Supporting Information

New Small γ-Turn Type *N*-Primary Amino Terminal Tripeptide Organocatalyst for solvent free Asymmetric Aldol Reaction of Various Ketones with Aldehydes

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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 under an inert atmosphere in flame dried and cooled glassware. The reaction progress was monitored by thin layer chromatography (TLC) using Merk silica plate gel 60 F_{254} aluminum sheet. The purification of products were carried out 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 the 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 was reported as: 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 was measured by JASCO DIP-360 polarimeter. The melting point was measured using a Yanaco micro melting point apparatus. High resolution mass spectra (HRMS) data was collected by electron impact (EI) using Hitachi RMG-GMG and JEOL JNK-DX303 sector instruments. The enantiomeric excess (*ee*) was determined using high pressure liquid chromatography (HPLC) principle by DAICEL CHIRALPAK AD-H, AS-H, IC columns.

2.Experimental procedure

2.1 General procedure for the synthesis of peptide organocatalysts 3a-d, 5a-h, 6a-j, 8, 9,12a,b, 13a,b and 14a,b

To a solution of *N*-Boc-L-Proline, **7** and **11a,b** (0.5mmol), *N,N'*-Dicyclohexylcarbodiimide (DCC) (0.6 mmol) was suspended in dry CH_2Cl_2 (5 ml) and stirred at 0 °C for 1 hour. The corresponding primary aromatic amines **2a-d** (0.55 mmol) 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, the insoluble by-product Dicyclohexyl urea (DCU) was filtered off and the filtrate was evaporated to dryness. The obtained oily residue was dissolved in $CHCl_3$ and washed consecutively with saturated aqueous $NaHCO_3$ solution, aqueous HCl (1.0 M) and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under a reduced pressure to afford the obtained crude products that were used for next step without further purification. To the solution of the crude products 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, DCM 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 on SiO_2 ($CHCl_3$: MeOH = 99:1 to 95: 5) to afford the corresponding amino amides **3a-d, 8** and **12a,b**.

2.1.1 L-Pro-Ph (3a)

Colorless solid. 90% yield. m p 73 °C. $[\alpha]_D^{20}$ = -71.87 (c = 0.64, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.73 (s, 1H), 7.60 (m, 2H), 7.30-7.34 (m, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 3.86 (dd, *J* = 9.0, 5.3 Hz, 1H), 3.06-3.11 (m, 1H), 2.96-3.00 (m, 1H), 2.18-2.25 (m, 1H), 2.01-2.08 (m, 1H), 1.70-1.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.5, 137.8, 128.9, 123.8, 119.2, 61.0, 47.3, 30.77, 26.3. MS (EI): m/z = 190 $[M]^+$, HRMS calculated for $C_{11}H_{14}N_2O_1$ $[M]^+$: 190.2460; found 190.1114.

2.1.2. L-Pro-1-Naph (3b)

Colorless solid. 95% yield. mp 63 °C. $[\alpha]_D^{20}$ = -11.11 (c = 0.81, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.59 (s, 1H), 8.24-8.32 (m, 1H), 7.83-7.90 (m, 2H), 7.63-7.68 (m, 1H), 7.47-7.55 (m, 3H), 4.02 (q, *J* = 4.8 Hz, 1H), 3.10-3.21 (m, 2H), 2.25-2.35 (m, 1H), 2.15 (m, 1H), 1.77-1.91 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.5, 134.0, 132.5, 128.8, 126.1, 126.0, 125.7, 124.4, 120.2, 117.7, 61.5, 47.6, 30.9, 26.5. MS (EI): m/z = 240 $[M]^+$, HRMS calculated for $C_{15}H_{16}N_2O$ $[M]^+$: 240.3060; found 240.1255.

2. 1.3. L-Pro-1-Anth (3c)

Yellow solid. 85% yield. mp 91 °C. $[\alpha]_D^{20}$ = -134.95 (c = 0.45, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.75 (s, 1H), 8.42 (d, *J* = 17.2 Hz, 2H), 8.27 (d, *J* = 6.9 Hz, 1H), 7.97-8.05 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.45-7.54 (m, 3H), 4.08 (q, *J* = 4.8 Hz, 1H), 3.17-3.28 (m, 2H), 2.28-2.36 (m, 1H), 2.20 (m, 1H), 1.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.6, 132.2, 132.1, 131.4, 128.4, 128.0, 127.2, 125.7, 125.4, 125.3, 124.6, 118.8, 116.4, 77.3, 77.0, 76.8, 61.6, 47.6, 30.9, 26.5. MS (EI): m/z = 290 $[M]^+$, HRMS calculated for $C_{19}H_{18}N_2O$ $[M]^+$: 290.3660, found 290.1414.

2.1.4. L-Pro-1-Pyr (3d)

Colorless solid. 93% yield. mp 141 °C. $[\alpha]_D^{20}$ = -75.55 (c = 0.45, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.85 (s, 1H), 8.79 (d, *J* = 8.0 Hz, 1H), 8.17 (q, *J* = 7.4 Hz, 3H), 8.09 (dd, *J* = 17.2, 9.7 Hz, 2H), 8.03-7.98 (m, 3H), 4.15-4.09 (m, 1H), 3.28-3.17 (m, 2H), 2.38-2.31 (m, 1H), 2.22 (m, 1H), 1.97-1.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.7, 131.6, 131.0, 130.9, 128.3, 127.8, 127.6, 126.3, 126.2, 125.6, 125.3, 125.3, 124.9, 124.8, 121.8, 119.9, 119.7, 77.4, 77.1, 76.9, 61.7, 47.7, 31.1, 26.6. MS (EI): m/z = 314 $[M]^+$, HRMS calculated for $C_{21}H_{18}N_2O$ $[M]^+$: 314.3880; found 314.1419.

2.1.5. D-Pro-1-Naph (8)

Colorless solid. 90% yield. mp 75 °C. $[\alpha]_D^{20}$ = 38.11 (c = 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.57 (s, 1H), 8.27 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.88-7.81 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.54-7.46 (m, 3H), 3.98 (q, *J* = 4.8 Hz, 1H), 3.17-3.06 (m, 2H), 2.29-2.22 (m, 2H), 2.13 (m, 1H), 1.87-1.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.6, 134.1, 132.7, 128.9, 126.2, 126.1, 126.1, 125.9, 124.5, 120.3, 117.8, 61.6, 47.6, 31.0, 29.8, 26.6. MS (EI): m/z = 314 $[M]^+$, HRMS calculated for $C_{21}H_{18}N_2O$ $[M]^+$: 240.3060; found 240.1267.

2.1.6. L-Aze-1-Naph (12a)

Colorless solid. 60% yield. mp 110 °C. $[\alpha]_D^{20}$ = -40.62 (c = 0.45, $CHCl_3$). ^{1}HNMR (500 MHz, $CDCl_3$, ppm): δ 10.41 (s, 1H), 8.28 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57-7.48 (m, 3H), 4.60 (dd, *J* = 9.2, 8.0 Hz, 1H), 3.96-3.88 (m, 1H), 3.50 (m, 1H), 2.84-2.77 (m, 1H), 2.61-2.53 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.2, 134.1, 132.3, 128.8, 126.1, 126.0, 125.9, 124.7, 120.2, 117.9, 60.0, 43.6, 26.7. MS (EI): m/z = 226 $[M]^+$, HRMS calculated for $C_{21}H_{18}N_2O$ $[M]^+$: 226.2790; found 226.1103.

2.1.7. L-Pip-1-Naph (12b)

Colorless solid. 70% yield. mp 99 °C. $[\alpha]_D^{20}$ = -28.96 (c = 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.61 (s, 1H), 8.17 (d, *J* = 6.9 Hz, 1H), 7.88-7.85 (m, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.55-7.46 (m, 3H), 3.51 (q, *J* = 4.6 Hz, 1H), 3.16 (m, 1H), 2.87-2.81 (m, 1H), 2.13-2.08 (m, 1H), 1.87-1.81 (m, 1H), 1.74-1.69 (m, 1H), 1.68-1.61 (m, 1H), 1.57-1.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.5, 134.1, 132.5, 128.9, 126.3, 126.2, 126.0, 126.0, 124.9, 120.4, 118.8, 60.7, 45.7, 29.8, 26.1, 23.8. MS (EI): m/z = 254 $[M]^+$, HRMS calculated for $C_{21}H_{18}N_2O$ $[M]^+$: 254.3330; found 254.1423.

2.2. General procedure for the synthesis of peptide organocatalysts 5a-h, 9 and 13a,b

N-Boc- amino acids **4a-e** (4.135 mmol) were stirred with *N, N* '-Dicyclohexylcarbodiimide DCC (4.55 mmol) in CH_2Cl_2 (15 mL) at 0 °C for 1 h. Corresponding amino amides **3a-d, 8 12a,b** (4.135 mmol) were added slowly and the reaction was stirred at 30 °C. After the reaction completion, as monitored by thin layer chromatography, insoluble by-product DCU was filtered off and the filtrate was evaporated to dryness. The obtained oily residue was dissolved in CH_2Cl_2, and washed sequentially with saturated aqueous $NaHCO_3$ solution, aqueous HCl (1.0 M), and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under a reduced pressure to afford the crude products that were used for next step without further purification. To the solution of the obtained crude products in dry CH_2Cl_2, TFA was added in dropwise over a period of times (2 mL) at 0 °C and successively stirred at room temperature (r.t.) for 4 h. After the reaction completion DCM 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 h 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 on SiO_2 ($CHCl_3$: MeOH = 99:1 to 95: 5) to obtain the corresponding dipeptide catalysts **5a-h**, **9** and **13a,b**.

2.2.1. L-Ala- L-Pro-1-Naph (5a)

Colorless solid. 88% yield. mp 96 °C. $[\alpha]_D^{20}$ = -115.6 (c = 0.50, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.93 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53-7.56 (m, 1H), 7.44-7.51 (m, 2H), 5.01 (d, *J* = 6.9 Hz, 1H), 3.77 (q, *J* = 6.7 Hz, 1H), 3.55-3.63 (m, 2H), 2.70-2.74 (m, 1H), 2.18-2.28 (m, 1H), 2.06-2.14 (m, 1H), 1.83-1.90 (m, 1H), 1.70 (s, 2H), 1.32 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 169.2, 133.98, 133.2, 128.6, 126.2, 126.1, 125.9, 125.7, 124.8, 120.9, 118.7, 60.7, 48.6, 47.1, 25.9, 25.3, 21.6. MS (EI): m/z = 311 $[M]^+$, HRMS calculated for $C_{18}H_{21}N_3O_2$ $[M]^+$: 311.3850; found 311.1638.

2.2.2. L-Val- L-Pro-1-Naph (5b)

Colorless solid. 91% yield. mp 111 °C. $[\alpha]_D^{20}$ = -84.13 (c = 0.57, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.02 (s, 1H), 8.19-8.21 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51-7.55 (m, 1H), 7.43-7.51 (m, 2H), 5.03 (d, *J* = 6.9 Hz, 1H), 3.58-3.64 (m, 2H), 3.40 (d, *J* = 6.3 Hz, 1H), 2.69-2.73 (m, 1H), 2.20-2.29 (m, 1H), 2.06-2.13 (m, 1H), 1.84-1.98 (m, 2H), 1.57 (s, 2H), 0.91 (q, *J* = 3.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 169.2, 133.9, 133.3, 128.5, 126.1, 125.8, 125.7, 124.7, 121.0, 118.2, 60.6, 58.5, 47.5, 32.6, 25.9, 25.3, 19.9, 17.1. MS (EI): m/z = 339 $[M]^+$, HRMS calculated for $C_{20}H_{25}N_3O_2$ $[M]^+$: 339.4390; found 339.1942.

2.2.3. L-Tle- L-Pro-1-Naph (5c)

Colorless solid. 92% yield. mp 121 °C. $[\alpha]_D^{20}$ = -110 (c = 0.63, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.02 (s, 1H), 8.22 (d, *J* = 6.9 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.85-7.83 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 5.03 (dd, *J* = 8.0, 1.1 Hz, 1H), 3.69-3.65 (m, 2H), 3.41 (s, 1H), 2.73-2.68 (m, 1H), 2.30-2.20 (m, 1H), 2.12-2.05 (m, 1H), 1.93-1.86 (m, 1H), 1.66 (s, 2H), 0.97 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.6, 169.2, 133.9, 133.3, 128.5, 126.1, 126.0, 125.8, 125.7, 124.6, 121.1, 118.1, 60.5, 60.4, 48.5, 35.5, 26.1, 25.3. MS (EI): m/z = 353 $[M]^+$, HRMS calculated for $C_{21}H_{27}N_3O_2$ $[M]^+$: 353.4660; found 353.2097.

2.2.4. L-Phg- L-Pro-1-Naph (5d)

Colorless solid. 78% yield. mp 101 °C. $[\alpha]_D^{20}$ = -29.60 (c = 0.42, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.77 (s, 1H), 8.03 (t, *J* = 8.9 Hz, 2H), 7.85-7.86 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.49-7.56 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.32-7.33 (m, 2H), 7.14-7.20 (m, 3H), 5.06 (d, *J* = 6.9 Hz, 1H), 4.70 (s, 1H), 3.58 (dd, *J* = 17.2, 9.7 Hz, 1H), 3.27-3.31 (m, 1H), 2.62-2.66 (m, 1H), 2.01-2.12 (m, 5H), 1.83-1.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 169.0, 140.4, 133.9, 133.0, 129.3, 128.5, 128.2, 126.9, 126.3, 126.2, 125.8, 125.6, 125.0, 121.1, 119.0, 61.0, 58.1, 46.9, 26.2, 25.1. MS (EI): m/z = 373 $[M]^+$, HRMS calculated for $C_{23}H_{23}N_3O_2$ $[M]^+$: 373.4560; found 373.1794.

2.2.5. L-Phe- L-Pro-1-Naph (5e)

Colorless solid. 60% yield. mp 99 °C. $[\alpha]_D^{20}$ = -88.00 (c = 0.40, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.99 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.58-7.62 (m, 1H), 7.44-7.53 (m, 2H), 7.02-7.05 (m, 3H), 6.96-6.98 (m, 2H), 4.99 (d, *J* = 6.9 Hz, 1H), 3.85 (t, *J* = 7.2 Hz, 1H), 3.48 (m, 1H), 3.02-3.08 (m, 1H), 2.96 (q, *J* = 6.9 Hz, 1H), 2.85 (q, *J* = 6.5 Hz, 1H), 2.64 (q, *J* = 5.9 Hz, 1H), 1.95-2.07 (m, 2H), 1.76-1.84 (m, 1H), 1.66 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 168.6, 136.7, 134.0, 133.3, 129.1, 128.6, 128.5, 126.8, 126.3, 125.9, 125.9, 125.7, 124.7, 120.9, 118.2, 60.6, 55.0, 47.1, 43.1, 25.9, 25.1**.** MS (EI): m/z = 387 $[M]^+$, HRMS calculated for $C_{24}H_{25}N_3O_2$ $[M]^+$: 387.4830; found 387.1950.

2.2.6. L-Tle- L-Pro-1-Ph (5f)

Colorless solid. 80% yield. mp 153 °C. $[\alpha]_D^{20}$ = -42.50 (c = 0.40, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 9.56 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.29 (m, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 4.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 3.60-3.63 (m, 2H), 3.37 (s, 1H), 2.55-2.59 (m, 1H), 2.11-2.21 (m, 1H), 1.98-2.05 (m, 1H), 1.80-1.88 (m, 1H), 1.71 (s, 2H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.4, 168.9, 138.3, 129.0, 124.0, 119.7, 60.5, 60.5, 48.5, 35.6, 26.2, 26.0, 25.3. MS (EI): m/z = 303 $[M]^+$, HRMS calculated for $C_{17}H_{25}N_3O_2$ $[M]^+$: 303.4060; found 303.1949.

2.2.7. L-Tle- L-Pro-1-Anth (5g)

Yellow solid. 91% yield. mp 91 °C. $[\alpha]_D^{20}$ = -134.95 (c = 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.23 (s, 1H), 8.77 (s, 1H), 8.42 (s, 1H), 8.29 (d, *J* = 7.4 Hz, 1H), 8.11 (dd, *J* = 5.4, 3.7 Hz, 1H), 7.99 (dd, *J* = 5.7, 4.0 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.41-7.50 (m, 3H), 5.09 (d, *J* = 6.9 Hz, 1H), 3.66-3.71 (m, 2H), 3.42 (s, 1H), 2.74 (m, 1H), 2.23-2.33 (m, 1H), 2.09-2.13 (m, 1H), 1.89-1.97 (m, 1H), 1.69 (s, 2H), 0.96 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.8, 169.3, 133.3, 132.1, 131.6, 131.4, 128.7, 127.7, 126.9, 125.7, 125.4, 125.2, 124.7, 124.7, 119.7, 116.3, 60.6, 60.4, 48.5, 35.5, 26.2, 26.1, 25.4. MS (EI): m/z = 403 $[M]^+$, HRMS calculated for $C_{25}H_{29}N_3O_2$ $[M]^+$: 403.5260; found 403.2269.

2.2.8. L-Tle- L-Pro-1-Pyr (5h)

Green solid. 91% yield. mp 95 °C. $[\alpha]_D^{20}$ = -151.78 (c = 0.56, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.35 (s, 1H), 8.75 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 9.2 Hz, 1H), 8.14-8.18 (m, 3H), 8.11 (t, *J* = 4.6 Hz, 1H), 7.95-8.02 (m, 3H), 5.12-5.14 (m, 1H), 3.67-3.74 (m, 2H), 3.44 (s, 1H), 2.74-2.79 (m, 1H), 2.26-2.35 (m, 1H), 2.13 (m, 1H), 1.91-1.99 (m, 1H), 1.63 (s, 2H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.9, 169.2, 131.6, 131.4, 130.9, 128.2, 127.7, 127.3, 126.3, 126.0, 125.2, 125.1, 124.8, 124.7, 121.6, 120.6, 119.7, 60.6, 60.5, 48.5, 35.6, 26.2, 26.1, 25.4. MS (EI): m/z = 427 $[M]^+$, HRMS calculated for $C_{27}H_{29}N_3O_2$ $[M]^+$: 427.5480; found 427.2254.

2.2.9. L-Tle-D-Pro-1-Naph (9)

Colorless solid. 85% yield. mp 153 °C. $[\alpha]_D^{20}$ = 10.96 (c = 0.40, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.07 (s, 1H), 8.16-8.10 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54-7.43 (m, 3H), 5.01 (d, *J* = 8.0 Hz, 1H), 3.73-3.59 (m, 2H), 3.40 (d, *J* = 11.5 Hz, 1H), 2.71 (q, *J* = 6.1 Hz, 1H), 2.26-2.16 (m, 1H), 2.08 (s, 1H), 1.90-1.82 (m, 1H), 1.63 (s, 2H), 1.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.6, 169.2, 133.9, 133.3, 128.5, 126.1, 126.0, 125.8, 125.7, 124.6, 121.1, 118.1, 60.5, 60.4, 48.5, 35.5, 26.1, 25.3. MS (EI): m/z = 353 $[M]^+$, HRMS calculated for $C_{27}H_{29}N_3O_2$ $[M]^+$: 353.4660; found 353.2097.

2.2.10. L-Tle- L-Aze-1-Naph (13a)

Colorless solid. 70% yield. mp 153 °C. $[\alpha]_D^{20}$ = -121.06 (c = 0.40, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.32 (s, 1H), 8.28 (d, *J* = 7.4 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 7.86-7.84 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.53-7.46 (m, 3H), 5.21 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.29 (m, 1H), 4.17 (m, 1H), 3.12 (s, 1H), 2.97-2.91 (m, 1H), 2.58-2.51 (m, 1H), 1.60 (s, 2H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 177.0, 169.1, 134.0, 133.2, 128.5, 126.2, 125.9, 125.7, 124.8, 121.1, 118.3, 62.9, 58.5, 49.5, 35.2, 26.1, 18.0. MS (EI): m/z = 339 $[M]^+$, HRMS calculated for $C_{27}H_{29}N_3O_2$ $[M]^+$: 339.4390; found 339.1951.

2.2.11. L-Tle- L-Pip-1-Naph (13b)

Colorless solid. 70% yield. mp 153 °C. $[\alpha]_D^{20}$ = -109.72 (c = 0.40, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.10 (s, 1H), 8.21 (d, *J* = 7.4 Hz, 1H), 7.98-7.95 (m, 1H), 7.85 (dd, *J* = 7.2, 2.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.47-7.44 (m, 1H), 5.50 (d, *J* = 5.2 Hz, 1H), 4.06 (d, *J* = 13.7 Hz, 1H), 3.66 (s, 1H), 3.21 (m, 1H), 2.36 (d, *J* = 13.7 Hz, 1H), 2.18-2.08 (m, 1H), 1.83-1.76 (m, 3H), 1.67 (s, 3H), 1.59 (m, 1H), 0.95 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 177.0, 169.7, 134.1, 132.9, 128.8, 126.3, 126.0, 125.9, 125.6, 124.8, 120.6, 118.2, 57.8, 52.9, 45.1, 36.0, 26.5, 25.7, 25.1, 20.3. MS (EI): m/z = 367 $[M]^+$, HRMS calculated for $C_{27}H_{29}N_3O_2$ $[M]^+$: 367.4930; found 367.2268.

2.3. General procedure for the synthesis of peptide organocatalysts 6a-j, 10 and 14a-b

To a solution of *N, N′*-Dicyclohexylcarbodiimide (DCC) (1.29 mmol) in dry CH_2Cl_2 (10 mL) were added *N*-Boc-L-amino acids **4’a-f** (0.86 mmol) at 0 °C and the reaction mixture was stirred for 1 hour. After 1 hour, corresponding dipeptides **5a-h, 9** and **13a-b** (0.95 mmol) were added and the reaction was stirred for another 24 hour at rt. The insoluble by-product DCU was filtered off and the filtrate evaporated to dryness. The obtained oily residue was dissolved in CH_2Cl_2 and extracted sequentially with saturated aqueous $NaHCO_3$ solution, aqueous HCl (1.0 M), and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under a reduced pressure to afford the crude products that were used for next step without further purification. To the solution of the crude products in dry CH_2Cl_2, TFA was added in dropwise over a period of times (0.4 mL) at 0 °C and successively stirred at room temperature (r.t.) for 4 h. After the reaction completion, DCM 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 h 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 on SiO_2 ($CHCl_3$: MeOH = 99:1 to 95: 5) to obtain the corresponding tripeptide catalysts **6a-j, 10** and **14a,b**.

2.3.1. L-Ala- L-Tle- L-Pro-1-Naph (6a)

White solid. 93% yield. mp 102 °C. $[\alpha]_D^{20}$ = -46.59 (c = 0.58, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.83 (s, 1H), 8.20 (d, *J* = 6.9 Hz, 1H), 8.15 (q, *J* = 4.6 Hz, 2H), 7.84-7.86 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.44-7.54 (m, 3H), 4.98 (dd, *J* = 7.4, 1.7 Hz, 1H), 4.65 (d, *J* = 9.2 Hz, 1H), 3.97 (m, 1H), 3.71-3.76 (m, 1H), 3.56 (q, *J* = 6.9 Hz, 1H), 2.65-2.69 (m, 1H), 2.20-2.30 (m, 1H), 2.05-2.13 (m, 1H), 1.87-1.95 (m, 1H), 1.57 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 175.7, 172.8, 169.1, 133.9, 133.2, 128.5, 126.1, 125.8, 125.8, 125.7, 124.7, 121.0, 118.2, 60.6, 56.5, 50.8, 48.8, 35.2, 26.3, 26.1, 25.3, 21.9. MS (EI): m/z = 424 $[M]^+$, HRMS calculated for $C_{24}H_{32}N_4O_3$ $[M]^+$: 424.5450; found 424.2467.

2.3.2. L-Val- L-Tle- L-Pro-1-Naph (6b)

White solid. 90% yield. mp 83 °C. $[\alpha]_D^{20}$ = -62.50 (c = 0.58, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.85 (s, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.83-7.87 (m, 1H), 7.64 (t, *J* = 8.3 Hz, 1H), 7.47-7.54 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 4.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.67 (d, *J* = 9.2 Hz, 1H), 4.00 (m, 1H), 3.71-3.75 (m, 1H), 3.31 (d, *J* = 4.0 Hz, 1H), 2.66 (m, 1H), 2.33-2.42 (m, 1H), 2.20-2.29 (m, 1H), 2.07-2.12 (m, 1H), 1.86-1.94 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 4H), 1.01 (s, 9H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 172.9, 169.1, 133.9, 133.2, 128.5, 126.1, 125.8, 125.8, 125.7, 124.7, 121.1, 118.2, 60.6, 60.2, 56.6, 48.8, 34.9, 30.6, 26.4, 26.1, 25.3, 19.7, 16.1. MS (EI): m/z = 452 $[M]^+$, HRMS calculated for $C_{26}H_{36}N_4O_3$ $[M]^+$: 452.5990; found 452.2781.

2.3.3. L-Tle- L-Tle- L-Pro-1-Naph (6c)

White solid. 96% yield. mp 177 °C. $[\alpha]_D^{20}$ = -70.31 (c = 0.40, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.02 (s, 9H), 1.05 (s, 9H), 1.57 (s, 2H), 1.84-1.98 (m, 1H), 2.04-2.15 (m, 1H), 2.17-2.32 (m, 1H), 2.66 (m, 1H), 3.20 (s, 1H), 3.68-3.77 (m, 1H), 3.99 (m, 1H), 4.67 (d, *J* = 9.2 Hz, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 7.41-7.56 (m, 3H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.78-7.90 (m, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 9.83 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.8, 173.0, 169.1, 133.9, 133.2, 128.5, 126.1, 125.8, 125.7, 124.7, 121.1, 118.2, 64.4, 60.5, 56.6, 48.8, 34.9, 34.2, 26.9, 26.5, 26.1, 25.3. MS (EI): m/z = 466 $[M]^+$, HRMS calculated for $C_{27}H_{38}N_4O_3$ $[M]^+$: 466.6260; found 466.2949.

2.3.4. L-Phg- L-Tle- L-Pro-1-Naph (6d)

White solid. 72% yield. mp 106 °C. $[\alpha]_D^{20}$ = +46.59 (c = 0.58, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.75 (s, 1H), 8.14 (dd, *J* = 23.8, 7.7 Hz, 2H), 7.83-7.85 (m, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.49-7.54 (m, 3H), 7.43-7.47 (m, 1H), 7.36-7.42 (m, 4H), 7.30-7.34 (m, 1H), 4.93 (dd, *J* = 7.7, 2.0 Hz, 1H), 4.68 (d, *J* = 9.7 Hz, 1H), 4.57 (s, 1H), 3.86 (m, 1H), 3.66-3.70 (m, 1H), 2.60-2.66 (m, 1H), 2.15-2.25 (m, 1H), 1.99-2.06 (m, 1H), 1.83-1.87 (m, 2H), 0.94 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_{3,}$ ppm): δ 172.8, 172.4, 169.1, 141.1, 134.0, 133.1, 129.0, 128.5, 128.2, 126.9, 126.1, 125.9, 125.8, 125.7, 124.8, 121.0, 118.4, 60.6, 59.9, 56.8, 48.7, 35.4, 26.3, 26.2, 25.2. MS (EI): m/z = 486 $[M]^+$, HRMS calculated for $C_{29}H_{34}N_4O_3$ $[M]^+$: 486.6160; found 486.2638.

2.3.5. L-Phe- L-Tle- L-Pro-1-Naph (6e)

White solid. 85% yield. mp 93 °C. $[\alpha]_D^{20}$ = +84.63 (c = 0.58, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.79 (s, 1H), 8.12-8.19 (m, 3H), 7.82 (dd, *J* = 9.5, 8.3 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.42-7.53 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (dd, *J* = 16.3, 7.2 Hz, 3H), 4.96 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.61-4.67 (m, 1H), 3.99 (m, 1H), 3.71-3.76 (m, 1H), 3.67 (q, *J* = 4.4 Hz, 1H), 3.28 (dd, *J* = 13.7, 3.4 Hz, 1H), 2.75 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.63-2.67 (m, 1H), 2.20-2.33 (m, 1H), 2.07-2.16 (m, 1H), 1.88-1.95 (m, 1H), 1.56 (d, *J* = 8.0 Hz, 2H), 0.93-1.02 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.3, 172.6, 169.1, 137.6, 133.9, 133.2, 129.3, 128.7, 128.5, 126.9, 126.1, 125.8, 125.7, 124.7, 121.1, 118.3, 60.6, 56.7, 56.5, 48.8, 40.9, 35.2, 26.3, 26.2, 25.3. MS (EI): m/z = 500 $[M]^+$, HRMS calculated for $C_{30}H_{36}N_4O_3$ $[M]^+$: 500.6430; found 500.2792.

2.3.6. Gly- L-Tle- L-Pro-1-Naph (6f)

White solid. 87% yield. mp 99 °C. $[\alpha]_D^{20}$ = -55.00 (c = 0.4, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.81 (s, 1H), 8.17 (dd, *J* = 26.6, 7.7 Hz, 2H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.84-7.85 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.43-7.54 (m, 3H), 4.97 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.72 (d, *J* = 9.2 Hz, 1H), 3.95 (m, 1H), 3.72-3.76 (m, 1H), 3.43 (dd, *J* = 21.8, 17.2 Hz, 2H), 2.66 (m, 1H), 2.20-2.30 (m, 1H), 2.04-2.12 (m, 1H), 1.88-1.95 (m, 1H), 1.60 (s, 2H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 172.6, 169.1, 133.9, 133.2, 128.5, 126.1, 125.8, 125.7, 124.7, 121.0, 118.3, 60.6, 56.5, 48.8, 44.6, 35.3, 26.3, 26.2, 25.3. MS (EI): m/z = 410 $[M]^+$, HRMS calculated for $C_{23}H_{30}N_4O_3$ $[M]^+$: 410.5180; found 410.2319.

2.3.7. L-Tle- L-Tle- L-Pro-Ph (6g)

White solid. 70% yield. mp 233 °C. $[\alpha]_D^{20}$ = -71.42 (c = 0.55, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.38 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.62-4.70 (m, 2H), 3.88 (q, *J* = 8.4 Hz, 1H), 3.71 (m, 1H), 3.37 (s, 1H), 2.40 (q, *J* = 3.6 Hz, 1H), 2.12-2.21 (m, 1H), 1.92-2.05 (m, 2H), 1.04 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 171.8, 168.9, 138.2, 129.0, 124.1, 119.5, 64.1, 60.7, 57.3, 48.8, 35.1, 33.6, 27.1, 26.6, 26.5, 25.1. MS (EI): m/z = 416 $[M]^+$, HRMS calculated for $C_{23}H_{36}N_4O_3$ $[M]^+$: 416.5660; found 416.2853.

2.3.8. L-Tle- L-Tle- L-Pro-1-Anth (6h)

Brown solid. 80% yield. mp 105 °C. $[\alpha]_D^{20}$ = -23.45 (c = 0.60, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.04 (s, 1H), 8.74 (s, 1H), 8.43 (s, 1H), 8.27 (d, *J* = 7.4 Hz, 1H), 8.09-8.11 (m, 1H), 8.00 (dd, *J* = 5.9, 3.9 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.48 (m, 2H), 7.43 (dd, *J* = 8.6, 7.4 Hz, 1H), 5.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.69 (d, *J* = 9.7 Hz, 1H), 4.02 (m, 1H), 3.74-3.78 (m, 1H), 3.24 (s, 1H), 2.69-2.72 (m, 1H), 2.23-2.33 (m, 1H), 2.12 (m, 1H), 1.91-1.99 (m, 1H), 1.60 (s, 2H), 1.08 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.9, 173.0, 169.2, 133.1, 132.1, 131.5, 131.4, 128.6, 127.8, 127.0, 125.7, 125.5, 125.2, 124.8, 124.7, 119.6, 116.6, 77.2, 77.0, 76.7, 64.5, 60.6, 56.7, 48.8, 34.8, 34.2, 26.9, 26.5, 26.1, 25.3. MS (EI): m/z = 516 $[M]^+$, HRMS calculated for $C_{31}H_{40}N_4O_3$ $[M]^+$: 516.6860; found 516.3094.

2.3.9. L-Tle- L-Tle- L-Pro-1-Pyr (6i)

Green solid. 83% yield. mp 115 °C. $[\alpha]_D^{20}$ = -8.0 (c = 0.50, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.16 (s, 1H), 8.72 (d, *J* = 8.6 Hz, 1H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.14-8.16 (m, 3H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.97-8.02 (m, 3H), 7.90 (d, *J* = 9.2 Hz, 1H), 5.07 (d, *J* = 8.0 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 4.02 (m, 1H), 3.74-3.79 (m, 1H), 3.22 (s, 1H), 2.72 (m, 1H), 2.24-2.34 (m, 1H), 2.09-2.17 (m, 1H), 1.92-2.00 (m, 1H), 1.58 (s, 4H), 1.06 (s, 9H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.0, 173.2, 169.3, 131.6, 131.5, 131.0, 128.4, 127.7, 127.4, 126.5, 126.1, 125.3, 125.2, 125.2, 124.9, 124.8, 121.8, 120.7, 120.0, 64.5, 60.7, 56.8, 48.9, 35.0, 34.3, 27.0, 26.6, 26.3, 25.5. MS (EI): m/z = 540 $[M]^+$, HRMS calculated for $C_{33}H_{40}N_4O_3$ $[M]^+$: 540.7080; found 540.3094.

