Asymmetric $\alpha$-Oxyacylation of Ketones

Supplementary Information

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General Procedures. All reaction were conducted in oven-dried (100 °C) glassware under an atmosphere of nitrogen. Commercially available solvents and reagents were used without further purification. Light petroleum refers to the fraction with bp 40–60 °C and ether refers to diethyl ether. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF\textsubscript{254} that were visualised under UV light (at 254 and/or 360 nm). Infra-red (IR) spectra were recorded in the range 4000–600 cm\textsuperscript{-1} using KBr disks for solid samples and thin films between NaCl plates for liquid samples or as a nujol mull and are reported in cm\textsuperscript{-1}. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl\textsubscript{3} at 18 °C unless stated otherwise and were reported in ppm; J values were recorded in Hz and multiplicities were expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using atmospheric pressure chemical ionization (APCI) unless otherwise stated. ES refers to electrospray ionization, CI refers to chemical ionization (ammonia) and EI refers to electron ionization. High-resolution mass spectra were obtained courtesy of the EPSRC Mass Spectrometry Service at University of Wales, Swansea, U.K. using the ionization methods specified. In vacuo refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump.
**$N$-(S)-$\alpha$-Methylbenzyl-$O$-benzoyl hydroxylamine hydrochloride 10·HCl.**

Compound 10 was synthesised from $N$-(S)-$\alpha$-methylbenzylamine 9 using General Procedure 1. Conversion to the HCl salt gave 10·HCl (3.52 g, 62%) as a white crystalline solid which was collected by filtration. mp 92–96 °C; IR (nujol)/cm$^{-1}$: 2925, 2293, 1765, 1458, 1378, 1263, 1052; $^1$H NMR (400 MHz, DMSO) δ 9.00–9.20 (br, 2H), 7.75 (d, 2H, $J$ 7.1 Hz), 7.60 (t, 1H, $J$ 6.7 Hz), 7.4–7.5 (m, 4H), 7.30 (m, 2H), 7.20 (m, 1H), 4.35 (q, 1H, $J$ 6.7 Hz), 1.35 (d, 3H, $J$ 6.7 Hz); $^{13}$C NMR (100 MHz, DMSO) δ 165.6, 142.8, 133.9, 129.3, 129.1, 128.9, 128.7, 127.8, 127.4, 59.9, 19.9 ppm; MS (ES): m/z 242 [M + H]$^+$; HRMS calculated for C$_{15}$H$_{16}$NO$_2$ [M + H]$^+$ 242.1176, found 242.1177.

**$N$-(S)-$\alpha$-Methyl benzyl-$O$-benzoyl hydroxylamine 10.**

pH 10.5 buffer (250 mL) was added quickly to a solution of $N$-(S)-$\alpha$-methylbenzyl-$O$-benzoyl hydroxylamine hydrochloride 10·HCl (500 mg, 1.8 mmol) in dichloromethane (250 mL), with vigorous stirring at room temperature for one hour. The reaction mixture was then separated and the aqueous layer was extracted with dichloromethane (3 x 100 mL). The organic extracts were then combined with the organic layer and washed with brine (250 mL), dried (Na$_2$SO$_4$) and concentrated to give $N$-(S)-$\alpha$-methylbenzyl-$O$-benzoyl hydroxylamine 10 (92%) as a clear colourless oil. IR (nujol)/cm$^{-1}$: 3233, 3063, 3031, 2977, 1719, 1601, 1584, 1493, 1451, 1373, 1316, 1268, 1177, 1090, 1066, 1025, 979, 762, 701; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, 2H, $J$ 7.1 Hz), 7.55 (t, 1H, $J$ 7.5 Hz), 7.30–7.50 (m, 7H), 4.25 (q, 1H, $J$ 6.7 Hz), 1.45 (d, 3H, $J$ 6.7 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 141.3, 133.4, 129.4, 128.7, 128.5, 128.4, 127.9, 127.2, 61.0, 19.8 ppm; MS (APCI): m/z 242 [M + H]$^+$; [α]$^\mathrm{D}$_2 $-80$ (c 1.0, CHCl$_3$).

**(±)-2-Benzoyloxy cyclohexanone 11.**

Cyclohexanone 2 (3.3 mL, 32 mmol) was added dropwise (over 5 min) to a stirred solution of $N$-methyl-$O$-benzoyl hydroxylamine hydrochloride (6.00 g, 32 mmol) in DMSO (45 mL). Stirring was continued at 25 °C overnight. The reaction mixture was diluted with brine (50 mL) and extracted with ethyl acetate (4 x 50 mL). The combined extracts were washed with brine (150 mL), dried (MgSO$_4$) and concentrated to give the crude product which was purified on silica, eluting with petroleum ether-ethyl acetate (3:1) to give (±)-2-benzoyloxy cyclohexanone 11 (4.74 g, 68%) as a white crystalline solid. mp 81–85 °C; [lit.$^2$ 81–83 °C]; IR (thin film)/cm$^{-1}$: 2945, 2867, 1743, 1719 1603, 1451, 1316, 1271, 1177, 1112, 1071, 1034; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, 2H, $J$ 8.3 Hz), 7.50 (t, 1H, $J$ 7.4 Hz), 7.35 (dd,
2H, J 7.7, 7.7 Hz), 5.35 (dd, 1H, J 12.0, 9.5 Hz), 2.45–2.55 (m, 1H), 2.30–2.45 (m, 2H), 2.00–2.10 (m, 1H), 1.90–2.00 (m, 1H), 1.70–1.90 (m, 2H), 1.55–1.70 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 204.4, 165.6, 133.2, 129.9, 129.7, 128.4, 77.0, 40.8, 33.2, 27.2, 23.8 ppm; MS (ES): \(m/z\) 219 [M + H]+; HRMS calculated for C\(_{13}\)H\(_{15}\)O\(_3\) [M + H]+ 219.1016, found 219.1015; Enantiomers separated on Chiracel OD 5% IPA/Hexane, 1.0 mL/min (t\(_1\) = 12.2 min; t\(_2\) = 16.5 min).

**N-(S)-\(\alpha\)-Methylbenzyl hydroxylamine 13.**

Ammonium hydroxide solution (33%, 3.5 mL) was added dropwise (over 5 min) to a solution of N-(S)-\(\alpha\)-methylbenzyl-O-benzoyl hydroxylamine 10 (3.28 g, 13.59 mmol) in methanol (7 mL) under nitrogen, and stirring was continued at room temperature overnight. The methanol was removed under reduced pressure and the residue dissolved in ethyl acetate (50 mL), washed with brine (30 mL), dried (MgSO\(_4\)) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (1:1) to give N-(S)-\(\alpha\)-methylbenzyl hydroxylamine 13 (1.29 g, 70%) as a white solid. mp 89–93 °C; IR (thin film)/cm\(^{-1}\): 3254, 3130, 2966, 2871, 1495, 1453, 1422, 1366, 1207, 1069, 1006; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.15–7.30 (m, 5H), 5.90–6.05 (br, 2H), 4.00 (q, 1H, J 6.7 Hz), 1.30 (d, 3H, J 6.7 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.0, 128.6, 127.7, 127.2, 61.8, 19.3 ppm; MS (ES): \(m/z\) 137 [M]; \([\alpha]^{23}_D\) –30.8 (c 1.0, CHCl\(_3\)).

**N-(S)-\(\alpha\)-Methylbenzyl-O-pivaloyl hydroxylamine 15.**

Synthesised from pivalic acid (1.0 g, 9.8 mmol) and N-(S)-\(\alpha\)-methylbenzyl hydroxylamine 13 (1.6 g, 11.8 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave N-(S)-\(\alpha\)-methylbenzyl-O-pivaloyl hydroxylamine 15 (51%) as a clear colourless oil. IR (thin film)/cm\(^{-1}\): 3233, 2975, 2867, 1727, 1480, 1455, 1368, 1280, 1146, 1025, 978, 760, 700; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65–7.75 (br, 1H), 7.30–7.35 (m, 4H), 7.25–7.30 (m, 1H), 4.20 (q, 1H, J 6.7 Hz), 1.45 (d, 3H, J 6.7 Hz), 1.10 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 178.3, 141.2, 128.5, 127.8, 127.1, 60.8, 38.3, 27.0, 19.4 ppm; MS (ES): \(m/z\) 222 [M + H]+; HRMS calculated for C\(_{13}\)H\(_{20}\)NO\(_2\) [M + H]+ 222.1494, found 222.1499; \([\alpha]^{23}_D\) –14.2 (c 1.0, CHCl\(_3\)).

**N-Methyl-O-pivaloyl hydroxylamine hydrochloride.**

Synthesised from pivalic acid (2.00 g, 19.6 mmol) and N-methyl hydroxylamine hydrochloride (1.96 g, 23.5 mmol) using General Procedure 2. Conversion to the HCl salt
gave *N*-methyl-*O*-pivaloyl hydroxylamine hydrochloride (37%) as a white solid which was collected by filtration. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.90–10.00\) (br, 2H), 2.80 (s, 3H), 1.25 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 178.5, 39.5, 38.2, 27.1\) ppm.

**\(N\)-(S)-\(\alpha\)-Methylbenzyl-*O*-3,5-di-tert-butybenzoyl hydroxylamine 16.**

Synthesised from 3,5-di-tert-butylbenzoic acid (1.0 g, 4.3 mmol) and \(N\)-(S)-\(\alpha\)-methyl benzyl hydroxylamine 13 (0.7 g, 5.2 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave \(N\)-(S)-\(\alpha\)-methylbenzyl-*O*-3,5-di-tert-butyl benzoyl hydroxylamine 16 (63%) as a white solid. mp 32–34 °C; IR (thin film)/cm\(^{-1}\): 3236, 2959, 2872, 1713, 1601, 1475, 1454, 1363, 1311, 1233, 1112, 895; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.80\) (s, 2H), 7.65 (s, 1H), 7.45–7.50 (m, 2H), 7.30–7.40 (m, 3H), 4.35 (q, 1H, \(J = 6.6\) Hz), 1.60 (d, 3H, \(J = 6.6\) Hz), 1.30 (s, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 167.6, 151.2, 141.0, 128.6, 128.0, 127.7, 127.6, 123.6, 61.0, 35.0, 31.3, 19.5 ppm; MS (ES): \(m/z\) 354 \([M + H]^+\); HRMS calculated for C\(_{23}\)H\(_{32}\)NO\(_2\) \([M + H]^+\) 354.2428, found 354.2430; \([\alpha]\)\(^{23}\)_D −44 (c 1.0, CHCl\(_3\)).

