Supporting Information for:

Chemoenzymatic and enantiodivergent routes to 1,2-ring-fused bicyclo[2.2.2]octane and related tricyclic frameworks

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Contents **Page**

Synthetic Studies

General Experimental Procedures

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian Gemini or Innova machine operating at 300 or 500 MHz, respectively. Unless otherwise specified, spectra were acquired at 20 °C in deuterochloroform ($CDCl_3$) that had been stored over anhydrous sodium carbonate. Chemical shifts are recorded as δ values in parts per million (ppm). Infrared spectra (ν_{max}) were normally recorded on a Perkin–Elmer 1800 Series FTIR Spectrometer and samples were analyzed as thin films on KBr plates (for liquids) or as a KBr disc (for solids). Low-resolution ESI mass spectra were recorded on a Micromass–Waters LC-ZMD single quadrupole liquid chromatograph-mass spectrometer while low- and high-resolution EI mass spectra were recorded on a VG Fisons AUTOSPEC three-sector double-focusing instrument. Melting points were measured on Reichert hot-stage microscope or a Stanford Research Systems Optimelt – Automated Melting Point System and are uncorrected. Analytical thin layer chromatography (TLC) was performed on aluminium-backed 0.2 mm thick silica gel 60 F254 plates as supplied by Merck. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included a mixture of vanillin: sulfuric acid: ethanol (1 g : 1 g : 18 mL) or phosphomolybdic acid : ceric sulfate : sulfuric acid (conc.) : water (37.5 g : 7.5 g : 37.5 g : 720 mL). The retardation factor (R_f) values cited here have been rounded at the first decimal point. Flash chromatographic separations were carried out following protocols defined by Still *et al.*[1] with silica gel 60 (0.040–0.0063 mm) as the stationary phase and using the AR- or HPLC-grade solvents indicated. Starting materials and reagents were generally available from the Sigma–Aldrich, Merck, TCI, Strem or Lancaster Chemical Companies and were either used as supplied or, in the case of liquids, distilled when required. Drying agents and other inorganic salts were purchased from the AJAX, BDH or Unilab Chemical Companies. THF, dichloromethane (DCM), acetonitrile and benzene were dried using a Glass Contour solvent purification system that is based upon a technology originally described by Grubbs *et al.*[2] Spectroscopic grade solvents were used for all analyses. Where necessary, reactions were performed under a nitrogen or argon atmosphere.

Specific Chemical Transformations

Compound 17

A suspension of (1*S*,2*S*)-3-iodocyclohexa-3,5-diene-1,2-diol [**7** (X=I)][3] (1.00 g, 4.20 mmol) and (1*S*)-(+)-10-camphorsulfonic acid monohydrate (20.0 mg, 0.08 mmol) in CH_2Cl_2 (30 mL) was cooled to –20 ºC then treated, dropwise, with benzaldehyde dimethylacetal (650 μL, 4.33 mmol). The ensuing mixture was allowed to warm to –10 ºC over 2 h then NaOH (20 mL of a 2.0 M aqueous solution) was added. The separated aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic fractions were washed with water (1 × 20 mL) and brine (1 × 20 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the *title acetal* ***17*** (containing traces of benzaldehyde) (1.29 g, *ca.* 85%) as an unstable, white solid (R_f = 0.6 in 3:7 *v/v* ethyl acetate/hexane).

^{1}H NMR (300 MHz) 7.50 (m, 2H), 7.37 (m, 3H), 6.70 (dt, *J* = 6.0 and 0.7 Hz, 1H), 6.09 (ddt, *J* = 9.5, 4.1 and 0.7 Hz, 1H), 5.81 (dd, *J* = 9.5 and 6.0 Hz, 1H), 5.77 (s, 1H), 4.83 (d, *J* = 9.2 Hz, 1H), 4.70 (dd, *J* = 9.2 and 4.1 Hz, 1H).

^{13}C NMR (75 MHz) 136.0 (C), 133.7 (CH), 129.6 (CH), 128.3 (CH), 127.2 (CH), 125.2 (CH), 123.7 (CH), 99.1 (CH), 98.5 (C), 77.9 (CH), 72.8 (CH).

IR ν_{max} 2880, 1458, 1395, 1364, 1333, 1312, 1284, 1216, 1087, 1059, 1009, 987, 927, 838, 762, 701 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 326 ($M^{+\bullet}$, 21%), 280 (76), 220 (90), 204 (65), 171 (50), 153 (82), 105 (92), 93 (90), 77 (99), 65 (100), 51 (69), 39 (75).

HREIMS Found: $M^{+\bullet}$, 325.9804. $C_{13}H_{11}O_2{}^{127}I$ requires $M^{+\bullet}$, 325.9804.

This material was sufficiently pure to be used as obtained in the next step of the reaction sequence.

Compound 18

A solution of (1*S*,2*S*)-3-iodo-6-methylcyclohexa-3,5-diene-1,2-diol[3] (2.0 g, 7.93 mmol) in 2,2-dimethoxypropane (40 mL) maintained at 18 °C was treated with *p*-TsOH•H_2O (*ca.* 30 mg, 0.16 mmol) and the ensuing mixture stirred at this temperature for 0.5 h then quenched with triethylamine (1.0 mL) and concentrated under reduced pressure. The resulting brown residue was partitioned between water (40 mL) and Et_2O (100 mL) and the separated aqueous phase was extracted with Et_2O (2 × 200 mL). The combined organic phases were washed with NaOH (1 × 100 mL of a 2.0 M solution) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure below 30 °C to give title acetonide **18**[4] (2.17 mg, 93%) as a pale-brown oil (R_f = 0.6 in 3:7 *v/v* ethyl acetate/hexane).

^{1}H NMR (300 MHz) 6.54 (d, *J* = 6.2 Hz, 1H), 5.49 (dq, *J* = 6.2 and 1.6 Hz, 1H), 4.73 (d, *J* = 8.4 Hz, 1H), 4.46 (dd, *J* = 8.4 and 0.7 Hz, 1H), 1.88 (broadened s, 3H), 1.43 (broadened s, 3H), 1.42 (broadened s, 3H).
^{13}C NMR (75 MHz) 134.6, 134.1, 120.4, 106.1, 96.2, 78.5, 75.8, 26.7, 25.2, 20.2.
Optical Rotation $[\alpha]_D$ = +37 (*c* 1.0, $CHCl_3$) [lit.[4] $[\alpha]_D$ = +69 (*c* 0.77, $CHCl_3$)].

This material was sufficiently pure to be used as obtained in the next step of the reaction sequence.

Compound 19

DDQ (12.8 g, 56.6 mmol) was added to a solution of 1,4-pentadien-3-ol[5] (5.0 mL, 51.4 mmol) in Et_2O (20 mL, 2.5 M) and the ensuing slurry was stirred at 18 ºC for 24 h. The resulting mixture was poured into pentane (100 mL) (to precipitate the $DDQH_2$) and the flask washed out with additional pentane (2 × 20 mL). The resulting solid was filtered off and washed with pentane (2 × 20 mL) then the combined filtrates were carefully concentrated under reduced pressure below 40 ºC and at *ca*. 750 mm Hg to give divinyl ketone **19**[6] as a *ca*. 60% solution in Et_2O/pentane (*ca.* 6 mL, 72%).

^{1}H NMR (300 MHz) 6.64 (dd, *J* = 17.4 and 10.6 Hz, 2H), 6.32 (dd, *J* = 17.4 and 1.3 Hz, 2H), 5.88 (dd, *J* = 10.6 and 1.3 Hz, 2H).
^{13}C NMR (75 MHz) 190.1 (C), 134.2 (CH), 129.4 (CH_2).
IR ν_{max} 2926, 2857, 1698, 1679, 1613, 1403, 1090, 989, 928 cm^{-1}.

Compound 20

Method 1:

Step i: Following a procedure established by Szymoniak *et al.*,[7] a solution of 3-methyl-but-2-enal (770 μL, 7.98 mmol) in THF (2 mL) was added, dropwise, to a solution of vinyl magnesium bromide (10 mL of a 1.0 M solution in THF, 10.0 mmol) in THF (5 mL) maintained at 18 ºC under a nitrogen atmosphere. The ensuing mixture was stirred at this temperature for 40 min then water (5 mL) was added and the separated aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give 5-methyl-1,4-hexadien-3-ol[8] (800 mg, *ca.* 89%) as a clear, orange oil.

^{1}H NMR (300 MHz) 5.88 (ddd, *J* = 17.1, 10.3 and 5.8 Hz, 1H), 5.22 (dt, *J* = 17.1 and 1.5 Hz, 1H), 5.18 (broad s, 1H), 5.07 (dt, *J* = 7.1 and 1.2 Hz, 1H), 4.84 (t, *J* = 7.1 Hz, 1H), 1.73 (d, *J* = 1.0 Hz, 3H), 1.70 (d, *J* = 1.0 Hz, 3H) 1.67 (br s, 1H).

This material was clean enough to be used directly in the next step of the reaction sequence.

Step ii: DDQ (555 mg, 2.44 mmol) was added to a magnetically stirred solution of 5-methyl-1,4-hexadien-3-ol (252 mg, 2.25 mmol) in Et_2O (1 mL) and the resulting slurry was stirred at 18 ºC for 24 h. The ensuing mixture was poured into pentane (10 mL) (to precipitate the $DDQH_2$), the flask washed with additional pentane (2 × 5 mL) and the residual solid filtered off and washed with pentane (2 × 5 mL). The combined filtrates were carefully concentrated under reduced pressure below 40 ºC and at *ca.* 750 mm Hg to give the very volatile ketone **20**[9] (101 mg, 41%) as a clear, yellow liquid.

^{1}H NMR (300 MHz) 6.39 (dd, *J* = 17.5 and 10.4 Hz, 1H), 6.27 (m, 1H), 6.19 (dd, *J* = 17.5 and 1.5 Hz, 1H), 5.73 (dd, *J* = 10.4 and 1.5 Hz, 1H), 2.17 (d, *J* = 1.3 Hz, 3H), 1.93 (d, *J* = 1.3 Hz, 3H).
^{13}C NMR (75 MHz) 190.4, 157.2, 138.2, 127.1, 122.0, 27.9, 21.0.

This material was clean enough to be used directly in the next step of the reaction sequence.

Method 2:
Following a procedure established by Mironov *et al.*,[10] diethylamine hydrochloride (6.85 g, 62.5 mmol), formaldehyde (5.1 mL of a 37% aqueous solution, 62.5 mmol), 4-hydroxy-4-methylpentan-2-one (7.75 mL, 62.5 mmol), HCl (250 μL of a 36% aqueous solution) and hydroquinone (125 mg, 1.14 mmol) were mixed in an Ace Glass™ reaction tube that was sealed then heated at 100 °C for 2 h. After cooling, the sealed tube was carefully opened and the reaction mixture transferred into a distillation apparatus. After distilling off the water, the hydrochloride salt of the Mannich base was decomposed at 150–210 °C to give the title divinyl ketone **20**[9] (2.4 g, 35%) as a bright-yellow liquid contaminated with mesityl oxide.

This material was used directly in the next step of the reaction sequence.

General Procedure for the Michael Addition of Ketals 12, 17 and 18 to Enones 19 and 20
A magnetically stirred solution of the relevant ketal (1.0 mole equiv.) in THF (0.2 M) was cooled to –30 °C then treated, dropwise, with *i*-PrMgCl (1.2–2.0 mole equiv. of a 2.0 M solution in THF). The ensuing mixture was warmed to 0 °C and stirred at this temperature until no starting material could be detected by ^{1}H NMR analysis (1–2 h). The reaction mixture was then cooled to –78 °C and treated with copper(I) bromide-dimethyl sulfide complex (0.1 mole equiv.) and HMPA (3.0 mole equiv.). A solution of the relevant enone (2.1 mole equiv.) and TMSCl (3.0 mole equiv.) in THF (*ca*. 2 mL) was then added *via* syringe pump over 1.5 h. The resulting mixture was allowed to warm to 18 ºC over 16 h then treated with NH_4Cl (*ca*. 20 mL of a saturated aqueous solution) and the

ensuing mixture stirred at 18 ºC for 10 min. The biphasic system was separated and the aqueous layer extracted with ethyl acetate (3 × 30 mL). The combined organic fractions were washed with water (2 × 10 mL) and brine (1 × 20 mL) then dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude material thus obtained was subjected to flash column chromatography using the conditions defined below for each individual case.

