

Supporting Information for

High-performance Anionic Stereogenic-at-cobalt(III) Complex/Halide Salts/Oxone Catalytic System for Enantioselective Halocyclization of Olefins

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1. Introduction

1.1. General Data

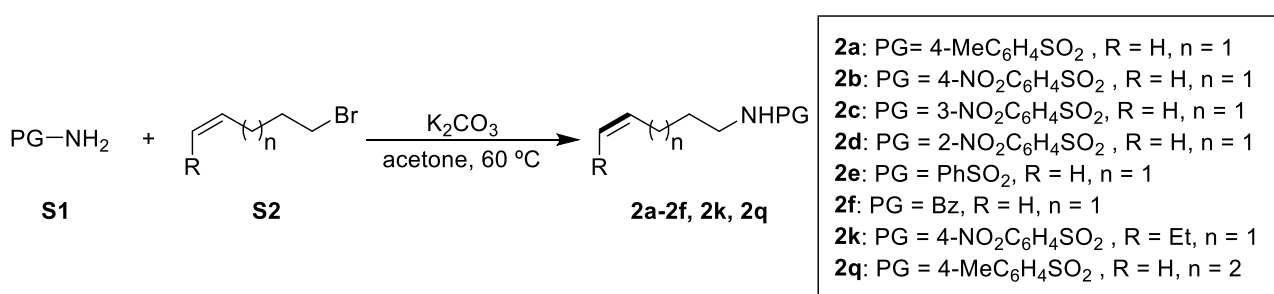
¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectrums were recorded on an Agilent 600 NMR spectrometer at 600 MHz, 151 MHz and 564 MHz using CDCl₃ as solvent, respectively. ¹H-NMR data are reported as follows: δ , chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Melting points were measured on a digital melting point apparatus and the temperature was uncorrected. High resolution mass spectrometric measurements (HRMS) were performed by the Waters Xevo G2-XS TOF (ESI Source). HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). Chiralpak IA, IC, ID and IE columns were purchased from Daicel Chemical Industries, Ltd. Single crystal structures of the compounds were determined by measuring X-ray intensity data on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at low and room temperature (172-203 K) during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were assigned in idealized locations. Optical rotations were recorded on an Anton Paar MCP-100 polarimeter.

1.2. Materials

Analytic grade solvents for the column chromatography and commercially available reagents were used as received. *n*-hexane, was dried over CaH₂ and distilled prior to use. Toluene was dried over Na and distilled prior to use. The catalysts (Λ -**1a** to Λ -**1e**)^[1] were known compounds and synthesized according to the literatures. Alkenes **2m**^[2], **2p**^[1b] β,γ -unsaturated hydrazones **2r-2v**^[3], tryptophols and tryptamine **2w-2z**^[1d] were known compounds and prepared according to following procedure, and the spectral data were in accordance with the literatures. Alkenes **2a-2l**, **2n-2o** and **2q** were new compounds and synthesized according to the procedure reported.^[1b]

2. General Procedure for Preparation of Alkenes 2

2.1 General Procedure for Preparation of Substrates 2a-2f, 2k, 2q



To an oven-dried round bottom flask with magnetic stir bar was added alkyl bromide **S2** (1.1 equiv), amide **S1** (1.0 equiv), K₂CO₃ (2.0 equiv) and acetone (1.0 M). The solution was heated at 60 °C. Upon completion of the reaction (16 h), the solution was cooled to room temperature, filtered through a plug of Celite™ and rinsed with EtOAc, and solvent was removed in vacuo to afford a crude product. Purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the substrate **2a-2f, 2k, 2q**.

4-Methyl-N-(pent-4-en-1-yl)benzenesulfonamide 2a: yield: 2.347 g (76%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.74 – 5.67 (m, 1H), 4.98 – 4.94 (m, 2H), 4.60 – 4.58 (m, 1H), 2.97 – 2.93 (m, 2H), 2.43 (s, 3H), 2.06 – 2.03 (m, 2H), 1.59 – 1.53 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 143.4, 137.3, 137.2, 129.8, 127.2, 115.6, 42.7, 30.7, 28.8, 21.6; HRMS (ESI) calculated for C₁₂H₁₇NO₂S [M+H]⁺: 240.1058, found: 240.1065.

4-Nitro-N-(pent-4-en-1-yl)benzenesulfonamide 2b: yield: 2.485 g (75%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); light yellow solid; m.p.: 107.7 – 109.2 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.37 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 5.78 – 5.66 (m, 1H), 5.05 – 4.94 (m, 2H), 4.69 (s, 1H), 3.04 (dd, *J* = 13.4, 6.8 Hz, 2H), 2.07 (q, *J* = 7.0 Hz, 2H), 1.60 (dd, *J* = 13.8, 6.6 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 150.2, 146.2, 136.9, 128.4, 124.5, 116.1, 42.9, 30.6, 28.9; HRMS (ESI) calculated for C₁₁H₁₄N₂O₄S [M+H]⁺: 271.0753, found: 271.0754.

3-Nitro-N-(pent-4-en-1-yl)benzenesulfonamide 2c: yield: 2.105 g (75%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); light yellow solid; m.p.: 100.5 – 101.7 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.71 (s, 1H), 8.44 (d, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 1H), 7.76 (t, *J* = 7.9 Hz, 1H), 5.78 – 5.65 (m, 1H), 5.05 – 4.92 (m, 2H), 4.81 (s, 1H), 3.09 – 3.00 (m, 2H), 2.07 (d, *J*

= 6.6 Hz, 2H), 1.64 – 1.56 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.5, 142.7, 137.0, 132.6, 130.1, 127.2, 122.3, 116.0, 42.9, 30.6, 28.9; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 271.0753, found: 271.0751.

2-Nitro-*N*-(pent-4-en-1-yl)benzenesulfonamide 2d: yield: 2.360 g (78%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); light yellow solid; m.p.: 100.5 – 101.7 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.18 – 8.09 (m, 1H), 7.87 (dd, J = 6.7, 2.1 Hz, 1H), 7.80 – 7.70 (m, 2H), 5.78 – 5.66 (m, 1H), 5.28 (s, 1H), 5.00 – 4.96 (m, 2H), 3.12 (q, J = 6.8 Hz, 2H), 2.09 (q, J = 7.0 Hz, 2H), 1.69 – 1.61 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.2, 37.0, 134.0, 133.6, 132.8, 131.2, 125.4, 115.9, 43.3, 30.6, 28.8; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 271.0753, found: 271.0753.

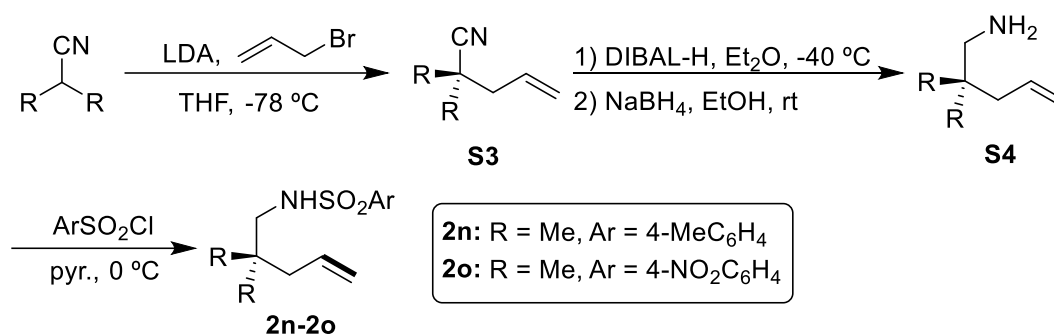
***N*-(pent-4-en-1-yl)benzenesulfonamide 2e**: yield: 2.601 g (74%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 6.8 Hz, 1H), 7.53 – 7.51 (m, 2H), 5.77 – 5.64 (m, 1H), 5.01 – 4.91 (m, 2H), 4.45 (s, 1H), 3.04 – 2.93 (m, 2H), 2.05 – 2.04 (m, 2H), 1.59 – 1.55 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 140.3, 137.2, 132.7, 129.2, 127.1, 115.7, 42.8, 30.7, 28.9; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 226.0902, found: 226.0910.

***N*-(pent-4-en-1-yl)benzamide 2f**: yield: 2.150 g (75%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.81 – 7.70 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.33 (m, 2H), 6.24 (s, 1H), 5.86 – 5.82 (m, 1H), 5.06 (dd, J = 17.1, 1.6 Hz, 1H), 5.00 (dd, J = 10.2, 1.6 Hz, 1H), 3.46 (q, J = 7.0 Hz, 2H), 2.21 – 2.12 (m, 2H), 1.78 – 1.67 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 167.6, 137.9, 134.9, 131.4, 128.6, 126.9, 115.4, 39.7, 31.3, 28.9; **HRMS (ESI)** calculated for $\text{C}_{12}\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 190.1232, found: 190.1235.

(*Z*)-*N*-(hept-4-en-1-yl)-4-nitrobenzenesulfonamide 2k: yield: 2.140 g (83%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); white solid; m.p.: 105.2 – 106.5 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.37 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.6 Hz, 2H), 5.42 – 5.38 (m, 1H), 5.24 – 5.19 (m, 1H), 4.65 (s, 1H), 3.03 (q, J = 6.4 Hz, 2H), 2.04 (q, J = 7.2 Hz, 2H), 2.00 – 1.92 (m, 2H), 1.60 – 1.51 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 150.2, 146.2, 133.4, 128.4, 127.0, 124.5, 43.2, 29.7, 24.2, 20.6, 14.3; **HRMS (ESI)** calculated for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 299.1066, found: 299.1072.

***N*-(hex-5-en-1-yl)-4-methylbenzenesulfonamide 2q**: yield: 2.160 g (67%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); colorless oil; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.75 (d, $J = 7.9$ Hz, 2H), 7.30 (d, $J = 7.5$ Hz, 2H), 5.77 – 5.65 (m, 1H), 4.96 – 4.91 (m, 2H), 4.52 (s, 1H), 2.99 – 2.89 (m, 2H), 2.43 (s, 3H), 1.99 (d, $J = 6.7$ Hz, 2H), 1.52 – 1.42 (m, 2H), 1.38 – 1.35 (m, 2H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 143.4, 138.2, 137.2, 129.8, 127.2, 115.0, 43.2, 33.1, 29.1, 25.8, 21.6; **HRMS (ESI)** calculated for $\text{C}_{16}\text{H}_{23}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 254.1215, found: 254.1218.

2.2 General Procedure for Preparation of Substrates 2n-2o



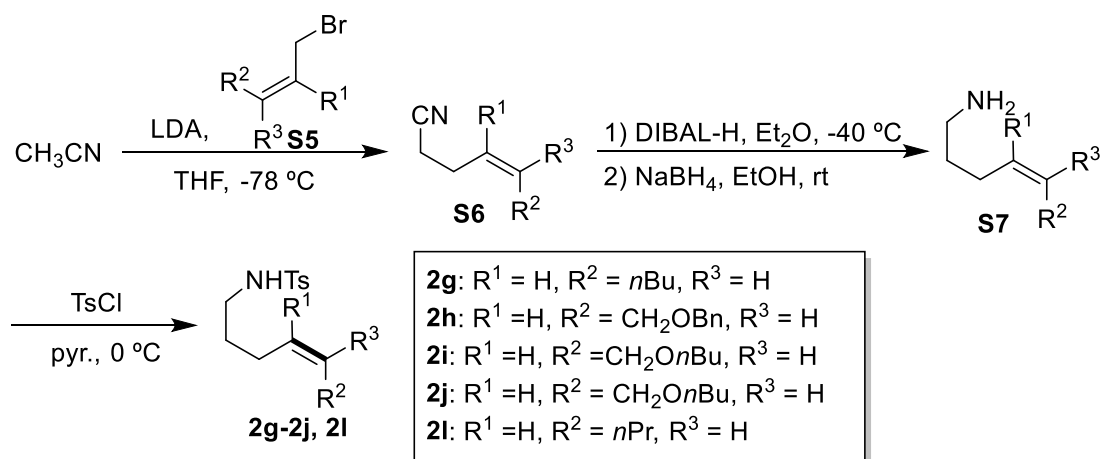
n-Butyllithium (2.4 M in hexane, 12 mmol, 1.2 equiv.) was added to the diisopropylamine (12 mmol, 1.2 equiv.) at 0 °C in THF (15 mL). The solution was stirred at 0 °C for 30 min, and then cooled to -78 °C. The solution of disubstituted acetonitrile (10 mmol, 1.0 equiv.) in THF (5 mL) was added to the reaction mixture slowly. The solution was stirred at -78 °C for another 2 h, to which the allyl bromide (12.5 mmol, 1.2 equiv.) was added. The reaction mixture was stirred overnight. The reaction was quenched with addition of saturated aqueous NH_4Cl , extracted with Et_2O and the organic layers were dried over Na_2SO_4 , and concentrated. The resultant oil was used without purification in the subsequent step. The DIBAL-H (1.5 M in toluene, 15 mmol, 1.5 equiv.) was added to the alkylated nitrile **S3** in Et_2O (20 mL) at -40 °C. The reaction mixture was stirred for 3 h and then NaBH_4 (30 mmol, 3.0 equiv.) was added. After 10 min, the EtOH (20 mL) was added to the solution carefully. The reaction mixture was allowed to warm to room temperature and stirred overnight then diluted with Et_2O (20 mL), extracted with 1 M HCl . The combined acidic extracts were made basic (pH > 13) with 15% NaOH (aq.) and extracted with CH_2Cl_2 . The combined organic extracts were dried over Na_2SO_4 and concentrated. The resultant oil was used without purification in the subsequent step. The amine **S4** (5.0 mmol, 1.0 equiv.) was dissolved in pyridine (10 mL) and cooled to 0 °C. Following addition of the sulfonyl chloride (5.5 mmol, 1.1 equiv.), the reaction mixture was stirred at room temperature for 4 h. The solution was diluted with Et_2O (20 mL), then washed with 1 M HCl , dried

over Na₂SO₄ and purified by column chromatography, EtOAc/Hexanes (5%→20% EtOAc) to afford the sulfonyl-protected γ -amino-alkene **2n-2o**.

N-(2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide 2n: yield: 3.317 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 7/1); white solid; m.p.: 107.4 – 109.7 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.72 (m, 1H), 5.01 (t, *J* = 13.7 Hz, 2H), 4.52 (s, 1H), 2.68 (d, *J* = 6.9 Hz, 2H), 2.43 (s, 3H), 1.96 (d, *J* = 7.4 Hz, 2H), 0.86 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 143.4, 137.2, 134.4, 129.8, 127.2, 118.0, 53.0, 44.2, 34.2, 25.0, 21.6; HRMS (ESI) calculated for C₁₄H₂₁NO₂S [M+H]⁺: 268.1371, found: 268.1371.

N-(2,2-dimethylpent-4-en-1-yl)-4-nitrobenzenesulfonamide 2o: yield: 2.150 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 5/1); white solid; m.p.: 105.2 – 106.5 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.37 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.7 Hz, 2H), 5.76 – 5.71 (m, 1H), 5.09 – 4.98 (m, 2H), 4.65 (s, 1H), 2.77 (d, *J* = 6.7 Hz, 2H), 1.97 (d, *J* = 7.4 Hz, 2H), 0.88 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 150.2, 146.1, 134.1, 128.3, 124.5, 118.3, 53.2, 44.2, 34.3, 25.0; HRMS (ESI) calculated for C₁₃H₁₈N₂O₄S [M+H]⁺: 299.1066, found: 299.1068.

2.3 General Procedure for Preparation of Substrates **2g-2j**, **2l**



n-Butyllithium (2.4 M in hexane, 12 mmol, 1.2 equiv.) was added to the diisopropylamine (12 mmol, 1.2 equiv.) at 0 °C in THF (15 mL). The solution was stirred at 0 °C for 30 min, and then cooled to -78 °C. The solution of acetonitrile (10 mmol, 1.0 equiv.) in THF (5 mL) was added to the reaction mixture slowly. The solution was stirred at -78 °C for 2 h, and then the substituted allyl bromide **S5** (12.5 mmol, 1.2 equiv.) was added. The reaction mixture was stirred overnight. The reaction was quenched with addition of saturated aqueous NH₄Cl, extracted with Et₂O and the organic layers were

dried over Na₂SO₄, and concentrated. The resultant oil was used without purification in the subsequent step. The DIBAL-H (1.5 M in toluene, 15 mmol, 1.5 equiv.) was added to the alkylated nitrile **S6** in Et₂O (20 mL) at -40 °C. The reaction mixture was stirred for 3 h and then NaBH₄ (30 mmol, 3.0 equiv.) was added. After 10 min, the EtOH (20 mL) was added to the solution carefully. The reaction mixture was allowed to warm to room temperature and stirred overnight then diluted with Et₂O (20 mL), extracted with 1 M HCl. The combined acidic extracts were made basic (pH > 13) with 15% NaOH (aq.) and extracted with CH₂Cl₂. The combined organic extracts were dried over Na₂SO₄ and concentrated. The resultant oil was used without purification in the subsequent step. The amine **S7** (5 mmol, 1.0 equiv.) was dissolved in pyridine (10 mL) and cooled to 0 °C. Following addition of the tosyl chloride (5.5 mmol, 1.1 equiv.), the reaction mixture was stirred at room temperature for 4 h. The solution was diluted with Et₂O (20 mL), then washed with 1 M HCl, dried over Na₂SO₄ and purified by column chromatography, EtOAc/Hexanes (5%→20% EtOAc) to afford the substrate **2g-2j, 2l**.

(Z)-4-Methyl-N-(non-4-en-1-yl)benzenesulfonamide 2g: yield: 2.160 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.39 – 5.35 (m, 1H), 5.26 – 5.22 (m, 1H), 4.37 (s, 1H), 2.95 (q, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.01 (q, *J* = 7.2 Hz, 2H), 1.98 – 1.95 (m, 2H), 1.55 – 1.48 (m, 2H), 1.31 – 1.27 (m, 4H), 0.88 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (151 MHz, cdcl₃) δ 143.4, 137.3, 131.5, 129.8, 127.9, 127.2, 43.1, 31.9, 29.7, 27.0, 24.4, 22.4, 21.6, 14.0; HRMS (ESI) calculated for C₁₆H₂₅NO₂S [M+H]⁺: 296.1684, found: 296.1692.

(Z)-N-(6-(Benzyloxy)hex-4-en-1-yl)-4-methylbenzenesulfonamide 2h: yield: 2.140 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.22 (m, 7H), 5.68 – 5.57 (m, 1H), 5.49 – 5.47 (m, 1H), 5.02 (s, 1H), 4.55 – 4.51 (m, 2H), 3.99 (d, *J* = 6.7 Hz, 2H), 2.96 – 2.85 (m, 2H), 2.40 (s, 3H), 2.10 – 2.08 (m, 2H), 1.59 – 1.51 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 143.2, 138.2, 137.4, 132.9, 129.7, 128.5, 128.0, 127.8, 127.1, 127.1, 72.5, 65.4, 42.3, 29.1, 24.4, 21.5; HRMS (ESI) calculated for C₂₀H₂₅NNaO₃S [M+Na]⁺: 382.1453, found: 382.1460.

(Z)-N-(6-Butoxyhex-4-en-1-yl)-4-methylbenzenesulfonamide 2i: yield: 1.150 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 5.59 (s, 1H), 5.46 – 5.44 (m, 1H), 4.92

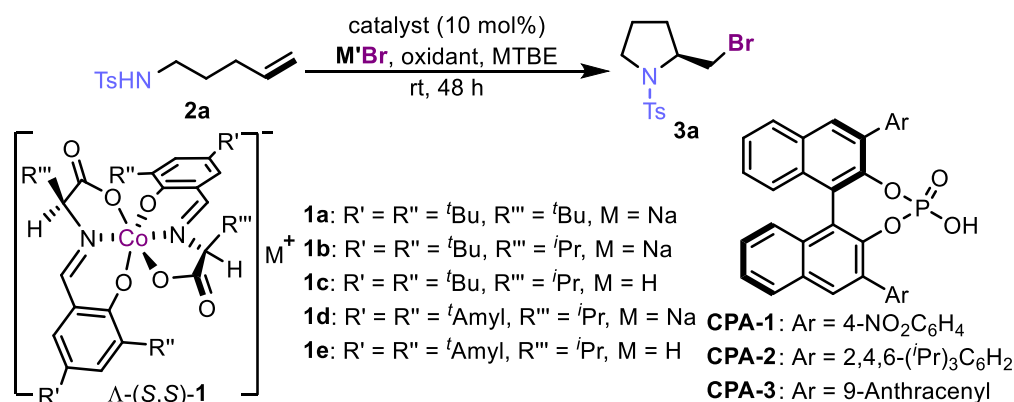
(s, 1H), 3.95 (d, $J = 5.8$ Hz, 2H), 3.44 (t, $J = 6.6$ Hz, 2H), 3.01 – 2.87 (m, 2H), 2.42 (s, 3H), 2.12 (d, $J = 6.5$ Hz, 2H), 1.56 (s, 4H), 1.36 (d, $J = 7.2$ Hz, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 143.3, 137.6, 132.3, 129.7, 127.5, 127.1, 70.7, 66.1, 42.3, 31.8, 29.2, 24.4, 21.6, 19.4, 14.0; **HRMS (ESI)** calculated for $\text{C}_{17}\text{H}_{27}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 348.1609, found: 348.1617.

(Z)-N-(6-(Allyloxy)hex-4-en-1-yl)-4-methylbenzenesulfonamide 2j: yield: 2.130 g (40%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 6.01 – 5.88 (m, 1H), 5.62 (dd, $J = 16.7$, 7.5 Hz, 1H), 5.48 (dd, $J = 17.3$, 8.3 Hz, 1H), 5.29 (d, $J = 17.2$ Hz, 1H), 5.21 (d, $J = 10.2$ Hz, 1H), 5.00 (s, 1H), 4.01 (d, $J = 5.4$ Hz, 2H), 3.97 (d, $J = 6.4$ Hz, 2H), 2.98 – 2.89 (m, 2H), 2.42 (s, 3H), 2.14 (d, $J = 6.8$ Hz, 2H), 1.63 – 1.55 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 143.3, 137.5, 134.7, 132.9, 129.7, 127.1, 127.0, 117.5, 71.6, 65.3, 42.2, 29.1, 24.4, 21.6; **HRMS (ESI)** calculated for $\text{C}_{16}\text{H}_{23}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 332.1296, found: 332.1297.

(E)-4-Methyl-N-(oct-4-en-1-yl)benzenesulfonamide 2l: yield: 1.120 g (80%); (Flash column chromatography eluent, petrol ether/EtOAc = 10/1); white solid; m.p.: 105.2 – 106.5 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 7.1$ Hz, 2H), 7.30 (d, $J = 7.3$ Hz, 2H), 5.41 – 5.31 (m, 1H), 5.31 – 5.20 (m, 1H), 4.38 (s, 1H), 2.94 (d, $J = 6.0$ Hz, 2H), 2.43 (s, 3H), 1.97 (d, $J = 6.4$ Hz, 2H), 1.91 (d, $J = 6.4$ Hz, 2H), 1.55 – 1.47 (m, 2H), 1.39 – 1.28 (m, 2H), 0.86 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 143.4, 137.3, 131.8, 129.8, 128.7, 127.2, 42.8, 34.7, 29.6, 29.4, 22.7, 21.6, 13.7; **HRMS (ESI)** calculated for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 282.1528, found: 282.1534.

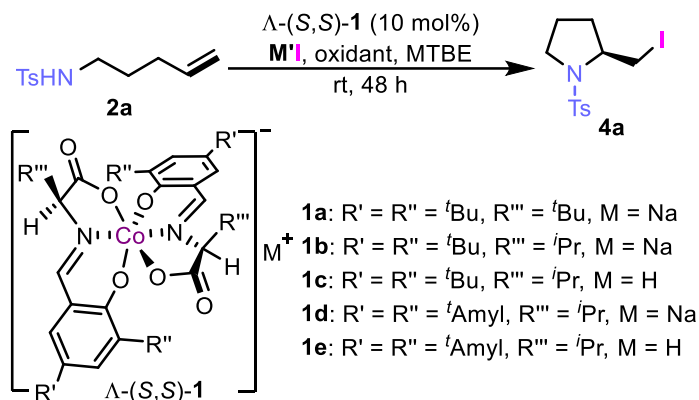
3. Detailed Optimization of the Reaction Conditions for Asymmetric Halocyclization

Table S1 | Optimization of oxidative bromocyclization conditions^[a]



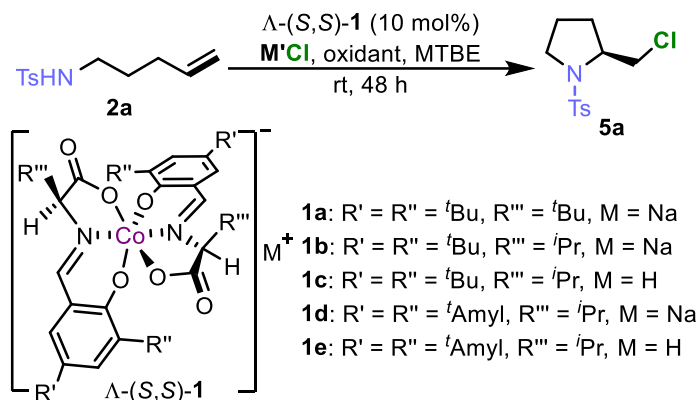
entry	catalyst	M'Br	oxidant	yield [%] ^[b]	e.r. ^[c]
1	Λ-1a	NaBr	Oxone	95	60:40
2	Λ-1b	NaBr	Oxone	97	94.5:5.5
3	Λ-1c	NaBr	Oxone	98	94:6
4	Λ-1d	NaBr	Oxone	91	90:10
5	Λ-1e	NaBr	Oxone	89	90.5:9.5
6	CPA-1	NaBr	Oxone	90	51:49
7	CPA-2	NaBr	Oxone	88	50.5:49.5
8	CPA-3	NaBr	Oxone	86	54:46
9	Λ-1b	KBr	Oxone	69	94:6
10	Λ-1b	LiBr	Oxone	88	93.5:6.5
11	Λ-1b	TBAB	Oxone	93	78.5:21.5
12	Λ-1b	NaBr	K ₂ S ₂ O ₈	51	89:11
13	Λ-1b	NaBr	<i>m</i> CPBA	trace	-
14	Λ-1b	NaBr	CAN	46	89:11
15 ^[d]	Λ-1b	NaBr	Oxone	97	97:3
16 ^[d,e]	Λ-1b	NaBr	Oxone	95	97:3
17 ^[d,f]	Λ-1b	NaBr	Oxone	95	97:3
18 ^[d,g]	Λ-1b	NaBr	Oxone	92	96.5:3.5

[a] Reaction conditions: **2a** (0.10 mmol), M'Br (0.10 mmol), oxidant (0.30 mmol), and catalyst (Λ-1 or CPA-1–3, 0.01 mmol) in MTBE (2.0 mL) at room temperature unless otherwise noted. [b] Isolated yields were based on **2a**. [c] e.r. values were determined by chiral stationary HPLC. [d] Run at 0 °C. [e] 1.0 mol% catalyst was used. [f] 0.5 mol% catalyst was used. [g] 0.1 mol% catalyst was used.

Table S2 | Optimization of oxidative iodocyclization conditions^[a]

Entry	Δ-(S,S)-1	M'I	yield [%] ^[b]	e.r. ^[c]
1	Δ-1a	NaI	71	60:40
2	Δ-1b	NaI	98	84.5:15.5
3	Δ-1c	NaI	94	84:16
4	Δ-1d	NaI	98	80.5:19.5
5	Δ-1e	NaI	87	80:20
6	Δ-1b	KI	94	84:16
7	Δ-1b	TBAI	94	78:22
8 ^[d]	Δ-1b	NaI	95	89.5:10.5
9 ^[d,f]	Δ-1b	NaI	95	89.5:10.5
10 ^[e,f]	Δ-1b	NaI	92	92.5:7.5
11 ^[e,f,g]	Δ-1b	NaI	92	92.5:7.5
12 ^[e,f,h]	Δ-1b	NaI	79	82:18

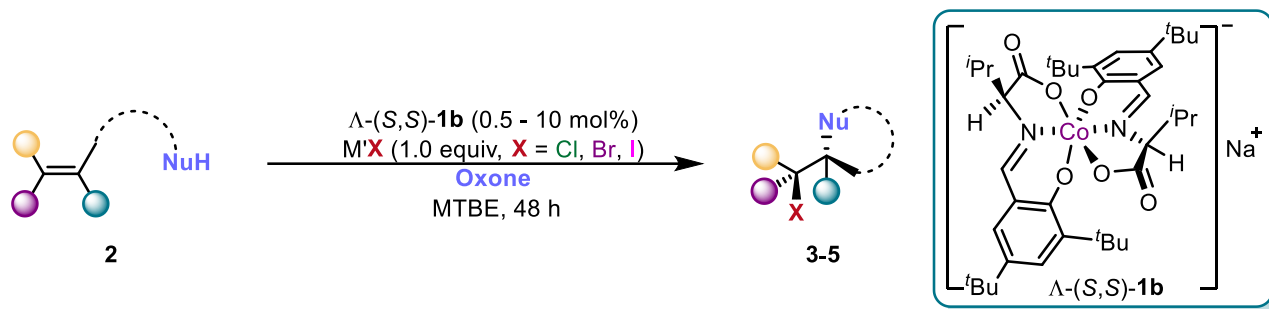
[a] Reaction conditions: **2a** (0.10 mmol), M'I (0.10 mmol), Oxone (0.30 mmol), and Δ-(S,S)-1 (0.01 mmol) in MTBE (2.0 mL) at room temperature unless otherwise noted. [b] Isolated yields were based on **2a**. [c] e.r. values were determined by chiral stationary HPLC. [d] Run at 0 °C. [e] Run at -15 °C. [f] Oxone (0.50 mmol) was employed. [g] 1.0 mol% catalyst was used. [h] 0.5 mol% catalyst was used.

Table S3 | Optimization of oxidative chlorocyclization conditions^[a]

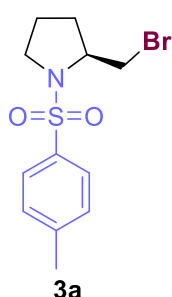
Entry	Λ -(<i>S,S</i>)-1	M'Cl	yield [%] ^[b]	e.r. ^[c]
1	Λ -1a	NH ₄ Cl	76	62.5:37.5
2	Λ -1b	NH ₄ Cl	83	83:17
3	Λ -1c	NH ₄ Cl	55	83.5:16.5
4	Λ -1d	NH ₄ Cl	59	81:19
5	Λ -1e	NH ₄ Cl	60	81:19
6	Λ -1b	NaCl	35	82.5:17.5
7	Λ -1b	KCl	37	83:17
8	Λ -1b	LiCl	86	79.5:20.5
9	Λ -1b	TBAC	37	56.5:43.5
10 ^[d]	Λ -1b	NH ₄ Cl	85	83.5:16.5
11 ^[d,e]	Λ -1b	NH ₄ Cl	81	77.5:22.5
12 ^[d,e,f]	Λ -1b	NH ₄ Cl	62	70.5:29.5
13 ^[d,e,g]	Λ -1b	NH ₄ Cl	60	60:40

[a] Reaction conditions: **2a** (0.10 mmol), M'Cl (0.10 mmol), Oxone (0.50 mmol), and Λ -(*S,S*)-1 (0.01 mmol) in MTBE (2.0 mL) at room temperature unless otherwise noted. [b] Isolated yields were based on **2a**. [c] e.r. values were determined by chiral stationary HPLC. [d] Oxone (1.00 mmol) was employed. [e] Run at 0 °C. [f] 5.0 mol% catalyst was used. [g] 1.0 mol% catalyst was used.

4. General Procedure for the Enantioselective Halocyclizations and Characterization Data

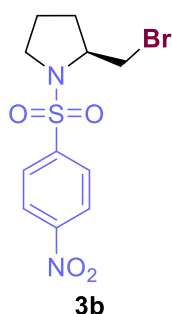


A 10mL oven-dried vial was charged with alkenes **2** (0.10 mmol), catalyst **1b** (0.5-10 mol%), $M'X$ (0.10 mmol), and MTBE (2 mL) at room temperature. The mixture was cooled to the corresponding temperature and stirred for 15 min. The Oxone (0.3-1.0 mmol) was added and the resulting solution was stirred vigorously until the reaction was complete (monitored by TLC). The reaction was saturated aqueous $Na_2S_2O_3$ (0.2 mL). The mixture was purified by flash column chromatography (silica gel, petrol ether/EtOAc = 5:1) to give the enantioenriched products.



(S)-2-(bromomethyl)-1-tosylpyrrolidine 3a: yield: 30.2 mg (95%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -29.4$ (c 0.30 CH_2Cl_2); 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 3.83 (t, $J = 8.7$ Hz, 1H), 3.77 (dd, $J = 9.8, 2.9$ Hz, 1H), 3.50 – 3.44 (m, 1H), 3.36 (t, $J = 9.7$ Hz, 1H), 3.18 – 3.14 (m, 1H), 2.44 (s, 3H), 1.96 – 1.93 (m, 1H), 1.89 – 1.79 (m, 1H), 1.76 – 1.72 (m, 1H), 1.58 – 1.52 (m, 1H); ^{13}C NMR

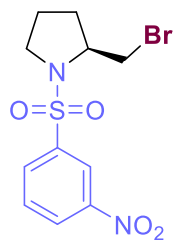
(151 MHz, $CDCl_3$) δ 143.8, 134.5, 129.9, 127.7, 60.5, 49.9, 36.1, 30.5, 23.9, 21.6; **HRMS (ESI)** calculated for $C_{12}H_{17}^{79}BrNO_2S$ $[M+H]^+$: 318.0163, found: 318.0158; **HRMS (ESI)** calculated for $C_{12}H_{17}^{81}BrNO_2S$ $[M+H]^+$: 320.0143, found: 320.0148; **Enantiomeric ratio**: 97:3, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, $T = 30$ °C, $\lambda = 254$ nm): $t_R = 7.17$ min (major), $t_R = 7.72$ min (minor).



(S)-2-(bromomethyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine 3b yield: 30.4 mg (87%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 114.5 – 115.7 °C; $[\alpha]_D^{20} = +50.7$ (c 0.30 CH_2Cl_2); 1H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, $J = 8.3$ Hz, 2H), 8.05 (d, $J = 8.3$ Hz, 2H), 3.90 (t, $J = 8.2$ Hz, 1H), 3.74 (d, $J = 9.9$ Hz, 1H), 3.58 – 3.49 (m, 1H), 3.42 (t, $J = 9.5$ Hz, 1H), 3.22 –

3.19 (m, 1H), 2.08 – 1.98 (m, 1H), 1.95 – 1.93 (m, 1H), 1.83 – 1.81 (m, 1H), 1.67 – 1.64 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 150.4, 143.4, 128.7, 124.5, 60.7, 49.9, 35.6, 30.5, 24.0; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{79}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 348.9858, found: 348.9866; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{81}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 350.9837, found: 350.9843; **Enantiomeric ratio**: 95:5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_{R} = 18.52 min (major), t_{R} = 16.64 min (minor).

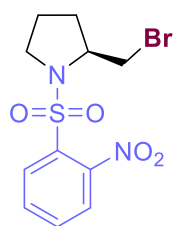
(S)-2-(bromomethyl)-1-((3-nitrophenyl)sulfonyl)pyrrolidine 3c: yield: 32.8 mg (94%); (Flash



3c

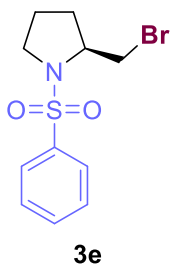
column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 105.3 – 106.5 °C; $[\alpha]_{\text{D}}^{20}$ = +75.7 (c 0.33 CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 8.69 (s, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 3.99 – 3.88 (m, 1H), 3.74 (dd, J = 10.1, 3.0 Hz, 1H), 3.59 – 3.50 (m, 1H), 3.44 (t, J = 9.5 Hz, 1H), 3.29 – 3.18 (m, 1H), 2.05 – 2.02 (m, 1H), 1.96 – 1.94 (m, 1H), 1.85 – 1.81 (m, 1H), 1.68 – 1.66 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.6, 140.1, 132.9, 130.7, 127.4, 122.6, 60.7, 50.0, 35.7, 30.5, 24.1; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{79}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 348.9858, found: 348.9860; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{81}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 350.9837, found: 350.9842; **Enantiomeric ratio**: 96:4, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_{R} = 19.28 min (major), t_{R} = 18.26 min (minor).

(S)-2-(bromomethyl)-1-((2-nitrophenyl)sulfonyl)pyrrolidine 3d: yield: 31.0 mg (89%); (Flash

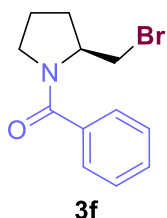


3d

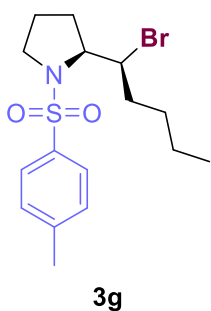
column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 100.1 – 101.3 °C; $[\alpha]_{\text{D}}^{20}$ = +29.4 (c 0.31 CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 8.03 (d, J = 7.5 Hz, 1H), 7.78 – 7.65 (m, 2H), 7.64 – 7.55 (m, 1H), 4.27 – 4.17 (m, 1H), 3.67 – 3.65 (m, 1H), 3.55 – 3.48 (m, 1H), 3.48 – 3.41 (m, 1H), 3.39 (t, J = 9.5 Hz, 1H), 2.12 – 2.02 (m, 2H), 2.03 – 1.93 (m, 1H), 1.84 – 1.81 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.6, 133.9, 131.8, 131.6, 131.0, 124.2, 60.5, 49.8, 35.4, 30.6, 24.1; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{79}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 348.9858, found: 348.9862; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}^{81}\text{BrN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 350.9837, found: 350.9843; **Enantiomeric ratio**: 95:5, determined by HPLC (Daicel Chirapak ID, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_{R} = 21.52 min (major), t_{R} = 23.04 min (minor).



(S)-2-(bromomethyl)-1-(phenylsulfonyl)pyrrolidine 3e: yield: 28.8 mg (95%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -110.3$ (c 0.29 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 3.87 (t, *J* = 8.5 Hz, 1H), 3.80 – 3.75 (m, 1H), 3.51 – 3.44 (m, 1H), 3.37 (t, *J* = 9.7 Hz, 1H), 3.21 – 3.17 (m, 1H), 1.99 – 1.92 (m, 1H), 1.88 – 1.84 (m, 1H), 1.78 – 1.74 (m, 1H), 1.56 (s, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 137.4, 133.0, 129.3, 127.6, 60.5, 49.9, 36.0, 30.4, 23.9; **HRMS (ESI)** calculated for C₁₁H₁₅⁷⁹BrNO₂S [M+H]⁺: 304.0007, found: 304.0002; **HRMS (ESI)** calculated for C₁₁H₁₅⁸¹BrNO₂S [M+H]⁺: 305.9986, found: 305.9984; **Enantiomeric ratio:** 96.5:3.5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.36 min (major), t_R = 11.31 min (minor).



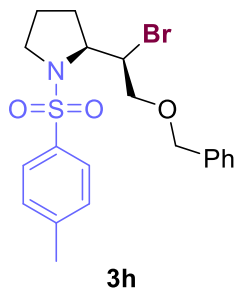
(S)-2-(bromomethyl)pyrrolidin-1-yl(phenyl)methanone 3f: yield: 24.1 mg (90%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -6.9$ (c 0.24 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 4.25 – 4.21 (m, 1H), 3.87 – 3.83 (m, 1H), 3.62 (t, *J* = 10.1 Hz, 1H), 3.52 (q, *J* = 6.5 Hz, 2H), 2.28 – 2.24 (m, 1H), 1.96 – 1.84 (m, 2H), 1.80 – 1.76 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 167.7, 134.7, 131.6, 128.7, 126.9, 52.2, 39.2, 36.1, 33.5, 27.3; **HRMS (ESI)** calculated for C₁₂H₁₅⁷⁹BrNO [M+H]⁺: 268.0337, found: 268.0340; **HRMS (ESI)** calculated for C₁₂H₁₅⁸¹BrNO [M+H]⁺: 270.0317, found: 270.0319; **Enantiomeric ratio:** 96:4, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 9.40 min (major), t_R = 10.97 min (minor).



(S)-2-((S)-1-bromopentyl)-1-tosylpyrrolidine 3g: yield: 33.3 mg (89%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -45.5$ (c 0.34 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.43 (d, *J* = 11.8 Hz, 1H), 3.90 – 3.88 (m, 1H), 3.42 – 3.38 (m, 1H), 3.28 – 3.17 (m, 1H), 2.37 (s, 3H), 1.99 – 1.89 (m, 2H), 1.79 – 1.64 (m, 2H), 1.56 – 1.52 (m, 2H), 1.39 – 1.29 (m, 3H), 1.29 – 1.23 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 143.8, 134.1, 129.9, 127.7, 64.4, 59.0, 51.0, 31.1, 30.3, 27.7, 24.5, 22.2, 21.6, 14.0; **HRMS (ESI)** calculated for C₁₆H₂₅⁷⁹BrNO₂S [M+H]⁺: 374.0789, found:

374.0798; **HRMS (ESI)** calculated for $C_{16}H_{25}^{81}BrNO_2S$ $[M+H]^+$: 376.0769, found: 376.0780; **Enantiomeric ratio**: 96.5:3.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 7.33\text{ min}$ (major), $t_R = 6.77\text{ min}$ (minor).

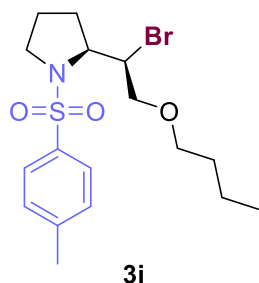
(S)-2-((R)-2-(benzyloxy)-1-bromoethyl)-1-tosylpyrrolidine 3h: yield: 37.2 mg (85%); (Flash



column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil;

$[\alpha]_D^{20} = +75.6$ (c 0.37 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.71 (t, $J = 9.7$ Hz, 2H), 7.39 – 7.30 (m, 7H), 4.65 (d, $J = 11.8$ Hz, 1H), 4.62 – 4.55 (m, 2H), 4.09 – 4.03 (m, 1H), 3.98 (dd, $J = 10.8, 4.9$ Hz, 1H), 3.87 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.46 – 3.38 (m, 1H), 3.30 (m, 1H), 2.43 (s, 3H), 2.09 – 2.00 (m, 1H), 1.82 – 1.69

(m, 2H), 1.39 – 1.29 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 138.0, 134.3, 129.9, 128.5, 127.9, 127.8, 127.7, 73.3, 70.6, 62.3, 55.0, 50.9, 29.0, 24.4, 21.6; **HRMS (ESI)** calculated for $C_{20}H_{25}^{79}BrNO_3S$ $[M+H]^+$: 438.0739, found: 438.0740; **HRMS (ESI)** calculated for $C_{20}H_{25}^{81}BrNO_3S$ $[M+H]^+$: 440.0718, found: 440.0721; **Enantiomeric ratio**: 95.5:4.5, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 10.64\text{ min}$ (major), $t_R = 8.73\text{ min}$ (minor).



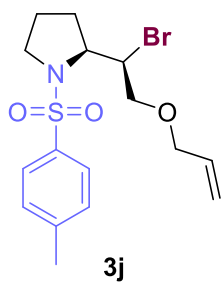
(S)-2-((R)-1-bromo-2-butoxyethyl)-1-tosylpyrrolidine 3i: yield: 36.7 mg

(91%); (Flash column chromatography eluent, petroleum ether/ethyl acetate =

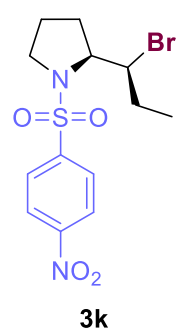
5/1); colorless oil; $[\alpha]_D^{20} = +100.4$ (c 0.37 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.59 – 4.51 (m, 1H), 4.04 – 4.02 (m, 1H), 3.91 – 3.88 (m, 1H), 3.82 – 3.78 (m, 1H), 3.57 – 3.43

(m, 3H), 3.30 (m, 1H), 2.44 (s, 3H), 2.10 – 2.06 (m, 1H), 1.81 – 1.73 (m, 2H), 1.63 – 1.55 (m, 2H), 1.45 – 1.35 (m, 3H), 0.93 (t, $J = 7.4$ Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 134.3, 129.9, 127.7, 71.2, 71.0, 62.5, 55.1, 50.9, 31.9, 28.8, 24.4, 21.6, 19.4, 14.0; **HRMS (ESI)** calculated for $C_{17}H_{27}^{79}BrNO_3S$ $[M+H]^+$: 404.0895, found: 404.0899; **HRMS (ESI)** calculated for $C_{17}H_{27}^{81}BrNO_3S$ $[M+H]^+$: 406.0875, found: 406.0885; **Enantiomeric ratio**: 96.5:3.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 10.54\text{ min}$ (major), $t_R = 7.69\text{ min}$ (minor).

(S)-2-((R)-2-(allyloxy)-1-bromoethyl)-1-tosylpyrrolidine 3j: yield: 34.9 mg (90%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = +55.7$ (c 0.35

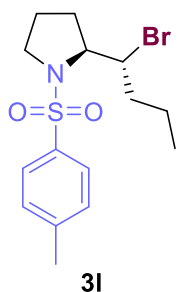


CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 5.95 – 5.89 (m, 1H), 5.33 – 5.30 (m, 1H), 5.22 (d, *J* = 12.6 Hz, 1H), 4.56 – 4.53 (m, 1H), 4.10 – 4.00 (m, 3H), 3.93 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.83 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.35 – 3.28 (m, 1H), 2.44 (s, 3H), 2.11 – 2.02 (m, 1H), 1.82 – 1.72 (m, 2H), 1.38 – 1.34 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 143.9, 134.5, 134.3, 129.9, 127.8, 117.4, 72.2, 70.4, 62.4, 55.0, 51.0, 28.9, 24.4, 21.6; **HRMS (ESI)** calculated for C₁₆H₂₃⁷⁹BrNO₃S [M+H]⁺:388.0582, found: 388.0588; **HRMS (ESI)** calculated for C₁₆H₂₃⁸¹BrNO₃S [M+H]⁺:390.0562, found: 390.0570; **Enantiomeric ratio**: 96.5:3.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 11.66 min (major), t_R = 9.35 min (minor).



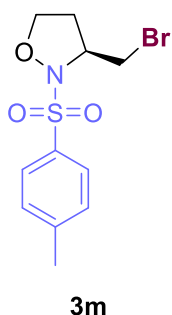
(S)-2-((S)-1-bromopropyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine 3k: yield: 33.5 mg (89%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 113.7 – 114.5 °C; [α]_D²⁰ = +18.9 (c 0.34 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 8.44 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 4.39 (d, *J* = 11.4 Hz, 1H), 4.03 – 3.95 (m, 1H), 3.57 – 3.48 (m, 1H), 3.34 – 3.26 (m, 1H), 2.12 – 1.99 (m, 2H), 1.87 – 1.84 (m, 2H), 1.63 – 1.53 (m, 1H), 1.47 (q, *J* = 6.2 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 150.4, 142.9, 128.8, 124.5, 64.8, 60.4, 51.1, 27.9, 25.0, 24.5, 13.0; **HRMS (ESI)** calculated for C₁₃H₁₈⁷⁹BrN₂O₄S [M+H]⁺: 377.0171, found: 377.0175; **HRMS (ESI)** calculated for C₁₃H₁₈⁸¹BrN₂O₄S [M+H]⁺: 379.0150, found: 379.0158; **Enantiomeric ratio**: 94.5:5.5, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 19.21 min (major), t_R = 16.63 min (minor).

(S)-2-((R)-1-bromobutyl)-1-tosylpyrrolidine 3l: yield: 32.0 mg (89%); (Flash column



chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; [α]_D²⁰ = -24.3 (c 0.32 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.59 – 4.56 (m, 1H), 3.79 – 3.72 (m, 1H), 3.43 – 3.29 (m, 2H), 2.44 (s, 3H), 2.00 – 1.98 (m, 1H), 1.90 – 1.86 (m, 1H), 1.83 – 1.70 (m, 3H), 1.70 – 1.62 (m, 1H), 1.46 – 1.42 (m, 1H), 1.40 – 1.33 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 143.7, 135.8, 129.8, 127.6, 64.0, 62.2, 49.5, 38.1, 28.1, 24.9, 21.6, 21.3, 13.5; **HRMS (ESI)** calculated for C₁₅H₂₃⁷⁹BrNO₂S [M+H]⁺: 360.0633, found: 360.0640; **HRMS (ESI)** calculated for C₁₅H₂₃⁸¹BrNO₂S [M+H]⁺: 362.0612, found: 362.0620; **Enantiomeric ratio**:

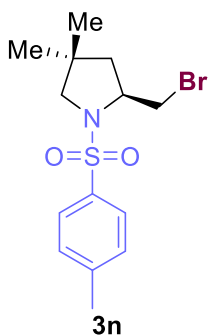
78:22, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.45 min (major), t_R = 9.66 min (minor).



3m

(S)-3-(bromomethyl)-2-tosylisoxazolidine 3m: yield: 28.4 mg (89%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$ = +47.4 (c 0.28 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 4.54 – 4.45 (m, 1H), 4.06 – 3.96 (m, 2H), 3.65 (dd, J = 10.0, 4.8 Hz, 1H), 3.35 (t, J = 9.6 Hz, 1H), 2.53 – 2.48 (m, 1H), 2.45 (s, 3H), 2.28 – 2.19 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 145.4, 132.8, 129.9, 129.3, 70.3, 60.0,

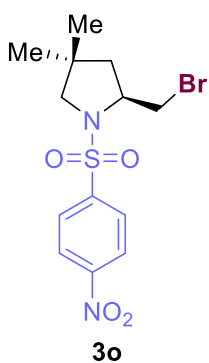
34.4, 34.3, 21.8; **HRMS (ESI)** calculated for C₁₁H₁₅⁷⁹BrNO₃S [M+H]⁺:319.9956, found: 319.9952; **HRMS (ESI)** calculated for C₁₁H₁₅⁸¹BrNO₃S [M+H]⁺:321.9936, found: 321.9945; **Enantiomeric ratio:** 93:7, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 11.43 min (major), t_R = 10.50 min (minor).



3n

(S)-2-(bromomethyl)-4,4-dimethyl-1-tosylpyrrolidine 3n: yield: 30.8 mg (89%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 113.7 – 114.8 °C; $[\alpha]_D^{20}$ = +56.5 (c 0.31 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.67 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.87 (dd, J = 9.7, 3.0 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.45 (t, J = 9.2 Hz, 1H), 3.10 (q, J = 10.6 Hz, 2H), 2.37 (s, 3H), 1.81 (dd, J = 12.8, 7.3 Hz, 1H), 1.64 (dd, J = 12.9, 8.3 Hz, 1H), 0.98

(s, 3H), 0.46 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 143.8, 135.3, 129.8, 127.7, 62.0, 60.2, 46.0, 37.6, 37.5, 26.2, 26.0, 21.6; **HRMS (ESI)** calculated for C₁₄H₂₁⁷⁹BrNO₂S [M+H]⁺: 346.0476, found: 346.0471; **HRMS (ESI)** calculated for C₁₄H₂₁⁸¹BrNO₂S [M+H]⁺: 348.0456, found: 348.0465; **Enantiomeric ratio:** 95:5, determined by HPLC (Daicel Chirapak ID, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 8.90 min (major), t_R = 10.54 min (minor).

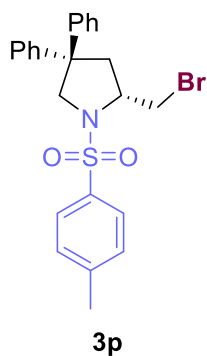


3o

(S)-2-(bromomethyl)-4,4-dimethyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine 3o: yield: 33.9 mg (90%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 117.9 – 119.0 °C; $[\alpha]_D^{20}$ = -44.7 (c 0.34 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 8.39 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H), 4.03 – 3.99 (m, 1H), 3.80 (dd, J = 10.1, 2.4 Hz, 1H), 3.62 (dd, J = 10.0, 7.7 Hz, 1H), 3.24 (d, J = 10.4 Hz, 1H), 3.19 (d, J = 10.4 Hz, 1H), 1.91 (dd, J = 12.9,

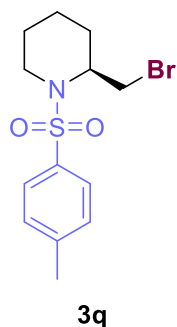
7.4 Hz, 1H), 1.78 (dd, J = 12.9, 8.6 Hz, 1H), 1.09 (s, 3H), 0.65 (s, 3H); ¹³C NMR (151 MHz, CDCl₃)

δ 150.3, 144.6, 128.7, 124.5, 61.9, 60.2, 45.5, 38.0, 37.1, 26.0, 25.7; **HRMS (ESI)** calculated for $C_{13}H_{17}^{79}BrN_2NaO_4S$ $[M+Na]^+$: 398.9990, found: 398.9986; **Enantiomeric ratio**: 91.5:8.5, determined by HPLC (Daicel Chirapak ID, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 8.79 min (major), t_R = 10.63 min (minor).



(R)-2-(bromomethyl)-4,4-diphenyl-1-tosylpyrrolidine 3p: yield: 39.9 mg (85%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 113.1 – 114.0 °C; $[\alpha]_D^{20}$ = -17.5 (c 0.40 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.23 – 7.05 (m, 8H), 4.41 (d, J = 10.3 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.79 (dd, J = 9.7, 3.1 Hz, 1H), 3.70 (d, J = 10.3 Hz, 1H), 2.92 (t, J = 9.9 Hz, 1H), 2.77 – 2.73 (m, 2H), 2.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 144.6, 143.7, 134.1, 129.9, 128.8, 128.7, 127.5, 126.9, 126.7, 126.6,

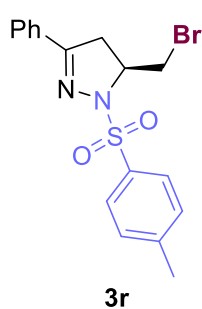
126.4, 60.2, 58.9, 52.4, 42.2, 35.9, 21.6; **HRMS (ESI)** calculated for $C_{24}H_{25}^{79}BrNO_2S$ $[M+H]^+$: 470.0789, found: 470.0783; **HRMS (ESI)** calculated for $C_{24}H_{25}^{81}BrNO_2S$ $[M+H]^+$: 472.0769, found: 472.0773; **Enantiomeric ratio**: 92:8, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 12.09 min (major), t_R = 9.96 min (minor).



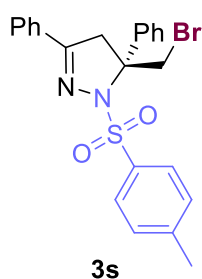
(S)-2-(bromomethyl)-1-tosylpiperidine 3q: yield: 28.5 mg (86%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$ = +17.2 (c 0.29 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 4.31 – 4.23 (m, 1H), 3.75 (d, J = 13.3 Hz, 1H), 3.51 (t, J = 10.1 Hz, 1H), 3.44 – 3.40 (m, 1H), 2.99 – 2.90 (m, 1H), 2.43 (s, 3H), 2.03 (d, J = 12.4 Hz, 1H), 1.58 – 1.51 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.29 (m, 1H); **^{13}C NMR** (151

MHz, $CDCl_3$) δ 143.4, 138.2, 129.9, 127.1, 53.5, 41.2, 30.4, 25.3, 24.4, 21.6, 18.0; **HRMS (ESI)** calculated for $C_{13}H_{19}^{79}BrNO_2S$ $[M+H]^+$: 332.0320, found: 332.0322; **HRMS (ESI)** calculated for $C_{13}H_{19}^{81}BrNO_2S$ $[M+H]^+$: 334.0299, found: 334.0307; **Enantiomeric ratio**: 87:13, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.42 min (major), t_R = 7.08 min (minor).

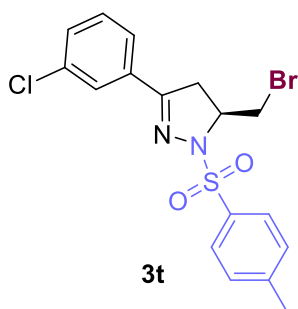
(S)-5-(bromomethyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole 3r: yield: 35.7 mg (91%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 140.2 –



141.1 °C; $[\alpha]_D^{20} = -74.2$ (c 0.36 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.20 – 4.14 (m, 1H), 4.00 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.61 (t, *J* = 9.6 Hz, 1H), 3.28 (dd, *J* = 17.5, 10.9 Hz, 1H), 3.12 (dd, *J* = 17.5, 8.7 Hz, 1H), 2.39 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 157.3, 144.7, 132.1, 130.9, 130.5, 129.7, 128.7, 128.7, 127.0, 61.9, 39.9, 35.2, 21.7; **HRMS (ESI)** calculated for C₁₇H₁₈⁷⁹BrN₂O₂S [M+H]⁺: 393.0272, found: 393.0274; **HRMS (ESI)** calculated for C₁₇H₁₈⁸¹BrN₂O₂S [M+H]⁺: 395.0252, found: 395.0256; **Enantiomeric ratio**: 95:5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 7.71 min (major), t_R = 9.19 min (minor).



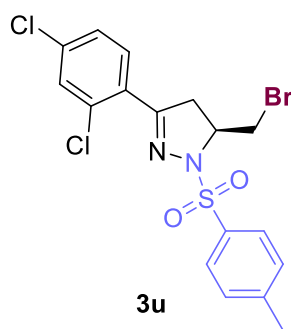
(R)-5-(bromomethyl)-3,5-diphenyl-1-tosyl-4,5-dihydro-1H-pyrazole 3s: yield: 38.4 mg (82%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = +100.7$ (c 0.38 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.76 (s, 2H), 7.44 (s, 3H), 7.25 – 7.22 (m, 3H), 7.14 – 7.11 (m, 4H), 7.00 – 6.97 (s, 2H), 4.66 (dd, *J* = 10.6, 4.2 Hz, 1H), 4.30 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.90 (dd, *J* = 17.8, 4.2 Hz, 1H), 3.67 (dd, *J* = 17.8, 4.1 Hz, 1H), 2.31 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 152.6, 143.0, 138.0, 136.1, 130.7, 130.5, 128.9, 128.8, 128.4, 128.3, 127.3, 127.0, 126.8, 73.8, 50.8, 38.0, 21.5; **HRMS (ESI)** calculated for C₂₃H₂₂⁷⁹BrN₂O₂S [M+H]⁺: 469.0580, found: 469.0585; **HRMS (ESI)** calculated for C₂₃H₂₂⁸¹BrN₂O₂S [M+H]⁺: 471.0560, found: 471.0569; **Enantiomeric ratio**: 89:11, determined by HPLC (Daicel Chirapak IE, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 24.32 min (major), t_R = 21.84 min (minor).



(S)-5-(bromomethyl)-3-(3-chlorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazole 3t: yield: 34.6 mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 140.4 – 141.3 °C; $[\alpha]_D^{20} = -11.3$ (c 0.35 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.30 (m, 3H), 4.25 – 4.15 (m, 1H), 3.97 (dd, *J* = 10.0 Hz, 1H), 3.62 (t, *J* = 9.4 Hz, 1H), 3.25 (dd, *J* = 17.3, 11.2 Hz, 1H), 3.10 (dd, *J* = 17.4, 8.6 Hz, 1H), 2.40 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 155.9, 144.8, 134.9, 132.3, 132.3, 130.8, 130.0, 129.8, 128.7, 127.0, 125.1, 62.0, 39.7, 35.1, 21.7; **HRMS (ESI)** calculated for C₁₇H₁₇⁷⁹Br³⁵ClN₂O₂S [M+H]⁺: 426.9883, found:

426.9884; **HRMS (ESI)** calculated for $C_{17}H_{17}^{81}Br^{35}ClN_2O_2S$ $[M+H]^+$: 428.9862, found: 428.9870; **HRMS (ESI)** calculated for $C_{17}H_{17}^{81}Br^{37}ClN_2O_2S$ $[M+H]^+$: 430.9833, found: 430.9834; **Enantiomeric ratio**: 95.5:4.5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 8.38\text{ min}$ (major), $t_R = 9.58\text{ min}$ (minor).

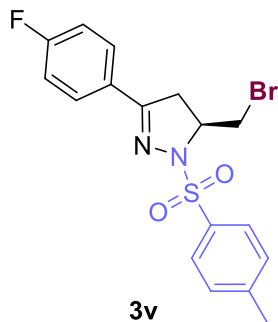
(S)-5-(bromomethyl)-3-(2,4-dichlorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazole 3u: yield: 37.4



mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: $155.0 - 156.2\text{ }^\circ\text{C}$; $[\alpha]_D^{20} = +24.3$ (c 0.37 CH_2Cl_2); 1H -NMR (600 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.1\text{ Hz}$, 2H), 7.57 (d, $J = 8.1\text{ Hz}$, 1H), 7.38 (s, 1H), 7.34 (d, $J = 7.0\text{ Hz}$, 2H), 7.26 (s, 1H), 4.21 – 4.20 (m, 1H), 3.96 (dd, $J = 9.7\text{ Hz}$, 1H), 3.66 (t, $J = 9.1\text{ Hz}$, 1H), 3.42 (dd, $J = 17.5, 11.0\text{ Hz}$, 1H), 3.29 (dd, $J = 17.7, 8.8\text{ Hz}$, 1H), 2.43 (s, 3H); ^{13}C -NMR

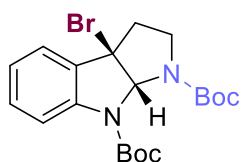
(151 MHz, $CDCl_3$) δ 156.1, 144.9, 136.8, 133.6, 132.3, 131.5, 130.6, 129.8, 128.7, 128.6, 127.5, 62.4, 42.6, 35.0, 21.7; **HRMS (ESI)** calculated for $C_{17}H_{16}^{79}Br^{35}Cl_2N_2O_2S$ $[M+H]^+$: 460.9493, found: 460.9497; **Enantiomeric ratio**: 95.5:4.5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 8.90\text{ min}$ (major), $t_R = 11.79\text{ min}$ (minor).

(S)-5-(bromomethyl)-3-(4-fluorophenyl)-1-tosyl-4,5-dihydro-1H-pyrazole 3v: yield: 37.4 mg



(91%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: $120.1 - 121.3\text{ }^\circ\text{C}$; $[\alpha]_D^{20} = -100.1$ (c 0.37 CH_2Cl_2); 1H -NMR (600 MHz, $CDCl_3$) δ 7.80 (d, $J = 7.9\text{ Hz}$, 2H), 7.68 – 7.62 (m, 2H), 7.30 (d, $J = 7.9\text{ Hz}$, 2H), 7.07 (t, $J = 8.3\text{ Hz}$, 2H), 4.21 – 4.16 (m, 1H), 4.02 – 3.97 (m, 1H), 3.62 (t, $J = 9.6\text{ Hz}$, 1H), 3.26 (dd, $J = 17.4, 10.9\text{ Hz}$, 1H), 3.11 (dd, $J = 17.4, 8.7\text{ Hz}$, 1H), 2.40 (s, 3H); ^{13}C -NMR (151 MHz, $CDCl_3$) δ 165.2, 163.5,

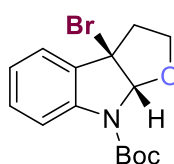
156.2, 144.7, 132.1, 129.8, 129.1 (d, $J = 8.6\text{ Hz}$), 128.7, 126.8 (d, $J = 3.5\text{ Hz}$), 115.9 (d, $J = 22.0\text{ Hz}$), 62.0, 39.9, 35.2, 21.7; ^{19}F -NMR (564 MHz, $CDCl_3$) δ -108.6; **HRMS (ESI)** calculated for $C_{17}H_{17}^{79}BrFN_2O_2S$ $[M+H]^+$: 411.0173, found: 411.0179; **HRMS (ESI)** calculated for $C_{17}H_{17}^{81}BrFN_2O_2S$ $[M+H]^+$: 413.0152, found: 413.0159; **Enantiomeric ratio**: 95:5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_R = 9.42\text{ min}$ (major), $t_R = 11.57\text{ min}$ (minor).



3w

di-tert-butyl (3aR,8aR)-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-
b]indole-1,8-dicarboxylate 3w: yield: 39.5 mg (90%); (Flash column
 chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.:

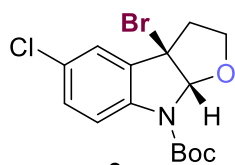
89.6 – 91.1 °C; $[\alpha]_D^{20} = -75.7$ (c 0.40 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.58 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 3.73 (dd, *J* = 10.4, 7.7 Hz, 1H), 2.81 – 2.79 (m, 2H), 2.76 – 2.68 (m, 1H), 1.59 (s, 9H), 1.49 (s, 9H); ¹³C-NMR (101 MHz, CDCl₃) δ 153.4, 152.1, 142.1, 132.7, 130.3, 124.0, 123.8, 117.4, 83.9, 82.1, 80.8, 62.2, 46.2, 28.4, 28.3; **HRMS (ESI)** calculated for C₂₀H₂₇⁷⁹BrN₂NaO₄ [M+Na]⁺: 461.1052, found: 461.1048; **Enantiomeric ratio:** 90:10, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 4.23 min (major), t_R = 4.69 min (minor).



3x

tert-butyl (3aR,8aS)-3a-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-
carboxylate 3x: yield: 30.6 mg (90%); (Flash column chromatography eluent,
 petroleum ether/ethyl acetate = 7/1); colorless oil; $[\alpha]_D^{20} = -64.2$ (c 0.31 CH₂Cl₂); ¹H-

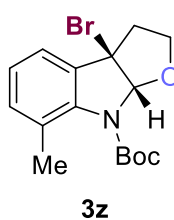
NMR (600 MHz, CDCl₃) δ 7.84 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.34 – 6.12 (m, 1H), 4.00 (t, *J* = 8.0 Hz, 1H), 3.53 – 3.45 (m, 1H), 2.94 – 2.86 (m, 1H), 2.80 (dd, *J* = 12.3, 3.8 Hz, 1H), 1.60 (s, 9H); ¹³C-NMR (151 MHz, CDCl₃) δ 151.9, 141.6, 132.0, 130.5, 124.9, 123.8, 115.0, 100.9, 81.2, 67.8, 61.6, 45.1, 28.5; **Enantiomeric ratio:** 96.5:3.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.22 min (major), t_R = 5.20 min (minor).



3y

tert-butyl (3aR,8aS)-3a-bromo-5-chloro-2,3,3a,8a-tetrahydro-8H-furo[2,3-
b]indole-8-carboxylate 3y: yield: 33.7 mg (90%); (Flash column
 chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$

= -39.9 (c 0.34 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.78 (s, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.24 (m, 1H), 6.19 – 6.15 (m, 1H), 4.01 (t, *J* = 8.0 Hz, 1H), 3.52 – 3.49 (m, 1H), 2.90 – 2.86 (m, 1H), 2.76 (dd, *J* = 12.5, 3.7 Hz, 1H), 1.59 (s, 9H); ¹³C-NMR (151 MHz, CDCl₃) δ 151.7, 130.6, 128.7, 125.0, 116.1, 110.1, 101.2, 82.8, 67.8, 60.7, 45.0, 28.4; **Enantiomeric ratio:** 94:6, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.05 min (major), t_R = 5.44 min (minor).



tert-butyl (3*aR*,8*aS*)-3*a*-bromo-7-methyl-2,3,3*a*,8*a*-tetrahydro-8*H*-furo[2,3-

b]indole-8-carboxylate **3z**: yield: 31.8 mg (90%); (Flash column chromatography

eluent, petroleum ether/ethyl acetate = 7/1); colorless oil; $[\alpha]_D^{20} = -109.3$ (c 0.32

CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 7.25 (d, $J = 7.2$ Hz, 1H), 7.16 – 7.08 (m,

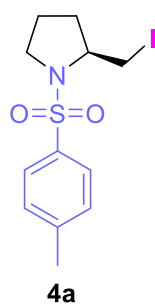
2H), 6.18 (s, 1H), 3.98 – 3.94 (m, 1H), 3.44 – 3.40 (m, 1H), 2.90 – 2.84 (m, 1H), 2.81

– 2.76 (m, 1H), 2.32 (s, 3H), 1.57 (s, 9H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 152.6, 140.6, 134.6, 133.0,

128.5, 125.7, 121.6, 103.0, 82.3, 68.0, 61.7, 43.6, 28.3, 20.2; **Enantiomeric ratio**: 96.5:3.5,

determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, T

= 30 °C, $\lambda = 254$ nm): $t_R = 6.85$ min (major), $t_R = 6.02$ min (minor).



(*S*)-2-(iodomethyl)-1-tosylpyrrolidine **4a**: yield: 31.7 mg (87%); (Flash column

chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -$

80.0 (c 0.32 CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.34 (d,

$J = 7.9$ Hz, 2H), 3.74 (m, 1H), 3.62 (dd, $J = 9.6, 2.9$ Hz, 1H), 3.52 – 3.44 (m, 1H), 3.22

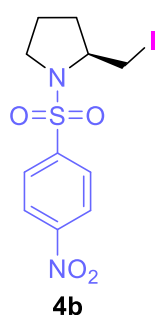
– 3.18 (m, 2H), 2.44 (s, 3H), 1.86 – 1.82 (m, 3H), 1.53 – 1.51 (m, 1H); $^{13}\text{C NMR}$ (151

MHz, CDCl_3) δ 143.8, 134.6, 129.9, 127.6, 60.8, 50.2, 32.2, 24.0, 21.6, 11.6; **HRMS**

(**ESI**) calculated for $\text{C}_{12}\text{H}_{17}\text{INO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 366.0025, found: 366.0032; **Enantiomeric ratio**:

92.5:7.5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0

mL/min, T = 30 °C, $\lambda = 254$ nm): $t_R = 6.32$ min (major), $t_R = 6.74$ min (minor).



(*S*)-2-(iodomethyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine **4b**: yield: 29.7 mg (75%);

(Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid;

m.p.: 101.2 – 102.5 °C; $[\alpha]_D^{20} = +20.3$ (c 0.30 CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3)

δ 8.40 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.9$ Hz, 2H), 3.83 – 3.76 (m, 1H), 3.59 (d, $J =$

9.8 Hz, 1H), 3.57 – 3.50 (m, 1H), 3.27 – 3.22 (m, 2H), 1.99 – 1.90 (m, 2H), 1.90 – 1.81

(m, 1H), 1.65 – 1.60 (m, 1H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.4, 143.5, 128.7,

124.6, 61.1, 50.2, 32.2, 24.1, 10.7; **HRMS (ESI)** calculated for $\text{C}_{11}\text{H}_{14}\text{IN}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 396.9719,

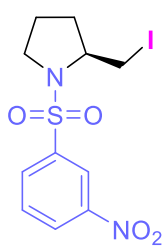
found: 396.9717; **Enantiomeric ratio**: 90.5:9.5, determined by HPLC (Daicel Chirapak IC,

isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, $\lambda = 254$ nm): $t_R = 18.05$ min (major),

$t_R = 16.16$ min (minor).

(*S*)-2-(iodomethyl)-1-((3-nitrophenyl)sulfonyl)pyrrolidine **4c**: yield: 30.1 mg (76%); (Flash

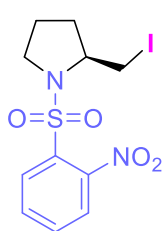
column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 108.2 –



4c

109.4 °C; $[\alpha]_D^{20} = +63.3$ (c 0.30 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 8.68 (d, *J* = 10.6 Hz, 1H), 8.45 (t, *J* = 9.8 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.77 (dd, *J* = 15.1, 7.1 Hz, 1H), 3.81 – 3.78 (m, 1H), 3.60 – 3.54 (m, 1H), 3.56 – 3.49 (m, 1H), 3.33 – 3.22 (m, 2H), 1.98 – 1.90 (m, 2H), 1.90 – 1.81 (m, 1H), 1.68 – 1.60 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 148.6, 140.1, 132.9, 130.7, 127.4, 122.6, 60.9, 50.2, 32.2, 24.1,

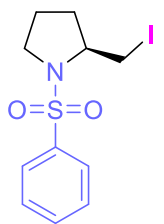
10.9; **HRMS (ESI)** calculated for C₁₁H₁₄IN₂O₄S [M+H]⁺: 396.9717, found: 396.9725; **Enantiomeric ratio**: 91:9, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 17.55 min (major), t_R = 16.60 min (minor).



4d

(S)-2-(iodomethyl)-1-((2-nitrophenyl)sulfonyl)pyrrolidine 4d: yield: 30.9 mg (78%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 105.8 – 107.0 °C; $[\alpha]_D^{20} = +29.7$ (c 0.31 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 8.05 (t, *J* = 10.0 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 1H), 4.11 (s, 1H), 3.59 – 3.44 (m, 3H), 3.24 (t, *J* = 9.6 Hz, 1H), 2.08 (d, *J* = 7.6 Hz,

1H), 1.99 (d, *J* = 11.1 Hz, 2H), 1.86 – 1.79 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 148.7, 133.9, 132.0, 131.6, 131.0, 124.2, 60.8, 50.1, 32.4, 24.1, 10.5; **HRMS (ESI)** calculated for C₁₁H₁₄IN₂O₄S [M+H]⁺: 396.9719, found: 396.9726; **Enantiomeric ratio**: 90:10, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 17.67 min (major), t_R = 19.86 min (minor).

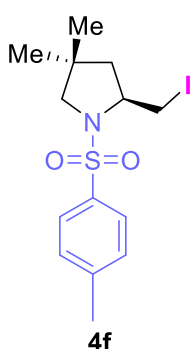


4e

(S)-2-(iodomethyl)-1-(phenylsulfonyl)pyrrolidine 4e: yield: 28.8 mg (82%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = -72.8$ (c 0.29 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 2H), 3.80 – 3.72 (m, 1H), 3.65 – 3.58 (m, 1H), 3.51 – 3.47 (m, 1H), 3.26 – 3.17 (m, 2H), 1.92 – 1.76 (m, 3H), 1.57 – 1.48 (m,

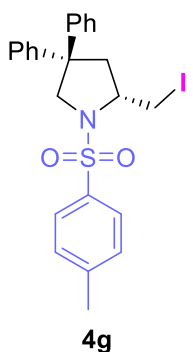
1H); ¹³C NMR (151 MHz, CDCl₃) δ 137.5, 133.0, 129.3, 127.5, 60.8, 50.1, 32.1, 24.0, 11.4; **HRMS (ESI)** calculated for C₁₁H₁₅INO₂S [M+H]⁺: 351.9868, found: 351.9869; **Enantiomeric ratio**: 91:9, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 8.32 min (major), t_R = 8.94 min (minor).

(S)-2-(iodomethyl)-4,4-dimethyl-1-tosylpyrrolidine 4f: yield: 34.6 mg (88%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 115.0 – 116.2 °C; $[\alpha]_D^{20} = +7.0$ (c 0.35 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* =



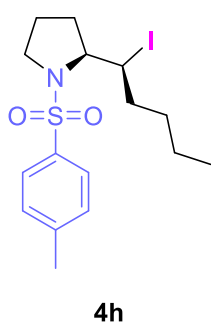
7.9 Hz, 2H), 3.75 (dd, $J = 9.5, 2.7$ Hz, 1H), 3.71 – 3.65 (m, 1H), 3.36 (t, $J = 9.2$ Hz, 1H), 3.26 – 3.12 (m, 2H), 2.42 (s, 3H), 1.90 (dd, $J = 12.5, 7.2$ Hz, 1H), 1.58 (dd, $J = 12.8, 8.6$ Hz, 1H), 1.03 (s, 3H), 0.50 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 143.7, 135.3, 129.8, 127.6, 62.1, 60.2, 47.9, 37.6, 26.1, 26.0, 21.6, 13.2; **HRMS (ESI)** calculated for $\text{C}_{14}\text{H}_{21}\text{INO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 394.0338, found: 394.0341; **Enantiomeric ratio**: 90.5:9.5, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} =$

7.25 min (major), $t_{\text{R}} = 7.88$ min (minor).



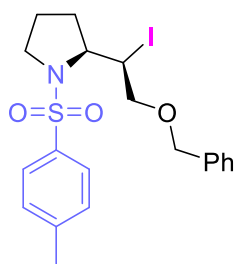
(R)-2-(iodomethyl)-4,4-diphenyl-1-tosylpyrrolidine 4g: yield: 46.3 mg (89%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 113.7 – 114.5 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} = -16.9$ (c 0.46 CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.30 – 7.25 (m, 4H), 7.18 (t, $J = 7.7$ Hz, 3H), 7.16 – 7.05 (m, 5H), 4.43 (d, $J = 10.3$ Hz, 1H), 3.90 – 3.83 (m, 1H), 3.76 (d, $J = 10.3$ Hz, 1H), 3.67 (dd, $J = 9.5, 3.1$ Hz, 1H), 2.82 (m, 2H), 2.66 (dd, $J = 13.1, 5.2$

Hz, 1H), 2.39 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 144.8, 144.5, 143.7, 134.4, 129.8, 128.8, 128.7, 127.5, 126.9, 126.7, 126.6, 126.4, 60.5, 59.3, 52.4, 44.1, 21.6, 11.4; **HRMS (ESI)** calculated for $\text{C}_{24}\text{H}_{25}\text{INO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 518.0651, found: 518.0641; **Enantiomeric ratio**: 91:9, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 7.45$ min (major), $t_{\text{R}} = 6.31$ min (minor).



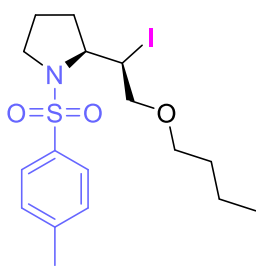
(S)-2-((S)-1-iodopentyl)-1-tosylpyrrolidine 4h: yield: 36.6 mg (87%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_{\text{D}}^{20} = -46.8$ (c 0.37 CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.64 (d, $J = 7.9$ Hz, 2H), 7.27 (d, $J = 7.9$ Hz, 2H), 4.53 (d, $J = 11.5$ Hz, 1H), 4.02 – 3.93 (m, 1H), 3.47 – 3.37 (m, 1H), 3.32 – 3.27 (m, 1H), 2.37 (s, 3H), 1.98 – 1.93 (m, 1H), 1.86 – 1.82 (m, 1H), 1.75 – 1.65 (m, 2H), 1.57 – 1.49 (m, 2H), 1.38 – 1.30 (m, 2H), 1.25 (dd,

$J = 13.2, 6.4$ Hz, 2H), 0.86 (t, $J = 6.9$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 143.8, 134.2, 129.9, 127.7, 65.9, 51.6, 41.1, 32.3, 32.0, 29.2, 24.4, 22.0, 21.6, 14.0; **HRMS (ESI)** calculated for $\text{C}_{16}\text{H}_{25}\text{INO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 422.0651, found: 422.0661; **Enantiomeric ratio**: 92:8, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 7.39$ min (major), $t_{\text{R}} = 6.78$ min (minor).



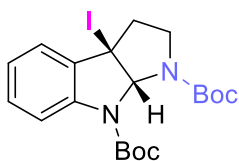
4i

(S)-2-((R)-2-(benzyloxy)-1-iodoethyl)-1-tosylpyrrolidine 4i: yield: 42.2 mg (87%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = +56.4$ (c 0.42 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.30 (dd, *J* = 15.1, 7.4 Hz, 3H), 4.70 (dd, *J* = 11.2, 5.6 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 3.99 (dd, *J* = 8.5, 3.9 Hz, 1H), 3.86 (d, *J* = 5.9 Hz, 2H), 3.47 – 3.39 (m, 1H), 3.36 – 3.28 (m, 1H), 2.43 (s, 3H), 2.08 – 2.03 (m, 1H), 1.86 – 1.80 (m, 1H), 1.75 – 1.72 (m, 1H), 1.34 – 1.30 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 143.9, 138.1, 134.3, 129.9, 128.5, 127.9, 127.8, 127.8, 73.1, 71.4, 63.4, 51.3, 35.8, 30.4, 24.3, 21.6; **HRMS (ESI)** calculated for C₂₀H₂₅INO₃S [M+H]⁺: 486.0600, found: 486.0594; **Enantiomeric ratio:** 91:9, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.90 min (major), t_R = 9.57 min (minor).



4j

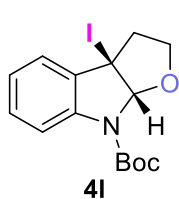
(S)-2-((R)-2-butoxy-1-iodoethyl)-1-tosylpyrrolidine 4j: yield: 38.3 mg (85%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20} = +64.5$ (c 0.38 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.85 – 3.69 (m, 2H), 3.59 – 3.42 (m, 3H), 3.35 – 3.27 (m, 1H), 2.44 (s, 3H), 2.09 (dd, *J* = 12.2, 6.0 Hz, 1H), 1.89 – 1.71 (m, 2H), 1.60 – 1.56 (m, 2H), 1.46 – 1.32 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 143.8, 134.3, 129.9, 127.7, 71.7, 71.0, 63.6, 51.3, 36.2, 31.9, 30.2, 24.3, 21.6, 19.5, 14.0; **HRMS (ESI)** calculated for C₁₇H₂₇INO₃S [M+H]⁺: 452.0756, found: 452.0761; **Enantiomeric ratio:** 88.5:11.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.88 min (major), t_R = 9.04 min (minor).



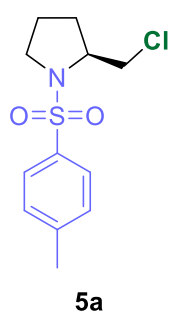
4k

di-tert-butyl (3aR,8aR)-3a-iodo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate 4k: yield: 35.0 mg (72%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); colorless oil; $[\alpha]_D^{20} = -43.6$ (c 0.35 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.44 (s, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.05 – 6.97 (m, 1H), 6.38 (s, 1H), 3.49 – 3.40 (m, 1H), 2.87 – 2.78 (m, 1H), 2.77 – 2.67 (m, 2H), 1.52 (s, 9H), 1.41 (s, 9H); ¹³C-NMR (151 MHz, CDCl₃) δ 153.3, 152.3, 141.2, 130.4, 129.7, 124.3, 123.8, 117.9, 86.3, 82.1, 80.8, 46.1, 37.2, 28.5, 28.4; **HRMS (ESI)** calculated for

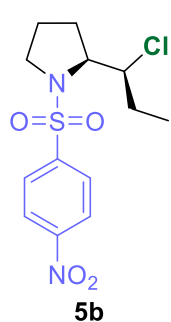
$C_{20}H_{27}IN_2NaO_4$ $[M+Na]^+$: 509.0913, found 509.0916; **Enantiomeric ratio**: 87:13, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 4.69 min (major), t_R = 5.07 min (minor).



tert-butyl (3aR,8aS)-3a-iodo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate 4l: yield: 35.2 mg (91%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 7/1); colorless oil; $[\alpha]_D^{20}$ = -79.2 (c 0.35 CH_2Cl_2); 1H -NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 7.0 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.45 – 6.17 (m, 1H), 3.85 – 3.76 (m, 1H), 3.45 – 3.32 (m, 1H), 2.99 – 2.86 (m, 2H), 1.61 (s, 9H); ^{13}C -NMR (151 MHz, $CDCl_3$) δ 151.9, 129.9, 125.2, 123.8, 115.0, 103.3, 82.3, 67.3, 47.9, 28.5; **HRMS (ESI)** calculated for $C_{15}H_{18}INNaO_3$ $[M+Na]^+$: 410.0229, found: 410.0223; **Enantiomeric ratio**: 94.5:5.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.32 min (major), t_R = 5.37 min (minor).

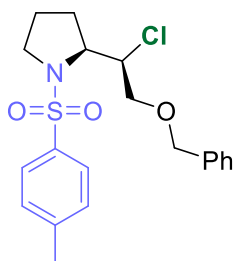


(S)-2-(chloromethyl)-1-tosylpyrrolidine 5a: yield: 22.2 mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$ = -41.4 (c 0.22 CH_2Cl_2); 1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.88 (d, J = 10.7 Hz, 1H), 3.81 (d, J = 8.5 Hz, 1H), 3.51 – 3.42 (m, 2H), 3.14 (q, J = 8.1 Hz, 1H), 2.44 (s, 3H), 1.93 (s, 1H), 1.89 – 1.78 (m, 1H), 1.78 – 1.66 (m, 1H), 1.63 – 1.59 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 134.3, 129.9, 127.7, 60.6, 49.7, 47.1, 29.4, 23.9, 21.6; **HRMS (ESI)** calculated for $C_{12}H_{17}ClINO_2S$ $[M+H]^+$: 274.0669, found: 274.0670; **Enantiomeric ratio**: 83:17, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.26 min (major), t_R = 11.26 min (minor).



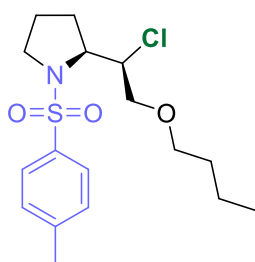
(S)-2-((S)-1-chloropropyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine 5b: yield: 26.9 mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); white solid; m.p.: 113.7 – 114.5 °C; $[\alpha]_D^{20}$ = +6.9 (c 0.27 CH_2Cl_2); 1H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 4.26 (d, J = 11.2 Hz, 1H), 3.97 – 3.88 (m, 1H), 3.54 – 3.46 (m, 1H), 3.31 – 3.27 (m, 1H), 2.09 – 1.94 (m, 2H), 1.87 – 1.73 (m, 2H), 1.54 – 1.45 (m, 2H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 143.0, 128.9, 124.5, 66.5, 64.4, 50.7, 27.2, 24.8, 24.6, 11.8; **HRMS (ESI)**

calculated for $C_{13}H_{18}ClN_2O_4S$ $[M+H]^+$: 333.0676, found: 333.0675; **Enantiomeric ratio**: 84.5:15.5, determined by HPLC (Daicel Chirapak IC, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 25.60 min (major), t_R = 20.38 min (minor).



5c

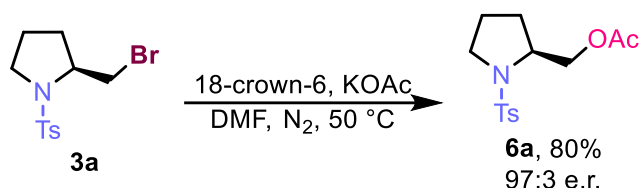
(S)-2-((R)-2-(benzyloxy)-1-chloroethyl)-1-tosylpyrrolidine 5c: yield: 31.9 mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$ = +30.5 (c 0.32 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.32 – 7.30 (m, 3H), 4.65 (d, J = 11.2 Hz, 1H), 4.59 – 4.53 (m, 2H), 4.06 – 4.04 (m, 1H), 3.97 – 3.94 (m, 1H), 3.80 – 3.77 (m, 1H), 3.42 – 3.38 (m, 1H), 3.33 – 3.29 (m, 1H), 2.44 (s, 3H), 2.03 – 1.99 (m, 1H), 1.77 – 1.70 (m, 1H), 1.38 – 1.32 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 138.1, 134.5, 129.9, 128.5, 127.9, 127.8, 127.8, 73.4, 70.6, 62.4, 62.0, 50.7, 28.2, 24.4, 21.6; **HRMS (ESI)** calculated for $C_{20}H_{25}ClNO_3S$ $[M+H]^+$: 394.1244, found: 394.1248; **Enantiomeric ratio**: 87.5:12.5, determined by HPLC (Daicel Chirapak IA, isopropanol / hexanel = 5/95, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 14.89 min (major), t_R = 14.05 min (minor).



5d

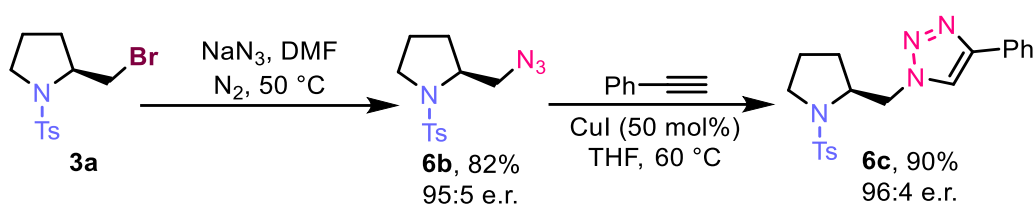
(S)-2-((R)-2-butoxy-1-chloroethyl)-1-tosylpyrrolidine 5d: yield: 29.1 mg (81%); (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1); colorless oil; $[\alpha]_D^{20}$ = +40.0 (c 0.29 CH_2Cl_2); **1H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 4.46 – 4.40 (m, 1H), 4.03 – 3.96 (m, 1H), 3.86 (dd, J = 10.6, 4.2 Hz, 1H), 3.72 (dd, J = 10.6, 7.0 Hz, 1H), 3.58 – 3.42 (m, 3H), 3.33 – 3.28 (m, 1H), 2.44 (s, 3H), 2.09 – 2.00 (m, 1H), 1.83 – 1.66 (m, 2H), 1.61 – 1.56 (m, 2H), 1.44 – 1.34 (m, 3H), 0.93 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.9, 134.4, 129.9, 127.8, 71.3, 71.0, 62.4, 62.2, 50.7, 31.9, 28.1, 24.4, 21.6, 19.6, 14.0; **HRMS (ESI)** calculated for $C_{17}H_{27}ClNO_3S$ $[M+H]^+$: 360.1400, found: 360.1395; **Enantiomeric ratio**: 88.5:11.5, determined by HPLC (Daicel Chirapak IE, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 11.50 min (major), t_R = 13.83 min (minor).

5. The Derivations of (S)-2-(Bromomethyl)-1-tosylpyrrolidine



(S)-(1-tosylpyrrolidin-2-yl)methyl acetate (6a):

To a solution of **3a** (0.10 mmol, 30mg) in DMF (1.0 mL) was added 18-crown-6 (0.2 mmol, 50 mg), KOAc (0.4 mmol, 41.6mg) and the reaction mixture was stirred under N₂ at 50 °C in the absence of light for 24 h. The mixture was diluted with Et₂O. Organic phase was washed with H₂O (2 × 5.0 mL), The organic volatile solvents were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **6a** (22.4 mg, 80% yield, 97:3 er). white solid; m.p.: 93.9 – 94.5 °C; $[\alpha]_D^{20} = +59.6$ (c 0.23 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.20 (dd, *J* = 11.0, 4.7 Hz, 1H), 4.13 – 4.10 (m, 1H), 3.93 – 3.86 (m, 1H), 3.47 – 3.40 (m, 1H), 3.17 (q, *J* = 8.9 Hz, 1H), 2.43 (s, 3H), 2.07 (s, 3H), 1.87 – 1.80 (m, 1H), 1.75 – 1.68 (m, 1H), 1.65 – 1.60 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 170.7, 143.6, 134.8, 129.8, 127.4, 66.2, 58.0, 49.2, 28.7, 24.1, 21.5, 20.9; HRMS (ESI) calculated for C₁₄H₁₉NNaO₄S [M+Na]⁺: 320.0932, found: 320.0934; **Enantiomeric ratio**: 97:3, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 14.46 min (major), t_R = 16.01 min (minor).