**\(N\)-Methyl-*O*-3,5-di-tert-butylbenzoyl hydroxylamine.**

Synthesised from 3,5-di-tert-butylbenzoic acid (2.00 g, 8.5 mmol) and \(N\)-methyl hydroxylamine hydrochloride (0.85 g, 10.2 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave \(N\)-methyl-*O*-3,5-di-tert-butylbenzoyl hydroxylamine (68%) as a clear colourless oil. IR (thin film)/cm\(^{-1}\): 3250, 2963, 2871, 1720, 1600, 1476, 1364, 1312, 1238, 1106; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.90\) (s, 2H), 7.65 (s, 1H), 6.90–7.05 (br, 1H), 3.00 (s, 3H), 1.40 (s, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 167.7, 151.3, 127.7, 127.6, 123.6, 40.0, 35.0, 31.4 ppm; MS (ES): \(m/z\) 264 \([M + H]^+\); HRMS calculated for C\(_{16}\)H\(_{26}\)NO\(_2\) \([M + H]^+\) 264.1694, found 264.1696.

**\(N\)-(S)-\(\alpha\)-Methylbenzyl-*O*-2,4,6-trimethylbenzoyl hydroxylamine 17.**

Synthesised from 2,4,6-trimethylbenzoic acid (1.4 g, 8.5 mmol) and \(N\)-(S)-\(\alpha\)-methyl benzyl hydroxylamine 13 (1.4 g, 10.2 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave \(N\)-(S)-\(\alpha\)-methylbenzyl-*O*-2,4,6-trimethylbenzoyl hydroxylamine 17 (5%) as a clear colourless oil. IR (thin film)/cm\(^{-1}\): 3234, 2976, 2925, 1722, 1611, 1453, 1374, 1260, 1166, 1066, 852, 762, 700; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.20–7.35\) (m, 5H), 6.70 (s, 2H), 4.25 (q, 1H, \(J = 6.7\) Hz), 2.15 (s, 3H), 2.00 (s, 6H), 1.40 (d, 3H, \(J = 6.7\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 170.1, 159.7, 138.3, 133.0, 131.6, 128.0, 127.7, 127.6, 126.0, 119.6, 112.8, 107.1, 29.8, 23.1 ppm; MS (ES): \(m/z\) 358 \([M + H]^+\); HRMS calculated for C\(_{23}\)H\(_{32}\)NO\(_2\) \([M + H]^+\) 358.2428, found 358.2428; \([\alpha]\)\(^{23}\)_D −33 (c 1.0, CHCl\(_3\)).
141.6, 139.9, 135.7, 128.6, 128.5, 128.4, 127.9, 127.0, 60.8, 21.2, 20.1, 19.5 ppm; MS (ES): m/z 284 [M + H]⁺; HRMS calculated for C₁₈H₂₂NO₂ [M + H]⁺ 284.1645, found 284.1648.

**N-Methyl-O-2,4,6-trimethylbenzoyl hydroxylamine.**

Synthesised from 2,4,6-trimethylbenzoic acid (2.00 g, 12.2 mmol) and N-methyl hydroxylamine hydrochloride (1.22 g, 14.6 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave N-methyl-O-2,4,6-trimethylbenzoyl hydroxylamine (6%) as a clear colourless oil. IR (thin film)/cm⁻¹: 3252, 2922, 1724, 1611, 1467, 1438, 1258, 1168, 1061, 847; ¹H NMR (400 MHz, CDCl₃) δ 7.60–7.80 (br, 1H), 6.75 (s, 2H), 2.90 (s, 3H), 2.25 (s, 6H), 2.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 140.1, 135.6, 128.5, 128.4, 39.8, 21.2, 19.6 ppm; MS (ES): m/z 194 [M + H]⁺; HRMS calculated for C₁₁H₁₆NO₂ [M + H]⁺ 194.1181, found 194.1190.

**N-(S)-α-Methylbenzyl-O-acetyl hydroxylamine 18.**

Synthesised from glacial acetic acid (0.4 g, 6.7 mmol) and N-(S)-α-methylbenzyl hydroxylamine 13 (1.1 g, 8.0 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave N-(S)-α-methylbenzyl-O-acetyloxy hydroxylamine 18 (49%) as a clear colourless oil. IR (thin film)/cm⁻¹: 3236, 3030, 2978, 2933, 2876, 1742, 1604, 1496, 1454, 1369, 1232, 1054, 946; ¹H NMR (400 MHz, CDCl₃) δ 7.20–7.30 (m, 5H), 4.10 (q, 1H, J 6.7 Hz), 1.95 (s, 3H), 1.35 (d, 3H, J 6.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 141.3, 128.6, 127.8, 127.0, 60.7, 19.7, 19.2 ppm; MS (EI): m/z 179 [M⁺]; HRMS calculated for C₁₀H₁₃NO₂ [M⁺] 179.0941, found 179.0942; [α]²³D −56.8 (c 1.0, CHCl₃).

**(+)-2-Pivaloyloxy cyclohexanone 20.**

Prepared by reaction of cyclohexanone 2 (59 mg, 0.6 mmol) and N-methyl-O-pivaloyl hydroxylamine hydrochloride (100 mg, 0.6 mmol) in DMSO (1.2 mL) using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave (+)-2-pivaloyloxy cyclohexanone 20 (71%) as a low melting crystalline solid. mp 26–31 °C; IR (thin film)/cm⁻¹: 2958, 2870, 1737, 1726, 1480, 1458, 1397, 1280, 1158, 1114, 1064; ¹H NMR (400 MHz, CDCl₃) δ 5.05 (dd, 1H, J 11.1, 6.3 Hz), 2.40–2.45 (m, 1H), 2.25–2.40 (m, 1H), 2.15–2.25 (m, 1H), 1.95–2.05 (m, 1H), 1.85–1.95 (m, 1H), 1.65–1.80 (m 2H), 1.50–1.65 (m, 1H), 1.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 204.6, 177.7, 176.2, 40.7, 38.7, 32.9, 27.19, 27.18, 23.7 ppm; MS (ES): m/z 199 [M + H]⁺; HRMS...
calculated for C₁₁H₁₉O₃ [M + H]⁺ 199.1329, found 199.1331; Enantiomers separated by ¹H NMR spectroscopy, using 0.1 equivalents of shift reagent Eu(hfc)₃, see Supplementary Information for full details.

(±)-2-(3,5-Di-tert-butylbenzoyloxy)cyclohexanone 21.

Prepared by reaction of cyclohexanone 2 (33 mg, 0.33 mmol) and N-methyl-O-3,5-di-tert-butylbenzoyl hydroxylamine (100 mg, 0.33 mmol) in DMSO (0.7 mL) using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave (±)-2-(3,5-di-tert-butylbenzoyloxy)cyclohexanone 21 (169 mg, 90%) as a white crystalline solid. mp 85–89 °C; IR (thin film)/cm⁻¹: 2962, 2868, 1735, 1718, 1598, 1476, 1459, 1364, 1319, 1241, 1114, 895; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 2H), 7.55 (s, 1H), 5.30 (dd, 1H, J 12.1, 6.3 Hz), 2.45–2.50 (m, 1H), 2.30–2.45 (m, 2H), 2.00–2.10 (m, 1H), 1.80–2.00 (m, 2H), 1.70–1.80 (m, 1H), 1.60–1.70 (m, 1H), 1.25 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 204.6, 166.4, 151.0, 129.0, 127.5, 124.1, 77.4, 40.8, 34.9, 33.2, 31.4, 27.2, 23.8 ppm; MS (ES): m/z 331 [M + H]⁺; HRMS calculated for C₂₁H₃₁O₃ [M + H]⁺ 331.2268, found 331.2267; Enantiomers separated by ¹H NMR spectroscopy, using 1.3 equivalents of shift reagent Eu(hfc)₃, see Supplementary Information for full details.

(±)-2-(2,4,6-Trimethylbenzoyloxy)cyclohexanone 22.

Prepared by reaction of cyclohexanone 2 (43 mg, 0.44 mmol) and N-methyl-O-2,4,6-trimethylbenzoyl hydroxylamine (100 mg, 0.44 mmol) in DMSO (0.9 mL) using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave (±)-2-(2,4,6-trimethylbenzoyloxy)cyclohexanone 22 (31 mg, 40%) as a white crystalline solid. mp 57–62 °C; IR (thin film)/cm⁻¹: 2944, 2866, 1736, 1722, 1611, 1451, 1428, 1313, 1263, 1169, 1090, 1034, 852; ¹H NMR (400 MHz, CDCl₃) δ 6.80 (s, 2H), 5.35 (dd, 1H, J 12.1, 6.4 Hz), 2.45–2.55 (m, 1H), 2.35–2.45 (m, 1H), 2.30 (s, 6H), 2.20 (s, 3H), 2.00–2.10 (m, 1H), 1.90–2.00 (m, 1H), 1.70–1.85 (m, 2H), 1.50–1.65 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 204.2, 168.9, 139.5, 135.7, 130.1, 128.5, 76.9, 40.9, 33.1, 27.2, 23.9, 21.2, 19.9 ppm; MS (APCI): m/z 261 [M + H]⁺; HRMS calculated for C₁₆H₁₇O₃ [M + H]⁺ 261.1491, found 261.1484; Enantiomers separated on Chiracel OD column, 5% IPA/Hexane, 1.0 mL/min (t₁ = 9.7 min; t₂ = 12.1 min).

(±)-2-Acetoxyloxy cyclohexanone 23.

Prepared by reaction of cyclohexanone 2 (78 mg, 0.80 mmol) and N-(S)-α-methyl benzyl-O-acetyl hydroxylamine (100 mg, 0.80 mmol) in DMSO (1.6 mL) using General
Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave (±)-2-acetoxyl-2-cyclohexanone 23 (44 mg, 50%) as a white crystalline solid. mp 25–29 °C; [lit.\textsuperscript{5} 35–36 °C]; IR (thin film) cm\textsuperscript{-1}: 2940, 2861, 1745, 1725, 1376, 1239, 1070; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 5.10 (dd, 1H, J 11.5, 6.4 Hz), 2.40–2.50 (m, 1H), 2.25–2.40 (m, 1H), 2.20–2.25 (m, 1H), 2.10 (s, 3H), 2.00–2.10 (m, 1H), 1.85–1.95 (m, 1H), 1.65–1.75 (m, 2H), 1.50–1.60 (m, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 204.6, 170.1, 76.6, 40.7, 33.1, 27.2, 23.8, 20.8 ppm; MS (ES) m/z 156 [M]+; HRMS calculated for C\textsubscript{8}H\textsubscript{12}O\textsubscript{3} [M]+ 156.0786, found 156.0786; Enantiomers separated by \textsuperscript{1}H NMR, using 0.3 equivalents of shift reagent Eu(hfc)\textsubscript{3}.


