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Stereoselective Aziridination of Cyclic Allylic Alcohols Using Chloramine-T

Susannah C. Coote, Peter O'Brien* and Adrian C. Whitwood

Department of Chemistry, University of York, Heslington, York YO10 5DD UK. Fax: +44 1904 432516; Tel: +44 1904 432535; E-mail: paob1@york.ac.uk

Supporting Information Available: Additional experimental procedures (synthesis of allylic alcohols) are available as supplementary data.

General:

All non-aqueous reactions were carried out under O_2-free N_2 or Ar using oven-dried glassware. CH_2Cl_2 was dried on an Mbraun SPS solvent purification system. Et_2O and THF were distilled from sodium and benzophenone. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C and was purchased in Winchester quantities. Brine refers to a saturated aqueous solution of NaCl. Water is distilled water.

Flash chromatography was carried out using Fluka Chemie GmbH silica (220-440 mesh). Thin layer chromatography was carried out using commercially available Merck F_{254} aluminium-backed silica plates. Proton (400 or 270 MHz) and carbon (100.6 or 67.9 MHz) NMR spectra were recorded on a Jeol ECX-400 instrument or a Jeol EX-270 instrument using an internal deuterium lock. For samples recorded as solutions in $CDCl_3$, chemical shifts are quoted in parts per million relative to $CHCl_3$ (δ_H 7.27) and $CDCl_3$ (δ_C 77.0, central line of triplet). For samples recorded as a solution in C_6D_6, chemical shifts are quoted in parts per million relative to C_6D_5H (δ_H 7.16) and C_6D_6 (δ_C 128.0, central line of the triplet). Carbon NMR spectra were recorded with broad band proton decoupling and were assigned using DEPT experiments. Coupling constants (*J*) are quoted in Hertz. Melting points were carried out on a Gallenkamp melting point apparatus. Boiling points given for compounds purified by Kugelrohr distillation correspond to the oven temperature during distillation. Infra-red spectra were recorded on a Nicolet IR100 FT-IR spectrometer or an ATI Mattson Genesis FT-IR spectrometer. Chemical ionization high and low

resolution mass spectra were recorded on a Fisons Analytical (VG) Autospec spectrometer. Electrospray high and low resolution mass spectra were recorded on a Bruker Daltronics micrOTOF spectrometer.

General Procedures:

General procedure A: preparation of 3-substituted enones

A solution of organolithium reagent (1.1 eq.) was added dropwise to a stirred solution of 3-ethoxy-2-cyclohexen-1-one (6.4 mmol) in THF (15 mL) at –78 ˚C under nitrogen. After sirring for 30 min at –78 ˚C, the reaction mixture was allowed to warm to 0 ˚C. 5% $H_2SO_{4(aq)}$ (5 mL) was added, and the resulting mixture stirred at 0 ˚C for 30 min. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with saturated $Na_2CO_{3(aq)}$ (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product.

General procedure B: Luche reduction of enones

$NaBH_4$ (1.2 eq.) was added portionwise to a stirred solution of enone (2.3 mmol) and $CeCl_3.7H_2O$ (1.2 eq.) in MeOH (10 mL) at 0 ˚C. The resulting suspension was allowed to warm to rt and stirred at rt for 30 min. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with water (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

General procedure C: preparation of tertiary alcohols using Grignard reagents

Grignard reagent (1.5 eq.) was added dropwise to a stirred solution of enone (1.7 mmol) in THF (8 mL) at 0 ˚C under nitrogen. The resulting solution was allowed to warm to rt and stirred at rt for 12 h. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

General procedure D: preparation of tertiary alcohols using organolithium reagents

Organolithium reagent (1.1 eq.) was added dropwise to a stirred solution of enone (10.2 mmol) in Et_2O (15 mL) at –78 ˚C under nitrogen. The resulting solution was stirred at –78 ˚C for 15 min, then water (1 mL) was added, and the reaction mixture was allowed to warm to rt. Saturated $NH_4Cl_{(aq)}$ (5 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product.

Synthesis and characterisation data of allylic alcohols:

3-Butylcyclohex-2-en-1-one 16

Using general procedure A, *n*-butyllithium (6.7 mL of a 1.06 M solution in hexanes, 7.0 mmol) and 3-ethoxy-2-cyclohexen-1-one **15** (900 mg, 6.4 mmol) in THF (15 mL) gave the crude product. Purification by Kugelrohr distillation gave enone **16** (681 mg, 70%) as a colourless oil, bp 130-150 ºC/35 mm Hg (lit.,[1] 92-95 ºC/26 mm Hg); R_F(1:1 petrol-Et_2O) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (s, 1H, =CH), 2.33 (t, J = 6.0, 2H, CH_2), 2.26 (t, J = 6.0, 2H, CH_2), 2.21 (t, J = 7.0, 2H, CH_2), 1.96 (app. quintet, J = 6.0, 2H, CH_2), 1.47 (app. quintet, J = 7.0, 2H, CH_2), 1.32 (app. sextet, J = 7.0, 2H, CH_2), 1.26 (t, J = 7.0, 3H, Me). Spectroscopic data consistent with those reported in the literature.[1]

3-Allylcyclohex-2-en-1-one 17

A solution of 3-ethoxy-2-cyclohexen-1-one **15** (1.0 g, 7.1 mmol) in THF (8 mL) was added dropwise *via* cannula to a stirred solution of allyl magnesium chloride (7.1 mL of a 2.00 M solution in THF, 14.2 mmol) in THF (20 mL) at 0 ˚C under nitrogen. The resulting solution was allowed to warm to rt and stirred for 4 h. The solution was cooled to 0 ˚C, 5% $H_2SO_{4(aq)}$ (5 mL) was added, and the resulting mixture was stirred for 30 min. The layers were separated, and the aqueous layer extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with saturated $Na_2CO_{3(aq)}$ (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone

17 as a colourless oil (902 mg, 93%), bp 115-135 ˚C/15 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90-5.85 (m, 1H, =CH), 5.83-5.71 (m, 1H, =CH), 5.16-5.09 (m, 2H, =CH_2), 2.95-2.93 (br m, 2H, CH_2CH=CH_2), 2.38-2.33 (m, 2H, CH_2), 2.32-2.28 (m, 2H, CH_2), 2.02-1.96 (m, 2H, CH_2). Spectroscopic data consistent with those reported in the literature.[2]

