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Supporting Information

New boro amino amide organocatalysts for asymmetric cross Aldol reaction of ketones with carbonyl compounds

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1. General Information

Reagents and dry solvents were of the commercially available maximum grade and used without further purification. Reactions were performed out under an inert atmosphere in flame dried and cooled glassware. The reaction was monitored by thin layer chromatography (TLC) using Merck silica plate gel 60 F_{254} aluminum sheet. Also, the purifications of products were confirmed using column chromatography techniques in silica gel 60 N (40–50 µm) purchased from Kanto Chemical Company. Visualization of the products was confirmed by ultraviolet light, iodine vapor and ninhydrin stain. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500 (^{1}H for 500 MHz and ^{13}C for 125 MHz). All spectra were recorded at 21 °C. Chemical shifts (δ) are reported in parts per million (ppm) relative to the signals of tetramethylsilane (TMS) using the residual solvents signals. Report data for ^{1}H NMR spectroscopy are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet and br = broad, coupling constants (J) and assimilation were measured in hertz (Hz). Optical rotation measured by JASCO DIP-360 polarimeter. The melting point were measured using a Yanaco micro melting point apparatus. High resolution mass spectra (HRMS) data were collected by electron impact (EI) using Hitachi RMG-GMG and JEOL JNK-DX303 sector instruments. The result values were determined for enantiomeric excess (*ee*) using high pressure liquid chromatography (HPLC) principle by DAICEL CHIRALPAK AD-H, OD-H, AS-H column.

2. Experimental procedure

2.1 General procedure for the synthesis of boro amino amide organocatalysts 4a, 4b-g, 4h

To a solution of Fmoc-t-Leucine **1a,** *N*-Boc amino acids **1b-f ,** *N*-Boc-L-Proline **1g** (1.0 mmol) respectively, HATU (1.2 mmol) and DIPEA (1.5 mmol) were added in dry DMF and stirred for 15min. The corresponding 2-pinacolyl boro phenyl amine **2a**,2-pinenyl boro phenyl amine **2b** (1.0 mmol) respectively were added slowly and the reaction mixture was gradually allowed to stir from 0 °C to 30 °C until the reaction completion. After the reaction was completed, as monitored by TLC, reaction mixture was diluted with water, the crude products were extracted with $CHCl_3$, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the corresponding N-protected boro amino amides **3a, 3b-g**.

(4a)

To a solution of **3a** (1.0 mmol) in acetonitrile was added 20% piperidine in DMF (5V) at 0 °C and the reaction mixture was gradually allowed to stir from 0 °C to 30 °C until the reaction completion. After the reaction was completed, as monitored by TLC, the solvent was removed under a reduced pressure and the obtained residue was subjected to flash column chromatography to afford the compound **4a**.

(4b-g)

To a solution of **3b-g** in dry CH_2Cl_2, TFA was added dropwise over a period of times (v/v) at 0 °C and successively stirred at room temperature (r.t.) for 4 h. After the reaction completion, CH_2Cl_2 and TFA were removed under a reduced pressure, the residue was basified by drop-wise addition of saturated $NaHCO_3$ solution at 0 °C and stirred for 1 hour at r.t.. The crude products were extracted with $CHCl_3$, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the corresponding boro amino amides **4b-g**.

(4h)

To a solution of **4b** (1.0 mmol) in acetonitrile was added K_2CO_3 (2.0 mmol) and methyl Iodide (1.2

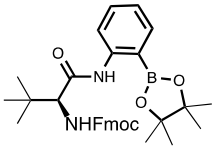
mmol) and the reaction was stirred at reflux condition until the reaction completion. After the reaction completion as monitored by T.L.C., the solvent was removed under a reduced pressure, the crude residue was diluted with water and extracted with $CHCl_3$, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the corresponding methylated boro amino amide **4h.**

2.2 General procedure for the asymmetric aldol reaction of various ketones with aromatic aldehydes

The boro amino amide catalyst **4b** (10 mol%) and benzoic acid (20 mol%) were added to a solution of ketones (0.4 mmol) and the aldehydes (0.1 mmol) under the sea water and tap water (1:1) as solvent reaction condition. The reaction mixture was stirred at 25 °C for appropriate time until the reaction completion, monitored by thin layer chromatography (TLC). The reaction mixture was directly purified by flash column chromatography on SiO_2 (*n*-hexane/CH_3CO_2Et) to afford the corresponding aldol products. The compounds are the known compounds and the structures were identified by spectral data which were in good agreement with those reported. The enantiomeric excess (*ee*) was determined using high pressure liquid chromatography (HPLC) principle by DAICEL CHIRALPAK AD-H, AS-H, OD-H columns.[11]

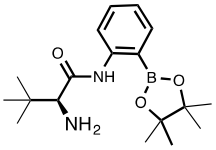
3. Experimental Data

(S)-2-AminoFmoc-N-(-pinacol phenyl boronate)-3,3-dimethylbutanamide (3a)



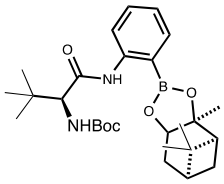
Colorless solid; 88% yield; mp 72-76 °C; $[\alpha]_D^{20}$ = -35.80 (c = 0.1, $CHCl_3$); IR (neat) 3362, 2972, 1614, 1581, 1447, 1351, 1140, 1119, 1072, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.55 (s, 1H), 8.52 (d, *J* = 8.6 Hz, 1H), 7.80-7.70 (m, 4H), 7.64-7.54 (m, 2H), 7.51-7.45 (m, 1H), 7.42-7.35 (m, 2H), 7.33-7.27 (m, 1H), 7.13-7.05 (m, 1H), 5.71 (d, *J* = 5.7 Hz, 1H), 4.47-4.39 (m, 1H), 4.38-4.29 (m, 1H), 4.27-4.20 (m, 1H), 4.02 (d, *J* = 9.2 Hz, 1H), 1.36 (d, *J* = 5.1Hz, 12H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 169.2, 156.4, 143.9, 143.5, 141.7, 136.8, 136.6, 133.3, 132.9, 127.8, 127.1, 125.3, 123.3, 120.2, 118.8, 84.7, 66.9, 64.2, 46.4, 35.4, 26.9, 25.03, 25.0, 24.8. MS (EI) *m/z* : 554 $[M]^+$, HRMS m/z: [EI] calculated for $C_{33}H_{39}BN_2O_5$ $[M]^+$: 554.2952; found 554.2944.

(S)-2-Amino-N-(-pinacol phenyl boronate)-3,3-dimethylbutanamide (4a)



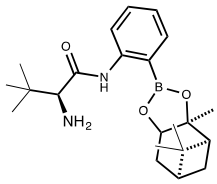
viscous liquid; 55% yield; $[\alpha]_D^{20}$ = -45.80 (c = 0.10, $CHCl_3$); IR (neat) 2971, 2360, 1607, 1445, 1152, 1021, 753cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.43 (s, 1H), 7.14-7.05 (m, 1H), 7.03-6.97 (m, 1H), 6.95-6.89 (m, 1H), 6.86-6.80 (m, 1H), 3.35 (s, 1H), 1.23 (s, 12H), 1.07 (s, 9H) ; ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.9, 143.6, 136.0, 132.3, 123.5, 118.8, 83.9, 75.2, 66.0, 34.7, 26.8, 25.1, 24.9; MS (EI): m/z = 332 $[M]^+$, HRMS m/z: [EI] calculated for $C_{18}H_{29}BN_2O_3$ $[M]^+$: 332.2271; found 332.2272.

(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide (3b)



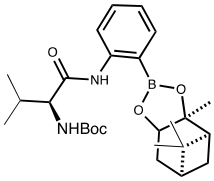
transparent liquid; 91% yield; mp 153 °C; $[\alpha]_D^{20}$ = -22.80 (c = 0.10, $CHCl_3$) ; IR (neat) 3367, 2966, 1692, 1478, 1447, 1357, 1342, 1162, 1055, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.42 (s, 1H), 8.44 (d, *J* = 8.59 Hz, 1H), 7.87-7.74 (m, 1H), 7.46-7.43 (m, 1H), 7.12-7.06 (m, 1H), 5.38 (d, *J* = 14.89 Hz, 1H), 4.52-4.42 (m, 1H), 3.93 (d, *J* = 9.16 Hz, 1H), 2.47-2.37 (m, 1H), 2.32-2.11 (m, 2H), 2.04-1.89 (m, 2H), 1.52 (s, 3H), 1.42 (s, 9H), 1.31 (s, 3H), 1.18-1.12 (m, 1H), 1.06 (s, 9H), 0.89 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 169.6, 155.8, 144.0, 136.4, 132.9, 123.3, 119.4, 87.5, 79.7, 78.2, 63.9, 51.4, 39.5, 38.4, 35.6, 33.4, 31.6, 28.8, 28.4, 27.1, 26.8, 26.5, 24.1, 22.7, 14.2; MS (EI): m/z = 484 $[M]^+$, HRMS m/z: [EI] calculated for $C_{27}H_{41}BN_2O_5$ $[M]^+$: 484.3109; found 484.3107.

(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide (4b)



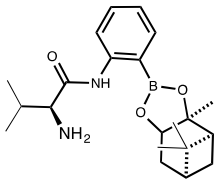
Colorless solid; 80% yield; mp 50-53 °C; $[\alpha]_D^{20}$ = -34.80 (c = 0.40, $CHCl_3$) ; IR (neat) 3674, 2925, 2359, 1632, 1600, 1480, 1447, 1370, 1166, 1054, 1033 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.49 (d, *J* = 8.59 Hz, 1H), 7.79-7.74 (m, 1H), 7.45-7.42 (m, 1H), 7.11-7.03 (m, 1H), 4.51-4.43 (m, 1H), 3.14 (s, 1H), 2.46-2.37 (m, 1H), 2.23-2.10 (m, 2H), 2.05-1.90 (m, 2H), 1.50 (s, 3H), 1.31 (s, 3H), 1.24-1.21 (m, 1H), 1.03 (s, 9H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 181.1, 172.9, 144.4, 136.4, 133.2, 123.8, 119.1, 86.9, 78.1, 65.6, 51.6, 39.6, 38.2, 35.5, 35.0, 28.8, 27.1, 26.9, 26.5, 23.8; MS (EI): m/z = 385 $[M+H]^+$ HRMS m/z: [EI] calculated for $C_{22}H_{33}BN_2O_3$ $[M]^+$: 384.2584 found $[M+1]^+$: 385.2659.

(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3-methyl butanamide (3c)



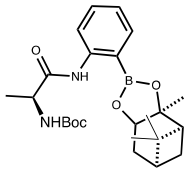
transparent liquid; 89% yield; mp 153 °C; $[\alpha]_D^{20}$ = -36.80 (c = 0.40, $CHCl_3$) ; IR (neat) 3346, 2928, 1688, 1613, 1480, 1447, 1343, 1159, 1076, 1041, 761 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.56 (s, 1H), 8.51-8.41 (m, 1H), 7.78 (d, *J* = 6.30 Hz, 1H), 7.51-7.39 (m, 1H), 7.14-7.04 (m, 1H), 5.19 (d, *J* = 8.59 Hz, 1H), 4.49 (d, *J* = 8.02 Hz, 1H), 4.20-4.08 (m, 1H), 2.47-2.41 (m, 1H), 2.33-2.16 (m, 2H), 2.03-1.91 (m, 2H), 1.59-1.57 (m, 1H), 1.52 (s, 3H), 1.49 (s, 9H), 1.32 (s, 3H), 1.20-1.13 (m, 1H), 1.00 (d, *J* = 6.87 Hz, 3H), 0.93 (d, *J* = 6.87 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 169.9, 155.8, 144.2, 136.6, 133.0, 123.3, 119.0, 87.2, 79.8, 78.2, 61.0, 51.5, 39.8, 38.4, 35.7, 31.7, 28.8, 28.3, 27.1, 26.5, 24.3, 19.3, 17.6; MS (EI): m/z = 470 $[M]^+$, HRMS m/z: [EI] calculated for $C_{26}H_{39}BN_2O_5$ $[M]^+$: 470.2952; found 470.2947.

(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3-methyl butanamide (4c)



transparent liquid; 80% yield; mp 153 °C; $[\alpha]_D^{20}$ = -54.80 (c = 0.10, $CHCl_3$); IR (neat) 3273, 2960, 2922, 2869, 1479, 1447, 1357, 1166, 1076, 1051, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.37-8.29 (m, 1H), 7.80-7.70 (m, 1H), 7.46-7.39 (m, 1H), 7.13-7.04 (m, 1H), 4.46 (d, *J* = 10.31 Hz, 1H), 3.34 (d, *J* = 4.01 Hz, 1H), 2.47-2.36 (m, 1H), 2.34-2.27 (m, 1H), 2.26-2.17 (m, 1H), 2.15-2.11 (m, 1H), 2.03-1.88 (m, 2H), 1.49 (s, 3H), 1.30 (s, 3H), 1.02 (d, *J* = 6.87 Hz, 3H), 1.24-1.22 (m, 1H), 0.93-0.83 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.8, 136.1, 132.1, 123.1, 119.3, 87.1, 78.2, 61.4, 51.3, 39.5, 38.1, 36.2, 31.6, 28.9, 27.3, 26.5, 24.1, 19.8, 16.5; MS (EI): m/z = 370 $[M]^+$, HRMS m/z: [EI] calculated for $C_{21}H_{31}BN_2O_3$ $[M]^+$: 370.2428; found 370.2430.

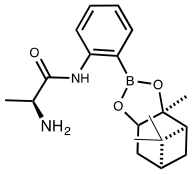
(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)- propenamide (3d)



white solid; 88% yield; mp 62-64 °C; $[\alpha]_D^{20}$ = -37.80 (c = 0.10, $CHCl_3$); IR (neat) 3334, 2923, 2359, 1693, 1579, 1447, 1344, 1161, 1077, 1040, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.59 (s,

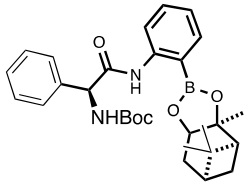
1H), 8.51-8.36 (m, 1H), 7.77 (d, *J* = 7.45 Hz, 1H), 7.47-7.40 (m, 1H), 7.14-6.97 (m, 1H), 5.35-5.16 (m, 1H), 4.49 (d, *J* = 8.59 Hz, 1H), 4.37-4.27 (m, 1H), 2.52-2.37 (m, 1H), 2.29-2.12 (m, 2H), 2.04-1.91 (m, 2H), 1.51 (s, 3H), 1.48-1.44 (m, 12H), 1.31 (s, 3H), 1.18 (d, *J* = 10.88 Hz, 1H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 170.9, 155.2, 144.3, 136.4, 132.9, 123.3, 119.5, 87.1, 79.9, 78.4, 51.2, 39.6, 38.3, 35.5, 28.8, 28.4, 27.0, 26.5, 24.1,19.5; MS (EI): m/z = 442 $[M]^+$, HRMS m/z: [EI] calculated for $C_{24}H_{35}BN_2O_5$ $[M]^+$: 442.2639; found 442.2633.

(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-propanamide (4d)



white solid; 80% yield; mp 109-111 °C; $[\alpha]_D^{20}$ = -34.80 (c = 0.10, $CHCl_3$); IR (neat) 3228, 2980, 2886, 1620, 1482, 1448, 1369, 1166, 1054, 1012 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.32-8.27 (m, 1H), 7.78-7.71 (m, 1H), 7.45-7.37 (m, 1H), 7.10-7.04 (m, 1H), 4.48-4.44 (m, 1H), 3.63-3.53 (m, 1H), 2.46-2.33 (m, 1H), 2.25-2.18 (m, 1H), 2.14-2.07 (m, 1H), 2.02-1.86 (m, 2H), 1.49 (s, 3H), 1.38 (d, *J* = 12.60 Hz, 3H), 1.29 (s, 3H), 1.27-1.23 (m, 1H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.5, 143.4, 135.9, 132.0, 123.2, 119.3, 86.4, 78.1, 52.1, 51.3, 39.6, 38.5, 35.7, 28.9, 27.0, 26.2, 24.1, 21.5; MS (EI): m/z = 342 $[M]^+$, HRMS m/z: [EI] calculated for $C_{19}H_{27}BN_2O_3$ $[M]^+$: 342.2115; found $[M]^+$: 342.2120.

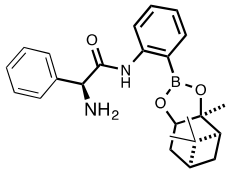
(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-2-phenylethanamide (3e)



Colorless solid. 90% yield; mp 66-68 °C; $[\alpha]_D^{20}$ = +10.20 (c = 0.10, $CHCl_3$) ; IR (neat) 3345, 2932, 1694, 1482, 1447, 1343, 1160, 1076, 1051, 754 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.48 (s, 1H), 8.55-8.45 (m, 1H), 7.78-7.76 (m, 1H), 7.46-7.42 (m, 3H), 7.38-7.32 (m, 3H), 7.09-7.06 (m, 1H), 5.96-5.91 (m, 1H), 5.31-5.18 (m, 1H), 4.49-4.28 (m, 1H), 2.53-2.34 (m, 1H), 2.28-2.11 (m, 2H), 2.00-1.82 (m, 2H), 1.48 (s, 3H), 1.42 (s, 9H), 1.33 (s, 3H), 1.13-1.10 (m, 1H), 0.89 (s, 3H) ; ^{13}C NMR

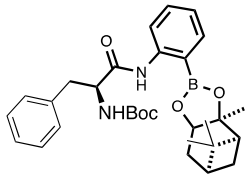
(125 MHz, $CDCl_3$, ppm): δ 168.5, 155.3, 144.3, 136.5, 136.4, 132.9, 129.0, 128.4, 128.3, 127.5, 123.3, 119.2, 87.2, 80.0, 78.3, 59.8, 51.4, 39.6, 39.4, 38.2, 35.4, 35.2, 28.8, 28.6, 28.4, 27.1, 26.7, 26.4, 24.1; MS (EI): m/z = 504 $[M]^+$, HRMS m/z: [EI] calculated for $C_{29}H_{37}BN_2O_5$ $[M]^+$: 504.2796; found 504.2796.

(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-2-phenylethanamide (4e)



pale yellow liquid; 80% yield; mp 153 °C; $[\alpha]_D^{20}$ = +15.20 (c = 0.10, $CHCl_3$); IR (neat) 3286, 2920, 1685, 1607, 1476, 1447, 1344, 1160, 1076, 1040, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.53-8.44 (m, 1H), 7.80-7.74 (m, 1H), 7.52-7.39 (m, 3H), 7.37-7.25 (m, 3H), 7.07-7.02 (m, 1H), 4.63 (s, 1H), 4.42-4.30 (m, 1H), 2.46-2.38 (m, 1H), 2.24-2.11 (m, 2H), 2.04-1.94 (m, 2H), 1.50 (s, 3H), 1.32 (s, 3H), 1.17 (d, *J* = 10.88 Hz, 1H), 0.89 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 171.8, 144.3, 141.1, 136.6, 132.8, 128.9, 128.1, 127.2, 122.9, 119.1, 87.2, 77.9, 61.2, 51.6, 39.4, 38.2, 35.3, 28.6, 27.3, 26.3, 24.1; MS (EI): m/z = 404 $[M]^+$, HRMS m/z: [EI] calculated for $C_{24}H_{29}BN_2O_3$ $[M]^+$: 404.2271; found $[M]^+$: 404.2264.

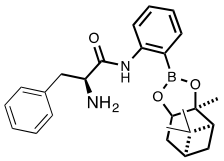
(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3-phenylpropanamide (3f)



transparent liquid; 80% yield; mp 153 °C; $[\alpha]_D^{20}$ = -50.80 (c = 0.10, $CHCl_3$) ; IR (neat) 3296, 2919, 1719, 1657, 1447, 1355, 1159, 1077, 1040, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.59 (s, 1H), 8.51-8.42 (m, 1H), 7.81-7.71 (m, 1H), 7.53-7.38 (m, 1H), 7.32-7.12 (m, 5H), 7.12-7.04 (m, 1H), 5.11-4.98 (m, 1H), 4.60-4.33 (m, 2H), 3.29-3.04 (m, 2H), 2.44-2.30 (m, 1H), 2.25-2.13 (m, 2H), 1.95-1.74 (m, 2H), 1.44 (s, 3H), 1.41 (s, 9H), 1.27 (s, 3H), 1.08 (d, *J* = 10.88 Hz, 1H), 0.86 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 169.6, 155.2, 144.2, 136.4, 136.3, 132.9, 129.5, 128.6, 127.0, 123.3, 119.6, 86.8, 80.1, 78.4, 56.7, 51.2, 39.5, 38.9, 38.2, 35.4, 31.6, 28.6, 28.4, 28.1, 26.9, 26.3,

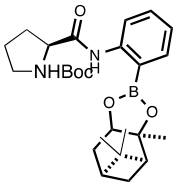
24.0; MS (EI): m/z = 518 $[M]^+$, HRMS m/z: [EI] calculated for $C_{30}H_{39}BN_2O_5$ $[M]^+$: 518.2952; found $[M]^+$: 518.2960.

(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3-phenylpropanamide (4f)



Colorless solid; 80% yield; mp 53-55 °C; $[\alpha]_D^{20}$ = -46.80 (c = 0.10, $CHCl_3$); IR (neat) 3262, 2918, 1676, 1605, 1478, 1447, 1345, 1160, 1076, 1040, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.46 (s, 1H), 8.46-8.38 (m, 1H), 7.80-7.72 (m, 1H), 7.48-7.44 (m, 1H), 7.34-7.29 (m, 2H), 7.27-7.20 (m, 3H), 7.12-7.05 (m, 1H), 4.47-4.40 (m, 1H), 3.77-3.70 (m, 1H), 3.38-3.30 (m, 1H), 2.82-2.76 (m, 1H), 2.46-2.35 (m, 1H), 2.25-2.17 (m, 1H), 2.12-2.07 (m, 1H), 1.97-1.90 (m, 2H), 1.48 (s, 3H), 1.29 (s, 3H), 1.21 (d, *J* = 10.88 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.8, 143.5, 138.1, 136.5, 132.1, 129.3, 128.8, 126.9, 123.1, 119.8, 86.4, 78.3, 57.7, 51.6, 41.5, 39.5, 38.3, 35.2, 29.0, 27.1, 26.4, 24.1; MS (EI): m/z = 418 $[M]^+$,HRMS m/z: [EI] calculated for $C_{25}H_{31}BN_2O_3$ $[M]^+$: 418.2428; found $[M]^+$: 418.2431;

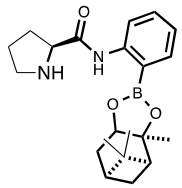
(S)-2-N-Boc pyrrolidine-N-((+)-2,3-pinanediol phenyl boronate)-carboxamide (3g)



transparent liquid; 80% yield; mp 153 °C; $[\alpha]_D^{20}$ = -133.80 (c = 0.10, $CHCl_3$); IR (neat) 3329, 2931, 2868, 1687, 1608, 1475, 1446, 1345, 1158, 1077, 1030, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.88 (s, 1H), 8.66 (d, *J* = 8.59 Hz, 1H), 7.78 (d, *J* = 7.45 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 4.60 (d, *J* = 8.02 Hz, 1H), 4.31-4.21 (m, 4H), 3.63-3.49 (m, 2H), 2.55-2.45 (m, 1H), 2.38-2.28 (m, 1H), 2.28-2.11 (m, 3H), 2.00-1.84 (m, 1H), 1.42 (s, 3H), 1.34 (s, 9H), 1.31 (s, 3H), 1.15 (d, *J* = 10.31 Hz, 1H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.4, 144.3, 136.4, 133.2, 123.3, 118.9, 86.1, 80.9, 78.7, 61.9, 51.3, 47.6, 39.2, 37.7, 35.3, 32.2, 28.9, 28.5, 27.2, 25.8,

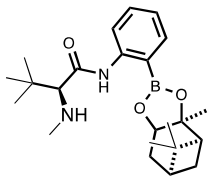
24.0, 23.5; MS (EI): m/z = 468 $[M]^+$, HRMS m/z: [EI] calculated for $C_{26}H_{37}BN_2O_5$ $[M]^+$: 468.2796; found $[M]^+$: 468.2803;

(S)-2-pyrrolidine-N-((+)-2,3-pinanediol phenyl boronate)-carboxamide (4g)



Colorless solid; 80% yield; mp 64-66 °C; $[\alpha]_D^{20}$ = -38.80 (c = 0.10, $CHCl_3$); IR (neat) 3319, 3168, 2917, 1654, 1517, 1447, 1359, 1283, 1078, 1041, 765 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.74 (s, 1H), 8.41 (d, *J* = 8.59 Hz, 1H), 7.80-7.73 (m, 1H), 7.45-7.36 (m, 1H), 7.13-7.02 (m, 1H), 4.52-4.17 (m, 1H), 3.93-3.82 (m, 1H), 3.11-2.95 (m, 2H), 2.48-2.36 (m, 1H), 2.29-2.09 (m, 3H), 2.07-1.89 (m, 3H), 1.85-1.68 (m, 2H), 1.49 (s, 3H), 1.31 (s, 3H), 1.29-1.25 (m, 1H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.6, 143.6, 136.0, 132.0, 123.0, 118.8, 86.3, 78.0, 60.6, 51.7, 47.8, 39.7, 38.3, 35.7, 31.1, 28.9, 27.2, 26.6, 26.2, 24.3; MS (EI): m/z = 368 $[M]^+$, HRMS m/z: [EI] calculated for $C_{21}H_{29}BN_2O_3$ $[M]^+$: 368.2271; found $[M]^+$: 368.2266;

(S)-2-Aminomethyl-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide (4h)

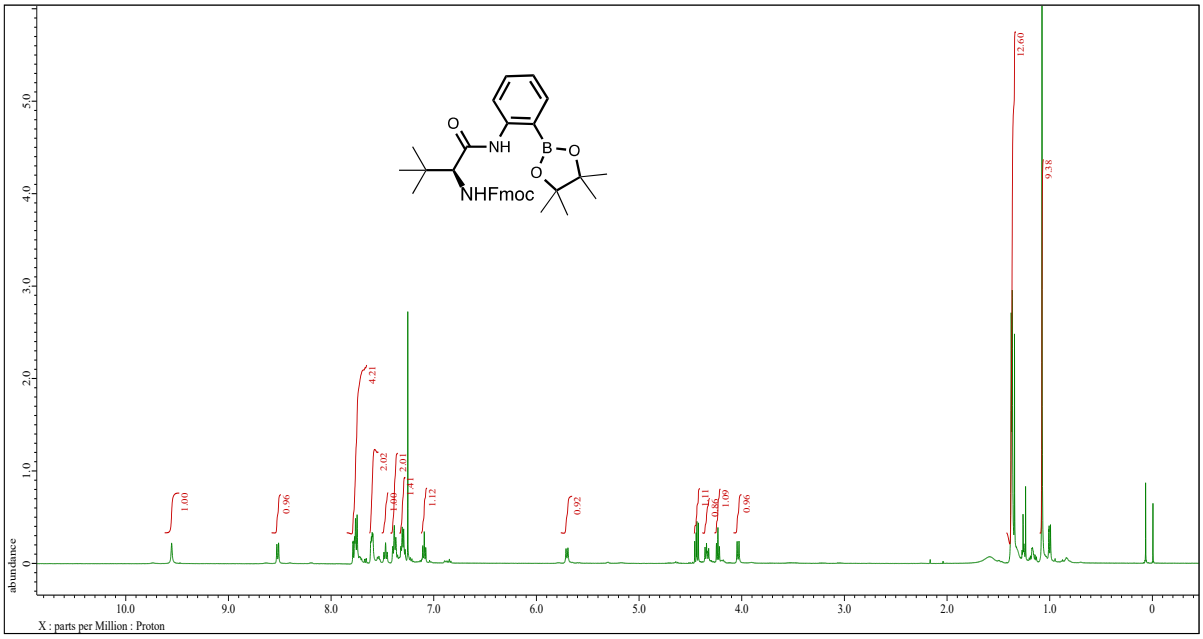


pale liquid; 84% yield; $[\alpha]_D^{20}$ = +80.00 (c = 0.10, $CHCl_3$); IR (neat) 2923, 2868, 1694, 1476, 1446, 1342, 1162, 1119, 1078, 1041, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.2 (s, 1H), 8.57 (d, *J* = 8.59 Hz, 1H), 7.81-7.76 (m, 1H), 7.47-7.40 (m, 1H), 7.11-7.04 (m, 1H), 4.47-4.42 (m, 1H), 2.72 (s, 1H), 2.47-2.39 (m, 1H), 2.37 (s, 3H), 2.26-2.19 (m, 1H), 2.17-2.12 (m, 1H), 2.03-1.92 (m, 2H), 1.56 (s, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 1.24 (d, *J* = 10.88 Hz, 1H), 1.03 (s, 9H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.2, 144.2, 136.2, 132.4, 123.1, 119.1, 86.9, 78.0, 76.2, 51.6, 39.8, 38.3, 36.0, 35.4, 34.0, 29.0, 27.4, 27.2, 26.6, 24.1; MS (EI): m/z = 398 $[M]^+$, HRMS m/z: [EI] calculated for $C_{23}H_{35}BN_2O_3$ $[M]^+$: 398.2741; found $[M]^+$: 398.2741;

