Supporting information


Fung Kei (Kathy) Cheung, Aidan M. Hayes, David J. Morris and Martin Wills.*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

m.wills@warwick.ac.uk.

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Preparation of reagents for synthetic processes and ketone reductions.

**General Experimental Details**

All reactions, unless otherwise stated, were run under an atmosphere of nitrogen at ambient temperature (18-22 °C). 0 °C refers to an ice slush bath and –78 °C refers to a dry ice-acetone bath. Heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by TLC using aluminium backed silica gel 60 (F254) plates, visualised using UV 254 nm and phosphomolybdic acid, ninhydrin, potassium permanganate or vanillin dips as appropriate. Flash column chromatography was carried out routinely using 60 Å silica gel (Merck). Reagents were used as received from commercial sources unless otherwise stated. NMR spectra were recorded on a Bruker DPX (300 or 400 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million downfield from TMS. Coupling constants (J) are measured in hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Golden Gate. Mass spectra were recorded on a 7070E VG mass spectrometer. Melting points were recorded on a Stuart Scientific SMP 1 instrument and are uncorrected. Optical rotations were measured with an AA1000 polarimeter and are given in 10⁻¹ deg cm² g⁻¹. Determination of enantiomeric excesses by HPLC analysis was achieved using a Merck-Hitachi L-6200A HPLC pump, Merck-Hitachi L-4000 UV absorbance detector, Axiomm 727 data module and a Daicel Chiralcel OD, OD-H or AD 4.6 x 25 cm column. Determination of enantiomeric excesses by GC analysis was achieved using a Chrompac cyclodextrin-β-236M-19 50m or Chiracel β-DEX-120 25m column.

**Synthesis of 3,4,4-trimethylpent-1-en-3-ol.**
To a stirred solution of 1 M vinylmagnesium bromide in THF (36 cm$^3$, 36.0 mmol) was added a solution of pinacolone (3.005 g, 30.0 mmol) in THF (9 cm$^3$) at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred overnight at reflux, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm$^3$), diluted with water (20 cm$^3$) and extracted with DCM (2 x 50 cm$^3$). The combined extracts were dried (MgSO$_4$), filtered and concentrated under vacuum at room temperature to give the crude product. The residue was purified by distillation to give the alcohol$^1$ (2.25 g, 59%) as a colourless oil; bp 61-63 °C / 50 mbar; $\nu_{\text{max}}$/cm$^{-1}$ (thin film) 3485 (OH), 1642 (C=C); $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 0.94 (9 H, s, C(CH$_3$)$_3$), 1.24 (3 H, s, CH$_3$), 1.40 (1 H, s, OH), 5.09 (1 H, dd, $J$ 11.1 and 1.5, $=CH_H$ trans to $=CR$), 5.22 (1 H, dd, $J$ 17.3 and 1.5, $=CH_H$ cis to $=CR$), 6.08 (1 H, dd, $J$ 17.3 and 11.1, $=CHR$); $\delta_C$ (100.6 MHz; CDCl$_3$; Me$_4$Si) 23.3 (q), 25.3 (q), 37.1 (s), 77.3 (s), 112.3 (t), 143.3 (d).

**Synthesis of 2-adamantan-1-ylbut-3-en-2-ol.**

To a stirred solution of 1 M vinylmagnesium bromide in THF (14.5 cm$^3$, 14.5 mmol) was added a solution of 1-adamantylmethyl ketone (2.150 g, 30.0 mmol) in THF (5 cm$^3$) at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred overnight at reflux, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm$^3$), diluted with water (20 cm$^3$) and extracted with DCM (2 x 30
cm\(^3\)). The combined extracts were dried (MgSO\(_4\)), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (2.5% EtOAc/hexane to 10% EtOAc/hexane) to give the alcohol\(^2\) (1.36 g, 55%) as a colourless oil; \(\nu_{\max}/\text{cm}^{-1}\) (thin film) 3489 (OH), 1640 (C=C); \(\delta_H\) (400 MHz; CDCl\(_3\); Me\(_4\)Si) 1.19 (3 H, s, CH\(_3\)), 1.36 (1 H, s, OH), 1.58-1.82 (12 H, m, adamantyl 6 x CH\(_2\)), 1.96-2.02 (3 H, m, adamantyl 3 x CH), 5.09 (1 H, dd, \(J\) 11.1 and 1.6, =CHH trans to =CR), 5.18 (1 H, dd, \(J\) 17.3 and 1.6, =CHH cis to =CR), 6.03 (1 H, dd, \(J\) 17.3 and 11.1, =CHR); \(\delta_C\) (100.6 MHz; CDCl\(_3\); Me\(_4\)Si) 22.1 (q), 28.6 (3 x d), 36.3 (3 x t), 37.1 (3 x t), 38.3 (s), 77.2 (s), 112.3 (t), 142.9 (d); Found (EI) 206.1652 [M]\(^+\), \(C_{14}H_{22}O\) requires 206.1671 (1.9 mDa error); \(m/z\) (EI) 188 (M-OH\(_2\))^+ (10%), 135 (100), 107 (15), 93 (30), 79 (30).