3-(3-Butenyl)-2-cyclohexen-1-one 18

Magnesium turnings (1.22 g, 50.0 mmol) were stirred for 30 min in a flame-dried flask at rt under argon. THF (30 mL) was added, and the resulting suspension stirred for 15 min. Then, a solution of 4-bromo-1-butene (3.0 mL, 30.0 mmol) in THF (20 mL) was added dropwise *via* cannula in order to maintain a gentle reflux. The resulting suspension was heated at reflux for 10 min, then cooled to 0 ºC. A solution of 3-ethoxy-2-cyclohexen-1-one **15** (3.5 mL, 25.0 mmol) in THF (10 mL) was added dropwise *via* cannula and the reaction mixture was heated at reflux for 30 min. The reaction mixture was allowed to cool to rt and saturated $NH_4Cl_{(aq)}$ (25 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with water (30 mL) and brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone **18** (2.58 g, 69%) as a colourless oil, bp 170-190 ºC/20 mm Hg, R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (br t, J = 1.0, 1H, =CH), 5.78 (ddt, J = 17.5, 10.5, 6.5, 1H, CH=CH_2), 5.05 (ddt, J = 17.5, 3.0, 1.0, 1H, CH=CH_AH$_B$), 5.00 (ddd, J = 10.5, 3.0, 1.0, 1H, CH=CH$_A$$H_B$), 2.36 (app. br t, J = 6.5, 2H, CH_2CH=CH_2), 2.31-2.26 (m, 6H, 6 x CH), 1.97 (quintet, J = 6.5, 2H, CH_2). Spectroscopic data consistent with those reported in the literature.[3]

3-Isopropylcyclohex-2-en-1-one 19

Using general procedure A, *iso*-propyllithium (16.3 mL of a 0.48 M solution in pentane, 7.8 mmol) and 3-ethoxy-2-cyclohexen-1-one **15** (1.0 g, 7.1 mmol) in THF (15 mL) gave the crude product. Purification by Kugelrohr distillation gave enone **19** (524 mg, 53%) as a colourless oil, bp 115-135 ºC/15 mm Hg (lit.,[4] 100 ºC/14 mm Hg); R_F(1:1 petrol-Et_2O) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H, =CH), 2.43 (septet, J = 7.0, 1H, CHMe$_2$), 2.34 (t, J = 7.0, 2H, CH_2), 2.28 (t, J = 6.5, 2H, CH_2),

1.96 (app. quintet, J = 7.0, 2H, CH_2), 1.077 (d, J = 7.0, 3H, Me), 1.075 (d, J = 7.0, 3H, Me). Spectroscopic data consistent with those reported in the literature.[5]

3-*tert*-Butylcyclohex-2-en-1-one 20

Using general procedure A, *tert*-butyllithium (8.5 mL of a 1.20 M solution in pentane, 9.0 mmol) and 3-ethoxy-2-cyclohexen-1-one **15** (1.2 g, 8.2 mmol) in THF (25 mL) gave the crude product. Purification by Kugelrohr distillation gave enone **20** (717 mg, 57%) as a colourless oil, bp 100-110 ºC/9 mm Hg (lit.,[6] 80-81 ºC/4 mm Hg); $R_F(Et_2O)$ 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (t, J = 1.0, 1H, =CH), 2.36-2.32 (m, 4H, 2 x CH_2), 1.95 (app. quintet, J = 6.5, 2H, CH_2), 1.11 (s, 9H, CMe_3). Spectroscopic data consistent with those reported in the literature.[7]

3-Phenylcyclohex-2-en-1-one 21

Using general procedure A, phenyllithium (2.5 mL of a 1.70 M solution in dibutyl ether, 4.3 mmol) and 3-ethoxy-2-cyclohexen-1-one **15** (543 mg, 3.9 mmol) in THF (10 mL) gave the crude product. Purification by Kugelrohr distillation (220-240 ºC/5 mm Hg (lit.,[8] 130-140 ºC/0.6 mm Hg)) gave enone **21** (453 mg, 68%) as a white solid, mp 64-65 ºC (lit.,[9] 64-65 ºC); R_F(1:1petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H, Ph), 7.43-7.40 (m, 3H, Ph), 6.43 (t, J = 1.5, 1H, =CH), 2.78 (td, J = 6.5, 1.5, 2H, CH_2), 2.49 (br t, J = 6.5, 2H, CH_2), 2.16 (app. quintet, J = 6.5, 2H, CH_2). Spectroscopic data consistent with those reported in the literature.[10]

3-(3-Butenyl)-2-cyclopenten-1-one 25

Magnesium turnings (457 mg, 18.8 mmol) were stirred for 1 h in a flame-dried flask at rt under argon. THF (10 mL) was added, and the resulting suspension stirred for 15 min. Then, a solution of 4-bromo-1-butene (1.1 mL, 10.9 mmol) in THF (5 mL) was added dropwise *via* cannula. The resulting suspension was heated at reflux for 30 min, then cooled to 0 ºC. A solution of 3-ethoxycyclopent-2-en-1-one **24** (1.0 mL, 8.4 mmol) in THF (2 mL) was added dropwise *via* cannula and the reaction mixture was stirred at rt for 2 h. Then, the reaction mixture was poured onto a mixture of ice (3 g) and 5% $H_2SO_{4(aq)}$ and the resulting mixture stirred for 30 min. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with saturated $NaHCO_{3(aq)}$ (20 mL), water (20 mL) and

brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone **25** (758 mg, 67%) as a colourless oil, bp 140-150 ºC/20 mm Hg, R_F(1:1 petrol-Et_2O) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.90 (m, 1H, =CH), 5.71-5.61 (m, 1H, C*H*=CH_2), 5.04 (ddt, *J* = 10.0, 2.0, 1.0, 1H, CH=CH_AH_B), 5.01 (app. dq, *J* = 17.0, 2.0, 1H, CH=CH_AH_B), 2.14-2.12 (m, 2H, 2 x CH), 2.02-1.92 (m, 4H, 4 x CH), 1.88-1.85 (m, 2H, 2 x CH). Spectroscopic data consistent with those reported in the literature.[11]