Compound 21

The Michael addition of the Grignard reagent derived from acetonide **12** (503 mg, 1.81 mmol) to enone **19** (591 μL of a 60% solution in Et_2O/pentane, *ca.* 3.80 mmol) was carried out as described in the general procedure and using 1.2 mole equiv. of *i*-PrMgCl (1.1 mL of a 2.0 M solution in THF, 2.2 mmol). The crude product thus obtained was subjected to flash column chromatography (1:9 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.4 in 3:7 *v/v* ethyl acetate/hexane) gave the *title enone **21*** (274 mg, 65%) as a clear, colourless oil.

^{1}H NMR (300 MHz) 6.37 (dd, *J* = 17.7 and 10.3 Hz, 1H), 6.23 (dd, *J* = 17.7 and 1.5 Hz, 1H), 5.96 (dd, *J* = 9.6 and 5.6 Hz, 1H), 5.84 (dd, *J* = 10.3 and 1.5 Hz, 1H), 5.79 (dd, *J* = 9.6 and 3.8 Hz, 1H), 5.71 (d, *J* = 5.6 Hz, 1H), 4.66 (dd, *J* = 8.7 and 3.8 Hz, 1H), 4.53 (d, *J* = 8.7 Hz, 1H), 2.83 (m, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.39 (s, 3H), 1.38 (s, 3H).
^{13}C NMR (75 MHz) 199.8 (C), 136.9 (C), 136.4 (CH), 128.2 (CH_2), 124.4 (CH), 123.1 (CH), 118.9 (CH), 105.3 (C), 73.4 (CH), 71.2 (CH), 37.4 (CH_2), 27.9 (CH_2), 26.8 (CH_3), 25.0 (CH_3).
IR ν_{max} 3044, 2985, 2933, 2894, 1700, 1681, 1614, 1402, 1378, 1369, 1208, 1158, 1096, 1031, 962, 838, 717 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 234 ($M^{+\bullet}$, <1%), 219 (5), 177 (40), 176 (48), 175 (44), 159 (70), 158 (75), 147 (40), 121 (75), 107 (100), 91 (46), 77 (52), 55 (95), 43 (62).
HREIMS Found: $M^{+\bullet}$, 234.1255. $C_{14}H_{18}O_3$ requires $M^{+\bullet}$, 234.1256.
Optical Rotation $[\alpha]_D$ = +89 (*c* 1.6, $CHCl_3$).

Compound 22

The Michael addition of the Grignard reagent derived from acetal **17** (690 mg, *ca.* 2.12 mmol) to enone **19** (691 μL of a 60% solution in Et_2O/pentane, *ca.* 4.44 mmol) was carried out as described in the general procedure using 2.0 mole equiv. of *i*-PrMgCl (2.1 mL of a 2.0 M solution in THF, 4.2 mmol). The crude product was subjected to flash column chromatography (1:9 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.3 in 3:7 *v/v* ethyl acetate/hexane) gave the *title enone **22*** (376 mg, 63%) as a clear, colourless oil.

^{1}H NMR (300 MHz) 7.45 (m, 2H), 7.35 (m, 3H), 6.34 (dd, *J* = 17.8 and 10.4 Hz, 1H), 6.19 (dd, *J* =

17.8 and 1.3 Hz, 1H), 6.02 (dd, *J* = 9.5 and 5.6 Hz, 1H), 5.89 (dd, *J* = 9.5 and 3.7 Hz, 1H), 5.80 (dd, *J* = 10.4 and 1.3 Hz, 1H), 5.80 (partially obscured d, *J* = 5.6, 1H), 5.70 (s, 1H), 4.73 (dd, *J* = 9.3 and 3.7 Hz, 1H), 4.60 (d, *J* = 9.3 Hz, 1H), 2.84 (m, 2H), 2.62 (m, 2H).

^{13}C NMR (75 MHz) 199.8 (C), 136.8 (C), 136.3 (CH), 135.9 (C), 129.4 (CH), 128.3 (CH), 128.2 (CH_2), 127.0 (CH), 124.5 (CH), 122.2 (CH), 119.4 (CH), 99.1 (CH), 74.1 (CH), 72.3 (CH), 37.5 (CH_2), 28.1 (CH_2).

IR ν_{max} 3045, 2891, 1711, 1459, 1402, 1374, 1312, 1294, 1218, 1089, 1065, 1025, 1000, 919, 761, 735, 699 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 282 ($M^{+\bullet}$, <1%), 175 (62), 158 (91), 147 (55), 133 (35), 121 (72), 105 (90), 91 (52), 77 (85), 65 (28), 55 (100), 39 (31).

HREIMS Found: $M^{+\bullet}$, 282.1254. $C_{18}H_{18}O_3$ requires $M^{+\bullet}$, 282.1256.

Optical Rotation $[\alpha]_D$ = +112 (*c* 1.5, $CHCl_3$).

Compound 23

The Michael addition of the Grignard reagent derived from acetonide **12** (1.00 g, 3.60 mmol) to enone **20** (945 μL, *ca.* 7.55 mmol) was carried out as described in the general procedure using 1.5 mole equiv. of *i*-PrMgCl (2.7 mL of a 2.0 M solution in THF, 5.4 mmol). The initially formed product was a silyl enol ether so this was dissolved in THF (7 mL) and the solution thus obtained treated with tetra-*n*-butylammonium fluoride (7 mL of a 1.0 M solution in THF, 7.00 mmol) and stirred at 18 ºC for 1 h. The reaction mixture was then concentrated under reduced pressure onto silica (*ca.* 2 g of 230–400 mesh material). The resulting free-flowing solid was subjected to flash column chromatography (silica, 1:9 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.4 in 3:7 *v/v* ethyl acetate/hexane) gave the *title enone* ***23*** (700 mg, 74%) as a clear, colourless oil.

1H NMR (300 MHz) 6.09 (m, 1H), 5.96 (dd, *J* = 9.7 and 5.6 Hz, 1H), 5.78 (dd, *J* = 9.7 and 3.7 Hz, 1H), 5.70 (d, *J* = 5.6 Hz, 1H), 4.66 (dd, *J* = 8.6 and 3.7 Hz, 1H), 4.53 (d, *J* = 8.6 Hz, 1H), 2.65 (m, 2H), 2.53 (m, 2H), 2.34 (d, *J* = 1.1 Hz, 3H), 1.89 (d, *J* = 1.1 Hz, 3H), 1.40 (s, 3H), 1.38 (s, 3H).

13C NMR (75 MHz) 199.9 (C) 155.4 (C), 137.3 (C), 124.5 (CH), 123.6 (CH), 122.9 (CH), 118.6 (CH), 105.3 (C), 73.5 (CH), 71.3 (CH), 41.8 (CH_2), 28.1 (CH_2), 27.7 (CH_3), 26.9 (CH_3), 25.0 (CH_3), 20.8 (CH_3).

IR ν_{max} 3044, 2948, 2933, 2912, 1688, 1620, 1445, 1378, 1369, 1234, 1209, 1159, 1109, 1031, 888, 708 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 262 ($M^{+\bullet}$, 2%), 247 (2), 204 (33), 189 (10), 149 (34), 148 (30), 121 (33), 107 (49), 104 (50), 91 (23), 83 (100), 77 (29), 55 (69), 43 (35), 39 (21).

HREIMS Found: $M^{+\bullet}$, 262.1558. $C_{16}H_{22}O_3$ requires $M^{+\bullet}$, 262.1569.

Optical Rotation $[\alpha]_D$ = +114 (*c* 0.3, $CHCl_3$).

Compound 24

The Michael addition of the Grignard reagent derived from acetonide **18** (1.00 g, 3.42 mmol) to enone **20** (900 μL, *ca.* 7.20 mmol) was carried out as described in the general procedure using 2.0 mole equiv. of *i*-PrMgCl (3.4 mL of a 2.0 M solution in THF, 6.8 mmol). The initially formed product was a silyl enol ether so this was dissolved in THF (7 mL) and the resulting solution treated with tetra-*n*-butylammonium fluoride (7 mL of a 1.0 M solution in THF, 7.00 mmol) then stirred at 18 ºC for 1 h. The ensuing mixture was concentrated under reduced pressure onto silica (*ca.* 2 g of 230–400 mesh material) and the resulting free-flowing solid subjected to flash column chromatography (silica, 1:9 *v/v* ethyl acetate/hexane elution). Concentration of the appropriate fractions (R_f = 0.4, 3:7 *v/v* ethyl acetate/hexane) gave the *title enone **24*** (568 mg, 60%) as a clear, colourless oil.

^{1}H NMR (300 MHz) 6.09 (m, 1H), 5.65 (s, 2H), 4.50 (AB q, *J* = 8.4 Hz, 2H), 2.63 (m, 2H), 2.51 (m, 2H), 2.13 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H).
^{13}C NMR (75 MHz) 200.0 (C), 155.1 (C), 134.1 (C), 132.3 (C), 123.6 (CH), 119.7 (CH), 119.6 (CH), 105.8 (C), 75.6 (CH), 74.3 (CH), 42.1 (CH_2), 28.3 (CH_2), 27.6 (CH_3), 27.0 (CH_3), 25.3 (CH_3), 20.7 (CH_3), 19.8 (CH_3).
IR ν_{max} 2982, 2933, 2912, 1688, 1620, 1447, 1378, 1369, 1235, 1208, 1158, 1110, 1062, 1039, 1013, 872 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 276 ($M^{+\bullet}$, 1%), 261 [$(M - CH_3\bullet)^+$, <1], 218 (49), 199 (19), 191 (22), 185 (18), 163 (39), 149 (58), 135 (55), 121 (90), 108 (26), 91 (39), 83 (100), 77 (35), 55 (81), 43 (82).
HREIMS Found: $M^{+\bullet}$, 276.1722. $C_{17}H_{24}O_3$ requires $M^{+\bullet}$, 276.1725.
Optical Rotation $[\alpha]_D$ = +19 (*c* 0.9, $CHCl_3$).

Compounds 25 and 26

A solution of enone **21** (258 mg, 1.10 mmol) and BHT (24.7 mg, 0.11 mmol) in toluene (110 mL) was heated at reflux for 16 h. The cooled reaction mixture was then concentrated under reduced pressure and the residue thus obtained was subjected to flash column chromatography (silica, 1:4 → 2:3 *v/v* ethyl acetate/hexane gradient elution) and so affording two fractions, A and B.

Concentration of fraction A (R_f = 0.2 in 3:7 *v/v* ethyl acetate/hexane) gave the title *anti*-adduct **25** (113 mg, 44%) as a white, crystalline solid, m.p. = 131–134 ºC.

^{1}H NMR (300 MHz) 6.29 (t, *J* = 7.3 Hz, 1H), 5.74 (d, *J* = 7.3 Hz, 1H), 4.28 (ddd, *J* = 7.1, 2.7 and 1.0 Hz, 1H), 4.23 (dd, *J* = 7.1 and 1.0 Hz, 1H), 2.88 (m, 1H), 2.51–2.18 (m, 3H), 1.99–1.88 (m, 2H), 1.65–1.47 (m, 2H), 1.33 (s, 3H), 1.28 (s, 3H).
^{13}C NMR (75 MHz) 215.2 (C), 135.7 (CH), 130.7 (CH), 109.1 (C), 83.3 (CH), 79.5 (CH), 50.1 (CH), 47.5 (C), 36.9 (CH_2), 35.7 (CH), 28.4 (CH_2), 25.5 (CH_3), 24.9 (CH_3), 23.5 (CH_2).
IR ν_{max} 2986, 2934, 2886, 2865, 1742, 1455, 1378, 1368, 1207, 1142, 1068, 1058, 883, 745, 717 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 234 ($M^{+\bullet}$, 12%), 219 (70), 177 (70), 176 (91), 175 (62), 147 (98), 133 (100), 120 (74), 105 (88), 100 (77), 91 (99), 85 (52), 77 (45), 43 (75).
HREIMS Found: $M^{+\bullet}$, 234.1256. $C_{14}H_{18}O_3$ requires $M^{+\bullet}$, 234.1256.
Elemental Analysis Found: C, 71.58; H, 7.73. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%.
Optical Rotation $[\alpha]_D$ = –102 (*c* 1.2, $CHCl_3$).

