Supporting Information

Chiral iron porphyrin (+)-D_4-(por)FeCl catalyzes highly enantioselective cyclopropanation of alkenes using *in situ* generated diazoacetonitrile with up to 35000 product turnover

Contents

1 General Information

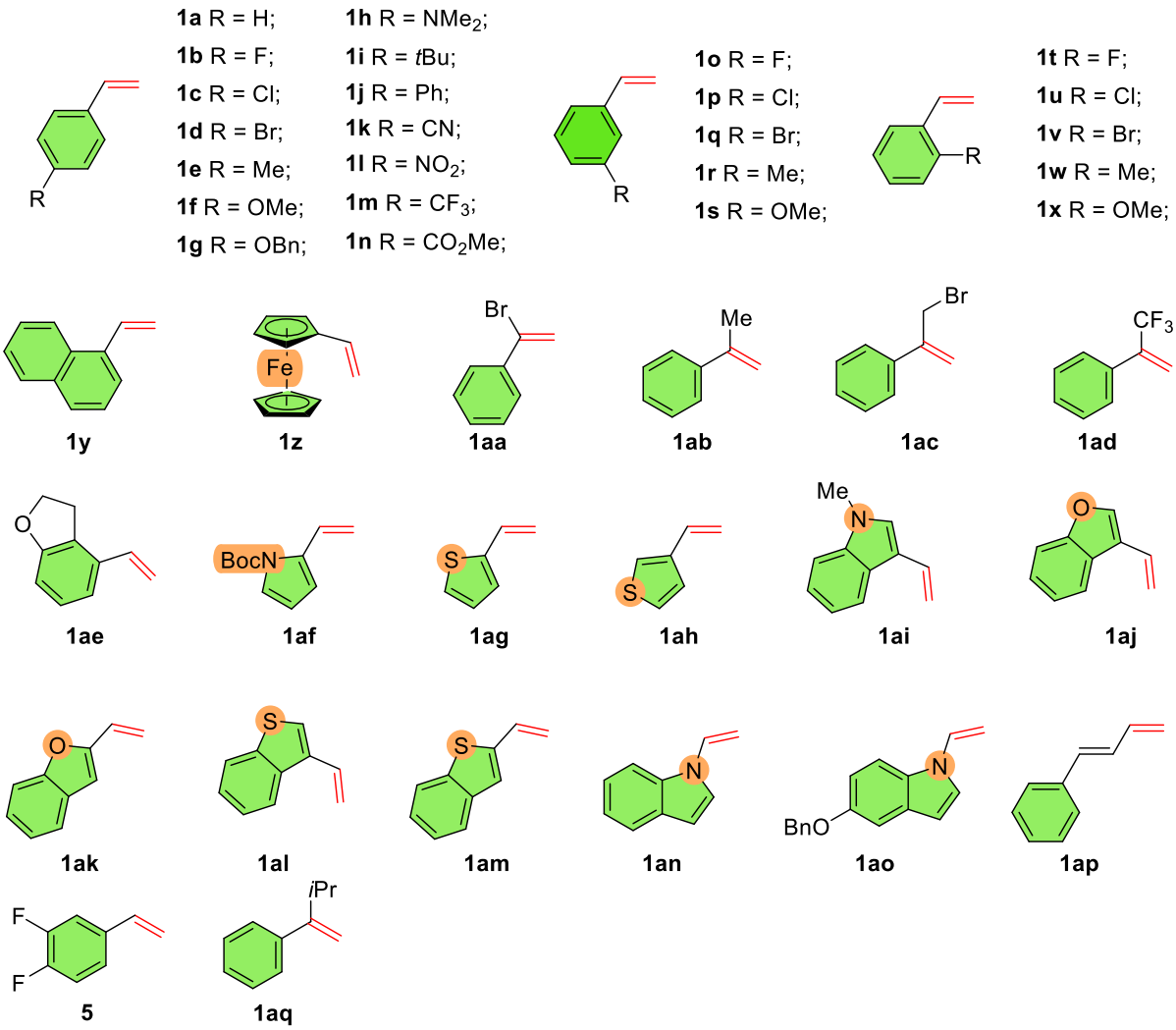
All catalytic reactions were performed using the standard Schlenk technique under an argon atmosphere. Reagents obtained commercially were used without further purification unless indicated otherwise. Anhydrous toluene and dichloromethane (DCM) were freshly distilled with Na/benzophenone and CaH_2, respectively. TLC analysis was performed on silica gel 60 F_{254} pre-coated plates. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a Bruker DPX-600, DPX-500 or DPX-400 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference or referenced to nondeuterated solvent residual signal, and coupling constants (*J*) were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. GC MS experiment was conducted using 7890B-5977A (Agilent). High resolution ESI-MS experiment was conducted using Q Exactive Mass Spectrometers (Thermo Fisher). HPLC measurements were carried out on an Agilent 1260 HPLC system with Chiralcel® AD-H, OD-H, OJ-H, IE or IG. t_R(minor) corresponds to the retention time of the minor isomer and t_R(major) corresponds to the retention time of the major isomer.

2 Synthesis

2.1 Preparation of Iron Catalysts

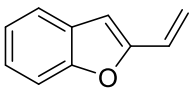
All chiral iron porphyrin catalysts were prepared according to our previous description in the literature.[1]

Alkenes studied in this work



2.2 General Procedure for Synthesis of Alkenes

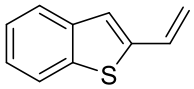
To a solution of methyltriphenylphosphonium bromide (1.2 equiv.) in freshly distilled THF (0.5 M) was slowly added *n*-butyllithium (2.5 M solution in hexanes, 1.2 equiv.) at room temperature. The resulting yellow suspension was stirred for 2 h at room temperature. A solution of aldehyde (5.0 mmol, 1.0 equiv.) in dry THF (5.0 mL) was added dropwise to the suspension and the reaction mixture was stirred for 4 h at room temperature. After the reaction was completed, the reaction mixture was quenched with sat. NH_4Cl aq. (20 mL) and extracted with AcOEt (30 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give the corresponding alkene derivatives.



2-Vinylbenzofuran (1x).[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 6.65 (dd, J = 17.5, 11.2 Hz, 1H), 6.60 (s, 1H), 6.00 (d, J = 17.4 Hz, 1H), 5.42

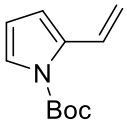
(d, *J* = 11.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.84, 154.75, 128.82, 125.29, 124.66, 122.80, 121.00, 115.74, 111.03, 104.77.

Spectral data were in accord with the literature values.[2]



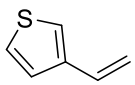
2-Vinylbenzo[*b*]thiophene (1y). [2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 1H), 7.71 – 7.63 (m, 1H), 7.33 – 7.25 (m, 2H), 7.16 (s, 1H), 6.91 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.66 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.10, 140.01, 138.86, 130.60, 124.79, 124.42, 123.57, 123.07, 122.28, 115.96.

Spectral data were in accord with the literature values.[2]



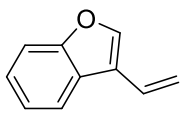
***tert*-Butyl 2-vinyl-1*H*-pyrrole-1-carboxylate (1aa).**[6] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 2H), 6.44 (s, 1H), 6.16 (t, *J* = 3.4 Hz, 1H), 5.54 (dd, *J* = 17.6, 1.7 Hz, 1H), 5.14 (dd, *J* = 11.1, 1.6 Hz, 1H), 1.62 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.42, 134.49, 128.04, 121.87, 113.36, 110.79, 110.75, 83.86, 28.03.

Spectral data were in accord with the literature values.[2]



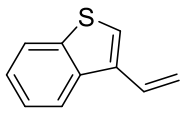
3-Vinylthiophene (1ai). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.24 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.17 (dd, *J* = 2.9, 1.3 Hz, 1H), 6.71 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.58 (dd, *J* = 17.5, 1.1 Hz, 1H), 5.19 (dd, *J* = 10.9, 1.1 Hz, 1H). **^{13}C NMR** (126 MHz, CDCl3) δ 140.53, 130.98, 125.99, 124.73, 122.34, 113.63.

Spectral data were in accord with the literature values.[3]



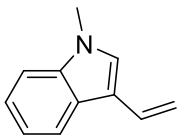
3-Vinylbenzofuran (1aj). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.16 (d, *J* = 6.8 Hz, 1H), 8.00 (s, 1H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.65 (td, *J* = 7.7, 1.6 Hz, 1H), 7.61 (td, *J* = 7.4, 1.3 Hz, 1H), 7.12 (dd, *J* = 17.8, 11.3 Hz, 1H), 6.17 (dd, *J* = 17.9, 1.2 Hz, 1H), 5.68 (dd, *J* = 11.3, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 155.82, 143.70, 126.45, 125.74, 124.65, 123.03, 120.82, 119.62, 114.82, 111.55.

Spectral data were in accord with the literature values.[4]



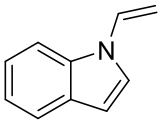
3-Vinylbenzo[b]thiophene (1ak). ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 1H), 7.45 (td, *J* = 7.2, 1.2 Hz, 2H), 7.40 (td, *J* = 7.6, 0.9 Hz, 2H), 7.08 (dd, *J* = 17.7, 11.2 Hz, 1H), 5.89 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.38 (dd, *J* = 11.1, 1.4 Hz, 1H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 140.45, 137.69, 134.39, 129.21, 124.58, 124.41, 122.87, 122.70, 121.89, 114.99.

Spectral data were in accord with the literature values.[4]



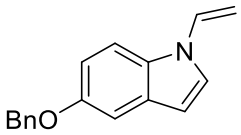
1-Methyl-3-vinyl-1H-indole (1al). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.48 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.61 (dd, *J* = 17.9, 1.6 Hz, 1H), 5.05 (dd, *J* = 11.3, 1.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 137.69, 130.17, 129.92, 126.01, 122.14, 120.18, 120.12, 113.43, 110.52, 109.60, 32.91.

Spectral data were in accord with the literature values.[5]



1-Vinyl-1*H*-indole (1ag). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 3.3 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.19 (dd, *J* = 15.7, 8.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 5.15 (d, *J* = 15.7 Hz, 1H), 4.73 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.51, 129.67, 129.16, 123.38, 122.73, 121.21, 120.81, 109.54, 104.97, 96.44.

Spectral data were in accord with the literature values.[6]



5-(Benzyloxy)-1-vinyl-1H-indole (1am). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (d, *J* = 3.3 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.48 (d, *J* = 6.6 Hz, 2H), 7.43 (dd, *J* = 15.7, 6.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 5.34 (dd, *J* = 15.6, 1.2 Hz, 1H), 5.12 (s, 2H), 4.72 (dd, *J* = 9.0, 1.1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 153.78, 138.03, 130.80, 130.62, 129.58, 128.86, 128.15, 128.10, 125.08, 113.21, 111.30, 104.94, 104.64, 96.41, 70.11. **HR-MS (ESI):** calcd. for $C_{17}H_{15}NO$ ($[M+H]^+$) 250.1226, found 250.1223.

3 Experimental Procedure for (+)-D$_4$-(por)FeCl Catalyzed Cyclopropanation Reactions

Alkene (0.2 mmol), (+)-D$_4$-(por)FeCl (1 mol%, 2 μmol) and 1-methimidazole (1 mol%, 2 μmol) were added in a reaction tube with a stirrer under argon atmosphere, followed by addition of degassed DCM (0.5 mL). Aminoacetonitrile hydrochloride (36.8 mg, 0.4 mmol) and sodium nitrite (53.4mg, 0.6 mmol) were dissolved in degassed H_2O (2.0 mL), respectively. The solution of aminoacetonitrile hydrochloride was transferred into the reaction tube and cooled down to 0 °C in the cold trap, followed by adding the pre-cooled solution of sodium nitrite. After 4 h stirring, a new batch of aminoacetonitrile hydrochloride (36.8 mg, 0.4 mmol) and sodium nitrite (53.4 mg, 0.6 mmol) powders were added. The reaction mixture was stirred for 14 h at 0 °C. The reaction tube was moved out and 0.5 mL $CDCl_3$ was added, followed by extracting with $CDCl_3$ (0.5 mL, 3 times), and then $CHBr_3$ was added as internal standard in the crude product mixture for ^{1}H-NMR determination of production yield and the ratio of *trans*/*cis* diastereomers. After drying over Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by column chromatography with PE/EA (2% to 30% EA) as eluent.

4 Mechanism Studies

General experimental procedure of preparing iron-carbene intermediate

Anhydrous and degassed solvents like THF, *n*-hexane and benzene were used throughout the experiments. Freeze-thawing method (at least 3 cycles) was used to degas the aforementioned solvents. For UV-vis experiments, air-tight UV cells with a quick-fit side arm were used whereas air-free J Young NMR tubes were used for ^{1}H NMR spectroscopy. ATR-FTIR spectroscopy was performed on all iron complexes as powdered solid samples, while diazoacetonitrile was analyzed in film form. All the glassware should be dried for at least 48 h at 100 °C prior to use.

Synthesis of Fe(II) carbene (–)-D$_4$-chiral porphyrin

In a well-circulated glovebox with O_2 and H_2O both < 1 ppm, an oven-dried seal tube was sequentially added with 10 mg of (–)-D$_4$-(por)FeCl (8.11 μmol), 10 equiv. of Zn dust (<10 μm, 98%, Merck) and 3 mL of degassed THF. The reaction was stirred for 24 h, followed by dilution with degassed *n*-hexane by 50% and filtration with a filter made of PTFE. The purple solution was then evaporated to dryness under high vacuum. Subsequently, a vial containing a benzene solution of [(–)-D$_4$-(por)Fe(THF)$_2$] (8.11 μmol) was added with 1 equiv. of diazo compound (0.07 M in PhMe). Within a minute, the generated red-orange solution was rapidly evaporated to dryness under high vacuum, affording [(–)-D$_4$-(por)Fe(:CHCN)]. The Fe(II) carbene intermediate was observed to undergo decomposition in air, as evidenced by the signal decay via monitoring by UV-vis spectroscopy (Figure S2). After adding styrene into the solution of iron(II) carbene intermediate in benzene, the reaction was monitored by UV-vis spectroscopy (Figure S3), It was found that the Fe(II) carbene was consumed by styrene and [(–)-D$_4$-(por)Fe(THF)$_2$] was regenerated.

UV-vis spectrum of [(–)-D$_4$-(por)Fe(THF)$_2$] in THF: 438, 547 nm; (Figure S1);

UV-vis spectrum of [(–)-D$_4$-(por)Fe(THF)$_2$] in benzene: 423, 448, 539 nm. (Figure 3 shown in main-text);

UV-vis spectrum of [(–)-D4-(por)Fe(:CHCN)] in benzene: 417, 518 nm (Figure 3 shown in main-text).

^{1}H NMR spectrum in C_6D_6 (key peaks shown here): 17.8 (s, 1H), 8.77–8.82 (d x 2, 8H) and 7.30 (s, 4H) ppm (Figure 4 shown in main-text);

HR ESI-MS (positive-ion mode) in DCM: calculated 1235.5523 *m/z*, found 1235.5517 *m/z* (Figure 4 shown in main-text);

ATR-FTIR of [(–)-D_4-(por)Fe(:CHCN)](υ(C≡N)): 2178 cm^{-1} (reference of diazoacetonitrile, 2100 cm^{-1}) (Figure 5 shown in main-text).

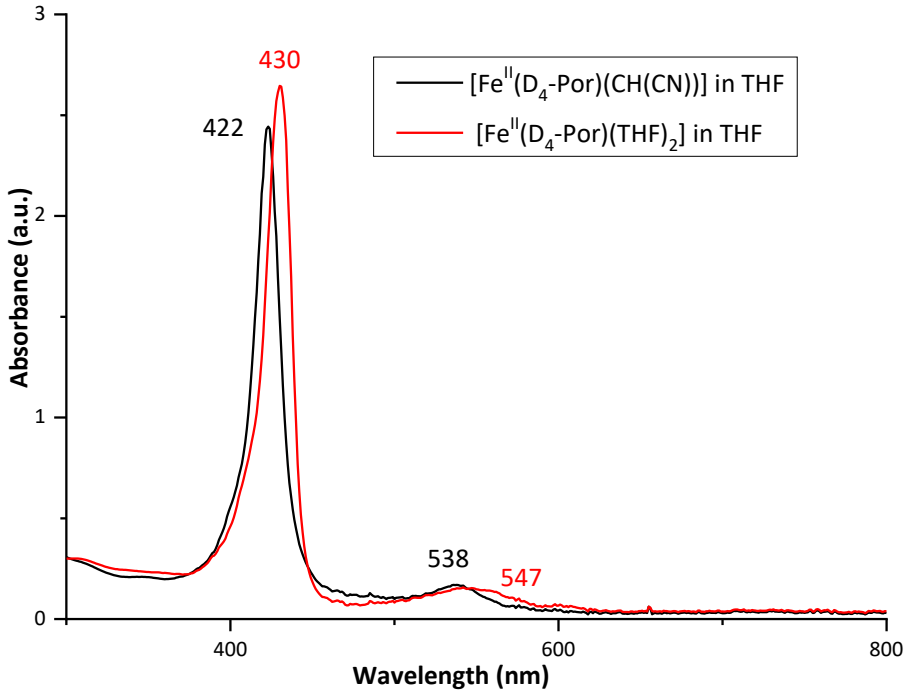


Figure S1. UV-vis absorbance specturm of [(–)-D_4-(por)Fe(THF)$_2$] and [(–)-D_4-(por)Fe(:CHCN)]

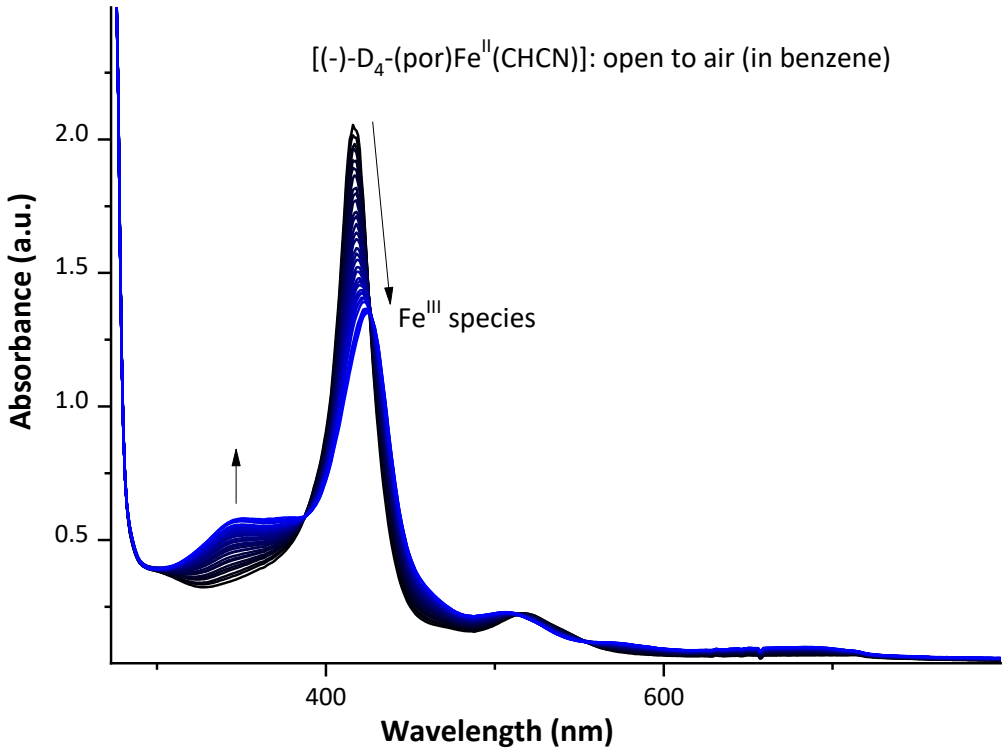


Figure. S2. UV-Vis absorbance specturm of Fe carbene decayed under air atmosphere.

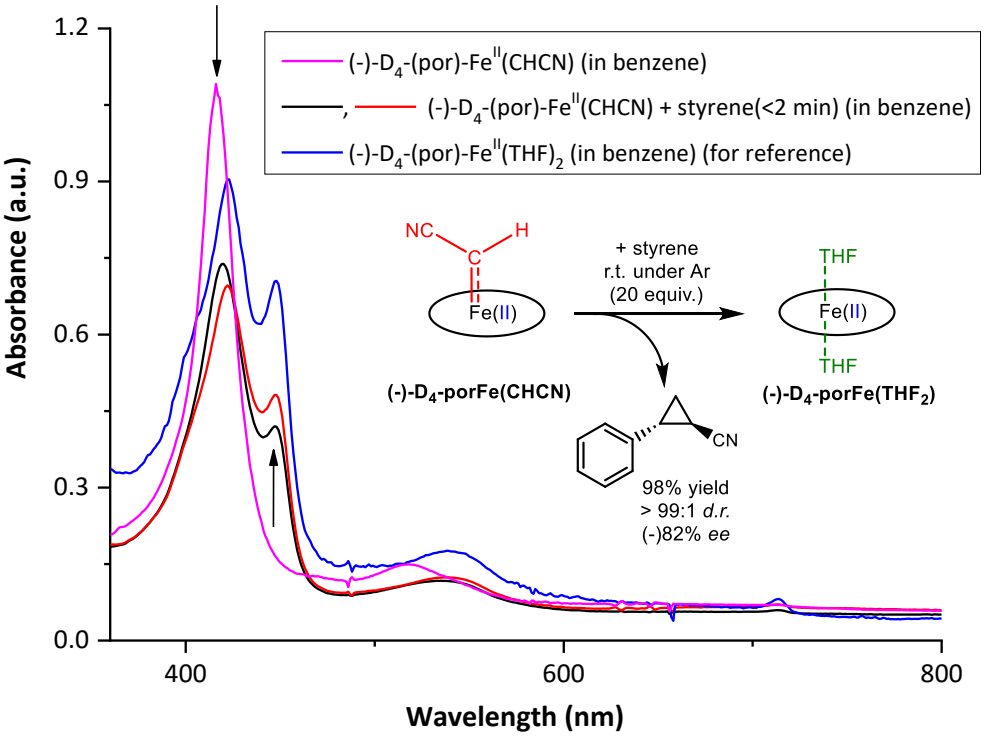


Figure. S3. UV-Vis absorbance specturm of process of (–)-D4-(por)Fe(:CHCN) reacted with styrene. From black line to red line referred to monitoring after adding styrene within 2 min.

Stoichiometric reaction of Fe(II) carbene (-)-D4-chiral porphyrin with styrene:

In a typical experiment, a vial containing a deuterated benzene solution of (–)-D4-(por)Fe(:CHCN) (8.11 μmol) was charged with 20 equiv. of freshly distilled styrene, followed by stirring at room temperature for overnight. The product yield was determined by ^{1}H-NMR with addition of trimethoxybenzene as an internal standard (Figure S4), and % ee was determined by HPLC (retention time confirmed by racemic mixture). (Figure S5).

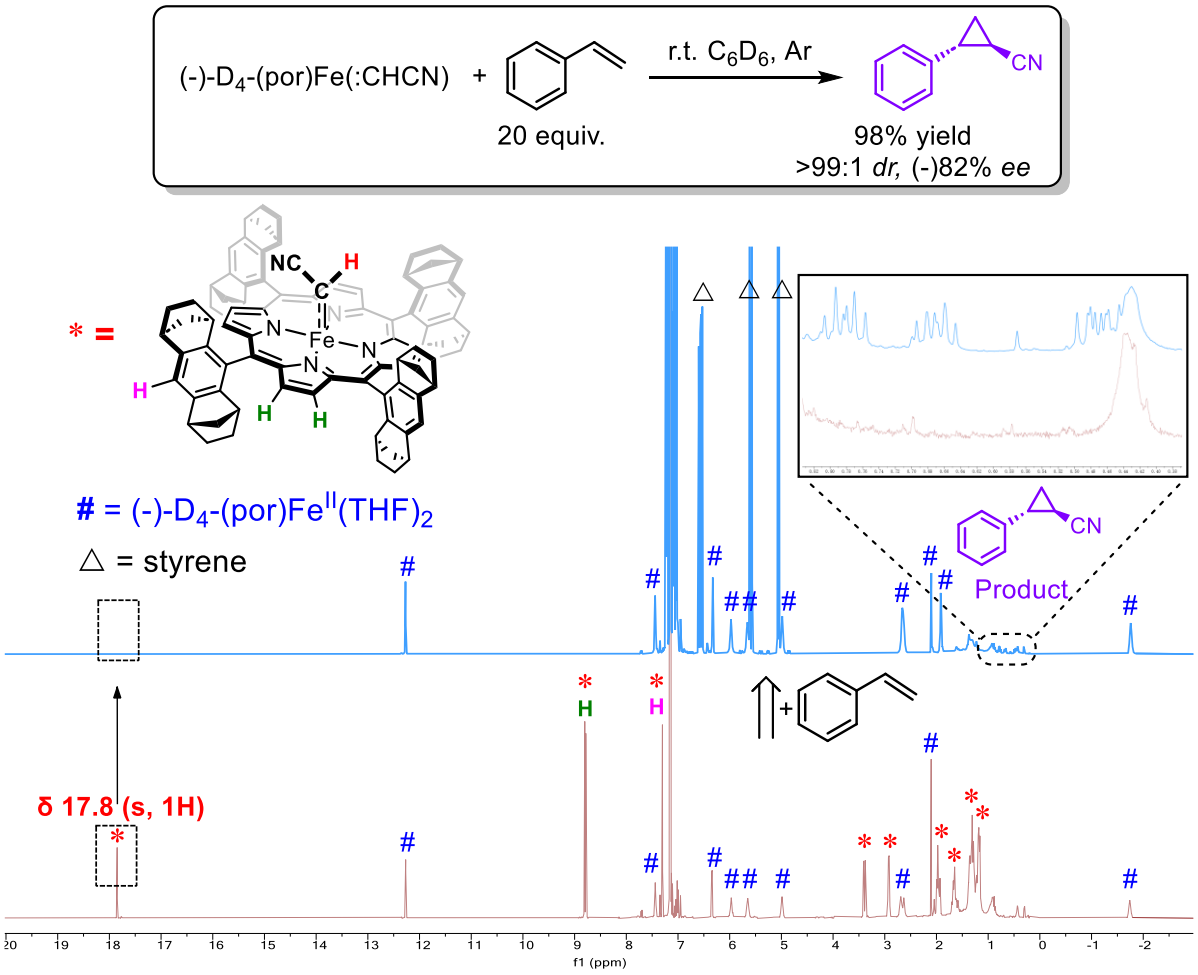
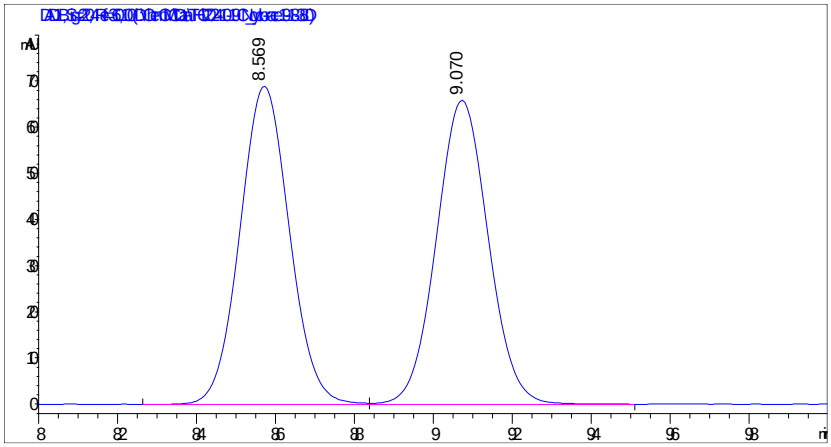
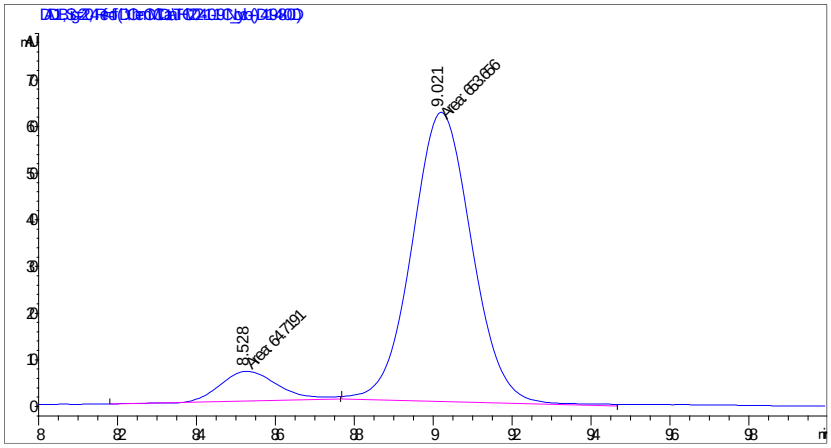


Figure S4. ^{1}H-NMR monitored stoichiometric reaction of Fe(II) carbene (–)-D4-chiral porphyrin with styrene.

HPLC: With **(–)-D4-(por)FeCl** as catalyst: -82% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**minor**) = 8.528 min., t_R (**major**) = 9.021 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.569	BV	0.1358	601.32690	68.93520	49.9163
2	9.070	VB	0.1408	603.34418	65.90099	50.0837
Totals :				1204.67108	134.83619	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.528	MM	0.1688	64.71913	6.39188	9.0091
2	9.021	MM	0.1757	653.65570	62.01051	90.9909
Totals :				718.37483	68.40238	

Figure 5. HPLC analysis for % *ee* determination of stoichiometric reaction.

(–)-D$_4$-porFe(:CHCN)(MeIm)

HRMS(ESI) (*m/z*) [M$^+$]: Calcd. for $C_{90}H_{83}FeN_7$ 1317.6054, found 1317.6057.

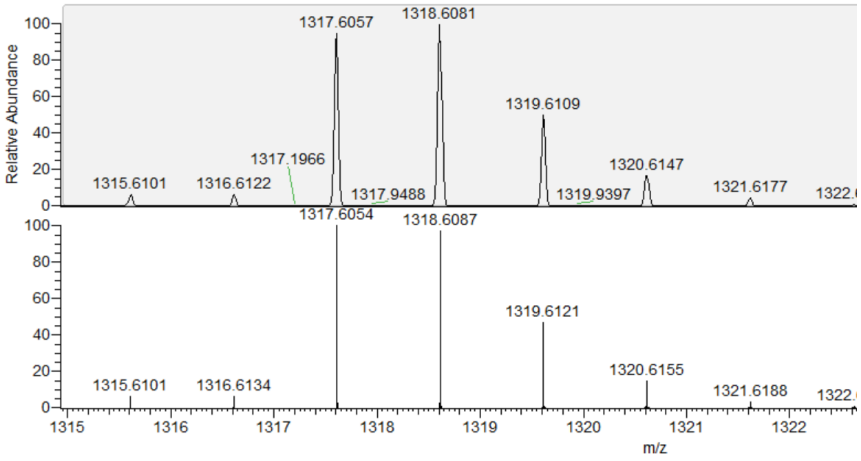
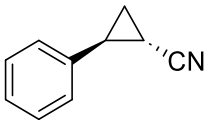


Figure S6. HR ESI-MS of **(–)-D$_4$-porFe(:CHCN)(MeIm)** intermediate**.**

5 Characterization of Products

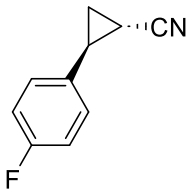


(1*S*,2*S*)-2-Phenylcyclopropane-1-carbonitrile (2a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.22 (m, 3H), 7.16–7.07 (m, 2H), 2.63 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.66–1.59 (m, 1H), 1.57–1.52 (m, 1H), 1.45 (ddd, *J* = 8.6, 6.7, 5.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.60, 128.80, 127.44, 126.35, 121.07, 24.93, 15.25, 6.63. **GC-MS** m/z (% relative intensity): 143.1(92.1), 142.1(22.7), 116.1(86.7), 115.1(100), 89(18.7), 77(15.2).

Spectral data were in accord with the literature values.[7]

With **(+)-D$_4$-(por)FeCl** as catalyst: 97% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 8.41 min., t_R (**minor**) = 8.89 min. $[\alpha]_D^{25}$ = +304.53 (c =1.00, $CHCl_3$).

With **(-)-D$_4$-(por)FeCl** as catalyst: -95% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**minor**) = 7.12 min., t_R (**major**) = 7.52 min. $[\alpha]_D^{25}$ = -288.47 (c =1.0, $CHCl_3$).

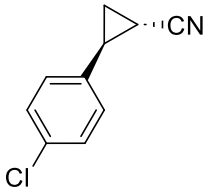


(1*S*,2*S*)-2-(4-Fluorophenyl)cyclopropane-1-carbonitrile (2b). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.62 (ddd, *J* = 9.3, 6.6, 4.7 Hz, 1H), 1.62 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.51 (dt, *J* = 8.8, 5.2 Hz, 1H), 1.43 – 1.40 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.09 (d, *J* = 246.3 Hz), 133.29 (d, *J* = 3.3 Hz), 128.16 (d, *J* = 8.1 Hz), 120.89, 115.72 (d, *J* = 21.4 Hz), 24.30, 15.10, 6.55. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.63. GC-MS

m/z (% relative intensity): 162(10.5), 161.1(90.8), 160.1(18.6), 135.1(12.1), 134(70.5), 133(100), 109(25.9), 107(20.6).

Spectral data were in accord with the literature values.[7]

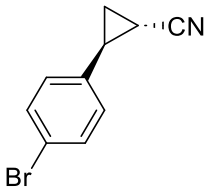
With **(+)-D$_4$-(por)FeCl** as catalyst: 98% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 10.75 min., t_R (**minor**) = 11.34 min. $[\alpha]_D^{25}$ = +302.33 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(4-Chlorophenyl)cyclopropane-1-carbonitrile (2c). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 2.61 (ddd, *J* = 9.2, 6.6, 4.6 Hz, 1H), 1.63 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.53 (dt, *J* = 8.9, 5.1 Hz, 1H), 1.42 (ddd, *J* = 8.9, 6.7, 5.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.07, 133.31, 128.95, 127.78, 120.70, 24.35, 15.20, 6.72. GC-MS m/z (% relative intensity): 179(10.7), 177(32.2), 142.1(71), 140.1(18.4), 116.1(16.2), 115.1(100), 114.1(8.6).

Spectral data were in accord with the literature values.[7]

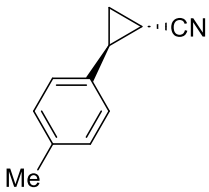
With **(+)-D$_4$-(por)FeCl** as catalyst: 93% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 11.87 min., t_R (**minor**) = 12.02 min. $[\alpha]_D^{25}$ = +264.73 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(4-Bromophenyl)cyclopropane-1-carbonitrile (2d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 2.62 (ddd, *J* = 9.1, 6.6, 4.7 Hz, 1H), 1.66 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.55 (dt, *J* = 8.7, 5.1 Hz, 1H), 1.45 (ddd, *J* = 8.9, 6.6, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.61, 131.90, 128.11, 121.29, 120.71, 24.42, 15.20, 6.73. GC-MS m/z (% relative intensity): 223(17.7), 221(18), 142.1(64.1), 141.1(9.2), 140.1(18.4), 116.1(18), 115.1(100).

Spectral data were in accord with the literature values.[7]

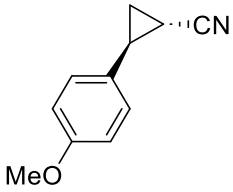
With **(+)-D$_4$-(por)FeCl** as catalyst: 95% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 12.85 min., t_R (**minor**) =13.39 min. $[\alpha]_D^{25}$ = +219.10 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(4-Tolyl)cyclopropane-1-carbonitrile (2e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 2.32 (s, 3H), 1.59 (dt, *J* = 9.2, 5.2 Hz, 1H), 1.50 (dt, *J* = 8.7, 5.1 Hz, 1H), 1.42 (ddd, *J* = 8.8, 6.7, 5.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.20, 134.55, 129.44, 126.28, 121.23, 24.70, 21.05, 15.14, 6.50. GC-MS m/z (% relative intensity): 157.1(98.8), 156.1(100), 142.1(73.6), 140.1(23.5), 129.1(44.7), 128.1(25.7), 116.1(21.8), 115.1(99.5), 91.1(30.5).

Spectral data were in accord with the literature values. [7]

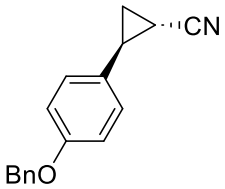
With **(+)-D4-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 7.78 min., t_R (**minor**) =8.21 min. $[\alpha]_D^{25}$ = +299.67 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(4-Methoxyphenyl)cyclopropane-1-carbonitrile (2f). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.59 (ddd, *J* = 9.2, 6.6, 4.7 Hz, 1H), 1.59 – 1.56 (m, 1H), 1.47 (dt, *J* = 8.8, 5.0 Hz, 1H), 1.40 (ddd, *J* = 8.8, 6.7, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.93, 129.51, 127.64, 121.28, 114.15, 55.34, 24.41, 14.93, 6.32. GC-MS m/z (% relative intensity): 173.1(77.8), 172.1(29.1), 158.1(41.2), 131.1(26.8), 130.1(100), 121.1(20.9), 115(18.8), 103.1(40).

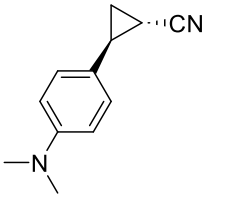
Spectral data were in accord with the literature values.[7]

With **(+)-D4-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 11.91 min., t_R (**minor**) =12.90 min. $[\alpha]_D^{25}$ = +293.87 (c =0.50, $CHCl_3$).



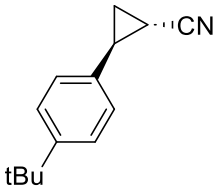
(1*S*,2*S*)-2-(4-(Benzyloxy)phenyl)cyclopropane-1-carbonitrile (2g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 4H), 7.39 – 7.32 (m, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.08 (s, 2H), 2.62 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.57 (dt, *J* = 9.2, 5.3 Hz, 1H), 1.50 (dt, *J* = 8.8, 5.0 Hz, 1H), 1.42 (ddd, *J* = 8.8, 6.7, 5.1 Hz, 1H). ^{13}C NMR (126 MH z, $CDCl_3$) δ 158.13, 136.78, 129.83, 128.66, 128.08, 127.68, 127.46, 121.28, 115.15, 70.10, 24.44, 14.97, 6.36. GC-MS m/z (% relative intensity): 249.1(7.5), 158(6.9), 103.1(7.2), 92.1(8.7), 91.1(100).

With **(+)-D4-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) = 15.99 min., t_R (**minor**) =16.95 min. $[\alpha]_D^{25}$ = +199.57 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(4-(Dimethylamino)phenyl)cyclopropane-1-carbonitrile (2h). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 2H), 2.93 (s, 6H), 2.59 – 2.54 (m, 1H), 1.53 (dt, *J* = 9.6, 5.0 Hz, 1H), 1.42 (dt, *J* = 9.7, 5.0 Hz, 1H), 1.40 – 1.34 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.97, 127.36, 125.02, 121.60, 112.67, 40.58, 24.53, 14.72, 6.08. GC-MS m/z (% relative intensity): 187.1(11), 186.1(88.3), 185.1(100), 144.1(10.8), 143.1(13), 142.1(13.8), 134.1(21.4), 118.1(12.8), 115.1(20.9).

With **(+)-D4-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 12.05 min., t_R (**minor**) =13.16 min. $[\alpha]_D^{25}$ = +276.20 (c =0.50, $CHCl_3$).

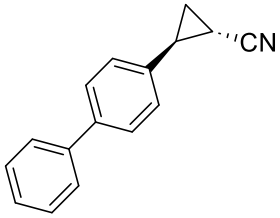


(1*S*,2*S*)-2-(4-(*tert*-Butyl)phenyl)cyclopropane-1-carbonitrile (2i). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 2.61 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.59 (dt, *J* = 9.2, 5.3 Hz, 1H), 1.54 – 1.51 (m, 1H), 1.43 (ddd, *J* = 8.7, 6.7, 5.1 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.54, 134.55, 126.06, 125.69, 121.21, 34.51, 31.27,

24.57, 15.14, 6.48. GC-MS m/z (% relative intensity): 199.1(12.8), 185.1(14.3), 184.1(100), 156.1(19.7), 144.1(16.6), 143.1(21.9), 128.1(15.7), 117.1(15.9), 116.1(19.3), 115.1(27.4).

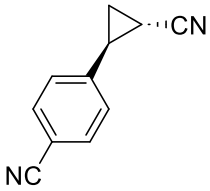
Spectral data were in accord with the literature values. [7]

With **(+)-D$_4$-(por)FeCl** as catalyst: 63% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 7.35 min., t_R (**minor**) =7.74 min. $[\alpha]_D^{25}$ = +176.00 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-([1,1'-Biphenyl]-4-yl)cyclopropane-1-carbonitrile (2j). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.10 (dt, *J* = 8.4, 2.3 Hz, 2H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.58 (dt, *J* = 9.2, 5.4 Hz, 1H), 1.52 (dt, *J* = 8.9, 4.8 Hz, 2H), 1.42 (ddd, *J* = 8.7, 6.7, 5.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.63, 140.57, 134.23, 128.80, 128.44, 127.38, 127.34, 127.10, 119.47, 22.96, 13.11, 6.54. GC-MS m/z (% relative intensity): 220.1(18.6), 219.1(100), 218.1(38.5), 217.1(23.1), 192.1(11.3), 191.1(21.2), 178.1(15.4), 165.1(33), 152(17.3).

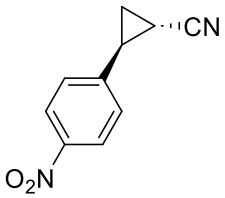
With **(+)-D$_4$-(por)FeCl** as catalyst: 89% *ee* (Chiral AS-H, 10% isopropanol-hexane, rate 0.8 mL/min): t_R (**minor**) = 11.43 min., t_R (**major**) =18.86 min. $[\alpha]_D^{25}$ = +267.00 (c =1.0, $CHCl_3$).



4-((1*S*,2*S*)-2-Cyanocyclopropyl)benzonitrile (2k). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.68 (ddd, *J* = 9.3, 6.6, 4.7 Hz, 1H), 1.74 (dt, *J* = 9.2, 5.6 Hz, 1H), 1.64 (ddd, *J* = 8.9, 5.7, 4.7 Hz, 1H), 1.51 (ddd, *J* = 8.9, 6.6, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.06, 132.61, 127.02, 120.11, 118.39, 111.37, 24.69, 15.75, 7.48. GC-MS m/z (% relative intensity): 168.1(100), 167.1(19.9), 142(15.5), 141.1(84.2), 140.1(70), 114.1(32.8).

Spectral data were in accord with the literature values. [8]

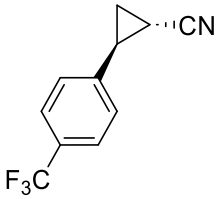
With **(+)-D$_4$-(por)FeCl** as catalyst: 85% *ee* (Chiral IA, 5% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) = 35.13 min., t_R (**minor**) =37.34 min. $[\alpha]_D^{25}$ = +353.33 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(4-Nitrophenyl)cyclopropane-1-carbonitrile (2l). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 2.73 (ddd, *J* = 9.2, 6.6, 4.6 Hz, 1H), 1.78 (dt, *J* = 9.2, 5.7 Hz, 1H), 1.69 (ddd, *J* = 8.9, 5.7, 4.6 Hz, 1H), 1.55 (ddd, *J* = 8.9, 6.7, 5.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.19, 145.14, 127.08, 124.08, 120.01, 24.52, 16.02, 7.71. GC-MS m/z (% relative intensity): 188.1(42.7), 158.1(28.9), 142(38.8), 141.1(59.5), 140.1(40), 116.1(35.2), 115.1(100), 103(33.7).

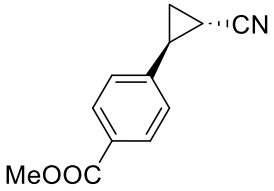
Spectral data were in accord with the literature values. [9]

With **(+)-D4-(por)FeCl** as catalyst: 85% *ee* (Chiral IA, 5% isopropanol-hexane, rate 0.8 mL/min): t_R (**minor**) = 47.82 min., t_R (**major**) =52.64 min. $[\alpha]_D^{25}$ = +298.00 (c =1.00, $CHCl_3$).



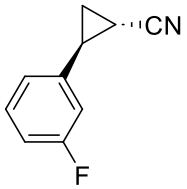
(1*S*,2*S*)-2-(4-(Trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (2m). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.71 (ddd, *J* = 9.2, 6.6, 4.7 Hz, 1H), 1.73 (dt, *J* = 9.2, 5.6 Hz, 1H), 1.64 (ddd, *J* = 8.9, 5.6, 4.7 Hz, 1H), 1.52 (ddd, *J* = 8.9, 6.7, 5.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.66, 129.77 (q, *J* = 32.6 Hz), 126.69, 125.78 (q, *J* = 3.8 Hz), 123.93 (d, *J* = 271.9 Hz), 120.45, 24.55, 15.51, 7.10. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.76. GC-MS m/z (% relative intensity): 211.1(99.5), 192.1(46.7), 191.1(27), 190.1(47.6), 151.1(27.8), 142.1(100), 141.1(39.9), 140.1(55.8), 116.1(23.4), 115.1(127.4).

With **(+)-D4-(por)FeCl** as catalyst: 83% *ee* (Chiral AS-H, 1% isopropanol-hexane, rate 0.8 mL/min): t_R (**minor**) = 24.17 min., t_R (**major**) =27.14 min. $[\alpha]_D^{25}$ = +144.80 (c =1.00, $CHCl_3$).



Methyl 4-((1*S*,2*S*)-2-Cyanocyclopropyl)benzoate (2n). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.94 (s,3H), 2.69 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.72 (dt, *J* = 9.1, 5.5 Hz, 1H), 1.65 (dt, *J* = 8.7, 5.2 Hz, 1H), 1.53 (ddd, *J* = 8.8, 6.6, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.58, 142.80, 130.08, 129.31, 126.19, 120.54, 52.21, 24.78, 15.71, 7.24. GC-MS m/z (% relative intensity): 201.1(22), 171(12.7), 170.1(100), 169.1(13.2), 142.1(27.5), 140.1(17), 116.1(24), 115.1(53.1).

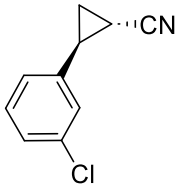
With **(+)-D4-(por)FeCl** as catalyst(-15 °C): 90% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**minor**) = 27.58 min., t_R (**major**) =29.21 min. $[\alpha]_D^{25}$ = +344.17 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(3-Fluorophenyl)cyclopropane-1-carbonitrile (2o). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (td, *J* = 8.0, 6.0 Hz, 1H), 6.96 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 6.91 (ddt, *J* = 7.7, 1.5, 0.7 Hz, 1H), 6.79 (dt, *J* = 9.8, 2.1 Hz, 1H), 2.63 (ddd, *J* = 9.2, 6.6, 4.6 Hz, 1H), 1.65 (dt, *J* = 9.1, 5.5 Hz, 1H), 1.57 (ddd, *J* = 8.9, 5.6, 4.7 Hz, 1H), 1.45 (ddd, *J* = 8.8, 6.7, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.00 (d, *J* = 247.0 Hz), 140.16 (d, *J* = 7.7 Hz), 130.38 (d, *J* = 8.5 Hz), 122.17 (d, *J* = 3.0 Hz), 120.66, 114.45 (d, *J* = 21.2 Hz), 113.31 (d, *J* = 22.2 Hz), 24.55 (d, *J* = 2.2 Hz), 15.37, 6.91. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.40. GC-MS m/z (% relative intensity): 162.1(9.4), 161.1(87.6), 160.1(14.9), 140.1(9), 135.1(12.2), 134.1(75), 133.1(100), 109.1(15.4), 107.1(16.6).

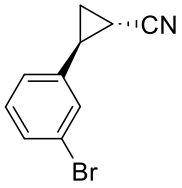
Spectral data were in accord with the literature values. [7]

With **(+)-D4-(por)FeCl** as catalyst: 86% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) = 8.06 min., t_R (**minor**) =8.35 min. $[\alpha]_D^{25}$ = +144.80 (c =1.00, $CHCl_3$).



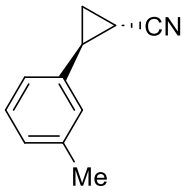
(1*S*,2*S*)-2-(3-Chlorophenyl)cyclopropane-1-carbonitrile (2p). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.08 (s, 1H), 7.03 – 6.99 (m, 1H), 2.61 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.65 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.61 – 1.53 (m, 1H), 1.45 (ddd, *J* = 8.8, 6.7, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.63, 134.74, 130.06, 127.68, 126.52, 124.75, 120.62, 24.47, 15.25, 6.81. GC-MS m/z (% relative intensity): 179(9), 177.1(27.4), 142.1(53.6), 140.1(17), 116.1(15.5), 115.1(100).

With **(+)-D4-(por)FeCl** as catalyst: 86% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) = 7.92 min., t_R (**minor**) =8.40 min. $[\alpha]_D^{25}$ = +255.37 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(3-Bromophenyl)cyclopropane-1-carbonitrile (2q). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.25 (t, *J* = 1.9 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.64 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.61 – 1.53 (m, 1H), 1.45 (ddd, *J* = 8.8, 6.7, 5.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.89, 130.62, 130.32, 129.45, 125.23, 122.87, 120.60, 24.41, 15.23, 6.81. GC-MS m/z (% relative intensity): 223(18.2), 221(18.4), 142.1(65.6), 140.1(18.1), 116.1(18.9), 115.1(100), 114.1(8.5).

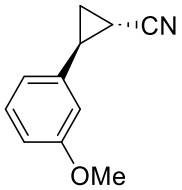
With **(+)-D4-(por)FeCl** as catalyst: 85% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) = 8.21 min., t_R (**minor**) =8.80 min. $[\alpha]_D^{25}$ = +216.50 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(3-Tolyl)cyclopropane-1-carbonitrile (2r). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.94 – 6.87 (m, 2H), 2.60 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 2.33 (s, 3H), 1.60 (dt, *J* = 9.2, 5.3 Hz, 1H), 1.56 – 1.51 (m, 1H), 1.44 (ddd, *J* = 8.7, 6.7, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.53, 137.52, 128.67, 128.17, 127.11, 123.29, 121.15, 24.88, 21.36, 15.20, 6.55. GC-MS m/z (% relative intensity): 157.1(46.1), 156.1(100), 142.1(30), 130.1(13.2), 129.1(33.1), 128.1(17.4), 115.1(58.6), 91.1(14.8).

Spectral data were in accord with the literature values. [7]

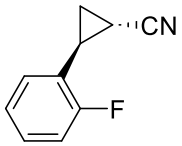
With **(+)-D4-(por)FeCl** as catalyst: 85% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =5.73 min., t_R (**minor**) =5.94 min. $[\alpha]_D^{25}$ = +282.17 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(3-Methoxyphenyl)cyclopropane-1-carbonitrile (2s). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 2.1 Hz, 1H), 3.80 (s, 3H), 2.61 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.61 (dt, *J* = 8.2, 4.8 Hz, 1H), 1.57 – 1.53 (m, 1H), 1.44 (ddd, *J* = 8.7, 6.7, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.90, 139.22,

129.86, 121.05, 118.48, 112.58, 112.46, 55.29, 24.94, 15.27, 6.67. GC-MS m/z (% relative intensity): 173.1(81.4), 172.1(18.1), 142.1(17), 131.1(34.4), 130.1(100), 115.1(26.9), 103.1(46.5).

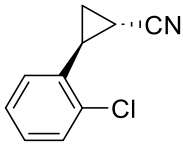
With **(+)-D4-(por)FeCl** as catalyst: 84% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =9.73 min., t_R (**minor**) =10.15 min. $[\alpha]_D^{25}$ = +246.67 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(2-Fluorophenyl)cyclopropane-1-carbonitrile (2t). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.12 – 7.02 (m, 2H), 6.98 (td, *J* = 7.6, 1.7 Hz, 1H), 2.77 – 2.69 (m, 1H), 1.69 – 1.61 (m, 2H), 1.54 – 1.46 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.71 (d, *J* = 247.2 Hz), 129.03 (d, *J* = 8.2 Hz), 127.28 (d, *J* = 3.6 Hz), 124.74 (d, *J* = 13.8 Hz), 124.31 (d, *J* = 3.6 Hz), 120.90, 115.70 (d, *J* = 21.4 Hz), 19.27 (d, *J* = 4.1 Hz), 14.22 (d, *J* = 1.8 Hz), 5.51 (d, *J* = 2.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.06. GC-MS m/z (% relative intensity): 161.1(100), 160.1(14), 140.1(14.5), 135.1(13.4), 134.1(73.7), 133.1(99.8), 109.1(24.6), 107(19.1).

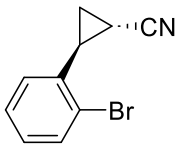
Spectral data were in accord with the literature values. [7]

With **(+)-D4-(por)FeCl** as catalyst: 88% *ee* (Chiral AD-H, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =6.98 min., t_R (**minor**) =7.28 min. $[\alpha]_D^{25}$ = +258.00 (c =1.00, $CHCl_3$).



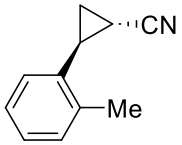
(1*S*,2*S*)-2-(2-Chlorophenyl)cyclopropane-1-carbonitrile (2u). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 1H), 7.27 – 7.11 (m, 2H), 7.01 (dd, *J* = 6.8, 2.2 Hz, 1H), 2.81 (ddd, *J* = 9.2, 6.8, 5.0 Hz, 1H), 1.68 (dt, *J* = 9.2, 5.1 Hz, 1H), 1.55 – 1.41 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.94, 135.27, 129.67, 128.85, 127.45, 126.97, 120.93, 23.34, 14.25, 5.82. GC-MS m/z (% relative intensity): 179(11.2), 177(34.2), 142.1(60.6), 140.1(29.9), 116.1(15.2), 115.1(100), 114.1(14.5).

With **(+)-D4-(por)FeCl** as catalyst: 88% *ee* (Chiral AD-H, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =7.31 min., t_R (**minor**) =7.66 min. $[\alpha]_D^{25}$ = +140.02 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(2-Bromophenyl)cyclopropane-1-carbonitrile (2v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.26 (t, *J* = 6.7 Hz, 1H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.7 Hz, 1H), 2.81 – 2.73 (m, 1H), 1.69 (dt, *J* = 9.4, 4.6 Hz, 1H), 1.55 – 1.43 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.94, 132.92, 129.14, 127.88, 127.58, 126.39, 120.95, 25.96, 14.54, 6.18. GC-MS m/z (% relative intensity): 223(21.4), 221(21.7), 142.1(61.1), 141.1(9.9), 140.1(31.4), 116.1(17.8), 115.1(100), 114.1(14.3).

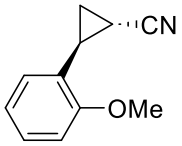
With **(+)-D4-(por)FeCl** as catalyst: 88% *ee* (Chiral AD-H, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =7.77 min., t_R (**minor**) =8.11 min. $[\alpha]_D^{25}$ = +123.83 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(2-Tolyl)cyclopropane-1-carbonitrile (2w). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 7.14 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 2.61 (dt, *J* = 9.1, 6.0 Hz, 1H), 2.45 (s, 3H), 1.66 – 1.60 (m, 1H), 1.49 – 1.40 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.25, 135.65, 130.20, 127.64, 126.13, 125.94, 121.44, 23.65, 19.60, 13.96, 5.12. GC-MS m/z (% relative intensity): 157.1(72.1), 156.1(71.2), 142.1(47.2), 130.1(29), 129.1(48.1), 128.1(21.4), 117.1(20.2), 116.1(28.6), 115.1(100), 91.1(32.8).

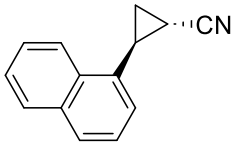
Spectral data were in accord with the literature values. [7]

With **(+)-D$_4$-(por)FeCl** as catalyst: 85% *ee* (Chiral IA, 1% isopropanol-hexane, rate 1.2 mL/min): t_R (**minor**) =6.85 min., t_R (**major**) =7.24 min. $[\alpha]_D^{25}$ = +199.67 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-(2-Methoxyphenyl)cyclopropane-1-carbonitrile (2x). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 1H), 6.93 – 6.84 (m, 3H), 3.87 (s, 3H), 2.76 (ddd, *J* = 9.1, 6.9, 5.0 Hz, 1H), 1.55 (dt, *J* = 9.3, 4.8 Hz, 1H), 1.52 – 1.48 (m, 1H), 1.45 (ddd, *J* = 8.4, 6.9, 4.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.48, 128.54, 126.40, 125.87, 121.74, 120.41, 110.38, 55.46, 20.50, 13.89, 5.25. GC-MS m/z (% relative intensity): 173.1(81.7), 158.1(97.9), 131.1(57.8), 130.1(100), 115.1(33.2), 103.1(47.5).

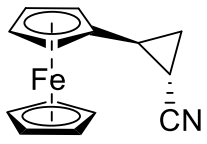
With **(+)-D$_4$-(por)FeCl** as catalyst: 90% *ee* (Chiral IA, 1% isopropanol-hexane, rate 1.2 mL/min): t_R (**minor**) =13.57 min., t_R (**major**) =15.19 min. $[\alpha]_D^{25}$ = +127.90 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(Naphthalen-1-yl)cyclopropane-1-carbonitrile (2y). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.57 (s, 1H), 7.48 (dtd, *J* = 7.9, 6.9, 5.3 Hz, 2H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.80 (ddd, *J* = 9.2, 6.7, 4.8 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.67 – 1.63 (m, 1H), 1.58 (ddd, *J* = 8.5, 6.7, 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.95, 133.25, 132.62, 128.66, 127.72, 127.53, 126.64, 126.10, 125.22, 124.33, 121.10, 25.22, 15.23, 6.66. GC-MS m/z (% relative intensity): 193.1(63.5), 192.1(30.9), 190.1(12.3), 166.1(36.6), 165.1(100), 153.1(43.5), 152.1(45.1), 151.1(12.9), 139.1(18.5), 115.1(12.6).

Spectral data were in accord with the literature values. [7]

With **(+)-D$_4$-(por)FeCl** as catalyst: 91% *ee* (Chiral IA, 0.5% isopropanol-hexane, rate 1.2 mL/min): t_R (**major**) =52.22 min., t_R (**minor**) =61.61 min. $[\alpha]_D^{25}$ = +112.00 (c =1.0, $CHCl_3$).

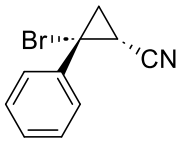


(1*S*,2*S*)-2-(Ferrocenyl)cyclopropane-1-carbonitrile (2z). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 5H), 4.14 – 4.07 (m, 3H), 4.01 – 4.00 (m, 1H), 2.29 (ddd, *J* = 9.1, 6.6, 4.6 Hz, 1H), 1.50 (dt, *J* = 9.1, 5.3 Hz, 1H), 1.41 (ddd, *J* = 8.7, 5.5, 4.6 Hz, 1H), 1.23 (ddd, *J* = 8.7, 6.6, 5.0 Hz, 1H). **^{13}C NMR** (126

MHz, $CDCl_3$) δ 121.28, 86.12, 68.75, 67.94, 67.68, 67.06, 66.40, 20.99, 16.06, 6.81. **HR-MS** (ESI): calcd. for $C_{14}H_{13}NFe$ ($[M]^+$) 251.0392, found 251.0388.

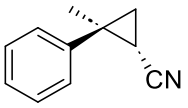
GC-MS m/z (% relative intensity): 252.1(18.1), 251.1(100), 186(66), 185(45.3), 159(15.9), 158(16.7), 121(22.9), 104.1(9.6), 103.1(18.7).

With **(+)-D_4-(por)FeCl** as catalyst: 48% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =9.75 min., t_R (**minor**) =11.29 min. $[\alpha]_D^{25}$ = +68.67 (c =0.50, $CHCl_3$).



(1*R*,2*R*)-2-Bromo-2-phenylcyclopropane-1-carbonitrile (2aa). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.24 (m, 3H), 1.97 – 1.88 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.16, 129.35, 129.05, 128.40, 118.43, 34.05, 24.03, 14.19. GC-MS m/z (% relative intensity): [M-Br]142.1(82.2), 141.1(9.9), 140.1(24.6), 116.1(21.1), 115.1(100), 102.1(10), 89.1(14.5).

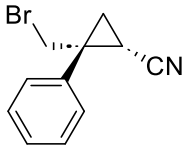
With **(+)-D_4-(por)FeCl** as catalyst: 77% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =8.89 min., t_R (**minor**) =9.15 min. $[\alpha]_D^{25}$ = +162.05 (c =1.00, $CHCl_3$).



(1*S*,2*S*)-2-Methyl-2-phenylcyclopropane-1-carbonitrile (2ab). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 1.67 (dd, *J* = 9.1, 5.5 Hz, 1H), 1.66 (s, 3H), 1.57 (dd, *J* = 9.3, 5.3 Hz, 1H), 1.31 (t, *J* = 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.71, 128.79, 127.41, 127.37, 120.31, 28.73, 23.50, 21.30, 11.28. GC-MS m/z (% relative intensity): 157.1(40.1), 156.1(46.2), 142.1(100), 129.1(35.8), 116.1(17.4), 115.1(84), 103.1(18.8), 78.1(19.6), 77.1(30.5), 51.1(25.3).

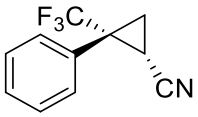
Spectral data were in accord with the literature values. [7]

With **(+)-D_4-(por)FeCl** as catalyst: 79% *ee* (Chiral IA, 1% isopropanol-hexane, rate 1.2 mL/min): t_R (**minor**) =6.20 min., t_R (**major**) =6.49 min. $[\alpha]_D^{25}$ = +40.00 (c =0.10, $CHCl_3$).



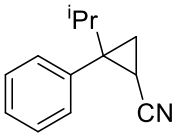
(1*S*,2*R*)-2-(Bromomethyl)-2-phenylcyclopropane-1-carbonitrile (2ac). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 5H), 3.71 (q, *J* = 11.0 Hz, 2H), 1.94 (dd, *J* = 8.9, 5.9 Hz, 1H), 1.69 (dd, *J* = 8.9, 5.6 Hz, 1H), 1.50 (t, *J* = 5.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.36, 129.25, 128.77, 128.46, 118.93, 39.33, 34.38, 22.01, 13.58. GC-MS m/z (% relative intensity): [M-Br]156.1(89.6), 142.1(28.6), 129.1(100), 128.1(34.8), 116.1(23.2), 115.1(81.2), 103.1(32), 102.1(31.7), 77.1(41.2).

With **(+)-D_4-(por)FeCl** as catalyst: 67% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =7.91 min., t_R (**minor**) =8.87 min. $[\alpha]_D^{25}$ = -43.51 (c =0.20, $CHCl_3$).



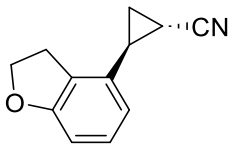
(1*S*,2*R*)-2-phenyl-2-(trifluoromethyl)cyclopropane-1-carbonitrile (2ad). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.46 – 7.43 (m, 3H), 2.30 (dd, *J* = 9.6, 6.1 Hz, 1H), 1.95 (dd, *J* = 9.6, 5.8 Hz, 1H), 1.75 (tq, *J* = 6.0, 1.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.41, 130.00, 129.70, 129.00, 124.16 (q, *J* = 275.2 Hz), 116.99, 34.76 (q, *J* = 34.3 Hz), 16.22 (q, *J* = 2.4 Hz), 8.28 (q, *J* = 3.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.16. GC-MS m/z (% relative intensity): 211.1(41.7), 161.1(12.2), 143.1(12.2), 142.1(100), 140.1(23), 116.1(19.7), 115.1(97.3), 77.1(10.5), 63.1(11.9), 51.1(14). Spectral data were in accord with the literature values. [7]

With **(+)-D$_4$-(por)FeCl** as catalyst: 89% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =6.89 min., t_R (**minor**) =7.31 min. $[\alpha]_D^{25}$ = +101.67 (c =1.00, $CHCl_3$).



2-isopropyl-2-phenylcyclopropane-1-carbonitrile (2ae) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 1.70 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.64 (p, *J* = 6.8 Hz, 1H), 1.43 (dd, *J* = 8.9, 4.7 Hz, 1H), 1.28 (t, *J* = 5.1 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.20, 131.09, 127.99, 127.59, 120.65, 39.10, 35.19, 21.15, 19.93, 19.38, 10.56. GC-MS m/z (% relative intensity): 185(5.1), 143(14.2), 132(100), 131(13.6), 117(85.6), 115(55.7),102(10.3), 91(32.7), 77(16.5), 63(11.6), 51(17.7).

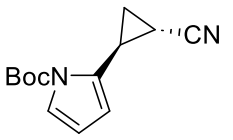
With **(+)-D$_4$-(por)FeCl** as catalyst: 60% *ee* (Chiral AS-H, 1% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =9.77 min., t_R (**minor**) =11.36 min. $[\alpha]_D^{25}$ = +132.44 (c =0.50, $CHCl_3$).



(1*S*,2*S*)-2-(2,3-Dihydrobenzofuran-4-yl)cyclopropane-1-carbonitrile (3a). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.98 (t, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 7.7 Hz, 1H), 4.56 (t, *J* = 8.8 Hz, 2H), 3.26 – 3.17 (m, 2H), 2.46 (ddd, *J* = 9.1, 6.8, 4.8 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.47 (dt, *J* = 8.4, 5.1 Hz, 1H), 1.39 (ddd, *J* = 8.6, 6.7, 5.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.14, 134.21, 128.62, 126.99, 121.06, 116.09, 108.54, 71.17, 28.53, 22.87, 14.46, 5.58. GC-MS m/z (% relative intensity): 185.1(100), 184.1(70.2), 156.1(27.5), 129.1(29.8), 128.1(26.1), 127.1(30.1), 117.1(25.2), 115.1(54.2).

Spectral data were in accord with the literature values. [10]

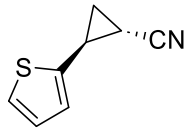
With **(+)-D$_4$-(por)FeCl** as catalyst: 90% *ee* (Chiral IE, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =18.08 min., t_R (**minor**) =18.97 min. $[\alpha]_D^{25}$ = +170.00 (c =0.10, $CHCl_3$).



***tert*-Butyl 2-((1*S*,2*S*)-2-cyanocyclopropyl)-1H-pyrrole-1-carboxylate (3b).** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.05 (t, *J* = 3.4 Hz, 1H), 6.06 – 5.89 (m, 1H), 3.00 – 2.92 (m, 1H), 1.64 (s, 9H), 1.55 (dt, *J* = 9.0, 5.2 Hz, 1H), 1.46 (dt, *J* = 8.7, 5.1 Hz, 1H), 1.37 (ddd, *J* = 8.7, 6.8, 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.05, 131.86, 122.48, 121.17, 111.13,

109.77, 84.47, 28.07, 27.98, 19.24, 14.30, 5.87. GC-MS m/z (% relative intensity): 232.2(15.3), 176.1(18.9), 159.1(15.3), 132.1(100), 131.1(64.7), 105.1(30), 104.1(29.1), 80.1(16.2).

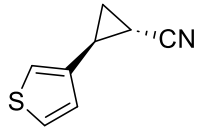
With **(+)-D$_4$-(por)FeCl** as catalyst: 89% *ee* (Chiral IA, 1% isopropanol-hexane, rate 1.2 mL/min): t_R (**minor**) =6.00 min., t_R (**major**) =6.38 min. $[\alpha]_D^{25}$ = +150.30 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(Thiophen-2-yl)cyclopropane-1-carbonitrile (3c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.2, 1.2 Hz,1H), 6.93 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.86 (d, *J* = 3.5 Hz, 1H), 2.80 (ddd, *J* = 9.1, 6.5, 4.9 Hz, 1H), 1.67 (dt, *J* = 9.0, 5.4 Hz, 2H), 1.64 – 1.57 (m, 1H), 1.47 (ddd, *J* = 8.8, 6.6, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.36, 127.11, 125.02, 124.31, 120.54, 20.33, 16.21, 7.66. GC-MS m/z (% relative intensity): 149(100), 148(42.2), 122(72.7), 121(37.1), 104.1(13.2), 97(44.4), 96(17.2), 69(19.9).

Spectral data were in accord with the literature values. [7]

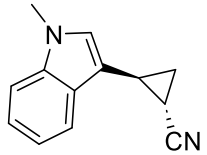
With **(+)-D$_4$-(por)FeCl** as catalyst: 83% *ee* (Chiral IA, 2% isopropanol-hexane, rate 0.8 mL/min): t_R (**major**) =8.77 min., t_R (**minor**) =9.98 min. $[\alpha]_D^{25}$ = +338.33 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(Thiophen-3-yl)cyclopropane-1-carbonitrile (3d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.0, 2.9 Hz, 1H), 6.93 – 6.92 (m, 1H), 6.86 (dd, *J* = 5.0, 1.4 Hz, 1H), 2.64 (ddd, *J* = 9.1, 6.6, 4.6 Hz, 1H), 1.64 – 1.56 (m, 1H), 1.52 (ddd, *J* = 8.7, 5.5, 4.6 Hz, 1H), 1.40 (ddd, *J* = 8.7, 6.6, 5.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.77, 126.68, 125.87, 121.06, 120.98, 20.70, 15.28, 6.35. GC-MS m/z (% relative intensity): 149.1(100), 148.1(39.6), 123.1(11.7), 122(75.4), 121(40.5), 104.1(12.7), 97.1(38.6), 69(16.3).

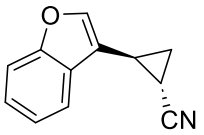
With **(+)-D$_4$-(por)FeCl** as catalyst: 86% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =8.99 min., t_R (**minor**) =9.63 min. $[\alpha]_D^{25}$ = +290.00 (c =0.10, $CHCl_3$).

Spectral data were in accord with the literature values. [11]



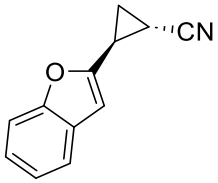
(1*S*,2*S*)-2-(1-Methyl-1H-indol-3-yl)cyclopropane-1-carbonitrile (3e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 6.85 (s, 1H), 3.77 (s, 3H), 2.76 – 2.71 (m, 1H), 1.63 (dt, *J* = 9.2, 4.8 Hz, 1H), 1.53 – 1.48 (m, 1H), 1.46 (ddd, *J* = 8.6, 6.6, 4.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.05, 131.86, 122.47, 121.14, 111.12, 109.76, 84.46, 28.06, 19.23, 14.30, 5.86.GC-MS m/z (% relative intensity): 196.1(100), 195.1(80.4), 181.1(16.6), 168.1(21.6), 154.1(17.7), 144.1(73.8), 143.1(15.1), 128.1(14.7), 127.1(16.6), 115.1(19.6).

With **(+)-D$_4$-(por)FeCl** as catalyst: 76% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =10.71 min., t_R (**minor**) =11.17 min. $[\alpha]_D^{25}$ = +95.00 (c =0.10, $CHCl_3$).



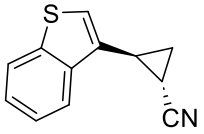
(1*S*,2*S*)-2-(Benzofuran-3-yl)cyclopropane-1-carbonitrile (3f). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.27 (td, *J* = 8.3, 7.8 Hz, 1H), 7.23 (td, *J* = 7.4, 1.1 Hz, 1H), 2.55 – 2.51 (m, 1H), 1.59 (dt, *J* = 9.0, 5.2 Hz, 1H), 1.55 – 1.48 (m, 1H), 1.40 (ddd, *J* = 8.6, 6.7, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.43, 141.80, 127.19, 125.09, 123.05, 120.95, 119.34, 118.42, 111.85, 15.17, 13.38, 4.47. GC-MS m/z (% relative intensity): 184.1(13.6), 183.1(100), 182.1(48.4), 156.1(20.8), 155.1(17.5), 154.1(46), 131.1(37.6), 128.1(28.7), 127.1(29.2), 115.1(19), 102.1(16.6).

With **(+)-D$_4$-(por)FeCl** as catalyst: 86% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =10.66 min., t_R (**minor**) =11.16 min. $[\alpha]_D^{25}$ = +61.00 (c =0.10, $CHCl_3$).



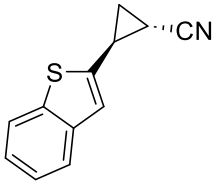
(1*S*,2*S*)-2-(Benzofuran-2-yl)cyclopropane-1-carbonitrile (3g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.17 (m, 2H), 6.57 (s, 1H), 2.73 (ddd, *J* = 9.3, 6.6, 4.5 Hz, 1H), 1.91 (ddd, *J* = 8.9, 5.9, 4.5 Hz, 1H), 1.72 – 1.67 (m, 1H), 1.66 – 1.61 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.31, 153.25, 128.32, 124.26, 123.12, 120.65, 120.29, 110.93, 103.88, 18.76, 13.98, 5.50. GC-MS m/z (% relative intensity): 183.1(100), 182.1(39.5), 156(16.1), 154.1(36.5), 131(40.9), 128.1(21.9), 127(19.7), 115.1(16.4), 102(18.6).

With **(+)-D$_4$-(por)FeCl** as catalyst: 64% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =7.17 min., t_R (**minor**) =7.93 min. $[\alpha]_D^{25}$ = +281.67 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(Benzo[b]thiophen-3-yl)cyclopropane-1-carbonitrile (3h). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.50 (td, *J* = 7.2, 1.3 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 (s, 1H), 2.80 – 2.78 (m, 1H), 1.73 (dt, *J* = 9.1, 4.4 Hz, 1H), 1.60 – 1.49 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.41, 138.75, 133.05, 125.09, 124.61, 123.04, 122.56, 121.68, 121.09, 77.32, 77.07, 76.81, 19.11, 13.61, 4.76. GC-MS m/z (% relative intensity): 200.1(15), 199.1(100), 198.1(33.3), 172(47.2), 171(42.2), 147.1(28.4), 115.1(11.5).

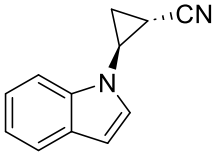
With **(+)-D$_4$-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =8.76 min., t_R (**minor**) =9.19 min. $[\alpha]_D^{25}$ = +104.67 (c =1.0, $CHCl_3$).



(1*S*,2*S*)-2-(Benzo[b]thiophen-2-yl)cyclopropane-1-carbonitrile (3i). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.64 (d, *J* = 7.0 Hz, 1H), 7.34 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 7.09 (s, 1H), 2.91 – 2.83 (m, 1H), 1.76 – 1.67 (m, 2H), 1.58 – 1.49 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.88, 139.46, 138.78, 124.72, 124.56, 123.29, 122.28, 121.67, 120.32, 21.08, 16.25, 7.65. GC-MS m/z (% relative intensity): 200.1(15.9),

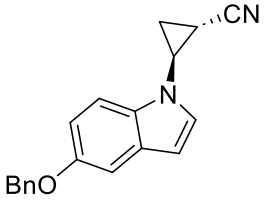
199.1(100), 198.1(30.4), 173.1(10.3), 172.1(55.5), 171.1(37.1), 147.1(30.7), 145.1(9.4), 115.1(8.4), 102.1(7.7).

With **(+)-D$_4$-(por)FeCl** as catalyst: 87% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =9.26 min., t_R (**minor**) =9.76 min. $[\alpha]_D^{25}$ = +320 (c =0.10, $CHCl_3$).



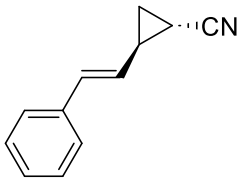
(1*S*,2*S*)-2-(1H-Indol-1-yl)cyclopropane-1-carbonitrile (3j). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 3.3 Hz, 1H), 6.42 (d, *J* = 3.3 Hz, 1H), 3.89 – 3.86 (m, 1H), 1.81 – 1.79 (m, 1H), 1.77 – 1.73 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.01, 128.96, 126.42, 122.68, 121.40, 120.81, 119.17, 109.75, 103.07, 34.26, 14.40, 5.94. GC-MS m/z (% relative intensity): 182.1(100), 156.1(18.8), 155.1(15.1), 154.1(37.8), 130.1(18.4), 116.1(24.1).

With **(+)-D$_4$-(por)FeCl** as catalyst: 87% *ee* (Chiral IE, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =11.10 min., t_R (**minor**) =12.46 min. $[\alpha]_D^{25}$ = +78.67 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(5-(Benzyloxy)-1H-indol-1-yl)cyclopropane-1-carbonitrile (3k). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.25 (t, *J* = 7.4 Hz,1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.91 (d, *J* = 3.1 Hz, 1H), 6.32 (d, *J* = 3.1 Hz, 1H), 5.03 (s, 2H), 3.86 – 3.83 (m, 1H), 1.81 – 1.75 (m, 1H), 1.75 – 1.70 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.10, 137.46, 132.38, 129.39, 128.61, 128.58, 127.87, 127.66, 127.53, 127.04, 119.20, 113.50, 110.41, 104.79, 102.74, 70.86, 34.36, 14.39, 5.92. GC-MS m/z (% relative intensity): 289.2(10.1), 288.1(44.3), 198.1(14.2), 197.1(100), 169.1(16.8), 168.1(10.9), 142.1(8.1), 103.1(9.1).

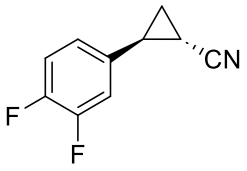
With **(+)-D$_4$-(por)FeCl** as catalyst: 90% *ee* (Chiral AS-H, 10% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) =19.576 min., t_R (**minor**) =22.543 min. $[\alpha]_D^{25}$ = +90.00 (c =0.10, $CHCl_3$).



(1*S*,2*R*)-2-((*E*)-Styryl)cyclopropane-1-carbonitrile (4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.23 (m, 3H), 7.19 – 7.15 (m, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.62 (dd, *J* = 15.9, 8.2 Hz, 1H), 2.20 – 2.17 (m, 1H), 1.45 – 1.41 (m,1H), 1.38 – 1.34 (m, 1H), 1.16 – 1.13 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.25, 132.25, 128.70, 127.82, 127.24, 126.05, 120.95, 24.08, 14.64, 5.11. GC-MS m/z (% relative intensity): 169.1(36), 168.1(53.5), 142.1(100), 141.1(51.8), 129.1(77.7), 128.1(76.7), 127.1(30.2), 116.1(66.9), 115.1(97.7).

Spectral data were in accord with the literature values. [12]

With **(+)-D$_4$-(por)FeCl** as catalyst: 65% *ee* (Chiral IA, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**major**) = 8.65 min., t_R (**minor**) = 9.57 min. $[\alpha]_D^{25}$ = +145.00 (c =0.10, $CHCl_3$).



(1*S*,2*S*)-2-(3,4-Difluorophenyl)cyclopropane-1-carbonitrile (6). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 – 7.00 (m, 1H), 6.87 – 6.82 (m, 1H), 6.81 – 6.78 (m, 1H), 2.52 (ddd, *J* = 9.2, 6.7, 4.7 Hz, 1H), 1.56 (dt, *J* = 9.2, 5.5 Hz, 1H), 1.48 – 1.46 (m, 1H), 1.34 (ddd, *J* = 8.9, 6.7, 5.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.98 (dd, *J* = 91.7, 12.7 Hz), 149.00 (dd, *J* = 91.0, 12.6 Hz), 134.65 (dd, *J* = 5.8, 3.9 Hz), 122.73 (dd, *J* = 6.3, 3.6 Hz), 120.54, 117.63 (d, *J* = 17.3 Hz), 115.54 (d, *J* = 18.0 Hz), 24.06 (d, *J* = 1.7 Hz), 15.19, 6.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.85 (d, *J* = 21.1 Hz), -139.19 (d, *J* = 21.1 Hz). GC-MS m/z (% relative intensity): 179.1(85.2), 178.1(11.4), 158(12.4), 152.1(61.5), 151.1(100), 133.1(12.1), 127.1(24.9), 125(16.4).

With **(+)-D$_4$-(por)FeCl** as catalyst: 88% *ee* (Chiral AS-H, 2% isopropanol-hexane, rate 1.0 mL/min): t_R (**minor**) =14.12 min., t_R (**major**) =16.04 min. $[\alpha]_D^{25}$ = +224.63 (c =1.00, $CHCl_3$).

6 Crystallographic Data

Table S6 Crystal data and structure refinement for **2g**.

Identification code	**2g**
Empirical formula	$C_{17}H_{15}NO$
Formula weight	249.30
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.1916(8)
b/Å	7.5616(9)
c/Å	27.676(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1295.7(3)
Z	4
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.396
F(000)	528.0
Crystal size/mm^3	0.4 × 0.18 × 0.1
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	10.552 to 146.53
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $-39 \le l \le 37$
Reflections collected	25804
Independent reflections	3919 [R_{int} = 0.0668, R_{sigma} = 0.0373]
Data/restraints/parameters	3919/0/172
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1111
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.1119
Largest diff. peak/hole / e Å^{-3}	0.43/-0.21
Flack parameter	-0.01(12)
CCDC	2349759

Table S7 Crystal data and structure refinement for **2l**.

Identification code	**2l**
Empirical formula	$C_{20}H_{16}N_4O_4$
Formula weight	376.37
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.2102(14)
b/Å	6.6977(10)
c/Å	14.702(2)
α/°	90
β/°	98.797(4)
γ/°	90
Volume/Å^3	896.3(2)
Z	2
ρ_{calc}g/cm^3	1.395
μ/mm^{-1}	0.528
F(000)	392.0
Crystal size/mm^3	0.2 × 0.12 × 0.08
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	5.292 to 121.124
Index ranges	-11 ≤ h ≤ 11, -8 ≤ k ≤ 8, -19 ≤ l ≤ 19
Reflections collected	20517
Independent reflections	3991 [R_{int} = 0.0538, R_{sigma} = 0.0531]
Data/restraints/parameters	3991/1/253
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.1064
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31
Flack parameter	0.07(6)
CCDC	2349760

Table S8 Crystal data and structure refinement for **2z**.

Identification code	**2z**
Empirical formula	$C_{28}H_{26}Fe_2N_2$
Formula weight	502.21
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.4077(10)
b/Å	7.4147(8)
c/Å	14.8363(16)
α/°	90
β/°	92.504(4)
γ/°	90
Volume/Å^3	1143.8(2)
Z	2
ρ_{calc}g/cm^3	1.458
μ/mm^{-1}	7.123
F(000)	520.0
Crystal size/mm^3	0.2 × 0.18 × 0.14
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	5.186 to 146.89
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -21 ≤ l ≤ 20
Reflections collected	25521
Independent reflections	6412 [R_{int} = 0.0407, R_{sigma} = 0.0373]
Data/restraints/parameters	6412/1/308
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0961
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0990
Largest diff. peak/hole / e Å^{-3}	0.76/-0.48
Flack parameter	0.128(12)
CCDC	2349761

Table S9 Crystal data and structure refinement for **2aa**.

Identification code	**2aa**
Empirical formula	$C_{10}H_8BrN$
Formula weight	222.08
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.0173(4)
b/Å	9.8390(6)
c/Å	12.9563(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	894.54(9)
Z	4
ρ_{calc}g/cm^3	1.649
μ/mm^{-1}	3.812
F(000)	440.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	9.82 to 142.244
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected	20294
Independent reflections	2614 [R_{int} = 0.0781, R_{sigma} = 0.0490]
Data/restraints/parameters	2614/0/110
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0332, wR_2 = 0.0560
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.0586
Largest diff. peak/hole / e Å^{-3}	0.56/-0.56
Flack parameter	0.00(2)
CCDC	2349764

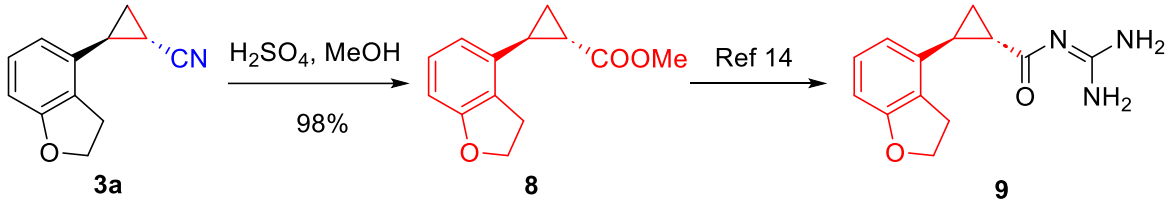
Table S10 Crystal data and structure refinement for **2ad**.

Identification code	**2ad**
Empirical formula	$C_{11}H_8F_3N$
Formula weight	211.18
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.1860(6)
b/Å	10.3981(8)
c/Å	12.9161(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	965.10(13)
Z	4
ρ_{calc}g/cm^3	1.453
μ/mm^{-1}	0.703
F(000)	432.0
Crystal size/mm^3	0.22 × 0.08 × 0.06
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	9.5 to 146.656
Index ranges	$-10 \le h \le 9$, $-14 \le k \le 13$, $-18 \le l \le 17$
Reflections collected	19415
Independent reflections	2901 [R_{int} = 0.0843, R_{sigma} = 0.0476]
Data/restraints/parameters	2901/0/137
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1063
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1077
Largest diff. peak/hole / e Å^{-3}	0.43/-0.25
Flack parameter	0.18(17)
CCDC	2351894

7 Diversification of Arylcyclopropanyl Nitriles

Preparation of 9

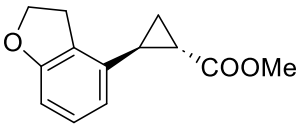
Alcoholysis of **3a** afforded the corresponding cyclopropyl carboxylic ester **8** with a yield of 98%.[13] In the presence of excess guanidine (free base) in DMF, **8** can be converted into **9** according to the reported procedure. [14]



3a **8** **9**

Preparation of arylcyclopropyl carboxylic ester 8

A mixture of **3a** (23 mg, 0.128 mmol), 98% H_2SO_4 (100 μL) and MeOH (0.5 mL) was heated to reflux for 3 h. After cooling down to room temperature, $NaHCO_3$ (aq) was added dropwise until pH = 7. Then the mixture was extracted by ethyl acetate, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography with PE/EA (2%-5% EA) to afford **8** as pale-yellow oil, yield 98%.

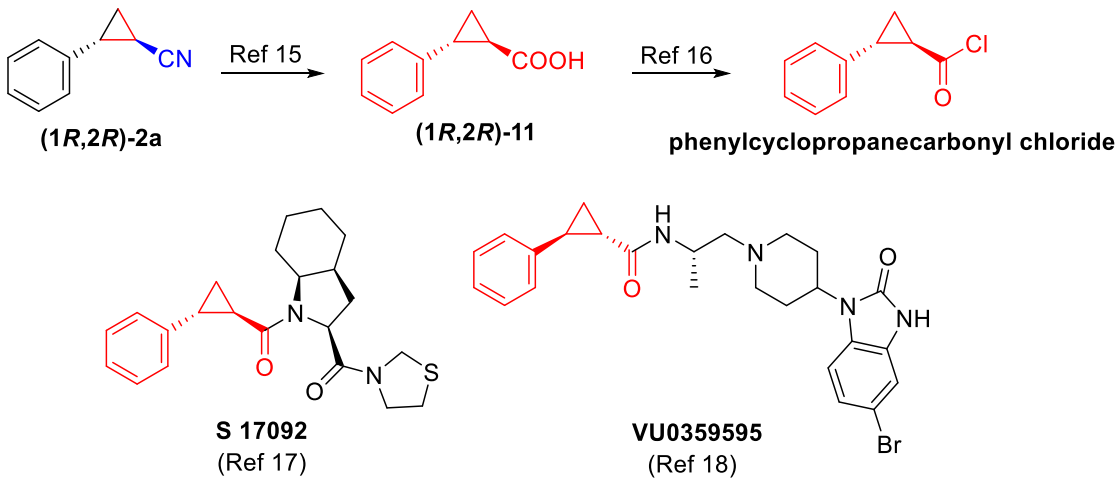


Methyl (1*S*,2*S*)-2-(2,3-dihydrobenzofuran-4-yl)cyclopropane-1-carboxylate (8). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (t, *J* = 7.8 Hz, 1H), 6.67 – 6.63 (m, 1H), 6.41 (dt, *J* = 7.8, 0.7 Hz, 1H), 4.59 (t, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 3.24 (t, *J* = 8.7 Hz, 2H), 2.42 (ddd, *J* = 9.2, 6.6, 4.2 Hz, 1H), 1.91 (ddd, *J* = 8.4, 5.2, 4.3 Hz, 1H), 1.58 (ddd, *J* = 9.4, 5.2, 4.4 Hz, 1H), 1.32 (ddd, *J* = 8.4, 6.6, 4.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.01, 159.86, 136.57, 128.30, 126.64, 116.22, 107.61, 71.10, 51.98, 28.57, 24.05, 22.61, 16.19. **GC-MS** m/z (% relative intensity): 218.2(91.8), 159.1(100), 158.1(80.3), 157.1(52), 144.1(78.1), 132.1(74.4), 131.1(68.3), 129.1(51.4), 115.1(88), 91.1(70.1).

7.1 Compounds in Figure 2

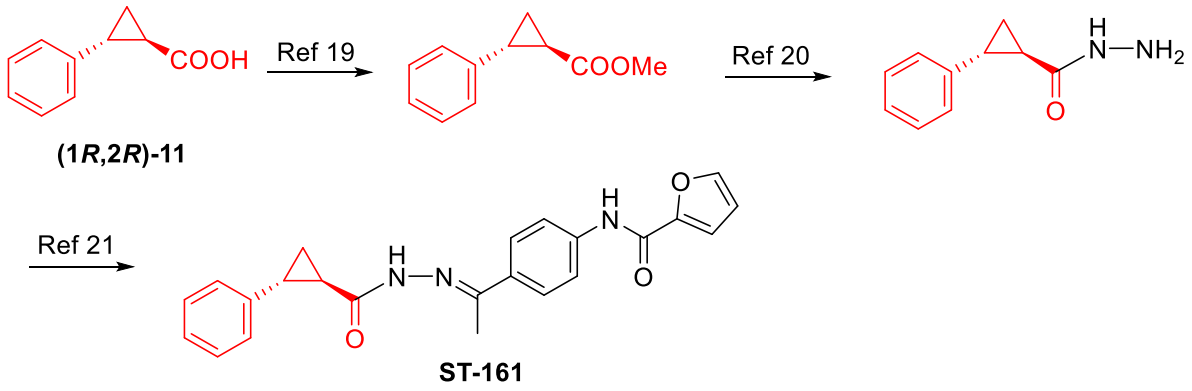
Preparation of S 17092, 11 and VU359595

According to the literature method,[15] phenyl cyclopropyl carboxylic acid **(1*R*,2*R*)-11** can be obtained via hydrolysis of **(1*R*,2*R*)-2a** under basic conditions in high yield. In the presence of $SOCl_2$, **(1*R*,2*R*)-11** can be converted into phenylcyclopropanecarbonyl chloride.[16] Coupling phenylcyclopropanecarbonyl chloride with the corresponding amines affords the desired product **S17092**,[17] and **VU359595** (using **(1*S*,2*S*)-2a** as starting material).[18]



Preparation of ST-161

Reaction of **(1*R*,2*R*)-11** with methanol affords the methyl ester,[19] followed by reaction of the ester with hydrazine hydrate to give phenylcyclopropane-1-carbohydrazide.[20] **ST-161** can be obtained by coupling the carbohydrazide with the corresponding ketone according to the reported procedure.[21]



7.2 Compounds in scheme 4 and figure 2

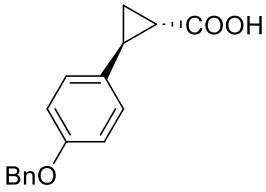
Preparation of phenylcyclopropylamines

Alkaline hydrolysis of **2a**, **2g**, **2l**, **2p** and **6** affords the corresponding carboxylic acids,[15] which can be further converted into the related *t*-butoxy carbamates via reaction with diphenylphosphoryl azide and *t*-butanol.[22] Hydrolysis of the *t*-butoxy carbamates with 6 M HCl afford the corresponding phenylcyclopropylamines (as HCl salt).[23]

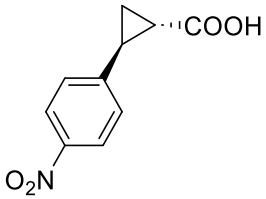
General Procedure for Hydrolysis of Cyclopropyl Nitriles to Cyclopropyl Carboxylic Acids

To a solution of KOH (50% w/w, 0.5 mL) and dioxane (0.1 mL) at room temperature was added cyclopropyl nitrile (**2g, 2l or 6**) (0.08 mmol). The mixture was heated to 90 °C. After

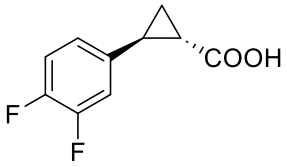
the reaction was completed as monitored by TLC. The reaction was cooled down to room temperature and neutralized by 3 M HCl. The crude product was extracted by ethyl acetate, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/hexanes to afford the product as solid.



(1*S*,2*S*)-2-(4-(Benzyloxy)phenyl)cyclopropane-1-carboxylic acid (11a), 82% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 4H), 7.35 – 7.27 (m, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.04 (s, 2H), 2.56 (ddd, *J* = 9.2, 6.7, 4.1 Hz, 1H), 1.82 (ddd, *J* = 8.3, 5.2, 4.1 Hz, 1H), 1.62 (dt, *J* = 9.5, 4.9 Hz, 1H), 1.35 (ddd, *J* = 8.3, 6.7, 4.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.63, 157.64, 136.93, 131.77, 128.59, 127.97, 127.49, 127.44, 114.93, 70.07, 26.61, 23.71, 17.23. HR-MS (ESI): calcd. for $C_{17}H_{16}O_3$ ([M-H]$^-$) 267.1016, found 267.1020.



(1*S*,2*S*)-2-(4-Nitrophenyl)cyclopropane-1-carboxylic acid (11b), 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 2.68 (ddd, *J* = 9.9, 6.5, 4.1 Hz, 1H), 2.01 (dt, *J* = 9.1, 4.8 Hz, 1H), 1.79 (dt, *J* = 9.8, 5.2 Hz, 1H), 1.50 – 1.47 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.21, 147.36, 146.79, 126.89, 123.89, 26.47, 24.69, 18.18. GC-MS m/z (% relative intensity): 207(16.6), 190.1(28.1), 162.1(9.2), 160.1(9.7), 136(9), 116.1(69.9), 115.1(100), 103.1(9.6). **HR-MS** (ESI): calcd. for $C_{10}H_9NO_4$ ([M-H]$^-$) 206.0448, found 206.0449.



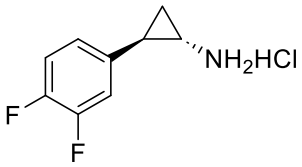
(1*S*,2*S*)-2-(3,4-Difluorophenyl)cyclopropane-1-carboxylic acid (11c), 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.70 (s, 1H), 7.10 – 7.02 (m, 1H), 6.91 – 6.86 (m, 1H), 6.85 – 6.82 (m, 1H), 2.55 (ddd, *J* = 9.3, 6.6, 4.1 Hz, 1H), 1.85 (dt, *J* = 8.9, 4.7 Hz, 1H), 1.65 (dt, *J* = 9.7, 5.1 Hz, 1H), 1.34 (ddd, *J* = 8.5, 6.6, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.62, 150.99 (dd, *J* = 105.9, 12.7 Hz), 148.53 (dd, *J* = 104.9, 12.7 Hz), 136.59 (dd, *J* = 5.9, 3.7 Hz), 122.44 (dd, *J* = 6.2, 3.5 Hz), 117.25 (d, *J* = 17.3 Hz), 115.23 (d, *J* = 17.7 Hz), 26.05 (d, *J* = 1.6 Hz), 23.94, 17.30. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -136.13 (d, *J* = 21.2 Hz), -137.84 (d, *J* = 21.3 Hz). GC-MS m/z (% relative intensity): 198.1(58), 180(23.1), 153.1(100), 152.1(50.8), 151.1(87), 143(17.2), 134.1(11.9), 133.1(77.3), 127.1(58.6), 125.1(13), 101.1(14.4). **HR-MS (ESI):** calcd. for $C_{10}H_8F_2O_2$ ([M-H]$^-$) 197.0409, found 197.0409.

Spectral data were in accord with the literature values.[24]

Preparation of cyclopropyl amine 14. [25]

A mixture of **11c** (0.13 mmol, 25.9 mg), diphenylphosporazidate (0.15 mmol, 41.5 mg), and triethylamine (0.18 mmol, 20.6 mg) in dry *tert*-BuOH (1.3 mL) was stirred at 90 °C under argon atmosphere for 48 h. The solution was concentrated and poured into 10% aqueous

Na_2CO_3 (5 mL) and extracted with Et_2O three times. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated. The resulting *tert*-butyl carbamate was dissolved in a mixture of MeOH (1 mL) and 6 M aqueous HCl (2 mL). The solution was maintained at reflux for 12 h. After concentration under reduced pressure, the residue was washed with Et_2O three times, and the white solid was obtained as the product as HCl salt.

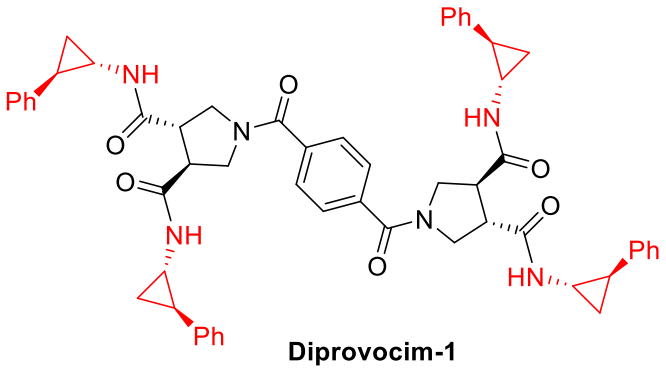


(1*S*,2*R*)-2-(3,4-Difluorophenyl)cyclopropan-1-amine hydrochloride (14), 92% yield. ^{1}H NMR (500 MHz, CD_3OD) δ 7.20 (m, 2H), 7.12 (m, 2H), 7.00 (m, 2H), 2.85 (m, 2H), 2.38 (ddd, *J* = 10.2, 6.5, 3.6 Hz, 2H), 1.43 (ddd, *J* = 10.2, 6.8, 4.5 Hz, 2H), 1.34 (dt, *J* = 7.9, 6.7 Hz, 2H), 1.29 (s, 1H). **^{13}C NMR** (126 MHz, CD_3OD) δ 150.63 (dd, *J* = 127.3, 12.9 Hz), 148.68 (dd, *J* = 126.4, 12.8 Hz), 136.03 (d, *J* = 9.5 Hz), 122.75 (dd, *J* = 6.4, 3.4 Hz), 117.05 (d, *J* = 17.7 Hz), 115.14 (d, *J* = 18.1 Hz), 30.57, 20.38 (d, *J* = 1.7 Hz), 12.48. **^{19}F NMR** (376 MHz, CD_3OD) δ -136.09 (d, *J* = 21.1 Hz), -137.80 (d, *J* = 21.1 Hz). GC-MS m/z (% relative intensity): 168(36.9), 153.1(36.1), 152.1(100), 151.1(73.3), 148(16.4), 140(18.8), 139(14.9), 132.9(17.7), 127(26.3), 125(12.2), 119(16.8), 114.1(18.3), 101(19.2). **HR-MS** (ESI): calcd. for $C_9H_{10}ClF_2N$ ([M-Cl]$^+$) 170.0776, found 170.0775.

Spectral data were in accord with the literature values.[26]

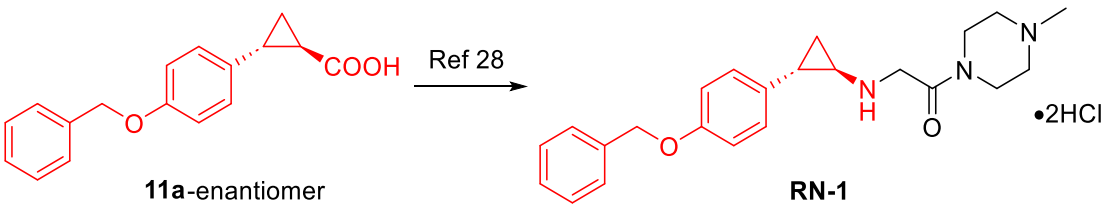
Diversification of aryl cyclopropyl nitriles to bio-active cyclopropyl carboxamides.

According to the reported procedures, coupling of phenylcyclopropylamine with the corresponding carboxylic acid affords **Diprovocim-1**.[27]



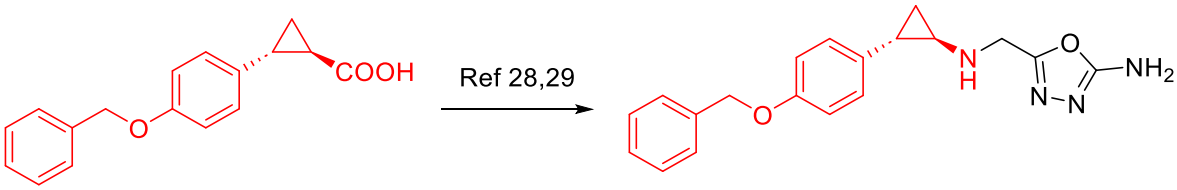
Diprovocim-1
(Ref 27)

Alkylation of *tert*-butyl ((1*R*,2*S*)-2-(4-(benzyloxy)phenyl)cyclopropyl)carbamate, which can be prepared from **11a**-enatniomer, with 2-chloro-1-(4-methylpiperazin-1-yl)ethan-1-one in the presence of NaH affords *tert*-butyl ((1*R*,2*S*)-2-(4-(benzyloxy)phenyl)cyclopropyl)(2-(4-methylpiperazin-1-yl)-2-oxoethyl)carbamate. Further deprotection of the Boc-group by ethereal HCl solution gives **RN-1** as a water soluble HCl salt.[28]



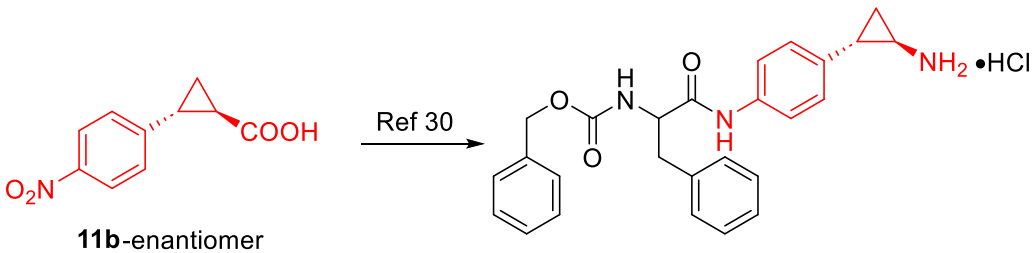
11a-enantiomer **RN-1**

(1*R*,2*S*)-2-(4-(benzyloxy)phenyl)cyclopropan-1-amine can be easily prepared from **11a**-enantiomer,[28] then coupling with *tert*-butyl (5-(chloromethyl)-1,3,4-oxadiazol-2-yl)carbamate under alkaline condition and followed by deprotection of the Boc group under acidic conditions affords **ORY-2001**.[29]



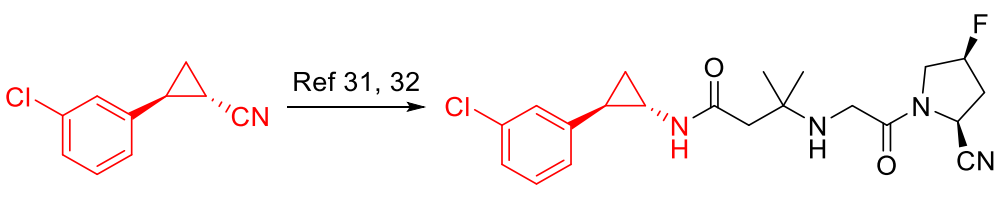
11a-enantiomer **ORY-2001 (Vafidemstat)**

According to the reported procedures, reducing the nitro group of *tert*-butyl ((1*R*,2*S*)-2-(4-nitrophenyl)cyclopropyl)carbamate, which can be prepared from **11b**-enantiomer,[30] followed by coupling with corresponding carboxylic acid affords *N*-Boc MC2580. Further deprotection of the Boc-group in the presence of 6 M HCl yields **MC2580**.[30]



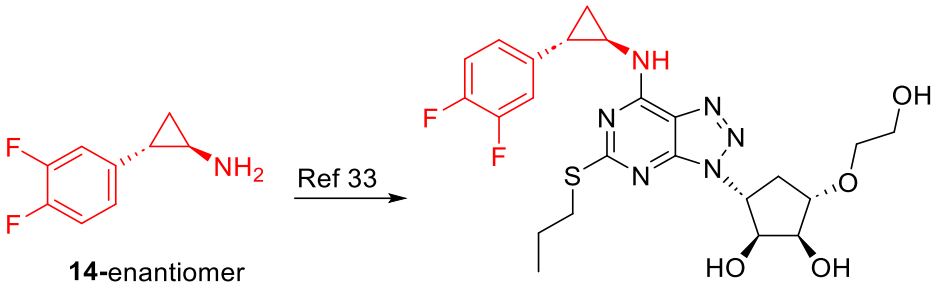
11b-enantiomer **MC2580**

According to the reported procedures, coupling of (1*S*,2*R*)-2-(3-chlorophenyl)cyclopropan-1-amine, which can be prepared from **2p**,[31] with 3-((tert-butoxycarbonyl)amino)-3-methylbutanoic acid affords amide *tert*-butyl (4-(((1*S*,2*R*)-2-(3-chlorophenyl)cyclopropyl)amino)-2-methyl-4-oxobutan-2-yl)carbamate. After deprotection of the Boc group under acidic condition and followed by coupling with (2*S*,4*S*)-1-(2-bromoacetyl)-4-fluoropyrrolidine-2-carbonitrile, **13** is obtained.[32]



2p **13**

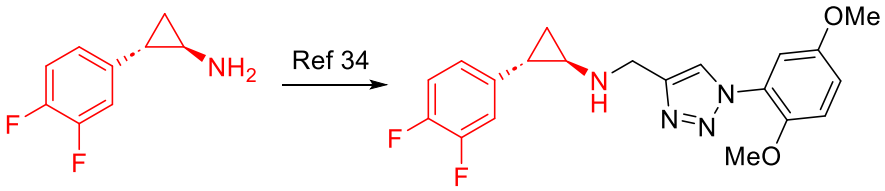
According to the reported procedures,[33] coupling of (1*R*,2*S*)-2-(3,4-difluorophenyl)cyclopropan-1-amine (**14**-enantiomer) with 7-chloro triazolopyrimidine and followed by deprotection of the ketal group affords **Ticagrelor (AZD6140).**



14-enantiomer

Ticagrelor (AZD6140)

According to the reported procedures,[34] reaction of *tert*-butyl ((1*R*,2*S*)-2-(3,4-difluorophenyl)cyclopropyl)carbamate (prepared from **14**-enantiomer) with propargyl bromide in the presence of NaH affords *tert*-butyl ((1*R*,2*S*)-2-(3,4-difluorophenyl)cyclopropyl)(prop-2-yn-1-yl)carbamate. Deprotection of the Boc group under acidic condition affords (1*R*,2*S*)-2-(3,4-difluorophenyl)-*N*-(prop-2-yn-1-yl)cyclopropan-1-amine, which react with 2-azido-1,4-dimethoxybenzene to give **7** via "Click Chemistry" reaction.