1-Allylcyclopent-2-en-1-ol 26

A solution of cyclopentenone **22** (5.1 mL, 60.9 mmol) in THF (10 mL) was added dropwise to a stirred solution of allylmagnesium chloride (36.5 mL of a 2.0 M solution in THF, 73.1 mmol) in THF (40 mL) at 0 °C under N_2. After being allowed to warm to rt the reaction mixture was stirred for 2 h, then cooled to 0 °C. Saturated $NH_4Cl_{(aq)}$ (40 mL) was added, the resulting mixture was stirred at rt for 15 min and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with brine (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave allylic alcohol **26** (7.13 g, 94%) as a colourless oil, bp 70-75 °C/1.5 mm Hg; R_F(1:1 petrol-EtOAc) 0.5; ^{1}H NMR (400 MHz, C_6D_6) δ 5.92 (ddt, *J* = 18.0, 10.0, 7.5, 1H, C*H*=CH_2), 5.66-5.62 (br m, 2H, CH=CH), 5.09-5.05 (m, 2H, CH=CH_2) 2.37 (d, *J* = 7.5, 2H, CH_2-CH=CH_2), 2.32-2.27 (m, 1H), 2.09-2.01 (m, 1H), 1.94-1.88 (m, 1H), 1.84 (s, 1H, OH), 1.80-1.74 (m, 1H). Spectroscopic data are comparable with those reported in $CDCl_3$ in the literature.[12]

3-Allyl-2-cyclopenten-1-one 27

PDC (9.87 g, 26.2 mmol) was added in one portion to a stirred solution of allylic alcohol **26** (1.63 g, 13.1 mmol) in CH_2Cl_2 (20 mL) at rt under N_2. The resulting brown suspension was stirred vigorously at rt for 6 h and then Et_2O (20 mL) was added. The solids were removed by filtration through a plug of silica and washed with Et_2O (200 mL). The filtrate was evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave enone **27** (986 mg, 62%) as a pale yellow oil, bp 110-115 °C/1.9 mm Hg; R_F(1:1 hexane-EtOAc) 0.4; ^{1}H NMR (400 MHz, C_6D_6) δ 5.84 (s, 1H, =CH), 5.51 (ddt, *J* = 18.0, 10.0, 7.0, 1H, C*H*=CH_2), 4.95 (dq, *J* =

10.0, 2.0, 1H, *cis*-CH=CH_AH$_B$), 4.88 (dq, *J* = 18.0, 2.0, 1H, *trans*-CH=CH$_A$$H_B$), 2.52 (d, *J* = 7.0, 2H, CH_2-CH=CH$_2$), 2.04-2.01 (m, 2H), 1.82-1.80 (m, 2H). Spectroscopic data are comparable with those reported in $CDCl_3$ in the literature.[13]

Cyclohex-2-en-1-ol 1

Using general procedure B, cyclohex-2-enone **13** (2.2 mL, 22.7 mmol), $CeCl_3.7H_2O$ (10.20 g, 27.2 mmol) and $NaBH_4$ (990 mg, 26.1 mmol) in MeOH (100 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **1** (960 mg, 43%) as a colourless oil, bp 140-150 ºC/75 mm Hg (lit.,[14] 68-70 ºC/20 mm Hg); R_F(Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (dtd, *J* = 10.0, 3.5 and 1.0, 1H, =CH), 5.75 (ddt, *J* = 10.0, 3.5 and 2.0, 1H, =CH), 4.20 (br s, 1H, CHO), 2.09-1.83 (m, 2H, 2 x CH and OH), 1.77-1.69 (m, 1H, CH), 1.64-1.54 (m, 3H, 3 x CH). Spectroscopic data consistent with those reported in the literature.[14]

3-Methylcyclohex-2-en-1-ol 28

Using general procedure B, 3-methylcyclohex-2-enone **14** (1.3 mL, 11.0 mmol), $CeCl_3.7H_2O$ (4.92 g, 13.2 mmol) and $NaBH_4$ (484 mg, 12.7 mmol) in MeOH (50 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **28** (790 mg, 64%) as a colourless oil, bp 175-185 ºC/75 mm Hg (lit.,[15] 56 ºC/1 mm Hg); R_F(Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52-5.50 (m, 1H, =CH), 4.21-4.16 (m, 1H, CHO), 2.01-1.82 (m, 2H, 2 x CH), 1.81-1.72 (m, 2H, 2 x CH), 1.70 (s, 3H, Me), 1.61-1.56 (m, 2H, 2 x CH), 1.39 (br s, 1H, OH). Spectroscopic data consistent with those reported in the literature.[15]

3-Butylcyclohex-2-en-1-ol 29

Using general procedure B, 3-butylcyclohex-2-en-1-one **16** (350 mg, 2.3 mmol), $CeCl_3.7H_2O$ (1.04 g, 2.8 mmol) and $NaBH_4$ (100 mg, 2.7 mmol) in MeOH (10 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **29** (289 mg, 81%) as a colourless oil, bp 150-160 ºC/10 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51-5.48 (br m, 1H, =CH), 4.21-4.18 (br m, 1H, CHO), 1.99-1.89 (m, 4H, 2 x CH_2), 1.83-1.69 (m, 2H, CH_2), 1.62-1.55 (m, 2H, CH_2), 1.43-1.35 (m, 2H, CH_2), 1.29 (app. br sextet, *J* =7.0, 2H, CH_2), 0.90 (t, *J* = 7.0, 3H, Me). Spectroscopic data consistent with those reported in the literature.[16]