Compound 24 was synthesised from 4-fluorobenzoic acid (0.50 g, 3.6 mmol) and N-(S)-\textit{α}-methylbenzyl hydroxylamine (0.59 g, 4.32 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave N-(S)-\textit{α}-methylbenzyl-\textit{O}-4-fluorobenzoyl hydroxylamine 24 (59%) as a clear colourless oil. IR (thin film) cm\textsuperscript{-1}: 3233, 2977, 1724, 1604, 1507, 1454, 1320, 1287, 1155, 1084, 1014, 852, 759; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 7.80–7.90 (m, 2H), 7.30–7.35 (m, 2H), 7.25–7.30 (m, 2H), 7.20–7.25 (m, 1H), 7.00 (dd, 2H, J 8.7, 8.7 Hz), 4.25 (q, 1H, J 6.7 Hz), 1.45 (d, 3H, J 6.7 Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 166.0, 165.9, 141.2, 132.0, 128.7, 128.0, 127.1, 124.6, 115.8, 61.0, 19.7 ppm; MS (ES) m/z 260 [M + H]+; HRMS calculated for C\textsubscript{15}H\textsubscript{15}NO\textsubscript{2}F [M + H]+ 260.1081, found 260.1084; [α]\textsuperscript{23}_D −71.6 (1 g/100 mL, CHCl\textsubscript{3}).

\textit{N}-Methyl-\textit{O}-4-fluorobenzoyl hydroxylamine.

The title compound was synthesised from 4-fluorobenzoic acid (0.75 g, 5.35 mmol) and N-methyl hydroxylamine hydrochloride using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:2), gave N-\textit{methyl}-\textit{O}-4-fluorobenzoyl hydroxylamine (42%) as a white solid. mp 26–28 °C; IR (thin film) cm\textsuperscript{-1}: 3246, 2969, 1724, 1603, 1508, 1474, 1436, 1414, 1272, 1239, 1156, 1080, 1014, 853, 760; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 8.00 (dd, 2H, J 9.0, 5.4 Hz), 7.05 (t, 2H, J 8.7 Hz), 6.95–7.05 (br, 1H), 2.90 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 166.0, 165.9, 132.0, 124.6, 115.8, 39.9 ppm; MS (ES) m/z 170 [M + H]+; HRMS calculated for C\textsubscript{8}H\textsubscript{9}NO\textsubscript{2}F [M + H]+ 170.0612, found 170.0612.
**N-(S)-α-Methylbenzyl-O-4-methoxybenzoyl hydroxylamine 25.**

Compound 25 was synthesised from 4-methoxybenzoic acid (0.60 g, 3.9 mmol) and N-(S)-α-methylbenzyl hydroxylamine (0.64 g, 4.7 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave N-(S)-α-methylbenzyl-O-4-methoxybenzoyl hydroxylamine 25 (81%) as a clear colourless oil. IR (thin film)/cm\(^{-1}\): 3232, 2975, 1714, 1606, 1581, 1510, 1455, 1421, 1317, 1258, 1169, 1089, 1027, 845, 762; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, 2H, \(J\) 9.0 Hz), 7.30–7.35 (m, 2H), 7.25 (dd, 2H, \(J\) 7.3, 7.3 Hz), 7.20–7.25 (m, 1H), 6.80 (d, 2H, \(J\) 9.0 Hz), 4.20 (q, 1H, \(J\) 6.7 Hz), 3.75 (s, 3H), 1.45 (d, 3H, \(J\) 6.7 Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.7, 163.7, 141.3, 131.4, 128.6, 127.9, 127.2, 120.6, 113.8, 55.5, 19.8 ppm; MS (EI): \(m/z\) 272 [M]\(^+\); HRMS calculated for C\(_{16}\)H\(_{18}\)NO\(_3\) [M + H]\(^+\) 272.1281, found 272.1278; [\(\alpha\)]\(^{23}\)\(_D\) −76 (1 g/100 mL, CHCl\(_3\)).

**N-Methyl-O-4-methoxybenzoyl hydroxylamine.**

The title compound was synthesised from 4-methoxybenzoic acid (5.0 g, 33 mmol) and N-methyl hydroxylamine hydrochloride (3.3 g, 39.6 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (1:1), gave N-methyl-O-4-methoxybenzoyl hydroxylamine (72%) as a white solid. mp 38–43 °C; IR (thin film)/cm\(^{-1}\): 3246, 2932, 1718, 1606, 1511, 1465, 1421, 1318, 1257, 1170, 1080, 1027, 846, 763; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, 2H, \(J\) 9.0 Hz), 6.85 (d, 2H, \(J\) 9.0 Hz), 3.80 (s, 3H), 2.85 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.7, 163.7, 141.3, 131.4, 128.6, 127.9, 127.2, 120.6, 113.8, 55.5, 39.9 ppm; MS (ES): \(m/z\) 182 [M + H]\(^+\).

**N-(S)-α-Methylbenzyl-O-4-dimethylaminobenzoyl hydroxylamine 26.**

Compound 26 was synthesised from 4-dimethylaminobenzoic acid (0.60 g, 3.6 mmol) and N-(S)-α-methylbenzyl hydroxylamine (0.59 g, 4.3 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (65:35), gave N-(S)-α-methylbenzyl-O-4-dimethylaminobenzoyl hydroxylamine 26 (84%) as a white solid. mp 54–58 °C; IR (thin film)/cm\(^{-1}\): 3230, 2928, 1701, 1607, 1529, 1445, 1370, 1275, 1184, 1068, 825, 762, 699; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, 2H, \(J\) 9.1 Hz), 7.45 (d, 2H, \(J\) 7.0 Hz), 7.35 (dd, 2H, \(J\) 7.3, 7.3 Hz), 7.30–7.35 (m, 1H), 6.65 (d, 2H, \(J\) 9.1 Hz), 3.80 (s, 3H), 2.85 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 153.5, 141.5, 131.1, 128.5, 127.8, 127.2, 114.8, 110.8, 60.9, 40.1, 19.8 ppm; MS (ES): \(m/z\)
285 [M + H]+; HRMS calculated for C_{17}H_{21}N_{2}O_{2} [M + H]^{+} 285.1598, found 285.1601; [α]^{23}_{D} −98 (1 g/100 mL, CHCl_{3}).

**N-Methyl-O-4-dimethylaminobenzoyl hydroxylamine.**

The title compound was synthesised from 4-dimethylaminobenzoic acid (1.00 g, 6.1 mmol) and N-methyl hydroxylamine hydrochloride (0.61 g, 7.3 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (1:1), gave *N*-methyl-*O*-4-dimethylaminobenzoyl hydroxylamine (41%) as a white solid. mp 103–108 °C; IR (thin film)/cm⁻¹: 3253, 2906, 1702, 1620, 1461, 1377, 1320, 1289, 1 236, 1190, 1098, 971, 826, 764; 

1H NMR (400 MHz, CDCl_{3}) δ 7.80 (d, 2H, J 9.0 Hz), 6.60 (d, 2H, J 9.0 Hz), 3.00 (s, 6H), 2.80 (s, 3H); 

13C NMR (100 MHz, CDCl_{3}) δ 167.4, 153.5, 131.1, 114.7, 110.7, 40.1, 40.0 ppm; MS (APCI): m/z 195 [M + H]^{+}; HRMS calculated for C_{10}H_{15}N_{2}O_{2} [M + H]^{+} 195.1134, found 195.1142.

**N-(S)-α-Methylbenzyl-O-3,4,5-trimethoxybenzoyl hydroxylamine 27.**

Compound 27 was synthesised from 3,4,5-trimethoxybenzoic acid (0.60 g, 2.8 mmol) and N-(S)-α-methylbenzyl hydroxylamine (0.46 g, 3.4 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave *N-(S)-α-methylbenzyl-O-3,4,5-trimethoxybenzoyl hydroxylamine 27* (88%) as a clear colourless oil. IR (thin film)/cm⁻¹: 3239, 2935, 1715, 1588, 1504, 1457, 1416, 1337, 1218, 1174, 1128, 1002, 754, 701; 

1H NMR (400 MHz, CDCl_{3}) δ 7.80–7.90 (br, 1H), 7.20 (s, 2H), 3.85 (s, 9H), 2.90 (s, 3H); 

13C NMR (100 MHz, CDCl_{3}) δ 166.6, 153.0, 142.4, 141.1, 128.6, 128.0, 127.2, 123.2, 106.5, 61.2, 61.0, 56.2, 19.6 ppm; MS (EI): m/z 331 [M]^{+}; HRMS calculated for C_{18}H_{22}NO_{5} [M]^{+} 332.1492, found 332.1494.

**N-Methyl-O-3,4,5-trimethoxybenzoyl hydroxylamine.**

The title compound was synthesised from 3,4,5-trimethoxybenzoic acid (1.00 g, 4.7 mmol) and N-methyl hydroxylamine hydrochloride (0.47 g, 5.6 mmol) using General Procedure 2. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (2:3), gave *N-methyl-O-3,4,5-trimethoxybenzoyl hydroxylamine* (42%) as a white solid. mp 71–74 °C; IR (thin film)/cm⁻¹: 3246, 2942, 1713, 1588, 1504, 1463, 1415, 1336, 1230, 1185, 1130, 993, 862, 754; 

1H NMR (400 MHz, CDCl_{3}) δ 7.70–7.80 (br, 1H), 7.20 (s, 2H), 3.85 (s, 9H), 2.90 (s, 3H); 

13C NMR (100 MHz, CDCl_{3}) δ 166.6, 153.0, 142.5, 123.2, 106.5, 61.0, 56.3,
40.0 ppm; MS (EI): m/z 241 [M]+; HRMS calculated for C_{11}H_{15}NO_{5} [M]^{+} 241.0950, found 241.0950.