2.3.10. D-Tle- L-Tle- L-Pro-1-Naph (6j)

White solid. 70% yield. mp 233 °C. $[\alpha]_D^{20}$ = 56.13 (c = 0.45, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.82 (s, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.85-7.84 (m, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.51 (m, 2H), 7.47-7.43 (m, 1H), 7.11 (d, *J* = 9.2 Hz, 1H), 4.96 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 3.96 (m, 1H), 3.74-3.70 (m, 1H), 3.12 (s, 1H), 2.69-2.66 (m, 1H), 2.29-2.20 (m, 1H), 2.10 (m, 1H), 1.94-1.87 (m, 1H), 1.55 (s, 2H), 1.03 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 173.8, 172.9, 169.2, 134.1, 133.3, 128.7, 126.2, 126.0, 125.9, 124.8, 121.2, 118.3, 64.8, 60.7, 56.8, 48.8, 35.2, 34.5, 26.8, 26.6, 26.3, 25.4. MS (EI): m/z = 466 $[M]^+$, HRMS calculated for $C_{33}H_{40}N_4O_3$ $[M]^+$: 466.6260; found 466.3142.

2.3.11. L-Tle- L-Tle-D-Pro-1-Naph (10)

White solid. 85% yield. mp 225 °C. $[\alpha]_D^{20}$ = 73.22 (c = 0.51, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 9.66 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.53-7.42 (m, 3H), 4.93 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 4.15-4.11 (m, 1H), 3.74-3.65 (m, 1H), 2.77 (s, 1H), 2.64 (q, *J* = 6.3 Hz, 1H), 2.29-2.19 (m, 1H), 2.13-2.08 (m, 1H), 2.01-1.93 (m, 1H), 1.12 (s, 9H), 0.80 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.4, 172.3, 169.7, 134.2, 133.3, 128.5, 127.2, 126.0, 125.8, 125.4, 122.0, 120.4, 64.3, 61.1, 57.6, 48.4, 34.6, 34.0, 28.1, 26.8, 26.7, 24.8. MS (EI): m/z = 466 $[M]^+$, HRMS calculated for $C_{33}H_{40}N_4O_3$ $[M]^+$: 466.6260; found 466.4930.

2.3.12. L-Tle- L-Tle- L-Aze-1-Naph (14a)

White solid. 90% yield. mp 168 °C. $[\alpha]_D^{20}$ = -89.70 (c = 0.55, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 10.15 (s, 1H), 8.25 (d, *J* = 6.9 Hz, 1H), 8.13-8.11 (m, 1H), 7.86-7.83 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.52-7.46 (m, 3H), 5.19 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.60 (dd, *J* = 15.8, 8.9 Hz, 1H), 4.30 (d, *J* = 9.2 Hz, 1H), 4.21 (td, *J* = 8.6, 5.7 Hz, 1H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.97-2.90 (m, 1H), 2.59-2.51 (m, 1H), 1.58 (s, 2H), 1.06 (s, 10H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.7, 174.1, 169.2, 134.1, 133.2, 128.7, 126.2, 126.0, 126.0, 125.9, 125.0, 121.2, 118.6, 64.5, 63.0, 55.0, 50.0, 34.4, 34.3, 27.0, 26.6, 18.1. MS (EI): m/z = 466 $[M]^+$, HRMS calculated for $C_{33}H_{40}N_4O_3$ $[M]^+$: 452.5990; found 452.2785.

2.3.13. L-Tle- L-Tle- L-Pip-1-Naph (14b)

White solid. 75% yield. mp 220 °C. $[\alpha]_D^{20}$ = -93.81 (c = 0.50, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.83 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.93-7.88 (m, 1H), 7.85-7.78 (m, 2H), 7.73-7.67 (m, 2H), 7.52-7.48 (m, 2H), 5.46 (d, *J* = 4.0 Hz, 1H), 5.04 (d, *J* = 9.7 Hz, 1H), 4.63 (d, *J* = 7.4 Hz, 1H), 4.21 (d, *J* = 14.9 Hz, 1H), 3.27 (m, 1H), 3.18 (s, 1H), 2.33 (d, *J* = 13.7 Hz, 1H), 2.09-1.62 (m, 2H), 1.56 (s, 2H), 1.04 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 174.7, 174.1, 169.2, 134.1, 133.2, 128.7, 126.2, 126.0, 126.0, 125.9, 125.0, 121.2, 118.6, 64.5, 63.0, 55.0, 50.0, 34.4, 34.3, 27.0, 26.6, 18.1. MS (EI): m/z = 480.6530 $[M]^+$, HRMS calculated for $C_{33}H_{40}N_4O_3$ $[M]^+$: 480.6530; found 480.3100.

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

The peptide catalyst **6c** (30 mol%) was added to a solution of ketones **15a-h** (0.4 mmol) and the aldehydes **16a-i** (0.1 mmol) under the neat reaction condition. The reaction mixture was stirred at 0 °C for appropriate time until the reaction completion, monitored by thin layer chromatography (TLC). The diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. Consequently, the reaction mixture was purified by flash column chromatography on SiO_2 (*n*-hexane/CH_3CO_2Et) to afford the corresponding aldol products **17a-p**. [6a-j]

Gram scale for the asymmetric aldol reaction of cyclohexanone (15a) with 4-nitrobenzaldehyde (16a)

The peptide catalyst **6c** (30 mol%) was added to a solution of cyclohexanone **15a** (2.06 ml, 19.851 mmol) and the 4-nitrobenzaldehyde **16a** (1g, 6.617 mmol) under neat reaction condition. The reaction mixture was stirred at 0 °C for appropriate time until the reaction completion, monitored by thin layer chromatography (TLC). The diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. Consequently, the reaction mixture was purified by flash column chromatography on SiO_2 (*n*-hexane/CH_3CO_2Et) to afford the 2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one **17a.** The enantiomeric excess (*ee*) of **17a** was determined by HPLC (CHIRALPAK-AD-H hexane/i-PrOH = 90:10 1.0mL /min, λ = 254 nm) (1.65g, 98% yield, dr= 24:76 and enantiomeric excess 93 %*ee*).

2.4.1. 2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one (**17a**) [6a,9]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.21-8.19 (m, 2H), 7.51-7.46 (m, 2H), 5.47 (s, H), 4.89 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.07 (d, *J* = 2.9 Hz, 1H), 3.18 (d, *J* = 2.9 Hz, H), 2.64-2.55 (m, 1H), 2.51-2.46 (m, 1H), 2.42-2.32 (m, 1H), 2.14-2.08 (m, 1H), 1.86-1.80 (m, 1H), 1.74-1.64 (m, 1H), 1.63-1.49 (m, 3H), 1.42-1.24 (m, 1H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm):* tmajor= 33.86 min, tminor= 25.58 min, *dr(syn/anti) =* 20*:*80*,* 98*% ee (anti).*

2.4.2. 2-[Hydroxy-(2-nitrophenyl)-methyl]-cyclohexan-1-one (**17b**) [6c]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.83 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.75 (dd*, J* = 8.0, 1.1 Hz, 1H), 7.64-7.58 (m, 1H), 7.43-7.40 (m, 1H), 5.43 (d, *J* = 6.9 Hz, 1H), 2.77-2.72 (m, 1H), 2.44 (m, 1H), 2.36-2.29 (m, 1H), 2.11-2.06 (m, 1H), 1.86-1.81 (m, 1H), 1.77-1.71 (m, 1H), 1.71-1.53 (m, 3H). The ee was determined by chiral HPLC: *AD-H column, n-hexane/iso-propanol: 90/10, flow rate = 1.0 mL/min,* λ=254 nm*):* tmajor= 22.84 min, tminor= 24.55 min, *dr(syn/anti) =* 22*:*78*,* 99*% ee (anti).*

2.4.3. 2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclohexan-1-one (**17c**) [6a]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.22-8.11 (m, 2H), 7.68-7.66 (m, 1H), 7.53 (td, *J* = 7.7, 4.6 Hz, 1H), 5.48 (s, H), 4.90 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.13 (d, *J* = 2.9 Hz, 1H), 3.20 (d, *J* = 3.4 Hz, H), 2.68-2.60 (m, 1H), 2.53-2.47 (m, 1H), 2.44-2.34 (m, 1H), 2.15-2.10 (m, 1H), 1.88-1.82 (m, 1H), 1.79-1.50 (m, 4H), 1.44-1.35 (m, 1H). The ee was determined by chiral HPLC: *(AD-H column, n-hexane/iso propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 21.76 min, tminor= 27.55 min, *dr(syn/anti) =* 20:80*,* 99*% ee (anti).*

2.4.4. 2-[Hydroxy-(2-bromophenyl)-methyl]-cyclohexan-1-one (**17d**) [6]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.58-7.49 (m, 2H), 7.36-7.30 (m, 1H), 7.13-7.07 (m, 1H), 5.30-5.21 (m, 1H), 3.85 (brs, 1H), 2.76-2.68 (m, 1H), 2.44-2.38 (m, 2H), 2.08-2.0 (m, 1H), 1.80-1.74 (m, 1H), 1.75-1.70 (m, 2H), 1.58-1.54 (m, 2H). The ee was determined by chiral HPLC: *AD-H column, n-hexane/iso propanol = 90/10, flow rate = 1.0 mL/min, λ=224 nm, dr(syn/anti) =* 25:75*,* 86*% ee (anti).*

2.4.5. 2-[Hydroxy-(3-bromophenyl)-methyl]-cyclohexan-1-one (**17e**) [6c]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.49-7.48 (m, 1H), 7.40 (m, 1H), 7.24-7.18 (m, 2H), 5.36 (d, *J* = 1.7 Hz, H), 4.74 (d, *J* = 8.6 Hz, 1H), 4.01 (s, 1H), 3.03 (d, *J* = 45.2 Hz, 0H), 2.61-2.55 (m, 1H), 2.50-2.44 (m, 1H), 2.41-2.32 (m, 1H), 2.10 (m, 1H), 1.88-1.78 (m, 1H), 1.73-1.63 (m, 2H), 1.63-1.48 (m, 2H). The ee was determined by chiral HPLC: *(AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 12.57 min, tminor= 14.67 min, *dr(syn/anti) =* 25:75*,* 93*% ee (anti).*

2.4.6. 2-[Hydroxy-(4-bromophenyl)-methyl]-cyclohexan-1-one (**17f**) [6c]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.48-7.47 (m, 2H), 7.21-7.18 (m, 2H), 5.35 (s, H), 4.75 (d, *J* = 7.4 Hz, 1H), 4.00 (d, *J* = 4.0 Hz, 1H), 3.06 (s, H), 2.56-2.47 (m, 2H), 2.37 (q, *J* = 5.5 Hz, 1H), 2.11 (d, *J* = 3.4 Hz, 1H), 1.84 (d, *J* = 24.6 Hz, 1H), 1.68 (t, *J* = 12.6 Hz, 2H), 1.56 (t, *J* = 11.5 Hz, 2H), 1.29 (t, *J* = 12.3 Hz, 1H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 18.35 min, tminor= 15.97 min, *dr(syn/anti) =* 23:77*,* 94*% ee (anti).*

2.4.7. 2-[Hydroxy-(4-chlorophenyl)-methyl]-cyclohexan-1-one (**17g**) [6c]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.32 (m, 2H), 7.27-7.23 (m, 3H), 5.36 (d, *J* = 2.3 Hz, H), 4.77 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.99 (d, *J* = 2.9 Hz, H), 3.06 (d, *J* = 3.4 Hz, 1H), 2.58-2.53 (m, 1H), 2.51-2.44 (m, 1H), 2.41-2.32 (m, 1H), 2.10 (m, 1H), 1.88-1.79 (m, 1H), 1.72-1.47 (m, 4H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 16.19 min, tminor= 14.30 min, *dr(syn/anti) =* 14:86*,* 98*% ee (anti).*

2.4.8. 2-[Hydroxy-(4-cyanophenyl)-methyl]-cyclohexan-1-one (**17h**) [6a]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.66-7.63 (m, 2H), 7.49-7.42 (m, 2H), 5.44 (s, H), 4.84 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.07 (d, *J* = 2.9 Hz, H), 3.16 (d, *J* = 3.4 Hz, 1H), 2.62-2.55 (m, 1H), 2.52-2.46 (m, 1H), 2.43-2.33 (m, 1H), 2.12 (m, 1H), 1.88-1.81 (m, 1H), 1.76-1.65 (m, 2H), 1.64-1.48 (m, 2H), 1.45-1.19 (m, 1H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 30.36 min, tminor= 24.62 min, *dr(syn/anti) =* 33:67*,* 94*% ee (anti).*

2.4.9. 2-[Hydroxy-phenyl-methyl]-cyclohexan-1-one (**17i**) [6c]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.35-7.26 (m, 5H), 5.37 (s, H), 4.78 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.98 (d, *J* = 2.9 Hz, 1H), 2.64-2.57 (m, 1H), 2.48-2.43 (m, 1H), 2.38-2.30 (m, 1H), 2.09-2.02 (m, 1H), 1.78-1.72 (m, 1H), 1.70-1.47 (m, 3H), 1.32-1.23 (m, 1H). The ee was determined by chiral HPLC: *(AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 15.9 min, tminor= 12.69 min, *dr(syn/anti) = 25:75, 60% ee (anti).*

2.4.10. 2-[Hydroxy-(4-(methoxyphenyl) methyl)-cyclopentan-1-one (**17j**) [8b,d]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.24 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.74 (dd, *J* = 8.9, 1.9 Hz, 1H), 3.93 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 2.64-2.30 (m, 3H), 2.13-2.05 (m, 1H), 1.81-1.23 (m, 5H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 98/2, flow rate = 0.4 mL/min, λ=254 nm):* tmajor= 165.78 min, tminor= 154.72 min, *dr(syn/anti) = 26:74, 58% ee (anti).*

2.4.10. 2-[Hydroxy-(4-(nitrophenyl) methyl)-cyclopentan-1-one (**17n**) [8b,d]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.25-8.20 (m, 2H), 7.57-7.52 (m, 2H), 5.43 (s, 1H), 4.85 (d, *J* = 9.2 Hz, 0H), 2.84 (s, 1H), 2.50-2.36 (m, 2H), 2.33-2.11 (m, 1H), 2.06-1.94 (m, 2H), 1.81-1.68 (m, 2H). The ee was determined by chiral HPLC: (*IC column, n-hexane/iso-propanol = 85/15, flow rate = 0.8 mL/min, λ=254 nm):* tmajor= 29.69 min, tminor= 24.63 min, *dr(syn/anti) = 15:85, 93% ee (anti).*

2.4.11. 2-[Hydroxy(4-nitrophenyl) methyl] cycloheptan-1-one (**17m**) [8b,d]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.28-8.21 (m, 2H), 7.60-7.54 (m, 2H), 4.87 (dd, *J*= 9.0, 1.0 Hz, 1H), 4.77 (d, *J* = 1.0 Hz, 1H), 2.56-2.26 (m, 3H), 2.11-1.99 (m, 1H), 1.85-1.71 (m, 2H), 1.62-1.53 (m, 1H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 48.1 min, tminor= 20.70 min, *dr (syn/anti) = 15:85, 91% ee (anti).*

2.4.12. 2-[-Hydroxy-(4-(nitrophenyl)-methyl)-4-methylcyclohexan-1-one (**17o**) [8b]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.51-7.46 (m, 2H), 4.89 (m, 1H), 4.00 (dd, *J* = 105.4, 2.9 Hz, 1H), 2.76-2.36 (m, 3H), 2.11-1.76 (m, 3H), 1.62-1.56 (m, 2H), 1.48-1.23 (m, 2H), 0.96 (dd, J = 81.3, 12.6 Hz, 3H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min, λ=254 nm):* tmajor= 32.36 min, tminor= 34.44 min, *dr (syn/anti) =21:79, 90% ee (anti).*

2.4.13. 6-[Hydroxy-(4-nitro-phenyl)-methyl]-2,2-dimethyl-1,3-dioxan-5-one (**17p**) [8a]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.21 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.61-7.55 (m, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.29 (dd, *J* = 17.5, 1.4 Hz, 1H), 4.22 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.09 (dd, *J* = 17.5, 2.6 Hz, 1H), 1.39 (s, 3H), 1.21 (s, 3H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol: 95/05, flow Rate = 1.0 mL/min, λ=254 nm):* tmajor= 55.87 min, tminor= 42.13 min, *dr(syn/anti) =30:70, 68% ee (anti).*

2.4.14. 3-[Hydroxy-[4-(nitrophenyl) methyl] dihydro-2H-pyran-4-one (**17q**) [8b]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.23 (m, 2H), 7.53-7.50 (m, 2H), 5.55 (s, H), 4.98 (d, *J* = 8.0 Hz, 1H), 4.27-4.19 (m, 1H), 3.85 (m, 1H), 3.78-3.69 (m, 2H), 3.47-3.41 (m, 1H), 2.96-2.87 (m, 1H), 2.76-2.65 (m, 1H), 2.55-2.46 (m, 1H). The ee was determined by chiral HPLC: (*AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm):* tmajor= 59.75 min, tminor= 50.60 min, *dr(syn/anti) = 13:87, 94% ee (anti).*

2.4.15. 3-Hydroxy-3-(4-nitrophenyl)-1-propan-1-one (**17r**) [8f]

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.21 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 5.29-5.25 (m, 1H), 3.65 (d, *J* = 3.4 Hz, 1H), 2.87-2.83 (m, 2H), 2.23 (s, 3H). The ee was determined by chiral HPLC: (*AS-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min,* λ=254 nm*):* tmajor= 18.36 min, tminor= 13.9 min, *dr(syn/anti) = n.d, 52% ee.*

2.4.16. 3-Hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**17s**) [8b]

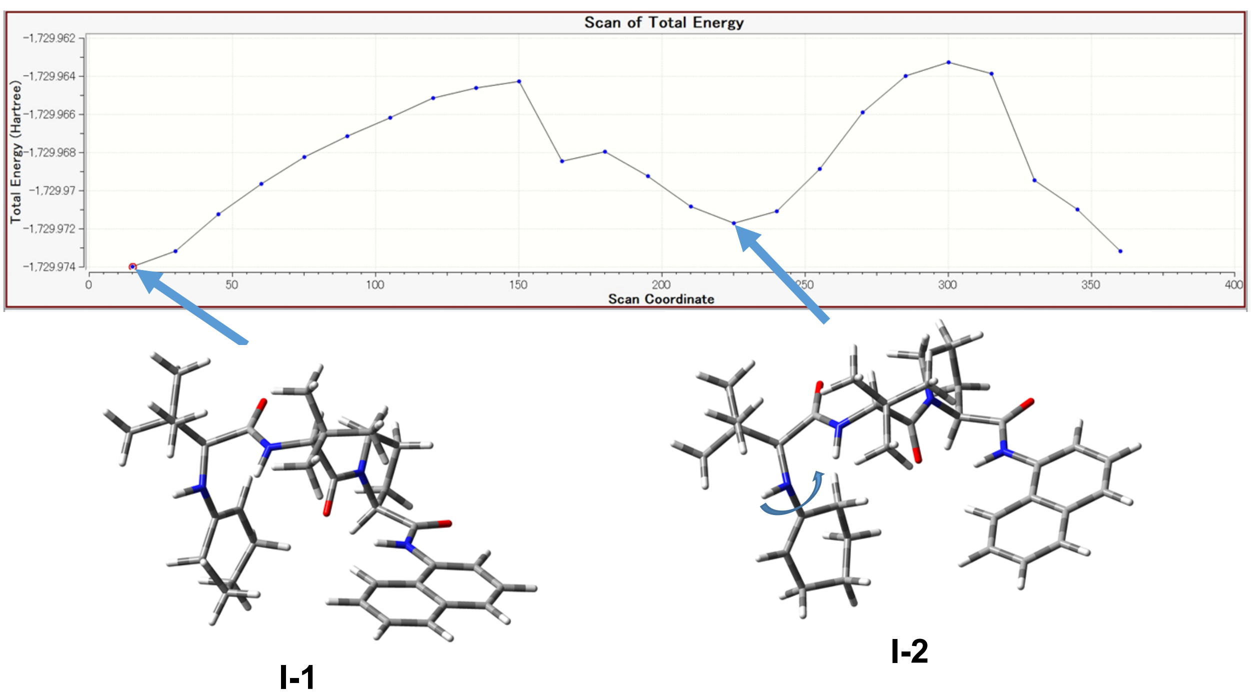
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.25–7.46 (m, 9H), 5.46 (d, *J* = 8.6 Hz, 1H), 3.90 (d, *J* = 2.9 Hz, 1H), 3.44–3.31 (m, 2H). The ee was determined by chiral HPLC: *(AD-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min,* λ=254 nm*):* tmajor= 34.14 min, tminor= 39.27 min, *dr(syn/anti) = n.d, 82% ee.*

3. 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 (for a ground state) or one (for a transition state) 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.



Ratio **I-1** : **I-2** = 96.14 : 3.86

Figure S1. The coordinate scan calculations (at the B3LYP/6-31G(d) level of theory) and total energies (in hartree, calculated at the B3LYP/6-31G(d) level of theory in gas phase) of **6c** generated by varying two torsion angles (the dihedral scans showed with u-shaped arrows, as shown in the bottom structures).

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

Total energy = -1729.297620 hartree

Symbol	X	Y	Z
C	-4.49757	-0.46142	1.037219
C	-3.41505	-0.88272	1.860457
C	-3.61771	-1.73187	2.927445
C	-4.91203	-2.20898	3.233678
C	-5.98055	-1.8197	2.460511
C	-5.81235	-0.94465	1.353602
C	-6.92297	-0.54508	0.565208
C	-6.74187	0.303832	-0.49938
C	-5.46032	0.791319	-0.83497
C	-4.34993	0.422096	-0.09184
N	-3.05418	0.889281	-0.39962
C	-2.66623	1.751865	-1.39003
O	-3.40928	2.298002	-2.19775
C	-1.1338	2.008465	-1.39628
C	-0.73191	3.060562	-2.43486
C	-0.50229	2.233577	-3.7091
C	0.155118	0.943637	-3.19688
N	-0.37235	0.806185	-1.81639
C	-0.01448	-0.12661	-0.90364
C	0.978817	-1.22341	-1.32241
O	-0.44021	-0.08936	0.265267
C	0.36532	-2.66443	-1.30656
C	0.070519	-3.16401	0.120565
C	1.376213	-3.61478	-1.97768
C	-0.93965	-2.65885	-2.1278
N	2.149876	-1.08598	-0.46259
C	3.273934	-0.43955	-0.89222
O	3.474703	-0.12178	-2.06289
C	4.320738	-0.14619	0.207987
N	3.654384	0.083426	1.486207
C	3.081032	1.341093	1.770359
C	2.714845	1.510583	3.231157
C	1.714723	2.651951	3.457827

C	2.135781	3.901499	2.677294
C	2.169967	3.608428	1.17064
C	2.8321	2.289543	0.847939
C	5.43236	-1.24934	0.314325
C	6.543652	-0.74213	1.260567
C	4.873876	-2.58406	0.846418
C	6.062742	-1.48112	-1.07398
H	-2.4022	-0.54559	1.667771
H	-2.77172	-2.03523	3.538323
H	-5.05899	-2.87835	4.077033
H	-6.98288	-2.17685	2.685536
H	-7.91082	-0.9201	0.820488
H	-7.59076	0.612848	-1.10349
H	-5.33245	1.458681	-1.67475
H	-2.27553	0.510829	0.137428
H	-0.81917	2.266964	-0.3798
H	0.196225	3.548387	-2.1159
H	-1.50872	3.816293	-2.5587
H	0.125779	2.741375	-4.44651
H	-1.468	2.011993	-4.17334
H	1.24761	1.021582	-3.169
H	-0.11375	0.07321	-3.80281
H	1.343051	-1.03492	-2.33211
H	-0.34853	-4.17632	0.077202
H	-0.64318	-2.51811	0.636879
H	0.985889	-3.21613	0.721453
H	0.988921	-4.64036	-1.98068
H	2.333306	-3.61827	-1.44579
H	1.5699	-3.32558	-3.0178
H	-1.34404	-3.67488	-2.19854
H	-0.77056	-2.30164	-3.15163
H	-1.71062	-2.03037	-1.66887
H	1.998529	-1.06114	0.54121
H	4.822879	0.770719	-0.13436
H	4.155623	-0.29597	2.280363

H	3.631359	1.695372	3.815079
H	2.299461	0.565286	3.606574
H	1.633507	2.86791	4.529957
H	0.720207	2.330421	3.12014
H	3.135167	4.214879	3.010734
H	1.455321	4.735992	2.886177
H	2.691152	4.420873	0.645036
H	1.140331	3.61859	0.773863
H	3.089748	2.121073	-0.1944
H	7.365438	-1.46643	1.294361
H	6.199094	-0.60264	2.292336
H	6.952249	0.21381	0.912904
H	5.680161	-3.32292	0.920909
H	4.106245	-2.99047	0.180664
H	4.429431	-2.48393	1.843608
H	6.892355	-2.19247	-0.98651
H	6.456516	-0.54894	-1.49345
H	5.342439	-1.88199	-1.79134

Table **S2**. Cartesian coordinates (Angstroms) for **TS-1** in gas phase.
Point Group: C1
Imaginary Freq: 1
Total energy = -1729.287407 hartree

Symbol	X	Y	Z
C	-0.00399	-0.00636	0.005573
C	-0.00781	-0.00926	1.42932
C	1.169509	-0.01472	2.146598
C	2.417601	-0.01743	1.484094
C	2.457533	-0.01665	0.109509
C	1.266011	-0.01241	-0.66477
C	1.318721	-0.01598	-2.0832
C	0.156552	-0.01447	-2.81542
C	-1.10528	-0.00603	-2.1827
C	-1.19929	0.000285	-0.7997
N	-2.44391	0.007678	-0.1342
C	-3.70351	-0.01238	-0.67117

O	-3.97383	-0.05627	-1.86609
C	-4.81809	0.007488	0.411421
C	-6.21547	-0.13097	-0.2012
C	-6.61464	1.320414	-0.50823
C	-6.04929	2.116858	0.677151
N	-4.88324	1.310144	1.117923
C	-4.09983	1.540797	2.198007
C	-4.3668	2.800531	3.041448
O	-3.2045	0.743699	2.531851
C	-3.1759	3.817824	3.036681
C	-1.95314	3.30016	3.818365
C	-3.6696	5.129292	3.678367
C	-2.7682	4.098161	1.576117
N	-4.74163	2.362394	4.380832
C	-6.0486	2.229016	4.750077
O	-6.99472	2.614513	4.063936
C	-6.27656	1.562508	6.126232
N	-5.18585	0.630115	6.413547
C	-5.14507	-0.63911	5.732577
C	-6.44784	-1.28514	5.295012
C	-6.27349	-2.77247	4.946704
C	-5.01932	-3.0022	4.096909
C	-3.764	-2.55873	4.860248
C	-3.95486	-1.22302	5.531392
C	-6.47009	2.601661	7.288813
C	-6.90722	1.844771	8.563655
C	-5.17716	3.388181	7.579138
C	-7.59589	3.589107	6.920364
H	-0.93899	-0.00567	1.985729
H	1.13464	-0.0174	3.23273
H	3.338793	-0.02132	2.060545
H	3.410688	-0.02058	-0.41426
H	2.289088	-0.02154	-2.57309
H	0.194015	-0.01879	-3.90153
H	-2.01126	-0.00559	-2.77102

H	-2.43687	0.089447	0.881374
H	-4.59555	-0.76746	1.152596
H	-6.89368	-0.57167	0.538441
H	-6.20057	-0.76051	-1.09191
H	-7.69485	1.458908	-0.6087
H	-6.13888	1.634389	-1.44214
H	-6.76828	2.202595	1.498894
H	-5.73466	3.123396	0.385016
H	-5.24299	3.323002	2.658237
H	-1.14798	4.043265	3.776217
H	-1.57754	2.36129	3.405599
H	-2.19176	3.141804	4.876686
H	-2.86085	5.869071	3.699901
H	-4.00488	4.967957	4.708023
H	-4.50533	5.562023	3.114924
H	-1.99409	4.873129	1.544307
H	-3.61769	4.458868	0.982219
H	-2.36095	3.207529	1.08566
H	-4.08392	1.80578	4.917137
H	-7.24647	1.0574	6.014455
H	-5.03137	0.518512	7.40864
H	-6.86378	-0.74588	4.430151
H	-7.19501	-1.18062	6.094116
H	-7.16865	-3.13969	4.430076
H	-6.18629	-3.35207	5.876392
H	-5.10051	-2.41946	3.168369
H	-4.93687	-4.05605	3.80494
H	-2.90806	-2.4973	4.175156
H	-3.49076	-3.3211	5.608069
H	-3.0609	-0.70025	5.868119
H	-7.13915	2.560291	9.360733
H	-6.13208	1.175802	8.956837
H	-7.80722	1.24572	8.380206
H	-5.33687	4.075445	8.418254
H	-4.86985	3.983202	6.713424

H	-4.34319	2.728519	7.842031
H	-7.77597	4.271026	7.759853
H	-8.53248	3.06359	6.703072
H	-7.34684	4.186745	6.040322

Table **S3**. Cartesian coordinates (Angstroms) for **I-2** in gas phase.
Point Group: C1
Imaginary Freq: 0
Total energy = -1729.294587 hartree

Symbol	X	Y	Z
C	-4.49281	1.137375	0.376766
C	-3.3592	1.921935	0.732478
C	-3.48268	3.027202	1.547174
C	-4.74453	3.412478	2.053158
C	-5.86085	2.678786	1.726615
C	-5.77443	1.534527	0.888494
C	-6.93387	0.787645	0.552845
C	-6.83175	-0.31389	-0.26141
C	-5.58419	-0.72921	-0.775
C	-4.42825	-0.02874	-0.4676
N	-3.16415	-0.41685	-0.96125
C	-2.85194	-1.4527	-1.80108
O	-3.65001	-2.23931	-2.29779
C	-1.33009	-1.54391	-2.10088
C	-1.01121	-2.62796	-3.13538
C	-0.8186	-3.89047	-2.28167
C	-0.0988	-3.37834	-1.02571
N	-0.55734	-1.9709	-0.90768
C	-0.12623	-1.05346	-0.01268
C	0.854866	-1.49911	1.088282
O	-0.48732	0.137221	-0.0794
C	0.241624	-1.43612	2.528278
C	-0.00228	0.009066	3.005741
C	1.222906	-2.12953	3.494006
C	-1.095	-2.20514	2.534514
N	2.069371	-0.70517	0.961448

C	3.079873	-1.07875	0.127608
O	3.113702	-2.15965	-0.46105
C	4.219468	-0.04356	-0.018
N	3.744635	1.309513	0.32777
C	3.376391	2.217244	-0.70188
C	2.376693	1.705218	-1.71662
C	2.205221	2.670375	-2.89953
C	2.06252	4.115402	-2.41037
C	3.324399	4.55316	-1.6521
C	3.812741	3.488878	-0.70053
C	5.506093	-0.44169	0.794647
C	6.623469	0.583081	0.497098
C	5.228496	-0.48125	2.310962
C	6.009382	-1.82698	0.338777
H	-2.36845	1.669451	0.369981
H	-2.59923	3.607226	1.799971
H	-4.82909	4.285446	2.694757
H	-6.83902	2.965004	2.106223
H	-7.89565	1.104173	0.948348
H	-7.71824	-0.88608	-0.52173
H	-5.51832	-1.59752	-1.41429
H	-2.34929	0.092487	-0.62361
H	-0.97356	-0.55181	-2.39599
H	-0.08377	-2.36853	-3.65821
H	-1.81583	-2.73216	-3.86454
H	-0.24115	-4.66922	-2.78783
H	-1.79822	-4.30228	-2.02086
H	0.990577	-3.39418	-1.13666
H	-0.37019	-3.94991	-0.13313
H	1.16187	-2.52939	0.907542
H	-0.44987	-0.00649	4.006437
H	-0.67471	0.549788	2.336244
H	0.934556	0.573827	3.08299
H	0.827117	-2.10851	4.516083
H	2.196789	-1.62953	3.499596

H	1.382339	-3.17926	3.218232
H	-1.50168	-2.24146	3.55134
H	-0.96632	-3.24088	2.195781
H	-1.84719	-1.72759	1.897447
H	2.047681	0.285957	1.181402
H	4.50593	-0.08848	-1.07611
H	4.357597	1.764399	0.994687
H	1.412958	1.539792	-1.21356
H	2.68549	0.71976	-2.09122
H	1.332305	2.371749	-3.49242
H	3.078592	2.597751	-3.56268
H	1.193134	4.183161	-1.74188
H	1.871164	4.79302	-3.25132
H	3.126367	5.483519	-1.10085
H	4.120833	4.804528	-2.3718
H	4.546948	3.794878	0.046514
H	7.555968	0.263535	0.976006
H	6.39977	1.588647	0.87074
H	6.809484	0.6632	-0.58025
H	6.150901	-0.71665	2.854338
H	4.488086	-1.2477	2.562021
H	4.859685	0.476761	2.697293
H	6.931686	-2.07576	0.877345
H	6.233567	-1.83316	-0.73403
H	5.275211	-2.61321	0.52349