3-Allylcyclohex-2-en-1-ol 30

Using general procedure B, 3-allylcyclohex-2-enone **17** (318 mg, 2.3 mmol), $CeCl_3.7H_2O$ (1.04 g, 2.8 mmol) and $NaBH_4$ (100 mg, 2.7 mmol) in MeOH (10 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **30** (209 mg, 66%) as a colourless oil, bp 140-150 ºC/10 mm Hg; R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83-5.79 (m, 1H, =CH), 5.53-5.52 (m, 1H, =CH), 5.07-5.02 (m, 2H, $=CH_2$), 4.20 (br s, 1H, CHO), 2.71 (app.br d, J = 7.0, 2H, $CH_2CH=CH_2$), 2.00-1.89 (m, 2H, CH_2), 1.84-1.69 (m, 2H, CH_2), 1.62-1.53 (m, 3H, CH_2 and OH). Spectroscopic data consistent with those reported in the literature.[17]

3-(3-Butenyl)-2-cyclohexen-1-ol 31

Using general procedure B, enone **18** (1.47 g, 9.8 mmol), $CeCl_3.7H_2O$ (4.5 g, 11.7 mmol) and $NaBH_4$ (426 mg, 11.3 mmol) in MeOH (60 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **31** (1.41 g, 95%) as a colourless oil, bp 130-135 ºC/2 mm Hg, R_F(1:1 petrol-Et_2O) 0.4; IR ($CHCl_3$) 3606 (OH), 3018, 2931, 2862, 1639 (C=C), 1439, 1219,1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.0, 10.5, 6.5, 1H, $CH=CH_2$), 5.50 (br t, J = 2.0, 1H, =CH), 5.01 (ddd, J = 17.0, 3.5, 1.5, 1H, $CH=CH_AH_B$), 4.95 (br d, J = 10.5, 1H, $CH=CH_AH_B$), 4.19 (br s, 1H, CHO), 2.20-2.14 (m, 2H, 2 x CH), 2.07-2.03 (m, 2H, 2 x CH), 1.98-1.86 (m, 2H, 2 x CH), 1.83-1.68 (m, 2H, 2 x CH), 1.65 (br s, 1H, OH), 1.62-1.53 (m, 2H, 2 x CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.6 (=C), 138.3 (=CH), 124.0 (=CH), 114.5 ($=CH_2$), 65.8 (CHO), 36.8 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 28.5 (CH_2), 19.4 (CH_2); MS (CI, NH_3) *m/z* 152 [$(M + H)^+$, 6], 137 (10), 134 (61), 123 (33), 119 (31), 110 (27), 97 (100), 91 (27), 79 (22), 67 (17), 55 (28), 41 (30); HRMS (CI, NH_3) *m/z* calcd for $C_{10}H_{16}O$ $(M + H)^+$ 152.1201, found 152.1206.

3-Isopropylcyclohex-2-en-1-ol 32

Using general procedure B, 3-isopropylcyclohex-2-en-1-one **19** (200 mg, 1.5 mmol), $CeCl_3.7H_2O$ (667 mg, 1.8 mmol) and $NaBH_4$ (63 mg, 1.7 mmol) in MeOH (10 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **32** (155 mg, 75%) as a colourless oil, bp 115-130 ºC/10 mm Hg; R_F(1:1 petrol-Et_2O) 0.5; IR (film) 3338 (OH), 2959, 2932, 2869, 1463, 1382, 1286, 1058, 1008, 999, 972, 911

cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48-5.46 (m, 1H, =CH), 4.18 (app. quintet, J = 3.5, 1H, CHO), 2.17 (septet, J = 7.0, 1H, C*H*Me_2), 2.10-1.84 (m, 2H, 2 x CH), 1.82-1.66 (m, 2H, 2 x CH), 1.60-1.53 (m, 3H, 2 x CH and OH), 1.00 (d, J = 7.0, 3H, Me), 0.99 (d, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 148.0 (=C), 121.3 (=CH), 66.0 (CHO), 34.9 (*C*HMe_2), 32.1 (CH_2), 26.1 (CH_2), 21.2 (Me), 21.1 (Me), 19.3 (CH_2); MS (CI, NH_3) *m/z* 123 [$(M - OH)^+$, 100]; HRMS (CI, NH_3) *m/z*: $[M - OH]^+$ calcd for $C_9H_{16}O$, 123.1174; found, 123.1173.

3-*tert*-Butylcyclohex-2-en-1-ol 33

Using general procedure B, 3-*tert*-butylcyclohex-2-en-1-one **20** (350 mg, 2.3 mmol), $CeCl_3.7H_2O$ (1.04 g, 2.8 mmol) and $NaBH_4$ (100 mg, 2.7 mmol) in MeOH (15 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **33** (301 mg, 85%) as a colourless oil, bp 200-230 ºC/65 mm Hg; R_F(1:1 petrol-Et_2O) 0.5; IR (film) 3328 (OH), 2935, 2867, 1478, 1364, 1248, 1058, 999, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 (dt, J = 3.5, 1.5, 1H, =CH), 4.24-4.20 (m, 1H, CHO), 2.10-2.02 (m, 1H, CH), 1.99-1.91 (m, 1H, CH), 1.85-1.79 (m, 1H, CH), 1.75-1.67 (m, 1H, CH), 1.62-1.52 (m, 2H, 2 x CH), 1.46 (br s, 1H, OH), 1.04 (s, 9H, CMe_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 150.1 (=C), 120.6 (=CH), 66.4 (CHO), 35.3 (*C*Me_3), 32.0 (CH_2), 28.9 (C*Me*$_3$), 24.6 (CH_2), 19.8 (CH_2); MS (CI, NH_3) *m/z* 154 [$(M)^+$, 20], 137 (100); HRMS (CI, NH_3) *m/z*: $[M]^+$ calcd for $C_{10}H_{18}O$, 154.1594; found, 154.1596.