14-enantiomer

7

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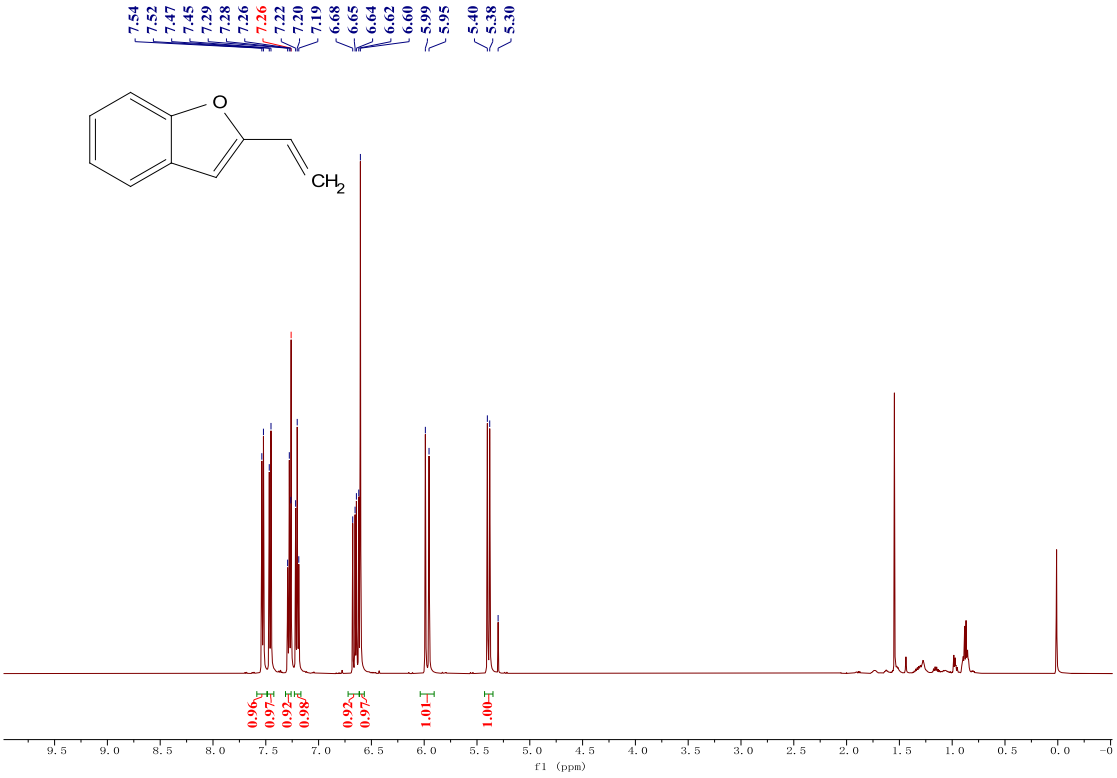
9 NMR Spectra

^{1}H NMR spectrum of **1x** in $CDCl_3$.



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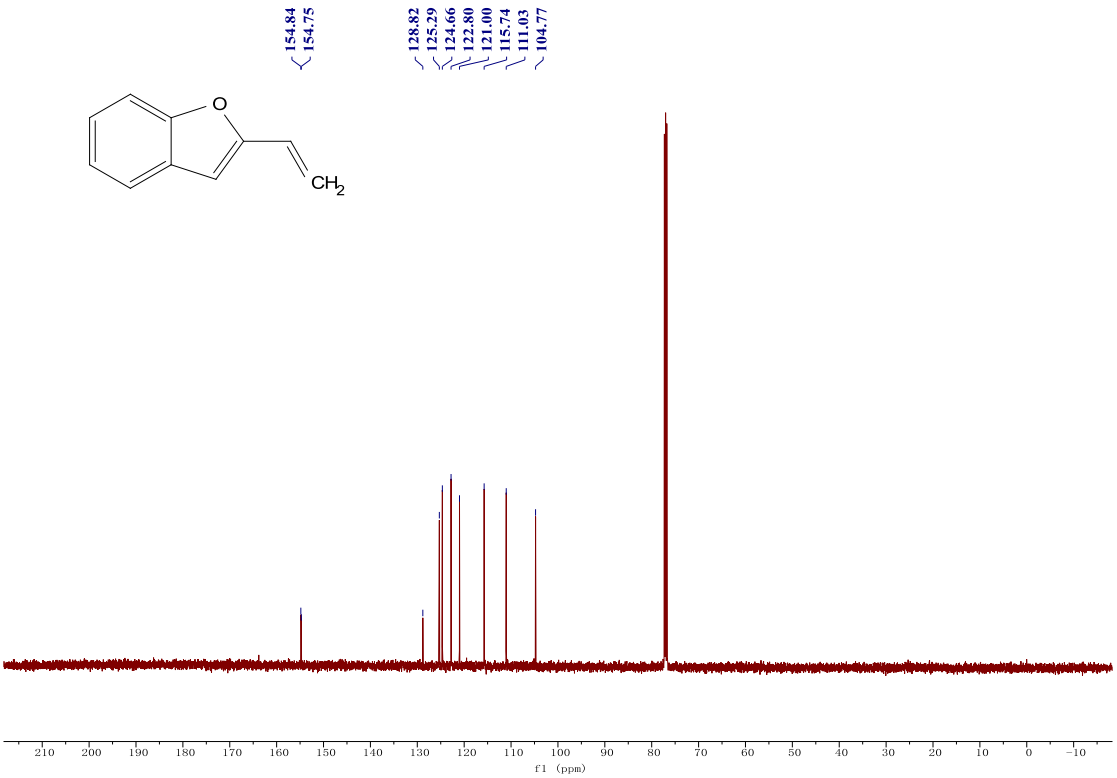

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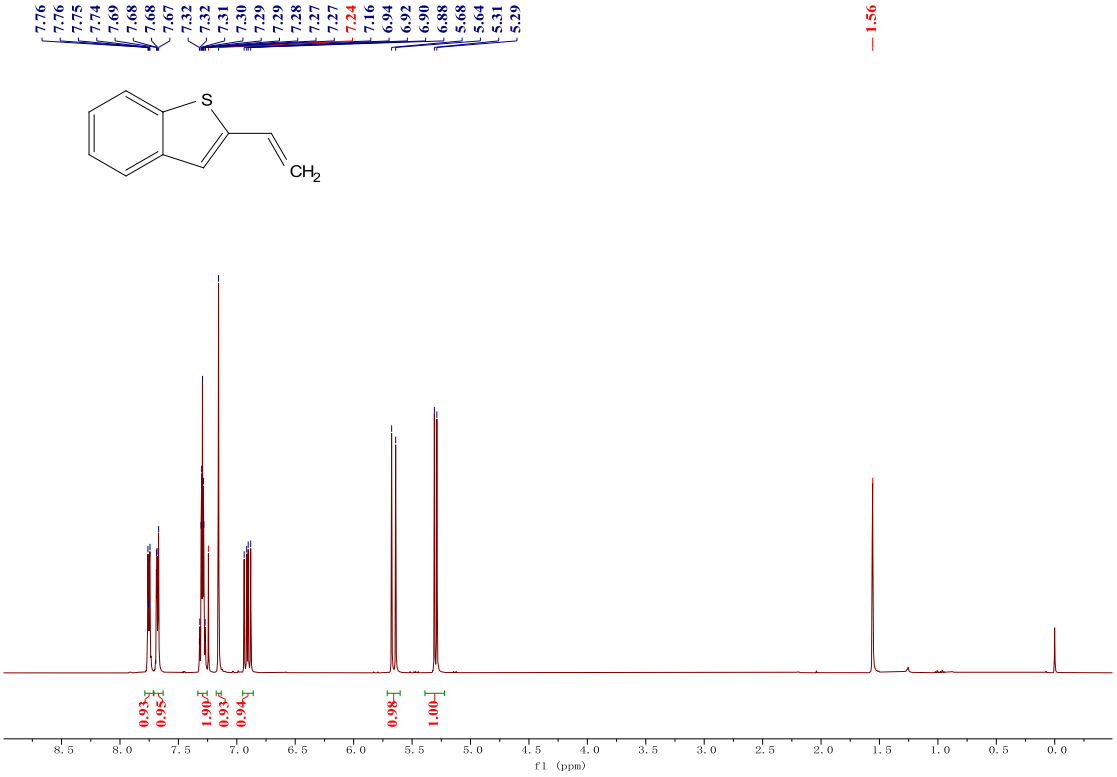

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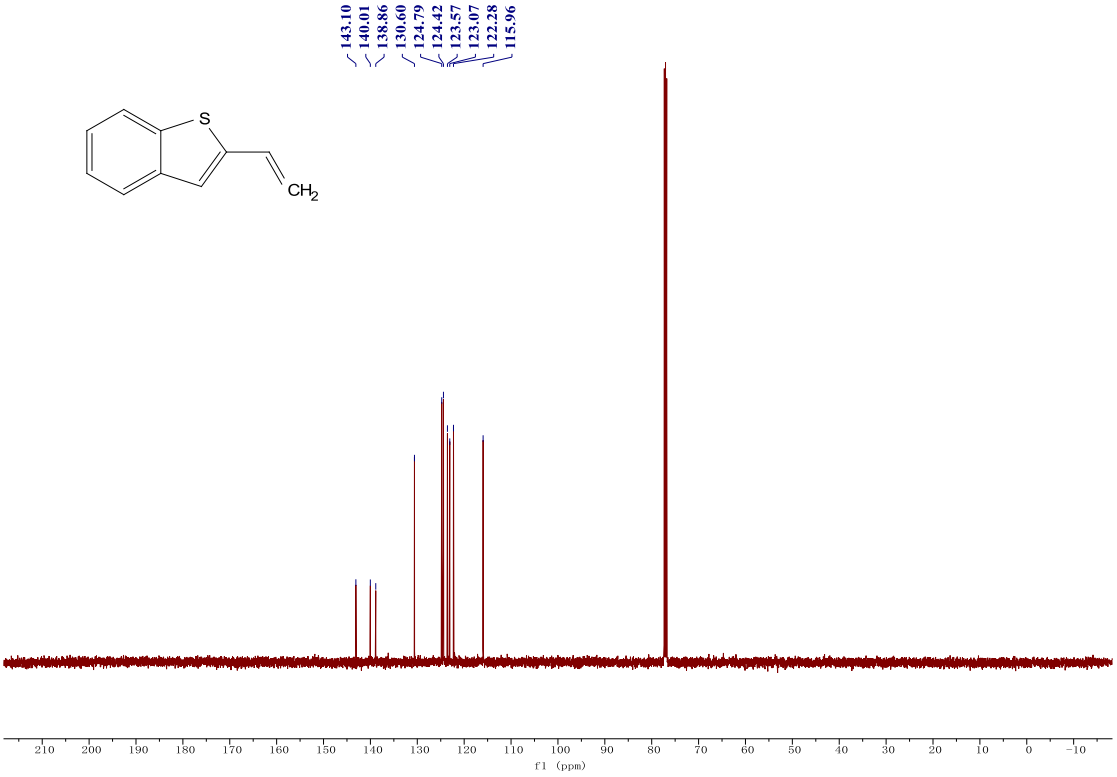

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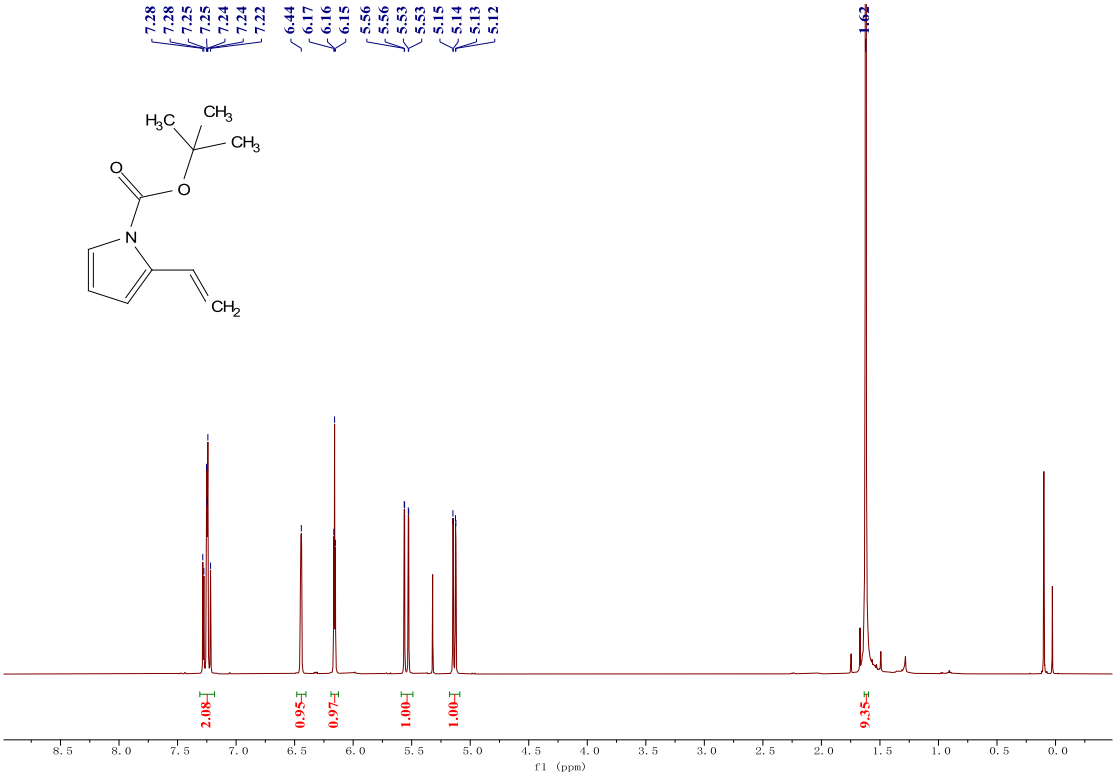

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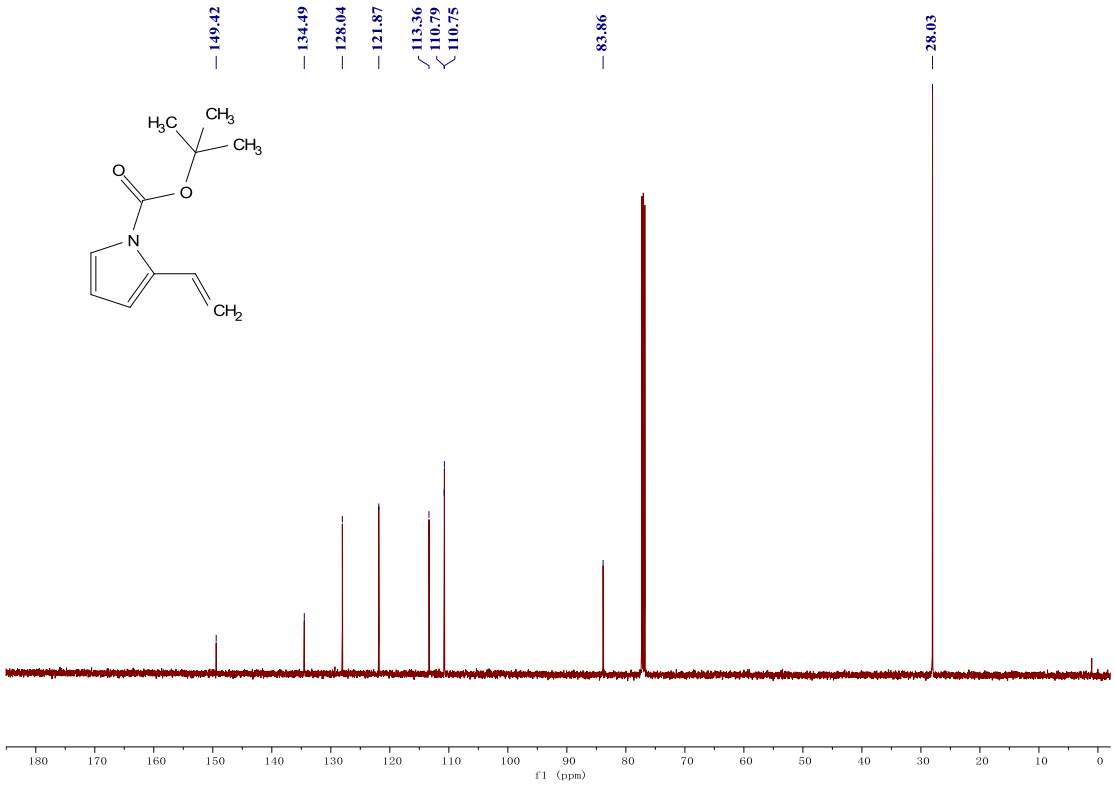

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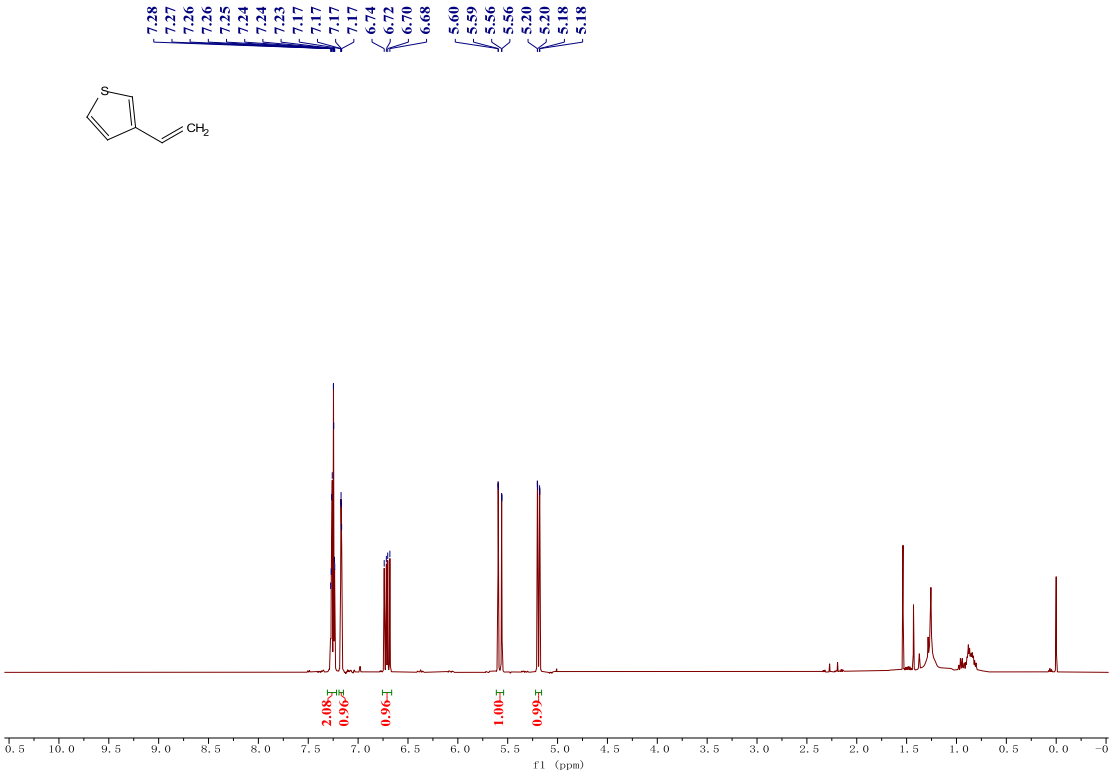

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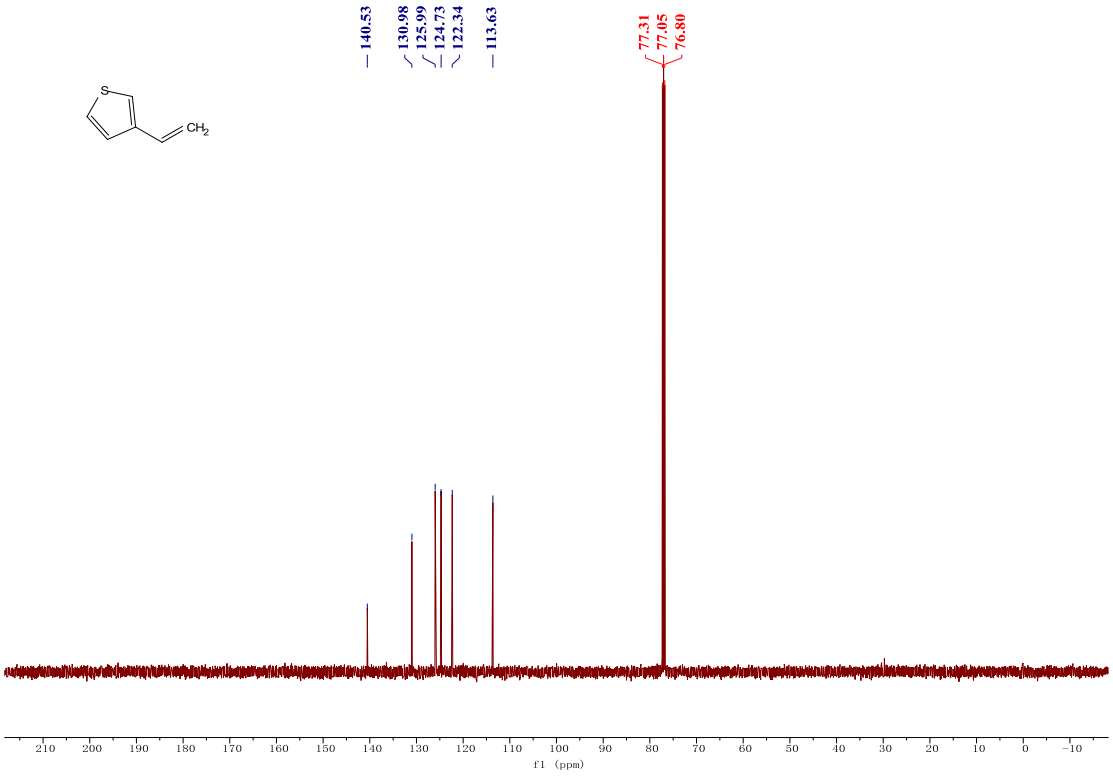

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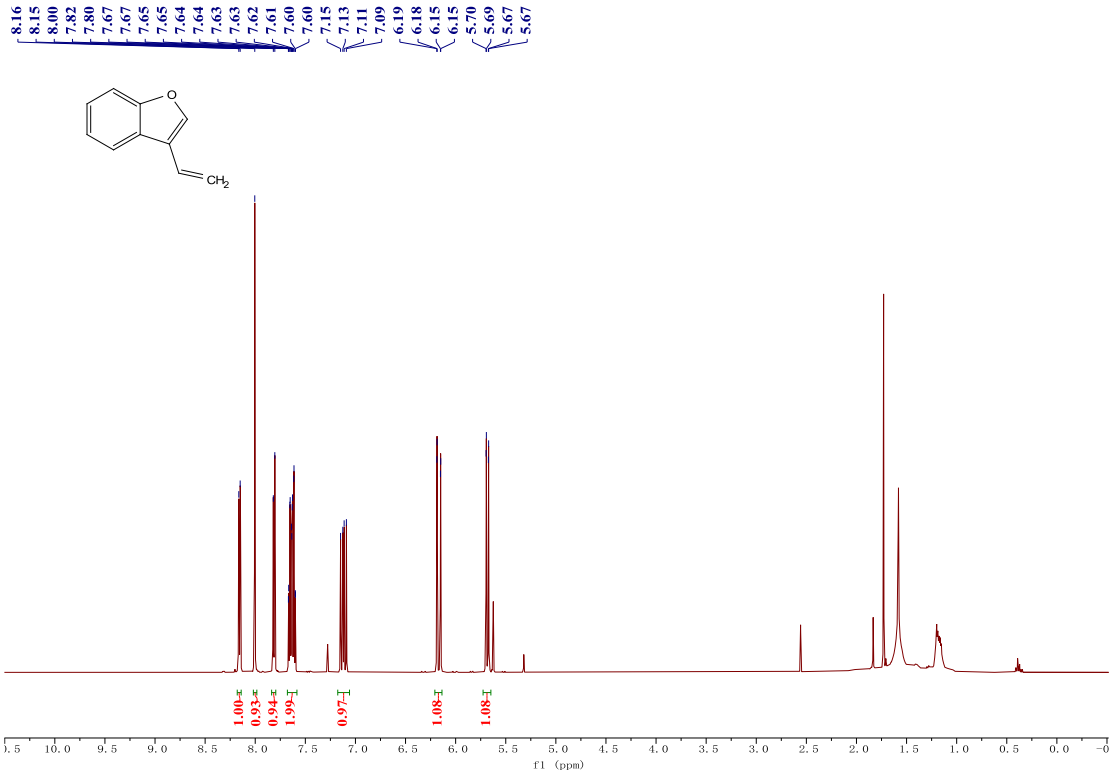

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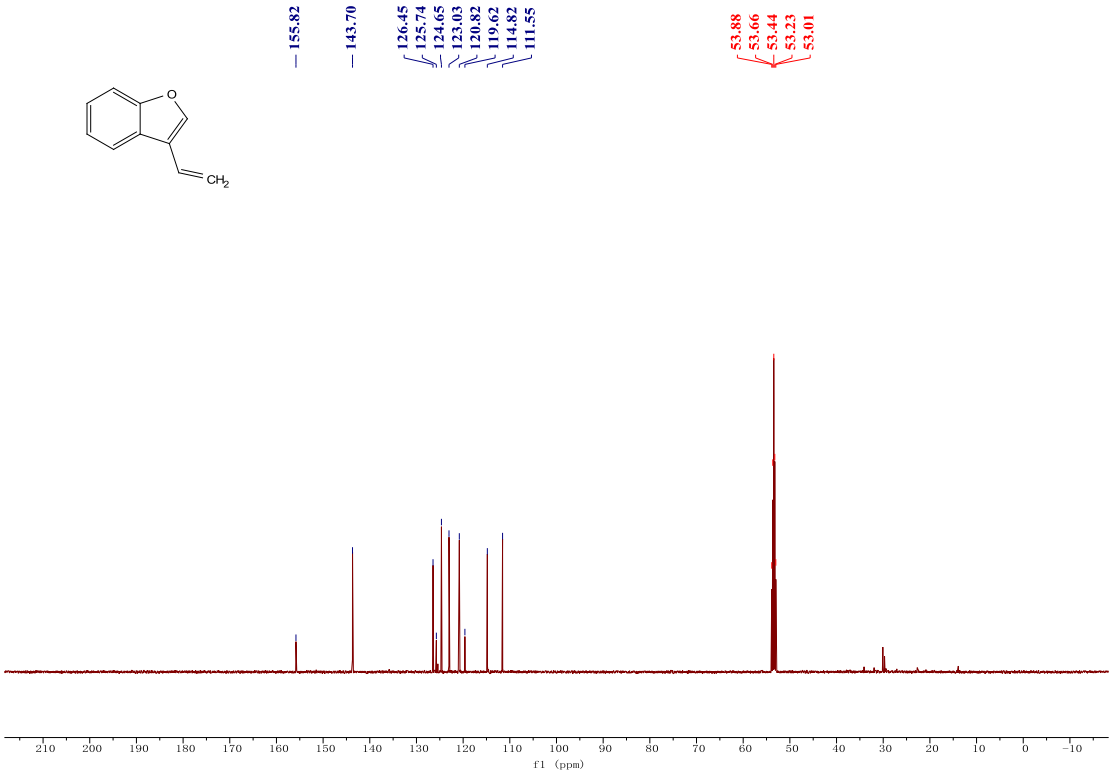
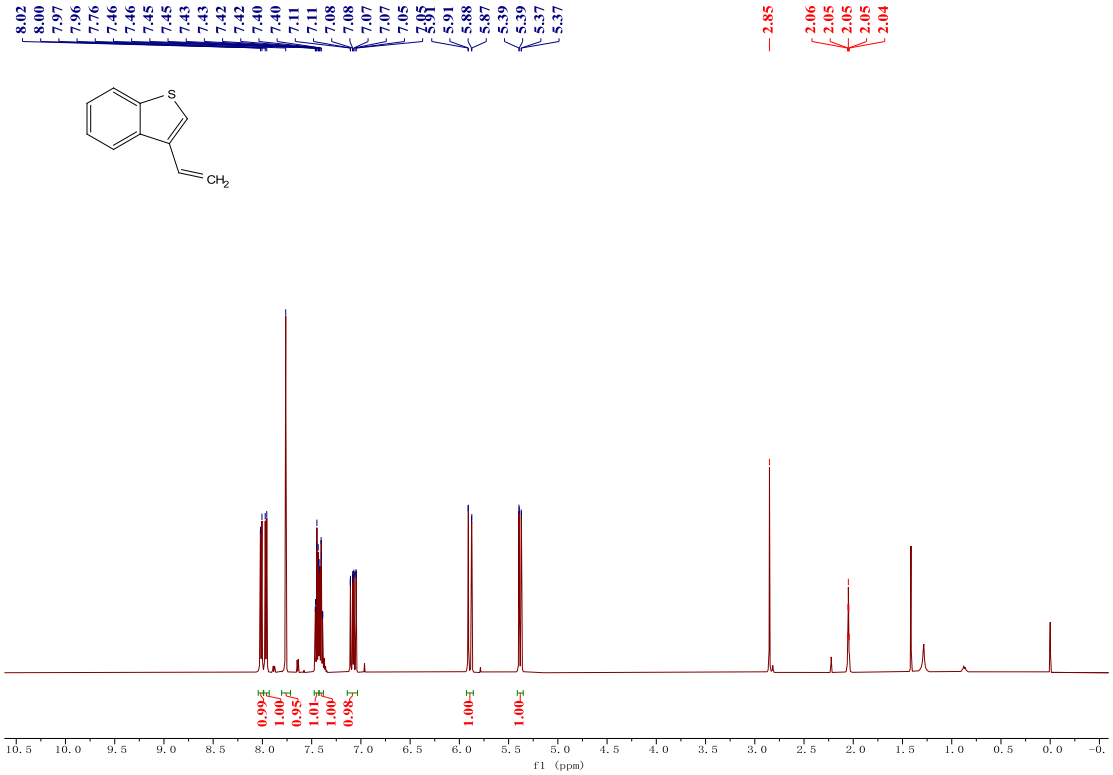


^{1}H NMR spectrum of **1ak** in Acetone-*d6*



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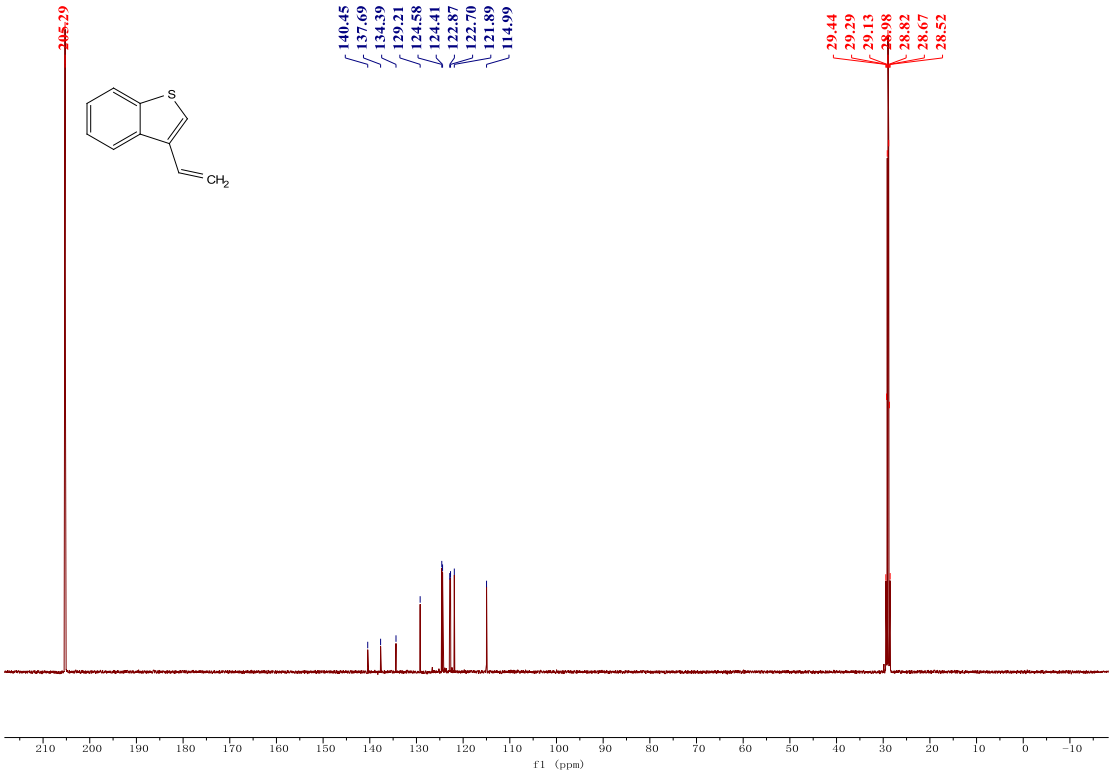

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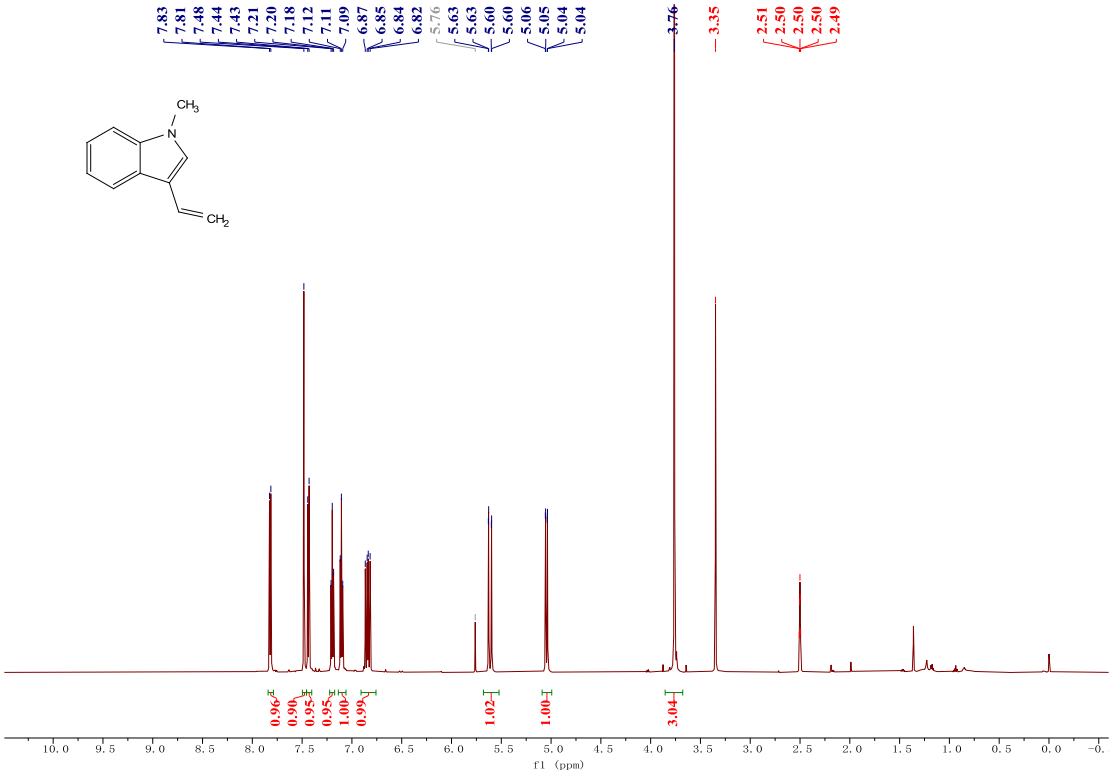
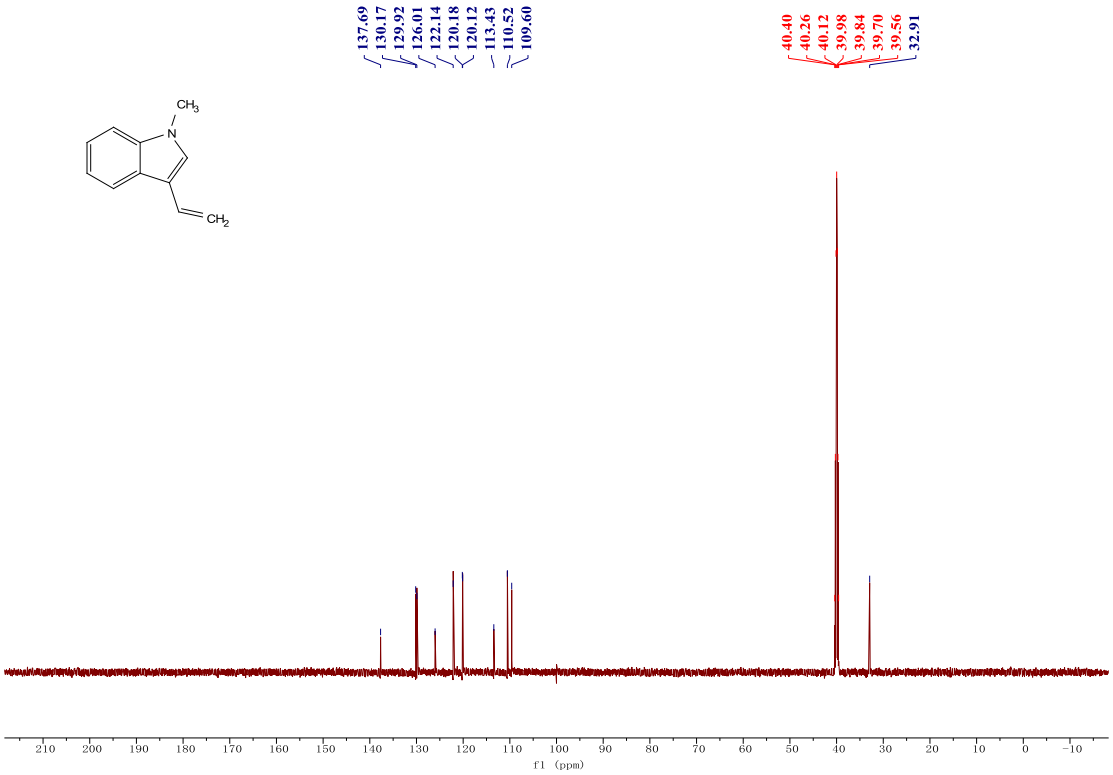
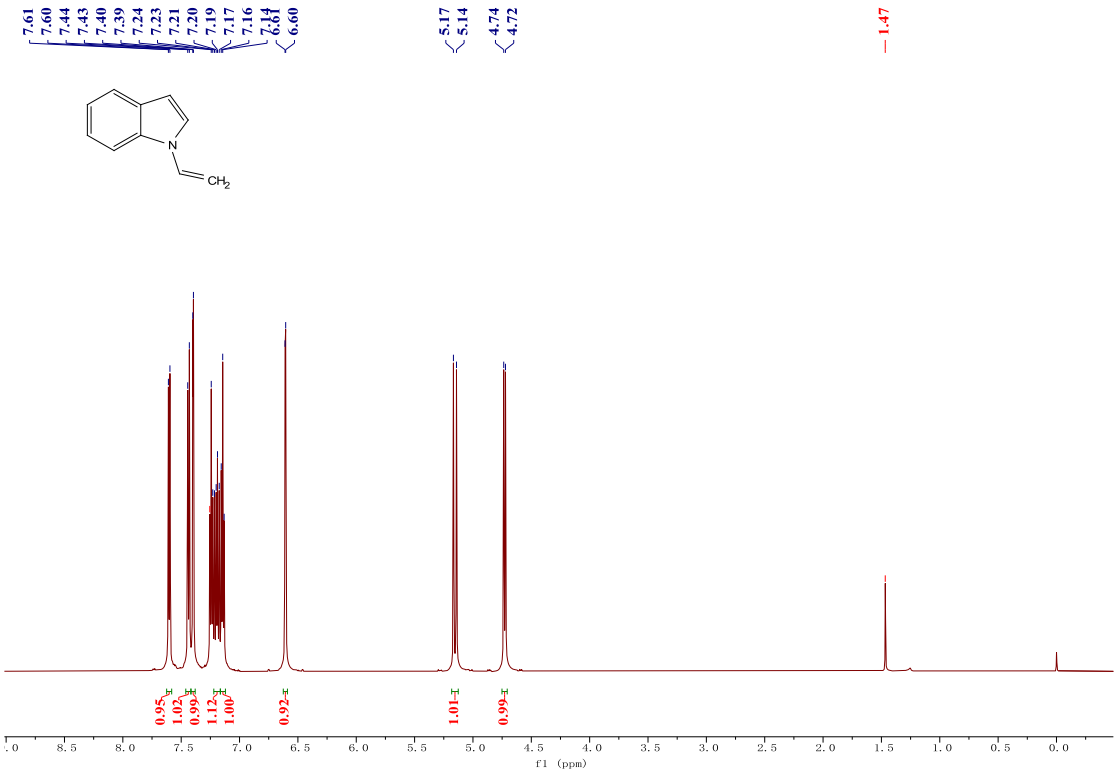


^{13}C NMR spectrum of **1al** in DMSO-*d*6



^{1}H NMR spectrum of **1ag** in $CDCl_3$



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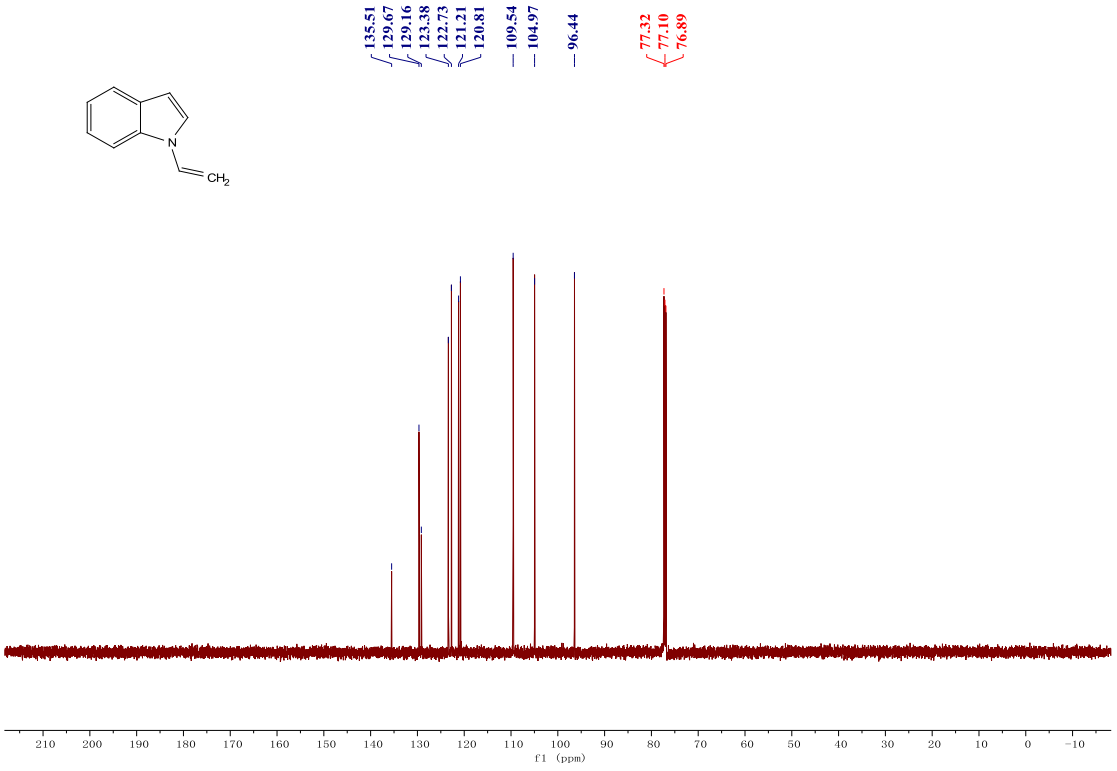

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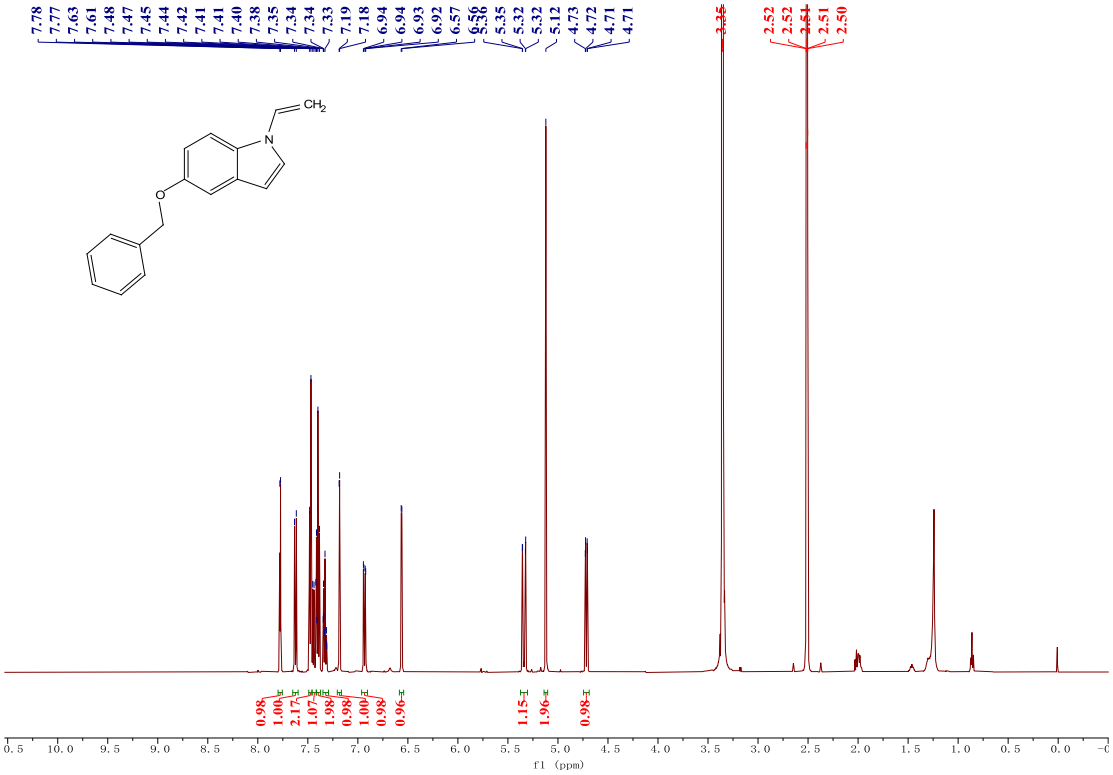

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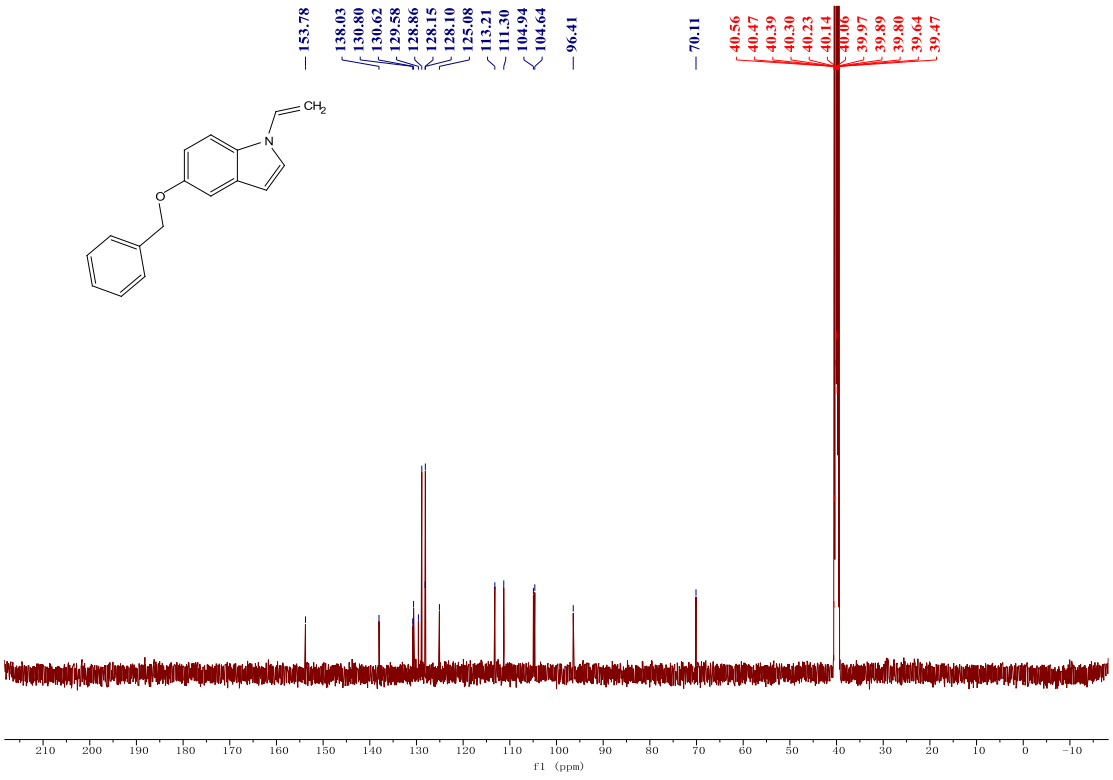
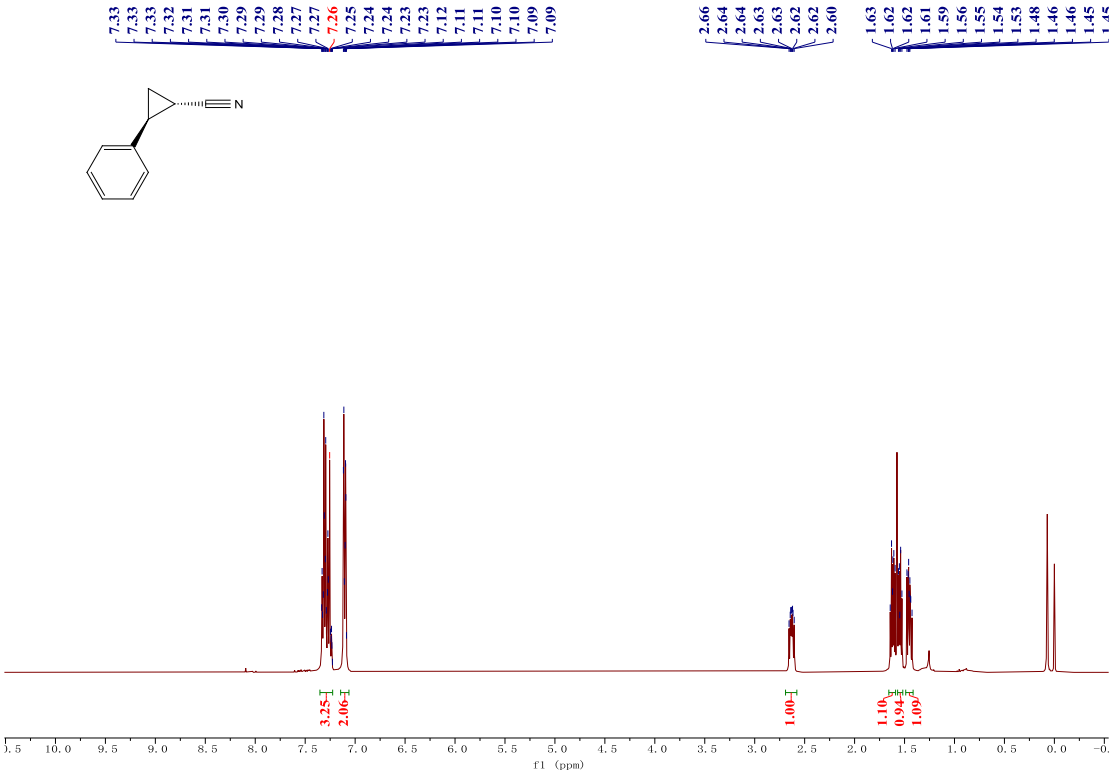


^{1}H NMR spectrum of **2a** in $CDCl_3$



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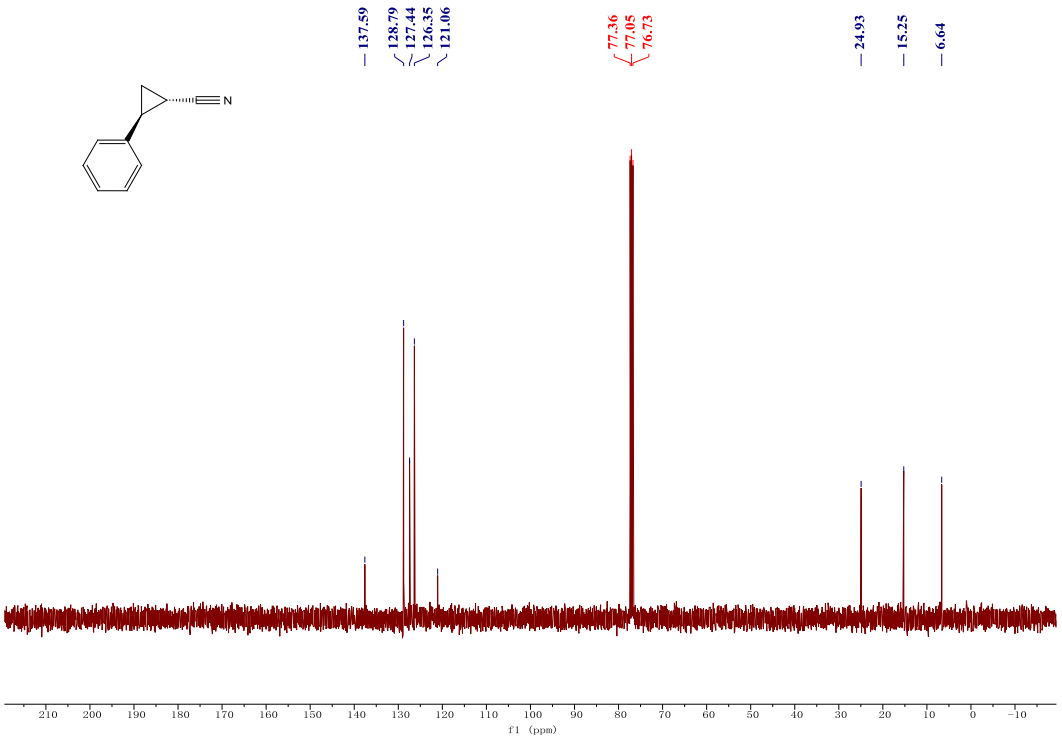

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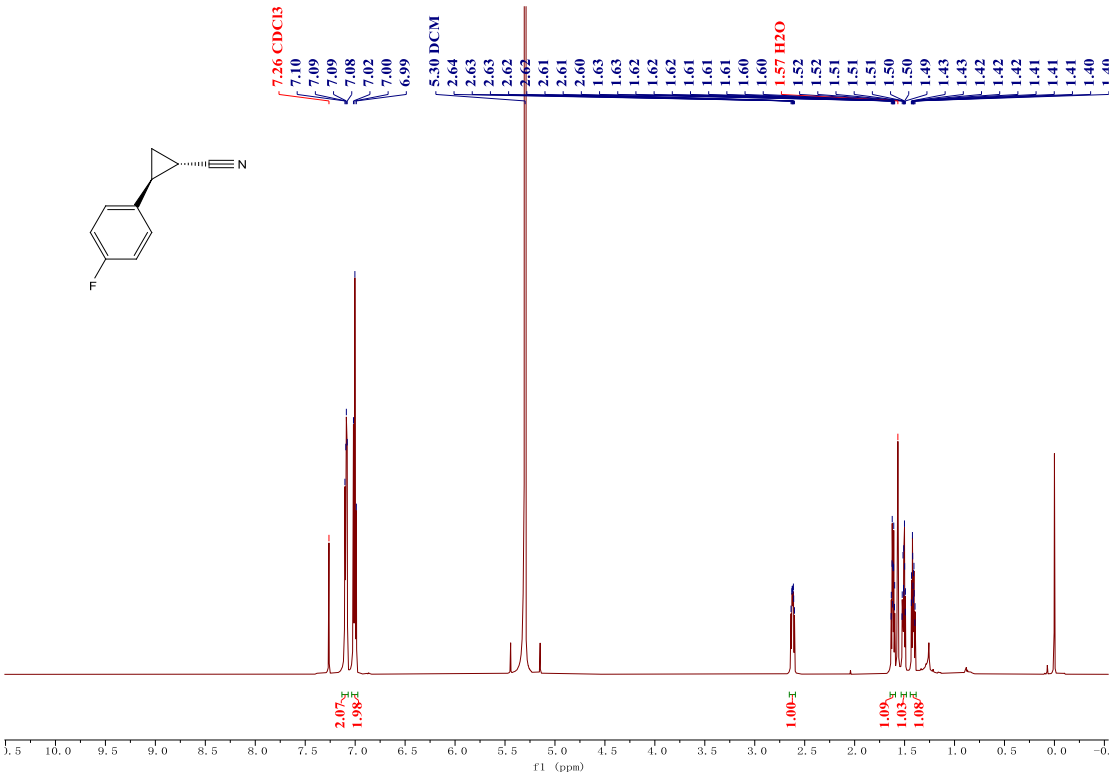
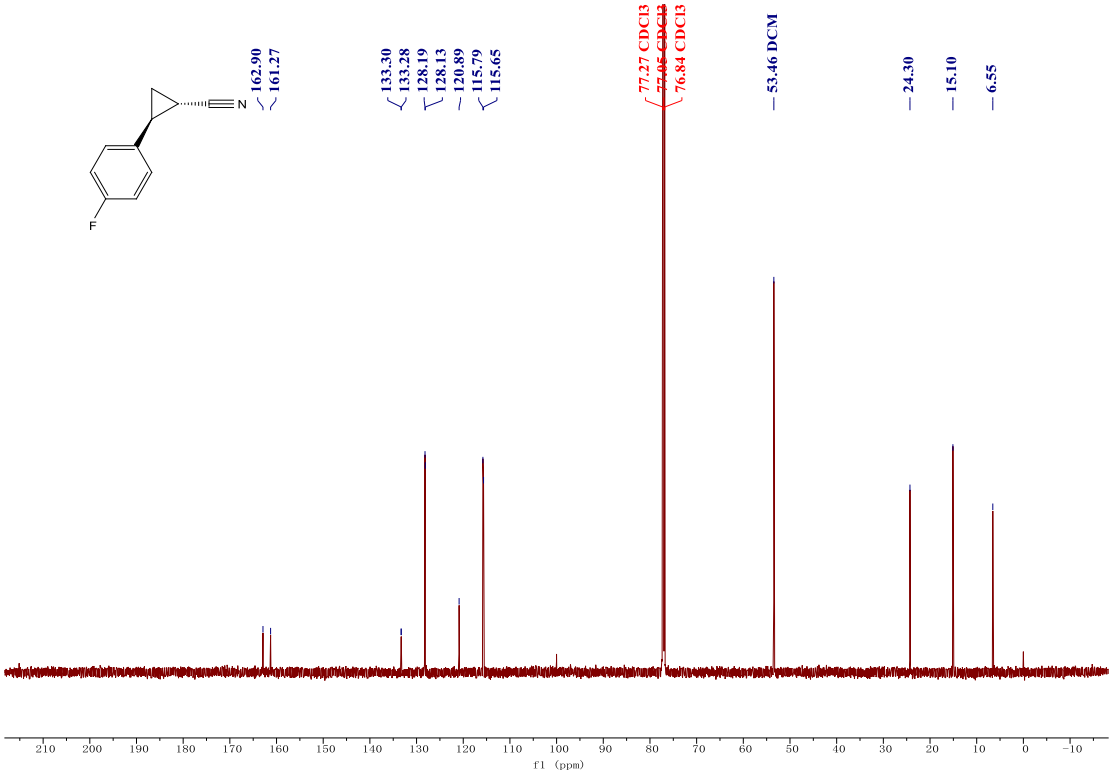
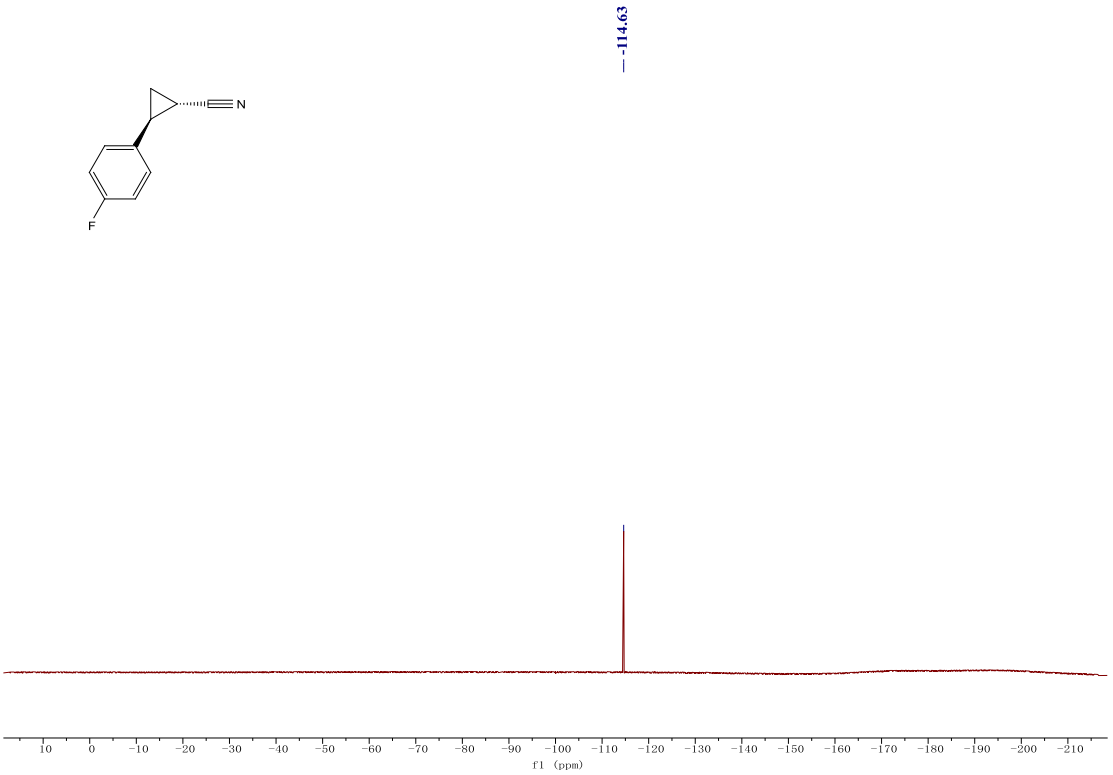


^{13}C NMR spectrum of **2b** in $CDCl_3$



^{19}F NMR spectrum of **2b** in $CDCl_3$



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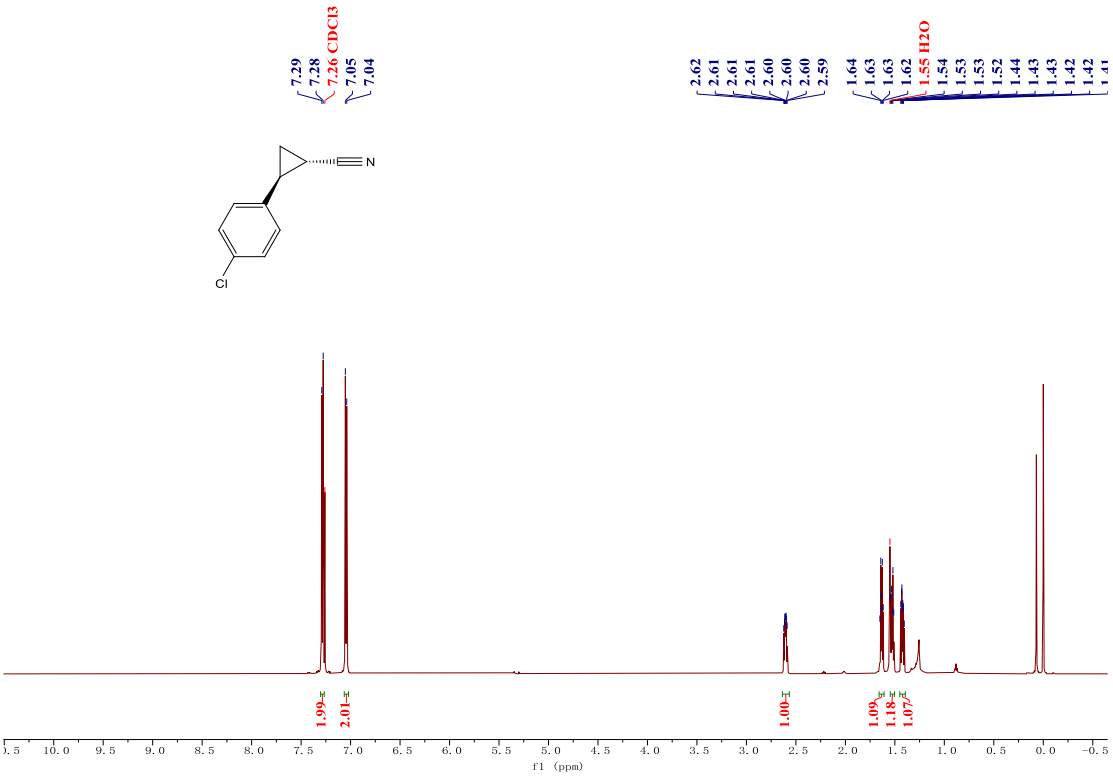
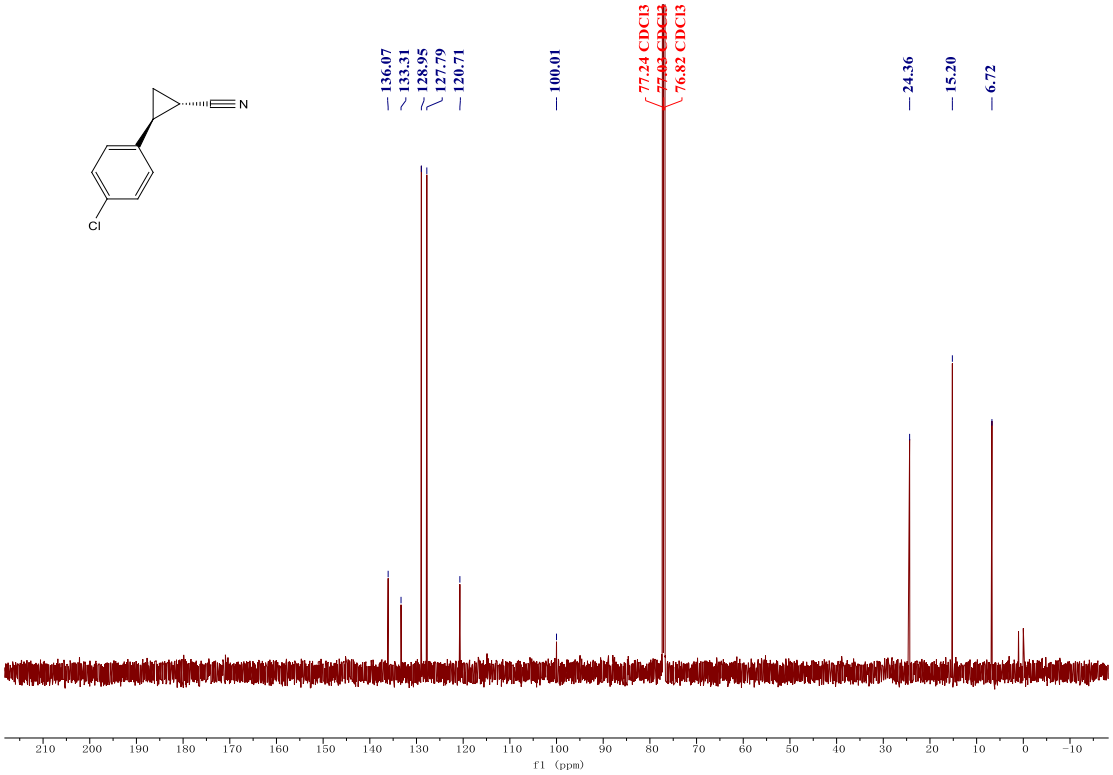


^{13}C NMR spectrum of **2c** in $CDCl_3$



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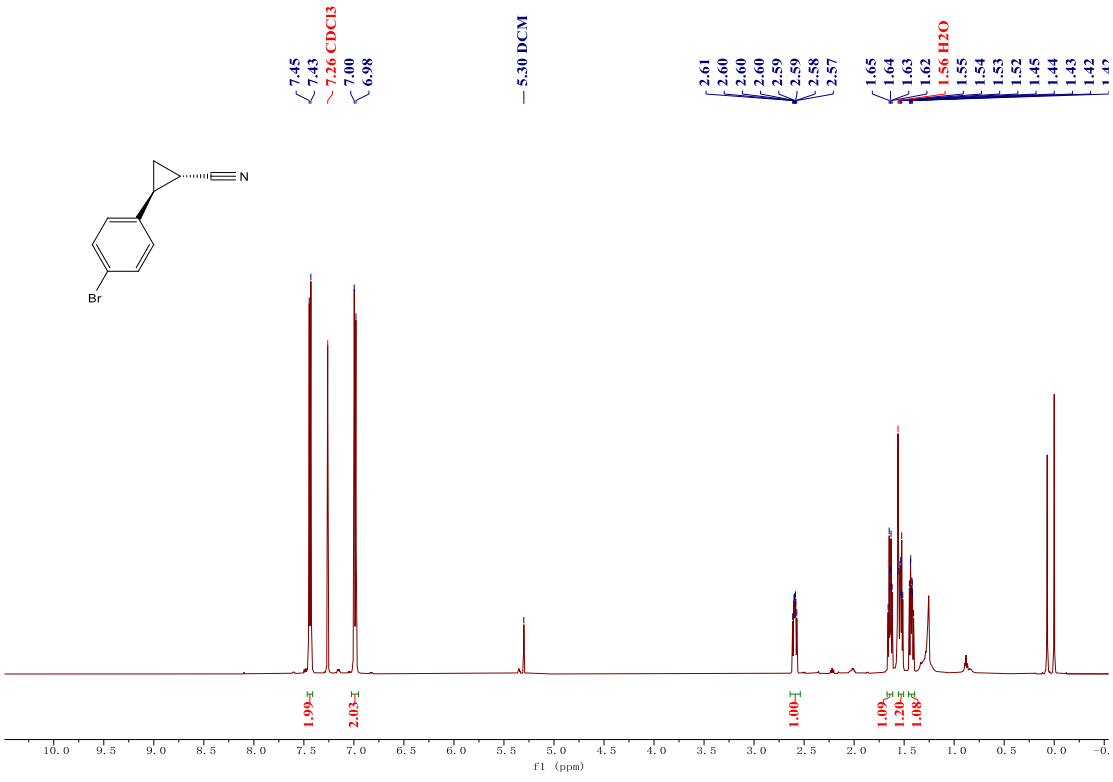

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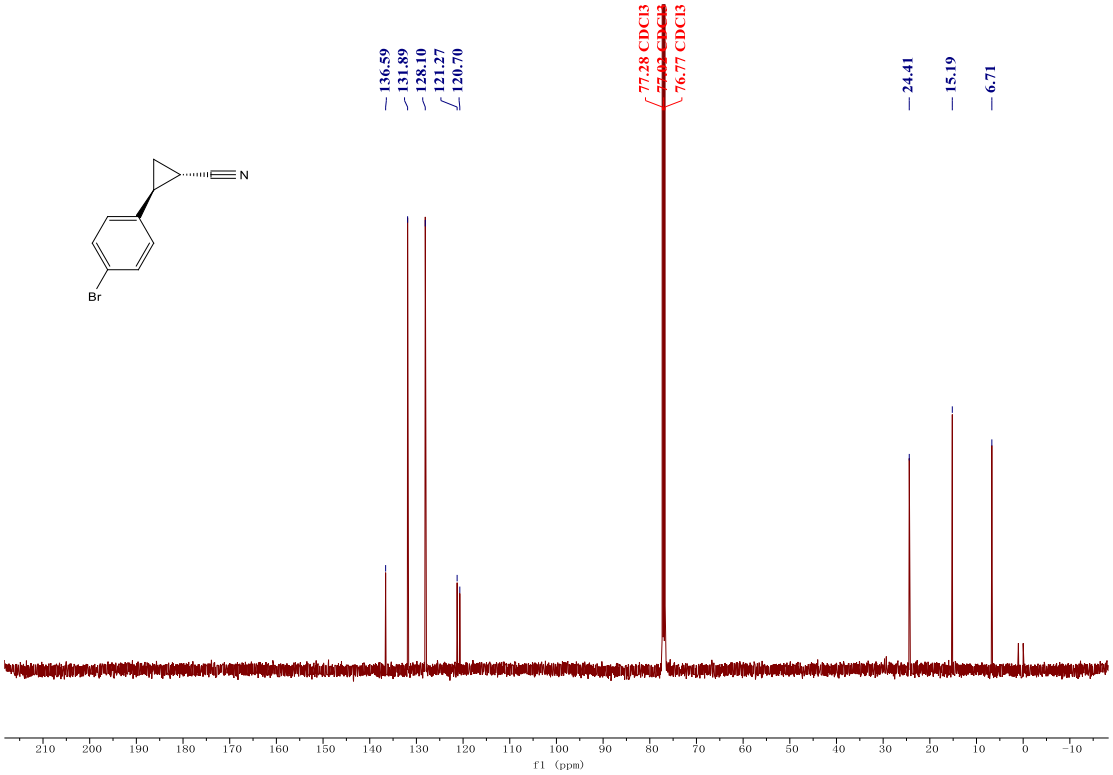

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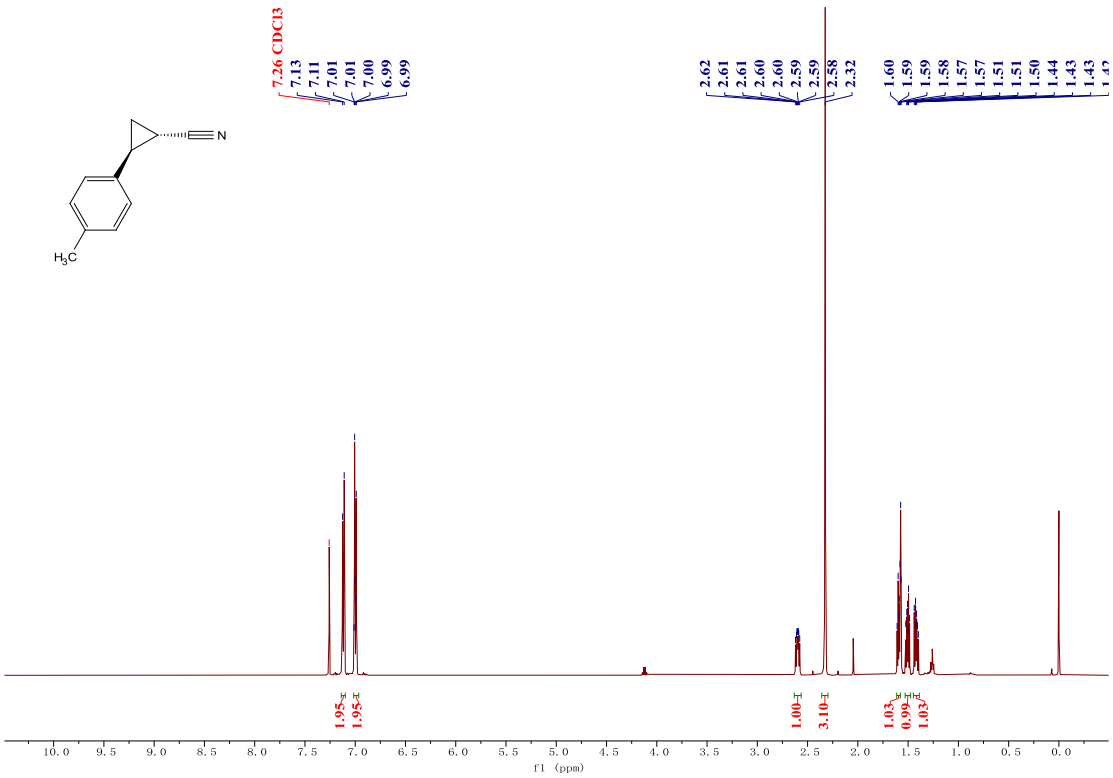

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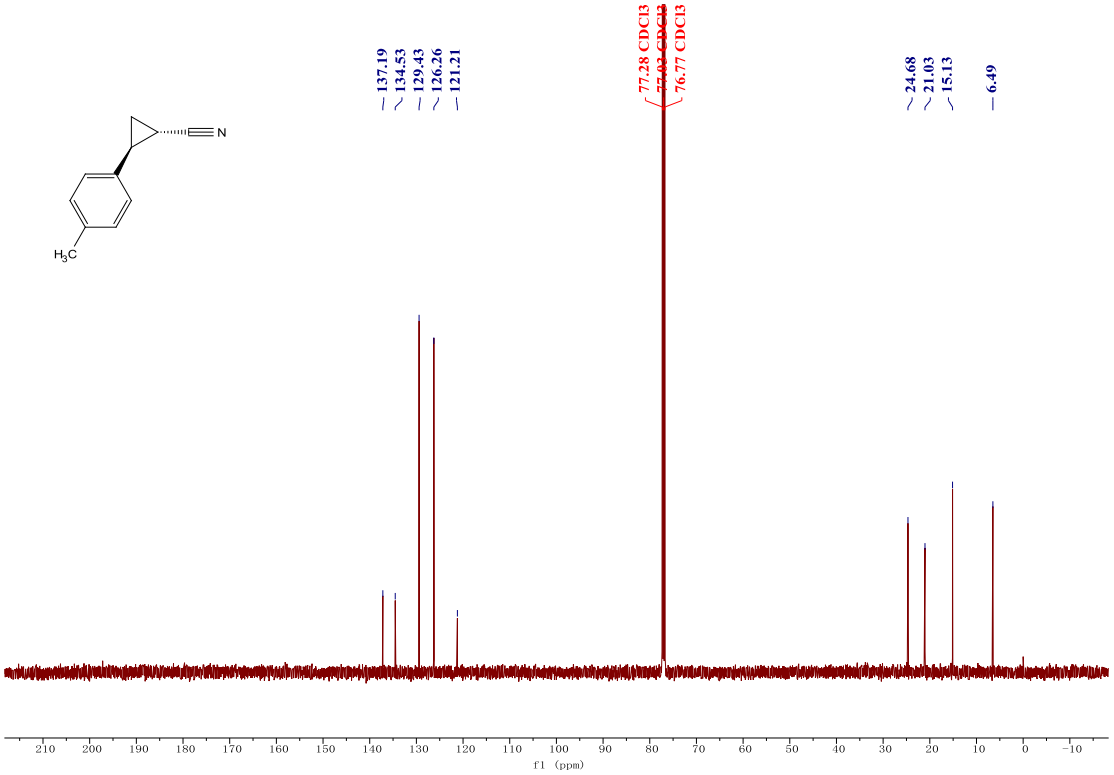

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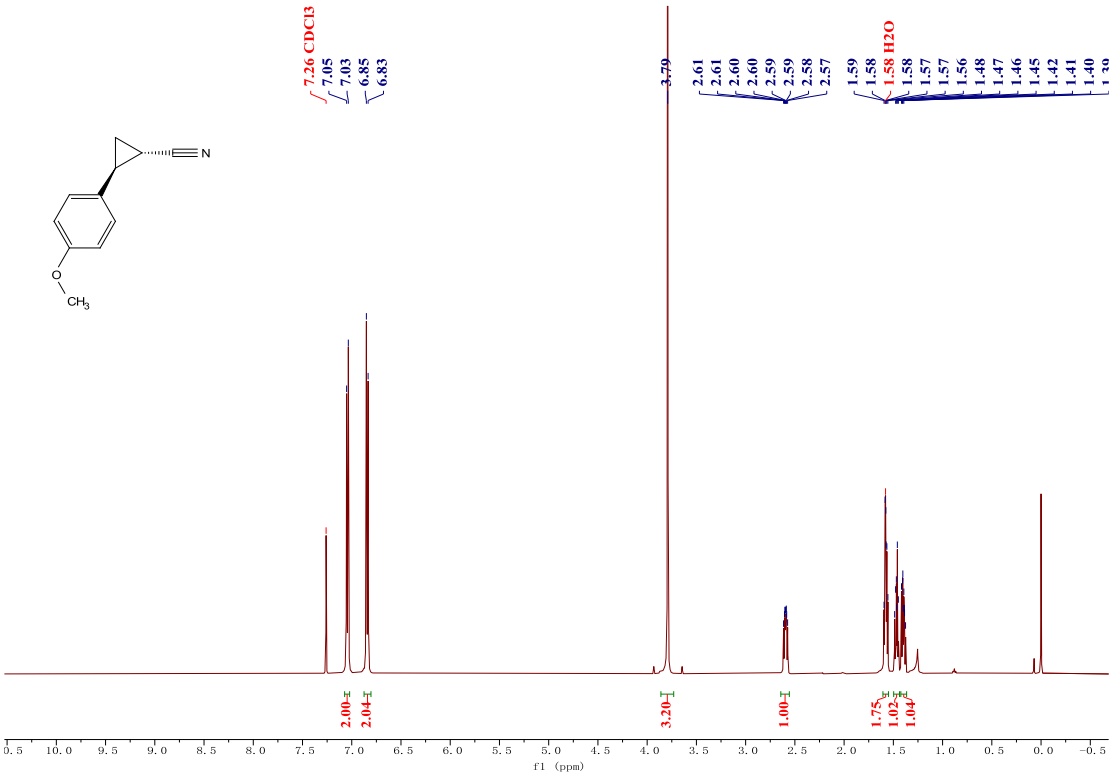
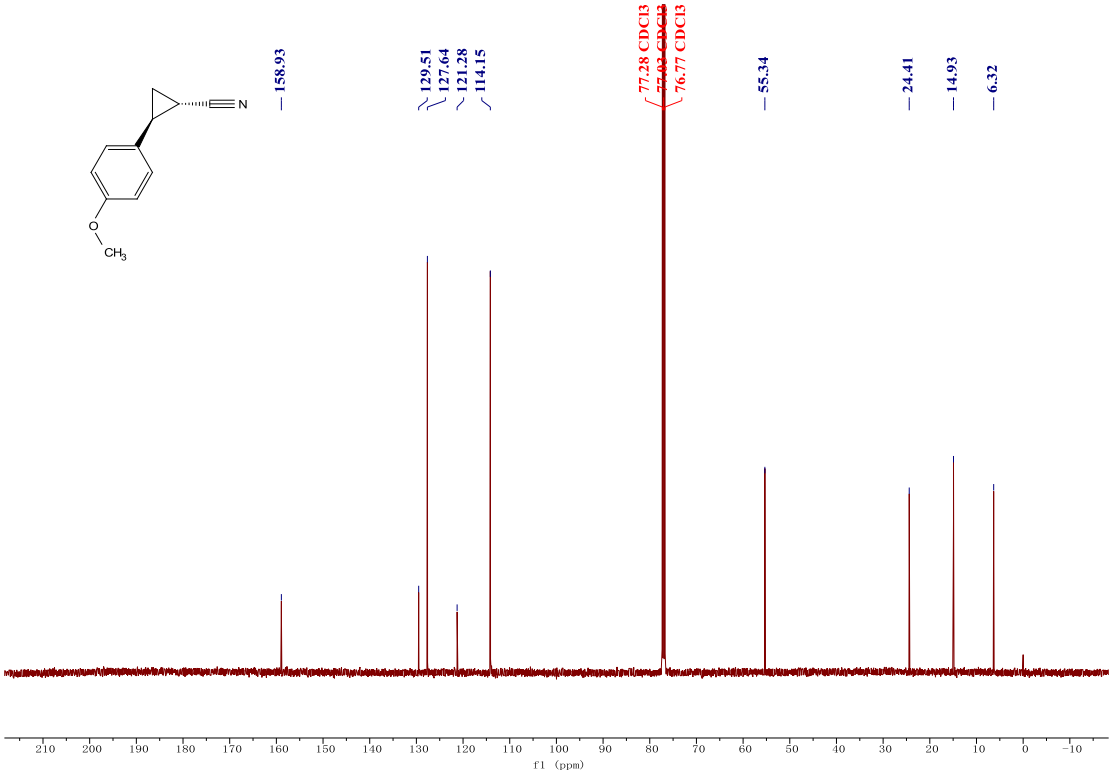
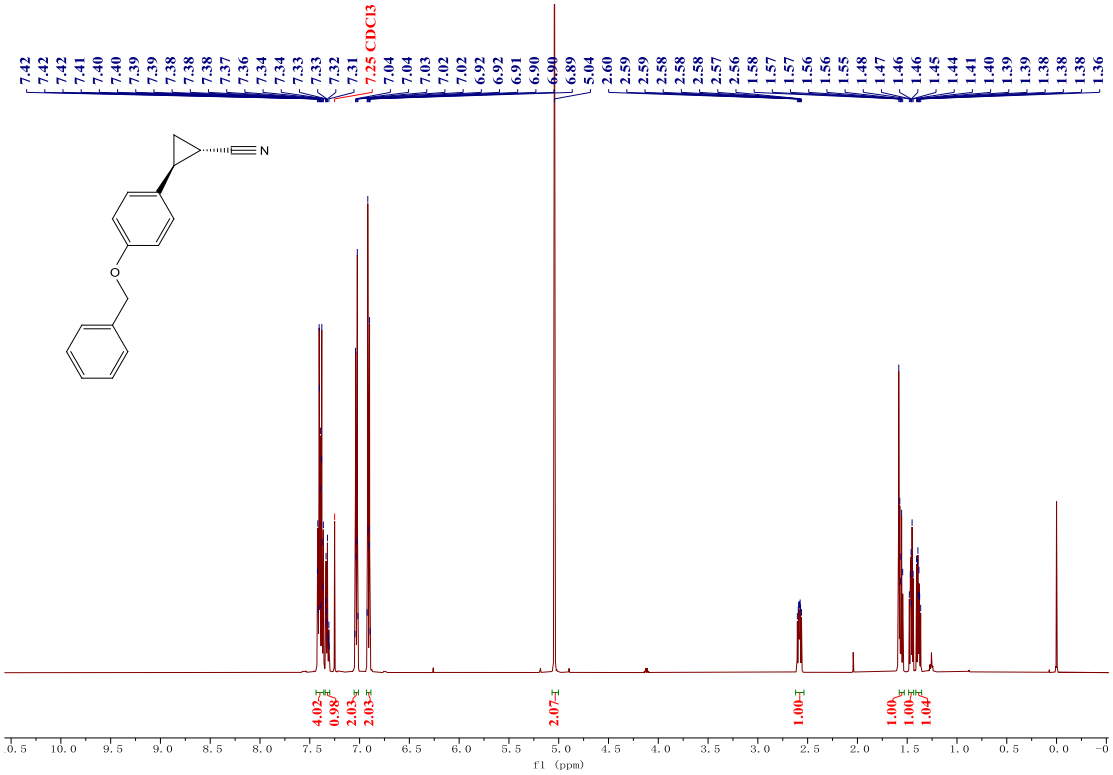


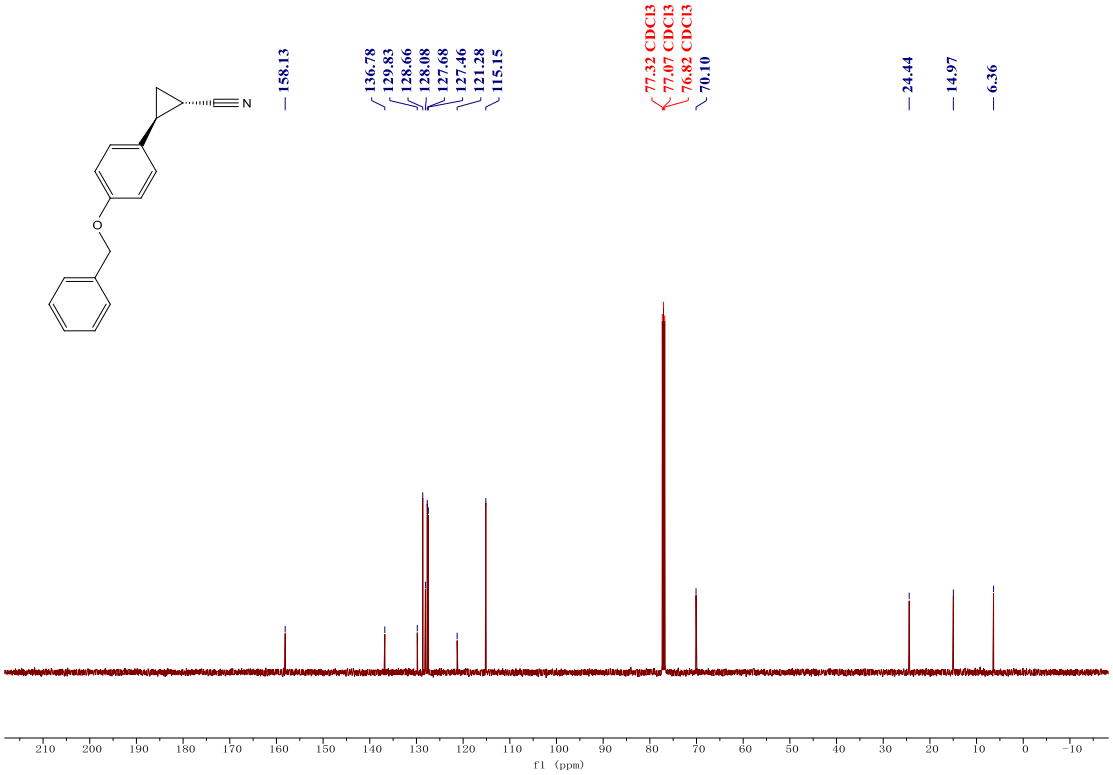
^{13}C NMR spectrum of **2f** in $CDCl_3$



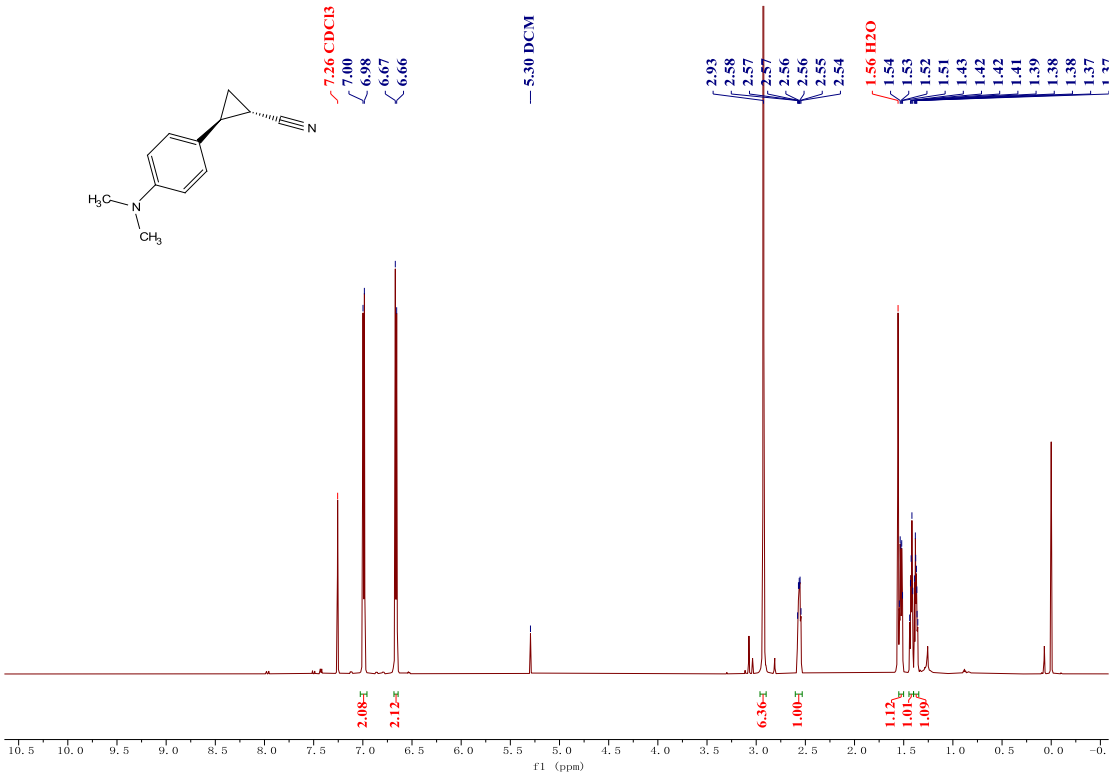
^{1}H NMR spectrum of **2g** in $CDCl_3$



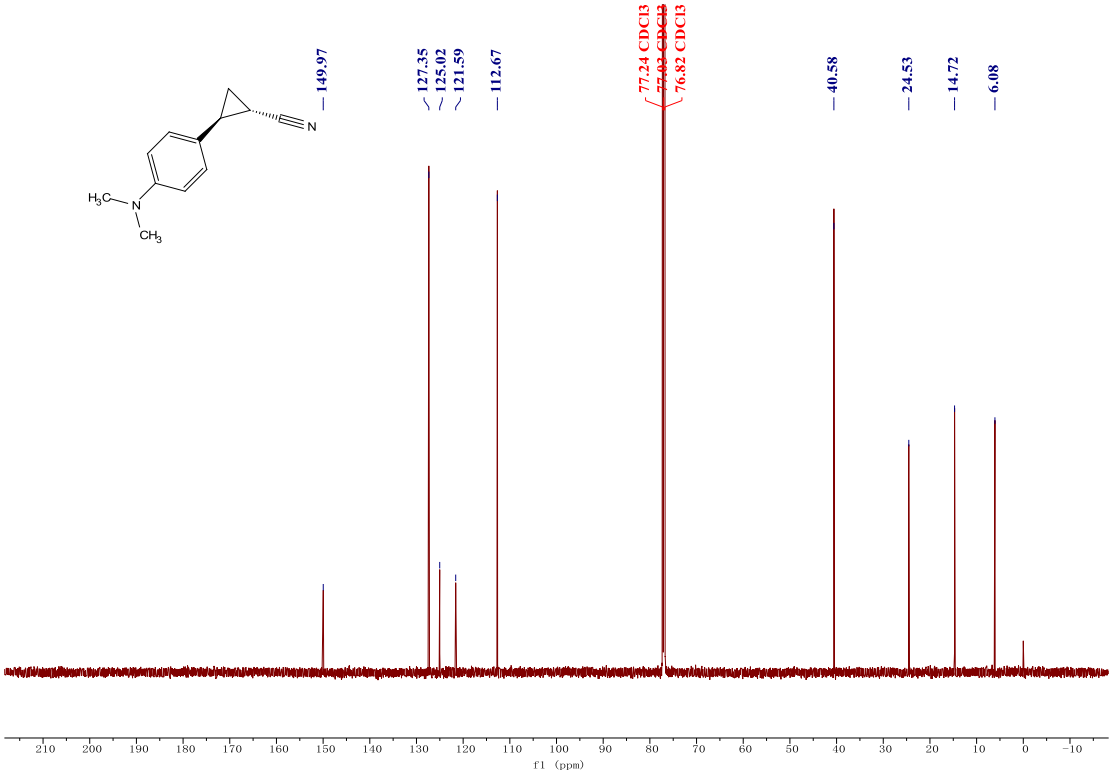
^{13}C NMR spectrum of **2g** in $CDCl_3$



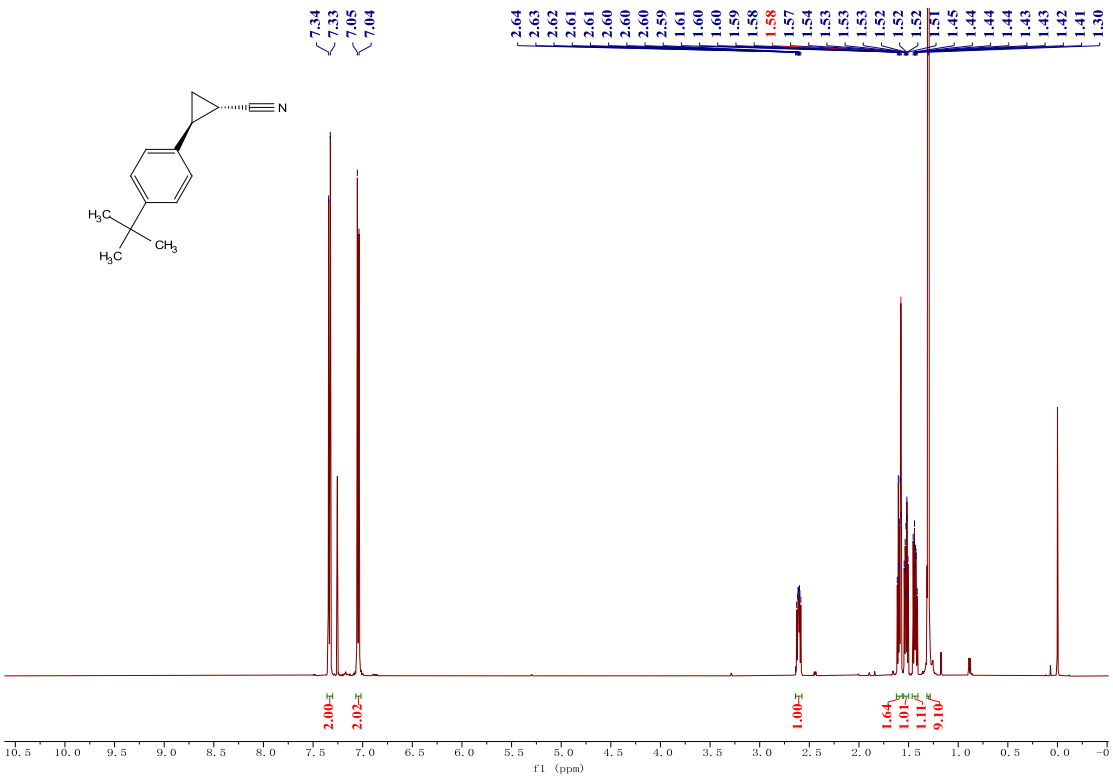
^{1}H NMR spectrum of **2h** in $CDCl_3$



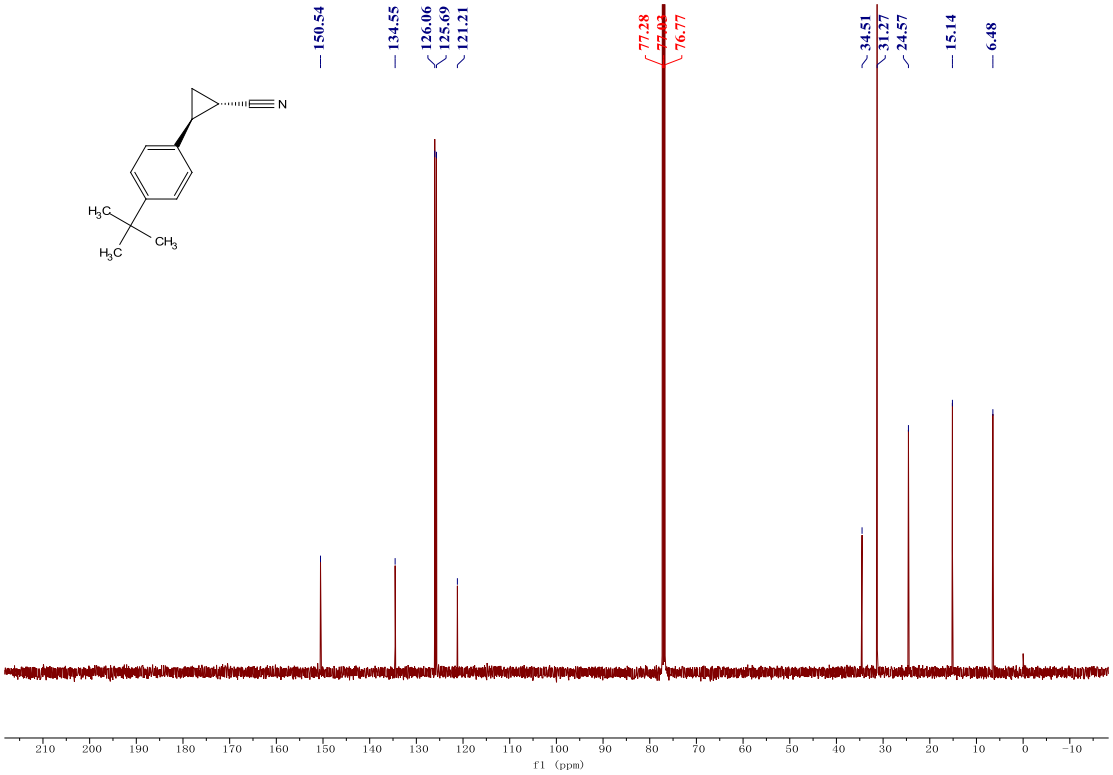
^{13}C NMR spectrum of **2h** in $CDCl_3$



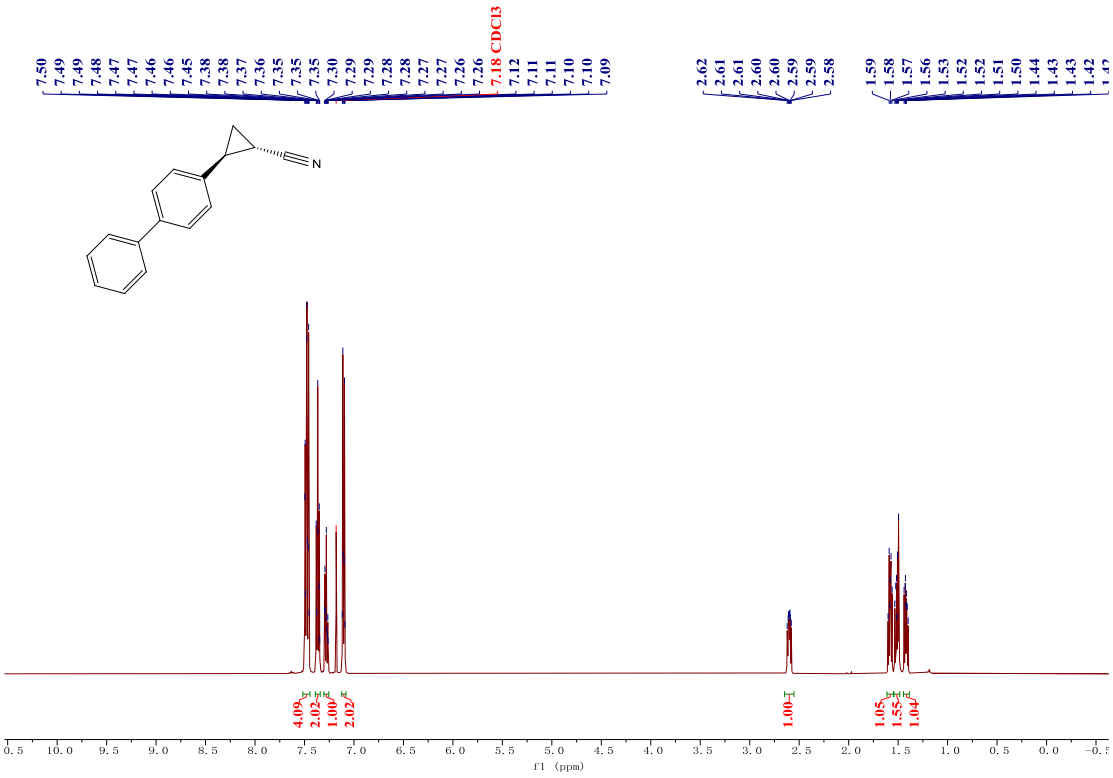
^{1}H NMR spectrum of **2i** in $CDCl_3$



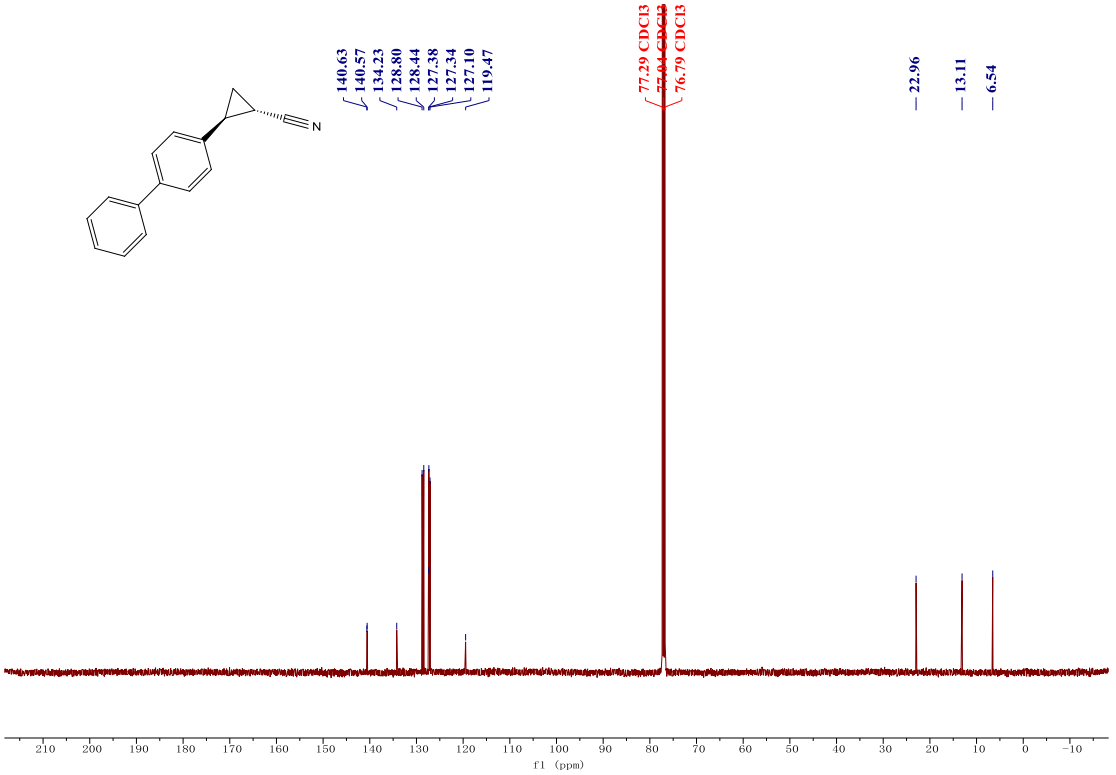
^{13}C NMR spectrum of **2i** in $CDCl_3$