**N-(S)-α-Methyl-4-fluorobenzyl-O-benzoyl hydroxylamine 28.**

Compound 28 was synthesised from (S)-α-methyl-4-fluorobenzylamine using General Procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave N-(S)-α-methyl-4-fluorobenzyl-O-benzoyl hydroxylamine 28 (2.41 g, 63%) as a white solid. mp 41–46 °C; IR (thin film)/cm\(^{-1}\): 3226, 2976, 1720, 1602, 1510, 1452, 1316, 1268, 1225, 1178, 1159, 1091, 1066, 1025, 997, 836; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, 2H, \(J\) 7.1 Hz), 7.50 (t, 1H, \(J\) 7.5 Hz), 7.30–7.40 (m, 4H), 6.95 (dd, 2H, \(J\) 8.7, 8.7 Hz), 4.20 (q, 1H, \(J\) 6.7 Hz), 1.45 (d, 3H, \(J\) 6.7 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8, 162.4, 137.0, 133.4, 129.3, 128.8, 128.6, 128.2, 115.5, 60.2, 19.8 ppm; MS (APCI): m/z 260 [M + H]\(^+\); HRMS calculated for C\(_{15}\)H\(_{15}\)NO\(_2\)F [M + H]\(^+\) 260.1081, found 260.1081; [\(\alpha\)]\(^{23}\)D −69.2 (1 g/100 mL, CHCl\(_3\)).

**N-(S)-α-Methyl-4-methylbenzyl-O-benzoyl hydroxylamine 29.**

Compound 29 was synthesised from (S)-α-methyl-4-methylbenzylamine using General Procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave N-(S)-α-methyl-4-methylbenzyl-O-benzoyl hydroxylamine 29 (2.61 g, 75%) as a white solid. mp 33–35 °C; IR (thin film)/cm\(^{-1}\): 3226, 2964, 1718, 1600, 1514, 1451, 137.0, 133.4, 129.3, 128.8, 128.6, 128.2, 115.5, 60.2, 19.8 ppm; MS (ES): m/z 256 [M + H]\(^+\); HRMS calculated for C\(_{16}\)H\(_{18}\)NO\(_2\) [M + H]\(^+\) 256.1332, found 256.1331; [\(\alpha\)]\(^{23}\)D −78 (1 g/100 mL, CHCl\(_3\)).

**N-(S)-α-Methyl-4-methoxybenzyl-O-benzoyl hydroxylamine 30.**

Compound 30 was synthesised from (S)-α-methyl-4-methoxybenzylamine using General Procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave N-(S)-α-methyl-4-methoxybenzyl-O-benzoyl hydroxylamine 30 (2.7 g, 74%) as a white solid. mp 34–37 °C; IR (thin film)/cm\(^{-1}\): 3235, 2973, 1719, 1611, 1514, 1451, 1264, 1248, 1177, 1088, 1059, 1025, 829; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, 2H, \(J\) 7.1 Hz), 7.45 (t, 1H, \(J\) 7.5 Hz), 7.30 (dd, 2H, \(J\) 7.7, 7.7 Hz), 7.20 (d, 2H, \(J\) 8.7 Hz), 7.10 (d, 2H, \(J\) 8.7 Hz), 4.20 (q, 1H, \(J\) 6.6 Hz), 2.25 (s, 3H), 1.45 (d, 3H, \(J\) 6.6 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.9, 138.1, 137.6, 133.3, 129.4, 129.3, 128.5, 128.4, 127.1, 60.7, 21.2, 19.7 ppm; MS (ES): m/z 256 [M + H]\(^+\); HRMS calculated for C\(_{16}\)H\(_{18}\)NO\(_2\) [M + H]\(^+\) 256.1332, found 256.1331; [\(\alpha\)]\(^{23}\)D −78 (1 g/100 mL, CHCl\(_3\)).
8.7 Hz), 4.20 (q, 1H, J 6.6 Hz), 3.70 (s, 3H), 1.45 (d, 3H, J 6.6 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 159.3, 133.3, 133.0, 129.3, 128.5, 128.36, 128.36, 114.0, 60.3, 55.3, 19.7 ppm; MS (ES): m/z 272 [M + H]$^+$; HRMS calculated for C$_{16}$H$_{18}$NO$_3$ [M + H]$^+$ 272.1281, found 272.1280; $\alpha$$^{23}$D $-82.2$ (1 g/100 mL, CHCl$_3$).

(±)-2-(4-Fluorobenzoyloxy)cyclohexanone 31.

Compound 31 was synthesised through reaction of cyclohexanone and N-methyl-O-4-fluorobenzoyl hydroxylamine, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave (±)-2-(4-fluorobenzoyloxy) cyclohexanone 31 (71 mg, 51%) as a white crystalline solid. mp 74–79 °C; IR (thin film)/cm$^{-1}$: 2948, 2865, 1731, 1716, 1604, 1507, 1312, 1270, 1150, 1112, 1091, 766; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00–8.10 (m, 2H), 7.05 (dd, 2H, J 8.7 Hz), 5.30 (dd, 1H, J 12.0, 6.4 Hz), 2.45–2.55 (m, 1H), 2.30–2.50 (m, 2H), 2.00–2.10 (m, 1H), 1.90–2.00 (m, 1H), 1.70–1.90 (m, 2H), 1.55–1.70 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.2, 167.0, 164.8, 132.5, 126.0, 115.5, 77.1, 40.8, 33.2, 21.2, 23.8 ppm; MS (ES): m/z 237 [M + H]$^+$; HRMS calculated for C$_{13}$H$_{14}$O$_3$F [M + H]$^+$ 237.0921, found 237.0919; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1$ = 10.5 min; $t_2$ = 12.6 min).

(±)-2-(4-Methoxybenzoyloxy)cyclohexanone 32.

Compound 32 was synthesised through reaction of cyclohexanone and N-methyl-O-4-methoxybenzoyl hydroxylamine, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (65:35), gave (±)-2-(4-methoxybenzoyloxy) cyclohexanone 32 (104 mg, 76%) as a white crystalline solid. mp 114–118 °C; IR (thin film)/cm$^{-1}$: 2944, 1727, 1702, 1604, 1511, 1320, 1280, 1260, 1173, 1109, 1038, 770; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, 2H, J 9.0 Hz), 6.85 (d, 2H, J 9.0 Hz), 5.30 (dd, 1H, J 11.2, 6.3 Hz), 3.80 (s, 3H), 2.45–2.55 (m, 1H), 2.30–2.45 (m, 2H), 2.00–2.10 (m, 1H), 1.90–2.00 (m, 1H), 1.70–1.90 (m, 2H), 1.55–1.70 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.6, 165.3, 163.6, 132.0, 122.1, 113.6, 76.9, 55.4, 40.8, 33.3, 27.3, 23.8 ppm; MS (APCI): m/z 249 [M + H]$^+$; HRMS calculated for C$_{14}$H$_{17}$O$_4$ [M + H]$^+$ 249.1121, found 249.1122; Enantiomers separated on OD chiral column, 10% IPA/Hexane, 1.0 mL/min ($t_1$ = 14.8 min; $t_2$ = 19.1 min).
(±)-2-(4-dimethylaminobenzoyloxy)cyclohexanone 33.

Compound 33 was synthesised through reaction of cyclohexanone and \(N\)-methyl-\(O\)-4-dimethylaminobenzoyl hydroxylamine, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave (±)-2-(4-dimethylaminobenzoyloxy) cyclohexanone 33 (64 mg, 48%) as a white crystalline solid. mp 107–112 °C; IR (thin film)/cm\(^{-1}\): 2941, 2867, 1731, 1702, 1607, 1528, 1448, 1368, 1183, 1107; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, 2H, \(J\) 9.0 Hz), 6.55 (d, 2H, \(J\) 9.0 Hz), 5.30 (dd, 1H, \(J\) 11.2, 6.3 Hz), 2.95 (s, 6H), 2.45–2.50 (m, 1H), 2.35–2.45 (m, 1H), 2.30–2.35 (m, 1H), 2.00–2.10 (m, 1H), 1.90–2.00 (m, 1H), 1.70–1.90 (m, 2H), 1.60–1.70 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 205.2, 165.9, 153.5, 131.7, 116.3, 110.7, 76.3, 40.8, 40.1, 33.4, 27.3, 23.9 ppm; MS (EI): \(m/z\) 261 \([M]^+\); HRMS calculated for \(C_{15}H_{19}NO_3\) \([M]^+\) 261.1359, found 261.1361; Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min (\(t_1\) = 22.9 min; \(t_2\) = 28.5 min).

(±)-2-(3,4,5-Trimethoxybenzoyloxy)cyclohexanone 34.

Compound 34 was synthesised through reaction of cyclohexanone and \(N\)-methyl-\(O\)-3,4,5-trimethoxybenzoyl hydroxylamine 27, using general procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:2), gave (±)-2-(3,4,5-trimethoxybenzoyloxy) cyclohexanone 34 (108 mg, 85%) as a white crystalline solid. mp 93–98 °C; IR (thin film)/cm\(^{-1}\): 2941, 1735, 1717, 1589, 1501, 1458, 1415, 1337, 1224, 1127; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 (s, 2H), 5.30 (dd, 1H, \(J\) 11.3, 6.4 Hz), 3.80 (s, 9H), 2.45–2.55 (m, 1H), 2.35–2.45 (m, 2H), 2.00–2.10 (m, 1H), 1.95–2.00 (m, 1H), 1.70–1.90 (m, 2H), 1.55–1.70 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 204.4, 165.3, 152.9, 142.6, 124.7, 107.1, 77.2, 61.0, 56.3, 40.8, 33.2, 27.2, 23.9 ppm; MS (EI): \(m/z\) 308 \([M]^+\); HRMS calculated for \(C_{16}H_{20}O_6\) \([M]^+\) 308.1254, found 308.1253; Enantiomers separated on OD chiral column, 2.5% IPA/Hexane, 0.5 mL/min (\(t_1\) = 48.2 min; \(t_2\) = 55.5 min).

\(N\)-(S)-\(\alpha\)-Ethylbenzyl-\(O\)-benzoyl hydroxylamine 38.

