

Supporting Information for

Enantioselective construction of functionalized oxazoles via anionic stereogenic-at-cobalt(III) complex-catalyzed Ugi-4CR/Wittig reaction sequences

Qi-Ming Wang, Chang-Min Peng, Yong-En Sun, Chuan-Zhi Yao, Hua-Jie Jiang* and Jie Yu*

Department of Applied Chemistry, Anhui Province Engineering Laboratory for Green Pesticide Development and Application, and Anhui Province Key Laboratory of Crop Integrated Pest Management, Anhui Agricultural University, Hefei 230036, China

E-mail: jieyu@ahau.edu.cn, jianghj@ahau.edu.cn

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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 IB and IF 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 (172-298 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

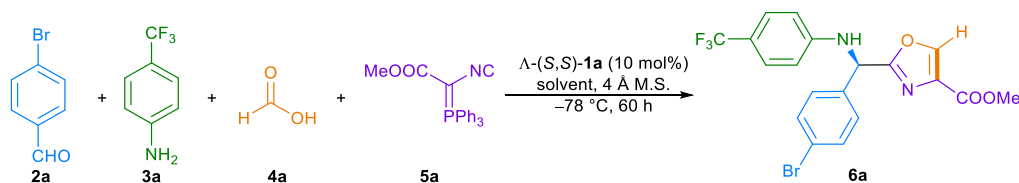
Analytic grade solvents for the column chromatography and commercially available reagents were used as received. Toluene were dried over Na and distilled prior to use. The catalysts (Λ-**1a** to Λ-**1g**)^[1] and substrates **5**^[2] were known compounds, and the spectral data were in accordance with the literature.

[1] (a) J. Yu, H.-J. Jiang, Y. Zhou, S.-W. Luo and L.-Z. Gong, *Angew. Chem., Int. Ed.*, 2015, **54**, 11209; (b) H.-J. Jiang, K. Liu, J. Yu, L. Zhang and L.-Z. Gong, *Angew. Chem., Int. Ed.*, 2017, **56**, 11931; (c) B.-B. Sun, K. Liu, Q. Gao, W. Fang, S. Lu, C.-R. Wang, C.-Z. Yao, H.-Q. Cao and J. Yu, *Nat. Commun.*, 2022, **13**, 7065.

[2] (a) Z.-L. Ren, Z.-R. Guan, H.-H. Kong and M.-W. Ding, *Org. Chem. Front.*, 2017, **4**, 2044; (b) Z.-L. Ren, W.-T. Lu, S. Cai, M.-M. Xiao, Y.-F. Yuan, P. He and M.-W. Ding, *J. Org. Chem.*, 2019, **84**, 14911; (c) M. Sun, L. Zhao and M.-W. Ding, *J. Org. Chem.*, 2019, **84**, 14313.

1.3. Reaction conditions optimization

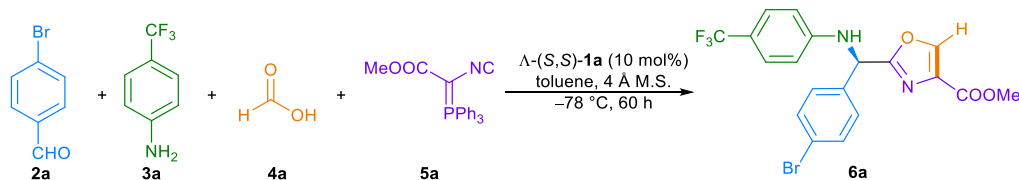
Supplementary Table S1. Optimization of the solvents^a.



entry	solvent	yield (%) ^b	er (%) ^c
1	toluene	58	89.5:10.5
2	CCl ₄	46	69:31
3	CHCl ₃	32	65:35
4	benzotrifluoride	50	60:40
5	cyclohexane	-	-
6	TBME	-	-

^a **2a** (0.12 mmol), **3a** (0.10 mmol), **4a** (1.5 mmol), **5a** (0.30 mmol), 4 Å MS (50.0 mg) and Δ -(S,S)-**1a** (0.01 mmol) in solvents (1.5 mL) for 60 h, **4a** was divided into three equal parts and added at 12 hours apart. ^b Isolated yields were based on **3a**. ^c er values were determined by chiral stationary HPLC.

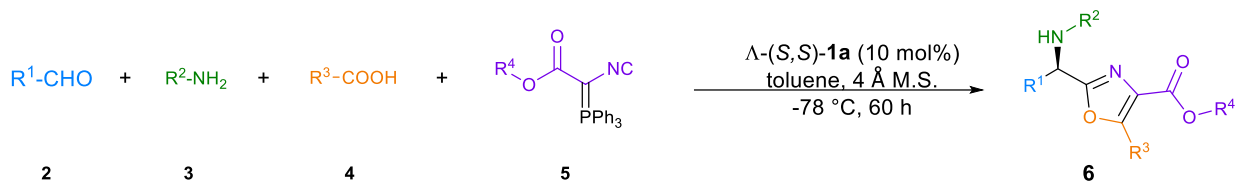
Supplementary Table S2. Optimization equivalents^a.



entry	2a:3a:4a:5a	yield (%) ^b	er (%) ^c
1	1.2:1.0:5.0:3.0	32	70:30
2	1.2:1.0:10:3.0	58	71:29
3	1.5:1.0:15:3.0	61	89.5:10.5
4	1.2:1.0:20:3.0	60	85:15

^a **2a**, **3a** (0.10 mmol), **4a**, **5a**, 4 Å MS (50.0 mg) and Δ -(S,S)-**1a** (0.01 mmol) in toluene (1.5 mL) for 60 h, **4a** was divided into three equal parts and added at 12 hours apart. ^b Isolated yields were based on **3a**. ^c er values were determined by chiral stationary HPLC.

2. Experimental Procedures of Asymmetric Ugi/Wittig Reaction and Characterization Data

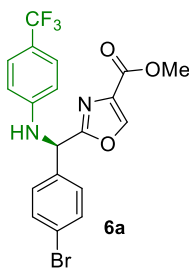


General Procedure A: Synthesis of racemic oxazole compounds via Ugi/Wittig reactions

To a 10-mL oven-dried tube was added aldehyde **2** (0.10 mmol), amine **3** (0.10 mmol), acid **4** (0.10 mmol), isocyanide (triphenylphosphoranylidene) acetates **5** (0.10 mmol) and MeOH (1.0 mL). The solution was stirred overnight and then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give the racemic oxazole compounds.

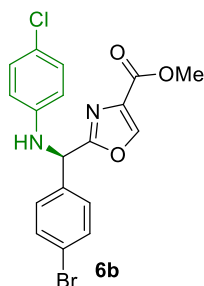
General Procedure B: Synthesis of chiral oxazole compounds via asymmetric Ugi/Wittig reactions

A 10-mL oven-dried tube was charged with aldehyde **2** (0.12 mmol), amine **3** (0.10 mmol), catalyst Δ-(*S,S*)-**1a** (0.01 mmol), 4 Å MS (50.0 mg), and toluene (1.5 mL) at room temperature and stirred for 30 min. Then isocyanide (triphenylphosphoranylidene)acetates **5** (0.30 mmol) was added. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and stirred for another 30 min. The carboxylic acid **4** (1.50 mmol) was divided into 0.5 mmol parts added at 12 hours intervals was stirred vigorously for 60 h. The reaction was then quenched with pre-cooled NEt_3 ($-78\text{ }^\circ\text{C}$, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether = 1:1) to give the enantioenriched oxazole compounds.

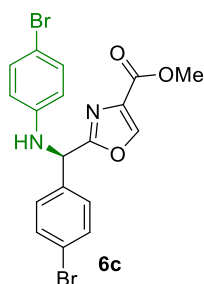


Methyl (*R*)-2-((4-bromophenyl)((4-(trifluoromethyl)phenyl)amino)methyl)oxazole-4-carboxylate **6a:** yield: 26.3 mg (58%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_{\text{D}}^{20} = -24.3$ (c 0.13 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.17 (s, 1H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.38 (dd, $J = 8.0, 4.7$ Hz, 4H), 6.65 (d, $J = 8.4$ Hz, 2H), 5.73 (d, $J = 5.8$ Hz, 1H), 5.41 (d, $J = 5.6$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.5, 161.2, 148.0, 144.6, 136.3, 133.5, 132.5, 128.7, 126.8 (q, $J = 3.8$ Hz), 124.7 (q, $J = 270.8$ Hz), 123.1, 120.8 (d, $J = 33.2$ Hz), 113.0, 55.7, 52.4; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -61.4 ; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{14}^{79}\text{BrF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 477.0038, found: 477.0035; **HRMS (ESI)** calculated for

$C_{19}H_{14}^{81}BrF_3N_2O_3$ $[M+Na]^+$: 479.0017, found: 479.0016; **Enantiomeric ratio**: 89.5:10.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.35 min (minor), t_R = 6.25 min (major).

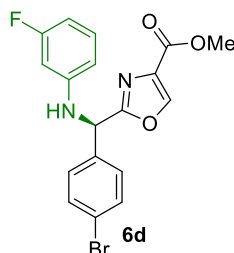


Methyl (*R*)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6b: yield: 25.2 mg (60%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20}$ = -12.7 (c 0.25 CH_2Cl_2); **1H -NMR** (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 5.66 (d, J = 5.8 Hz, 1H), 5.03 (d, J = 5.6 Hz, 1H), 3.91 (s, 3H); **^{13}C -NMR** (151 MHz, $CDCl_3$) δ 163.9, 161.3, 144.6, 144.2, 136.7, 133.5, 132.4, 129.3, 128.8, 123.9, 123.0, 115.0, 56.2, 52.4; **HRMS (ESI)** calculated for $C_{18}H_{14}^{79}Br^{35}ClN_2O_3$ $[M+Na]^+$: 442.9774, found: 442.9772; **HRMS (ESI)** calculated for $C_{18}H_{14}^{81}Br^{35}ClN_2O_3$ $[M+Na]^+$: 444.9754, found: 442.9757; **HRMS (ESI)** calculated for $C_{18}H_{14}^{81}Br^{37}ClN_2O_3$ $[M+Na]^+$: 446.9724, found: 446.9714; **Enantiomeric ratio**: 93:7, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.82 min (minor), t_R = 7.97 min (major).

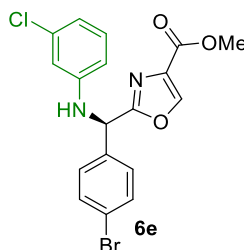


Methyl (*R*)-2-((4-bromophenyl)((4-bromophenyl)amino)methyl)oxazole-4-carboxylate 6c: yield: 23.2 mg (50%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20}$ = -6.3 (c 0.37 CH_3OH); **1H -NMR** (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.50 (d, J = 8.6 Hz, 2H), 5.66 (d, J = 6.0 Hz, 1H), 5.06 (d, J = 5.8 Hz, 1H), 3.91 (s, 3H); **^{13}C -NMR** (151 MHz, $CDCl_3$) δ 163.8, 161.3, 144.6, 144.6, 136.6, 133.5, 132.4, 132.2, 128.8, 122.9, 115.4, 110.9, 56.1, 52.4; **HRMS (ESI)** calculated for $C_{18}H_{14}^{79}Br_2N_2O_3$ $[M+Na]^+$: 486.9269, found: 486.9274; **HRMS (ESI)** calculated for $C_{18}H_{14}^{79}Br^{81}BrN_2O_3$ $[M+Na]^+$: 488.9248, found: 488.9251; **HRMS (ESI)** calculated for $C_{18}H_{14}^{81}Br_2N_2O_3$ $[M+Na]^+$: 490.9228, found: 490.9231; **Enantiomeric ratio**: 91:9, determined by

HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 7.01 min (minor), t_R = 8.05 min (major).

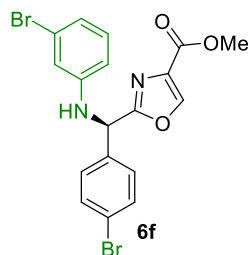


Methyl (*R*)-2-((4-bromophenyl)((3-fluorophenyl)amino)methyl)oxazole-4-carboxylate 6d: yield: 20.3 mg (50%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20}$ = -10.0 (c 0.15 CH₃OH); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.08 (dd, J = 15.0, 7.9 Hz, 1H), 6.42 (dd, J = 20.0, 8.2 Hz, 2H), 6.30 (d, J = 11.2 Hz, 1H), 5.67 (d, J = 5.9 Hz, 1H), 5.16 (d, J = 5.6 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.8 (d, J = 243.8 Hz), 163.6, 161.1, 147.2 (d, J = 10.4 Hz), 144.4, 136.5, 133.3, 132.3, 130.4 (d, J = 10.2 Hz), 128.6, 122.7, 109.3, 105.4 (d, J = 21.5 Hz), 100.6 (d, J = 25.7 Hz), 55.8, 52.2; **¹⁹F-NMR** (564 MHz, CDCl₃) δ -112.1; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹BrFN₂O₃ [M+Na]⁺: 427.0070, found: 427.0066; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹BrFN₂O₃ [M+Na]⁺: 429.0049, found: 429.0048; **Enantiomeric ratio:** 89:11, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.19 min (minor), t_R = 7.04 min (major).

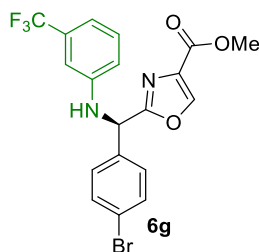


Methyl (*R*)-2-((4-bromophenyl)((3-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6e: yield: 22.3 mg (53%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20}$ = -43.3 (c 0.05 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.05 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.60 (s, 1H), 6.50 (d, J = 8.2 Hz, 1H), 5.68 (d, J = 6.0 Hz, 1H), 5.12 (d, J = 6.0 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.8, 161.2, 146.7, 144.5, 136.6, 135.2, 133.5, 132.4, 130.4, 128.8, 122.9, 119.0, 113.6, 111.9, 55.9, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹Br³⁷ClN₂O₃ [M+Na]⁺: 444.9745, found: 444.9748; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 444.9754, found: 446.9749; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 446.9724, found: 446.9729;

Enantiomeric ratio: 85.5:14.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.49 min (minor), t_R = 6.97 min (major).

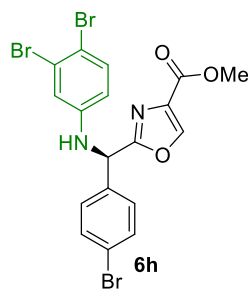


Methyl (*R*)-2-((4-bromophenyl)((3-bromophenyl)amino)methyl)oxazole-4-carboxylate 6f: yield: 23.2 mg (50%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20}$ = -25.9 (c 0.12 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.77 (s, 1H), 6.54 (dd, J = 8.1, 1.6 Hz, 1H), 5.67 (d, J = 6.1 Hz, 1H), 5.11 (d, J = 6.0 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.8, 161.3, 146.9, 144.6, 136.6, 133.5, 132.5, 130.7, 128.8, 123.4, 123.0, 121.9, 116.6, 112.3, 55.9, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹Br₂N₂O₃ [M+Na]⁺: 486.9269, found: 486.9261; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹Br⁸¹BrN₂O₃ [M+Na]⁺: 488.9248, found: 488.9256; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br₂N₂O₃ [M+Na]⁺: 490.9228, found: 490.9231; **Enantiomeric ratio:** 85.5:14.5, determined by HPLC (Daicel Chirapak IB, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 7.08 min (major), t_R = 10.29 min (minor).

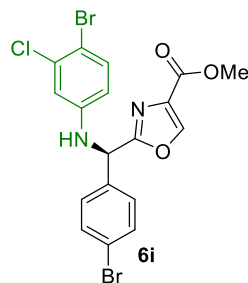


Methyl (*R*)-2-((4-bromophenyl)((3-(trifluoromethyl)phenyl)amino)methyl)oxazole-4-carboxylate 6g: yield: 19.1 mg (42%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20}$ = -9.8 (c 0.37 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.23 (t, J = 7.9 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.72 (d, J = 6.0 Hz, 1H), 5.27 (d, J = 5.8 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.7, 161.2, 145.8, 144.6, 136.4, 133.5, 132.5, 131.7 (q, J = 31.9 Hz), 129.9, 128.8, 125.4 (q, J = 272.5 Hz), 123.2, 123.0, 121.43, 116.4, 115.5 (q, J = 3.9 Hz), 110.3 (q, J = 4.0 Hz), 55.9, 52.3; **¹⁹F-NMR** (564 MHz, CDCl₃) δ -63.0; **HRMS (ESI)** calculated for C₁₉H₁₄⁷⁹BrF₃N₂O₃ [M+Na]⁺: 477.0038, found: 477.0035; **HRMS (ESI)** calculated for C₁₉H₁₄⁸¹BrF₃N₂O₃ [M+Na]⁺: 479.0017, found: 479.0016; **Enantiomeric ratio:** 82.5:17.5, determined

by HPLC (Daicel Chirapak IB, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 10.12 min (major), t_R = 11.76 min (minor).

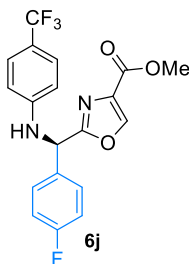


Methyl (*R*)-2-(((4-bromophenyl)((3,4-dibromophenyl)amino)methyl)oxazole-4-carboxylate 6h: yield: 31.1 mg (57%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_D^{20}$ = -18.0 (c 0.11 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.7 Hz, 1H), 6.89 (d, J = 2.6 Hz, 1H), 6.44 (dd, J = 8.7, 2.7 Hz, 1H), 5.63 (d, J = 6.1 Hz, 1H), 5.16 (d, J = 6.0 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.5, 161.2, 145.6, 144.7, 136.2, 133.9, 133.5, 132.6, 128.8, 125.4, 123.1, 118.4, 114.2, 113.0, 55.9, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₃⁷⁹Br₃N₂O₃ [M+H]⁺: 542.8555, found: 542.8555; **Enantiomeric ratio:** 77:23, determined by HPLC (Daicel Chirapak IB, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 8.57 min (major), t_R = 9.80 min (minor).

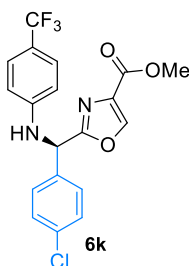


Methyl (*R*)-2-(((4-bromo-3-chlorophenyl)amino)(4-bromophenyl)methyl)oxazole-4-carboxylate 6i: yield: 20.0 mg (40%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_D^{20}$ = -25.5 (c 0.08 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.7 Hz, 1H), 6.71 (d, J = 2.6 Hz, 1H), 6.40 (dd, J = 8.7, 2.6 Hz, 1H), 5.63 (d, J = 6.1 Hz, 1H), 5.18 (d, J = 5.9 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.5, 161.2, 145.7, 144.7, 136.2, 135.1, 134.1, 133.5, 132.6, 128.8, 123.1, 115.2, 113.7, 110.6, 55.9, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₃⁷⁹Br₂³⁵ClN₂O₃ [M+Na]⁺: 520.8879, found: 520.8871; **HRMS (ESI)** calculated for C₁₈H₁₃⁷⁹Br₂³⁷ClN₂O₃ [M+Na]⁺: 522.8850, found: 522.8848; **HRMS (ESI)** calculated for C₁₈H₁₃⁷⁹Br⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 524.8829, found: 524.8827; **Enantiomeric ratio:** 78:22, determined by HPLC (Daicel Chirapak IB, isopropanol/*n*-

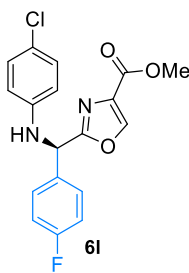
hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 8.10 min (major), t_R = 9.02 min (minor).



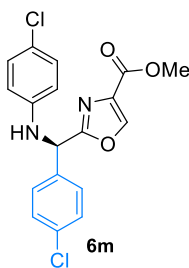
Methyl (R)-2-((4-fluorophenyl)((4-(trifluoromethyl)phenyl)amino)methyl)oxazole-4-carboxylate 6j: yield: 20.1 mg (51%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_D^{20}$ = -17.7 (c 0.11 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 7.47 (dd, J = 7.4, 5.4 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.07 (t, J = 8.3 Hz, 2H), 6.65 (d, J = 8.2 Hz, 2H), 5.76 (d, J = 5.6 Hz, 1H), 5.38 (d, J = 5.2 Hz, 1H), 3.92 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 163.9, 163.8, 162.1, 161.2, 148.1, 144.6, 133.4, δ 133.1 (q, J = 3.3 Hz), 128.9, 128.8, 127.4, 126.8 (q, J = 3.7 Hz), 124.7 (q, J = 270.6 Hz), 120.6 (q, J = 32.5 Hz), 116.4, 116.2, 113.0, 55.5, 52.4; ¹⁹F-NMR (564 MHz, CDCl₃) δ -112.6, -61.4; **HRMS (ESI)** calculated for C₁₉H₁₄F₄N₂O₃ [M+Na]⁺: 417.0838, found: 417.0840; **Enantiomeric ratio**: 92:8, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 4.87 min (minor), t_R = 5.62 min (major).



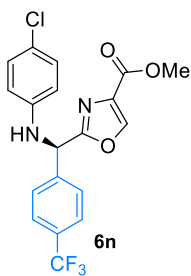
Methyl (R)-2-((4-chlorophenyl)((4-(trifluoromethyl)phenyl)amino)methyl)oxazole-4-carboxylate 6k: yield: 20.5 mg (50%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_D^{20}$ = -20.9 (c 0.17 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 18.2, 8.4 Hz, 4H), 6.65 (d, J = 8.4 Hz, 2H), 5.75 (d, J = 5.8 Hz, 1H), 5.40 (d, J = 5.6 Hz, 1H), 3.92 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 163.6, 161.2, 148.1, 144.6, 135.8, 134.9, 133.5, 129.5, 128.4, 127.4, δ 126.8 (q, J = 3.7 Hz), 124.7 (q, J = 270.6 Hz), 122.0, 120.7 (q, J = 32.8 Hz), 113.0, 55.6, 52.4; ¹⁹F-NMR (564 MHz, CDCl₃) δ -61.4; **HRMS (ESI)** calculated for C₁₉H₁₄³⁵ClF₃N₂O₃ [M+Na]⁺: 433.0543, found: 433.0540; **HRMS (ESI)** calculated for C₁₉H₁₄³⁷ClF₃N₂O₃ [M+Na]⁺: 435.0513, found: 435.0504; **Enantiomeric ratio**: 92:8, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.15 min (minor), t_R = 6.02 min (major).



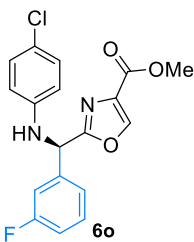
Methyl (*R*)-2-(((4-chlorophenyl)amino)(4-fluorophenyl)methyl)oxazole-4-carboxylate 6l: yield: 21.2 mg (56%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow flocculent; $[\alpha]_D^{20} = -25.5$ (c 0.08 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.16 (s, 1H), 7.46 (dd, $J = 8.4, 5.3$ Hz, 2H), 7.15 – 6.96 (m, 4H), 6.56 (d, $J = 8.7$ Hz, 2H), 5.69 (d, $J = 6.0$ Hz, 1H), 5.00 (d, $J = 5.9$ Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.7, 162.8 (d, $J = 443.0$ Hz), 162.0, 144.5, 144.2, 133.4, 133.4, 129.3, 128.9, 128.9, 123.7, 116.3 (d, $J = 21.8$ Hz), 114.9, 56.0, 52.3; **¹⁹F-NMR** (564 MHz, CDCl₃) δ -112.9; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵ClFN₂O₃ [M+Na]⁺: 383.0575, found: 383.0578; **HRMS (ESI)** calculated for C₁₈H₁₄³⁷ClFN₂O₃ [M+Na]⁺: 385.0545, found: 385.0547; **Enantiomeric ratio:** 90:10, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.00 min (minor), t_R = 6.88 min (major).



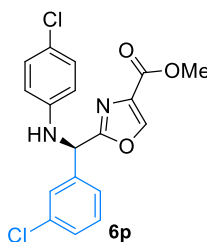
Methyl (*R*)-2-(((4-chlorophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6m: yield: 22.3 mg (59%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20} = -36.0$ (c 0.11 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.16 (s, 1H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 8.6$ Hz, 2H), 6.55 (d, $J = 8.6$ Hz, 2H), 5.68 (d, $J = 5.9$ Hz, 1H), 5.03 (d, $J = 5.7$ Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 164.0, 161.3, 144.5, 144.2, 136.1, 134.8, 133.4, 129.4, 129.3, 128.5, 123.8, 114.9, 56.1, 52.3; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl₂N₂O₃ [M+Na]⁺: 399.0279, found: 399.0284; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl³⁷ClN₂O₃ [M+Na]⁺: 401.0250, found: 401.0250; **Enantiomeric ratio:** 89.5:10.5 (The enantioselectivity could be improved to 94.5:5.5 or via recrystallization in DCM:heptane = 1:5), determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.32 min (minor), t_R = 7.31 min (major).



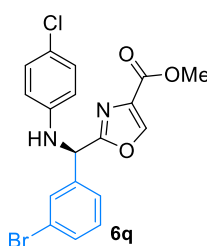
Methyl (*R*)-2-(((4-chlorophenyl)amino)(4-(trifluoromethyl)phenyl)methyl)oxazole-4-carboxylate 6n: yield: 22.2 mg (54%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_{\text{D}}^{20} = -14.2$ (c 0.19 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.17 (s, 1H), 7.63 (d, $J = 8.3$ Hz, 4H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.56 (d, $J = 8.8$ Hz, 2H), 5.77 (d, $J = 6.0$ Hz, 1H), 5.11 (d, $J = 5.9$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.6, 161.2, 144.6, 144.0, 141.6, 133.5, 131.17 (q, $J = 32.6$ Hz), 129.3, 127.6, 126.2 (q, $J = 3.6$ Hz), 124.0, 123.8 (q, $J = 272.3$ Hz), 114.9, 56.3, 52.4; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -62.7; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{14}^{35}\text{ClF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 433.0543, found: 433.0545; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{14}^{37}\text{ClF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 435.0513, found: 435.0514; **Enantiomeric ratio**: 91:9, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 5.29$ min (minor), $t_{\text{R}} = 6.17$ min (major).



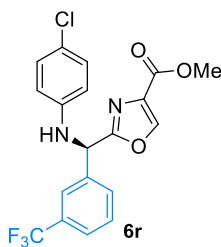
Methyl (*R*)-2-(((4-chlorophenyl)amino)(3-fluorophenyl)methyl)oxazole-4-carboxylate 6o: yield: 22.7 mg (63%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow flocculent; $[\alpha]_{\text{D}}^{20} = -25.6$ (c 0.06 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.17 (s, 1H), 7.33 (dd, $J = 7.8, 5.9$ Hz, 1H), 7.27 (s, 1H), 7.20 (d, $J = 9.4$ Hz, 1H), 7.09 (d, $J = 8.7$ Hz, 2H), 7.05 – 6.98 (m, 1H), 6.57 (d, $J = 8.7$ Hz, 2H), 5.70 (d, $J = 6.1$ Hz, 1H), 5.05 (d, $J = 6.0$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 164.1, 162.5 (d, $J = 388.9$ Hz), 162.4, 144.6, 144.1, 140.2 (d, $J = 6.7$ Hz), 133.4, 130.8, 130.8, 129.3, 123.8, 122.8, 122.8, 115.8 (d, $J = 21.2$ Hz), 114.9, 114.3, 114.1, 56.2, 56.2, 52.3; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -111.3; **HRMS (ESI)** calculated for $\text{C}_{18}\text{H}_{14}^{35}\text{ClFN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 383.0575, found: 383.0577; **HRMS (ESI)** calculated for $\text{C}_{18}\text{H}_{14}^{37}\text{ClFN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 385.0545, found: 385.0544; **Enantiomeric ratio**: 91.5:8.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 5.81$ min (minor), $t_{\text{R}} = 6.32$ min (major).



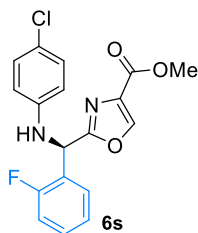
Methyl (*R*)-2-((3-chlorophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6p: yield: 18.5 mg (49%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -8.8$ (c 0.19 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 3.9 Hz, 1H), 7.30 (d, *J* = 4.8 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 5.67 (d, *J* = 6.0 Hz, 1H), 5.05 (d, *J* = 5.8 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.8, 161.2, 144.6, 144.1, 139.7, 135.2, 133.5, 130.5, 129.3, 129.1, 127.3, 125.3, 123.9, 114.9, 56.2, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl₂N₂O₃ [M+Na]⁺: 399.0279, found: 399.0285; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl³⁷ClN₂O₃ [M+Na]⁺: 401.0250, found: 401.0255; **Enantiomeric ratio:** 89:11, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): *t*_R = 5.76 min (minor), *t*_R = 6.30 min (major).



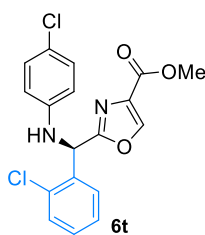
Methyl (*R*)-2-((3-bromophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6q: yield: 20.2 mg (48%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -13.9$ (c 0.09 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.64 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.66 (d, *J* = 6.0 Hz, 1H), 5.05 (d, *J* = 5.8 Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.8, 161.2, 144.6, 144.1, 139.9, 133.5, 132.0, 130.7, 130.2, 129.3, 125.7, 123.9, 123.3, 114.9, 56.2, 52.4; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 442.9774, found: 442.9778; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 444.9754, found: 444.9754; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 446.9724, found: 446.9724; **Enantiomeric ratio:** 87:13, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): *t*_R = 5.97 min (minor), *t*_R = 6.55 min (major).



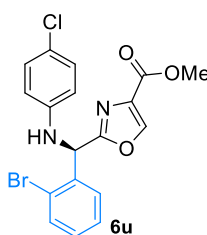
Methyl (R)-2-(((4-chlorophenyl)amino)(3-(trifluoromethyl)phenyl)methyl)oxazole-4-carboxylate 6r: yield: 24.2 mg (59%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -8.6$ (c 0.15 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.18 (s, 1H), 7.76 (s, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.59 (d, $J = 7.7$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 8.7$ Hz, 2H), 6.57 (d, $J = 8.7$ Hz, 2H), 5.76 (d, $J = 6.0$ Hz, 1H), 5.09 (d, $J = 5.9$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.6, 161.2, 144.6, 144.0, 138.8, 133.5, 131.7 (q, $J = 32.5$ Hz), 130.5, 129.8, 129.3, 125.7 (q, $J = 3.8$ Hz), 124.0 (q, $J = 7.3, 3.5$ Hz), 123.8 (q, $J = 272.4$ Hz), 121.1, 114.9, 56.4, 52.4; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -62.6; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{14}^{35}\text{ClF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 433.0543, found: 433.0547; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{14}^{37}\text{ClF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 435.0513, found: 435.0515; **Enantiomeric ratio**: 89:11, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 8.06$ min (minor), $t_{\text{R}} = 9.09$ min (major).



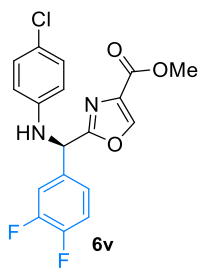
Methyl (R)-2-(((4-chlorophenyl)amino)(2-fluorophenyl)methyl)oxazole-4-carboxylate 6s: yield: 15.5 mg (43%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -13.4$ (c 0.20 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.17 (s, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.31 (dd, $J = 13.5, 7.1$ Hz, 1H), 7.11 (dd, $J = 17.9, 8.5$ Hz, 4H), 6.59 (d, $J = 8.7$ Hz, 2H), 6.06 (d, $J = 6.7$ Hz, 1H), 5.09 (d, $J = 6.4$ Hz, 1H), 3.92 (s, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.8, 161.3, 160.6 (d, $J = 248.1$ Hz), 144.5, 144.1, 133.4, 130.5, 130.5, 129.3, 128.4 (d, $J = 3.2$ Hz), 125.0 (d, $J = 3.5$ Hz), 123.7, 116.1, 116.0, 114.8, 52.3, 50.0, 50.0; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -118.6; **HRMS (ESI)** calculated for $\text{C}_{18}\text{H}_{14}^{35}\text{ClFN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 383.0575, found: 383.0579; **HRMS (ESI)** calculated for $\text{C}_{18}\text{H}_{14}^{37}\text{ClFN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 385.0545, found: 385.0548; **Enantiomeric ratio**: 88.5:11.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 5.41$ min (minor), $t_{\text{R}} = 6.21$ min (major).



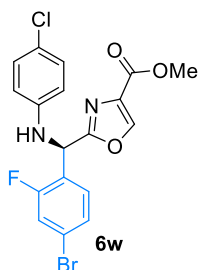
Methyl (*R*)-2-((2-chlorophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6t: yield: 15.0 mg (40%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow flocculent; $[\alpha]_D^{20} = -12.3$ (c 0.18 CH₂Cl₂); **¹H-NMR** (600 MHz, CDCl₃) δ 8.16 (s, 1H), 7.50 – 7.40 (m, 2H), 7.27 (s, 1H), 7.26 – 7.20 (m, 1H), 7.09 (d, $J = 8.7$ Hz, 2H), 6.55 (d, $J = 8.7$ Hz, 2H), 6.21 (d, $J = 6.3$ Hz, 1H), 5.14 (d, $J = 6.0$ Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.9, 161.3, 144.6, 144.1, 135.3, 133.8, 133.4, 130.2, 130.0, 129.3, 128.5, 127.7, 123.7, 114.8, 53.1, 52.3; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl₂N₂O₃ [M+Na]⁺: 399.0279, found: 399.0280; **HRMS (ESI)** calculated for C₁₈H₁₄³⁵Cl³⁷ClN₂O₃ [M+Na]⁺: 401.0250, found: 401.0257; **Enantiomeric ratio:** 91:9, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.37 min (minor), t_R = 5.88 min (major).



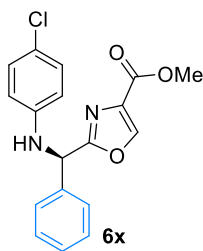
Methyl (*R*)-2-((2-bromophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6u: yield: 20.1 mg (48%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white solid; $[\alpha]_D^{20} = -7.5$ (c 0.19 CH₂Cl₂); m.p.: 58.1-67.1 °C; **¹H-NMR** (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.45 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.21 – 7.15 (m, 1H), 7.09 (d, $J = 8.8$ Hz, 2H), 6.55 (d, $J = 8.8$ Hz, 2H), 6.18 (d, $J = 6.1$ Hz, 1H), 5.16 (d, $J = 6.0$ Hz, 1H), 3.92 (s, 3H); **¹³C-NMR** (151 MHz, CDCl₃) δ 163.9, 161.3, 144.6, 144.1, 136.9, 133.5, 133.4, 130.2, 129.3, 128.7, 128.4, 124.0, 123.7, 114.8, 55.7, 52.3; **HRMS (ESI)** calculated for C₁₈H₁₄⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 442.9774, found: 442.9777; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 444.9754, found: 444.9755; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 446.9724, found: 446.9727; **Enantiomeric ratio:** 90:10, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.48 min (minor), t_R = 5.90 min (major).



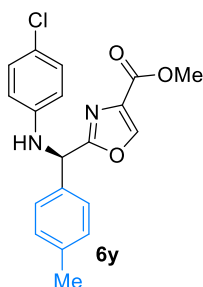
Methyl (R)-2-(((4-chlorophenyl)amino)(3,4-difluorophenyl)methyl)oxazole-4-carboxylate 6v: yield: 17.0 mg (45%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20} = -6.1$ (c 0.12 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.33 (t, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.16 (dd, *J* = 17.7, 8.4 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.66 (d, *J* = 5.8 Hz, 1H), 5.06 (d, *J* = 5.5 Hz, 1H), 3.92 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 162.4 (d, *J* = 365.1 Hz), 151.6 (d, *J* = 13.1 Hz), 151.3 (d, *J* = 12.7 Hz), 150.0 (d, *J* = 12.9 Hz), 149.7 (d, *J* = 12.4 Hz), 144.6, 144.0, 134.6, 133.5, 129.3, 124.0, 123.2, 123.2, 123.2, 123.2, 118.1 (d, *J* = 17.6 Hz), 116.3 (d, *J* = 18.4 Hz), 114.9, 55.8, 52.4; ¹⁹F-NMR (564 MHz, CDCl₃) δ -135.5, -137.1; **HRMS (ESI)** calculated for C₁₈H₁₃³⁵ClF₂N₂O₃ [M+Na]⁺: 401.0480, found: 401.0485; **HRMS (ESI)** calculated for C₁₈H₁₃³⁷ClF₂N₂O₃ [M+Na]⁺: 403.0451, found: 403.0459; **Enantiomeric ratio:** 91:9, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.53 min (minor), t_R = 6.11 min (major).



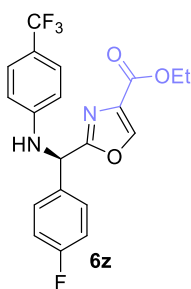
Methyl (R)-2-(((4-bromo-2-fluorophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6w: yield: 17.5 mg (40%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_D^{20} = -20.9$ (c 0.17 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.17 (s, 1H), 7.32 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.27 (s, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 5.99 (d, *J* = 6.6 Hz, 1H), 5.10 (d, *J* = 6.3 Hz, 1H), 3.92 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 163.2, 161.2, 160.3 (d, *J* = 252.5 Hz), 144.6, 143.7, 133.5, 129.6 (d, *J* = 3.8 Hz), 129.4, 128.4 (d, *J* = 3.6 Hz), 124.2 (d, *J* = 13.5 Hz), 124.1, 124.1, 123.2, 123.1, 119.8, 119.7, 114.8, 52.4, 49.7, 49.7; ¹⁹F-NMR (564 MHz, CDCl₃) δ -115.9; **HRMS (ESI)** calculated for C₁₈H₁₃⁷⁹Br³⁵ClFN₂O₃ [M+Na]⁺: 460.9680, found: 460.9680; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁵ClFN₂O₃ [M+Na]⁺: 464.9630, found: 464.9637; **HRMS (ESI)** calculated for C₁₈H₁₄⁸¹Br³⁷ClFN₂O₃ [M+Na]⁺: 446.9724, found: 446.9714; **Enantiomeric ratio:** 87:13, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.54 min (minor), t_R = 6.65 min (major).



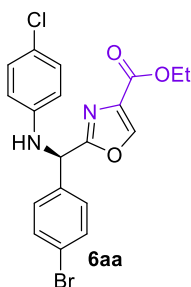
Methyl (*R*)-2-(((4-chlorophenyl)amino)(phenyl)methyl)oxazole-4-carboxylate 6x: yield: 18.8 mg (55%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -17.9$ (c 0.17 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.16 (s, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 5.71 (d, *J* = 6.1 Hz, 1H), 4.99 (d, *J* = 5.9 Hz, 1H), 3.91 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 164.5, 161.4, 144.5, 144.5, 137.6, 133.4, 129.2, 129.2, 128.8, 127.1, 123.5, 114.8, 56.7, 52.3; **HRMS (ESI)** calculated for C₁₈H₁₅³⁵ClN₂O₃ [M+Na]⁺: 365.0669, found: 365.0665; **HRMS (ESI)** calculated for C₁₈H₁₅³⁷ClN₂O₃ [M+Na]⁺: 367.0639, found: 367.0639; **Enantiomeric ratio:** 91:9, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.32 min (minor), t_R = 7.11 min (major).



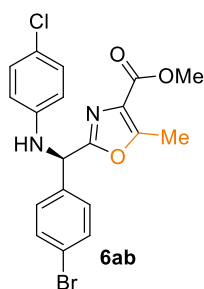
Methyl (*R*)-2-(((4-chlorophenyl)amino)(p-tolyl)methyl)oxazole-4-carboxylate 6y: yield: 18.2 mg (51%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white flocculent; $[\alpha]_{\text{D}}^{20} = -25.4$ (c 0.13 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.15 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 5.67 (d, *J* = 6.1 Hz, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 3.91 (s, 3H), 2.33 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 164.7, 161.4, 144.5, 144.4, 138.7, 134.6, 133.3, 129.9, 129.2, 127.0, 123.4, 114.8, 56.5, 52.3, 21.1; **HRMS (ESI)** calculated for C₁₉H₁₇³⁵ClN₂O₃ [M+Na]⁺: 379.0825, found: 379.0823; **HRMS (ESI)** calculated for C₁₉H₁₇³⁷ClN₂O₃ [M+Na]⁺: 381.0796, found: 381.0794; **Enantiomeric ratio:** 83.5:16.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.29 min (minor), t_R = 7.44 min (major).



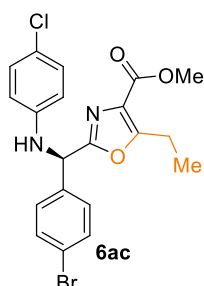
Ethyl (R)-2-((4-fluorophenyl)((4-(trifluoromethyl)phenyl)amino)methyl)oxazole-4-carboxylate 6z: yield: 28.2 mg (69%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_{\text{D}}^{20} = -12.1$ (c 0.14 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.16 (s, 1H), 7.47 (dd, $J = 8.3, 5.3$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.06 (t, $J = 8.5$ Hz, 2H), 6.65 (d, $J = 8.5$ Hz, 2H), 5.76 (d, $J = 5.8$ Hz, 1H), 5.40 (d, $J = 5.6$ Hz, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.8, 162.9 (d, $J = 248.3$ Hz), 160.8, 148.2, 144.4, 133.7, 133.1 (d, $J = 3.1$ Hz), 128.9 (d, $J = 8.3$ Hz), 126.7 (q, $J = 3.8$ Hz), 124.7 (q, $J = 270.7$ Hz), 120.6 (d, $J = 32.7$ Hz), 116.4, 116.2, 112.9, 61.5, 55.5, 14.3; $^{19}\text{F-NMR}$ (564 MHz, CDCl_3) δ -61.3, -112.6; **HRMS (ESI)** calculated for $\text{C}_{20}\text{H}_{16}\text{F}_4\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 431.0995, found: 431.0990; **Enantiomeric ratio:** 90.5:9.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 7.72$ min (major), $t_{\text{R}} = 9.67$ min (minor).



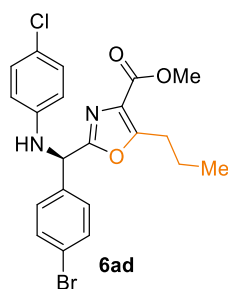
Ethyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6aa: yield: 23.4 mg (54%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_{\text{D}}^{20} = -18.2$ (c 0.16 CH_2Cl_2); $^1\text{H-NMR}$ (600 MHz, CDCl_3) δ 8.14 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 8.7$ Hz, 2H), 6.55 (d, $J = 8.7$ Hz, 2H), 5.66 (d, $J = 6.0$ Hz, 1H), 5.05 (d, $J = 5.8$ Hz, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl_3) δ 163.8, 160.9, 144.4, 144.2, 136.7, 133.7, 132.4, 129.3, 128.8, 123.8, 122.8, 114.9, 61.5, 56.2, 14.3; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{16}^{79}\text{Br}^{35}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 456.9931, found: 456.9932; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{16}^{81}\text{Br}^{35}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 458.9910, found: 458.9917; **HRMS (ESI)** calculated for $\text{C}_{19}\text{H}_{16}^{81}\text{Br}^{37}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 460.9881, found: 460.9884; **Enantiomeric ratio:** 90:10, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ\text{C}$, $\lambda = 254$ nm): $t_{\text{R}} = 5.83$ min (minor), $t_{\text{R}} = 6.71$ min (major).



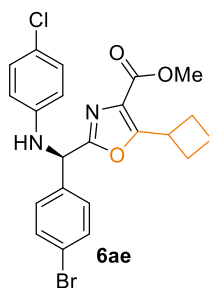
Methyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-methyloxazole-4-carboxylate 6ab: yield: 17.0 mg (39%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20} = -5.1$ (c 0.27 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.59 (d, *J* = 6.0 Hz, 1H), 4.99 (d, *J* = 5.8 Hz, 1H), 3.91 (s, 3H), 2.58 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 162.4, 160.9, 157.2, 144.2, 137.0, 132.3, 129.2, 128.8, 127.6, 123.6, 122.7, 114.9, 56.0, 52.1, 12.1; **HRMS (ESI)** calculated for C₁₉H₁₆⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 456.9931, found: 456.9933; **HRMS (ESI)** calculated for C₁₉H₁₆⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 458.9910, found: 458.9915; **HRMS (ESI)** calculated for C₁₉H₁₆⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 460.9881, found: 460.9888; **Enantiomeric ratio:** 84.5:15.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.49 min (major), t_R = 7.69 min (minor).



Methyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-ethyloxazole-4-carboxylate 6ac: yield: 12.1 mg (27%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20} = -6.8$ (c 0.12 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 5.60 (d, *J* = 5.9 Hz, 1H), 5.01 (d, *J* = 5.7 Hz, 1H), 3.91 (s, 3H), 3.09 – 2.92 (m, 2H), 1.22 (t, *J* = 7.5 Hz, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 162.4, 161.9, 160.8, 144.3, 137.0, 132.3, 129.2, 128.8, 126.7, 123.7, 122.7, 114.9, 56.1, 52.1, 19.7, 11.9; **HRMS (ESI)** calculated for C₂₀H₁₈⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 471.0087, found: 471.0083; **HRMS (ESI)** calculated for C₂₀H₁₈⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 473.0067, found: 473.0065; **HRMS (ESI)** calculated for C₂₀H₁₈⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 475.0037, found: 475.0038; **Enantiomeric ratio:** 79:21, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 9.69 min (minor), t_R = 15.86 min (major).

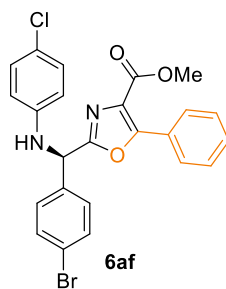


Methyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-propyloxazole-4-carboxylate 6ad: yield: 17.1 mg (37%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20} = 1.2$ (c 0.74 CH₂Cl₂); $^1\text{H-NMR}$ (600 MHz, CDCl₃) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.55 (d, $J = 8.5$ Hz, 2H), 5.60 (d, $J = 6.0$ Hz, 1H), 4.99 (d, $J = 5.9$ Hz, 1H), 3.91 (s, 3H), 2.96 (m, $J = 31.4, 14.9, 7.4$ Hz, 2H), 1.65 (dd, $J = 14.7, 7.4$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C-NMR}$ (151 MHz, CDCl₃) δ 162.4, 160.9, 160.9, 144.3, 137.0, 132.3, 129.2, 128.8, 127.3, 122.7, 114.9, 110.1, 56.1, 52.1, 27.8, 21.1, 13.5; **HRMS (ESI)** calculated for C₂₁H₂₀⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 485.0244, found: 485.0243; **HRMS (ESI)** calculated for C₂₁H₂₀⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 487.0223, found: 487.0225; **HRMS (ESI)** calculated for C₂₁H₂₀⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 489.0194, found: 489.0198; **Enantiomeric ratio:** 86:14, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.60 min (minor), t_R = 9.76 min (major).

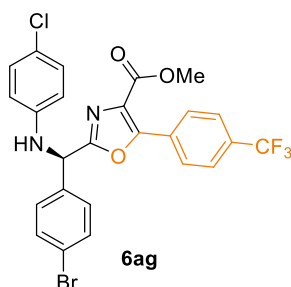


Methyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-cyclobutyloxazole-4-carboxylate 6ae: yield: 19.9 mg (42%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20} = 3.1$ (c 0.29 CH₂Cl₂); $^1\text{H-NMR}$ (600 MHz, CDCl₃) δ 7.50 (d, $J = 8.3$ Hz, 1H), 7.39 (d, $J = 8.3$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 6.56 (d, $J = 8.6$ Hz, 1H), 5.63 (d, $J = 6.0$ Hz, 1H), 5.03 (d, $J = 5.8$ Hz, 1H), 4.23 – 4.15 (m, 1H), 3.90 (s, 3H), 2.30 (dt, $J = 17.6, 8.2$ Hz, 3H), 2.23 – 2.17 (m, 1H), 2.04 (dd, $J = 12.6, 6.2$ Hz, 1H), 1.94 – 1.88 (m, 1H); $^{13}\text{C-NMR}$ (151 MHz, CDCl₃) δ 160.7, 144.3, 137.1, 132.3, 129.3, 128.8, 125.9, 123.6, 122.7, 114.9, 56.1, 52.1, 31.1, 27.8, 27.6, 18.5; **HRMS (ESI)** calculated for C₂₂H₂₀⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 497.0244, found: 497.0245; **HRMS (ESI)** calculated for C₂₂H₂₀⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 499.0223, found: 499.0227; **HRMS (ESI)** calculated for C₂₂H₂₀⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 501.0194, found: 501.0199; **Enantiomeric ratio:**

74.5:25.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.62 min (minor), t_R = 11.79 min (major).

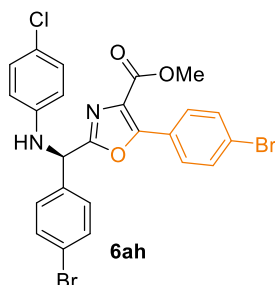


Methyl (*R*)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-phenyloxazole-4-carboxylate 6af: yield: 20.3 mg (41%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20}$ = 17.1 (c 0.43 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 2.8 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 2.9 Hz, 3H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 5.71 (d, *J* = 5.9 Hz, 1H), 5.01 (d, *J* = 5.8 Hz, 1H), 3.94 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 162.2, 161.1, 156.3, 144.2, 136.8, 132.4, 130.7, 129.3, 128.8, 128.5, 126.7, 126.5, 123.8, 122.8, 114.9, 56.1, 52.4; **HRMS (ESI)** calculated for C₂₄H₁₈⁷⁹Br³⁵ClN₂O₃ [M+Na]⁺: 519.0087, found: 519.0085; **HRMS (ESI)** calculated for C₂₄H₁₈⁸¹Br³⁵ClN₂O₃ [M+Na]⁺: 521.0067, found: 521.0067; **HRMS (ESI)** calculated for C₂₄H₁₈⁸¹Br³⁷ClN₂O₃ [M+Na]⁺: 523.0037, found: 523.0039; **Enantiomeric ratio:** 83.5:16.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 6.37 min (minor), t_R = 15.66 min (major).

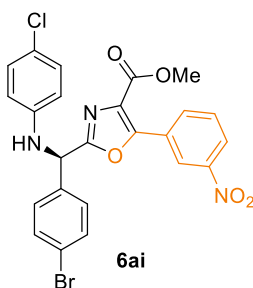


Methyl (*R*)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate 6ag: yield: 25.4 mg (45%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20}$ = 13.7 (c 0.31 CH₂Cl₂); ¹H-NMR (600 MHz, CDCl₃) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 5.9 Hz, 1H), 4.98 (d, *J* = 5.8 Hz, 1H), 3.96 (s, 3H); ¹³C-NMR (151 MHz, CDCl₃) δ 162.0, 161.9, 154.5, 144.1, 136.6, 132.5, 132.3 (q, *J* = 32.8 Hz), 131.8, 129.8, 129.4, 129.0 (q, *J* = 269.2 Hz), 128.8, 128.8, 125.5 (q, *J* = 3.5 Hz), 124.0, 123.0, 115.0, 56.2, 52.6; ¹⁹F-NMR (564 MHz, CDCl₃) δ -63.1; **HRMS (ESI)** calculated for C₂₅H₁₇⁷⁹Br³⁵ClF₃N₂O₃ [M+Na]⁺: 586.9961, found: 586.9965; **HRMS (ESI)** calculated for

$C_{25}H_{17}^{81}Br^{35}ClF_3N_2O_3$ $[M+Na]^+$: 588.9940, found: 588.9947; **HRMS (ESI)** calculated for $C_{25}H_{17}^{81}Br^{37}ClF_3N_2O_3$ $[M+Na]^+$: 590.9911, found: 590.9919; **Enantiomeric ratio**: 76:24, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 5.77 min (minor), t_R = 10.69 min (major).

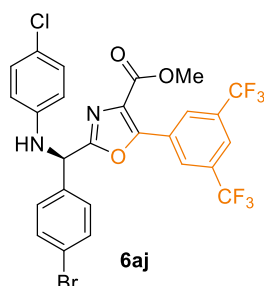


Methyl (*R*)-5-(4-bromophenyl)-2-((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6ah: yield: 17.2 mg (30%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20}$ = 15.5 (c 0.14 CH_2Cl_2); **1H -NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 5.71 (d, J = 5.8 Hz, 1H), 4.97 (d, J = 5.7 Hz, 1H), 3.94 (s, 3H); **^{13}C -NMR** (151 MHz, $CDCl_3$) δ 162.1, 161.3, 155.2, 144.2, 136.7, 132.5, 131.8, 129.9, 129.3, 128.8, 127.2, 125.4, 125.3, 123.9, 122.9, 114.9, 56.2, 52.5; **HRMS (ESI)** calculated for $C_{24}H_{17}^{79}Br^{35}ClN_2O_3$ $[M+Na]^+$: 596.9192, found: 596.9185; **HRMS (ESI)** calculated for $C_{24}H_{17}^{81}Br^{37}ClN_2O_3$ $[M+Na]^+$: 602.9122, found: 602.9114; **Enantiomeric ratio**: 71:29, determined by HPLC (Daicel Chirapak IA, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_R = 7.04 min (minor), t_R = 15.96 min (major).

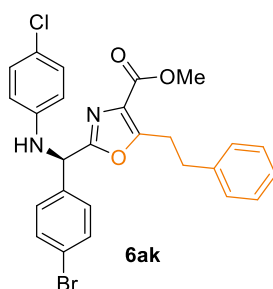


Methyl (*R*)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-(3-nitrophenyl)oxazole-4-carboxylate 6ai: yield: 24.3 mg (45%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); yellow oil; $[\alpha]_D^{20}$ = 16.5 (c 0.45 CH_2Cl_2); **1H -NMR** (600 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.32 – 8.26 (m, 1H), 7.65 (t, J = 8.1 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.61 (d, J = 8.7 Hz, 2H), 5.76 (d, J = 6.1 Hz, 1H), 4.97 (d, J = 6.1 Hz, 1H), 3.98 (s, 3H); **^{13}C -NMR** (151 MHz, $CDCl_3$) δ 162.1, 161.8, 153.4, 148.3, 144.0, 136.4, 134.0, 132.5, 129.7, 129.3, 128.8, 128.4, 128.0, 125.0, 124.0, 123.4, 123.1, 114.9, 56.2, 52.8; **HRMS (ESI)** calculated for $C_{24}H_{17}^{79}Br^{35}ClN_3O_5$ $[M+Na]^+$: 563.9938, found: 563.9935; **HRMS (ESI)**

calculated for $C_{24}H_{17}^{81}Br^{37}ClN_3O_5$ $[M+Na]^+$: 567.9888, found: 567.9889; **Enantiomeric ratio**: 79:21, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ C$, $\lambda = 254$ nm): $t_R = 9.37$ min (minor), $t_R = 16.54$ min (major).



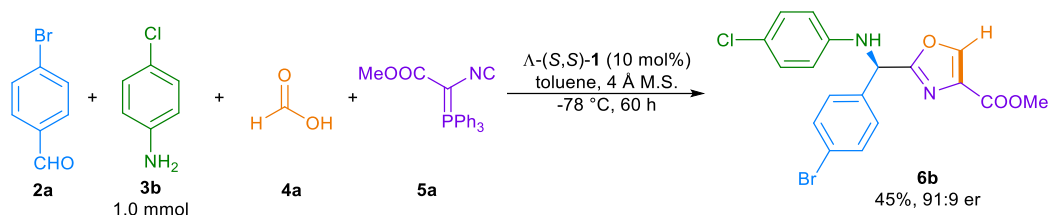
Methyl (R)-5-(3,5-bis(trifluoromethyl)phenyl)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)oxazole-4-carboxylate 6aj: yield: 28.4 mg (45%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20} = 15.7$ (c 0.74 CH_2Cl_2); 1H -NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.95 (s, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.8$ Hz, 2H), 6.61 (d, $J = 8.8$ Hz, 2H), 5.77 (d, $J = 6.4$ Hz, 1H), 4.95 (d, $J = 6.3$ Hz, 1H), 3.98 (s, 3H); ^{13}C -NMR (151 MHz, $CDCl_3$) δ 162.5, 161.6, 152.7, 144.0, 136.3, 132.6, 132.0 (q, $J = 33.8$ Hz), 129.4, 129.0, 128.8, 128.6 – 128.4 (m), 124.1, 123.8 (q, $J = 3.6$ Hz), 123.2, 121.2 (q, $J = 272.9$ Hz), 115.0, 56.2, 52.9; ^{19}F -NMR (564 MHz, $CDCl_3$) δ -63.0; **HRMS (ESI)** calculated for $C_{26}H_{16}^{79}Br^{35}ClF_6N_2O_3$ $[M+Na]^+$: 654.9835, found: 654.9835; **HRMS (ESI)** calculated for $C_{26}H_{16}^{81}Br^{37}ClF_6N_2O_3$ $[M+Na]^+$: 658.9785, found: 658.9789; **Enantiomeric ratio**: 80:20, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, $T = 30^\circ C$, $\lambda = 254$ nm): $t_R = 5.25$ min (minor), $t_R = 5.86$ min (major).



Methyl (R)-2-((4-bromophenyl)((4-chlorophenyl)amino)methyl)-5-phenethyloxazole-4-carboxylate 6ak: yield: 21.5 mg (41%); (Flash column chromatography eluent, petroleum ether/diethyl ether = 1/1); white oil; $[\alpha]_D^{20} = -2.9$ (c 0.44 CH_2Cl_2); 1H -NMR (600 MHz, $CDCl_3$) δ 7.48 (d, $J = 8.4$ Hz, 2H), 7.30 – 7.24 (m, 3H), 7.19 (d, $J = 6.5$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 2H), 7.04 – 6.96 (m, 2H), 6.53 (d, $J = 8.8$ Hz, 2H), 5.56 (d, $J = 6.2$ Hz, 1H), 4.89 (d, $J = 6.1$ Hz, 1H), 3.88 (s, 3H), 3.31 (t, $J = 7.5$ Hz, 2H), 2.93 (t, $J = 7.5$ Hz, 2H); ^{13}C -NMR (151 MHz, $CDCl_3$) δ 162.2, 161.0, 159.8, 144.2, 139.6, 136.9, 132.3, 129.2, 128.7, 128.5, 128.3, 127.6, 126.5, 123.6, 122.7, 114.8, 56.0, 52.1, 33.7, 27.8; **HRMS (ESI)** calculated for $C_{26}H_{22}^{79}Br^{35}ClN_2O_3$ $[M+Na]^+$: 547.0400, found: 547.0405; **HRMS**

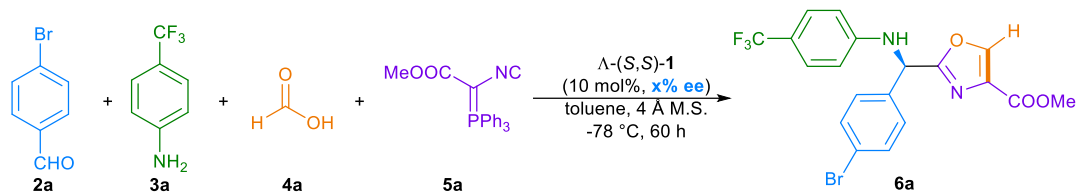
(ESI) calculated for $\text{C}_{26}\text{H}_{22}^{81}\text{Br}^{37}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{Na}]^+$: 551.0350, found: 551.0359; **Enantiomeric ratio:** 79.5:20.5, determined by HPLC (Daicel Chirapak IF, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, T = 30 °C, λ = 254 nm): t_{R} = 6.68 min (minor), t_{R} = 10.08 min (major).

3. Asymmetric Ugi-4CR/Wittig reaction sequences in large-scale



A 50-mL oven-dried tube was charged with 4-bromobenzaldehyde **2a** (1.2 mmol), 4-chloroaniline **3b** (1.0 mmol), catalyst Δ -(S,S)-**1a** (0.1 mmol), 4 Å MS (100.0 mg), and toluene (10.0 mL) at room temperature and stirred for 30 min. Then isocyano(triphenylphosphoranylidene)-acetates **5a** (3.0 mmol) was added. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and stirred for another 30 min. The formic acid **4a** (15.0 mmol) was divided into 5.0 mmol parts added at 12 hours intervals was stirred vigorously for 60 h. The reaction was then quenched with pre-cooled NEt_3 ($-78\text{ }^{\circ}\text{C}$, 1.0 mL). The organic layer was separated, and the aqueous phase was extracted with EtOAc ($3 \times 30\text{ mL}$). The combined organic layers were washed with water (50 mL) and brine (50 mL). The solution was then dried over Na_2SO_4 and filtered. The volatiles were then evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether/ ethyl acetate = 1:1) to give the desired product **6b** (189.0 mg, 45% yield, 91:9 er).

4. Nonlinear Effect Studies



A 10-mL oven-dried tube was charged with 4-bromobenzaldehyde **2b** (0.12 mmol), 4-trifluoroaniline **3a** (0.10 mmol), scalemic catalyst **1a** (0.01 mmol), 4 Å MS (50 mg), and toluene (1.5 mL) at room temperature and stirred for 30 min. Then isocyano(triphenylphosphoranylidene)-acetates **5a** (1.50 mmol) was added in one portion. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and stirred for another 30 min. The formic acid **4a** (0.30 mmol) was divided into three equal parts added at 12 hours intervals and the resulting solution was stirred vigorously for 60 h. The reaction was then quenched with pre-cooled NEt_3 ($-78\text{ }^{\circ}\text{C}$, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether = 1:1) to give the multisubstituted oxazoles **6a**.

