Electronic Supporting Information

Enantioenrichment of Racemic BINOL by Way of Excited State Proton Transfer

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Materials

N(α)-benzyloxycarbonyl-L-tryptophan (Z-Trp-OH) and N,N'-dicyclohexylcabodiimide (DCC) were purchased from Alfa Aesar and used without further purification. 4-(dimethylamino)pyridine (DMAP), N-(tert-butoxycarbonyl)-L-phenylalanine (Boc-Phe-OH), N-(tert-butoxycarbonyl)-L-2-phenylglycine (Boc-Phg-OH), N-benzyloxycarbonyl-L-proline (Z-Pro-OH), N- (tert-butoxycarbonyl)-L-proline (Boc-Pro-OH), N-(tert-Butoxycarbonyl)-L-alanine (Boc-Ala-OH), (1S)-(+)-Menthyl chloroformate, triethylamine, diisopropylethylamine, pyridine, and isopropylamine were all purchased from Sigma Aldrich and used without further purification. Racemic 1,1'-Bi-2-naphthol, (R)- 1,1'-Bi-2-naphthol, and (S)- 1,1'-Bi-2-naphthol were purchased from TCI and used without further purification. HPLC grade CH_2Cl_2 was purchased from Sigma-Aldrich and used without further purification. Dry solvents were obtained from a Pure Process Technology solvent purification system.

Instrumentation

Absorption spectroscopy. The UV-visible spectra were recorded using an Agilent 8453 UV-Vis photo diode array spectrophotometer with a special optical glass 1 cm × 1 cm cuvette.

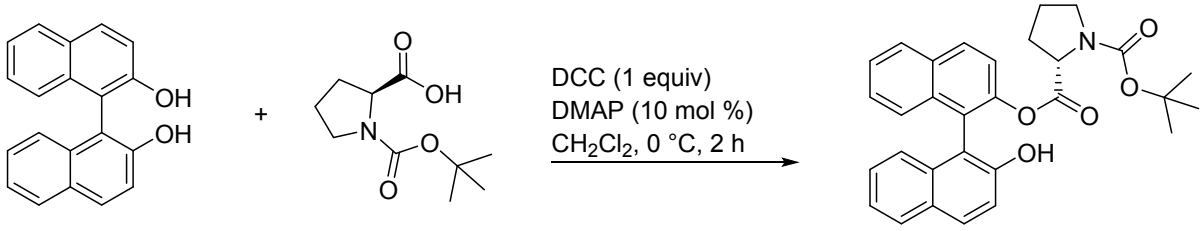
Light Source. A ThorLabs M365L2- UV (365 nm, fwhm = 7.5 nm) mounted LED was used as the light source for UV reactions and was controlled by ThorLabs LEDD1B T-Cube series LED driver. The light intensity was measured using an Ophir power meter (Vega 7Z01560) and sensor (3A-FS 7Z02628).

^{1}H and ^{13}C NMR. Nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm) relative to residual chloroform peak (7.26 (s) ppm). Chemical shifts for ^{13}C are reported in parts per million (ppm) relative to residual chloroform peak (77.16 ppm).

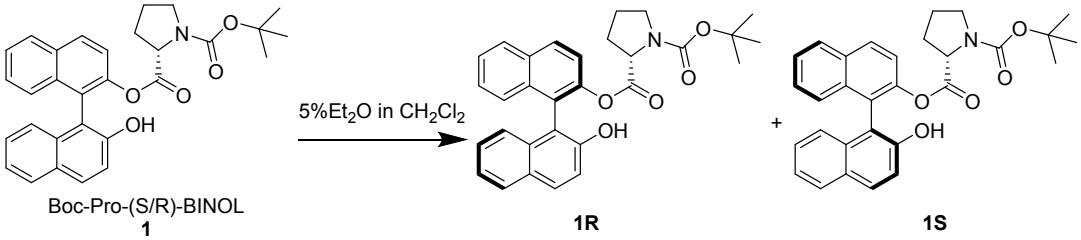
CD Spectroscopy. Circular Dichroism spectra were obtained using an AVIV 202 CD spectrometer with a 2 mm × 1 cm quartz cuvette.

Chiral Chromatography. Supercritical fluid chromatography (SFC) was performed using a JASCO SFC-4000 analytical SFC system with ~1mg/mL of sample in HPLC grade CH_2Cl_2.

Synthesis:

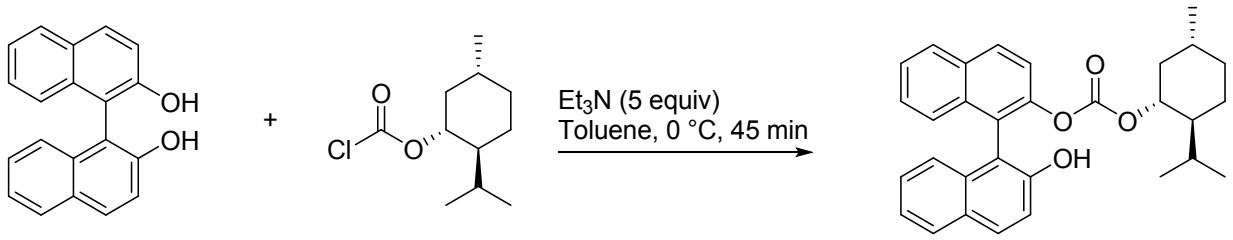


*Boc-Pro-BINOL (**1**):* (R/S)BINOL (1 g, 3.49 mmol, 1 equiv), dicyclohexylcarbodiimide (0.86 mg, 4.19 mmol, 1.2 equiv), N,N-dimethylaminopyridine (0.05 mg, 0.42 mmol, 0.12 equiv), and N-(tert-Butoxycarbonyl)-L-proline (0.9 g, 4.19 mmol, 1.2 equiv) were added to a 250mL three neck round bottom flask equipped with a magnetic stir bar. The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 100 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. Seconds to minutes after the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that most or all of the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 60 grams of 400-600 mesh silica with hexanes in a 40 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 25% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **1** (1.61 g, 95% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 – 7.8 (m, 4H), 7.6 – 7.2 (m, 7H), 7.1 – 7.0 (m, 1H), 5.3 – 5.2 (m, 1H), 4.3 – 4.1 (m, 1H), 3.4 – 2.9 (m, 2H), 1.5 – 1.4 (m, 10H), 1.4 – 0.9 (m, 2H), 0.9 – 0.3 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 153.6, 151.8, 147.8, 147.8, 133.5, 131.1, 130.6, 130.5, 129.1, 128.5, 128.1, 128.0, 128.0, 127.7, 127.3, 127.1, 127.0, 126.7, 126.5, 126.4, 126.2, 125.9, 125.7, 125.7, 124.9, 124.7, 124.5, 123.9, 123.8, 121.4, 121.4, 118.5, 118.4, 118.2, 100.1, 80.3, 80.1, 80.0, 76.9, 59.0, 58.9, 58.5, 46.3, 46.1, 30.1, 29.8, 29.3, 28.7, 28.6, 28.5, 23.8, 23.4, 23.1, 22.5. HRMS (ESI+) *m/z* calcd. For $C_{30}H_{29}NNaO_5$ ([M+Na]$^+$) 506.19434, found 506.19446.

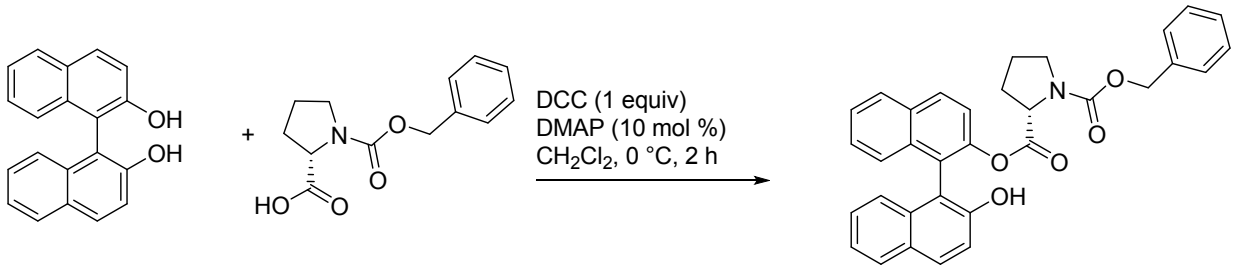


Separation of R and S diastereomers of Boc-Pro-BINOL (**1R** and **1S**): For irradiation experiments a large quantity of **1R** and **1S** were necessary to repeat measurements. Instead of synthesizing these from enantiopure starting materials, 1g of (R/S) Boc-Pro-BINOL was synthesized according to the above procedure and then subjected to silica column chromatography to separate the diastereomers following a modified literature procedure.[1] A 5% Et_2O in CH_2Cl_2 solution was used as the solvent. Due to the difficulty of the separation, several of the fractions were found to contain traces of both **1R** and **1S**, and

therefore great care was taken to only combine fractions which contained only one diastereomer. Chiral SFC analysis of **1R** and **1S** confirmed their enantiopurity. The fractions which contained some quantity of both diastereomers were combined to constitute the racemic sample. Chiral SFC indicated a slight excess of **1R** which was adjusted by adding small amounts of **1S** until the SFC trace showed a 50/50 ratio of diastereomers.

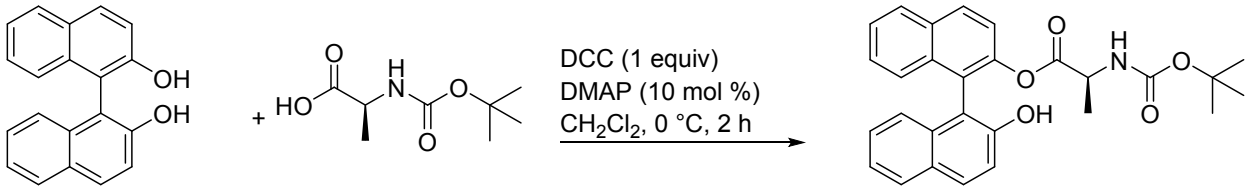


*Synthesis of Menthyl-BINOL (**2**):* (R/S)BINOL (250 mg, 0.873 mmol, 1 equiv) and (S) menthyl chloroformate (210 mg, 0.960 mmol, 1.1 equiv) were added to a 250 mL 3 neck round bottom flask equipped with a magnetic stir bar. The flask was purged and backfilled with N_2 three times. 60 mL of toluene was added to the flask and stirred until the BINOL was completely dissolved. Et_3N (0.609 mL, 4.366 mmol, 5 equiv) was added slowly via syringe with stirring. The reaction mixture was stirred at room temperature until TLC indicated completion of the reaction, ~45 minutes. The reaction was quenched with 10 mL of 4 M HCl, extracted with water 3 times, dried over anhydrous sodium sulfate, and evaporated to dryness. A silica gel column was prepared by wet packing 12 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 10% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **2** (0.301 g, 74% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 – 8.1 (m, 1H), 8.0 – 8.0 (m, 1H), 8.0 – 7.8 (m, 2H), 7.6 – 7.5 (m, 2H), 7.4 – 7.3 (m, 4H), 7.3 – 7.2 (m, 1H), 7.1 (ddt, *J* = 7.7, 4.5, 1.1 Hz, 1H), 5.3 (d, *J* = 5.3 Hz, 1H), 4.4 (qd, *J* = 11.0, 4.6 Hz, 1H), 1.8 – 1.5 (m, 4H), 1.4 – 1.2 (m, 2H), 1.0 – 0.7 (m, 7H), 0.7 – 0.5 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.9, 152.0, 151.9, 148.1, 133.6, 133.5, 132.5, 132.4, 131.0, 131.0, 130.6, 130.6, 129.3, 128.4, 128.1, 128.1, 127.6, 127.6, 126.9, 126.9, 126.5, 126.5, 126.0, 126.0, 124.7, 124.7, 123.7, 123.7, 123.6, 123.4, 121.6, 118.5, 118.4, 113.9, 79.8, 46.8, 46.6, 40.4, 39.9, 34.1, 34.0, 31.4, 31.3, 26.7, 26.1, 23.6, 23.4, 22.0, 22.0, 20.6, 20.5, 16.6, 16.2. HRMS (ESI+) *m/z* calcd. For $C_{31}H_{32}NaO_4$ ([M+Na]$^+$) 491.21983, found 491.22072.



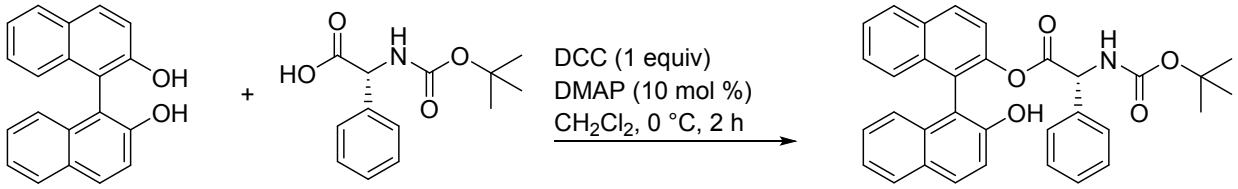
*Synthesis of Z-Pro-BINOL (**3**):* (R/S)BINOL (100 mg, 0.349 mmol, 1 equiv), dicyclohexylcarbodiimide (0.086 mg, 0.419 mmol, 1.2 equiv), N,N-dimethylaminopyridine (0.005 mg, 0.042 mmol, 0.12 equiv), and N-

[(Benzyloxy)carbonyl]-L-proline (104 mg, 0.419 mmol, 1.2 equiv) were added to a 50mL three neck round bottom flask equipped with a magnetic stir bar. The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 10 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. After the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that most or all of the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5 mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 12 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 33% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **3** (0.141 g, 78% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 – 7.8 (m, 4H), 7.6 – 7.5 (m, 1H), 7.5 – 7.3 (m, 9H), 7.3 – 7.1 (m, 2H), 7.1 – 7.0 (m, 1H), 5.3 – 5.1 (m, 2H), 5.1 – 5.0 (m, 1H), 4.3 – 4.2 (m, 1H), 3.7 – 3.0 (m, 2H), 2.2 – 1.6 (m, 2H), 1.4 – 1.0 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 171.7, 154.9, 154.1, 154.0, 151.9, 151.7, 147.8, 147.5, 136.6, 136.5, 133.5, 133.4, 133.3, 132.3, 131.0, 130.8, 130.7, 130.6, 130.4, 130.4, 130.2, 128.9, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.5, 127.5, 127.3, 127.0, 126.9, 126.7, 126.4, 126.2, 125.7, 125.6, 125.6, 124.8, 124.6, 124.5, 124.4, 123.7, 123.7, 123.7, 123.5, 122.9, 122.9, 122.8, 122.1, 121.9, 121.5, 118.3, 118.3, 118.1, 114.1, 113.8, 67.2, 67.1, 67.0, 60.4, 59.2, 58.8, 58.7, 58.4, 46.8, 46.6, 46.3, 46.1, 30.1, 29.9, 29.1, 28.9, 23.7, 23.3, 23.0, 22.3, 14.2, -16.9. HRMS (ESI+) *m/z* calcd. For $C_{33}H_{27}NNaO_5$ ([M+Na]$^+$) 540.17869, found 540.17921.

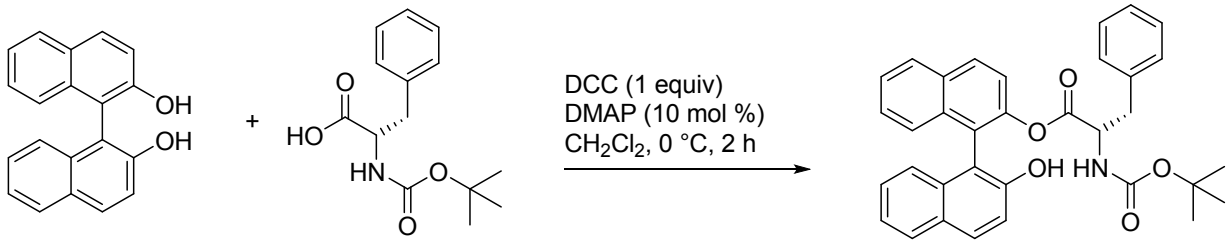


*Synthesis of Boc-Ala-BINOL (**4**):* (R/S)BINOL (100 mg, 0.349 mmol, 1 equiv), dicyclohexylcarbodiimide (0.108 mg, 0.524 mmol, 1.5 equiv), N,N-dimethylaminopyridine (0.006 mg, 0.052 mmol, 0.15 equiv), and N-(tert-Butoxycarbonyl)-L-alanine (0.099 mg, 0.524 mmol, 1.5 equiv) were added to a 50mL three neck round bottom flask equipped with a magnetic stir bar. (Note: the R_f values of Boc-Ala-BINOL and BINOL are very similar. To compensate, large excess of Boc-Ala-OH was used to ensure that all the BINOL was reacted making the separation much easier). The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 10 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. Seconds to minutes after the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that all the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 16 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 25% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and

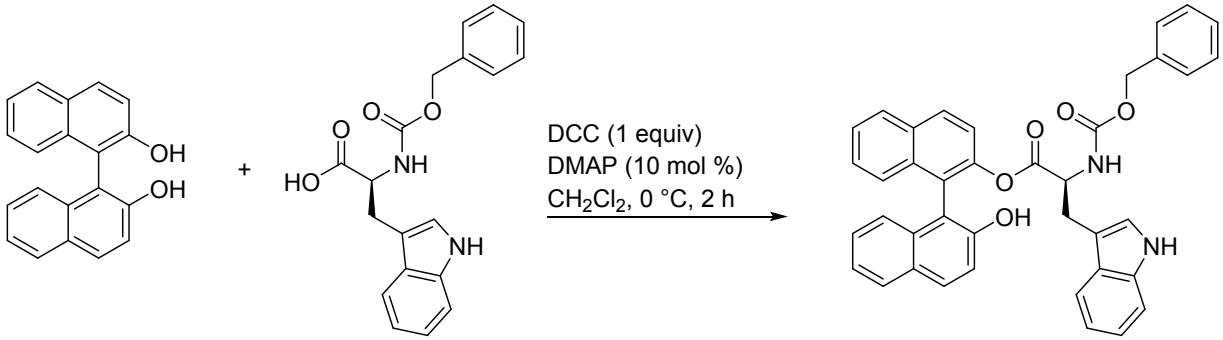
evaporated to dryness to obtain **4** (0.065 g, 41% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 (t, *J* = 9.2 Hz, 1H), 8.0 – 7.9 (m, 1H), 7.9 – 7.8 (m, 2H), 7.5 (ddt, *J* = 10.0, 6.0, 1.9 Hz, 1H), 7.5 – 7.2 (m, 7H), 7.0 (dq, *J* = 8.4, 0.9 Hz, 1H), 5.4 (s, 1H), 4.2 (t, *J* = 7.5 Hz, 1H), 1.4 (s, 9H), 0.6 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 151.7, 147.7, 147.5, 133.4, 133.4, 132.4, 131.1, 130.6, 130.5, 130.4, 129.0, 128.4, 128.4, 128.0, 127.6, 126.9, 126.5, 126.3, 125.8, 125.6, 124.7, 124.3, 123.7, 123.5, 122.9, 121.6, 118.2, 113.8, 79.9, 77.2, 28.3, 28.3, 17.1, 17.0. HRMS (ESI+) *m/z* calcd. For $C_{28}H_{27}NNaO_5$ ([M+Na]$^+$) 480.17869, found 480.17681.



*Synthesis of Boc-Phg-BINOL (**5**):* (R/S)BINOL (100 mg, 0.349 mmol, 1 equiv), dicyclohexylcarbodiimide (0.108 mg, 0.524 mmol, 1.5 equiv), N,N-dimethylaminopyridine (0.006 mg, 0.052 mmol, 0.15 equiv), and N-(tert-Butoxycarbonyl)-D-phenylglycine (0.110 mg, 0.524 mmol, 1.5 equiv) were added to a 50 mL three neck round bottom flask equipped with a magnetic stir bar. (Note: the R_f values of Boc-Phg-BINOL and BINOL are very similar. To compensate, large excess of Boc-Phg-OH was used to ensure that all the BINOL was reacted making the separation much easier). The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 10 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. Seconds to minutes after the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that all the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 16 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 25% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **5** (0.094 g, 52% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 13.5, 9.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 15.9, 8.5 Hz, 1H), 7.74 (t, *J* = 8.3 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.42 – 6.96 (m, 9H), 6.93 – 6.79 (m, 3H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.17 (q, *J* = 7.1 Hz, 1H), 1.43 (d, *J* = 11.9 Hz, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.79, 155.06, 154.88, 151.82, 151.61, 147.69, 135.05, 134.83, 133.60, 133.49, 132.40, 131.08, 130.73, 130.65, 130.51, 129.12, 129.03, 128.93, 128.56, 128.46, 128.37, 128.17, 128.07, 127.62, 127.44, 126.99, 126.64, 126.55, 126.38, 126.00, 125.73, 124.74, 124.22, 123.55, 123.47, 123.39, 121.53, 121.46, 118.37, 118.12, 113.68, 80.56, 80.38, 77.37, 76.90, 58.24, 57.73, 28.40, 28.38; HRMS (ESI+) *m/z* calcd. For $C_{33}H_{29}NNaO_5$ ([M+Na]$^+$) 542.19434, found 542.19383.



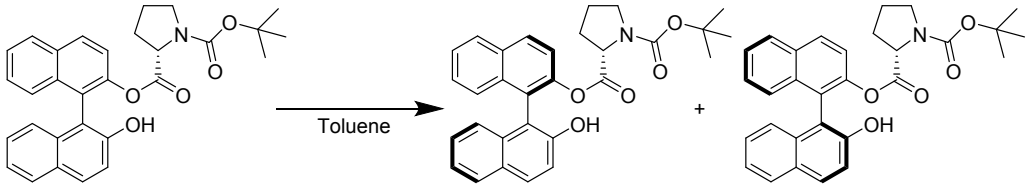
*Synthesis of Boc-Phe-BINOL (**6**):* (R/S)BINOL (100 mg, 0.349 mmol, 1 equiv), dicyclohexylcarbodiimide (0.108 mg, 0.524 mmol, 1.5 equiv), N,N-dimethylaminopyridine (0.006 mg, 0.052 mmol, 0.15 equiv), and N-(tert-Butoxycarbonyl)-L-phenylalanine (0.139 mg, 0.524 mmol, 1.5 equiv) were added to a 50mL three neck round bottom flask equipped with a magnetic stir bar. (Note: the R_f values of Boc-Phe-BINOL and BINOL are very similar. To compensate, large excess of Boc-Phe-OH was used to ensure that all the BINOL was reacted making the separation much easier). The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 10 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. Seconds to minutes after the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that all the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 16 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 25% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **6** (0.117 g, 63% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.1 (dd, *J* = 11.4, 8.9 Hz, 1H), 8.0 (dd, *J* = 8.1, 4.1 Hz, 1H), 7.9 – 7.8 (m, 2H), 7.5 (ddd, *J* = 8.2, 5.8, 2.3 Hz, 1H), 7.5 – 7.2 (m, 6H), 7.2 – 7.1 (m, 3H), 7.1 – 7.1 (m, 1H), 6.9 – 6.8 (m, 1H), 6.8 – 6.7 (m, 1H), 4.6 (d, *J* = 8.4 Hz, 1H), 4.4 (td, *J* = 8.8, 4.3 Hz, 1H), 2.2 – 1.8 (m, 2H), 1.3 (d, *J* = 11.9 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 155.1, 151.8, 147.8, 147.6, 135.9, 133.5, 133.3, 132.4, 131.1, 130.6, 129.0, 128.9, 128.5, 128.4, 128.1, 127.6, 127.4, 127.0, 126.9, 126.8, 126.5, 125.7, 124.5, 123.8, 122.9, 121.6, 118.2, 113.8, 80.2, 80.0, 77.3, 54.1, 36.9, 28.2. HRMS (ESI+) *m/z* calcd. For $C_{34}H_{31}NNaO_5$ ($[M+Na]^+$) 556.20999, found 556.21032.



*Synthesis of Z-Trp-BINOL (**7**):* (R/S)BINOL (100 mg, 0.349 mmol, 1 equiv), dicyclohexylcarbodiimide (0.086 mg, 0.419 mmol, 1.2 equiv), N,N-dimethylaminopyridine (0.005 mg, 0.042 mmol, 0.12 equiv), and N-[(Benzyloxy)carbonyl]-L-tryptophan (118 mg, 0.419 mmol, 1.2 equiv) were added to a 50mL three neck

round bottom flask equipped with a magnetic stir bar. The flask was purged and backfilled with N_2 three times and submerged in an ice bath. 10 mL of cold CH_2Cl_2 (~0° C) was added via syringe to the reaction flask. Seconds to minutes after the solvent was added dicyclohexyl urea can be seen precipitating from solution. The solution was stirred at 0° C until TLC indicated that most or all of the BINOL had reacted (~2 hours). The reaction mixture was then rotary evaporated to remove 2/3^{rds} of the solvent volume, causing more dicyclohexyl urea to precipitate from solution. The resulting slurry was vacuum filtered and washed with three 5 mL portions of cold CH_2Cl_2. The filtrate was then rotary evaporated to dryness. A silica gel column was prepared by wet packing 12 grams of 400-600 mesh silica with hexanes in a 15 mm column. The crude product was wet loaded with minimal CH_2Cl_2 onto the column and eluted with 33% EtOAc/hexanes until the monosubstituted product was obtained. The fractions were combined and evaporated to dryness to obtain **7** (0.138 g, 65% yield) as an off-white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.9 – 7.8 (m, 3H), 7.8 – 7.7 (m, 2H), 7.4 (dt, *J* = 8.2, 4.0 Hz, 1H), 7.3 – 7.1 (m, 13H), 7.1 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.0 – 6.9 (m, 2H), 6.3 (d, *J* = 2.5 Hz, 1H), 5.6 (s, 1H), 4.9 (s, 2H), 4.8 (d, *J* = 7.8 Hz, 1H), 4.4 (td, *J* = 7.7, 4.8 Hz, 1H), 2.6 (dd, *J* = 15.2, 4.9 Hz, 1H), 2.3 (dd, *J* = 15.2, 7.7 Hz, 1H), 1.8 (dd, *J* = 12.5, 4.0 Hz, 1H), 1.6 (dddd, *J* = 13.3, 5.8, 3.9, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 155.9, 151.9, 147.6, 136.1, 136.0, 133.6, 133.5, 132.3, 130.6, 130.5, 129.0, 128.5, 128.4, 128.2, 128.1, 128.1, 127.4, 127.3, 126.9, 126.3, 125.9, 124.8, 123.6, 123.0, 122.7, 122.2, 121.7, 119.6, 118.5, 118.3, 113.8, 111.2, 109.3, 67.0, 54.5, 49.2, 33.9, 26.6, 24.9. HRMS (ESI+) *m/z* calcd. For $C_{30}H_{29}NNaO_5$ ($[M+Na]^+$) 629.20524, found 629.20570.

Boc-Pro-BINOL Enantioenrichment:



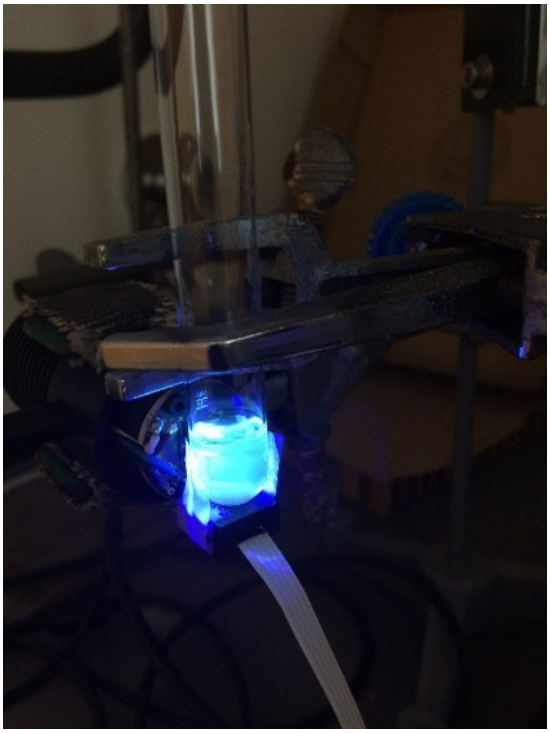
(S)-Boc-Pro-(S/R)-BINOL
1

(S)-Boc-Pro-(R)-BINOL
>50%

(S)-Boc-Pro-(S)-BINOL
<50%

5 mg of racemic Boc-Pro-(S/R)-BINOL added to test-tube with a magnetic stir bar. 1 mL of dry toluene and 0.1 mL of dry triethylamine were added to the test tube and the reaction vessel was capped with a rubber septum. The solution was vigorously stirred with a magnetic stir plate and irradiated with a 365 nm LED at 8 mW/cm^2 for 60 minutes. 0.1 mL aliquots were removed at 10, 20, 40, and 60 minutes. Each aliquot was evaporated to dryness, dissolved in 1 mL of toluene, then evaporated to dryness a second time to remove residual triethylamine. Silica gel columns were prepared by wet packing 400-600 mesh silica gel in 25% ethyl acetate in hexanes. Samples were dissolved in 1mL of 25% ethyl acetate in hexanes and flashed through the column. After separation, fractions containing Boc-Pro-BINOL were dried under reduced pressure. Purified samples were dissolved in 1mL of HPLC grade dichloromethane and analyzed by supercritical fluid chromatography.

Reaction set-up:



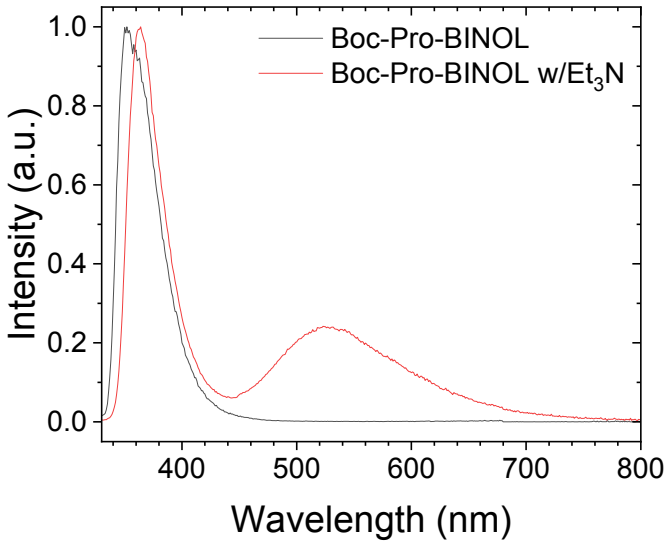


Figure S1. Emission spectra for Boc-Pro-BINOL in toluene with and without Et_3N (λ_{ex} = 320 nm).

Solvent Dependence: 5 mg of racemic Boc-Pro-BINOL added to test-tube with a magnetic stir bar. 1 mL of dry solvent (see table below) and 0.1 mL of dry triethylamine were added to the test tube and the reaction vessel was capped with a rubber septum. The solution was vigorously stirred with a magnetic stir plate and irradiated with a 365nm LED at 8mW/cm^2 for 60 minutes. 0.1 mL aliquots were removed at 20 and 60 minutes. Each aliquot was evaporated to dryness, dissolved in 1 mL of toluene, then evaporated to dryness a second time to remove residual triethylamine. Silica gel columns were prepared by wet packing 400-600 mesh silica gel in 25% ethyl acetate in hexanes. Samples were dissolved in 1 mL of 25% ethyl acetate in hexanes and flashed through the column. After separation, fractions containing Boc-Pro-BINOL were dried under reduced pressure. Purified samples were dissolved in 1 mL of HPLC grade dichloromethane and analyzed by supercritical fluid chromatography (Daicel CHIRALPAK® IA column, 35% CH_2Cl_2 in CO_2, 1.5 mL/min flow rate)

Table S1. Enantioenrichment of Boc-Pro-BINOL in various solvents[a]

Solvent	ee **1R** (%) @ 20 mins[b]	ee **1R** (%) @ 60 mins[b]
Toluene	15	31
Mesitylene	8	17
Hexanes[c]	10	24
MeCN	7	13
THF	15	17
MeOH	4	2
CH_2Cl_2	18	18

[a]10 mM Boc-Pro-(S/R)-BINOL under 365 nm irradiation (8 mW/cm^2) at room temperature for 60 minutes with stirring. [b]ee was determined using SFC (Daicel CHIRALPAK® IA column, 35% CH_2Cl_2 in CO_2, 1.5 mL/min flow rate). [c] Boc-Pro-BINOL was insoluble at the standard solvent volume, therefore 3mL of hexanes and 0.3mL of triethylamine was used to fully dissolve the compound.

