

Electronic Supplementary Information

Asymmetric Michael addition of aldehydes to nitroalkenes using a primary amino acid lithium salt

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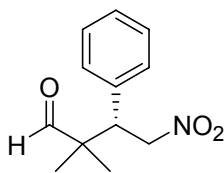
(C) References

(A) General comments

IR spectra were recorded using a JASCO FT/IR-5300 or FT/IR-410 spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM-A400II or ECX-400P FT NMR. Chemical shifts, δ are referred to TMS. EI and ESI high-resolution mass spectra were measured on a JEOL JMS-700TZ or JMS-T100LP spectrometer. Optical rotation was measured by a JASCO DIP-360 or P-2200. Melting points are measured by Yanagimoto micro melting point apparatus and are uncorrected. HPLC was carried out using a JASCO PU-2089 Plus intelligent pump and a UV-2075 Plus UV detector.

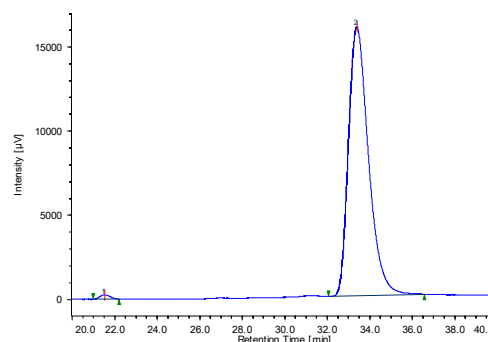
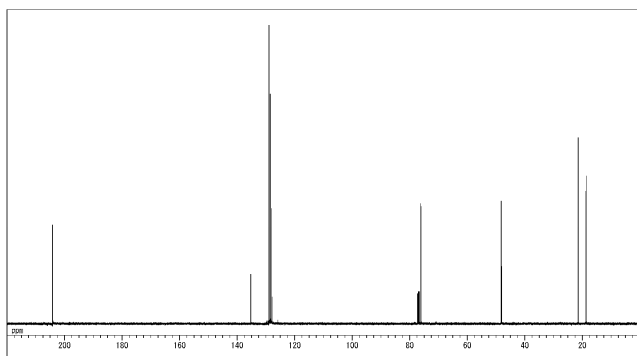
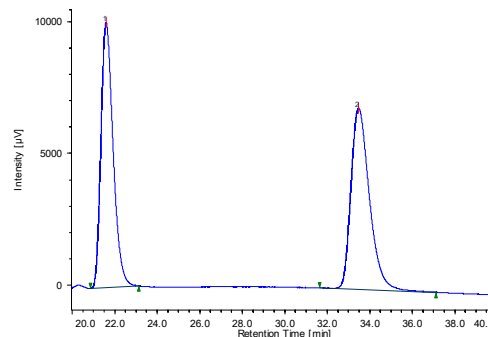
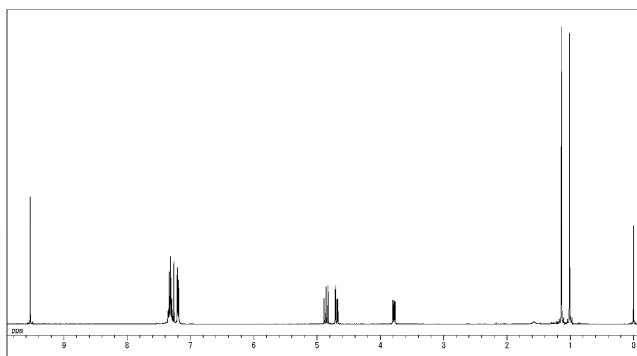
(B) Compound characterization data of the Michael adducts

(S)-2,2-Dimethyl-4-nitro-3-phenylbutanal (3a)

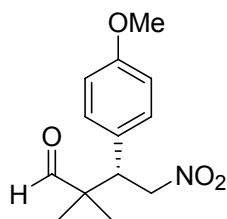


The enantioselectivity was determined by HPLC analysis [98% ee, DAICEL CHIRALCEL OD-H, 10% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 33.5 min, t_r (minor enantiomer) = 21.6 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.¹ $[\alpha]^{26}_D = -4.9^\circ$ ($c = 1.0$, CHCl_3), light yellow oil, $\delta_H(\text{CDCl}_3)$ 1.01 (3H, s), 1.14 (3H, s), 3.79 (1H, dd, J 4.2, 11.3 Hz), 4.69 (1H, dd, J 4.2, 13.1 Hz), 4.86 (1H, dd, J 11.3, 13.1 Hz), 7.20-7.21 (2H, m), 7.30-7.36 (3H, m), 9.53 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.7, 21.5, 48.1, 48.3, 76.2, 128.0, 128.5, 128.9, 135.3, 204.2; $\nu(\text{neat})/\text{cm}^{-1}$ 3065, 3034, 2975, 2934, 2878, 2820, 2720, 1725, 1603, 1555, 1495, 1468, 1456, 1435, 1379, 1337, 1314, 1206, 1159, 1144, 1090, 1032, 1005, 976, 912, 883, 831, 804, 781, 750, 706, 648; [HR EI-MS: Calc. for $\text{C}_{12}\text{H}_{15}\text{NO}_3$ (M): 221.1052. Found: M^+ , 221.1044].

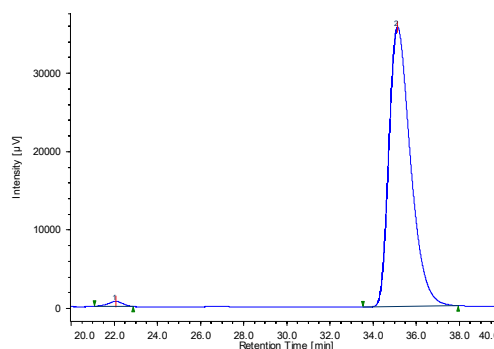
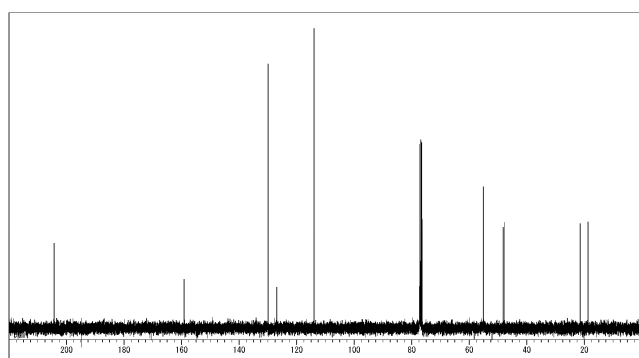
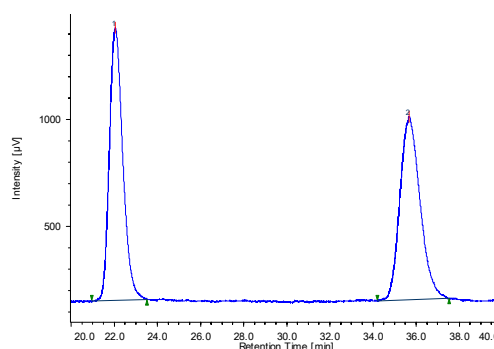
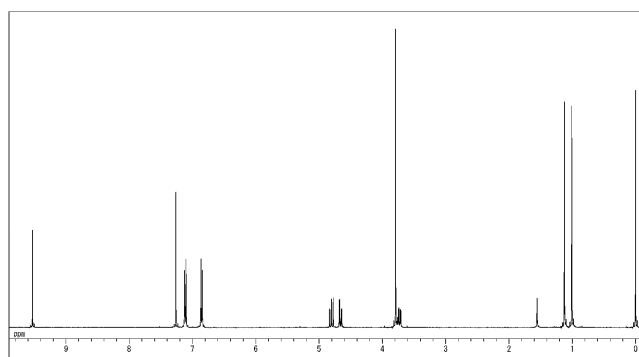


(S)-2,2-Dimethyl-3-(4-methoxyphenyl)-4-nitrobutanal (3b)

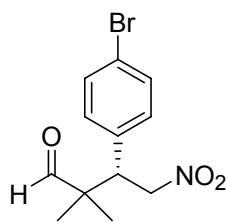


The enantioselectivity was determined by HPLC analysis [98% ee, DAICEL CHIRALCEL OD-H, 10% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 35.6 min, t_r (minor enantiomer) = 22.1 min]. The absolute configuration was determined by comparison of the optical rotation with that of the literature.^{1f,g}

$[\alpha]^{26}_D = +1.7^\circ$ ($c = 1.0$, CHCl_3), white solid, Mp. 58-59 °C, $\delta_H(\text{CDCl}_3)$ 1.00 (3H, s), 1.13 (3H, s), 3.73 (1H, dd, J 4.2, 11.5 Hz), 3.79 (3H, s), 4.66 (1H, dd, J 4.2, 12.8 Hz), 4.81 (1H, dd, J 11.5, 12.8 Hz), 6.86 (2H, d, J 8.7 Hz), 7.11 (2H, d, J 8.7 Hz), 9.53 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.7, 21.4, 47.7, 48.2, 55.1, 76.4, 113.9, 126.9, 130.0, 159.2, 204.3; $\nu(\text{KBr})/\text{cm}^{-1}$ 2976, 2919, 2841, 2718, 1725, 1611, 1582, 1553, 1516, 1468, 1441, 1379, 1290, 1250, 1188, 1119, 1028, 889, 839, 812, 747, 635; [HR EI-MS: Calc. for $\text{C}_{13}\text{H}_{17}\text{NO}_4$ (M): 251.1158. Found: M^+ , 251.1152].



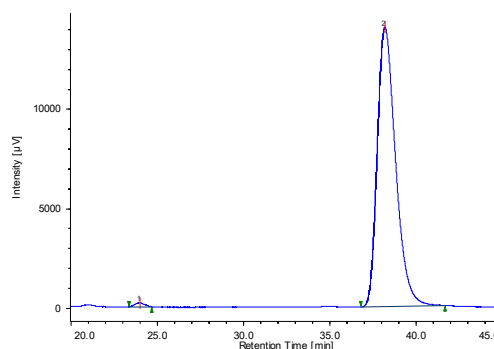
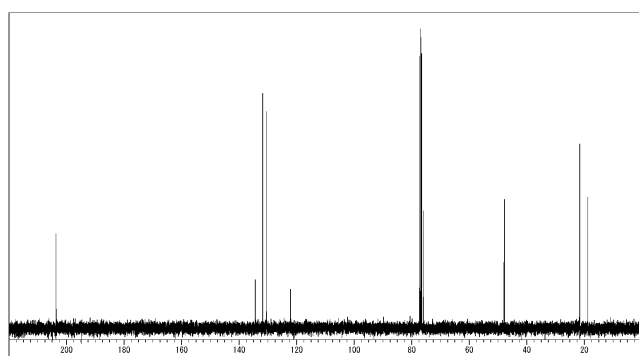
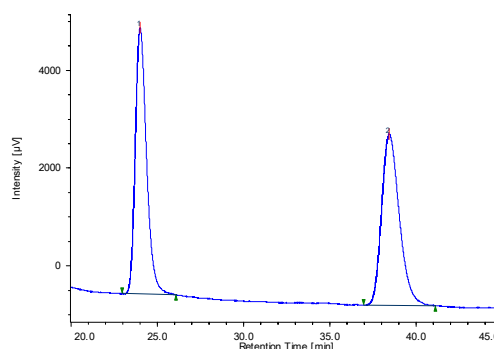
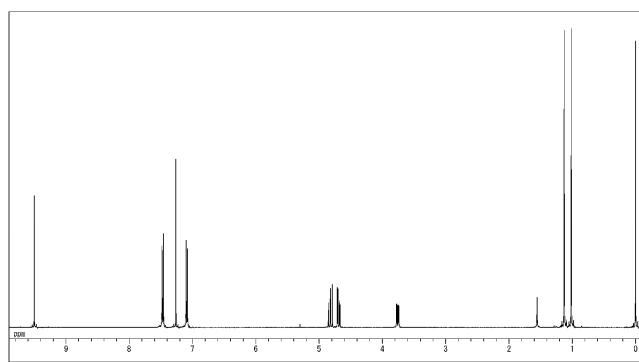
(S)-3-(4-Bromophenyl)-2,2-dimethyl-4-nitrobutanal (3c)



