Supplementary Information

Stereodivergent Synthesis of Enantioenriched Azepino[3,4,5-*cd*]-Indoles via Cooperative Cu/Ir-Catalyzed Asymmetric Allylic Alkylation and Intramolecular Friedel-Crafts Reaction

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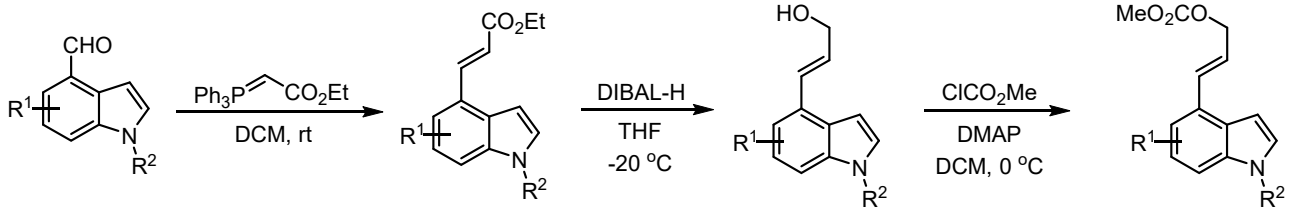
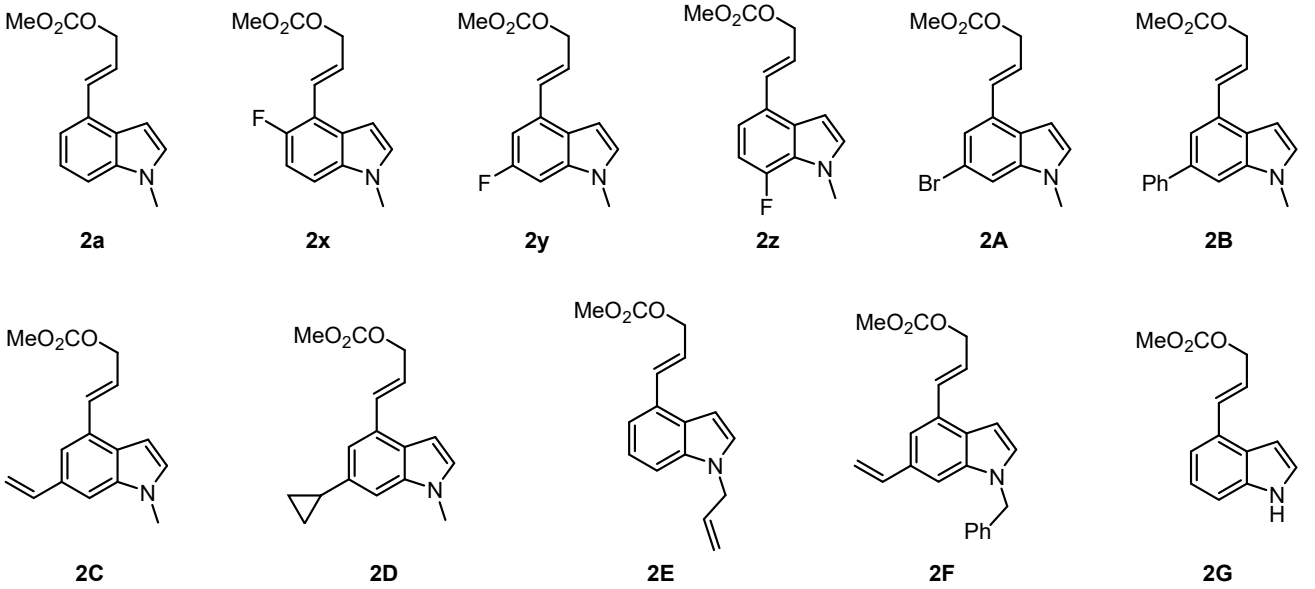
1. General Remarks

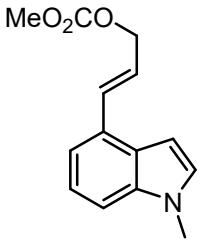
^{1}H NMR spectra were recorded on a Bruker Mercury 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data were reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, and brs = broad single). ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal CF_3COOH signal at -76.55 ppm. The data were reported as (s = single, d = double, t = triple, q = quarter, m = multiple or unresolved, br s = broad single, coupling constant (s) in Hz, integration). Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise stated, all reactions were set up under nitrogen atmosphere in oven-dried glassware using standard Schlenk techniques, monitored by TLC with silica-gel coated plates and purified by flash column chromatography. The enantiomeric excesses (ee) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent 1200 Series chromatographs using a Diacel chiral column (25 cm). Optical rotations were measured on an Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]^{30}_{D}$ values reported in degrees; concentration (c) is in 0.5 g/100 mL. Aldimine esters,[1] 4-indolyl allylic carbonates[2] chiral ligands **L1**-**L3**[3], **L4**[4], **L5**[5] and **L6**[6] were prepared according to the literature procedure. The racemic products were obtained by blending equal amount of two enantiomers. The absolute configuration of the products (6*S*,7*S*,9*R*)-**3a**, (6*R*,7*R*,9*R*)-**3a**, and (6*R*,7*S*,9*R*)-**3a** were assigned by X-ray diffraction analysis.