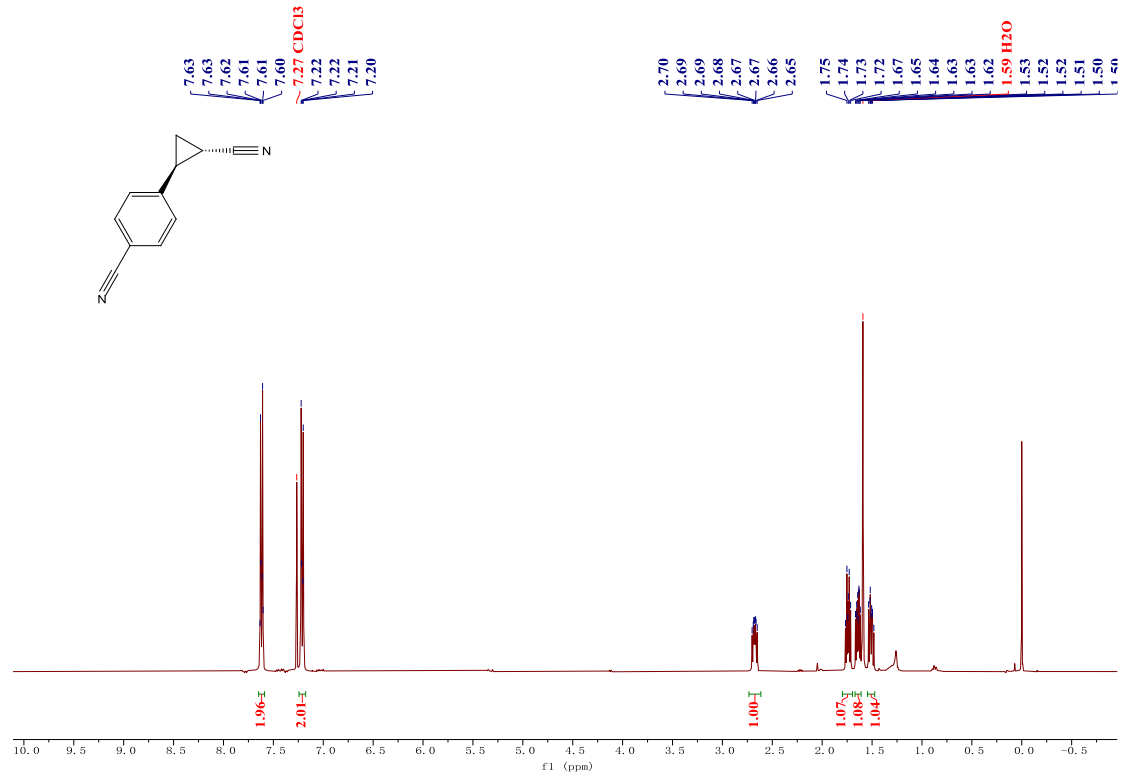
^{1}H NMR spectrum of **2j** in $CDCl_3$



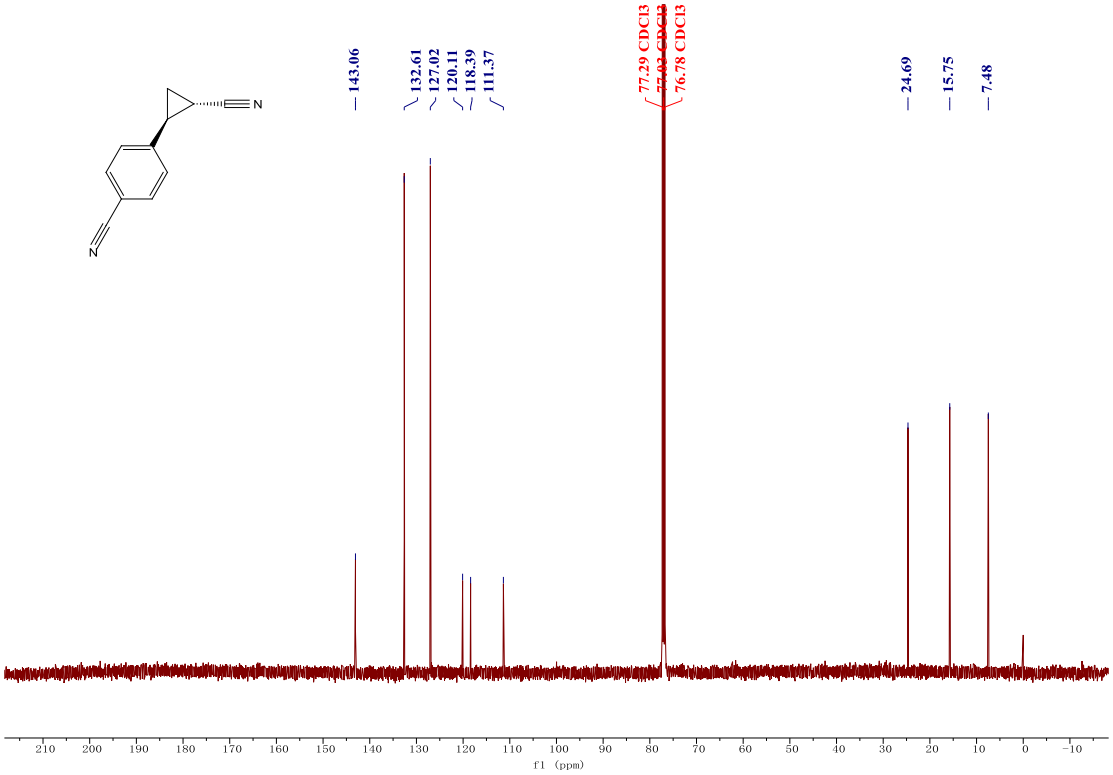
^{13}C NMR spectrum of **2j** in $CDCl_3$



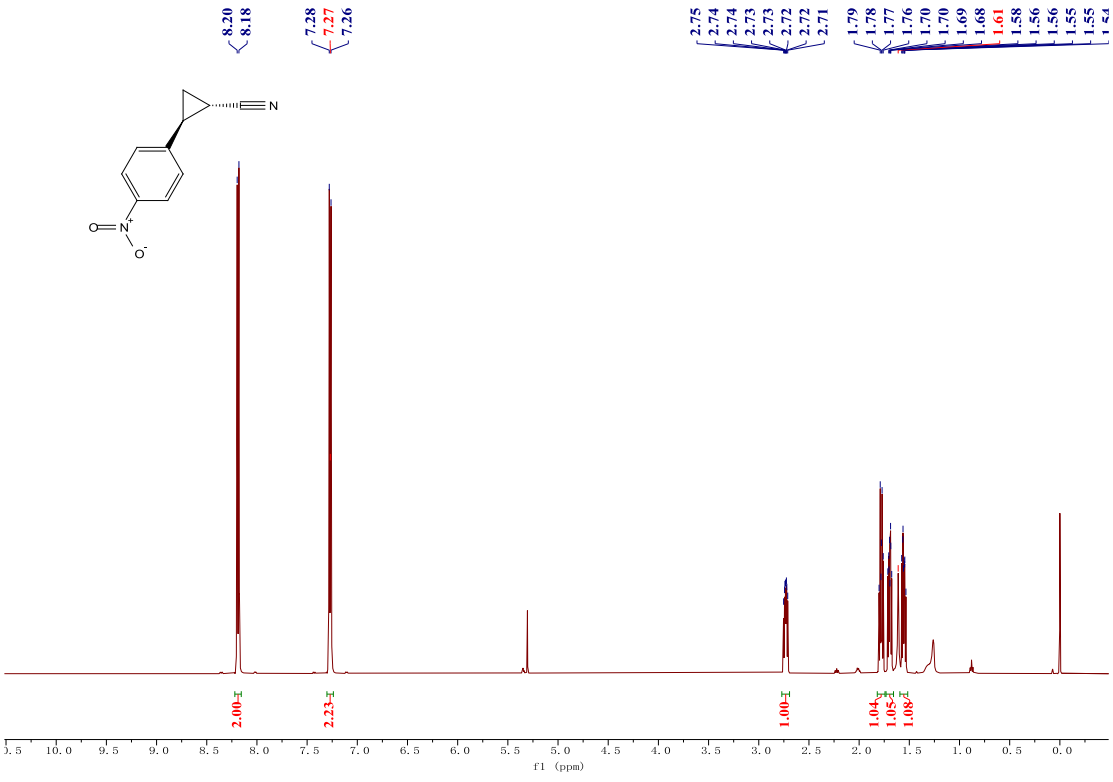
^{1}H NMR spectrum of **2k** in $CDCl_3$



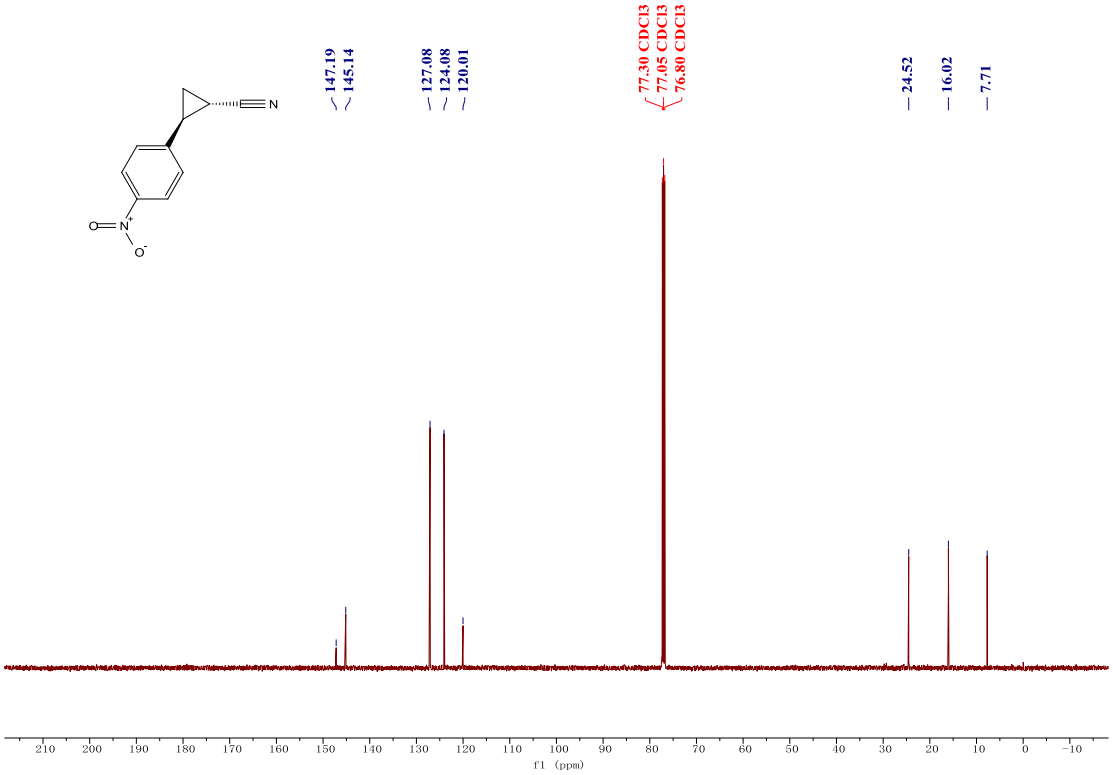
^{13}C NMR spectrum of **2k** in $CDCl_3$



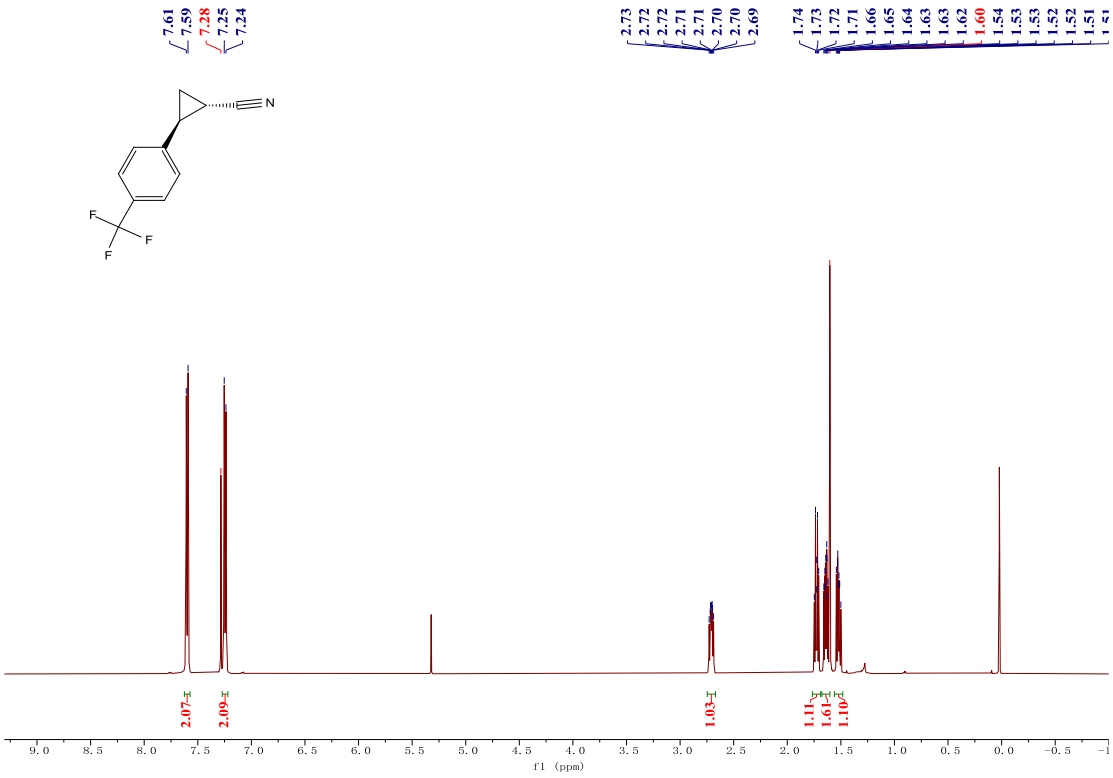
^{1}H NMR spectrum of **2l** in $CDCl_3$



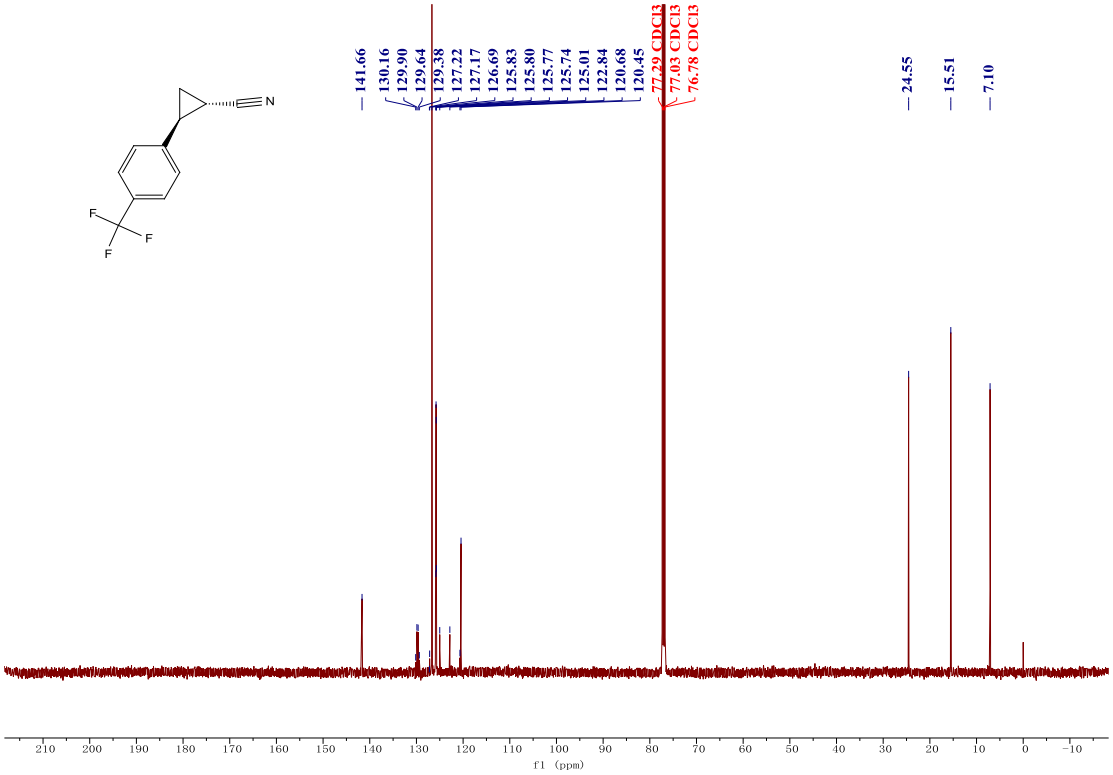
^{13}C NMR spectrum of **2l** in $CDCl_3$



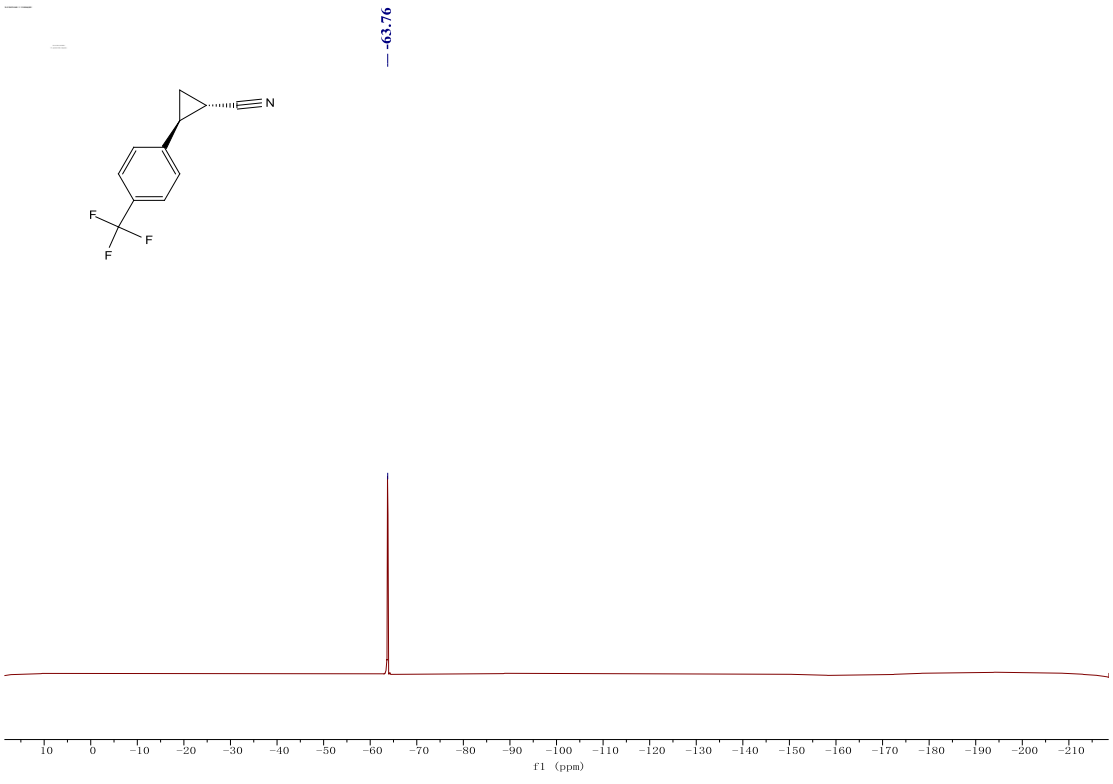
^{1}H NMR spectrum of **2m** in $CDCl_3$



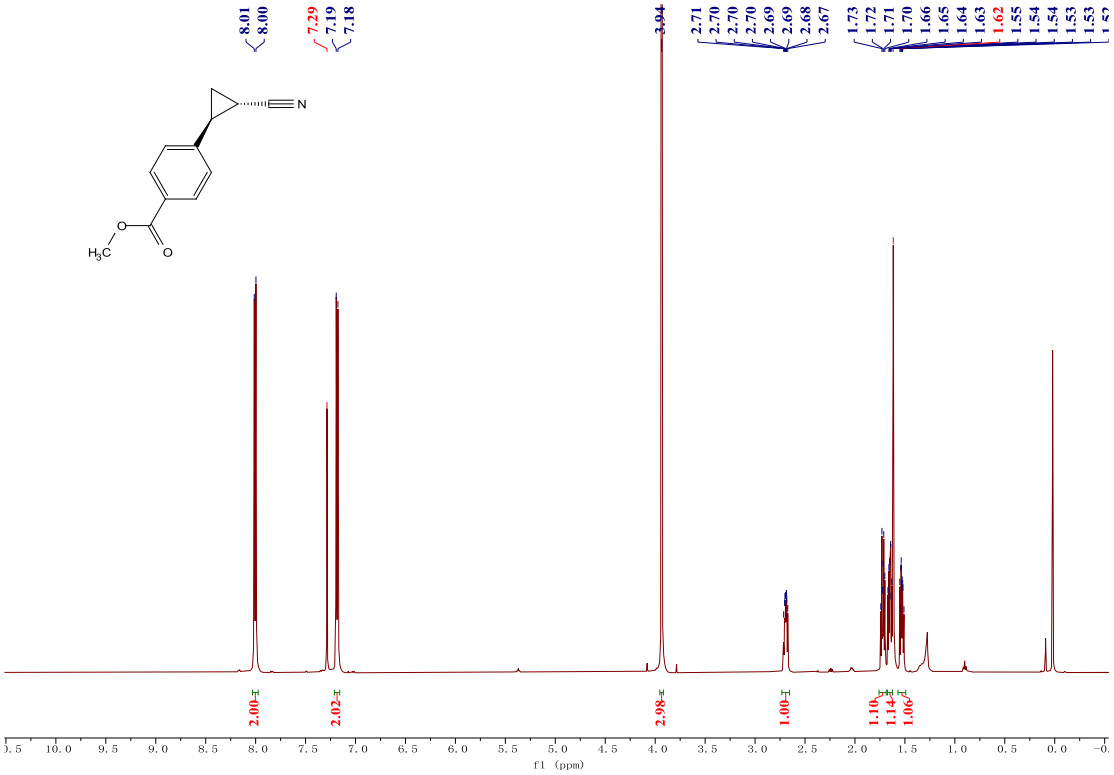
^{13}C NMR spectrum of **2m** in $CDCl_3$



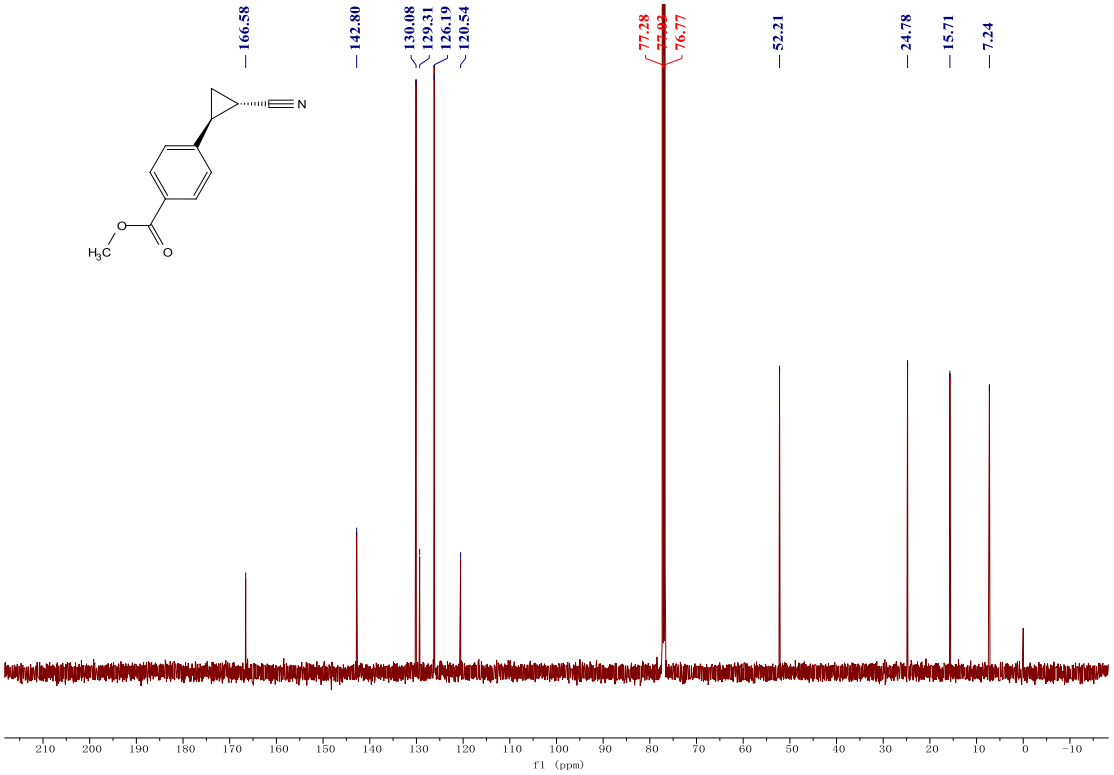
^{19}F NMR spectrum of **2m** in $CDCl_3$



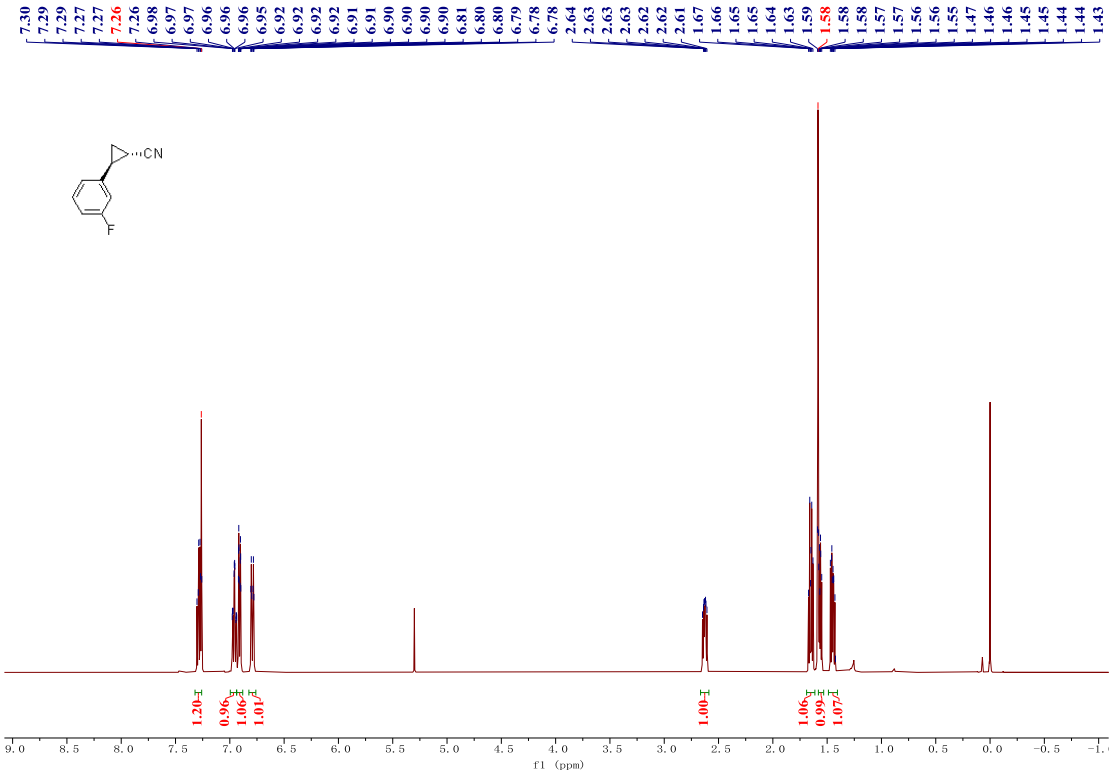
^{1}H NMR spectrum of **2n** in $CDCl_3$



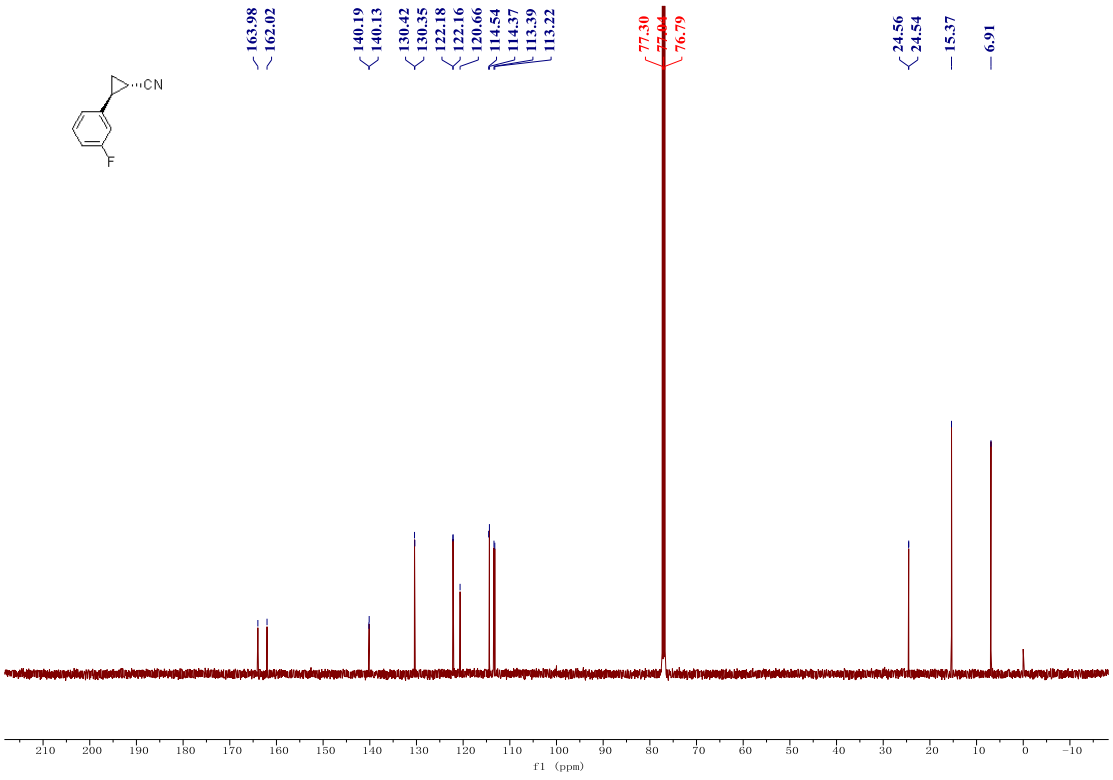
^{13}C NMR spectrum of **2n** in $CDCl_3$



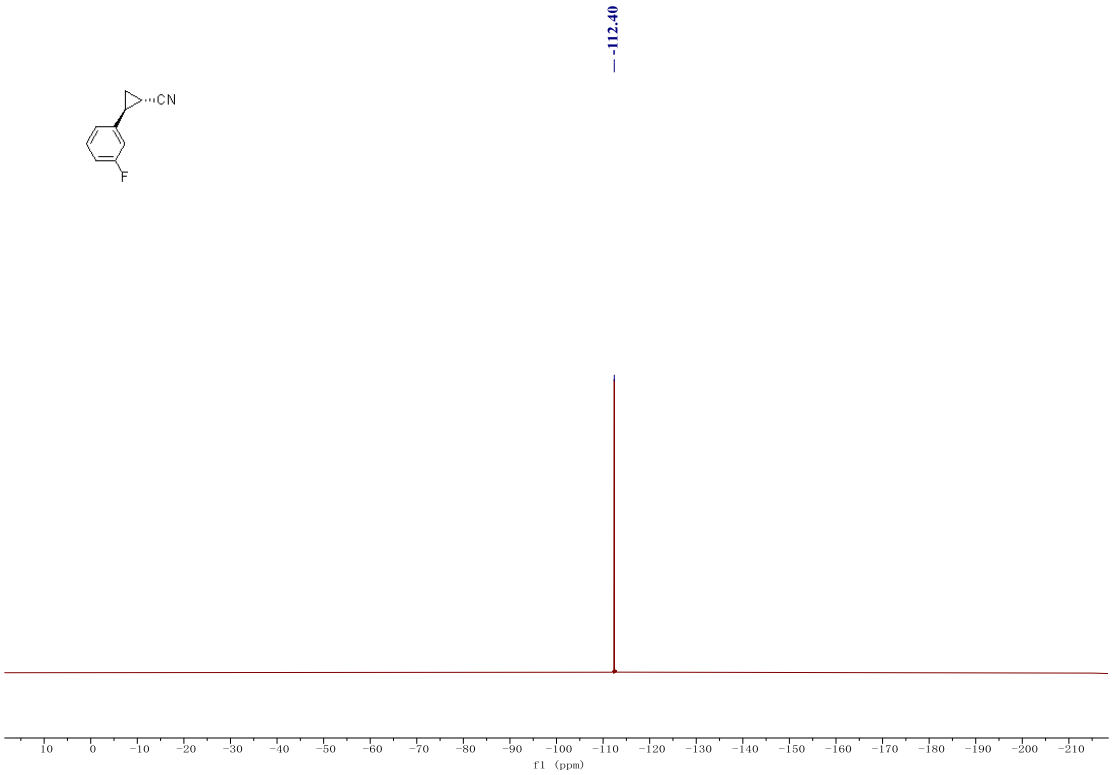
^{1}H NMR spectrum of **2o** in $CDCl_3$



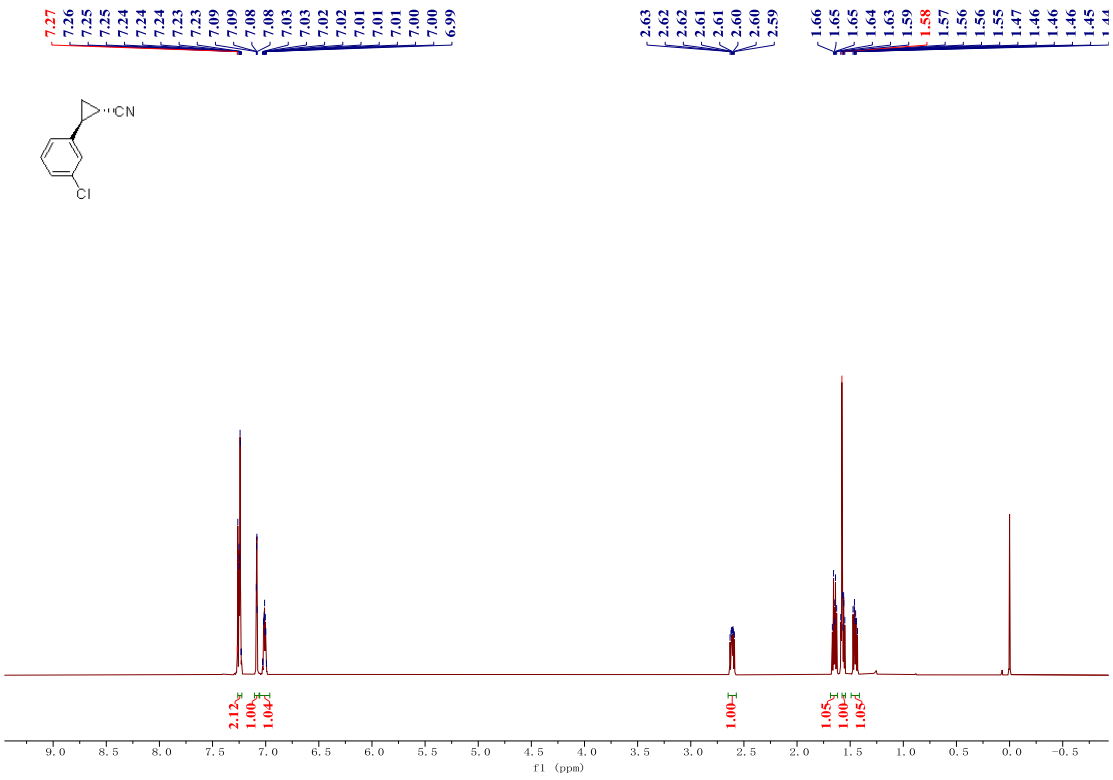
^{13}C NMR spectrum of **2o** in $CDCl_3$



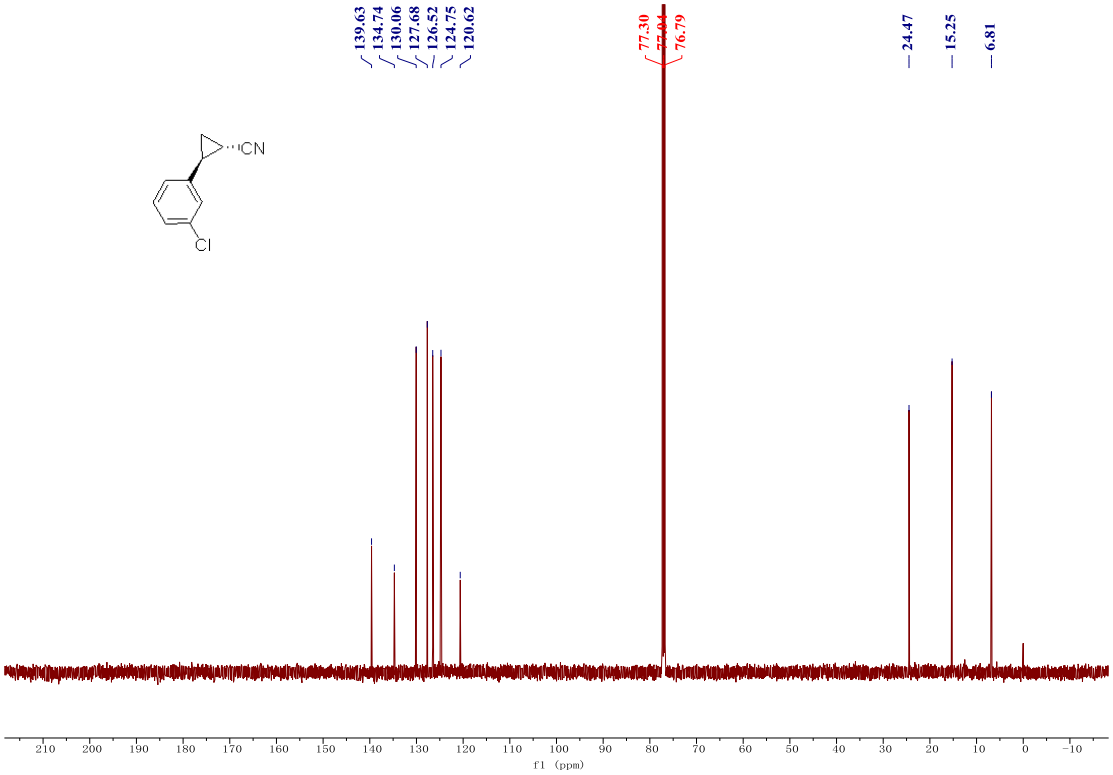
^{19}F NMR spectrum of **2o** in $CDCl_3$



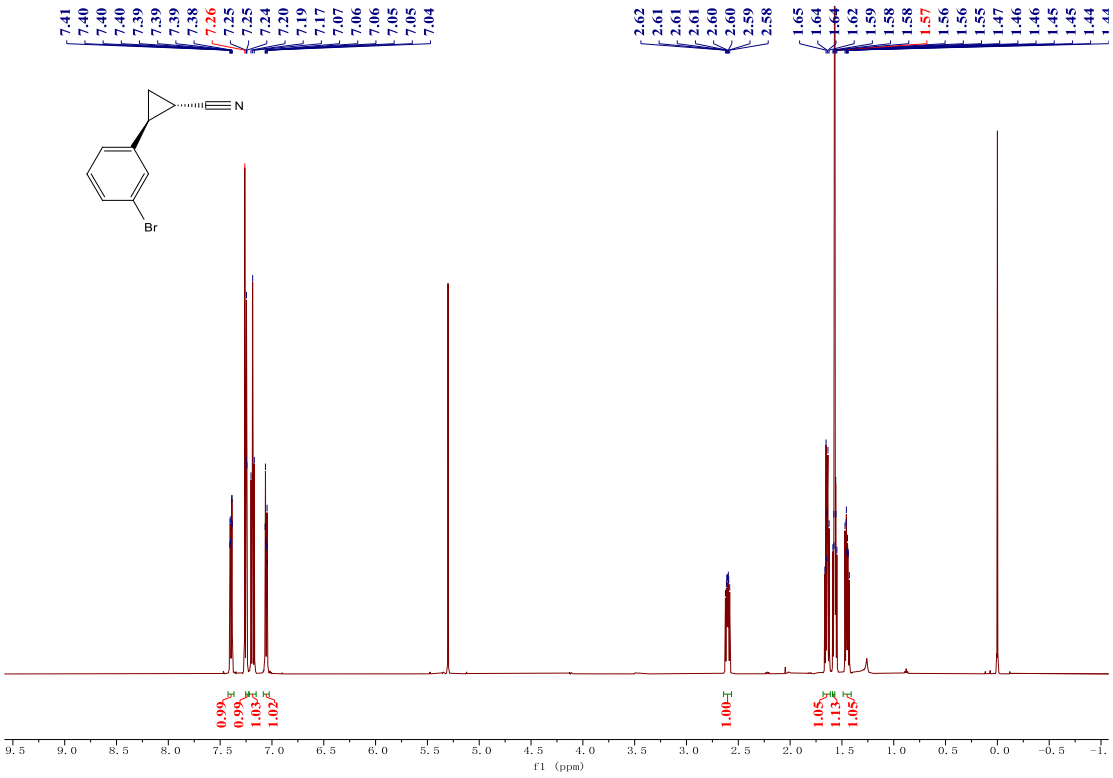
^{1}H NMR spectrum of **2p** in $CDCl_3$



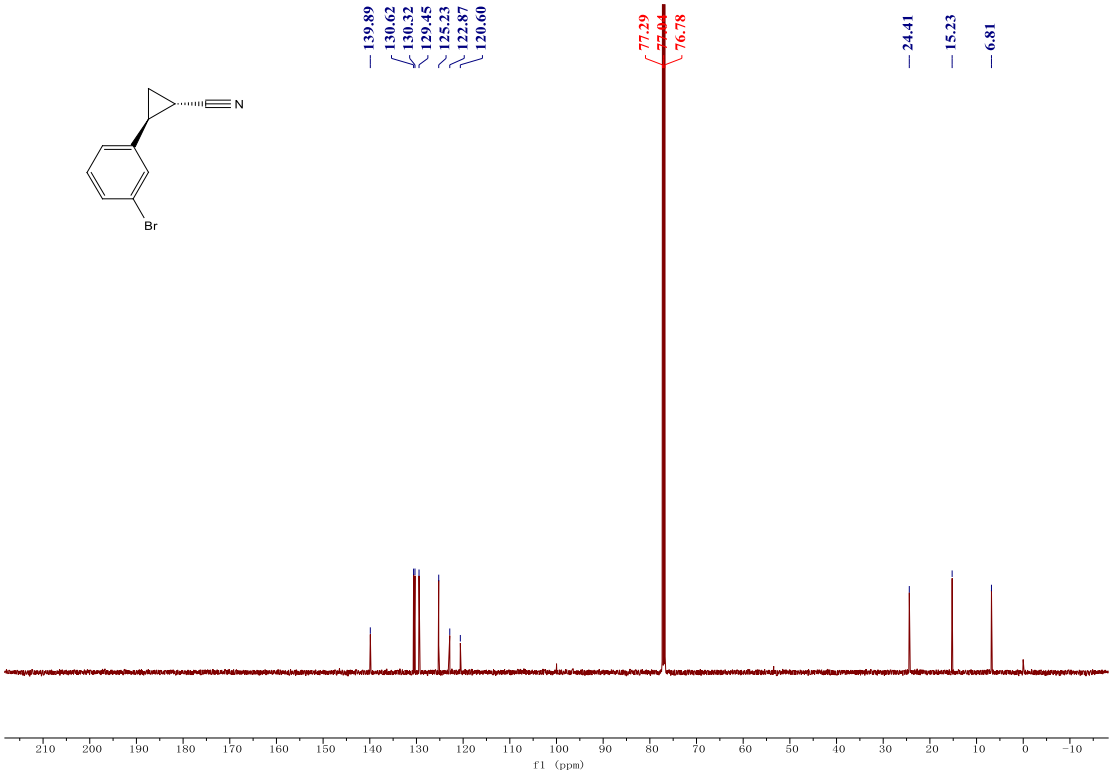
^{13}C NMR spectrum of **2p** in $CDCl_3$



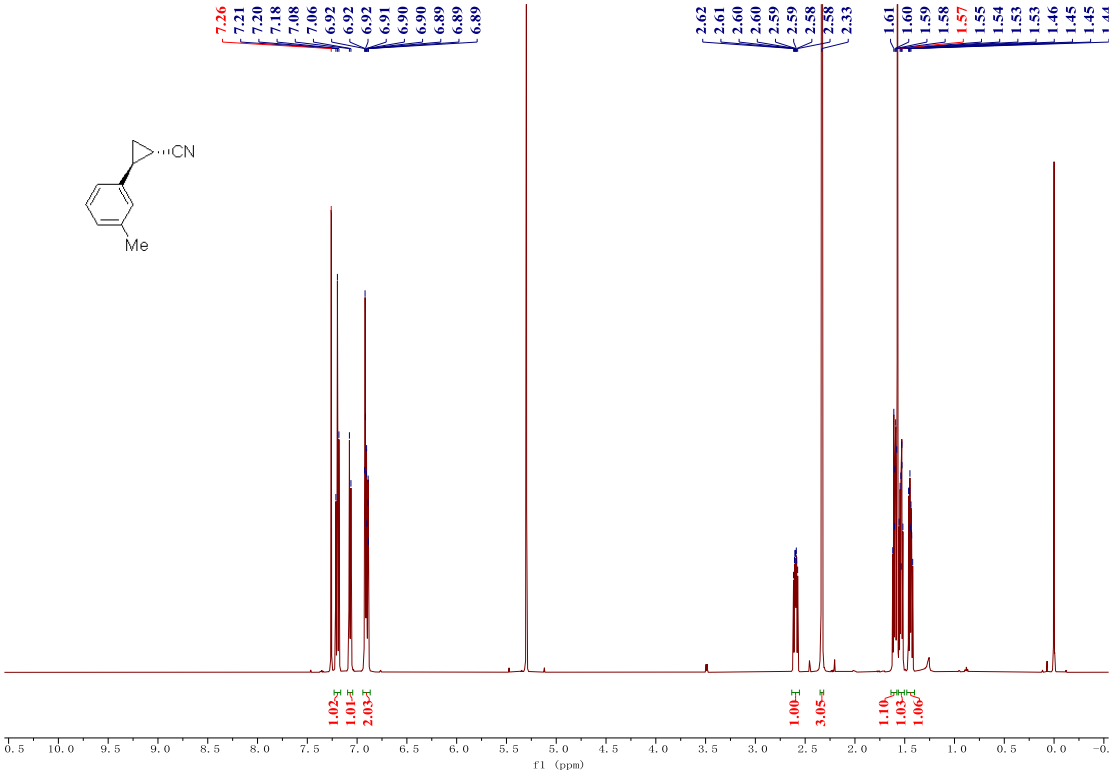
^{1}H NMR spectrum of **2q** in $CDCl_3$



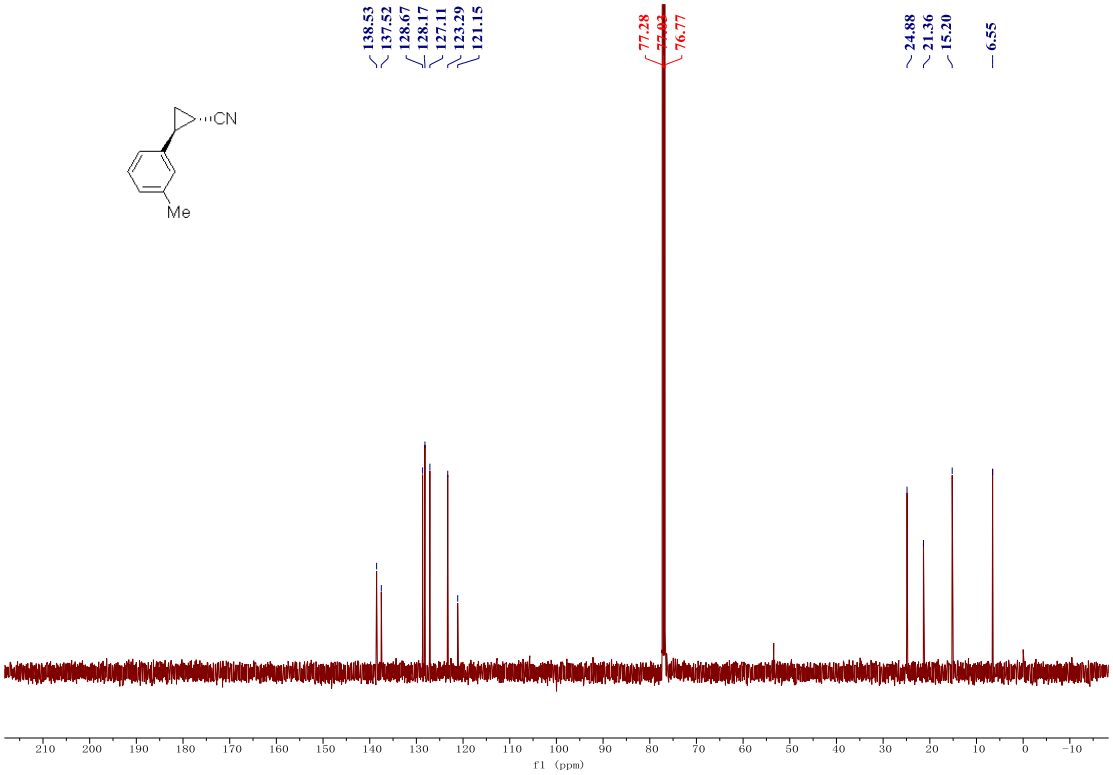
^{13}C NMR spectrum of **2q** in $CDCl_3$



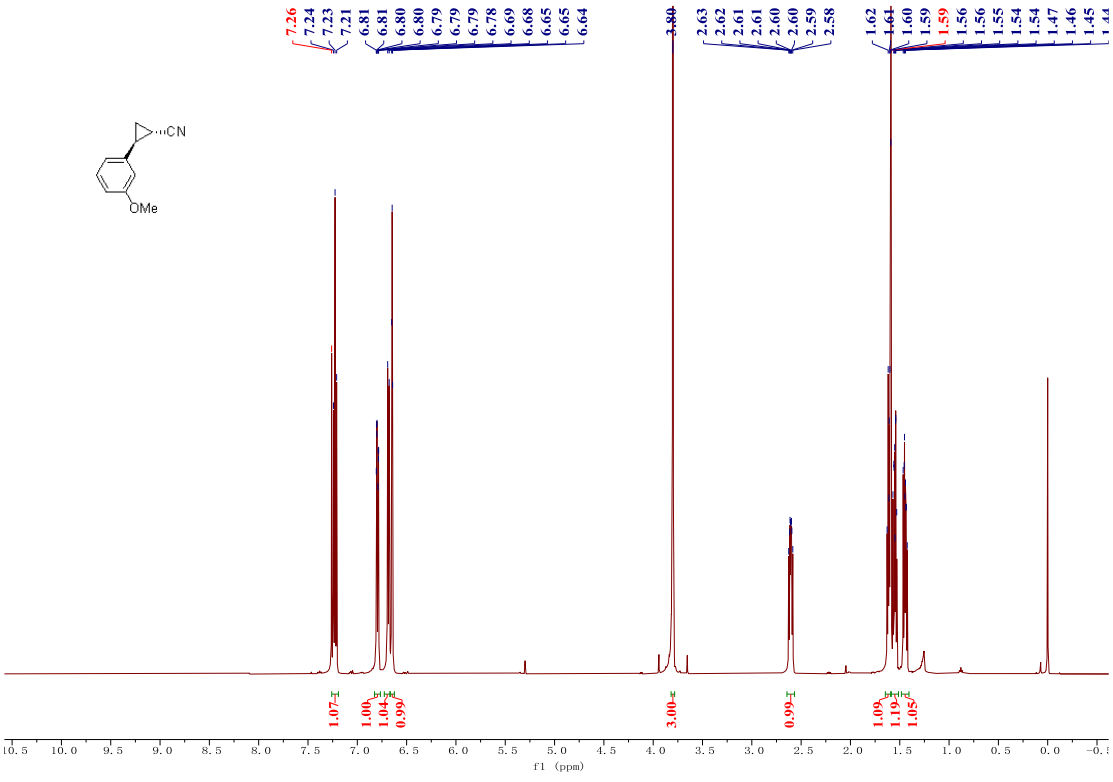
^{1}H NMR spectrum of **2r** in $CDCl_3$



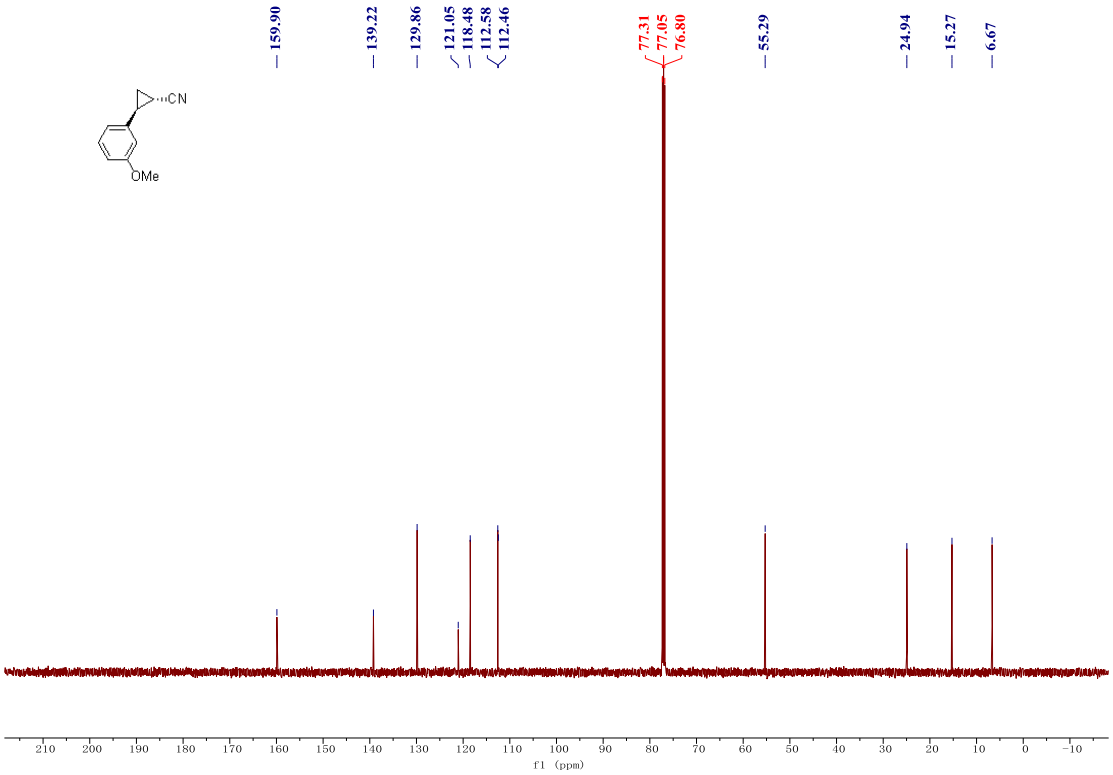
^{13}C NMR spectrum of **2r** in $CDCl_3$



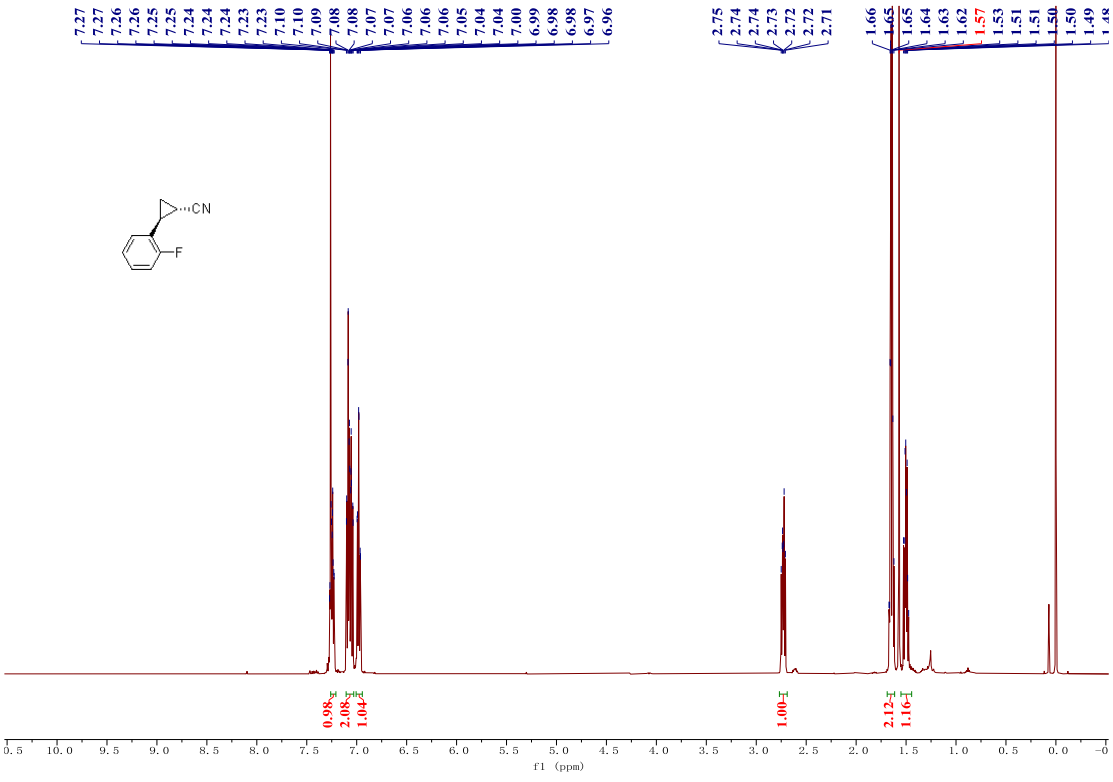
^{1}H NMR spectrum of **2s** in $CDCl_3$



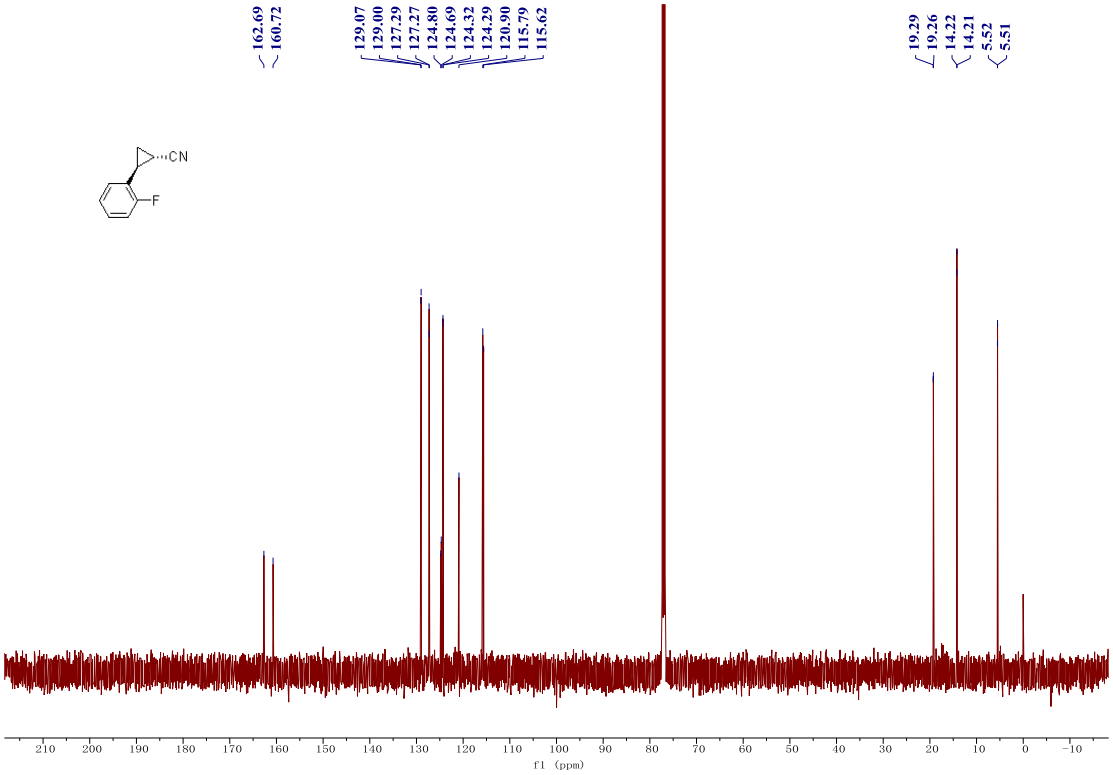
^{13}C NMR spectrum of **2s** in $CDCl_3$



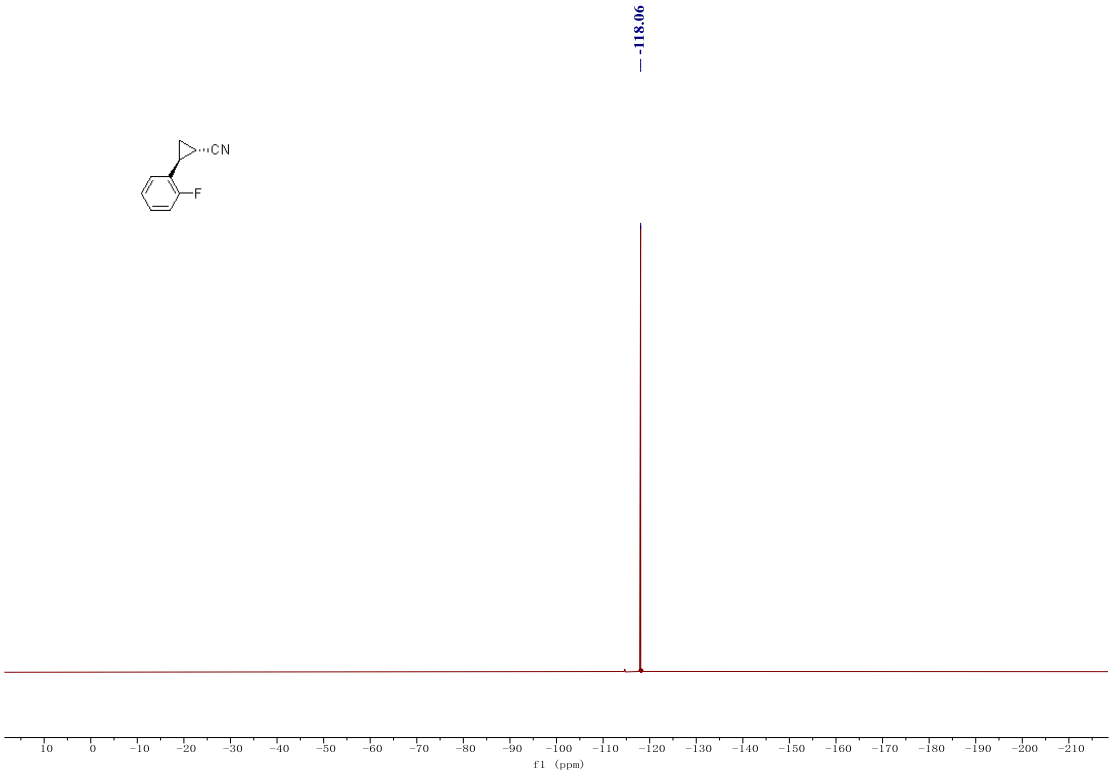
^{1}H NMR spectrum of **2t** in $CDCl_3$



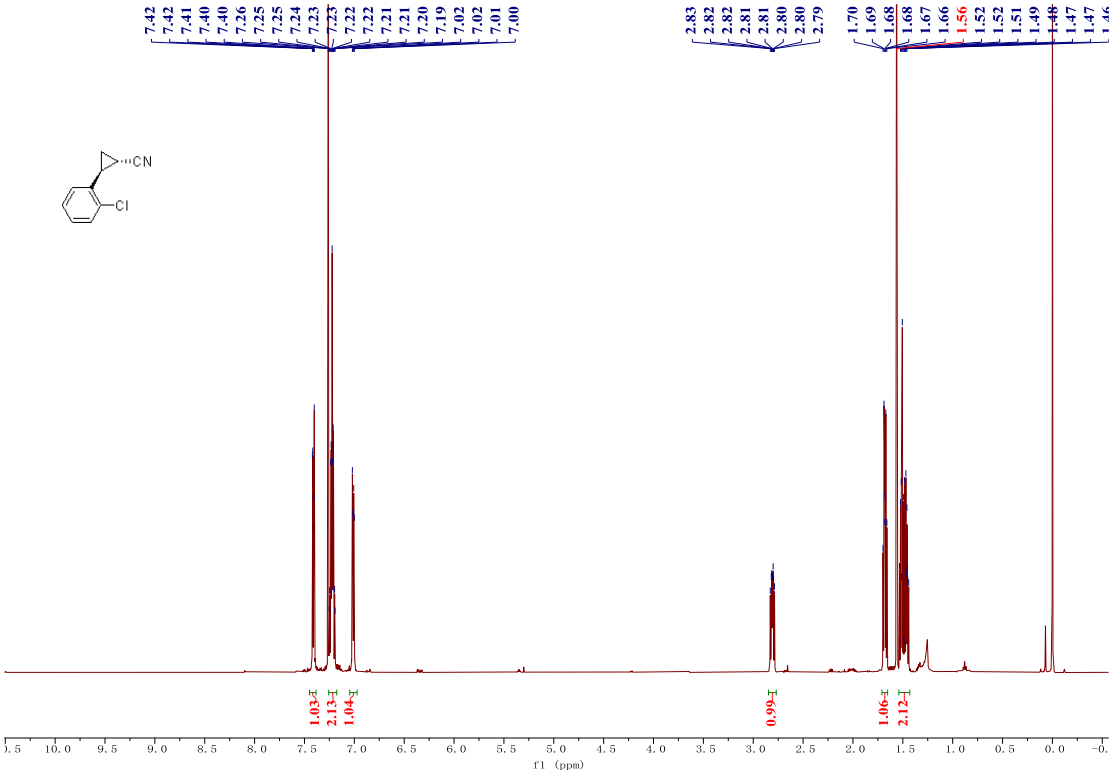
^{13}C NMR spectrum of **2t** in $CDCl_3$



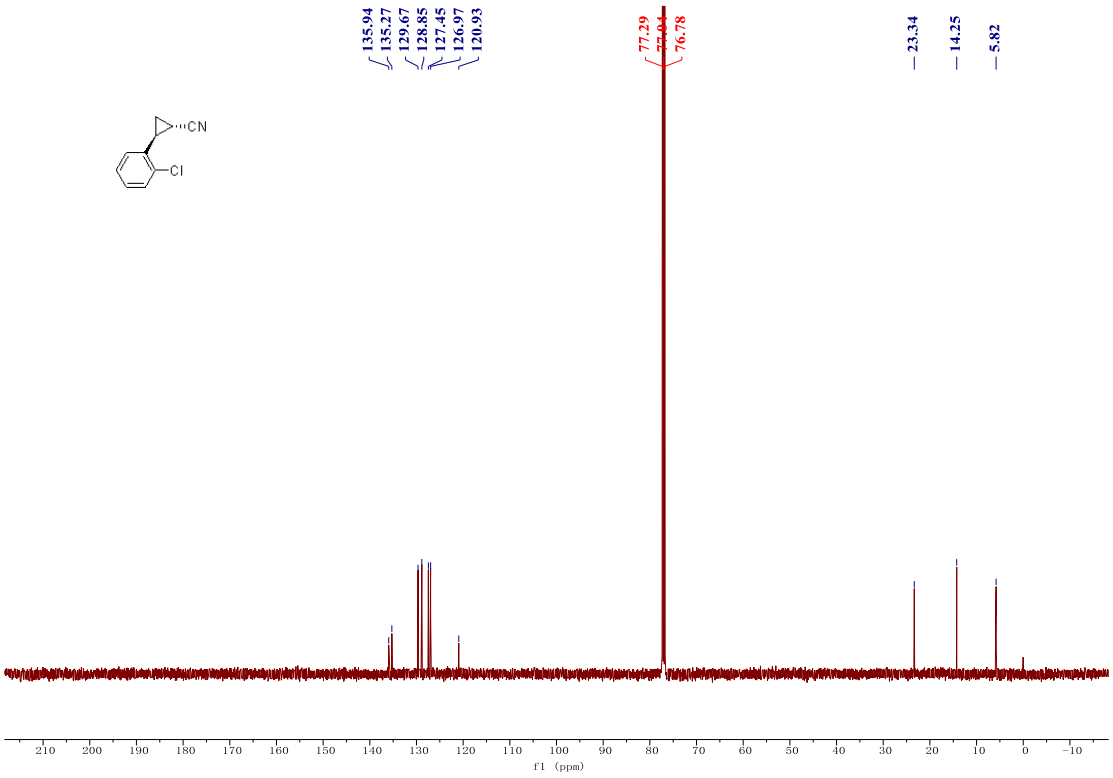
^{19}F NMR spectrum of **2t** in $CDCl_3$



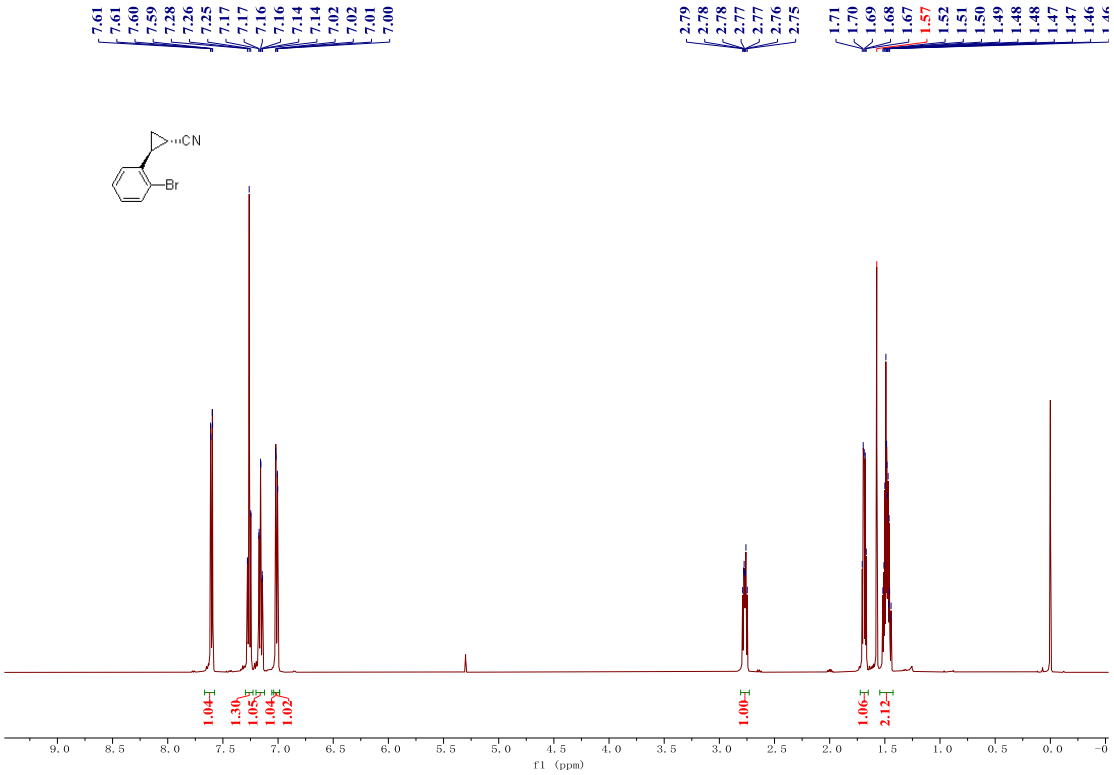
^{1}H NMR spectrum of **2u** in $CDCl_3$



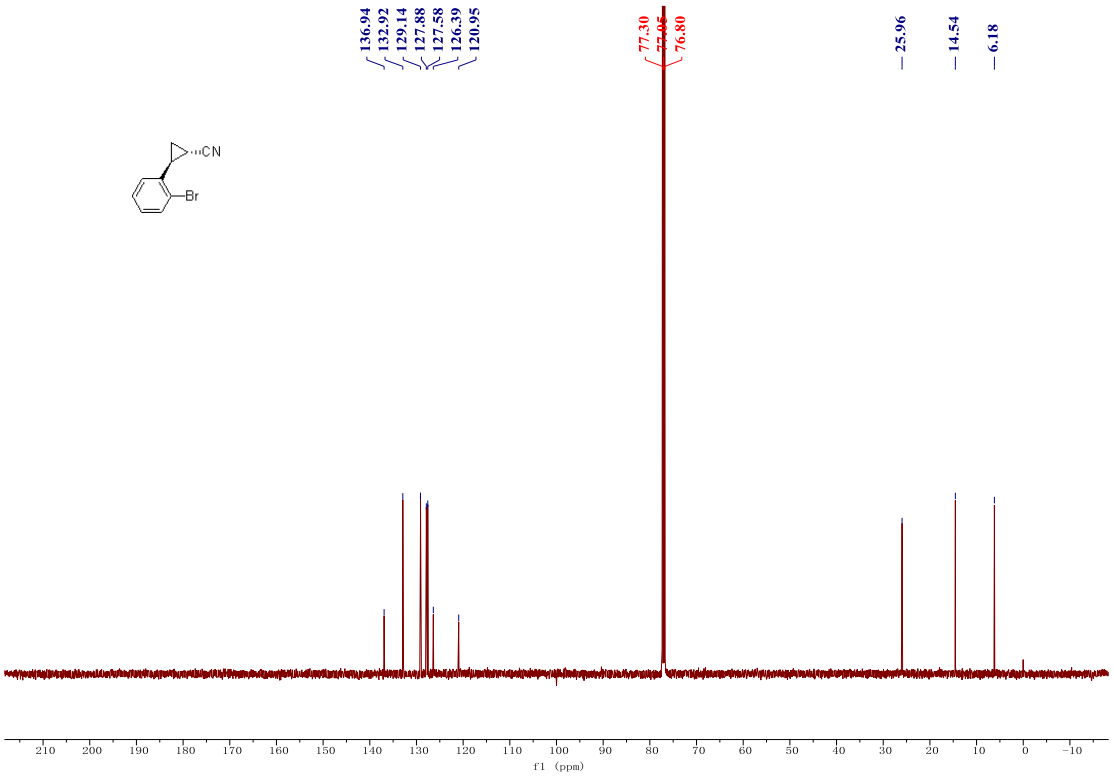
^{13}C NMR spectrum of **2u** in $CDCl_3$



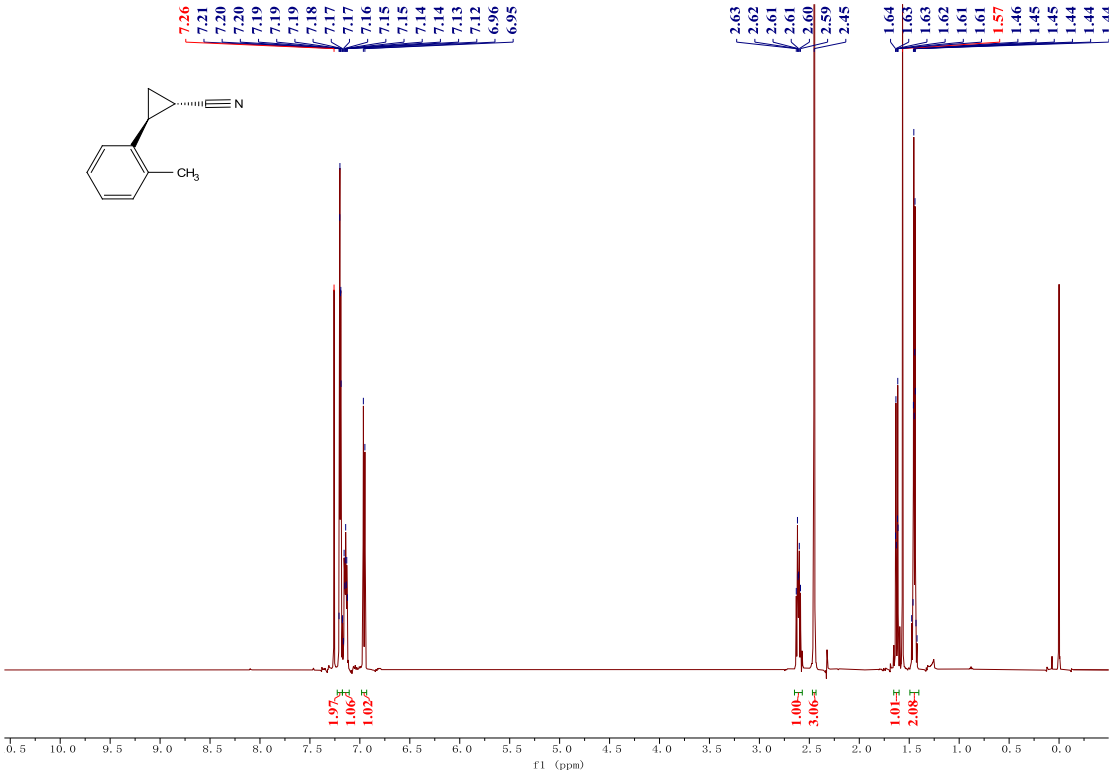
^{1}H NMR spectrum of **2v** in $CDCl_3$



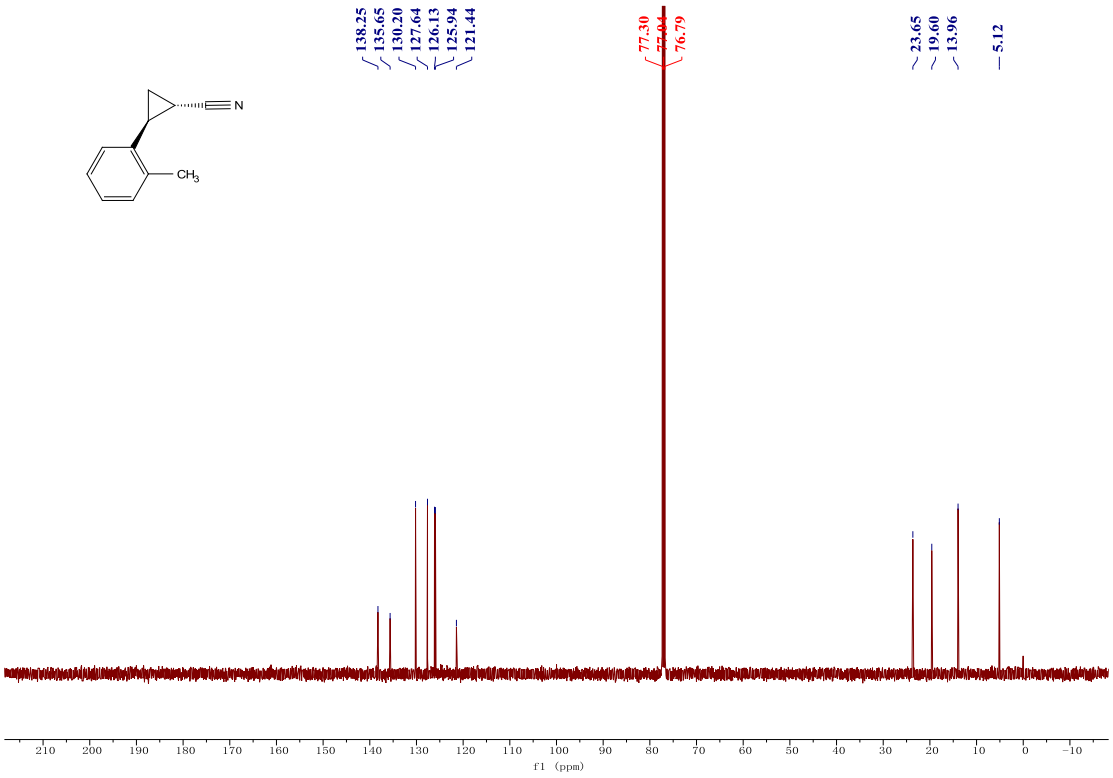
^{13}C NMR spectrum of **2v** in $CDCl_3$



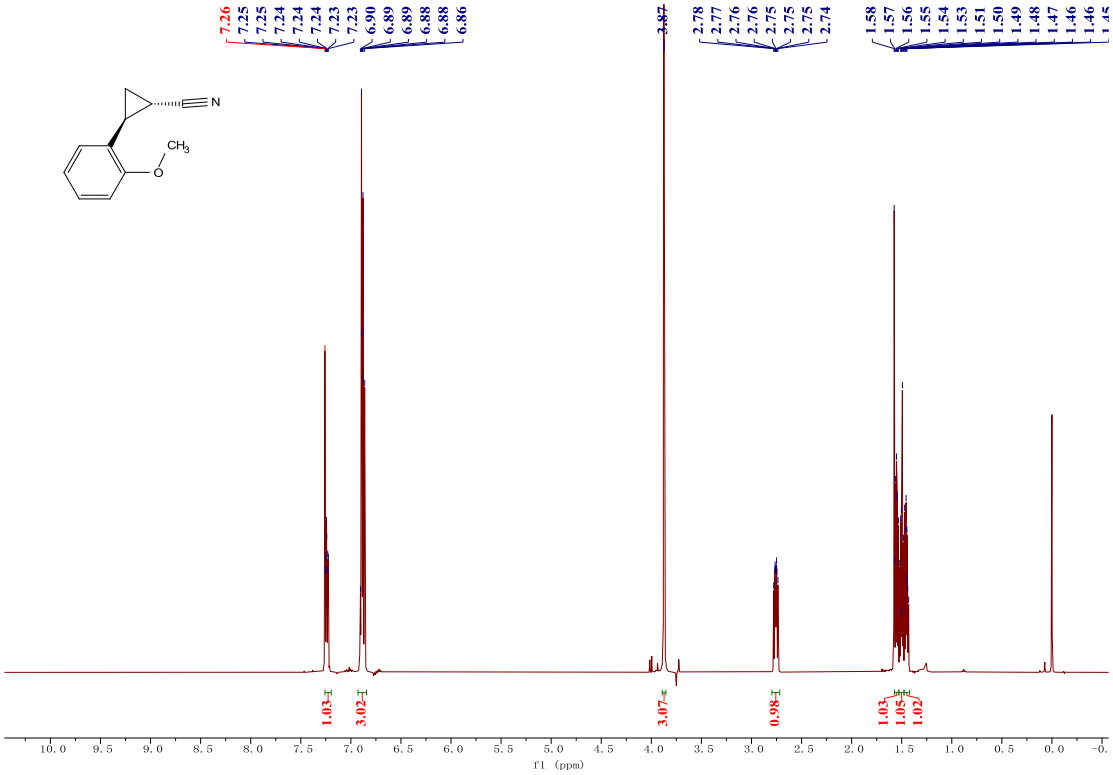
^{1}H NMR spectrum of **2w** in $CDCl_3$



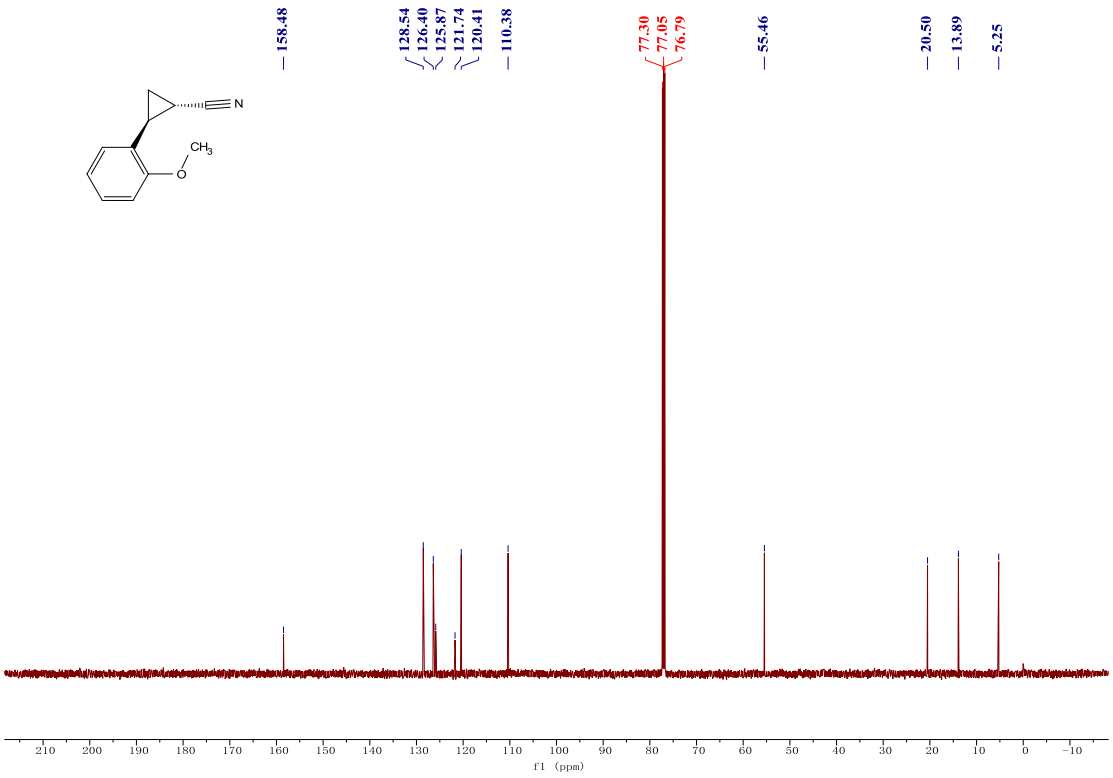
^{13}C NMR spectrum of **2w** in $CDCl_3$



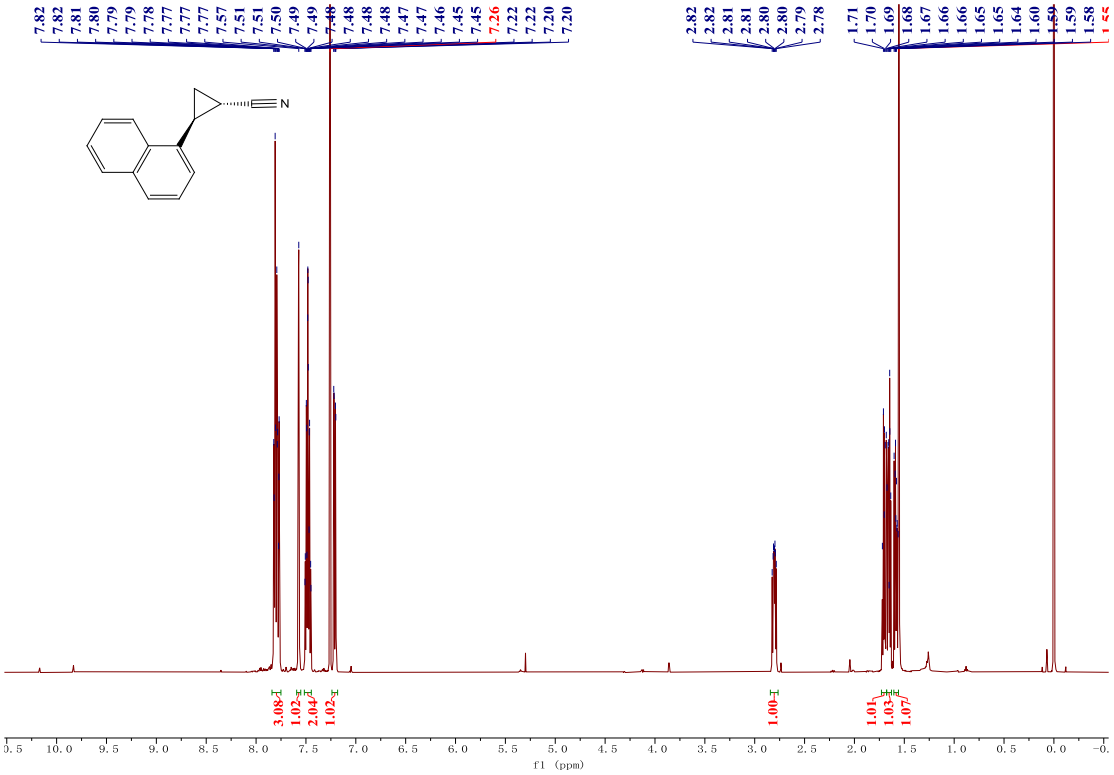
^{1}H NMR spectrum of **2x** in $CDCl_3$



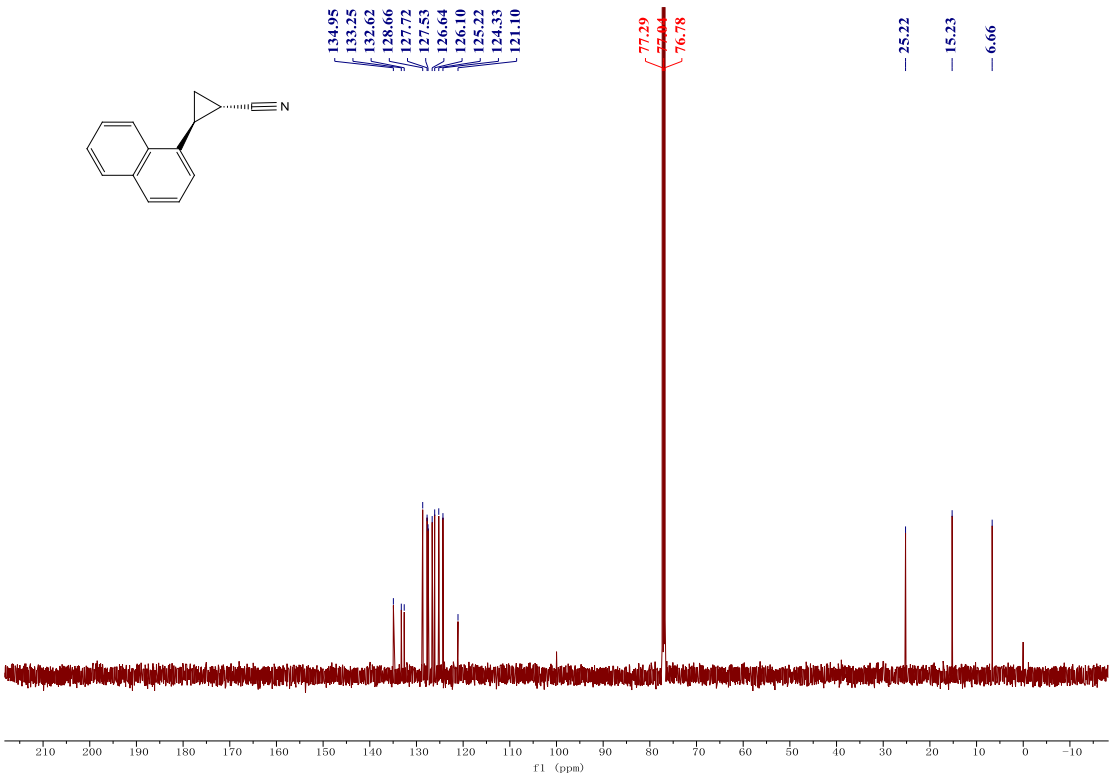
^{13}C NMR spectrum of **2x** in $CDCl_3$



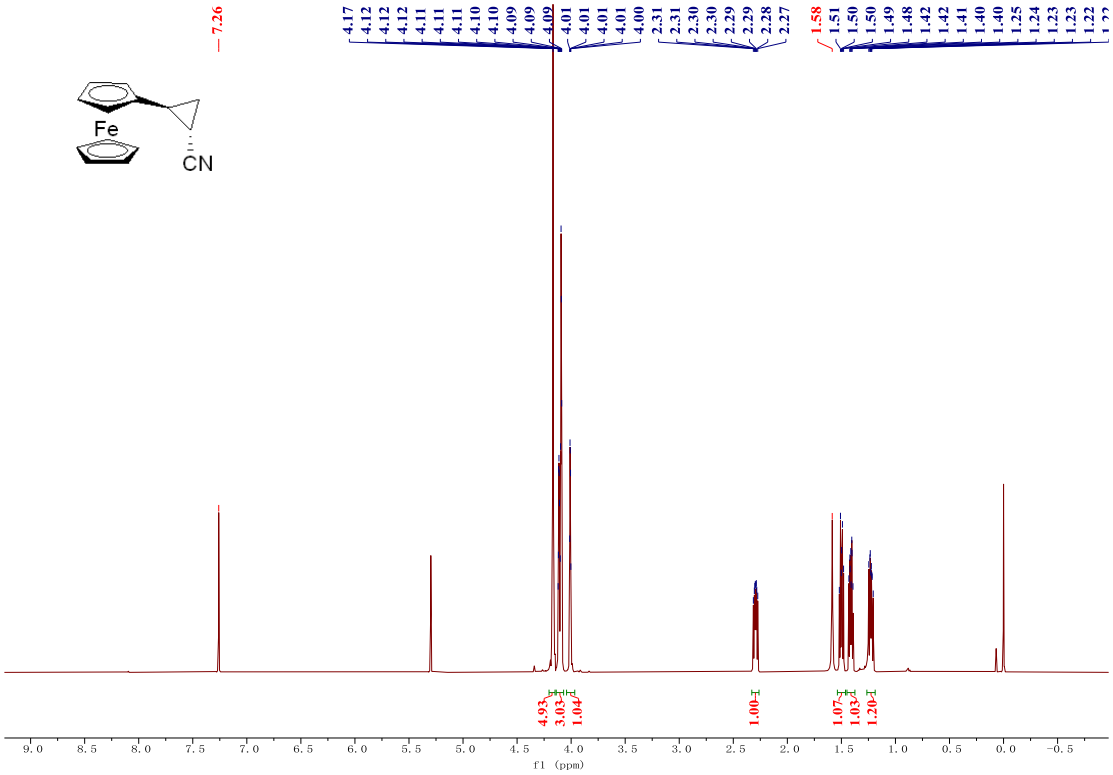
^{1}H NMR spectrum of **2y** in $CDCl_3$



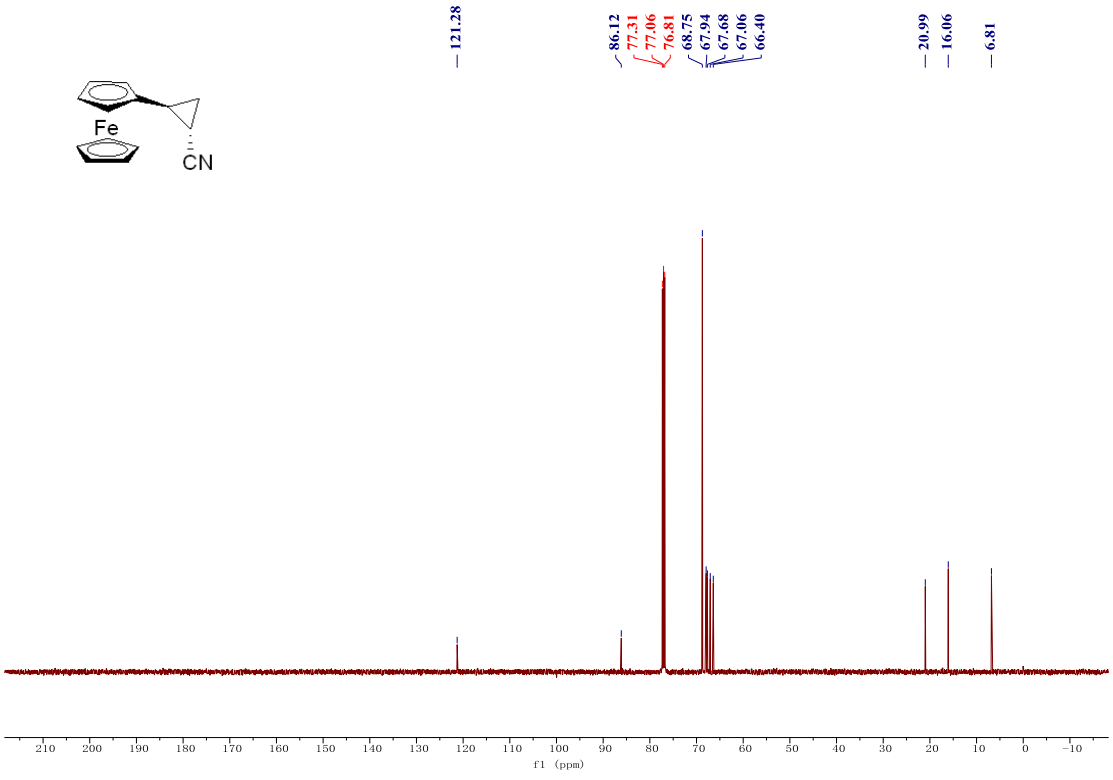
^{13}C NMR spectrum of **2y** in $CDCl_3$



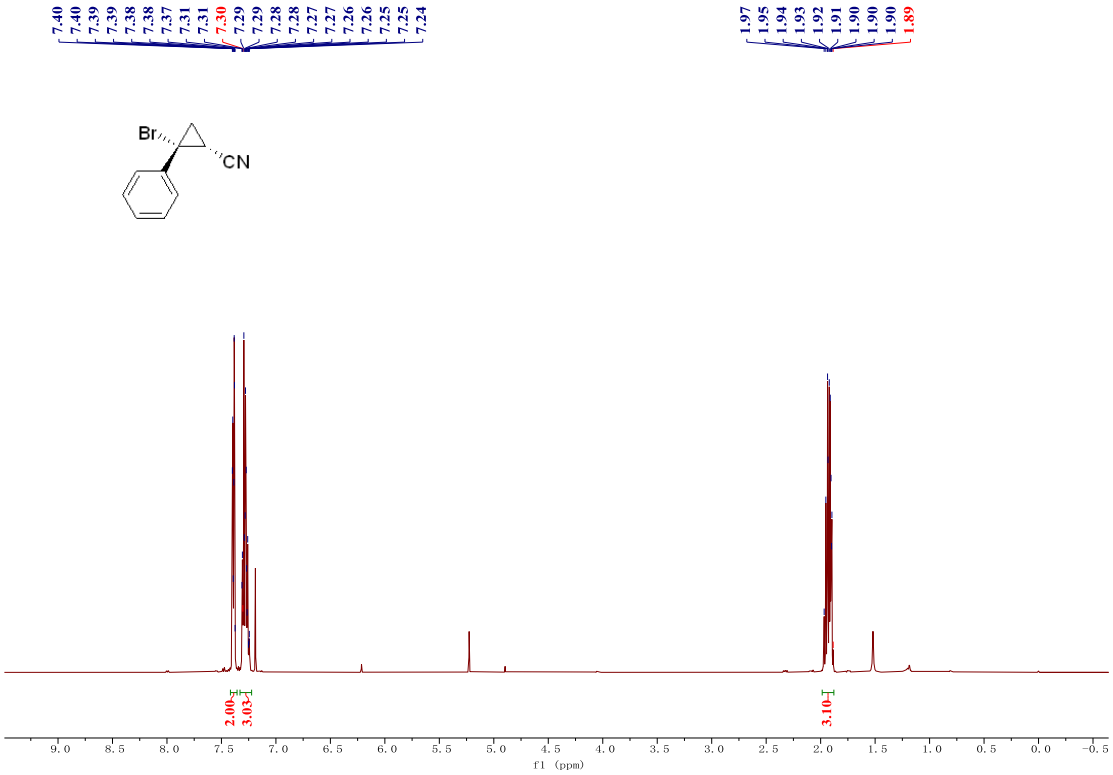
^{1}H NMR spectrum of **2z** in $CDCl_3$



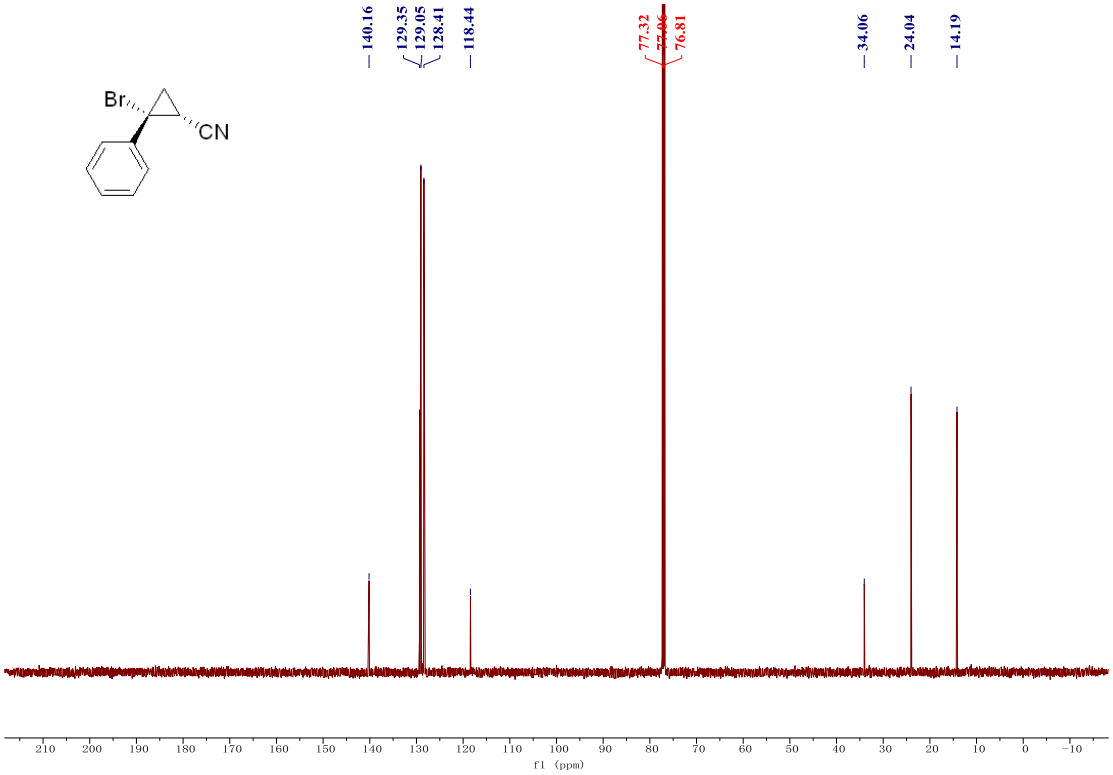
^{13}C NMR spectrum of **2z** in $CDCl_3$



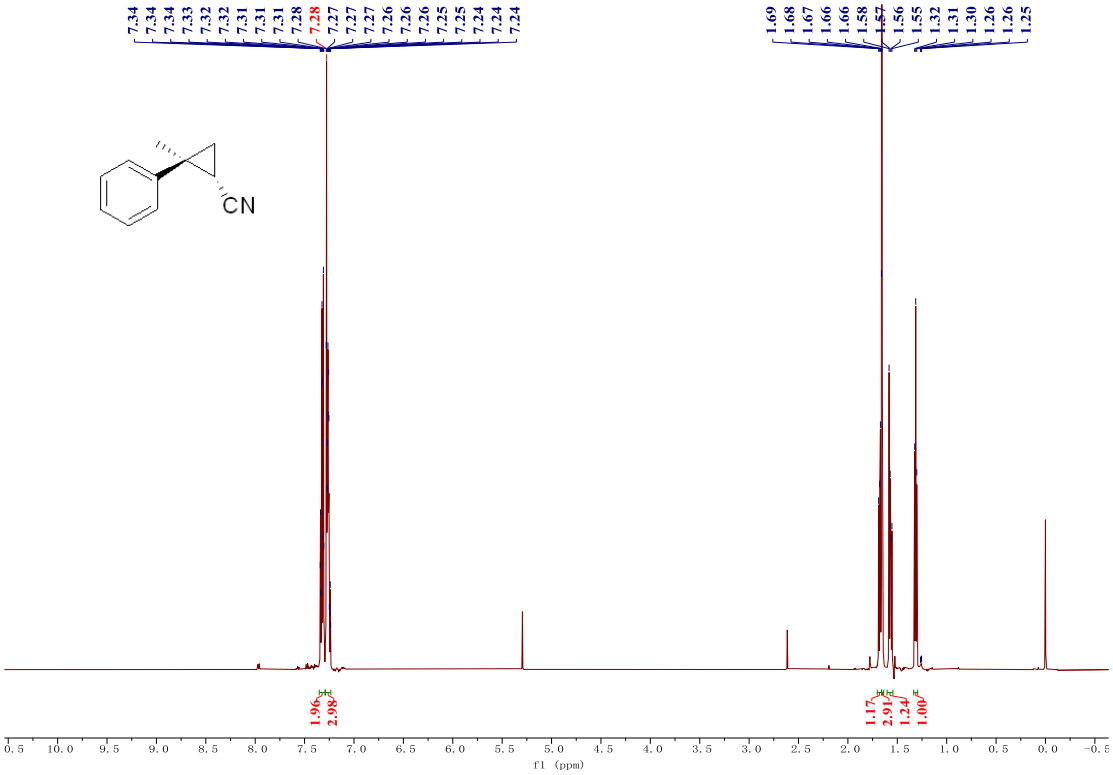
^{1}H NMR spectrum of **2aa** in $CDCl_3$



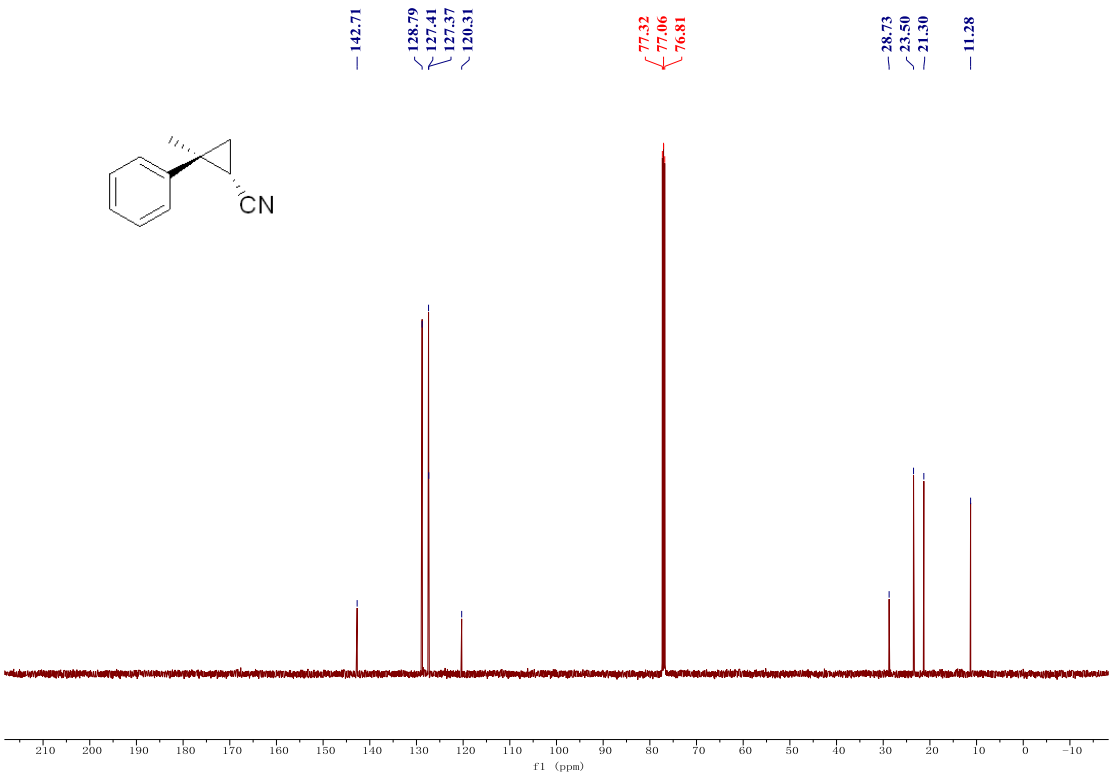
^{13}C NMR spectrum of **2aa** in $CDCl_3$



