Supporting Information
Mechanistic Studies Inform Design of Improved Ti(salen) Catalysts for Enantioselective [3+2] Cycloaddition
(Experimental Part)

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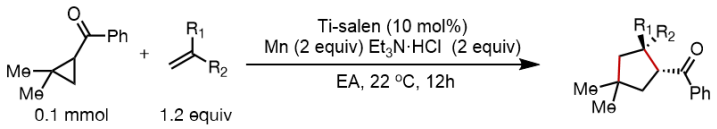
Section 1. General information

All reactions were conducted under a nitrogen atmosphere, unless otherwise noted. Flash chromatography was performed using silica gel P60, 40 - 63 μm, 60 Å (R12030B) from SiliCycle. Commercial reagents purchased from Alfa Aesar, Acros, AK Scientific, Combi-blocks, Oakwood, Sigma Aldrich, Strem and TCI were used as received with the following exceptions: toluene, dichloromethane, tetrahydrofuran, diethyl ether, and acetonitrile were dried by passing through columns of activated alumina; dimethylformamide was dried by passing through columns of activated molecular sieves; ethyl acetate are distilled and dried over activated molecular sieves. Manganese powder was purchased form Alfa Aesar 325 mesh, 99.95% (metals basis). Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz) and Inova-500 (500 MHz) spectrometers. 2D NMR spectra were collected on Inova-600 (600 mHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16). Data are represented as follows: chemical shift, multiplicity (br. s = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Yields and diastereomeric ratios were determined based on ^{1}H NMR spectra of crude reaction mixture using dibromomethane as the internal standard. Infrared (IR) spectra were obtained using a Thermo Scientific Nicolet is 10 FTIR spectrometer. Cyclic voltammetry data were measured with a BASi Epsilon potentiostat. The mass spectral data were obtained on a ThermoFisher Scientific Exactive series DART Mass Spectrometer. GC–MS data was collected on *J* MS-GC Mate II GCMS system. Enantiomeric excesses were determined by chiral HPLC of isolated material using a SHIMADZU system with CHIRALPAK® columns

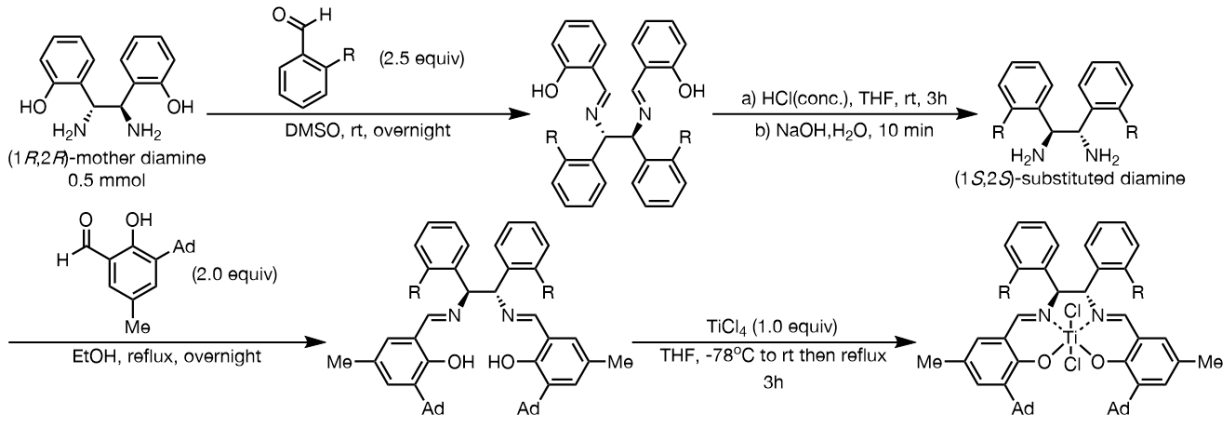
Abbreviations: ^{t}Bu—*tert*-butyl, DMAP—4-dimethylaminopyridine, DCM—dichloromethane, dr—diastereomeric ratio, ee—enantiomeric excess, Et_2O—diethyl ether, Et_3N—triethylamine, EtOAc—ethyl acetate, EtOH-ethanol, MeCN—acetonitrile, MeOH—methanol, THF—tetrahydrofuran, rt—room temperature

Section 2. General procedures for Ti-catalyzed [3+2] cycloaddition of cyclopropyl ketones and alkenes



Method A (0.1 mmol scale): *Ti-catalyzed [3+2] cycloaddition of cyclopropyl ketones and alkenes.* In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Mn (11.0 mg, 0.2 mmol, 2.0 equiv), $Et_3N{\cdot}HCl$ (27.4 mg, 0.2 mmol, 2.0 equiv) and Ti-salen complex (0.01 mmol, 10 mol%). The solids were suspended in 1 mL of EtOAc. The mixture was stirred for 15 min to allow reduction of the pre-catalyst. (Note: Depending on the solubility and reduction potential of each catalyst, the color change of solution from dark red to deep green could be observed for sometimes. However, the absence of color change has no effect on the success of reaction.) Subsequently, the alkene substrate (1.2 equiv) and cyclopropyl ketone substrate (0.10 mmol, 1.0 equiv) were added. The resulting mixture was capped and sealed with parafilm, then was removed from the glovebox and stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then all transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10 mL in total) to remove the inorganic salts and other insoluble solids. The product solution was concentrated under vacuo and dissolved in $CDCl_3$ to analyze the NMR yields and diastereomeric ratio(dr) using ^1H NMR. The purified products were obtained by flash chromatography on silica gel using hexanes/EtOAc or other solvents combination. Enantiomeric excesses were determined by chiral HPLC of isolated product.

Section 3. Preparation and characterization of catalysts

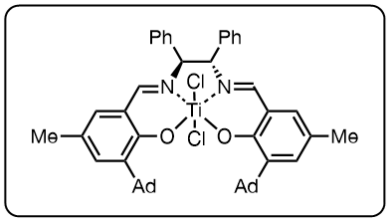


Method B (0.5 mmol scale): *Synthesis of Ti-salen complex with different backbone.* The substituted diamines and 3-(adamantan-1-yl)-5-methylsalicylaldehyde were synthesized according to literature with minor modification[1].

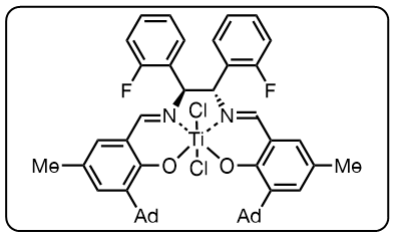
Synthesis of substituted diamine: To a clear solution of (1R,2R)-bis(2-hydroxylphenyl)-1,2-diaminoethane (0.5 mmol, 122 mg) DMSO (2.5 mL) was added corresponding aryl aldehyde (1.25 mmol, 2.5equiv). The resulting mixture was stirred overnight at room temperature, and then the mixture was poured into water. The aqueous layer was extracted with Et_2O (30 mL x3). The combined organic layer was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was dried on a high vacuum pump. The crude product was subsequently hydrolyzed under acidic conditions. To a clear solution of crude diimine product in THF (5 mL) was added concentrated HCl (37%, 0.15 mL). The reaction mixture was stirred at room temperature for 3 h. The mixture was diluted with 1M HCl and extracted with Et_2O (30 mL x2). The combined organic layer was extracted with 1M HCl (30 mL x3), and the combined aqueous layer was neutralized with NaOH to pH=12. The neutralized solution was extracted with Et_2O (50 mL x3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude diamine was further dried on a high vacuum pump before subsequent synthesis.

Schiff base condensation: To an oven-dried round-bottomed flask was added diamine and the previously synthesized diamine (0.5 mmol) and 3-(adamantan-1-yl)-5-methylsalicylaldehyde (1.0 mmol, 2.0 equiv). The mixture was suspended in EtOH (5 mL) and heated up to reflux. The solution was kept under reflux condition for 12h. After cooling down, precipitate was filtered and washed with a small portion of cold EtOH. If no precipitate formed, then one drop of water was added to the solution.

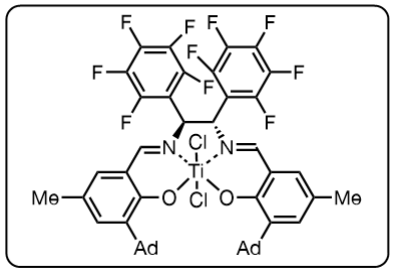
Ti-salen complex synthesis: In an oven-dried round bottom flask, the salen ligand (358 mg, 0.5 mmol, 1 equiv) was dissolved in THF (5 mL) to afford a yellow solution, which was cooled to -78 ^oC under N_2. Then $TiCl_4$ solution (1.0 M in toluene; 0.5 mL, 0.5 mmol, 1.0 equiv) was added carefully into the above solution at -78 ^oC. This red solution was warmed up to room temperature and heated under reflux for 3 h. After the reaction was cooled to room temperature, the dark red solid was filtered off and washed with hexanes and Et_2O to afford catalyst. If no solid formed after reaction, the solvent was removed under vacuum. Pentane or hexanes was added to the dark red residue and sonication was applied to facilitate the formation of precipitate.



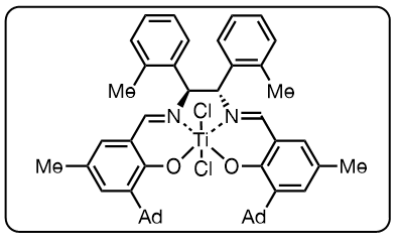
Catalyst **(*S*,*S*)-4a**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4a** as a dark red powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.33 (d, *J* = 2.2 Hz, 2H), 7.31 – 7.27 (m, 6H), 7.15 – 7.08 (m, 4H), 6.80 (d, *J* = 2.2 Hz, 2H), 5.55 (s, 2H), 2.27 – 2.23 (m, 12H), 2.22 (s, 7H), 2.15 – 2.09 (m, 5H), 1.86 – 1.79 (m, 6H), 1.79 – 1.72 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.97, 160.98, 137.76, 136.31, 136.13, 133.88, 131.50, 129.39, 129.11, 126.40, 41.82, 37.96, 37.08, 29.06, 20.63.



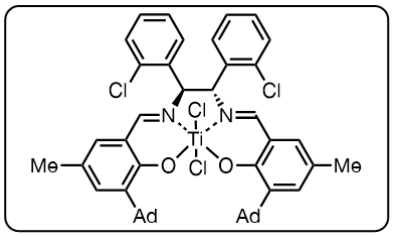
Catalyst **(*S*,*S*)-4b**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4b** as a light red powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.34 (d, *J* = 2.2 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.20 – 7.11 (m, 2H), 7.02 – 6.93 (m, 2H), 6.85 (d, *J* = 2.2 Hz, 2H), 6.02 (s, 2H), 2.30 – 2.19 (m, 18H), 2.15 – 2.09 (m, 6H), 1.86 – 1.79 (m, 6H), 1.79 – 1.71 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.40, 161.15, 137.81, 136.24, 133.94, 131.47, 126.30, 125.43, 116.05, 41.84, 37.99, 37.10, 29.07, 20.64. ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.87.



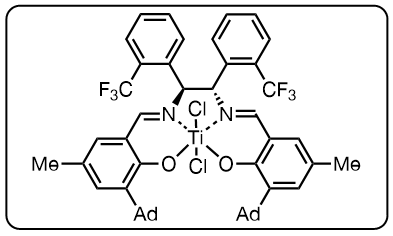
Catalyst **(*S*,*S*)-4aa**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4aa** as a light red powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.41 (s, 2H), 6.96 (s, 2H), 6.39 (s, 2H), 2.29 (s, 6H), 2.26 – 2.19 (m, 12H), 2.15 – 2.07 (m, 6H), 1.84 – 1.78 (m, 6H), 1.78 – 1.71 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.05, 161.33, 138.16, 137.30, 134.28, 131.98, 125.84, 63.17, 41.81, 38.06, 37.02, 29.01, 20.67. ^{19}F NMR (470 MHz, $CDCl_3$) δ -133.89, -139.44, -146.89, -146.93, -146.97, -157.42.



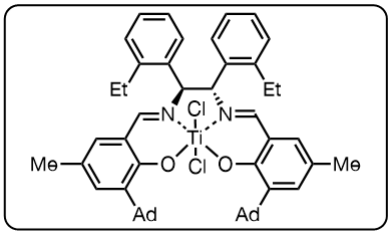
Catalyst **(*S*,*S*)-4c**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4c** as a dark red powder. ^{1}H NMR δ 7.70 (s, 2H), 7.42 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.32 (d, *J* = 2.2 Hz, 3H), 7.25 – 7.12 (m, 4H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 2.2 Hz, 3H), 5.91 (s, 2H), 2.26 – 2.24 (m, 12H), 2.22 (s, 6H), 2.15 – 2.09 (m, 6H), 1.89 (s, 6H), 1.86 – 1.80 (m, 6H), 1.79 – 1.72 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.66, 160.93, 138.95, 137.70, 135.94, 135.02, 133.83, 131.37, 130.69, 129.18, 128.90, 127.38, 126.52, 72.05, 41.81, 37.94, 37.10, 29.06, 20.63, 19.30.



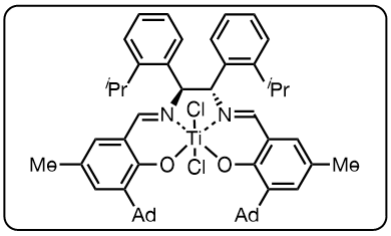
Catalyst **(*S*,*S*)-4d**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4d** as a dark red powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.28 (M, 4H), 6.83 (d, *J* = 2.2 Hz, 2H), 6.30 (s, 2H), 2.28 – 2.20 (m, 18H), 2.14 – 2.09 (m, 6H), 1.85 – 1.79 (m, 6H), 1.78 – 1.71 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.48, 161.08, 137.75, 136.30, 136.18, 133.93, 133.36, 131.47, 130.99, 130.63, 129.81, 128.28, 126.37, 71.16, 41.80, 37.95, 37.08, 29.04, 20.64.



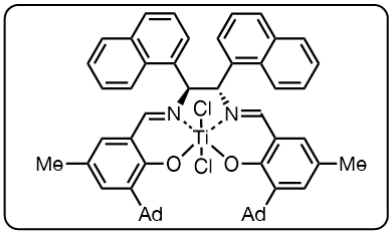
Catalyst **(*S*,*S*)-1e.** Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-1e** as a dark red powder. ^{1}H NMR δ 7.82 – 7.75 (m, 2H), 7.65 – 7.58 (m, 4H), 7.51 (s, 2H), 7.48 – 7.41 (m, 2H), 7.33 (d, *J* = 2.2 Hz, 2H), 6.74 (d, *J* = 2.2 Hz, 2H), 6.23 (s, 2H), 2.26 – 2.18 (m, 18H), 2.11 (s, 6H), 1.85 – 1.78 (m, 6H), 1.78 – 1.71 (m, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.56, 160.95, 137.79, 136.41, 134.66, 134.01, 133.45, 132.00, 131.54, 129.62, 126.39, 126.13, 71.31, 41.80, 37.96, 37.06, 29.04, 20.61. ^{19}F NMR (470 MHz, $CDCl_3$) δ -58.12.



Catalyst **(*S*,*S*)-4f**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4f** as a red powder. ^{1}H NMR δ 7.65 (s, 2H), 7.43 – 7.39 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 4H), 7.12 – 7.06 (m, 2H), 6.77 (d, *J* = 2.2 Hz, 2H), 6.00 (s, 2H), 2.44 (dq, *J* = 15.0, 7.5 Hz, 2H), 2.27 – 2.23 (m, 12H), 2.22 (s, 6H), 2.20 – 2.15 (m, 1H), 2.11 (s, 6H), 1.85 – 1.79 (m, 6H), 1.78 – 1.70 (m, 6H), 0.95 (t, *J* = 7.5 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.45, 160.91, 144.97, 137.69, 135.90, 134.05, 133.80, 131.35, 129.16, 129.14, 129.02, 127.35, 126.51, 71.52, 41.80, 37.94, 37.09, 29.06, 25.41, 20.62, 15.20.



Catalyst **(*S*,*S*)-4g**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4g** as a red powder. ^{1}H NMR δ 7.68 (s, 2H), 7.46 – 7.41 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.14 (m, 7H), 6.78 – 6.72 (m, 2H), 6.06 (s, 2H), 2.77 (hept, *J* = 6.8 Hz, 2H), 2.27 – 2.23 (m, 12H), 2.22 (s, 6H), 2.15 – 2.08 (m, 6H), 1.87 – 1.79 (m, 6H), 1.79 – 1.72 (m, 6H), 1.09 (d, *J* = 6.8 Hz, 6H), 0.55 (d, *J* = 6.7 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.74, 160.85, 149.76, 137.70, 135.95, 133.77, 133.57, 131.40, 129.22, 127.28, 126.56, 125.80, 71.59, 41.81, 37.94, 37.09, 29.05, 28.57, 25.49, 22.77, 20.62.

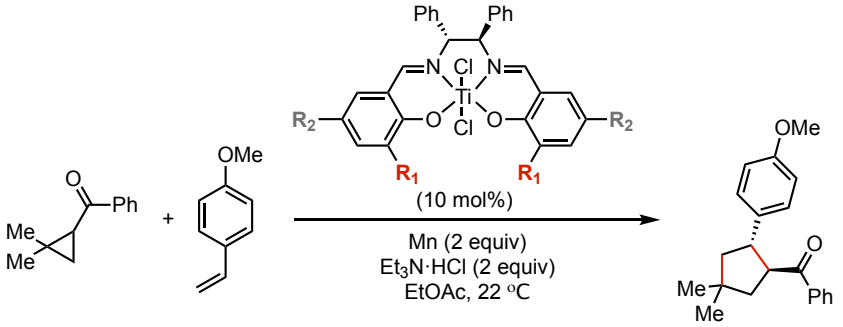


Catalyst **(*S*,*S*)-4h**. Followed General Method B, the crude solid was washed with hexanes and Et_2O to afford catalyst **(*S*,*S*)-4h** as a red powder. The catalyst shows 3 different distereomers in a ratio of 4:3:2, in which two are C_2-symmetric and one is not C_2-symmetric. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.64 (s, free phenol), 9.82 (s, free phenol), 8.63 (d, *J* = 8.6 Hz, 0H), 8.49 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 0H), 7.97 (d, *J* = 2.2 Hz, 0H), 7.93 (s, 1H), 7.88 – 7.83 (m, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.73 (s, 0H), 7.73 – 7.68 (m, 1H), 7.68 – 7.62 (m, 2H), 7.62 – 7.56 (m, 1H), 7.56 – 7.43 (m, 3H), 7.34 – 7.29 (m, 2H), 7.18 (q, *J* = 6.2, 4.6 Hz, 1H), 7.02 – 6.97 (m, 0H), 6.96 (s, 0H), 6.93 (t, *J* = 5.8 Hz, 1H), 6.90 (s, 0H), 6.89 – 6.83 (m, 1H), 6.77 (ddd, *J* = 8.6, 6.8, 1.4 Hz, 0H), 6.67 (d, *J* = 2.2 Hz, 0H), 6.63 (d, *J* = 2.2 Hz, 0H), 6.59 (d, *J* = 2.2 Hz, 1H),

6.52 (s, 1H), 6.49 (dd, J = 7.0, 1.2 Hz, 1H), 6.11 (dd, J = 11.5, 2.2 Hz, 1H), 2.34 – 2.22 (m, 13H), 2.19 – 2.11 (m, 14H), 1.90 – 1.74 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.13, 164.74, 164.43, 161.23, 161.08, 160.91, 137.82, 137.76, 137.67, 137.57, 136.21, 136.16, 136.12, 135.88, 135.61, 134.54, 134.50, 133.91, 133.81, 133.59, 133.17, 132.96, 132.90, 132.43, 131.47, 131.37, 131.33, 131.14, 130.47, 130.43, 130.28, 129.81, 129.61, 129.57, 129.47, 129.37, 129.18, 129.07, 128.48, 128.37, 127.97, 127.79, 127.71, 127.26, 126.85, 126.70, 126.48, 126.44, 126.40, 126.19, 126.02, 125.89, 125.72, 125.44, 125.23, 124.82, 124.72, 122.35, 121.66, 80.95, 76.49, 69.61, 67.68, 41.90, 41.87, 41.83, 41.79, 40.32, 38.00, 37.12, 29.10, 29.08, 20.55.

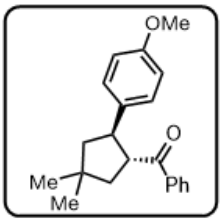
Section 4. Probing the effect of ortho and para substituents

Followed General Method A using Ti-salen complex with different ortho/para substituents and *p*-methoxystyrene as alkene, the crude of reaction mixture was analyzed by NMR. Enantio excess(ee) was analyzed by HPLC after purification. All results were obtained with two parallel experiments. The preliminary results suggested modifications at these positions are not effective for improving the catalyst performance.

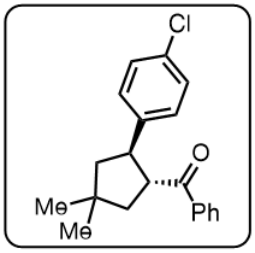


ortho (R_1) \ para (R_2)	Cl	F	H	Me	*t*-Bu	OMe
H	- / -	- / -	dr 1:1.5 / 2% ee	dr 1:1.4 / 1% ee	dr 1:1.5 / 1% ee	- / -
Me	- / -	- / -	dr 1:1.6 / -16% ee	dr 1:1.7 / -3% ee	- / -	- / -
Ph	dr 1:2.1 / 1% ee	dr 1:2.2 / 2% ee	dr 1:2 / 1% ee	dr 1:2.3 / 3% ee	dr 1:2.2 / 6% ee	dr 1:2.1 / 6% ee
t-Bu	dr 1.8:1 / 48-63% ee	dr 1.6:1 / 45% ee	dr 2.2:1 / 84% ee	dr 2.1:1 / 74% ee	dr 2.1:1 / 78% ee	dr 1.9:1 / 76% ee
Ad	dr >19:1 / 94% ee	dr >19:1 / 90% ee	dr >19:1 / 93% ee	dr >19:1 / 94% ee	dr >19:1 / 92% ee	dr >19:1 / 93% ee
CEt_3	- / -	- / -	dr 1.3:1 / 83% ee	- / -	- / -	- / -

Section 5. Characterization of products

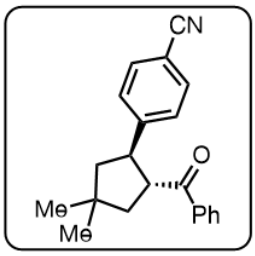


((1R,2R)-2-(4-methoxyphenyl)-4,4-dimethylcyclopentyl)(phenyl)methanone ((*R,R*)-3a). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:19, EtOAc/hexanes) to give 16.0 mg (52% yield) of **(*R,R*)-3a** as a yellow solid. . The dr was determined to be 17:1, trans diastereoisomer: -94% ee [AS, 2.5% ^{i}PrOH in hexanes, 0.4 mL/min, 254 nm; t1 = 12.61 min, t2 = 13.40 min]. Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 69%, dr was determined to be >19:1, trans diastereoisomer: -90% ee [AS, 2.5% ^{i}PrOH in hexanes, 0.4 mL/min, 254 nm; t1 = 12.65 min, t2 = 13.43 min]. The spectra data is consistent with previous literature report, the product was isolated together with around 3% cis diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.56 (d, J = 7.7 Hz, cis diastereoisomer), 7.54 – 7.45 (m, 1H), 7.43 – 7.34 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.5 Hz, cis diastereoisomer), 6.78 (d, J = 8.6 Hz, 1H), 6.53 (d, J = 8.5 Hz, cis diastereoisomer), 4.32 (q, J = 9.1 Hz, cis diastereoisomer), 3.90 (td, J = 8.5, 7.7, 4.4 Hz, 2H), 3.74 (s, 3H), 3.65 (s, cis diastereoisomer), 2.10 (dd, J = 12.8, 7.3 Hz, 1H), 2.01 (dd, J = 12.7, 6.5 Hz, 1H), 1.83 (dd, J = 12.8, 6.5 Hz, 1H), 1.72 (dd, J = 12.8, 7.3 Hz, 1H), 1.21 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.05, 158.07, 137.21, 136.22, 132.89, 132.15(cis diastereoisomer), 129.53(cis diastereoisomer), 128.55, 128.54, 128.40, 128.11(cis diastereoisomer), 128.08(cis diastereoisomer), 113.89, 113.27(cis diastereoisomer), 55.36, 55.20, 49.66, 46.85, 46.27, 38.98, 30.78, 29.74. The absolute configuration is assigned according to previous literature report[2].

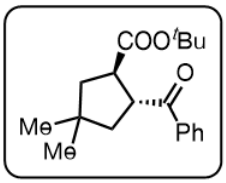


((1R,2R)-2-(4-chlorophenyl)-4,4-dimethylcyclopentyl)(phenyl)methanone ((*R,R*)-3b). Followed General Method A with Ti-salen complex **(*S,S*)-1e** and corresponding alkene, the crude product was purified by column chromatography (3:97, EtOAc/hexanes) to give 22.7 mg (73% yield) of **(*R,R*)-3b** as a white solid. The dr was determined to be 12:1, trans diastereoisomer: -94% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 7.78 min, t2 = 15.27 min]. $[\alpha]_D^{22}$ -60.0 (c0.46, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 93%, dr was determined to be 14:1, trans diastereoisomer: -90% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 7.52 min, t2 = 14.07 min]. The spectra data is consistent with previous literature report, the product was isolated together with around 4% cis diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.58 – 7.55 (m, cis diastereoisomer), 7.51 (t, *J* =7.6 Hz, 1H), 7.40 (t, *J* =7.7 Hz, 2H), 7.19 (s, 4H), 6.95 (d, *J* =8.5 Hz, cis diastereoisomer), 6.88 (d, *J* =8.5 Hz, cis diastereoisomer), 4.38 – 4.32 (ddd, cis diastereoisomer, the coupling constant is hard to be resolved), 3.95 (ddd, *J* =11.4, 9.8, 7.3 Hz, 1H),

3.87 (td, *J* =9.8, 8.1 Hz, 1H), 3.77 (td, *J* =10.5, 7.7 Hz, cis diastereoisomer), 2.33 – 2.26 (m, cis diastereoisomer), 2.13 (dd, *J* =13.0, 9.8 Hz, 1H), 2.02 (dd, *J* =12.7, 7.3 Hz, 1H), 1.96 – 1.91 (m, cis diastereoisomer), 1.81 (t, *J* =12.1 Hz, 1H), 1.72 (dd, *J* =12.9, 8.1 Hz, 1H), 1.22 (s, 3H), 1.18 (s, cis diastereoisomer), 1.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.11(cis diastereoisomer), 201.54, 142.65, 137.00, 133.08, 132.45(cis diastereoisomer), 131.91, 129.88(cis diastereoisomer), 128.88, 128.65, 128.59, 128.52(cis diastereoisomer), 128.24(cis diastereoisomer), 128.06(cis diastereoisomer), 127.93, 55.06, 50.92(cis diastereoisomer), 49.38, 48.95(cis diastereoisomer), 47.90(cis diastereoisomer), 46.86, 46.18, 43.44(cis diastereoisomer), 39.09, 38.67(cis diastereoisomer), 30.71, 29.68, 29.52(cis diastereoisomer), 28.64(cis diastereoisomer). The absolute configuration is assigned according to previous literature report[2].