Table S3. Relation between *e.e.* of [**1a**] and *e.e.* of [**6a**]

entry	Δ - 1a (mg)	Λ - 1a (mg)	<i>ee</i> ₁ of 1a (%) ^b	c (g/100 mL) ^c	$[\alpha]^{20}$	yield of 6a (%) ^e	<i>ee</i> ₂ of 6a (%) ^f
1	--	2.1	100	0.0084	-3785.71	60	79
2	2.5	47.5	86	0.0084	-3198.41	50	67
3	5.5	45.0	77	0.0084	-2873.02	53	58
4	7.5	42.5	73	0.0084	-2730.16	55	51
5	10.0	40.0	58	0.008	-2170.83	51	43
6	15.0	35.0	38	0.008	-1420.83	55	28
7	20.0	30.5	18	0.008	-675.00	55	13
8	2.0	--	--	0.008	+3662.50	56	-79

^a The scalemic catalyst **1a** was prepared by mixing the two enantiopure catalysts Δ -(*R,R*)-**1a** and Λ -(*S,S*)-**1a**, which were completely dissolved in MeOH and then the solvent was evaporated in vacuo before used. ^b The *ee*₁ of **1a** were calculated by the quality of Δ -(*R,R*)-**1a** and Λ -(*S,S*)-**1a**. ^c The samples were dissolved in MeOH. ^d The *ee*₂ of **1a** were calculated according to the optical rotation values of different scalemic catalysts **1a** divided by the average optical rotation values of Δ -(*R,R*)-**1a** and Λ -(*S,S*)-**1a**. The *ee*₂ values were used as the horizontal coordinate in **Table S1**. ^e Isolated yield. ^f Determined by HPLC analysis.

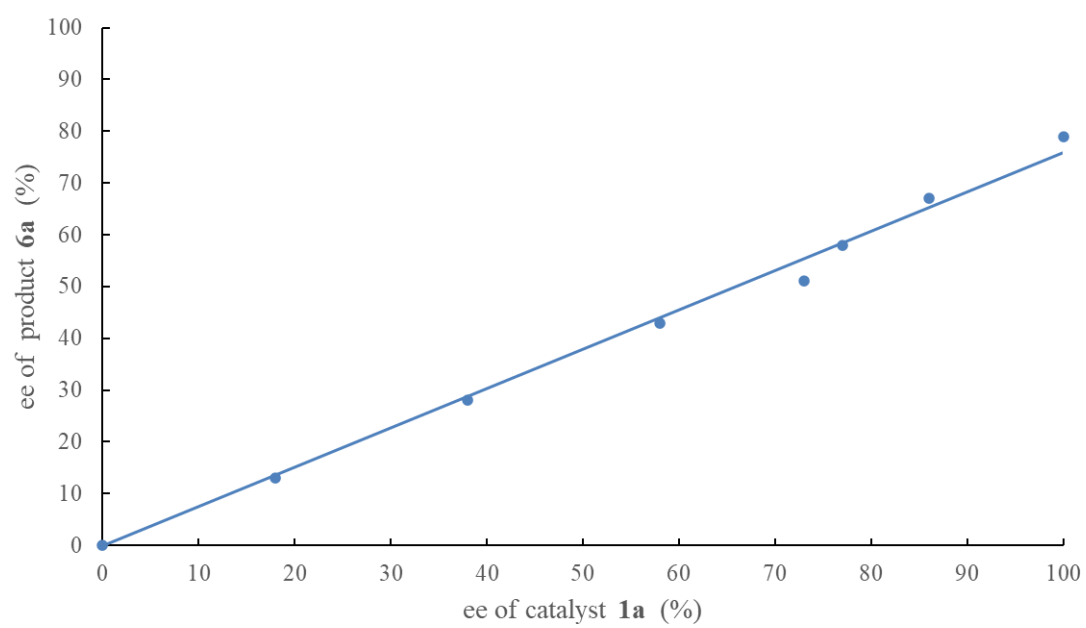


Figure S1. Nonlinear effect studies with catalyst **1a**.

5. X-ray single crystal data for 6u

Sample preparation for crystal growth: Compound **6u** (60.0 mg) was dissolved in *n*-hexane/DCM/diethyl ether (v/v = 3/1/1, 5.0 mL), while slow evaporation of solvent at room temperature white crystals were grown. Thermal ellipsoids are shown at 50% probability.

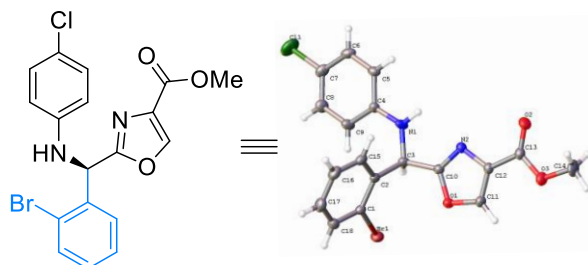
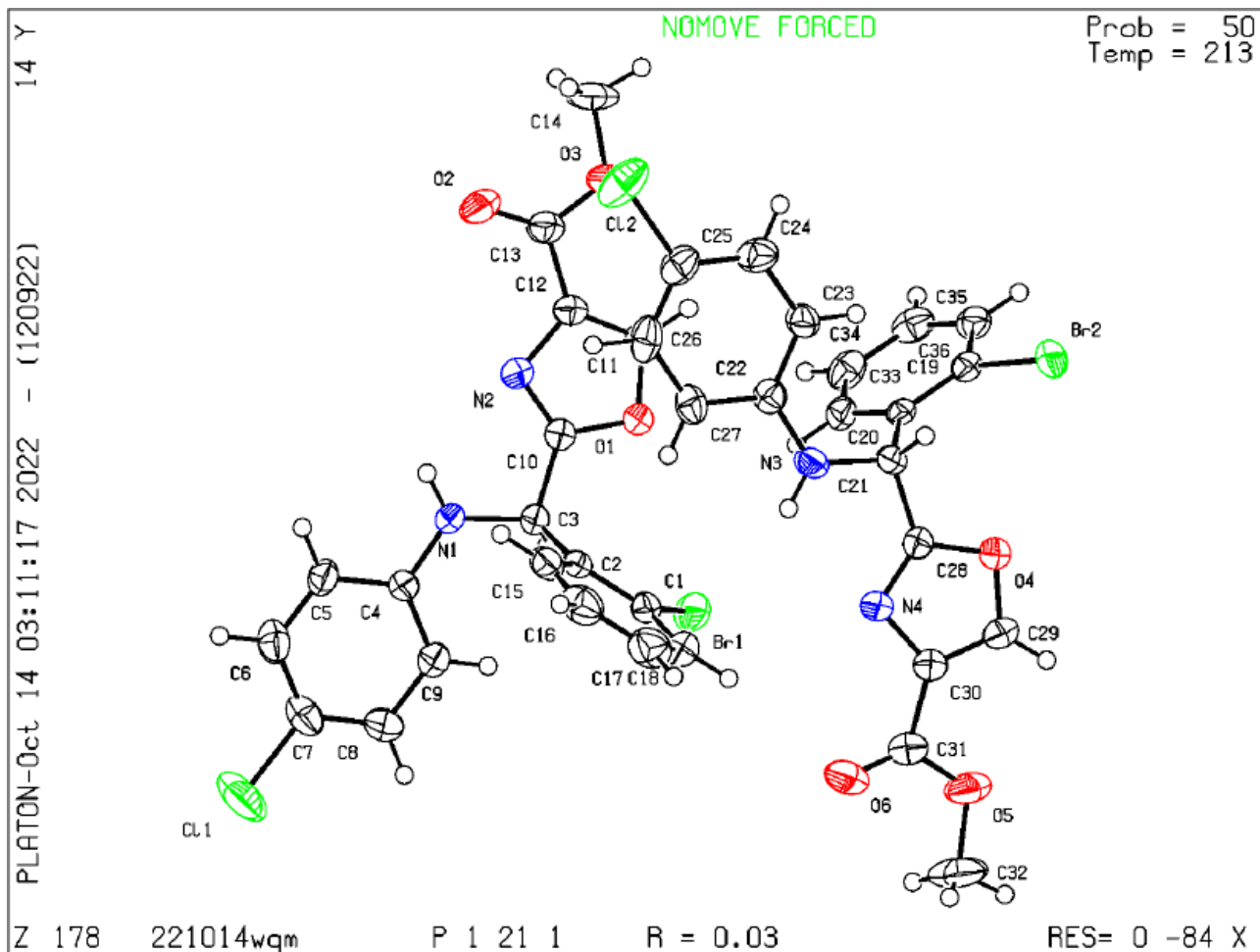
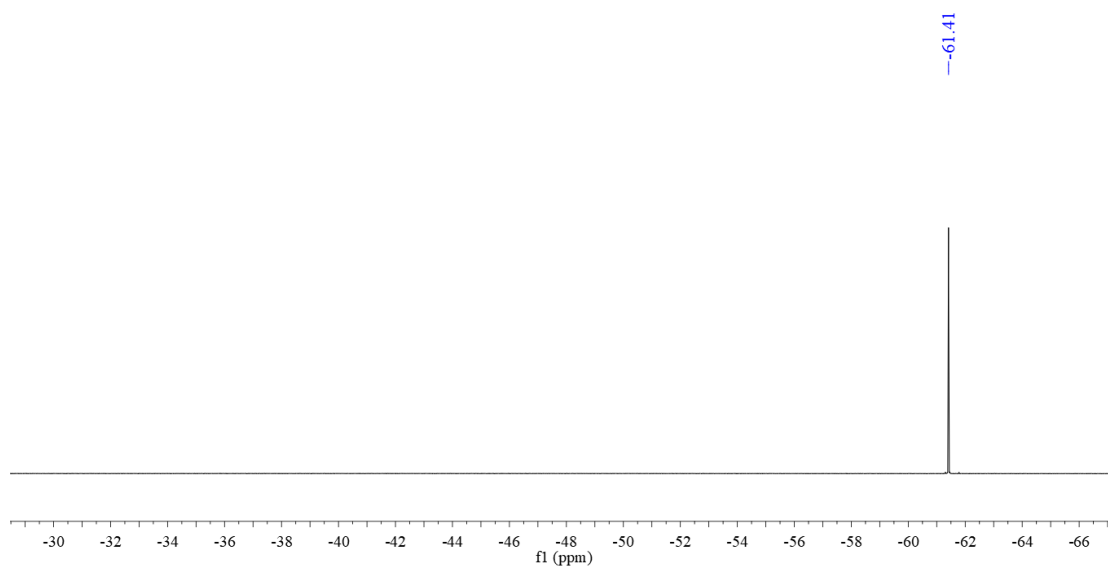
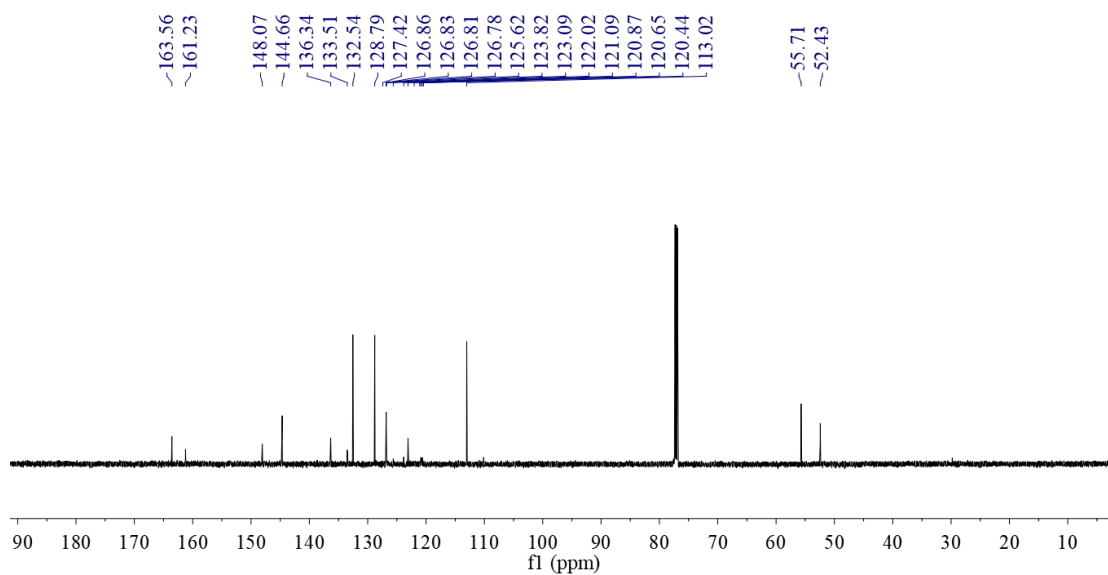
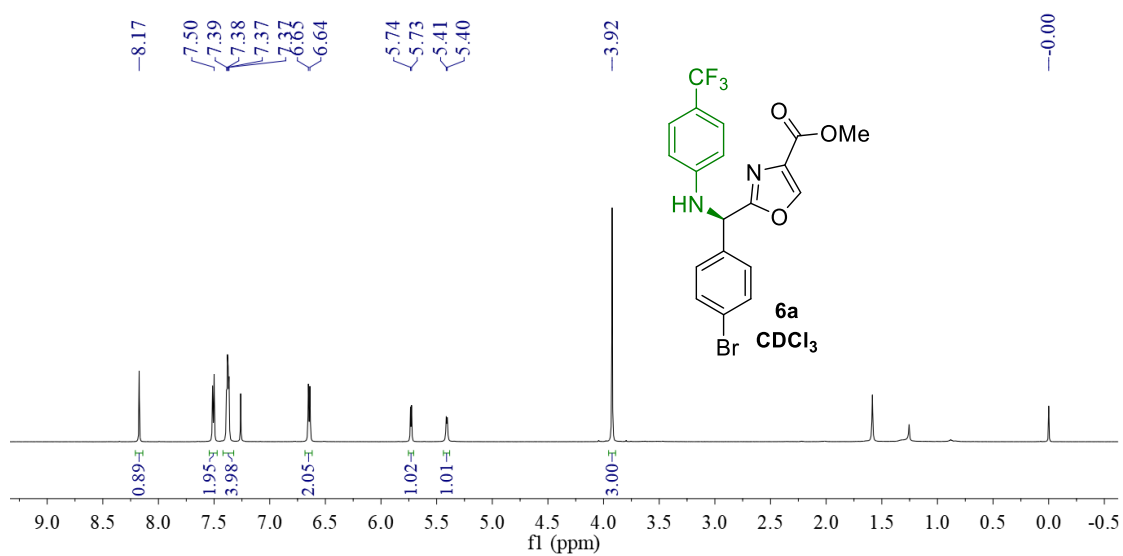


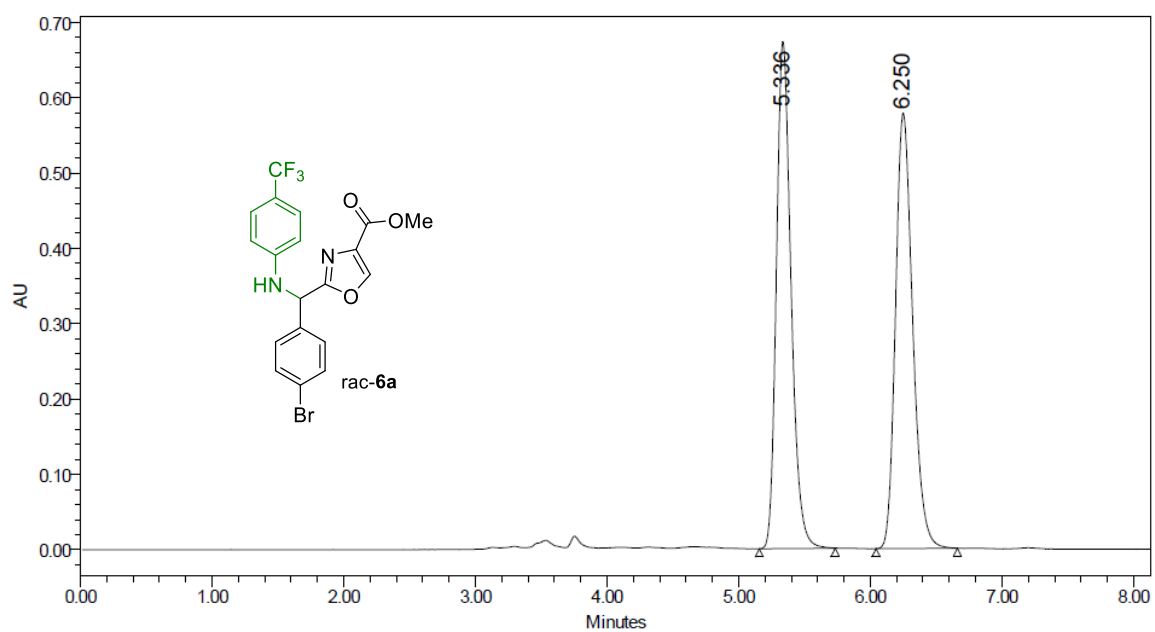
Table S4. Crystal data and structure refinement for **6u** (CCDC 2422261)

Empirical formula	C ₁₈ H ₁₄ BrClN ₂ O ₃
Formula weight	421.67
Temperature/K	213.0
Crystal system	monoclinic
Space group	P2 ₁
a/Å	11.1043(3)
b/Å	13.4026(4)
c/Å	12.0631(4)
α/°	90
β/°	90.368(2)
γ/°	90
Volume/Å ³	1795.27(9)
Z	4
ρ _{calc} /cm ³	1.506
μ/mm ⁻¹	3.083
F(000)	848.0
Crystal size/mm ³	0.07 × 0.07 × 0.05
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	3.463 to 55.120
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -12 ≤ l ≤ 14
Reflections collected	24195
Independent reflections	6784 [R _{int} = 0.0458, R _{sigma} = 0.0408]
Data/restraints/parameters	6784/1/453
Goodness-of-fit on F ²	1.065
Final R indexes [I > 2σ (I)]	R ₁ = 0.0258, wR ₂ = 0.0625
Final R indexes [all data]	R ₁ = 0.0274, wR ₂ = 0.0638
Largest diff. peak/hole / e Å ⁻³	0.278/-0.356
Flack parameter	0.041(7)

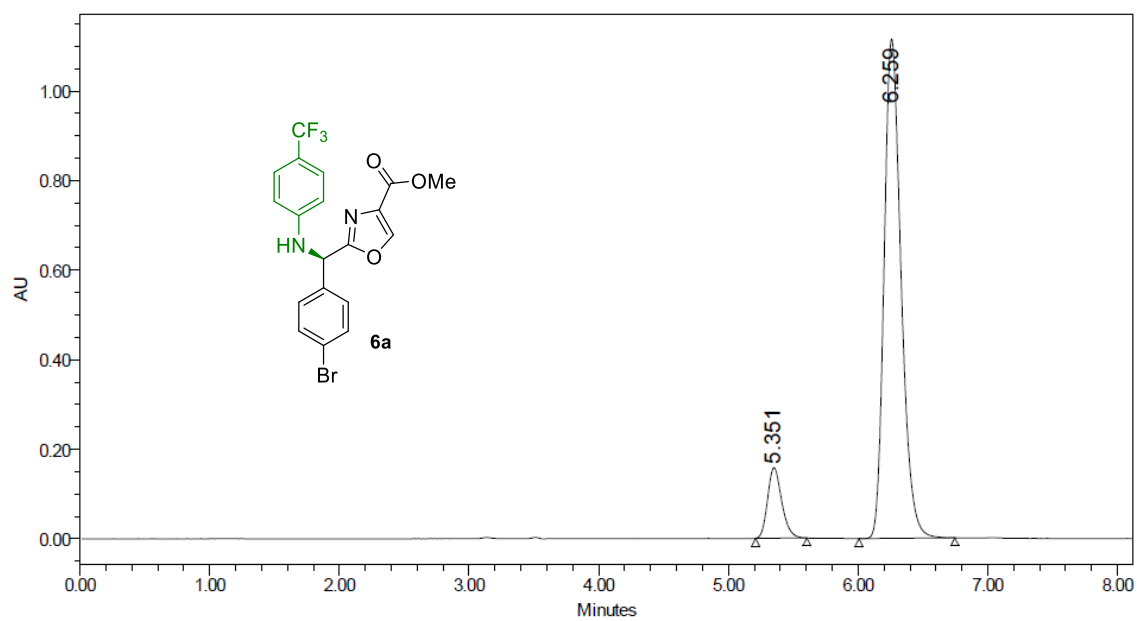


6. NMR spectra and HPLC traces

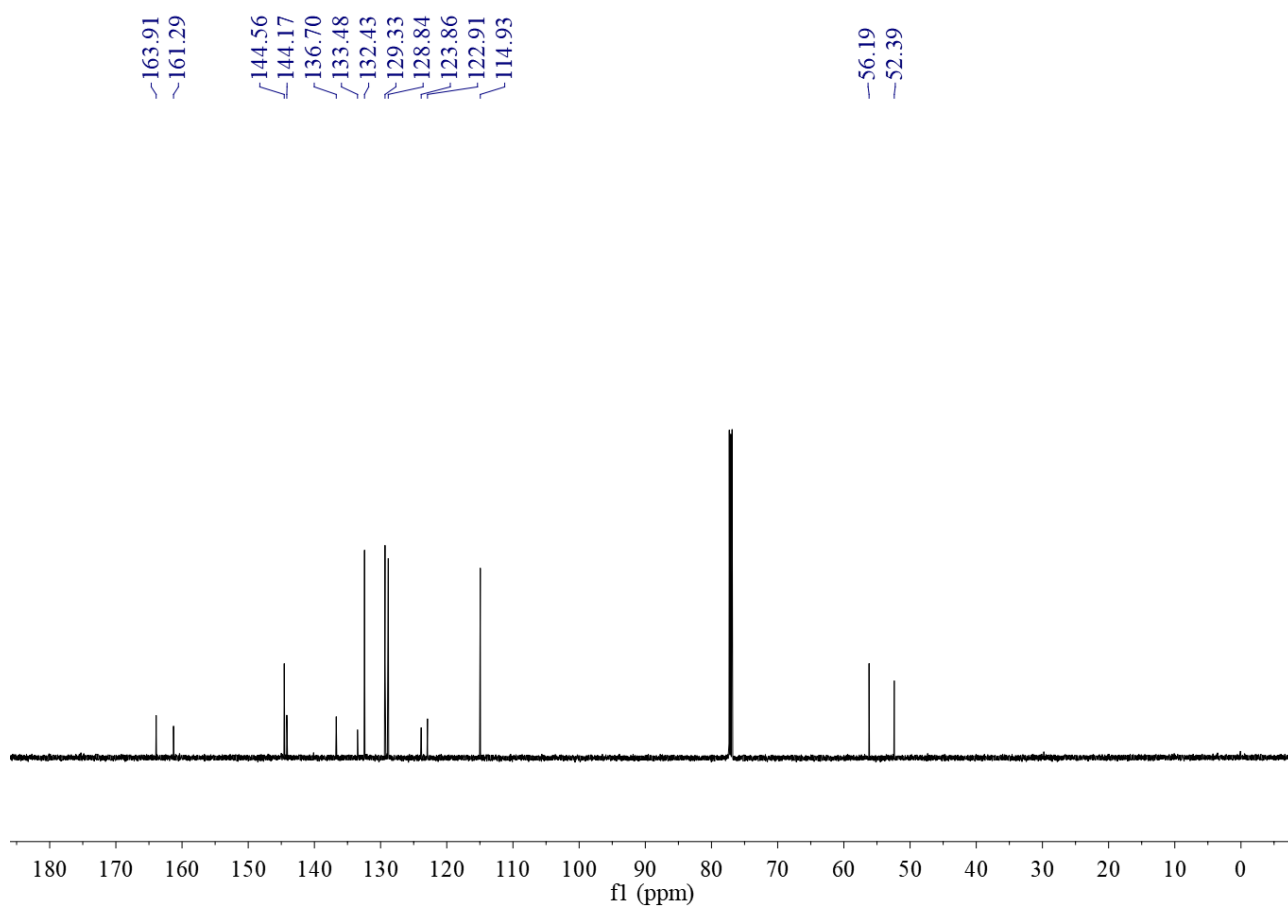
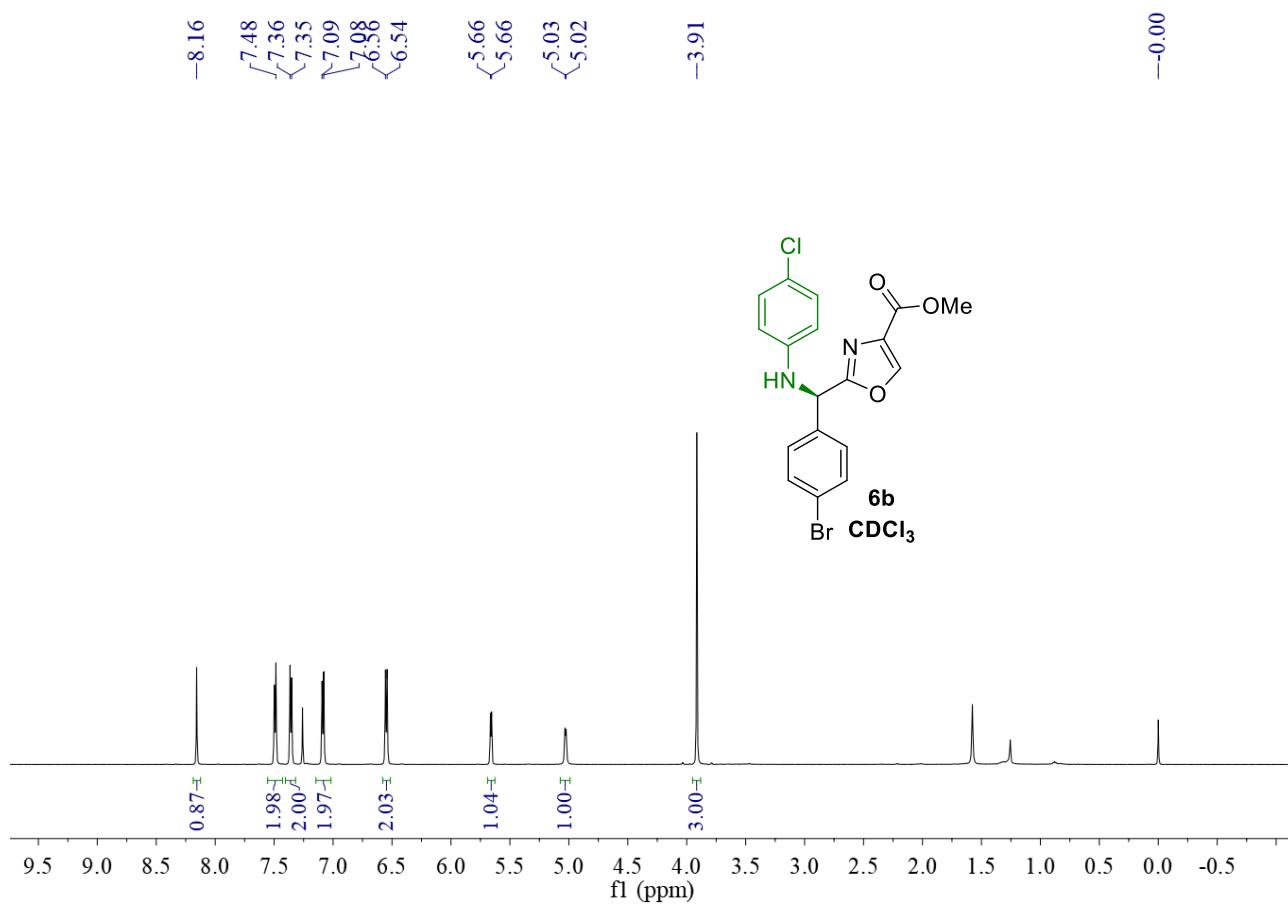


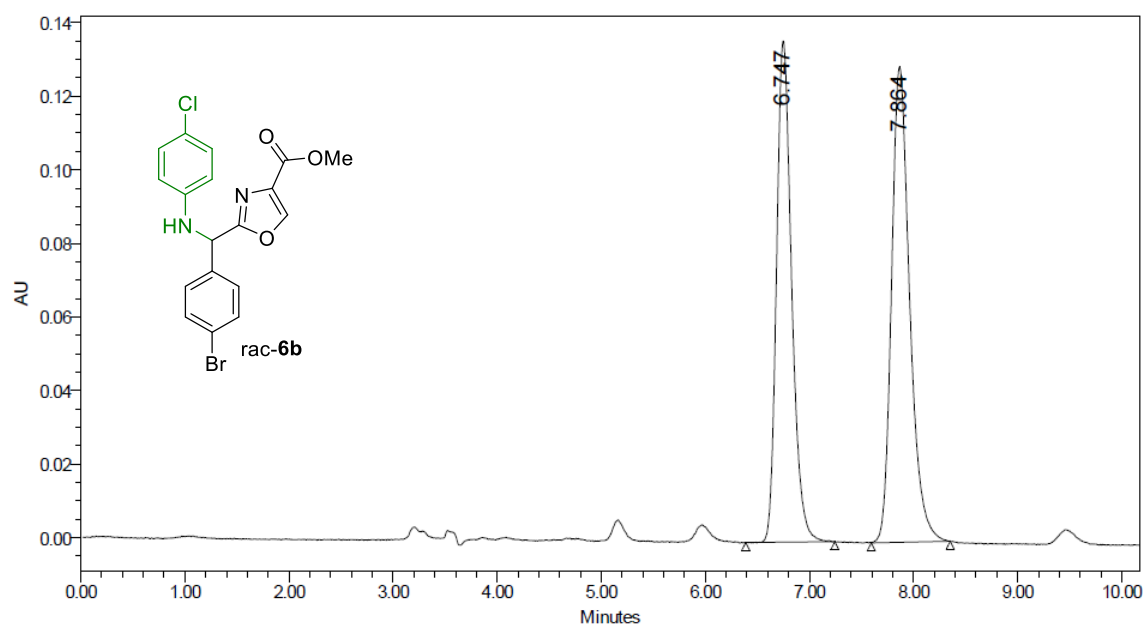


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.336	Unknown	5208342	49.93	673305	53.82	BB	346	5.157	5.733
2	6.250	Unknown	5223962	50.07	577789	46.18	BB	371	6.043	6.662

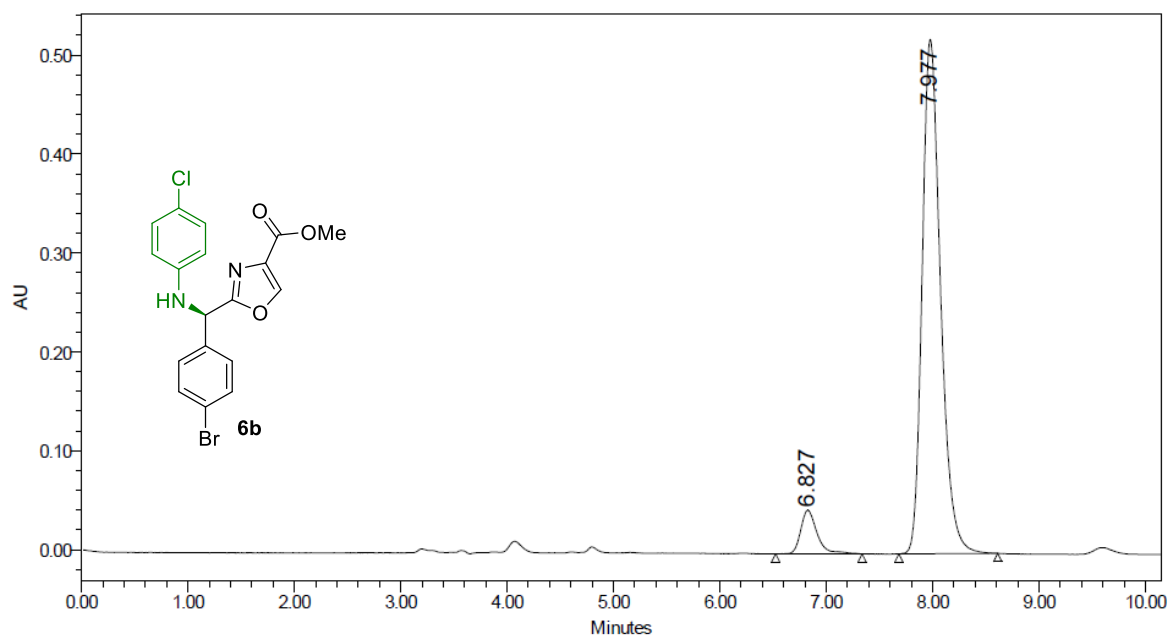


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.351	Unknown	1190854	10.51	157429	12.37	bb	237	5.210	5.605
2	6.259	Unknown	10134669	89.49	1115100	87.63	bB	443	6.007	6.745

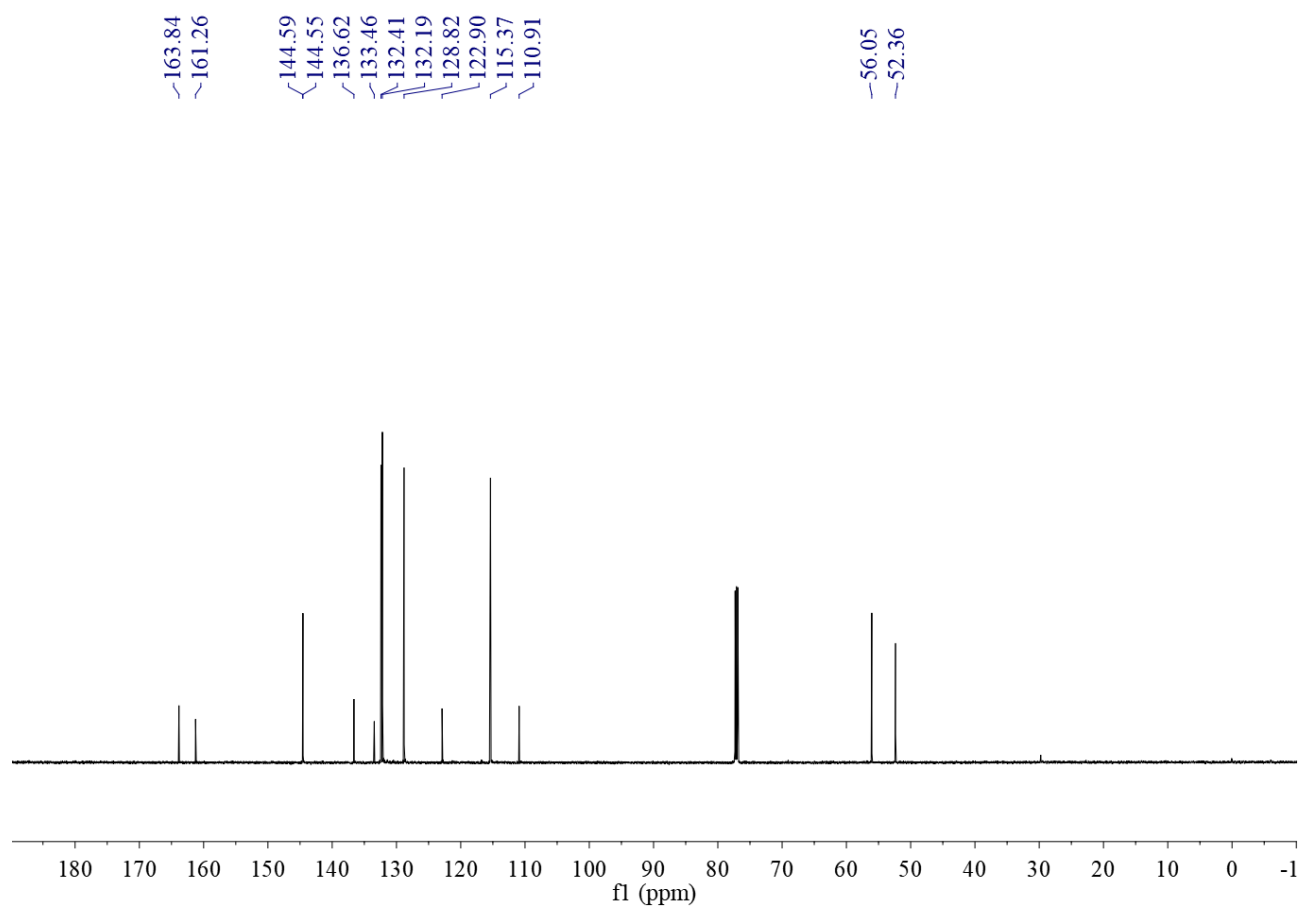
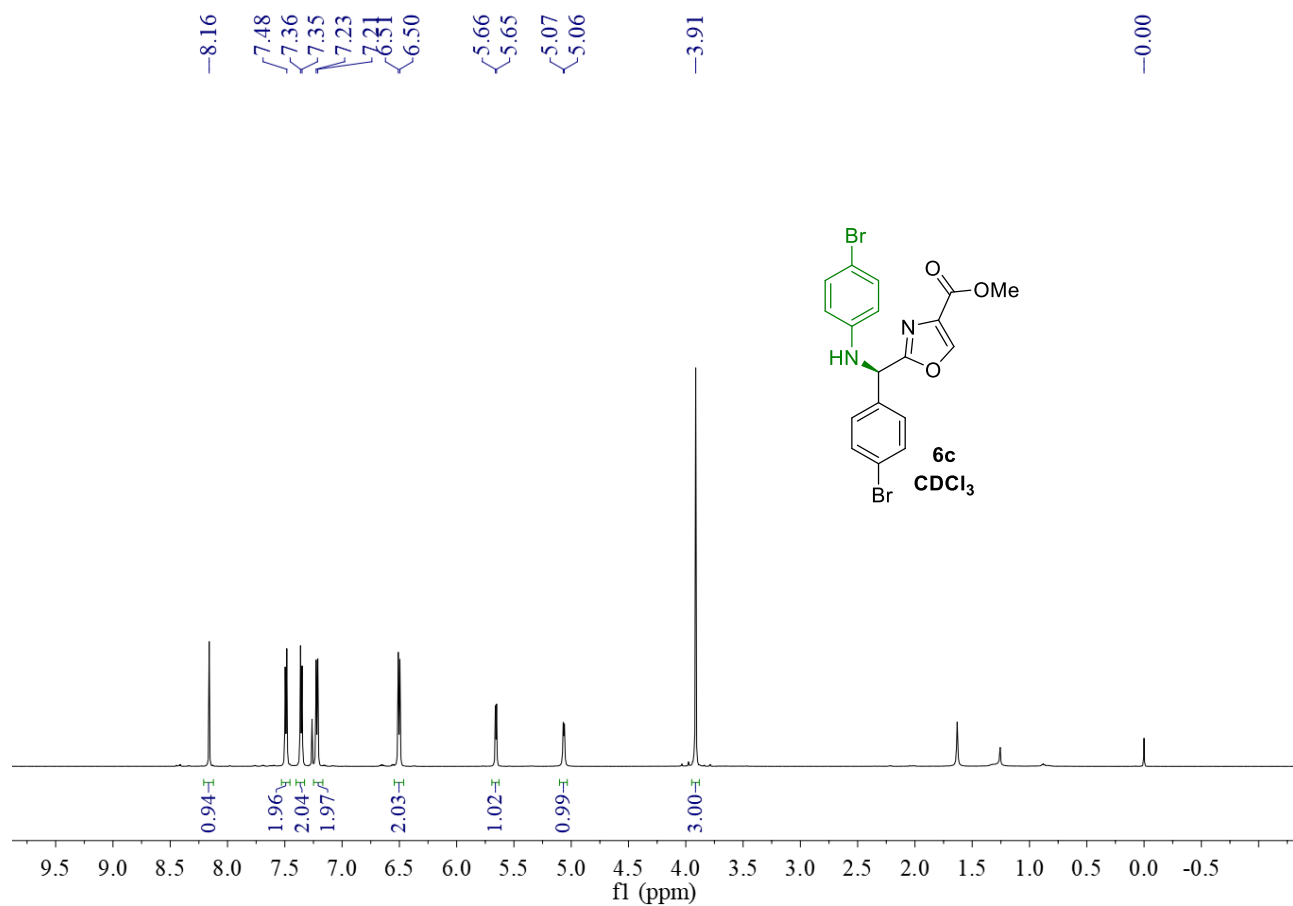


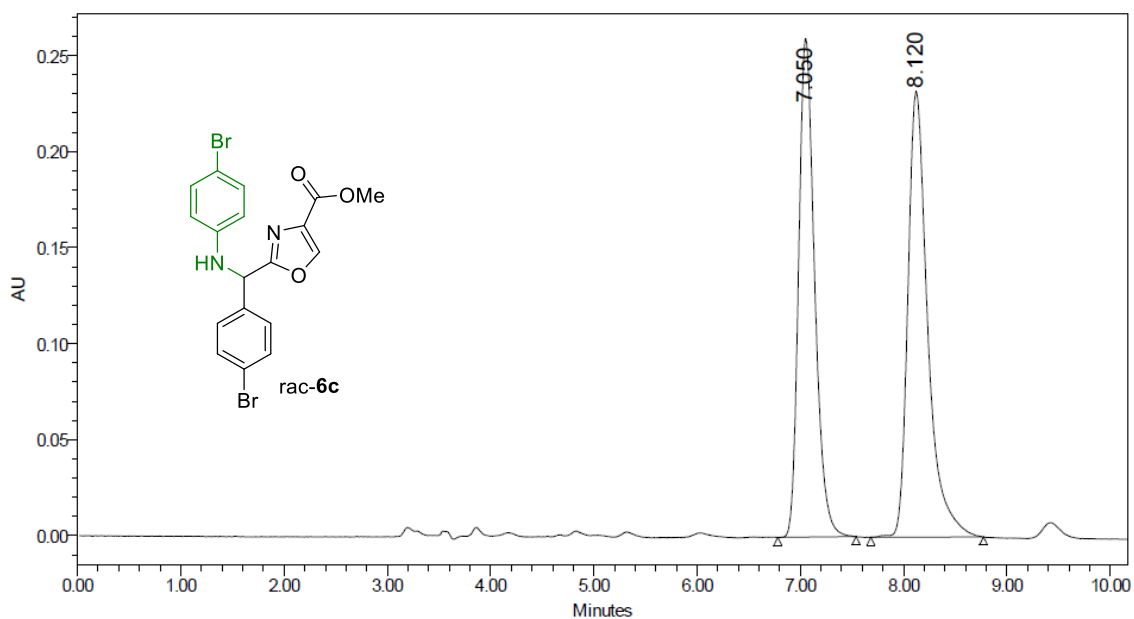


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.747	Unknown	1373395	46.79	136239	51.32	bb	514	6.387	7.243
2	7.864	Unknown	1561869	53.21	129213	48.68	Bb	455	7.593	8.352

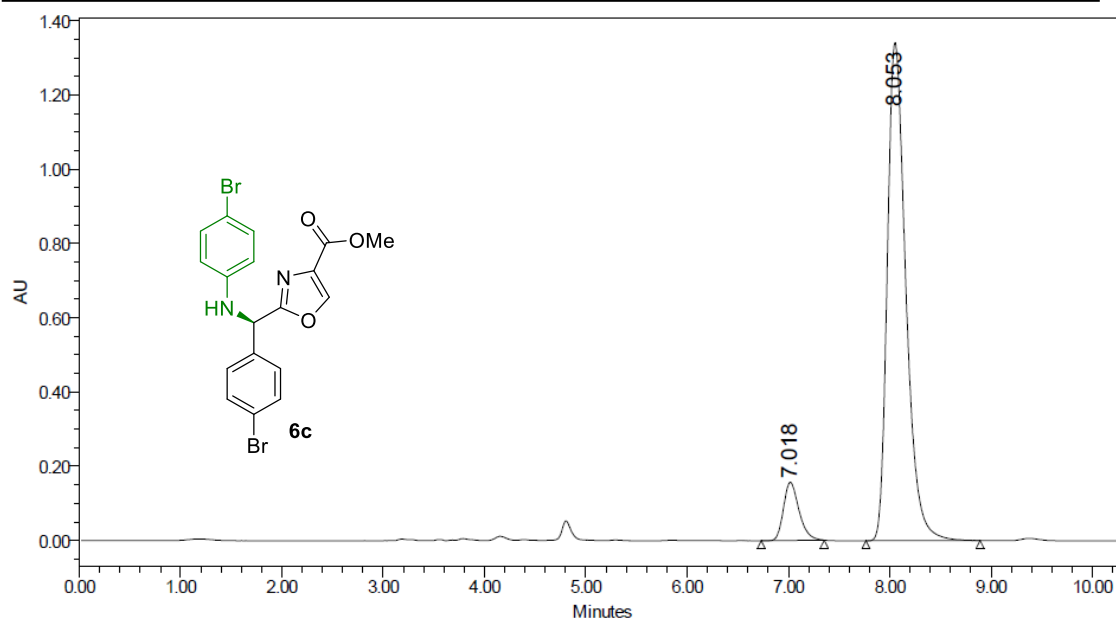


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.827	Unknown	468922	7.00	43941	7.79	bB	487	6.525	7.337
2	7.977	Unknown	6230899	93.00	520014	92.21	BB	558	7.682	8.612

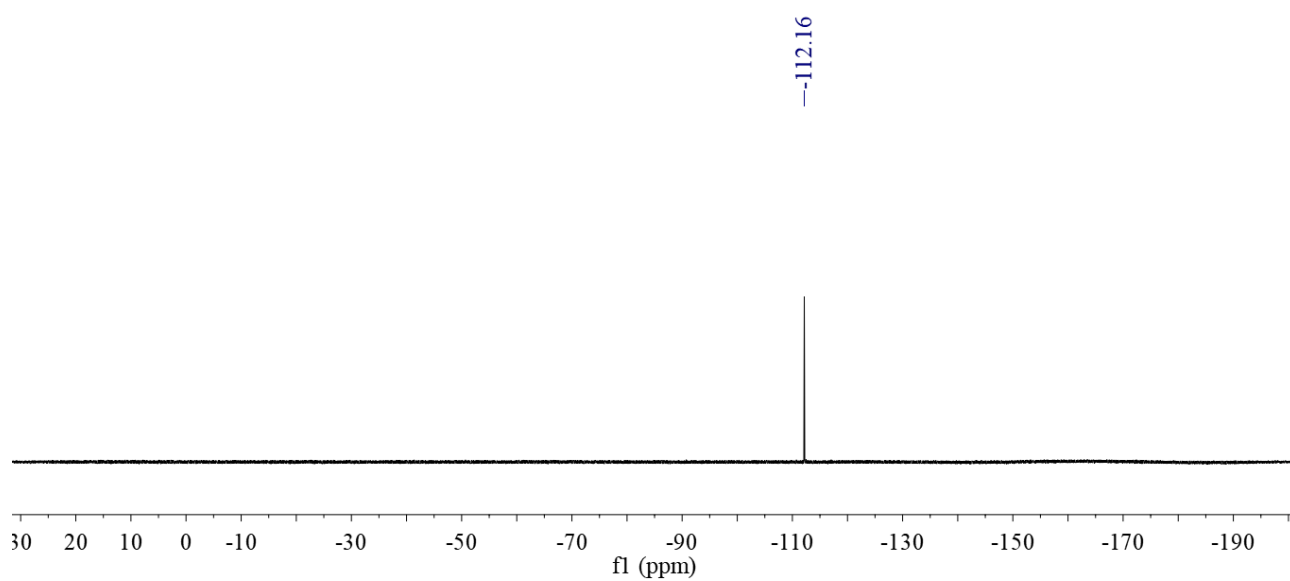
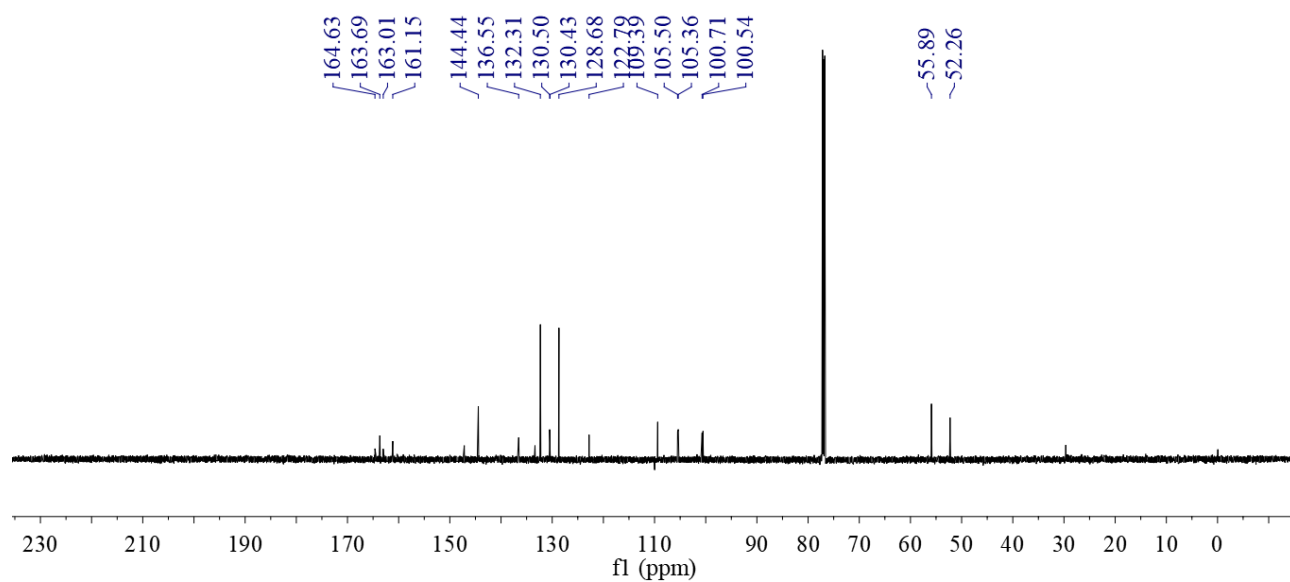
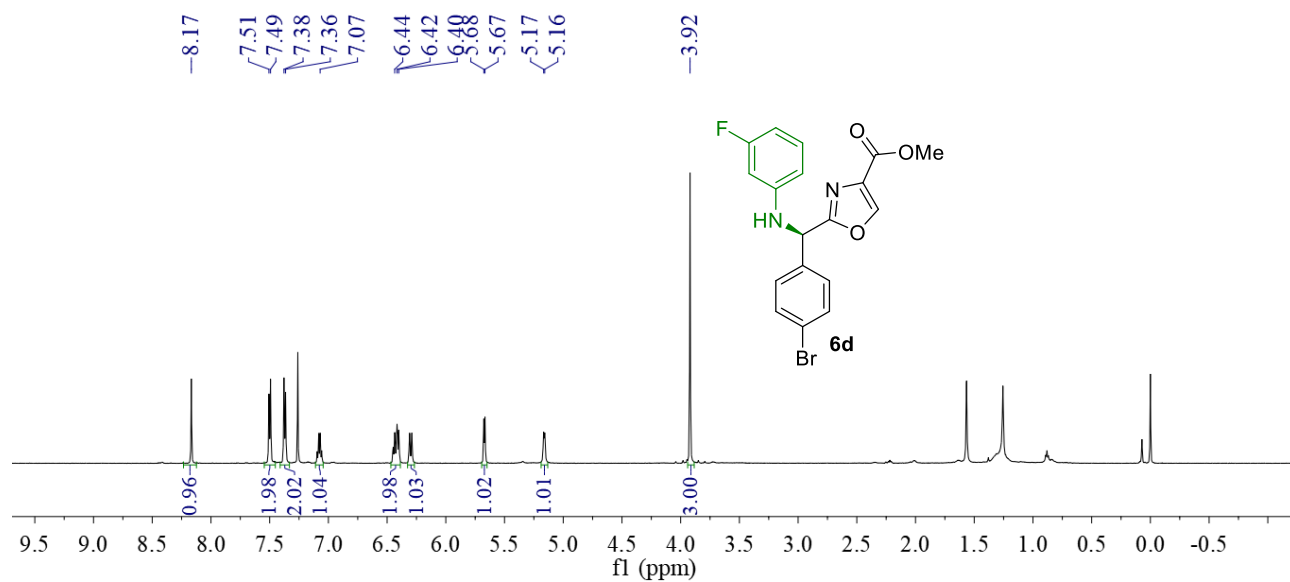


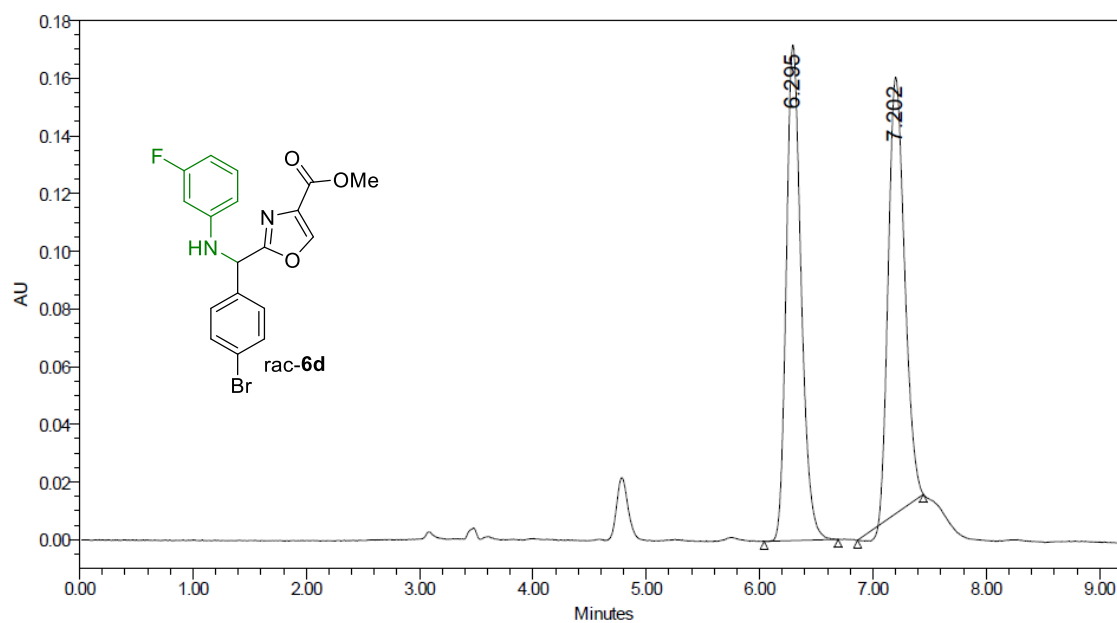


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.050	Unknown	2793206	47.41	259612	52.80	bb	454	6.782	7.538
2	8.120	Unknown	3097862	52.59	232059	47.20	bb	654	7.682	8.772

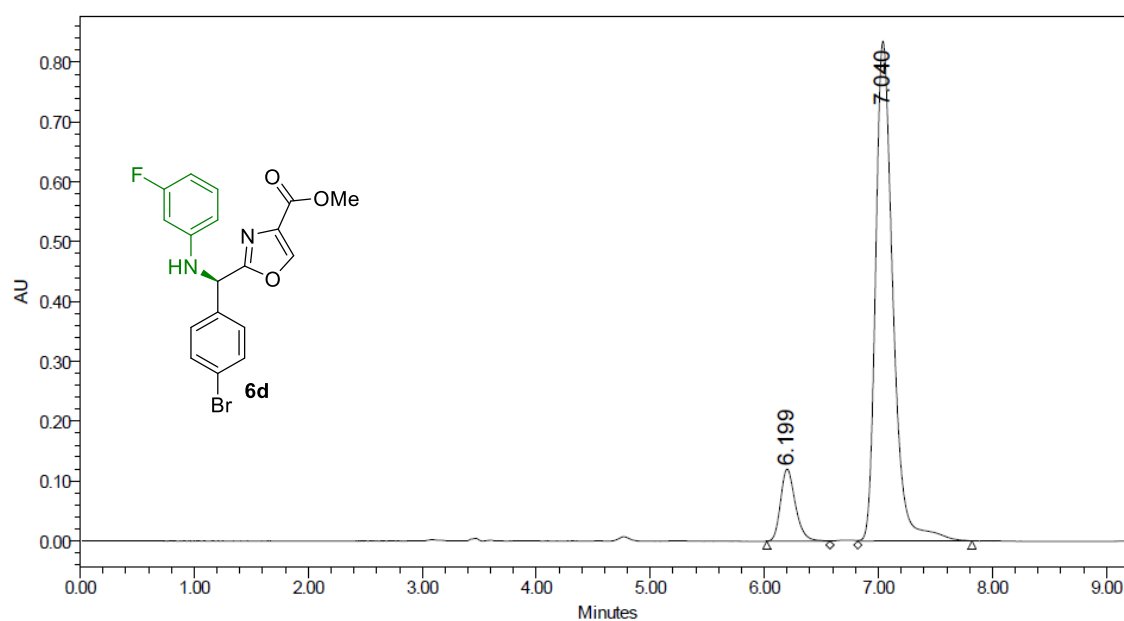


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.018	Unknown	1667350	8.92	156620	10.46	bb	373	6.732	7.353
2	8.053	Unknown	17022657	91.08	1341359	89.54	bb	676	7.765	8.892

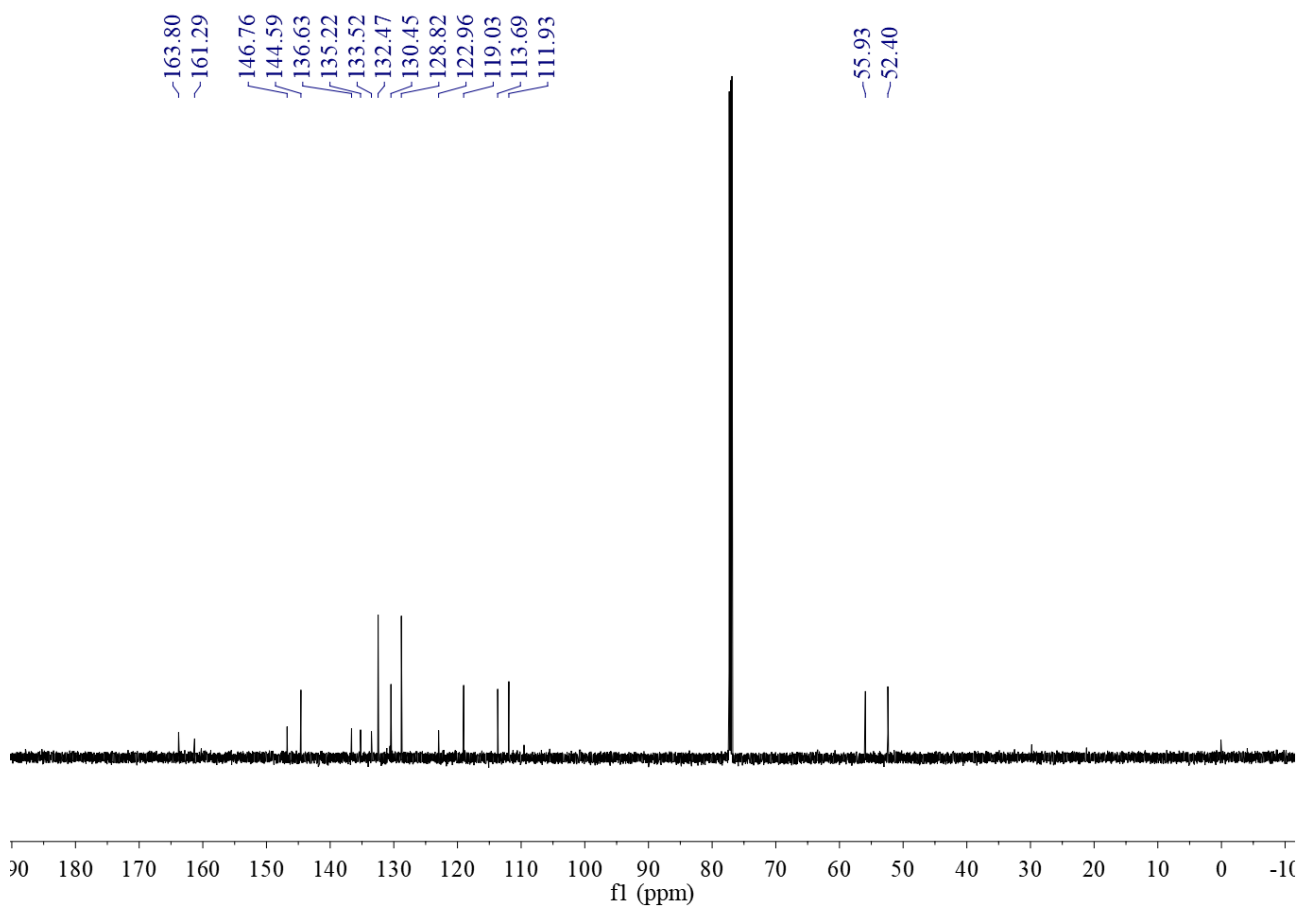
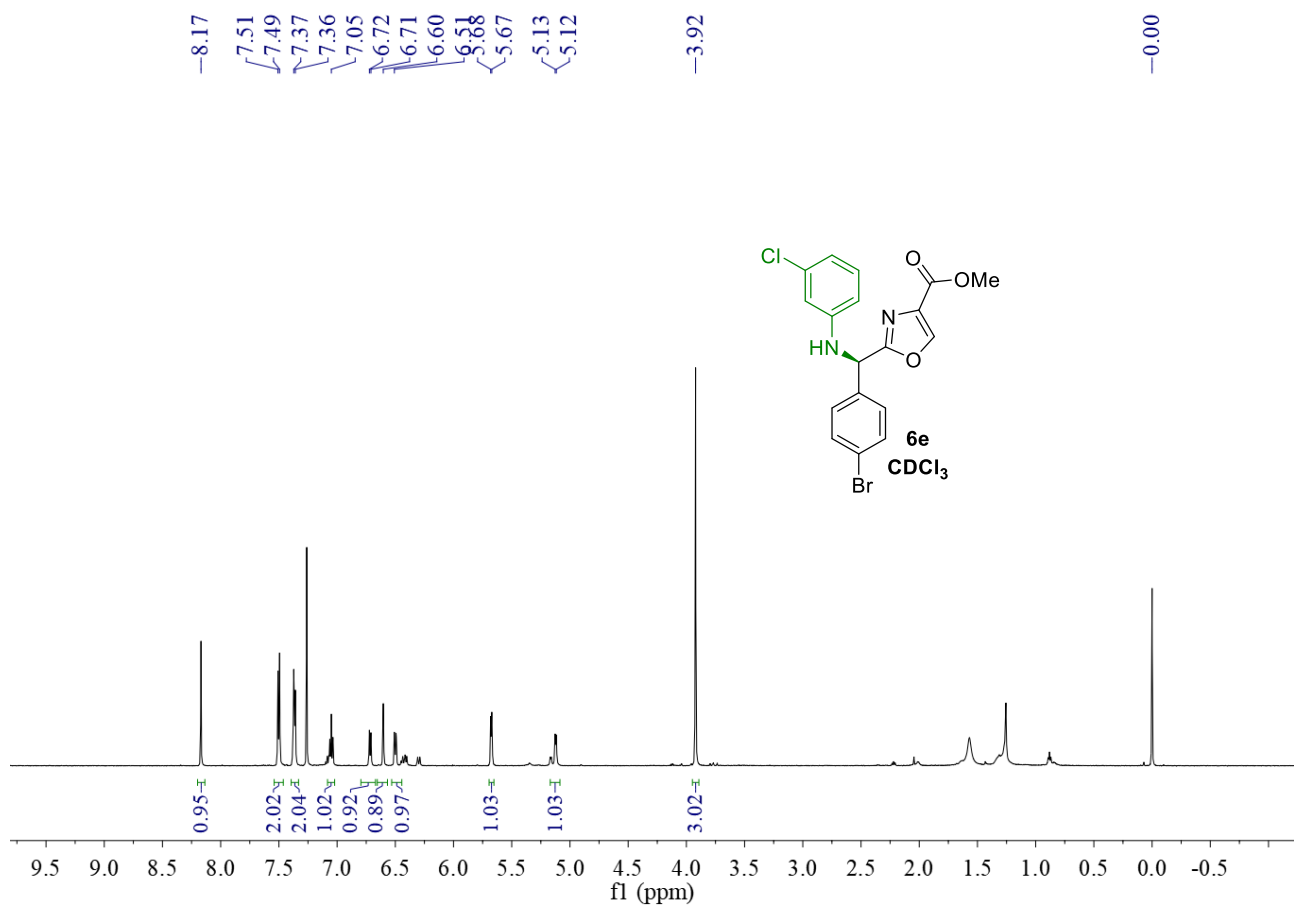