Concentration of fraction B (R_f = 0.3 in 3:7 *v/v* ethyl acetate/hexane) gave the title *syn*-adduct **26** (101 mg, 39%) as a white, crystalline solid, m.p. = 93–96 ºC.

^{1}H NMR (300 MHz) 6.35 (dd, *J* = 8.0 and 6.8 Hz, 1H), 5.81 (dd, *J* = 8.0 and 1.0 Hz, 1H), 4.08 (ddd, *J* = 8.0, 4.2 and 1.0 Hz, 1H), 3.99 (d, *J* = 8.0 Hz, 1H), 2.84 (m, 1H), 2.66 (ddd, *J* = 10.0, 6.1 and 1.7 Hz, 1H), 2.49–2.36 (m, 1H), 2.23–1.95 (complex m, 4H), 1.49 (s, 3H), 1.40 (ddd, *J* = 6.1, 2.4 and 1.0 Hz, 1H), 1.35 (s, 3H).
^{13}C NMR (75 MHz) 217.8 (C), 137.0 (CH), 133.7 (CH), 112.3 (C), 77.1 (CH), 75.0 (CH), 47.7 (C), 45.9 (CH), 36.2 (CH_2), 35.0 (CH), 26.5 (CH_3), 25.2 (CH_2), 24.4 (CH_3), 22.8 (CH_2).
IR ν_{max} 2993, 2965, 2932, 2861, 1739, 1450, 1376, 1268, 1209, 1144, 1069, 1058, 1016, 872, 723 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 234 ($M^{+\bullet}$, 4%), 219 [$(M - CH_3\bullet)^+$, 50], 205 (37), 177 (48), 176 (85), 175 (82), 159 (71), 147 (99), 134 (97), 133 (98), 120 (78), 117 (77), 105 (95), 100 (97), 91 (100), 77 (55), 55 (45), 43 (79).
HREIMS Found: $(M - CH_3\bullet)^+$, 219.1021. $C_{14}H_{18}O_3$ requires $(M - CH_3\bullet)^+$, 219.1021.
Elemental Analysis Found: C, 71.50; H, 7.75. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%.
Optical Rotation $[\alpha]_D$ = +128 (*c* 1.04, $CHCl_3$).

Compounds 27 and 28

A solution of enone **22** (129 mg, 0.46 mmol) and BHT (10 mg, 0.05 mmol) in toluene (45 mL) was heated at reflux for 24 h. The cooled reaction mixture was then concentrated under reduced pressure and the residue thus obtained was subjected to flash column chromatography (silica, 1:9 → 3:7 *v/v* ethyl acetate/hexane gradient elution) and so affording two fractions, A and B.

Concentration of fraction A (R_f = 0.1 in 3:7 *v/v* ethyl acetate/hexane) afforded the anti-*adduct **27*** (76 mg, 59%) as a white, crystalline solid, m.p. = 174–179 ºC.

^{1}H NMR (300 MHz) 7.47 (m, 2H), 7.35 (m, 3H), 6.44 (broad t, *J* = 7.3 Hz, 1H), 5.89 (d, *J* = 7.3 Hz, 1H), 5.63 (s, 1H), 4.34 (dd, *J* = 7.4 and 2.7 Hz, 1H), 4.28 (d, *J* = 7.4 Hz, 1H), 3.08 (m, 1H), 2.49 (m, 2H), 2.29 (m, 1H), 2.01 (m, 2H), 1.65 (m, 2H).
^{13}C NMR (75 MHz) 214.9 (C), 136.2 (CH), 136.1 (C), 131.1 (CH), 129.8 (CH), 128.3 (CH), 127.5 (CH), 103.5 (CH), 83.8 (CH), 80.1 (CH), 50.3 (CH), 47.6 (C), 36.9 (CH_2), 35.6 (CH), 28.4 (CH_2), 23.7 (CH_2).
IR ν_{max} 2922, 2873, 1732, 1462, 1404, 1358, 1313, 1218, 1150, 1112, 1084, 1062, 994, 920, 853, 759, 752, 705, 698 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 282 ($M^{+\bullet}$, 9%), 281 [$(M - H\bullet)^+$, 12], 253 (9), 176 (69), 147 (68), 133 (58), 120 (40), 105 (100), 91 (67), 77 (45), 55 (21).
HREIMS Found: $(M - H\bullet)^+$, 281.1176. $C_{18}H_{18}O_3$ requires $(M - H\bullet)^+$, 281.1178.
Optical Rotation $[\alpha]_D$ = –75 (*c* 0.5, $CHCl_3$).

Concentration of fraction B (R_f = 0.3 in 3:7 *v/v* ethyl acetate/hexane) afforded the syn-*adduct **28*** (27 mg, 21%) as a clear, colourless oil.

^{1}H NMR (300 MHz) (7.50 (m, 2H), 7.41 (m, 3H), 6.41 (dd, *J* = 8.1 and 6.8 Hz, 1H), 5.94 (s, 1H), 5.89 (d, *J* = 8.1 Hz, 1H), 4.14 (dd, *J* = 8.4 and 3.9 Hz, 1H), 4.07 (d, *J* = 8.4 Hz, 1H), 3.02 (m, 1H), 2.84 (ddd, *J* = 9.8, 6.1 and 1.5 Hz, 1H), 2.49–1.99 (m, 5H), 1.50 (ddd, *J* = 12.7, 6.8 and 1.5 Hz, 1H).
^{13}C NMR (75 MHz) 217.4 (C), 137.3 (CH), 136.4 (C), 134.1 (CH), 129.8 (CH), 128.6 (CH), 126.8 (CH), 106.2 (CH), 77.8 (CH), 76.3 (CH), 47.8 (C), 46.1 (CH), 36.2 (CH_2), 35.0 (CH), 25.2 (CH_2), 23.2 (CH_2) .
IR ν_{max} 3041, 2917, 2869, 1740, 1458, 1405, 1298, 1220, 1444, 1108, 1086, 1063, 1025, 991, 761, 743, 700 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 282 ($M^{+\bullet}$, 5%), 253 (51), 176 (71), 147 (82), 133 (82), 120 (40), 105 (96), 91 (100), 77 (61), 55 (32).
HREIMS Found: $M^{+\bullet}$, 282.1255. $C_{18}H_{18}O_3$ requires $M^{+\bullet}$, 282.1256.
Optical Rotation $[\alpha]_D$ = +59 (*c* 0.3, $CHCl_3$).

Compound 29

A solution of enone **23** (129 mg, 0.46 mmol) and BHT (10 mg, 0.05 mmol) in mesitylene (45 mL)

was heated at reflux for 4 days. The cooled reaction mixture was then concentrated under reduced pressure and subjected to flash column chromatography (silica, 1:9 → 3:7 *v/v* ethyl acetate/hexane gradient elution) to afford compound **29** (58.1 mg, 45%) as a white, crystalline solid, m.p. = 101–104 ºC.

^{1}H NMR (300 MHz) 6.31 (t, *J* = 8.0 Hz, 1H), 5.81 (d, *J* = 8.0 Hz, 1H), 4.62 (ddd, *J* = 7.1, 2.9 and 1.0 Hz, 1H), 4.18 (dd, *J* = 7.1 and 1.0 Hz, 1H), 2.47 (ddd, *J* = 6.6, 2.9 and 1.0 Hz, 1H), 2.36–2.22 (m, 3H), 1.76 (m, 1H), 1.49 (s, 1H), 1.33 (s, 3H), 1.29 (s, 3H), 1.20 (s, 3H), 1.00 (s, 3H).
^{13}C NMR (75 MHz) 214.6 (C), 136.5 (CH), 129.5 (CH), 109.0 (C), 83.5 (CH), 77.1 (CH), 59.8 (CH), 49.7 (C), 49.5 (CH), 38.6 (CH_2), 37.4 (C), 29.9 (CH_3), 28.5 (CH_2), 25.4 (CH_3), 25.0 (two signals overlapping, 2 × CH_3).
IR ν_{max} 2965, 2937, 2910, 2883, 1734, 1381, 1367, 1265, 1206, 1088, 1066, 879, 738 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 262 ($M^{+\bullet}$, <1%), 247 [$(M - CH_3\bullet)^+$, 25], 204 (100), 175 (49), 147 (46), 119 (49), 91 (46), 55 (41), 43 (54).
HREIMS Found: $(M - CH_3\bullet)^+$, 247.1339. $C_{16}H_{22}O_3$ requires $(M - CH_3\bullet)^+$, 247.1334.
Optical Rotation $[\alpha]_D$ = –107 (*c* 0.95, $CHCl_3$).

Compound 30

A solution of enone **23** (100 mg, 0.40 mmol) in MeOH (4 mL) was cooled to 0 ºC and treated with $NaBH_4$ (29 mg, 0.77 mmol). The ensuing mixture was stirred at 0 ºC for 1 h then warmed to 18 ºC and stirred at this temperature for a further 1 h. Water (1 mL) was then added and the resulting mixture concentrated under reduced pressure. The residue thus obtained was partitioned between half brine (10 mL) and CH_2Cl_2 (20 mL) then the separated aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic fractions were washed with brine (1 × 10 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. Subjection of the resulting yellow oil to flash column chromatography (silica, 1:9 → 3:7 *v/v* ethyl acetate/hexane gradient elution) and concentration of the appropriate fractions (R_f = 0.4 in 1:1 *v/v* ethyl acetate/hexane) gave a *ca.* 1:1 mixture of the epimeric forms of *alcohol **30*** (88 mg, 84%) as a clear, colourless oil.

^{1}H NMR (300 MHz) 5.96 (ddd, *J* = 9.6, 5.6 and 1.6 Hz 1H), 5.76 (m, 2H), 5.19 (m, 1H), 4.66 (dd, *J* = 8.6 and 3.7 Hz, 1H), 5.12 (dd, *J* = 8.6 and 2.6 Hz, 1H), 4.37 (m, 1H), 2.26 (m, 2H), 1.83–1.55 (m, 2H), 1.72 (s, 3H), 1.68 (s, 1.5H), 1.66 (1.5H), 1.40 (s, 3H), 1.38 (s, 1.5H), 1.37 (s, 1.5H) (resonance due to OH group proton not observed).
^{13}C NMR (75 MHz) 138.0 (C), 137.8 (C), 135.6 (C), 135.2 (C), 127.9 (CH), 127.8 (CH), 124.5 (two signals overlapping, 2 × CH), 122.8(4) (CH), 122.7(7) (CH), 118.6 (CH), 118.5 (CH), 105.2(4)

(C), 105.1(8) (C), 73.4(9) (CH), 73.4(7) (CH), 71.4(4) (CH), 71.4(0) (CH), 68.4 (CH), 68.1 (CH), 35.2 (CH_2), 35.0 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 26.9 (CH_3), 26.8 (CH_3), 25.7(9) (CH_3), 25.7(7) (CH_3), 25.1 (CH_3), 25.0 (CH_3), 18.3(2) (CH_3), 18.2(5) (CH_3).

IR ν_{max} 3435, 3044, 2984, 2931, 1448, 1377, 1235, 1209, 1158, 1046, 886, 716 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 246 [$(M - H_2O)^{+\bullet}$, 1%), 231 [$(M - H_2O - CH_3\bullet)^+$, 4], 206 (60), 188 (42), 173 (51), 145 (35), 133 (41), 107 (100), 95 (52), 94 (51), 85 (54), 79 (59), 43 (71).

HREIMS Found: $(M - H_2O)^{+\bullet}$, 246.1614. $C_{16}H_{24}O_3$ requires $(M - H_2O)^{+\bullet}$, 246.1620.