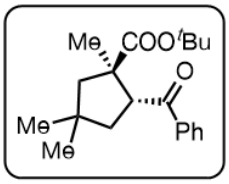


4-((1R,2R)-2-benzoyl-4,4-dimethylcyclopentyl)benzonitrile ((*R,R*)-3d). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:9, EtOAc/hexanes) to give 25.2 mg (83% yield) of **(*R,R*)-3d** as a white solid. The dr was determined to be >19:1, trans diastereoisomer: 99% ee [AD, 5.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 6.36 min, t2 = 9.78 min]. $[\alpha]_D^{22}$-60.3 (c0.47, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 87%, dr was determined to be >19:1, trans diastereoisomer: 79% ee [AD, 5.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 6.39 min, t2 = 9.83 min]. The spectra data is consistent with previous literature report. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.08 – 4.00 (m, 1H), 3.89 (q, *J* = 9.5 Hz, 1H), 2.17 (dd, *J* = 13.1, 10.1 Hz, 1H), 2.05 (dd, *J* = 12.7, 7.5 Hz, 1H), 1.83 (t, *J* = 12.2 Hz, 1H), 1.73 (dd, *J* = 13.1, 8.3 Hz, 1H), 1.23 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.96, 149.90, 136.68, 133.29, 132.35, 128.74, 128.52, 128.38, 119.12, 110.12, 54.89, 49.01, 46.83, 46.53, 39.24, 30.61, 29.83, 29.59. The absolute configuration is assigned according to previous literature report[2].

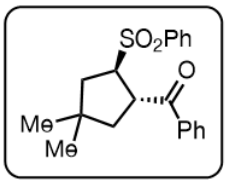


***tert*-butyl (1*R*,2*R*)-2-benzoyl-4,4-dimethylcyclopentane-1-carboxylate ((*R,R*)-3e).** Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:19, EtOAc/hexanes) to give 27.7 mg (92% yield) of **(*R,R*)-3e** as a yellow oil. The dr was determined to be 19:1, trans diastereoisomer: 83% ee [IA, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 8.68 min, t2 = 9.60 min]. $[\alpha]_D^{22}$ -30.7 (c0.55, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 93%, dr was determined to be >19:1, trans diastereoisomer: 43% ee. [IA, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 8.15 min, t2 = 9.06 min]. The spectra

data is consistent with previous literature report. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 (m, 2H), 4.22 (q, *J* = 8.9 Hz, 1H), 3.54 (q, *J* = 8.8 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.78 (dd, *J* = 12.8, 8.8 Hz, 1H), 1.60 (dd, *J* = 12.6, 8.5 Hz, 1H), 1.36 (s, 9H), 1.10 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.61, 174.78, 136.98, 133.07, 128.71, 128.67, 80.49, 49.17, 46.78, 46.11, 44.78, 40.08, 29.23, 28.94, 28.13. The absolute configuration is assigned according to previous literature report[2].

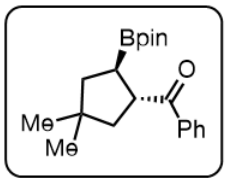


***tert*-butyl (1R,2R)-2-benzoyl-1,4,4-trimethylcyclopentane-1-carboxylate ((*R,R*)-3f).** Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:19, EtOAc/hexanes) to give 28.6 mg (91% yield) of **(*R,R*)-3f** as a yellow oil. The dr was determined to be 19:1, trans diastereoisomer: 92% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 3.67 min, t2 = 4.30 min]. $[\alpha]_D^{22}$ -61.4 (c0.57, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 91%, the dr was determined to be >19:1, trans diastereoisomer: 60% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 3.64 min, t2 = 4.26 min]. The spectra data is consistent with previous literature report, there is also small portion of unreacted cyclopropyl ketone substrate which cannot be separated by chromatography, its peaks are assigned accordingly. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.96 – 7.92 (m, cyclopropyl ketone), 7.52 (m, 1H), 7.47 (d, cyclopropyl ketone)7.42 (m, 2H), 4.65 (dd, *J* = 11.4, 6.8 Hz, 1H), 2.48 (dd, *J* = 7.5, 5.7 Hz, cyclopropyl ketone), 2.22 (t, *J* = 12.1 Hz, 1H), 2.13 (dd, *J* = 13.5, 1.5 Hz, 1H), 1.66 (ddd, *J* = 12.9, 6.8, 1.6 Hz, 1H), 1.53 (d, *J* = 13.4 Hz, 1H), 1.38 (s, 9H), 1.14 (s, 3H), 1.10 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.98, 177.01, 138.47, 132.91, 132.54(cyclopropyl ketone), 128.76, 128.58, 128.12(cyclopropyl ketone), 80.78, 55.13, 53.54, 50.88, 43.87, 37.92, 33.02(cyclopropyl ketone), 30.45, 29.13, 27.97, 27.20(cyclopropyl ketone), 22.64, 22.15(cyclopropyl ketone), 18.62(cyclopropyl ketone). The absolute configuration is assigned according to previous literature report[2].

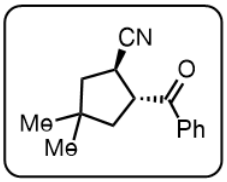


((1S,2R)-4,4-dimethyl-2-(phenylsulfonyl)cyclopentyl)(phenyl)methanone ((*R,R*)-3g). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:4, EtOAc/hexanes) to give 21.3 mg (62% yield) of **(*R,R*)-3g** as a white solid. The dr was determined to be 17:1, trans diastereoisomer: 79% ee [AD, 6.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 11.07 min, t2 = 14.30 min]. $[\alpha]_D^{22}$ -14.9 (c0.43, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 83%, the dr was determined to be 5:1, trans diastereoisomer: 25% ee [AD, 6.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 11.11 min, t2 = 14.19 min]. The spectra data is consistent with previous literature report. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 4H), 7.53 (dt, *J* = 19.7, 7.4 Hz, 2H), 7.42 (dt, *J* = 15.0, 7.6 Hz, 4H), 4.62 (q, *J* = 8.8 Hz, 1H), 4.35

(dt, *J* = 10.6, 7.4 Hz, 1H), 2.18 (dt, *J* = 12.5, 9.3 Hz, 2H), 1.90 (dd, *J* = 13.1, 8.7 Hz, 1H), 1.59 (dd, *J* = 12.7, 6.6 Hz, 1H), 1.18 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.49, 138.89, 135.58, 133.67, 133.52, 129.23, 128.74, 128.63, 128.50, 64.74, 47.28, 46.52, 40.99, 40.64, 28.87, 28.19. The absolute configuration is assigned according to previous literature report[2].

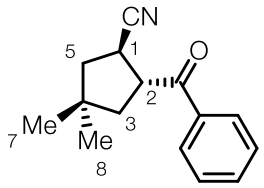


((1R,2R)-4,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)(phenyl)methanone ((*R,R*)-3h). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:19, EtOAc/hexanes) to give 11.0 mg (50% yield) of **(*R,R*)-3h** as a white solid. The dr was determined to be 7:1, trans diastereoisomer: 82% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 5.03 min, t2 = 6.54 min]. $[\alpha]_D^{22}$ -30.5 (c0.22, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 44%, the dr was determined to be 7:1, trans diastereoisomer: 20% ee [AD, 0.5% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 5.19 min, t2 = 6.74 min]. The spectra data is consistent with previous literature report, the product was isolated together with around 6% of cis diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.94 – 7.91 (m, cis diastereoisomer), 7.71 (dd, *J* = 5.7, 3.3 Hz, cis diastereoisomer), 7.52 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.22 (dd, *J* = 8.5, 5.9 Hz, cis diastereoisomer), 3.97 (q, *J* = 8.9 Hz, 1H), 2.03 (q, *J* = 9.1 Hz, 1H), 1.83 (dd, *J* = 12.7, 9.2 Hz, 1H), 1.75 (dd, *J* = 12.3, 9.2 Hz, 1H), 1.67 (dd, *J* = 12.7, 8.7 Hz, 1H), 1.53 (dd, *J* = 12.3, 9.1 Hz, 1H), 1.19 (d, *J* = 2.9 Hz, 12H), 1.07 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.13, 137.55, 132.64, 128.80, 128.47, 83.37, 49.05, 46.26, 43.84, 40.85, 29.19, 28.93, 24.90, 24.80. The absolute configuration is assigned according to previous literature report[2].

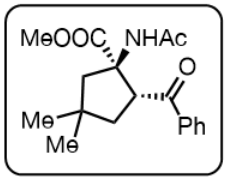


(1R,2R)-2-benzoyl-4,4-dimethylcyclopentane-1-carbonitrile ((*R,R*)-3i). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:9, EtOAc/hexanes) to give 16.0 mg (70% yield) of **(*R,R*)-3i** as a white solid. The dr was determined to be 11:1, trans diastereoisomer: 52% ee [AS, 5.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 11.34 min, t2 = 15.60 min]. $[\alpha]_D^{22}$ -54.7 (c0.32, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 69%, the dr was determined to be 3:1, trans diastereoisomer: 30% ee [AS, 5.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 11.35 min, t2 = 15.57 min]. IR(Film) 2958, 2932, 2869, 1681, 1597, 1580, 1464, 1448, 1371, 1240, 1223, 1010, 849, 772, 699, 669, 656 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.65 – 7.57 (m, 1H), 7.54 – 7.46 (m, 2H), 4.18 (dt, *J* = 9.9, 8.1 Hz, 1H), 3.74 (q, *J* = 8.3 Hz, 1H), 2.12 (dd, *J* = 13.1, 9.9 Hz, 1H), 2.05 (dd, *J* = 12.9, 8.9 Hz, 1H), 1.93 (dd, *J* = 12.9, 8.2 Hz, 1H), 1.61 – 1.54 (m, 1H), 1.22 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.40, 135.63, 133.86, 128.99, 128.81, 122.81, 77.16, 51.74,

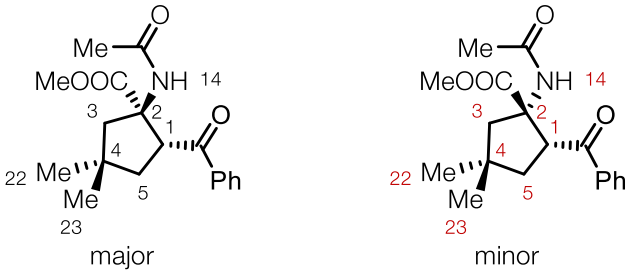
46.06, 45.23, 40.78, 28.87, 28.52, 28.34. MS (DART) exact mass calculated for [$C_{15}H_{18}NO^+$]: 228.1379, found 228.1377.



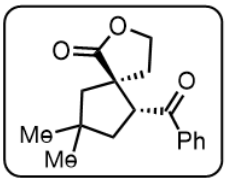
Relative stereochemistry assignments were based on 1D 1H supported by ROESY and HSQC. Major product trans: ROE from H2, H3' (top), H5' (top) to H7 defines "top". ROE from H8 to H3'' (bottom), H5'' (bottom) and H1 defines "bottom" and shows that H2 is trans to H1. The absolute configuration is assigned according to previous literature report[2].



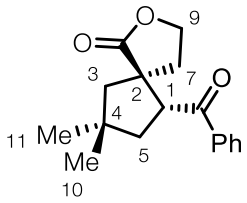
methyl (1R,2R)-1-acetamido-2-benzoyl-4,4-dimethylcyclopentane-1-carboxylate ((*R,R*)-3j). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (2:3, EtOAc/hexanes) to give 24.8 mg (83% yield, containing another diastereoisomer in a ratio of 10:1) of **(*R,R*)-3j** as a white solid. The dr was determined to be 10:1, trans diastereoisomer: 95% ee [AS, 3.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 10.92 min, t2 = 14.64 min]. $[\alpha]_D^{22}$ -72.8 (c0.50, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 58%, the dr was determined to be 6:1, trans diastereoisomer: 87% ee[AS, 3.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 10.93 min, t2 = 14.60 min]. IR(Film) 3294, 3209, 3062, 2979, 2953, 2868, 1738, 1679, 1655, 1596, 1580, 1539, 1448, 1370, 1318, 1275, 1244, 1215, 1181, 1136, 1071, 1018, 1001, 983, 837, 55, 697, 663 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, minor diastereoisomer), 7.92 – 7.83 (m, 2H), 7.60 (t, *J* = 7.6 Hz, minor diastereoisomer), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.47 (m, minor diastereoisomer), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (s, minor diastereoisomer), 6.78 (s, 1H), 5.43 (dd, *J* = 13.4, 7.3 Hz, 1H), 4.23 (dd, *J* = 12.4, 6.9 Hz, minor diastereoisomer), 3.84 (s, 3H), 3.39 (s, minor diastereoisomer), 2.56 (d, *J* = 14.4 Hz, minor diastereoisomer), 2.52 (d, *J* = 14.0 Hz, 1H), 2.44 (d, *J* = 14.3 Hz, minor diastereoisomer), 2.25 (t, *J* = 12.9 Hz, 1H), 2.18 (t, *J* = 12.7 Hz, minor diastereoisomer), 1.98 (dd, *J* = 11.0, 3.9 Hz, 1H, in this region it contains one methine and one methyl peak from minor diastereoisomer), 1.93 (s, 3H), 1.46 (s, 3H), 1.18 (d, *J* = 7.0 Hz, methyl groups from minor diastereoisomer), 1.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.88(minor diastereoisomer), 199.95, 175.87, 172.89(minor diastereoisomer), 170.21(minor diastereoisomer), 169.42, 136.89, 134.16(minor diastereoisomer), 133.40, 128.97(minor diastereoisomer), 128.75, 128.67(minor diastereoisomer), 128.61, 128.39(minor diastereoisomer), 69.26(minor diastereoisomer), 68.02, 52.98, 52.84, 52.39(minor diastereoisomer), 50.46(minor diastereoisomer), 50.00(minor diastereoisomer), 48.06, 45.59, 45.53, 38.08, 36.89(minor diastereoisomer), 32.15, 31.63(minor diastereoisomer), 31.59(minor diastereoisomer), 30.55, 24.69, 23.53(minor diastereoisomer). MS (DART) exact mass calculated for [$C_{18}H_{24}NO_4^+$]: 318.1694, found 318.1690.



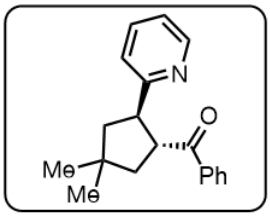
Relative stereochemistry assignments were based on 1D 1H supported by ROESY and HSQC. Major product: NOE from H3' (top)to H14 defines "top" and shows H1 is on the same side of H14. Minor product: NOE from H14 to H3'' (bottom), H5'' (bottom) and H1 defines "bottom" and shows that H1 is on the opposite side of H14. The absolute configuration is assigned according to previous literature report[2].



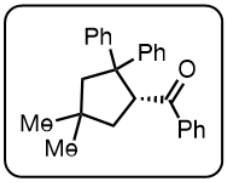
(5S,6R)-6-benzoyl-8,8-dimethyl-2-oxaspiro[4.4]nonan-1-one ((*R,R*)-3k). Followed General Method A with Ti-salen complex **(*S,S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:9, EtOAc/hexanes) to give 24.7 mg (90% yield) of **(*R,R*)-3k** as a white solid. The dr was determined to be 7:1, <u>trans diastereoisomer:</u> 91% ee [AS, 10.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 7.79 min, t2 = 9.72 min]. $[\alpha]_D^{22}$ -48.8 (c0.49, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S,S*)-4a** and corresponding alkene, the yield was determined to be 85%, the dr was determined to be 6:1, <u>trans diastereoisomer:</u> 66% ee[AS, 10.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 7.77 min, t2 = 9.68 min]. IR(Film) 2954, 2928, 2868, 1758, 1668, 1595, 1579, 1463, 1447, 1367, 1314, 1268, 1247, 1165, 1021, 967, 836, 807, 731, 688 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.40 (m, 2H), 4.40 (dd, *J* = 11.9, 6.8 Hz, 1H), 4.09 (dt, *J* = 8.8, 7.3 Hz, 1H), 3.93 (td, *J* = 8.6, 4.9 Hz, 1H), 2.35 (dt, *J* = 12.9, 7.7 Hz, 1H), 2.24 – 2.15 (m, 2H), 2.04 (ddd, *J* = 12.7, 7.3, 5.0 Hz, 1H), 1.85 (dd, *J* = 12.9, 6.8 Hz, 1H), 1.75 (d, *J* = 13.3 Hz, 1H), 1.22 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.33, 181.42, 136.94, 133.83, 129.04, 128.68, 77.16, 65.90, 53.79, 52.94, 51.18, 44.75, 38.16, 33.82, 30.61, 30.03, 29.82. MS (DART) exact mass calculated for [$C_{17}H_{21}O_3^+$]: 273.1480, found 273.1474.



Relative stereochemistry assignments were based on 1D 1H supported by ROESY and HSQC. Major product trans: ROE from H1, H3' (top), H5' (top) to H10 defines "top". ROE from H3'' (bottom), H5'' (bottom) to H11 defines "bottom". Key NOE correlation is from H7'' to H3'', indicating that two methylene groups are on the same side of benzoyl group. The absolute configuration is assigned according to previous literature report[2].



((1R,2R)-4,4-dimethyl-2-(pyridin-2-yl)cyclopentyl)(phenyl)methanone ((*R*,*R*)-3l). Followed General Method A with Ti-salen complex **(*S*,*S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (1:9, EtOAc/hexanes) to give 18.6 mg (67% yield) of **(*R*,*R*)-3l** as a white solid. The dr was determined to be 10:1, trans diastereoisomer: 94% ee [OD, 3.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 5.51 min, t2 = 8.23 min]. $[\alpha]_D^{22}$ -57.8 (c0.37, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S*,*S*)-4a** and corresponding alkene, the yield was determined to be 85%, the dr was determined to be >19:1, trans diastereoisomer: 39% ee[OD, 3.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 5.41 min, t2 = 7.94 min]. IR(Film). 3048, 3006, 2952, 2925, 2865, 2856, 1681, 1589, 1567, 1472, 1448, 1436, 1339, 1276, 1257, 1223, 1209, 1179, 1011, 993, 788, 772, 758, 706, 686, 669, 652, 531 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 – 8.48 (m, 1H), 7.93 – 7.85 (m, 2H), 7.48 (tq, *J* =5.4, 1.6 Hz, 2H), 7.38 (t, *J* =7.6 Hz, 2H), 7.17 (d, *J* =7.7 Hz, 1H), 7.07 – 6.99 (m, 1H), 4.42 – 4.33 (m, 1H), 4.05 (ddd, *J* =11.4, 9.4, 7.5 Hz, 1H), 2.19 (dd, *J* =12.9, 10.6 Hz, 1H), 2.07 – 1.93 (m, 2H), 1.74 (dd, *J* =13.0, 8.1 Hz, 1H), 1.20 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.16, 162.96, 149.52, 137.07, 136.29, 132.85, 128.71, 128.51, 123.66, 121.44, 53.03, 48.91, 48.75, 46.39, 39.55, 30.26, 29.84, 29.71. MS (DART) exact mass calculated for $[C_{19}H_{22}NO^+]$: 280.1691, found 280.1685. The absolute configuration is assigned according to previous literature report[2].

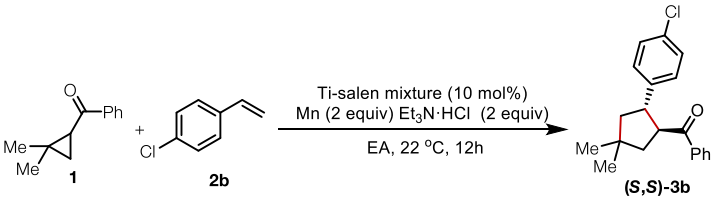


(R)-(4,4-dimethyl-2,2-diphenylcyclopentyl)(phenyl)methanone ((*R*,*R*)-3m). Followed General Method A with Ti-salen complex **(*S*,*S*)-4e** and corresponding alkene, the crude product was purified by column chromatography (2:3, DCM/hexanes) to give 10.0 mg (29% yield) of **(*R*,*R*)-3m** as a white solid. 82% ee [OD, 1.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 6.72 min, t2 = 7.79 min]. $[\alpha]_D^{22}$ -142.5 (c0.2, $CHCl_3$). Followed General Method A with Ti-salen complex **(*S*,*S*)-4a** and corresponding alkene, the yield was determined to be 74%, 32% ee[OD, 1.0% ^{i}PrOH in hexanes, 1.0 mL/min, 254 nm; t1 = 6.53 min, t2 = 7.57 min]. The spectra data is consistent with previous literature report. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.48 – 7.42 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.16 (d, *J* = 8.7 Hz, 1H), 3.27 (d, *J* = 12.6 Hz, 1H), 2.43 (d, *J* = 12.6 Hz, 1H), 2.22 (dd, *J* = 13.9, 8.7 Hz, 1H), 1.97 (dd, *J* = 13.8, 1.8 Hz, 1H), 1.21 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.10, 148.79, 147.30, 138.67, 132.32, 128.47, 128.39, 128.13, 127.91, 127.50, 126.93, 125.87, 125.50, 59.94, 53.57, 52.04, 44.26, 38.28, 32.38, 31.97. The absolute configuration is assigned according to previous literature report[2].

Section 6. Non-linear effect study and diffusion NMR experiments

Non-linear effect study

Non-linear effect study was conducted to verify whether this system operates through a monomeric or multiple center. Catalysts made from (1R,2R)-1,2-diphenylethane-1,2-diamine and (1S,2S)-1,2-diphenylethane-1,2-diamine are mixed in different ratios (roughly 3:2, 7:3, 4:1, 9:1). The accurate enantiomeric excess (ee) of the mixed catalysts was determined by HPLC. Subsequently, following General Method A, each portion mixture of catalysts was dissolved in 2 mL EA and 1 mL of catalyst mixture was used as catalyst to conduct standard reaction. Considering the solubility of the Ti catalysts, para-tBu-ortho-tBu Ti-catalysts were used for the study. The crude product was purified, and isolated product was submitted to HPLC to test the ee of product. The ee of products then was plotted versus the ee of the catalysts.



Ratio of catalysts	ee of catalyst(%)	ee of product(%)
10:0	99	82
9:1	84	68
8:2	67	53
7:3	44	35
6:4	24	20
5:5	2	1
racemic	0	0

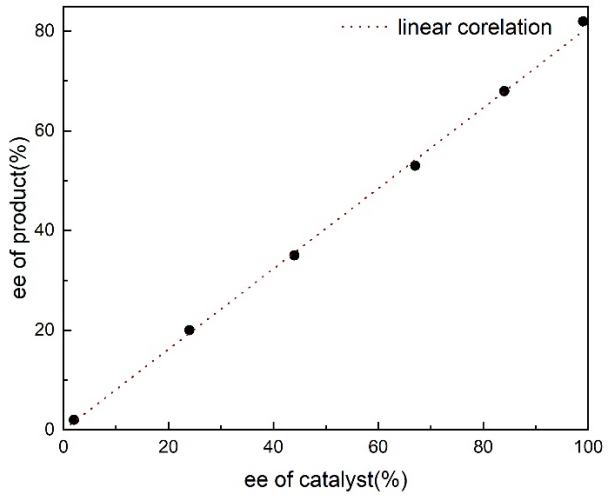


Figure S1. Non-linear effect plot. No obvious non-linear effect was observed for p-^{t}Bu-o-^{t}Bu Ti catalysts.

Diffusion NMR

Diffusion NMR spectra were acquired on a Varian INOVA 600 MHz spectrometer equipped with a 5 mm HCN inverse detection triple resonance probe with single-axis pulsed field gradients using the DgcsteSL_cc stimulated echo sequence with self-compensating gradient schemes and convection compensation[3] as provided in VnmrJ 3.2A. The diffusion delay was set at 150 ms, and the strength of the diffusion gradient with duration of 1.4 ms was varied from 3 to 76 G/cm in 32 square spaced increments. Spectra for each PFG increment were collected with 4 steady state scans and 8 scans, 1.6 s acquisition time and 3 s relaxation delay. Diffusion datasets were analyzed in MNova 14.0.1 (Mestrelab Research) with single exponential fitting of integrals of multiple resonances in each compound after careful phasing and 7th order polynomial baseline correction. The ligand and complex were chosen because they are structurally similar to optimal catalyst and have good solubilities. The diffusion coefficients for salen and complex were found to be 3.8 x 10^{-6} cm^2/s and 4.0 x 10^{-6} cm^2/s, respectively, indicating that the aggregation states of both compounds are similar.

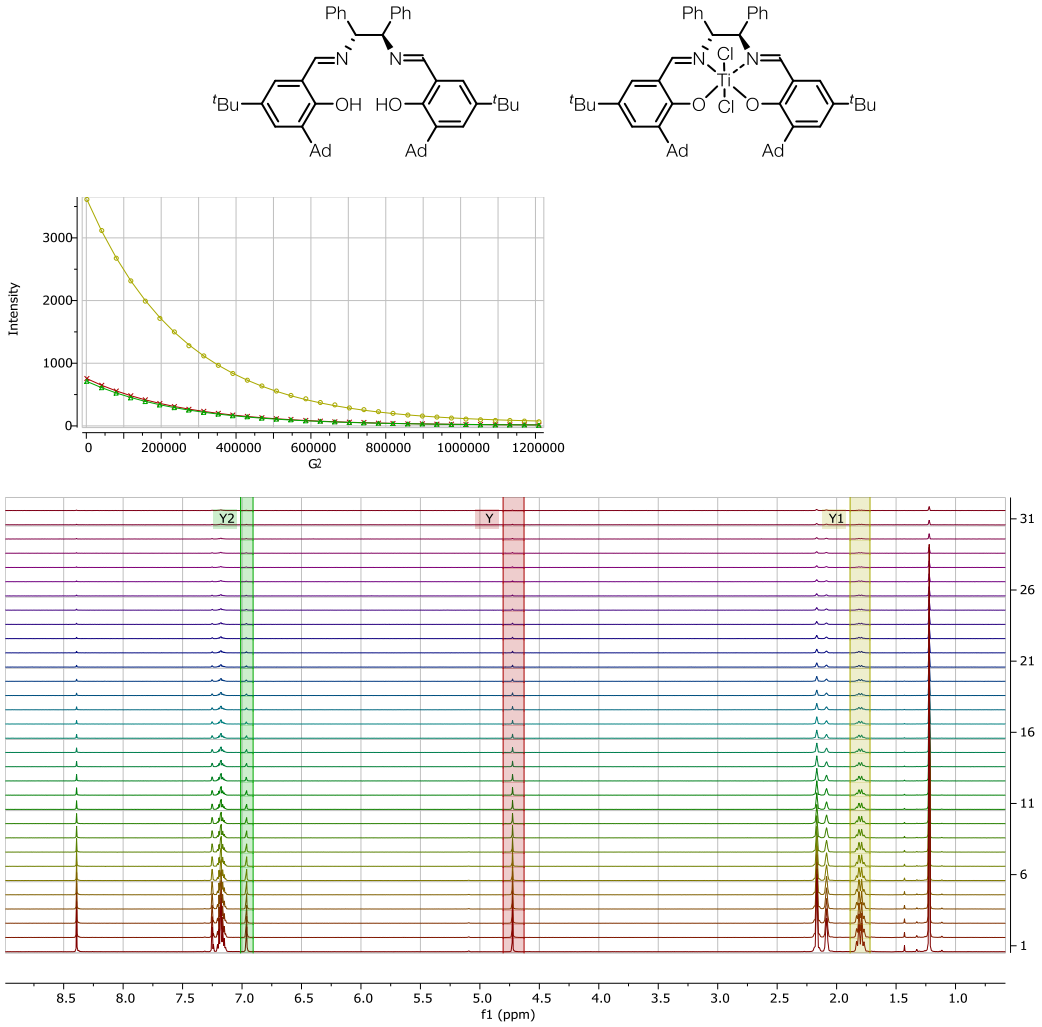


Figure S2. Diffusion NMR spectrum of ortho-Ad para-tBu salen ligand

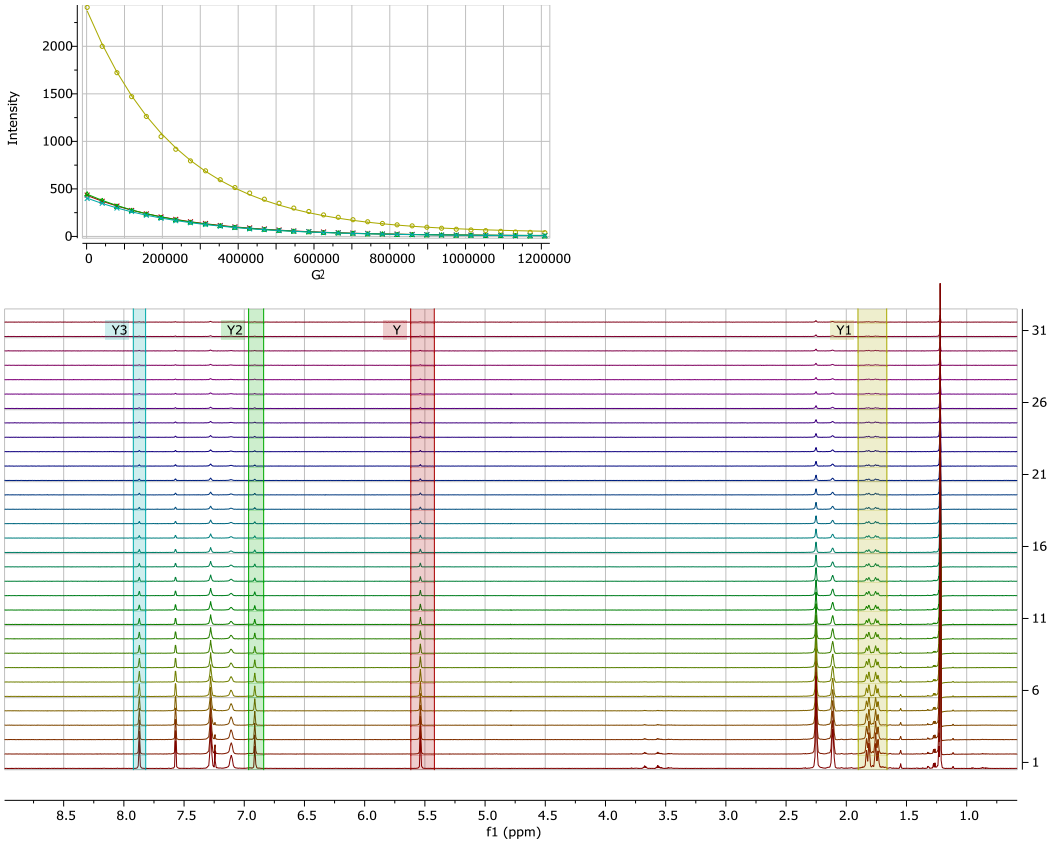


Figure S3. Diffusion NMR spectrum of ortho-Ad para-tBu Ti complex

Section 7. Electrochemical studies of catalysts

Cyclic voltammetry study

Cyclic voltammetry (CV) experiments were conducted in a N_2-filled glovebox with a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a nonaqueous Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M Bu_4PF_6/MeCN) reference electrode, and a platinum wire counter electrode. The catalyst of interest was dissolved in anhydrous DCM with Bu_4NPF_6 as electrolyte. Current was reported in µA, while all potentials were reported in mV against the $Fc^{+/0}$ redox couple. The CV study revealed that there is a weak correlation between the electronic properties of para-substituents and redox potentials of Ti-catalysts, ranging from -0.95 V to -1.13 V. But complex with electron-neutral or electron-rich substituents have almost same redox potential. Notably, para-CF_3 complex has a less reversible redox activity.

