Enantioselective Synthesis of Nitroalkanes Bearing All-Carbon Quaternary Stereogenic Centers through Cu-Catalyzed Asymmetric Conjugate Additions

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Supporting Information

General. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer, $\nu_{\max}$ in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m) or weak (w). ^1H NMR spectra are recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal standard (CDCl_3 : δ 7.26). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and assignment. ^{13}C NMR spectra are recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16). Enantiomer ratios are determined by chiral GLC analysis; (Alltech Associates Chiraldex GTA column, 30m x 0.25mm or Supelco Betadex 120 column, 30m x 0.25 mm) or by analytical liquid chromatography (HPLC) on a Shimadzu chromatograph with a Chiralpack OD (4.6 x 250 mm) chiral column by Chiral Technologies in comparison to authentic racemic materials. Racemic samples are made with a 1:1 mixture of D,D and L,L ligands. Elemental analyses are performed by Robertson MicroLit Laboratories (Madison, New Jersey). High resolution mass spectrometry is performed by the University of Illinois Mass Spectrometry Laboratories (Urbana, Illinois) and at the Mass Spectrometry Facility, Boston College (on a Micromass LCT ESI-MS (positive mode)). Optical rotation values are recorded on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise stated, all reactions are carried out under an inert atmosphere of N_2 in flame dried glassware. Solvents are purified under a positive pressure of dry argon by a modified Advanced ChemTech purification system. Toluene is purified through Cu and alumina columns and CH_2Cl_2 , Et_2O and THF are purified by passage through two alumina columns. Diethylzinc (neat), dimethylzinc (1 N in toluene) and sodium nitrite are purchased from Aldrich and used without further purification. Dibutylzinc (1 N in heptane) is purchased from Fluka and used without further purification. Other alkylzincs are prepared based on reported methods.^{1a,b} Copper (I) triflate (benzene complex, 2:1) is prepared by known methods.² Nitroalkenes **1a–1c**, **4** and **5** are synthesized according to a modified literature procedure.³ Stereochemistry of

1) a) Knochel, P.; Singer, P. R. *Chem. Rev.* **1993**, 93, 2117–2188 and references cited therein.

2) a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, 95, 1889–1897. b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, 95, 3300–3310.

3) Ohta, H.; Kobayashi, N.; Ozaki, K. *J. Org. Chem.* **1989**, 1802–1804.

nitroalkenes has been ascertained previously.⁴ Peptide-based phosphine ligands are prepared as previously disclosed.⁵

Representative procedure for the synthesis of nitroalkenes. To a stirred mixture of acetic anhydride (75.7 g, 742 mmol) and 69% aqueous nitric acid (8.63 g, 94 mmol) is added 2-(4-chlorophenyl)propene (6.56 g, 43 mmol) at $-20\text{ }^{\circ}\text{C}$ (dry ice/acetone bath) and the mixture is allowed to stir between -20 and $-10\text{ }^{\circ}\text{C}$ for 10 min. After the reaction is complete (as judged by TLC analysis), ice water (25.0 mL) is added and the mixture is allowed to stir at $0\text{ }^{\circ}\text{C}$ for 15 min and then washed with diethyl ether (3 x 30 mL). The combined organic layers are washed with saturated aqueous NaHCO_3 and brine, dried over MgSO_4 , filtered and concentrated to afford a brown residue. Purification by silica gel chromatography (10:1 hexanes:ethyl acetate) affords 2-acetoxy-1-nitro-2-(4-chlorophenyl)propane (9.23 g, 35.8 mmol, 83% yield) as a yellow oil.

A solution of the nitroacetate, 2-acetoxy-1-nitro-2-(4-chlorophenyl)propane (3 g, 11.6 mmol) in 15% aqueous NaOH (60 mL) and chloroform (100 mL) is allowed to stir at $22\text{ }^{\circ}\text{C}$ for 24 h. The mixture is washed with CH_2Cl_2 (3 x 20 mL). The organic layers are combined and washed with 10% aqueous HCl , brine, dried over MgSO_4 , filtered and concentrated to afford a brown residue. Purification by silica gel chromatography (20:1 hexanes:ethyl acetate to elute product) affords (*E*)-1-nitro-2-(4-chlorophenyl)propene (**1b**, 1.66 g, 73% yield based on the nitro acetate used) as a yellow oil.

Representative procedure for the Cu-catalyzed conjugate addition of dialkyl zinc reagents to nitroalkene. (CAUTION: Et_2Zn is pyrophoric! Use extreme caution!) In a glovebox, a 13 x 100 mm test tube is charged with $(\text{CuOTf})_2\cdot\text{C}_6\text{H}_6$ (1.6 mg, 3.2 μmol) and **3** (4.6 mg, 6.4 μmol), sealed with a septum. After the test tube is removed from the glovebox, toluene (1.0 mL) is added and the mixture is allowed to stir for 5 min at $22\text{ }^{\circ}\text{C}$, and then cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice/acetone bath. Et_2Zn (50.0 μL , 0.49 mmol) is added to the mixture in a dropwise fashion and the resulting solution is allowed to stir at $-78\text{ }^{\circ}\text{C}$ for 10 min. A solution of (*E*)-1-nitro-2-phenylpropene (**1a**, 26 mg, 0.16 mmol) in 1.0 mL of toluene is added by syringe and the reaction is allowed to stir at $-78\text{ }^{\circ}\text{C}$. After 24 h, the reaction is quenched at $-30\text{ }^{\circ}\text{C}$ by the dropwise addition of a saturated aqueous solution of NH_4Cl (5.0 mL). The mixture is washed with Et_2O (2 x 2.0 mL). The combined organic layers are passed through a short plug of silica gel eluting with Et_2O . Volatiles are removed under reduced pressure and the toluene solution is purified by silica gel chromatography (100% pentane to elute toluene followed by 20:1 pentane: Et_2O to elute product) to afford a colorless oil (27 mg, 0.14 mmol, 87% yield).