Compound 31

Alcohol **31** was prepared in the same manner as described immediately above for congener **30** but now using enone **24** (107 mg, 0.39 mmol) as the starting material. In this manner a *ca.* 1:1 mixture of the epimeric forms of the *title alcohol **31*** (89 mg, 83%) was obtained as a clear colourless oil (R_f = 0.2 in 3:7 *v/v* ethyl acetate/hexane).

^{1}H NMR (300 MHz) 5.69 (m, 2H), 5.19 (m, 1H), 4.51 (s, 2H), 4.37 (m, 1H), 2.25 (m, 2H), 1.87 (s, 3H), 1.84–1.57 (m, 2H), 1.72 (s, 3H), 1.68 (s, 1.5H), 1.66 (s, 1.5H), 1.42 (s, 3H), 1.37 (s, 1.5H), 1.35 (s, 1.5H) (resonance due to OH group proton not observed).

^{13}C NMR (75 MHz) 135.5 (C), 135.2 (C), 134.8 (C), 134.6 (C), 132.2 (C), 132.1 (C), 128.0 (CH), 127.9 (CH), 119.7 (CH), 119.6 (three signals overlapping, 3 × CH), 105.7(9) (C), 105.7(6) (C), 75.8 (CH), 75.7 (CH), 74.4 (CH), 74.3 (CH), 68.4 (CH), 68.1 (CH), 35.4 (CH_2), 35.3 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 27.0(3) (CH_3), 26.9(9) (CH_3), 25.8 (two signals overlapping, 2 × CH_3), 25.4(3) (CH_3), 25.3(6) (CH_3), 19.8 (two signals overlapping, 2 × CH_3), 18.3(3) (CH_3), 18.2(6) (CH_3).

IR ν_{max} 3434, 2983, 2932, 2914, 2879, 1448, 1377, 1235, 1209, 1159, 1064, 1045, 1021, 872, 849 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 260 [$(M - H_2O)^{+\bullet}$, 6%], 245 [$(M - H_2O - CH_3\bullet)^+$, 10], 220 (92), 202 (52), 187 (67), 147 (48), 121 (100), 108 (59), 95 (69), 91 (53), 85 (68), 77 (51), 55 (40), 43 (65).

HREIMS Found: $(M - H_2O)^{+\bullet}$, 260.1777. $C_{17}H_{26}O_3$ requires $(M - H_2O)^{+\bullet}$, 260.1776.

Compound 32

A solution of a *ca.* 1:1 mixture of the epimeric forms of alcohol **30** (43.3 mg, 0.16 mmol) and BHT (3.5 mg, 0.02 mmol) in mesitylene (35 mL) was heated at reflux for 4 days then cooled and concentrated under reduced pressure to give a yellow oil. Purification of this material by flash column chromatography (silica, 3:7 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.3 in 1:1 *v/v* ethyl acetate/hexane) afforded the *title compound **32*** (19.1 mg, 44%) as a clear, colourless oil.

^{1}H NMR (300 MHz) 6.11 (dd, *J* = 8.1 and 6.5 Hz, 1H), 5.70 (dd, *J* = 8.1 and 1.0 Hz, 1H), 4.59 (ddd, *J* = 7.1, 3.0 and 1.0 Hz, 1H), 4.07 (dd, *J* = 7.1 and 1.0 Hz, 1H), 3.87 (m, 1H), 2.42 (ddd, *J* = 6.5, 3.0 and 1.0 Hz, 1H), 2.21 (m, 1H), 1.90 (m, 2H), 1.60 (m, 1H), 1.30 (s, 3H), 1.27 (s, 3H), 1.23 (d, *J* = 9.3 Hz, 1H), 1.14 (s, 3H), 1.00 (s, 3H) (resonance due to OH group proton not observed).

^{13}C NMR (75 MHz) 133.0 (CH), 132.3 (CH), 108.4 (C), 84.0 (CH), 77.2 (CH), 74.7 (CH), 59.8 (CH), 50.6 (C), 49.0 (CH), 35.1 (C), 34.0 (CH_2), 30.9 (CH_3), 30.1 (CH_2), 25.4(3) (CH_3), 25.3(6) (CH_3), 25.0 (CH_3).

IR ν_{max} 3435, 3042, 2931, 2869, 1456, 1378, 1368, 1264, 1206, 1174, 1161, 1091, 1064, 1029, 1006, 983, 967, 902, 884, 830, 816, 735, 702 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 264 ($M^{+\bullet}$, <1%), 249 (55), 206 (52), 188 (95), 173 (89), 164 (64), 159 (94), 147 (78), 145 (80), 133 (82), 120 (69), 107 (79), 105 (79), 100 (54), 91 (71), 85 (82), 69 (50), 55 (60), 43 (100).

HREIMS Found: $M^{+\bullet}$, 264.1726. $C_{16}H_{24}O_3$ requires $M^{+\bullet}$, 264.1725.

Compound 33

A solution of *ca.* 1:1 mixture of the epimeric forms of alcohol **31** (53.1 mg, 0.19 mmol) and BHT (4.0 mg, 0.02 mmol) in mesitylene (40 mL) was heated at reflux for 96 h then cooled and concentrated under reduced pressure to give a yellow oil. Subjection of this material to flash column chromatography (silica, 3:7 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.3 in 1:1 *v/v* ethyl acetate/hexane) afforded the *title compound **33*** (24.3 mg, 46%) as a colourless, semi-solid.

^{1}H NMR (300 MHz) 5.68 (AB quartet, *J* = 8.3 Hz, 2H), 4.24 (d, *J* = 7.2 Hz, 1H), 4.08 (d, *J* = 7.2 Hz, 1H), 3.90 (m, 1H), 2.20 (m, 1H), 1.87 (m, 2H), 1.60 (m, 1H), 1.30 (s, 3H), 1.27 (s, 3H), 1.22 (d, *J* = 8.1 Hz, 1H), 1.19 (s, 3H), 1.02 (s, 3H), 0.94 (s, 3H) (resonance due to OH group proton not observed).

^{13}C NMR (75 MHz) 137.9 (CH), 132.2 (CH), 108.3 (C), 84.9 (CH), 81.4 (CH), 74.8 (CH), 61.0 (CH), 49.4 (C), 46.3 (C), 37.4 (C), 34.0 (CH_2), 30.0 (CH_2), 27.0 (CH_3), 25.6 (CH_3), 25.0 (CH_3), 21.6 (CH_3), 15.0 (CH_3).

IR ν_{max} 3429, 3036, 2967, 2872, 1455, 1370, 1255, 1207, 1167, 1085, 1056, 1017, 898, 870, 733 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 263 [$(M - CH_3\bullet)^+$, 19%], 220 (73), 202 (28), 187 (31), 178 (99), 163 (48), 121 (65), 119 (100), 105 (42), 91 (41), 77 (27), 43 (64).

HREIMS Found: $(M - CH_3\bullet)^+$, 263.1647. $C_{17}H_{26}O_3$ requires $(M - CH_3\bullet)^+$, 263.1647.

Optical Rotation $[\alpha]_D$ = –5 (*c* 0.4, $CHCl_3$).

Compound 34

A solution of alcohol **33** (9.8 mg, 0.04 mmol), triethylamine (20 μL, 0.14 mmol) and DMAP [4-(*N*,*N*- dimethylamino)pyridine] (17.3 mg, 0.14 mmol) in CH_2Cl_2 (1.0 mL) maintained at 18 ºC was treated with 3,5-dinitrobenzoyl chloride (24.2 mg, 0.105 mmol). The ensuing mixture was stirred at 18 ºC for 16 h then $NaHCO_3$ (2 mL of a saturated aqueous solution) and CH_2Cl_2 (5 mL) were added. The separated aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic fractions were washed with brine (1 × 2 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. Subjection of the resulting yellow oil to flash column chromatography (silica, 1:19 *v/v* ethyl acetate/hexane elution) and concentration of the appropriate fractions (R_f = 0.6, 3:7 *v/v* ethyl acetate/hexane) afforded the *title ester **34*** (10.1 mg, 61%) as a white crystalline solid, m.p. = 178–182 º.

^{1}H NMR (500 MHz) 9.24 (t, *J* = 2.2 Hz, 1H), 9.12 (d, *J* = 2.2 Hz, 2H), 5.78 (AB quartet, *J* = 8.0 Hz, 2H), 5.09 (m, 1H), 4.32 (d, *J* = 7.1 Hz, 1H), 4.19 (d, *J* = 7.1 Hz, 1H), 2.54 (m, 1H), 2.08 (m, 1H), 1.93 (m, 1H), 1.80 (d, *J* = 9.0 Hz, 1H), 1.74 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H), 1.08 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (75 MHz) 162.1 (C), 148.7 (C), 138.8 (CH), 134.0 (C), 131.1 (CH), 129.3 (CH), 122.4 (CH), 108.7 (C), 84.5 (CH), 81.3 (CH), 80.2 (CH), 58.0 (CH), 49.2 (C), 46.3 (C), 37.6 (C), 31.1 (CH_2), 30.4 (CH_2), 26.9 (CH_3), 25.6 (CH_3), 25.0 (CH_3), 22.2 (CH_3), 15.1 (CH_3).

IR ν_{max} 3103, 2922, 2851, 1729, 1628, 1547, 1461, 1370, 1344, 1276, 1208, 1168, 1075, 1018, 920, 873, 730, 721 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 457 [$(M - CH_3•)^+$, 11%], 414 (22), 202 (100), 187 (39), 173 (50), 160 (58), 145 (79), 121 (45), 69 (40), 57 (51), 55 (48), 43 (77).

HREIMS Found: $(M - CH_3•)^+$, 457.1609. $C_{24}H_{28}N_2O_8$ requires $(M - CH_3•)^+$, 457.1611.

Optical Rotation $[\alpha]_D$ = –57 (*c* 0.15, $CHCl_3$).

Compound 35

L-Selectride® (0.68 mL of a 1.0 M solution in THF, 0.68 mmol, 2.0 molar equiv.) was slowly added to a magnetically stirred solution of ketone **26** (80 mg, 0.34 mmol) in dry CH_2Cl_2 (10 mL) maintained at –78 ºC under a nitrogen atmosphere. The ensuing mixture was stirred at –78 °C for 1 h then quenched with NH_4Cl (20 mL of a saturated aqueous solution) and diluted with CH_2Cl_2 (10 mL). After the reaction mixture had warmed to room temperature the separated aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL) and the combined organic fractions were then dried ($MgSO_4$), filtered, concentrated under reduced pressure. The ensuing light-yellow oil was subjected to flash column chromatography (silica 3:7 v/v ethyl acetate/hexane elution) to give, after concentration of

the relevant fractions (R_f = 0.3 in 2:3 v/v ethyl acetate/hexane) a crystalline solid. Recrystallisation (ethyl acetate) of this material gave the *title compound **35*** (70 mg, 87%) as a colourless, crystalline solid, m.p. = 90.9 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (dd, *J* = 7.8 and 6.6 Hz, 1H), 5.88 (d, *J* = 7.8 Hz, 1H), 4.02–3.96 (m, 2H), 3.84 (d, *J* = 7.8 Hz, 1H), 2.82 (m, 1H), 2.34–2.04 (m, 3H), 1.72–1.60 (m, 3H), 1.44 (s, 3H), 1.28 (s, 3H), 1.32–1.25 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 135.0, 112.2, 77.6, 75.3, 73.3, 49.3, 39.9, 36.1, 35.9, 28.0, 26.7, 24.7, 22.3.
IR ν_{max} 3481, 3046, 2937, 1614, 1455, 1372, 1263, 1206, 1163, 1134, 1059, 976, 944, 876, 804, 703, 649 cm^{-1}.
Mass spectrum (EI, 70 eV) *m/z* 236 ($M^{+\bullet}$, 3%), 221 (17), 207 (12), 178 (31), 160 (88), 136 (67), 131 (100), 118 (65), 117 (72), 105 (51), 100 (41), 91 (68), 43 (44).
HREIMS Found: $M^{+\bullet}$, 236.1414 $C_{14}H_{20}O_3$ requires $M^{+\bullet}$, 236.1412.
Optical Rotation $[\alpha]_D$ = –5.1 (*c* 0.82, CH_2Cl_2).