Table **S4**. Cartesian coordinates (Angstroms) for **TS-2** in gas phase.
Point Group: C1
Imaginary Freq: 1
Total energy = -1729.285376 hartree

Symbol	X	Y	Z
C	-4.53233	1.041345	0.406089
C	-3.42473	1.821816	0.843175
C	-3.58989	2.859493	1.73566
C	-4.86993	3.177425	2.242724
C	-5.96206	2.445736	1.838985

C	-5.83255	1.370096	0.919471
C	-6.96725	0.624912	0.504919
C	-6.82323	-0.40955	-0.38727
C	-5.55664	-0.75687	-0.90472
C	-4.42363	-0.05592	-0.52198
N	-3.1417	-0.37726	-1.01704
C	-2.78934	-1.33883	-1.92679
O	-3.55977	-2.10175	-2.49844
C	-1.26038	-1.37385	-2.20038
C	-0.89591	-2.37096	-3.30477
C	-0.6946	-3.68941	-2.54259
C	-0.01327	-3.25818	-1.23565
N	-0.50046	-1.87081	-1.02625
C	-0.10237	-1.01092	-0.0618
C	0.873322	-1.51368	1.019951
O	-0.49434	0.17211	-0.04975
C	0.244371	-1.54342	2.454006
C	-0.01319	-0.13309	3.020298
C	1.21615	-2.29359	3.386446
C	-1.08842	-2.31722	2.395034
N	2.087751	-0.71271	0.954462
C	3.09529	-1.01607	0.089926
O	3.116666	-2.0367	-0.59873
C	4.252332	0.007607	0.047571
N	3.770251	1.3423	0.459673
C	3.325126	2.243728	-0.59488
C	1.913054	2.762043	-0.43889
C	1.400877	3.478277	-1.69839
C	2.472126	4.400704	-2.29152
C	3.722751	3.597705	-2.67874
C	4.124034	2.617053	-1.60327
C	5.496908	-0.45984	0.888644
C	6.66612	0.519911	0.642289
C	5.176915	-0.50915	2.395965
C	5.956988	-1.85689	0.423343

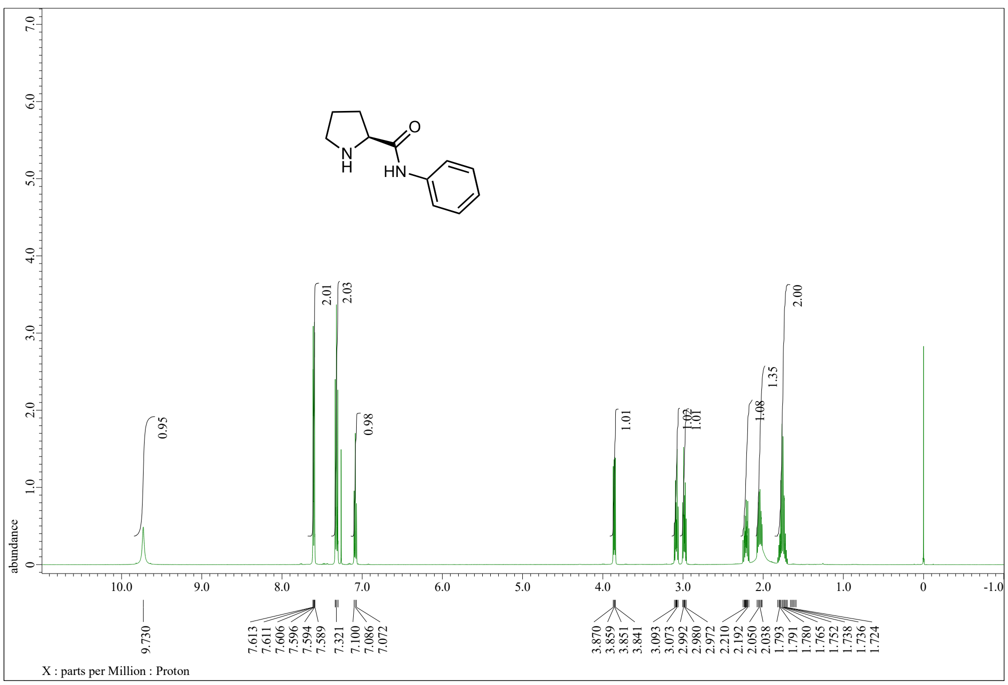
H	-2.42171	1.61903	0.48333
H	-2.72542	3.438141	2.049867
H	-4.98746	3.997386	2.946111
H	-6.9538	2.680657	2.218603
H	-7.94366	0.889058	0.903028
H	-7.69066	-0.9803	-0.70803
H	-5.45798	-1.57266	-1.60594
H	-2.34527	0.123138	-0.62614
H	-0.92157	-0.35488	-2.4135
H	0.037081	-2.05458	-3.78448
H	-1.68185	-2.43653	-4.05843
H	-0.08905	-4.41612	-3.09154
H	-1.67047	-4.13944	-2.33659
H	1.078158	-3.24577	-1.32057
H	-0.29535	-3.89774	-0.3938
H	1.184084	-2.53085	0.779884
H	-0.47339	-0.21533	4.012021
H	-0.68011	0.44557	2.377769
H	0.918978	0.430601	3.146883
H	0.804371	-2.3435	4.401201
H	2.18631	-1.78957	3.441774
H	1.387431	-3.32149	3.043741
H	-1.50504	-2.42346	3.4029
H	-0.95063	-3.32718	1.988778
H	-1.83652	-1.80147	1.783609
H	2.095189	0.244213	1.293928
H	4.571632	0.01232	-1.00247
H	4.481972	1.80987	1.011819
H	1.881927	3.443695	0.426963
H	1.243817	1.931491	-0.18512
H	0.489362	4.04075	-1.46369
H	1.119876	2.725682	-2.44844
H	2.747	5.161372	-1.54737
H	2.083209	4.938256	-3.16487
H	4.561881	4.276393	-2.88529

H	3.546008	3.055895	-3.62172
H	5.129483	2.201318	-1.66795
H	7.562409	0.168886	1.166257
H	6.465467	1.535921	1.002745
H	6.908408	0.585213	-0.42521
H	6.071461	-0.7965	2.960892
H	4.394675	-1.24348	2.613066
H	4.840141	0.459782	2.782269
H	6.863531	-2.14419	0.969515
H	6.190277	-1.86259	-0.64725
H	5.19458	-2.61955	0.593736

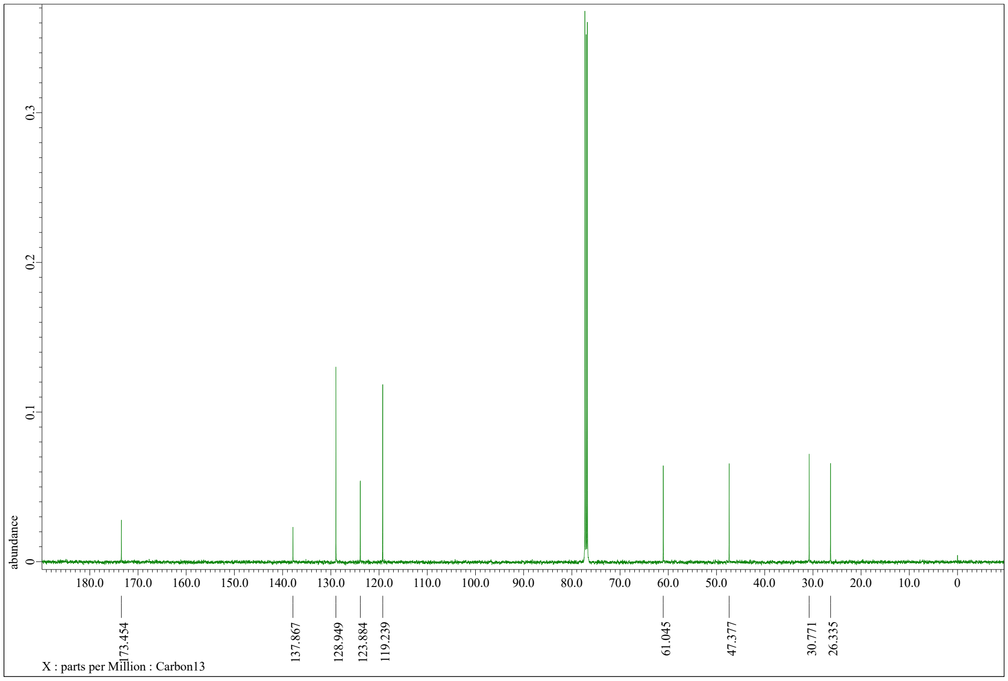
4. ^{1}H & ^{13}C NMR SPECTRA

L-Pro-Ph (3a) (Chemical Formula: $C_{11}H_{14}N_2O$)

^{1}H-NMR

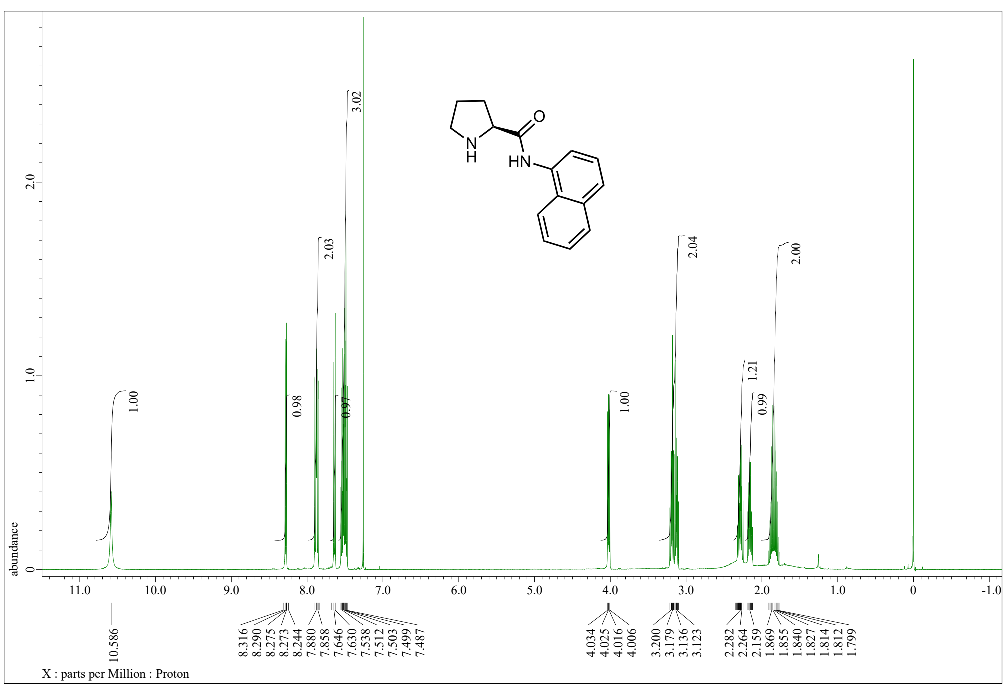


13C-NMR



L-Pro-1-Naph (3b) (Chemical Formula: $C_{15}H_{16}N_2O$)

[1]H-NMR



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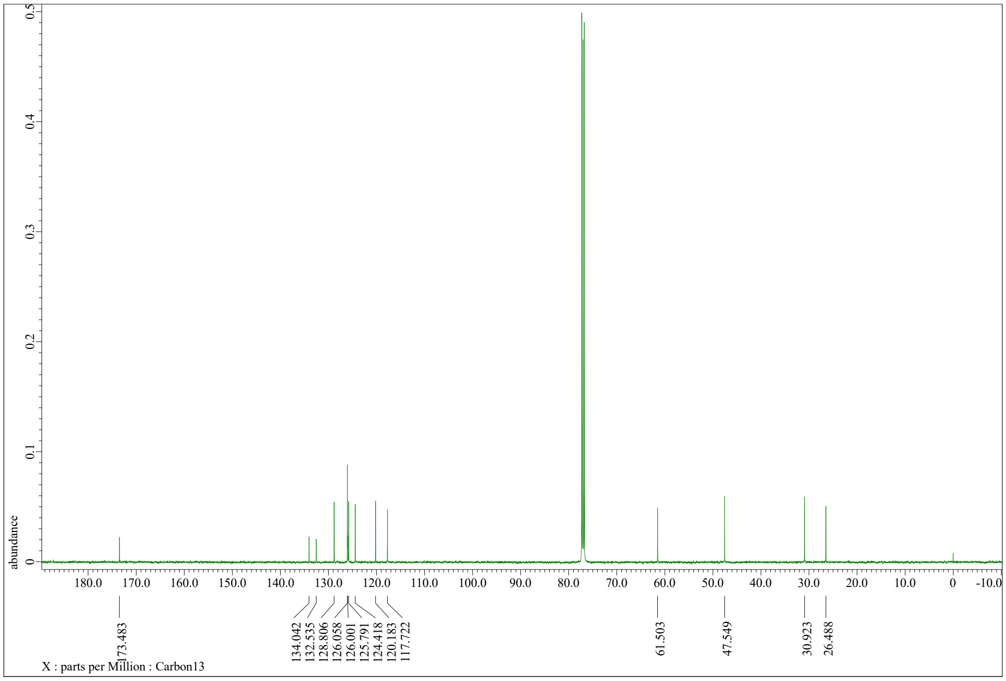
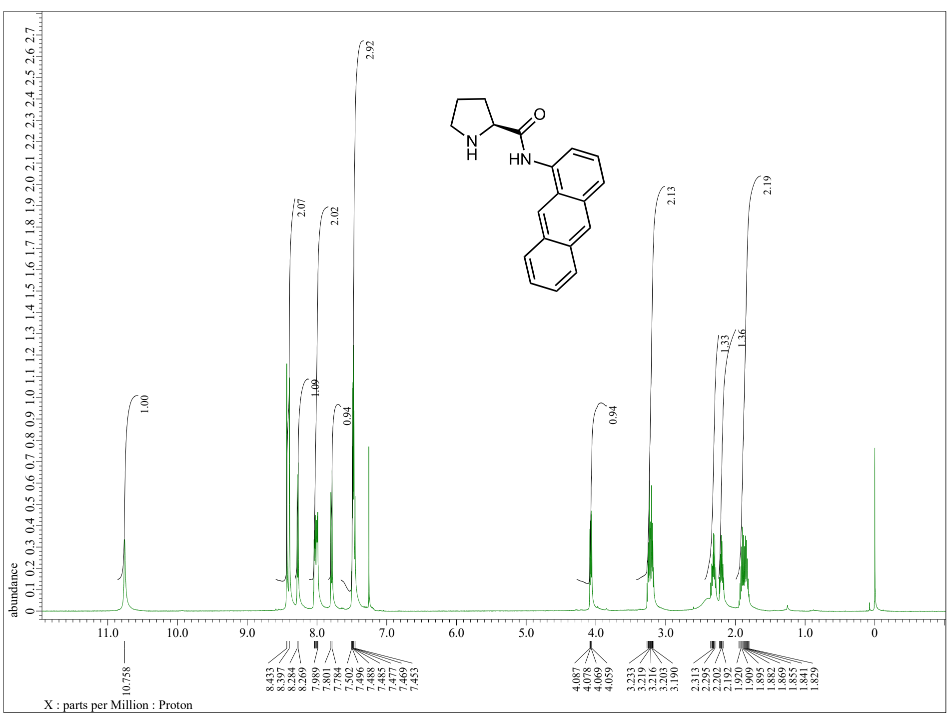
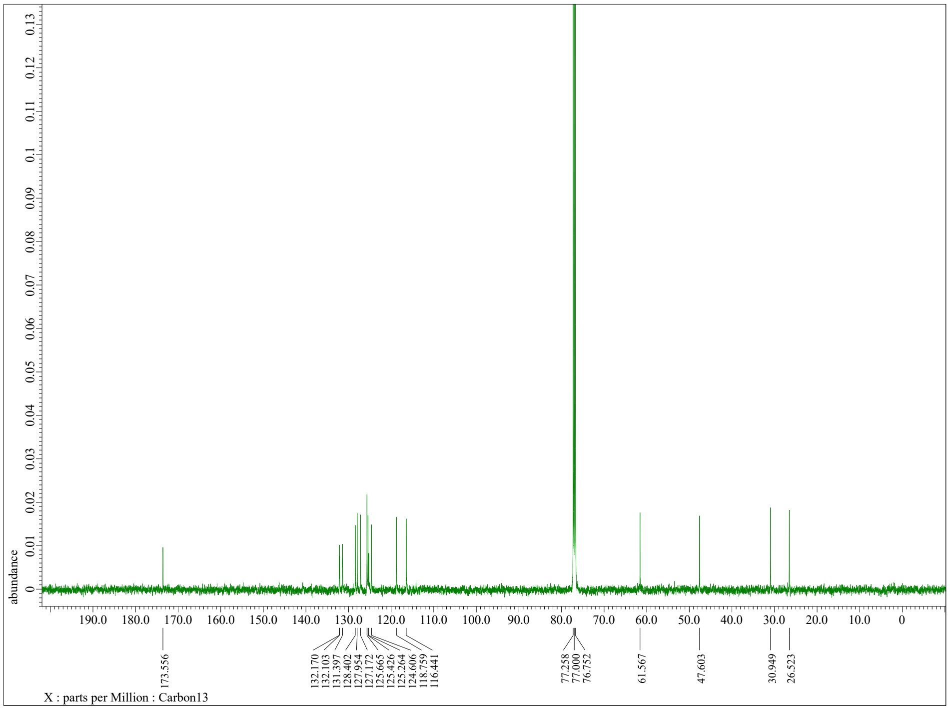


L-Pro-1-Anth (3c) (Chemical Formula: $C_{19}H_{18}N_2O$)

^{1}H-NMR

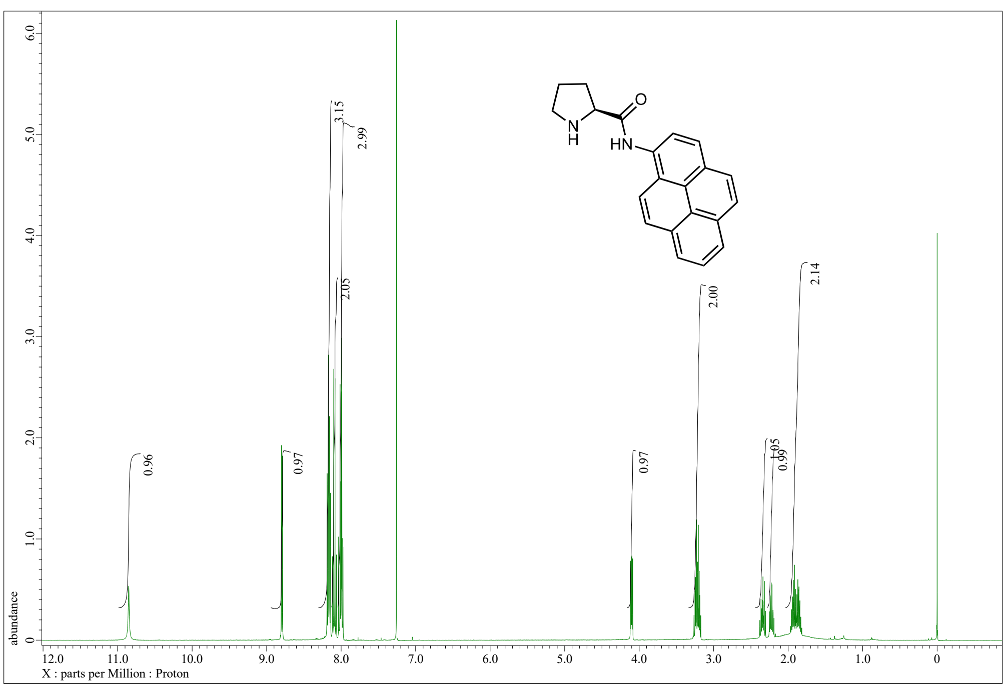


13C-NMR

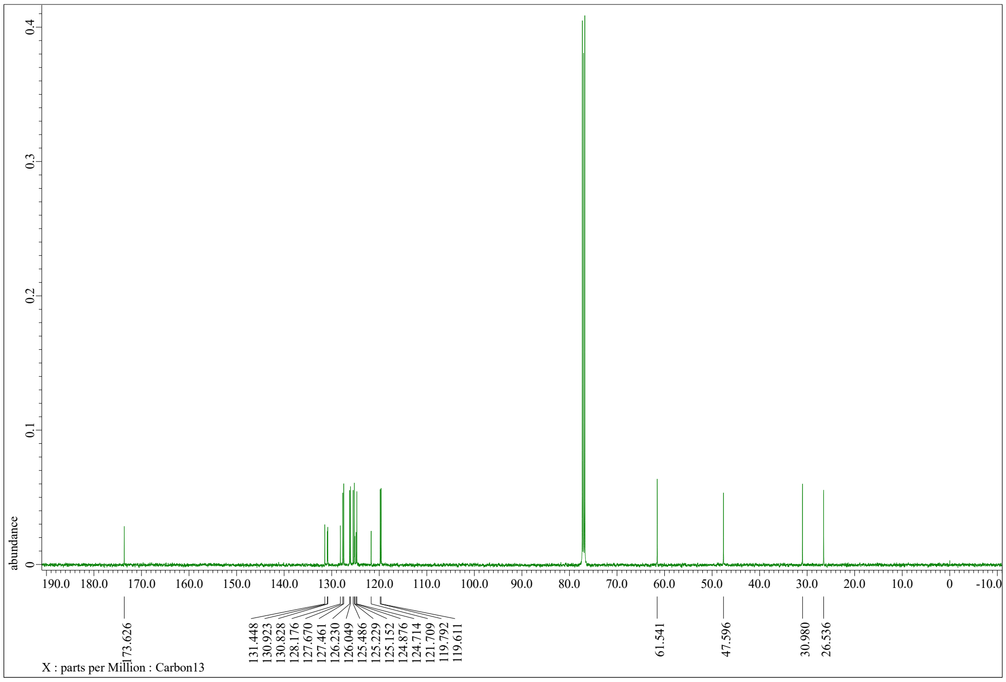


L-Pro-1-Pyr (3d) (Chemical Formula: $C_{21}H_{18}N_2O$)

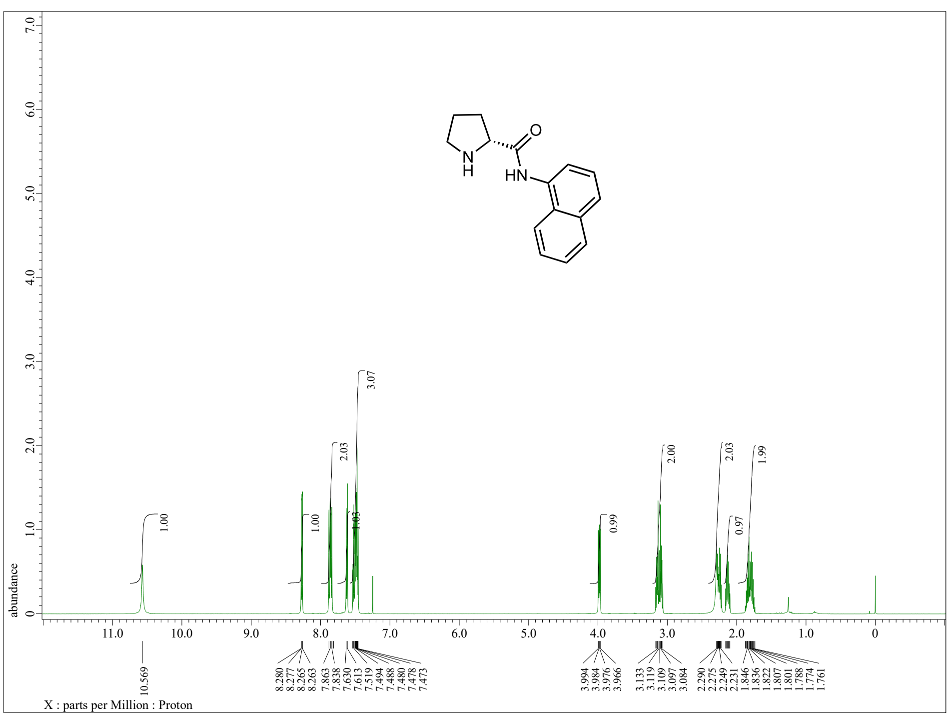
^{1}H-NMR



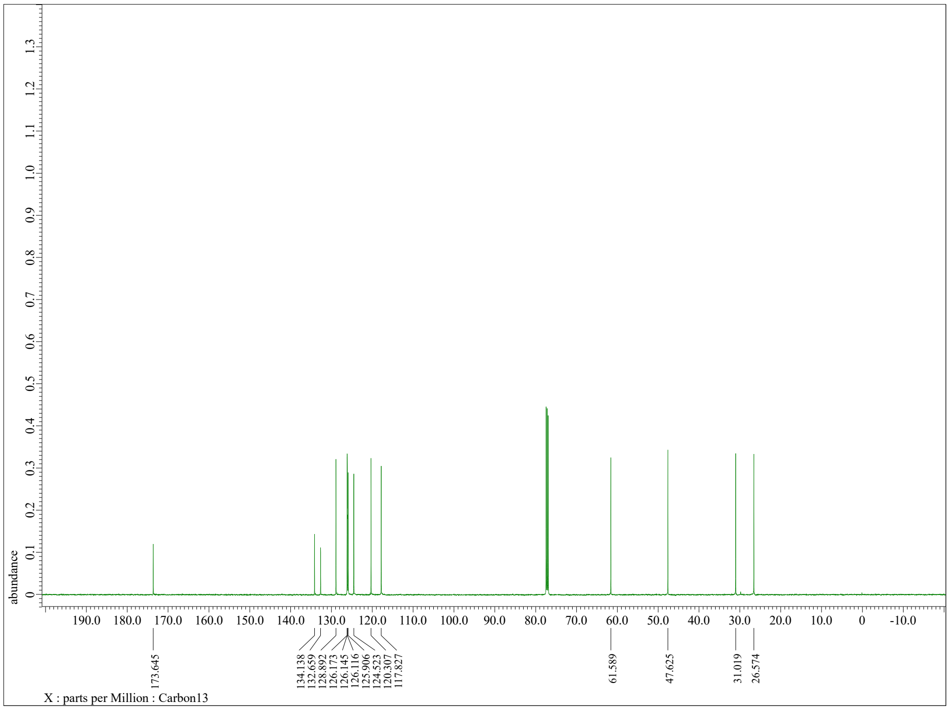
13C-NMR



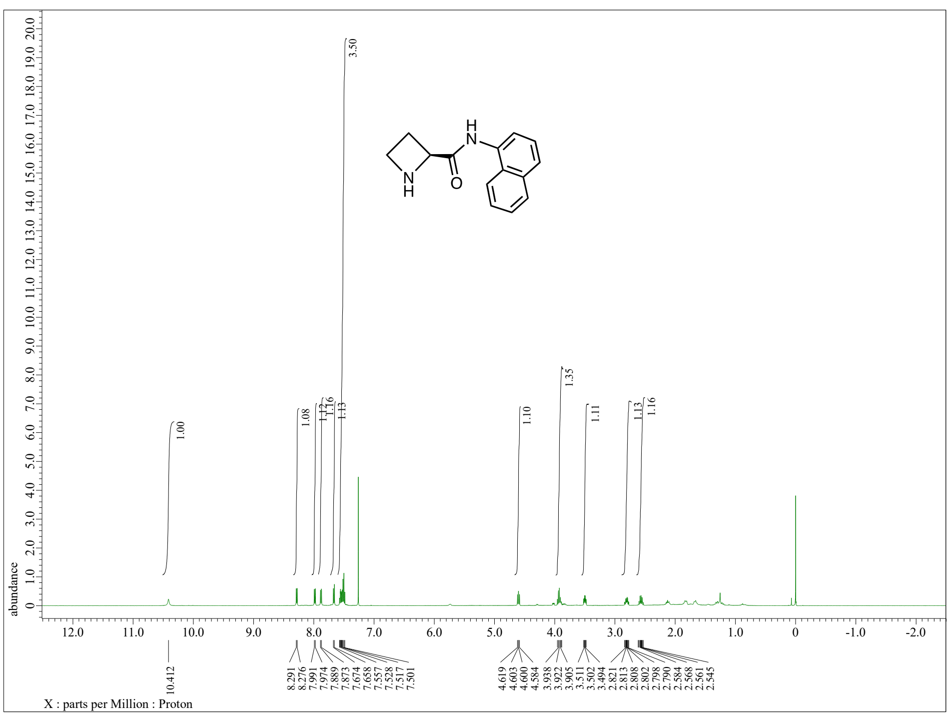
$_D$**Pro-1-Naph (8)** (Chemical Formula: $C_{15}H_{16}N_2O$)
^{1}H-NMR



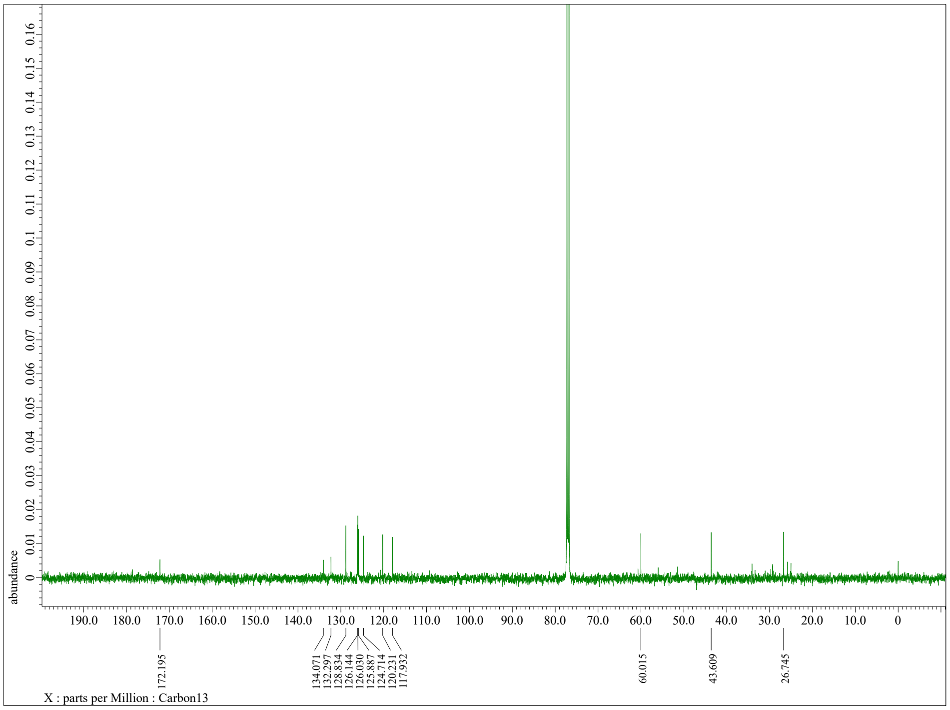
13C-NMR



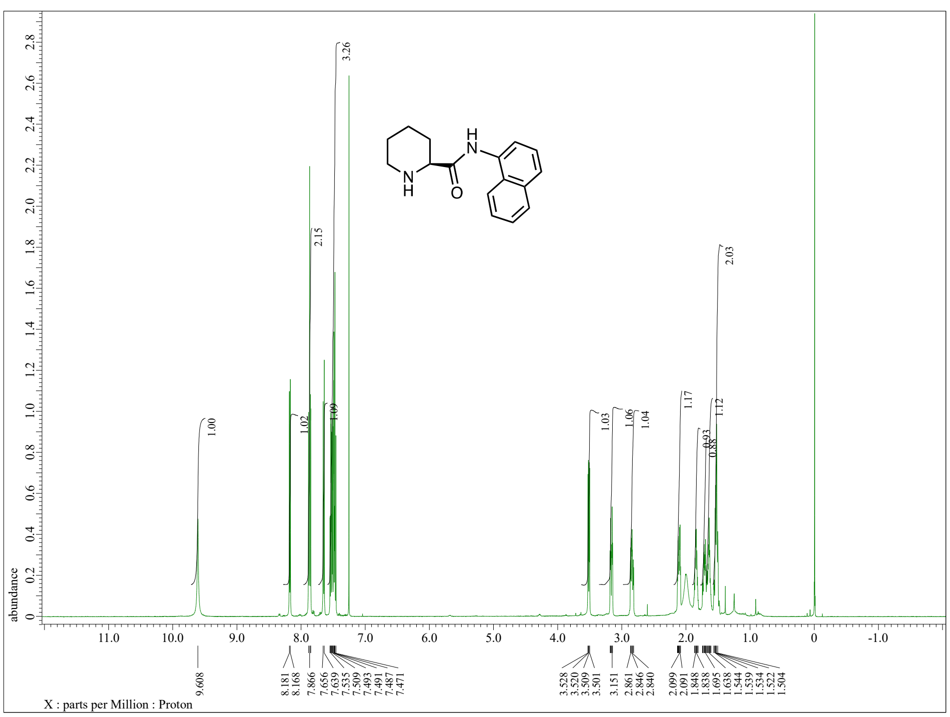
L-Aze-1-Naph (12a) (Chemical Formula: $C_{14}H_{14}N_2O$)
^{1}H-NMR