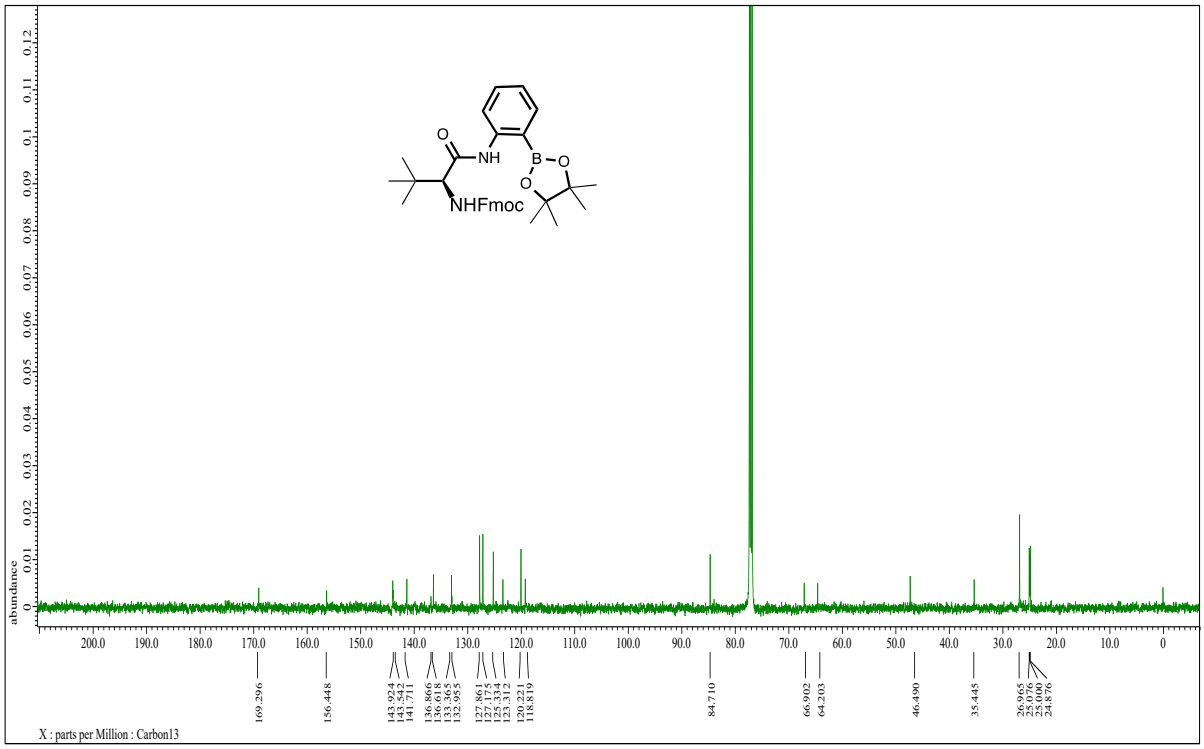
4 ^{1}H NMR and ^{13}C NMR Spectra

(S)-2-AminoFmoc-N-(-pinacol phenyl boronate)-3,3-dimethylbutanamide

^{1}H-NMR

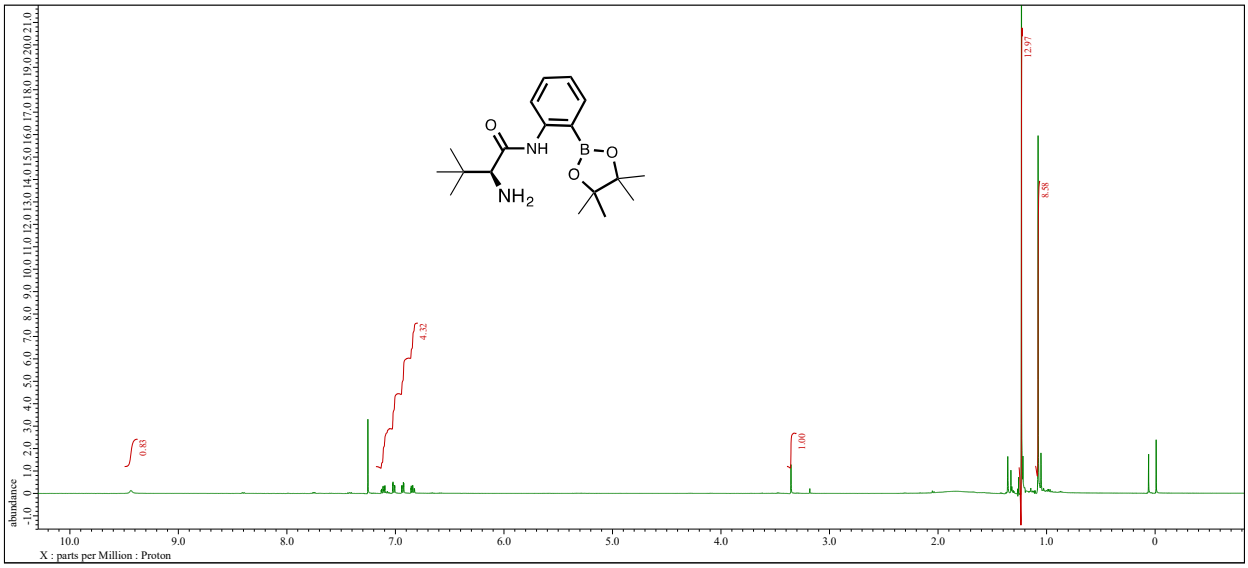


^{13}C-NMR

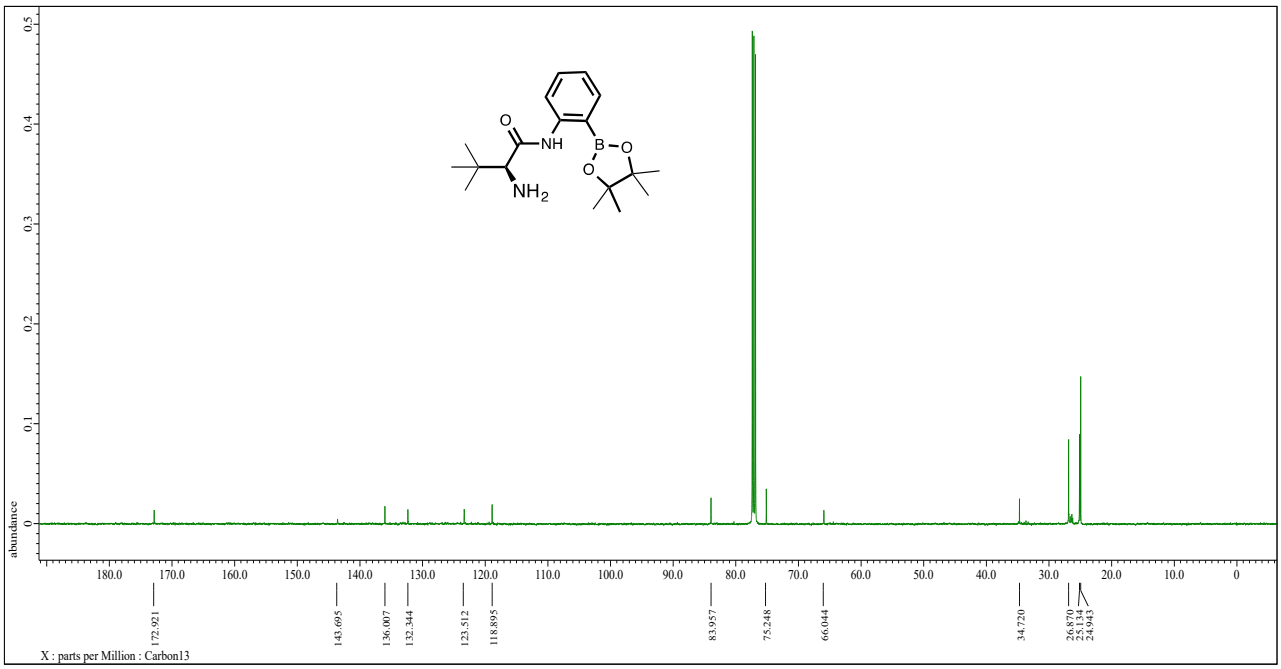


(S)-2-Amino-N-(-pinacol phenyl boronate)-3,3-dimethylbutanamide

^{1}H-NMR

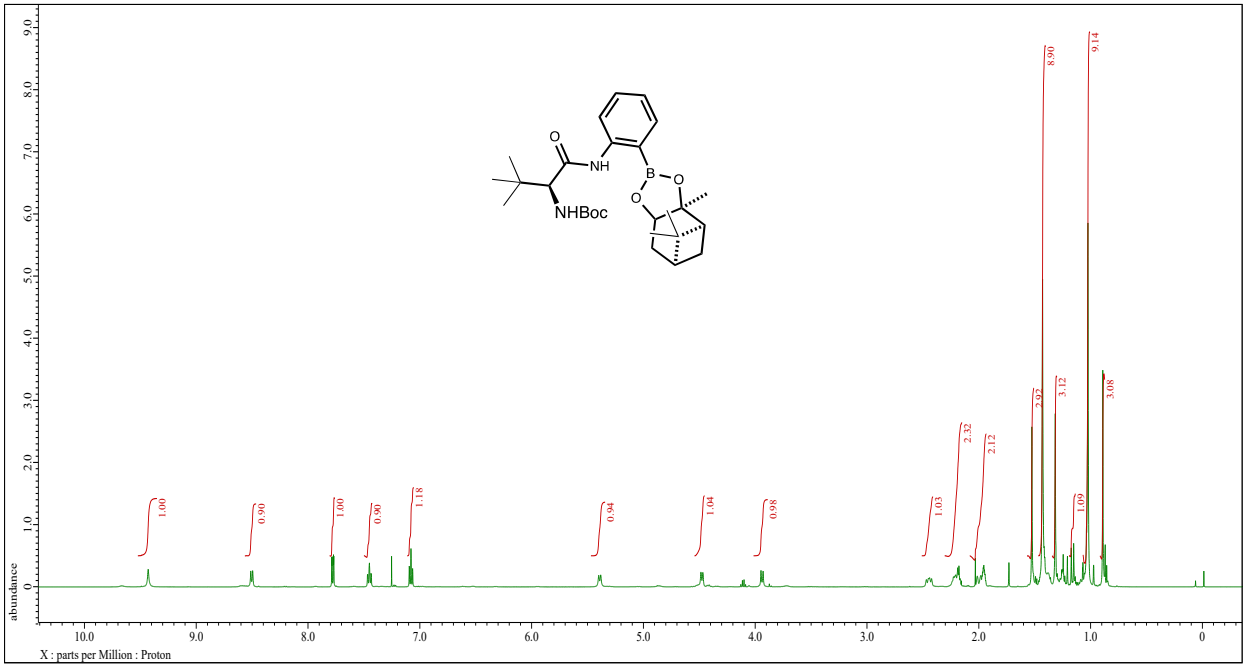


^{13}C-NMR

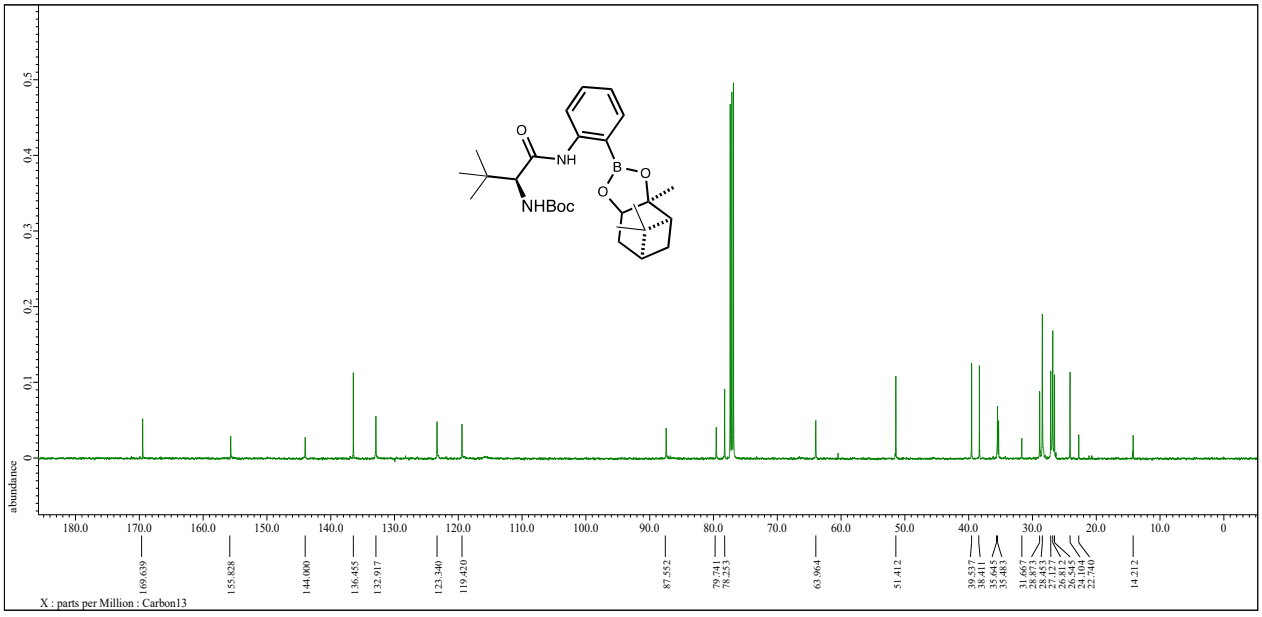


(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide

^{1}H-NMR

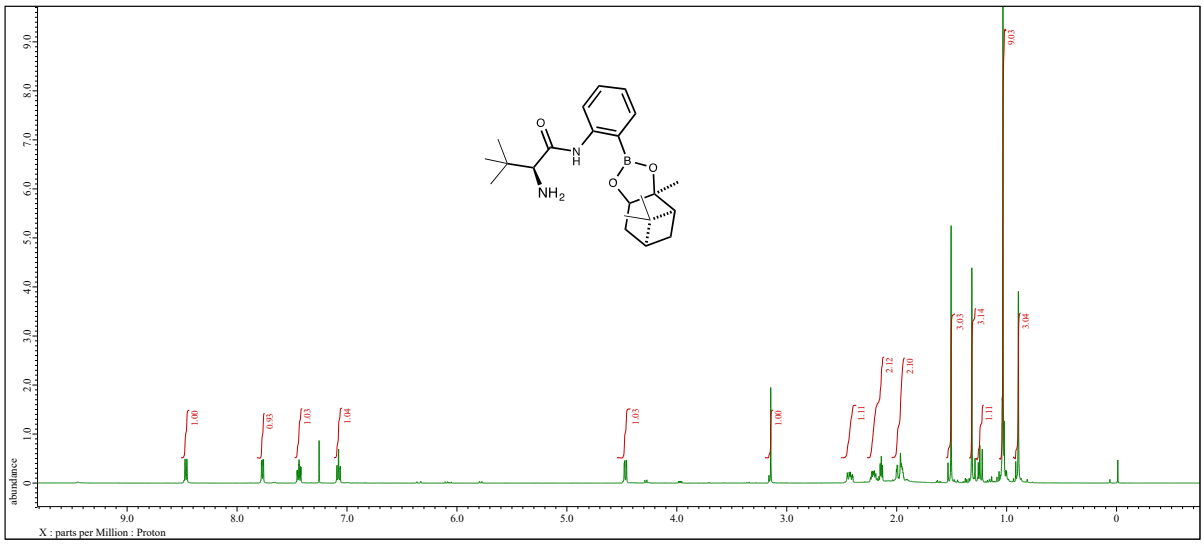


^{13}C-NMR

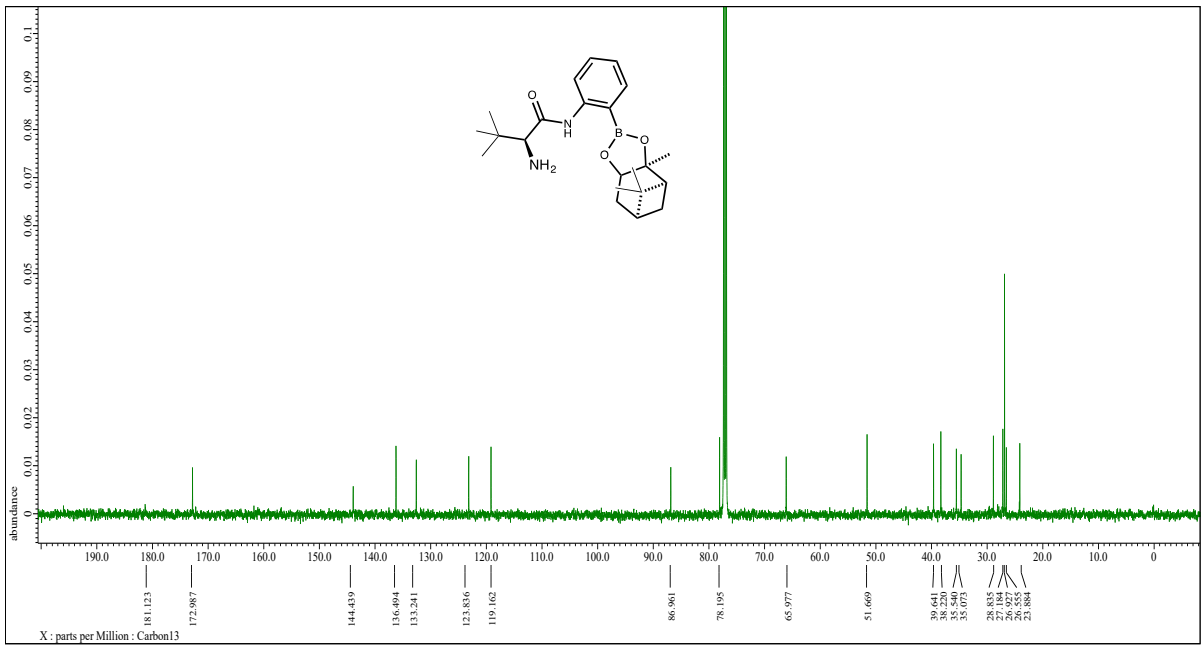


(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide

^{1}H-NMR

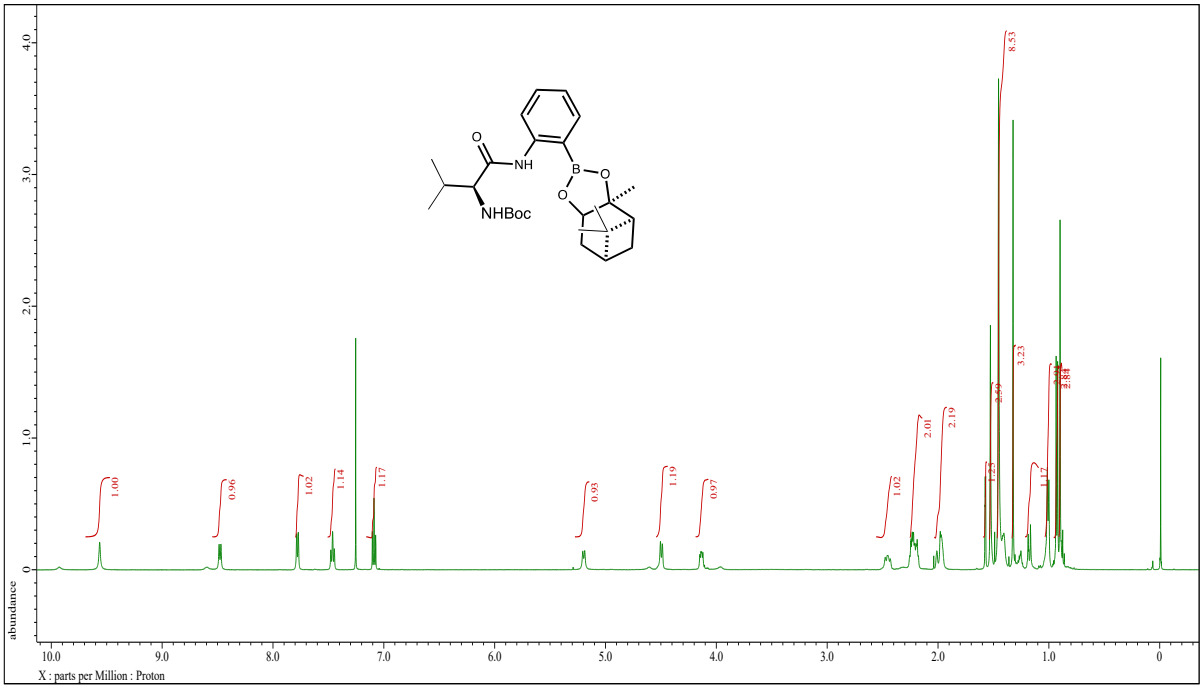


^{13}C-NMR

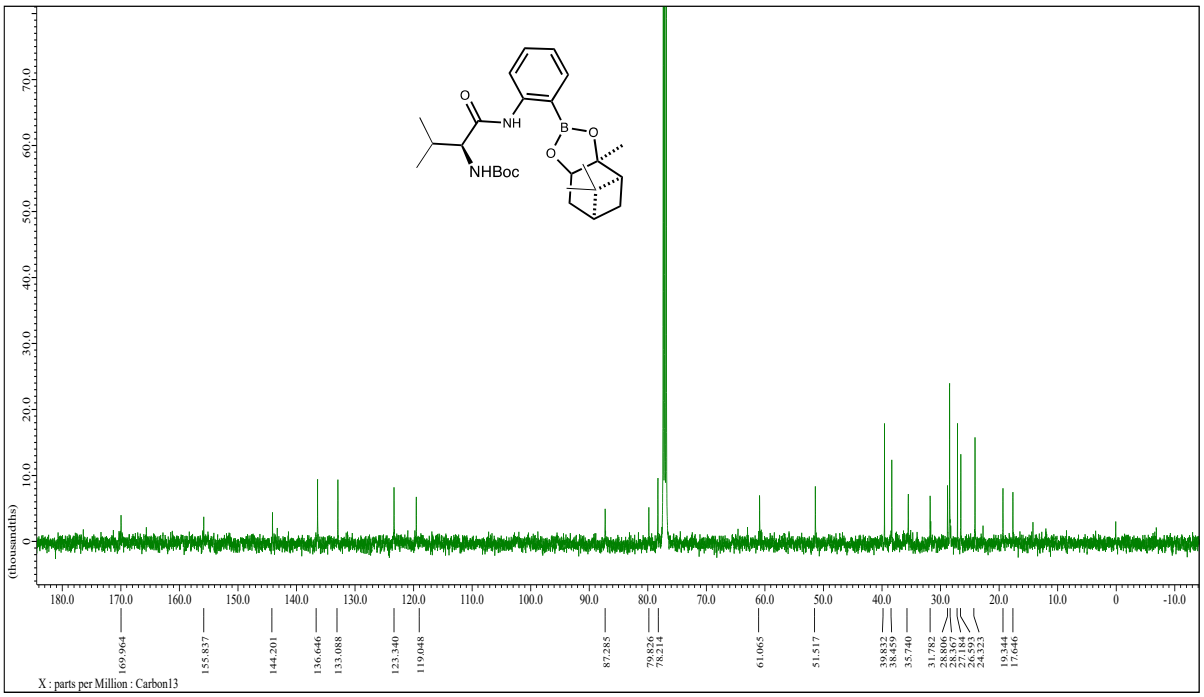


(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3-methyl butanamide

^{1}H-NMR

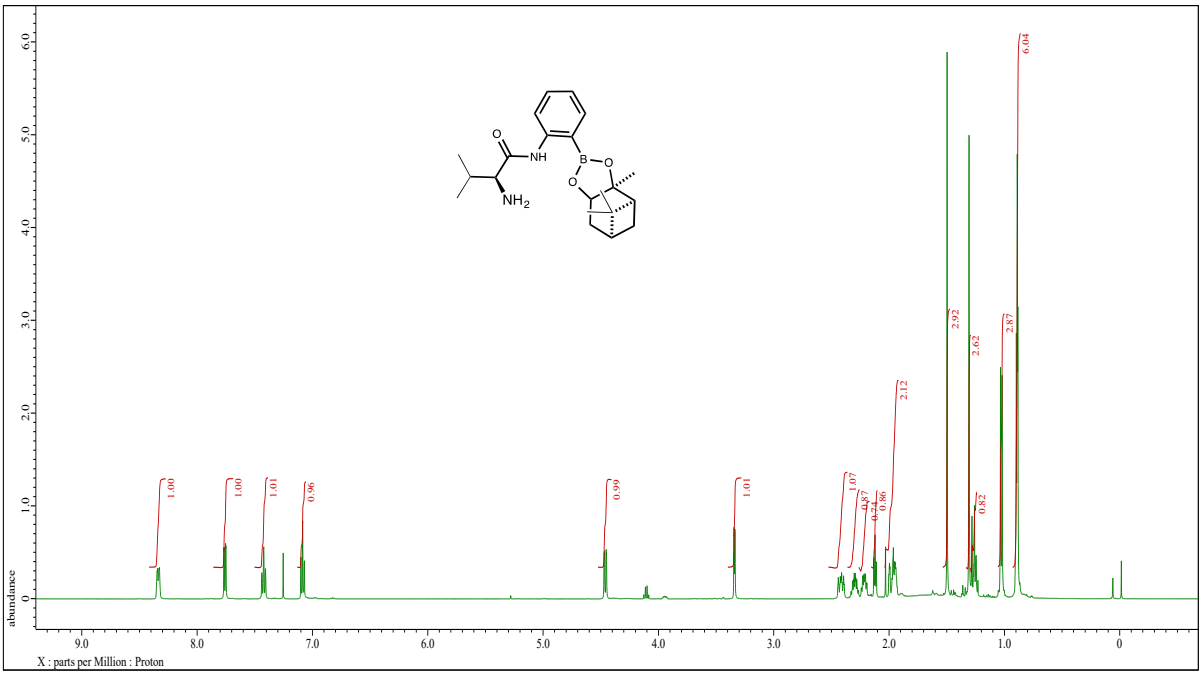


^{13}C-NMR

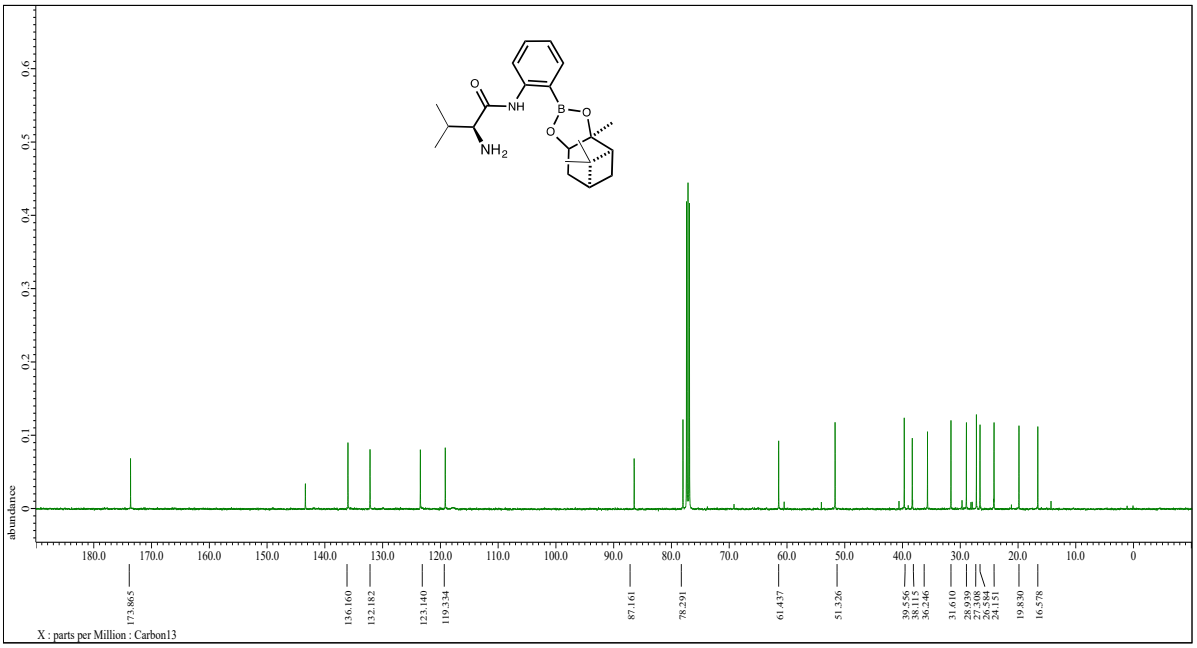


(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3-methyl butanamide

^{1}H-NMR

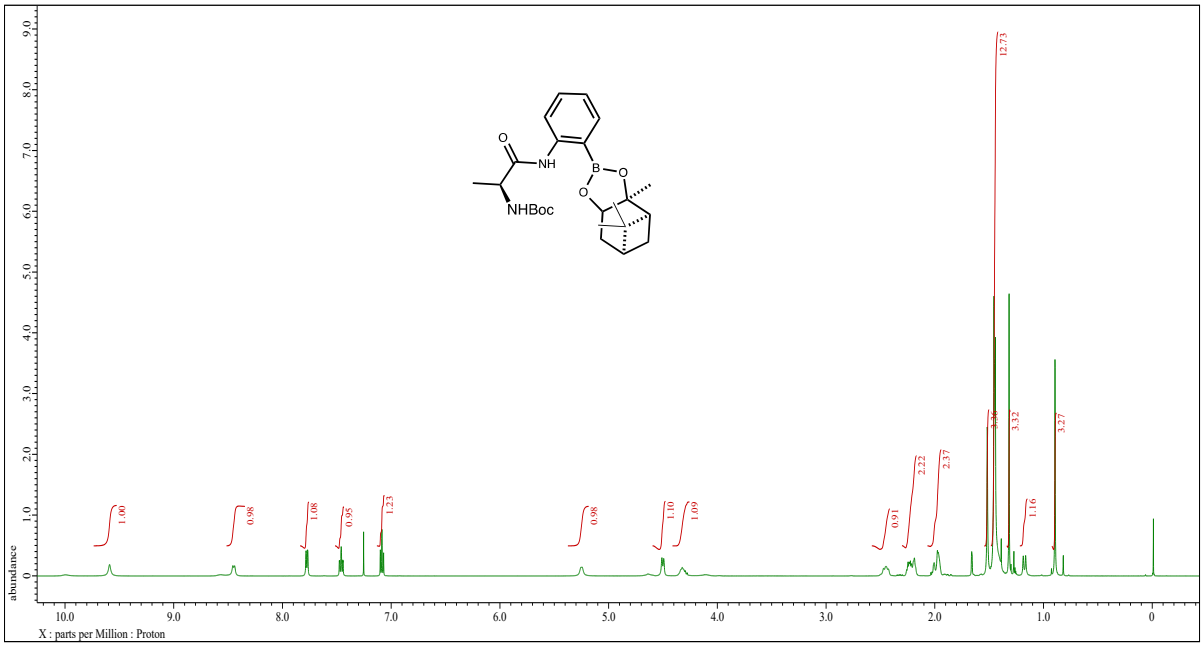


^{13}C-NMR

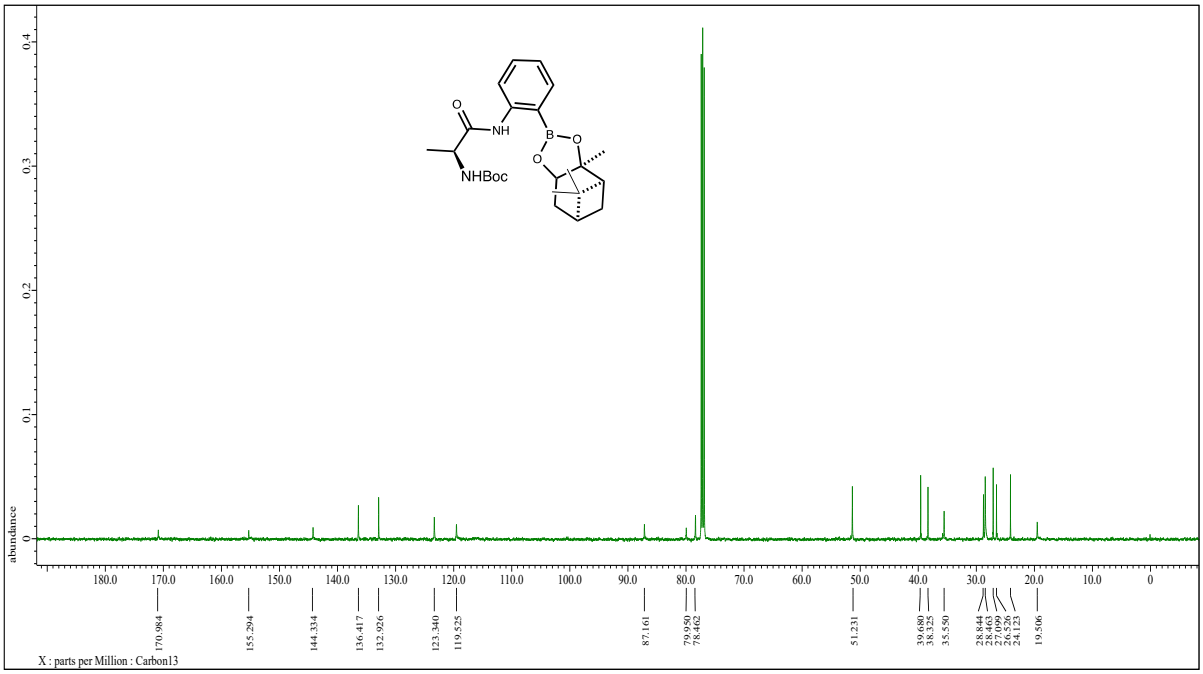


(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)- propanamide