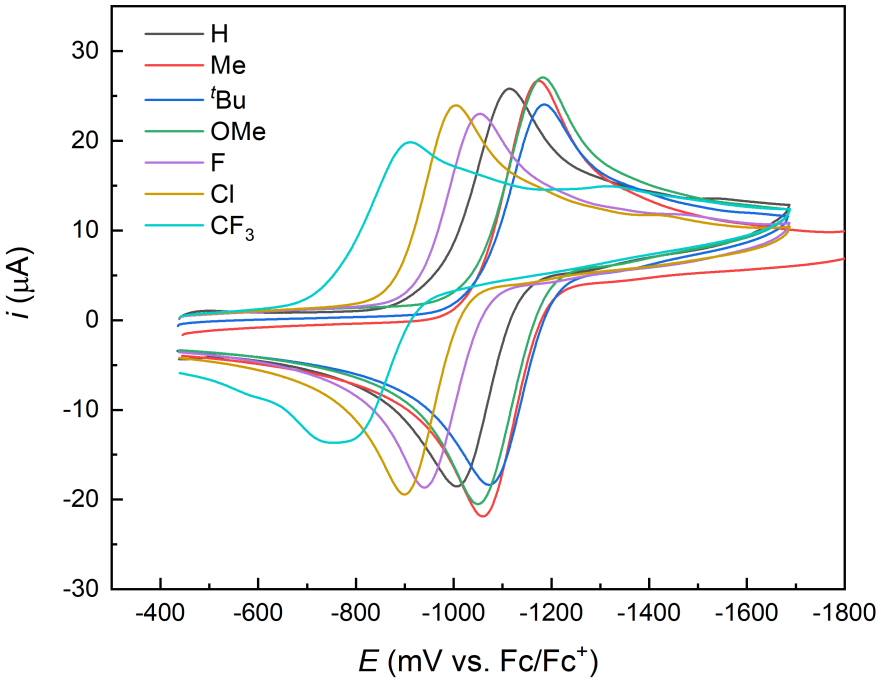


Figure S4. Cyclic voltammogram of *ortho*-Ad Ti(salen) complexes. Para-substituents of catalysts were varied, and CVs were recorded respectively. Conditions: Ti-complexes (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

Stability test with bulk electrolysis

Electrochemical stability experiments were conducted in a nitrogen filled glovebox using 1 mM solutions of catalyst in 0.1 M Bu_4PF_6/DCM. A Pine Wavenow potentiostat was employed for controlled potential bulk electrolysis and cyclic voltammograms. Reticulated vitreous carbon (RVC) (100 PPI, 4 x 0.5 x 0.5 cm^3) was purchased from ERG Aerospace and used as received. Fresh anodes and cathodes were prepared for each experiment by affixing nickel wire to RVC. A custom divided cell separated with a fine frit and additional two ports on the anodic side to accommodate a reference electrode and glassy carbon working electrode (3 mm) was used for controlled potential bulk electrolysis. A nonaqueous Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M Bu_4PF_6/MeCN) reference electrode was used for bulk electrolysis experiments and was kept proximal to the working electrode during controlled potential electrolysis. CVs were collected

using a glassy carbon working electrode (0.071 cm^2), platinum wire auxiliary electrode, and nonaqueous Ag/Ag^+ reference electrode.

To the cathodic compartment was added 0.1 M Bu_4PF_6/DCM (5 mL) and a magnetic stir bar. To the anodic side was added a stir bar and 1 mM solution of catalyst in 0.1 M Bu_4PF_6/DCM (5 mL). The glassy carbon electrode, platinum wire auxiliary electrode, and nonaqueous Ag/Ag^+ reference electrode were then immersed in the anodic side solution and a CV was recorded at 500 mV/s. The platinum wire electrode and glassy carbon electrode were removed. The RVC anode and cathode were then inserted into the anodic and cathodic solutions, respectively. The RVC anode and cathode were submerged such that 2 cm of the RVC was in contact with the solution. Controlled potential bulk electrolysis was then performed at -1.3 V vs. $Ag/AgNO_3$ until the current plateaued at 0 A. At this point, controlled potential electrolysis was initiated at 0 V vs. $Ag/AgNO_3$ until the current plateaued at 0 A to return all of the reduced Ti^{III}(salen) to the original Ti^{IV}(salen) redox state. After electrolysis was stopped, the glassy carbon electrode and platinum wire auxiliary electrode were inserted into the anodic solution and the "After Electrolysis" CV was recorded at 50 mVs. Overlay of the "Before Electrolysis" and "After Electrolysis" CVs revealed a diminish in current after electrolysis for *p*-CF_3 Ti(salen), indicative that this complex is unstable to reduction.

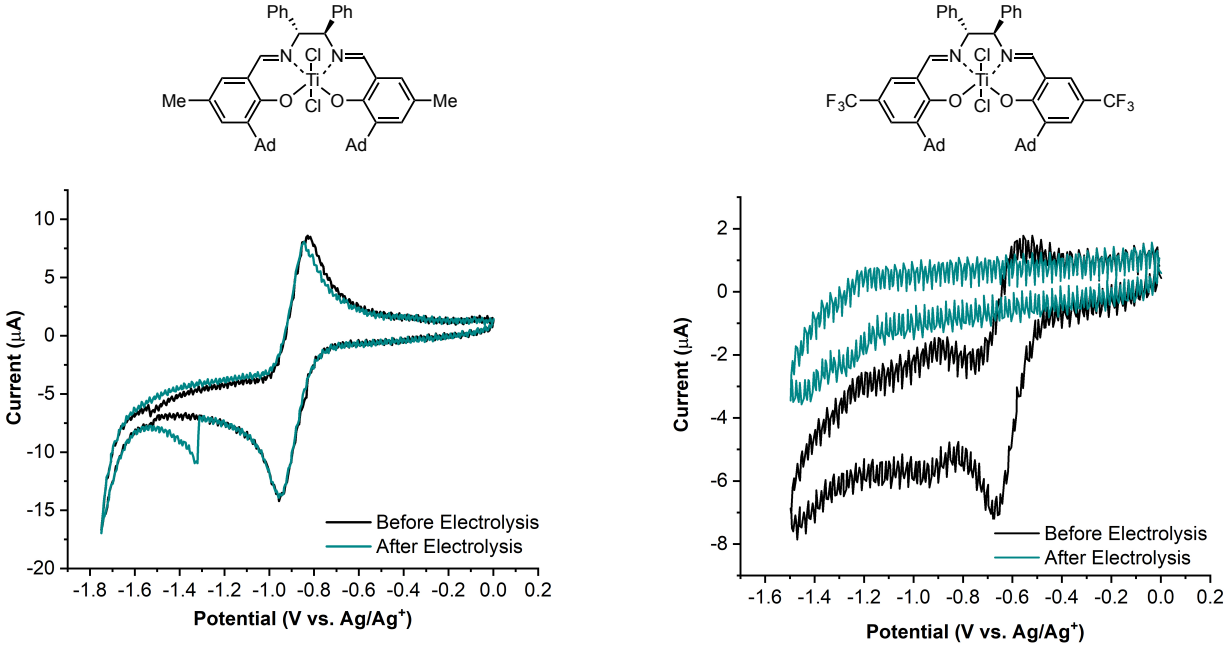


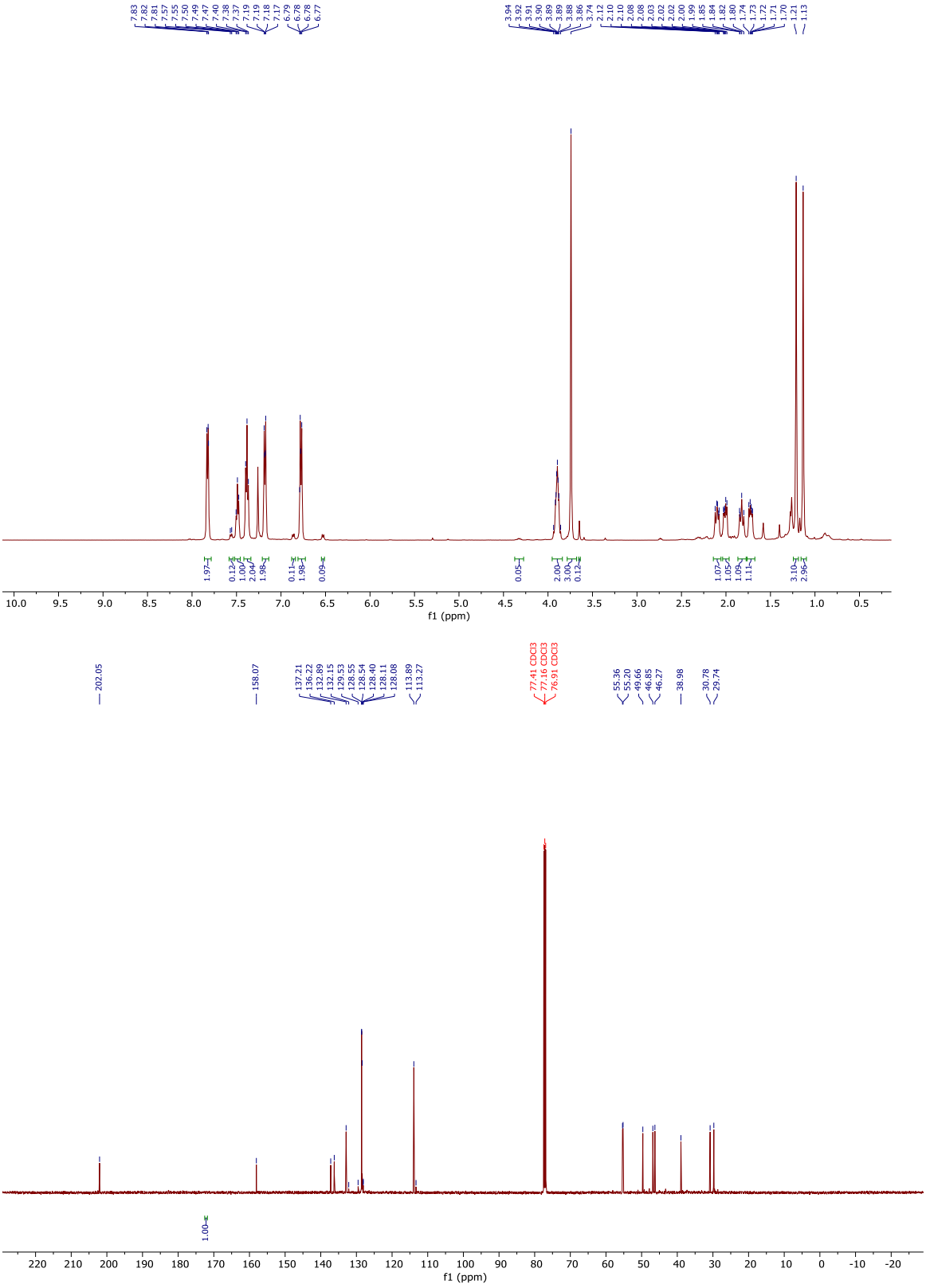
Figure S5. Before and after electrolysis CVs of (left) *p*-Me Ti(salen) and (right) *p*-CF_3 Ti(salen).

Section 8. Reference

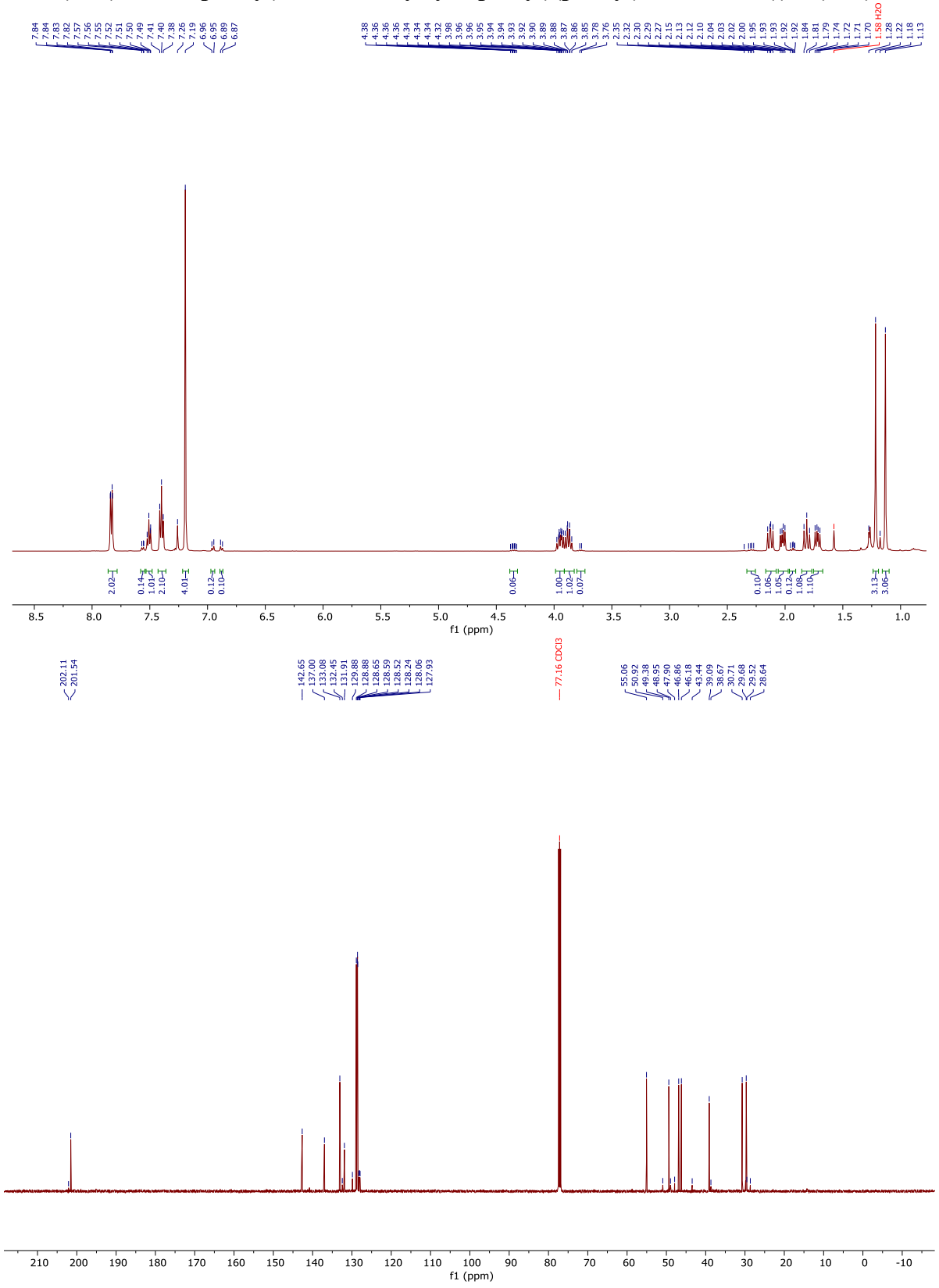
1. Kim, H.; Nguyen, Y.; Yen, C. P. H.; Chagal, L.; Lough, A. J.; Kim, B. M.; Chin, J. Stereospecific synthesis of C 2 symmetric diamines from the mother diamine by resonance-assisted hydrogen-bond directed diaza-Cope rearrangement. *J. Am. Chem. Soc.* **2008**, *130*, 12184-12191.
2. Hao, W.; Harenberg, J. H.; Wu, X.; MacMillan, S. N.; Lin, S. Diastereo-and enantioselective formal [3+ 2] cycloaddition of cyclopropyl ketones and alkenes via Ti-catalyzed radical redox relay *J. Am. Chem. Soc.* **2018**, *140*, 3514-3517.
3. Jerschow, A.; Müller, N. Suppression of Convection Artifacts in Stimulated-Echo Diffusion Experiments. Double-Stimulated-Echo Experiments *J. Magn. Reson.* **1997**, *125*, 372-375.

Section 9. Spectral data for products

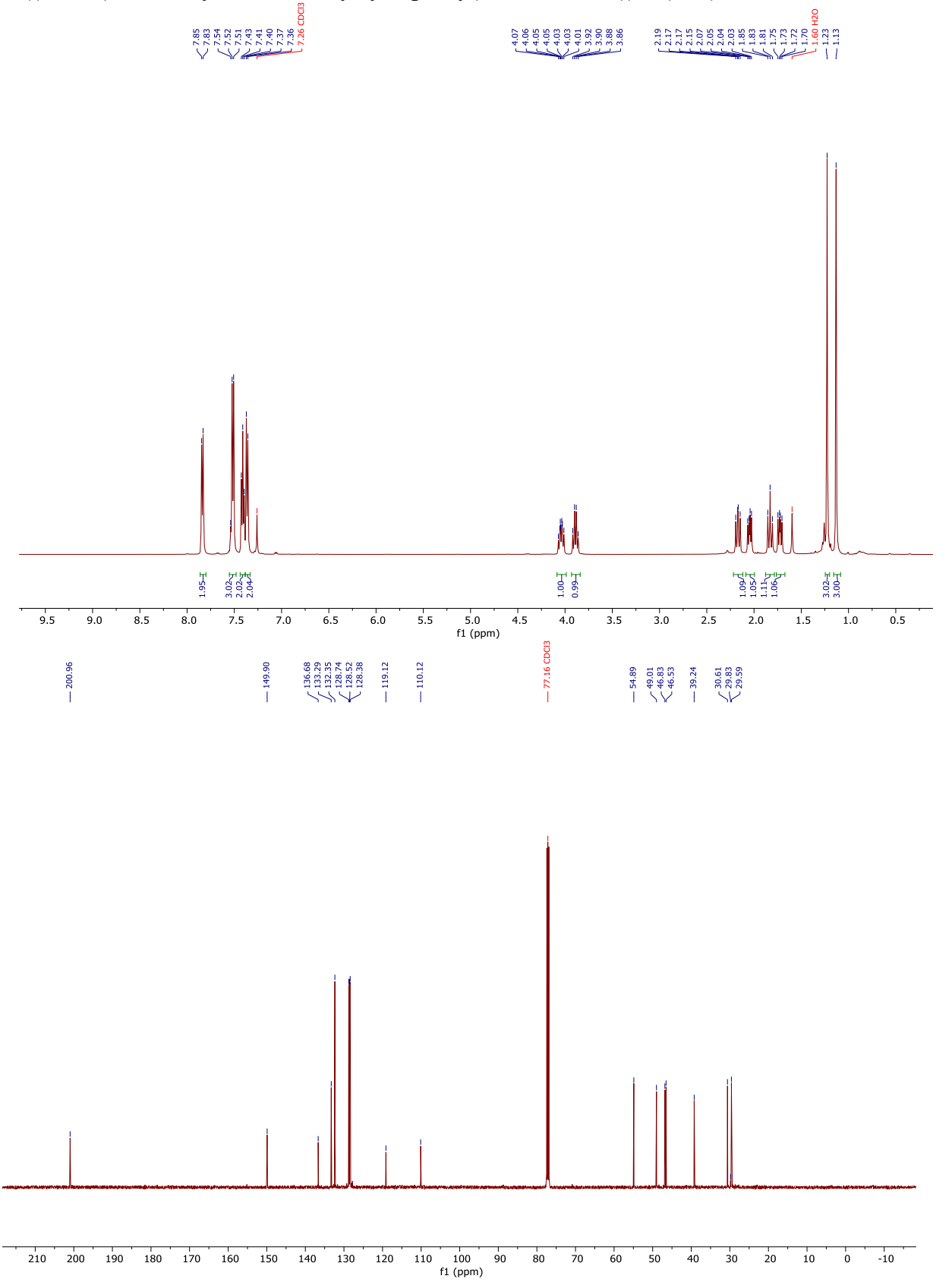
((1R,2R)-2-(4-methoxyphenyl)-4,4-dimethylcyclopentyl)(phenyl)methanone ((*R,R*)-3a).



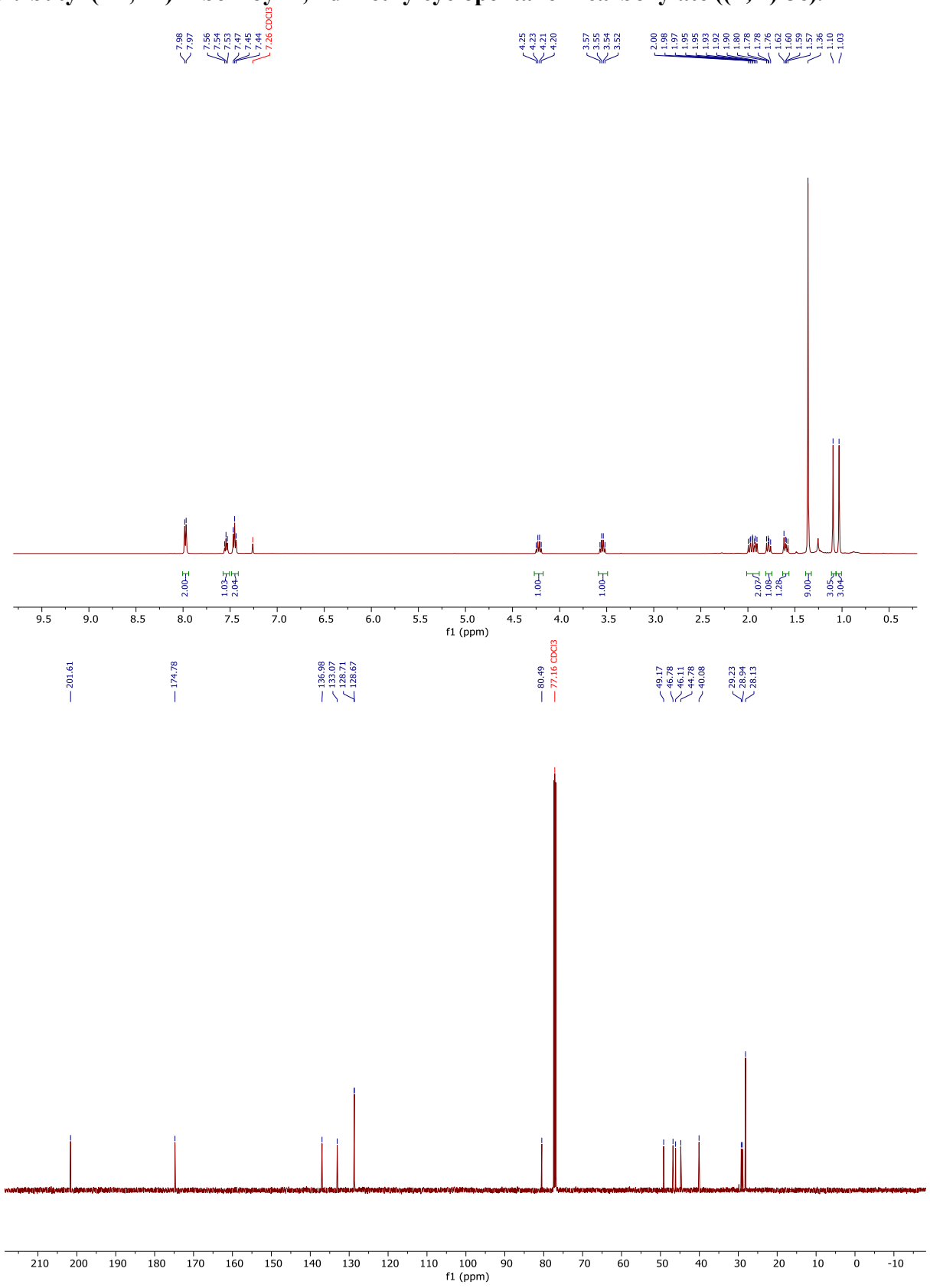
((1R,2R)-2-(4-chlorophenyl)-4,4-dimethylcyclopentyl)(phenyl)methanone ((*R*,*R*)-3b).