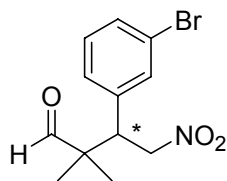
The enantioselectivity was determined by HPLC analysis [99% ee, DAICEL CHIRALCEL OD-H, 10% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 38.2 min, t_r (minor enantiomer) = 24.0 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.² $[\alpha]^{26}_D = -3.3^\circ$ ($c = 1.0$, CHCl_3), white solid, Mp. 86-87 °C, $\delta_H(\text{CDCl}_3)$ 1.02 (3H, s), 1.13 (3H, s), 3.76 (1H, dd, J 4.2, 11.3 Hz), 4.69 (1H, dd, J 4.2, 13.2 Hz), 4.82 (1H, dd, J 11.3, 13.2 Hz), 7.09 (2H, d, J 8.6 Hz), 7.47 (2H, d, J 8.6 Hz), 9.50 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.8, 21.6, 47.8, 48.0, 75.9, 122.1, 130.6, 131.8, 134.3, 203.7;

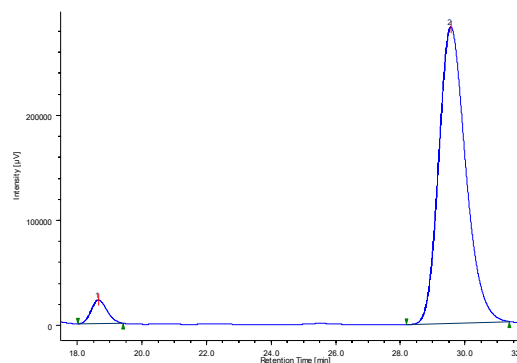
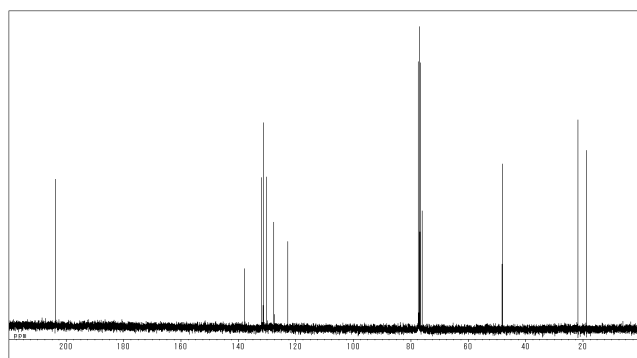
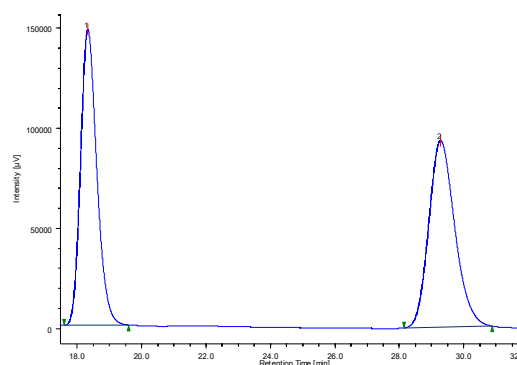
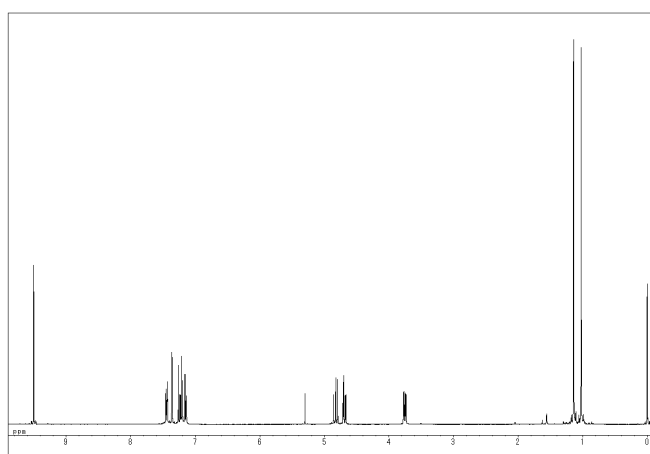
$\nu(\text{KBr})/\text{cm}^{-1}$ 3030, 2973, 2934, 2874, 2818, 2718, 1728, 1559, 1487, 1468, 1441, 1410, 1381, 1350, 1306, 1206, 1144, 1113, 1074, 1009, 889, 845, 781, 721, 702, 664; [HR EI-MS: Calc. for $\text{C}_{12}\text{H}_{14}\text{BrNO}_3$ (M): 299.0157. Found: M^+ , 299.0145].



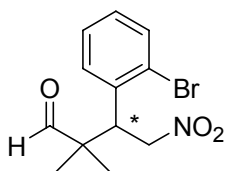
3-(3-Bromophenyl)-2,2-dimethyl-4-nitrobutanal (3d)³



The enantioselectivity was determined by HPLC analysis [92% ee, DAICEL CHIRALCEL OD-H, 10% ethanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 29.3 min, t_r (minor enantiomer) = 18.3 min]. $[\alpha]_D^{23} = +4.0^\circ$ ($c = 1.0$, CHCl_3), yellow oil, $\delta_{\text{H}}(\text{CDCl}_3)$ 1.02 (3H, s), 1.14 (3H, s), 3.77 (1H, dd, J 4.0, 11.3 Hz), 4.69 (1H, dd, J 4.0, 13.2 Hz), 4.83 (1H, dd, J 11.3, 13.2 Hz), 7.14-7.24 (2H, m), 7.36 (1H, s), 7.43-7.46 (1H, m), 9.50 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 18.8, 21.8, 47.9, 48.2, 76.0, 122.8, 127.7, 130.2, 131.3, 132.1, 137.9, 203.7; $\nu(\text{neat})/\text{cm}^{-1}$ 3073, 2975, 2936, 2877, 2812, 2710, 1727, 1558, 1475, 1434, 1380, 1348, 1295, 1213, 1141, 1067, 997, 978, 881, 840, 811, 783, 702, 646; [HR ESI-MS: Calc. for $\text{C}_{12}\text{H}_{14}\text{BrNNaO}_3$ ($M+\text{Na}$): 322.0055. Found: $M+\text{Na}$, 322.0044].



3-(2-Bromophenyl)-2,2-dimethyl-4-nitrobutanal (**3e**)³



The enantioselectivity was determined by HPLC analysis [92% ee, DAICEL CHIRALCEL OD-H, 10% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 47.0 min, t_r (minor enantiomer) = 16.4 min].

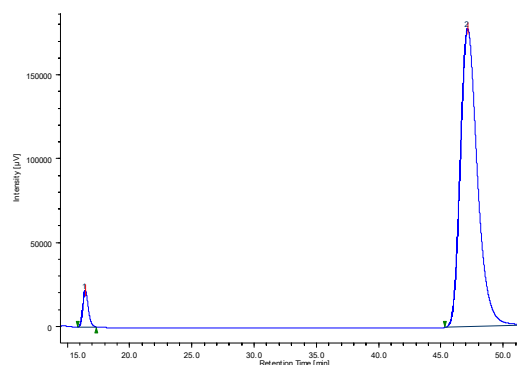
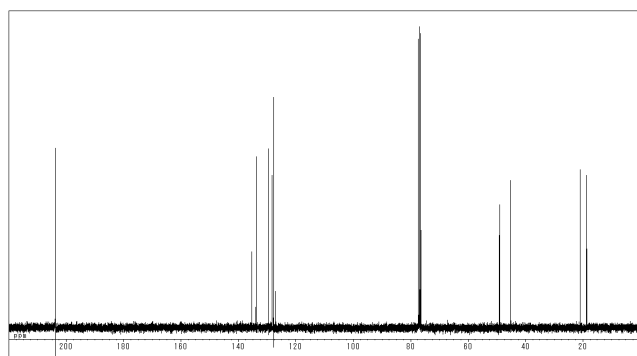
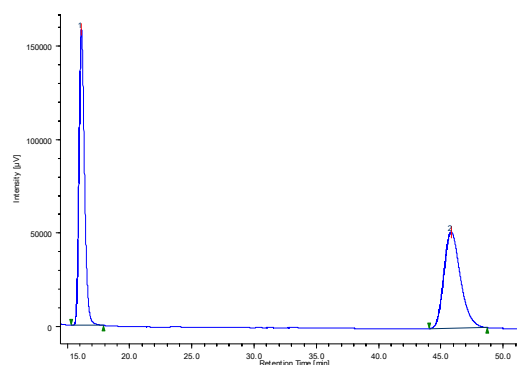
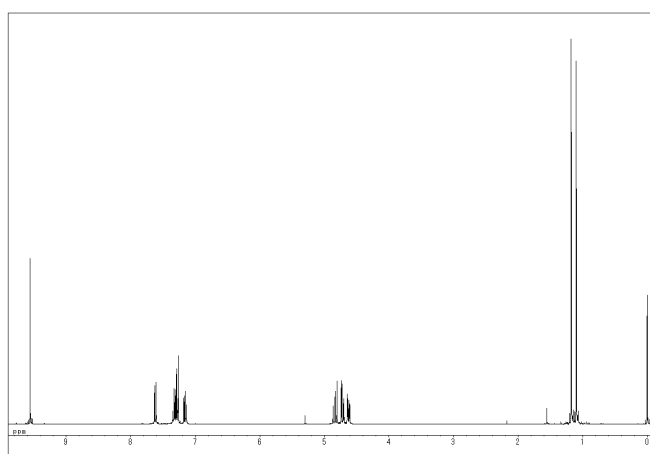
$[\alpha]_{D}^{23} = -13.0^\circ$ ($c = 1.0$, CHCl_3), orange solid, Mp. 60-61 °C, $\delta_{\text{H}}(\text{CDCl}_3)$ 1.10

(3H, s), 1.18 (3H, s), 4.63 (1H, dd, J 4.1, 11.4 Hz), 4.72 (1H, dd, J 4.1, 13.3 Hz), 4.84 (1H, dd, J 11.4, 13.3 Hz), 7.14-7.18 (1H, m), 7.26-7.35 (2H, m), 7.61-7.63 (1H, m), 9.50 (1H, s);

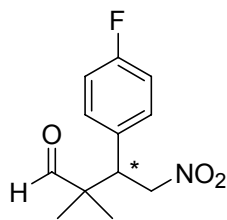
$\delta_{\text{C}}(\text{CDCl}_3)$ 18.7, 20.9, 45.2, 49.1, 76.4, 127.1, 127.8, 128.3, 129.4, 133.9, 135.4, 203.8;

$\nu(\text{KBr})/\text{cm}^{-1}$ 3068, 3033, 2970, 2935, 2874, 2818, 2725, 1730, 1554, 1472, 1438, 1402, 1379, 1273, 1201, 1065, 1024, 910, 891, 801, 752, 723, 662, 625; [HR ESI-MS: Calc. for

$\text{C}_{12}\text{H}_{14}\text{BrNNaO}_3$ ($M^+\text{Na}$): 322.0055. Found: $M^+\text{Na}$, 322.0052].