^{1}H-NMR

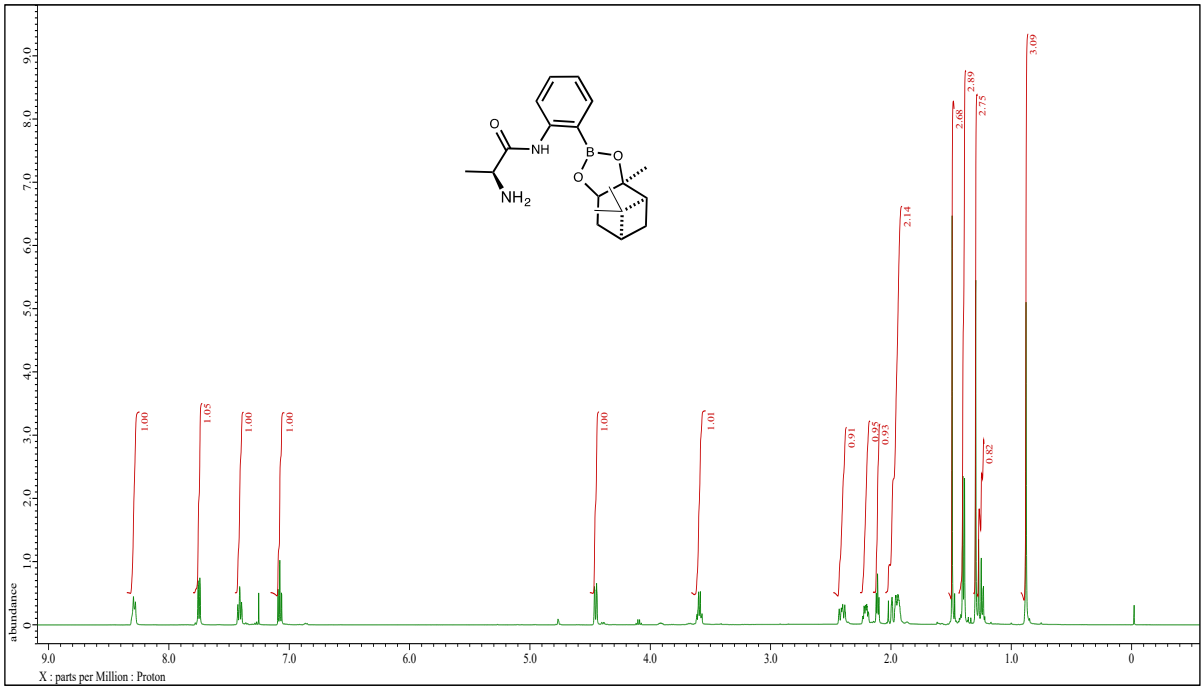


^{13}C-NMR

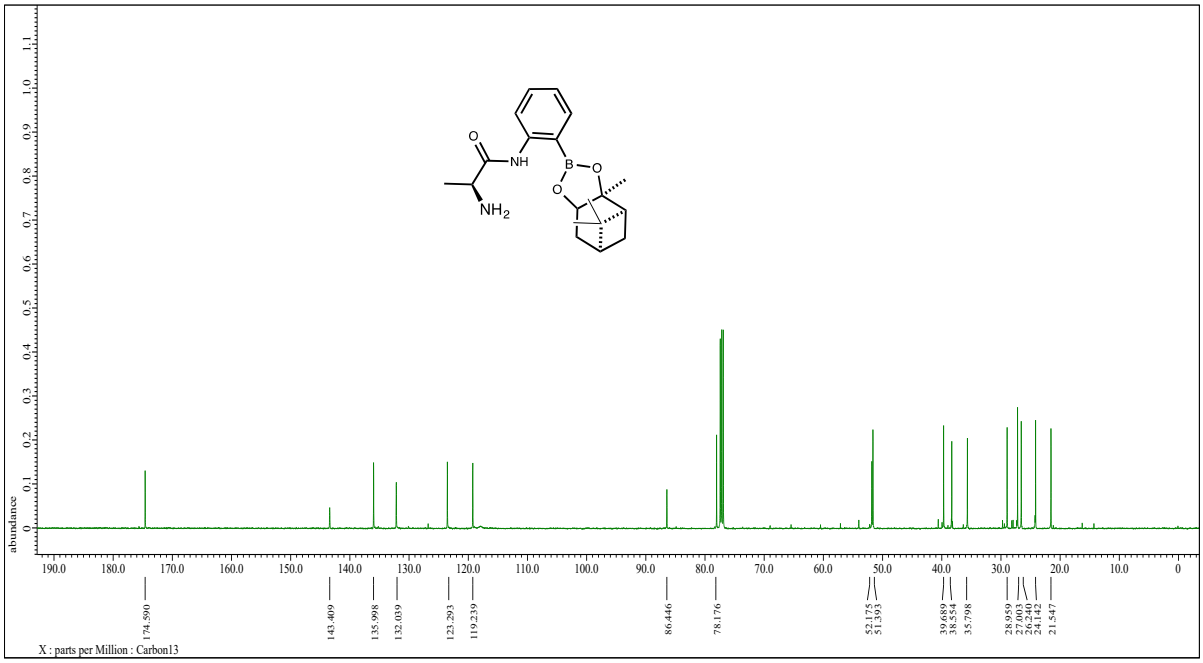


(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-propanamide

^{1}H-NMR

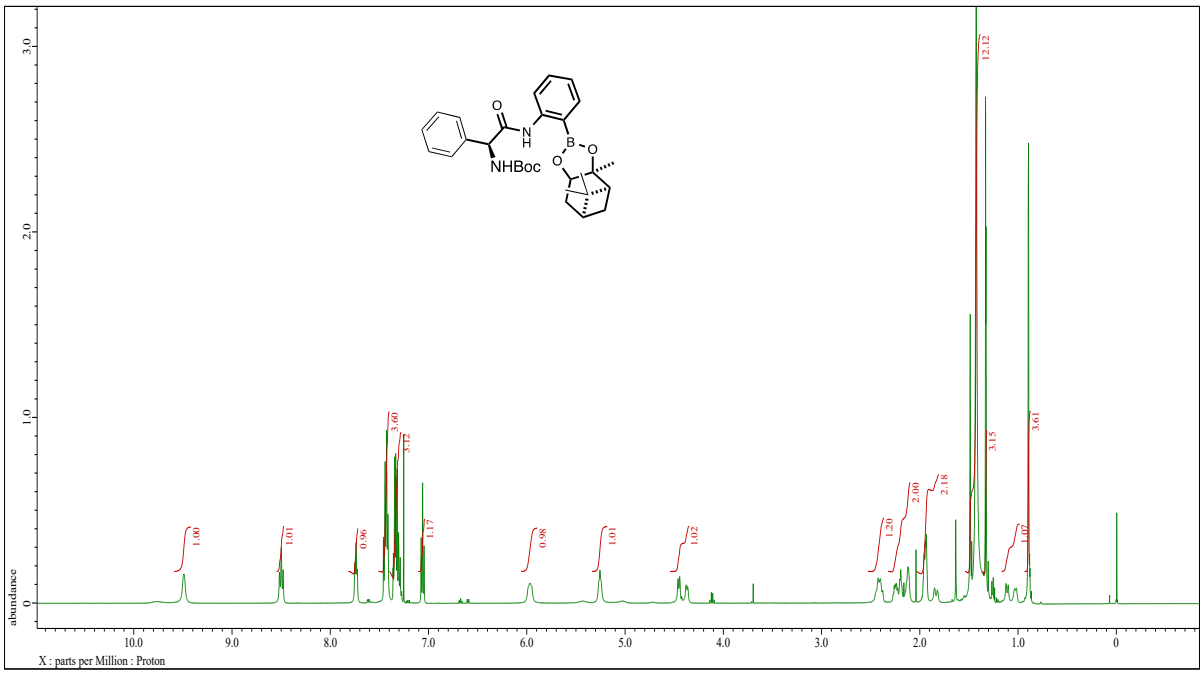


^{13}C-NMR

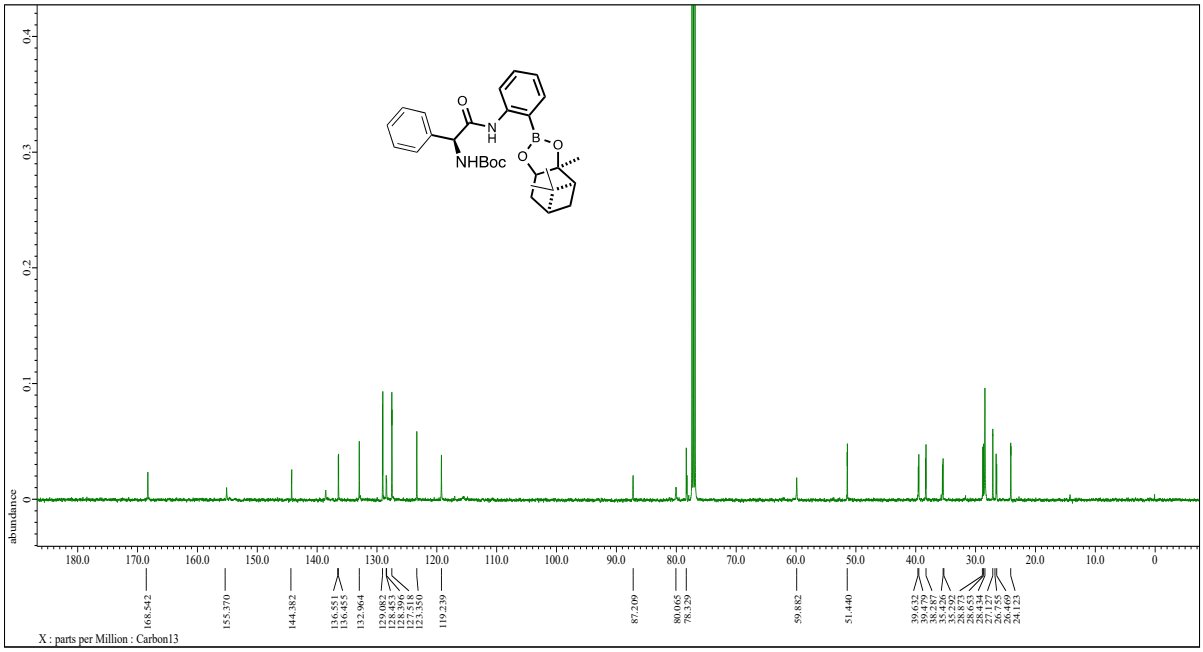


(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-2-phenylethanamide

^{1}H-NMR

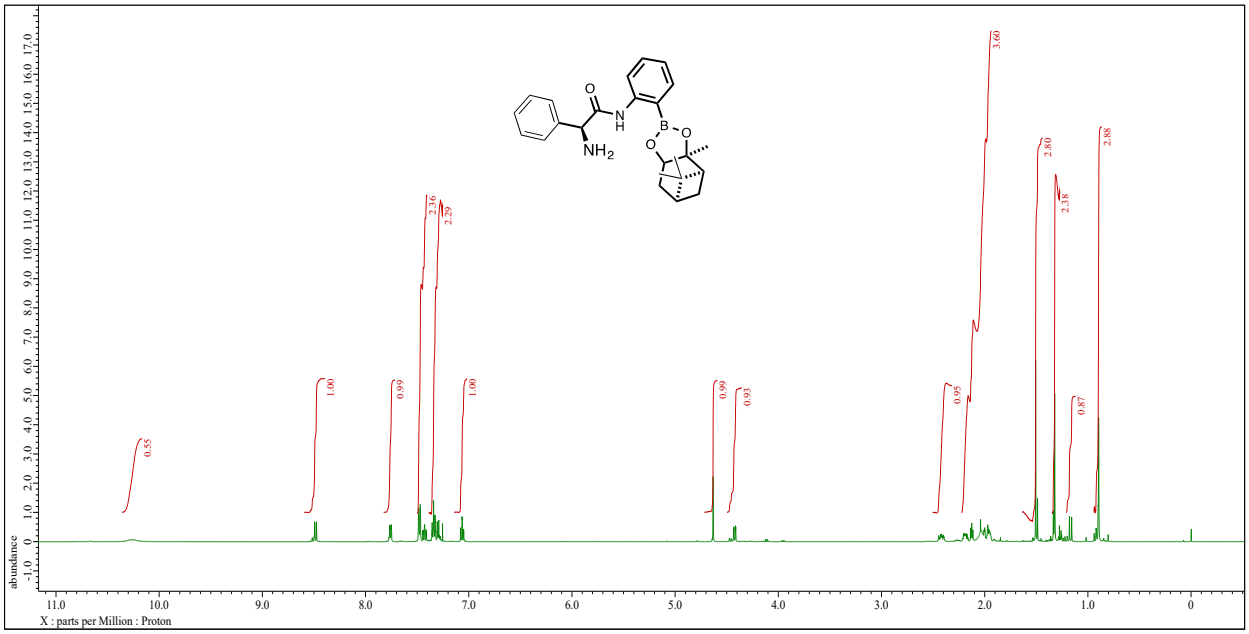


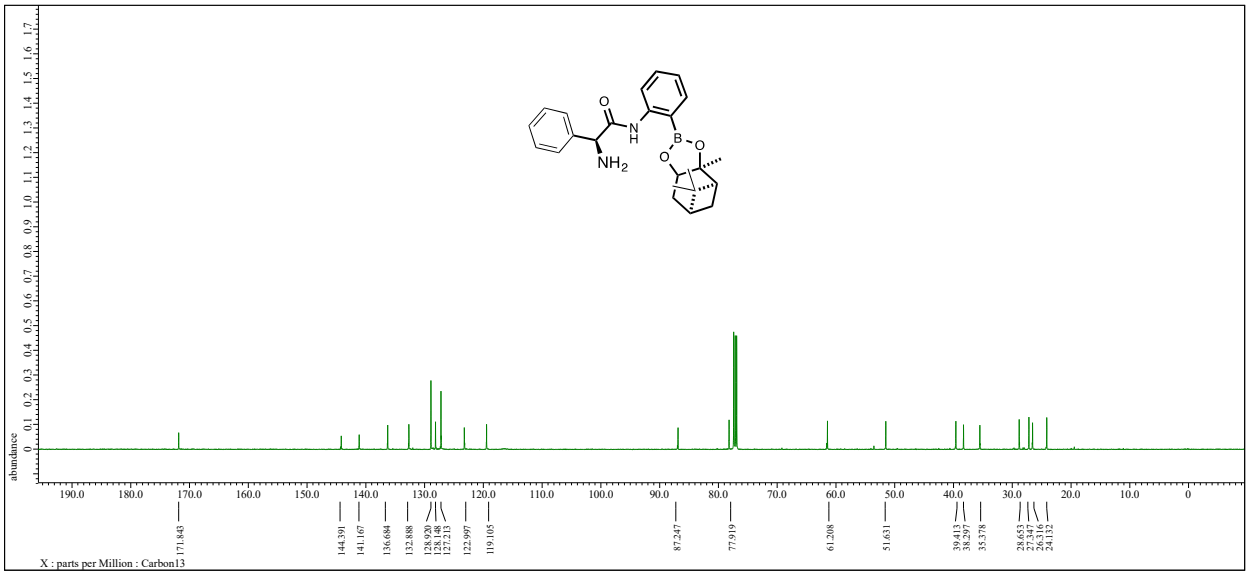
^{13}C-NMR



(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-2-phenylethanamide

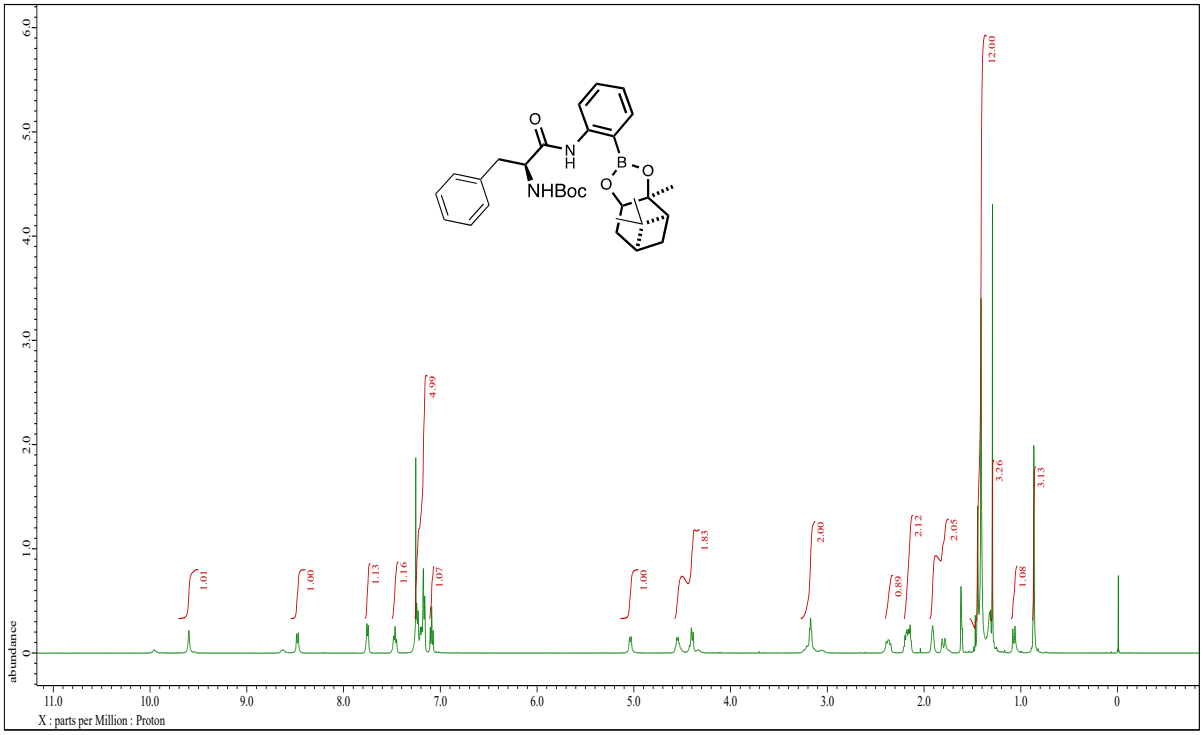
^{1}H-NMR



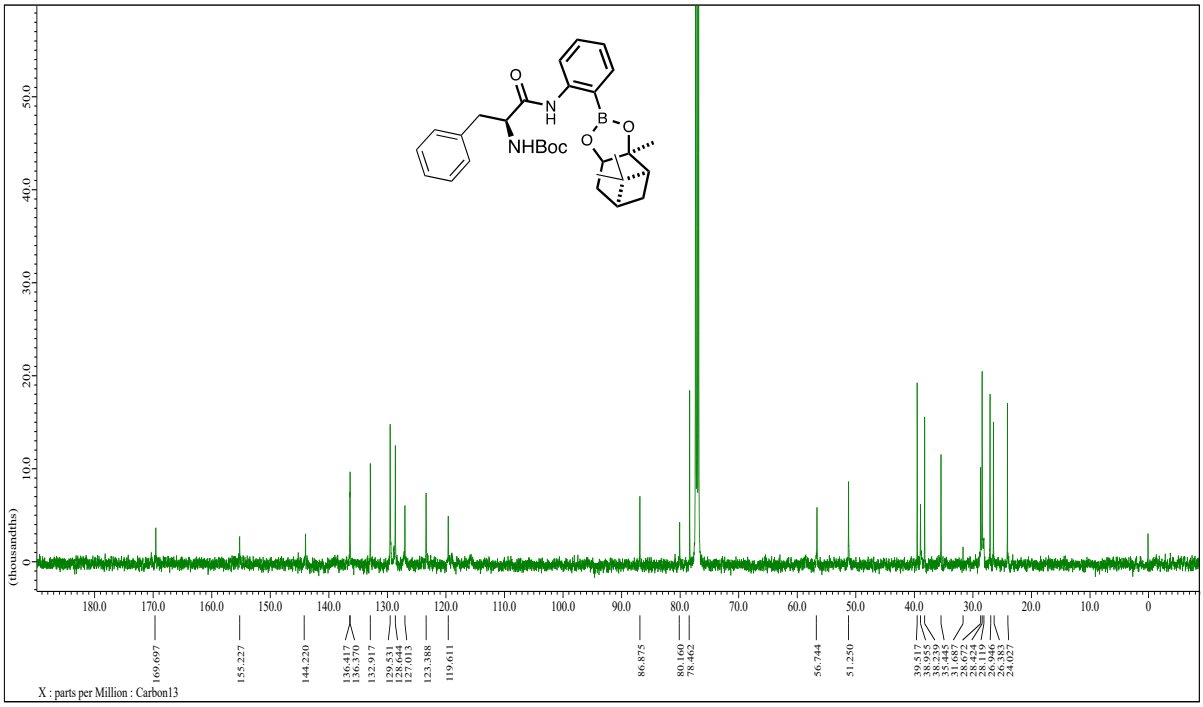


(S)-2-Aminoboc-N-((+)-2,3-pinanediol phenyl boronate)-3-phenylpropanamide

^{1}H-NMR

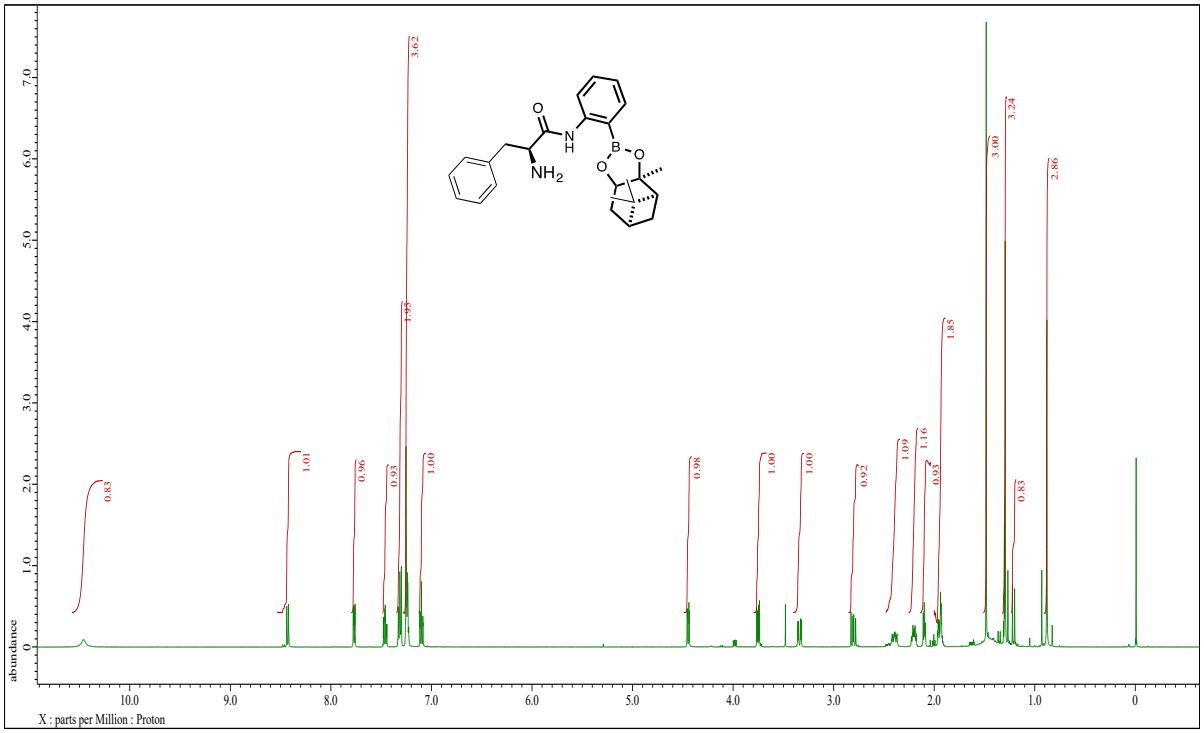


^{13}C-NMR

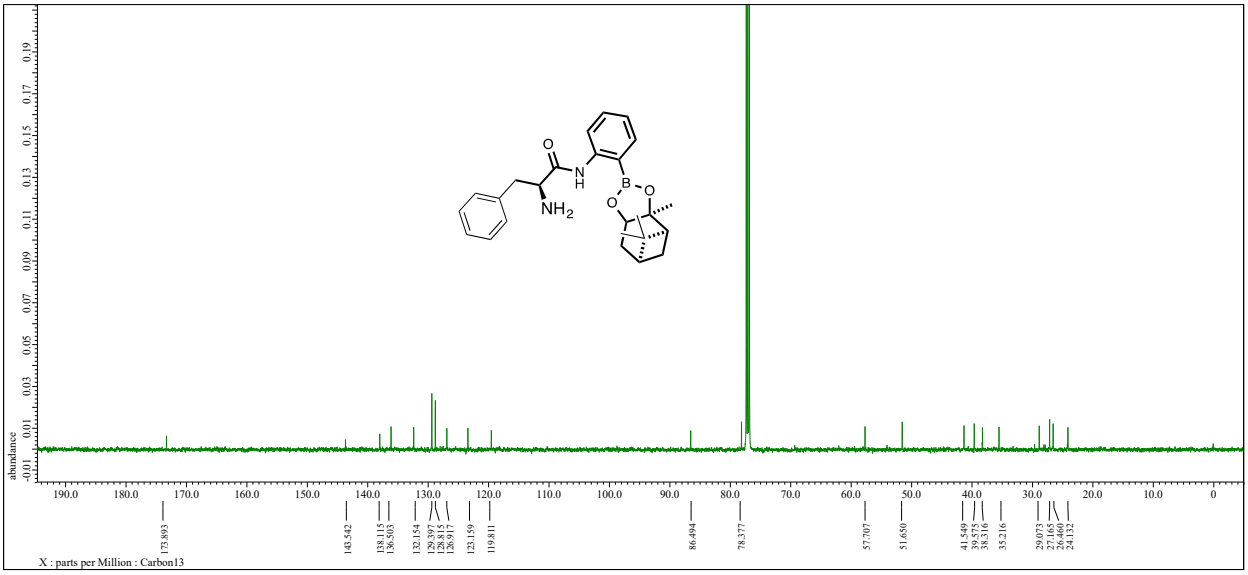


(S)-2-Amino-N-((+)-2,3-pinanediol phenyl boronate)-3-phenylpropanamide

^{1}H-NMR

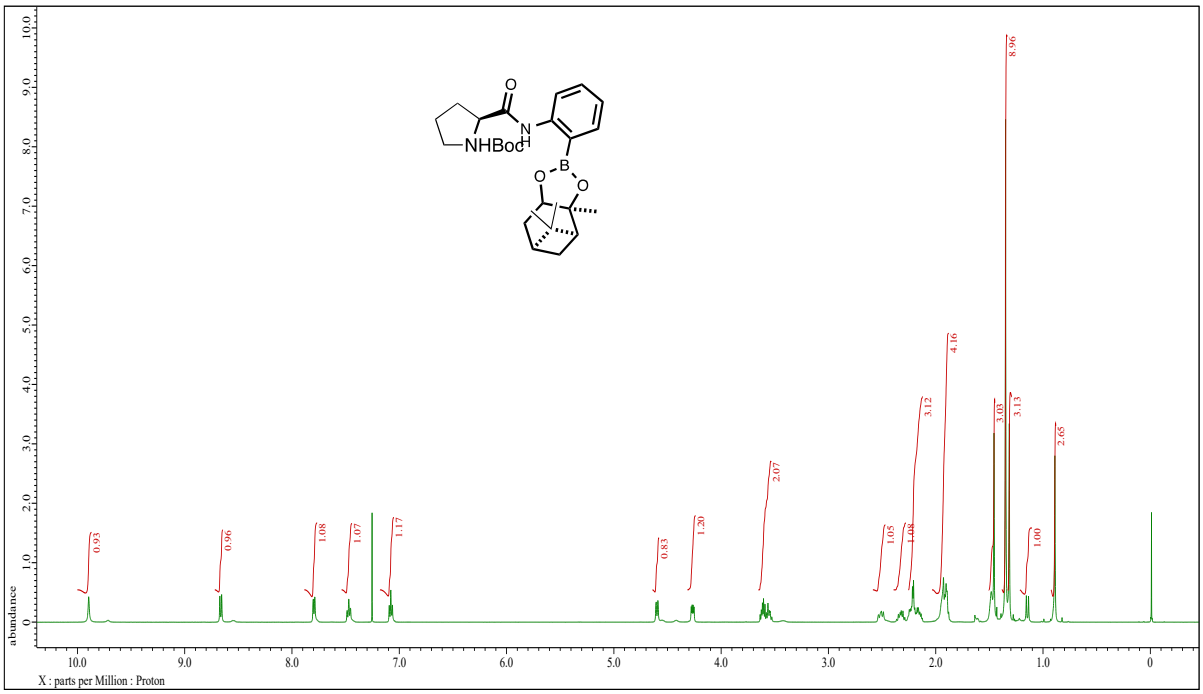


^{13}C-NMR

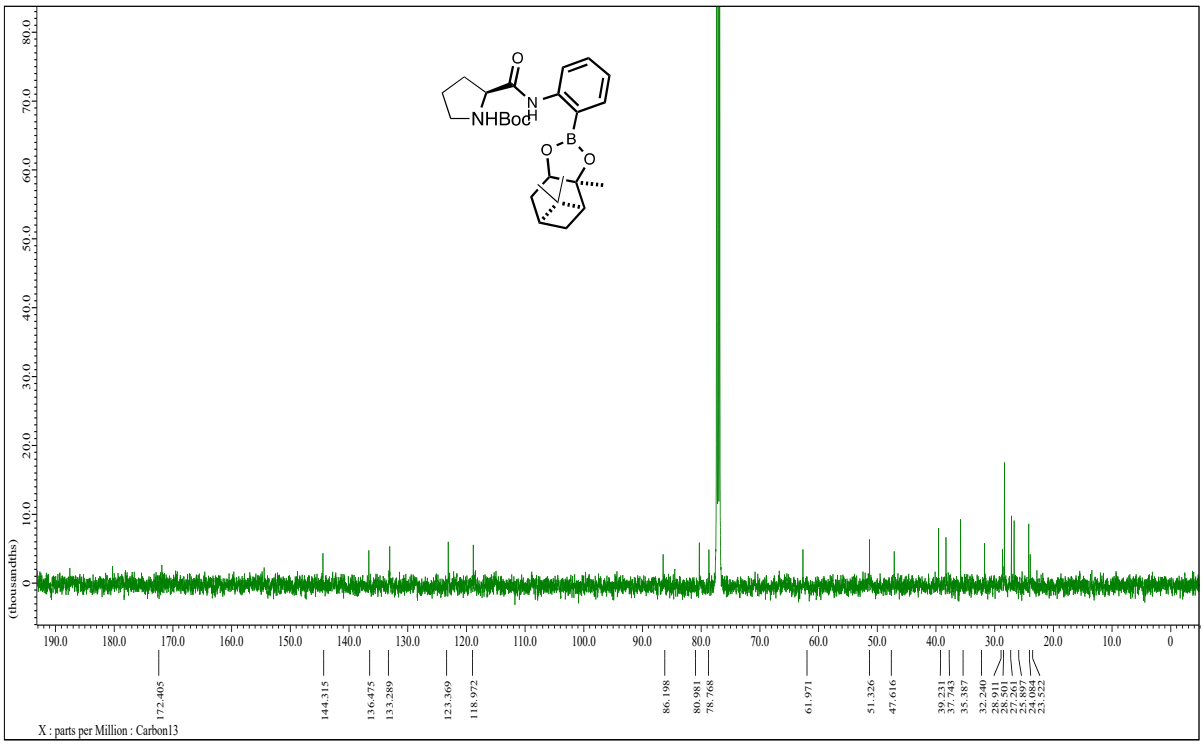


(S)-2-NBocpyrrolidine-N-((+)-2,3-pinanediol phenyl boronate)-carboxamide.

^{1}H-NMR

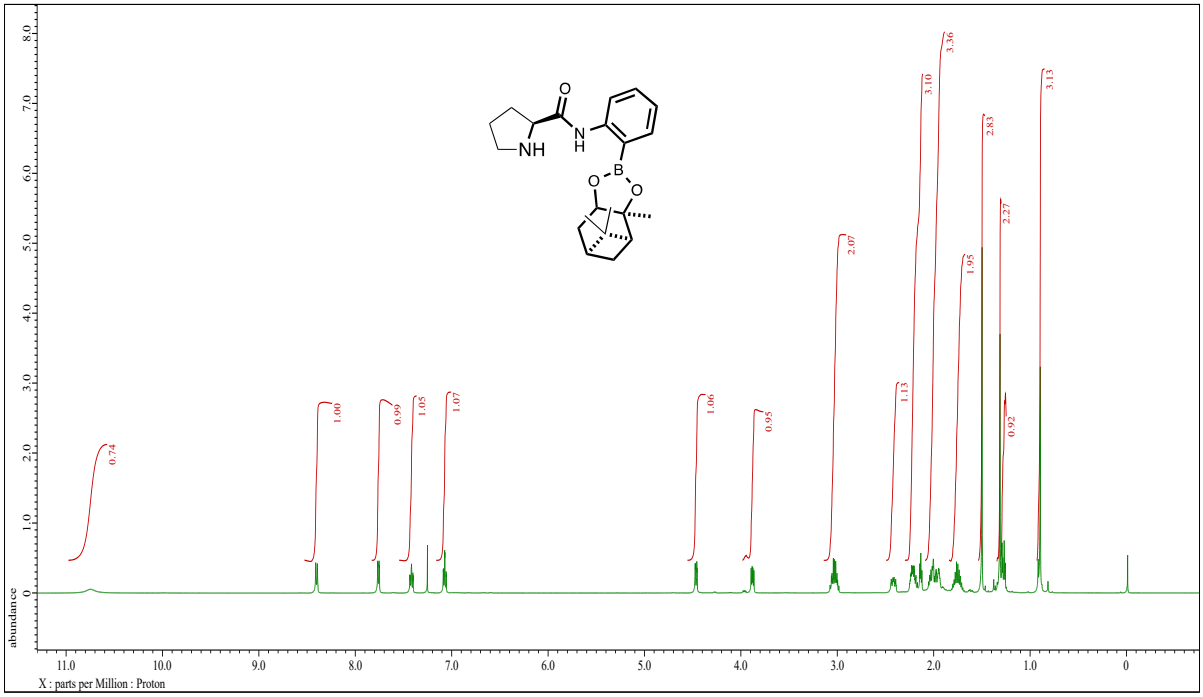


^{13}C-NMR