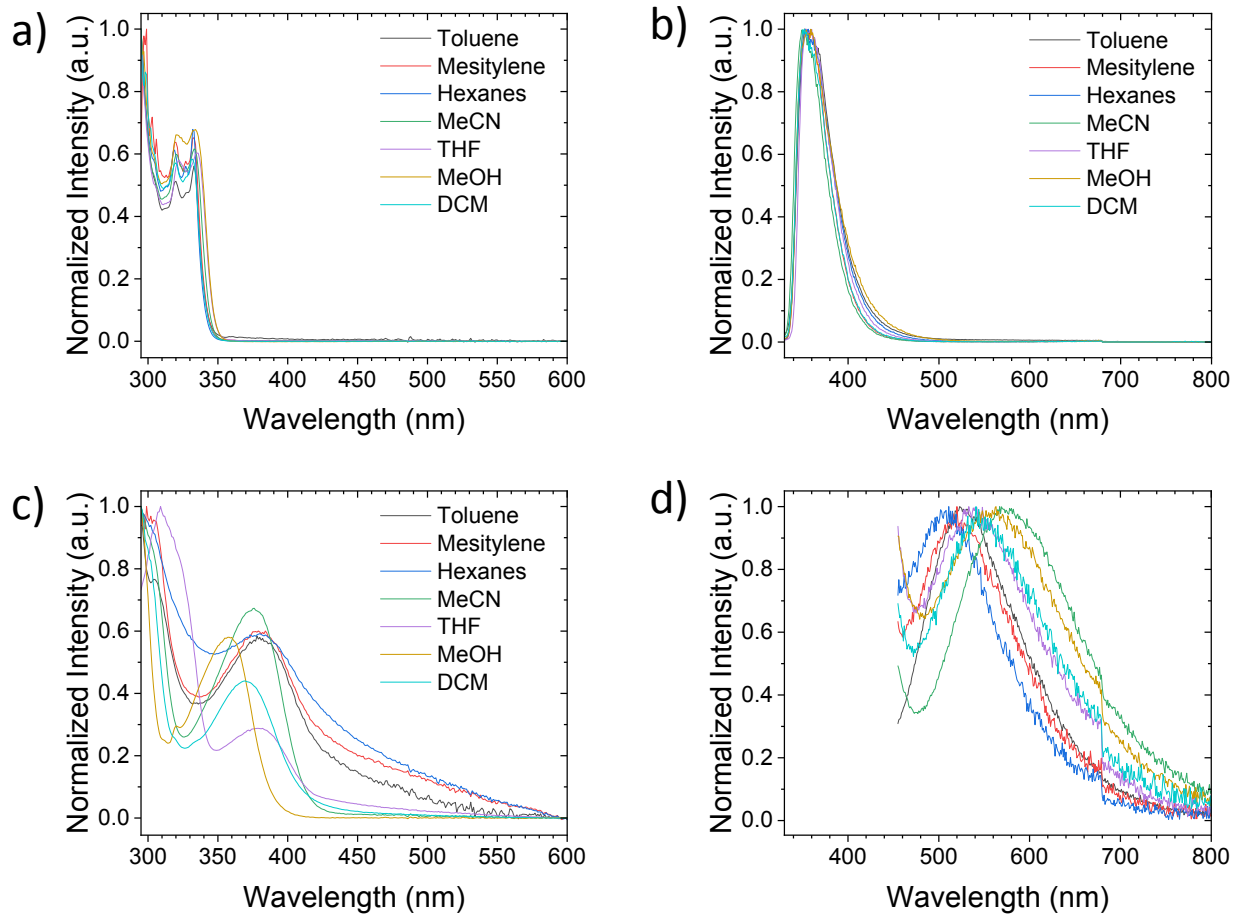


Figure S2. Solvent dependent absorption (a, c) and emission (b, d) of Boc-Pro-BINOL without (a, b) and with excess KOH (c) or Et_3N (d) (λ_{ex} = 320 nm).

ΔpK$_a$ Determination: ΔpK_a, the difference in pK_a between the ground and excited states, was calculated by utilizing the Förster cycle equation displayed below:

$$\Delta pK_a = \frac{Nh\Delta\nu}{\ln(10)RT}$$

Where N is Avogadro's number, h is Planck's constant, $\Delta\nu$ is the difference in energy between the 0-0 transition of the protonated and deprotonated form of the ESPT dye, R is the gas constant, and T is temperature. The $E_{0\text{-}0}$ was determined by the intercept of the normalized absorption and emission spectra of the protonated and deprotonated forms of the dyes as depicted in Figure S2. The resulting $E_{0\text{-}0}$ and ΔpKa's are summarized in Table S2.

Table S2. $E_{0\text{-}0}$ and ΔpKa for Boc-Pro-BINOL in various solvents.

Solvent	Enol $E_{0\text{-}0}$ (eV)	Keto $E_{0\text{-}0}$ (eV)	ΔpKa
Toluene	3.65	2.99	11.2
Mesitylene	3.65	2.95	11.8
Hexanes	3.66	2.99	11.3
MeCN	3.65	2.97	11.4
THF	3.62	2.99	10.6
MeOH	3.63	3.17	7.69
CH_2Cl_2	3.65	3.05	10.0

Base Dependence: 5 mg of Boc-Pro-(S)-BINOL added to test-tube with a magnetic stir bar. (Note: Boc-Pro-(S)-BINOL was used instead of racemic Boc-Pro-BINOL to amplify the differences in rate and ee.) 1 mL of dry toluene and dry base (see table below) were added to the test tube and the reaction vessel was capped with a rubber septum. The solution was vigorously stirred with a magnetic stir plate and irradiated with a 365 nm LED at 8mW/cm^2 for 60 minutes. 0.1 mL aliquots were removed at 60 minutes. Each aliquot was evaporated to dryness, dissolved in 1mL of toluene, then evaporated to dryness a second time to remove residual base. Silica gel columns were prepared by wet packing 400-600 mesh silica gel in 25% ethyl acetate in hexanes. Samples were dissolved in 1 mL of 25% ethyl acetate in hexanes and flashed through the column. After separation, fractions containing Boc-Pro-BINOL were dried under reduced pressure. Purified samples were dissolved in 1 mL of HPLC grade dichloromethane and analyzed by supercritical fluid chromatography (Daicel CHIRALPAK® IA column, 35% CH_2Cl_2 in CO_2, 1.5 mL/min flow rate)

Table S3. Enantioenrichment of Boc-Pro-BINOL with various bases[a]

Base	Volume added (mL)	ee (%) at 60 mins[b]
Triethylamine	0.100	17 of R
Diisopropylethylamine	0.125	26 of S
Pyridine	0.058	84 of S
Isopropylamine	0.061	76 of S

[a]10 mM Boc-Pro-(S)-BINOL under 365 nm irradiation (8 mW/cm^2) at room temperature for 60 minutes with stirring. [b]ee was determined using SFC (Daicel CHIRALPAK® IA column, 35% CH2Cl2 in CO2, 1.5 mL/min flow rate).

Table S4. Enantioenrichment of Boc-Pro-BINOL with various concentrations of triethylamine[a]

Toluene:Triethylamine (v:v)	ee **1R** (%) at 60 mins[b]
10:1	31
20:1	29
40:1	26
100:1	19

[a]10 mM Boc-Pro-(S/R)-BINOL under 365 nm irradiation (8 mW/cm^2) at room temperature for 60 minutes with stirring. [b]ee was determined using SFC (Daicel CHIRALPAK® IA column, 35% CH_2Cl_2 in CO_2, 1.5 mL/min flow rate).

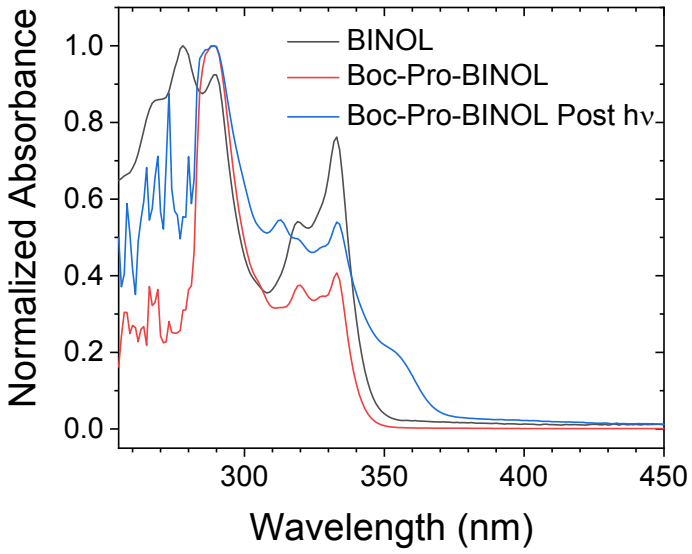


Figure S3. UV-Vis absorption spectra of BINOL, Boc-Pro-BINOL, and Boc-Pro-BINOL after 60 minutes of irradiation with 365nm at 8mW/cm^3. Spectra were normalized to set the λ_{max} = 1. The peak that appears at 360 nm after irradiation corresponds to the photodecomposition product responsible for the internal filtering effect.

Isolation of the side products: Boc-Pro-BINOL was irradiated 4 hours under standard conditions. Upon completion the mixture containing product and side products was separated using a 15 mm diameter column wet-packed with 12g of silica in 10% EtOAc in Hexanes. The reaction mixture was wet loaded

with CH_2Cl_2 and eluted with a gradient from 10% to 25% EtOAc in Hexanes. One major fraction, other than the desired product was isolated (R_f = 0.5, 20% EtOAc/80% hexanes) and the absorption spectrum after chiral group deprotection can be seen in Figure S4.

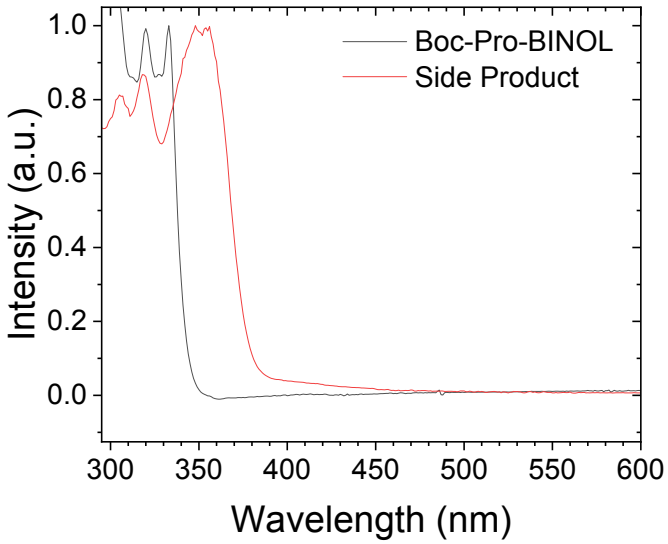
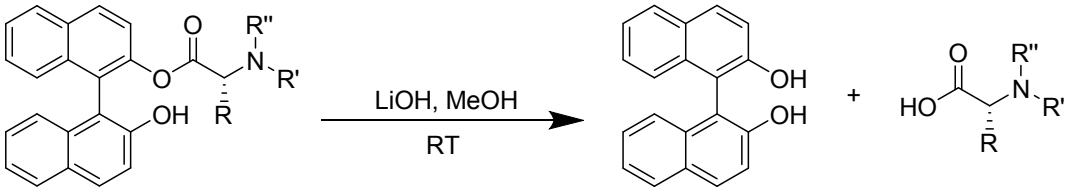


Figure S4. UV-Vis absorption spectra of Boc-Pro-BINOL and isolated side product (R_f = 0.5 in 20% EtOAc/80% Hexanes) after 4 hours of photolysis.



Chiral auxiliary-BINOL Cleavage: ~5mg of Boc-Pro-(S)-BINOL was dissolved in 1 mL of MeOH, then 0.1 mL of a 1 M solution of LiOH in MeOH was added and the solution was stirred at RT for 30 mins to 2 hours until TLC indicated completion of the reaction, as evidenced by the disappearance of the coupled BINOL and the reappearance of BINOL. The reaction was quenched by adding an equimolar amount of trifluoroacetic acid in MeOH. The reaction was stirred an additional 5 minutes and then evaporated to dryness. The resulting amorphous solid was dissolved in CH_2Cl_2 and run through a silica plug with CH_2Cl_2 until all the BINOL was eluted to yield (S)-BINOL in 90% yield with 100% ee.

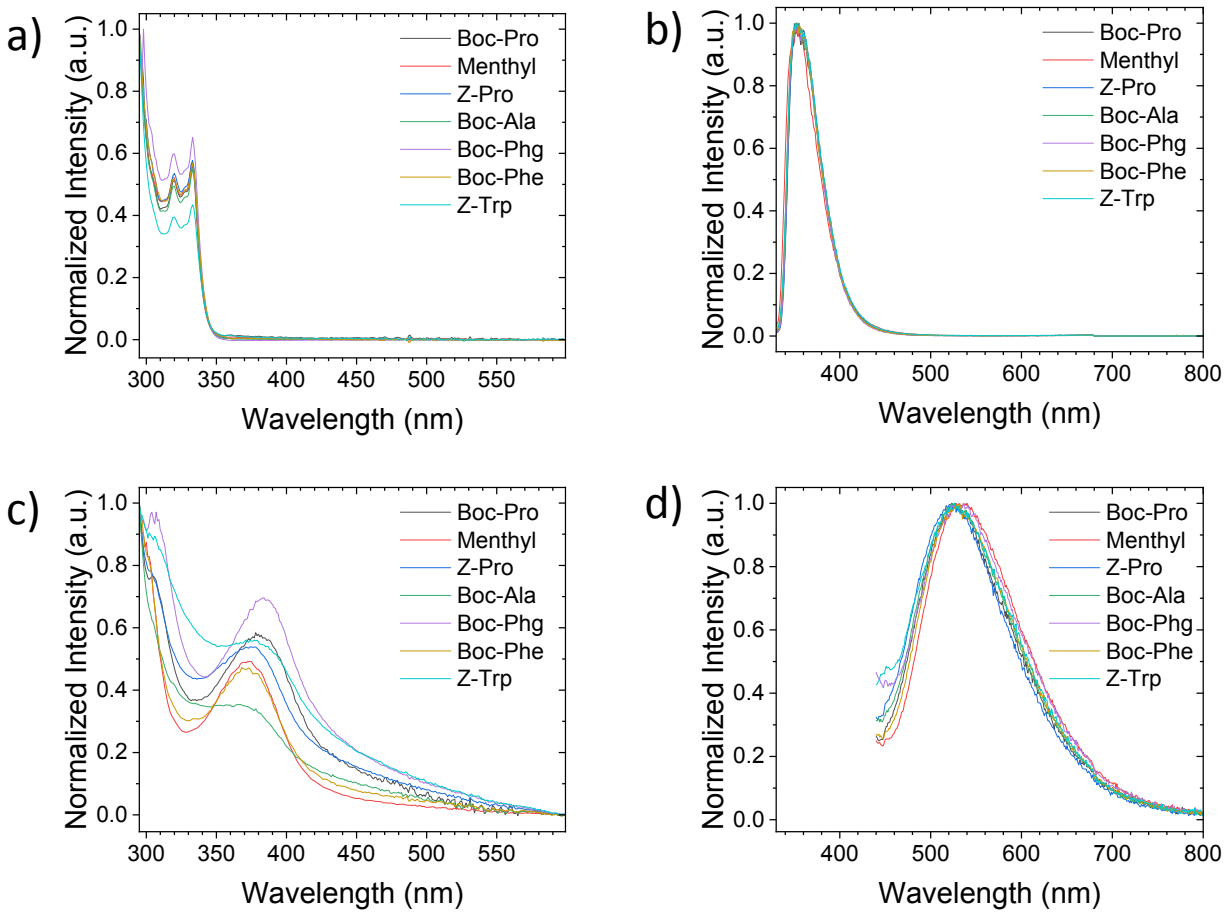


Figure S5. Absorption (a, c) and emission (b, d) of BINOL derivatives in toluene without (a, b) and with excess KOH (c) or Et_3N (d) (λ_{ex} = 320 nm).

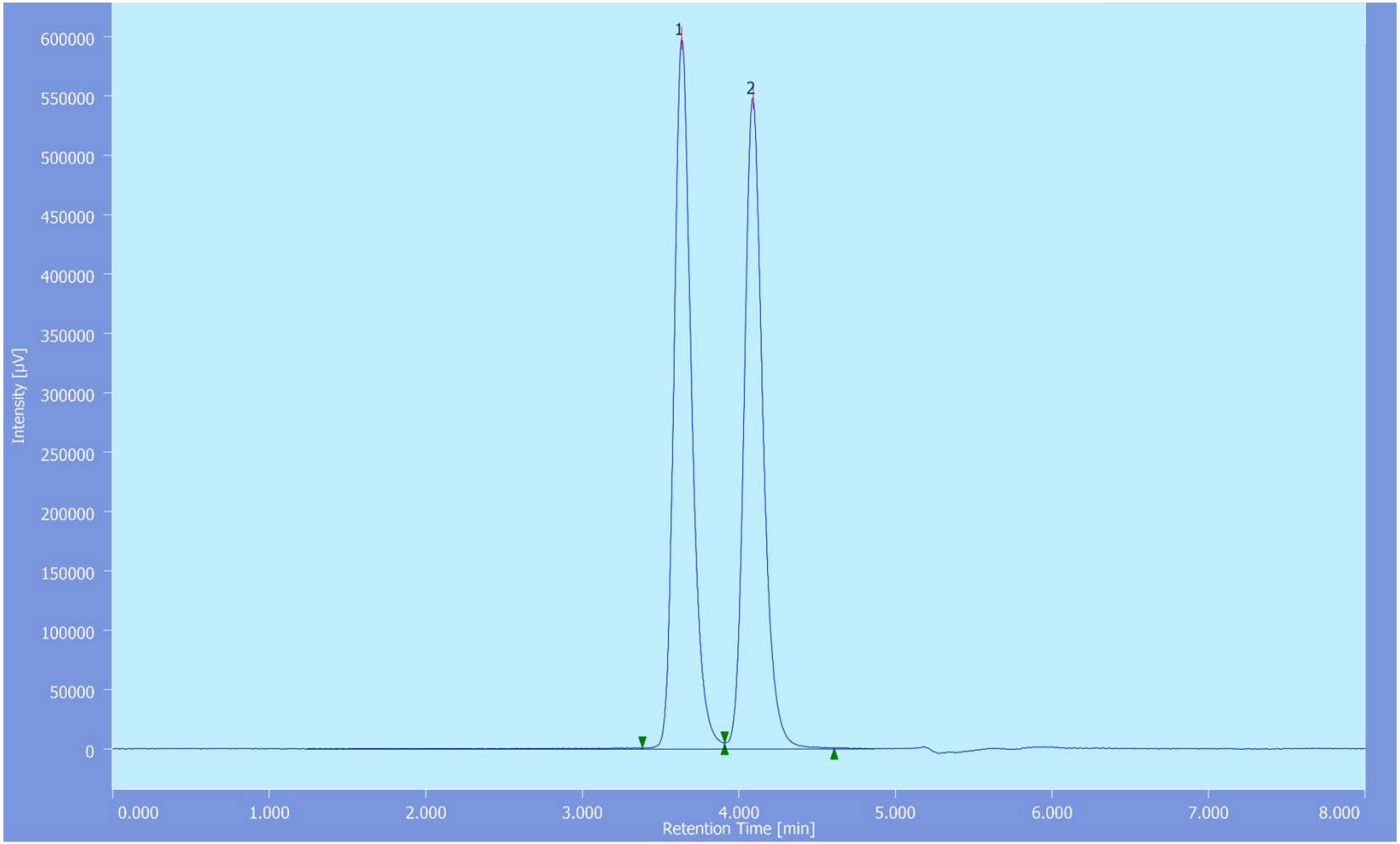
Table S5. $E_{0\text{-}0}$ and ΔpK_a for BINOL derivatives in toluene.

Chiral Auxiliary	Enol $E_{0\text{-}0}$ (eV)	Keto $E_{0\text{-}0}$ (eV)	ΔpK_a
Boc-Pro	3.65	2.99	11.2
Menthyl	3.67	3.02	10.9
Z-Pro	3.65	3.02	10.5
Boc-Ala	3.65	3.05	10.2
Boc-Phg	3.65	2.99	11.2
Boc-Phe	3.65	3.02	10.7
Z-Trp	3.65	2.97	11.5

References

[1] B. M. Panchal, C. Einhorn, J. Einhorn, *Tetrahedron Letters,* **2002***, 43*, 9245-9248.

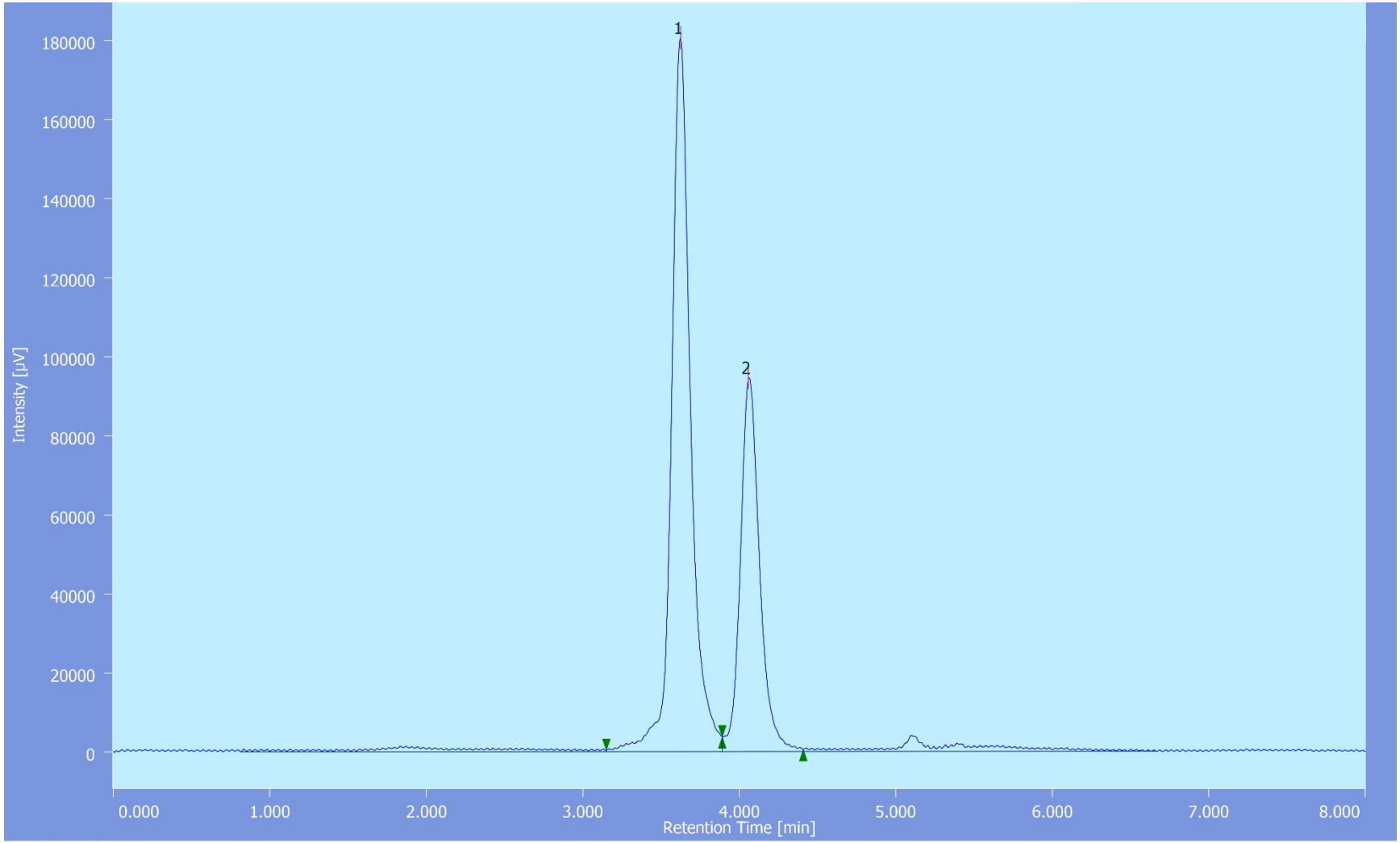
SFC Traces:



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.633	4659307	598149	50.547	52.157	N/A	5419	2.255	1.283	
2	Unknown	1	4.092	4558478	548668	49.453	47.843	N/A	6070	N/A	1.181	

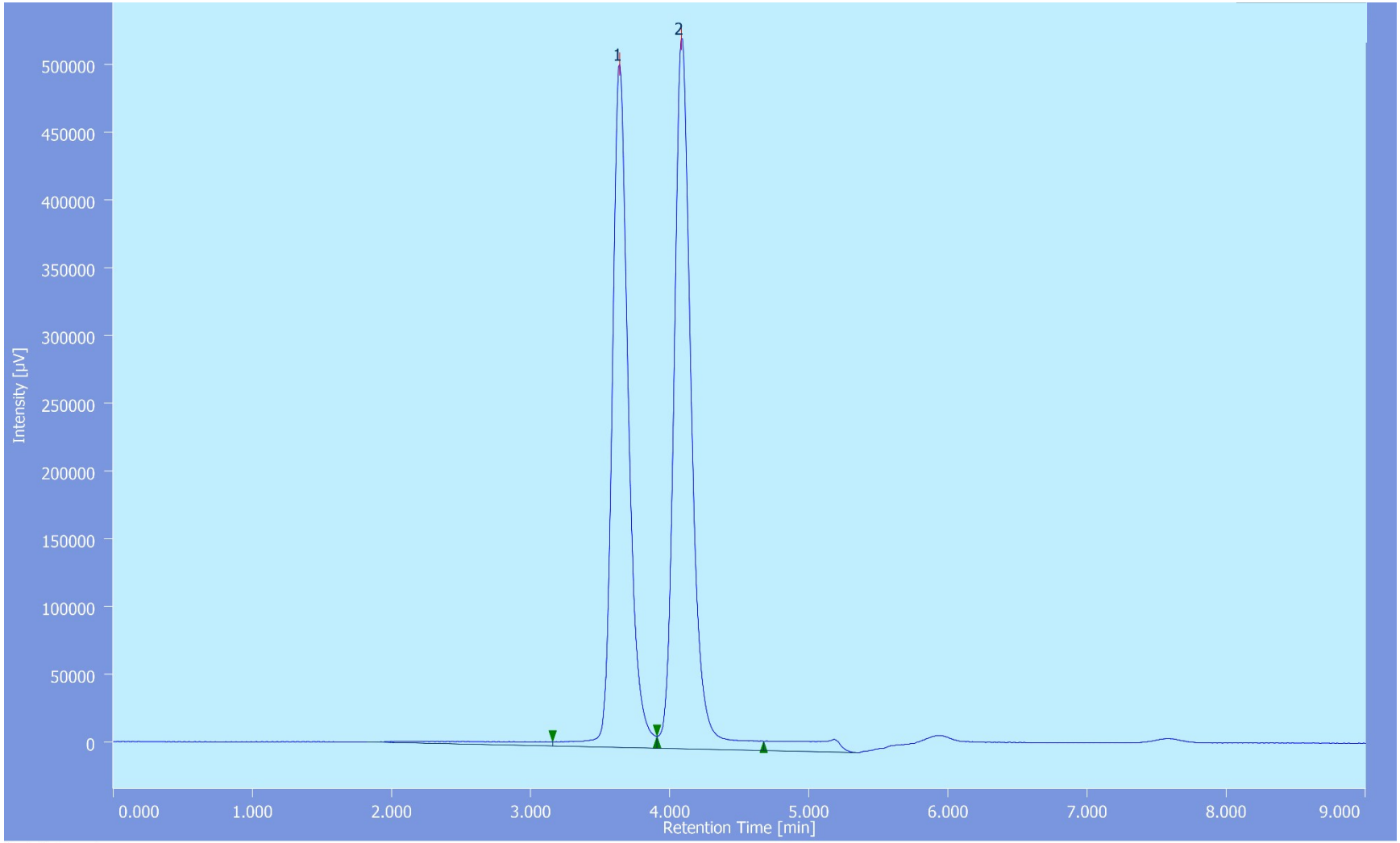
Figure S6. SFC trace of Racemic Boc-Pro-BINOL. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa,10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.625	1528573	180545	65.465	65.618	N/A	5278	2.117	1.244	
2	Unknown	1	4.058	806378	94600	34.535	34.382	N/A	5928	N/A	1.238	

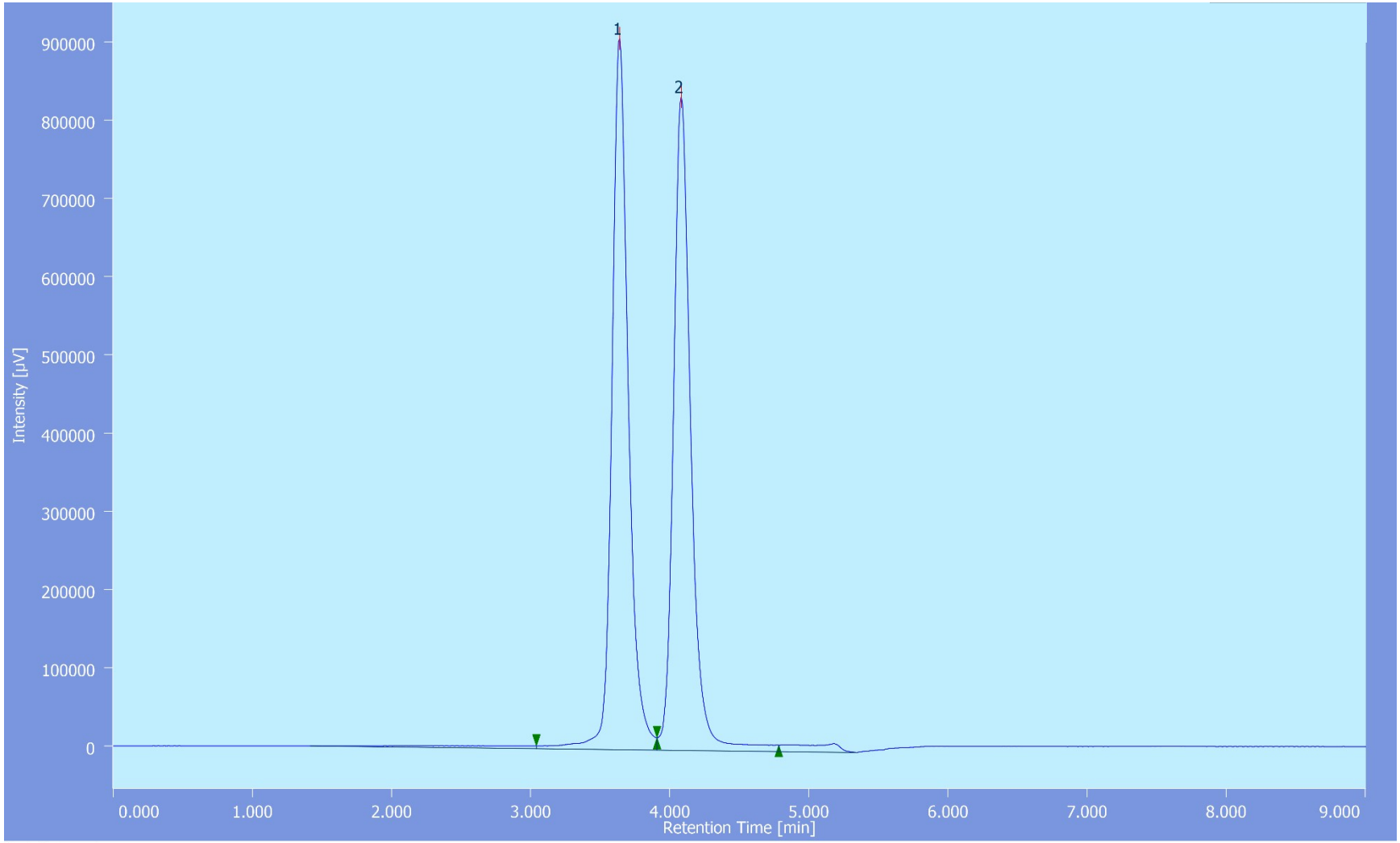
Figure S7. SFC trace of Racemic Boc-Pro-BINOL after irradiation. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.642	4139641	504254	47.383	49.033	N/A	5215	2.136	1.240	
2	Unknown	1	4.083	4596850	524139	52.617	50.967	N/A	5881	N/A	1.267	