3-Phenylcyclohex-2-en-1-ol 34

Using general procedure B, 3-phenylcyclohex-2-enone **21** (450 mg, 2.6 mmol), $CeCl_3.7H_2O$ (1.19 g, 3.1 mmol) and $NaBH_4$ (113 mg, 3.0 mmol) in MeOH (10 mL) gave the crude product. Purification by flash chromatography on silica with petrol-Et_2O (1:1) as eluent gave allylic alcohol **34** (359 mg, 79%) as a white solid, mp 60-62 ºC (lit.,[18] 60-61 ºC), R_F(1:1 petrol-Et_2O) 0.3; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.28 (m, 5H, Ph), 6.14 (dt, J = 3.5, 2.0, 1H, =CH), 4.43-4.38 (m, 1H, CHO), 2.53-2.44 (m, 1H, CH), 2.42-2.34 (m, 1H, CH), 2.00-1.88 (m, 2H, CH_2), 1.80-1.65 (m, 2H, CH_2), 1.59 (br s, 1H, OH). Spectroscopic data consistent with those reported in the literature.[19]

Cyclopent-2-en-1-ol 35

Using general procedure B, cyclopent-2-enone **22** (2.5 mL, 30.0 mmol), $CeCl_3.7H_2O$ (13.40 g, 36.0 mmol) and $NaBH_4$ (1.30 g, 34.5 mmol) in MeOH (120 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **35** (903 mg, 36%) as a colourless oil, bp 150-160 ºC/75 mm Hg (lit.,[14] 57-59 ºC/25 mm Hg); R_F(Et_2O) 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.90 (m, 1H, =CH), 5.78-5.75 (m, 1H, =CH), 4.82-4.78 (m, 1H, CHO), 2.75 (br s, 1H, OH), 2.49-2.40 (m, 1H, CH), 2.25-2.12 (m, 2H, 2 x CH), 1.67-1.59 (m, 1H, CH). Spectroscopic data consistent with those reported in the literature.[14]

3-Methylcyclopent-2-en-1-ol 36

Using general procedure B, 3-methylcyclopent-2-enone **23** (1.1 mL, 11.0 mmol), $CeCl_3.7H_2O$ (4.92 g, 13.2 mmol) and $NaBH_4$ (484 mg, 12.7 mmol) in MeOH (50 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **36** (575 mg, 53%) as a colourless oil, bp 140-150 ºC/30 mm Hg (lit.,[20] 70-71 ºC/12 mm Hg); R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (app. septet, J = 2.0, 1H, =CH), 4.81 (br d, J = 6.0, 1H, CHO), 2.48-2.40 (m, 1H, CH), 2.34-2.25 (m, 1H, CH), 2.20-2.12 (m, 1H, CH), 1.78 (s, 3H, Me), 1.76-1.69 (m, 1H, CH), 1.48 (br s, 1H, OH). Spectroscopic data consistent with those reported in the literature.[21]

3-Allylcyclopent-2-en-1-ol 37

Using general procedure B, 3-allylcyclopent-2-en-1-one **27** (200 mg, 1.6 mmol), $CeCl_3.7H_2O$ (774 mg, 2.0 mmol) and $NaBH_4$ (71 mg, 1.9 mmol) in MeOH (10 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **37** (151 mg, 74%) as a colourless oil, bp 130-140 ºC/7 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; IR (film) 3325 (OH), 2931, 2895, 2848, 1638, 1429, 1412, 1034, 994, 968, 913 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94-5.84 (m, 1H, =CH), 5.56 (app. sextet, J = 1.5, 1H, =CH), 5.16-5.10 (m, 2H, =CH_2), 4.82 (br m, 1H, CHO), 2.82-2.71 (m, 2H, CH_2CH=CH_2), 2.39-2.31 (m, 1H, CH), 2.24-2.15 (m, 1H, CH), 2.09-2.01 (m, 1H, CH), 1.81-1.73 (m, 1H, CH), 1.70 (s, 1H, OH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.2 (=C), 136.2 (=CH), 129.0 (=CH), 116.6 (=CH_2), 78.0 (CHO), 36.5 (CH_2), 34.8 (CH_2), 34.0 (CH_2); MS (CI, NH_3) *m/z* 107 [(M – OH)$^+$, 100]; HRMS (CI, NH_3) *m/z*: [M – OH]$^+$ calcd for $C_8H_{12}O$, 107.0861; found, 107.0865.

3-(3-Butenyl)-2-cyclopent-2-en-1-ol 38

Using general procedure B, 3-(3-butenyl)-2-cyclopenten-1-one **25** (459 mg, 3.3 mmol), $CeCl_3.7H_2O$ (1.5 g, 4.0 mmol) and $NaBH_4$ (143 mg, 3.8 mmol) in MeOH (15 mL) gave the crude product. Purification by flash chromatography on silica with petrol-Et_2O (1:1) as eluent gave allylic alcohol **38** (364 mg, 80%) as a colourless oil, R_F(1:1 petrol-Et_2O) 0.3; IR (film) 3340 (OH), 2927, 2847, 1642, 1448, 1329, 1039, 910 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.86 (ddt, J = 17.0, 10.0, 6.0, 1H, C*H*=CH_2), 5.49 (app. sextet, J = 2.0, 1H, =CH), 5.13 (app. dq, J = 17.0, 2.0, 1H, CH=CH_AH_B), 5.10 (ddt, J = 10.0, 2.0, 1.0, 1H, CH=CH_AH_B), 4.81-4.77 (m, 1H, CHO), 2.34-2.26 (m, 1H, CH), 2.24-2.14 (m, 3H, 3 x CH), 2.13-2.08 (m, 2H, 2 x CH), 2.05-1.97 (m, 1H, CH), 1.77-1.69 (m, 1H, CH), 0.98 (br s, 1H, OH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 147.9 (=C), 138.4 (=CH), 127.9 (=CH), 114.7 (=CH_2), 77.6 (CHO), 34.3 (CH_2), 33.6 (CH_2), 32.0 (CH_2), 30.7 (CH_2); MS (CI, NH_3) *m/z* 138 [$(M - H_2O + NH_4)^+$, 30], 121 (100); HRMS (CI, NH_3) *m/z*: $[M - H_2O + NH_4]^+$ calcd for $C_9H_{14}O$, 138.1283; found, 138.1284.