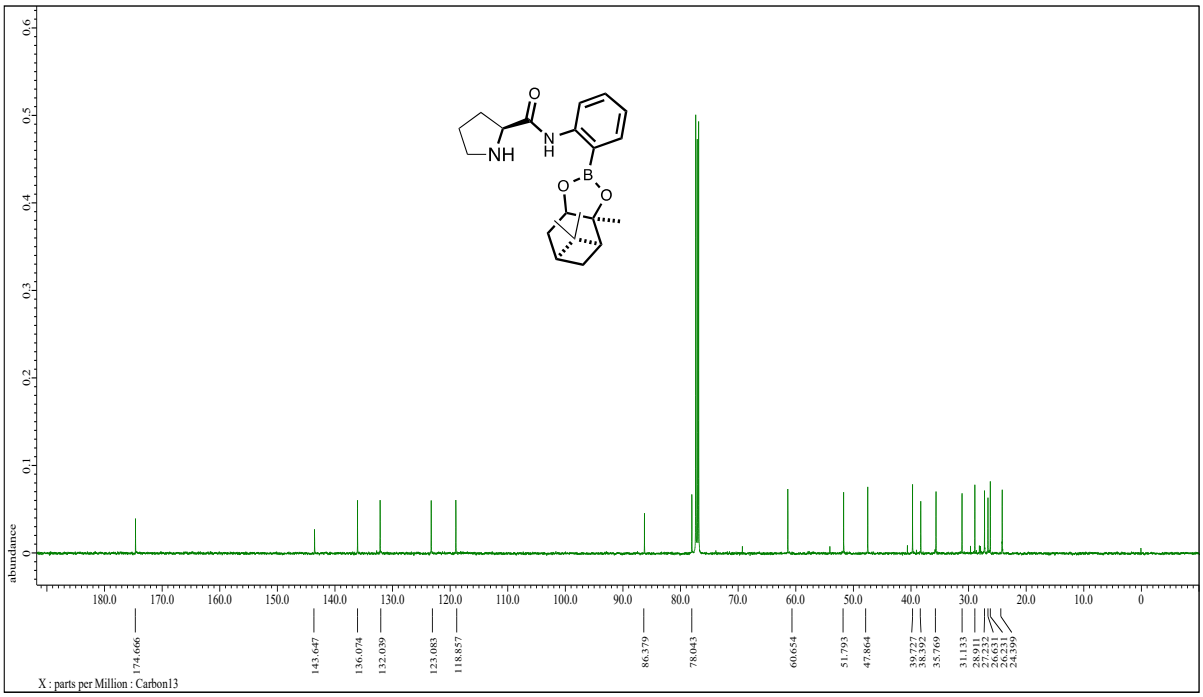


(S)-2-pyrrolidine-N-((+)-2,3-pinanediol phenyl boronate)-carboxamide.

^{1}H-NMR

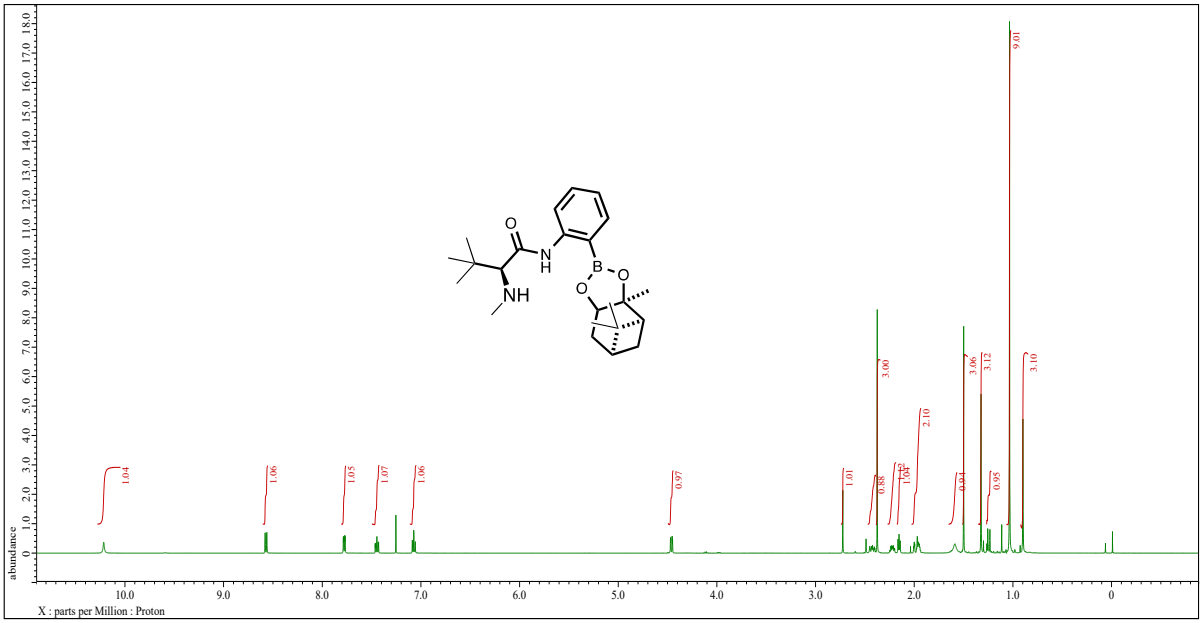


^{13}C-NMR

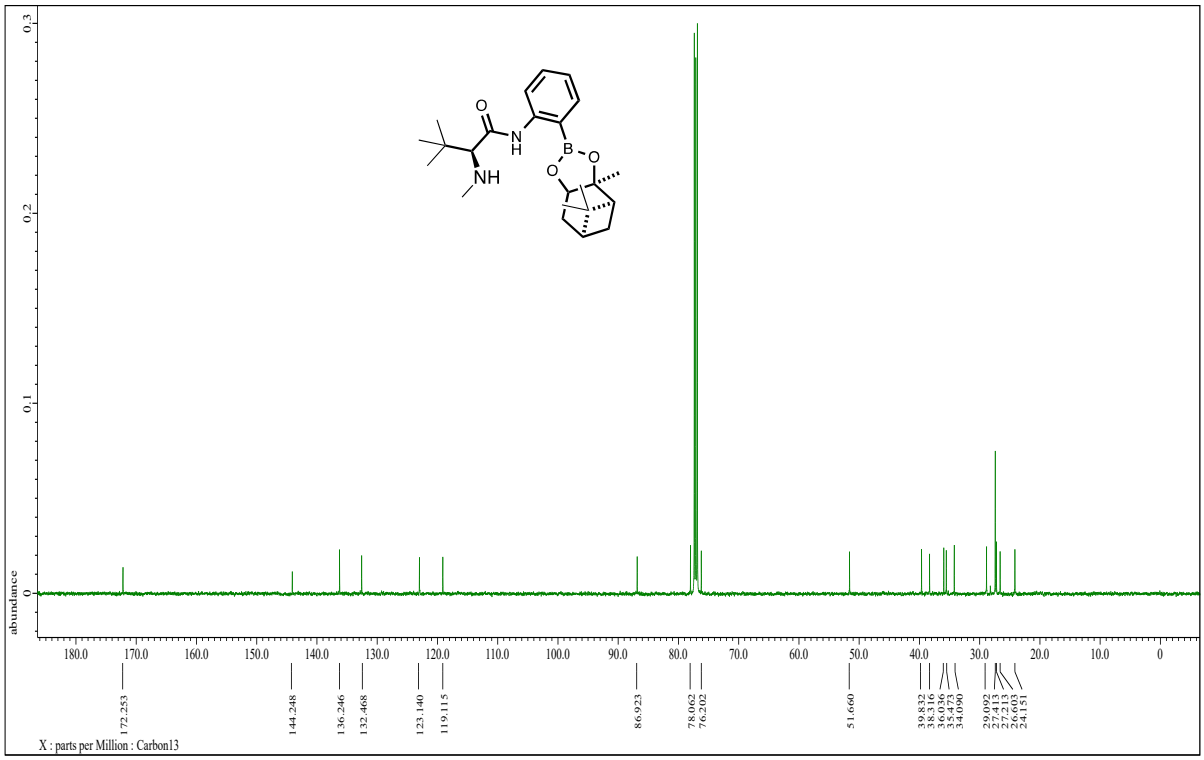


(S)-2-Aminomethyl-N-((+)-2,3-pinanediol phenyl boronate)-3,3-dimethylbutanamide

^{1}H-NMR

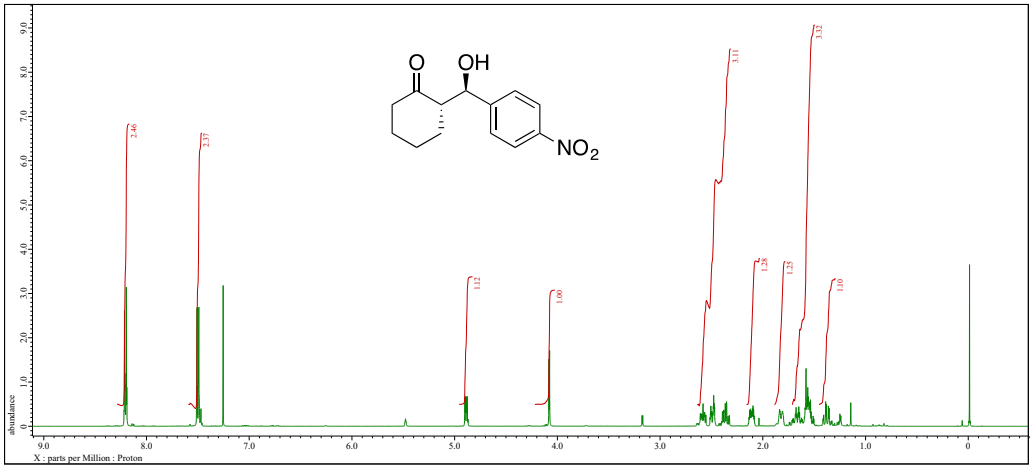


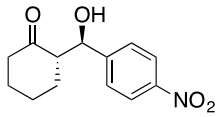
^{13}C-NMR



H[1] NMR and Mass data of the Aldol products

2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one (**7a**)



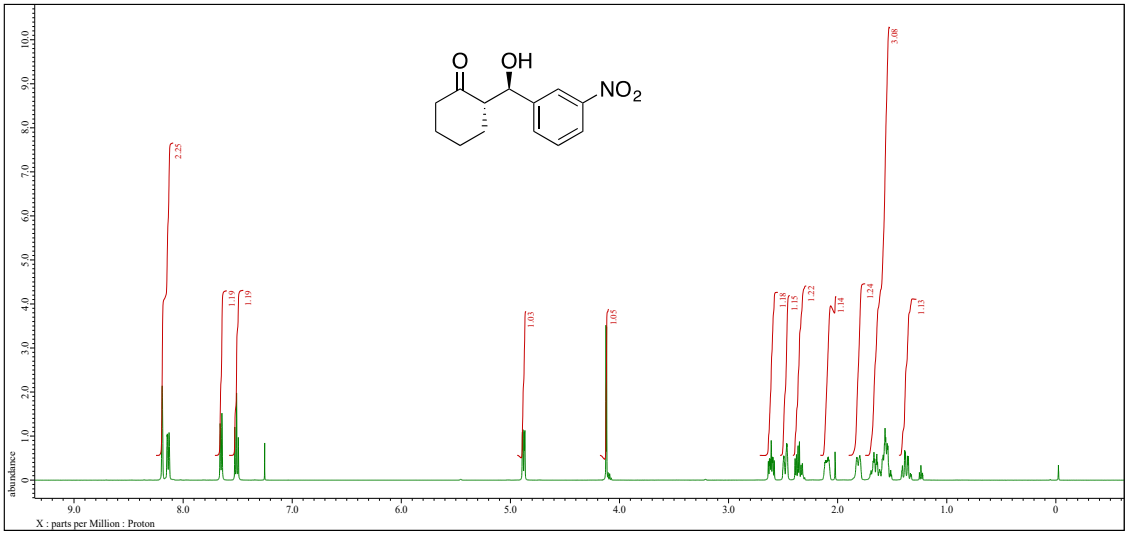


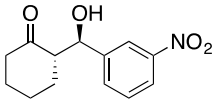
Chemical Formula: $C_{13}H_{15}NO_4$
Exact Mass: 249.1001

MS (EI) *m/z* : 249 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{13}H_{15}N_1O_4$ $[M]^+$: 249.1001; Found $[M]^+$: 249.1006.

2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclohexan-1-one (**7b**)



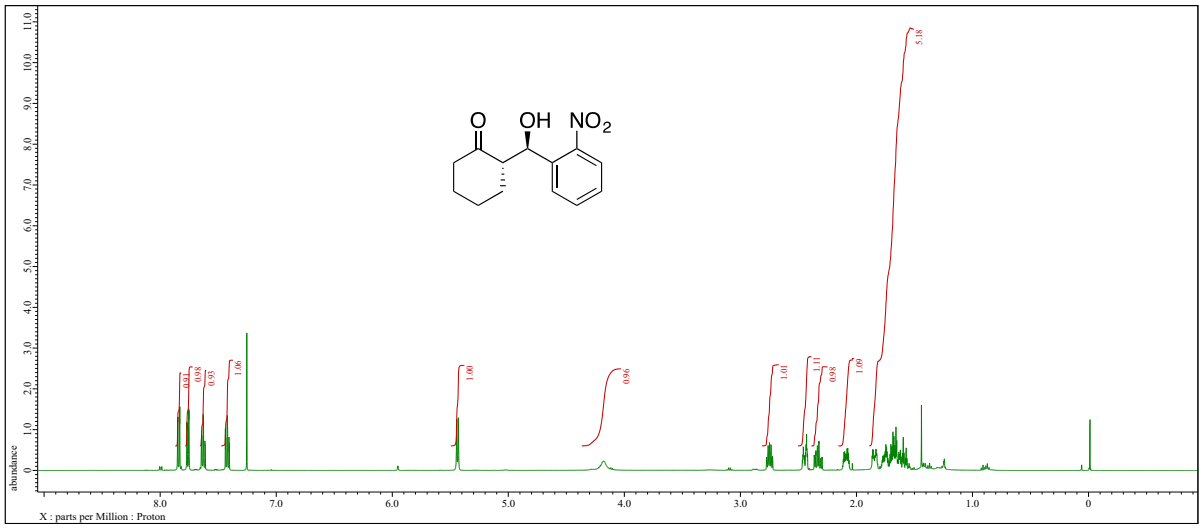


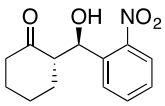
Chemical Formula: $C_{13}H_{15}NO_4$
Exact Mass: 249.1001

MS (EI) *m/z* : 249 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{13}H_{15}N_1O_4$ $[M]^+$: 249.1001, Found $[M]^+$: 249.1006.