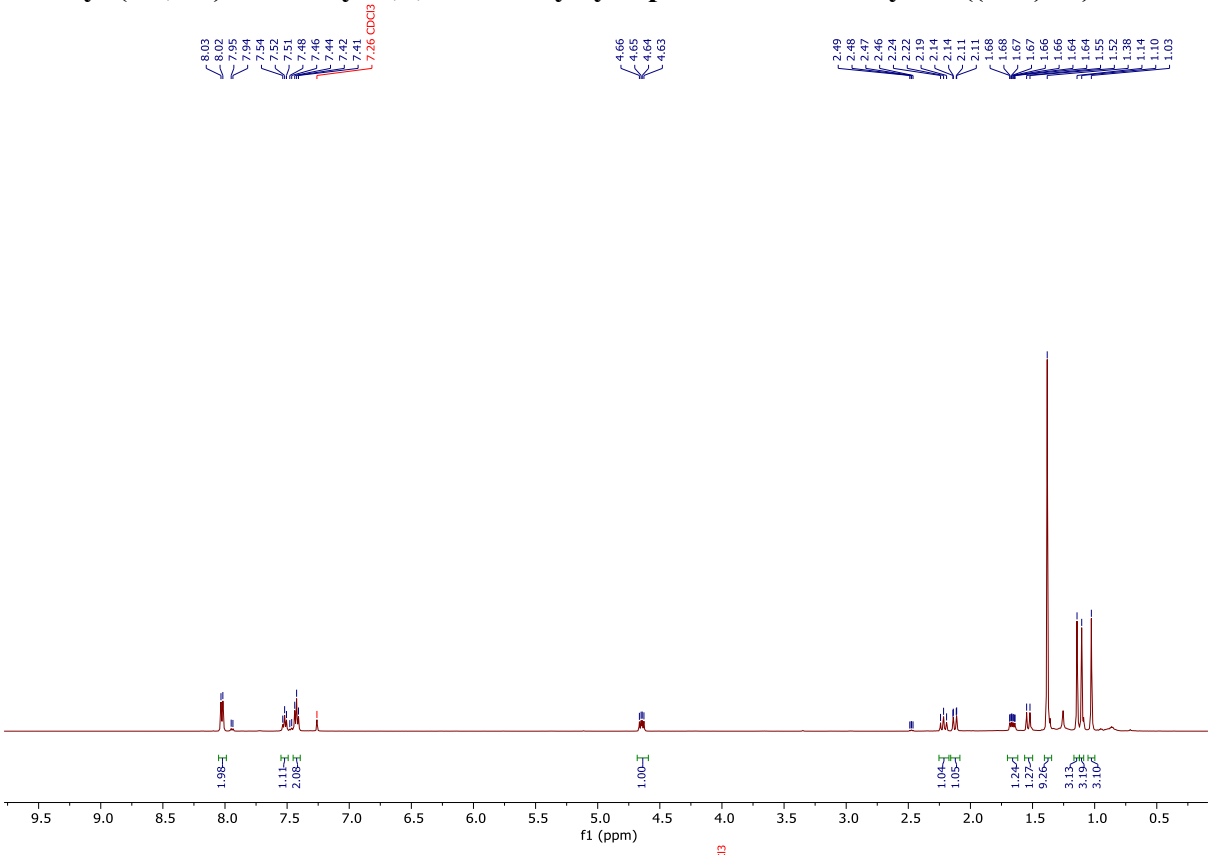
4-((1R,2R)-2-benzoyl-4,4-dimethylcyclopentyl)benzonitrile ((*R*,*R*)-3d).

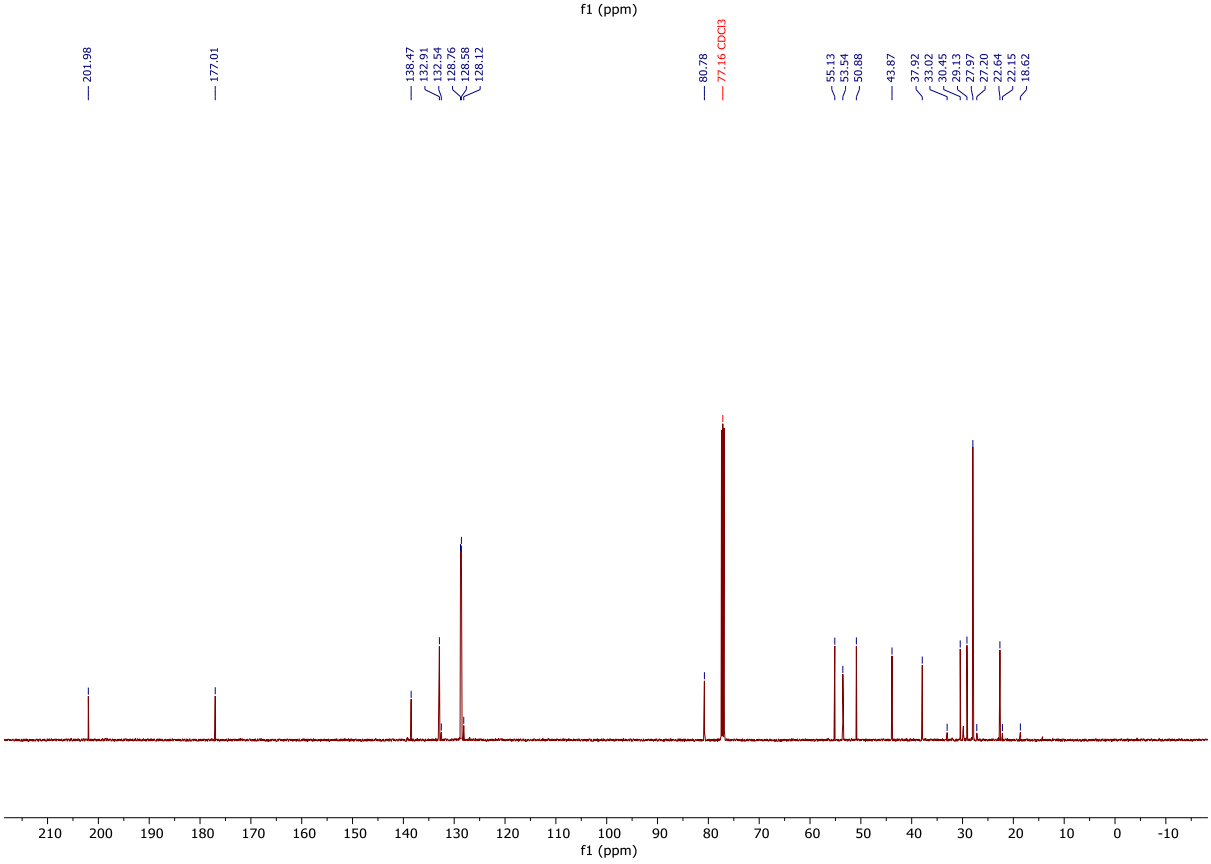


***tert*-butyl (1R,2R)-2-benzoyl-4,4-dimethylcyclopentane-1-carboxylate ((*R,R*)-3e).**

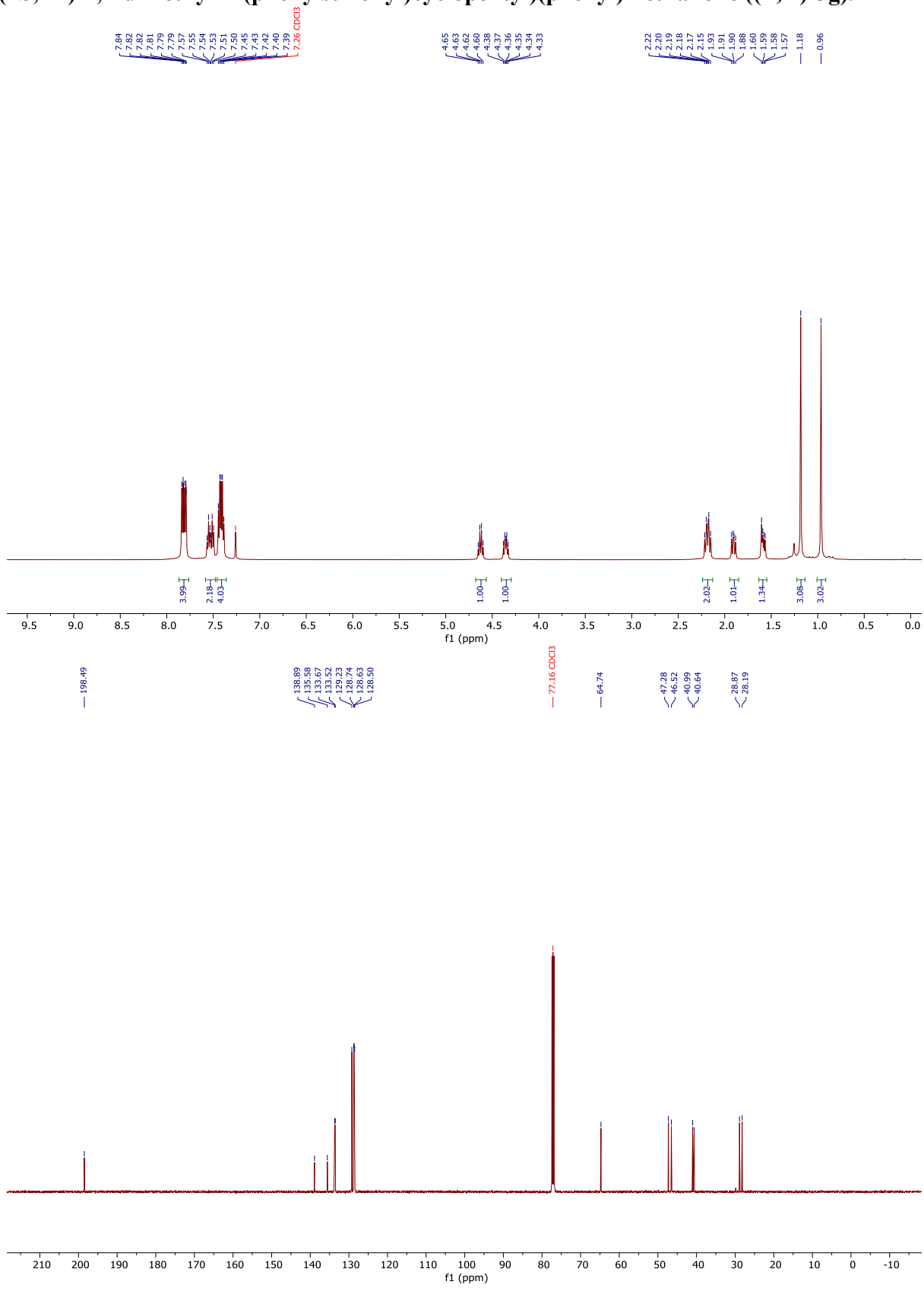


***tert*-butyl (1R,2R)-2-benzoyl-1,4,4-trimethylcyclopentane-1-carboxylate ((*R*,*R*)-3f).**

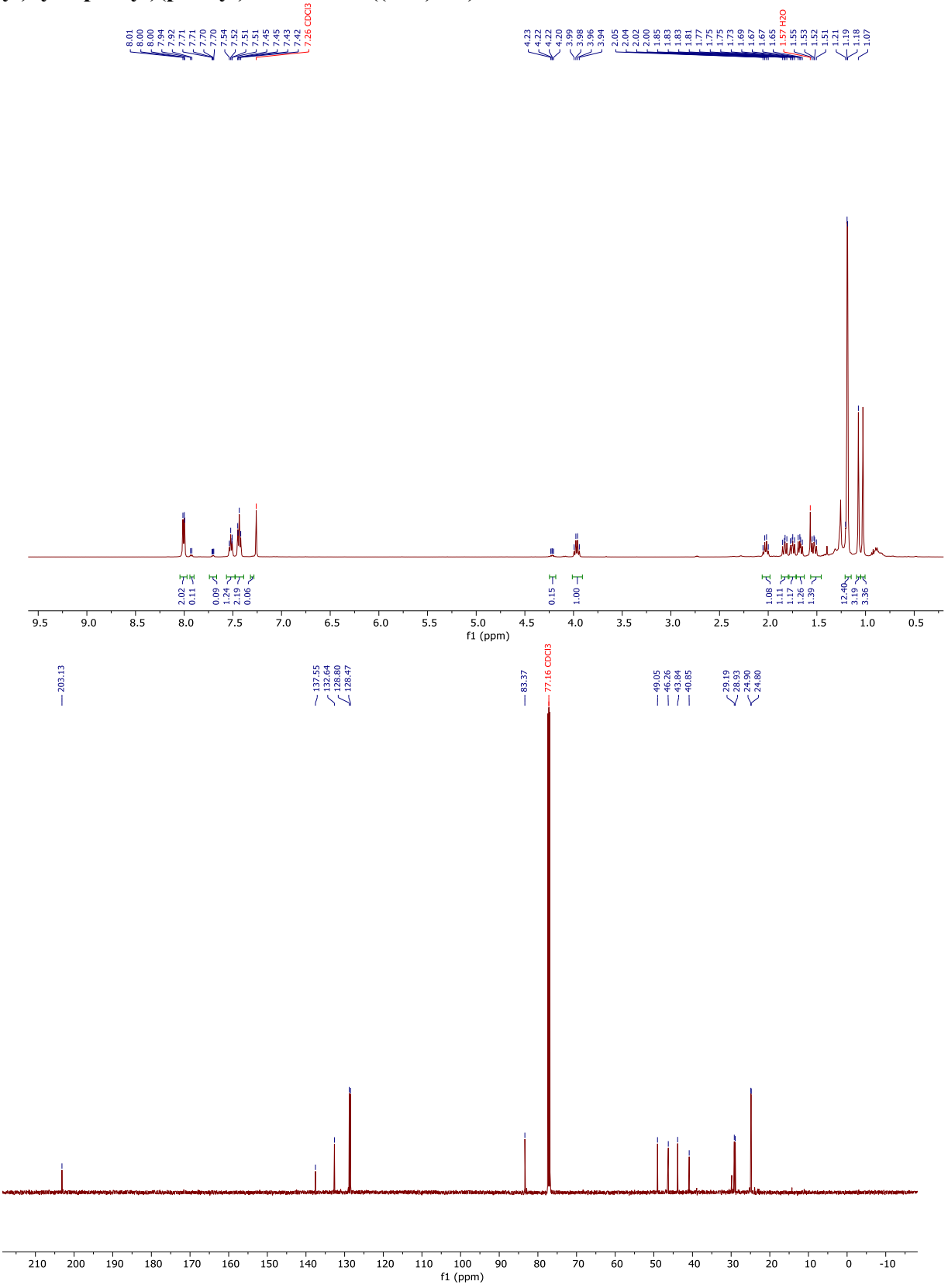




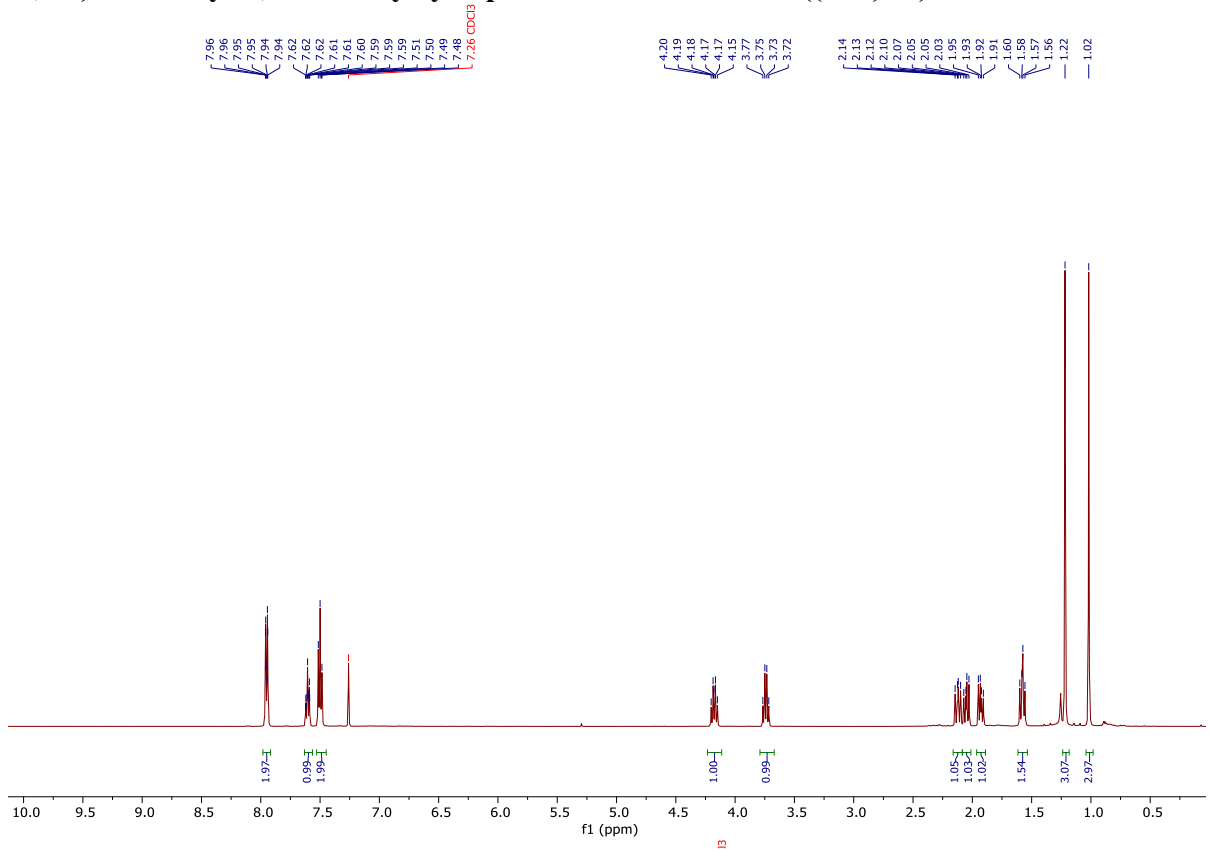
((1S,2R)-4,4-dimethyl-2-(phenylsulfonyl)cyclopentyl)(phenyl)methanone ((*R*,*R*)-3g).

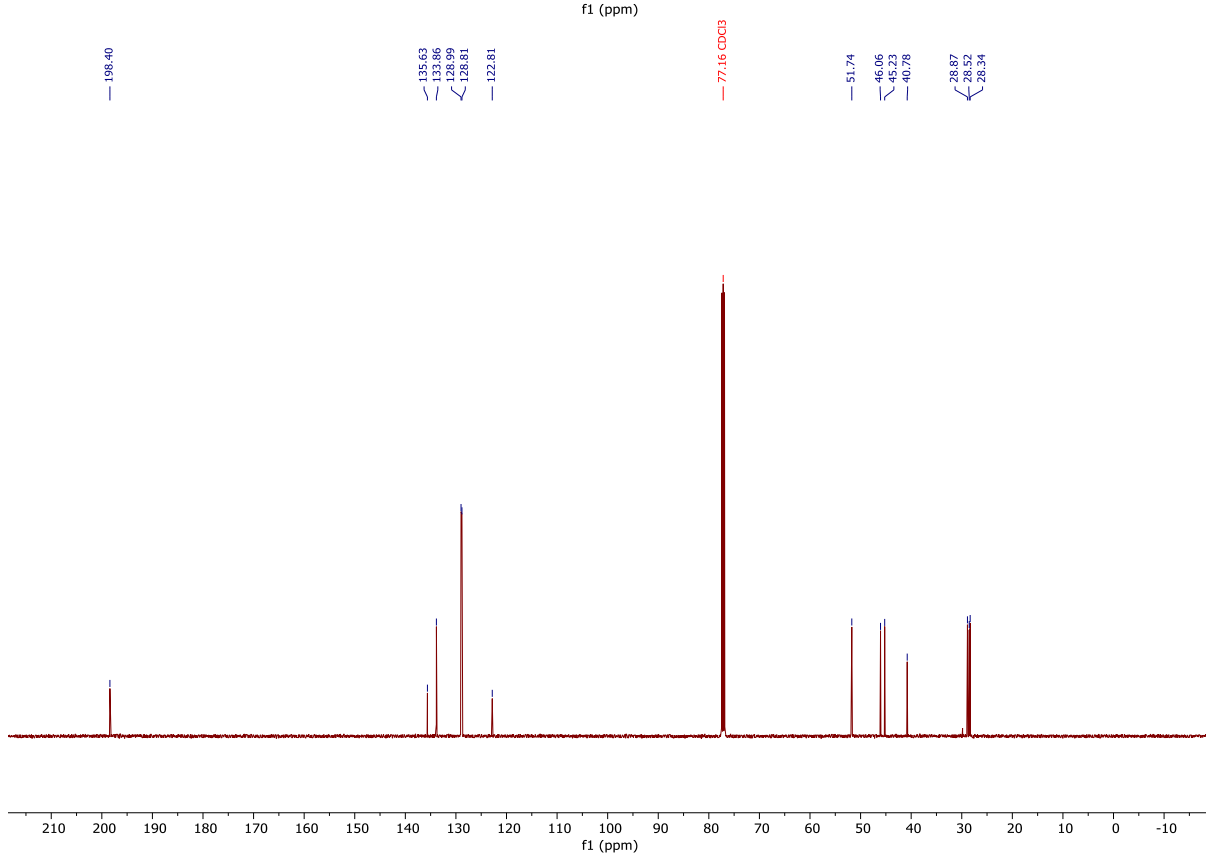


((1R,2R)-4,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)(phenyl)methanone ((*R,R*)-3h).

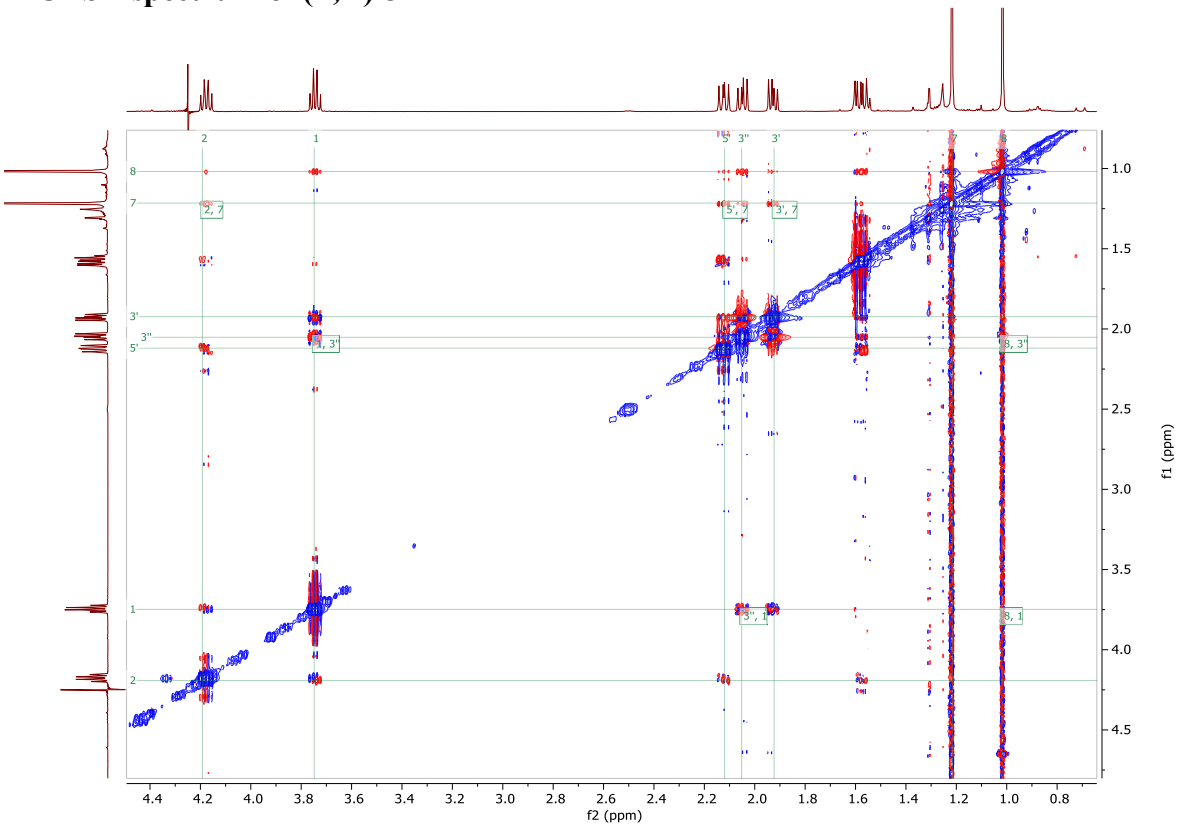


(1R,2R)-2-benzoyl-4,4-dimethylcyclopentane-1-carbonitrile ((*R*,*R*)-3i).