Compound 31 was synthesised from (S)-\(\alpha\)-ethylbenzylamine (1.0 g, 7.4 mmol) using general procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave \(N\)-(S)-\(\alpha\)-ethylbenzyl-\(O\)-benzoyl hydroxylamine 38 (75%) as a white solid. mp 28–33 °C; IR (thin film)/cm\(^{-1}\): 3229, 2963, 2931, 2876, 1720, 1452, 1268, 1089, 1065; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90–8.00 (br, 1H), 7.80 (d, 2H, \(J\) 7.1 Hz), 7.45 (t, 1H, \(J\) 7.5 Hz), 7.35–7.40 (m, 3H), 7.25–7.30 (m, 2H), 7.10–7.20 (m, 3H), 6.95 (s, 1H), 6.85–6.95 (m, 2H), 6.75–6.85 (m, 2H), 6.65–6.75 (m, 2H), 4.00–4.10 (m, 2H), 3.80–3.90 (m, 2H), 3.70–3.80 (m, 2H), 3.60–3.70 (m, 2H), 3.50–3.60 (m, 2H), 3.40–3.50 (m, 2H), 3.30–3.40 (m, 2H), 3.20–3.30 (m, 2H), 3.10–3.20 (m, 2H), 3.00–3.10 (m, 2H), 2.90–3.00 (m, 2H), 2.80–2.90 (m, 2H), 2.70–2.80 (m, 2H), 2.60–2.70 (m, 2H), 2.50–2.60 (m, 2H), 2.40–2.50 (m, 2H), 2.30–2.40 (m, 2H), 2.20–2.30 (m, 2H), 2.10–2.20 (m, 2H), 2.00–2.10 (m, 2H), 1.90–2.00 (m, 2H), 1.80–1.90 (m, 2H), 1.70–1.80 (m, 2H), 1.60–1.70 (m, 2H), 1.50–1.60 (m, 2H), 1.40–1.50 (m, 2H), 1.30–1.40 (m, 2H), 1.20–1.30 (m, 2H), 1.10–1.20 (m, 2H), 1.00–1.10 (m, 2H), 0.90–1.00 (m, 2H), 0.80–0.90 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 204.5, 165.7, 152.9, 142.6, 124.7, 107.1, 77.2, 61.0, 56.3, 40.8, 33.2, 27.2, 23.9 ppm; MS (EI): \(m/z\) 308 \([M]^+\); HRMS calculated for \(C_{16}H_{20}O_6\) \([M]^+\) 308.1254, found 308.1253; Enantiomers separated on OD chiral column, 2.5% IPA/Hexane, 0.5 mL/min (\(t_1\) = 48.2 min; \(t_2\) = 55.5 min).
7.20–7.35 (m, 7H), 3.95 (dd, 1H, $J$ 8.3, 5.8 Hz), 1.90–2.00 (m, 1H), 1.70–1.80 (m, 1H), 0.80 (t, 3H, $J$ 7.5 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 140.0, 133.3, 129.3, 128.53, 128.49, 128.4, 127.9, 127.7, 67.7, 26.8, 10.6 ppm; MS (ES): $m/z$ 256 [M + H]$^+$; HRMS calculated for C$_{16}$H$_{18}$NO$_2$ [M + H]$^+$ 256.1338, found 256.1341; $[\alpha]_{23}^{2}$D +64 (1 g/100 mL, CHCl$_3$).

**N-(S)-α-Methylcyclohexyl-O-benzoyl hydroxylamine hydrochloride 39·HCl.**

Compound 39·HCl was synthesised from N-(S)-α-methylcyclohexylamine (1.0 g, 7.9 mmol) using General Procedure 1. Conversion to the HCl salt gave N-(S)-α-methylcyclohexyl-O-benzoyl hydroxylamine hydrochloride 39·HCl (76%) as a white solid, which was collected by filtration. mp 105–109 °C; IR (thin film)/cm$^{-1}$: 2925, 2843, 1718, 1446, 1270, 1064, 1020, 767, 707; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.40–9.70 (br, 2H), 7.95 (d, 2H, $J$ 7.1 Hz), 7.65 (t, 1H, $J$ 7.5 Hz), 7.55 (dd, 2H, $J$ 7.7, 7.7 Hz), 3.00–3.10 (m, 1H), 1.65–1.80 (m, 4H), 1.55–1.65 (m, 1H), 1.44–1.55 (m, 1H), 1.10–1.25 (m, 4H), 1.05 (d, 3H, $J$ 6.6 Hz), 1.00–1.05 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 134.1, 129.5, 129.3, 128.7, 60.5, 40.1, 29.8, 28.1, 26.6, 26.5, 26.3, 14.6 ppm; MS (APCI): $m/z$ 248 [M + H]$^+$; HRMS calculated for C$_{15}$H$_{22}$NO$_2$ [M + H]$^+$ 248.1645, found 248.1645.

**N-(S)-1,2,3,4-Tetrahydronaphthyl-O-benzoyl hydroxylamine hydrochloride 40·HCl.**

Compound 40·HCl was synthesised from N-(S)-1,2,3,4-tetrahydronaphthylamine (0.5 mL, 3.5 mmol) using General Procedure 1. Conversion to the HCl salt gave N-(S)-1,2,3,4-tetrahydronaphthyl-O-benzoyl hydroxylamine hydrochloride 40·HCl (11%) as a white crystalline solid, which was collected by filtration. mp 90–93 °C; IR (thin film)/cm$^{-1}$: 2939, 1717, 1450, 1315, 1268, 1089, 1065, 1025, 707; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, 2H, $J$ 7.0 Hz), 7.65 (m, 1H), 7.55 (t, 2H, $J$ 7.8 Hz), 7.50 (d, 1H, $J$ 6.9 Hz), 7.15–7.25 (m, 2H), 7.10–7.15 (m, 1H), 6.10–6.50 (br, 2H), 4.30 (t, 1H, $J$ 4.5 Hz), 2.65–2.85 (m, 2H), 1.90–2.10 (m, 2H), 1.80–1.90 (m, 1H), 1.65–1.75 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 138.7, 134.1, 134.0, 130.1, 129.44, 129.41, 129.3, 128.9, 127.9, 126.1, 57.9, 29.2, 26.7, 18.7 ppm; MS (ES): $m/z$ 268 [M + H]$^+$; HRMS calculated for C$_{17}$H$_{22}$NO$_2$ [M + H]$^+$ 268.1332, found 268.1330.

**N-(R)-3,3-Dimethyl-2-butyl-O-benzoyl hydroxylamine hydrochloride 41·HCl.**

Compound 41·HCl was synthesised from N-(R)-3,3-dimethyl-2-butylamine (2.0 g, 19.8 mmol) using General Procedure 1. Conversion to the HCl salt gave N-(R)-3,3-dimethyl-2-butyl-O-benzoyl hydroxylamine hydrochloride 41·HCl (81%) as a white
crystalline solid, which was collected by filtration. mp 95–99 °C; IR (thin film)/cm$^{-1}$: 2962, 1719, 1602, 1451, 1364, 1315, 1271, 1177, 1089, 1066, 1026, 707; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.90–10.20 (br, 2H), 7.95 (d, 2H, $J$ 7.2 Hz), 7.70 (t, 1H, $J$ 7.5 Hz), 7.55 (dd, 2H, $J$ 7.7, 7.7 Hz), 2.90 (q, 1H, $J$ 7.0 Hz), 1.10 (d, 3H, $J$ 7.0 Hz), 0.95 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.2, 134.0, 129.4, 129.2, 128.8, 64.4, 34.0, 27.2, 13.7 ppm; MS (APCI): m/z 222 [M + H]$^+$; HRMS calculated for C$_{13}$H$_{20}$NO$_2$ [M + H]$^+$ 222.1489, found 222.1489.

$N$-($R$)-3,3-Dimethyl-2-butyl-$O$-benzoyl hydroxylamine 41.

Compound 41 was synthesised from ($R$)-3,3-dimethyl-2-butylamine (2.0 g, 19.8 mmol) using General Procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave $N$-($R$)-3,3-dimethyl-2-butyl-$O$-benzoyl hydroxylamine 41 (81%) as a clear colourless oil. IR (thin film)/cm$^{-1}$: 3247, 2963, 2860, 1720, 1602, 1452, 1365, 1316, 1272, 1178, 1089, 1067, 1026, 707; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, 2H, $J$ 7.1 Hz), 7.60 (t, 1H, $J$ 7.5 Hz), 7.45 (dd, 2H, $J$ 7.7, 7.7 Hz), 2.85 (q, 1H, $J$ 6.5 Hz), 1.10 (d, 3H, $J$ 6.5 Hz), 0.95 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.1, 133.3, 129.3, 129.1, 128.5, 65.1, 33.7, 26.8, 13.7 ppm; MS (APCI): m/z 222 [M + H]$^+$; $[\alpha]_{23}^D$ −44.2 (1 g/100 mL, CHCl$_3$).

$N$-($S$)-3,3-Dimethyl-2-butyl-$O$-benzoyl hydroxylamine 42.

Compound 42 was synthesised from ($S$)-3,3-dimethyl-2-butylamine (2.5 g, 24.7 mmol) using General Procedure 1. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1) gave $N$-($S$)-3,3-dimethyl-2-butyl-$O$-benzoyl hydroxylamine 42 (85%) as a clear colourless oil. IR (thin film)/cm$^{-1}$: 3281, 2961, 2871, 1464, 1396, 1372, 1340, 997, 880; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, 2H, $J$ 6.8 Hz), 7.95–8.00 (br, 1H), 7.55 (t, 1H, $J$ 7.3 Hz), 7.45 (dd, 2H, $J$ 8.0, 8.0 Hz), 2.90 (q, 1H, $J$ 6.6 Hz), 2.05 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.1, 133.3, 129.3, 129.3, 128.5, 65.0, 33.7, 26.8, 13.7 ppm; MS (APCI): m/z 222 [M + H]$^+$; $[\alpha]_{23}^D$ +39.6 (1 g/100 mL, CHCl$_3$).

$N$-($R$)-3,3-Dimethyl-2-butyl hydroxylamine.

Ammonium hydroxide (33%, 6 mL) was added dropwise (over 5 min) to a solution of $N$-($R$)-3,3-dimethyl-2-butyl-$O$-benzoyl hydroxylamine 41 (5.79 g, 26.16 mmol) in methanol (12 mL) under nitrogen, with stirring at room temperature overnight. The methanol was then removed under reduced pressure and the residue dissolved in ethyl acetate (20 mL), washed with brine (20 mL), dried (MgSO$_4$) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (3:2) to give $N$-($R$)-3,3-dimethyl-2-butyl hydroxylamine (1.32 g, 43%) as a clear, pale yellow oil. IR (thin film)/cm$^{-1}$: 3281, 2961, 2871, 1464, 1396, 1372, 1340, 997, 880; $^1$H NMR (400 MHz,
CDCl$_3$ δ 5.60–5.90 (br, 2H, NH and OH), 2.65 (q, 1H, $J$ 6.4 Hz, CHN), 1.05 (d, 3H, $J$ 6.4 Hz, CH$_3$CN), 0.85 (s, 9H, tBu); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 65.7, 33.1, 26.7, 13.1 ppm.