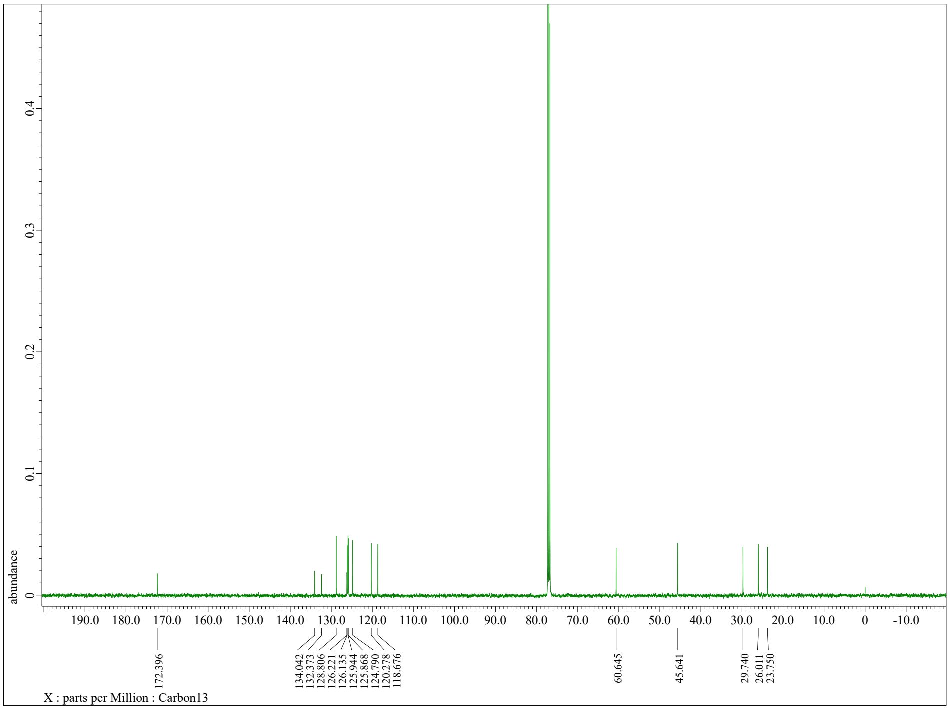
13C-NMR



L-Pip-1-Naph (12b) (Chemical Formula: $C_{16}H_{18}N_2O$)
¹H-NMR

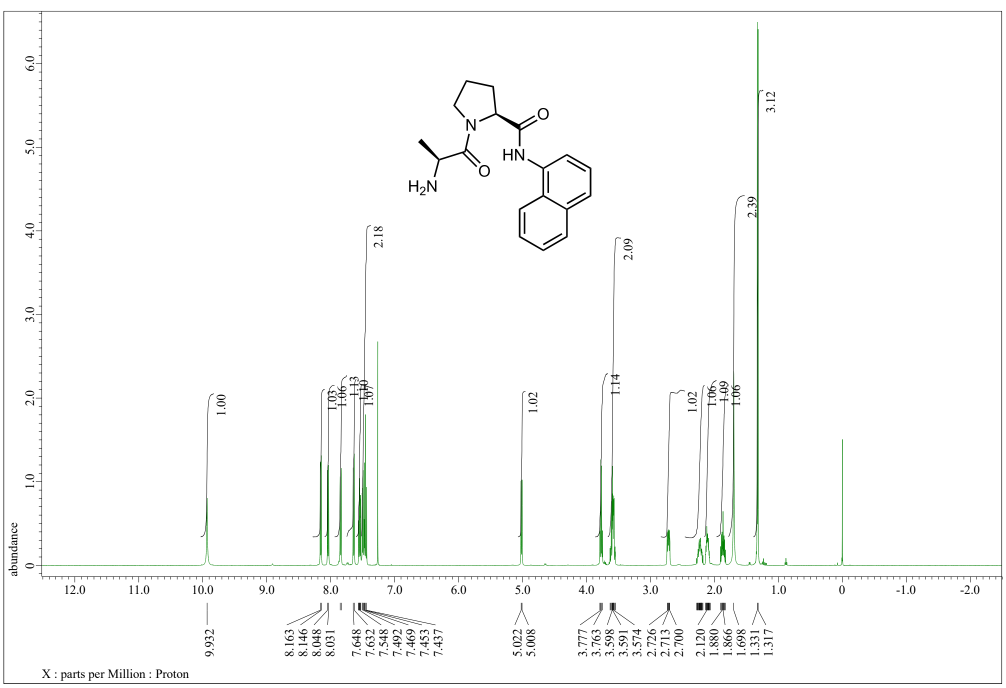


13C-NMR

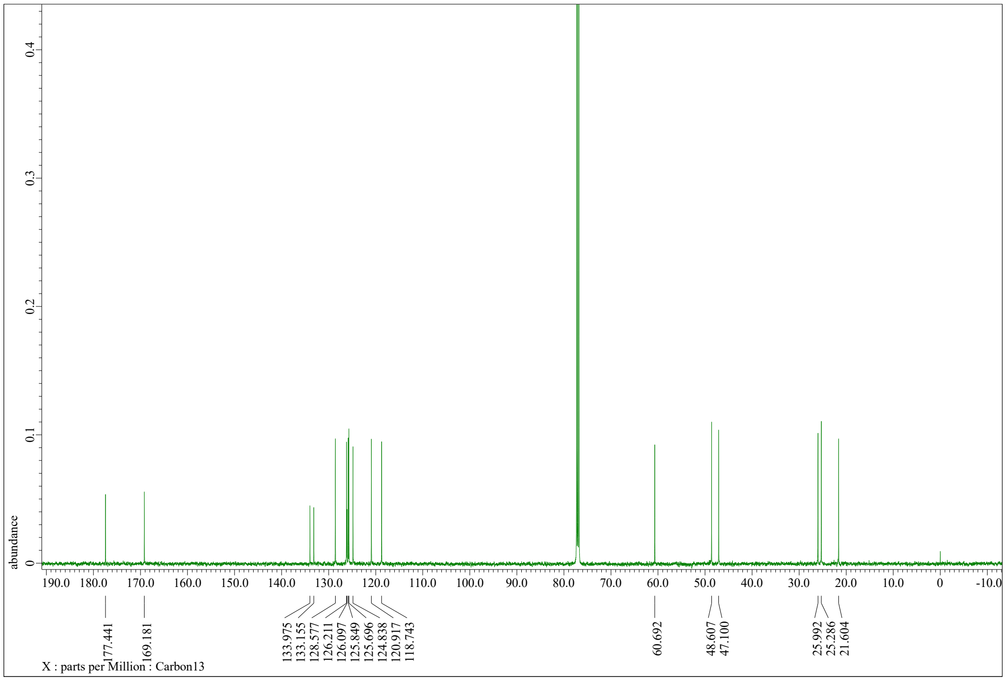


L-Ala- L-Pro-1-Naph (5a) (Chemical Formula: $C_{18}H_{18}N_3O_2$)

^{1}H-NMR

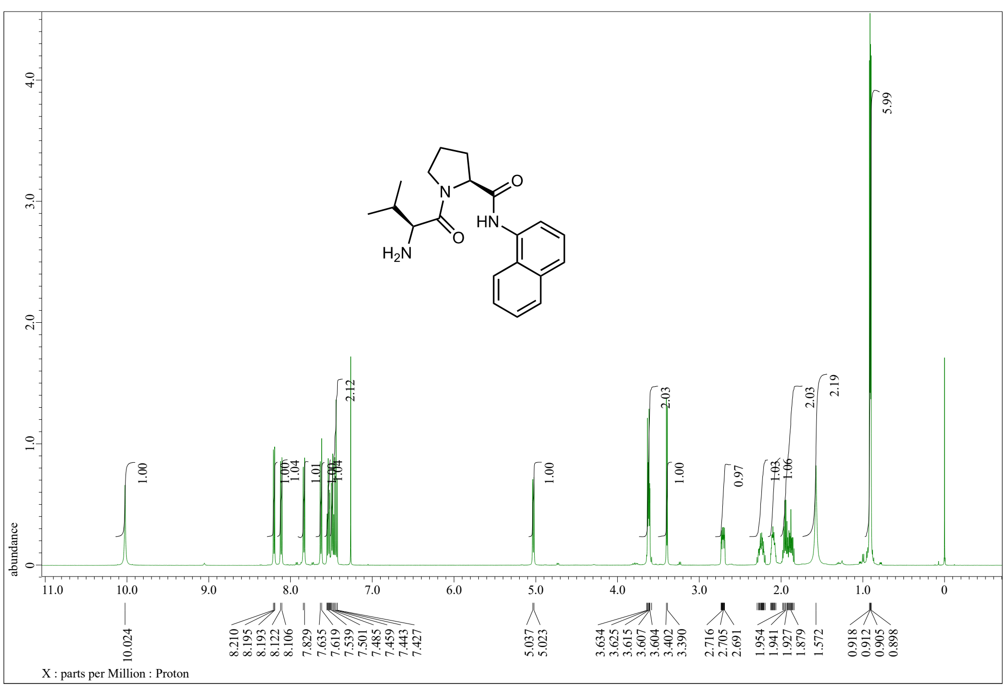


13C-NMR

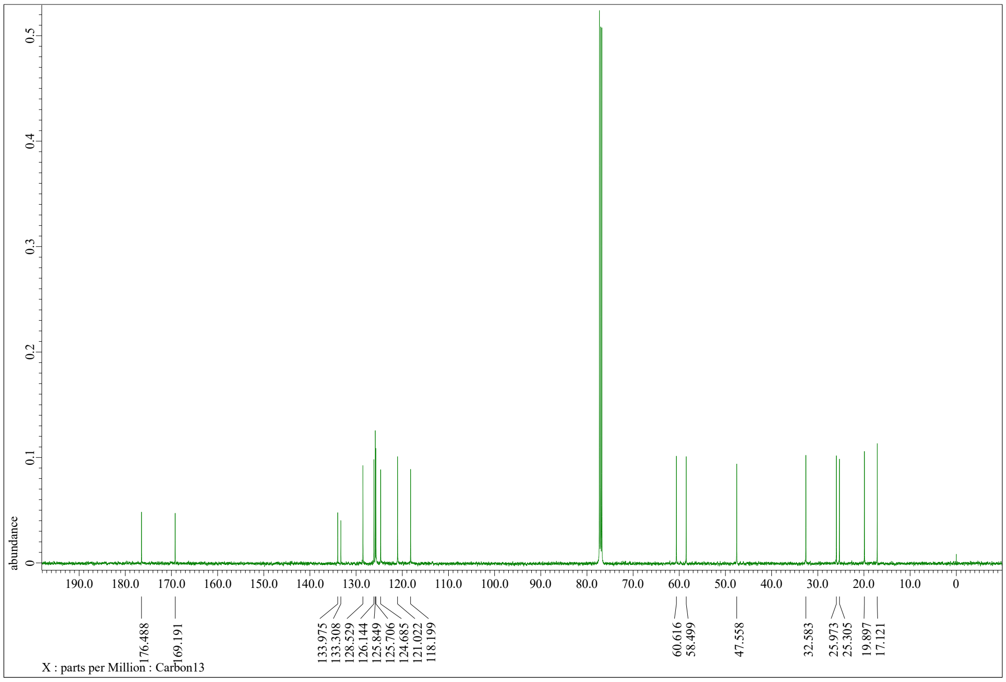


L-Val- L-Pro-1-Naph (5b) (Chemical Formula: $C_{20}H_{25}N_3O_2$)

[1]H-NMR

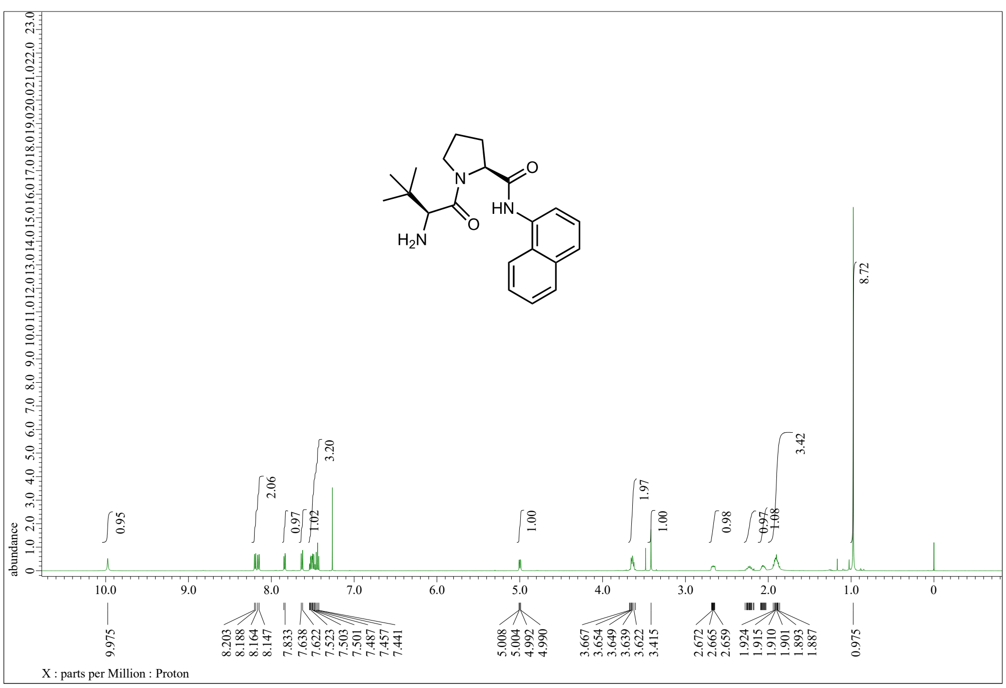


13C-NMR

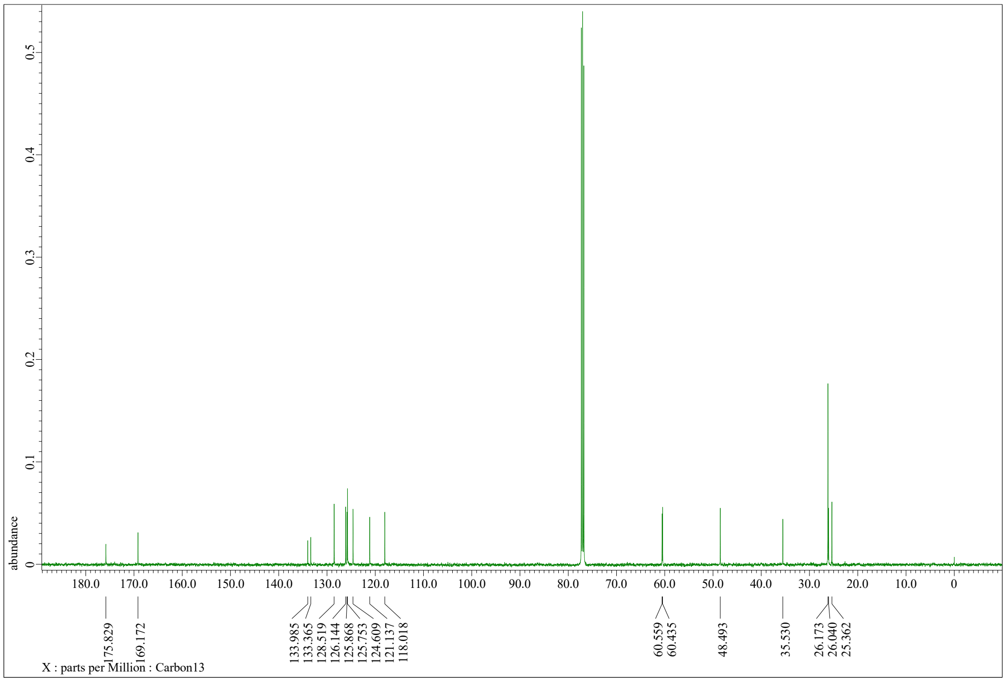


L-Tle- L-Pro-1-Naph (5c) (Chemical Formula: $C_{21}H_{27}N_3O_2$)

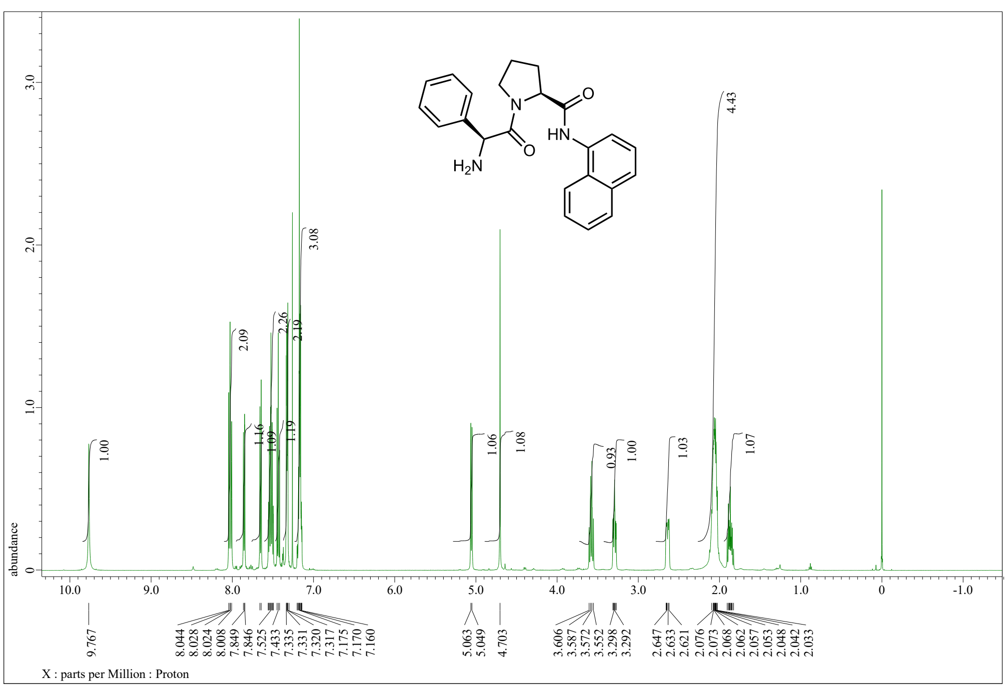
[1]H-NMR



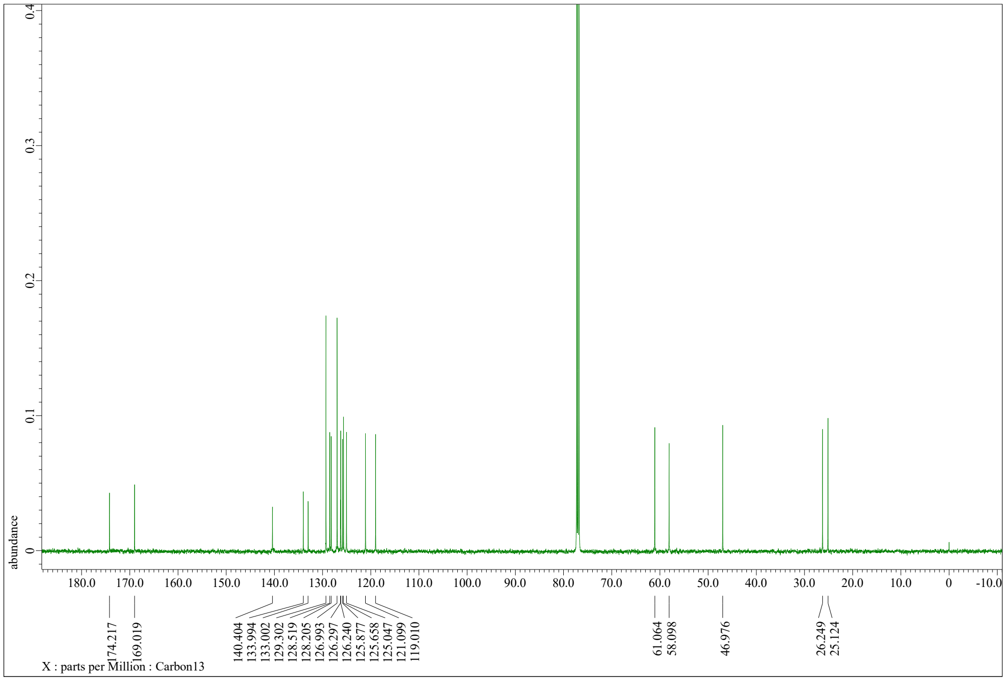
13C-NMR



L-Phg- L-Pro-1-Naph (5d) (Chemical Formula: $C_{23}H_{23}N_3O_2$)
^{1}H-NMR

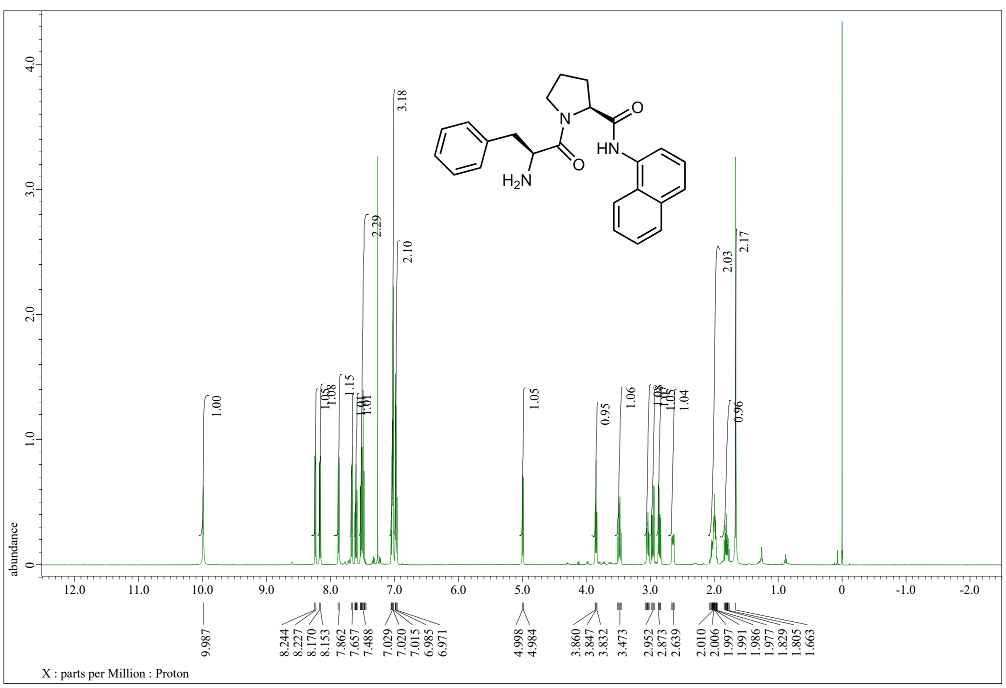


13C-NMR

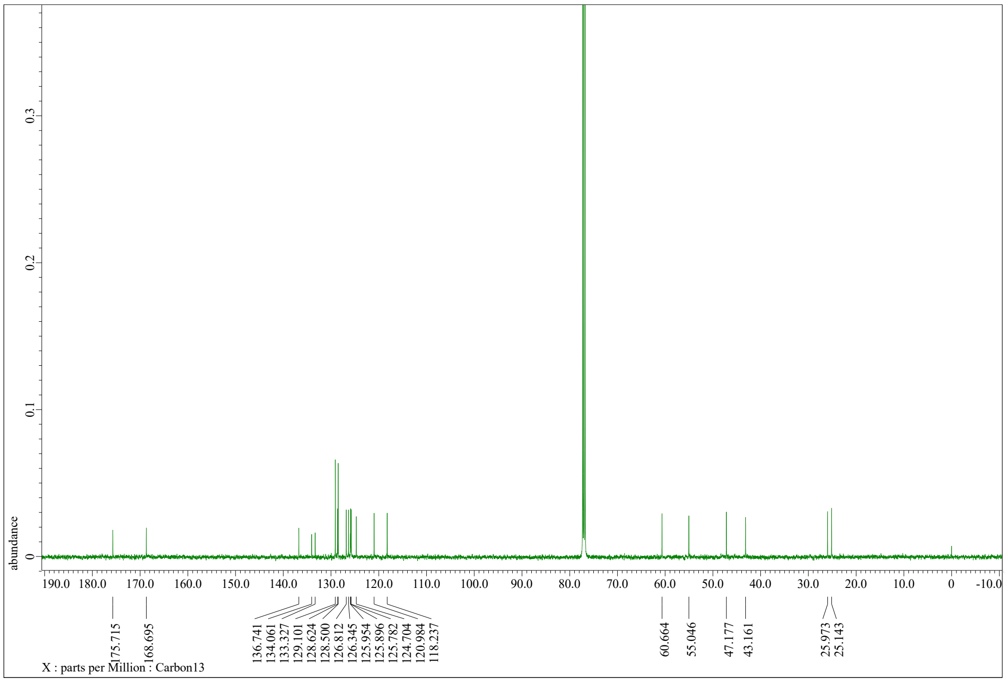


L-Phe- L-Pro-1-Naph (5e) (Chemical Formula: $C_{24}H_{25}N_3O_2$)

^{1}H-NMR

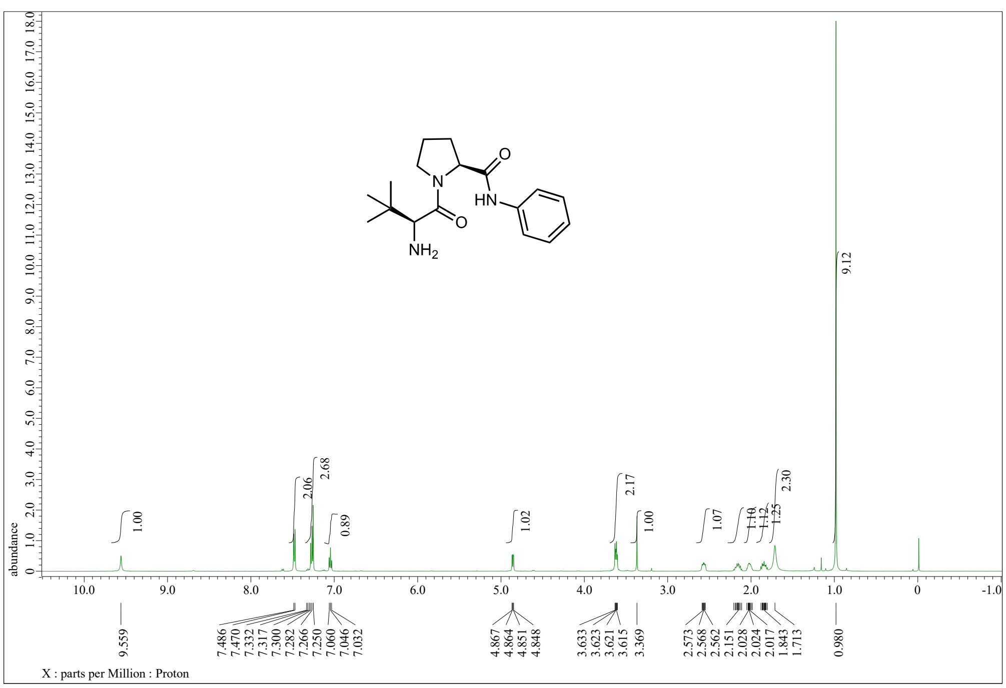


13C-NMR

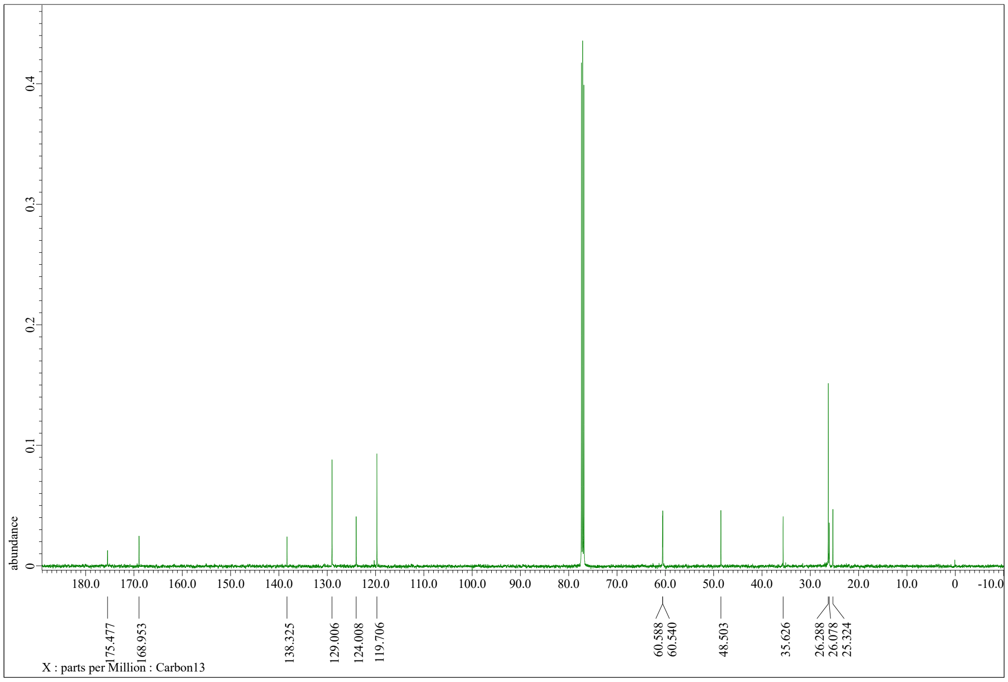


L-Tle- L-Pro-1-Ph (5f) (Chemical Formula: $C_{17}H_{25}N_3O_2$)

^{1}H-NMR

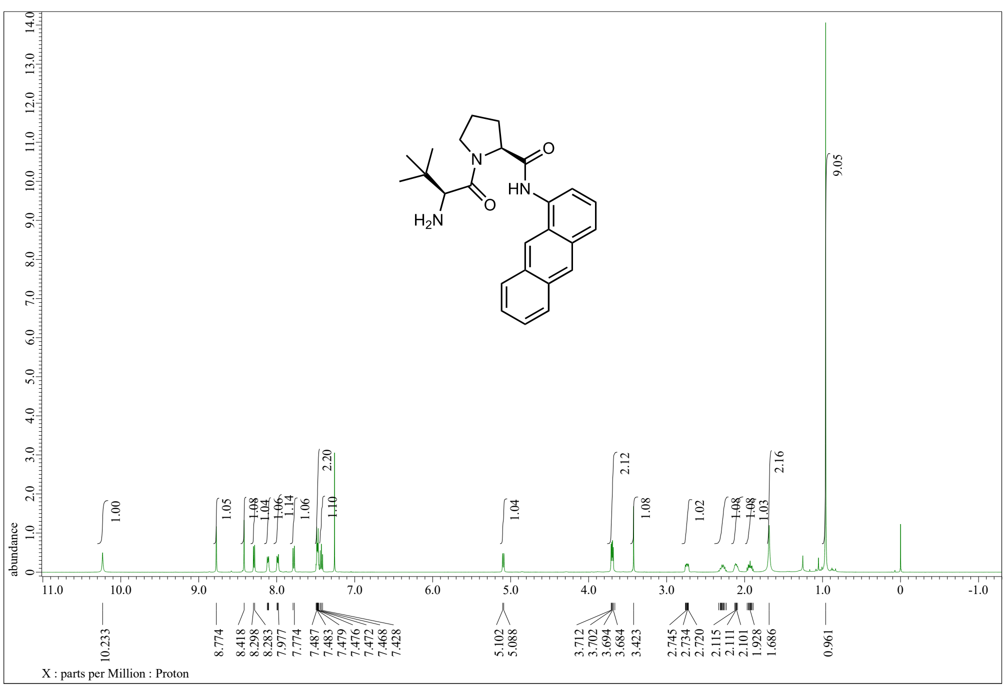


13C-NMR

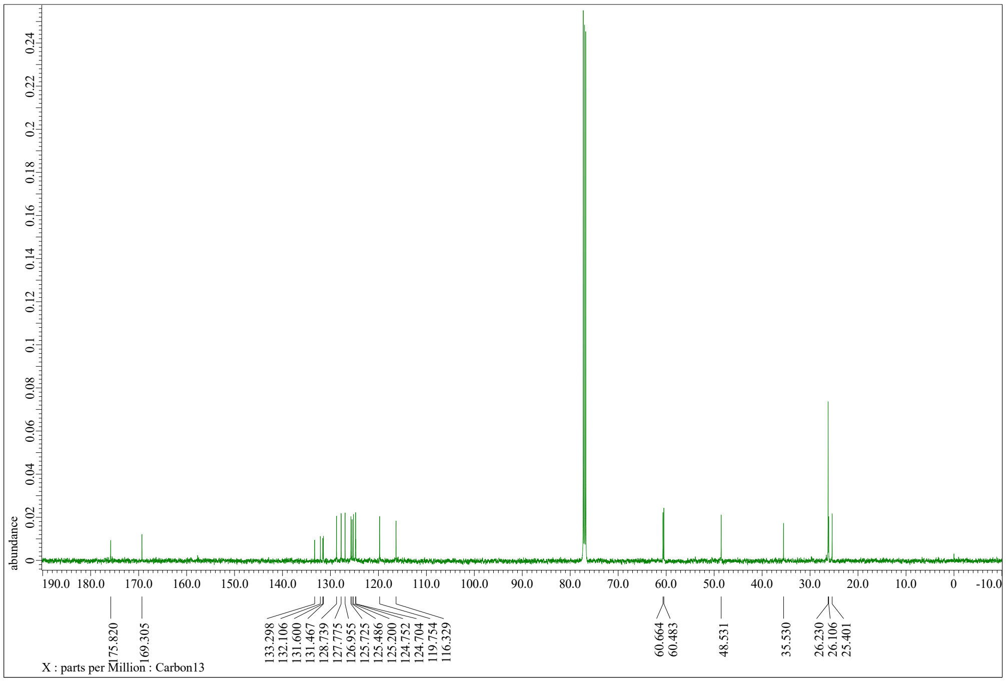


L-Tle- L-Pro-1-Anth (5g) (Chemical Formula: $C_{25}H_{29}N_3O_2$)