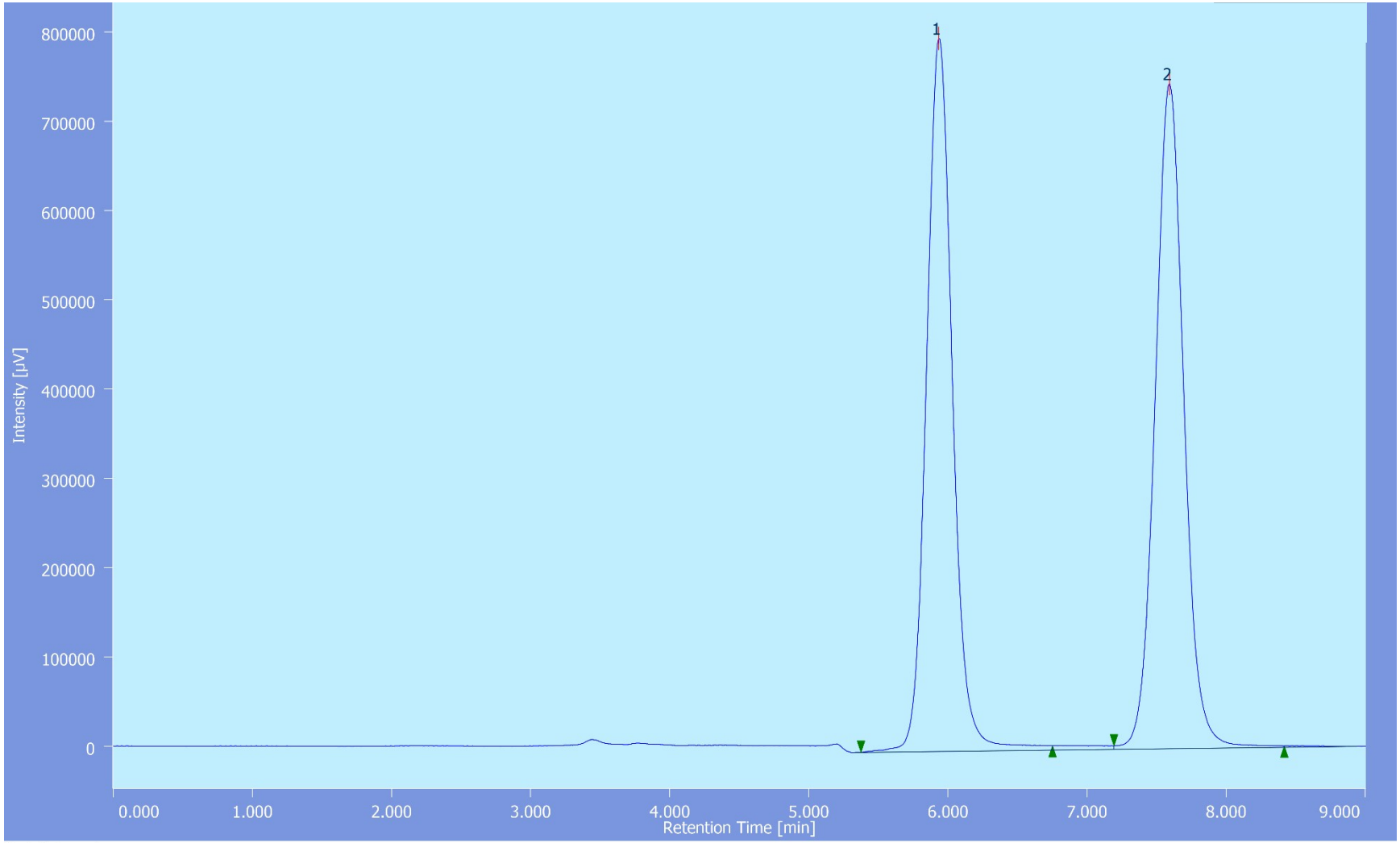
Figure S8. SFC trace of Racemic Boc-Pro-BINOL photodynamic resolution control without light. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.642	7532685	909056	50.817	52.104	N/A	5254	2.147	1.207	
2	Unknown	1	4.083	7290403	835639	49.183	47.896	N/A	5959	N/A	1.223	

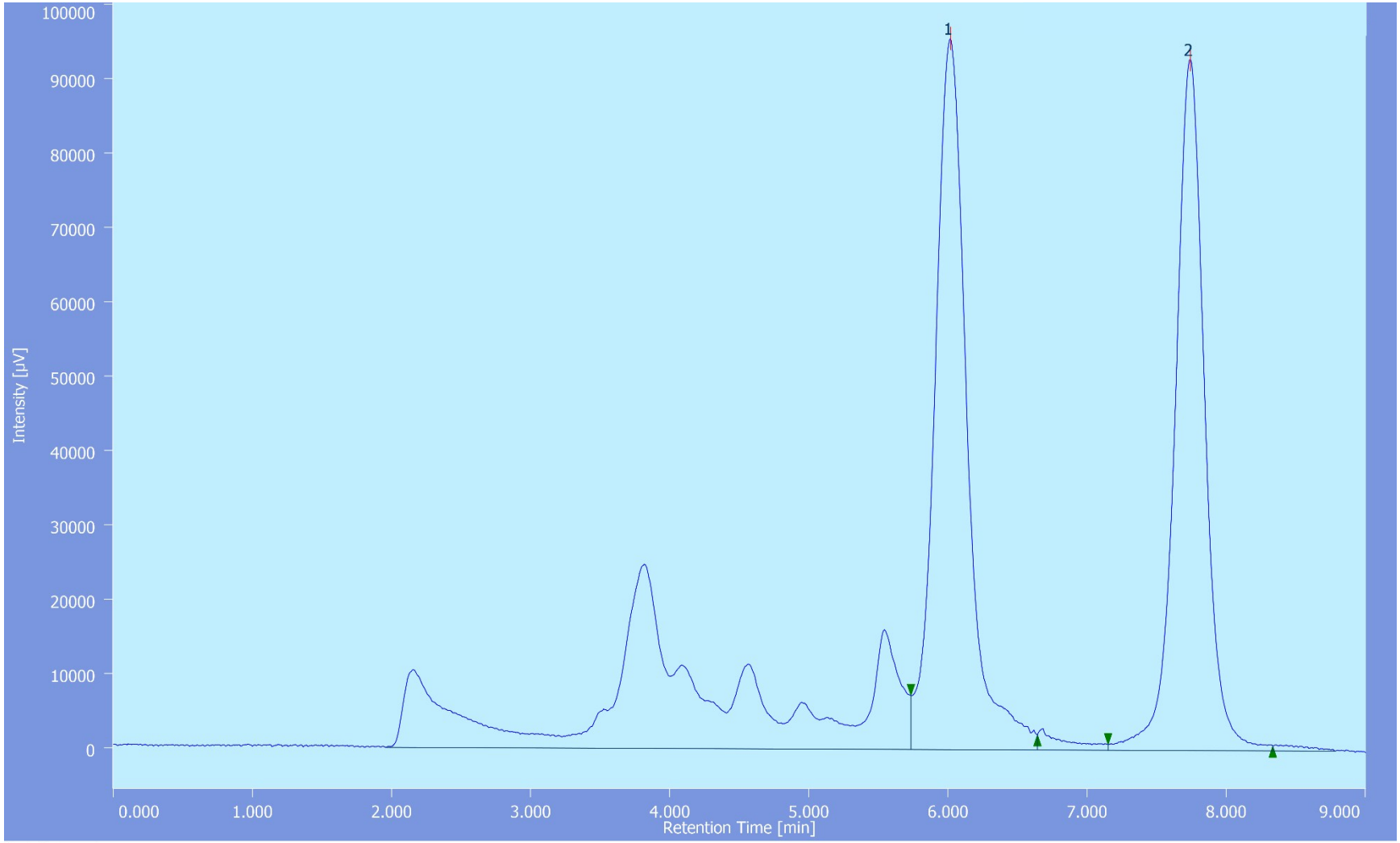
Figure S9. SFC trace of Racemic Boc-Pro-BINOL photodynamic resolution control without base. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	5.933	10403710	798460	49.363	51.751	N/A	5180	4.770	1.110	
2	Unknown	1	7.592	10672041	744423	50.637	48.249	N/A	6831	N/A	1.051	

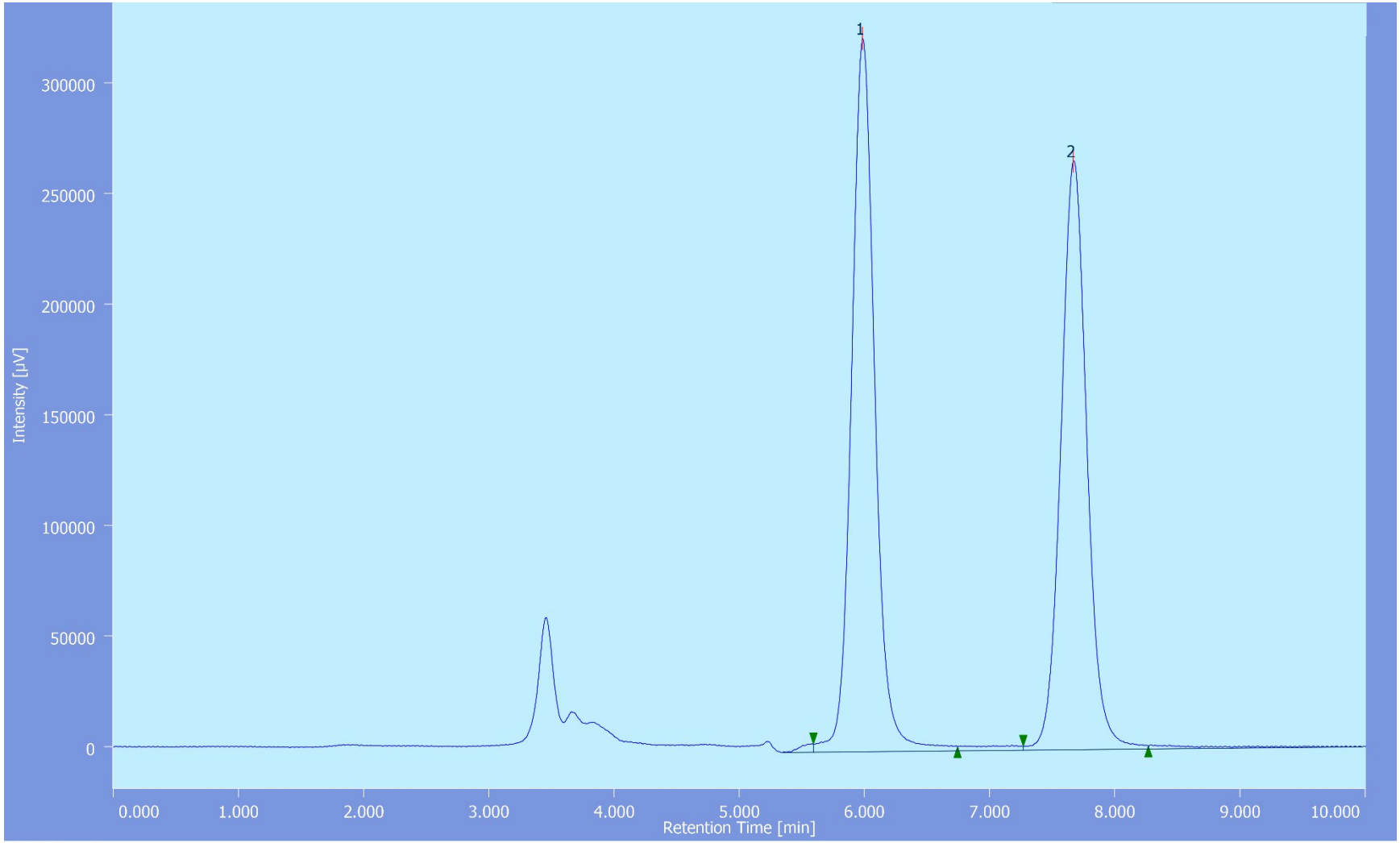
Figure S10. SFC trace of Racemic Boc-Pro-BINOL without light, heated to 100° C. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	6.017	1536080	95610	52.760	50.724	N/A	3862	4.620	N/A	
2	Unknown	1	7.742	1375361	92880	47.240	49.276	N/A	7335	N/A	0.994	

Figure S11. SFC trace of Racemic BINOL and Boc-Pro-OH after irradiation. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
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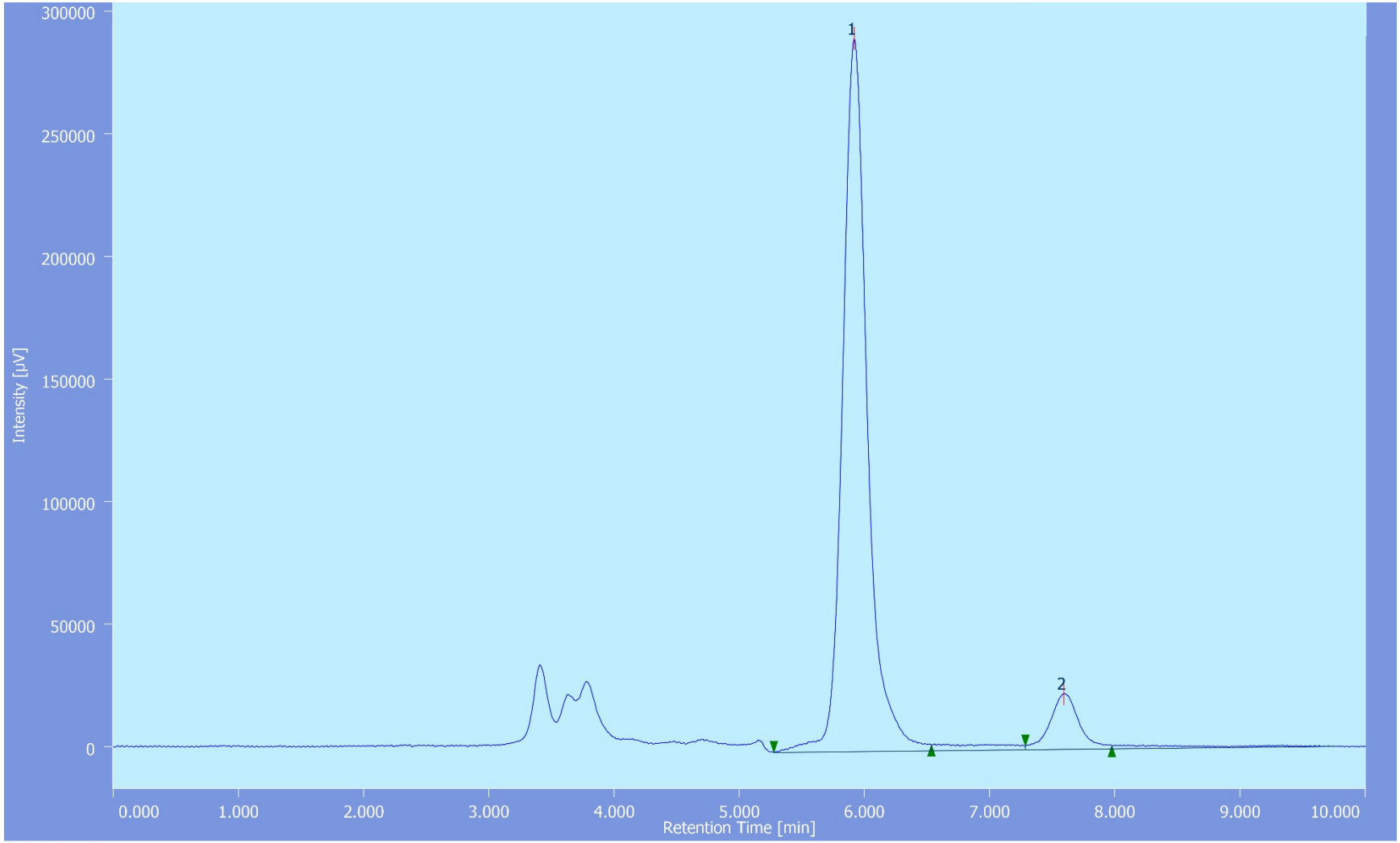
2	Unknown	1	7.667	3840735	266039	47.845	45.216	N/A	6981	N/A	1.081	

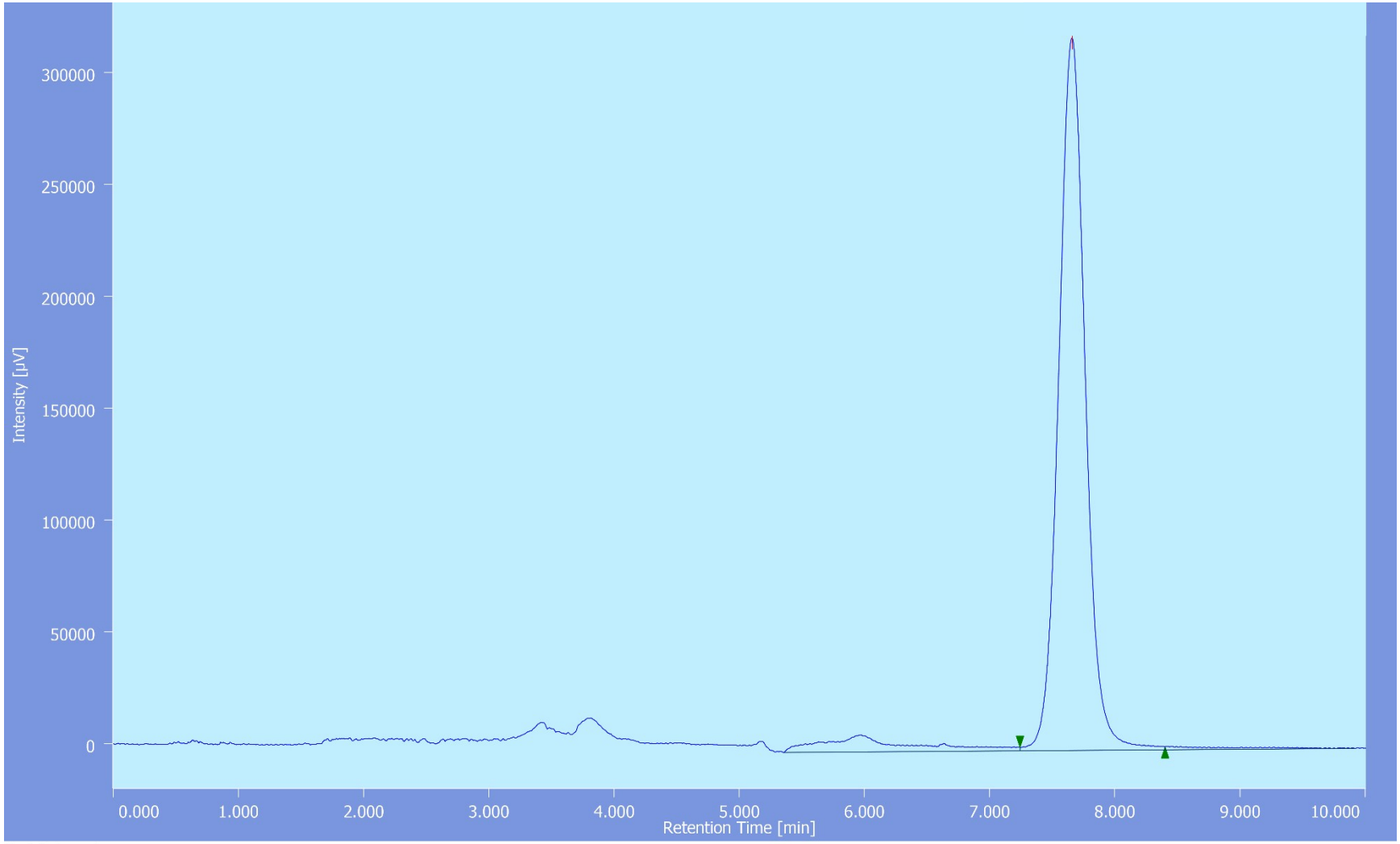
Figure S12. SFC trace of Racemic Boc-Pro-BINOL after cleavage reaction. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	5.917	3992560	290927	91.661	92.702	N/A	5055	4.665	1.277	
2	Unknown	1	7.592	363247	22903	8.339	7.298	N/A	6150	N/A	N/A	

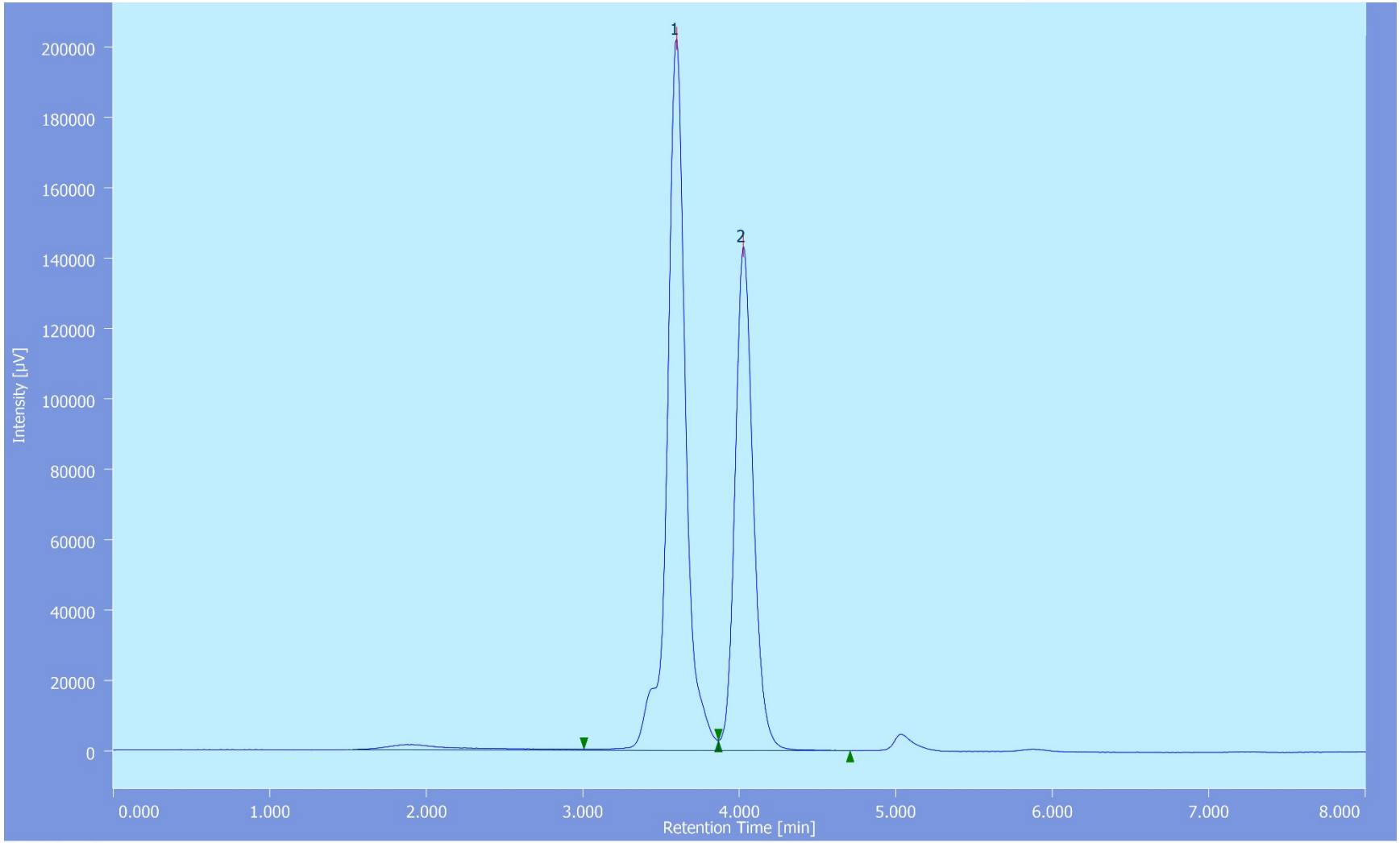
Figure S13. SFC trace of Boc-Pro-(R)-BINOL after cleavage reaction. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	7.658	4700304	318484	100.000	100.000	N/A	6649	N/A	1.047	

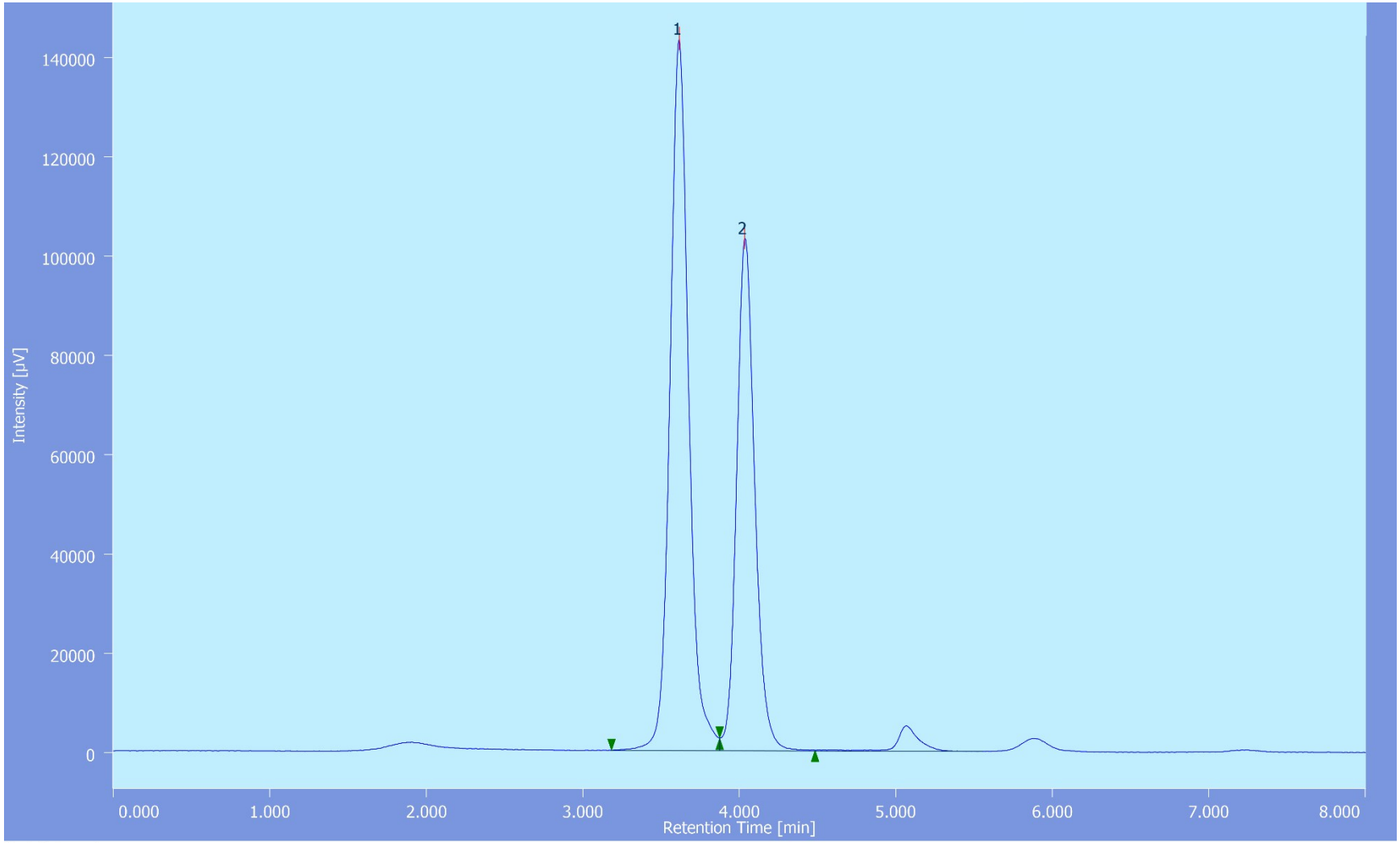
Figure S14. SFC trace of Boc-Pro-(S)-BINOL after cleavage reaction. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.600	1667998	202145	59.110	58.512	N/A	5735	2.151	0.942	
2	Unknown	1	4.025	1153873	143332	40.890	41.488	N/A	6103	N/A	1.178	

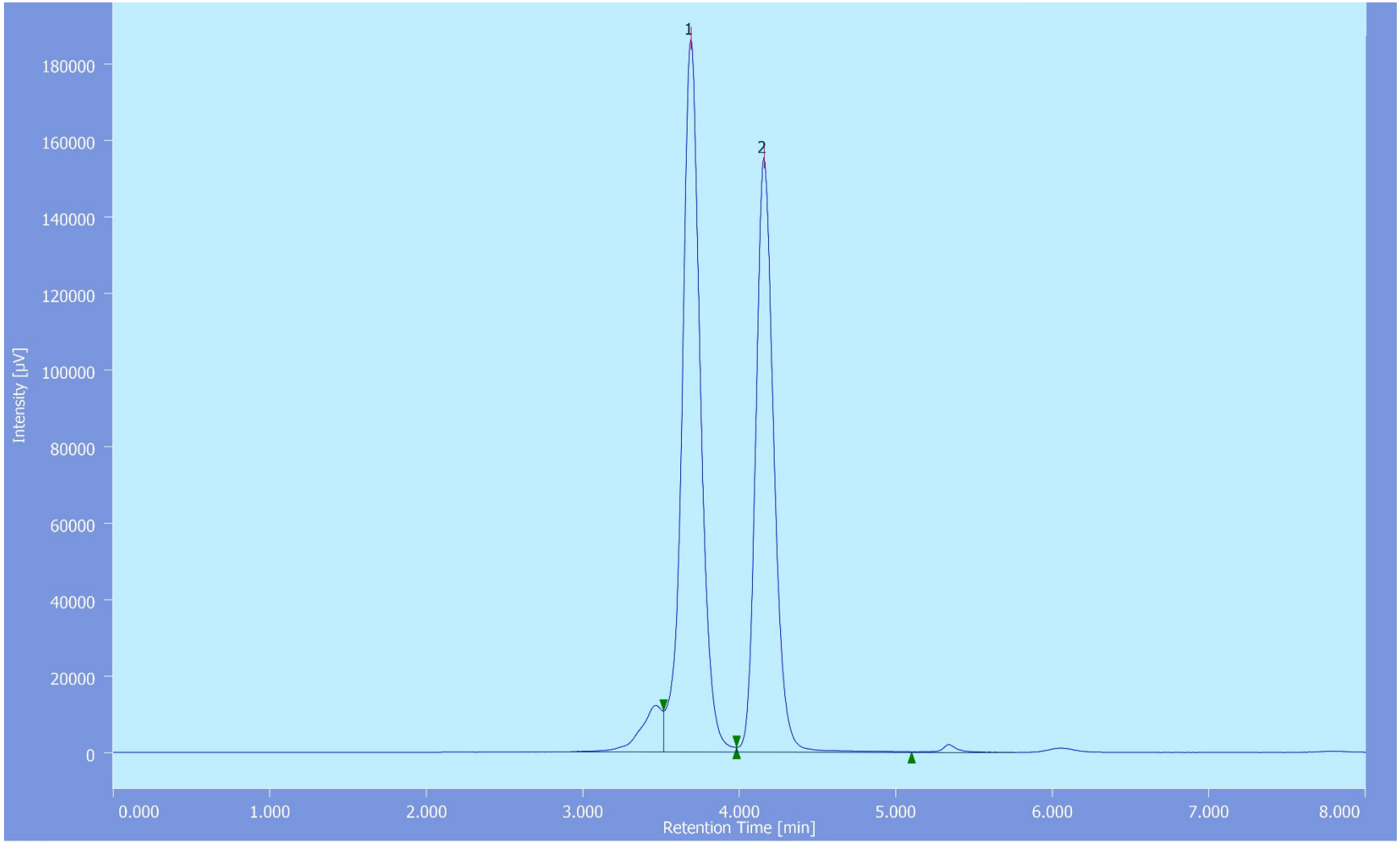
Figure S15. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in CH_2Cl_2 (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.617	1188398	143416	58.809	58.130	N/A	4847	2.026	1.115	
2	Unknown	1	4.033	832391	103302	41.191	41.870	N/A	6218	N/A	1.192	