(S)-2-(azidomethyl)-1-tosylpyrrolidine (6b):

To a solution of **3** (0.10 mmol) in DMF (1.0 mL) was added NaN₃ (0.11 mmol), and the reaction mixture was stirred under N₂ at 50 °C in the absence of light for 24 h. Then the mixture was diluted with Et₂O. Organic phase was washed with H₂O (2 × 5.0 mL), The organic volatile solvents were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **6b** (75% yield, 95:5 er). white solid; m.p.: 124.5 – 125.2 °C; $[\alpha]_D^{20} = -36.9$ (c 0.35 CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.73 – 3.69 (m, 1H), 3.56 (dd, *J* = 12.2, 3.4 Hz, 1H), 3.53 – 3.42 (m,

2H), 3.18 – 3.14 (m, 1H), 2.44 (s, 3H), 1.91 – 1.83 (m, 1H), 1.82 – 1.80 (m, 1H), 1.72 – 1.65 (m, 1H), 1.60 – 1.55 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 143.8, 134.4, 129.9, 127.7, 59.0, 55.4, 49.6, 29.5, 24.2, 21.6; **HRMS (ESI)** calculated for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 303.0892, found: 303.0893; **Enantiomeric ratio**: 95:5, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 20/80, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_{\text{R}} = 7.63\text{ min}$ (major), $t_{\text{R}} = 8.10\text{ min}$ (minor).

(S)-4-phenyl-1-((1-tosylpyrrolidin-2-yl)methyl)-1H-1,2,3-triazole (6c):

To an oven-dried round bottom flask with magnetic stir bar was added **6b** (0.107 mmol, 30 mg), phenyl acetylene (0.214 mmol, 21.85 mg), CuI (0.0214 mmol, 4.1 mg) and THF (2ml) The solution was heated at $60\text{ }^\circ\text{C}$ for 4 h. The reaction mixture was diluted with CH_2Cl_2 (10.0 mL) and H_2O (5.0 mL). Organic was separated and the aqueous was extracted with CH_2Cl_2 ($2 \times 10.0\text{ mL}$). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **6c** (37.8mg, 90% yield, 96:4 er). white solid; m.p.: $133.6 - 134.4\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} = +110.7$ (c 0.38 CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3) δ 8.02 (s, 1H), 7.92 – 7.82 (m, 2H), 7.76 (d, $J = 8.2\text{ Hz}$, 2H), 7.44 (t, $J = 7.7\text{ Hz}$, 2H), 7.39 – 7.29 (m, 3H), 4.76 – 4.72 (m, 2H), 3.91 (dd, $J = 11.9, 8.4\text{ Hz}$, 1H), 3.28 – 3.24 (m, 1H), 3.09 – 3.00 (m, 1H), 2.45 (s, 3H), 2.00 – 1.95 (m, 1H), 1.76 – 1.60 (m, 2H), 1.41 – 1.37 (m, 1H), 1.24 – 1.19 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 147.9, 144.2, 133.6, 130.0, 128.9, 128.3, 127.7, 125.9, 121.4, 59.4, 54.4, 49.7, 29.2, 23.8, 21.6; **HRMS (ESI)** calculated for $\text{C}_{20}\text{H}_{23}\text{N}_4\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 383.1543, found: 383.1542; **Enantiomeric ratio**: 96:4, determined by HPLC (Daicel Chirapak IB, isopropanol / hexanel = 30/70, flow rate = 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$, $\lambda = 254\text{ nm}$): $t_{\text{R}} = 17.33\text{ min}$ (major), $t_{\text{R}} = 14.80\text{ min}$ (minor).

6. General Procedure for Nonlinear Effect Studies

Combining the certain amounts of optically pure Λ -(*S,S*)-**1b** with pure Δ -(*R,R*)-**1b** leads to the formation of the specified *ee* values of catalyst **1b** (preferentially in Λ -(*S,S*)-**1b**). Eight reactions containing the mixed catalyst of racemic, 17%, 33%, 54%, 67%, 89% and >99% optical purity were performed in parallel (Figure S1). As shown in Figure S1, a positive nonlinear effect was found for the bromocyclization.

General procedure: A 10-mL oven-dried vial was charged with alkene **2a** (0.10 mmol), activated NaBr (11 mg), catalyst **1b** with different *ee* values (0.0005 mmol, 0.5 mol%) and MTBE (2.0 mL) at room temperature. The mixture was cooled to 0 °C and stirred for 15 min. The Oxone (0.30 mmol) was added and the resulting solution was stirred vigorously. After 48 h, the reaction was then saturated aqueous Na₂S₂O₃ (0.2 mL). The mixture was purified by flash column chromatography (silica gel, petrol ether/EtOAc = 5:1) to give the enantioenriched product **3a**.

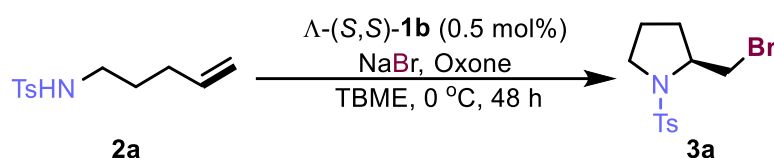


Table S4 | Nonlinear effect studies

Entry	<i>ee</i> of Λ -(<i>S,S</i>)- 1b (%)	<i>ee</i> of 3a (%)
1	0	0
2	17	79
3	33	87
4	54	88
5	67	91
7	89	91
8	100	94

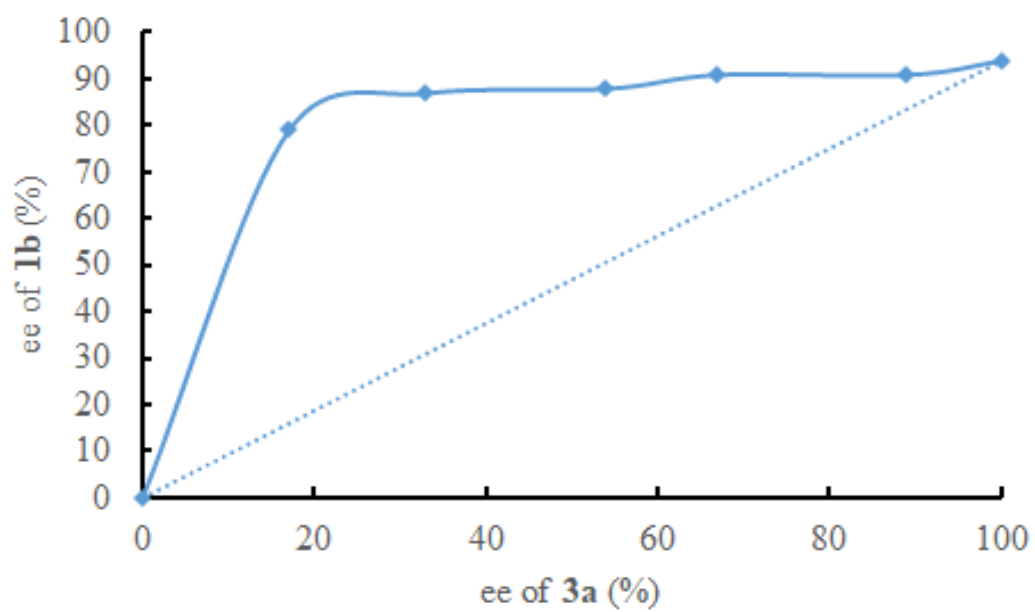


Figure S1. Nonlinear effect studies

7. X-Ray Diffraction Data

7.1. X-ray single crystal data for 3k

Sample preparation for crystal growth: absolute configuration of Compound **3k** (40.0 mg) was dissolved in DCM/*n*-hex (v/v = 1/3, 4.0 mL), while slow evaporation of solvent at room temperature dark brown red crystals were grown. Thermal ellipsoids are shown at 50% probability.

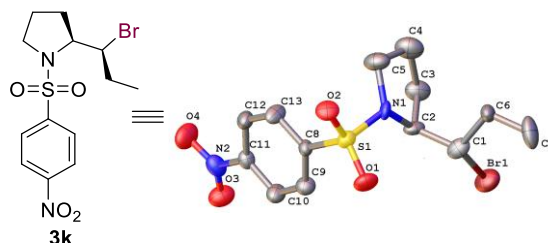
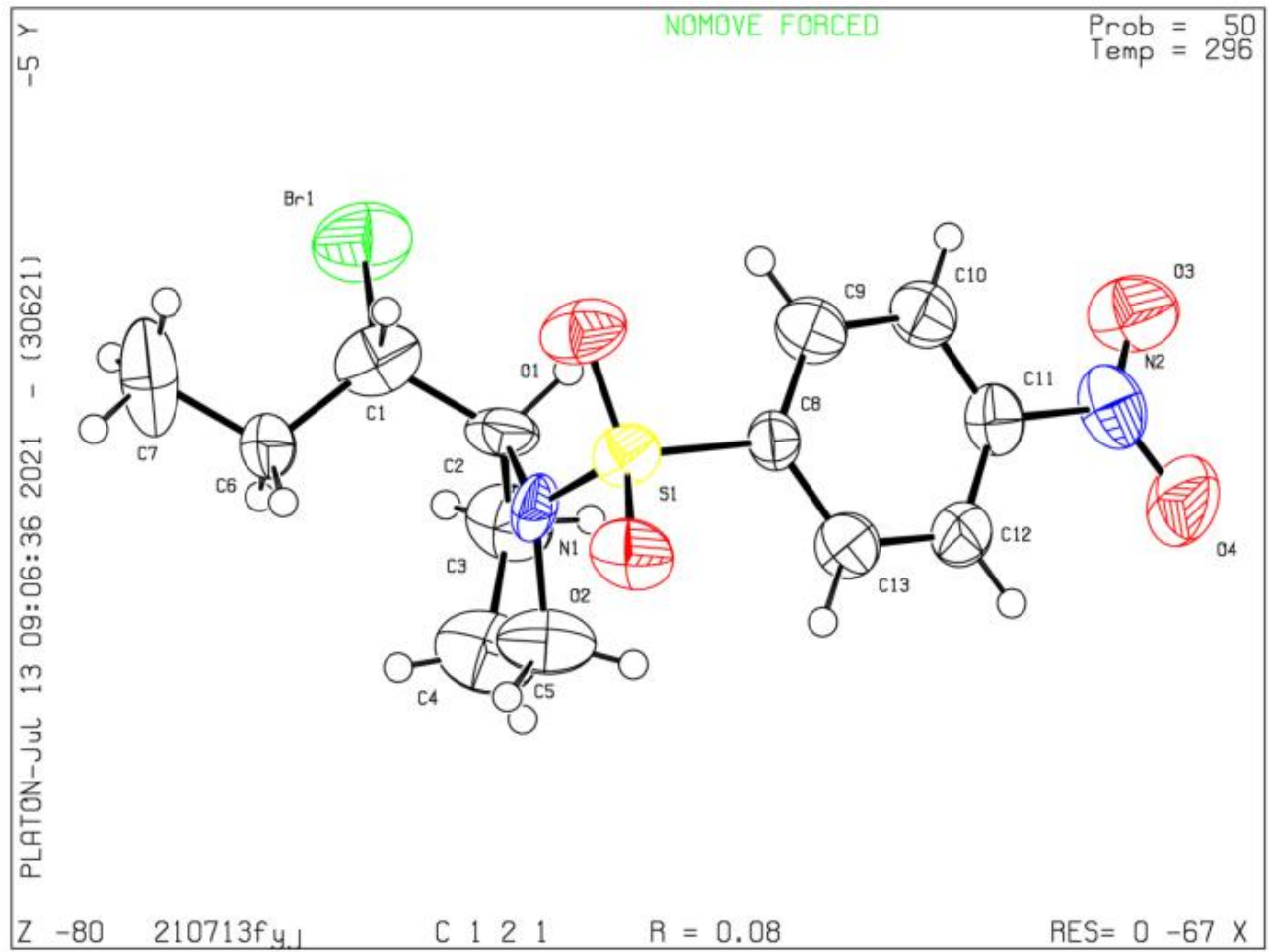


Table S5. Crystal data and structure refinement for **3k** (CCDC 2376580)

Empirical formula	C ₁₃ H ₁₇ BrN ₂ O ₄ S
Formula weight	377.25
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2
a/Å	12.403(11)
b/Å	5.914(4)
c/Å	22.599(16)
α/°	90
β/°	104.87(2)
γ/°	90
Volume/Å ³	1602(2)
Z	4
ρ _{calc} /cm ³	1.564
μ/mm ⁻¹	2.712
F(000)	768.0
Crystal size/mm ³	0.15 × 0.05 × 0.01
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.596 to 51.35
Index ranges	-14 ≤ h ≤ 14, -7 ≤ k ≤ 7, -27 ≤ l ≤ 27
Reflections collected	5439
Independent reflections	2581 [R _{int} = 0.1062, R _{sigma} = 0.1727]
Data/restraints/parameters	2581/19/191

Goodness-of-fit on F^2	0.968
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0782$, $wR_2 = 0.1750$
Final R indexes [all data]	$R_1 = 0.1754$, $wR_2 = 0.2212$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.91/-0.41
Flack parameter	0.11(3)



7.2. X-ray single crystal data for **3o**

Sample preparation for crystal growth: absolute configuration of Compound **3o** (40.0 mg) was dissolved in Et₂O/DCM (v/v = 3/1, 4.0 mL), while slow evaporation of solvent at room temperature white crystals were grown. Thermal ellipsoids are shown at 50% probability.

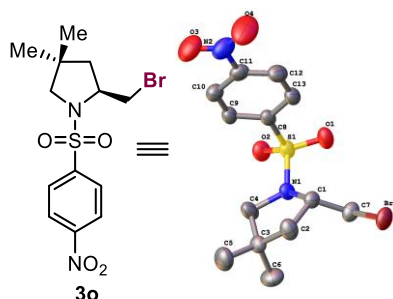
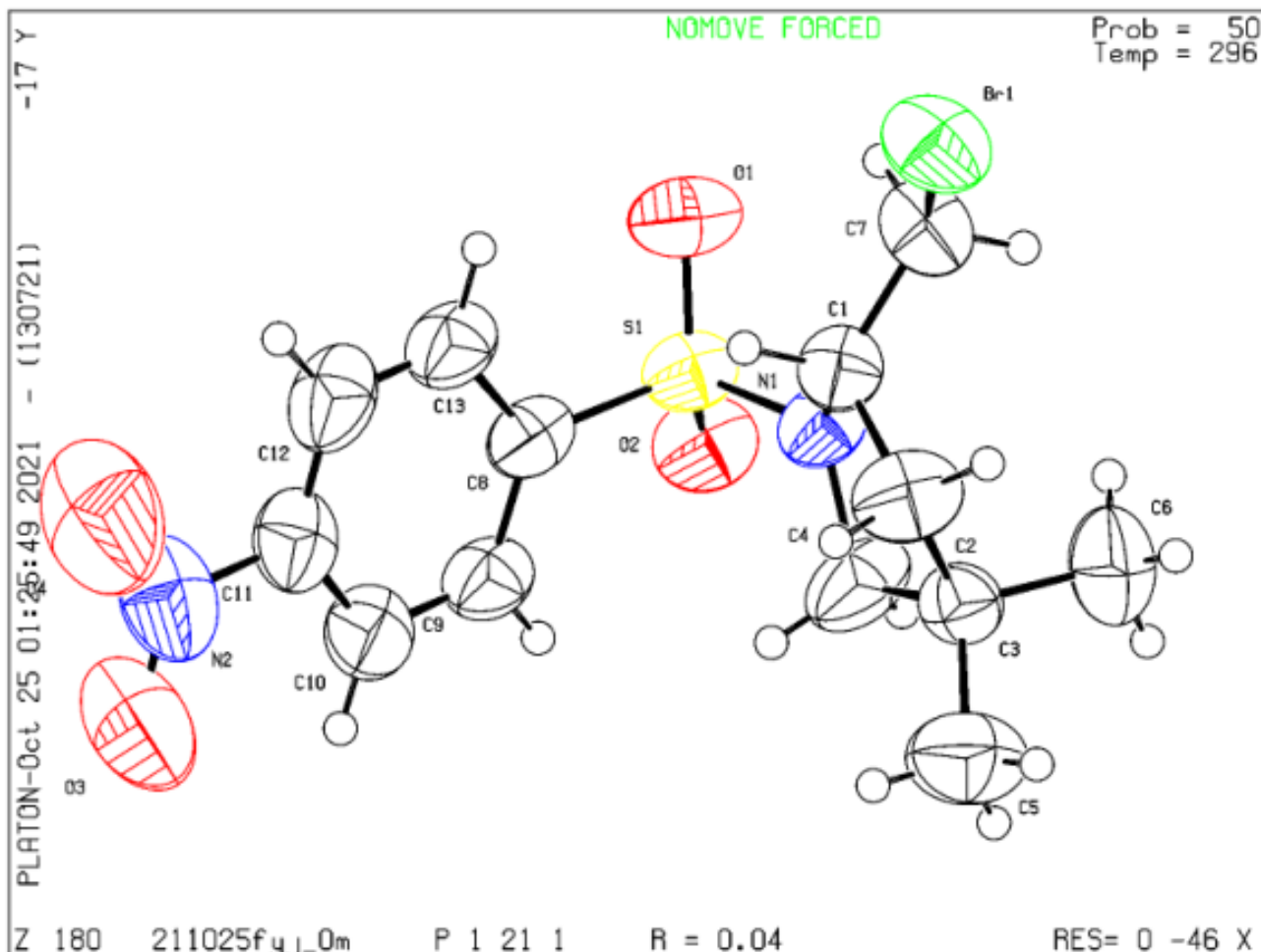


Table S6. Crystal data and structure refinement for **3o** (CCDC 2376475)

Empirical formula	C ₁₃ H ₁₇ BrN ₂ O ₄ S
Formula weight	377.25
Temperature/K	296
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.0954(2)
b/Å	6.18390(10)
c/Å	13.3904(2)
α/°	90
β/°	106.3620(10)
γ/°	90
Volume/Å ³	802.09(2)
Z	2
ρ _{calc} /cm ³	1.562
μ/mm ⁻¹	3.212
F(000)	384.0
Crystal size/mm ³	0.15 × 0.02 × 0.01
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.984 to 109.784
Index ranges	-12 ≤ h ≤ 11, -7 ≤ k ≤ 7, -15 ≤ l ≤ 16
Reflections collected	12282
Independent reflections	3034 [R _{int} = 0.0442, R _{sigma} = 0.0339]
Data/restraints/parameters	3034/1/192

Goodness-of-fit on F^2	1.033
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0437$, $wR_2 = 0.1146$
Final R indexes [all data]	$R_1 = 0.0521$, $wR_2 = 0.1239$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.46/-0.41
Flack parameter	0.032(16)



7.3. X-ray single crystal data for **3p**

Sample preparation for crystal growth: absolute configuration of Compound **3p** (40.0 mg) was dissolved in *n*-hexane/DCM (v/v = 3/1, 4.0 mL), while slow evaporation of solvent at room temperature white crystals were grown. Thermal ellipsoids are shown at 50% probability.

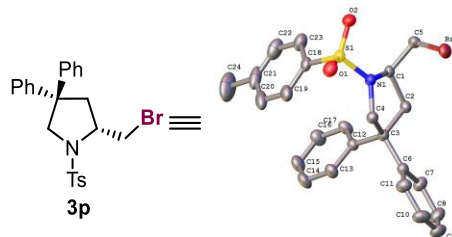
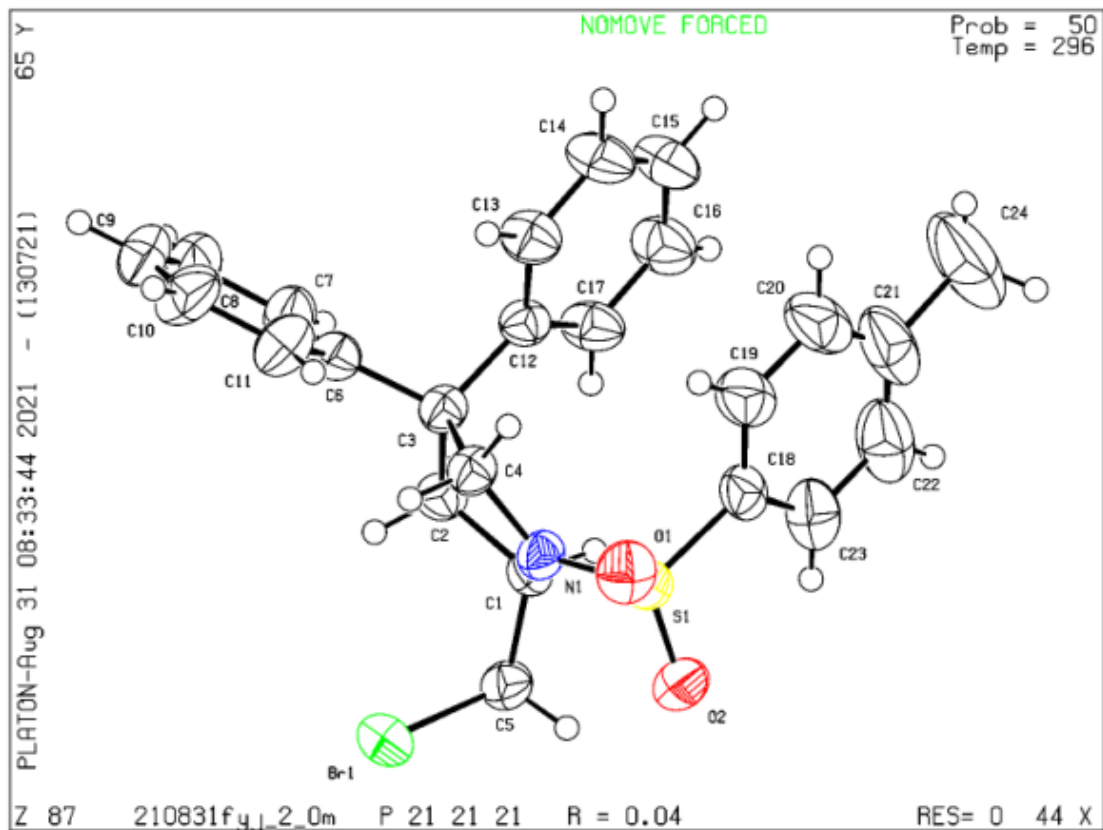


Table S7. Crystal data and structure refinement for **3p** (CCDC 2376474)

Empirical formula	C ₂₄ H ₂₄ BrNO ₂ S
Formula weight	470.41
Temperature/K	296
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.8681(2)
b/Å	10.6446(2)
c/Å	21.1836(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2225.17(7)
Z	4
ρ _{calc} /cm ³	1.404
μ/mm ⁻¹	2.397
F(000)	968.0
Crystal size/mm ³	0.08 × 0.08 × 0.05
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	7.262 to 109.956
Index ranges	-10 ≤ h ≤ 12, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25
Reflections collected	23732
Independent reflections	4220 [R _{int} = 0.0871, R _{sigma} = 0.0537]
Data/restraints/parameters	4220/0/263
Goodness-of-fit on F ²	1.070

Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0383$, $wR_2 = 0.0931$
Final R indexes [all data]	$R_1 = 0.0418$, $wR_2 = 0.0966$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.34/-0.77
Flack parameter	0.021(15)



7.4. X-ray single crystal data for **5b**

Sample preparation for crystal growth: relative configuration of Compound **5b** (40.0 mg) was dissolved in Et₂O/DCM/acetone (v/v/v = 4/1/1, 6.0 mL), while slow evaporation of solvent at room temperature white crystals were grown. Thermal ellipsoids are shown at 50% probability.

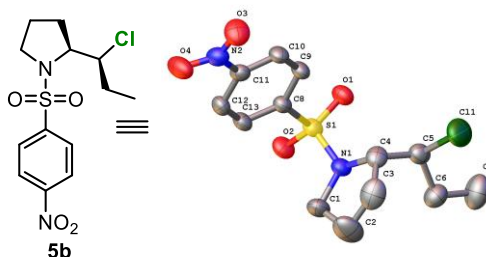
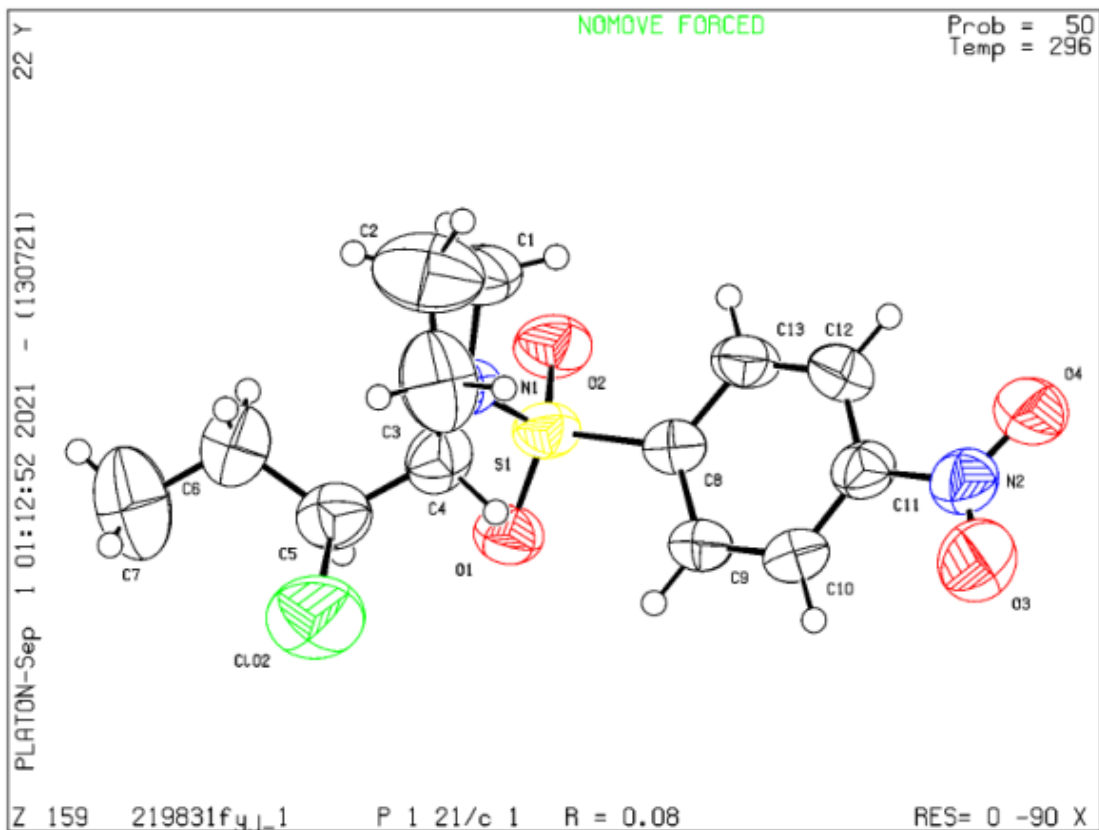


Table S8. Crystal data and structure refinement for **5b** (CCDC 2386476)

Empirical formula	C ₁₃ H ₁₇ ClN ₂ O ₄ S
Formula weight	332.79
Temperature/K	296
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	22.112(7)
b/Å	5.910(2)
c/Å	12.384(4)
α/°	90
β/°	103.404(17)
γ/°	90
Volume/Å ³	1574.4(9)
Z	4
ρ _{calc} /cm ³	1.404
μ/mm ⁻¹	2.322
F(000)	696.0
Crystal size/mm ³	0.08 × 0.03 × 0.01
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	7.15 to 109.95
Index ranges	-26 ≤ h ≤ 26, -4 ≤ k ≤ 7, -15 ≤ l ≤ 15
Reflections collected	12569
Independent reflections	2911 [R _{int} = 0.0778, R _{sigma} = 0.0577]
Data/restraints/parameters	2911/0/191

Goodness-of-fit on F^2	1.094
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0757$, $wR_2 = 0.2055$
Final R indexes [all data]	$R_1 = 0.1195$, $wR_2 = 0.2448$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.50/-0.51

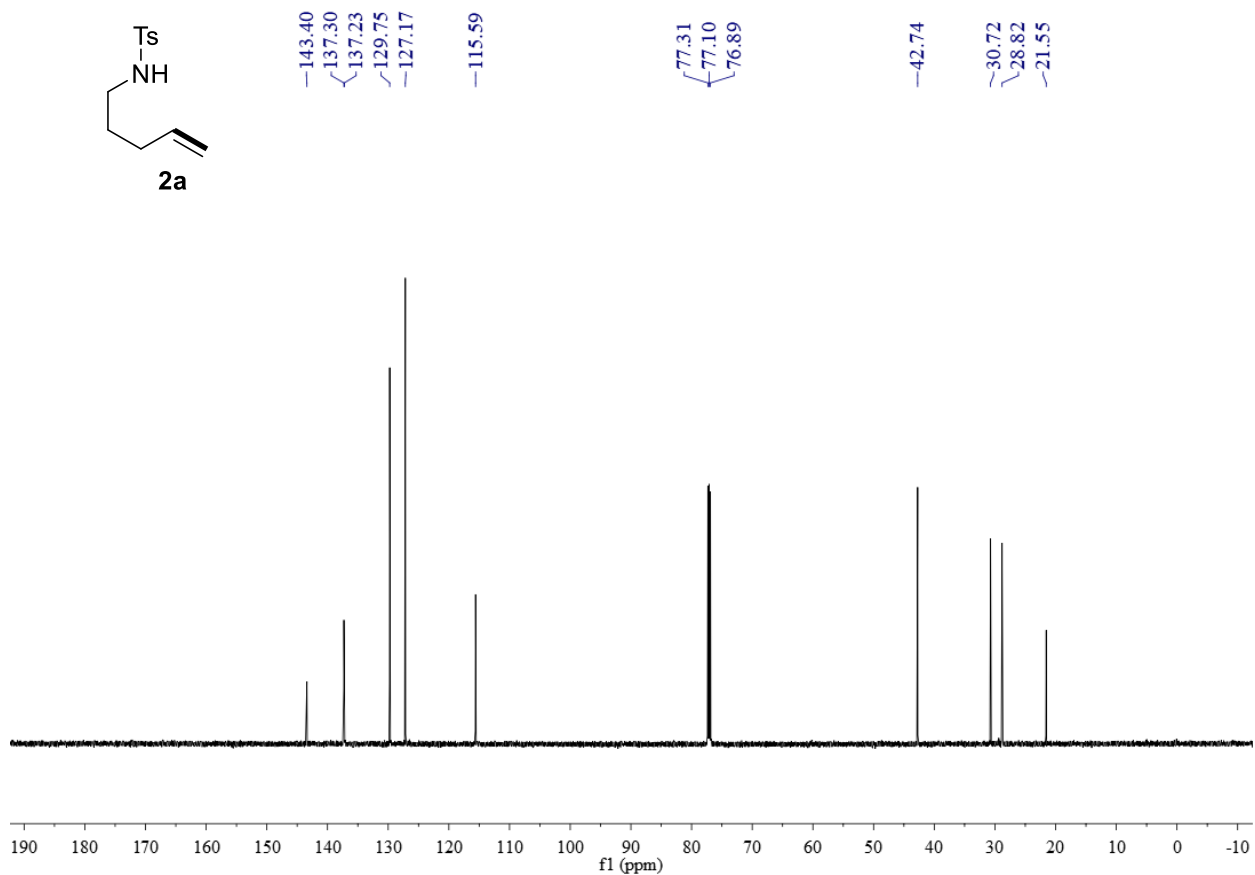
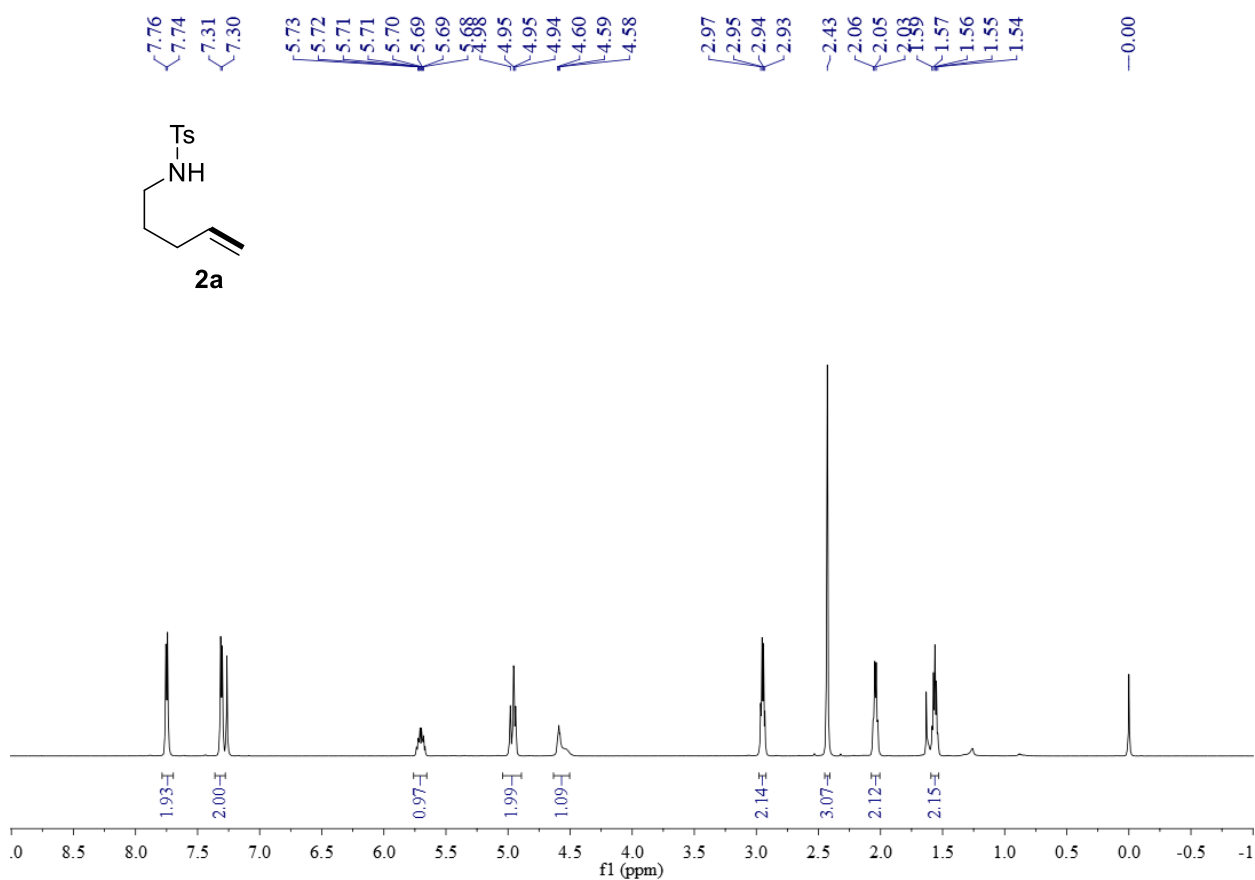


8. References

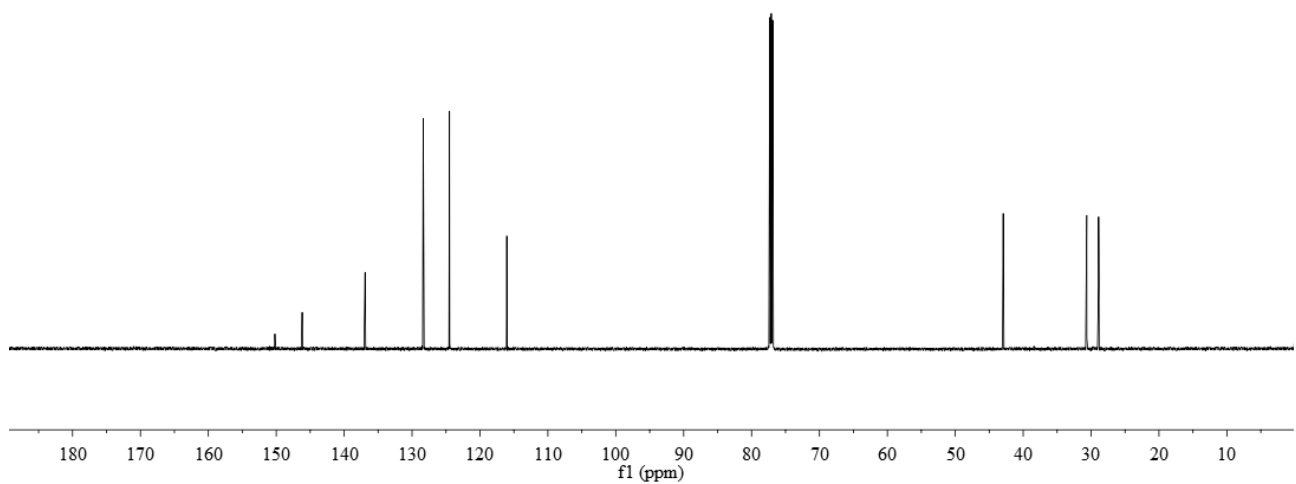
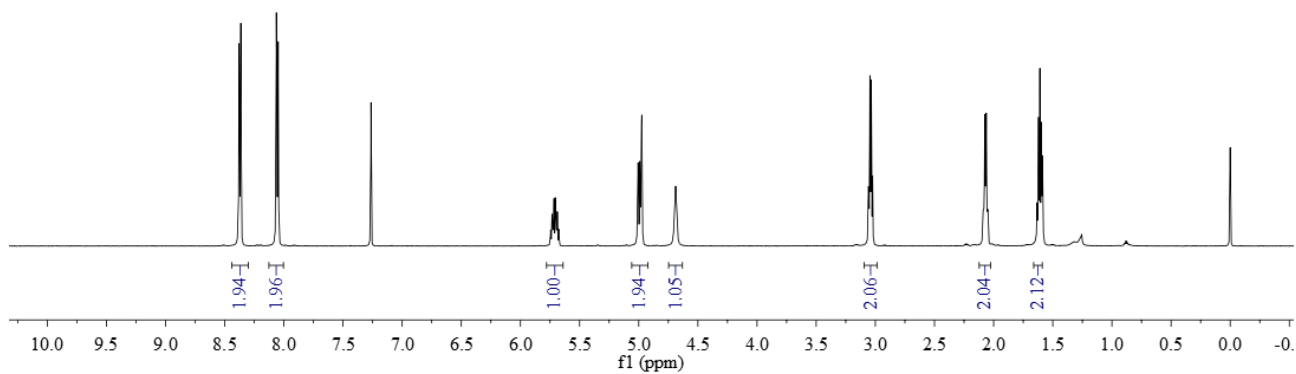
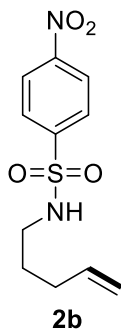
- [1](a) Yu, J.; Jiang, H.-J.; Zhou, Y.; Luo, S.-W.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2015**, *54*, 11209. (b) Jiang, H.-J.; Liu, K.; Yu, J.; Zhang, L.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2017**, *56*, 11931. (c) Jiang, H.-J.; Zhong, X.-M.; Y, J.; Zhang, Y.; Zhang, X.; Wu, Y.-D.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2019**, *58*, 1803. (d) Sun, T.-T.; Liu, K.; Zhang, S.-X.; Wang, C.-R.; Yao, C.-Z.; Yu, J. *Synlett* **2021**, *32*, 701.
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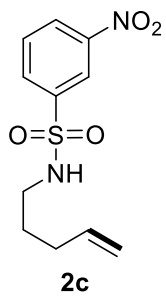
9. Selected NMR and HPLC

9.1. NMR of the Substrates 2



8.38
8.36
8.06
8.05
5.74
5.73
5.73
5.72
5.72
5.70
5.70
5.69
5.69
5.68
5.01
5.01
4.99
4.99
4.98
4.97
4.69
3.06
3.05
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1.61
1.60
1.59
0.00



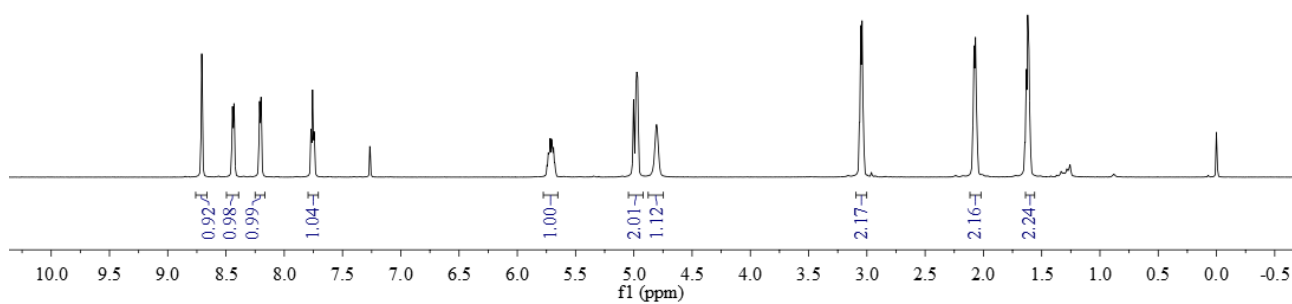


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 8.44
 8.43
 8.21
 8.20
 7.77
 7.76
 7.74

5.72
 5.71
 5.69
 5.00
 4.97
 4.97
 4.81

3.06
 3.05
 3.04
 2.08
 2.07
 1.64
 1.63
 1.62
 1.61

-0.00

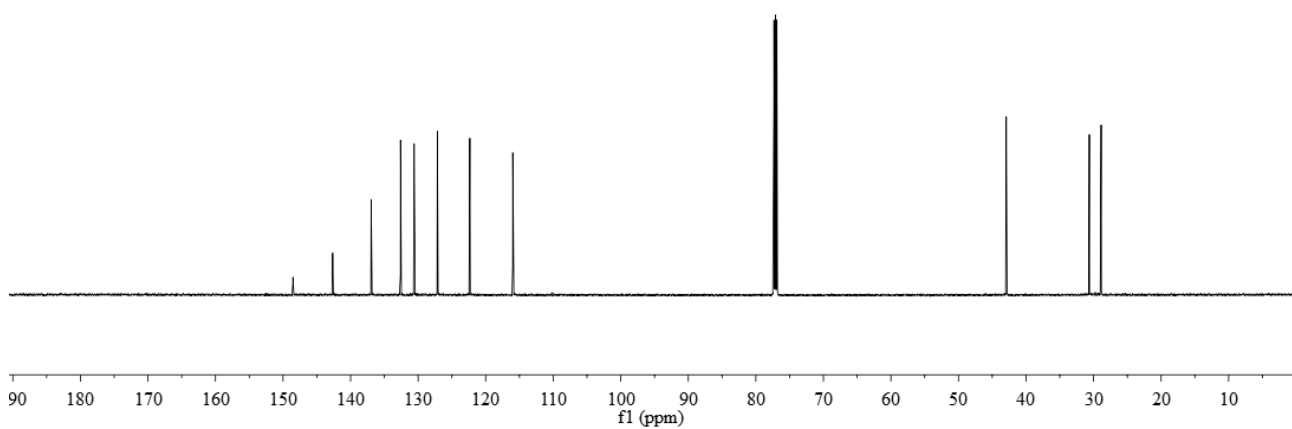
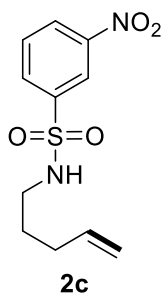


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 136.95
 132.60
 130.59
 127.15
 122.34
 115.98

77.31
 77.10
 76.89

-42.93

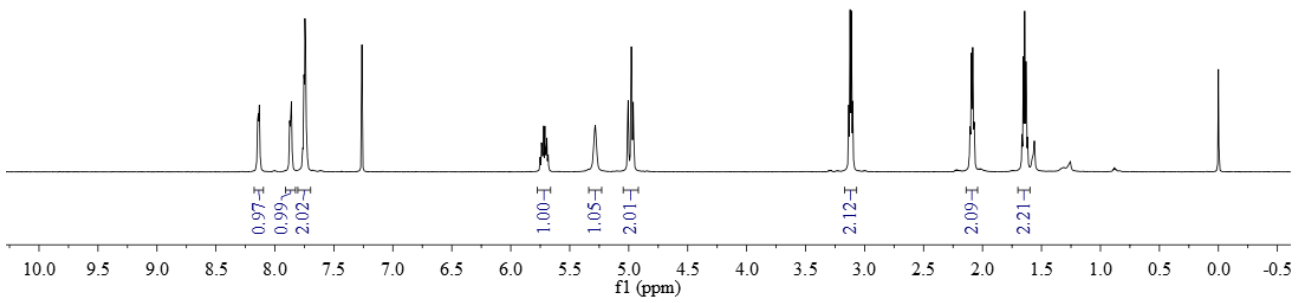
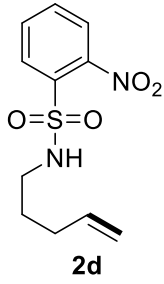
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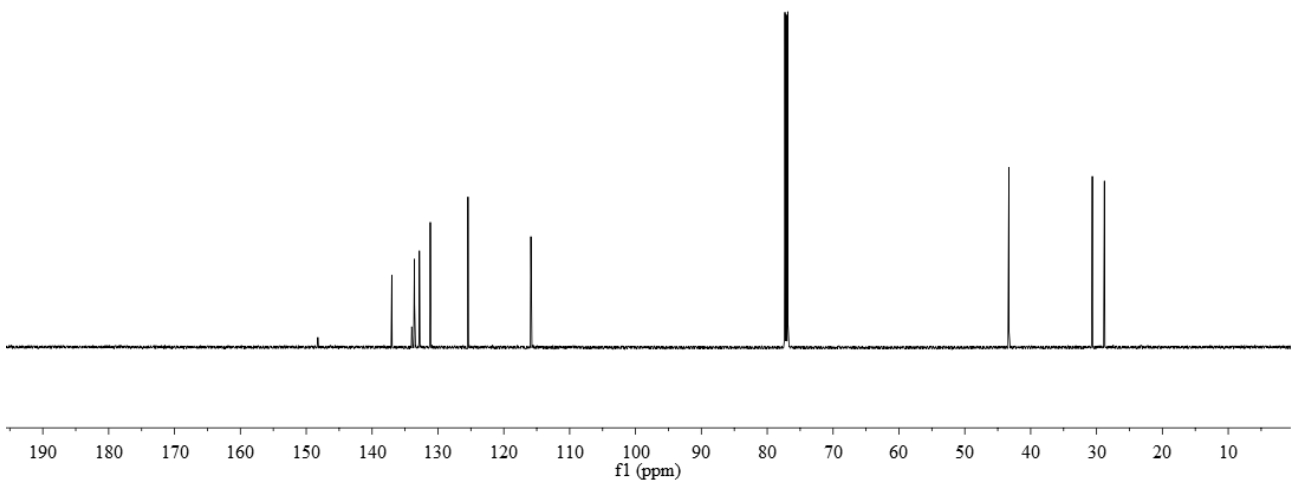
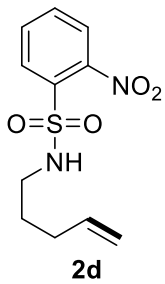
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7.74
7.73

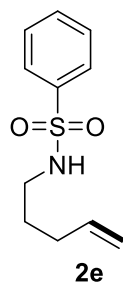
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5.28
5.01
4.98
4.98
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3.13
3.12
3.11
3.10
2.11
2.09
2.08
2.07
1.67
1.65
1.64
1.63
1.62

---0.00



148.23
137.01
133.98
133.57
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131.16
125.44
115.89
77.31
77.10
76.89
43.30
30.64
28.80



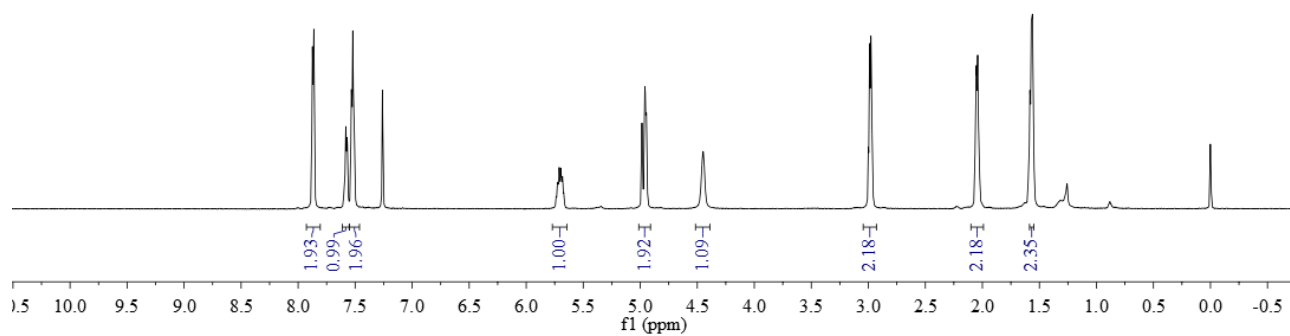


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7.86
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7.57
7.53
7.52
7.51

5.74
5.73
5.71
5.70
5.68
4.98
4.96
4.95
-4.45

3.00
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2.05
2.04
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1.58
1.57
1.56

-0.00



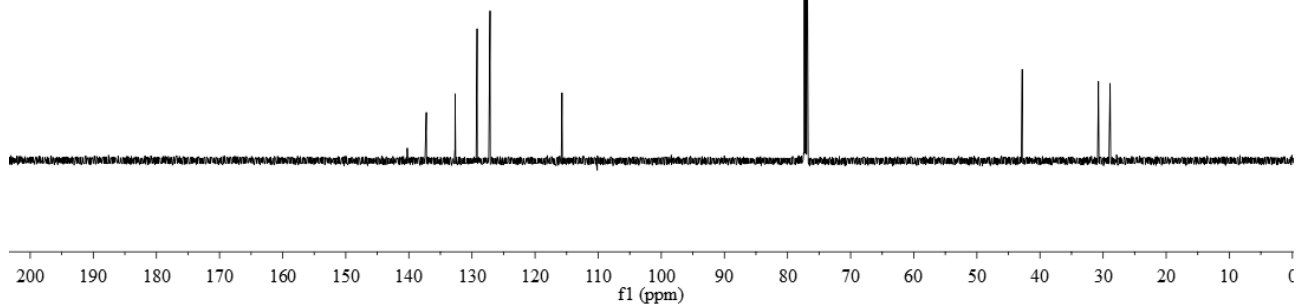
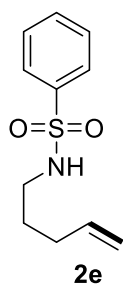
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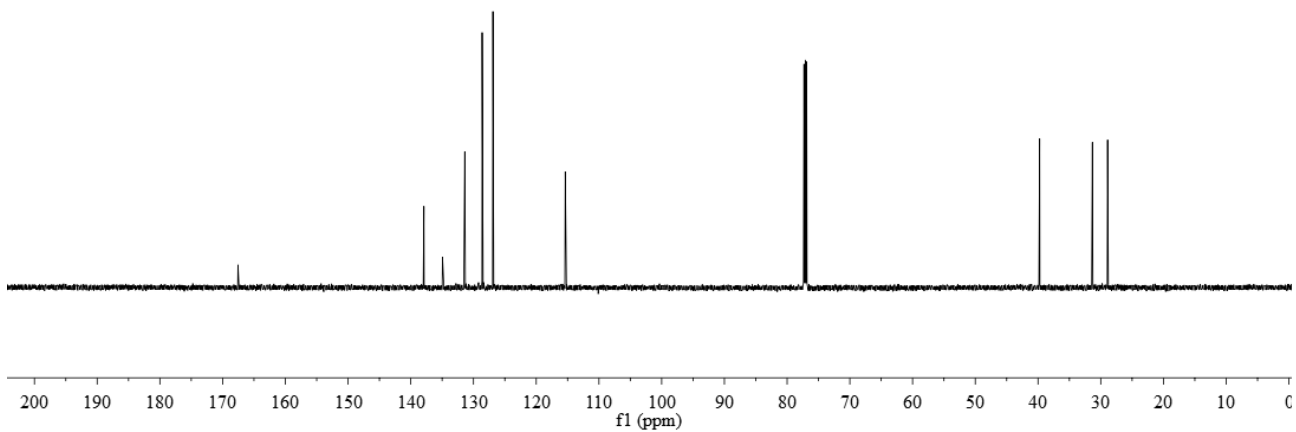
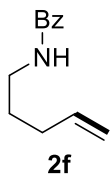
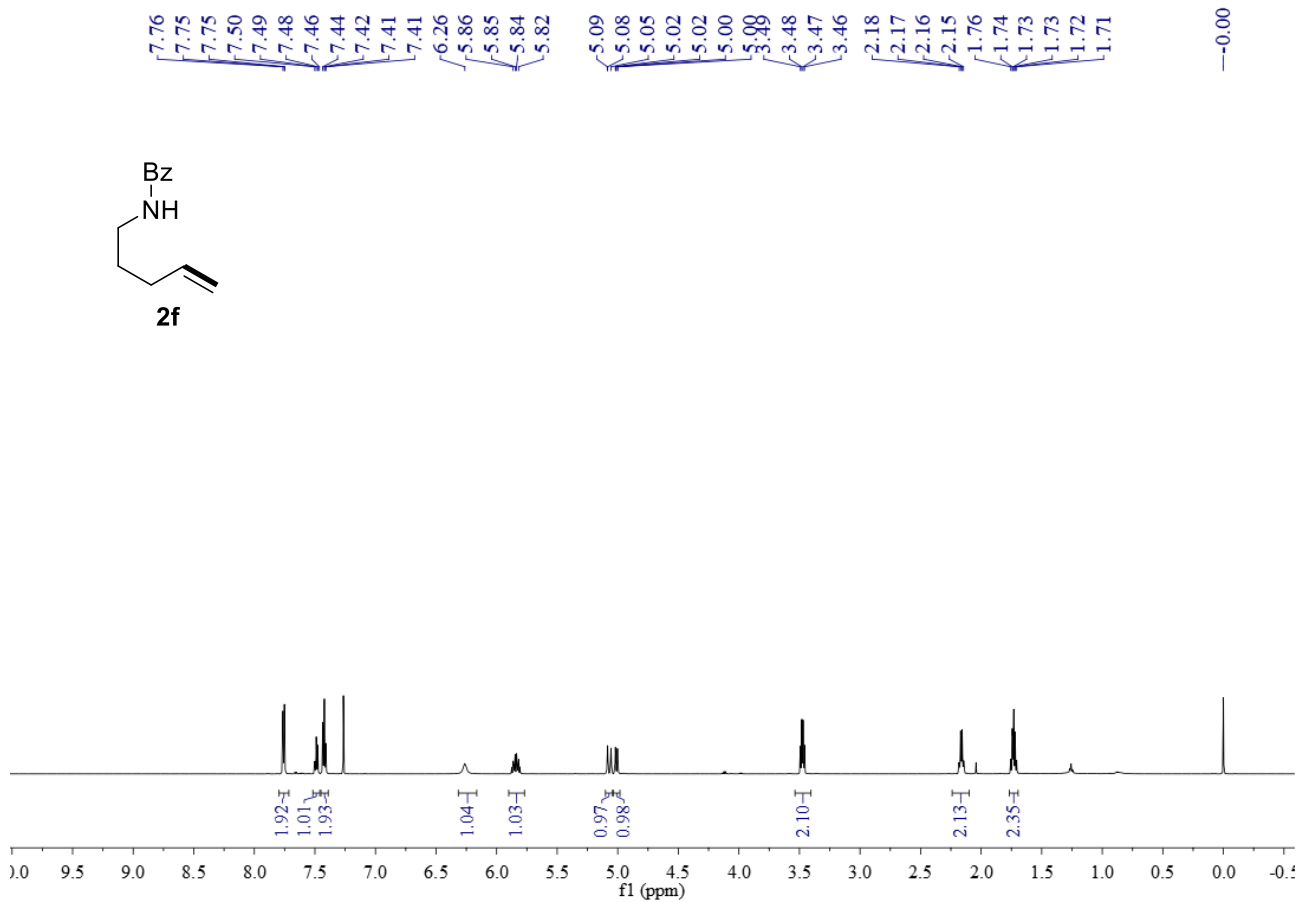
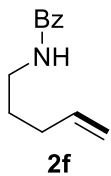
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42.81

30.74
28.88





7.75
7.73
7.31
7.30

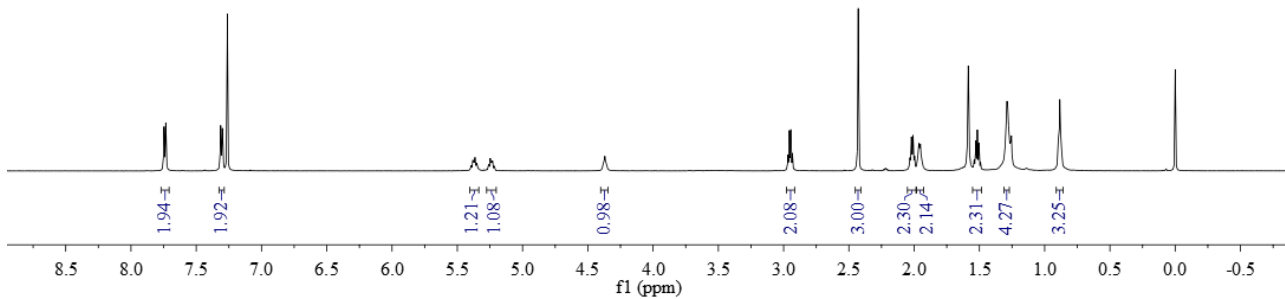
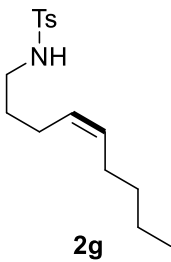
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2.01

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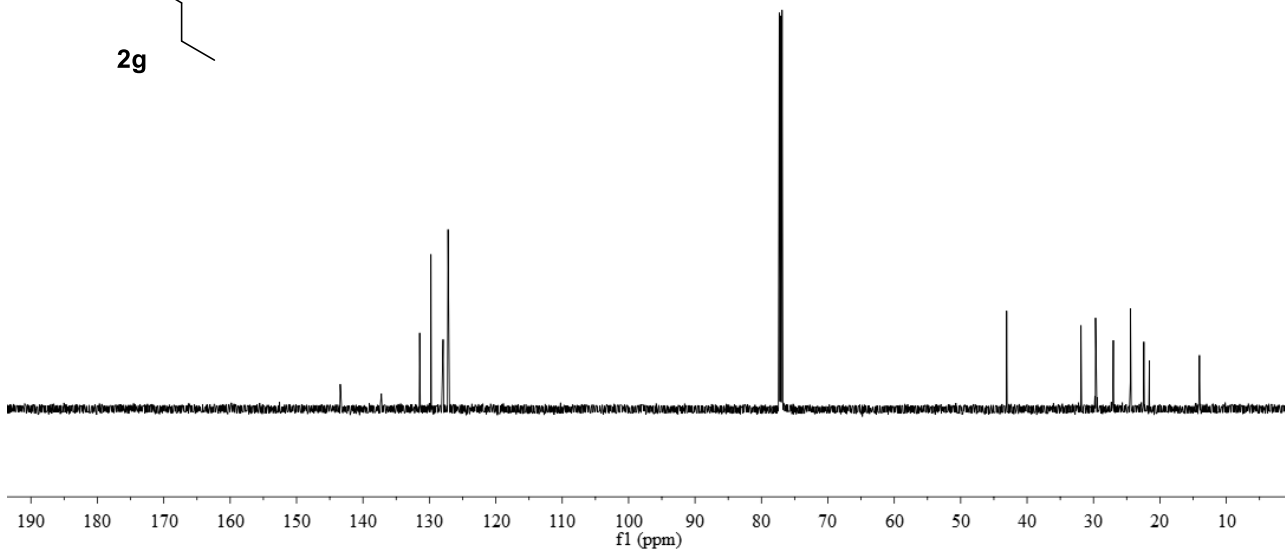
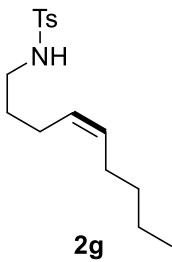


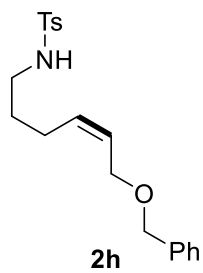
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77.31
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76.89

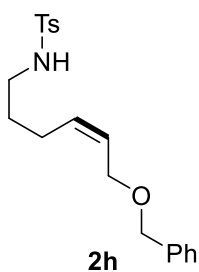
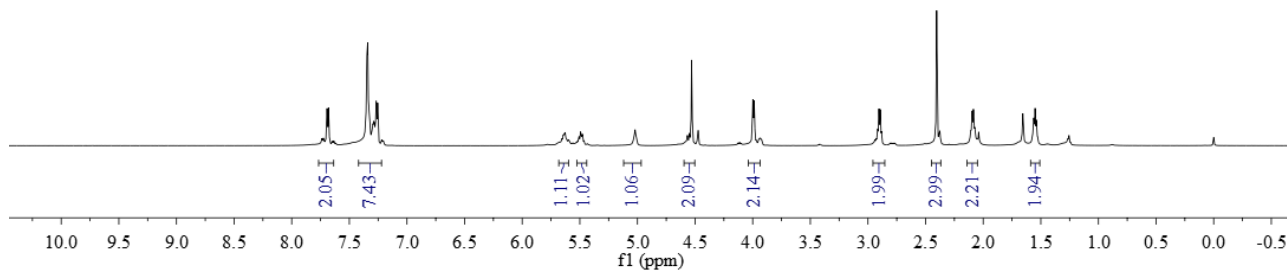
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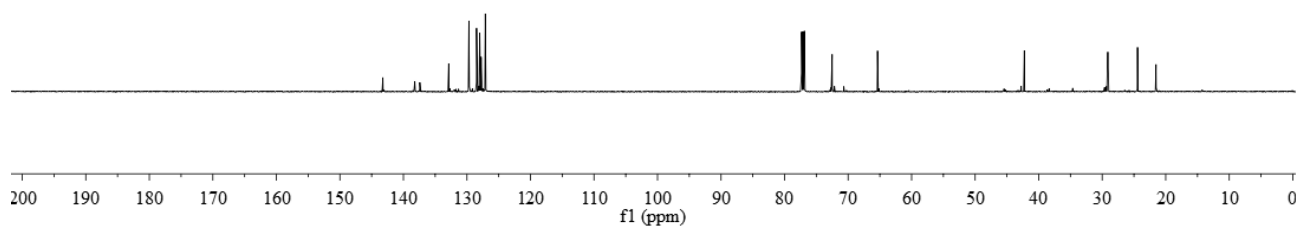


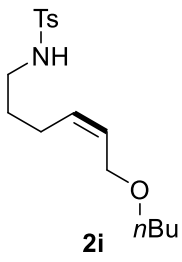


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7.29

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5.46
5.45

4.92

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3.94

3.44
3.43

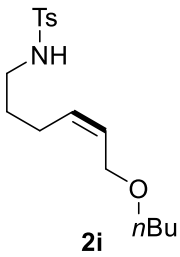
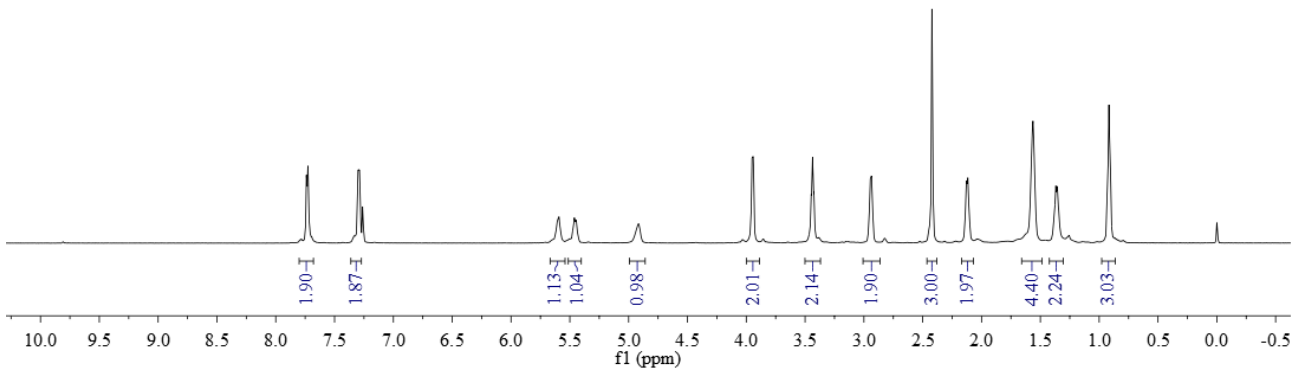
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0.90

-0.00

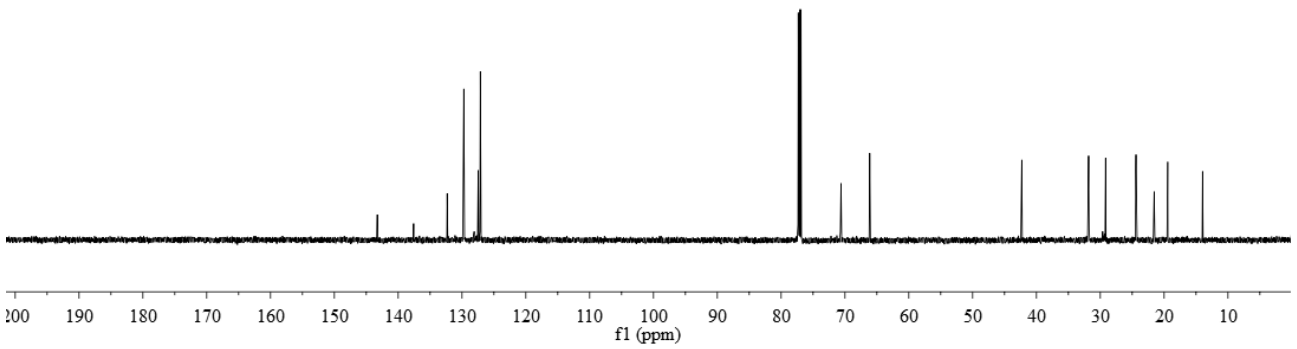


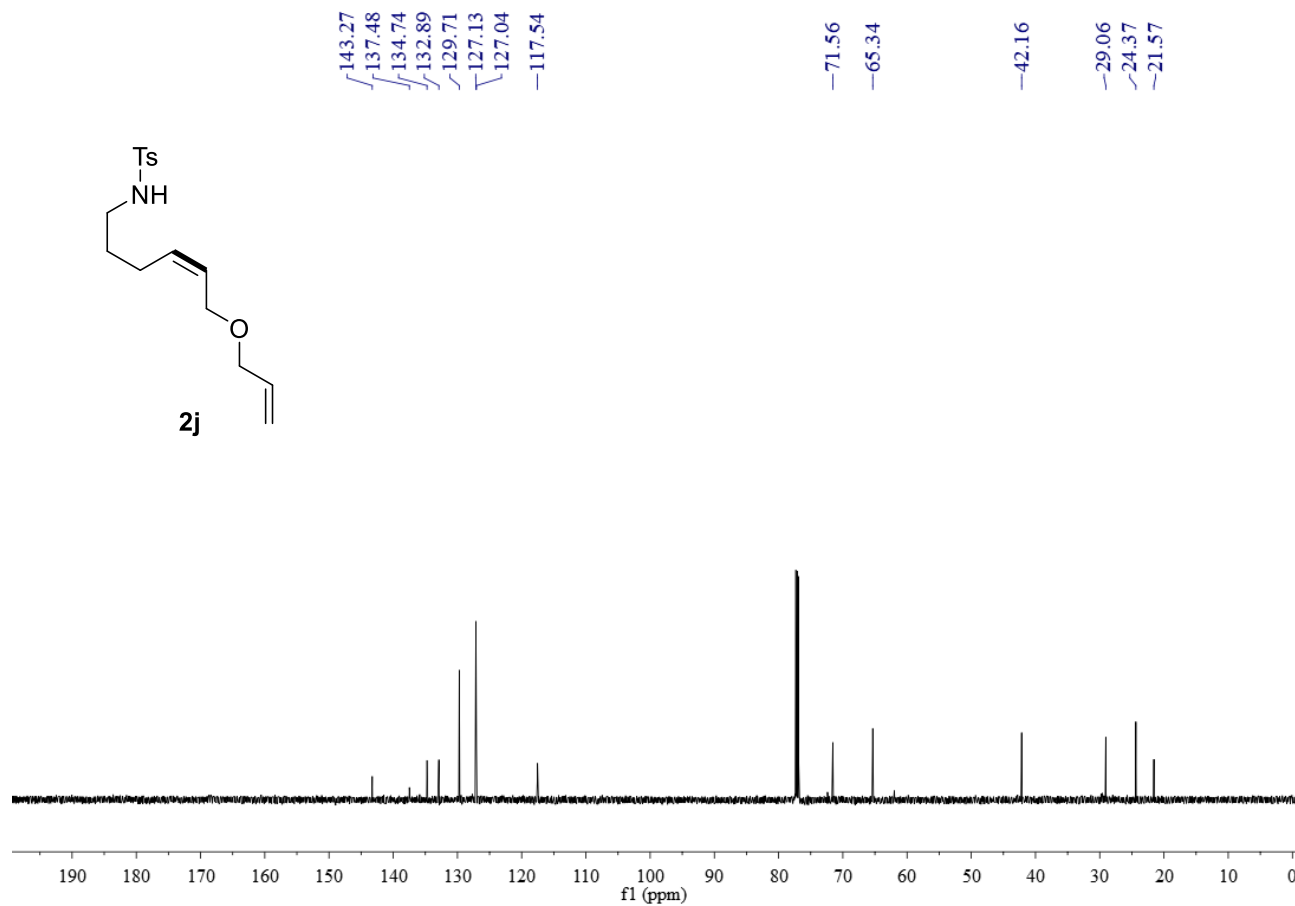
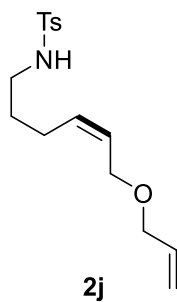
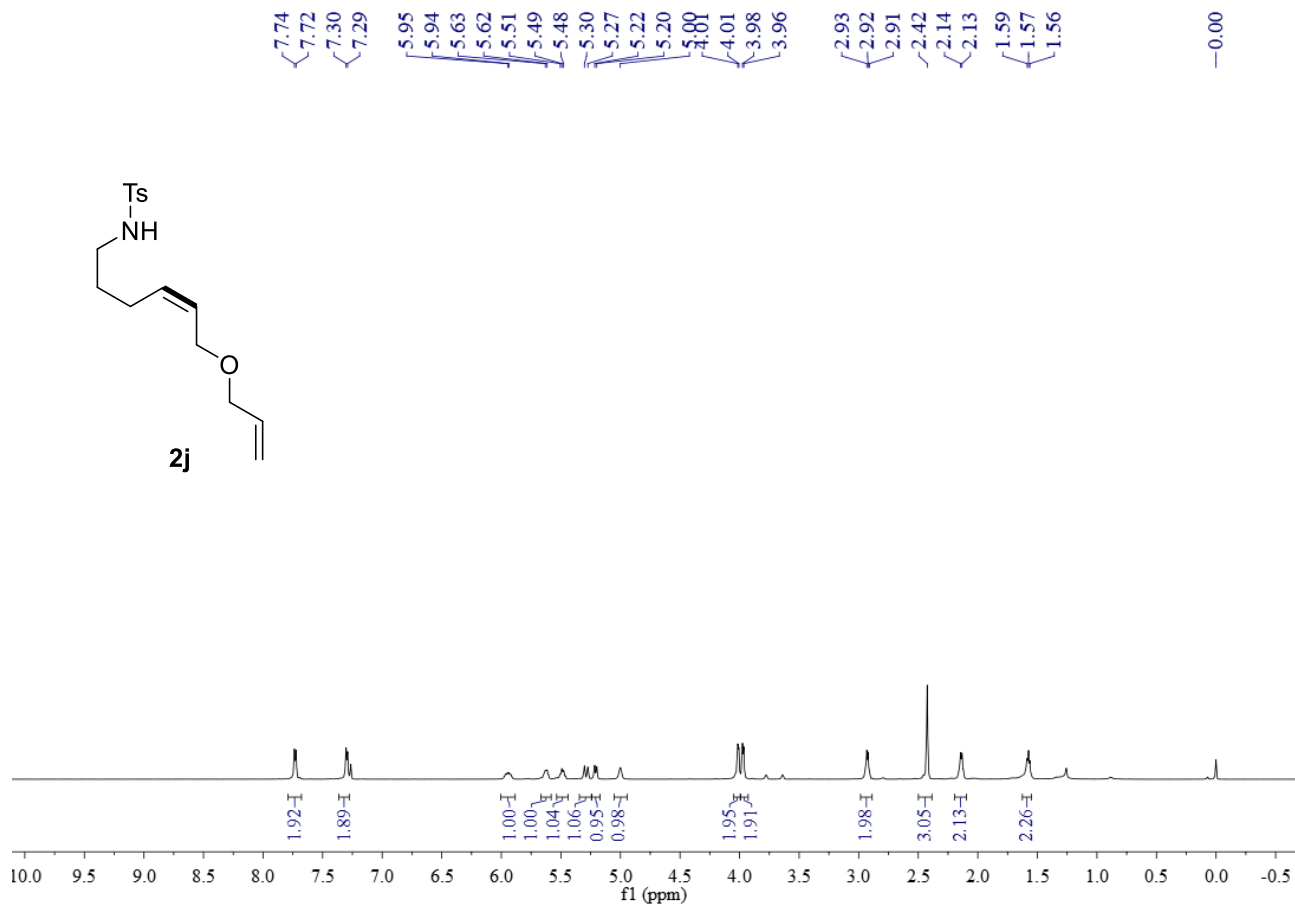
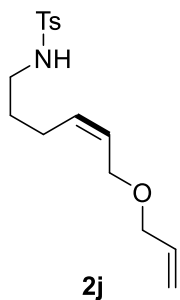
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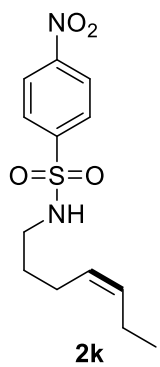
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76.89
70.62
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42.30

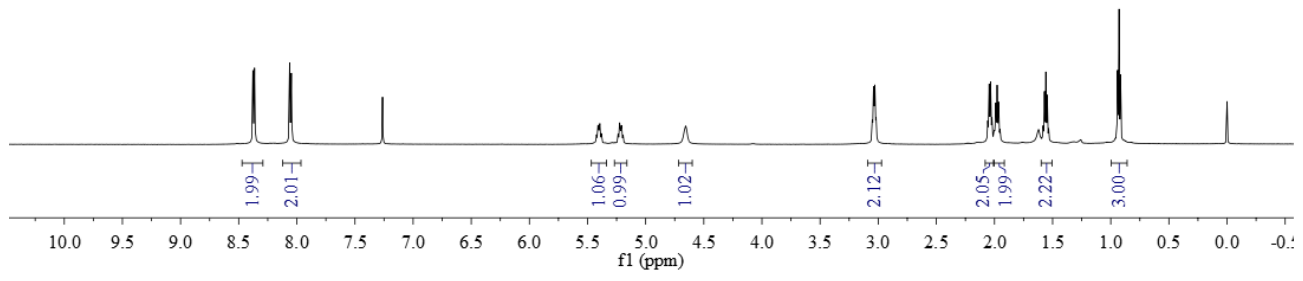
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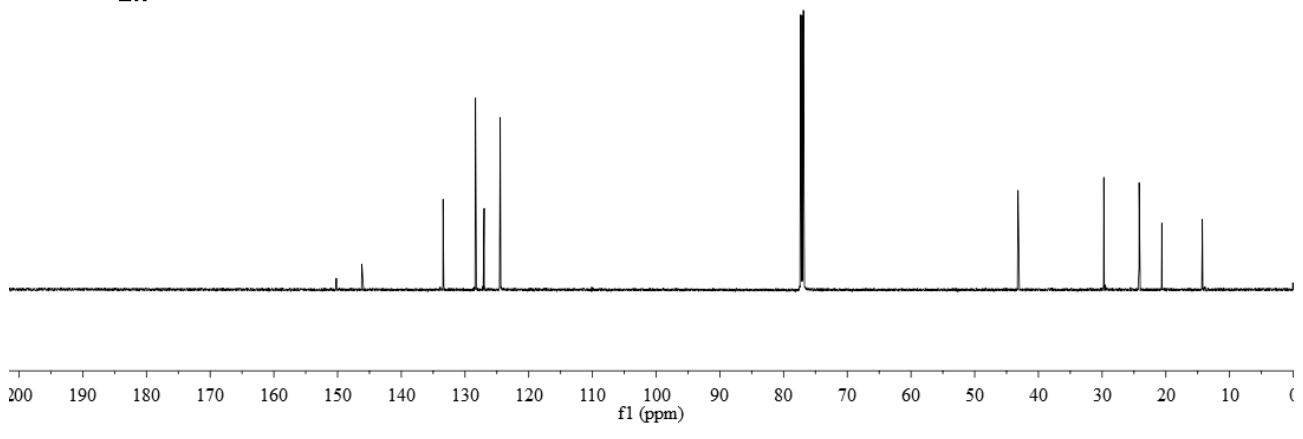
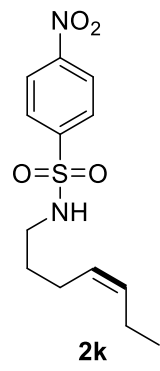


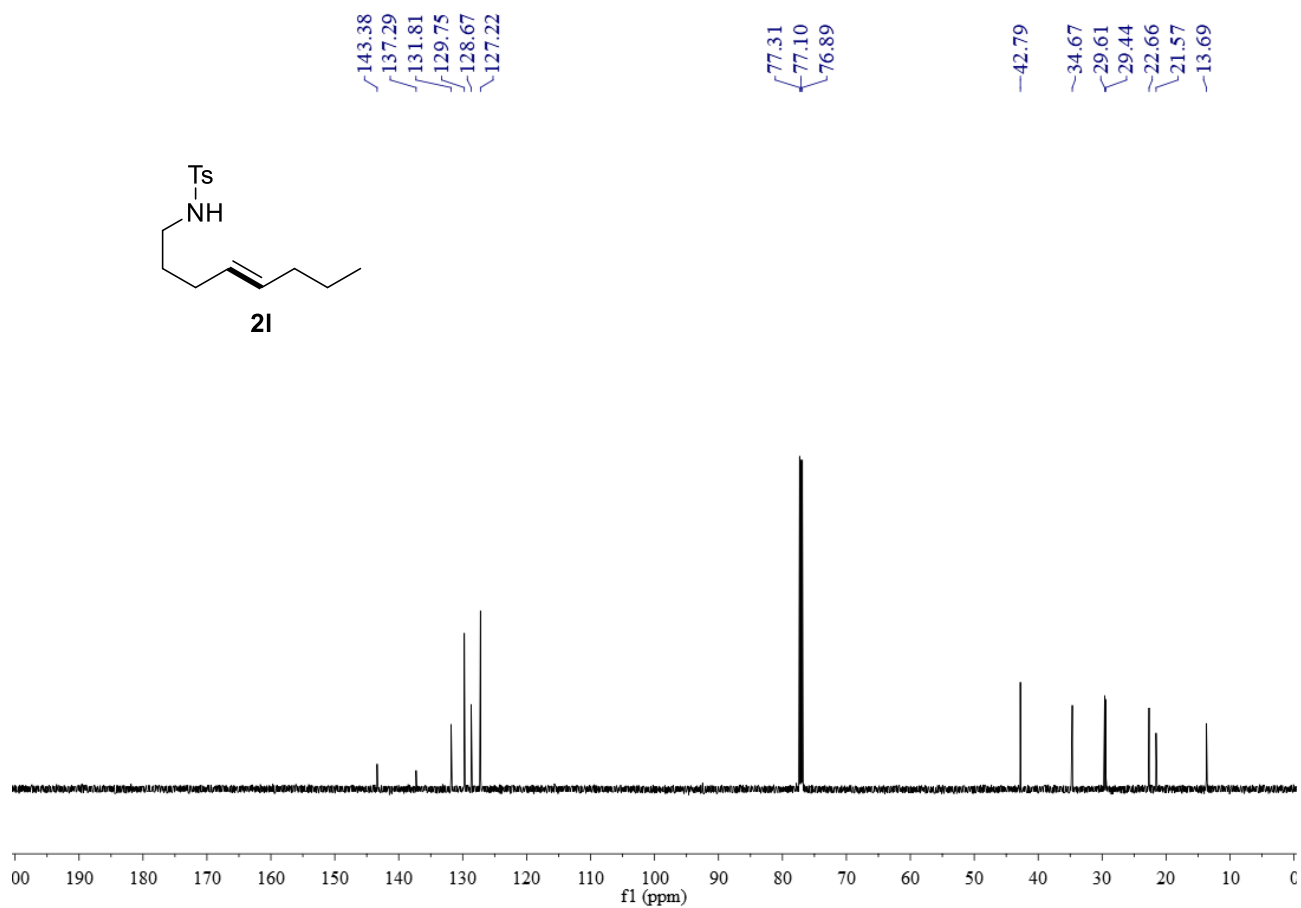
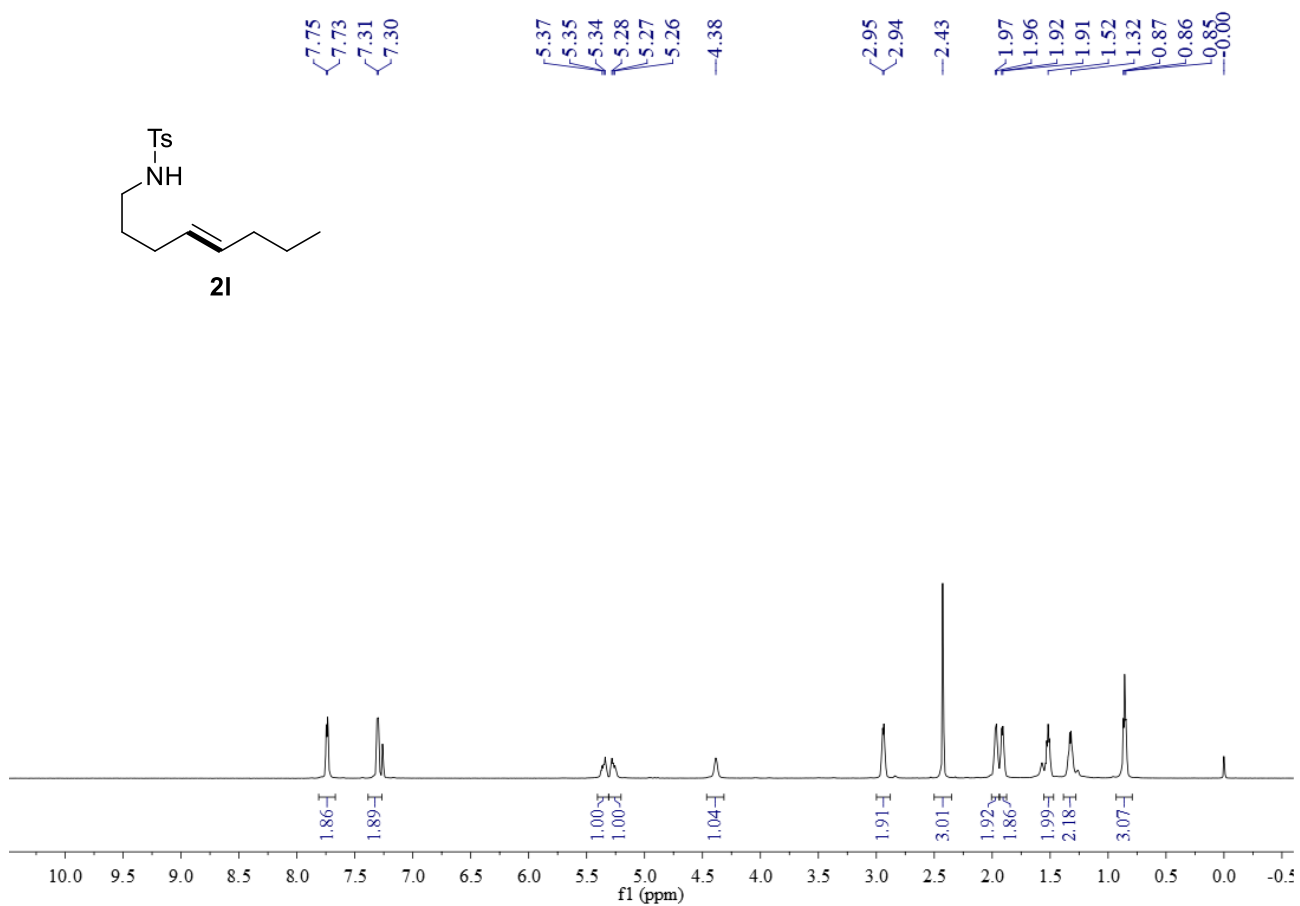