[1]H-NMR

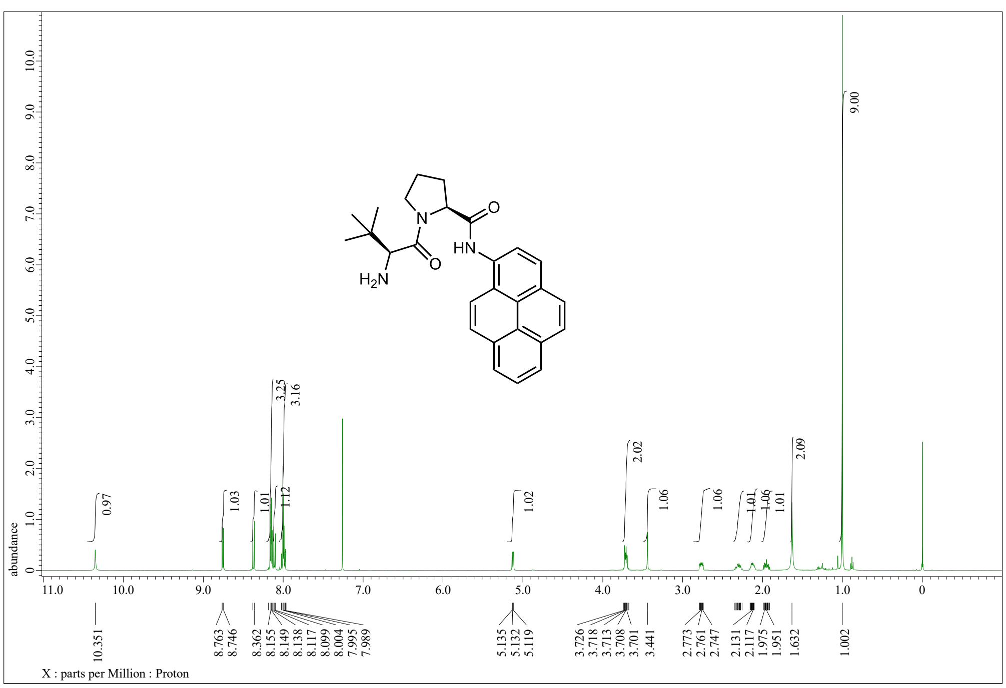


13C-NMR

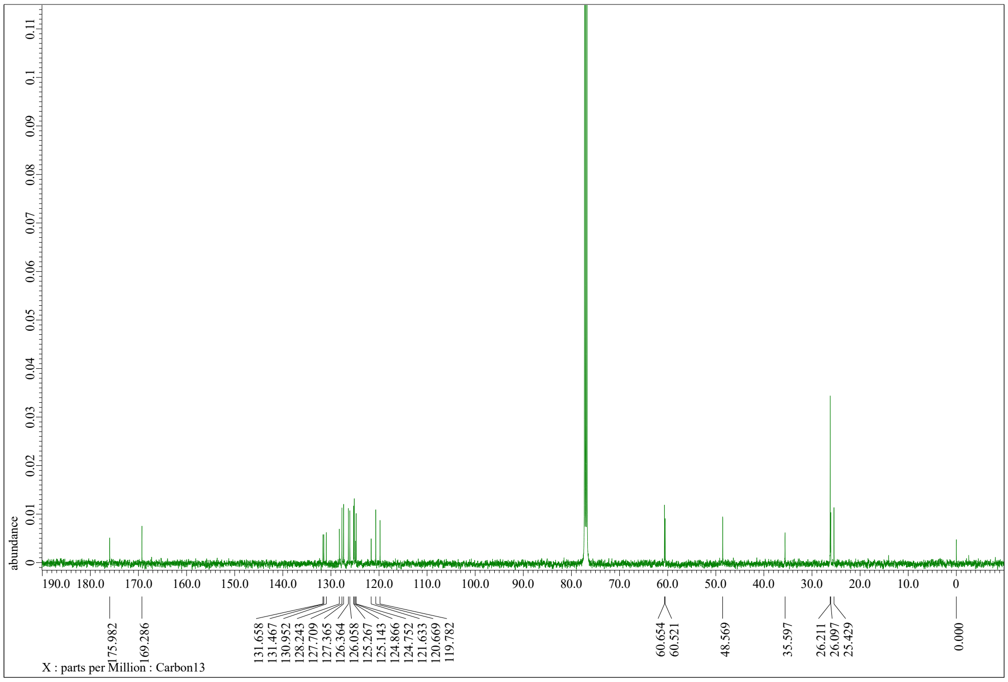


L-Tle- L-Pro-1-Pyr (5h) (Chemical Formula: $C_{27}H_{29}N_3O_2$)

^{1}H-NMR

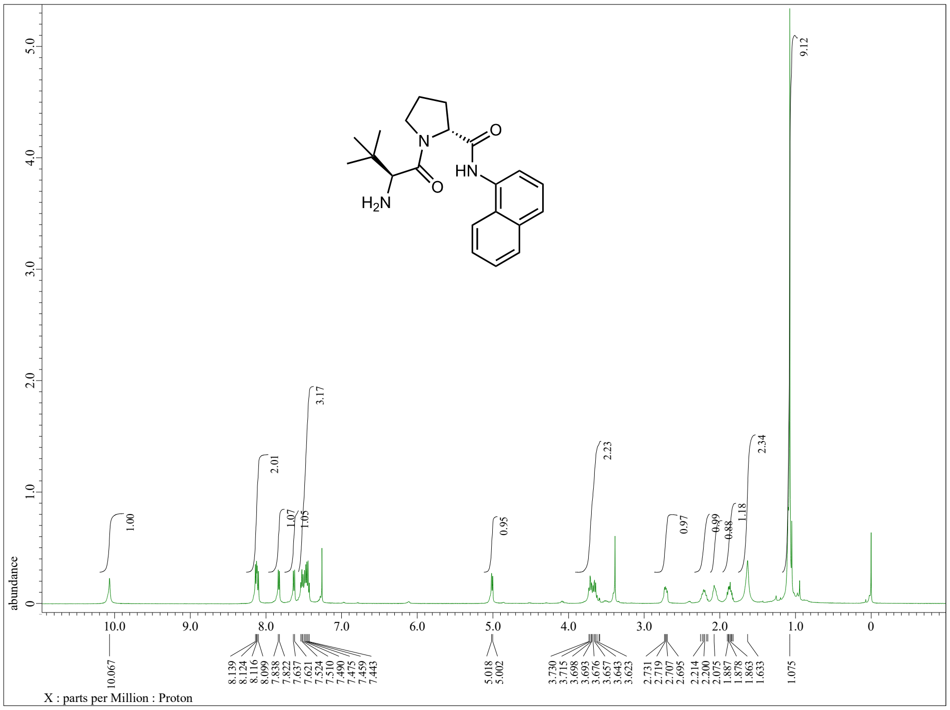


13C-NMR

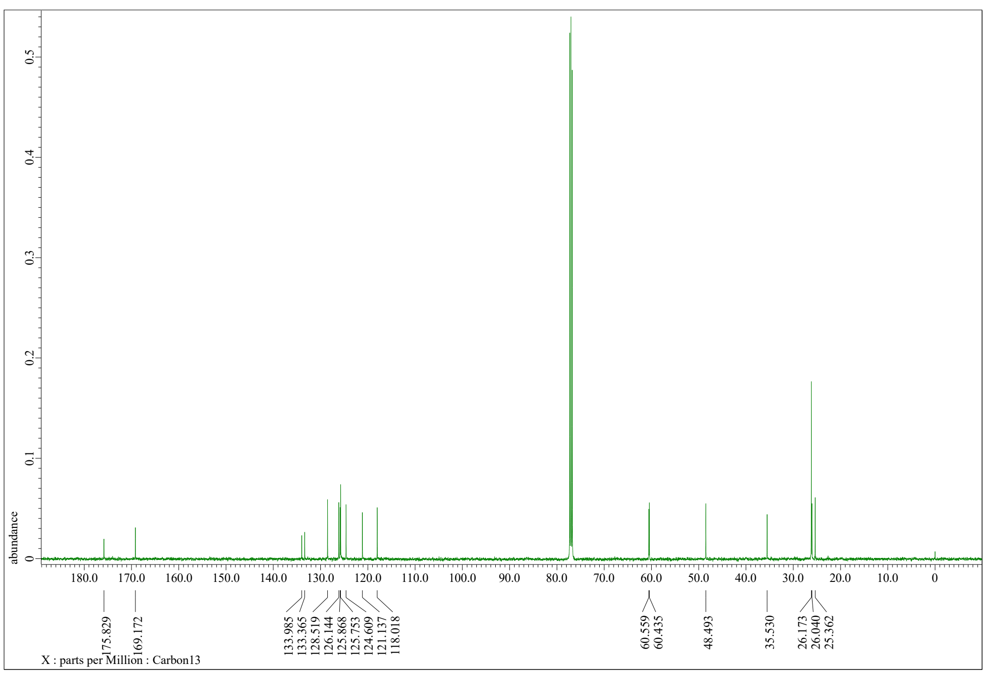


L-Tle-$_D$Pro-1-Naph (9) (Chemical Formula: $C_{21}H_{27}N_3O_2$)

[1]H-NMR

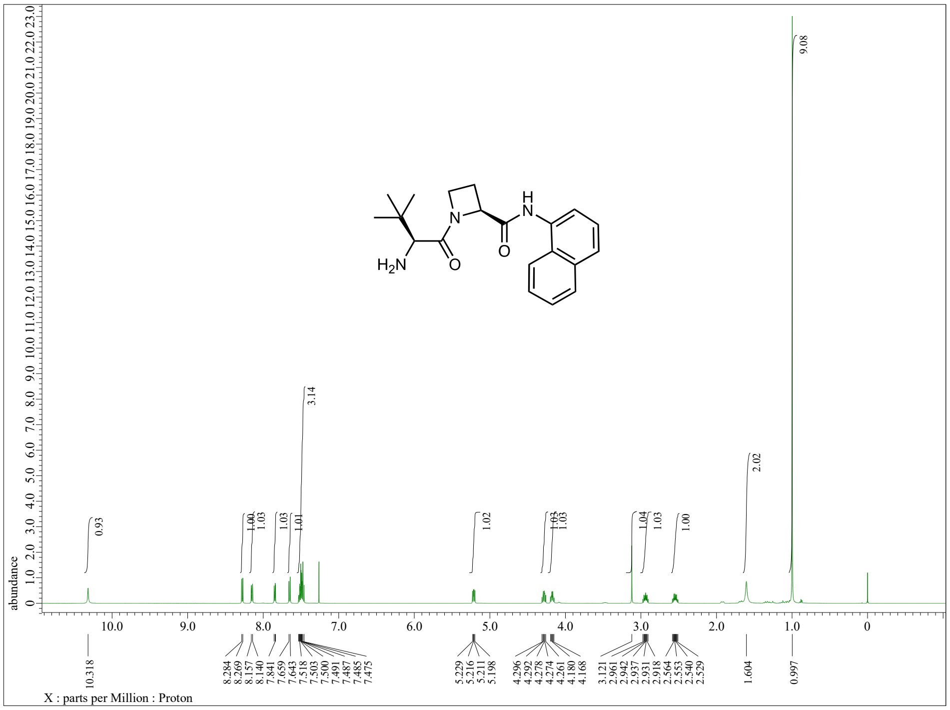


13C-NMR

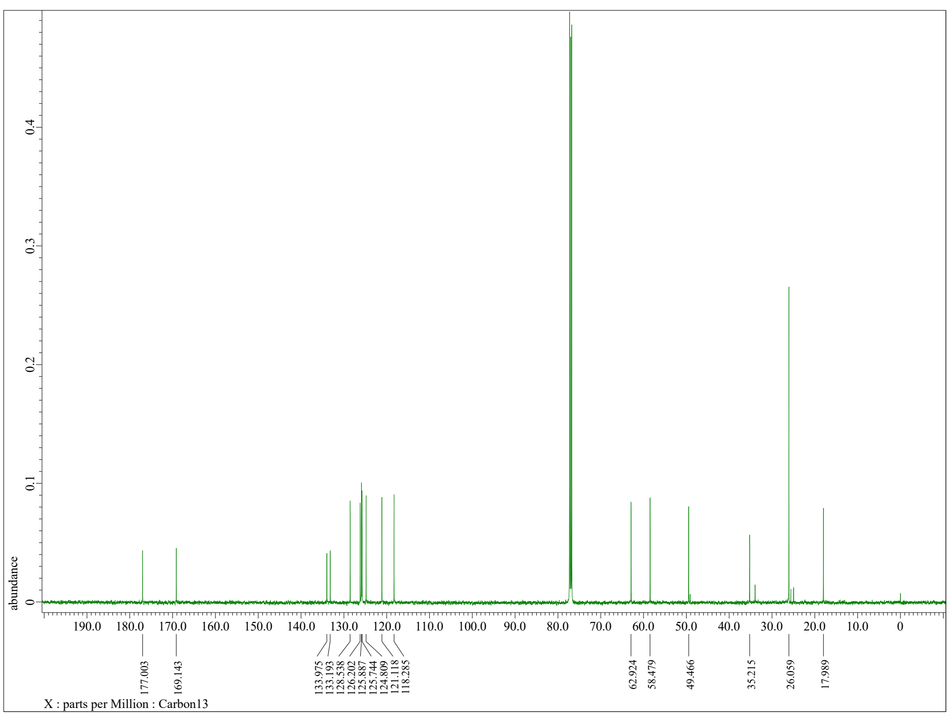


L-Tle- L-Aze-1-Naph (13a) (Chemical Formula: $C_{20}H_{25}N_3O_2$)

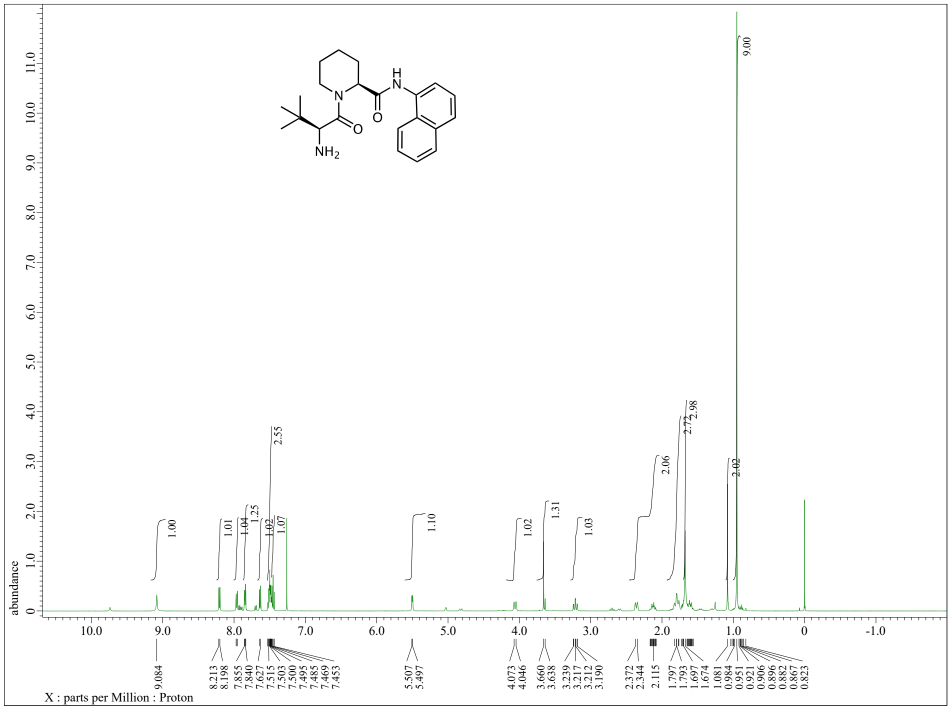
^{1}H-NMR



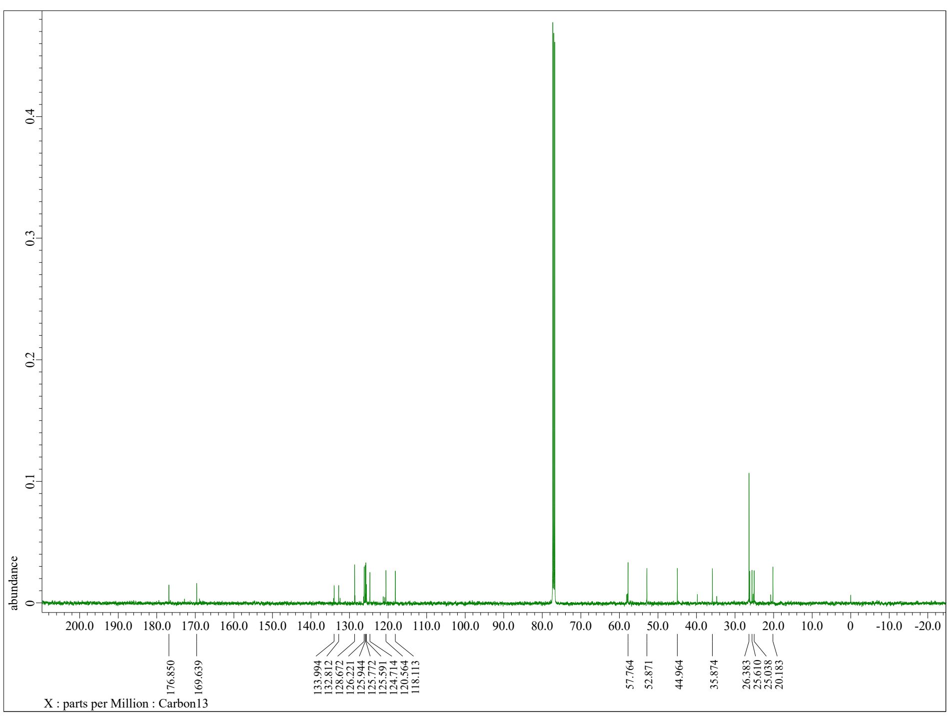
13C-NMR



L-Tle- L-Pip-1-Naph (13b) (Chemical Formula: $C_{22}H_{29}N_3O_2$)
^{1}H-NMR

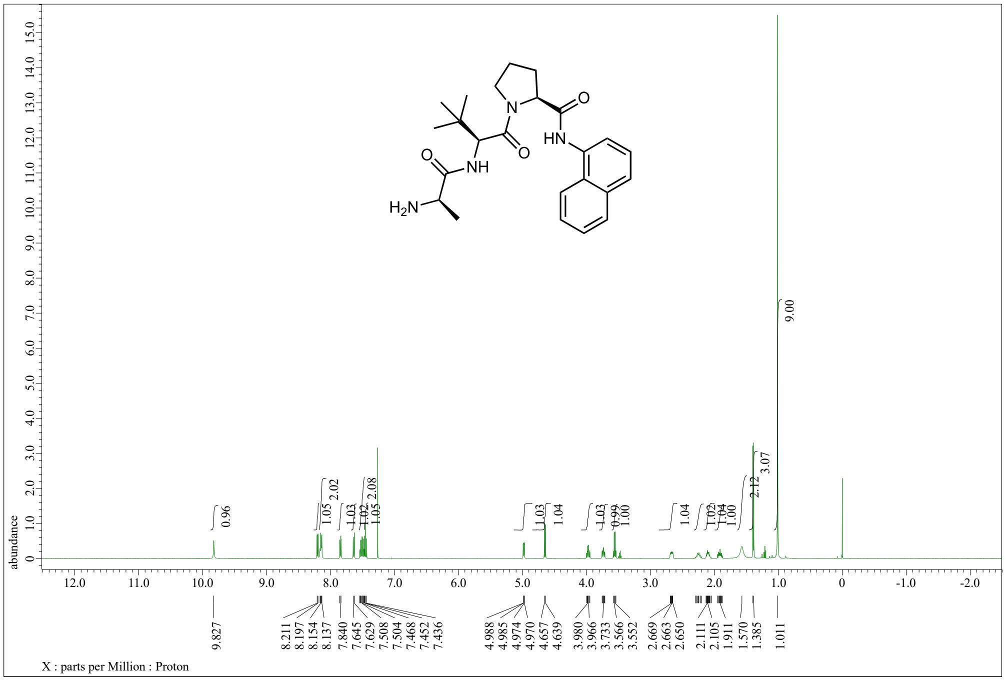


13C-NMR

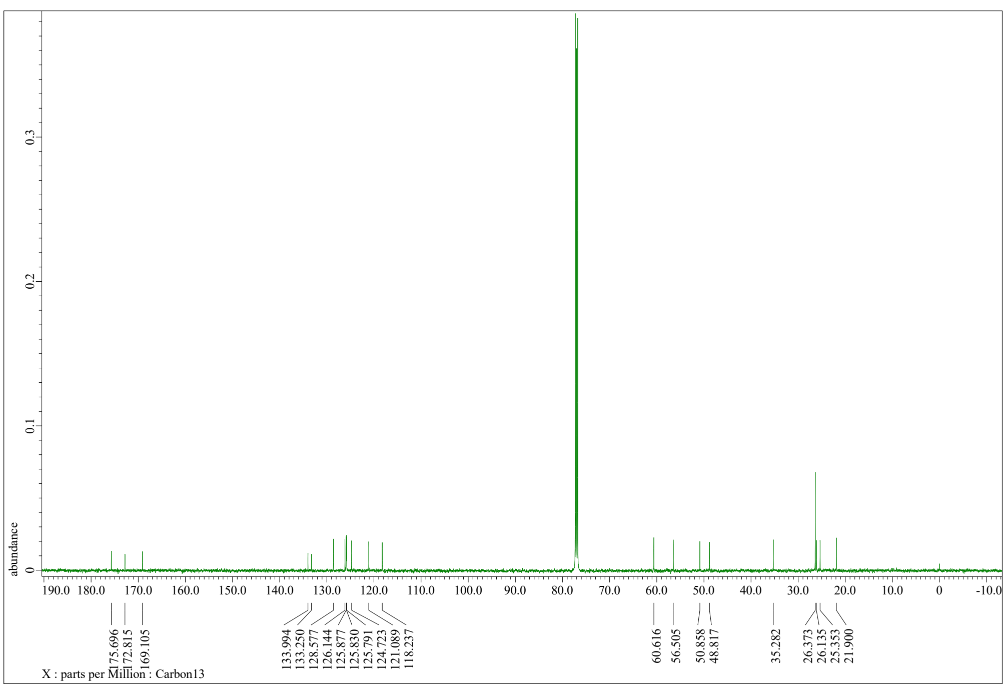


L-Ala- L-Tle- L-Pro-1-Naph (6a) (Chemical Formula: $C_{24}H_{32}N_4O_3$)

[1]H-NMR

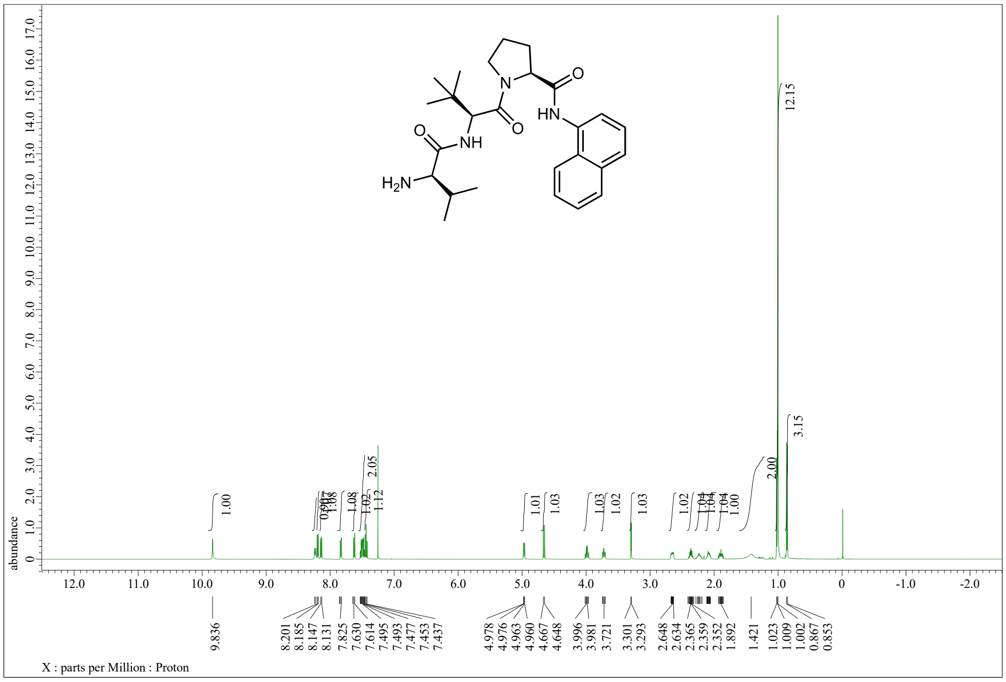


13C-NMR

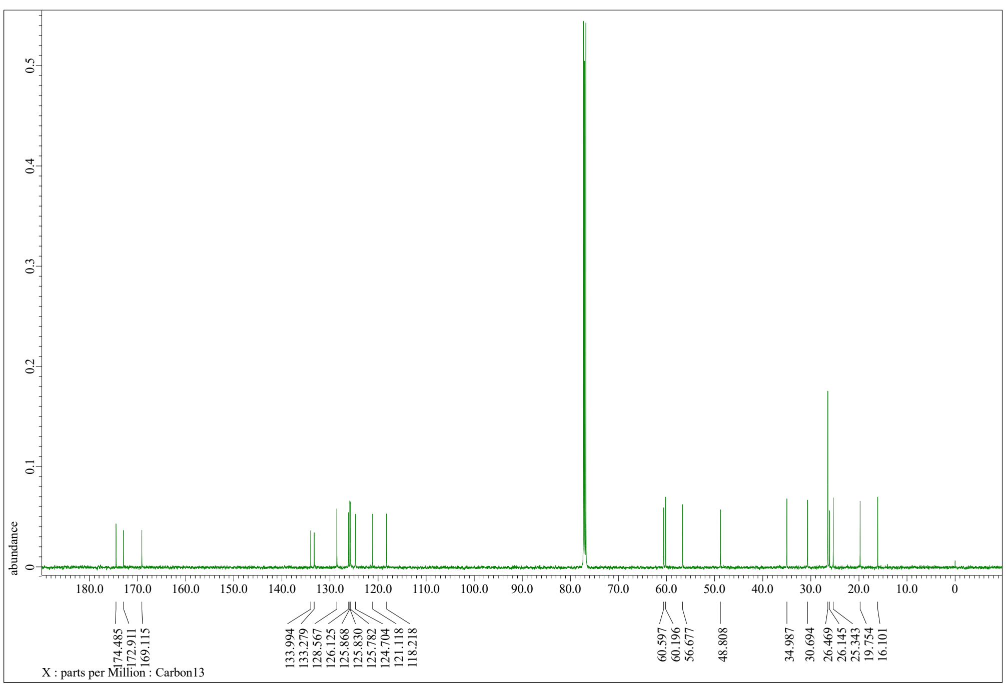


L-Val- L-Tle- L-Pro-1-Naph (6b) (Chemical Formula: $C_{26}H_{36}N_4O_3$)

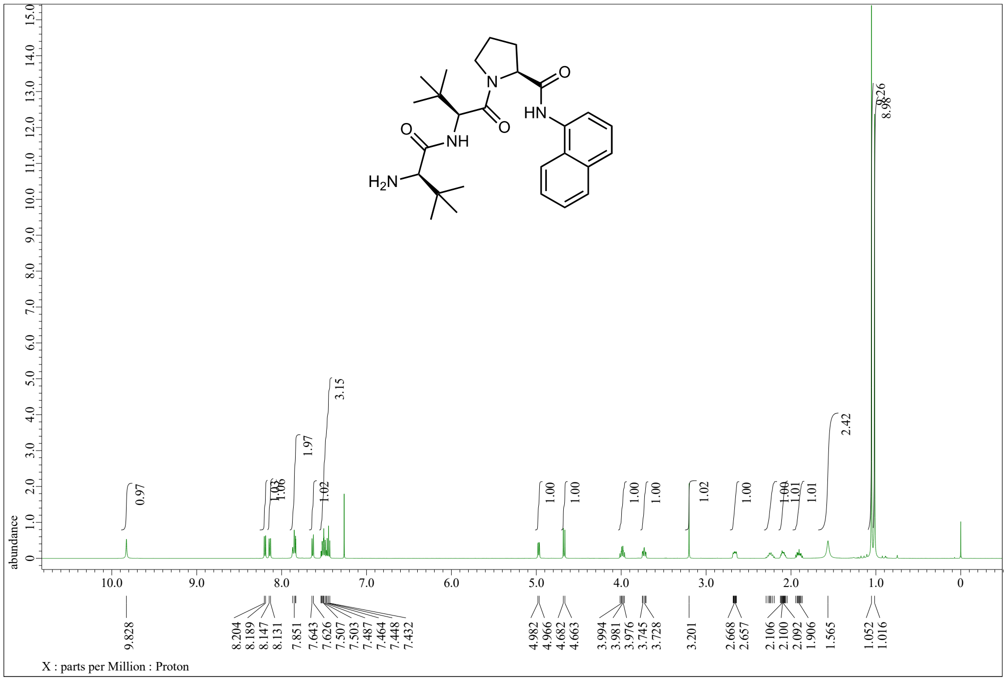
^{1}H-NMR



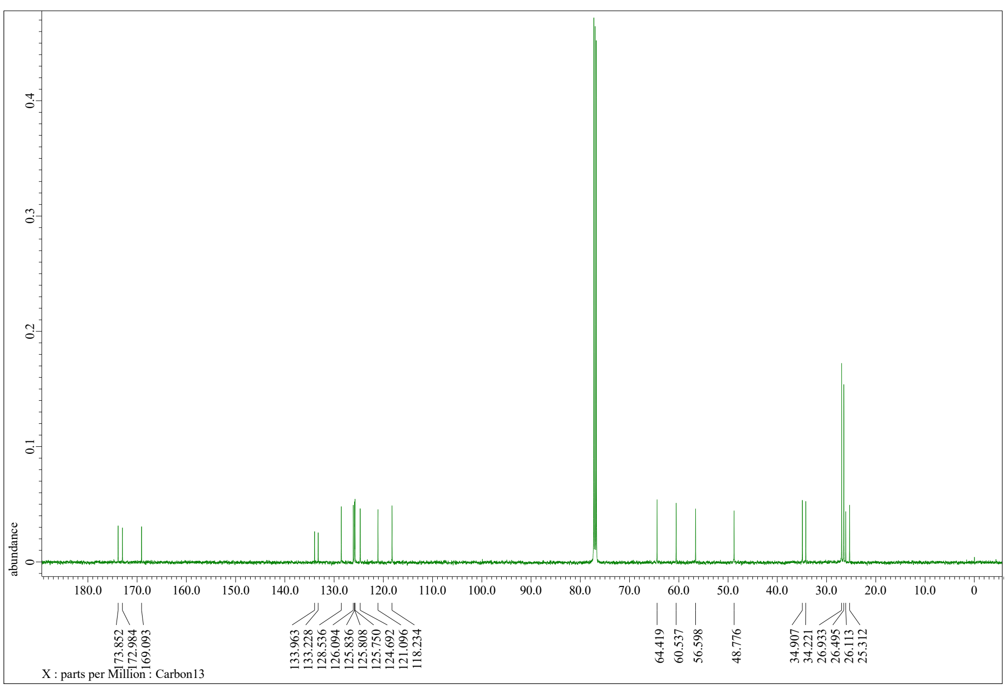
13C-NMR



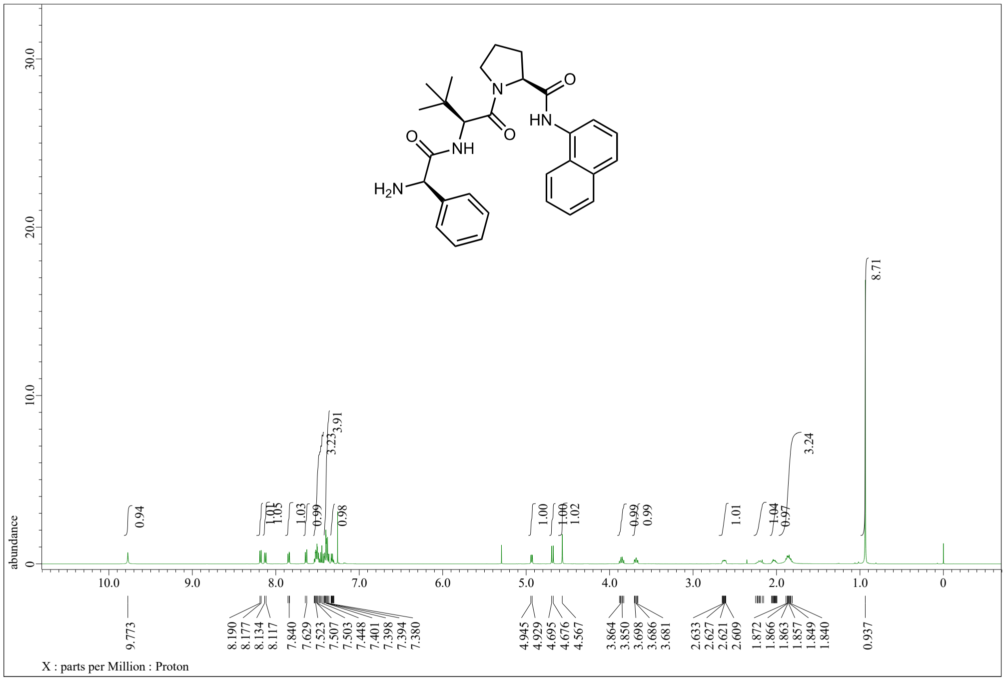
L-Tel- L-Tle- L-Pro-1-Naph (6c) (Chemical Formula: $C_{27}H_{38}N_4O_3$)
^{1}H-NMR