2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclohexan-1-one (**7c**)



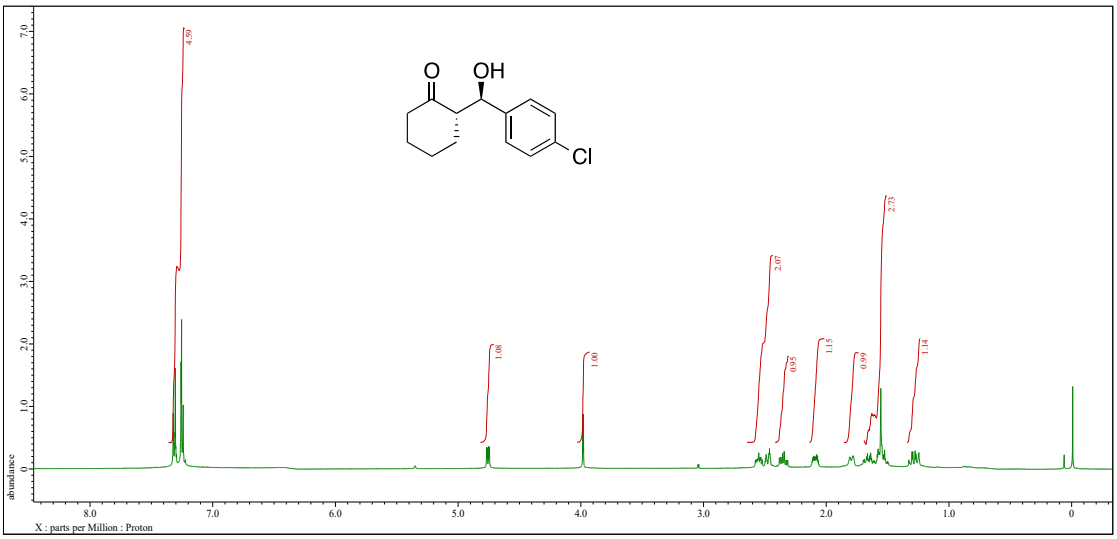


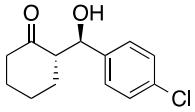
Chemical Formula: $C_{13}H_{15}NO_4$
Exact Mass: 249.1001

MS (EI) *m/z* : 249 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{13}H_{15}N_1O_4$ $[M]^+$: 249.1001, Found $[M]^+$: 249.1005.

2-[Hydroxy-(4-chlorophenyl)-methyl]-cyclohexan-1-one (**7d**)



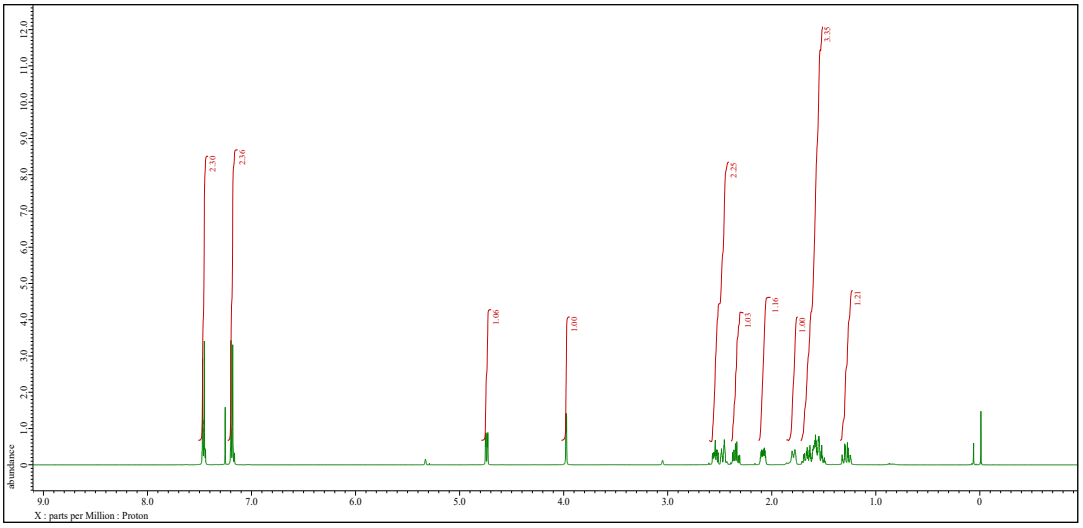


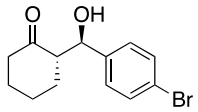
Chemical Formula: $C_{13}H_{15}ClO_2$
Exact Mass: 238.0761

MS (EI) *m/z* : 238 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{13}H_{15}ClO_2$ $[M]^+$: 238.0761; Found 238.0752 and [M+2] 240.0721

2-[Hydroxy-(4-bromophenyl)-methyl]-cyclohexan-1-one (**7e**)



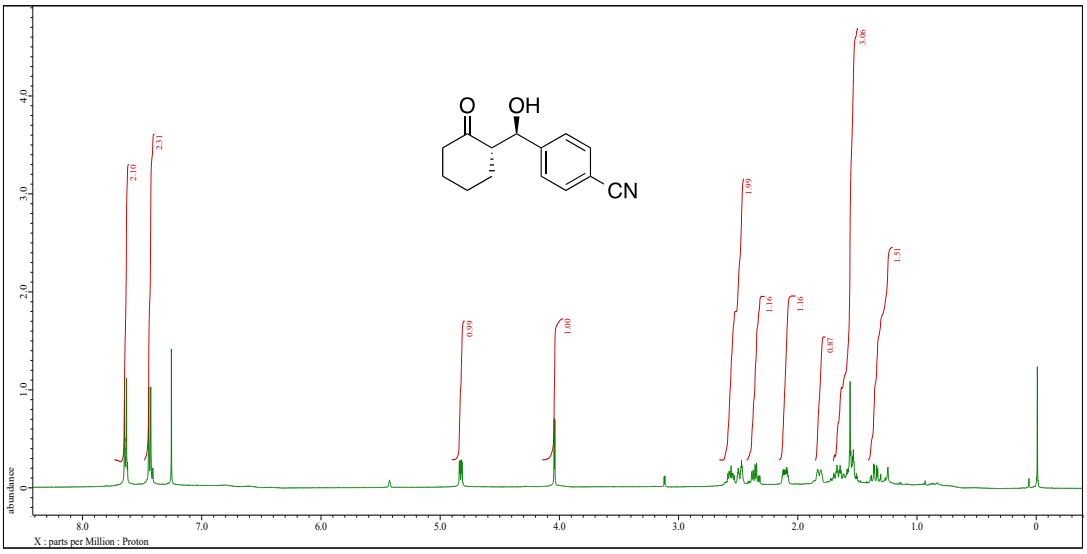


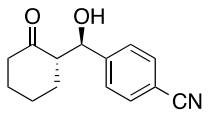
Chemical Formula: $C_{13}H_{15}BrO_2$
Exact Mass: 282.0255

MS (EI) *m/z* : 282 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{13}H_{15}BrO_2$ $[M]^+$: 282.0255; Found $[M]^+$: 282.0259 and [M+2] 284.0231

2-[Hydroxy-(4-cyanophenyl)-methyl]-cyclohexan-1-one (**7f**)



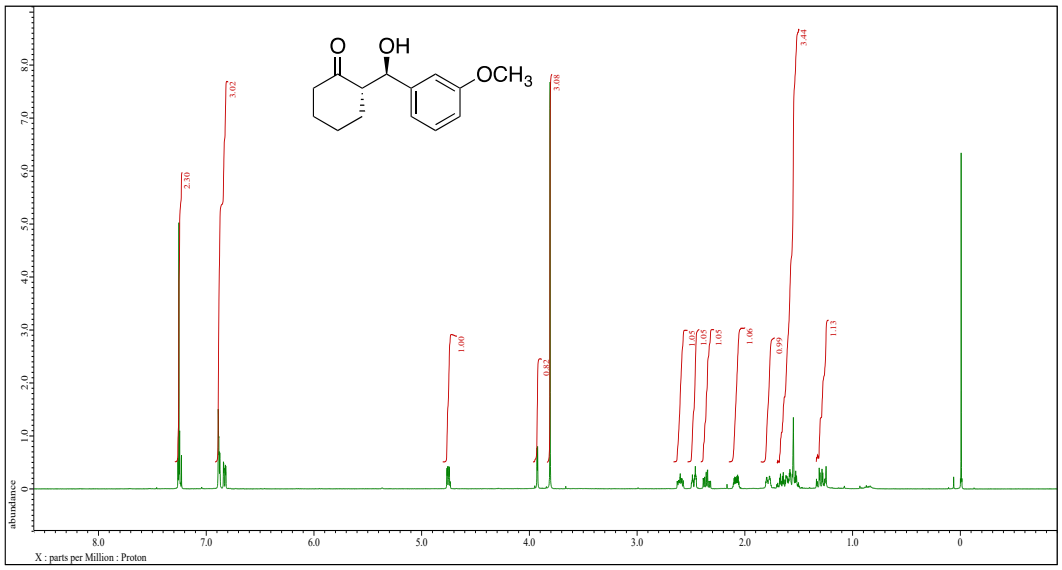


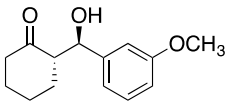
Chemical Formula: $C_{14}H_{15}NO_2$
Exact Mass: 229.1103

MS (EI) *m/z* : 229 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{15}NO_2$ $[M]^+$: 229.1103, Found $[M]^+$: 229.1107

2-[Hydroxy-(3-methoxyphenyl)-methyl]-cyclohexan-1-one (**7g**)



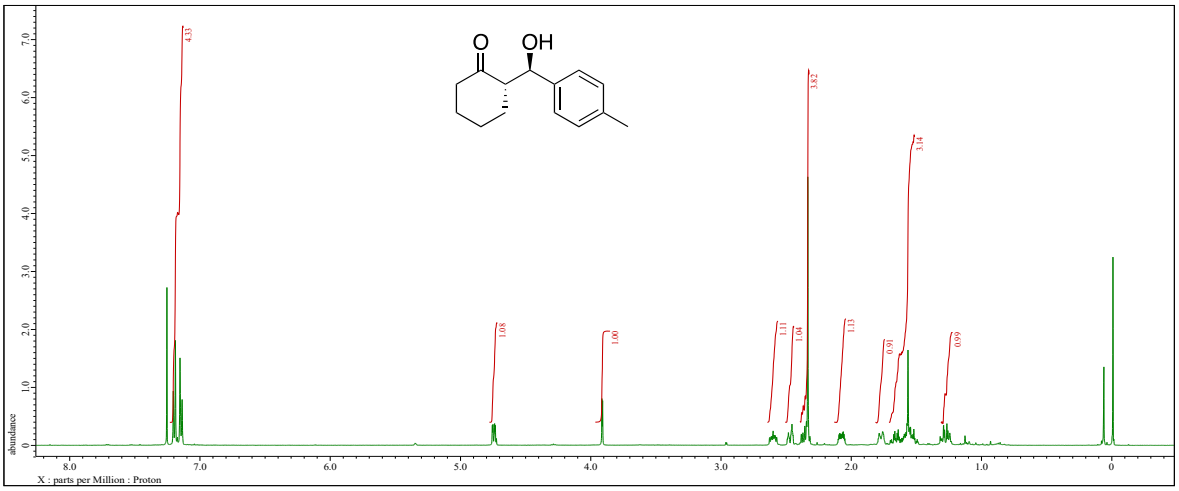


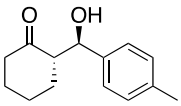
Chemical Formula: $C_{14}H_{18}O_3$
Exact Mass: 234.1256

MS (EI) *m/z* : 234 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{18}O_3$ $[M]^+$: 234.1256, Found $[M]^+$: 234.1251

2-[Hydroxy-(4-methylphenyl)-methyl]-cyclohexan-1-one (**7h**)



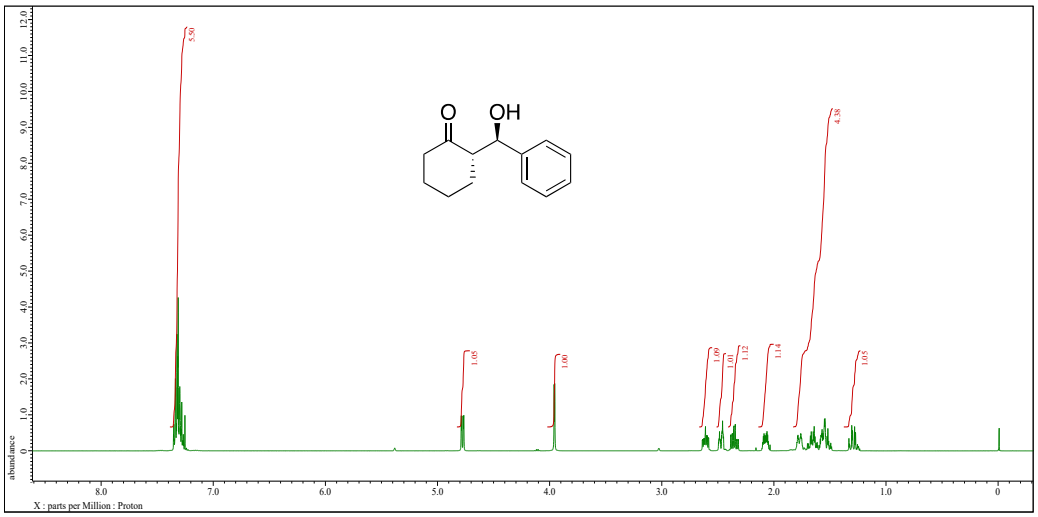


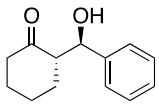
Chemical Formula: $C_{14}H_{18}O_2$
Exact Mass: 218.1307

MS (EI) *m/z* : 218 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{18}O_2$ $[M]^+$: 218.1307, Found $[M+1]^+$: 218.1396

2-[Hydroxy-(phenyl)-methyl]-cyclohexan-1-one (**7i**)



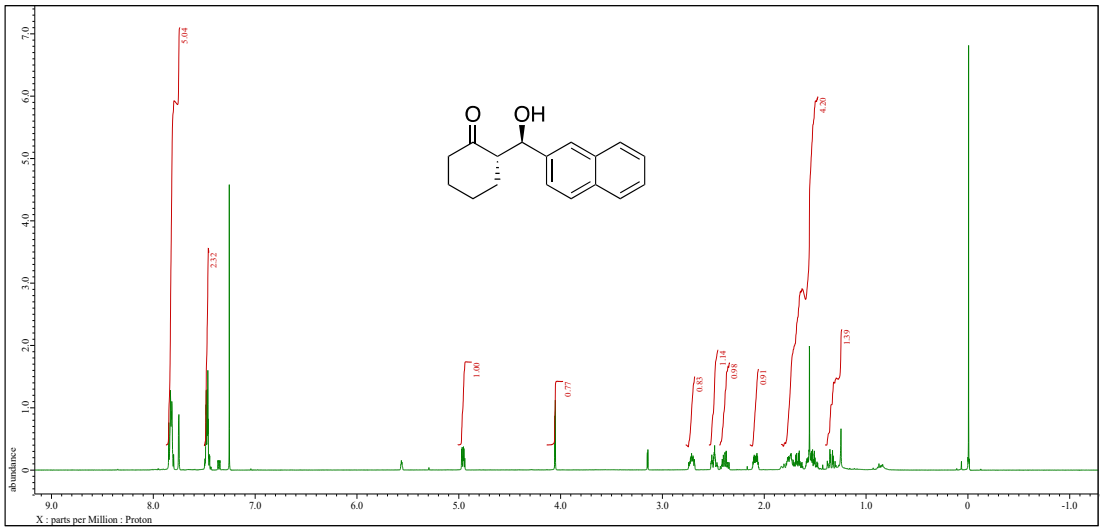


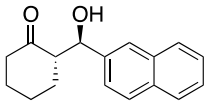
Chemical Formula: $C_{13}H_{16}O_2$
Exact Mass: 204.1150

MS (EI) *m/z* : 204 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{18}O_3$ $[M]^+$: 204.1150, Found $[M]^+$: 204.1151

2-[Hydroxy-(napthyl)-methyl]-cyclohexan-1-one (**7j**)



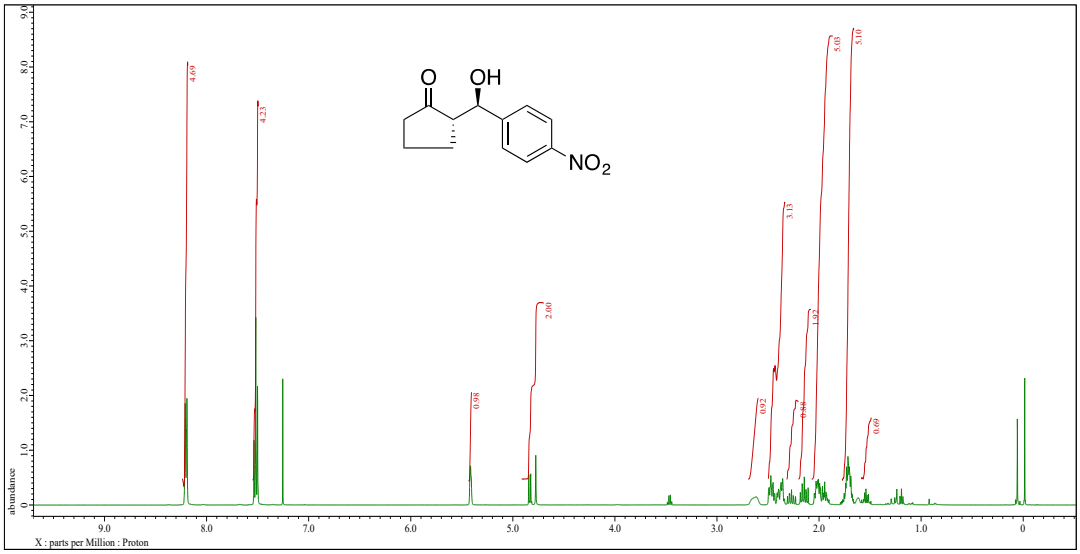


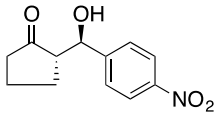
Chemical Formula: $C_{17}H_{18}O_2$
Exact Mass: 254.1307

MS (EI) *m/z* : 254 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{18}O_3$ $[M]^+$: 254.1307, Found $[M]^+$: 254.1315

2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclopentan-1-one (**7k**)



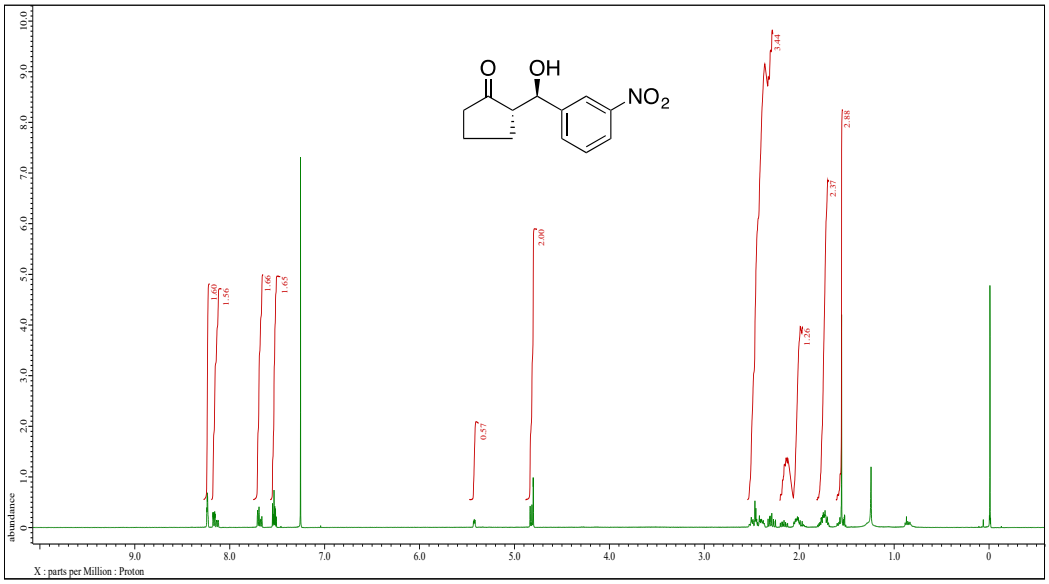


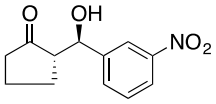
Chemical Formula: $C_{12}H_{13}NO_4$
Exact Mass: 235.0845

MS (EI) *m/z* : 254 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{12}H_{13}NO_4$ $[M]^+$: 235.0845, Found $[M]^+$: 235.0837

2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclopentan-1-one (**7l**)



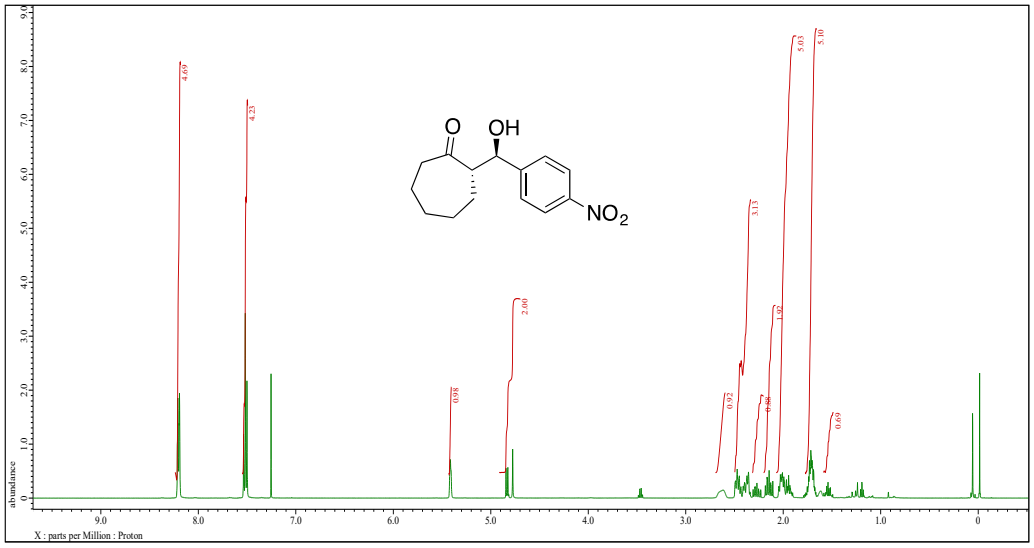


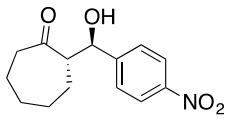
Chemical Formula: $C_{12}H_{13}NO_4$
Exact Mass: 235.0845

MS (EI) *m/z* : 235 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{12}H_{13}NO_4$ $[M]^+$: 235.0845, Found $[M]^+$: 235.0849

2-[Hydroxy-(4-nitrophenyl)-methyl]-cycloheptan-1-one(**7m**)



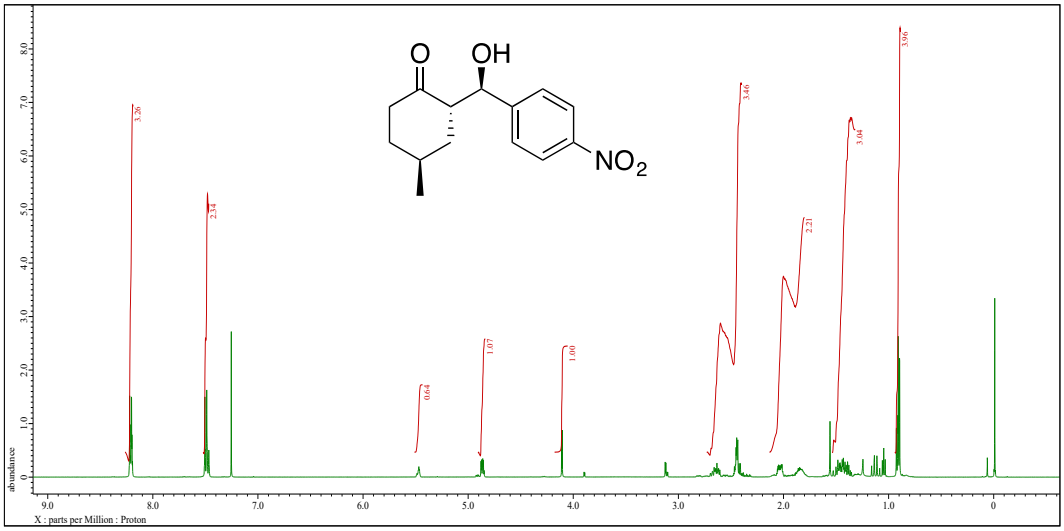


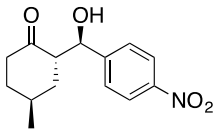
Chemical Formula: $C_{14}H_{17}NO_4$
Exact Mass: 263.1158

MS (EI) *m/z* : 263 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{17}NO_4$ $[M]^+$: 263.1158, Found $[M]^+$: 263.1155

2-[Hydroxy-(4-nitrophenyl)-methyl]-4-methylcyclohexan-1-one(**7n**)



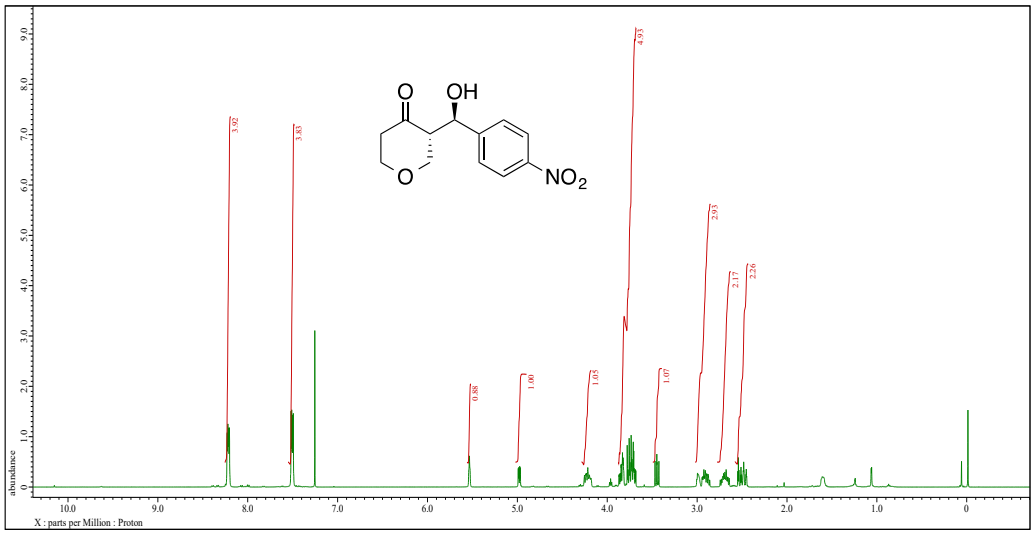


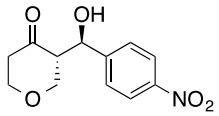
Chemical Formula: $C_{14}H_{17}NO_4$
Exact Mass: 263.1158

MS (EI) *m/z* : 263 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{14}H_{17}NO_4$ $[M]^+$: 263.1158, Found $[M]^+$: 263.1153

2-[Hydroxy-(4-nitrophenyl)-methyl]-dihydro-2H-pyran-4-one (**7o**)



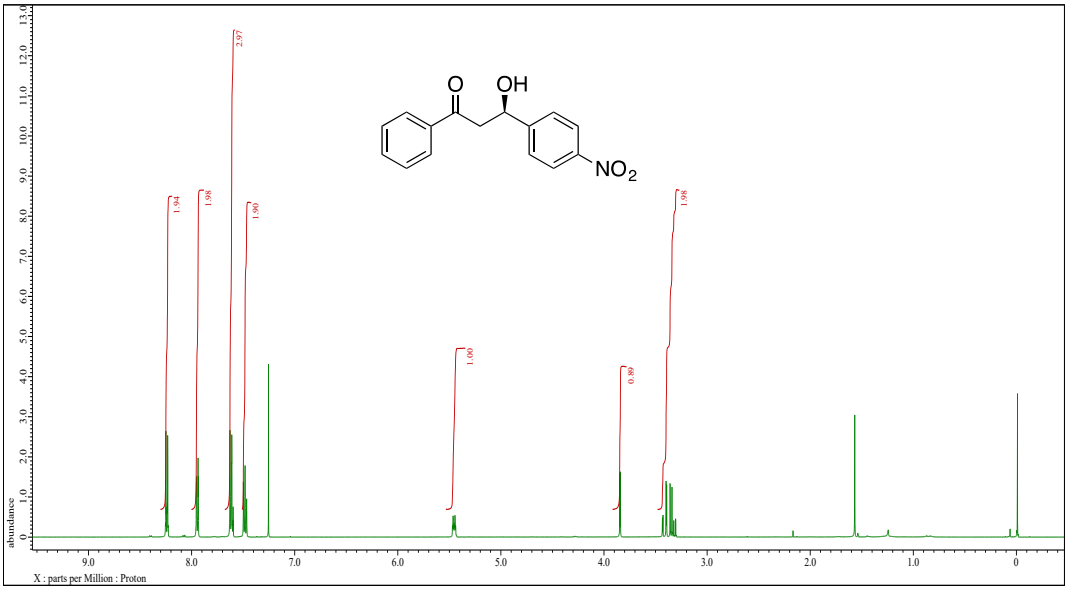


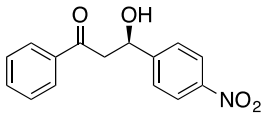
Chemical Formula: $C_{12}H_{13}NO_5$
Exact Mass: 251.0794