**Synthesis of 2-phenylbut-3-en-2-ol.**

![OH](image)

To a stirred solution of 1 M vinylmagnesium bromide in THF (36 cm\(^3\), 36.0 mmol) was added a solution of acetopheneone (3.60 g, 30.0 mmol) in THF at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred at reflux for 1 hour, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm\(^3\)), diluted with water (20 cm\(^3\)) and extracted with DCM (2 x 50 cm\(^3\)). The combined extracts were dried (MgSO\(_4\)), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (5% EtOAc/hexane to 10% EtOAc/hexane) to give the alcohol\(^3\) (2.73 g, 61%) as a colourless
oil; δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.65 (3 H, s, CH<sub>3</sub>), 1.96 (1 H, s, OH), 5.13 (1 H, dd, <i>J</i> 10.8 and 1.3, =CH<sub>H</sub> trans to =CR), 5.29 (1 H, dd, <i>J</i> 17.3 and 1.3, =CH<sub>H</sub> cis to =CR), 6.16 (1 H, dd, <i>J</i> 17.3 and 10.8, =CHR), 7.22-7.27 (1 H, m, Ph), 7.31-7.36 (2 H, m, Ph), 7.44-7.48 (2 H, m, Ph); δ<sub>C</sub> (100.6 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 29.4 (q), 74.8 (s), 112.4 (t), 125.2 (2 x d), 127.0 (d), 128.3 (2 x d), 144.9 (d), 146.5 (s).

Synthesis of 4,4-dimethyl-3-methylenepent-1-ene.

To a stirred solution of tetrabutylammonium perrhenate (0.531 g, 1.08 mmol) and para-toluenesulphonic acid mono-hydrate (0.103 g, 0.54 mmol) in DCM (40 cm<sup>3</sup>) was added a solution of 3,4,4-trimethylpent-1-en-3-ol (1.015 g, 4.92 mmol) in DCM (20 cm<sup>3</sup>). The reaction mixture was stirred overnight, diluted with diethyl ether (75 cm<sup>3</sup>) and saturated NaHCO<sub>3</sub> (75 cm<sup>3</sup>) added. The layers were separated and the organic layer was dried (MgSO<sub>4</sub>), filtered and concentrated to a small volume by distillation at ambient pressure. The residue was filtered (silica) and washed with pentane (50 cm<sup>3</sup>) and again concentrated to a small volume by distillation at ambient pressure. The residue was then distilled under reduced pressure (30 mbar) at room temperature, collecting the product in a trap at -78 °C to give the diene<sup>4</sup> (0.163 g, 14%) as a colourless oil; δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.09 (9 H, s, C(CH<sub>3</sub>)<sub>3</sub>), 4.79 (1 H, d, <i>J</i> 1.8, CH<sub>r</sub>H<sub>r</sub>CR<sub>r</sub>), 5.01 (1 H, dd, <i>J</i> 10.8 and 2.3, CHR=CHH trans to CR), 5.06 (1 H, m, CH<sub>r</sub>H<sub>r</sub>CR<sub>r</sub>), 5.39 (1 H, dd, <i>J</i> 17.1 and 2.3, CHR=CHH cis to CR), 6.42 (1 H, dd, <i>J</i> 17.1 and 10.8, CHR=CH<sub>2</sub>); δ<sub>C</sub> (100.6 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 29.3 (3 x q), 35.0 (s), 107.1 (t), 114.6 (t), 137.0 (d), 156.7 (s).
Synthesis of 1-(1-methyleneallyl)-adamantane.