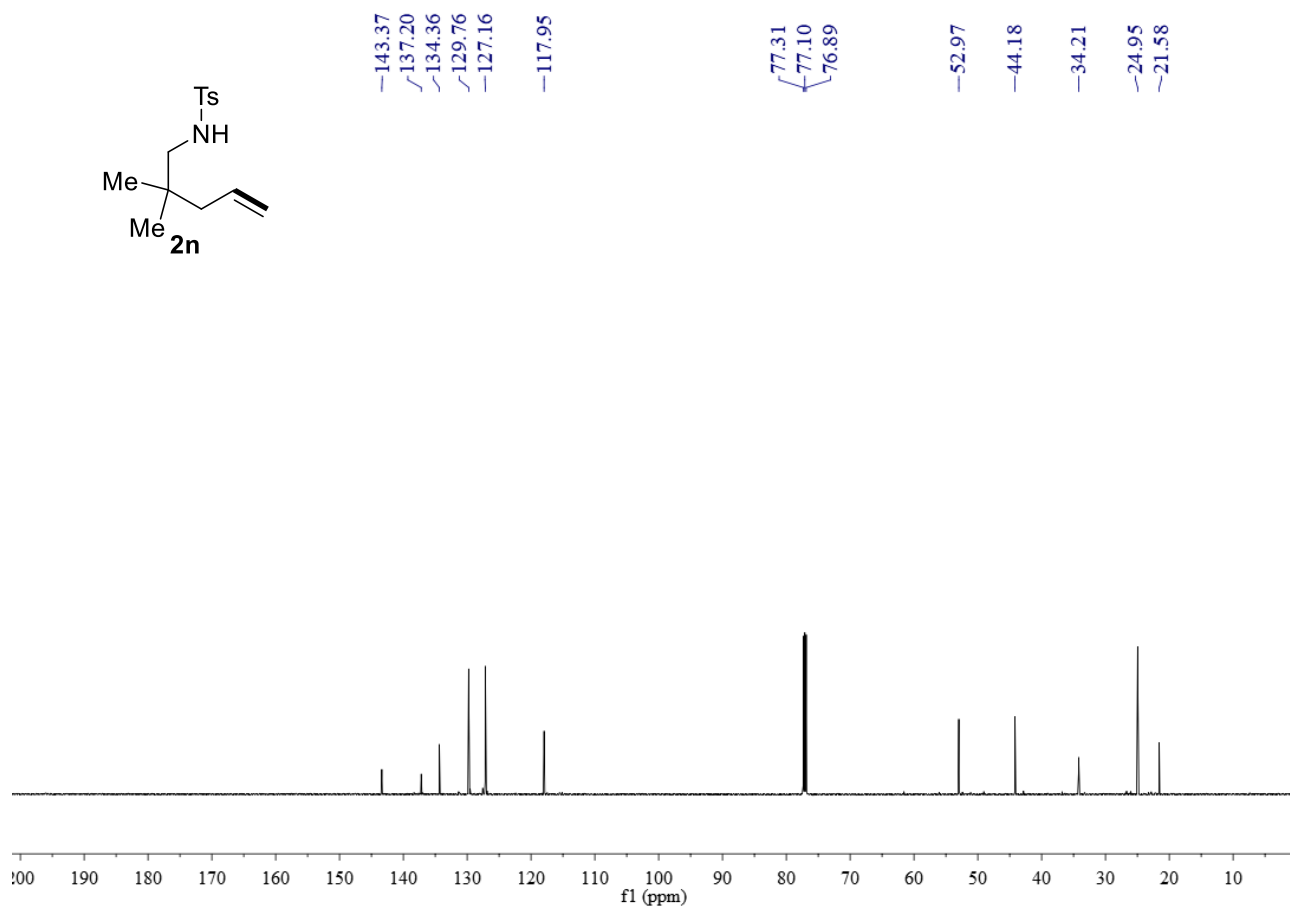
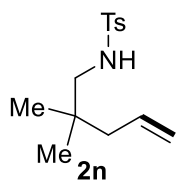
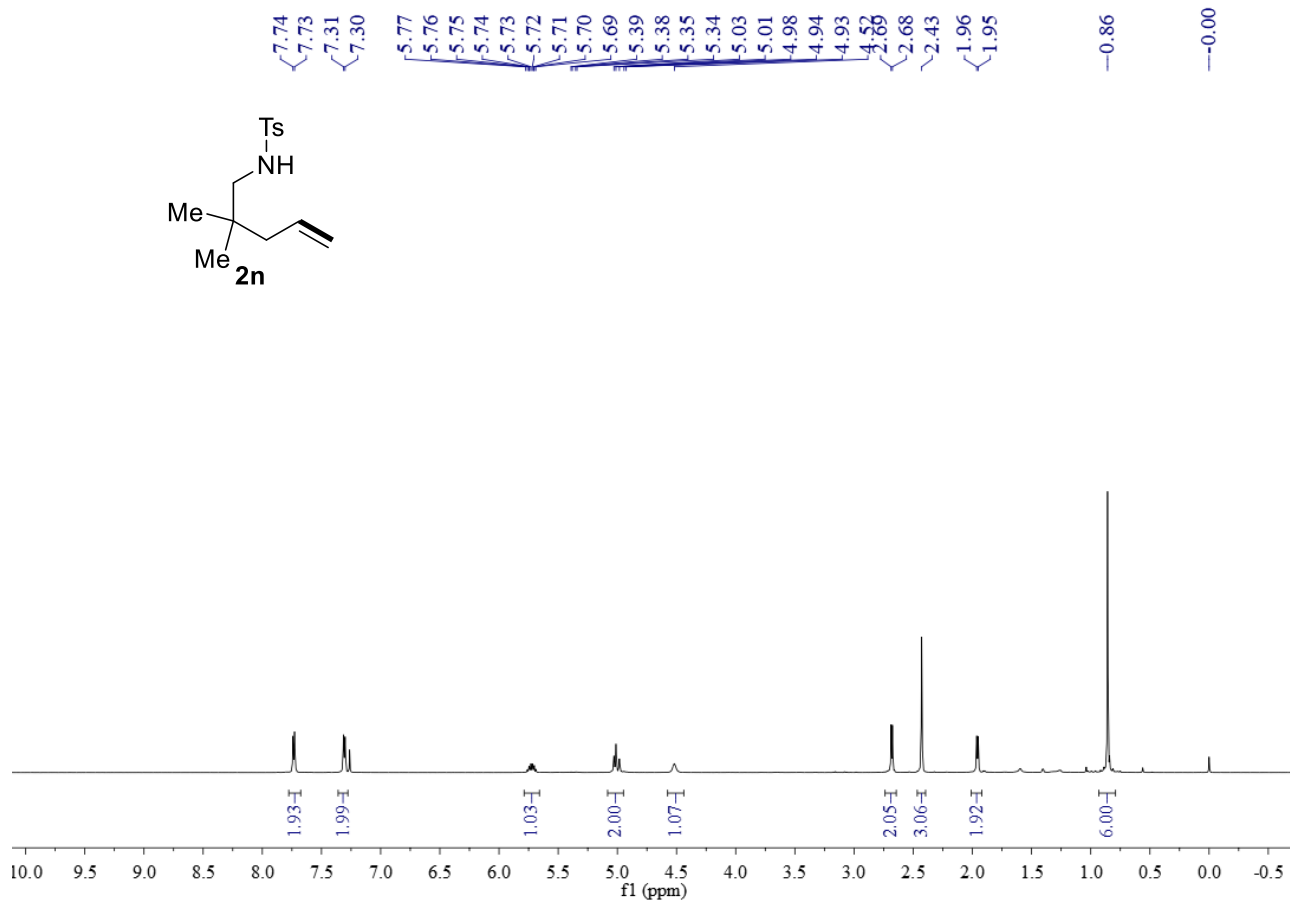
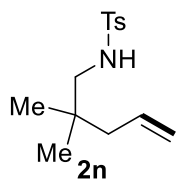
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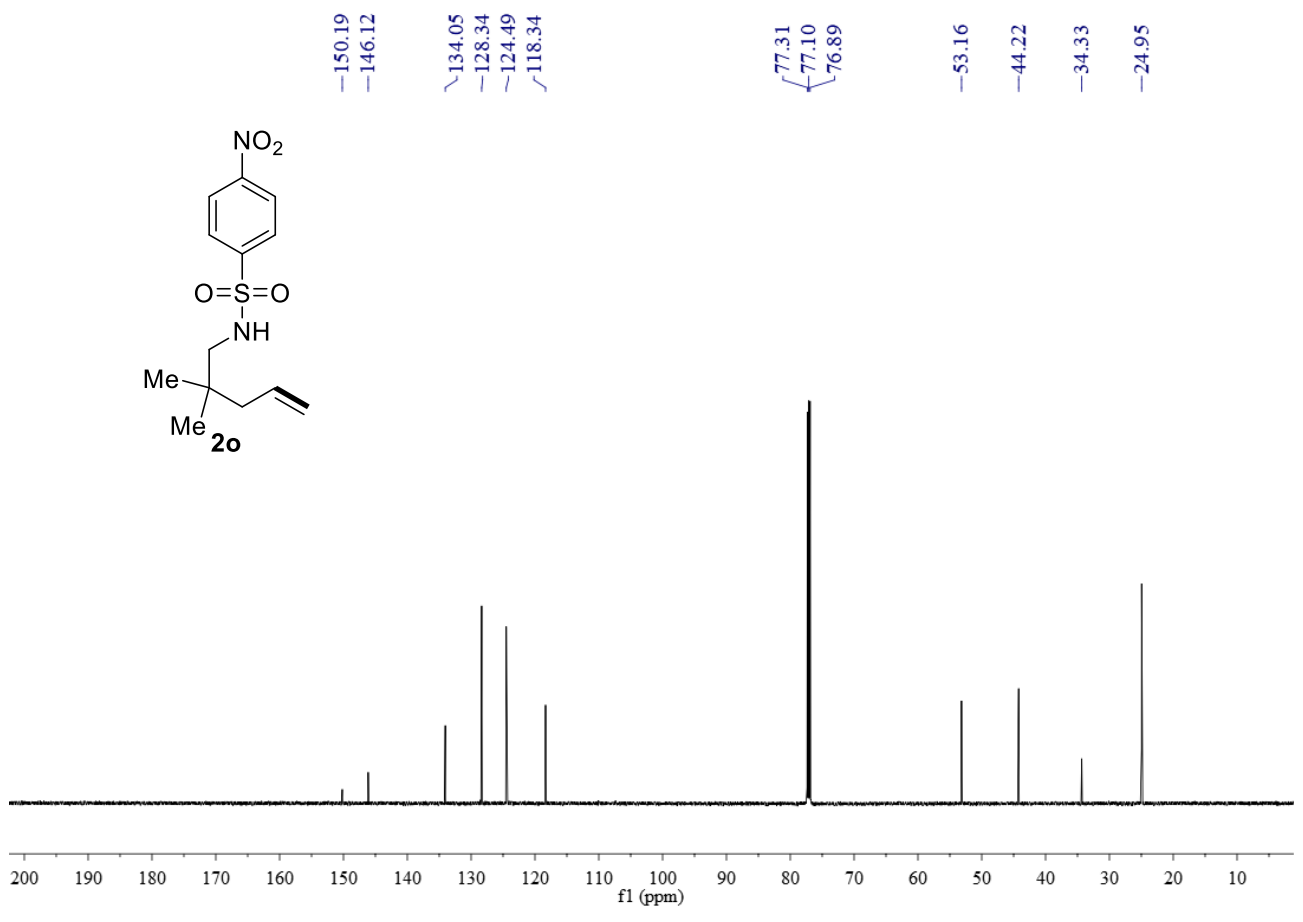
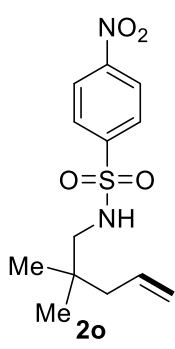
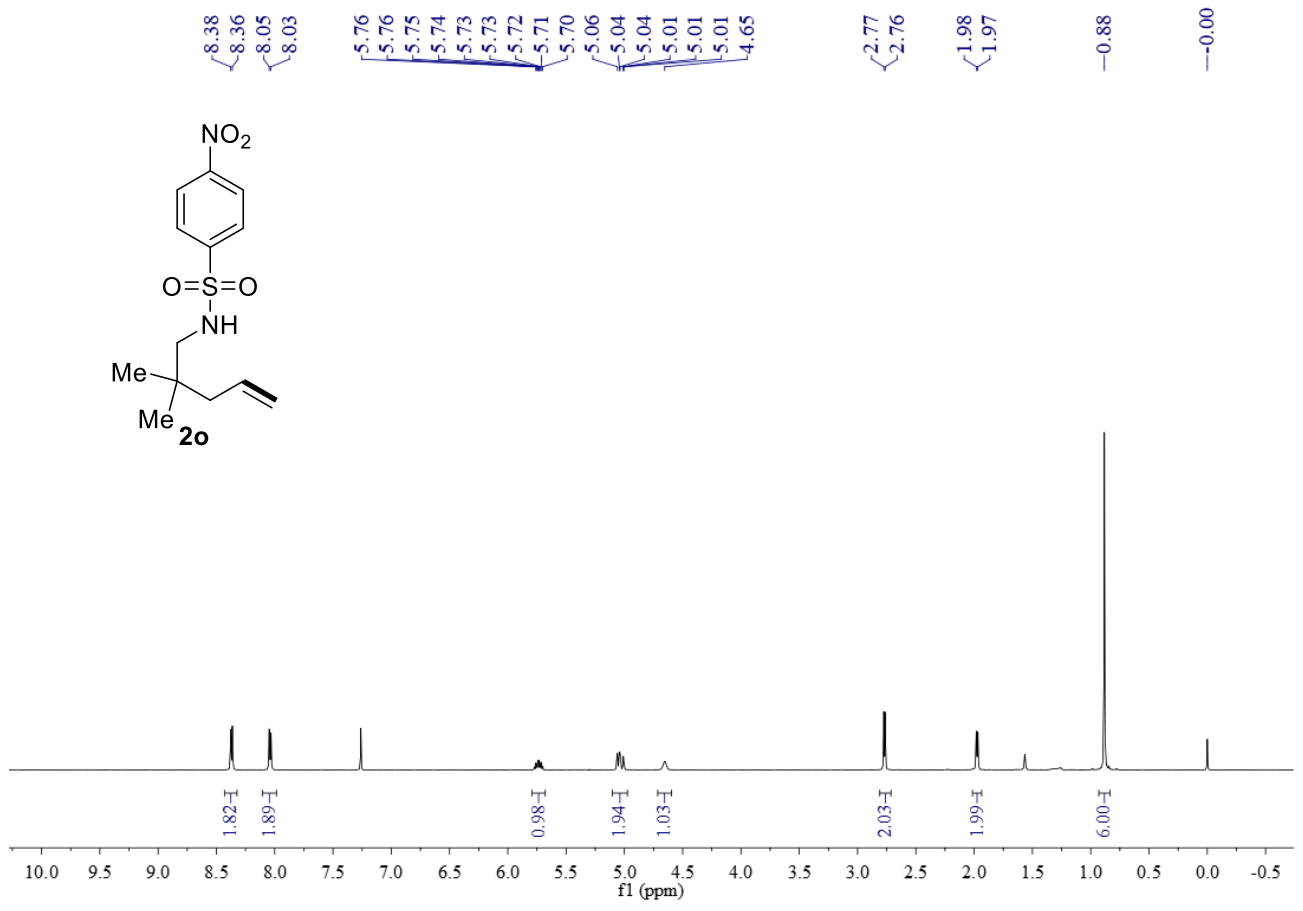
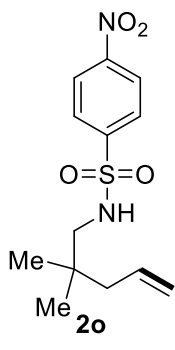


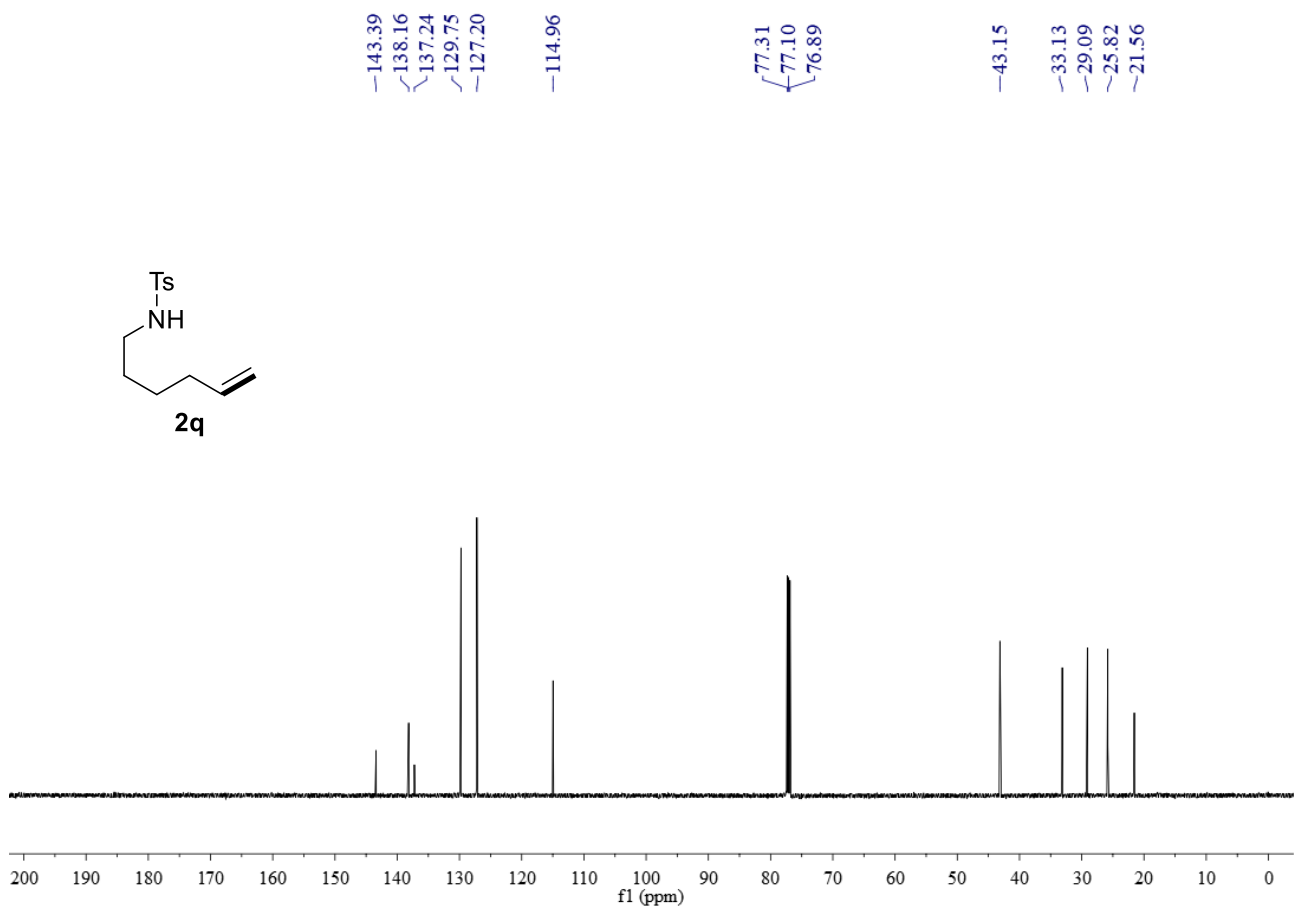
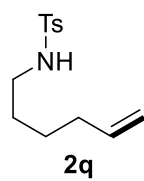
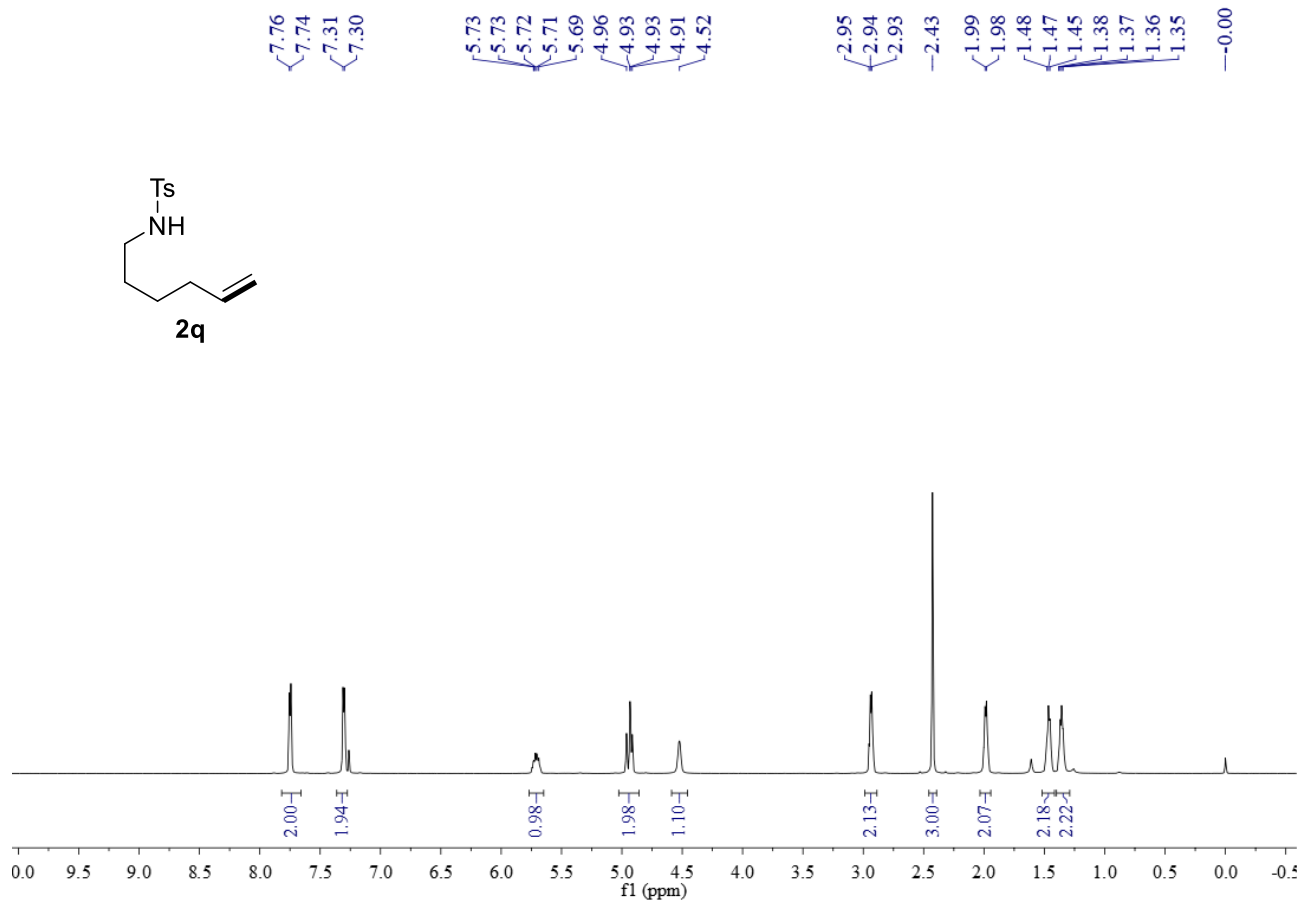
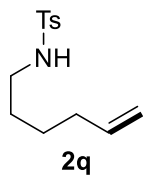
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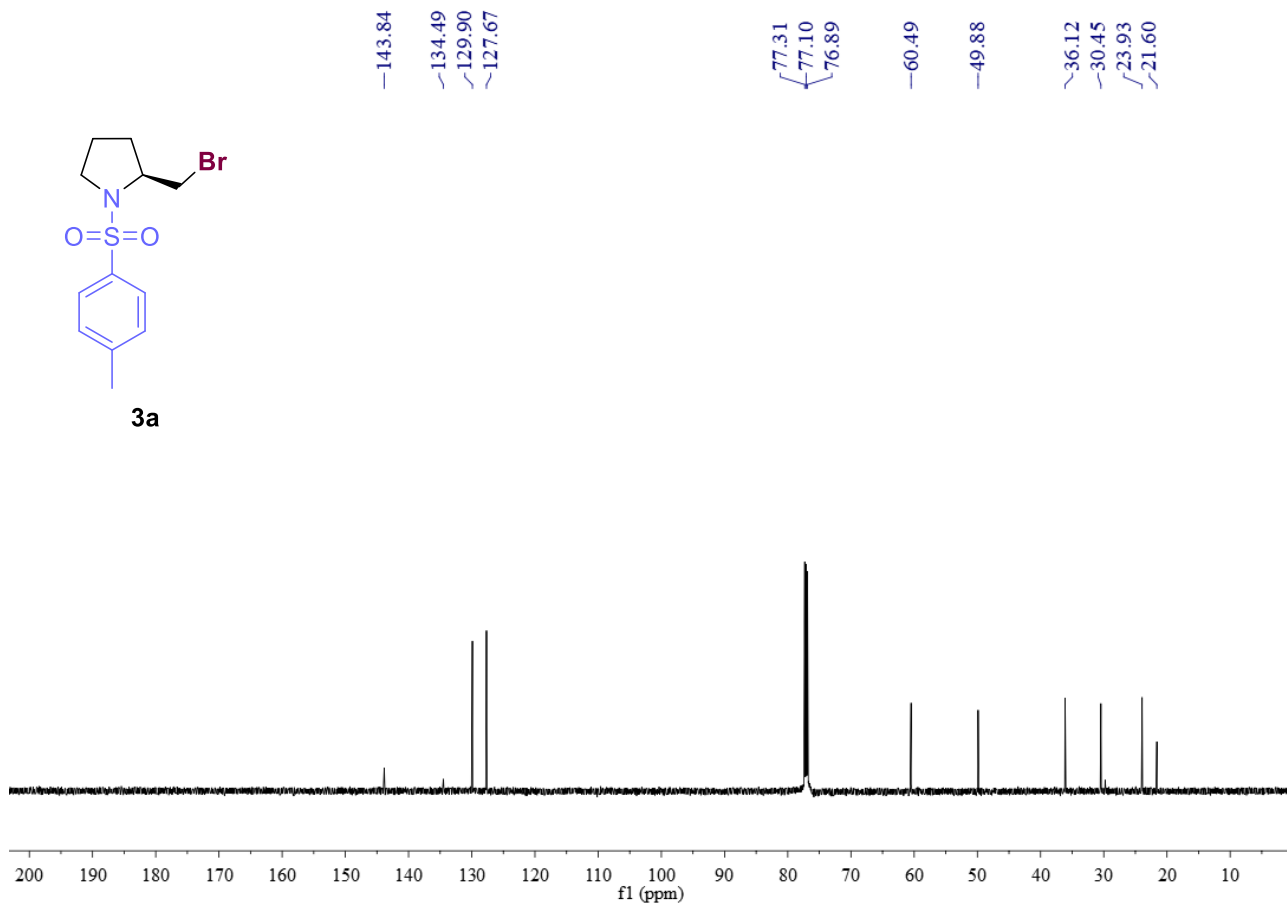
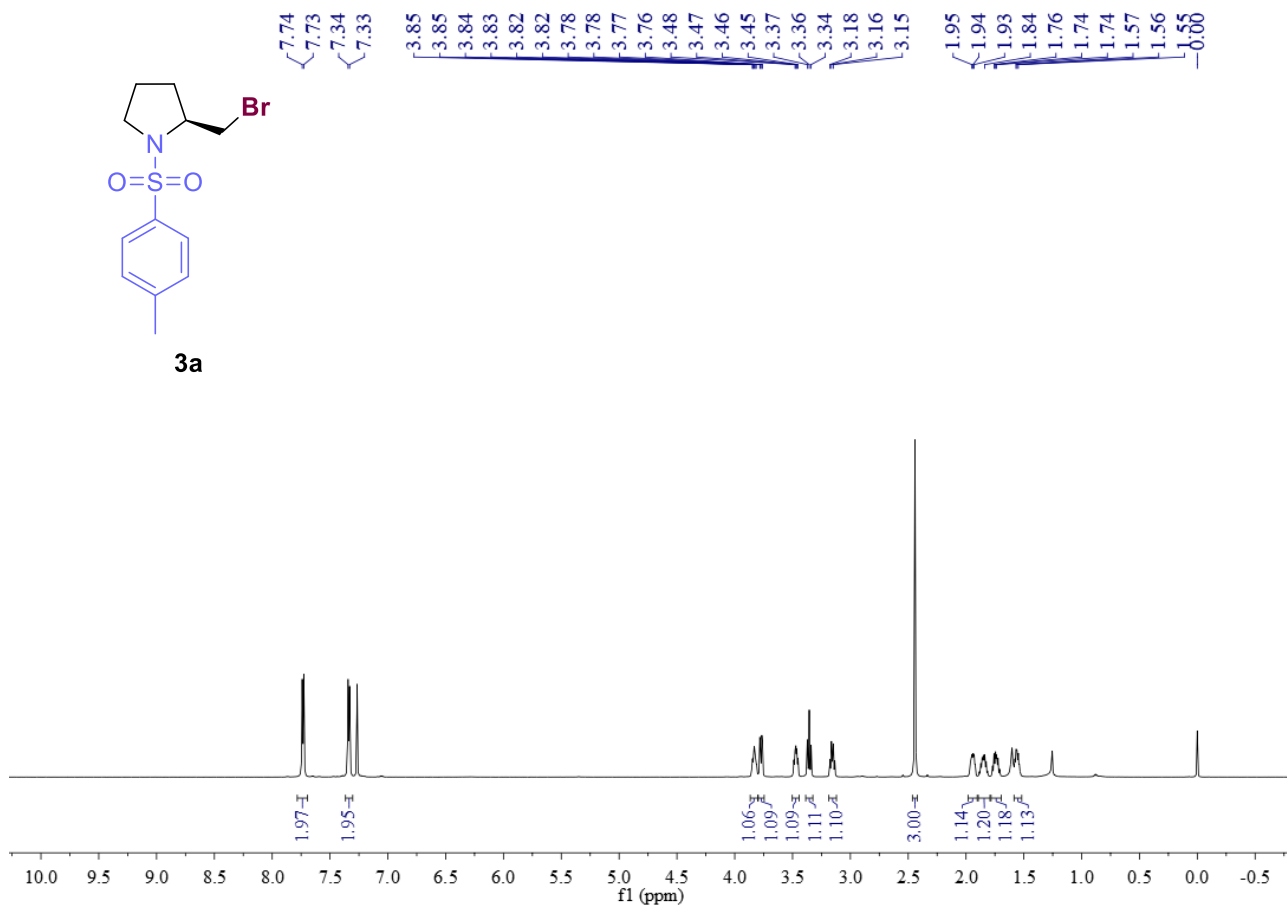


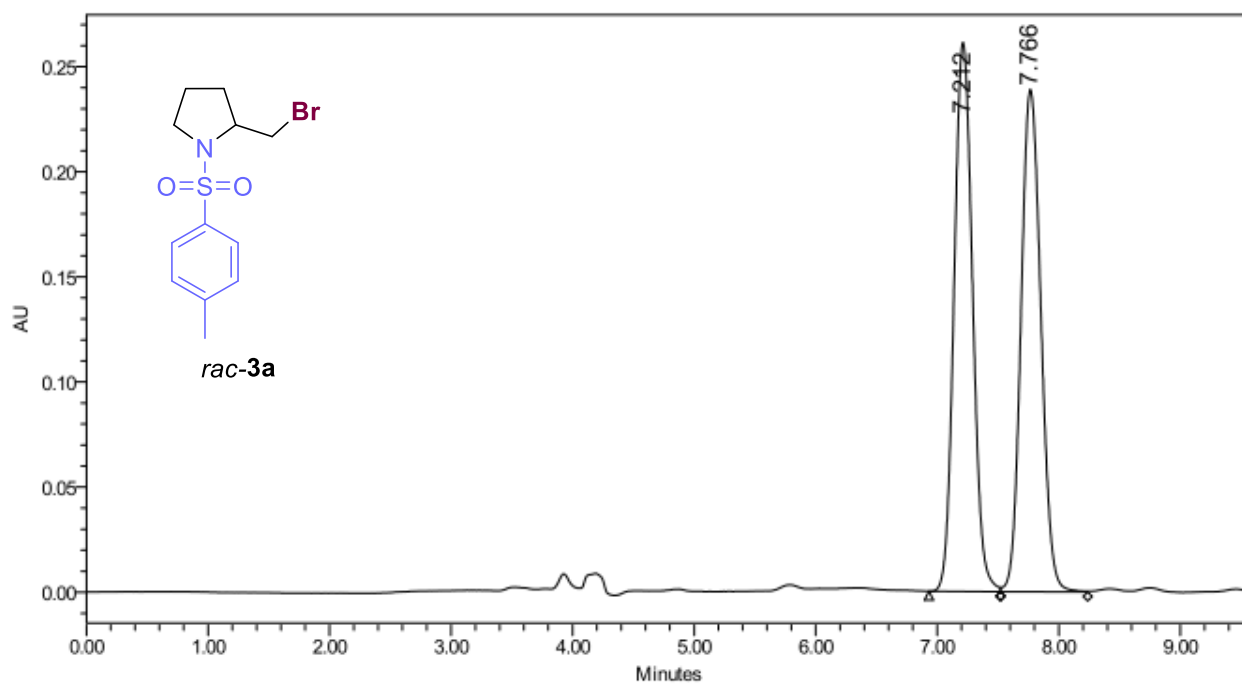




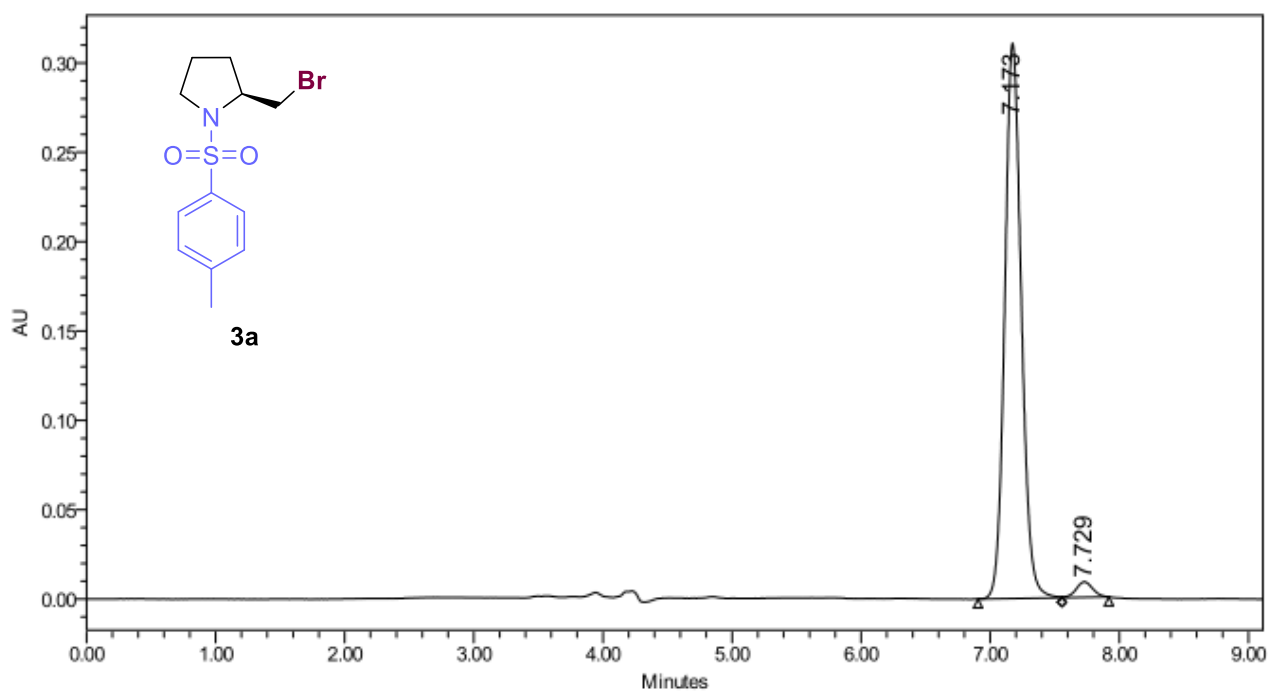


9.2. NMR and HPLC of the Products 3-6

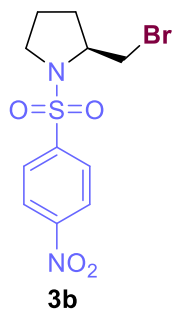




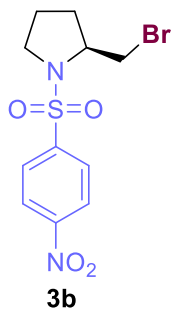
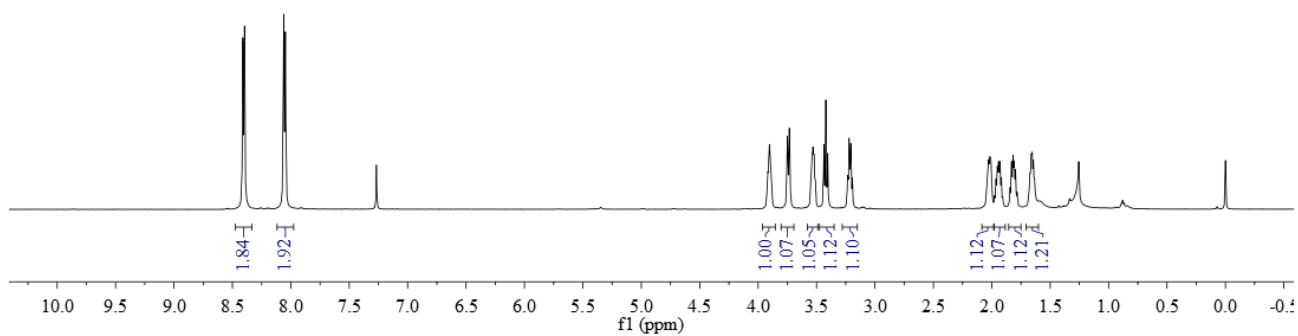
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.212	Unknown	2754123	50.34	261164	52.23	BV	354	6.932	7.522
2	7.766	Unknown	2716646	49.66	238854	47.77	VV	430	7.522	8.238



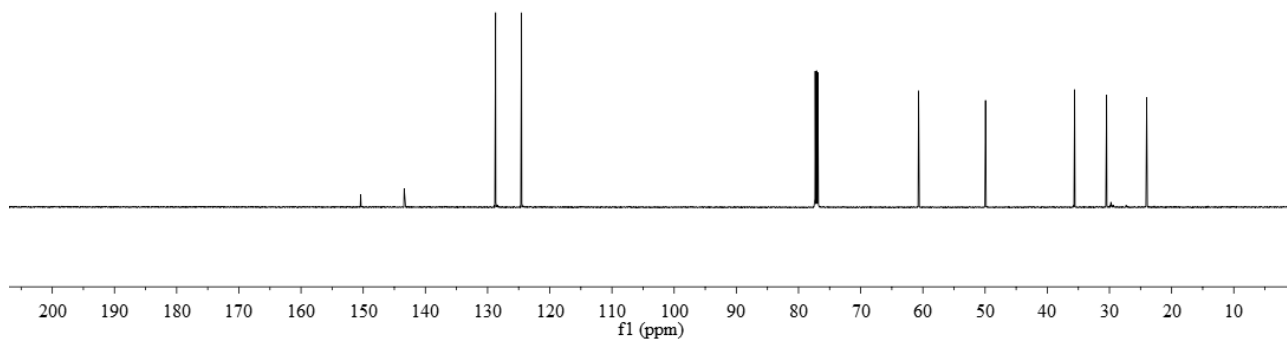
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.173	Unknown	2770574	97.26	310760	97.29	BV	390	6.905	7.555
2	7.729	Unknown	77923	2.74	8655	2.71	Vb	218	7.555	7.918

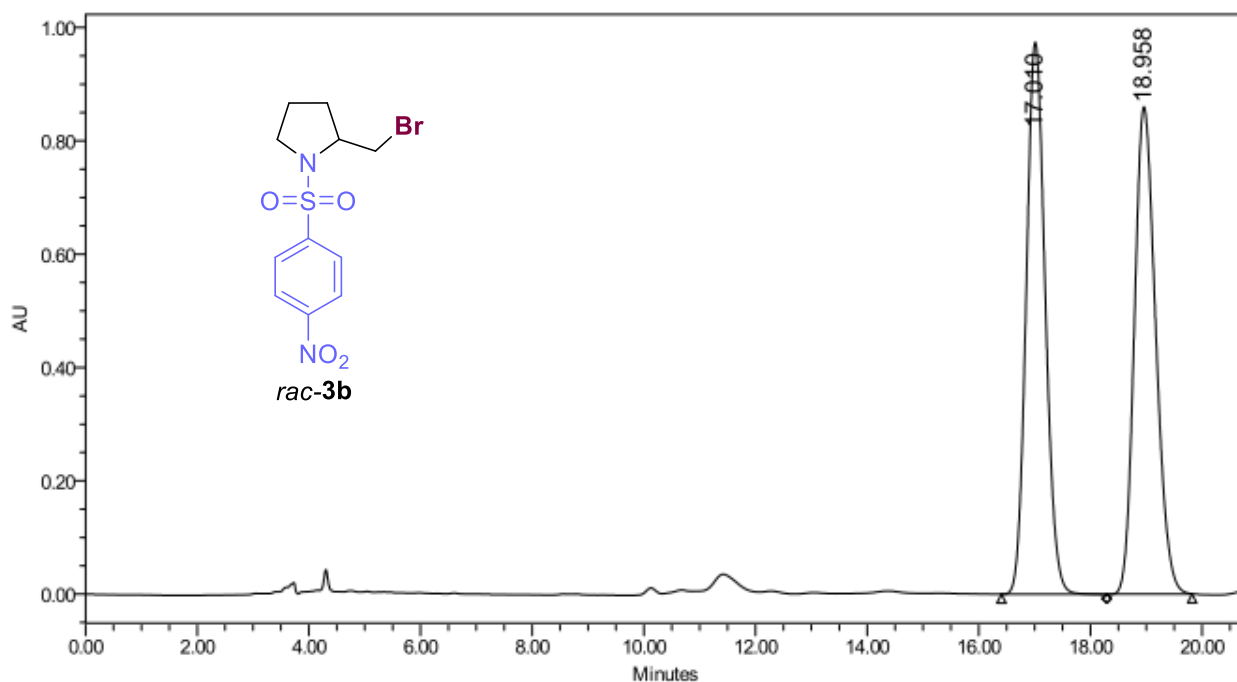


8.41, 8.40, 8.06, 8.05, -7.27, 3.92, 3.90, 3.89, 3.75, 3.73, 3.55, 3.54, 3.53, 3.52, 3.51, 3.44, 3.42, 3.40, 3.23, 3.22, 3.21, 3.19, 2.03, 2.02, 2.01, 1.94, 1.93, 1.83, 1.82, 1.81, 1.66, 1.65, 1.64, 0.00

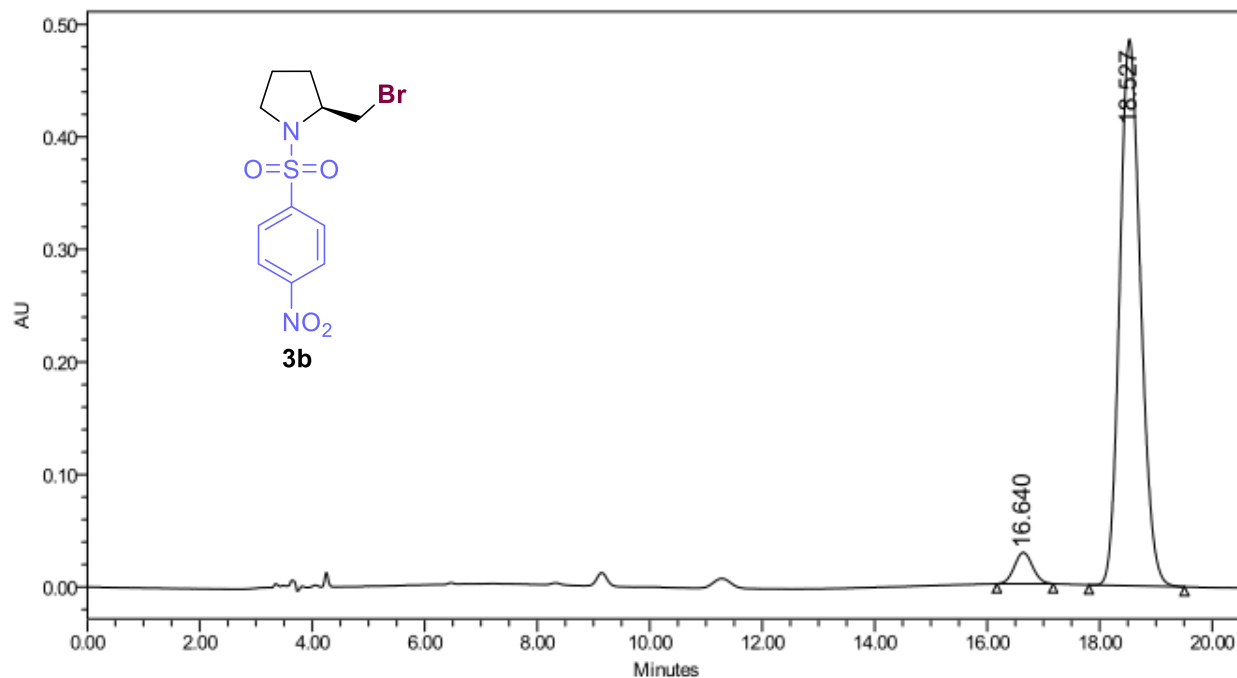


-150.41, -143.41, -128.71, -124.54, 77.31, 77.10, 76.89, -60.69, -49.93, 35.60, 30.46, 24.01

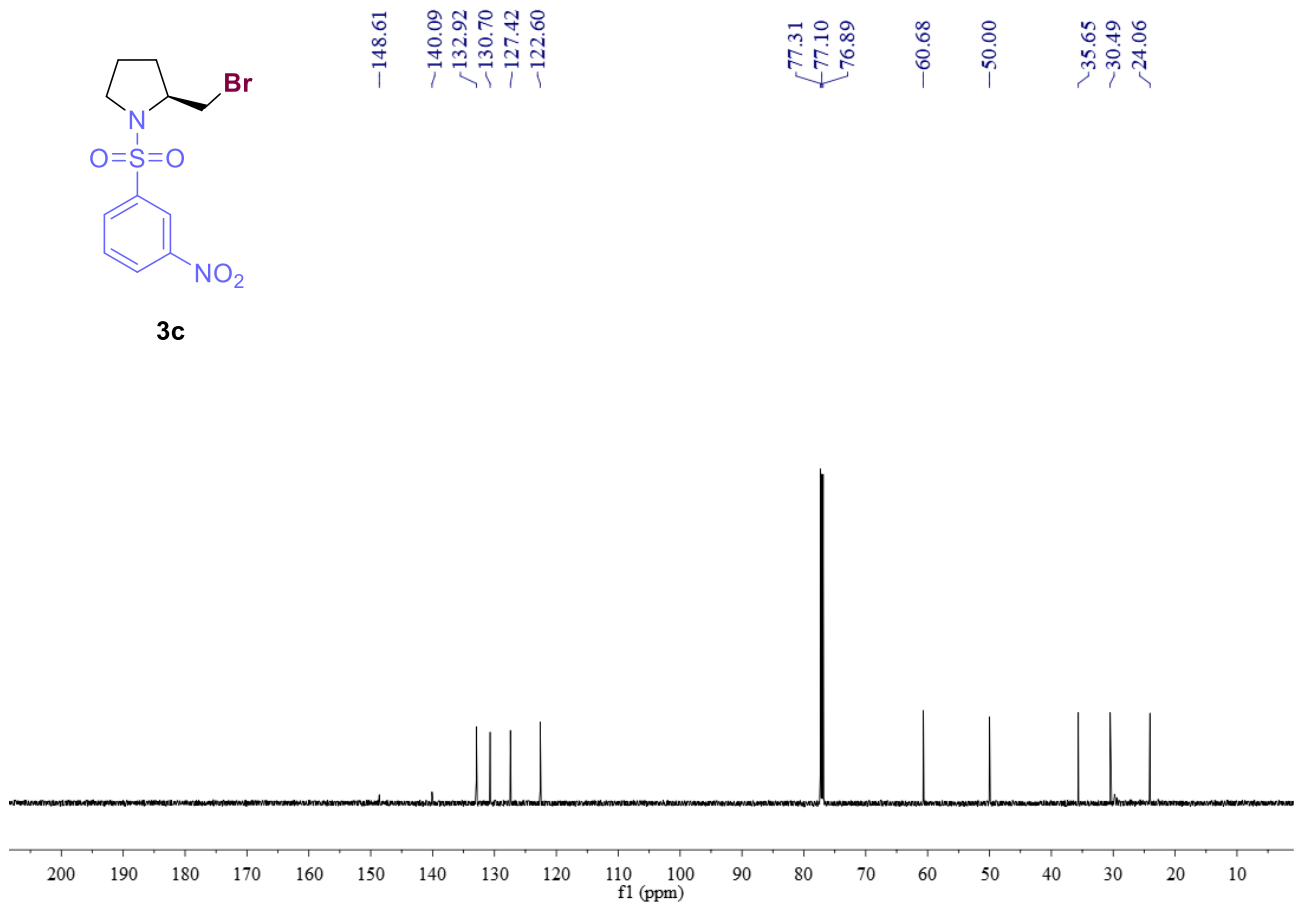
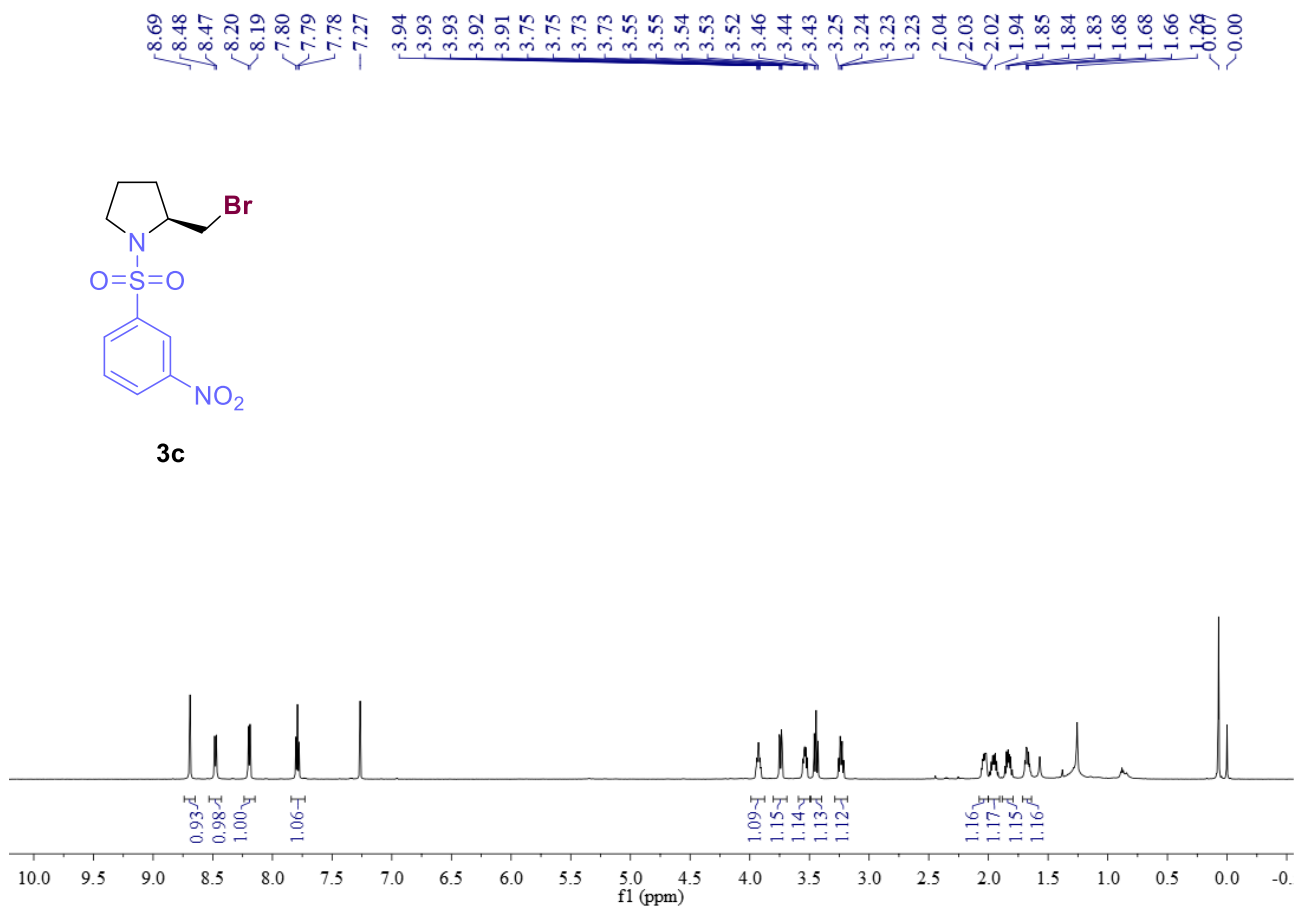
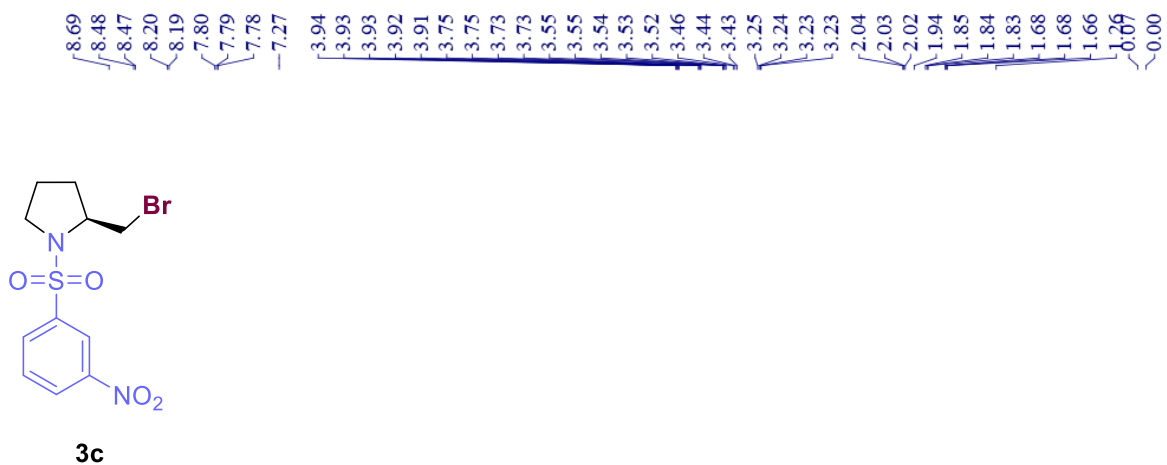


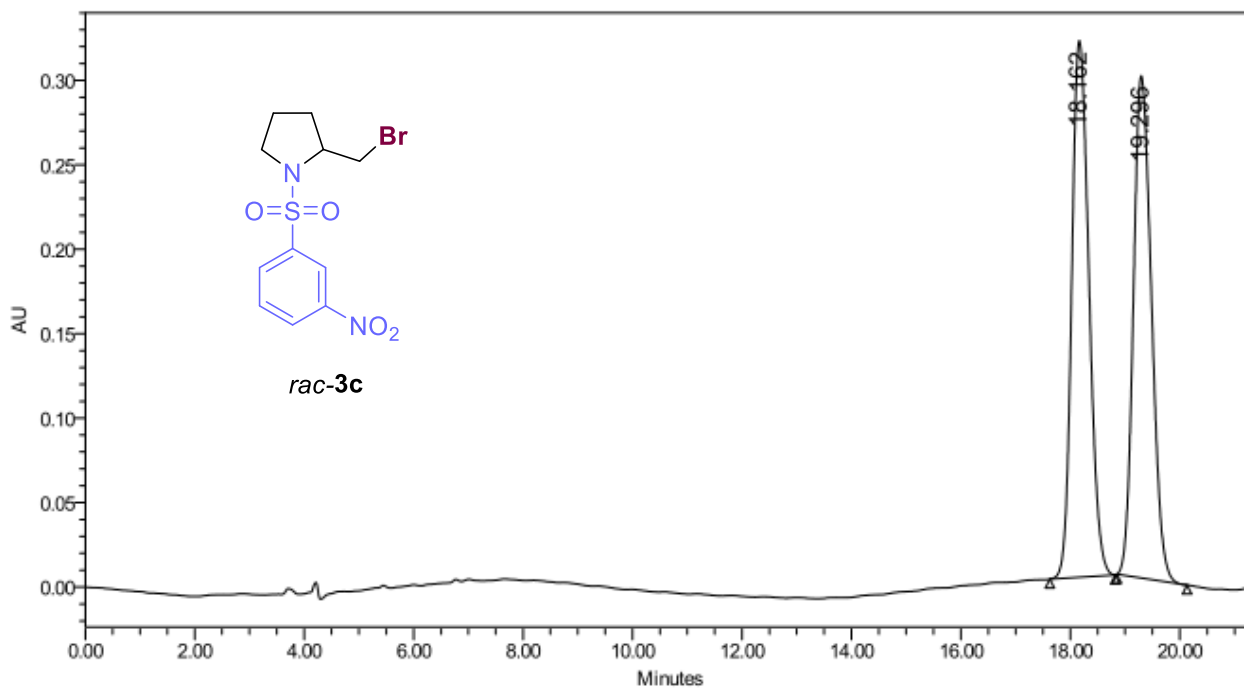


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	17.010	Unknown	22977601	50.19	974305	53.13	BV	1133	16.403	18.292
2	18.958	Unknown	22803197	49.81	859508	46.87	Vb	917	18.292	19.820

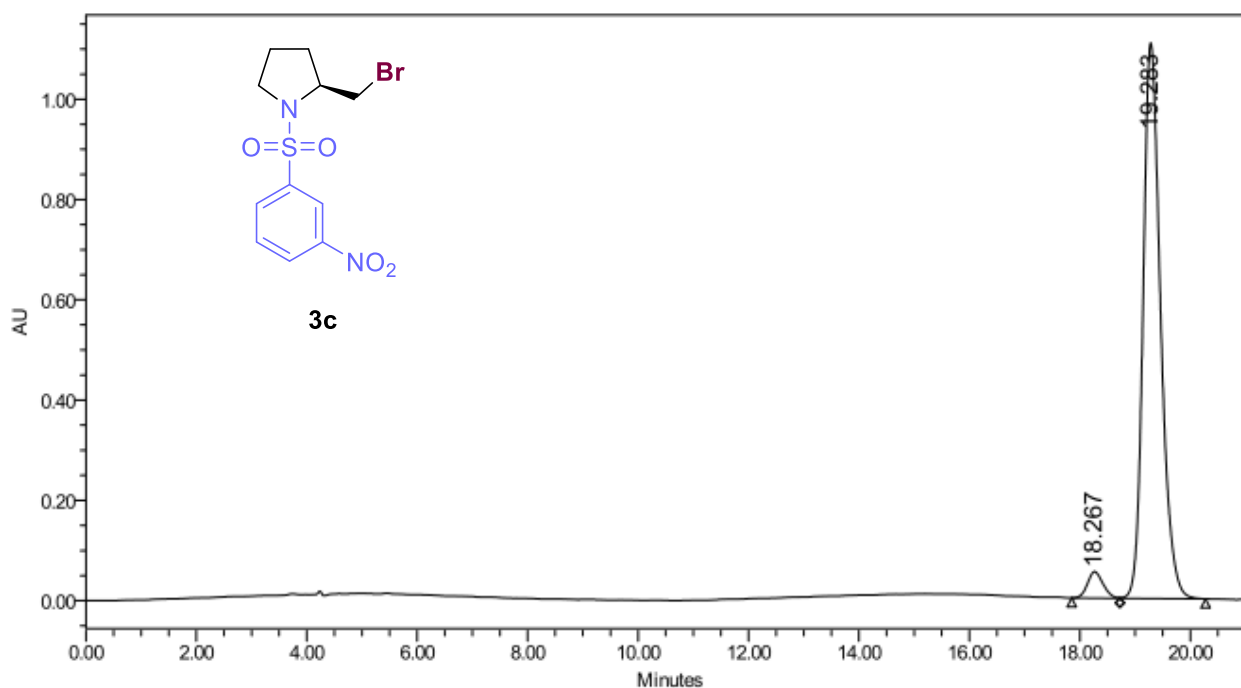


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.640	Unknown	626426	4.76	27689	5.39	bb	599	16.173	17.172
2	18.527	Unknown	12541441	95.24	485641	94.61	bb	1020	17.807	19.507



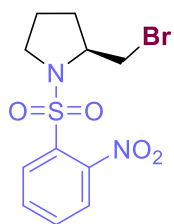


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	18.162	Unknown	6932889	50.45	317655	51.65	bb	718	17.623	18.820
2	19.296	Unknown	6809223	49.55	297384	48.35	bb	769	18.850	20.132

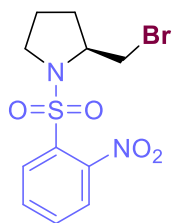
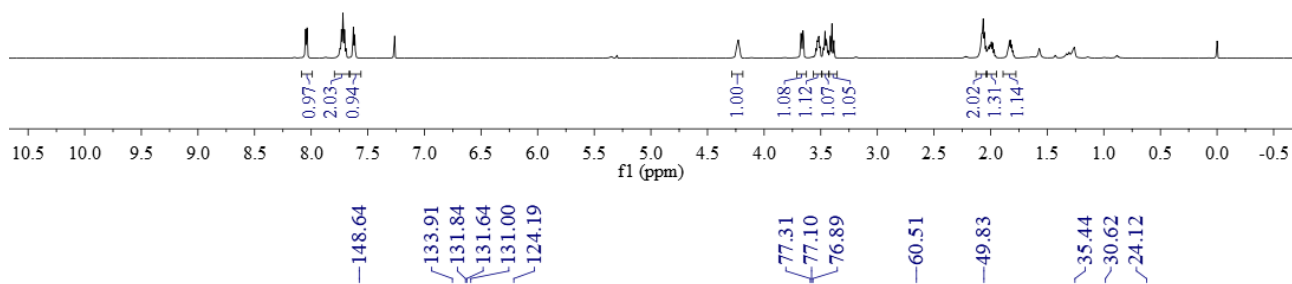


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)
1	18.267	Unknown	1033428	4.08	52859	4.55	bV	523	17.853
2	19.283	Unknown	24267039	95.92	1108063	95.45	VB	931	18.725

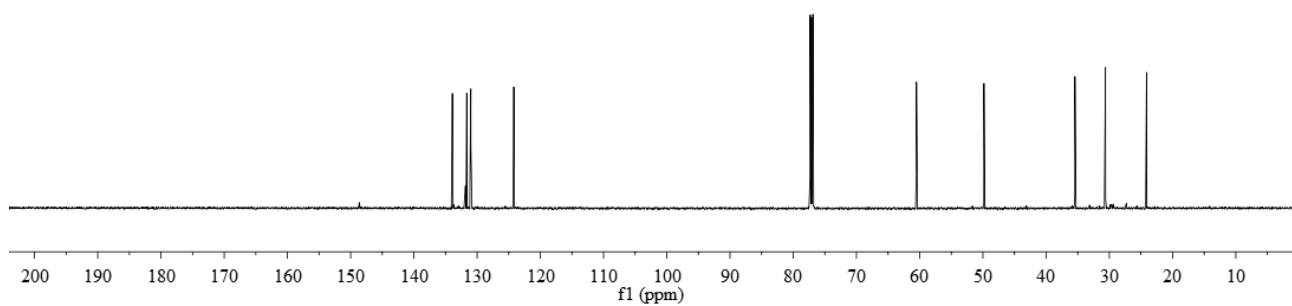
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7.72
7.71
7.70
7.69
7.63
7.63
7.62
4.24
4.23
4.23
3.67
3.67
3.66
3.65
3.54
3.53
3.53
3.52
3.52
3.52
3.50
3.47
3.46
3.45
3.45
3.42
3.40
3.38
2.08
2.08
2.06
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1.99
1.98
1.84
1.83
1.82
1.81
0.00

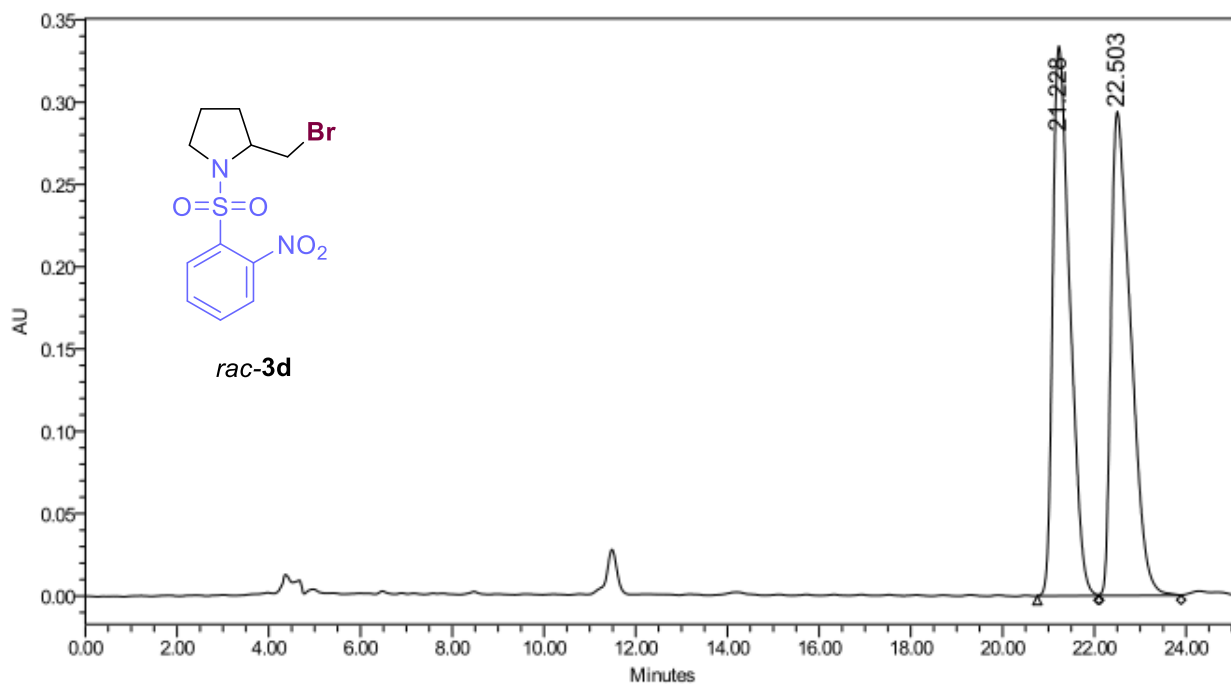


3d

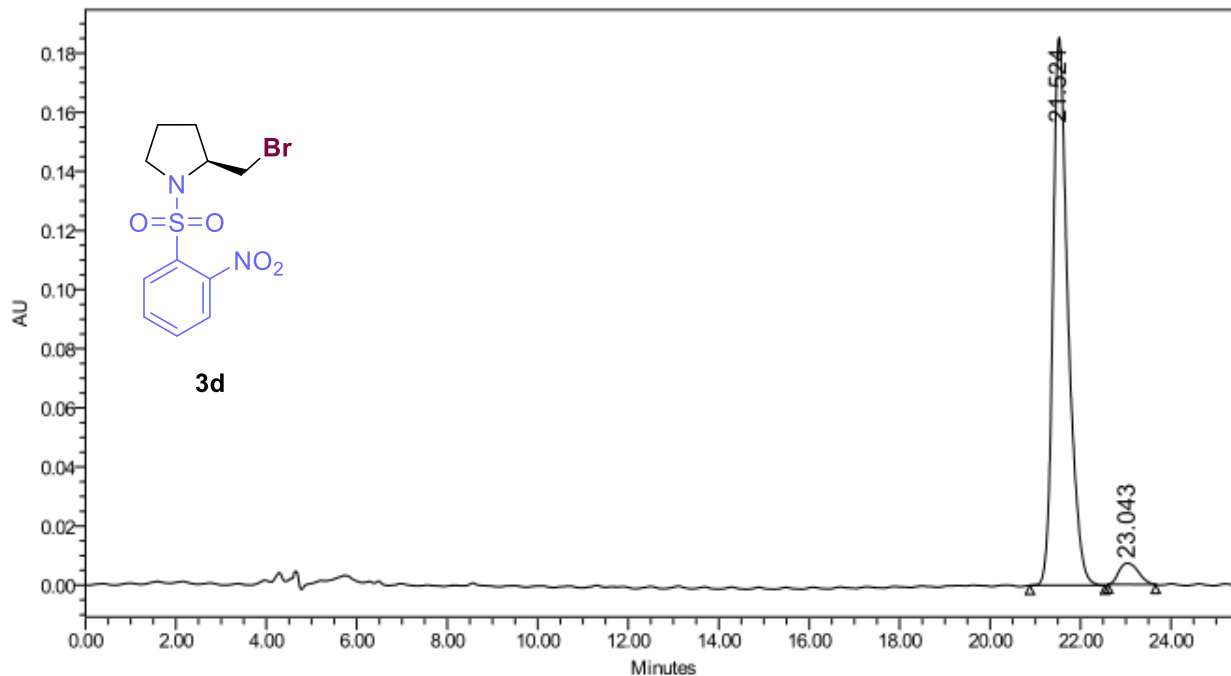


3d

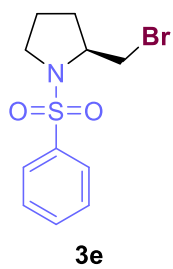




	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	21.228	Unknown	8634985	49.66	333875	53.18	BV	805	20.757	22.098
2	22.503	Unknown	8752488	50.34	293975	46.82	VV	1076	22.098	23.892

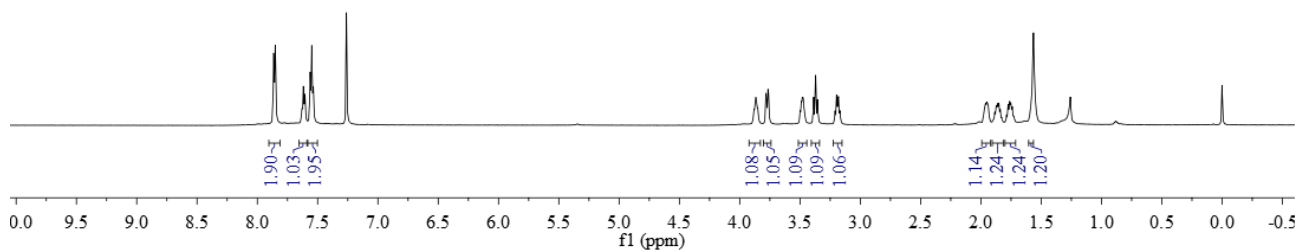


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	21.524	Unknown	4310338	95.21	185400	96.24	bb	996	20.880	22.540
2	23.043	Unknown	217015	4.79	7250	3.76	bb	628	22.612	23.658



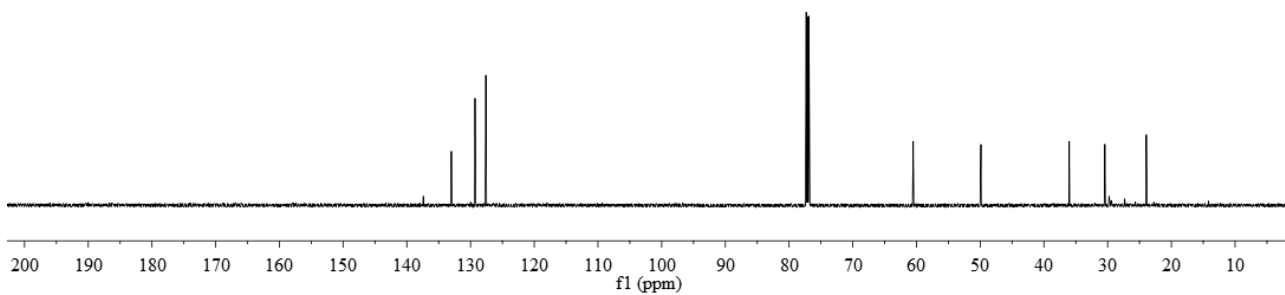
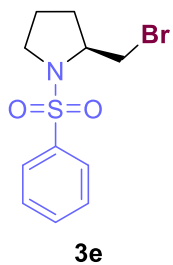
7.86
 7.85
 7.56
 7.55
 7.26

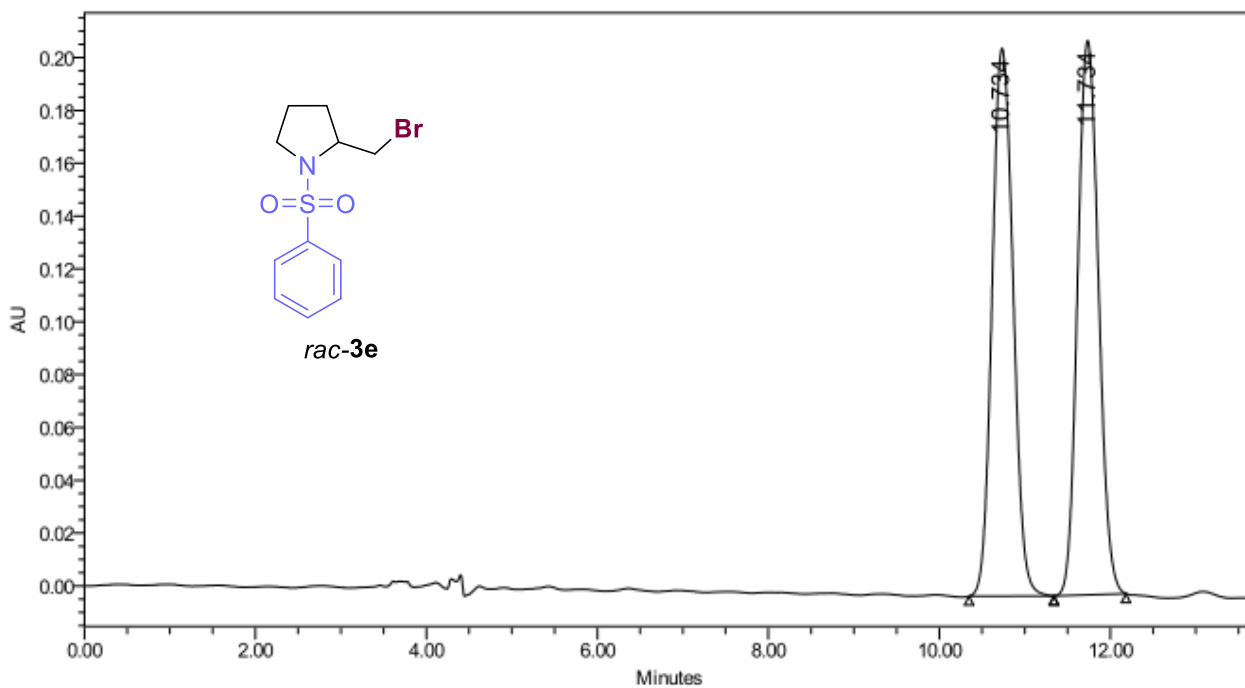
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 1.89
 1.87
 1.86
 1.85
 1.84
 1.83
 1.79
 1.77
 1.76
 1.75
 1.74
 1.73
 1.56
 1.26
 -0.00



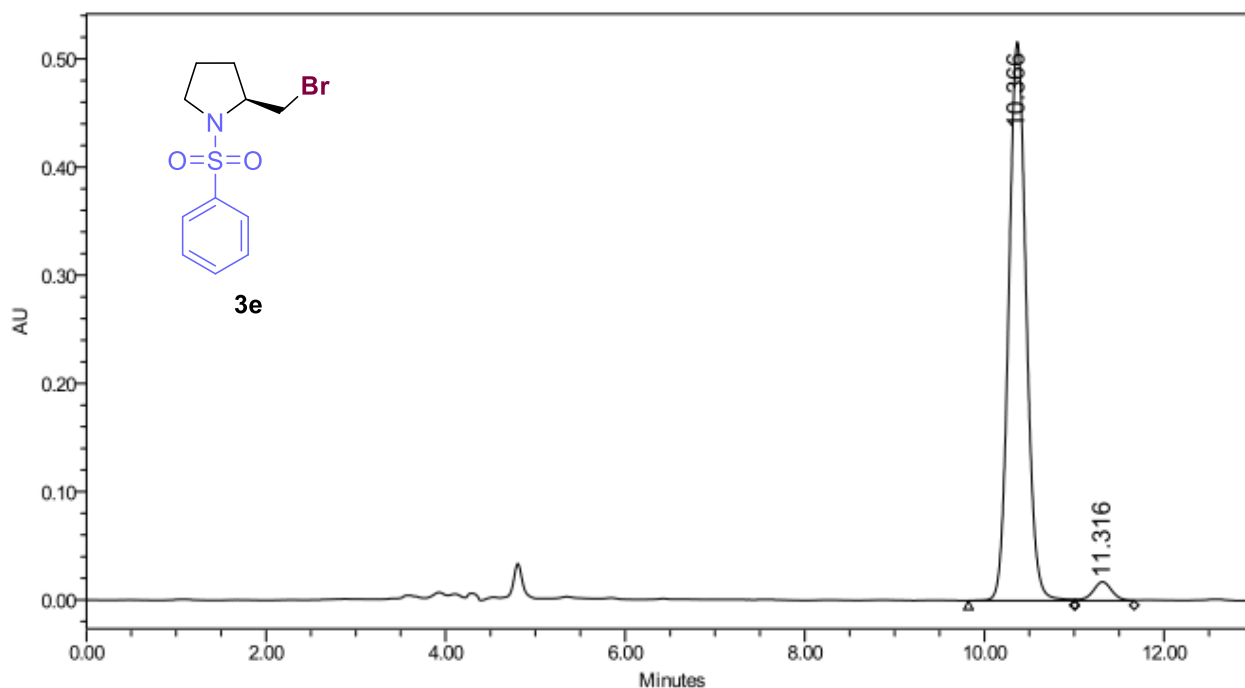
137.40
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 129.29
 127.60

77.31
 77.10
 76.89
 60.52
 49.88
 36.03
 30.44
 23.93



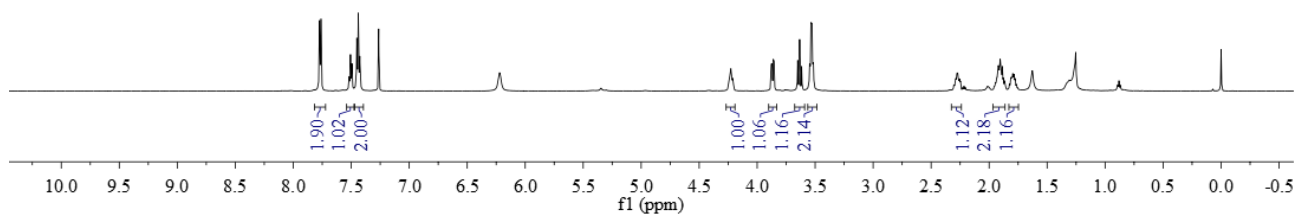
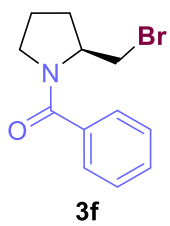


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.734	Unknown	3538195	49.85	207406	49.72	BB	596	10.347	11.340
2	11.734	Unknown	3559904	50.15	209782	50.28	BB	505	11.340	12.182



	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.366	Unknown	6986778	96.42	516596	96.73	BV	710	9.822	11.005
2	11.316	Unknown	259345	3.58	17476	3.27	VV	397	11.005	11.667

7.77
7.76
7.52
7.51
7.49
7.45
7.44
7.43
4.24
4.23
4.23
4.21
3.88
3.87
3.86
3.85
3.65
3.63
3.62
3.55
3.54
3.53
3.52
2.30
2.29
2.28
2.27
2.26
2.26
2.25
2.25
1.96
1.94
1.92
1.92
1.90
1.89
1.89
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1.81
1.80
1.79
1.78
1.76
1.75
-0.00



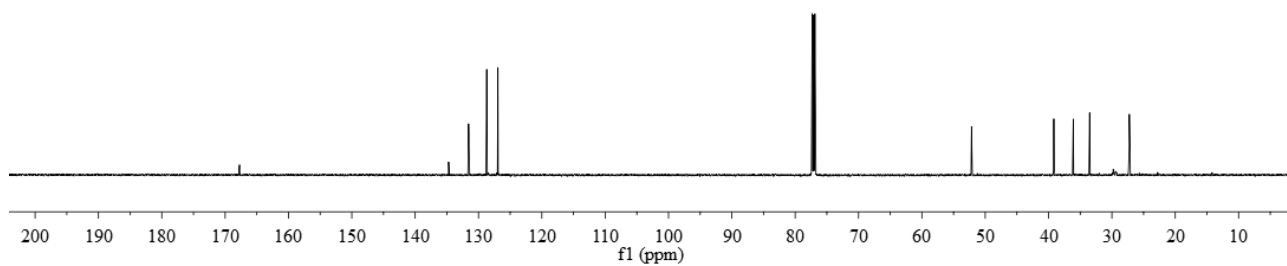
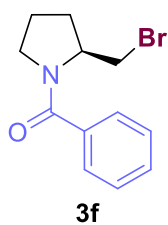
167.73

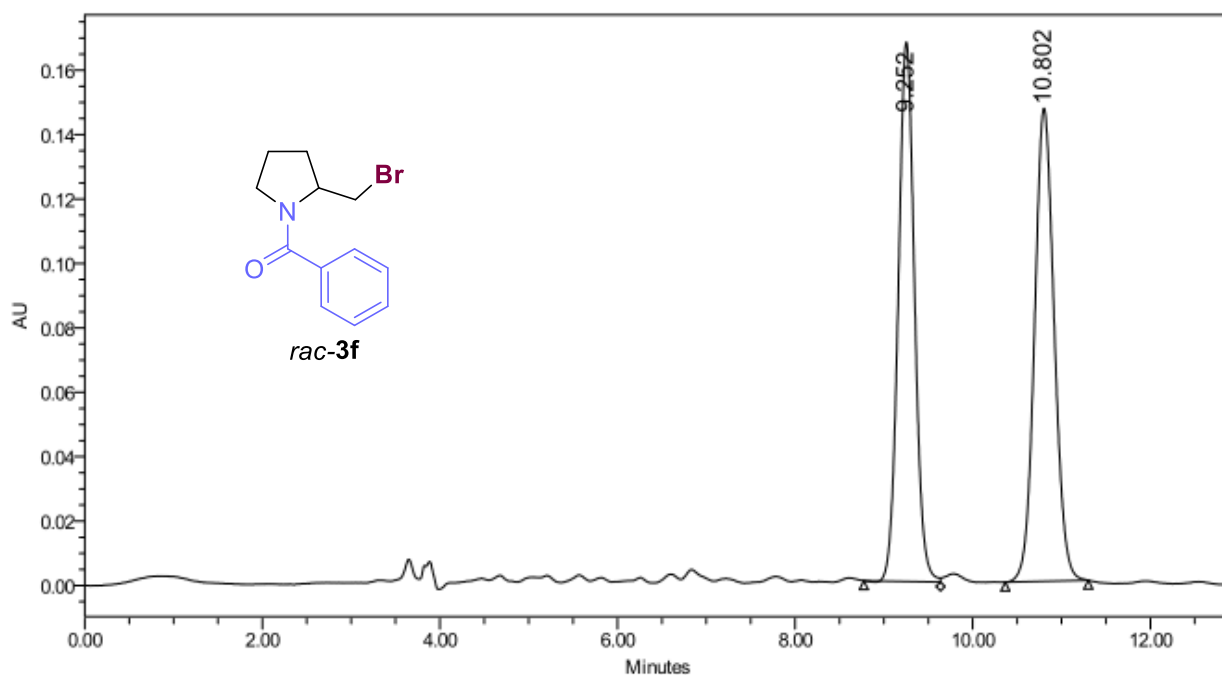
134.72
131.56
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126.93

77.31
77.10
76.89

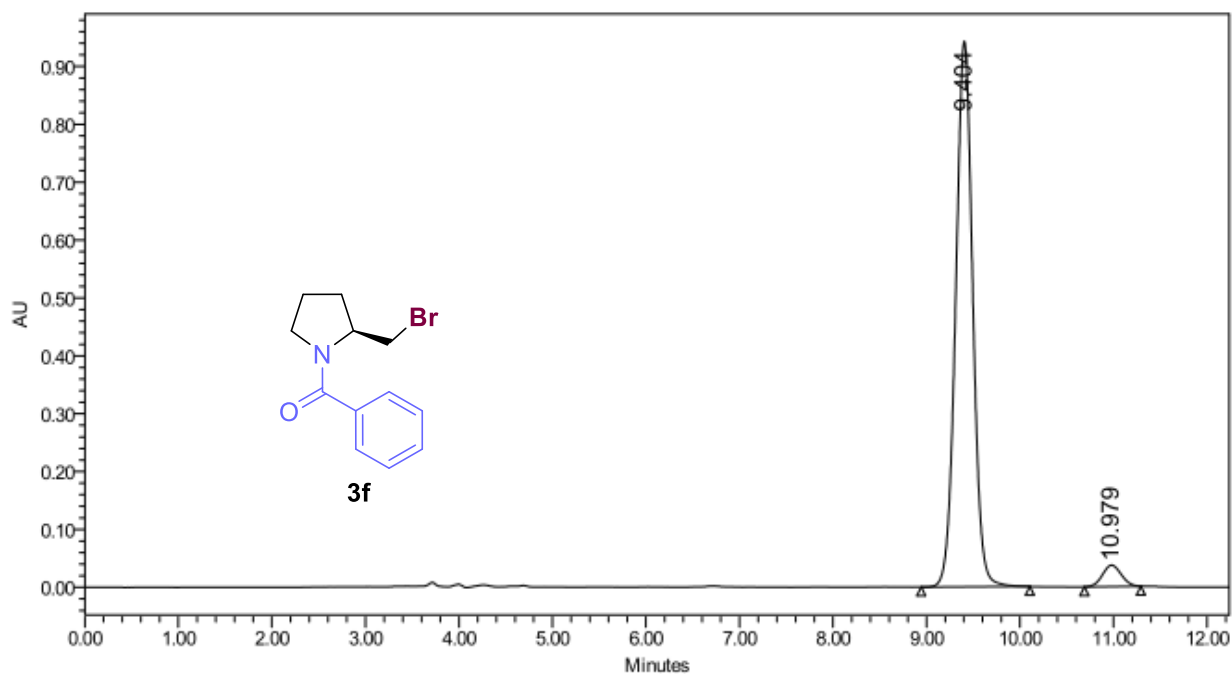
52.16

39.17
36.10
33.51
27.25



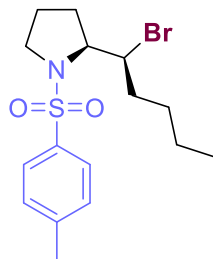


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.252	Unknown	2131632	48.59	167428	53.27	bV	518	8.773	9.637
2	10.802	Unknown	2255527	51.41	146863	46.73	Bb	560	10.367	11.300

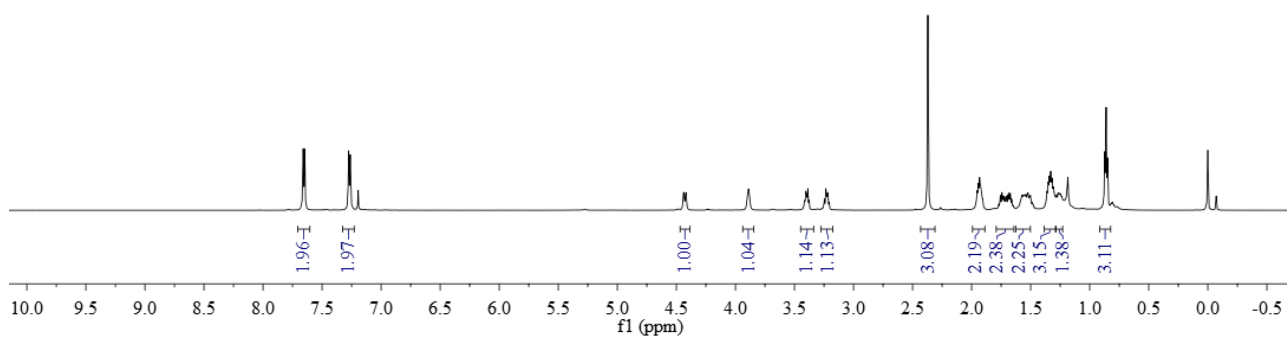


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.404	Unknown	11924274	95.83	942576	96.21	Bb	696	8.943	10.103
2	10.979	Unknown	518473	4.17	37086	3.79	bb	363	10.687	11.292

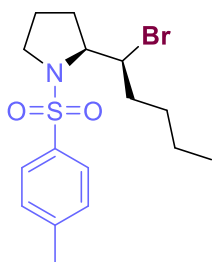
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7.26
4.44
4.42
3.90
3.89
3.88
3.40
3.40
3.39
3.23
3.23
3.22
3.22
2.37
1.95
1.94
1.93
1.92
1.76
1.74
1.73
1.69
1.68
1.67
1.57
1.56
1.56
1.55
1.54
1.52
1.50
1.36
1.35
1.34
1.33
1.32
1.31
1.29
1.28
1.27
1.26
1.25
1.24
0.87
0.86
0.85
0.00



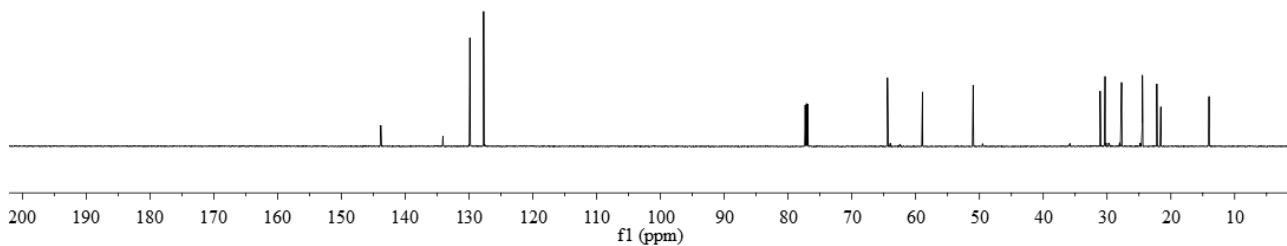
3g

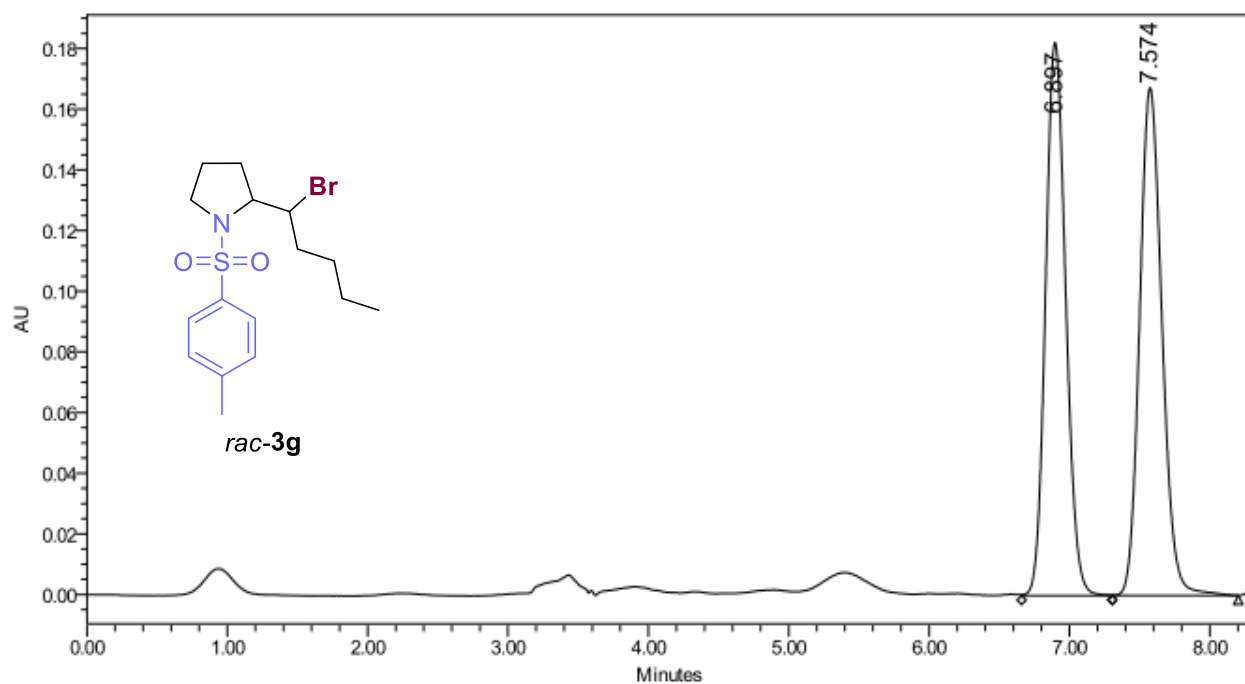


143.83
134.10
129.87
127.71
77.31
77.10
76.89
64.41
58.93
50.99
31.08
30.31
27.72
24.45
22.19
21.58
14.02