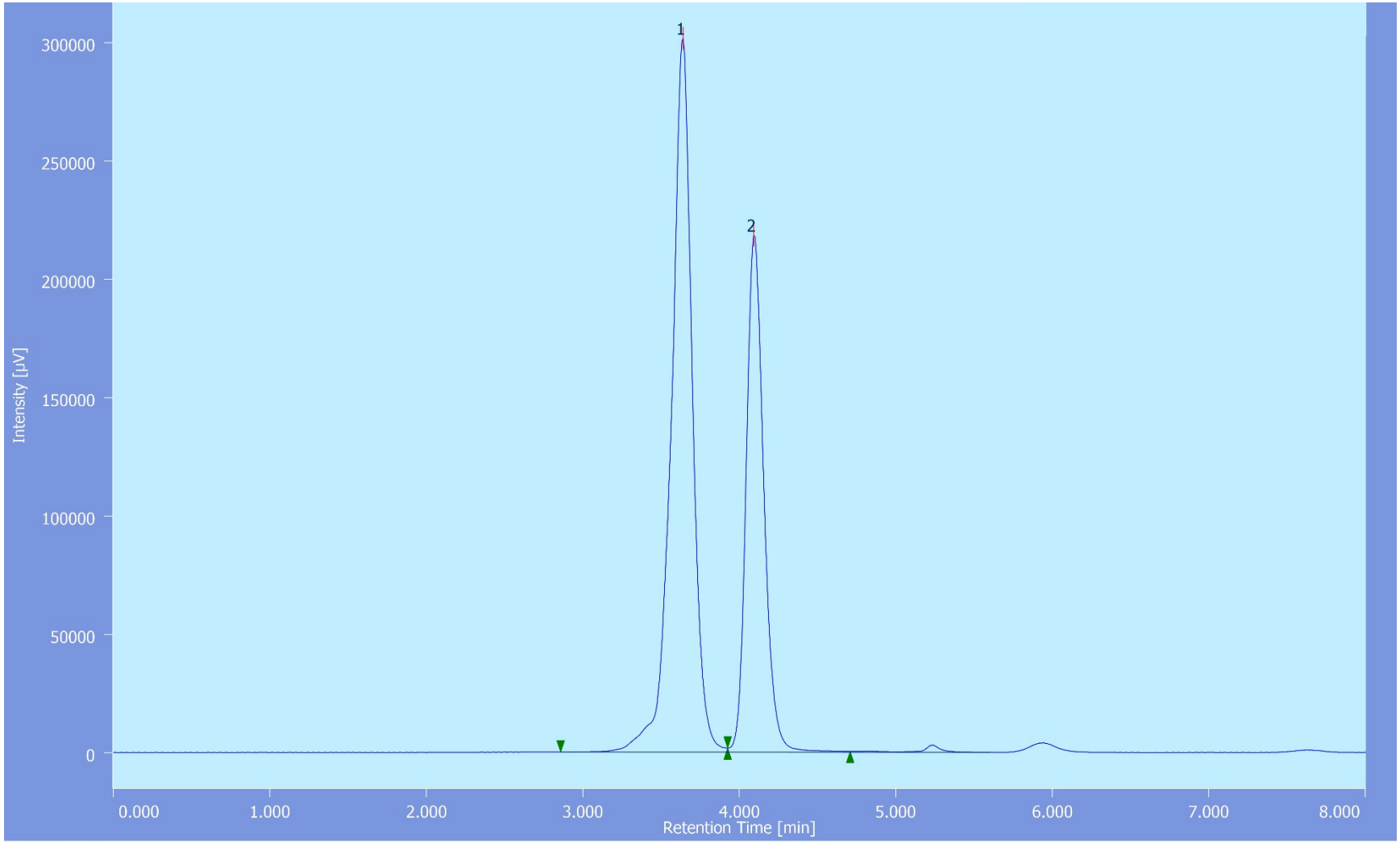
Figure S16. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in CH_2Cl_2 (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.692	1529784	186389	55.032	54.512	N/A	5386	2.303	N/A	
2	Unknown	1	4.158	1250003	155536	44.968	45.488	N/A	6573	N/A	1.188	

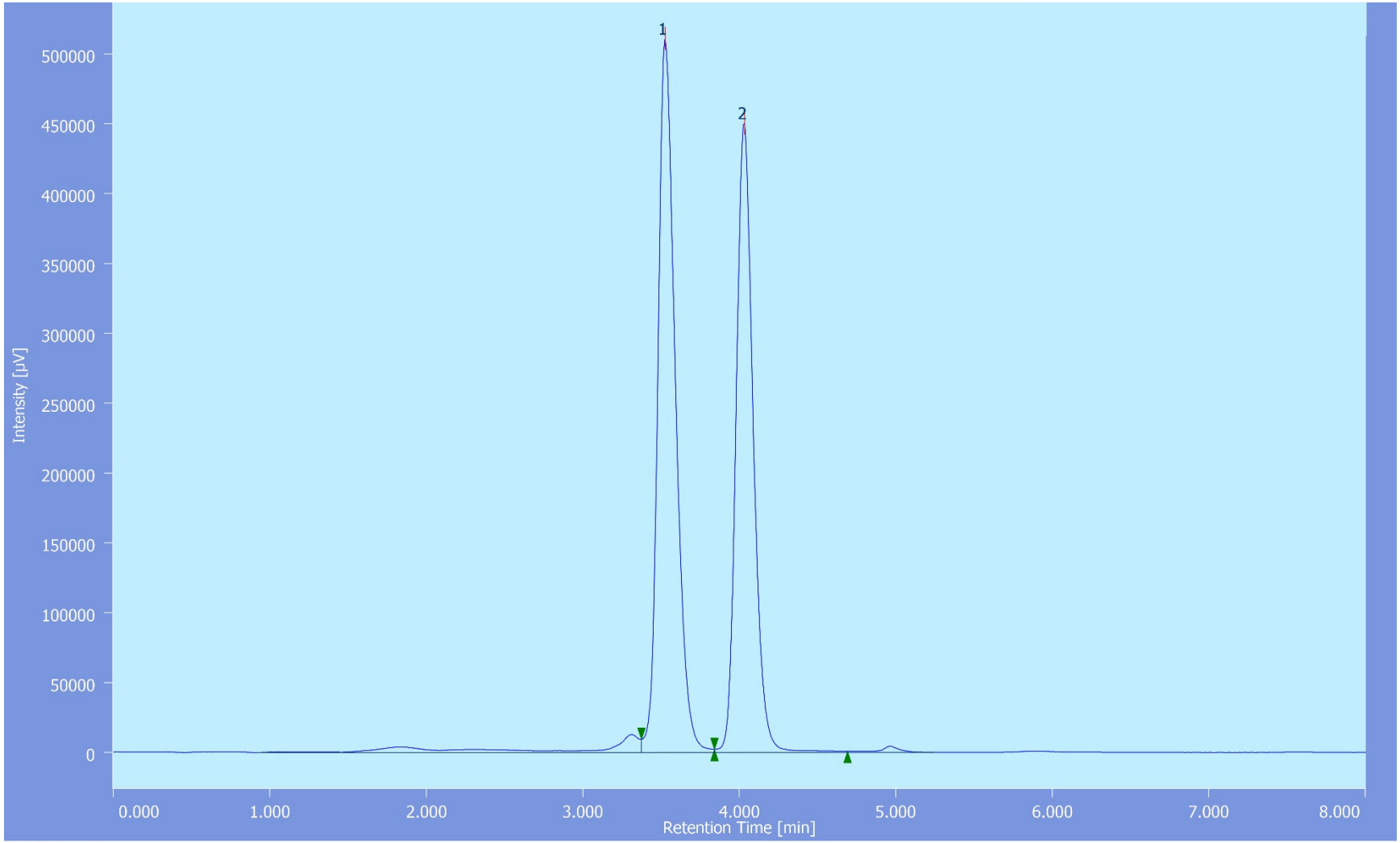
Figure S17. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in hexanes (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.642	2816517	301452	62.205	57.996	N/A	4285	2.135	0.918	
2	Unknown	1	4.092	1711317	218332	37.795	42.004	N/A	6687	N/A	1.241	

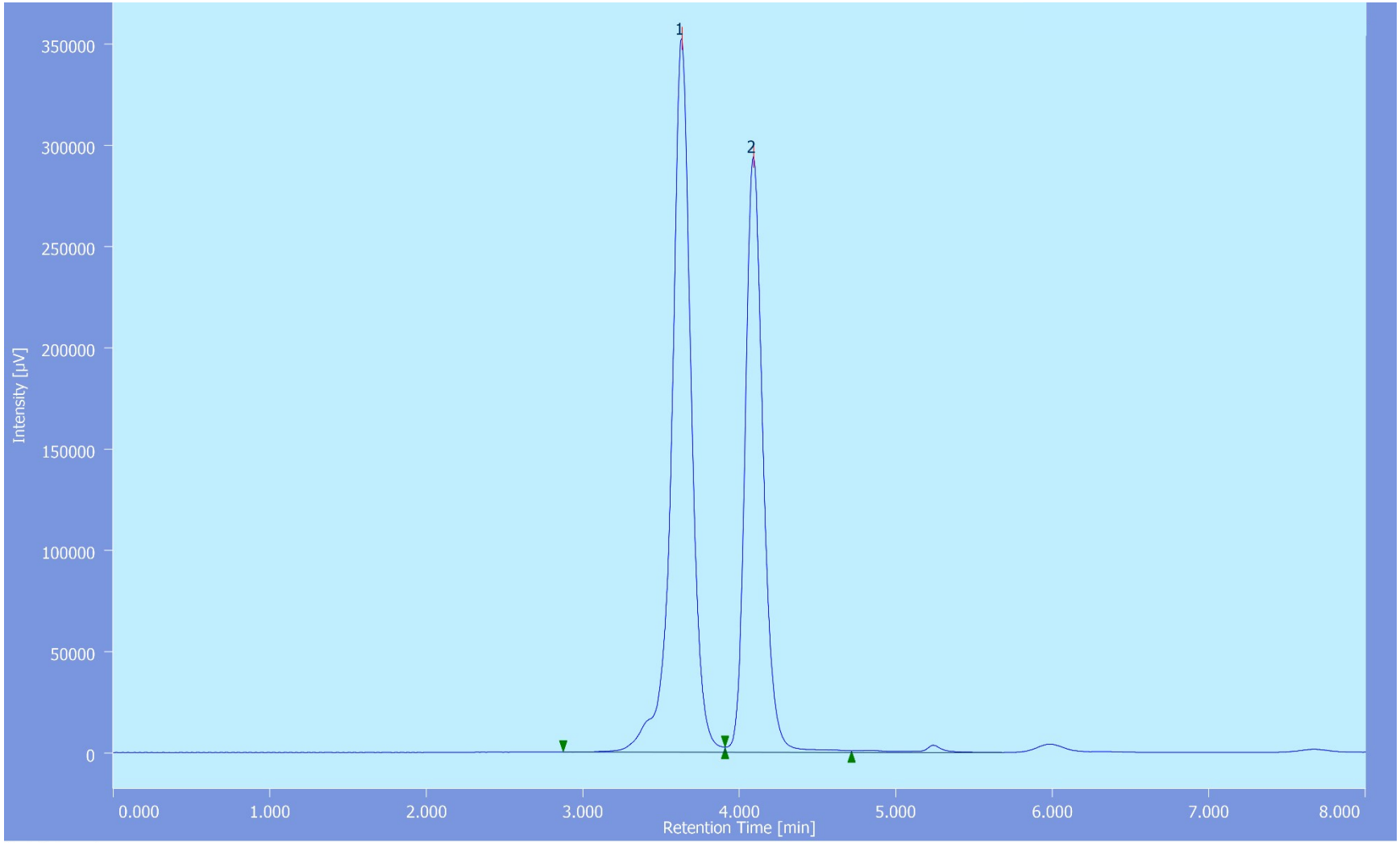
Figure S18. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in hexanes (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.525	3956897	510983	53.600	53.143	N/A	5052	2.594	1.297	
2	Unknown	1	4.033	3425355	450532	46.400	46.857	N/A	6876	N/A	1.157	

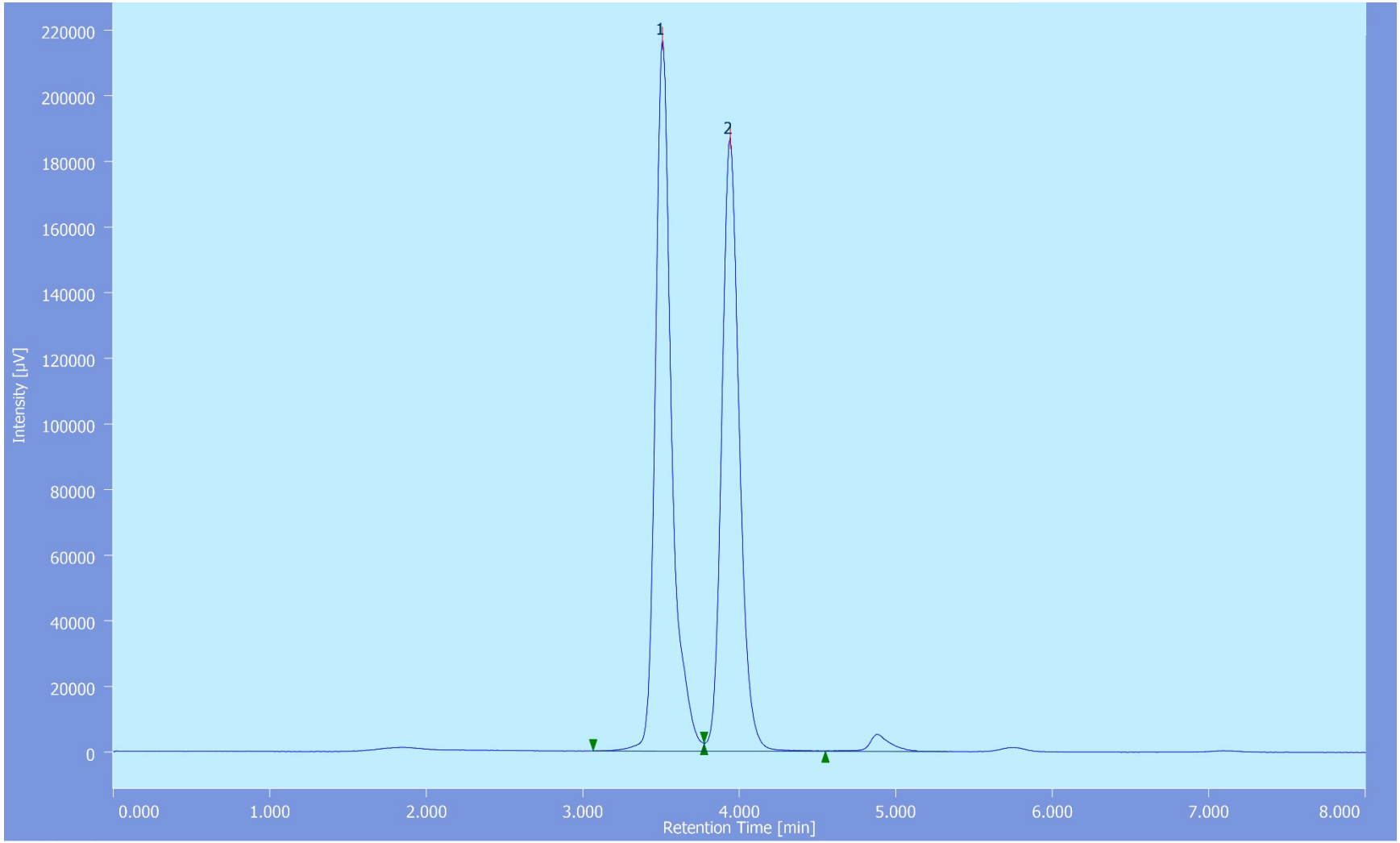
Figure S19. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in MeCN (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.633	3068539	352236	56.659	54.500	N/A	4981	2.254	0.918	
2	Unknown	1	4.092	2347294	294063	43.341	45.500	N/A	6579	N/A	1.176	

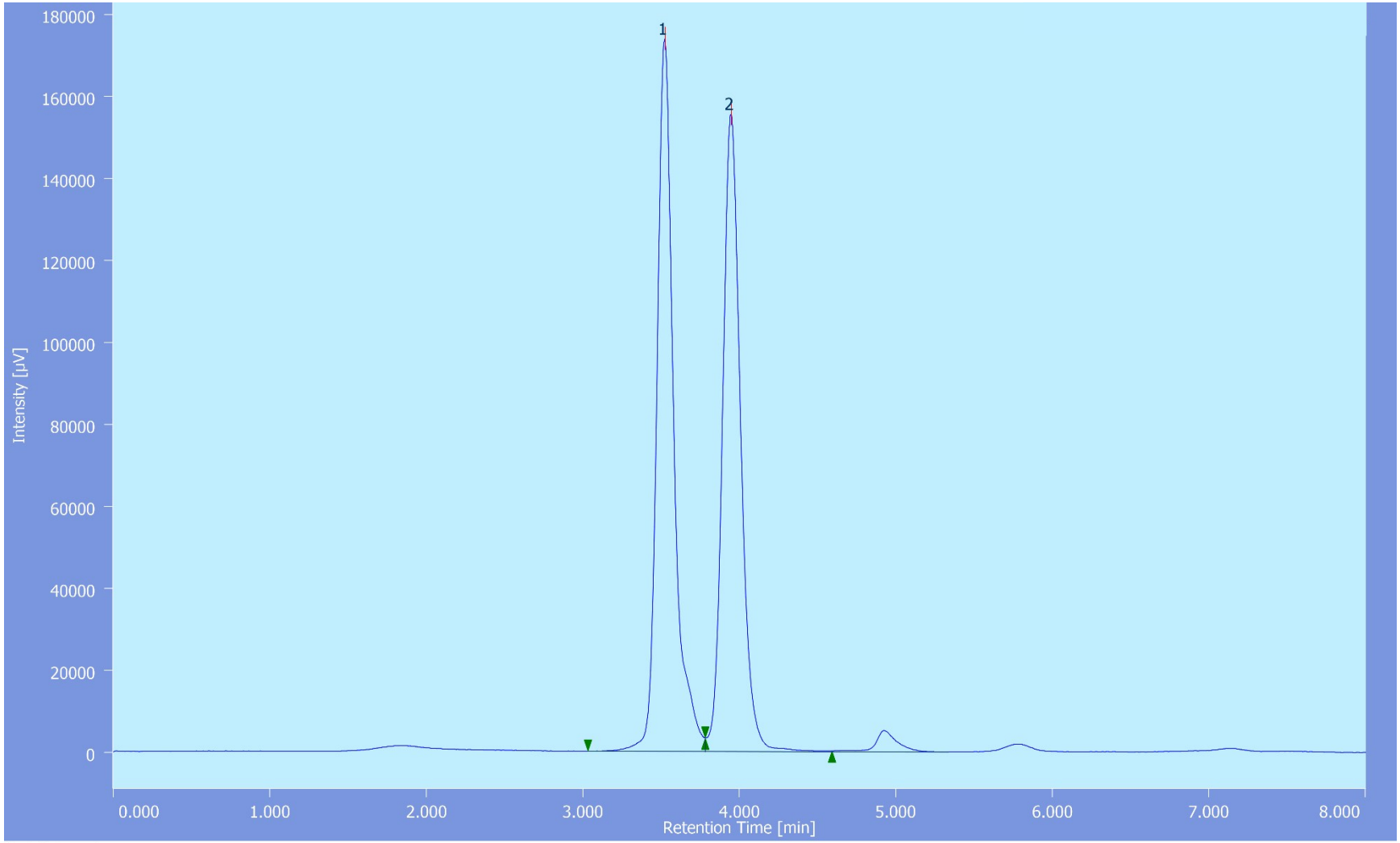
Figure S20. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in MeCN (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.508	1572256	217110	51.949	53.739	N/A	6629	2.339	1.421	
2	Unknown	1	3.942	1454269	186896	48.051	46.261	N/A	6266	N/A	1.158	

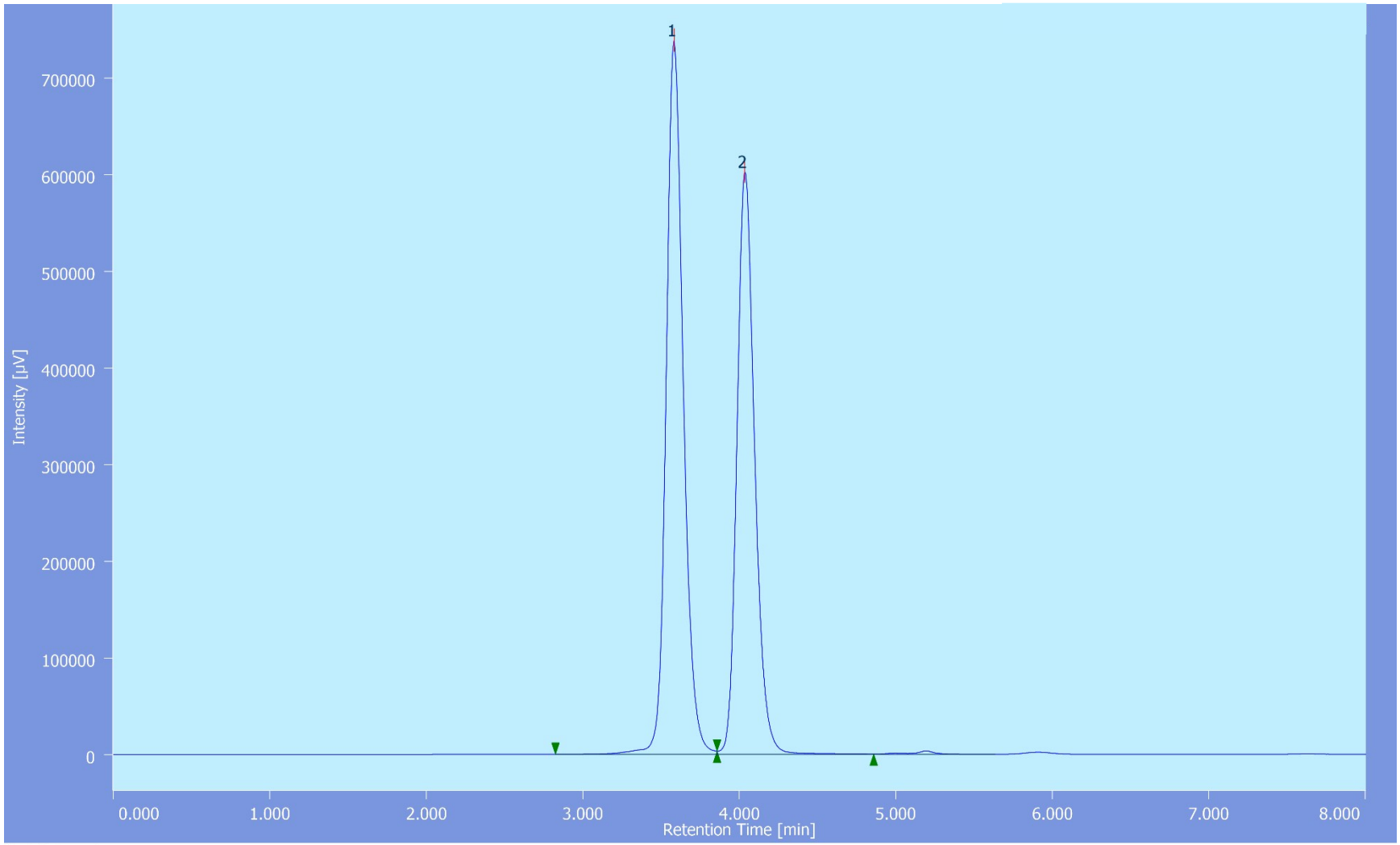
Figure S21. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in MeOH (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.525	1295656	173860	51.075	52.776	N/A	6215	2.237	1.369	
2	Unknown	1	3.950	1241091	155568	48.925	47.224	N/A	6110	N/A	1.130	

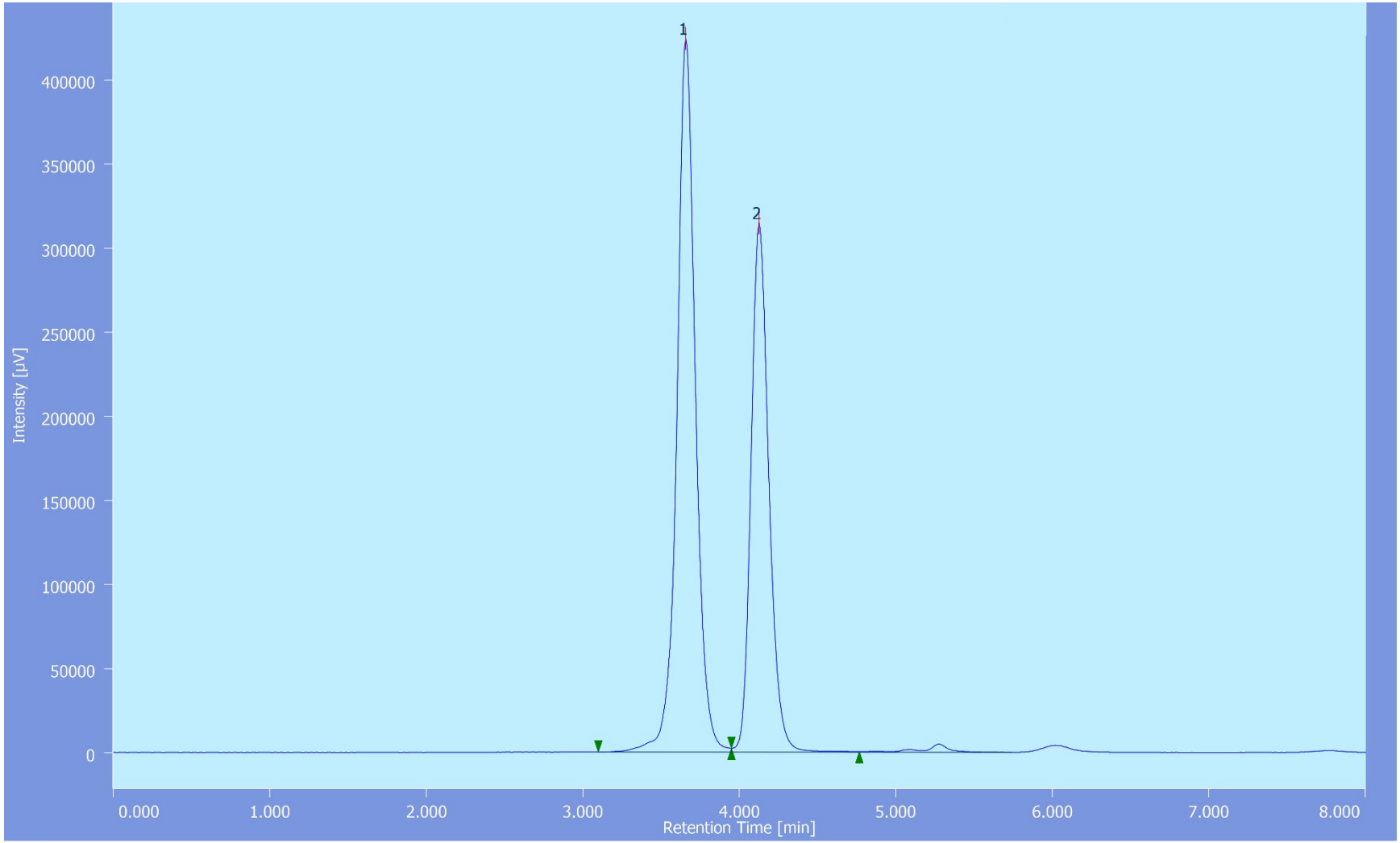
Figure S22. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in MeOH (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.583	5608754	738748	54.169	55.062	N/A	5545	2.291	1.176	
2	Unknown	1	4.033	4745395	602921	45.831	44.938	N/A	6416	N/A	1.237	

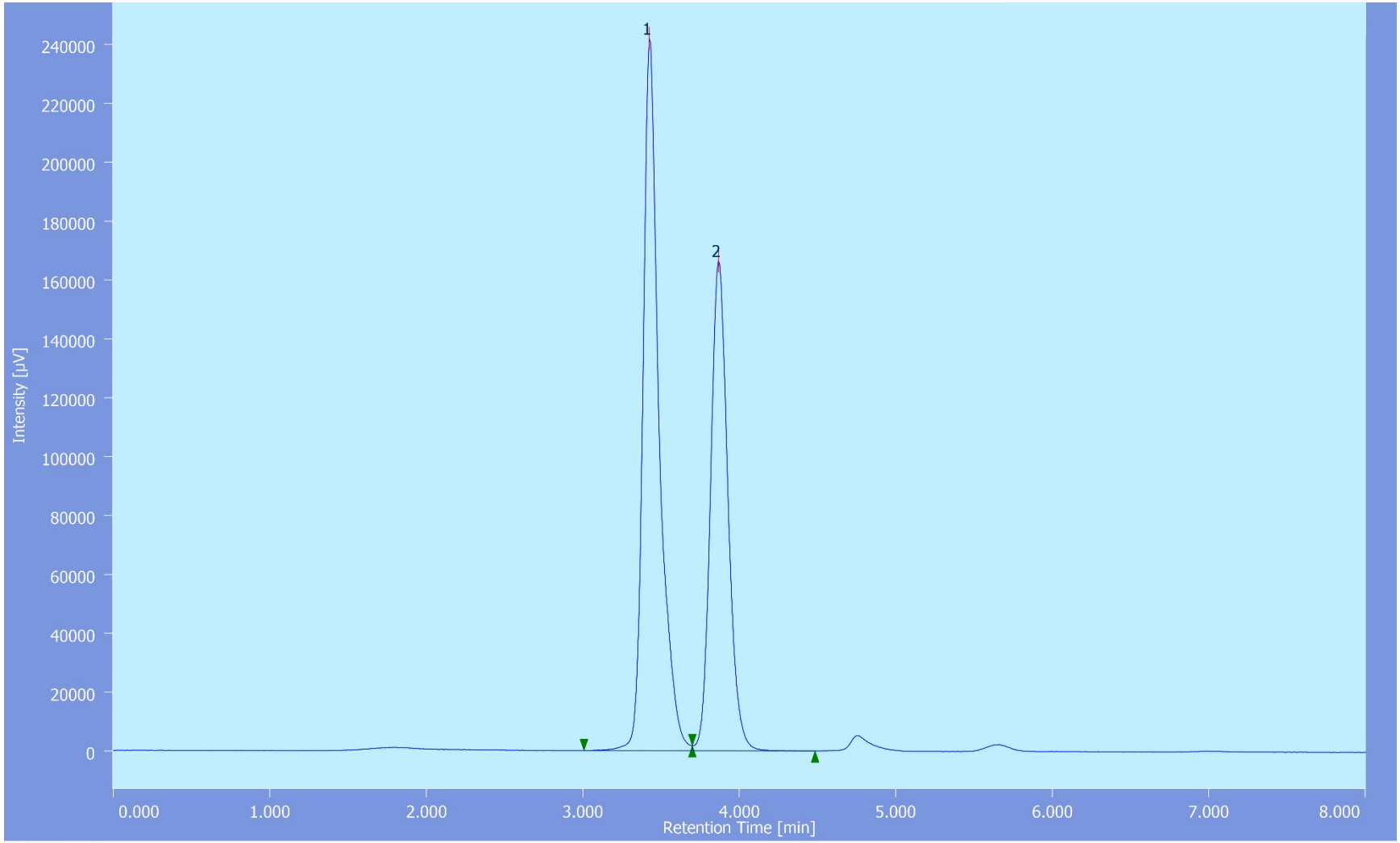
Figure S23. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in mesitylene (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.658	3486687	424309	58.344	57.415	N/A	5346	2.321	1.035	
2	Unknown	1	4.125	2489423	314706	41.656	42.585	N/A	6600	N/A	1.220	