To a stirred solution of tetrabutylammonium perrhenate (0.242 g, 0.49 mmol) and para-toluenesulphonic acid mono-hydrate (0.047 g, 0.25 mmol) in DCM (30 cm³) was added a solution of 2-adamantan-1-ylbut-3-en-2-ol (1.015 g, 4.92 mmol) in DCM (20 cm³). The reaction mixture was stirred overnight, diluted with diethyl ether (20 cm³) and saturated NaHCO₃ (50 cm³) added. The layers were separated and the organic layer was dried (MgSO₄), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (pentane) to give the diene (1.36 g, 55%) as a colourless oil; δ_H (400 MHz; CDCl₃; Me₄Si) 1.62-1.76 (12 H, m, adamantyl 6 x CH₂), 1.97-2.05 (3 H, m, adamantyl 3 x CH), 4.72 (1 H, d, J 1.5, CH₆H₆CR₂), 5.00 (1 H, dd, J 10.8 and 2.3, CHR=CH trans to CR), 5.08 (1 H, m, CH₆H₆CR₂), 5.37 (1 H, dd, J 17.1 and 2.3, CHR=CHH cis to CR), 6.44 (1 H, dd, J 17.1 and 10.8, CHR=CH₂); δ_C (100.6 MHz; CDCl₃; Me₄Si) 28.7 (3 x d), 36.9 (3 x t), 40.5 (s), 41.2 (3 x t), 107.1 (t), 114.7 (t), 136.4 (d), 157.1 (s).

Synthesis of (1-methyleneallyl)-benzene.

To a stirred solution of 2-phenylbut-3-en-2-ol (1.870 g, 12.6 mmol) in THF (30 cm³) was added para-toluenesulphonic acid mono-hydrate (0.480 g, 2.5 mmol). The reaction
mixture was stirred overnight at 60 °C, diluted with saturated NaHCO₃ (50 cm³) and extracted with DCM (2 x 50 cm³). The combined extracts were dried (MgSO₄), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (pentane) to give the product⁶ (0.528 g, 33%) as a colourless oil; δ_H (400 MHz; CDCl₃; Me₄Si) 5.16-5.23 (3 H, m, CHR=CH₂ and CH₆H₆CR₂), 5.29-5.31 (1 H, m, CH₆H₆CR₂), 6.62 (1 H, dd, J 17.1 and 10.8, CHR=CH₂), 7.27-7.38 (5 H, m, Ph); δ_C (100.6 MHz; CDCl₃; Me₄Si) 116.9 (t), 117.2 (t), 127.5 (d), 128.1 (2 x d), 128.3 (2 x d), 138.2 (d), 139.8 (s), 148.3 (s).

Synthesis of methanesulfonic acid but-3-ynyl ester.

To a stirred solution of 3-butyn-1-ol (4.63 g, 66.1 mmol) and triethylamine (10.01 g, 99.1 mmol) in DCM (60 cm³) was added a solution of methanesulphonyl chloride (11.36 g, 99.1 mmol) in DCM (30 cm³). The reaction mixture was stirred overnight, diluted with 2M HCl solution (30 cm³) and extracted with DCM (30 cm³). The combined extracts were washed with 1M HCl solution (30 cm³), saturated sodium hydrogen carbonate solution (30 cm³), and brine (30 cm³) and then dried (MgSO₄), filtered and concentrated under vacuum to give the product (9.64 g, 98%) as a clear oil; ν_max/cm⁻¹ (thin film) 3286 (≡CH), 1333 and 1168 (SO₂O); δ_H (300 MHz; CDCl₃; Me₄Si) 2.08 (1 H, t, J 2.7, ≡CH), 2.67 (2 H, dt, J 6.8 and 2.7, ≡CCH₂), 3.07 (3 H, s, CH₃), 4.32 (2 H, t, J 6.8, CH₂OSO₂); δ_C(75.5 MHz; CDCl₃; Me₄Si) 19.5 (t), 37.5 (q), 66.9 (t), 70.7 (d), 78.4 (s). Found (EI)
149.0257 [MH]$^+$, C$_3$H$_9$O$_3$S requires 149.0272 (1.5 mDa error); m/z (EI) 149 (MH$^+$, 50%), 109 (50), 79 (100), 70 (45).