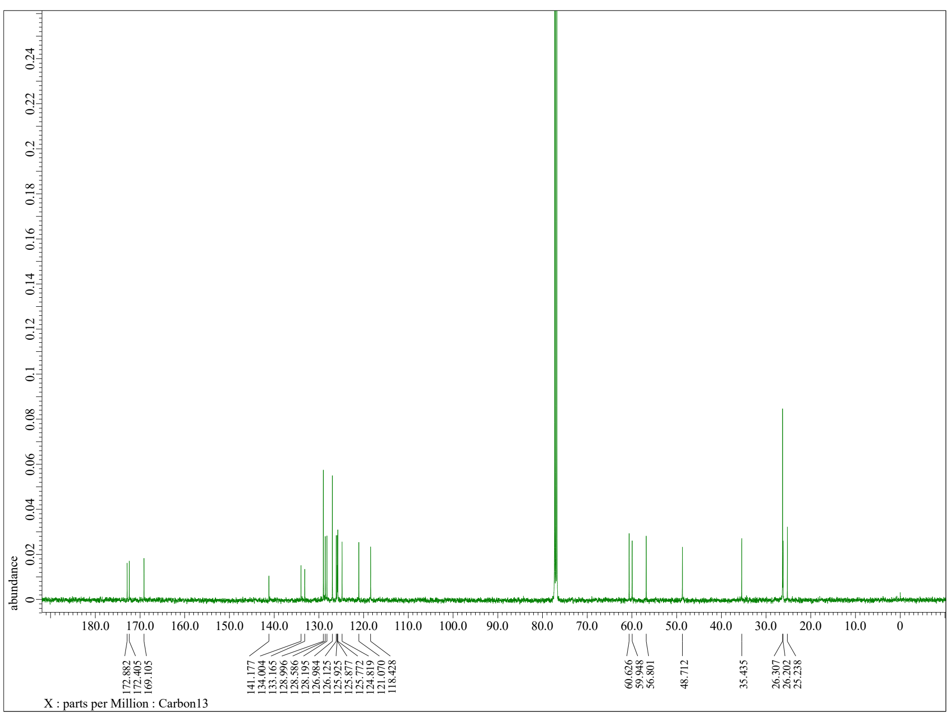
13C-NMR



L-Phg- L-Tle- L-Pro-1-Naph (6d) (Chemical Formula: $C_{29}H_{34}N_4O_3$)
^{1}H-NMR

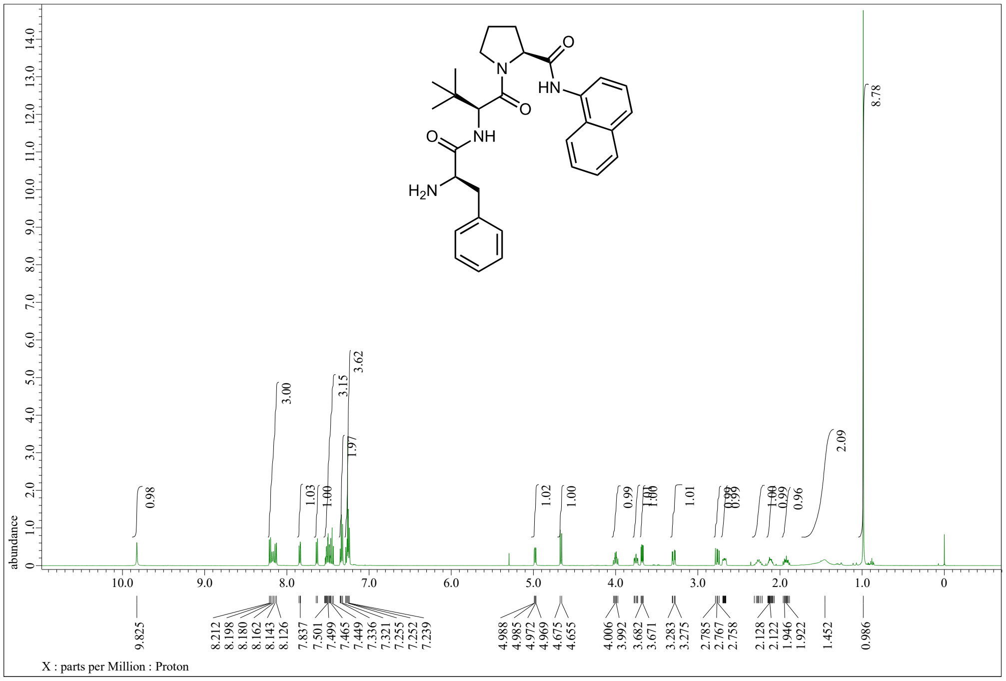


13C-NMR

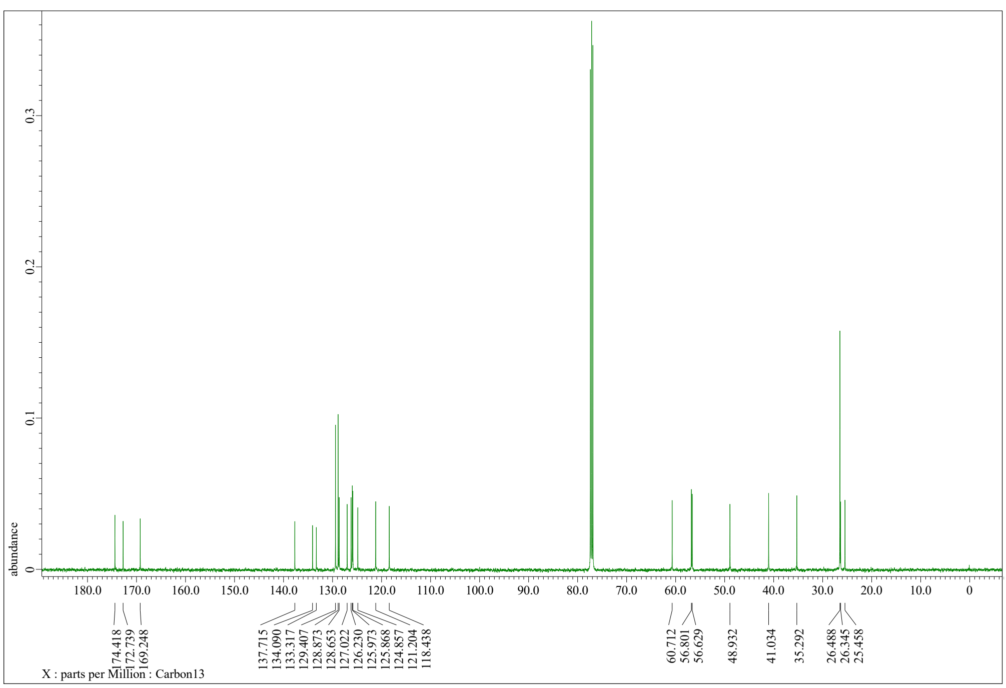


L-Phe- L-Tle- L-Pro-1-Naph (6e) (Chemical Formula: $C_{30}H_{36}N_4O_3$)

[1]H-NMR

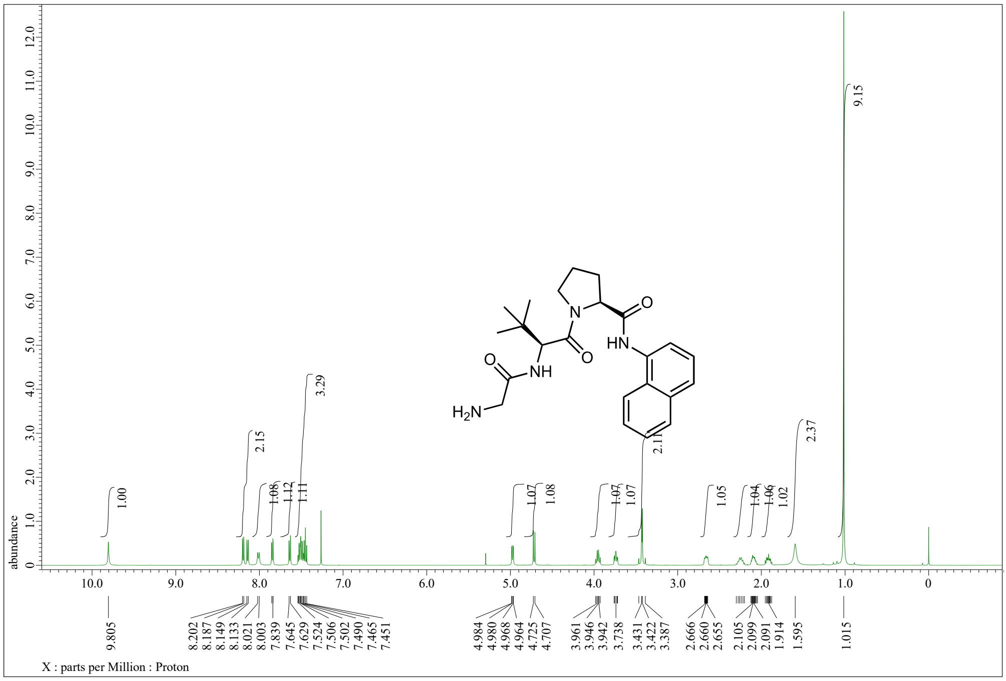


13C-NMR

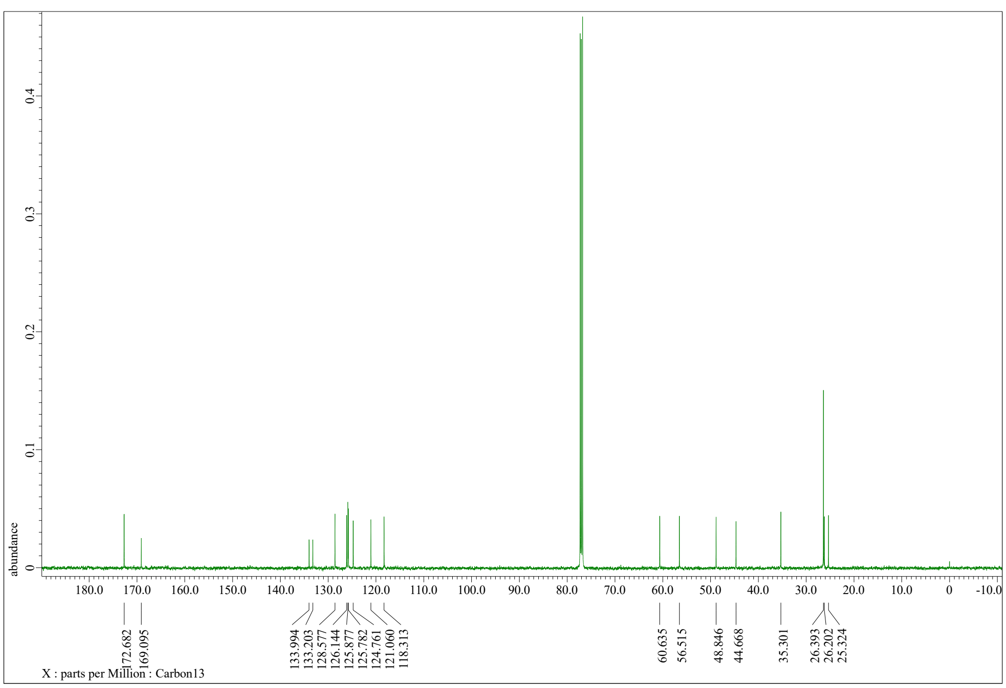


Gly- L-Tle- L-Pro-1-Naph (6f) (Chemical Formula: $C_{23}H_{30}N_4O_3$)

¹H-NMR

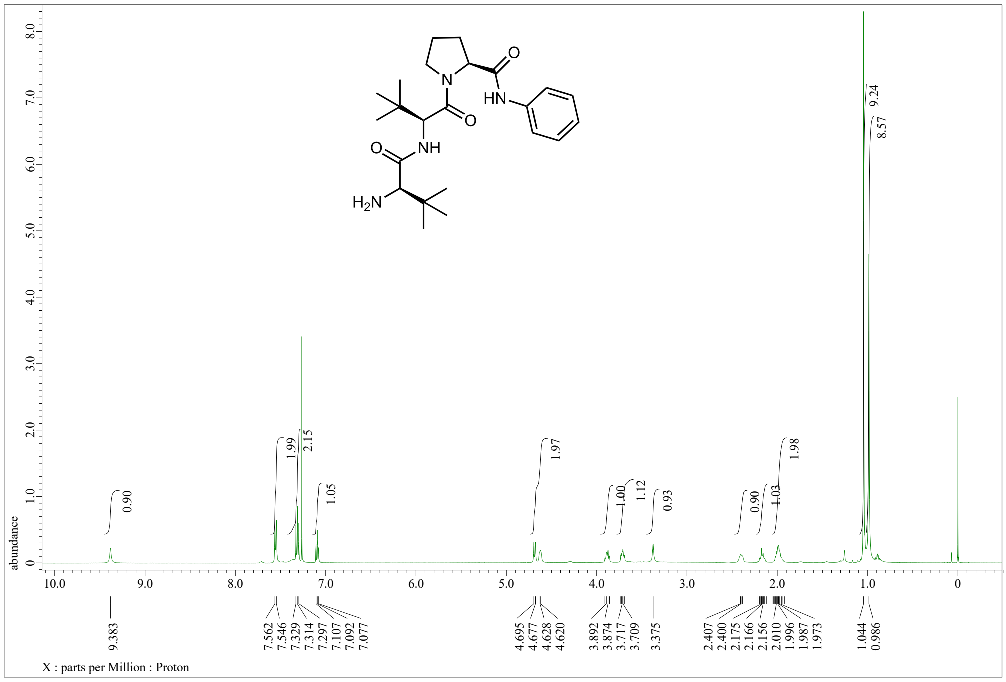


13C-NMR

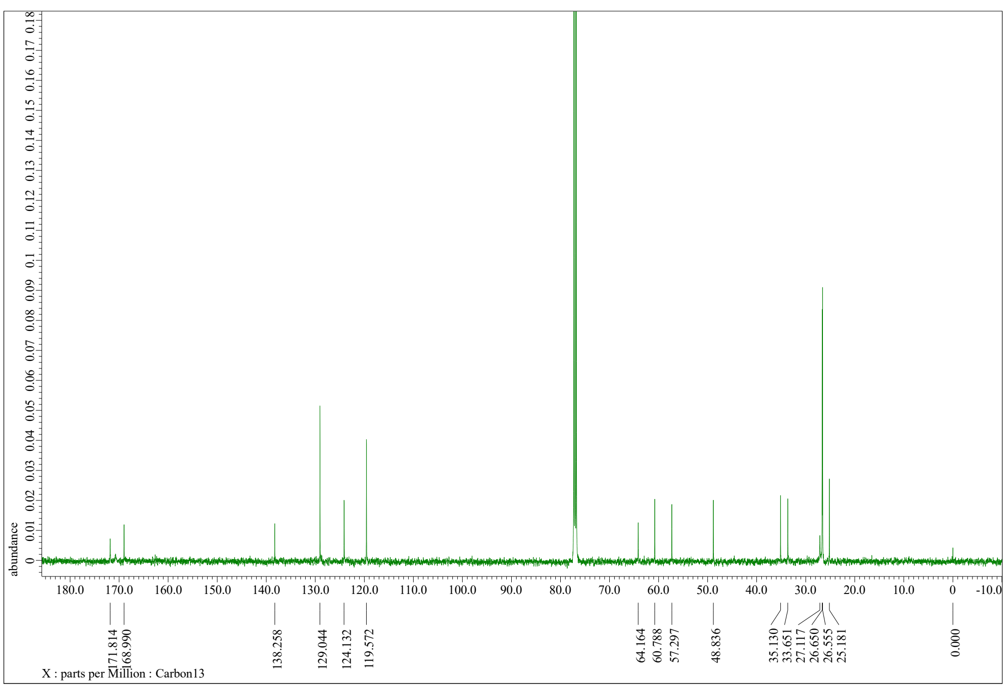


L-Tle- L-Tle- L-Pro-Ph (6g) (Chemical Formula: $C_{23}H_{36}N_4O_3$)

[1]H-NMR

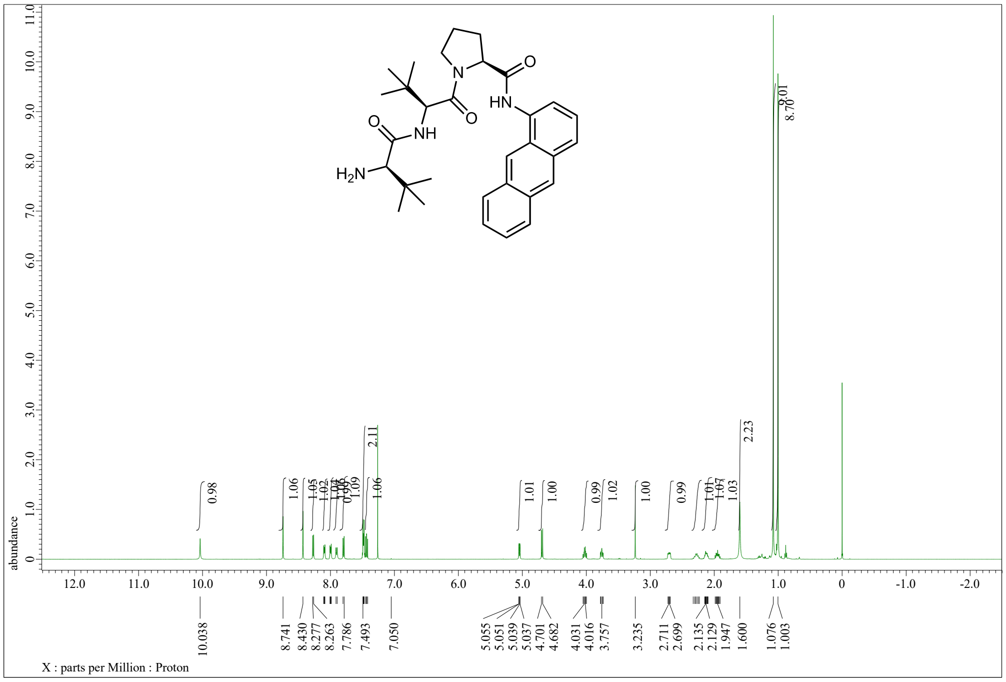


13C-NMR

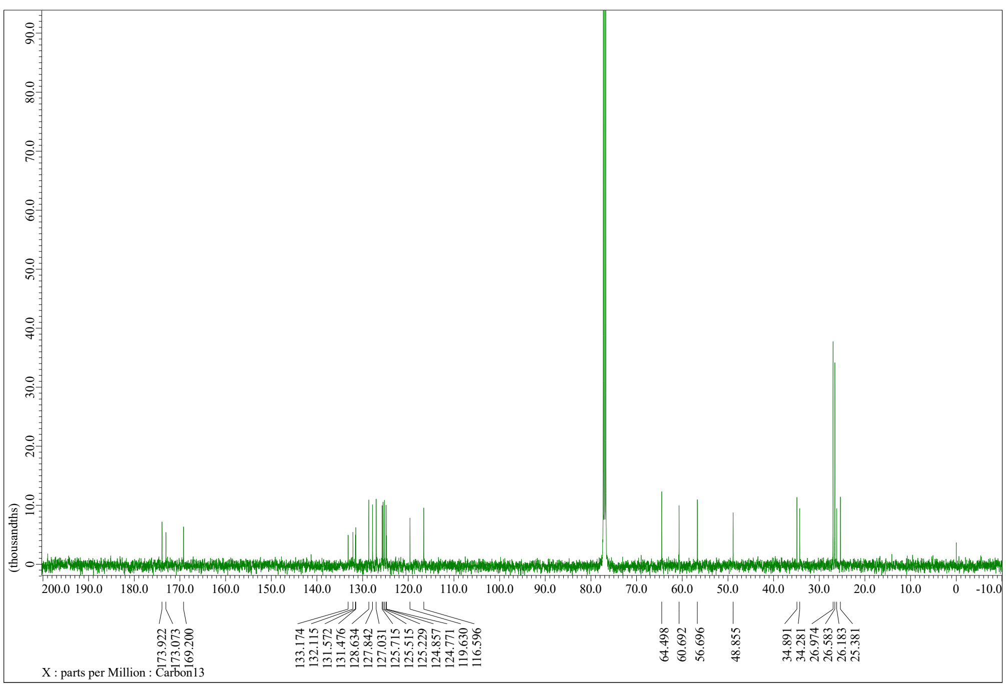


L-Tle- L-Tle- L-Pro-1-Anth (6h) (Chemical Formula: $C_{31}H_{40}N_4O_3$)

^{1}H-NMR

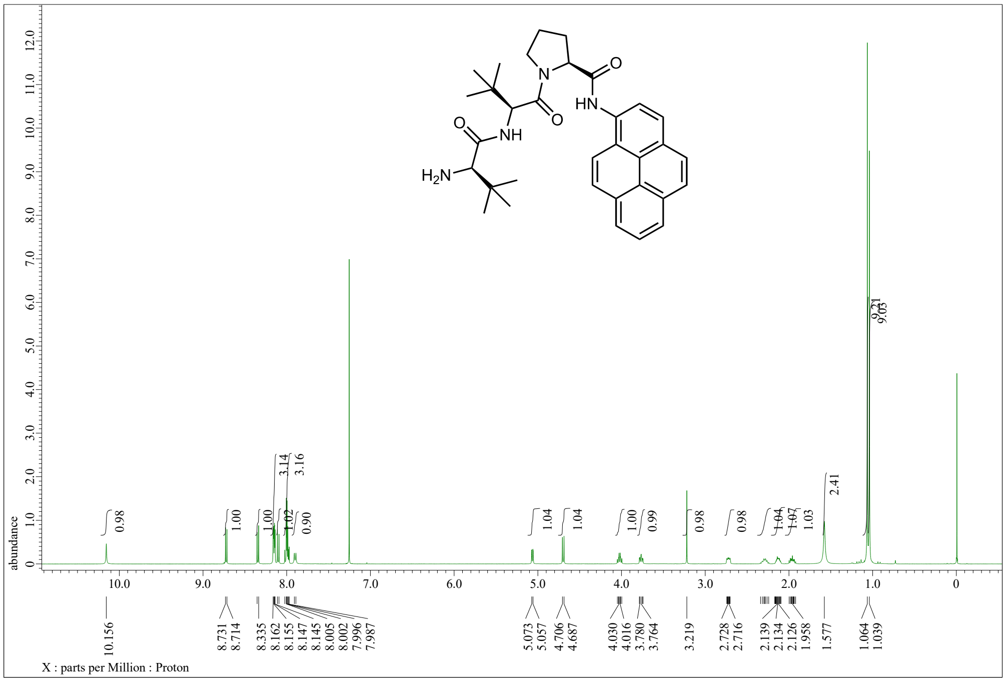


13C-NMR

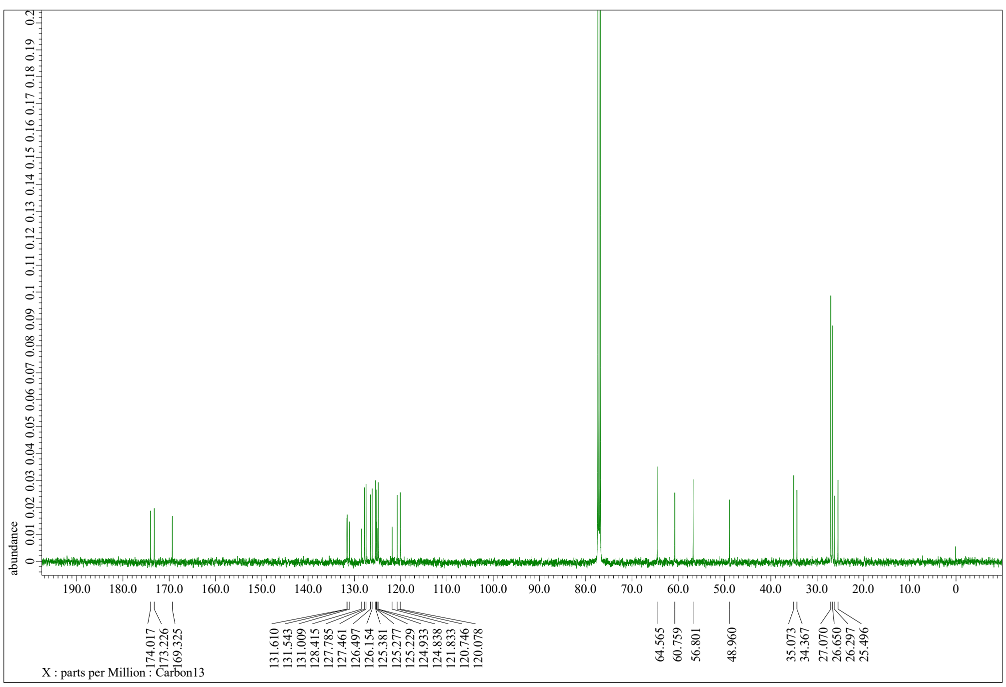


L-Tle- L-Tle- L-Pro-1-Pyr (6i) (Chemical Formula: $C_{33}H_{40}N_4O_3$)

¹H-NMR

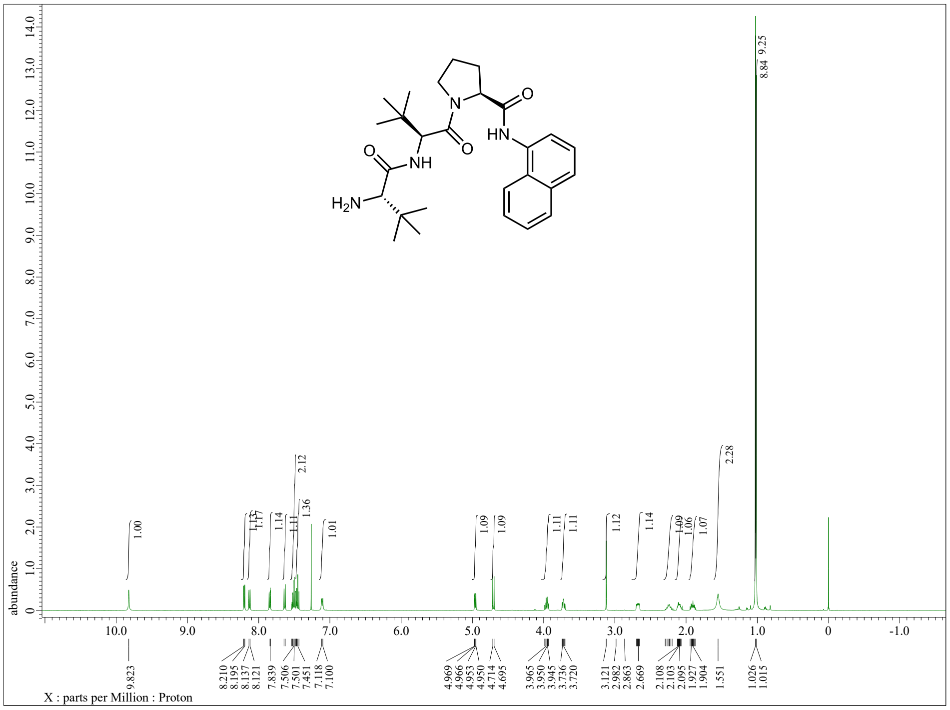


13C-NMR

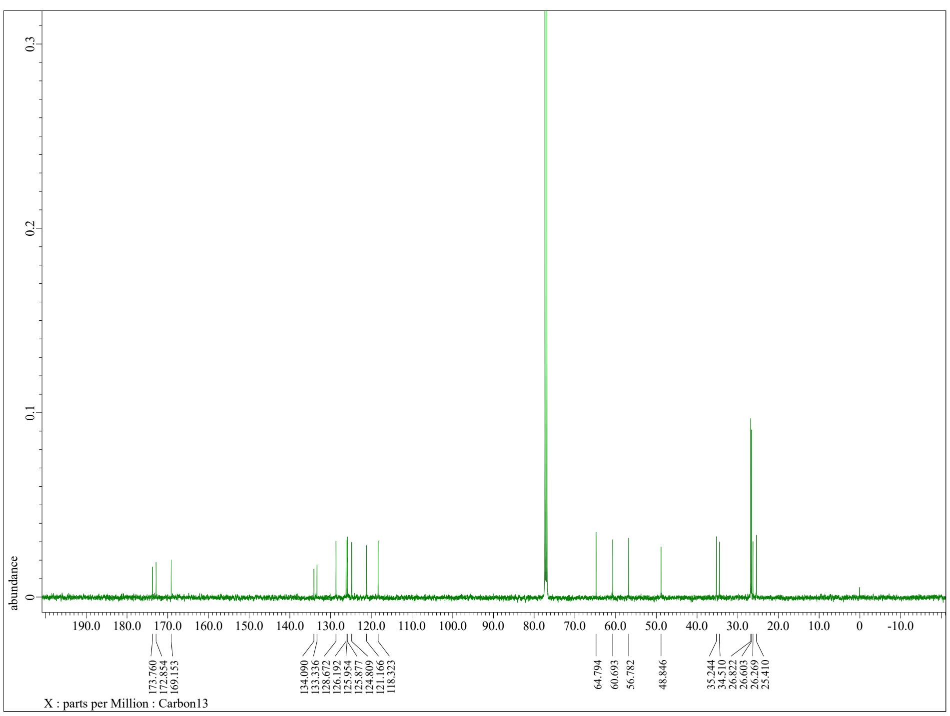


D-Tle- L-Tle- L-Pro-1-Naph (6j) (Chemical Formula: $C_{27}H_{38}N_4O_3$)