1-Methylcyclohex-2-en-1-ol 39

Using general procedure C, cyclohex-2-enone **13** (0.5 mL, 5.2 mmol) and methyl magnesium chloride (1.9 mL of a 3.00 M solution in THF, 5.7 mmol) in THF (20 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **39** (399 mg, 69%) as a colourless oil, bp 80-90 ºC/20 mm Hg (lit.,[22] 60-61ºC/15 mm Hg); R_F(1:1 petrol-Et_2O) 0.5; ^1H NMR (400 MHz, C_6D_6) δ 5.75-5.71 (m, 1H, =CH), 5.67 (ddd, J = 10.0, 4.0, 3.5, 1H, =CH), 1.94-1.51 (m, 7H, 3 x CH_2 and OH), 1.36 (s, 3H, Me). Spectroscopic data consistent with those reported in the literature.[23]

1-Butylcyclohex-2-en-1-ol 40

Using general procedure D, cyclohex-2-enone **13** (0.5 mL, 5.2 mmol) and *n*-butyllithium (6.1 mL of a 0.93 M solution in hexanes, 5.7 mmol) in Et_2O (8 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (1:1) as eluent gave allylic alcohol **40** (591 mg, 74%) as a colourless oil, R_F(1:1 petrol-Et_2O) 0.4; ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddd, J = 10.0, 4.0, 3.0, 1H, =CH), 5.64-5.60 (m, 1H, =CH), 2.08-2.00 (m, 1H, CH), 1.98-1.88 (m, 1H, CH), 1.71-

1.64 (m, 4H, 4 x CH), 1.56-1.48 (m, 3H, CH_2 and OH), 1.36-1.30 (m, 4H, 2 x CH_2), 0.91 (t, J = 7.0, 3H, Me). Spectroscopic data consistent with those reported in the literature.[24]

1-Allylcyclohex-2-en-1-ol 41

Using general procedure C, cyclohex-2-enone **13** (0.5 mL, 5.2 mmol) and allyl magnesium chloride (2.8 mL of a 2.00 M solution in THF, 5.7 mmol) in THF (20 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **41** (458 mg, 64%) as a colourless oil, bp 140-150 ºC/35 mm Hg (lit.,[25] 40-42ºC/0.05 mm Hg); R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, C_6D_6) δ 6.07 (ddt, J = 17.5, 10.5, 7.5, 1H, C*H*=CH_2), 5.73-5.70 (m, 2H, 2 x =CH), 5.20 (ddt, J = 10.5, 2.5, 1.5, 1H, CH=C*H*$_A$H$_B$), 5.17 (ddt, J = 17.5, 2.5, 1.5, 1H, CH=CH$_A$*H*$_B$), 2.38 (app. dt, J = 7.5, 1.5, 2H, C*H*$_2$CH=CH_2), 1.94-1.45 (m, 7H, 3 x CH_2 and OH). Spectroscopic data consistent with those reported in the literature.[25]

1-Isopropylcyclohex-2-en-1-ol 42

Using general procedure D, cyclohex-2-enone **13** (0.3 mL, 3.1 mmol) and *i*-propyllithium (7.1 mL of a 0.48 M solution in pentane, 3.4 mmol) in Et_2O (6 mL) gave the crude product. Purification by flash column chromatography on silica with petrol-Et_2O (8:2) as eluent gave allylic alcohol **42** (279 mg, 64%) as a colourless oil, R_F(8:2 petrol-Et_2O) 0.5; IR (film) 3438 (OH), 2957, 2875, 1466, 1439, 1384, 1170, 976, 952 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, J = 10.0, 5.0, 2.5, 1H, =CH), 5.61 (ddt, J = 10.0, 3.0, 1.5, 1H, =CH), 2.10-2.00 (m, 1H, CH), 1.96-1.87 (m, 1H, CH), 1.73 (septet, 7.0, 1H, C*H*Me_2), 1.71-1.54 (m, 4H, 2 x CH_2), 1.47 (s, 1H, OH), 0.96 (d, J = 7.0, 3H, Me), 0.89 (d, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 132.1 (=C), 130.6 (=CH), 71.7 (C(O)), 37.5 (*CH*Me_2), 30.7 (CH_2), 25.3 (CH_2), 18.6 (CH_2), 17.5 (Me), 16.4 (Me); MS (CI, NH_3) *m/z* 123 [(M – OH)$^+$, 100]; HRMS (CI, NH_3) *m/z*: [M – OH]$^+$ calcd for $C_9H_{16}O$, 123.1174; found, 123.1174.

1-Methylcyclopent-2-en-1-ol 43

Using general procedure C, cyclopent-2-enone **22** (0.5 mL, 6.0 mmol) and methyl magnesium chloride (2.2 mL of a 3.00 M solution in THF, 6.6 mmol) in THF (20 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **43** (249 mg, 42%) as a colourless oil, bp 70-80 ºC/25 mm Hg (lit.,[26] 47-49 ºC/15 mm

Hg); R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, C_6D_6) δ 5.77 (dt, *J* = 5.5, 2.5, 1H, =CH), 5.70 (dt, *J* = 5.5, 2.5, 1H, =CH), 2.41 (app. dddt, *J* = 16.5, 8.0, 4.5, 2.5, 1H, =CH), 2.39 (s, 1H, OH), 2.19 (app. dddt, *J* = 16.5, 8.0, 5.0, 2.5, 1H, CH), 1.99 (ddd, *J* = 13.0, 8.0, 5.0, 1H, CH), 1.91 (ddd, *J* = 13.0, 8.0, 4.5, 1H, CH), 1.46 (s, 3H, Me). Spectroscopic data consistent with those reported in the literature.[27]

1-Butylcyclopent-2-en-1-ol 44

Using general procedure D, cyclopent-2-enone **22** (0.5 mL, 6.0 mmol), *n*-butyllithium (6.2 mL of a 1.06 M solution in hexanes, 6.6 mmol) in Et_2O (8 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **44** (485 mg, 62%) as a colourless oil, bp 80-90 ºC/4 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; IR (film) 3351 (OH), 2957, 2931, 2860, 1456, 1378, 1085, 1048, 1027, 957, 749 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 5.76-5.71 (m, 2H, 2 x =CH), 2.41-2.33 (m, 1H, CH), 2.21-2.13 (m, 1H, CH), 1.97 (ddd, *J* = 13.5, 8.5, 4.0, 1H, CH), 1.84 (dddd, *J* = 13.5, 8.5,5.0, 1.0, 1H, CH), 1.76-1.64 (m, 2H, CH_2), 1.53-1.36 (m, 4H, 2 x CH_2), 1.15 (br s, 1H, OH), 1.27 (t, *J* = 7.5, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 138.0 (=C), 132.9 (=CH), 86.1 (CO), 41.5 (CH_2), 38.5 (CH_2), 31.8 (CH_2), 27.4 (CH_2), 24.1 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 123 [$(M - OH)^+$, 100], 83 (20); HRMS (CI, NH_3) *m/z*: $[M - OH]^+$ calcd for $C_9H_{16}O$, 123.1174; found, 123.1171.