**Synthesis of thioacetic acid S-but-3-ynyl ester.**

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To a stirred solution of methanesulfonic acid but-3-ynyl ester (18.73 g, 126.5 mmol) in acetonitrile (400 cm$^3$) was added potassium thioacetate (28.88 g, 253.0 mmol). The reaction mixture was stirred for 2 days, diluted with water (100 cm$^3$) and extracted with diethyl ether (3 x 200 cm$^3$). The combined extracts were dried (MgSO$_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by distillation to give the thioester (8.70 g, 54%) as a clear oil; bp 76-78°C / 30 mm Hg; $\nu_{\text{max}}$/cm$^{-1}$ (thin film) 3291 (≡C-H), 2938 (CH$_2$), 1686 (C=O); $\delta_{\text{H}}$ (300 MHz; CDCl$_3$; Me$_4$Si) 2.03 (1 H, t, J 2.6, ≡CH), 2.35 (3 H, s, CH$_3$), 2.49 (2 H, dt, J 7.0 and 2.6, ≡CCH$_2$), 3.04 (2 H, t, J 7.0, CH$_2$S); $\delta_{\text{C}}$ (100.6 MHz; CDCl$_3$; Me$_4$Si) 17.6 (t), 26.2 (t), 28.7 (q), 67.8 (d), 80.2 (s), 193.4 (s). Found (EI) 127.0202 [M-H]$^+$, C$_6$H$_7$OS requires 127.0218 (1.5 mDa error); m/z (EI) 129 (MH$^+$, 5%), 128 (M$^+$, 5), 127 (10), 113 (35), 79 (70), 78 (100), 63 (55), 61 (15).

**Synthesis of but-3-yn-1-sulfonic acid sodium salt.**

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To a stirred solution of thioacetic acid S-but-3-ynyl ester (5.00 g, 39.1 mmol) in acetic acid (65 cm$^3$) at 60 °C was added dropwise 30% hydrogen peroxide solution in water (25 cm$^3$, 196.0 mmol) and the reaction mixture was stirred for 3 hours, cooled and concentrated under vacuum to give the crude product, using heptane to azeotropically
remove any traces of acetic acid. The residue was dissolved in water (50 cm$^3$) and neutralized with 2M sodium hydroxide solution. The solution was then concentrated under vacuum to give the sulfonate ester (5.98 g, 99%) as an off-white solid; mp >320 °C; $\nu_{\text{max}}$/cm$^{-1}$ (solid) 3307 (≡CH), 1321 and 1155 (SO$_2$O); $\delta_H$ (300 MHz; CDCl$_3$; Me$_4$Si) 2.31 (1 H, t, $J$ 2.6, ≡CH), 2.54 (2 H, dt, $J$ 7.3 and 2.6, ≡CCH$_2$), 2.99 (2 H, t, $J$ 7.3, CH$_2$SO$_3$Na); $\delta_C$ (75.5 MHz; CDCl$_3$; Me$_4$Si) 14.5 (t). Found (LSIMS) 132.9967 [M$^-$], C$_4$H$_5$O$_3$S requires 132.9959 (0.8 mDa error); m/z (LSIMS) 133 (M$^-$, 100%).

**Synthesis of but-3-yne-1-sulfonyl chloride 15.**

![Image of but-3-yne-1-sulfonyl chloride 15]

To a suspension of but-3-yne-1-sulfonic acid sodium salt (7.05 g, 45.5 mmol) in DCM (15 cm$^3$) and thionyl chloride (23 cm$^3$) was added dimethylformamide (15 drops). The reaction mixture was refluxed for 5 hours, cooled to room temperature and concentrated under vacuum to give the crude product. The residue was purified by distillation to give 15 (2.38 g, 34%) as a pale yellow oil; bp 44-45 °C / 0.5 mm Hg; $\nu_{\text{max}}$/cm$^{-1}$ (thin film) 3295 (≡C-H), 2994 and 2930 (CH$_2$), 1368 and 1166 (SO$_2$Cl); $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 2.17 (1 H, t, $J$ 2.5, ≡CH), 2.93-2.98 (2 H, m, ≡CCH$_2$), 3.85 (2 H, t, $J$ 7.5, CH$_2$SO$_2$Cl); $\delta_C$ (75.5 MHz; CDCl$_3$; Me$_4$Si) 14.6 (t), 62.6 (t), 71.8 (d), 77.3 (s). Found (EI) 149 (5%), 78 (75), 63 (100).