2. Preparation and characterization data of 4-indolyl allyl carbonates 2

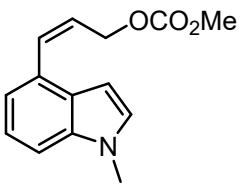
In general, 4-indolyl allyl carbonates **2** were prepared according to the procedure as shown below.[2]



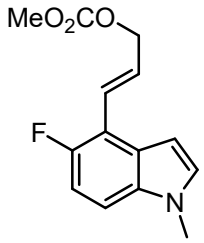




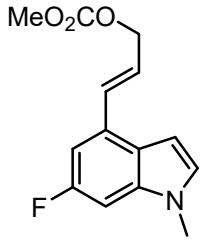
(*E*)-methyl (3-(1-methyl-1*H*-indol-4-yl)allyl) carbonate (2a): Yield (88% yield, overall 3 steps); white solid; m.p. 66-68 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 3H), 7.12 – 7.01 (m, 2H), 6.68 – 6.64 (m, 1H), 6.52 – 6.42 (m, 1H), 4.86 (dd, J = 6.4, 1.2 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 137.0, 133.7, 129.2, 128.3, 126.7, 122.8, 121.5, 117.7, 109.2, 99.3, 69.0, 54.7, 32.9. HRMS (ESI+) Calcd. For $C_{14}H_{16}NO_3^+$ ($[M+H]^+$): 246.1125, found: 246.1123. IR (thin film) v (cm^{-1}) 3054, 2986, 2305, 1748, 1442, 1265, 969, 739.



(*Z*)-methyl (3-(1-methyl-1*H*-indol-4-yl)allyl) carbonate[7] **(2a'):** Yield (93% yield, from the corresponding allyl alcohol); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.23 – 7.17 (m, 1H), 7.06 (d, *J* = 3.2 Hz, 1H), 7.03 (s, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.47 (dd, *J* = 3.2, 0.4 Hz, 1H), 5.95 (dt, *J* = 11.6, 6.4 Hz, 1H), 4.92 (dd, *J* = 6.4, 1.6 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 136.6, 131.6, 128.9, 128.1, 127.5, 125.1, 121.3, 119.5, 108.9, 99.5, 65.4, 54.7, 32.9. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2304, 1748, 1421, 1265, 896, 740.

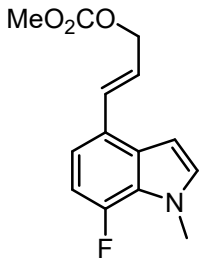


(*E*)-3-(5-fluoro-1-methyl-1*H*-indol-4-yl)allyl methyl carbonate (2x): Yield (86% yield, overall 3 steps); white solid; m.p. 58-60 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m 1H), 7.12 (d, *J* = 3.2 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.96 (dd, *J* = 11.2, 8.8 Hz, 1H), 6.66 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.64 – 6.57 (m, 1H), 4.88 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (d, *J* = 235.6 Hz), 155.7, 133.4, 130.6, 126.97 (dd, *J* = 21.2, 4.0 Hz), 126.29 (d, *J* = 7.2 Hz), 114.22 (d, *J* = 13.6 Hz), 110.3, 110.0, 109.63 (d, *J* = 10.6 Hz), 100.11 (d, *J* = 5.2 Hz), 69.3, 54.8, 33.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.2. HRMS (ESI+) Calcd. For $C_{14}H_{14}FNNaO_3^+$ ($[M+Na]^+$): 286.0850, found: 386.0847. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2305, 1750, 1442, 1265, 869, 740.