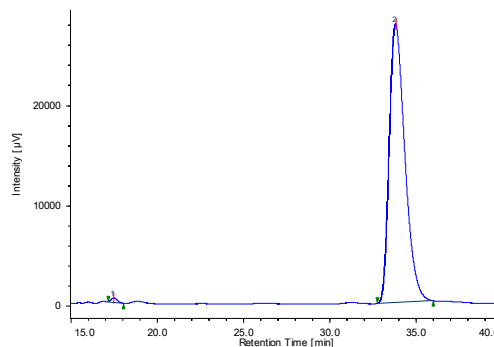
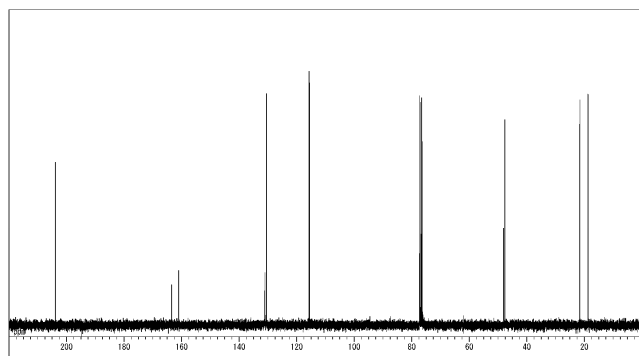
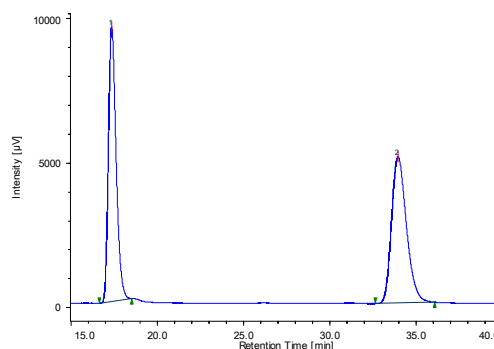
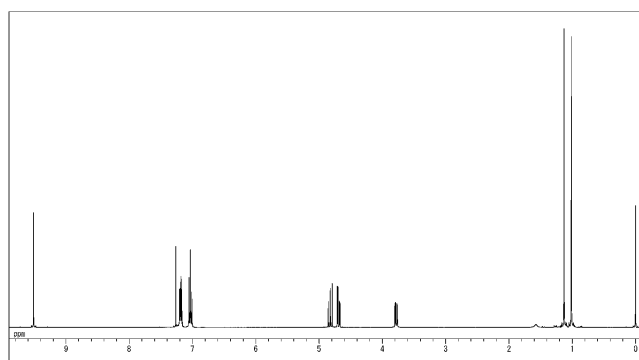


2,2-Dimethyl-3-(4-fluorophenyl)-4-nitrobutanal (3f)

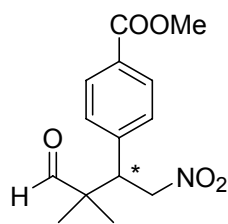


The enantioselectivity was determined by HPLC analysis [99% ee, DAICEL CHIRALCEL OD-H, 10% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 33.9 min, t_r (minor enantiomer) = 17.4 min].

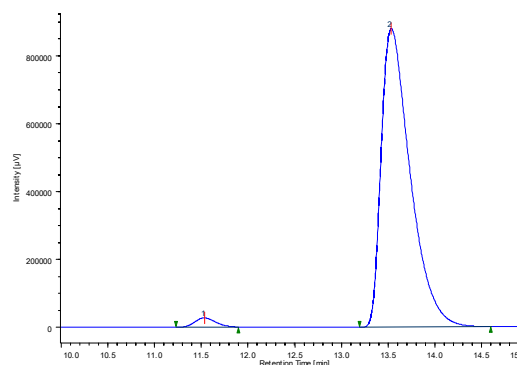
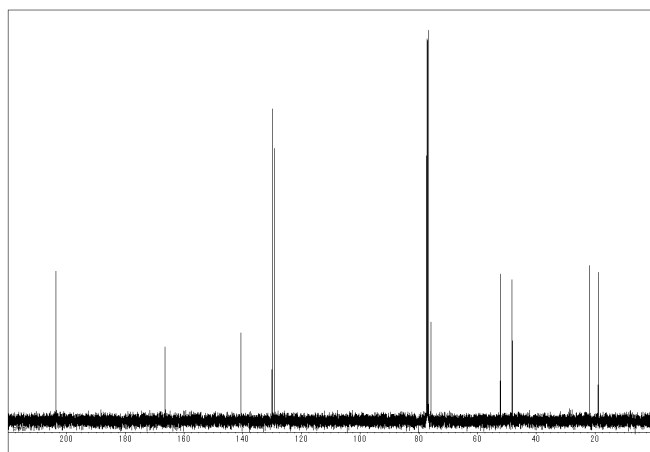
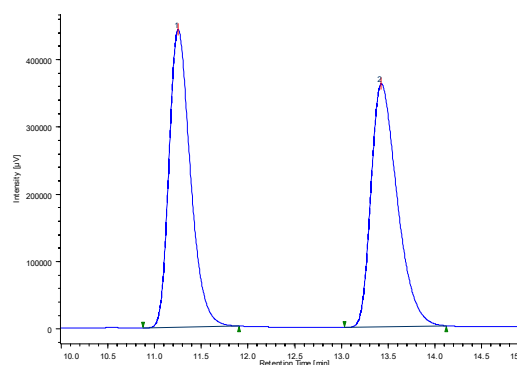
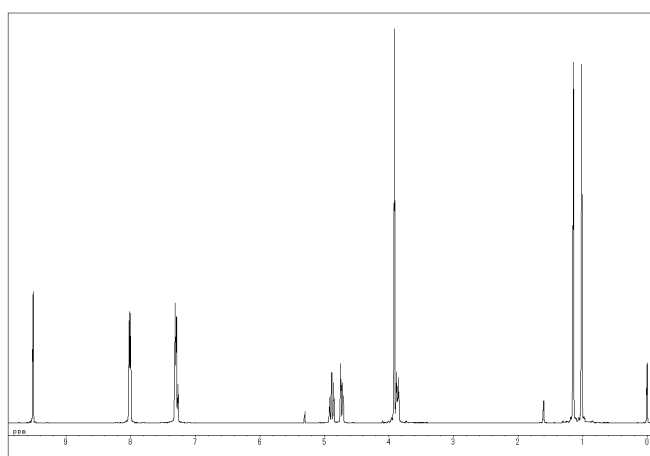
$[\alpha]^{26}_D = -1.5^\circ$ ($c = 1.0$, CHCl_3), light yellow oil, $\delta_H(\text{CDCl}_3)$ 1.01 (3H, s), 1.13 (3H, s), 3.78 (1H, dd, J 4.2, 11.5 Hz), 4.69 (1H, dd, J 4.2, 13.1 Hz), 4.82 (1H, dd, J 11.5, 13.1 Hz), 7.01-7.06 (2H, m), 7.17-7.21 (2H, m), 9.51 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.7, 21.5, 47.6, 48.1, 76.2, 115.6 (d, J 21.5 Hz), 130.5 (d, J 8.1 Hz), 131.0 (d, J 3.3 Hz), 162.3 (d, J 247.0 Hz), 203.9; $\nu(\text{neat})/\text{cm}^{-1}$ 3045, 2976, 2936, 2878, 2820, 2722, 1725, 1605, 1555, 1512, 1470, 1437, 1379, 1304, 1229, 1165, 1105, 1017, 883, 843, 750, 689, 646; [HR EI-MS: Calc. for $\text{C}_{12}\text{H}_{14}\text{FNO}_3$ (M): 239.0958. Found: M^+ , 239.0954].



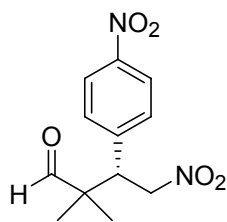
Methyl 4-(3,3-dimethyl-1-nitro-4-oxobutan-2-yl)benzoate (3g)



The enantioselectivity was determined by HPLC analysis [96% ee, DAICEL CHIRALPAK AD-H, 20% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 13.5 min, t_r (minor enantiomer) = 11.5 min]. $[\alpha]_D^{23} = +7.9^\circ$ ($c = 1.0$, CHCl_3), white solid, Mp. 88-89 °C, $\delta_{\text{H}}(\text{CDCl}_3)$ 1.01 (3H, s), 1.14 (3H, s), 3.86 (1H, dd, J 4.1, 11.4 Hz), 3.92 (3H, s), 4.73 (1H, dd, J 4.1, 13.2 Hz), 4.89 (1H, dd, J 11.4, 13.2 Hz), 7.30 (2H, d, J 8.2 Hz), 8.01 (2H, d, J 8.2 Hz), 9.52 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 18.9, 21.8, 48.1, 48.2, 52.2, 75.9, 129.2, 129.9, 130.1, 140.7, 166.5, 203.6; $\nu(\text{neat})/\text{cm}^{-1}$ 3101, 3060, 3031, 2975, 2952, 2816, 2723, 1723, 1611, 1553, 1436, 1378, 1284, 1192, 1112, 1020, 962, 900, 862, 797, 762, 710, 630; [HR ESI-MS: Calc. for $\text{C}_{14}\text{H}_{17}\text{NNaO}_5$ ($M+\text{Na}$): 302.1004. Found: $M+\text{Na}$, 302.1007].



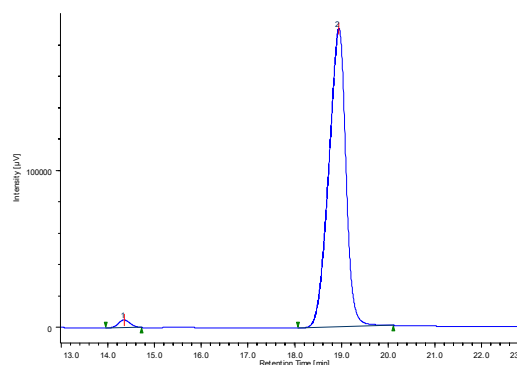
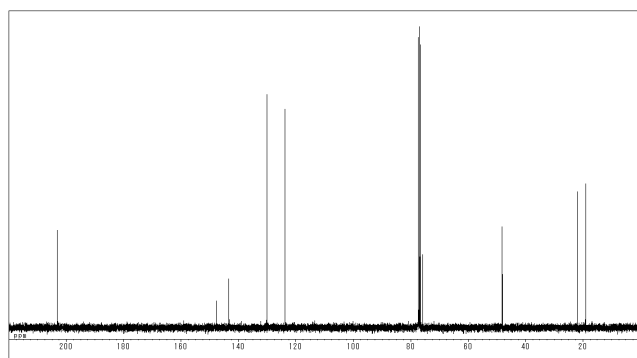
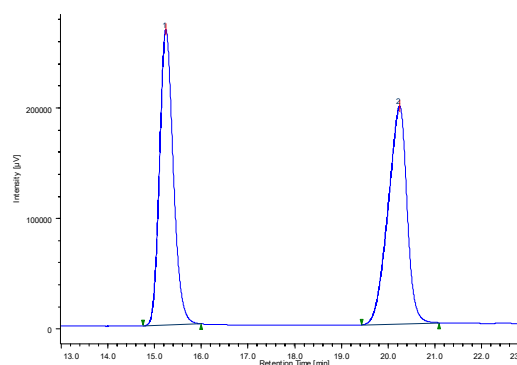
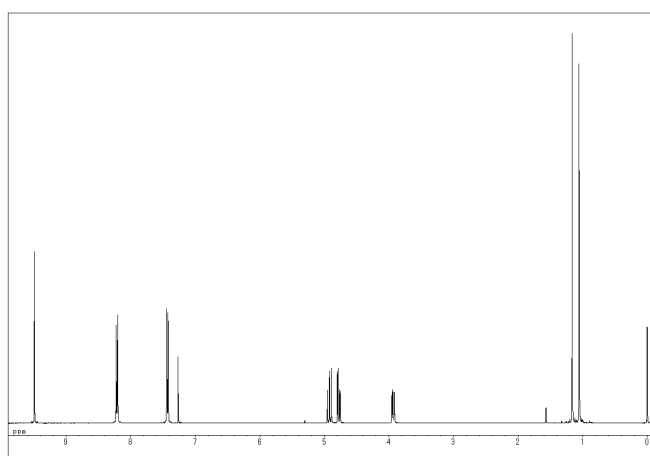
(S)-2,2-Dimethyl-4-nitro-3-(4-nitrophenyl)butanal (3h)



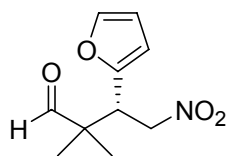
The enantioselectivity was determined by HPLC analysis [97% ee, DAICEL CHIRALPAK AD-H, 20% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 20.6 min, t_r (minor enantiomer) = 15.5 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.^{1f,g} $[\alpha]^{23}_D = -7.6^\circ$ (c = 1.0, CHCl₃),

orange solid, Mp. 57-59 °C, δ_H (CDCl₃) 1.06 (3H, s), 1.16 (3H, s), 3.93 (1H, dd, J 4.1, 11.4 Hz), 4.78 (1H, dd, J 4.1, 13.7 Hz), 4.92 (1H, dd, J 11.4, 13.7 Hz), 7.43 (2H, d, J 8.7 Hz), 8.22 (2H, d, J 8.7 Hz), 9.49 (1H, s); δ_C (CDCl₃) 19.1, 21.9, 48.1, 48.2, 75.8, 123.8, 130.1, 143.3, 147.7, 203.1; ν (KBr)/cm⁻¹ 3112, 3083, 2974, 2939, 2876, 2825, 2719, 1729, 1606, 1561, 1469, 1440, 1348, 1205, 1187, 1110, 1012, 887, 859, 747, 704, 656.