**Synthesis of pent-4-ynyl 4-methylbenzenesulfonate 26.**
To a solution of 4-penty-1-ol (8.52 g, 101 mmol) and triethylamine (11.25 g, 111 mmol) in acetonitrile (85 cm³) was added para-toluene sulphonyl chloride (18.68 g, 98 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred overnight, filtered and concentrated under vacuum. The residue was dissolved in dichloromethane (200 cm³), washed with 2 M HCl (200 cm³), sat. NaHCO₃ solution (200 cm³) and sat. NaCl solution (200 cm³), dried (MgSO₄), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash chromatography (5 % EtOAc/hexane to 30 % EtOAc/hexane) to give 26 (17.34 g, 74%) as a colourless oil. (Found: C, 60.11; H, 5.92. C₁₂H₁₄O₃S requires C, 60.48; H, 5.92%); ν max/cm⁻¹ (thin film) 3289 (≡CH), 1356 and 1173 (SO₂O), 812 (disubstituted benzene); δ H(300 MHz; CDCl₃; Me₄Si) 1.82-1.91 (3 H, m, CH₂CH₂C≡CH and =CH), 2.26 (2 H, dt, J 7.0 and 2.6, CH₂C≡CH), 2.45 (3 H, s, CH₃), 4.15 (2 H, t, J 6.2, CH₂OSO₂), 7.35 (2 H, d, J 8.2, ArH o to CH₃), 7.80 (2 H, d, J 8.2, ArH o to SO₂); δ C(75.5 MHz; CDCl₃; Me₄Si) 14.3 (t), 21.3 (q), 27.4 (t), 68.6 (t), 69.4 (d), 81.9 (s), 127.6 (2 x d), 129.7 (2 x d), 132.5 (s), 144.7 (s). Found (LSIMS): 239.0737 [MH]+, C₁₂H₁₅O₃S requires 239.0742 (2.2 ppm error); m/z (CI) 256 (MNH₄⁺, 100%), 239 (MH⁺, 5), 174 (10), 91 (5).

**Synthesis of cobalt cycloaddition catalyst 18.**
To a stirred solution of 1,2-bis(diphenylphosphino)ethane (2.000 g, 5.02 mmol) in THF (60 cm$^3$) was added cobalt(II) bromide (1.098 g, 5.02 mmol). The resulting brown solution was stirred overnight to give a green precipitate, which was collected by vacuum filtration to give $\text{18}^7$ (2.870 g) as a green solid, which was used in the cycloaddition reactions without further purification or characterisation.

**Synthesis of rhodium cycloaddition catalyst 19.**

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To a suspension of [Rh(cyclooctadiene)Cl]$_2$ (0.098 g, 0.20 mmol) in acetone (15 cm$^3$) was added naphthalene (0.102 g, 0.80 mmol) followed by silver tetrafluoroborate (0.077 g, 0.40 mmol). The reaction mixture was stirred for 1 hour, filtered (celite) and concentrated under vacuum to give $\text{19}^8$ (0.182 g) as a yellow/orange solid which was used in the cycloaddition reactions without further purification or characterisation.

**Reduction of ketones in isopropyl alcohol using tethered ruthenium aminoalcohol chiral ligands, typical procedure:**

To a suspension of ruthenium dimer (0.00425 mmol) in isopropanol (15 cm$^3$) was added a 0.1 M solution of potassium hydroxide (0.85 cm$^3$, 0.085 mmol) and the solution stirred at 28 °C for 20 minutes. Substrate (1.70 mmol) was added and the reaction mixture stirred at 28 °C for 2 hours, diluted with hexane (30 cm$^3$), filtered (silica), washed (50% EtOAc/hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash chromatography where necessary.
Reduction of ketones in formic acid/triethylamine using tethered ruthenium diamine chiral ligands, typical procedure:

A solution of ruthenium dimer (0.0075 mmol) or pre-formed ruthenium monomer (0.015 mmol) in formic acid : triethylamine 5 : 2 azeotrope (1.5 cm³) was stirred in a flame dried Schlenk tube at 28 °C for 30 minutes. Substrate (3.00 mmol) was added and the reaction mixture was stirred at 28 °C for 22 hours. The reaction mixture was filtered (silica), washed (50% EtOAc/hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash chromatography where necessary.

1-Phenylethanol KPA.