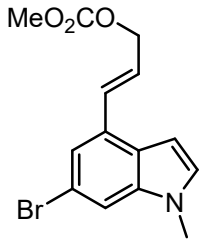


(*E*)-3-(6-fluoro-1-methyl-1*H*-indol-4-yl)allyl methyl carbonate (2y): Yield (89% yield, overall 3 steps); yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 1H), 7.05 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.99 – 6.95 (m, 1H), 6.50 – 6.47 (m, 1H), 6.47 – 6.39 (m, 1H), 4.86 (dd, *J* = 6.4, 1.2 Hz, 2H), 4.06 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ160.04 (d, *J* = 239.0 Hz), 155.6, 132.07 (d, *J* = 12.8 Hz), 131.25 (d, *J* = 2.4 Hz), 129.86 (d, *J* = 9.6 Hz), 124.9, 123.51 (d, *J* =

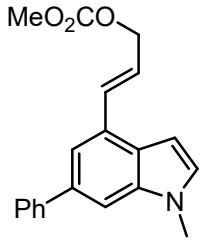
3.6 Hz), 119.0, 106.24 (d, J = 25.2 Hz), 96.6, 94.53 (d, J = 27.6 Hz), 68.4, 65.9, 54.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.9. IR (thin film) ν (cm^{-1}) 3054, 2986, 2305, 1749, 1442, 1265, 949, 740.



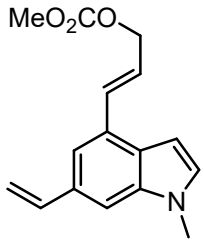
(*E*)-3-(7-fluoro-1-methyl-1*H*-indol-4-yl)allyl methyl carbonate (2z): Yield (87% yield, overall 3 steps); white solid; m.p. 64-66 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 6.94 (m, 3H), 6.86 – 6.78 (m, 1H), 6.70 – 6.65 (m, 1H), 6.44 – 6.23 (m, 1H), 4.90 – 4.80 (m, 2H), 3.99 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 150.35 (d, J = 245.6 Hz), 132.9, 130.8, 130.70 (d, J = 5.6 Hz), 124.60 (d, J = 14.0 Hz), 122.2, 118.11 (d, J = 6.8 Hz), 107.24 (d, J = 18.6 Hz), 107.24 (d, J = 18.6 Hz), 100.3, 69.0, 54.8, 35.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.6. HRMS (ESI+) Calcd. For $C_{14}H_{14}FNNaO_3^+$ ($[M+Na]^+$): 286.0850, found: 386.0847. IR (thin film) ν (cm^{-1}) 3054, 2986, 2305, 1748, 1442, 1265, 896, 739.



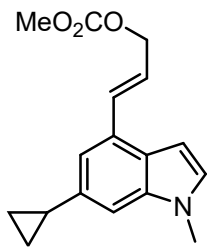
(*E*)-3-(6-bromo-1-methyl-1*H*-indol-4-yl)allyl methyl carbonate (2A): Yield (89% yield, overall 3 steps); white solid; m.p. 60-62 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.35 – 7.32 (m, 1H), 7.06 (d, J = 3.2 Hz, 1H), 6.98 (d, J = 16.0 Hz, 1H), 6.61 (dd, J = 3.2, 0.8 Hz, 1H), 6.50 – 6.40 (m, 1H), 4.86 (dd, J = 6.4, 1.2 Hz, 2H), 3.82 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 137.8, 131.9, 129.8, 127.8, 125.7, 124.4, 120.4, 115.2, 112.0, 99.7, 68.6, 54.8, 33.1. HRMS (ESI+) Calcd. For $C_{14}H_{14}{}^{78.9183}BrNO_3^+$ ($[M+H]^+$): 346.0049, found: 346.0047; $C_{14}H_{14}{}^{80.9163}BrNO_3^+$ ($[M+H]^+$): 348.0029, found: 348.0030. IR (thin film) ν (cm^{-1}) 3054, 2986, 2305, 1750, 1442, 1264, 896, 744.



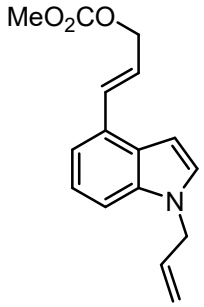
(*E*)-methyl (3-(1-methyl-6-phenyl-1*H*-indol-4-yl)allyl) carbonate (2B): Yield (85% yield, overall 3 steps); white solid; m.p. 80-82 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.49 – 7.41 (m, 4H), 7.36 – 7.30 (m, 1H), 7.16 – 7.08 (m, 2H), 6.67 (d, *J* = 3.2 Hz, 1H), 6.58 – 7.48 (m, 1H), 4.89 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 142.2, 137.6, 135.3, 133.6, 129.9, 128.7, 128.5, 127.4, 126.7, 126.0, 123.3, 117.8, 107.8, 99.4, 69.0, 54.8, 33.0. HRMS (ESI+) Calcd. For $C_{20}H_{19}NNaO_3^+$ ($[M+Na]^+$): 344.1257, found: 344.1254. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2305, 1748, 1442, 1265, 895, 739.