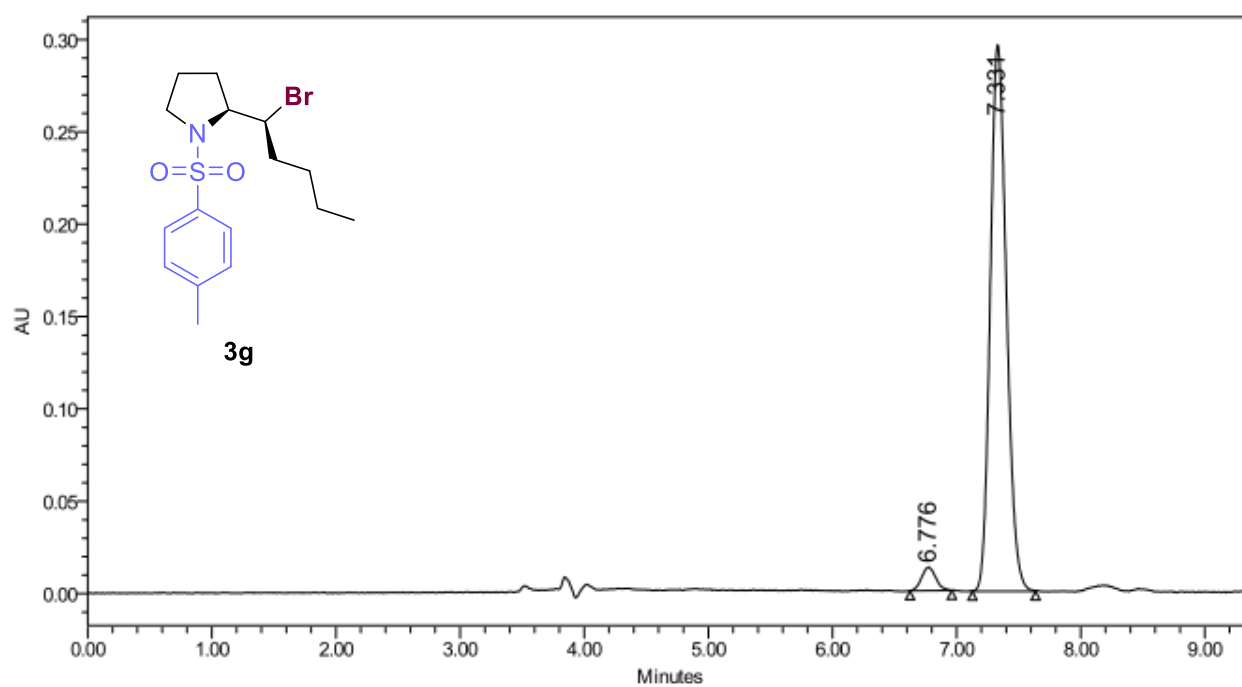


3g

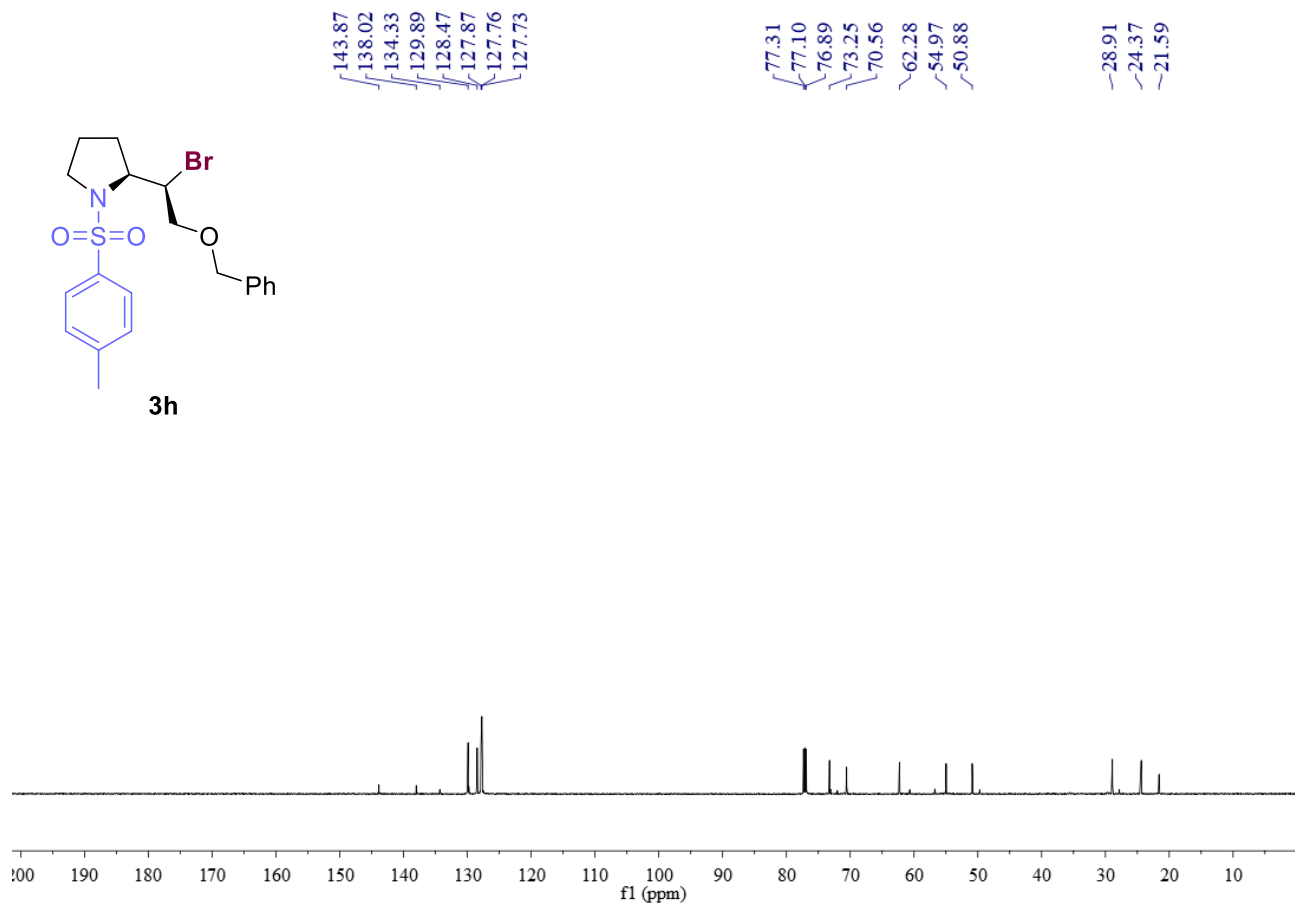
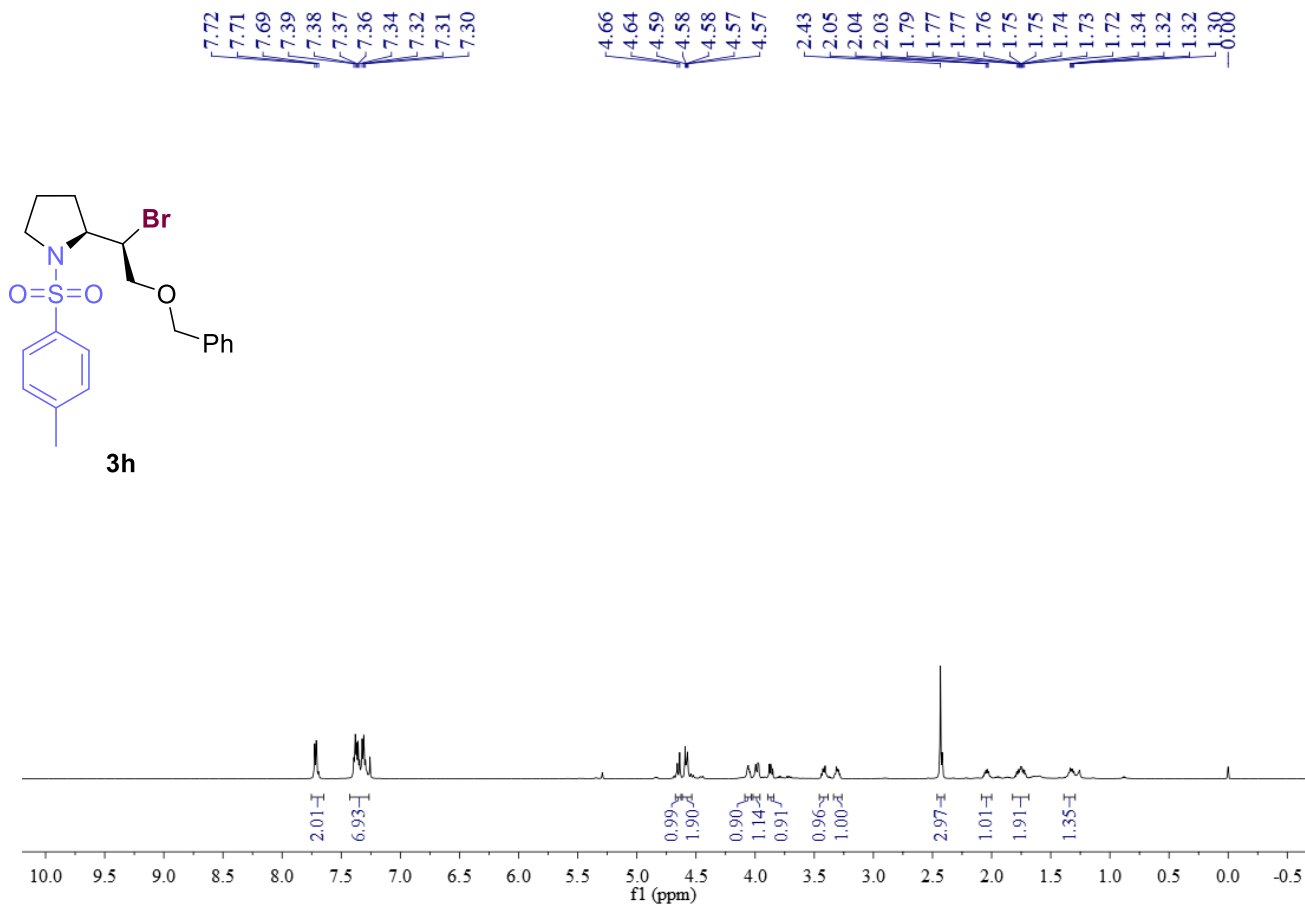


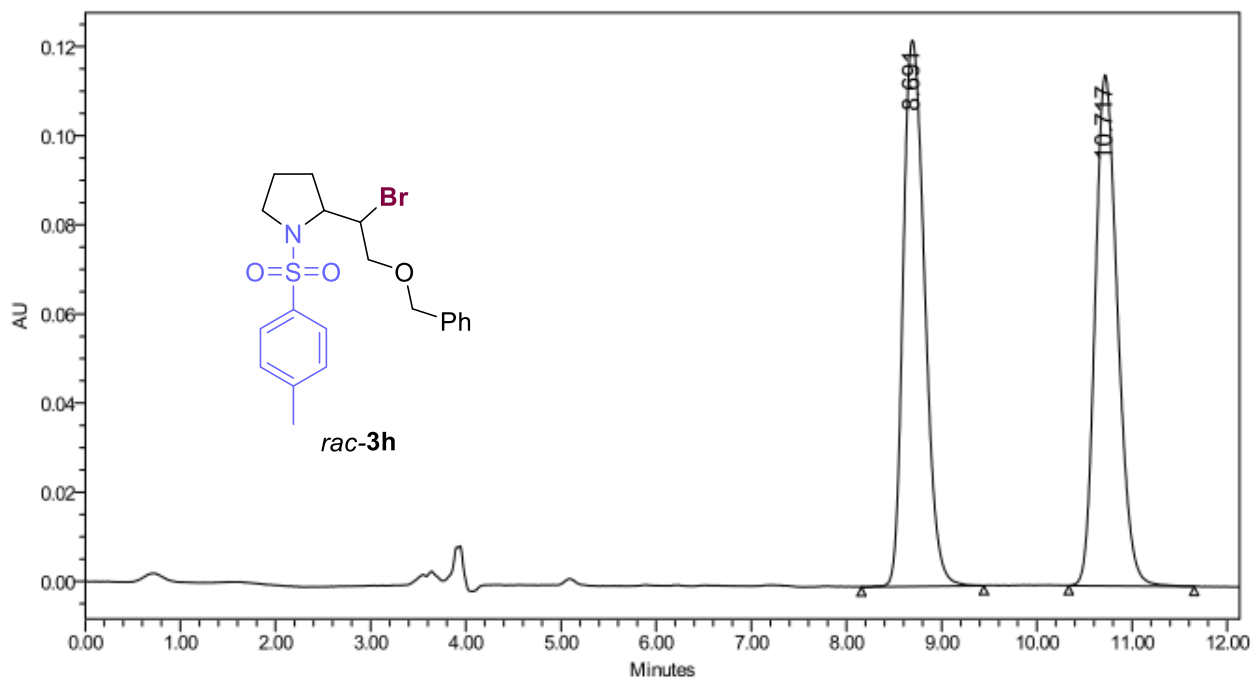


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.897	Unknown	1818293	49.51	182331	52.13	VV	388	6.658	7.305
2	7.574	Unknown	1854482	50.49	167404	47.87	VB	538	7.305	8.202

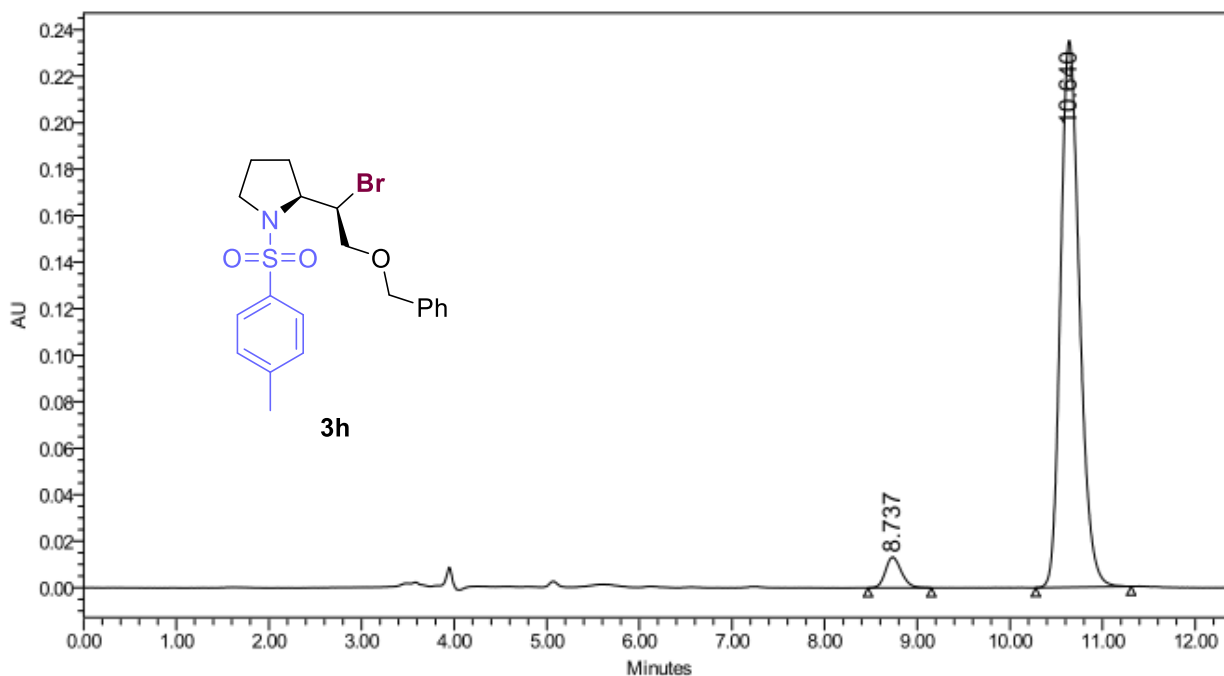


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.776	Unknown	101361	3.65	12714	4.12	BB	202	6.625	6.962
2	7.331	Unknown	2676001	96.35	295913	95.88	BB	306	7.127	7.637

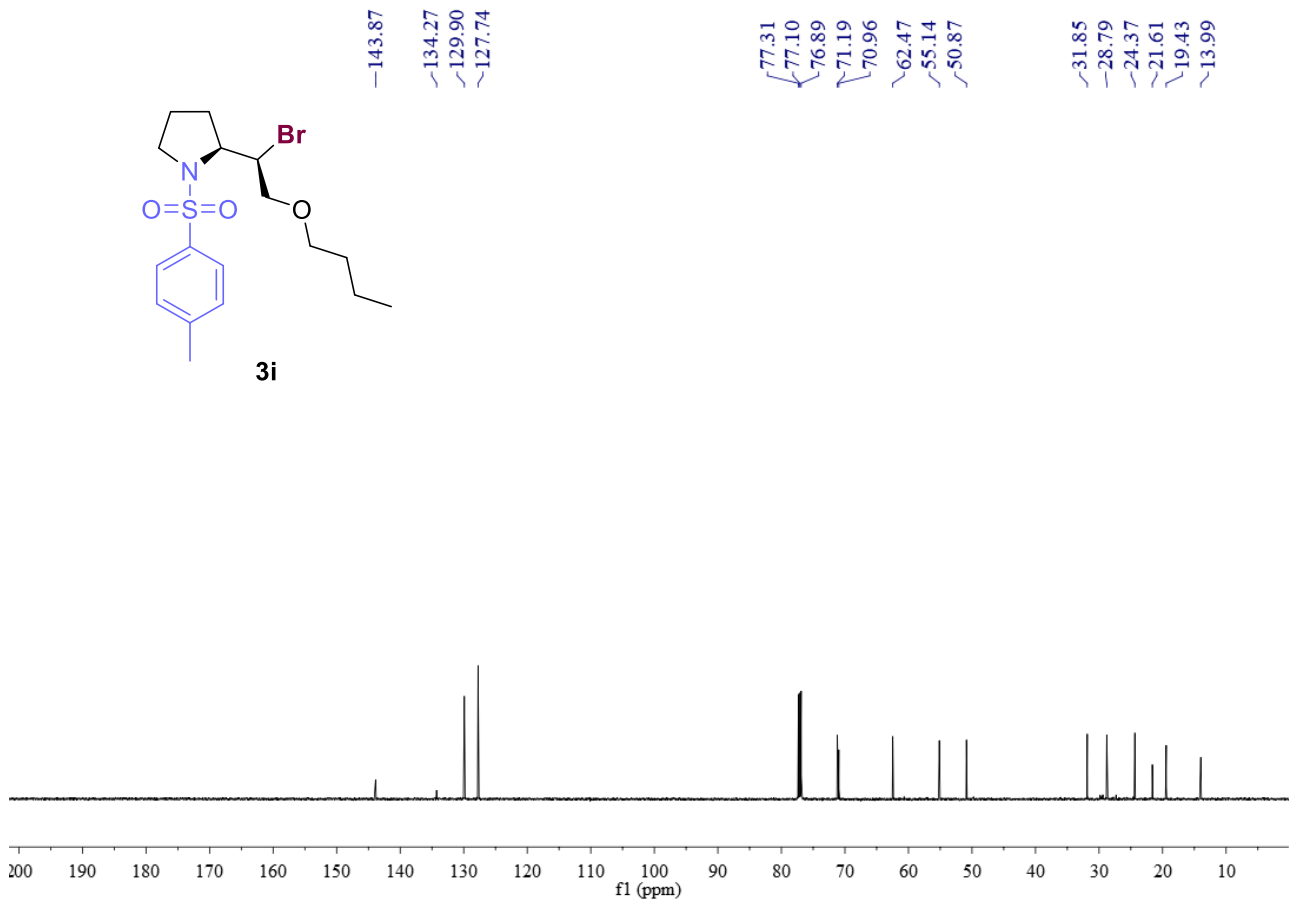
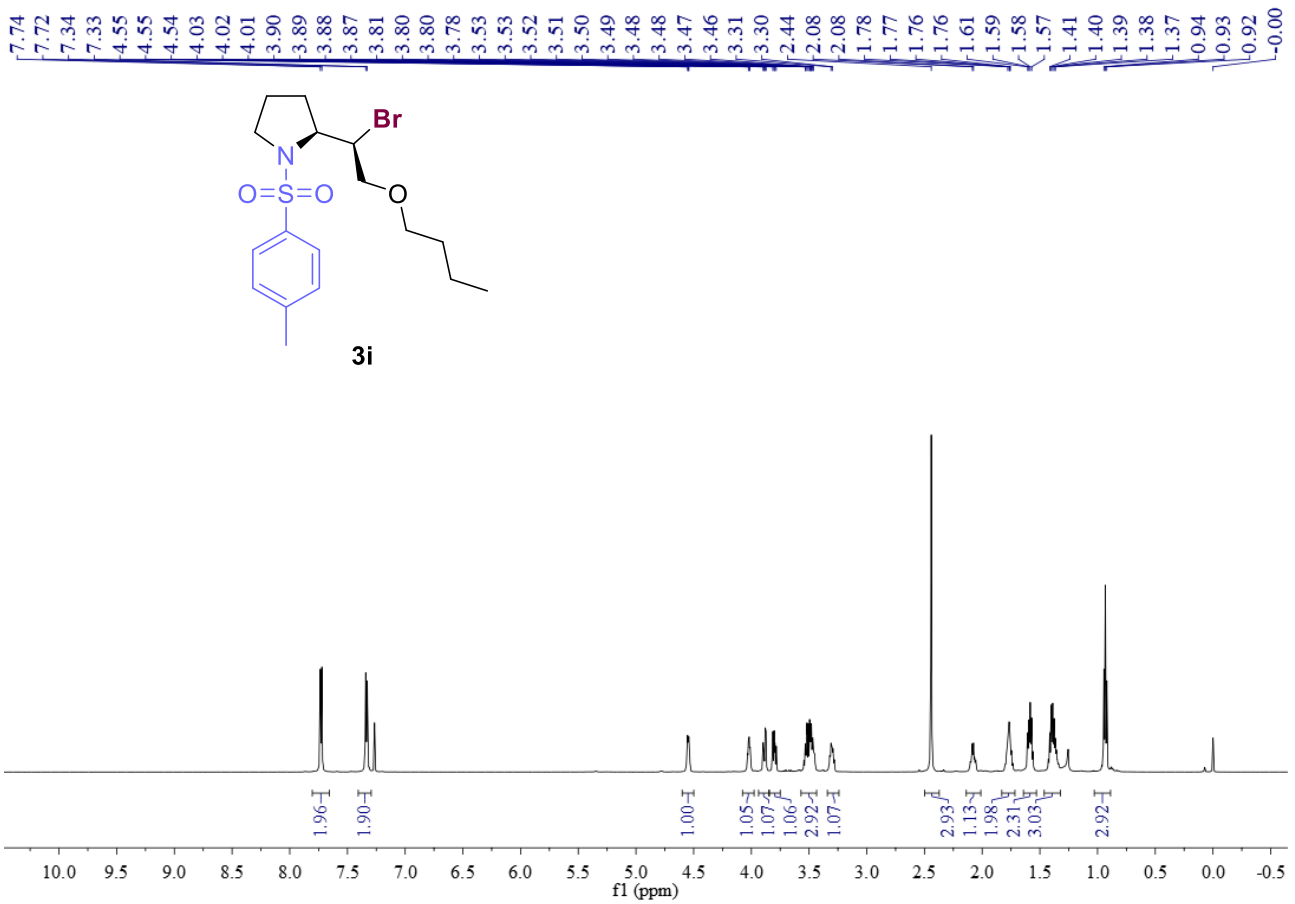


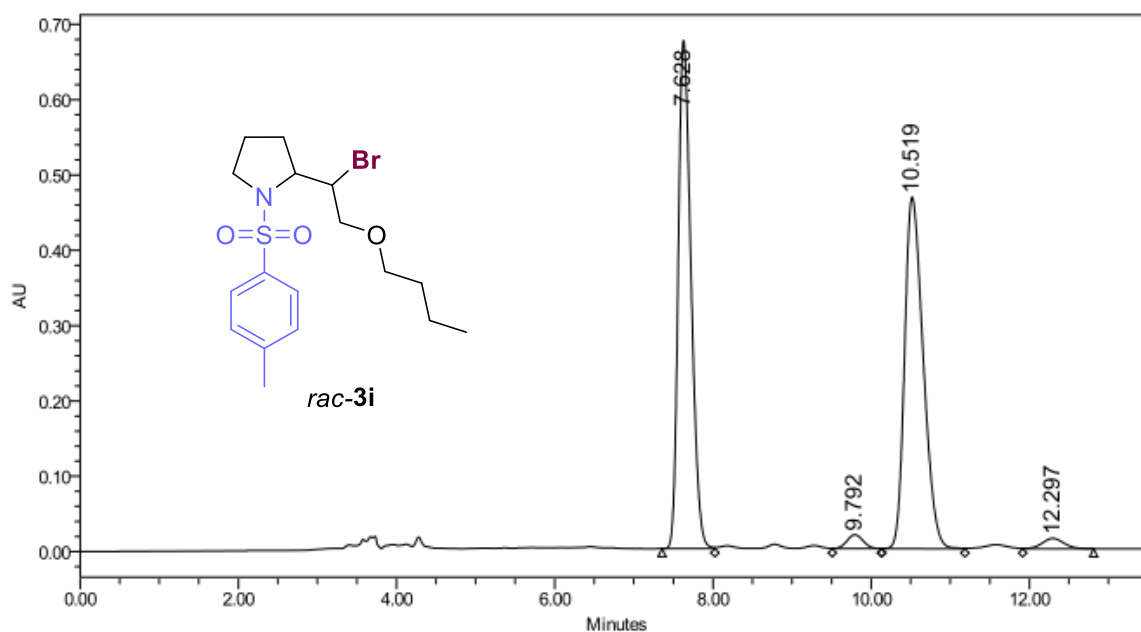


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.691	Unknown	1927469	50.55	122577	51.66	BB	772	8.157	9.443
2	10.717	Unknown	1885257	49.45	114688	48.34	BB	791	10.335	11.653

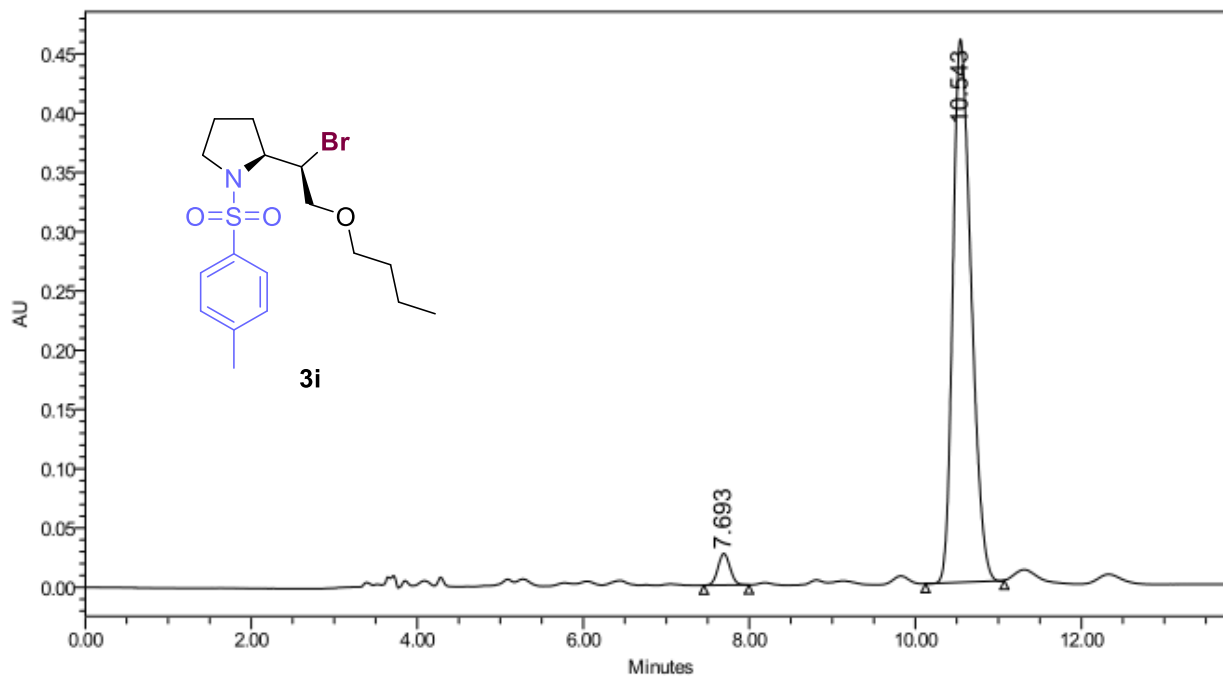


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.737	Unknown	159463	4.55	13211	5.32	BB	410	8.468	9.152
2	10.640	Unknown	3342767	95.45	235102	94.68	BB	618	10.280	11.310



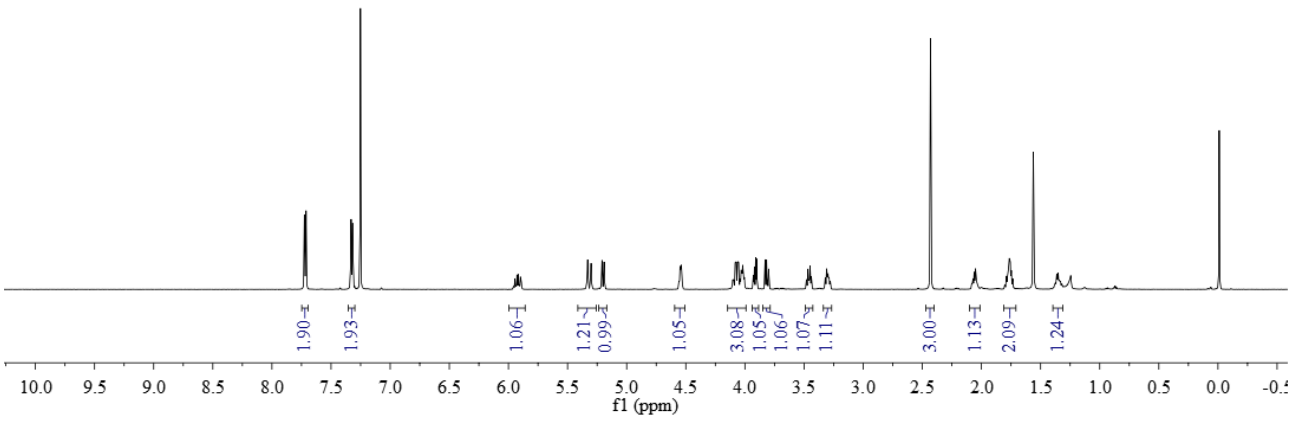
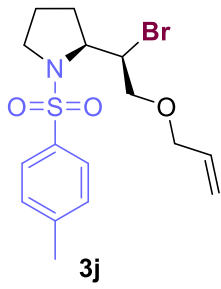


Peak	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.628	Unknown	7577702	48.12	674812	57.48	BV	402	7.355	8.025
2	9.792	Unknown	268121	1.70	18598	1.58	VV	374	9.510	10.133
3	10.519	Unknown	7637927	48.50	466861	39.77	VV	632	10.133	11.187
4	12.297	Unknown	264972	1.68	13759	1.17	VB	538	11.915	12.812

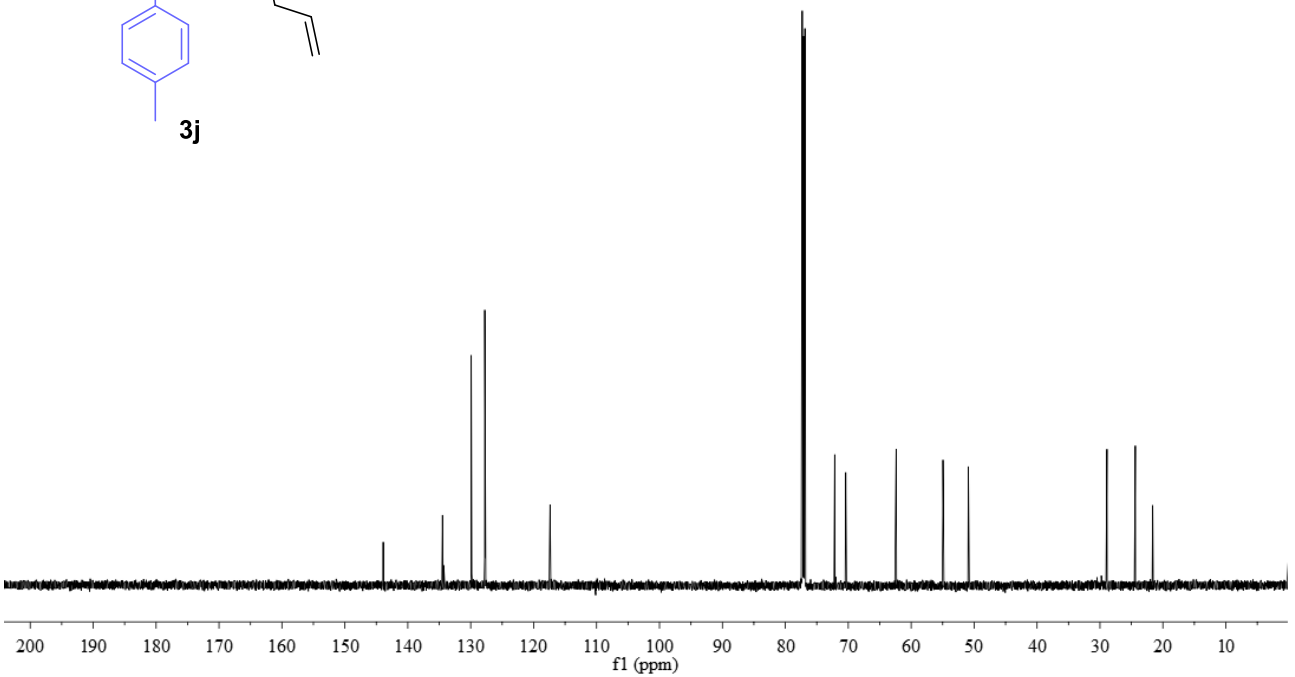
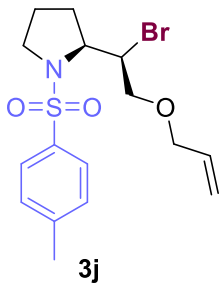


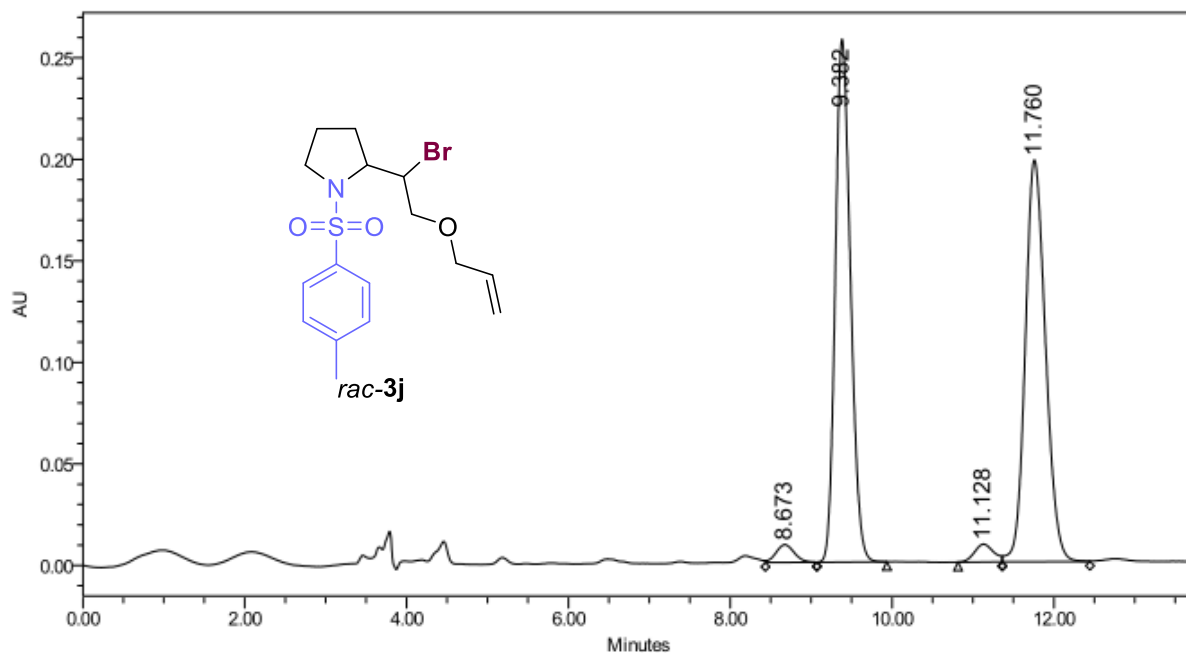
Peak	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.693	Unknown	271973	3.73	26664	5.50	bb	325	7.453	7.995
2	10.543	Unknown	7019269	96.27	458256	94.50	bb	570	10.122	11.072

7.73
7.71
7.33
7.32
5.93
5.92
5.33
5.33
5.30
5.30
5.21
5.19
4.55
4.54
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3.82
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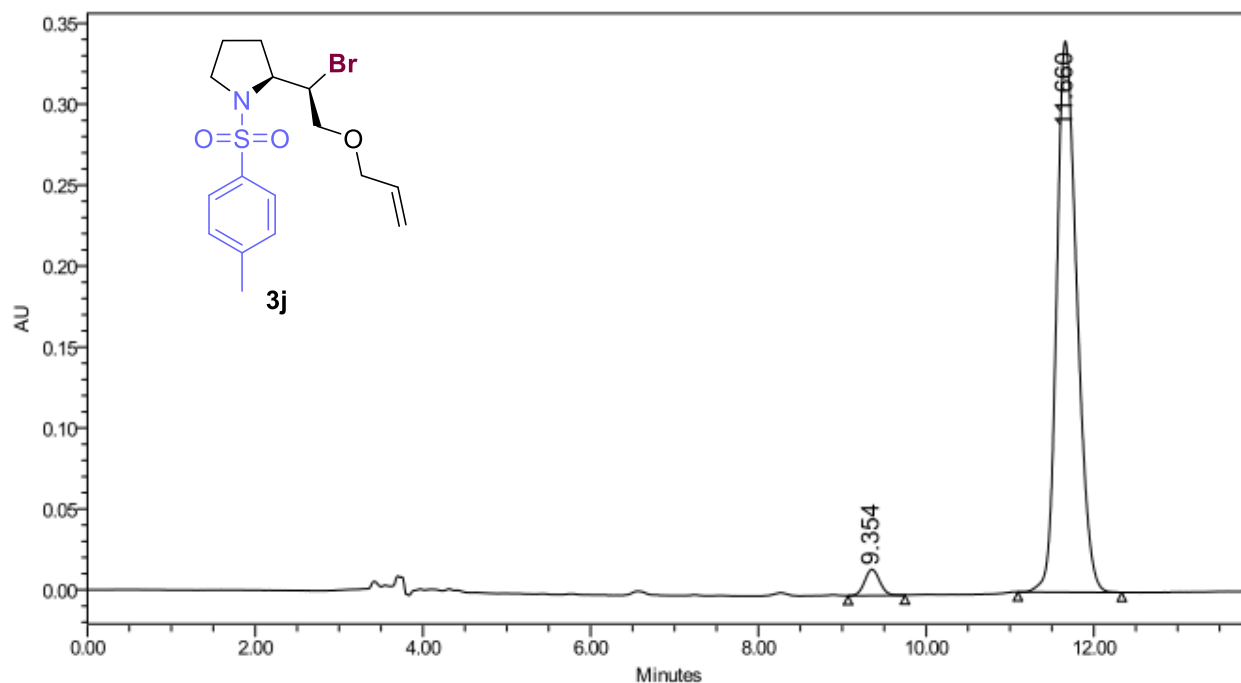


143.90
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24.38
21.62



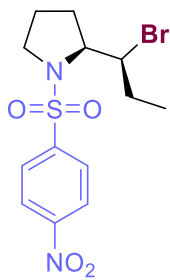


RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)	
1	8.673	Unknown	135911	1.92	8715	1.84	VV	382	8.435	9.072
2	9.382	Unknown	3358354	47.43	257478	54.46	VB	519	9.072	9.937
3	11.128	Unknown	143962	2.03	8786	1.86	BV	329	10.815	11.363
4	11.760	Unknown	3442517	48.62	197783	41.84	VV	650	11.363	12.447

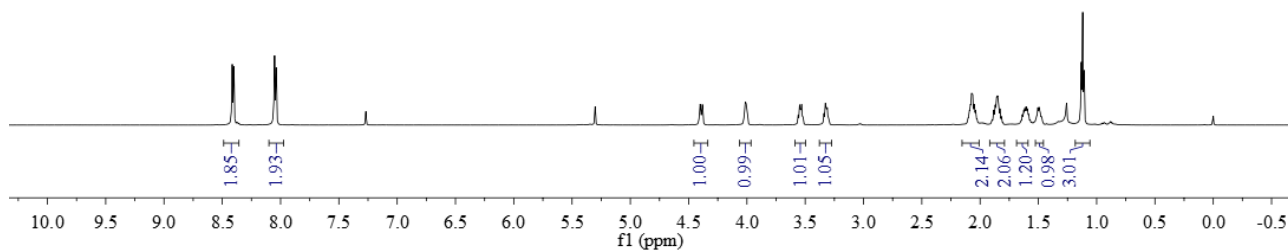


RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)	
1	9.354	Unknown	200196	3.38	16077	4.51	BB	407	9.070	9.748
2	11.660	Unknown	5718735	96.62	340391	95.49	bB	744	11.093	12.333

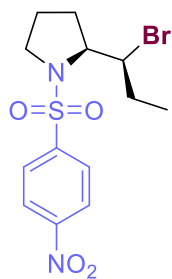
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4.01
4.00
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3.52
3.34
3.33
3.32
3.31
3.30
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.64
1.63
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1.11
-0.00



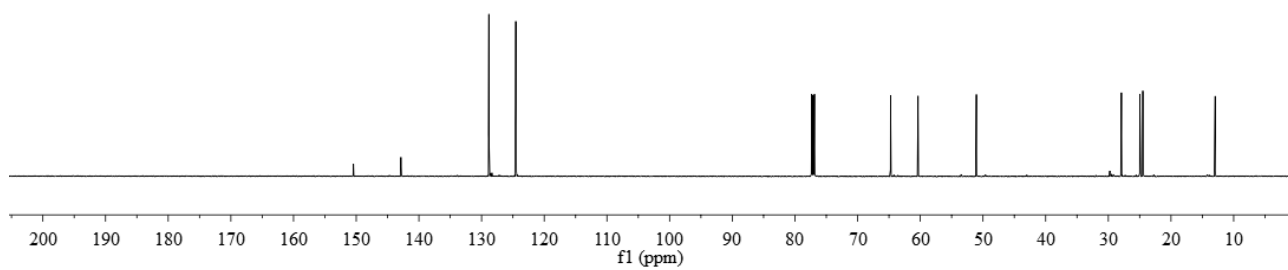
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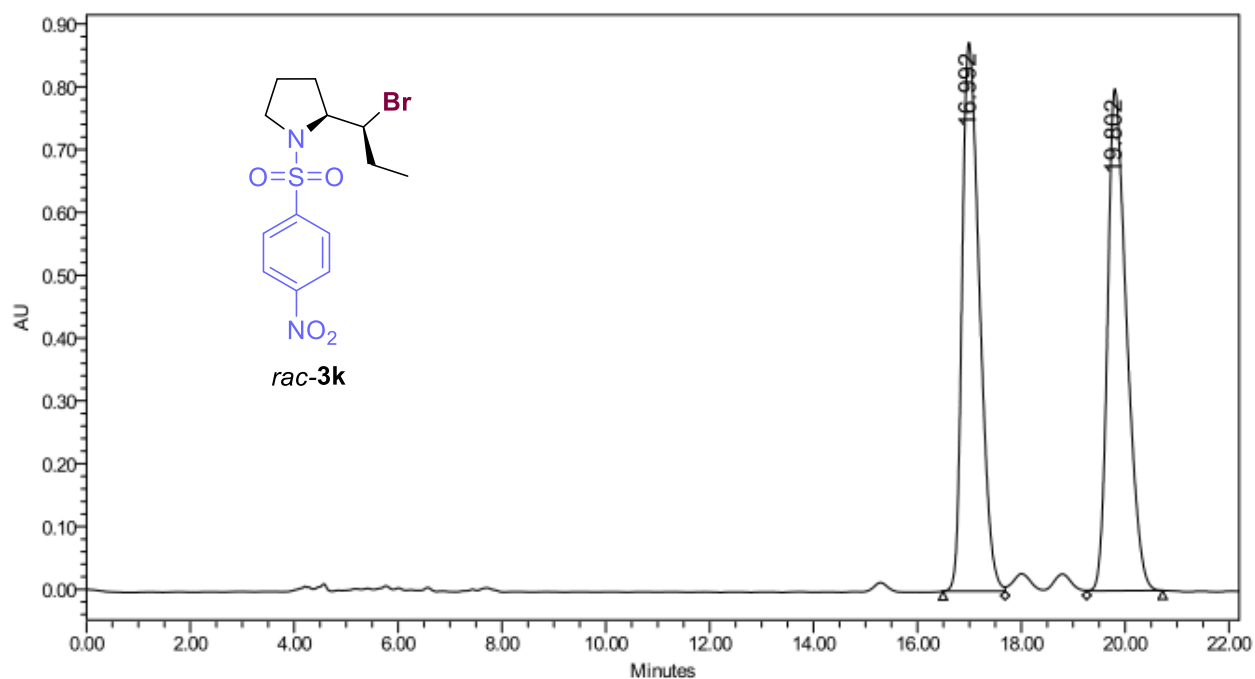


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24.49
12.96

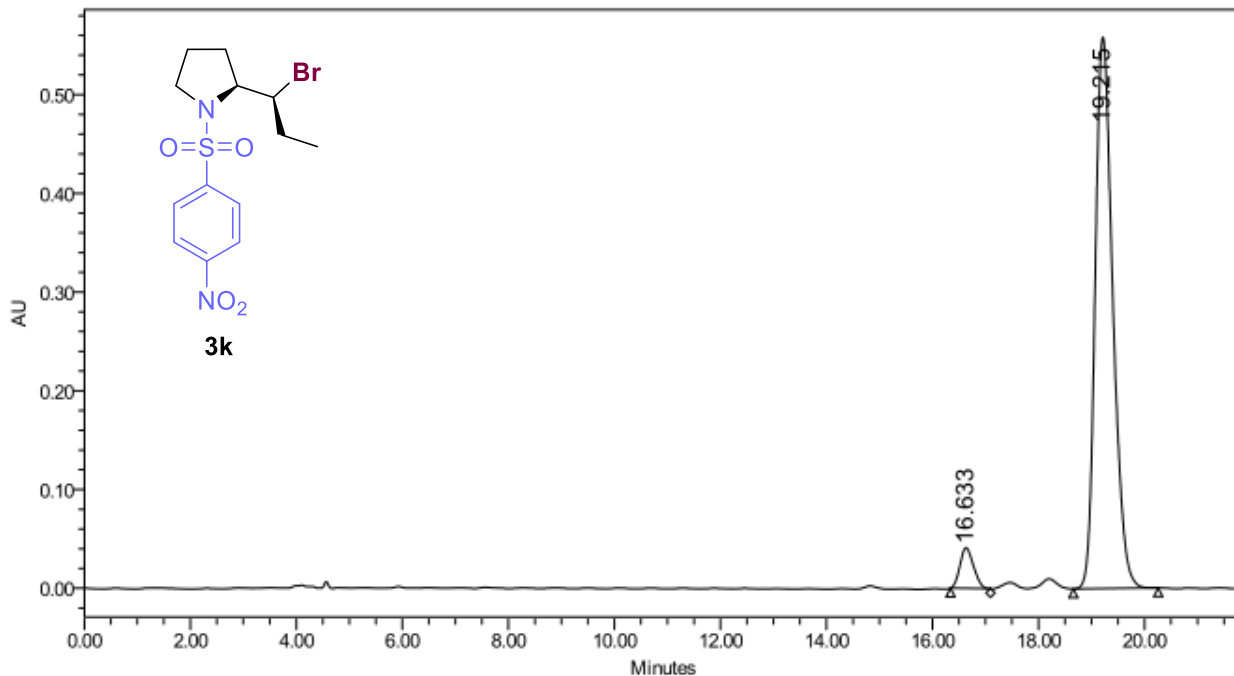


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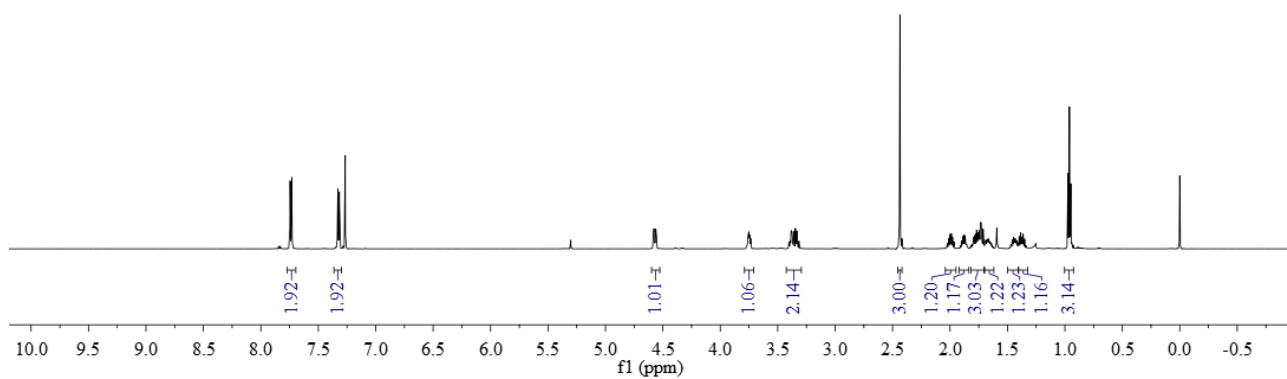
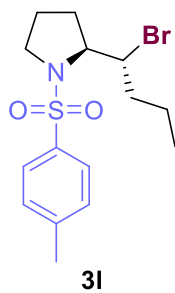


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.992	Unknown	20299309	49.92	873636	52.23	BV	717	16.493	17.688
2	19.802	Unknown	20361278	50.08	799067	47.77	VB	877	19.260	20.722

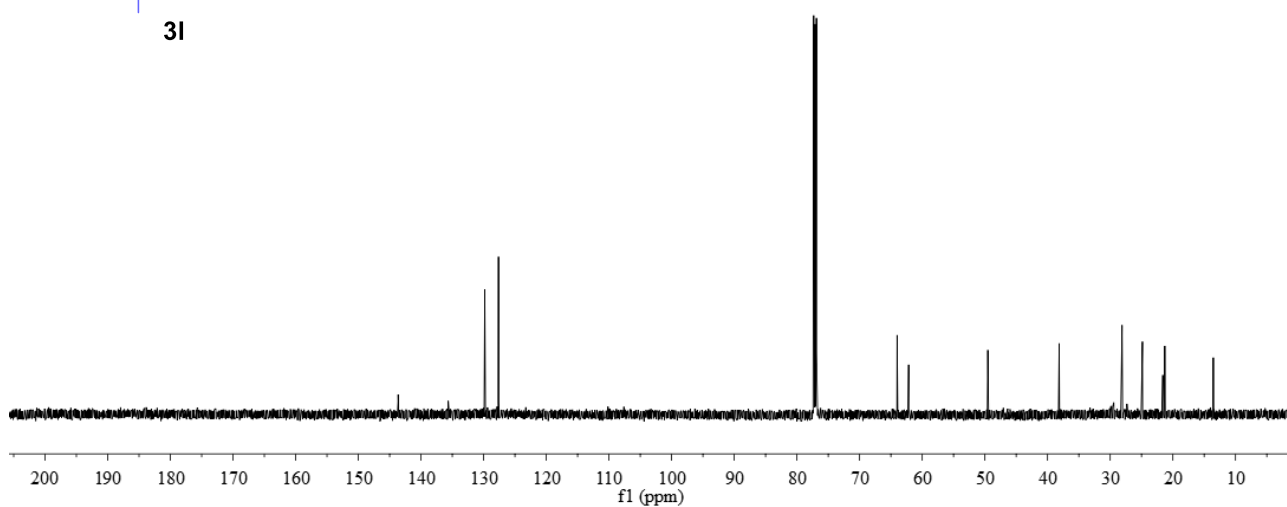
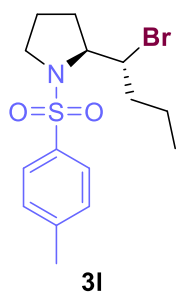


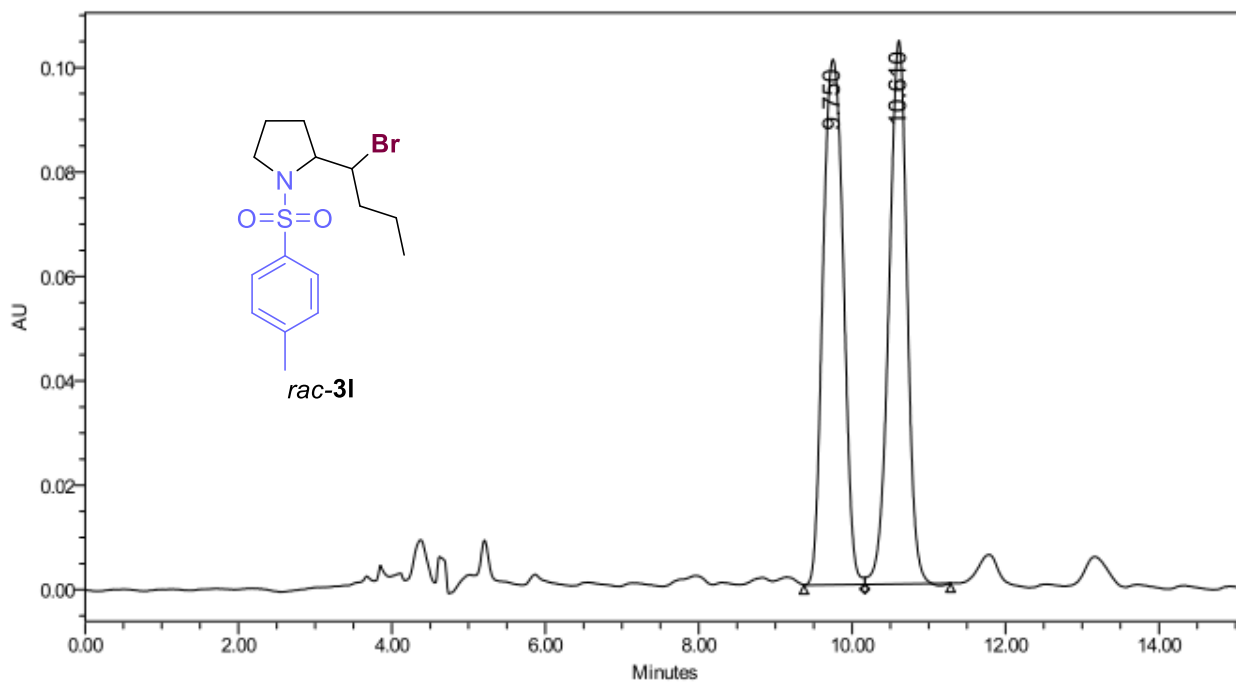
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.633	Unknown	725248	5.34	41090	6.85	bV	453	16.340	17.095
2	19.215	Unknown	12851672	94.66	558378	93.15	Bb	960	18.657	20.257

7.74
7.73
7.33
7.32
4.58
4.57
4.57
4.56
3.76
3.76
3.75
3.75
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1.87
1.79
1.78
1.78
1.77
1.76
1.76
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1.74
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0.95
0.00

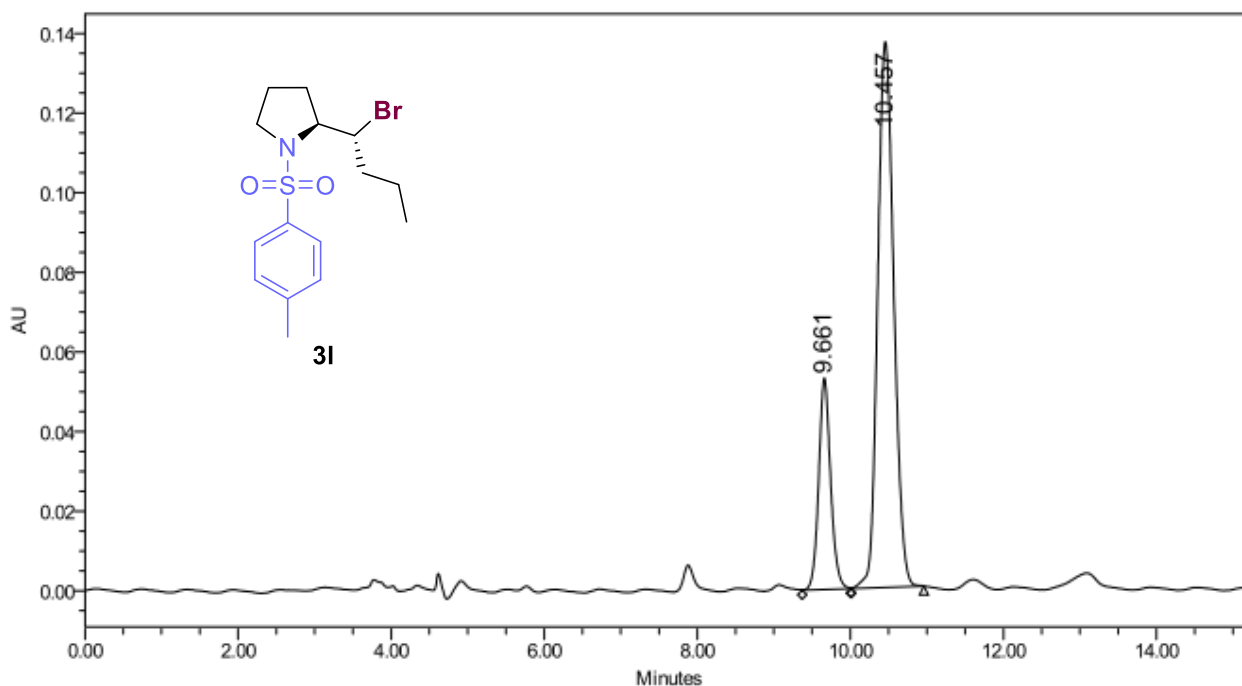


143.65
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21.28
13.54

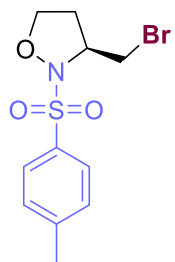




	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.750	Unknown	1862878	52.15	100622	49.15	BV	477	9.372	10.167
2	10.610	Unknown	1709492	47.85	104092	50.85	Vb	670	10.167	11.283



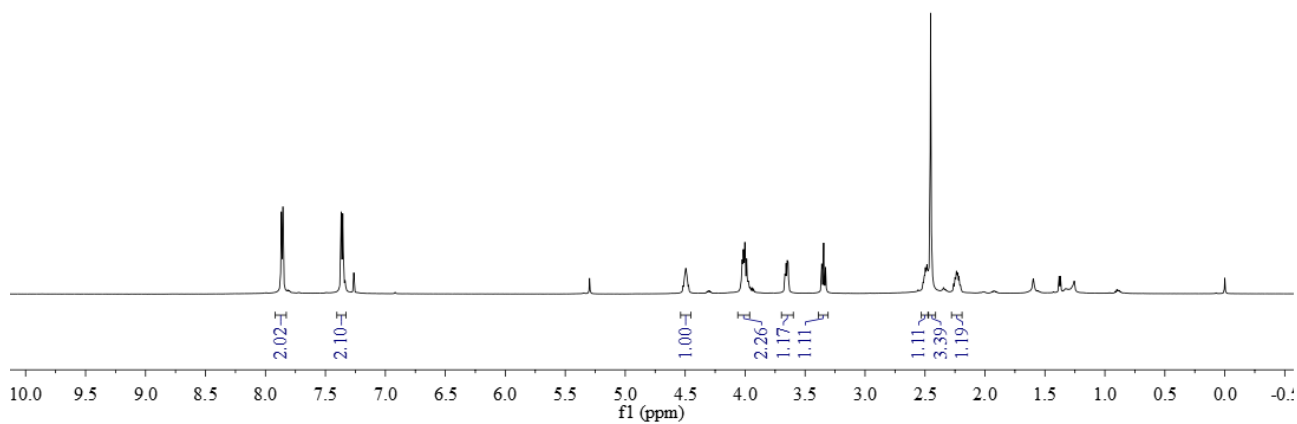
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.661	Unknown	570579	22.15	53030	27.90	VV	384	9.370	10.010
2	10.457	Unknown	2005120	77.85	137046	72.10	VB	571	10.010	10.962



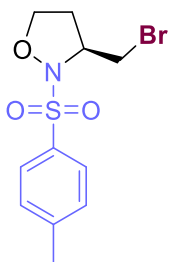
3m

7.87
7.85
7.37
7.36

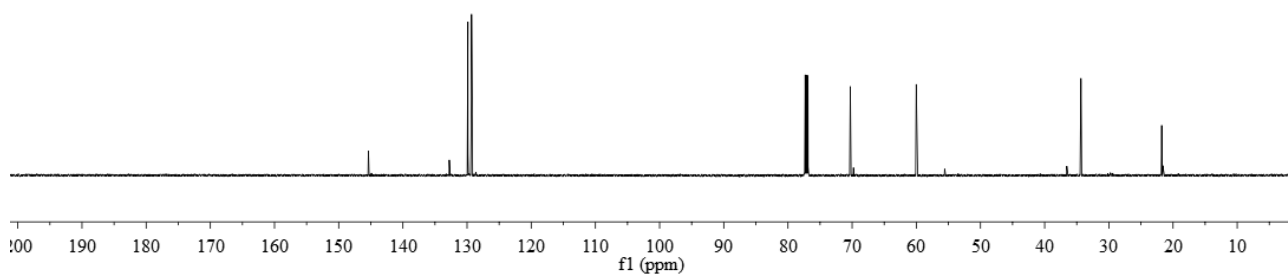
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4.02
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2.47
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2.25
2.24
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2.23
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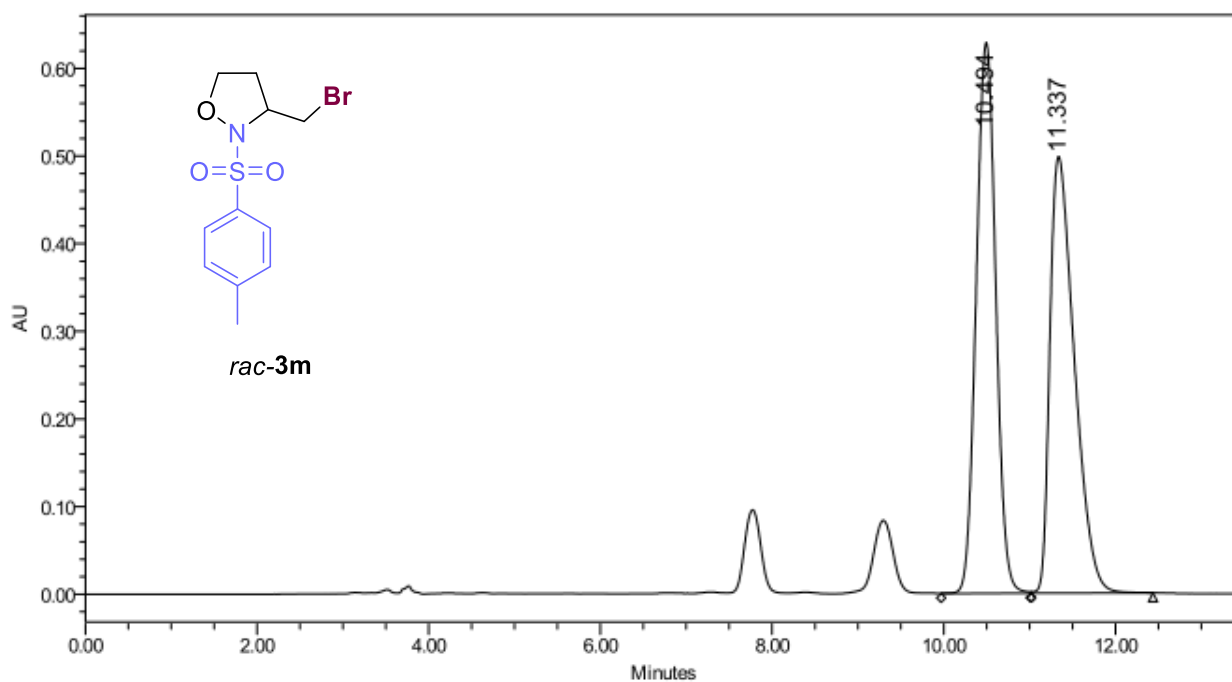


145.37
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77.10
76.89
70.28
60.01
34.35
34.33
21.77

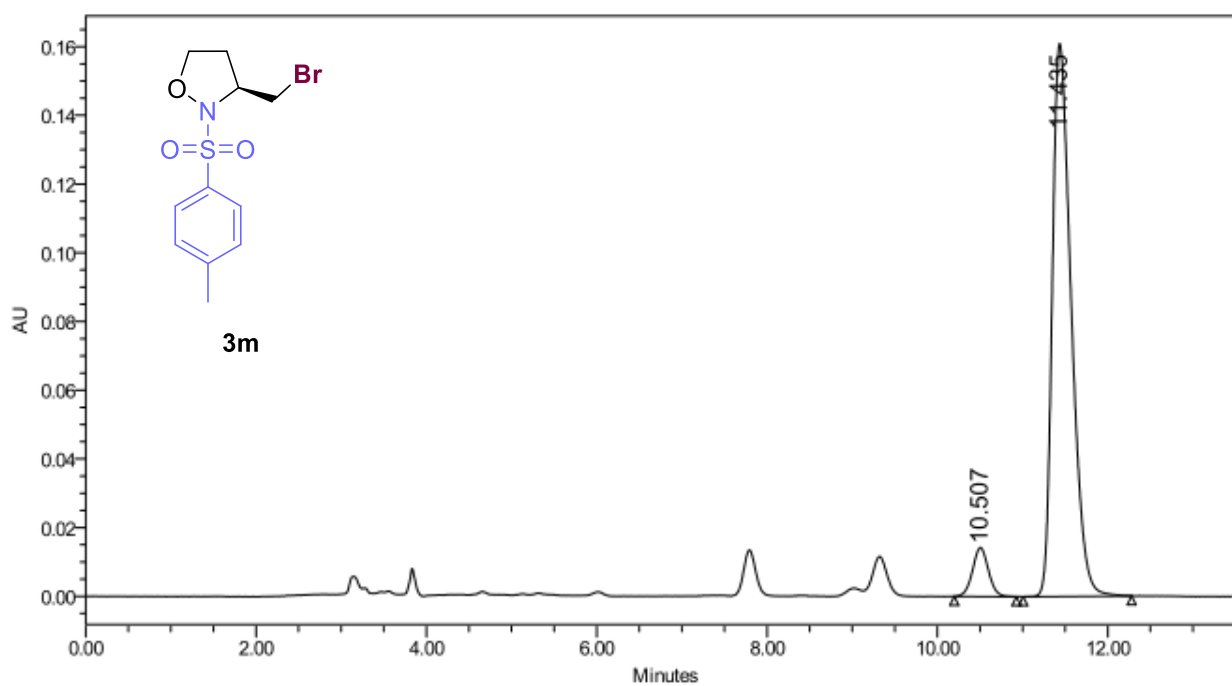


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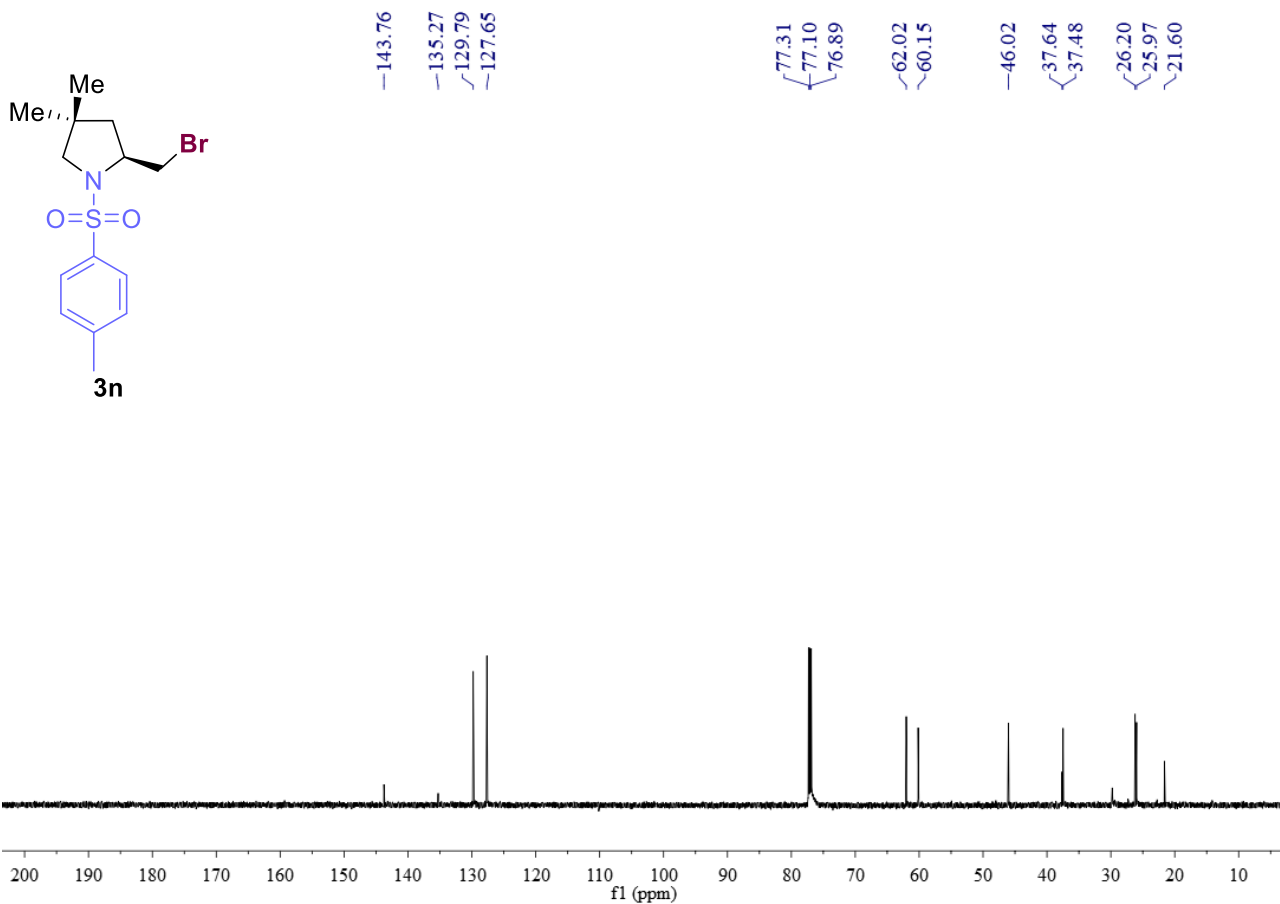
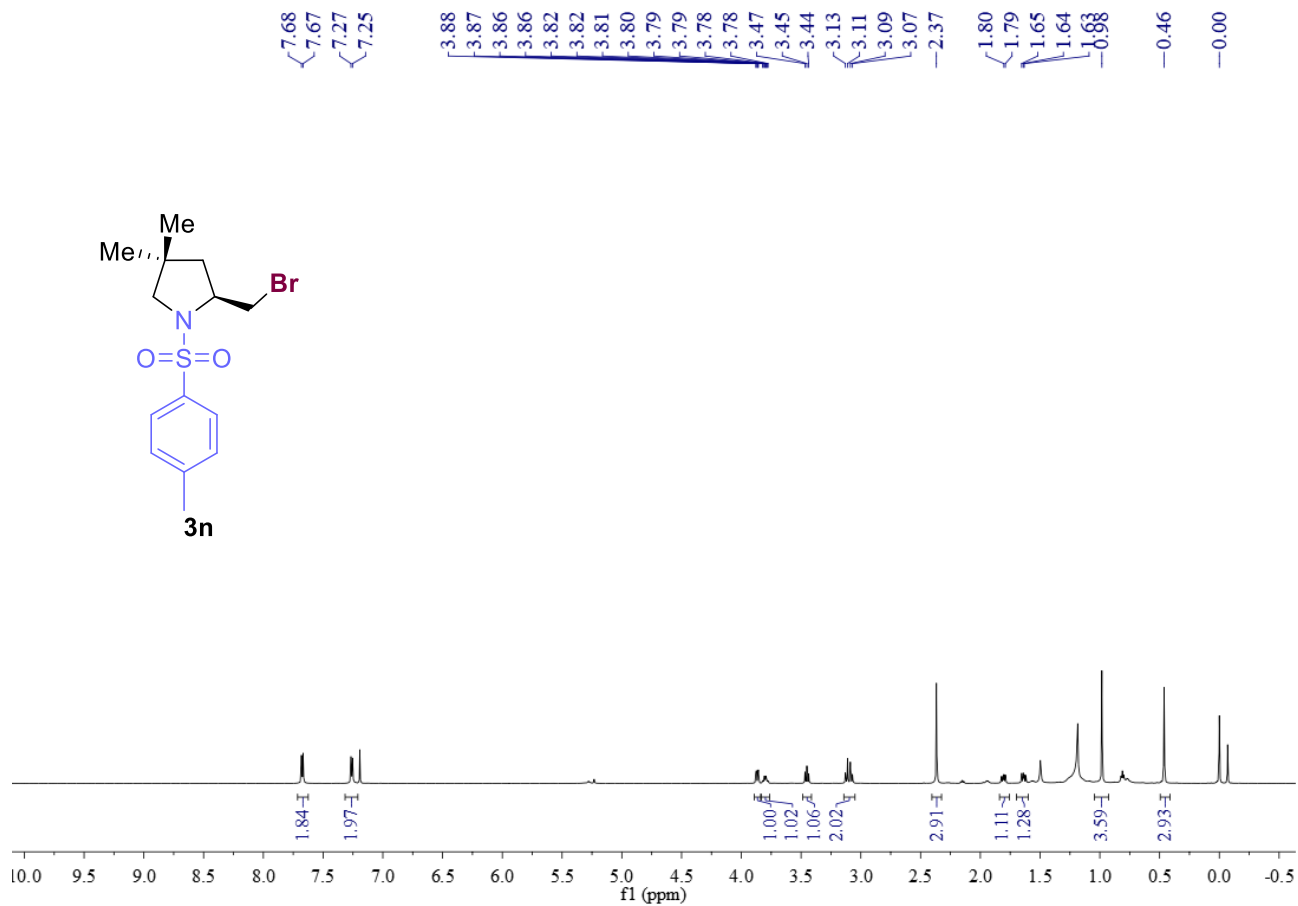
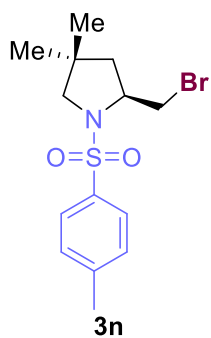


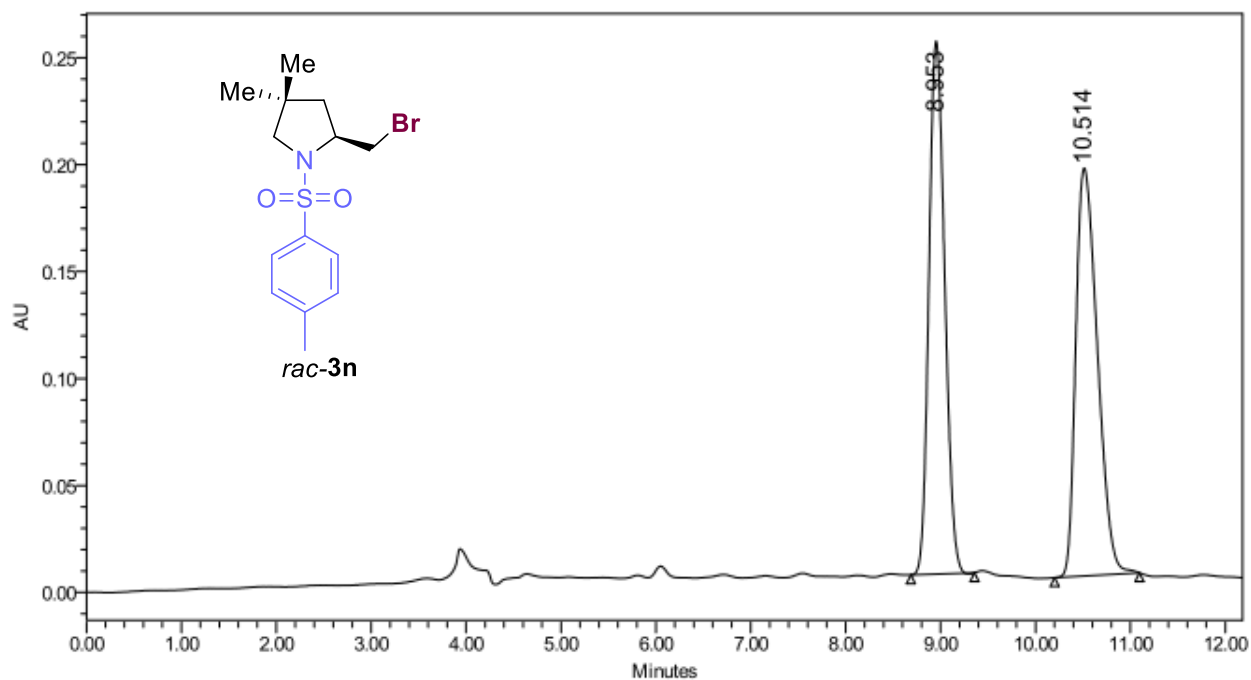


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.494	Unknown	9943508	50.22	628475	55.79	VV	629	9.968	11.017
2	11.337	Unknown	9856768	49.78	498067	44.21	Vb	852	11.017	12.437

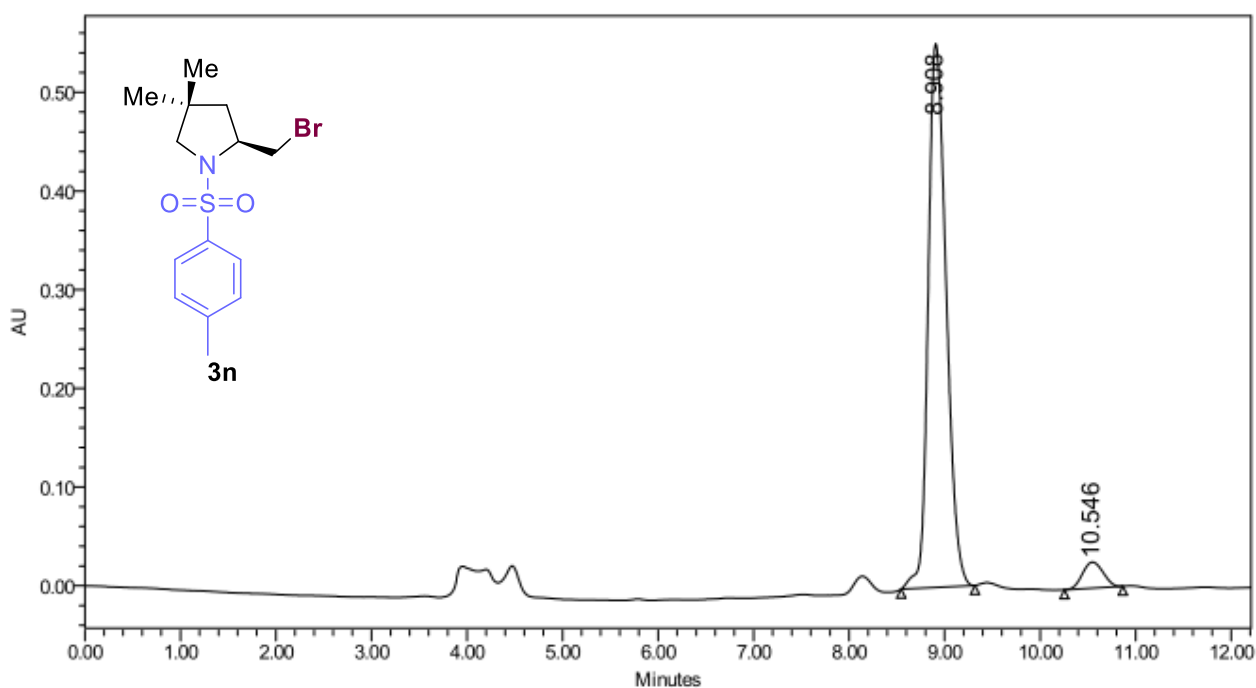


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.507	Unknown	184986	6.95	14247	8.13	BB	438	10.198	10.928
2	11.435	Unknown	2478292	93.05	160948	91.87	BB	764	11.007	12.280

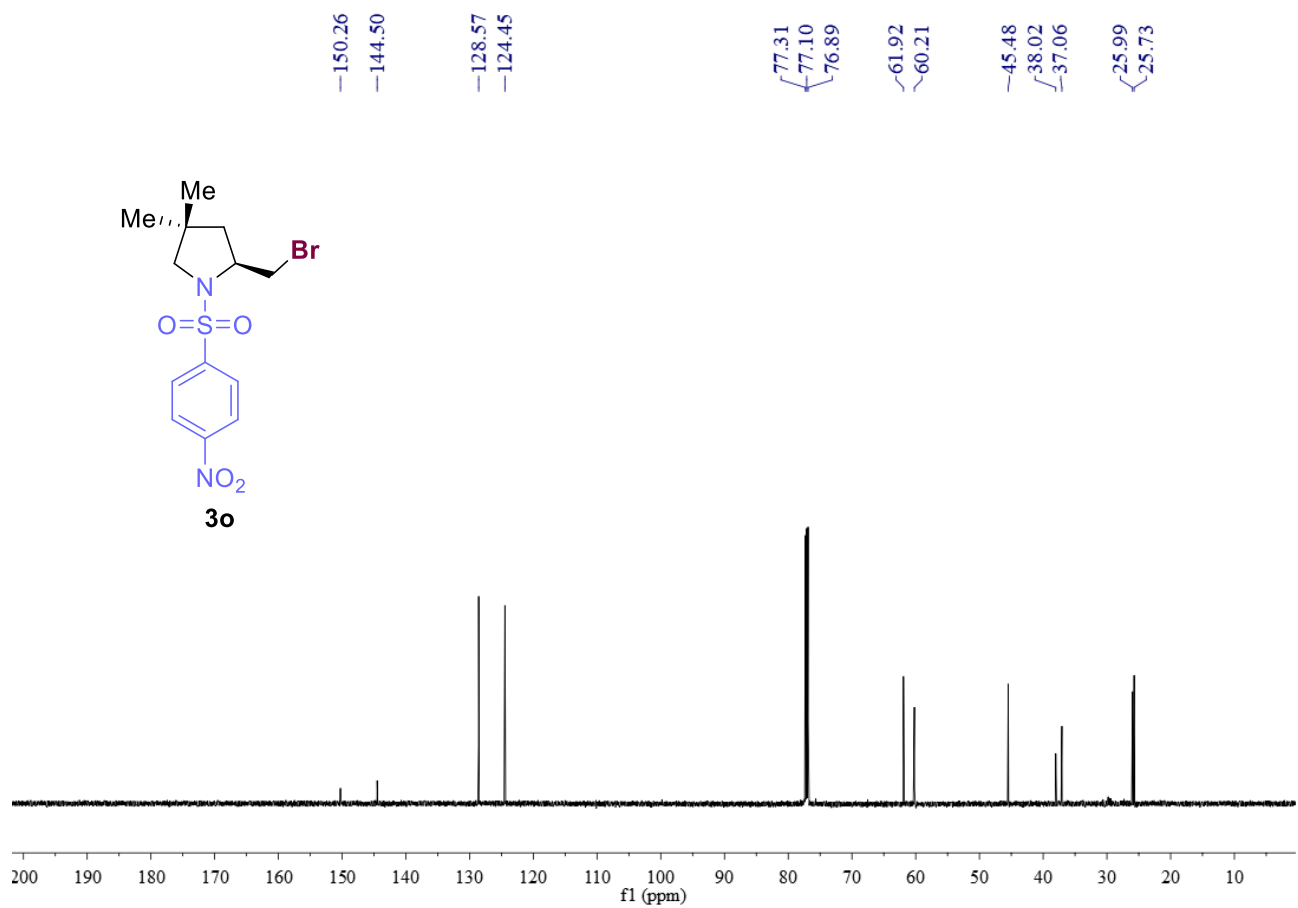
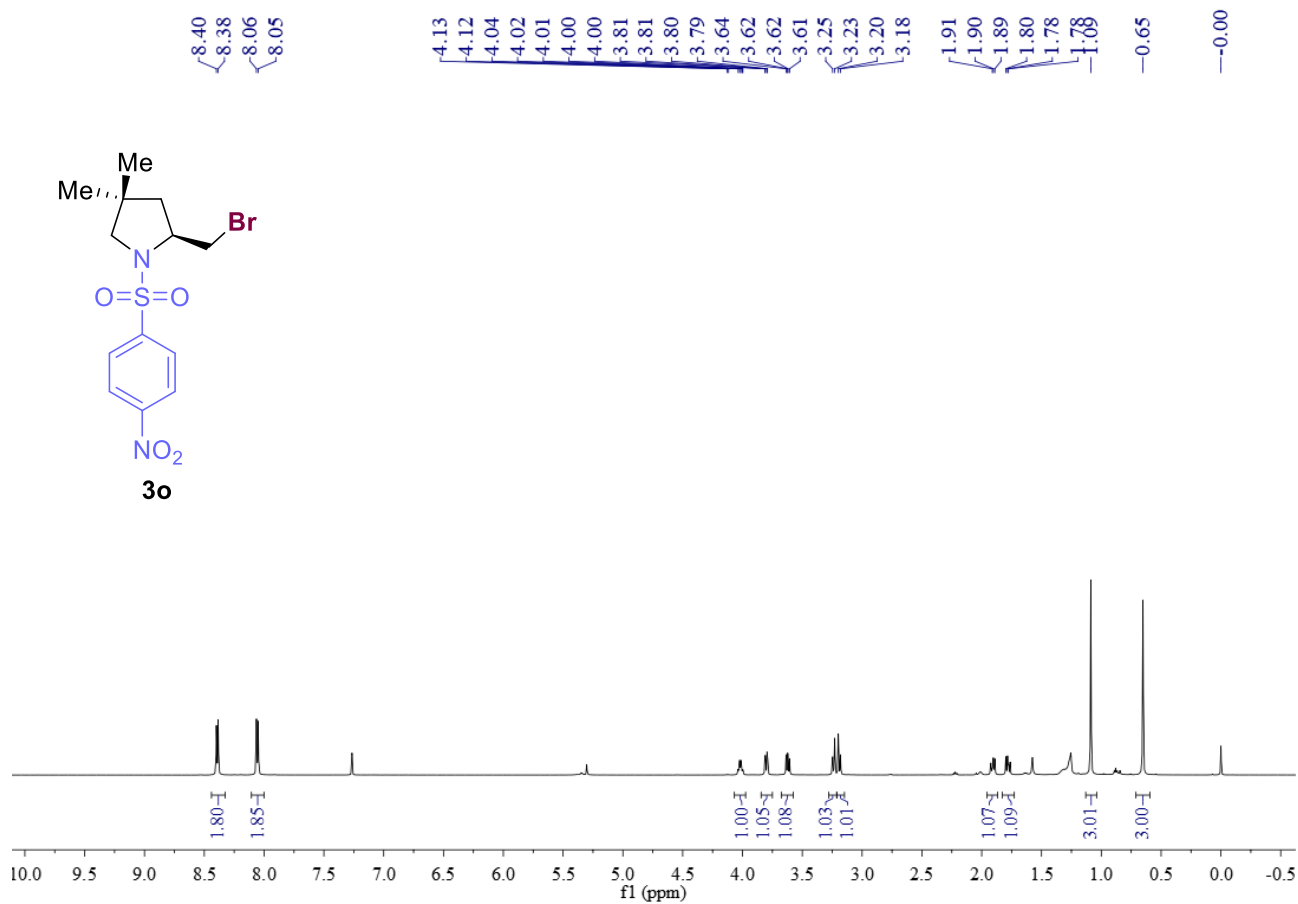


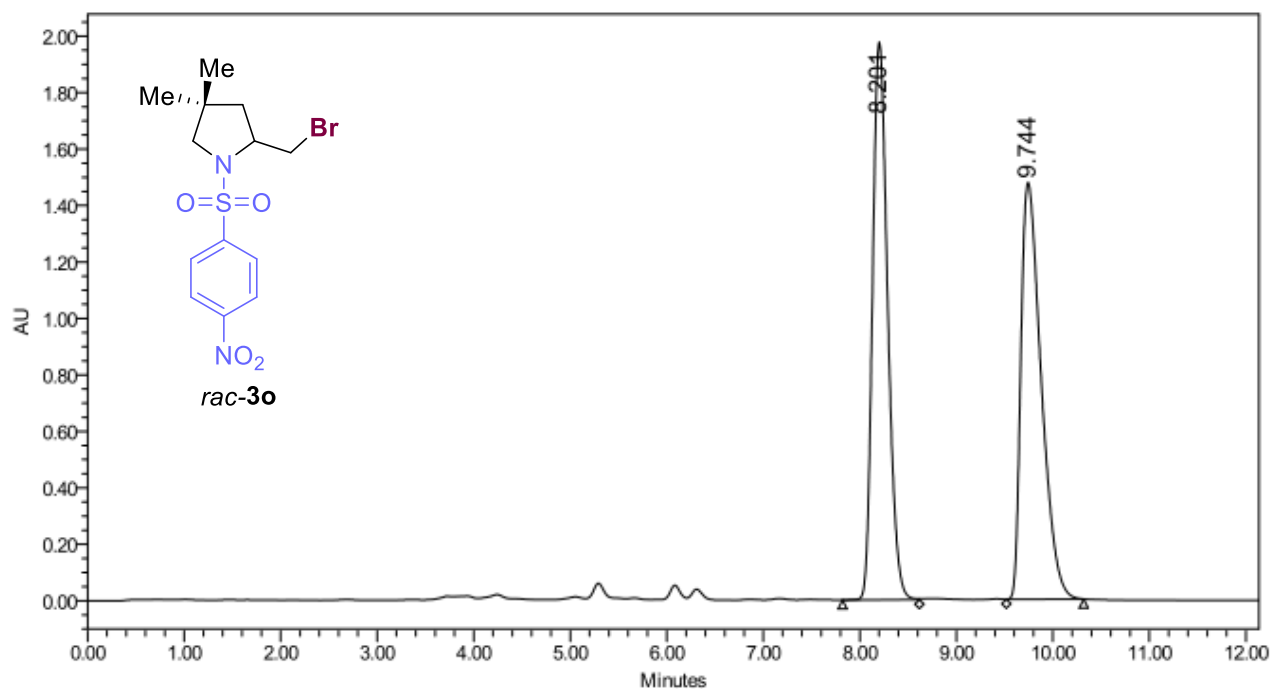


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.953	Unknown	2875152	48.81	249110	56.64	bb	402	8.687	9.357
2	10.514	Unknown	3015418	51.19	190665	43.36	bb	536	10.202	11.095

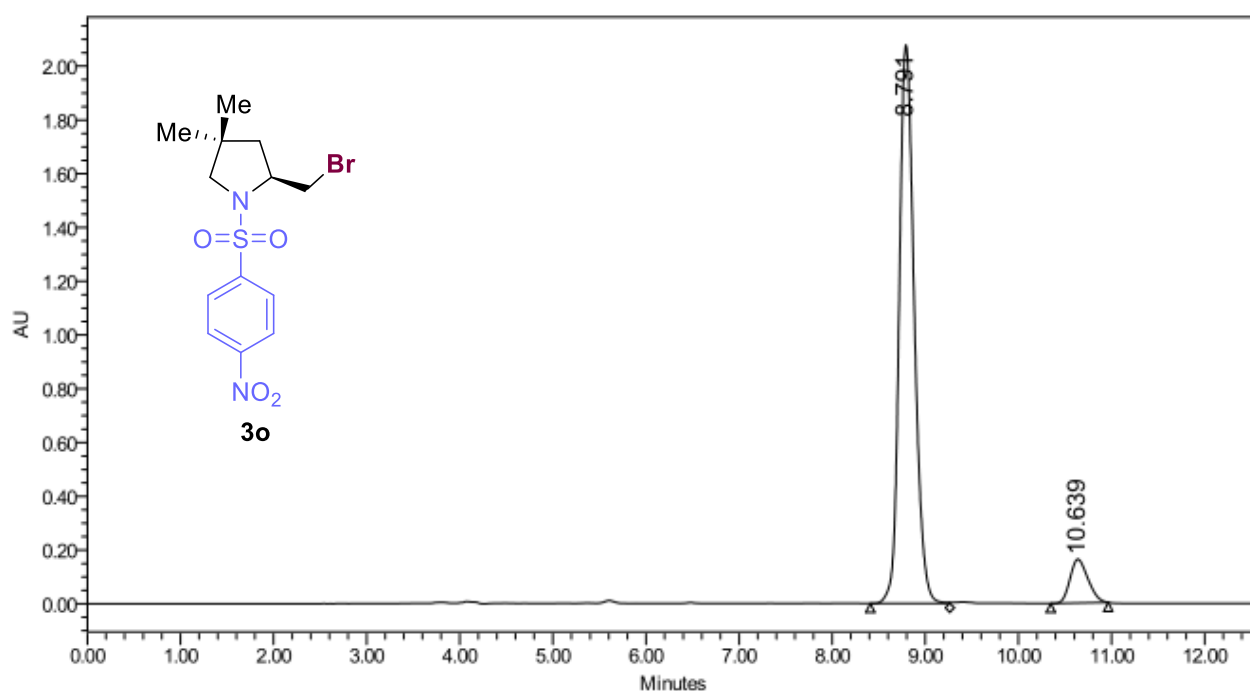


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.908	Unknown	7224560	94.84	550942	95.44	bb	464	8.545	9.318
2	10.546	Unknown	393155	5.16	26300	4.56	bb	367	10.255	10.867