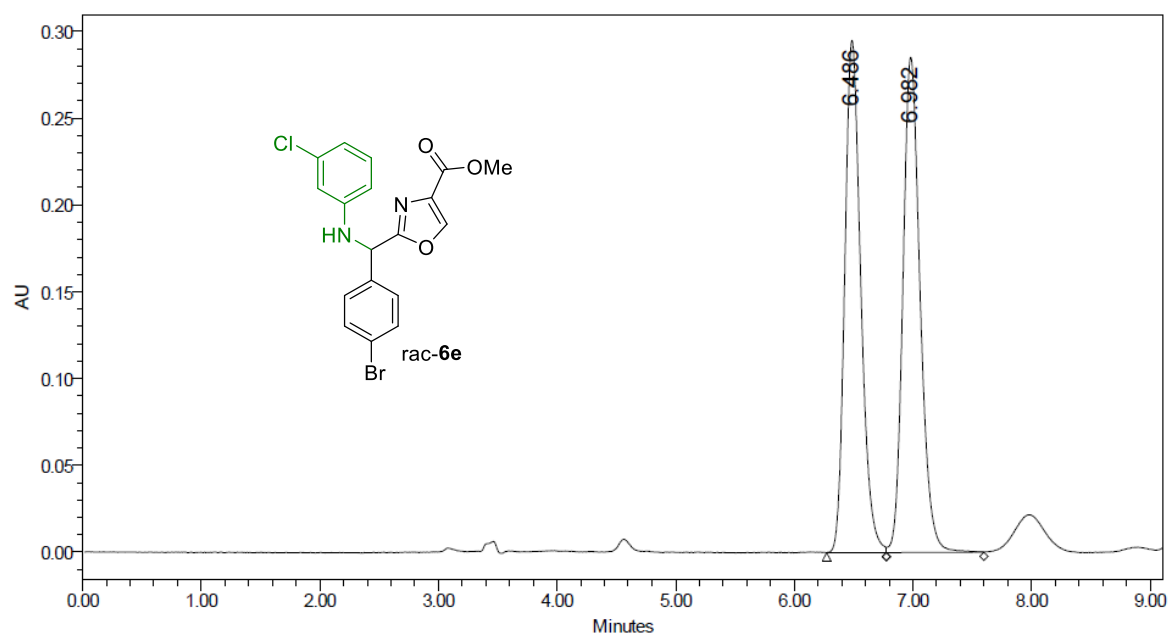


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.295	Unknown	1565188	50.37	171801	53.19	bb	392	6.040	6.693
2	7.202	Unknown	1541945	49.63	151217	46.81	bb	348	6.865	7.445

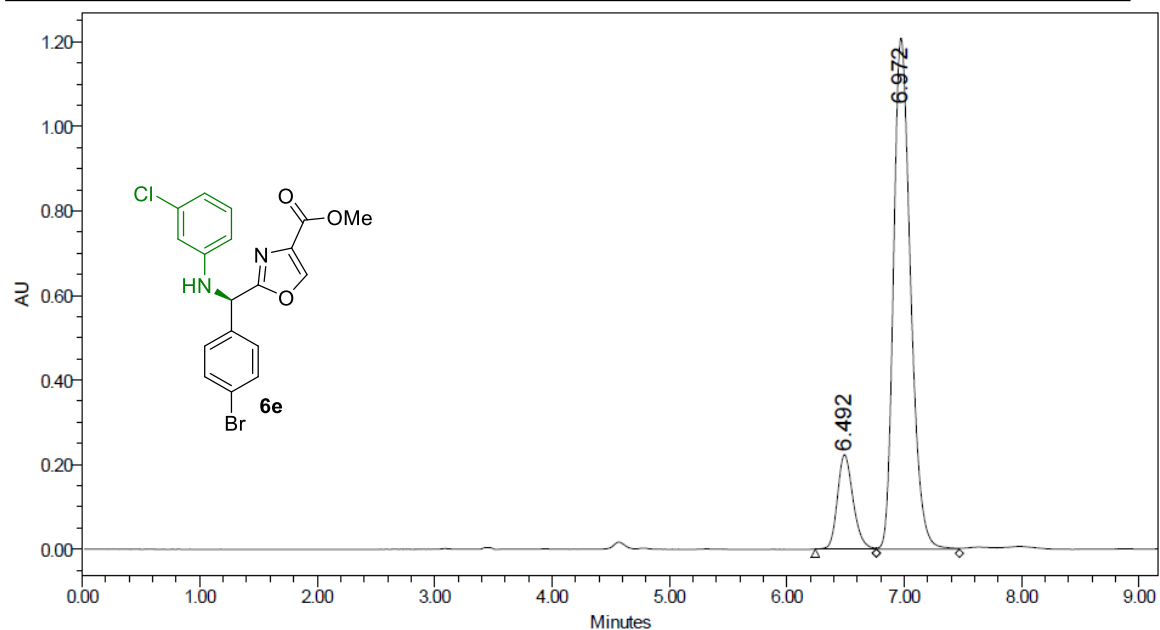


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.199	Unknown	1086079	11.00	120296	12.59	bV	332	6.022	6.575
2	7.040	Unknown	8783832	89.00	835464	87.41	Vb	601	6.818	7.820

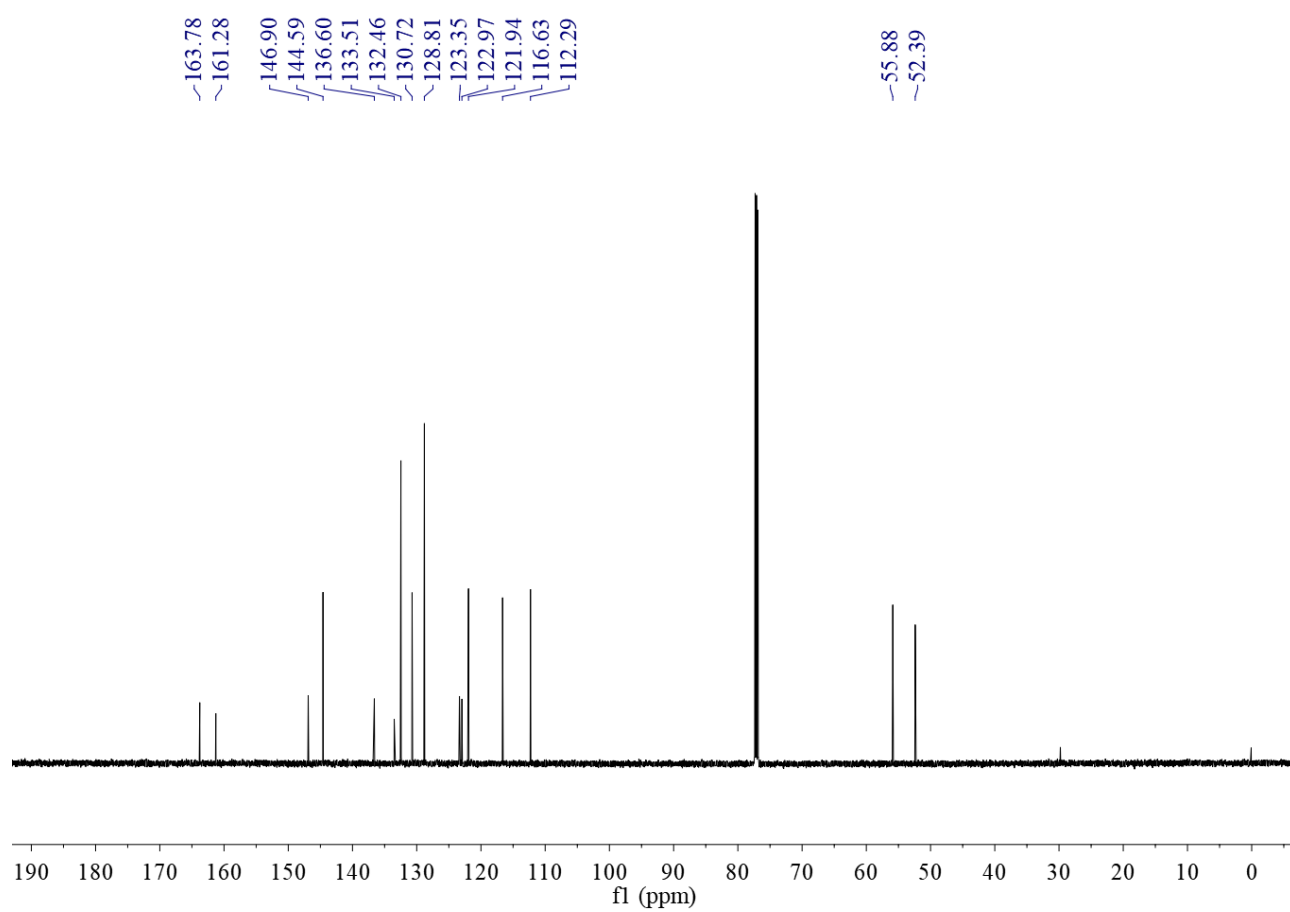
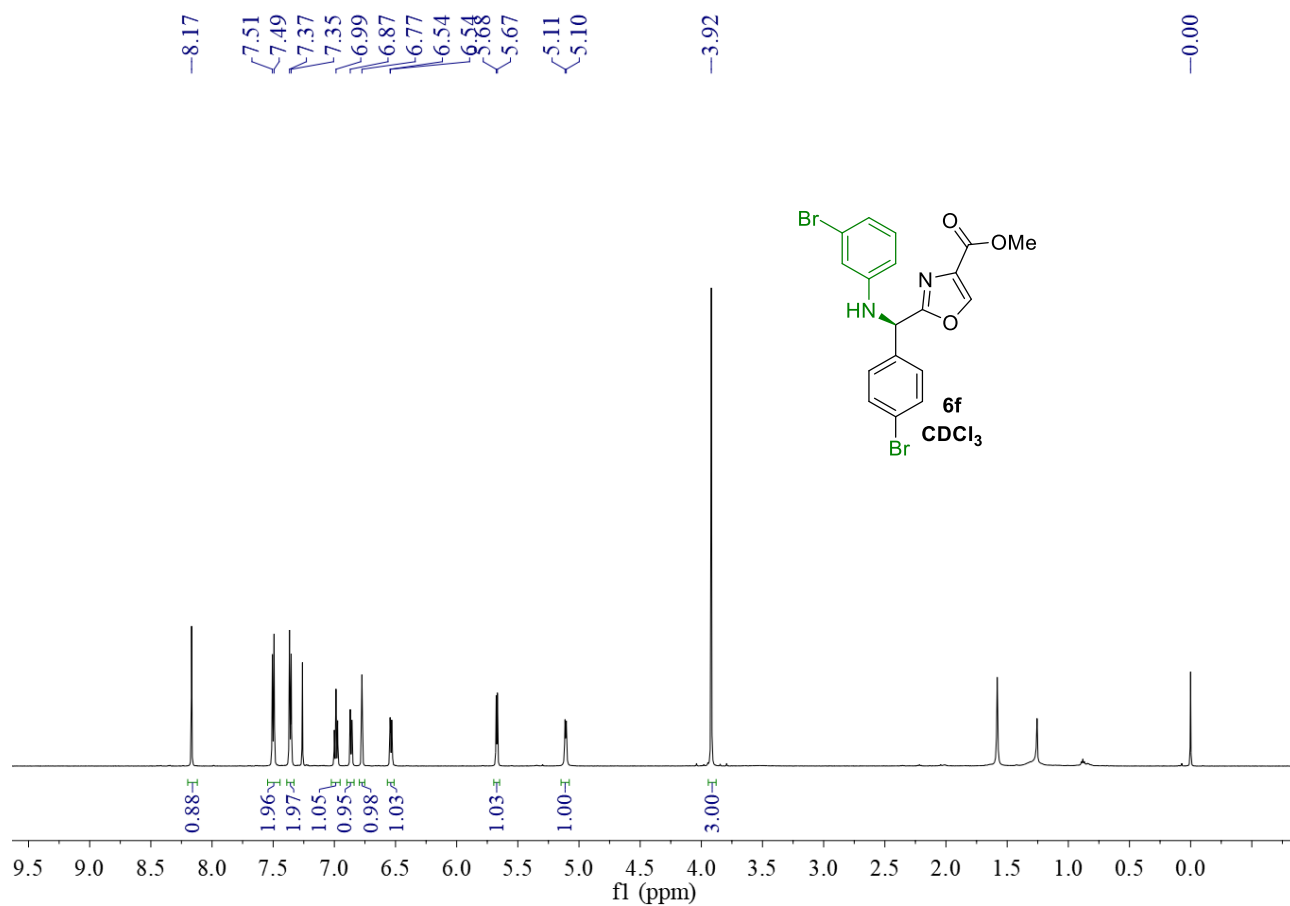


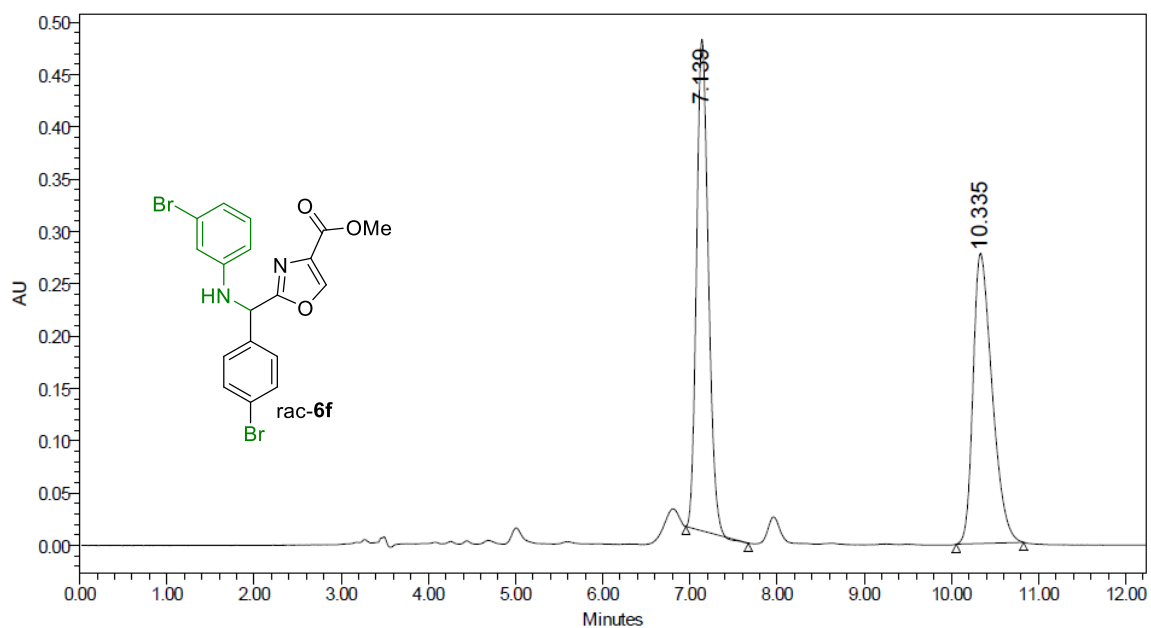


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.486	Unknown	2771834	49.06	295207	50.84	BV	302	6.273	6.777
2	6.982	Unknown	2877986	50.94	285472	49.16	VV	493	6.777	7.598

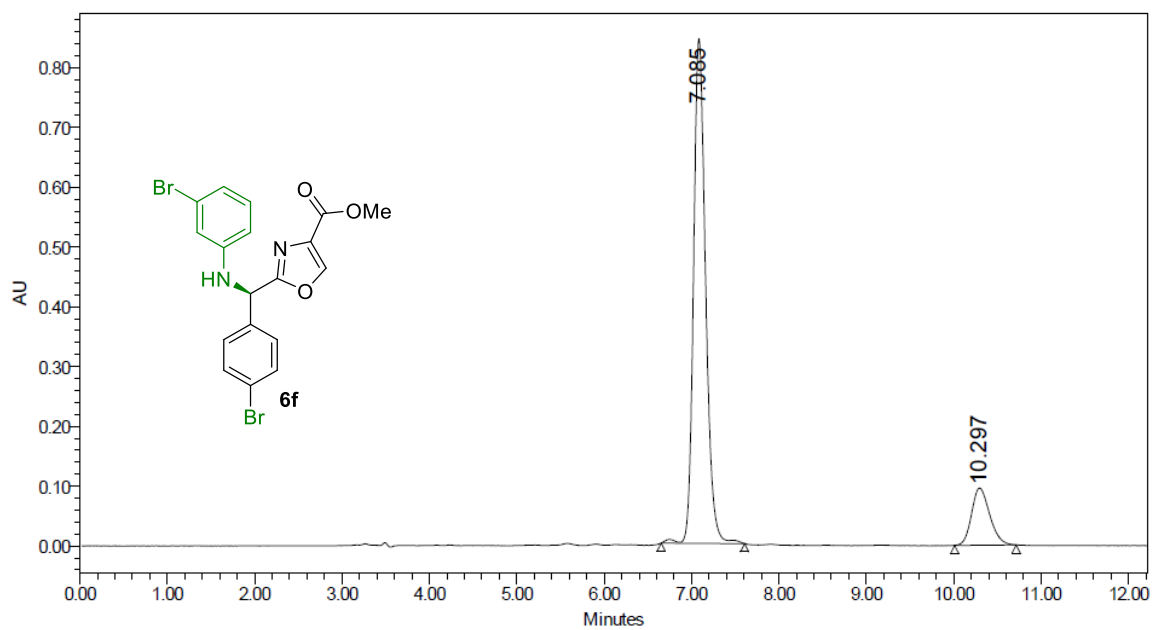


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.492	Unknown	2068294	14.50	223417	15.60	bV	311	6.243	6.762
2	6.972	Unknown	12200559	85.50	1208828	84.40	VV	425	6.762	7.470

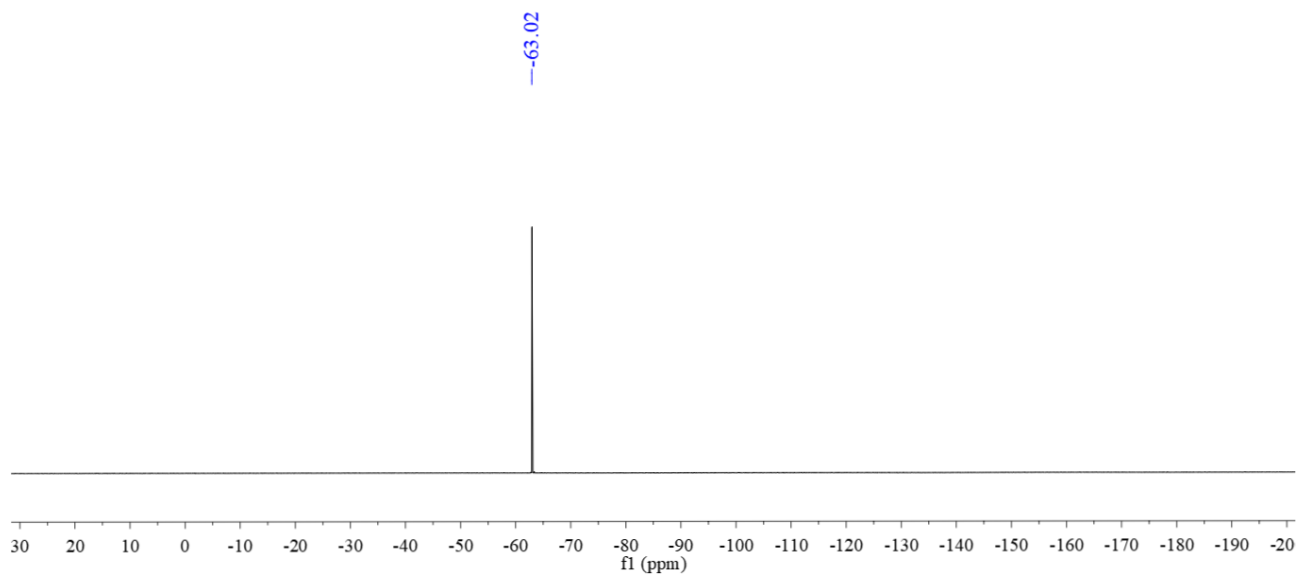
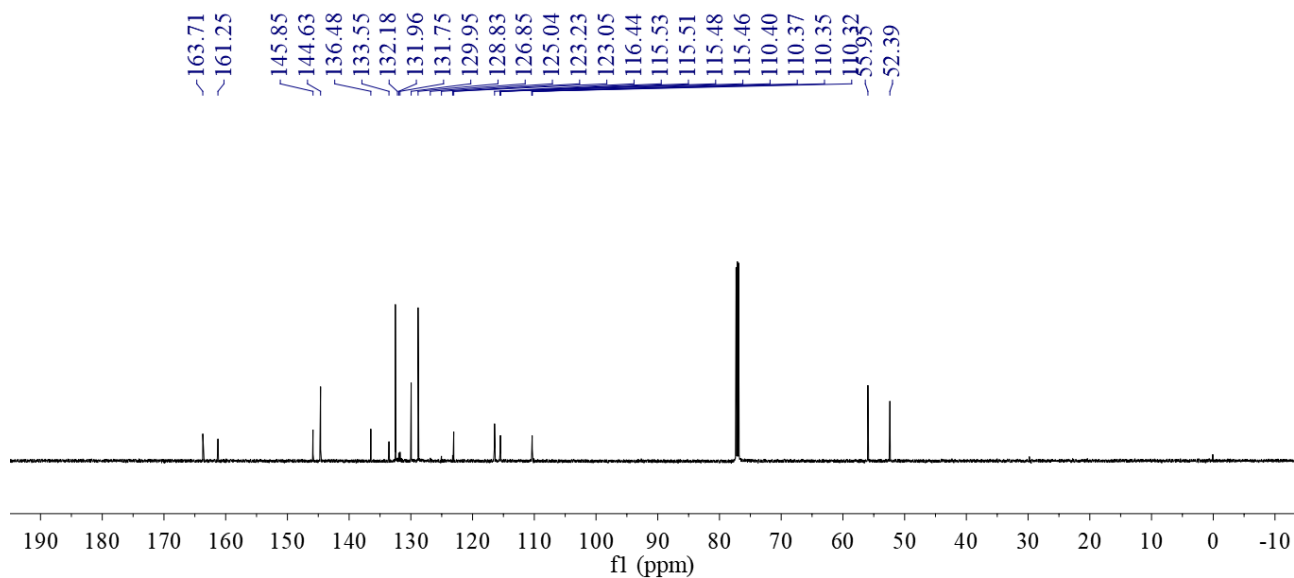
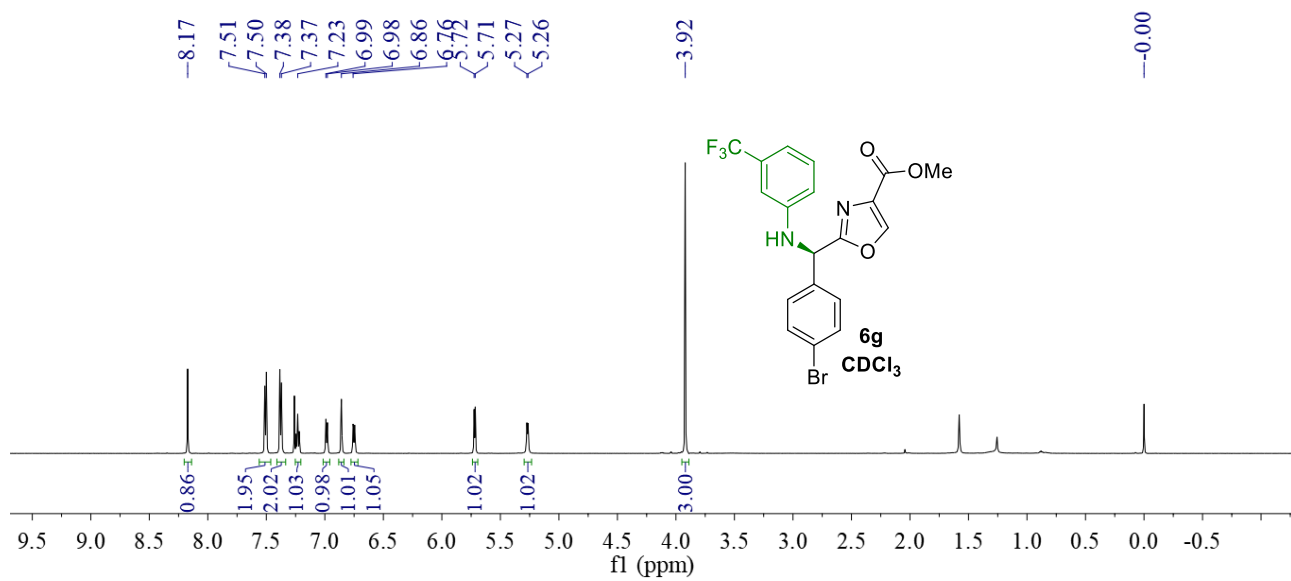


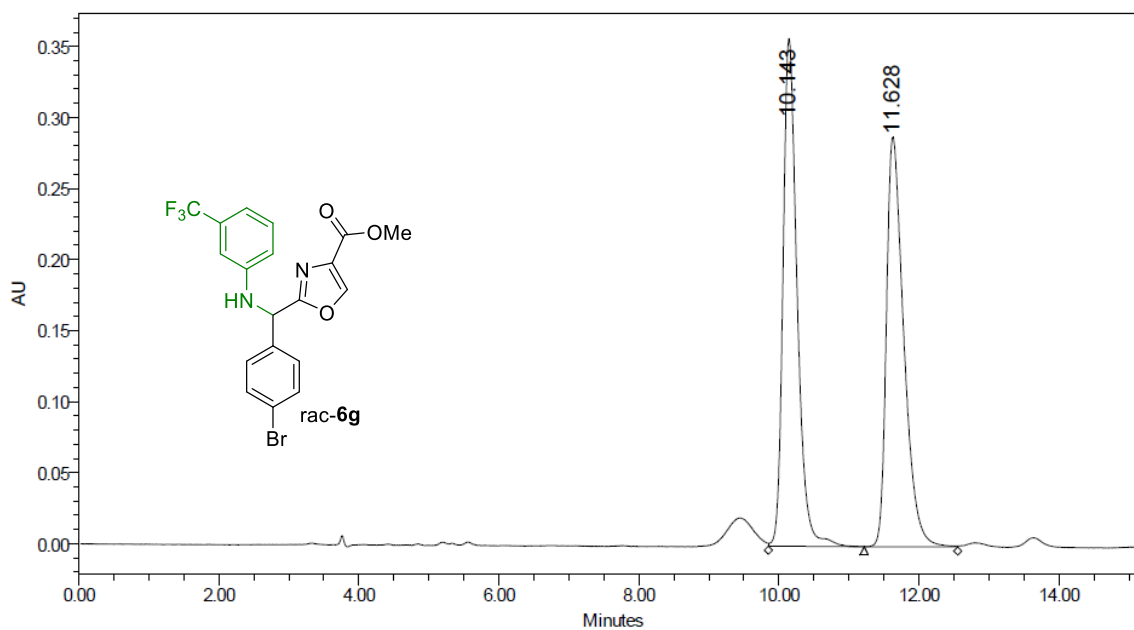


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.139	Unknown	4450754	51.35	469947	62.91	bb	429	6.957	7.672
2	10.335	Unknown	4215913	48.65	277074	37.09	bb	463	10.057	10.828

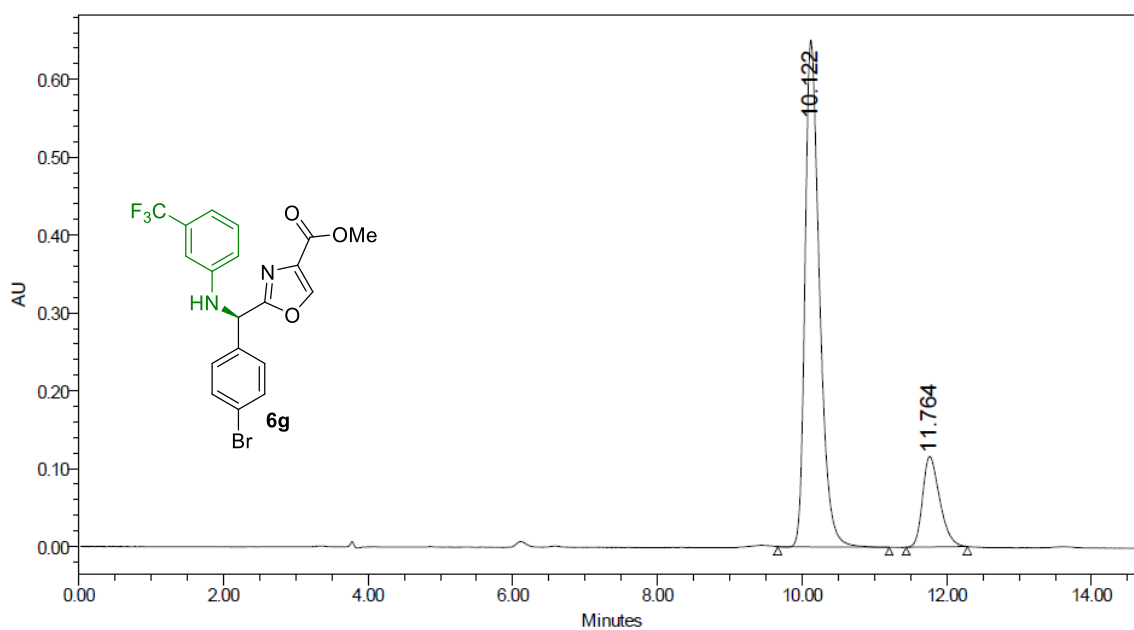


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.085	Unknown	8096127	85.51	844184	89.83	bb	572	6.653	7.607
2	10.297	Unknown	1372140	14.49	95611	10.17	bb	422	10.010	10.713

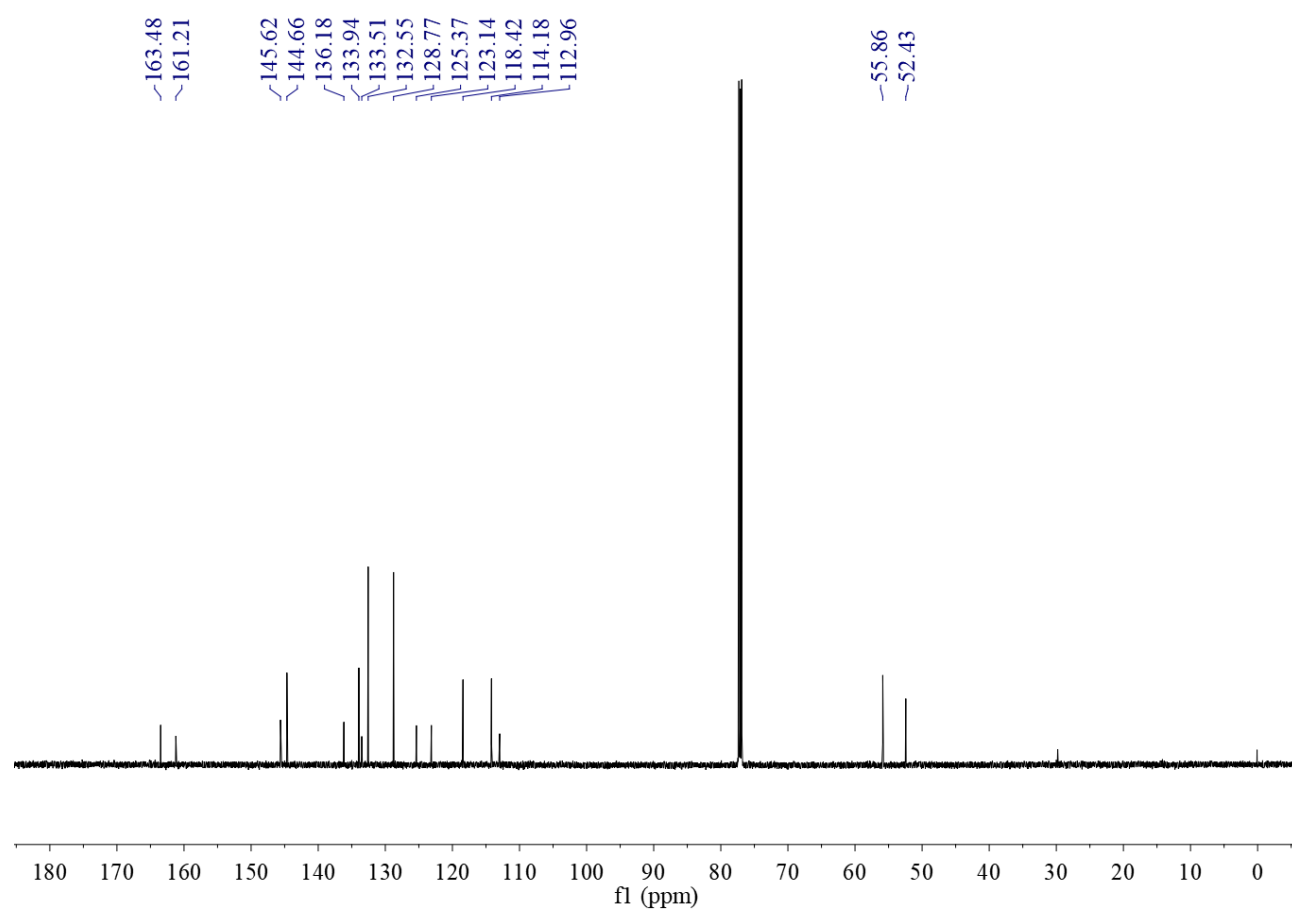
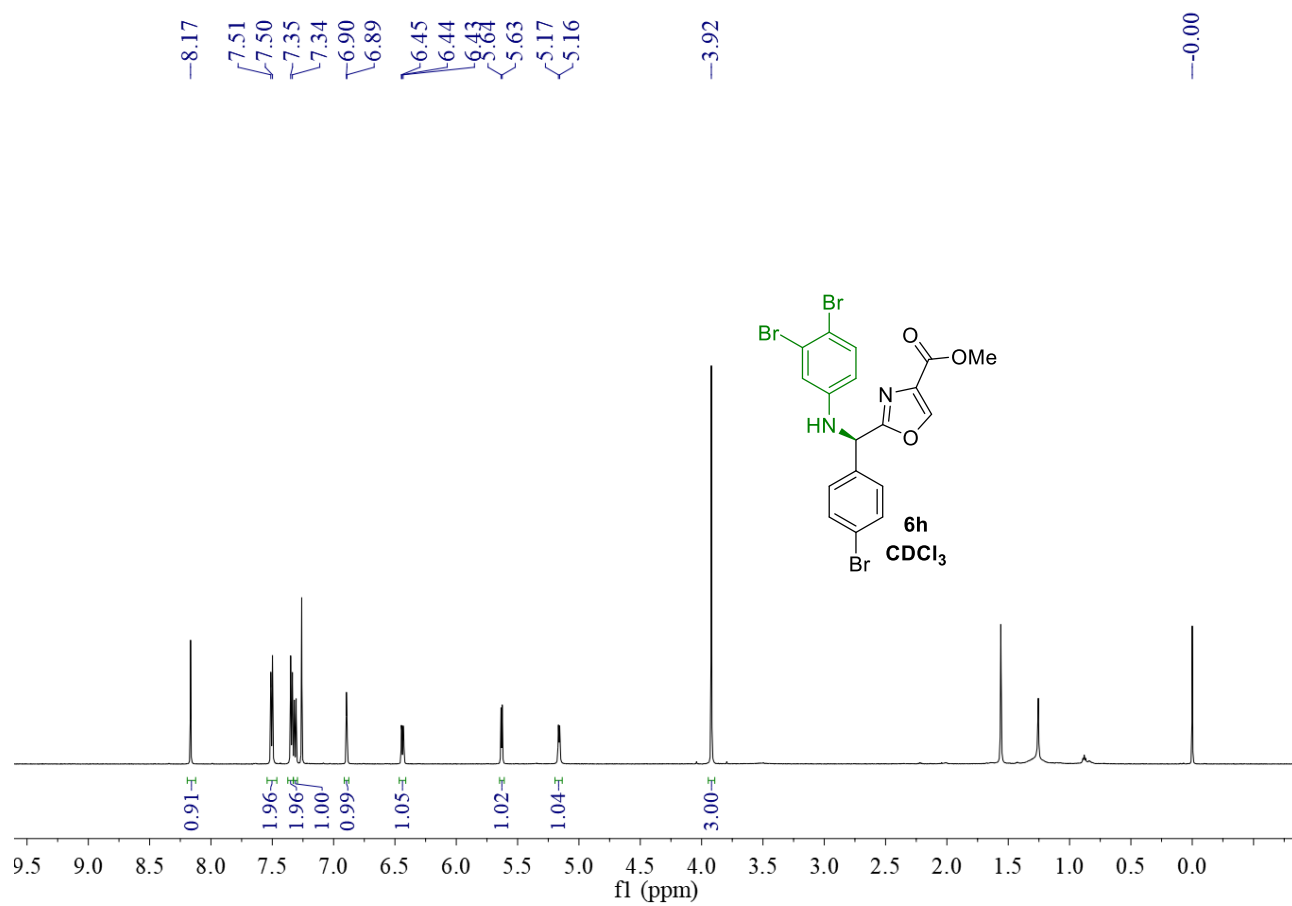


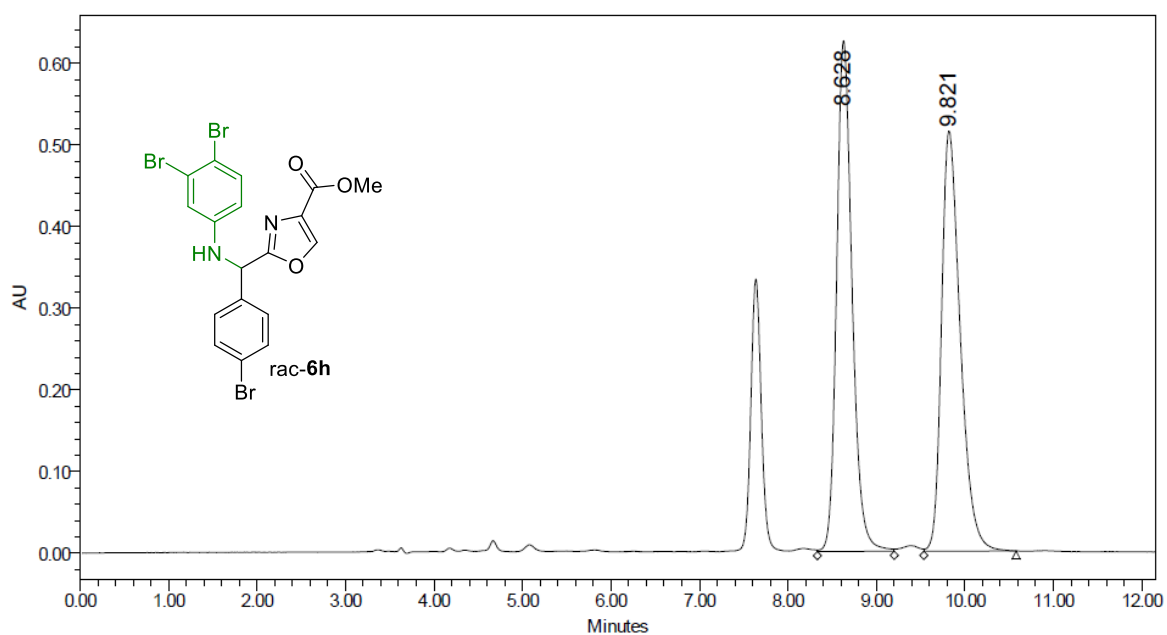


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.143	Unknown	5010725	50.18	357416	55.36	VB	822	9.848	11.218
2	11.628	Unknown	4974166	49.82	288253	44.64	BV	801	11.218	12.553

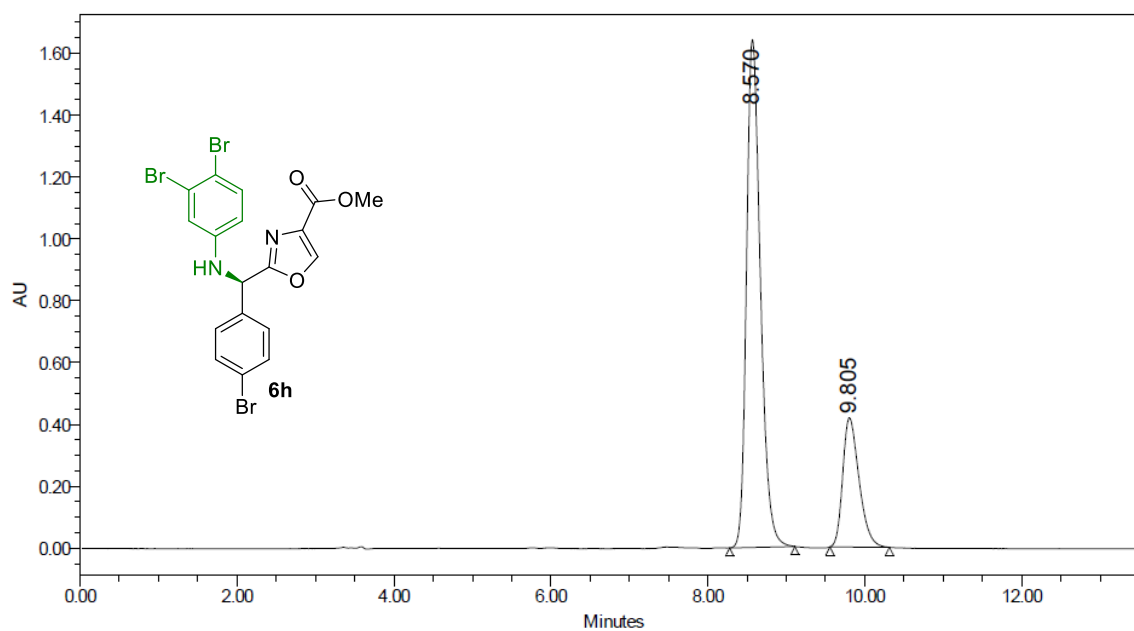


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.122	Unknown	9046425	82.52	650737	84.85	bb	923	9.665	11.203
2	11.764	Unknown	1916779	17.48	116216	15.15	Bb	508	11.438	12.285

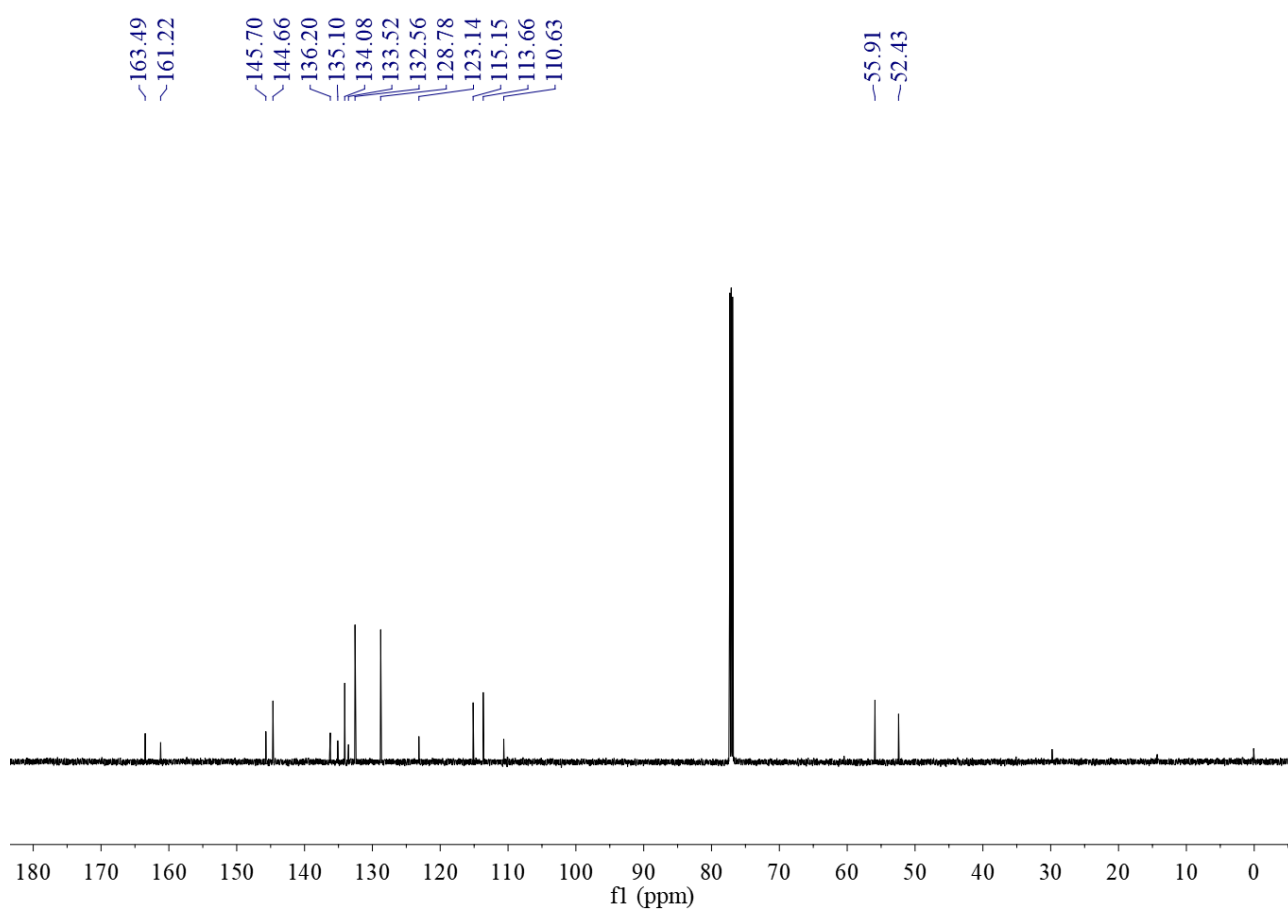
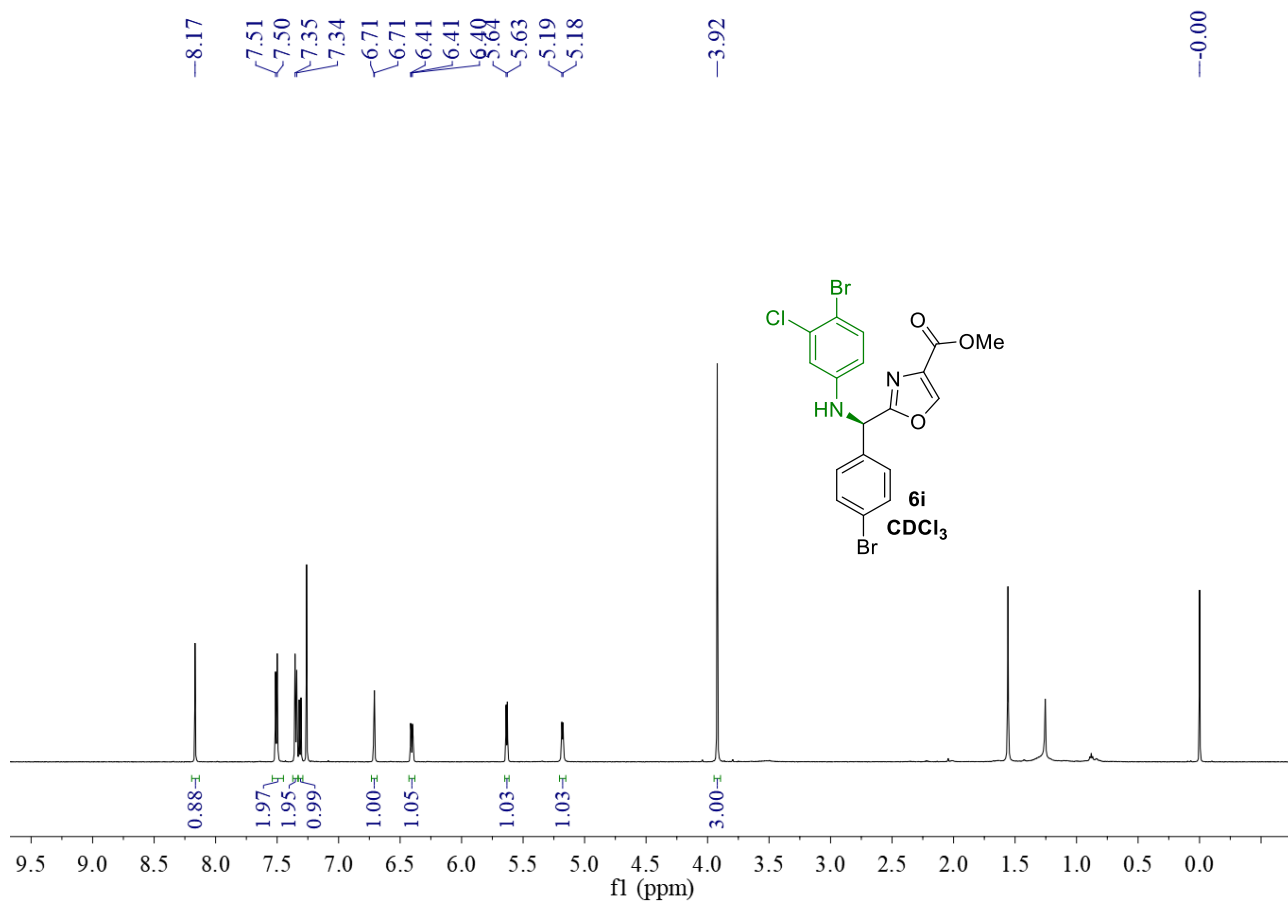


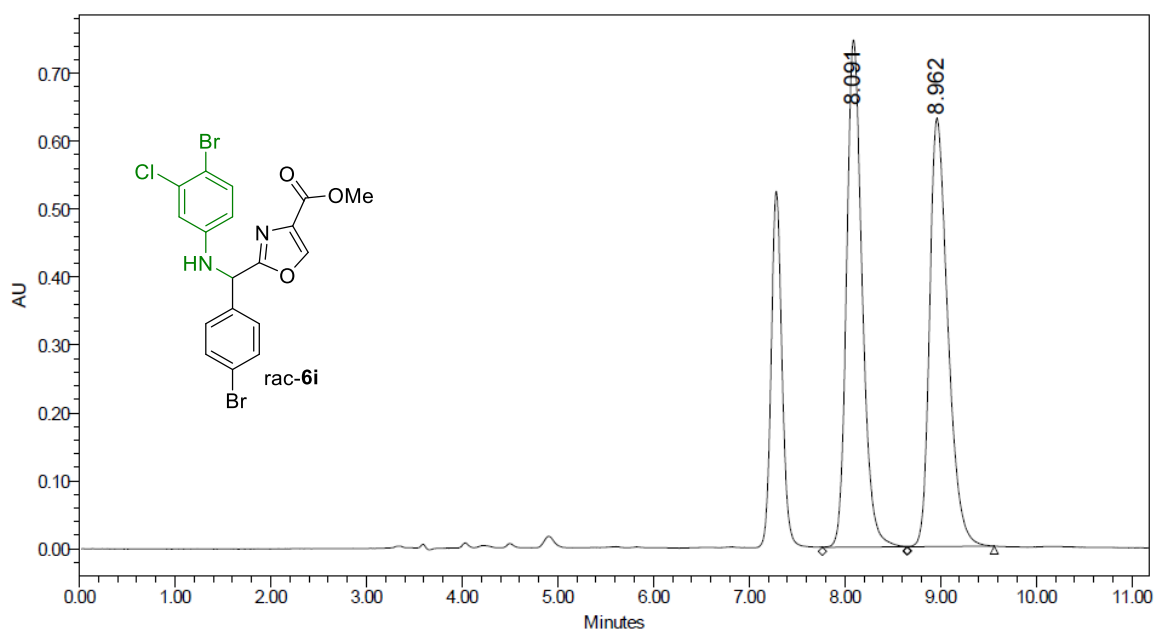


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.628	Unknown	7609185	50.12	625375	54.88	VV	521	8.332	9.200
2	9.821	Unknown	7572540	49.88	514174	45.12	VB	626	9.535	10.578

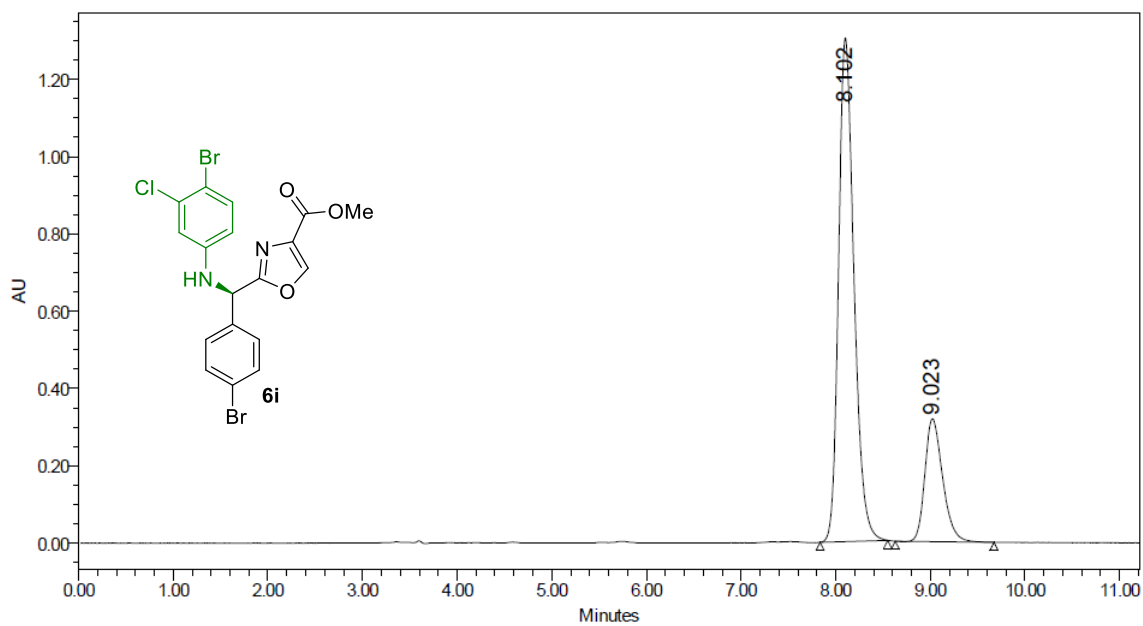


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.570	Unknown	20247277	77.01	1640850	79.69	bb	499	8.278	9.110
2	9.805	Unknown	6043951	22.99	418227	20.31	bb	455	9.557	10.315

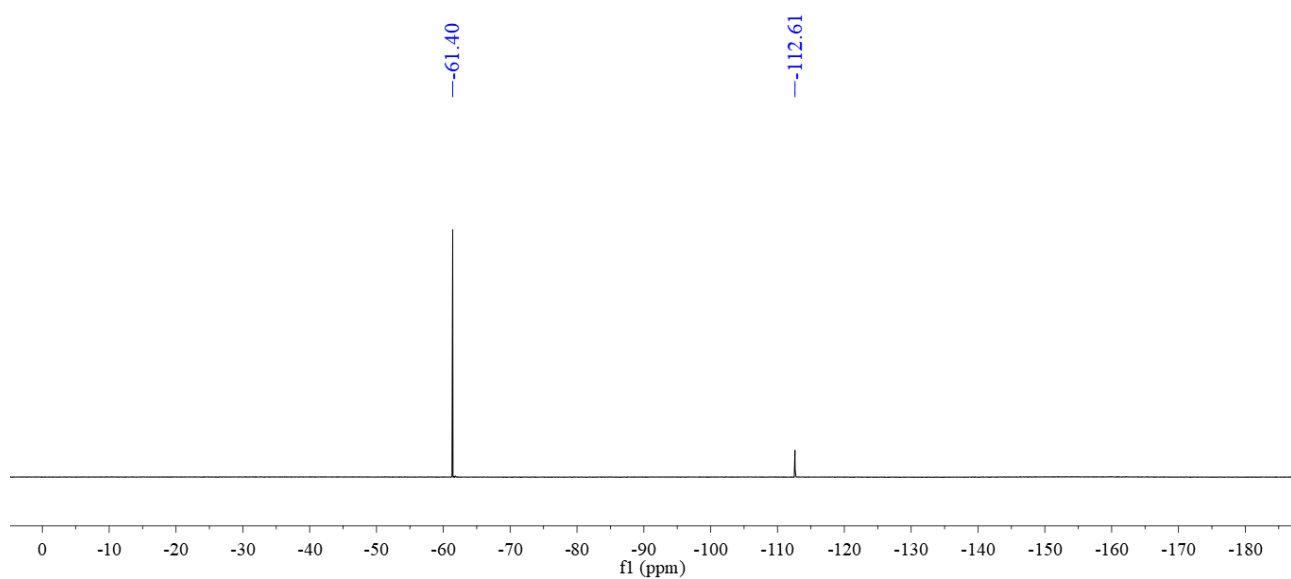
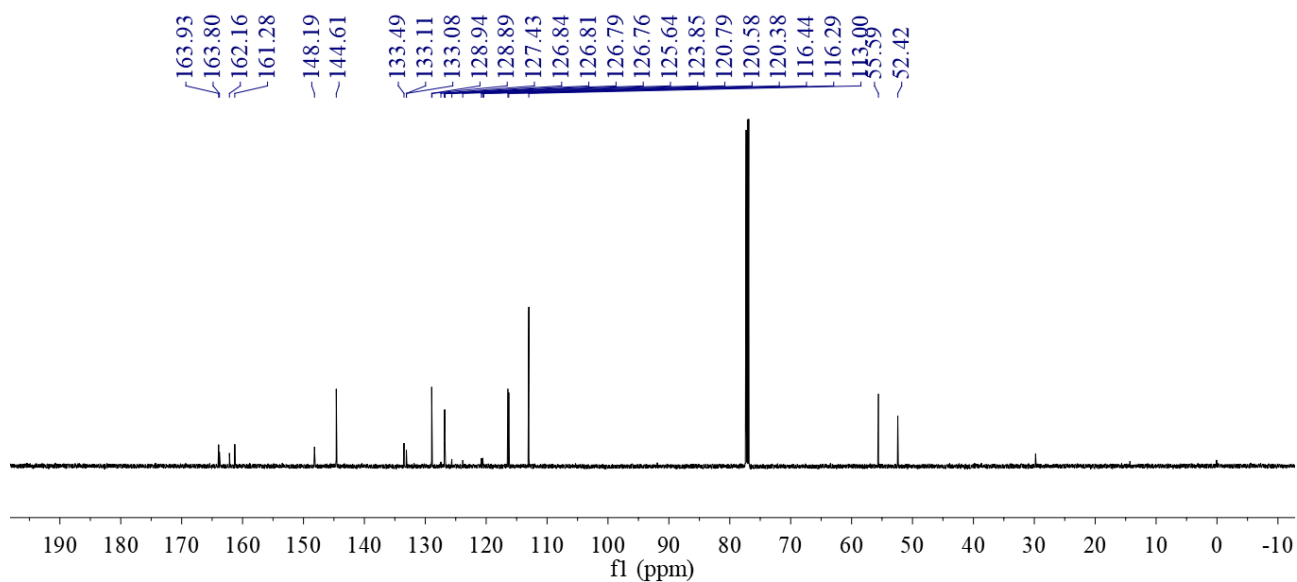
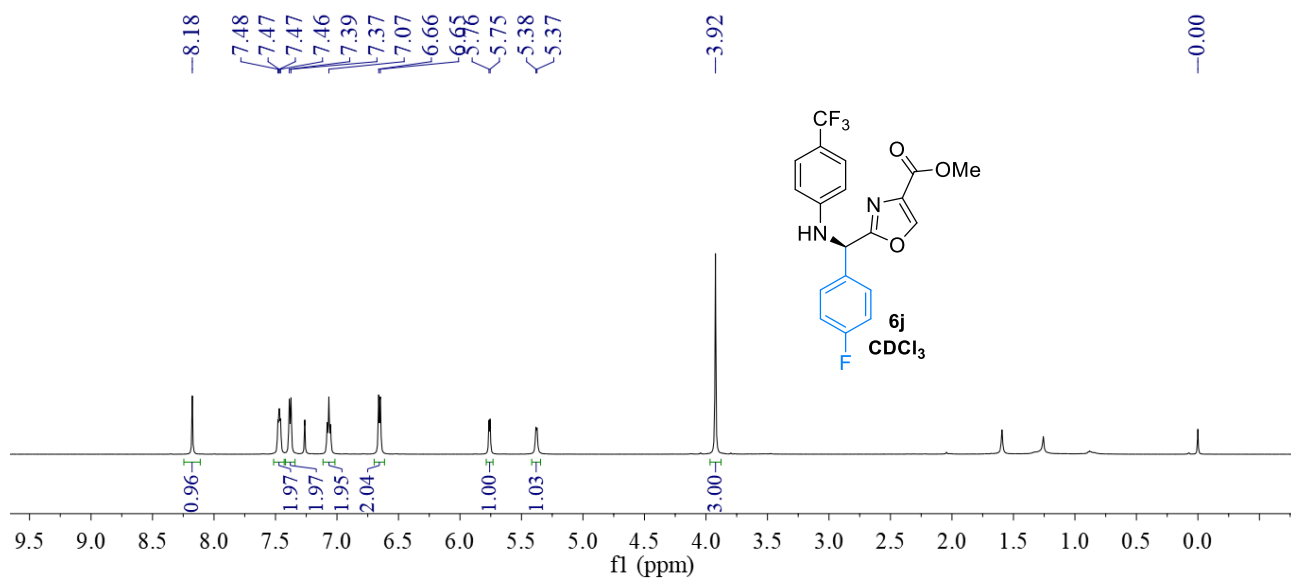