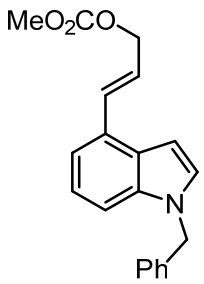
(*E*)-methyl (3-(1-methyl-6-vinyl-1*H*-indol-4-yl)allyl) carbonate (2C): Yield (86% yield, overall 3 steps); yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 6.83 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.62 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.52 – 6.44 (m, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.25 – 5.14 (m, 1H), 4.87 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 137.6, 137.3, 133.5, 131.5, 130.0, 128.3, 126.6, 123.2, 116.3, 112.0, 107.3, 99.6, 68.9, 54.8, 32.9. HRMS (ESI+) Calcd. For $C_{16}H_{17}NNaO_3^+$ ($[M+H]^+$): 294.1101, found: 294.1097. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2305, 1748, 1442, 1265, 896, 739.



(*E*)-3-(6-cyclopropyl-1-methyl-1*H*-indol-4-yl)allyl methyl carbonate (2D): Yield (88% yield, overall 3 steps); yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 6.94 (m, 4H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.50 – 6.40 (m, 1H), 4.85 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 2.07 – 1.97 (m, 1H), 1.02 – 0.90 (m, 2H), 0.78 – 0.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 137.5, 137.4, 133.8, 128.8, 128.0, 124.9, 122.8, 116.7, 106.4, 99.2, 69.1, 54.8, 32.9, 29.7, 15.8, 8.8. HRMS (ESI+) Calcd. For $C_{17}H_{19}NNaO_3^+$ ($[M+Na]^+$): 308.1257, found: 308.1254. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2305, 1748, 1422, 1265, 896, 740.

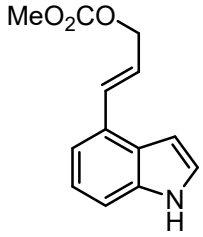


(*E*)-3-(1-allyl-1*H*-indol-4-yl)allyl methyl carbonate (2E): Yield (84% yield, overall 3 steps); yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.20 – 7.16 (m, 1H), 7.15 – 7.12 (m, 1H), 7.08 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.52 – 6.40 (m, 1H), 6.05 – 5.84 (m, 1H), 5.19 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.11 – 5.01 (m, 1H), 4.87 (dd, *J* = 6.6, 1.2 Hz, 2H), 4.74 – 4.70 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 136.4, 133.6, 133.3, 128.4, 128.3, 126.9, 122.9, 121.6, 117.8, 117.3, 109.6, 99.8, 69.0, 54.8, 48.9. HRMS (ESI+) Calcd. For $C_{16}H_{18}NO_3^+$ ($[M+H]^+$): 272.1281, found: 264.0788. HRMS (ESI+) Calcd. For $C_{16}H_{17}NNaO_3^+$ ($[M+Na]^+$): 294.1101, found: 294.1098. IR (thin film) *v* (cm^{-1}) 3054, 2986, 2306, 1747, 1442, 1265, 941, 740.



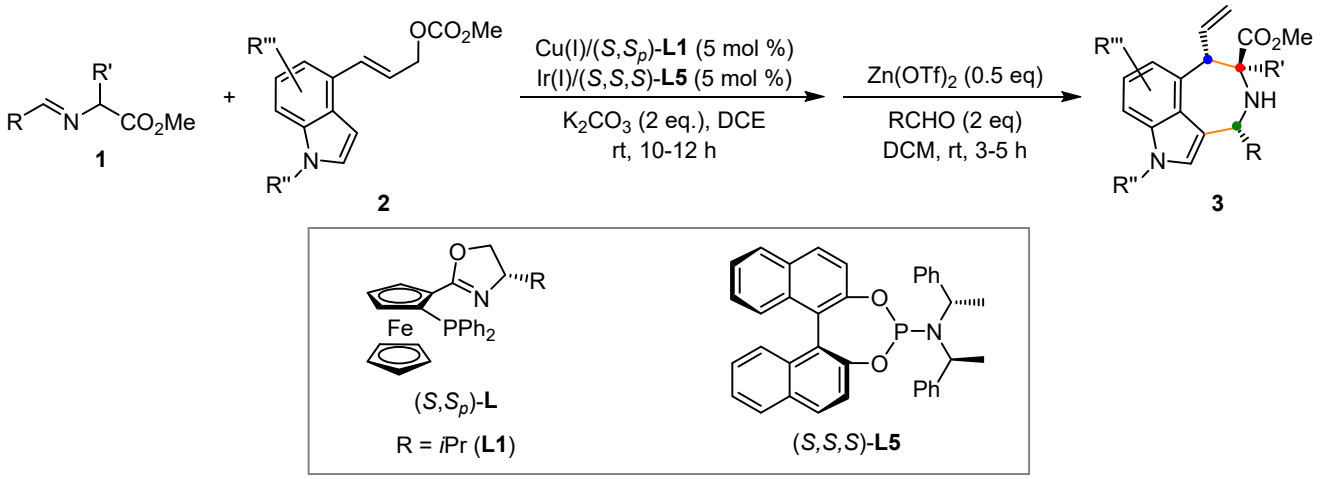
(*E*)-3-(1-benzyl-1*H*-indol-4-yl)allyl methyl carbonate (2F): Yield (86% yield, overall 3 steps); white solid; m.p. 78-80 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H),