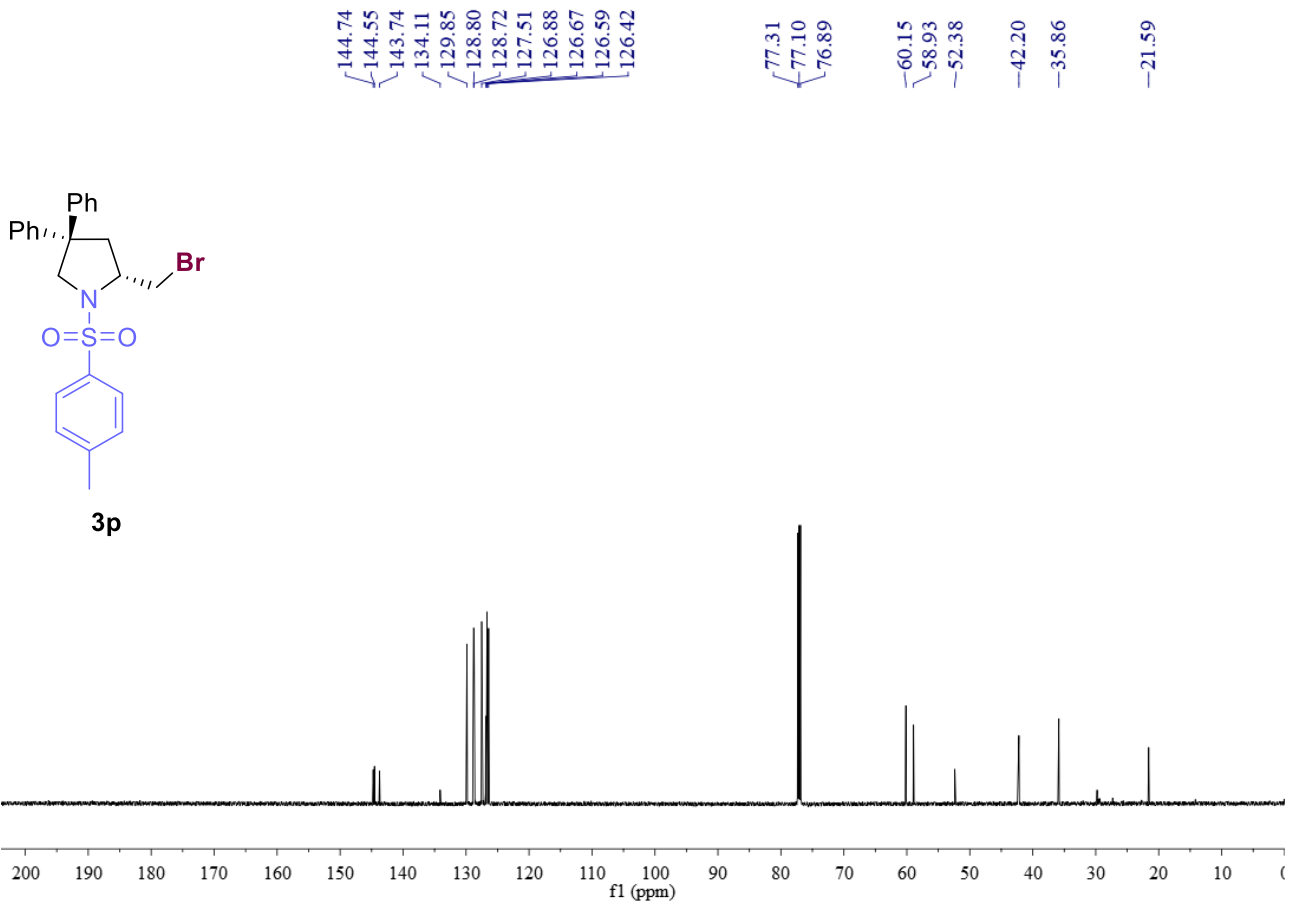
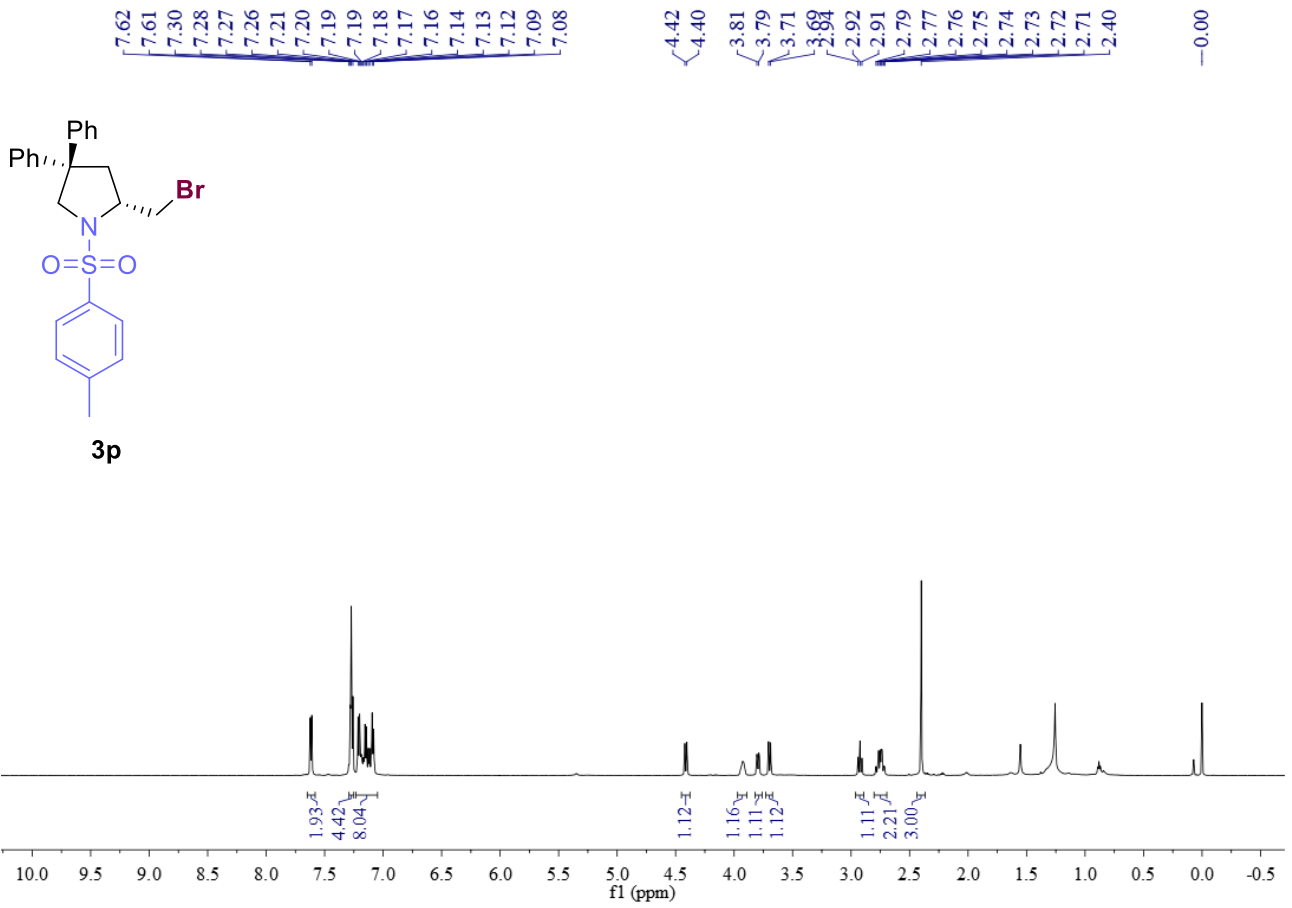


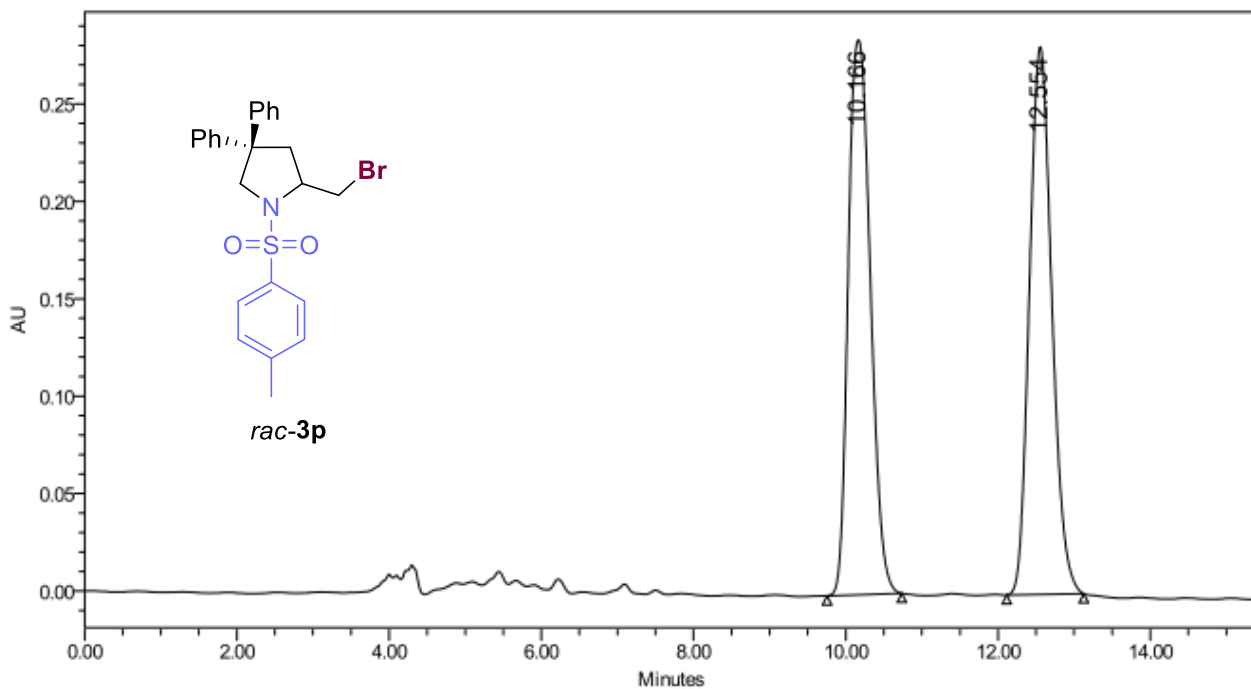


RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	21473839	49.96	1975694	57.25	BV	477	7.822	8.617
2	Unknown	21510713	50.04	1475567	42.75	Vb	481	9.517	10.318

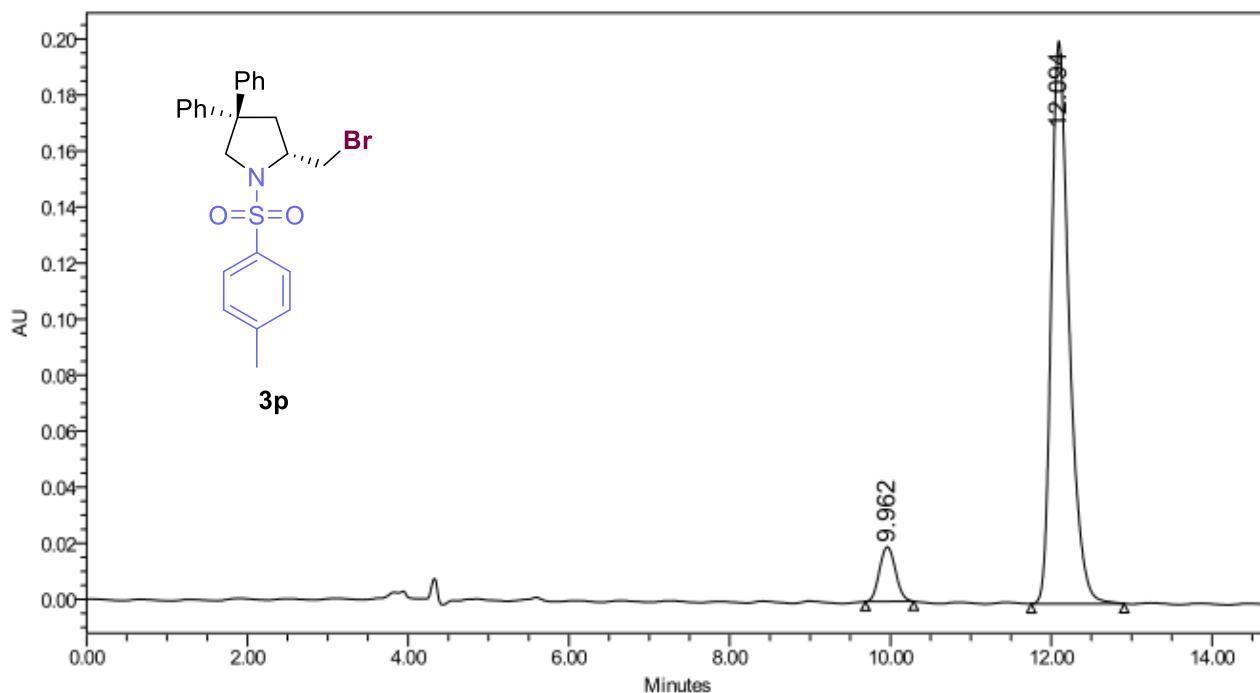


RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	23333174	91.46	2077536	92.74	BV	512	8.410	8.410
2	Unknown	2179861	8.54	162698	7.26	Bb	371	10.347	10.347

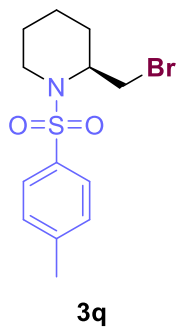




	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.166	Unknown	5754113	50.06	284794	50.32	BB	589	9.753	10.735
2	12.554	Unknown	5740089	49.94	281162	49.68	BB	608	12.113	13.127

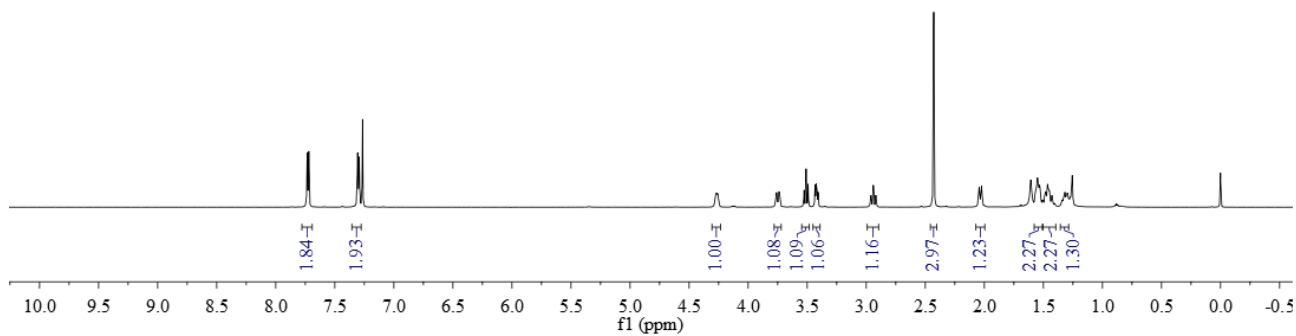


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.962	Unknown	268938	7.98	19404	8.81	bb	360	9.688	10.288
2	12.094	Unknown	3099779	92.02	200850	91.19	BB	694	11.752	12.908



7.73
7.72
7.31
7.29
7.27

4.27
4.26
4.26
3.51
3.49
3.42
2.94
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1.55
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1.45
1.45
0.66



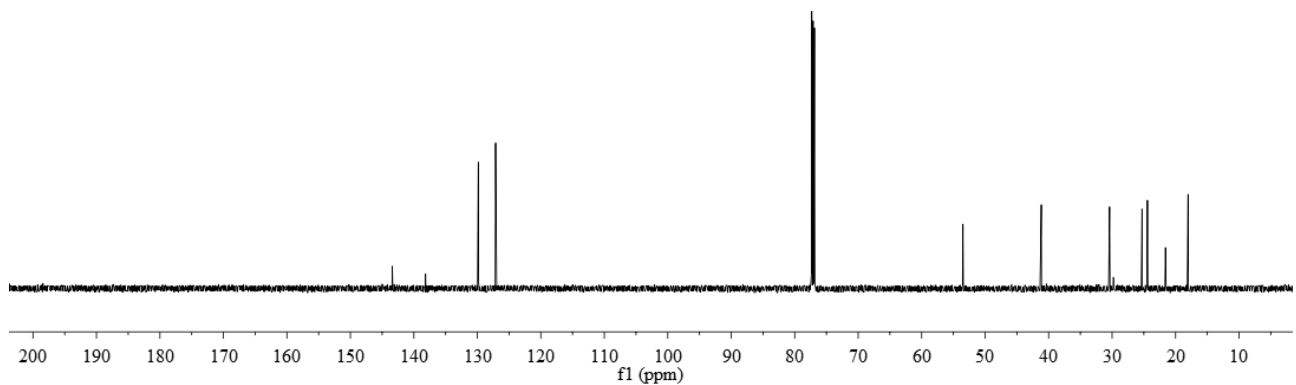
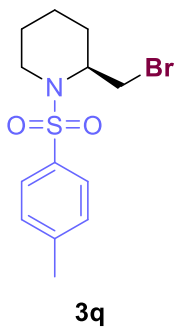
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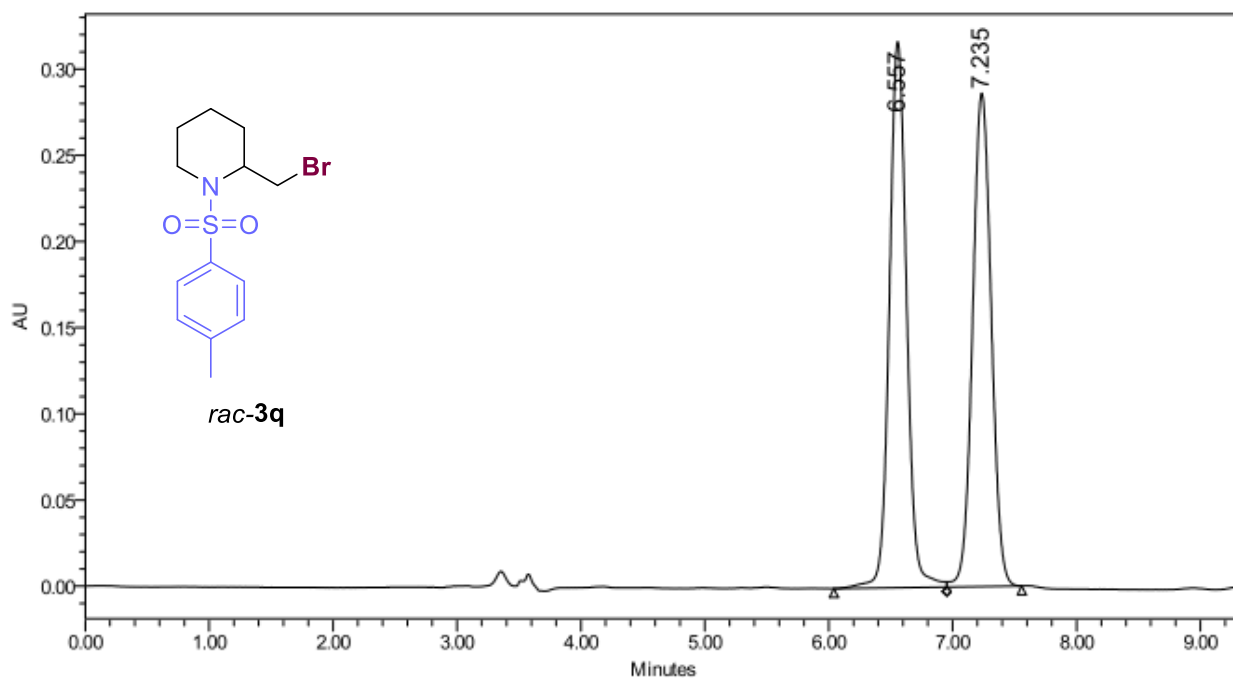
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-53.50

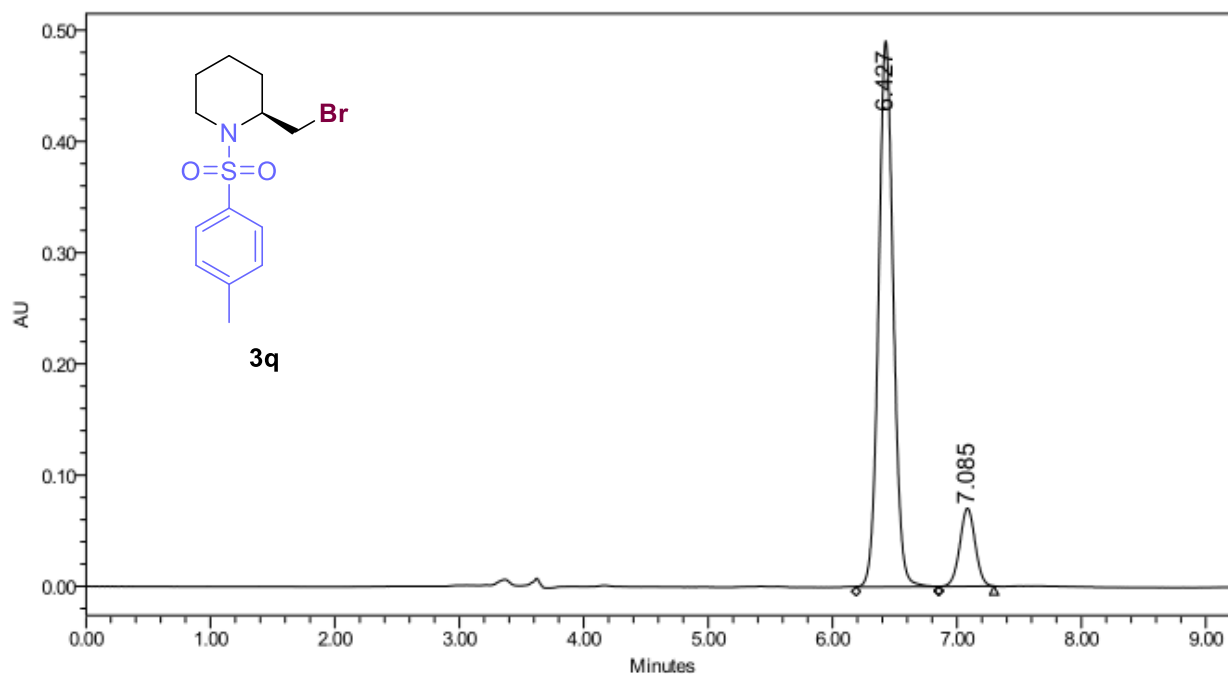
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30.40
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21.59
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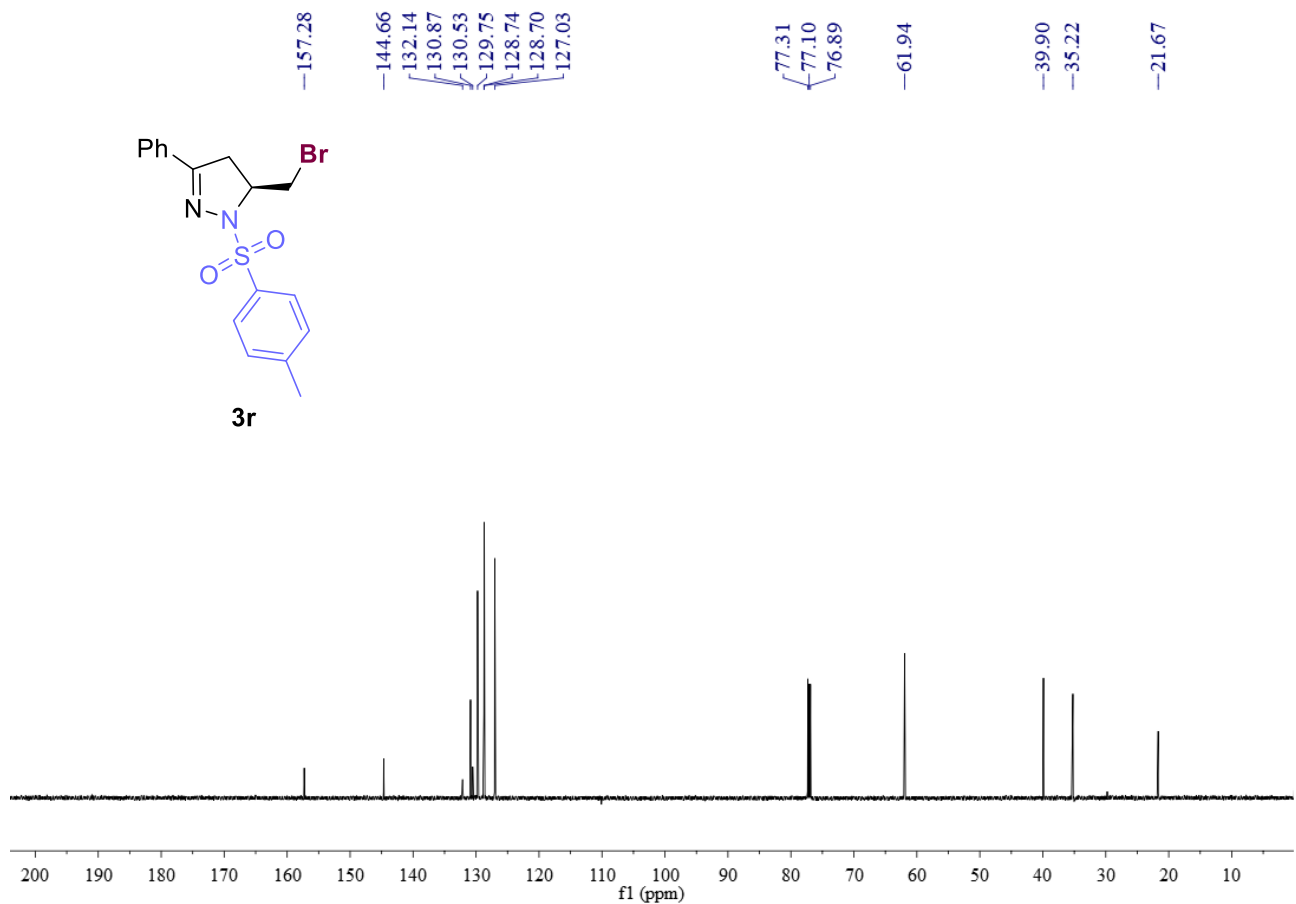
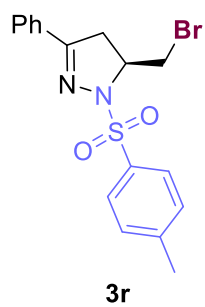
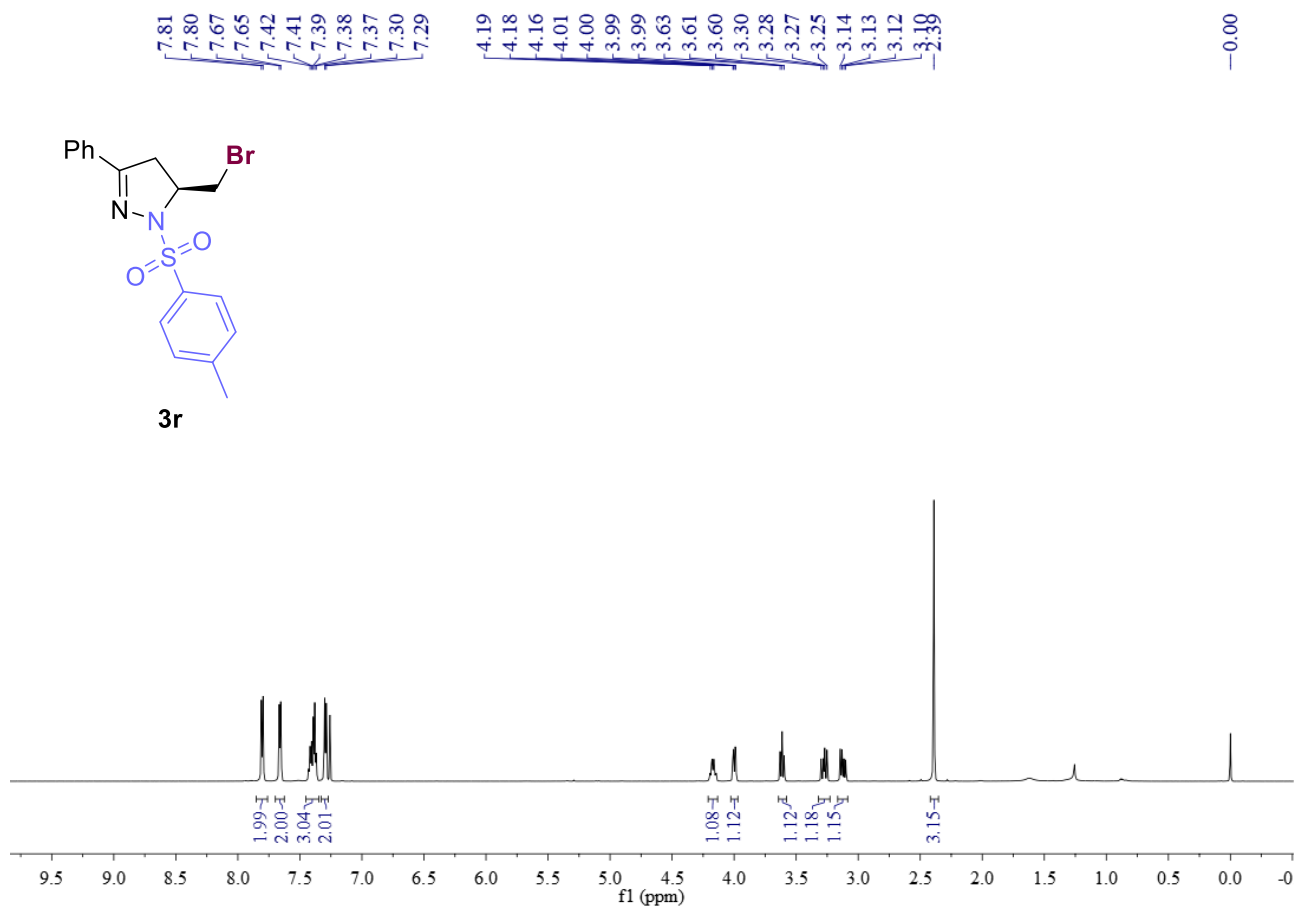
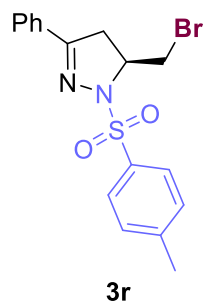


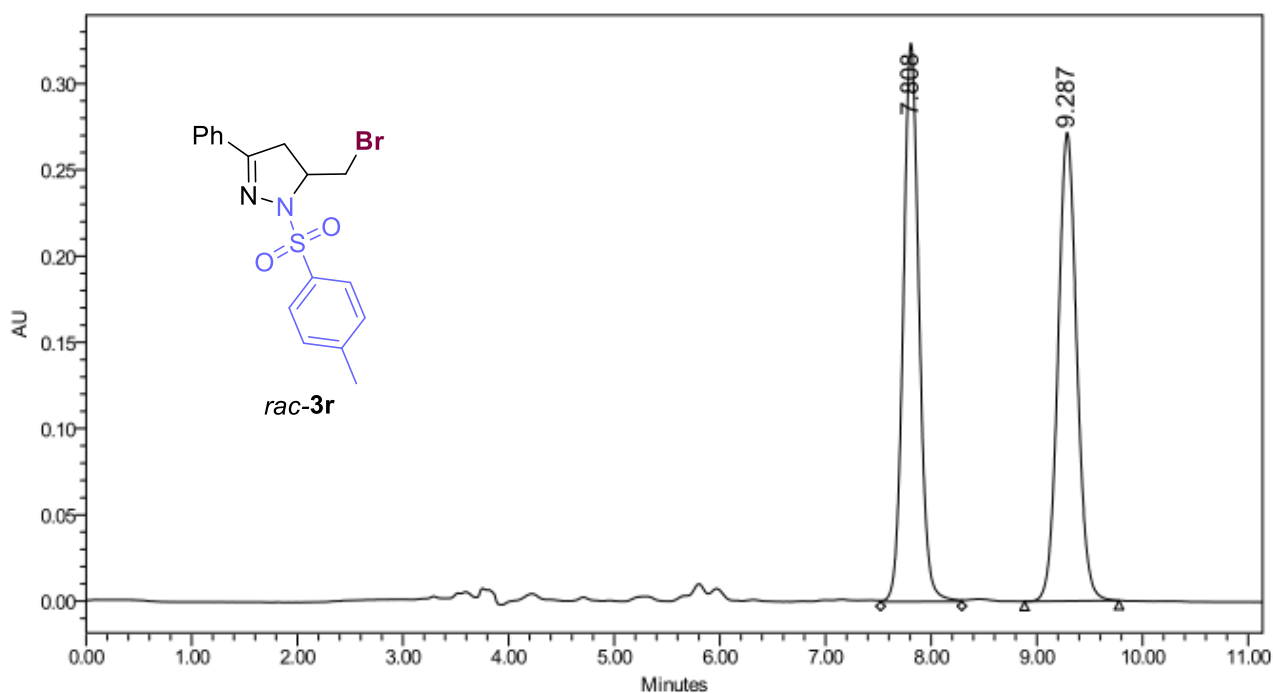


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.557	Unknown	3071504	50.62	316829	52.53	BV	547	6.042	6.953
2	7.235	Unknown	2996666	49.38	286254	47.47	VB	363	6.953	7.558

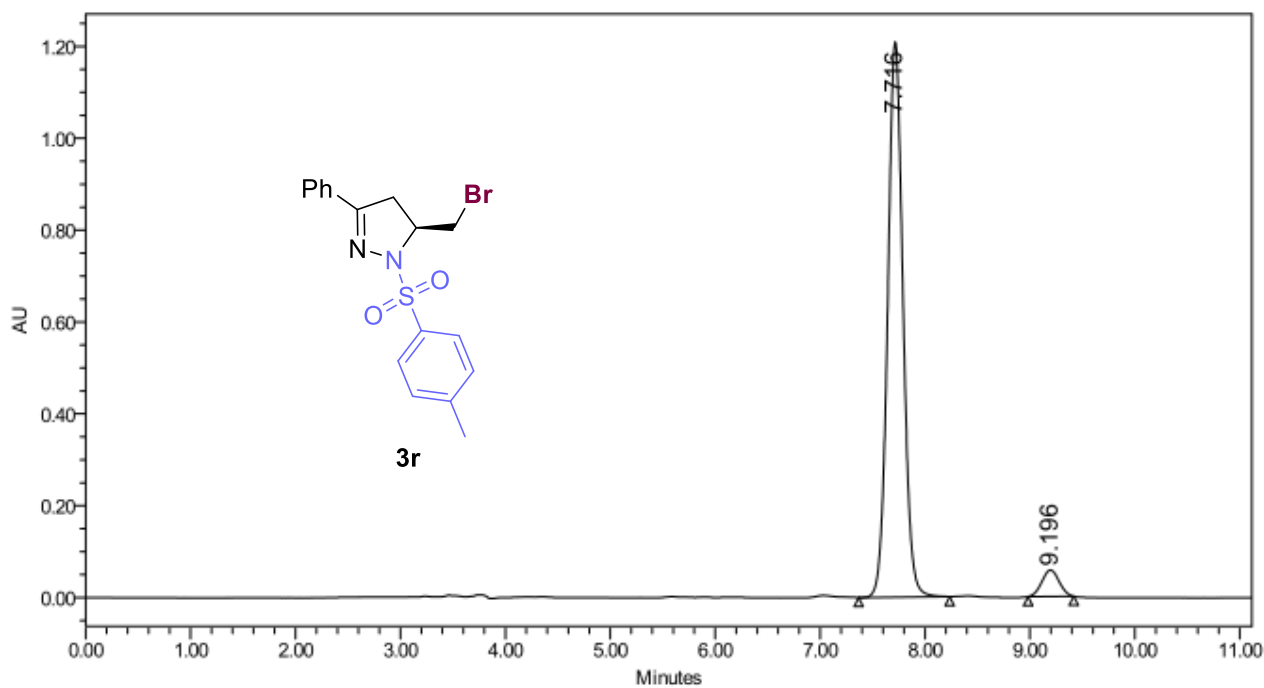


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.427	Unknown	4056508	87.03	490738	87.48	VV	398	6.188	6.852
2	7.085	Unknown	604434	12.97	70217	12.52	Vb	268	6.852	7.298

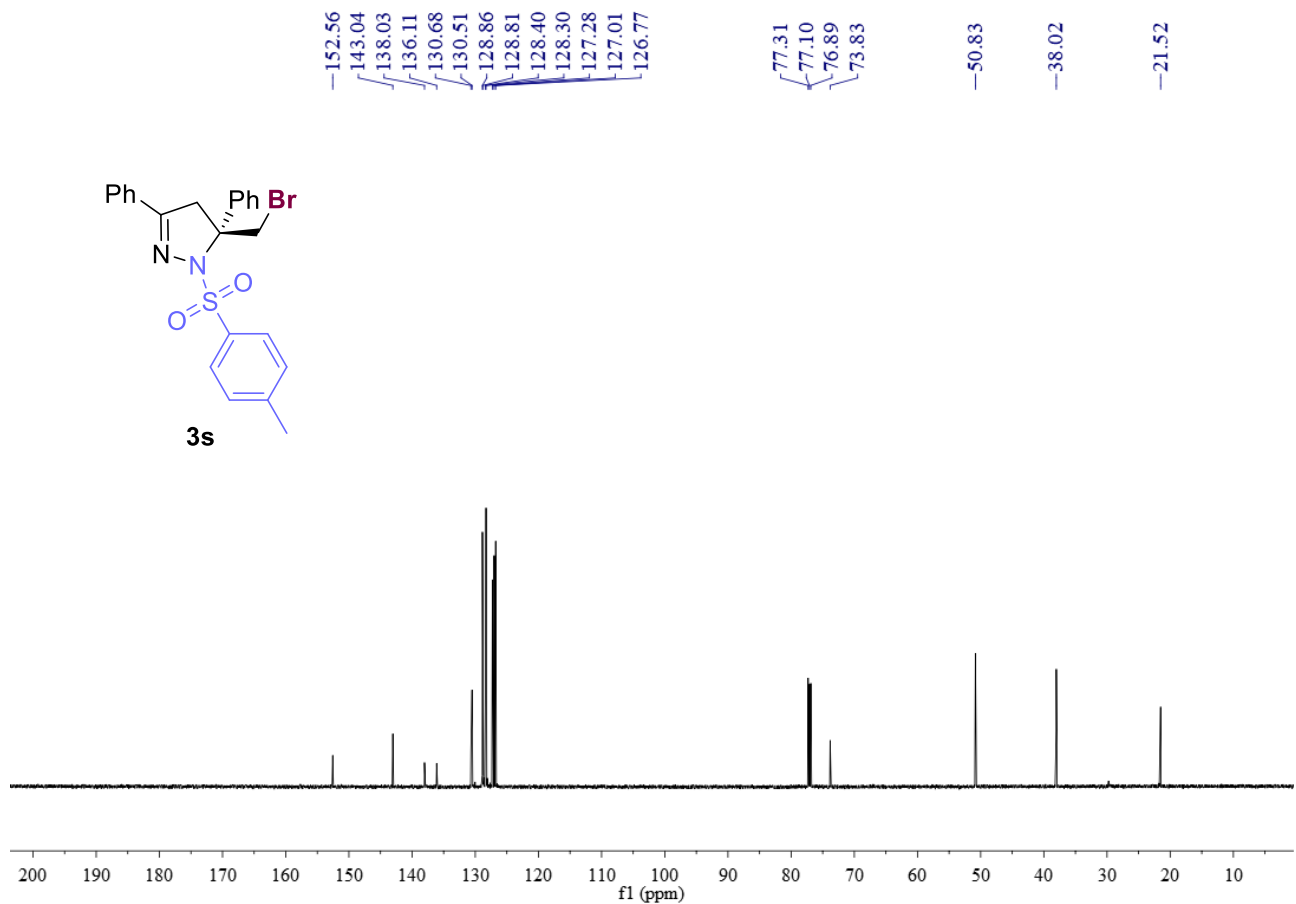
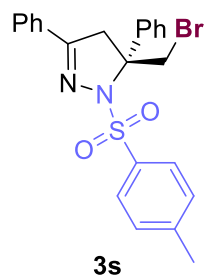
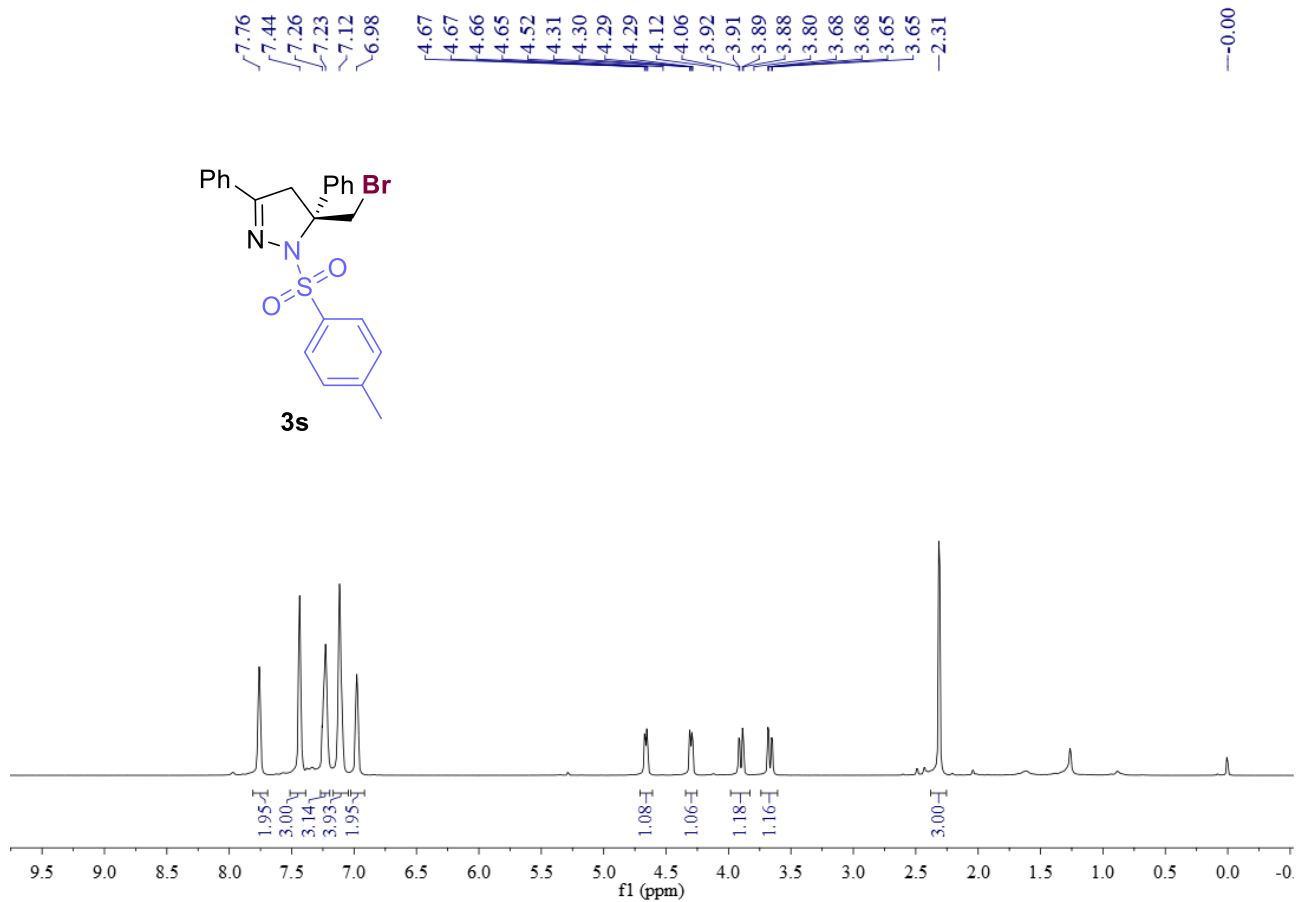
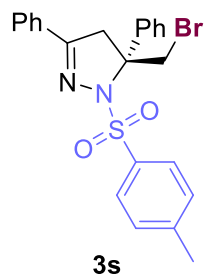


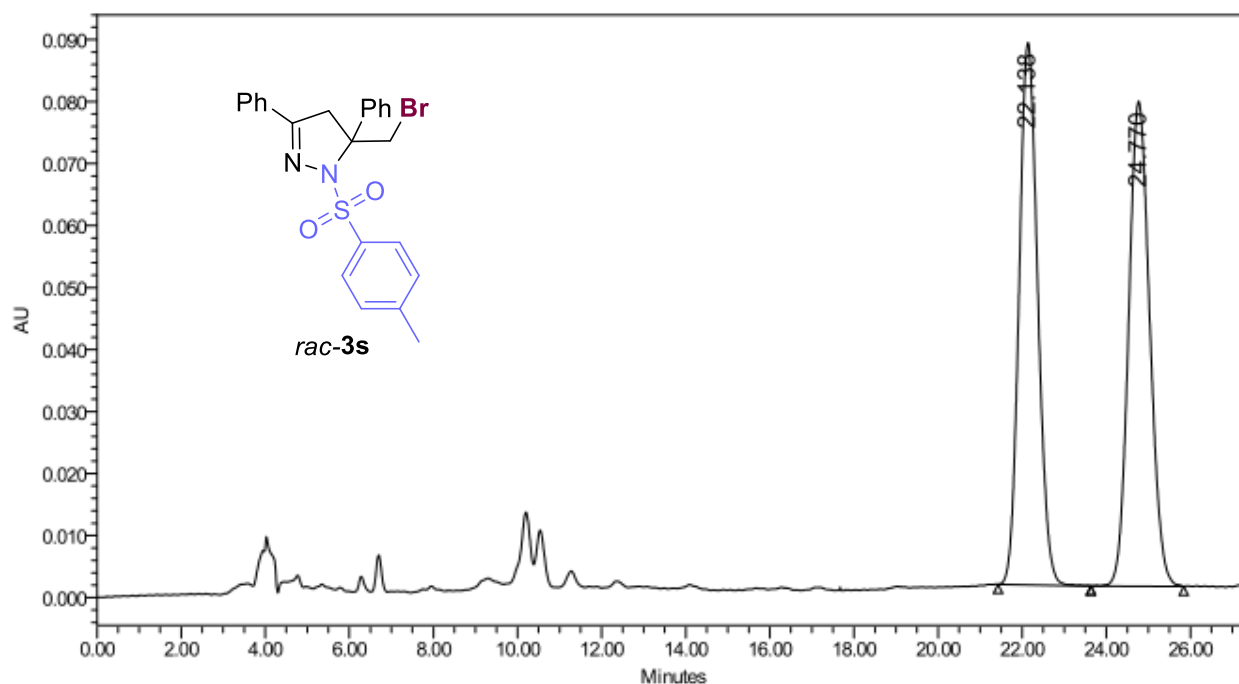


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.808	Unknown	3367452	49.99	323710	54.38	VV	461	7.522	8.290
2	9.287	Unknown	3368899	50.01	271591	45.62	Bb	537	8.883	9.778

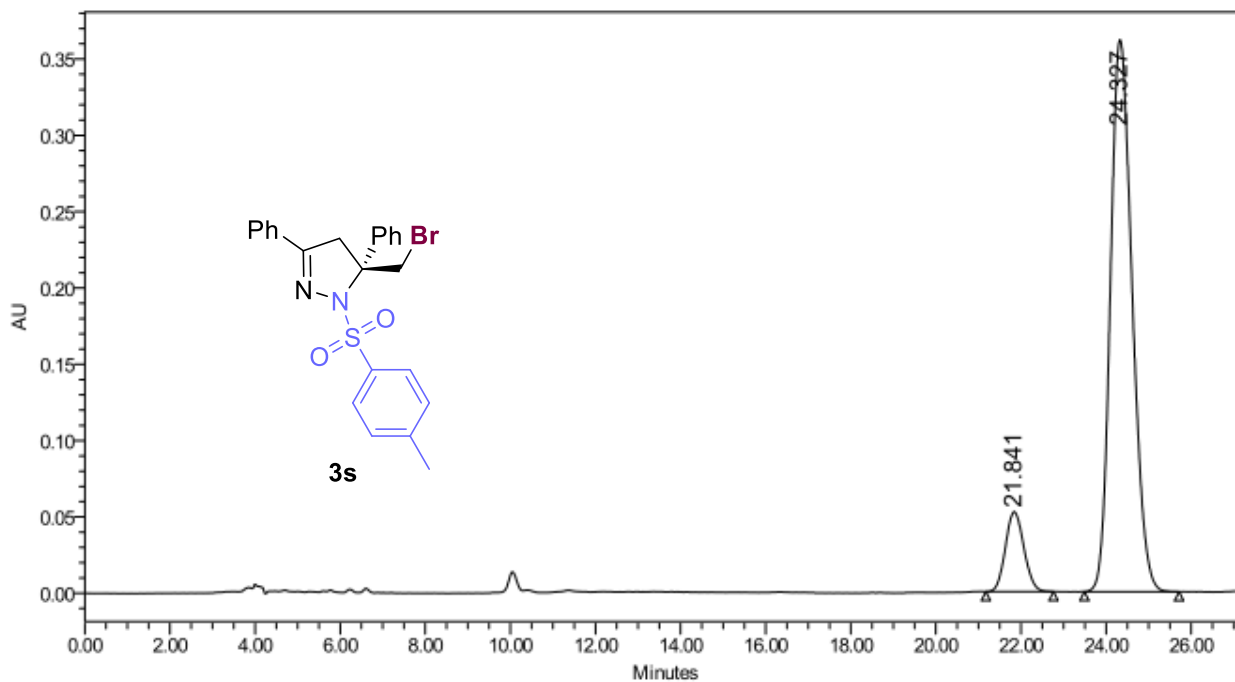


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.716	Unknown	12225838	94.90	1209146	95.47	bb	521	7.367	8.235
2	9.196	Unknown	656865	5.10	57423	4.53	bb	260	8.983	9.417

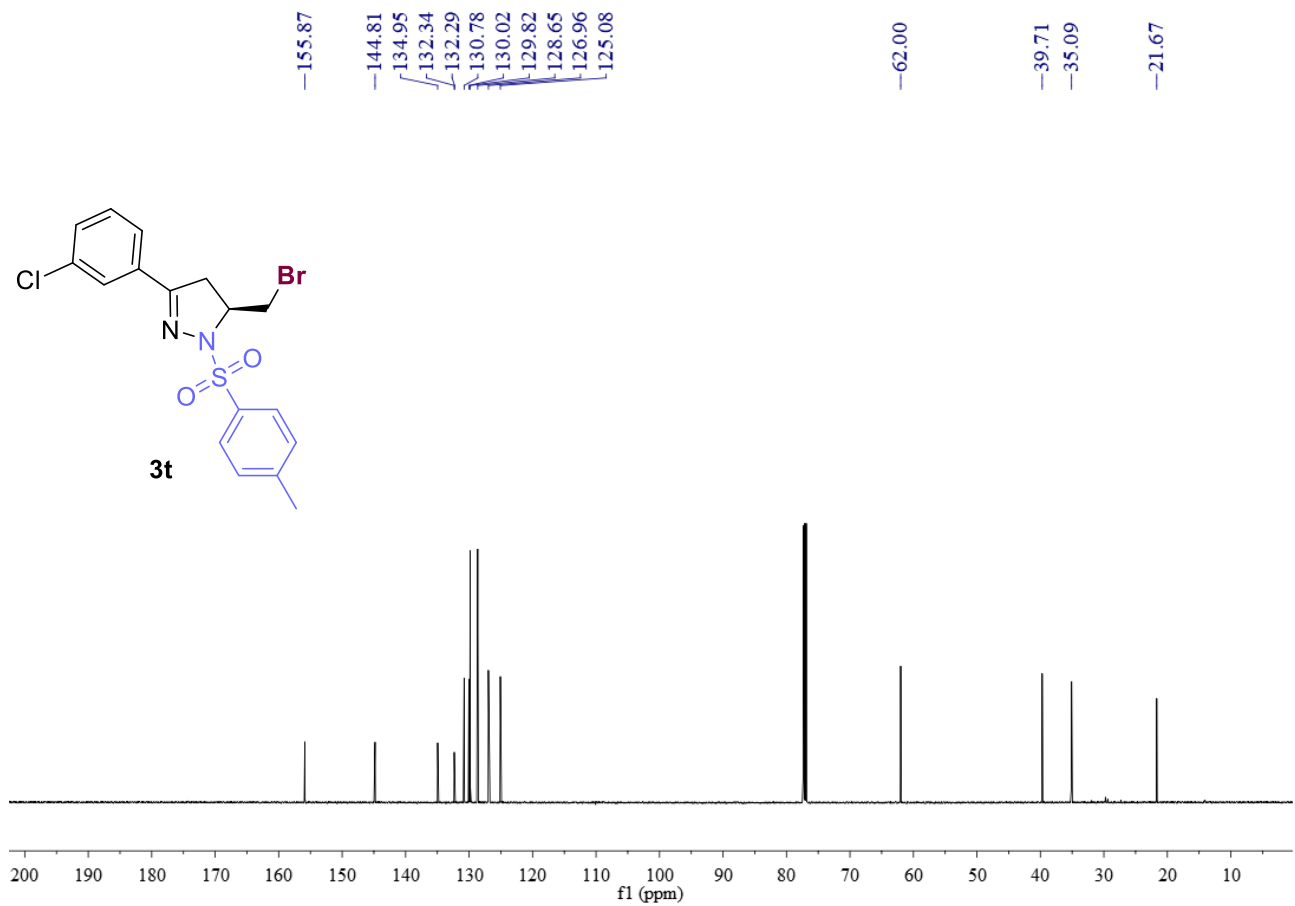
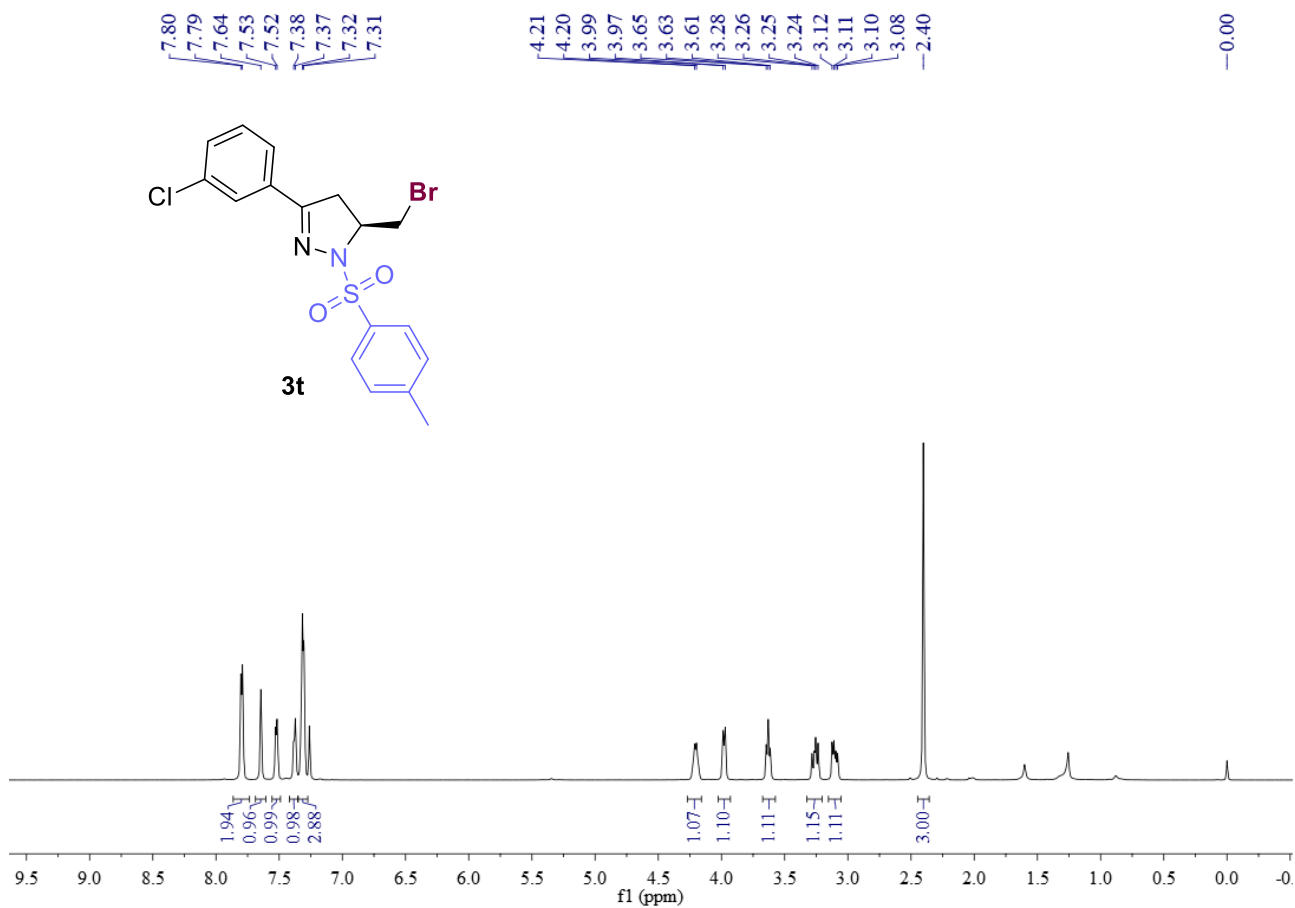


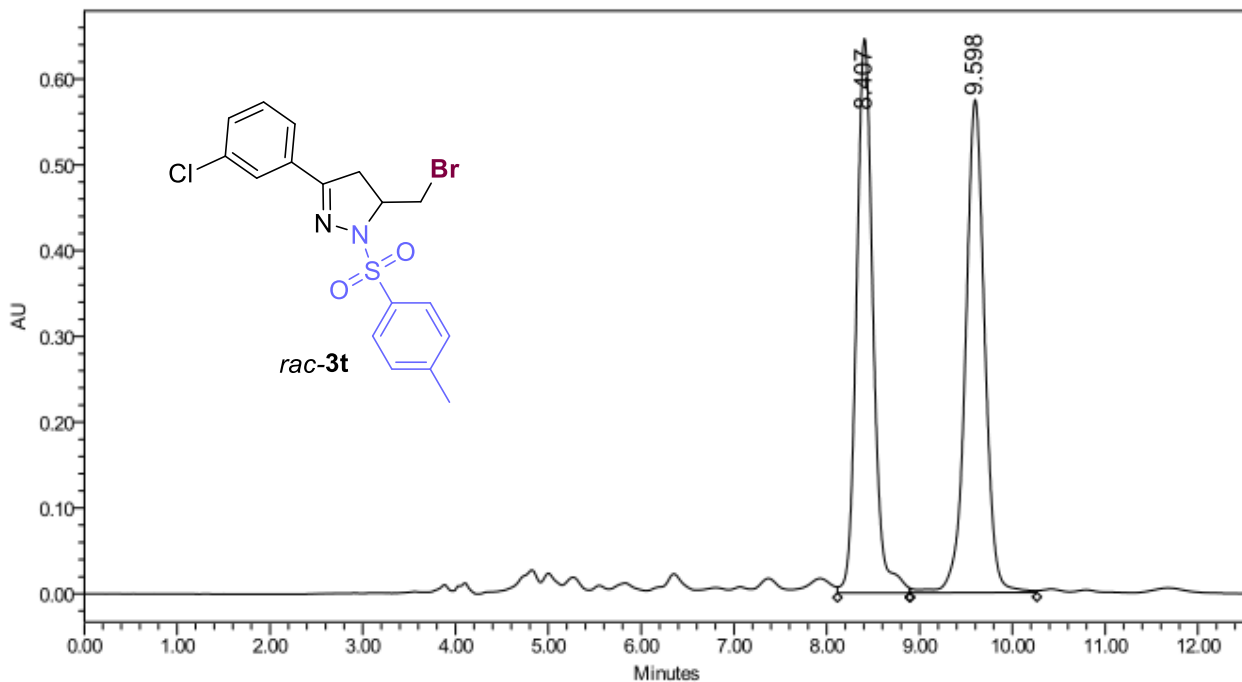


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	22.138	Unknown	2689415	49.71	87448	52.79	BB	1327	21.423	23.635
2	24.770	Unknown	2720816	50.29	78200	47.21	BB	1323	23.635	25.840

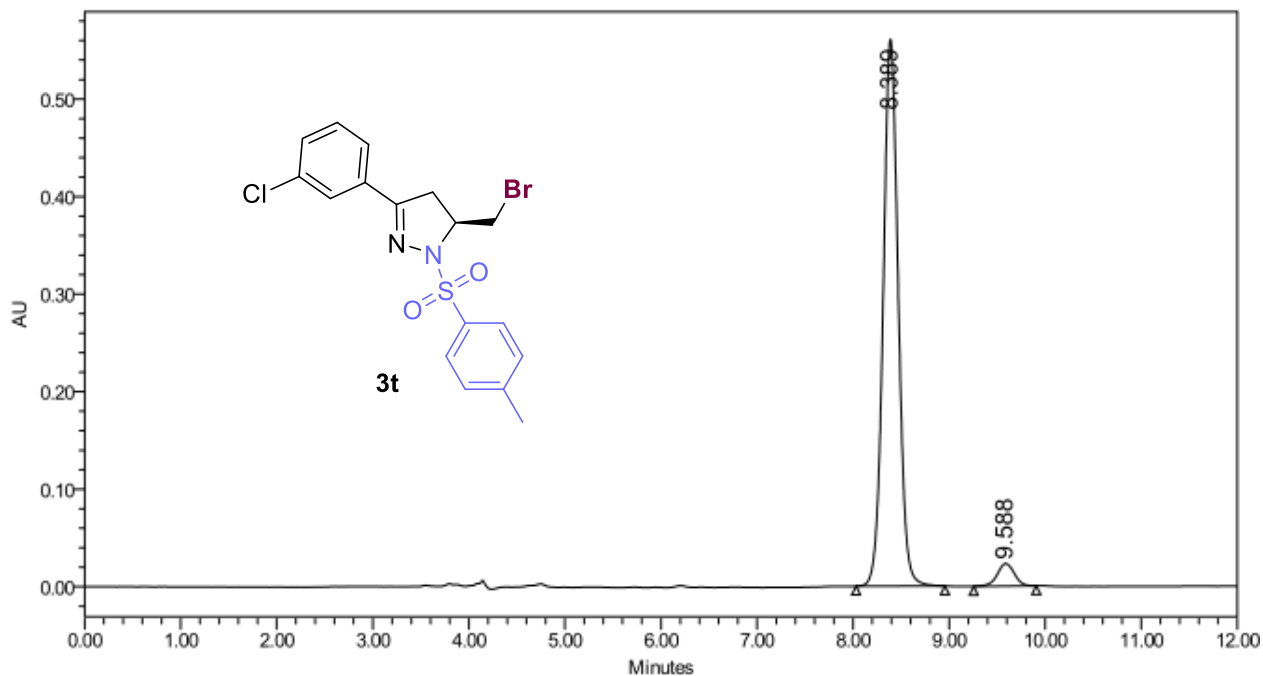


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	21.841	Unknown	1585364	11.00	52331	12.64	BB	951	21.177	22.762
2	24.327	Unknown	12832494	89.00	361588	87.36	BB	1336	23.488	25.715

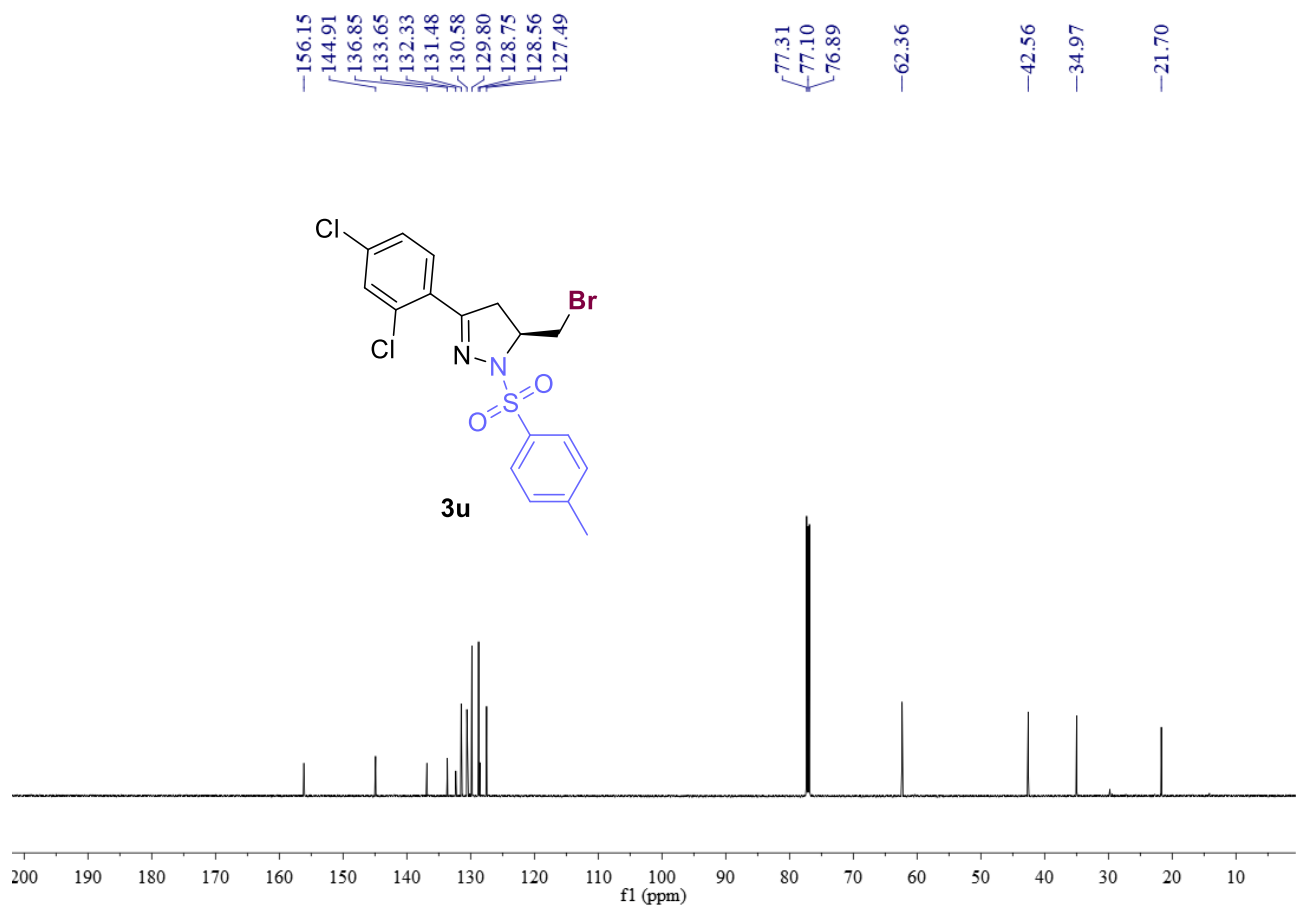
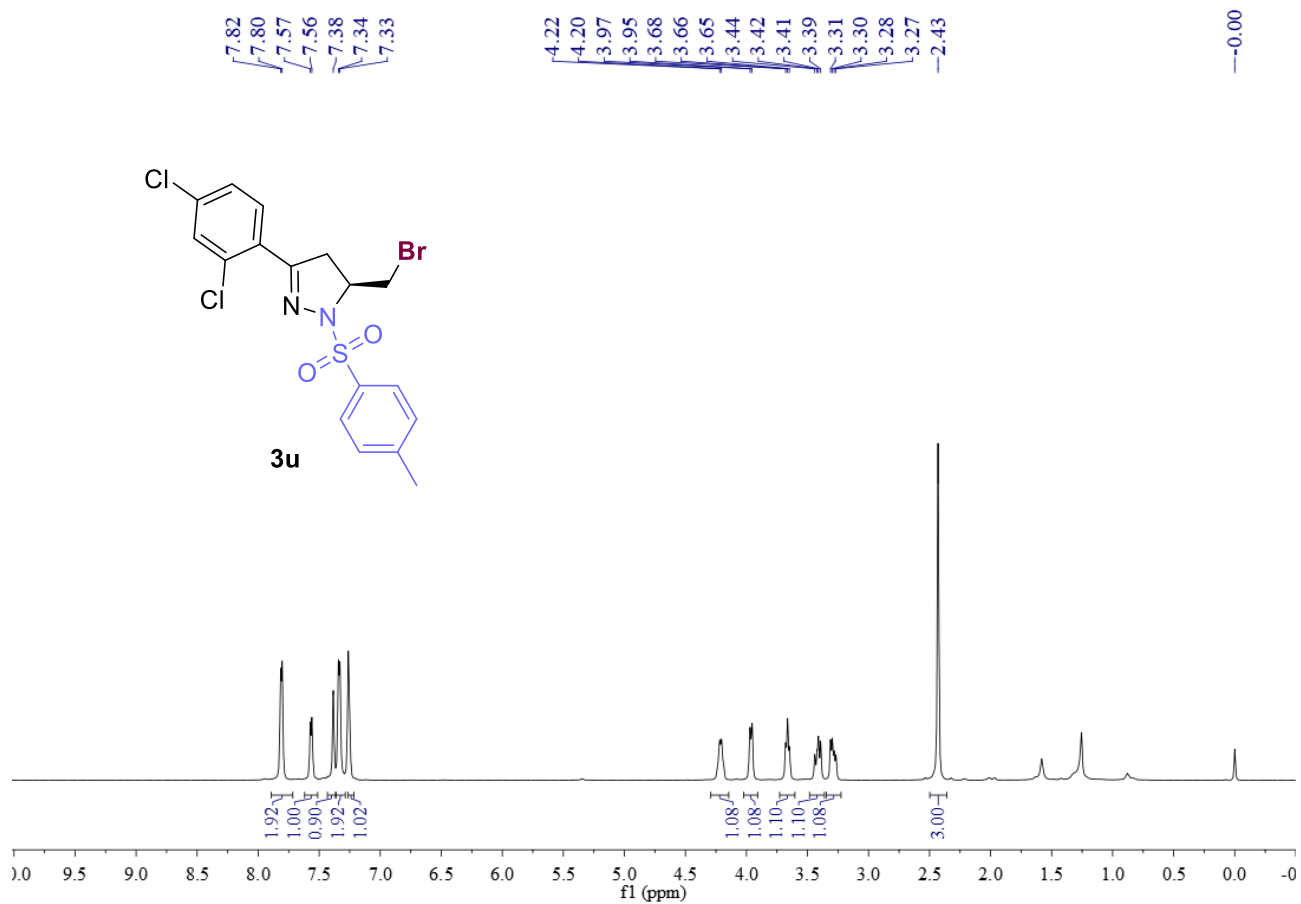


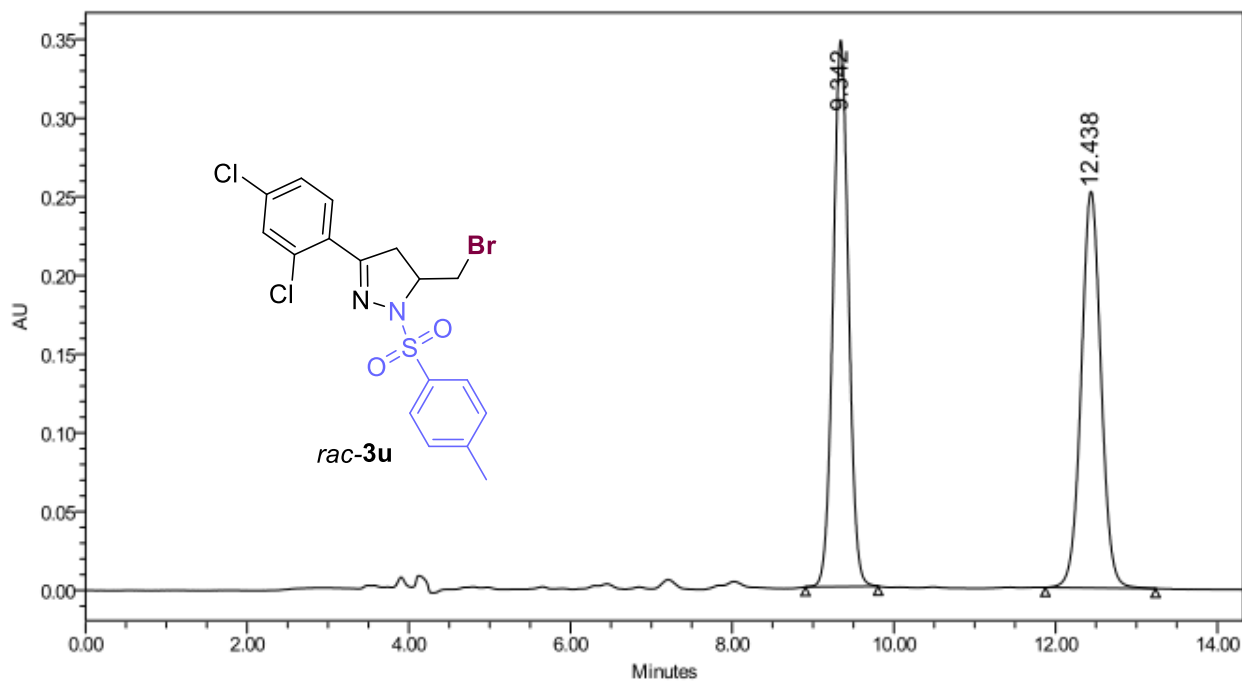


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.407	Unknown	8000839	49.22	646115	52.93	Vv	468	8.115	8.895
2	9.598	Unknown	8254799	50.78	574482	47.07	vV	822	8.895	10.265

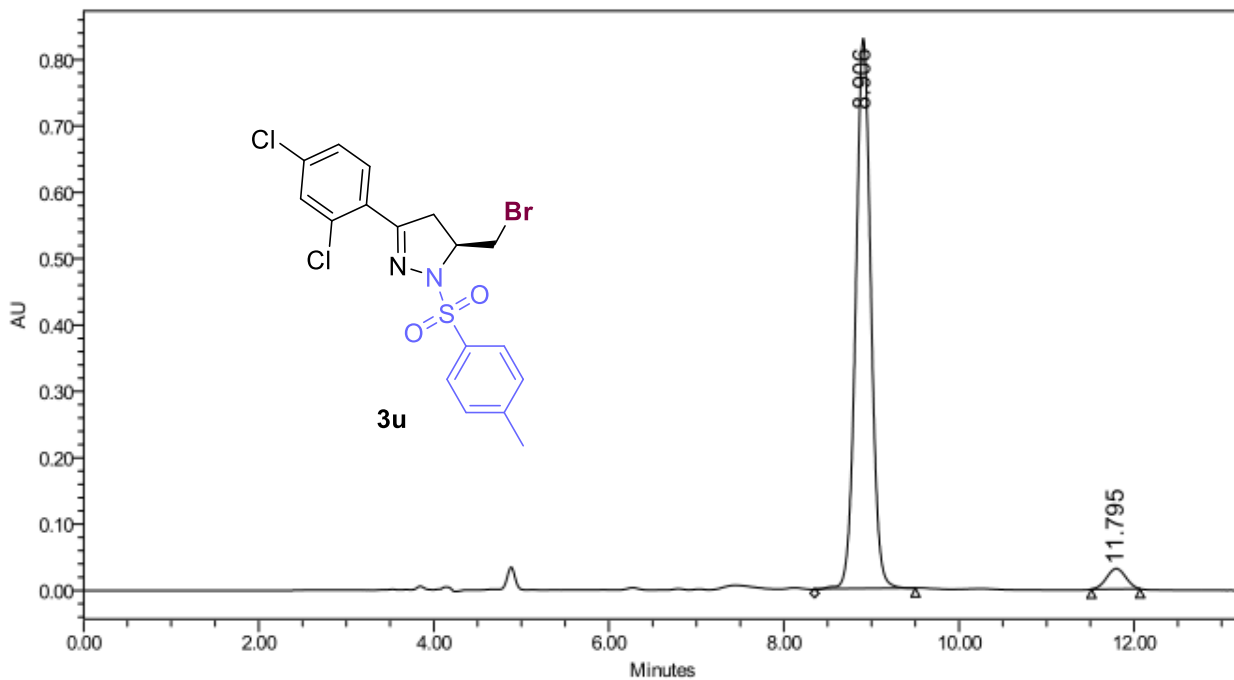


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.389	Unknown	6094271	95.56	560813	96.07	BB	554	8.032	8.955
2	9.588	Unknown	282894	4.44	22932	3.93	BB	391	9.255	9.907

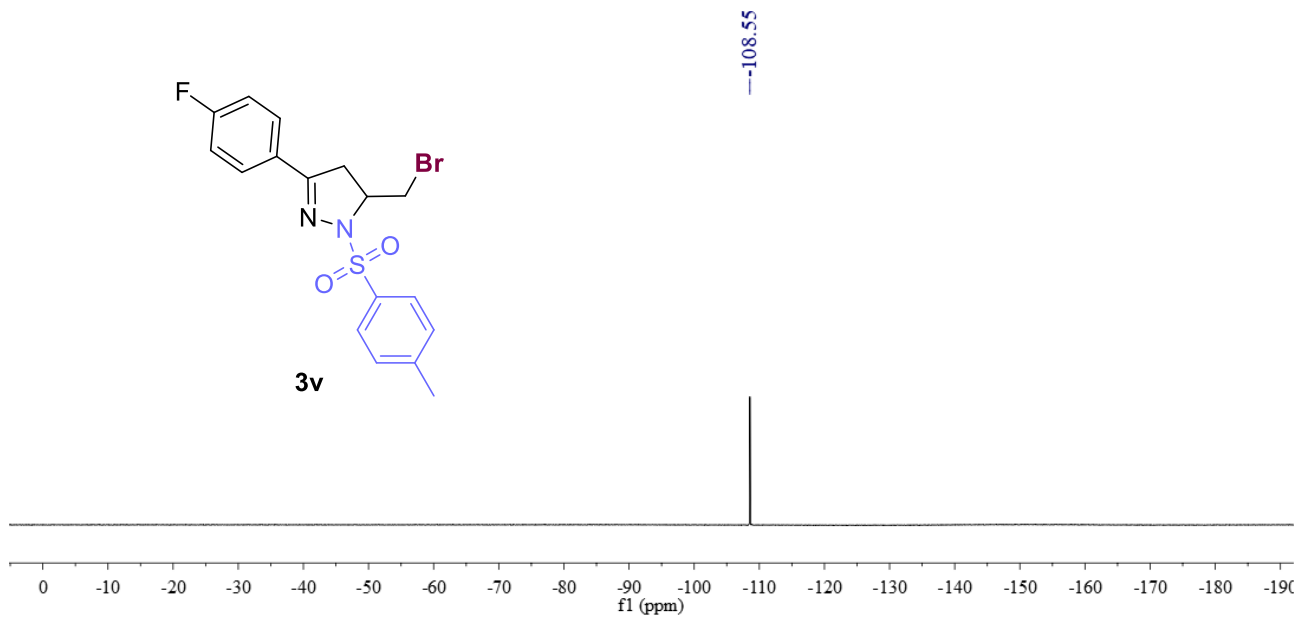
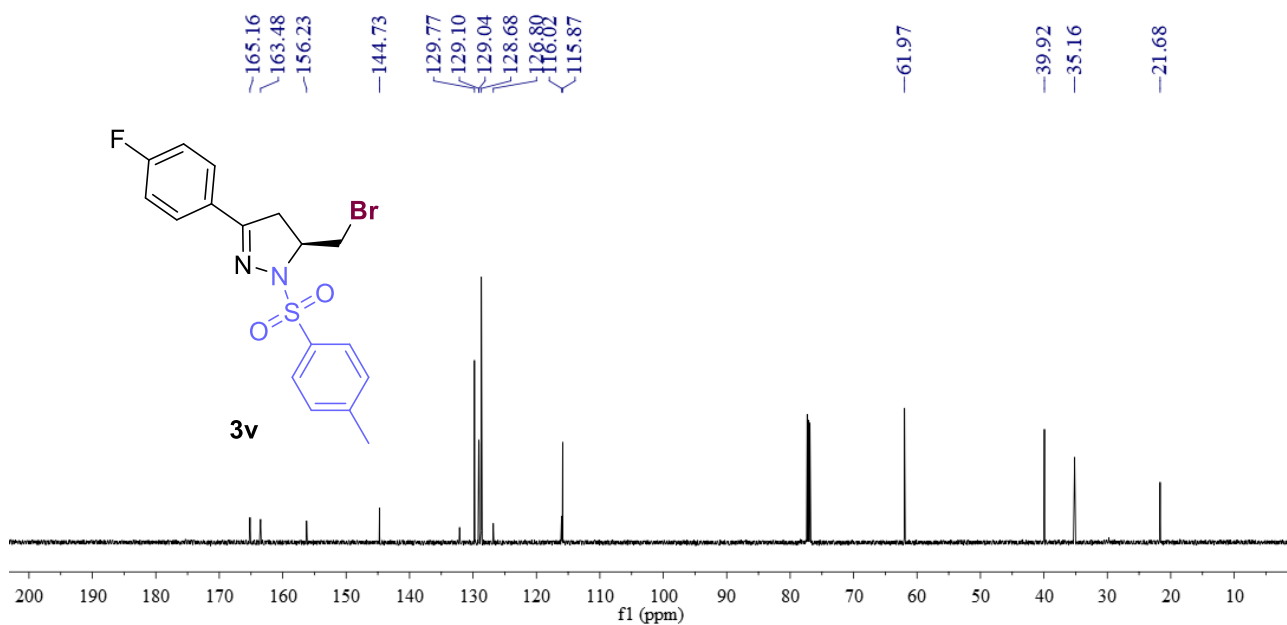
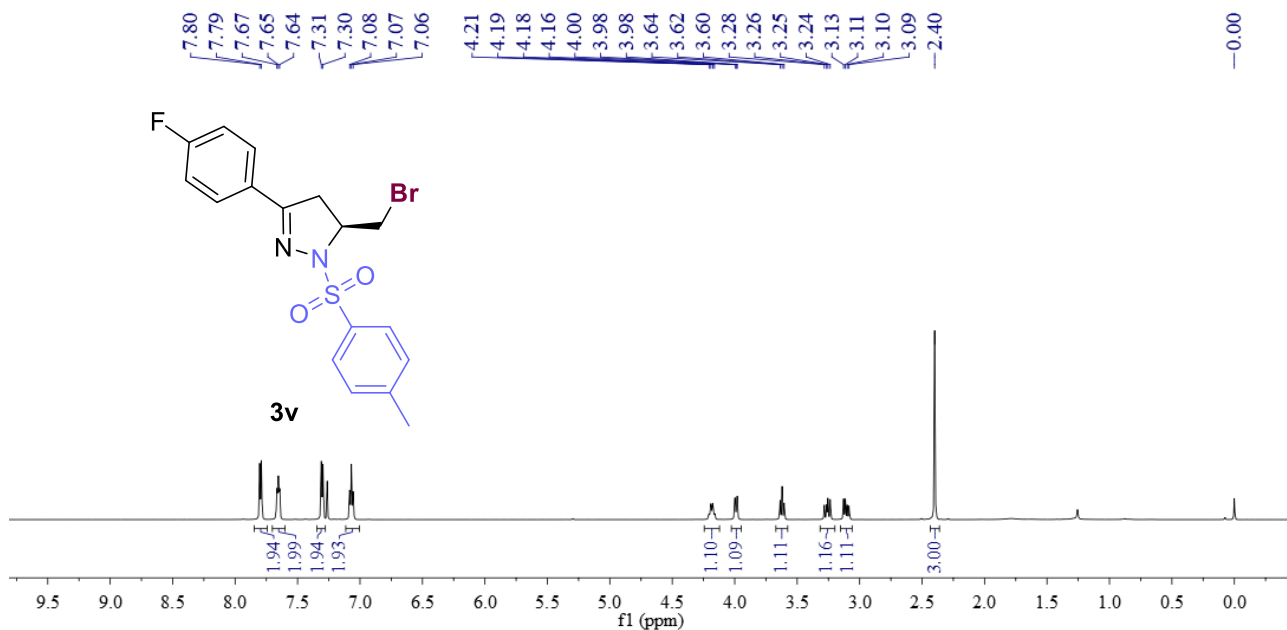


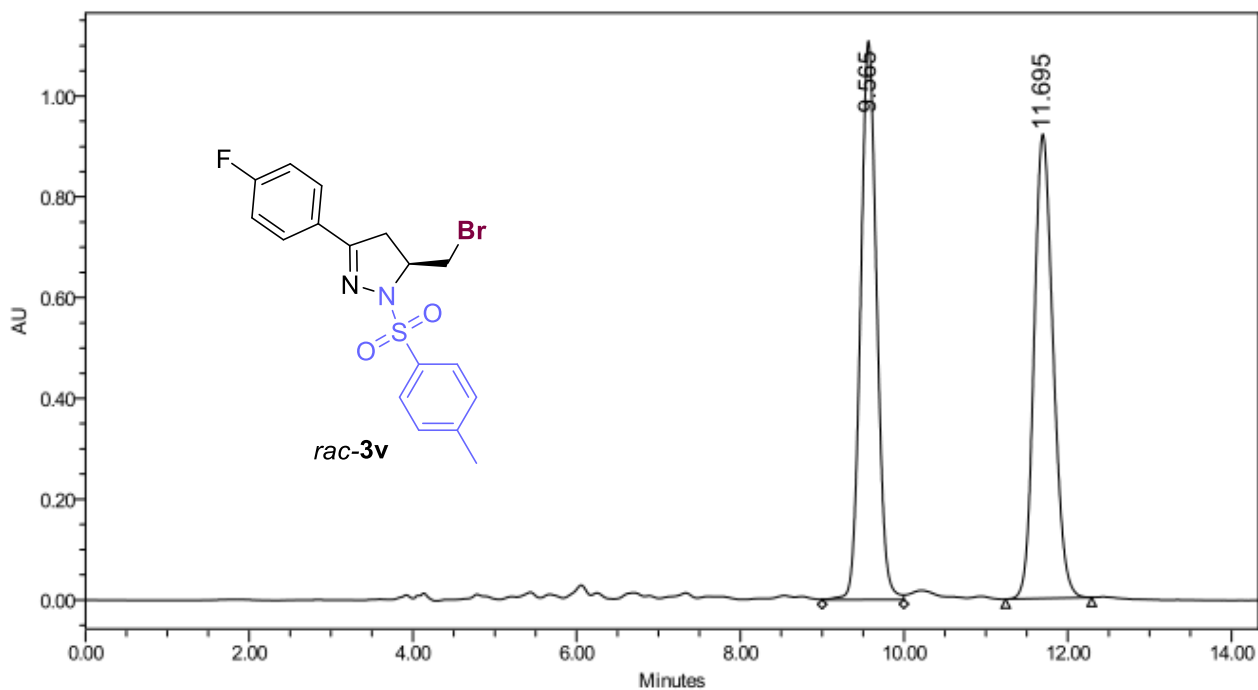


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.342	Unknown	4623967	51.89	347138	57.95	bb	539	8.907	9.805
2	12.438	Unknown	4286547	48.11	251912	42.05	bb	819	11.873	13.238

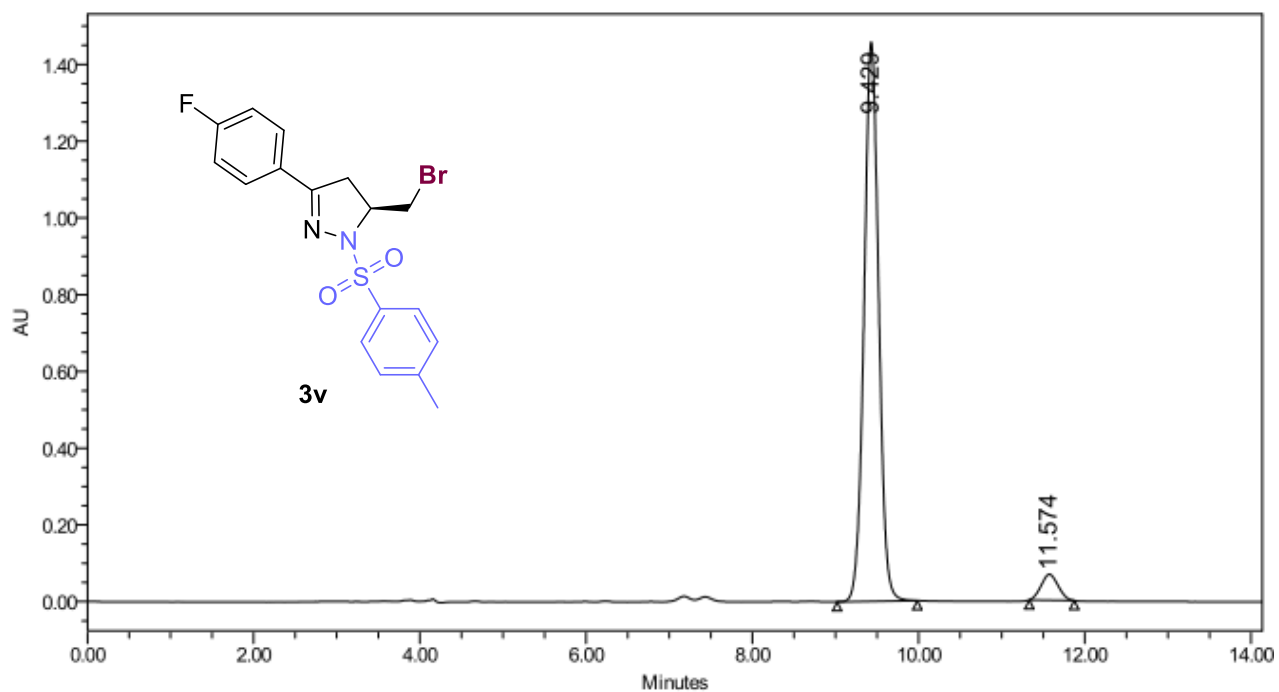


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.906	Unknown	9969301	95.51	828834	96.42	Vb	691	8.350	9.502
2	11.795	Unknown	468976	4.49	30817	3.58	bb	334	11.512	12.068