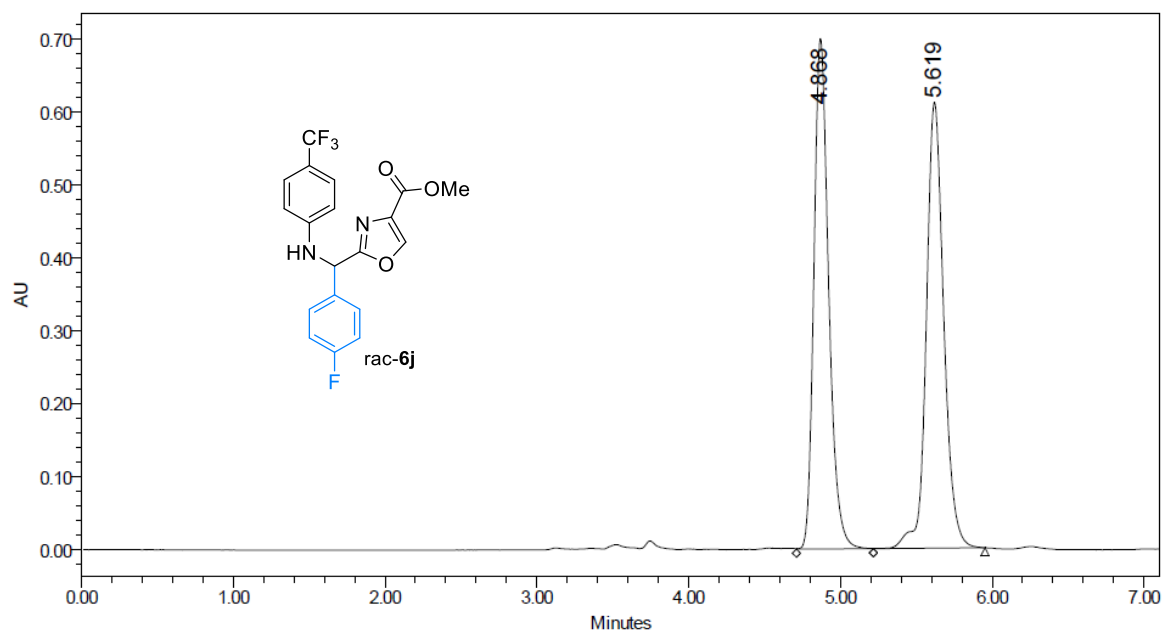


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.091	Unknown	8463046	50.37	746180	54.22	VV	532	7.765	8.652
2	8.962	Unknown	8340327	49.63	630111	45.78	VB	546	8.652	9.562

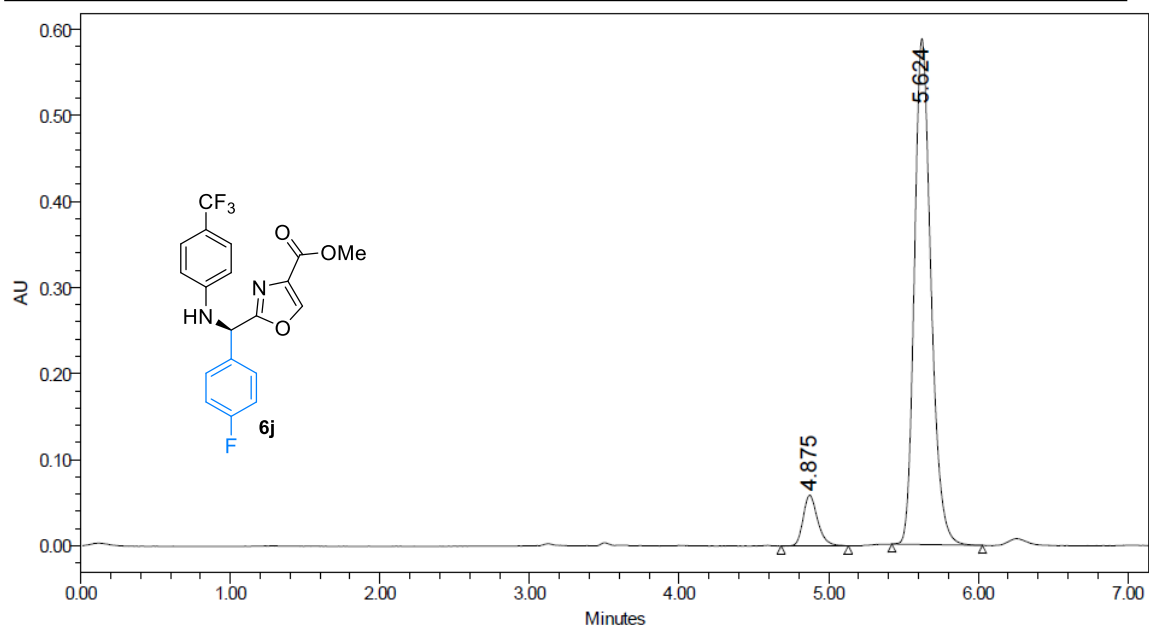


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.102	Unknown	14732193	78.00	1303208	80.39	bb	429	7.835	8.550
2	9.023	Unknown	4154235	22.00	317980	19.61	bb	626	8.630	9.673

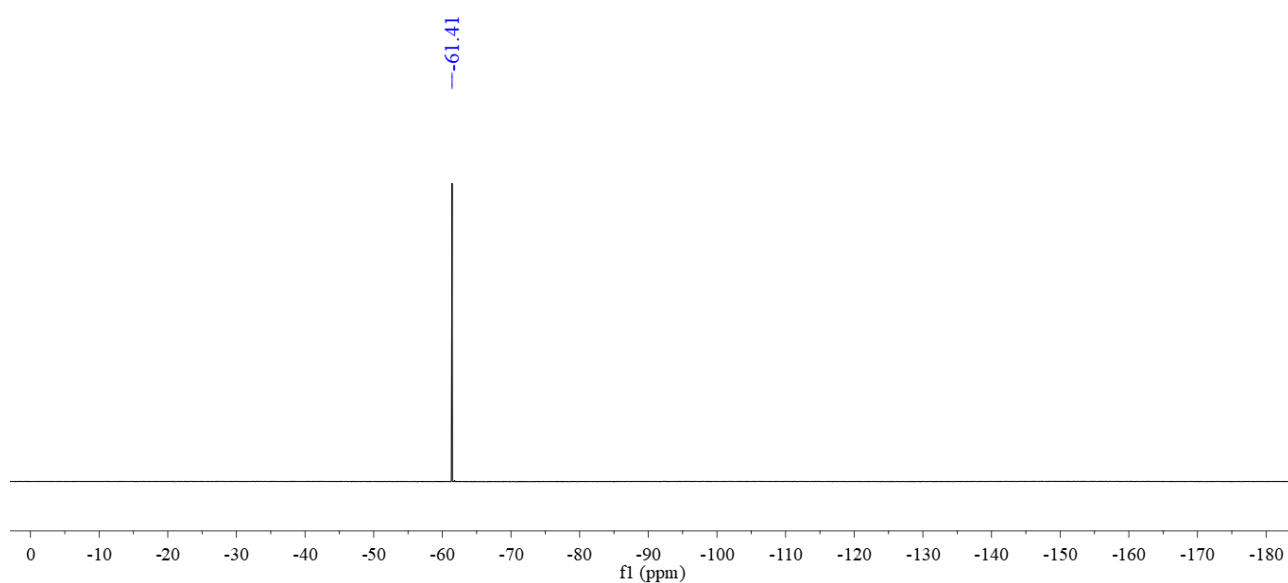
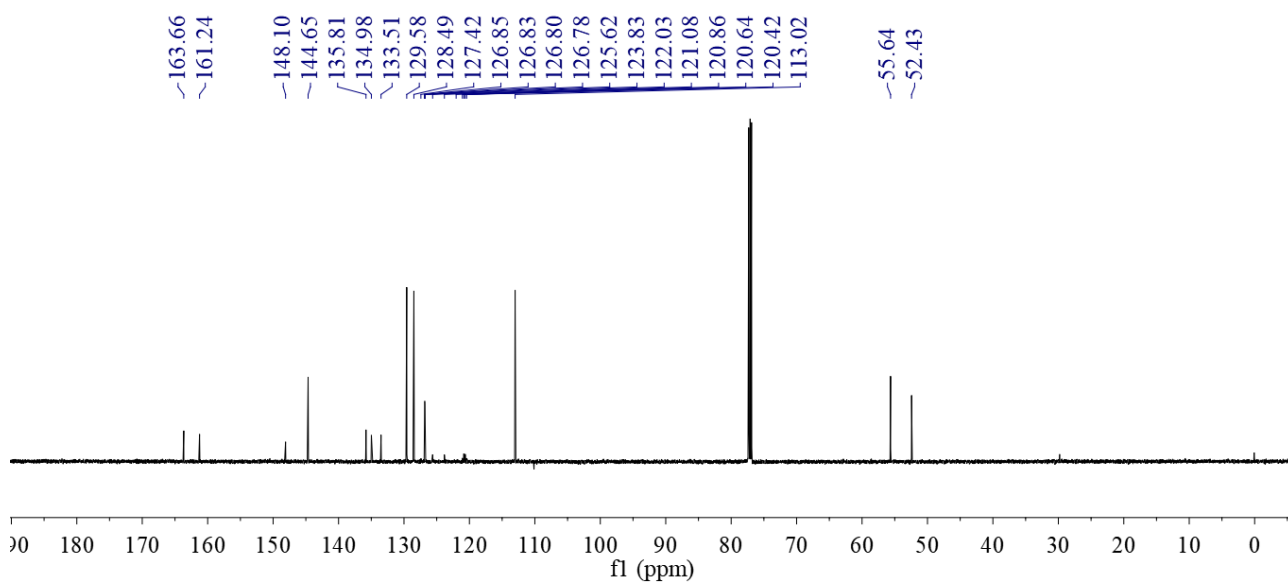
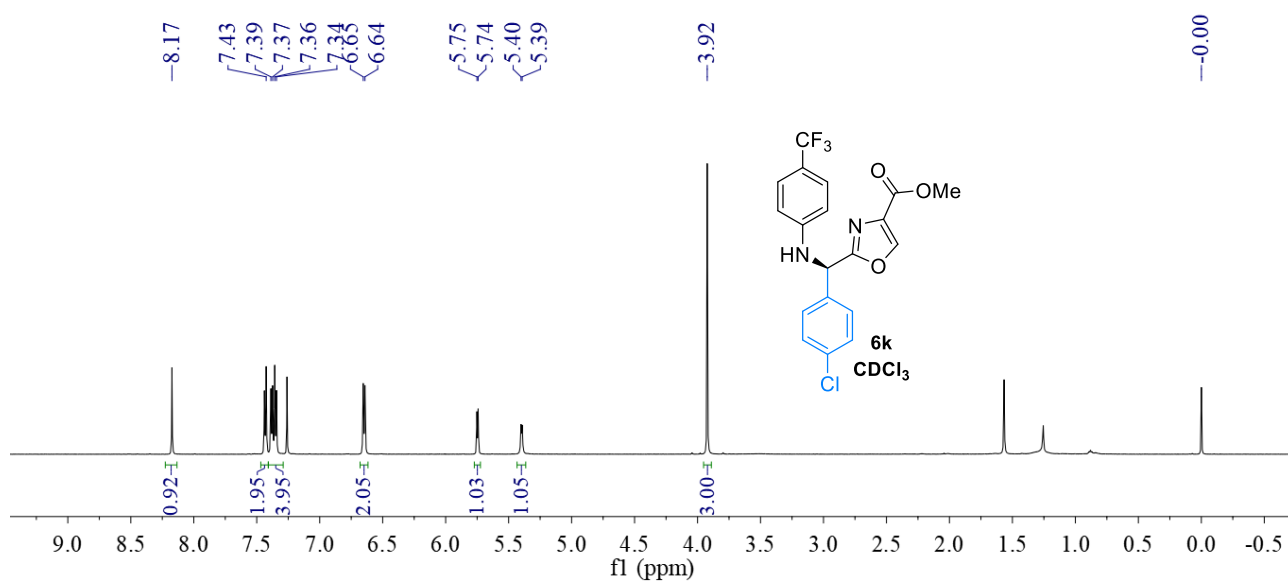


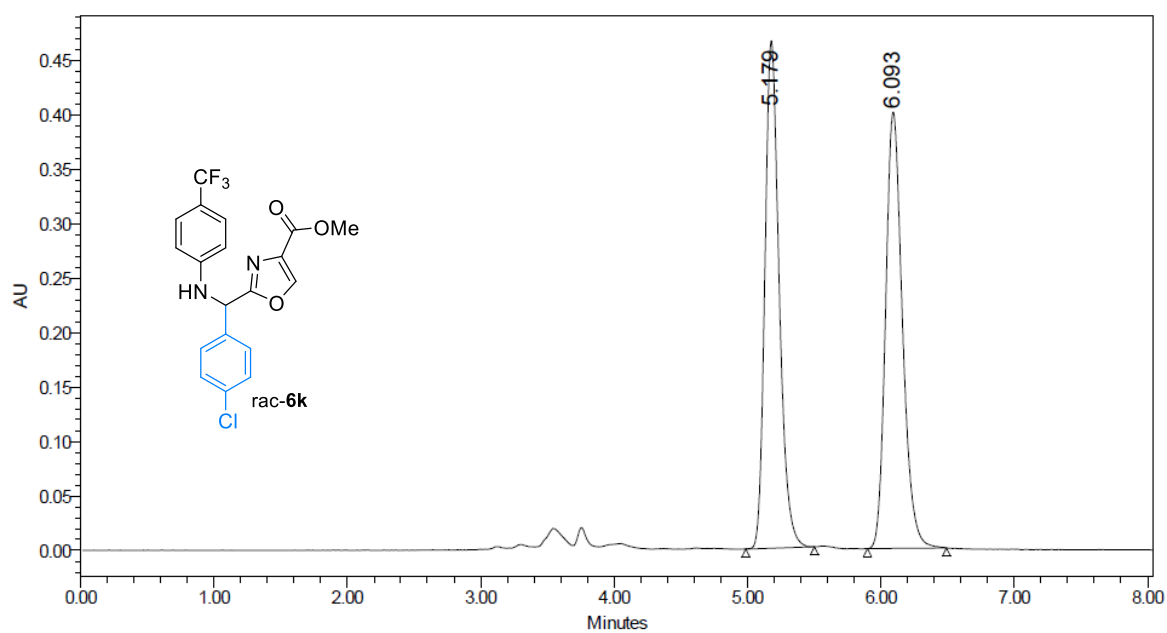


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	4.868	Unknown	4733277	49.17	699925	53.36	VV	304	4.710	5.217
2	5.619	Unknown	4893203	50.83	611701	46.64	VB	441	5.217	5.952

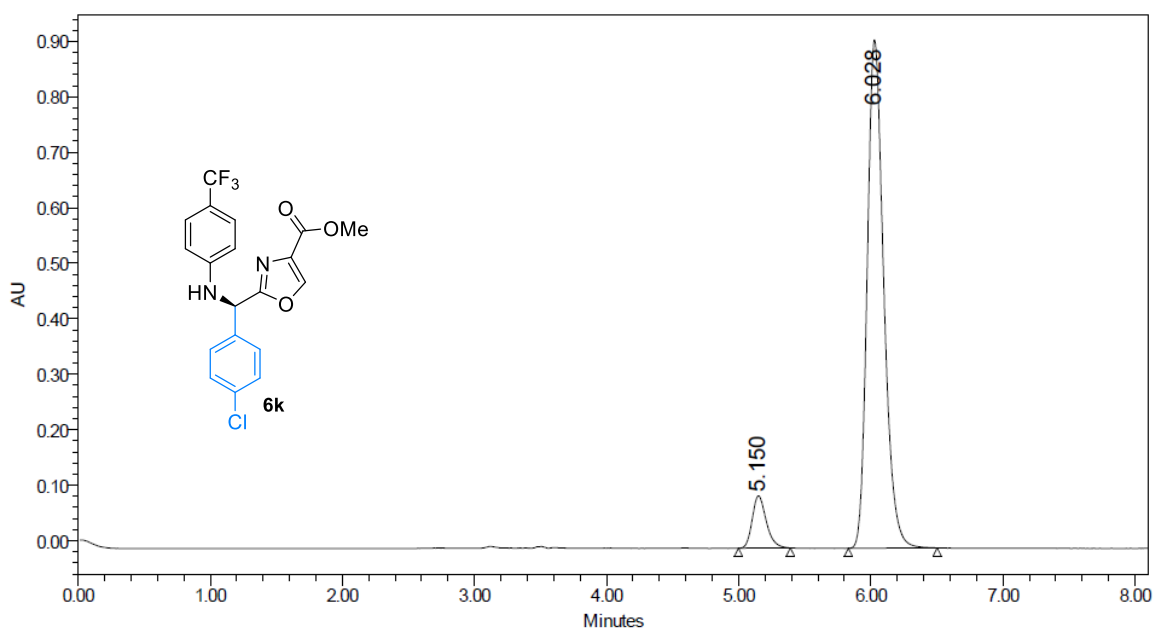


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	4.875	Unknown	393590	7.99	58793	9.09	bb	269	4.683	5.132
2	5.624	Unknown	4530544	92.01	587767	90.91	bb	363	5.423	6.028

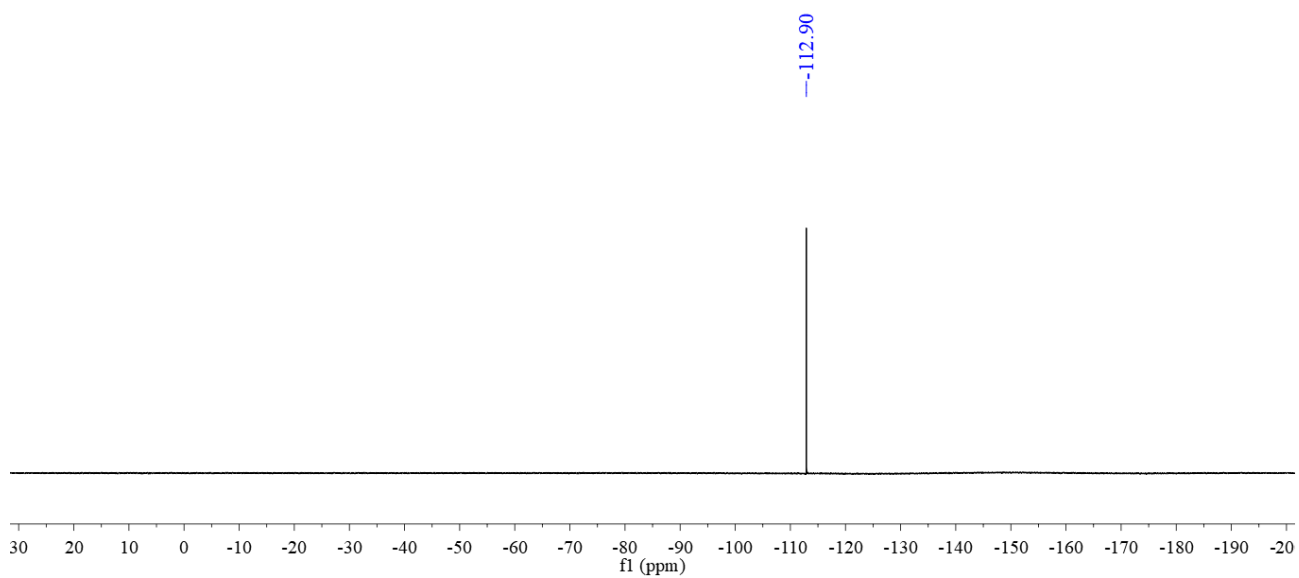
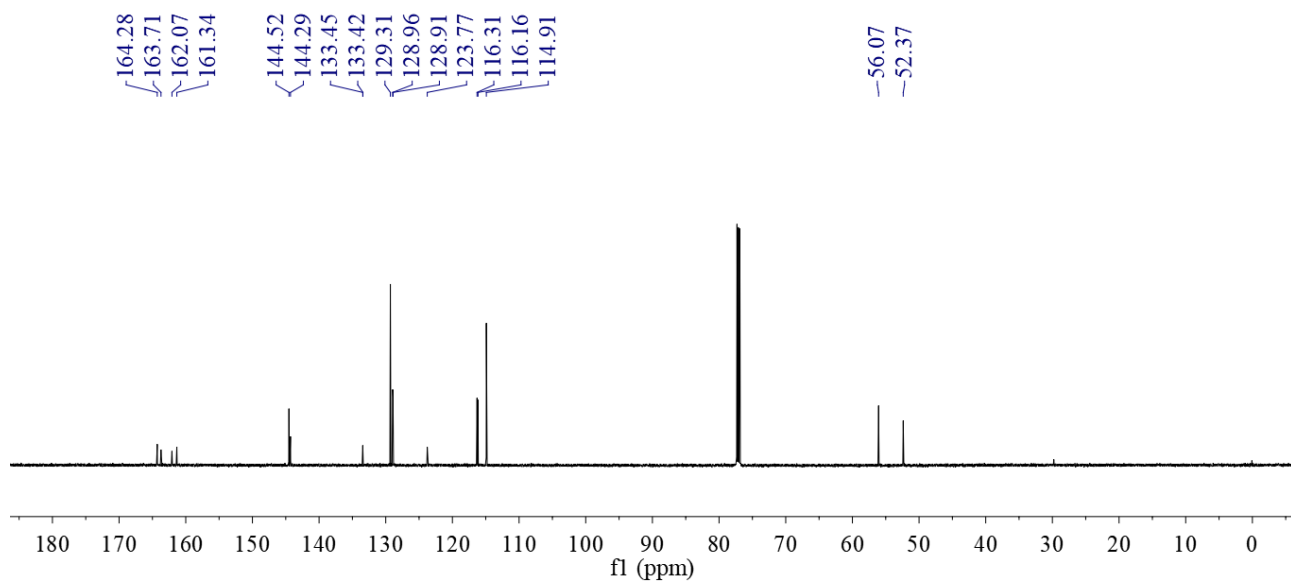
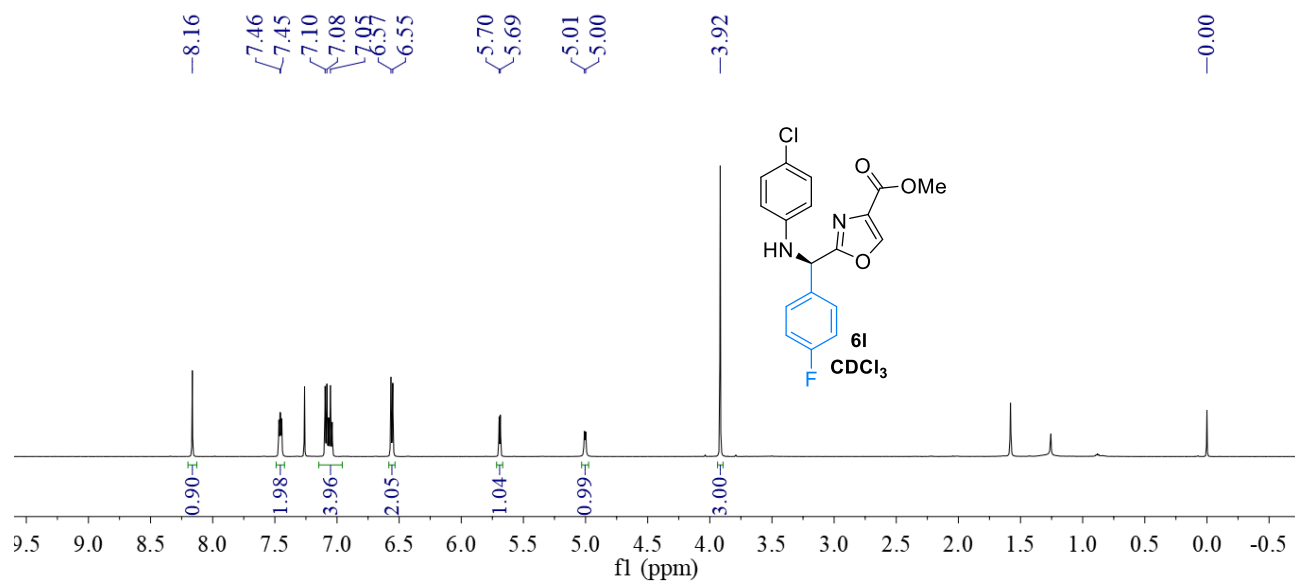


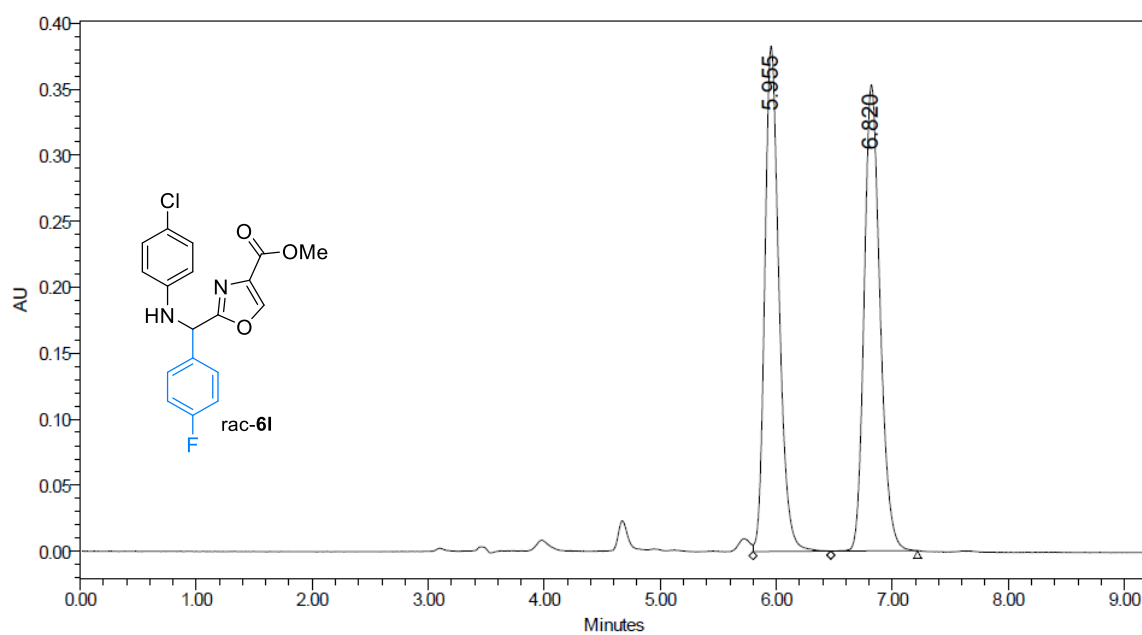


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.179	Unknown	3468611	49.68	465859	53.77	BB	308	4.988	5.502
2	6.093	Unknown	3512908	50.32	400592	46.23	BB	355	5.900	6.492

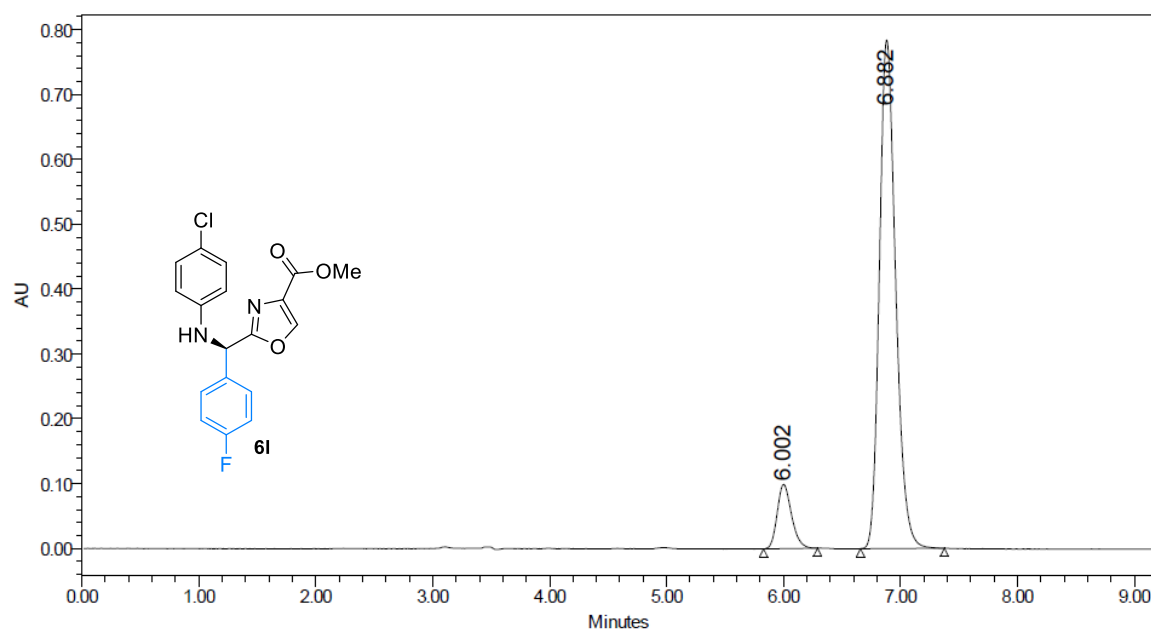


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.150	Unknown	691992	8.00	94181	9.32	bb	236	4.998	5.392
2	6.028	Unknown	7954645	92.00	915912	90.68	BB	403	5.830	6.502

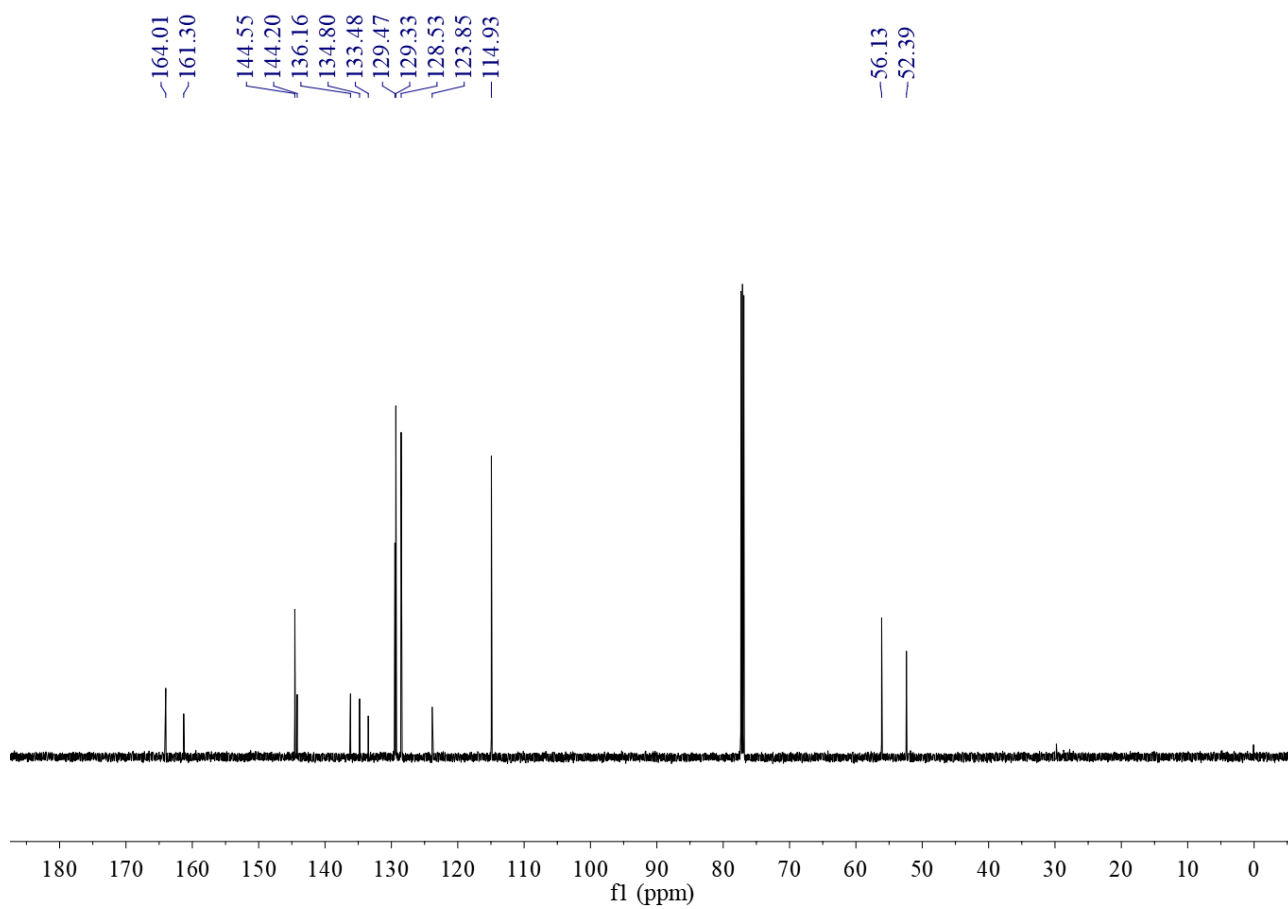
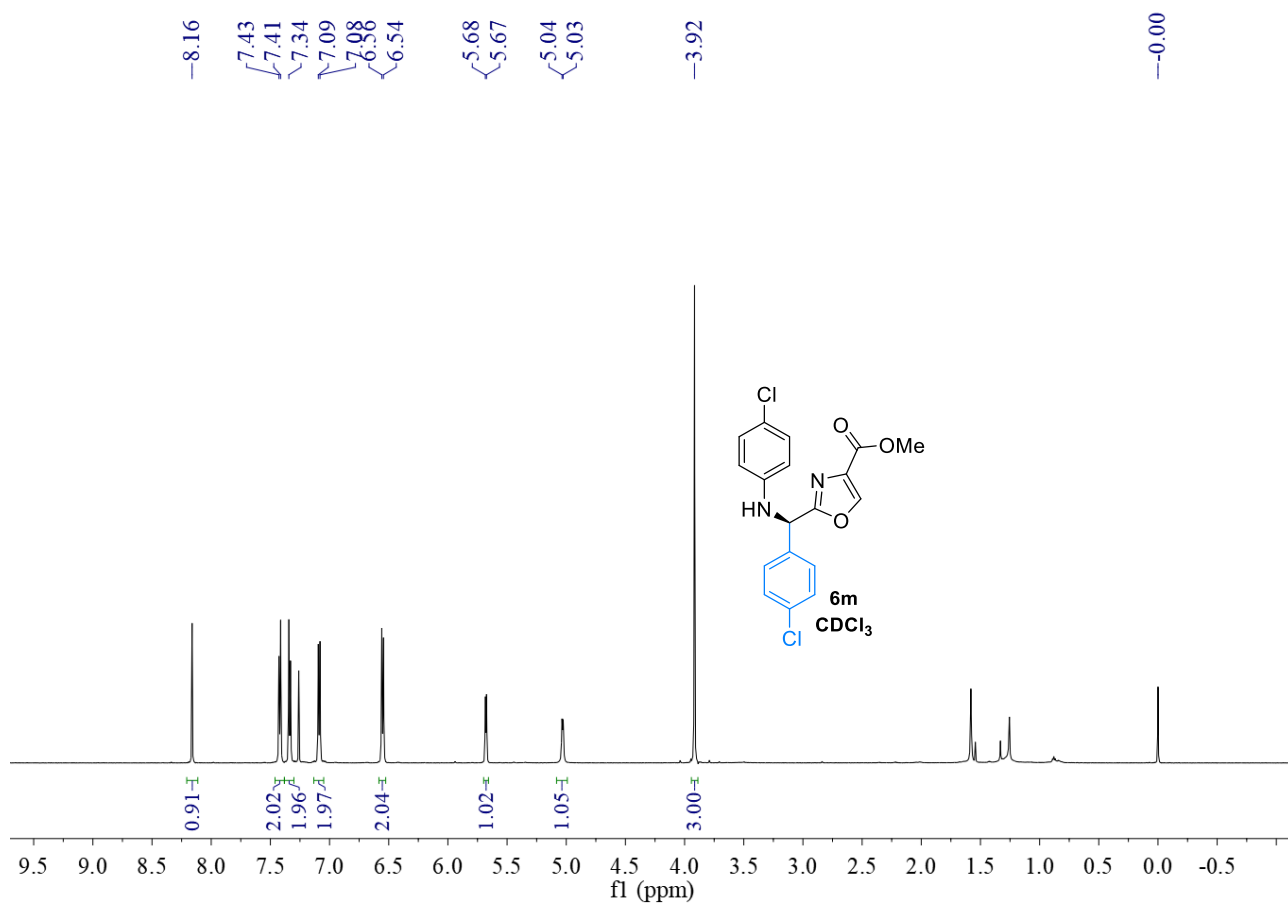


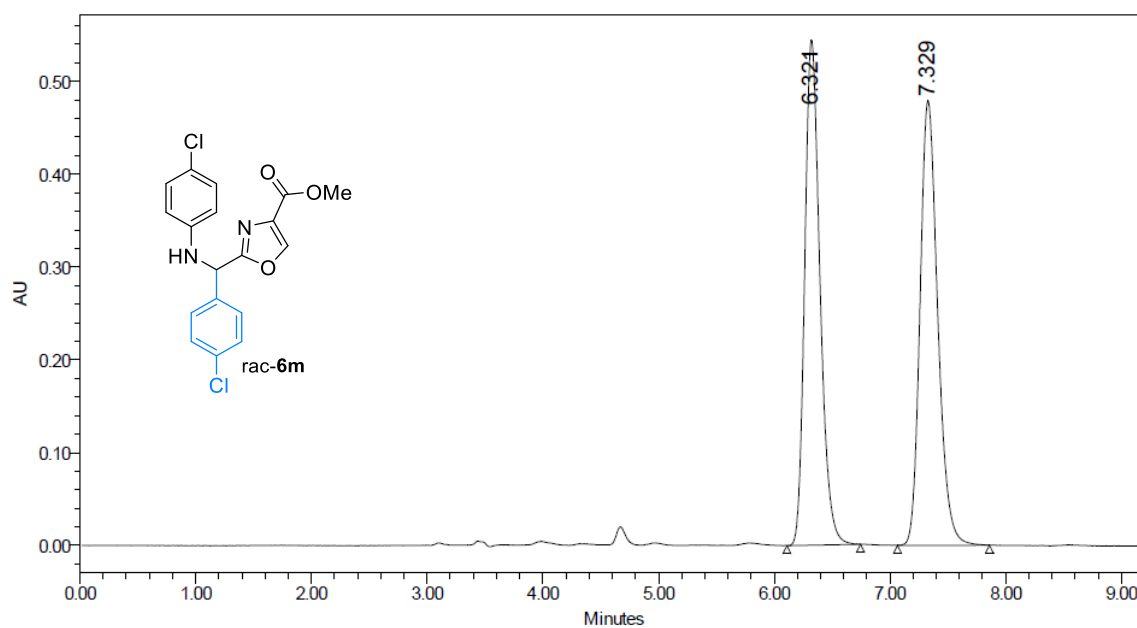


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.955	Unknown	3263993	49.27	382855	52.02	VV	403	5.798	6.470
2	6.820	Unknown	3360158	50.73	353138	47.98	VB	448	6.470	7.217

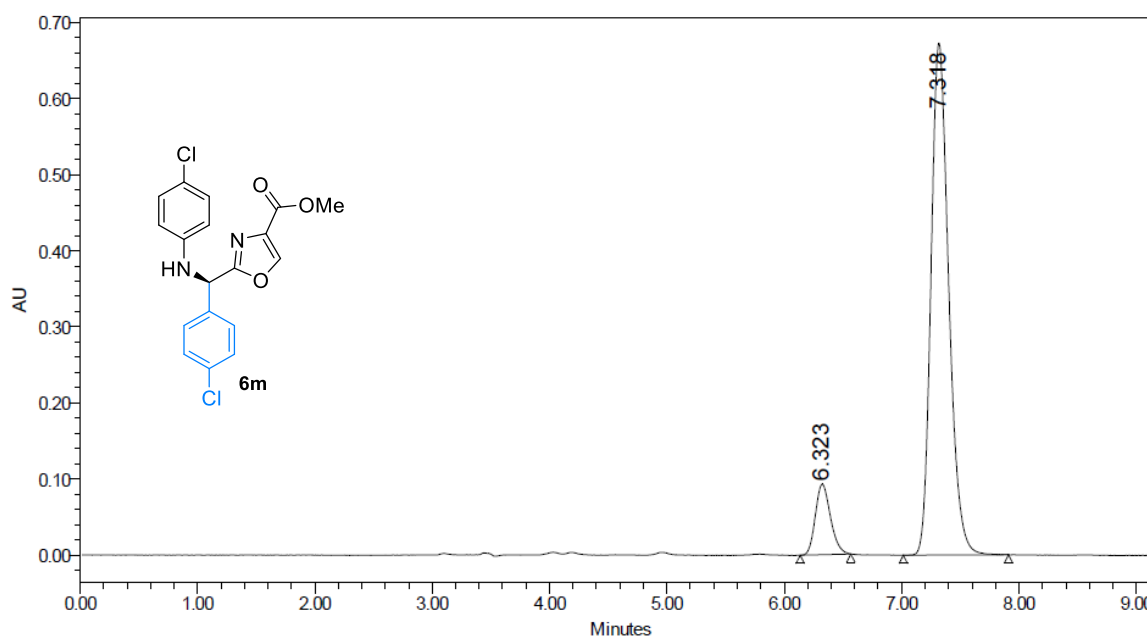


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.002	Unknown	841452	9.99	98748	11.19	BB	277	5.830	6.292
2	6.882	Unknown	7580106	90.01	784056	88.81	BB	431	6.658	7.377

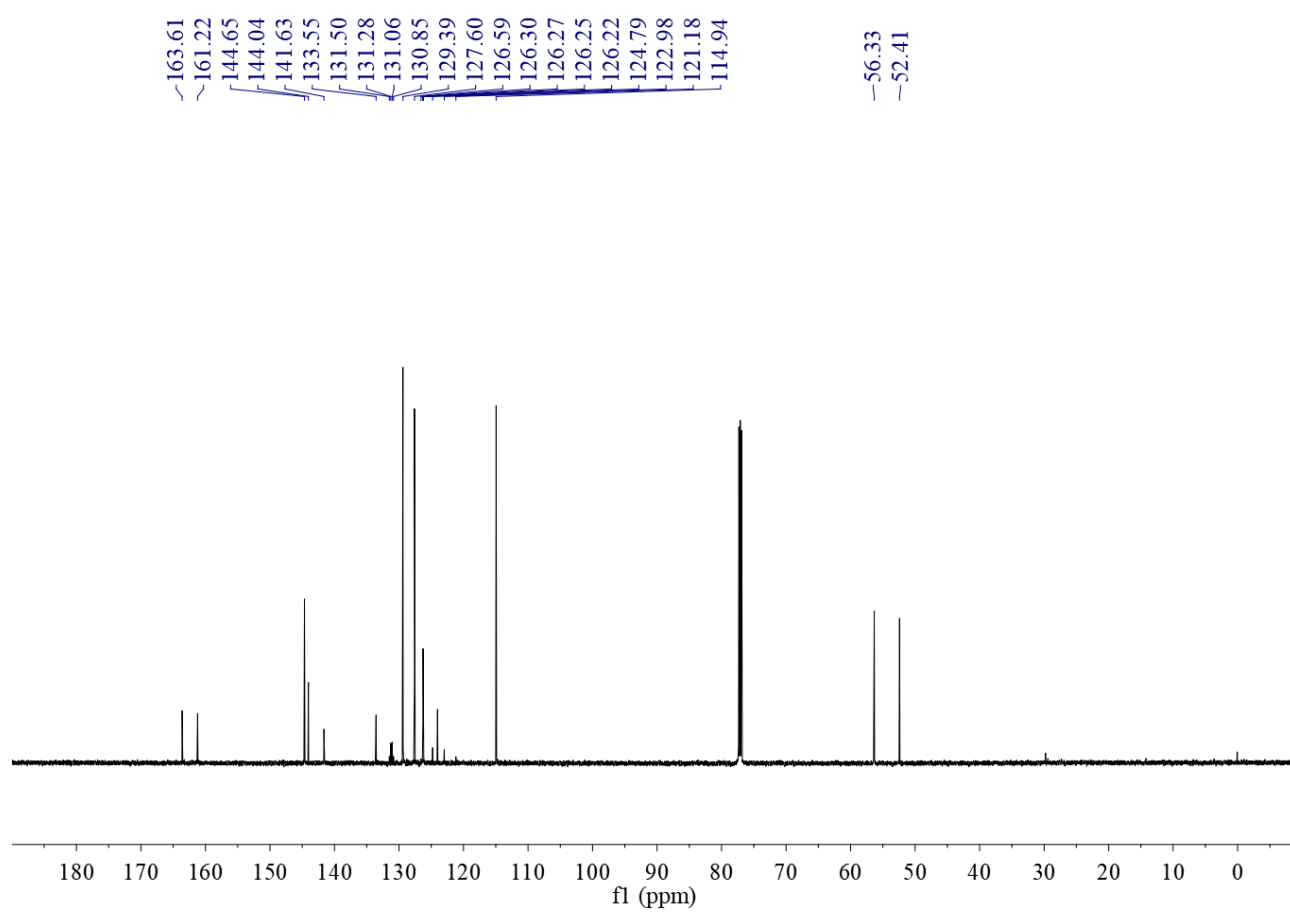
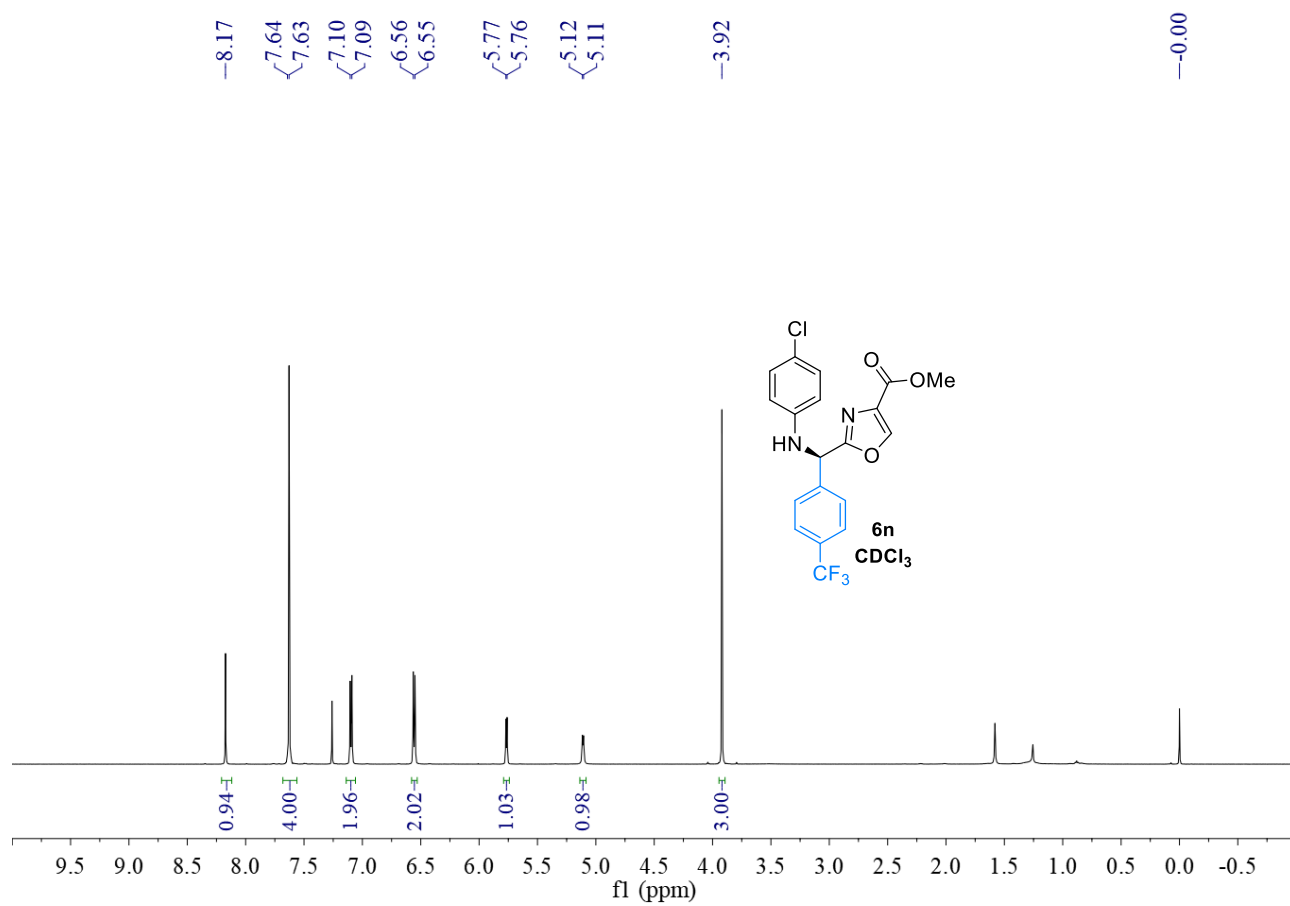


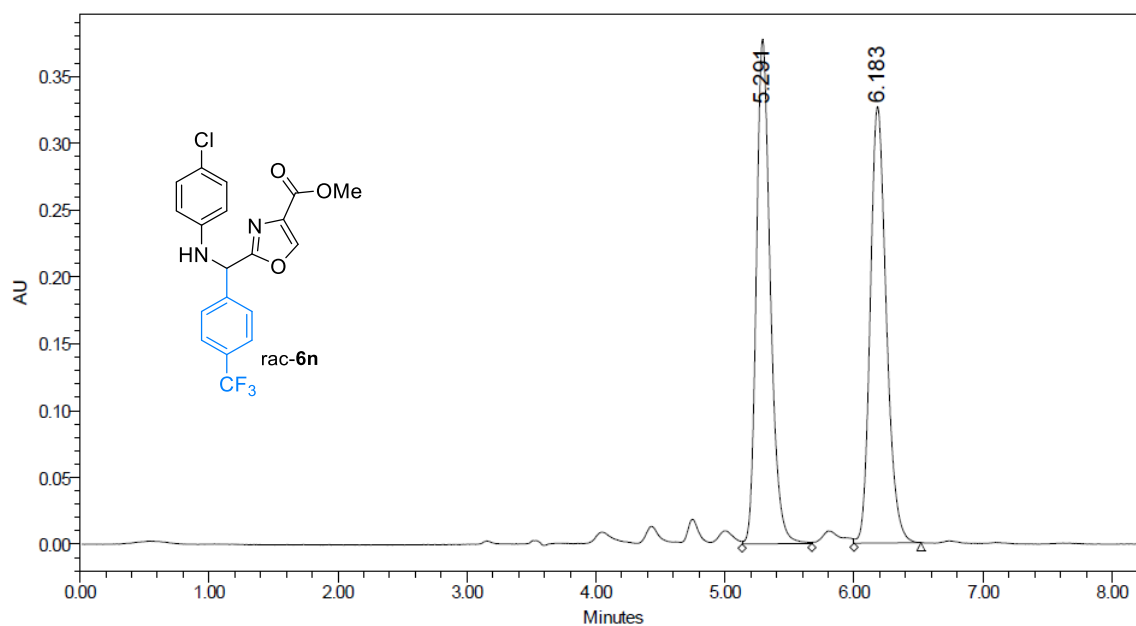


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1	6.321	Unknown	4990044	49.57	544579	53.20	BB	381	6.110	6.745
2	7.329	Unknown	5075954	50.43	479111	46.80	BB	477	7.065	7.860

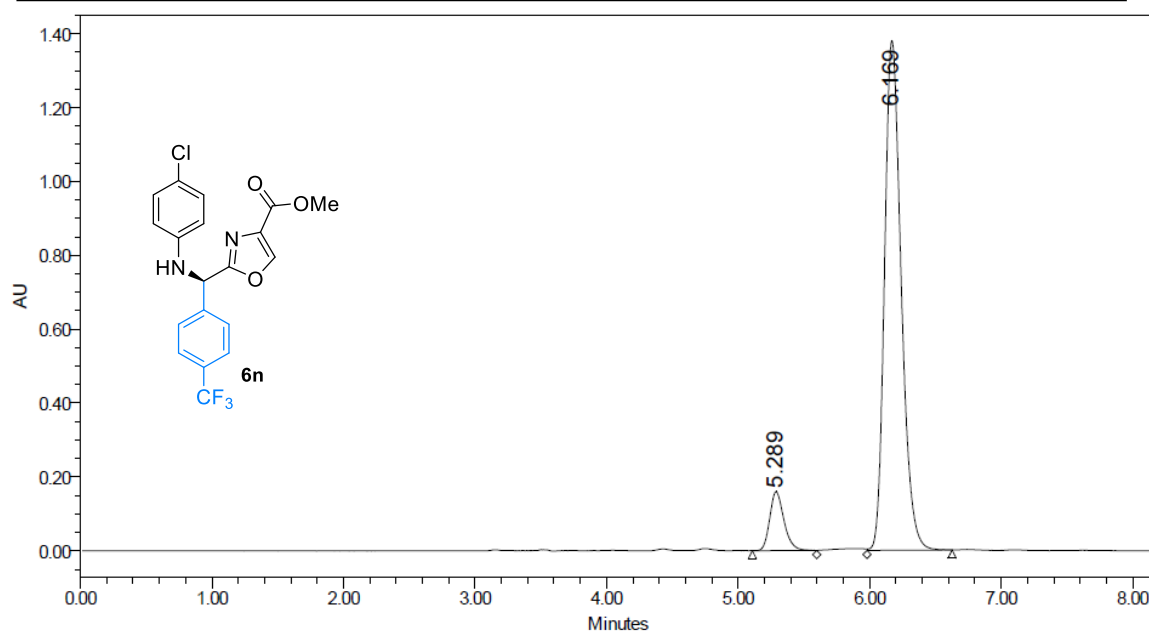


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.323	Unknown	831178	10.54	92735	12.11	bb	259	6.137	6.568
2	7.318	Unknown	7055228	89.46	672795	87.89	bb	538	7.015	7.912

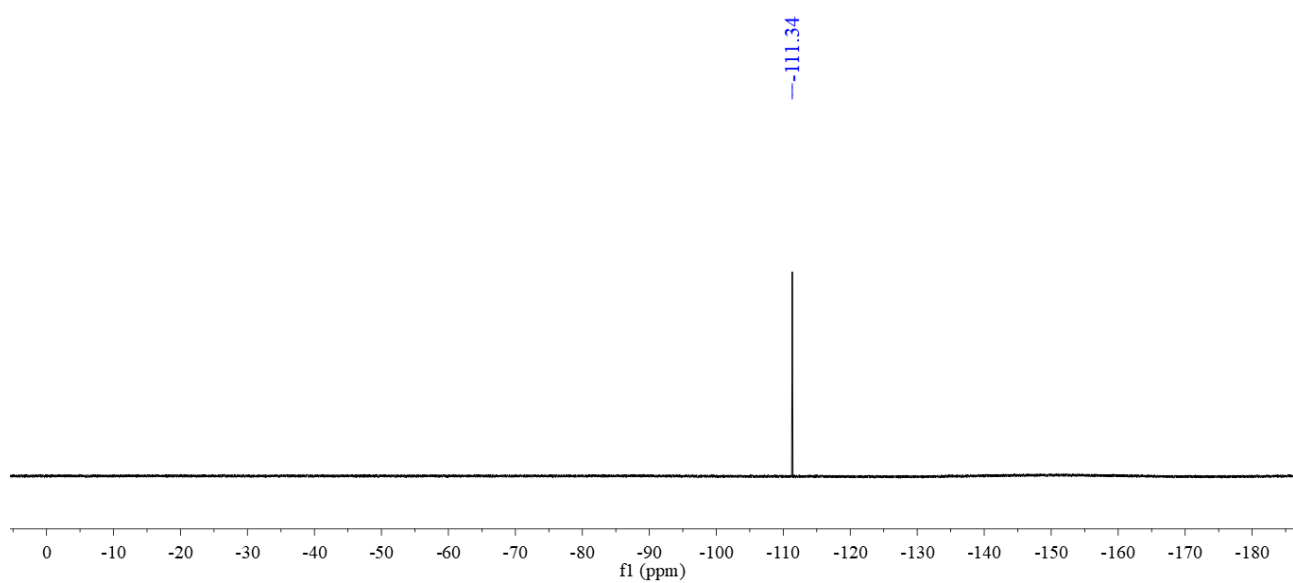
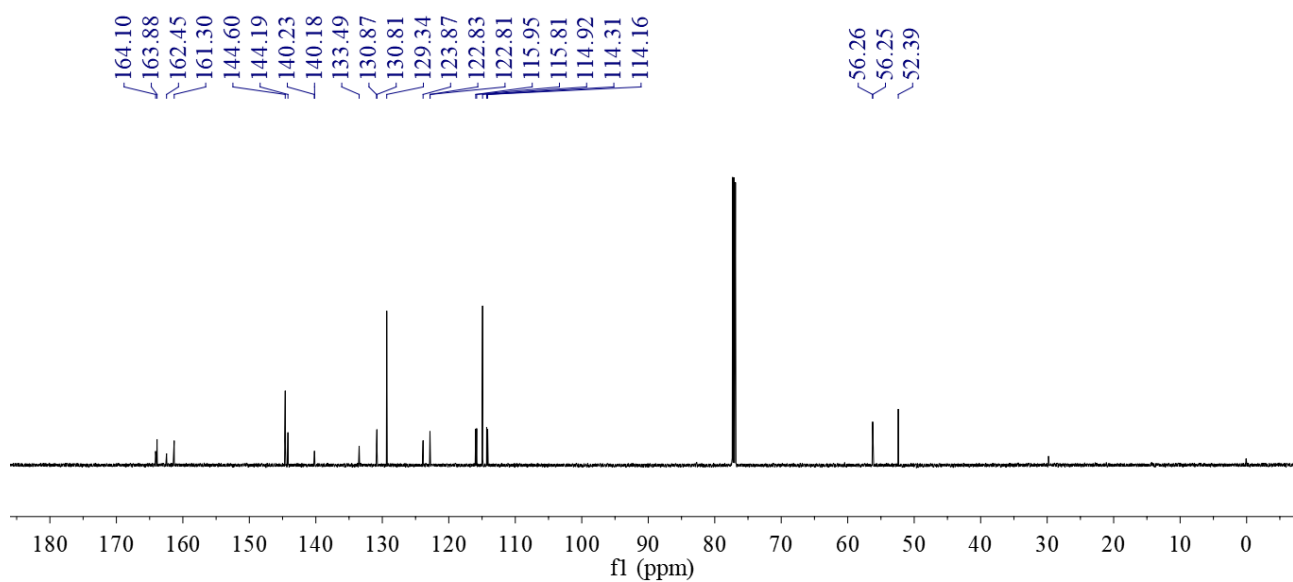
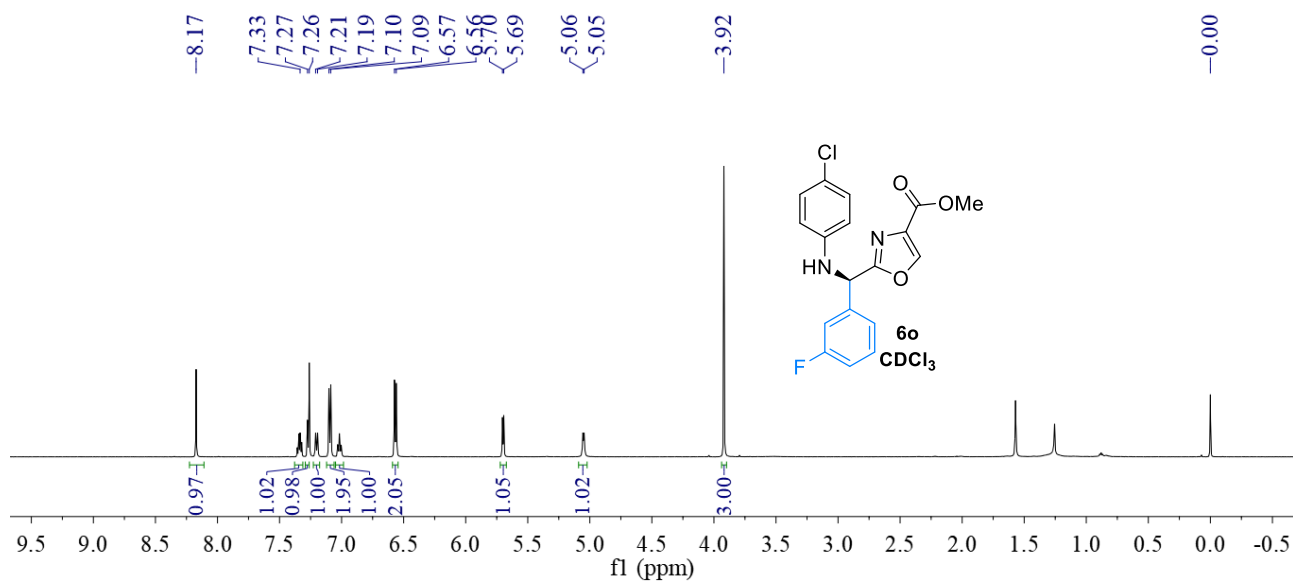