(±)-2-Benzoyloxy cyclopentanone.$^4$

The title compound was synthesised from cyclopentanone and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave (±)-2-benzoyloxy cyclopentanone (79 mg, 72%) as a white crystalline solid. mp 82–86 °C; Lit. ref. mp 88–91 °C; IR (thin film)/cm$^{-1}$: 2915, 2846, 1751, 1716, 1451, 1287, 1269, 1117, 709; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, 2H, $J$ 7.1 Hz), 7.50 (t, 1H, $J$ 7.4 Hz), 7.35 (dd, 2H, $J$ 7.8, 7.8 Hz), 5.25 (dd, 1H, $J$ 10.1, 8.6 Hz), 2.40–2.50 (m, 1H), 2.20–2.40 (m, 2H), 2.05–2.15 (m, 1H), 1.80–2.00 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 212.4, 165.8, 133.4, 130.0, 129.4, 128.4, 76.1, 35.0, 28.6, 17.2 ppm; MS (APCI): m/z 205 [M + H$^+$]; HRMS calculated for C$_{12}$H$_{13}$O$_3$ [M + H]$^+$ 205.0859, found 205.0861; Enantiomers separated on OD chiral column, 2.5% IPA/Hexane, 0.5 mL/min (t$_1$ = 45.5 min; t$_2$ = 48.9 min).

(±)-2-Benzoyloxy cycloheptanone.$^6$

The title compound was synthesised from cycloheptanone and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave (±)-2-benzoyloxy cycloheptanone (89 mg, 72%) as a white crystalline solid. mp 52–56 °C; Lit.$^5$ ref. mp 58–61 °C; IR (thin film)/cm$^{-1}$: 2932, 2861, 1734, 1714, 1448, 1315, 1272, 1107; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, 2H, $J$ 7.1 Hz), 7.50 (t, 1H, $J$ 7.5 Hz), 7.35 (dd, 2H, $J$ 7.7, 7.7 Hz), 5.40 (dd, 1H, $J$ 9.6, 3.3 Hz), 2.60–2.70 (m, 1H), 2.35–2.50 (m, 1H), 2.00–2.10 (m, 1H), 1.60–1.90 (m, 6H), 1.30–1.40 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.5, 165.8, 133.4, 130.0, 129.4, 128.4, 76.1, 35.0, 28.6, 17.2 ppm; MS (ES): m/z 233 [M + H$^+$]; HRMS calculated for C$_{14}$H$_{17}$O$_3$ [M + H]$^+$ 233.1172, found 233.1172; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min (t$_1$ = 11.5 min; t$_2$ = 13.5 min).

(±)-2-Benzoyloxy tetrahydropyran-4-one.$^6$

The title compound was synthesised from tetrahydropyran-4-one and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (1:1), gave (±)-2-benzoyloxy tetrahydropyran-4-one (99 mg, 84%) as a white crystalline solid. mp 76–79 °C; IR (thin
film/cm$^{-1}$: 2913, 2856, 1736, 1719, 1597, 1451, 1315, 1275, 1204, 1121, 1096; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, 2H, $J$ 7.2 Hz), 7.50 (t, 1H, $J$ 7.5 Hz), 7.35 (dd, 2H, $J$ 7.7, 7.7 Hz), 5.45 (dd, 1H, $J$ 9.9, 7.1 Hz), 4.30–4.40 (m, 1H), 4.20–4.30 (m, 1H), 3.60–3.70 (m, 2H), 2.70–2.85 (m, 1H), 2.50–2.60 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.5, 165.1, 133.6, 130.0, 129.0, 128.5, 74.1, 70.6, 68.6, 42.3 ppm; MS (EI): $m/z$ 221 [M + H]$^+$; HRMS calculated for C$_{12}$H$_{13}$O$_4$ [M + H]$^+$ 221.0814, found 221.0809; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1$ = 16.2 min; $t_2$ = 21.8 min).

(±)-2-Benzoyloxy tetrahydrothiopyran-4-one.$^6$

The title compound was synthesised from tetrahydrothiopyran-4-one and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using general procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:2), gave (±)-2-benzoyloxy tetrahydrothiopyran-4-one (255 mg, 68%) as an off-white solid. mp 73–78 °C; IR (thin film)/cm$^{-1}$: 2912, 1736, 1721, 1602, 1451, 1300, 1267, 1177, 1112, 1070, 1028, 772, 710; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, 2H, $J$ 7.1 Hz), 7.50 (t, 1H, $J$ 7.4 Hz), 7.35 (dd, 2H, $J$ 7.6, 7.6 Hz), 5.50 (dd, 1H, $J$ 11.0, 6.3 Hz), 3.05–3.15 (m, 2H), 2.85–2.95 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.6, 165.2, 133.5, 130.0, 129.2, 128.5, 77.2, 44.8, 34.7, 30.4 ppm; MS (EI): $m/z$ 236 [M]$^+$; HRMS calculated for C$_{12}$H$_{13}$O$_3$S [M + H]$^+$ 237.0580, found 237.0579; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1$ = 16.0 min; $t_2$ = 19.4 min).

(±)-2-Benzoyloxy-N-Boc-4-piperidinone.

The title compound was synthesised from N-Boc-4-piperidinone using and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave (±)-2-benzoyloxy-N-Boc-4-piperidinone (461 mg, 68%) as a white crystalline solid. mp 93–97 °C; IR (thin film)/cm$^{-1}$: 2976, 1739, 1724, 1700, 1472, 1452, 1420, 1367, 1297, 1272, 1236, 1164, 1112, 711; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, 2H, $J$ 7.2 Hz), 7.50 (t, 1H, $J$ 7.4 Hz), 7.35 (dd, 2H, $J$ 7.7, 7.7 Hz), 5.30 (dd, 1H, $J$ 10.4, 6.5 Hz), 4.35–4.65 (br, 1H), 4.20–4.30 (br, 1H), 3.20–3.35 (br, 1H), 3.10–3.20 (m, 1H), 2.45–2.65 (m, 2H), 1.40 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.5, 165.1, 154.2, 133.5, 130.0, 129.1, 128.5, 81.2, 73.9, 48.0, 43.5, 40.5, 28.3 ppm; MS (ES): $m/z$ 320 [M + H]$^+$; HRMS calculated for C$_{17}$H$_{22}$NO$_5$ [M + H]$^+$ 320.1498, found 320.1492; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1$ = 24.6 min; $t_2$ = 28.4 min).
(±)-2-Benzoyloxy-4,4-dimethylcyclohexanone.  

The title compound was synthesised from 4,4-dimethylcyclohexanone and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (4:1), gave (±)-2-benzoyloxy-4,4-dimethylcyclohexanone (85 mg, 65%) as a white crystalline solid. mp 63–66 °C; IR (thin film)/cm\(^{-1}\): 2946, 2862, 1739, 1713, 1602, 1585, 1450, 1392, 1365, 1284, 1266, 1172, 1106, 1023; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, 2H, \(J\) 7.5 Hz), 7.50 (t, 1H, \(J\) 7.4 Hz), 7.35 (dd, 2H, \(J\) 7.7, 7.7 Hz), 5.50 (dd, 1H, \(J\) 13.1, 6.4 Hz), 2.55–2.65 (m, 1H), 2.30–2.40 (m, 1H), 2.00–2.10 (m, 1H), 1.85 (t, 1H, \(J\) 12.9 Hz), 1.80–1.60 (m, 2H), 1.25 (s, 3H), 1.05 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 205.0, 165.7, 133.2, 129.9, 129.7, 128.4, 74.2, 45.3, 39.6, 37.0, 32.1, 31.4, 24.7 ppm; MS (ES): \(m/z\) 247 [M + H]\(^+\); Enantiomers separated on OD chiral column, 10% IPA/Hexane, 0.5 mL/min.

(±)-2-Benzoyloxy-4,4-dicarbethoxyxyclohexane.

The title compound was synthesised from 4,4-dicarbethoxyxyclohexanone and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (3:1), gave (±)-2-benzoyloxy-4,4-dicarbethoxyxyclohexanone (104 mg, 73%) as a clear colourless oil. IR (thin film)/cm\(^{-1}\): 2981, 2938, 1750, 1732, 1720, 1602, 1452, 1368, 1284, 1236, 1180, 1113, 1027, 861, 712; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, 2H, \(J\) 7.1 Hz), 7.50 (t, 1H, \(J\) 7.4 Hz), 7.40 (dd, 2H, \(J\) 7.7, 7.7 Hz), 5.50 (dd, 1H, \(J\) 12.5, 6.2 Hz), 4.30 (q, 2H, \(J\) 7.1 Hz), 4.10–4.20 (m, 2H), 2.90–3.00 (m, 1H), 2.60–2.70 (m, 2H), 2.45–2.55 (m, 1H), 2.35 (t, 1H, \(J\) 12.9 Hz), 2.05–2.15 (m, 1H), 1.25 (t, 3H, \(J\) 7.1 Hz), 1.15 (t, 3H, \(J\) 7.2 Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 202.6, 169.82, 169.75, 165.2, 133.4, 129.9, 129.3, 128.4, 73.3, 62.34, 62.25, 54.5, 36.9, 36.7, 31.6, 14.1, 14.0 ppm; MS (EI): \(m/z\) 362 [M]\(^+\); HRMS calculated for C\(_{19}\)H\(_{22}\)O\(_{7}\) [M]\(^+\) 362.1360, found 362.1364; Enantiomers separated on OD chiral column, 5% IPA/Hexane, 0.3 mL/min (\(t_1 = 28.1\) min; \(t_2 = 32.8\) min).

(±)-2-Benzoyloxy cyclohexane-1,4-dione monoethylene ketal.