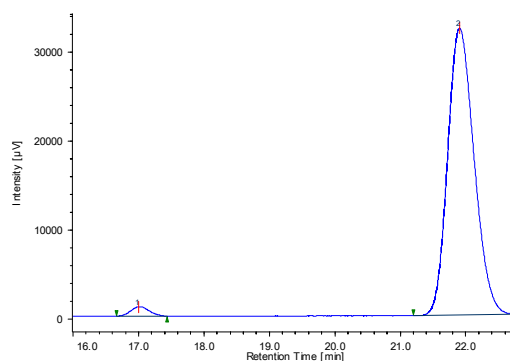
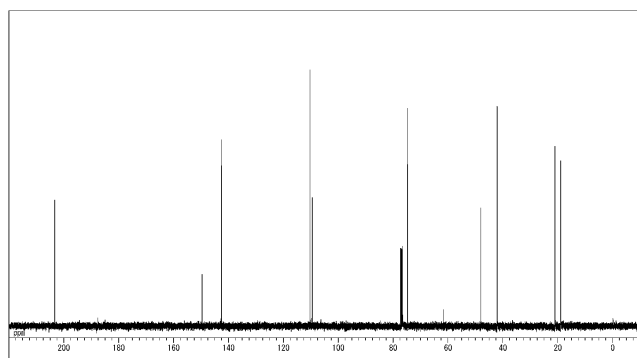
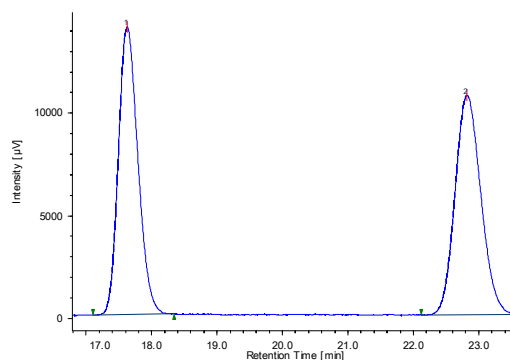
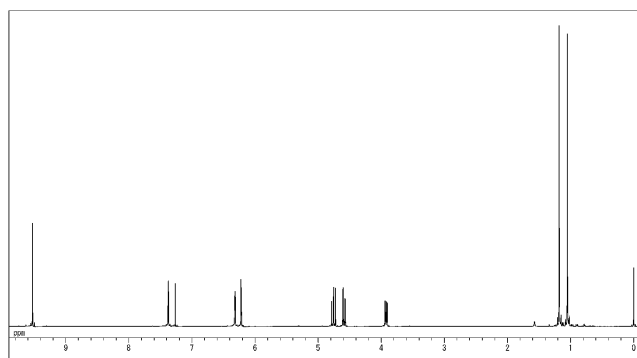
(S)-2,2-Dimethyl-3-(furan-2-yl)-4-nitrobutanal (3i)



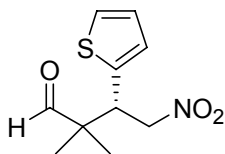
The enantioselectivity was determined by HPLC analysis [96% ee, DAICEL CHIRALPAK AD-H, 1% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 21.9 min, t_r (minor enantiomer) = 17.0 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.^{1f,g,2a}

$[\alpha]^{26}_D = +20.2^\circ$ ($c = 1.0$, CHCl_3), light yellow oil, $\delta_H(\text{CDCl}_3)$ 1.05 (3H, s), 1.18 (3H, s), 3.92 (1H, dd, J 3.9, 11.0 Hz), 4.59 (1H, dd, J 3.9, 12.8 Hz), 4.76 (1H, dd, J 11.0, 12.8 Hz), 6.22 (1H, d, J 3.2 Hz), 6.31 (1H, dd, J 1.6, 3.2 Hz), 7.38 (1H, d, J 1.6 Hz), 9.51 (1H, s); $\delta_C(\text{CDCl}_3)$ 19.0, 21.1, 42.2, 48.1, 74.8, 109.6, 110.4, 142.7, 149.7, 203.4; $\nu(\text{neat})/\text{cm}^{-1}$ 3151, 3123, 2975, 2935, 2877, 2821, 2720, 1772, 1727, 1556, 1505, 1469, 1433, 1377, 1344, 1294, 1181, 1148, 1078, 1016, 973, 915, 886, 819, 742, 700, 599; [HR EI-MS: Calc. for $\text{C}_{10}\text{H}_{13}\text{NO}_4$ (M): 211.0845. Found: M^+ , 211.0853].

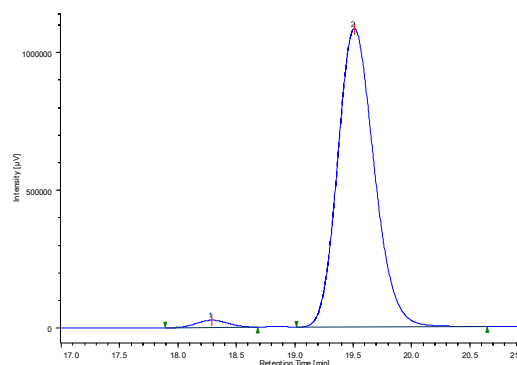
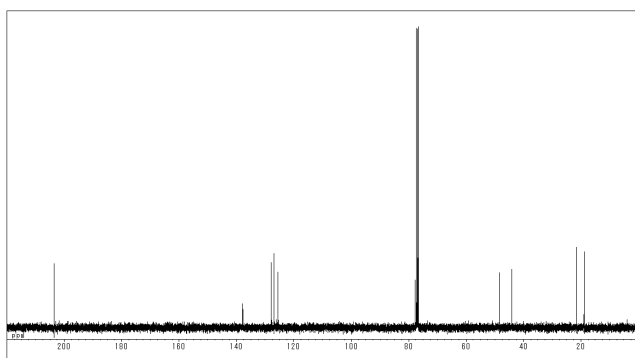
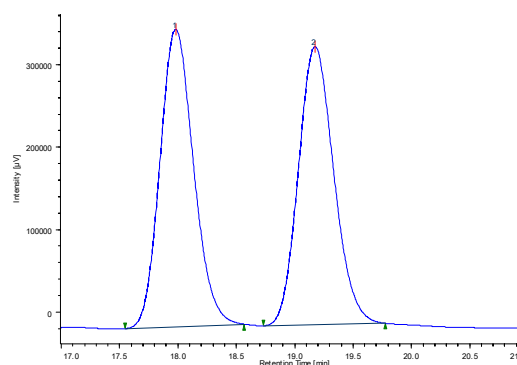
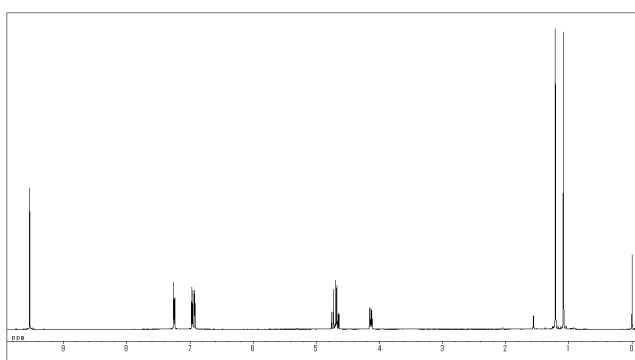


(S)-2,2-Dimethyl-4-nitro-3-(thiophen-2-yl)butanal (3j)

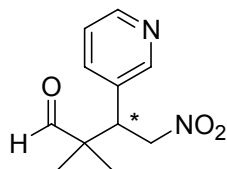


The enantioselectivity was determined by HPLC analysis [95% ee, DAICEL CHIRALPAK AD-H, 10% isopropanol/hexane, 0.5 mL/min, 209 nm; t_r (major enantiomer) = 19.5 min, t_r (minor enantiomer) = 18.3 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.^{1f,g} $[\alpha]^{23}_D = -5.1^\circ$ ($c = 1.0$, CHCl_3), light yellow oil, $\delta_H(\text{CDCl}_3)$ 1.09 (3H, s), 1.21 (3H, s), 4.14 (1H, dd, J 4.3, 10.6 Hz), 4.66 (1H, dd, J 4.3, 12.8 Hz), 4.73 (1H, dd, J 10.6, 12.8 Hz), 6.93 (1H, d, J 3.6 Hz), 6.97 (1H, dd, J 3.6, 5.0 Hz), 7.25 (1H, d, J 5.0 Hz), 9.54 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.9, 21.5, 44.0, 48.3, 77.8, 125.5, 126.9, 127.9, 137.8, 203.6; $\nu(\text{neat})/\text{cm}^{-1}$ 3110, 2974, 2930, 2880, 2819, 2719, 1724, 1556, 1468, 1434, 1379, 1341, 1249, 1206, 1162, 1064, 883, 851, 706.

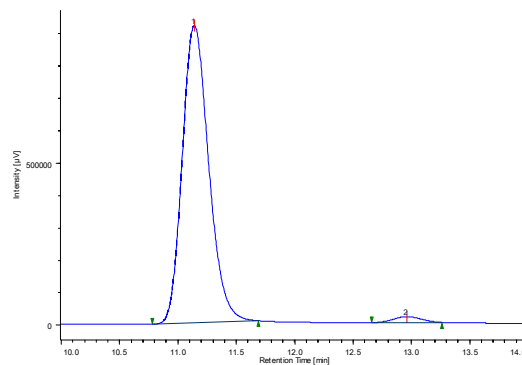
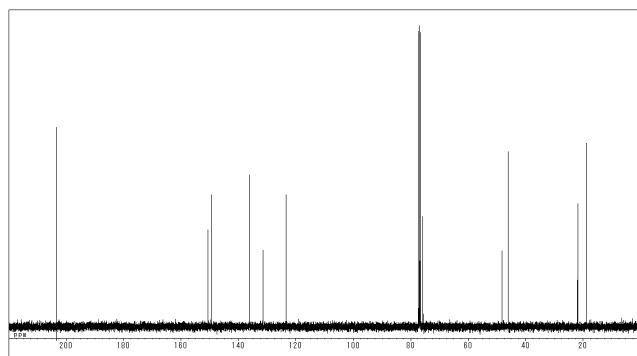
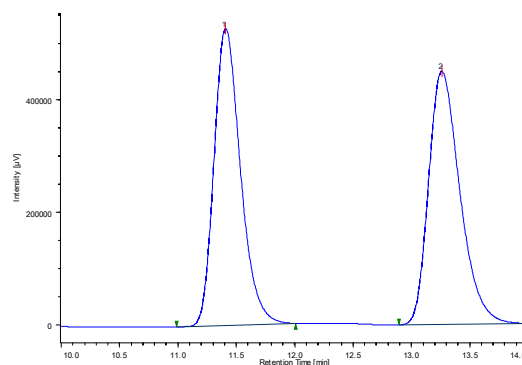
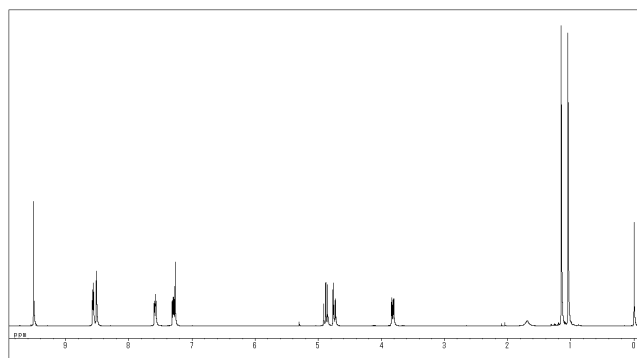


2,2-Dimethyl-4-nitro-3-(3-pyridyl)butanal (3k)

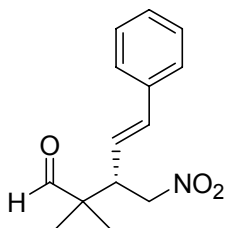


The enantioselectivity was determined by HPLC analysis [93% ee, DAICEL CHIRALPAK AD-H, 20% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 11.1 min, t_r (minor enantiomer) = 13.0 min].