MS (EI) *m/z* : 251 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{12}H_{13}NO_5$ $[M]^+$: 251.0794, Found $[M]^+$: 251.0796

3-Hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**7p**)



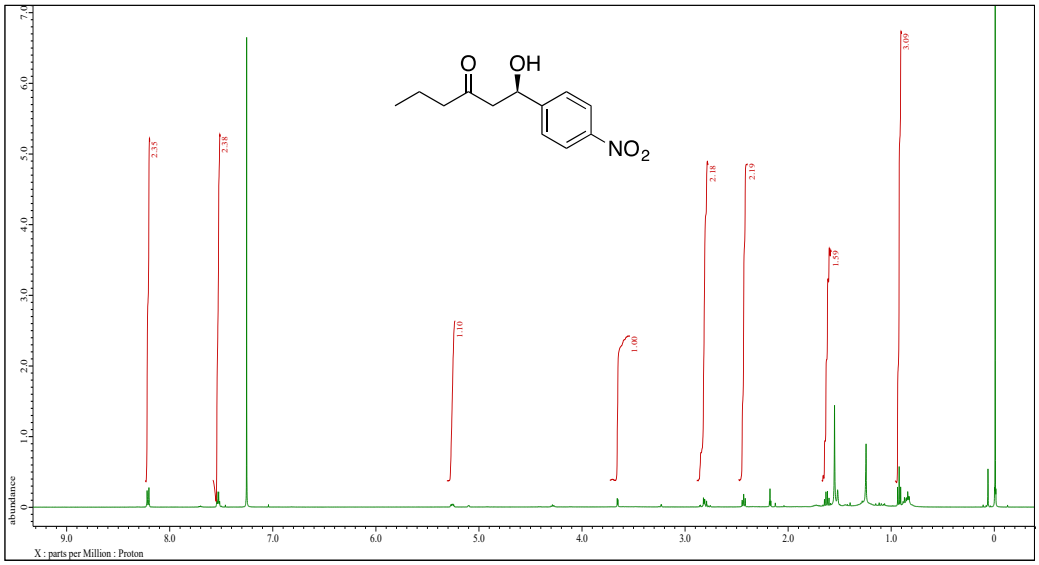


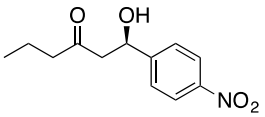
Chemical Formula: $C_{15}H_{13}NO_4$
Exact Mass: 271.0845

MS (EI) *m/z* : 271 $[M]^+$,

HRMS m/z: [EI] calculated for $C_{15}H_{13}NO_4$ $[M]^+$: 271.0845, Found $[M]^+$: 271.0848

3-Hydroxy-3-(4-nitrophenyl)-1-propylpropan-1-one (**7q**)



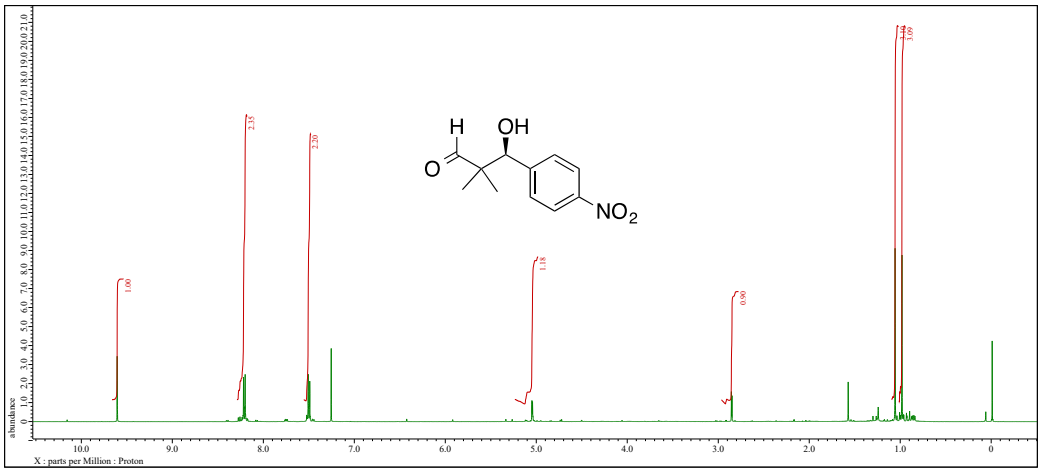


Chemical Formula: $C_{12}H_{15}NO_4$
Exact Mass: 237.1001

MS (EI) *m/z* : 237 $[M]^+$,

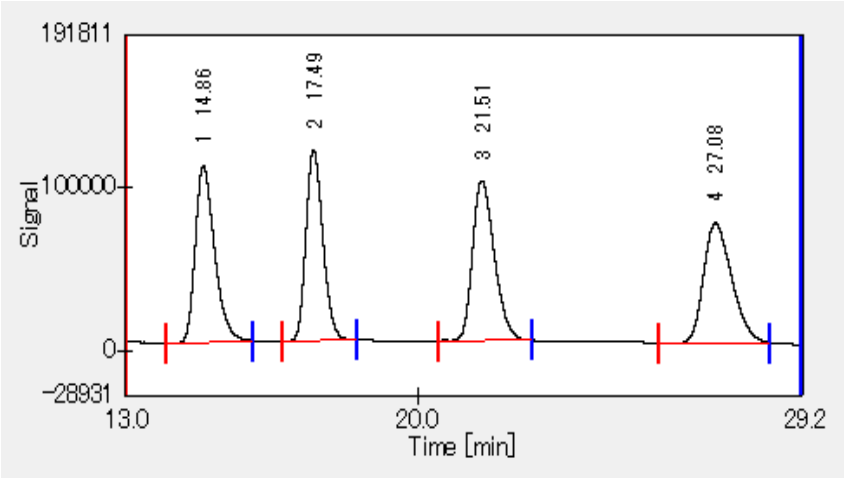
HRMS m/z: [EI] calculated for $C_{12}H_{15}NO_4$ $[M]^+$: 237.1001, Found $[M]^+$: 237.1004

3-Hydroxy-3-(4-nitrophenyl)-2,3-dimethylpropan-1-one (**7r**)

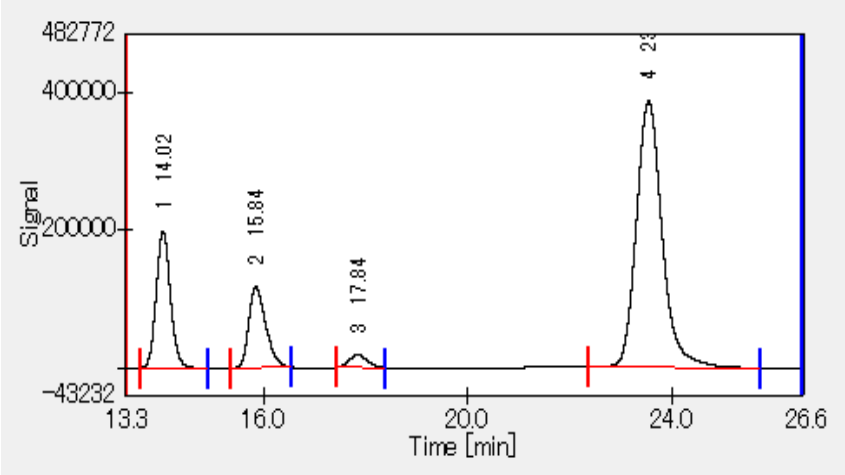


5. HPLC SPECTRA FOR ALDOL PRODUCTS

2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one (**7a**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 94% ee*

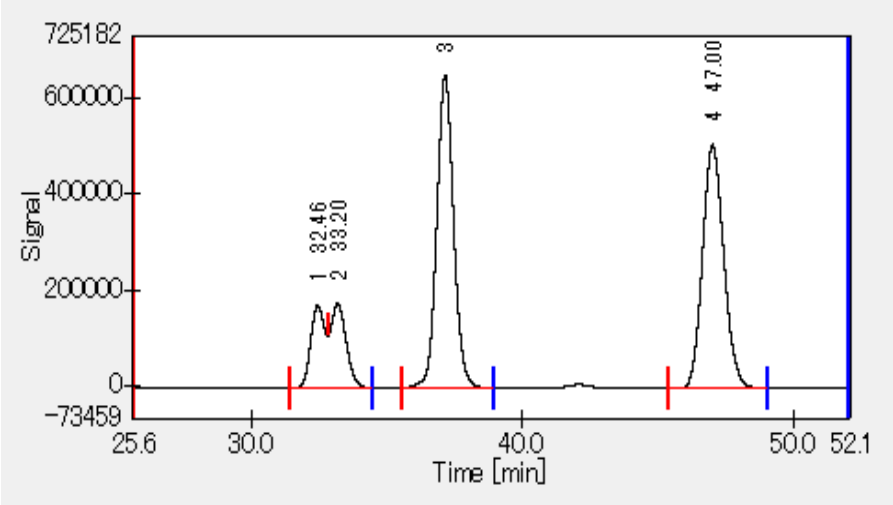


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	14.86	3433024	25.1286	107483	4692.4	1.383	3.243
2	17.49	3293264	24.1056	116990	8616.9	1.221	4.659
3	21.51	3528271	25.8258	97740	7861.7	1.293	5.003
4	27.08	3407248	24.94	73146	7420.4	1.314	*****
		13661806	100	395359			

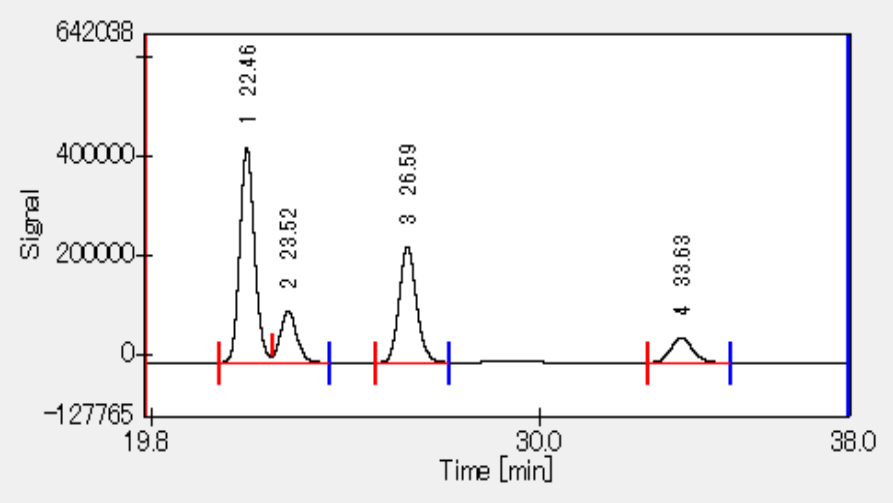


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	14.02	3822203	18.6025	198677	11710.5	1.119	3.162
2	15.84	2725808	13.2664	117306	10094.8	1.373	3.118
3	17.84	447108	2.1761	18551	12038.3	1.135	7.24
4	23.54	13551636	65.9551	387246	10356.2	1.195	*****
		20546755	100	721780			

2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclohexan-1-one (**7b**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 57% ee*

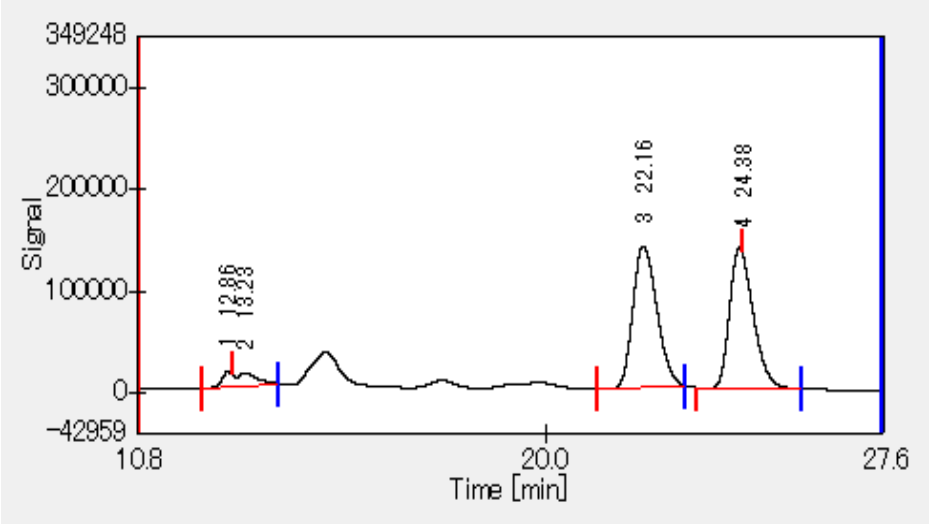


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	32.46	6582385	9.5258	172614	16392.8	*****	0.728
2	33.2	6704357	9.7024	176725	17323.7	*****	3.664
3	37.15	28108368	40.6777	651659	16600.3	1.07	7.53
4	47	27705162	40.0941	508669	16531.8	1.129	*****
		69100272	100	1509667			

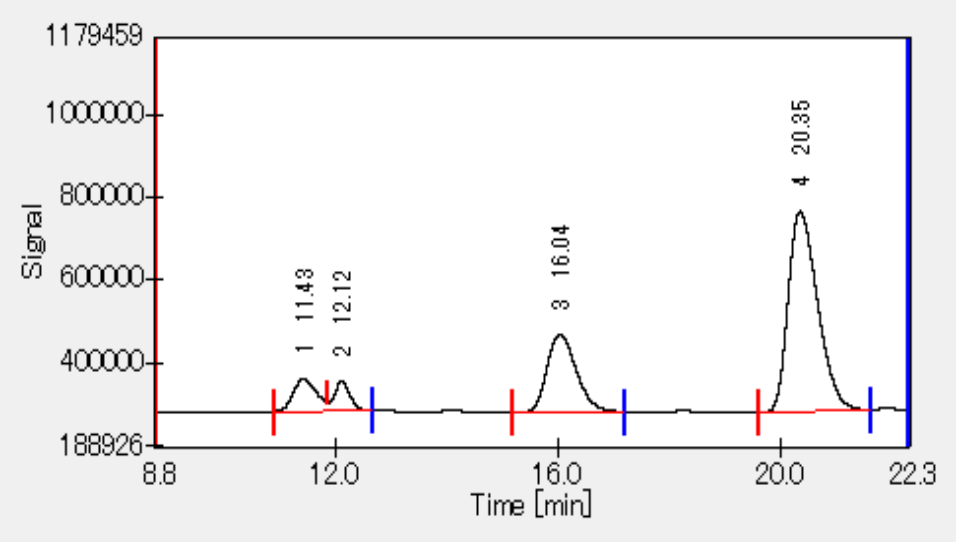


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	22.46	11431713	48.3788	431737	16270	1.135	1.448
2	23.52	2982209	12.6207	104312	15304.7	*****	3.869
3	26.59	7254575	30.7012	232930	16026.7	1.126	7.42
4	33.63	1961091	8.2993	50503	16184.9	1.128	*****
		23629588	100	819482			

2-[Hydroxy-(2-nitrophenyl)-methyl]-cyclohexan-1-one (**7c**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 44% ee*

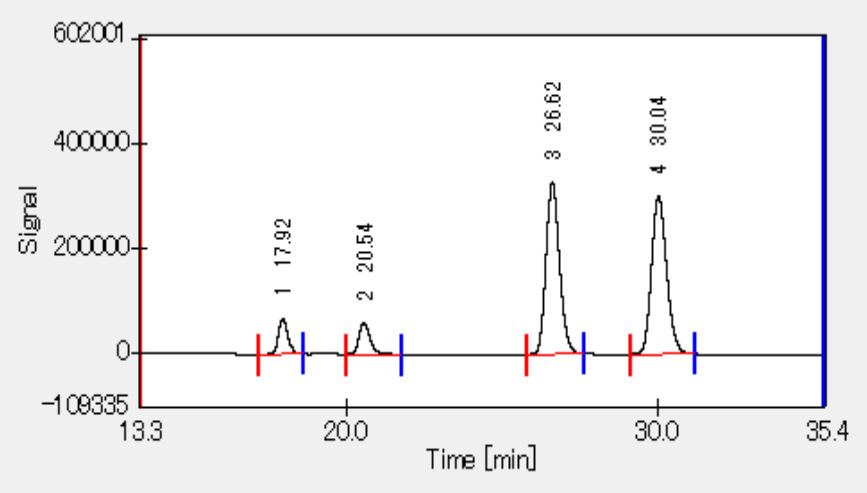


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	12.86	209456.1	2.5024	14825	18730.2	*****	0.597
2	13.23	425709.4	5.086	12778	3568.8	*****	9.487
3	22.16	5227444	62.4524	139703	7830.9	1.258	*****
4	24.38	2507674	29.9592	134800	*****	*****	*****
		8370283	100	302106			

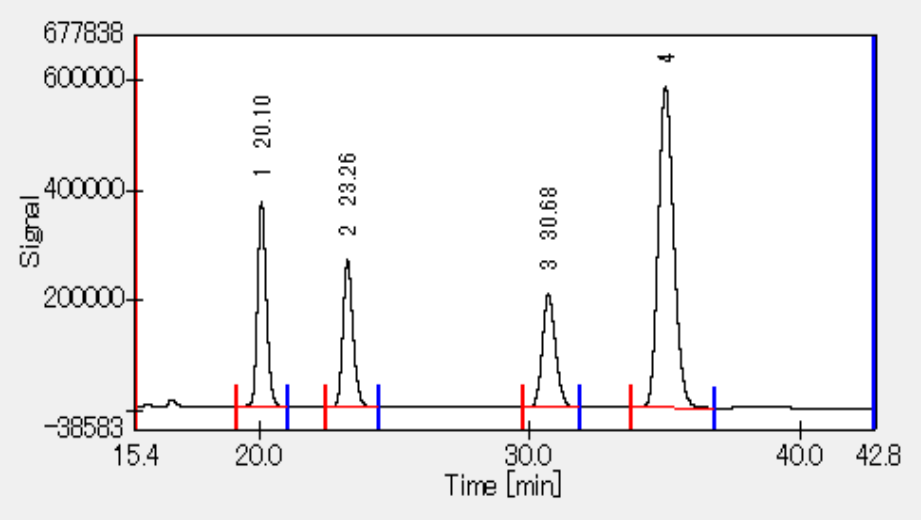


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	11.43	2224224	7.874	77191	3561.3	*****	1.084
2	12.12	1341442	4.7489	70488	9179.4	*****	5.262
3	16.04	6958953	24.6356	188601	4274.6	1.273	4.404
4	20.35	17722970	62.7415	482426	6913.4	1.366	*****
		28247590	100	818706			

2-[Hydroxy-(4-chlorophenyl)-methyl]-cyclohexan-1-one (**7d**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm,* 54*% ee*

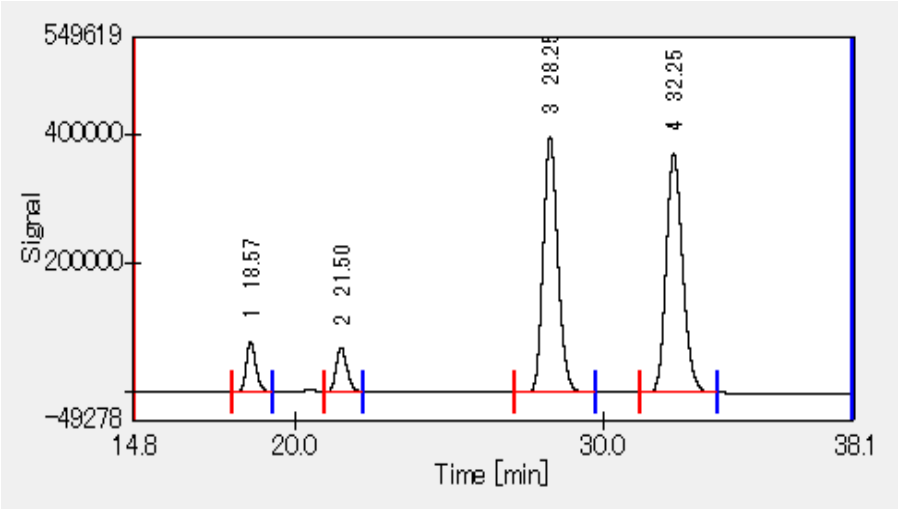


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	17.92	1427074	6.1949	68079	15406.1	1.237	4.228
2	20.54	1480476	6.4267	60301	15346.9	1.201	8.222
3	26.62	9913909	43.0361	327524	17078.6	1.157	3.968
4	30.04	10214813	44.3423	302860	17405	1.17	*****
		23036272	100	758764			

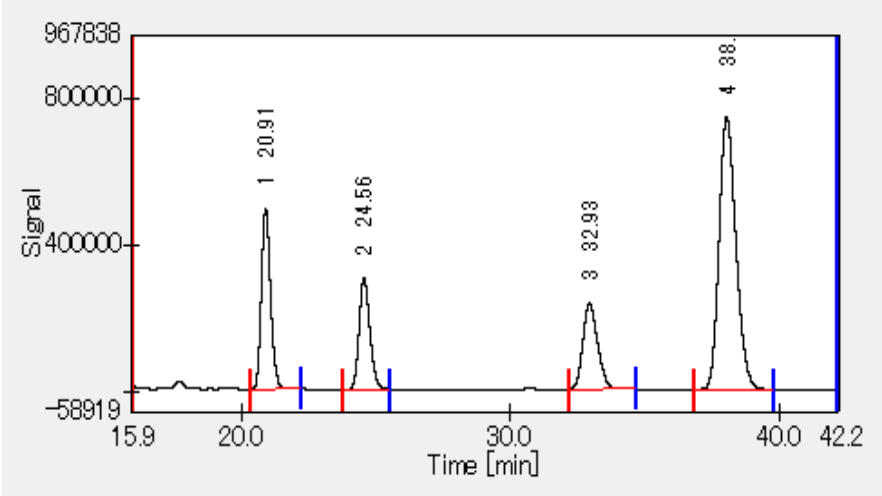


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	20.1	8406709	18.611	372449	17380.6	1.162	4.811
2	23.26	6872339	15.2142	266300	17334.5	1.206	9.137
3	30.68	6897315	15.2695	205260	17895.5	1.141	4.348
4	35	22994285	50.9054	582019	17179.3	1.164	*****
		45170647	100	1426028			

2-[Hydroxy-(4-bromophenyl)-methyl]-cyclohexan-1-one (**7e**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 57% ee*

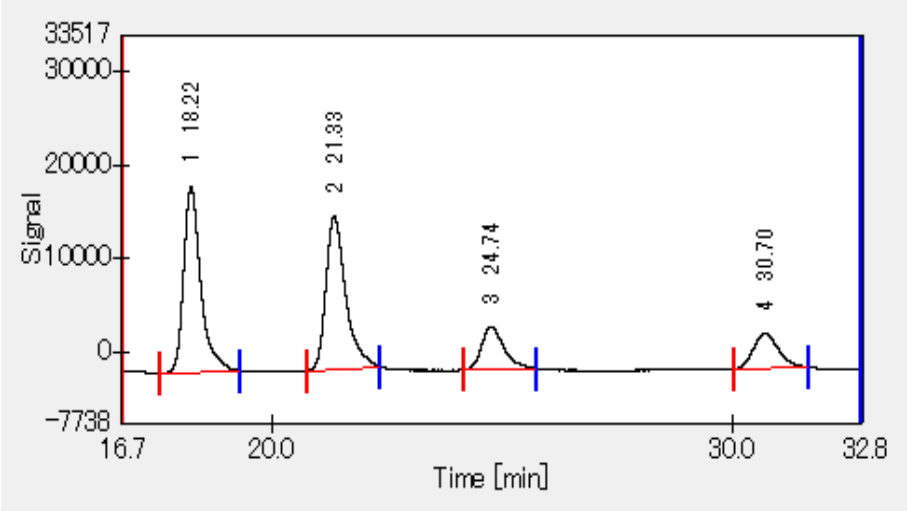


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.57	1738472	5.7133	80017	15708.4	1.231	4.633
2	21.5	1721194	5.6565	70077	16509.3	1.214	8.668
3	28.25	13152200	43.2232	400422	16153.7	1.177	4.228
4	32.25	13816668	45.4069	372298	16541.6	1.183	*****
		30428534	100	922814			

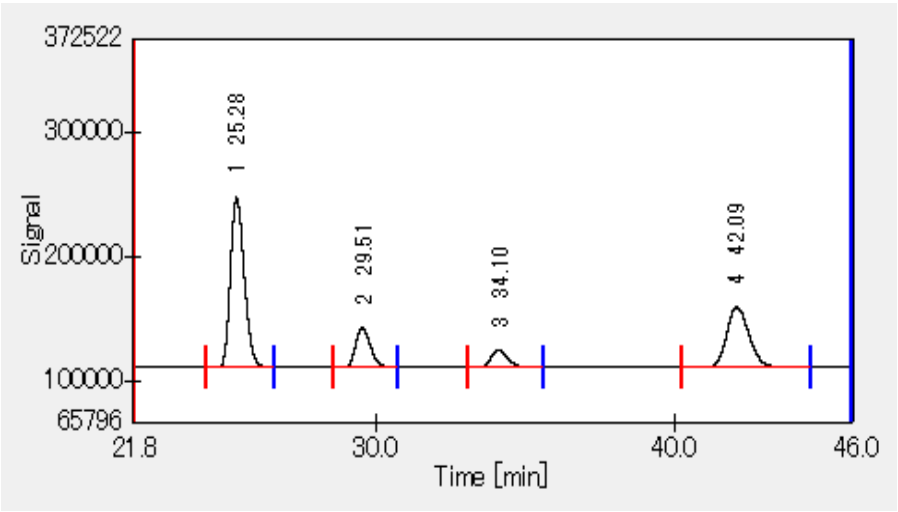


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	20.91	11635711	19.0473	493845	17170.3	1.192	5.276
2	24.56	8406015	13.7604	305910	17378.5	1.2	*****
3	32.93	8823700	14.4441	234793	16644.3	1.177	4.643
4	38.01	32223206	52.7483	743538	16969.7	1.194	*****
		61088632	100	1778086			

2-[Hydroxy-(4-cyanophenyl)-methyl]-cyclohexan-1-one (**7f**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm,* 65*% ee*

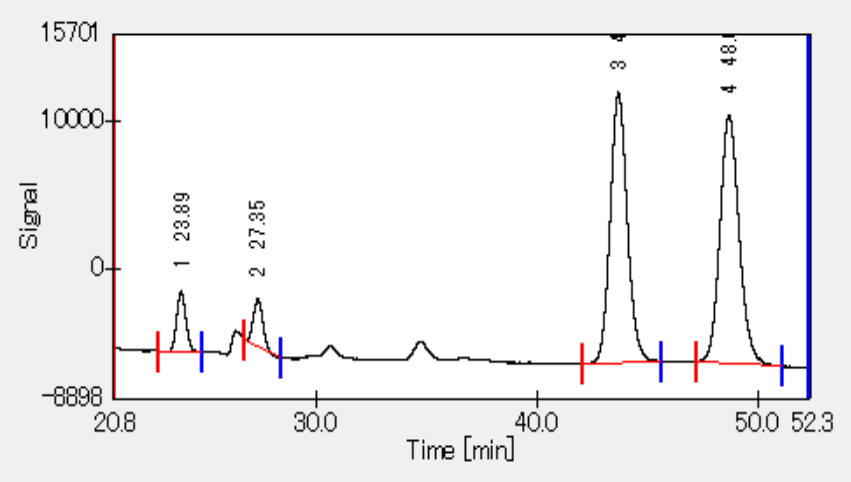


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.22	508061.2	39.5133	19766	10313.7	1.489	3.999
2	21.33	484747.5	37.7002	16262	10329	1.499	3.836
3	24.74	152003.3	11.8217	4512	11125.7	1.392	6.002
4	30.7	140984.4	10.9648	3687	13732.3	1.215	*****
		1285796	100	44227			