Representative procedure for the transformation of nitroalkanes to corresponding carboxylic acids. A solution of 1-nitro-2-methyl-2-(4-chlorophenyl)butane (**7**, 19 mg, 0.083 mmol), sodium nitrite (17.3 mg, 0.25 mmol) and acetic acid (50.1 mg, 0.83 mmol) in dimethyl sulfoxide (250 μL) is allowed to stir at $35\text{ }^{\circ}\text{C}$ for 48 h. After acidification with a 10% aqueous solution of hydrochloric acid (2 mL), the product is washed with diethyl ether (3 x 5 mL). The combined organic layers are dried over MgSO_4 , filtered and concentrated to afford a yellow residue. Purification by silica gel chromatography (10:1 pentane: Et_2O to elute product) delivers 2-methyl-2-(4-chlorophenyl)butanoic acid (**19**) as a colorless oil (14.3 mg, 0.067 mmol, 81% yield).

Representative procedure for the transformation of nitroalkanes to corresponding primary amines. 1-Nitro-2-methyl-2-(4-chlorophenyl)butane (**7**, 80 mg, 0.35 mmol), $\text{Pd}(\text{C})$

4) Czekelius, C.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2003**, 42, 4793–4795.

5) Mampreian, D. M.; Hoveyda, A. H. *Org. Lett.* **2004**, 6, 2829–2832.

(10%, 8.0 mg) and MeOH (2 mL) are charged into a autoclave equipped with a magnetic stirring bar. Hydrogen is initially introduced into the autoclave at a pressure of 300 psi before being reduced to 10–20 psi by carefully releasing the stop valve. After this procedure is repeated three times, the vessel is pressurized to 600 psi. The reaction mixture is allowed to stir at 22 °C for 40 h. After releasing the hydrogen gas and filtering off the solid catalyst, the solution is evaporated to dryness. The residue is purified by silica gel chromatography (1:1 pentane:Et₂O to elute product) to afford 1-amino-2-methyl-2-(4-chlorophenyl)butane as a colorless oil (43.6 mg, 0.22 mmol, 63% yield).

2-(Diphenylphosphino)-L-Tle-D-Tyr(OBn)-NEt₂ (4). M.p. = 63–68 °C. IR (neat): 3396 (w), 3276 (br), 3056 (m), 2974 (m), 2930 (m), 2867 (w), 1954 (w), 1885 (w), 1810 (w), 1646 (s), 1583 (w), 1508 (s), 1464 (s), 1438 (s), 1382 (m), 1369 (w), 1269 (s), 1243 (s), 1180 (m), 1143 (w), 1105 (w), 1029 (m), 746 (s), 620 (s) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 8.59 (1H, d, *J* = 4.4 Hz, N=CH), 7.93 (1H, ddd, *J* = 6.8, 4.0, 1.2 Hz, ArH), 7.59 (1H, d, *J* = 7.2 Hz, ArH), 7.45–7.22 (17H, m, ArH and NH), 7.04–7.02 (2H, m, ArH), 6.90 (1H, ddd, *J* = 7.6, 4.4, 1.2 Hz, ArH), 6.73–6.71 (2H, m, ArH), 5.04–4.97 (1H, m, NHCHCO), 4.93 (2H, s, PhCH₂O), 3.39–3.21 (4H, m, CH₃CHHNCH₂CH₃ and NCH₂*t*-Bu), 3.09–2.97 (2H, m, CH₃CHHNCH₂CH₃ and CHCHHAr), 2.82 (1H, dd, *J* = 13.2, 6.0 Hz, CHCHHAr), 1.03 (3H, t, *J* = 7.2 Hz, NCH₂CH₃), 0.97 (3H, t, *J* = 7.2 Hz, NCH₂CH₃), 0.68 (9H, s, *t*-Bu). ¹³C NMR (CDCl₃, 100 MHz): δ 170.3, 170.2, 160.6, 160.4, 157.5, 138.7, 138.5, 137.8, 137.6, 137.1, 137.0, 136.9, 136.2, 136.1, 134.5, 134.3, 133.9, 133.7, 130.6, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 127.9, 127.5, 114.7, 84.5, 70.0, 50.0, 41.9, 40.7, 38.7, 35.3, 27.2, 14.8, 13.1. HRMS Calcd. for C₄₅H₄₉N₃O₃PH [M+H⁺]: 712.3668. Found: 712.3649. Anal. Calcd for C₄₅H₄₉N₃O₃P: C, 75.92; H, 7.08; N, 5.90. Found: C, 75.85; H, 7.24; N, 5.90. [α]_D²⁰ + 13.2° (*c* = 1.22, CHCl₃).