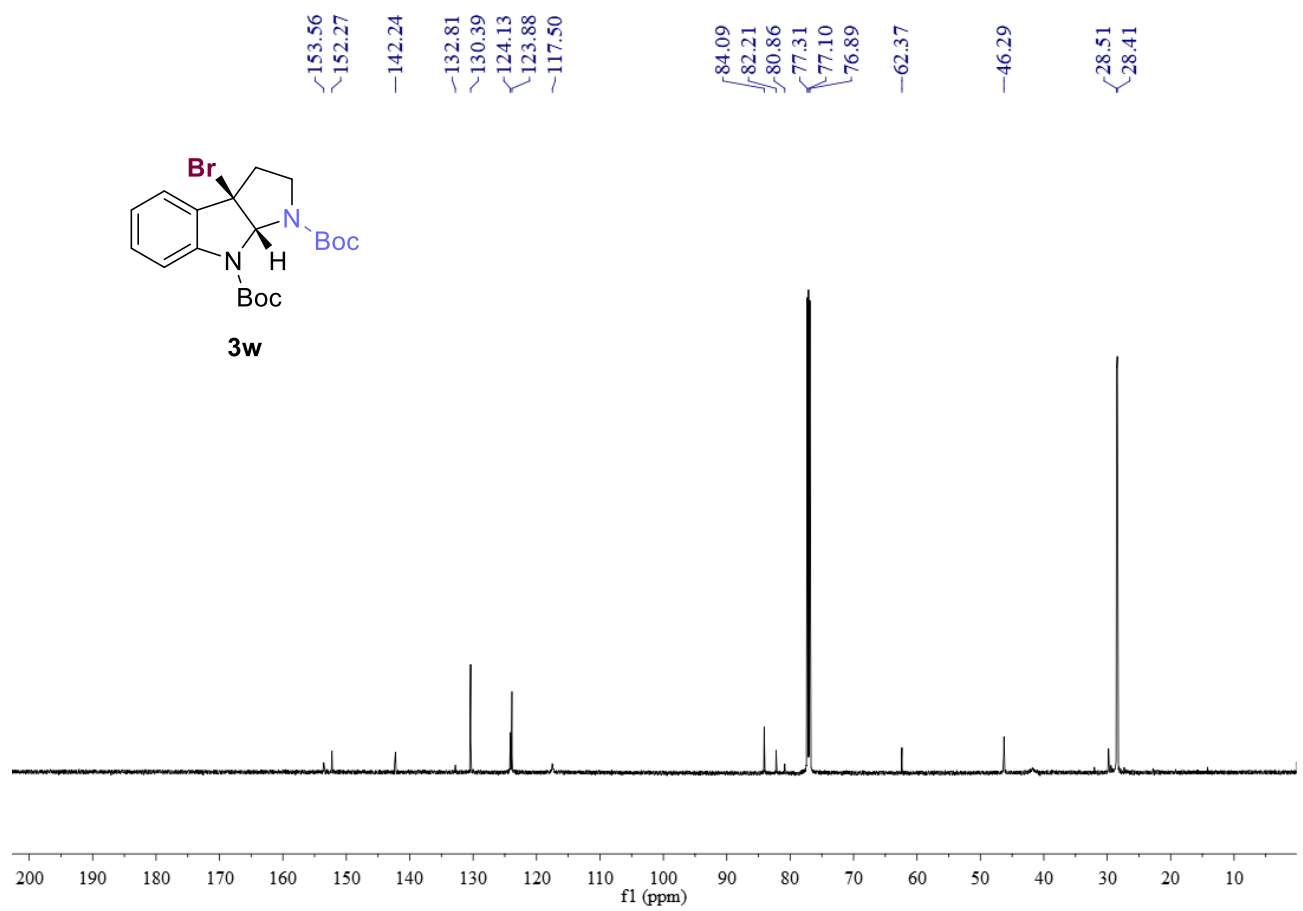
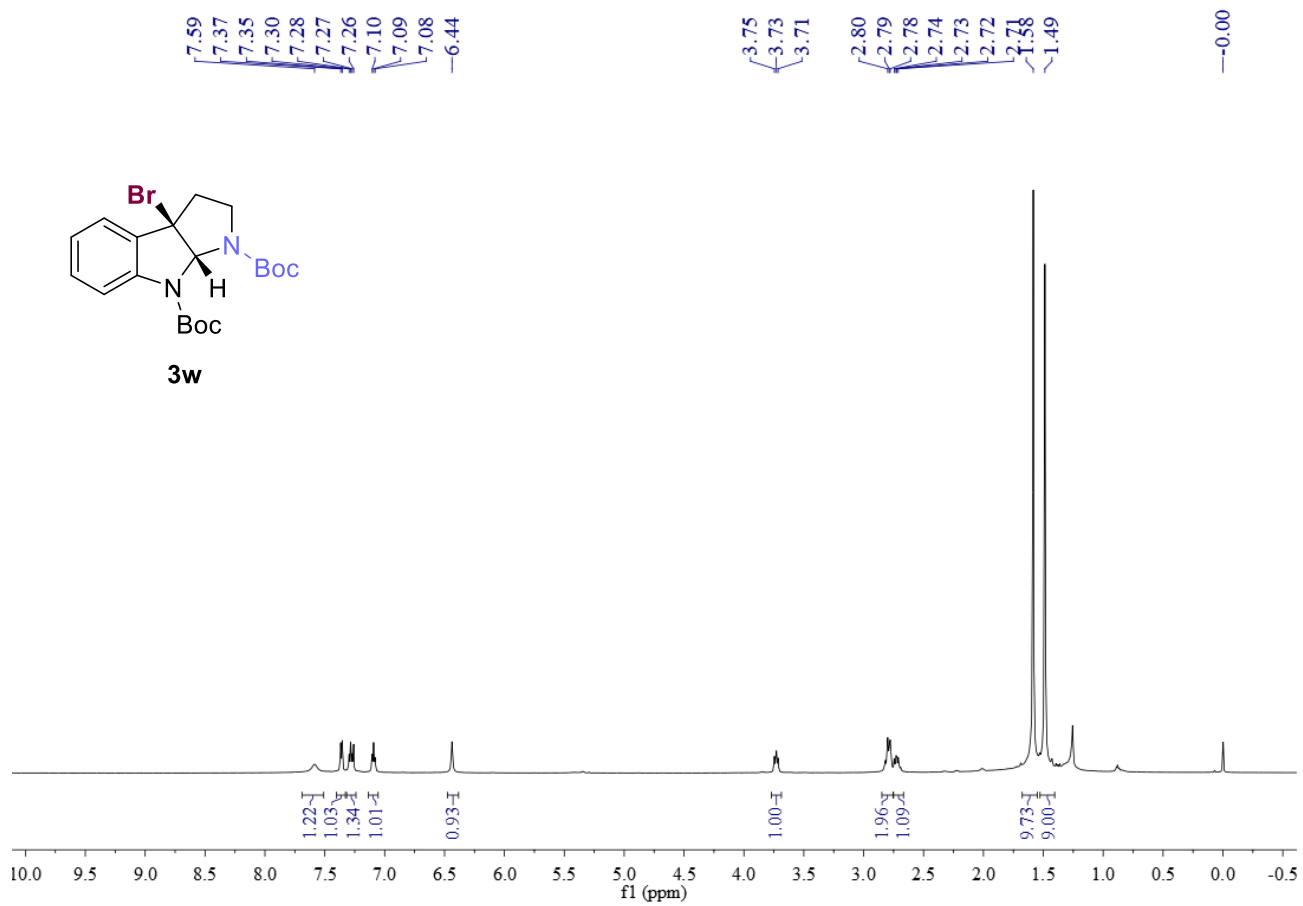


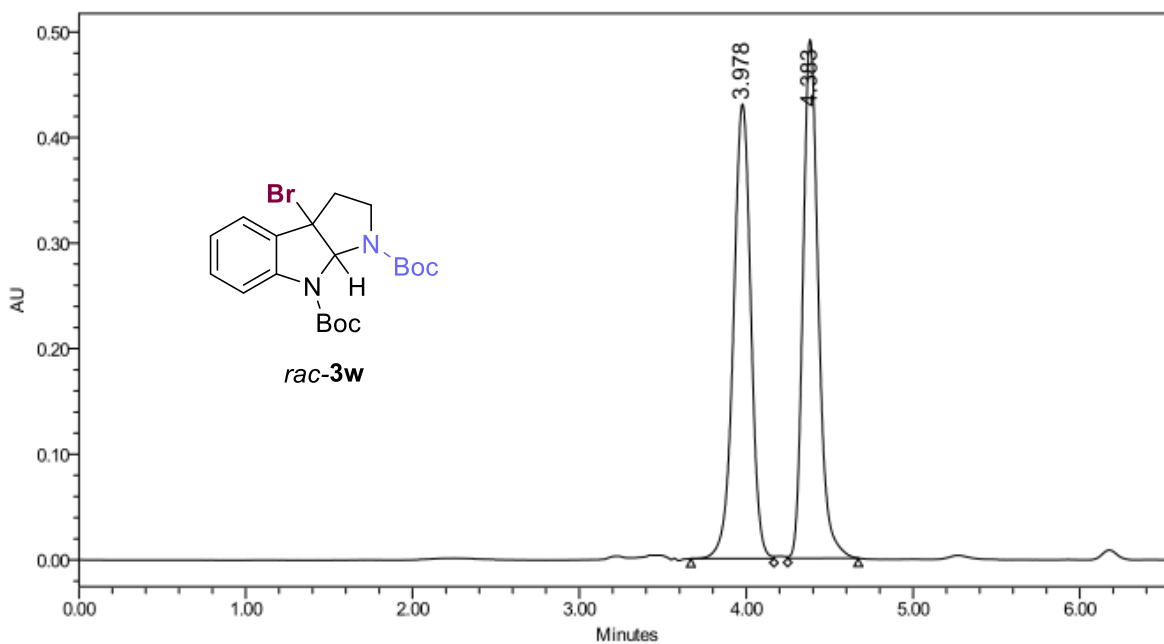


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)
1	9.565	Unknown	15185821	50.44	1108497	54.62	VV	598	9.000
2	11.695	Unknown	14923500	49.56	920857	45.38	BB	631	11.242

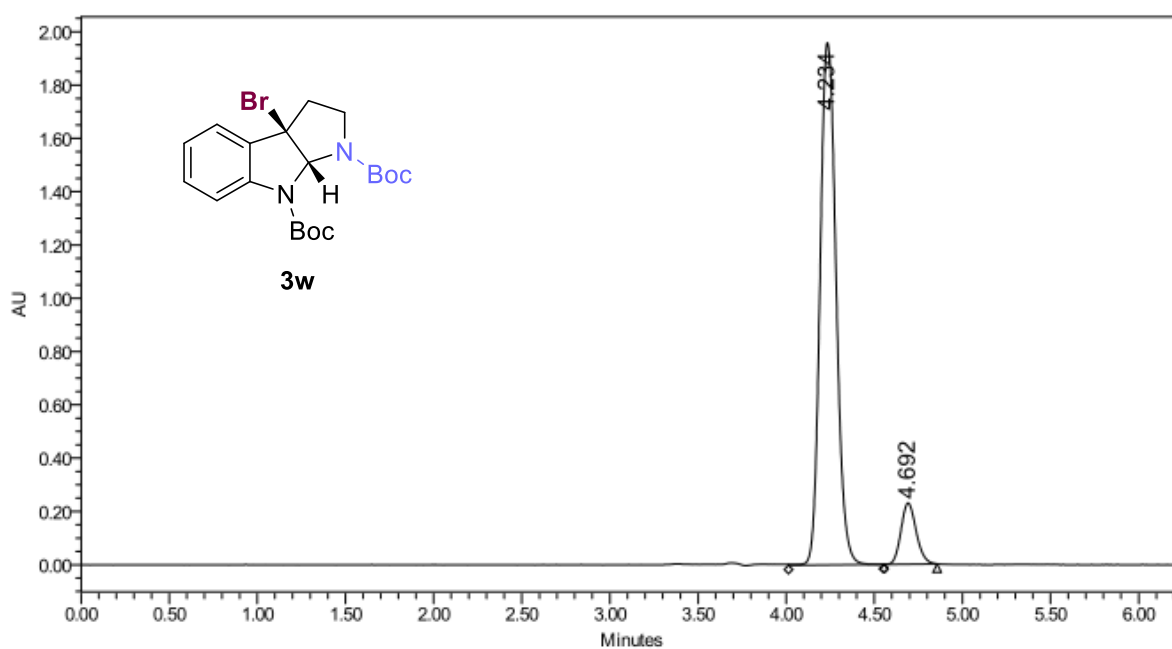


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)
1	9.429	Unknown	17768472	94.88	1457285	95.57	Bb	579	9.020
2	11.574	Unknown	958708	5.12	67612	4.43	bb	323	11.333

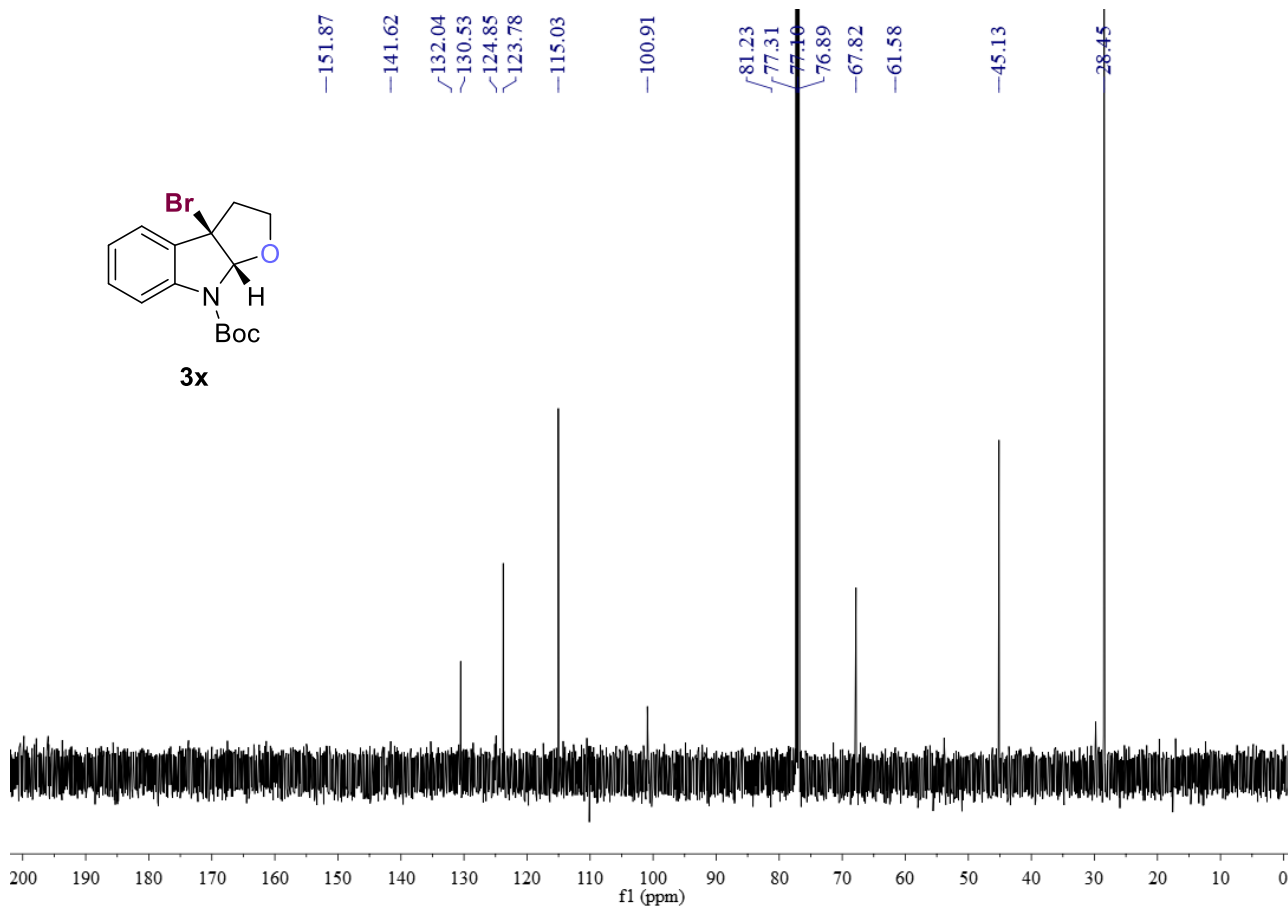
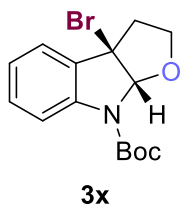
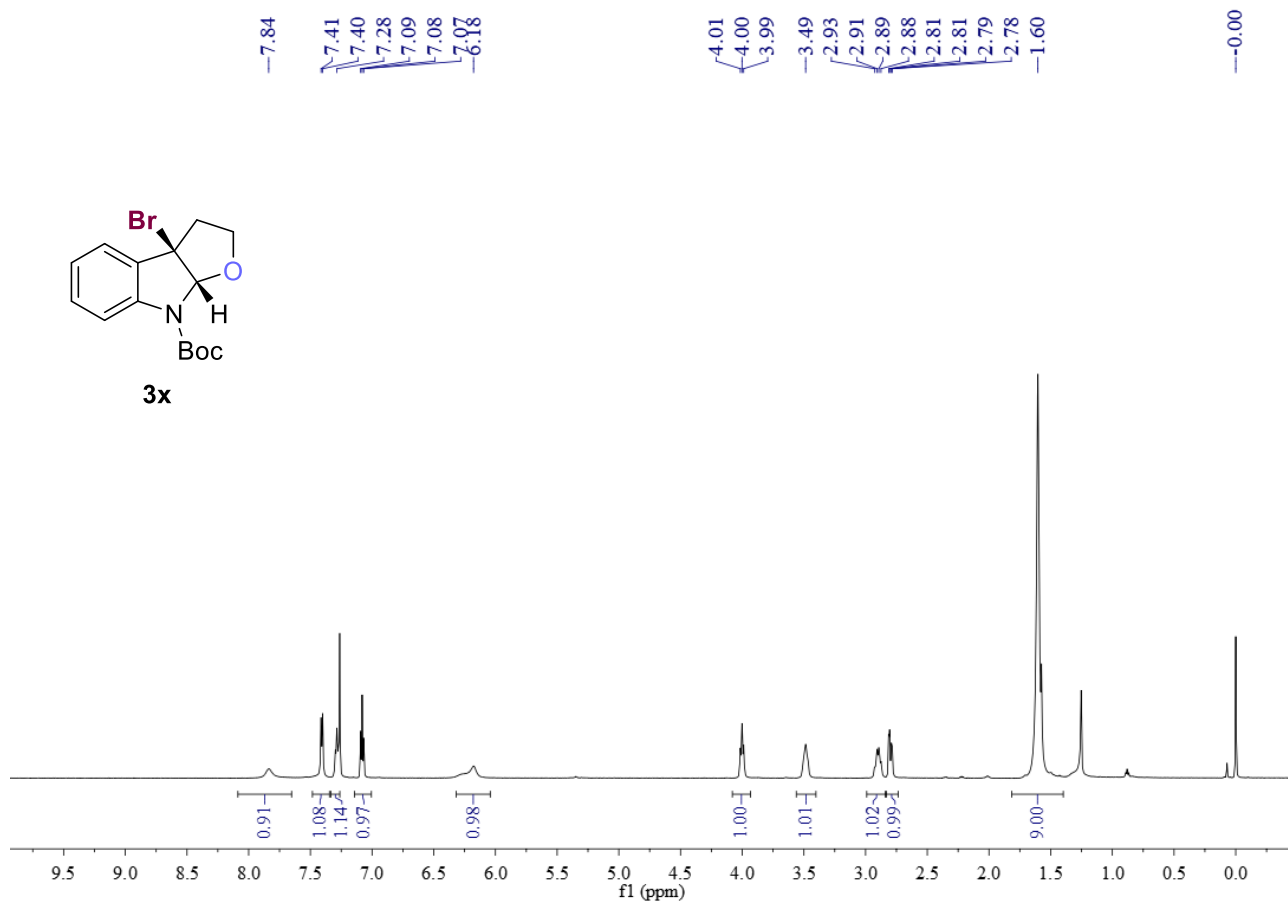
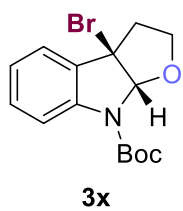


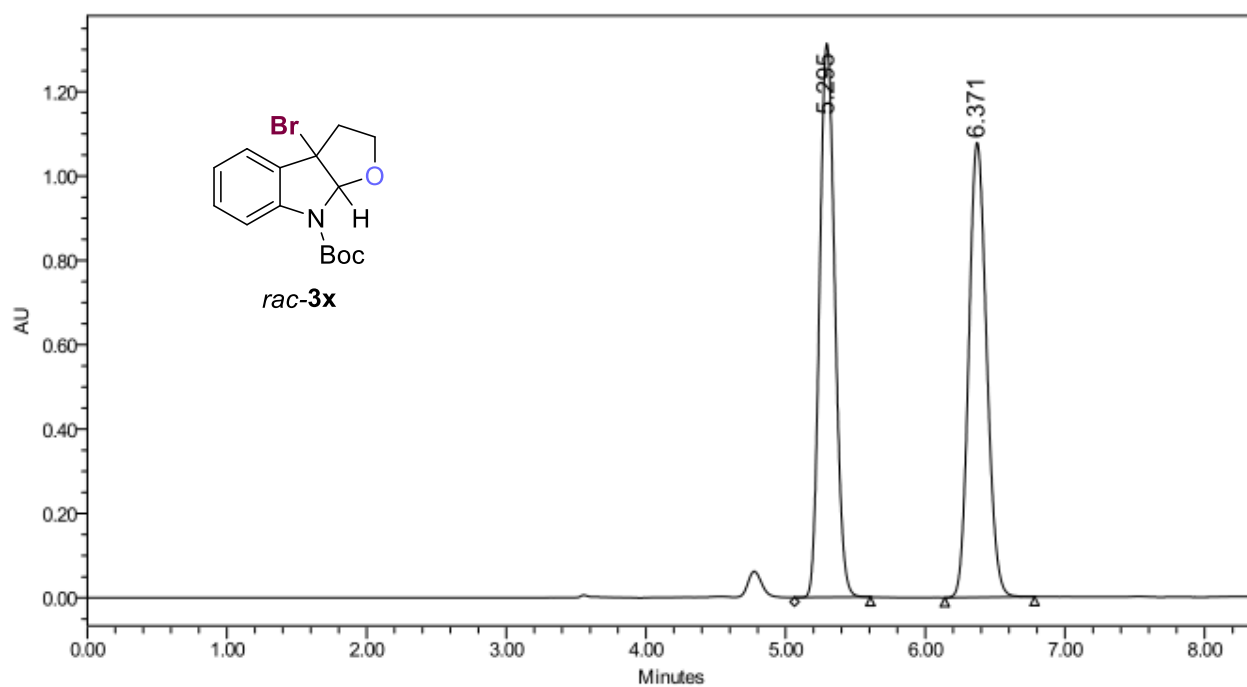


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	3.978	Unknown	3114367	49.91	430486	46.70	bV	299	3.668	4.167
2	4.383	Unknown	3125923	50.09	491379	53.30	Vb	254	4.248	4.672

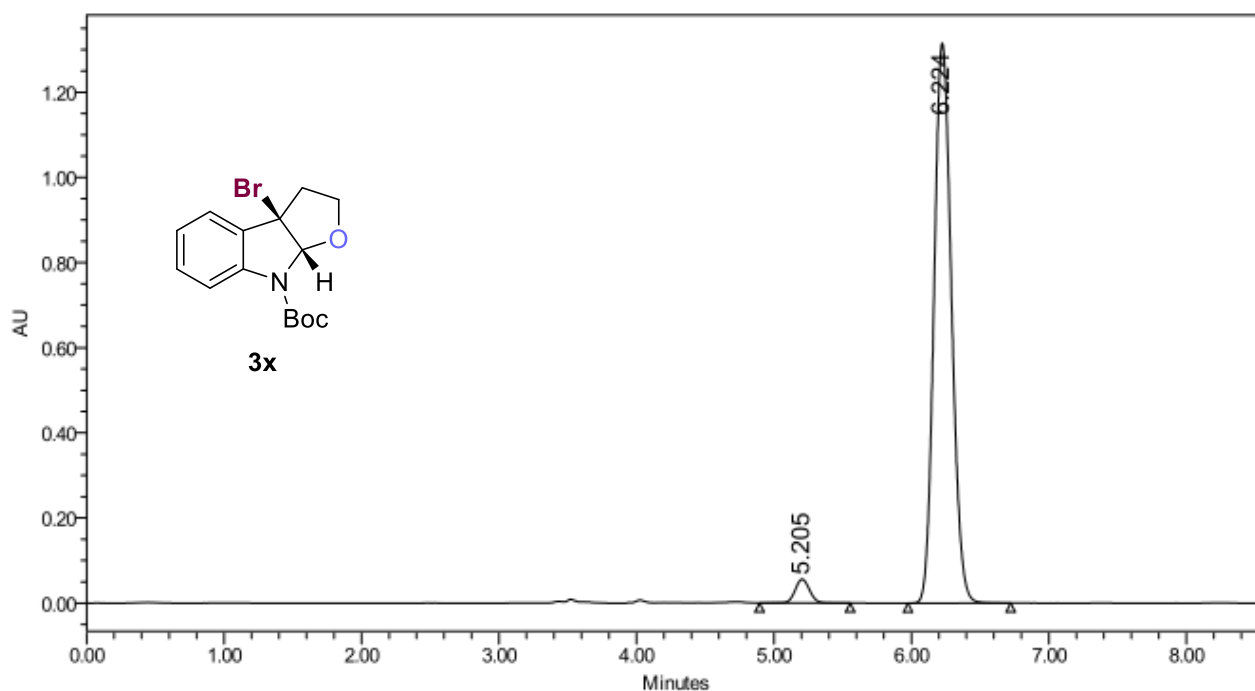


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	4.234	Unknown	12329235	89.95	1958707	89.50	VV	325	4.013	4.555
2	4.692	Unknown	1376851	10.05	229757	10.50	Vb	181	4.555	4.857



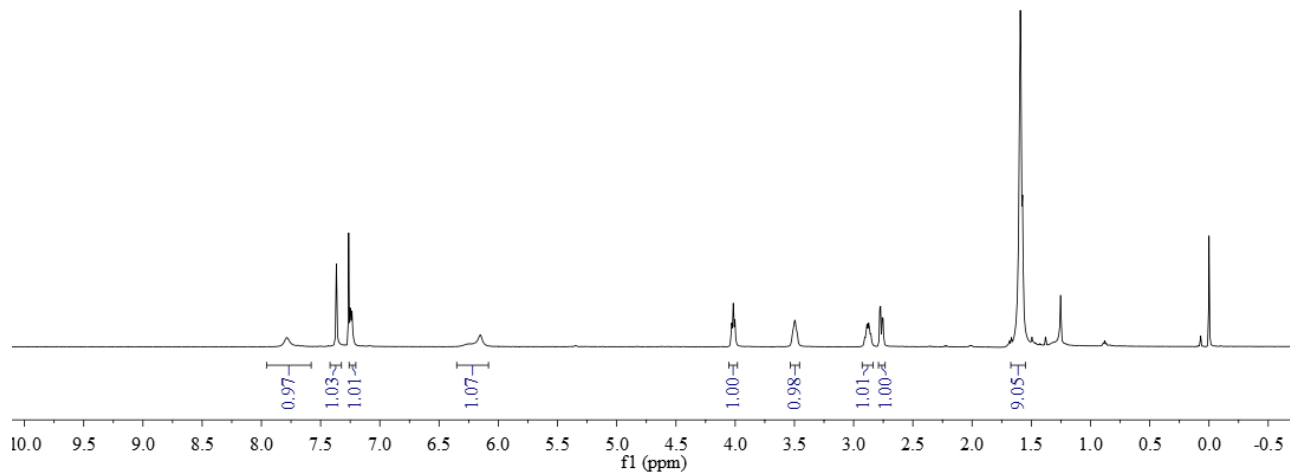
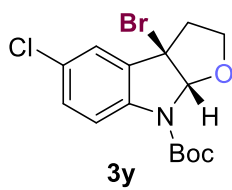


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.295	Unknown	9939263	50.94	1312917	54.90	Vb	326	5.063	5.607
2	6.371	Unknown	9574075	49.06	1078510	45.10	BB	385	6.140	6.782

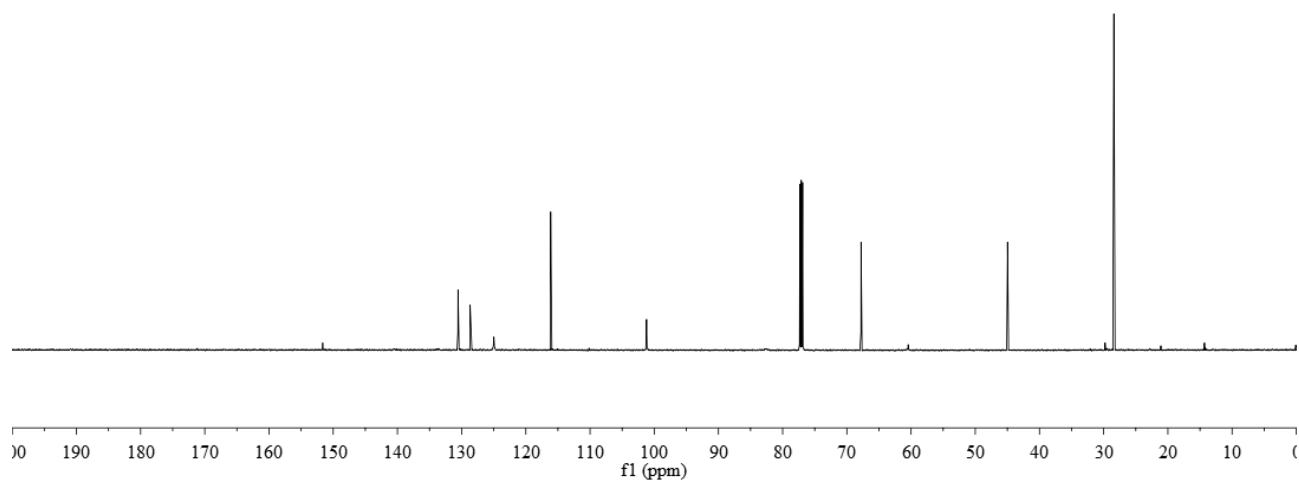
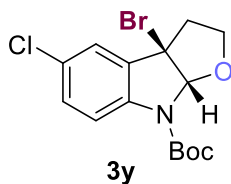


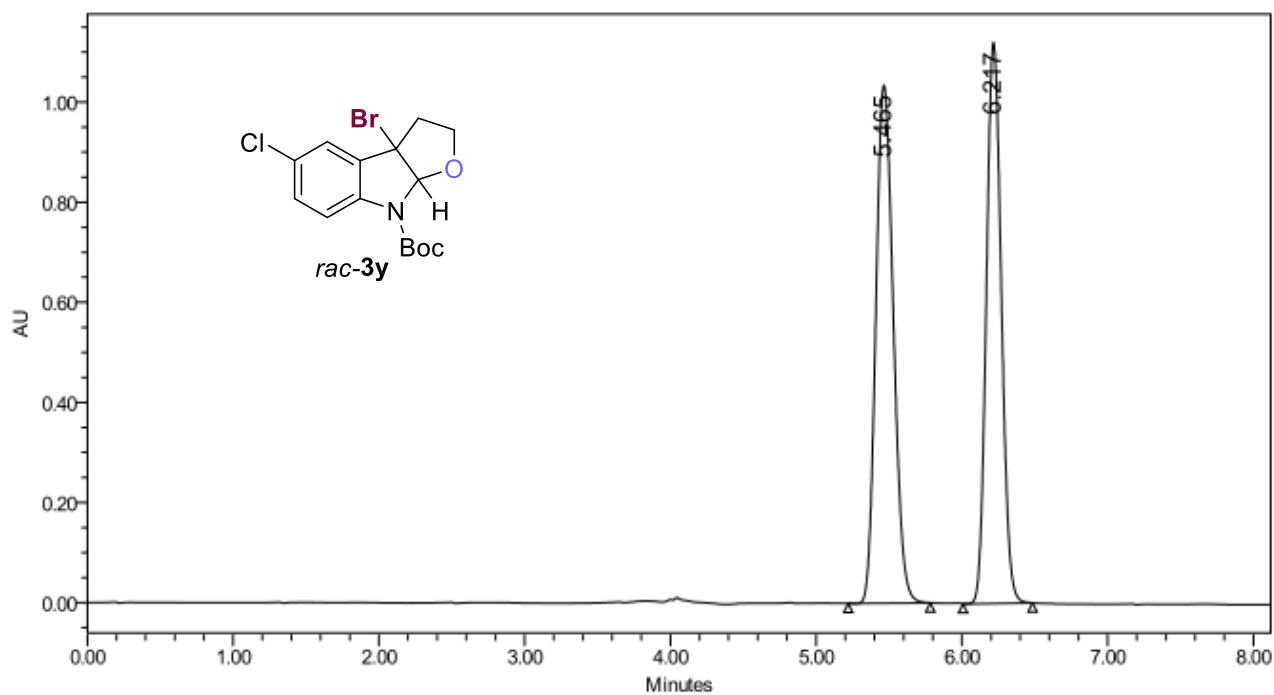
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.205	Unknown	411805	3.43	55880	4.07	BB	396	4.895	5.555
2	6.224	Unknown	11593217	96.57	1315584	95.93	BB	448	5.975	6.722

7.78, 7.37, 7.26, 7.25, 7.24, -6.15, 4.03, 4.02, 4.00, -3.50, 2.89, 2.87, 2.86, 2.78, 2.77, 2.76, 2.75, -1.59, -0.00

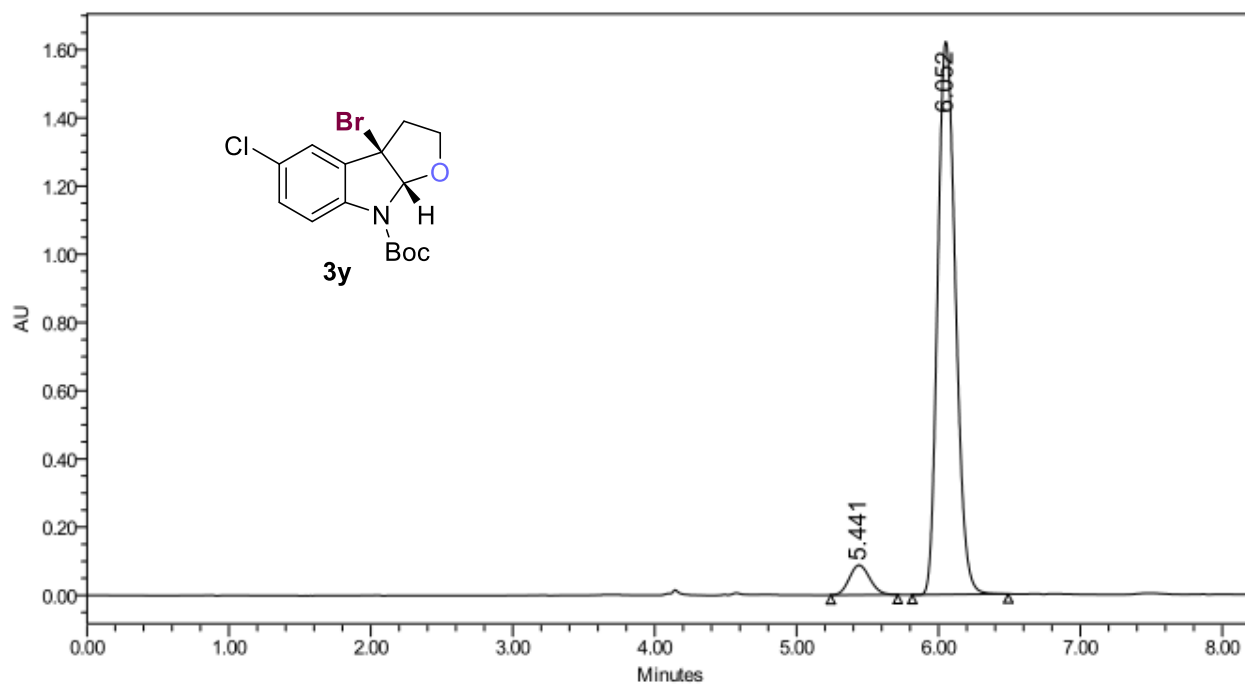


151.64, 130.56, 128.68, 124.98, 116.13, 101.20, 67.79, 60.44, 44.97, 29.78, 28.41

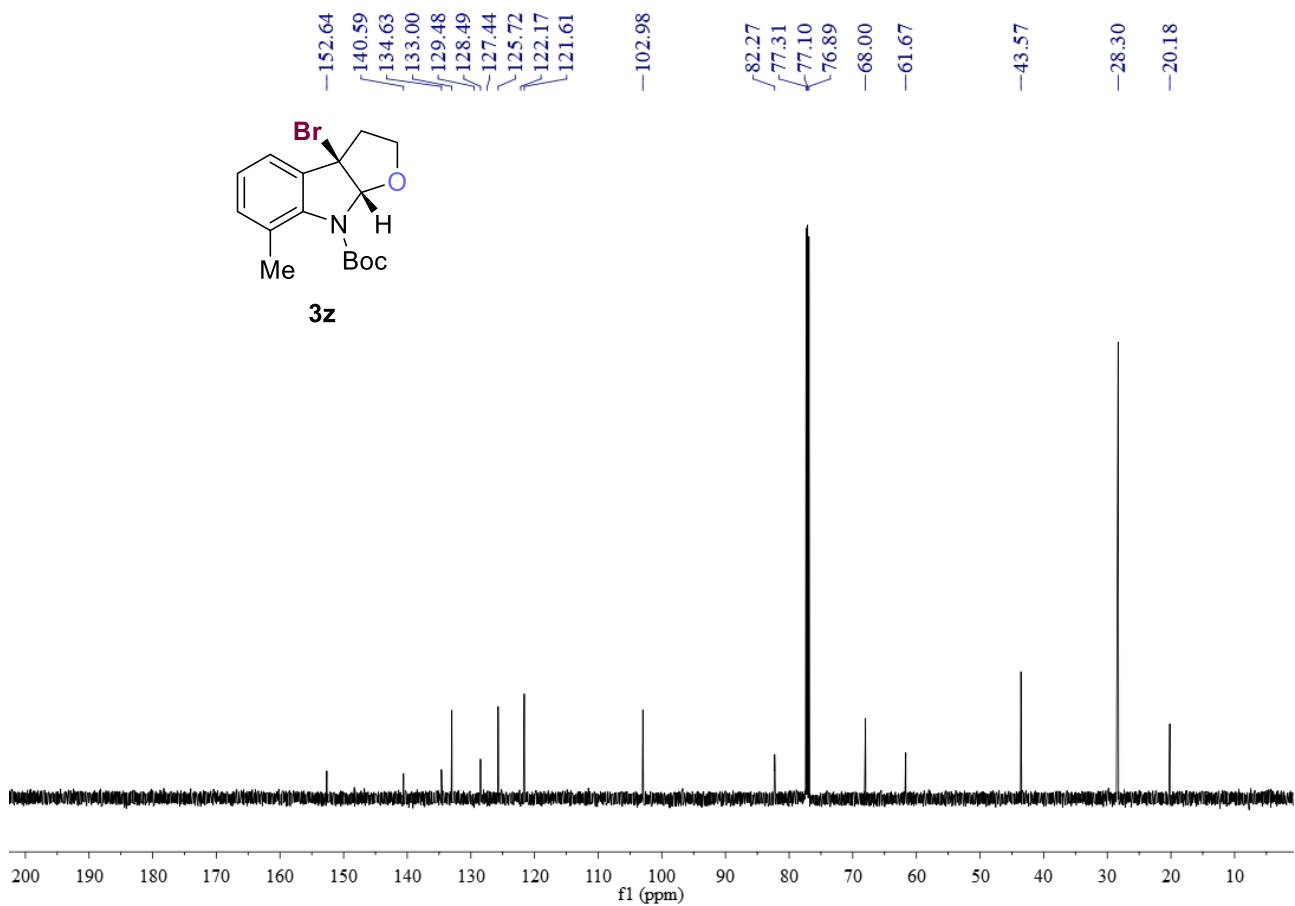
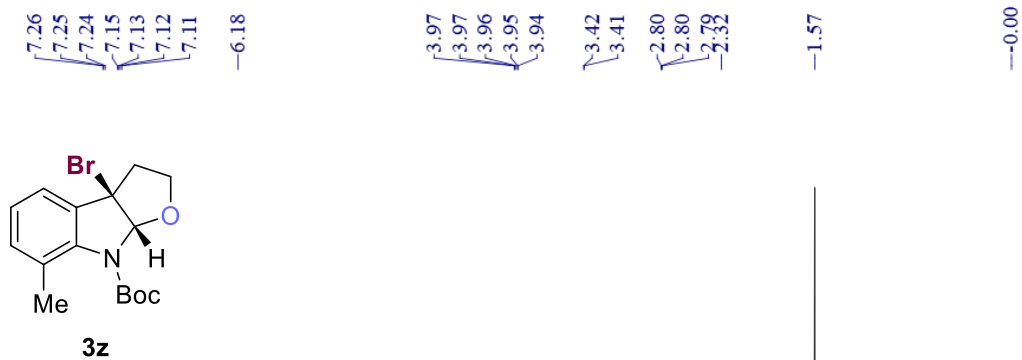


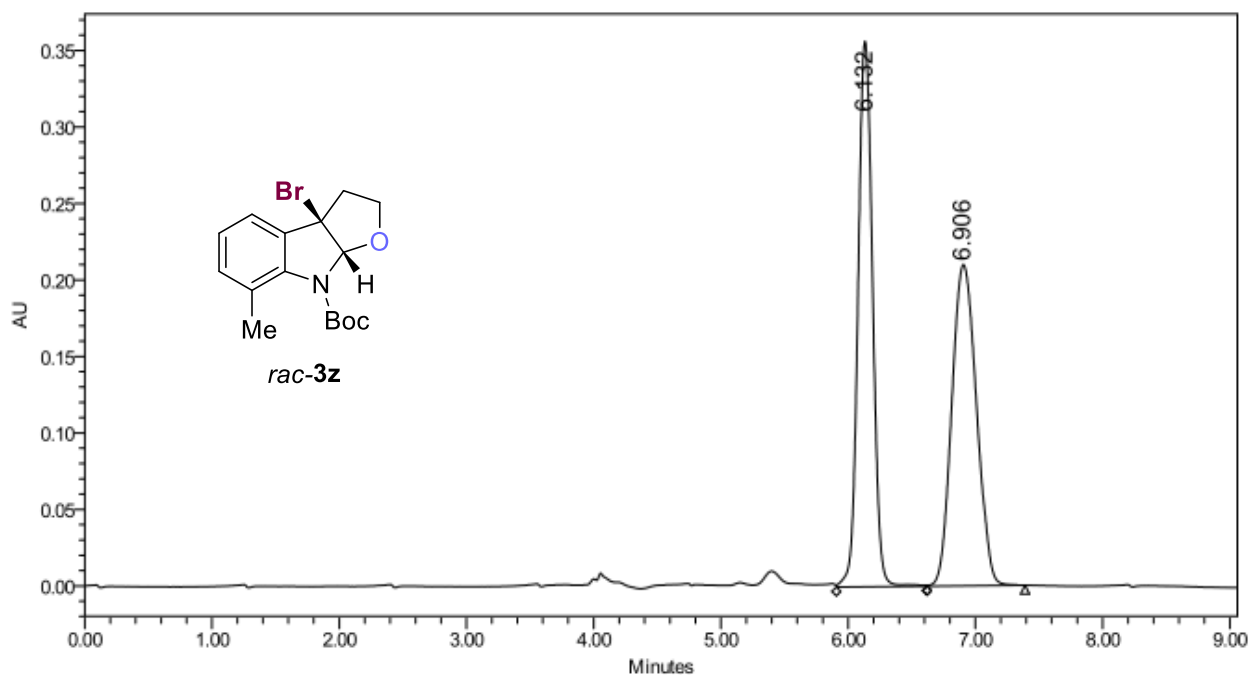


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.465	Unknown	8647626	51.94	1034828	48.00	bb	338	5.220	5.783
2	6.217	Unknown	8000157	48.06	1121083	52.00	bb	286	6.008	6.485

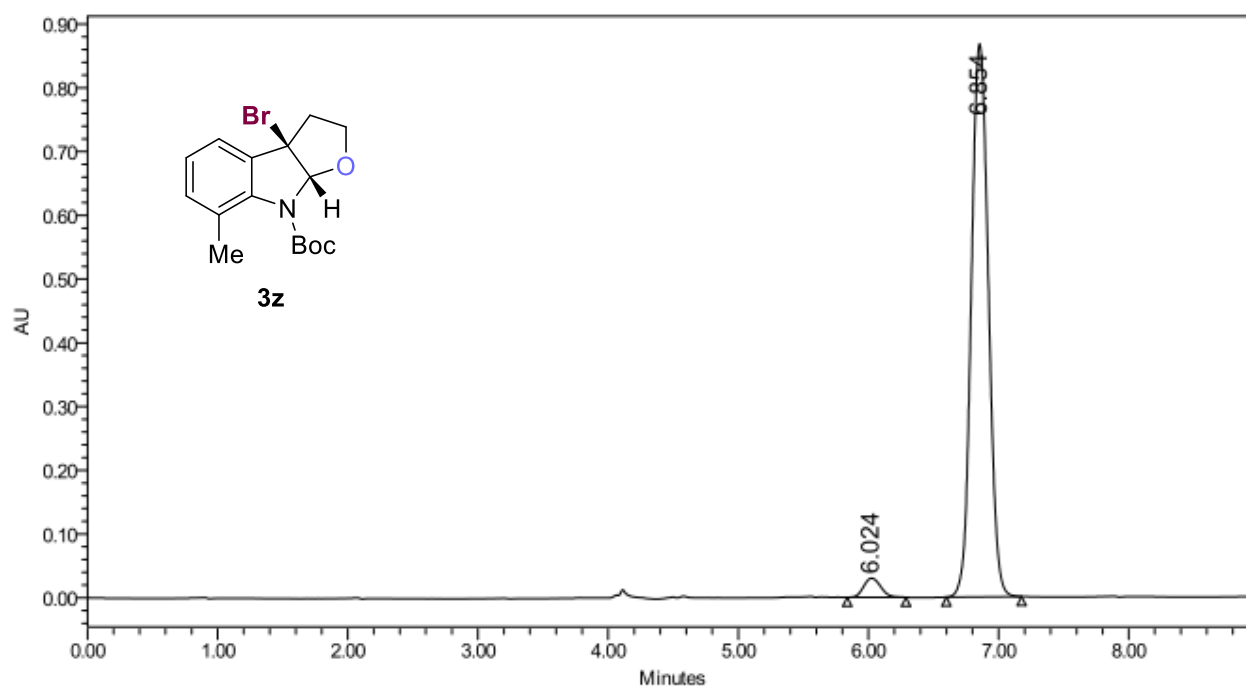


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.441	Unknown	873218	5.81	86965	5.09	bb	283	5.242	5.713
2	6.052	Unknown	14159091	94.19	1621699	94.91	bb	406	5.815	6.492

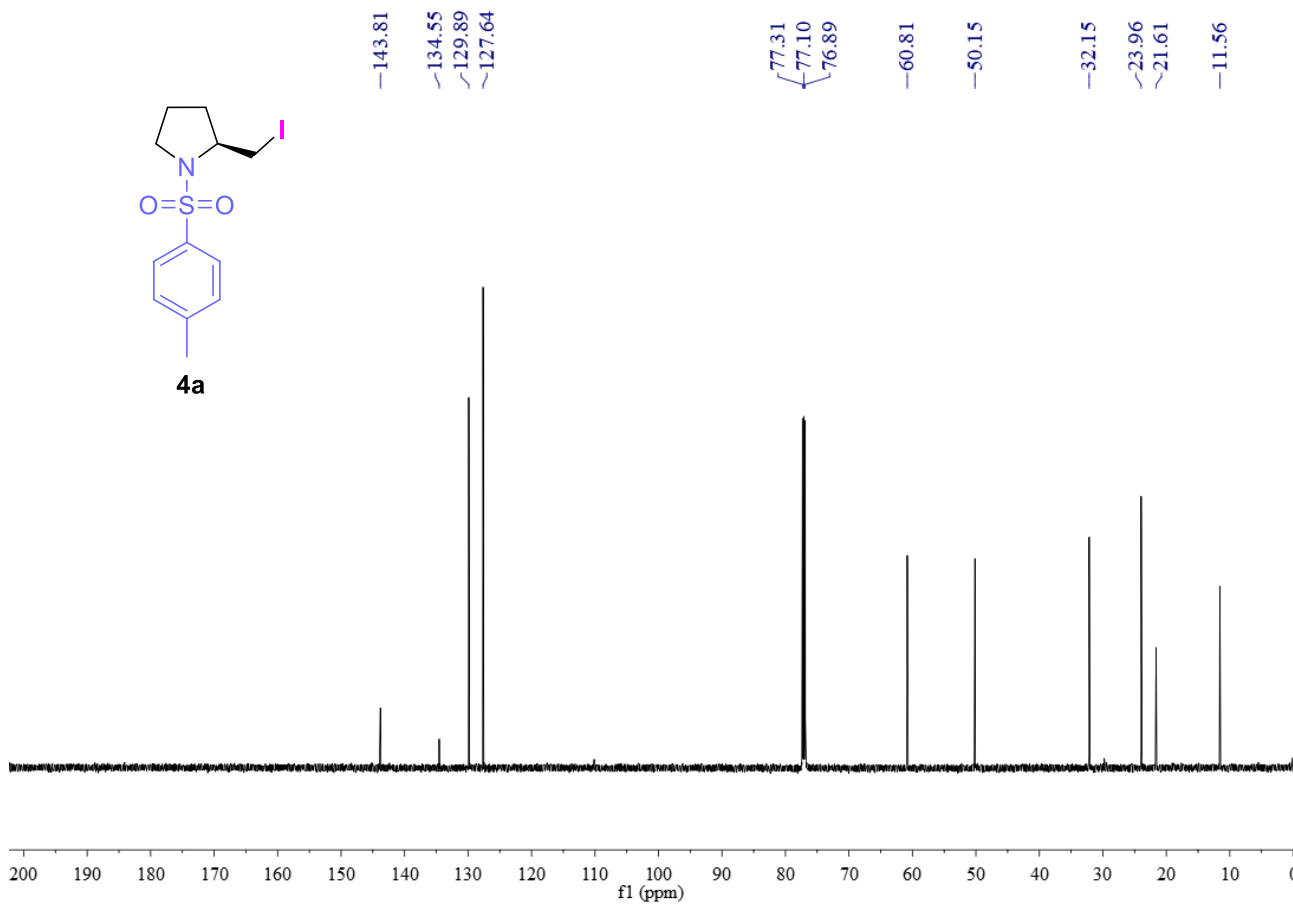
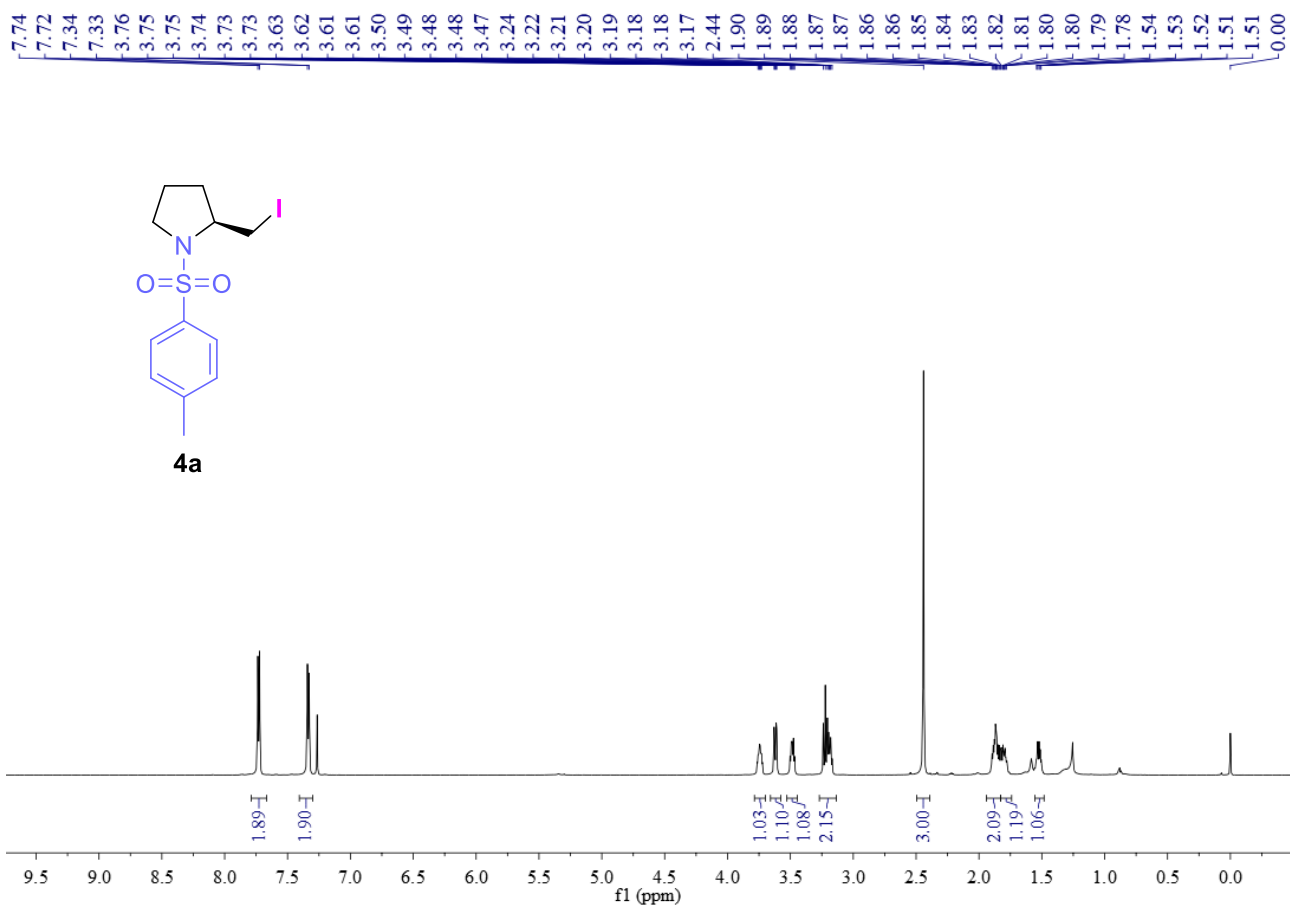


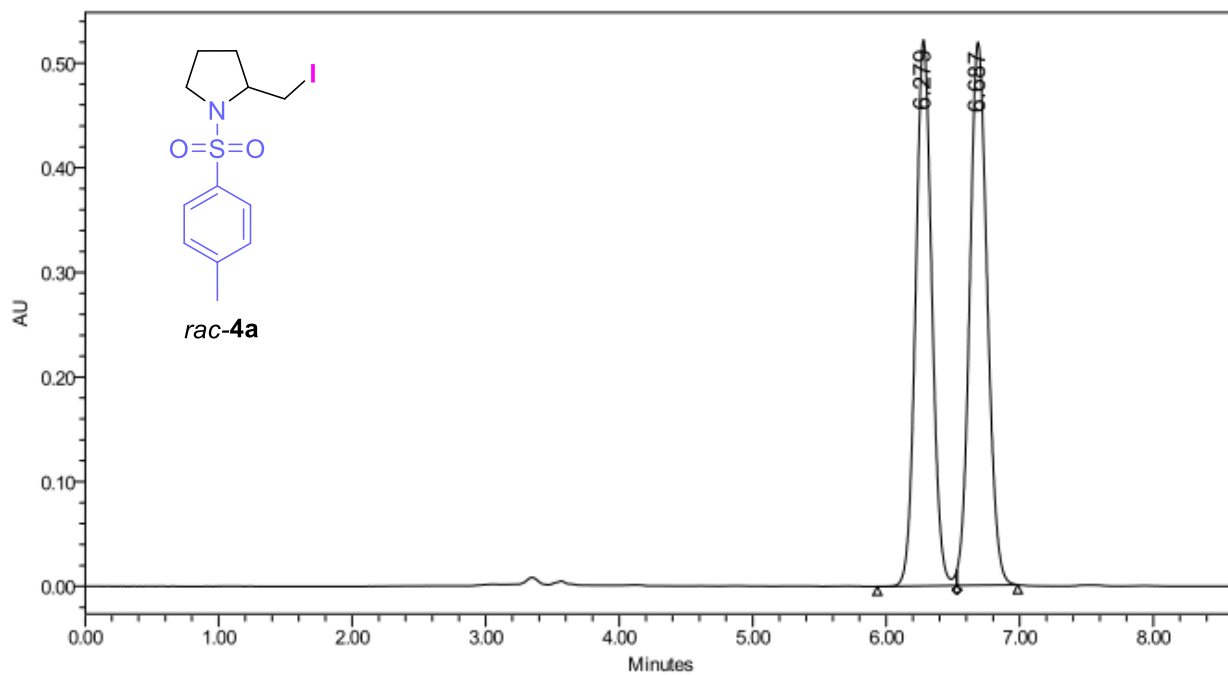


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.132	Unknown	2836301	50.12	356496	62.94	VV	428	5.907	6.620
2	6.906	Unknown	2822566	49.88	209867	37.06	VB	462	6.620	7.390

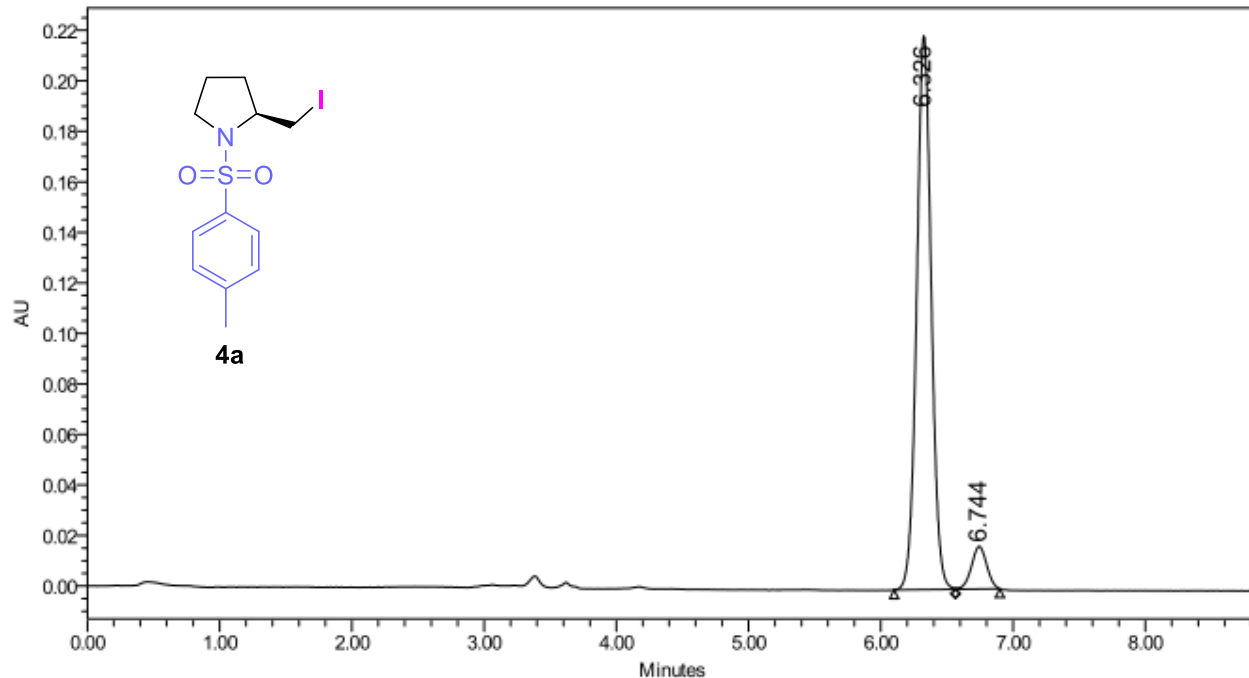


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.024	Unknown	272030	3.33	29926	3.34	Bb	271	5.837	6.288
2	6.854	Unknown	7902478	96.67	867164	96.66	bb	347	6.598	7.177

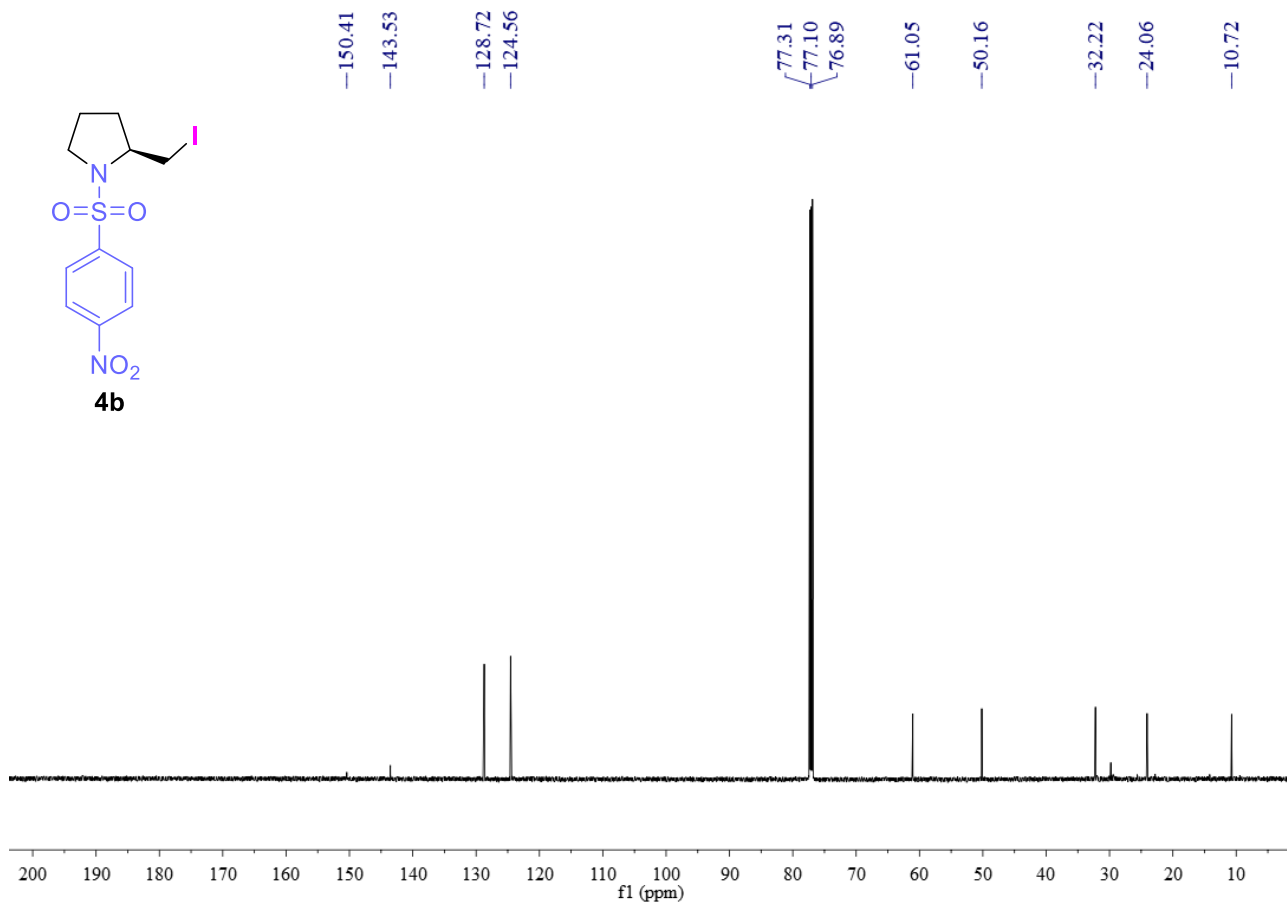
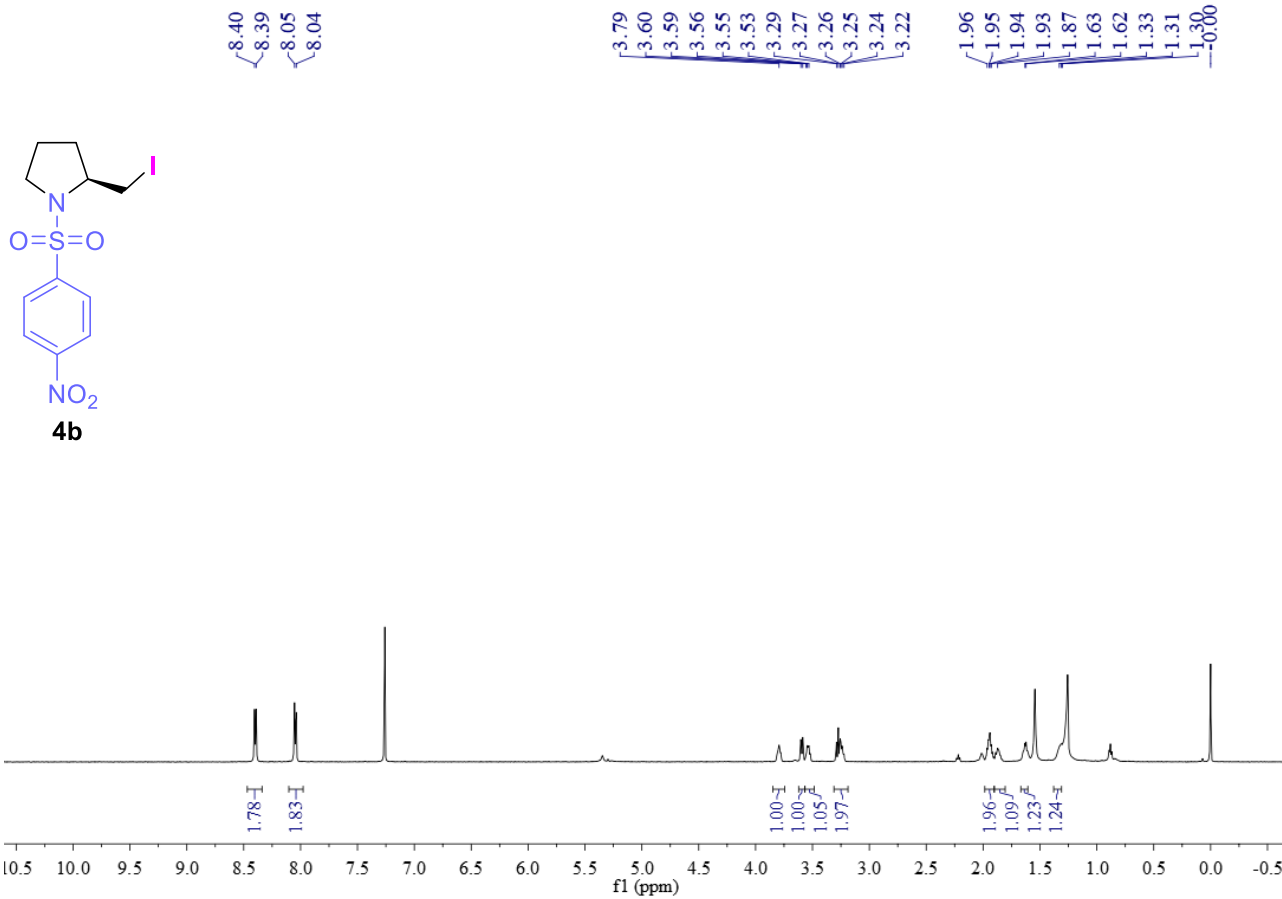


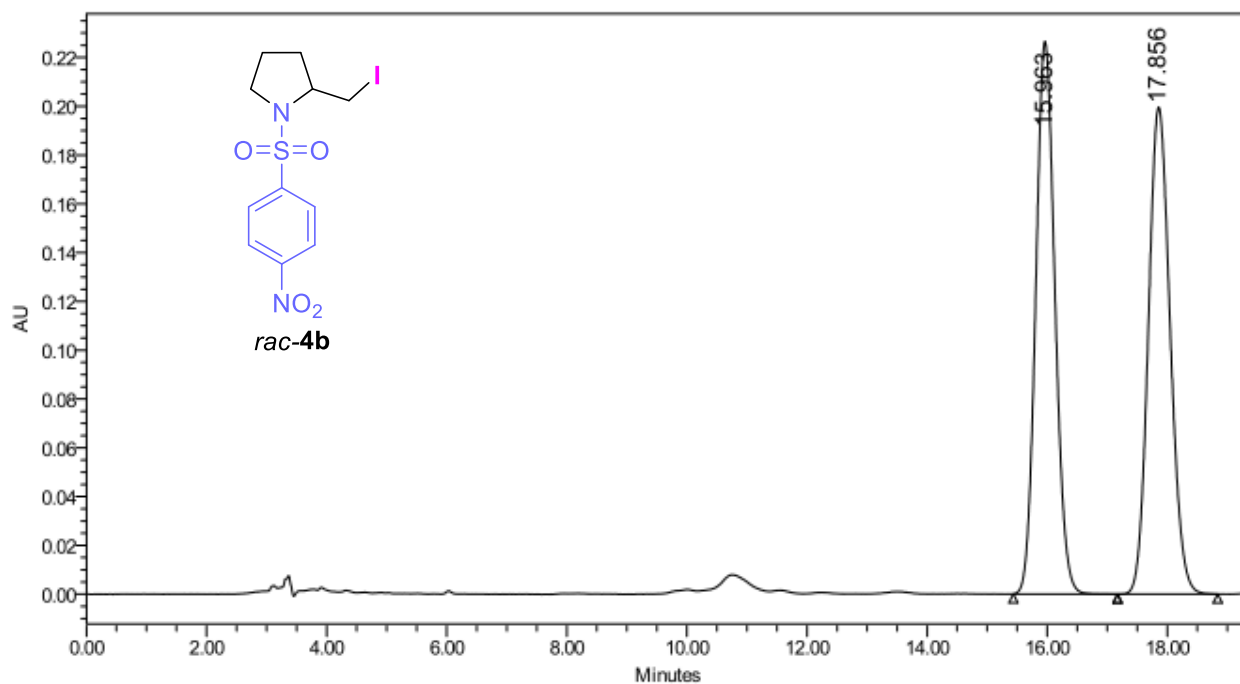


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.279	Unknown	4407613	48.16	521893	50.14	bv	357	5.933	6.528
2	6.687	Unknown	4744857	51.84	519038	49.86	vb	274	6.528	6.985

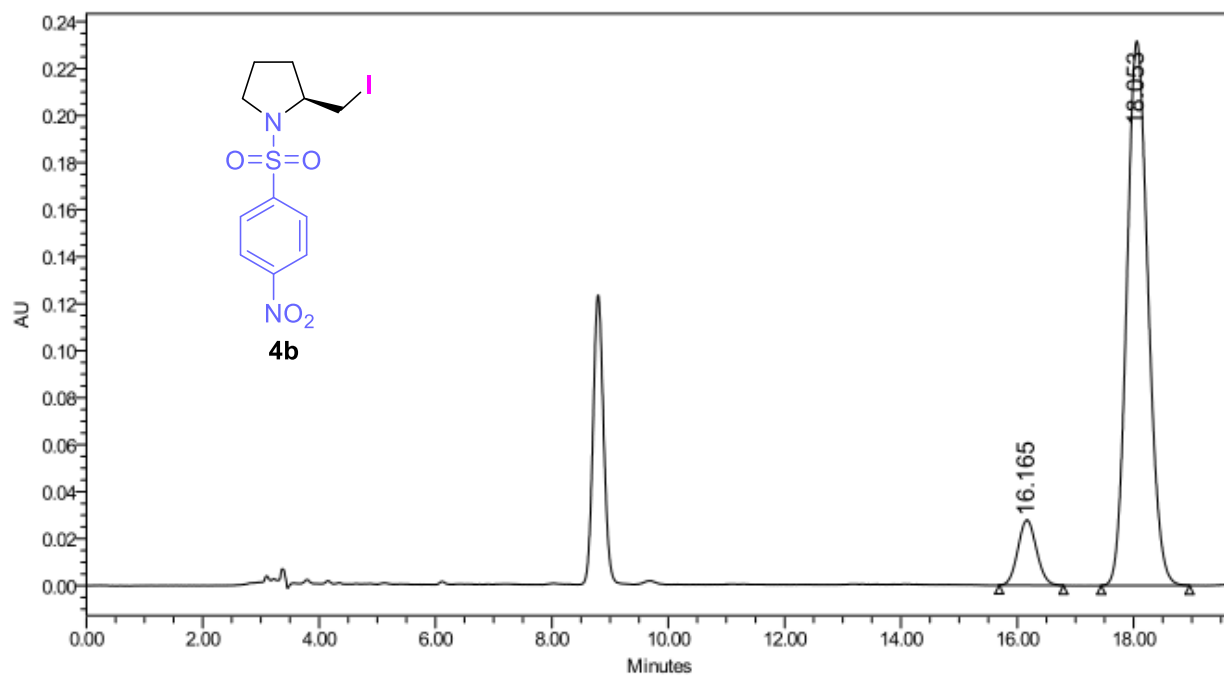


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.326	Unknown	1678334	92.53	219338	92.89	BV	279	6.100	6.565
2	6.744	Unknown	135577	7.47	16795	7.11	Vb	201	6.565	6.900



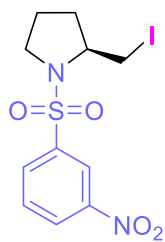


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	15.963	Unknown	5031406	49.98	226477	53.15	BB	1040	15.437	17.170
2	17.856	Unknown	5035463	50.02	199623	46.85	BB	1001	17.170	18.838

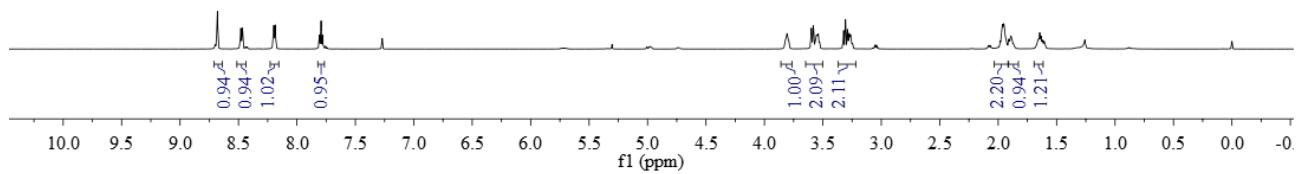


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.165	Unknown	617925	9.52	27772	10.70	BB	664	15.687	16.793
2	18.053	Unknown	5873340	90.48	231674	89.30	BB	909	17.443	18.958

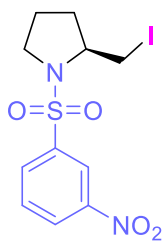
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1.62
1.61
0.00



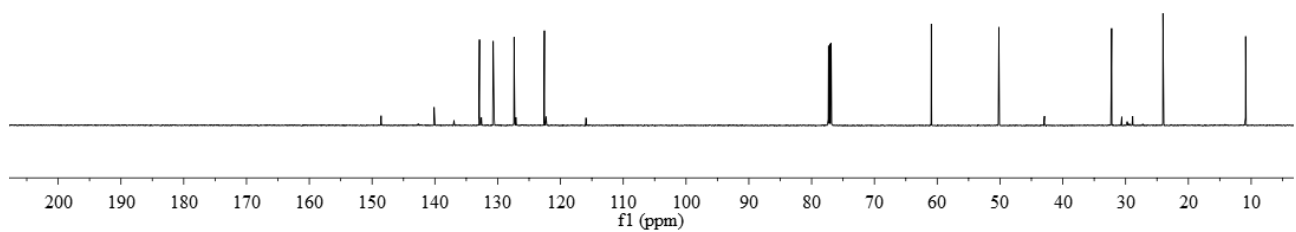
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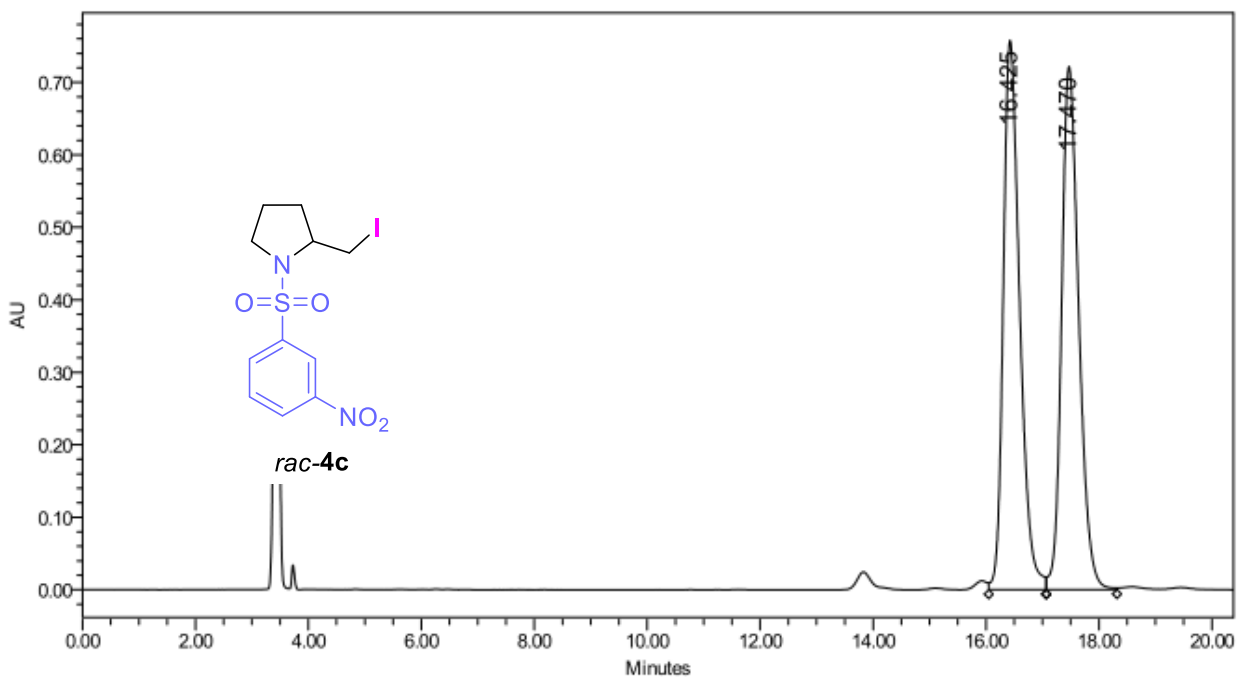


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140.11
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77.10
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60.94
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32.22
24.05
10.89

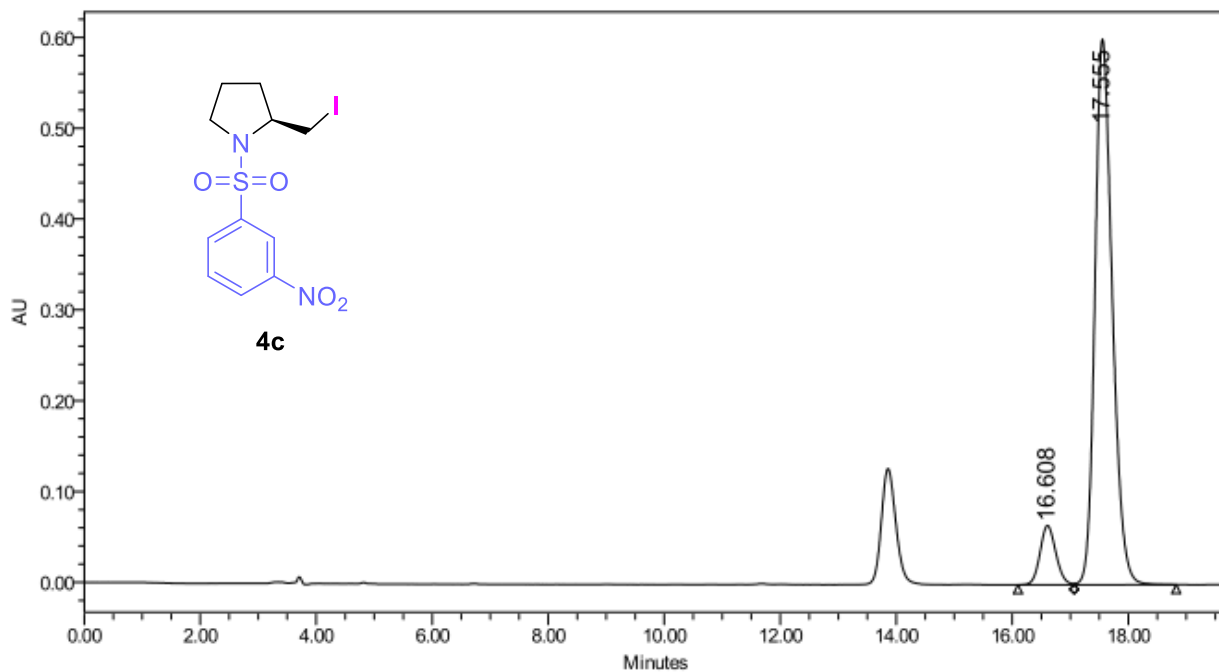


4c





	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.425	Unknown	15287232	50.04	758039	51.22	VV	612	16.047	17.067
2	17.470	Unknown	15265416	49.96	721834	48.78	VV	751	17.067	18.318

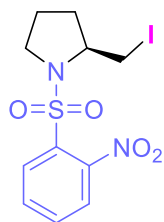


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.608	Unknown	1238630	9.01	65414	9.82	BV	582	16.097	17.067
2	17.555	Unknown	12514615	90.99	600829	90.18	VB	1055	17.067	18.825

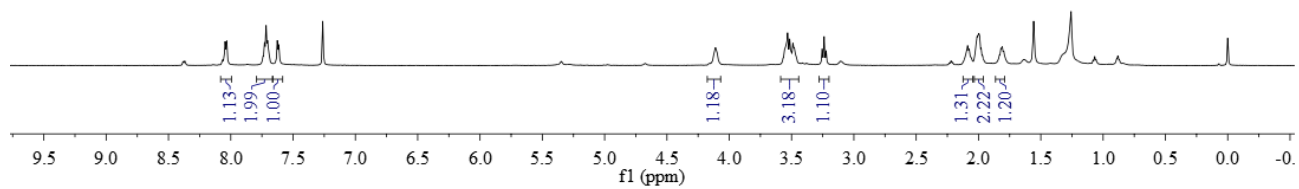
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7.72
7.70
7.63
7.61

-4.11
3.54
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3.49
3.48
3.24
2.09
2.07
2.00
1.98
1.82
1.81
1.80

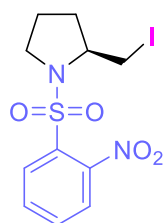
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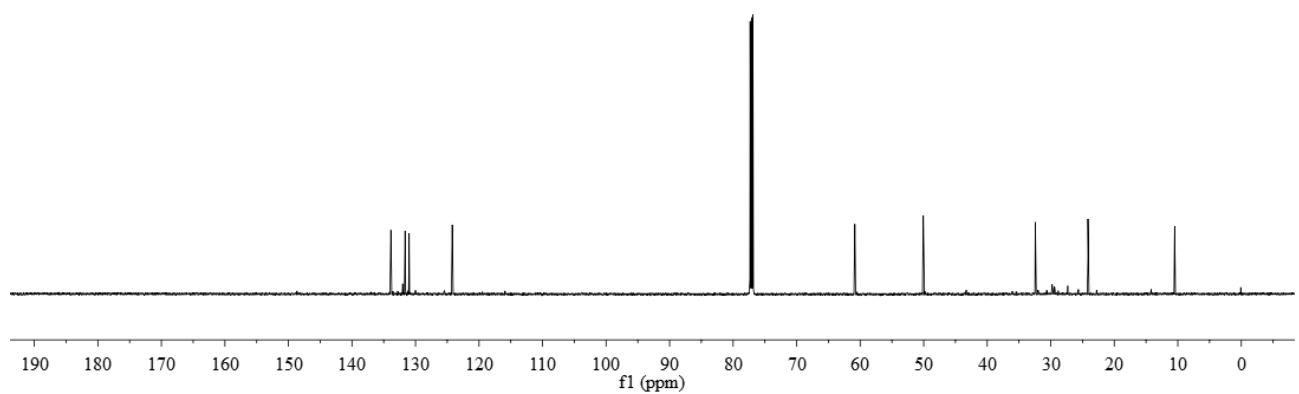
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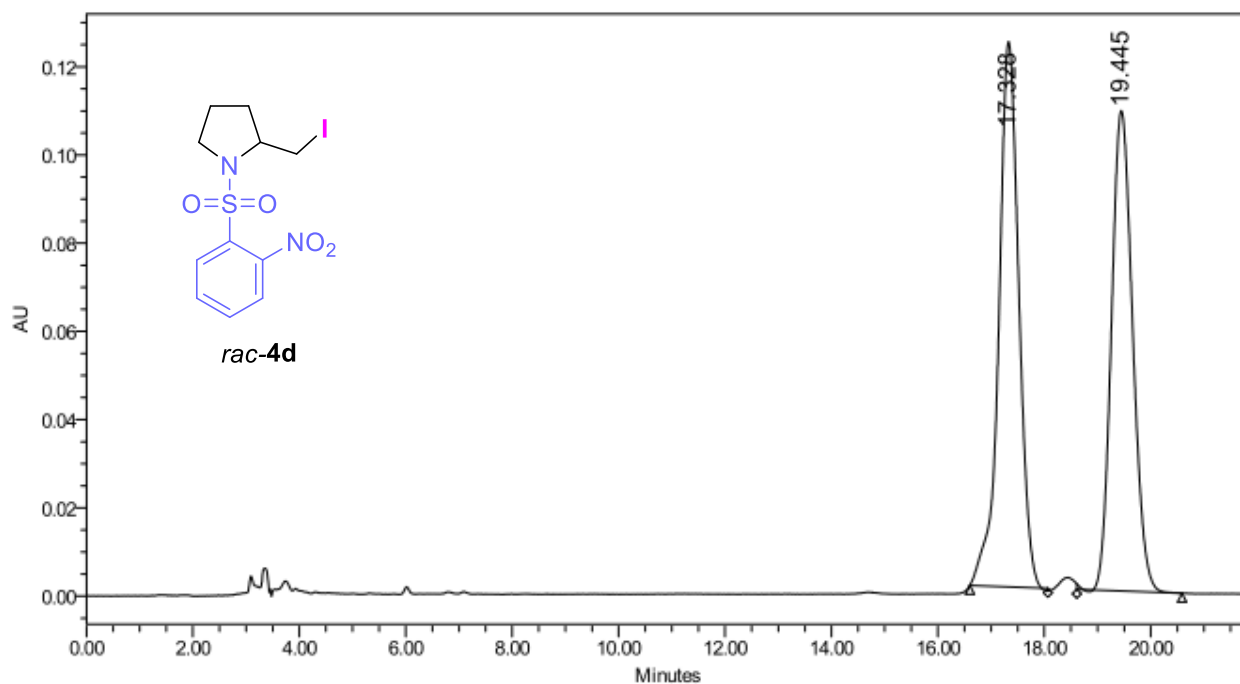


148.68
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24.14
10.49

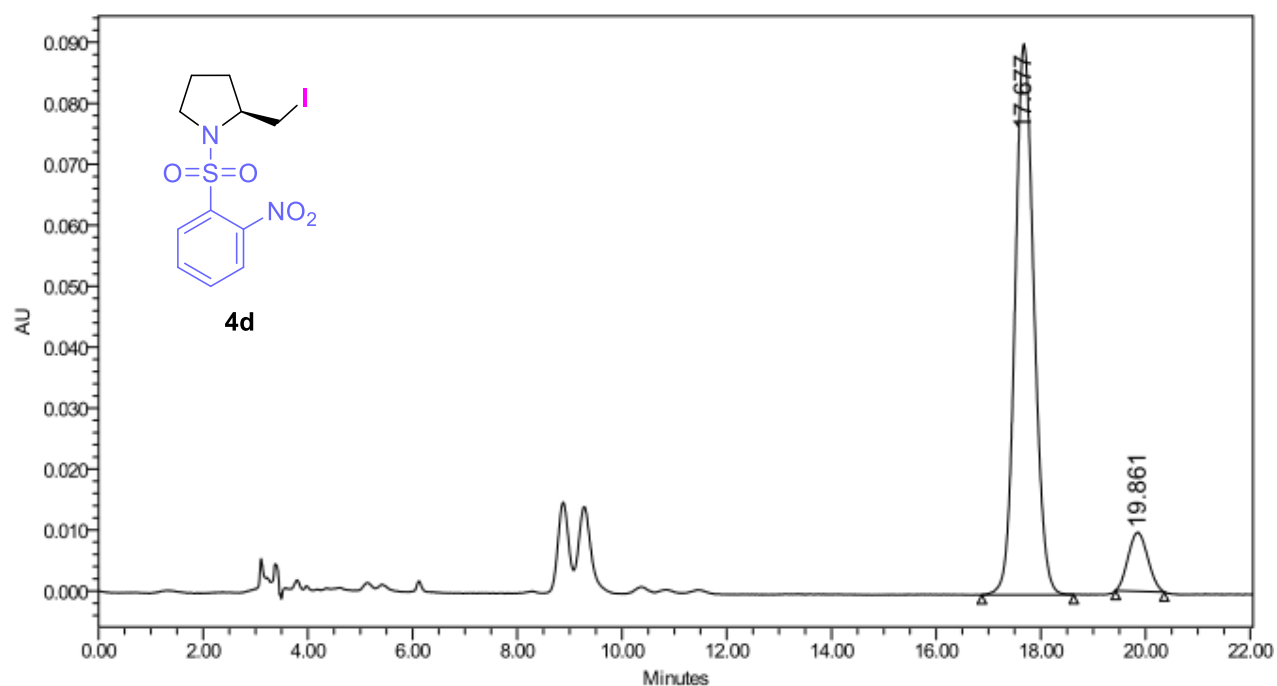


4d





RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	3224435	51.68	123574	53.15	bV	880	16.598	18.065
2	Unknown	3015153	48.32	108920	46.85	vb	1185	18.610	20.585