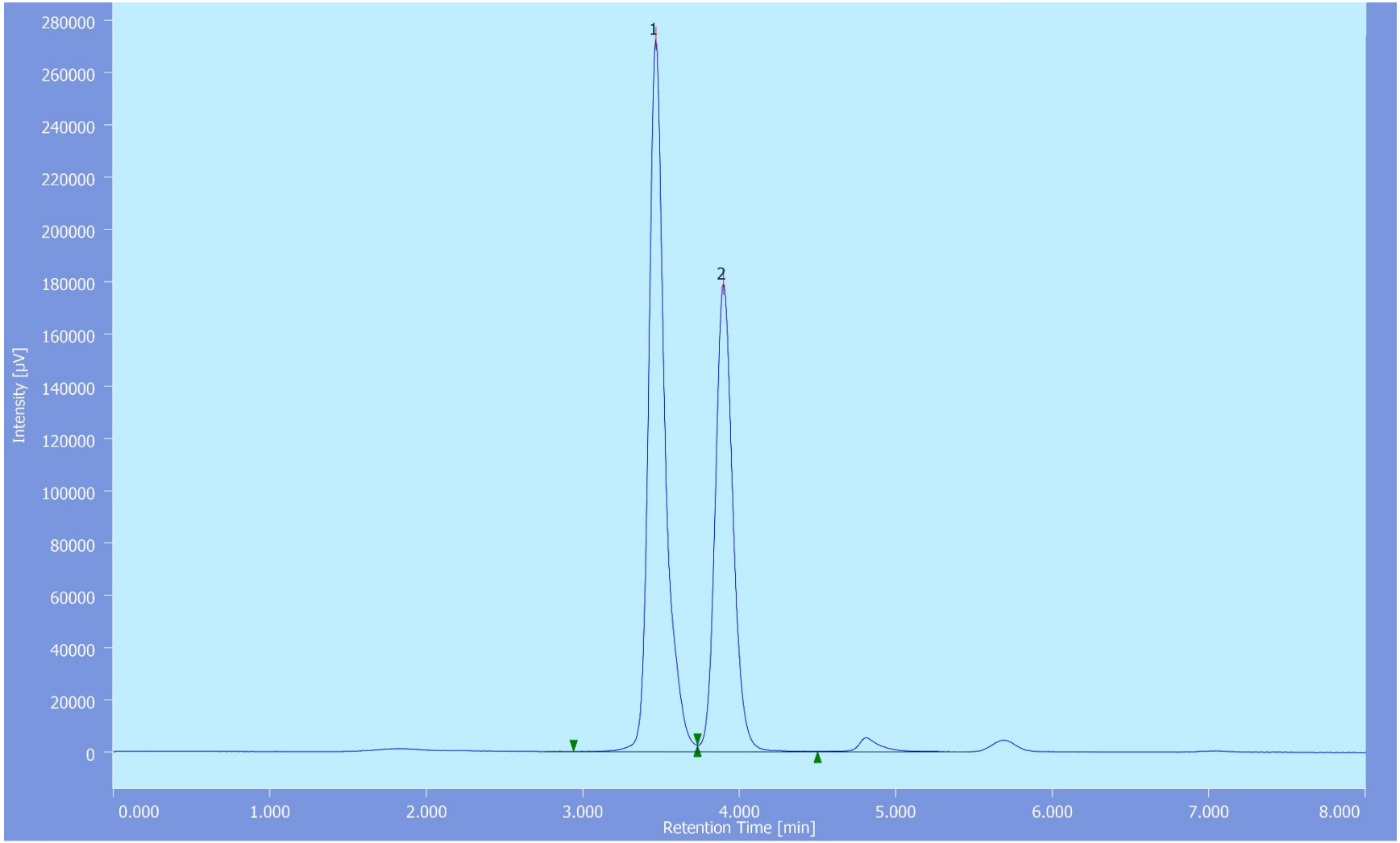
Figure S24. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in mesitylene (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.425	1736068	241950	57.465	59.240	N/A	6641	2.415	1.453	
2	Unknown	1	3.867	1285012	166472	42.535	40.760	N/A	6068	N/A	1.167	

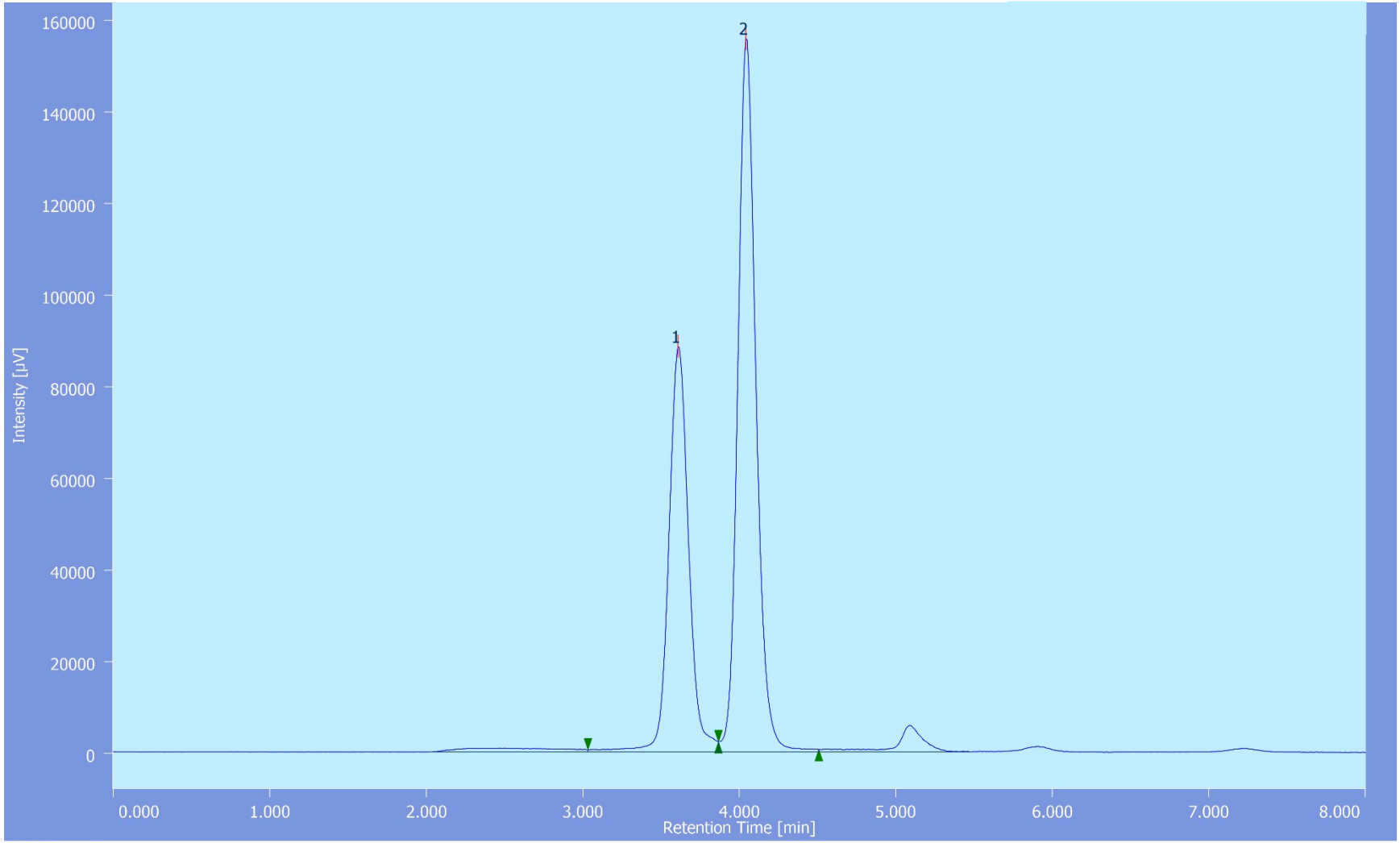
Figure S25. SFC trace of racemic Boc-Pro-BINOL after 20 minutes of irradiation in THF (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.467	1966511	272817	58.331	60.347	N/A	6562	2.337	1.377	
2	Unknown	1	3.900	1404794	179267	41.669	39.653	N/A	6045	N/A	1.151	

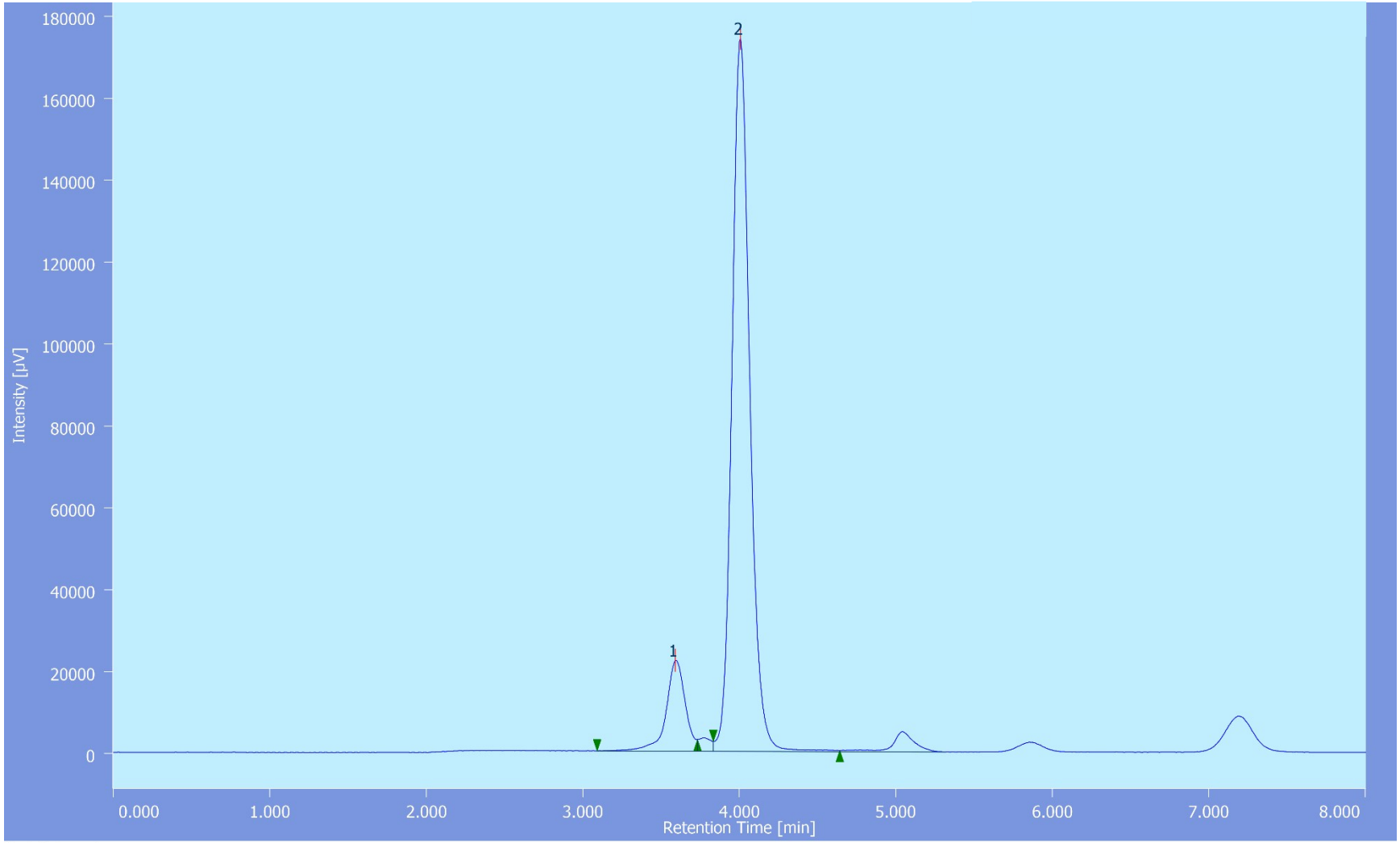
Figure S26. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation in THF (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.608	779084	88536	38.350	36.251	N/A	4271	2.044	1.126	
2	Unknown	1	4.042	1252413	155696	61.650	63.749	N/A	6267	N/A	1.182	

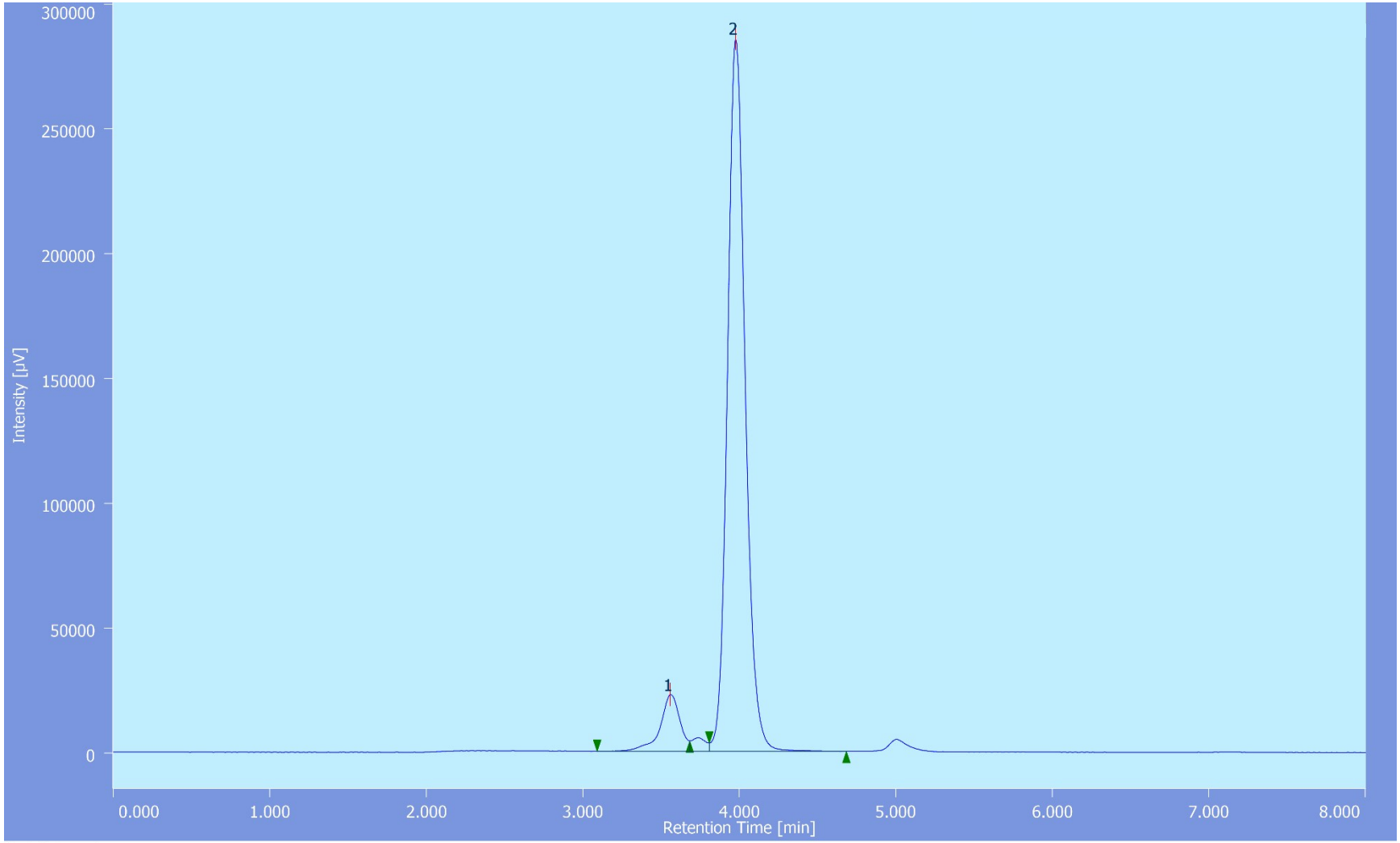
Figure S27. SFC trace of Boc-Pro-(S)-BINOL after 60 minutes of irradiation with diisopropylethylamine as base (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.592	188414	22215	12.031	11.320	N/A	4920	2.055	N/A	
2	Unknown	1	4.008	1377619	174019	87.969	88.680	N/A	6311	N/A	1.127	

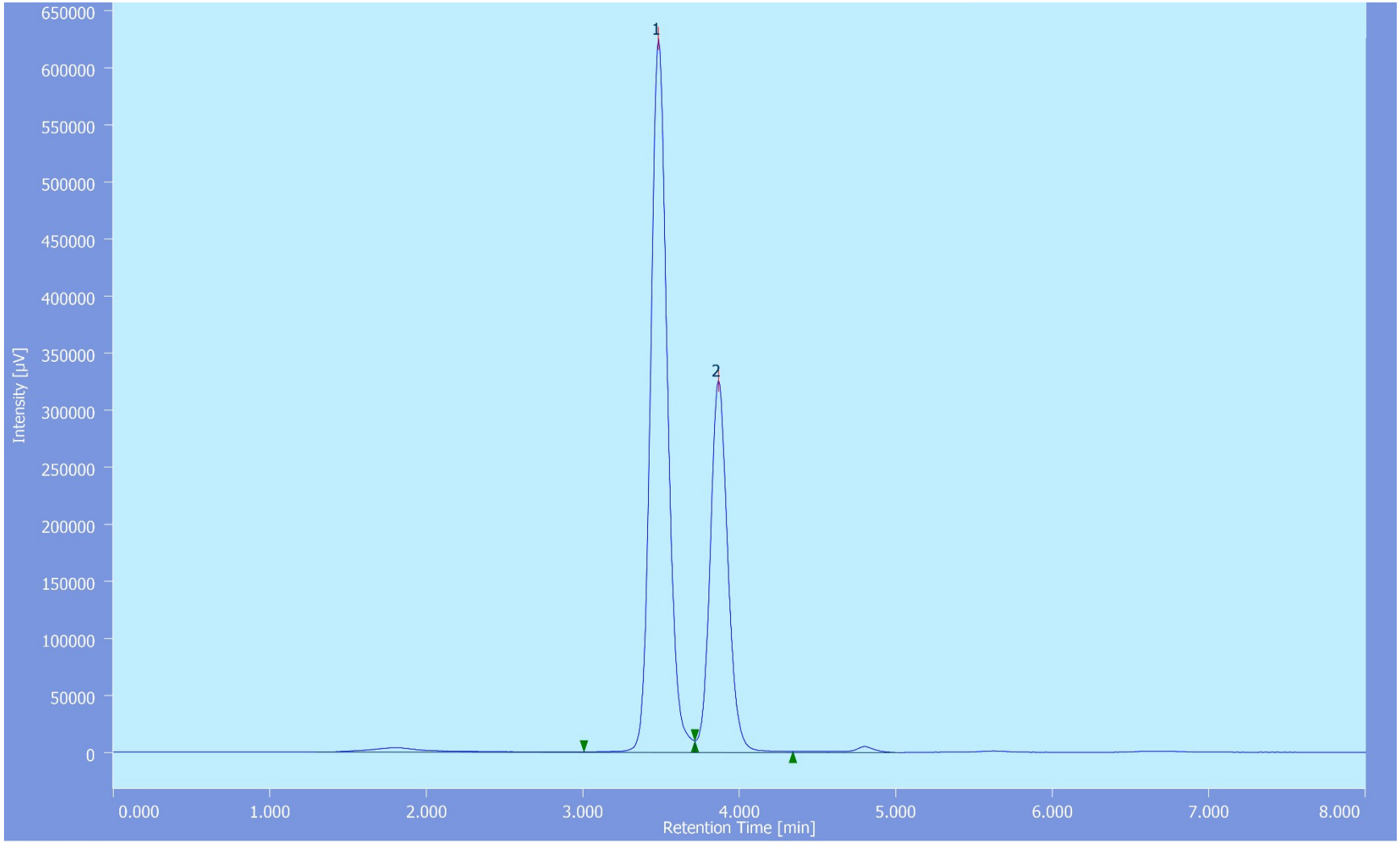
Figure S28. SFC trace of Boc-Pro-(S)-BINOL after 60 minutes of irradiation with isopropylamine as base (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.558	201072	22756	8.245	7.383	N/A	4590	2.032	N/A	
2	Unknown	1	3.975	2237641	285483	91.755	92.617	N/A	6257	N/A	1.166	

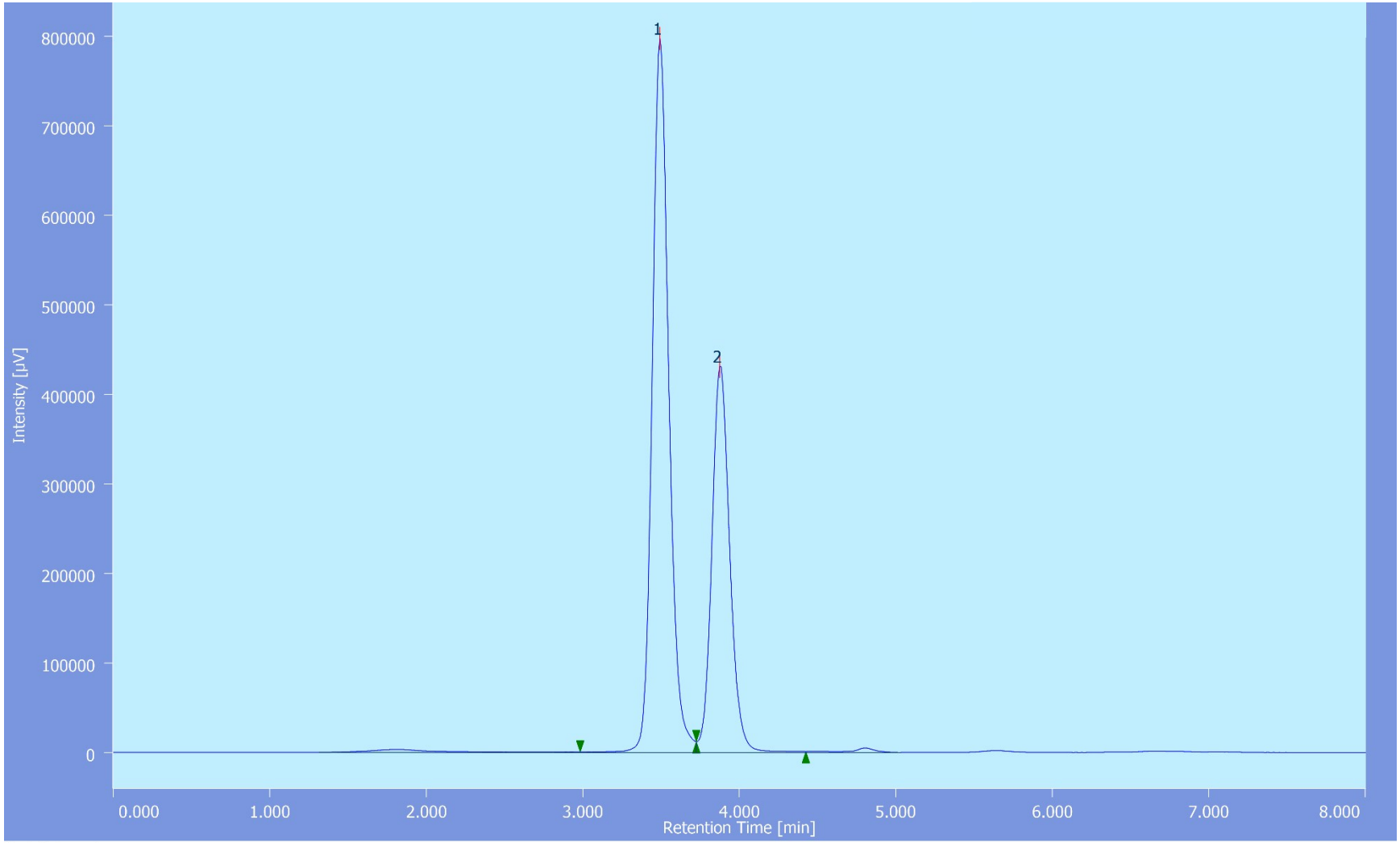
Figure S29. SFC trace of Boc-Pro-(S)-BINOL after 60 minutes of photodynamic resolution with pyridine as base (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.483	4702334	625544	64.768	65.736	N/A	5264	1.960	1.144	
2	Unknown	1	3.867	2557925	326050	35.232	34.264	N/A	5969	N/A	1.111	

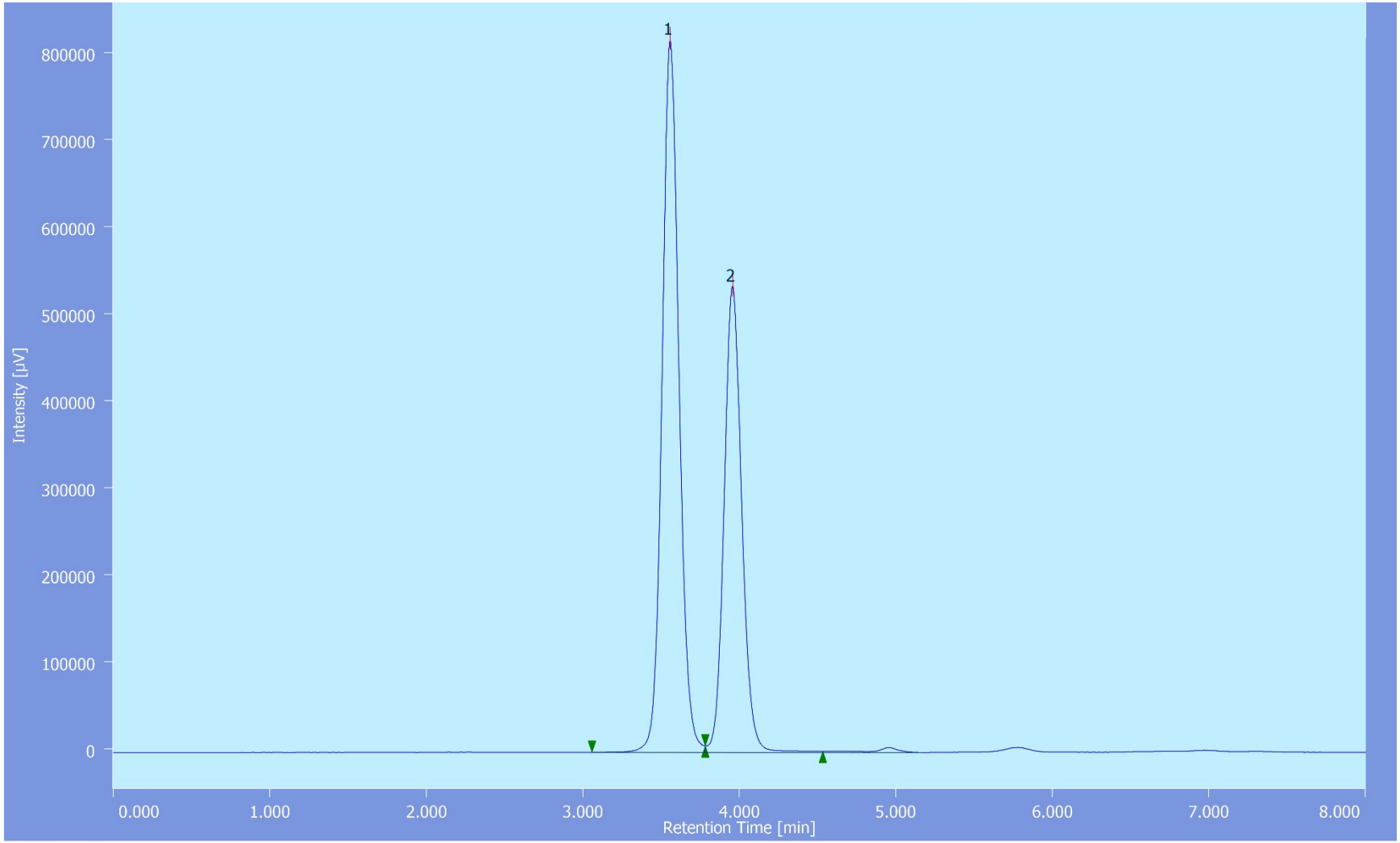
Figure S30. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation with a 20:1 v:v ratio of toluene to triethylamine. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.492	5873249	797019	63.149	64.897	N/A	5563	1.971	1.185	
2	Unknown	1	3.875	3427338	431117	36.851	35.103	N/A	5850	N/A	1.151	

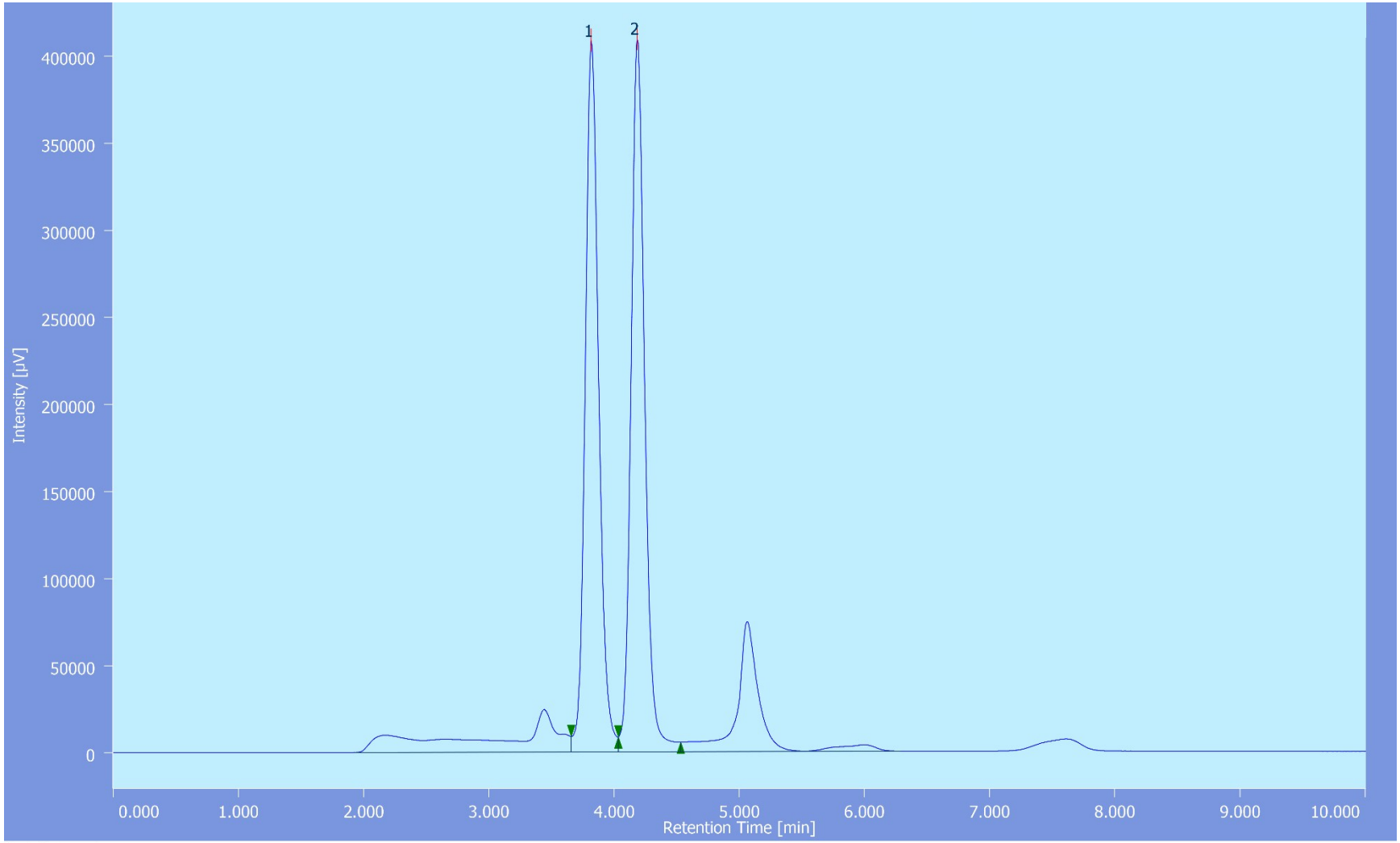
Figure S31. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation with a 40:1 v:v ratio of toluene to triethylamine. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.558	6131970	820115	59.413	60.437	N/A	5475	2.044	1.098	
2	Unknown	1	3.958	4188942	536861	40.587	39.563	N/A	6264	N/A	1.090	