Compound 36

Sodium hydride (26 mg of a 60% dispersion in oil, 0.66 mmol, 1.2 molar equiv.) was added to a magnetically stirred solution of alcohol **35** (130 mg, 0.55 mmol) in dry THF (5 mL) maintained at 0 ºC under a nitrogen atmosphere. The ensuing mixture was allowed to warm to 18 °C and stirred at this temperature for 0.5 h before being treated, dropwise, with iodomethane (0.11 mL, 1.65 mmol, 3.0 molar equiv.). After being stirred at 18 °C for a further 18 h the reaction mixture was quenched with NH_4Cl (25 mL of a saturated aqueous solution) then diluted with Et_2O (25 mL). The separated aqueous layer was extracted with Et_2O (2 × 30 mL) and the combined organic fractions were dried ($MgSO_4$), filtered, concentrated under reduced pressure. The resulting light-yellow oil was subjected to flash column chromatography (silica gel, 1:9 v/v ethyl acetate/hexane) to give, after concentration of the appropriate fractions (R_f = 0.6 in 3:7 v/v ethyl acetate/hexane), the *title compound **36*** (117 mg, 85%) as a clear, colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 7.8 and 6.6 Hz, 1H), 5.81 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 8.1 and 4.1 Hz, 1H), 3.88 (d, *J* = 8.1 Hz, 1H), 3.58 (m, 1H), 3.20 (s, 3H), 2.81 (m, 1H), 2.24 (m, 1H), 2.10–1.97 (m, 2H), 1.75–1.61 (m, 3H), 1.50 (s, 3H), 1.40 (m, 1H), 1.33 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 132.7, 111.9, 81.8, 77.8, 75.6, 57.3, 49.4, 38.7, 35.8, 32.1, 28.3, 26.7, 24.7, 22.2.
IR ν_{max} 3045, 2976, 2938, 2900, 2871, 2819, 1611, 1455, 1380, 1371, 1263, 1207, 1084, 1059, 973, 929, 877, 717, 698, 649 cm^{-1}.

Mass spectrum (EI, 70 eV) *m/z* 250 ($M^{+\bullet}$, 21%), 235 (15), 221 (12), 192 (27), 160 (83), 150 (65), 131 (93), 118 (72), 117 (67), 105 (51), 91 (65), 86 (62), 84 (86), 49 (100).
HREIMS Found: $M^{+\bullet}$, 250.1564. $C_{15}H_{22}O_3$ requires $M^{+\bullet}$, 250.1569.
Optical Rotation $[\alpha]_D$ = –44.1 (*c* 0.70, CH_2Cl_2).

Compound 37

DOWEX® 50WX8-100 ion exchange resin (500 mg of freshly activated material obtained by successive washing with saturated aqueous $NaHCO_3$, H_2O, 1 M HCl and H_2O) was added to a magnetically stirred solution of acetonide **36** (250 mg, 1.00 mmol) in MeOH:H_2O (18 mL of 5:1 v/v mixture) maintained at 18 °C. The resulting mixture was heated at reflux (*ca*. 110 ºC) for 72 h then cooled and filtered. The solids thus retained were sonicated with MeOH (3 × 15 mL) and CH_2Cl_2 (3 × 15 mL) and then filtered. The combined filtrates were concentrated under reduced pressure and the residue thus obtained was partitioned between NaCl (50 mL of a 1.5 M aqueous solution) and CH_2Cl_2 (50 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic phases were then dried ($MgSO_4$), filtered, concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash column chromatography (silica gel, 3:7 → 2:3 v/v ethyl acetate/hexane gradient elution) gave two fractions, A and B.

Concentration of fraction A (R_f = 0.6 in 3:7 v/v ethyl acetate/hexane) gave the starting acetonide **36** (25 mg, 10% recovery) as a clear, colourless oil. This material was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.1 in 3:7 v/v ethyl acetate/hexane) gave *title compound **37*** (162 mg, 77% at 90% conversion) as a clear, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.14 (dd, *J* = 8.1 and 6.6 Hz, 1H), 5.82 (d, *J* = 8.1 Hz, 1H), 3.64 (m, 1H), 3.56 (m, 1H), 3.44–3.37 (m, 2H), 3.28 (d, *J* = 4.5 Hz, 1H), 3.19 (s, 3H), 2.71 (m, 1H), 2.09–1.93 (m, 3H), 1.82–1.58 (m, 3H), 1.38 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 131.7, 81.9, 67.3, 64.8, 57.3, 49.9, 38.4, 37.9, 32.3, 27.9, 22.1.
IR ν_{max} 3361, 3042, 2939, 2821, 1616, 1456, 1392, 1368, 1286, 1199, 1144, 1110, 1078, 1039, 923, 864, 809, 707, 689 cm^{-1}.
Mass spectrum (ESI, +ve ionisation) *m/z* 233 [$(M + Na)^+$, 6%], 126 (95), 102 (100).
HRMS Found: $(M + Na)^+$, 233.1150. $C_{12}H_{18}O_3$ requires $(M + Na)^+$, 233.1154.
Optical Rotation $[\alpha]_D$ = –31.6 (*c* 2.07, CH_2Cl_2).

Compound 38

p-TsOH•H_2O (320 mg, 1.68 mmol, 2.2 molar equiv.) was added to a magnetically stirred solution of diol **37** (0.77 mmol, 161 mg) in dry CH_2Cl_2 (12 mL) maintained at 0 ºC under a nitrogen atmosphere. 4-Acetamido-TEMPO (359 mg, 1.68 mmol, 2.2 molar equiv.) was then added (in *ca*. 5 × 72 mg portions at 0.5 h intervals) and the resulting solution stirred at 18 °C for 1 h before being quenched with $NaHCO_3$ (20 mL of a saturated aqueous solution) then diluted with CH_2Cl_2 (20 mL). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL) then the combined organic fractions were dried ($MgSO_4$), filtered, concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash column chromatography (silica gel, 3:7 v/v ethyl acetate/hexane elution) gave, after concentration of the appropriate fractions (R_f = 0.2) a white solid. Recrystallisation (ethyl acetate/hexane) of this material afforded the *title compound **38*** (134 mg, 84%) as a colourless, crystalline solid, m.p. = 71.4 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 8.1 and 6.0 Hz, 1H), 6.05 (d, *J* = 8.1 Hz, 1H), 3.55 (m, 1H), 3.48 (s, 1H), 3.15 (s, 3H), 3.03 (m, 1H), 2.78 (s, 1H), 2.23 (m, 1H), 2.06 (m, 1H), 1.96–1.72 (m, 5H, m).

^{13}C NMR (75 MHz, $CDCl_3$) δ 216.0, 139.8, 128.1, 80.6, 73.6, 57.1, 53.9, 47.1, 40.4, 32.8, 28.5, 27.0.

IR ν_{max} 3439, 2936, 2874, 2824, 1729, 1610, 1457, 1364, 1206, 1137, 1109, 1080, 926, 876, 839, 766, 693 cm^{-1}.

Mass spectrum (ESI, +ve ionisation) *m/z* 231 [$(M + Na)^+$, 100%], 163 (55), 131 (92).

HRMS Found: $(M + Na)^+$, 231.0998. $C_{12}H_{16}O_3$ requires $(M + Na)^+$, 231.0997.

Optical Rotation $[\alpha]_D$ = –204.0 (*c* 1.54, CH_2Cl_2).

Compound 39

Benzoyl chloride (0.22 mL, 1.93 mmol, 3.0 molar equiv.) was slowly added to a magnetically stirred solution of acyloin **38** (134 mg, 0.64 mmol) and DMAP (314 mg, 2.57 mmol, 4.0 molar equiv.) in dry CH_2Cl_2 (10 mL) maintained at 0 ºC under a nitrogen atmosphere. The resulting solution was stirred at 0 ºC for 2 h and at 18 °C for 18 h before being quenched with HCl (15 mL of a 1 M aqueous solution) then diluted with CH_2Cl_2 (10 mL). The separated aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL and the combined organic fractions were then dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting light-yellow oil was subjected to flash column chromatography (silica gel, 3:17 → 1:4 v/v ethyl acetate/hexane gradient elution). Concentration of the appropriate fractions (R_f = 0.4 in 3:7 v/v ethyl acetate/hexane) gave the *title compound **39*** (200 mg, 99%) as a white solid, m.p. = 96.0 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12–7.97 (m, 2H), 7.56 (m, 1H), 7.49–7.38 (m, 2H), 6.36 (dd, *J* = 8.1 and 6.3 Hz, 1H), 6.18 (d, *J* = 8.1 Hz, 1H), 5.20 (s, 1H), 3.66 (m, 1H), 3.23 (s, 3H), 3.20 (m, 1H), 2.45 (m, 1H), 2.18–2.04 (m, 2H), 1.99–1.81 (m, 3H), 1.60 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.1, 166.2, 138.7, 133.6, 130.4, 130.1, 129.4, 128.7, 80.1, 73.4, 57.2, 52.8, 47.9, 42.0, 32.8, 27.6, 27.2.

IR ν_{max} 3060, 2943, 2902, 2875, 2828, 1739, 1726, 1601, 1585, 1453, 1315, 1267, 1106, 1071, 711 cm^{-1}.

Mass spectrum (ESI, +ve ionisation) *m/z* 335 [$(M + Na)^+$, 100%], 313 [$(M + H)^+$, 2], 163 (42), 131 (36).

HRMS Found: $(M + Na)^+$, 335.1258. $C_{19}H_{20}O_4$ requires $(M + Na)^+$, 335.1259.

Optical Rotation $[\alpha]_D$ = –129.8 (*c* 2.37, CH_2Cl_2).

Compounds 40 and 41

A solution of enone **39** (49 mg, 0.15 mmol) in dry benzene (10 mL) was irradiated at 300 nm in a Rayonet photochemical apparatus for 2 h at which point all of the starting material had been consumed. Accordingly, the reaction mixture was concentrated under reduced pressure and the resulting light-yellow oil was subjected to flash column chromatography (silica gel, 1:9 → 1:4 v/v ethyl acetate/hexane gradient elution) and thereby affording two fractions, A and B.

Concentration of fraction A (R_f = 0.4 in 3:7 v/v ethyl acetate/hexane) afforded the *title compound **40*** (30 mg, 61%) as a clear, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–7.99 (m, 2H), 7.54 (m, 1H), 7.42–7.19 (m, 2H), 6.00 (m, 1H), 5.86 (d, *J* = 2.1 Hz, 1H), 5.73 (m, 1H), 3.69 (m, 1H), 3.45 (m, 1H), 3.18 (s, 3H), 2.34 (m, 1H), 2.25–1.98 (m, 4H), 1.85 (m, 1H), 1.70 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 165.2, 134.0, 130.2, 130.1, 129.8, 128.9, 119.1, 85.9, 84.2, 57.9, 55.9, 43.1, 37.4, 32.5, 28.4, 20.6.

IR ν_{max} 3034, 2931, 1789, 1726, 1601, 1584, 1451, 1314, 1264, 1116, 1063, 1025, 927, 709 cm^{-1}.

Mass spectrum (ESI, +ve ionisation) *m/z* 335 [$(M + Na)^+$, 100%], 313 [$(M + H)^+$, 78], 159 (80) 101 (87).

HRMS Found: $(M + Na)^+$, 335.1259. $C_{19}H_{20}O_4$ requires $(M + Na)^+$, 335.1259.

Optical Rotation $[\alpha]_D$ = +233.7 (*c* 0.32, CH_2Cl_2).