¹H-NMR

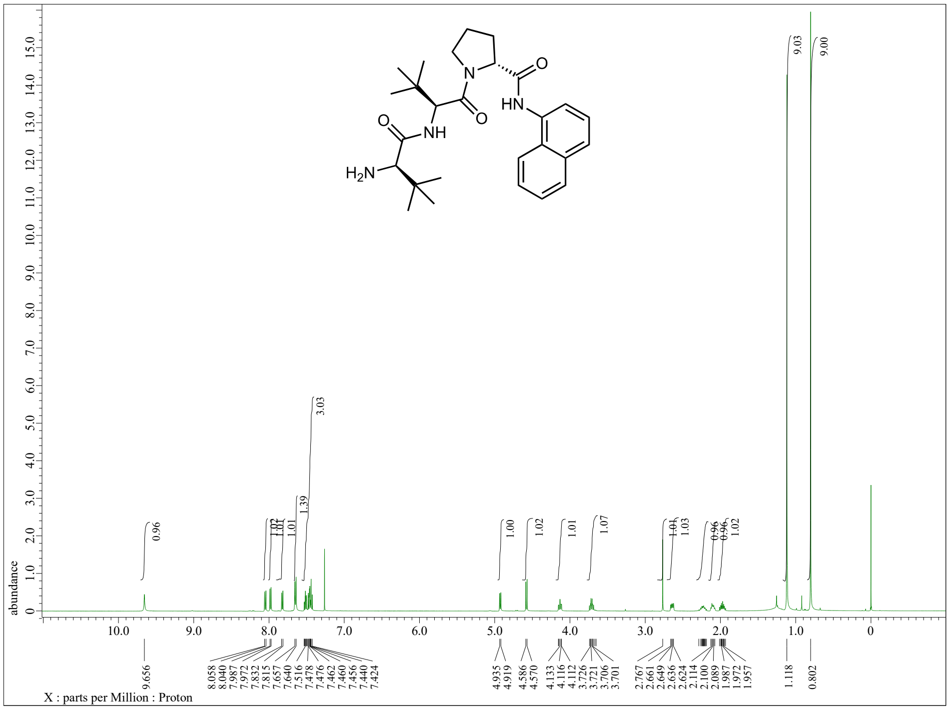


13C-NMR

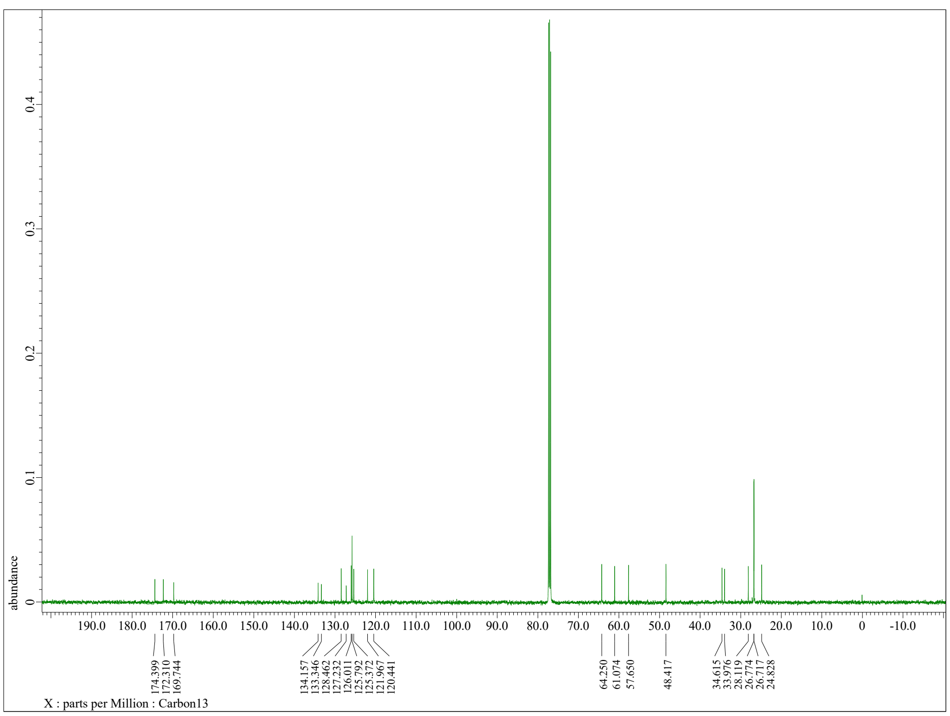


L-Tle- L-Tle-$_D$Pro-1-Naph (10) (Chemical Formula: $C_{27}H_{38}N_4O_3$)

[1]H-NMR

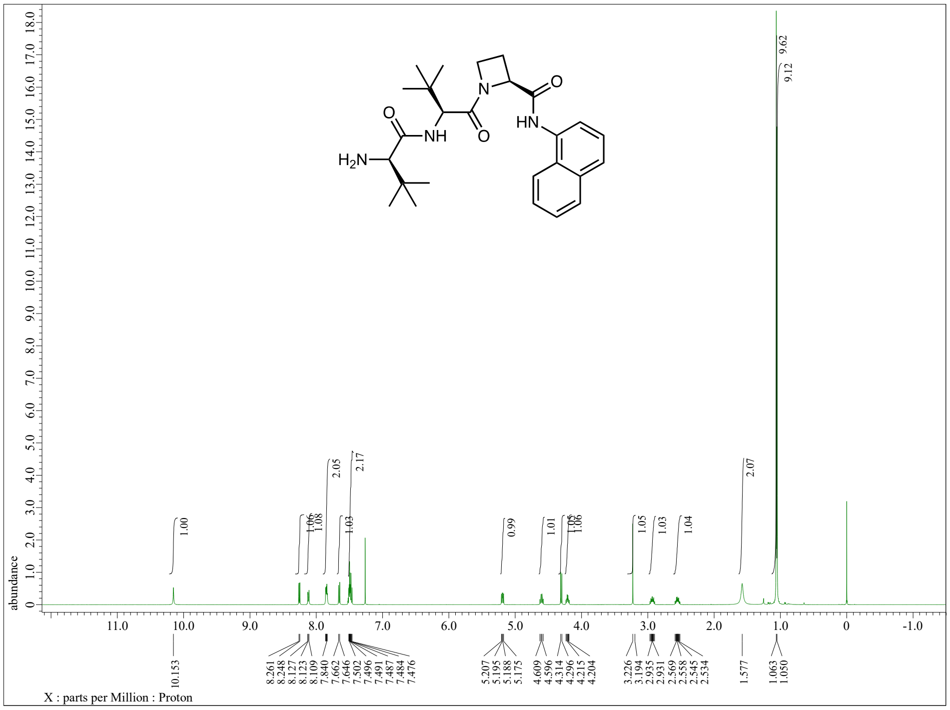


13C-NMR

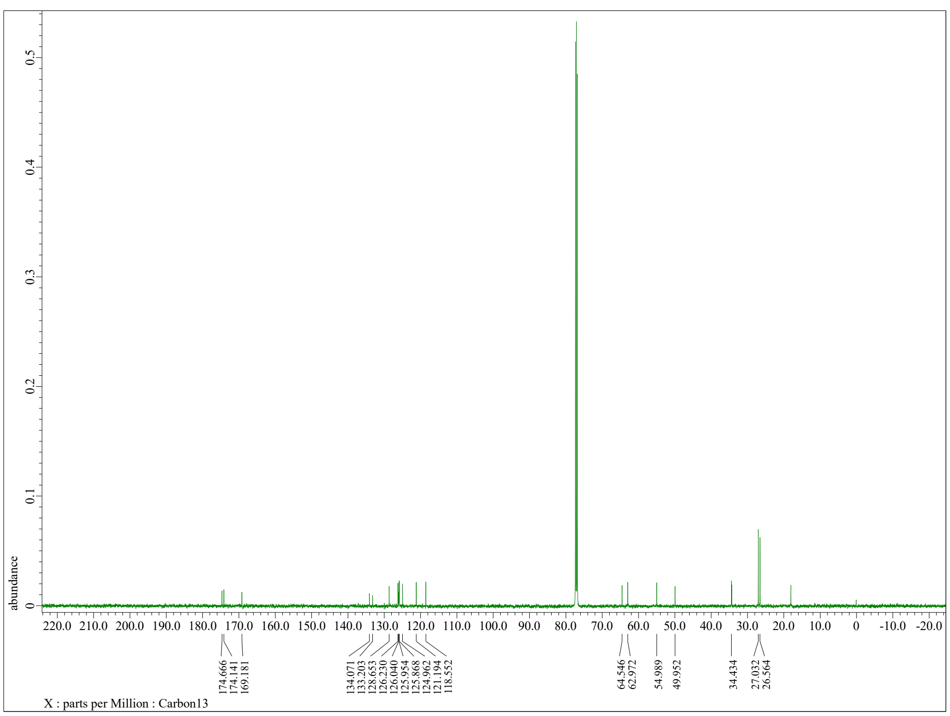


L-Tle- L-Tle- L-Aze-1-Naph (14a) (Chemical Formula: $C_{26}H_{36}N_4O_3$)

[1]H-NMR

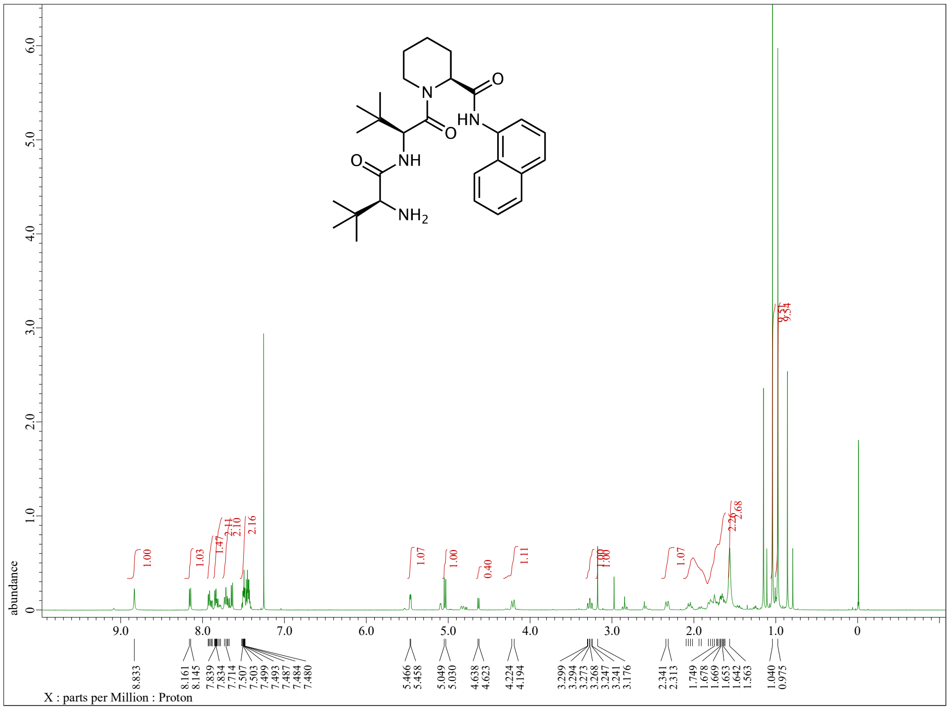


13C-NMR

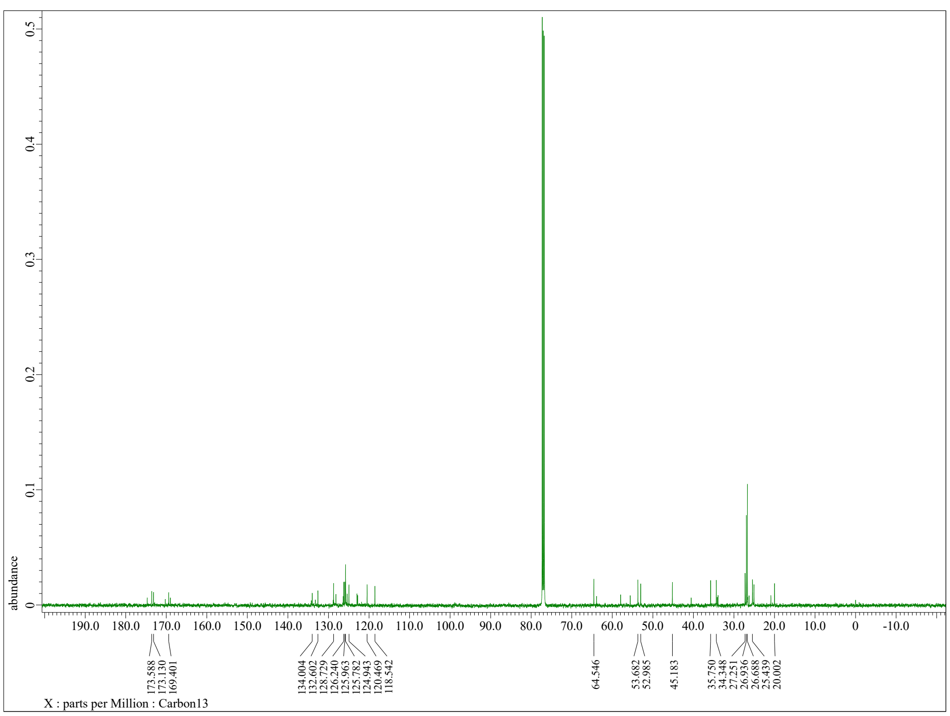


L-Tle- L-Tle- L-Pip-1-Naph (14b) (Chemical Formula: $C_{26}H_{36}N_4O_3$)

^{1}H-NMR



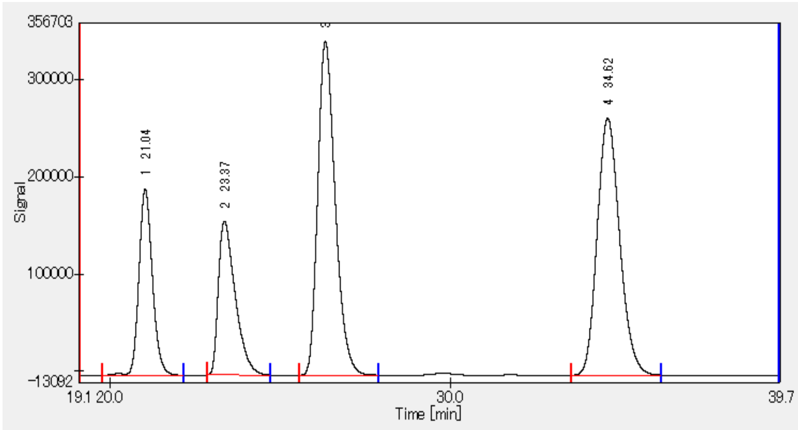
13C-NMR



5. HPLC SPECTRA FOR ALDOL PRODUCTS

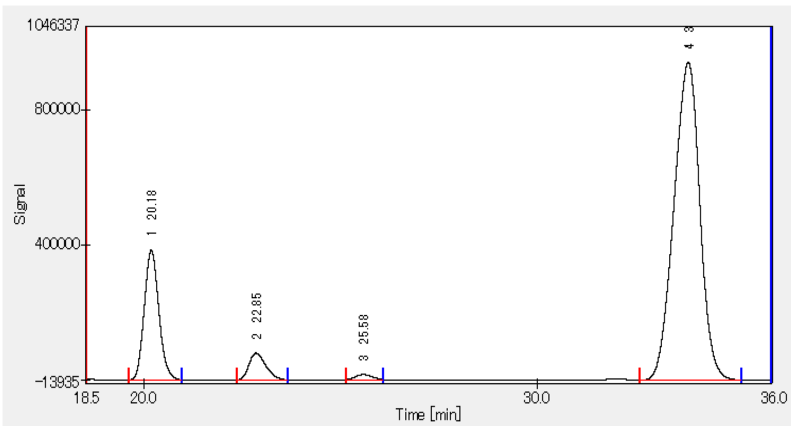
2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one (**17a**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min,* λ*=254 nm, dr(syn/anti) = 20:80, 98% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	21.04	5240452	14.9537	191121	13076.6	1.18	2.769
2	23.37	5438855	15.5198	158075	9795.3	1.668	3.093
3	26.33	12231672	34.9032	342773	11799.8	1.3	7.509
4	34.62	12133538	34.6232	264130	12496.6	1.171	*****
		35044517	100	956099			

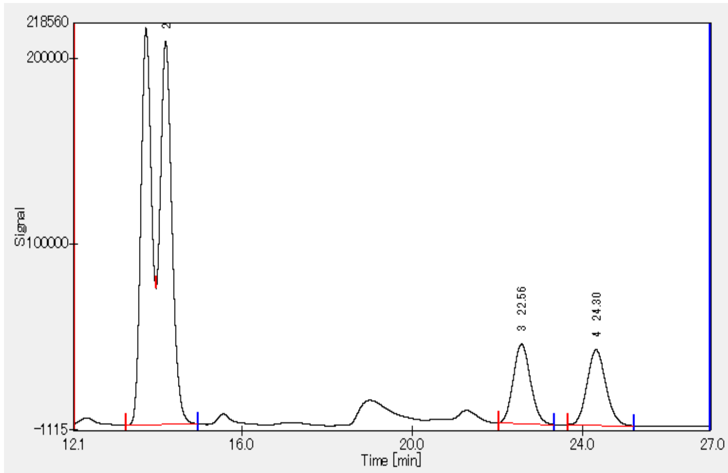
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	20.18	9978690	17.8164	386306	13386.5	1.124	3.527
2	22.85	2386523	4.261	79647	12585.2	1.327	3.463
3	25.58	442223.8	0.7896	15253	17842	1.083	8.292
4	33.86	43201037	77.133	942262	12132.5	0.946	*****
		56008473	100	1423468			

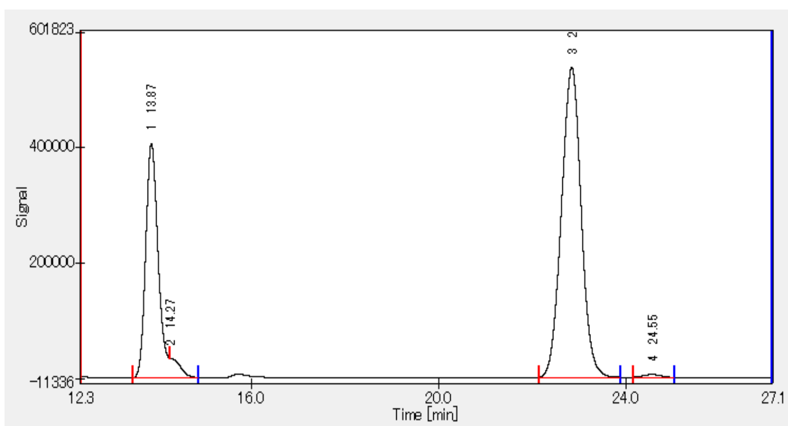
2-[Hydroxy-(2-nitrophenyl)-methyl]-cyclohexan-1-one (**17b**): *AD-H column, n-hexane/iso-propanol: 90/10, flow rate = 1.0 mL/min,* λ=254 nm, *dr(syn/anti) = 22:78, 99% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.76	3755605	36.7729	213745	13879.1	*****	0.935
2	14.22	4014459	39.3075	206530	12111.5	*****	13.196
3	22.56	1199921	11.749	42778	14202.5	1.121	2.207
4	24.3	1242980	12.1706	40664	13856.4	1.125	*****
		10212964	100	503717			

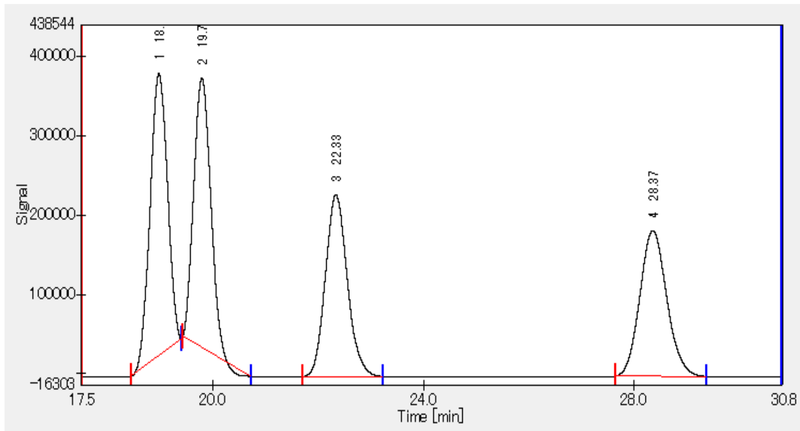
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.87	7491683	31.4608	407179	12854.3	*****	0.899
2	14.27	498899.6	2.0951	33153	20339.9	*****	14.58
3	22.84	15692161	65.8982	537934	13554.5	1.007	2.315
4	24.55	129992.9	0.5459	4947	20103.5	1.1	*****
		23812737	100	983213			

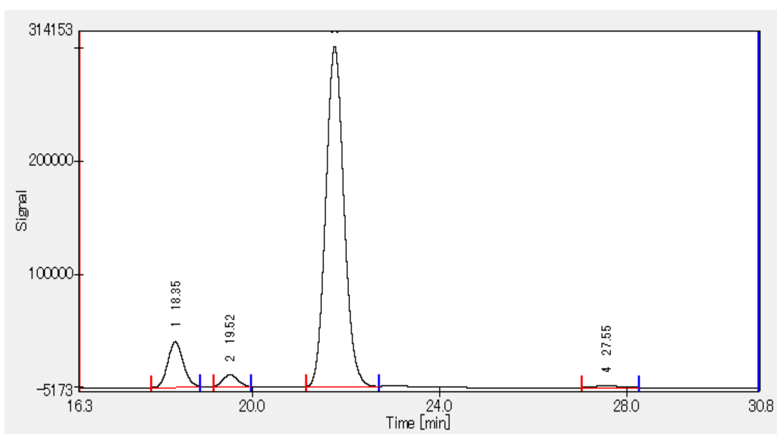
2-[Hydroxy-(3-nitrophenyl)-methyl]-cyclohexan-1-one (**17c**): *AD-H column, n-hexane/iso propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti)* = 20:80, *99% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.96	8195506	28.2962	356520	15202.6	0.992	1.348
2	19.78	7550894	26.0706	339909	17291.7	1.124	3.67
3	22.33	6661845	23.001	229403	12859.2	1.14	6.884
4	28.37	6554983	22.6321	183740	13819.8	1.118	*****
		28963229	100	1109572			

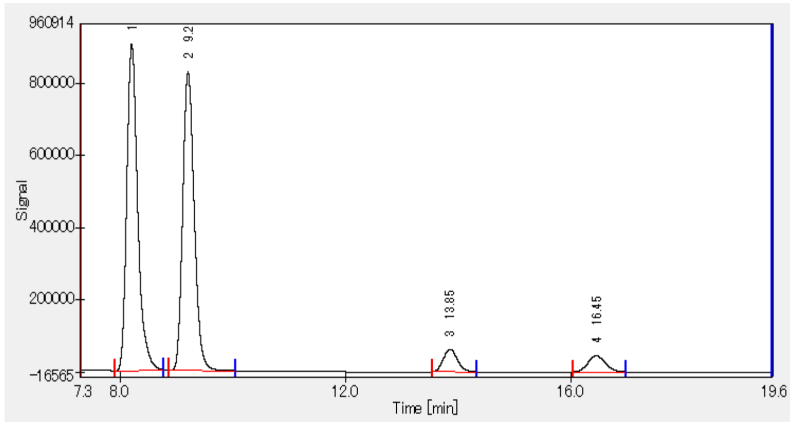
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.35	913986.4	9.822	40176	14255.7	1.1	1.932
2	19.52	233222.6	2.5063	10505	17166.7	1.129	3.379
3	21.76	8102028	87.067	301345	14369.2	1.093	7.259
4	27.55	56273	0.6047	1742	16035.2	1.149	*****
		9305510	100	353768			

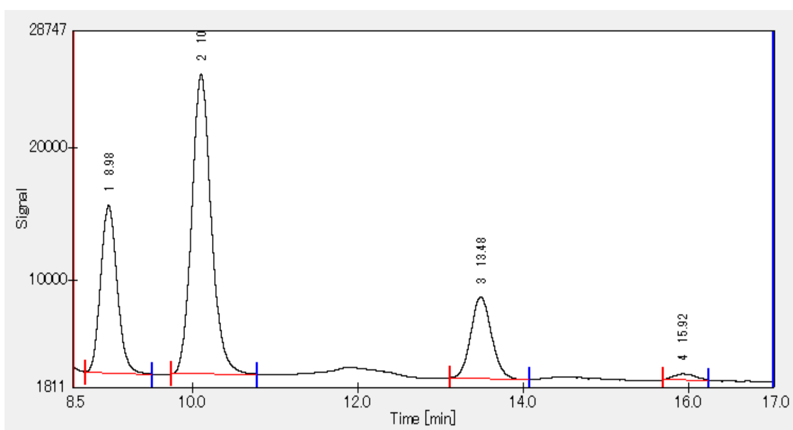
2-[Hydroxy-(2-bromophenyl)-methyl]-cyclohexan-1-one (**17d**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 25:75, 86% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	8.21	12151134	46.9446	903908	8094.4	1.321	2.695
2	9.2	11685035	45.1439	826335	9644	1.191	11.028
3	13.85	1087515	4.2015	62664	14024.9	1.135	4.942
4	16.45	960282.2	3.7099	44662	12733.2	1.086	*****
		25883966	100	1837569			

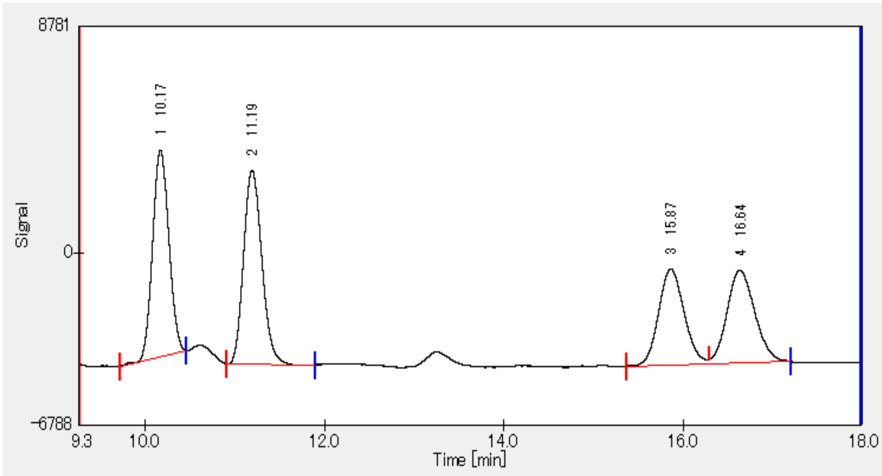
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	8.98	174521	26.4294	12623	9518.8	1.12	2.73
2	10.1	371724	56.2939	22626	8055.3	1.137	7.391
3	13.48	106086	16.0657	6163	13371.1	1.094	5.223
4	15.92	7996.8	1.211	452	18529	1.182	*****
		660327.8	100	41864			

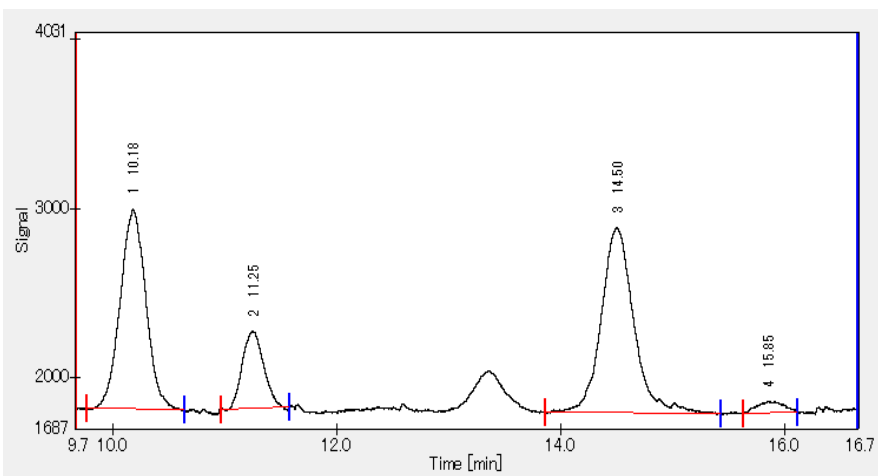
2-[Hydroxy-(3-bromophenyl)-methyl]-cyclohexan-1-one (**17e**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 25:75, 93% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	10.17	101584.5	28.2445	8074	14428.4	1.076	2.861
2	11.19	106307.2	29.5576	7574	14119.4	1.166	10.33
3	15.87	73941.53	20.5586	3746	14615.5	1.131	1.41
4	16.64	77828.37	21.6393	3620	13549.7	1.091	*****
		359661.6	100	23014			

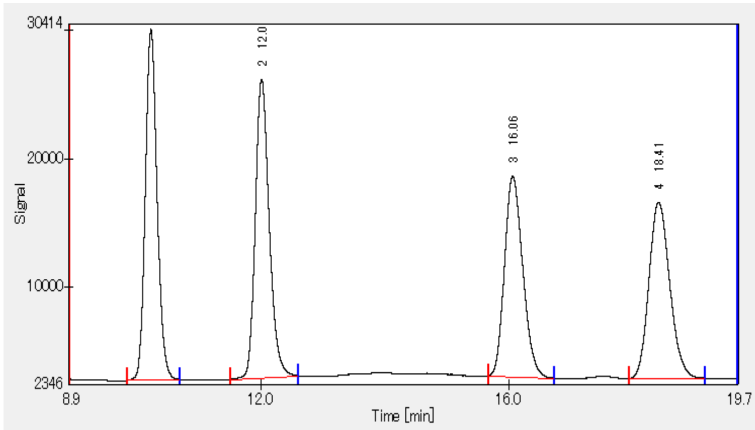
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	10.18	18803	39.2727	1178	9001.4	1.024	2.725
2	11.25	5898.4	12.3196	454	15990.6	1.08	7.282
3	14.5	22094.8	46.2481	1093	11685.5	1.136	2.843
4	15.85	1081.8	1.7595	66	23814.8	1.191	*****
		47878	100	2791			

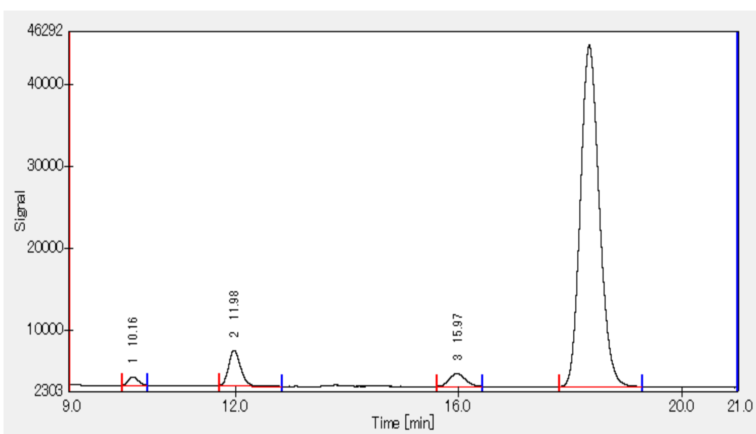
2-[Hydroxy-(4-bromophenyl)-methyl]-cyclohexan-1-one (**17f**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 23:77, 94% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	10.23	358767	26.3765	27284	13113.7	1.144	4.588
2	12.01	360795.8	26.5256	23255	13087.1	1.227	8.316
3	16.06	320899.5	23.5925	15654	13484	1.198	3.983
4	18.41	319716.4	23.5055	13723	13799.9	1.158	*****
		1360178.7	100	79916			

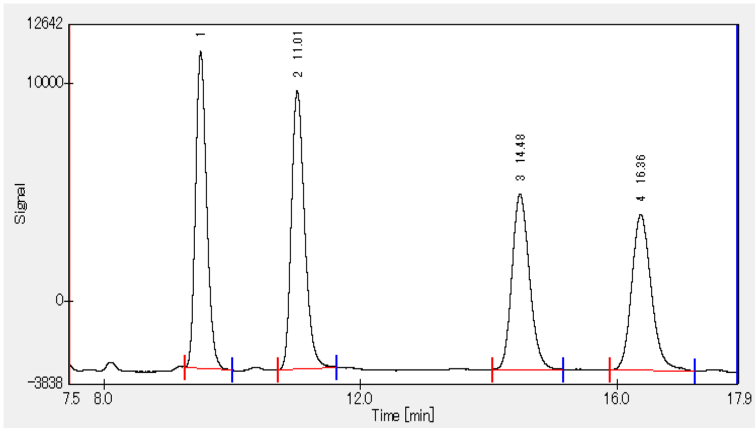
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	10.16	12889.3	1.1854	1064	15408.8	1.205	4.983
2	11.98	64080.1	5.8933	4345	14236.7	1.172	8.503
3	15.97	31433.2	2.8909	1596	14121.6	1.137	4.055
4	18.35	978930.6	90.0304	41703	13446.5	1.149	*****
		1087333.2	100	48708			

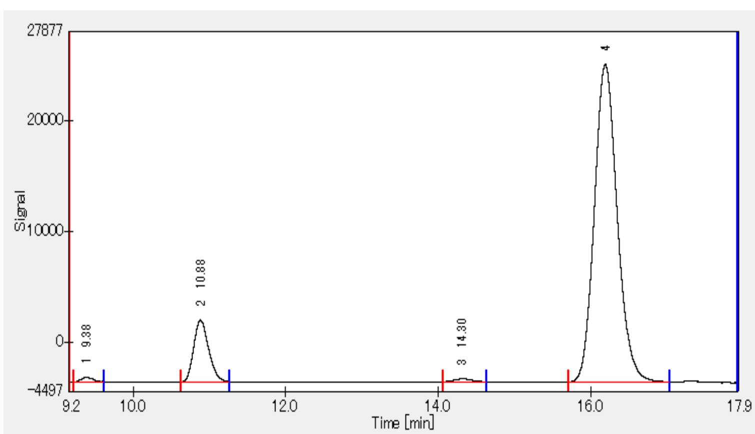
2-[Hydroxy-(4-chlorophenyl)-methyl]-cyclohexan-1-one (**17g**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) =* 14:86, *98% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	9.51	174051	26.3917	14503	13752.2	1.205	4.256
2	11.01	182351.5	27.6504	12750	13177.2	1.266	7.802
3	14.48	151525.2	22.9761	8054	13120.7	1.169	3.504
4	16.36	151562.6	22.9818	7129	13307.9	1.174	*****
		659490.3	100	42436			