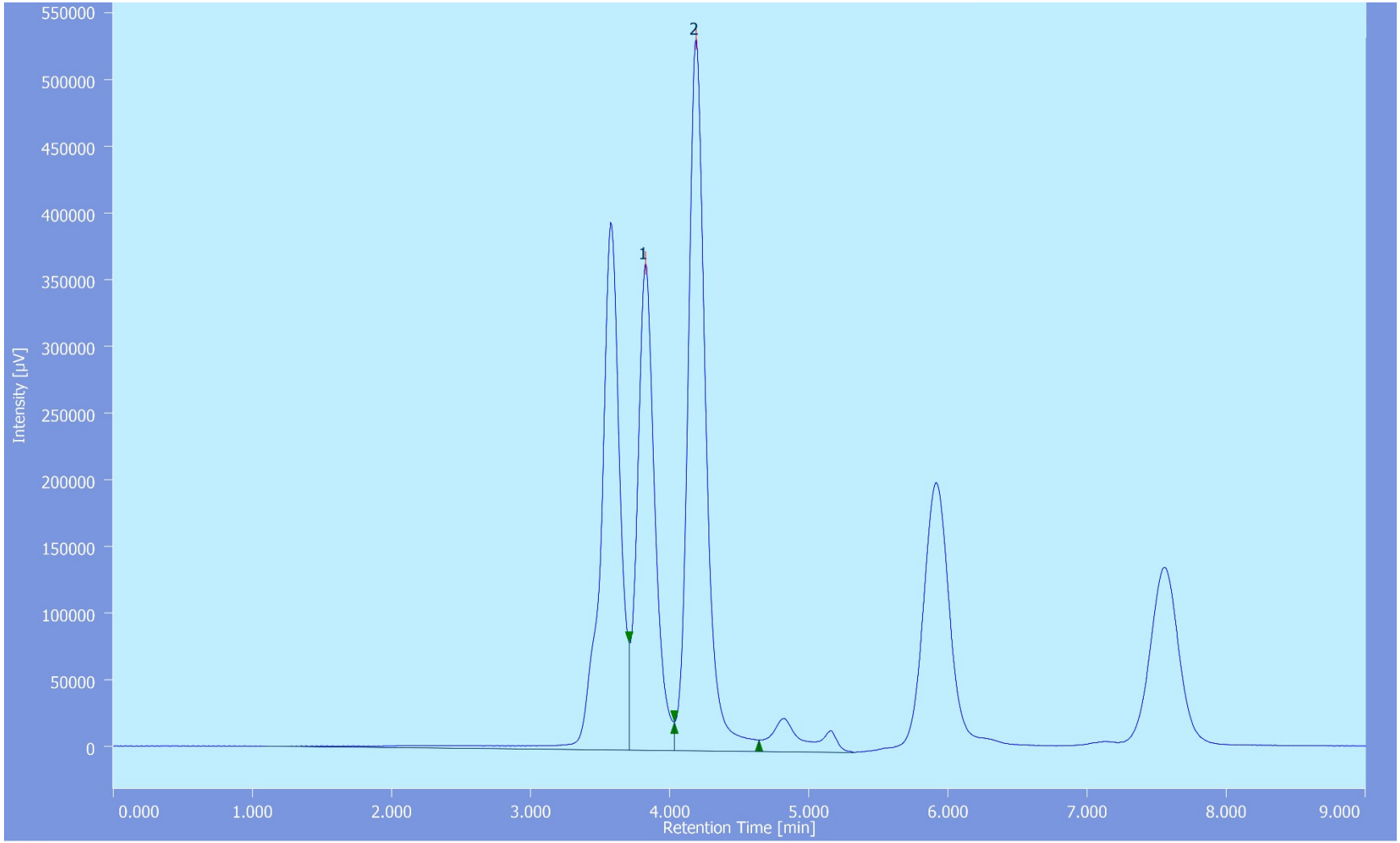
Figure S32. SFC trace of racemic Boc-Pro-BINOL after 60 minutes of irradiation with a 100:1 v:v ratio of toluene to triethylamine. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.817	3061152	408415	49.607	49.935	N/A	6401	1.925	1.197	
2	Unknown	1	4.183	3109602	409471	50.393	50.065	N/A	7661	N/A	1.185	

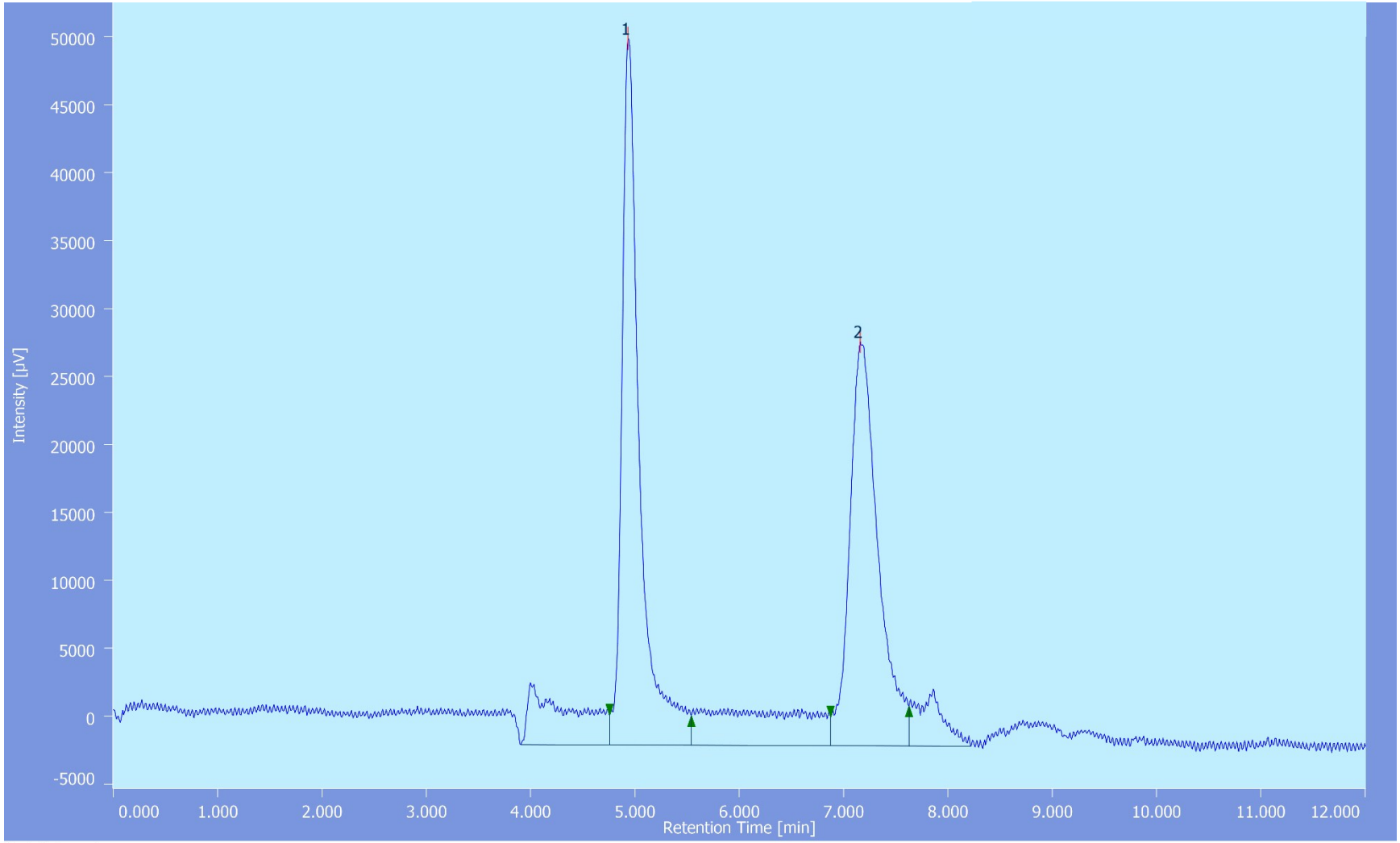
Figure S33. SFC trace of Racemic Boc-Ala-BINOL. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.825	3187168	365385	40.267	40.621	N/A	4891	1.696	N/A	
2	Unknown	1	4.192	4727960	534108	59.733	59.379	N/A	6090	N/A	1.175	

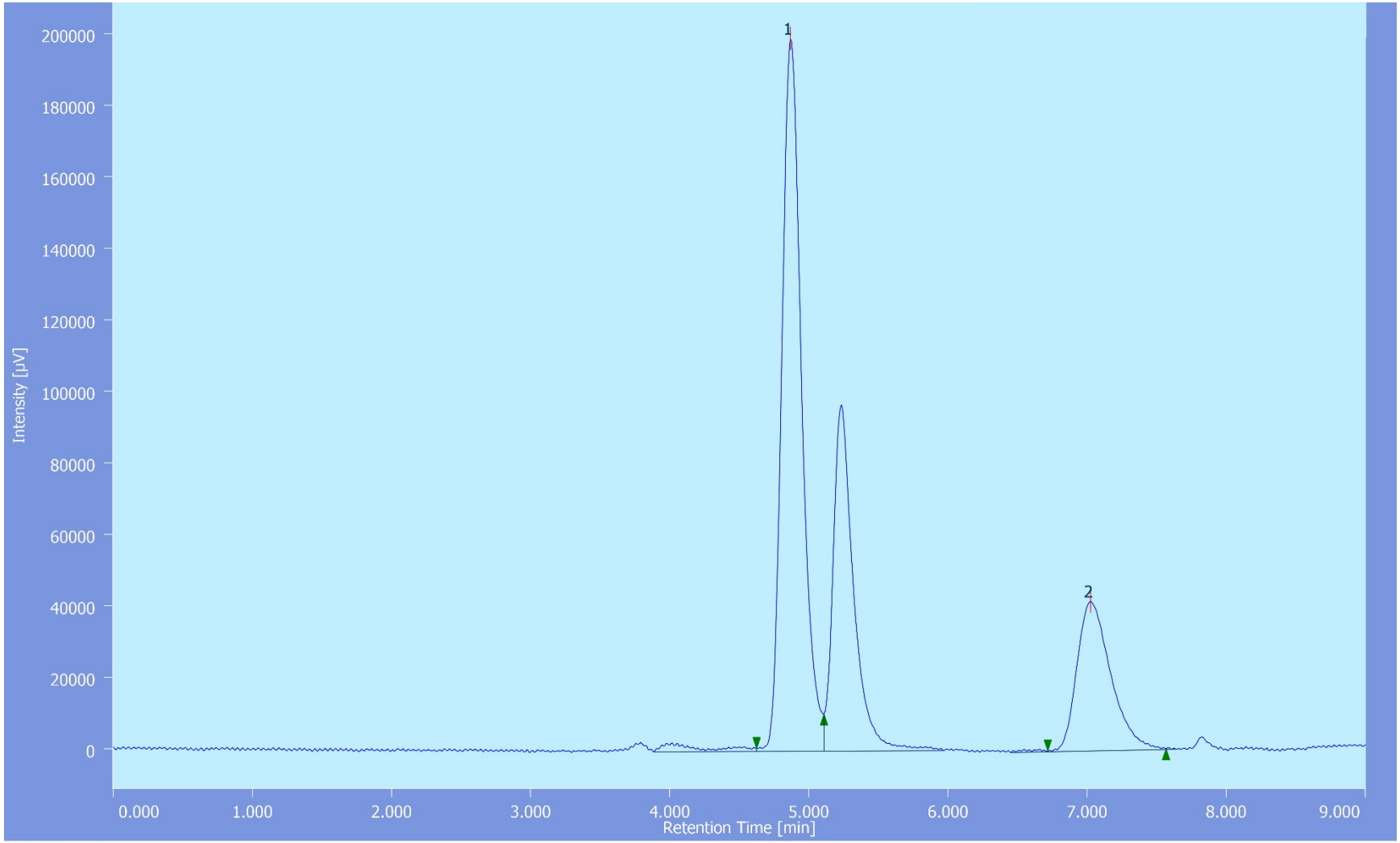
Figure S34. SFC trace of Boc-Ala-BINOL after irradiation. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	4.933	617340	51980	52.306	63.608	N/A	5761	6.190	2.613	
2	Unknown	1	7.158	562902	29740	47.694	36.392	N/A	3862	N/A	N/A	

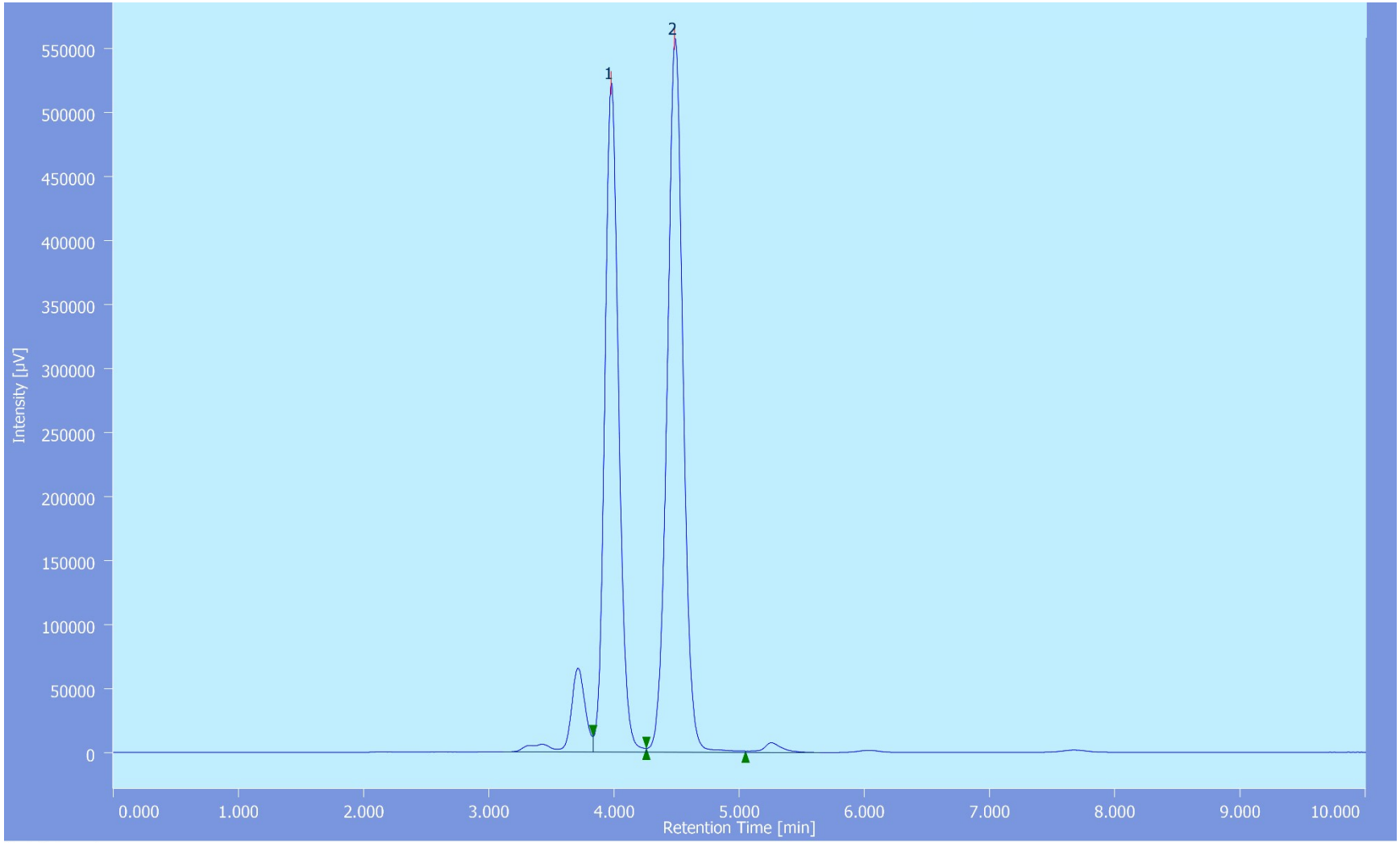
Figure S35. SFC trace of Racemic Boc-Phe-BINOL. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	4.867	1976114	199347	73.661	82.627	N/A	5813	6.254	N/A	
2	Unknown	1	7.025	706583	41915	26.339	17.373	N/A	4140	N/A	1.430	

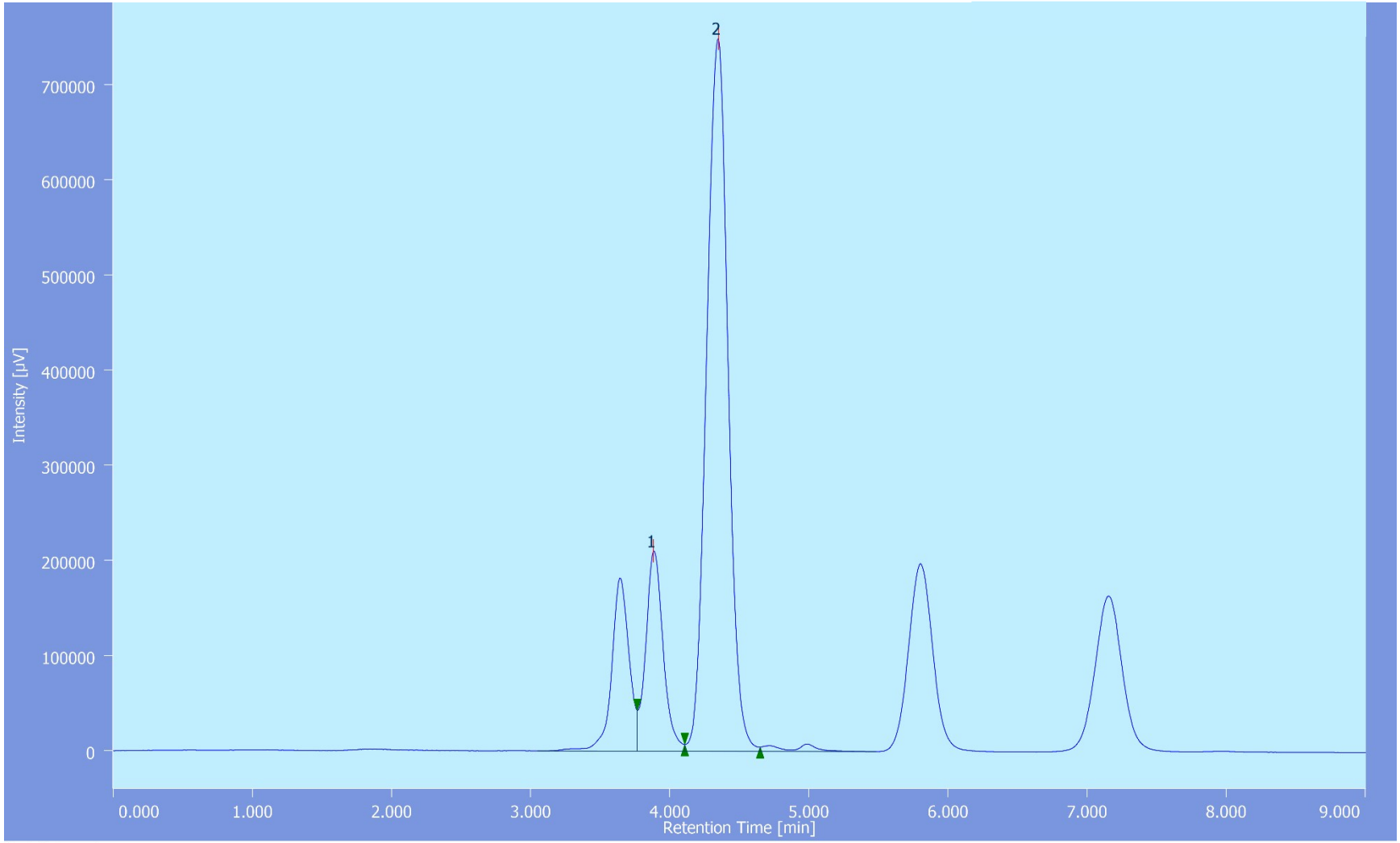
Figure S36. SFC trace of Boc-Phe-BINOL after irradiation. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.975	4017285	522629	44.985	48.391	N/A	6444	2.405	1.153	
2	Unknown	1	4.483	4913049	557393	55.015	51.609	N/A	6307	N/A	1.046	

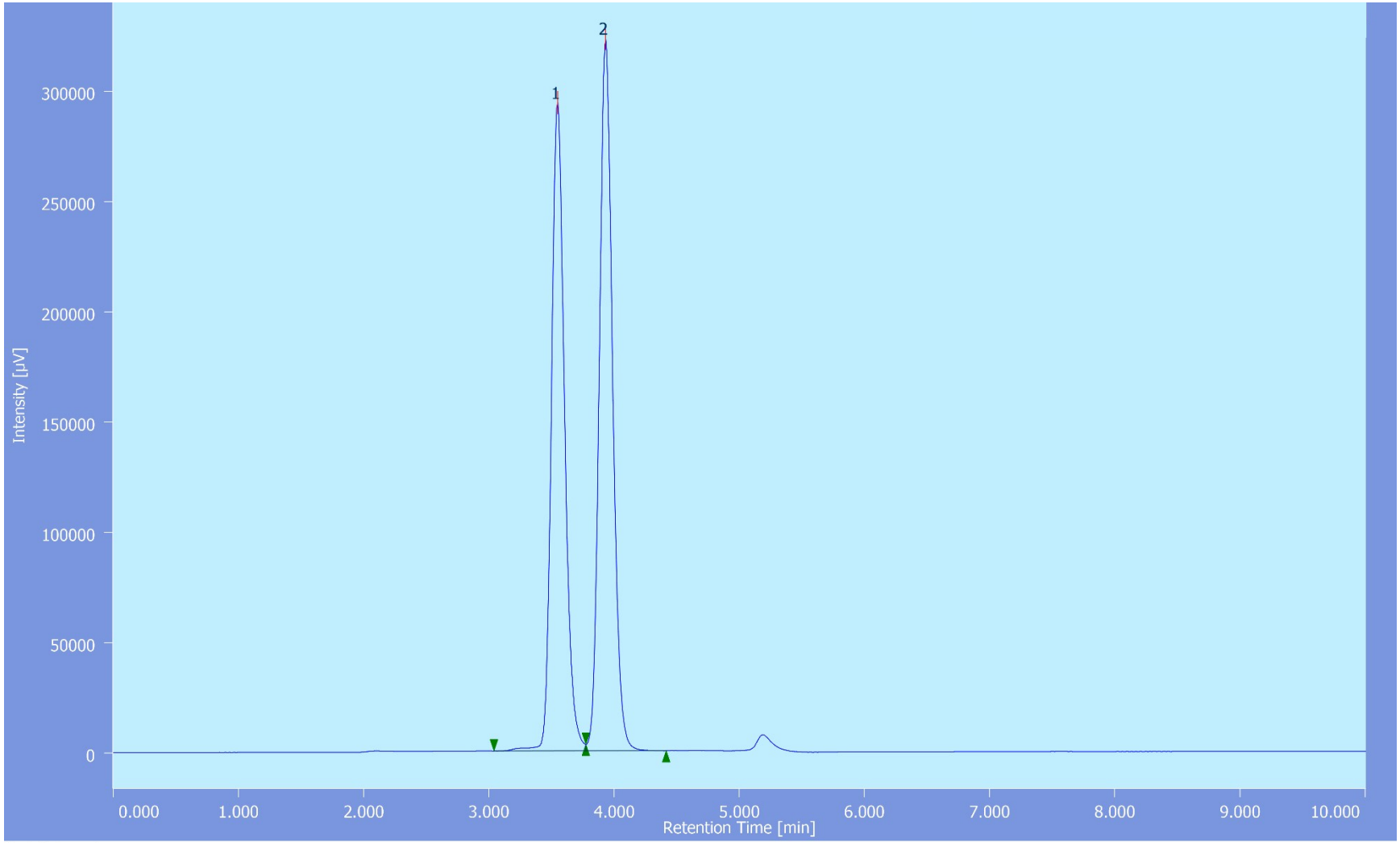
Figure S37. SFC trace of Racemic Boc-Phg-BINOL. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.883	1834150	210735	18.574	21.952	N/A	4949	1.850	N/A	
2	Unknown	1	4.350	8040530	749256	81.426	78.048	N/A	3724	N/A	1.002	

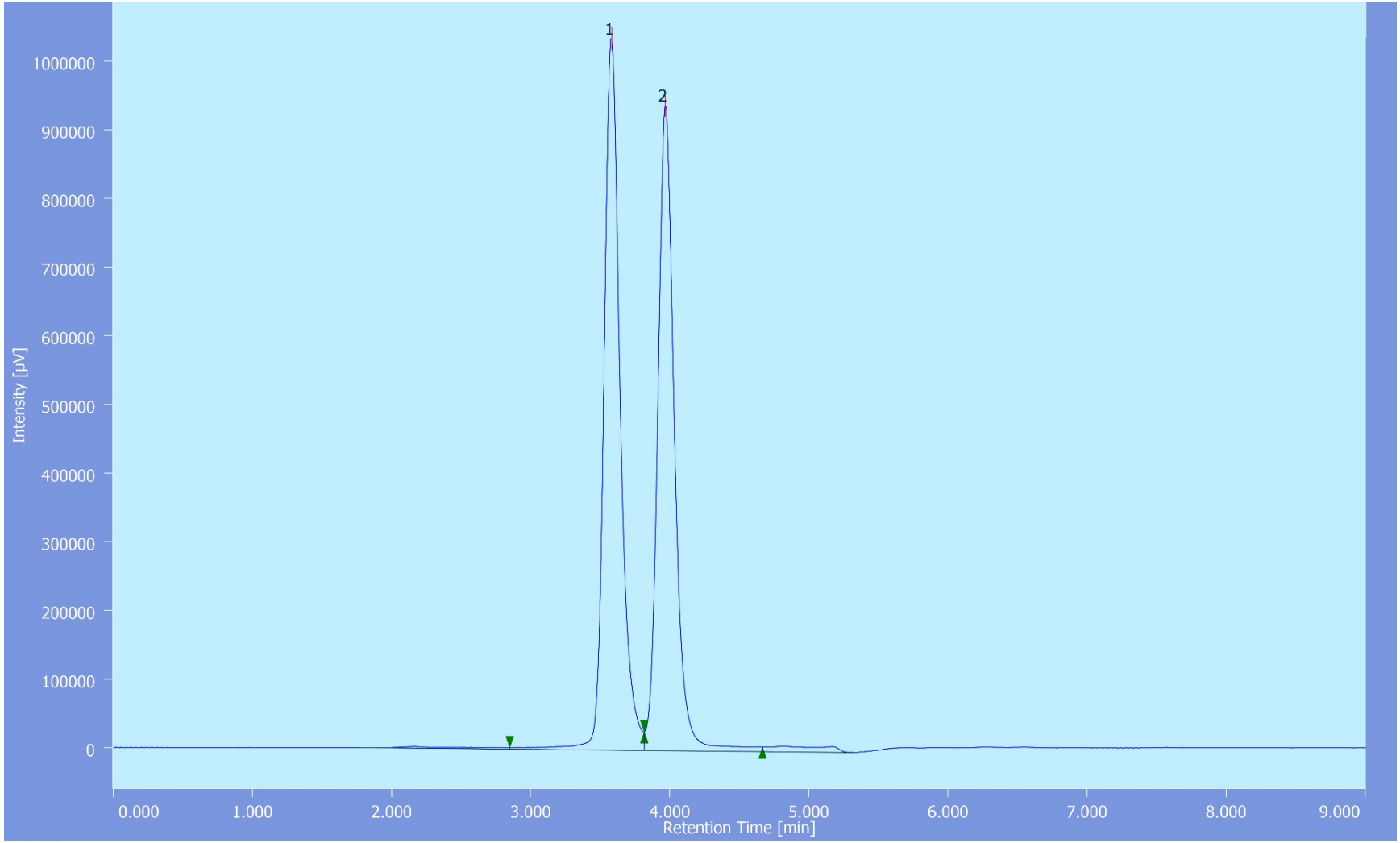
Figure S38. SFC trace of Boc-Phg-BINOL after irradiation. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.550	2158854	293807	47.586	47.641	N/A	5708	2.027	1.185	
2	Unknown	1	3.933	2377935	322899	52.414	52.359	N/A	6771	N/A	1.126	

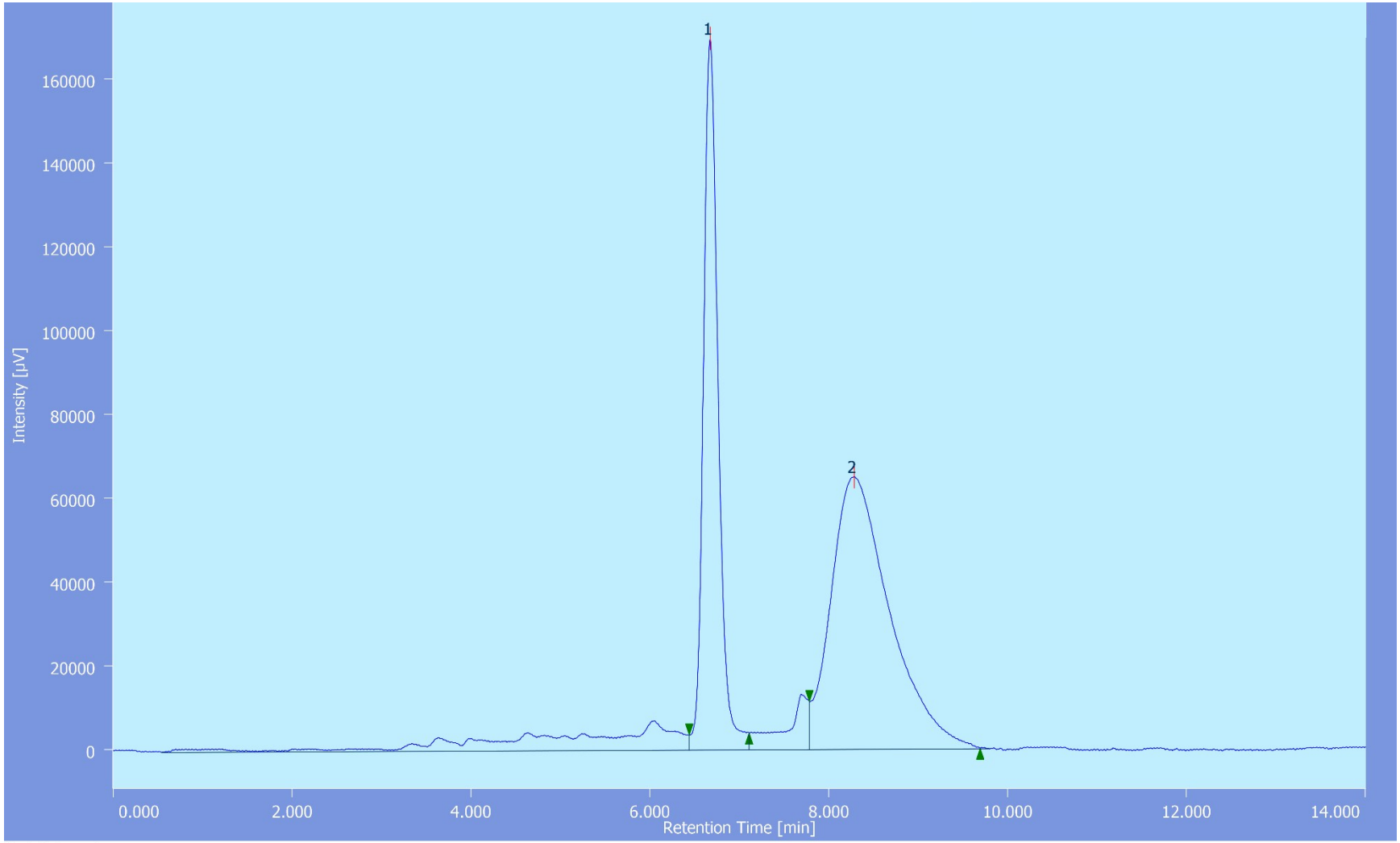
Figure S39. SFC trace of Racemic Menthyl-BINOL. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	3.583	8428401	1036244	51.778	52.445	N/A	5124	1.893	1.256	
2	Unknown	1	3.967	7849684	939634	48.222	47.555	N/A	5939	N/A	1.194	