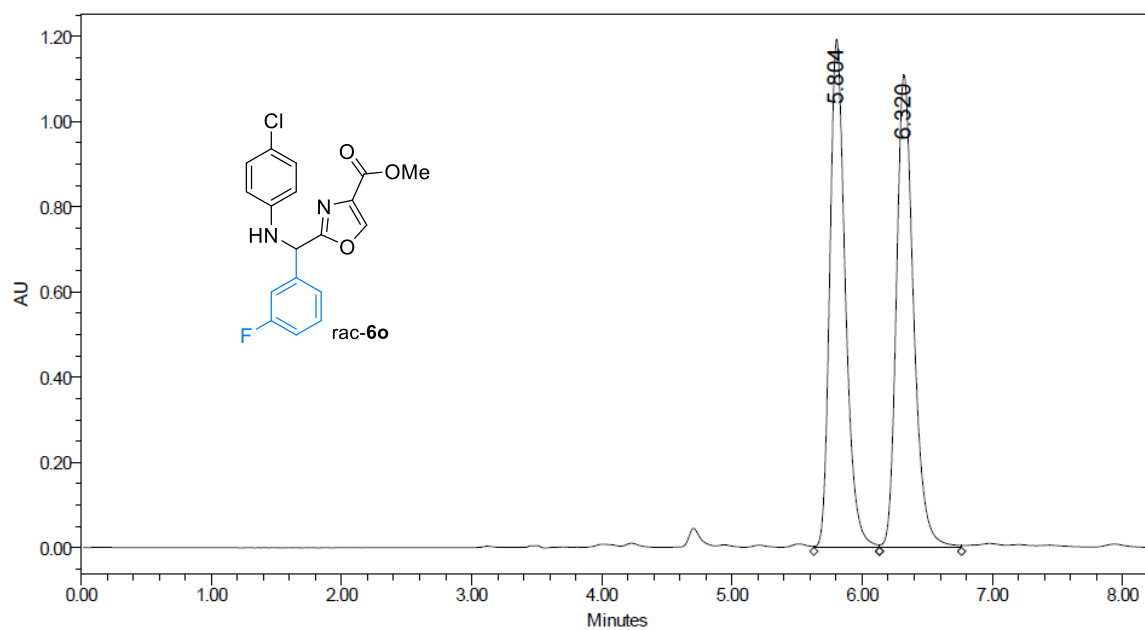


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.291	Unknown	2846615	50.14	377667	53.63	VV	324	5.133	5.673
2	6.183	Unknown	2831047	49.86	326601	46.37	VB	311	6.000	6.518

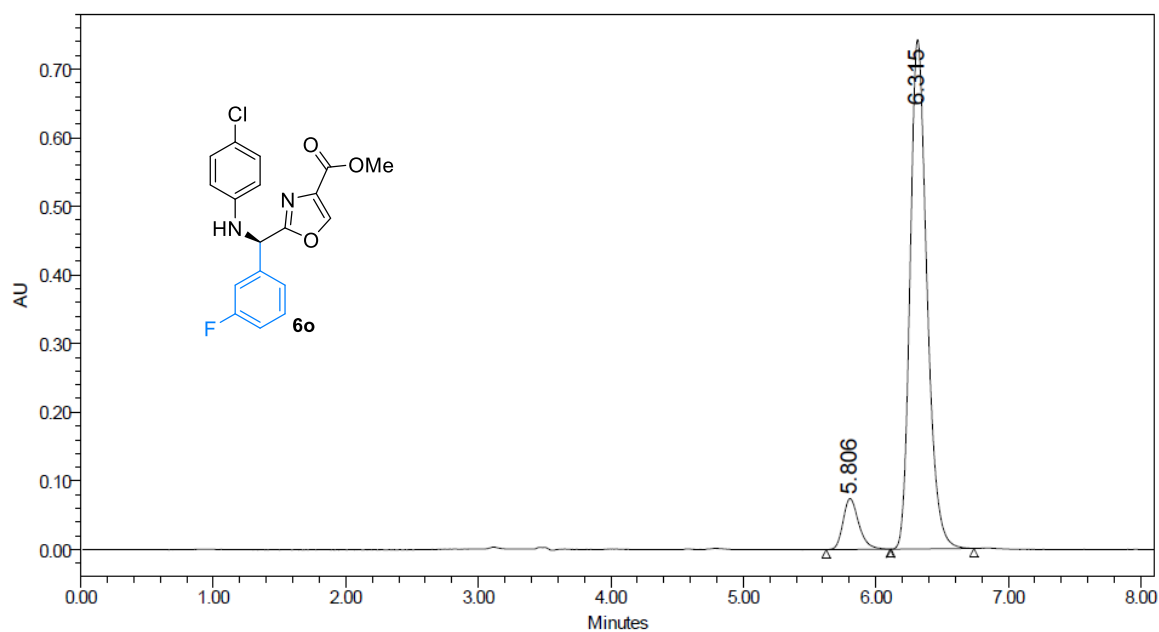


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.289	Unknown	1197102	8.97	159485	10.36	BV	294	5.108	5.598
2	6.169	Unknown	12151204	91.03	1380141	89.64	VB	388	5.980	6.627

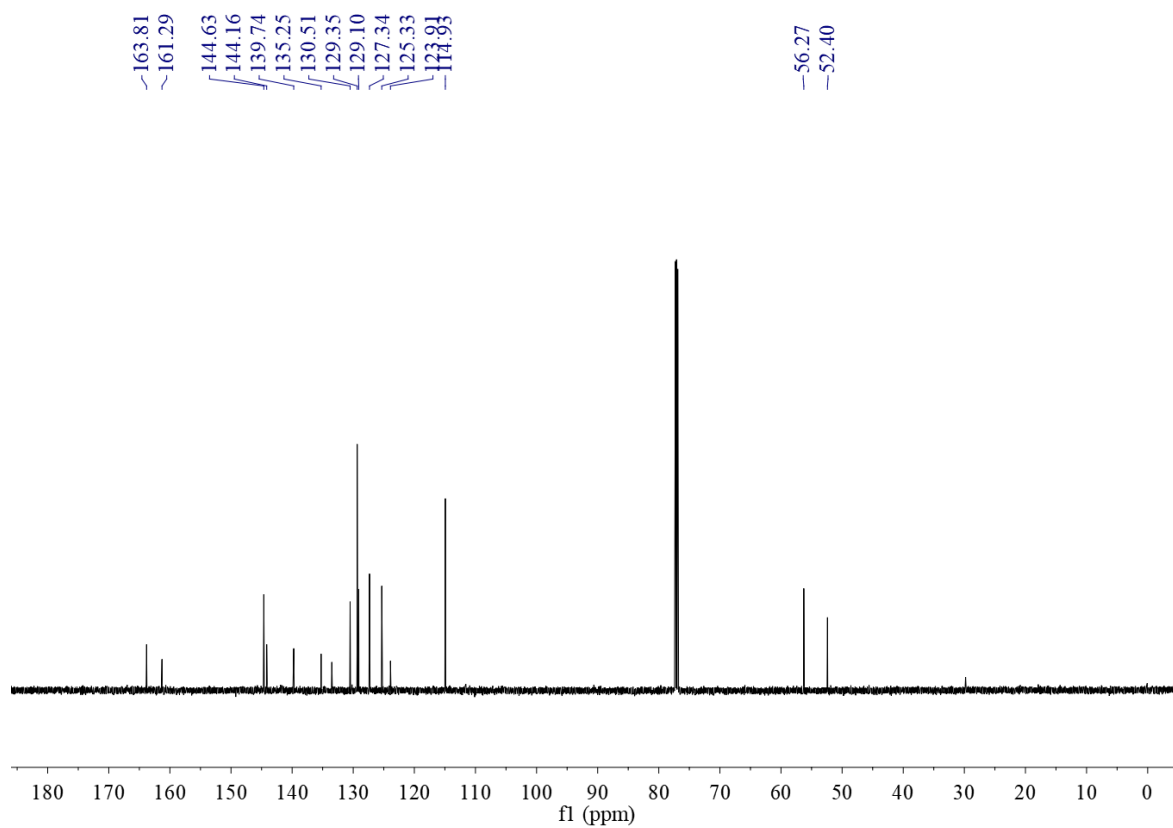
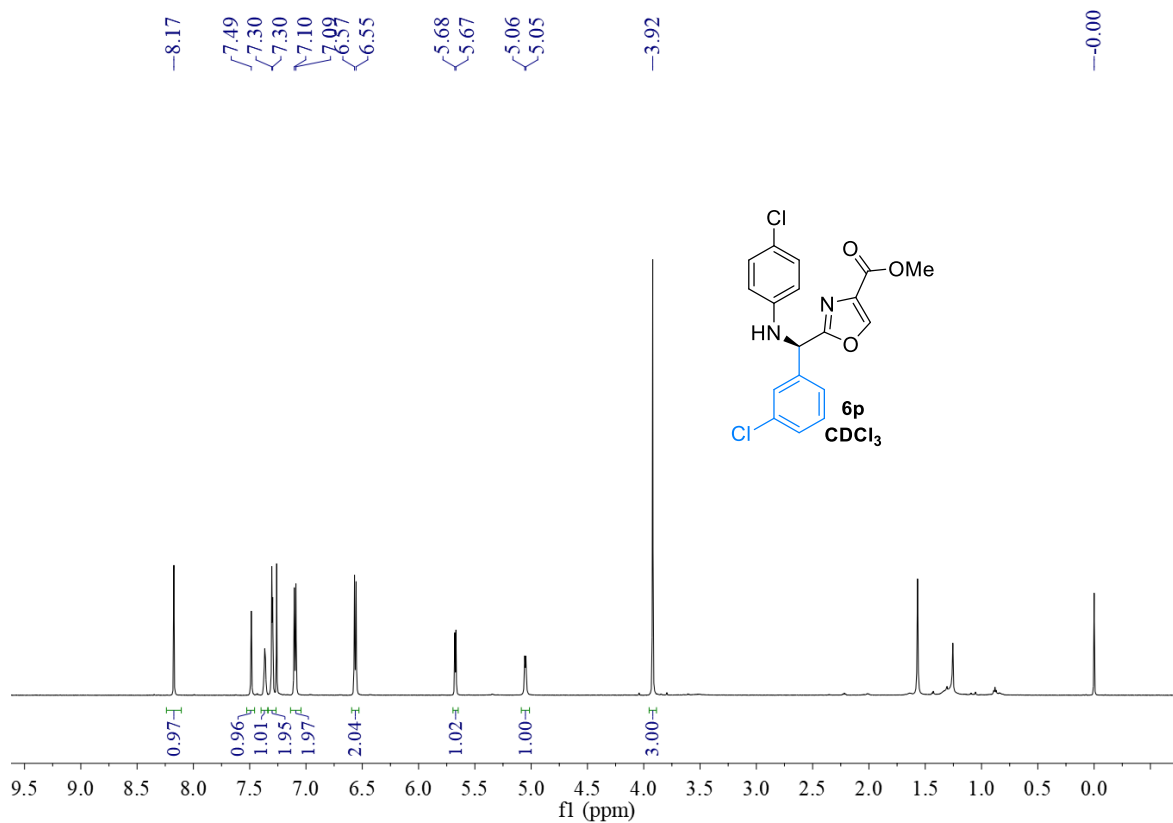


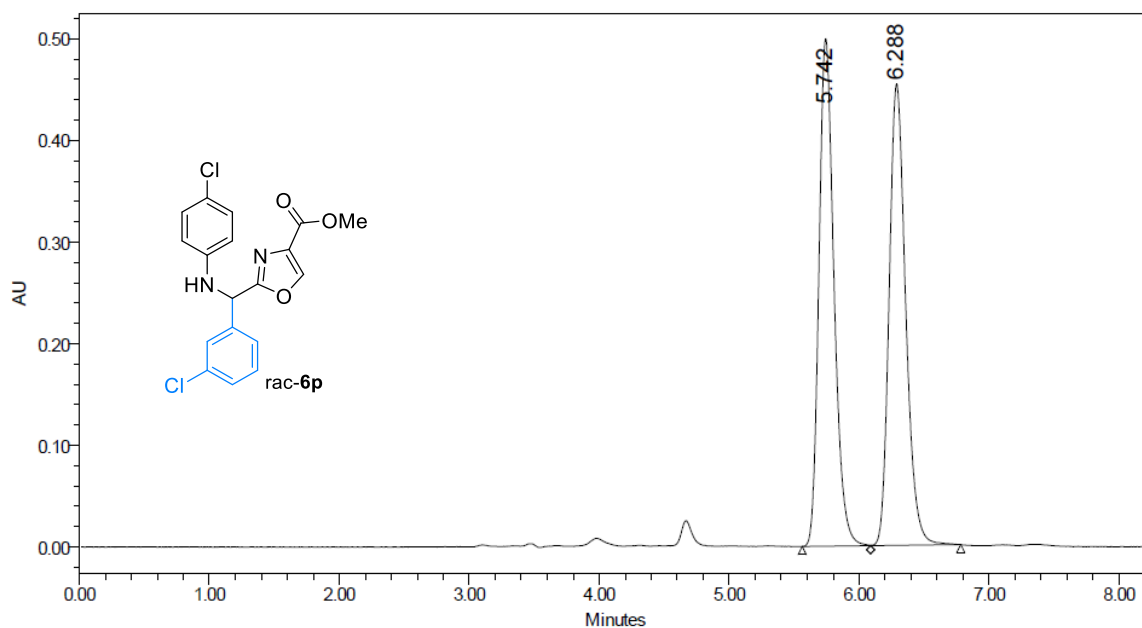


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.804	Unknown	9891739	49.44	1191975	51.80	VV	303	5.628	6.133
2	6.320	Unknown	10117214	50.56	1109172	48.20	VV	378	6.133	6.763

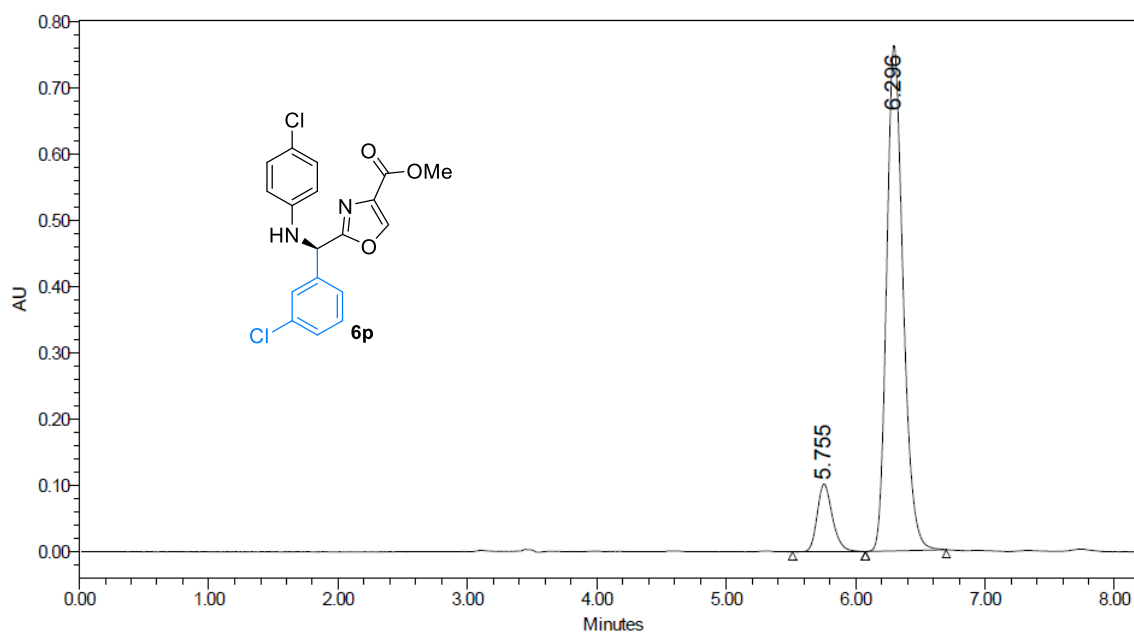


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.806	Unknown	610956	8.51	74102	9.08	BB	290	5.625	6.108
2	6.315	Unknown	6571600	91.49	742033	90.92	BB	375	6.115	6.740

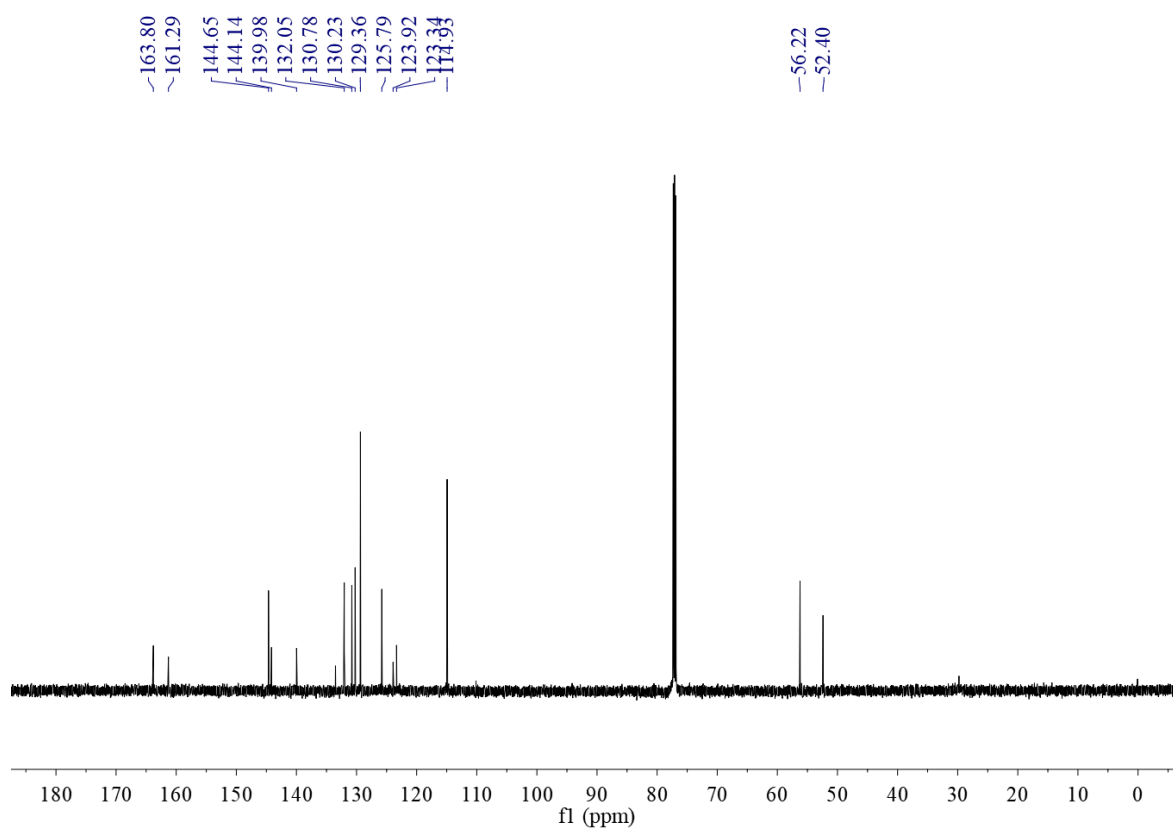
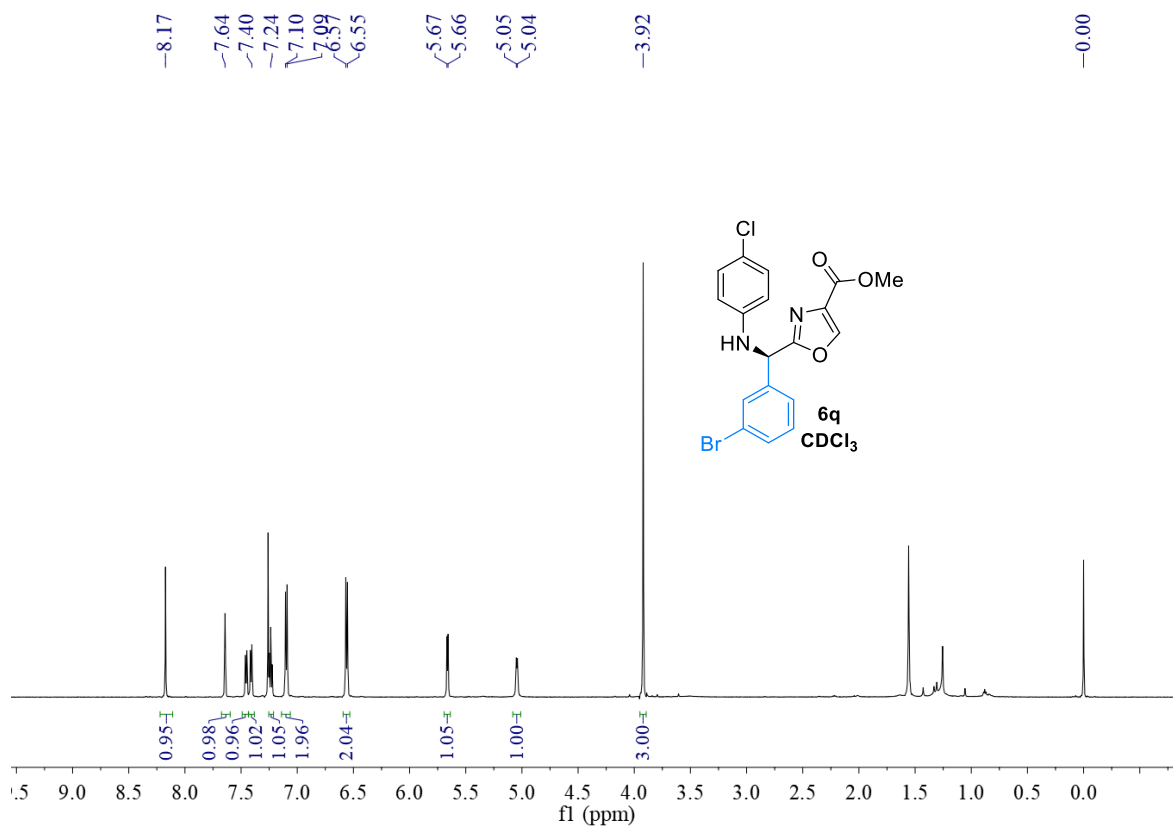


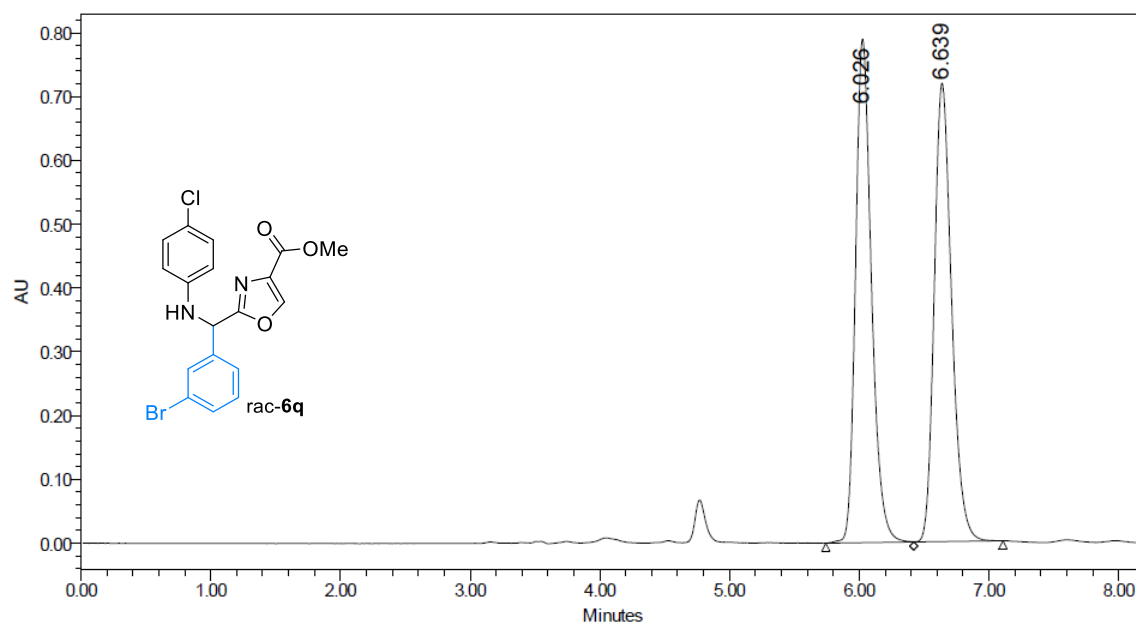


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.742	Unknown	4021552	50.03	499718	52.39	BV	316	5.562	6.088
2	6.288	Unknown	4016528	49.97	454095	47.61	VB	416	6.088	6.782

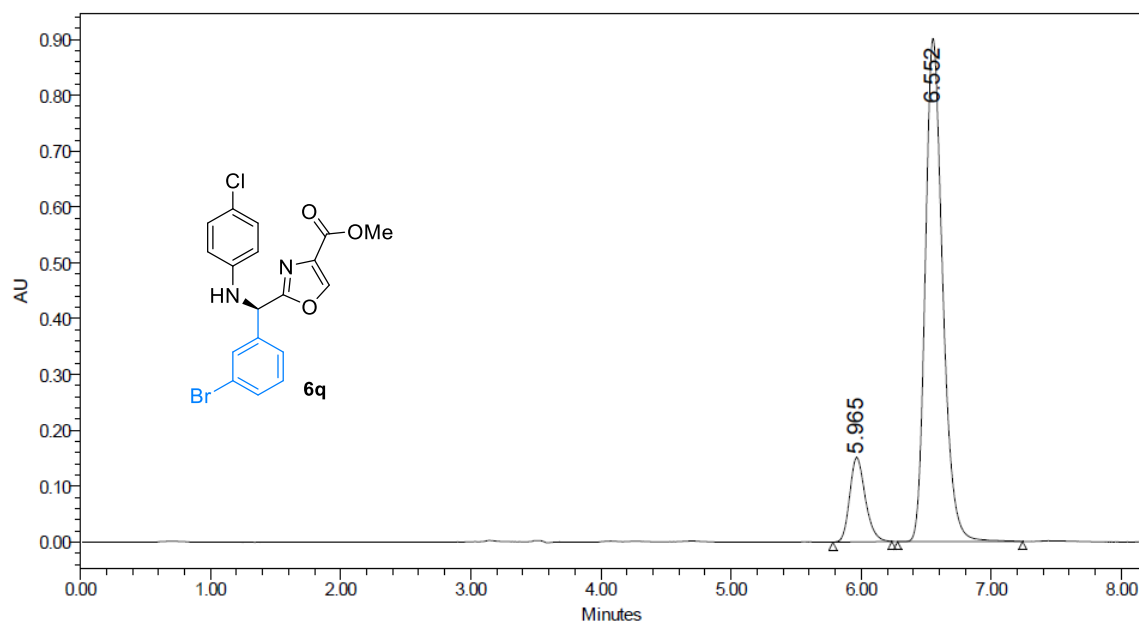


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.755	Unknown	829514	10.95	101703	11.77	bb	337	5.512	6.073
2	6.296	Unknown	6747963	89.05	762477	88.23	Bb	374	6.077	6.700

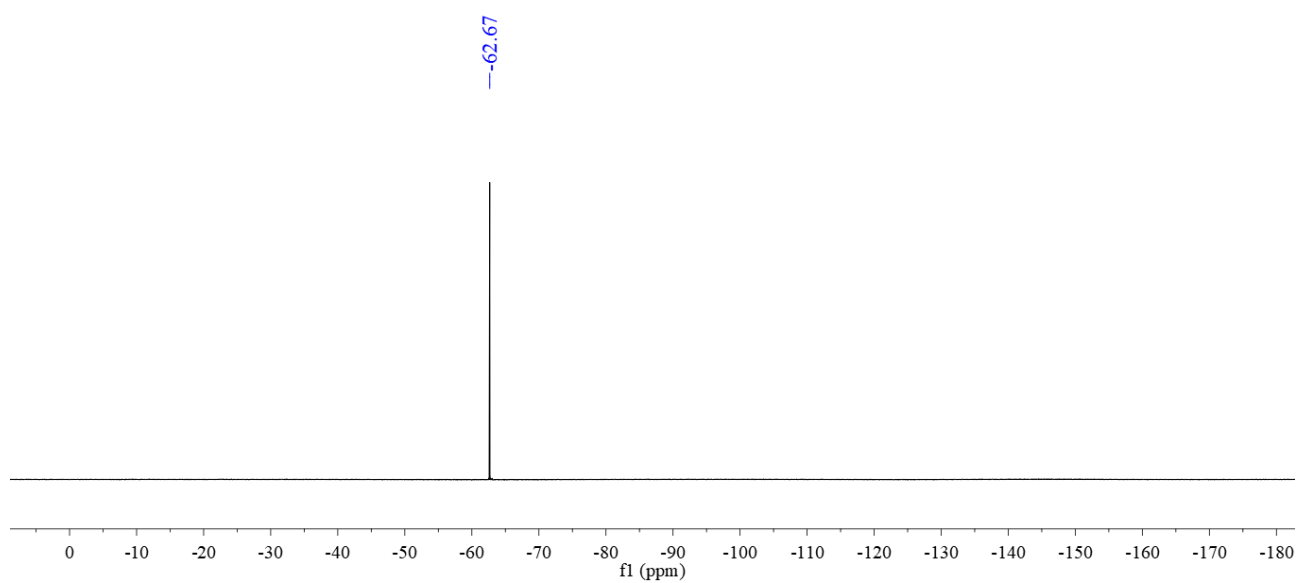
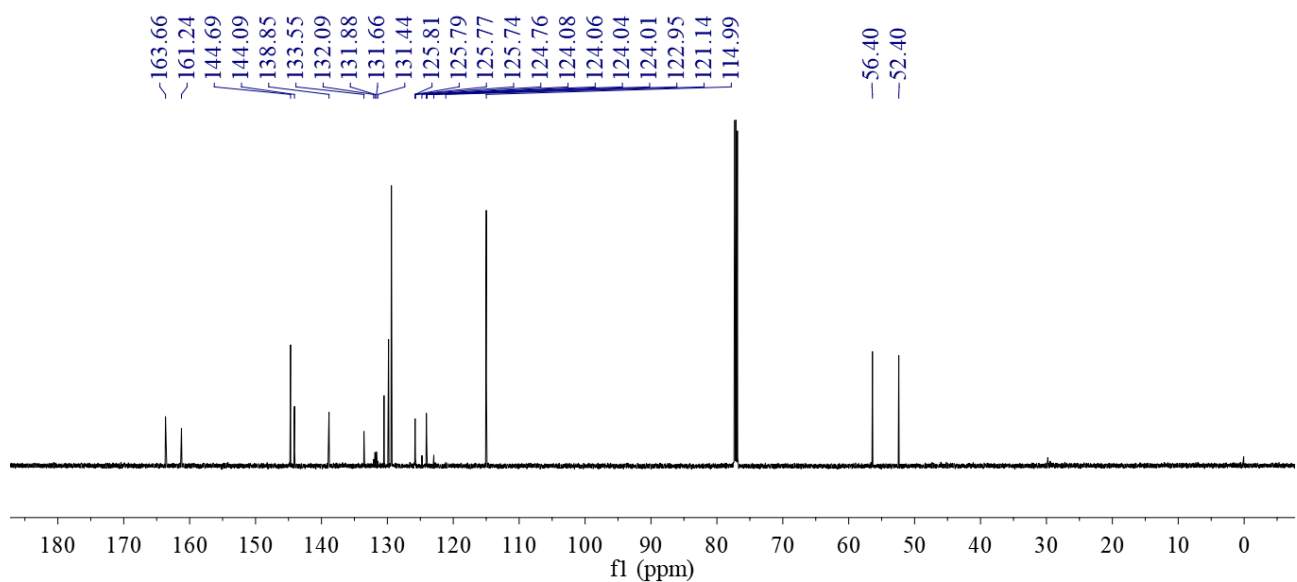
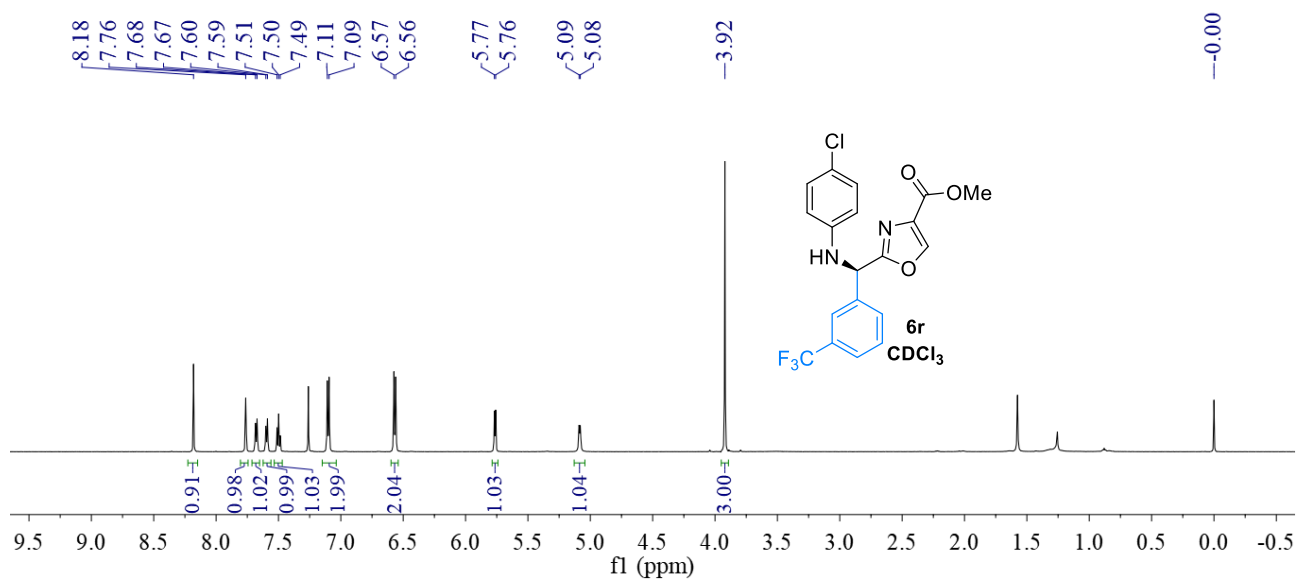


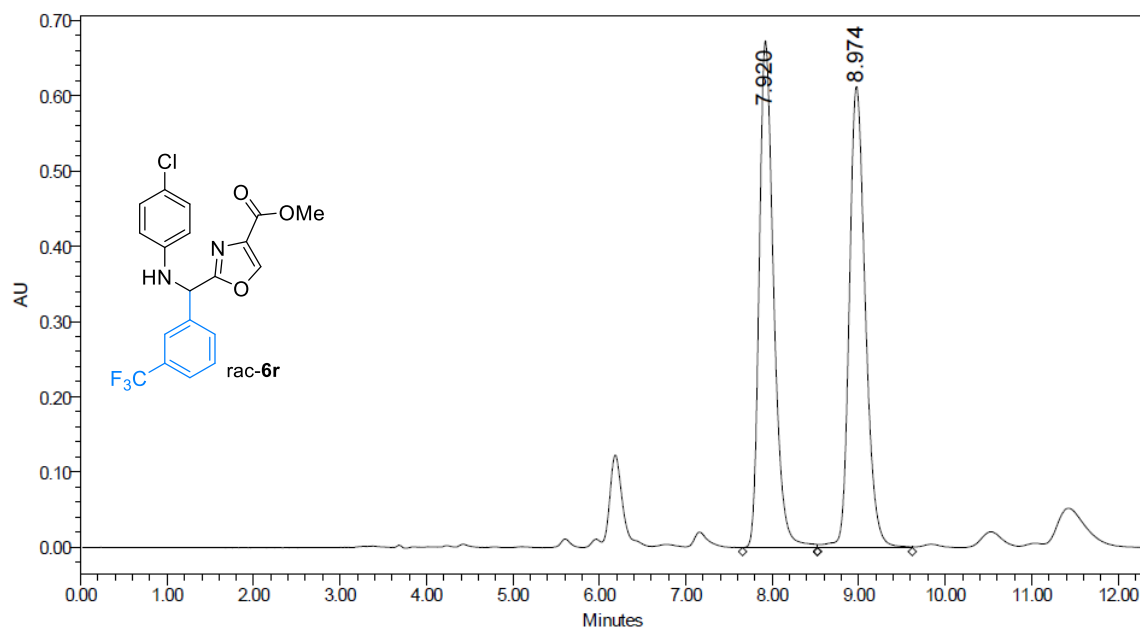


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.026	Unknown	6741296	50.21	789436	52.35	BV	406	5.743	6.420
2	6.639	Unknown	6684189	49.79	718634	47.65	VB	413	6.420	7.108

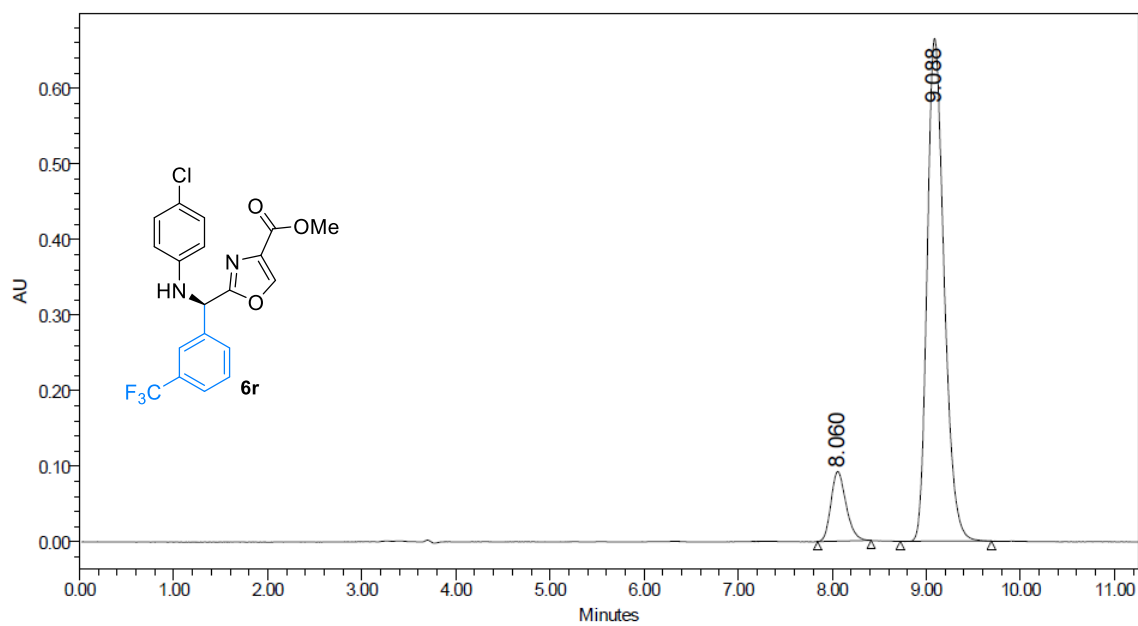


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.965	Unknown	1260213	13.09	150831	14.34	bb	272	5.783	6.237
2	6.552	Unknown	8363624	86.91	901064	85.66	bb	576	6.280	7.240

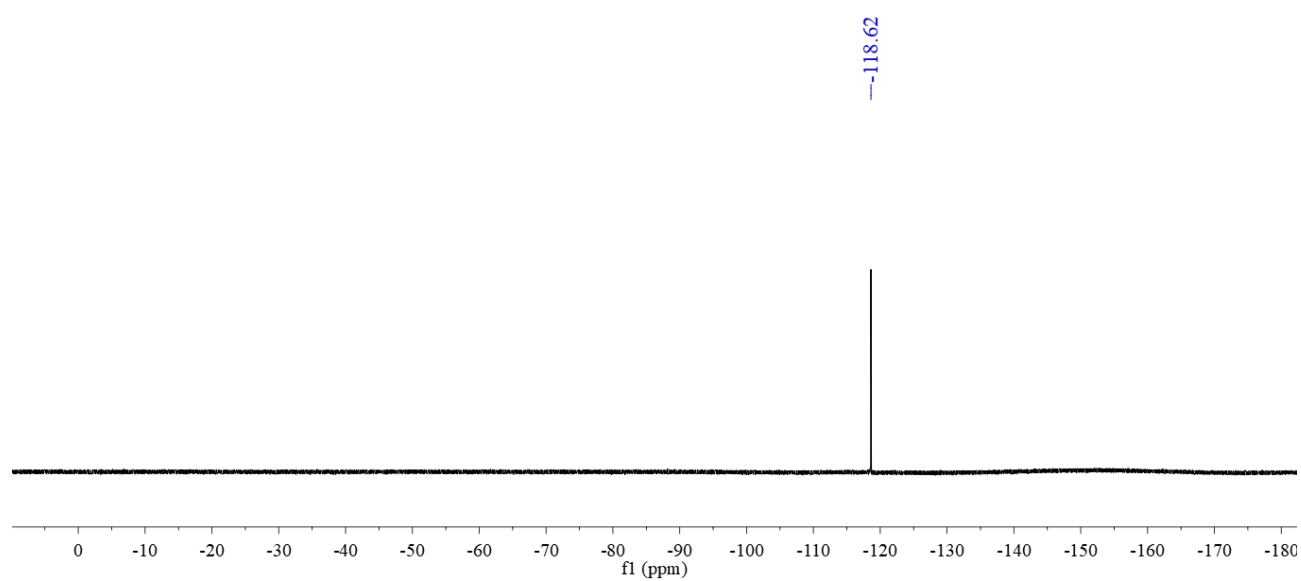
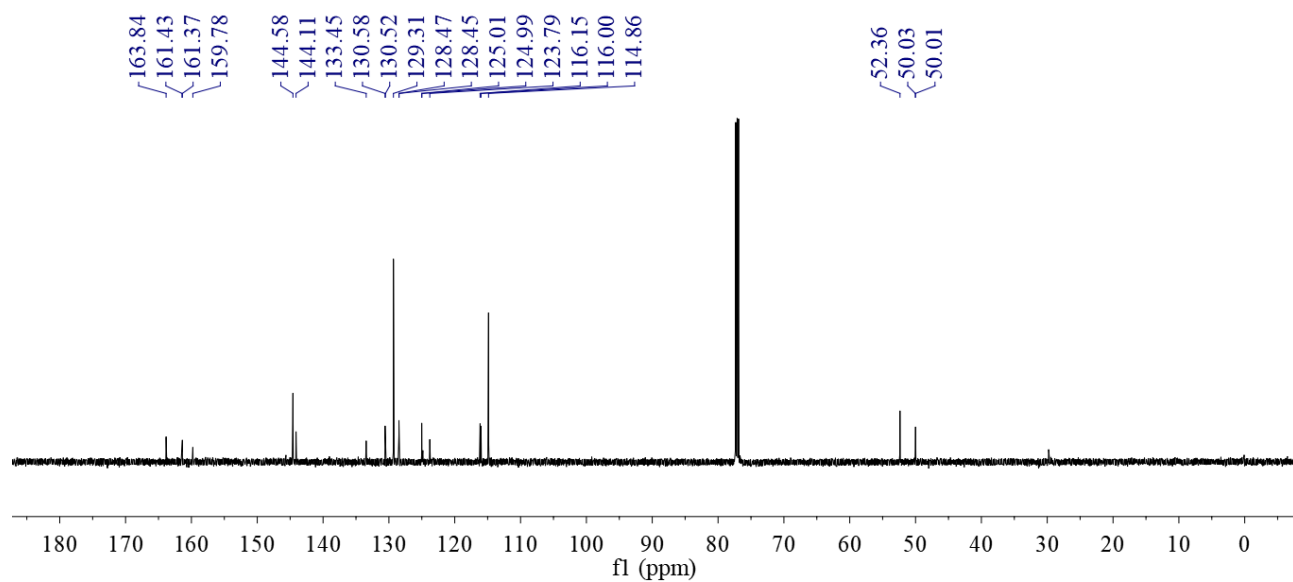
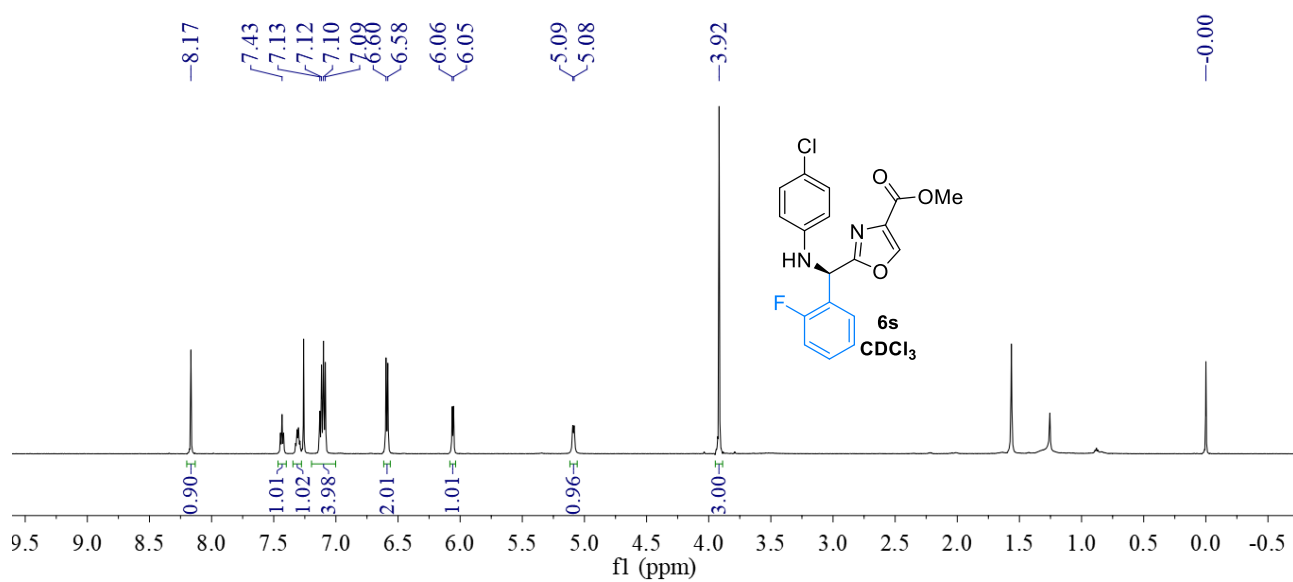


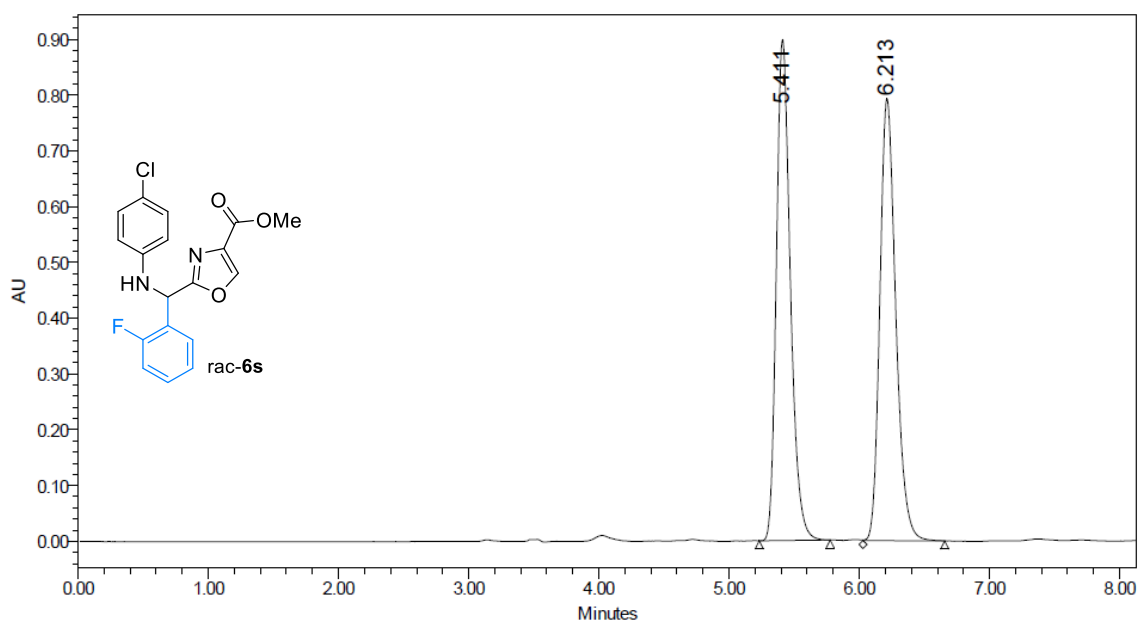


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.920	Unknown	7831919	49.71	673549	52.36	VV	519	7.657	8.522
2	8.974	Unknown	7922505	50.29	612751	47.64	VV	658	8.522	9.618

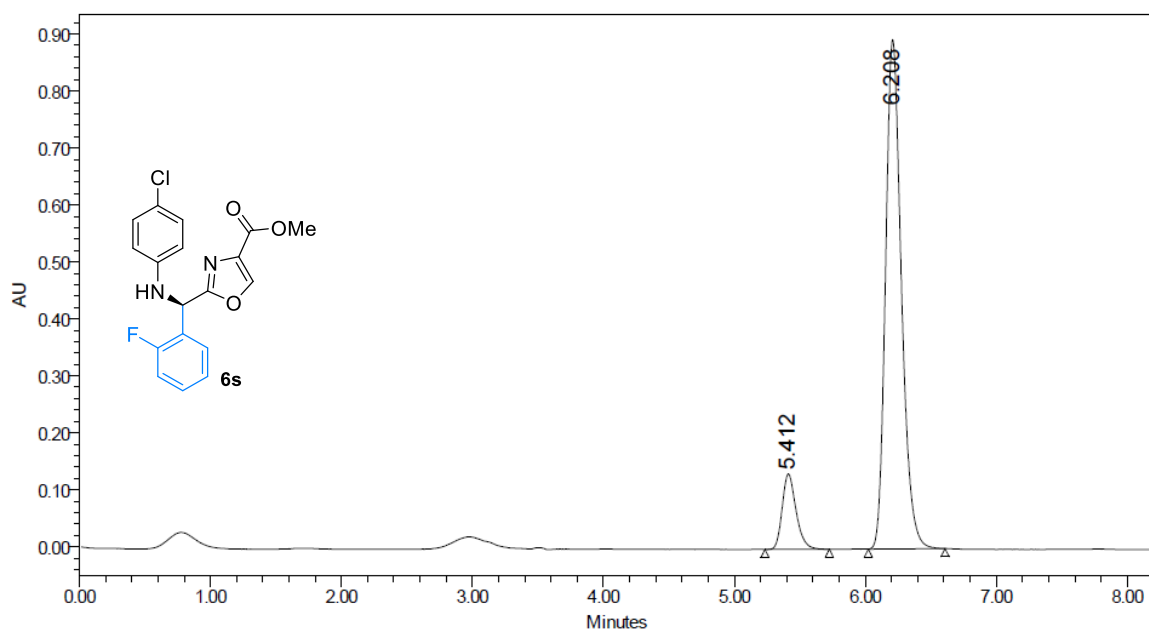


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	8.060	Unknown	1027960	11.00	92048	12.16	bb	341	7.845	8.413
2	9.088	Unknown	8320045	89.00	664739	87.84	bB	581	8.723	9.692

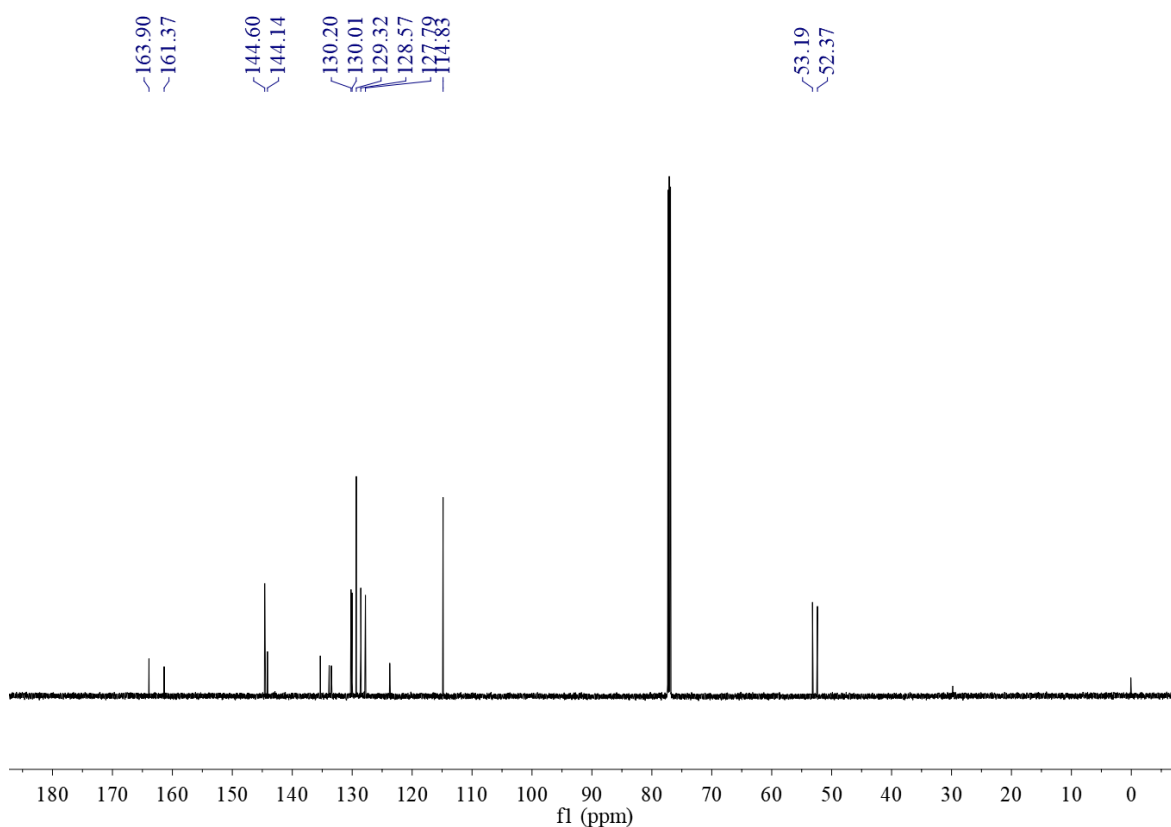
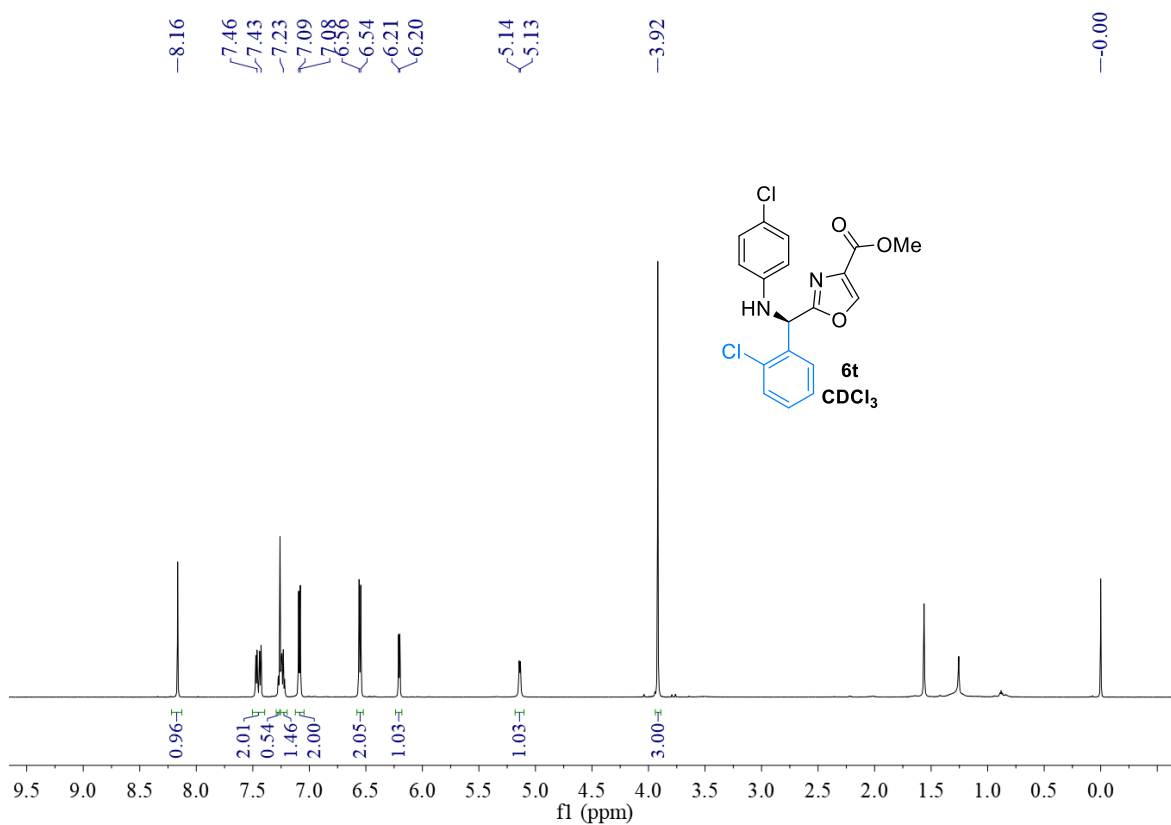


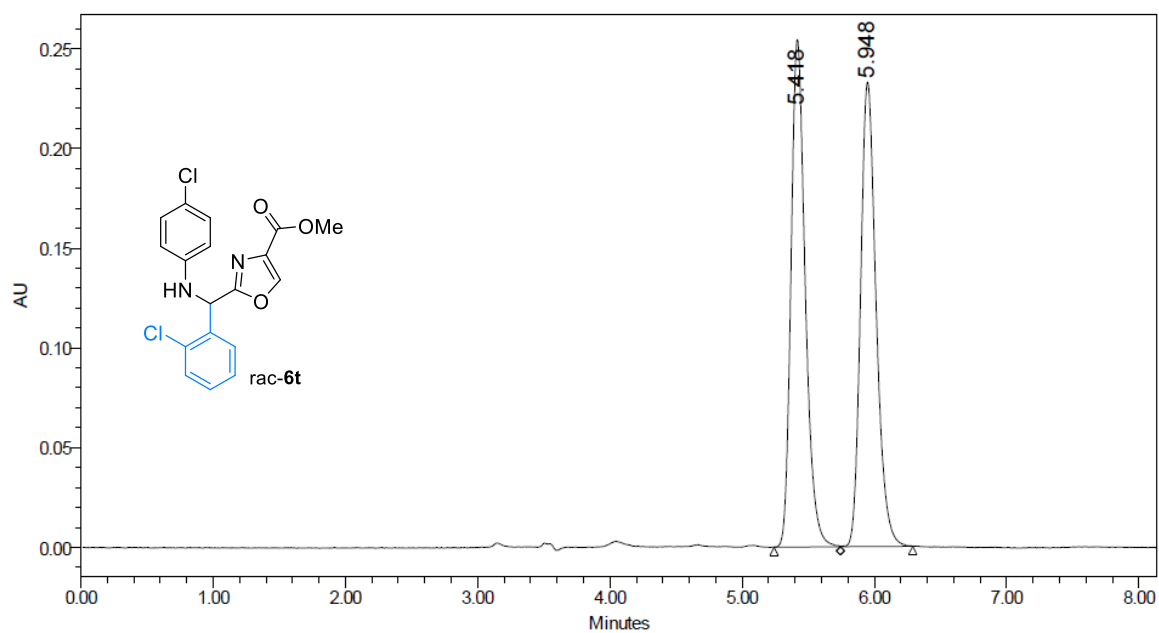


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.411	Unknown	6704658	49.92	898134	53.13	BB	327	5.232	5.777
2	6.213	Unknown	6725713	50.08	792216	46.87	VB	377	6.028	6.657