The title compound was synthesised from cyclohexanedione monoethylene ketal and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave (±)-2-benzoyloxy cyclohexane-1,4-dione monoethylene ketal (110 mg, 75%) as a white crystalline solid. mp 114–116 °C; Lit. ref. mp 114–116 °C; \(^9\) IR (thin film)/cm\(^{-1}\): 2961, 1719,
The title compound was synthesised from 4-tert-butylocyclohexanone and N-methyl-O-benzoyl hydroxylamine hydrochloride, in DMSO, using General Procedure 3. Purification by column chromatography, eluting with petroleum ether-ethyl acetate (7:3), gave (+)-2-benzoyloxy-4-tert-butylcyclohexanone (101 mg, 69%). IR (thin film)/cm\(^{-1}\): 2959, 2870, 1733, 1719, 1454, 1272, 1120; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.02\) (d, 2H, \(J 7.4\) Hz), 7.37 (dd, 2H, \(J 7.4\) Hz), 5.40 (dd, 1H, \(J 11.8, 6.3\) Hz), 2.40–2.47 (m, 3H), 2.05–2.16 (m, 1H), 1.45–1.75 (m, 3H), 0.87 (s, 9H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 156.1, 140.6, 134.7, 128.7, 128.64, 128.62, 128.4, 128.0, 127.2, 70.4, 60.9, 19.5\) ppm; MS (ESI): \(m/z\) 275 [M + H]; HRMS calculated for C\(_{16}\)H\(_{23}\)O\(_3\) [M + H]\(^+\) 275.1284, found 275.1282; \([\alpha]_D^{23}\) = –40.8 (1 g/100 mL, CHCl\(_3\)).
N-(R)-3,3-Dimethyl-2-butyl-O-benzylcarbonate hydroxylamine 49.

N-(R)-3,3-Dimethyl-2-butyl hydroxylamine (500 mg, 4.3 mmol) was dissolved in dry dichloromethane (8.5 mL) under nitrogen, and cooled to 0 °C. Triethylamine (0.71 mL, 5.12 mmol) and benzyl chloroformate (0.73 mL, 5.12 mmol) were then added dropwise (over 5 min) with stirring overnight warming to room temperature. The reaction mixture was diluted with 1M HCl (10 mL) and extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (40 mL), dried (MgSO₄) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (4:1), to give N-(R)-3,3-dimethyl-2-butyl-O-benzylcarbonate hydroxylamine 49 (502 mg, 47%) as a clear colourless oil. IR (thin film)/cm⁻¹: 3267, 2962, 1748, 1456, 1378, 1268, 1243; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.35 (m, 5H), 6.10–6.30 (br, 1H), 5.10 (s, 2H), 2.80 (q, 1H, J 6.5 Hz), 1.00 (d, 3H, J 6.5 Hz), 0.85 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 134.9, 128.7, 128.66, 128.4, 70.3, 65.0, 33.5, 26.7, 13.5 ppm; MS (ES): m/z 252 [M + H]⁺; HRMS calculated for C₁₄H₂₂NO₃ [M + H]⁺ 252.1600, found 252.1611; [α]²³D −42 (1 g/100 mL, CHCl₃).

N-(S)-α-Methylbenzyl-O-diphenylcarbamoyl hydroxylamine 50.

N-(S)-α-Methylbenzyl hydroxylamine 13 (1.0 g, 7.29 mmol) was dissolved in dry dichloromethane (14.6 mL) under nitrogen, and cooled to 0 °C. DMAP (890 mg, 7.29 mmol), triethylamine (1.22 mL, 8.75 mmol) and diphenylcarbamoyl chloride (2.03 g, 8.75 mmol) were then added with stirring overnight warming to room temperature. The reaction mixture was diluted with 1M HCl (15 mL) and extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with brine (50 mL), dried (MgSO₄) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (4:1), to give N-(S)-α-methylbenzyl-O-diphenylcarbamoyl hydroxylamine 50 (1.85 g, 77%) as a white solid. mp 62–65 °C; IR (thin film)/cm⁻¹: 3227, 2975, 1716, 1591, 1491, 1340, 1300, 1198, 1010, 757, 696; ¹H NMR (400 MHz, CDCl₃) δ 7.15–7.30 (m, 10H), 7.10–7.15 (m, 2H), 4.15 (q, 1H, J 6.7 Hz), 1.30 (d, 3H, J 6.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 155.6, 141.6, 141.2, 129.0, 128.5, 127.8, 127.3, 126.7, 60.9, 19.4 ppm; MS (ES): m/z 333 [M + H]⁺; HRMS calculated for C₂₁H₂₁N₂O₂ [M + H]⁺ 333.1603, found 333.1607; [α]²³D −28 (1 g/100 mL, CHCl₃).

N-(R)-3,3-Dimethyl-2-butyl-O-diphenylcarbamoyl hydroxylamine 51.

N-(R)-3,3-Dimethyl-2-butyl hydroxylamine (500 mg, 4.27 mmol) was dissolved in dry
dichloromethane (8.5 mL) under nitrogen, and cooled to 0 °C. DMAP (521 mg, 4.27 mmol), triethylamine (0.71 mL, 5.12 mmol) and diphenylcarbamoyl chloride (1.186 g, 5.12 mmol) were then added with stirring overnight warming to room temperature. The reaction mixture was diluted with 1M HCl (10 mL) and extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (40 mL), dried (MgSO₄) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (4:1), to give \textit{N-(R)-3,3-dimethyl-2-butyl-O-diphenylcarbamoyl hydroxylamine} \textit{51} (1.201 g, 90%) as a white solid. \textit{mp 60–65 °C; IR} (thin film)/ cm⁻¹: 3233, 2957, 2867, 1716, 1592, 1492, 1450, 1340, 1299, 1201, 1014, 756, 694; \textit{¹H NMR} (400 MHz, CDCl₃) δ 7.25 (t, 4H, \textit{J} 7.8), 7.10–7.20 (m, 6H), 2.70 (q, 1H, \textit{J} 6.5 Hz), 0.90 (d, 3H, \textit{J} 6.5 Hz), 0.80 (s, 9H); \textit{¹³C NMR} (100 MHz, CDCl₃) δ 156.1, 141.7, 129.1, 126.8, 126.6, 65.1, 33.5, 26.6, 13.5 ppm; \textit{MS} (ES): \textit{m/z} 313 [M + H]⁺; \textit{HRMS} calculated for C₁₉H₂₅N₂O₂ [M + H]⁺ 313.1916, found 313.1923; \textit{[α]}²³D −15.2 (1 g/100 mL, CHCl₃).

(±)-2-(Benzylcarbonoyloxy) cyclohexanone.\textsuperscript{10}

Cyclohexanone (0.048 mL, 0.459 mmol) was added dropwise (over 5 min) to a stirred solution of \textit{N}-methyl-\textit{O}-benzylcarbonate hydroxylamine hydrochloride\textsuperscript{6} (100 mg, 0.459 mmol) in THF-toluene (1:1, 0.66 mL). Stirring was continued at 25 °C overnight. The reaction mixture was diluted with brine (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (30 mL), dried (MgSO₄) and concentrated to give the crude product, which was purified on silica, eluting with petroleum ether-ethyl acetate (7:3), to give (±)-2-(benzylcarbonoyloxy) cyclohexanone (92 mg, 81%) as a white crystalline solid. \textit{mp 47–51 °C; IR} (thin film)/ cm⁻¹: 2944, 2866, 1752, 1728, 1499, 1455, 1386, 1300, 1262, 1216, 1115, 1017, 902, 889, 784, 744; \textit{¹H NMR} (400 MHz, CDCl₃) δ 7.20–7.35 (m, 5H), 5.10 (s, 2H), 4.95 (dd, 1H, \textit{J} 11.9, 6.5 Hz), 2.40–2.50 (m, 1H), 2.25–2.40 (m, 2H), 1.95–2.05 (m, 1H), 1.85–1.95 (m, 1H), 1.65–1.80 (m, 2H), 1.50–1.65 (m, 1H); \textit{¹³C NMR} (100 MHz, CDCl₃) δ 204.2, 154.3, 135.0, 128.6, 128.5, 128.3, 79.5, 70.0, 40.6, 33.0, 27.0, 23.6 ppm; \textit{MS} (EI): \textit{m/z} 248 [M]⁺; \textit{HRMS} calculated for C₁₄H₁₆O₄ [M]⁺ 248.1049, found 248.1048; Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min (\textit{t}₁ = 11.5 min; \textit{t}₂ = 14.6 min).

(±)-2-(Diphenylcarbamoyloxy) cyclohexanone.\textsuperscript{11}

Cyclohexanone 2 (0.037 mL, 0.359 mmol) was added dropwise (over 5 min) to a stirred solution of \textit{N}-methyl-\textit{O}-diphenylcarbamoyl hydroxylamine hydrochloride\textsuperscript{11} (100 mg, 0.359
mmol) in THF-toluene (1:1, 0.51 mL). Stirring was continued at 25 °C overnight. The reaction mixture was diluted with brine (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (30 mL), dried (MgSO₄) and concentrated to give the crude product which was purified on silica, eluting with petroleum ether-ethyl acetate (7:3), to give (±)-2-(diphenylcarbamoyloxy) cyclohexanone (101 mg, 91%) as a white crystalline solid. mp 138–141 °C; IR (thin film)/cm⁻¹: 2938, 1729, 1709, 1587, 1492, 1446, 1373, 1341, 1280, 1212, 1091, 760, 694; ¹H NMR (400 MHz, CDCl₃) δ 7.20–7.30 (m, 8H), 7.05–7.15 (m, 2H), 5.15 (dd, 1H, J 12.4, 6.3 Hz), 2.35–2.45 (m, 1H), 2.25–2.35 (m, 1H), 2.10–2.20 (m, 1H), 1.90–2.00 (m, 1H), 1.80–1.90 (m, 1H), 1.60–1.75 (m, 1H), 1.45–1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 205.1, 153.9, 142.6, 128.8, 127.1, 126.1, 78.0, 40.6, 32.9, 27.1, 23.7 ppm; MS (ES): m/z 310 [M + H]+; HRMS calculated for C₁₉H₂₀NO₃ [M + H]+ 310.1443, found 310.1433; Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min (t₁ = 11.6 min; t₂ = 19.6 min).

References

(9) T. C. Jones and N. C. O. Tomkinson, Org. Synth., 2007, 84, 233
$N$-(S)-$\alpha$-Methyl benzyl-$O$-benzoyl hydroxylamine 10.

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \]

\begin{align*}
\text{ppm} & \quad \delta \\
7.996 & \quad 7.978 \\
7.592 & \quad 7.573 \\
7.555 & \quad 7.490 \\
7.384 & \quad 7.359 \\
7.316 & \quad 4.399 \\
4.382 & \quad 4.366 \\
4.349 & \quad 1.591 \\
1.574 & \\
1.00 & \\
3.01 & \\
2.92 & \\
1.01 & \\
5.97 & \\
1.00 & \\
\end{align*}
$^{13}$C NMR (100 MHz, CDCl$_3$)

ppm (f1)
(±)-2-Benzyloxy cyclohexanone 11.

\[
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)}
\]

---

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$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on Chiracel OD 5% IPA/Hexane, 1.0 mL/min ($t_1 = 12.2$ min; $t_2 = 16.5$ min).
\textit{N-(S)-a-Methylbenzyl hydroxylamine 13.}

\begin{center}
\includegraphics[width=0.8\textwidth]{n-(s)-alpha-methylbenzyl-hydroxylamine-13.png}
\end{center}
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(S)-α-Methylbenzyl-O-pivaloyl hydroxylamine 15.