2-(Diphenylphosphino)-L-Tle-Gly-NEt₂ (5). M.p. = 68–72 °C. IR (neat): 3383 (br), 3050 (m), 2967 (m), 2924 (m), 2873 (m), 2320 (w), 1967 (w), 1652 (s), 1507 (m), 1483 (s), 1464 (m), 1438 (s), 1394 (m), 1375 (m), 1249 (m), 1313 (w), 1269 (m), 1224 (w), 1155 (w), 1123 (w), 1073 (w), 1029 (w), 746 (s), 696 (s) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 8.73 (1H, d, *J* = 5.2 Hz, N=CH), 8.13 (1H, ddd, *J* = 7.6, 4.0, 1.2 Hz, ArH), 7.48–7.42 (2H, m, ArH), 7.36–7.22 (11H, m, ArH and NH), 6.87 (1H, ddd, *J* = 7.6, 4.4, 1.2 Hz, ArH), 4.06 (1H, dd, *J* = 17.2, 4.8 Hz, NCHHCO), 3.94 (1H, dd, *J* = 17.2, 4.4 Hz, NCHHCO), 3.44–3.38 (3H, m, NCH₂*t*-Bu and NCH₂CH₃), 3.27 (2H, dq, *J* = 7.2, 2.4 Hz, NCH₂CH₃), 1.19 (3H, t, *J* = 7.2 Hz, NCH₂CH₃), 1.14 (3H, t, *J* = 6.8 Hz, NCH₂CH₃), 0.85 (9H, s, *t*-Bu). ¹³C NMR (CDCl₃, 100 MHz): δ 171.7, 167.2, 160.7, 160.5, 138.9, 137.9, 136.8, 136.4, 134.3, 134.1, 133.6, 130.7, 129.2, 128.9, 128.8, 128.7, 128.6, 84.3, 41.1, 40.9, 40.4, 35.3, 27.2, 14.2, 13.1. HRMS Calcd. for C₃₁H₃₈N₃O₂PH [M+H⁺]: 516.2780. Found: 516.2783. Anal. Calcd for C₃₁H₃₈N₃O₂P: C, 72.21; H, 7.43; N, 8.15. Found: C, 71.98; H, 7.04; N, 7.81. [α]_D²⁰ –27.86° (*c* = 0.787, CHCl₃).

2-(Diphenylphosphino)-phenyl-Gly-L-Tyr(OBn)-NEt₂ (6). M.p. 58–62 °C. IR (neat): 3377 (w), 3283 (br), 3056 (m), 2980 (m), 2930 (m), 2873 (w), 1960 (w), 1885 (w), 1810 (w), 1678 (s), 1640 (s), 1583 (m), 1508 (s), 1463 (m), 1438 (m), 1382 (m), 1243 (s), 1180

(m), 1142 (w), 1099 (w), 1067 (w), 1029 (m), 740 (s), 702 (s) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 8.84 (1H, d, $J = 4.8$ Hz, $\text{N}=\text{CH}$), 8.00 (1H, ddd, $J = 7.6, 4.0, 1.6$ Hz, ArH), 7.80 (1H, d, $J = 8.4$ Hz, ArH), 7.44-7.21 (17H, m, ArH and NH), 7.10-7.07 (2H, m, ArH), 6.92 (1H, ddd, $J = 7.6, 4.8, 1.2$ Hz, ArH), 6.83-6.79 (2H, m, ArH), 5.09-5.03 (1H, m, NHCHCO), 4.99 (2H, s, PhCH_2O), 4.15-4.04 (2H, m, $\text{C}=\text{NCH}_2\text{CO}$), 3.53 (1H, dq, $J = 13.6, 7.2$ Hz, $\text{CH}_3\text{CHHNCH}_2\text{CH}_3$), 3.08-2.95 (4H, m, $\text{CH}_3\text{CHHNCH}_2\text{CH}_3$ and CHCHHAr), 2.91 (1H, dd, $J = 13.2, 5.6$ Hz, CHCHHAr), 1.01 (3H, t, $J = 7.2$ Hz, NCH_2CH_3), 0.96 (3H, t, $J = 7.2$ Hz, NCH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.4, 169.4, 162.4, 162.2, 157.8, 138.8, 138.6, 138.2, 138.0, 137.2, 136.6, 136.5, 134.2, 134.0, 133.9, 131.0, 130.8, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.0, 127.6, 115.0, 70.2, 63.0, 50.1, 41.8, 40.6, 39.3, 14.4, 13.0. HRMS Calcd for $\text{C}_{41}\text{H}_{42}\text{N}_3\text{O}_3\text{P}$ [$\text{M}+\text{H}^+$]: 656.3042. Found: 656.3047. Anal. Calcd for $\text{C}_{41}\text{H}_{42}\text{N}_3\text{O}_3\text{P}$: C, 75.09; H, 6.46; N, 6.41. Found: C, 74.87; H, 6.60; N, 6.18. $[\alpha]_D^{20} +11.93^\circ$ ($c = 0.487$, CHCl_3).

2-(Diphenylphosphino)-phenyl-L-Tle-NEt₂ (7). IR (neat): 3377 (w), 3270 (w), 3056 (w), 2968 (m), 2899 (w), 2867 (w), 1698 (m), 1640 (s), 1501 (m), 1476 (m), 1464 (m), 1438 (m), 1369 (m), 1269 (m), 1218 (m), 1143 (w), 1099 (w), 1073 (w), 1029 (w), 746 (s), 696 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 8.72 (1H, d, $J = 4.8$ Hz, $\text{N}=\text{CH}$), 8.05 (1H, ddd, $J = 7.6, 3.6, 0.8$ Hz, ArH), 7.59 (1H, d, $J = 9.6$ Hz, ArH), 7.45 (1H, ddd, $J = 8.0, 8.0, 0.4$ Hz, ArH), 7.33-7.20 (10H, m, ArH), 6.86 (1H, ddd, $J = 7.6, 4.8, 0.8$ Hz, ArH), 3.68-3.54 (2H, m, NCH_2CH_3), 3.38 (1H, s, $\text{NCH}t\text{-Bu}$), 3.27 (1H, dq, $J = 14.4, 7.2$ Hz, NCHHCH_3), 2.98 (dq, $J = 14.4, 7.2$ Hz, NCHHCH_3), 1.17 (3H, t, $J = 6.8$ Hz, NCH_2CH_3), 1.04 (3H, t, $J = 7.2$ Hz, NCH_2CH_3), 0.78 (9H, s, $t\text{-Bu}$). ^{13}C NMR (CDCl_3 , 100 MHz): δ 171.3, 170.4, 161.1, 160.8, 139.0, 138.9, 137.9, 137.7, 136.7, 136.6, 136.3, 134.6, 134.4, 134.0, 133.9, 133.5, 130.7, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 84.3, 54.1, 42.9, 40.4, 35.7, 35.2, 27.2, 14.6, 13.0. $[\alpha]_D^{20} +2.0^\circ$ ($c = 2.0$, CHCl_3).