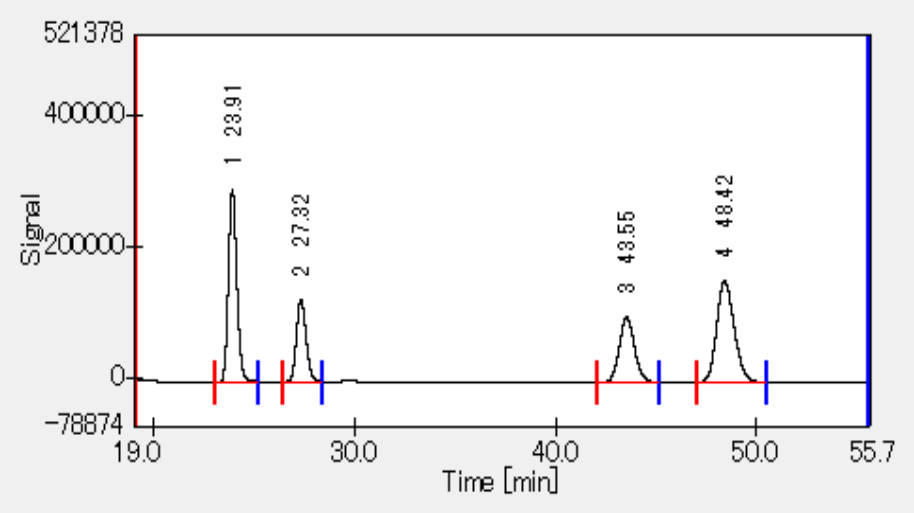


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	25.28	4392204	51.168	135856	13831.2	1.231	4.709
2	29.51	1111447	12.948	31940	15887.8	1.223	4.558
3	34.1	547062.3	6.3731	13632	16035.4	1.173	6.457
4	42.09	2533183	29.5109	48441	14550.8	1.195	*****
		8583896	100	229869			

2-[Hydroxy-(3-methoxyphenyl)-methyl]-cyclohexan-1-one (**7g**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm, 29% ee*

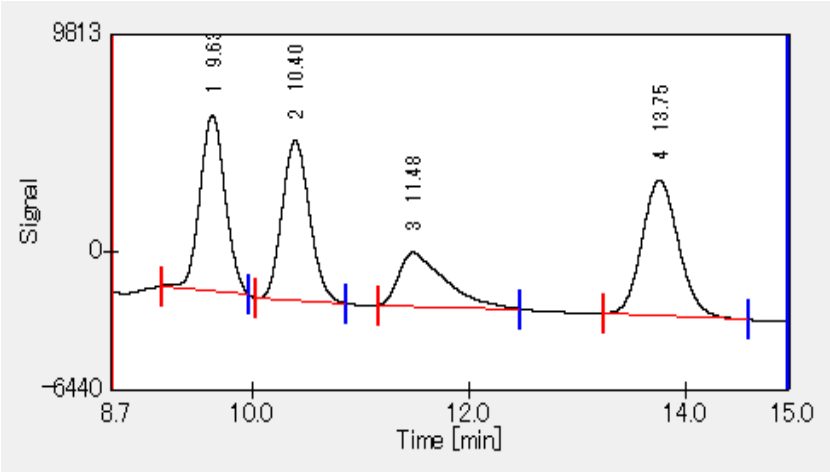


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	23.89	117216.5	5.3369	4083	15131.4	1.137	4.406
2	27.35	92323.8	4.2036	3140	19058	1.104	14.512
3	43.66	976892.6	44.4785	18222	14397.1	1.106	3.243
4	48.65	1009891	45.981	16749	14330.3	1.138	*****
		2196324	100	42194			

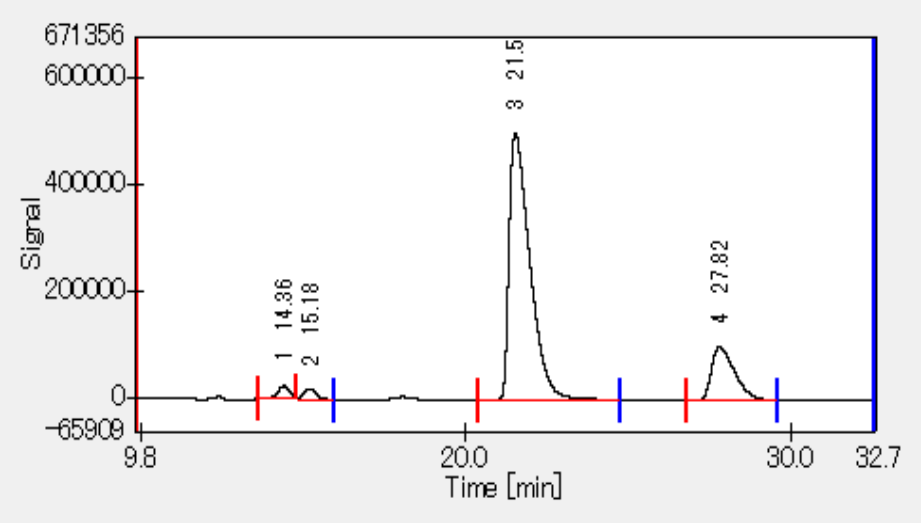


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	23.91	8614209	31.2178	295362	14872.7	1.162	4.032
2	27.32	4258499	15.4327	125999	14455.3	1.174	13.977
3	43.55	5251424	19.0311	100274	15200	1.091	3.192
4	48.42	9469792	34.3184	155599	13935.1	1.199	*****
		27593924	100	677234			

2-[Hydroxy-(4-methylphenyl)-methyl]-cyclohexan-1-one (**7h**)**:** *AS-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 63% ee*

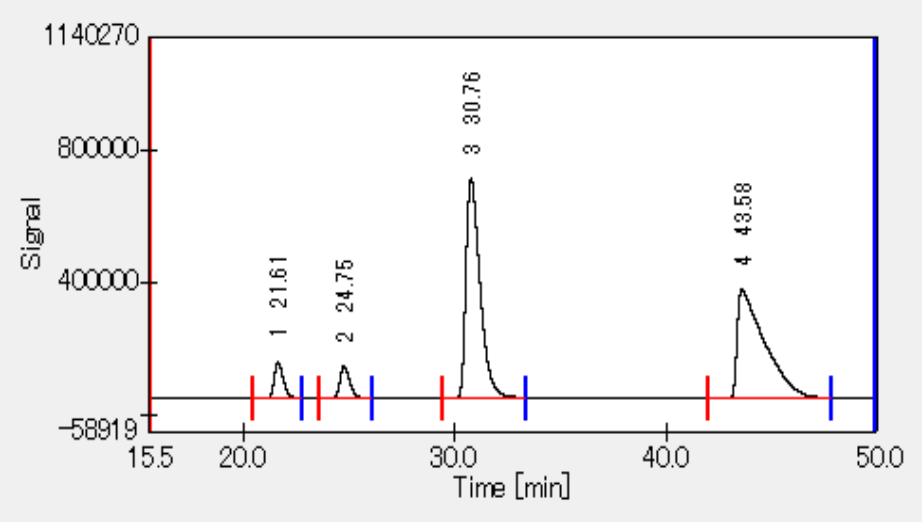


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	9.63	128755.1	29.4393	8062	8041.6	1.095	1.716
2	10.4	124406.8	28.445	7247	8181.5	1.098	2.179
3	11.48	39635.4	9.0625	1996	7465.3	1.197	3.931
4	13.75	144561.2	33.0533	6208	7739.9	1.112	*****
		437358.5	100	23513			

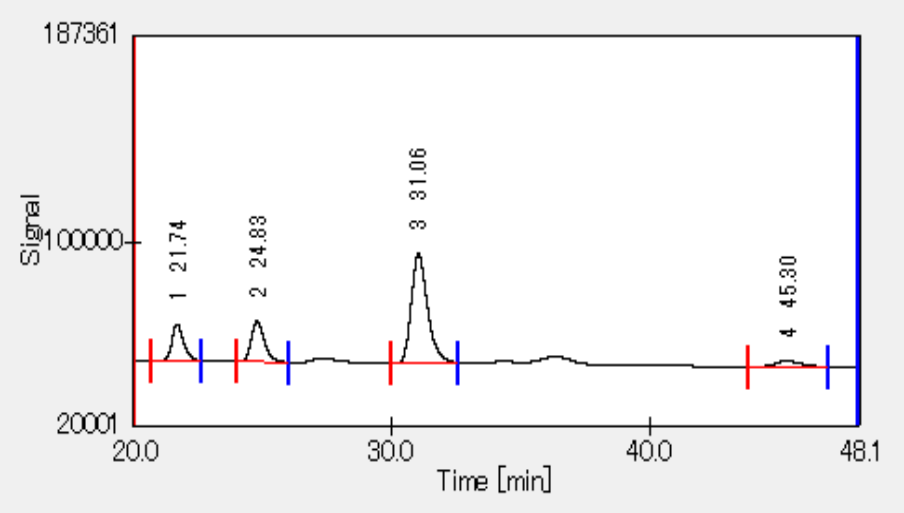


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	14.36	658185.9	2.3275	24178	6297	*****	1.153
2	15.18	522114.3	1.8464	20038	7677.2	*****	6.757
3	21.52	22148323	78.3231	498128	5206.2	2.093	4.968
4	27.82	4949514	17.503	99344	6846.8	1.628	*****
		28278138	100	641688			

2-[Hydroxy-(phenyl)-methyl]-cyclohexan-1-one (**7i**)**:** *OD-H column, n-hexane/iso-propanol = 97/3, flow rate = 0.8mL/min,* λ*=254 nm, 87% ee*

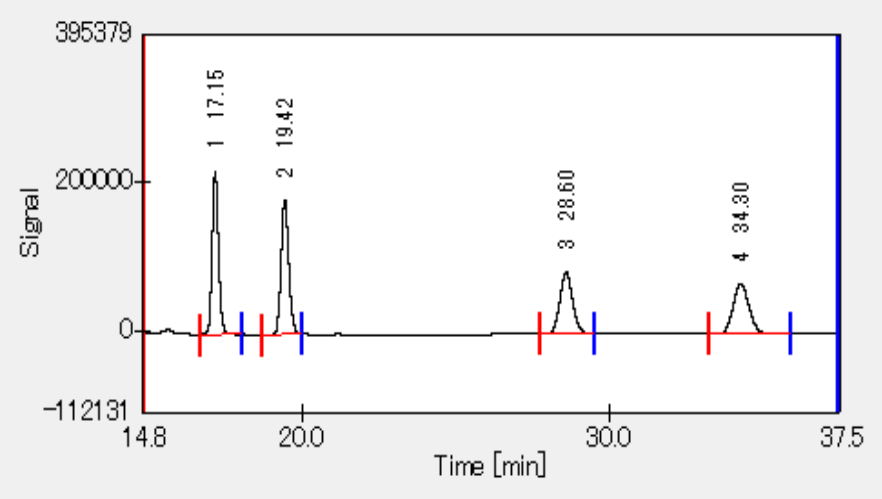


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	21.61	3358867	4.9644	109482	11022.9	1.358	3.644
2	24.75	3204930	4.7369	96711	12147.5	1.327	5.606
3	30.76	31051137	45.8935	668264	9735.3	1.664	6.624
4	43.58	30044127	44.4052	332902	4415.1	3.916	*****
		67659061	100	1207359			

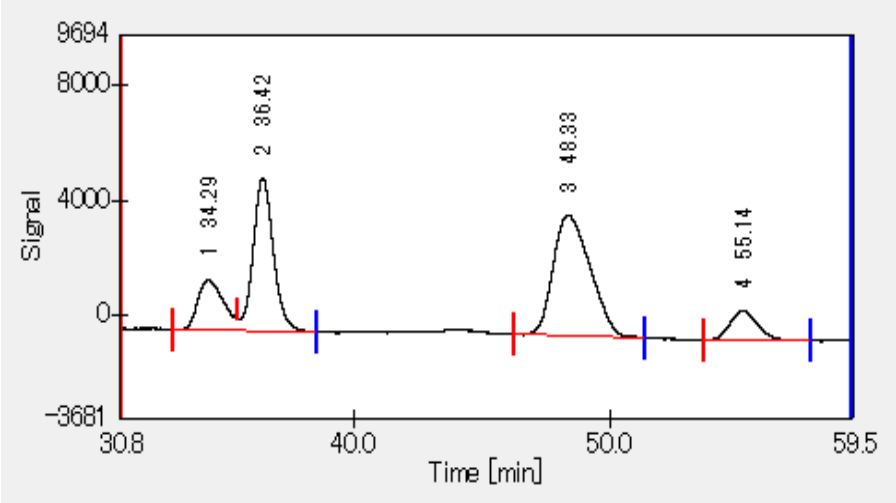


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	21.74	492189	14.8773	15896	10455	1.281	3.439
2	24.83	598316.3	18.0852	17391	11054.5	1.31	5.787
3	31.06	2069215	62.5457	46952	10527.3	1.288	10.13
4	45.3	148602.2	4.4918	2528	12828	1.155	*****
		3308323	100	82767			

2-[Hydroxy-(napthyl)-methyl]-cyclohexan-1-one (**7j**)**:** *AS-H column, n-hexane/iso-propanol = 98/2, flow rate = 1.0 mL/min,* λ*=254 nm,* 69*% ee*

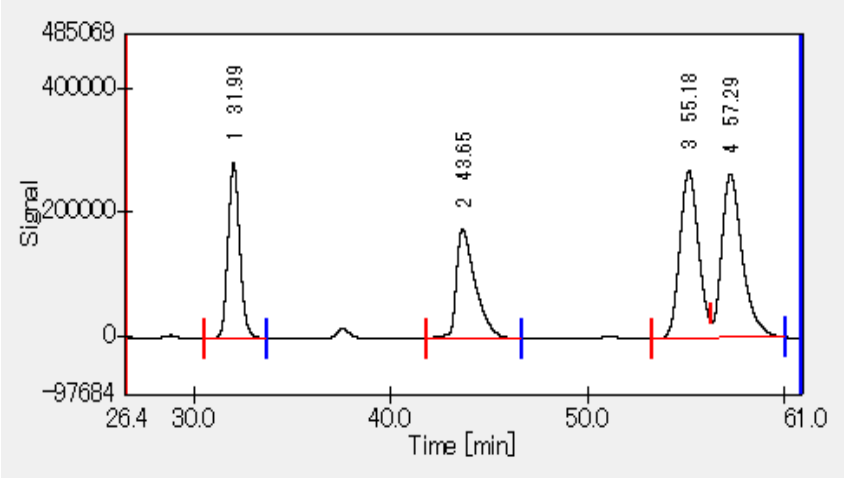


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	17.15	3111221	28.1379	217115	31437.6	1.141	5.274
2	19.42	3115565	28.1772	180675	26995.9	1.139	14.681
3	28.6	2405972	21.7596	83236	21602.4	1.086	6.519
4	34.3	2424289	21.9253	67295	19989.7	1.103	*****
		11057047	100	548321			

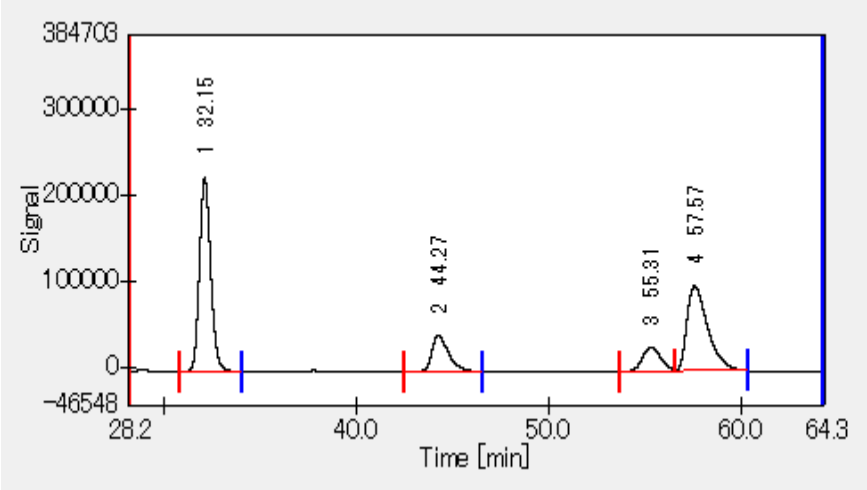


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	34.29	127028.2	13.8648	1790	5281.1	*****	1.268
2	36.42	295663.4	32.2708	5359	9855	*****	5.792
3	48.33	417777.2	45.5992	4199	5473.8	1.297	2.945
4	55.14	75725.4	8.2652	1022	11989.3	1.168	*****
		916194.2	100	12370			

2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclopentan-1-one (**7k**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 0.5 mL/min, λ=265 nm,* 60*% ee*

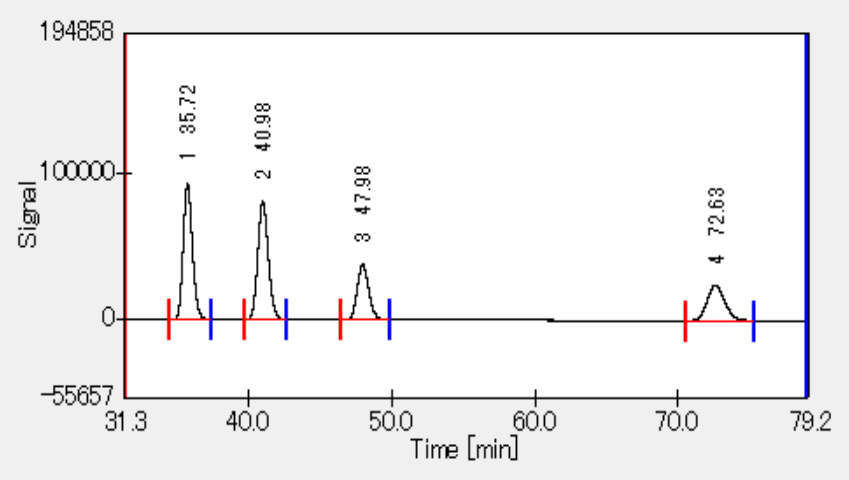


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	31.99	11669120	19.1996	282137	13232.8	1.13	7.819
2	43.65	11844749	19.4886	176378	8700.9	1.855	6.235
3	55.18	17853665	29.3753	269628	15708	*****	1.136
4	57.29	19410305	31.9365	264079	13741.8	*****	*****
		60777840	100	992222			

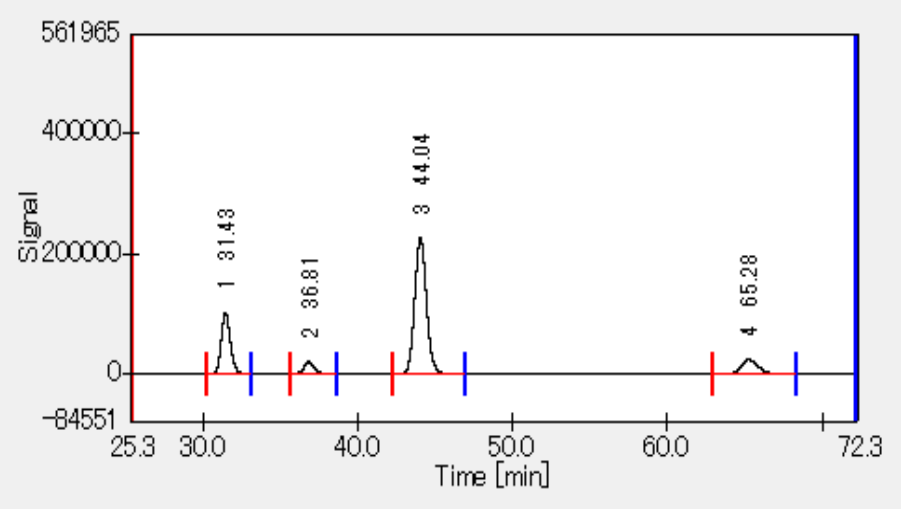


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	32.15	9092081	43.5549	224853	14034.8	1.167	8.916
2	44.27	2454550	11.7583	41166	11779.7	1.497	6.478
3	55.31	1856040	8.8912	28279	16061.7	*****	1.205
4	57.57	7472323	35.7956	99083	13179.9	1.693	*****
		20874994	100	393381			

2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclopentan-1-one (**7l**)**:** *AD-H column, n-hexane/iso-propanol = 95/5, flow rate = 1.0 mL/min, λ=269 nm, 73% ee*

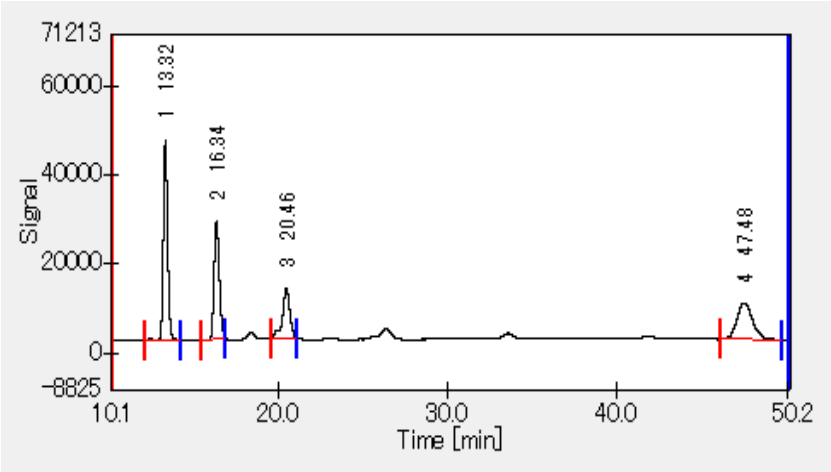


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	35.72	4227655	33.3948	93431	13657.3	1.167	4.039
2	40.98	4180548	33.0227	81112	14002.1	1.117	4.798
3	47.98	2146403	16.9547	38023	15735.6	1.119	12.757
4	72.63	2105033	16.6279	24382	15471.1	1.13	*****
		12659639	100	236948			

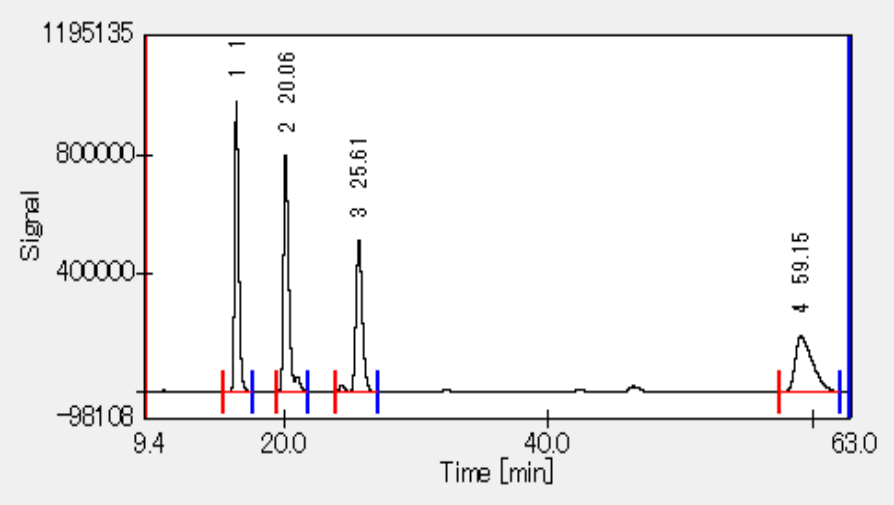


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	31.43	4156267	21.712	101429	13012.3	1.202	4.546
2	36.81	954999.1	4.9888	20486	13584.4	1.142	5.376
3	44.04	12130349	63.3679	228867	15242	1.088	11.906
4	65.28	1901118	9.9313	23962	14870.4	1.171	*****
		19142734	100	374744			

2-[Hydroxy-(4-nitrophenyl)-methyl]-cycloheptan-1-one(**7m**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm,* 14*% ee*

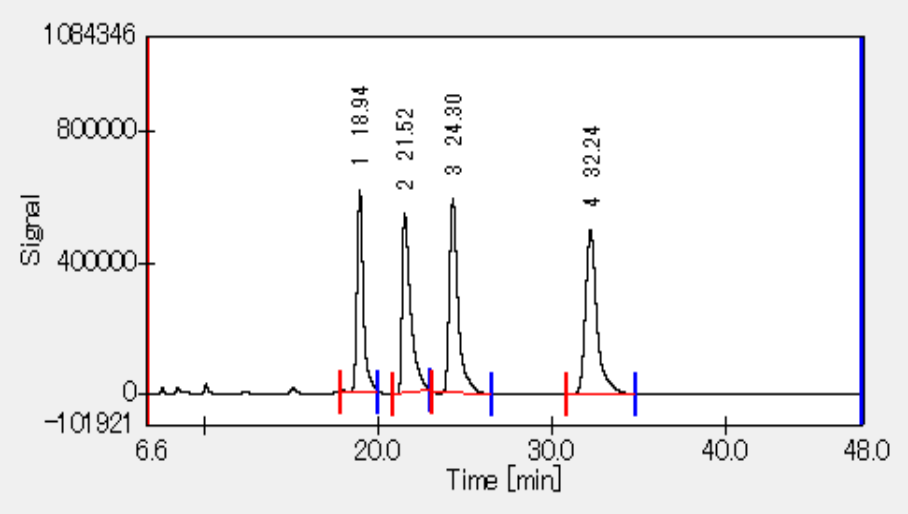


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.32	786752.4	35.5983	44893	13010	1.161	5.822
2	16.34	558078.5	25.2515	26504	13120.1	1.167	5.255
3	20.46	339727.3	15.3717	11406	6700.9	0.824	19.862
4	47.48	525524.6	23.7785	8224	12184.7	1.161	*****
		2210083	100	91027			

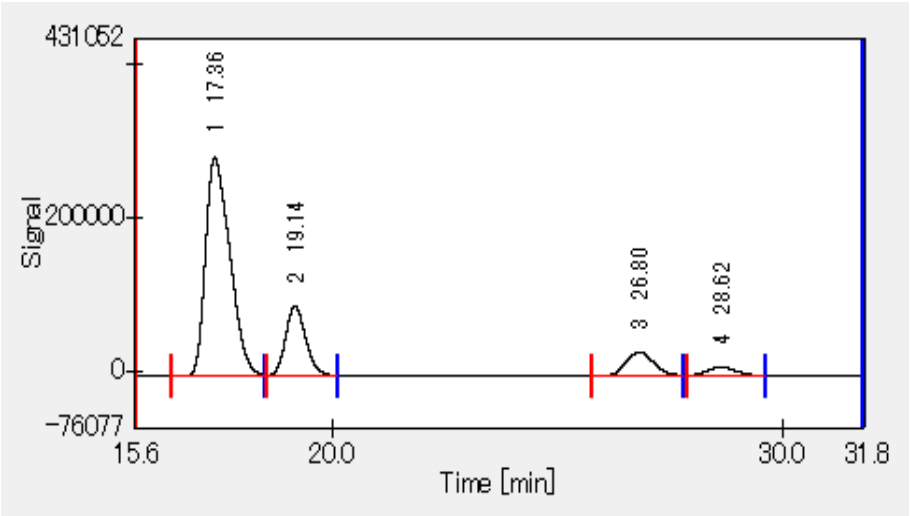


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	16.32	21194419	26.853	982267	12752	1.311	5.724
2	20.06	22732271	28.8014	799711	12159.4	1.418	6.818
3	25.61	17728896	22.4622	510098	12886.2	1.204	19.732
4	59.15	17272030	21.8834	191068	8979.3	1.723	*****
		78927616	100	2483144			

2-[Hydroxy-(4-nitrophenyl)-methyl]-4-methylcyclohexan-1-one(**7n**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm,* 58*% ee*