$[\alpha]_D^{23} = +9.9^\circ$ ($c = 1.0$, CHCl_3), orange oil, $\delta_{\text{H}}(\text{CDCl}_3)$ 1.05 (3H, s), 1.15 (3H, s), 3.82 (1H, dd, J 4.1, 11.4 Hz), 4.75 (1H, dd, J 4.1, 13.7 Hz), 4.88 (1H, dd, J 11.4, 13.7 Hz), 7.27-7.31 (1H, m), 7.57-7.60 (1H, m), 8.51-8.52 (1H, m), 8.56-8.58 (1H, m), 9.51 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 18.9, 21.8, 46.0, 48.2, 75.7, 123.5, 131.4, 136.1, 149.6, 150.6, 203.4; $\nu(\text{neat})/\text{cm}^{-1}$ 3420, 2975, 2934, 2872, 2822, 2722, 1725, 1555, 1469, 1430, 1379, 1186, 1027, 883, 822, 718; [HR ESI-MS: Calc. for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_3$ ($M+H$): 223.1083. Found: $M+H$, 223.1081].

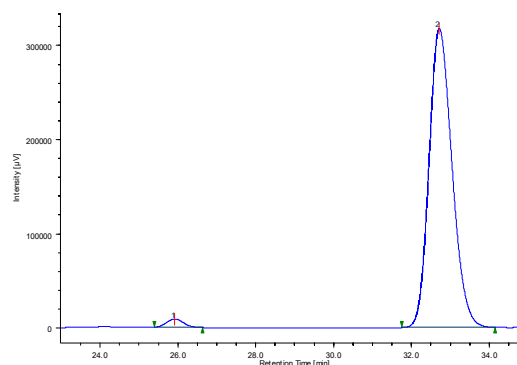
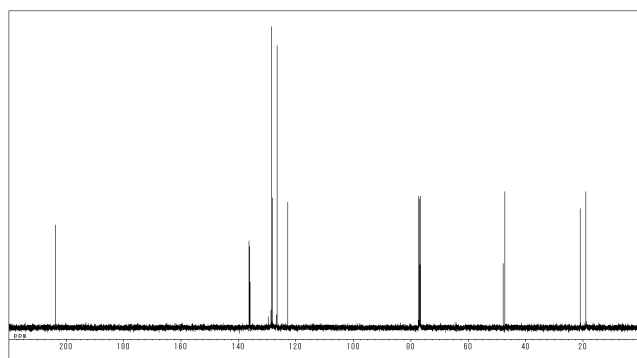
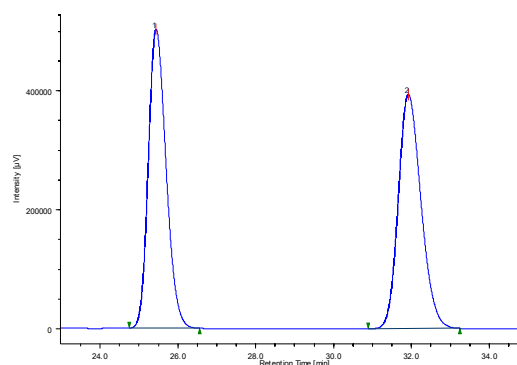
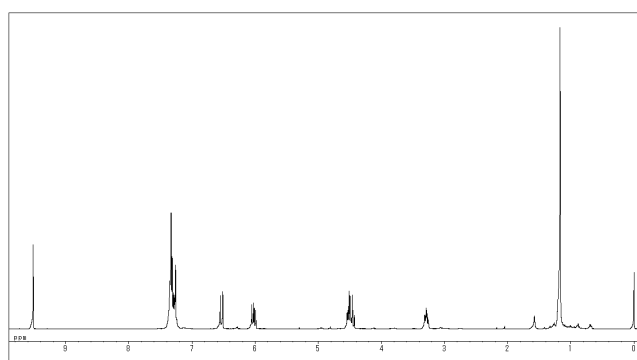


(S)-(E)-2,2-Dimethyl-3-(nitromethyl)-5-phenylpent-4-enal (3l)

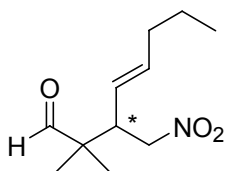


The enantioselectivity was determined by HPLC analysis [96% ee, DAICEL CHIRALPAK AD-H, 5% ethanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 32.8 min, t_r (minor enantiomer) = 25.9 min]. The absolute configuration was determined by comparison of the optical rotation with that of the literature.^{1f,g} $[\alpha]^{28}_D = +22.6^\circ$ ($c = 1.0$, CHCl_3),

yellow oil, $\delta_H(\text{CDCl}_3)$ 1.167 (3H, s), 1.172 (3H, s), 3.27 (1H, ddd, J 4.1, 9.9, 10.4 Hz), 4.46 (1H, dd, J 10.4, 12.2 Hz), 4.52 (1H, dd, J 4.1, 12.2 Hz), 6.02 (1H, dd, J 9.9, 15.9 Hz), 6.53 (1H, d, J 15.9 Hz), 7.27-7.35 (5H, m), 9.51 (1H, s); $\delta_C(\text{CDCl}_3)$ 19.0, 20.9, 47.2, 47.7, 76.6, 122.8, 126.5, 128.2, 128.6, 135.9, 136.3, 203.7; $\nu(\text{neat})/\text{cm}^{-1}$ 3060, 3028, 2974, 2932, 2875, 2817, 2716, 1723, 1554, 1494, 1468, 1449, 1434, 1380, 1200, 1075, 972, 887, 749, 694.

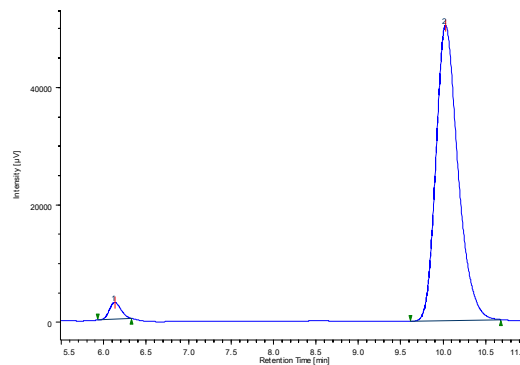
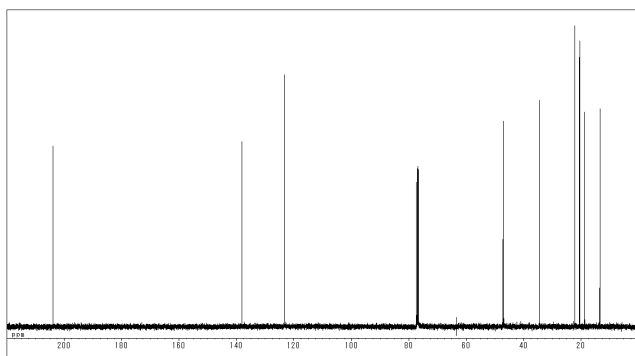
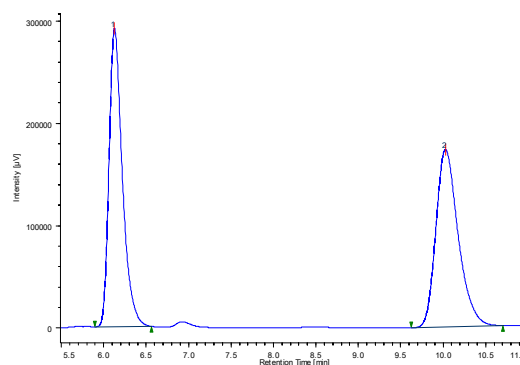
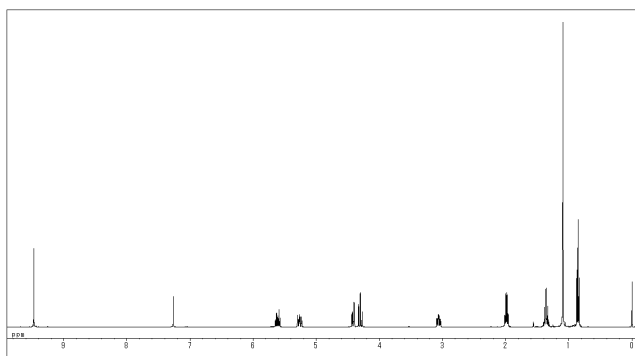


(E)-2,2-Dimethyl-3-(nitromethyl)oct-4-enal (3m)

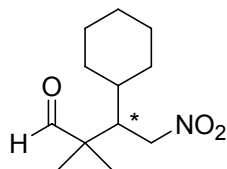


The enantioselectivity was determined by HPLC analysis [94% ee, DAICEL CHIRALCEL OD-H, 20% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 10.0 min, t_r (minor enantiomer) = 6.1 min].

$[\alpha]_{28}^{28} = -20.3^\circ$ ($c = 1.0$, CHCl_3), colorless oil, $\delta_{\text{H}}(\text{CDCl}_3)$ 0.86 (3H, t, J 7.3 Hz), 1.09 (6H, s), 1.31-1.41 (2H, m), 1.98 (2H, dt, J 6.8, 7.3 Hz), 3.05 (1H, ddd, J 3.9, 9.8, 10.7 Hz), 4.30 (1H, dd, J 10.7, 11.7 Hz), 4.42 (1H, dd, J 3.9, 11.7 Hz), 5.26 (1H, dd, J 9.8, 15.1 Hz), 5.59 (1H, dt, J 6.8, 15.1 Hz), 9.47 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.4, 18.8, 20.5, 22.1, 34.5, 46.9, 47.3, 76.9, 123.2, 138.1, 204.0; $\nu(\text{neat})/\text{cm}^{-1}$ 2963, 2931, 2873, 2714, 1728, 1556, 1466, 1436, 1380, 1339, 1202, 1056, 934, 887, 780, 718, 634.