(E)-1-Nitro-2-phenyl-1-propene (1a). ^1H NMR (CDCl_3 , 400 MHz): δ 7.45-7.37 (5H, m, ArH), 7.32 (1H, s, CHNO_2), 2.63 (3H, s, ArCCH_3).

(E)-1-Nitro-2-(4-chlorophenyl)-1-propene (1b). ^1H NMR (CDCl_3 , 400 MHz): δ 7.43-7.38 (4H, m, ArH), 7.28 (1H, q, $J = 1.6$ Hz, CHNO_2), 2.62 (3H, d, $J = 1.6$ Hz, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.6, 136.8, 136.6, 129.5, 128.4, 128.3, 18.6.

(E)-1-Nitro-2-(2'-naphthyl)-1-propene (1c). IR (neat): 3100 (w), 3049 (w), 2962 (w), 2930 (m), 2861 (w), 1621 (m), 1514 (s), 1470 (w), 1439 (w), 1388 (m), 1344 (s), 1281 (w), 1231 (w), 1199 (w), 1143 (w), 1029 (w), 960 (w), 828 (m), 759 (m), 708 (w) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.96 (1H, d, $J = 1.6$ Hz, ArH), 7.91-7.86 (3H, m, ArH), 7.58-7.52 (3H, m, ArH), 7.46 (1H, m, CHNO_2), 2.76 (3H, d, $J = 1.6$ Hz, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.0, 136.8, 135.6, 134.1, 133.2, 129.1, 128.7, 127.9, 127.7, 127.20, 127.18, 123.8, 18.7. HRMS Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: 213.0790. Found: 213.0788.

(E)-1-Nitro-2-phenyl-1-pentene (1d). ^1H NMR (CDCl_3 , 400 MHz): δ 7.44-7.39 (5H, m, ArH), 7.19 (1H, s, CHNO_2), 3.06-3.02 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.57-1.47

(2H, m, CH₂CH₂CH₃), 0.96 (3H, t, J = 7.4 Hz, CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 154.5, 137.5, 136.3, 130.3, 129.2, 127.2, 33.1, 21.9, 14.2.

(E)-1-Nitro-3-methyl-2-phenyl-1-butene (1e). ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.36 (3H, m, ArH), 7.24-7.21 (3H, m, ArH), 6.88 (1H, s, CHNO₂), 3.96 (1H, qq, J = 6.8, 6.8 Hz, CH(CH₃)₂), 1.13 (6H, d, J = 6.8 Hz, CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz): δ 159.2, 136.4, 135.8, 128.9, 128.4, 128.0, 29.4, 20.9.

(S)-1-Nitro-2-methyl-2-phenylbutane (2a). IR (neat): 3106 (w), 3074 (w), 2974 (s), 2936 (w), 2892 (w), 1552 (s), 1501 (m), 1451 (m), 1381 (s), 1331 (w), 1250 (w), 1180 (w), 1048 (w), 1004 (w), 916 (w), 765 (s), 708 (s), 645 (m), 557 (m) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.37-7.23 (5H, m, ArH), 4.59 (H, d, J = 10.8 Hz, CHHNO₂), 4.54 (H, d, J = 10.8 Hz, CHHNO₂), 1.95 (1H, dq, J = 14.8, 7.2 Hz, CHHCH₃), 1.74 (1H, dq, J = 14.8, 7.2 Hz, CHHCH₃), 1.52 (3H, s, ArCCH₃), 0.73 (3H, t, J = 7.4 Hz, CH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 142.2, 128.7, 127.1, 126.3, 86.3, 42.8, 32.5, 22.0, 8.4. HRMS Calcd for C₁₁H₁₅NO₂: 193.1103. Found: 193.1103. Anal. Calcd for C₁₁H₁₅NO₂: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.02; H, 7.61; N, 7.19. $[\alpha]_D^{20}$ -31.6° (c = 1.50, CHCl₃) for a sample that is 94% ee.

Optical purity is established by chiral GLC analysis (Chiraldex GTA, 110 °C, 20 psi); chromatograms are illustrated below for a 94% ee sample:

1-Nitro-2-methyl-2-phenylhexane (2b). IR (neat): 3094 (w), 3069 (w), 3031 (w), 2955 (s), 2873 (w), 1948 (w), 1879 (w), 1797 (w), 1741 (w), 1602 (w), 1558 (s), 1508 (w), 1476 (m), 1451 (w), 1382 (s), 1344 (m), 1269 (m), 1193 (w), 1155 (m), 1080 (m), 1042 (s), 973 (w), 910 (m), 790 (s), 696 (s), 658 (s), 570 (m) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.37-7.23 (5H, m, ArH), 4.58 (1H, d, J = 10.4 Hz, CHHNO₂), 4.54 (1H, d, J = 10.4 Hz, CHHNO₂), 1.88 (1H, dt, J = 12.8, 4.0 Hz, CHH(CH₂)₂CH₃), 1.68 (1H, dt, J = 12.8, 4.4 Hz, CHH(CH₂)₂CH₃), 1.53 (3H, s, ArCCH₃), 1.30-0.94 (4H, m, CH₂(CH₂)₂CH₃), 0.82 (3H, t, J = 7.2 Hz, (CH₂)₃CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 142.6, 128.7, 127.1, 126.2, 86.6, 42.5, 39.6, 26.1, 23.2, 22.6, 14.0. HRMS Calcd for C₁₃H₁₉NO₂: 221.1416. Found: 221.1416. Anal. Calcd for C₁₃H₁₉NO₂: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.48; H, 8.83; N, 6.33. $[\alpha]_D^{20}$ -30.5° (c = 1.70, CHCl₃) for a sample that is 93% ee.