7.18 (d, J = 3.2 Hz, 1H), 7.16 – 7.05 (m, 4H), 6.74 (d, J = 3.2 Hz, 1H), 6.50 – 6.44 (m, 1H), 5.33 (s, 2H), 4.87 (dd, J = 6.4, 1.2 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 137.4, 136.7, 133.6, 128.8, 128.5, 127.7, 127.0, 126.7, 123.0, 121.8, 118.0, 109.8, 100.1, 69.1, 54.8, 50.2. HRMS (ESI+) Calcd. For $C_{20}H_{19}NNaO_3^+$ ([M+Na]$^+$): 344.1257, found: 344.1255. IR (thin film) v (cm^{-1}) 3054, 2986, 2305, 1748, 1422, 1265, 896, 740.



(*E*)-3-(1*H*-indol-4-yl)allyl methyl carbonate (2G): Yield (80% yield, overall 3 steps); yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20-7.14 (m, 1H), 7.09 (d, J = 16.0 Hz, 1H), 6.75 – 6.72 (m, 1H), 6.55 – 6.40 (m, 1H), 4.87 (dd, J = 6.4, 1.2 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 136.1, 133.7, 128.3, 126.1, 124.6, 122.9, 122.0, 118.1, 111.0, 101.0, 69.0, 54.8. HRMS (ESI+) Calcd. For $C_{13}H_{13}NNaO_3^+$ ([M+Na]$^+$): 254.0788, found: 254.0787. IR (thin film) v (cm^{-1}) 3365, 3054, 2986, 2305, 1747, 1422, 1265, 896, 739.

3. General Procedures and Characterization for Azepino[3,4,5-*cd*]-Indoles

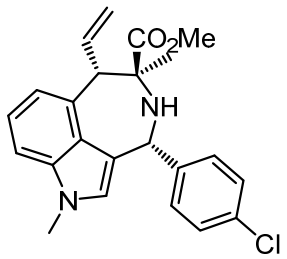


A flame dried Schlenk tube **A** was cooled to room temperature and filled with N_2. To this flask were added $[Ir(COD)Cl]_2$ (0.005 mmol), (*S*,*S*,*S*)-**L5** (0.010 mmol), degassed THF (0.5 mL) and

degassed *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 ºC for 30 min and then the volatile solvents were removed under vacuum to gain a pale-yellow solid. Meanwhile, $Cu(MeCN)_4BF_4$ (0.01 mmol) and (S,S_p)-^{i}Pr-Phosferrox-**L1** (0.011 mmol) were dissolved in 1.0 mL of DCE in a Schlenk tube **B**, and stirred at room temperature for about 40 min. Then, aldimine ester **1** (0.30 mmol), 4-indolyl allylic carbonate **2** (0.20 mmol) and K_2CO_3 (0.40 mmol) were added into the Schlenk tube **A** and filled with N_2. The Cu/**L1** complex solution was then transferred from the Schlenk tube **B** to the Schlenk tube **A** *via* syringe. Finally, the reaction mixture was continuously stirred at room temperature under N_2 atmosphere. Once starting material was consumed (monitored by TLC), the residue was separated by flash column chromatography to give the crude product. The crude product was dissolved in dichloromethane and two equivalent of the corresponding aldehyde and $Zn(OTf)_2$ (50 mol%) were added. Once starting material was consumed (monitored by TLC), the reaction was quenched with 1 mol of HCl solution (1 mL). The layers were separated, and the aqueous layer was extracted with DCM (5 mL x 3). The combined organic components were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtration and evaporated in vacuum. After evaporation of the solvent under vacuum, the crude mixture was flushed with short silica gel plug to remove the metal complex and the diastereoselectivity was determined with ^{1}H NMR analysis. Then, the whole residue was further purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess.