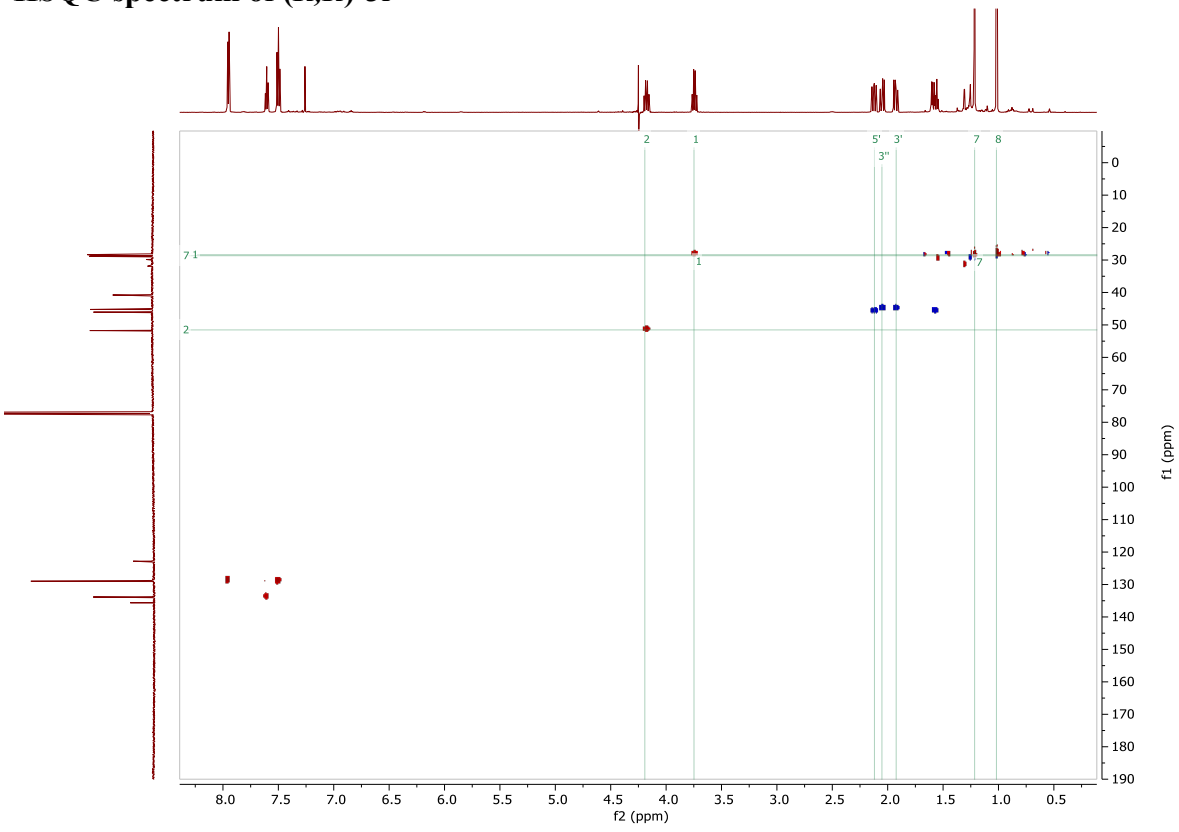




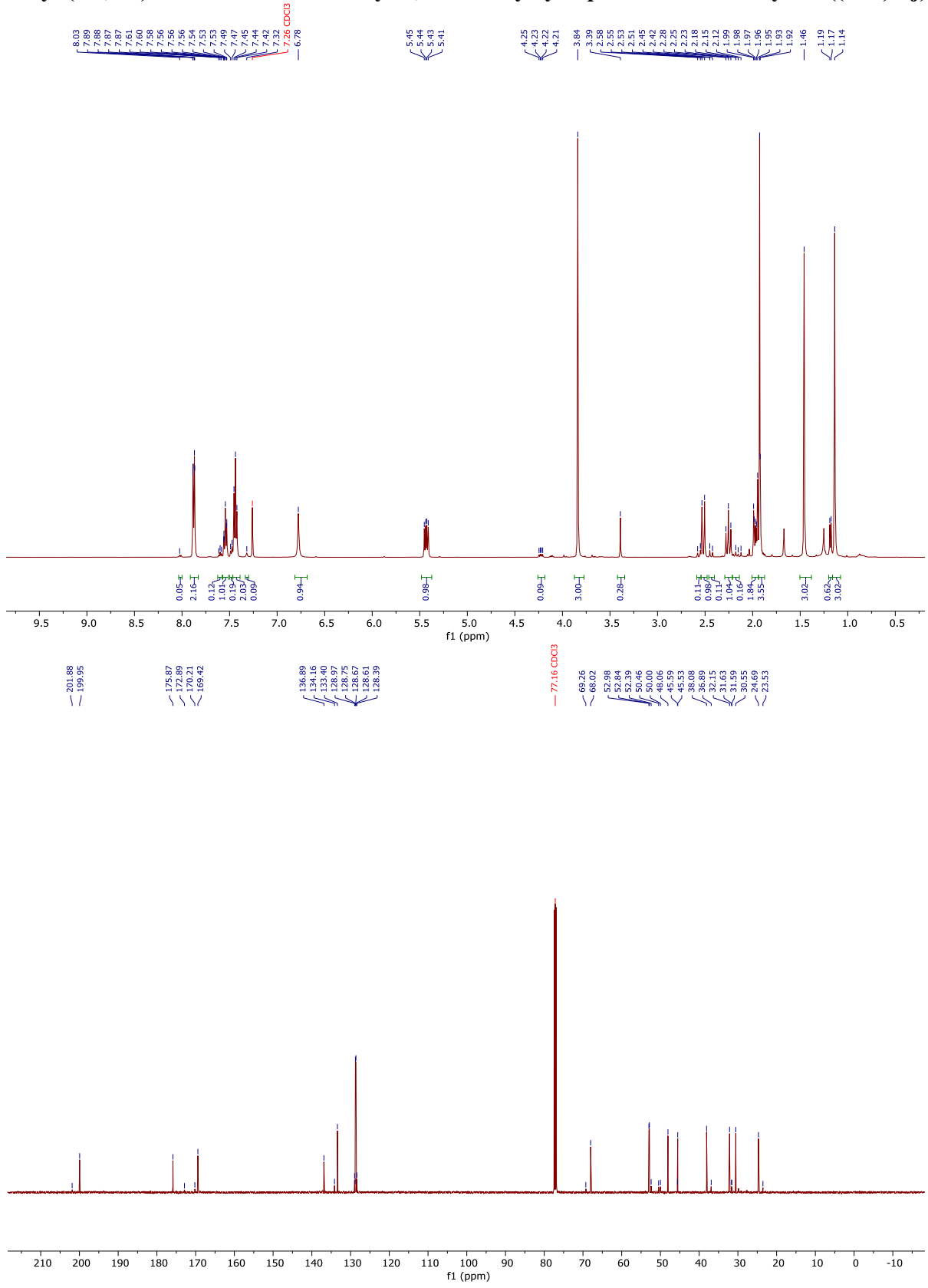
2D ROESY spectrum of (*R*,*R*)-3i



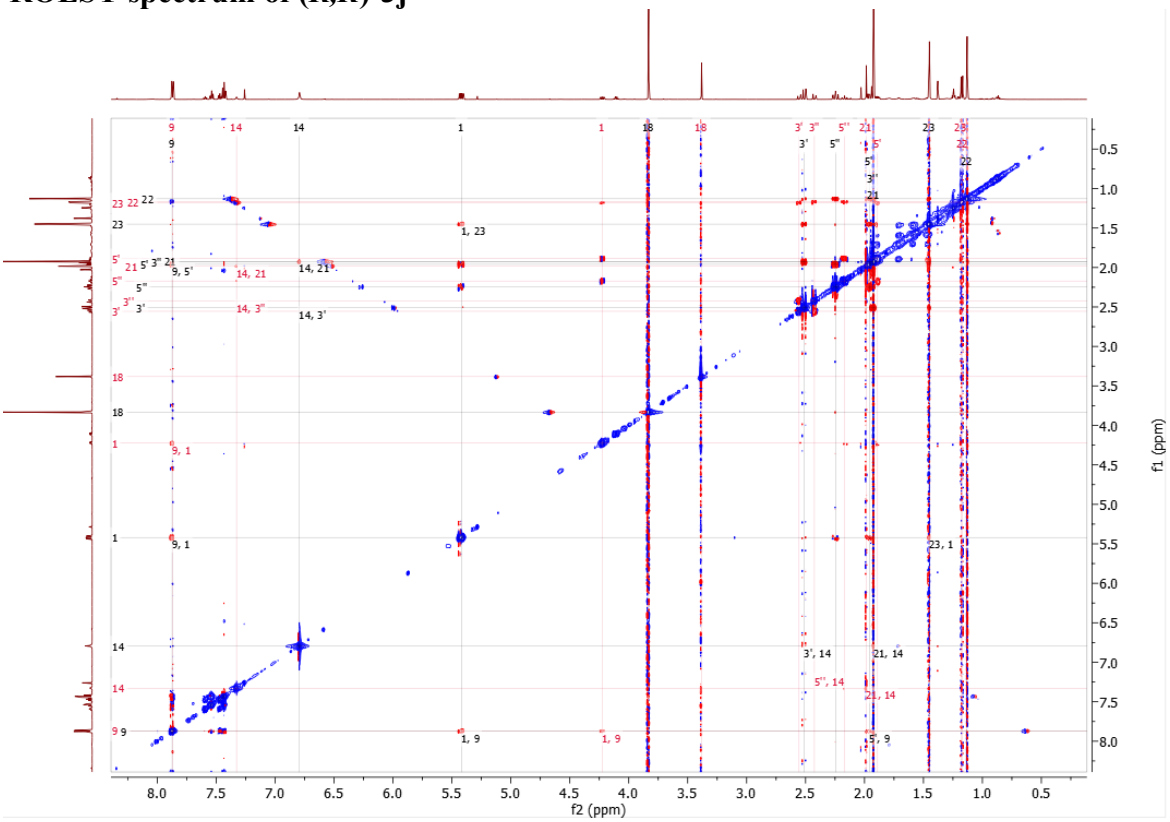
2D HSQC spectrum of (*R*,*R*)-3i



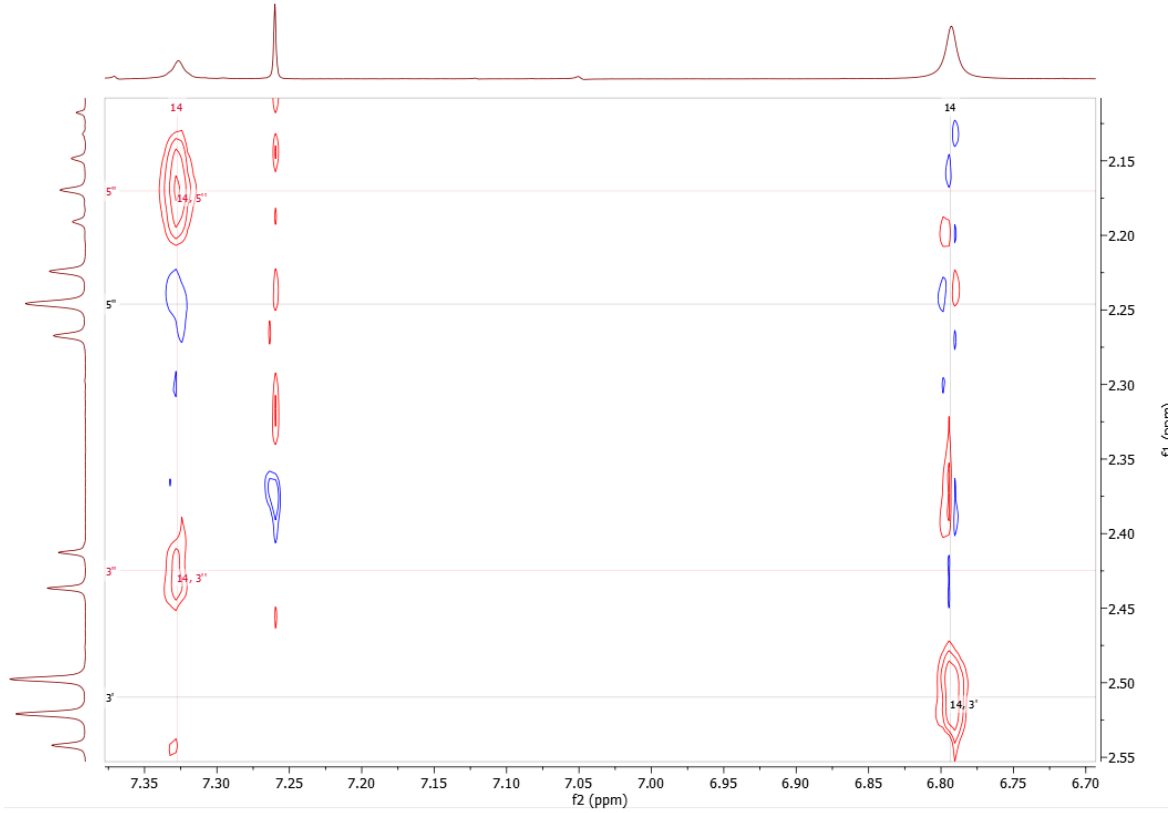
methyl (1R,2R)-1-acetamido-2-benzoyl-4,4-dimethylcyclopentane-1-carboxylate ((*R*,*R*)-3j).



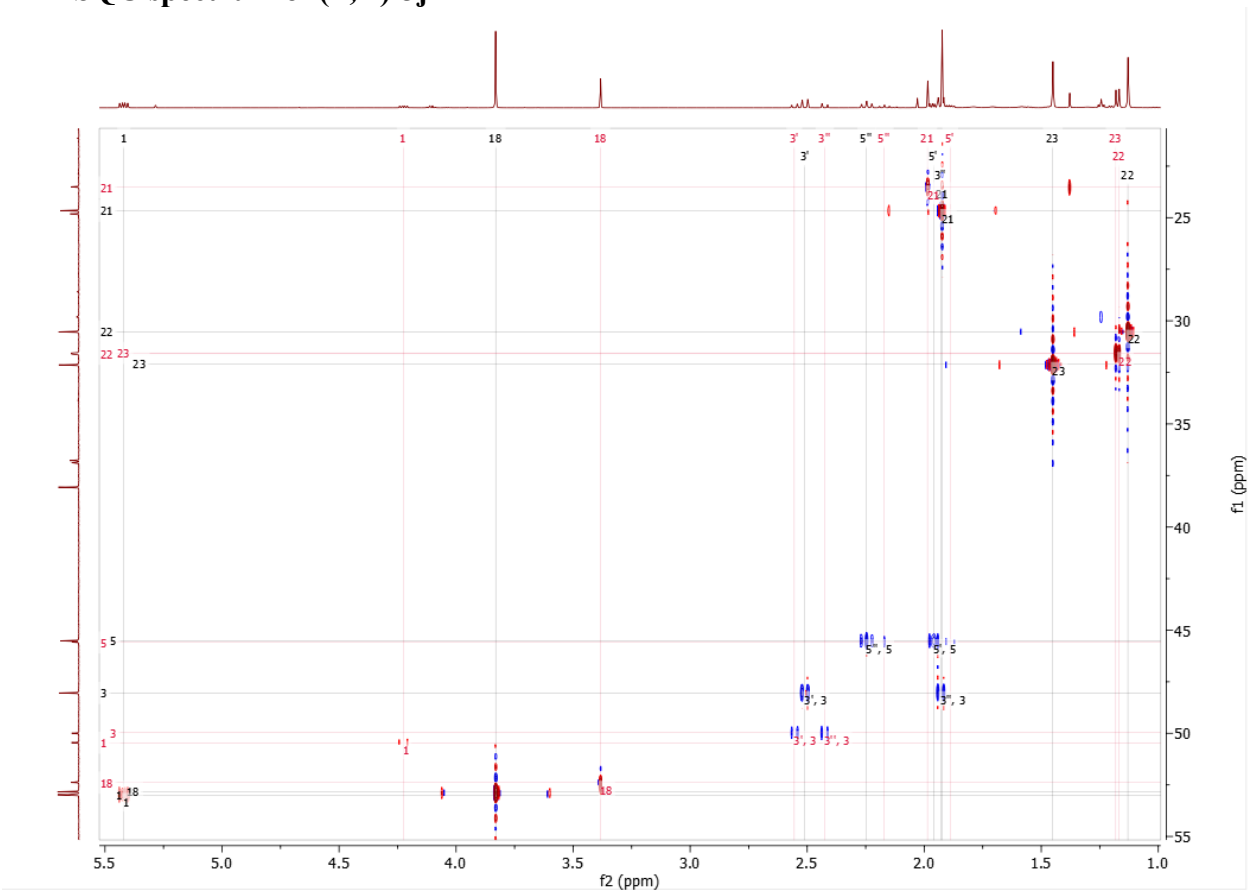
2D ROESY spectrum of (*R*,*R*)-3j



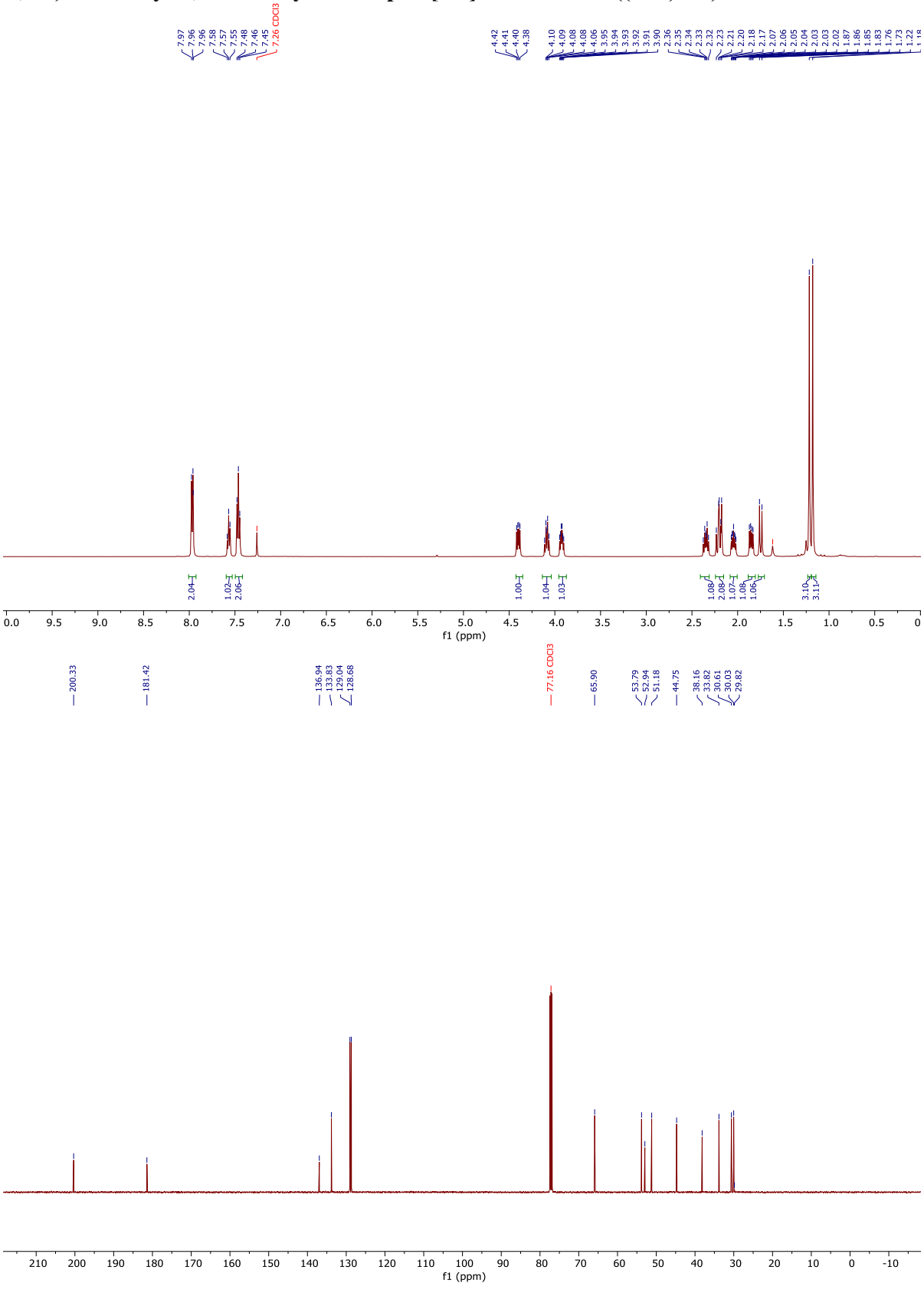
2D ROESY spectrum of (*R*,*R*)-3j (zoomed in key region)



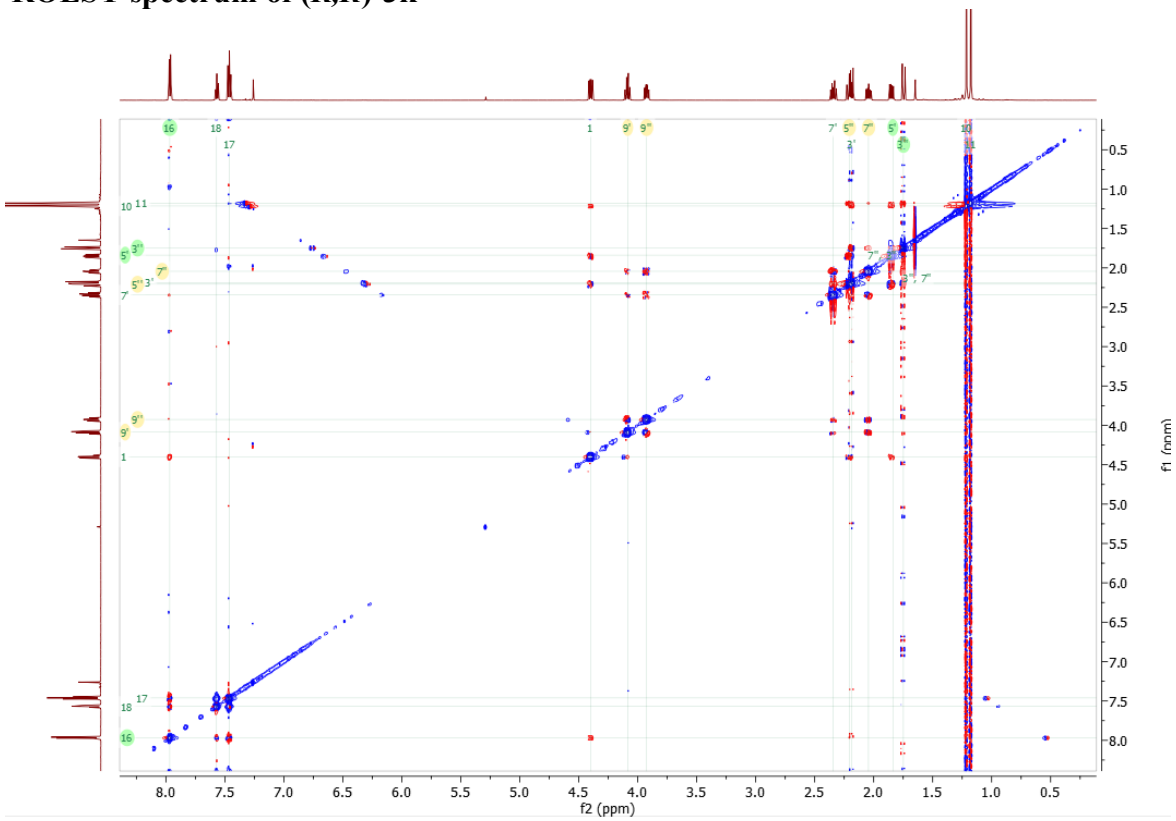
2D HSQC spectrum of (*R*,*R*)-3j



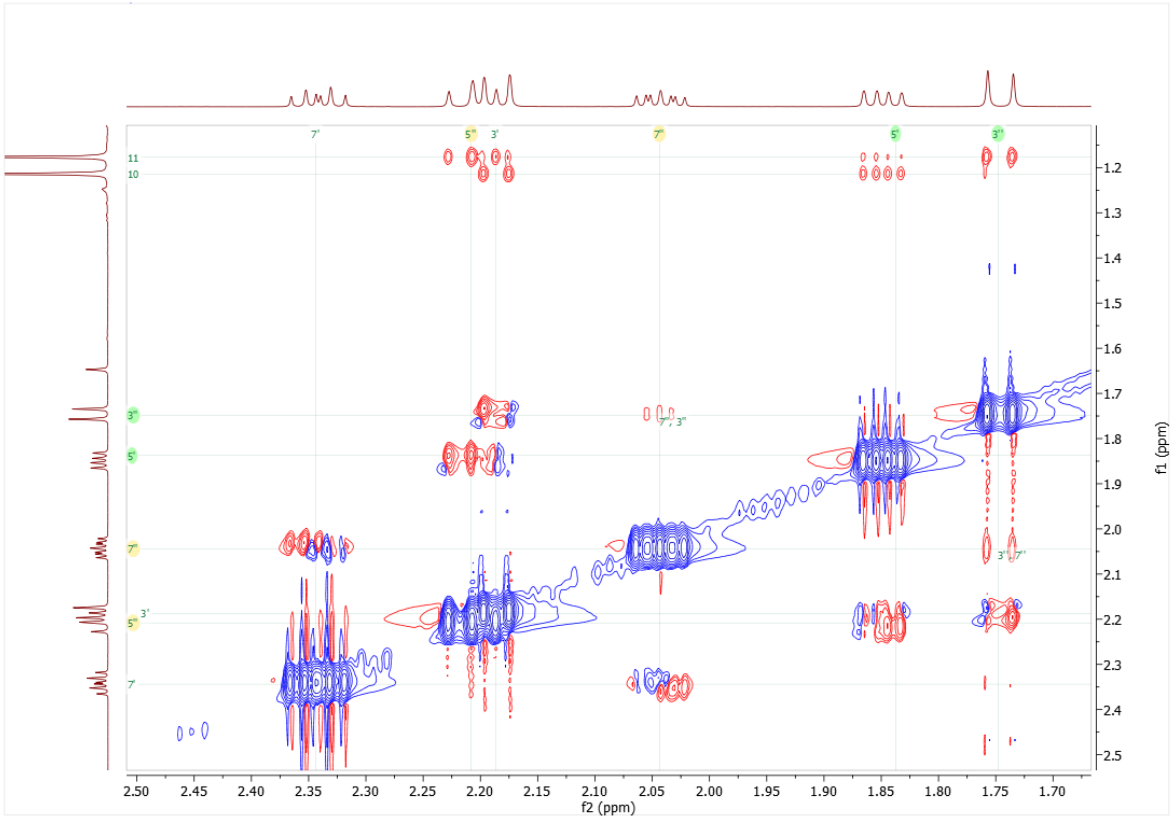
(5S,6R)-6-benzoyl-8,8-dimethyl-2-oxaspiro[4.4]nonan-1-one ((*R*,*R*)-3k).



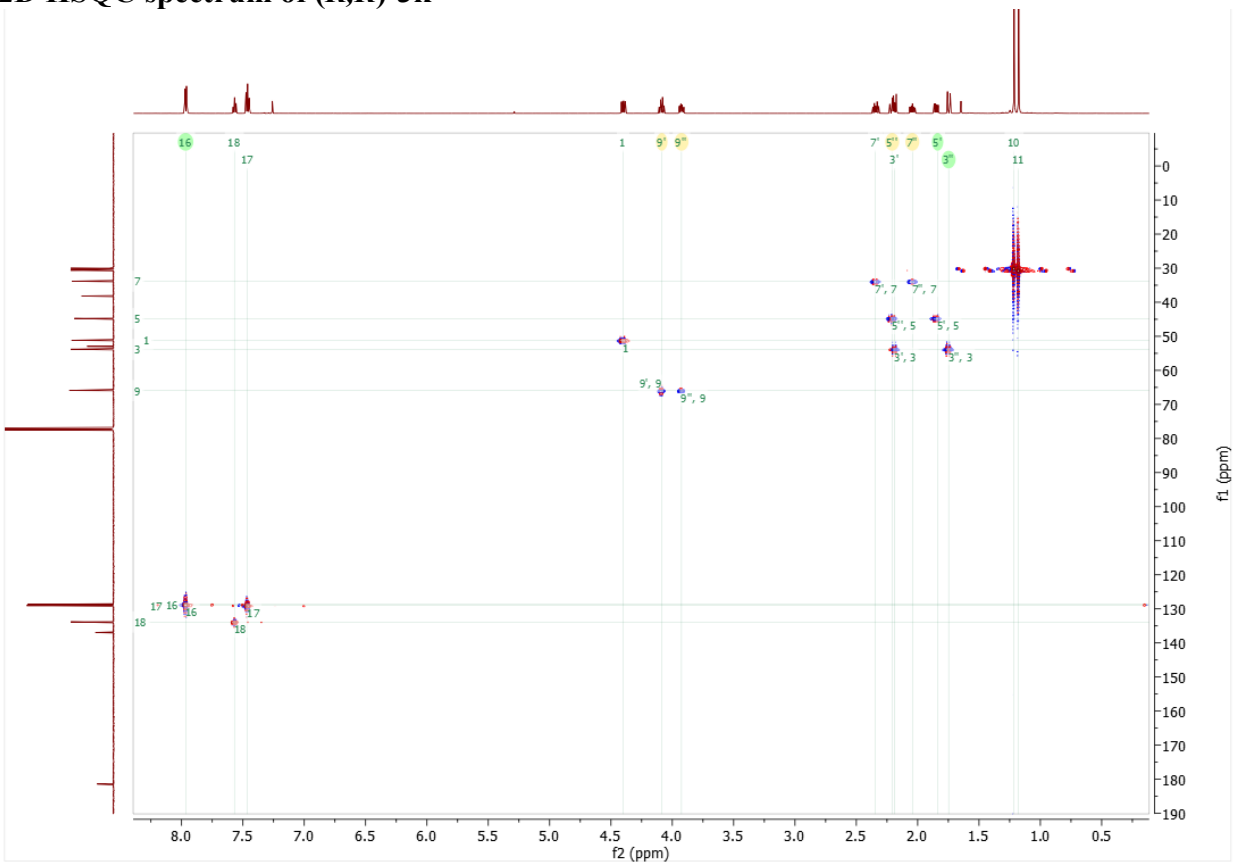
2D ROESY spectrum of (*R*,*R*)-3k



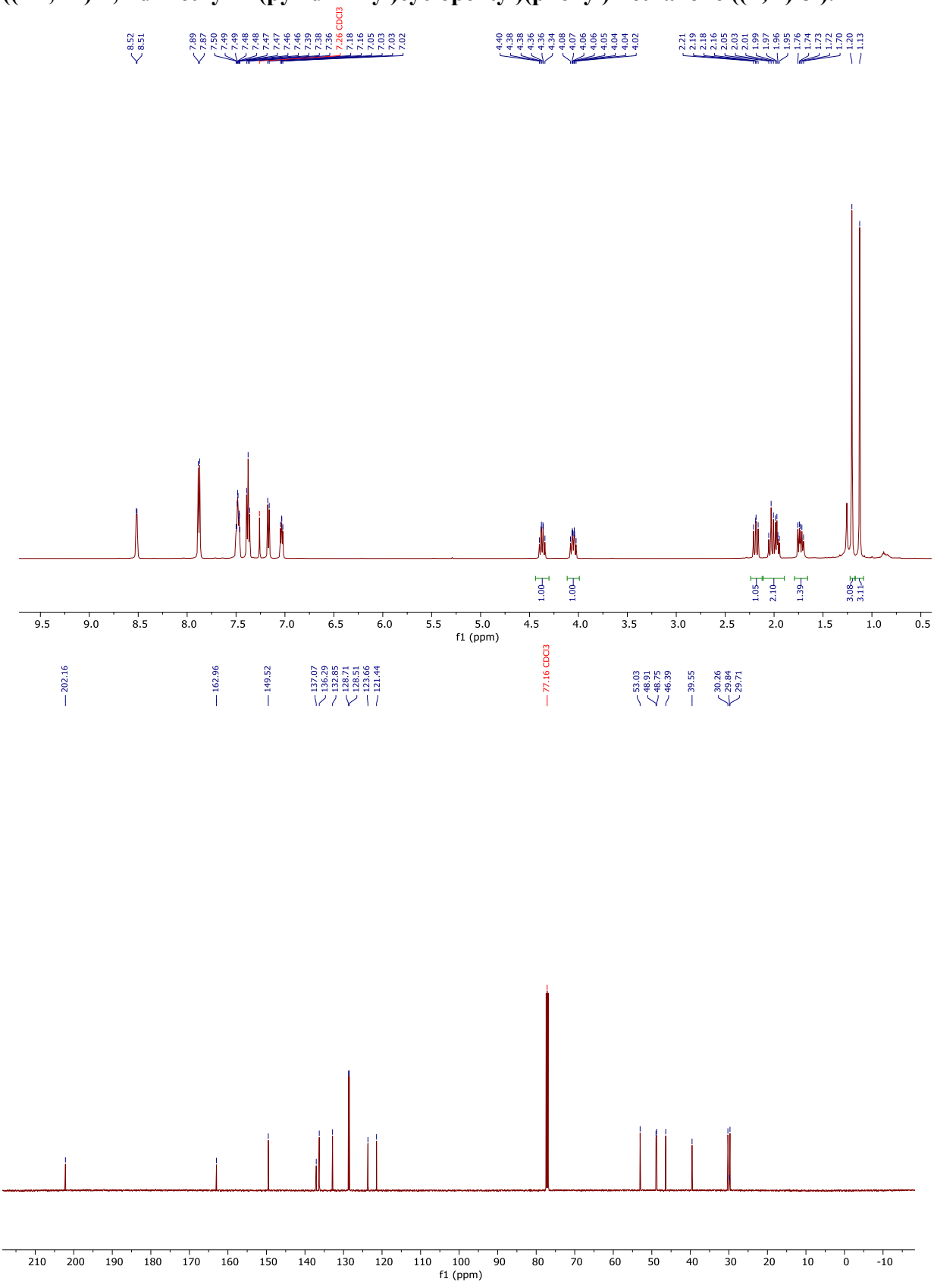
2D ROESY spectrum of (*R*,*R*)-3k(zoomed in key region)