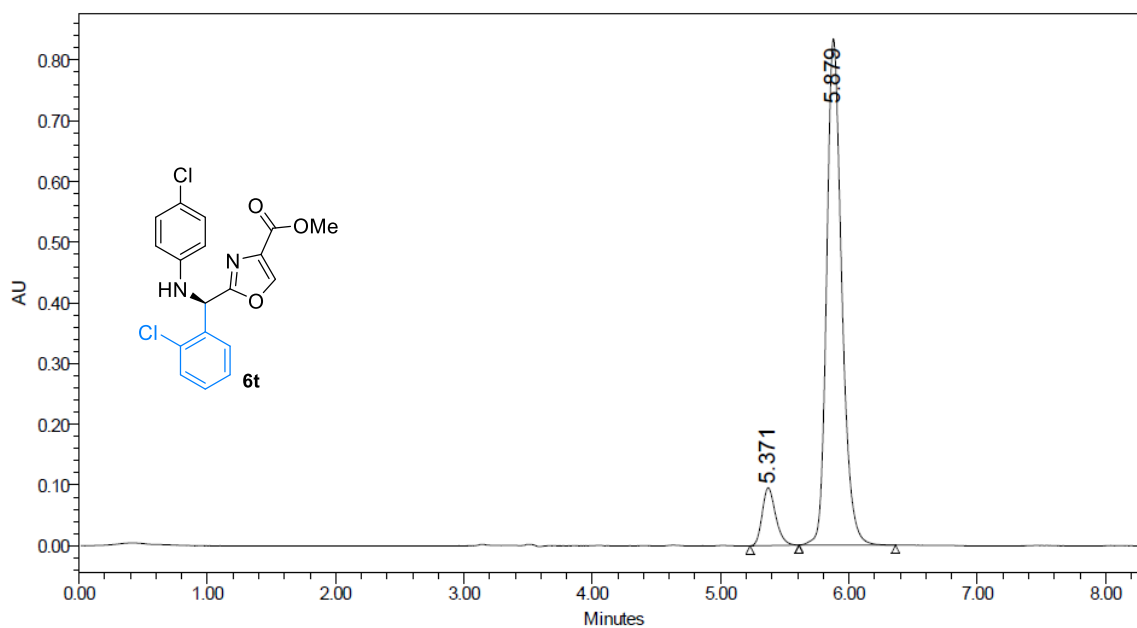


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.412	Unknown	972842	11.47	132305	12.89	Bb	295	5.233	5.725
2	6.208	Unknown	7511682	88.53	894072	87.11	Bb	351	6.023	6.608

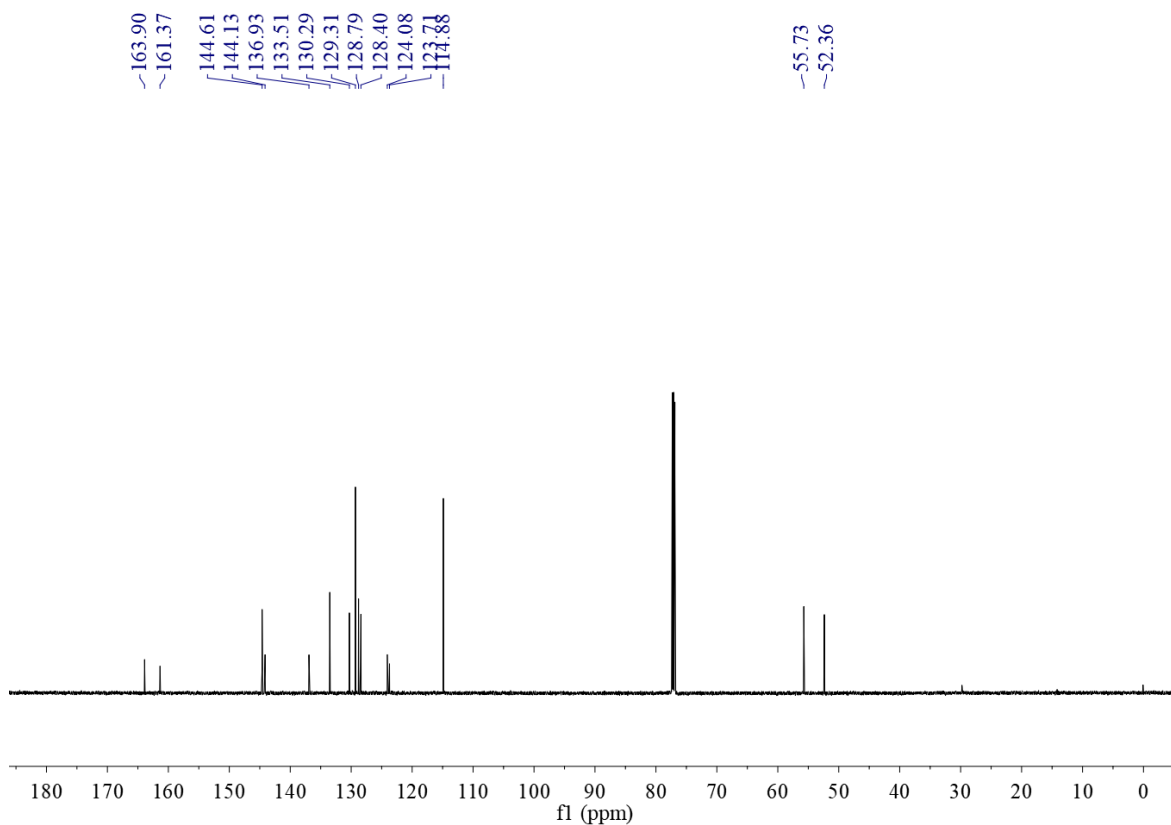
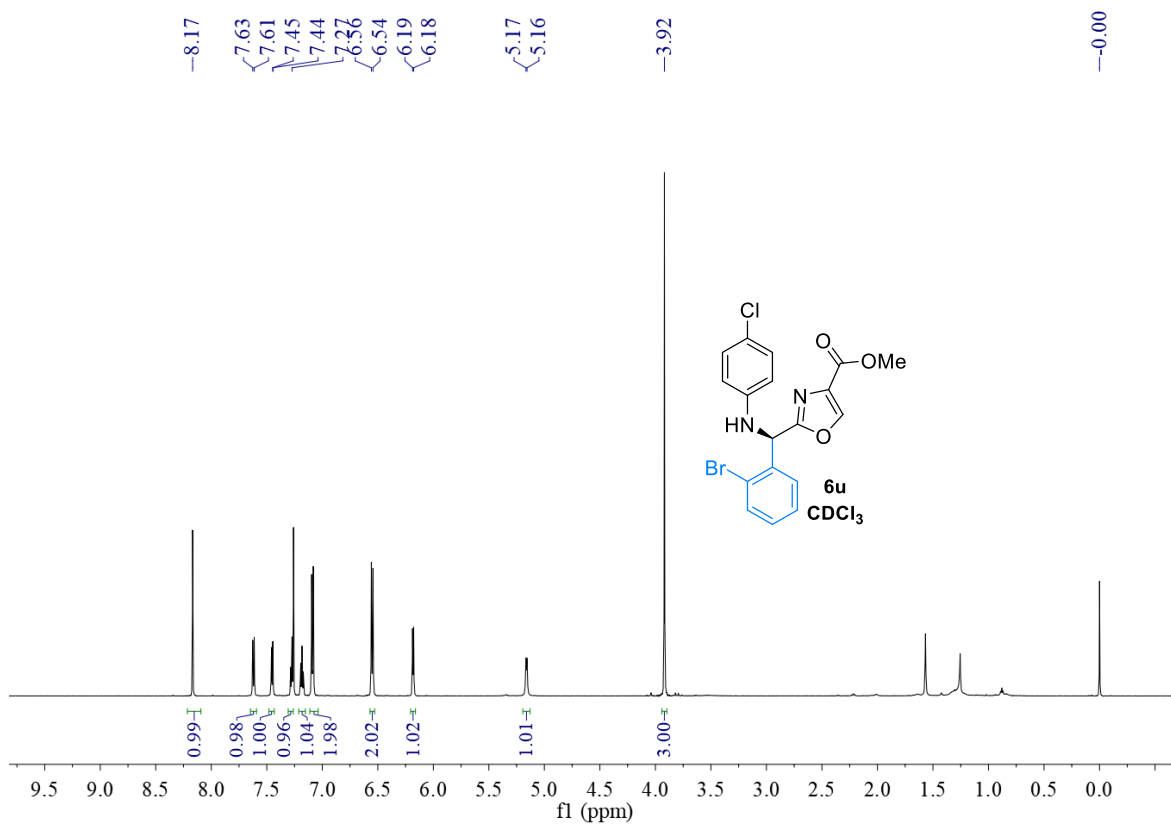


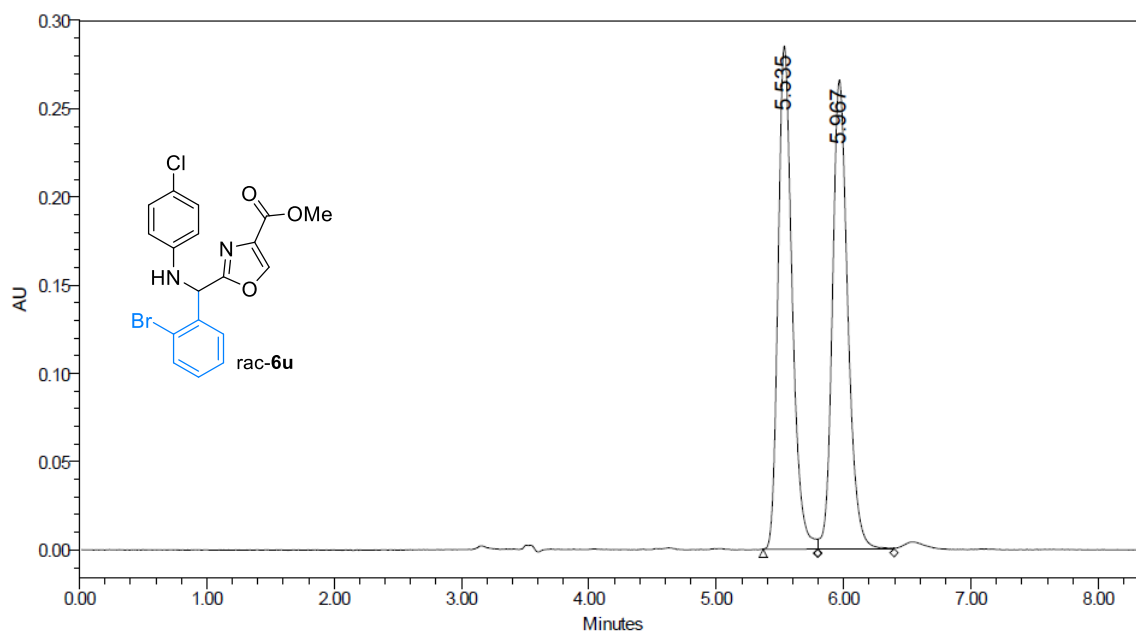


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.418	Unknown	1905748	50.04	254310	52.21	BV	301	5.242	5.743
2	5.948	Unknown	1902985	49.96	232819	47.79	VB	328	5.743	6.290

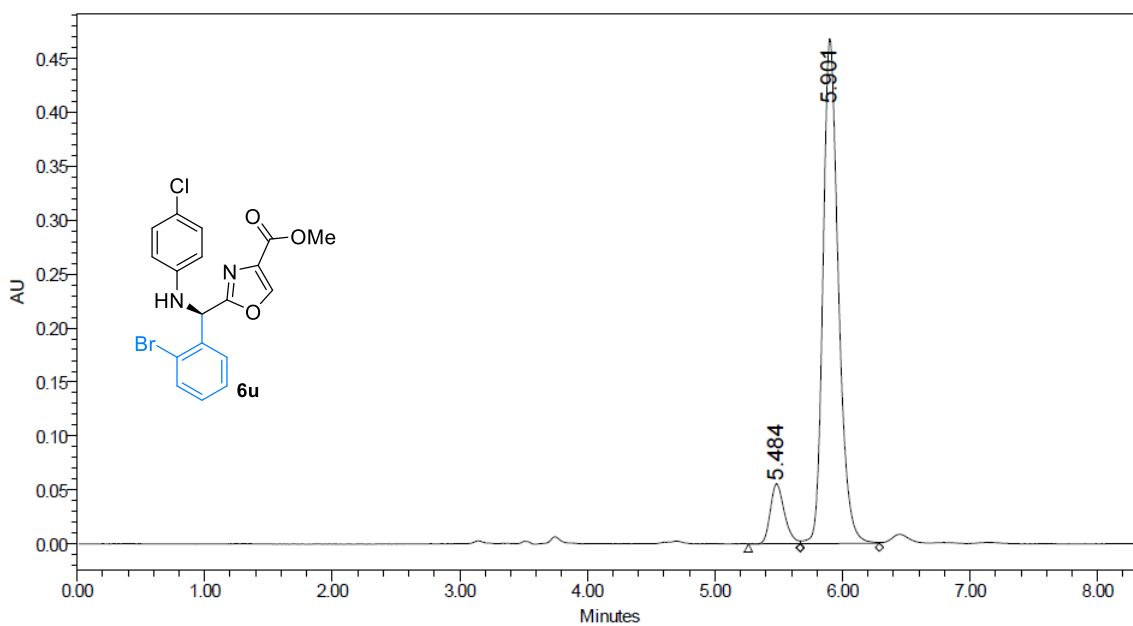


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.371	Unknown	691882	9.19	95104	10.23	bb	229	5.230	5.612
2	5.879	Unknown	6833493	90.81	834378	89.77	bb	451	5.612	6.363

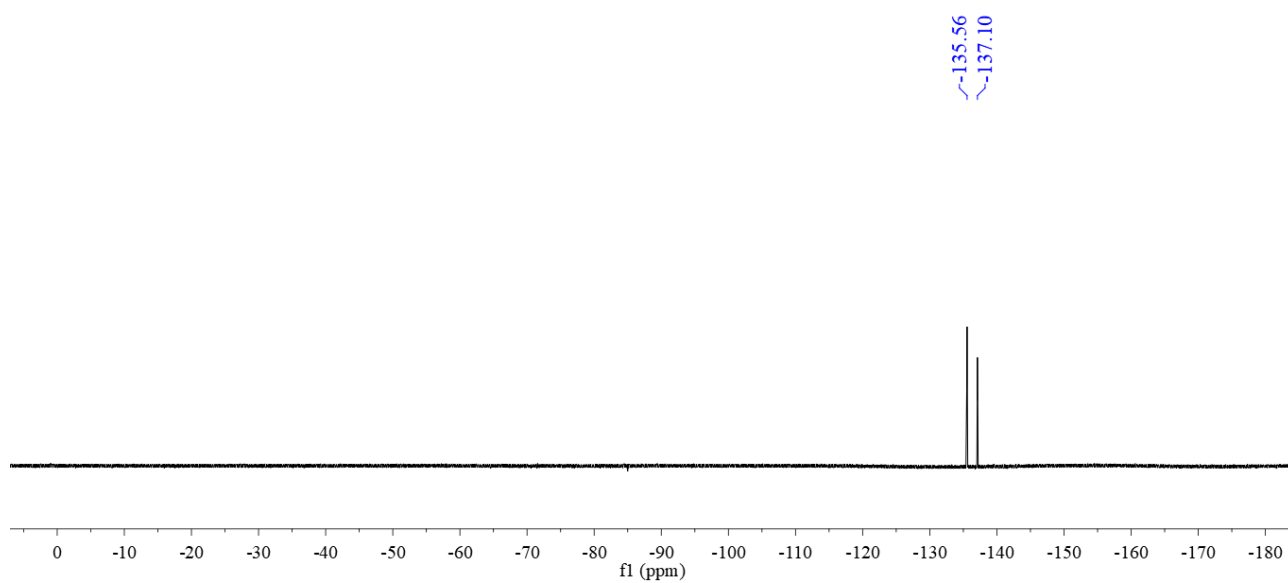
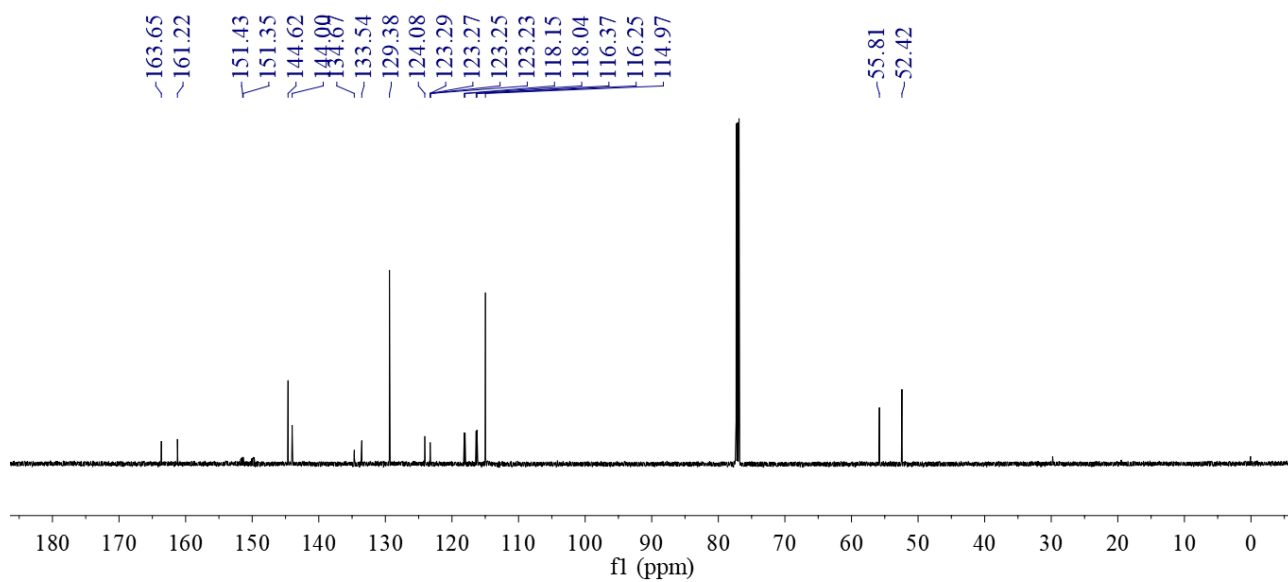
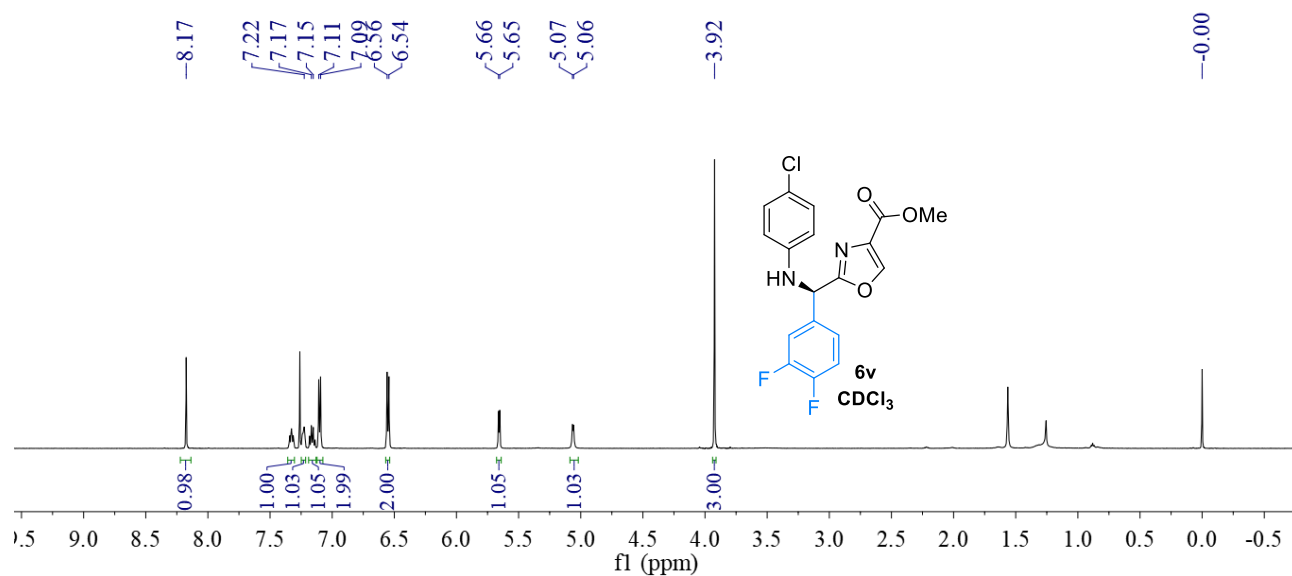


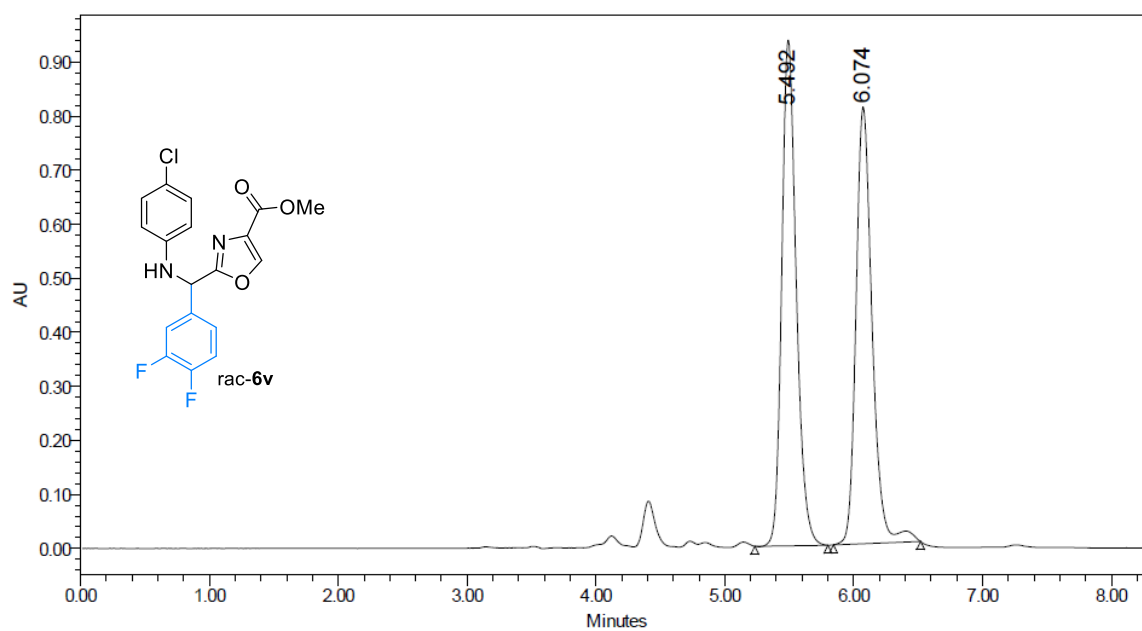


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.535	Unknown	2193016	49.68	285151	51.74	BV	257	5.368	5.797
2	5.967	Unknown	2221494	50.32	265928	48.26	VV	360	5.797	6.397

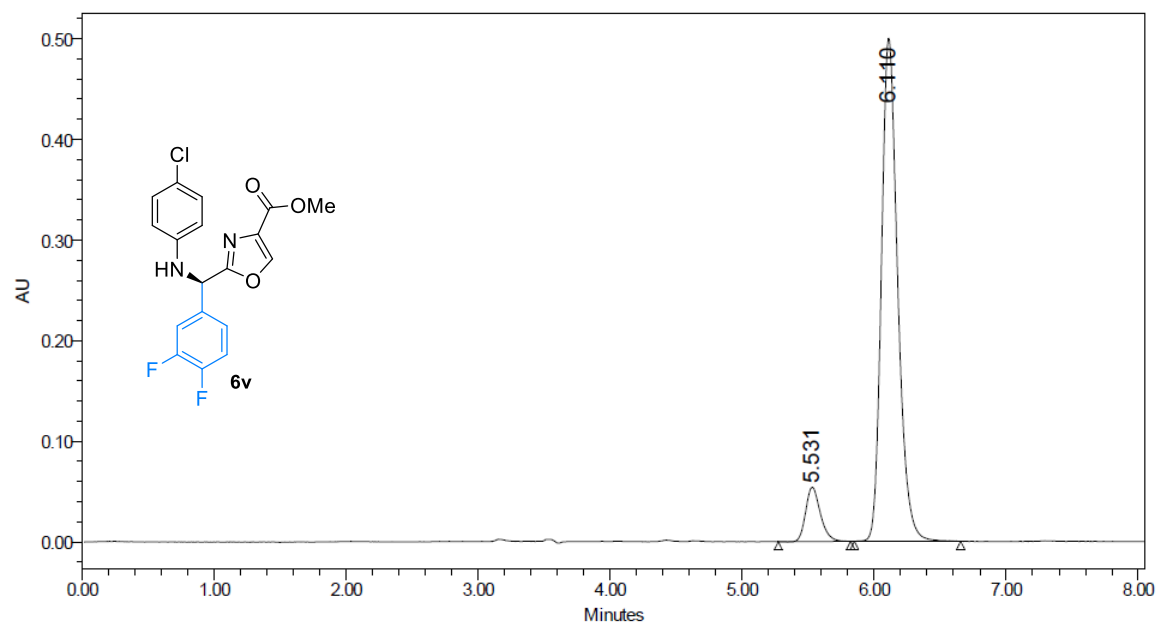


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.484	Unknown	425013	9.75	55312	10.57	bV	243	5.263	5.668
2	5.904	Unknown	3934039	90.25	467776	89.43	VV	373	5.668	6.290

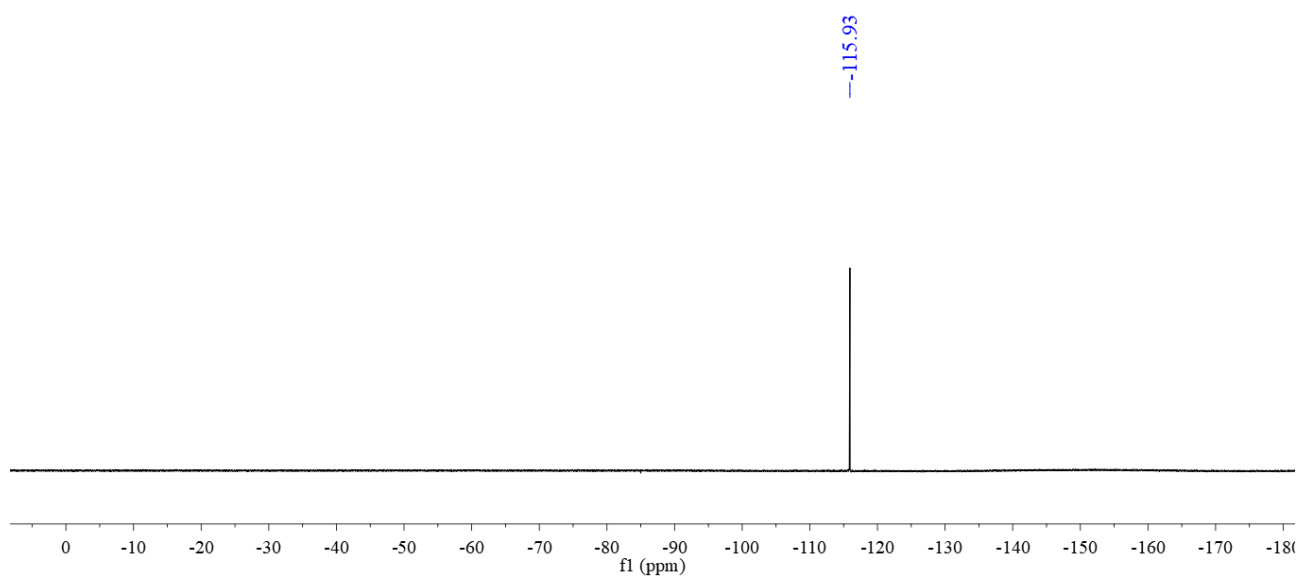
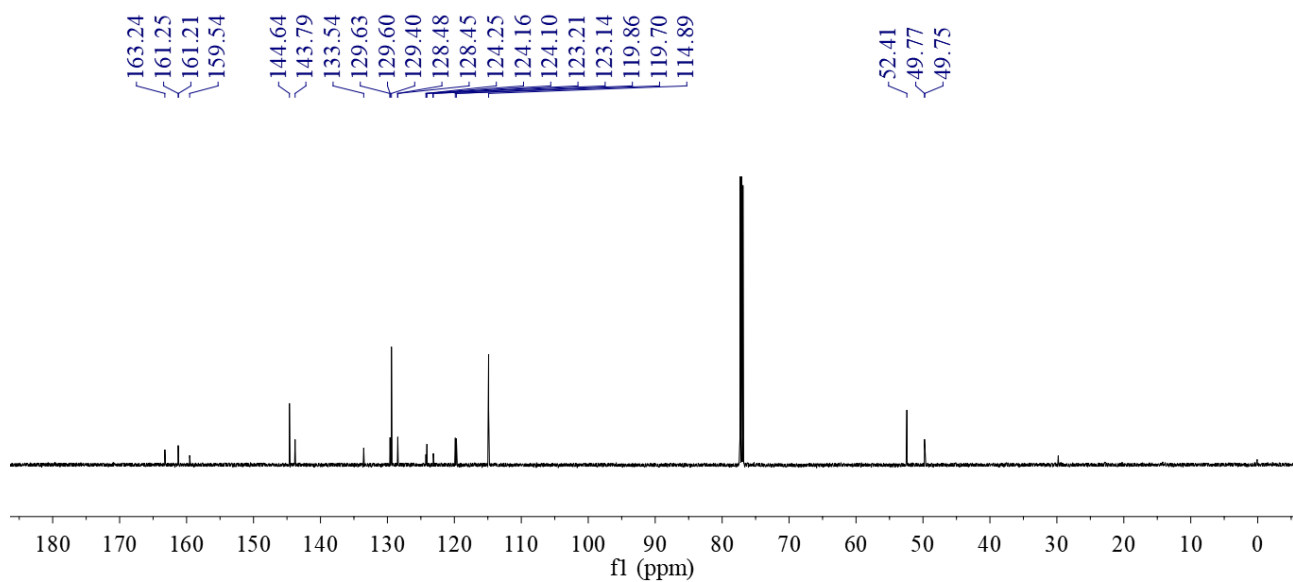
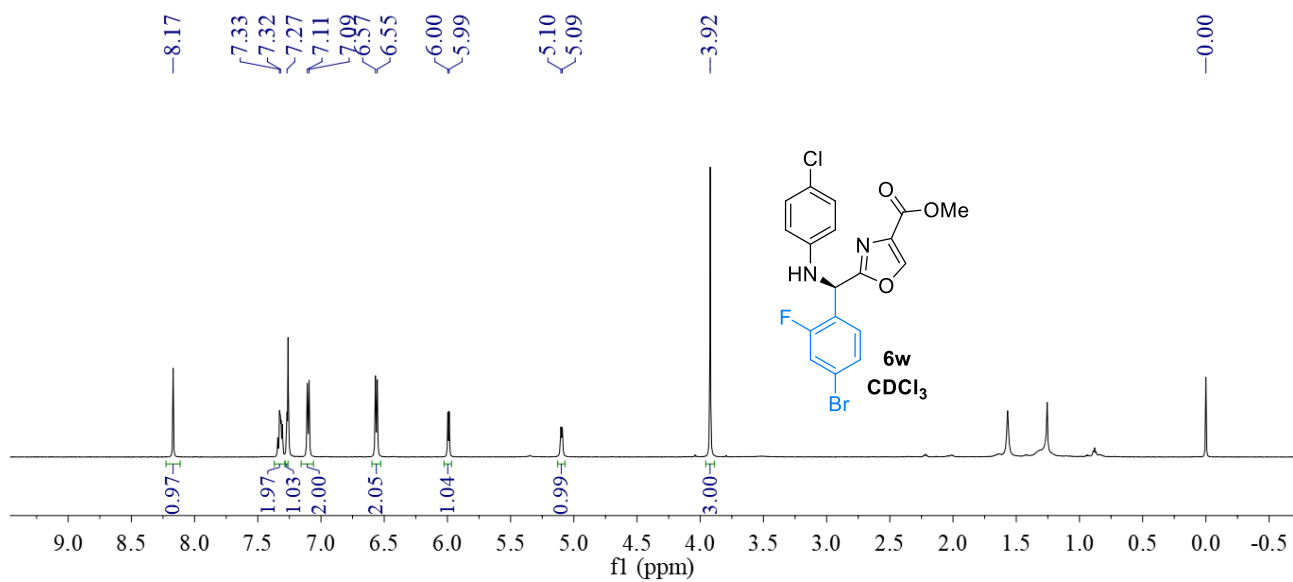


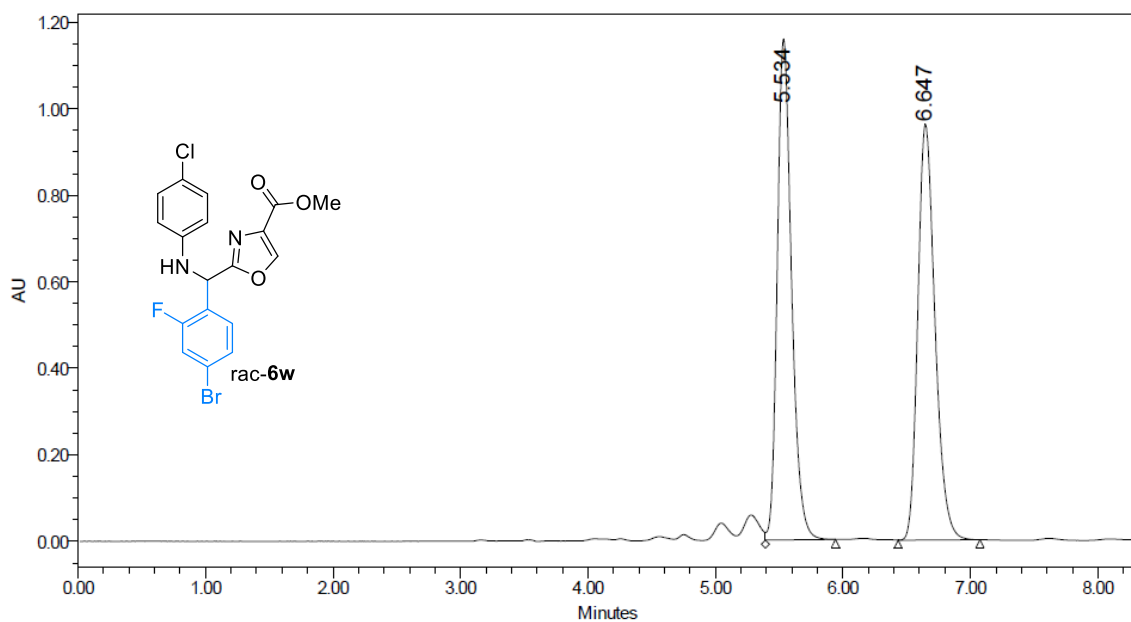


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.492	Unknown	7321522	50.94	935628	53.66	bb	340	5.233	5.800
2	6.074	Unknown	7051889	49.06	807910	46.34	bb	406	5.843	6.520

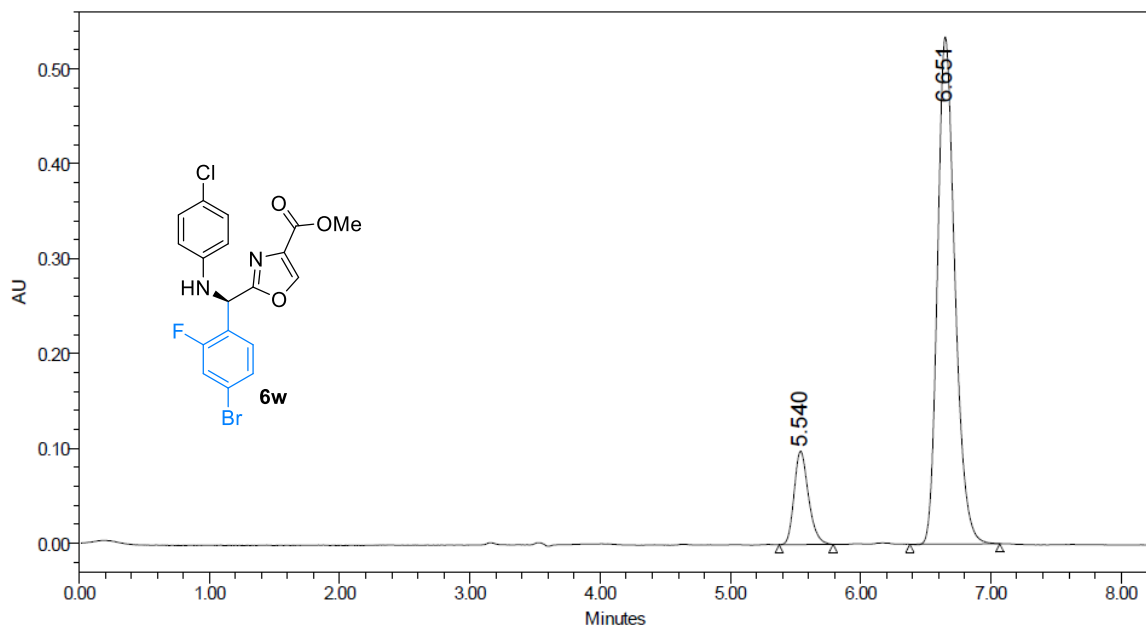


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.531	Unknown	418340	8.90	53909	9.73	bb	329	5.273	5.822
2	6.110	Unknown	4283383	91.10	499940	90.27	bb	483	5.850	6.655

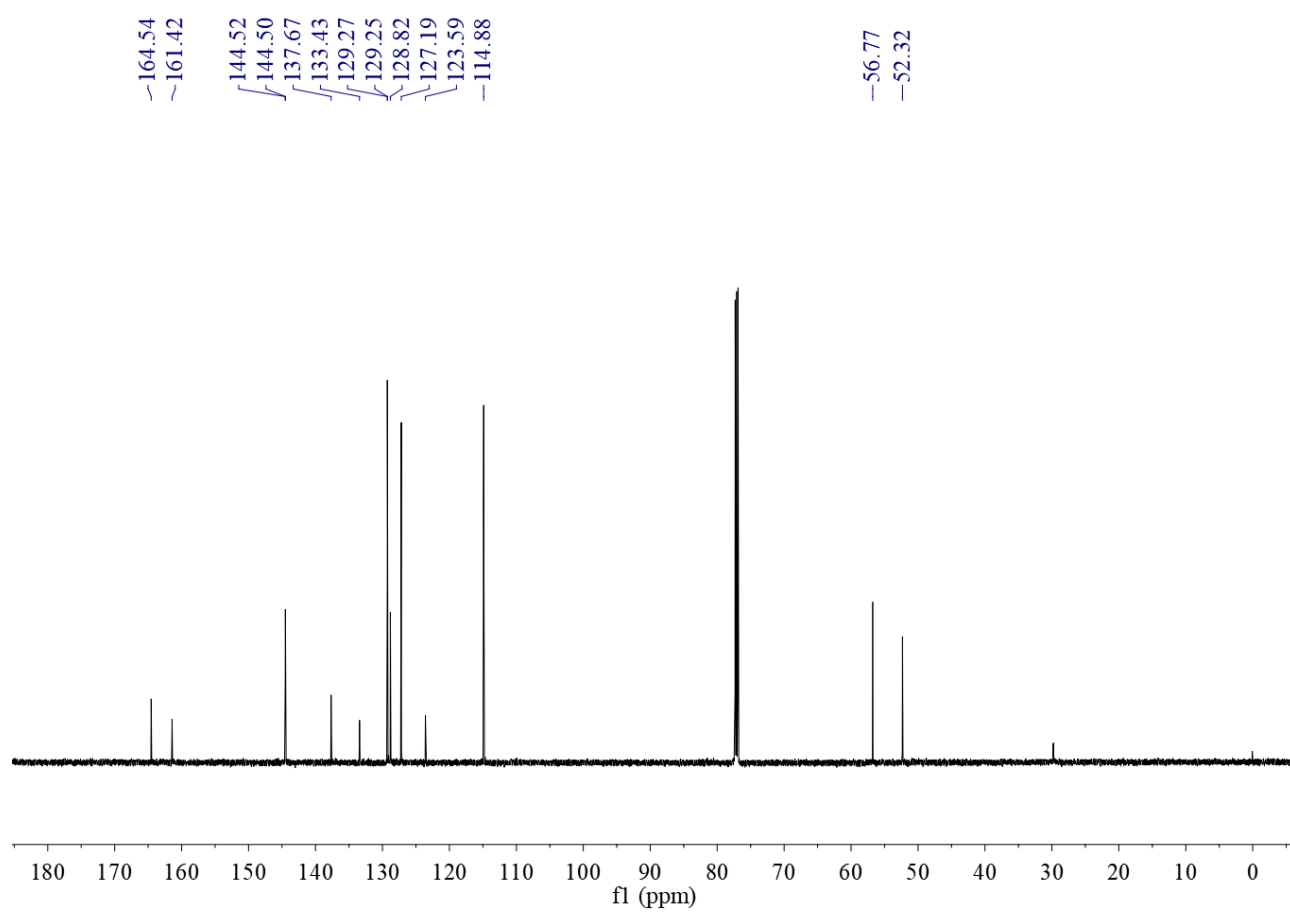
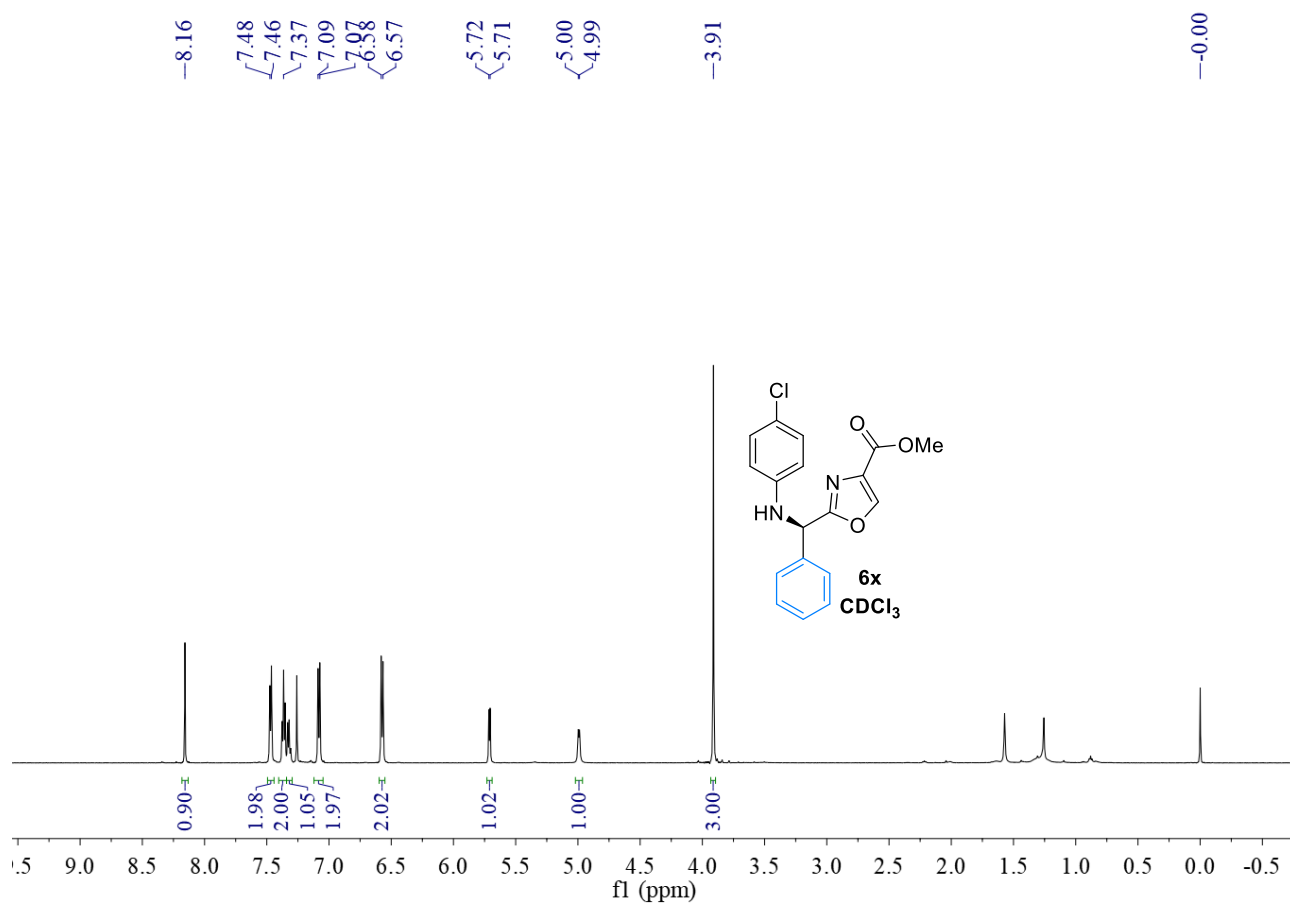


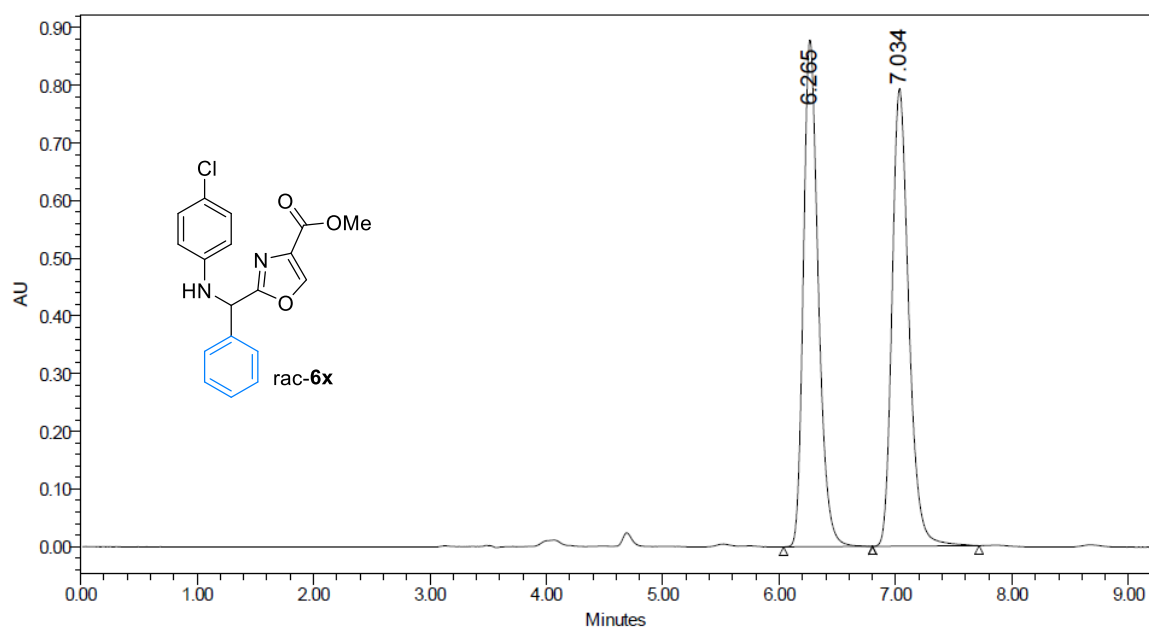


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.534	Unknown	9007040	50.02	1158268	54.66	VB	330	5.392	5.942
2	6.647	Unknown	8999358	49.98	960785	45.34	BB	385	6.433	7.075

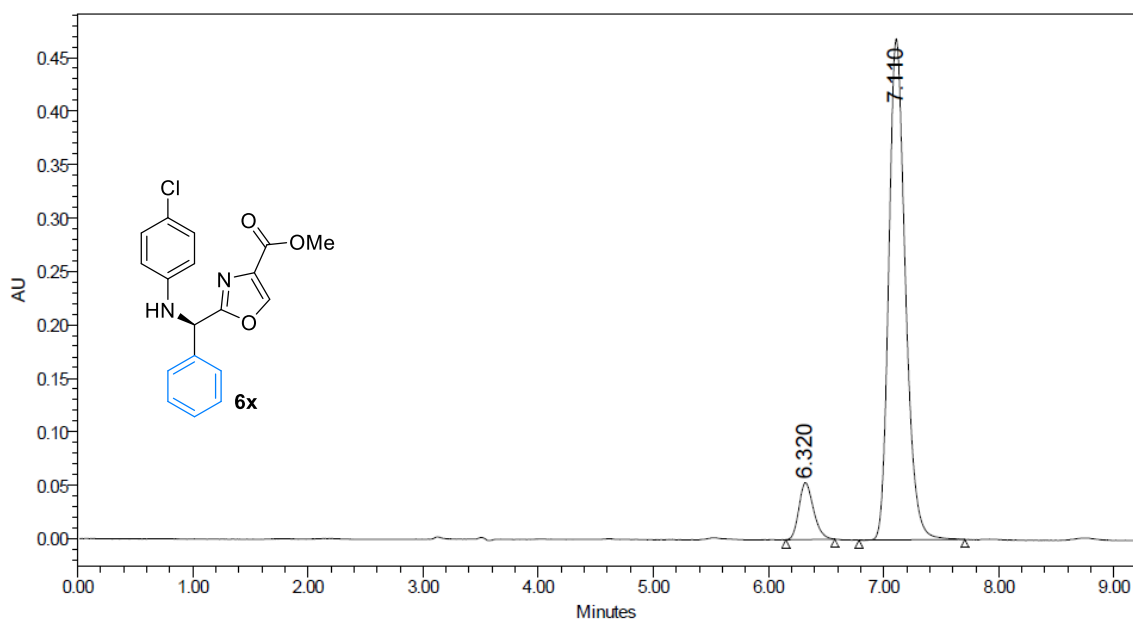


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.540	Unknown	753364	13.14	98317	15.54	bb	249	5.375	5.790
2	6.651	Unknown	4978399	86.86	534536	84.46	bB	414	6.378	7.068

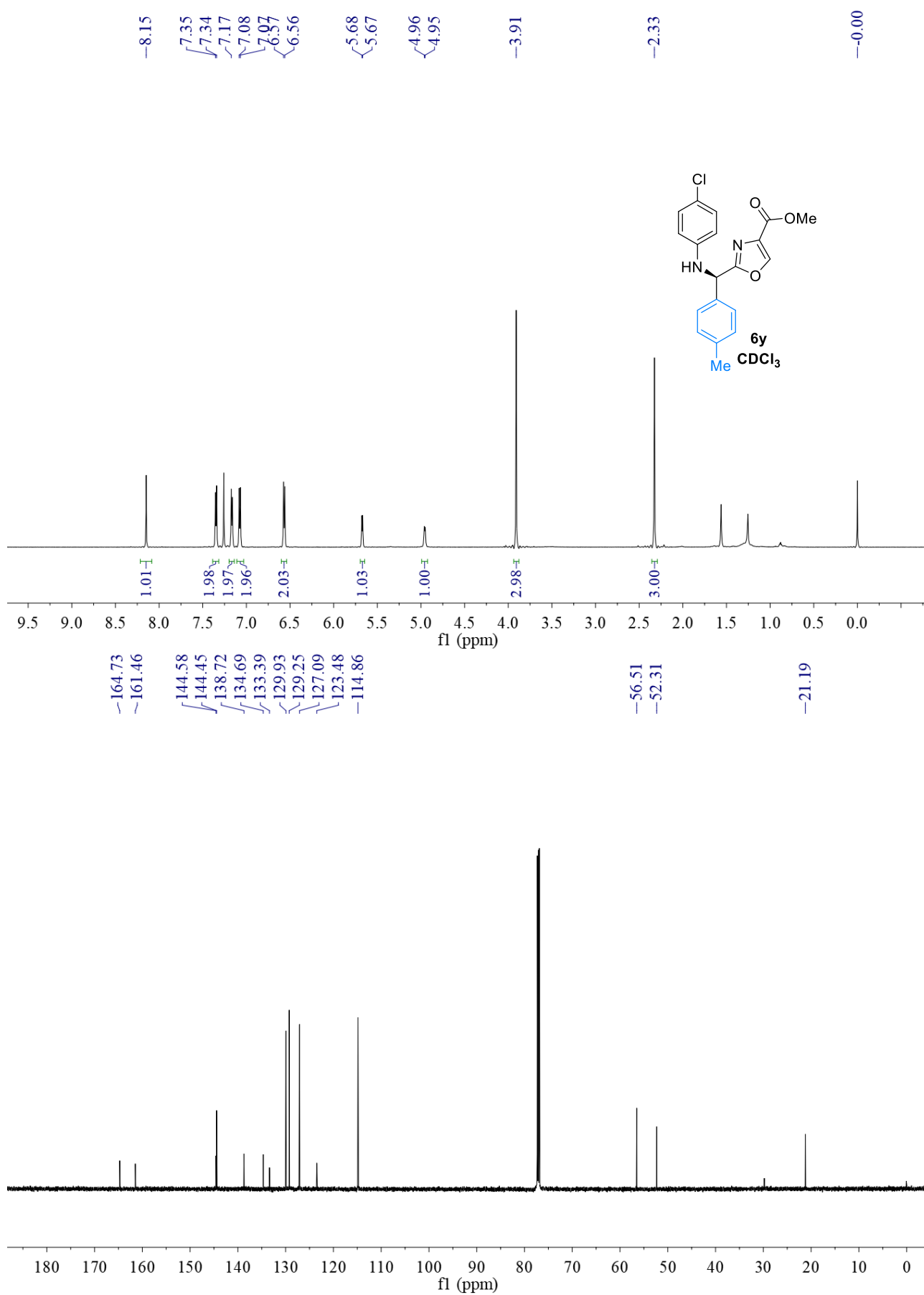


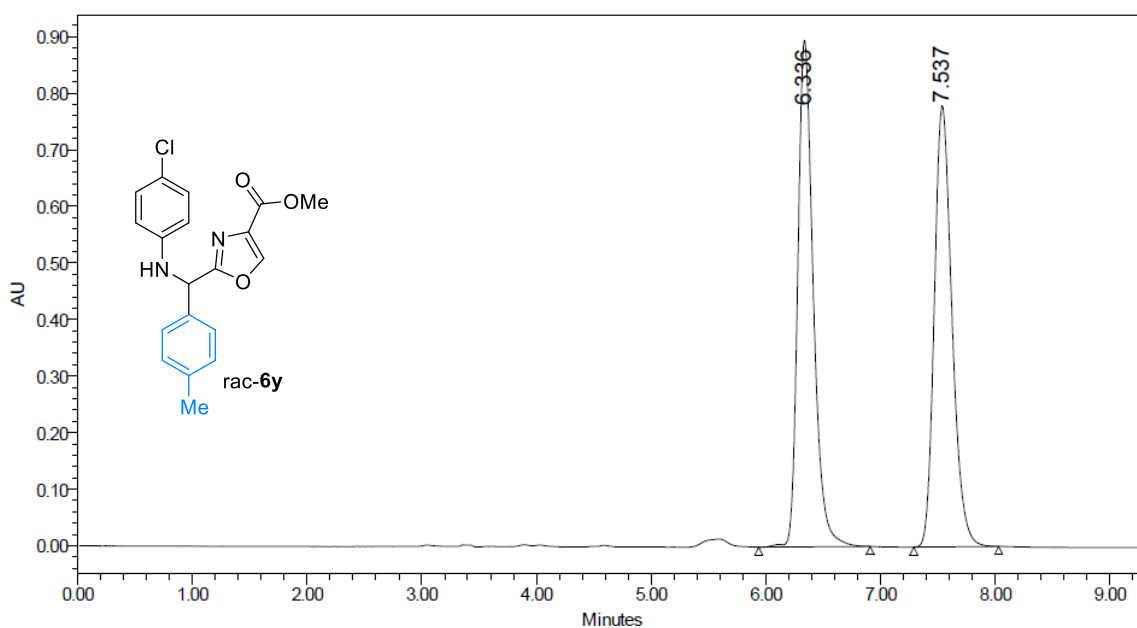


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.265	Unknown	7817319	49.62	878293	52.55	BB	458	6.038	6.802
2	7.034	Unknown	7937904	50.38	793110	47.45	BB	549	6.802	7.717

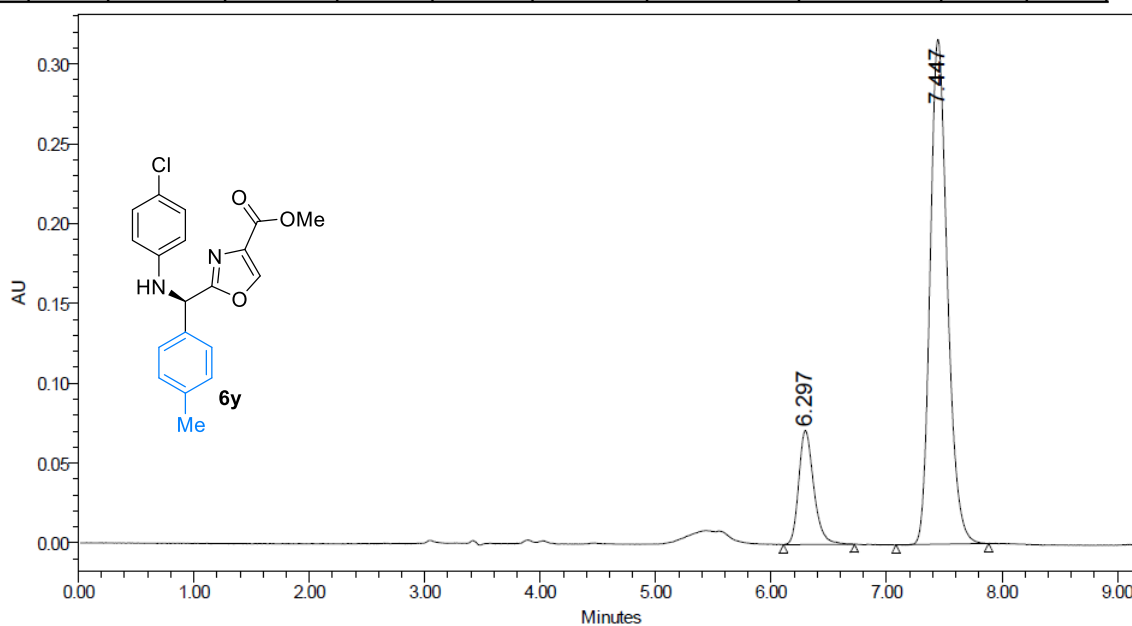


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.320	Unknown	467263	9.04	53090	10.17	Bb	255	6.152	6.577
2	7.110	Unknown	4701232	90.96	468960	89.83	bb	551	6.787	7.705