Characterization for Azepino[3,4,5-*cd*]-Indoles:

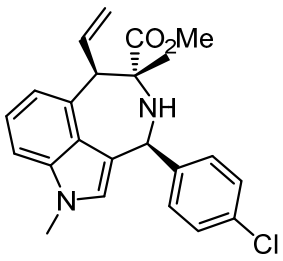
Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3a)



Yield (67%); 18:1 dr; white solid; m.p. 198-200 ℃; $[\alpha]^{30}_D$ = 63.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.12 (m, 1H), 7.12 – 7.06 (m,

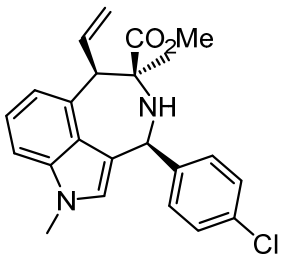
1H), 6.98 – 6.92 (m, 1H), 6.41 – 6.30 (m, 1H), 6.16 (s, 1H), 5.79 (s, 1H), 5.19 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.10 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.35 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 3.58 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 144.1, 138.2, 136.9, 134.8, 132.9, 129.5, 128.5, 125.9, 124.9, 122.0, 120.0, 118.9, 116.5, 107.2, 64.9, 56.7, 56.4, 51.7, 32.6, 26.5. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 395.1521, found: 395.1518; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 397.1491, found: 397.1498. IR (thin film) *v* (cm^{-1}) 3334, 3047, 2929, 1727, 1576, 1486, 1135, 1089, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.66 and 6.18 min.

Methyl (6*R*,7*R*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*S*)-3a)



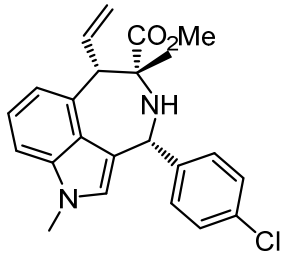
Yield (62%); 17:1 dr; white solid; m.p. 198-200 ℃; $[\alpha]^{30}_D$ = -61.4 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 395.1521, found: 395.1521; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 397.1491, found: 397.1497. IR (thin film) *v* (cm^{-1}) 3329, 3053, 2945, 1734, 1606, 1487, 1241, 1109, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.66 and 6.18 min.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-3a)



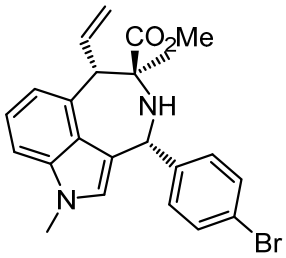
Yield (63%); 20:1 dr; white solid; m.p. 68-70 °C; $[\alpha]^{30}_D$ = -110.8 (*c* 0.50, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.10 (m, 2H), 6.99 – 6.95 (m, 1H), 6.34 (ddd, *J* = 17.2, 10.4, 8.8 Hz, 1H), 6.23 (s, 1H), 5.32 (s, 1H), 5.03 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.93 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 144.5, 140.9, 137.0, 133.0, 132.8, 129.9, 128.5, 126.6, 124.7, 121.8, 121.3, 119.9, 114.4, 107.4, 64.8, 60.1, 56.1, 52.6, 32.7, 20.8. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1523; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1495. IR (thin film) *v* (cm^{-1}) 3340, 2924, 2867, 1729, 1580, 1486, 1239, 1114, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AS-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.01 and 5.51 min.

Methyl (6*S*,7*R*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*R*)-3a)



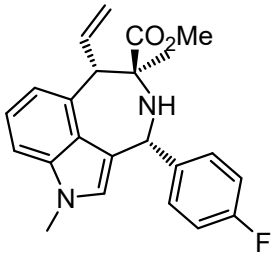
Yield (66%); 20:1 dr; white solid; m.p. 68-70 °C; $[\alpha]^{30}_D$ = 107.4 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1519; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1490. IR (thin film) *v* (cm^{-1}) 3337, 3049, 2947, 1730, 1487, 1457, 1246, 1088, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AS-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.01 and 5.51 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-bromophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3b)



Yield (68%); 19:1 dr; white solid; m.p. 208-210 °C; $[\alpha]^{30}_D$ = 47.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.12 (m, 1H), 7.12 – 7.08 (m, 1H), 6.97 – 6.93 (m, 1H), 6.36 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.17 (s, 1H), 5.79 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 3.61 (s, 3H), 3.59 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 144.6, 138.2, 136.9, 134.8, 131.4, 129.9, 125.9, 124.9, 122.0, 121.0, 119.9, 118.9, 116.5, 107.2, 65.0, 56.7, 56.5, 51.7, 32.7, 26.5. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{78.9183}BrN_2O_2^+$ ($[M+H]^+$): 439.1016, found: 439.1013; $C_{23}H_{24}{}^{80.9163}BrN_2O_2^+$ ($[M+H]^+$): 441.0995, found: 441.0996. IR (thin film) *v* (cm^{-1}) 3333, 3055, 2946, 1729, 1484, 1452, 1244, 1134, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.02 and 6.75 min.