Optical purity is established by chiral GLC analysis (Chiraldex GTA, 140 °C, 15 psi); chromatograms are illustrated below for a 93% ee sample:

1-Nitro-2-methyl-2-(4-chlorophenyl)butane (2c). IR (neat): 3062 (w), 3031(w), 2974 (s), 2943 (s), 2886 (s), 2734 (w), 1898 (m), 1558 (s), 1508 (s), 1457 (s), 1432 (m), 1376 (s), 1325 (m), 1250 (m), 1199 (m), 1174 (w), 1105 (s), 1010 (s), 903 (m), 821 (s), 790 (m), 765 (m), 740 (s), 721 (s), 664 (m), 551 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.32-7.30 (2H, m, ArH), 7.24-7.21 (2H, m, ArH), 4.57 (1H, d, J = 10.8 Hz, CHHNO₂), 4.50 (1H, d, J = 10.8 Hz, CHHNO₂), 1.90 (1H, dq, J = 13.6, 7.6 Hz, CHHCH₃), 1.71 (1H, dq, J = 14.0, 7.6 Hz, CHHCH₃), 1.50 (3H, s, CCH₃), 0.73 (3H, t, J = 7.6 Hz, CH₂CH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 140.7, 133.0, 128.9, 127.8, 86.1, 42.6, 32.6, 22.0, 8.3. HRMS Calcd for $\text{C}_{11}\text{H}_{14}\text{ClNO}_2$: 227.0713. Found: 227.0717. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{ClNO}_2$: C, 58.03; H, 6.20; N, 6.15. Found: C, 58.16; H, 6.32; N, 6.19. $[\alpha]_D^{20}$ -45.5° (c = 0.840, CHCl_3) for a sample that is 98% ee.

Optical purity is established by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 254 nm, 98:2 hexanes/*i*-PrOH, 0.3 mL/min); chromatograms are illustrated below for a 98% ee sample:

1-Nitro-2-methyl-2-(4-chlorophenyl)hexane (2d). IR (neat): 3037 (w), 2974 (s), 2955 (s), 2924 (s), 2860 (s), 2735 (w), 1898 (w), 1558 (s), 1489 (s), 1470 (s), 1432 (m), 1382 (s), 1331 (m), 1281 (w), 1250 (w), 1187 (w), 1149 (w), 1099 (s), 1010 (s), 897 (m), 828 (s), 740 (s), 664 (m), 564 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.32-7.29 (2H, m, ArH), 7.24-7.21 (2H, m, ArH), 4.56 (1H, d, J = 10.8 Hz, CHHNO₂), 4.49 (1H, d, J = 10.8 Hz, CHHNO₂), 1.82 (1H, dt, J = 13.0, 4.4 Hz, CHH(CH₂)₂CH₃), 1.64 (1H, dt, J = 13.0, 4.4 Hz, CHH(CH₂)₂CH₃), 1.51 (3H, s, CCH₃), 1.29-0.90 (4H, m, CH₂(CH₂)₂CH₃), 0.82 (3H, t, J = 7.2 Hz, (CH₂)₃CH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 141.1, 133.0, 128.9, 127.7, 86.3, 42.3, 39.7, 26.0, 23.1, 22.5, 14.0. HRMS Calcd for

$C_{13}H_{18}ClNO_2$: 255.1026. Found: 255.1035. Anal. Calcd for $C_{13}H_{18}ClNO_2$: C, 61.05; H, 7.09; N, 5.48. Found: C, 61.28; H, 7.32; N, 5.26. $[\alpha]_D^{20} -37.6^\circ$ ($c = 0.910$, $CHCl_3$) for a sample that is 96% ee.

Optical purity is established by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 254 nm, 98:2 hexanes/*i*-PrOH, 0.3 mL/min); chromatograms are illustrated below for a 96% ee sample:

PK#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	32.696		0.0000	0.000	4603400.0	50.284	BB	1.125	68176.30	56.327
2	40.600		0.0000	0.000	4551359.0	49.716	BB	1.435	52860.39	43.673

PK#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	32.988		0.0000	0.000	191811.0	2.337	BB	0.958	3337.25	3.593
2	40.479		0.0000	0.000	7994842.0	98.243	BB	1.494	89213.69	96.041

1-Nitro-6-acetoxy-2-methyl-2-(4-chlorophenyl)hexane (2e). IR (neat): 3446 (w), 2955 (s), 2924 (s), 2855 (m), 1904 (w), 1741 (s), 1551 (s), 1495 (s), 1470 (m), 1432 (m), 1376 (s), 1331 (w), 1243 (s), 1143 (w), 1099 (m), 1042 (s), 1017 (s), 966 (w), 897 (w), 834 (s), 746 (m), 651 (m), 557 (w) cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.31 (2H, m, ArH), 7.24-7.21 (2H, m, ArH), 4.57 (1H, d, $J = 11.2$ Hz, CHHNO₂), 4.52 (1H, d, $J = 10.8$ Hz, CHHNO₂), 3.98 (2H, t, $J = 6.8$ Hz, CH₂OAc), 2.00 (3H, s, OCOCH₃), 1.88 (1H, dt, $J = 13.0$, 4.4 Hz, CHH(CH₂)₃OAc), 1.70 (1H, dt, $J = 13.0$, 4.4 Hz, CHH(CH₂)₃OAc), 1.60-1.01 (7H, m, CCH₃ and CH₂(CH₂)₂CH₂OAc). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 140.7, 133.2, 129.0, 127.7, 86.2, 63.9, 42.3, 39.4, 28.9, 22.5, 21.1, 20.4. HRMS Calcd for $C_{15}H_{20}ClNO_4$: 313.1081. Found: 313.1084. $[\alpha]_D^{20} -22.0^\circ$ ($c = 0.907$, $CHCl_3$) for a sample that is 85% ee.