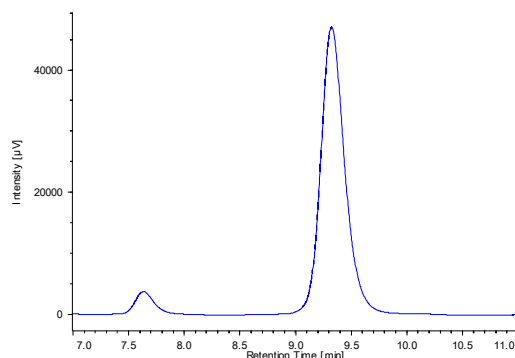
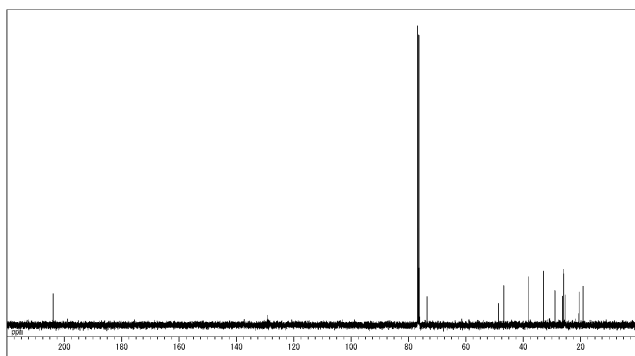
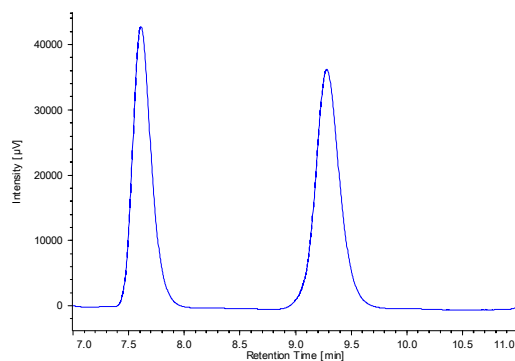
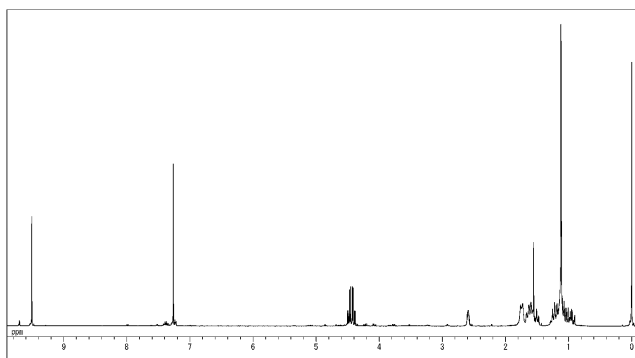


3-Cyclohexyl-2,2-dimethyl-4-nitrobutanal (3n)

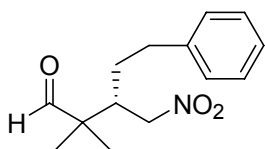


The enantioselectivity was determined by HPLC analysis [88% ee, DAICEL CHIRALCEL OD-H, 5% isopropanol/hexane, 1.0 mL/min, 210 nm; t_r (major enantiomer) = 9.3 min, t_r (minor enantiomer) = 7.6 min].

$[\alpha]_D^{26} = -11.3^\circ$ ($c = 1.0$, CHCl_3), colorless oil, $\delta_{\text{H}}(\text{CDCl}_3)$ 0.90-1.29 (1H, m), 1.47-1.76 (6H, m), 2.57-2.61 (1H, m), 4.40 (1H, dd, J 5.0, 14.0 Hz), 4.48 (1H, dd, J 6.5, 14.0 Hz), 9.51 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 19.2, 20.5, 25.4, 25.9, 26.3, 29.0, 32.9, 38.2, 46.8, 48.7, 73.5, 203.9; $\nu(\text{neat})/\text{cm}^{-1}$ 2929, 2855, 2709, 1724, 1554, 1449, 1373, 1308, 1249, 1103, 1025, 893, 841, 760, 704.

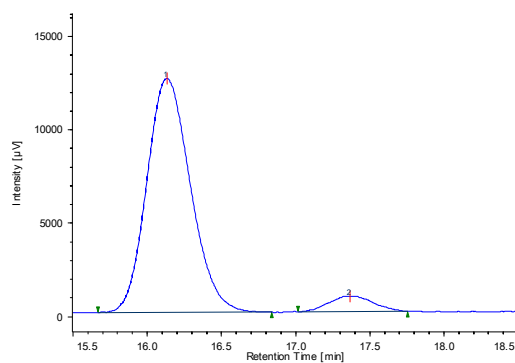
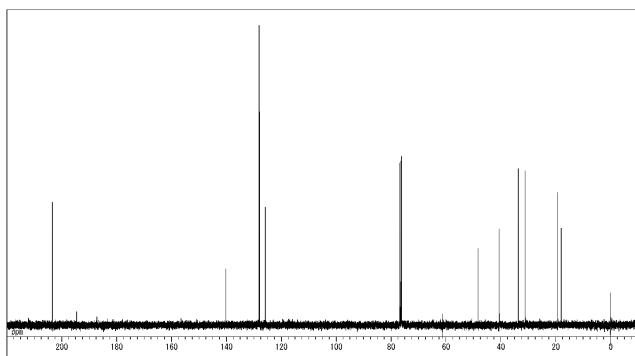
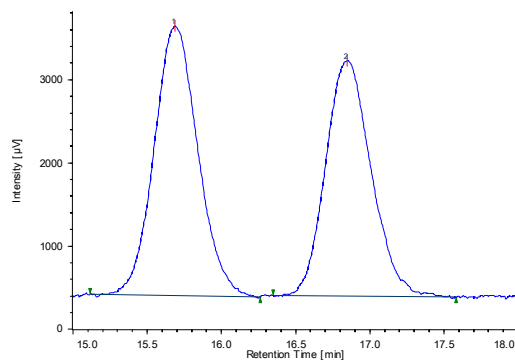
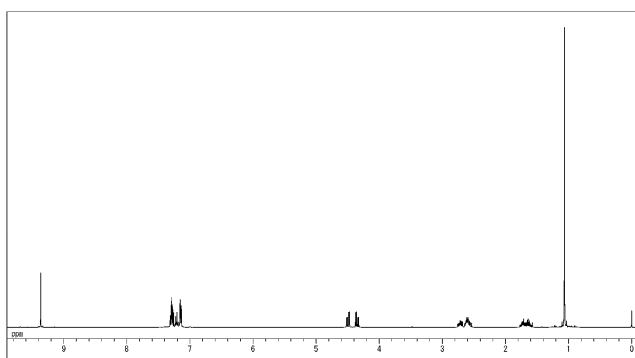


(S)-2,2-Dimethyl-3-(nitromethyl)-5-phenylpentanal (3o)

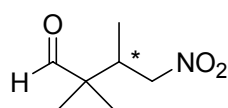


The enantioselectivity was determined by HPLC analysis [88% ee, DAICEL CHIRALPAK AD-H, 1% isopropanol/hexane, 1.0 mL/min, 254 nm; t_r (major enantiomer) = 16.1 min, t_r (minor enantiomer) = 17.4 min].

The absolute configuration was determined by comparison of the optical rotation with that of the literature.³ $[\alpha]^{26}_D = -22.5^\circ$ ($c = 1.0$, CHCl_3), colorless oil, $\delta_H(\text{CDCl}_3)$ 1.07 (6H, s), 1.57-1.77 (2H, m), 2.54-2.65 (2H, m), 2.68-2.76 (1H, m), 4.35 (1H, dd, J 6.5, 13.1 Hz), 4.49 (1H, dd, J 5.1, 13.1 Hz), 7.14-7.31 (5H, m), 9.37 (1H, s); $\delta_C(\text{CDCl}_3)$ 18.0, 19.3, 31.1, 33.6, 40.6, 48.3, 76.2, 125.9, 127.9, 128.1, 140.2, 203.4; $\nu(\text{neat})/\text{cm}^{-1}$ 3062, 3028, 2971, 2949, 2871, 2817, 2711, 1725, 1603, 1555, 1496, 1455, 1381, 1211, 1091, 1030, 885, 751, 701; [HR ESI-MS: Calc. for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ ($M+H$): 250.1443. Found: $M+H$, 250.1424].

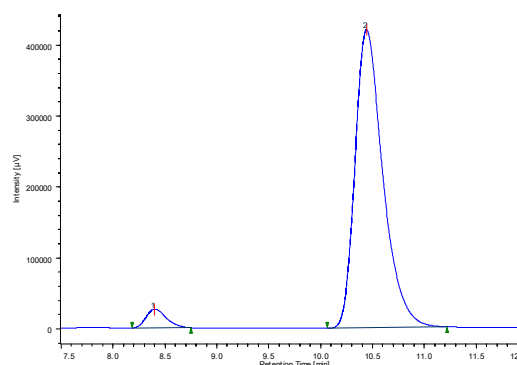
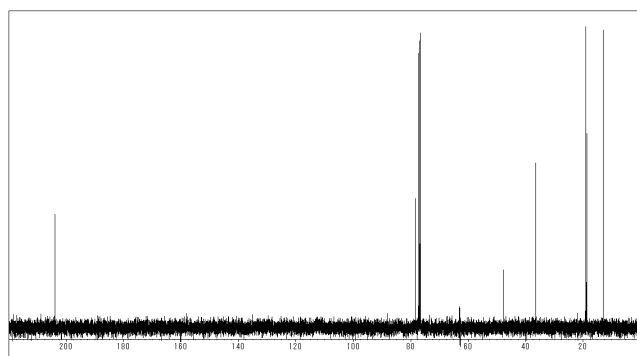
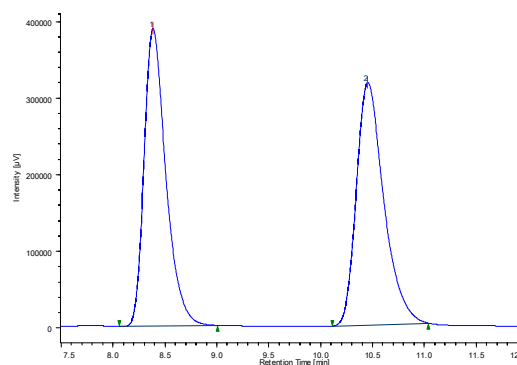
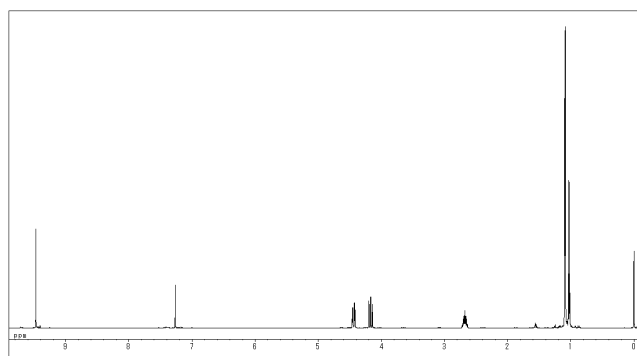


2,2,3-Trimethyl-4-nitrobutanal (3p)

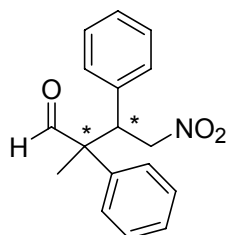


The enantioselectivity was determined by HPLC analysis [91% ee, DAICEL CHIRALCEL OD-H, 20% isopropanol/hexane, 1.0 mL/min, 209 nm; t_r (major enantiomer) = 10.5 min, t_r (minor enantiomer) = 8.4 min].

$[\alpha]_{26}^D = -20.0^\circ$ ($c = 1.0$, CHCl_3), colorless oil, $\delta_{\text{H}}(\text{CDCl}_3)$ 1.03 (3H, d, J 6.8 Hz), 1.09 (3H, s), 1.10 (3H, s), 2.65-2.71 (1H, m), 4.17 (1H, dd, J 10.2, 12.2 Hz), 4.44 (1H, dd, J 3.9, 12.2 Hz), 9.47 (1H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 12.9, 18.7, 19.1, 36.5, 47.6, 78.3, 203.9; $\nu(\text{neat})/\text{cm}^{-1}$ 2977, 2942, 2883, 2820, 2716, 1725, 1556, 1469, 1436, 1380, 1241, 1128, 1050, 885, 847, 778, 717.