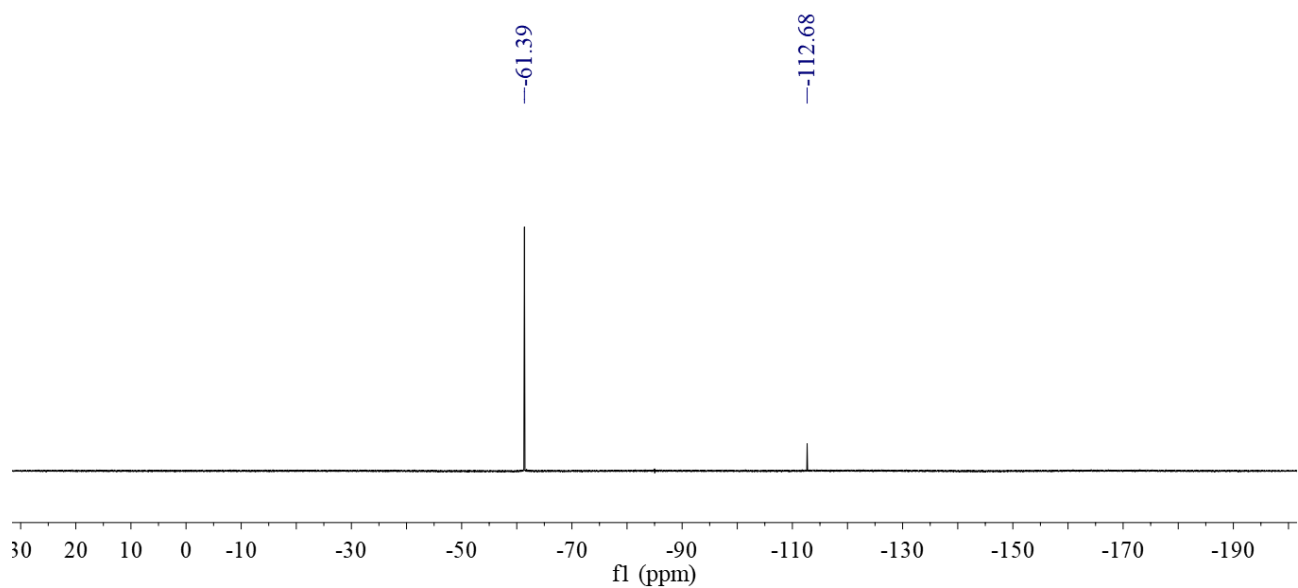
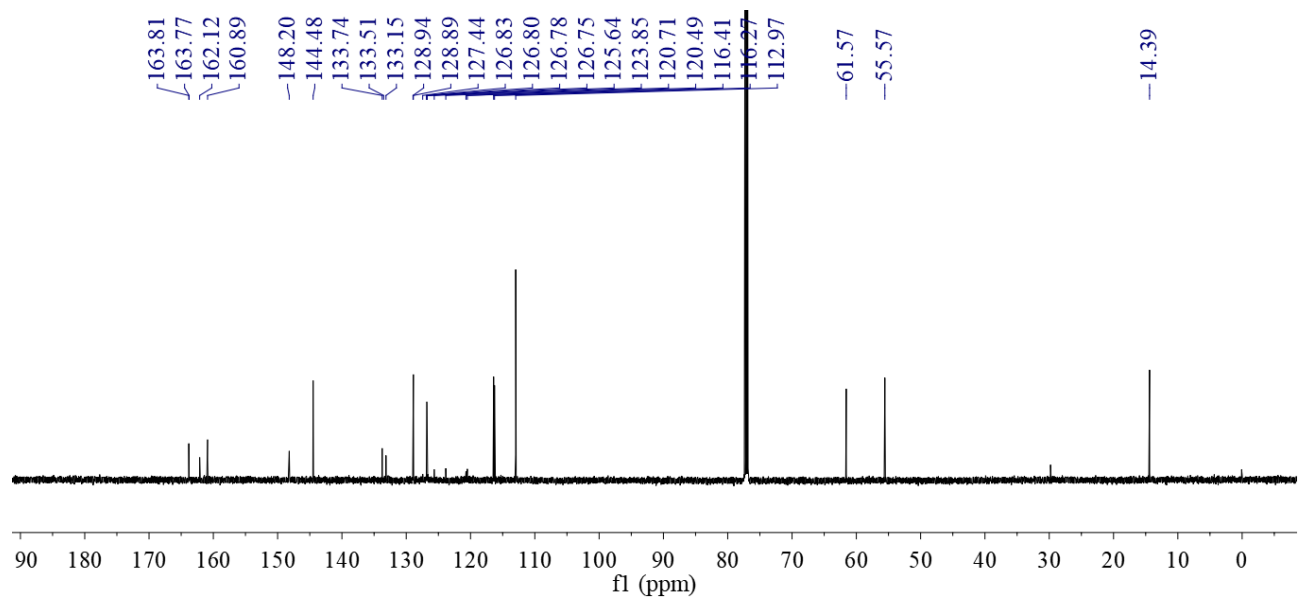
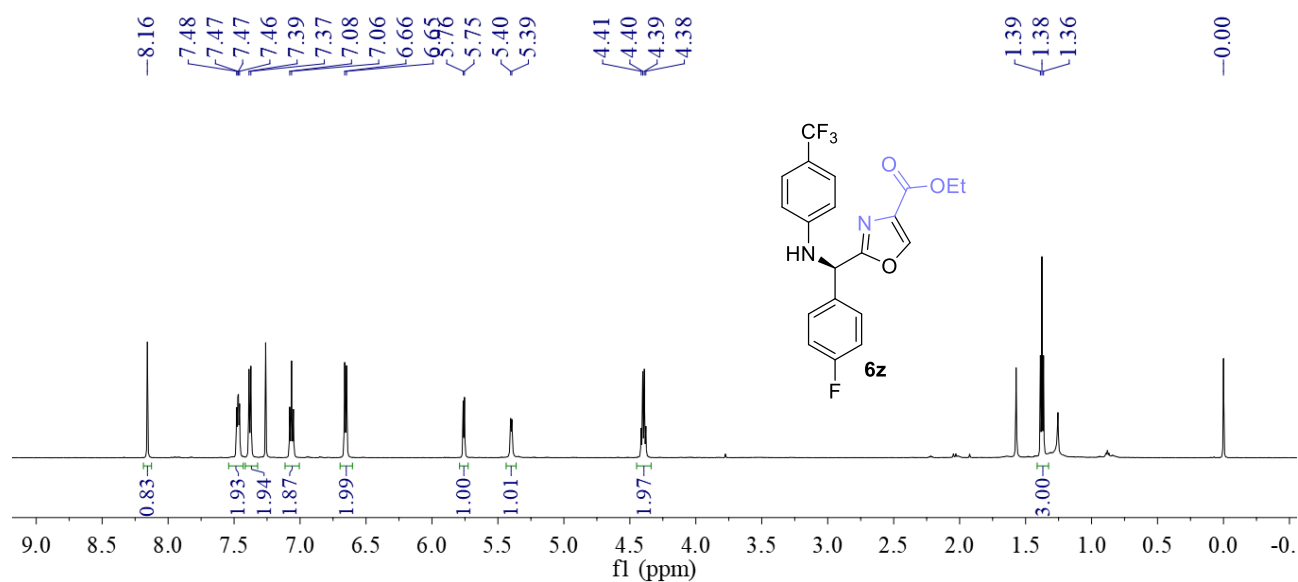


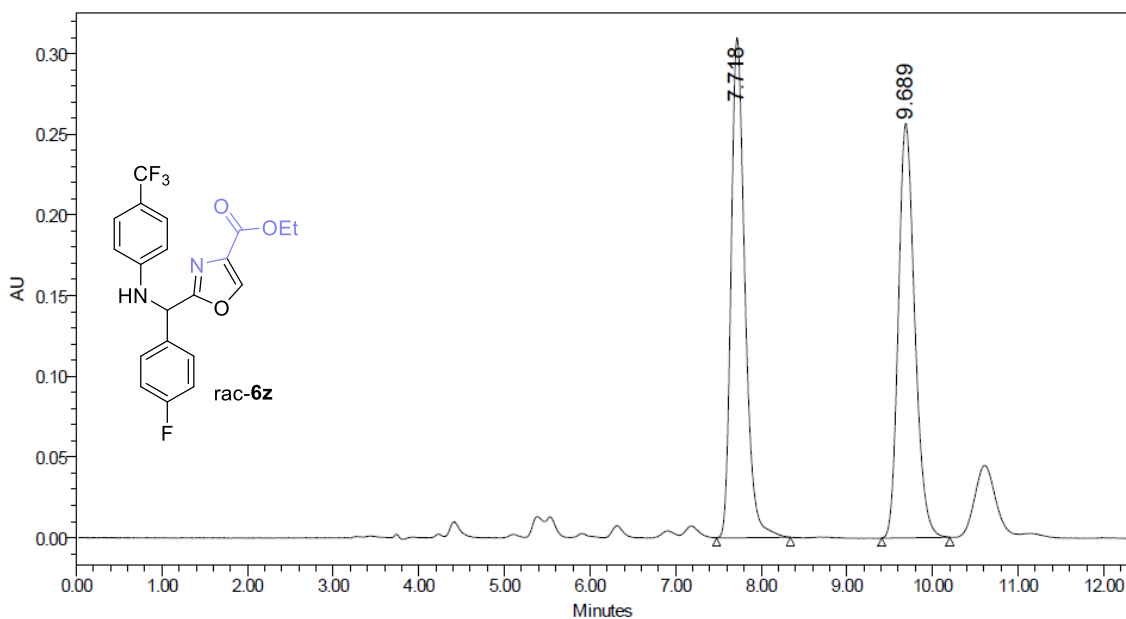


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.336	Unknown	8402080	50.21	895523	53.48	BB	583	5.937	6.908
2	7.537	Unknown	8331825	49.79	779070	46.52	BB	444	7.288	8.028

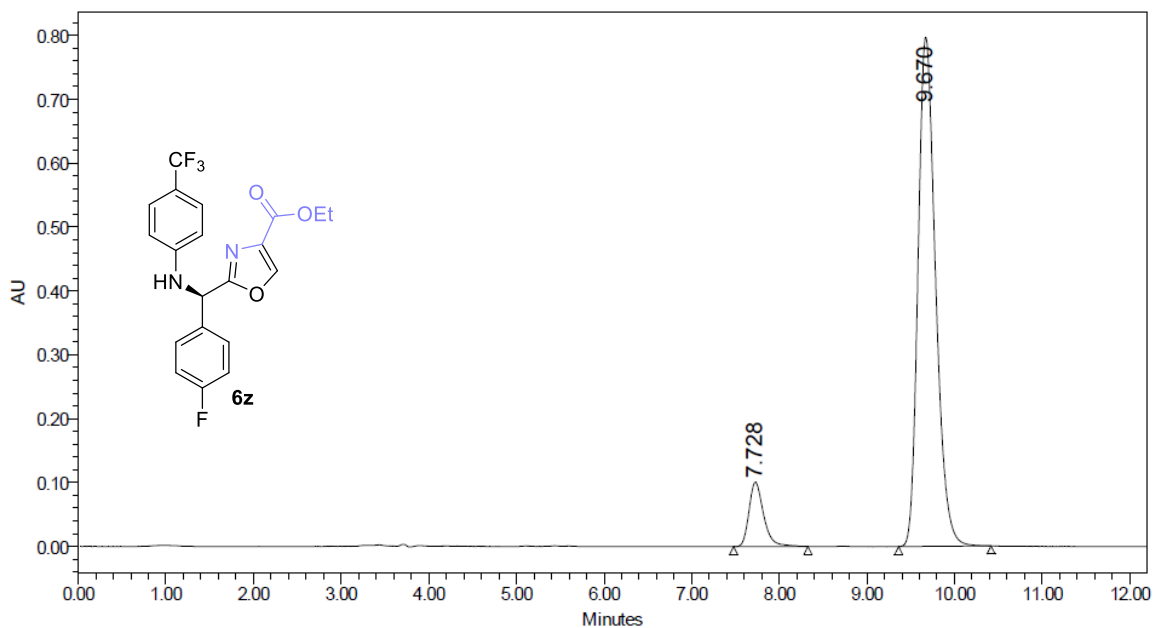


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.297	Unknown	649842	16.49	71521	18.44	Bb	369	6.108	6.723
2	7.447	Unknown	3292137	83.51	316310	81.56	bB	481	7.083	7.885

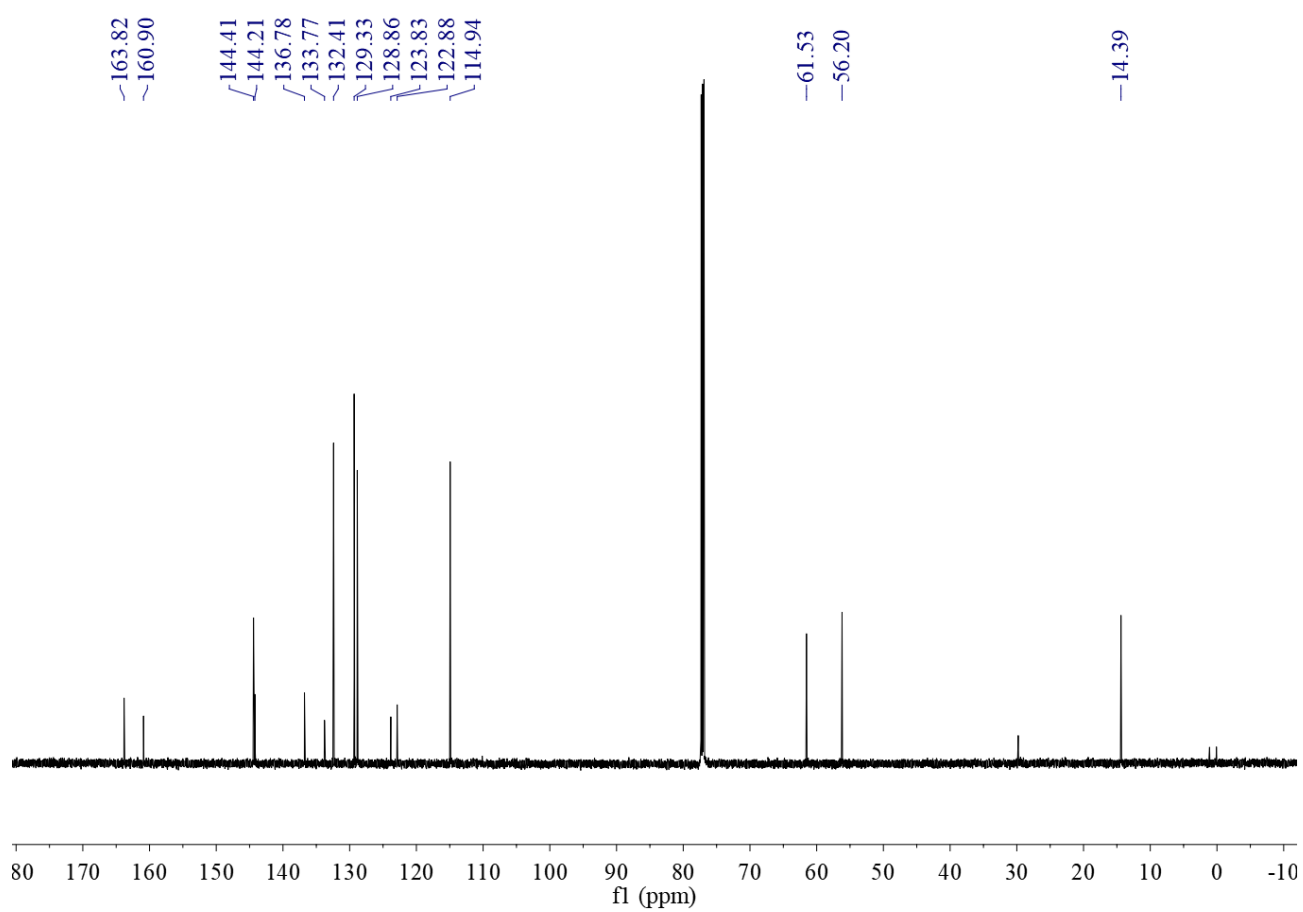
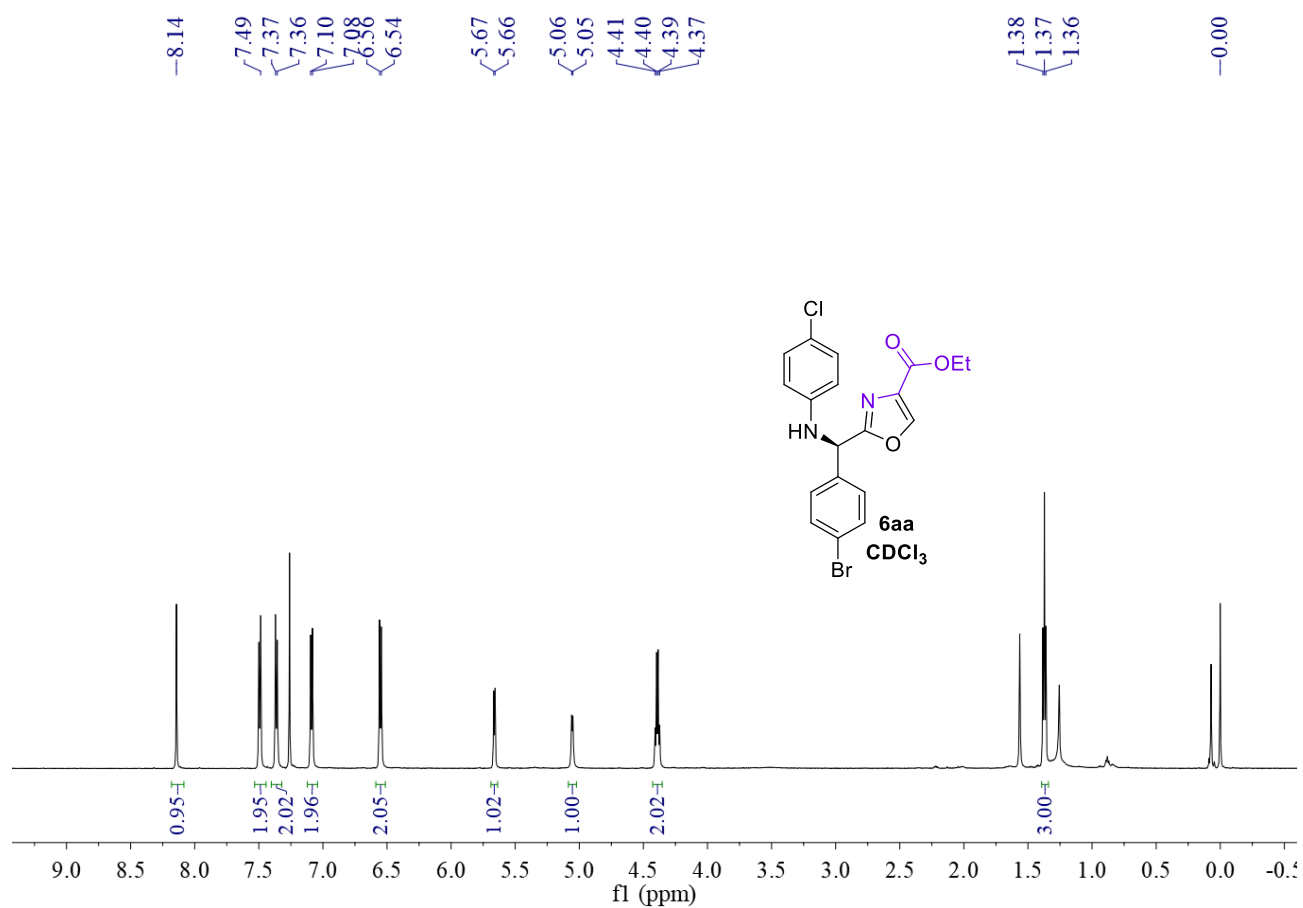


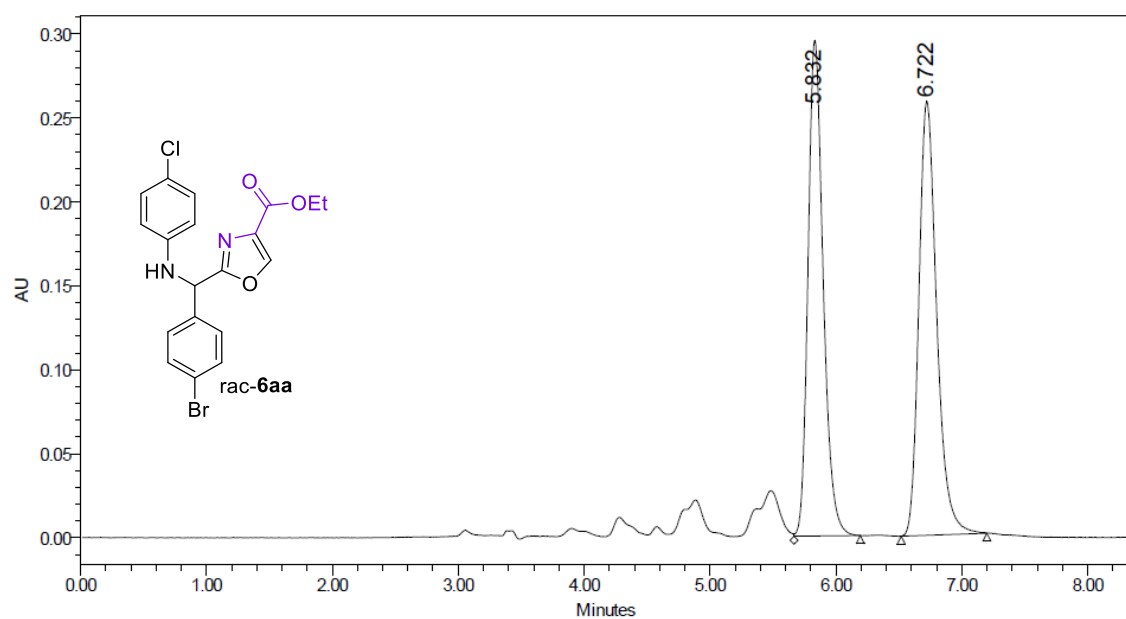


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.718	Unknown	3482899	50.49	309875	54.68	BB	519	7.477	8.342
2	9.689	Unknown	3415538	49.51	256811	45.32	BB	477	9.408	10.203

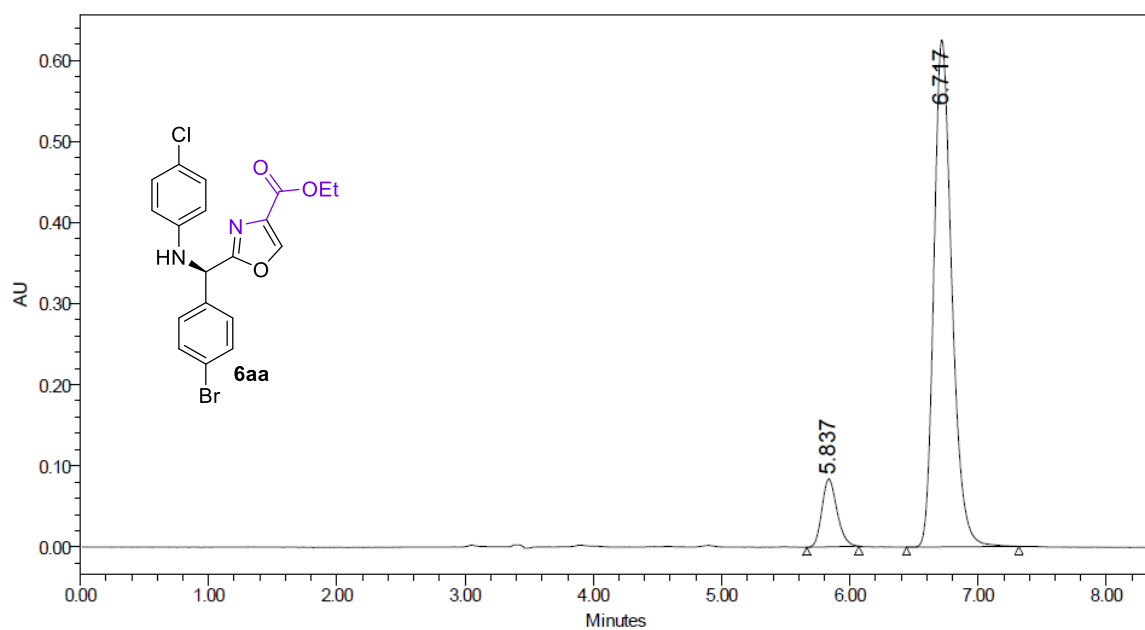


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.728	Unknown	1172023	9.58	100688	11.21	BB	508	7.478	8.325
2	9.670	Unknown	11061418	90.42	797263	88.79	BB	632	9.362	10.415

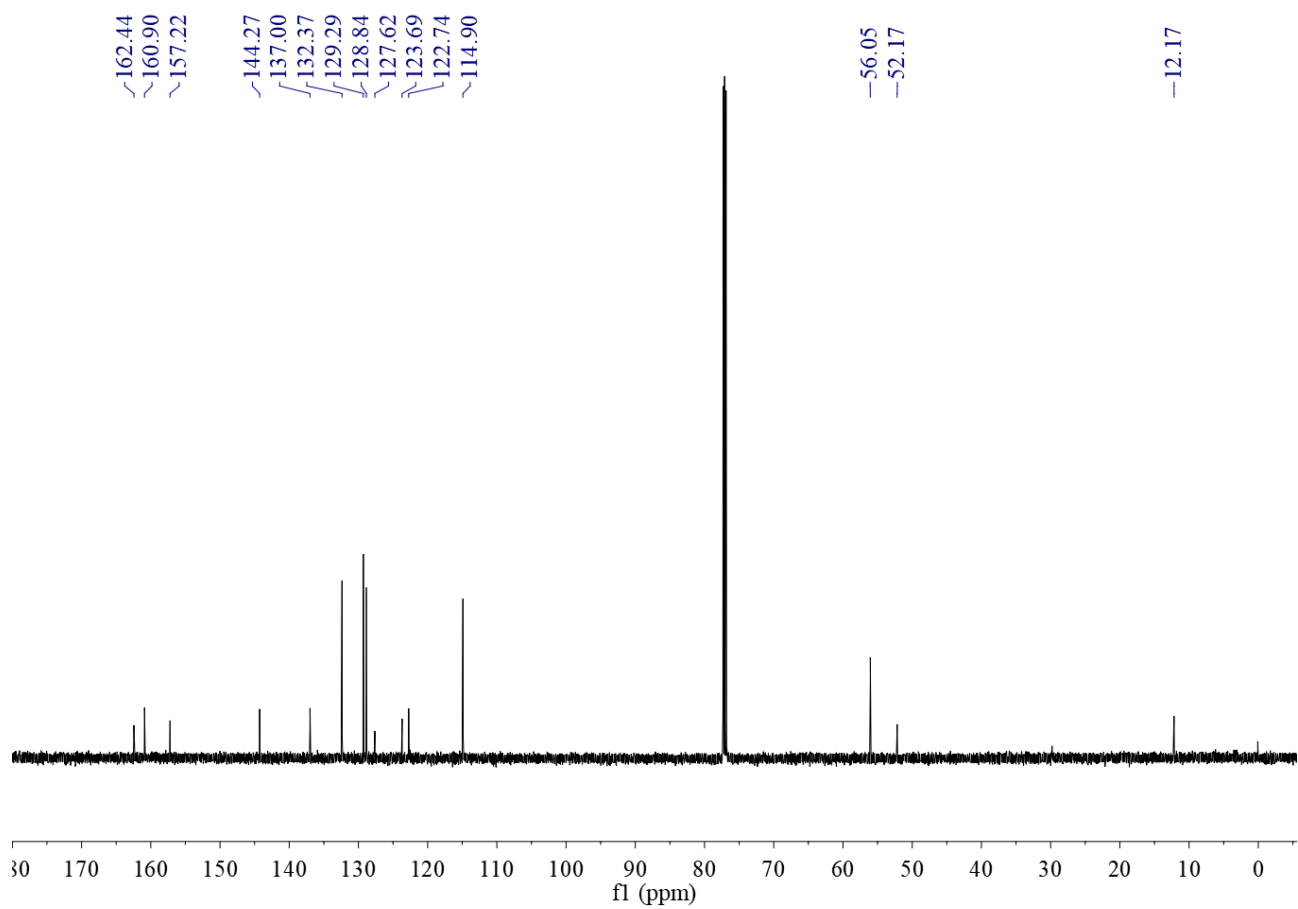
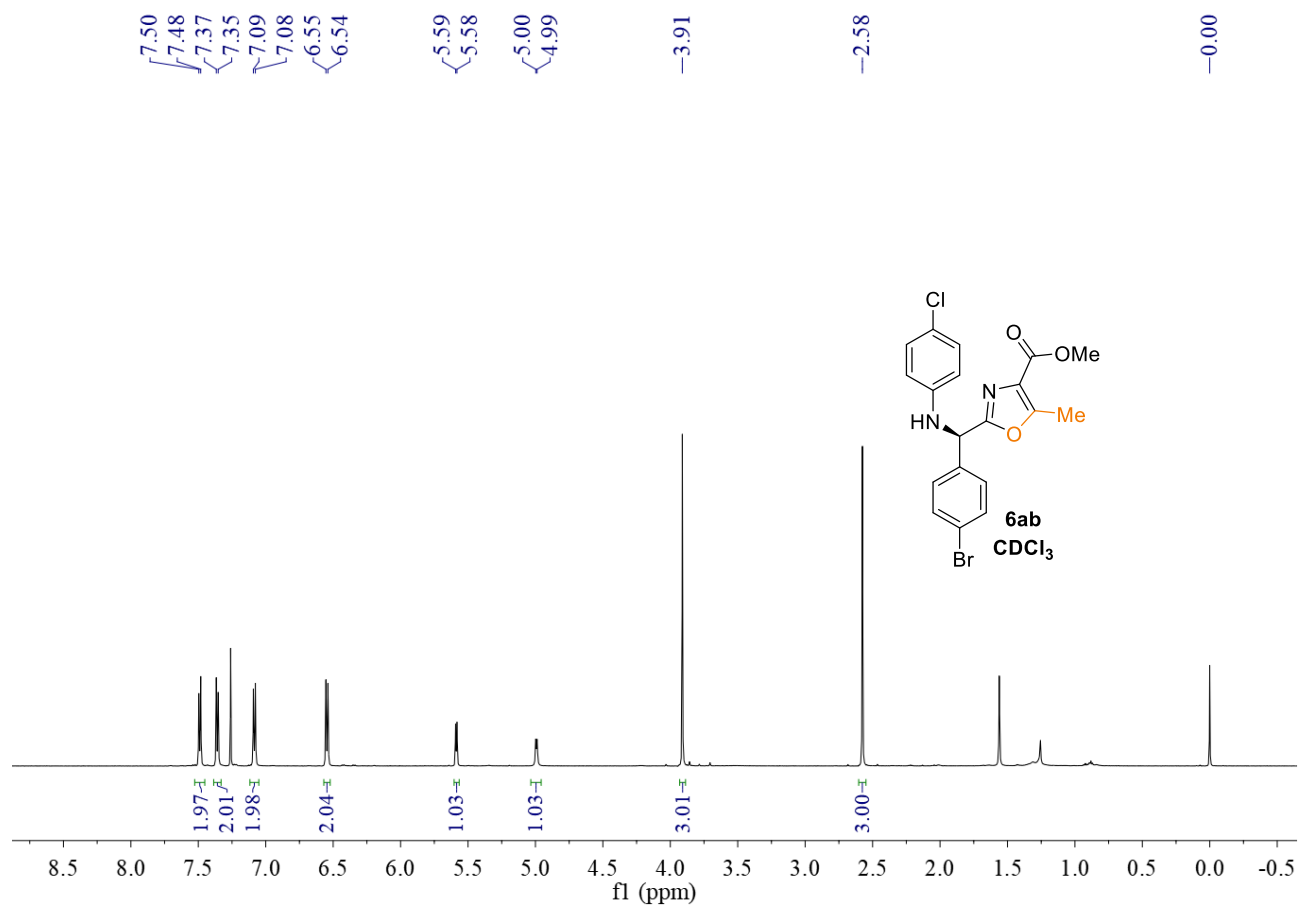


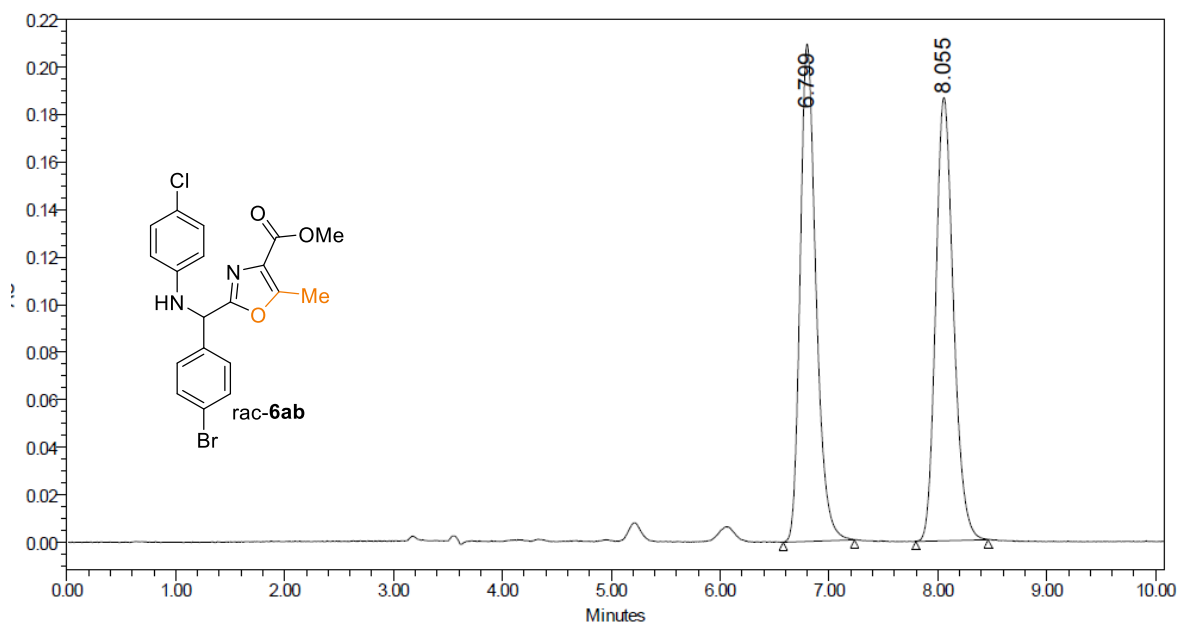


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.832	Unknown	2468357	49.20	295260	53.32	VB	316	5.667	6.193
2	6.722	Unknown	2548437	50.80	258503	46.68	BB	408	6.518	7.198

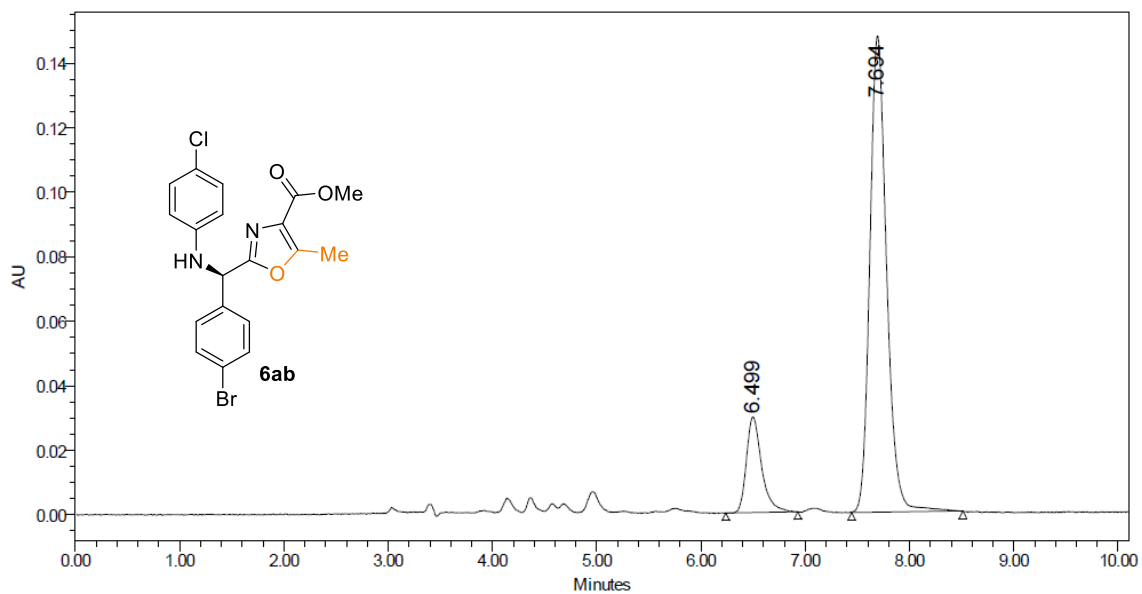


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.837	Unknown	686617	10.15	83692	11.81	bb	243	5.665	6.070
2	6.717	Unknown	6075144	89.85	625130	88.19	bb	526	6.442	7.318

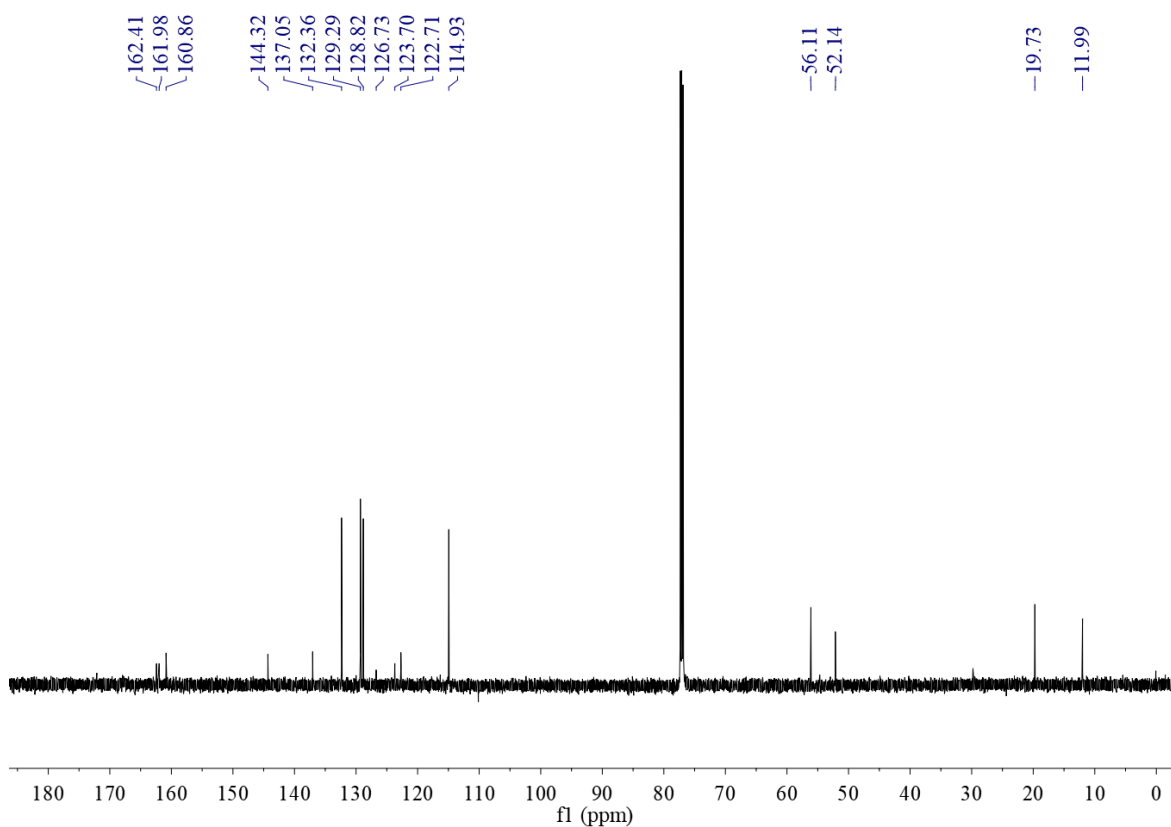
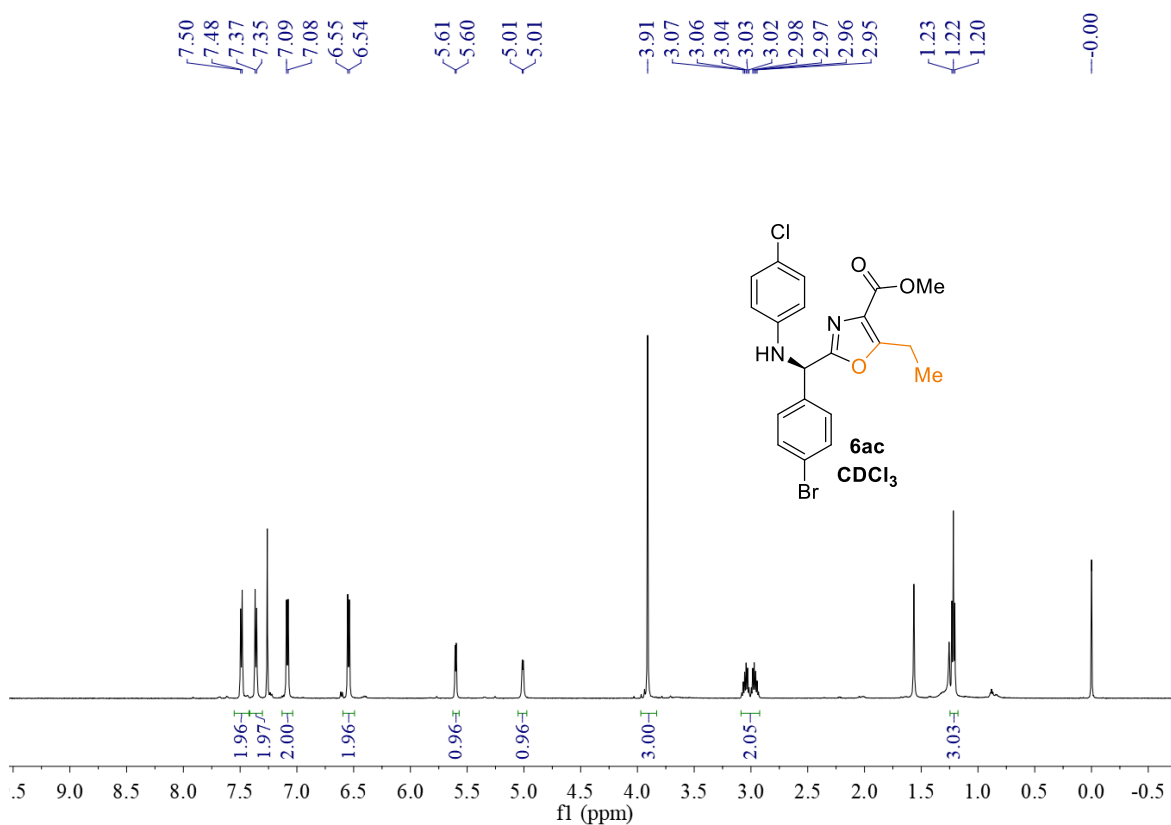


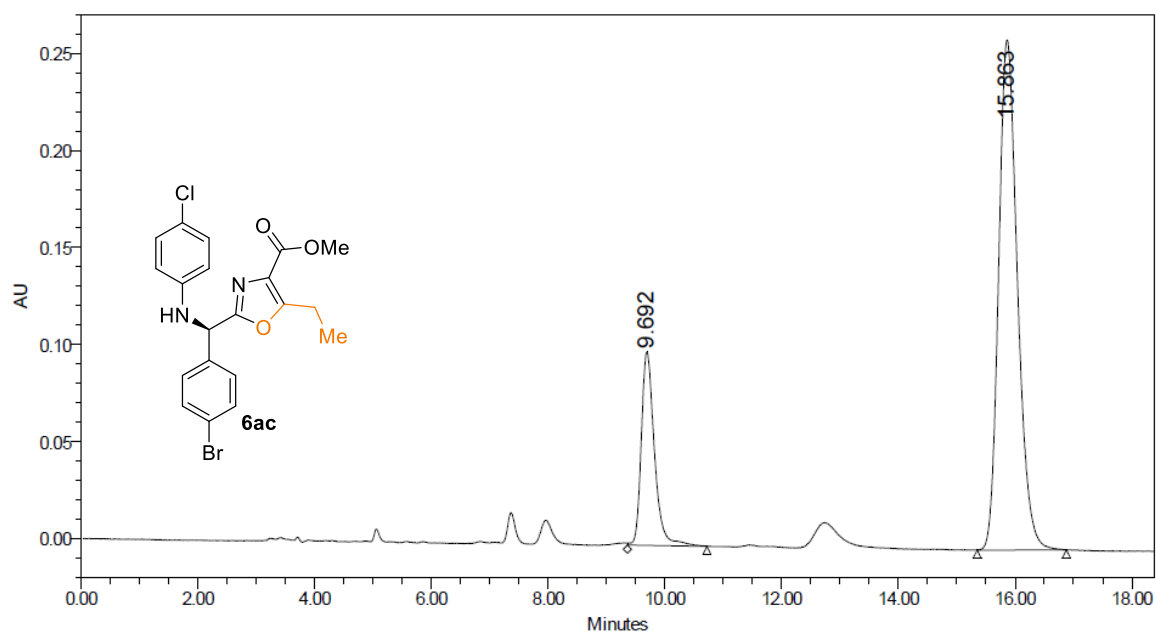
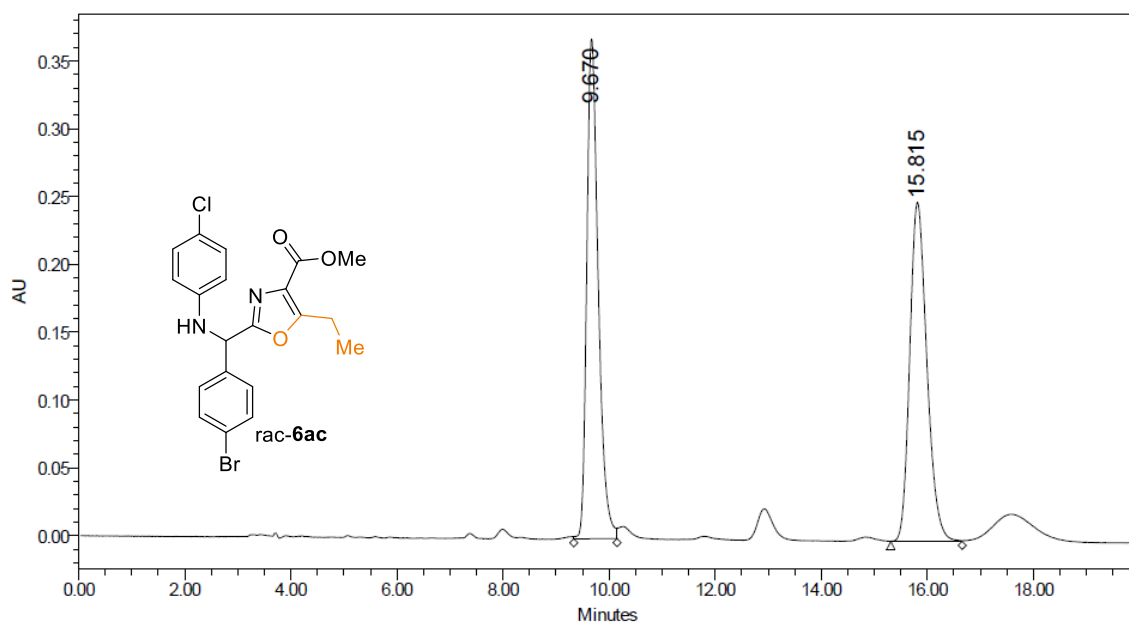


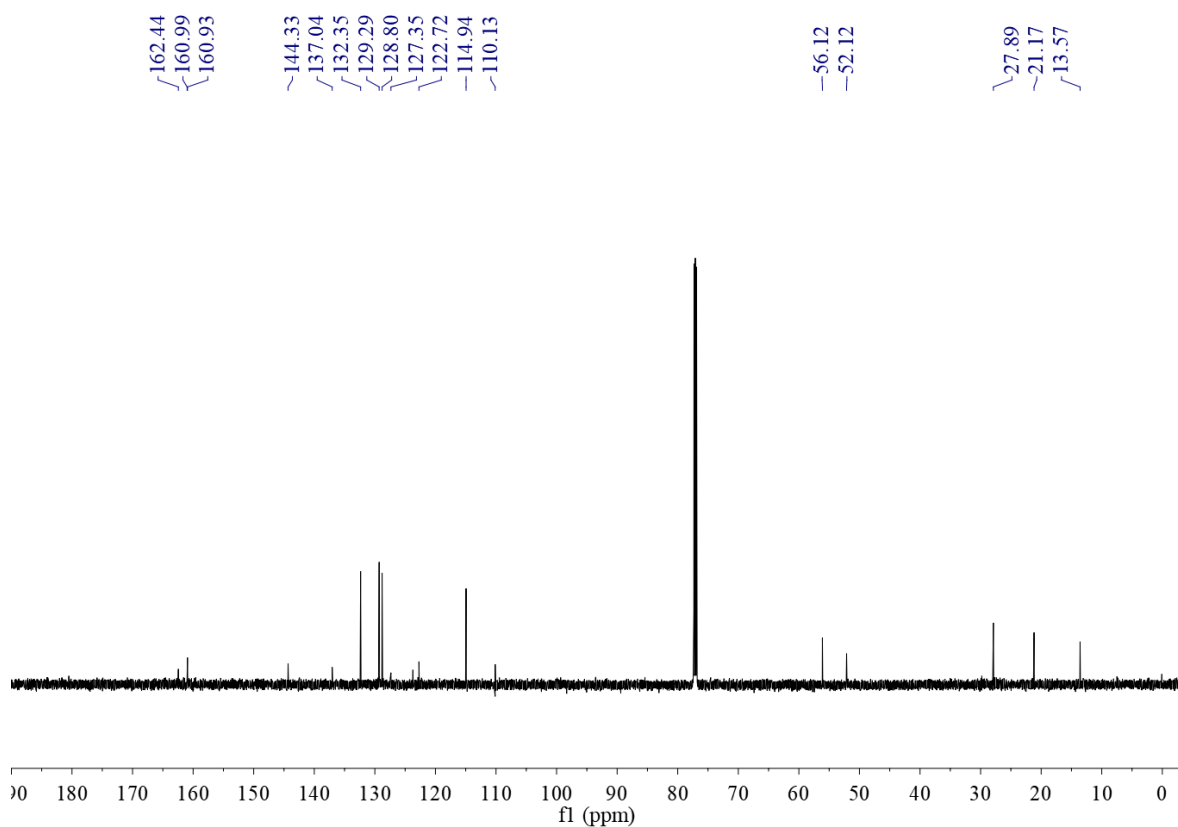
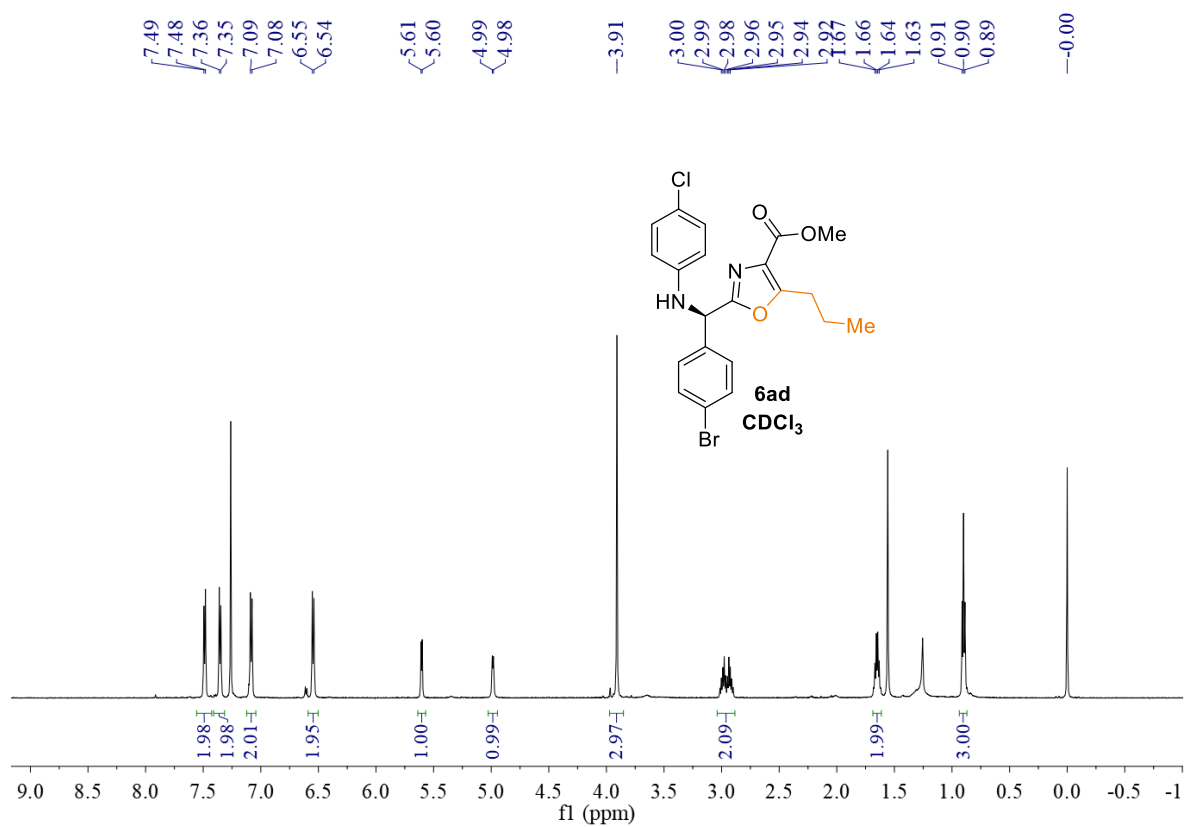
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	6.799	2119740	49.99	209261	52.88
2	8.055	2120767	50.01	186463	47.12

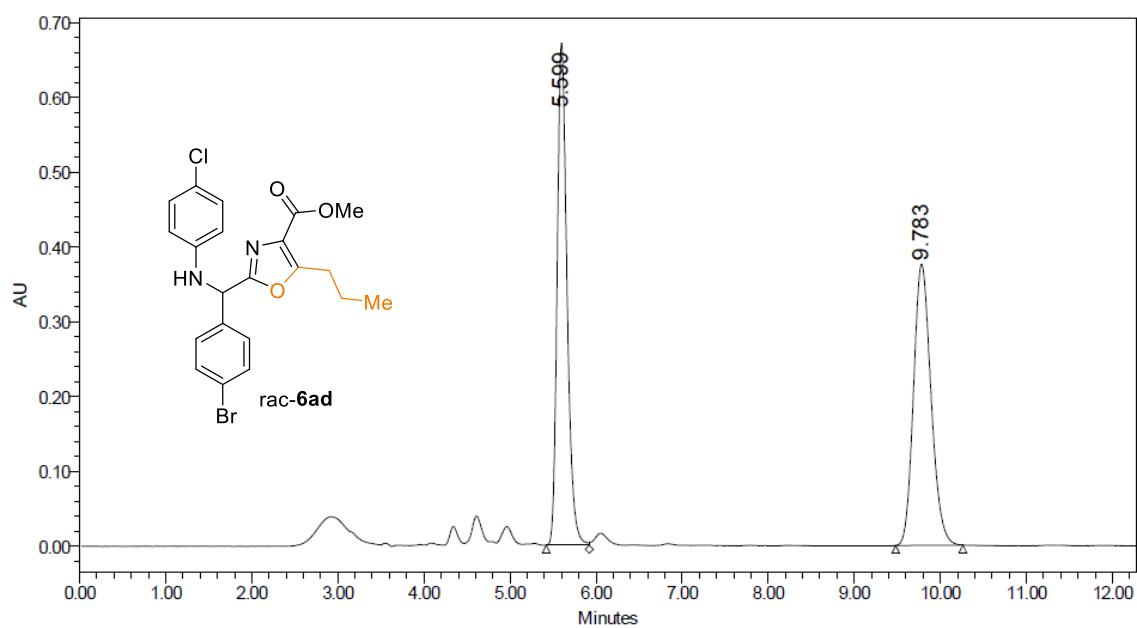


	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	6.499	300229	15.43	29634	16.72
2	7.694	1645872	84.57	147589	83.28

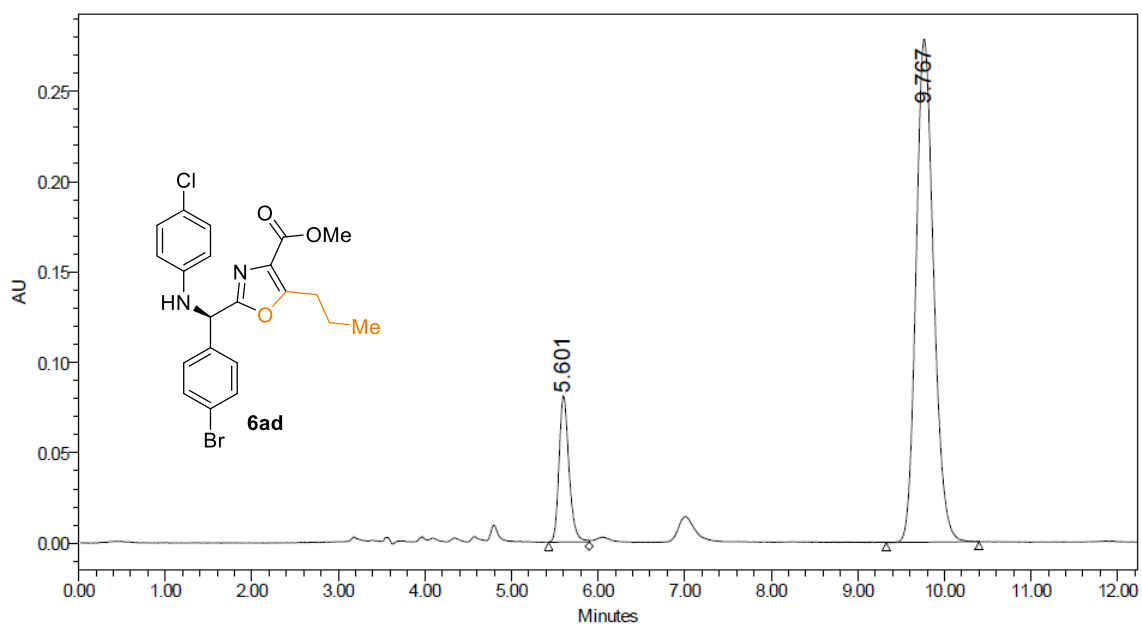




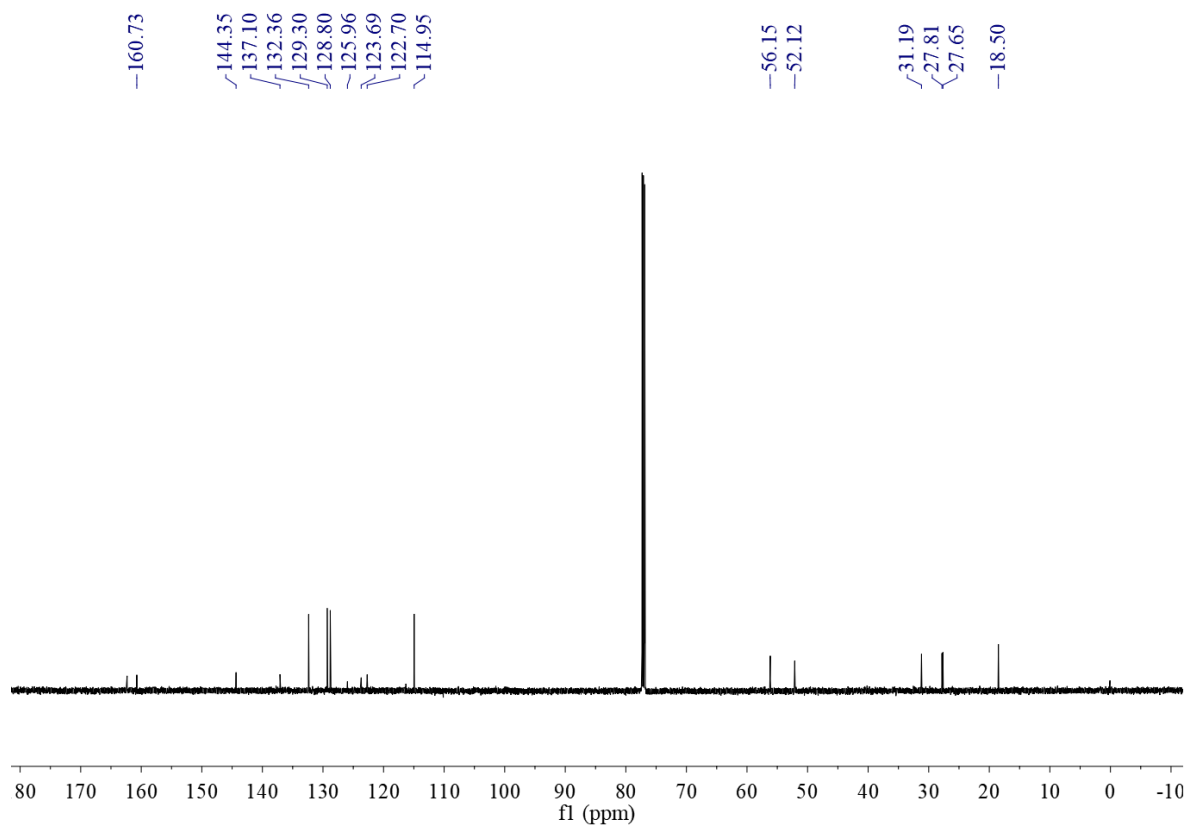
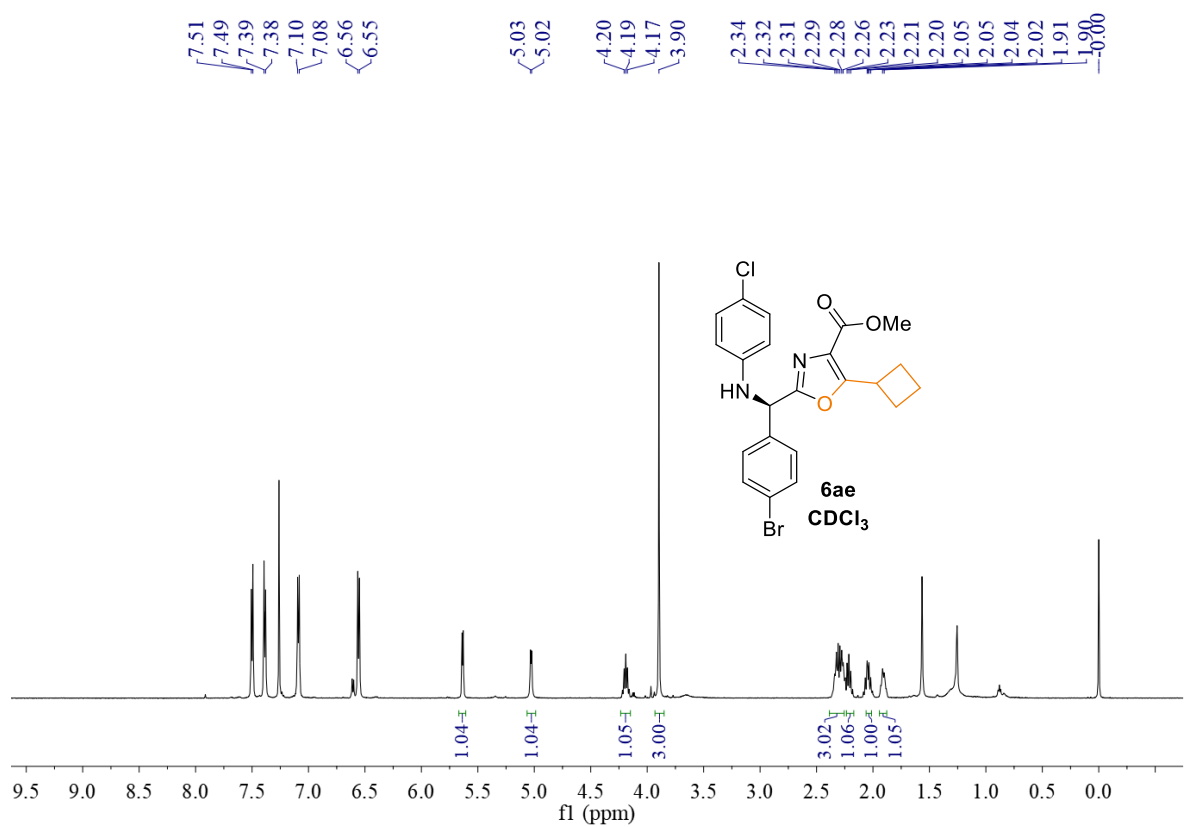