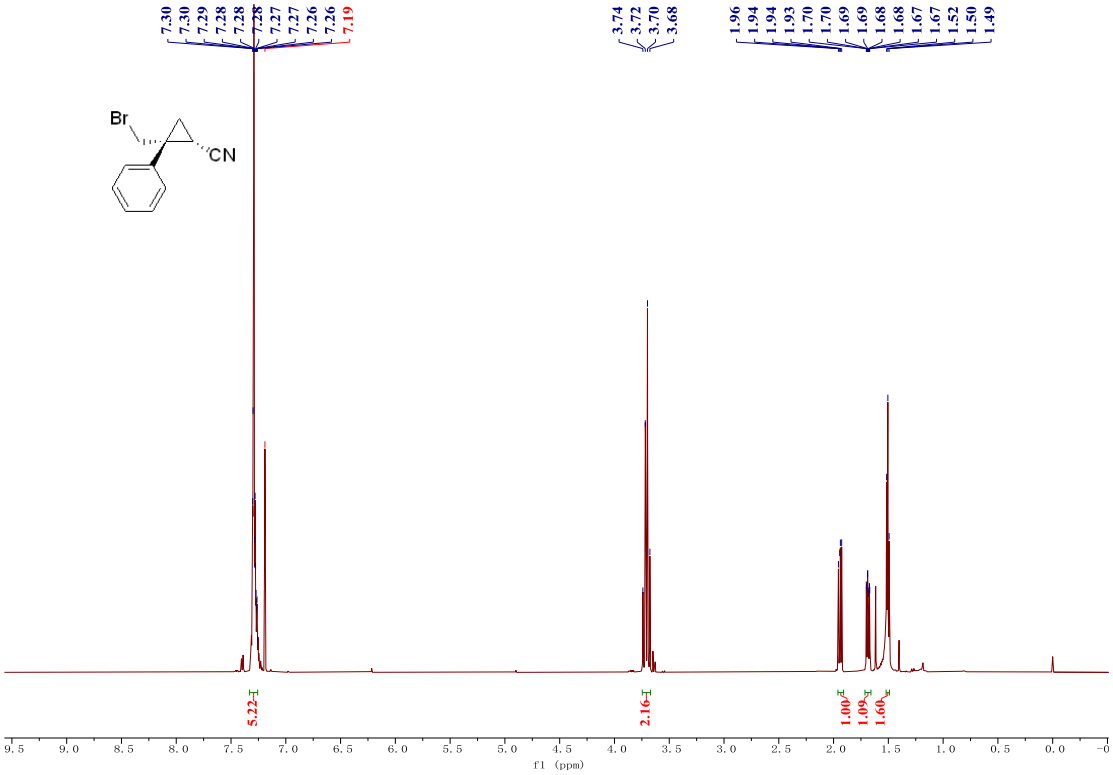
^{1}H NMR spectrum of **2ab** in $CDCl_3$



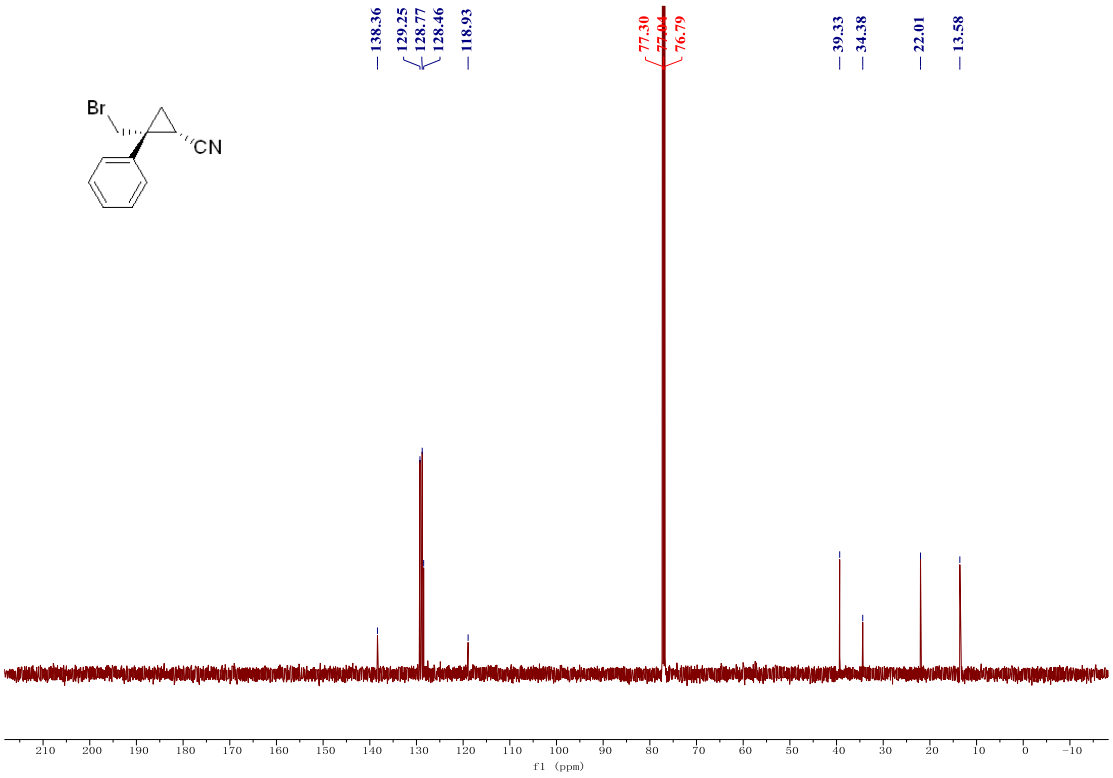
^{13}C NMR spectrum of **2ab** in $CDCl_3$



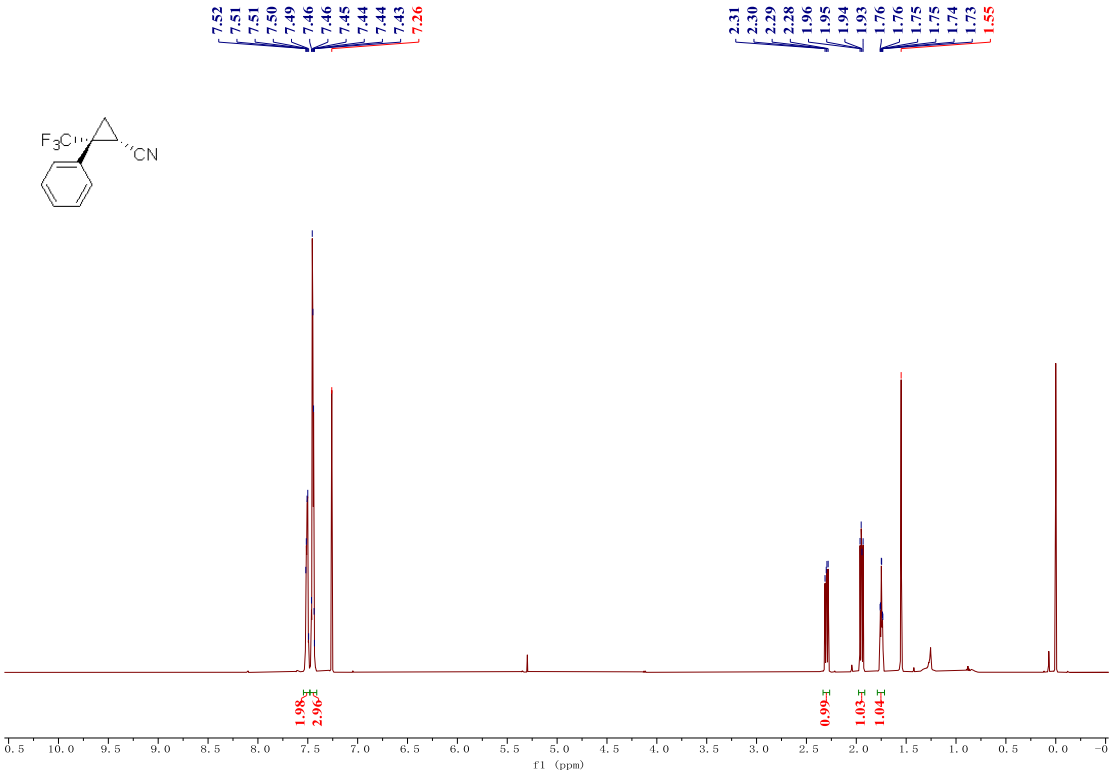
^{1}H NMR spectrum of **2ac** in $CDCl_3$



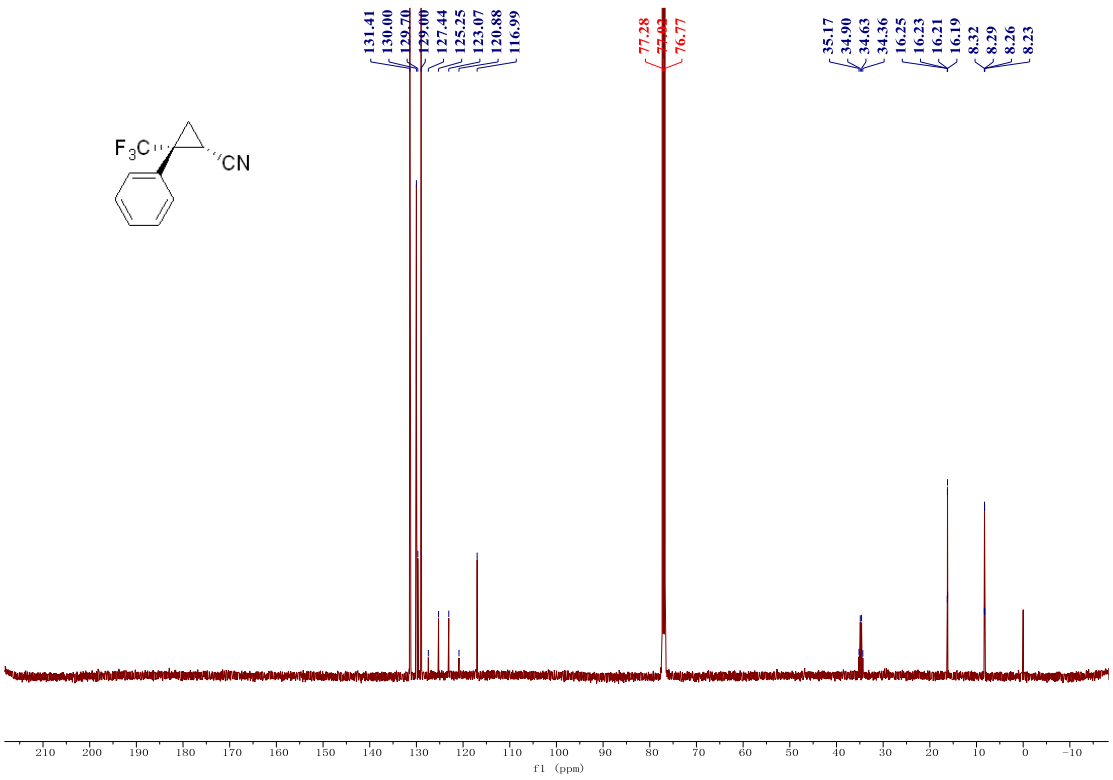
^{13}C NMR spectrum of **2ac** in $CDCl_3$



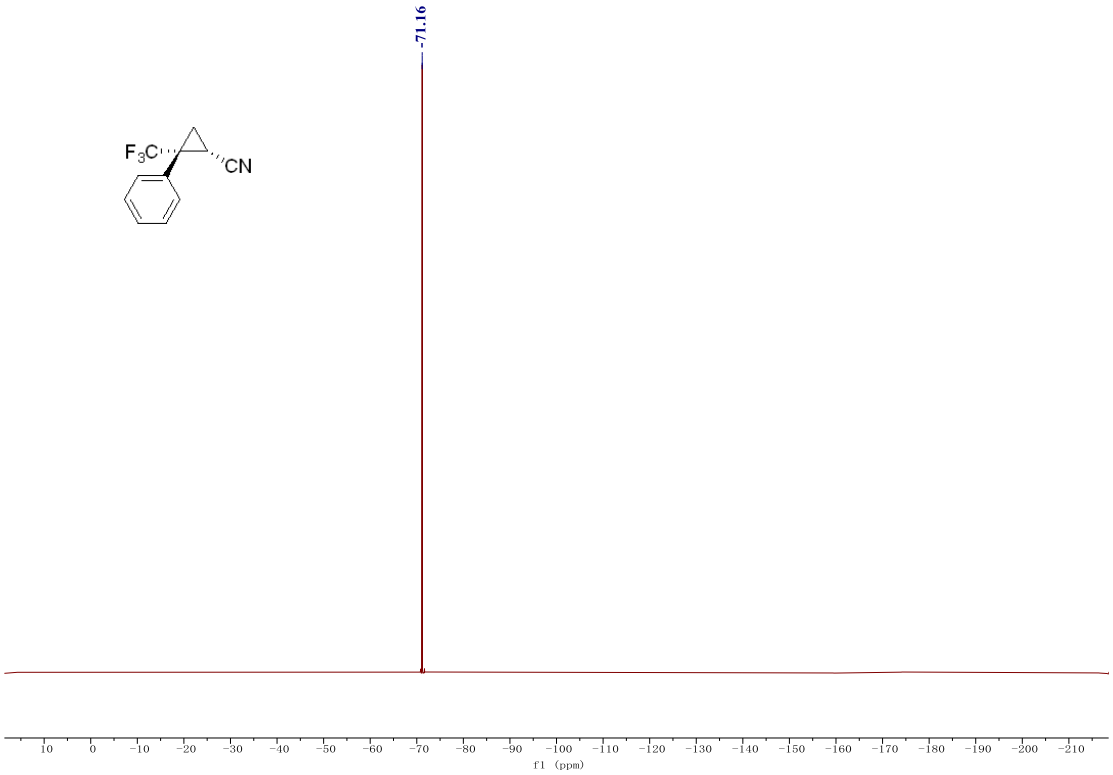
^{1}H NMR spectrum of **2ad** in $CDCl_3$



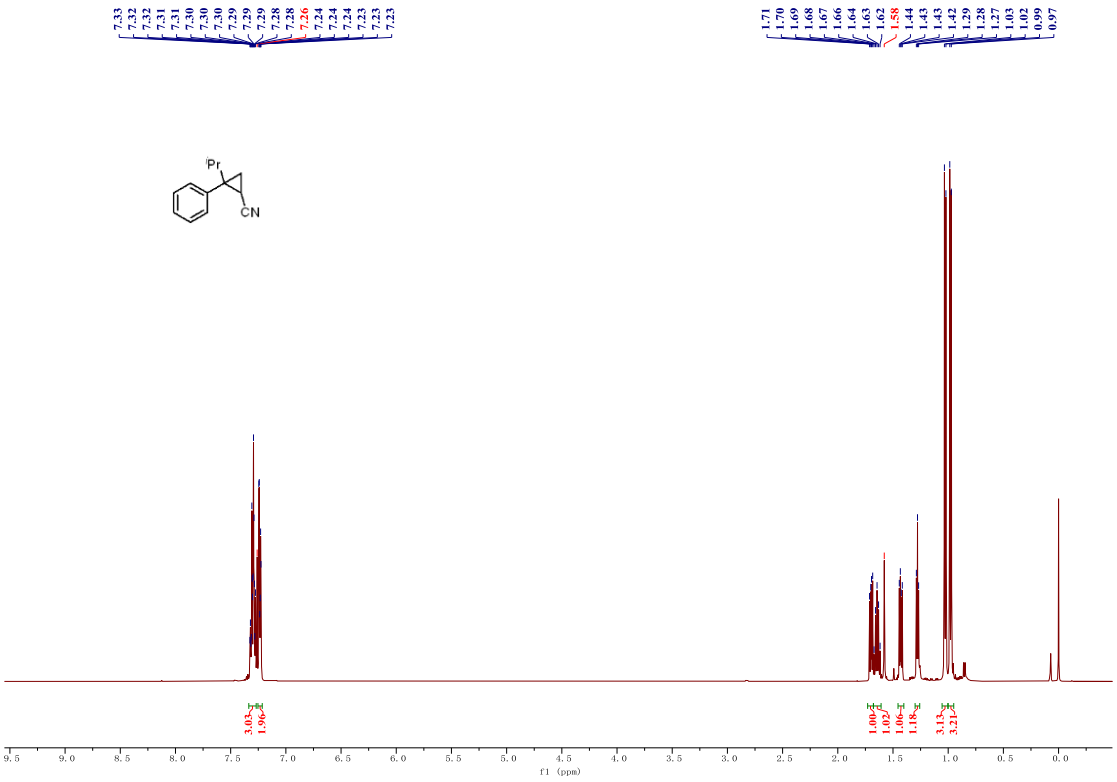
^{13}C NMR spectrum of **2ad** in $CDCl_3$



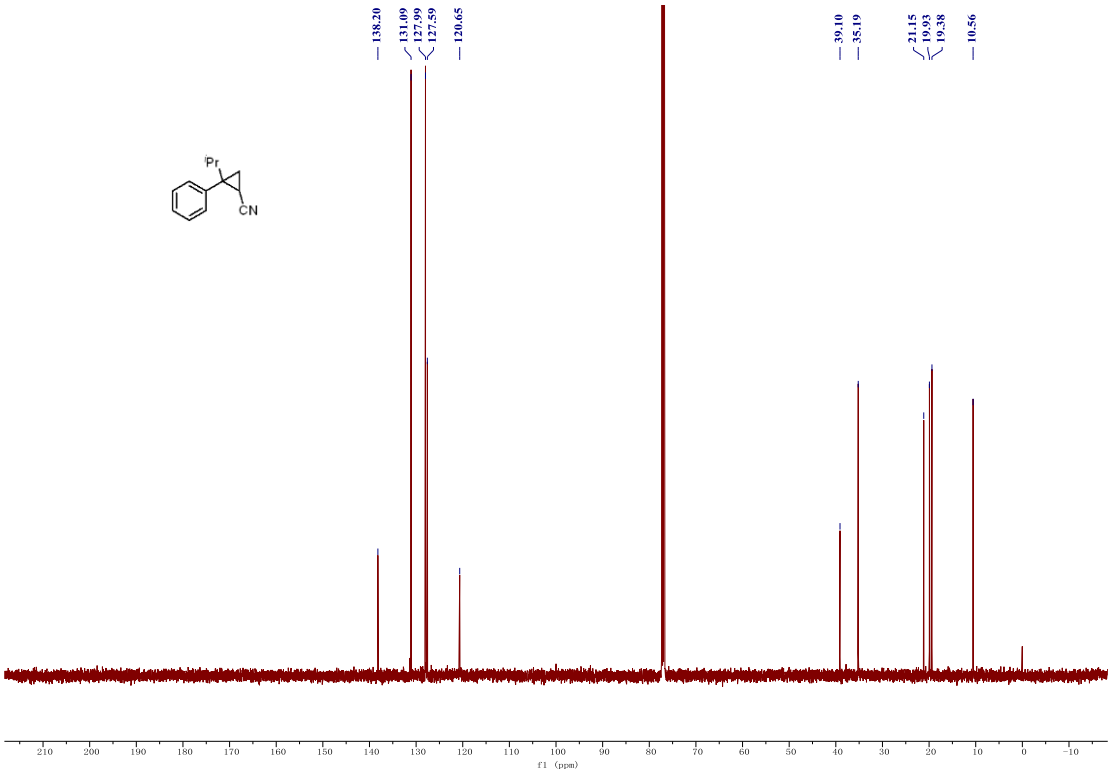
^{19}F NMR spectrum of **2ad** in $CDCl_3$



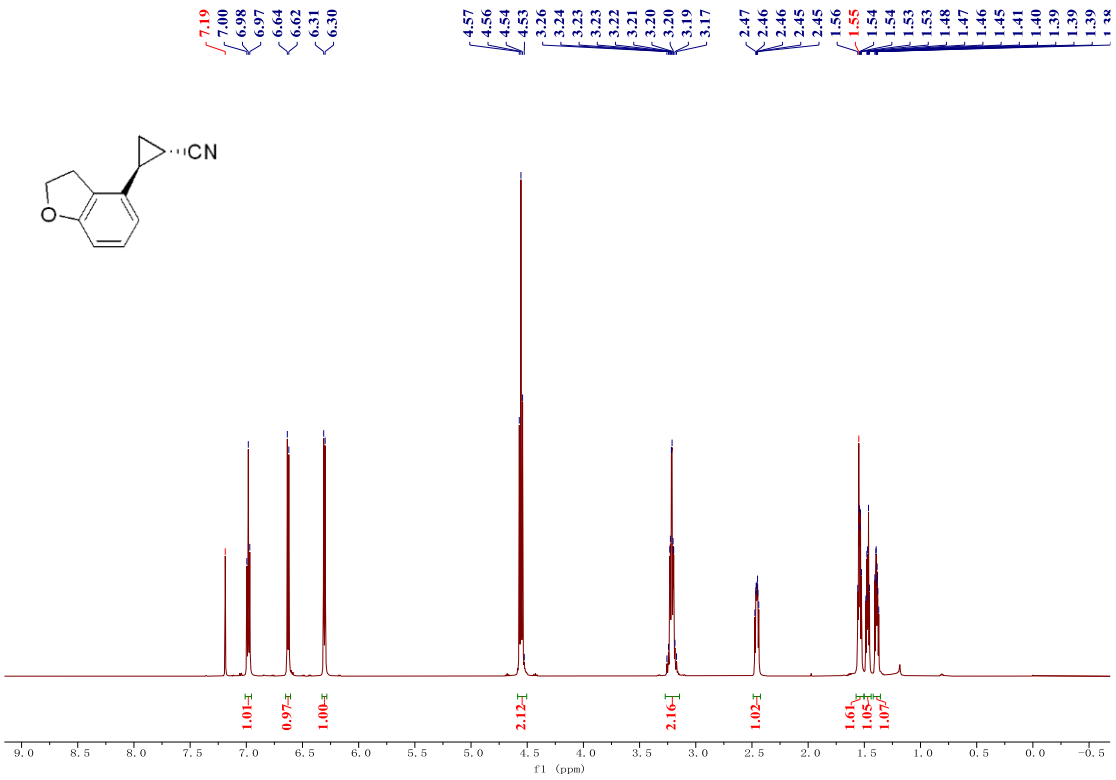
^{1}H NMR spectrum of **2ae** in $CDCl_3$



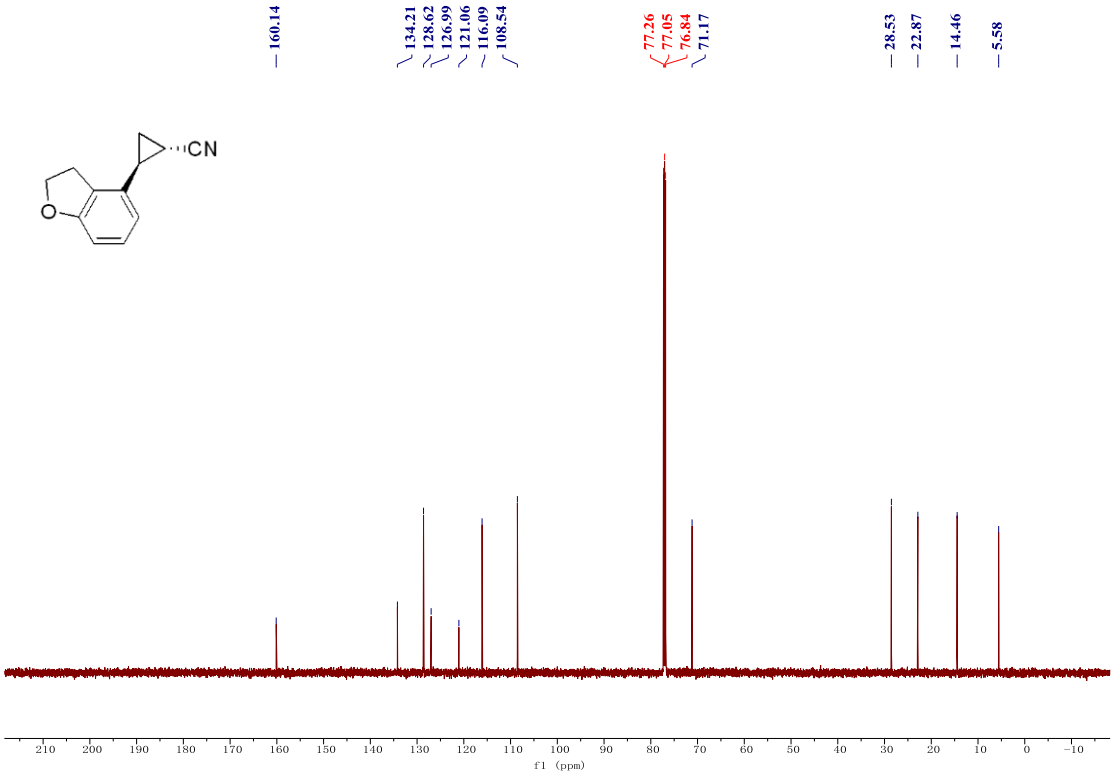
^{13}C NMR spectrum of **2ae** in $CDCl_3$



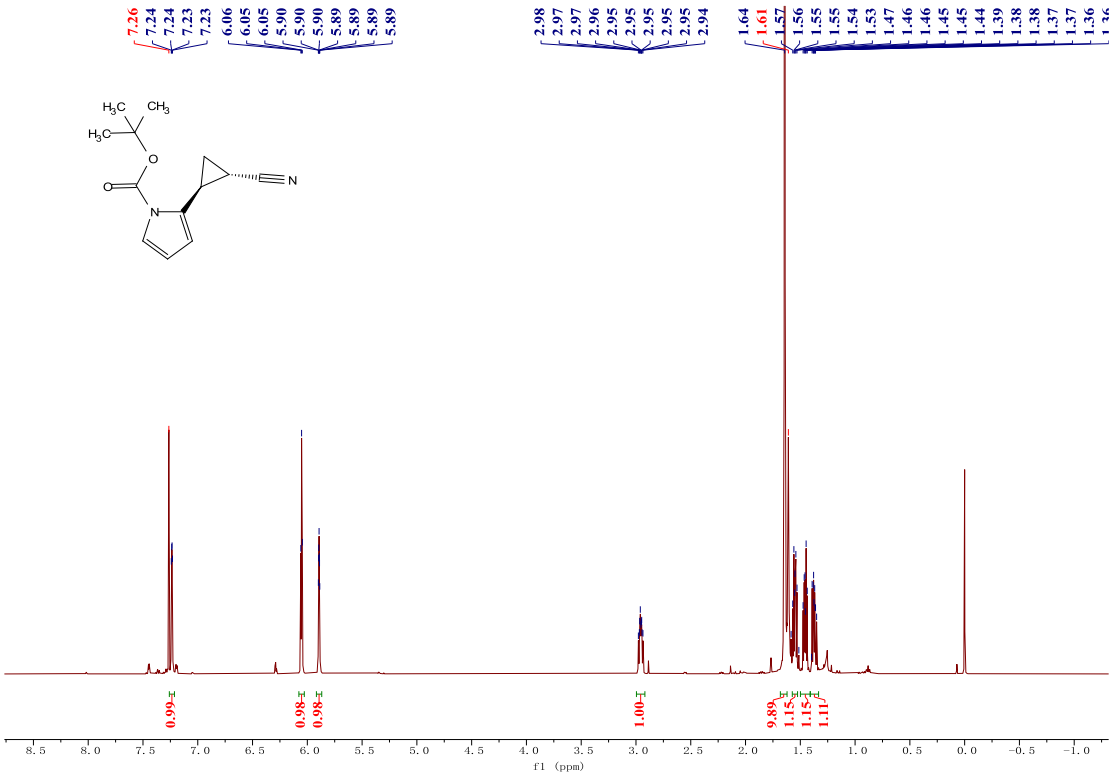
^{1}H NMR spectrum of **3a** in $CDCl_3$



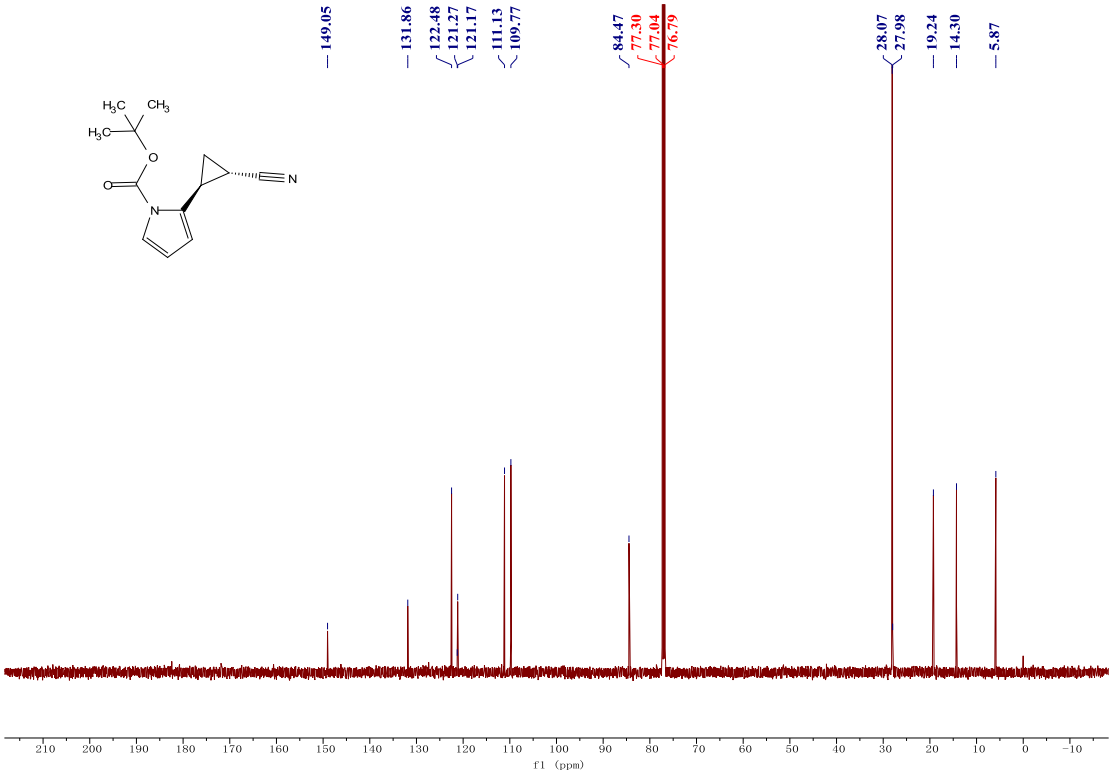
^{13}C NMR spectrum of **3a** in $CDCl_3$



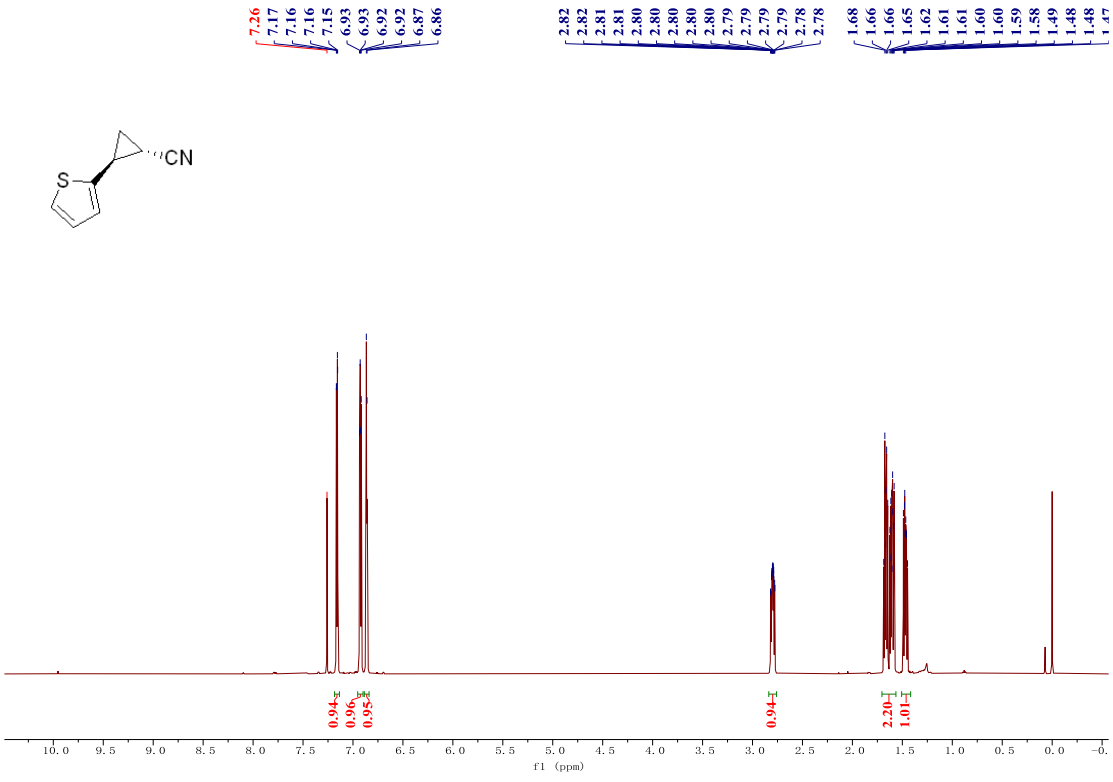
^{1}H NMR spectrum of **3b** in $CDCl_3$



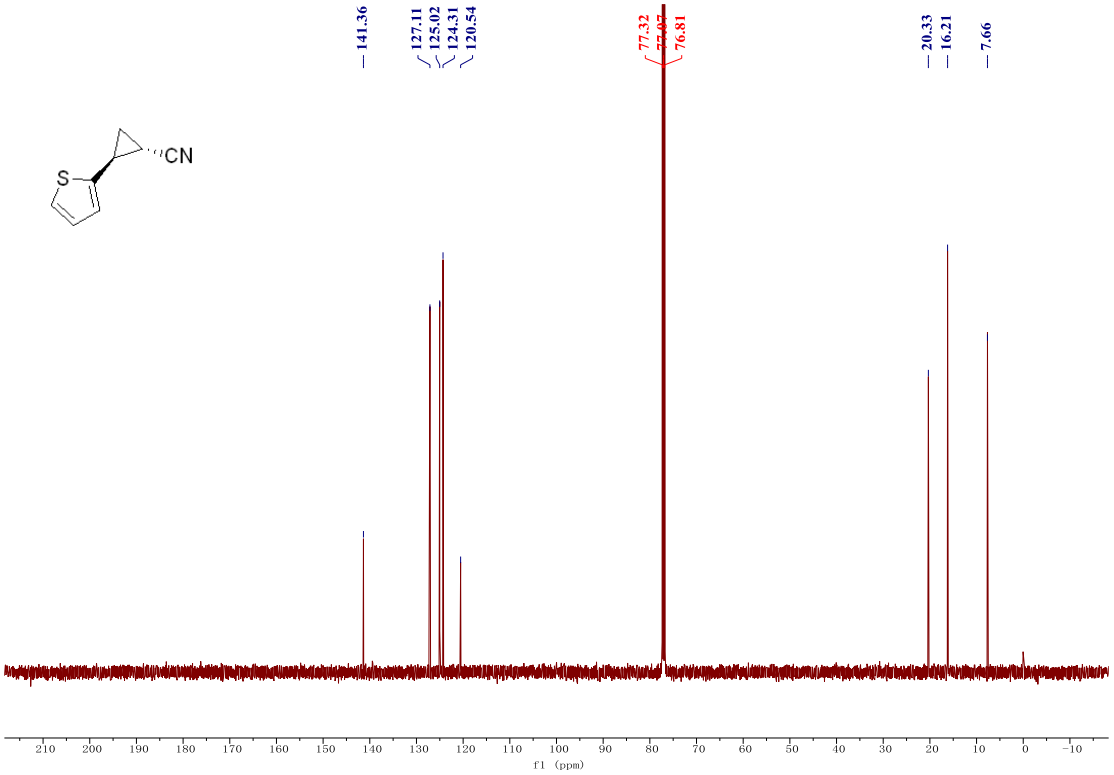
^{13}C NMR spectrum of **3b** in $CDCl_3$



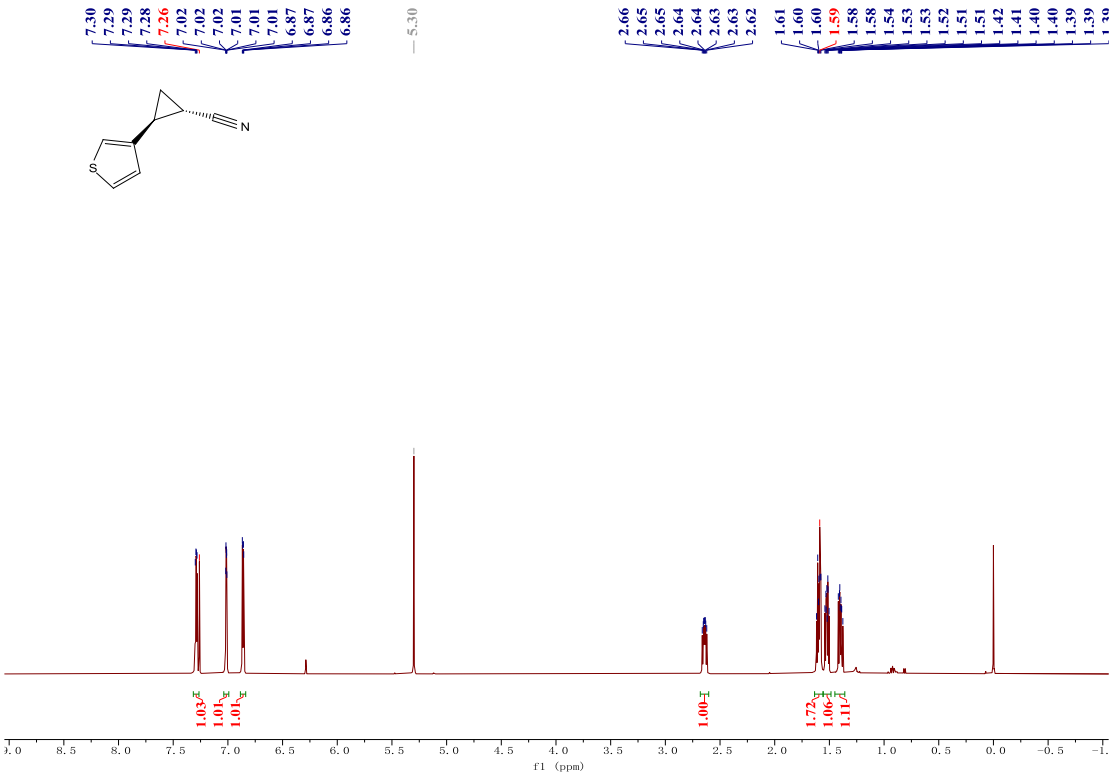
^{1}H NMR spectrum of **3c** in $CDCl_3$



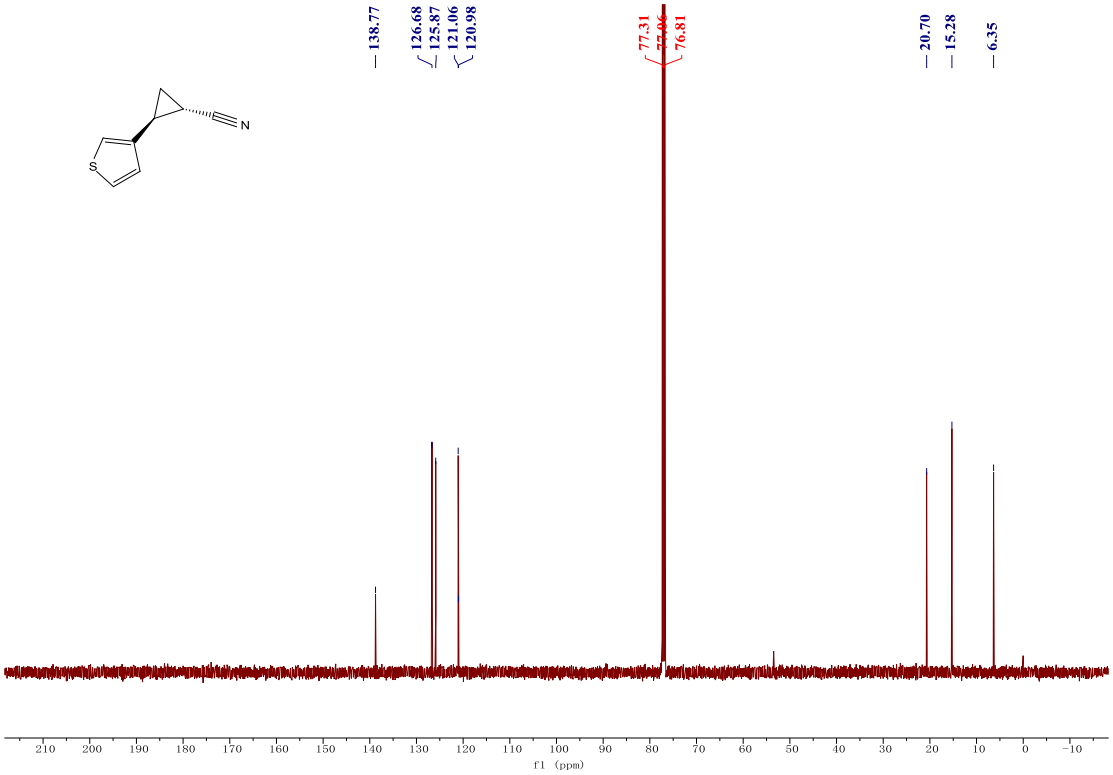
^{13}C NMR spectrum of **3c** in $CDCl_3$



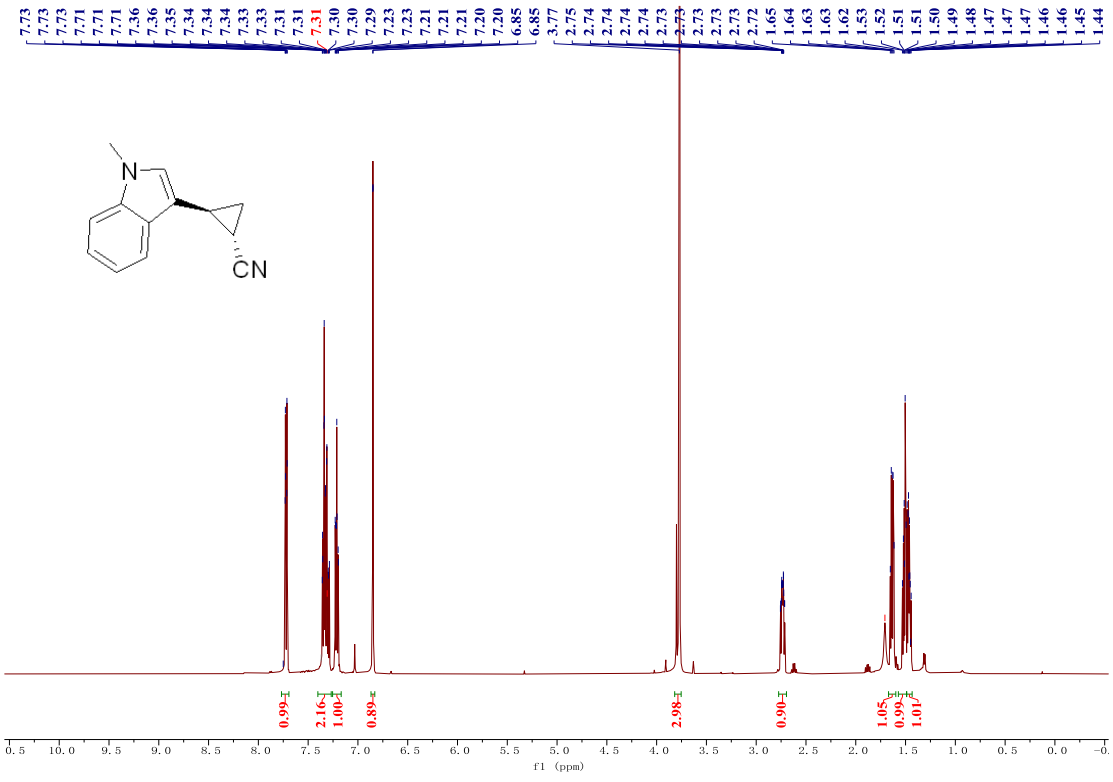
^{1}H NMR spectrum of **3d** in $CDCl_3$



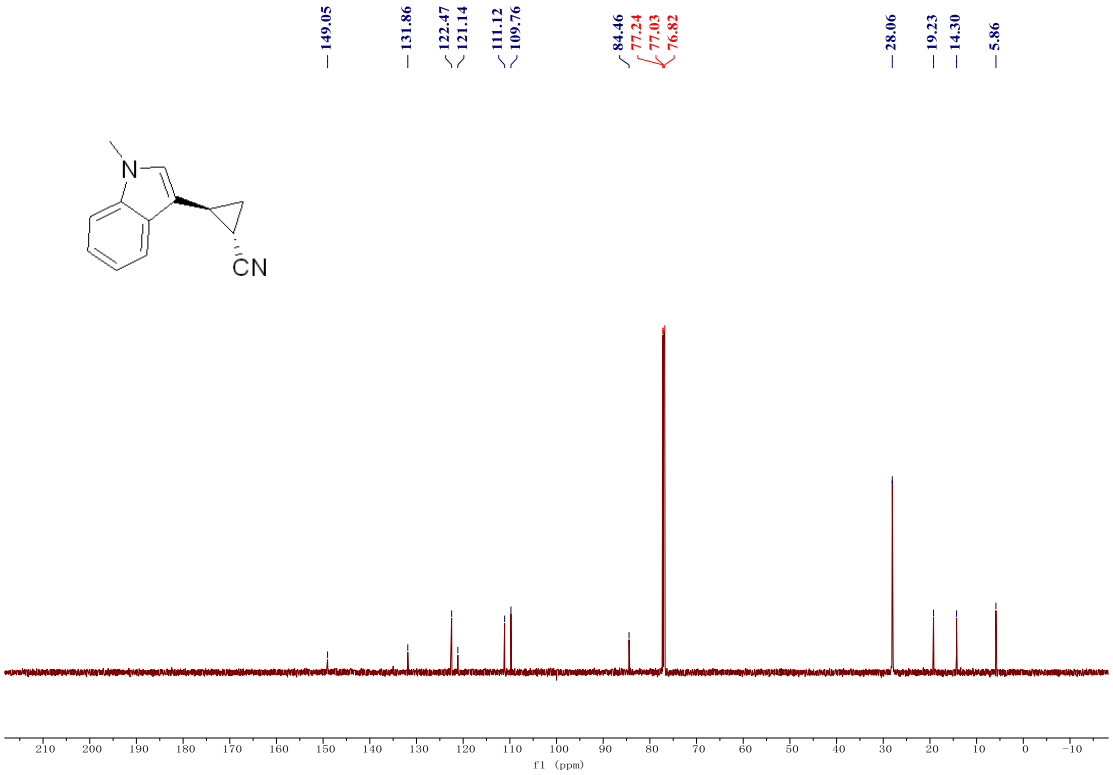
^{13}C NMR spectrum of **3d** in $CDCl_3$



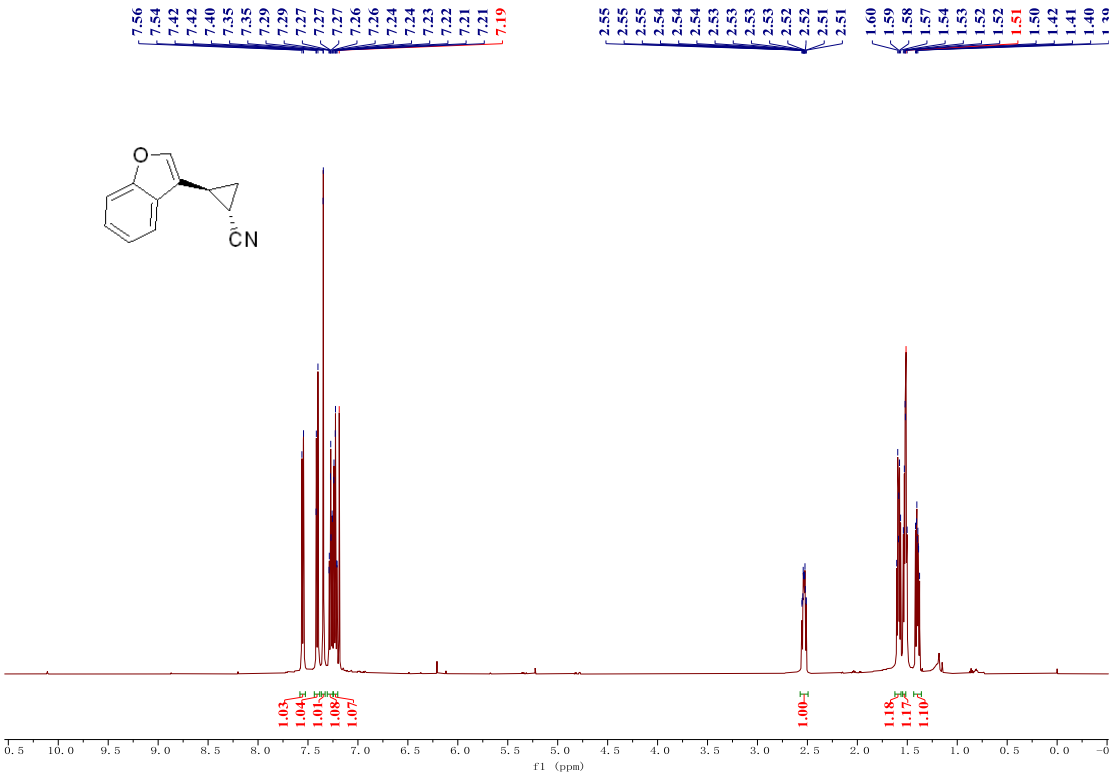
^{1}H NMR spectrum of **3e** in $CDCl_3$



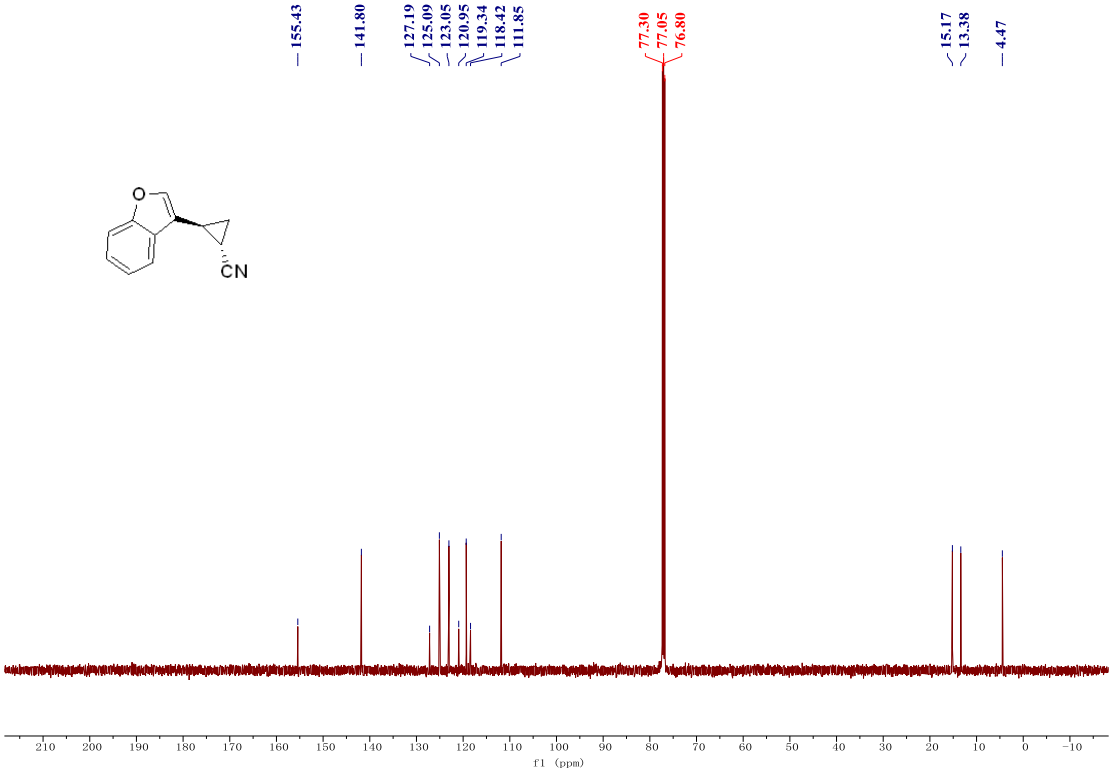
^{13}C NMR spectrum of **3e** in $CDCl_3$



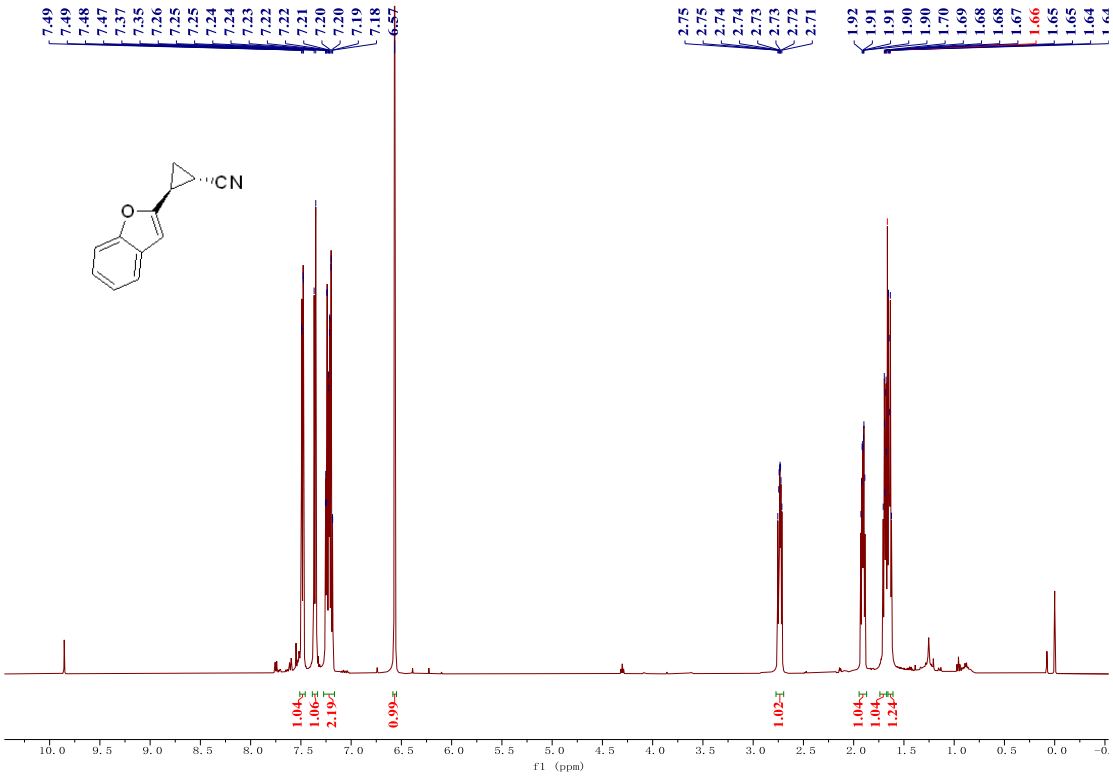
^{1}H NMR spectrum of **3f** in $CDCl_3$



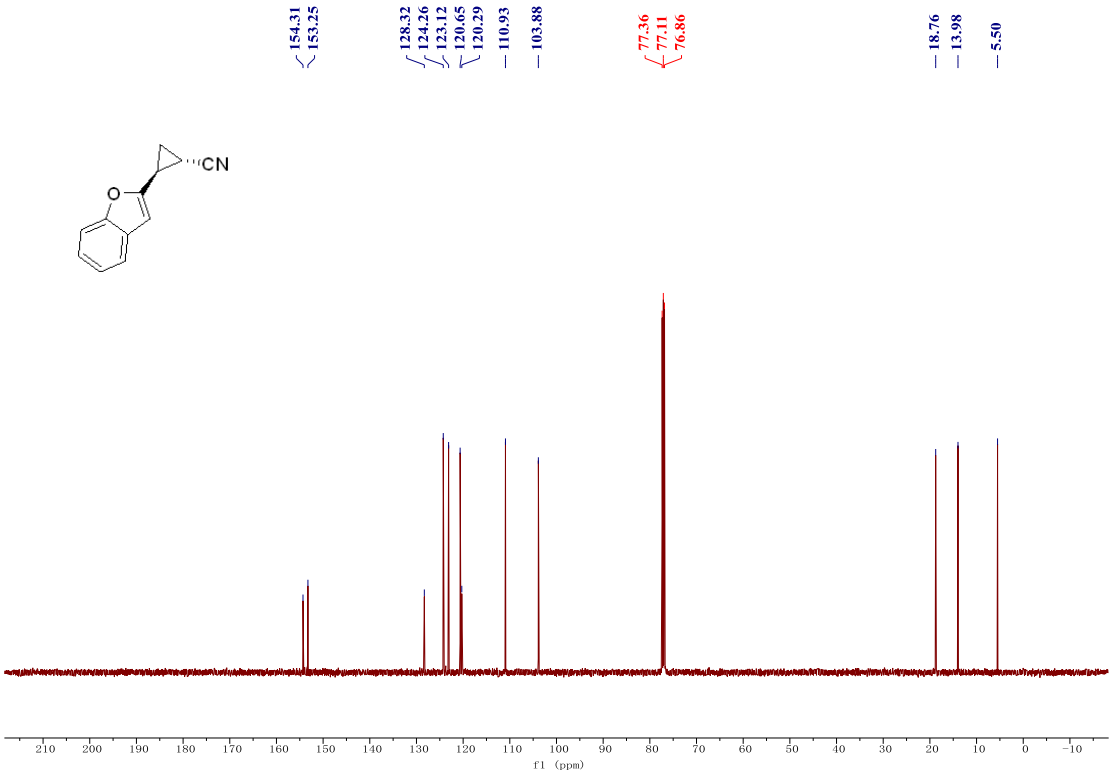
^{13}C NMR spectrum of **3f** in $CDCl_3$



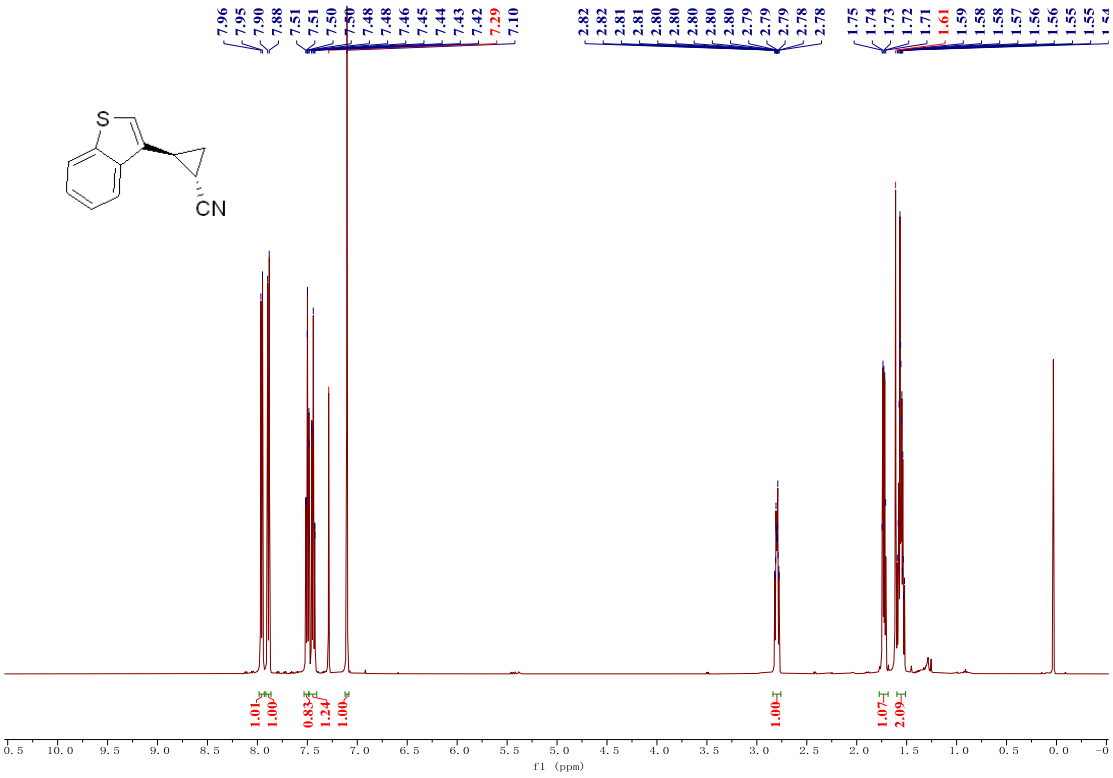
^{1}H NMR spectrum of **3g** in $CDCl_3$



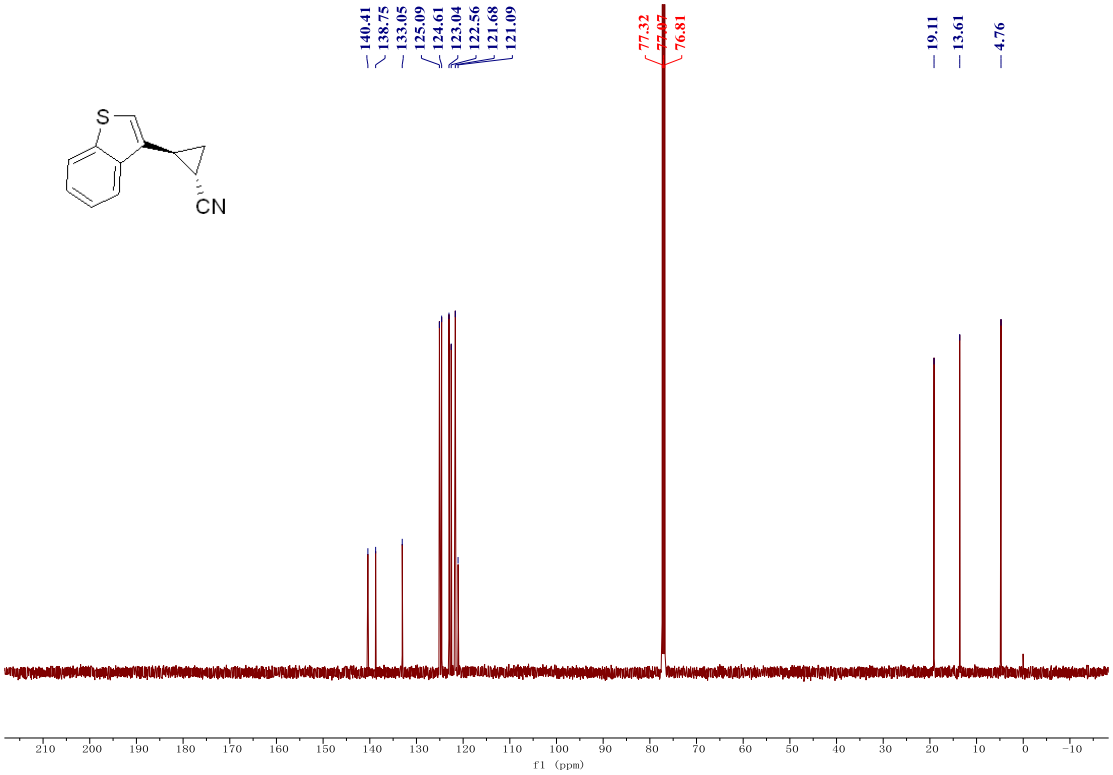
^{13}C NMR spectrum of **3g** in $CDCl_3$



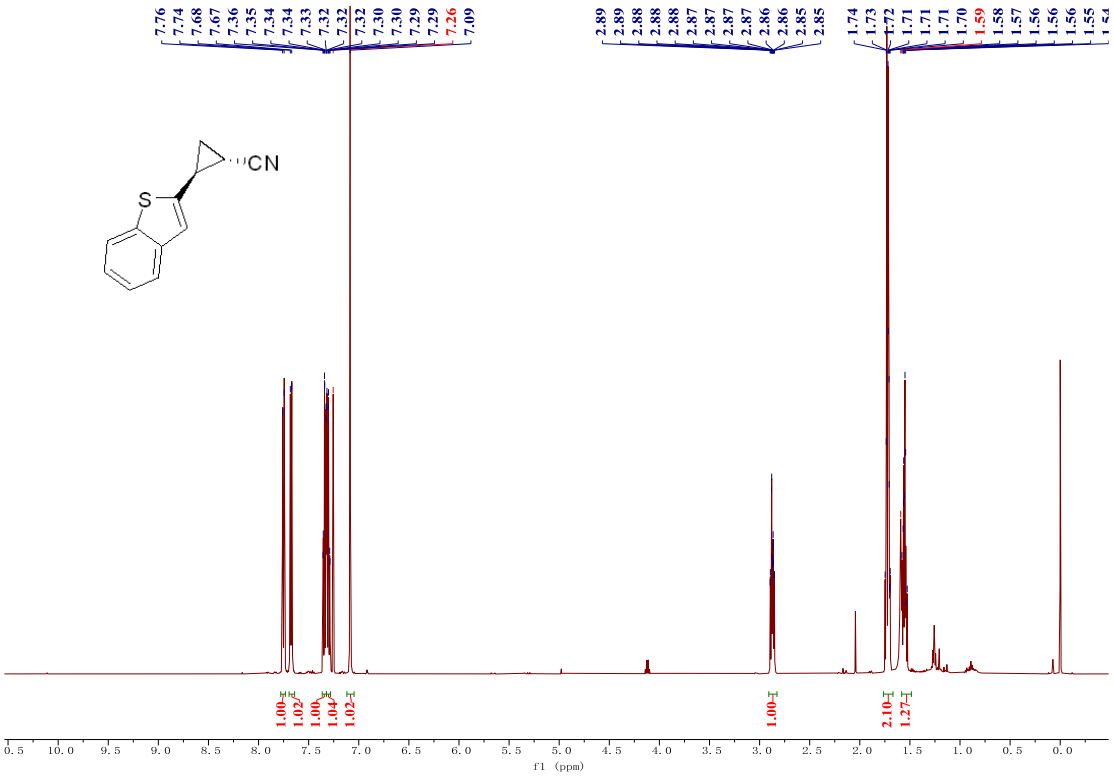
^{1}H NMR spectrum of **3h** in $CDCl_3$



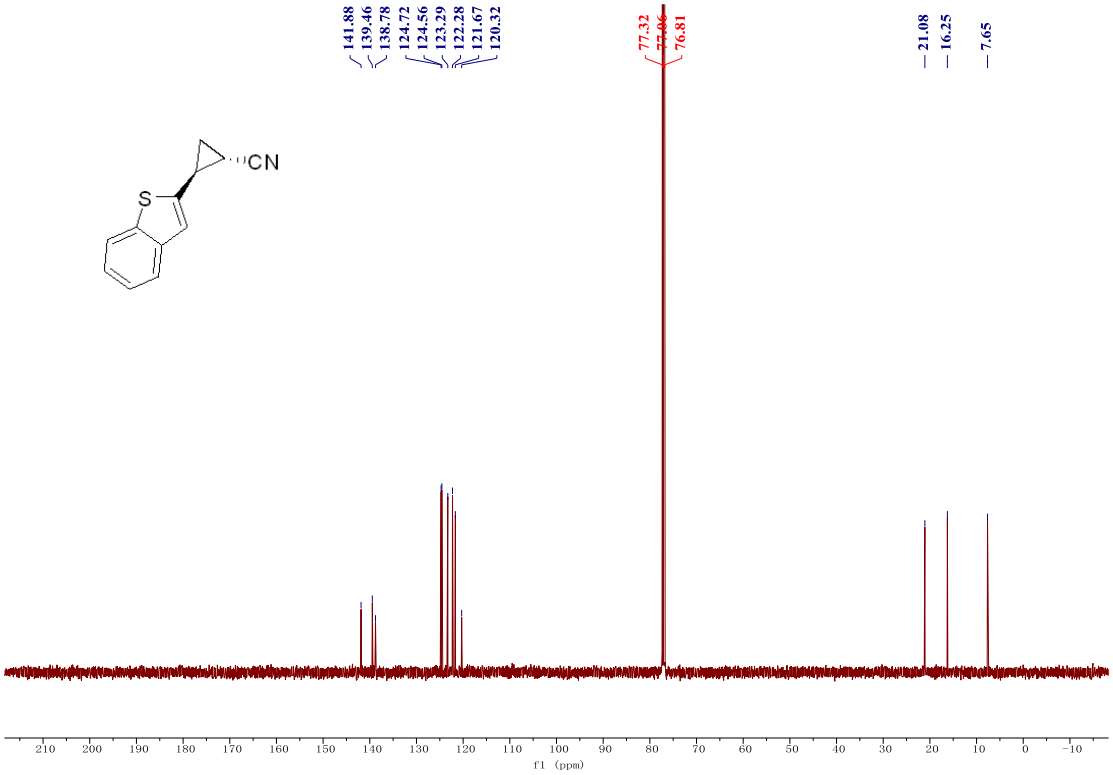
^{13}C NMR spectrum of **3h** in $CDCl_3$



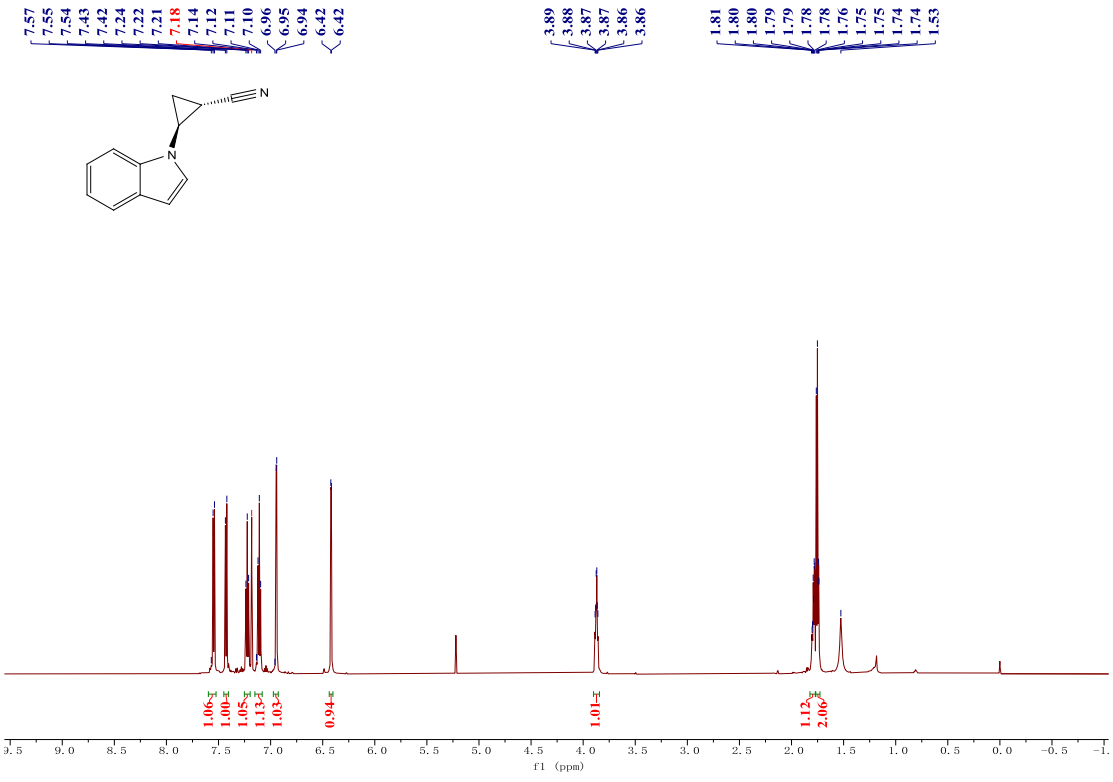
^{1}H NMR spectrum of **3i** in $CDCl_3$



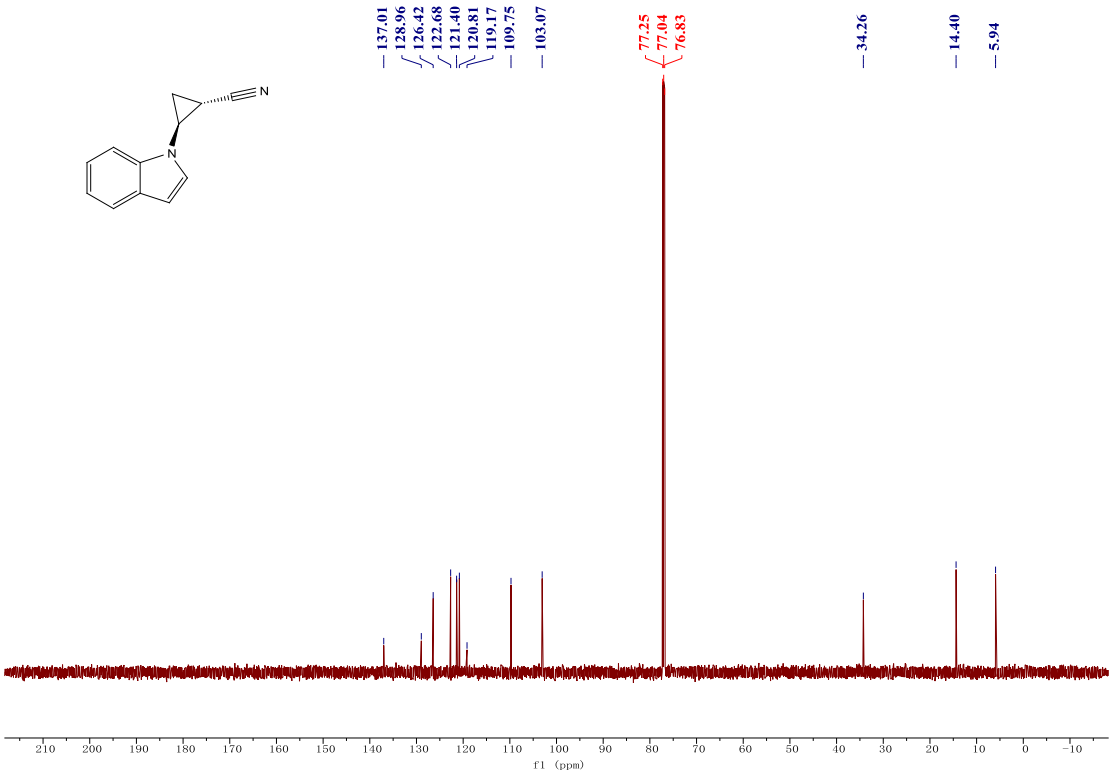
^{13}C NMR spectrum of **3i** in $CDCl_3$



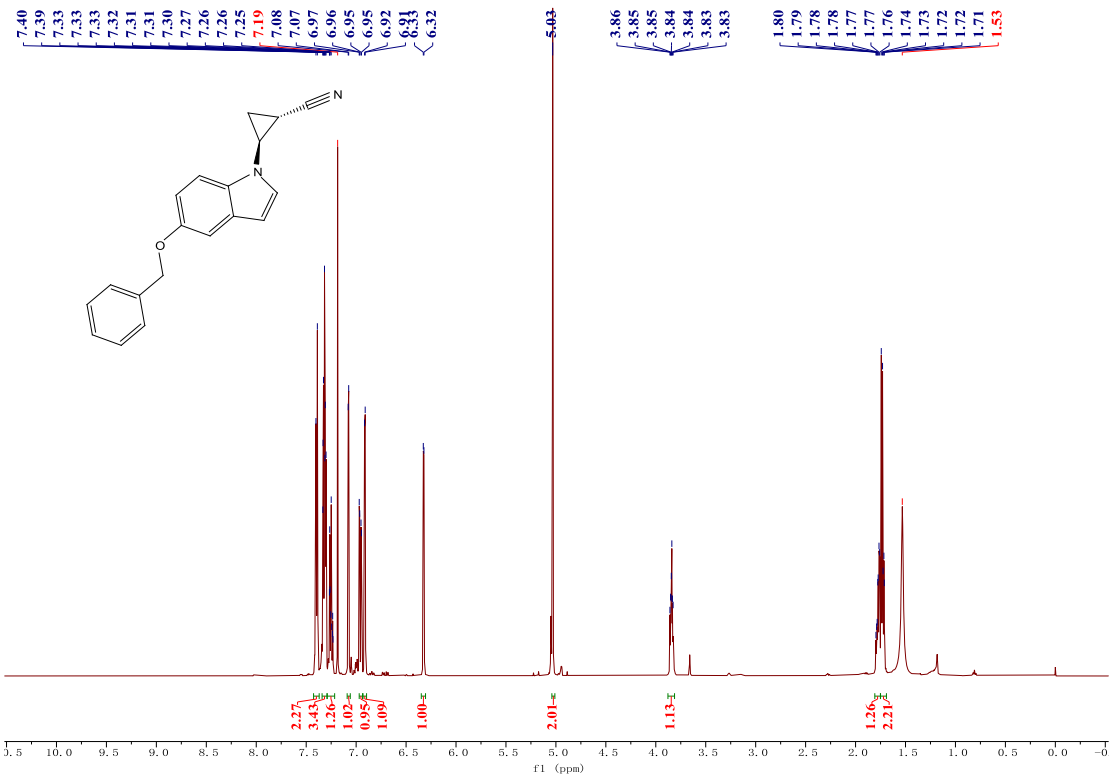
^{1}H NMR spectrum of **3j** in $CDCl_3$



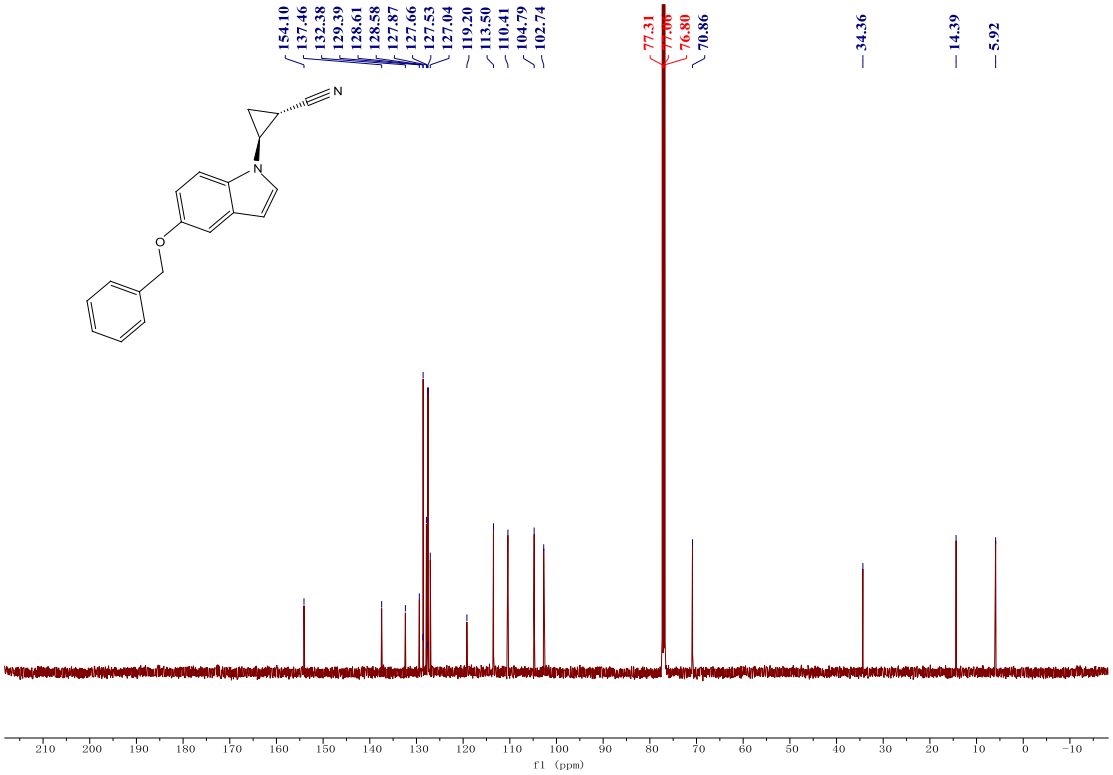
^{13}C NMR spectrum of **3j** in $CDCl_3$



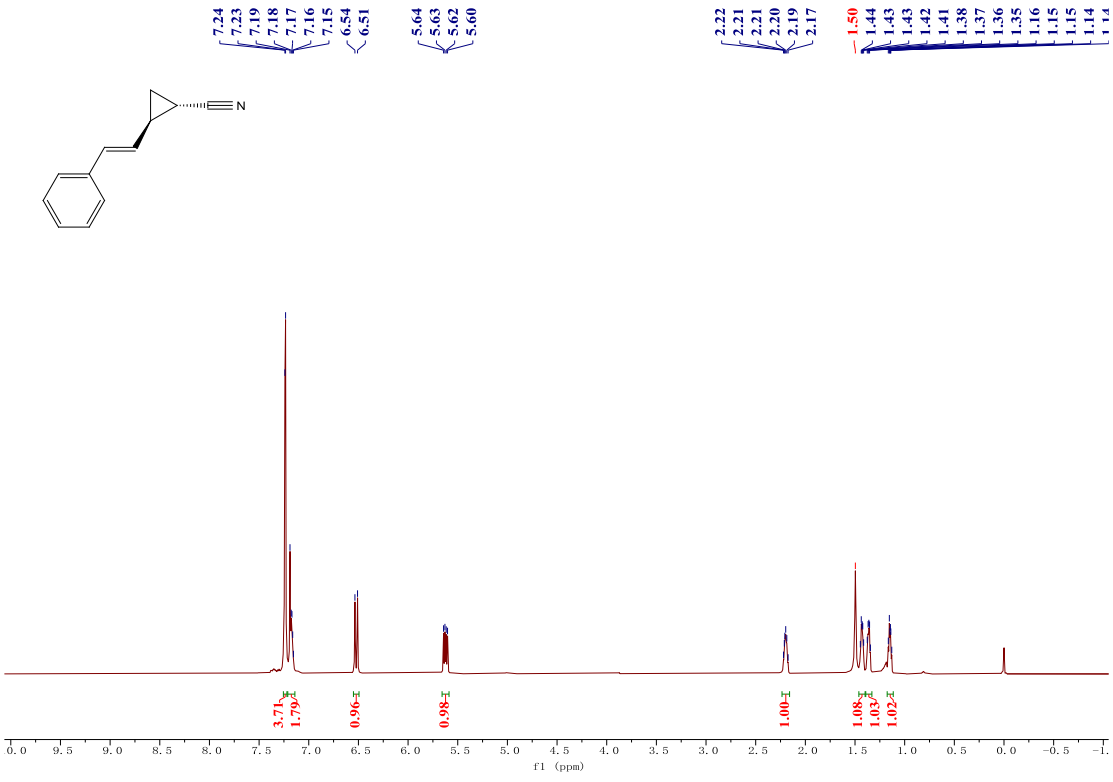
^{1}H NMR spectrum of **3k** in $CDCl_3$



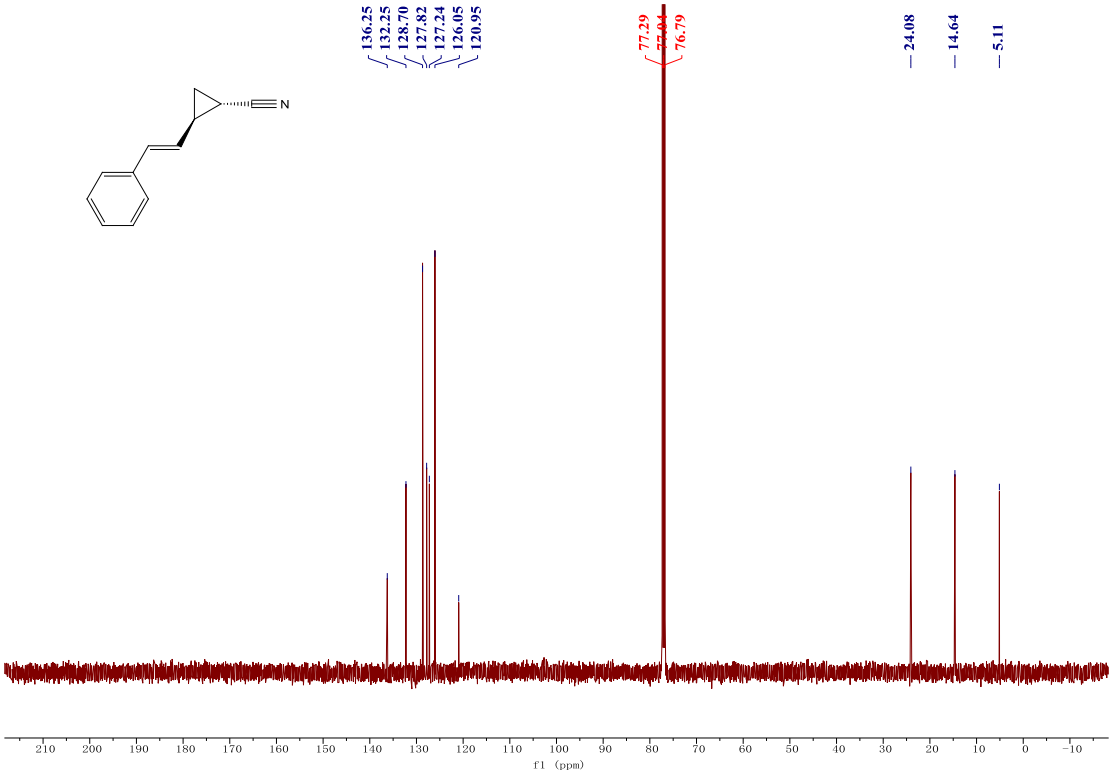
^{13}C NMR spectrum of **3k** in $CDCl_3$



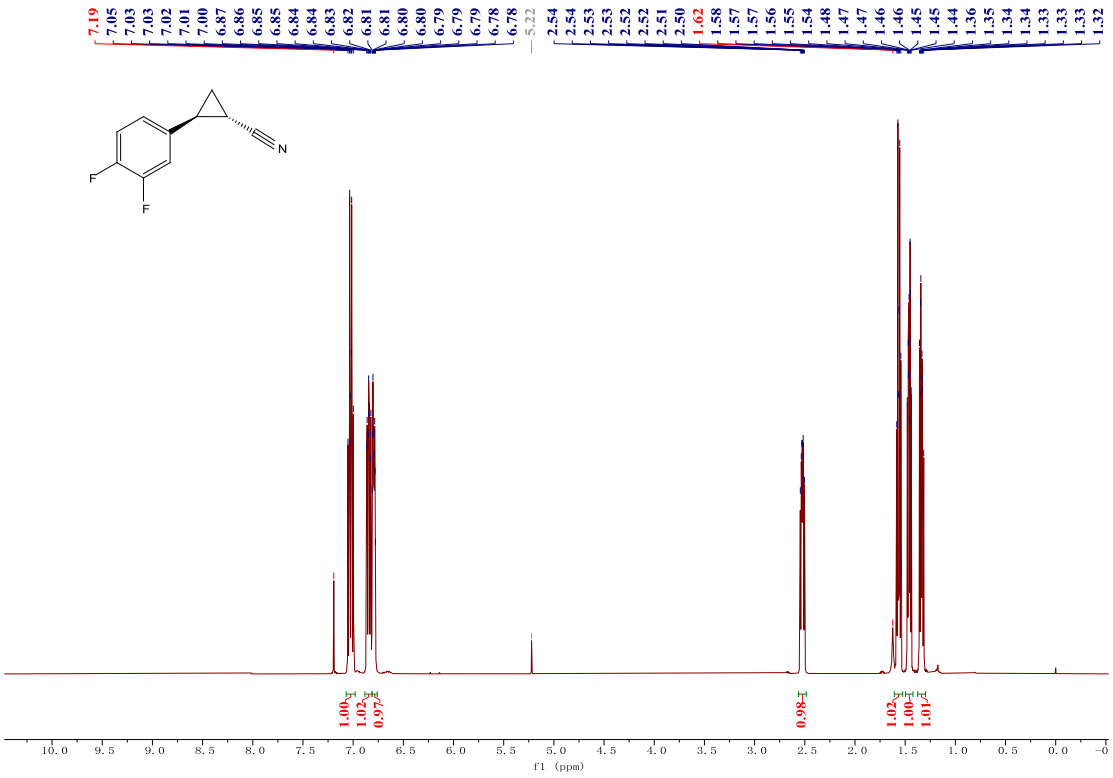
^{1}H NMR spectrum of **4** in $CDCl_3$



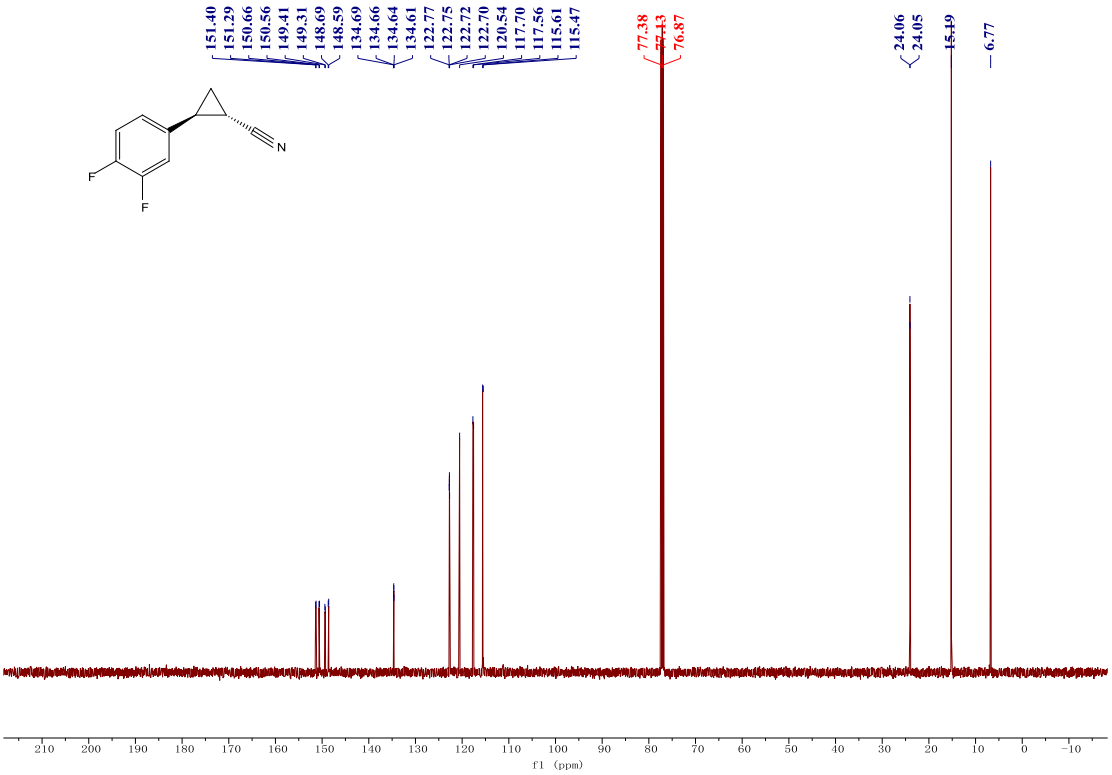
^{13}C NMR spectrum of **4** in $CDCl_3$



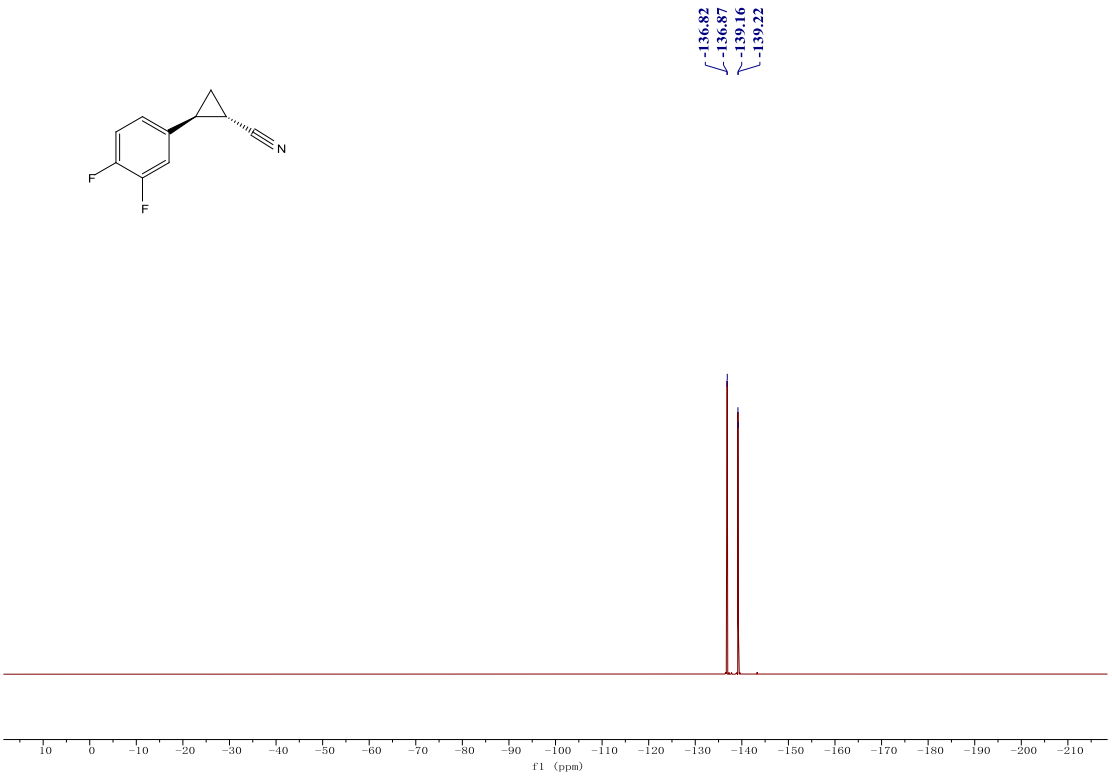
^{1}H NMR spectrum of **6** in $CDCl_3$



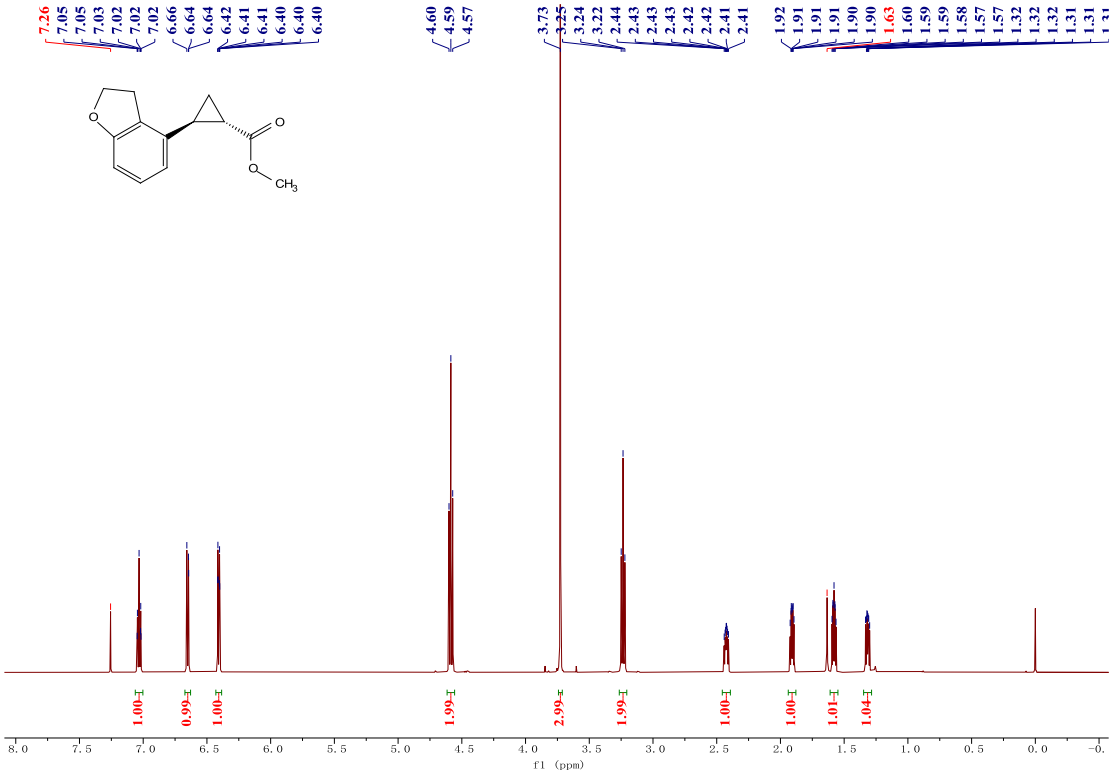
^{13}C NMR spectrum of **6** in $CDCl_3$



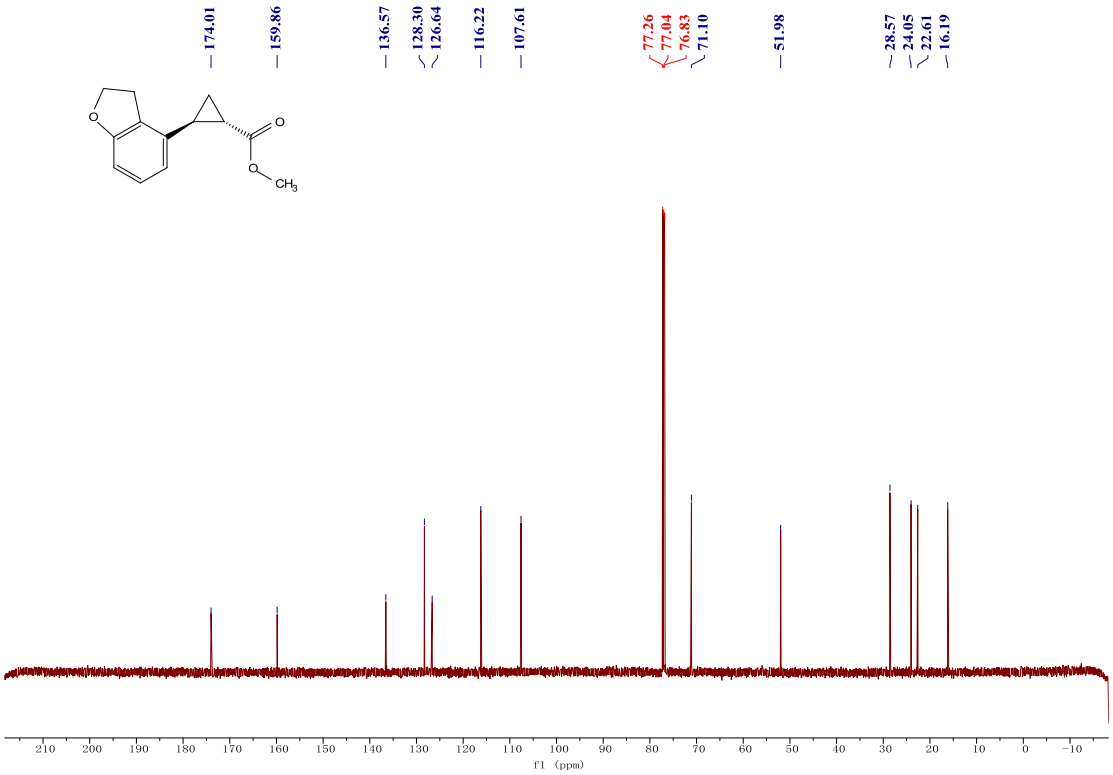
^{19}F NMR spectrum of **6** in $CDCl_3$



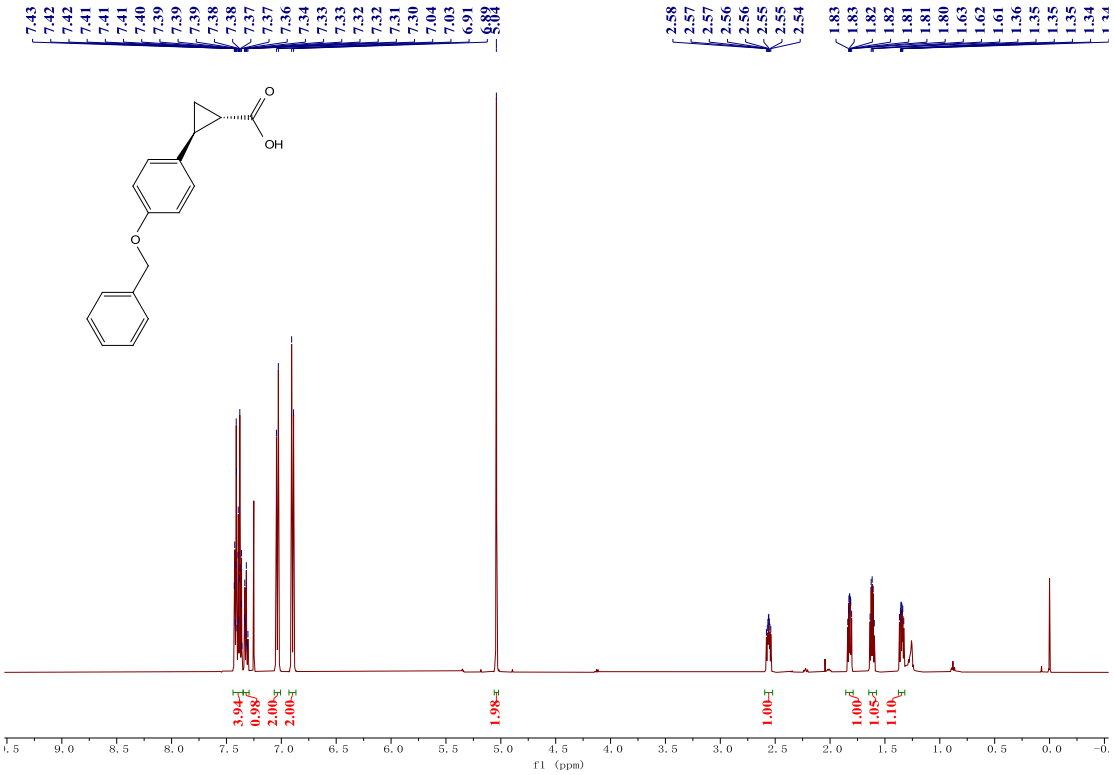
^{1}H NMR spectrum of **8**in $CDCl_3$



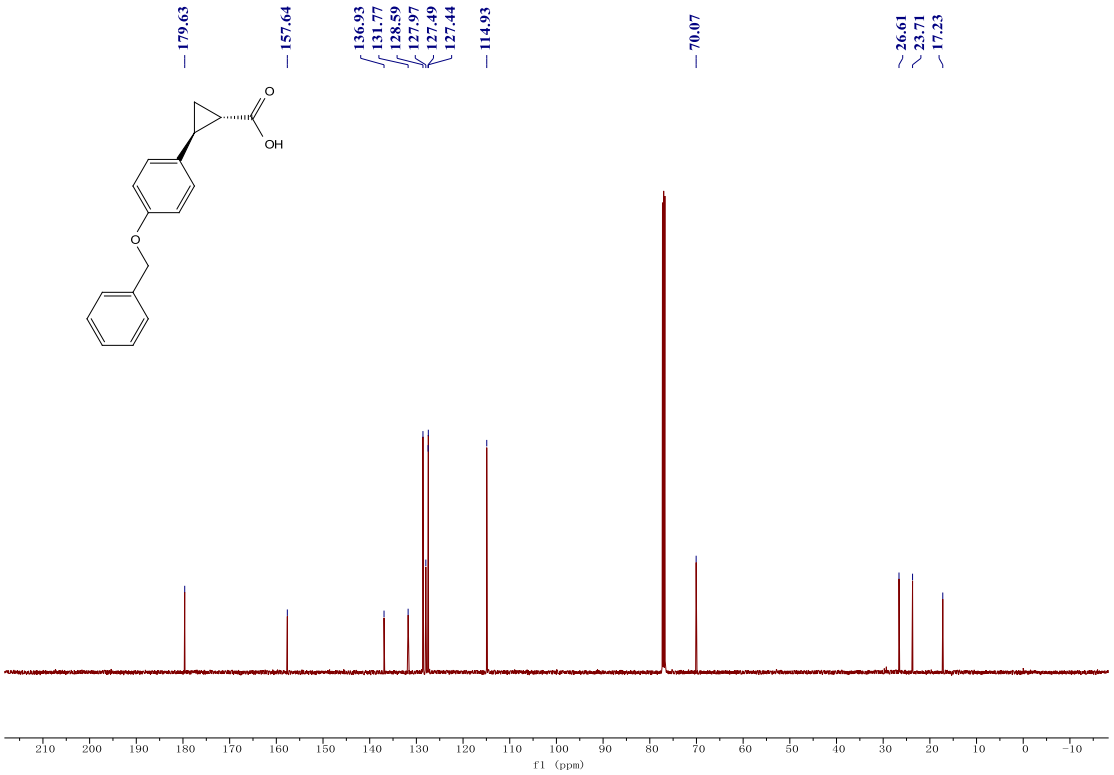
^{13}C NMR spectrum of **8** in $CDCl_3$