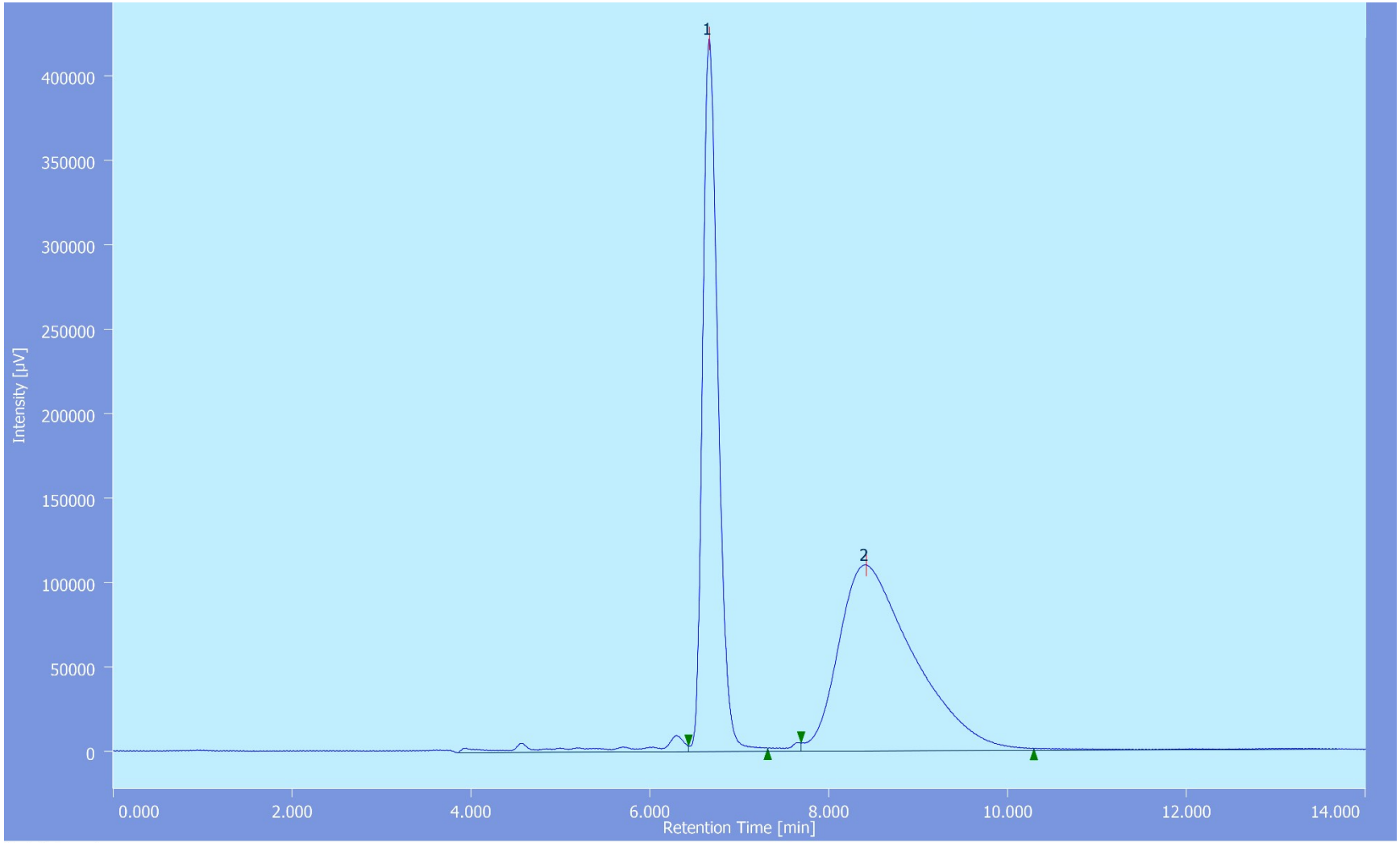
Figure S40. SFC trace of Menthyl-BINOL after irradiation. (Daicel CHIRALPAK® IA Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	6.675	1947073	169777	39.548	72.284	N/A	8486	2.224	1.201	
2	Unknown	1	8.283	2976289	65099	60.452	27.716	N/A	816	N/A	N/A	

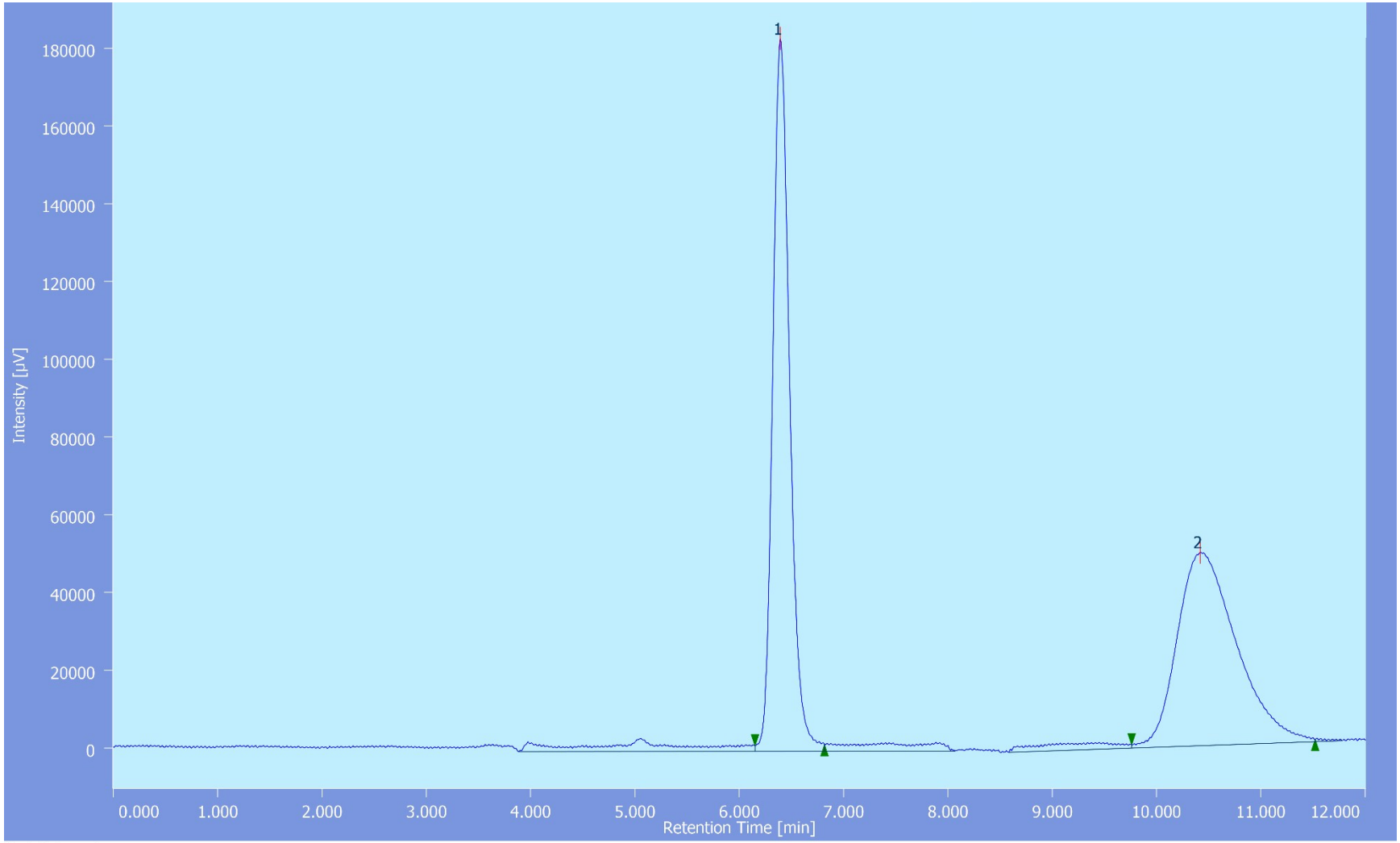
Figure S41. SFC trace of Racemic Z-Pro-BINOL. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	6.667	5047916	422042	44.063	79.281	N/A	7394	1.942	1.276	
2	Unknown	1	8.417	6408193	110298	55.937	20.719	N/A	506	N/A	1.569	

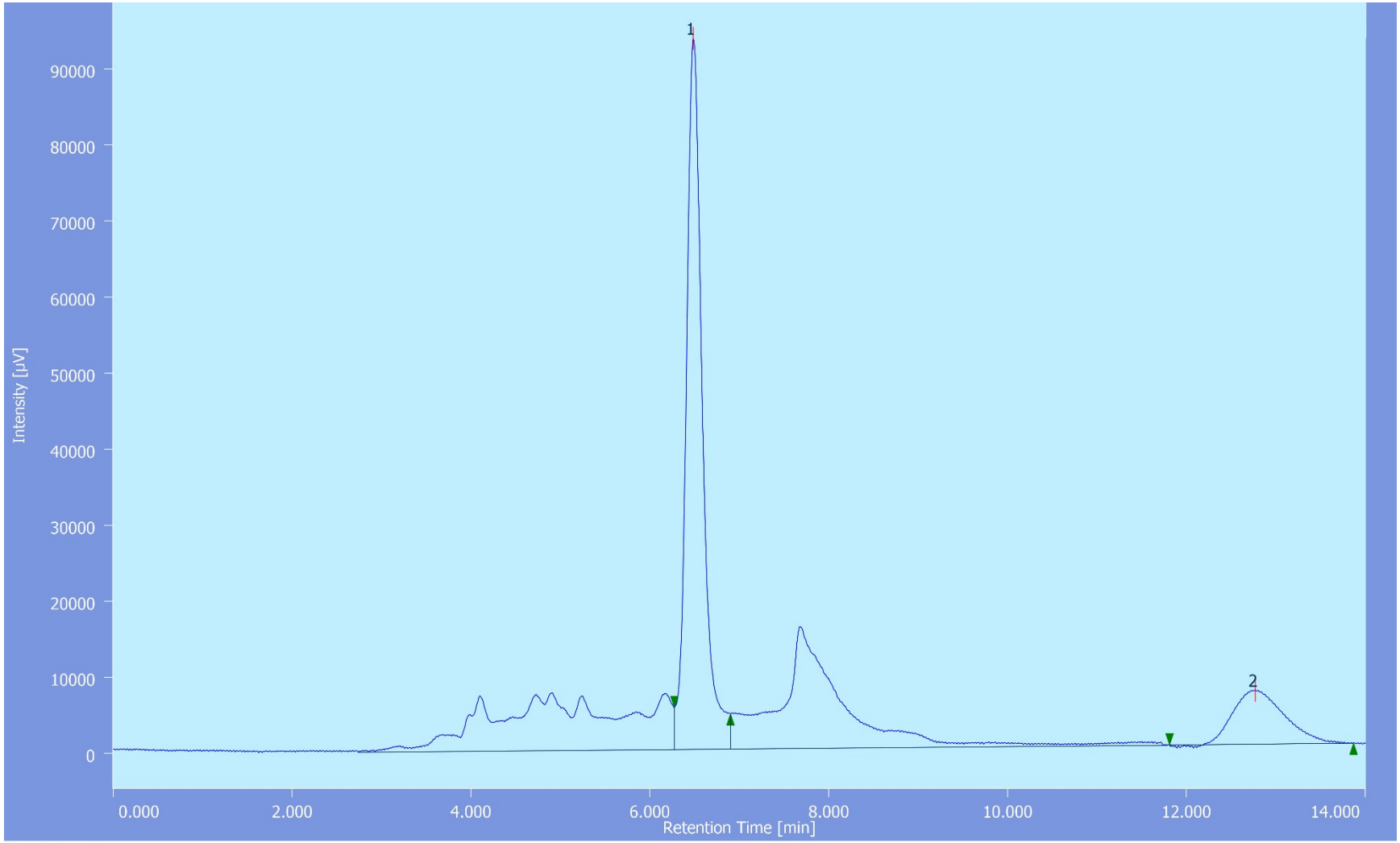
Figure S42. SFC trace of Z-Pro-BINOL after irradiation. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	6.392	2062150	183303	51.231	78.630	N/A	7917	6.172	1.236	
2	Unknown	1	10.417	1963051	49819	48.769	21.370	N/A	1667	N/A	1.422	

Figure S43. SFC trace of Racemic Z-Trp-BINOL. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	6.483	1173252	93487	80.542	92.937	N/A	7249	9.248	N/A	
2	Unknown	1	12.767	283449	7105	19.458	7.063	N/A	2331	N/A	1.279	

Figure S44. SFC trace of Z-Trp-BINOL after irradiation. (Daicel CHIRALPAK® IF Column, CO_2: CH_2Cl_2 = 65:35, Flowrate = 1.5 mL/min, CO_2 backpressure = 10 mPa, Column oven = 30°C)

[1]HNMR spectra :

Figure S45. [1]HNMR spectra for Boc-Pro-BINOL (400 MHz, Chloroform-d)

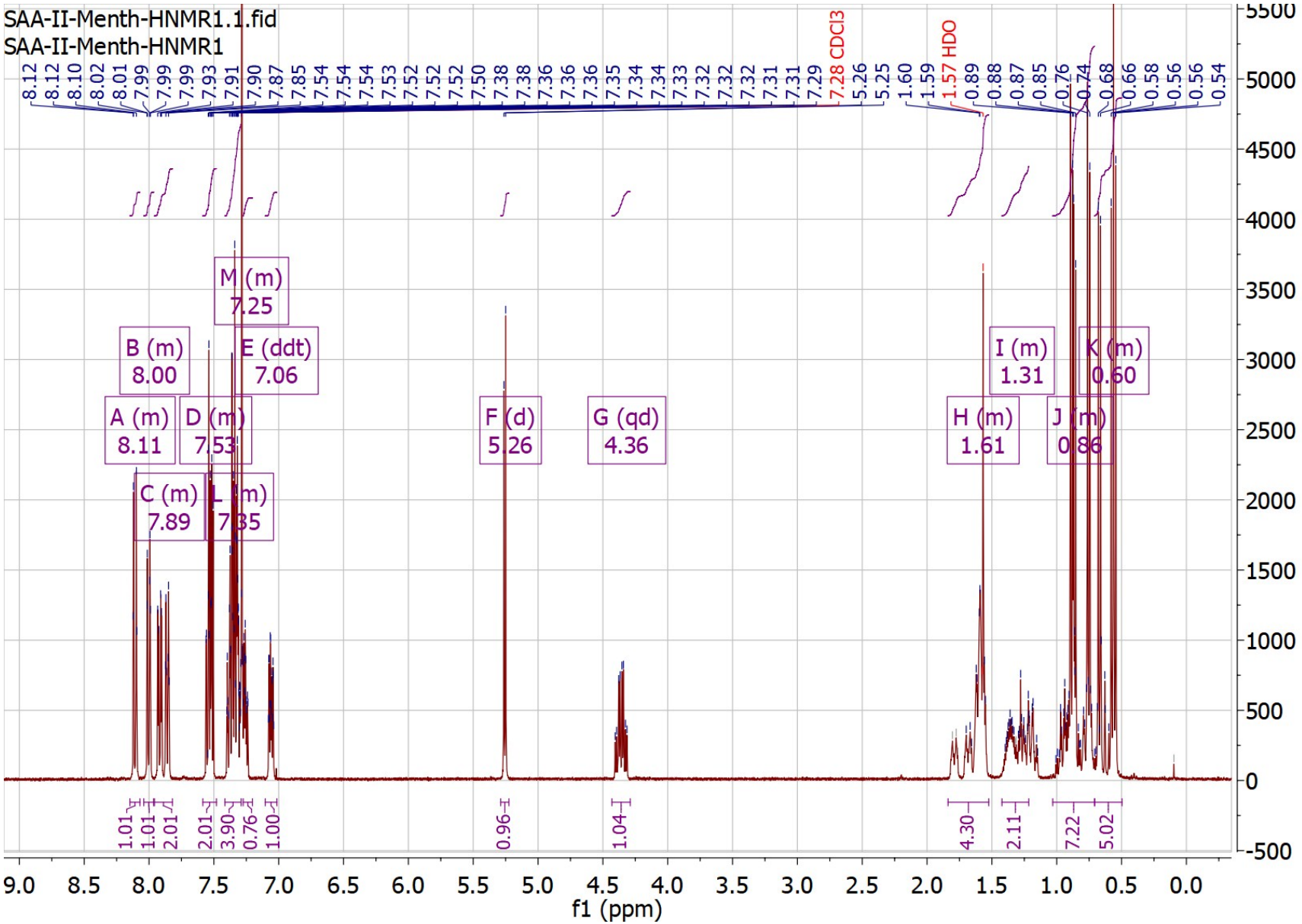


Figure S46. [1]HNMR spectra for Menthyl-BINOL (400 MHz, Chloroform-d)

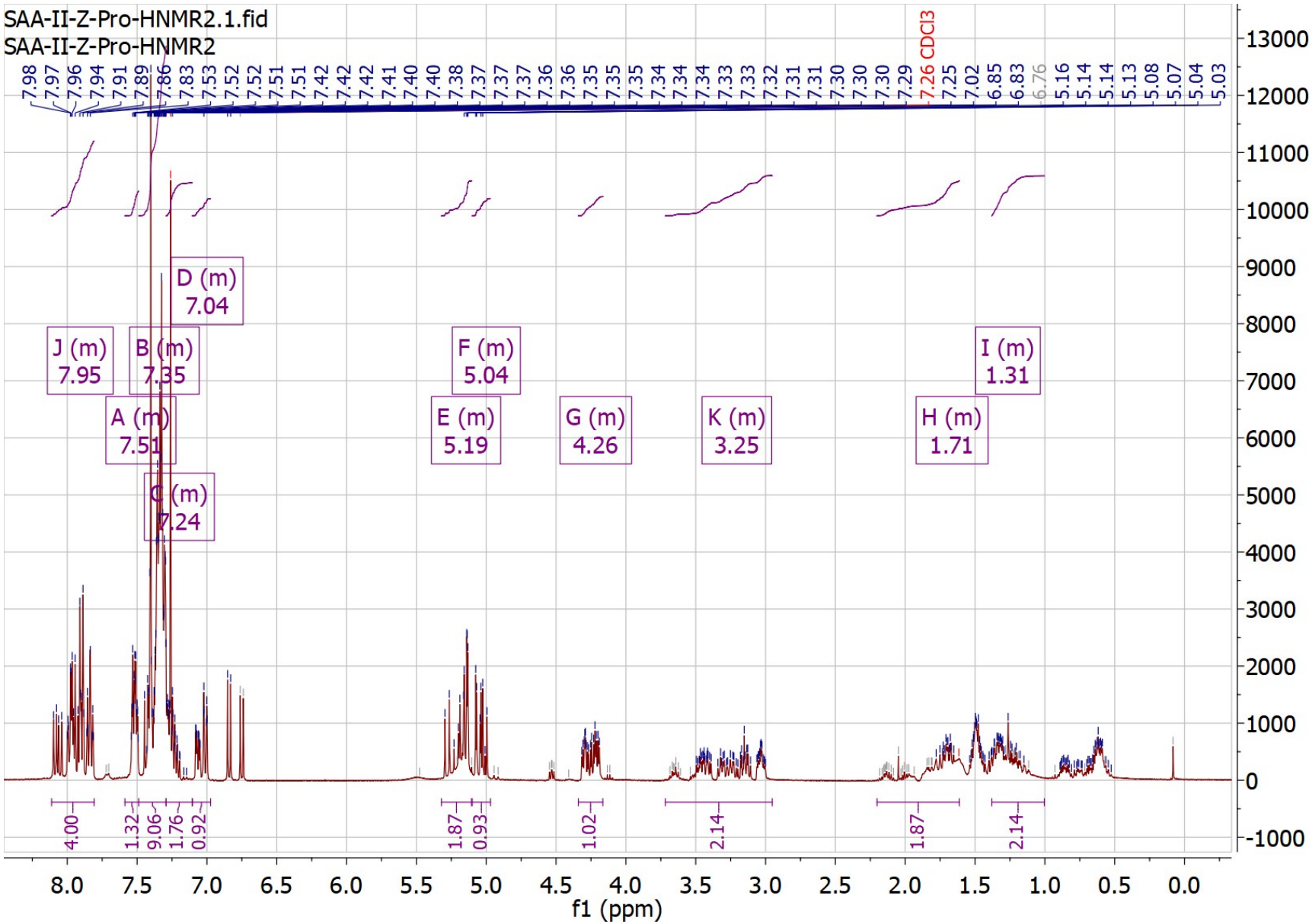


Figure S47. [1]HNMR spectra for Z-Pro-BINOL (400 MHz, Chloroform-d)

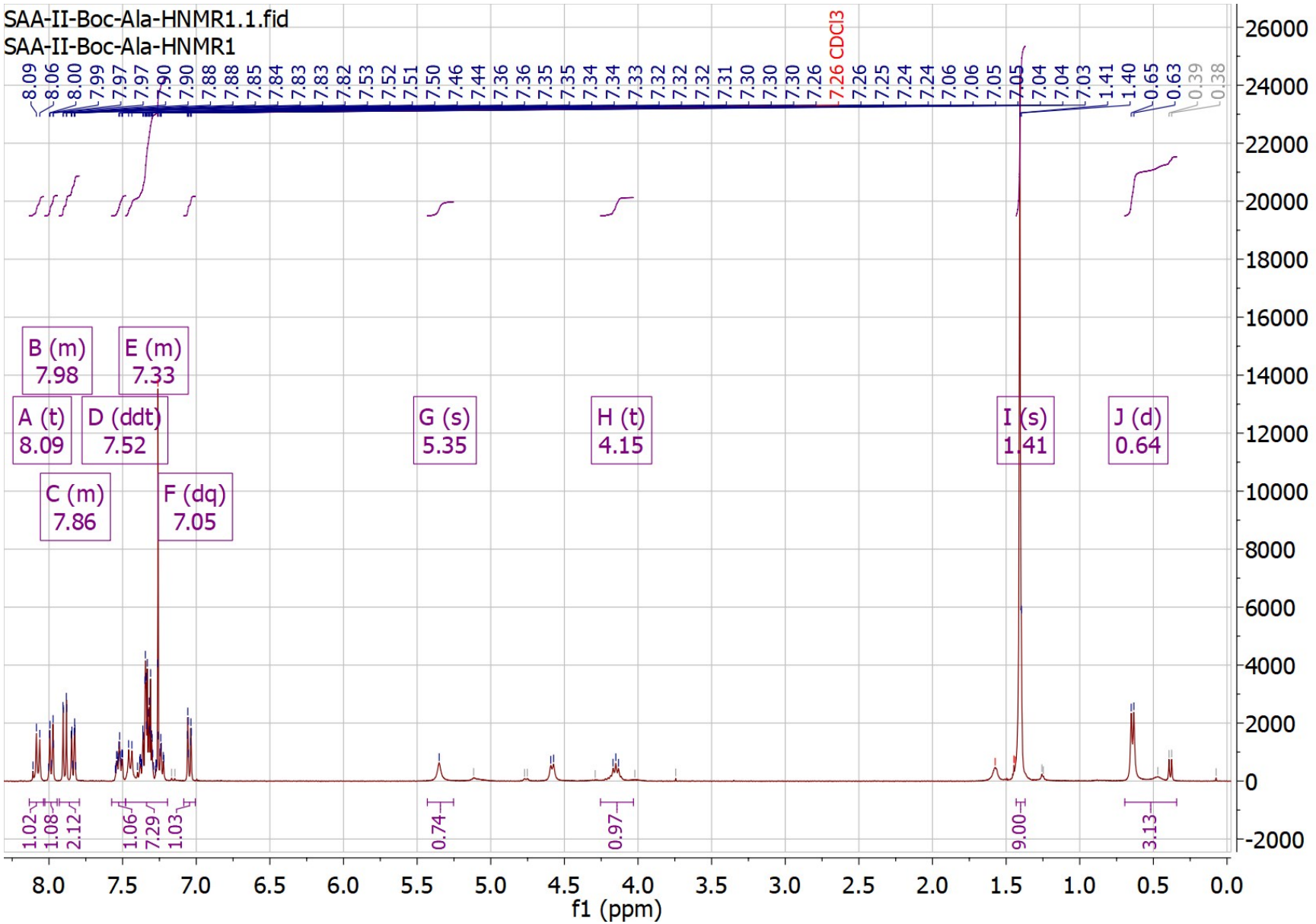


Figure S48. [1]HNMR spectra for Boc-Ala-BINOL (400 MHz, Chloroform-d)

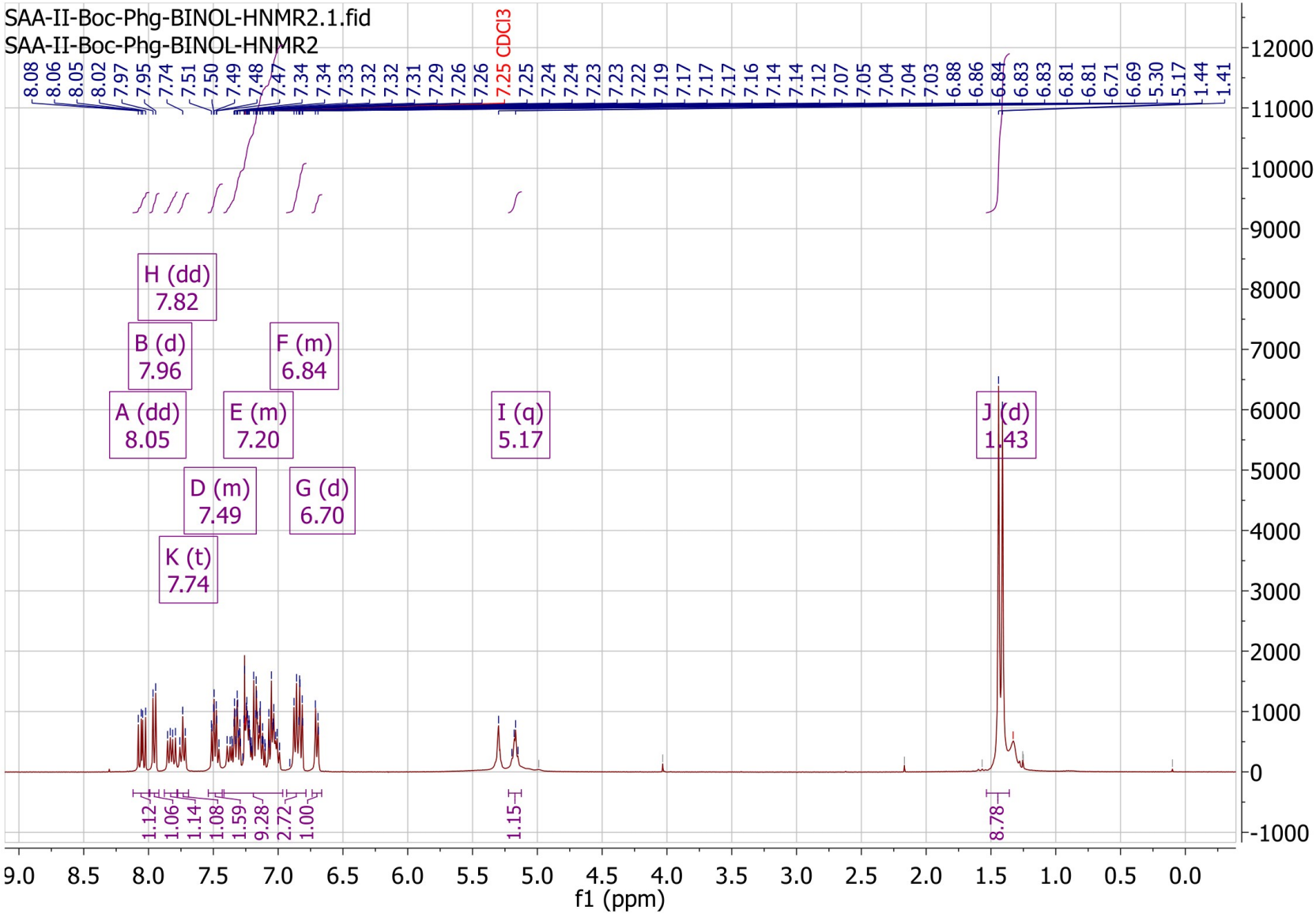


Figure S49. [1]HNMR spectra for Boc-Phg-BINOL (400 MHz, Chloroform-d)

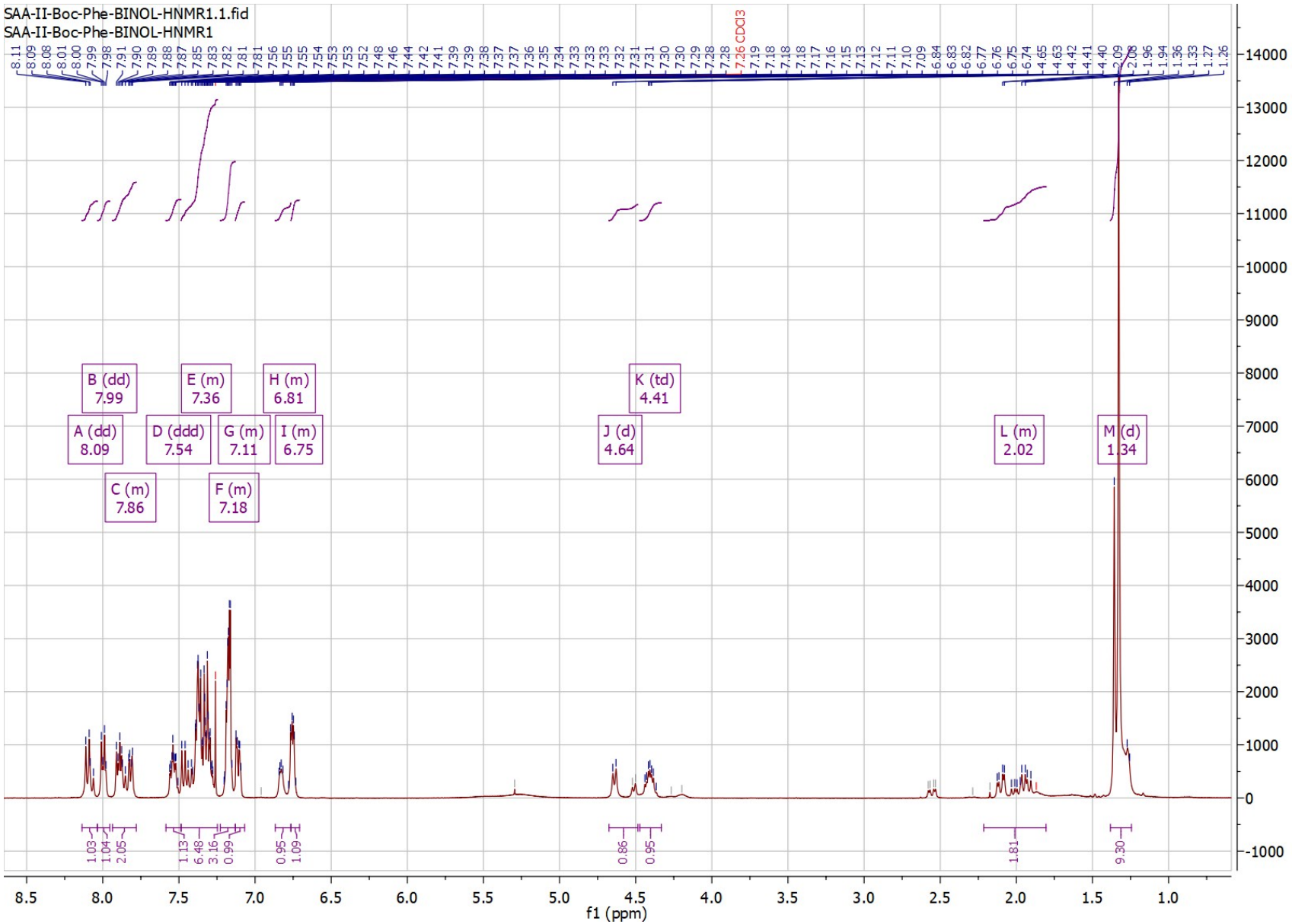


Figure S50. [1]HNMR spectra for Boc-Phe-BINOL (400 MHz, Chloroform-d)