1,3-Dimethylcyclohex-2-en-1-ol 45

Using general procedure D, 3-methylcyclohex-2-enone **14** (0.5 mL, 4.4 mmol) and methyllithium (4.9 mL of a 0.99 M solution in Et_2O, 4.9 mmol) in Et_2O (8 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **45** (362 mg, 65%) as a colourless oil, bp 75-85 ºC/5 mm Hg (lit.,[28] 68 ºC/5 mm Hg); R_F(1:1 petrol-Et_2O) 0.4; ^{1}H NMR (400 MHz, C_6D_6) δ 5.44 (app. septet, *J* = 1.0, 1H, =CH), 1.82-1.68 (m, 4H, 2 x CH_2), 1.64 (s, 3H, Me), 1.60-1.49 (m, 2H, CH_2), 1.37 (s, 3H, Me), 1.19 (s, 1H, OH). Spectroscopic data consistent with those reported in the literature.[28]

1-Butyl-3-methylcyclohex-2-en-1-ol 46

Using general procedure D, 3-methylcyclohex-2-enone **14** (2.0 mL, 17.6 mmol) and *n*-butyllithium (18.3 mL of a 1.06 M solution in hexanes, 19.4 mmol) in Et_2O (30 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **46**

(2.43 g, 82%) as a colourless oil, bp 100-110 ºC/3 mm Hg; R_F(1:1 petrol-Et_2O) 0.6; IR (film) 3379 (OH), 2932, 2863, 1666, 1456, 1378, 963 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.48 (app. quintet, J = 1.5, 1H, =CH), 1.82-1.70 (m, 4H, 2 x CH_2), 1.68 (br s, 3H, Me), 1.66-1.50 (m, 6H, 3 x CH_2), 1.47-1.39 (m, 2H, CH_2), 1.26 (s, 1H, OH), 1.05 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 137.0 (=C), 129.2 (=CH), 70.2 (CO), 43.4 (CH_2), 36.1 (CH_2), 30.9 (CH_2), 26.7 (CH_2), 24.3 (CH_2), 20.2 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 169 [$(M + H)^+$, 15], 151 (100), 111 (15); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{20}O$, 169.1592; found, 169.1596.

3-Butyl-1-methylcyclohex-2-en-1-ol 47

Using general procedure D, 3-butylcyclohex-2-enone **16** (1.0 g, 6.6 mmol) and methyllithium (7.3 mL of a 0.99 M solution in Et_2O, 7.2 mmol) in Et_2O (15 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **47** (752 mg, 68%) as a colourless oil, bp 135-145 ºC/5 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; IR (film) 3354 (OH), 2959, 2930, 2871, 1457, 1374, 1176, 1157, 1113 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.50-5.49 (m, 1H, =CH), 1.98 (app. t, J = 7.5, 2H, CH_2), 1.87-1.70 (m, 4H, 2 x CH_2), 1.64-1.54 (m, 2H, CH_2), 1.48-1.34 (m, 5H, 2 x CH_2 and OH), 1.41 (s, 3H, Me), 1.02 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 140.2 (=C), 129.4 (=CH), 68.4 (C(OH)), 38.7 (CH_2), 38.1 (CH_2), 30.6 (Me), 30.5 (CH_2), 29.2 (CH_2), 23.2 (CH_2), 20.7 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 151 [$(M –OH)^+$, 100]; HRMS (CI, NH_3) *m/z*: $[M – OH]^+$ calcd for $C_{11}H_{20}O$, 151.1487; found, 151.1489.

3-Allyl-1-butylcyclohex-2-en-1-ol 48

Using general procedure D, 3-allylcyclohex-2-enone **17** (300 mg, 2.2 mmol) and *n*-butyllithium (2.3 mL of a 1.06 M solution in hexanes, 2.4 mmol) in Et_2O (4 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **48** (300 mg, 70%) as a colourless oil, 130-150 ºC/10 mm Hg; R_F(1:1 petrol-Et_2O) 0.7; IR (film) 3371 (OH), 2933, 2863, 1664, 1638, 972, 912 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.88 (ddt, J = 17.5, 9.5, 7.0, 1H, C*H*=CH_2), 5.53-5.52 (m, 1H, =CH), 5.18-5.11 (m, 2H, CH=C*H*$_2$), 2.710 (d, J = 7.0, 1H, C*H*$_A$H$_B$C=CH_2), 2.708 (d, J = 7.0, 1H, CH$_A$*H*$_B$C=CH_2), 1.90-1.40 (m, 12H, 6 x CH_2), 1.35 (br s, 1H, OH), 1.05 (t, J = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 139.2 (=C), 136.9 (=CH), 129.6 (=CH),

116.7 (=CH_2), 70.2 (C(OH)), 43.4 (CH_2), 42.9 (CH_2), 36.2 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 24.3 (CH_2), 20.2 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 177 [(M - OH)$^+$, 100], 137 (25); HRMS (CI, NH_3) *m/z*: [M – OH]$^+$ calcd for $C_{13}H_{22}O$, 177.1643; found, 177.1646.