Concentration of fraction B (R_f = 0.5 in 3:7 v/v ethyl acetate/hexane) afforded a 4:1 mixture (as determined by ^{13}C NMR analysis) of the epimeric forms of *compound **41*** (8 mg, 16%) as a clear, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.10–7.90 (m, 2H), 7.49 (m, 1H), 7.40–7.33 (m, 2H), 5.80 (m, 1H), 5.62 (m, 1H), 4.10 (d, *J* = 6.9 Hz, 1H), 3.77 (m, 1H), 3.28 (s, 3H), 2.22 (m, 1H), 2.08 (m, 1H), 2.00–1.73 (m, 3H), 1.67–1.47 (m, 2H), 1.19 (m, 1H) (most of the signals arising from the minor diastereoisomer were obscured by those due to the major one).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 132.1, 132.0, 129.0, 128.5(0), 128.4(6), 128.3, 127.4(0), 127.3(6), 123.1, 119.4, 83.5, 83.1, 64.5, 61.4, 56.5, 56.3, 40.9, 35.3, 30.8, 28.7, 28.1, 27.6, 27.2, 26.0, 25.4, 23.6, 22.4, 20.9, 19.9 (two signals obscured or overlapping).
IR ν_{max} 3005, 2933, 2829, 2802, 1724, 1602, 1451, 1270, 1111, 710 cm^{-1}.
Mass spectrum (ESI, +ve ionisation) *m/z* 307 [$(M + Na)^+$, 13%], 247 (44), 102 (100).
HRMS Found: $(M + Na)^+$, 307.1311. $C_{18}H_{20}O_3$ requires $(M + Na)^+$, 307.1310.

Photochemically-induced Conversion of Cyclobutanone 40 into Cyclopropane 41

A solution of cyclobutanone **40** (6 mg, 0.02 mmol) in benzene-d_6 (1.5 mL) was irradiated at 300 nm in a Rayonet photochemical apparatus for 2 h. ^{1}H NMR analysis of the reaction mixture after this time indicated that all the starting material had been consumed. Accordingly, the reaction mixture was concentrated under reduced pressure and the resulting light-yellow oil subjected to flash column chromatography (silica gel, 1:9 v/v ethyl acetate/hexane) to give, after concentration of the appropriate fractions (R_f = 0.5 in 3:7 v/v ethyl acetate/hexane) cyclopropane **41** (4 mg, 73%) as a clear, colourless oil. This material was identical, in all respects, with an authentic sample.

Compounds 41 and 42

A solution of ketone **39** (52 mg, 0.17 mmol) in acetone (6mL of dry, degassed material) was irradiated at 300 nm in a Rayonet photochemical apparatus for 10 h. The reaction mixture was then concentrated under reduced pressure and the resulting light-yellow oil subjected to flash column chromatography (silica gel, 1:9 → 35:65 v/v ethyl acetate/hexane gradient elution) and thereby affording two fractions, A and B.

Concentration of fraction A (R_f = 0.5 in 3:7 v/v ethyl acetate/hexane) gave the *title compound **41*** (4 mg, 8%) as a clear, colourless oil. This material was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.3 in 3:7 v/v ethyl acetate/hexane) gave the *title compound* ***42*** (28 mg, 54%) as a clear, colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.96 (m, 2H), 7.53 (m, 1H), 7.44–7.35 (m, 2H), 5.62 (d, *J* = 1.5 Hz, 1H), 3.56 (m, 1H), 3.26 (s, 3H), 2.50 (m, 1H), 2.36 (ddd, *J* = 14.4, 6.3 and 2.4 Hz, 1H), 2.21–2.01 (m, 3H), 1.98–1.63 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.7, 165.8, 133.6, 130.3, 130.1, 128.7, 84.3, 81.2, 59.4, 57.4, 51.9, 35.6, 33.7, 32.3, 31.8, 30.6, 26.5.

IR ν_{max} 2935, 1723, 1451, 1268, 1122, 1096, 1025, 710 cm^{-1}.

Mass spectrum (ESI, +ve ionisation) *m/z* 335 [$(M + Na)^+$, 100%], 159 (28), 104 (31).

HRMS Found: $(M + Na)^+$, 335.1263. $C_{19}H_{20}O_4$ requires $(M + Na)^+$, 335.1259.

Optical Rotation $[\alpha]_D$ = +57.0 (*c* 0.31, CH_2Cl_2).

X-ray Crystallographic Studies

Data for Compound 25

$C_{14}H_{18}O_3$, M = 234.30, T = 200 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 6.3882(1), b = 10.3973(2), c = 18.3495(4) Å, V = 1218.77(4) Å^3, D_x = 1.277 g cm^{-3}, 1631 unique data ($2\theta_{max}$ = 55°), refinement on F using 1293 reflections with $I > 3.0\sigma(I)$; R = 0.0258, Rw = 0.0301, S = 1.1495.

Data for Compound 26

$C_{14}H_{18}O_3$, M = 234.30, T = 200 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 6.2050(1), b = 11.5001(3), c = 17.0648(5) Å, V = 1217.71(5) Å^3, D_x = 1.278 g cm^{-3}, 1612 unique data ($2\theta_{max}$ = 55°), refinement on F using 1169 reflections with $I > 3.0\sigma(I)$; R = 0.0286, Rw = 0.0331, S = 1.1573.

Data for Compound 27

$C_{18}H_{18}O_3$, M = 282.34, T = 200 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 9.7159(2), b = 9.7758(2), c = 14.8253(4) Å, V = 1408.12(6) Å^3, D_x = 1.332 g cm^{-3}, 2326 unique data ($2\theta_{max}$ = 60°), refinement on F^2 using all data, R = 0.030 [for 2075 reflections with $I > 2.0\sigma(I)$]; Rw = 0.081, S = 0.96.

Data for Compound 29

$C_{16}H_{22}O_3$, M = 262.35, T = 200 K, monoclinic, space group $P2_1$, Z = 4, a = 6.3467(2), b = 21.7077(6), c = 10.3198(3) Å, β = 90.9585(16)°, V = 1421.58(7) Å^3, D_x = 1.226 g cm^{-3}, 2589 unique data ($2\theta_{max}$ = 50°), refinement on F using 2064 reflections with $I > 2.0\sigma(I)$; R = 0.028, Rw = 0.031, S = 1.19.

Data for Compound 34

$C_{24}H_{28}N_2O_8$, M = 472.49, T = 200 K, monoclinic, space group $P2_1$, Z = 2, a = 9.1347(6), b = 6.1641(4), c = 21.3826(15) Å, β = 98.820(3)°, V = 1189.76(14) Å^3, D_x = 1.319 g cm^{-3}, 2322 unique data ($2\theta_{max}$ = 50°), refinement on F using 1661 reflections with $I > 1.5\sigma(I)$; R = 0.082, Rw = 0.077, S = 1.15.

Data for Compound 35

$C_{14}H_{20}O_3$, M = 236.31, T = 200 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 6.3638(1), b = 12.4427(3), c = 15.6175(4) Å, V = 1236.64.(5) Å^3, D_x = 1.269 g cm^{-3}, 2075 unique data ($2\theta_{max}$ = 60°), refinement on F^2 using all data, R = 0.032 [for 1595 reflections with $I > 2.0\sigma(I)$]; Rw = 0.070, S = 0.81.

Structure Determination

Images were measured on a Nonius Kappa CCD diffractometer (MoKa, graphite monochromator, l = 0.71073 Å) and data extracted using the DENZO package.[11] Structure solution was by direct methods (SIR92).[12] The structures of the abovementioned compounds were refined using the CRYSTALS program package.[13] Atomic coordinates, bond lengths and angles, and displacement parameters for these compounds have been deposited at the Cambridge Crystallographic Data Centre. Deposition numbers are: 747028 (for **25**), 747029 (for **26**), 747030 (for **27**), 747031 (for **29**), 747032 (for **34**) and 750107 (for **35**). These data can be obtained free-of-charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

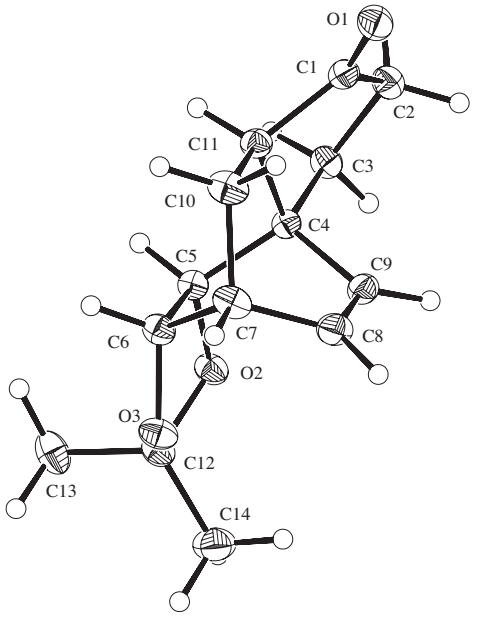

Figure S1. Molecular structure of $C_{14}H_{18}O_3$ (compound **25**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

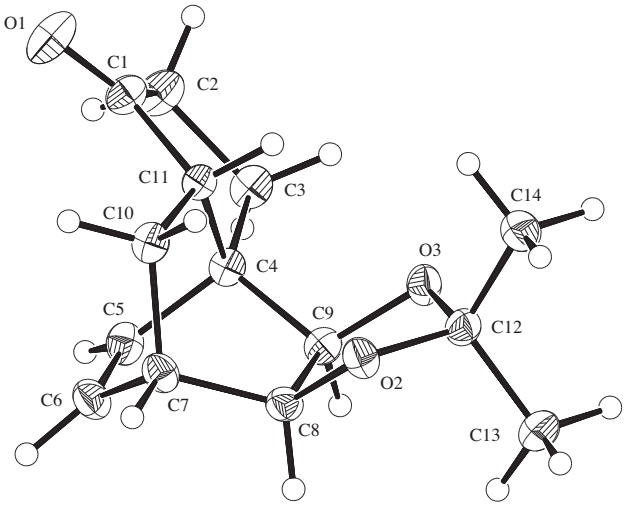

Figure S2. Molecular structure of $C_{14}H_{18}O_3$ (compound **26**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

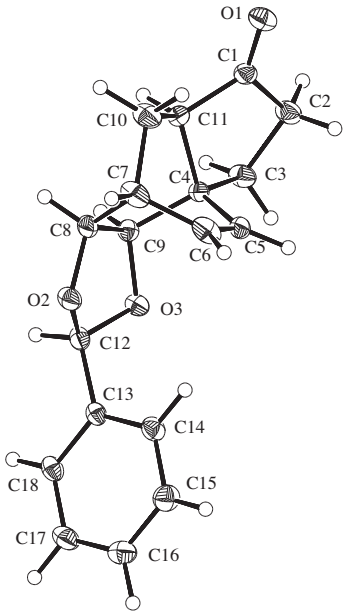

Figure S3. Molecular structure of $C_{18}H_{18}O_3$ (compound **27**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

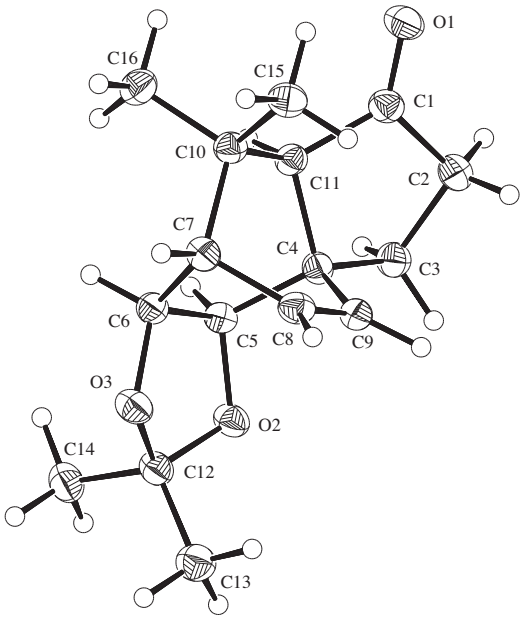

Figure S4. Molecular structure of <u>molecule one</u> of $C_{16}H_{22}O_3$ (compound **29**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