Optical purity is established by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 254 nm, 99:1 hexanes/*i*-PrOH, 0.3 mL/min); chromatograms are illustrated below for a 85% ee sample:

PK#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	219.201		0.0000	0.000	2985011.0	50.384	BV	7.459	6669.88	52.998
2	235.988		0.0000	0.000	2939489.0	49.616	VB	8.282	5915.22	47.002

PK#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	220.795		0.0000	0.000	1444270.0	7.697	BV	6.245	3854.43	12.593
2	232.428		0.0000	0.000	17319960.0	92.303	VB	10.790	26752.52	87.407

1-Nitro-2-methyl-2-(2'-naphthyl)butane (2f). IR (neat): 3056 (m), 2980 (s), 2924 (s), 2880 (m), 1646 (w), 1608 (m), 1558 (s), 1508 (s), 1463 (s), 1432

(m), 1388 (s), 1331 (m), 1268 (m), 1143 (w), 954 (w), 821 (s), 790 (m), 765 (m), 740 (s), 721 (s), 664 (m), 551 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.87-7.82 (3H, m, ArH), 7.71 (1H, d, J = 2.0 Hz, ArH), 7.52-7.45 (3H, m, ArH), 4.71 (1H, d, J = 10.8 Hz, CHHNO₂), 4.66 (1H, d, J = 10.8 Hz, CHHNO₂), 2.07 (1H, dq, J = 14.4, 7.2 Hz, CHHCH₃), 1.83 (1H, dq, J = 14.4, 7.2 Hz, CHHCH₃), 1.65 (3H, s, CCH₃), 0.76 (3H, t, J = 7.2 Hz, CH₂CH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.5, 133.4, 132.4, 128.5, 128.2, 127.6, 126.4, 126.3, 125.7, 124.1, 86.2, 43.1, 32.4, 22.1, 8.4. HRMS Calcd for C₁₅H₁₇NO₂: 243.1259. Found: 243.1259. Anal. Calcd for C₁₅H₁₇NO₂: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.31; H, 6.82; N, 5.49. $[\alpha]_{\text{D}}^{20}$ -53.7° (c = 0.940, CHCl₃) for a sample that is 95% ee.

Optical purity is established by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 254 nm, 98:2 hexanes/*i*-PrOH, 1.0 mL/min); chromatograms are illustrated below for a 95% ee sample:

1-Nitro-2-methyl-2-(2'-naphthyl)hexane (2g). IR (neat): 3056 (m), 3018 (w), 2962 (s), 2930 (s), 2867 (m), 2735 (w), 1917 (w), 1634 (w), 1602 (m), 1552 (s), 1508 (m), 1470 (s), 1432 (m), 1376 (s), 1331 (m), 1275 (m), 1250 (w), 1212 (w), 1137 (w), 948 (w), 904 (m), 859 (s), 828 (s), 752 (s), 671 (m), 476 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.87-7.82 (3H, m, ArH), 7.71 (1H, d, J = 1.6 Hz, ArH), 7.52-7.45 (3H, m, ArH), 4.70 (1H, d, J = 10.8 Hz, CHHNO₂), 4.65 (1H, d, J = 10.8 Hz, CHHNO₂), 2.00 (1H, dt, J = 13.0, 4.0 Hz, CHH(CH₂)₂CH₃), 1.76 (1H, dt, J = 13.0, 4.4 Hz, CHH(CH₂)₂CH₃), 1.67 (3H, s, CCH₃), 1.31-0.92 (4H, m, CH₂(CH₂)₂CH₃), 0.82 (3H, t, J = 7.2 Hz, (CH₂)₃CH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.9, 133.4, 132.3, 128.5, 128.2, 127.6, 126.4, 126.3, 125.5, 124.0, 86.4, 42.8, 39.5, 26.2, 23.2, 22.6, 14.0. HRMS Calcd for C₁₇H₂₁NO₂: 271.1572. Found: 271.1576. Anal. Calcd for C₁₇H₂₁NO₂: C, 75.25; H, 7.80; N, 5.16. Found: C, 74.98; H, 8.05; N, 4.99. $[\alpha]_{\text{D}}^{20}$ -51.2° (c = 0.57, CHCl₃) for a sample that is 85% ee.

The optical purity is established by chiral HPLC analysis (Chiral Technologies Chiralpak OD, 254 nm, 97:3 hexanes/*i*-PrOH, 1.0 mL/min); chromatograms are illustrated below for an 85% ee sample:

1-Nitro-2-methyl-2-phenylpentane (2h). IR (neat): 3087 (w), 3062 (w), 3018 (w), 2962 (s), 2930 (s), 2873 (s), 2735 (w), 1955 (w), 1879 (w), 1804 (w), 1608 (m), 1552 (s), 1495 (m), 1470 (m), 1445 (s), 1376 (s), 1331 (w), 1287 (w), 1243 (w), 1199 (w), 1149 (w), 1036 (m), 841 (w), 771 (m), 746 (m), 702 (s), 652 (m), 576 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.38-7.54 (5H, m, ArH), 4.59 (1H, d, $J = 10.8$ Hz, CHHNO₂), 4.55 (1H, d, $J = 10.8$ Hz, CHHNO₂), 1.87 (1H, dt, $J = 13.0, 4.4$ Hz, CHHCH₂CH₃), 1.68 (1H, dt, $J = 12.8, 4.4$ Hz, CHHCH₂CH₃), 1.55 (3H, s, CCH₃), 1.26-1.16 (1H, m, CH₂CHHCH₃), 1.10-0.97 (1H, m, CH₂CHHCH₃), 0.87 (3H, t, $J = 7.2$ Hz, (CH₂)₂CH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 142.6, 128.8, 127.1, 126.2, 86.5, 42.6, 42.2, 22.6, 17.3, 14.6. HRMS Calcd for C₁₂H₁₇NO₂: 207.1259. Found: 207.1259. Anal. Calcd for C₁₂H₁₇NO₂: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.48; H, 8.47; N, 6.48. $[\alpha]_D^{20}$ -41.9° ($c = 0.45$, CHCl₃) for a sample that is 85% ee.