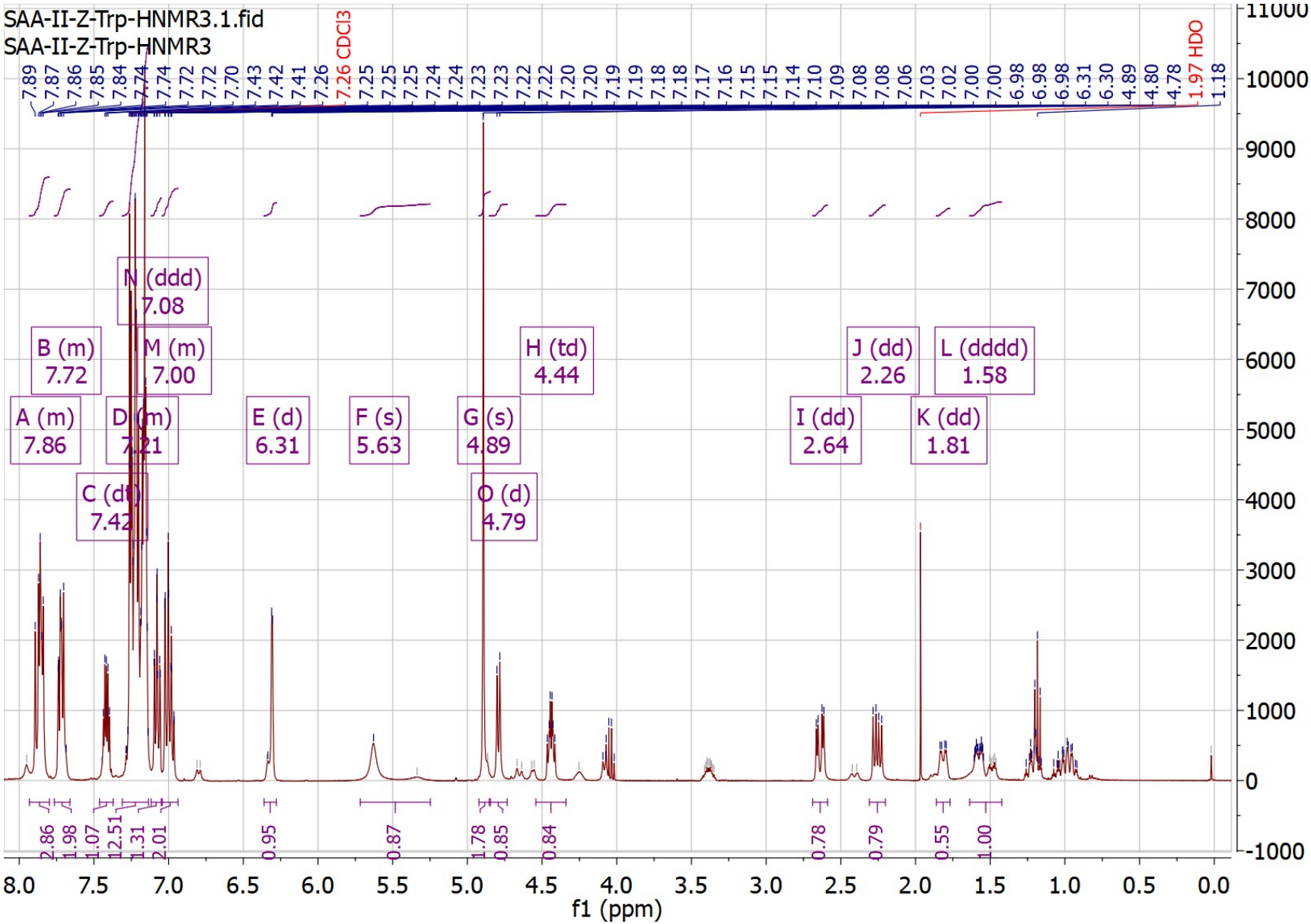


Figure S51. [1]HNMR spectra for Z-Trp-BINOL (400 MHz, Chloroform-d)

^{13}CNMR spectra :

Figure S52. ^{13}CNMR spectra for Boc-Pro-BINOL (101 MHz, Chloroform-*d*)

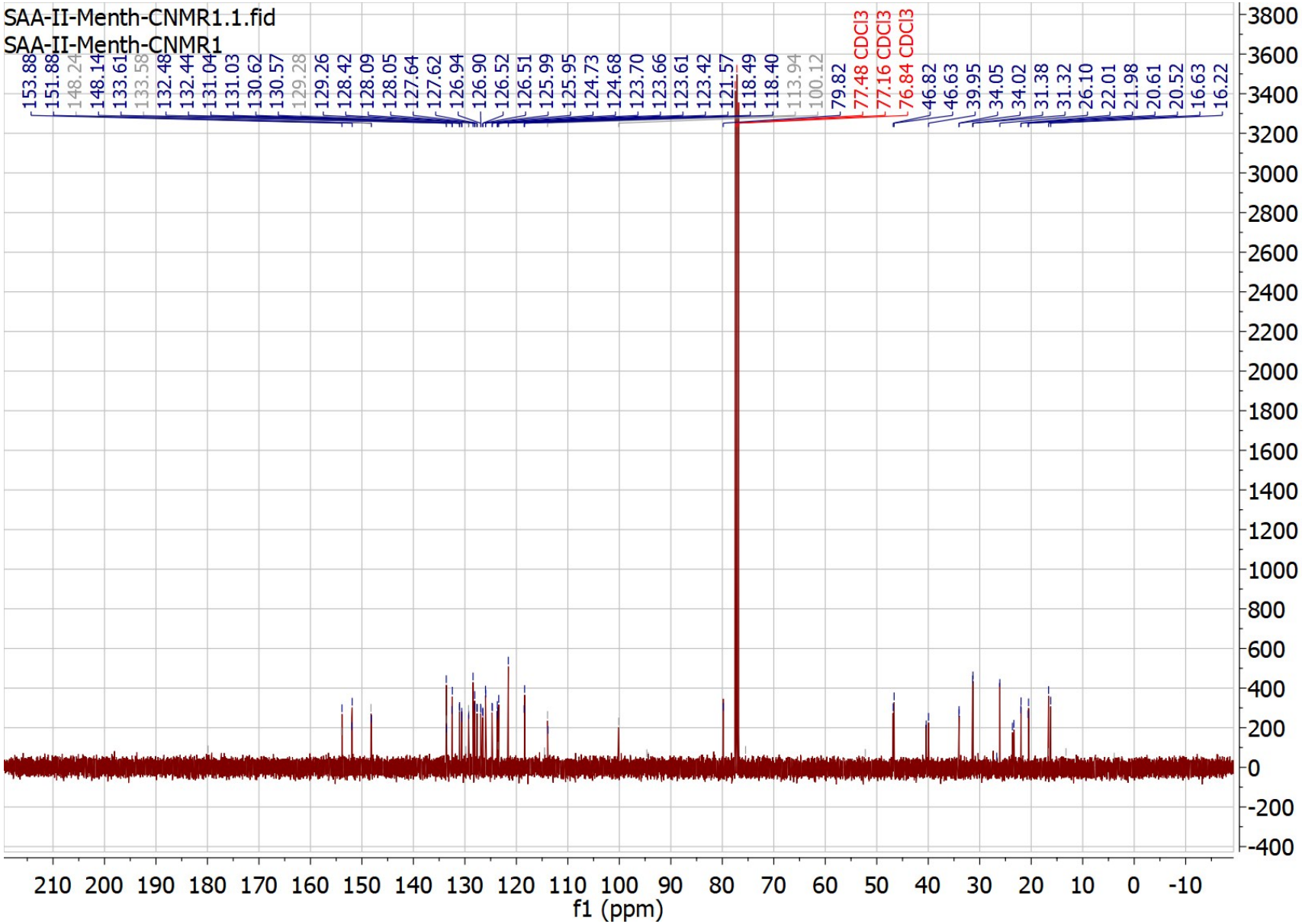


Figure S53. ^{13}CNMR spectra for Menthyl-BINOL (101 MHz, Chloroform-*d*)

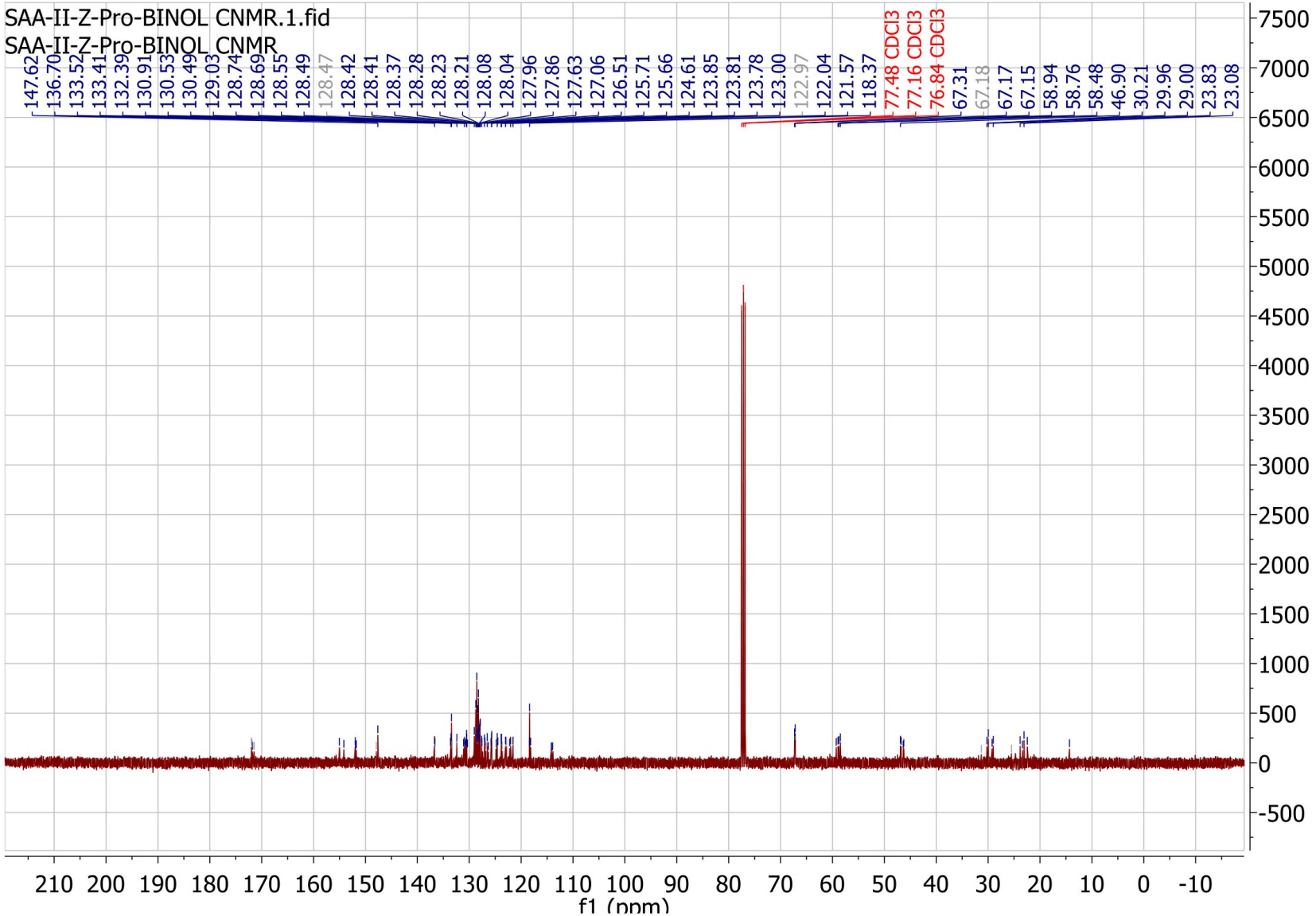


Figure S54. ^{13}CNMR spectra for Z-Pro-BINOL (101 MHz, Chloroform-*d*)

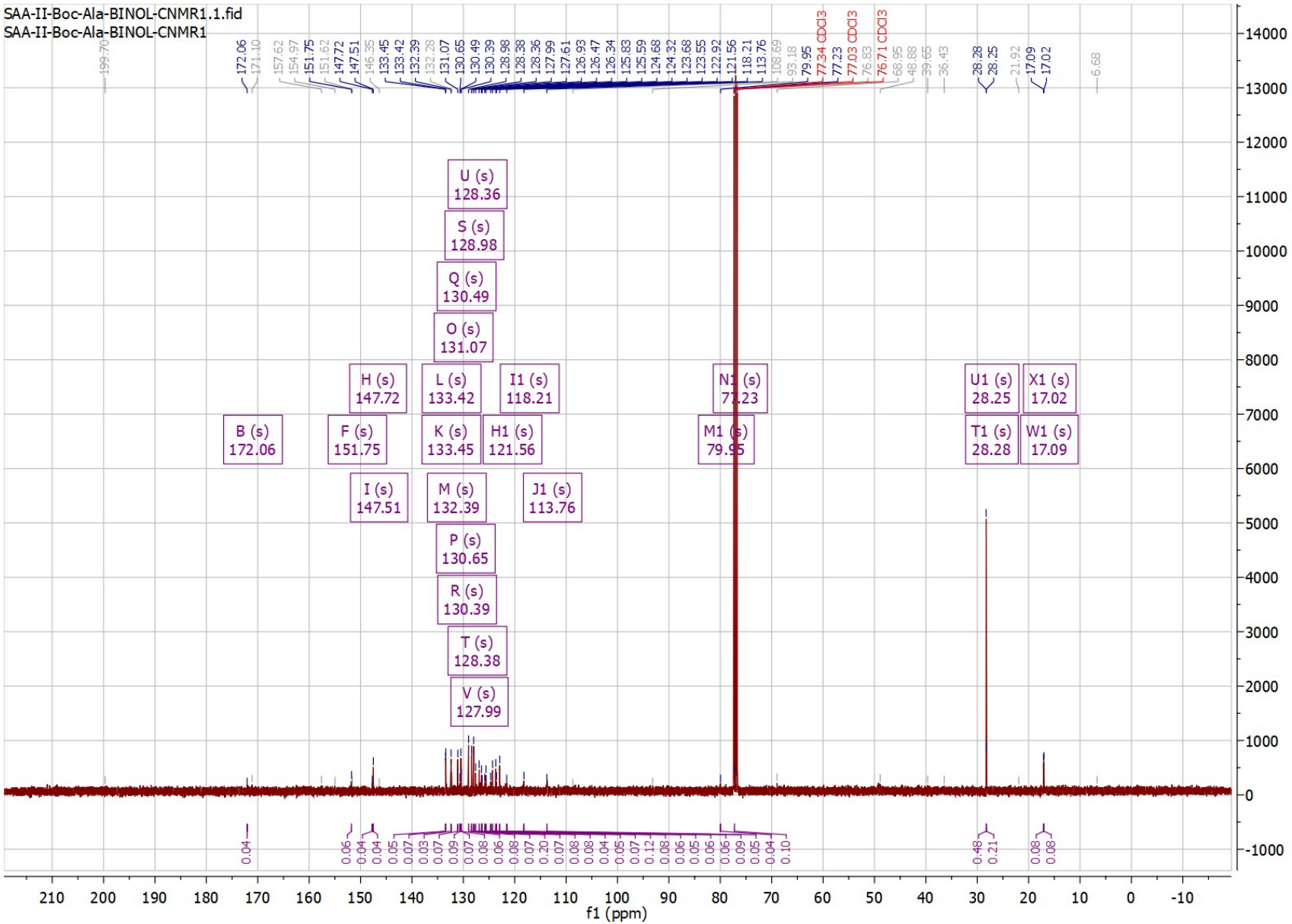


Figure S55. ^{13}CNMR spectra for Boc-Ala-BINOL (101 MHz, Chloroform-*d*)

Figure S56. [13]CNMR spectra for Boc-Phg-BINOL (101 MHz, Chloroform-*d*)

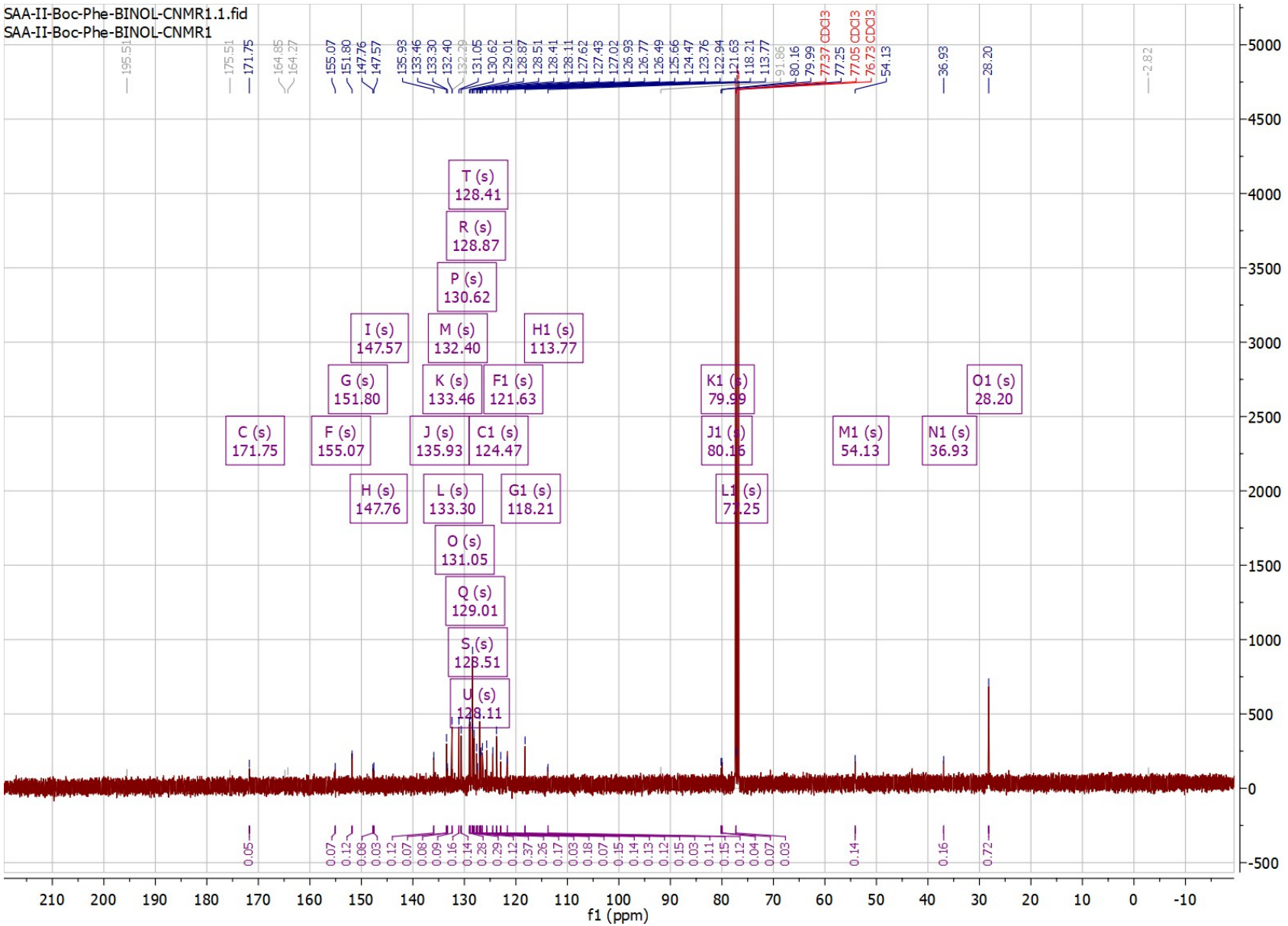


Figure S57. ^{13}CNMR spectra for Boc-Phe-BINOL (101 MHz, Chloroform-*d*)

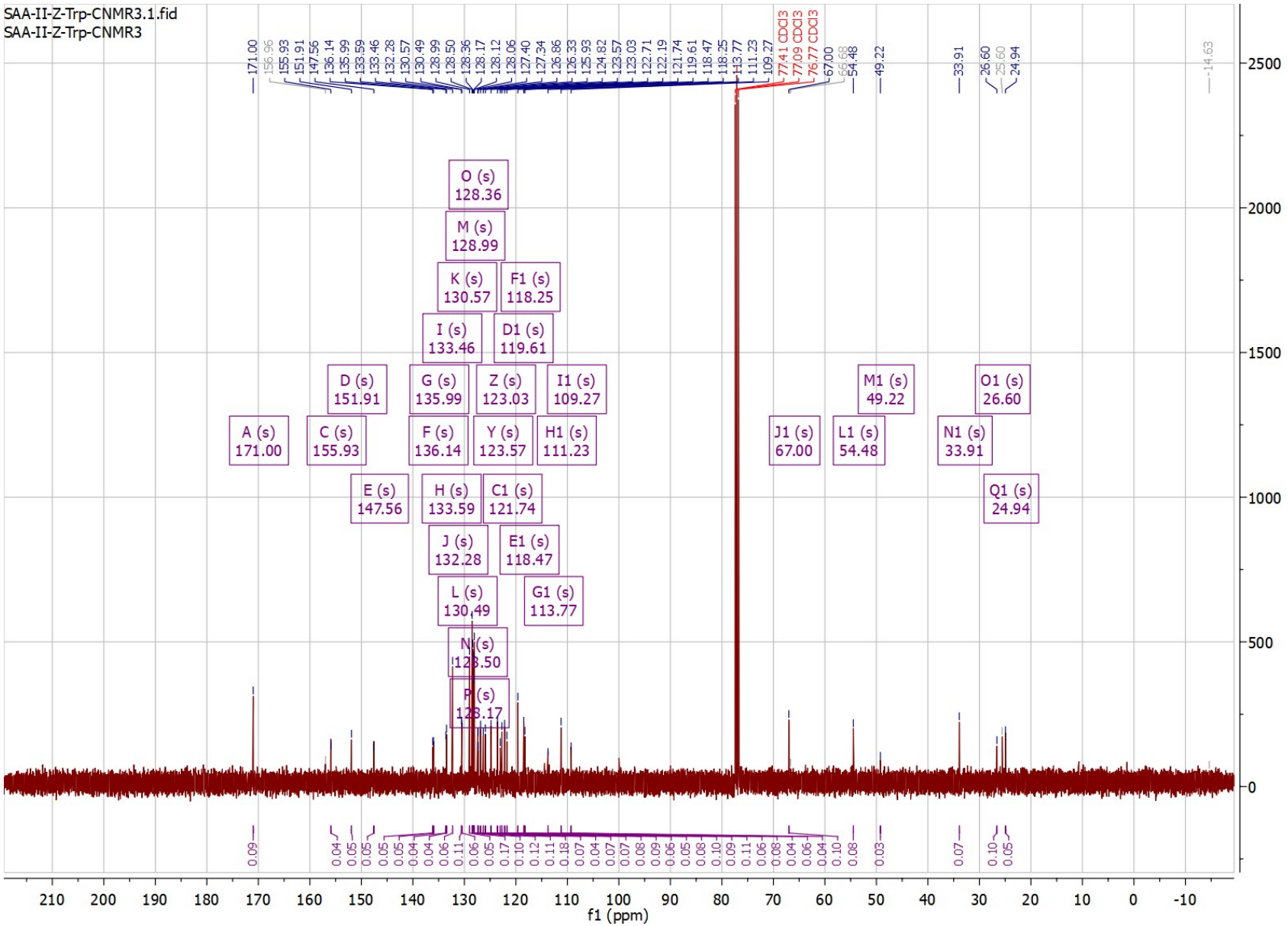


Figure S58. ^{13}CNMR spectra for Z-Trp-BINOL (101 MHz, Chloroform-*d*

Computational Methods

In this work, we used time-dependent density functional theory (TD-DFT) with the B3LYP functional and 6-31g** basis set, as implemented in Gaussian 09, to calculate optimized geometries for first excited, singlet state (R) and (S) configurations of basic (charge = -1) Boc-Pro-BINOL with no solvent present. Optimized geometries for the (R) and (S) configurations are provided in Table S4 and S5, respectively, and a plot of the optimized geometries are provided in Figure S54.

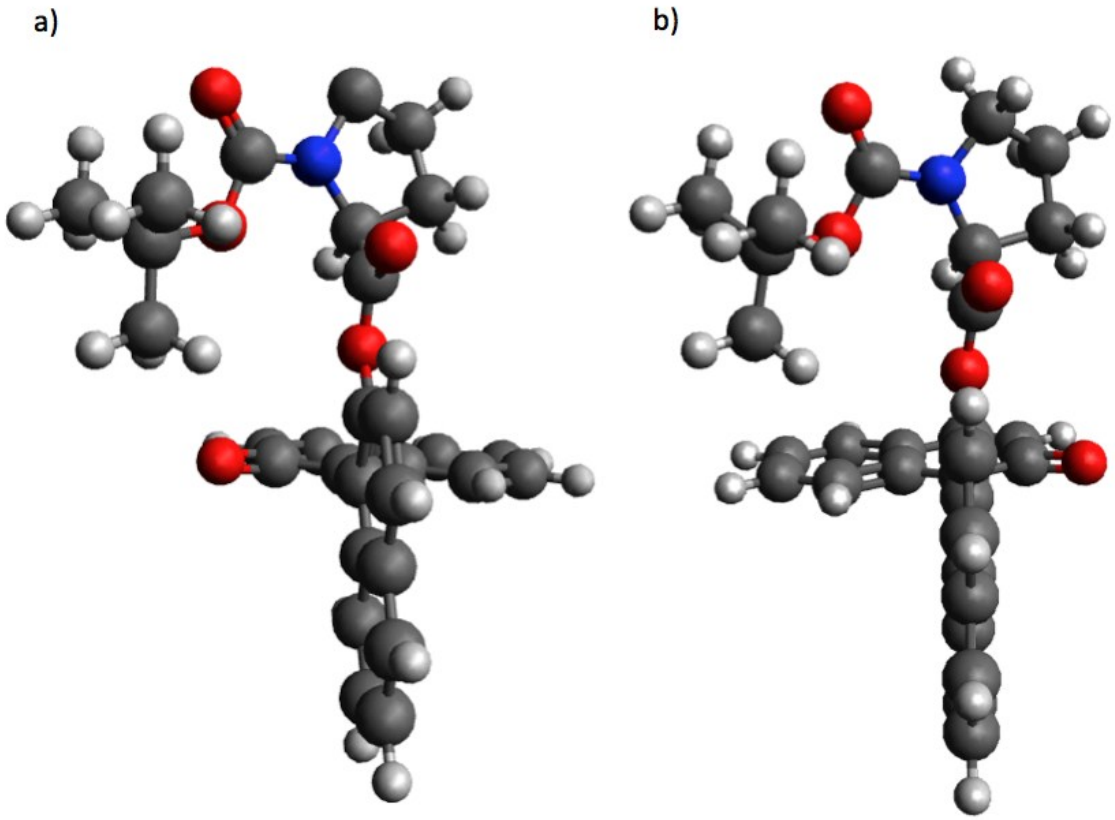


Figure S59. First excited singlet state geometries for deprotonated a) (R)-Boc-Pro-BINOL and b) (S)-Boc-Pro-BINOL using TD-DFT with B3LYP functional and 6-31g** basis set.

Table S6, S7. XYZ coordinates (in Angstroms) for (R)-Boc-Pro-BINOL and (S)-Boc-Pro-BINOL.

	(R)-Boc-Pro-BINOL			**(S)-Boc-Pro-BINOL**		
	X	Y	Z	X	Y	Z
C	-2.9578	-1.5504	-0.2635	3.2676	-1.1516	0.4248
C	-1.8399	-0.6706	-0.1454	2.0412	-0.4300	0.5444
C	-1.8716	0.5078	0.7777	1.9964	1.0588	0.3841
C	-2.3883	1.7616	0.3572	1.8474	1.6593	-0.8937
C	-3.4116	4.2614	-0.4945	1.5443	2.8478	-3.4469
C	-2.9137	4.1250	0.7913	1.6509	3.6513	-2.3238
C	-2.4001	2.8960	1.2454	1.8035	3.0917	-1.0412
C	-2.9150	1.9390	-0.9569	1.7433	0.8650	-2.0745
C	-3.4115	3.1559	-1.3717	1.5932	1.4430	-3.3164
C	-1.8843	2.7496	2.5771	1.9171	3.9205	0.1249
C	-1.3883	1.5613	3.0016	2.0563	3.3689	1.3558
C	-1.3477	0.3831	2.1329	2.0884	1.9189	1.5573
C	-2.8644	-2.6606	-1.1938	3.2306	-2.5970	0.5551
C	-1.6681	-2.8266	-1.9402	1.9833	-3.2293	0.7977
C	-0.5740	-1.9572	-1.8137	0.7850	-2.5092	0.9202
C	-0.6802	-0.8979	-0.9234	0.8376	-1.1283	0.7929
C	-3.9716	-3.5359	-1.3280	4.4406	-3.3259	0.4305
C	-5.1514	-3.3503	-0.5852	5.6660	-2.6822	0.1821
C	-5.2432	-2.2868	0.3039	5.7019	-1.2995	0.0512
C	-4.1677	-1.3948	0.4672	4.5240	-0.5386	0.1666
O	0.3396	0.0534	-0.6837	-0.2885	-0.2753	0.8788
O	-0.8553	-0.6859	2.5650	2.1692	1.4590	2.7212
H	-4.2660	-0.5765	1.1711	4.5825	0.5386	0.0635
H	-2.9167	1.0819	-1.6179	1.7909	-0.2104	-1.9628

H	-1.6027	-3.6611	-2.6344	1.9621	-4.3121	0.8961
H	-1.9033	3.6166	3.2346	1.8887	5.0005	-0.0063
H	0.3251	-2.0967	-2.3936	-0.1495	-3.0038	1.1351
H	-0.9922	1.4269	4.0035	2.1422	3.9752	2.2526
H	-3.8880	-4.3661	-2.0263	4.4009	-4.4084	0.5338
H	-2.9148	4.9740	1.4710	1.6176	4.7341	-2.4209
H	-6.1516	-2.1348	0.8837	6.6450	-0.7922	-0.1429
H	-3.8083	3.2647	-2.3768	1.5180	0.8162	-4.2000
H	-5.9851	-4.0386	-0.7096	6.5783	-3.2684	0.0915
H	-3.8049	5.2185	-0.8260	1.4269	3.2986	-4.4284
C	1.5189	0.1492	-1.2992	-1.5129	-0.5957	1.2999
C	2.2860	1.3519	-0.7315	-2.3676	0.6773	1.3478
O	1.9510	-0.5404	-2.2048	-1.9260	-1.6868	1.6465
N	3.7158	1.0676	-0.5579	-3.7629	0.4339	0.9614
C	4.2286	-0.0142	0.0968	-4.1670	-0.2178	-0.1638
O	5.4242	-0.2840	0.1212	-5.3318	-0.5243	-0.3909
O	3.2362	-0.6914	0.7179	-3.1091	-0.4303	-0.9862
C	3.4467	-2.0402	1.2673	-3.1834	-1.3989	-2.0860
C	3.9792	-2.9652	0.1673	-3.6223	-2.7652	-1.5478
C	4.3927	-1.9570	2.4700	-4.1229	-0.8697	-3.1754
C	2.0384	-2.4569	1.6940	-1.7364	-1.4539	-2.5832
H	1.3667	-2.5099	0.8338	-1.0688	-1.8157	-1.7966
H	2.0726	-3.4435	2.1681	-1.6619	-2.1283	-3.4424
H	1.6093	-1.7445	2.4019	-1.3961	-0.4607	-2.8897
H	5.3786	-1.6058	2.1626	-5.1426	-0.7896	-2.7970
H	3.9874	-1.2717	3.2212	-3.7912	0.1176	-3.5133
H	4.4910	-2.9459	2.9312	-4.1105	-1.5463	-4.0371
H	4.9896	-2.6827	-0.1321	-4.6583	-2.7376	-1.2071

H	3.9911	-3.9977	0.5324	-3.5283	-3.5184	-2.3374
H	3.3225	-2.9148	-0.7059	-2.9820	-3.0552	-0.7101
C	2.2937	2.5296	-1.7376	-2.5013	1.1962	2.8015
H	1.8303	1.6380	0.2208	-1.9110	1.4278	0.6959
C	3.6732	3.1819	-1.5493	-3.9202	1.7844	2.8624
H	2.2123	2.1245	-2.7518	-2.4234	0.3458	3.4870
H	1.4555	3.2105	-1.5720	-1.7112	1.9071	3.0518
C	4.5877	1.9781	-1.2954	-4.7293	0.8192	1.9880
H	3.9868	3.7740	-2.4144	-4.3097	1.8542	3.8824
H	3.6690	3.8401	-0.6726	-3.9367	2.7894	2.4244
H	4.9221	1.5223	-2.2383	-5.0623	-0.0587	2.5592
H	5.4778	2.2112	-0.7055	-5.6122	1.2691	1.5267

Electronic energies were calculated to be -1591.023462 a.u. and -1591.023144 a.u. for the (R) and (S) enantiomers, respectively, corresponding to a difference $\Delta E(S - R) = 0.199$ kcal/mol. Thermal, rotational, and vibrational contributions to total internal energy were assumed to be equal as a first approximation, giving rise to the following equations for enatiomeric excess (%ee):

$$\Delta E(S\text{-}R) = -RT \ln(K)$$

$$K = \frac{f_S}{1 - f_S}$$

$$\%ee = \left|\frac{f_R - f_S}{f_R + f_S}\right| * 100\%$$

where f_S is the fraction of (S) enantiomer, and $f_R = 1 - f_S$ is the fraction of (R) enantiomer. With $\Delta E(S - R) = 0.199$ kcal/mol, the above treatment gives rise to a 17% ee for the (R) enantiomer. While the enatiomeric excess value was calculated using ΔE in vacuum, as opposed to ΔG in toluene, the results are qualitatively consistent with measured ee values, suggesting DFT may be a useful tool in predicting and designing alternative auxiliary groups. Efforts are underway to expand the theory to model both

ground and excited states of protonated and deprotonated forms of BINOL derivatives, taking solvent into account.