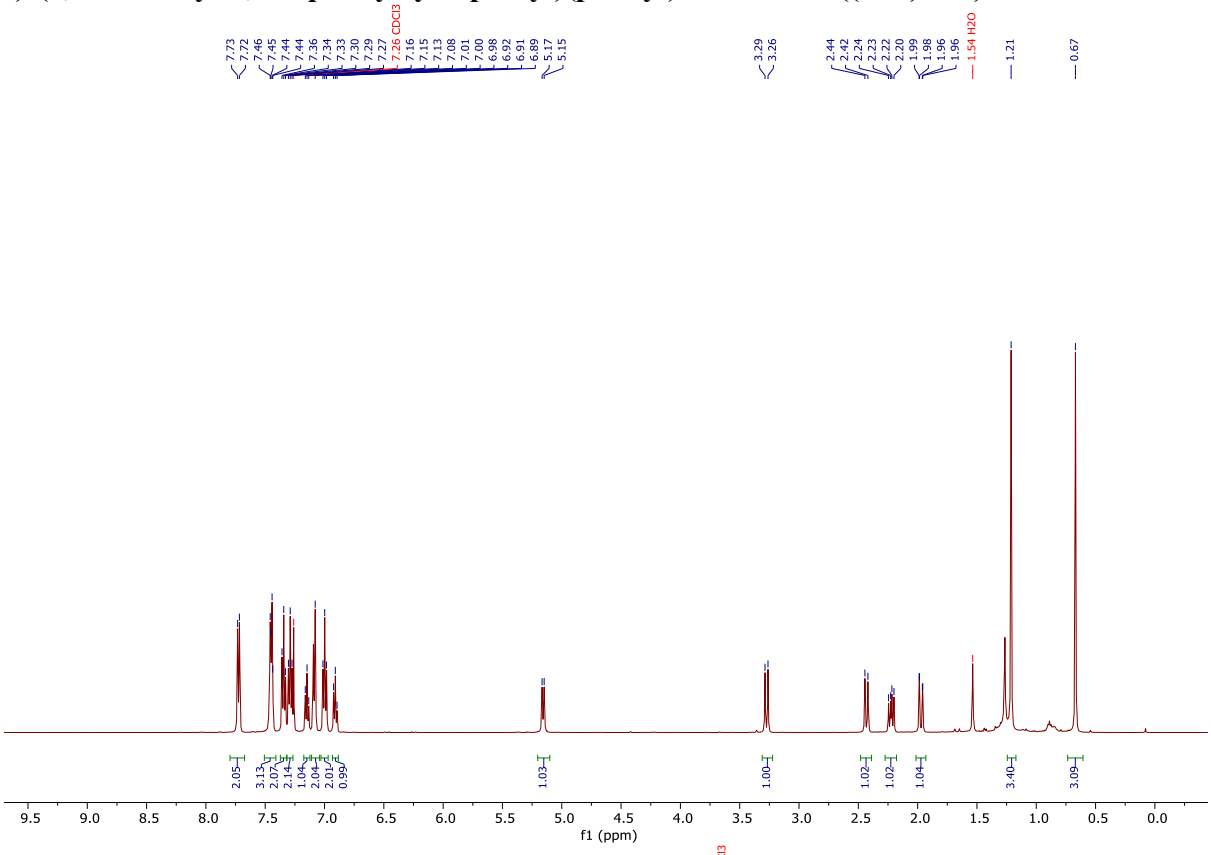
2D HSQC spectrum of (*R*,*R*)-3k

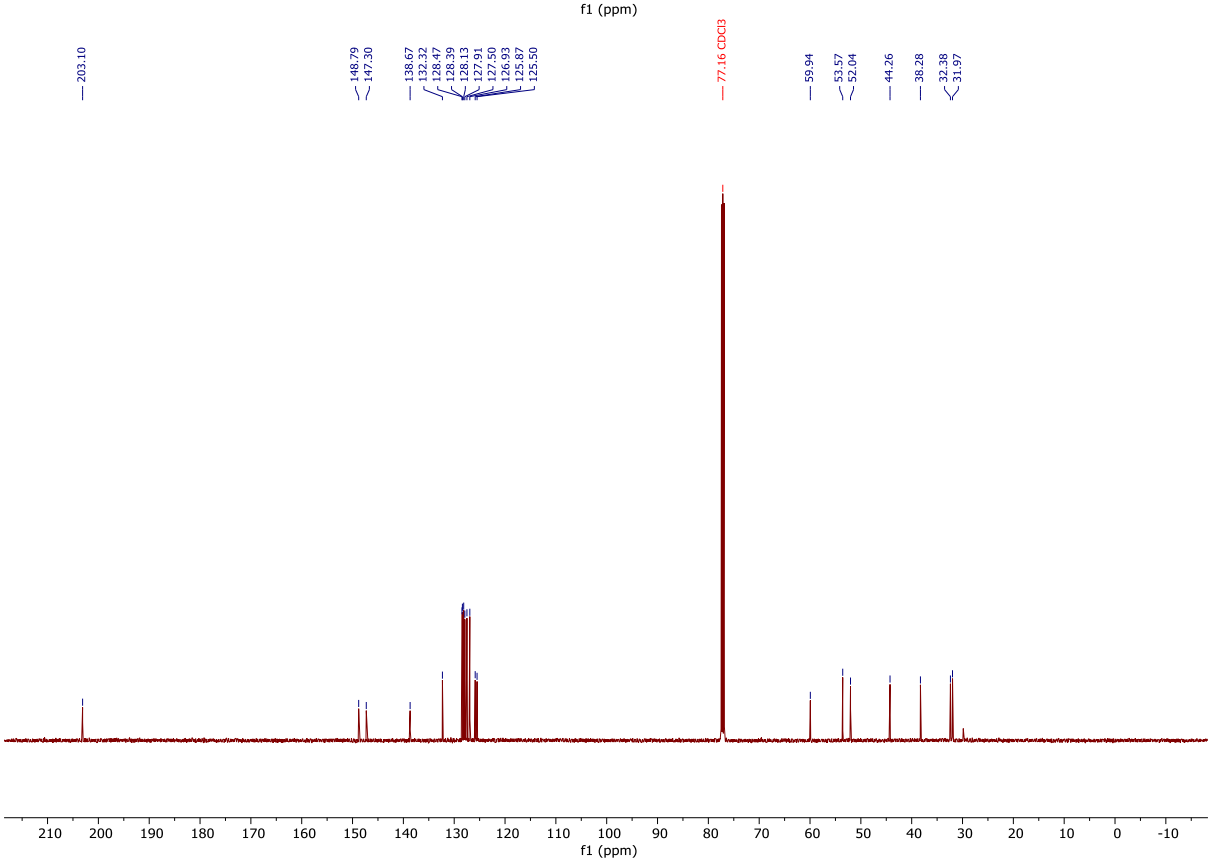


((1R,2R)-4,4-dimethyl-2-(pyridin-2-yl)cyclopentyl)(phenyl)methanone ((*R*,*R*)-3l).

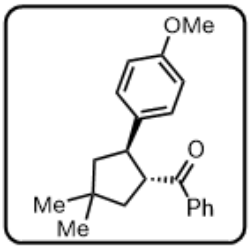


(R)-(4,4-dimethyl-2,2-diphenylcyclopentyl)(phenyl)methanone ((*R*,*R*)-3m).



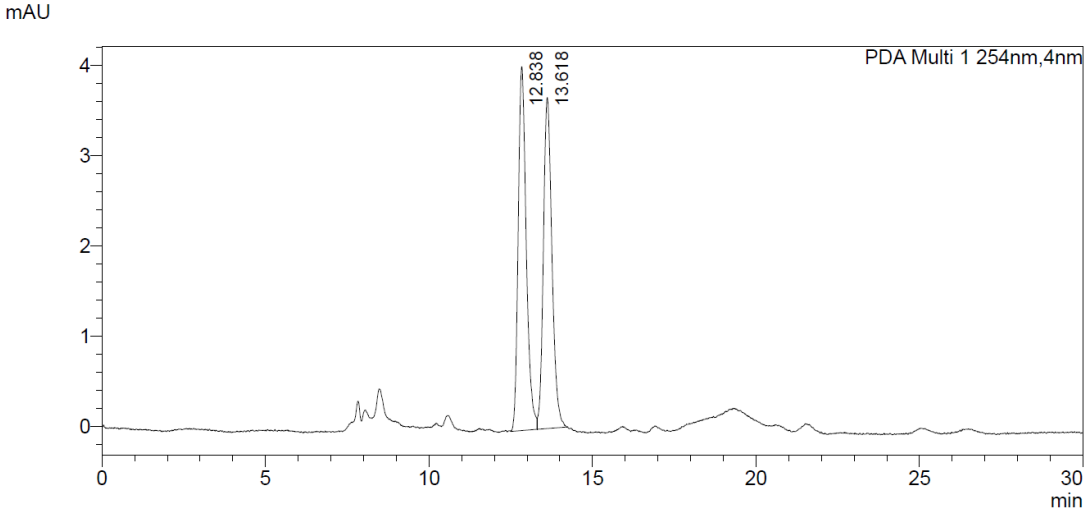


Section 10. HPLC traces



((*R*,*R*)-3a)

Racemic

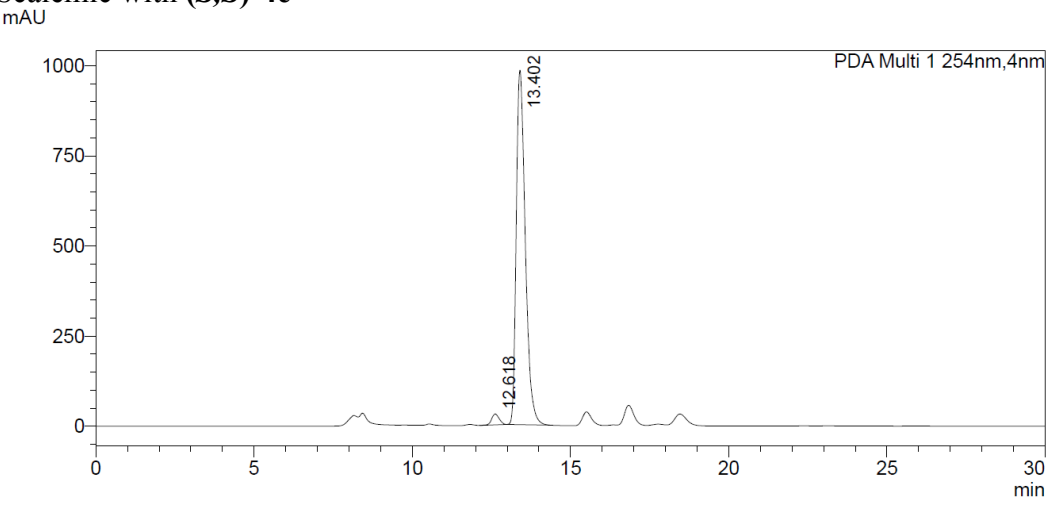


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.838	68968	4025	50.792
2	13.618	66817	3664	49.208
Total		135785	7689	100.000

Scalemic with **(*S*,*S*)-4e**

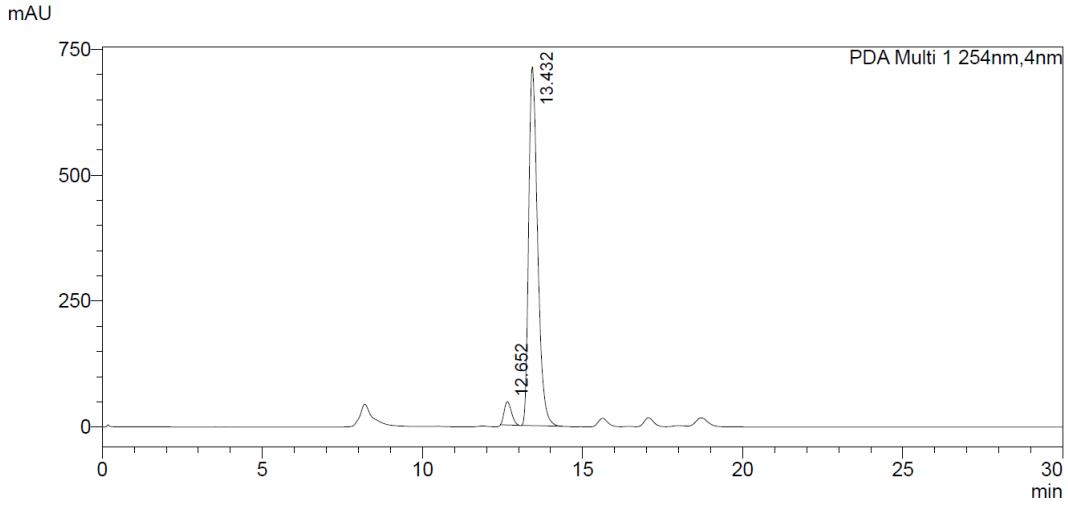


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.618	503414	30282	2.514
2	13.402	19520273	983155	97.486
Total		20023688	1013437	100.000

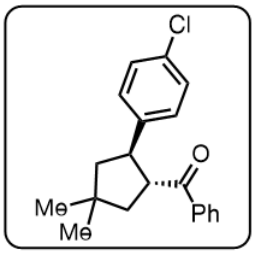
Scalemic with ***(S,S)*-4a**



<Peak Table>

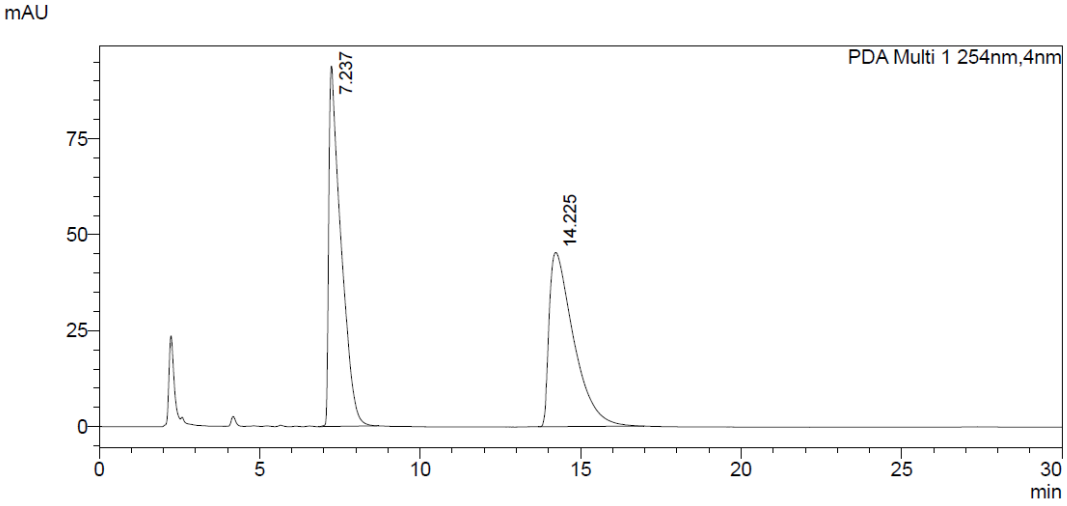
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.652	726534	46361	4.976
2	13.432	13873141	712957	95.024
Total		14599675	759319	100.000



((*R*,*R*)-3b)

Racemic

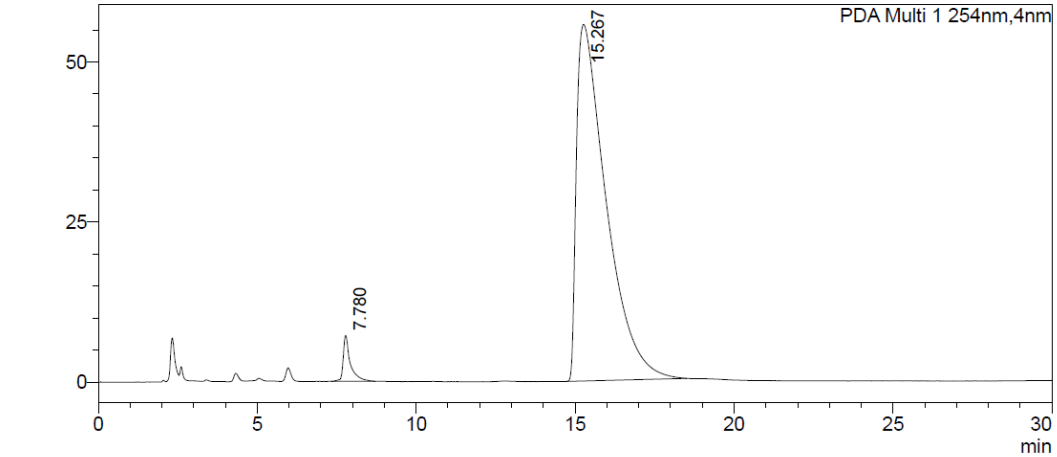


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.237	2482125	93918	50.756
2	14.225	2408200	45390	49.244
Total		4890324	139309	100.000

Scalemic with **(*S*,*S*)-4e**

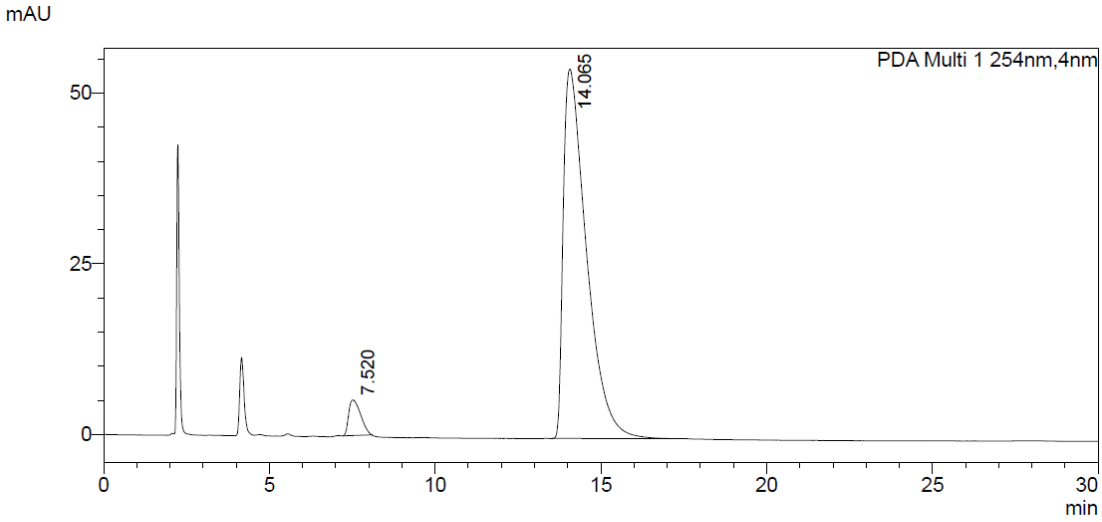


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.780	109878	7142	2.951
2	15.267	3614081	55647	97.049
Total		3723959	62789	100.000

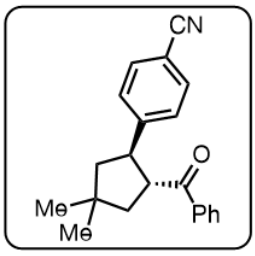
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

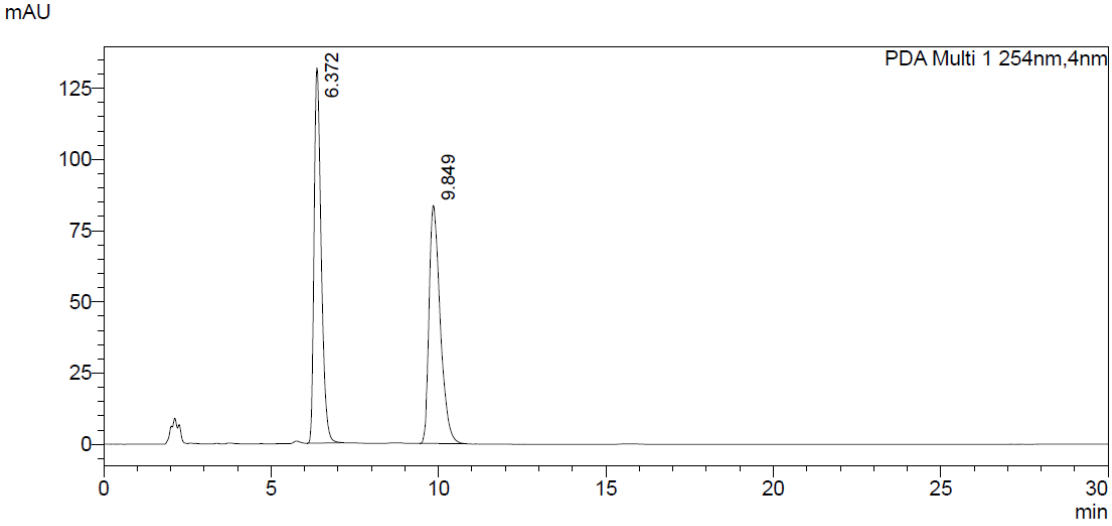
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.520	130112	5209	4.719
2	14.065	2627241	54104	95.281
Total		2757352	59313	100.000



((*R*,*R*)-3d)

Racemic

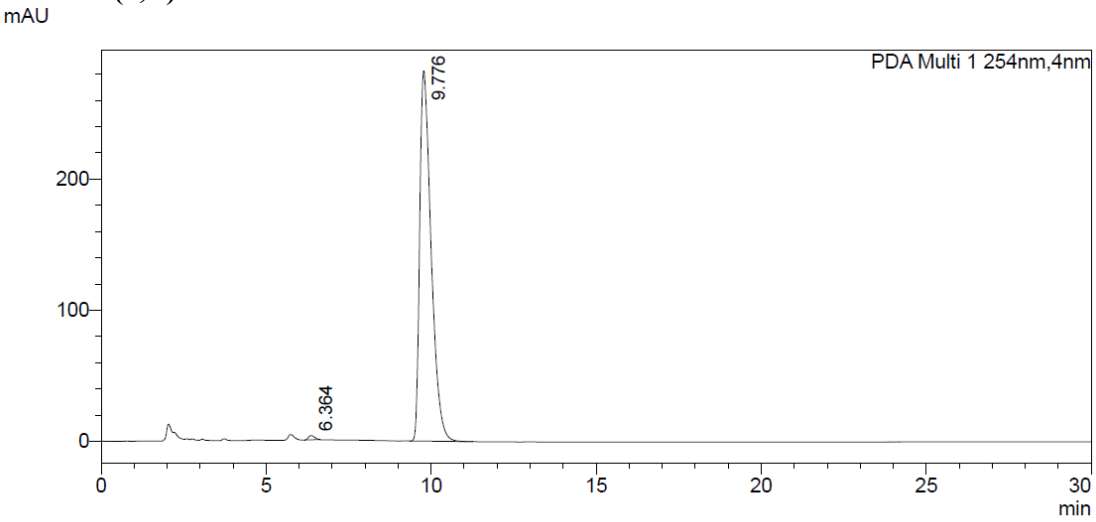


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.372	1943628	131762	50.085
2	9.849	1936996	83542	49.915
Total		3880624	215304	100.000

Scalemic with **(*S*,*S*)-4e**

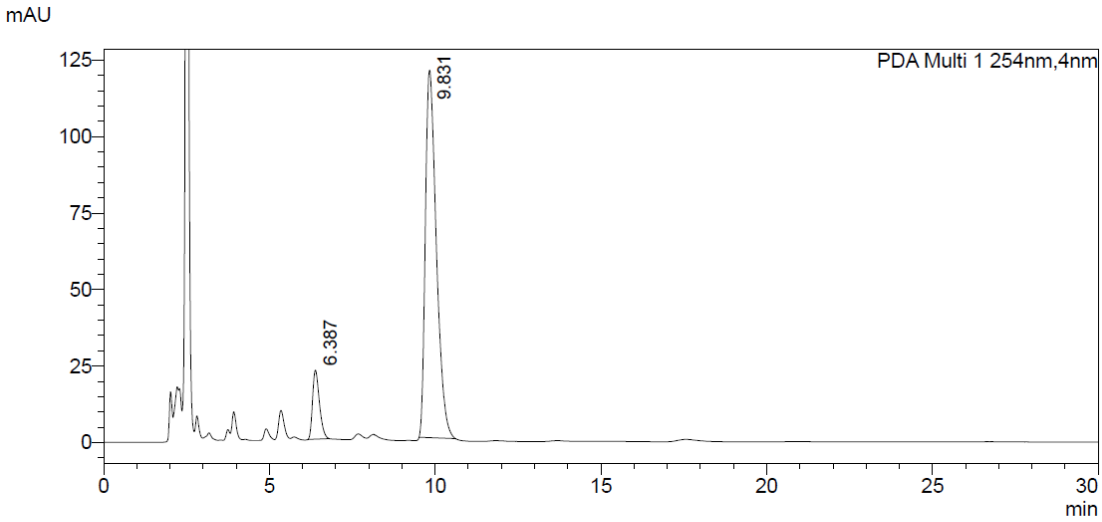


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.364	41405	3246	0.605
2	9.776	6798515	282477	99.395
Total		6839919	285723	100.000