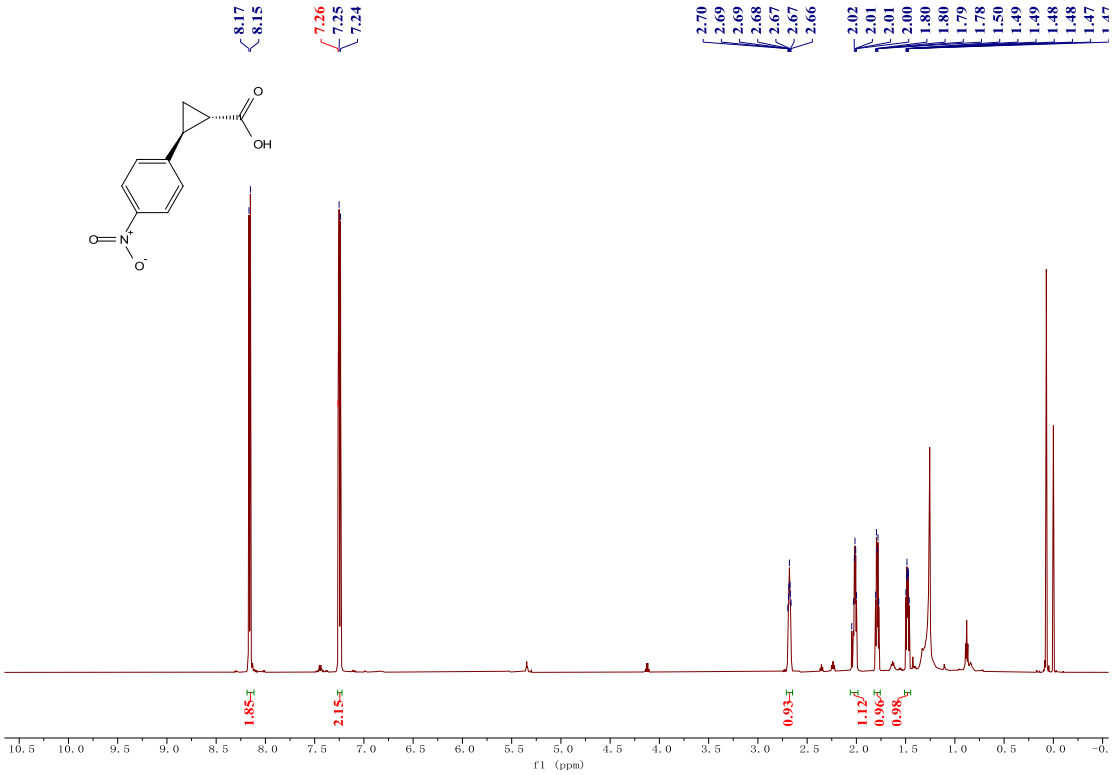
^{1}H NMR spectrum of **11a** in $CDCl_3$



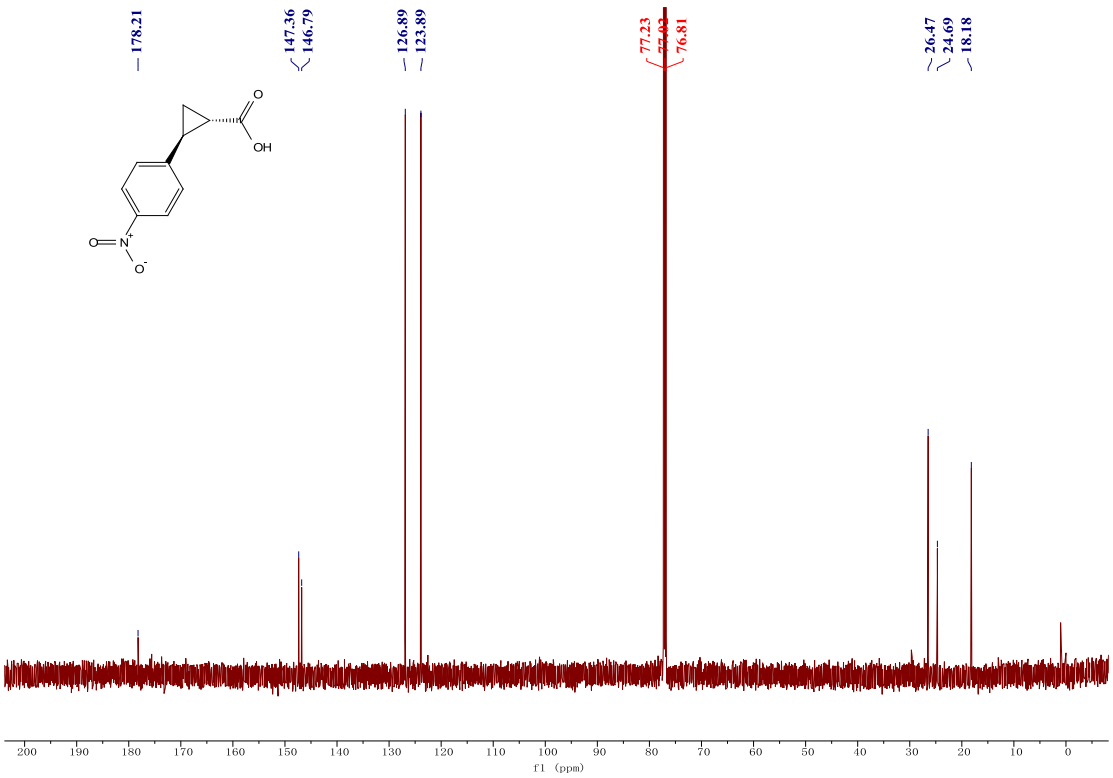
^{13}C NMR spectrum of **11a** in $CDCl_3$



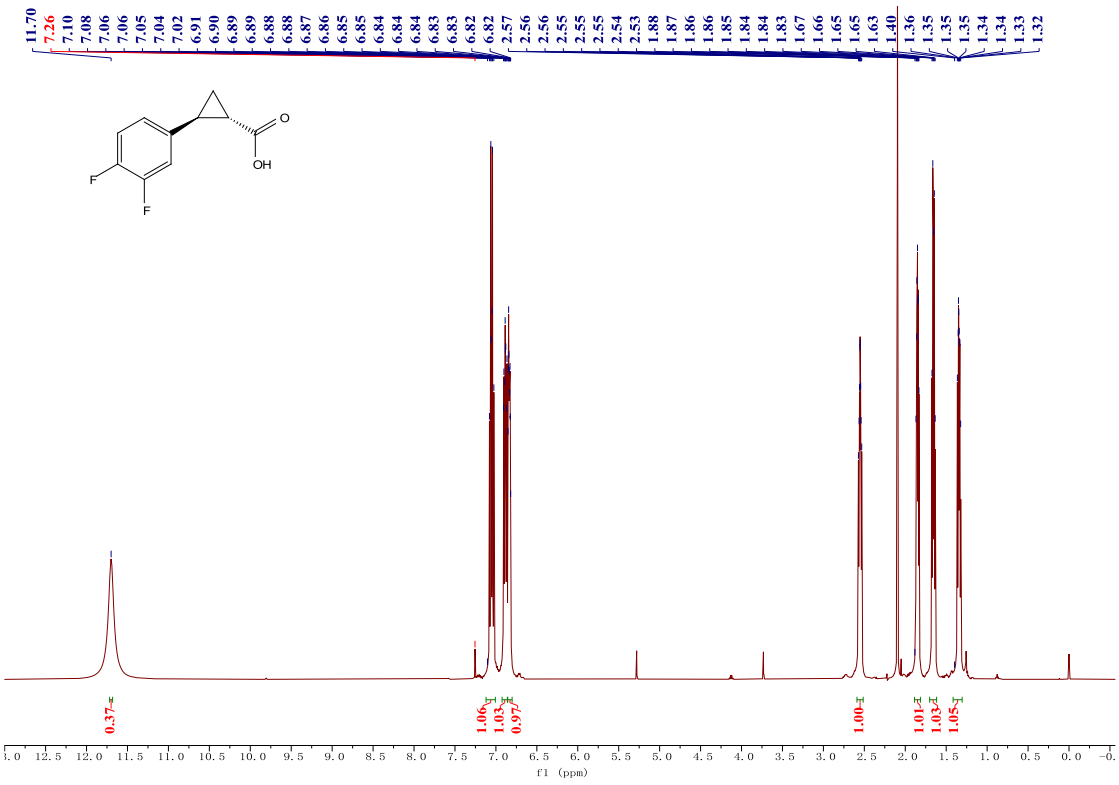
^{1}H NMR spectrum of **11b** in $CDCl_3$



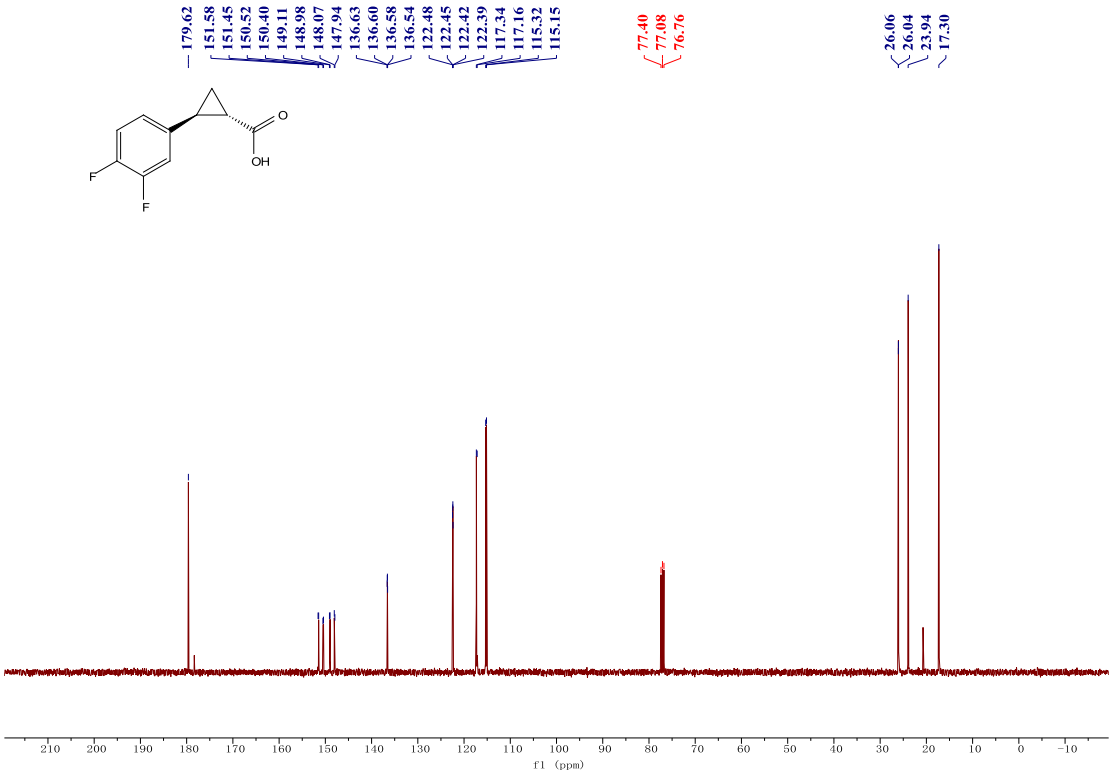
^{13}C NMR spectrum of **11b** in $CDCl_3$



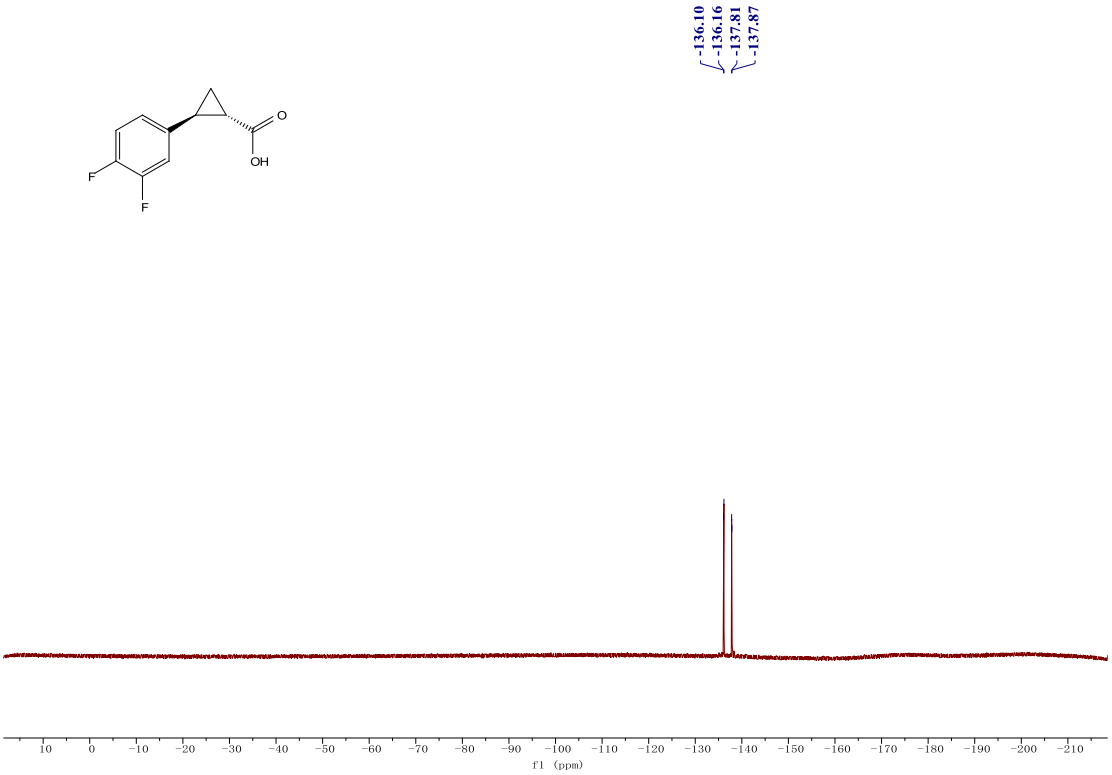
^{1}H NMR spectrum of **11c** in $CDCl_3$



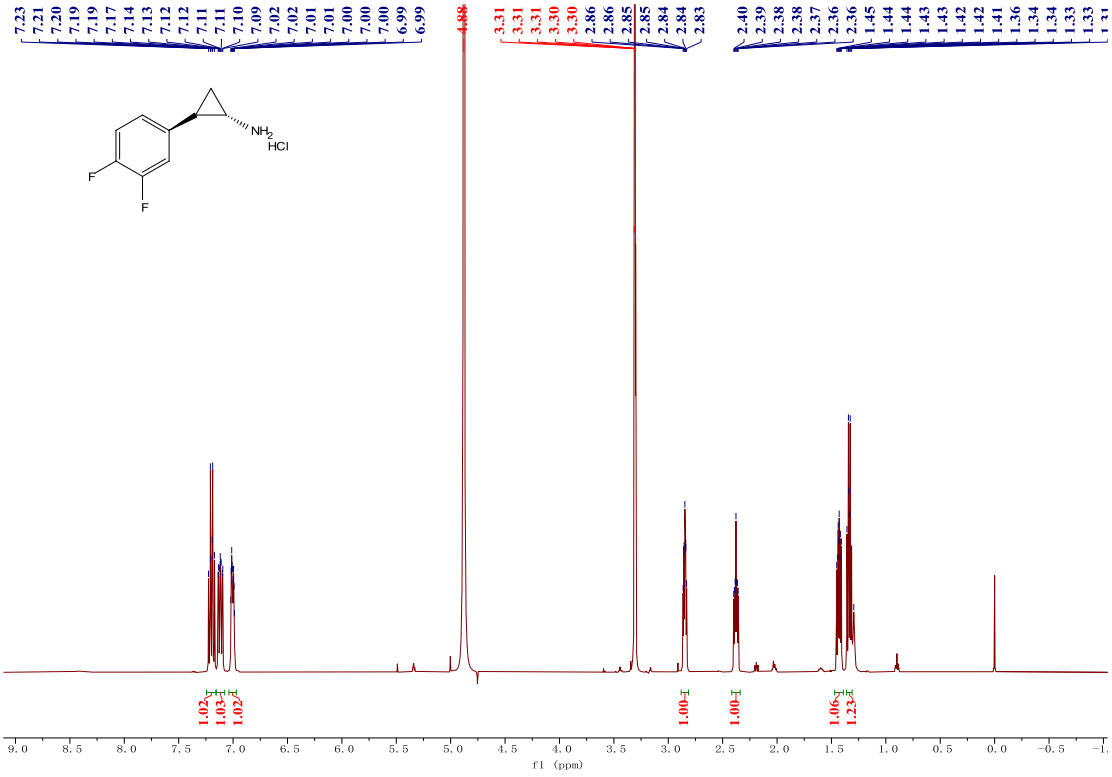
^{13}C NMR spectrum of **11c** in $CDCl_3$



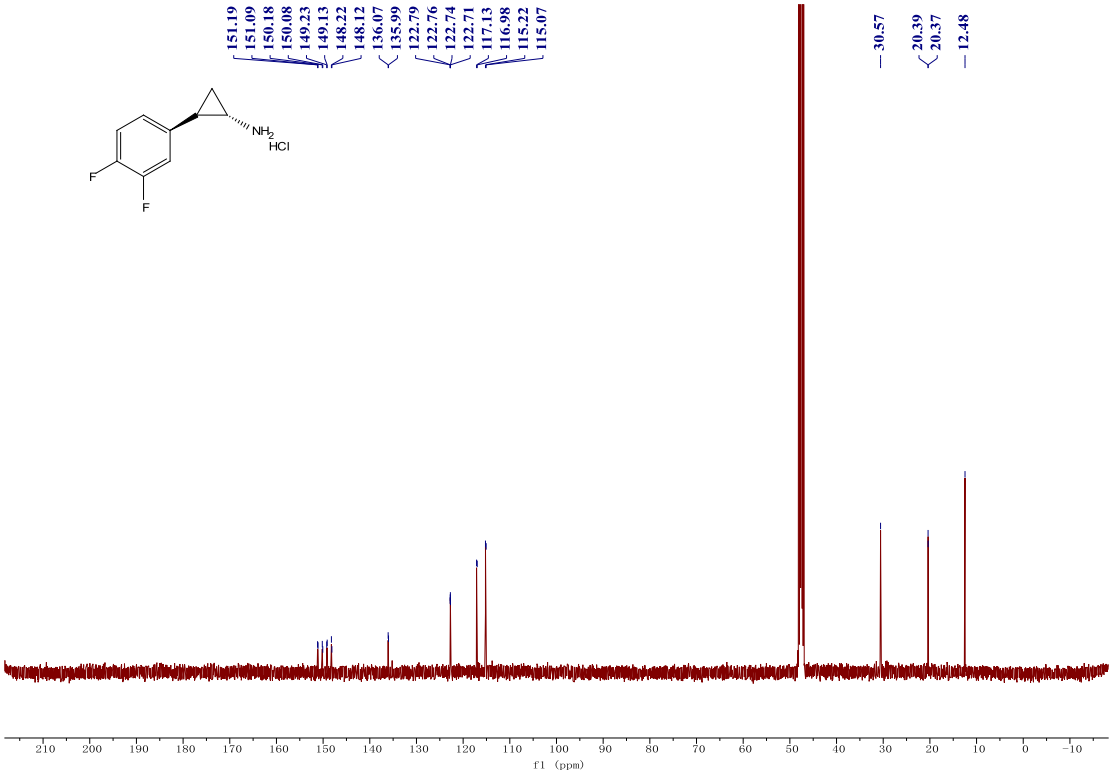
^{19}F NMR spectrum of **11c** in $CDCl_3$



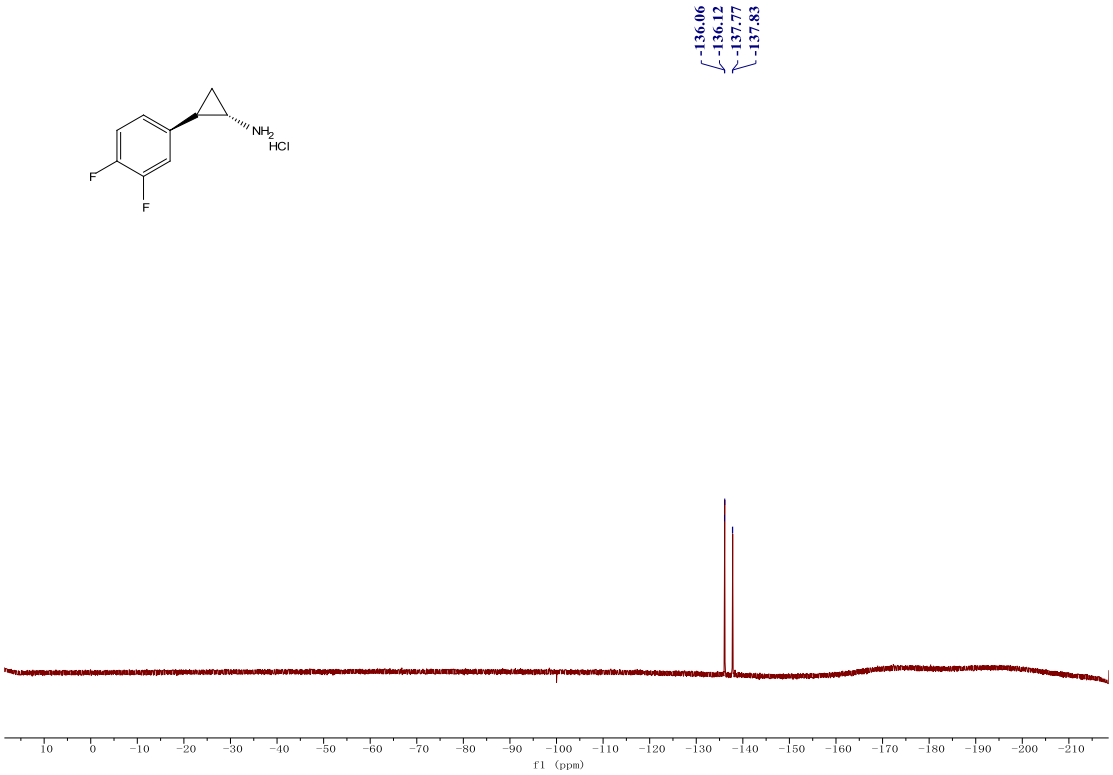
^{1}H NMR spectrum of **14** in CD_3OD



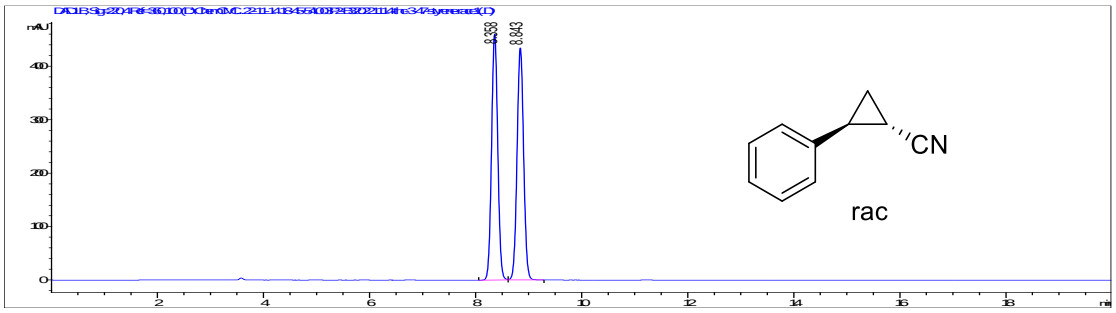
^{13}C NMR spectrum of **14** in CD_3OD



^{19}F NMR spectrum of **14** in CD_3OD

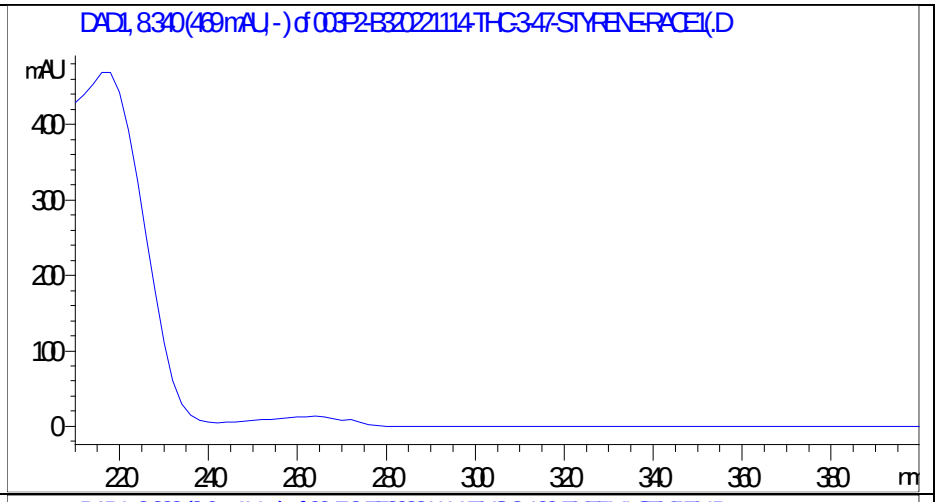
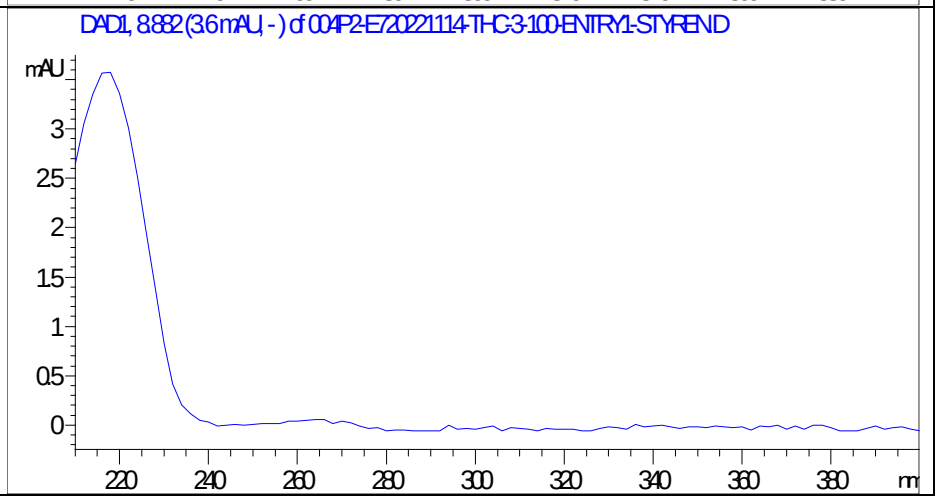


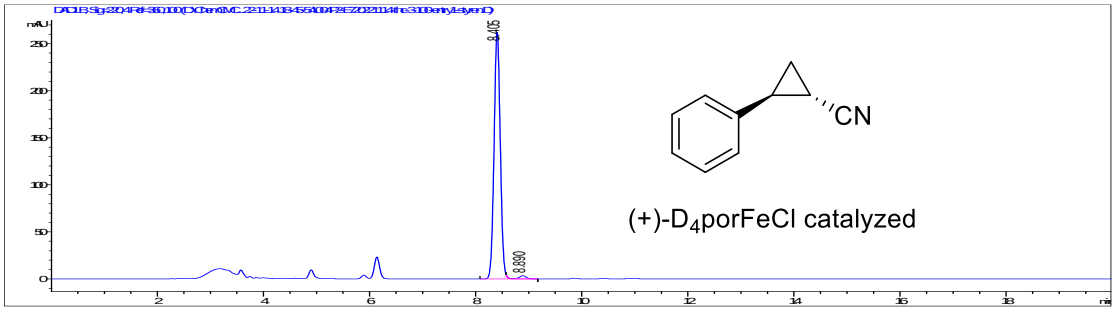
10 HPLC Spectra



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.358	BV	0.1268	3738.18262	460.26599	49.9722
2	8.843	VB	0.1324	3742.33691	434.73175	50.0278

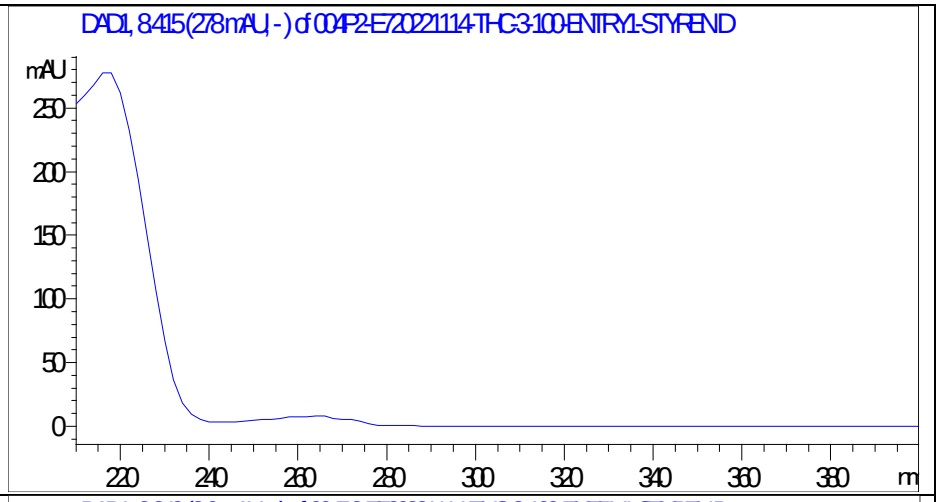
UV spectrum of the peak at 8.340 min.	
UV spectrum of the peak at 8.882 min.	



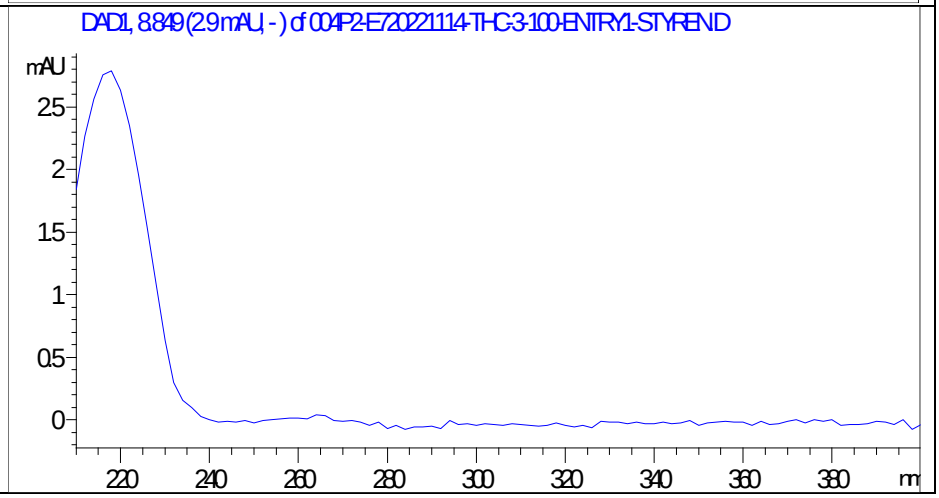
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

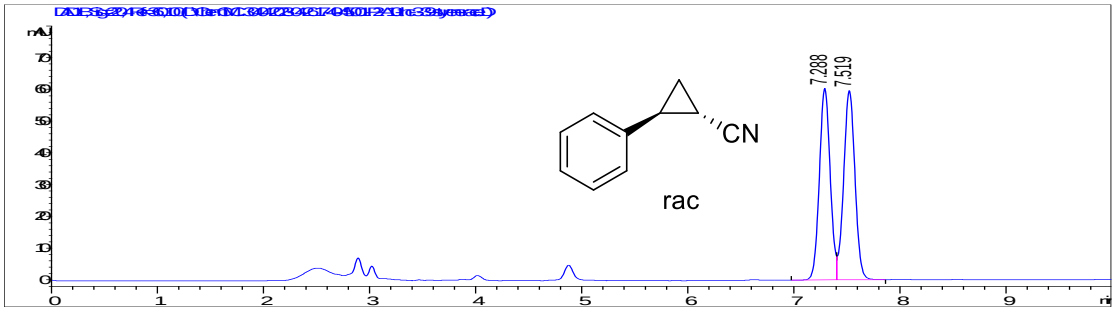
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.405	BV R	0.1271	2138.83667	262.50372	98.4865
2	8.890	VB E	0.1464	32.86850	3.35196	1.5135

UV spectrum of the peak at 8.415 min.



UV spectrum of the peak at 8.849 min.

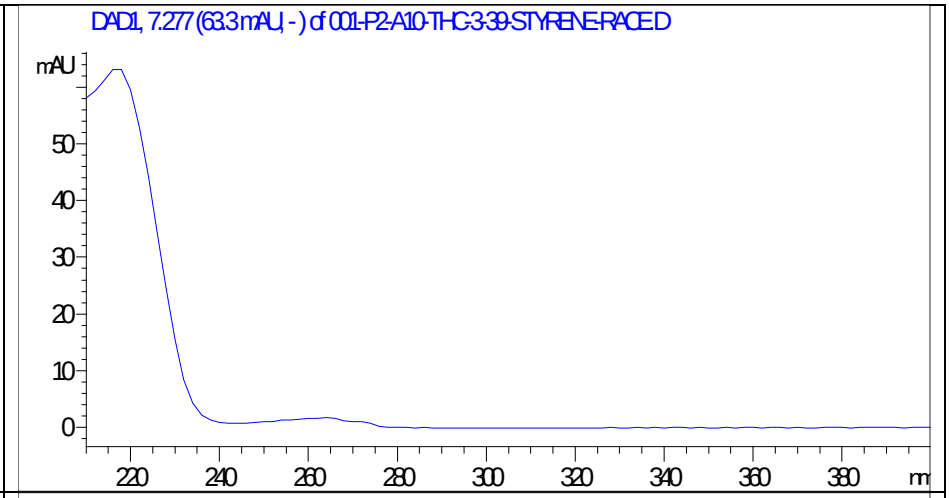




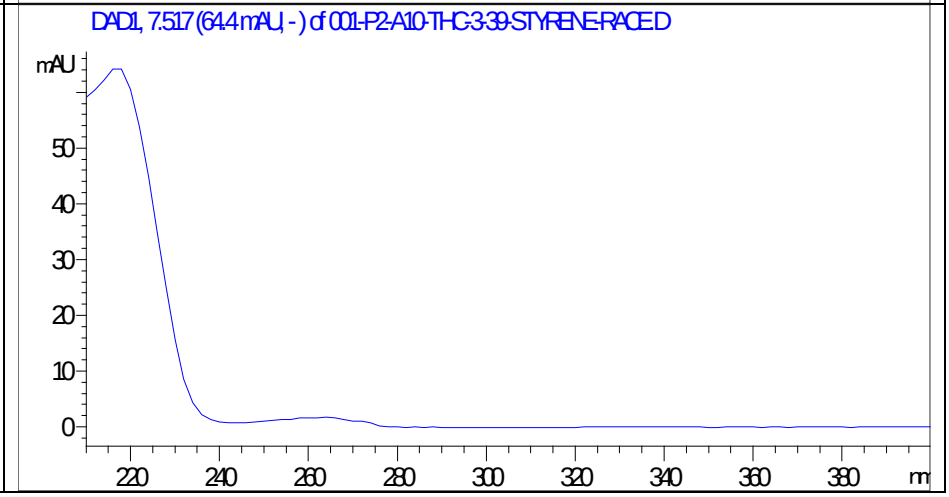
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

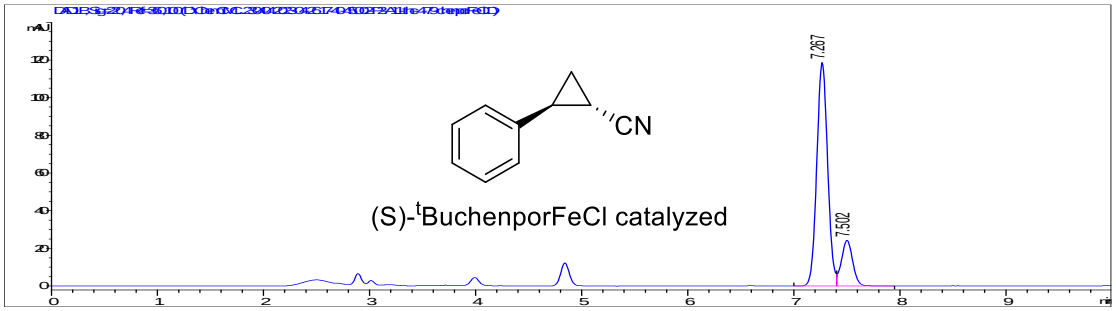
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.288	BV	0.1108	428.09802	60.32639	49.3285
2	7.519	VB	0.1140	439.75351	59.63026	50.6715
Totals :				867.85153	119.95665	

UV spectrum of the peak at 7.277 min.



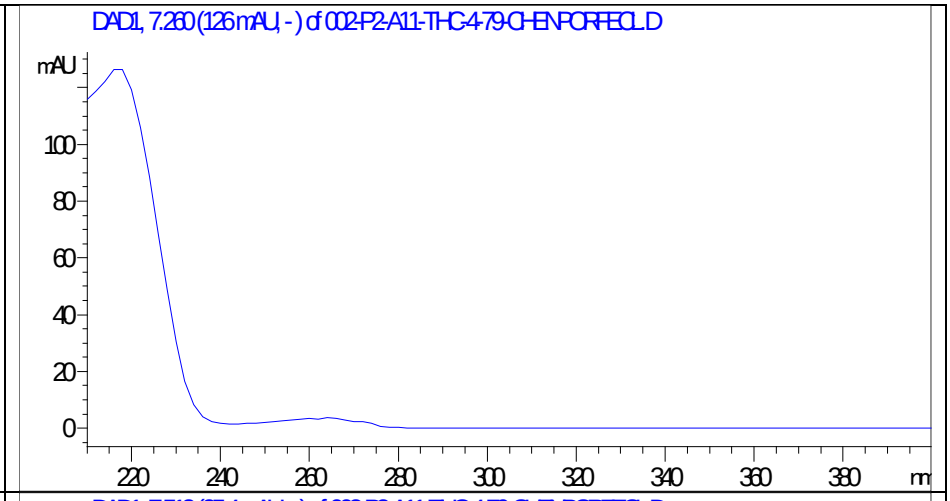
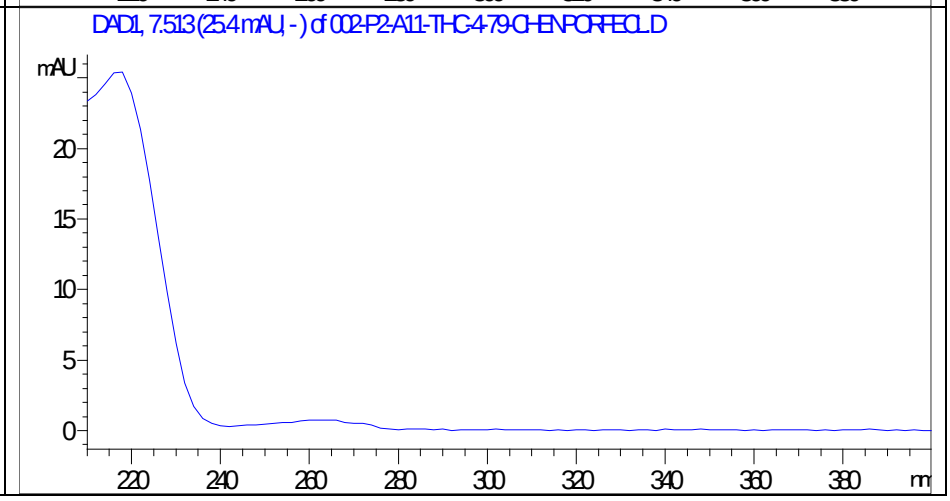
UV spectrum of the peak at 7.517 min.

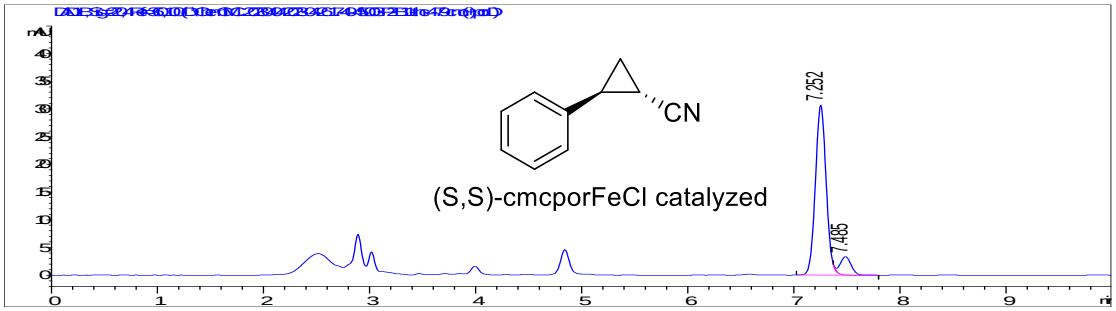




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

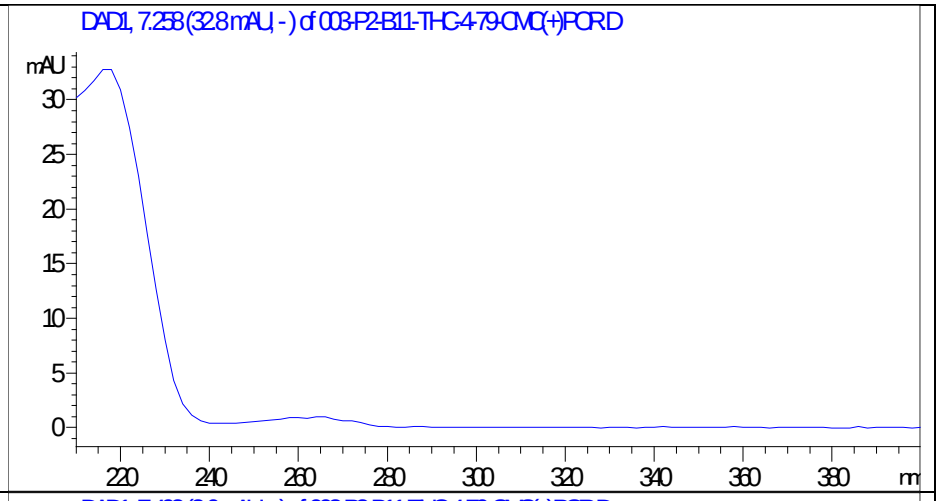
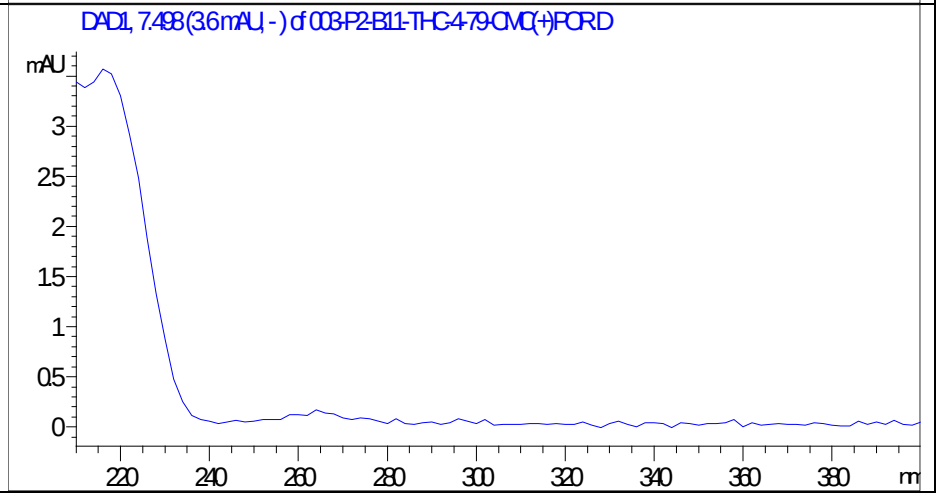
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.267	BV	0.1090	843.73010	118.55739	82.5258
2	7.502	VB	0.1141	178.65297	24.21816	17.4742
Totals :				1022.38307	142.77555	

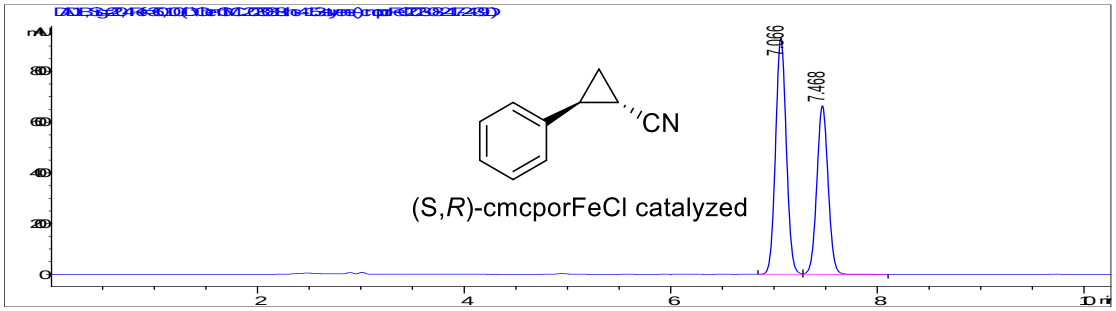
UV spectrum of the peak at 7.260 min.	
UV spectrum of the peak at 7.513 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

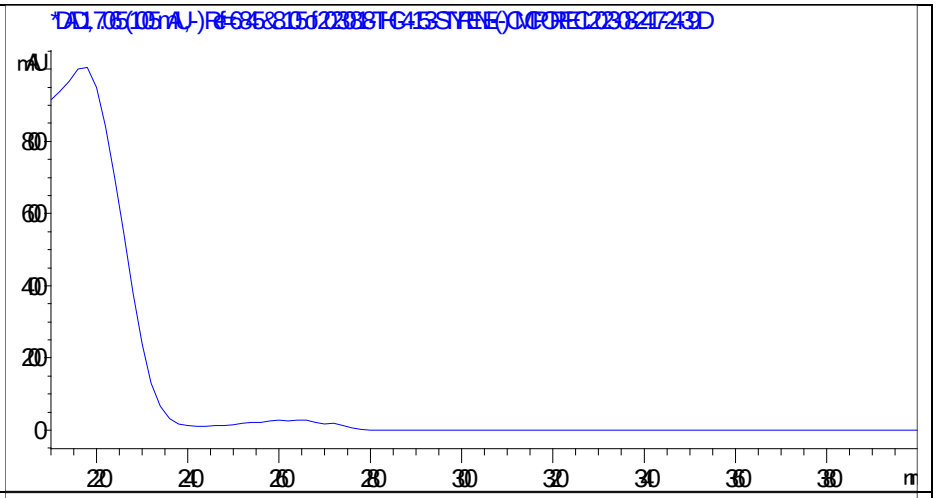
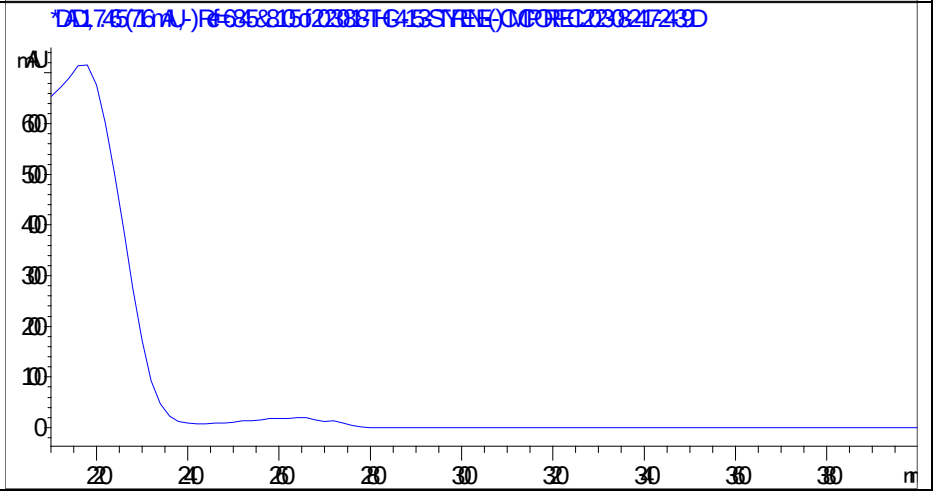
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.252	BV R	0.1092	218.77281	30.68597	90.3355
2	7.485	VB E	0.1109	23.40534	3.29465	9.6645
Totals :				242.17815	33.98062	

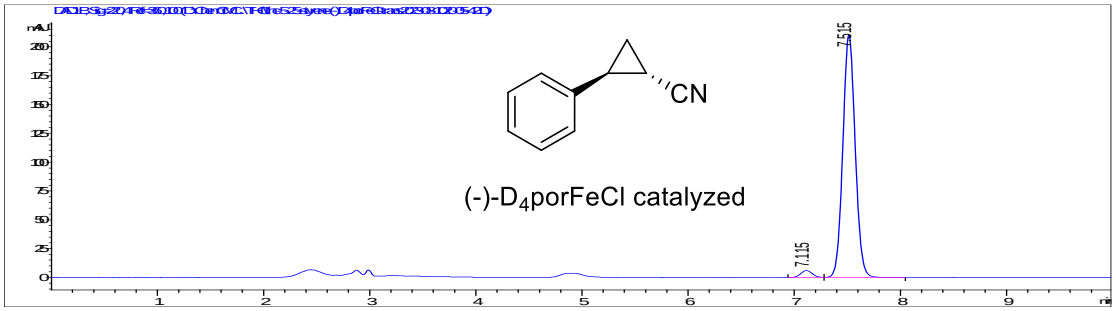
UV spectrum of the peak at 7.258 min.	
UV spectrum of the peak at 7.498 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

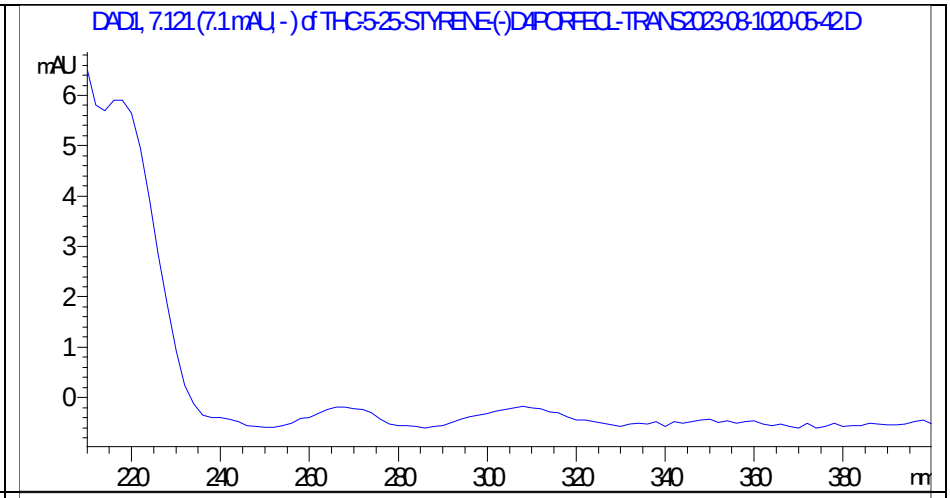
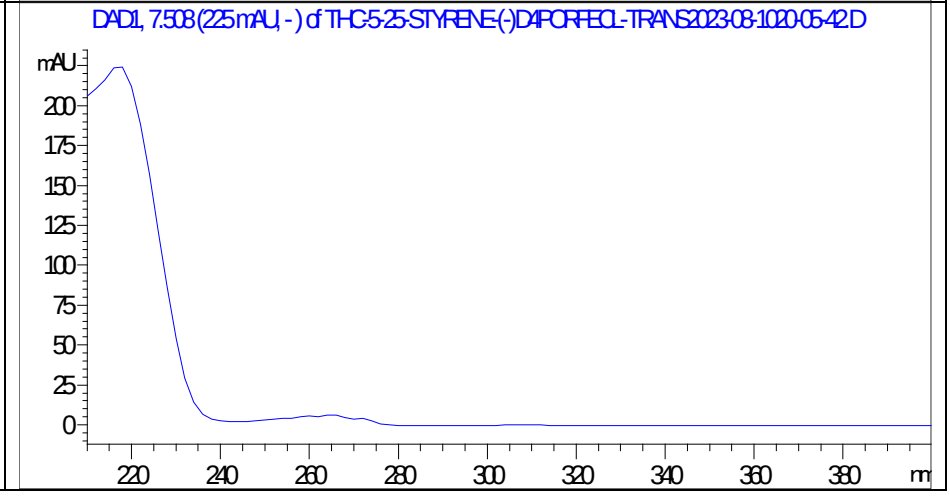
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.066	BV	0.1122	6735.76709	932.75519	57.1676
2	7.468	VB	0.1165	5046.71436	665.38782	42.8324
Totals :				1.17825e4	1598.14301	

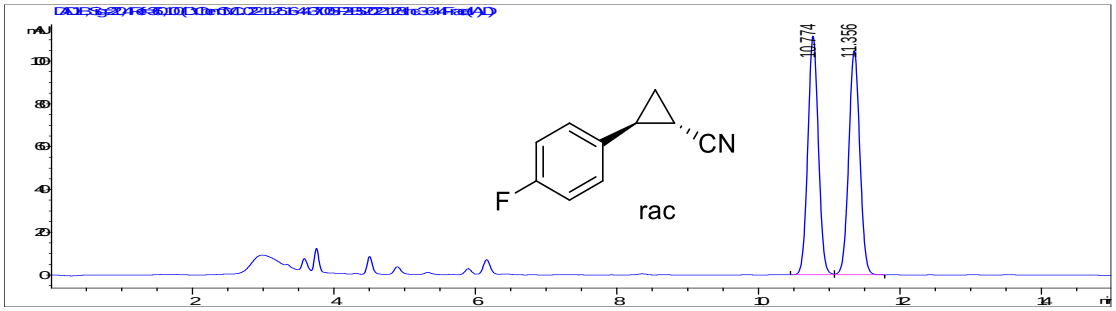
UV spectrum of the peak at 7.258 min.	
UV spectrum of the peak at 7.498 min.	



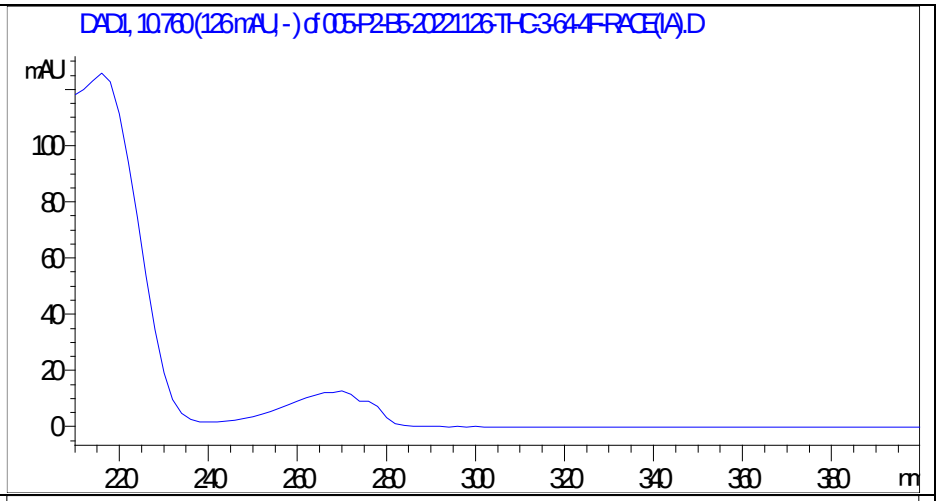
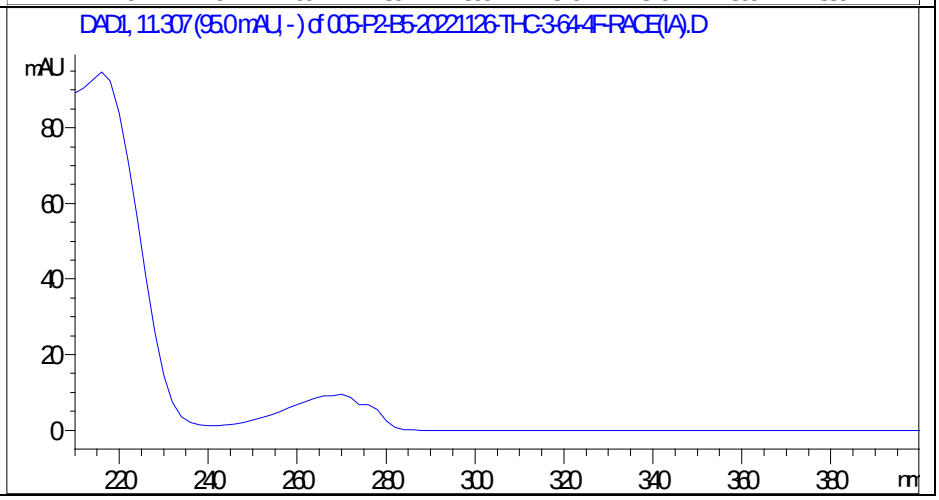
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

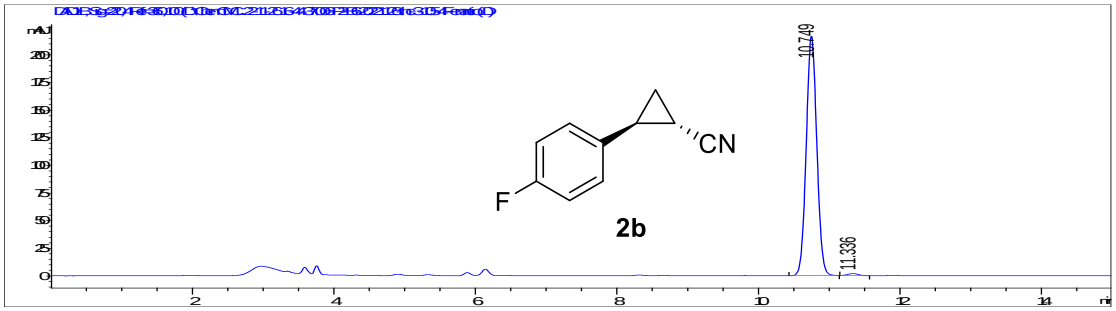
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.115	BV	0.1183	46.00865	6.07749	2.6219
2	7.515	VB	0.1245	1708.79126	210.87675	97.3781
Totals :				1754.79991	216.95425	

UV spectrum of the peak at 7.121 min.	
UV spectrum of the peak at 7.515 min.	



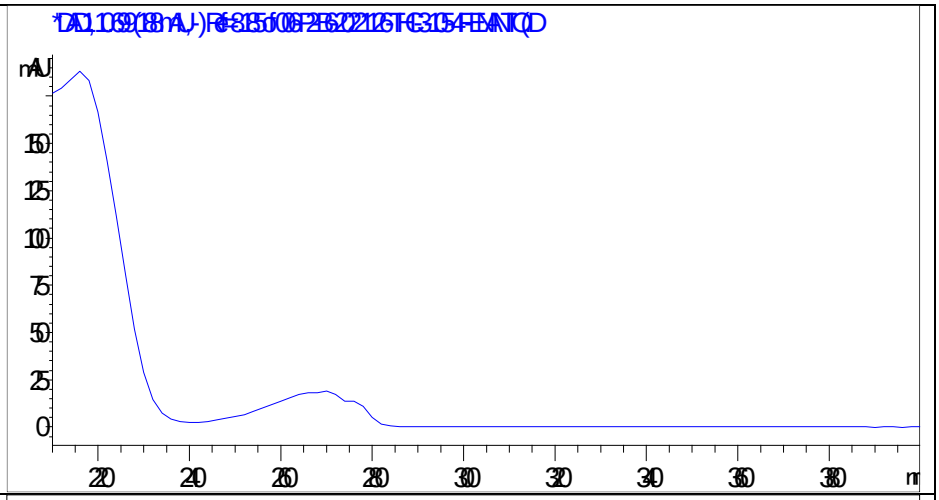
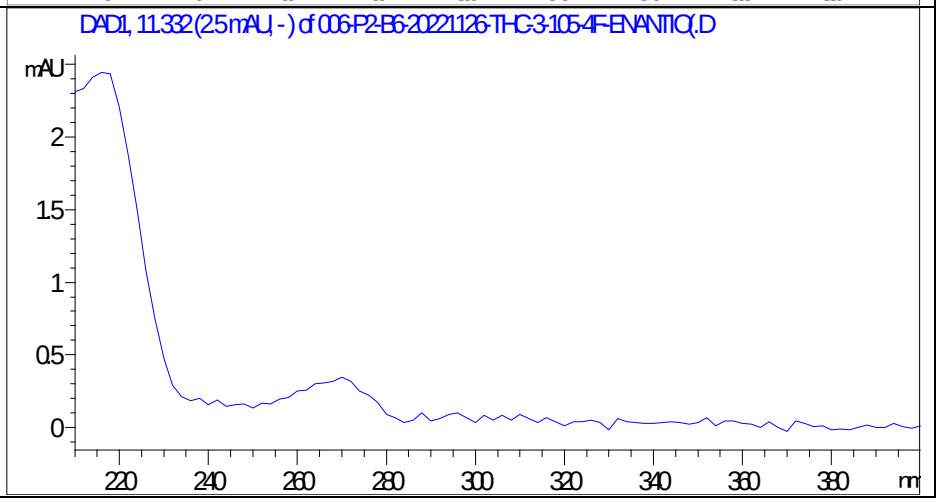
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.774	BV	0.1630	1156.28296	111.52898	50.3171
2	11.356	VB	0.1692	1141.71021	104.74861	49.6829

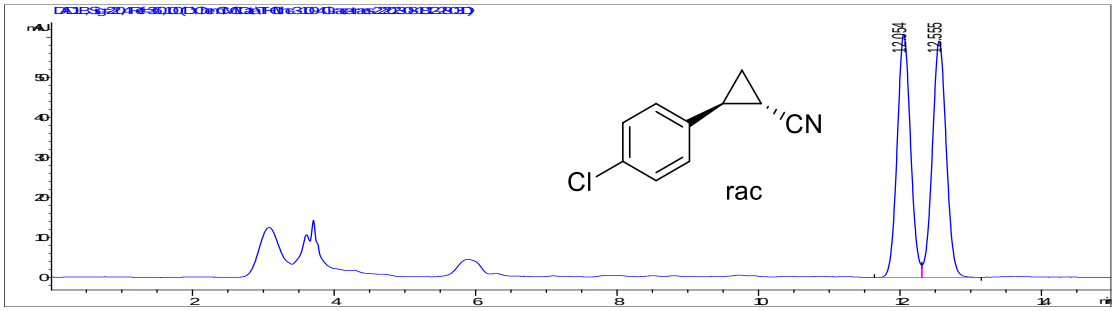
UV spectrum of the peak at 10.760 min.	
UV spectrum of the peak at 11.307 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

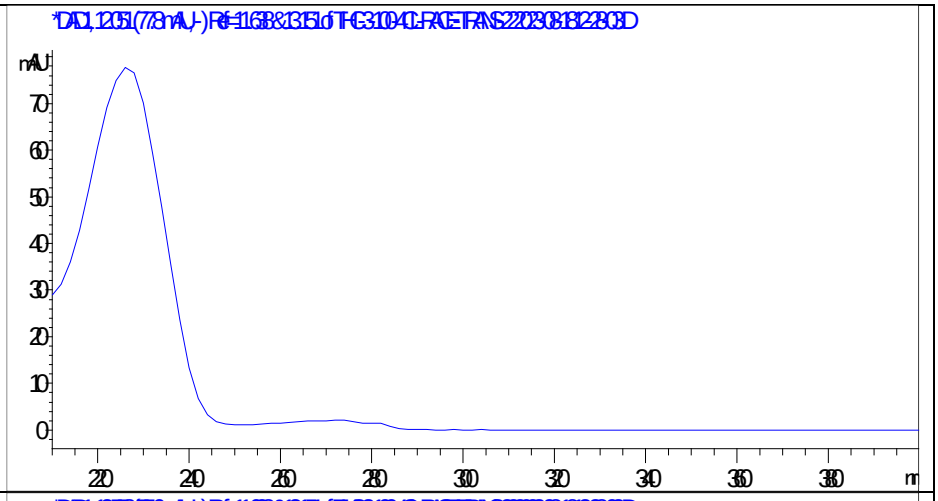
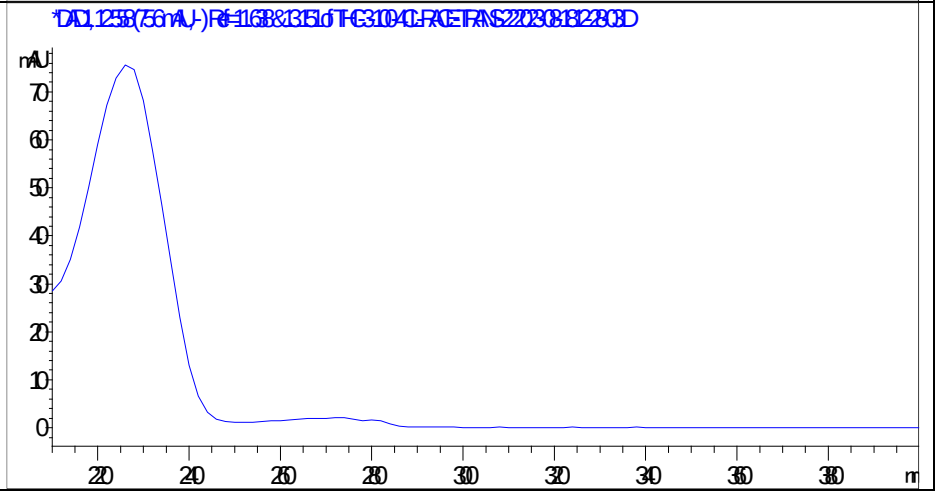
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.749	BB	0.1611	2249.52563	216.78615	99.1958
2	11.336	BB	0.1629	18.23635	1.78959	0.8042

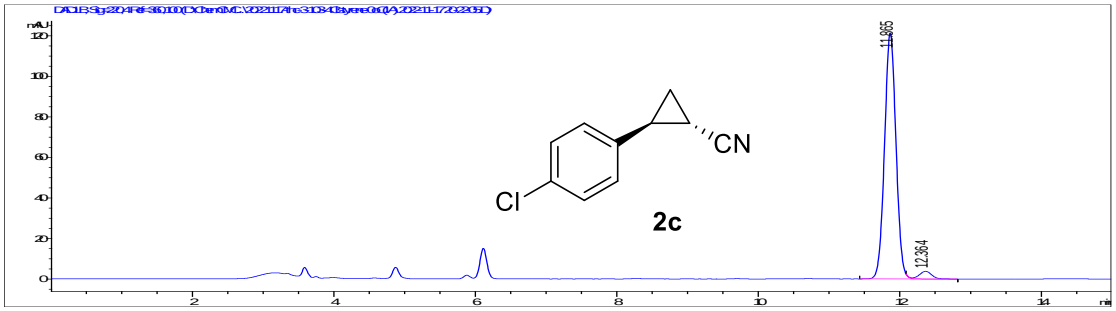
UV spectrum of the peak at 10.699 min.	
UV spectrum of the peak at 11.332 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

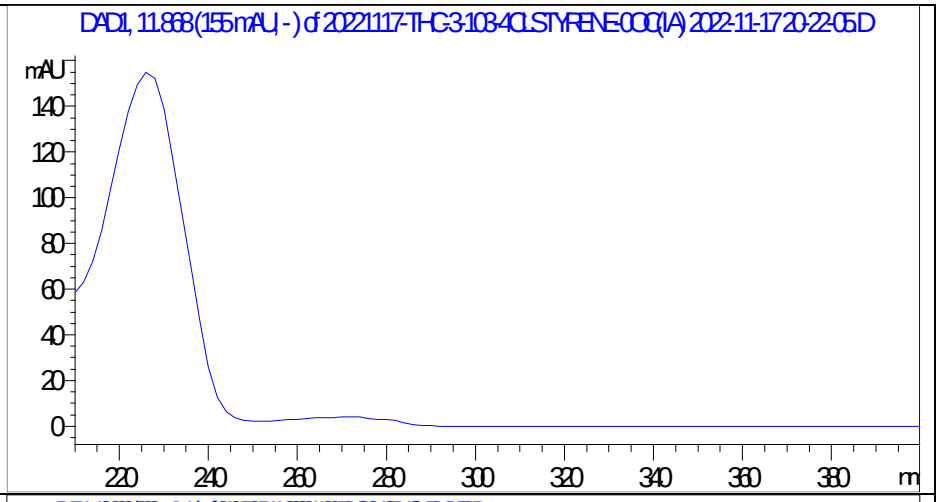
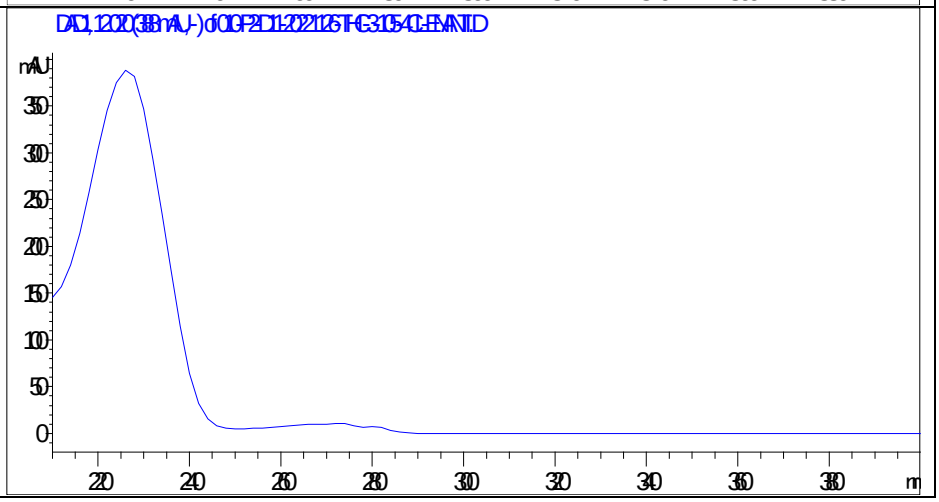
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.054	BV	0.2054	799.13135	60.78931	49.7701
2	12.555	VB	0.2112	806.51440	59.10039	50.2299
Totals :				1605.64575	119.88970	

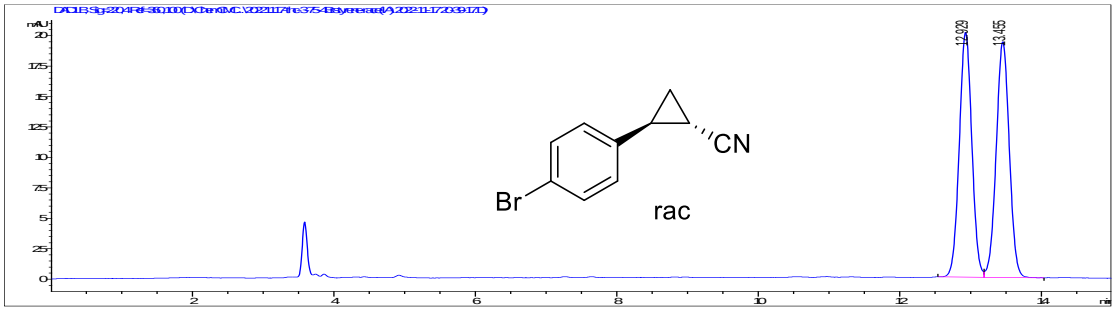
UV spectrum of the peak at 12.051 min.	
UV spectrum of the peak at 12.558 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

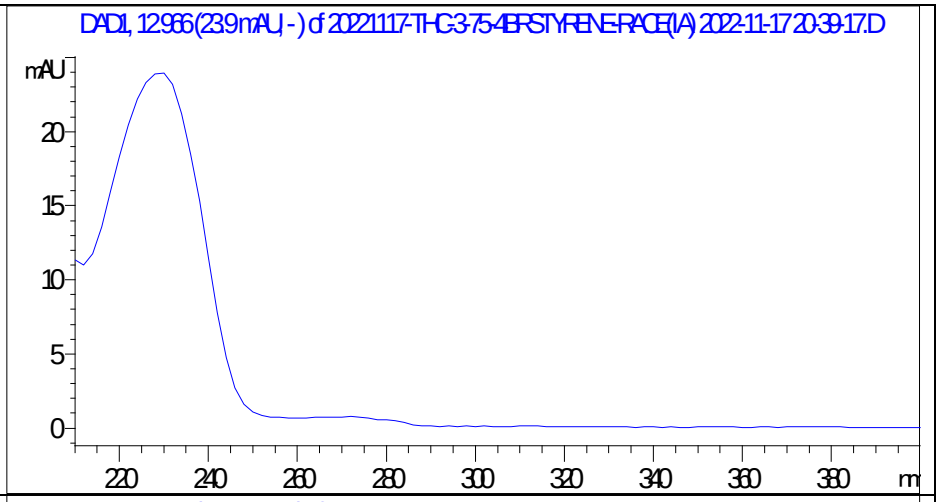
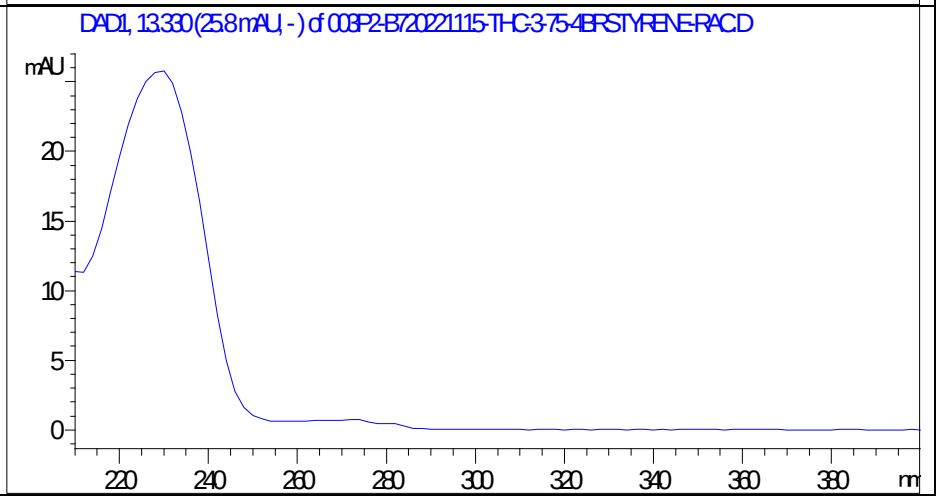
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.865	BV R	0.1752	1364.97131	121.40476	96.7389
2	12.364	VB E	0.1865	46.01299	3.76718	3.2611

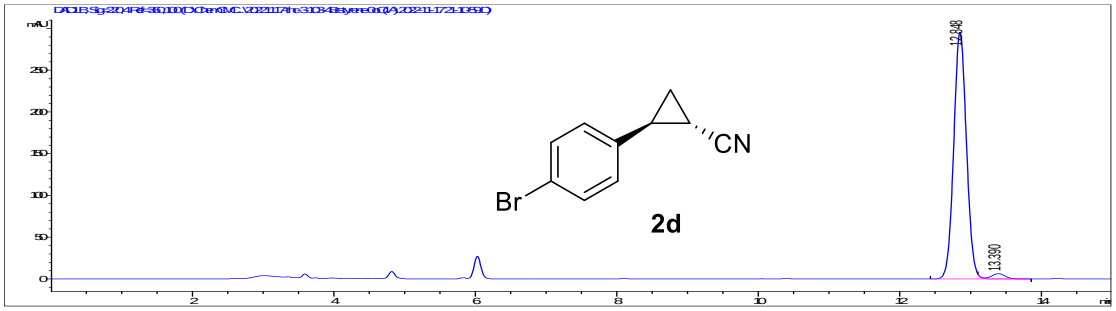
UV spectrum of the peak at 11.868 min.	
UV spectrum of the peak at 12.020 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.929	BV	0.1917	247.64742	20.10974	49.8365
2	13.455	VB	0.1982	249.27260	19.36331	50.1635

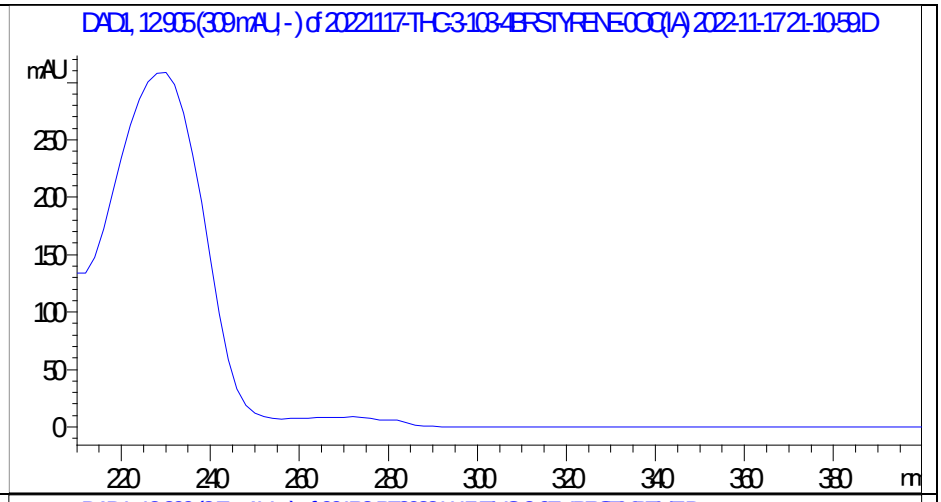
UV spectrum of the peak at 12.966 min.	
UV spectrum of the peak at 13.330 min.	



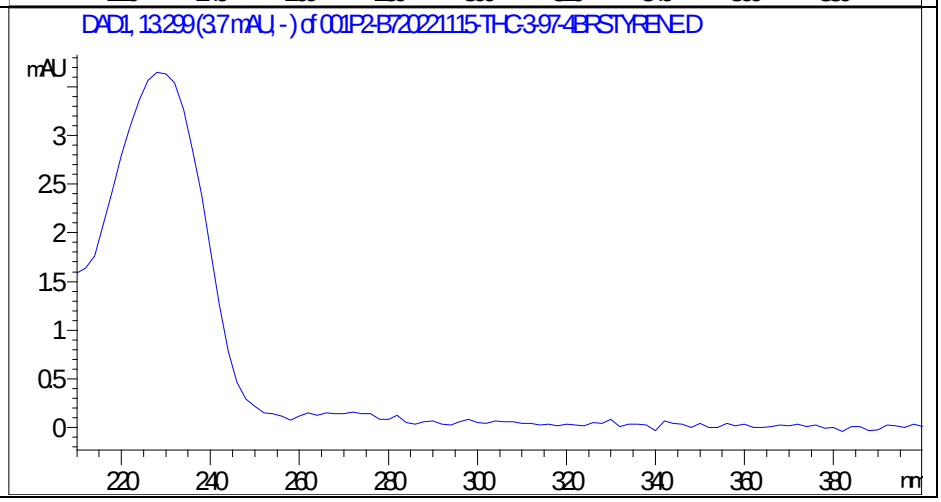
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

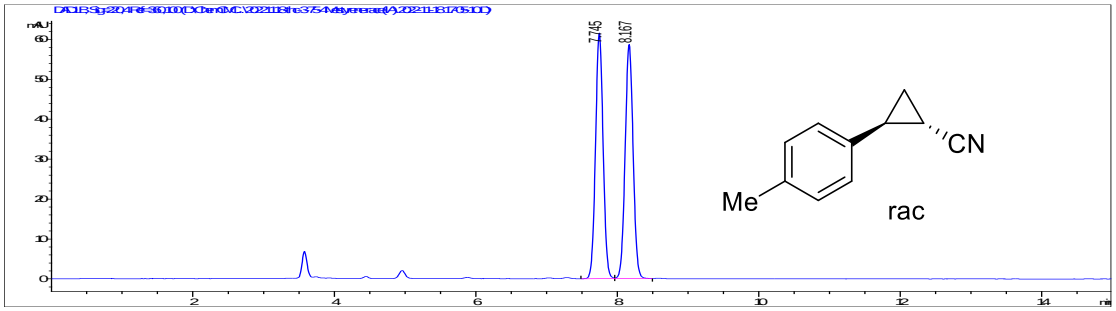
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.848	BV R	0.1940	3699.18579	295.65503	97.7488
2	13.390	VB E	0.2047	85.19280	6.34462	2.2512

UV spectrum of the peak at 12.905 min.



UV spectrum of the peak at 13.299 min.

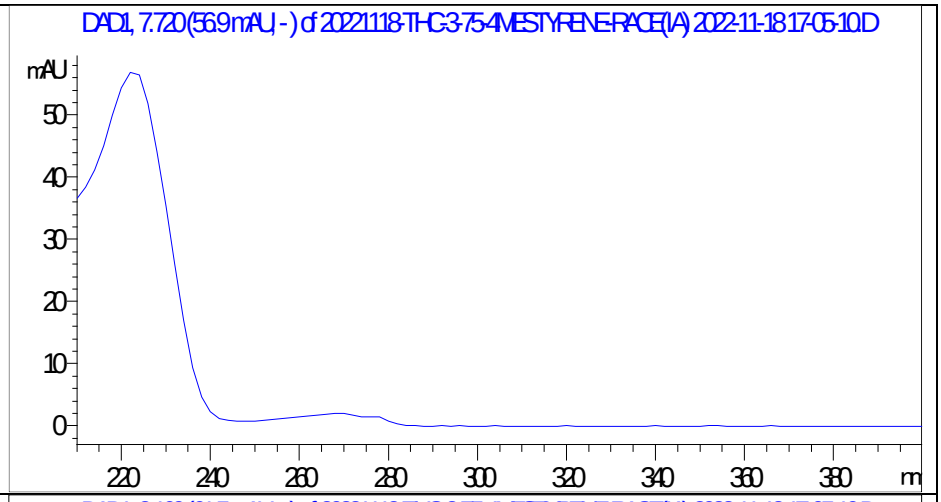




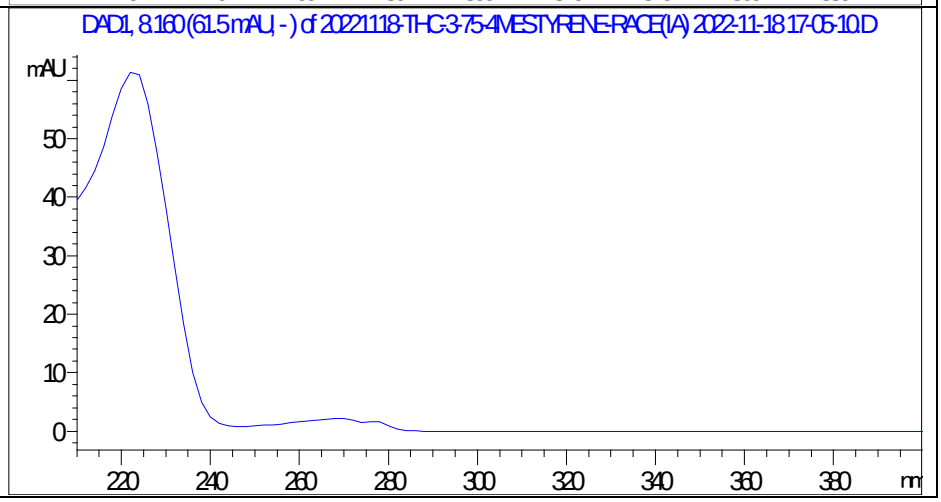
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

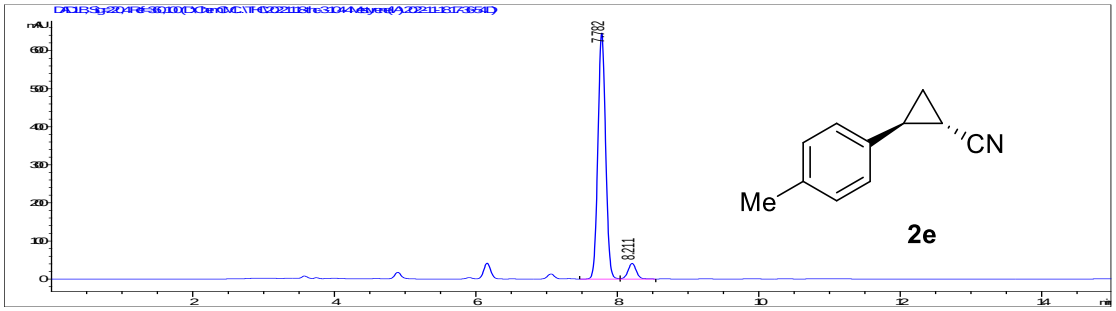
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.745	BV	0.1148	458.16516	61.58786	49.9986
2	8.167	VB	0.1212	458.19089	58.61942	50.0014

UV spectrum of the peak at 7.72 min.



UV spectrum of the peak at 8.160 min.

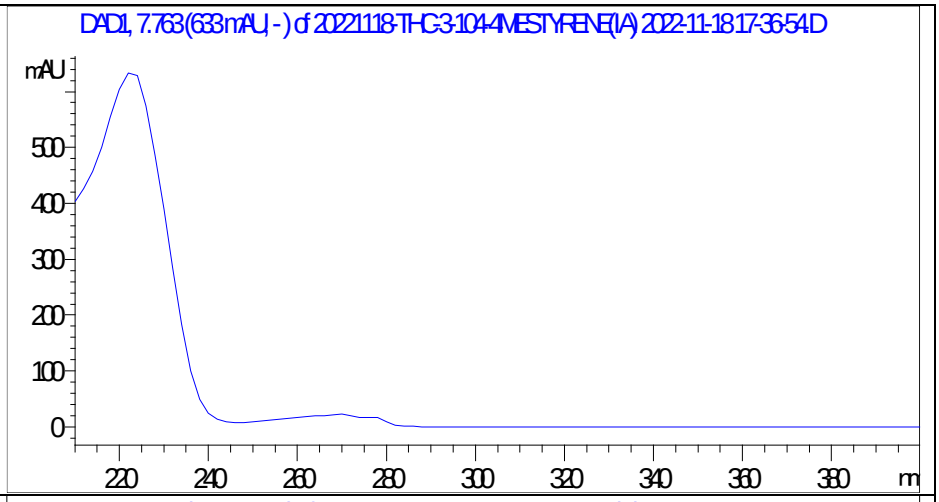




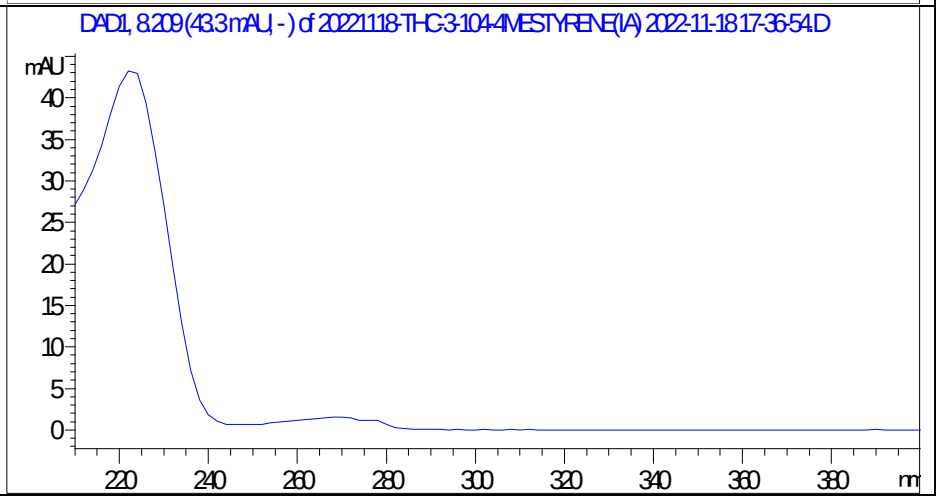
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

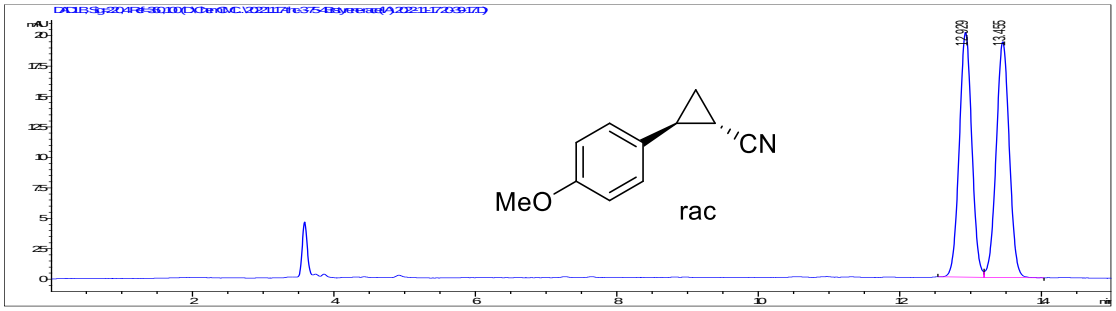
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.782	BV	0.1180	4873.56152	646.07538	93.6428
2	8.211	VB	0.1264	330.85565	40.90814	6.3572

UV spectrum of the peak at 7.763 min.



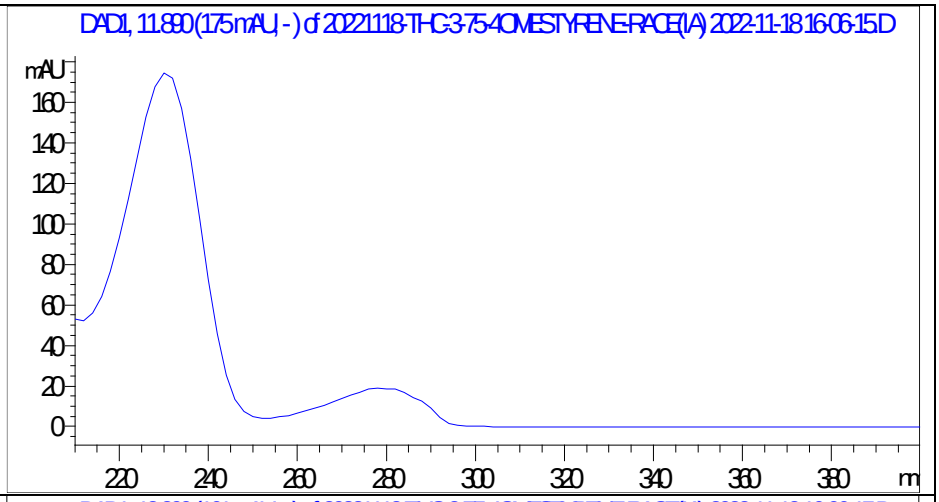
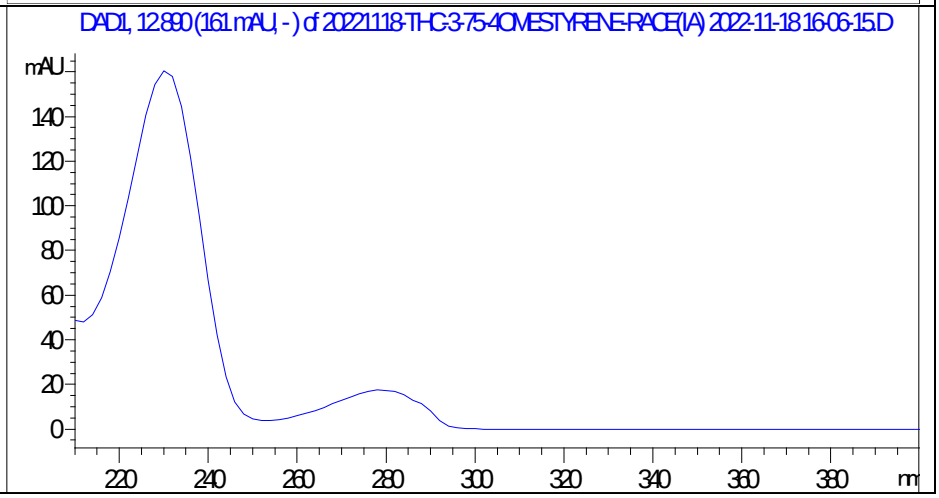
UV spectrum of the peak at 8.209 min.

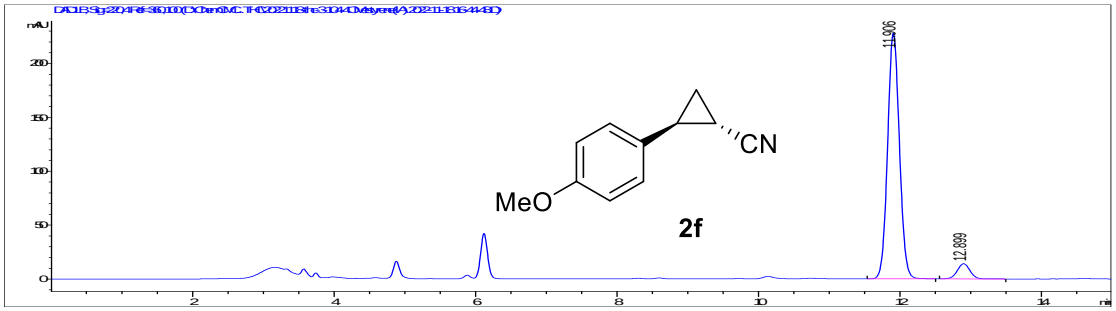




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.898	BB	0.1782	1092.20374	94.97186	50.1159
2	12.883	BB	0.1932	1087.15002	87.32882	49.8841

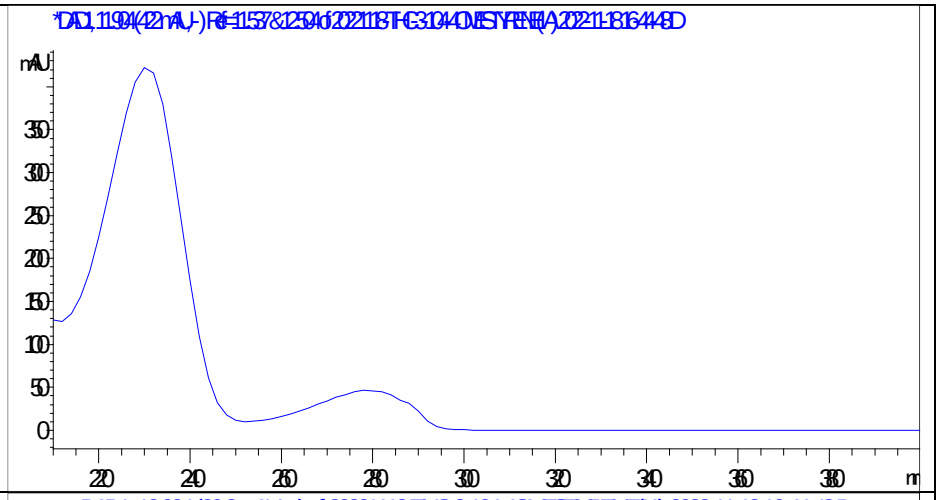
UV spectrum of the peak at 11.890 min.	
UV spectrum of the peak at 12.890 min.	



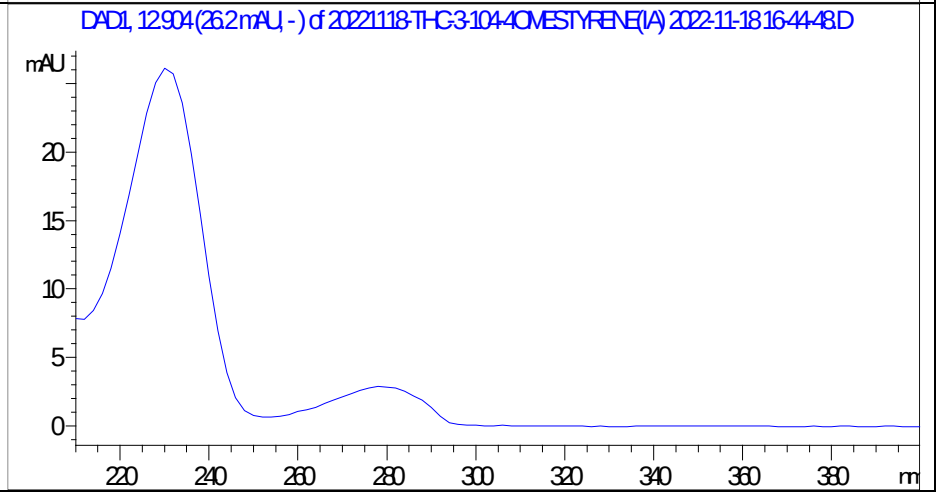
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

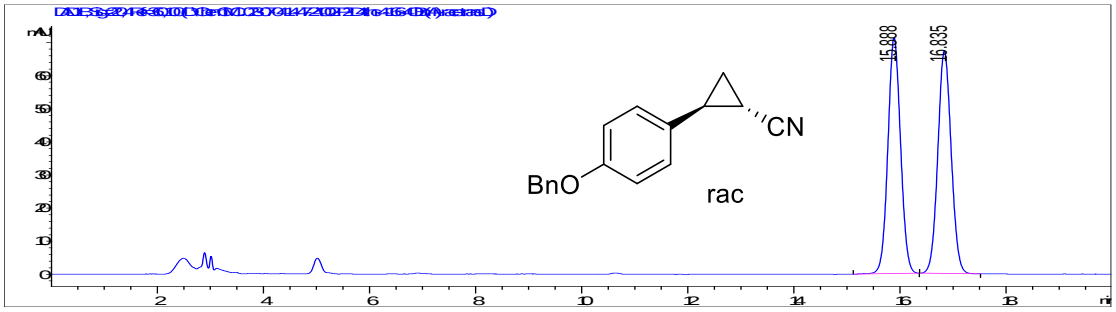
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.906	BB	0.1789	2638.82642	228.16277	93.7862
2	12.899	BB	0.1930	174.83577	14.06879	6.2138

UV spectrum of the peak at 11.904 min.



UV spectrum of the peak at 12.904 min.

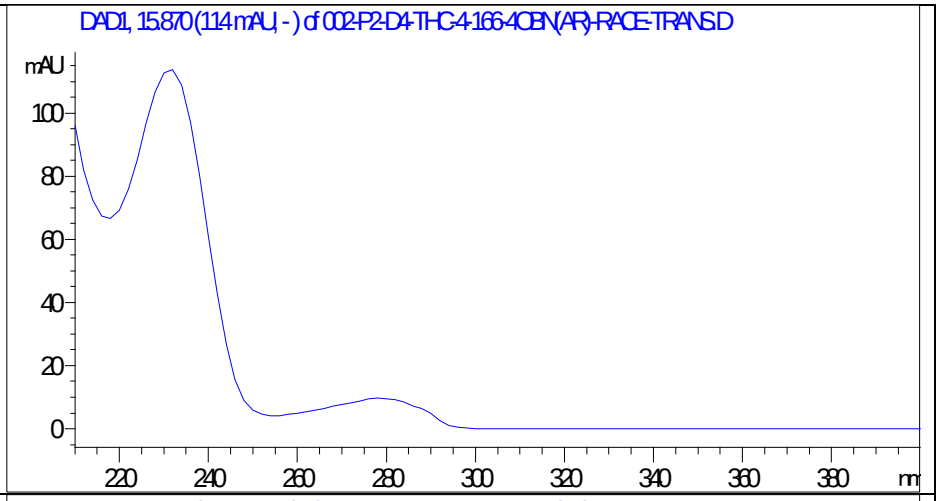




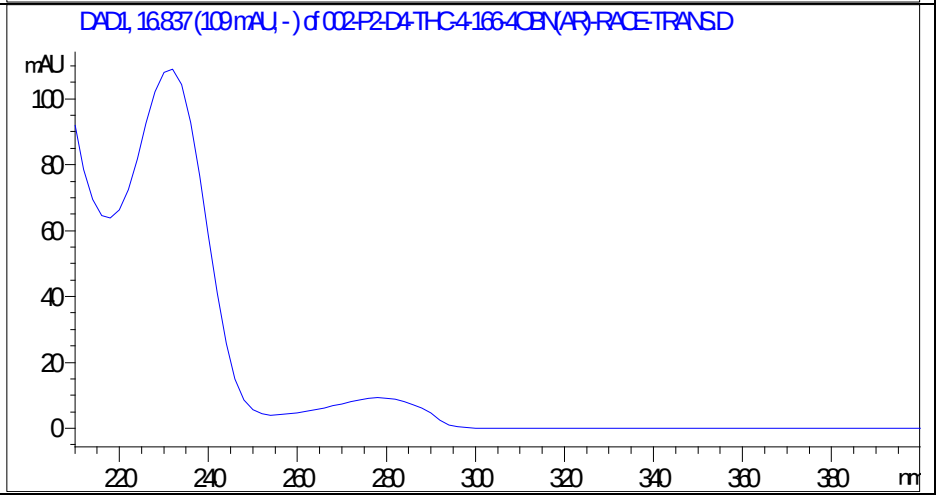
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

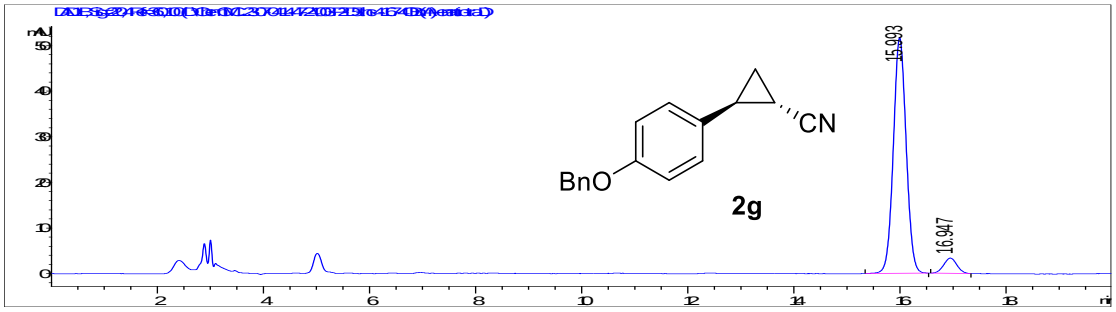
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.888	BB	0.2578	1183.47192	71.23291	50.0959
2	16.835	BB	0.2726	1178.93958	67.21091	49.9041
Totals :				2362.41150	138.44382	

UV spectrum of the peak at 15.870 min.



UV spectrum of the peak at 16.837 min.

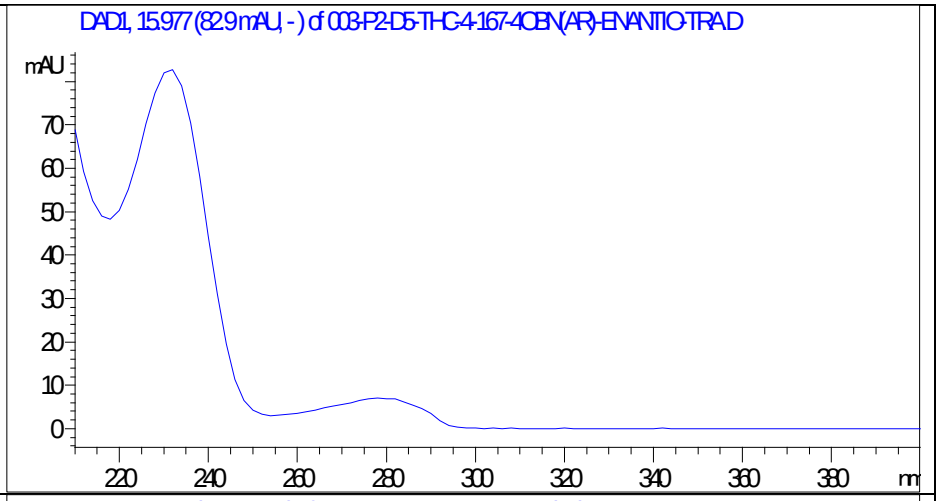




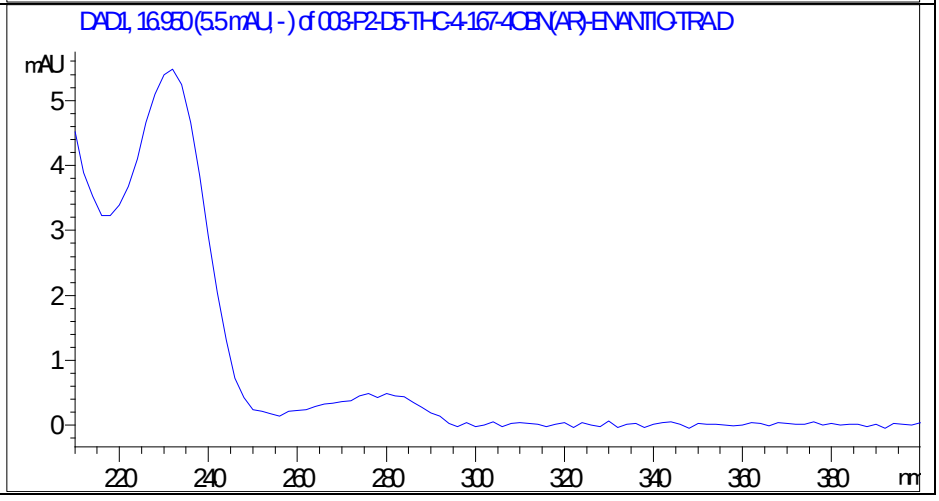
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

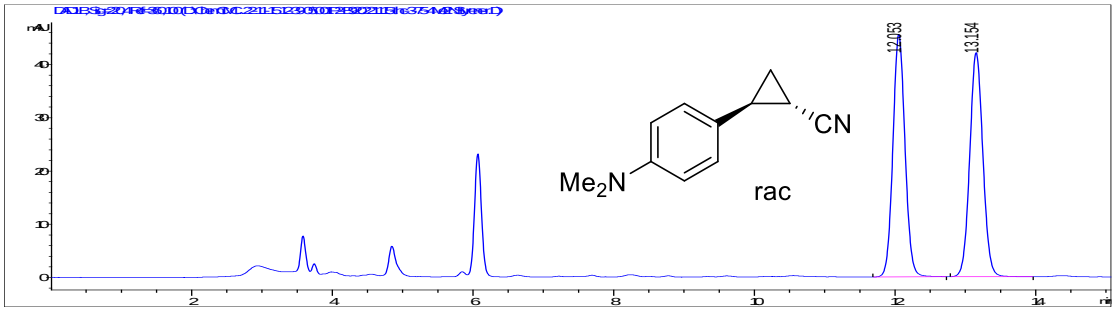
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.993	BB	0.2601	868.77472	51.69202	93.7621
2	16.947	BB	0.2668	57.79848	3.35882	6.2379
Totals :				926.57320	55.05084	

UV spectrum of the peak at 15.977 min.