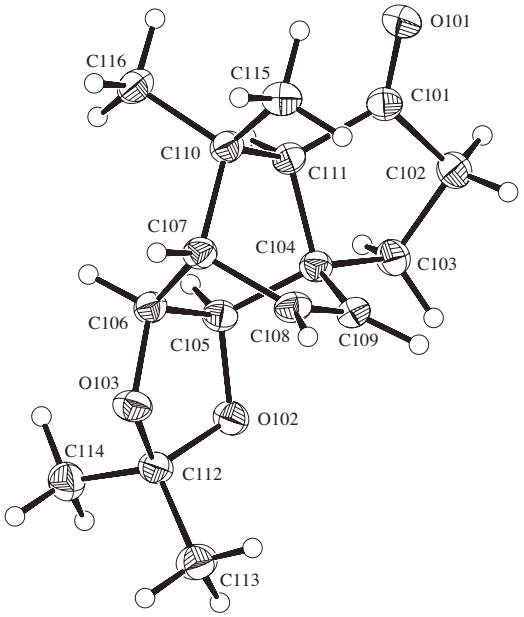

Figure S5. Molecular structure of <u>molecule two</u> of $C_{16}H_{22}O_3$ (compound **29**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

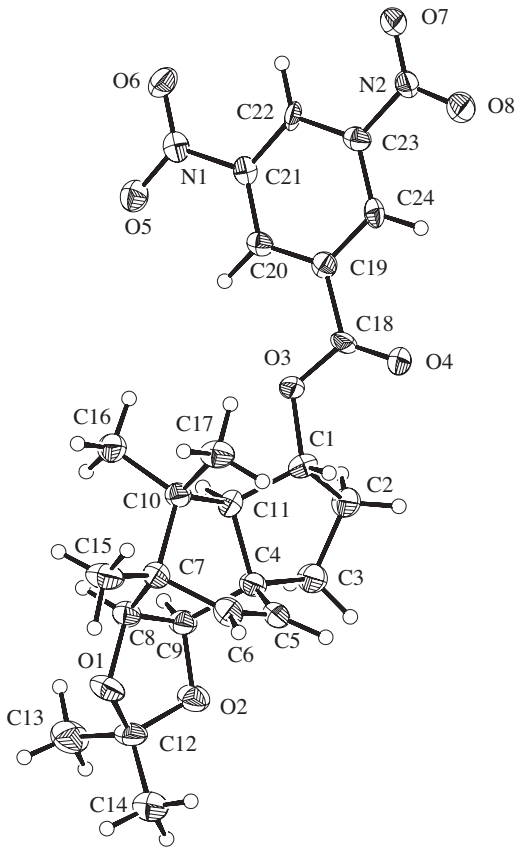

Figure S6. Molecular structure of $C_{24}H_{28}N_2O_8$ (compound **34**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

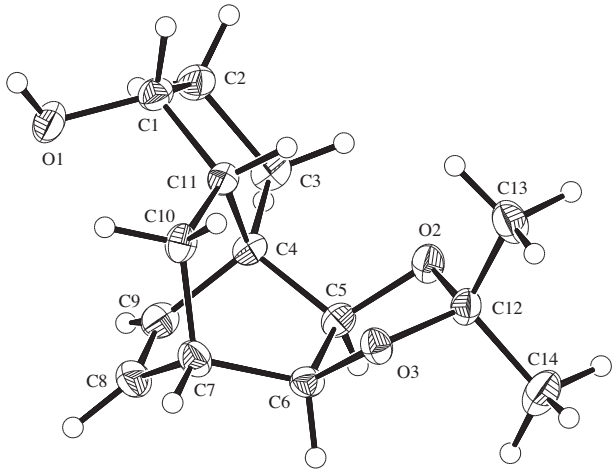

Figure S7. Molecular structure of $C_{14}H_{20}O_3$ (compound **35**) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

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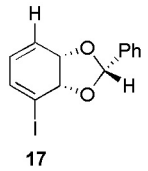
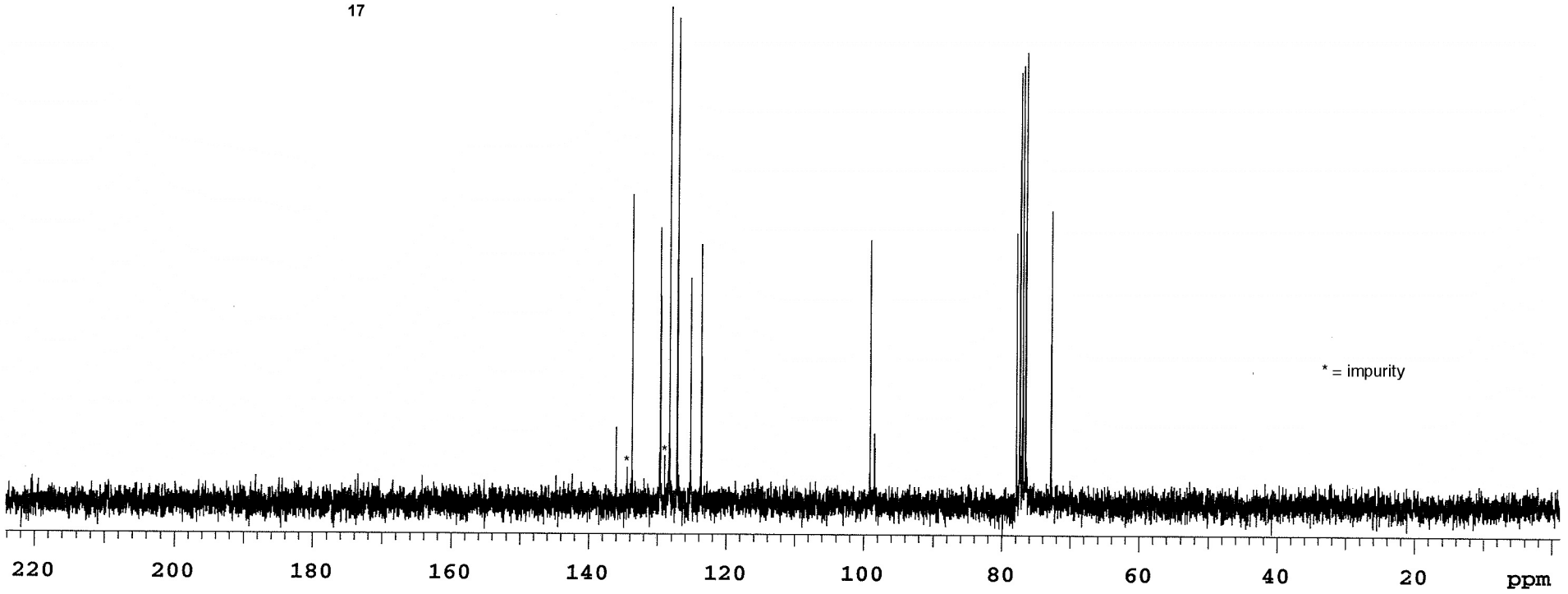
Selected ^{1}H and/or ^{13}C NMR Spectra of Compounds 17–42

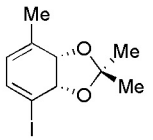
75 MHz ^{13}C NMR Spectrum of Compound **17** Recorded in $CDCl_3$



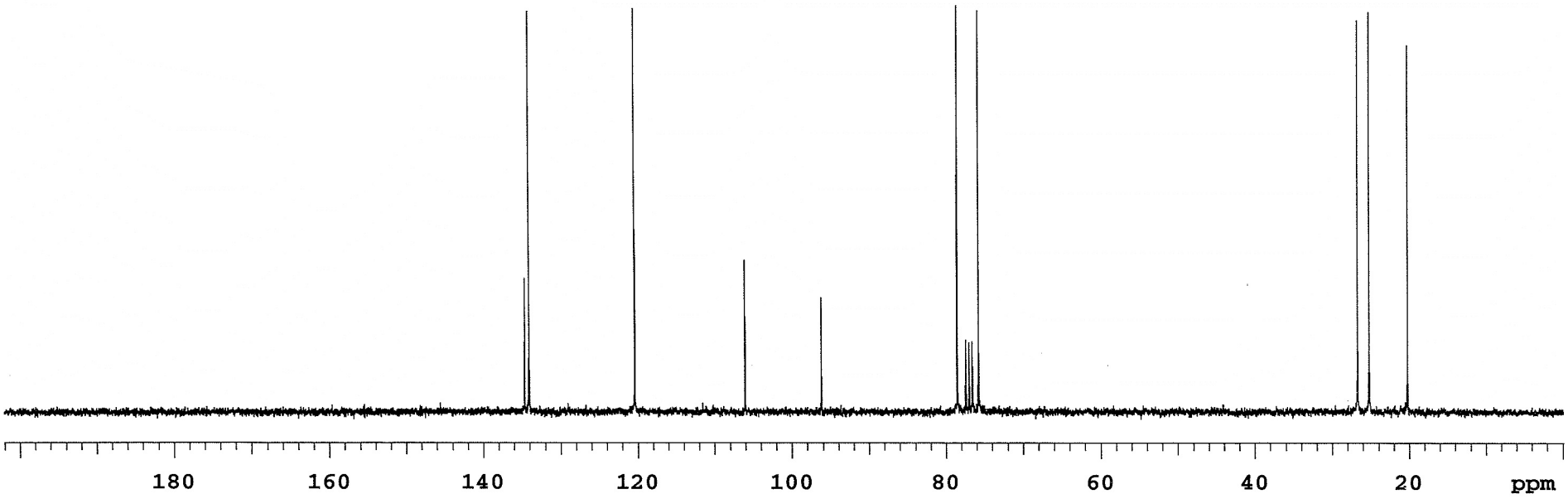
17



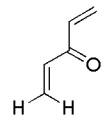
75 MHz ^{13}C NMR Spectrum of Compound **18** Recorded in $CDCl_3$