Optical purity is established by chiral GLC analysis (Chiraldex GTA, 128 °C, 20 psi); chromatograms are illustrated below for a 85% ee sample:

1-Nitro-2,3-dimethyl-2-phenylbutane (2i). IR (neat): 3106 (m), 3056 (m), 3037 (m), 2980 (s), 2880 (m), 1602 (m), 1558 (s), 1501 (m), 1476 (m), 1457 (m), 1382 (s), 1262 (s), 1187 (m), 1111 (m), 1042 (m), 916 (w), 834 (m), 759 (s), 708 (s), 645 (m), 557 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.34-7.21 (5H, m, ArH), 4.80 (1H, d, $J = 11.2$ Hz, CHHNO₂), 4.61 (1H, d, $J = 11.2$ Hz, CHHNO₂), 2.13 (1H, qq, $J = 6.8$ Hz, CH(CH₃)₂), 1.50 (3H, s, ArCCH₃), 0.94 (3H, d, $J = 6.8$ Hz, CH₃CHCH₃), 0.67 (3H, d, $J = 6.8$ Hz, CH₃CHCH₃). ^{13}C NMR (CDCl_3 , 100 MHz): δ 142.2, 128.4, 127.0, 126.6, 85.2, 45.7, 36.8, 17.9, 17.6, 17.0. HRMS Calcd. for C₁₂H₁₇NO₂: 207.1259. Found: 207.1259. $[\alpha]_D^{20}$ -53.1° ($c = 3.70$, CHCl₃) for a sample that is 73% ee.

Optical purity is established by chiral GLC analysis (Chiraldex GTA, 140 °C, 15 psi); chromatograms are illustrated below for a 73% ee sample:

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	28.467	MF	0.4815	1.25202e5	4333.40576	50.55159
2	31.043	FM	0.5525	1.22469e5	3694.68970	49.44841

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	28.123	MF	0.6002	7.91157e5	2.19710e4	86.47108
2	31.040	FM	0.5660	1.23781e5	3644.67969	13.52892

1-Nitro-2-ethyl-2-phenyl-3-methyl-butane (2j). IR (neat): 3094 (w), 3074 (w), 2987 (s), 2892 (w), 1552 (s), 1501 (m), 1476 (m), 1445 (m), 1376 (s), 1237 (m), 1155 (w), 1073 (w), 934 (w), 841 (w), 784 (s), 708 (s), 639 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.37-7.18 (5H, m, ArH), 5.04 (1H, d, $J = 11.2$ Hz, CHHNO_2), 4.84 (1H, d, $J = 11.2$ Hz, CHHNO_2), 2.23 (1H, dq, $J = 14.8, 7.6$ Hz, CCHHCH_3), 2.08 (1H, m, $\text{CH}(\text{CH}_3)_2$), 1.87 (1H, dq, $J = 14.8, 7.6$ Hz, CCHHCH_3), 0.92 (3H, t, $J = 7.2$ Hz, CH_2CH_3), 0.87 (3H, d, $J = 6.8$ Hz, CH_3CHCH_3), 0.79 (3H, d, $J = 6.8$ Hz, CH_3CHCH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 128.2, 127.5, 126.8, 78.6, 49.1, 34.1, 26.2, 17.9, 17.6, 8.7. HRMS Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: 221.1416. Found: 221.1416. Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.27; H, 8.33; N, 6.05. $[\alpha]_D^{20} -4.4^\circ$ ($c = 4.50$, CHCl_3) for a sample that is 93% ee.

Optical purity is established by chiral GLC analysis (β -dex, 130 °C, 20 psi); chromatograms are illustrated below for a 93% ee sample:

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	110.078	MF	0.8469	2.66331e5	5241.42578	50.05088
2	112.351	FM	0.8044	2.65790e5	5506.68604	49.94912

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	109.733	MM	0.8200	2.74138e5	5571.77832	96.52447
2	111.734	MM	0.7325	9870.79785	224.58093	3.47553

2-Methyl-2-(4-chlorophenyl)butanoic acid (8). IR (neat): 3075 (s, br), 2974 (s), 2930 (s), 2879 (s), 2634 (s), 1904 (w), 1709 (s), 1590 (w), 1495 (s), 1464 (s), 1401 (s), 1319 (m), 1275 (s), 1162 (m), 1143 (m), 1105 (s), 1048 (m), 1020 (s), 941 (m), 866 (w), 828 (m), 784 (m), 740 (s), 721 (m), 677 (m), 570 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.31 (4H, s, ArH), 2.07 (1H, dq, $J = 14.4, 7.2$ Hz, CHHCH_3), 1.96 (1H, dq, $J = 14.4, 7.2$ Hz, CHHCH_3), 1.54 (3H, s, CCH_3), 0.83 (3H, t, $J = 7.2$ Hz, CH_2CH_3).