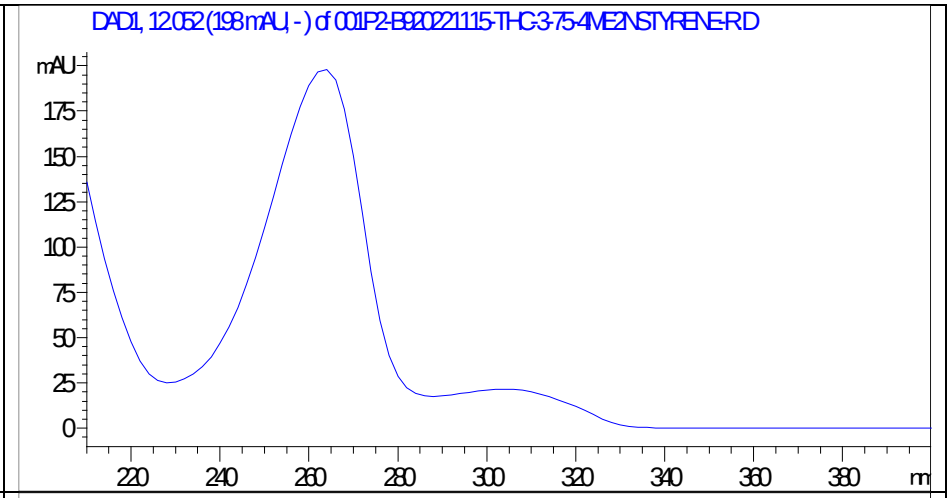
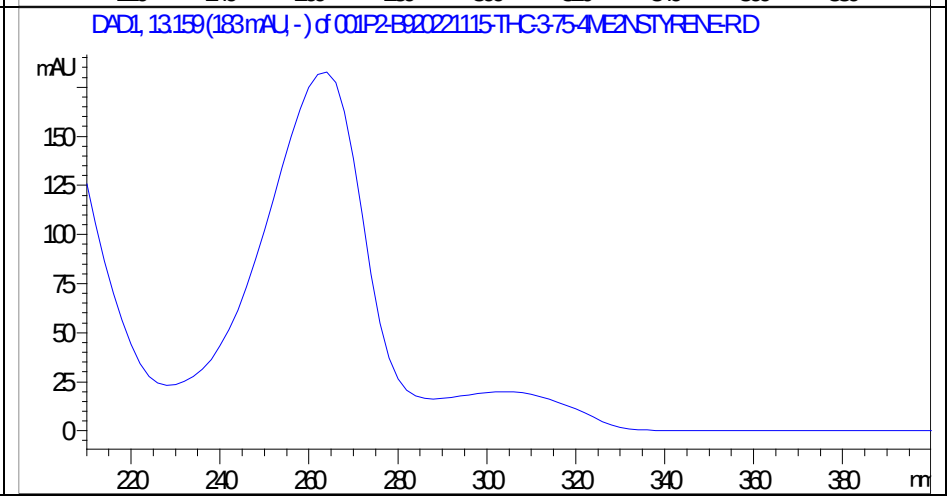
UV spectrum of the peak at 16.950 min.

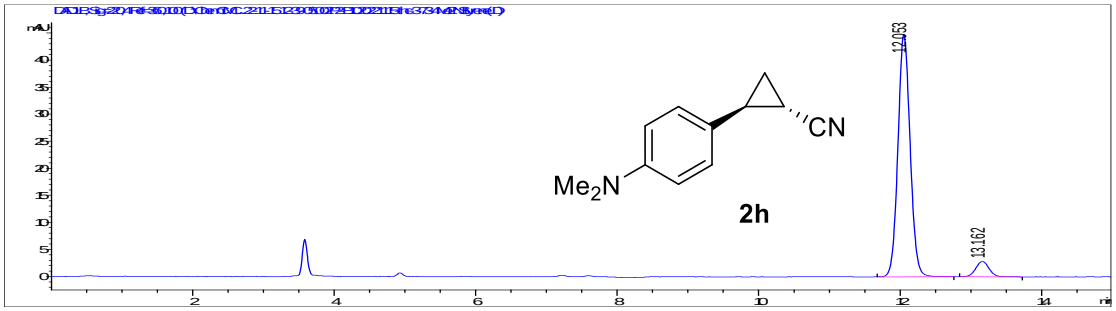




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.053	BB	0.1859	545.90417	45.53460	50.0171
2	13.154	BB	0.2013	545.53186	42.06537	49.9829
Totals :				1091.43604	87.59996	

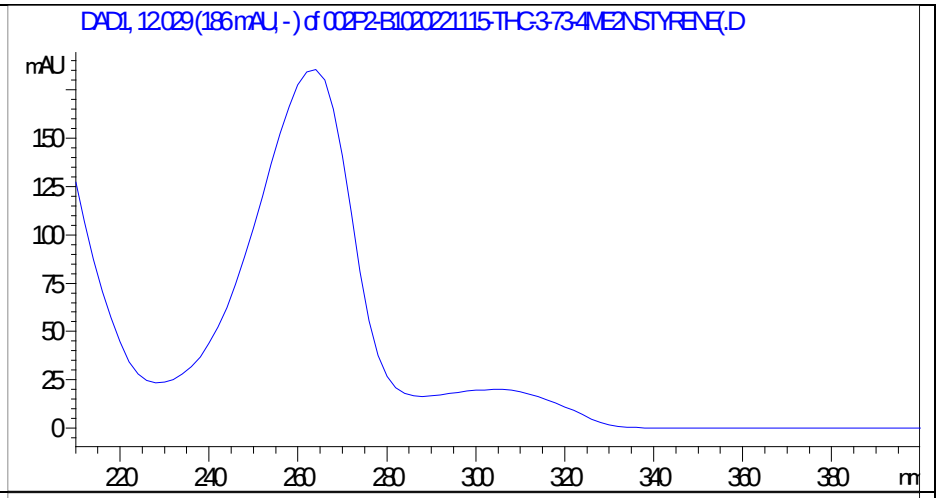
UV spectrum of the peak at 12.052 min.	
7UV spectrum of the peak at 13.159 min.	



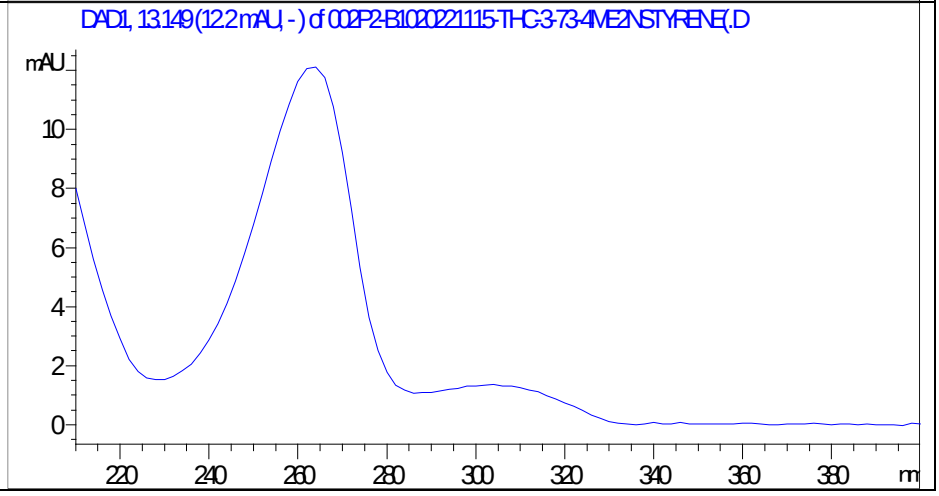
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

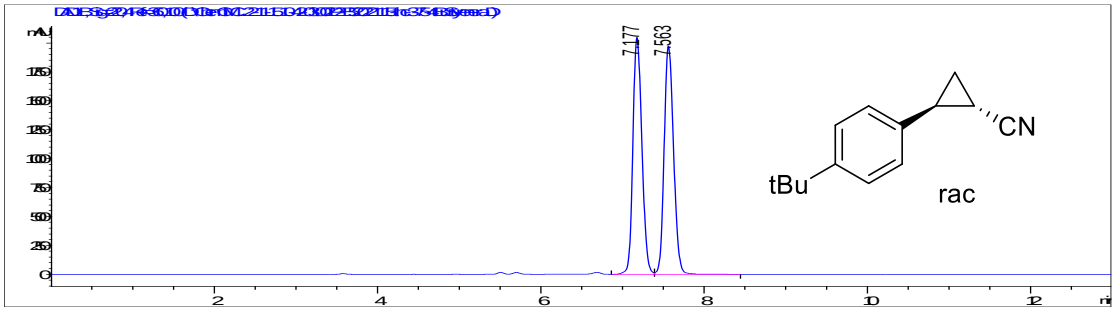
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.053	BB	0.1858	537.00049	44.82771	93.5647
2	13.162	BB	0.2021	36.93428	2.83232	6.4353
Totals :				573.93477	47.66003	

UV spectrum of the peak at 12.029 min.



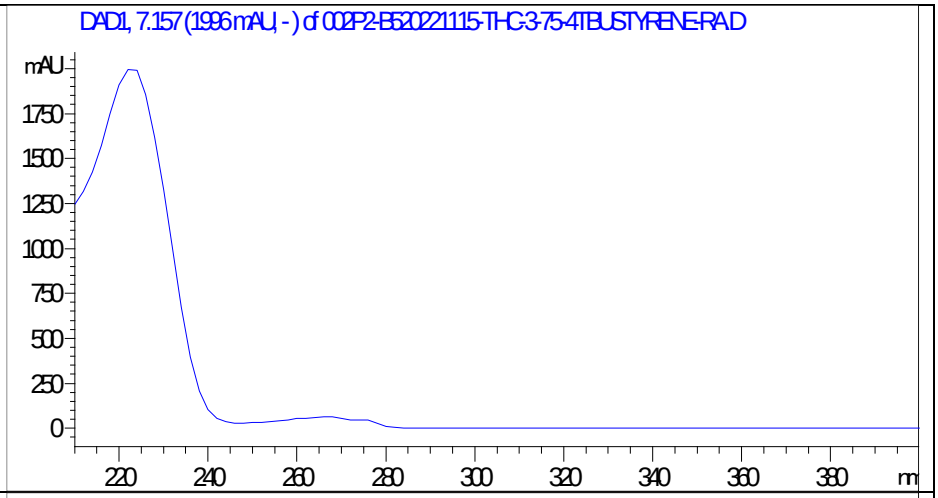
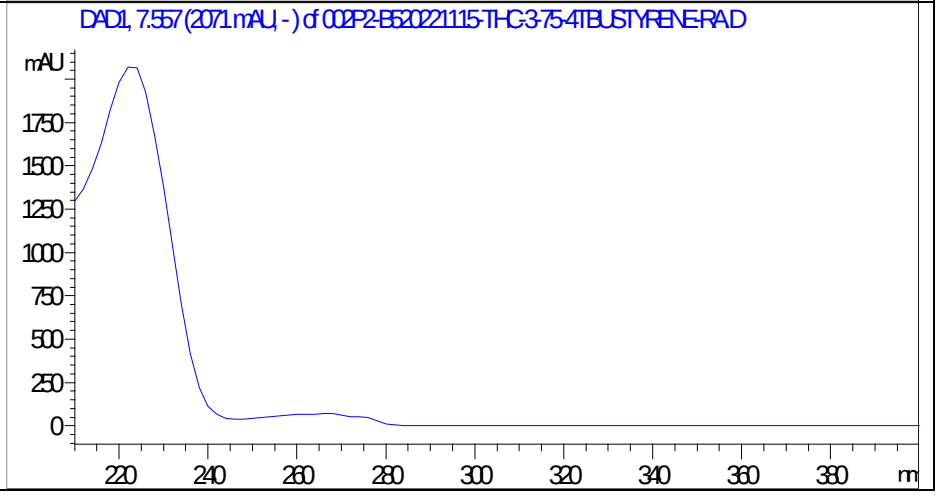
UV spectrum of the peak at 13.149 min.

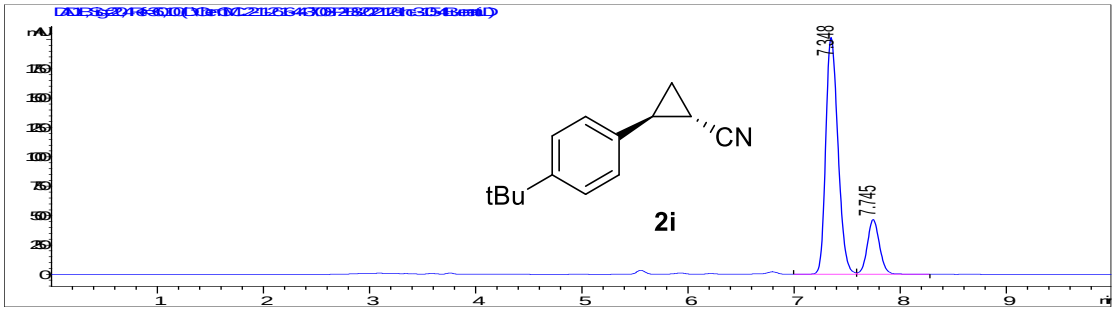




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

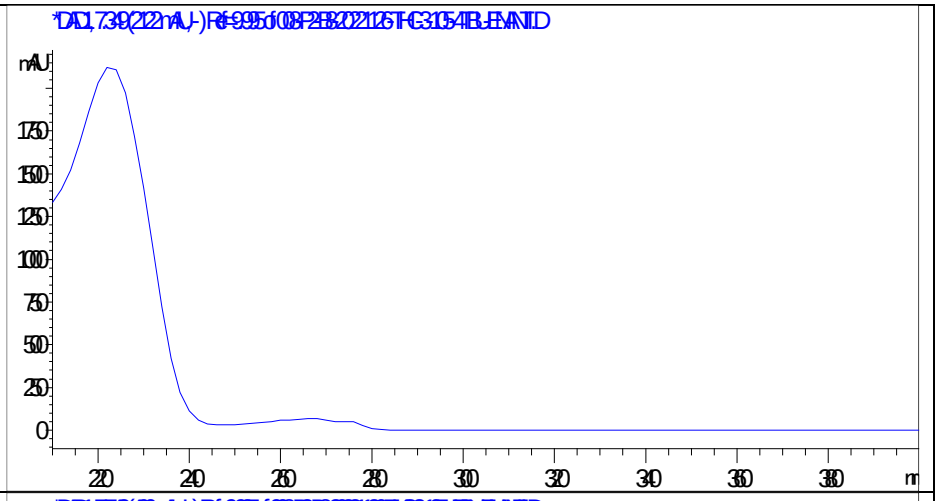
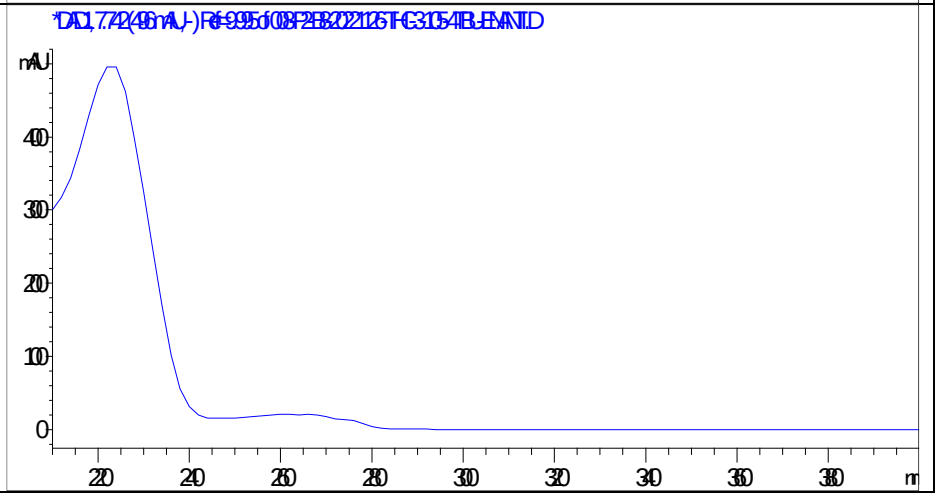
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.177	BV	0.1217	1.57375e4	2045.77515	49.7779
2	7.563	VB	0.1258	1.58779e4	1973.96167	50.2221
Totals :				3.16155e4	4019.73682	

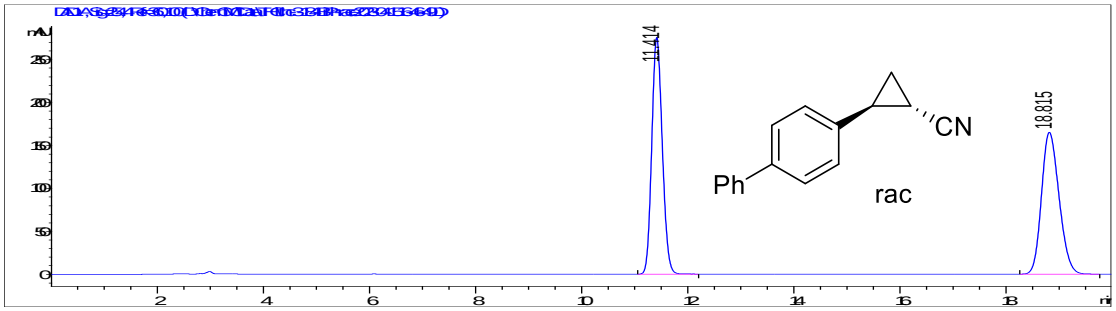
UV spectrum of the peak at 7.157 min.	
UV spectrum of the peak at 7.557 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.348	BV	0.1258	1.61877e4	2014.08997	81.1857
2	7.745	VB	0.1256	3751.38818	467.62555	18.8143
Totals :				1.99391e4	2481.71552	

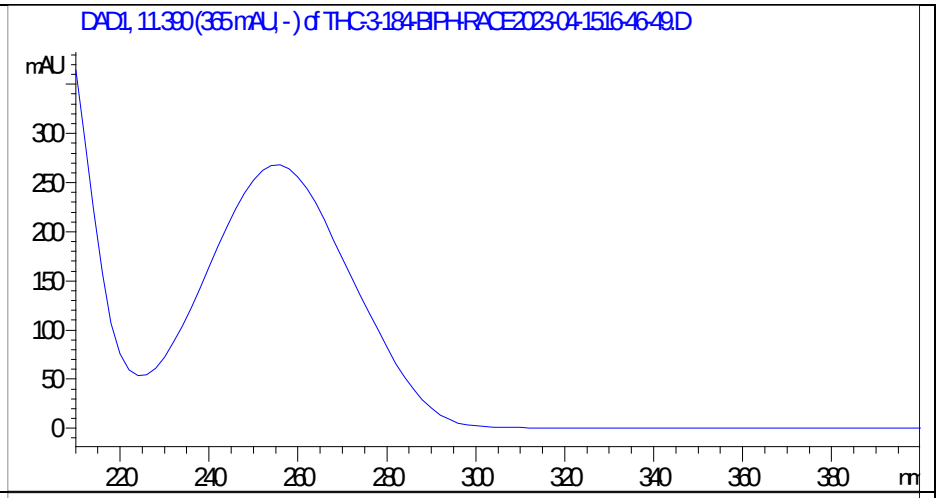
UV spectrum of the peak at 7.349 min.	
UV spectrum of the peak at 7.742 min.	



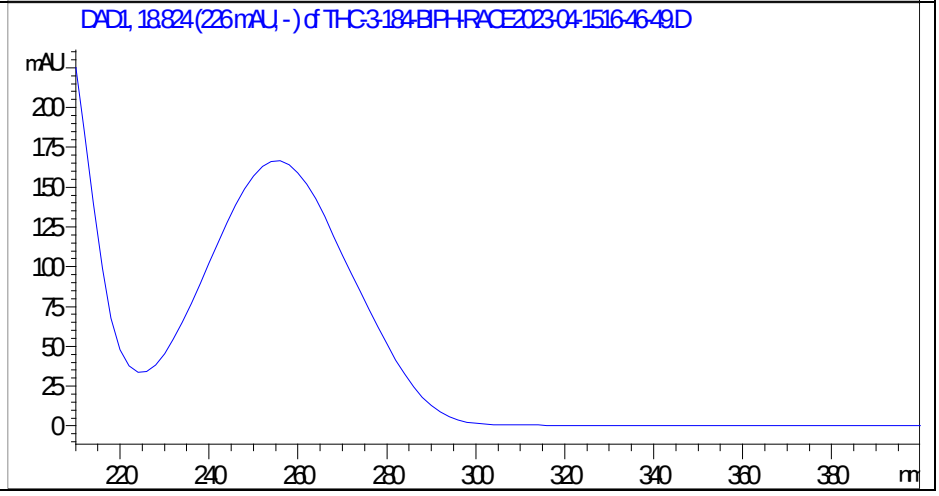
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

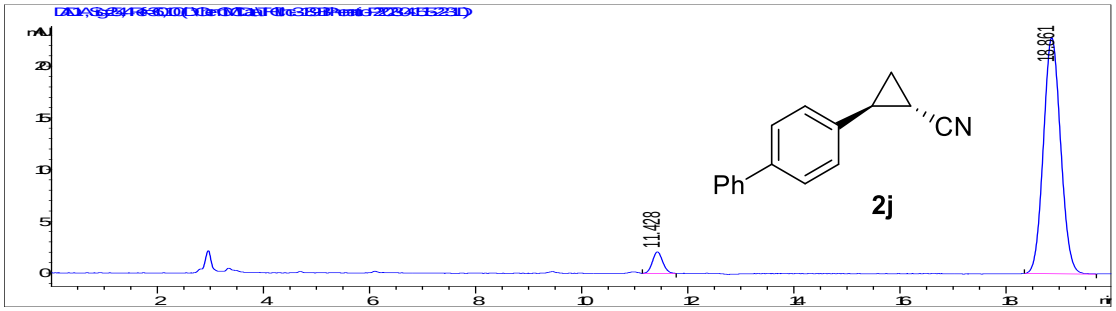
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.414	BB	0.2145	3785.87866	275.20950	49.9679
2	18.815	BB	0.3579	3790.74463	165.06760	50.0321
Totals :				7576.62329	440.27710	

UV spectrum of the peak at 11.390 min.



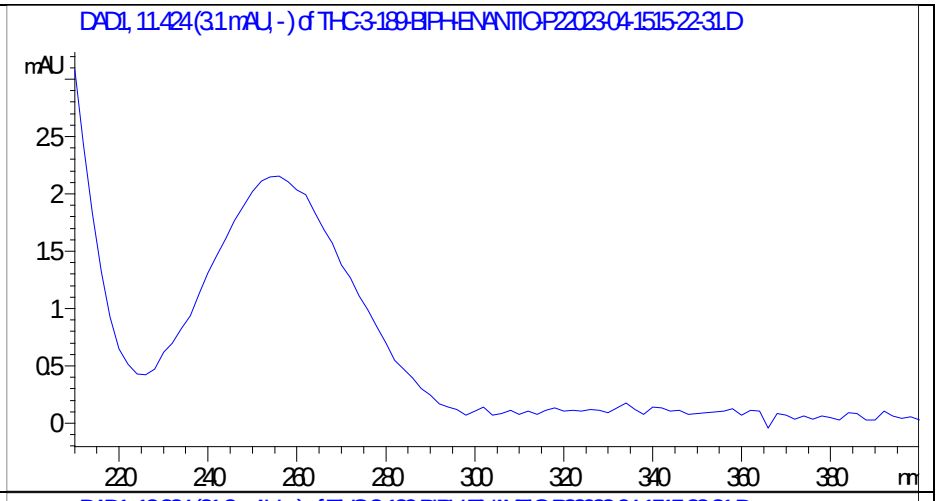
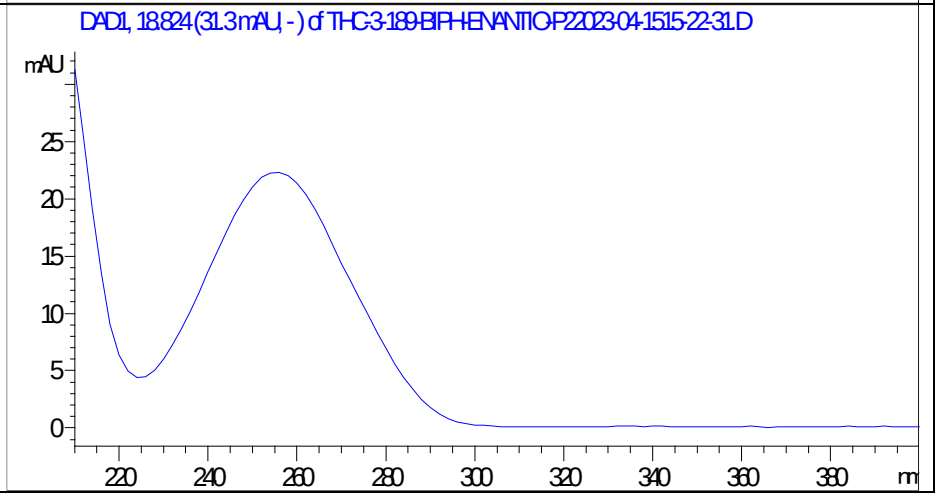
UV spectrum of the peak at 18.824 min.

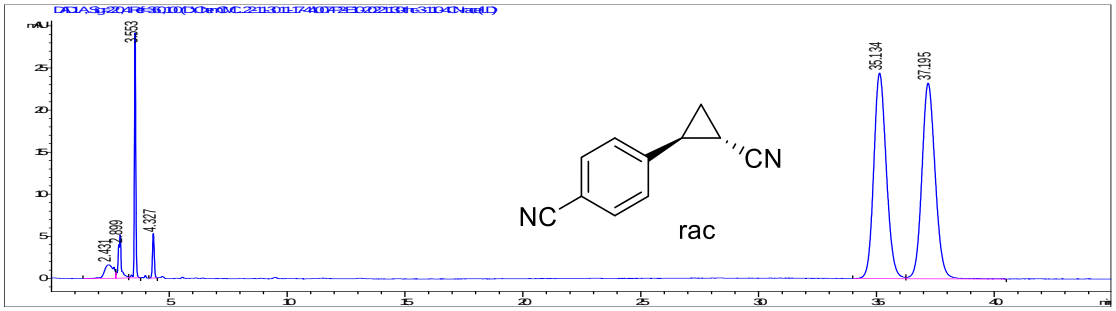




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

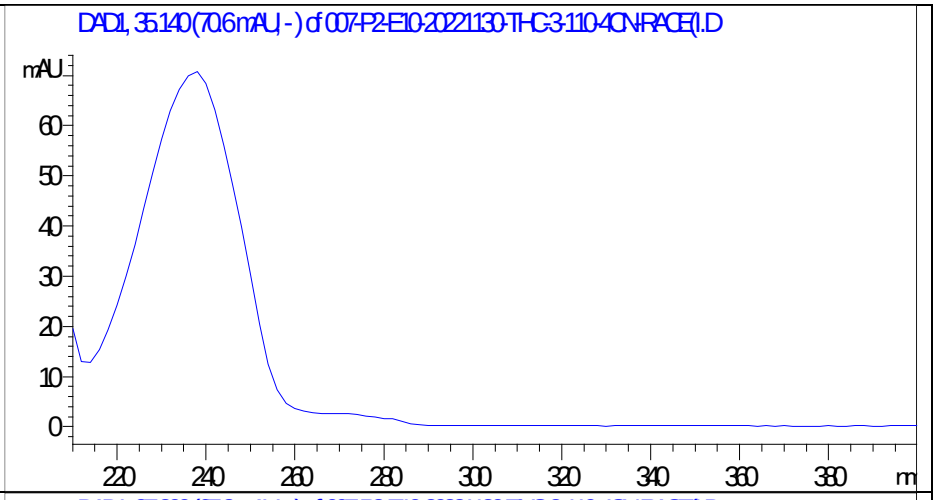
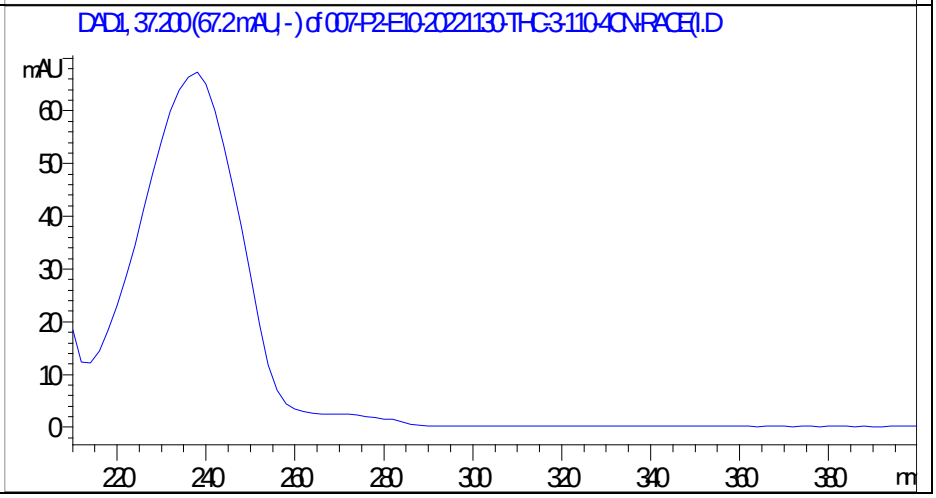
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.428	BB	0.2063	27.93940	2.08539	5.1449
2	18.861	BB	0.3513	515.11182	22.82504	94.8551
Totals :				543.05122	24.91042	

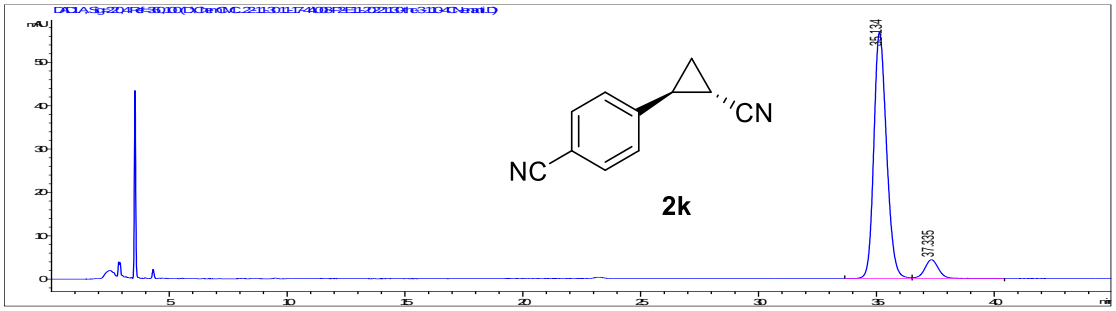
UV spectrum of the peak at 11.424 min.	
UV spectrum of the peak at 18.824 min.	



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

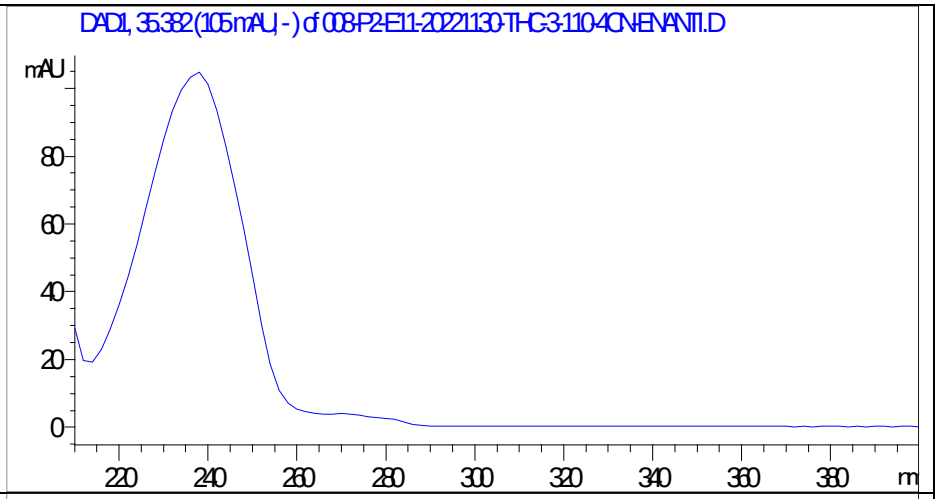
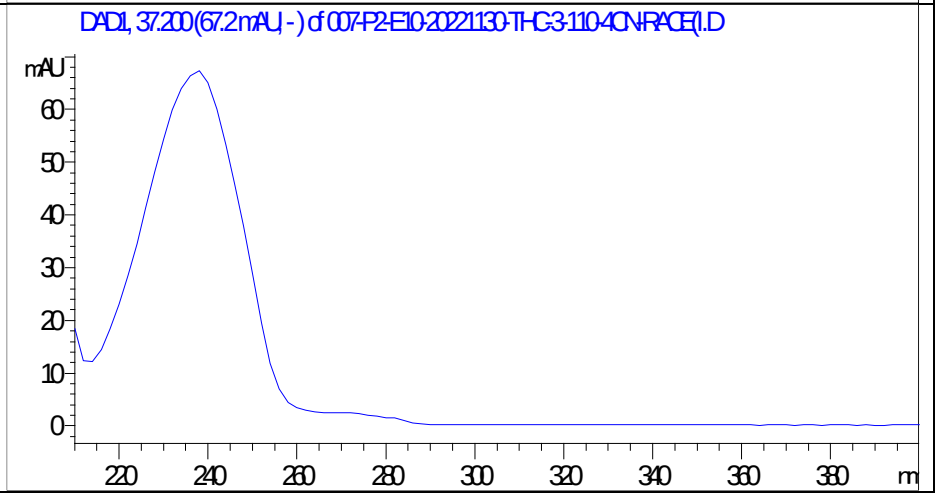
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.134	BV	0.5748	901.77655	24.42255	49.7761
2	37.195	VB	0.6009	909.88953	23.23388	50.2239

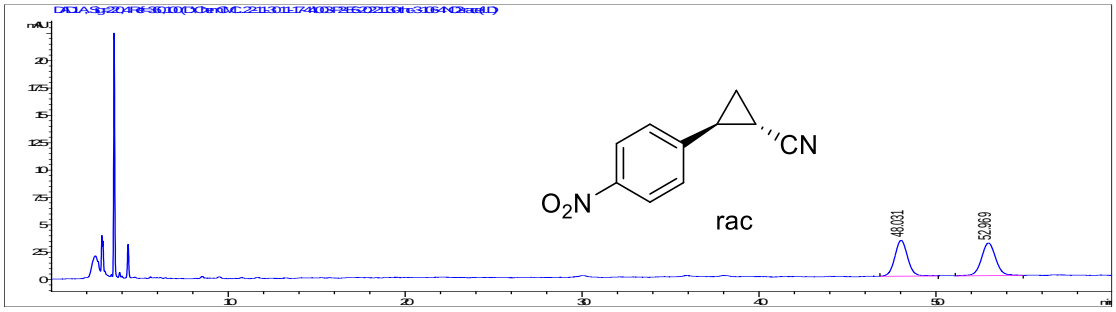
UV spectrum of the peak at 35.134 min.	
UV spectrum of the peak at 37.195 min.	



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

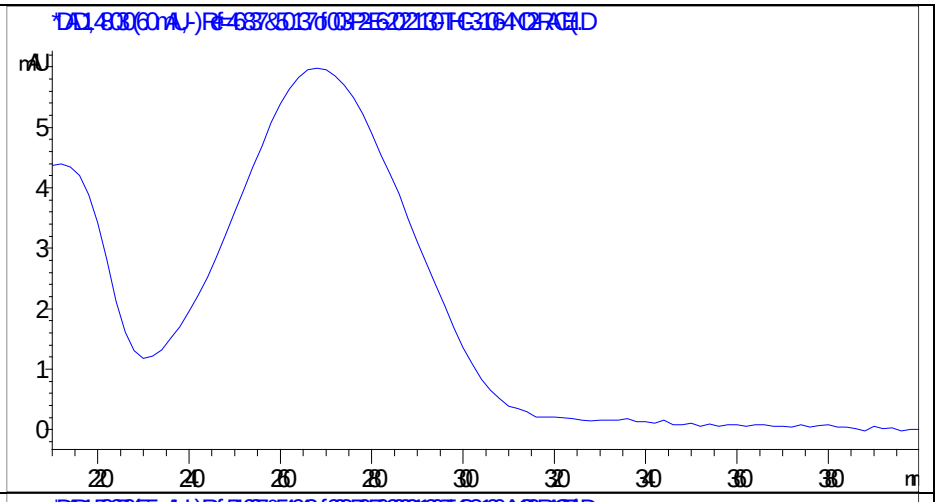
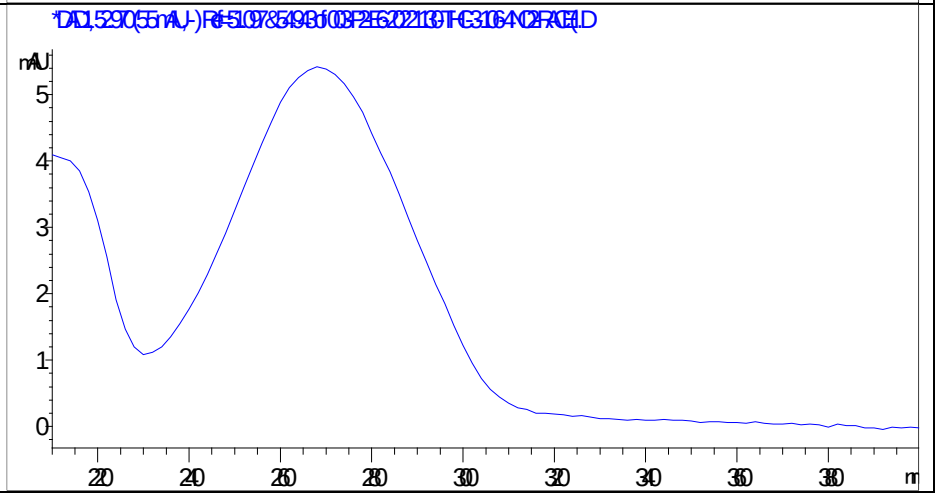
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.134	BV	0.5806	2123.56812	56.74883	92.3736
2	37.335	VB	0.6254	175.32161	4.32044	7.6264

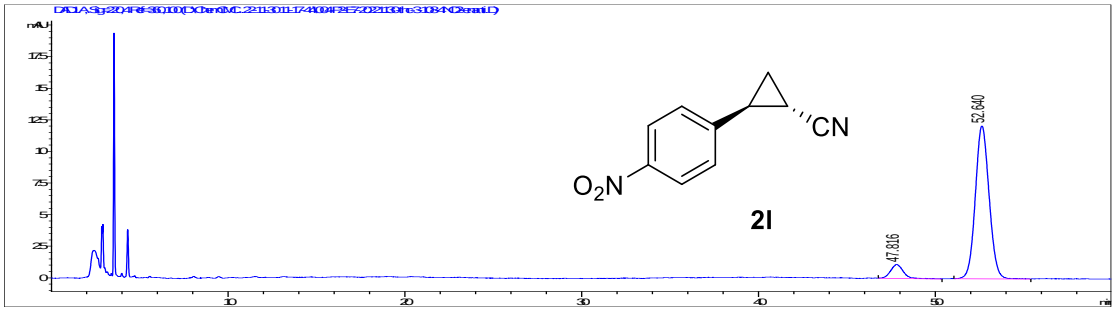
UV spectrum of the peak at 35.382 min.	
UV spectrum of the peak at 37.200 min.	



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

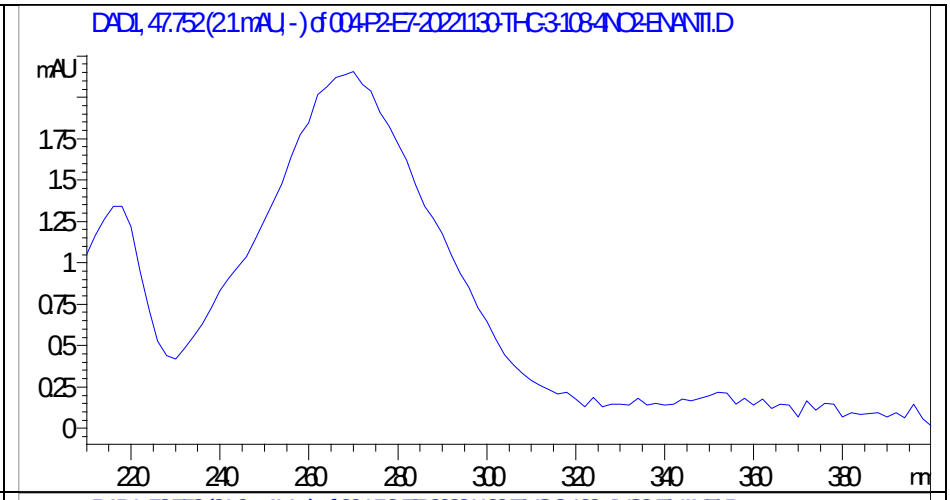
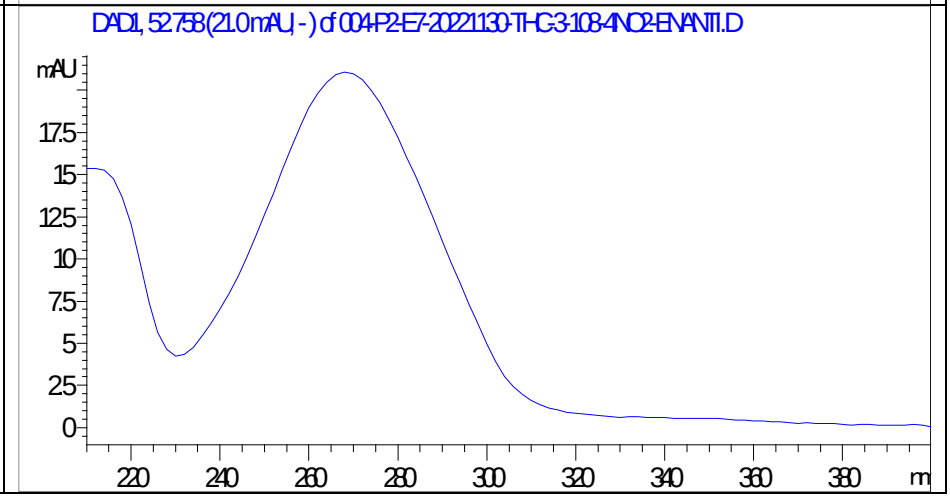
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.031	BB	0.7834	163.74664	3.27465	49.3782
2	52.969	BB	0.8719	167.87090	2.98595	50.6218

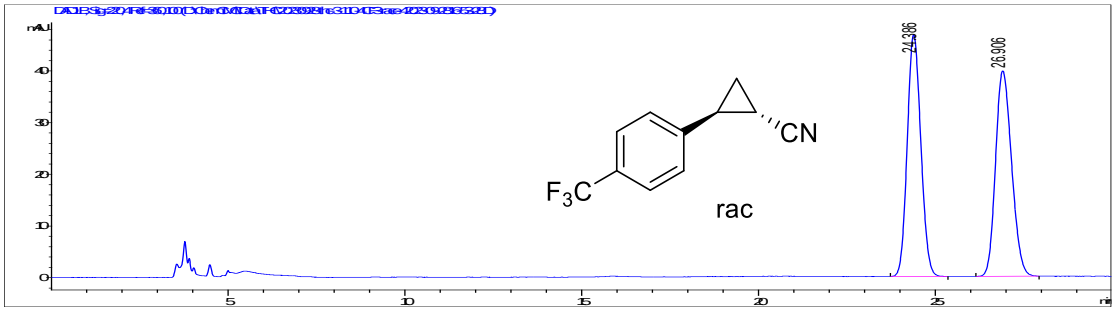
UV spectrum of the peak at 48.030 min.	
UV spectrum of the peak at 52.970 min.	



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.816	BB	0.7588	55.11494	1.10329	7.7482
2	52.640	BB	0.8405	656.21204	12.10418	92.2518

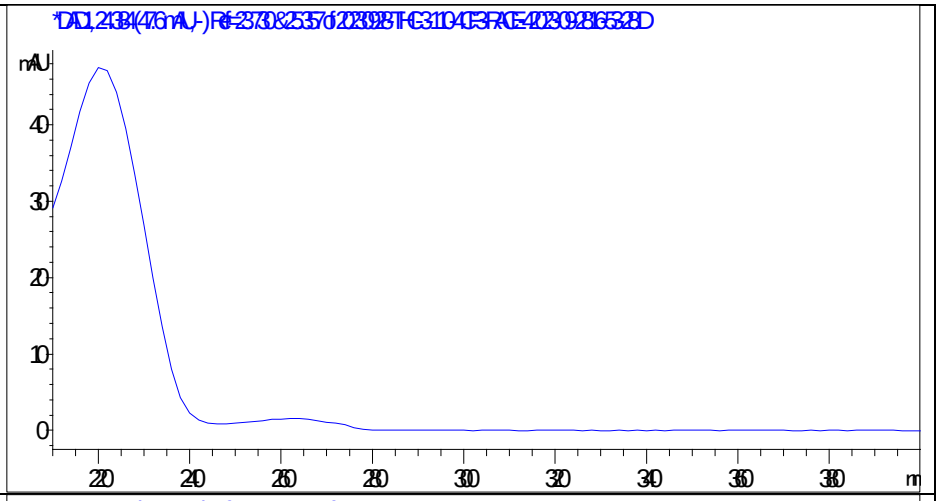
UV spectrum of the peak at 47.752 min.	
UV spectrum of the peak at 52.758 min.	



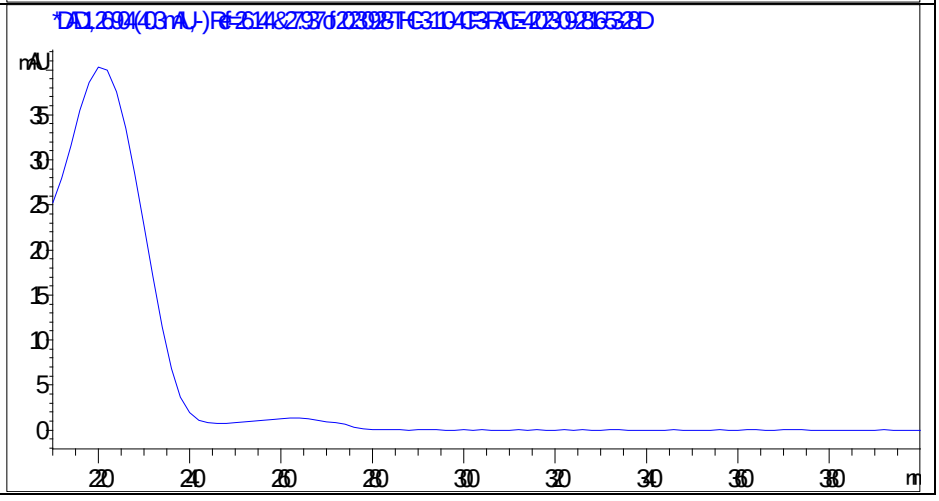
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

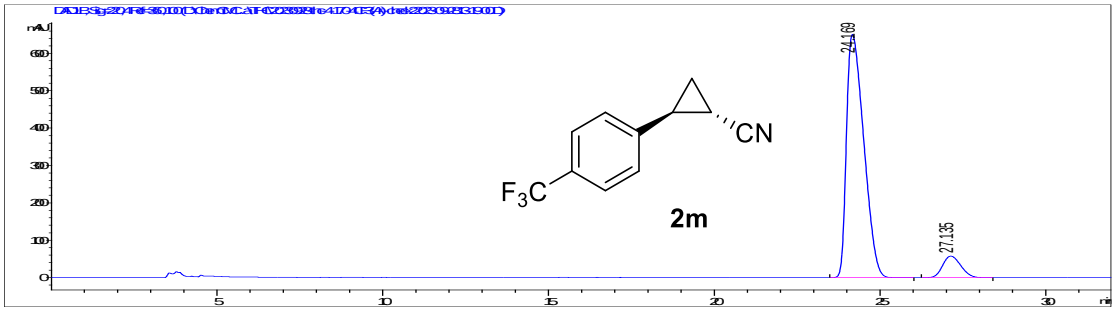
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.386	BB	0.4175	1250.55371	46.83601	49.9815
2	26.906	BB	0.4954	1251.48120	39.74575	50.0185
Totals :				2502.03491	86.58176	

UV spectrum of the peak at 24.384 min.



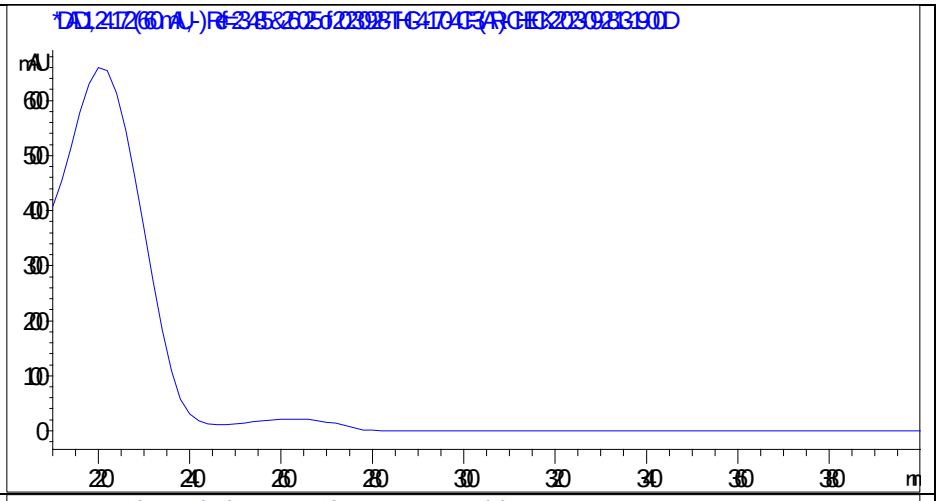
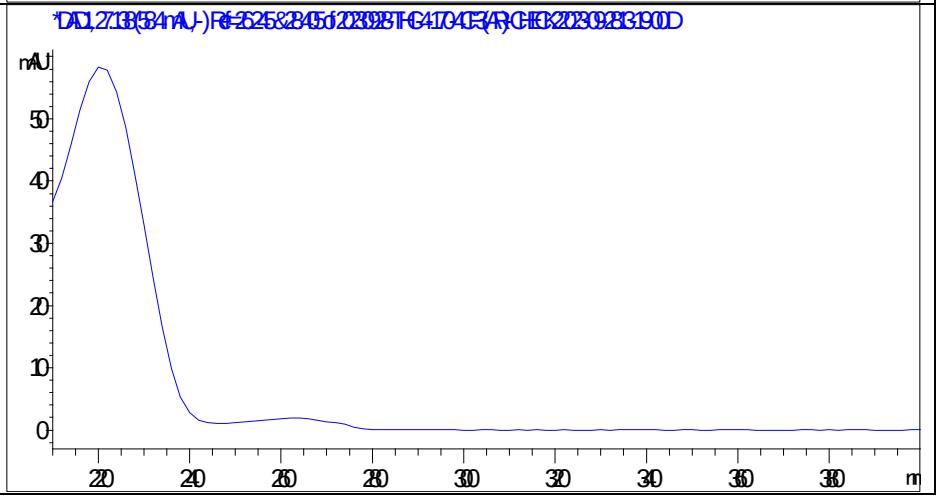
UV spectrum of the peak at 26.906min.

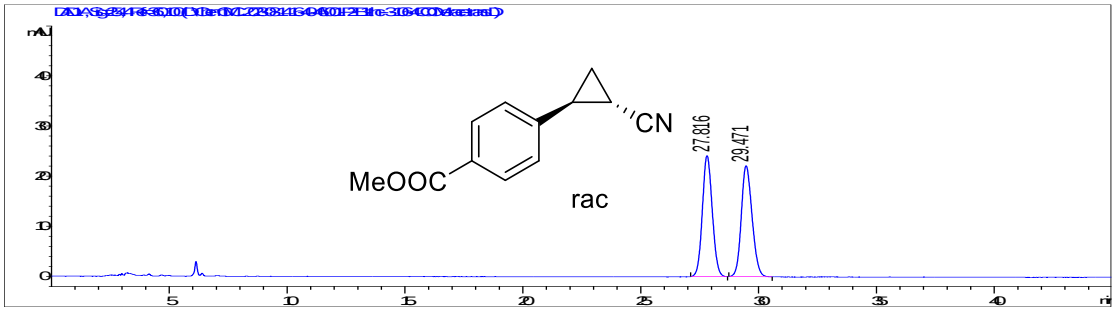




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

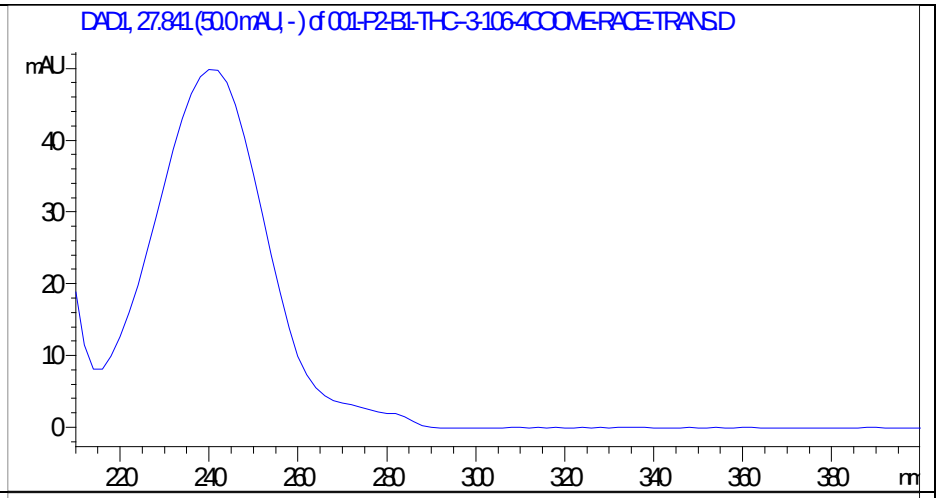
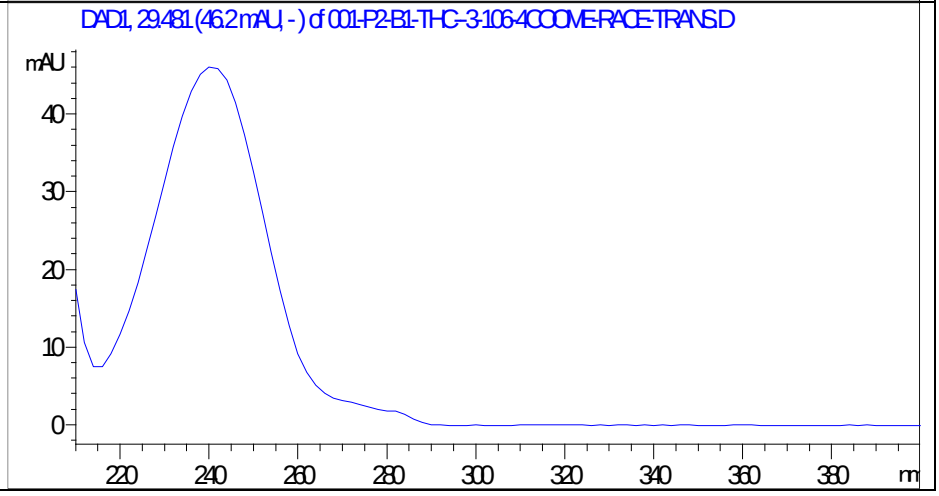
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.169	BB	0.5718	2.35248e4	650.73853	91.5108
2	27.135	BB	0.6005	2182.33496	57.54416	8.4892
Totals :				2.57071e4	708.28269	

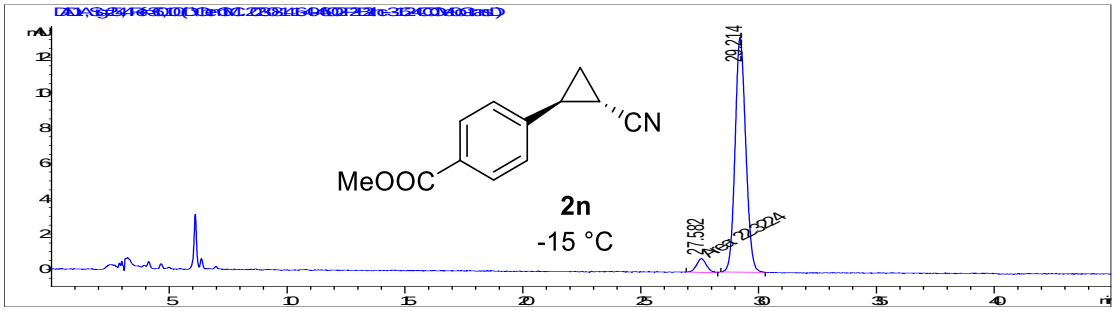
UV spectrum of the peak at 24.172 min.	
UV spectrum of the peak at 27.138 min.	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.816	BB	0.4482	703.97186	24.13935	49.9870
2	29.471	BB	0.4895	704.33820	22.11845	50.0130
Totals :				1408.31006	46.25780	

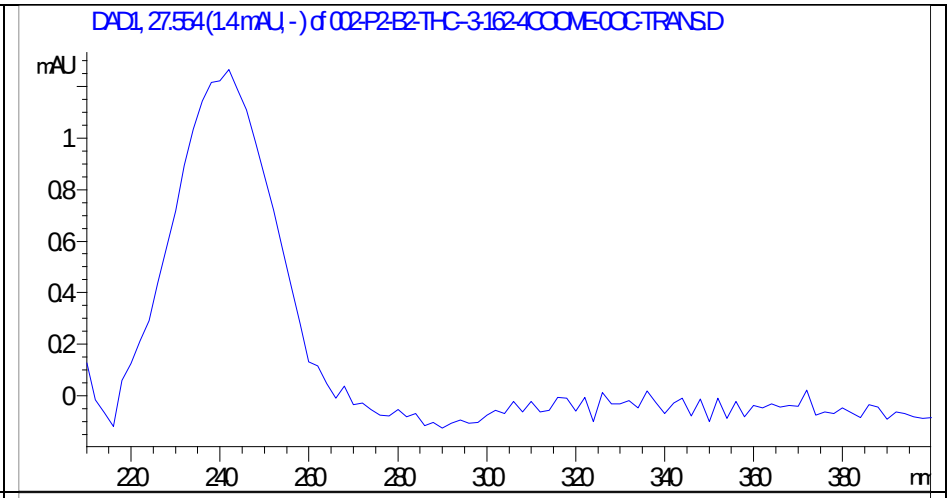
UV spectrum of the peak at 27.841 min.	
UV spectrum of the peak at 29.481 min.	



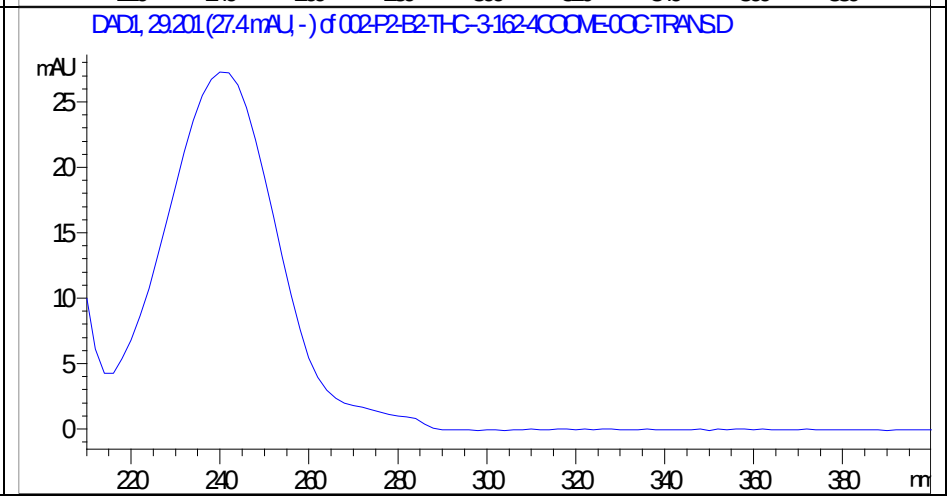
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

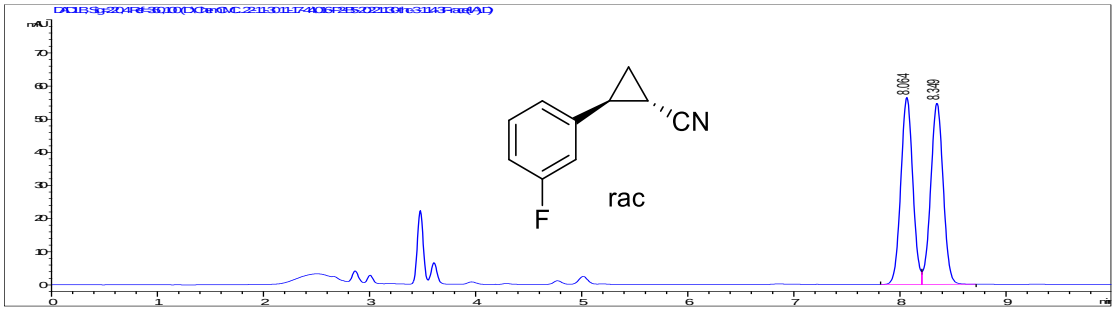
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.582	MM	0.4803	22.32240	7.74545e-1	5.0776
2	29.214	BB	0.4713	417.30176	13.25626	94.9224
Totals :				439.62416	14.03081	

UV spectrum of the peak at 27.554 min.



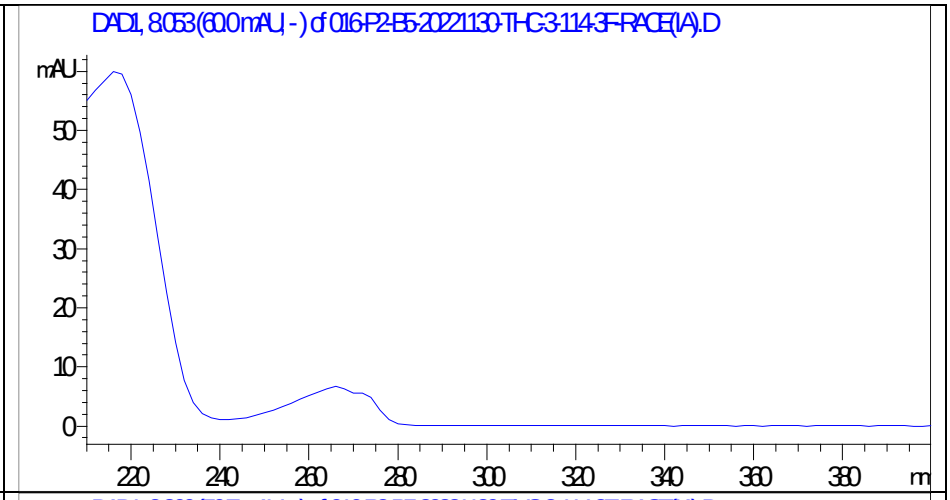
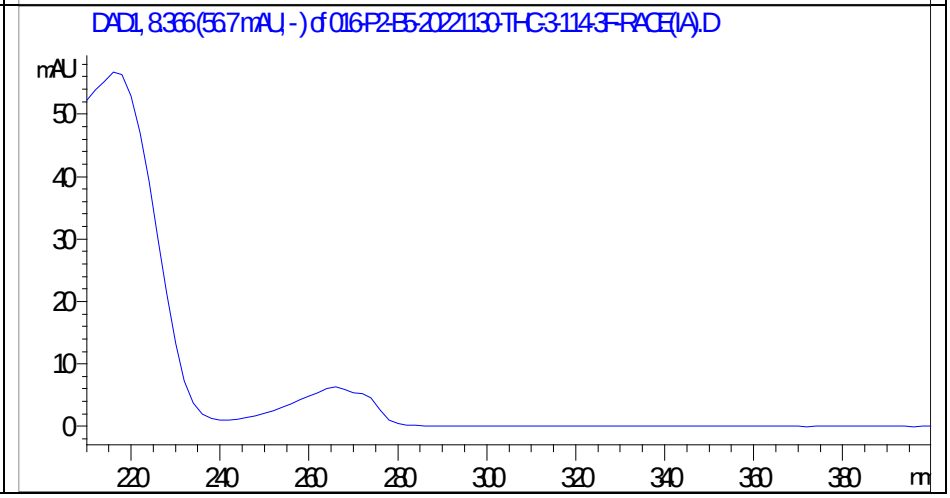
UV spectrum of the peak at 29.201 min.

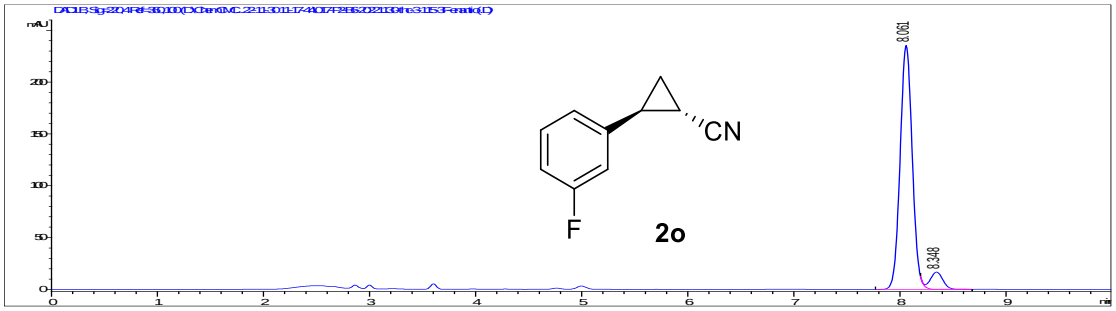




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

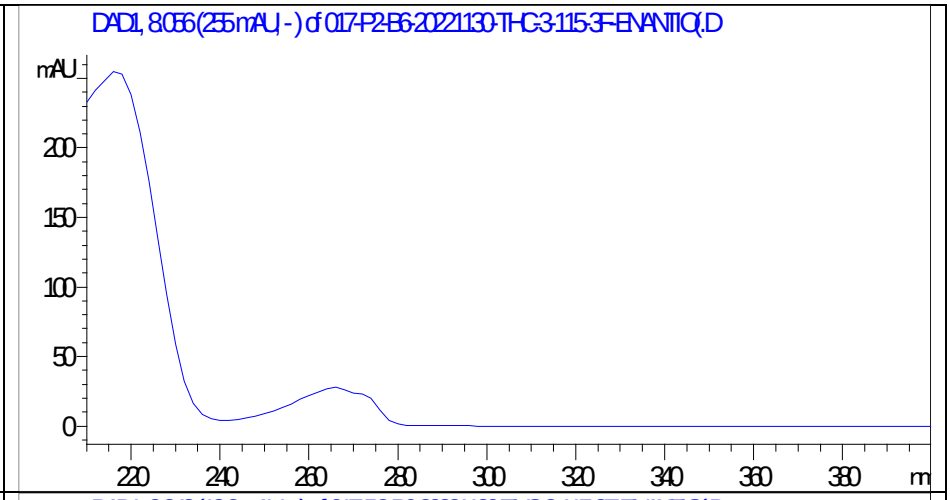
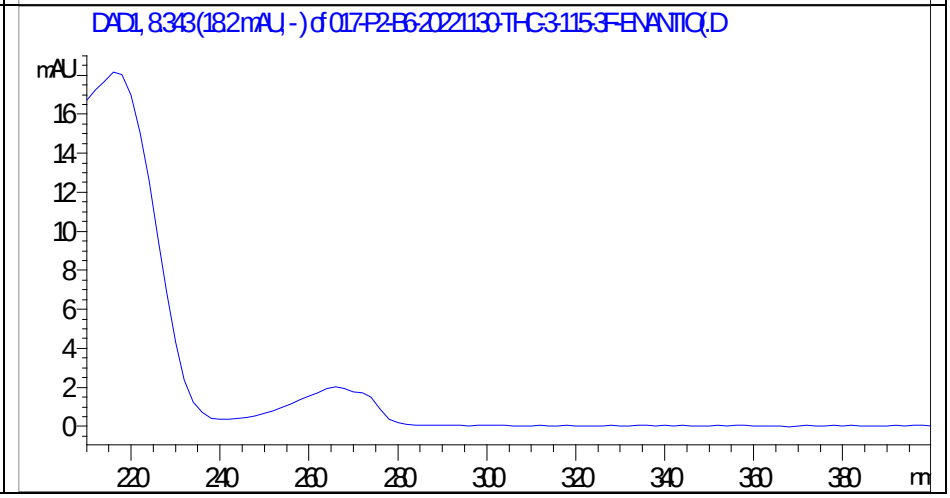
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.064	BV	0.1216	443.10165	56.41275	49.8390
2	8.349	VB	0.1271	445.96466	54.69624	50.1610

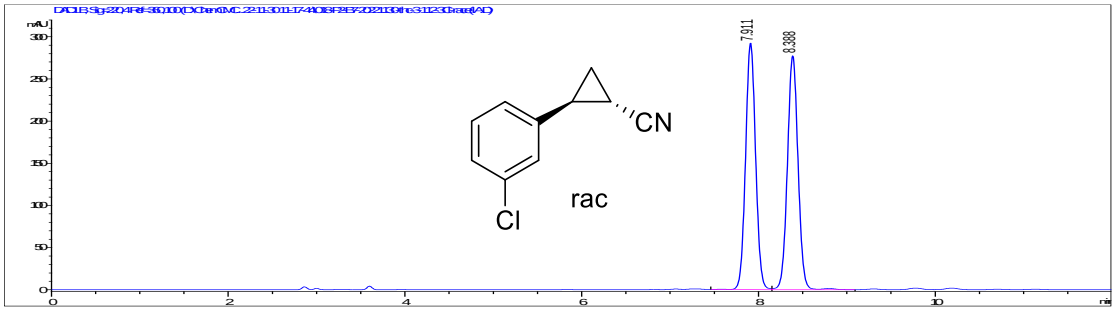
UV spectrum of the peak at 8.053 min.	
UV spectrum of the peak at 8.366 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

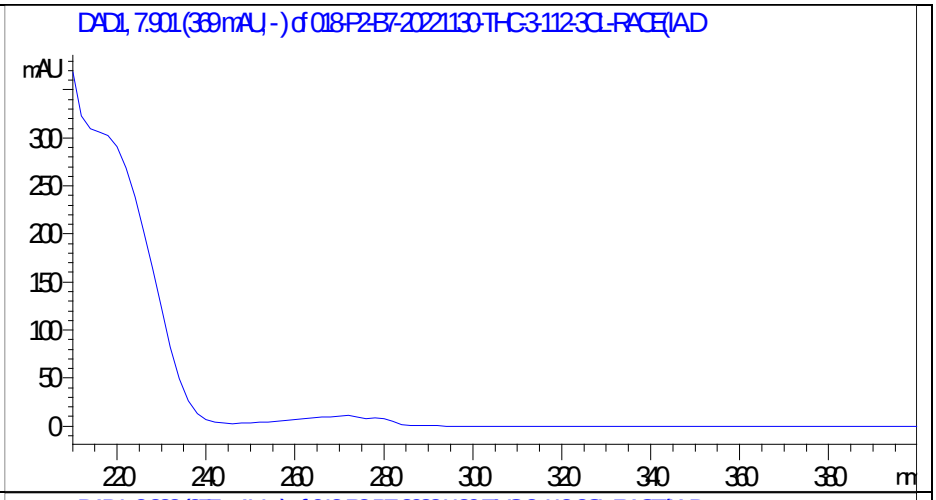
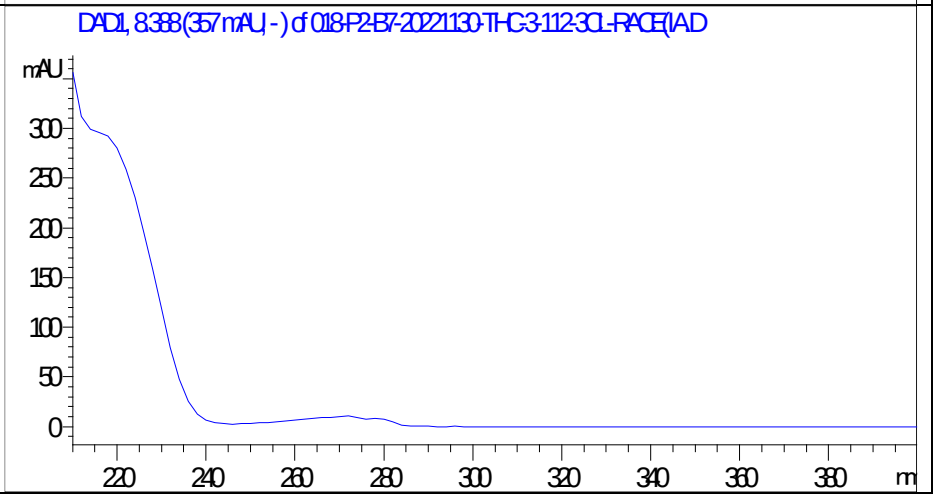
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.061	BV R	0.1226	1868.47803	235.39308	93.2476
2	8.348	VB E	0.1248	135.30270	16.65599	6.7524

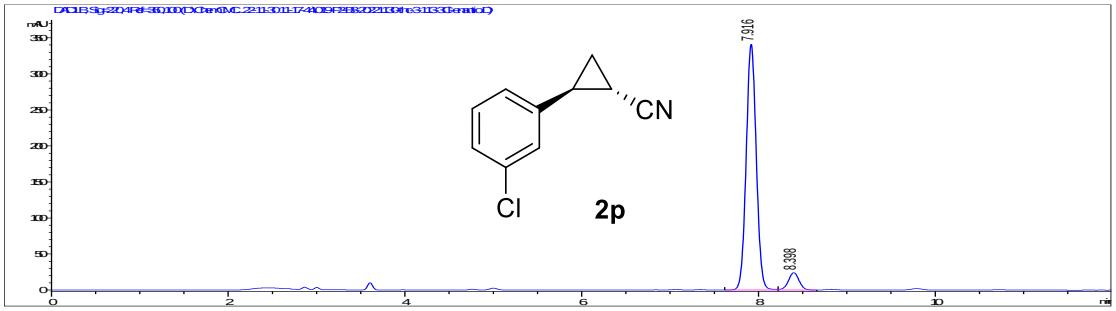
UV spectrum of the peak at 8.056 min.	
UV spectrum of the peak at 8.343 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

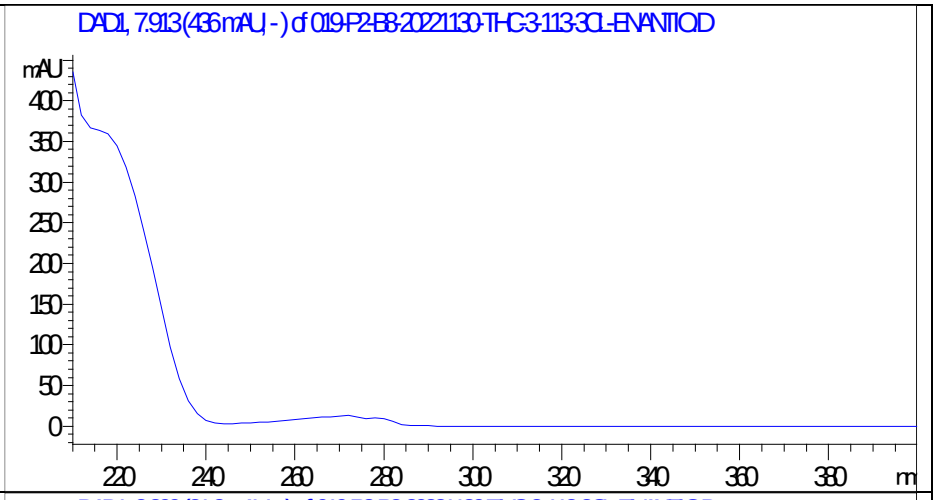
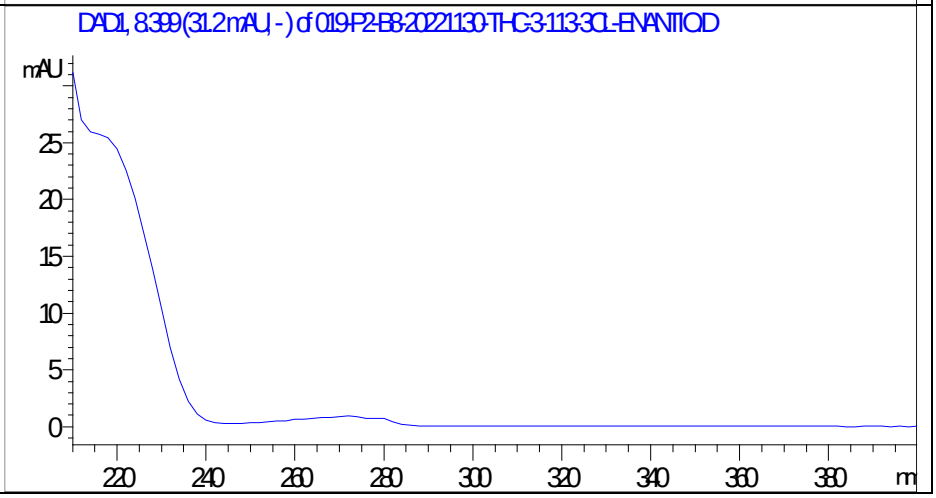
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.911	VV R	0.1240	2307.95044	292.69135	49.8343
2	8.388	VV R	0.1291	2323.29663	277.31989	50.1657

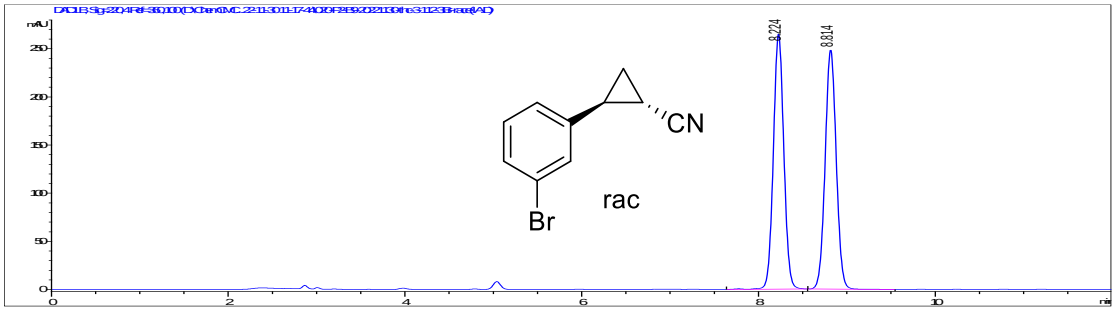
UV spectrum of the peak at 7.901 min.	
UV spectrum of the peak at 8.388 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.916	BV	0.1244	2705.49512	341.52234	93.0210
2	8.398	VB	0.1301	202.98412	24.13394	6.9790

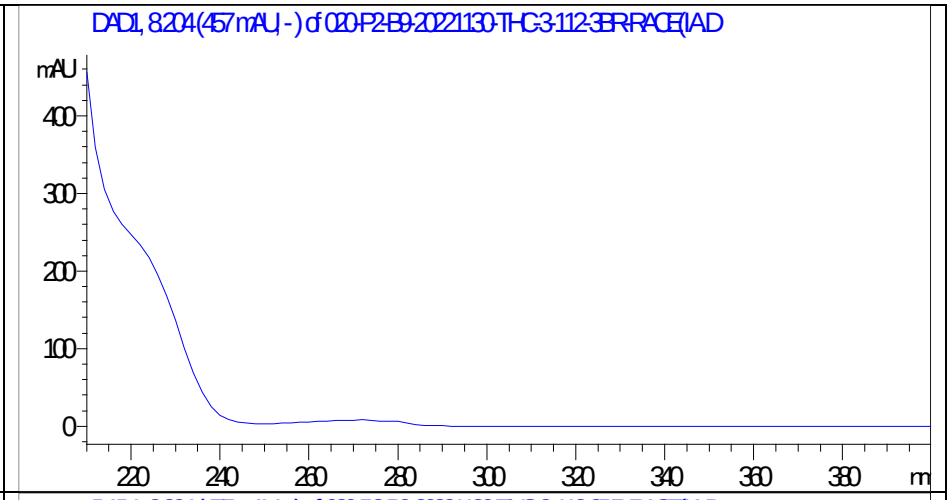
UV spectrum of the peak at 7.913 min.	
UV spectrum of the peak at 8.399 min.	



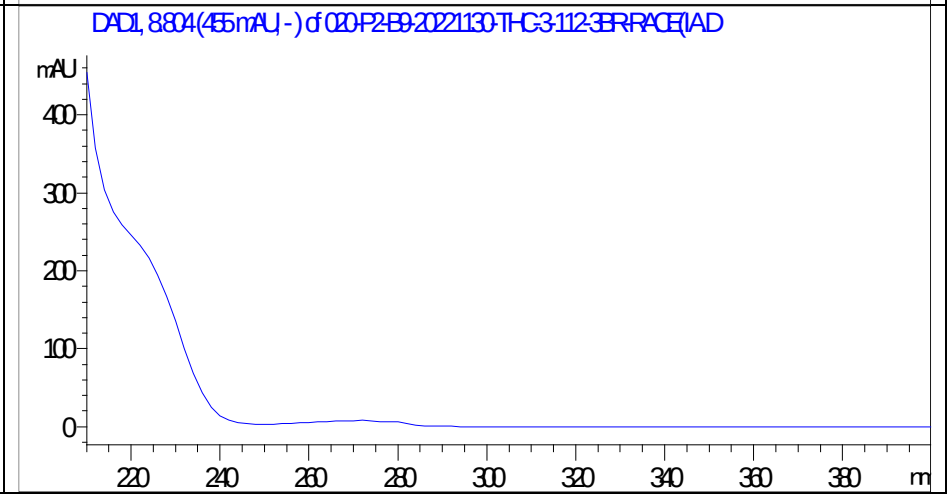
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

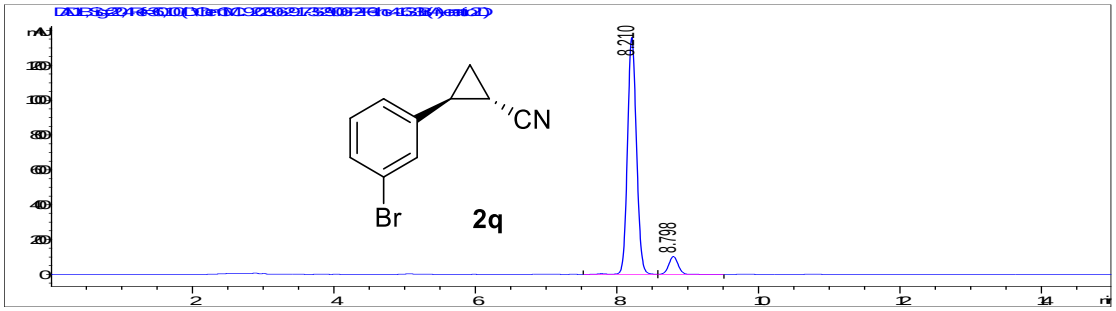
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.224	VB R	0.1261	2181.67310	264.82584	50.1396
2	8.814	BB	0.1338	2169.52197	248.52733	49.8604

UV spectrum of the peak at 8.204 min.



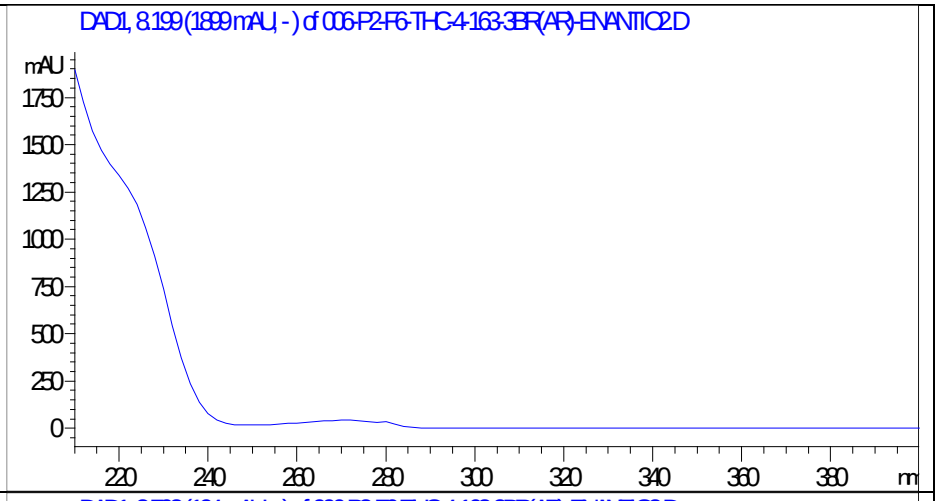
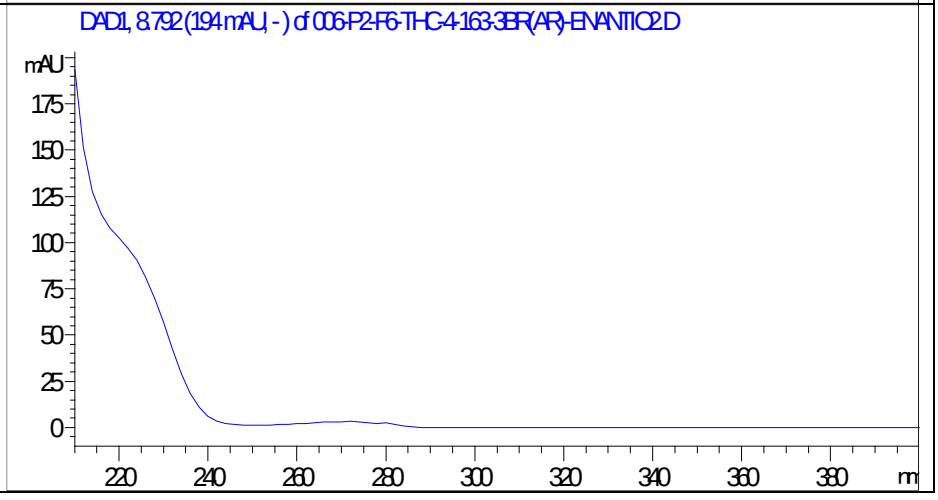
UV spectrum of the peak at 8.804 min.

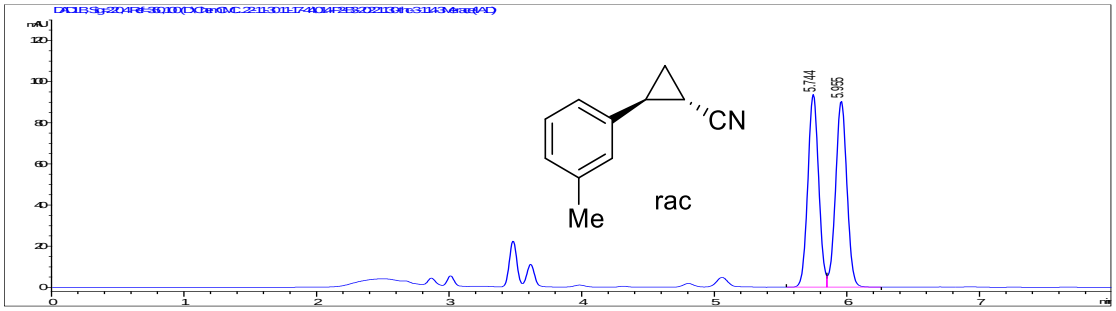




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

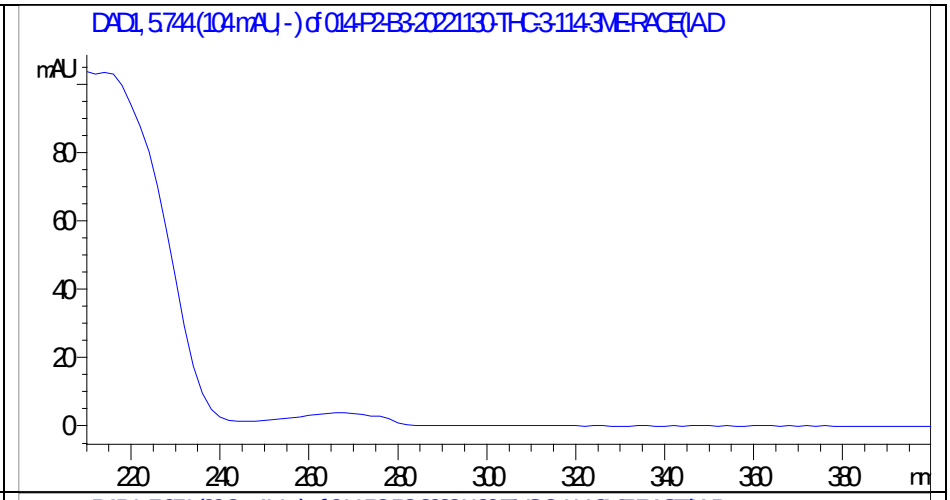
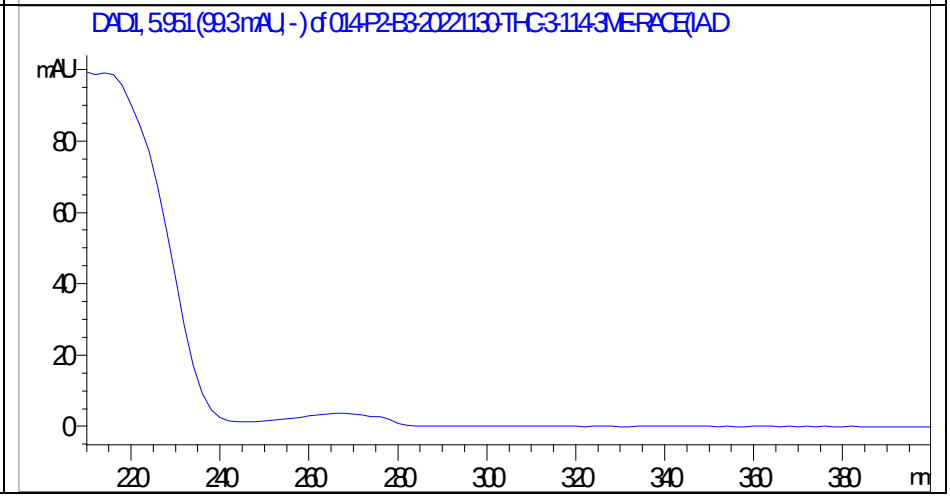
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.210	VV R	0.1367	1.20178e4	1359.58752	92.6660
2	8.798	VB	0.1419	951.14648	102.85929	7.3340
Totals :				1.29689e4	1462.44682	

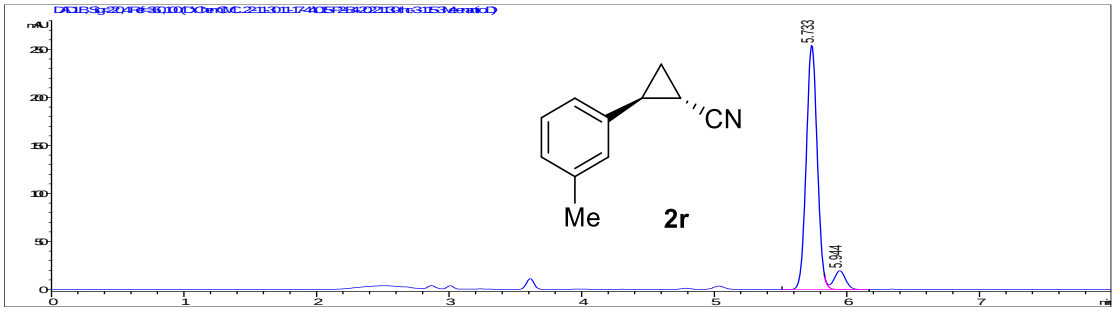
UV spectrum of the peak at 8.199 min.	
UV spectrum of the peak at 8.792 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.744	BV	0.0886	534.45844	93.59595	49.9108
2	5.955	VB	0.0932	536.36884	90.37561	50.0892

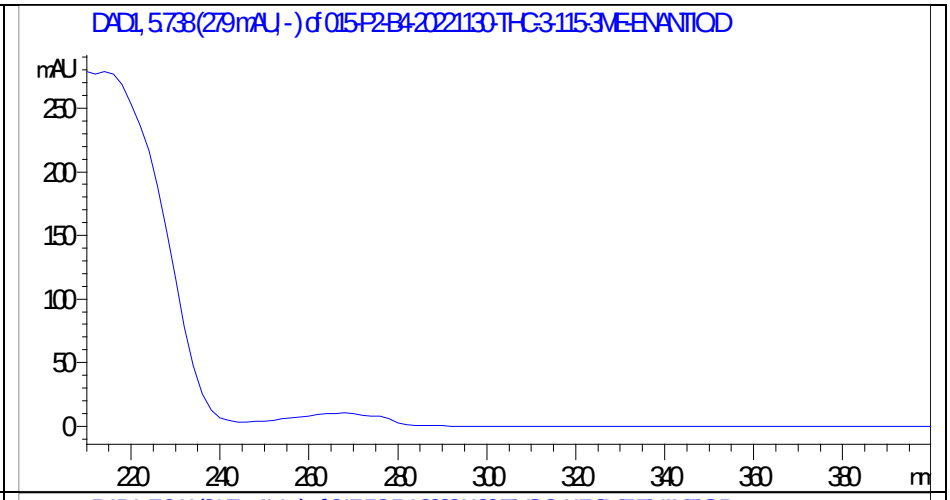
UV spectrum of the peak at 5.744 min.	
UV spectrum of the peak at 5.951 min.	



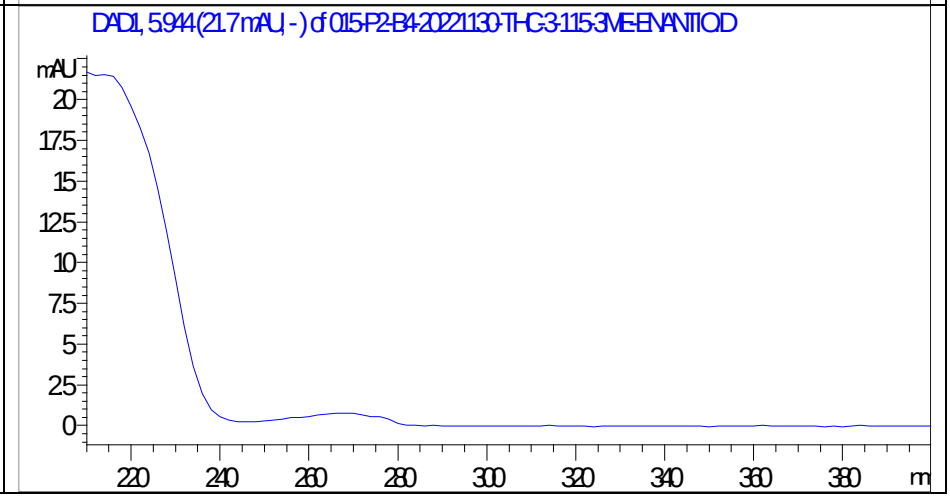
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

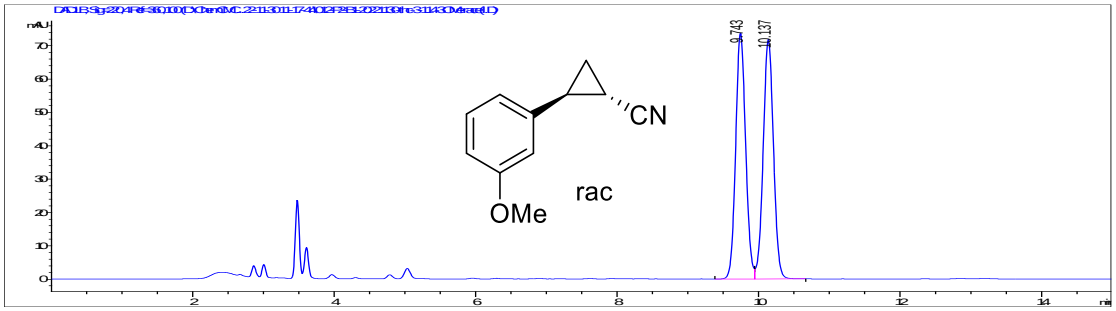
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.733	BV R	0.0895	1473.93152	254.60228	92.7164
2	5.944	VB E	0.0915	115.78822	19.44386	7.2836

UV spectrum of the peak at 5.738 min.



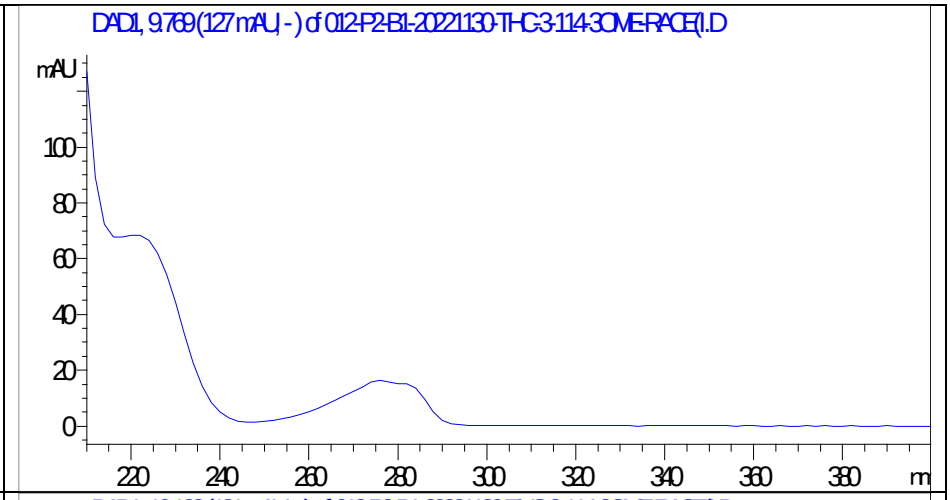
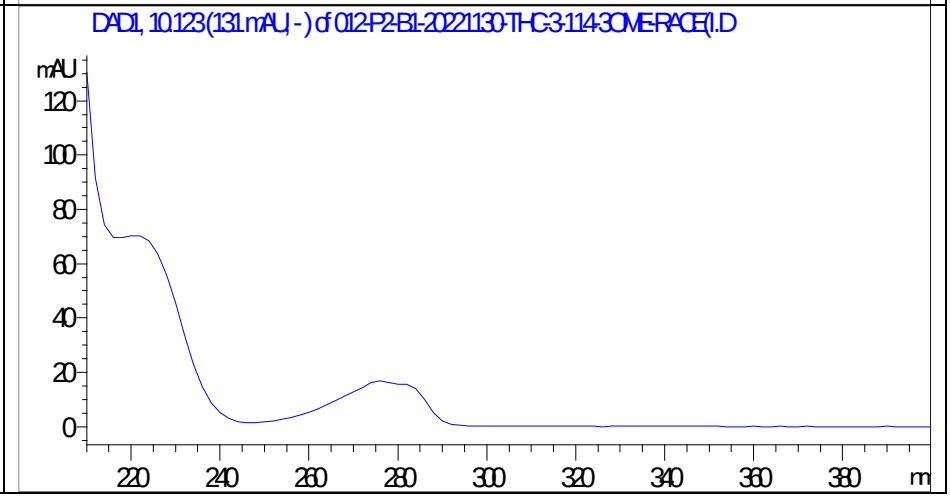
UV spectrum of the peak at 5.944 min.

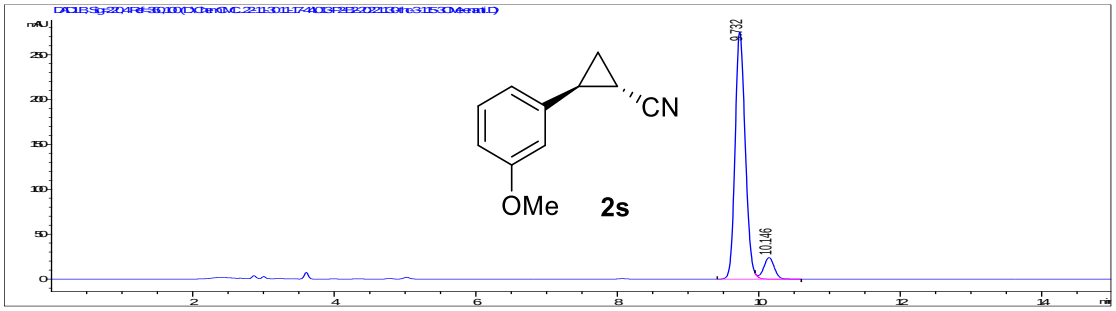




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

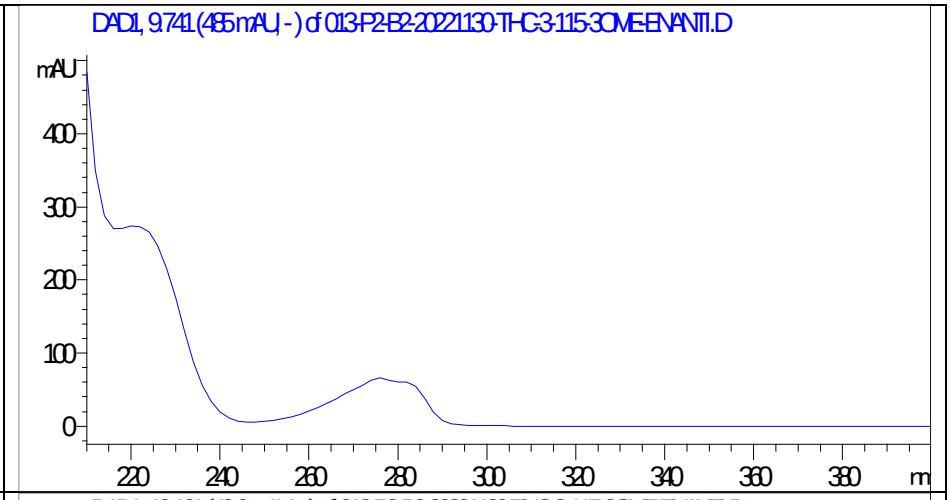
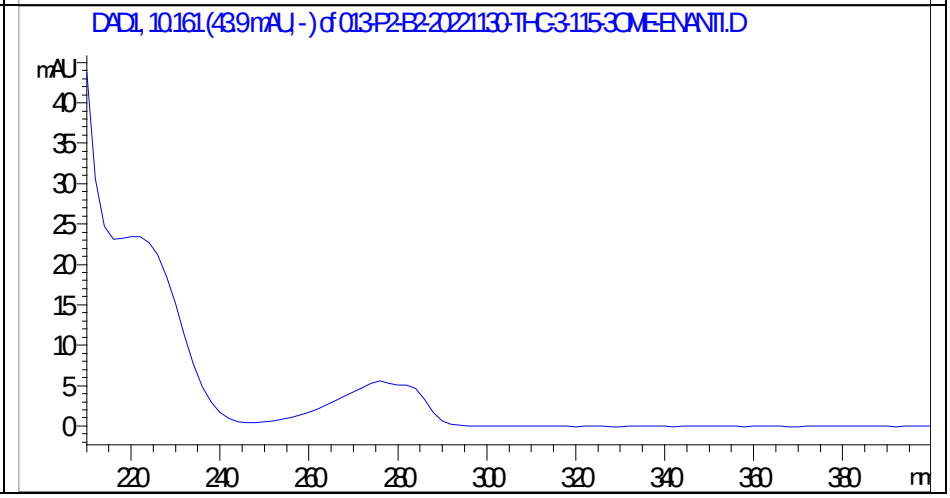
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.743	BV	0.1519	720.48077	73.78410	49.8485
2	10.137	VB	0.1557	724.86090	71.82605	50.1515

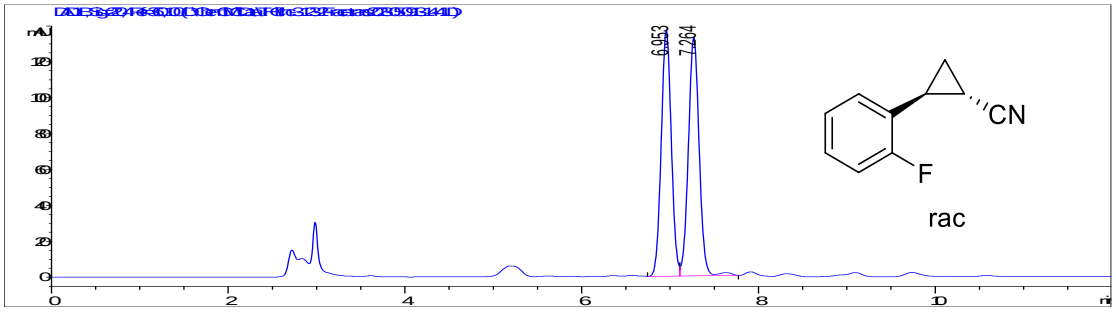
UV spectrum of the peak at 9.769 min.	
UV spectrum of the peak at 10.123 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

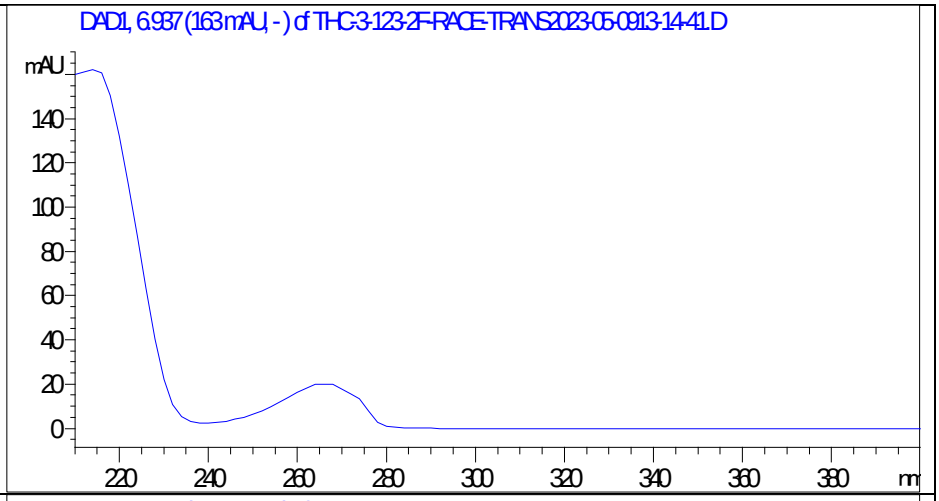
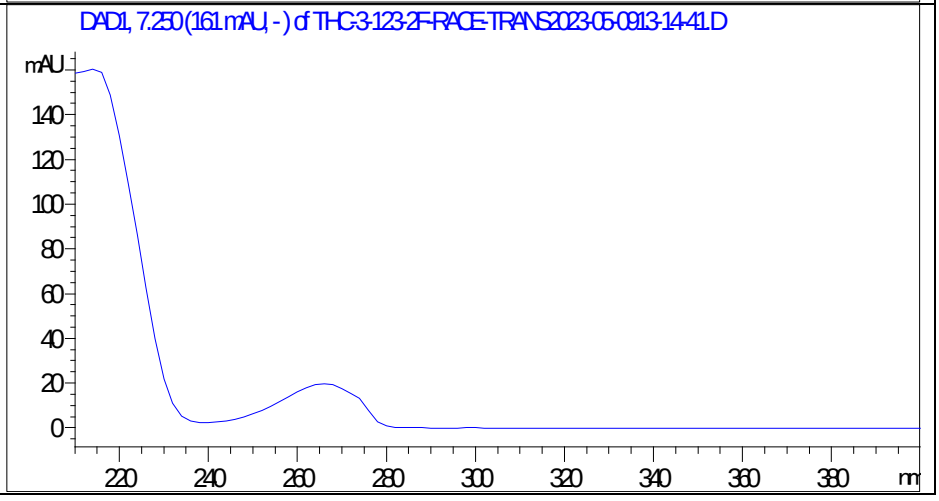
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.732	BV R	0.1546	2749.81689	275.22052	91.8887
2	10.146	VB E	0.1561	242.73505	23.98028	8.1113

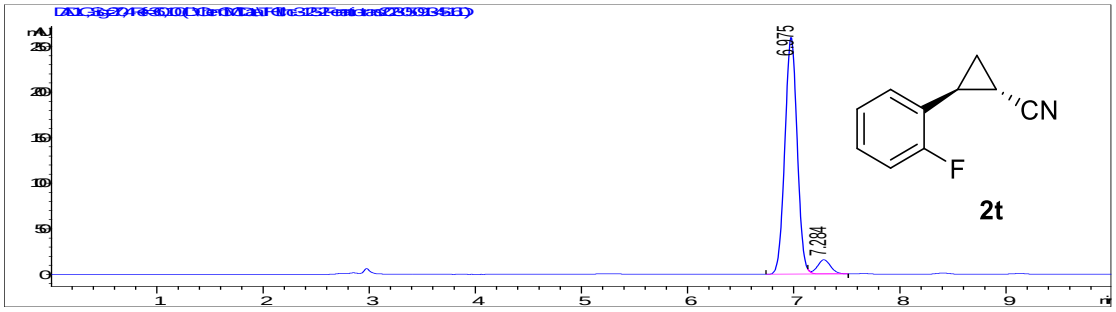
UV spectrum of the peak at 9.741 min.	
UV spectrum of the peak at 10.161 min.	