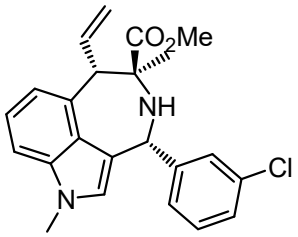
Methyl (6*S*,7*S*,9*R*)-9-(4-fluorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3c)



Yield (64%); 17:1 dr; white solid; m.p. 152-154 °C; $[\alpha]^{30}_D$ = 65.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.17 – 7.11 (m, 1H), 7.10 – 7.00 (m, 3H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.36 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.15 (s, 1H), 5.78 (s, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.34 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 3.58 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 162.0 (d, *J* = 241.0 Hz), 141.4, 138.4, 136.9, 134.9, 129.65 (d, *J* = 7.8 Hz), 125.9, 124.9, 122.0, 120.2, 118.9, 116.4, 115.1 (d, *J* = 21.8 Hz), 107.1, 64.9, 56.8, 56.4, 51.7,

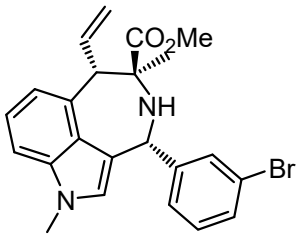
32.6, 26.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5. HRMS (ESI+) Calcd. For $C_{23}H_{24}FN_2O_2^+$ ($[M+H]^+$): 379.1816, found: 379.1813. IR (thin film) *v* (cm^{-1}) 3322, 3041, 2925, 1730, 1504, 1452, 1221, 1133, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.18 and 5.62 min.

Methyl (6*S*,7*S*,9*R*)-9-(3-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3d)



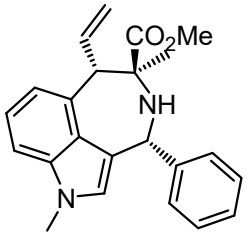
Yield (62%); 14:1 dr; white solid; m.p. 78-80 °C; $[\alpha]^{30}_D$ = 39.4 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49(m, 1H), 7.43 – 7.37 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.13 (m, 1H), 7.12-7.08 (m, 1H), 6.96 – 6.93 (m, 1H), 6.37 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.19 (s, 1H), 5.80 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.12 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 3.61 (s, 3H), 3.59 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 147.6, 138.2, 136.9, 134.8, 134.1, 129.6, 128.3, 127.4, 126.3, 125.9, 124.9, 122.0, 119.8, 118.9, 116.5, 107.2, 65.0, 60.1, 56.7, 51.7, 32.7, 26.4. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1516; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1503. IR (thin film) *v* (cm^{-1}) 3337, 3057, 2922, 1730, 1482, 1456, 1244, 1088, 747. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 4.62 and 4.96 min.

Methyl (6*S*,7*S*,9*R*)-9-(3-bromophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3e)



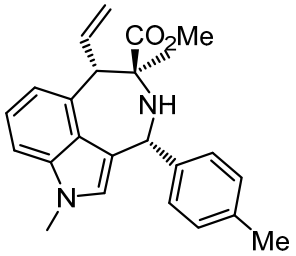
Yield (70%); 16:1 dr; white solid; m.p. 128-130 °C; $[\alpha]^{30}_D$ = 52.4 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 1H), 7.49 – 7.44 (m, 2H), 7.26 – 7.23 (m, 1H), 7.21 – 7.15 (m, 1H), 7.14 – 7.10 (m, 1H), 6.99 – 6.94 (m, 1H), 6.39 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.21 (s, 1H), 5.81 (s, 1H), 5.22 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.38 (d, *J* = 9.6 Hz, 1H), 3.63 (s, 3H), 3.61 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 147.9, 138.2, 136.9, 134.8, 131.2, 130.4, 129.9, 126.8, 126.0, 124.9, 122.4, 122.0, 119.7, 118.9, 116.5, 107.2, 645.0, 56.7, 51.7, 32.7, 26.5, 22.8. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{78.9183}BrN_2O_2^+$ ($[M+H]^+$): 439.1016, found: 439.1010; $C_{23}H_{24}{}^{80.9163}BrN_2O_2^+$ ($[M+H]^+$): 441.0996, found: 441.0996. IR (thin film) *v* (cm^{-1}) 3339, 3055, 2944, 1729, 1453, 1423, 1230, 1128, 746. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 4.68 and 5.15 min.