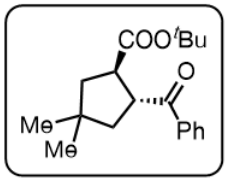
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

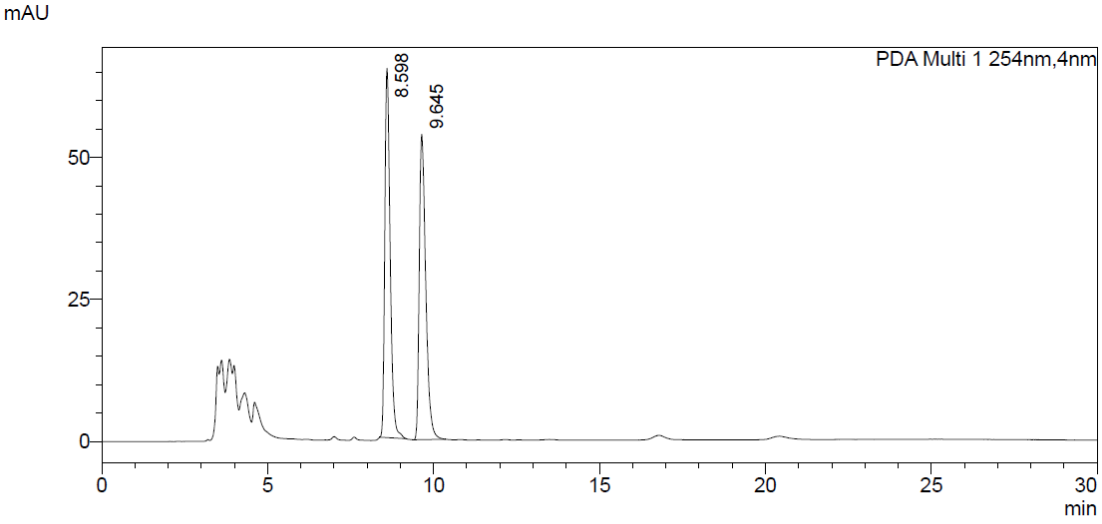
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.387	325002	22539	10.513
2	9.831	2766375	120225	89.487
Total		3091377	142765	100.000



((*R*,*R*)-3e)

Racemic

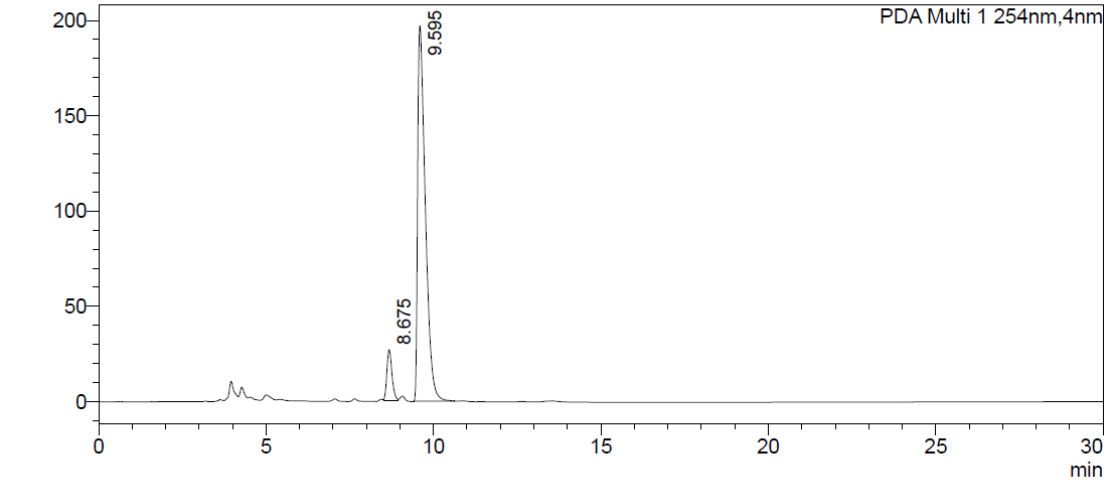


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.598	728058	64933	49.958
2	9.645	729291	53662	50.042
Total		1457349	118595	100.000

Scalemic with **(*S*,*S*)-4e**

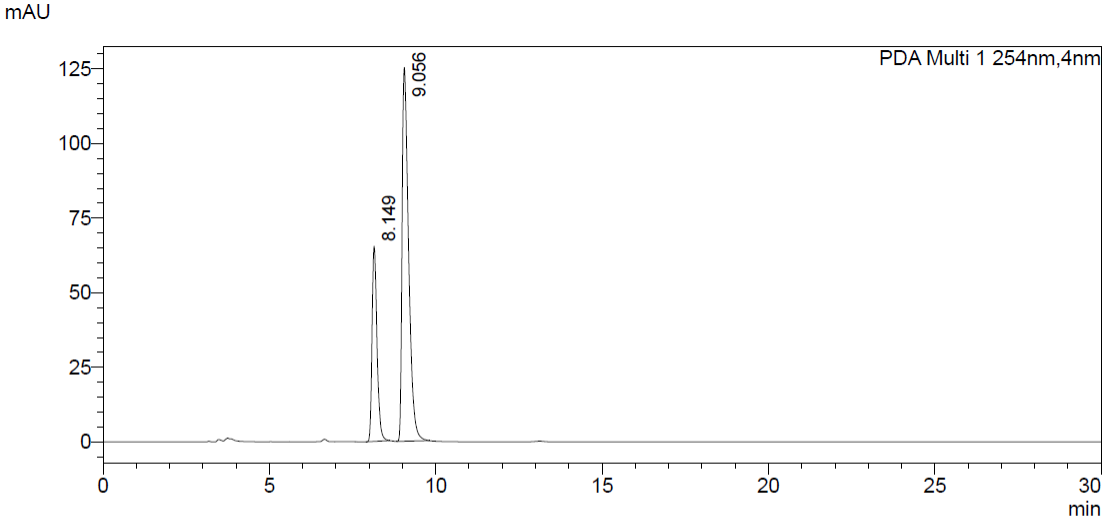


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.675	286737	26826	8.346
2	9.595	3148756	196920	91.654
Total		3435493	223746	100.000

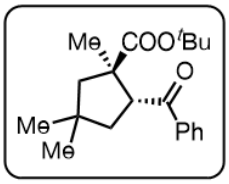
Scalemic with ***(S,S)*-4a**



<Peak Table>

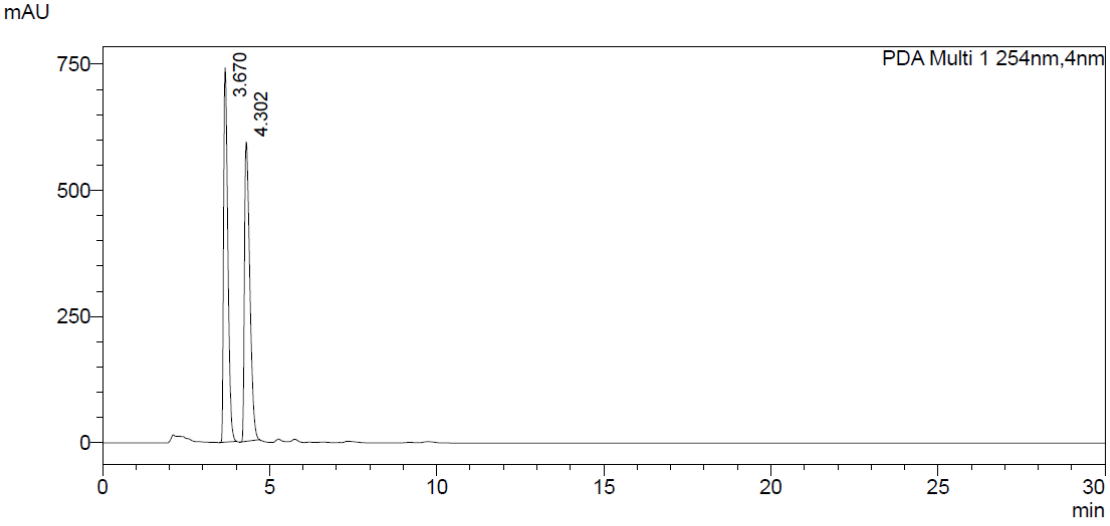
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.149	674306	65436	28.438
2	9.056	1696805	125271	71.562
Total		2371111	190708	100.000



((*R*,*R*)-3f)

Racemic

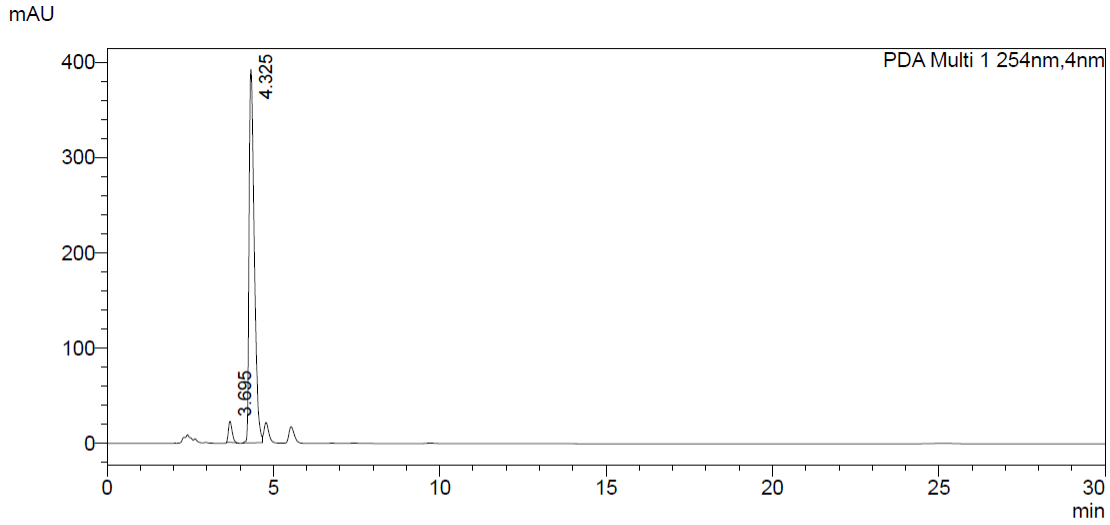


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	3.670	6521074	741765	49.722
2	4.302	6594006	592959	50.278
Total		13115080	1334724	100.000

Scalemic with **(*S*,*S*)-4e**

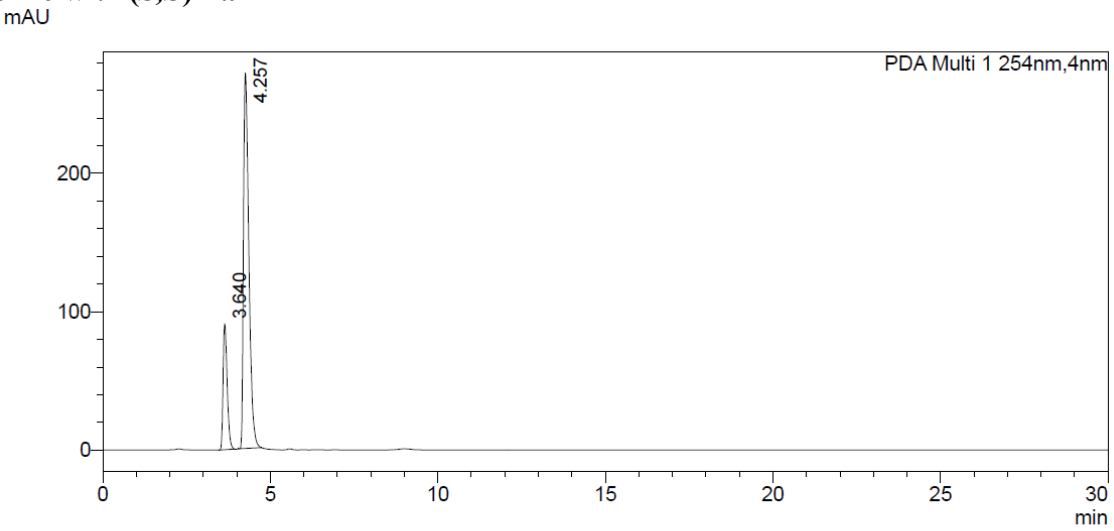


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	3.695	169268	22107	3.818
2	4.325	4264556	392002	96.182
Total		4433824	414109	100.000

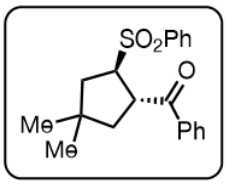
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

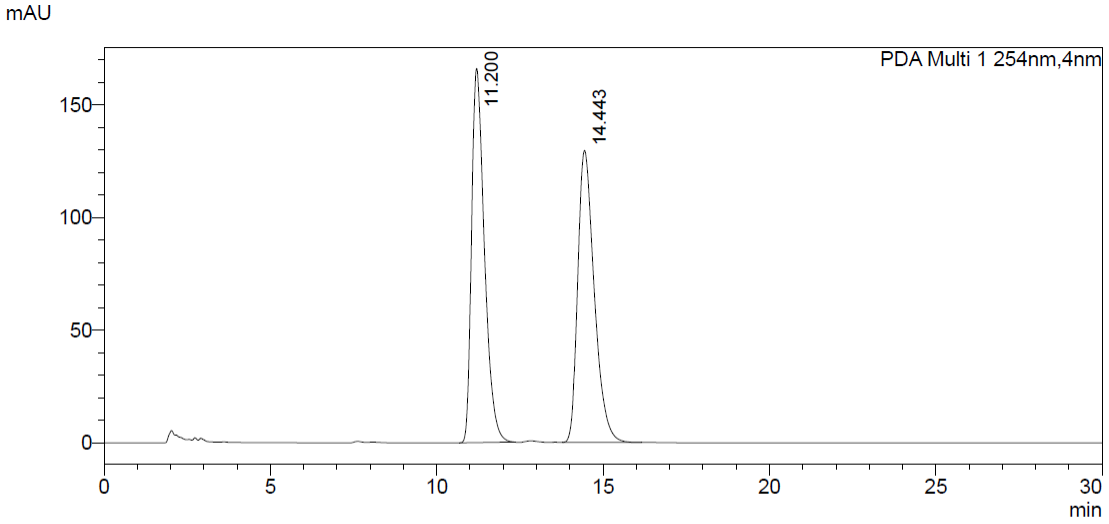
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	3.640	770593	90916	20.299
2	4.257	3025543	271397	79.701
Total		3796136	362313	100.000



((*R*,*R*)-3g)

Racemic

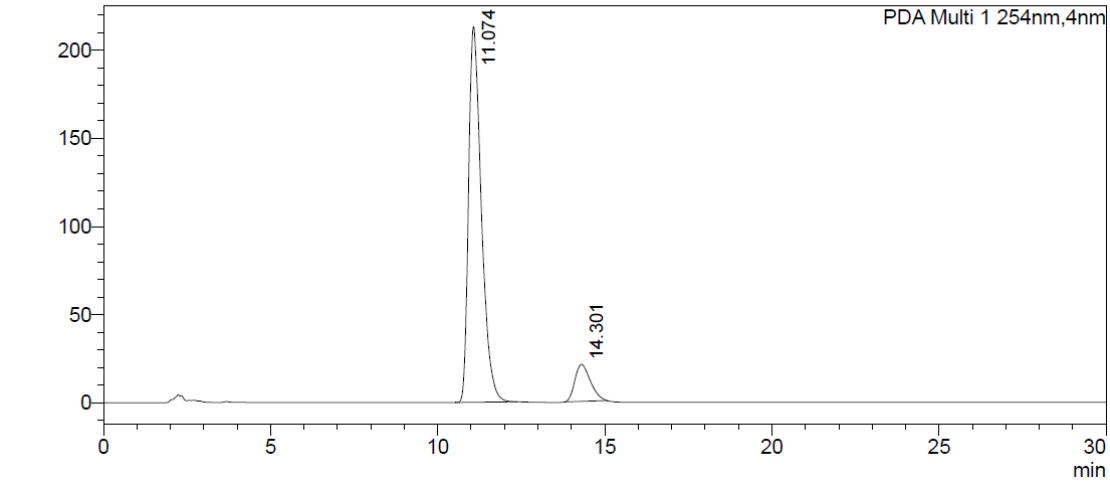


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.200	4462641	165995	49.994
2	14.443	4463677	129537	50.006
Total		8926318	295532	100.000

Scalemic with **(*S*,*S*)-4e**

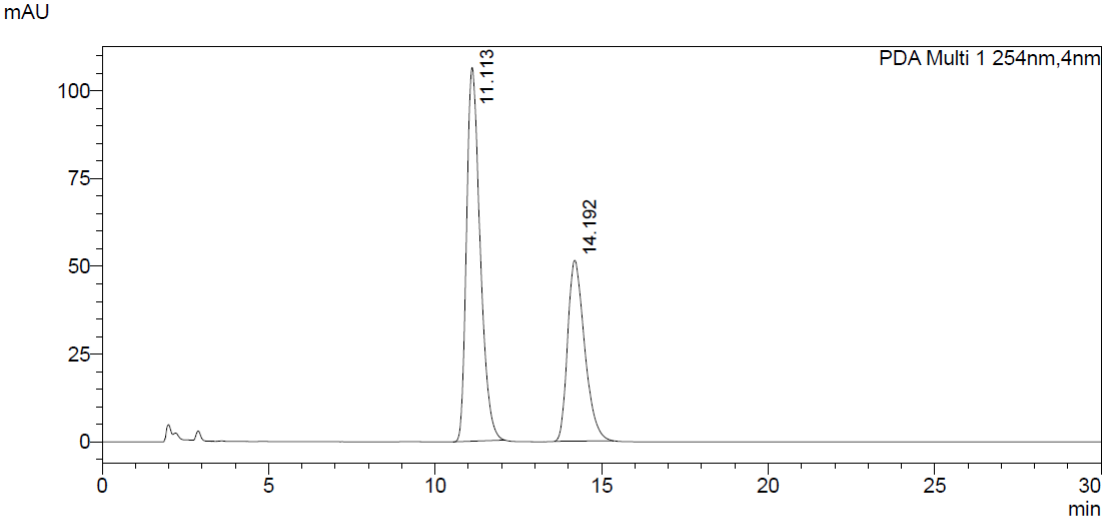


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.074	5670933	212883	89.377
2	14.301	673999	20956	10.623
Total		6344931	233839	100.000

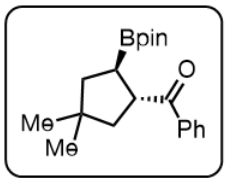
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

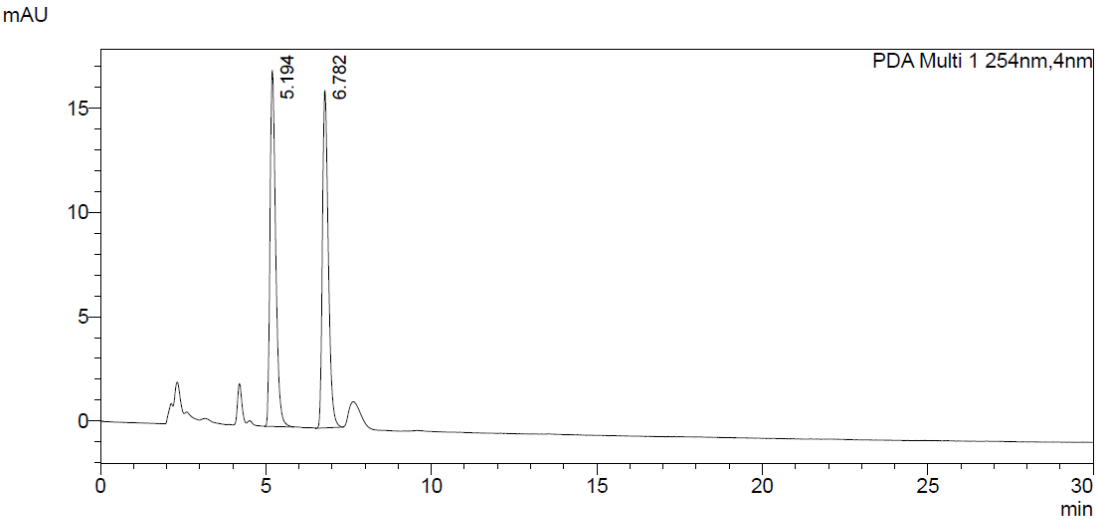
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.113	3020968	106421	62.340
2	14.192	1825001	51467	37.660
Total		4845969	157888	100.000



((*R*,*R*)-3h)

Racemic

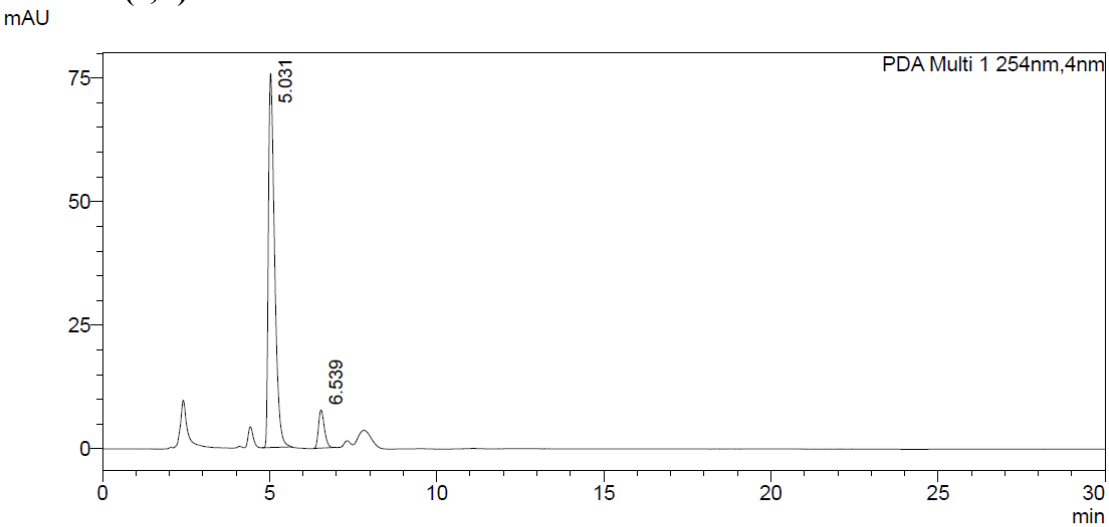


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.194	203303	17092	50.269
2	6.782	201124	16179	49.731
Total		404427	33271	100.000

Scalemic with **(*S*,*S*)-4e**

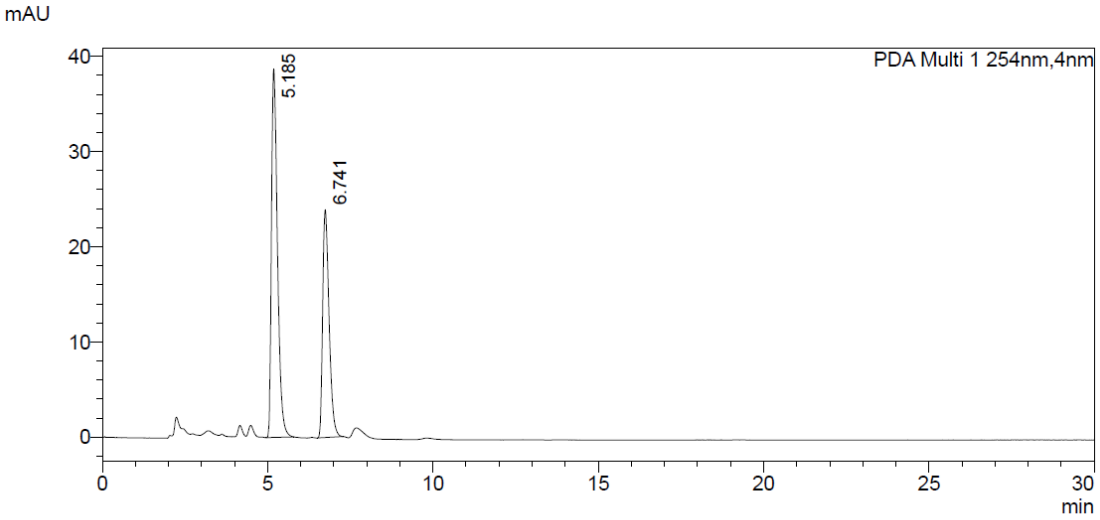


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.031	979355	75599	91.262
2	6.539	93772	7700	8.738
Total		1073128	83299	100.000

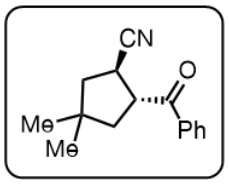
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

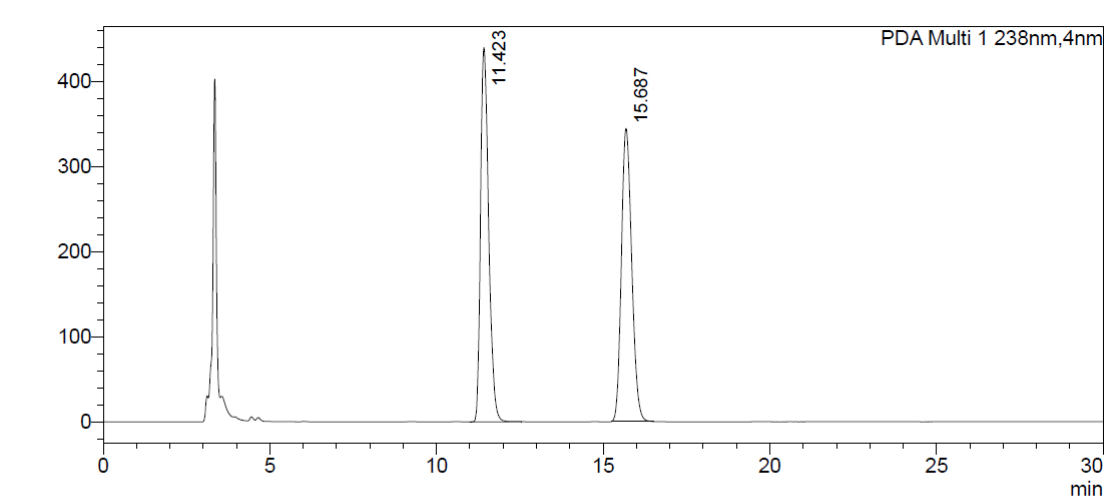
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.185	490266	38703	60.398
2	6.741	321456	23914	39.602
Total		811722	62617	100.000



((*R*,*R*)-3i)

Racemic

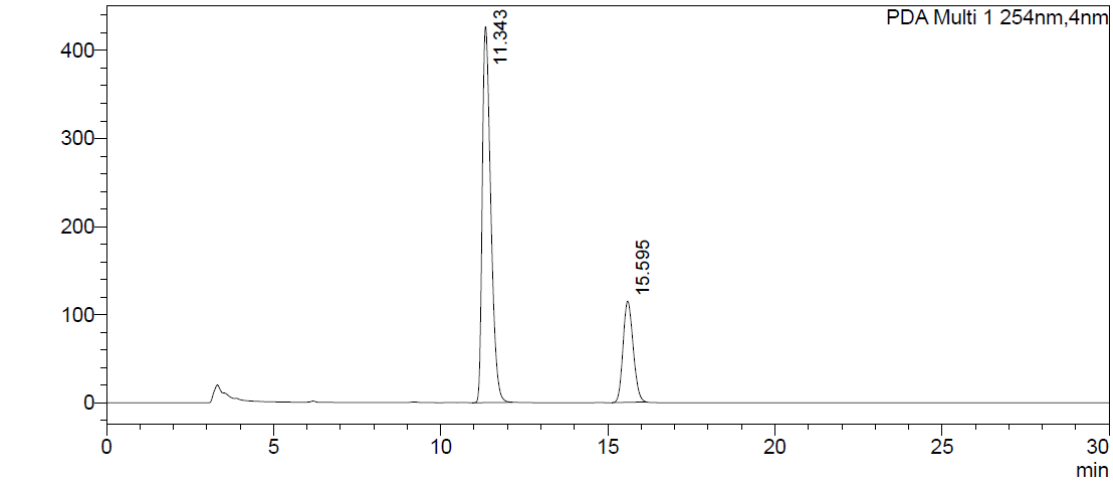


<Peak Table>

PDA Ch1 238nm

Peak#	Ret. Time	Area	Height	Area%
1	11.423	7437902	439562	50.081
2	15.687	7413777	344081	49.919
Total		14851679	783643	100.000