Signal 3: DAD1 G, Sig=270,4 Ref=360,100

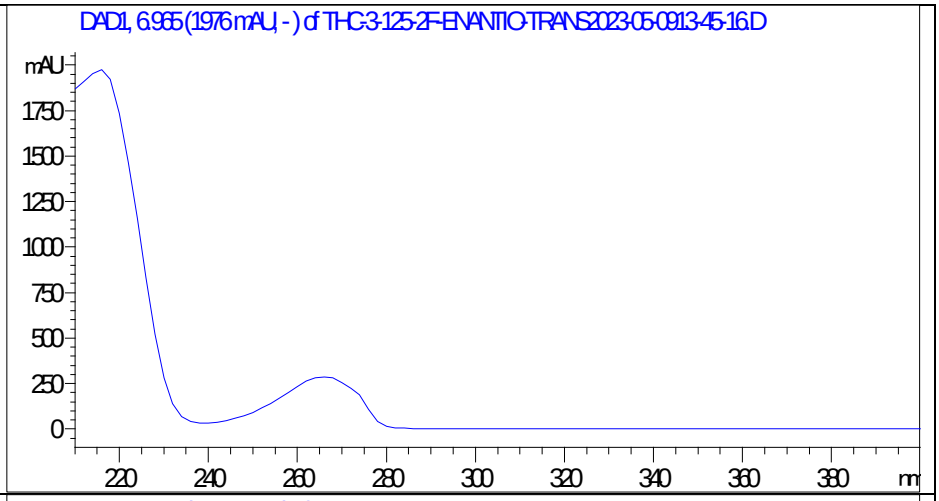
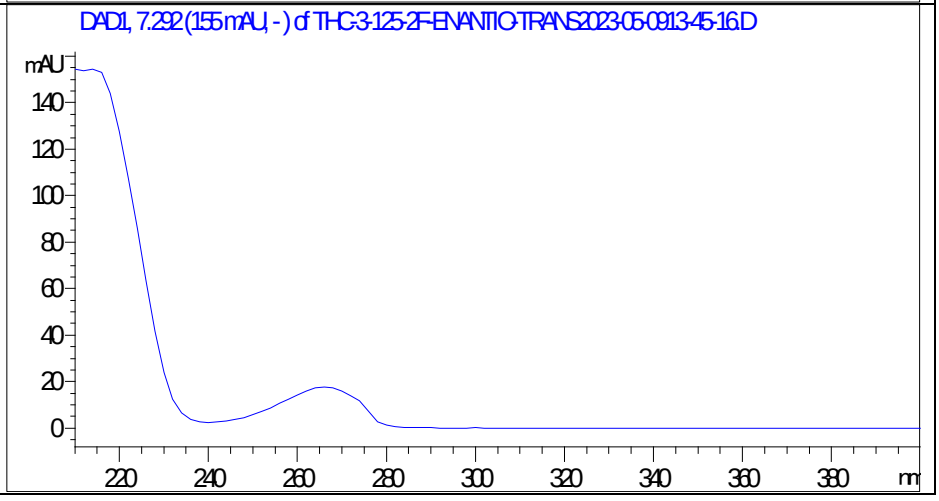
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.953	BV	0.1245	150.14729	18.92816	49.9093
2	7.264	VB	0.1285	150.69302	18.20991	50.0907
Totals :				300.84032	37.13807	

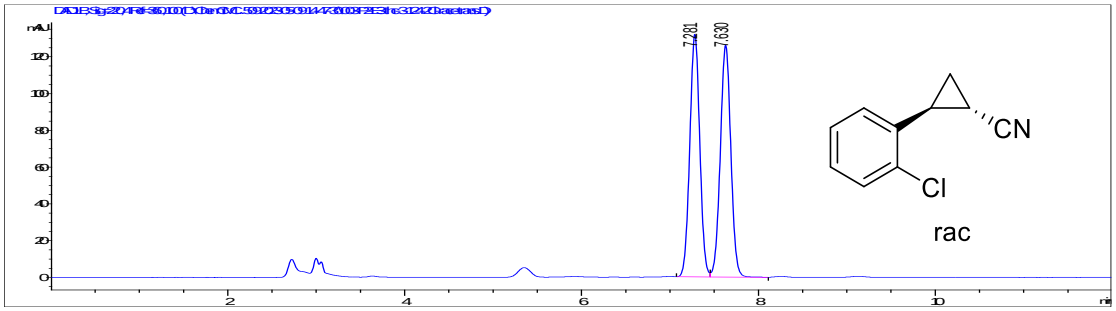
UV spectrum of the peak at 6.937 min.	
UV spectrum of the peak at 7.250 min.	



Signal 3: DAD1 G, Sig=270,4 Ref=360,100

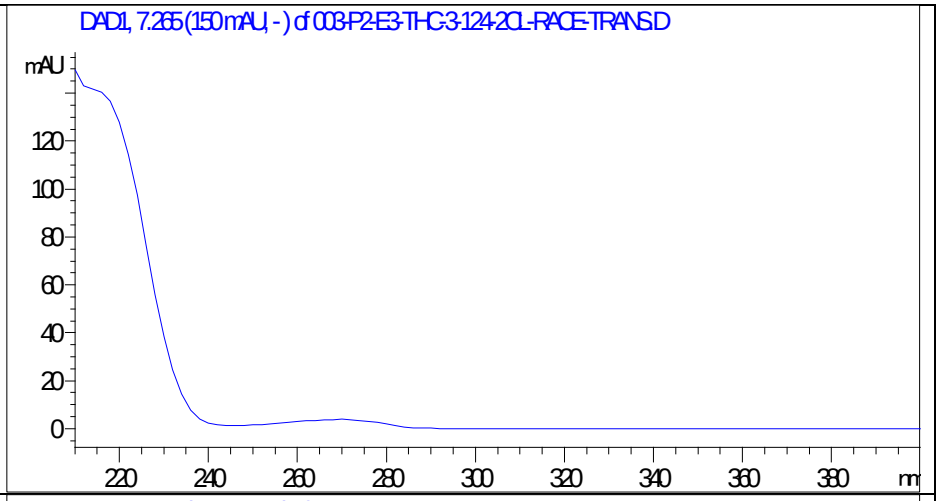
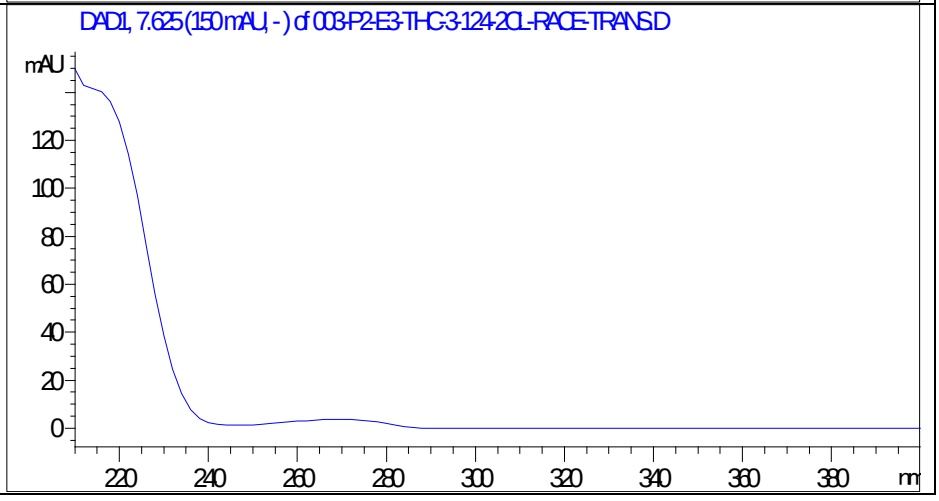
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.975	BV R	0.1263	2101.94922	259.91483	94.0511
2	7.284	VB E	0.1314	132.95180	15.60615	5.9489
Totals :				2234.90102	275.52098	

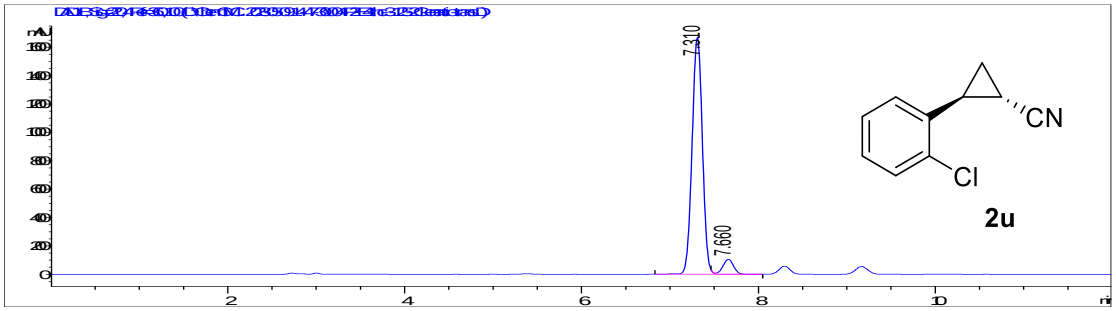
UV spectrum of the peak at 6.965 min.	
UV spectrum of the peak at 7.292 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.281	BV	0.1216	1036.61121	131.99013	49.8440
2	7.630	VB	0.1284	1043.10193	126.22614	50.1560
Totals :				2079.71313	258.21627	

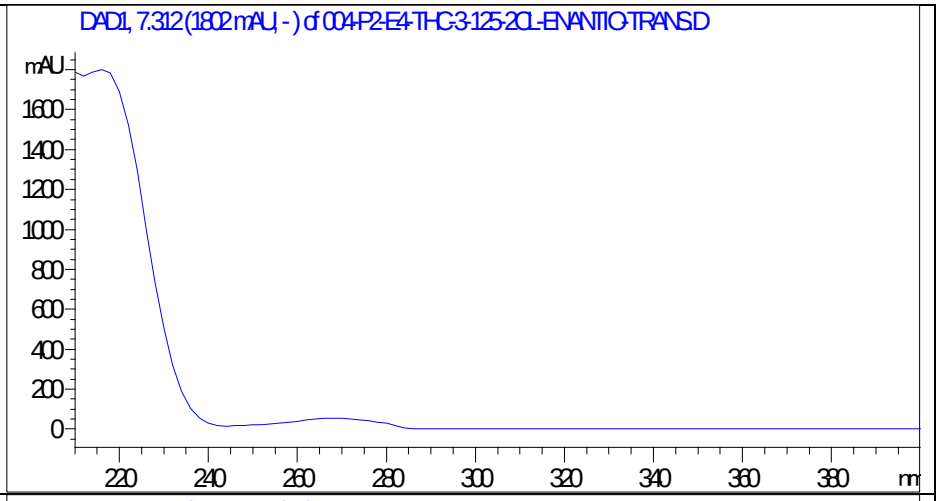
UV spectrum of the peak at 7.265 min.	
UV spectrum of the peak at 7.625 min.	



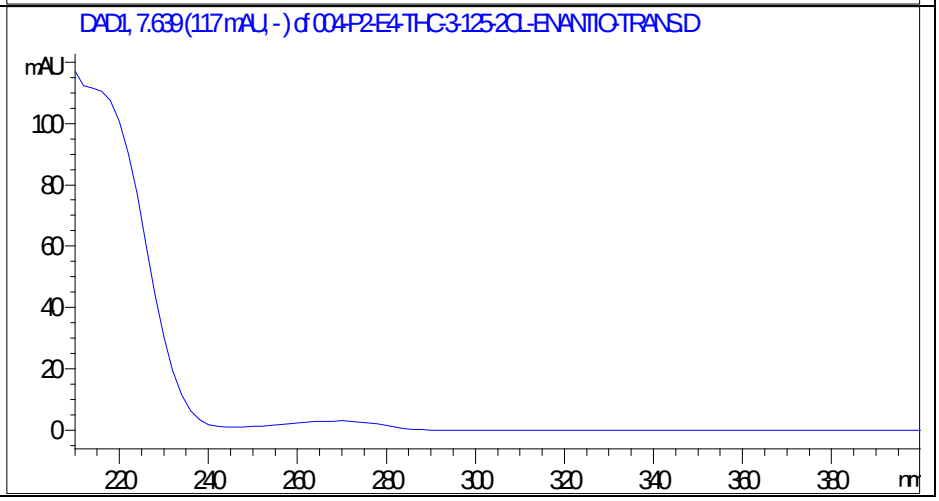
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

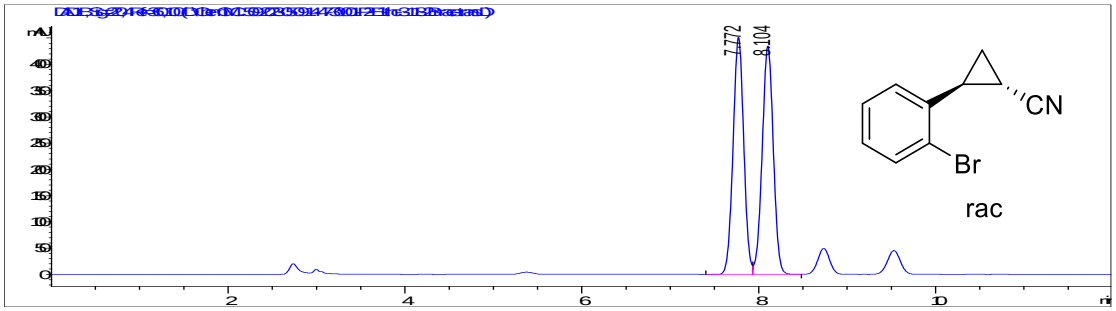
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.310	VV R	0.1266	1.35633e4	1668.44995	93.7907
2	7.660	VB E	0.1301	897.94684	106.74031	6.2093
Totals :				1.44612e4	1775.19026	

UV spectrum of the peak at 7.312 min.



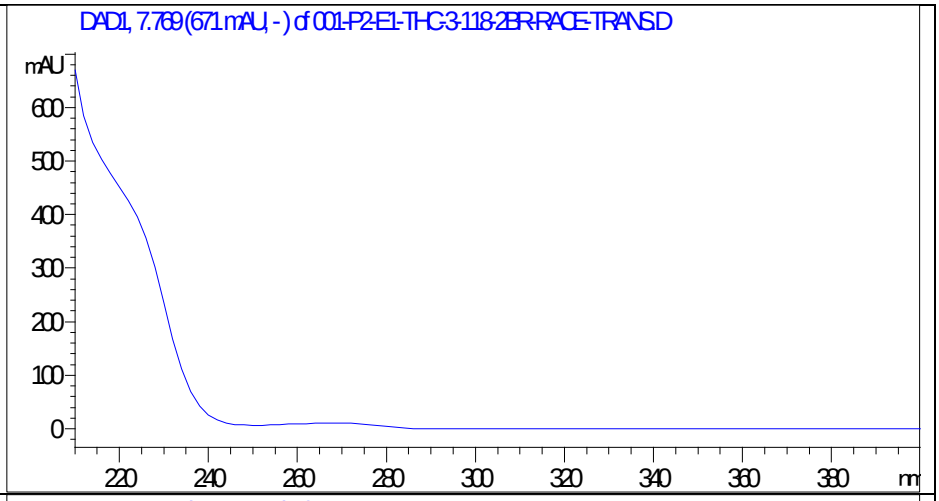
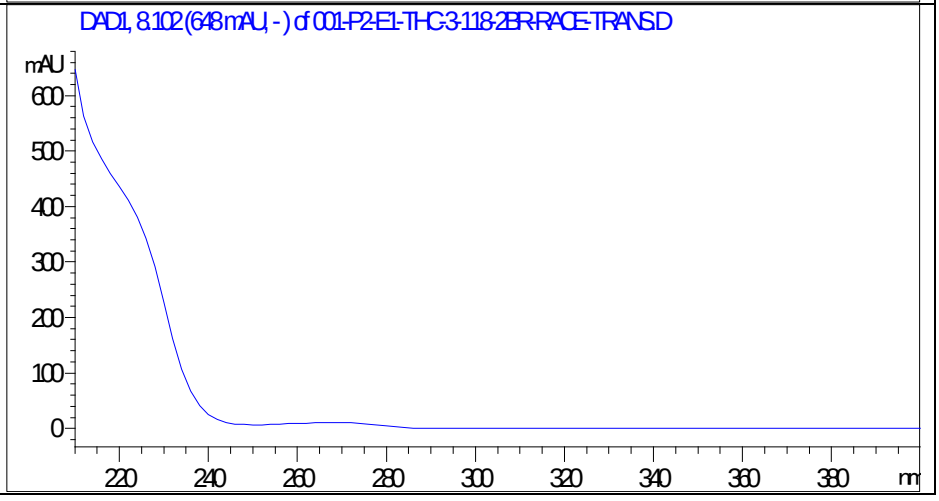
UV spectrum of the peak at 7.639 min.

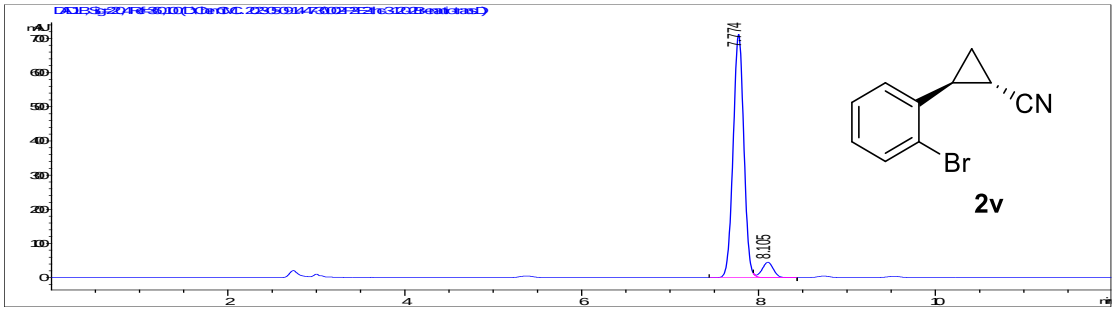




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

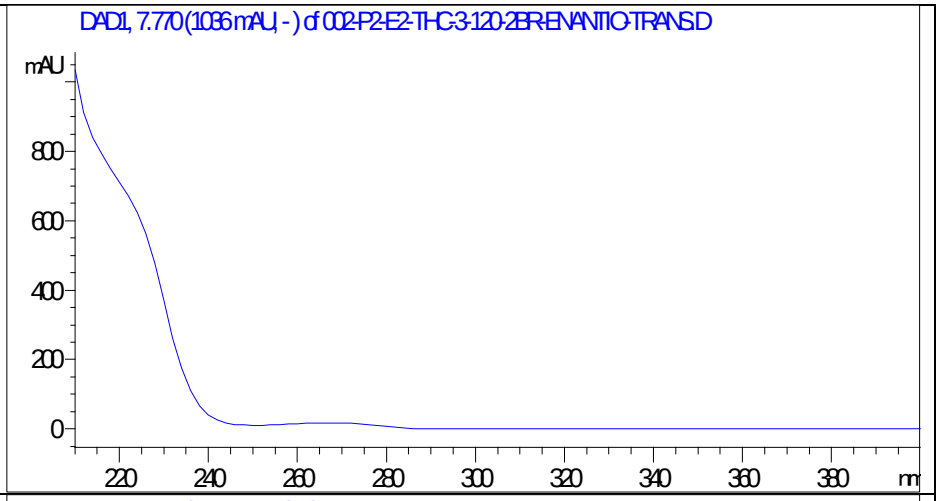
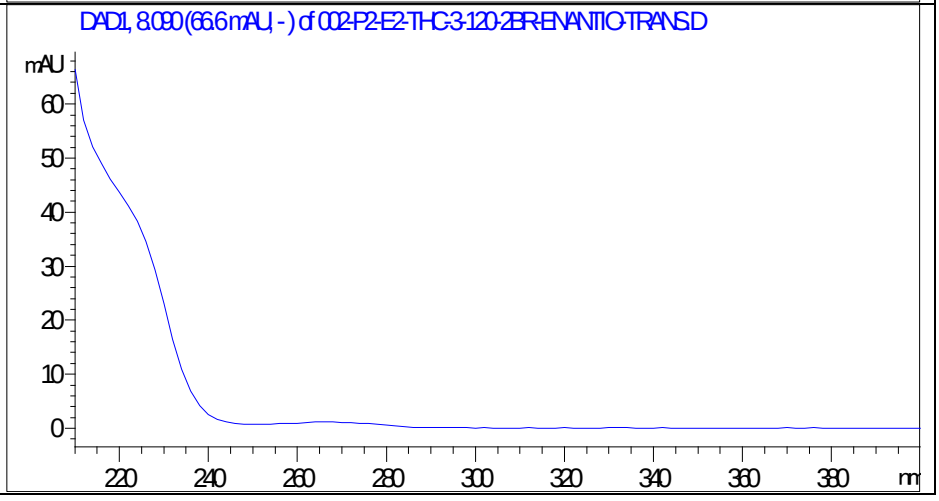
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.772	BV	0.1302	3797.23901	451.33765	49.8960
2	8.104	VV	0.1363	3813.06665	434.93875	50.1040
Totals :				7610.30566	886.27640	

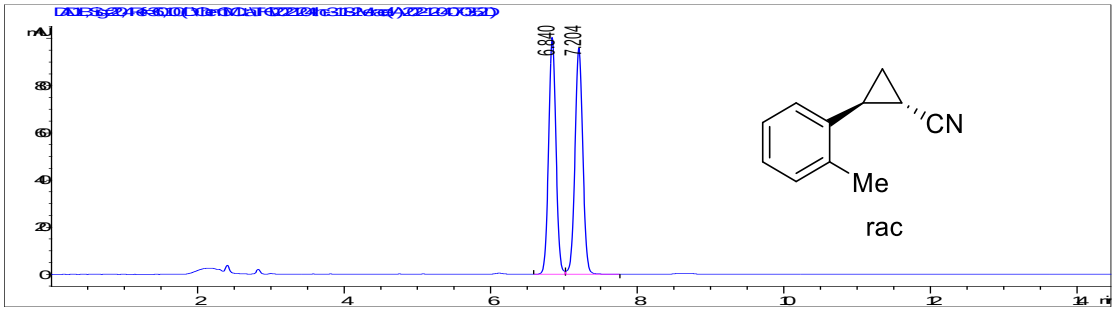
UV spectrum of the peak at 7.769 min.	
UV spectrum of the peak at 8.102 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.774	BV R	0.1304	6005.46777	712.33051	93.9152
2	8.105	VB E	0.1353	389.09775	44.83159	6.0848
Totals :				6394.56552	757.16210	

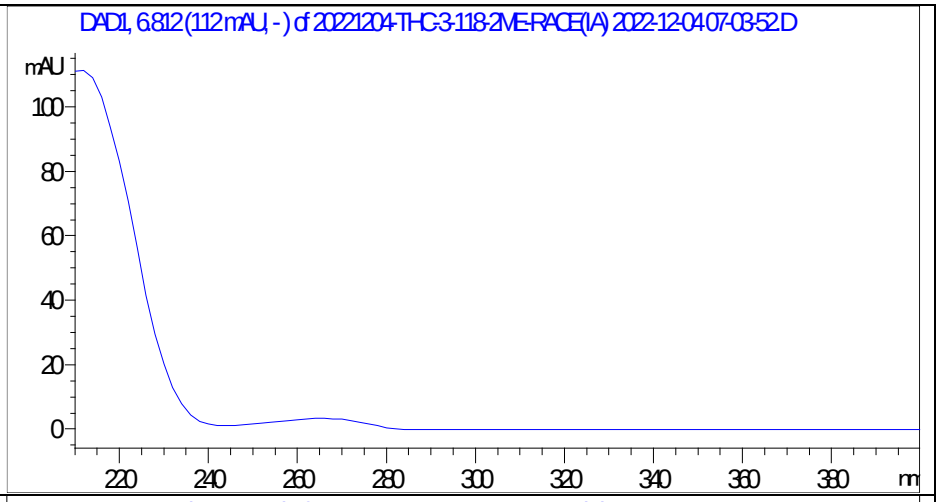
UV spectrum of the peak at 7.770 min.	
UV spectrum of the peak at 8.090 min.	



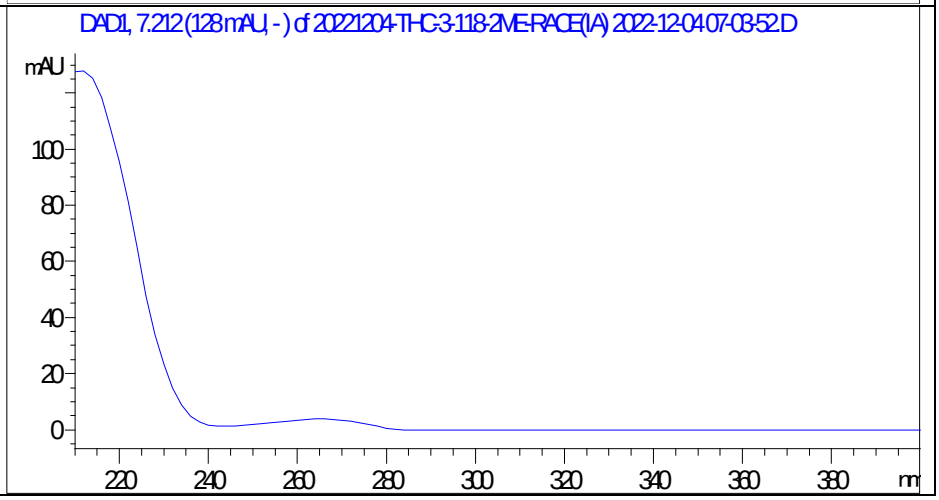
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

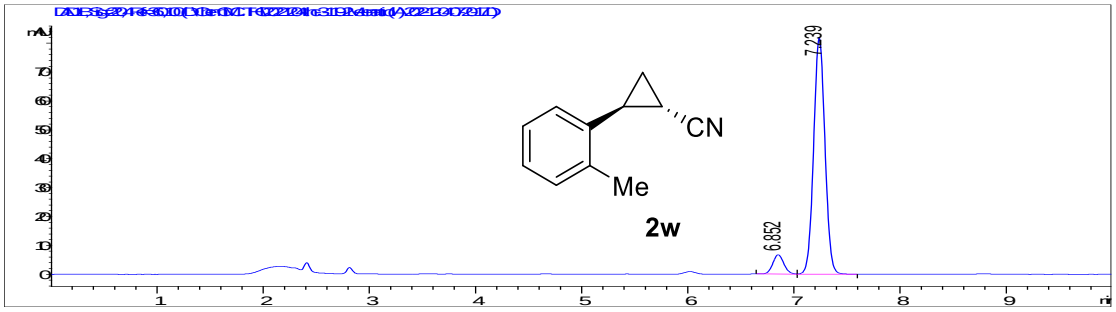
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.840	BV	0.1071	697.29077	100.31239	49.5165
2	7.204	VB	0.1144	710.90729	96.02797	50.4835

UV spectrum of the peak at 6.812 min.



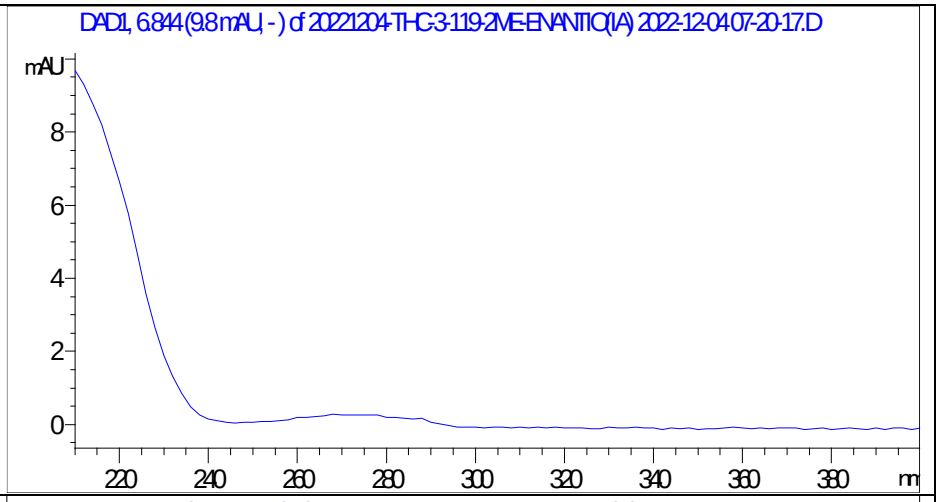
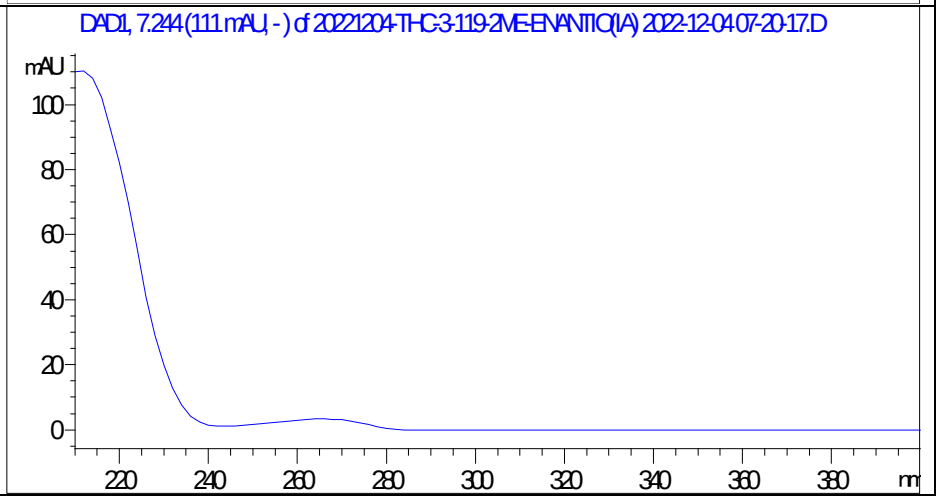
UV spectrum of the peak at 7.212 min.

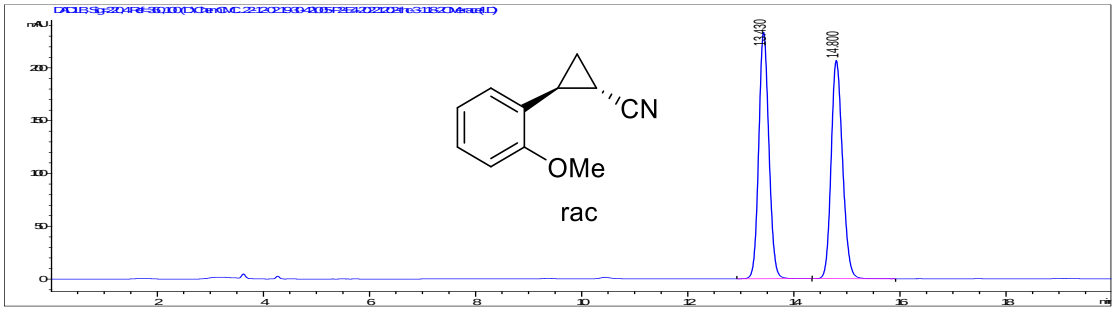




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

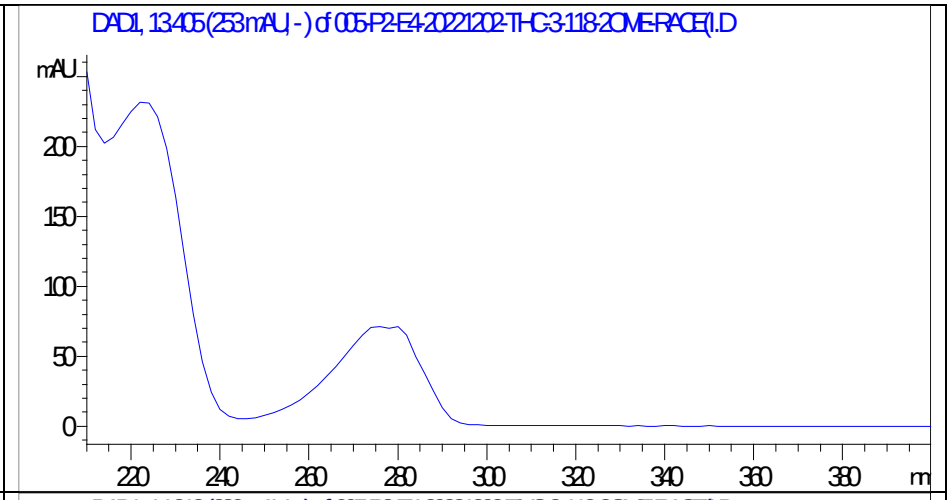
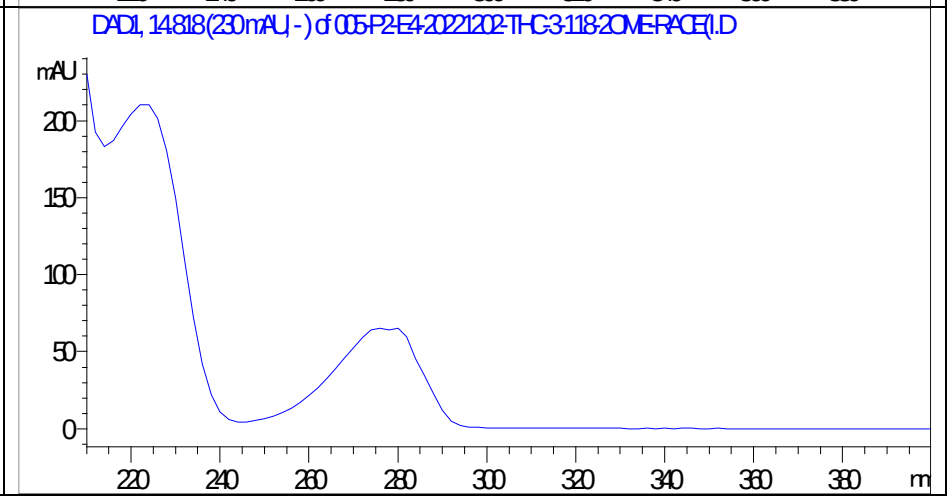
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.852	BV	0.1125	48.29411	6.66576	7.3775
2	7.239	VB	0.1144	606.32281	81.86349	92.6225

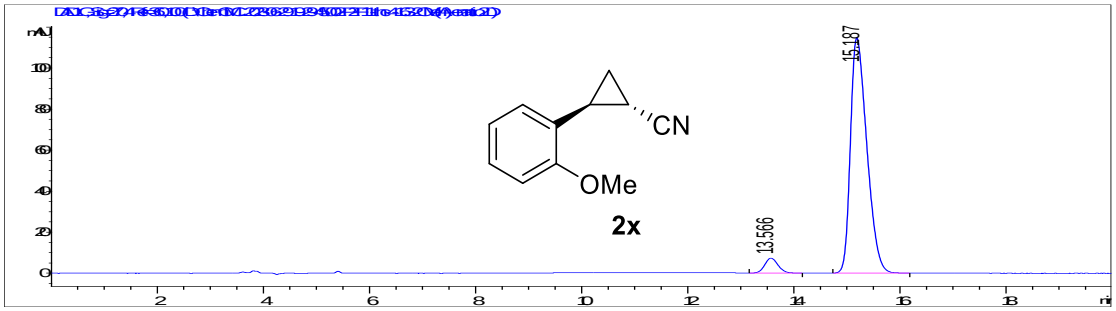
UV spectrum of the peak at 6.844 min.	
UV spectrum of the peak at 7.244 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

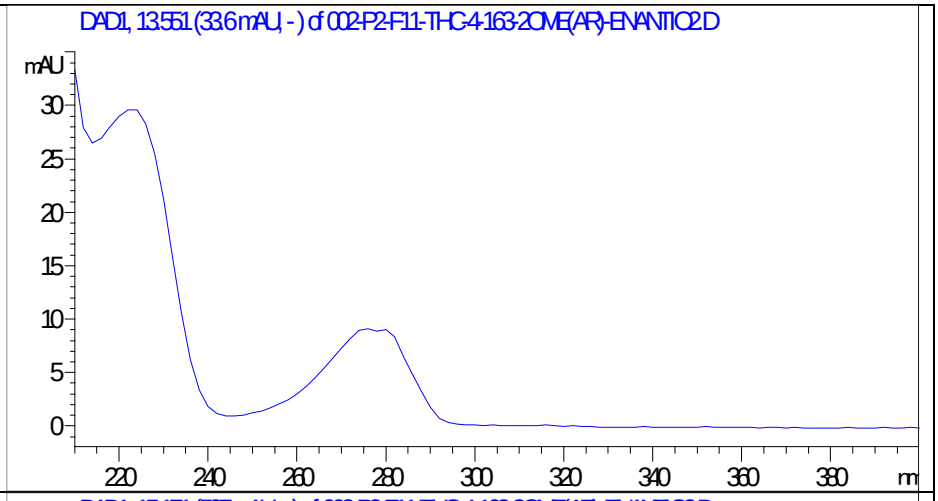
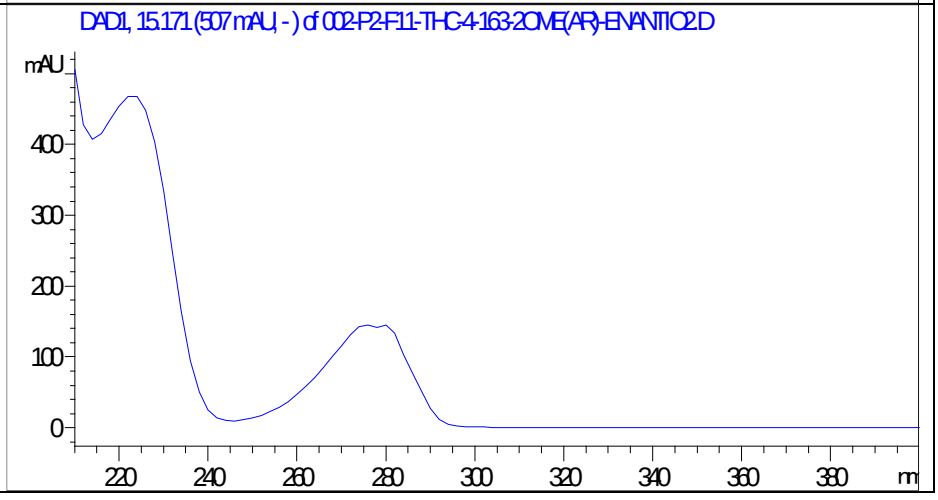
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.430	BB	0.2050	3101.74609	233.49612	50.1144
2	14.800	BB	0.2323	3087.57983	206.67609	49.8856

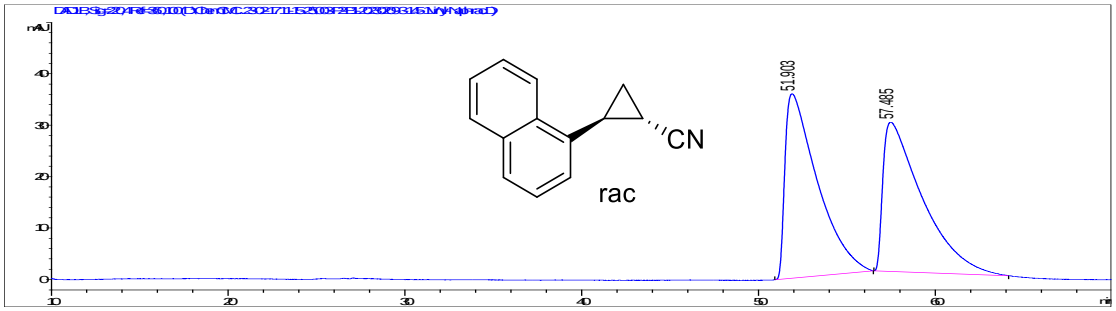
UV spectrum of the peak at 13.405 min.	
UV spectrum of the peak at 14.818 min.	



Signal 3: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.566	BB	0.2677	127.73721	7.31752	4.9328
2	15.187	BB	0.3283	2461.80908	114.76523	95.0672
Totals :				2589.54629	122.08275	

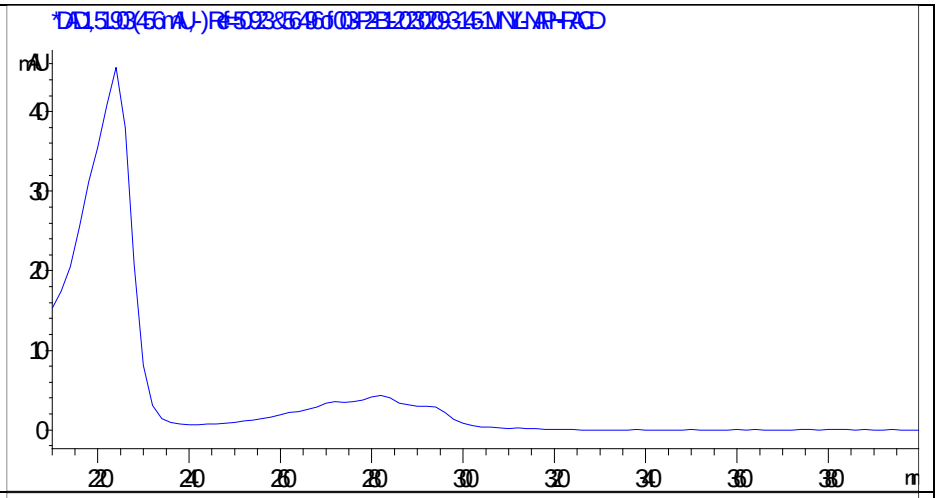
UV spectrum of the peak at 13.551 min.	
UV spectrum of the peak at 15.171 min.	



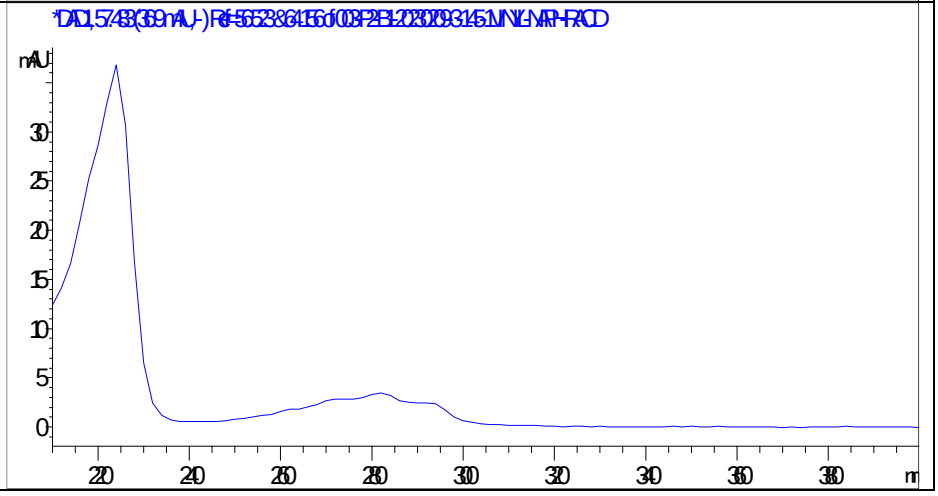
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

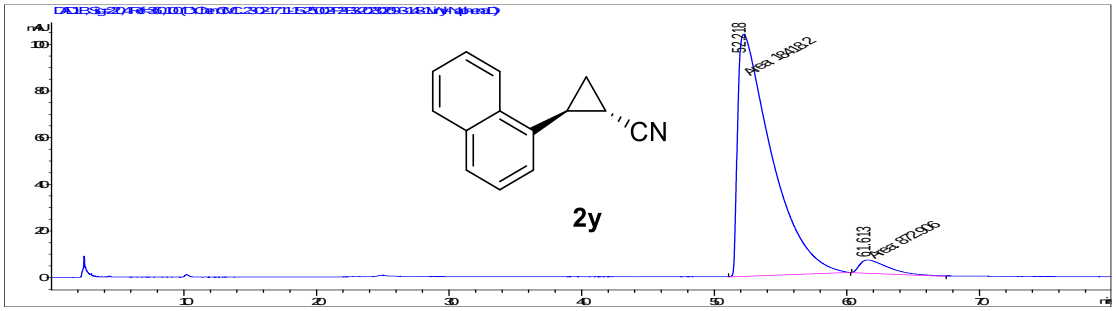
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.903	BB	1.6606	4571.13867	35.87472	50.4606
2	57.485	BB	1.8160	4487.68945	28.99006	49.5394
Totals :				9058.82813	64.86478	

UV spectrum of the peak at 51.903 min.



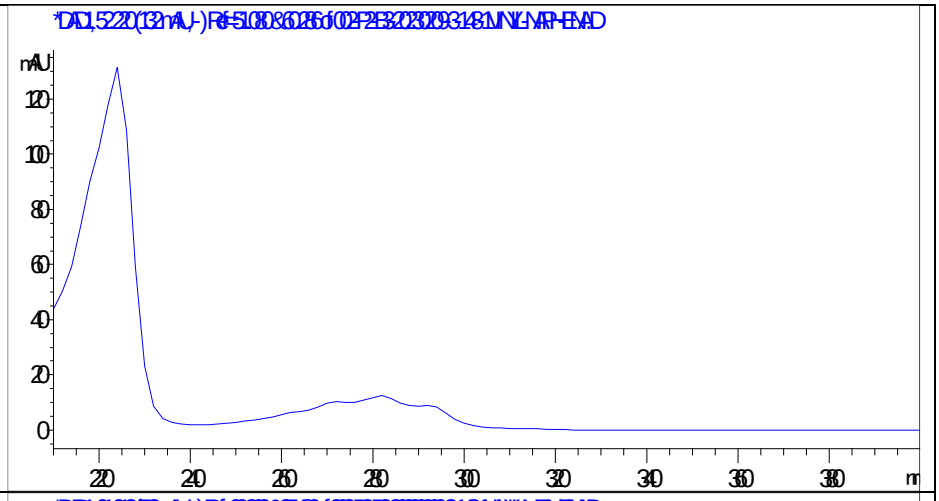
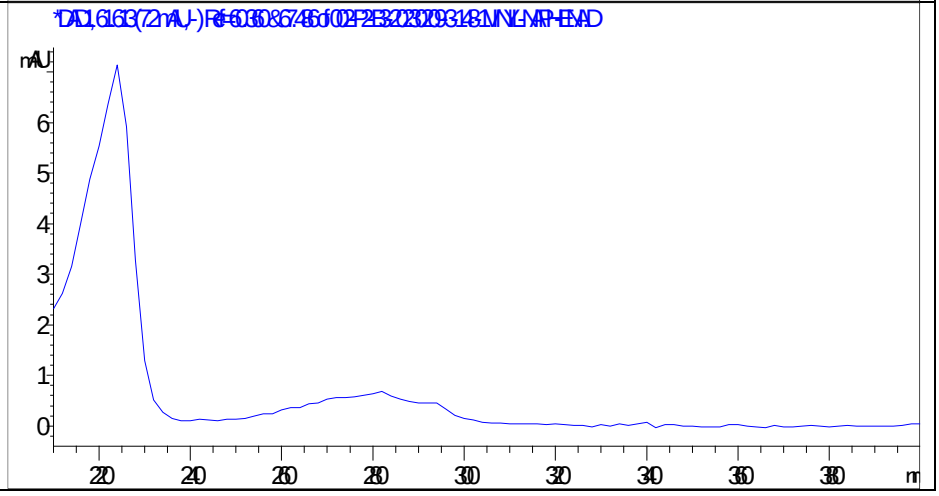
UV spectrum of the peak at 57.483 min.

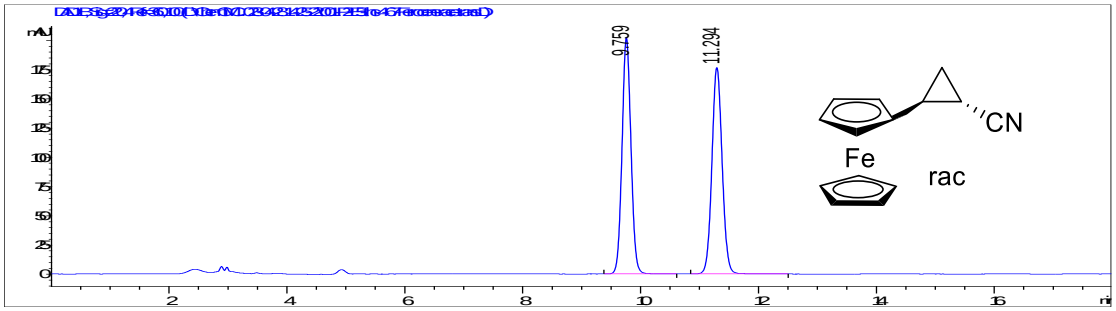




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

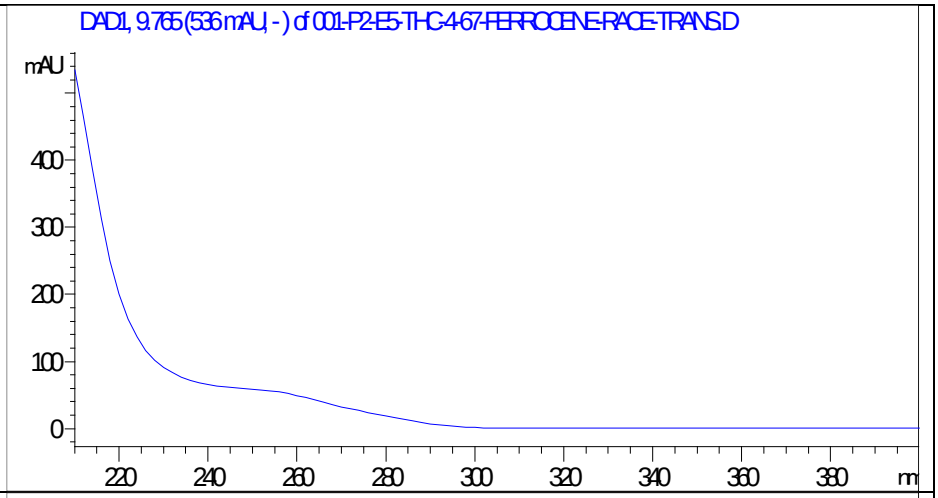
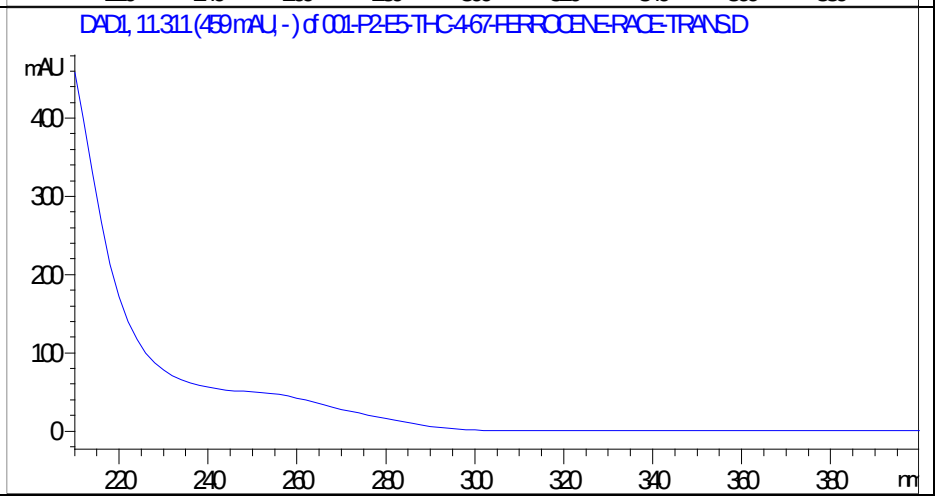
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.218	MM	2.9606	1.84182e4	103.68552	95.4751
2	61.613	MM	2.5277	872.90637	5.75550	4.5249
Totals :				1.92911e4	109.44102	

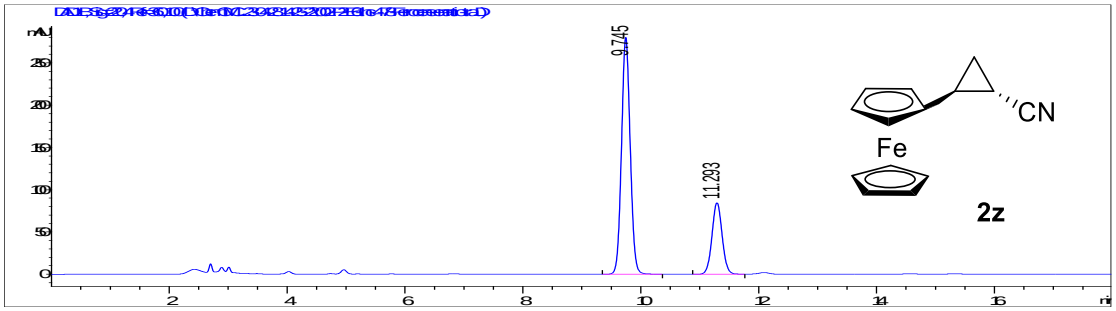
UV spectrum of the peak at 52.220 min.	
UV spectrum of the peak at 61.613 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.759	BB	0.1628	2127.03174	202.09837	49.9156
2	11.294	BB	0.1891	2134.22119	176.49176	50.0844
Totals :				4261.25293	378.59013	

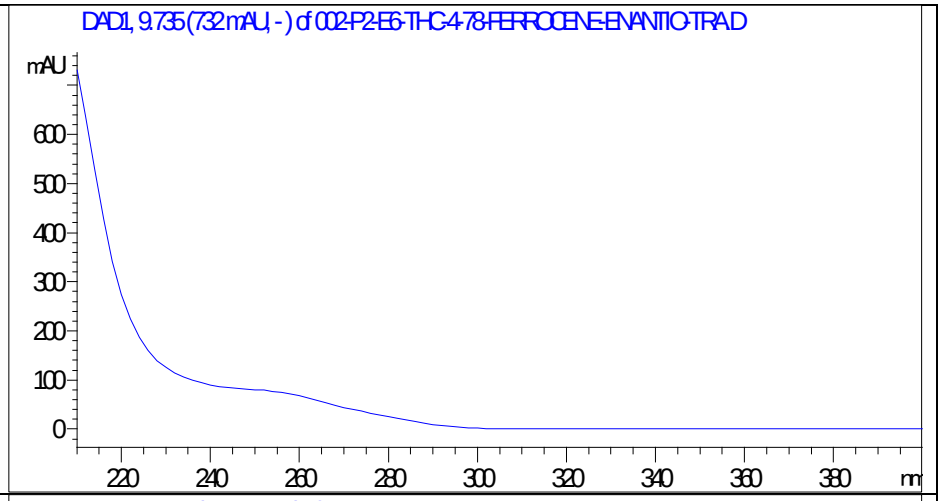
UV spectrum of the peak at 9.765 min.	
UV spectrum of the peak at 11.311 min.	



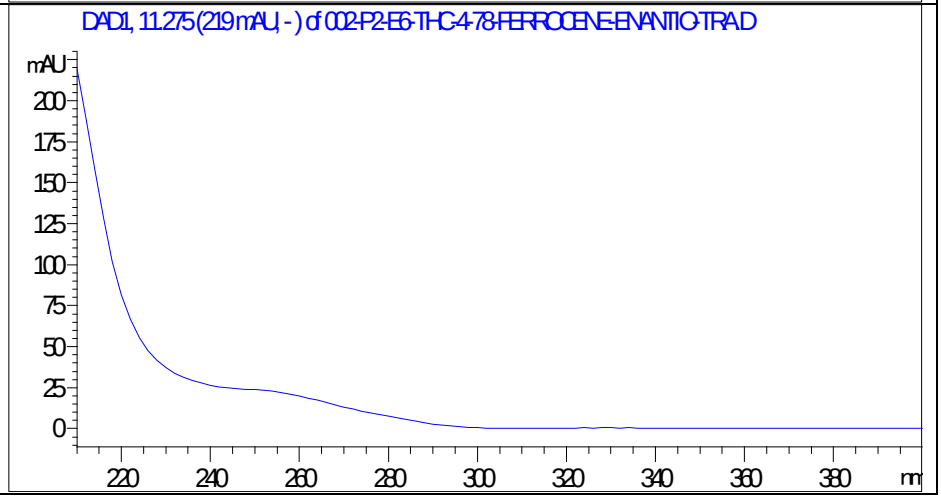
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

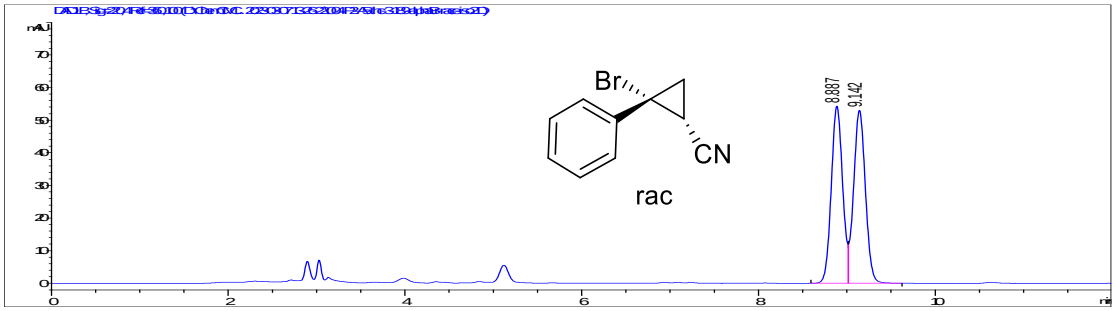
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.745	BB	0.1598	2874.11719	280.00967	73.9844
2	11.293	BB	0.1855	1010.64520	84.50397	26.0156
Totals :				3884.76239	364.51364	

UV spectrum of the peak at 9.735 min.



UV spectrum of the peak at 11.275 min.

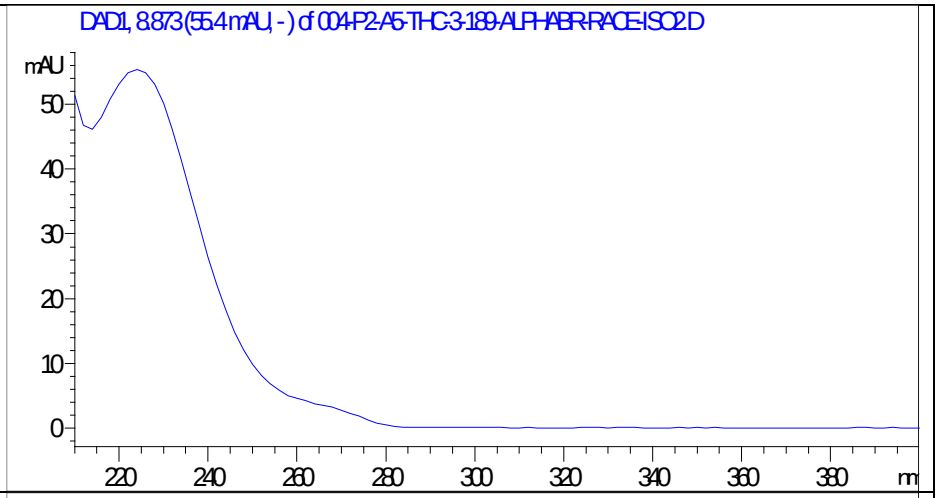




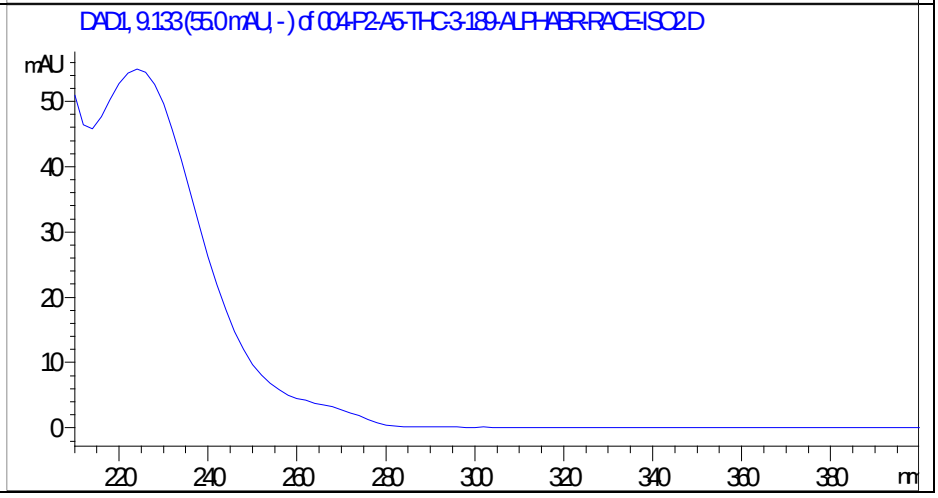
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

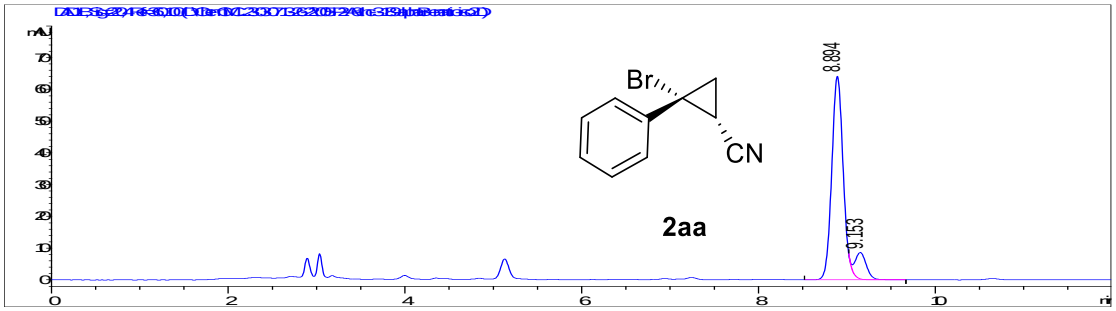
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.887	BV	0.1381	484.47955	54.32221	49.5650
2	9.142	VB	0.1444	492.98447	53.04028	50.4350
Totals :				977.46402	107.36248	

UV spectrum of the peak at 8.873 min.



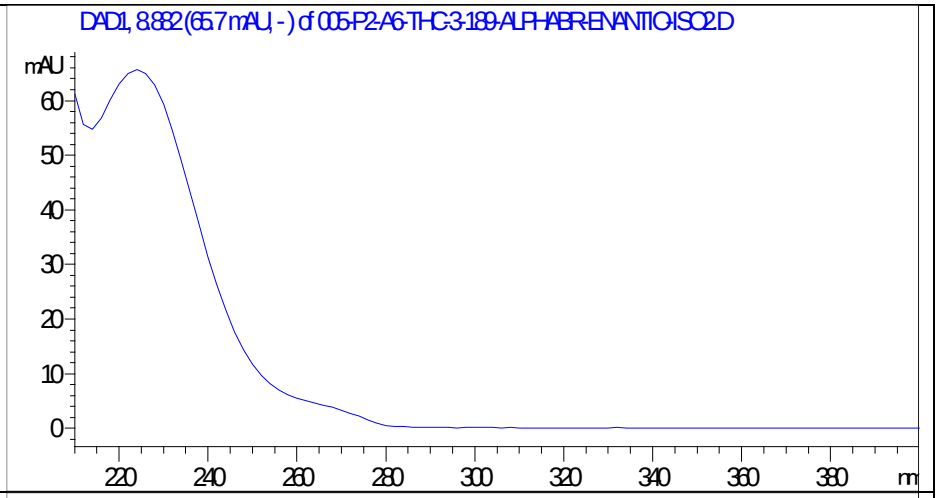
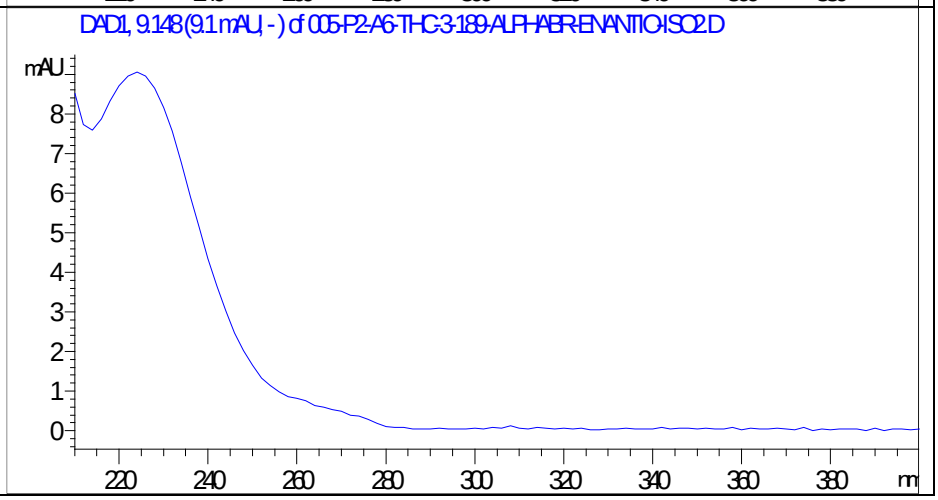
UV spectrum of the peak at 9.133 min.

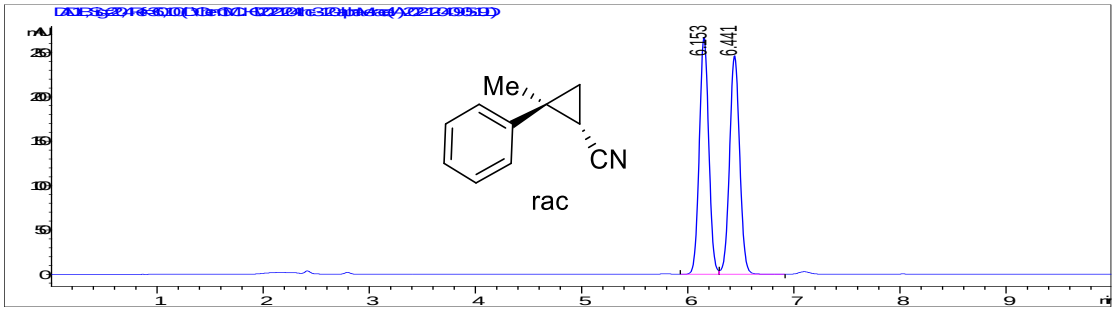




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

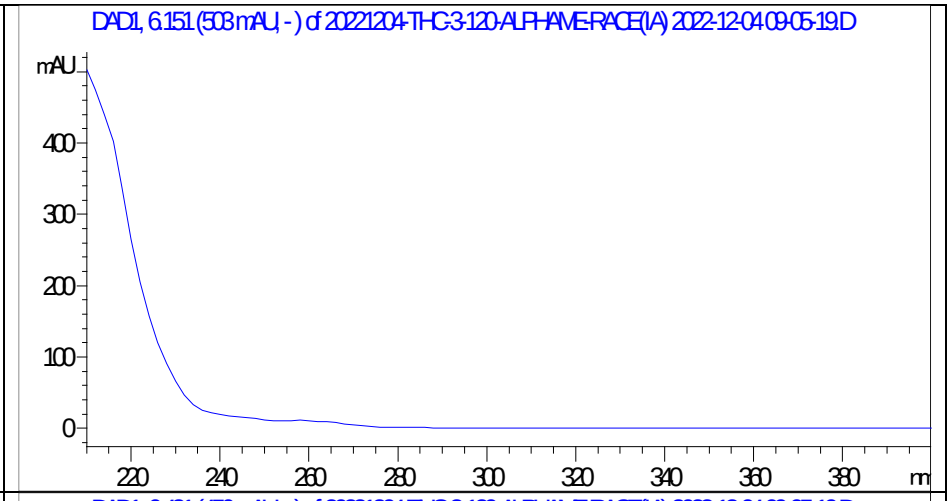
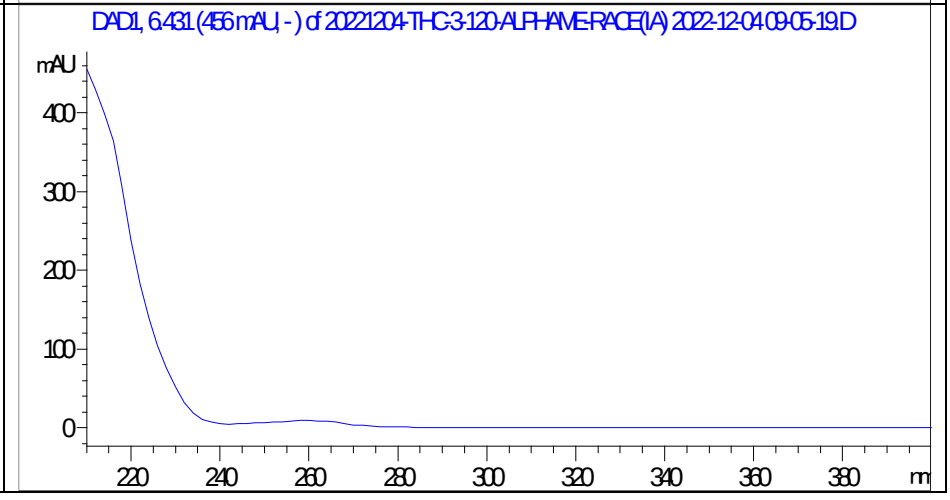
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.894	BV R	0.1394	579.69989	64.16592	88.8201
2	9.153	VB E	0.1344	72.96787	8.31648	11.1799
Totals :				652.66776	72.48240	

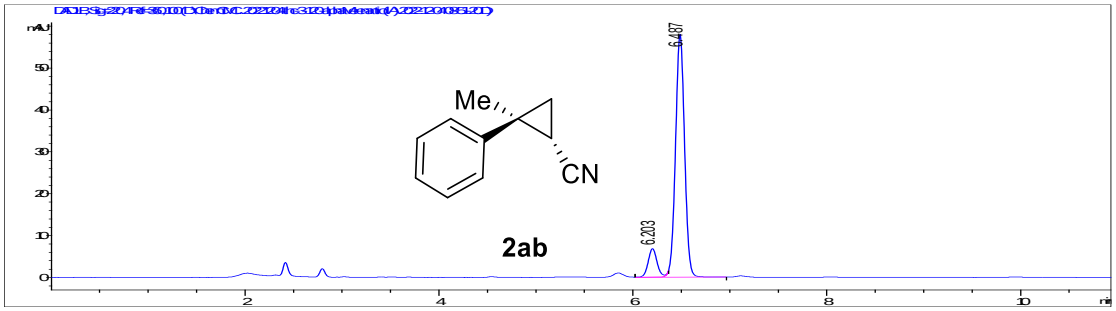
UV spectrum of the peak at 8.882 min.	
UV spectrum of the peak at 9.148 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.153	BV	0.0960	1647.75720	266.89063	50.2155
2	6.441	VB	0.1013	1633.61365	246.65681	49.7845
Totals :				3281.37085	513.54744	

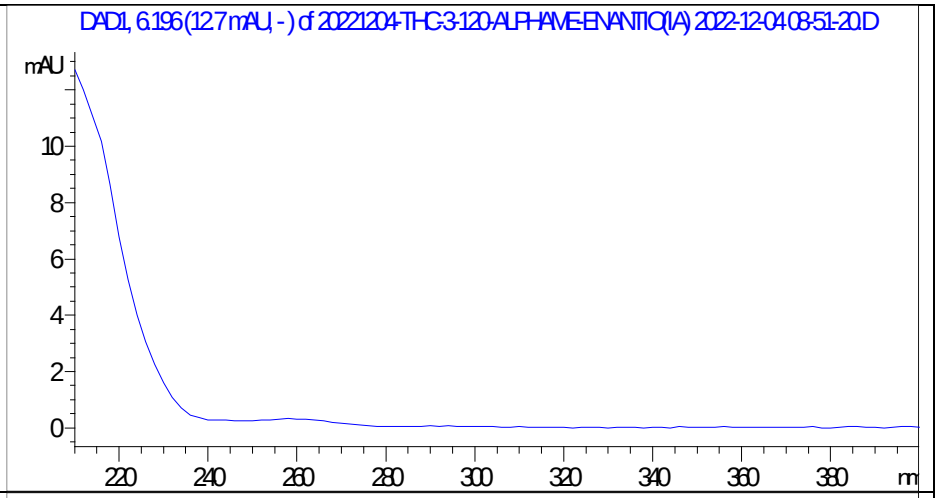
UV spectrum of the peak at 6.151 min.	
UV spectrum of the peak at 6.431 min.	



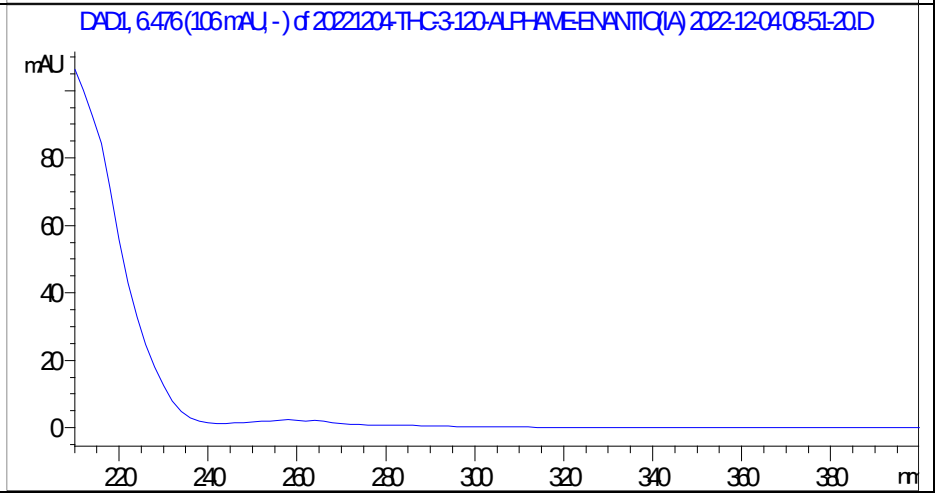
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

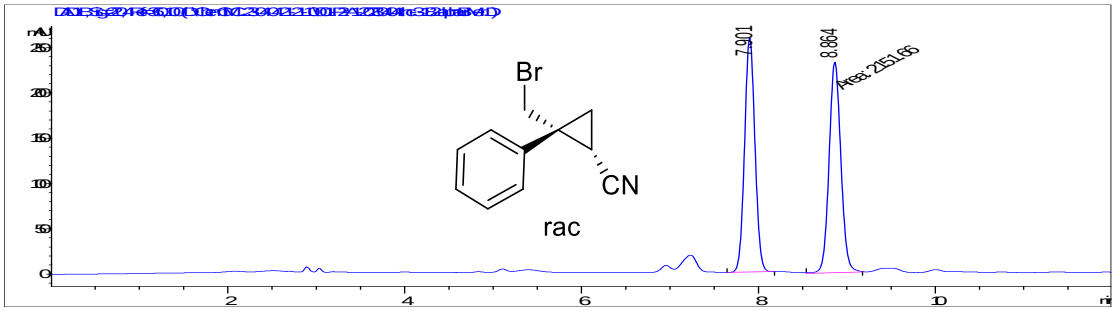
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.203	BV E	0.0977	43.11644	6.82424	10.2652
2	6.487	VB R	0.0998	376.90762	58.01847	89.7348
Totals :				420.02407	64.84271	

UV spectrum of the peak at 6.196 min.



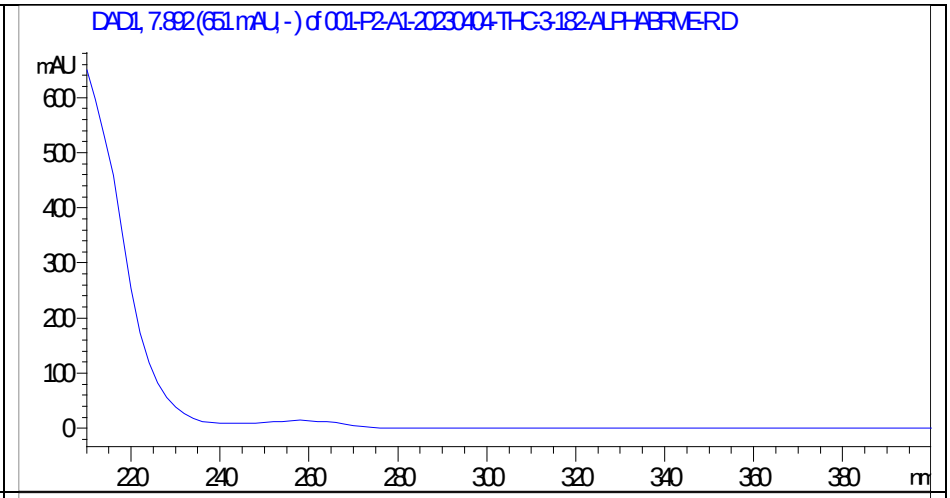
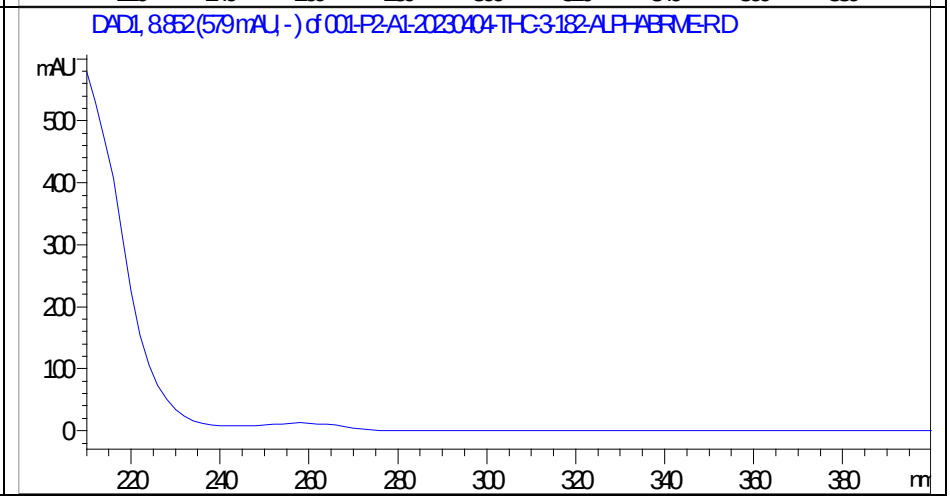
UV spectrum of the peak at 6.476 min.



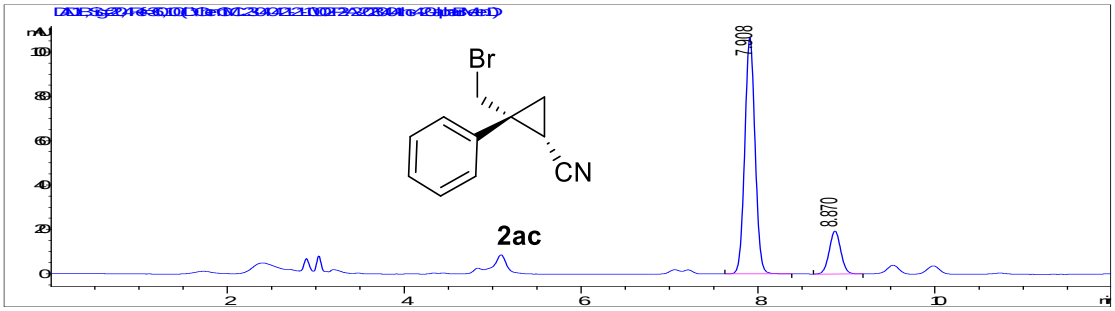


Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.901	BB	0.1270	2108.15820	258.87531	49.4894
2	8.864	MM	0.1543	2151.65820	232.36948	50.5106
Totals :				4259.81641	491.24478	

UV spectrum of the peak at 7.892 min.	
UV spectrum of the peak at 8.852 min.	

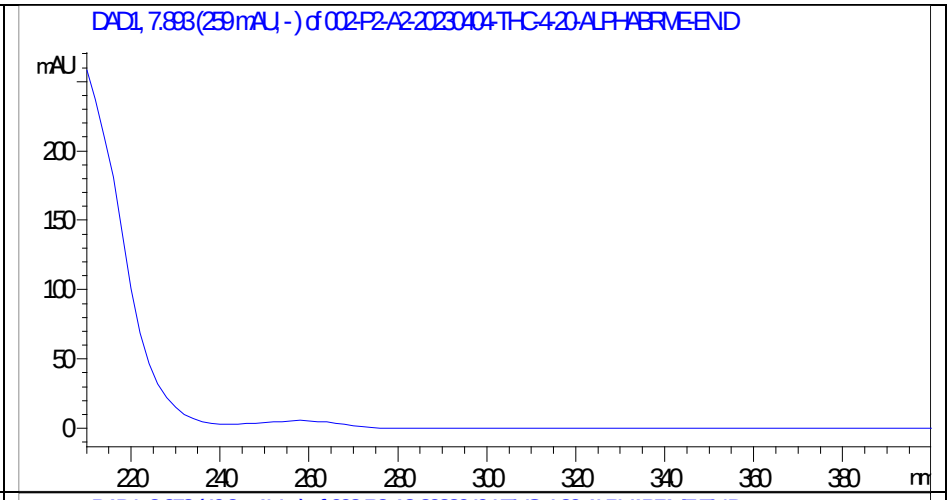
4c



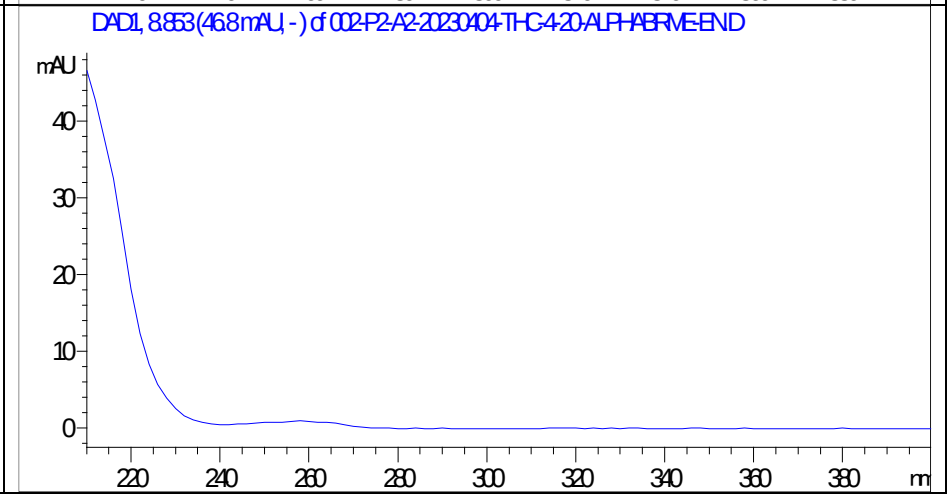
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

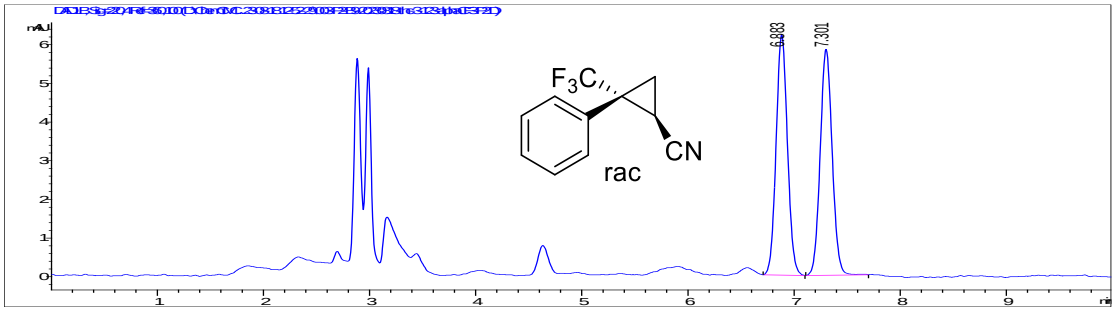
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.908	BB	0.1265	863.15405	106.60487	83.1257
2	8.870	BB	0.1412	175.21829	19.42529	16.8743

UV spectrum of the peak at 7.893 min.



UV spectrum of the peak at 8.853 min.

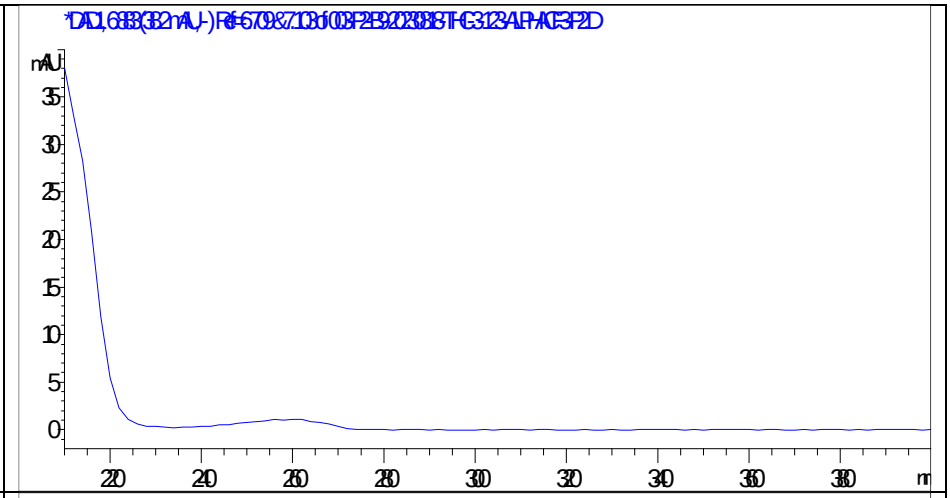




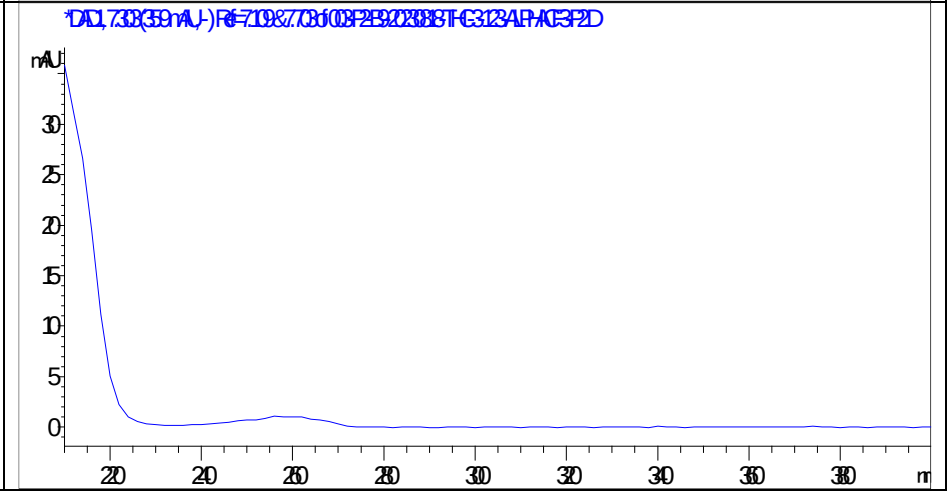
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

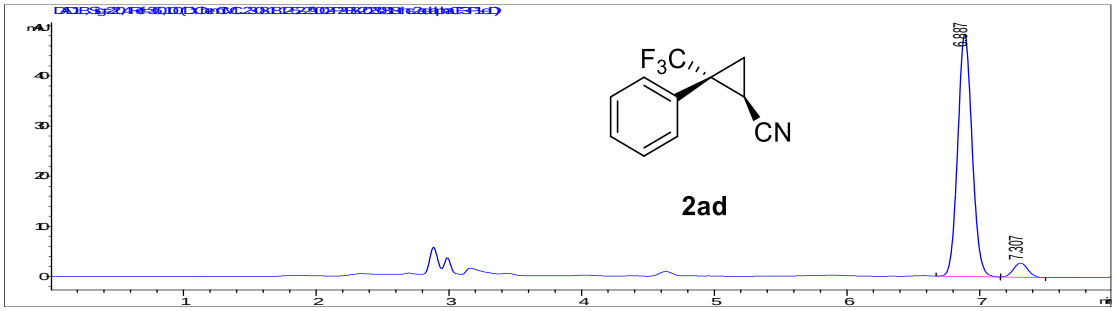
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.883	BB	0.1145	46.13209	6.22356	50.1792
2	7.301	BB	0.1215	45.80258	5.84057	49.8208
Totals :				91.93467	12.06414	

UV spectrum of the peak at 6.883 min.



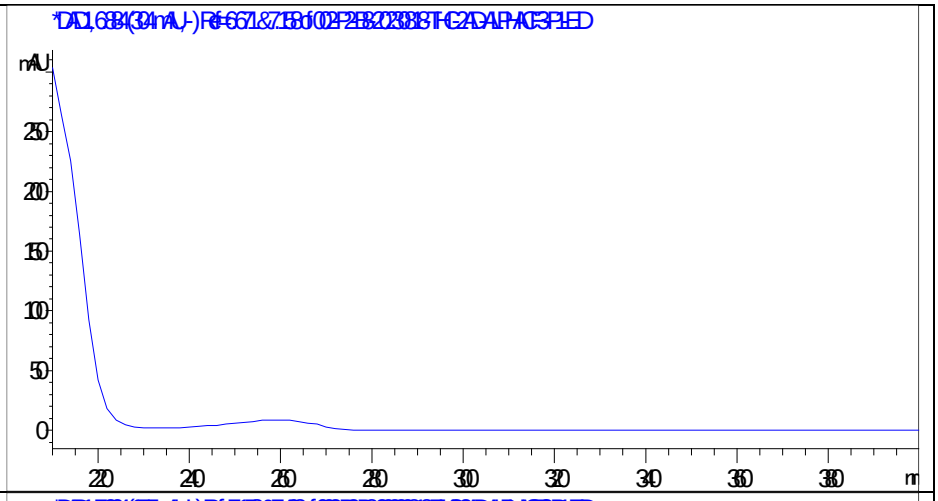
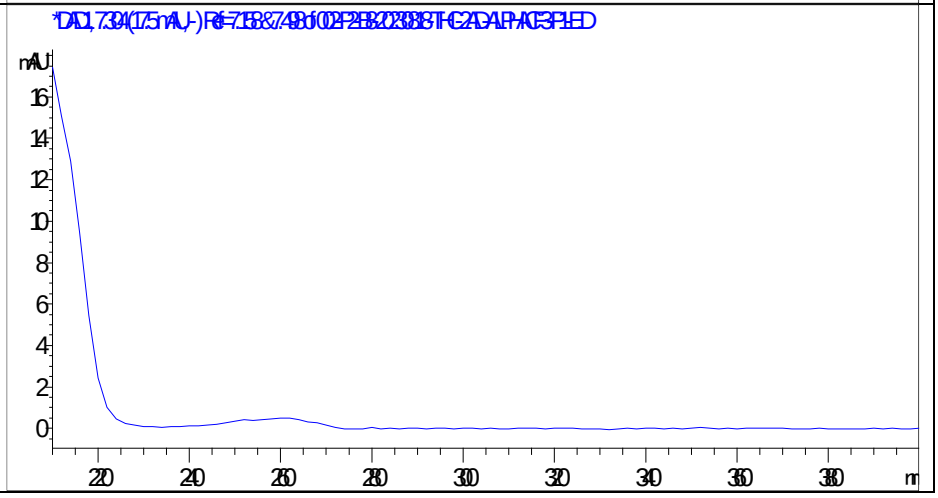
UV spectrum of the peak at 7.303 min.

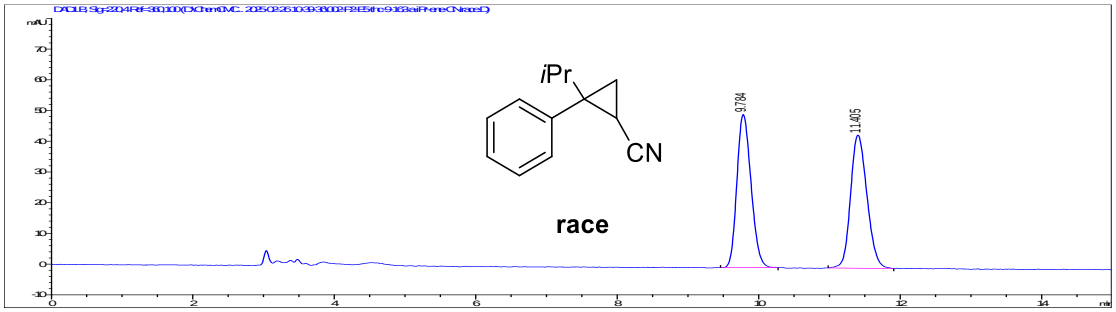




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

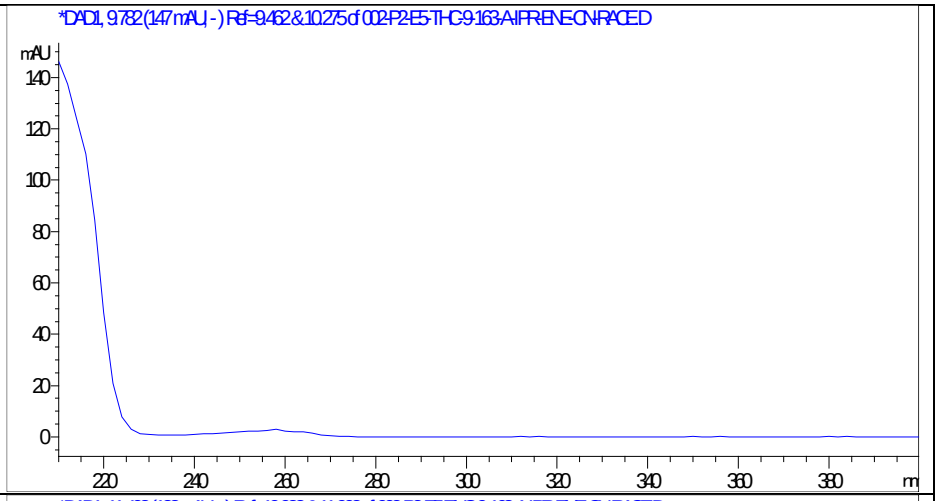
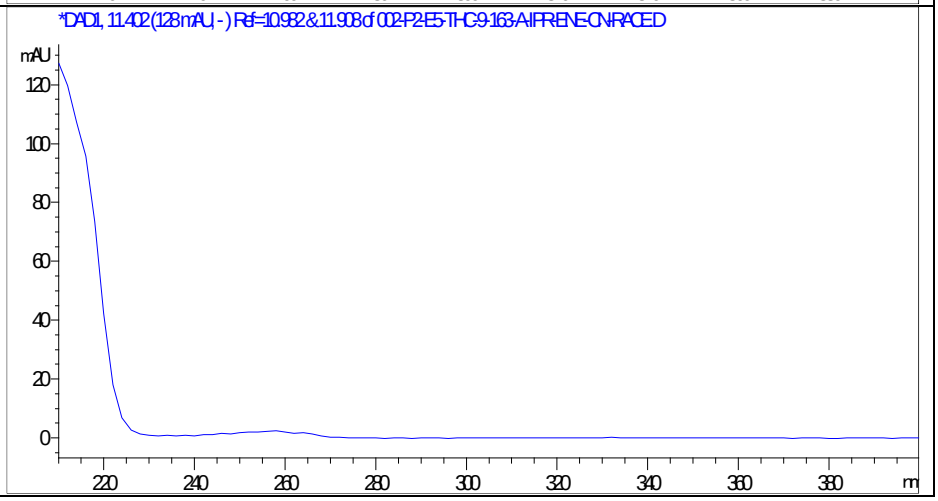
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.887	BB	0.1155	363.06436	48.38609	94.4647
2	7.307	BB	0.1156	21.27419	2.83213	5.5353
Totals :				384.33855	51.21822	

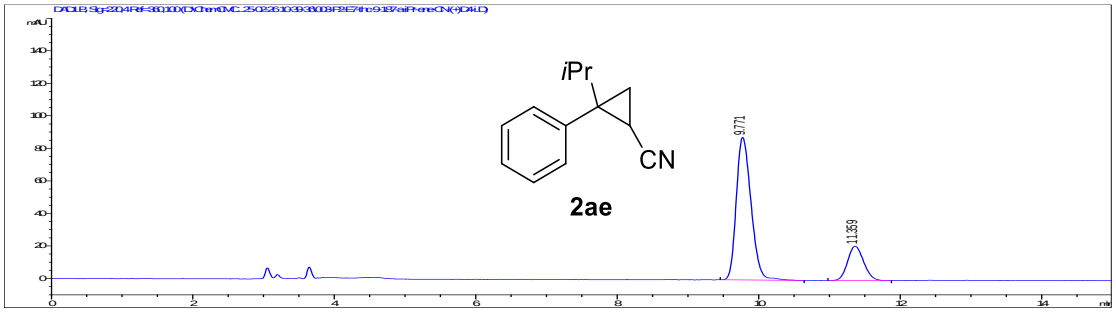
UV spectrum of the peak at 6.884 min.	
UV spectrum of the peak at 7.304 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

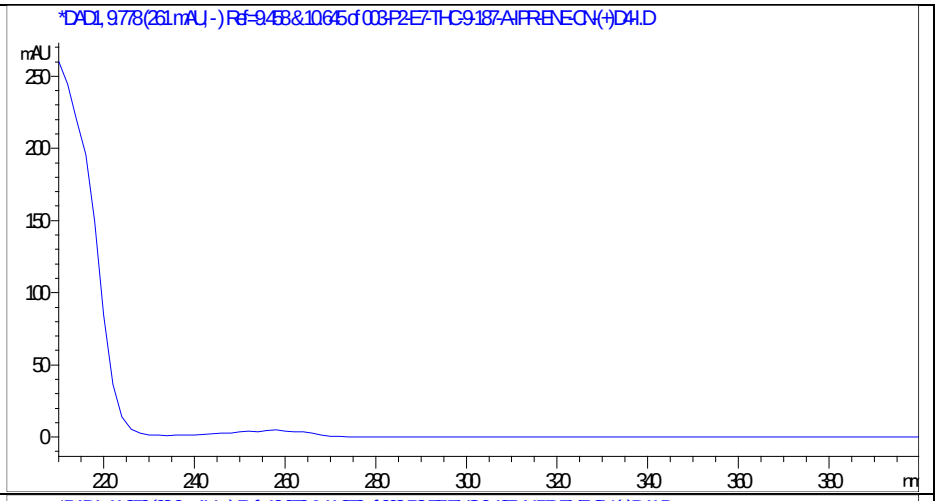
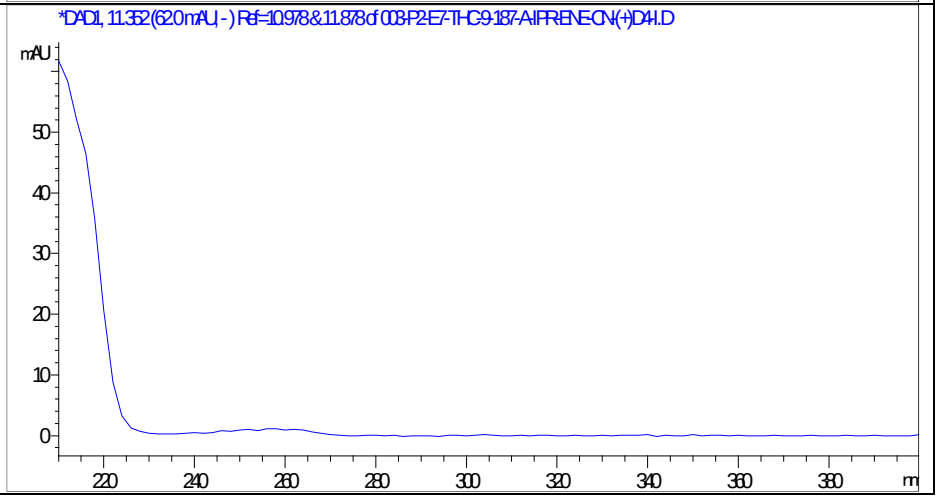
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.784	BB	0.2184	693.74658	49.82636	49.7728
2	11.405	BB	0.2504	700.07880	43.35533	50.2272
Totals :				1393.82538	93.18169	

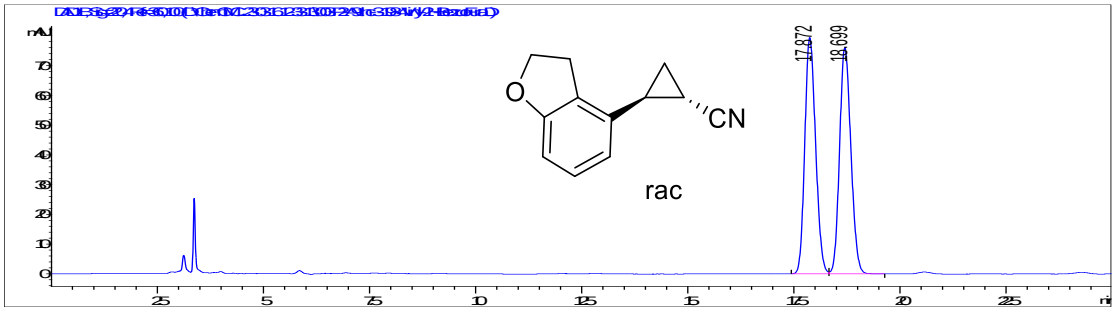
UV spectrum of the peak at 9.782 min.	
UV spectrum of the peak at 11.402 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

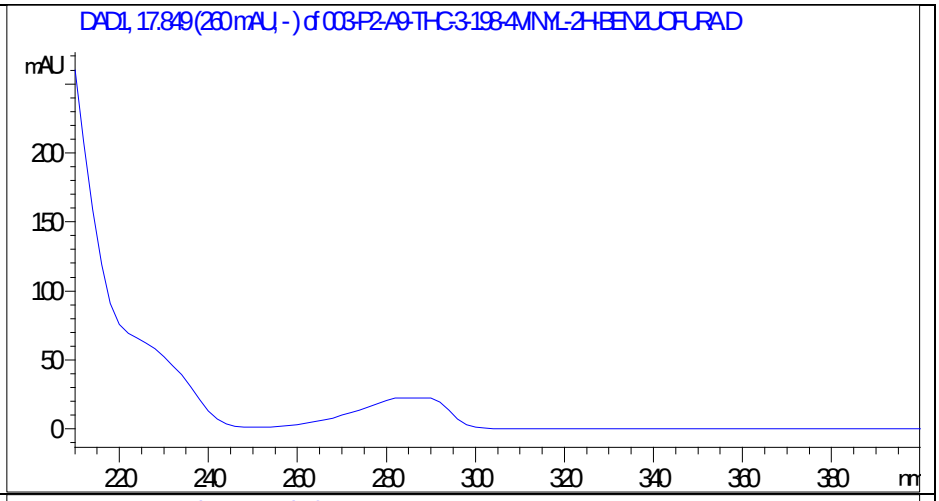
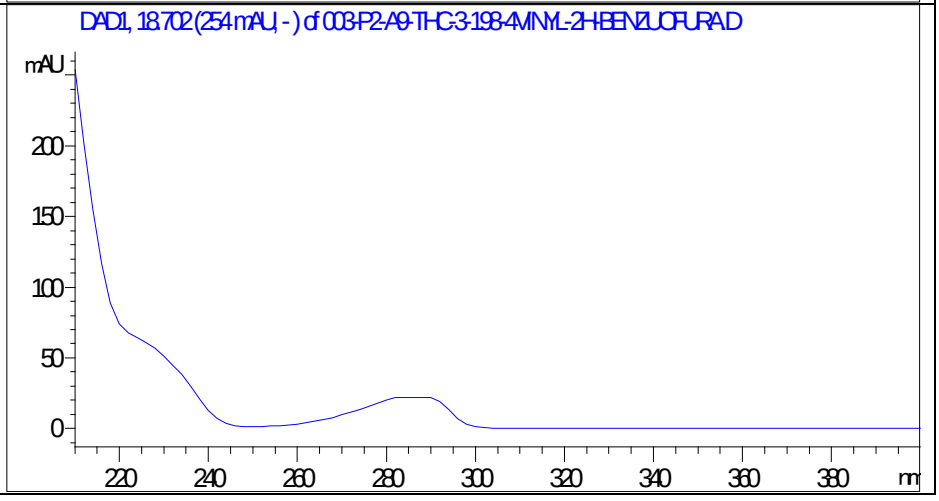
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.771	BB	0.2271	1271.04102	87.68533	79.0813
2	11.359	BB	0.2509	336.21808	21.20934	20.9187
Totals :				1607.25909	108.89466	

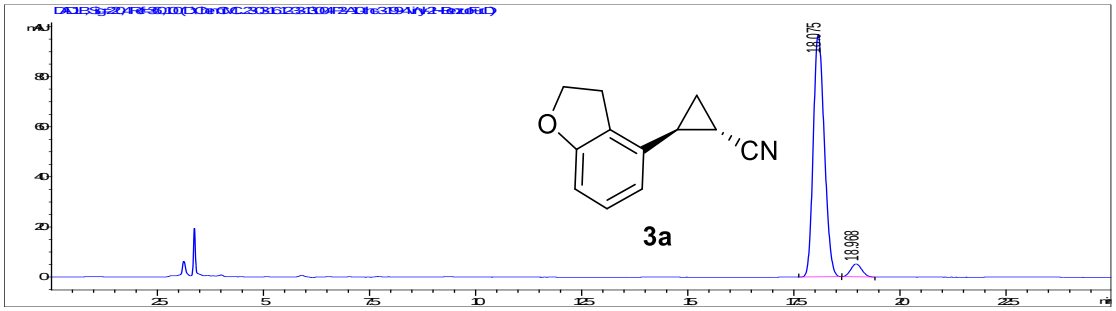
UV spectrum of the peak at 9.778 min.	
UV spectrum of the peak at 11.352 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

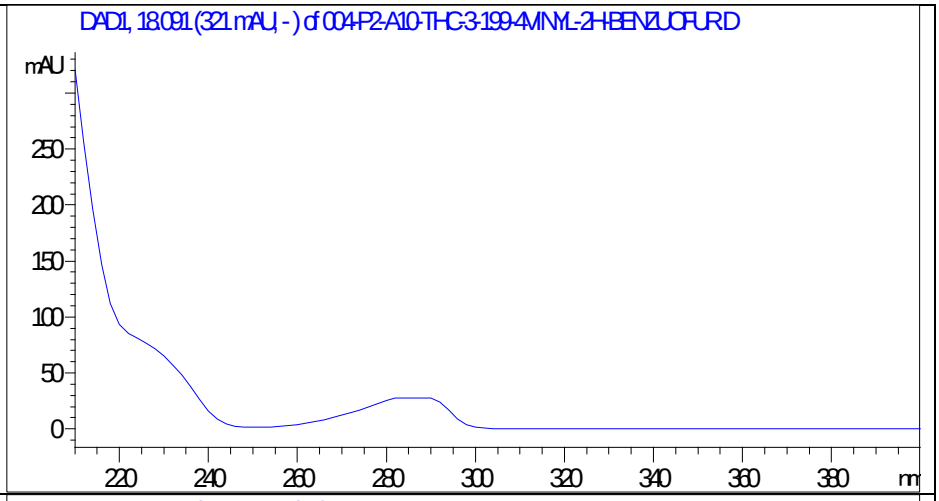
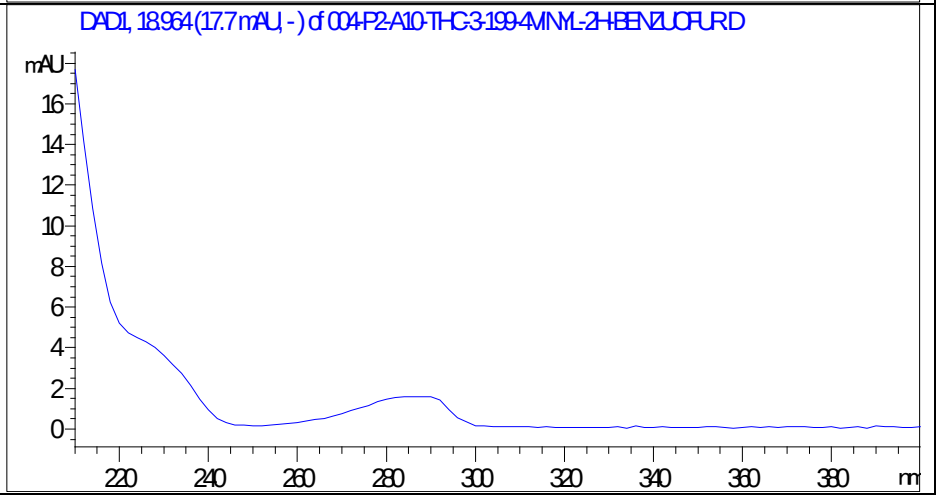
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.872	BV	0.2768	1407.23340	79.38653	49.9152
2	18.699	VB	0.2907	1412.01355	76.02368	50.0848
Totals :				2819.24695	155.41021	

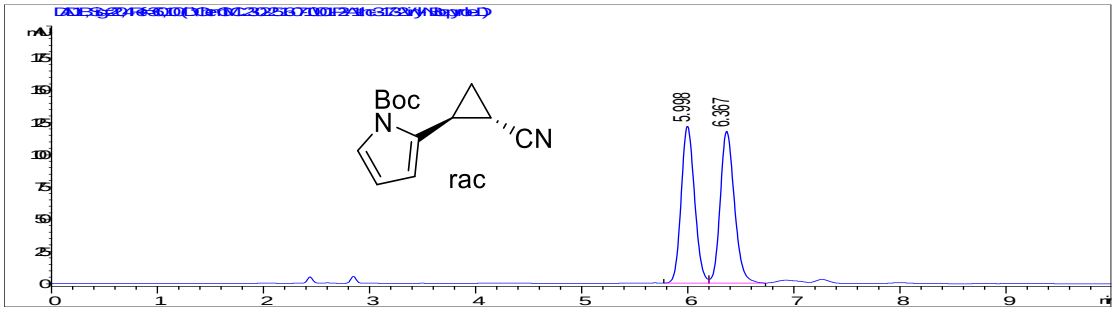
UV spectrum of the peak at 17.849 min.	
UV spectrum of the peak at 18.702 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

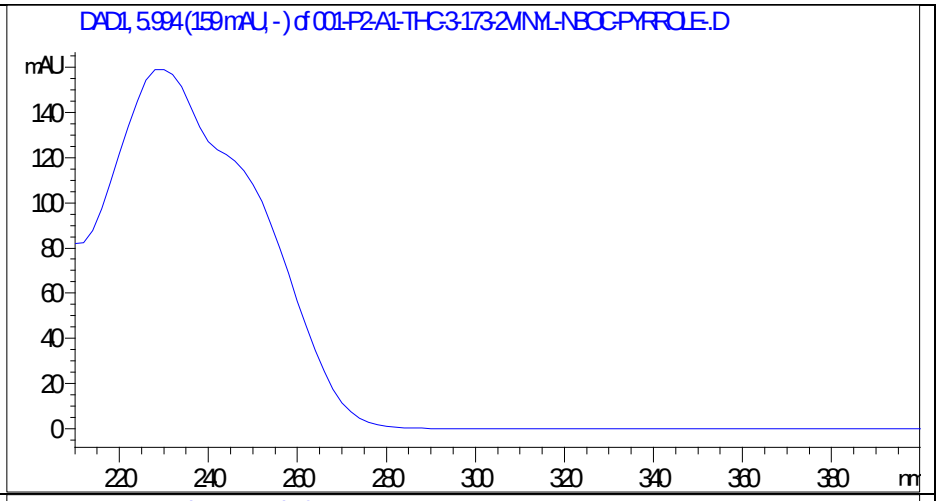
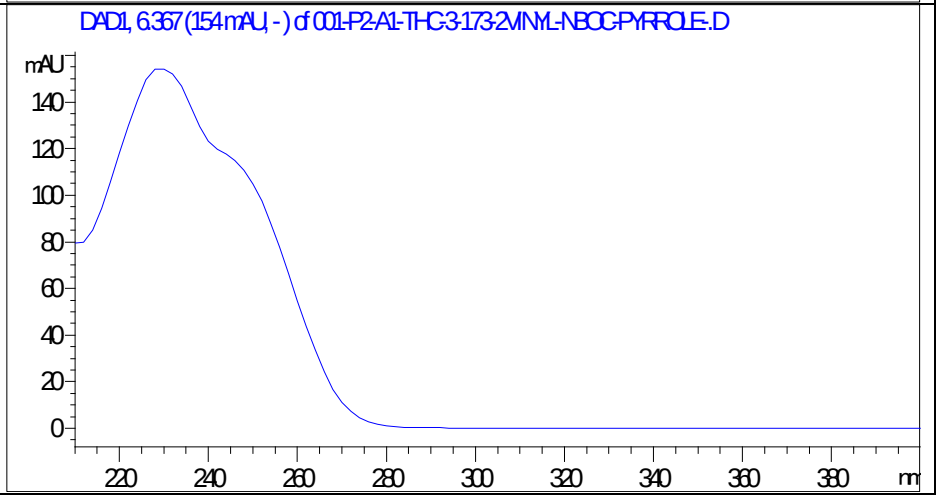
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.075	BB	0.2816	1757.06409	96.85848	94.9425
2	18.968	BB	0.2850	93.59703	5.17640	5.0575
Totals :				1850.66112	102.03488	

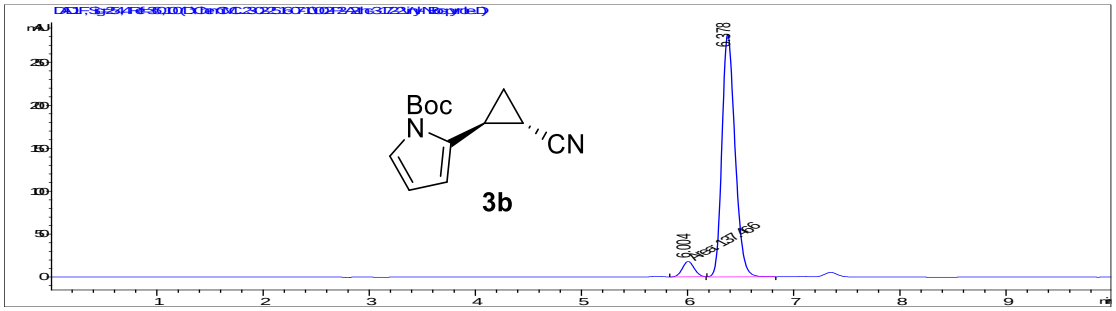
UV spectrum of the peak at 18.091 min.	
UV spectrum of the peak at 18.964 min.	