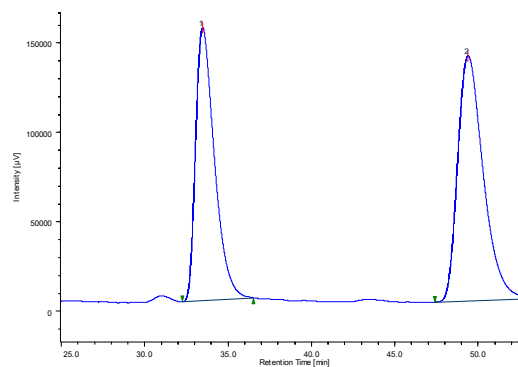
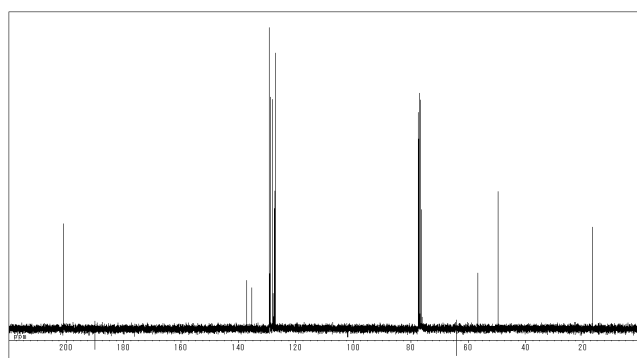
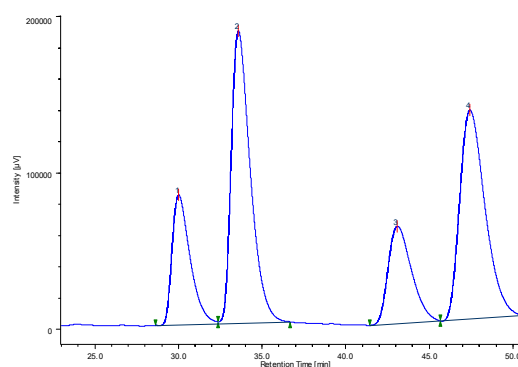
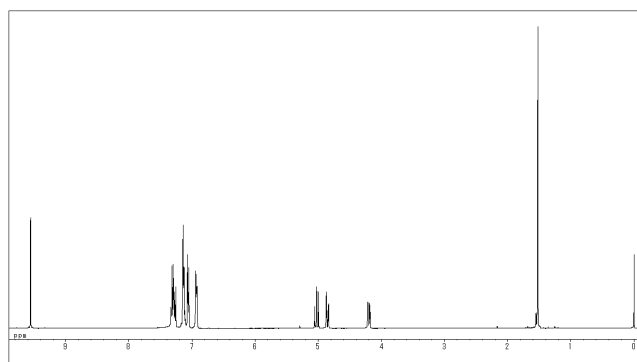


2-Methyl-4-nitro-2,3-diphenylbutanal (**3q**)^{2a}

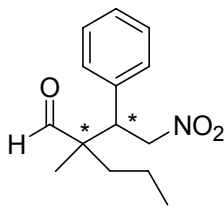


The enantioselectivity was determined by HPLC analysis [10% ee, DAICEL CHIRALCEL OD-H, 2% isopropanol/hexanes, 1.2 mL/min, 209 nm; t_r (major enantiomer, anti) = 30.0 min, t_r (minor enantiomer, syn) = 33.6 min, t_r (minor enantiomer, anti) = 43.1 min, t_r (major enantiomer, syn) = 47.4 min]. white solid, Mp. 98-100 °C, Characterization data for syn

isomer: δ_H (CDCl₃): 1.52 (3H, s), 4.20 (1H, dd, J 3.9, 11.2 Hz), 4.86 (1H, dd, J 3.9, 13.1 Hz), 5.03 (1H, dd, J 11.2, 13.1 Hz), 6.92-6.94 (2H, m), 7.05-7.07 (2H, m), 7.10-7.14 (3H, m), 7.25-7.33 (3H, m), 9.56 (1H, s); δ_C (CDCl₃) 16.7, 49.6, 56.6, 76.1, 127.2, 127.6, 128.0, 128.1, 129.0, 129.2, 135.3, 137.2, 201.0; ν (KBr)/cm⁻¹ 3086, 3065, 3028, 3000, 2980, 2921, 2827, 2724, 1962, 1886, 1811, 1718, 1600, 1557, 1494, 1455, 1430, 1379, 1205, 1097, 1078, 1029, 1003, 992, 919, 903, 865, 783, 747, 700.

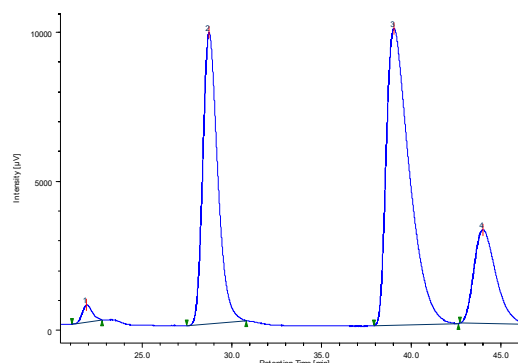
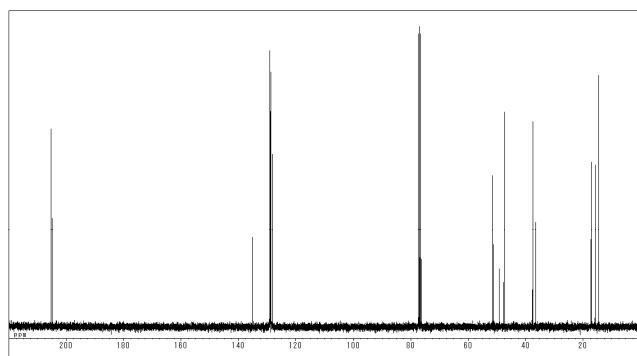
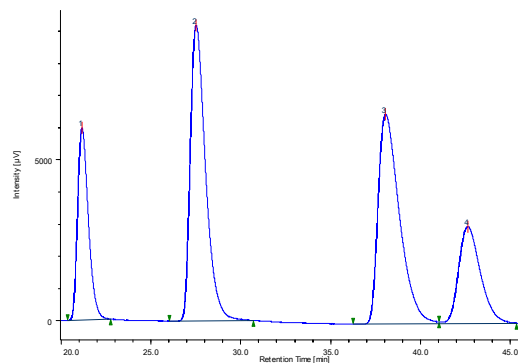
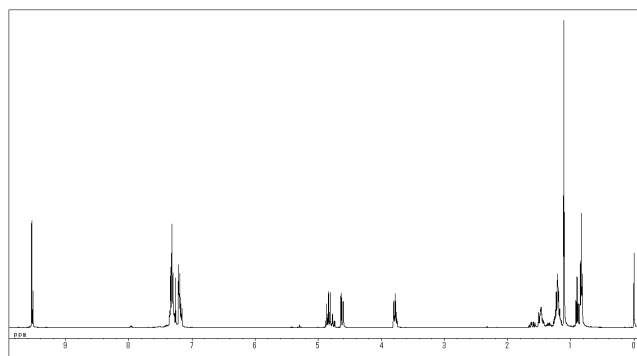


2-Methyl-2-(2-nitro-1-phenylethyl)pentanal (**3r**)^{1c,d}

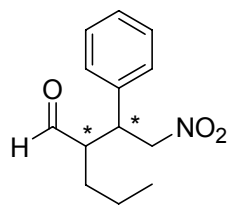


The enantioselectivity was determined by HPLC analysis [22% ee, DAICEL CHIRALCEL OD-H, 4% isopropanol/hexanes, 1.0 mL/min, 254 nm; t_r (minor enantiomer, anti) = 21.9 min, t_r (minor enantiomer, syn) = 28.7 min, t_r (major enantiomer, syn) = 39.0 min, t_r (major enantiomer, anti) = 44.0 min]. light yellow oil, δ_H (CDCl₃): 0.84 (syn) and 0.90 (anti) (3H, t, J

6.8 Hz), 1.10 (anti) and 1.11 (syn) (3H, s), 1.15-1.66 (syn and anti) (4H, m), 3.77 (anti) and 3.79 (syn) (1H, dd, J 4.4, 11.2 and 3.9, 11.7 Hz), 4.62 (syn) and 4.76 (anti) (1H, dd, J 3.9, 13.2 and 4.4, 12.7 Hz), 4.84 (syn) and 4.85 (anti) (1H, dd, J 11.7, 13.2 and 11.2, 12.7 Hz), 7.16-7.21 (syn and anti) (2H, m), 7.28-7.35 (syn and anti) (3H, m), 9.52 (anti) and 9.54 (syn) (1H, s); δ_C (CDCl₃) 14.4 (syn), 14.6 (anti), 15.7 (syn), 17.0 (syn), 17.1 (anti), 17.3 (anti), 36.5 (anti), 37.5 (syn), 47.5 (syn), 49.1 (anti), 51.0 (anti), 51.6 (syn), 76.2 (anti), 76.7 (syn), 128.10 (syn), 128.13 (anti), 128.7 (syn and anti), 129.0 (anti), 129.1 (syn), 205.0 (anti), 205.4 (syn); ν (neat)/cm⁻¹ 3064, 3032, 2962, 2935, 2874, 2720, 1730, 1603, 1555, 1497, 1455, 1379, 1205, 1092, 1033, 1005, 982, 913, 851, 798, 751, 704.

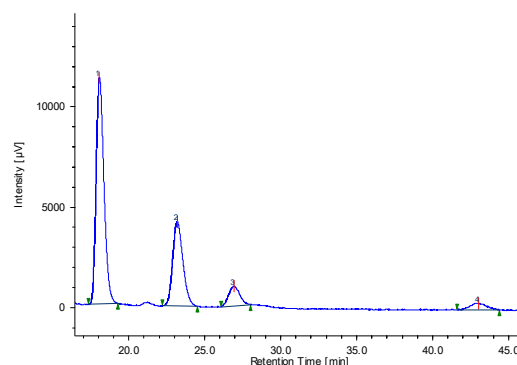
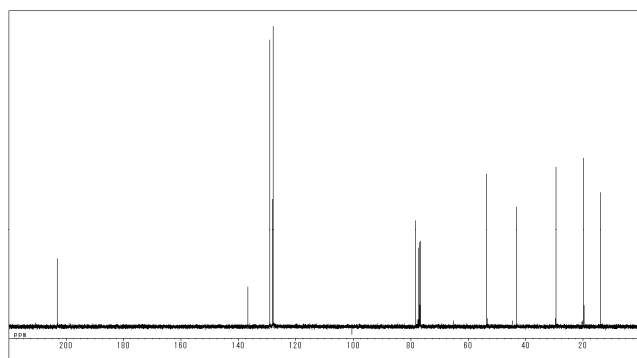
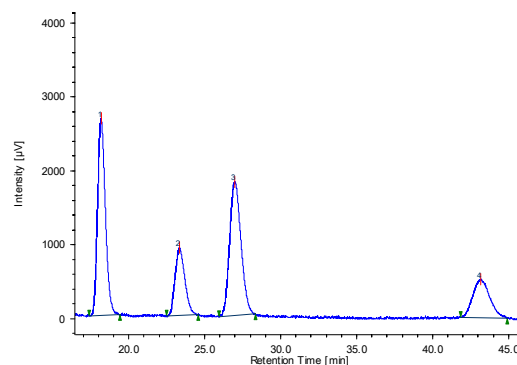
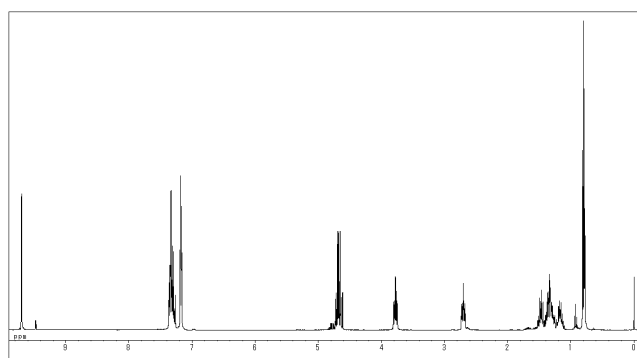