1-Butyl-3-isopropylcyclohex-2-en-1-ol 49

Using general procedure D, 3-isopropylcyclohex-2-enone **19** (200 mg, 1.5 mmol) and *n*-butyllithium (1.4 mL of a 1.06 M solution in hexanes, 1.6 mmol) in Et_2O (3 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **49** (249 mg, 87%) as a colourless oil, bp 130-140 ºC/10 mm Hg; R_F(1:1 petrol-Et_2O) 0.7; IR (film) 3358 (OH), 2931, 1664, 1464, 1381, 1164, 968 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 5.52 (app. sextet, *J* = 1.0, 1H, =CH), 2.27-2.16 (m, 1H, C*H*Me_2), 1.95-1.51 (m, 10H, 5 x CH_2), 1.44 (app. sextet, *J* = 7.0, 2H, CH_2), 1.30 (s, 1H, OH), 1.10 (d, *J* = 7.0, 3H, CH*Me$_A$*Me$_B$), 1.09 (d, *J* = 7.0, 3H, CHMe$_A$*Me$_B$*), 1.05 (t, *J* = 7.0, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 146.5 (=C), 126.4 (=CH), 70.2 (C(OH)), 43.6 (*C*HMe_2), 36.4 (CH_2), 35.8 (CH_2), 27.1 (CH_2), 26.7 (CH_2), 24.3 (CH_2), 22.1 (CH*Me$_A$*Me$_B$), 21.8 (CHMe$_A$*Me$_B$*), 20.4 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 179 [(M – OH)$^+$, 100], 139 (35); HRMS (CI, NH_3) *m/z*: [M – OH]$^+$ calcd for $C_{13}H_{22}O$, 179.1800; found, 179.1802.

1,3-Dimethylcyclopent-2-en-1-ol 50

Using general procedure C, 3-methylcyclopent-2-enone **23** (0.5 mL, 5.1 mmol) and methyl magnesium chloride (1.9 mL of a 3.00 M solution in THF, 5.6 mmol) in THF (20 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **50** (255 mg, 44%) as a colourless oil, 55-65 ºC/5 mm Hg; R_F(1:1 petrol-Et_2O) 0.5; ^{1}H NMR (400 MHz, C_6D_6) δ 5.42 (app. sextet, *J* = 1.5, 1H, =CH), 2.38-2.30 (m, 1H, CH), 2.15-1.97 (m, 4H, 3 x CH and OH), 1.67 (app. q, *J* = 1.5, 3H, Me), 1.50 (s, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 142.2 (=C), 133.8 (=CH), 83.8 (CO), 41.5 (CH_2), 35.9 (CH_2), 28.6 (Me), 17.2 (Me); MS (CI, NH_3) *m/z* 113 [(M + H)$^+$, 20], 95 (100); HRMS (CI, NH_3) *m/z*: [M]$^+$ calcd for $C_7H_{12}O$, 112.1126; found, 112.1130.

1-Butyl-3-methylcyclopent-2-en-1-ol 51

Using general procedure D, 3-methylcyclopent-2-enone **23** (0.5 mL, 5.1 mmol) and *n*-butyllithium (5.3 mL of a 1.06 M solution in hexanes, 5.6 mmol) in Et_2O (8 mL) gave

the crude product. Purification by Kugelrohr distillation gave allylic alcohol **51** (473 mg, 60%) as a colourless oil, bp 100-120 ºC/7 mm Hg; R_F(1:1 petrol-Et_2O) 0.4; IR (film) 3359 (OH), 2958, 2931, 2860, 1455, 1378, 1093, 1001 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.41 (app. sextet, *J* = 1.5, 1H, =CH), 2.37-2.28 (m, 1H, CH), 2.14-2.04 (m, 2H, 2 x CH), 2.00-1.93 (m, 1H, CH), 1.77-1.73 (m, 2H, 2 x CH), 1.70 (app.q, *J* = 1.5, 3H, Me), 1.59-1.50 (m, 2H, CH_2), 1.48-1.39 (m, 2H, CH_2), 1.37 (s, 1H, OH), 1.05 (t, *J* = 7.5, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 143.0 (=C), 132.4 (=CH), 86.4 (C(O)), 41.9 (CH_2), 39.6 (CH_2), 35.9 (CH_2), 27.6 (CH_2), 24.2 (CH_2), 17.3 (Me), 14.9 (Me); MS (CI, NH_3) *m/z* 155 [$(M + H)^+$, 25], 137 (100); HRMS (CI, NH_3) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{18}O$, 155.1436; found, 155.1431.

3-Allyl-1-butylcyclopent-2-en-1-ol 52

Using general procedure D, 3-allylcyclopent-2-enone **27** (220 mg, 1.8 mmol) and *n*-butyllithium (1.5 mL of a 1.35 M solution in hexanes, 2.0 mmol) in Et_2O (3 mL) gave the crude product. Purification by Kugelrohr distillation gave allylic alcohol **52** (147 mg, 45%) as a colourless oil, bp 130-140 ºC/7 mm Hg; R_F(1:1 petrol-Et_2O) 0.5; IR (film) 3385 (OH), 2957, 2930, 2860, 1701, 1675, 1638, 1457, 1378, 1179, 912 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.95 (m, 1H, =CH), 5.48 (app. quintet, *J* = 1.5, 1H, =CH), 5.18-5.13 (m, 2H, $=CH_2$), 2.78 (app. dquintet, *J* = 7.0, 1.5, 2H, $CH_2C=CH_2$), 2.41-2.33 (m, 1H, CH), 2.19-2.11 (m, 1H, CH), 2.06 (ddd, *J* = 13.0, 8.5, 4.5, 1H, CH), 1.95 (ddd, *J* = 13.0, 8.0, 4.5, 1H, CH), 1.76-1.71 (m, 2H, CH_2), 1.57-1.50 (m, 2H, CH_2), 1.44 (app. sextet, *J* = 7.5, 2H, CH_2), 1.04 (t, *J* = 7.5, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 145.5 (=C), 136.3 (=CH), 132.1 (=CH), 116.5 ($=CH_2$), 86.1 (C(O)), 41.8 (CH_2), 39.2 (CH_2), 36.6 (CH_2), 34.2 (CH_2), 27.5 (CH_2), 24.2 (CH_2), 14.9 (Me); MS (CI, NH_3) *m/z* 163 [$(M - OH)^+$, 100], 123 (35); HRMS (CI, NH_3) *m/z*: $[M - OH]^+$ calcd for $C_{12}H_{20}O$, 163.1487; found, 163.1493.

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