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\text{\textbf{Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-\(\beta\)-236M-19 50m, } T = 115 °C, P = 7 psi, \text{ ketone 13.2 min.}, \text{ } R \text{ isomer 19.3 min.}, \text{ } S \text{ isomer 20.3 min.}); \\
[\text{\(\alpha\)}]_D^{22} +49.0 \text{ (c 1.0 in CHCl}_3\text{) 98% ee } (R) \text{ (lit.}\ [\text{\(\alpha\)}]_D^{23} +48.6 \text{ (c 1.0 in CH}_2\text{Cl}_2\text{) 96% ee } (R)); \text{ } \delta_{\text{H}}(300 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si}) 1.47 \text{ (3 H, d, } J \text{ 6.4, CH}_3\text{), 2.04 (1 H, br s, OH), 4.86 (1 H, q, } J \text{ 6.4, PhCHCH}_3\text{), 7.33-7.35 (5 H, m, Ph); } \delta_{\text{C}}(75.5 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si}) 24.9 \text{ (q), 70.2 (d), 125.2 (2 x d), 127.2 (d), 128.3 (2 x d), 145.6 (s).}
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1-Cyclohexylethanol.
Method A: Enantiomeric excess by HPLC of 2-naphtholate ester derivative (Chialcel OD-H, 4% iso-propanol/hexane (0.7 mL min⁻¹), R isomer 8.3 min., S isomer 9.6 min.), conversion by ¹H-NMR; Method B: Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 100 °C, P = 7 psi, ketone 17.6 min., R isomer 26.3 min., S isomer 26.9 min.); [α]D¹⁸ -1.61 (c 1.80 in CHCl₃) 19% ee (R) (lit.¹⁰ [α]D +3.51 (c 3.1 in CHCl₃) 95% ee (S)); δH (400 MHz; CDCl₃; Me₄Si) 0.92-1.32 (6 H, m, cyclohexyl), 1.15 (3 H, d, J 6.3, CH₃), 1.46 (1 H, br s, OH), 1.63-1.88 (5 H, m, cyclohexyl), 3.54 (1 H, dt, J 6.3 and 6.3, CH(OH)CH₃); δC (100.6 MHz; CDCl₃; Me₄Si) 20.4 (q), 26.2 (2 x overlapping t), 26.5 (t), 28.4 (t), 28.7 (t), 45.1 (d), 72.2 (d).

3,3-Dimethylbutan-2-ol.

Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 80 °C, P = 7 psi, ketone 5.5 min., R isomer 8.7 min., S isomer 8.9 min.); [α]D²³ +2.0 (c 0.9 in CCl₄) 63% ee (S) (lit.¹¹ [α]D²⁹ -43.0 (c 1.5 in CCl₄) 99% ee (R)); δH (400 MHz; CDCl₃; Me₄Si) 0.89 (9 H, s, C(CH₃)₃), 1.12 (3 H, d, J 6.5, CH₃), 1.58-1.82 (1 H, br s, OH), 3.44-3.52 (1 H, m, CHOH); δC (100.6 MHz; CDCl₃; Me₄Si) 17.8 (q), 25.4 (3 x q), 34.9 (s), 75.6 (d).

1-Adamantanylethanol.
Enantiomeric excess by GC analysis (Chiracel β-DEX-120 25m, T = 115 °C, P = 48 psi, 
R isomer 57.1 min., S isomer 58.4 min.), conversion by 1H-NMR; [α]D18 +0.4 (c 1.5 in 
CHCl3) 12% ee (R) (lit.12 [α]D25 -1.6 (c 2.2 in CHCl3) 99.8% ee (S)); δH(400 MHz; 
CDCl3; Me4Si) 1.10 (3 H, d, J 6.5, CH3), 1.32 (1 H, br s, OH), 1.45-1.75 (12 H, m, 
adamantyl 6 x CH2), 1.96-2.02 (3 H, m, adamantyl 3 x CH), 3.28 (1 H, q, J 6.5, CHOH); 
δC(100.6 MHz; CDCl3; Me4Si) 16.5 (q), 28.4 (3 x d), 36.6 (s), 37.3 (3 x t), 37.7 (3 x t), 
75.8 (d).

1-Cyclohexylpropan-1-ol.

Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 
50m, T = 100 °C, P = 15 psi, ketone 19.9 min., S isomer 31.5 min., R isomer 32.1 min.); 
[α]D23 -1.92 (c 0.65 in CHCl3) 28% ee (S) (lit.13 [α]D25 -3.9 (c 3.05 in CHCl3) 99% ee 
(S)); δH(400 MHz; CDCl3; Me4Si) 0.95 (3 H, t, J 7.4, CH2CH3), 0.99-1.82 (14 H, m, 
CH2CH3, OH and cyclohexyl), 3.25-3.30 (1 H, m, CHOH); δC(100.6 MHz; CDCl3; 
Me4Si) 10.2 (q), 26.2 (t), 26.4 (t), 26.6 (t), 26.8 (t), 27.7 (t), 29.3 (t), 77.6 (d).