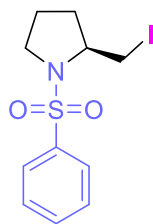


RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	2264749	90.02	90367	90.34	BB	1052	16.875	18.628
2	Unknown	251177	9.98	9662	9.66	bb	556	19.430	20.357

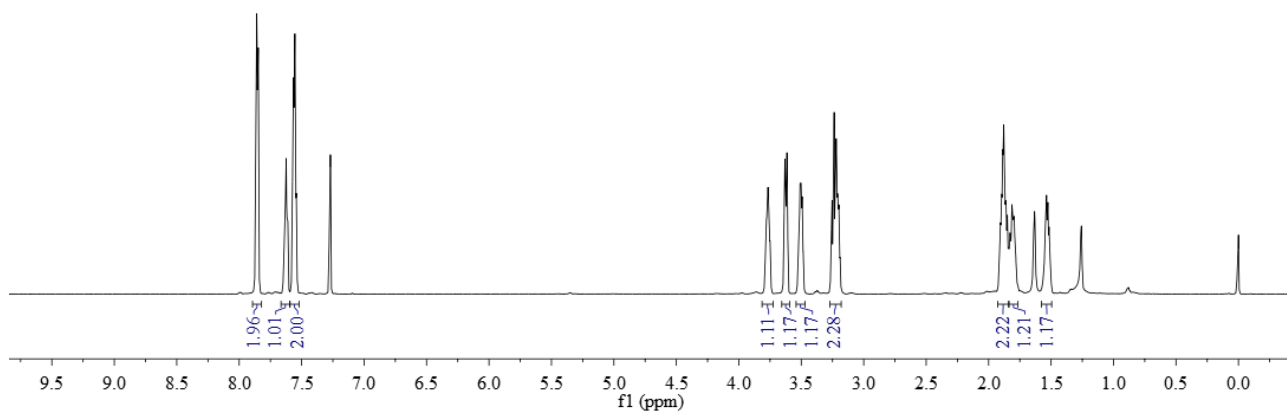
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7.27

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3.61
3.52
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3.24
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3.22
3.21
3.20
3.20

1.90
1.89
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1.85
1.81
1.81
1.80
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1.53
0.00



4e



137.48
132.97
129.27
127.54

77.31
77.10
76.89

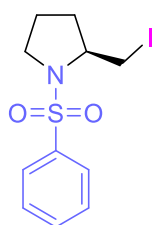
60.82

50.12

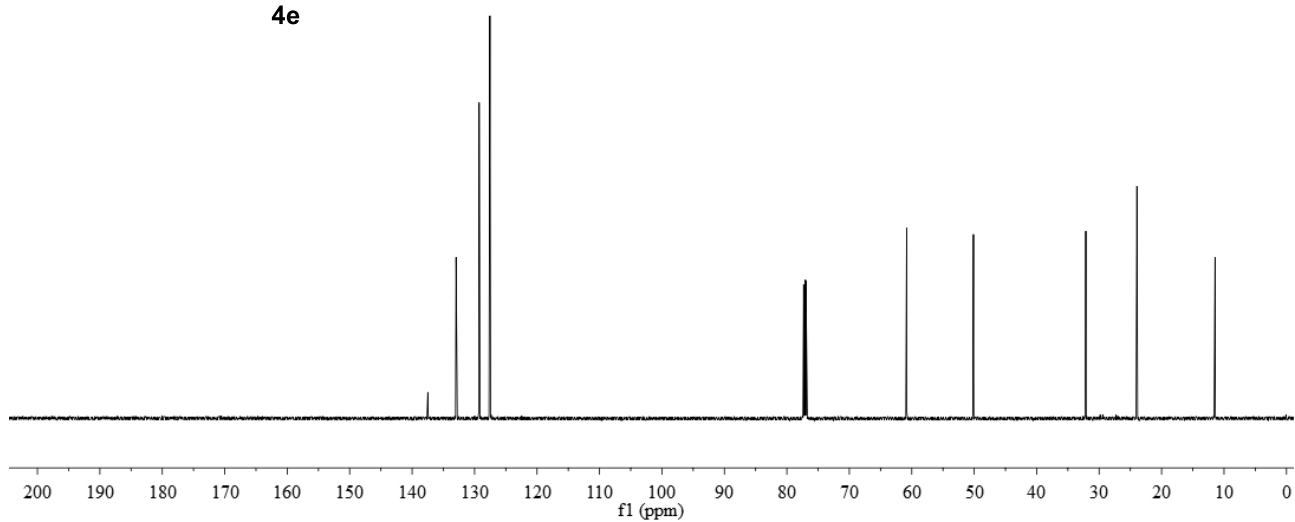
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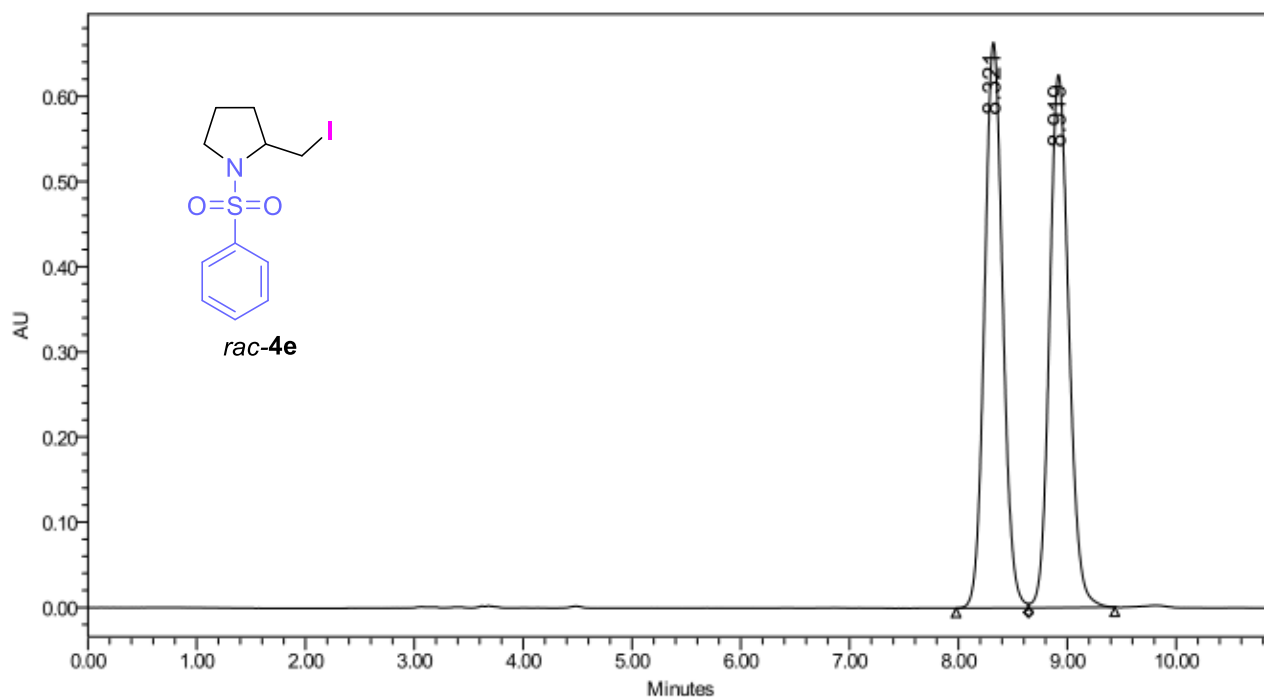
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11.44

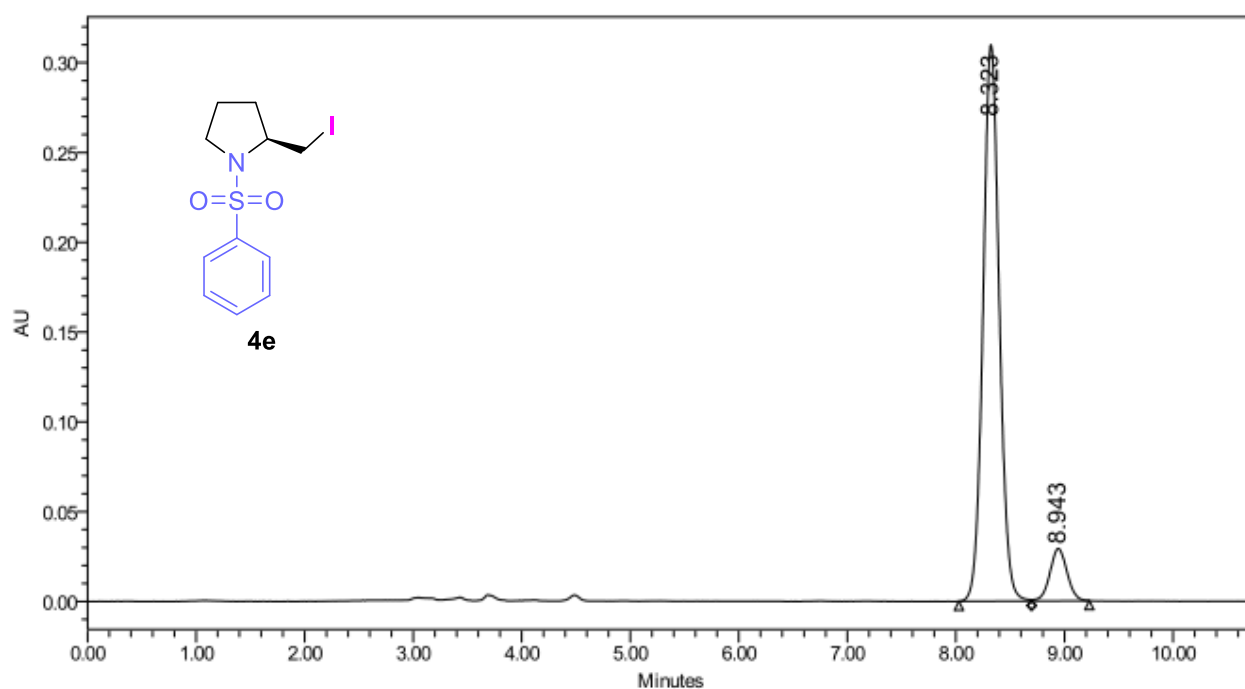


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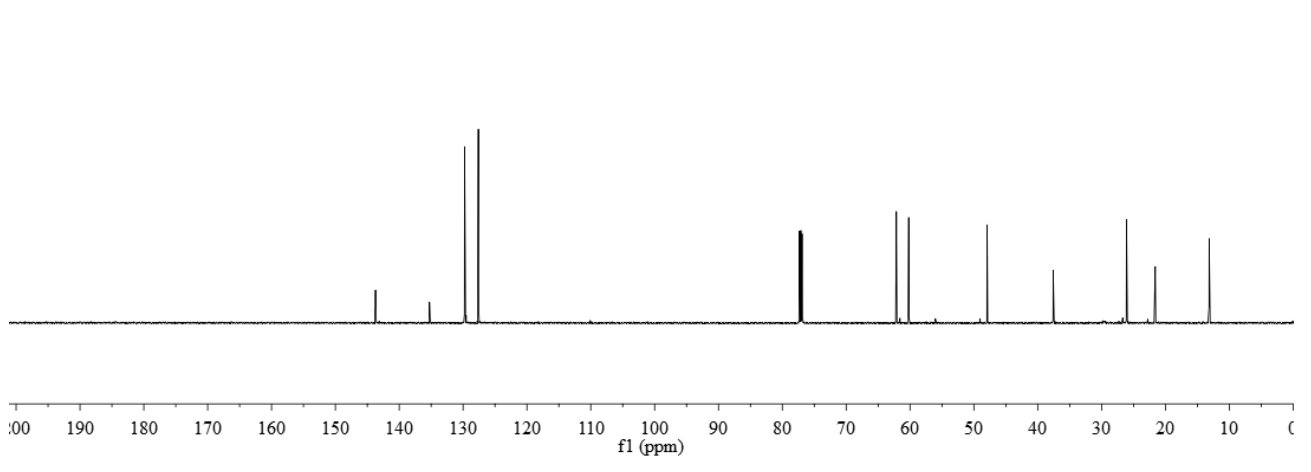
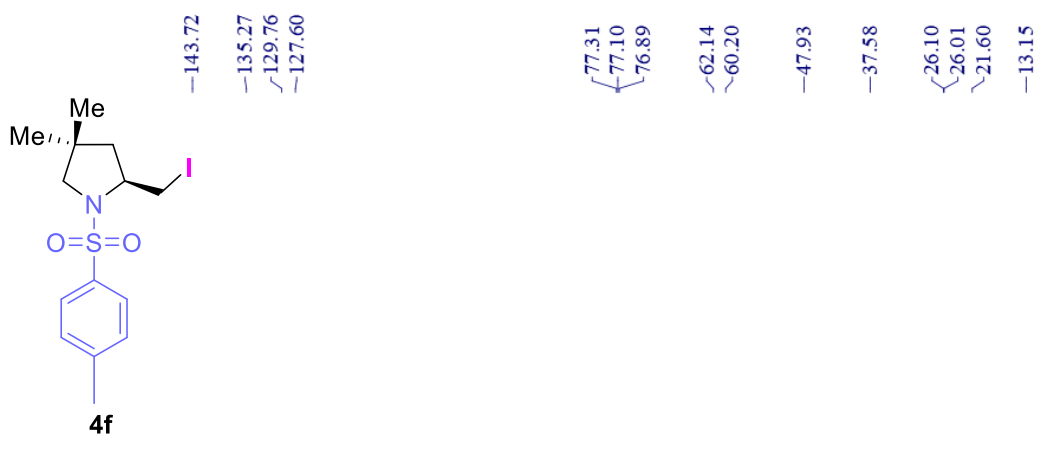
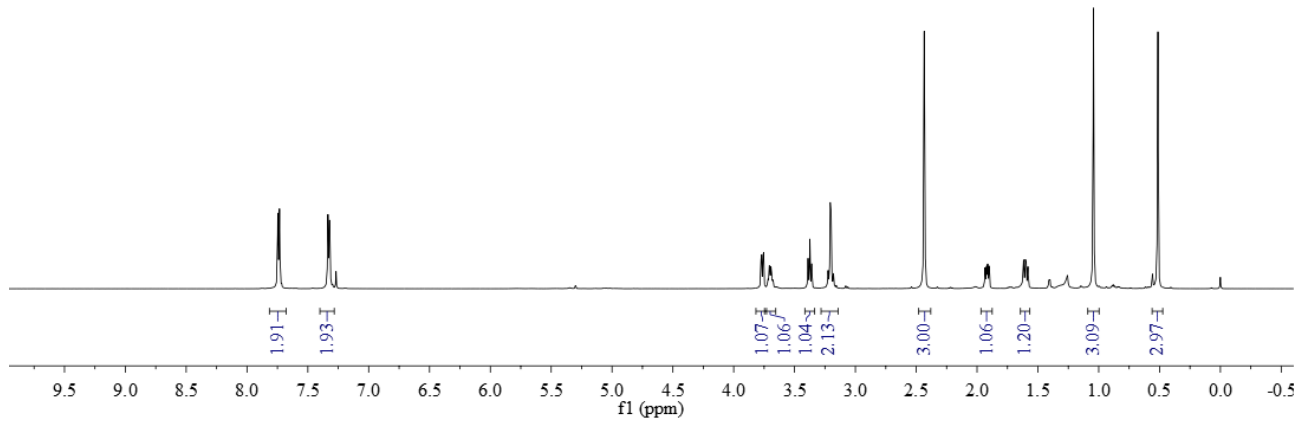
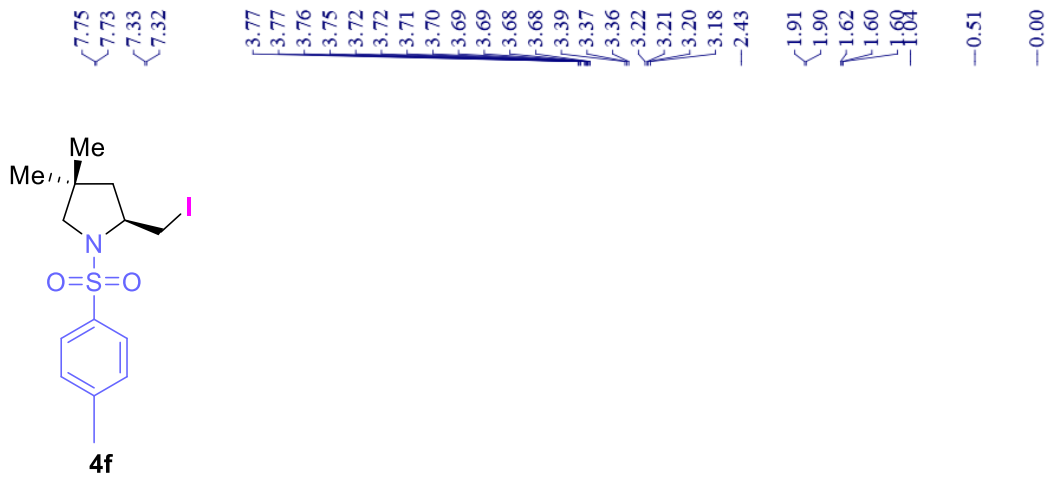


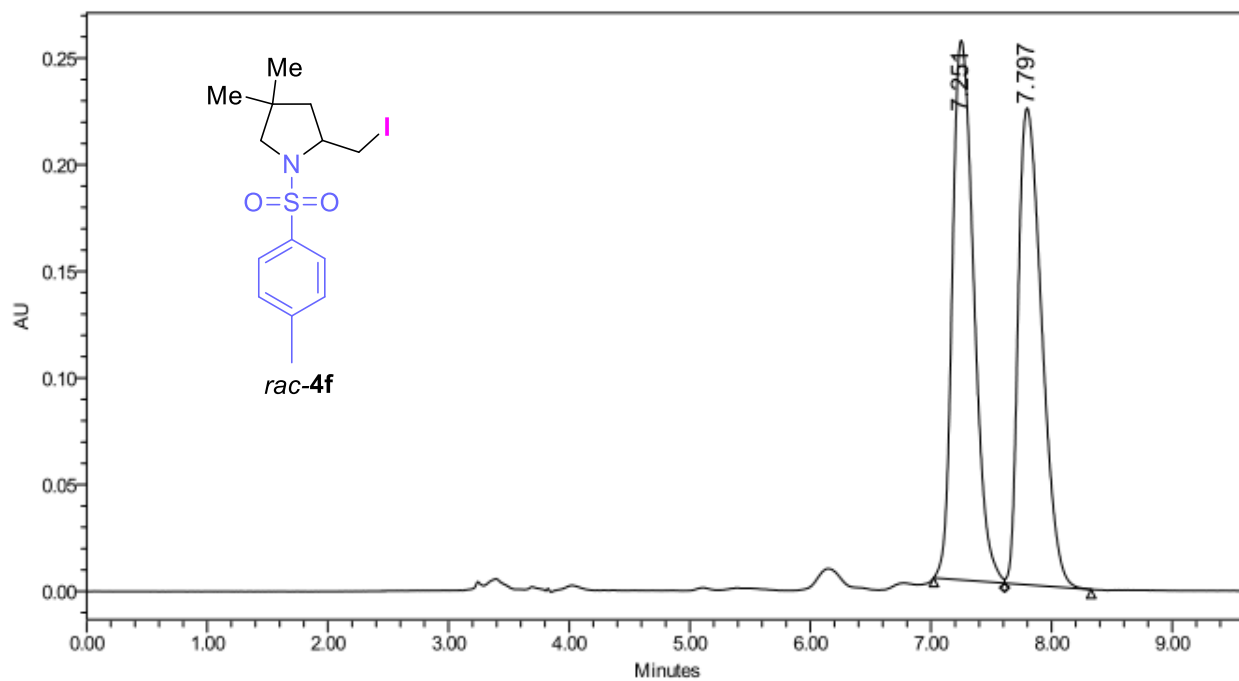


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.321	Unknown	7725308	50.04	663466	51.48	BV	399	7.978	8.643
2	8.919	Unknown	7712286	49.96	625284	48.52	Vb	476	8.643	9.437

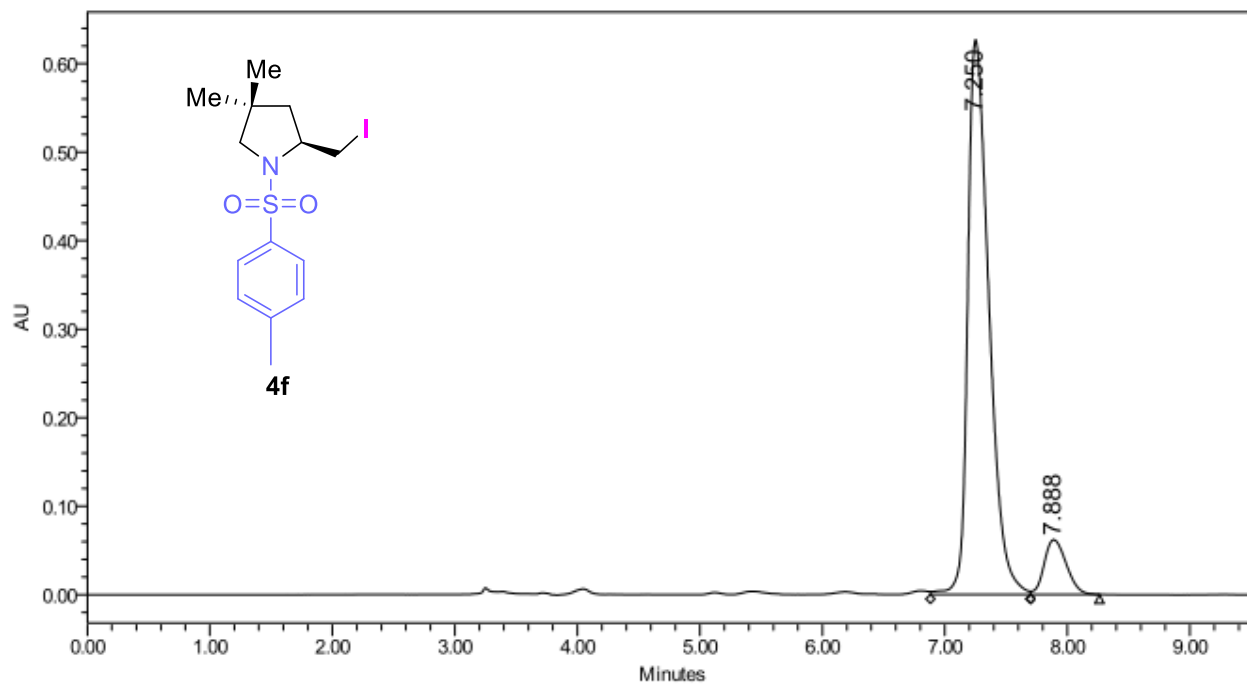


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.323	Unknown	3211549	90.93	309855	91.40	BV	402	8.027	8.697
2	8.943	Unknown	320170	9.07	29141	8.60	Vb	319	8.697	9.228

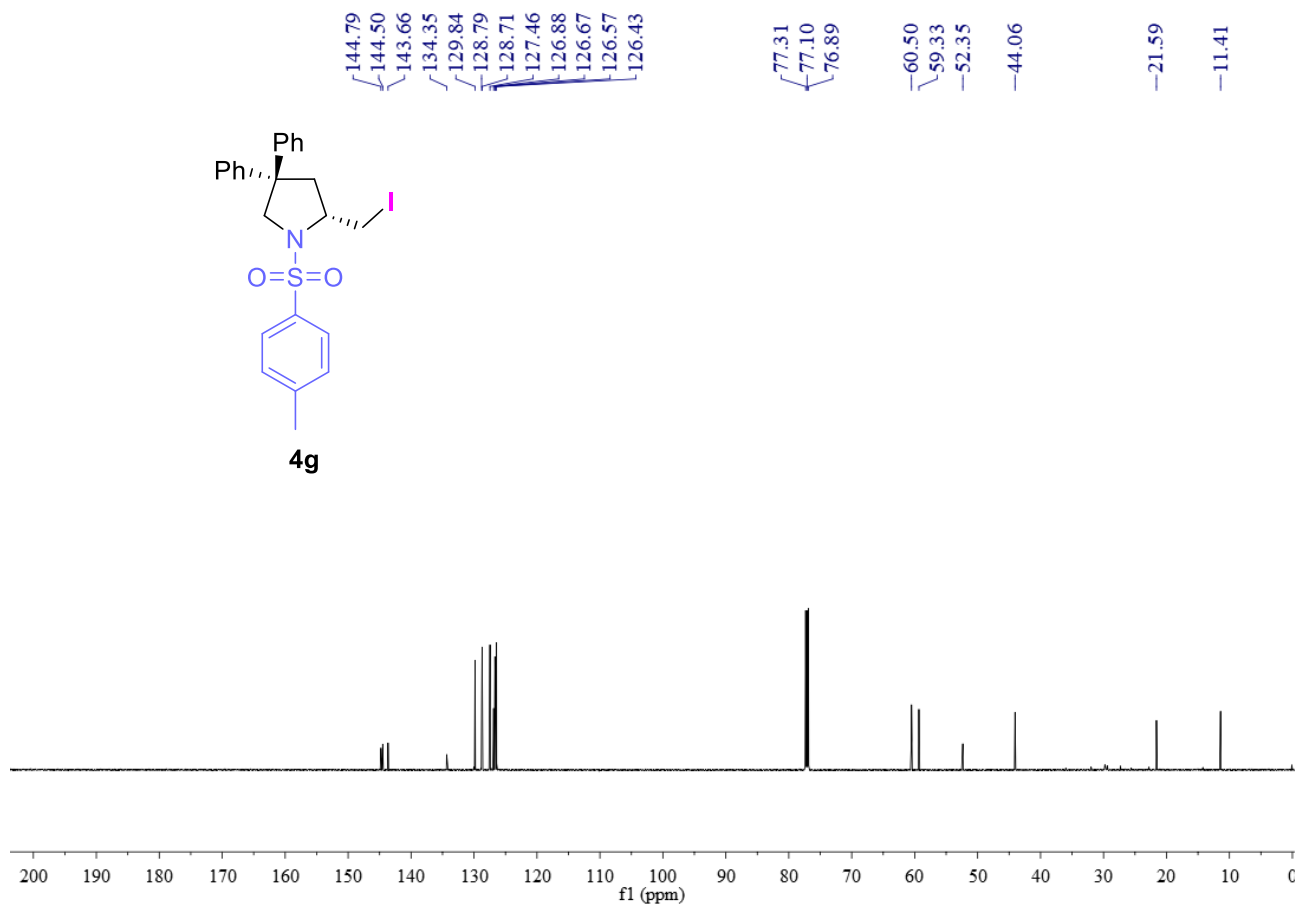
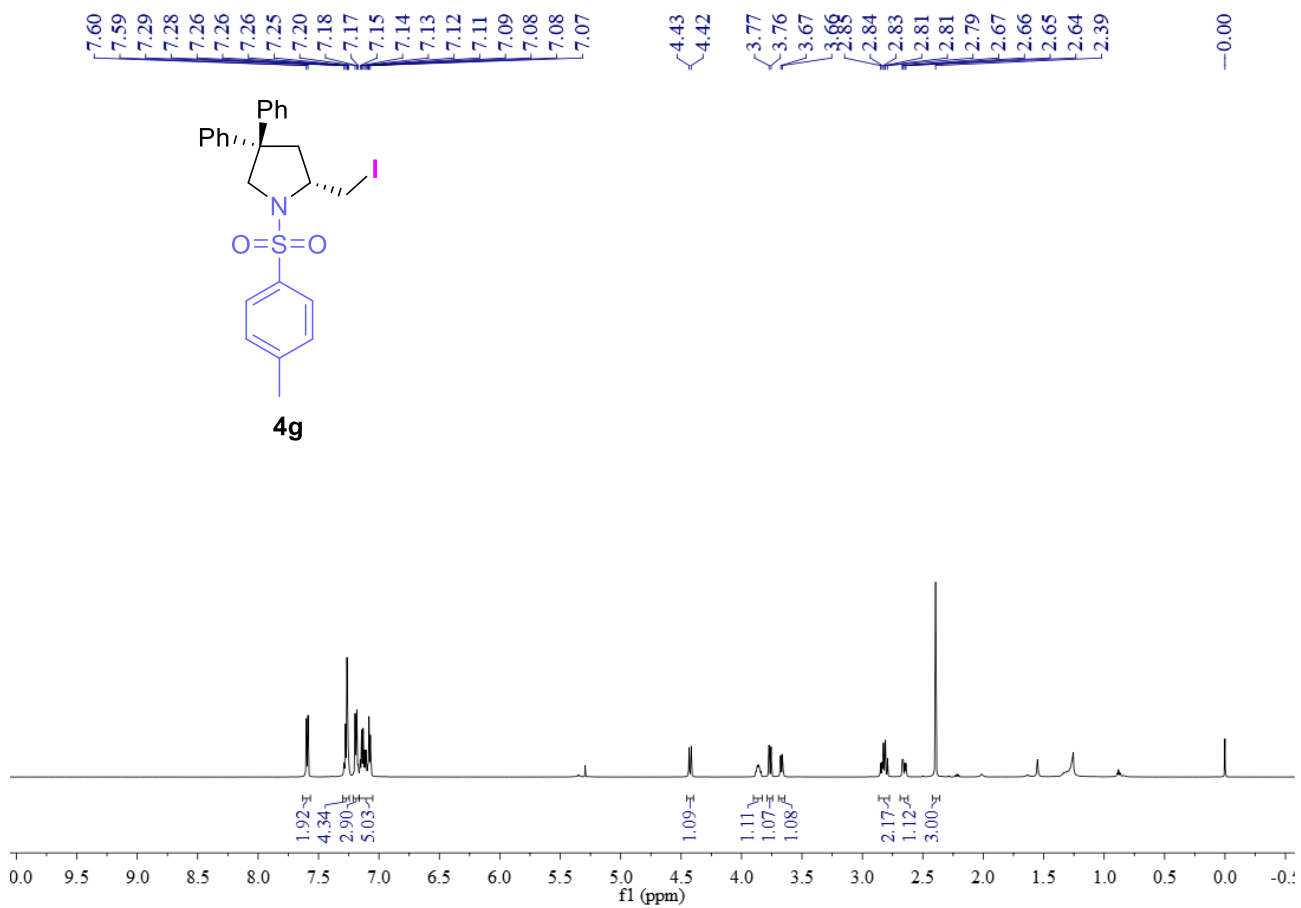


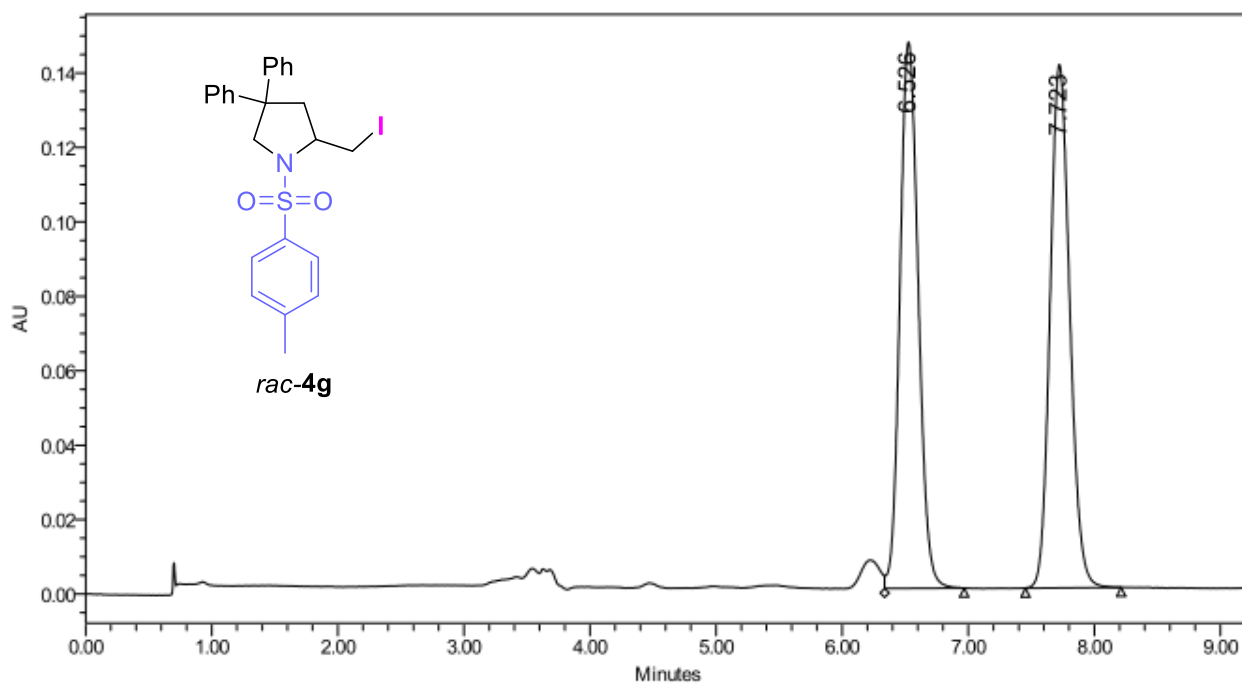


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.251	Unknown	3131971	51.00	252991	53.10	bV	352	7.023	7.610
2	7.797	Unknown	3009659	49.00	223463	46.90	Vb	431	7.610	8.328

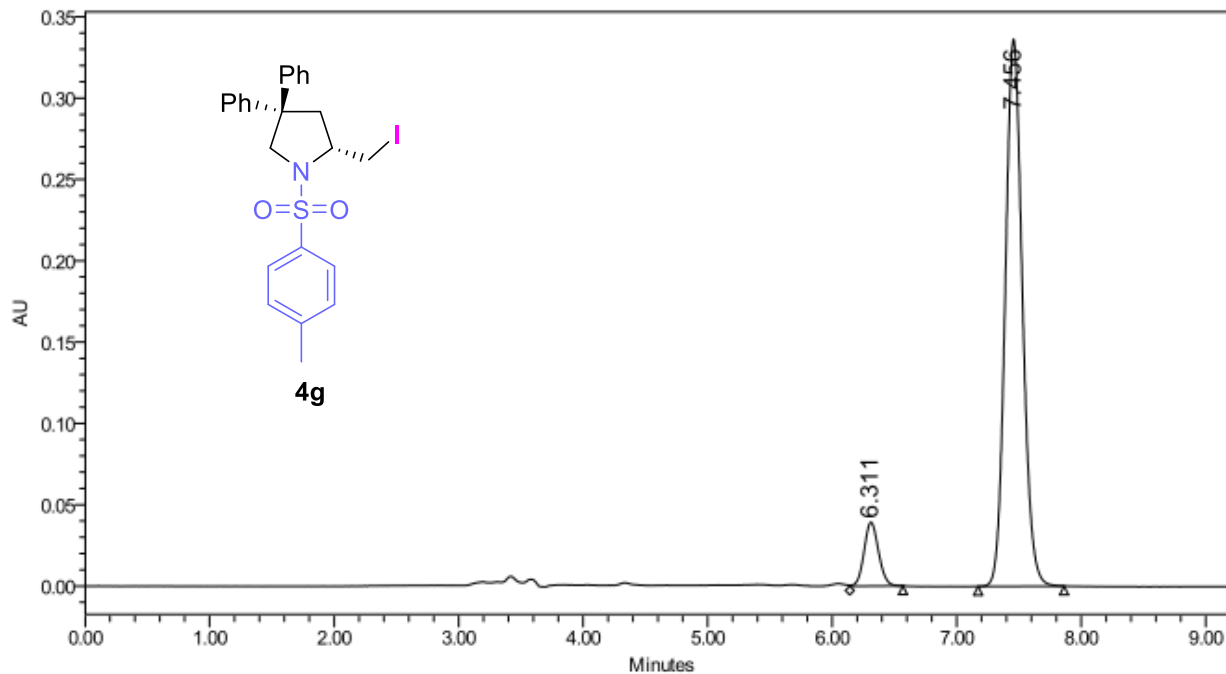


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.250	Unknown	7532174	90.68	626572	91.04	VV	491	6.882	7.700
2	7.888	Unknown	774300	9.32	61652	8.96	Vb	337	7.700	8.262

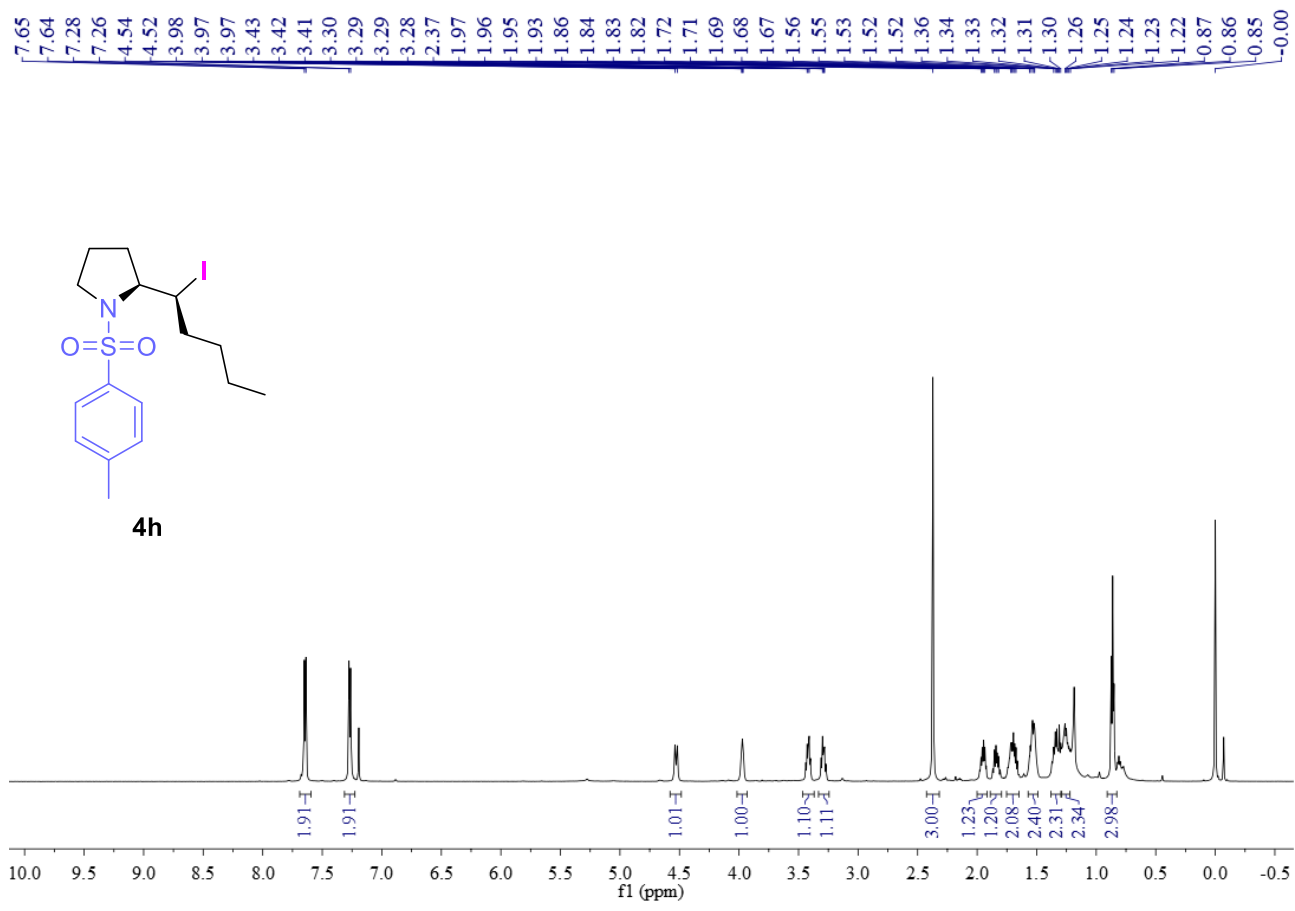




	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.526	Unknown	1485517	49.42	146753	51.06	VB	379	6.337	6.968
2	7.723	Unknown	1520529	50.58	140634	48.94	BB	456	7.453	8.213

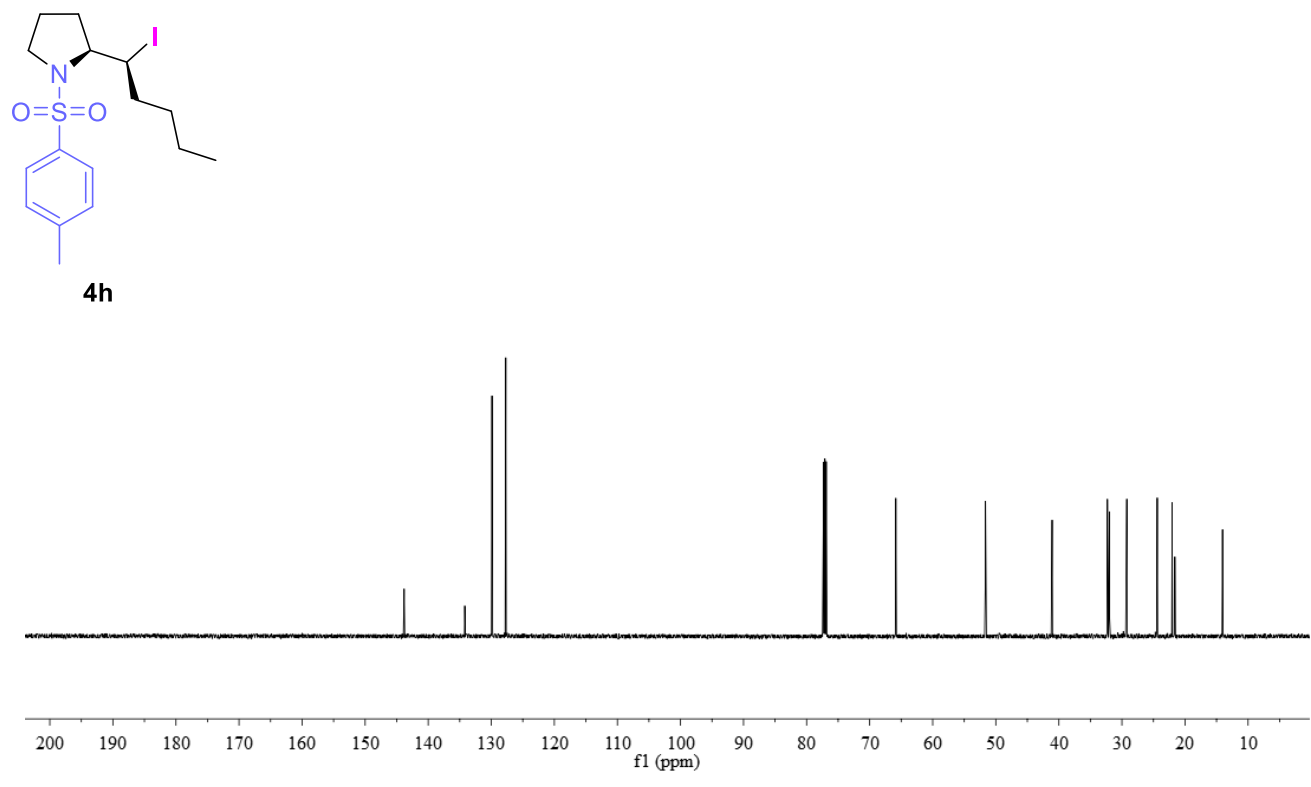


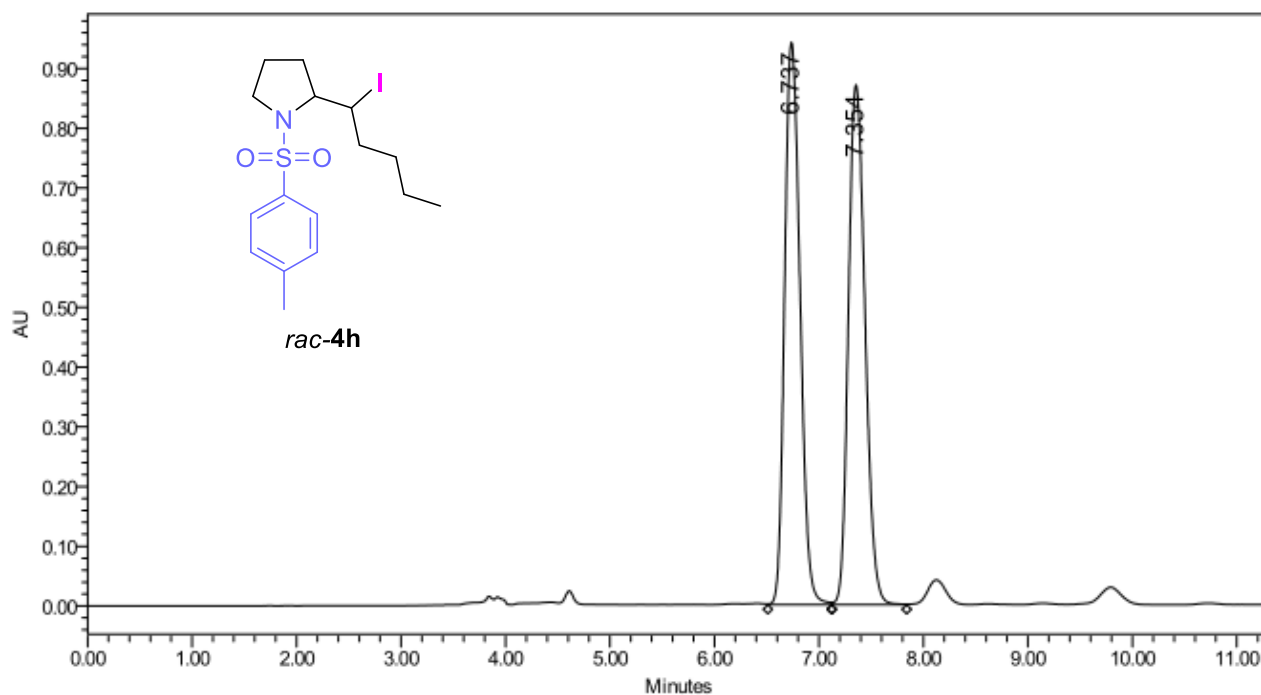
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.311	Unknown	316353	8.96	39120	10.42	Vb	256	6.140	6.567
2	7.456	Unknown	3212963	91.04	336355	89.58	BB	414	7.172	7.862



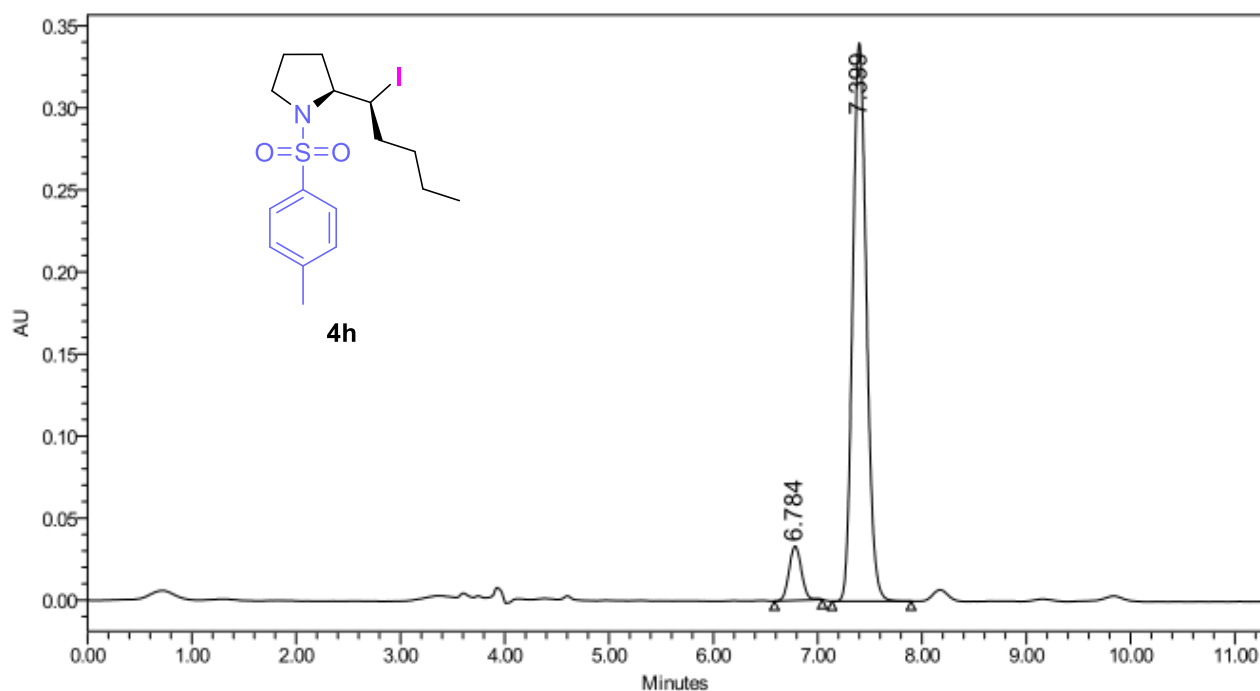
Chemical Shifts (ppm):

- 143.81
- 134.20
- 129.89
- 127.70
- 77.31
- 77.10
- 76.89
- 65.85
- 51.63
- 41.06
- 32.30
- 31.98
- 29.23
- 24.40
- 22.03
- 21.60
- 14.04



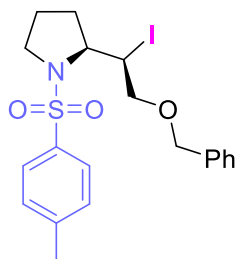


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.737	Unknown	9678607	50.08	942031	51.97	VV	368	6.510	7.123
2	7.354	Unknown	9649408	49.92	870759	48.03	VV	430	7.123	7.840

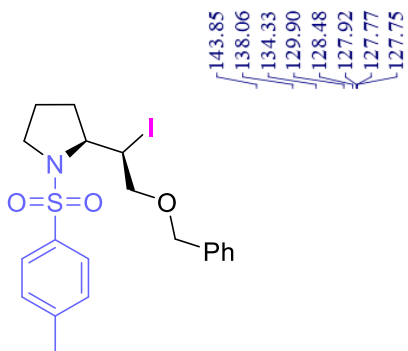
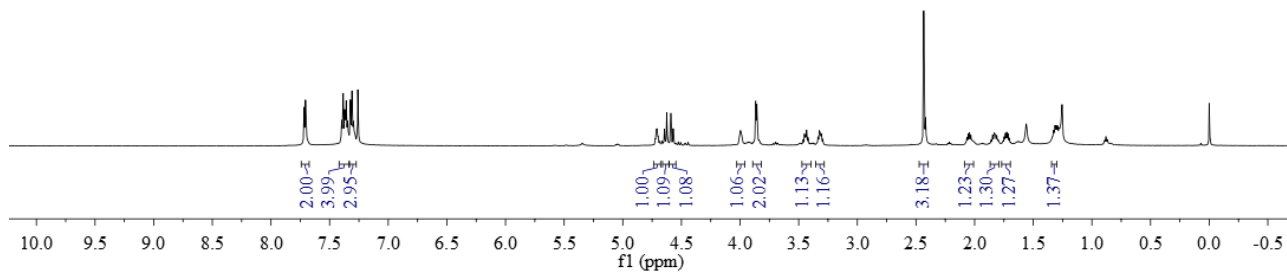


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.784	Unknown	272737	8.02	33064	8.86	bb	274	6.587	7.043
2	7.399	Unknown	3126090	91.98	340194	91.14	bb	455	7.138	7.897

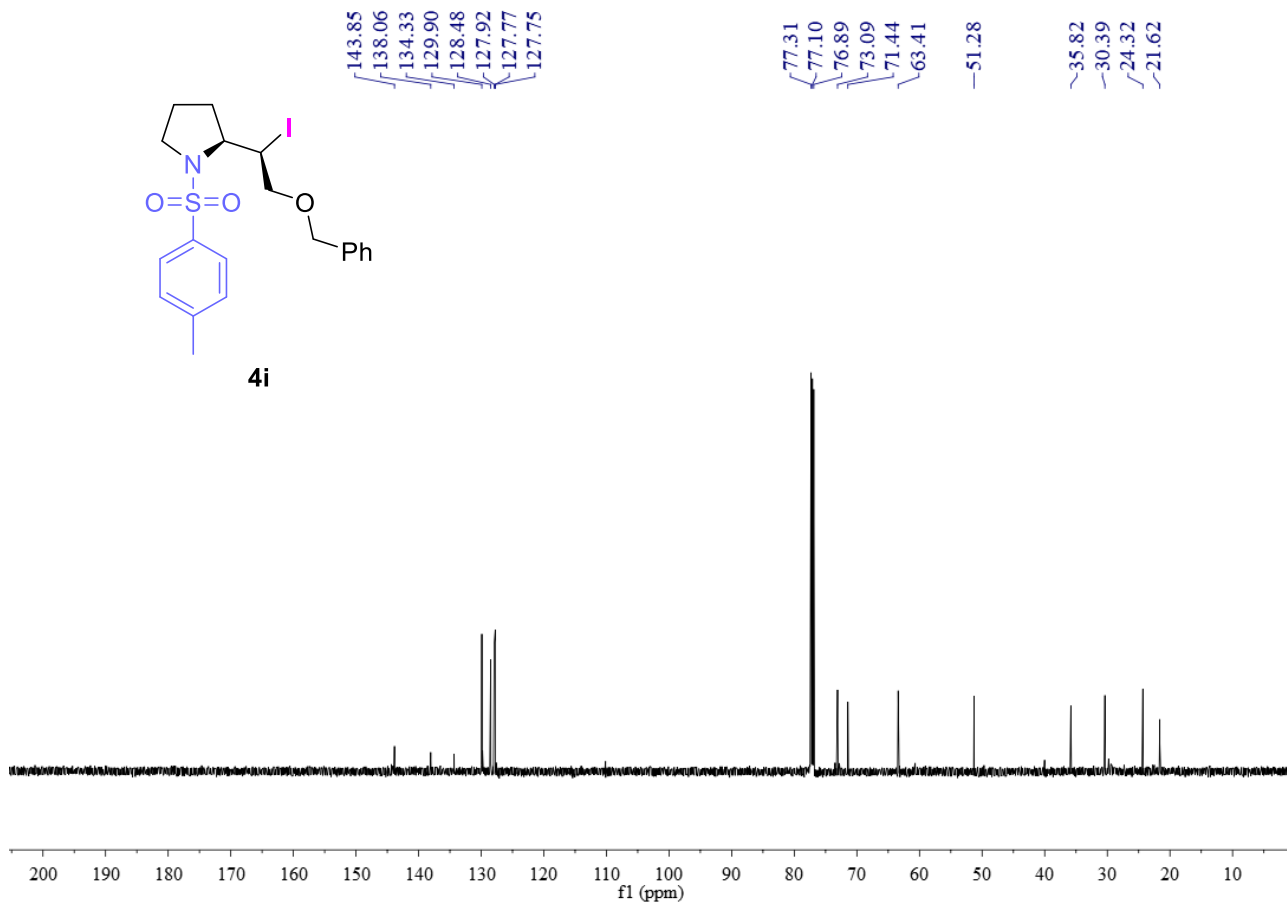
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7.71
7.40
7.38
7.37
7.36
7.35
7.32
7.31
7.30
7.28
4.71
4.71
4.70
4.64
4.63
4.59
4.57
4.57
4.00
4.00
3.99
3.98
3.87
3.86
3.45
3.44
3.43
3.42
3.34
3.32
3.31
3.31
2.43
2.05
2.04
2.03
1.85
1.83
1.82
1.81
1.75
1.74
1.73
1.72
1.33
1.31
1.30
1.29
1.28
0.00

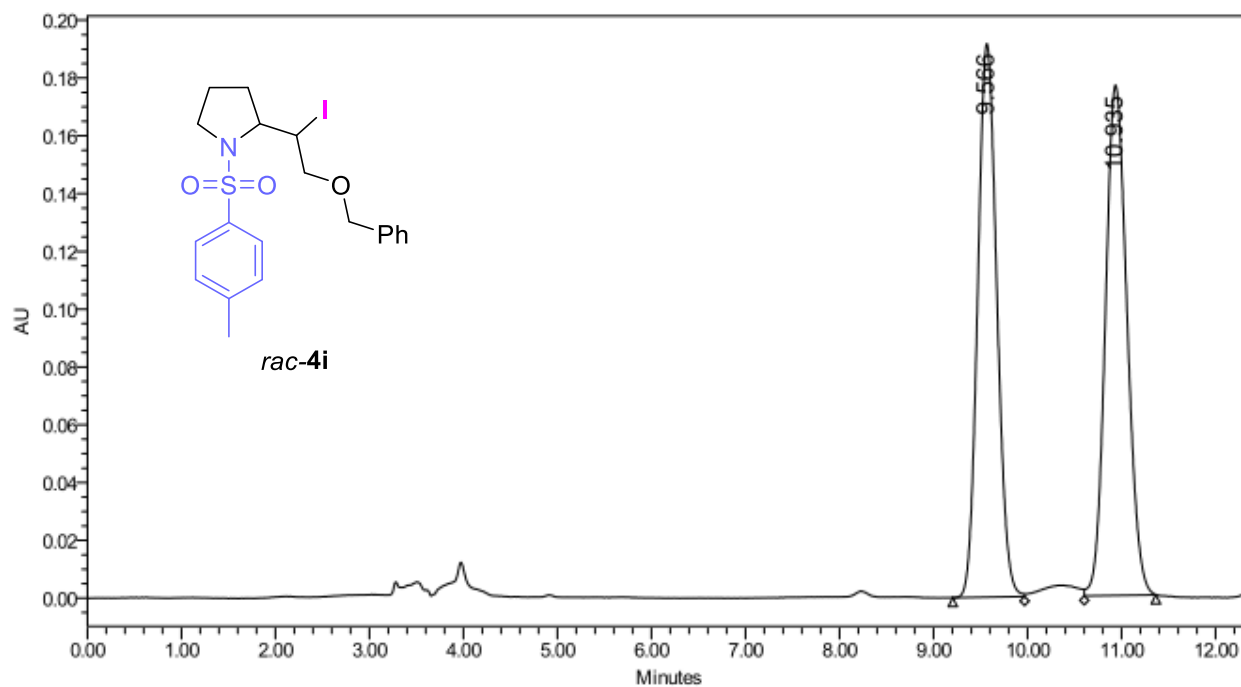


4i

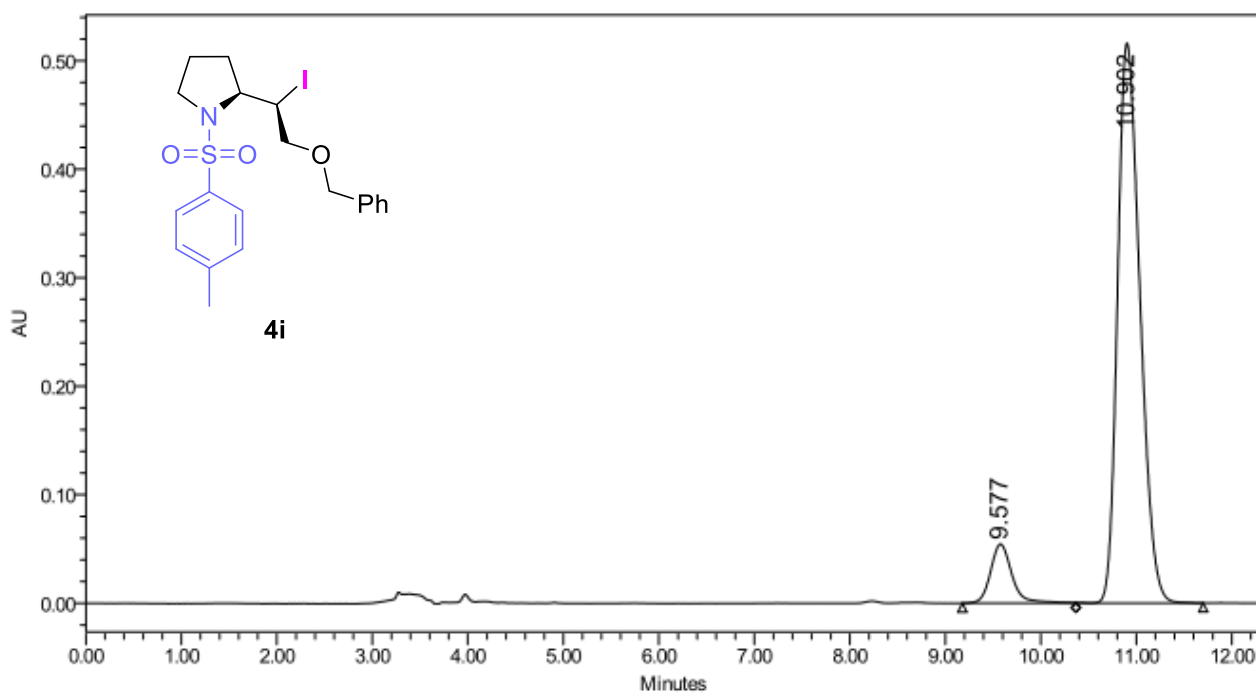


4i



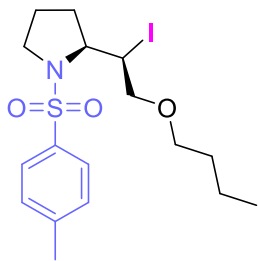


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.566	Unknown	2705543	49.00	191504	52.03	bV	459	9.203	9.968
2	10.935	Unknown	2816259	51.00	176571	47.97	Vb	457	10.602	11.363

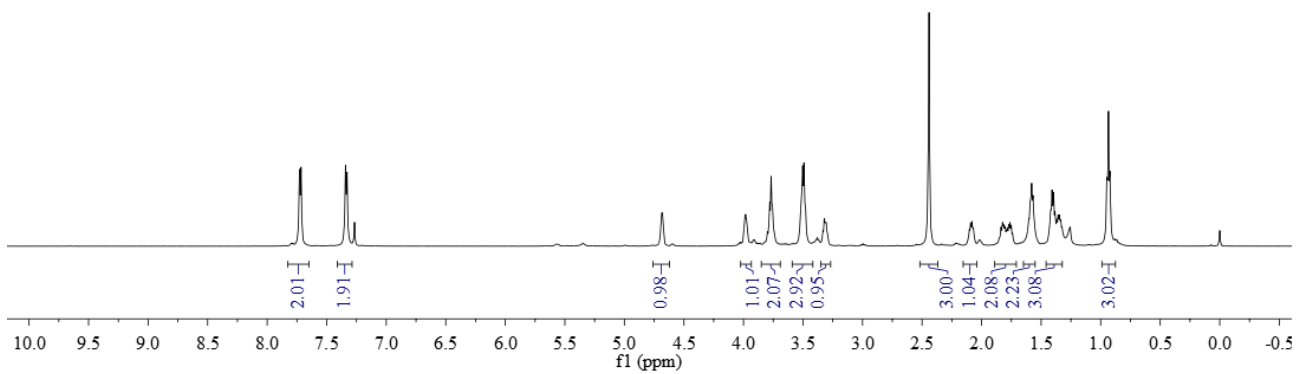


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.577	Unknown	847602	9.16	54319	9.52	Bv	713	9.178	10.367
2	10.902	Unknown	8405895	90.84	516178	90.48	vB	800	10.367	11.700

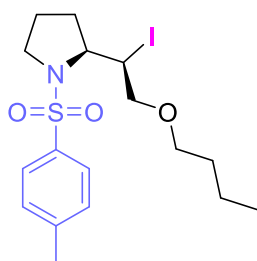
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7.33
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4.68
3.99
3.98
3.98
3.78
3.77
3.76
3.50
3.49
3.48
3.33
3.32
3.31
3.30
2.44
2.10
2.09
2.08
2.07
1.84
1.82
1.82
1.80
1.79
1.78
1.77
1.76
1.75
1.60
1.59
1.58
1.57
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1.37
1.36
1.35
1.34
1.33
0.95
0.92



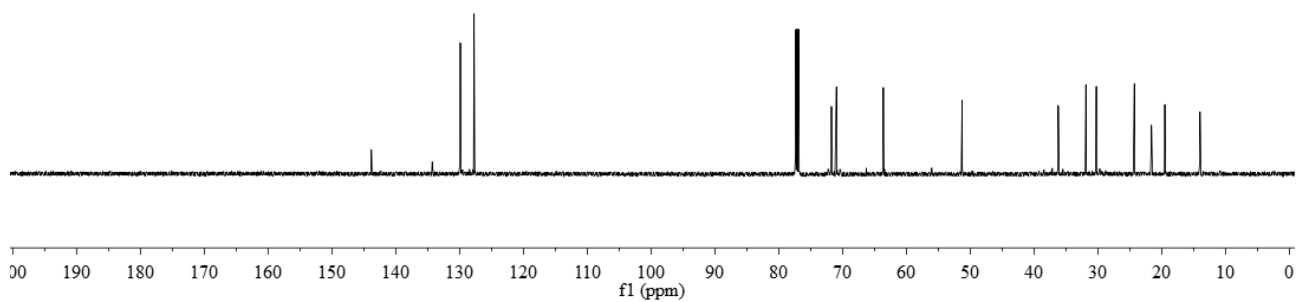
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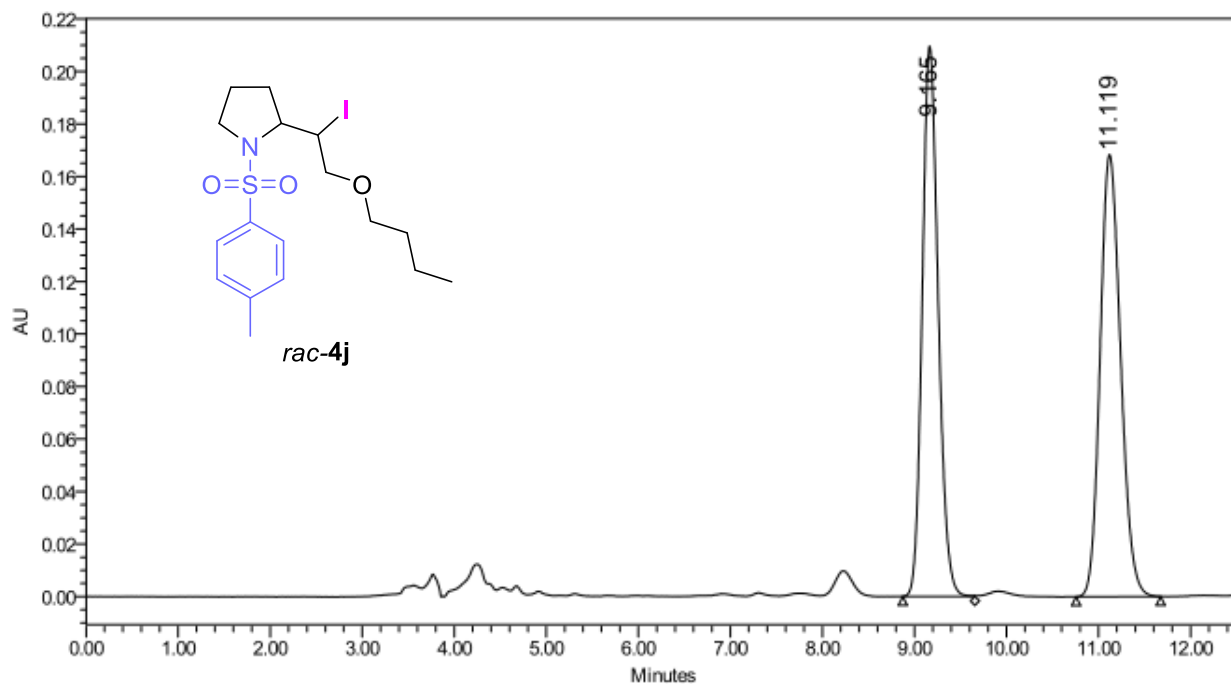


143.82
134.28
129.88
127.73
77.31
77.10
76.89
71.74
70.95
63.61
51.27
36.21
31.87
30.24
24.28
21.61
19.51
14.00

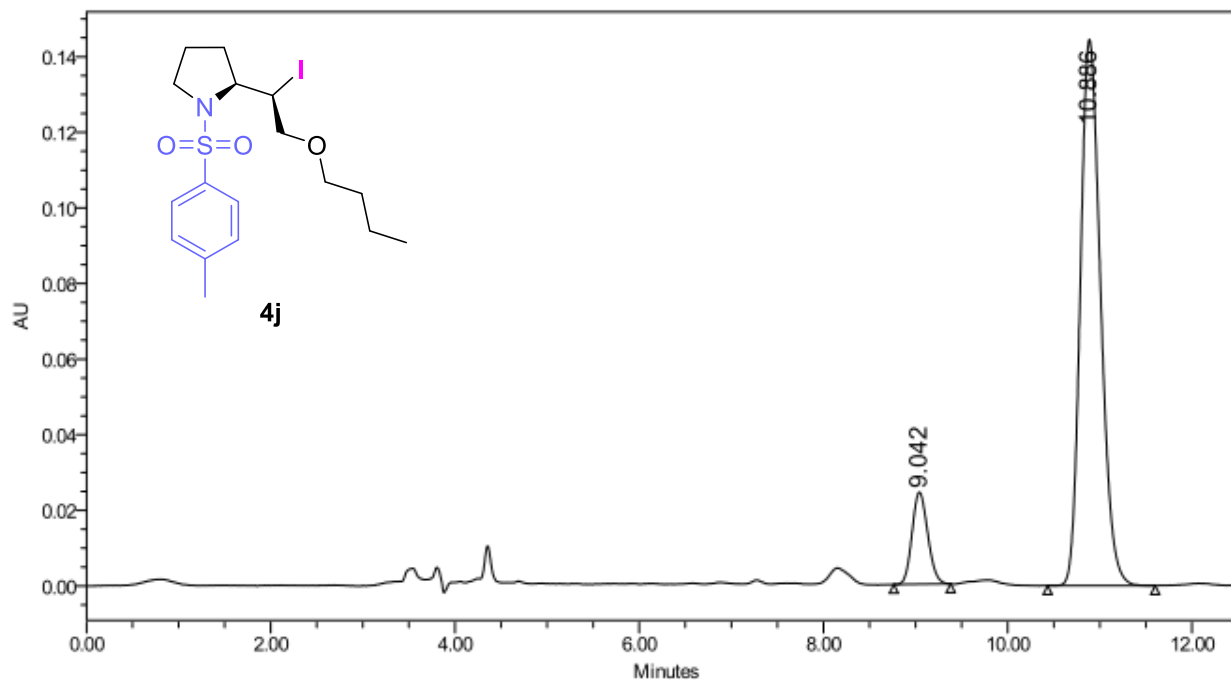


4j

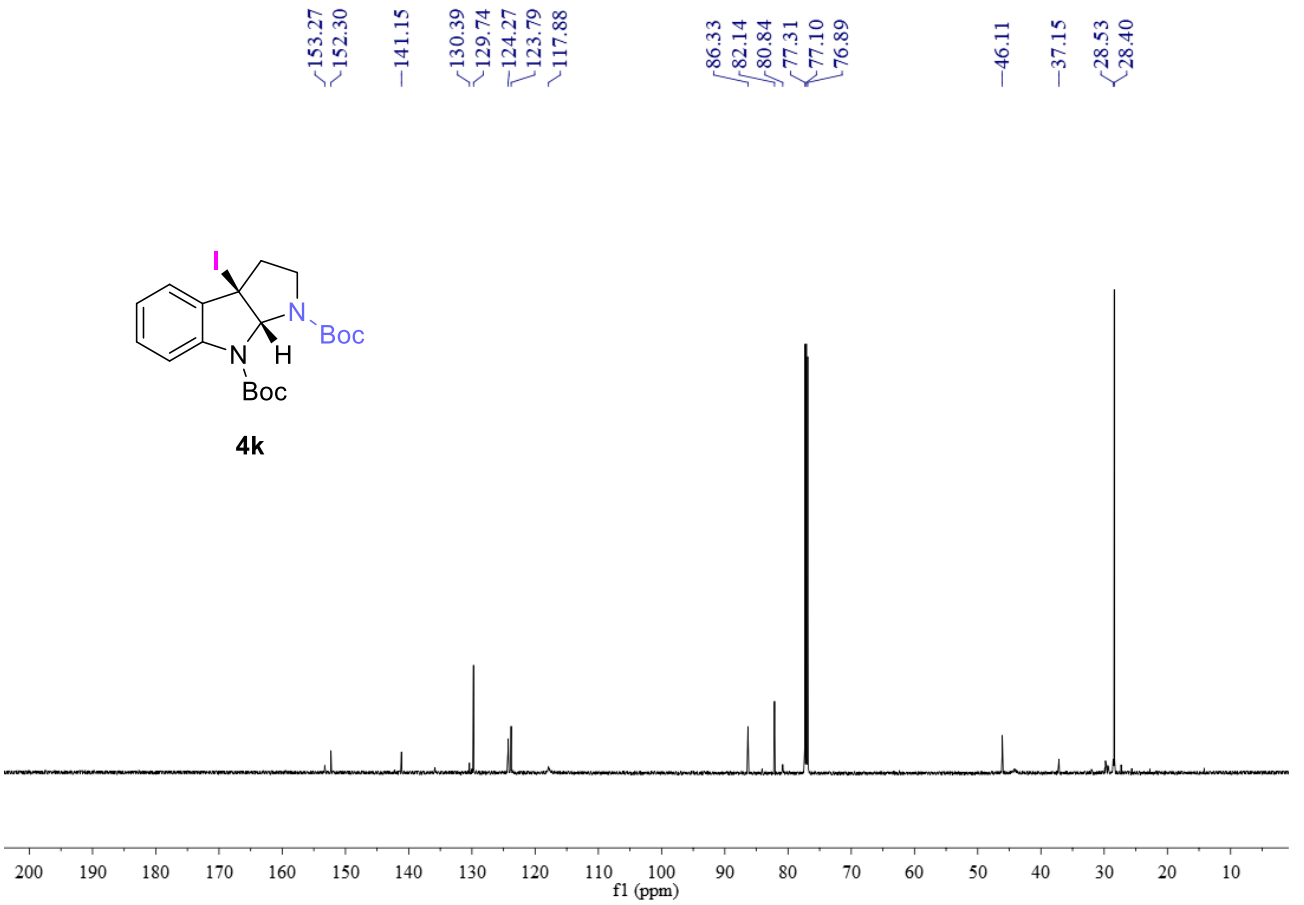
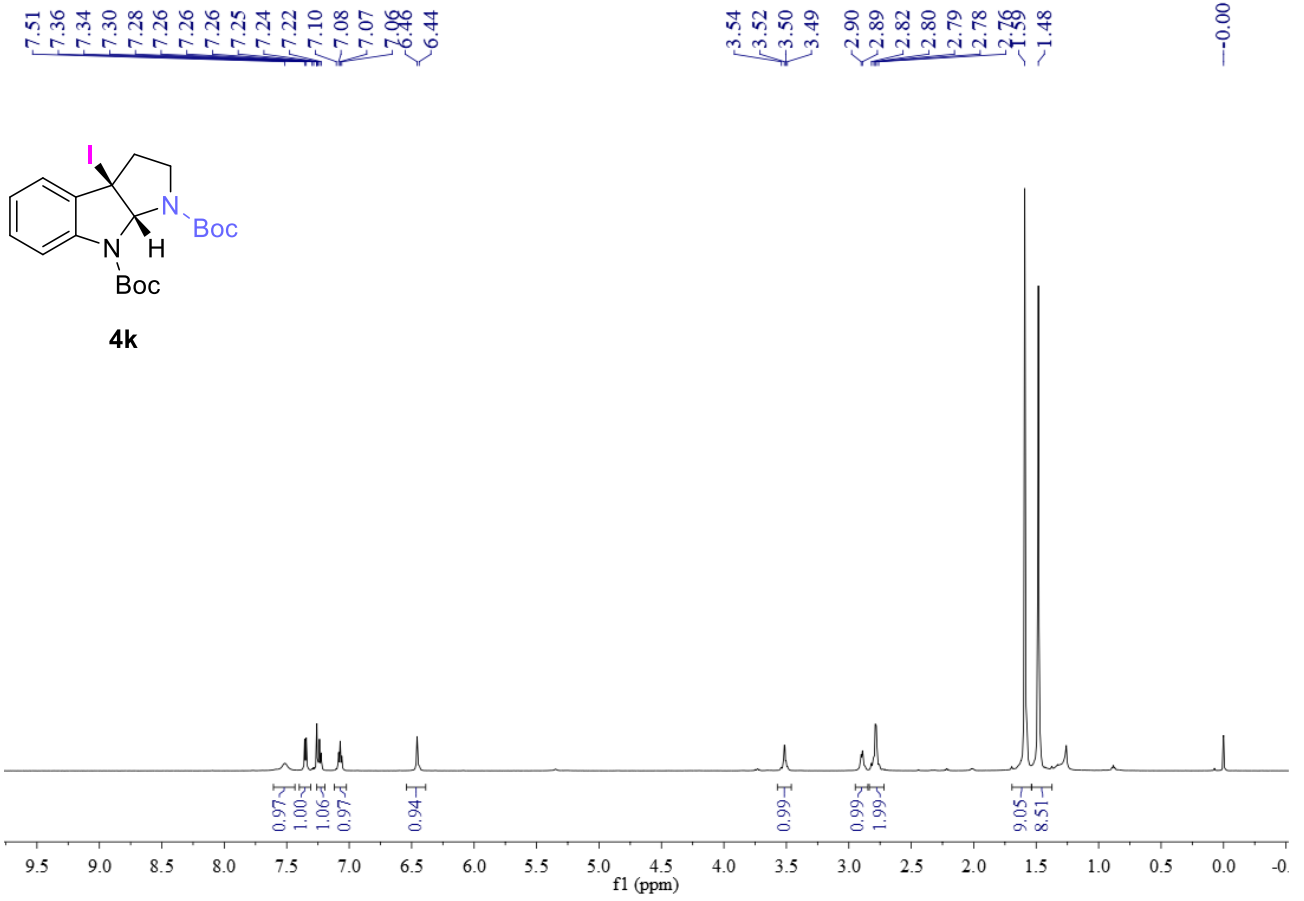


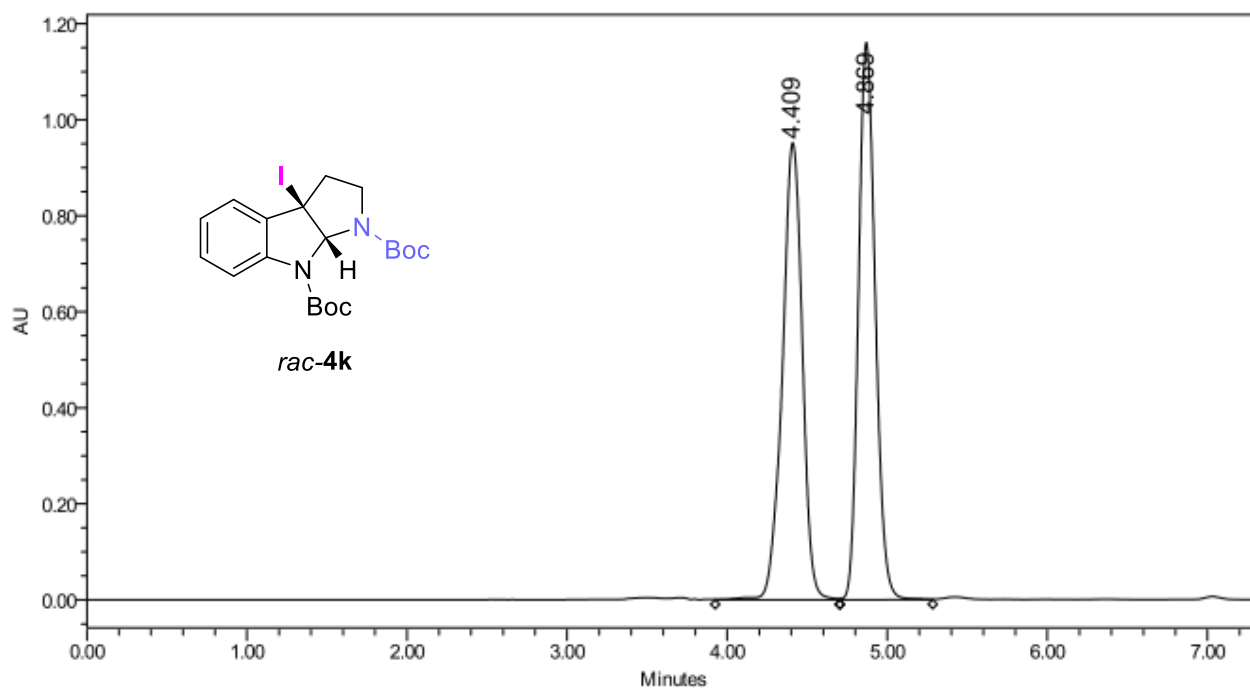


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.165	Unknown	2533606	49.31	209570	55.46	BV	471	8.872	9.657
2	11.119	Unknown	2604999	50.69	168326	44.54	BB	551	10.757	11.675

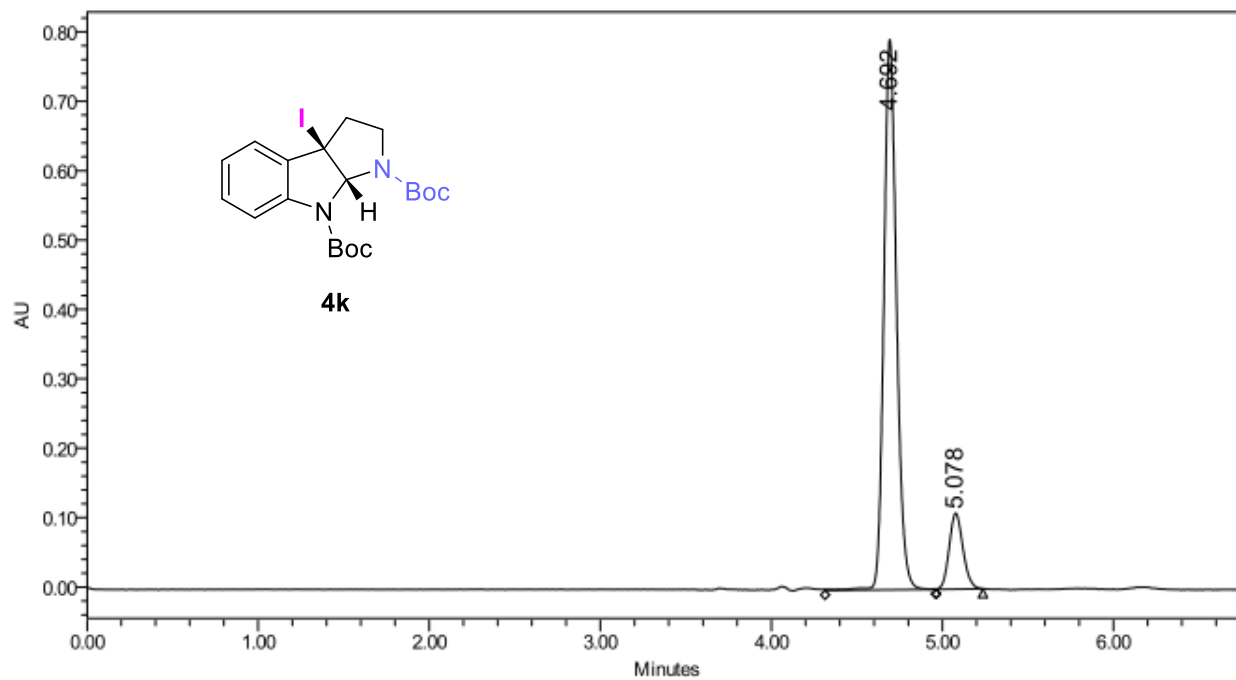


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.042	Unknown	287380	11.55	24278	14.38	bb	370	8.763	9.380
2	10.886	Unknown	2199915	88.45	144503	85.62	bb	701	10.432	11.600

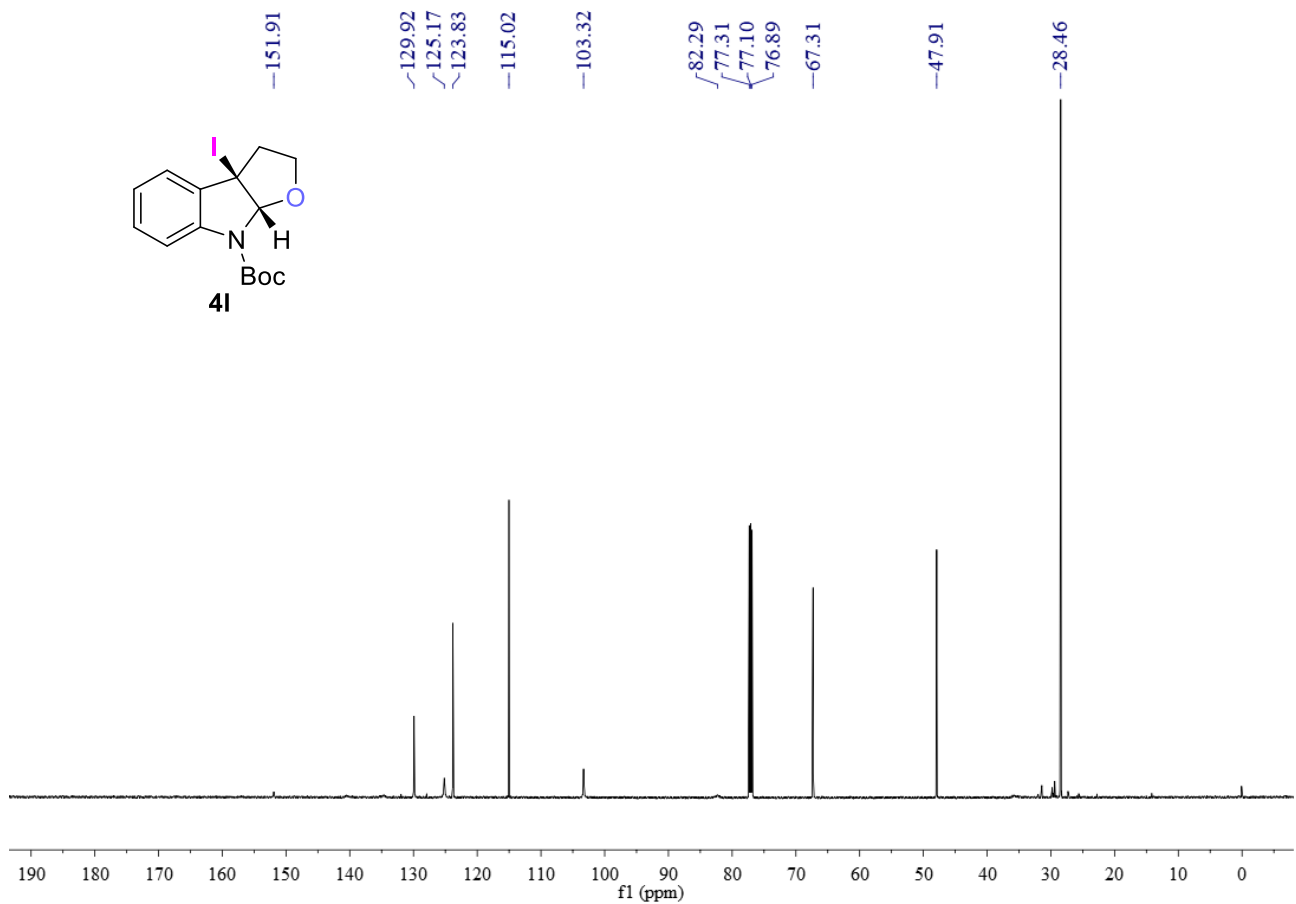
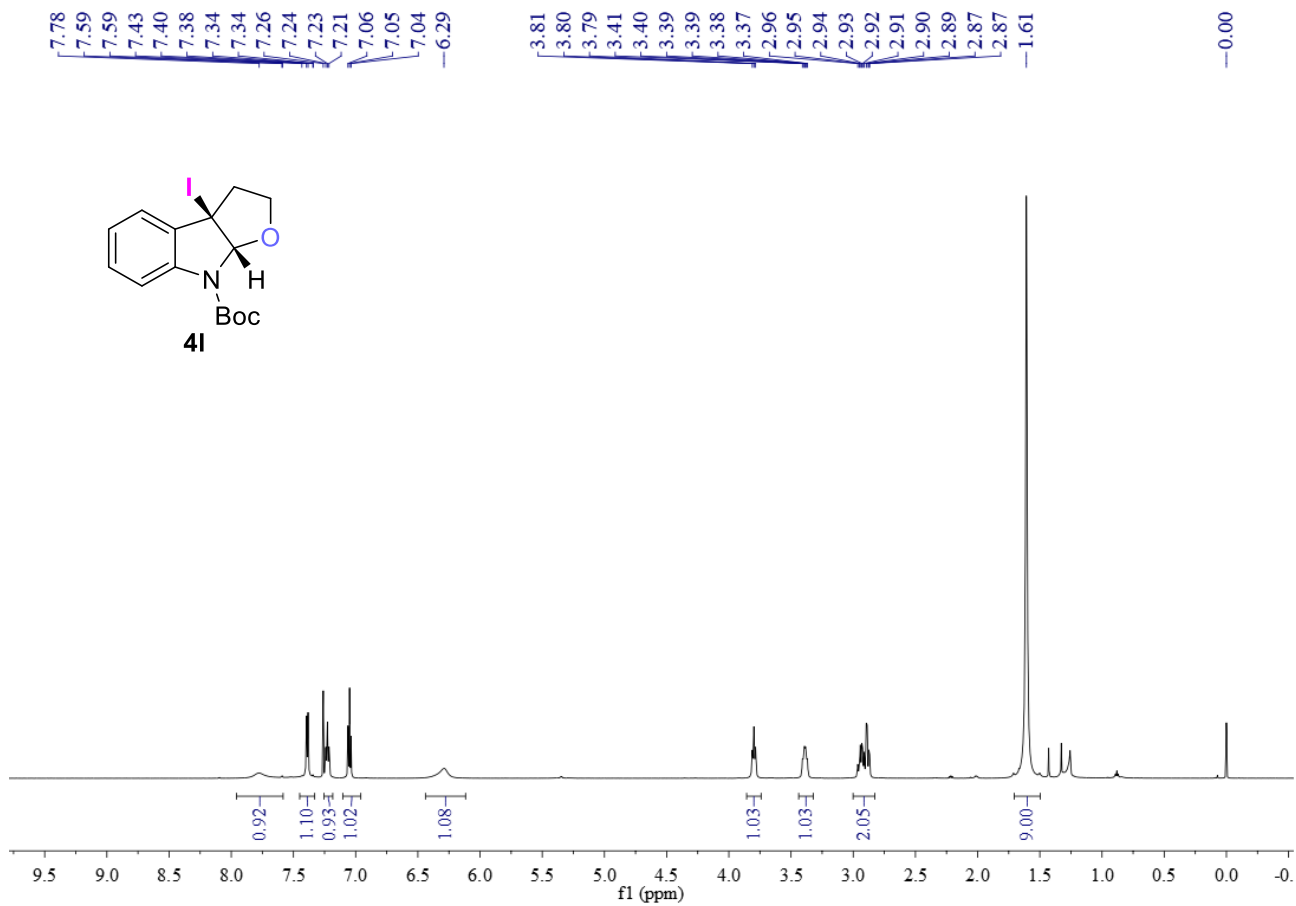