Scalemic with **(*S*,*S*)-4e**

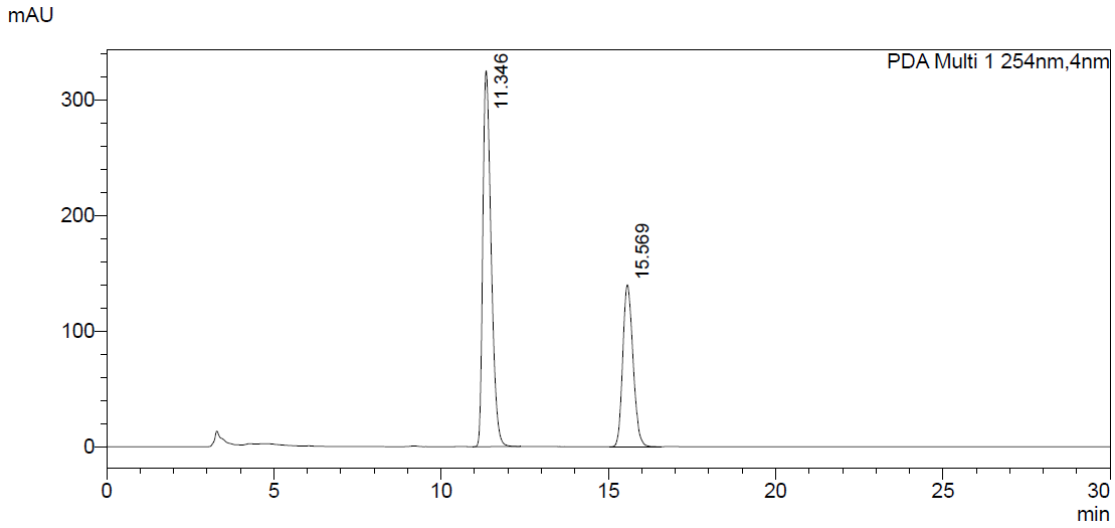


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.343	7544140	426518	75.717
2	15.595	2419525	114886	24.283
Total		9963666	541404	100.000

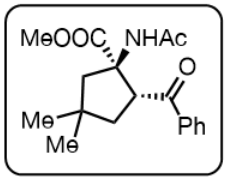
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

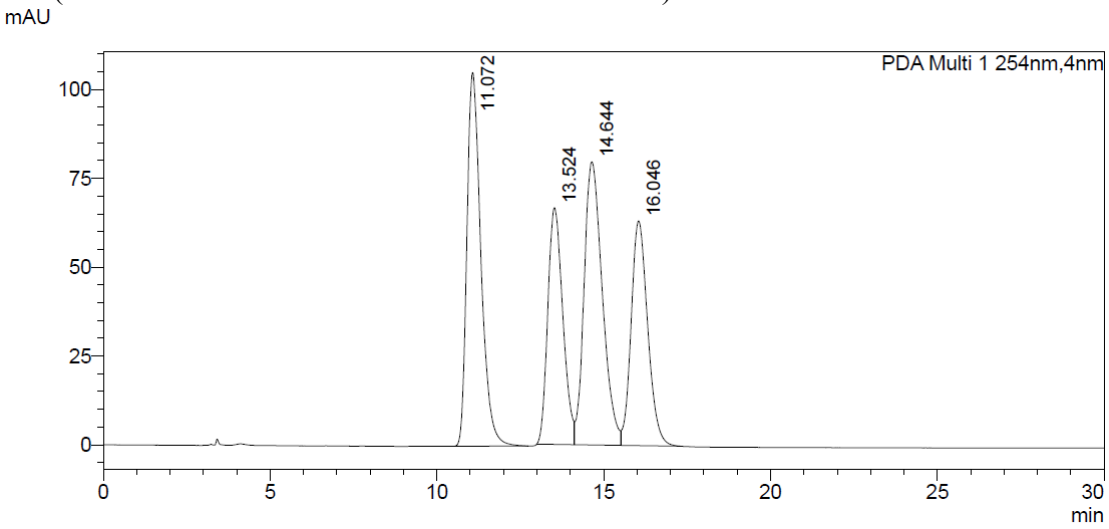
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.346	5620685	324850	65.272
2	15.569	2990512	139886	34.728
Total		8611197	464736	100.000



((*R*,*R*)-3j)

Racemic (contains two diastereomers in a ratio about 3:2)

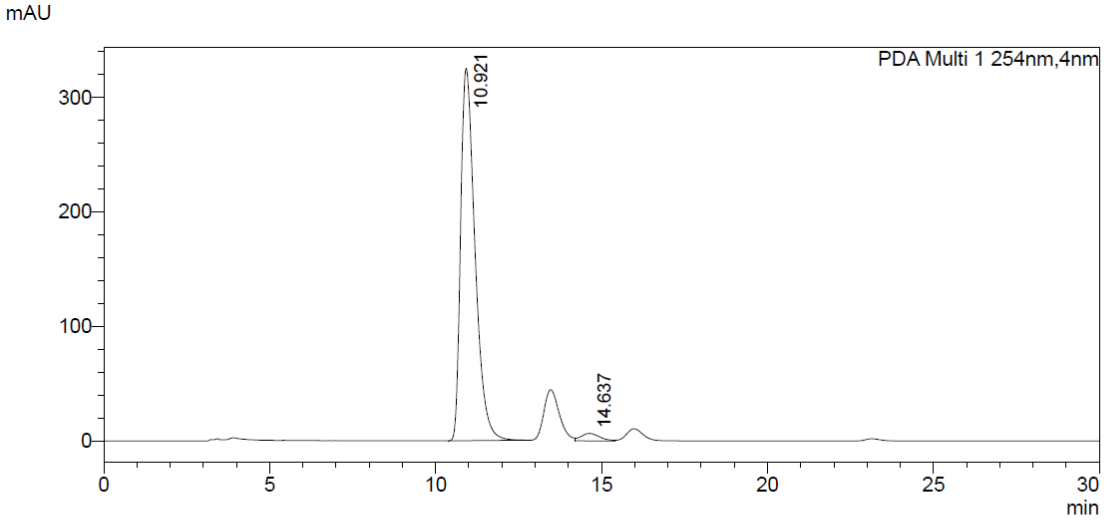


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.072	3064627	105167	29.524
2	13.524	2091581	66639	20.150
3	14.644	3039385	79707	29.280
4	16.046	2184666	63246	21.046
Total		10380258	314759	100.000

Scalemic with **(*S*,*S*)-4e**

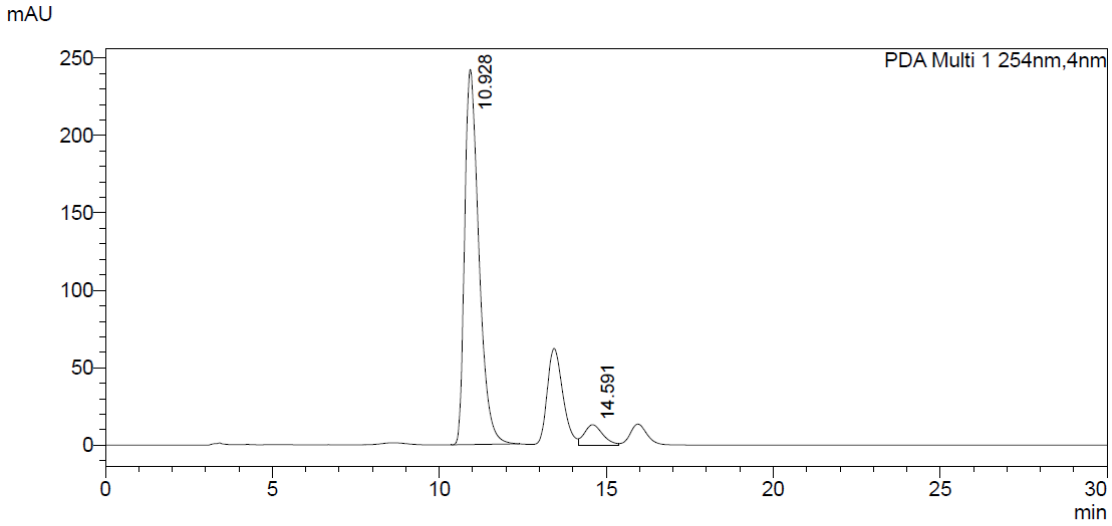


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.921	9768325	324941	97.486
2	14.637	251913	6543	2.514
Total		10020238	331485	100.000

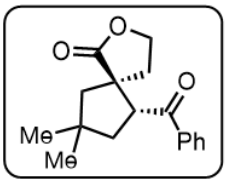
Scalemic with ***(S,S)*-4a**



<Peak Table>

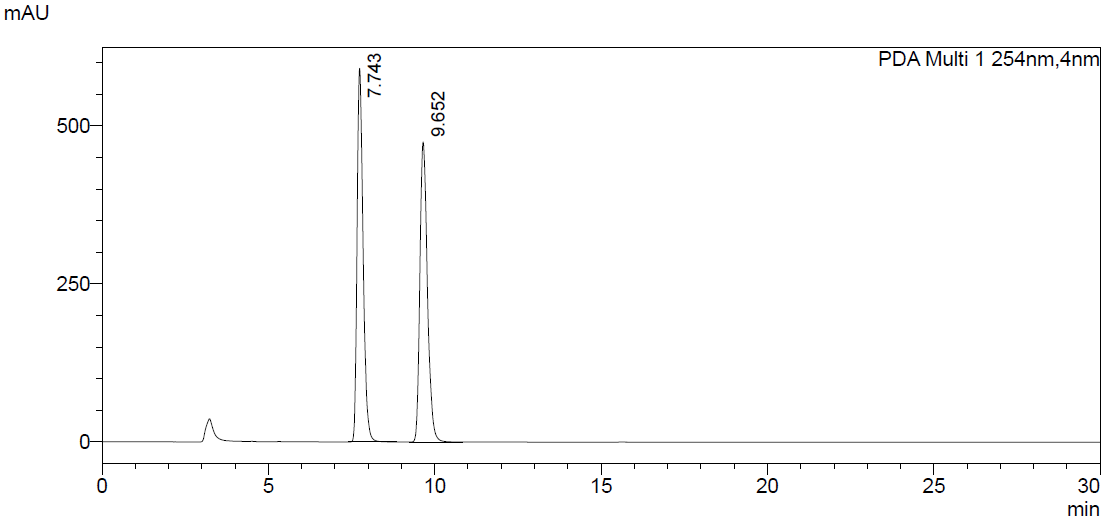
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.928	7203933	242083	93.530
2	14.591	498361	13087	6.470
Total		7702294	255170	100.000



((*R*,*R*)-3k)

Racemic

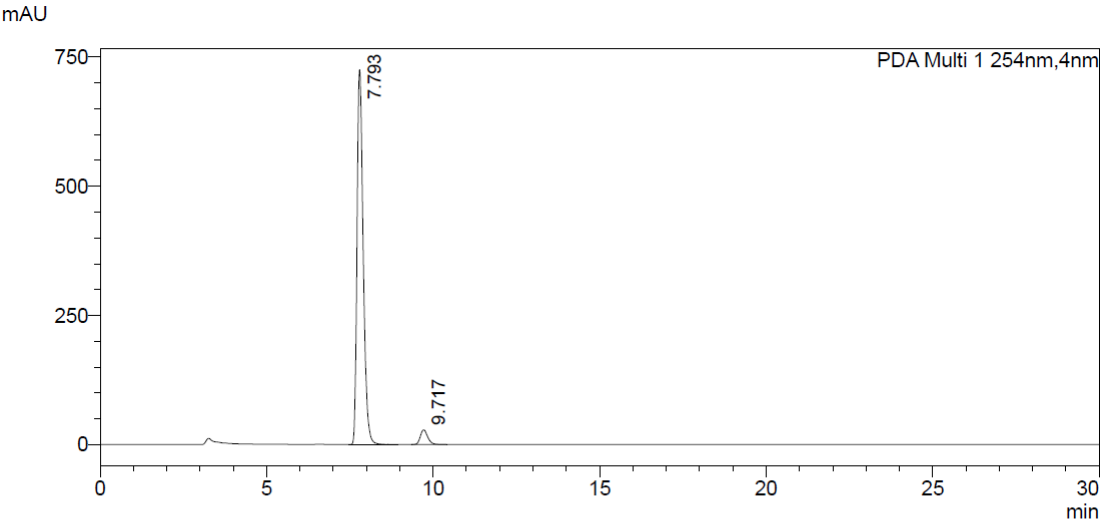


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.743	7447217	591382	49.926
2	9.652	7469328	474998	50.074
Total		14916545	1066380	100.000

Scalemic with **(*S*,*S*)-4e**

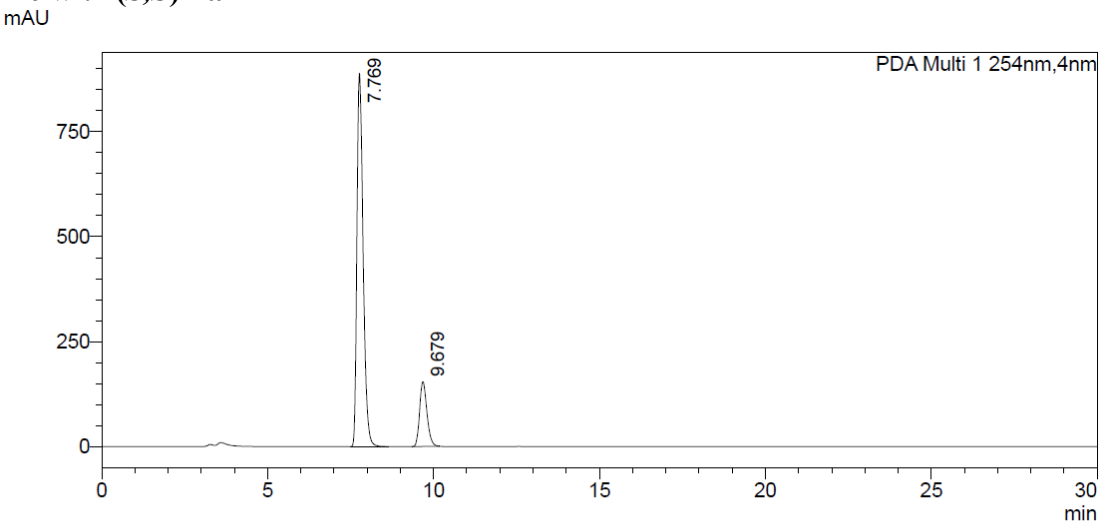


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.793	9331842	725655	95.516
2	9.717	438067	28461	4.484
Total		9769909	754116	100.000

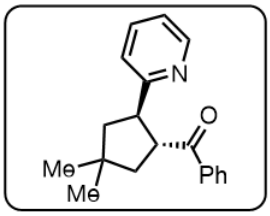
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

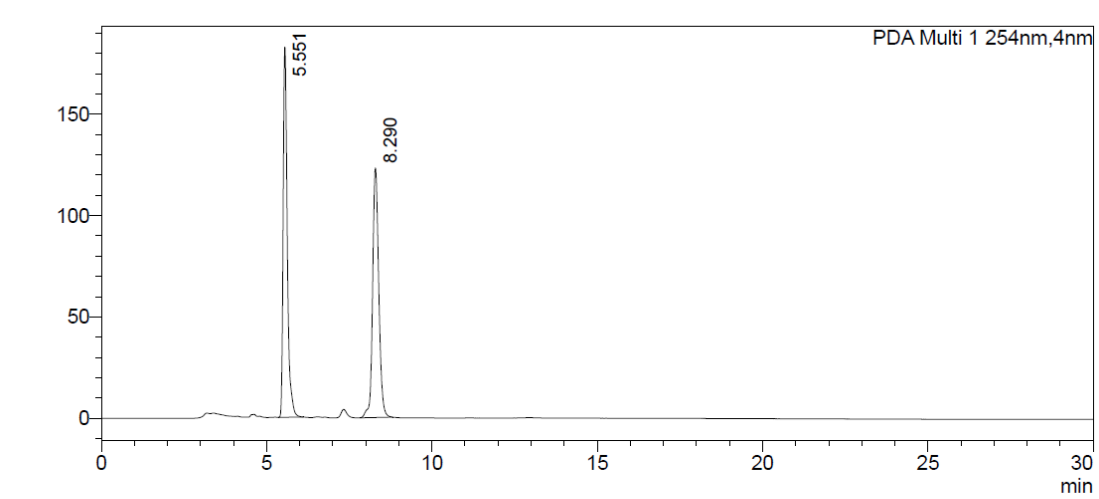
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.769	11574298	888782	83.037
2	9.679	2364373	154123	16.963
Total		13938670	1042905	100.000



((*R*,*R*)-3l)

Racemic

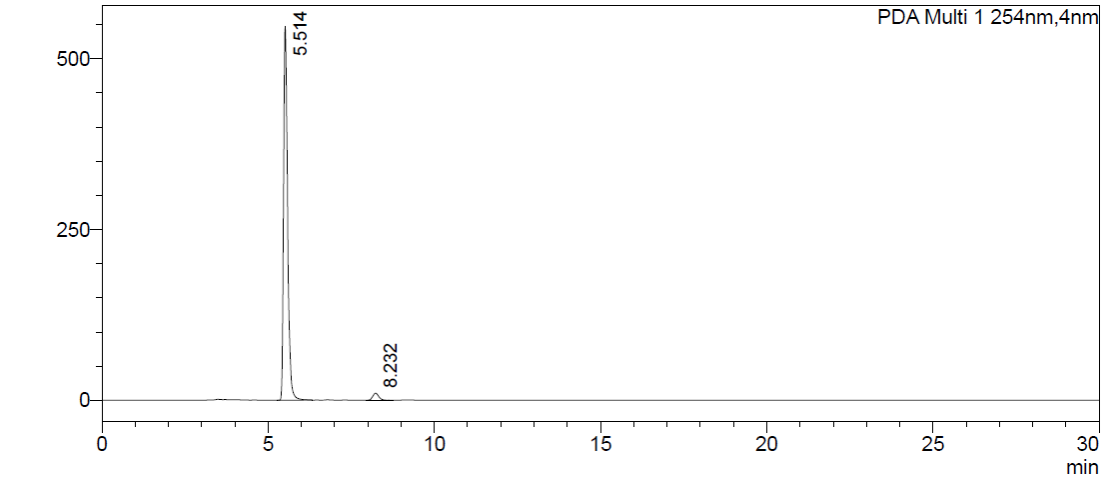


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.551	1588456	182544	50.037
2	8.290	1586081	123013	49.963
Total		3174537	305557	100.000

Scalemic with **(*S*,*S*)-4e**

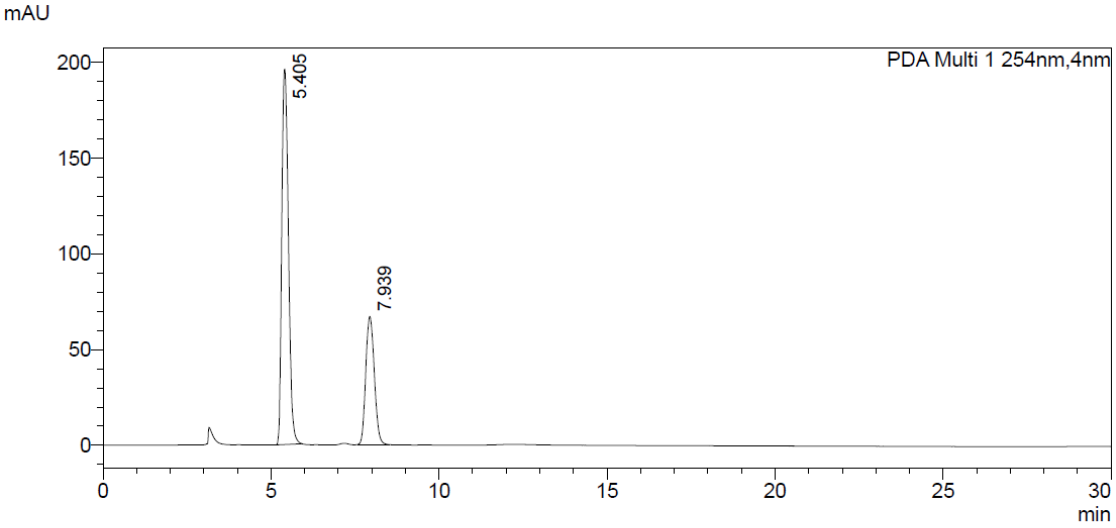


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.514	4625198	547306	97.312
2	8.232	127771	10331	2.688
Total		4752969	557636	100.000

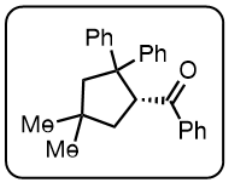
Scalemic with **(*S*,*S*)-4a**



<Peak Table>

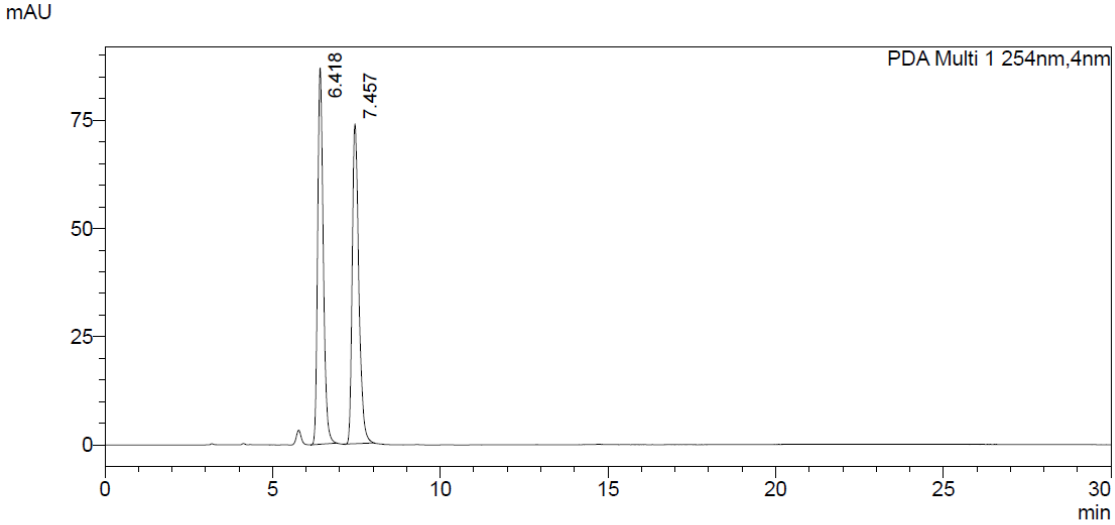
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.405	2694035	196189	69.407
2	7.939	1187481	66963	30.593
Total		3881517	263151	100.000



((*R*,*R*)-3m)

Racemic

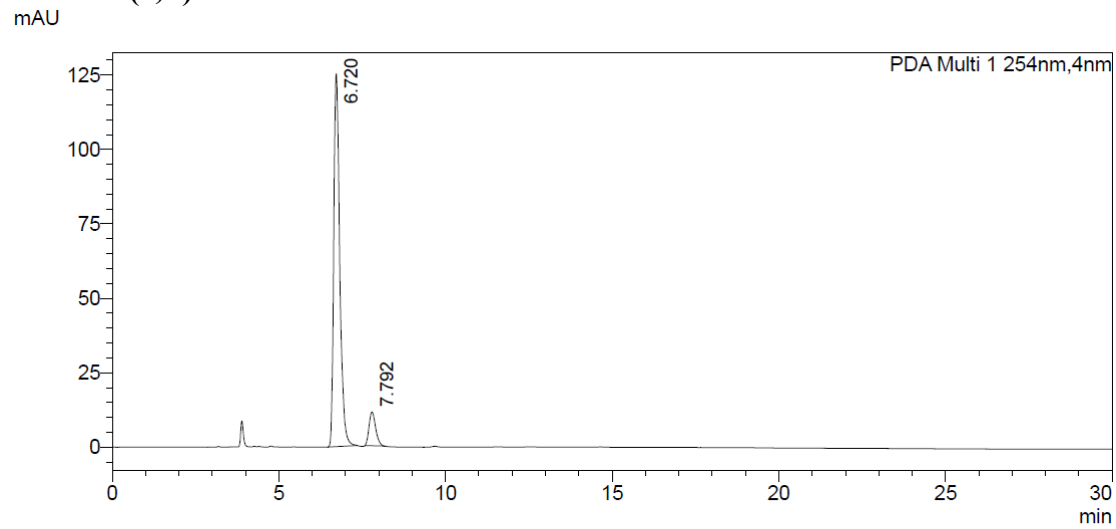


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.418	1014159	86903	50.130
2	7.457	1008912	73880	49.870
Total		2023071	160783	100.000

Scalemic with **(*S*,*S*)-4e**

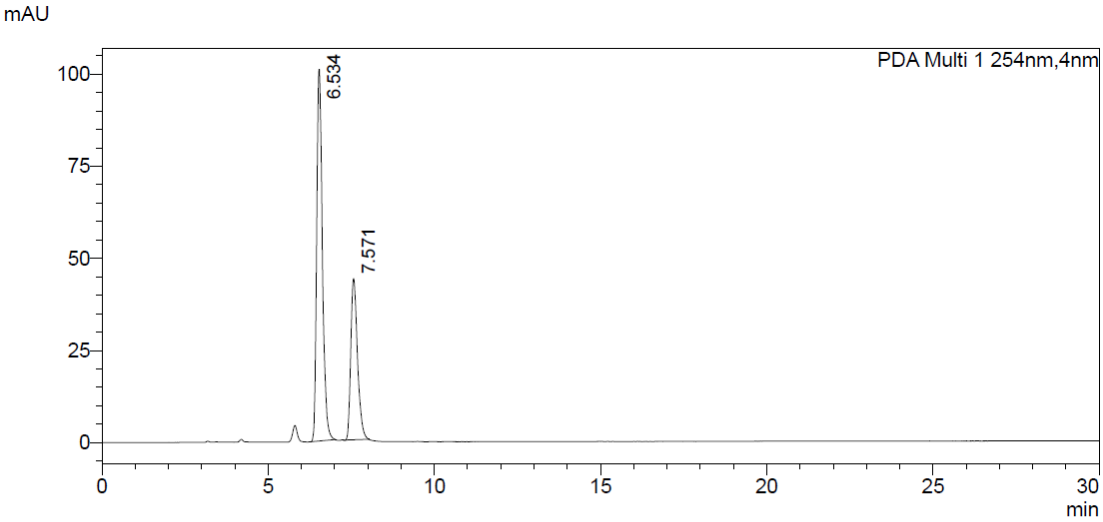


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.720	1556977	125253	90.901
2	7.792	155847	11296	9.099
Total		1712824	136548	100.000

Scalemic with **(*S*,*S*)-4a**



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.534	1199551	100841	66.193
2	7.571	612640	43729	33.807
Total		1812191	144570	100.000