Octan-2-ol.

Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 
50m, T = 70 °C, P = 10 psi, ketone 29.3 min., R isomer 54.1 min., S isomer 55.1 min.); 
[α]D23 +3.31 (c 0.65 in CHCl3) 24% ee (S) (lit.14 [α]D25 +9.0 (c 1.23 in CHCl3) 99% ee
\( \delta_H(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) 0.89 \) (3 H, t, \( J = 6.8 \), \( \text{CH}_2\text{CH}_3 \)), 1.18 (3 H, d, \( J = 6.3 \), \( \text{CH}_3\text{CHOH} \)), 1.27-1.47 (10 H, m, 5 x \( \text{CH}_2 \)), 1.57 (1 H, br s, \text{OH}), 3.78 (1 H, m, \( \text{CHOH} \)); 
\( \delta_C(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si}) 14.1 \) (q), 22.6 (t), 23.4 (q), 25.7 (t), 29.3 (t), 31.8 (t), 39.4 (t), 68.1 (d).

References


ii) 1H-NMR spectra of compounds lacking CHN analyses.

[(R,R)-2-(but-3-yne-1-sulfonylamino)-1,2-diphenylethyl]-carbamic acid tert-butyl ester 17.
{(R,R)-2-[2-(4-methylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-1,2-diphenylethyl}carbamic acid tert-butyl ester 20a.
\{(R,R)-2-[2-(4-tert-buty cyclohexa-1,4-dienyl)-ethanesulfonylamino]-1,2-diphenylethyl\}-carbamic acid tert-butyl ester 20b.
{(R,R)-2-[2-(4-adamantan-1-ylcyclohexa-1,4-dienyl)-ethanesulfonamido]-1,2-diphenylethyl}-carbamic acid tert-butyl ester 20c.
{(R,R)-1,2-diphenyl-2-[2-(4-phenylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-ethyl}-carbamic acid tert-butyl ester 20d.
2-(4-tert-butyl-phenyl)-ethanesulfonic acid \((R,R)-2\text{-amino-1,2-diphenylethyl})\text{-amide}

ammonium chloride ruthenium dimer 21b.
2-(4-adamantan-1-yl-phenyl)-ethanesulfonic acid ((R,R)-2-amino-1,2-diphenylethyl)-amide ammonium chloride ruthenium dimer 21c.
tert-butyl (1R,2S)-1-hydroxy-1-phenylprop-2-yl(pent-4-ynyl) carbamate 25.
[3-(4-tert-butyldimethylsilyloxy)-1-methyl-2-phenylethyl]-carbamic acid tert-butyl carbamate 28b.
[3-(4-adamantan-1-yl)cyclohexa-1,4-dienyl)-propyl]-((S,2R,2)-2-(tert-butyldimethylsilyl)oxy)-1-methyl-2-phenylethyl-carbamate tert-butylicarboxylate
[(1S,2R)-2-(tert-butyldimethylsilanyloxy)-1-methyl-2-phenylethyl]-[3-(4-phenylcyclohexa-1,4-dienyl)-propyl]-carbamic acid tert-butyl carbamate 28d.
[3-(4-tert-butylcyclohexa-1,4-dienyl)-propyl]-(1S,2R)-2-hydroxy-1-methyl-2-phenylethyl)-carbamic acid tert-butyl carbamate.
[3-(4-adamantan-1-yl-cyclohexa-1,4-dienyl)-propyl]-((1S,2R)-2-hydroxy-1-methyl-2-phenylethyl)-carbamic acid tert-butyl carbamate.
((1S,2R)-2-hydroxy-1-methyl-2-phenylethyl)-[3-(4-phenylcyclohexa-1,4-dienyl)-propyl]-carbamic acid tert-butyl carbamate.
(1R,2S)-2-[3-(4-tert-butylphenyl)-propylamino]-1-phenylpropan-1-ol ruthenium dimer 29b.
(1R,2S)-2-(3-biphenyl-4-yl-propylamino)-1-phenylpropan-1-ol ruthenium dimer

29d.