Hz, CH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 182.1, 141.4, 133.0, 128.7, 128.0, 50.2, 31.8, 21.2, 9.1. HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{ClO}_2$: 212.0604. Found: 212.0604. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{ClO}_2$: C, 62.12; H, 6.16. Found: C, 62.12; H, 6.16. $[\alpha]_{\text{D}}^{20} +10.0^\circ$ ($c = 0.88$, CHCl_3) for a sample that is 98% ee.

2-Methyl-2-phenylhexanoic acid (9). IR (neat): 3068 (br), 2962 (s), 2923 (s), 2873 (s), 2634 (w), 1948 (w), 1703 (s), 1602 (w), 1552 (w), 1495 (w), 1470 (m), 1451 (m), 1407 (m), 1388 (m), 1281 (s), 1224 (w), 1162 (w), 1143 (w), 1029 (w), 941 (m), 853 (w), 759 (w), 728 (m), 702 (s), 664 (w), 633 (w) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.31 (4H, m, ArH), 7.27-7.23 (1H, m, ArH), 2.04 (1H, dt, $J = 12.6$, 5.2 Hz, $\text{CHH}(\text{CH}_2)_2\text{CH}_3$), 1.93 (1H, dt, $J = 12.4$, 5.2 Hz $\text{CHH}(\text{CH}_2)_2\text{CH}_3$), 1.57 (3H, s, CCH_3), 1.35-1.16 (4H, m, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 0.88 (3H, t, $J = 7.2$ Hz, $(\text{CH}_2)_3\text{CH}_3$). ^{13}C NMR (CDCl_3 , 100 MHz): δ 181.7, 143.3, 128.5, 127.0, 126.3, 50.1, 38.9, 27.0, 23.3, 22.6, 14.1. HRMS Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.1307. Found: 206.1310. $[\alpha]_{\text{D}}^{20} +8.93^\circ$ ($c = 0.27$, CHCl_3) for a sample that is 93% ee.

(S)-2-Methyl-2-phenylbutanoic acid (10). IR (neat): 3081 (br), 3056 (s), 3024 (s), 2980 (s), 2936 (s), 2917 (s), 2634 (w), 2663 (w), 1961 (w), 1697 (s), 1602 (w), 1495 (m), 1451 (m), 1401 (m), 1376 (m), 1269 (s), 1162 (m), 1080 (w), 1029 (w), 929 (m), 803 (w), 771 (m), 734 (m), 702 (s), 633 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.32 (4H, m, ArH), 7.28-7.24 (1H, m, ArH), 2.14-1.97 (2H, m, CH_2CH_3), 1.57 (3H, s, CCH_3), 0.86 (3H, t, $J = 7.4$ Hz, CH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 182.7, 143.0, 128.5, 127.0, 126.4, 50.5, 31.8, 21.9, 9.2. HRMS Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: 178.0994. Found: 178.0995. Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 73.99; H, 7.89. $[\alpha]_{\text{D}}^{20} +23.5^\circ$ ($c = 0.51$, C_6H_6) for a sample that is 94% ee. Literature value: $[\alpha]_{\text{D}}^{23} +30.2^\circ$ ($c = 4.5$, C_6H_6) for optically pure (S) product.⁶

2,3-Dimethyl-2-phenylbutanoic acid (11). IR (neat): 3062 (w), 2968 (s, br), 2924 (s), 2873 (m), 2848 (m), 2641 (w), 2521 (w), 1697 (s), 1602 (w), 1552 (m), 1495 (w), 1464 (m), 1394 (m), 1376 (m), 1275 (s), 1130 (m), 1105 (m), 929 (m), 866 (w), 765 (w), 727 (m), 696 (s), 652 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.48-7.45 (2H, m, ArH), 7.35-7.30 (2H, m, ArH), 7.25-7.22 (1H, m, ArH), 2.70 (1H, qq, $J = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.49 (3H, s, CCH_3), 1.01 (3H, d, $J = 6.4$ Hz, CH_3CHCH_3), 0.62 (3H, d, $J = 6.8$ Hz, CH_3CHCH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ 182.0, 142.2, 128.4, 127.1, 126.8, 53.7, 34.7, 19.1, 17.2, 14.9. HRMS Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1150. Found: 192.1156. Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.42. $[\alpha]_{\text{D}}^{20} +21.1^\circ$ ($c = 0.75$, CHCl_3) for a sample that is 73% ee.

1-Amino-2-methyl-2-(4-chlorophenyl)butane. IR (neat): 3390 (br), 3289 (br), 2962 (s), 2924 (s), 2880 (s), 2855 (s), 1898 (w), 1590 (w), 1489 (s), 1464 (s), 1407 (w), 1394 (w), 1294 (w), 1105 (m), 1017 (m), 897 (w), 822 (s), 734 (w), 576 (w), 551 (w) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.31-7.27 (2H, m, ArH), 7.24-7.22

(6) a) Walborsky, H. M.; Allen, L. E. *J. Am. Chem. Soc.* **1971**, 93, 5465-5468. b) Cram, D. J.; Knight, J. D. *J. Am. Chem. Soc.* **1952**, 74, 5835-5838.

(2H, m, ArH), 2.90 (1H, d, $J = 13.2$ Hz, CHHNO₂), 2.69 (1H, d, $J = 13.2$ Hz, CHHNO₂), 1.75 (1H, dq, $J = 14.4, 7.2$ Hz, CHHCH₃), 1.52 (1H, dq, $J = 14.4, 7.2$ Hz, CHHCH₃), 1.28 (3H, s, CCH₃), 0.87 (2H, br, NH₂), 0.70 (3H, t, $J = 7.2$ Hz, CH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 144.3, 131.7, 128.5, 128.4, 54.0, 43.4, 32.6, 21.4, 8.5. HRMS Calcd for C₁₁H₁₆ClN: 197.0971. Found: 197.0970.