18

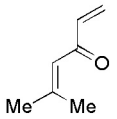


75 MHz ^{13}C NMR Spectrum of Compound **19** as a 60% solution in Et_2O/Pentane Recorded in $CDCl_3$



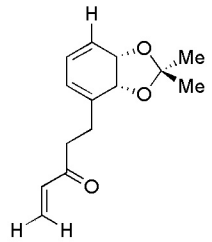
19

300 MHz ^{1}H NMR Spectrum of Compound **20** Recorded in $CDCl_3$



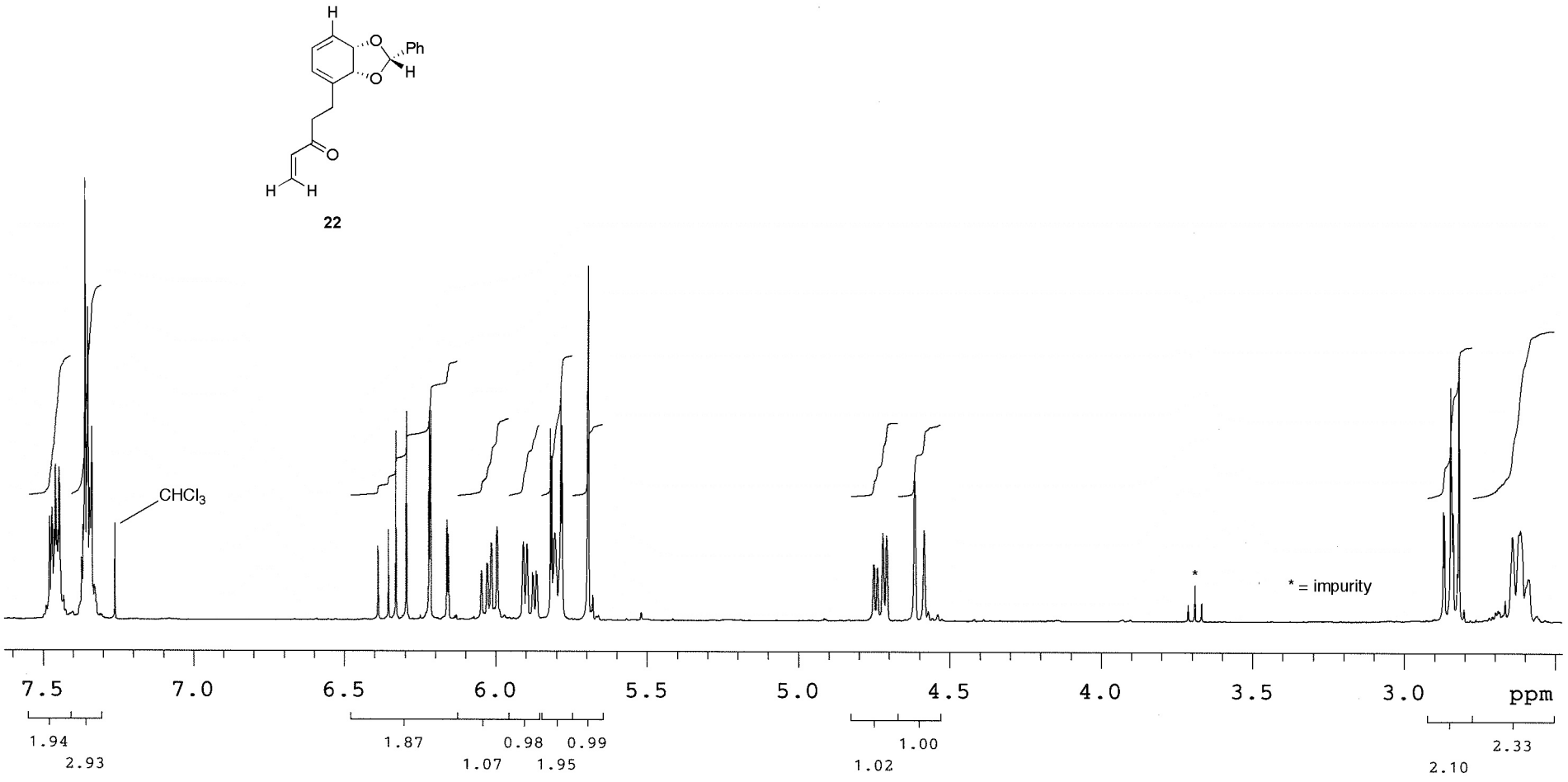
20

300 MHz ^{1}H NMR Spectrum of Compound **21** Recorded in $CDCl_3$

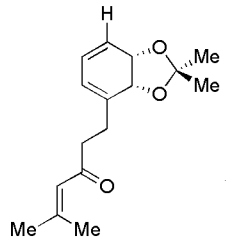


21

300 MHz ^{1}H NMR Spectrum of Compound **22** Recorded in $CDCl_3$

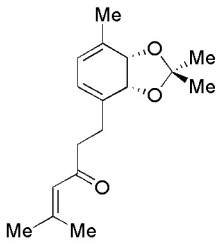


75 MHz ^{13}C NMR Spectrum of Compound **23** Recorded in $CDCl_3$



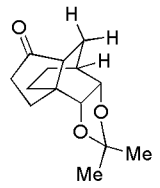
23

300 MHz ^{1}H NMR Spectrum of Compound **24** Recorded in $CDCl_3$



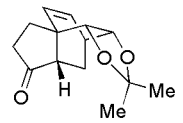
24

300 MHz ^{1}H NMR Spectrum of Compound **25** Recorded in $CDCl_3$



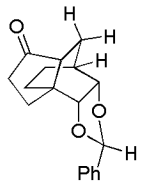
25

300 MHz ^{1}H NMR Spectrum of Compound **26** Recorded in $CDCl_3$



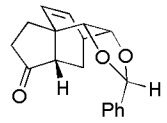
26

75 MHz ^{13}C NMR Spectrum of Compound **27** Recorded in $CDCl_3$



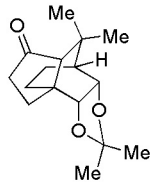
27

75 MHz ^{13}C NMR Spectrum of Compound **28** Recorded in $CDCl_3$

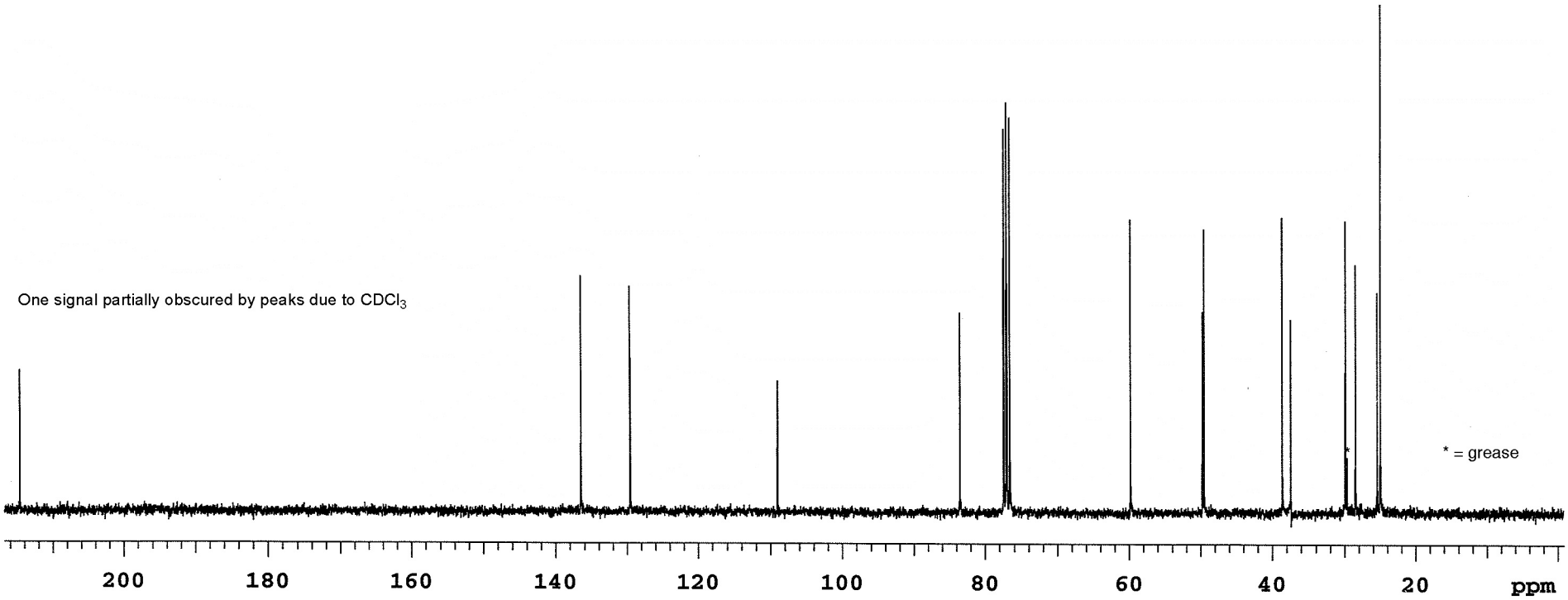


28

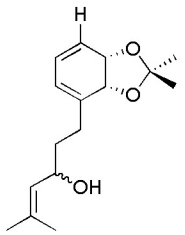
75 MHz ^{13}C NMR Spectrum of Compound **29** Recorded in $CDCl_3$



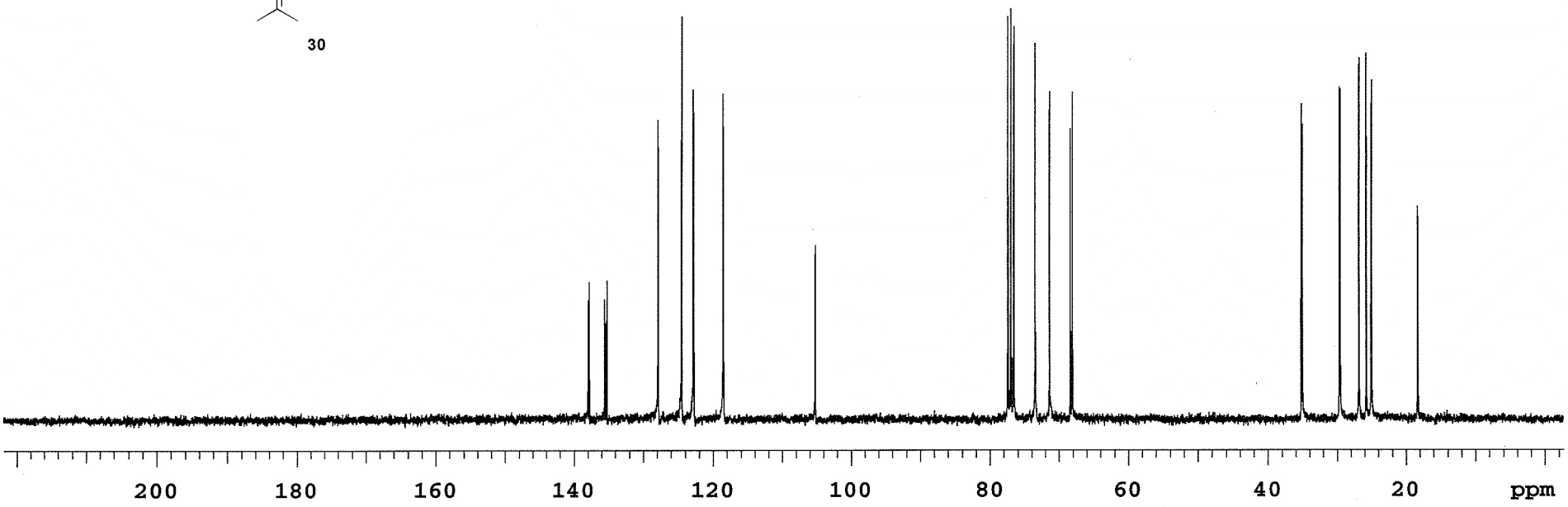
29



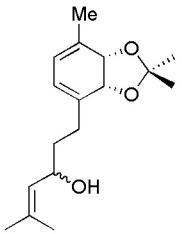
75 MHz ^{13}C NMR Spectrum of a *ca.* 1:1 Mixture of the Diastereoisomeric Forms of Compound **30** Recorded in $CDCl_3$



30

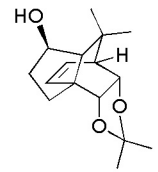


75 MHz ^{13}C NMR Spectrum of a *ca.* 1:1 Mixture of the Diastereoisomeric Forms of Compound **31** Recorded in $CDCl_3$



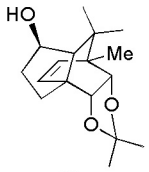
31

300 MHz ^{1}H NMR Spectrum of Compound **32** Recorded in $CDCl_3$



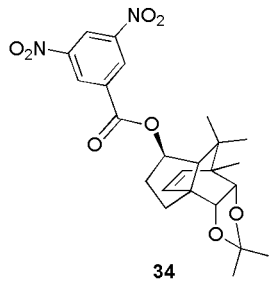
32

75 MHz ^{13}C NMR Spectrum of Compound **33** Recorded in $CDCl_3$



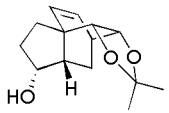
33

500 MHz ^{1}H NMR Spectrum of Compound **34** Recorded in $CDCl_3$



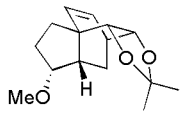
34

300 MHz ^{1}H NMR Spectrum of Compound **35** Recorded in $CDCl_3$



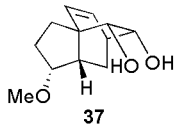
35

300 MHz ^{1}H NMR Spectrum of Compound **36** Recorded in $CDCl_3$



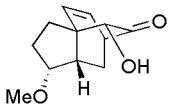
36

300 MHz ^{1}H NMR Spectrum of Compound **37** Recorded in $CDCl_3$



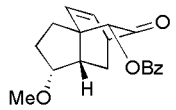
37

75 MHz ^{13}C NMR Spectrum of Compound **38** Recorded in $CDCl_3$



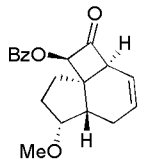
38

300 MHz ^{1}H NMR Spectrum of Compound **39** Recorded in $CDCl_3$



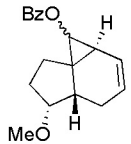
39

75 MHz ^{13}C NMR Spectrum of Compound **40** Recorded in $CDCl_3$



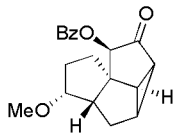
40

75 MHz ^{13}C NMR Spectrum of a *ca.* 4:1 Mixture of the Diastereoisomeric Forms of Compound **41** Recorded in $CDCl_3$



41

300 MHz ^{1}H NMR Spectrum of Compound **42** Recorded in $CDCl_3$



42