Chiral

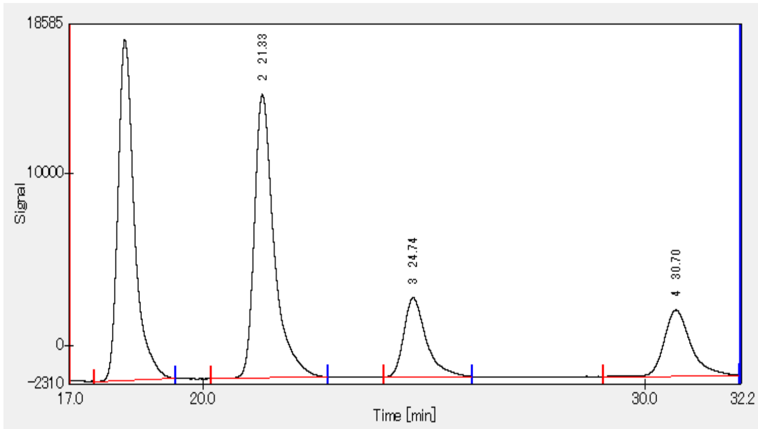


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	9.38	4476.2	0.6585	406	17170.7	1.23	4.591
2	10.88	75408	11.0934	5561	14065.5	1.199	8.609
3	14.3	4368.4	0.6426	285	17972.8	1.151	3.806
4	16.19	595500.9	87.6054	28552	13144.6	1.138	*****

679753.5	100	34804

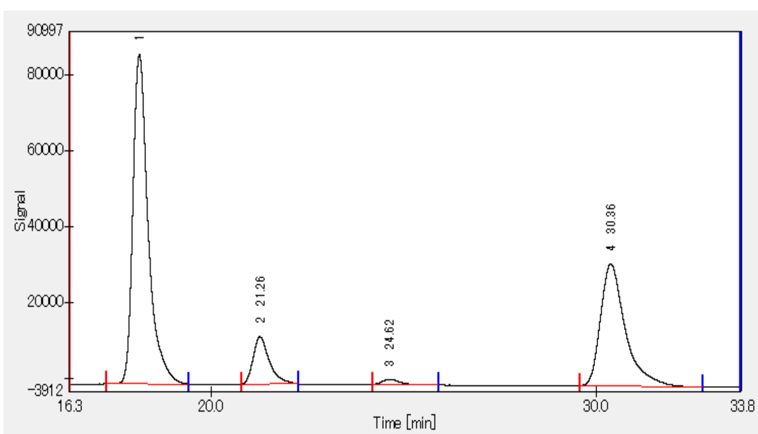
2-[Hydroxy-(4-cyanophenyl)-methyl]-cyclohexan-1-one (**17h**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 36:67, 94% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.22	508859.8	37.9291	19769	10292.2	1.496	3.903
2	21.33	510804.8	38.074	16448	9458.9	1.591	3.627
3	24.74	162379.9	12.1034	4586	9728.1	1.534	5.521
4	30.7	159564.6	11.8935	3827	11286.7	1.368	*****
		1341609	100	44630			

Chiral

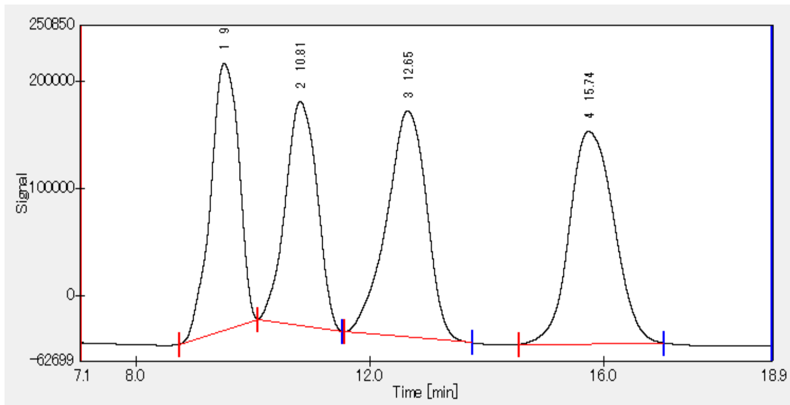


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	18.13	2393442	56.2981	86913	9005.6	1.513	3.954
2	21.26	363774	8.5566	12441	10731.6	1.467	4.019
3	24.62	45147.8	1.062	1449	13440.7	1.46	5.455
4	30.36	1449008	34.0833	32243	9325.3	1.582	*****

4251372	100	133046

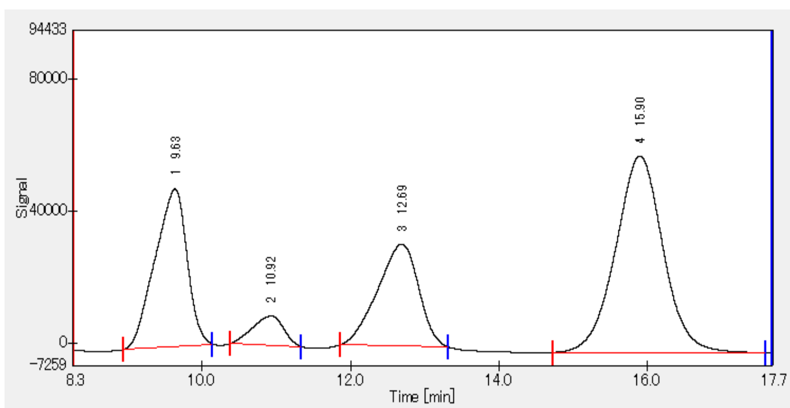
2-[Hydroxy-phenyl-methyl]-cyclohexan-1-one (**17i**): *OD-H column, n-hexane/iso-propanol = 90/10, flow rate = 0.5 mL/min, λ=220 nm, dr(syn/anti) = 25:75, 60% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	9.51	8371984	22.7175	249127	1795.1	0.92	1.369
2	10.81	7922735	21.4985	209345	1869.5	0.978	1.599
3	12.65	10048378	27.2664	211531	1514.4	0.889	2.319
4	15.74	10509479	28.5176	198335	2132	1.101	*****
		36852575	100	868338			

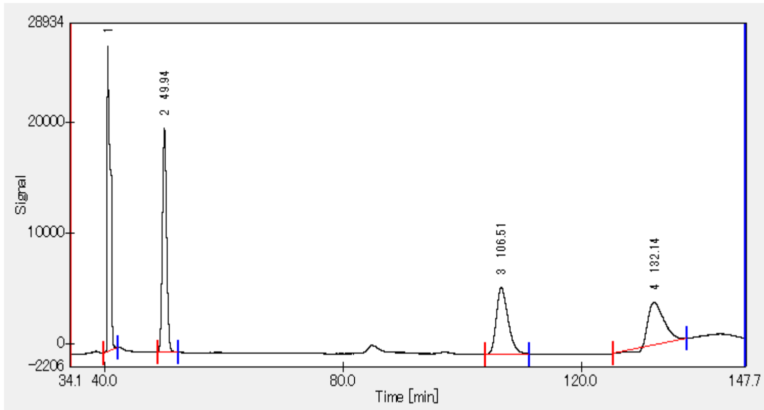
Chiral



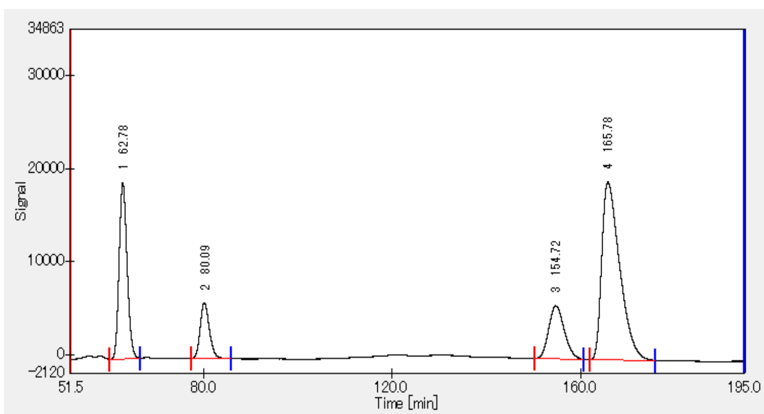
No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	9.63	1432053	25.89	47698	2260.8	0.847	1.64
2	10.92	257567.9	4.6566	8881	3240.3	0.862	1.956
3	12.69	1189169	21.4989	30971	2372.2	0.857	2.85
4	15.9	2652509	47.9545	59521	2764.3	1.01	*****

		5531299	100	147071			

2-[Hydroxy-(4-(Methoxyphenyl)-methyl]-cyclopentan-1-one (**17j**): *AD column, n-hexane/iso-propanol = 98/2, flow rate = 0.4 mL/min, λ=254 nm, dr(syn/anti) = 26:74, 58% ee anti.*



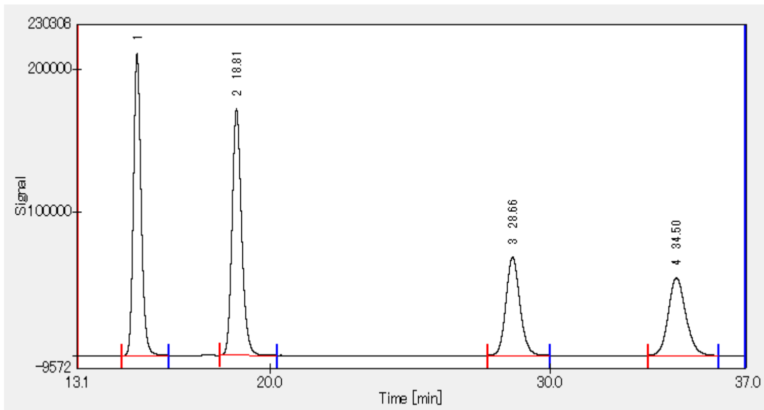
No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	40.41	1007122	28.7766	27575	30966	2.799	8.526
2	49.94	993246.2	28.3801	20243	23063.2	1.086	22.747
3	106.51	817996.4	23.3727	6035	13559.2	1.337	5.911
4	132.14	681436	19.4707	3875	11113.8	1.646	*****
		3499801	100	57728			



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	62.78	2233025	23.6718	18898	6391.6	1.162	5.11
2	80.09	807392.2	8.559	5959	7769.2	1.192	15.039
3	154.72	1327962	14.0774	5731	9679.7	1.176	1.638
4	165.78	5064899	53.6918	19127	8435.6	1.701	*****
		9433278	100	49715			

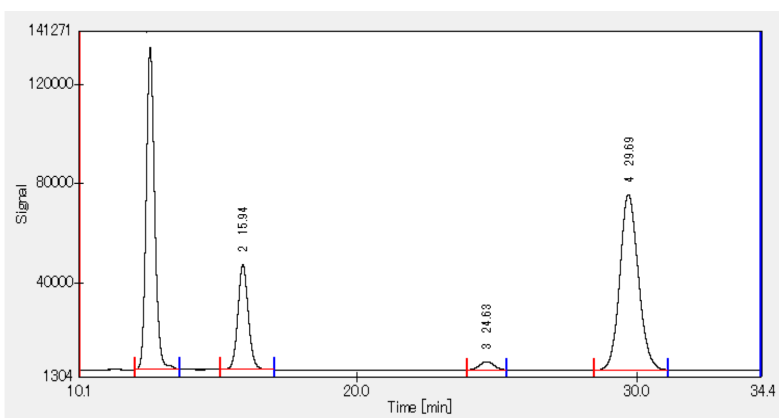
2-[Hydroxy-(4-(nitrophenyl)-methyl]-cyclopentan-1-one (**17m**): *IC column, n-hexane/iso-propanol = 85/15, flow rate = 0.8 mL/min, λ=254 nm, dr(syn/anti) = 15:85, 93% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	15.27	3987374	31.2444	210514	14288.7	1.174	6.157
2	18.81	4063273	31.8391	172008	13772.7	1.187	12.497
3	28.66	2365768	18.5378	68392	15046	1.12	5.534
4	34.5	2345470	18.3787	54082	13744.1	1.145	*****
		12761884	100	504996			

Chiral

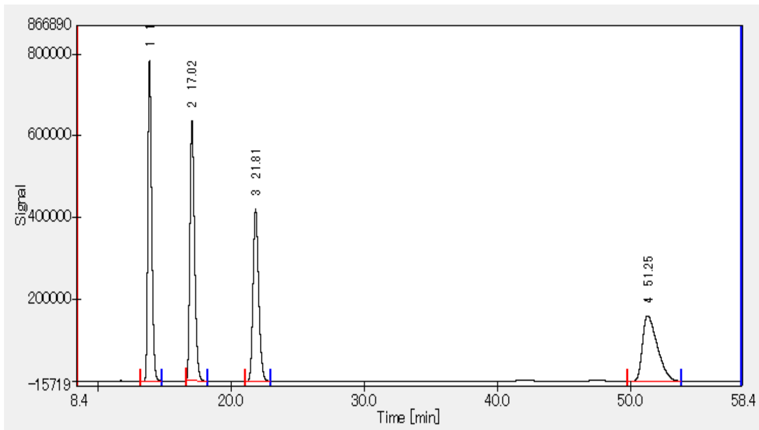


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	12.64	2731639	37.8848	130327	7998.9	1.133	5.241
2	15.94	1094448	15.1788	42609	8449.1	1.088	10.577
3	24.63	119718	1.6604	3432	10795	1.032	4.611

4	29.69	3264572	45.276	71105	9074.3	1.111	*****
		7210377	100	247473			

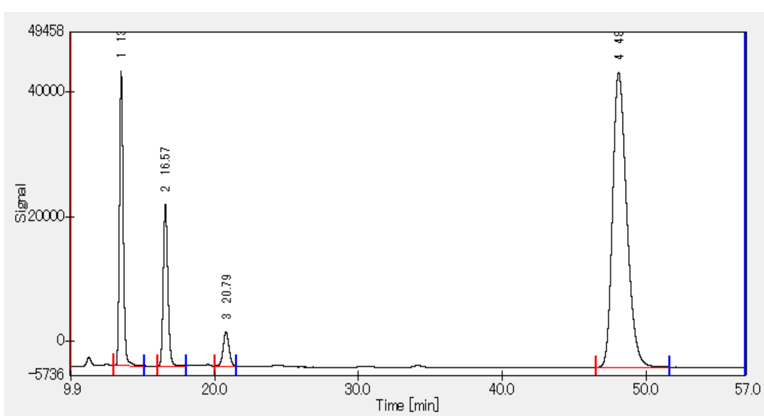
2-[Hydroxy(4-nitrophenyl)-methyl]-cycloheptan-1-one (**17n**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, (syn/anti) = 15:85, 91% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.84	15607317	27.8346	784338	10337.7	1.321	5.304
2	17.02	15382574	27.4338	636843	10781.7	1.328	6.576
3	21.81	12465413	22.2313	421084	11888.9	1.206	20.16
4	51.25	12616274	22.5003	161437	9346	1.601	*****
		56071579	100	2003702			

Chiral

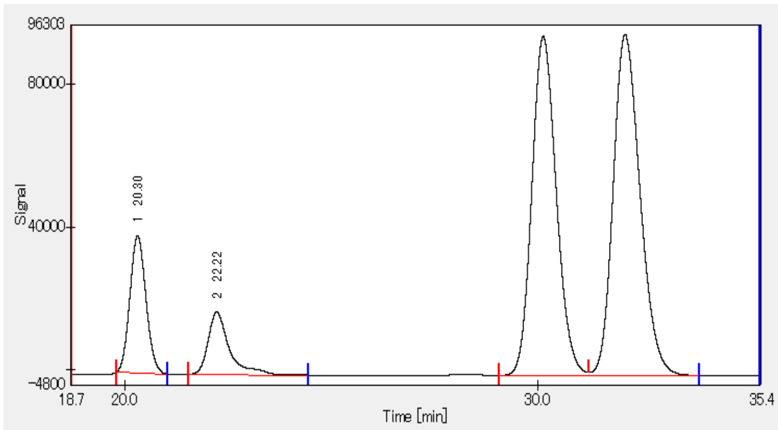


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.49	865645.6	17.913	47269	12289.6	1.165	5.676
2	16.57	578449.8	11.97	25978	12362.9	1.175	6.258
3	20.79	154673.9	3.2007	5507	12140.8	1.037	21.068
4	48.1	3233735	66.9163	47364	10962.4	1.293	*****

4832505	100	126118

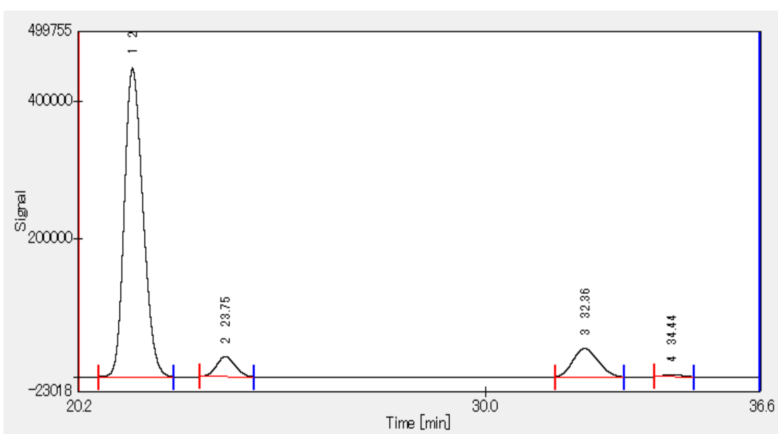
2-[-Hydroxy-(4-(nitrophenyl)-methyl]-4-methylcyclohexan-1-one (**17o**): *AD-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min, λ=254 nm, (syn/anti) =21:79, 90% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	20.3	1048193	10.5526	38680	12286.6	1.1	2.232
2	22.22	626136.4	6.3036	17500	8088.4	1.774	7.557
3	30.14	3922313	39.4875	95190	12102.3	1.146	1.727
4	32.13	4336401	43.6563	95707	11372.1	1.219	*****
		9933043	100	247077			

Chiral

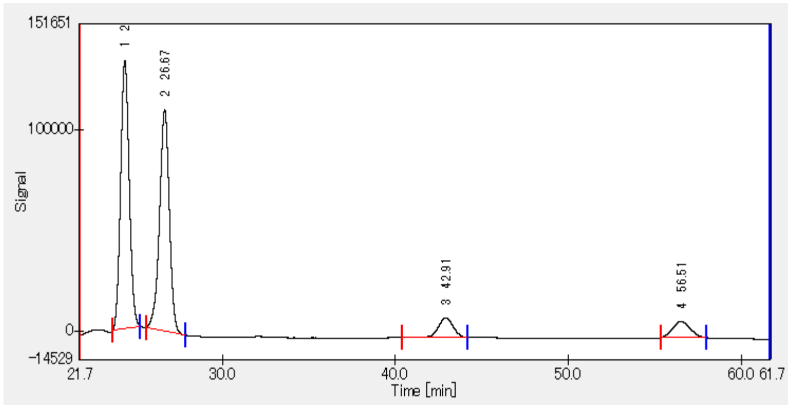


No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	21.53	13881921	83.4334	447870	10875.4	1.22	2.658
2	23.75	918263.4	5.519	29761	12507.1	1.075	8.677
3	32.36	1745002	10.4878	41387	13024.4	1.145	2.126

4	34.44	93137.8	0.5598	2798	27833.2	1.164	*****
		16638324	100	521816			

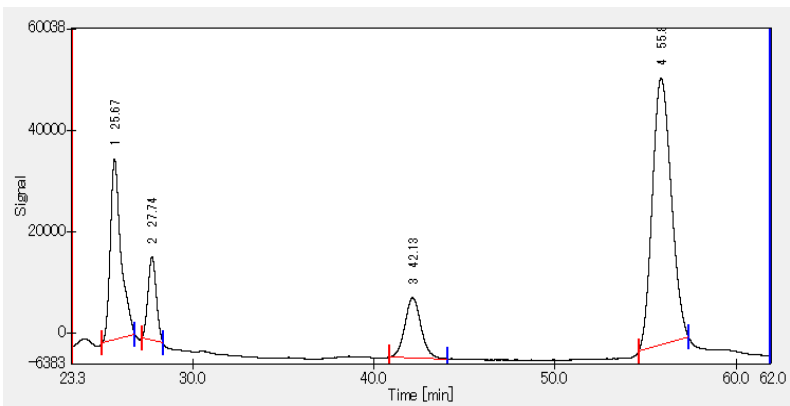
6-[Hydroxy-(4-nitro-phenyl)-methyl]-2,2-dimethyl-1,3-dioxan-5-one (**17p**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 30:70, 68% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	24.36	4570692	45.6075	132166	10993.2	1.083	2.303
2	26.67	4297609	42.8826	109336	9875.9	0.928	12.319
3	42.91	584345.3	5.8307	9773	12064.8	1.025	7.85
4	56.51	569147.4	5.6791	7958	14105.4	1.092	*****
		10021794	100	259233			

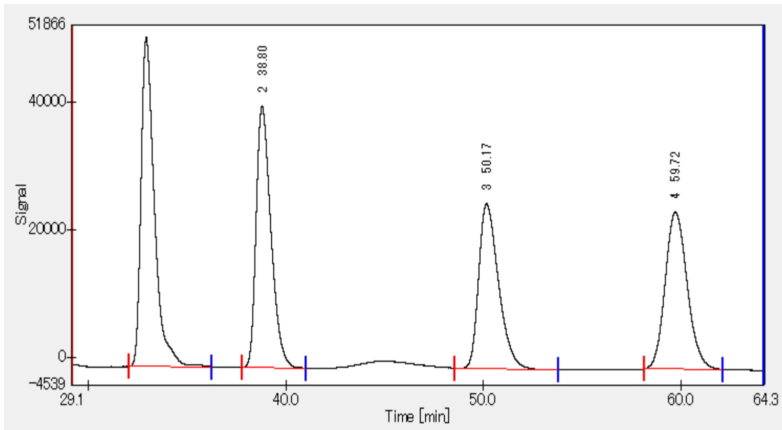
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	25.67	1464435	22.3966	35764	6690.1	1.445	1.965
2	27.74	522822.1	7.9959	16511	16972.3	1.06	11.415
3	42.13	731068.2	11.1807	11874	10180.2	1.08	7.594
4	55.87	3820323	58.4268	52735	13165.2	1.132	*****
		6538649	100	116884			

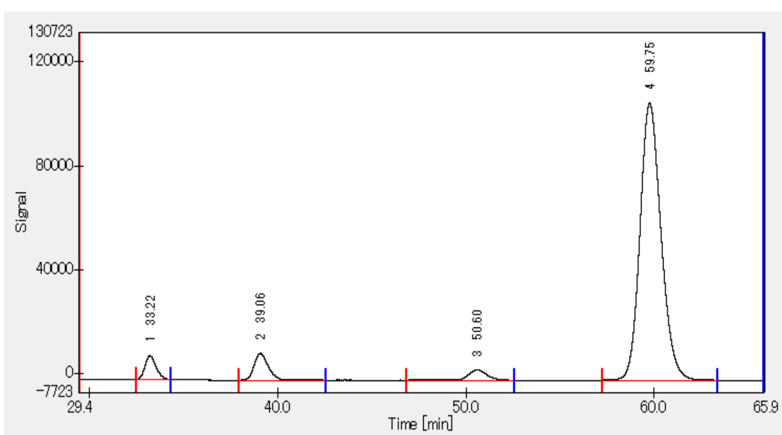
3-[Hydroxy-[4-(nitrophenyl)-methyl]-dihydro-2H-pyran-4-one (**17q**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti) = 13:87, 94% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	32.93	2427987	29.3593	51563	11220.2	1.71	4.428
2	38.8	2129583	25.751	40954	12179.1	1.416	6.895
3	50.17	1803880	21.8126	25839	11240	1.416	4.799
4	59.72	1908462	23.0772	24589	13101.9	1.165	*****
		8269912	100	142945			

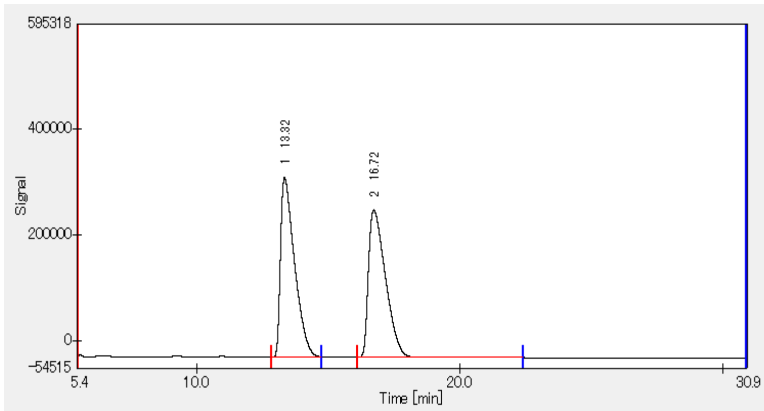
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	33.22	379003.8	4.0031	9122	13950.5	1.199	4.621
2	39.06	557366.2	5.887	10272	12404.9	1.263	7.145
3	50.6	274502.8	2.8994	3940	12280.2	1.16	4.673
4	59.75	8256819	87.2105	106565	13044.6	1.165	*****
		9467691	100	129899			

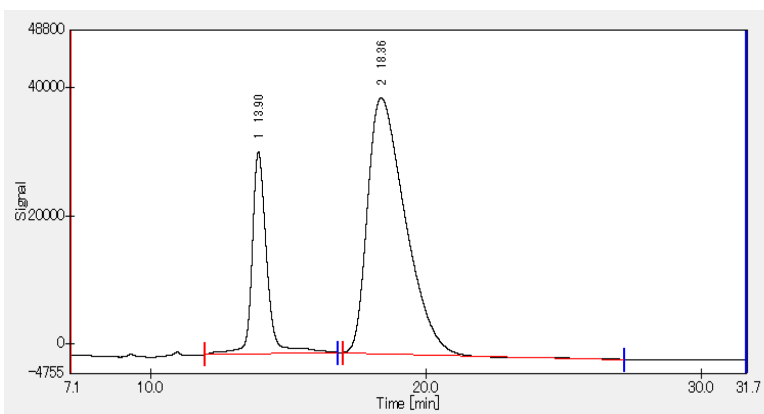
3-Hydroxy-3-(4-nitrophenyl)-1-propan-1-one (**17r**): *(AS-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min,* λ=254 nm, *dr(syn/anti) = n.d, 52% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.32	12536501	50.047	338398	2679.4	2.091	3.046
2	16.72	12512958	49.953	278010	3094.3	1.853	*****
		25049459	100	616408			

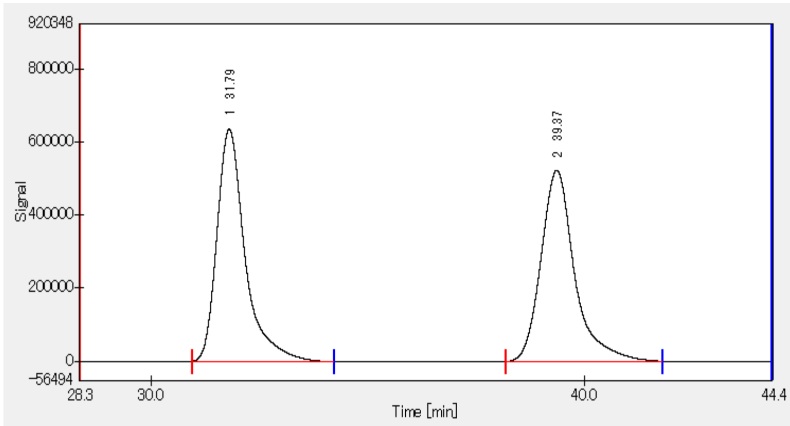
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	13.9	1174817	23.7938	31507	3668.6	1.226	2.553
2	18.36	3762670	76.2062	39886	814.2	1.602	*****
		4937487	100	71393			

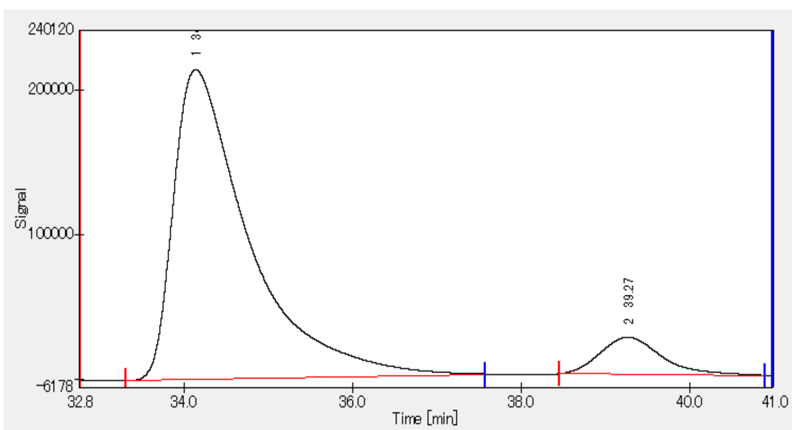
3-Hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**17s**): *AD-H column, n-hexane/iso-propanol: 90/10, flow Rate = 1.0 mL/min,* λ=254 nm*, dr(syn/anti) = n.d, 82% ee anti.*

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	31.79	28749255	50.3207	635412	10376.5	1.506	5.518
2	39.37	28382754	49.6793	523630	11074.9	1.346	*****
		57132009	100	1159042			

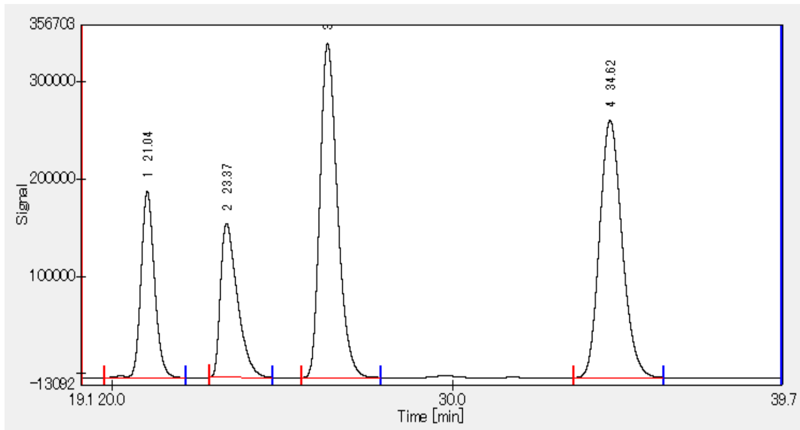
Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	34.14	13262031	91.0873	213711	5836.2	2.452	3.227
2	39.27	1297658	8.9127	25604	12738.8	1.34	*****
		14559689	100	239315			

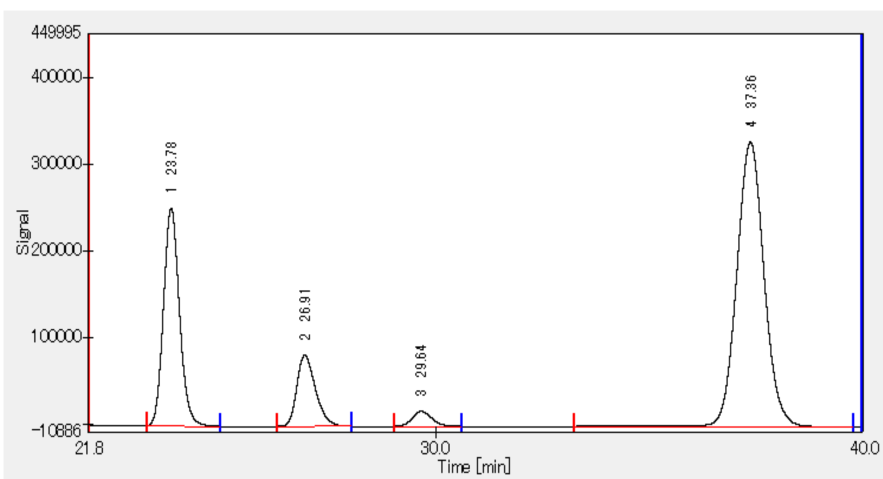
2-[Hydroxy-(4-nitrophenyl)-methyl]-cyclohexan-1-one (**17a**): *AD-H column, n-hexane/iso-propanol = 90/10, flow rate = 1.0 mL/min, λ=254 nm, dr(syn/anti)* = 24:76, 93*% ee anti.* (**1-gram Scale**)

Racemic



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	21.04	5240452	14.9537	191121	13076.6	1.18	2.769
2	23.37	5438855	15.5198	158075	9795.3	1.668	3.093
3	26.33	12231672	34.9032	342773	11799.8	1.3	7.509
4	34.62	12133538	34.6232	264130	12496.6	1.171	*****
		35044517	100	956099			

Chiral



No	Rt(min)	Area	Area%	Height	NTP	Symmetry	Resolution
1	23.78	6549061	27.0478	252299	18549.7	1.141	4.109
2	26.91	2508992	10.3622	82344	16947.7	1.328	3.22
3	29.64	551944.9	2.2796	17238	18626	1.171	7.52
4	37.36	14602882	60.3104	328677	15936.7	1.067	*****

24212880	100	680558