Signal 2: DAD1 F, Sig=254,4 Ref=360,100

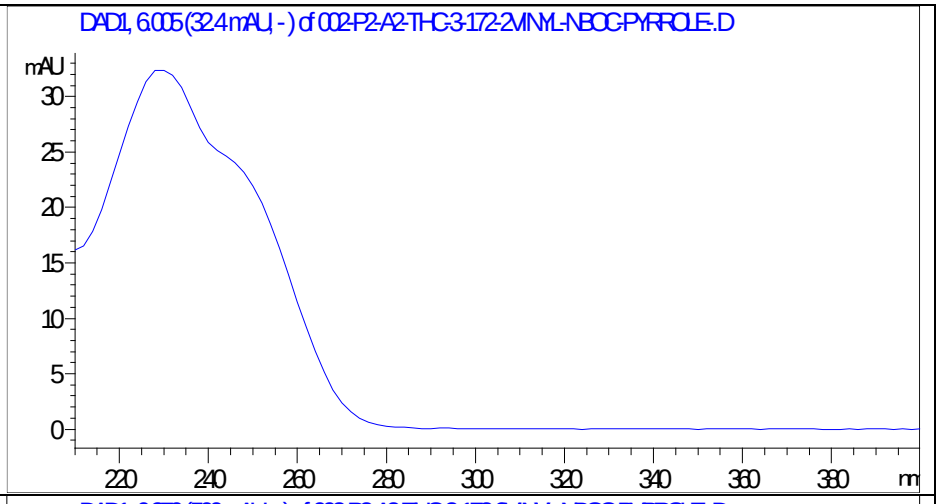
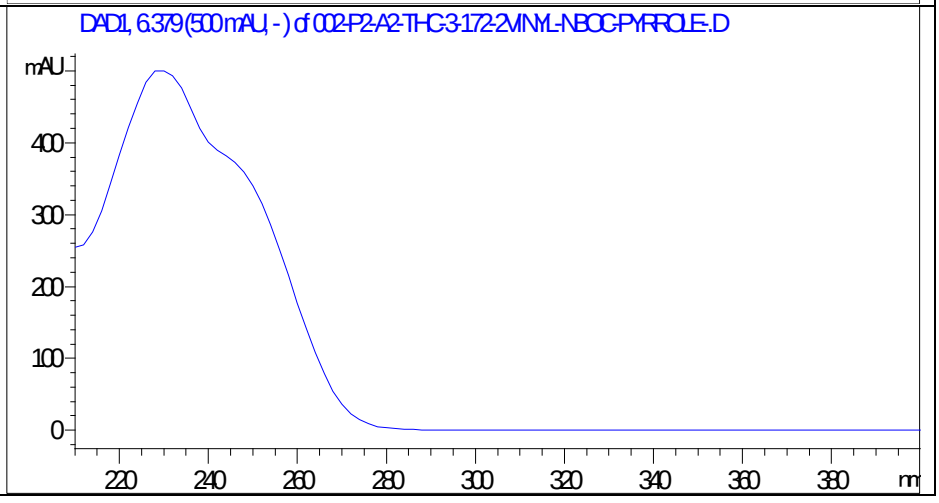
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.997	BV	0.1363	787.65656	89.80572	48.9098
2	6.367	VB	0.1444	822.77008	86.94878	51.0902
Totals :				1610.42664	176.75450	

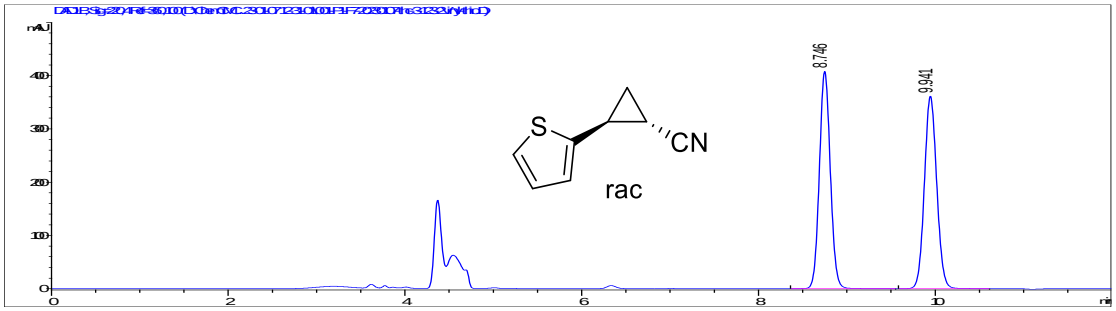
UV spectrum of the peak at 5.994 min.	
UV spectrum of the peak at 6.367 min.	



Signal 2: DAD1 F, Sig=254,4 Ref=360,100

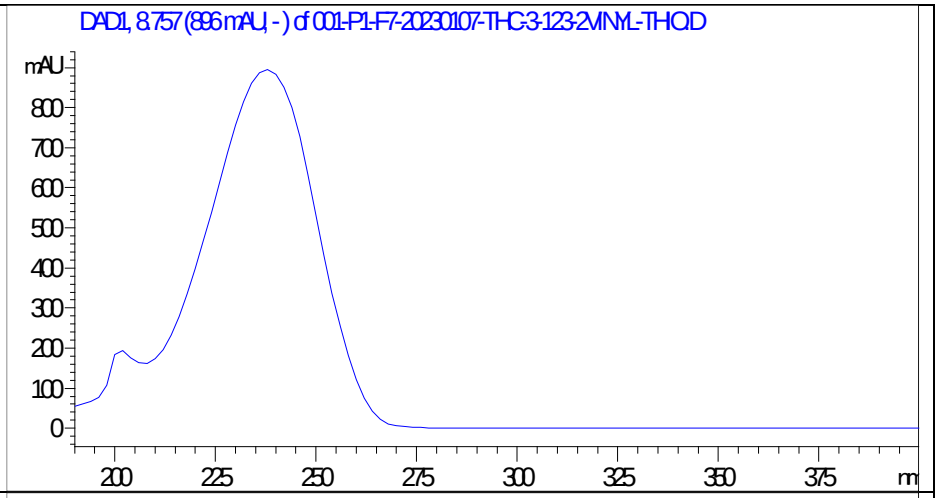
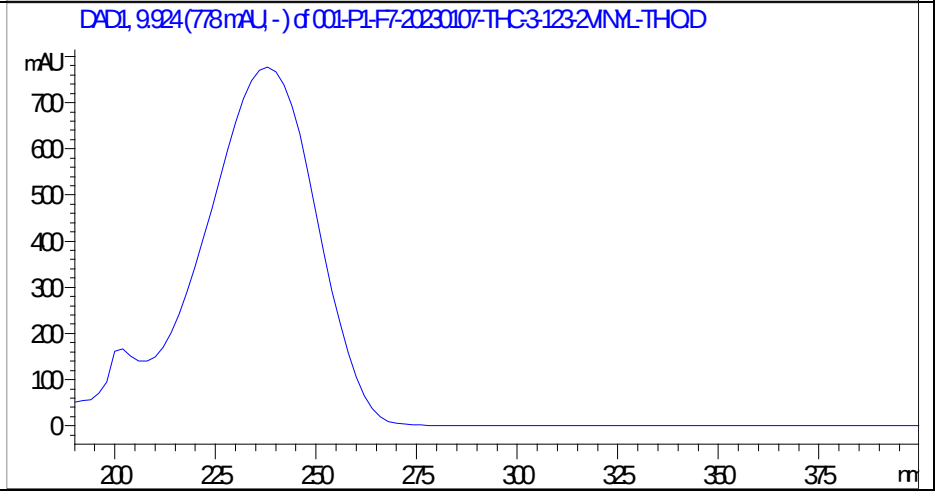
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.004	MM	0.1283	137.46602	17.86091	5.3750
2	6.378	VB	0.1340	2420.02856	282.32422	94.6250

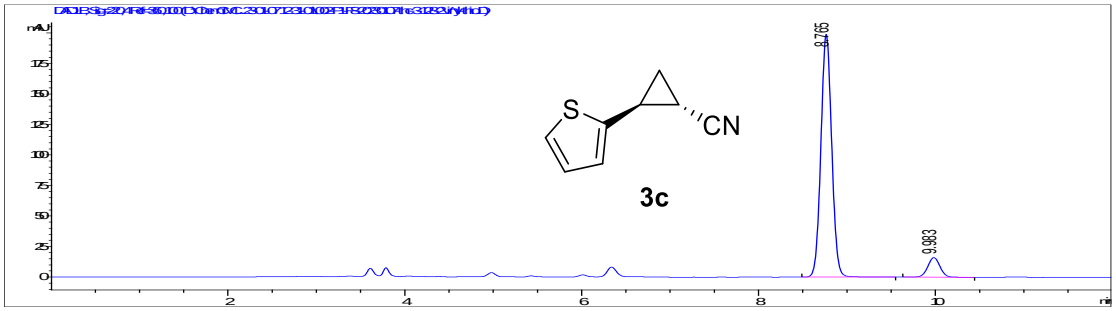
UV spectrum of the peak at 6.005 min.	
UV spectrum of the peak at 6.379 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.746	BB	0.1325	3515.72974	408.13284	50.0248
2	9.941	BB	0.1514	3512.23926	361.39297	49.9752
Totals :				7027.96899	769.52582	

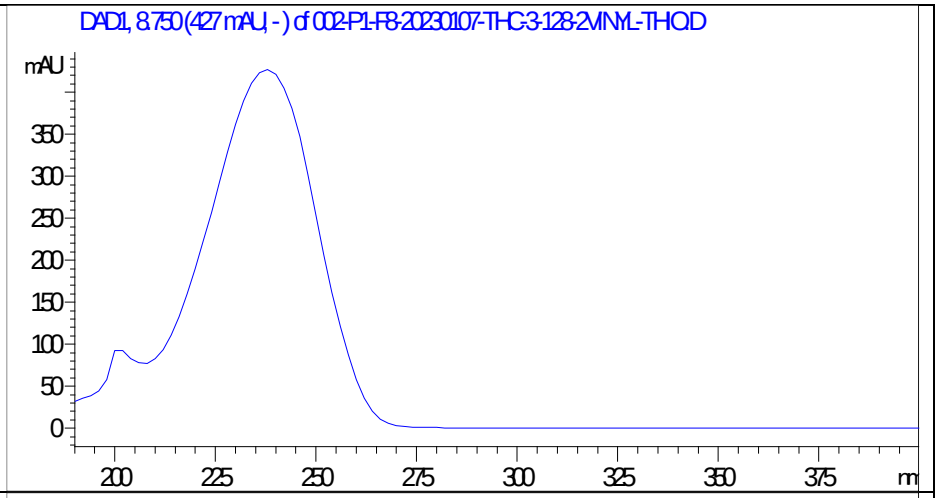
UV spectrum of the peak at 8.757 min.	
UV spectrum of the peak at 9.924 min.	



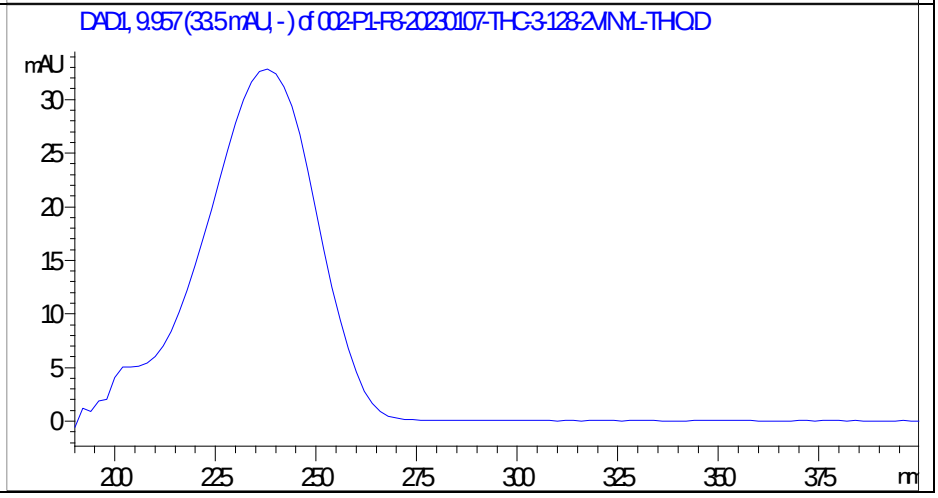
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

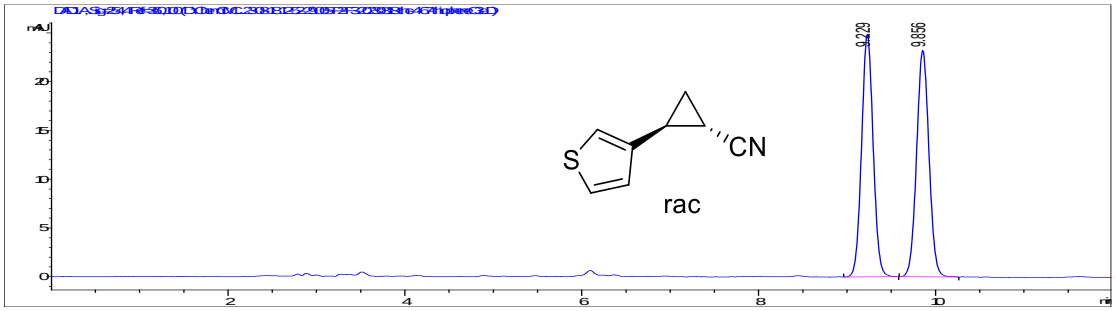
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.765	BB	0.1310	1686.91882	198.83720	91.6297
2	9.983	BB	0.1500	154.09937	16.04809	8.3703
Totals :				1841.01819	214.88529	

UV spectrum of the peak at 8.750 min.



UV spectrum of the peak at 9.957 min.

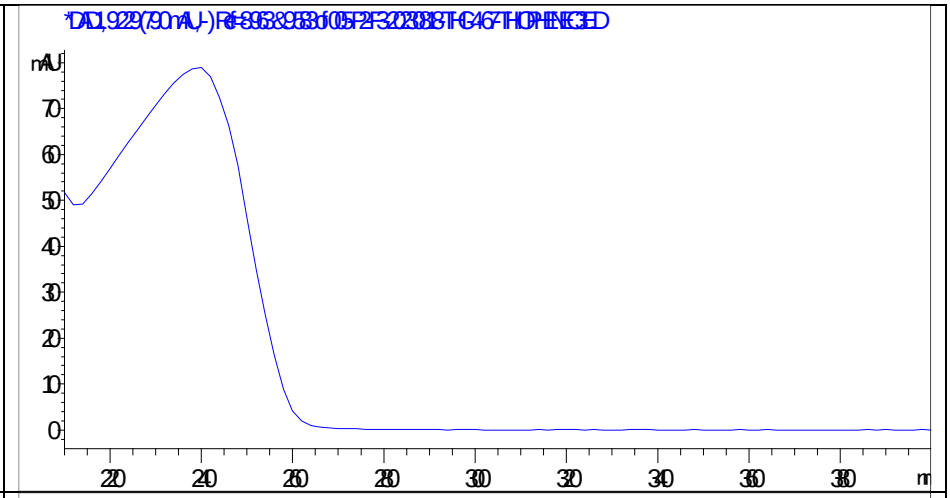




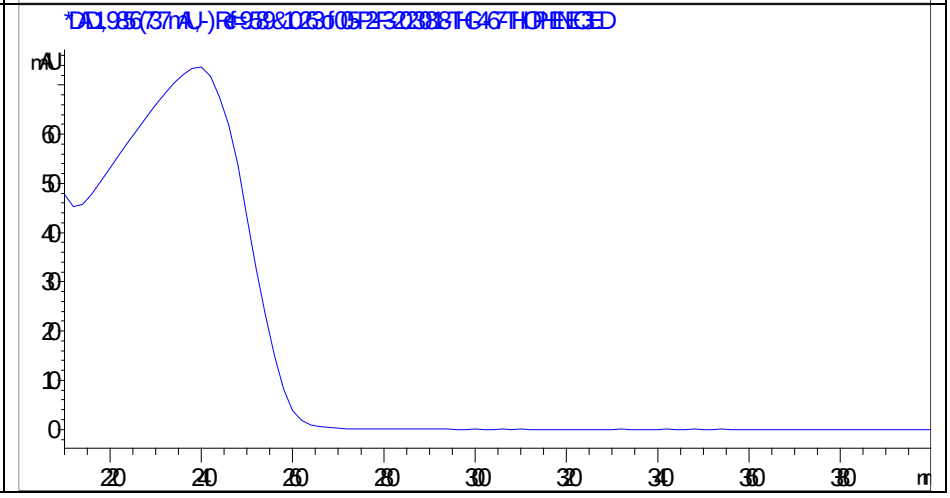
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

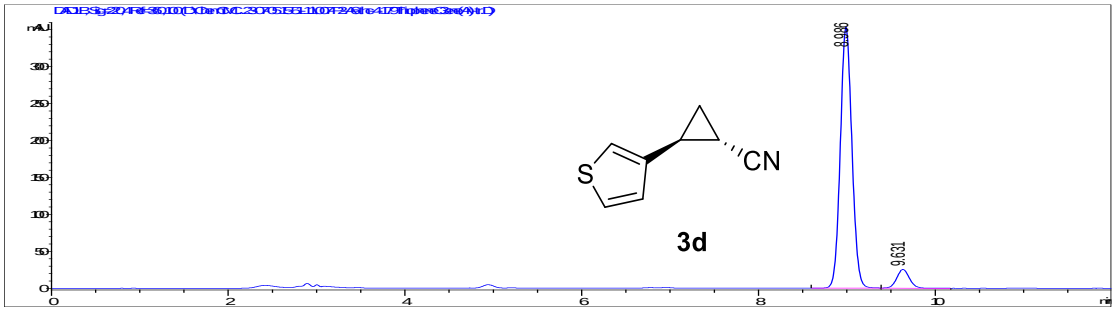
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.229	BB	0.1404	226.80244	24.87332	50.0527
2	9.856	BB	0.1518	226.32446	23.20526	49.9473
Totals :				453.12691	48.07858	

UV spectrum of the peak at 9.229 min.



UV spectrum of the peak at 9.856 min.

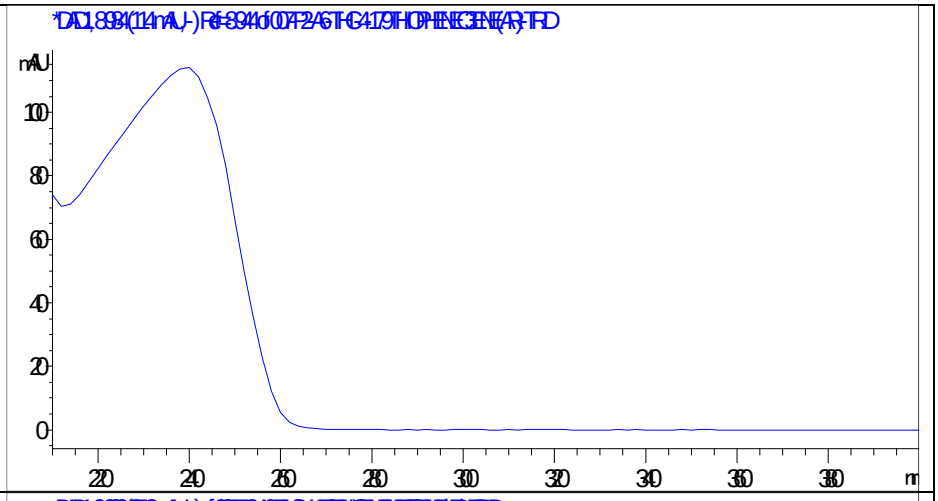




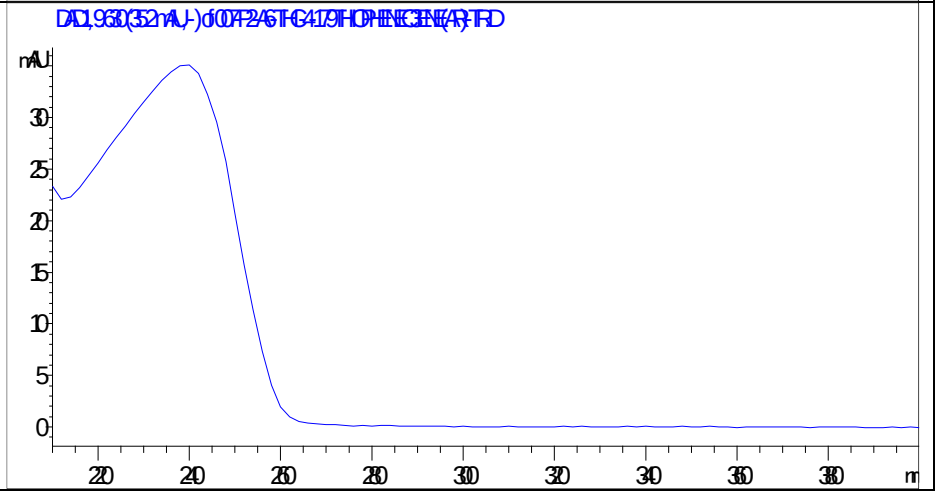
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

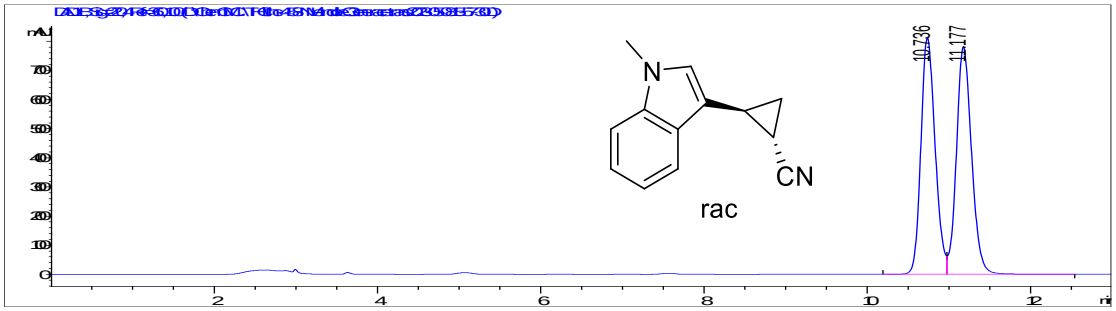
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.986	BB	0.1428	1400.42358	152.91766	92.9485
2	9.630	BB	0.1505	106.24218	11.02199	7.0515
Totals :				1506.66576	163.93965	

UV spectrum of the peak at 8.984 min.



UV spectrum of the peak at 9.630 min.

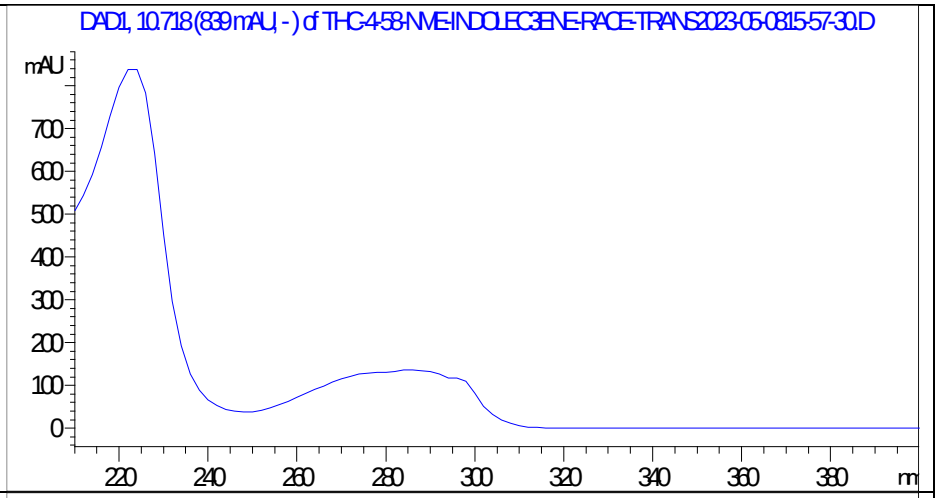




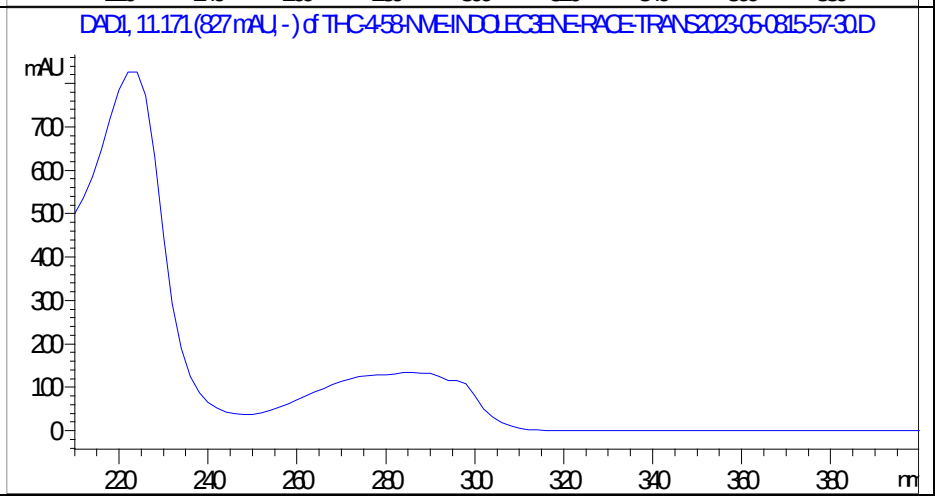
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

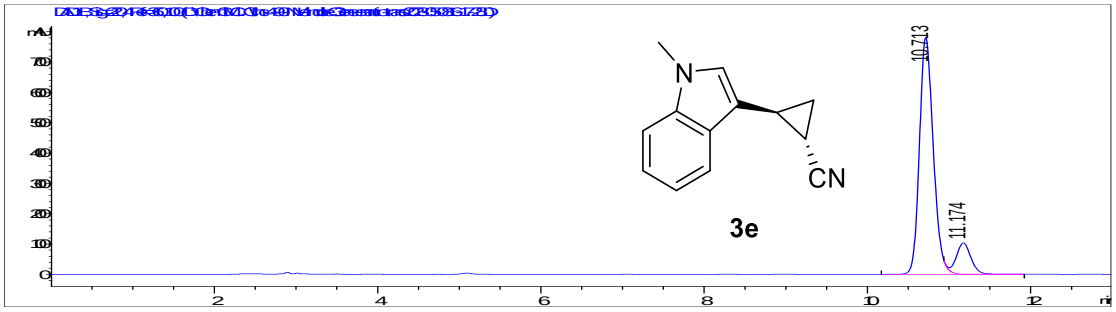
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.736	BV	0.1875	9851.07129	812.37018	49.4258
2	11.177	VB	0.1984	1.00800e4	781.74933	50.5742
Totals :				1.99310e4	1594.11951	

UV spectrum of the peak at 10.718 min.



UV spectrum of the peak at 11.171 min.

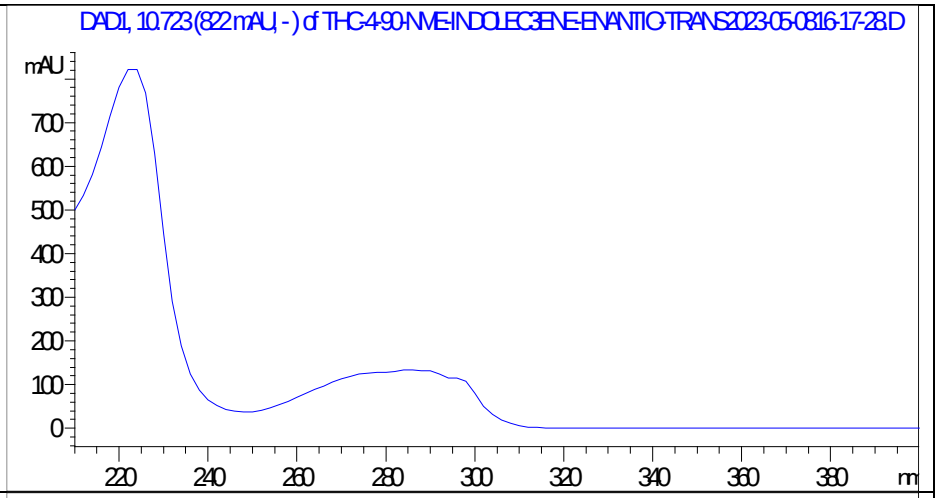




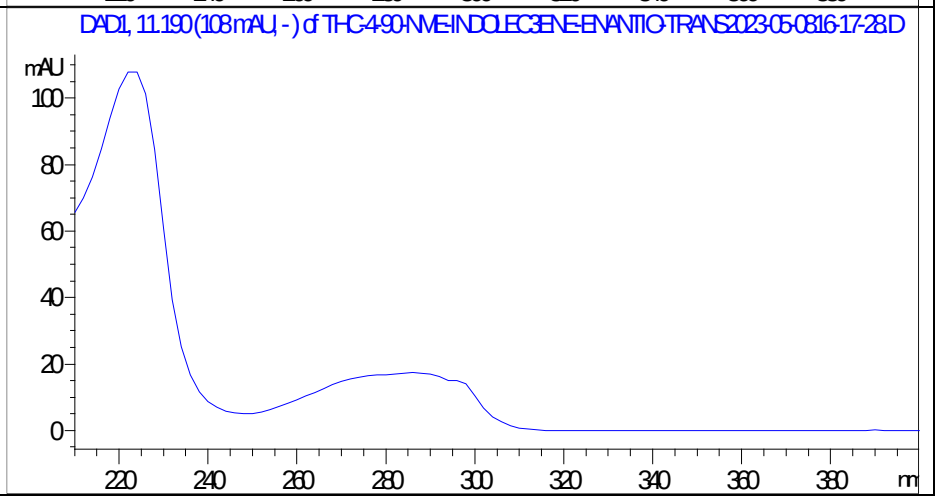
Signal 2: DAD1 B, Sig=220,4 Ref=360,100

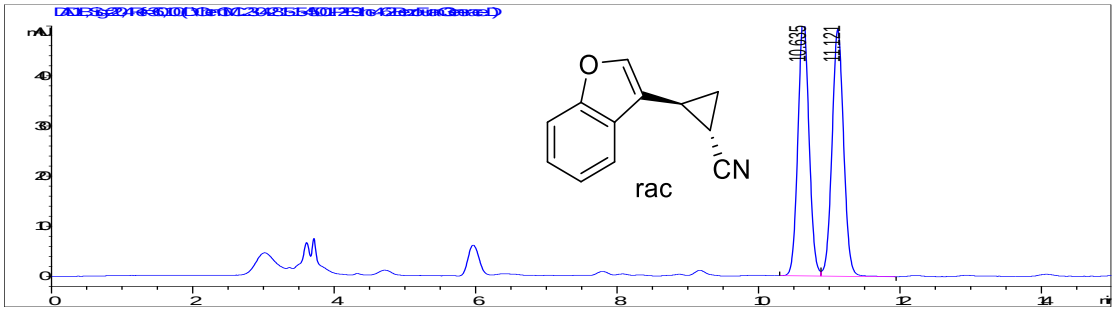
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.713	BV R	0.1818	9219.45605	780.82458	87.8113
2	11.174	VB E	0.1907	1279.71216	103.15018	12.1887
Totals :				1.04992e4	883.97477	

UV spectrum of the peak at 10.723 min.



UV spectrum of the peak at 11.190 min.

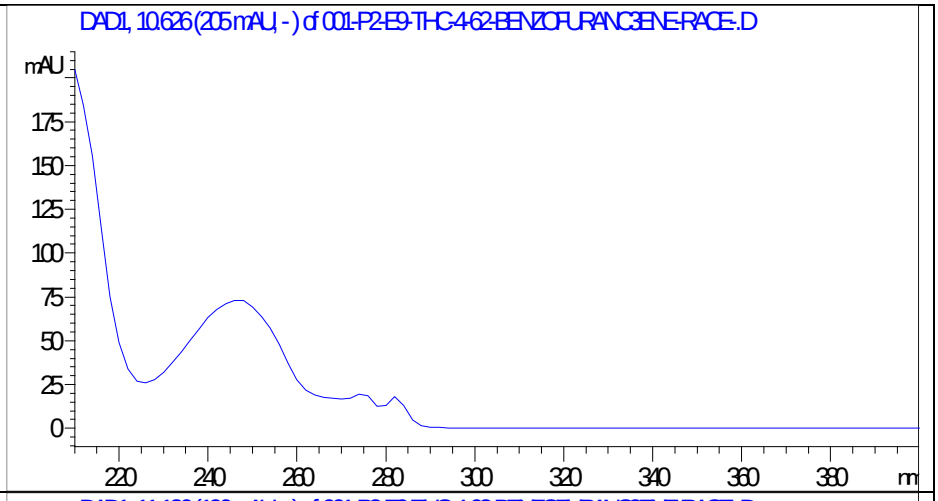
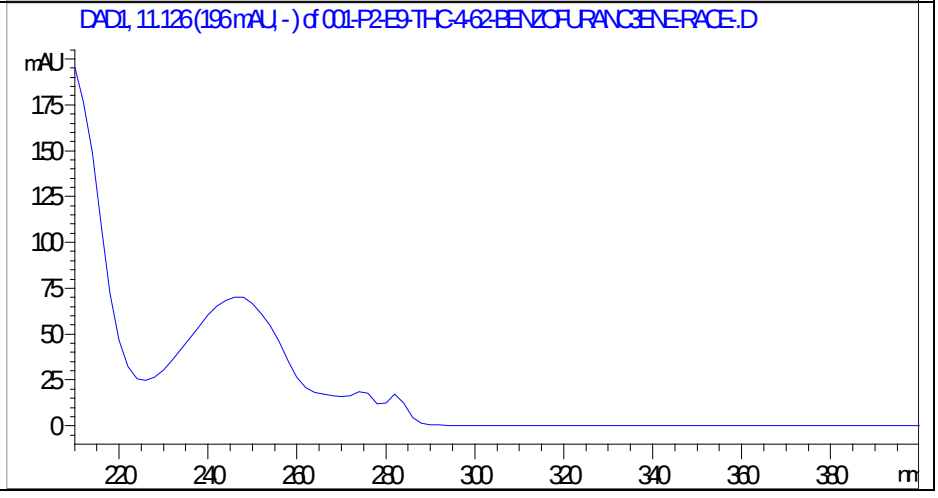


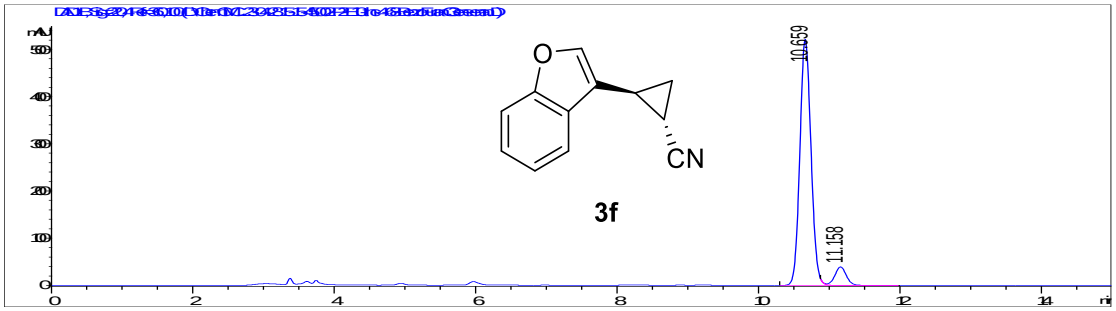


Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.635	BV	0.1680	558.58093	51.70343	49.8343
2	11.121	VB	0.1771	562.29523	49.27409	50.1657

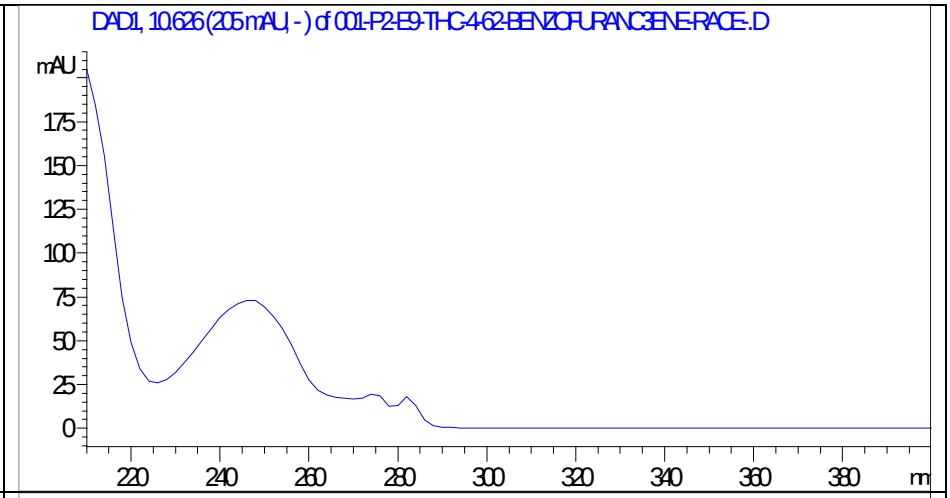
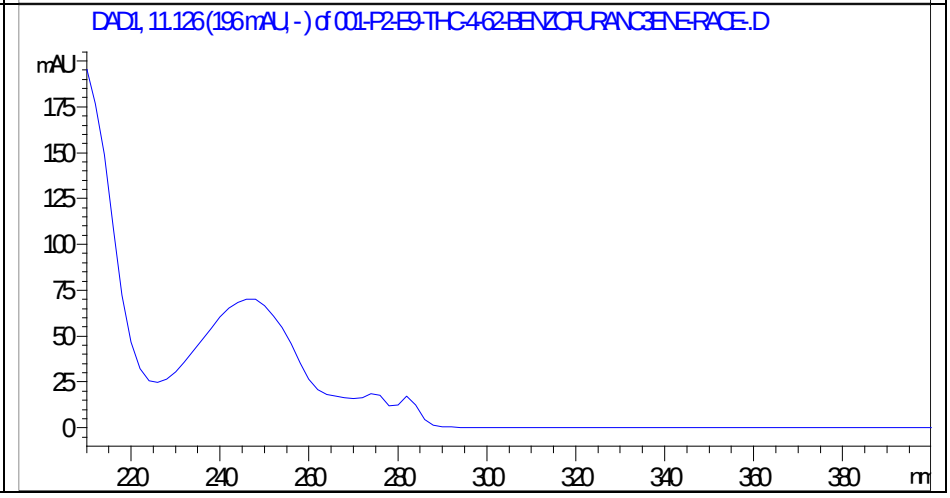
Totals : 1120.87616 100.97752

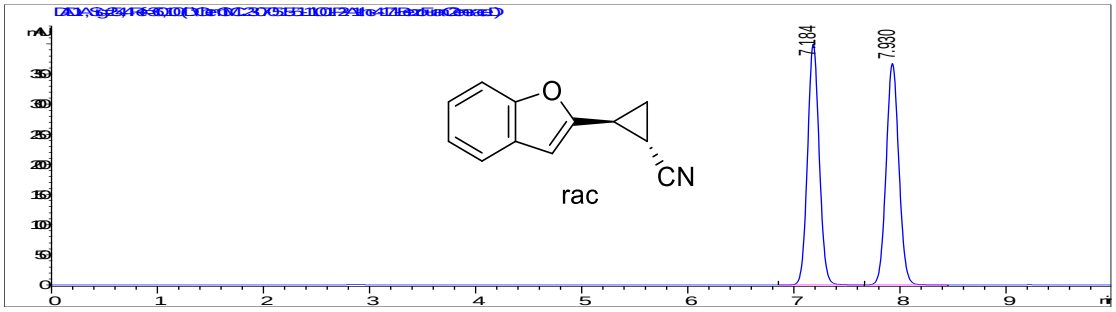
UV spectrum of the peak at 10.626 min.	
UV spectrum of the peak at 11.126 min.	



Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.659	BV R	0.1697	5706.90332	521.55060	92.8005
2	11.158	VB E	0.1744	442.74252	39.02752	7.1995
Totals :				6149.64584	560.57811	

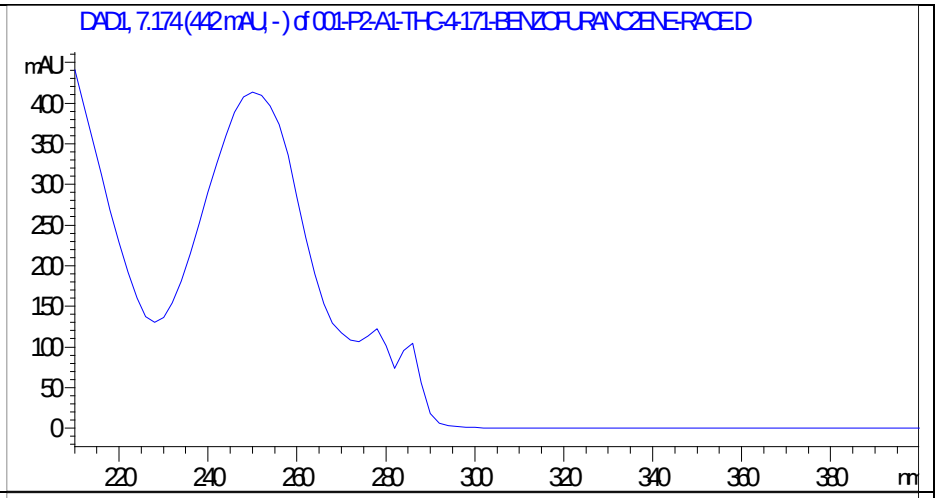
UV spectrum of the peak at 10.626 min.	
UV spectrum of the peak at 11.126 min.	



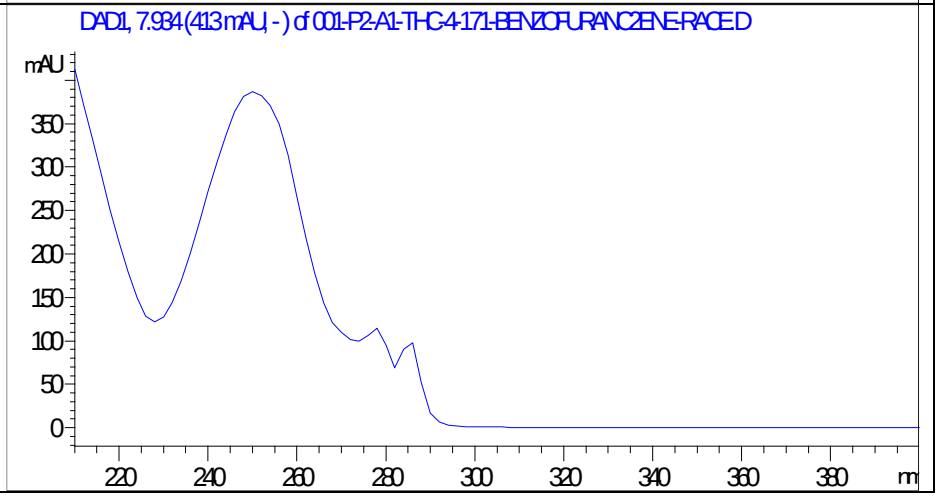
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

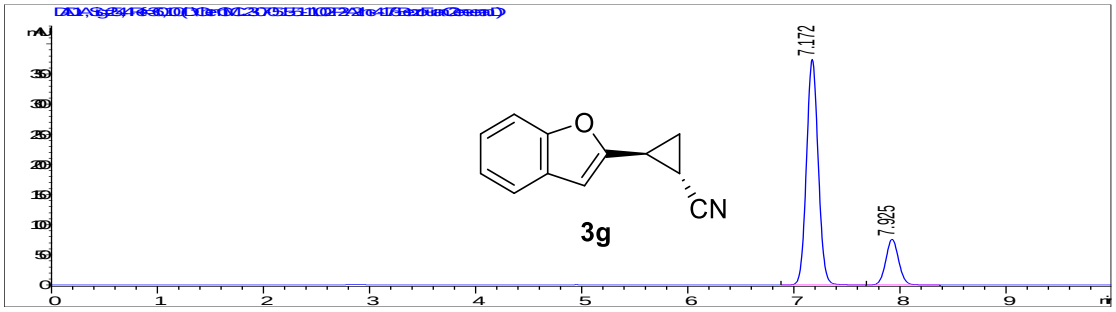
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.184	BB	0.1172	3062.05566	400.50577	50.0264
2	7.930	BB	0.1290	3058.82422	367.93192	49.9736
Totals :				6120.87988	768.43768	

UV spectrum of the peak at 7.174 min.



UV spectrum of the peak at 7.934 min.

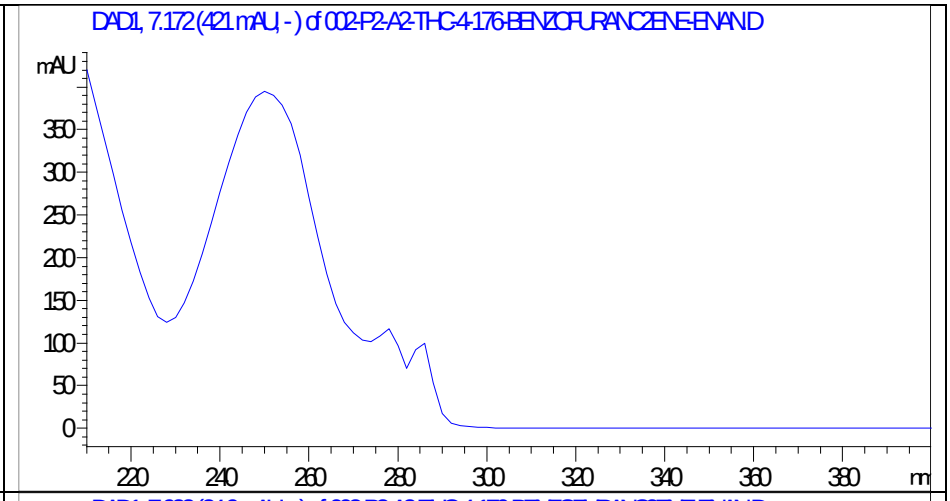




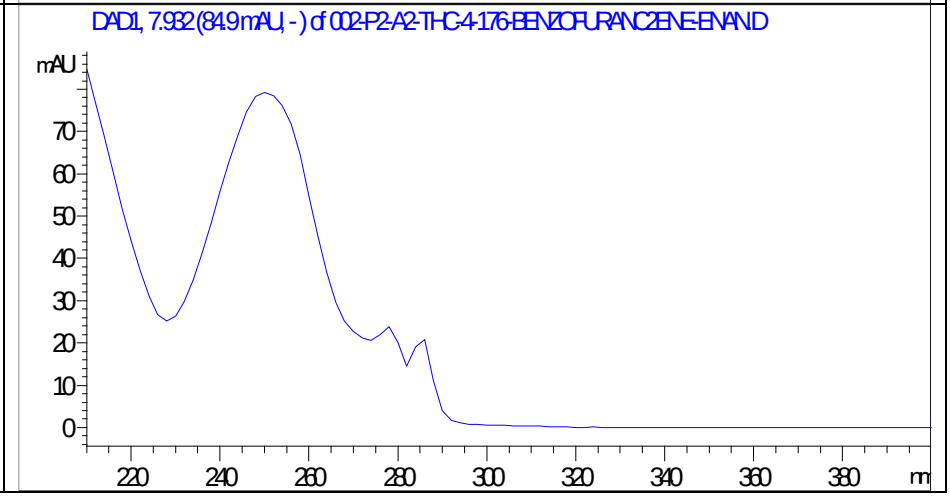
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

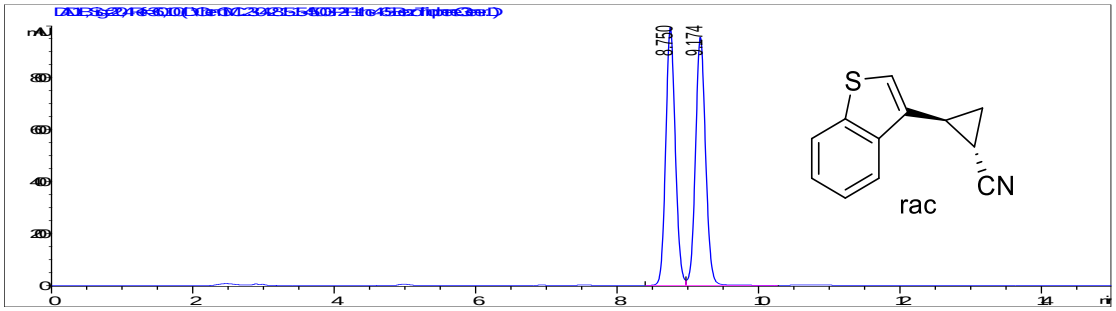
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.172	BB	0.1195	2873.82666	374.43591	81.8649
2	7.925	BB	0.1320	636.62195	75.78748	18.1351
Totals :				3510.44861	450.22340	

UV spectrum of the peak at 7.172 min.



UV spectrum of the peak at 7.932 min.

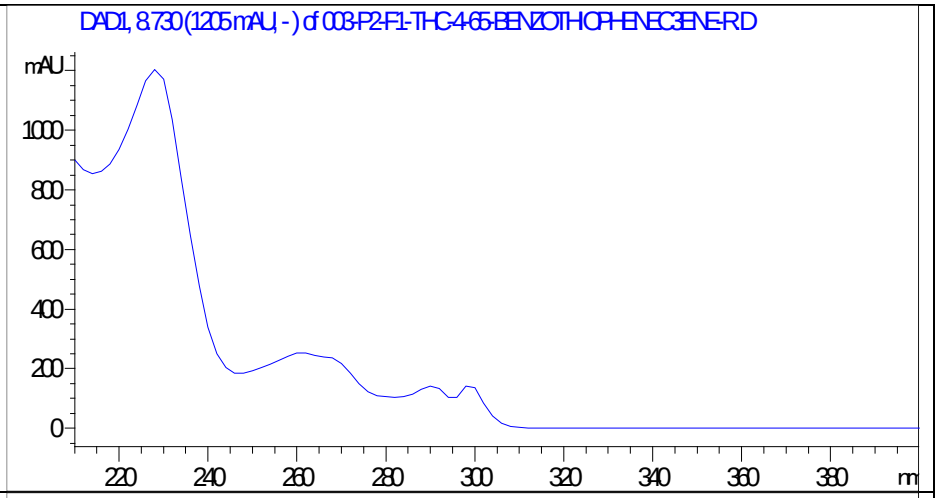




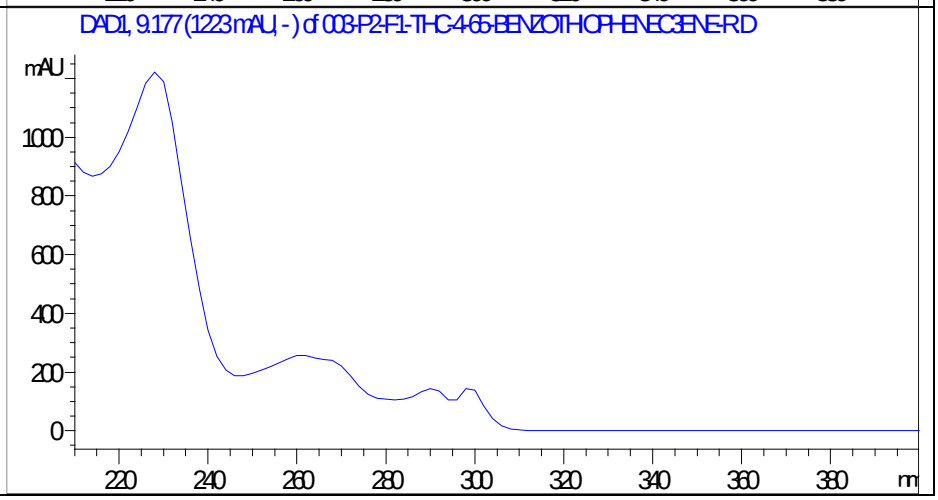
Signal 1: DAD1 B, Sig=220,4 Ref=360,100

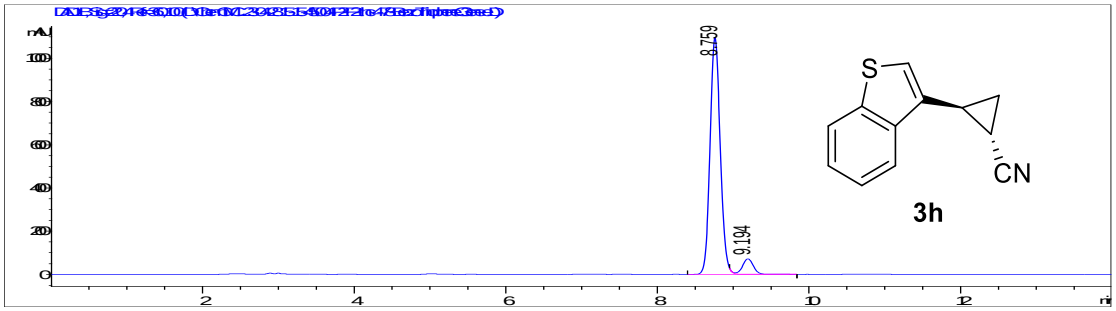
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.750	BV	0.1476	9314.12109	991.08868	49.7556
2	9.174	VB	0.1530	9405.60645	954.40765	50.2444
Totals :				1.87197e4	1945.49634	

UV spectrum of the peak at 8.730 min.



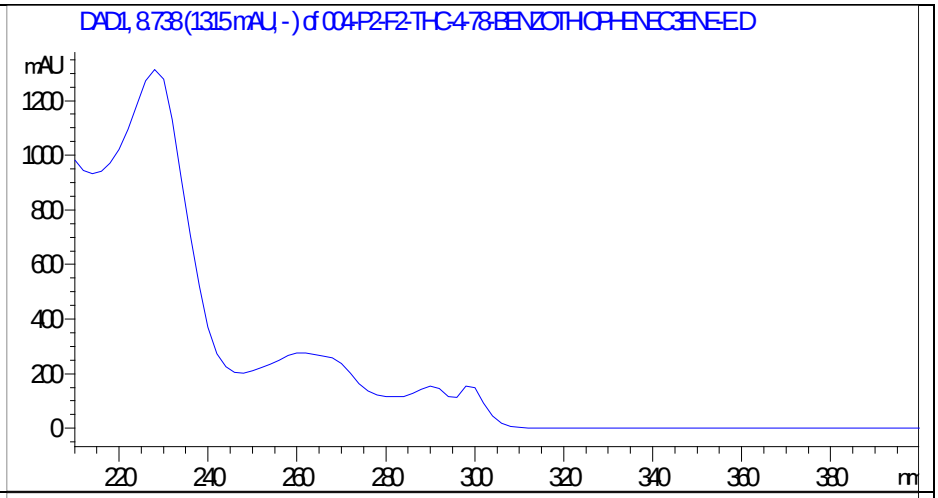
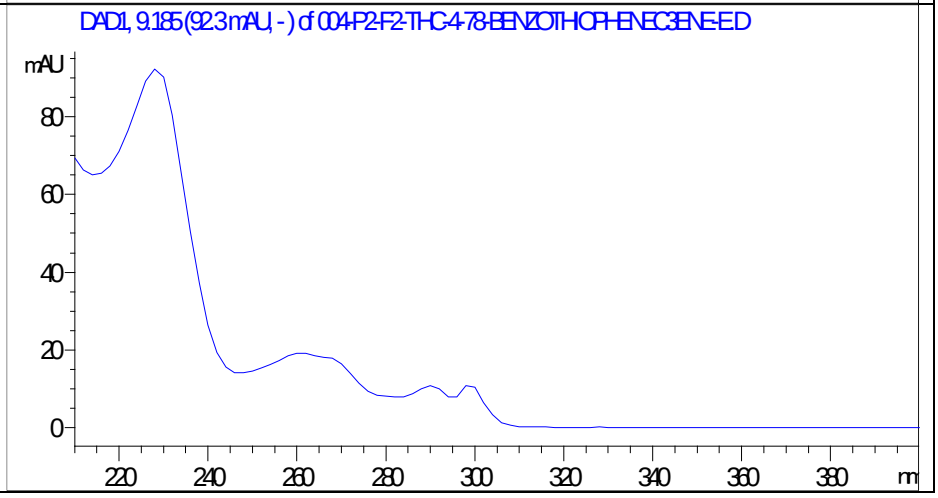
UV spectrum of the peak at 9.117 min.

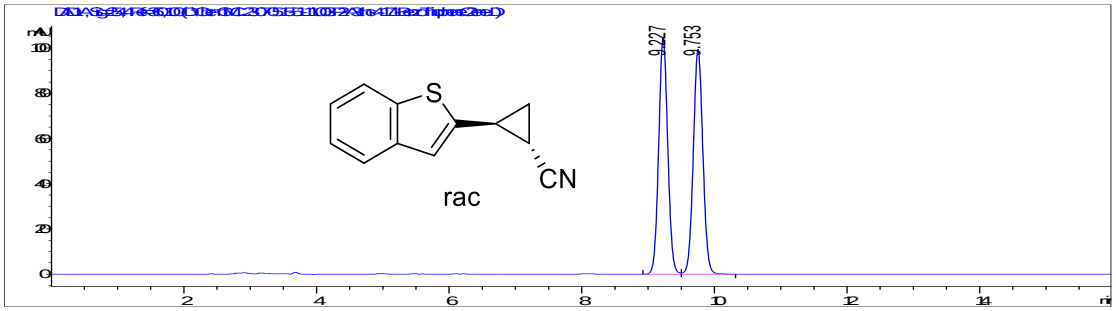




Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.759	BV R	0.1452	1.02474e4	1095.24194	93.4769
2	9.194	VB E	0.1518	715.09003	72.05999	6.5231
Totals :				1.09625e4	1167.30193	

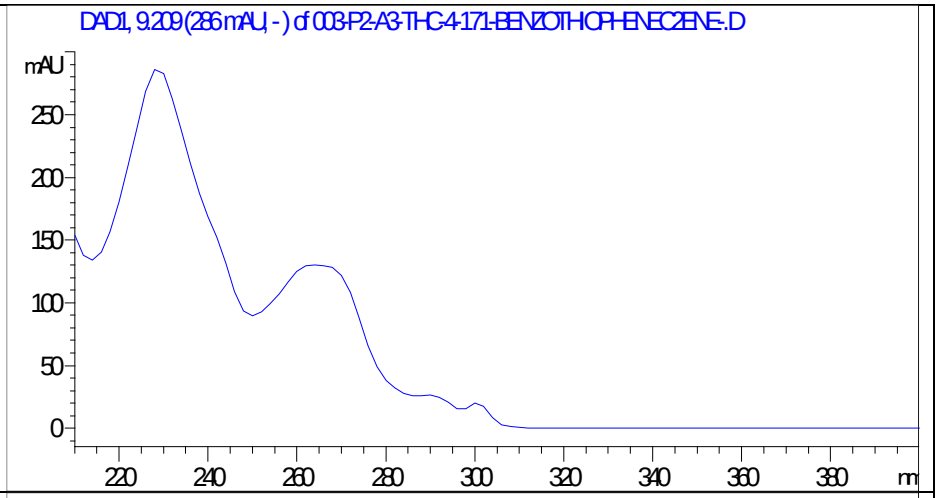
UV spectrum of the peak at 8.738 min.	
UV spectrum of the peak at 9.185 min.	



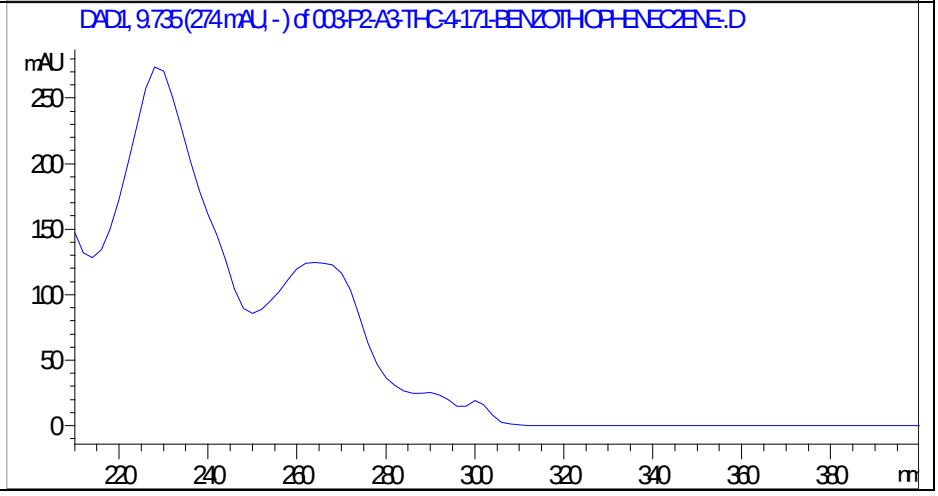
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

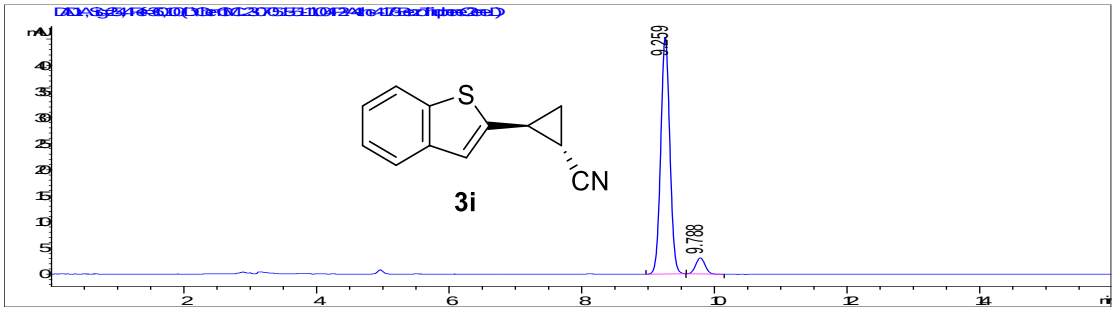
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.227	BV	0.1466	992.39050	104.64063	49.9302
2	9.753	VB	0.1548	995.16687	99.44022	50.0698
Totals :				1987.55737	204.08086	

UV spectrum of the peak at 9.209 min.



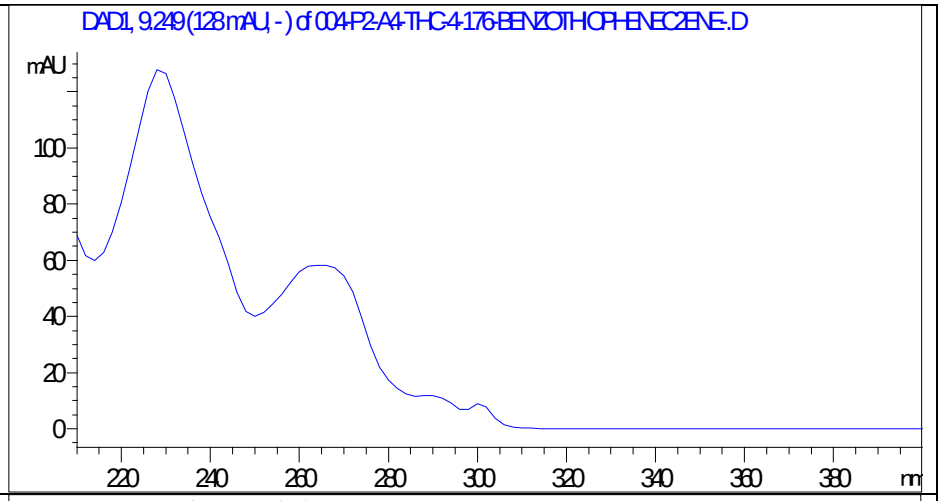
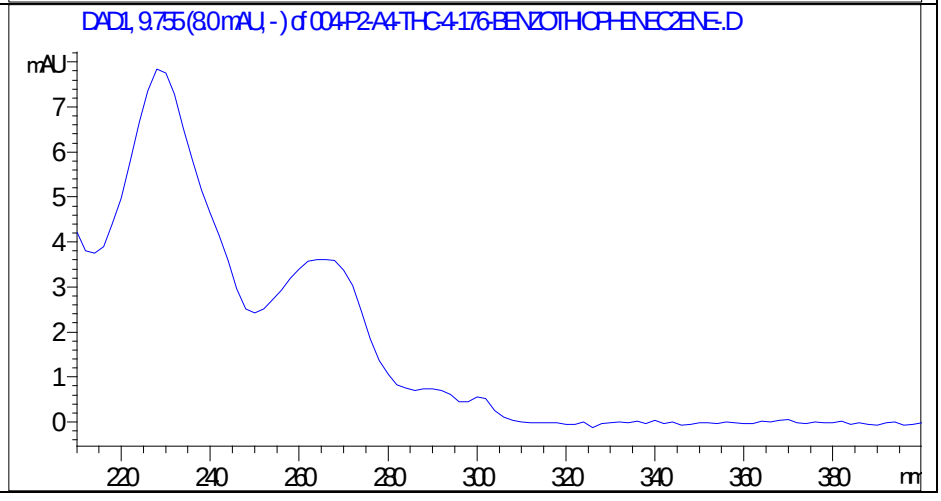
UV spectrum of the peak at 9.735 min.

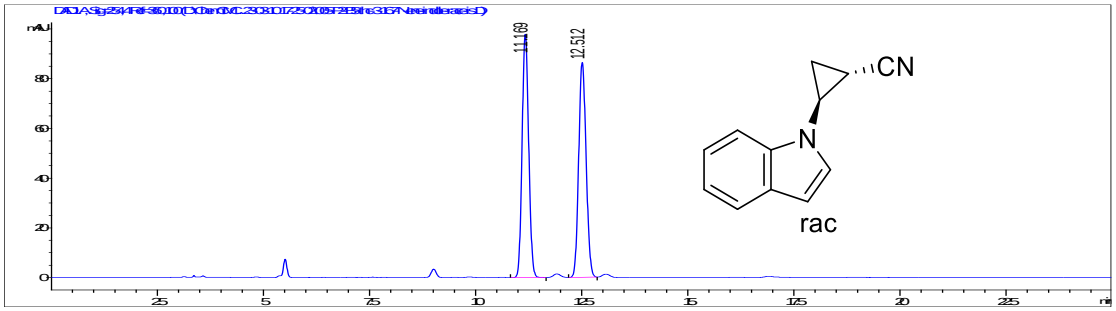




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.259	BB	0.1468	430.47971	45.33131	93.3520
2	9.788	BB	0.1554	30.65653	3.09949	6.6480
Totals :				461.13623	48.43080	

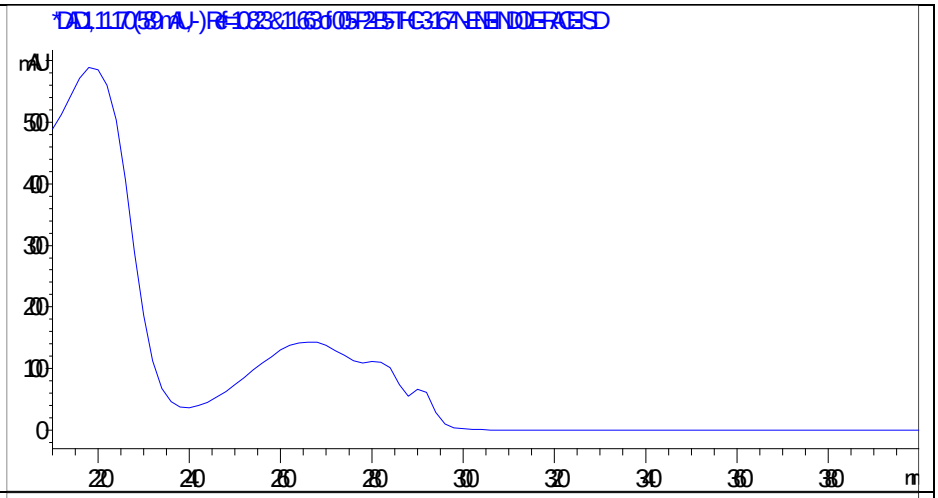
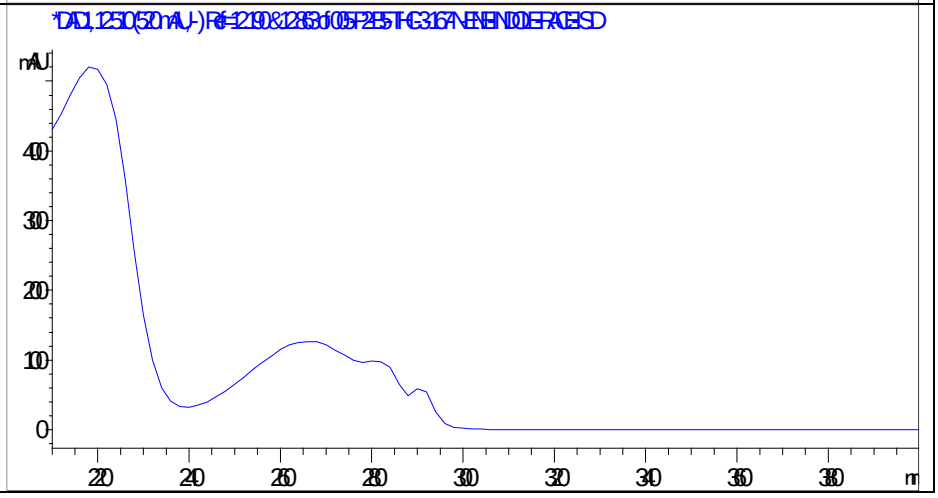
UV spectrum of the peak at 9.249 min.	
UV spectrum of the peak at 9.755 min.	

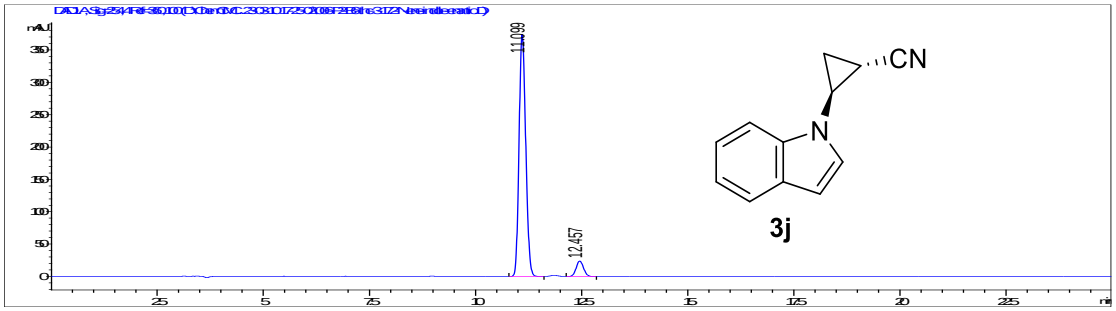


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.169	BB	0.1680	1056.21240	97.78936	50.0959
2	12.512	BB	0.1900	1052.17053	86.44945	49.9041

Totals :	2108.38293 184.23881

UV spectrum of the peak at 11.170 min.	
UV spectrum of the peak at 12.510 min.	

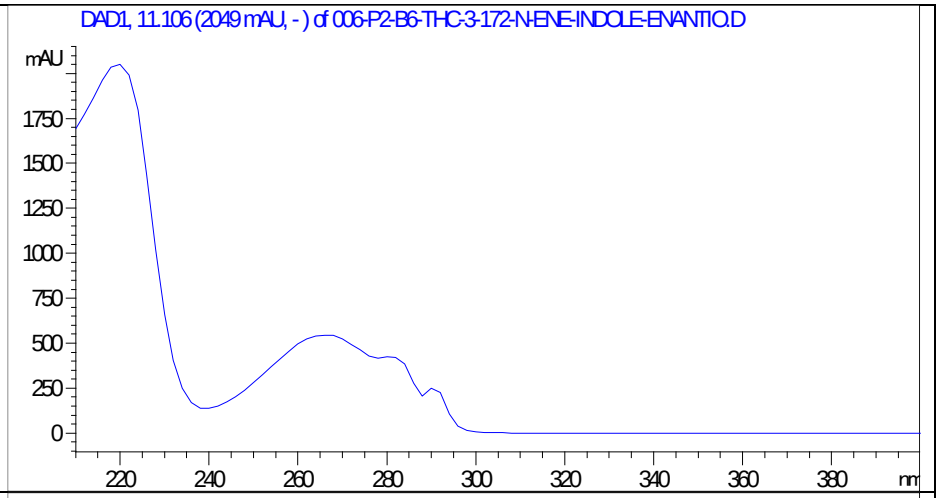


3j

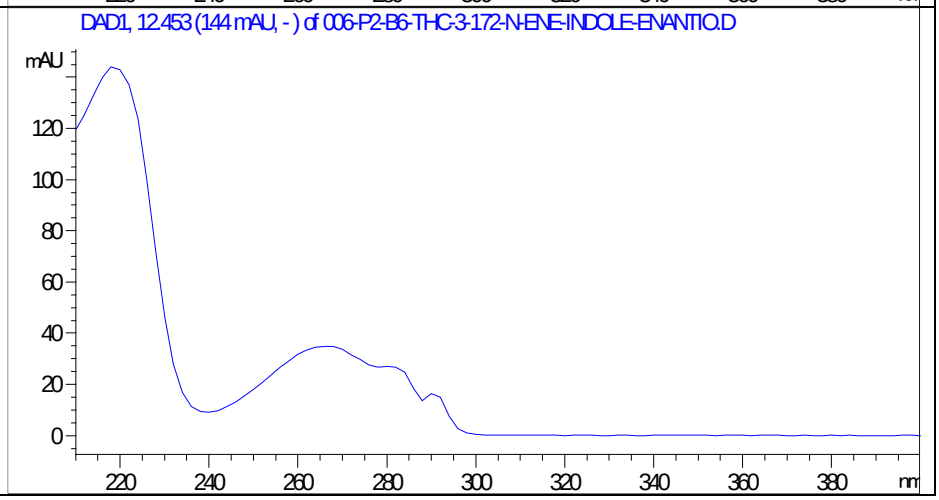
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

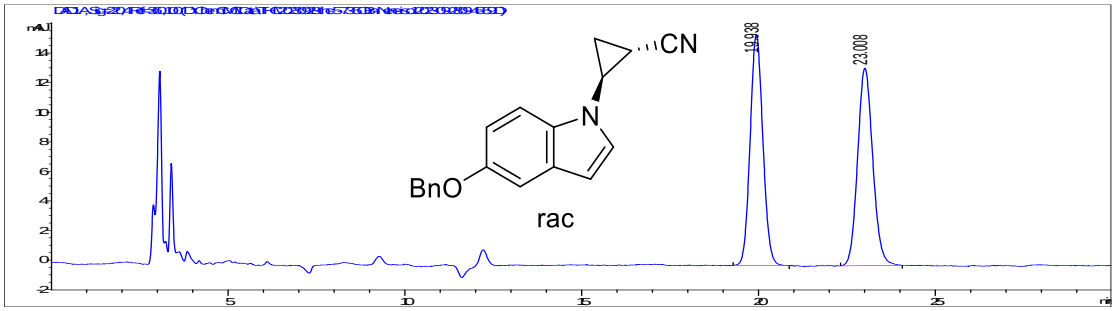
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.099	BB	0.1696	4089.52930	373.85950	93.4586
2	12.457	BB	0.1882	286.23572	23.81979	6.5414
Totals :				4375.76501	397.67929	

UV spectrum of the peak at 11.106 min.



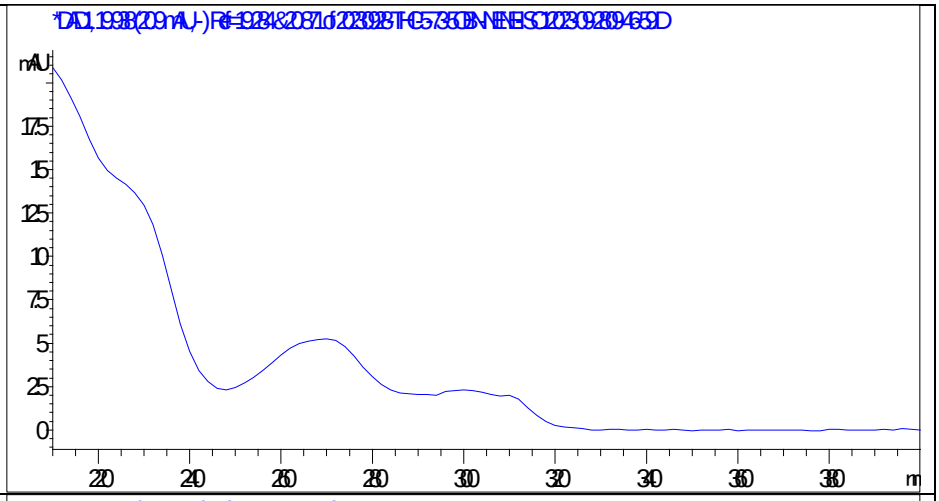
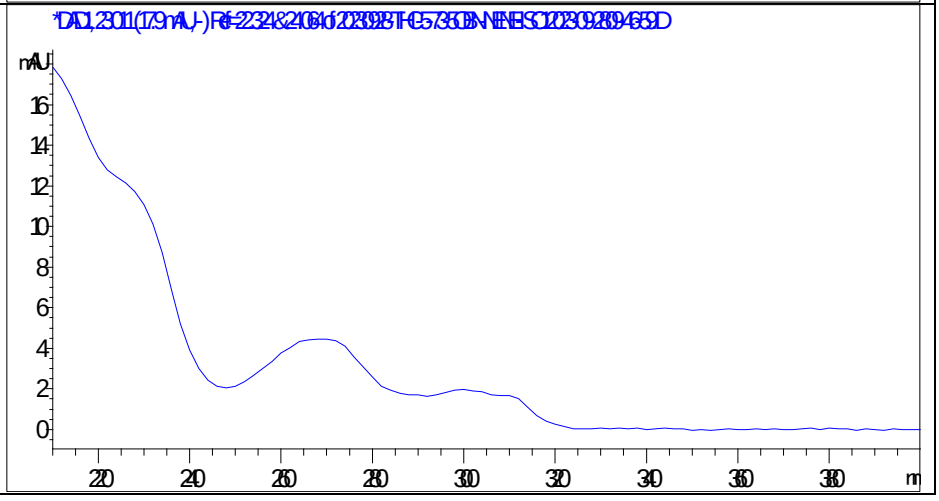
UV spectrum of the peak at 12.453 min.

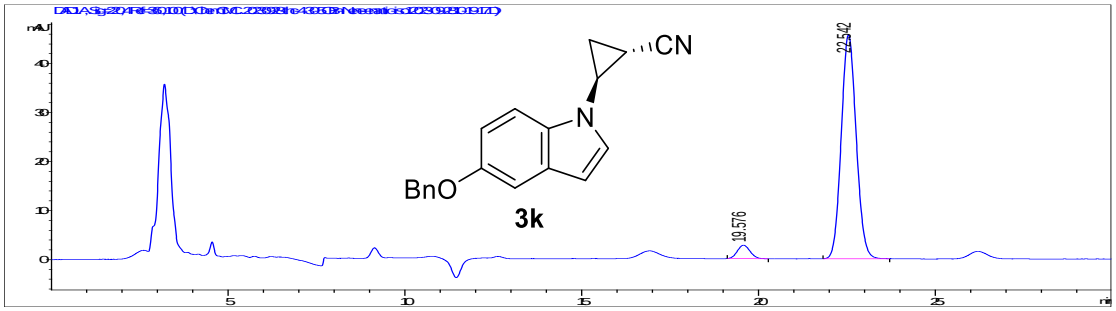




Signal 1: DAD1 A, Sig=220,4 Ref=360,100

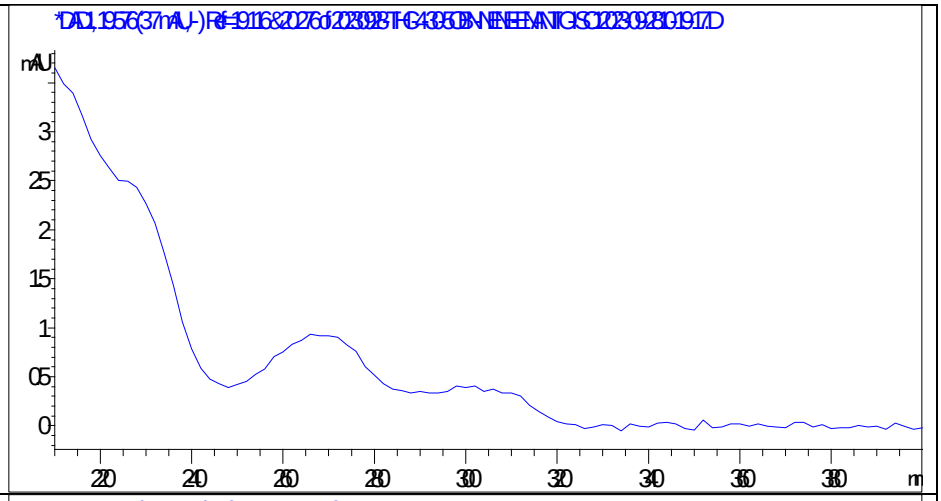
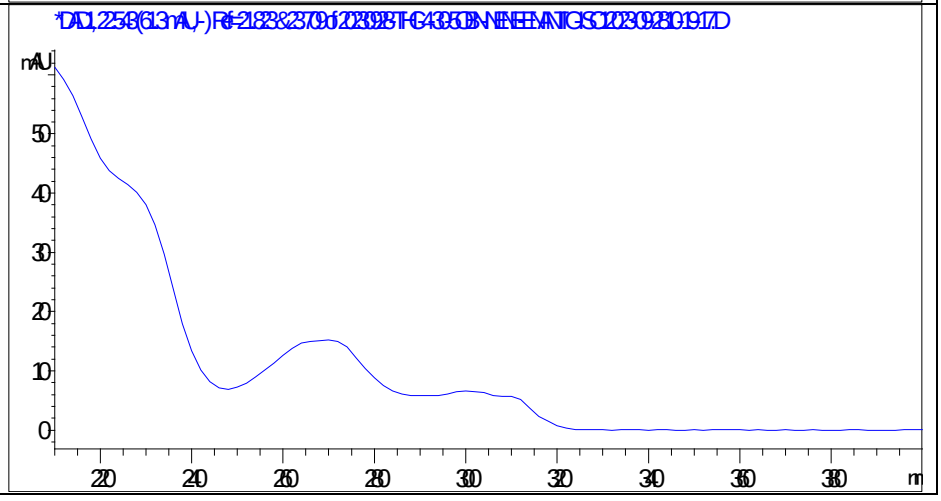
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.938	BB	0.3883	391.51315	15.62528	49.6507
2	23.008	BB	0.4507	397.02155	13.35999	50.3493
Totals :				788.53470	28.98527	

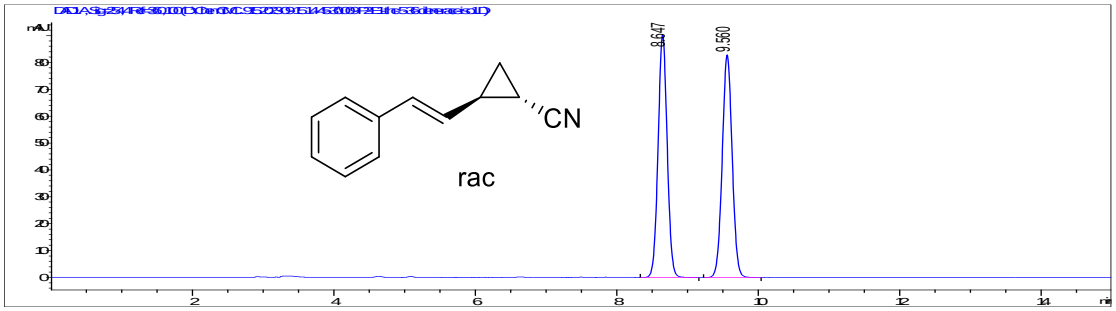
UV spectrum of the peak at 19.938 min.	
UV spectrum of the peak at 23.011 min.	



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.576	BB	0.3703	68.54966	2.73560	4.8589
2	22.542	BB	0.4564	1342.24390	45.74011	95.1411
Totals :				1410.79356	48.47571	

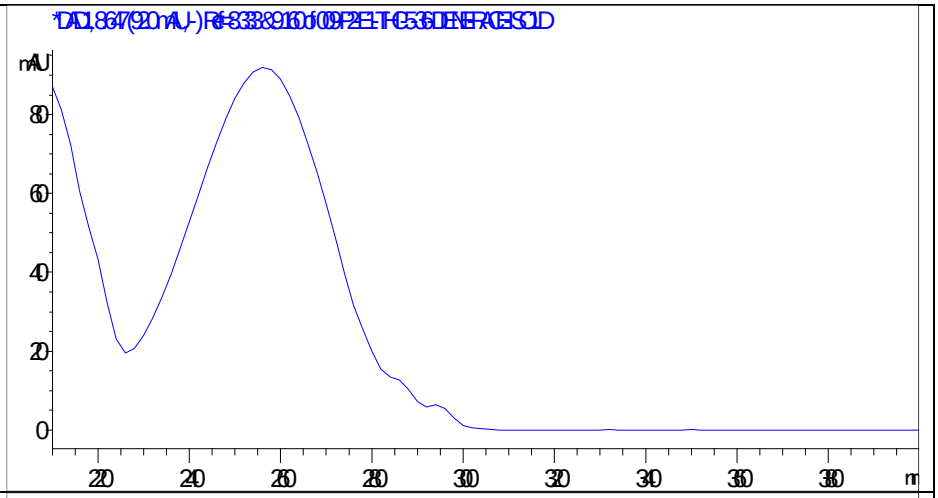
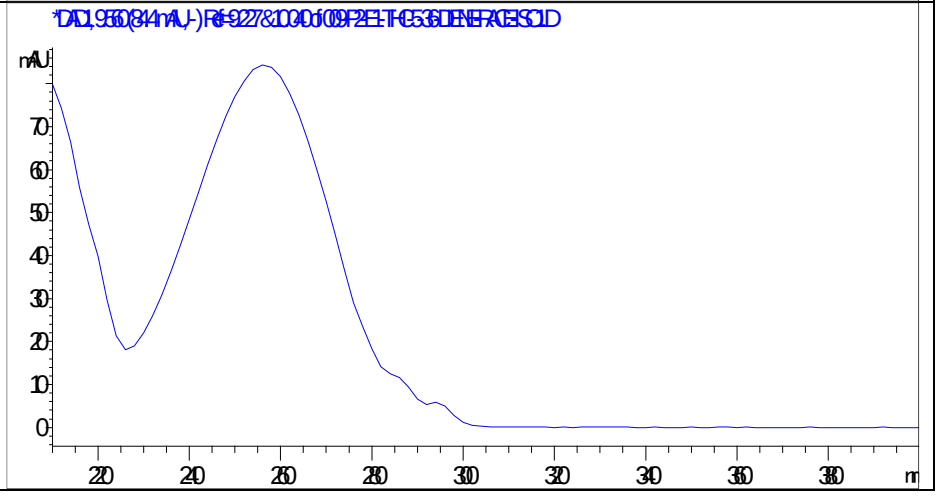
UV spectrum of the peak at 19.576 min.	
UV spectrum of the peak at 22.543 min.	

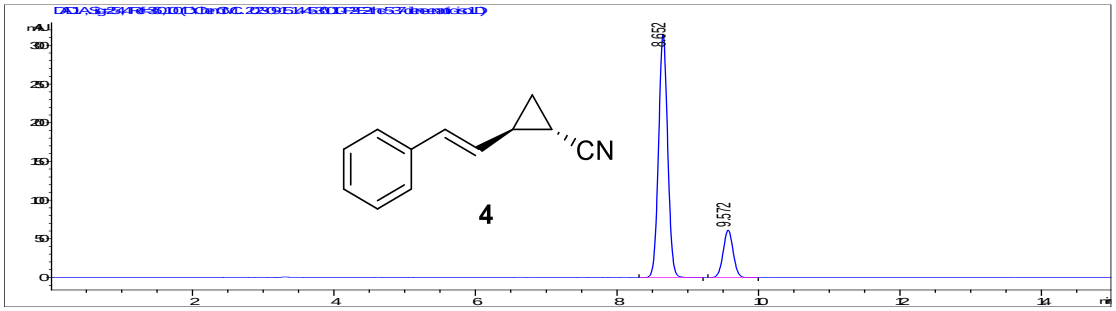


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.647	BB	0.1382	808.08203	90.43688	49.9581
2	9.560	BB	0.1519	809.43829	82.91582	50.0419

Totals : 1617.52032 173.35270

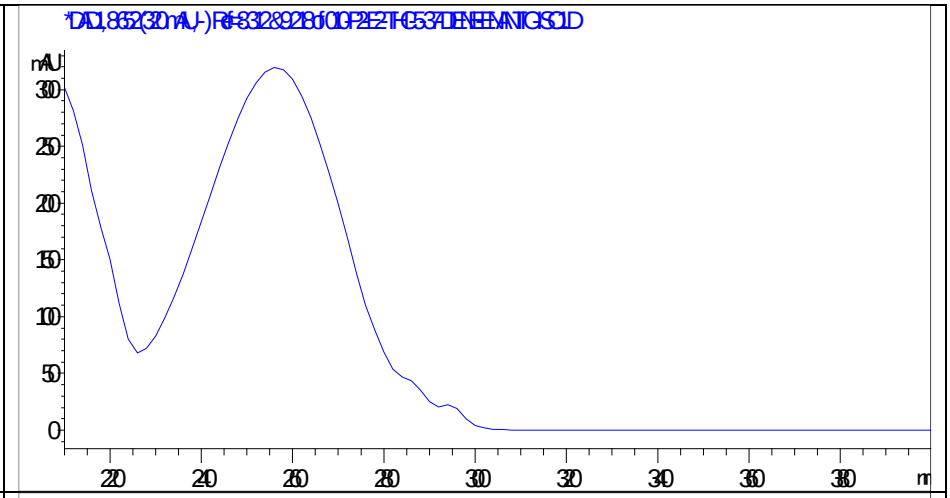
UV spectrum of the peak at 8.647 min.	
UV spectrum of the peak at 9.560 min.	



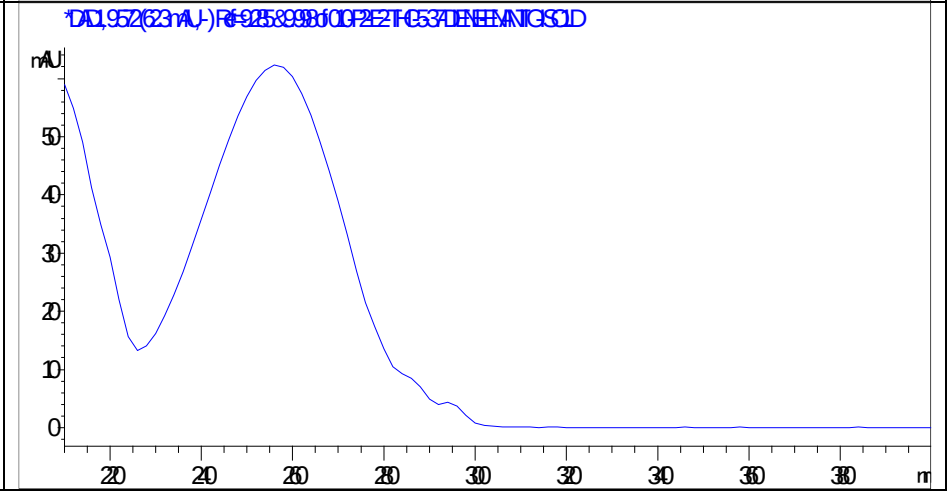
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

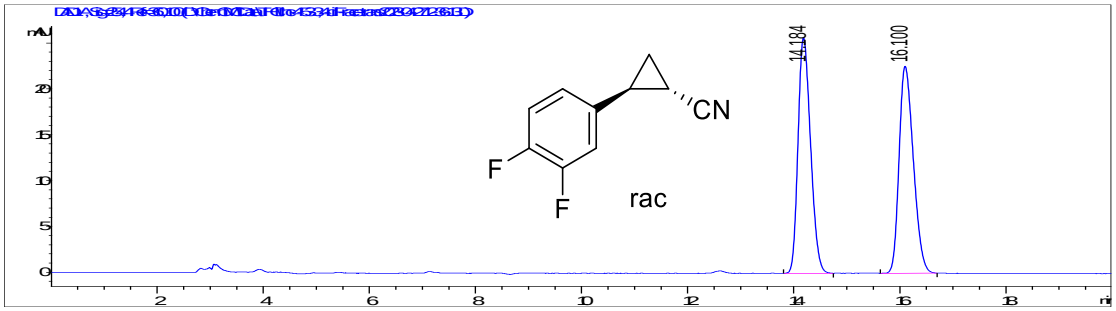
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.652	BB	0.1387	2818.75977	314.14737	82.4277
2	9.572	BB	0.1524	600.91553	61.25808	17.5723
Totals :				3419.67529	375.40545	

UV spectrum of the peak at 8.652min.



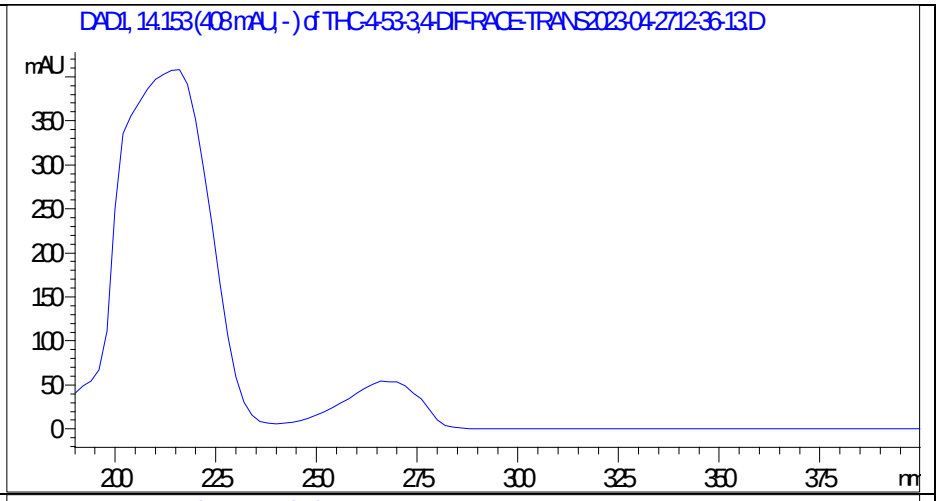
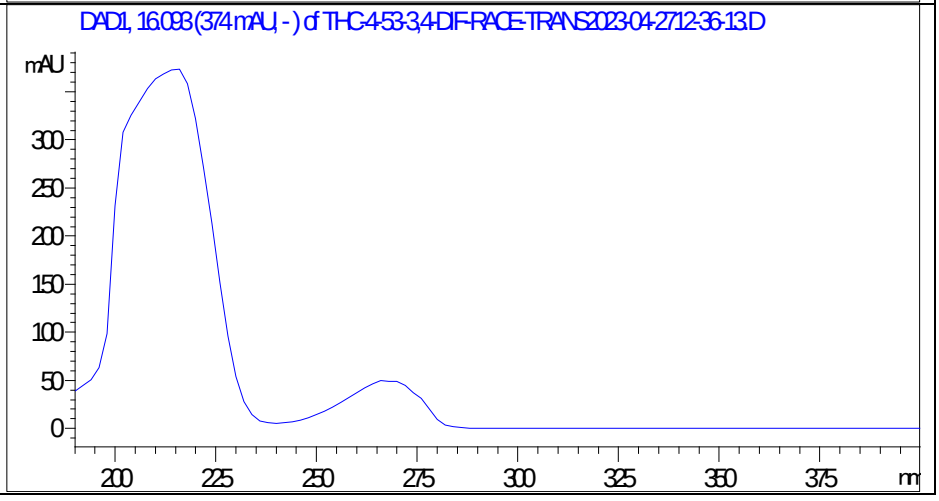
UV spectrum of the peak at 9.572 min.

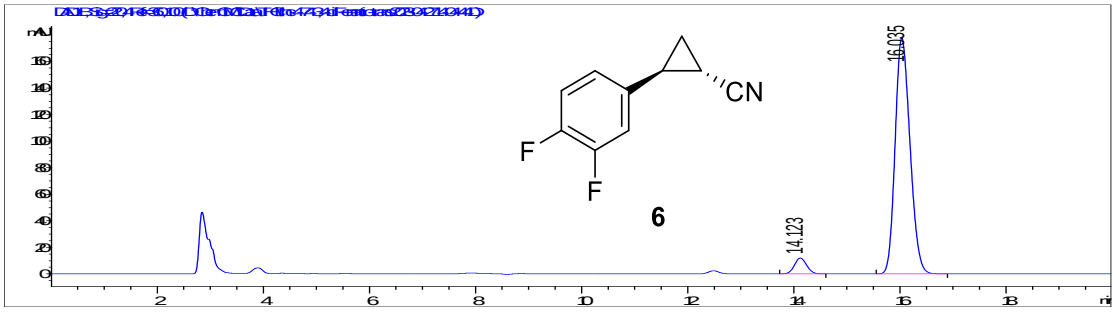




Signal 2: DAD1 B, Sig=220,4 Ref=360,100

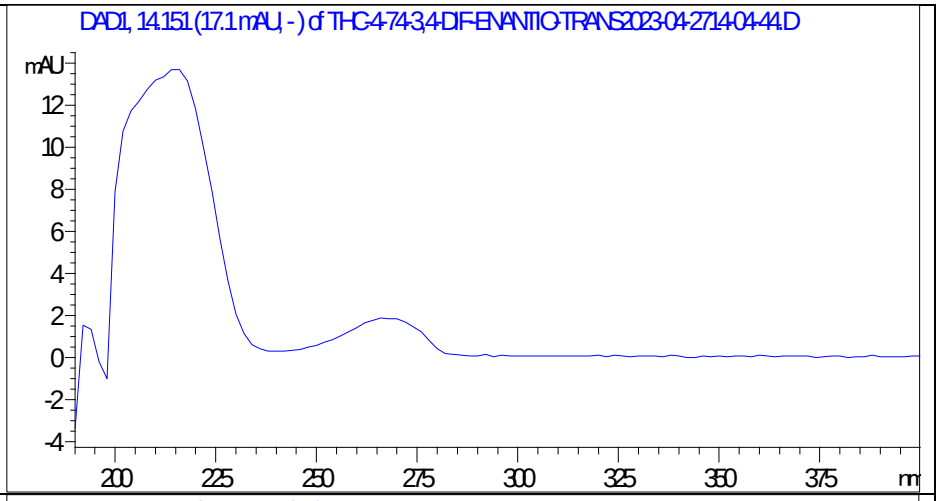
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.184	BB	0.2554	5940.68115	362.05548	49.9788
2	16.100	BB	0.2922	5945.72949	317.89932	50.0212
Totals :				1.18864e4	679.95480	

UV spectrum of the peak at 14.153 min.	
UV spectrum of the peak at 16.093 min.	



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.123	BB	0.2475	189.45961	11.91333	5.1897
2	16.035	BB	0.3030	3461.21533	177.87962	94.8103
Totals :				3650.67494	189.79296	

UV spectrum of the peak at 14.151 min.	
UV spectrum of the peak at 16.045 min.