2-(2-nitro-1-phenylethyl)pentanal (3s)⁴

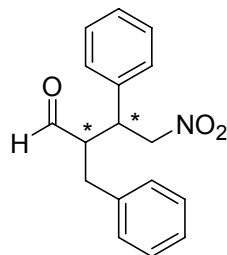


The enantioselectivity was determined by HPLC analysis [78% ee, DAICEL CHIRALCEL OD-H, 15% isopropanol/hexanes, 1.0 mL/min, 254 nm; t_r (major enantiomer, syn) = 18.1 min, t_r (major enantiomer, anti) = 23.2 min, t_r (minor enantiomer, syn) = 26.9 min, t_r (minor enantiomer, anti) = 43.0 min]. colorless oil, δ_H (CDCl₃): 0.80 (syn) and 0.93 (anti) (3H, t,

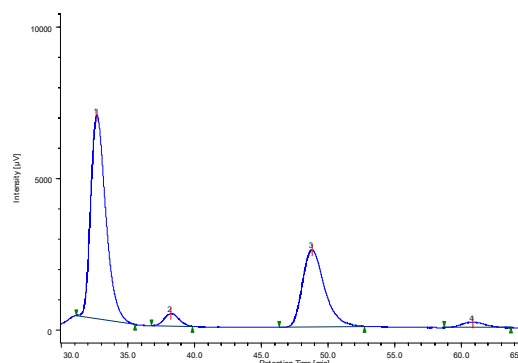
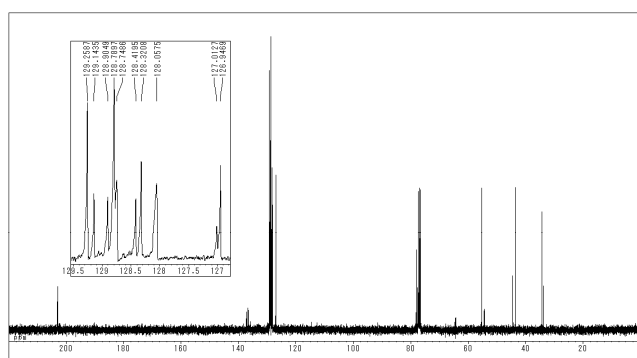
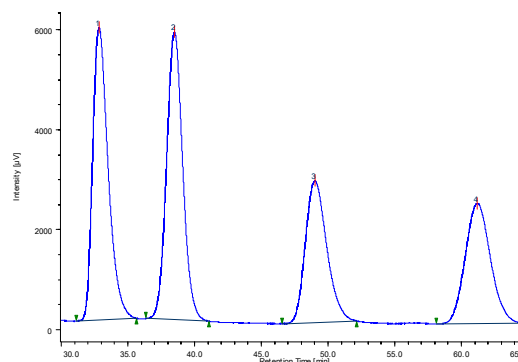
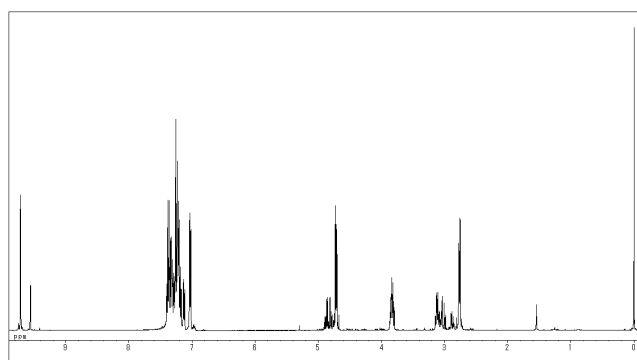
J 6.2 Hz), 1.11-1.74 (syn and anti) (4H, m), 2.60-2.66 (anti) and 2.67-2.74 (syn) (1H, m), 3.75-3.83 (syn and anti) (1H, m), 4.65 (syn) and 4.75 (anti) (1H, dd, J 9.6, 12.7 and 9.1, 13.0 Hz), 4.71 (syn) and 4.82 (anti) (1H, dd, J 4.5, 12.7 and 6.2, 13.0 Hz), 7.16-7.19 (syn and anti) (2H, m), 7.26-7.37 (syn and anti) (3H, m), 9.48 (anti) and 9.71 (syn) (1H, d, J 3.1 and 3.0 Hz); δ_C (CDCl₃) 13.90 (syn), 13.95 (anti), 19.7 (syn), 20.3 (anti), 29.4 (syn), 29.6 (anti), 43.1 (syn), 44.4 (anti), 53.2 (anti), 53.8 (syn), 77.8 (anti), 78.4 (syn), 128.0 (syn), 128.1 (syn), 128.17 (anti), 128.19 (anti), 129.05 (anti), 129.08 (syn), 136.2 (anti), 136.7 (syn), 203.2 (anti), 203.3 (syn); ν (neat)/cm⁻¹ 3064, 3032, 2961, 2931, 2873, 2729, 1723, 1604, 1555, 1496, 1455, 1434, 1380, 1203, 1119, 1090, 990, 913, 844, 763, 703.



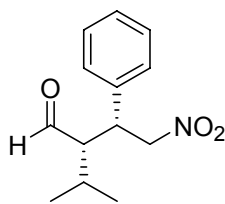
2-Methyl-2-(2-nitro-1-phenylethyl)pentanal (3t)⁵



The enantioselectivity was determined by HPLC analysis [89% ee, DAICEL CHIRALCEL OD-H, 20% isopropanol/hexanes, 1.0 mL/min, 254 nm; t_r (major enantiomer, syn) = 32.7 min, t_r (major enantiomer, anti) = 38.2 min, t_r (minor enantiomer, syn) = 48.8 min, t_r (minor enantiomer, anti) = 60.8 min]. yellow oil, δ_H (CDCl₃): 2.73-3.15 (syn and anti) (4H, m), 3.80-3.87 (syn and anti) (1H, m), 4.70 (syn) and 4.74 (anti) (2H, dd, J 8.5, 12.7 and 6.1, 12.7 Hz), 6.97-6.98 (syn) and 7.02-7.40 (syn and anti) (10H, m), 9.56 (anti) and 9.71 (syn) (1H, d, J 2.0 and 2.4 Hz); δ_C (CDCl₃) 33.6 (anti), 34.2 (syn), 43.4 (syn), 44.4 (anti), 54.4 (anti), 55.3 (syn), 77.6 (anti), 78.0 (syn), [(126.9, 127.0, 128.1, 128.3, 128.4, 128.7, 128.8, 128.9, 129.1, 129.3, 136.7, 137.2) (syn and anti)], 203.0 (syn), 203.1 (anti); ν (neat)/cm⁻¹ 3063, 3030, 2920, 2848, 2736, 1724, 1603, 1555, 1496, 1455, 1434, 1380, 1202, 1089, 1031, 913, 848, 759, 701.

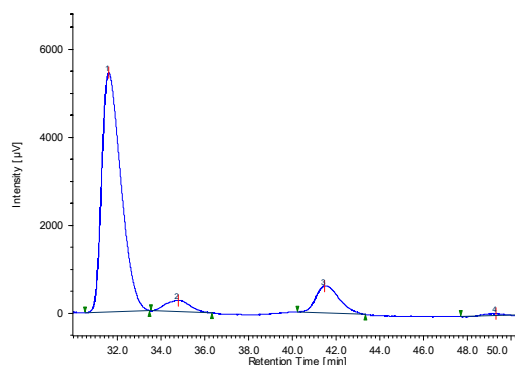
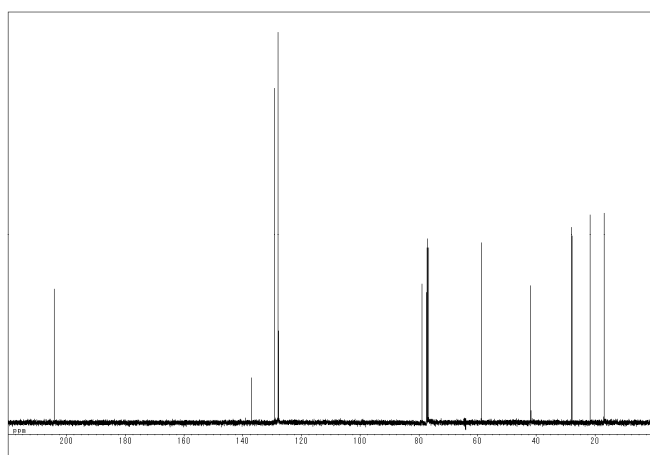
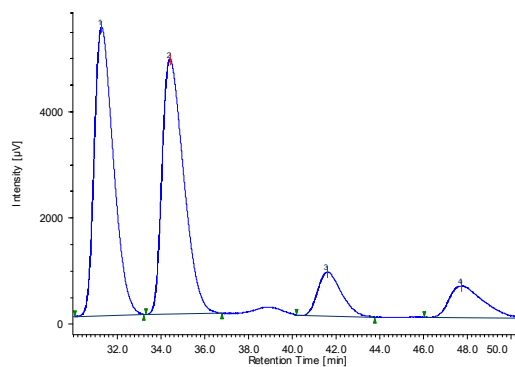
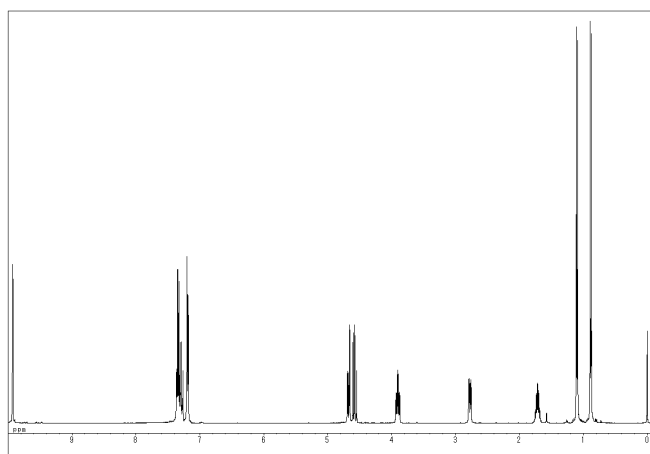


(2*S*,3*R*)-2-(Prop-2-yl)-3-phenylbutanal (3u)



The enantioselectivity was determined by HPLC analysis [89% ee, DAICEL CHIRALPAK AS-H, 1% isopropanol/hexanes, 1.2 mL/min, 254 nm; t_r (major enantiomer, syn) = 31.6 min, t_r (minor enantiomer, syn) = 34.8 min, t_r (major enantiomer, anti) = 41.5 min, t_r (minor enantiomer, anti) = 49.3 min]. The absolute configuration was determined by

comparison of the optical rotation with that of the literature.^{2a} $[\alpha]^{22}_D = -41.9^\circ$ ($c = 0.8$, CHCl_3), light yellow oil, Characterization data for syn isomer: $\delta_H(\text{CDCl}_3)$: 0.88 (3H, d, J 6.8 Hz), 1.10 (3H, d, J 7.3 Hz), 1.68-1.76 (1H, m), 2.75-2.80 (1H, m), 3.87-3.93 (1H, m), 4.57 (1H, dd, J 10.2, 12.7 Hz), 4.67 (1H, dd, J 4.4, 12.7 Hz), 7.18-7.20 (2H, m), 7.27-7.36 (3H, m), 9.93 (1H, d, J 2.4 Hz); $\delta_C(\text{CDCl}_3)$ 16.9, 21.6, 27.9, 41.9, 58.7, 79.0, 127.9, 128.1, 129.1, 137.0, 204.3; $\nu(\text{neat})/\text{cm}^{-1}$ 3058, 3031, 2964, 2921, 2875, 2742, 1717, 1604, 1553, 1496, 1456, 1432, 1379, 1241, 1206, 1144, 1110, 1073, 1031, 994, 913, 815, 760, 703.



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