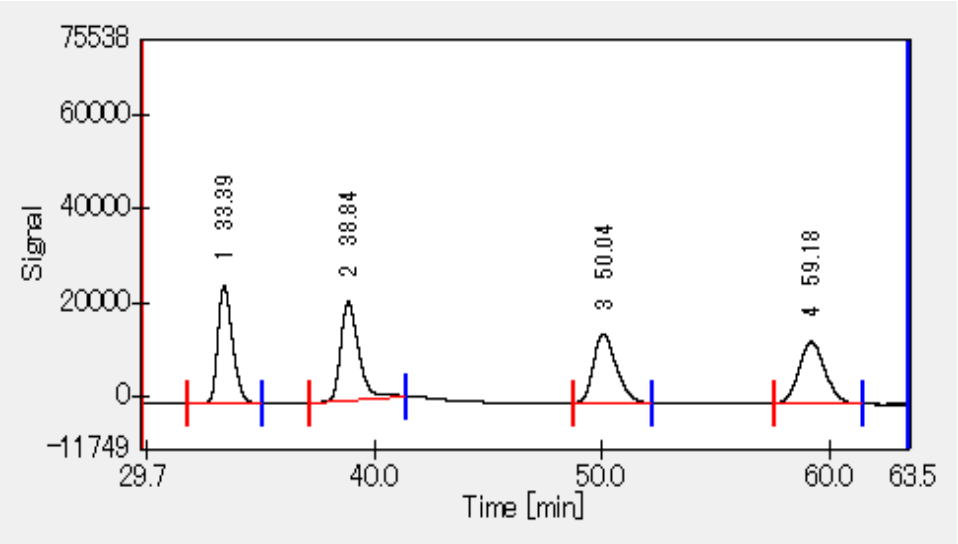


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.94	15406185	19.7134	613926	11992.6	1.467	3.054
2	21.52	18723599	23.9583	547440	7404.6	2.403	2.811
3	24.3	20687513	26.4713	591091	9880.7	1.712	6.996
4	32.24	23333454	29.857	499508	9973.7	1.539	*****
		78150751	100	2251965			

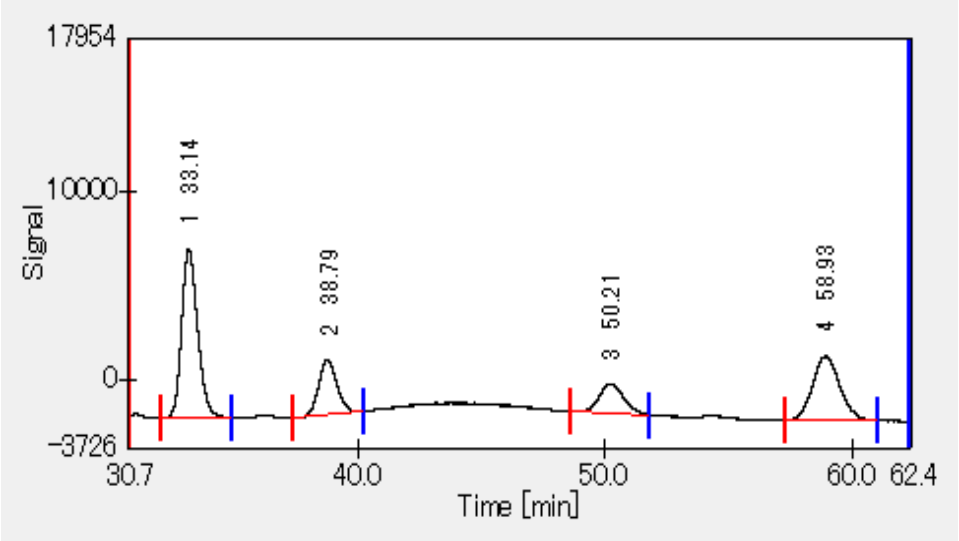


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	17.36	10667100	69.8405	284295	4869.3	1.42	1.95
2	19.14	2801843	18.3445	90374	8363.9	1.187	7.659
3	26.8	1344215	8.801	30967	8498.4	1.086	1.565
4	28.62	460348.8	3.014	10530	9700.1	1.098	*****
		15273507	100	416166			

2-[Hydroxy-(4-nitrophenyl)-methyl]-dihydro-2H-pyran-4-one (**7o**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 43% ee*



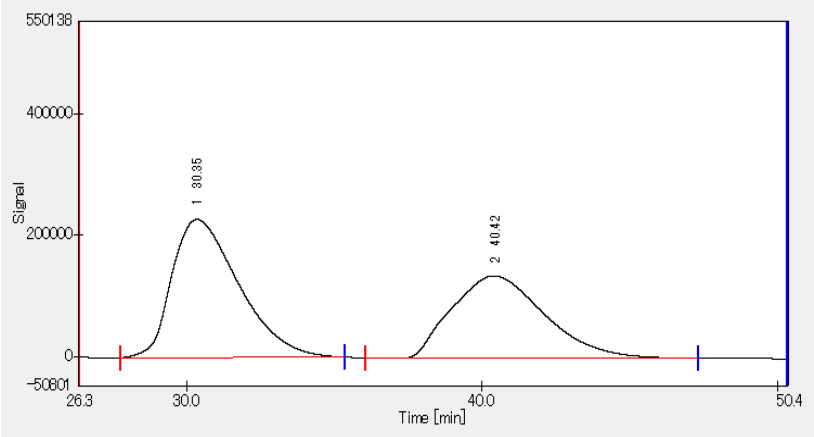
No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	33.39	1129277	26.0882	25069	12015.4	1.323	4.117
2	38.84	1125845	26.0089	20874	11798.3	1.349	6.79
3	50.04	1021881	23.6071	14801	11476.3	1.285	4.522
4	59.18	1051692	24.2958	13129	11891.8	1.133	*****
		4328696	100	73873			



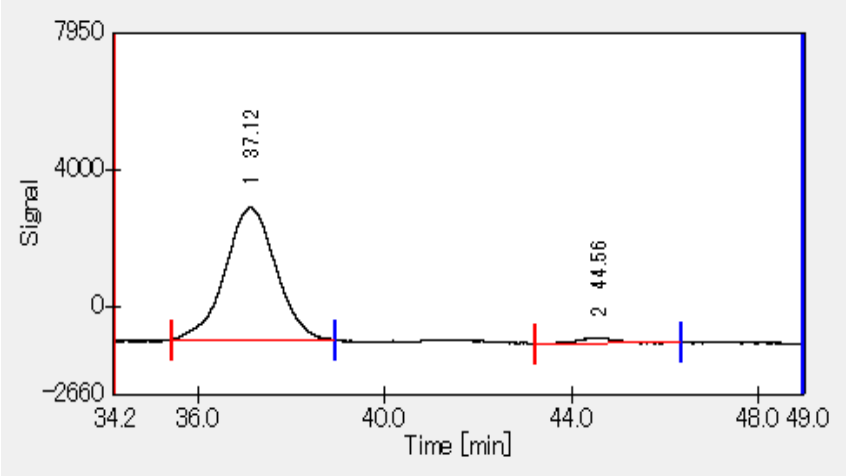
No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	33.14	401302.2	43.9729	8940	12015.9	1.243	4.334
2	38.79	147973.6	16.2143	2880	12342.2	1.086	7.03
3	50.21	104768.5	11.4801	1536	11745.1	1.126	4.436
4	58.93	258567.4	28.3327	3390	12847.9	1.092	*****

912611.7 100 16746

3-Hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**7p**)**:** *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, 94% ee*

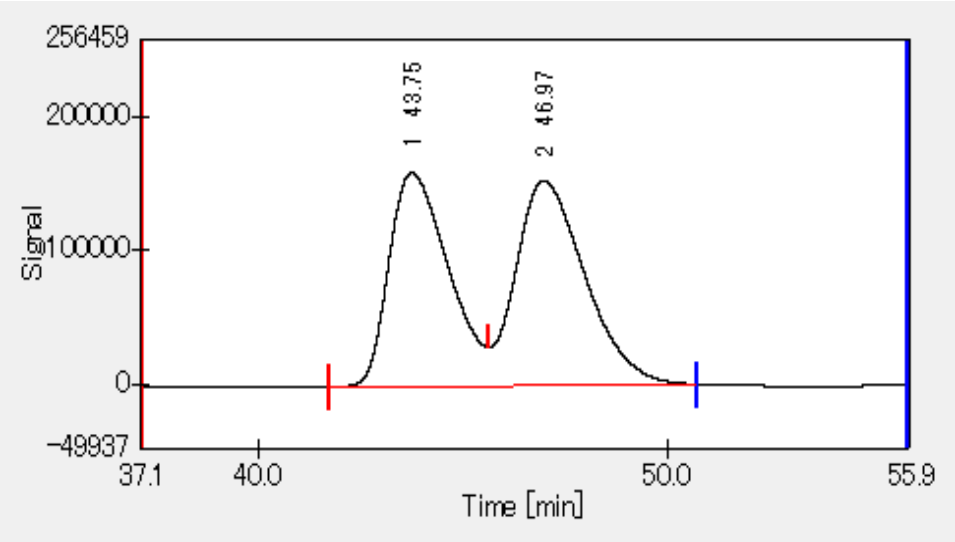


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	30.35	35834005	54.9044	227552	832.2	1.498	2.012
2	40.42	29432132	45.0956	135561	776.4	1.311	*****
		65266137	100	363113			



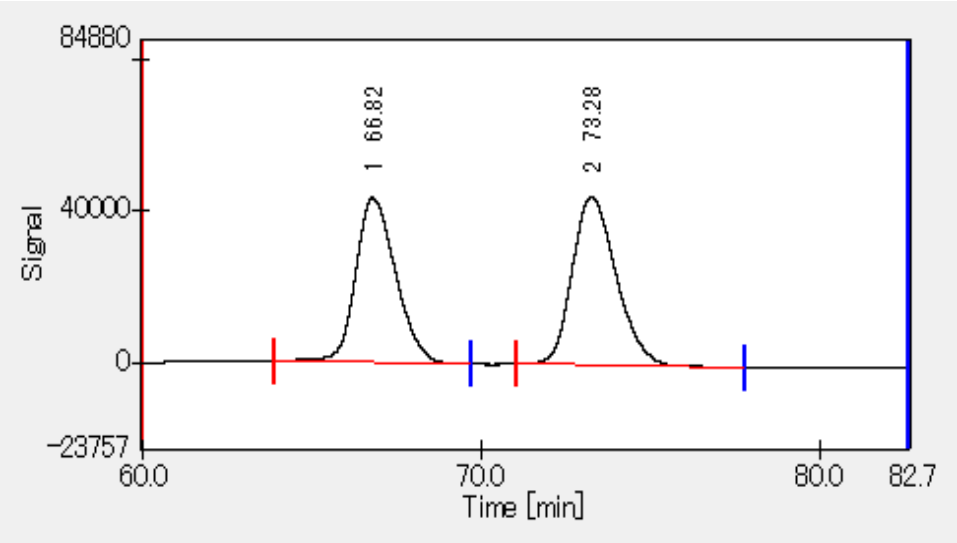
No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	37.12	293439	97.0904	3873	5178.9	0.991	4.288
2	44.56	8793.8	2.9096	164	15982.2	1.022	*****
		302232.8	100	4037			

3-Hydroxy-3-(4-nitrophenyl)-1-propylpropan-1-one (**7q**)**:** *AS-H column, n-hexane/iso-propanol = 70/30, flow rate = 0.6 mL/min, λ=254 nm.*



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	43.75	16132516	47.1717	159998	4257.9	*****	1.109
2	46.97	18067061	52.8283	153055	3581.8	*****	*****
		34199577	100	313053			

3-Hydroxy-3-(4-nitrophenyl)-2,3-dimethylpropan-1-one (**7r**)**:** *AS-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm*



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	66.82	3590435	47.1853	43595	14871.6	1.209	2.792
2	73.28	4018792	52.8147	44329	14505.8	1.221	*****
		7609227	100	87924			

6. Theoretical Calculations

The DFT method (at the B3LYP/6-31G(d) level of theory) was used to perform the conformational analysis with Gaussian 16 program package. The Gas phase geometry optimizations were performed using the B3LYP hybrid density functional and the 6-31G(d) basis set as implemented in the Gaussian 16. Vibrational mode analysis was performed for all structures to ensure that they have zero imaginary frequency.

1) Gaussian 16, Revision A.03,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Table S1. Cartesian coordinates (Angstroms) for **I-1** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -1451.8108 hartree

Symbol	X	Y	Z
C	-1.6391	2.398025	-0.6255
C	-0.34922	2.964355	-0.43233
C	-0.14475	4.297524	-0.83399
C	-1.15548	5.062136	-1.40685
C	-2.41269	4.48404	-1.58879
C	-2.662	3.168441	-1.20627
H	0.840728	4.730491	-0.68639
H	-0.96824	6.089158	-1.70763
H	-3.21835	5.06114	-2.03629
H	-3.63564	2.723825	-1.35198
B	0.866687	2.221639	0.182829
O	0.856929	0.908032	0.589817

O	2.090839	2.82013	0.357701
C	2.163409	0.552592	1.125952
C	3.020069	1.861102	0.898201
H	3.354585	2.255949	1.863968
C	1.932908	0.220714	2.600973
H	1.219148	-0.60582	2.68319
H	2.853889	-0.0705	3.110332
H	1.509858	1.087628	3.120604
C	2.708244	-0.62398	0.302201
H	2.082501	-1.5109	0.45238
C	4.241131	1.707032	-0.05513
H	4.126448	2.454966	-0.84742
H	5.163268	1.957795	0.482479
C	4.353455	0.306862	-0.67606
H	5.191974	0.256439	-1.38129
C	2.95093	-0.14283	-1.15554
H	2.980045	-0.96717	-1.87051
H	2.282097	0.62653	-1.55078
C	4.273674	-0.80589	0.424279
C	4.70289	-2.18501	-0.10682
H	5.789056	-2.21458	-0.25958
H	4.449053	-2.9699	0.616619
H	4.228661	-2.44837	-1.05638
C	5.018027	-0.57159	1.744245
H	4.767694	-1.34433	2.481661
H	6.100387	-0.6306	1.570834
H	4.820837	0.400956	2.202587
N	-1.86647	1.067949	-0.21451
H	-1.07226	0.558628	0.172652
C	-3.0144	0.32479	-0.31042
O	-4.06365	0.69364	-0.83021
C	-2.92737	-1.08145	0.333842
H	-3.51567	-1.72443	-0.33211
C	-3.64621	-1.1325	1.734625
C	-2.95318	-0.20931	2.758131

H	-3.00193	0.840016	2.449352
H	-3.44789	-0.29426	3.732644
H	-1.89602	-0.46084	2.90786
C	-3.63135	-2.58878	2.251108
H	-4.20764	-2.65813	3.180748
H	-4.08658	-3.27	1.522657
H	-2.6244	-2.96201	2.469279
C	-5.12176	-0.70483	1.593677
H	-5.62265	-0.8021	2.564494
H	-5.22201	0.327114	1.253156
H	-5.65167	-1.33983	0.874808
N	-1.54128	-1.56097	0.423518
H	-1.29551	-1.86196	1.358632
C	-1.01229	-2.44109	-0.5475
C	-0.22146	-3.4757	-0.20374
C	-1.31925	-2.10597	-1.99335
C	0.453765	-4.39305	-1.1937
H	-0.03729	-3.67006	0.854257
C	-0.35105	-2.79319	-2.96812
H	-2.35203	-2.40147	-2.23186
H	-1.27922	-1.01865	-2.1297
C	-0.14916	-4.26682	-2.60029
H	0.3759	-5.43307	-0.84672
H	1.53545	-4.18033	-1.23622
H	-0.72844	-2.69414	-3.99297
H	0.618626	-2.27669	-2.93657
H	0.494562	-4.76486	-3.33582
H	-1.1202	-4.78078	-2.62761

Table S2. Cartesian coordinates (Angstroms) for **I-2** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -1451.8010 hartree

Symbol	X	Y	Z
C	0.855865	2.24676	0.822282
C	-0.49461	2.431446	0.458758

C	-0.90956	3.758068	0.224152
C	-0.069	4.856253	0.387647
C	1.250408	4.646836	0.788618
C	1.708558	3.350335	0.992273
H	-1.93716	3.920128	-0.08737
H	-0.43884	5.861756	0.207345
H	1.92741	5.485316	0.929502
H	2.74567	3.181274	1.275473
B	-1.63858	1.362443	0.355989
O	-2.6054	1.509058	-0.61069
O	-1.9745	0.432226	1.313743
C	-3.75681	0.701434	-0.2569
C	-3.23621	-0.16782	0.949088
H	-3.89684	-0.03284	1.812063
C	-4.85716	1.687013	0.146721
H	-5.0484	2.380201	-0.67929
H	-5.79345	1.181318	0.396257
H	-4.54033	2.273827	1.0167
C	-4.13905	-0.16613	-1.46581
H	-4.53654	0.464374	-2.27038
C	-3.08187	-1.68743	0.647239
H	-2.02021	-1.93306	0.723137
H	-3.60449	-2.26773	1.417984
C	-3.57939	-2.08504	-0.75261
H	-3.47253	-3.1658	-0.91032
C	-2.95519	-1.11766	-1.78959
H	-2.99112	-1.49941	-2.8121
H	-1.94732	-0.75049	-1.58852
C	-4.9742	-1.44912	-1.07392
C	-5.62777	-2.07473	-2.31899
H	-5.98816	-3.08668	-2.09407
H	-6.49294	-1.47956	-2.63806
H	-4.94733	-2.14855	-3.17167
C	-6.03629	-1.42368	0.032466
H	-6.90858	-0.83052	-0.27008

H	-6.39243	-2.44465	0.223129
H	-5.68008	-1.02602	0.985849
N	1.451966	0.981111	1.026965
H	2.403756	0.998669	1.385835
C	1.179893	-0.19619	0.386624
O	0.205734	-0.40156	-0.33015
C	2.236	-1.29712	0.647498
H	2.135906	-1.97378	-0.21148
C	1.930634	-2.15739	1.928843
C	2.172283	-1.37351	3.235849
H	1.526869	-0.49204	3.298812
H	1.944884	-2.01522	4.094906
H	3.211048	-1.04145	3.347846
C	2.831569	-3.41203	1.902769
H	2.612884	-4.04802	2.768099
H	2.65585	-4.00431	0.997187
H	3.901312	-3.17394	1.941135
C	0.461422	-2.618	1.900499
H	0.278412	-3.32046	2.7222
H	-0.22654	-1.77647	2.01584
H	0.219222	-3.12529	0.960082
N	3.590429	-0.71363	0.715897
H	4.152727	-1.18712	1.415006
C	4.341143	-0.57549	-0.4855
C	5.625384	-0.96679	-0.55162
C	3.637485	0.100501	-1.64452
C	6.505532	-0.78116	-1.76251
H	6.07936	-1.44002	0.320657
C	4.618895	0.581154	-2.72579
H	2.902006	-0.58828	-2.08601
H	3.05654	0.952813	-1.27189
C	5.68545	-0.47736	-3.02427
H	7.112423	-1.68404	-1.91743
H	7.22931	0.031849	-1.58606
H	4.063373	0.844328	-3.63361

H	5.113096	1.499937	-2.38068
H	6.344619	-0.14327	-3.83481
H	5.19555	-1.39816	-3.37029

Table S3. Cartesian coordinates (Angstroms) for **I-A** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -1872.6596 hartree

Symbol	X	Y	Z
C	-0.88121	-2.4083	0.617541
C	-2.24912	-2.63383	0.928211
C	-2.61503	-3.90409	1.40783
C	-1.68285	-4.92251	1.582031
C	-0.34506	-4.67383	1.271949
C	0.063569	-3.43071	0.792977
H	-3.65971	-4.08152	1.647522
H	-1.99221	-5.89465	1.955132
H	0.398817	-5.45566	1.402825
H	1.100536	-3.24081	0.557609
B	-3.37136	-1.56833	0.787131
O	-3.17144	-0.28312	0.325356
O	-4.68018	-1.81431	1.108992
C	-4.42678	0.46149	0.399013
C	-5.47075	-0.63891	0.839691
H	-5.93002	-0.34778	1.790081
C	-4.20569	1.550357	1.449182
H	-3.36006	2.181214	1.155884
H	-5.08373	2.188431	1.570641
H	-3.97035	1.09872	2.419225
C	-4.74063	1.005385	-1.00207
H	-4.00431	1.767433	-1.28414
C	-6.58079	-0.96629	-0.20128
H	-6.51271	-2.03729	-0.42181
H	-7.56668	-0.80008	0.248463
C	-6.44833	-0.16074	-1.50228
H	-7.22846	-0.4431	-2.21928

C	-4.97038	-0.19252	-1.96511
H	-4.83845	0.078144	-3.01405
H	-4.40171	-1.10695	-1.77499
C	-6.26587	1.367386	-1.20582
C	-6.4549	2.233384	-2.46381
H	-7.51517	2.273492	-2.74252
H	-6.12361	3.261868	-2.27396
H	-5.89971	1.864035	-3.33043
C	-7.10585	1.994244	-0.08669
H	-6.78611	3.023488	0.11742
H	-8.15702	2.039575	-0.39923
H	-7.07675	1.444476	0.857541
N	-0.52105	-1.13241	0.12723
H	-1.30175	-0.4911	0.026042
C	0.698882	-0.62603	-0.20678
O	1.752605	-1.26511	-0.10129
C	0.66761	0.824709	-0.74401
H	-0.30292	1.262219	-0.47976
C	0.741025	0.884265	-2.31417
C	2.090286	0.380054	-2.86165
H	2.280645	-0.65919	-2.57649
H	2.082818	0.43166	-3.95715
H	2.929485	0.987061	-2.50932
C	0.534375	2.351745	-2.73872
H	0.583808	2.440058	-3.83069
H	-0.44696	2.723316	-2.41682
H	1.298638	2.999018	-2.30118
C	-0.39321	0.028973	-2.91546
H	-0.41766	0.156936	-4.00382
H	-0.25855	-1.03943	-2.71411
H	-1.37583	0.325094	-2.52573
N	1.682912	1.643211	-0.11863
H	2.63968	1.394381	-0.36718
C	1.559115	2.064602	1.214408
C	0.458232	1.93386	1.983367

C	2.813958	2.750327	1.724164
C	0.347665	2.477407	3.389426
H	-0.42136	1.419538	1.604896
C	2.562511	3.600586	2.975482
H	3.576383	1.98595	1.933962
H	3.231458	3.367561	0.918719
C	1.713572	2.832131	3.993002
H	-0.15988	1.742169	4.030381
H	-0.29888	3.372056	3.404396
H	3.520491	3.905124	3.41524
H	2.037362	4.523531	2.691222
H	1.58318	3.417156	4.912359
H	2.238592	1.908342	4.273803
C	7.429198	0.727756	-0.72564
C	8.810212	0.569424	-0.80893
C	9.372495	-0.70745	-0.72758
C	8.550917	-1.82526	-0.56267
C	7.168178	-1.67054	-0.47887
C	6.601701	-0.39093	-0.5605
H	6.970006	1.708904	-0.78604
H	9.448901	1.439097	-0.93699
H	10.45044	-0.83116	-0.79248
H	8.988368	-2.81788	-0.49911
H	6.521773	-2.53154	-0.35045
C	5.128716	-0.17679	-0.47589
O	4.616262	0.936545	-0.54265
O	4.435026	-1.30324	-0.32516
H	3.460152	-1.10817	-0.26546

Table S4. Cartesian coordinates (Angstroms) for **I-A'** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -1872.6558 hartree

Symbol	X	Y	Z
C	-0.91509	-2.31679	0.807286
C	-2.28741	-2.51931	1.11485

C	-2.66179	-3.75332	1.676057
C	-1.73398	-4.75824	1.932111
C	-0.39207	-4.53312	1.622053
C	0.025005	-3.32639	1.06387
H	-3.70998	-3.91331	1.912539
H	-2.05004	-5.70211	2.367047
H	0.348652	-5.30489	1.815445
H	1.064602	-3.15612	0.825607
B	-3.40925	-1.47049	0.878768
O	-3.20372	-0.21317	0.347117
O	-4.72585	-1.70772	1.174657
C	-4.46843	0.518967	0.325311
C	-5.51677	-0.55962	0.807778
H	-6.00536	-0.2113	1.723782
C	-4.29565	1.681905	1.302514
H	-3.45573	2.309721	0.986837
H	-5.18845	2.308361	1.358511
H	-4.07692	1.302558	2.306779
C	-4.73842	0.957438	-1.12128
H	-3.99677	1.702362	-1.43374
C	-6.59388	-0.96459	-0.2403
H	-6.51795	-2.04856	-0.38001
H	-7.5934	-0.76945	0.165597
C	-6.42195	-0.25521	-1.5916
H	-7.17602	-0.59504	-2.31148
C	-4.92909	-0.30907	-2.00161
H	-4.76321	-0.11404	-3.06242
H	-4.36229	-1.20298	-1.72708
C	-6.2577	1.29188	-1.40174
C	-6.40865	2.062263	-2.72536
H	-7.45908	2.073472	-3.04145
H	-6.08967	3.104499	-2.60045
H	-5.82249	1.635006	-3.54358
C	-7.13822	1.992156	-0.36005
H	-6.8293	3.035235	-0.21916

H	-8.17803	2.008881	-0.71097
H	-7.14025	1.511208	0.621458
N	-0.54477	-1.07458	0.242687
H	-1.31889	-0.43005	0.116646
C	0.671143	-0.62382	-0.1816
O	1.708028	-1.29317	-0.10021
C	0.654597	0.814579	-0.74553
H	-0.32751	1.244523	-0.52637
C	0.779308	0.856736	-2.31034
C	2.159988	0.388908	-2.80833
H	2.366279	-0.64592	-2.51981
H	2.19255	0.444999	-3.90321
H	2.967082	1.017544	-2.42081
C	0.545234	2.312589	-2.75861
H	0.641947	2.394963	-3.8478
H	-0.46175	2.655335	-2.4862
H	1.269001	2.985107	-2.29095
C	-0.31048	-0.04153	-2.93016
H	-0.30353	0.06044	-4.02155
H	-0.15212	-1.10107	-2.69915
H	-1.31323	0.23504	-2.57862
N	1.654252	1.647784	-0.08929
H	2.602771	1.3024	-0.23736
C	1.477762	2.094458	1.242833
C	2.507121	2.109219	2.111305
C	0.1287	2.692656	1.592713
C	2.469081	2.776583	3.46376
H	3.450494	1.660699	1.806081
C	0.002457	3.046693	3.083633
H	-0.03139	3.586629	0.970104
H	-0.68465	2.001313	1.33387
C	1.27152	3.725321	3.605098
H	3.405428	3.328248	3.630642
H	2.432474	2.017716	4.263623
H	-0.87676	3.685936	3.23423

H	-0.17355	2.127924	3.660507
H	1.144629	4.032337	4.650973
H	1.458249	4.638967	3.023325
C	7.431869	0.506109	-0.58982
C	8.807884	0.321077	-0.69754
C	9.335552	-0.97152	-0.7604
C	8.484401	-2.07841	-0.71502
C	7.106569	-1.89699	-0.60694
C	6.574869	-0.60155	-0.54417
H	6.998852	1.499671	-0.53928
H	9.469602	1.182233	-0.7325
H	10.4096	-1.11604	-0.84448
H	8.89498	-3.08331	-0.76364
H	6.437345	-2.74935	-0.57049
C	5.108595	-0.35792	-0.42904
O	4.624467	0.767656	-0.37314
O	4.383194	-1.47585	-0.39712
H	3.418528	-1.25015	-0.30647

Table S5. Cartesian coordinates (Angstroms) for **6a** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -550.0714 hartree

Symbol	X	Y	Z
C	1.705107	0.22009	-2.1E-05
C	1.101116	-1.04673	0.000034
C	-0.28321	-1.15924	0.000031
C	-1.04631	0.010139	-5E-06
C	-0.47394	1.280261	-5.1E-05
C	0.914902	1.376822	-6.9E-05
H	1.73579	-1.927	0.000081
H	-0.78105	-2.12095	0.000049
H	-1.11183	2.155192	-6.2E-05
H	1.389592	2.355022	-0.00013
N	-2.51864	-0.10282	0.000003
C	3.18703	0.33683	-1.9E-05

H	3.572977	1.37923	-0.0001
O	3.945275	-0.61132	0.000062
O	-3.00166	-1.23338	-0.00014
O	-3.16901	0.940845	0.000166