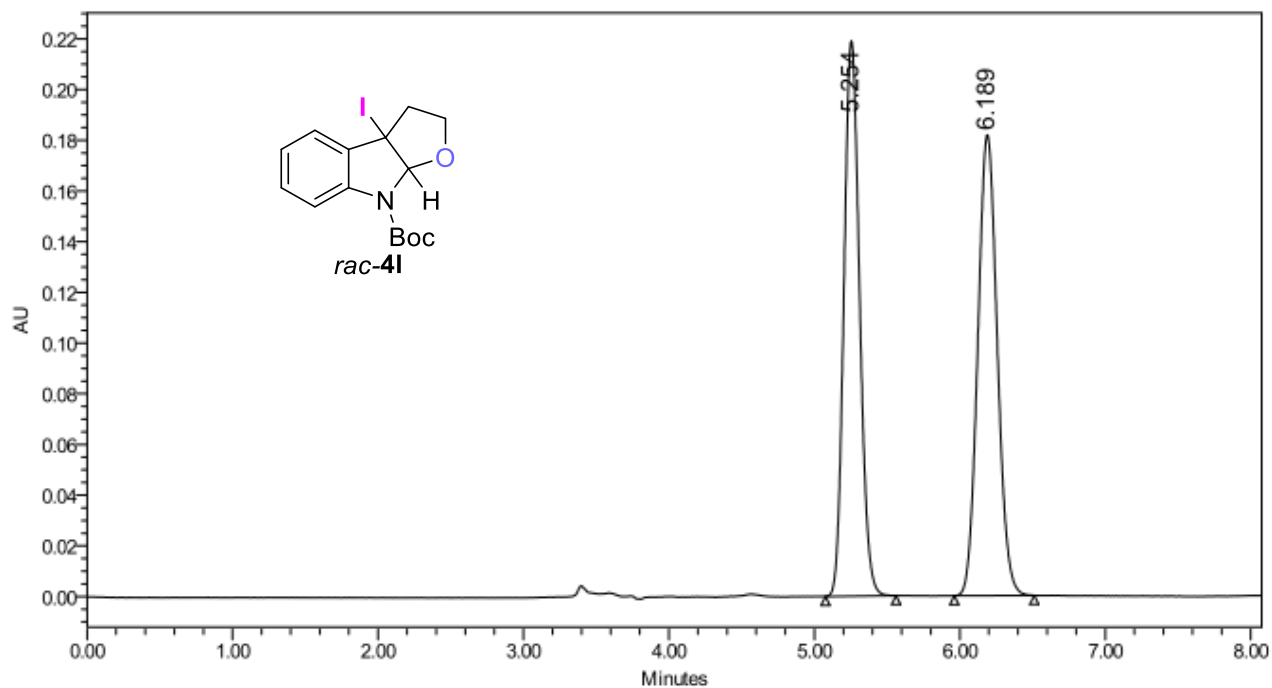


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	4.409	Unknown	8245129	49.33	951590	45.06	VV	467	3.925	4.703
2	4.869	Unknown	8469532	50.67	1160456	54.94	VV	348	4.703	5.283

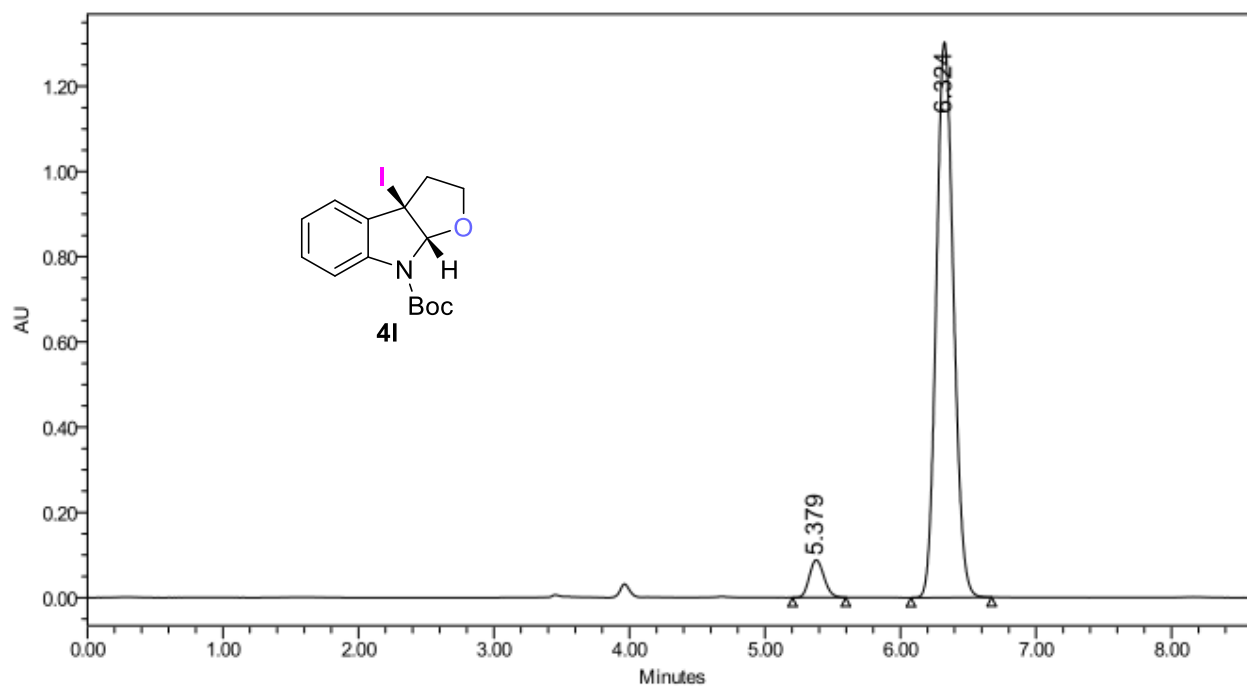


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	4.692	Unknown	4077522	86.97	792806	87.90	VV	390	4.313	4.963
2	5.078	Unknown	611083	13.03	109157	12.10	VB	164	4.963	5.237





RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	1634392	49.17	219062	54.64	BB	291	5.077	5.562
2	Unknown	1689816	50.83	181835	45.36	BB	330	5.962	6.512

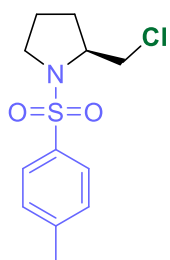


RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	Unknown	667761	5.47	88344	6.35	Bb	236	5.203	5.597
2	Unknown	11532057	94.53	1303663	93.65	Bb	357	6.078	6.673

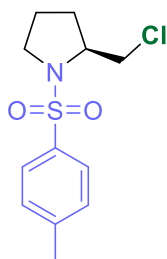
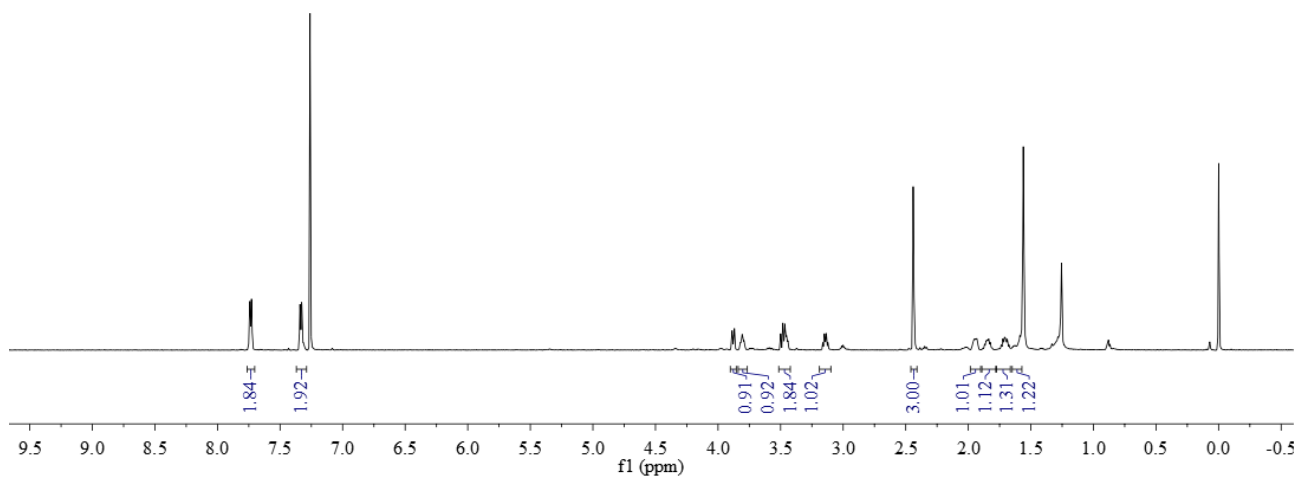
7.74
7.73
7.34
7.33
7.26

3.89
3.87
3.82
3.81
3.50
3.48
3.47
3.45
3.44
3.16
3.15
3.13
3.12
2.44

1.93
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1.84
1.82
1.72
1.71
1.69
1.59
1.56
0.00



5a



5a

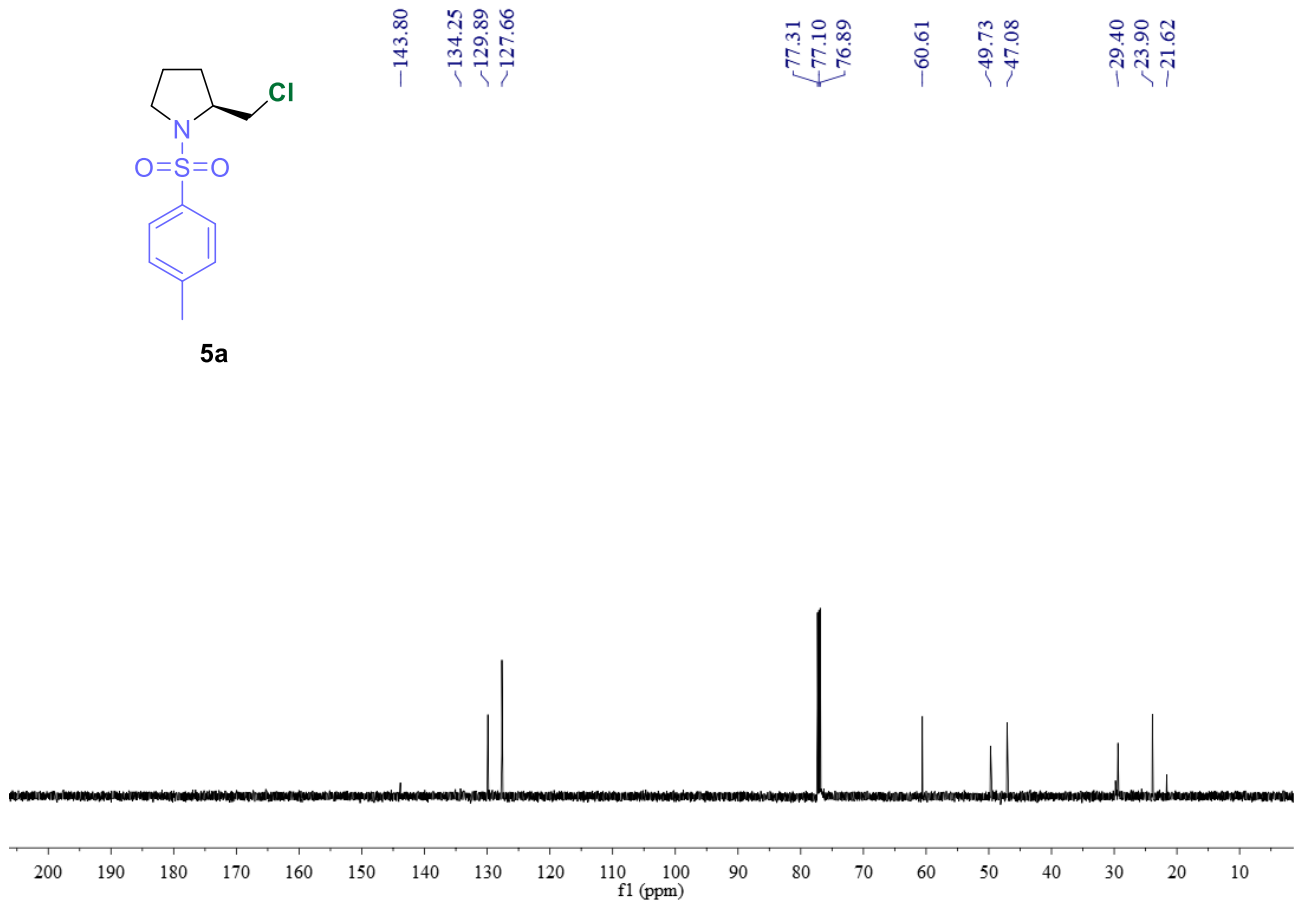
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127.66

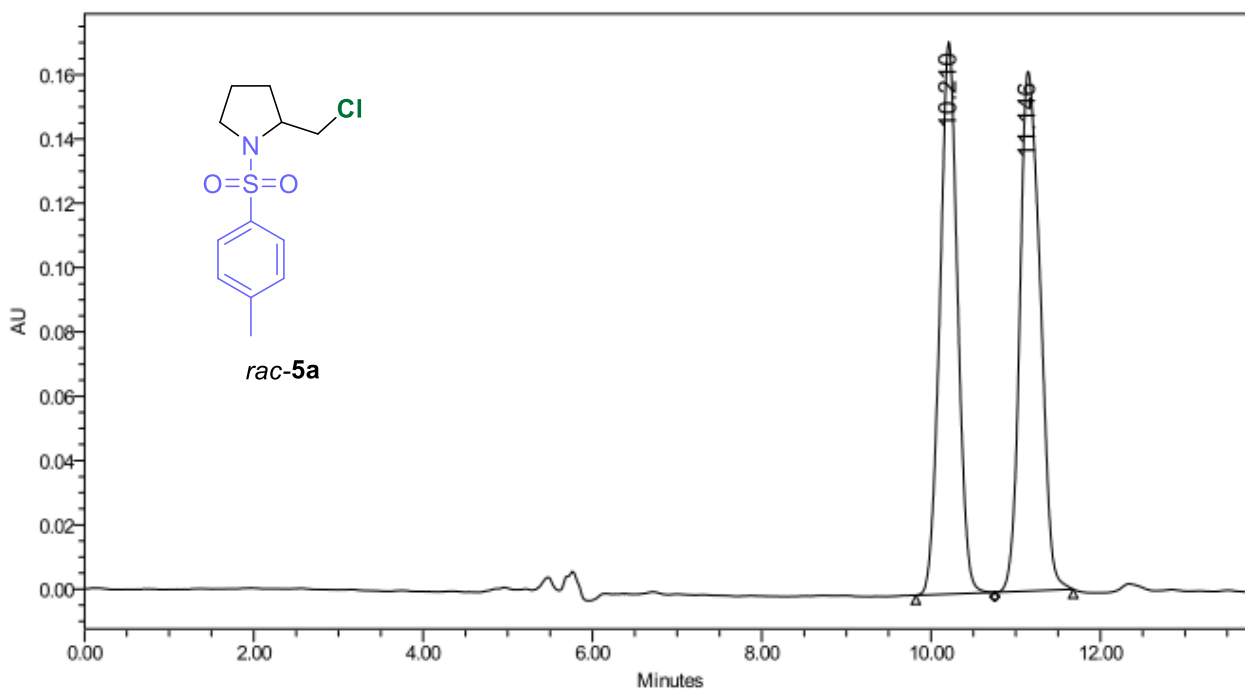
77.31
77.10
76.89

60.61

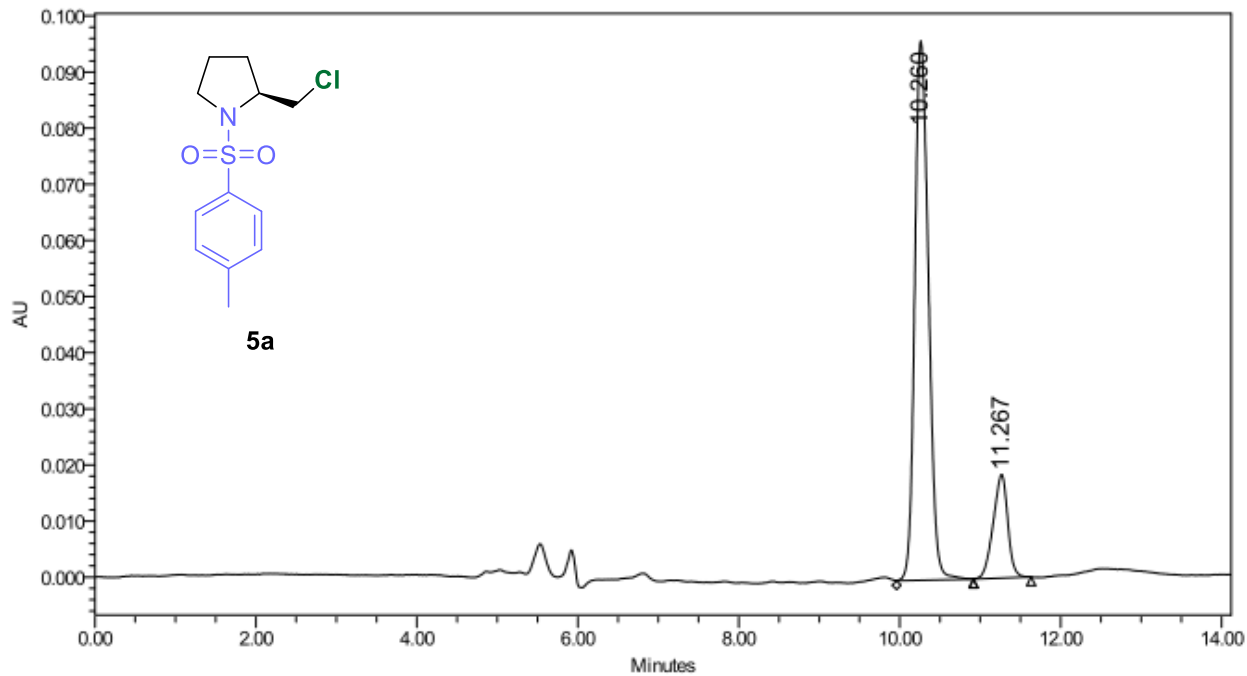
49.73
47.08

29.40
23.90
21.62

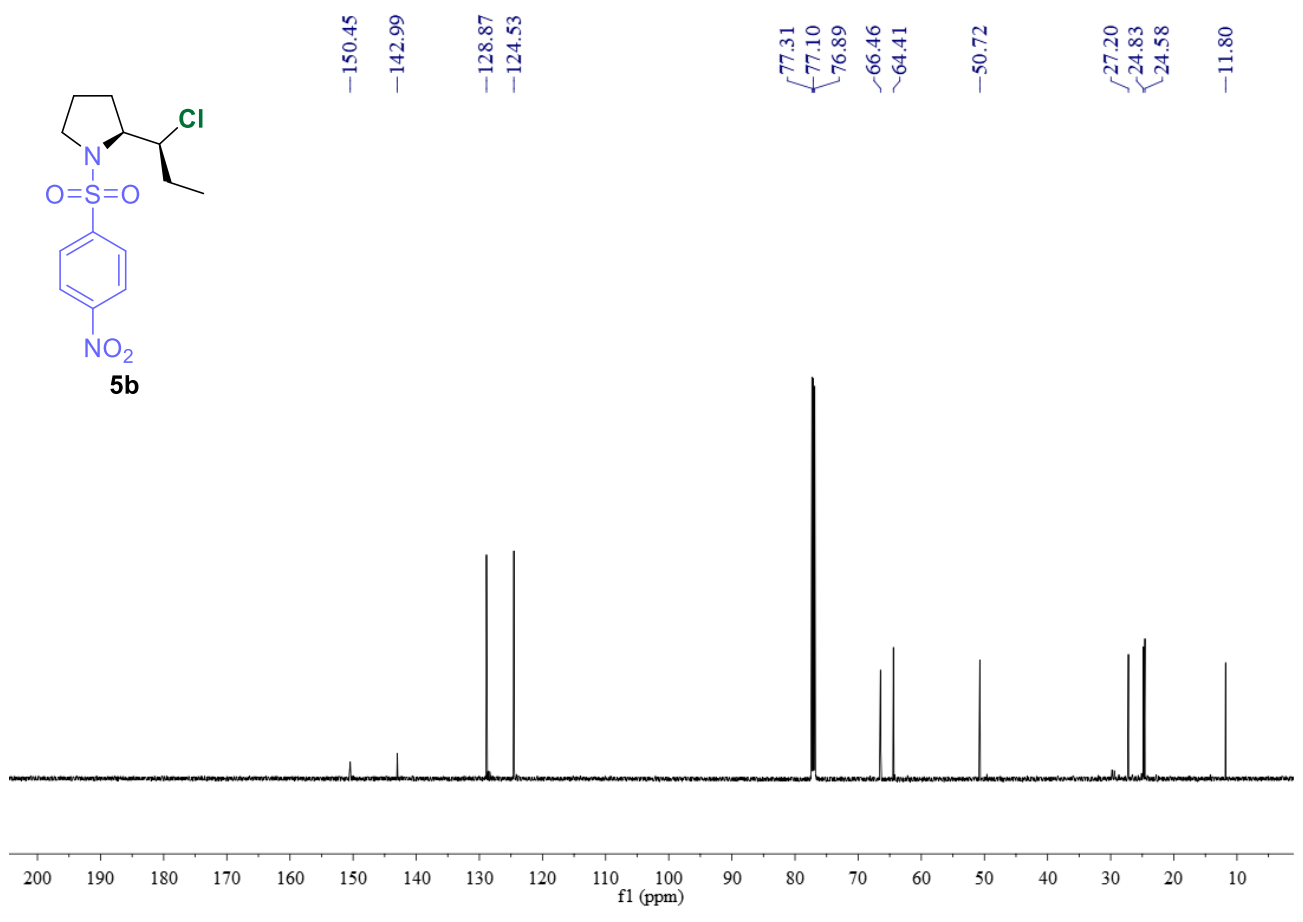
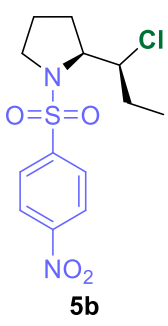
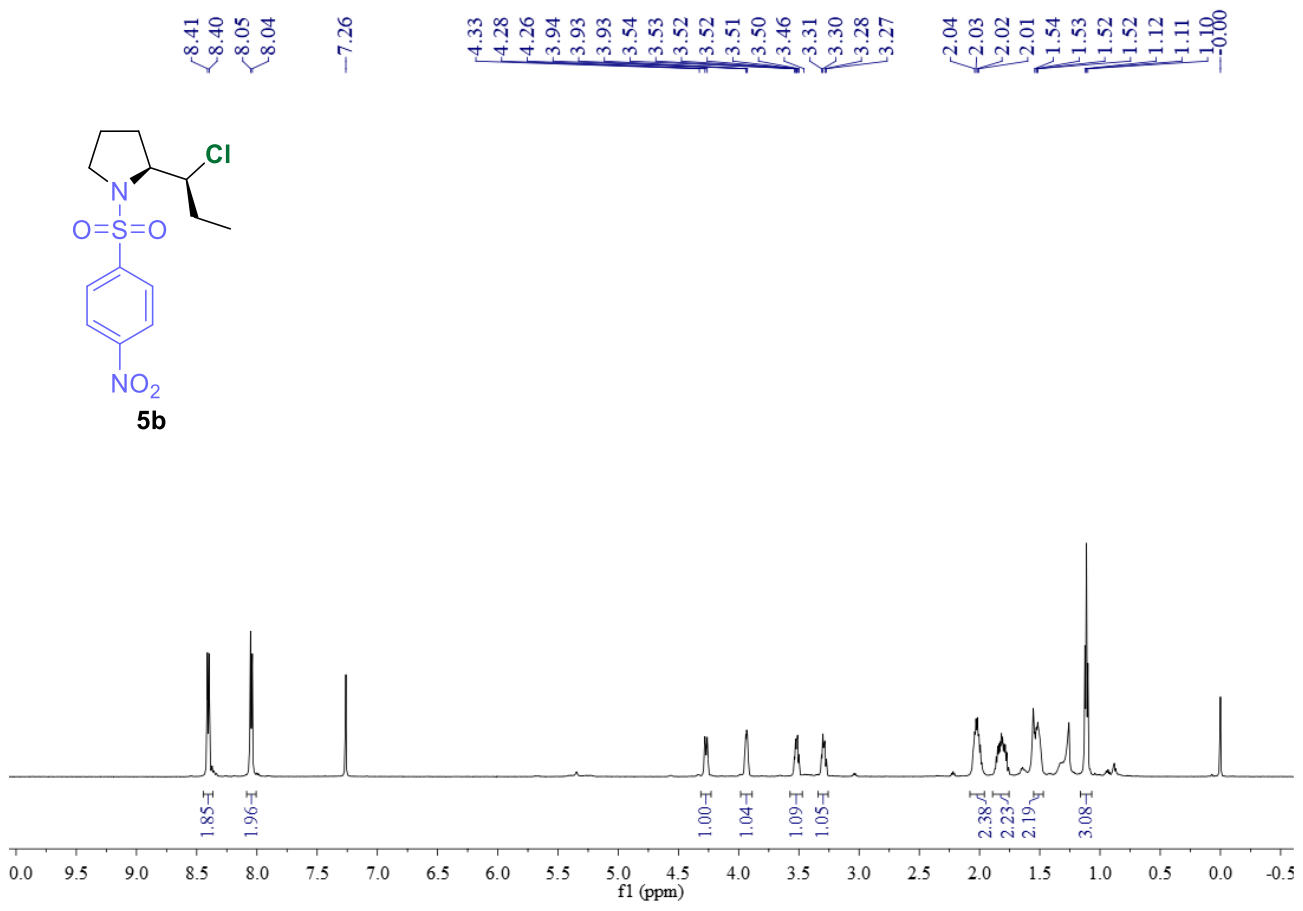
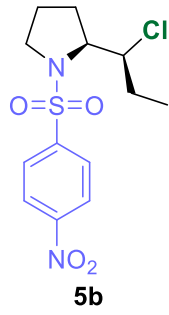


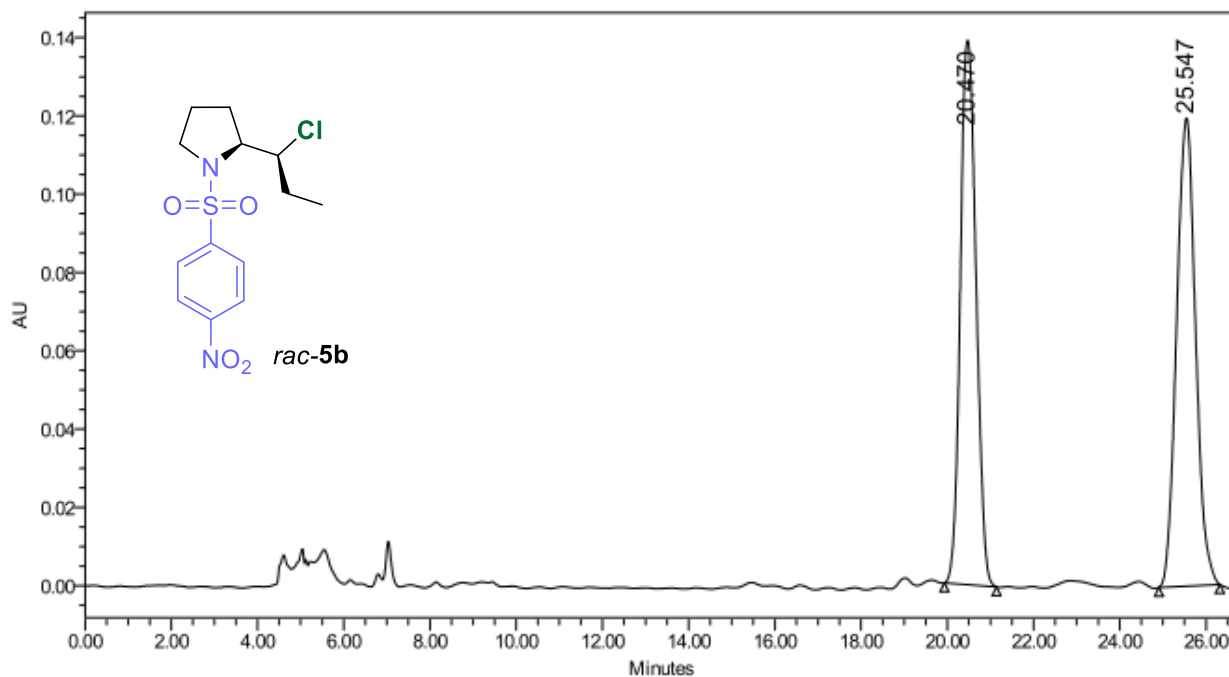


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.210	Unknown	2493592	47.96	171759	51.53	BV	560	9.820	10.753
2	11.146	Unknown	2705395	52.04	161566	48.47	Vb	555	10.753	11.678

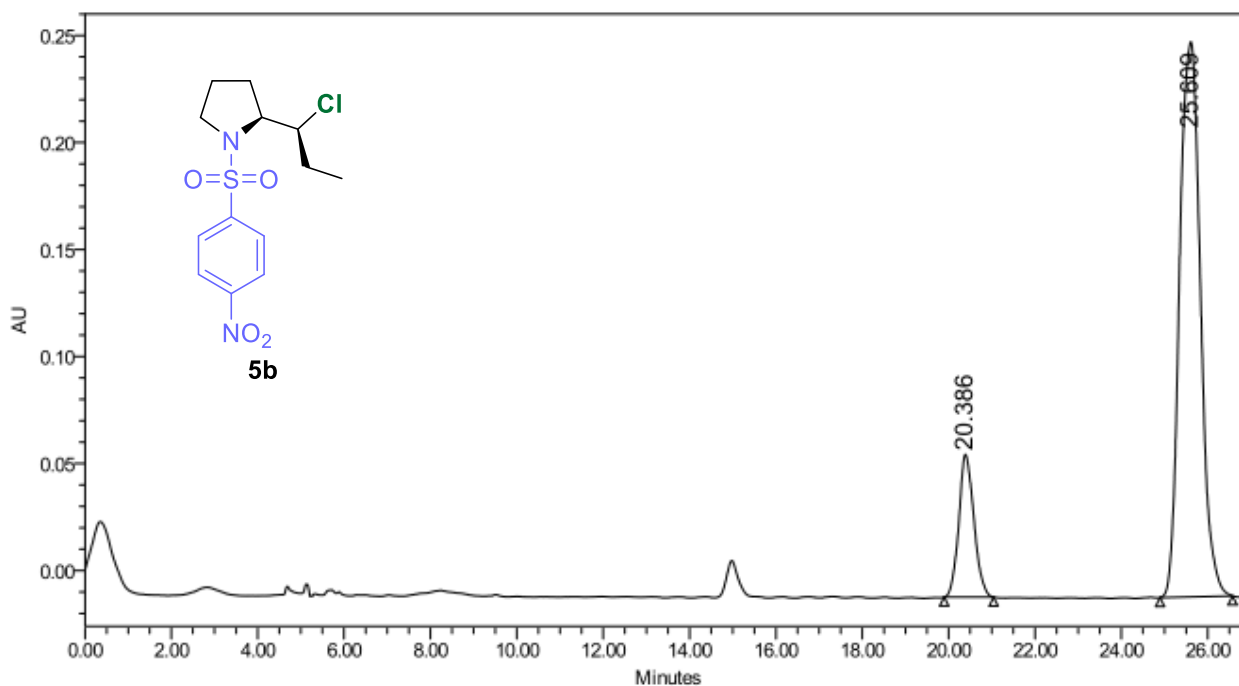


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.260	Unknown	1135240	82.99	96112	83.89	VB	574	9.960	10.917
2	11.267	Unknown	232663	17.01	18460	16.11	BB	429	10.917	11.632

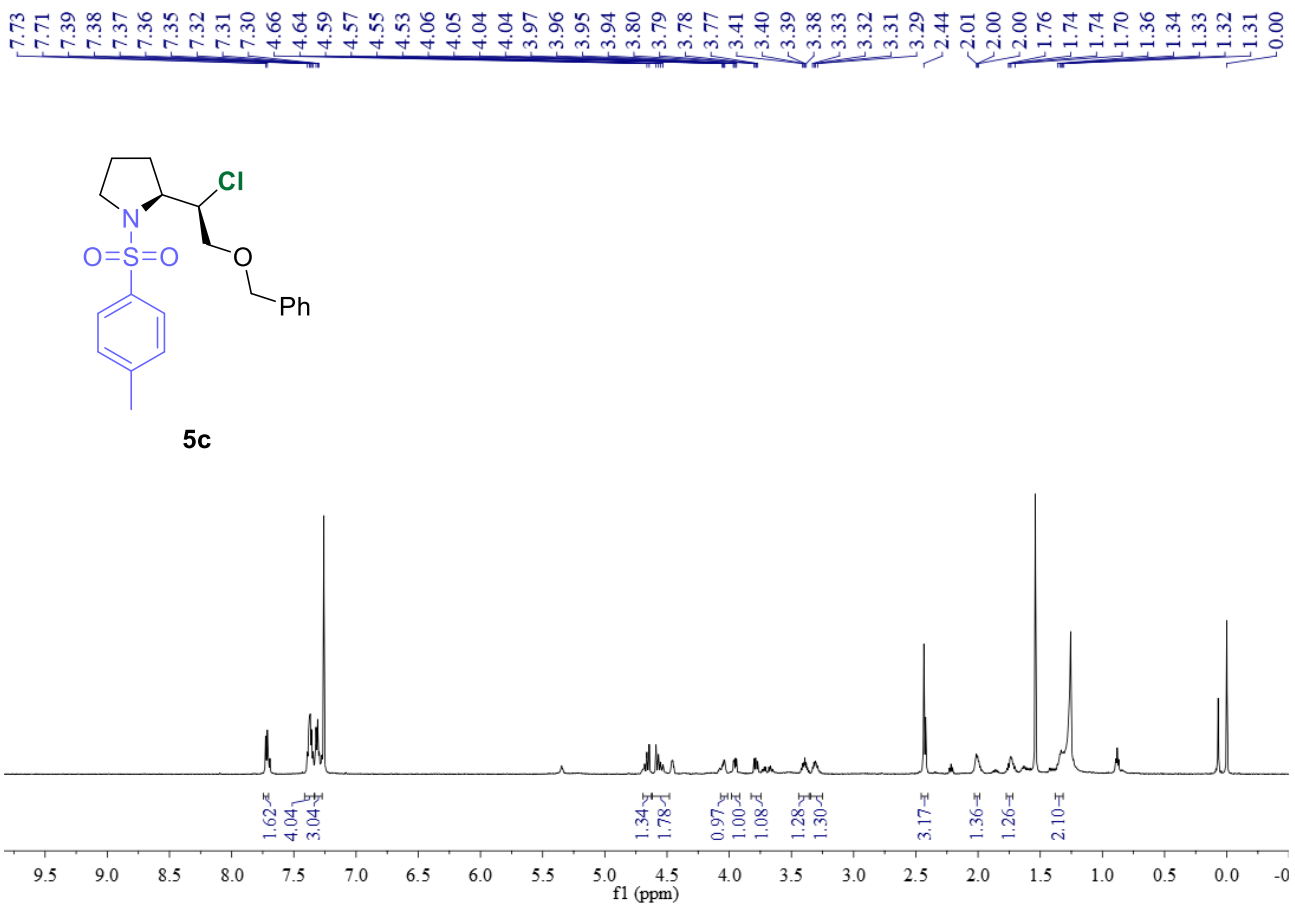




	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	20.470	Unknown	3526494	49.12	139042	53.76	BB	726	19.932	21.142
2	25.547	Unknown	3653283	50.88	119598	46.24	BB	850	24.905	26.322



	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	20.386	Unknown	1619863	15.75	66620	20.44	Bb	684	19.898	21.038
2	25.609	Unknown	8668218	84.25	259309	79.56	Bb	1009	24.893	26.575

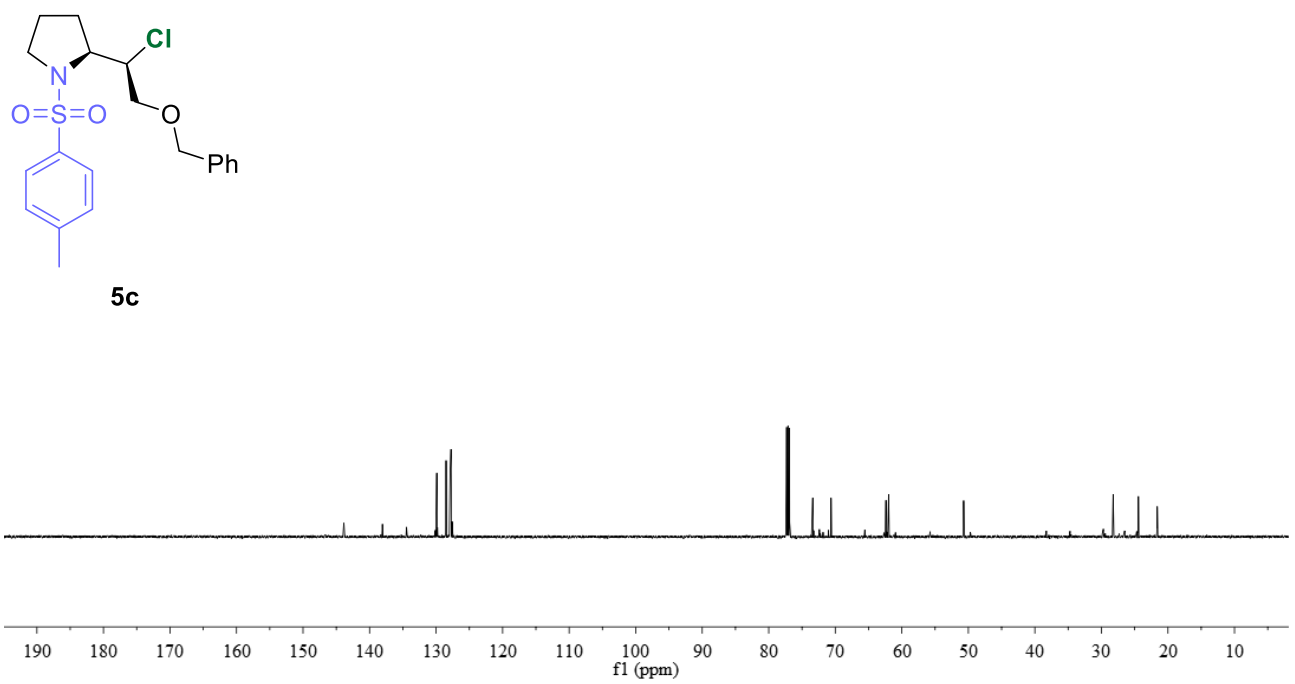


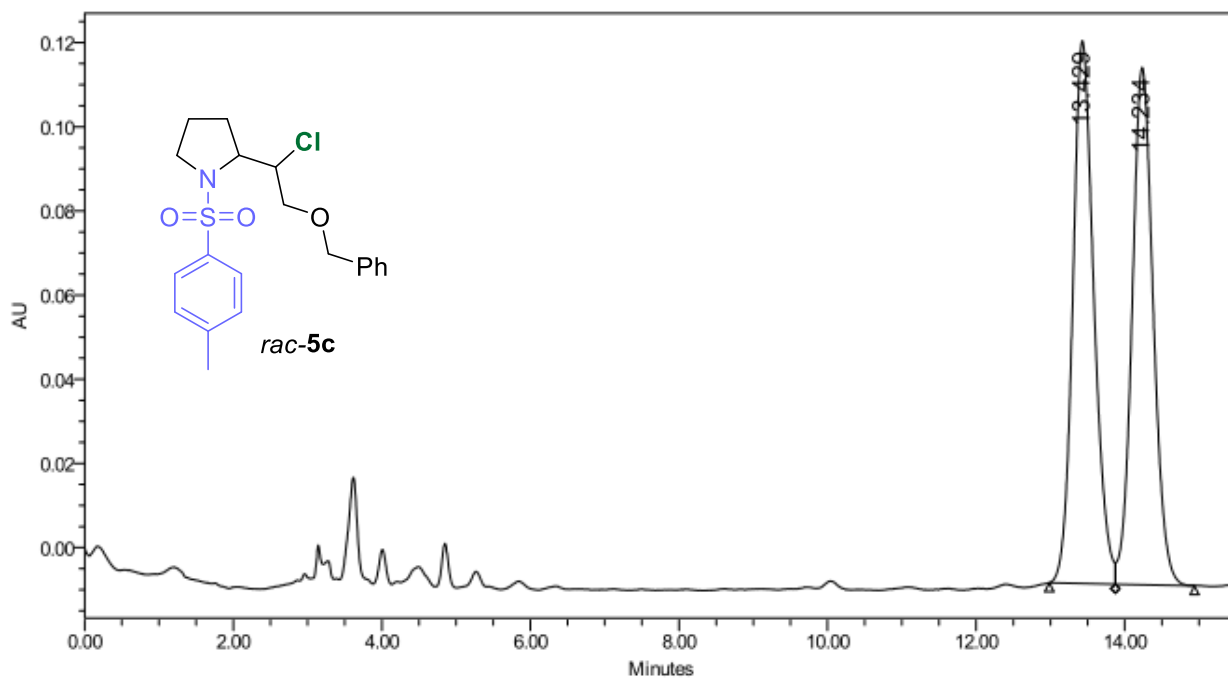
143.86
138.07
134.45
129.90
128.50
127.90
127.78
127.76

77.31
77.10
76.89
73.39
70.63
62.38
61.98

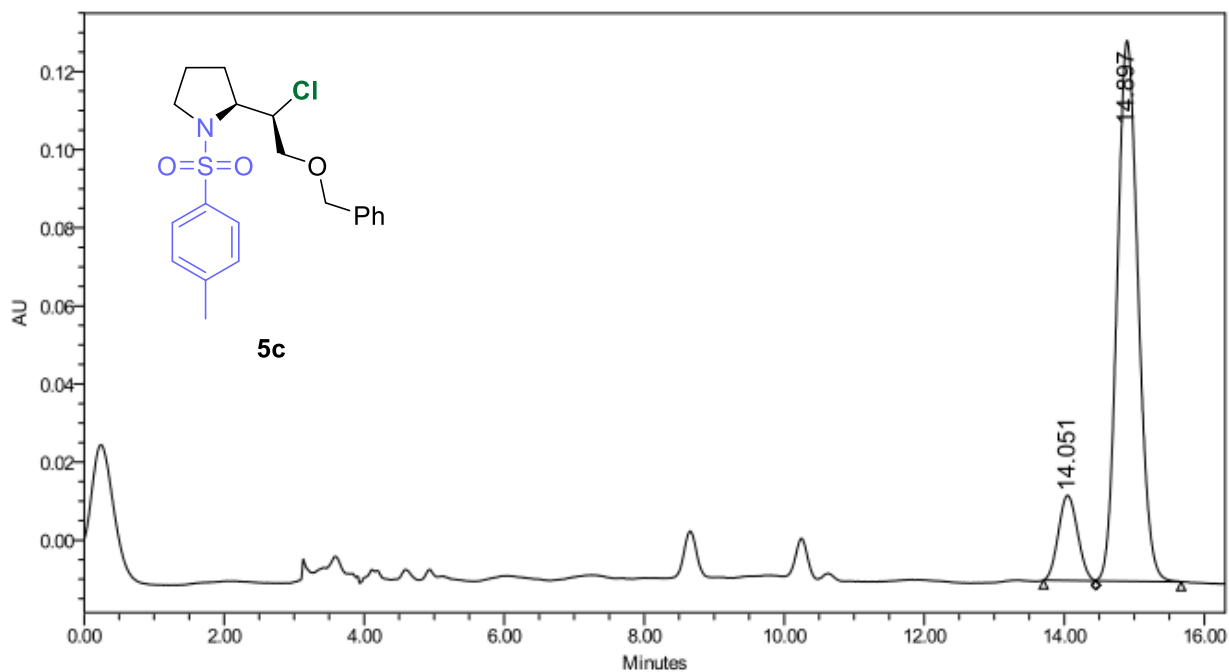
-50.70

-28.23
-24.44
-21.61



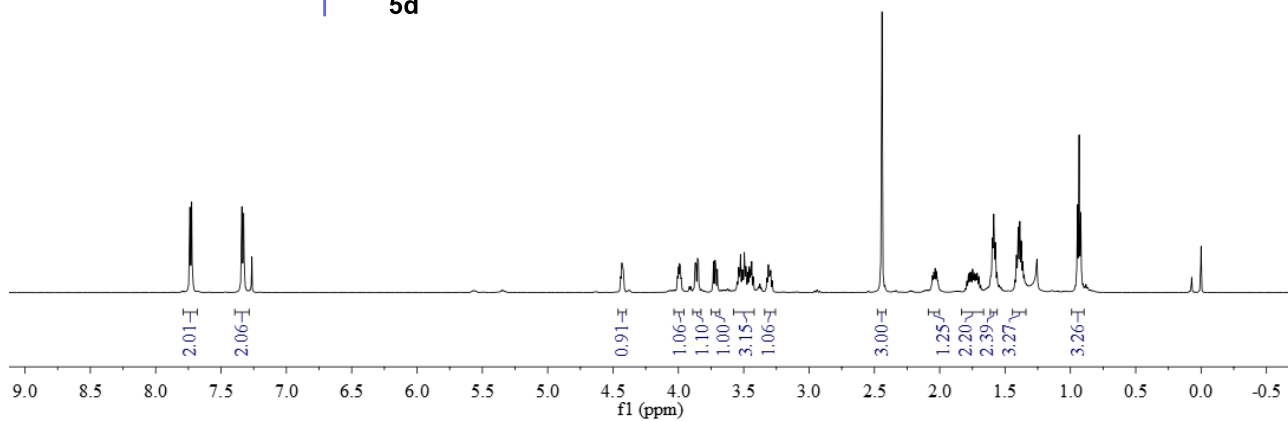
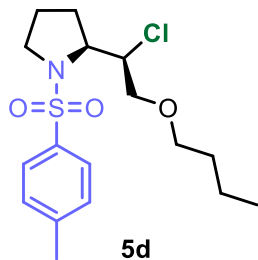


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.429	Unknown	2532340	51.10	128946	51.20	bV	533	12.985	13.873
2	14.234	Unknown	2423180	48.90	122885	48.80	VB	638	13.873	14.937

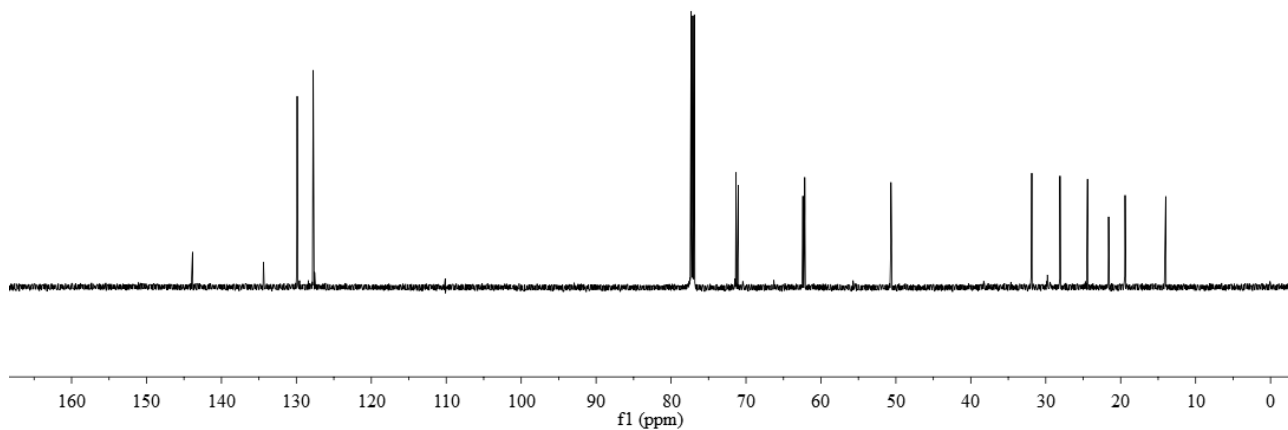
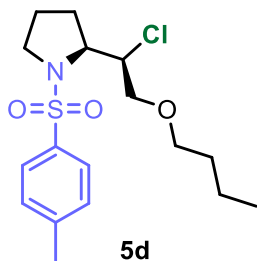


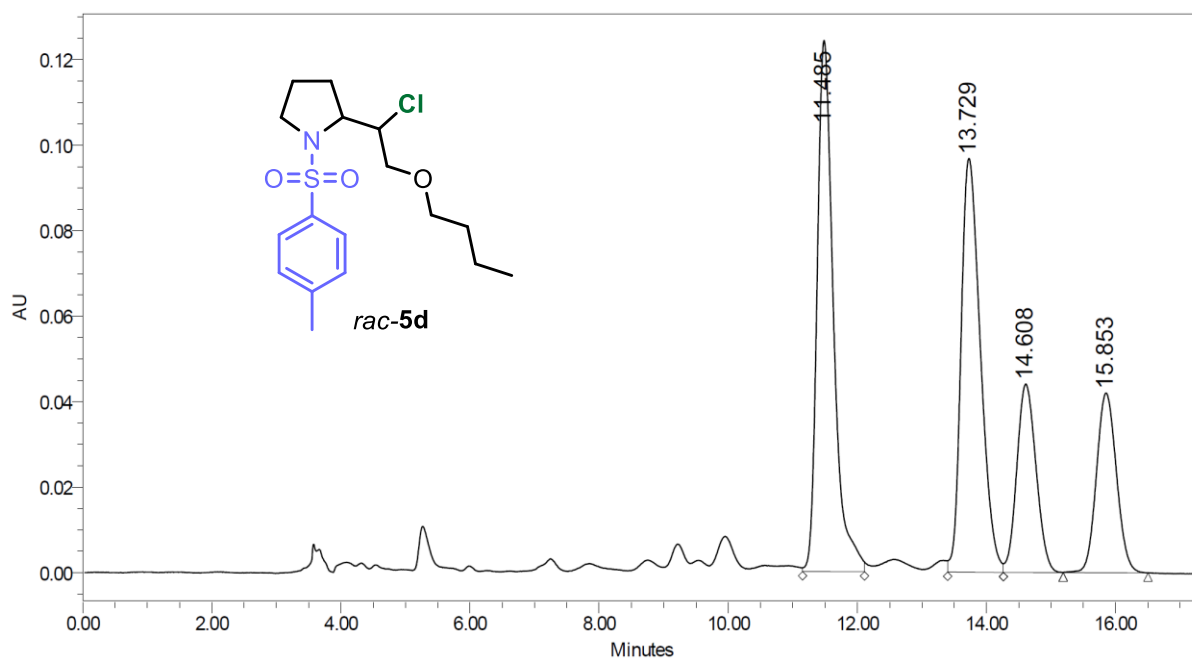
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.051	Unknown	414576	12.59	21718	13.56	bV	449	13.703	14.452
2	14.897	Unknown	2877358	87.41	138434	86.44	Vb	731	14.452	15.670

7.74
7.72
7.34
7.33
4.43
4.43
4.42
4.00
3.99
3.99
3.87
3.86
3.85
3.85
3.73
3.72
3.71
3.70
3.54
3.54
3.52
3.51
3.51
3.50
3.48
3.48
3.47
3.46
3.45
3.44
3.31
3.30
3.29
2.44
2.04
2.03
2.02
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1.60
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1.57
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1.40
1.39
1.38
1.36
0.95
0.92
0.00

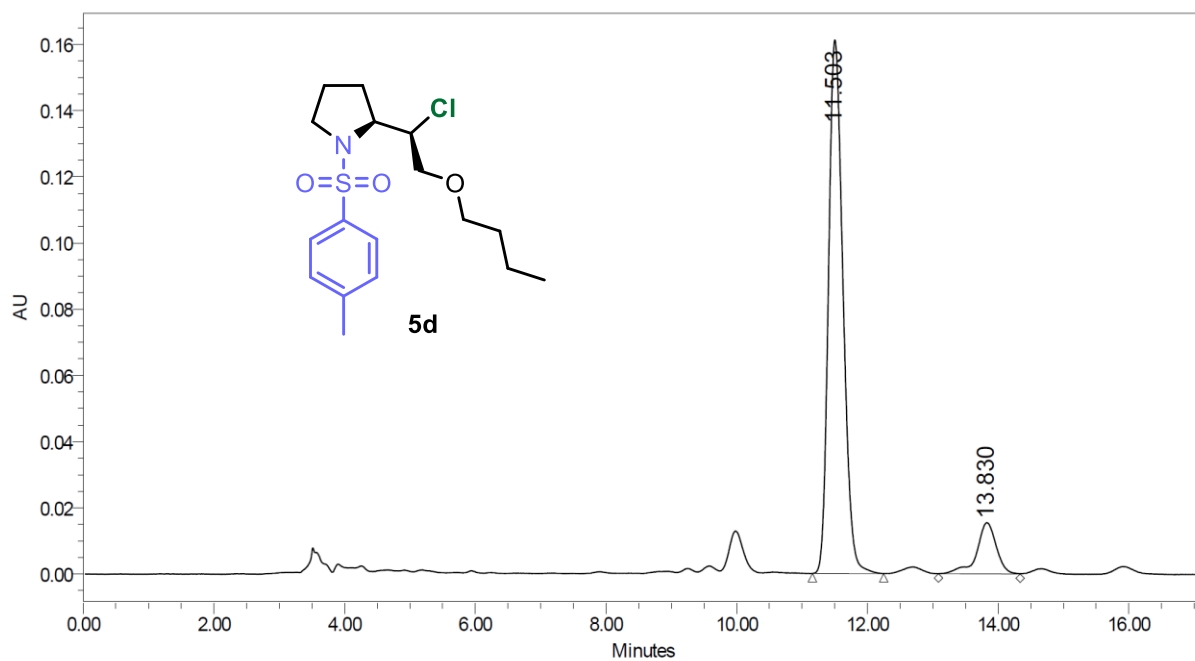


143.86
134.39
129.89
127.75
71.32
71.03
62.41
62.16
50.65
31.86
28.10
24.42
21.61
19.41
13.99

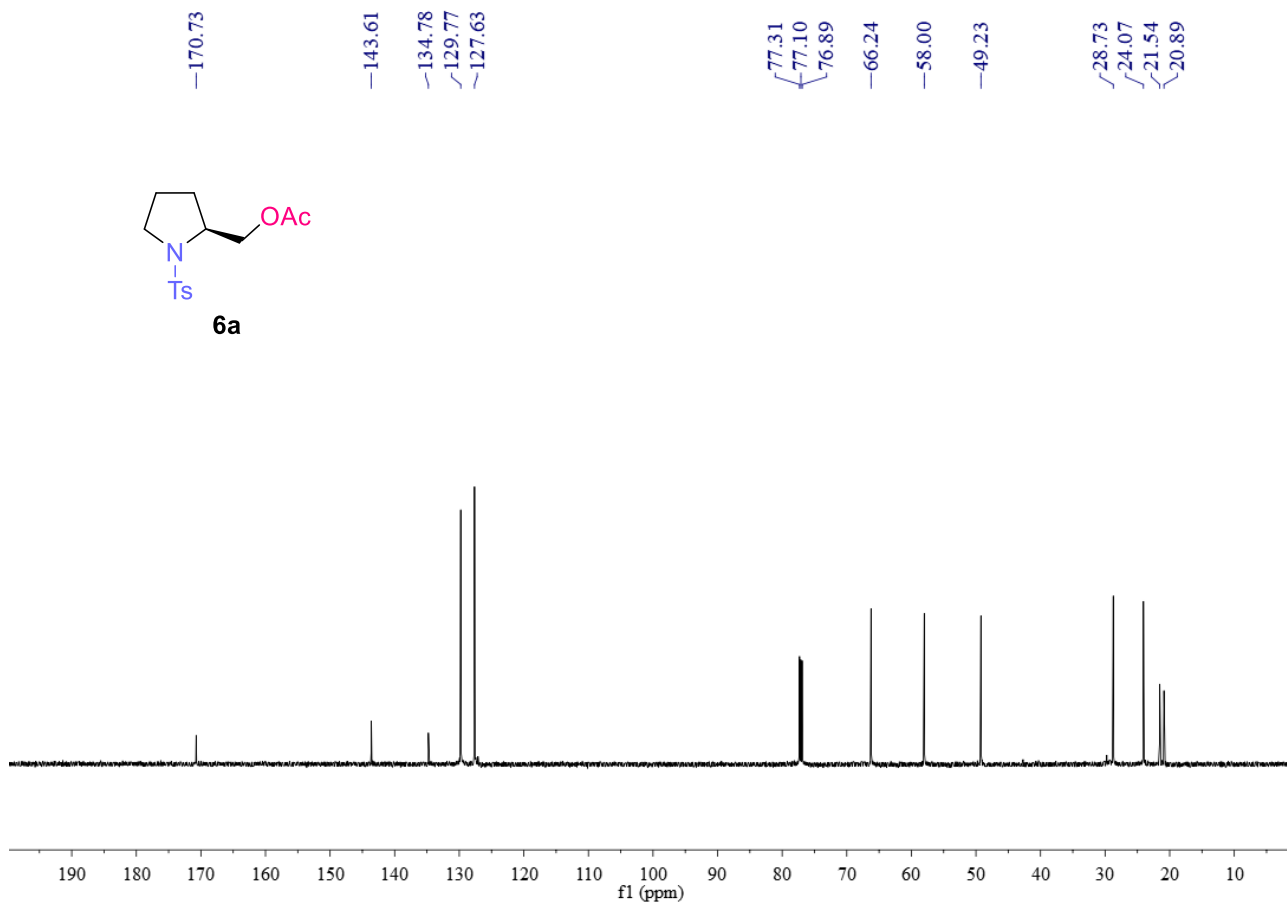
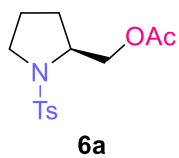
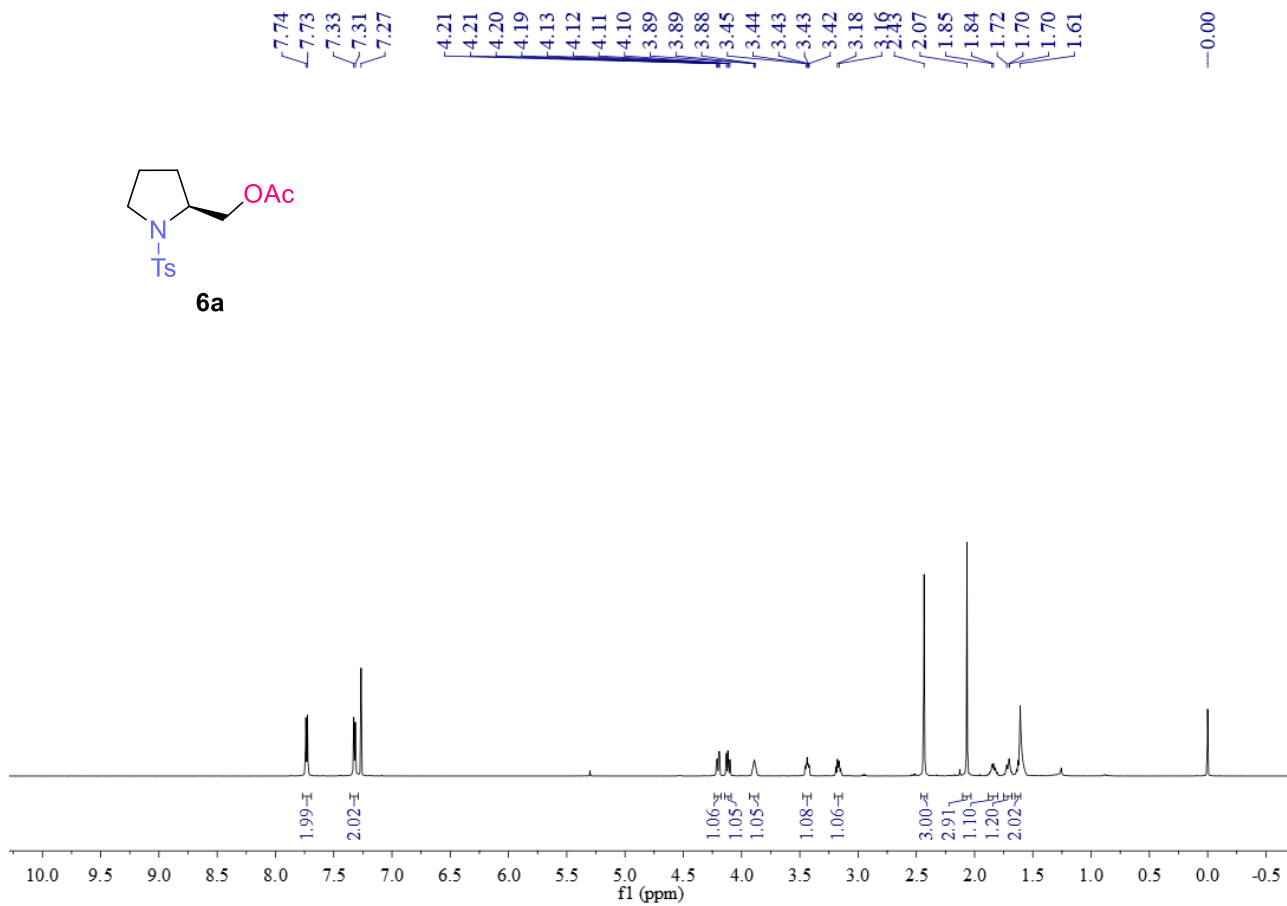
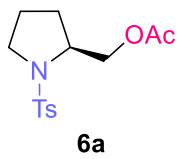


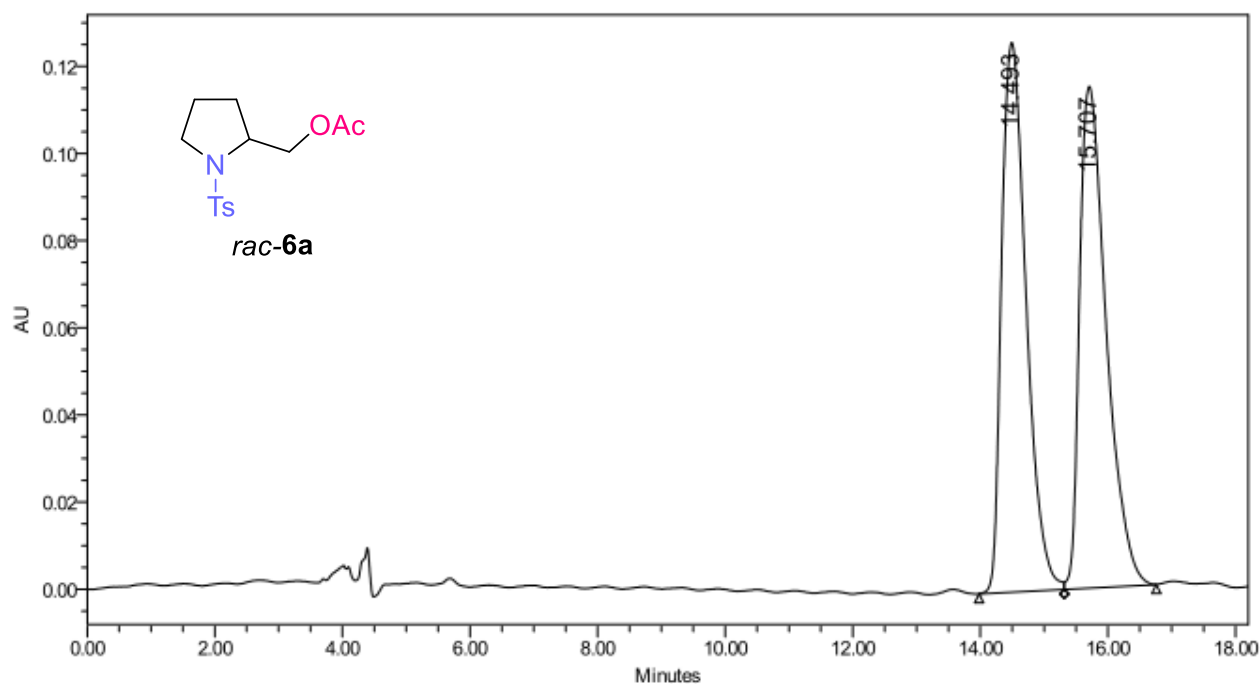


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.485	Unknown	2178687	36.22	124250	40.45	Vv	576	11.152	12.112
2	13.729	Unknown	2014191	33.49	96802	31.51	VV	518	13.398	14.262
3	14.608	Unknown	913987	15.20	44085	14.35	VB	557	14.262	15.190
4	15.853	Unknown	907994	15.10	42038	13.69	BB	787	15.190	16.502

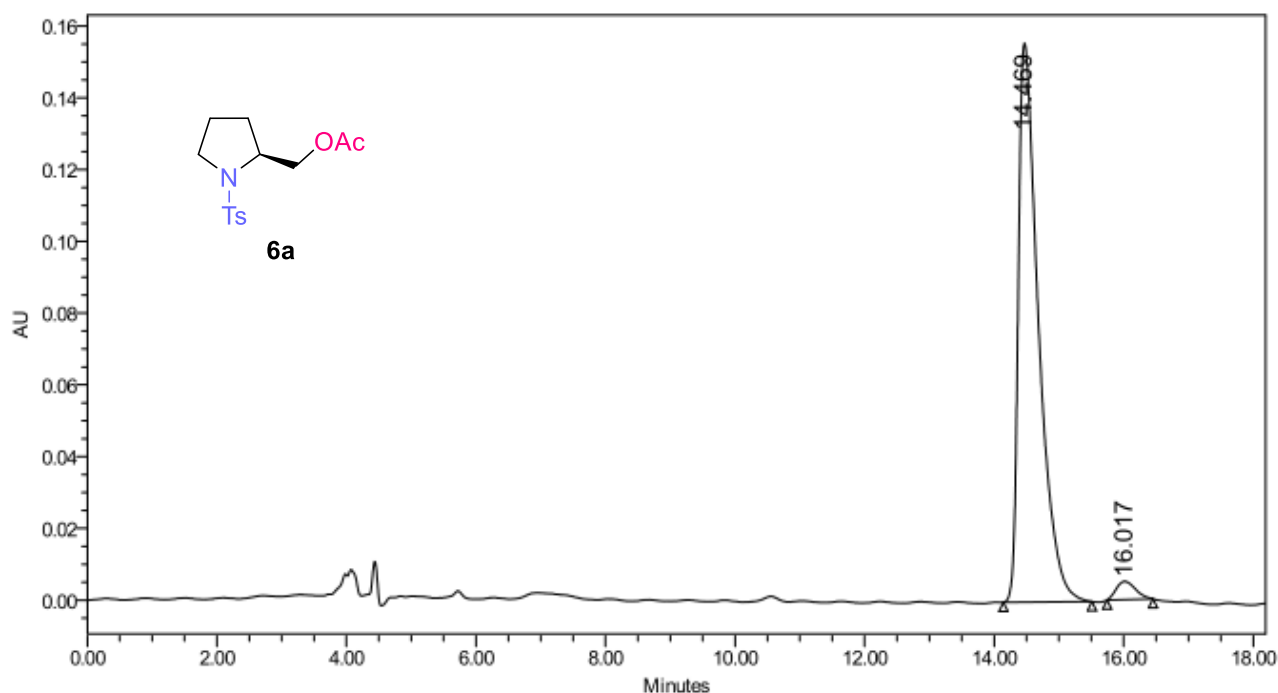


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.503	Unknown	2483743	88.49	161210	91.24	BB	654	11.158	12.248
2	13.830	Unknown	323185	11.51	15487	8.76	VV	750	13.088	14.338



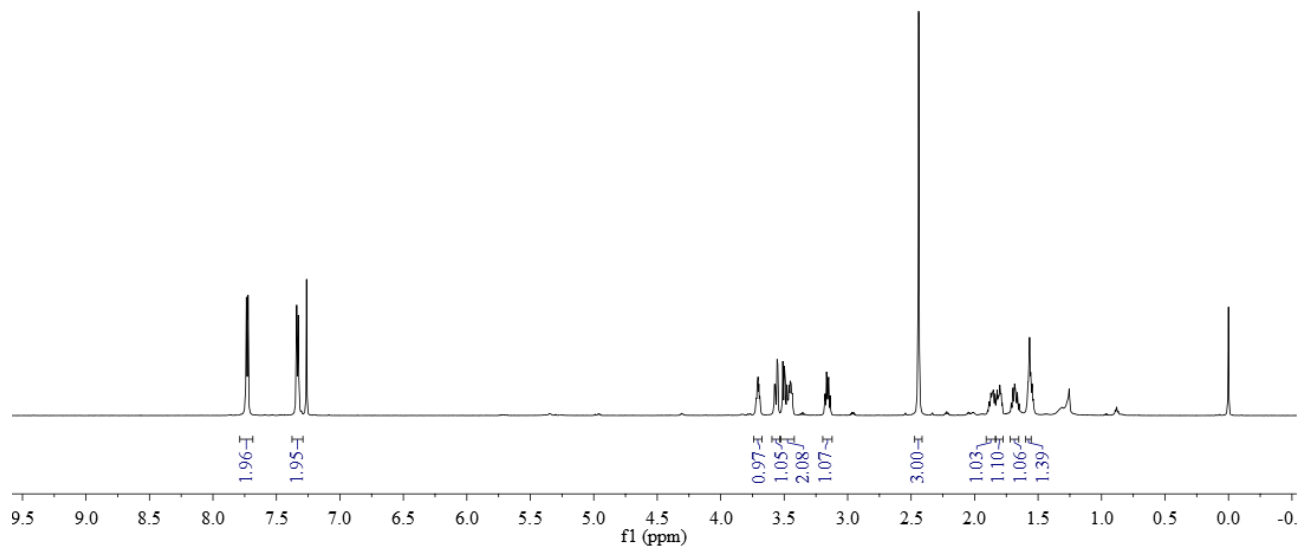
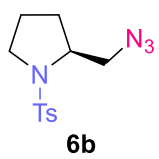


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.493	Unknown	3373248	50.13	126143	52.28	BV	801	13.980	15.315
2	15.707	Unknown	3355126	49.87	115135	47.72	VB	865	15.315	16.757

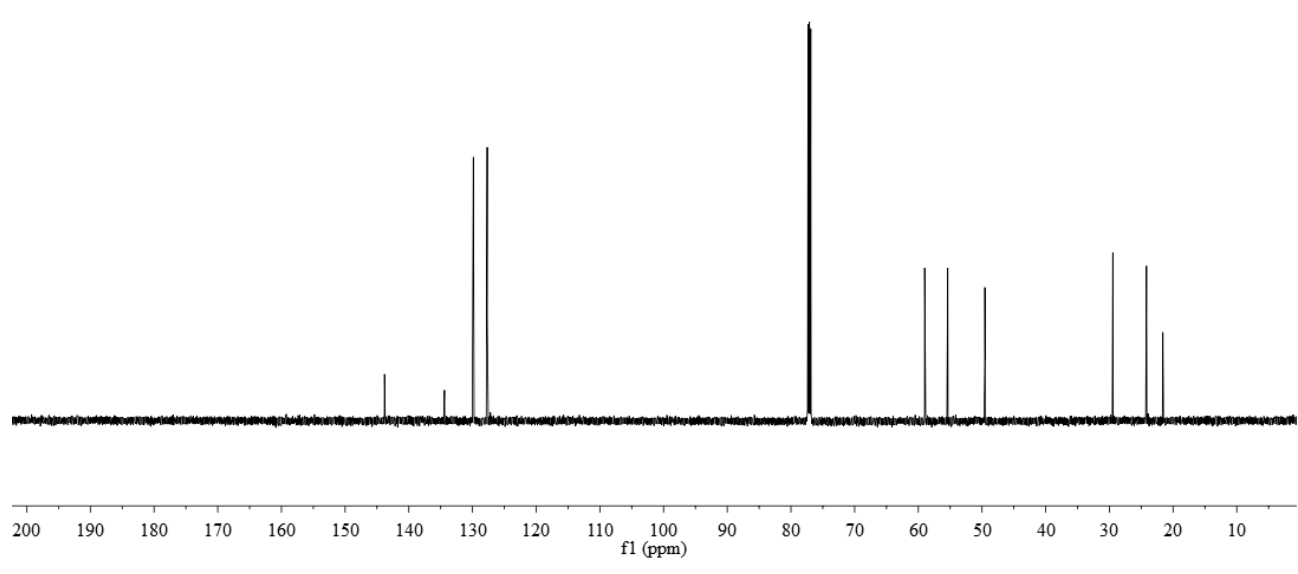
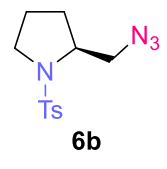


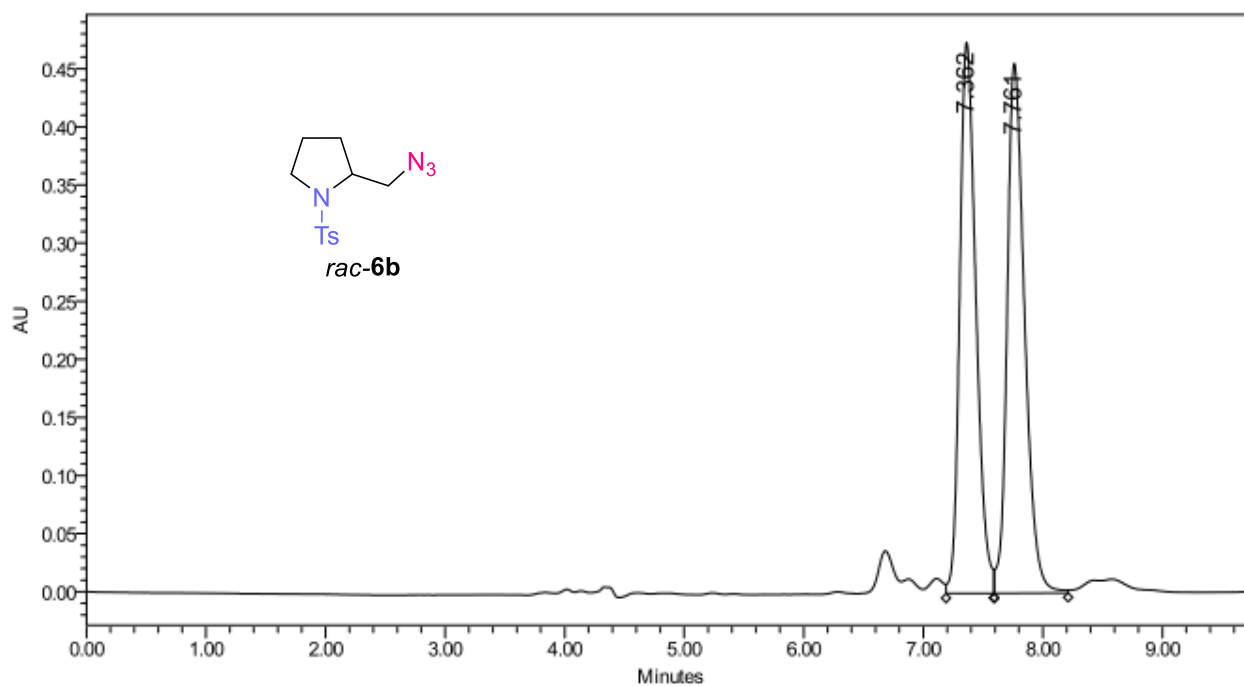
	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.469	Unknown	3370963	96.99	155784	96.85	Bb	820	14.143	15.510
2	16.017	Unknown	104446	3.01	5059	3.15	bB	425	15.743	16.452

7.74
7.72
7.34
7.33
3.72
3.71
3.71
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3.57
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3.46
3.46
3.45
3.45
3.44
3.43
3.18
3.17
3.16
3.15
3.15
2.44
1.87
1.86
1.85
1.84
1.83
1.82
1.81
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1.57
1.56
1.55
1.55
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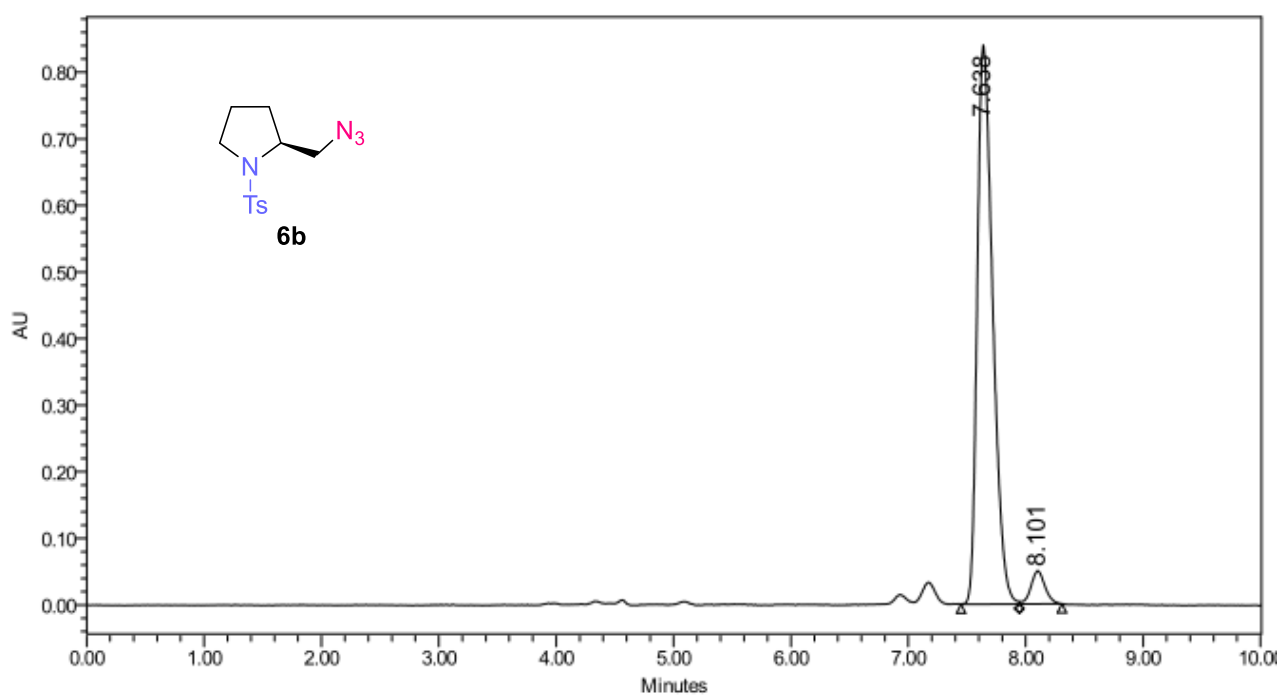


143.82
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 76.89
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 49.55
 29.46
 24.17
 21.60



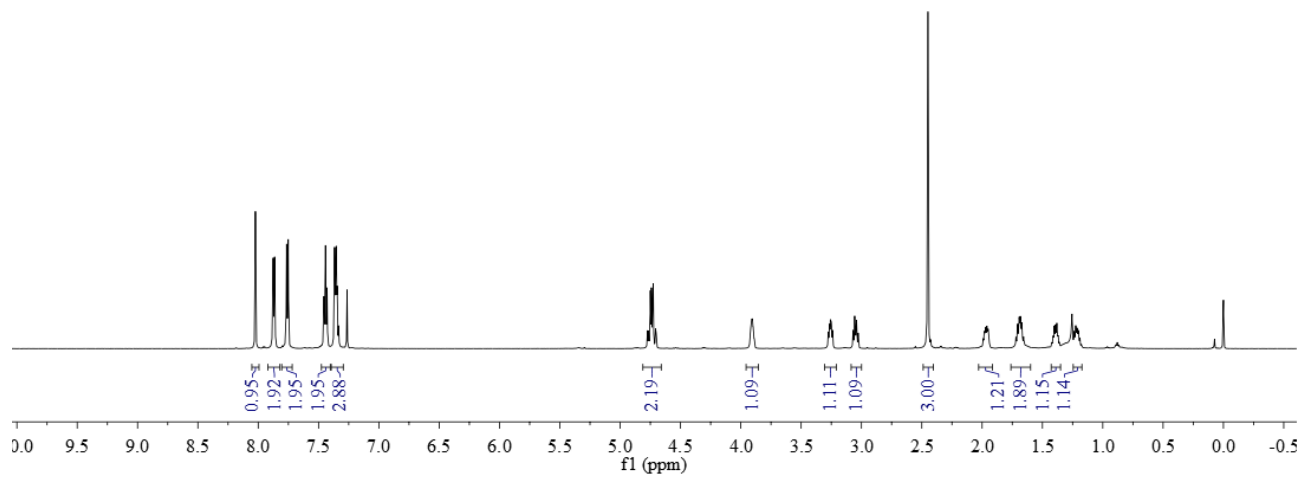
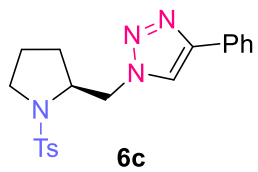


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.362	Unknown	4479883	49.15	474195	50.99	VV	242	7.190	7.593
2	7.761	Unknown	4634425	50.85	455713	49.01	VV	371	7.593	8.212



	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.638	Unknown	7702935	94.92	839549	94.41	bV	299	7.448	7.947
2	8.101	Unknown	412463	5.08	49730	5.59	Vb	217	7.947	8.308

8.02
7.88
7.88
7.86
7.76
7.75
7.45
7.44
7.43
7.37
7.35
7.35
7.35
4.77
4.76
4.75
4.74
4.73
4.73
4.71
4.71
3.91
3.90
3.27
3.26
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3.25
3.24
3.07
3.06
3.04
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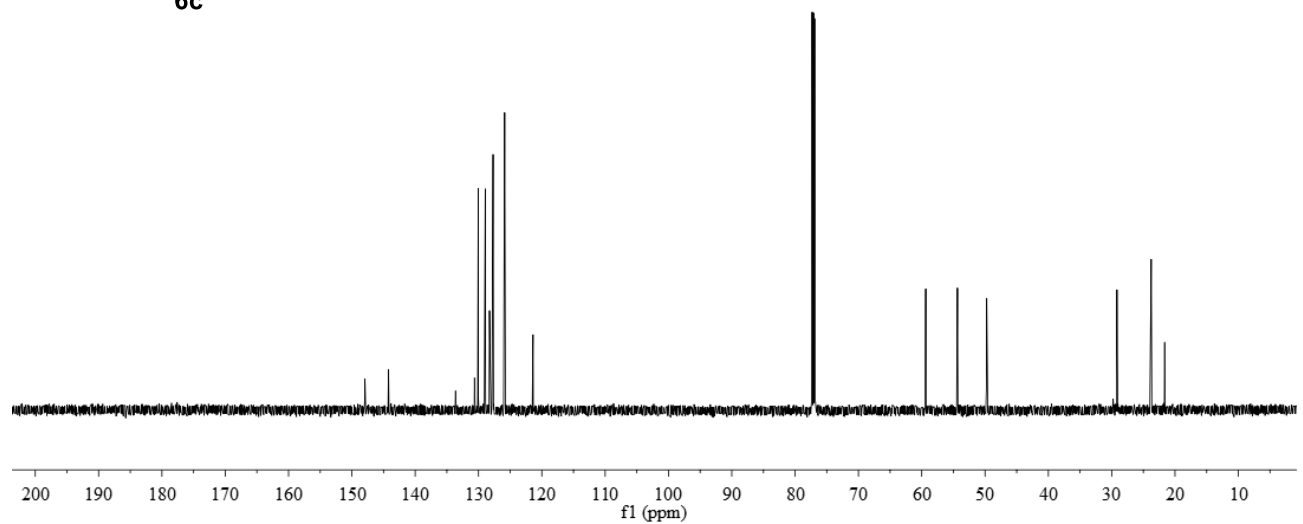
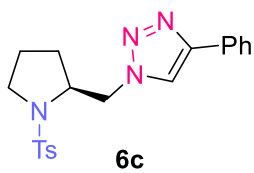


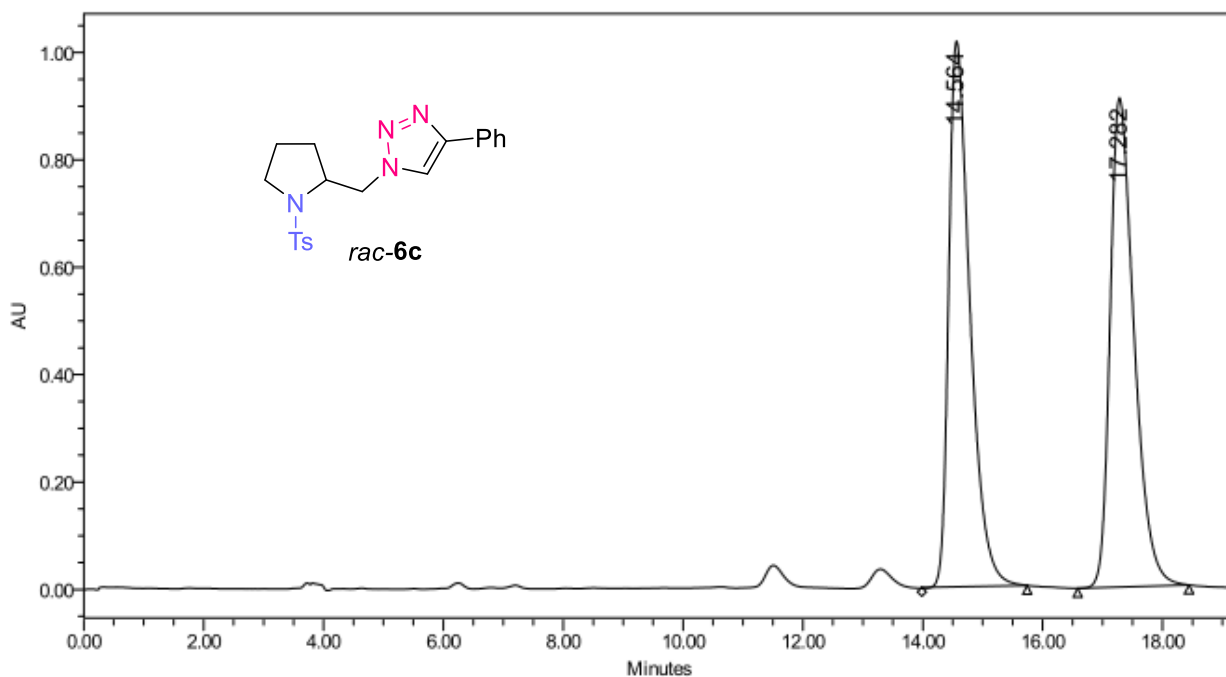
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125.87
121.39

77.31
77.10
76.89

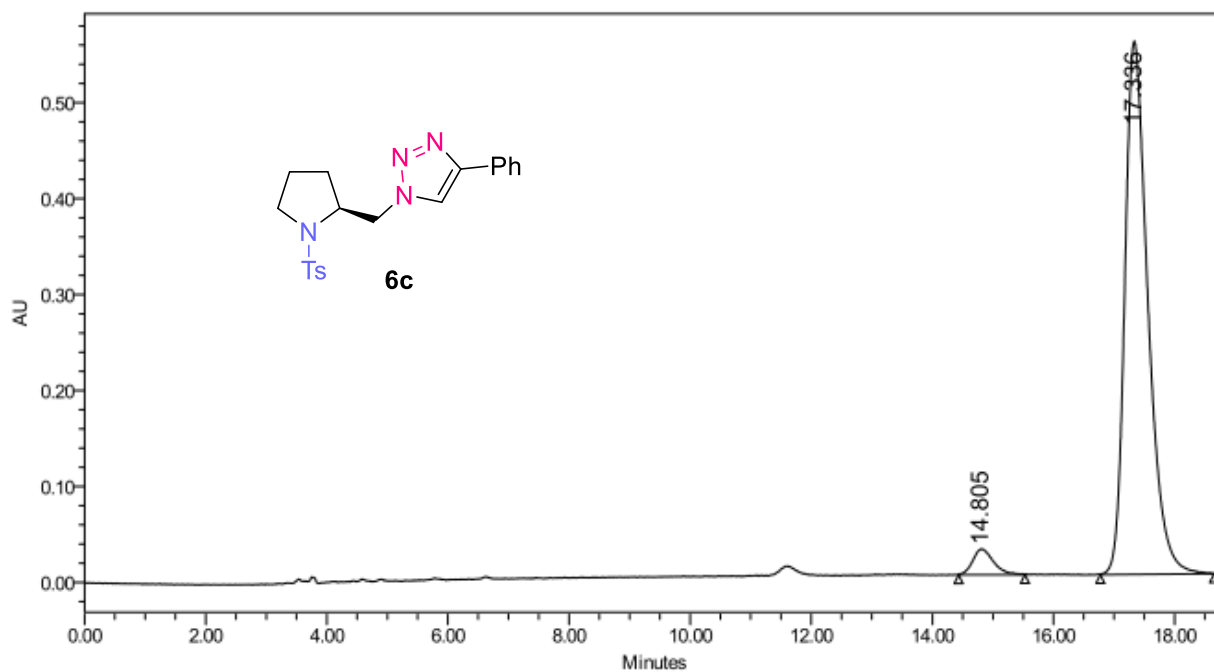
59.37
54.35
49.74

29.16
23.76
21.63





	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)
1	14.564	Unknown	25049489	49.78	1015752	52.73	Vb	1054	13.985
2	17.282	Unknown	25274650	50.22	910689	47.27	Bb	1115	16.583



	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.805	Unknown	632673	4.13	26852	4.61	BB	658	14.432	15.528
2	17.336	Unknown	14669961	95.87	555724	95.39	BB	1128	16.773	18.653