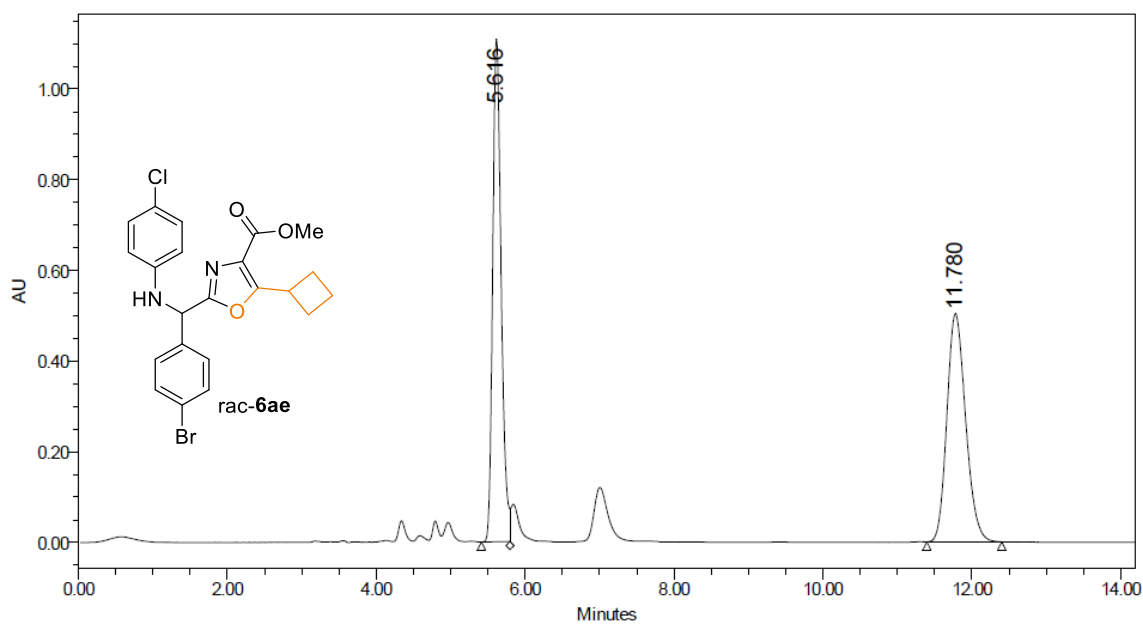


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.599	Unknown	5325804	50.05	671192	64.11	BV	300	5.422	5.922
2	9.783	Unknown	5314123	49.95	375798	35.89	BB	468	9.482	10.262

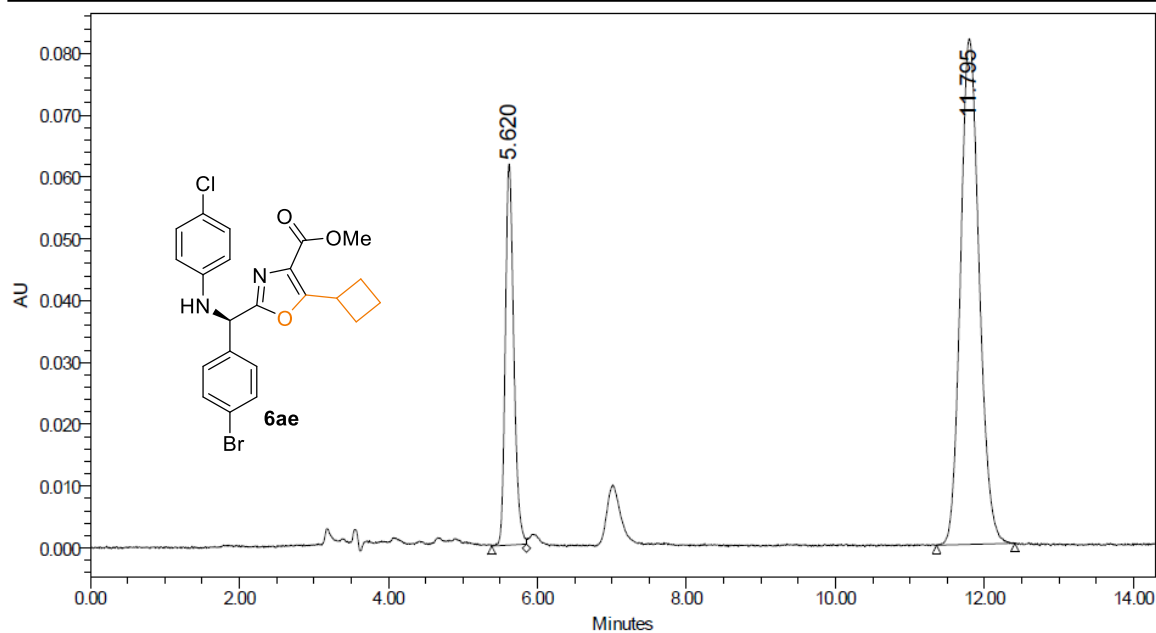


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.601	Unknown	647164	14.14	80745	22.49	BV	281	5.428	5.897
2	9.767	Unknown	3928812	85.86	278324	77.51	bb	643	9.328	10.400

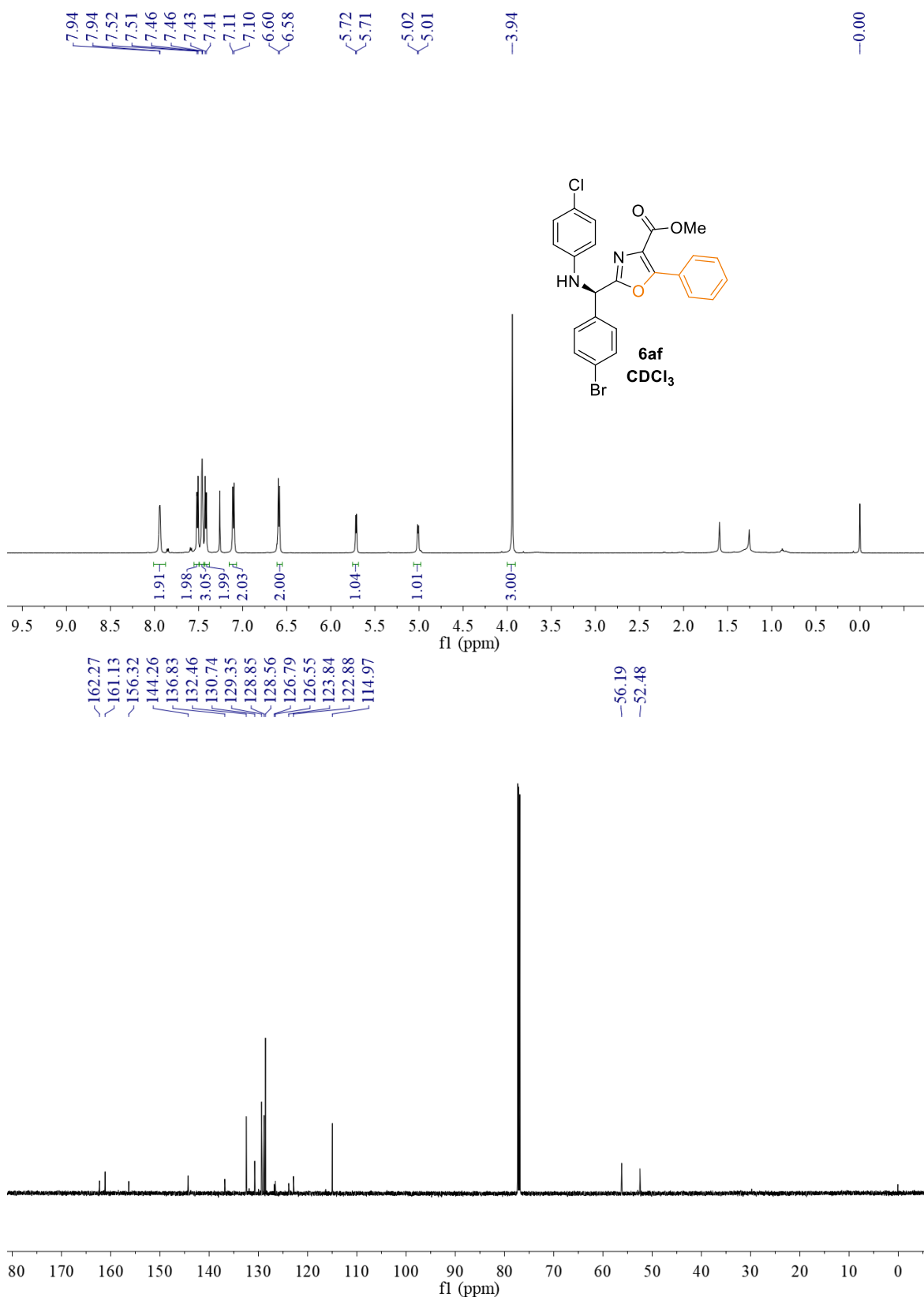


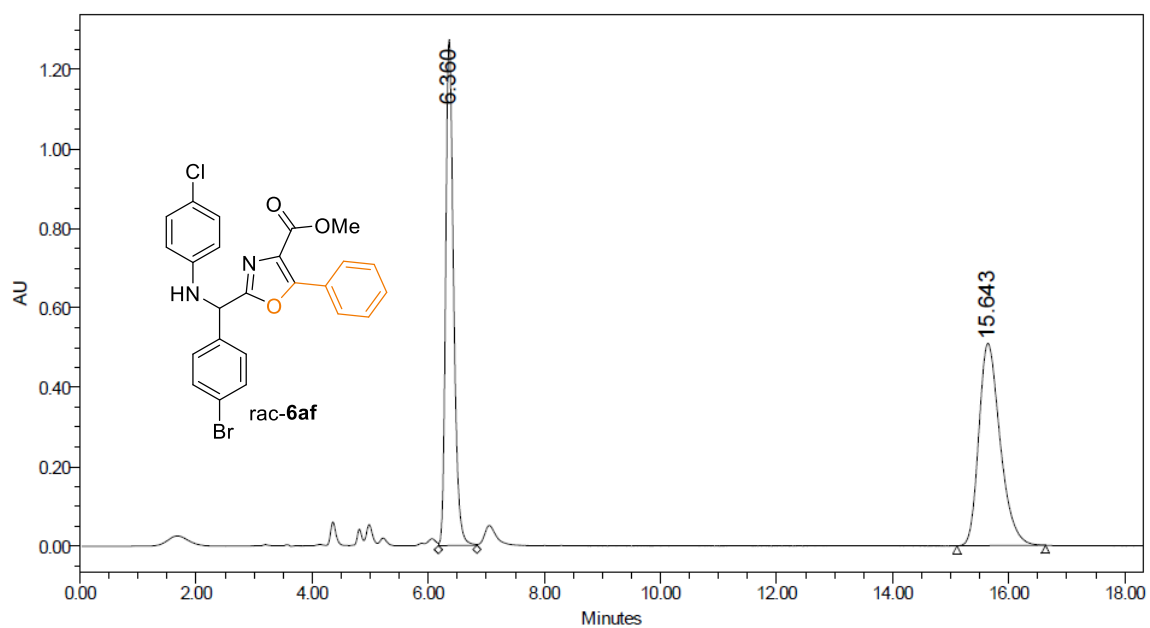


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.616	Unknown	8743051	49.78	1108615	68.79	BV	230	5.413	5.797
2	11.780	Unknown	8819711	50.22	502942	31.21	BB	603	11.397	12.402

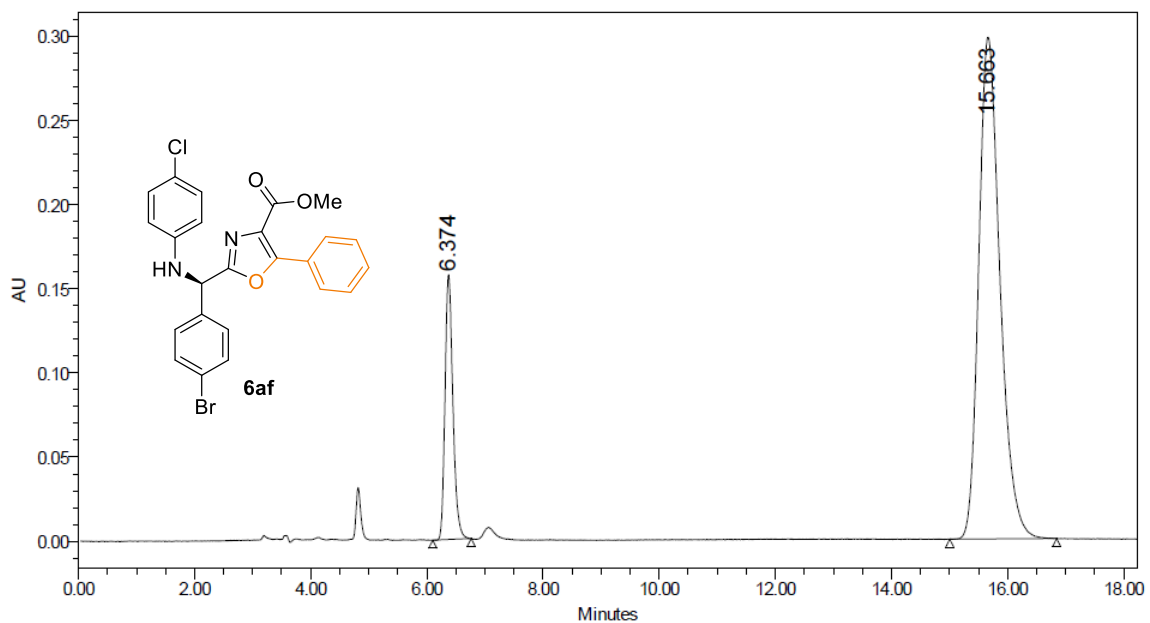


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.620	Unknown	488140	25.48	61640	42.97	BV	279	5.387	5.852
2	11.795	Unknown	1427801	74.52	81809	57.03	bb	630	11.357	12.407

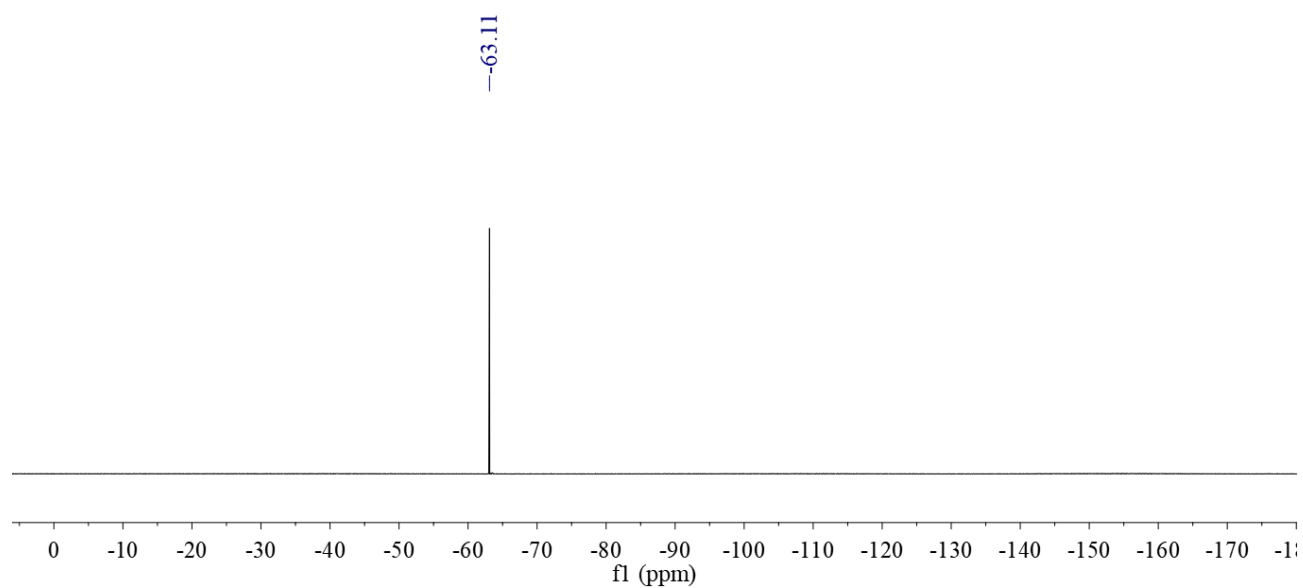
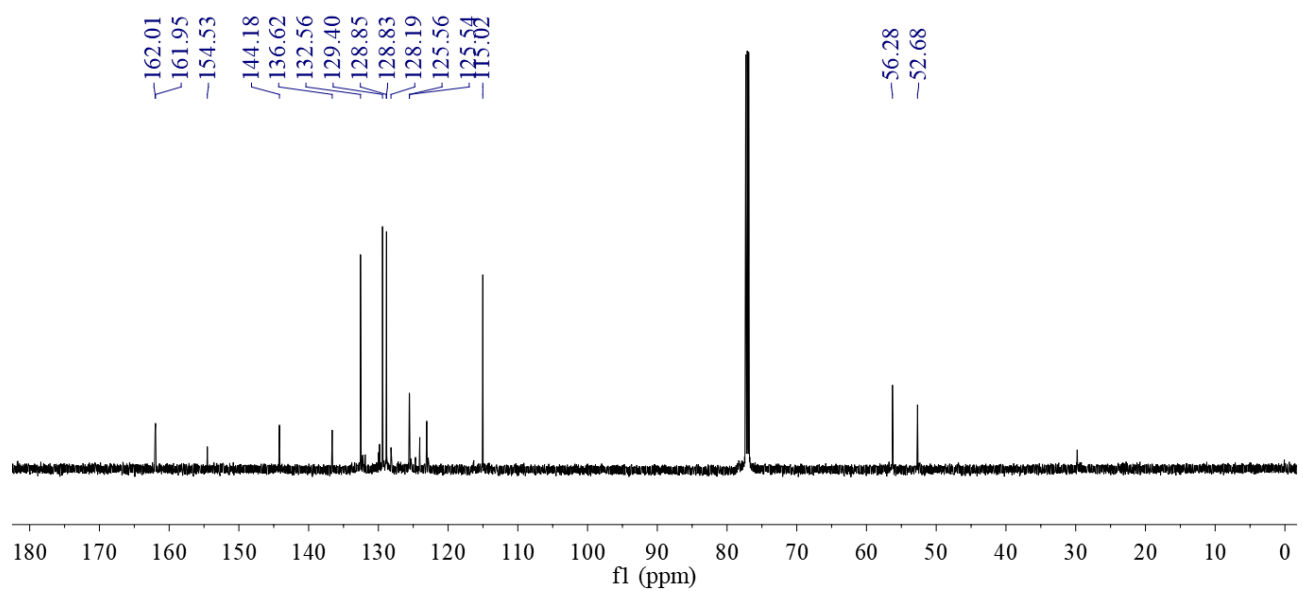
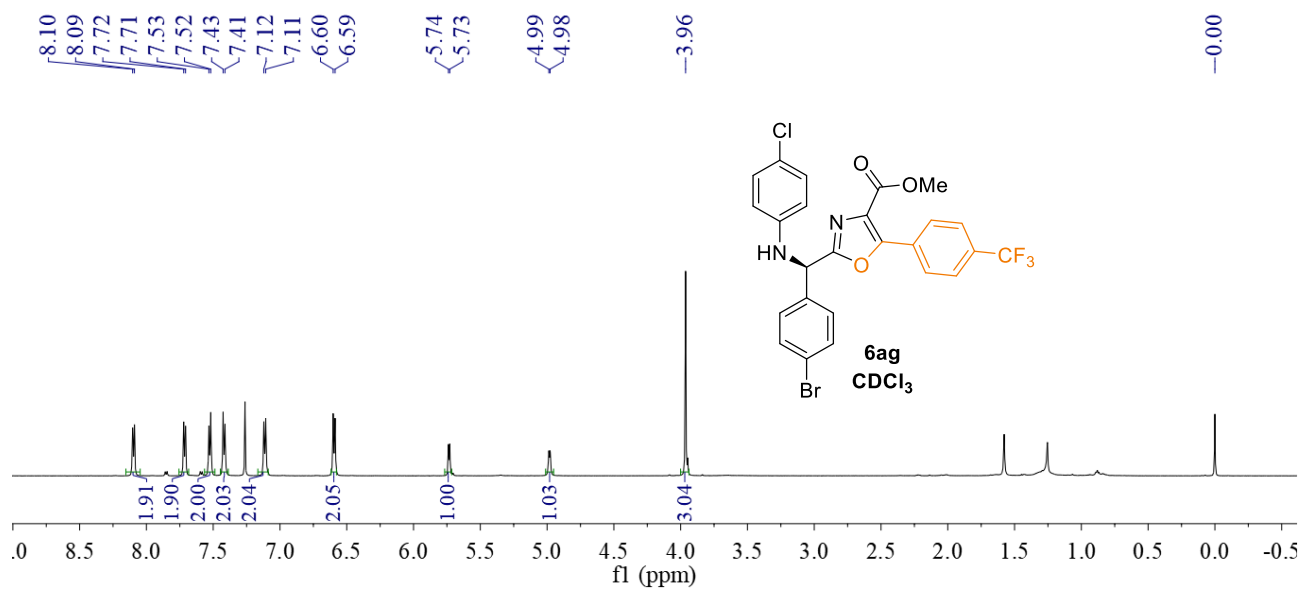


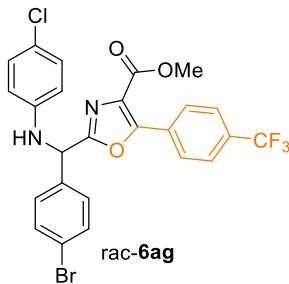


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)
1	6.360	Unknown	12090148	48.23	1273493	71.45	VV	400	6.175
2	15.643	Unknown	12978803	51.77	508875	28.55	BB	915	15.110

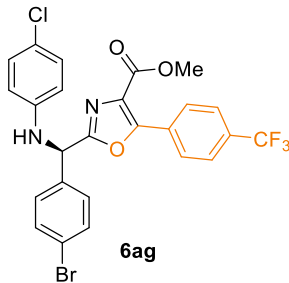


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	6.374	Unknown	1483428	16.37	157413	34.57	bb	397	6.102	6.763
2	15.663	Unknown	7578644	83.63	297990	65.43	bb	1105	15.005	16.847

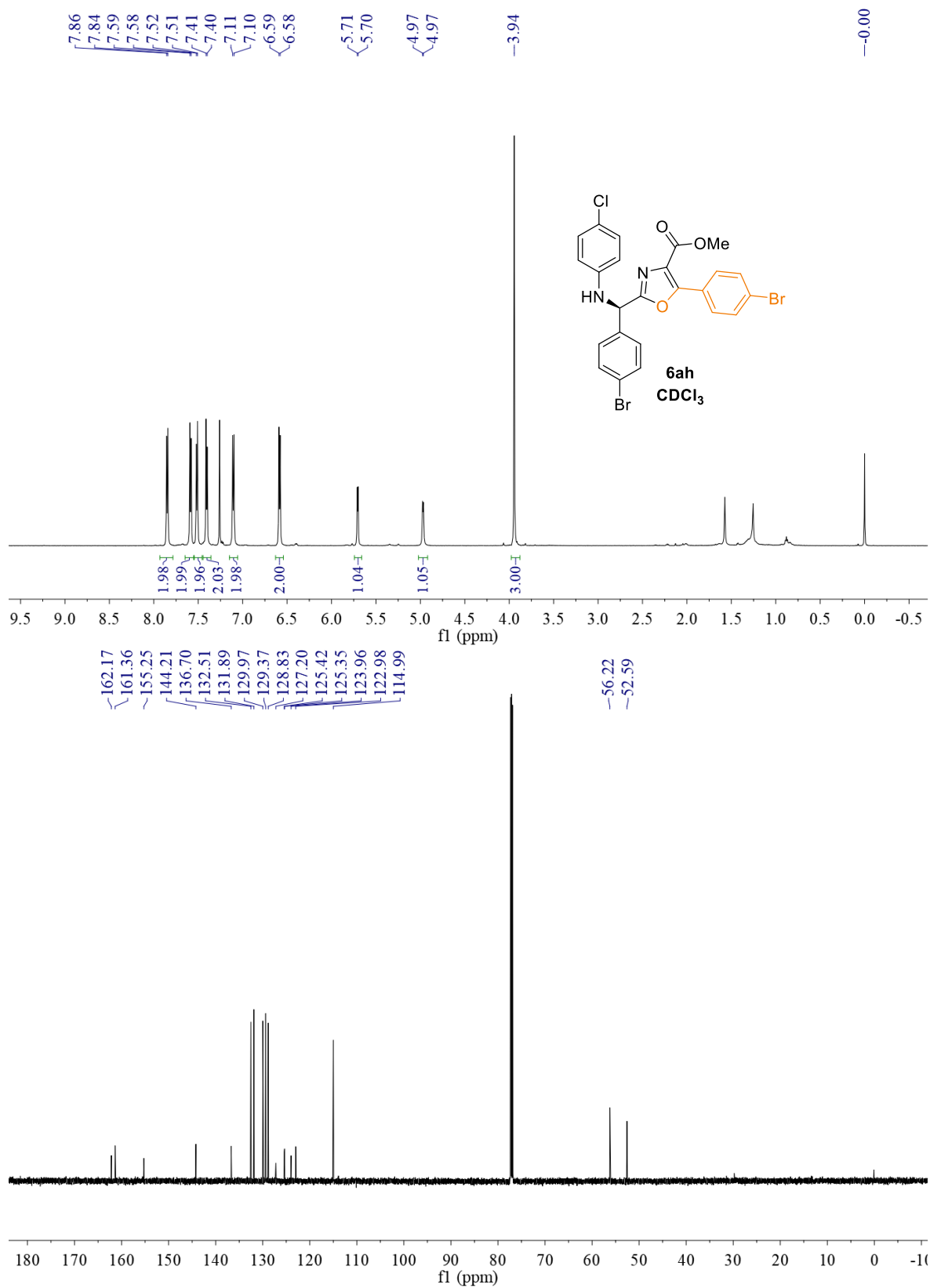


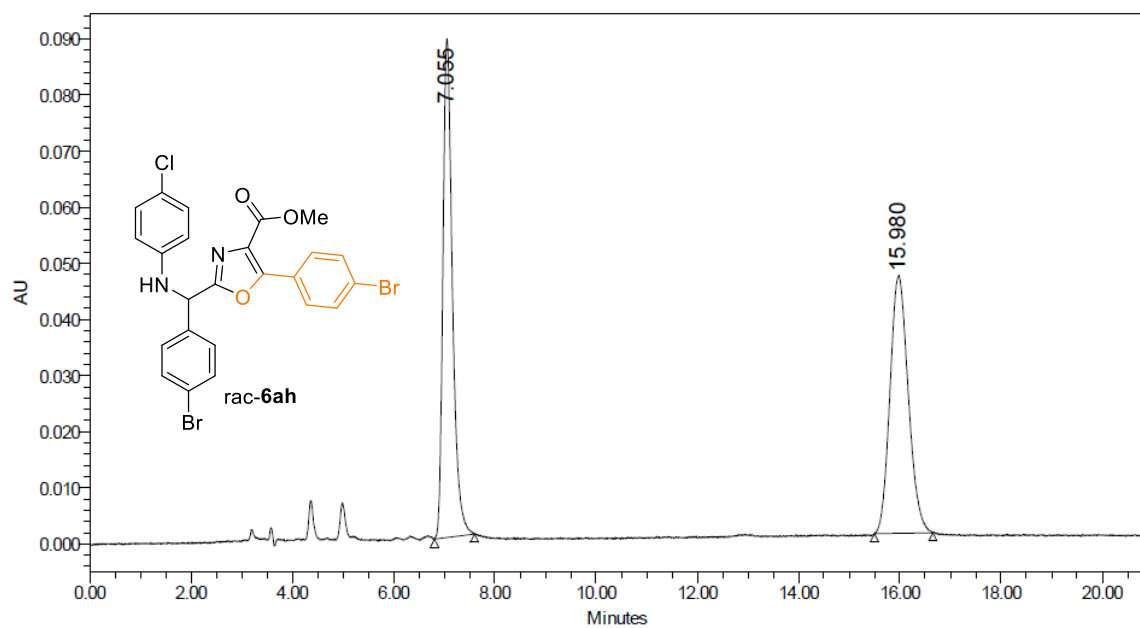


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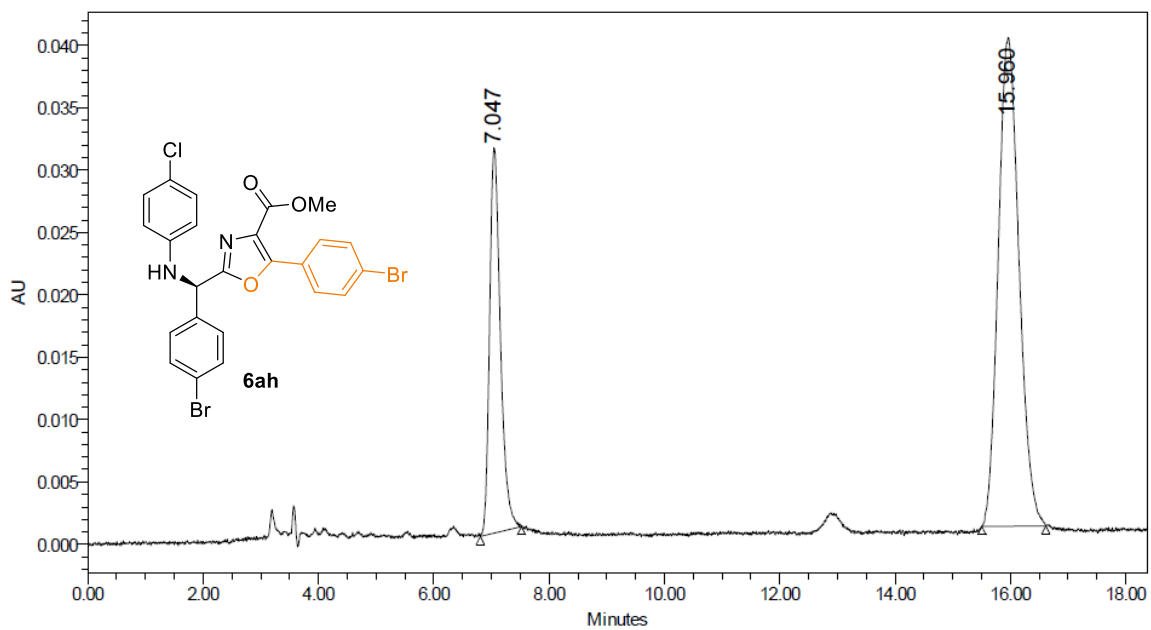


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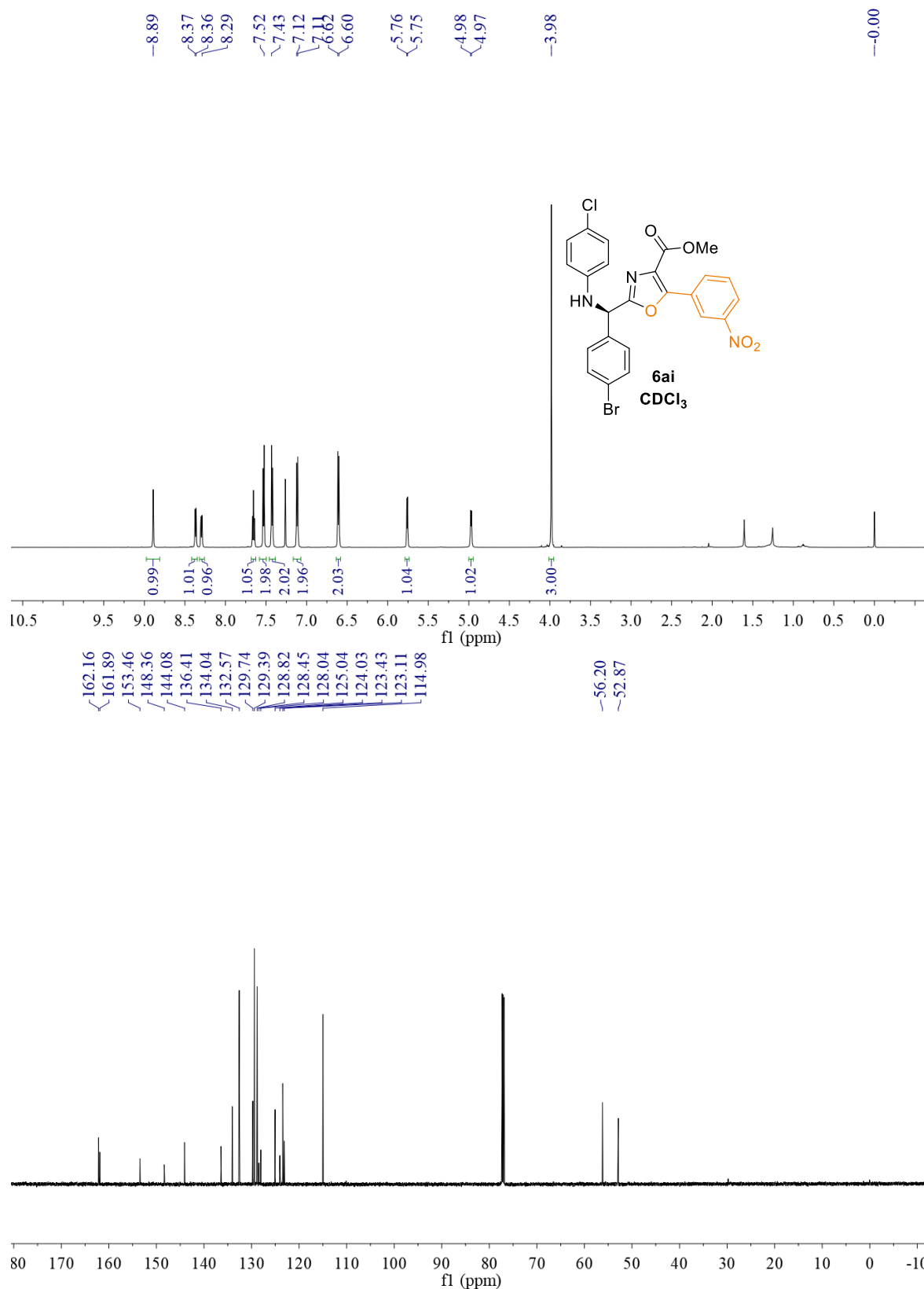


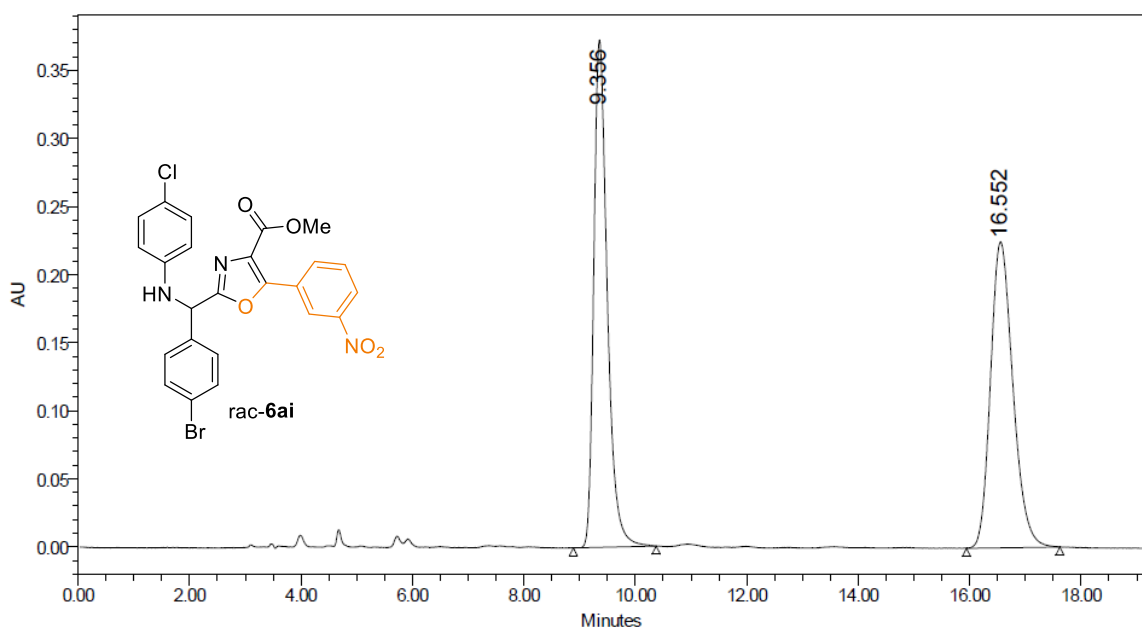


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.055	Unknown	1155061	50.07	88876	65.92	BB	475	6.810	7.602
2	15.980	Unknown	1151972	49.93	45941	34.08	BB	693	15.500	16.655

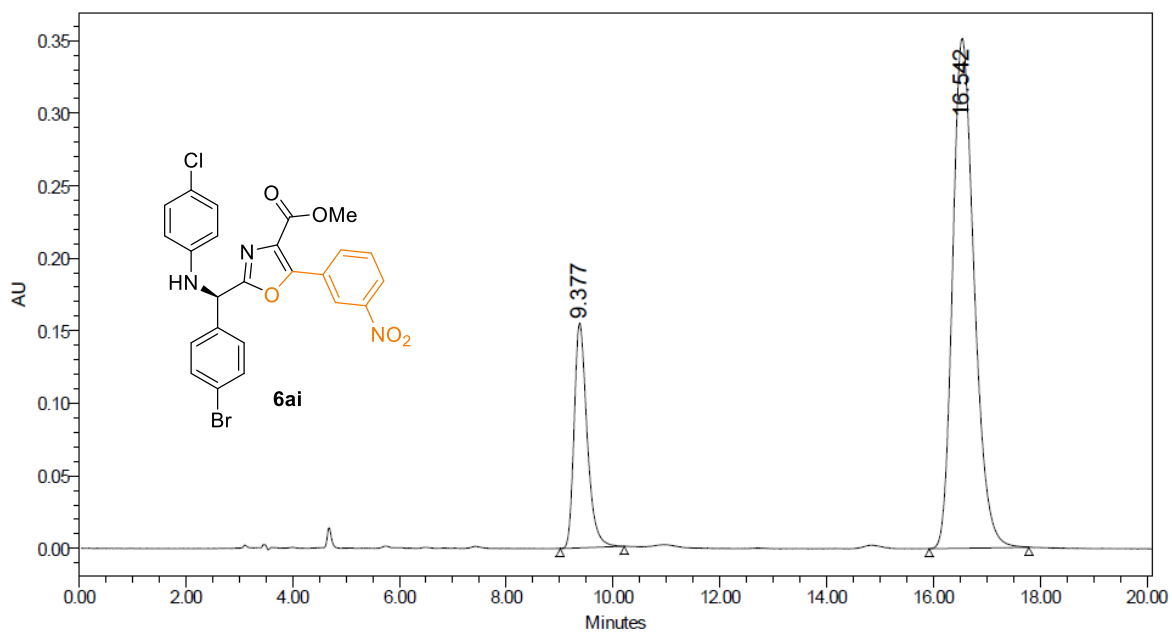


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.047	Unknown	401380	29.05	30870	44.06	BB	427	6.808	7.520
2	15.960	Unknown	980273	70.95	39192	55.94	BB	665	15.505	16.613

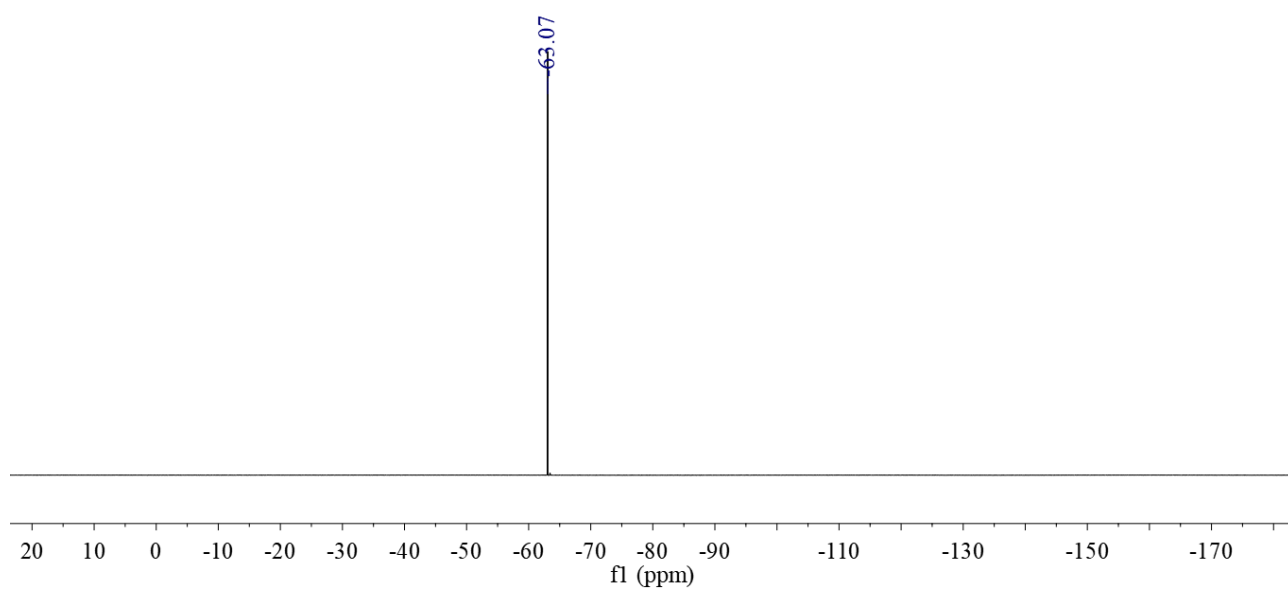
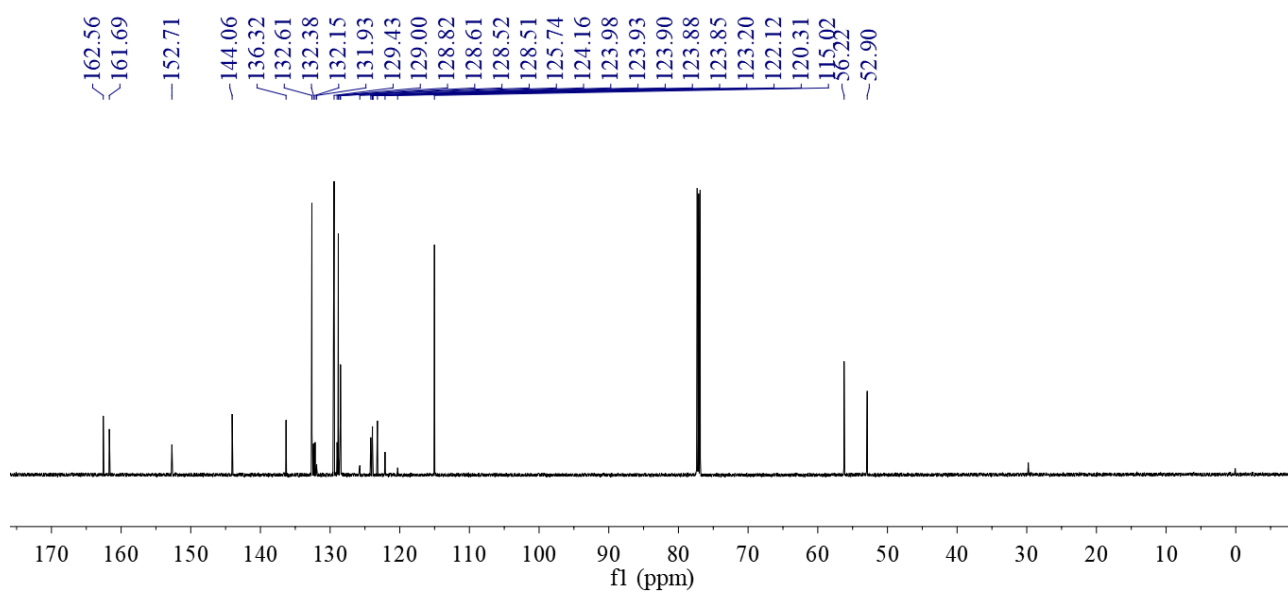
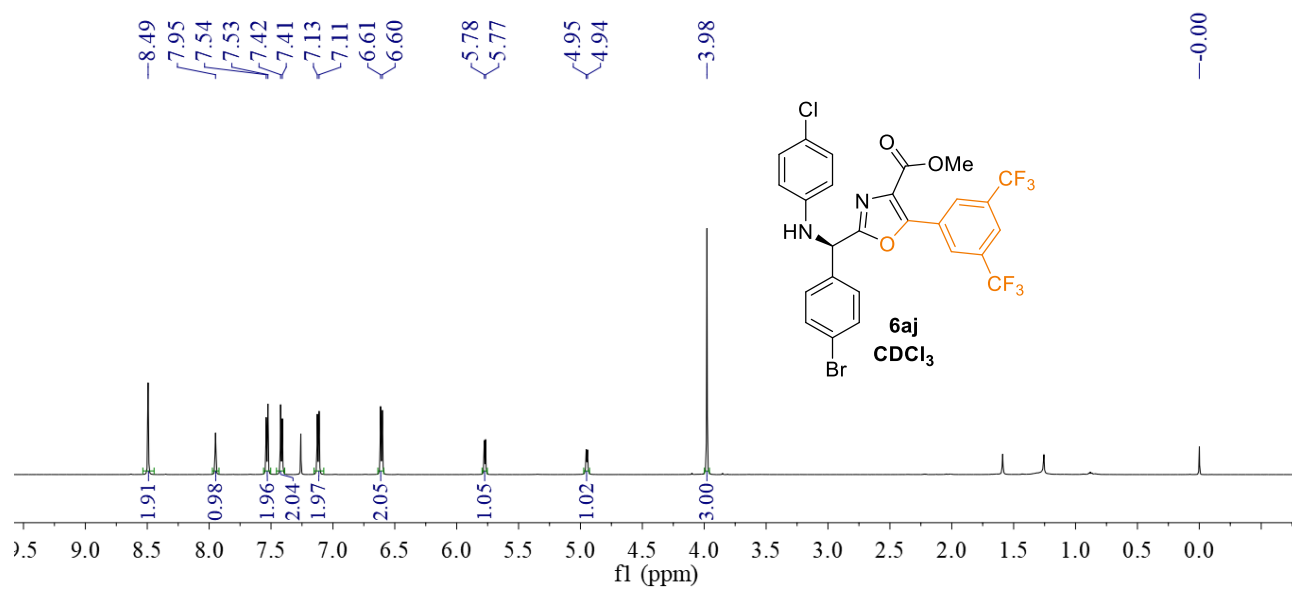


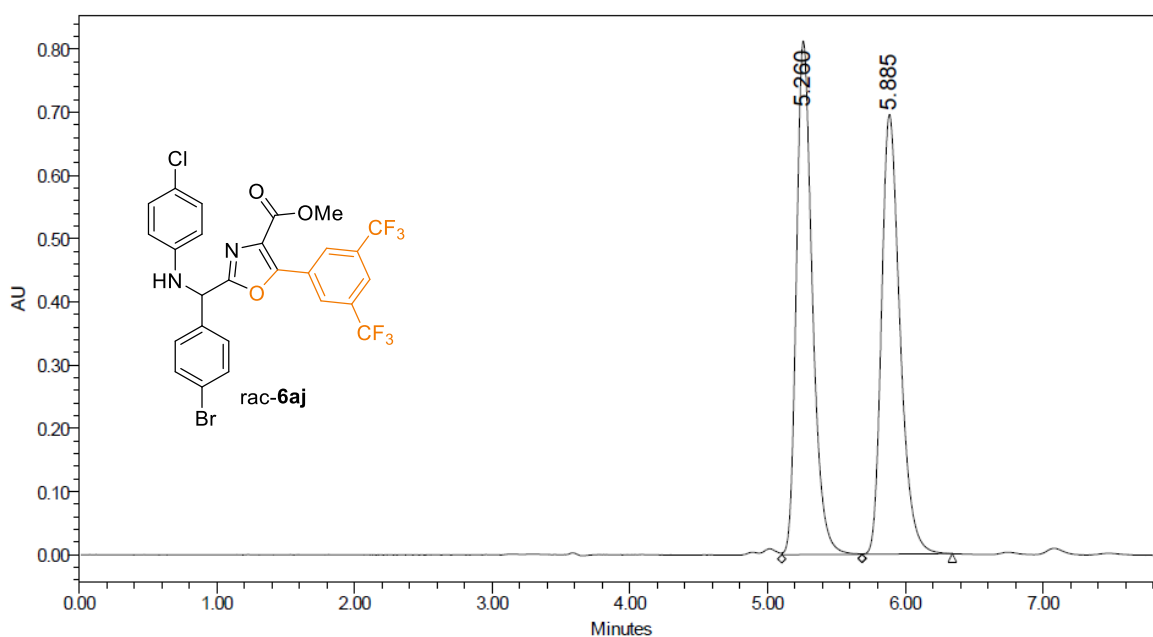


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.356	Unknown	6255941	49.93	372688	62.37	BB	891	8.888	10.373
2	16.552	Unknown	6274082	50.07	224816	37.63	BB	1004	15.945	17.618

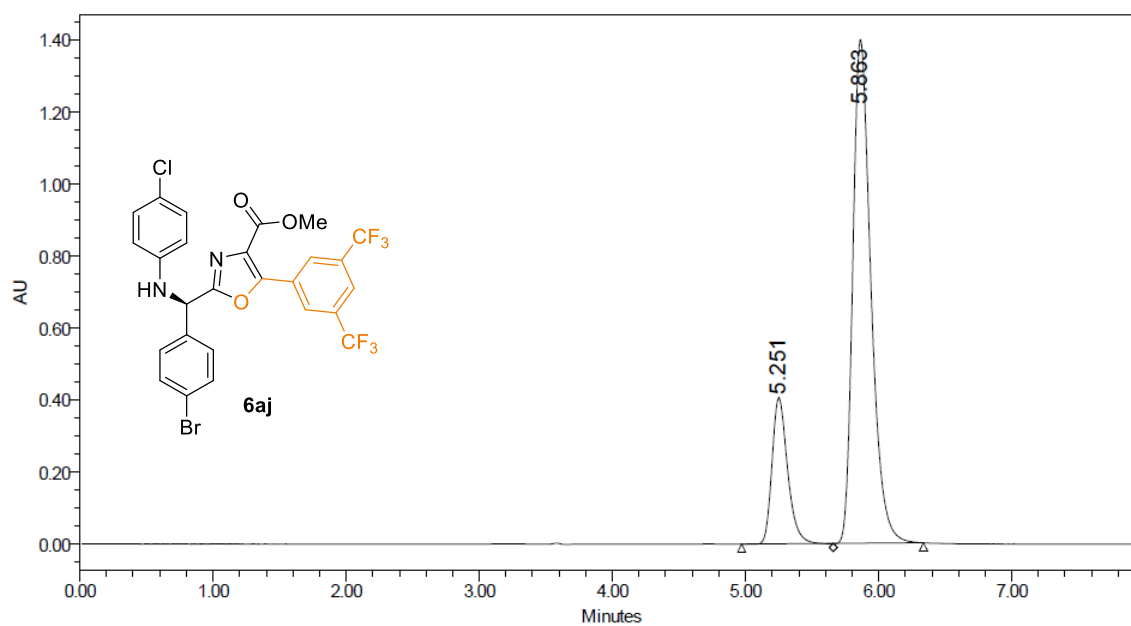


	RT (min)	Peak Type	Area (μV*sec)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	9.377	Unknown	2618267	20.99	154828	30.57	BB	720	9.010	10.210
2	16.542	Unknown	9857913	79.01	351614	69.43	BB	1120	15.923	17.790

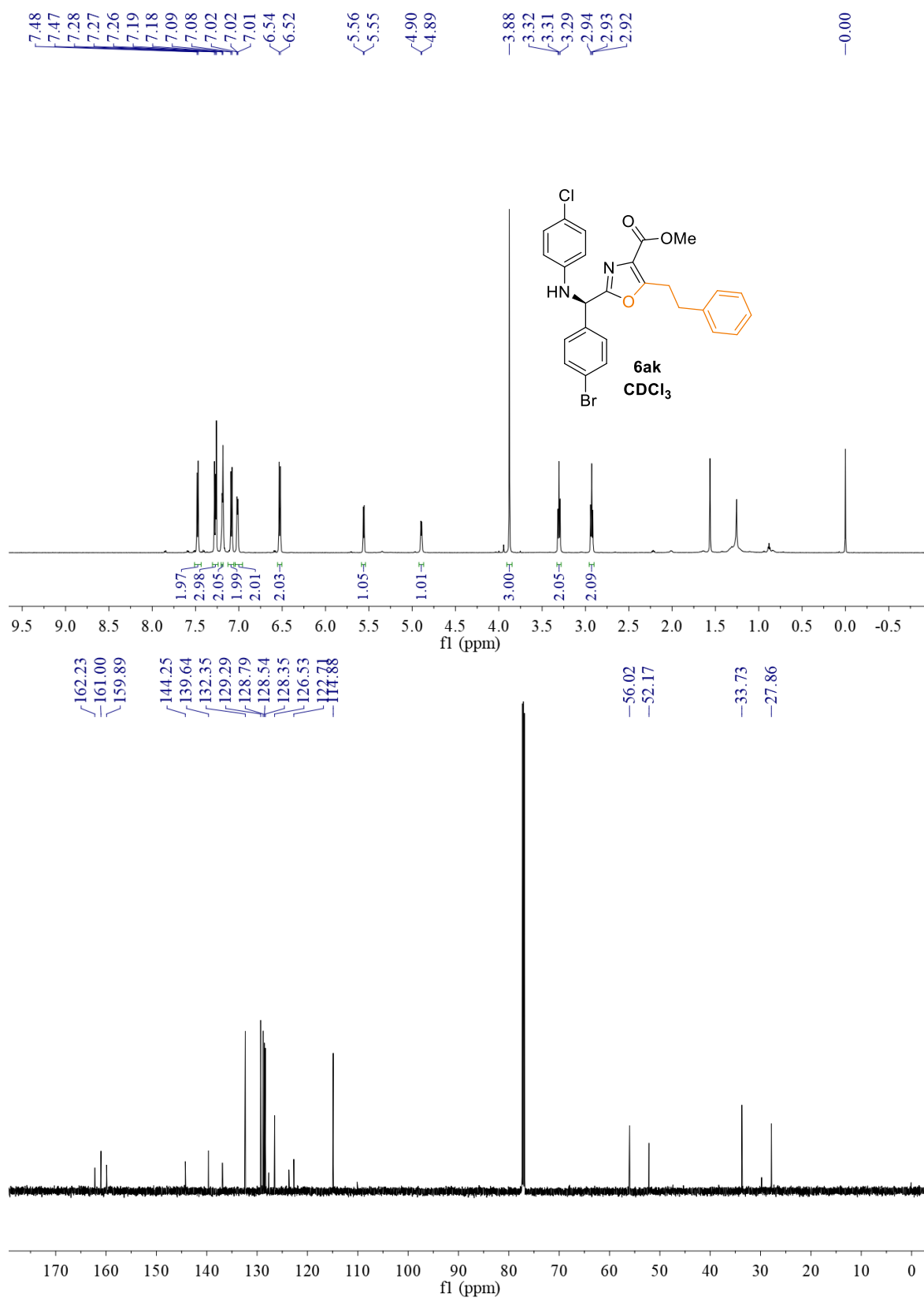


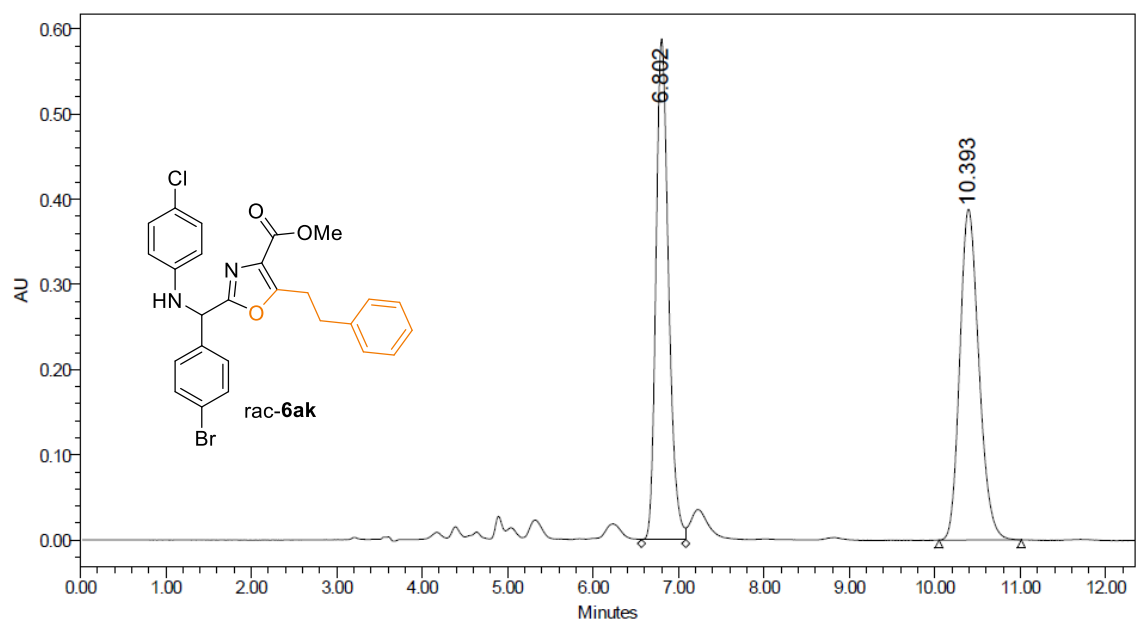


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.260	Unknown	6531271	50.21	812230	53.88	VV	350	5.103	5.687
2	5.885	Unknown	6477819	49.79	695287	46.12	VB	393	5.687	6.342

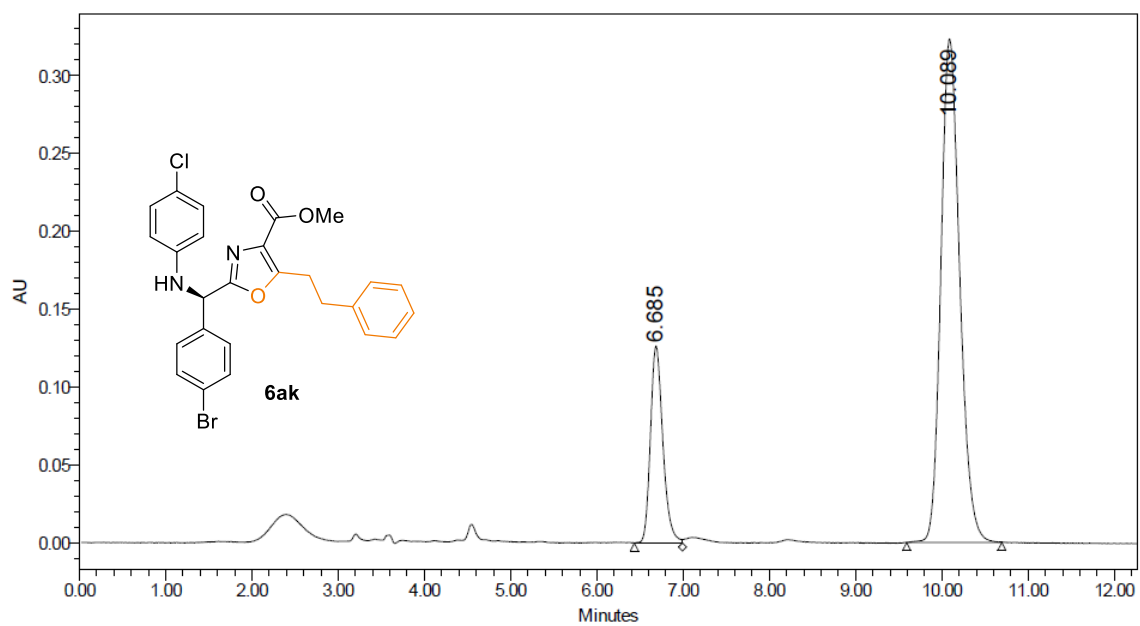


	RT (min)	Peak Type	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	5.251	Unknown	3293738	19.94	405530	22.47	bV	412	4.972	5.658
2	5.863	Unknown	13228646	80.06	1399026	77.53	Vb	407	5.658	6.337





	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	6.802	Unknown	6006064	49.84	587565	60.21	VV	311	6.567	7.085
2	10.393	Unknown	6044836	50.16	388232	39.79	BB	578	10.048	11.012



	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	6.685	Unknown	1264745	20.46	126440	28.11	BV	335	6.435	6.993
2	10.089	Unknown	4917443	79.54	323293	71.89	BB	663	9.592	10.697