$\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-Methyl-O-pivaloyl hydroxylamine hydrochloride.

$\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR (100 MHz, CDCl$_3$)
**N-(S)-a-Methylbenzyl-O-3,5-di-tert-butylbenzoyl hydroxylamine 16.**

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]
N-Methyl-O-3,5-di-tert-butylbenzoyl hydroxylamine.

^1H NMR (400 MHz, CDCl₃)
*N*-\((S)\)-\(\alpha\)-Methylbenzyl-\(O\)-2,4,6-trimethylbenzoyl hydroxylamine 17.

\[\text{H NMR (400 MHz, CDCl}_3)\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-Methyl-O-2,4,6-trimethylbenzoyl hydroxylamine.

\[
\begin{align*}
\text{-H NMR (400 MHz, CDCl}_3) \\
\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
\( N-(S)-\alpha\text{-Methylbenzyl-}\text{-O-acetyl hydroxylamine 18.} \)

\( \text{\H NMR (400 MHz, CDCl}_3\text{)} \)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{(±)-2-Pivaloyloxy cyclohexanone 20.}$

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) & \\
\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated by $^1$H NMR spectroscopy, using 0.1 equivalents of shift reagent Eu(hfc)$_3$
(±)-2-(3,5-Di-tert-butylbenzoyloxy)cyclohexanone 21.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated by $^1$H NMR spectroscopy, using 1.3 equivalents of shift reagent Eu(hfc)$_3$. 
(±)-2-(2,4,6-Trimethylbenzoyloxy)cyclohexanone 22.

$\text{H NMR (400 MHz, CDCl}_3$)}
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on Chiracel OD column, 5% IPA/Hexane, 1.0 mL/min ($t_1 = 9.7$ min; $t_2 = 12.1$ min).
(±)-2-Acetoxy cyclohexanone 23.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

ppm (t1)

204.635 170.087 76.593 40.737 33.105 27.195 23.805 20.794

ppm (t1)

-1000 0 1000 2000 3000 4000 5000 6000 7000

ppm (t1)

-3000 -2000 -1000 0 1000 2000 3000 4000
Enantiomers separated by $^1$H NMR, using 0.3 equivalents of shift reagent Eu(hfc)$_3$. 
*N-(S)-α-Methylbenzyl-O-4-fluorobenzoyl hydroxylamine 24.*

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)}
\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-Methyl-O-4-fluorobenzoyl hydroxylamine.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3) \\
\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(S)-α-Methylbenzyl-O-4-methoxybenzoyl hydroxylamine 25.

1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100 MHz, CDCl$_3$)

ppm (f1)

166.659, 163.859, 141.291, 131.429, 128.610, 127.872, 127.161, 120.593, 113.813, 60.954, 55.481, 19.771
**N-Methyl-O-4-methoxybenzoyl hydroxylamine.**

\[
\text{H NMR (400 MHz, CDCl}_3)\]

![NMR Spectrum](image)
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(S)-α-Methylbenzyl-O-4-dimethylaminobenzoyl hydroxylamine 26.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]

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$^{13}$C NMR (100 MHz, CDCl$_3$)
N-Methyl-\textit{O}-4-dimethylaminobenzoyl hydroxylamine.

\[
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3)\]

\[
\begin{align*}
7.905 & \quad 7.883 & \quad 7.260 & \quad 2.905 \\
2.0 & \quad 5.3 & \quad 6.9 & \quad 3.0
\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(S)-α-Methylbenzyl-O-3,4,5-trimethoxybenzoyl hydroxylamine 27.
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-Methyl-O-3,4,5-trimethoxybenzoyl hydroxylamine.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$N$-(S)-$\alpha$-Methyl-4-fluorobenzyl-$O$-benzoyl hydroxylamine 28.

$\text{H NMR (400 MHz, CDCl}_3\text{)}$

ppm (11)
$^{13}$C NMR (100 MHz, CDCl$_3$)
**N-(S)-α-Methyl-4-methylbenzyl-O-benzoyl hydroxylamine 29.**

\[ \text{NHN}O \]

**H NMR (400 MHz, CDCl}_3\)]

- 7.969 ppm
- 7.951 ppm
- 7.906 ppm
- 7.583 ppm
- 7.564 ppm
- 7.546 ppm
- 7.448 ppm
- 7.428 ppm
- 7.410 ppm
- 7.329 ppm
- 7.309 ppm
- 7.187 ppm
- 7.167 ppm
- 4.321 ppm
- 4.306 ppm
- 4.290 ppm
- 4.275 ppm
- 2.353 ppm
- 1.544 ppm
- 1.527 ppm
N-(S)-α-Methyl-4-methoxybenzyl-O-benzoyl hydroxylamine 30.

\[
\text{MeO} \quad \overset{\text{O}}{\text{N}} \quad \overset{\text{O}}{\text{O}} \quad \overset{\text{N}}{\text{N}} \\
\text{MeO}
\]

\(^1\text{H NMR (400 MHz, CDCl}_3\)}
$^{13}$C NMR (100 MHz, CDCl$_3$)
(±)-2-(4-Fluorobenzyloxy)cyclohexanone 31.

$\begin{align*}
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{O}
\end{align*}$

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min (t₁ = 10.5 min; t₂ = 12.6 min).
(±)-2-(4-Methoxybenzoyloxy)cyclohexanone 32.

$^1$H NMR (400 MHz, CDCl$_3$)
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3 \]
Enantiomers separated on OD chiral column, 10% IPA/Hexane, 1.0 mL/min ($t_1 = 14.8$ min; $t_2 = 19.1$ min).
(±)-2-(4-dimethylaminobenzoyloxy)cyclohexanone 33.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]

ppm
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min ($t_1 = 22.9$ min; $t_2 = 28.5$ min).
(±)-2-(3,4,5-Trimethoxybenzoyloxy)cyclohexanone 34.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 2.5% IPA/Hexane, 0.5 mL/min ($t_1 = 48.2$ min; $t_2 = 55.5$ min).
$N$-(S)-$\alpha$-Ethylbenzyl-$O$-benzoyl hydroxylamine 38.

$^1$H NMR (400 MHz, CDCl$_3$)
N-(S)-α-Methylcyclohexyl-O-benzoyl hydroxylamine hydrochloride 39·HCl.

1H NMR (400 MHz, CDCl₃)
$^13$C NMR (100 MHz, CDCl$_3$)
$N$-(S)-1,2,3,4-Tetrahydronaphthyl-O-benzoyl hydroxylamine hydrochloride 40·HCl.

$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (100 MHz, CDCl$_3$)

ppm (f1)
$N$-(R)-3,3-Dimethyl-2-butyl-O-benzoyl hydroxylamine 41.

![NMR spectra](image-url)
$^{13}$C NMR (100 MHz, CDCl$_3$)
\[ N-(R)-3,3\text{-dimethyl-2-butyl hydroxylamine}. \]
$^{13}$C NMR (100 MHz, CDCl$_3$)
(±)-2-Benzoyloxy cyclopentanone.

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \]

![NMR Spectrogram]
$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$
Enantiomers separated on OD chiral column, 2.5% IPA/Hexane, 0.5 mL/min (t_1 = 45.5 min; t_2 = 48.9 min).
(±)-2-Benzoyloxy cycloheptanone.

\[\text{H NMR (400 MHz, CDCl}_3\text{)}\]
$^{13}$C NMR (100 MHz, CDCl$_3$)

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Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1 = 11.5 \text{ min}$; $t_2 = 13.5 \text{ min}$).
(±)-2-Benzoyloxy tetrahydropyran-4-one.

\[ \text{H NMR (400 MHz, CDCl}_3) \]

ppm
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min (t₁ = 16.2 min; t₂ = 21.8 min).
(±)-2-Benzoyloxy tetrahydrothiopyran-4-one.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1 = 16.0$ min; $t_2 = 19.4$ min).
(±)-2-Benzoyloxy-N-Boc-4-piperidinone.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 1.0 mL/min ($t_1 = 24.6$ min; $t_2 = 28.4$ min).

![Graph of enantiomer separation](attachment:image.png)
(±)-2-Benzoyloxy-4,4-dimethylcyclohexanone.

$^1$H NMR (400 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 10% IPA/Hexane, 0.5 mL/min $t_1 = 13.8$ min; $t_2 = 16.1$ min).
(±)-2-Benzoyloxy-4,4-dicarbethoxycyclohexanone.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 0.3 mL/min \( t_1 = 28.1 \) min; \( t_2 = 32.8 \) min.
(±)-2-Benzoyloxy cyclohexane-1,4-dione monoethylene ketal.

\[
\text{H NMR (400 MHz, CDCl}_3\text{)}
\]
$^{13}\text{C NMR (100 MHz, CDCl}_3$)
Enantiomers separated on OD chiral column, 5% IPA/Hexane, 0.3 mL/min ($t_1 = 55.8$ min; $t_2 = 63.0$ min).
(±)-2-Benzoyloxy-4-tert-butylcyclohexanone.

$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(R)-3,3-Dimethyl-2-butyl-O-benzylcarbonate hydroxylamine 49.

\[\text{\begin{align*}
\text{N-} & \text{O} \\
\text{O} & \text{O} \\
\end{align*}}\]

\[\text{\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)}
\end{align*}}\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(S)-α-Methylbenzyl-O-diphenylcarbamoyl hydroxylamine 50.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3)\end{align*}
\]
$^{13}$C NMR (100 MHz, CDCl$_3$)
N-(R)-3,3-Dimethyl-2-butyl-O-diphenylcarbamoyl hydroxylamine 51.

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \]
$^{13}$C NMR (100 MHz, CDCl$_3$)
(±)-2-(Benzylcarbonoyloxy) cyclohexanone.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min ($t_1 = 11.5$ min; $t_2 = 14.6$ min).
(±)-2-(Diphenylcarbamoyloxy) cyclohexanone.

H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100 MHz, CDCl$_3$)
Enantiomers separated on OD chiral column, 20% IPA/Hexane, 1.0 mL/min ($t_1 = 11.6$ min; $t_2 = 19.6$ min).