Methyl (6*S*,7*S*,9*R*)-2,7-dimethyl-9-phenyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3f)



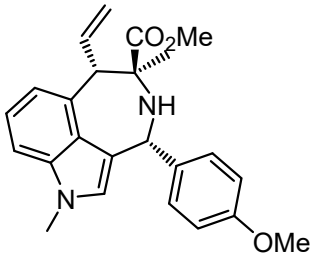
Yield (68%); 15:1 dr; white solid; m.p. 128-130 °C; $[\alpha]^{30}_D$ = 61.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.41 – 7.34 (m, 2H), 7.31 (m, 1H), 7.17 – 7.12 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.44 – 6.34 (m, 1H), 6.17 (s, 1H), 5.78 (s, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 3.58 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 142.0, 138.4, 136.9, 134.9, 128.3, 128.1, 127.3, 126.0, 125.1 121.9, 120.5, 118.8, 116.3, 107.1, 65.0, 57.1, 56.7, 51.7, 32.6, 26.5. HRMS (ESI+) Calcd. For $C_{23}H_{25}N_2O_2^+$ ($[M+H]^+$): 361.1911, found: 361.1907. IR (thin film) *v* (cm^{-1}) 3341, 2923, 2854, 1730, 1452, 1420, 1231, 1133, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.27 and 5.88 min.

Methyl (6*S*,7*S*,9*R*)-2,7-dimethyl-9-(*p*-tolyl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3g)



Yield (60%); 12:1 dr; white solid; m.p. 118-120 °C; $[\alpha]^{30}_D$ = 86.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.39 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.20 (s, 1H), 5.75 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.35 (d, *J* = 9.6 Hz, 1H), 3.60 (s, 6H), 2.38 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 142.7, 138.5, 136.9, 136.8, 135.0, 129.0, 128.1, 126.0, 125.1, 121.9, 120.6, 118.7, 116.3, 107.1, 64.9, 56.8, 51.6, 32.6, 26.5, 21.2, 14.1. HRMS (ESI+) Calcd. For $C_{24}H_{27}N_2O_2^+$ ($[M+H]^+$): 375.2067, found: 375.2068. IR (thin film) *v* (cm^{-1}) 3351, 2944, 2854, 1731, 1601, 1484, 1220, 1084, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.62 and 6.57 min.

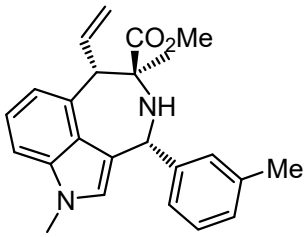
Methyl (6*S*,7*S*,9*R*)-9-(4-methoxyphenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3h)



Yield (66%); 18:1 dr; white solid; m.p. 126-128 °C; $[\alpha]^{30}_D$ = 85.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.18 – 7.12 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.38 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.19 (s, 1H), 5.72 (s, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.09 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.33 (d, *J* = 9.6 Hz, 1H), 3.83 (s, 3H), 3.60 (s, 3H), 3.60 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 158.8, 138.6, 138.0, 137.0,

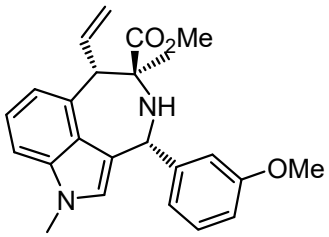
135.0, 129.2, 126.0, 125.0, 121.9, 120.6, 118.78, 116.2, 113.7, 107.1, 64.9, 56.9, 56.5, 55.3, 51.7, 32.6, 26.7. HRMS (ESI+) Calcd. For $C_{24}H_{27}N_2O_3^+$ ([M+H]$^+$): 391.2016, found: 391.2019. IR (thin film) *v* (cm^{-1}) 3342, 2946, 2863, 1730, 1609, 1510, 1243, 1177, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.95 and 9.29 min.

Methyl (6*S*,7*S*,9*R*)-2,7-dimethyl-9-(*m*-tolyl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3i)



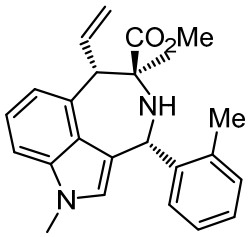
Yield (58%); 15:1 dr; white solid; m.p. 124-126℃; $[\alpha]^{30}_D$ = 106.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 3H), 7.18 – 7.08 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.40 (ddd, *J* = 17.2, 10.8, 7.2 Hz, 1H), 6.19 (s, 1H), 5.74 (s, 1H), 5.21 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.11 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.61 (s, 3H), 3.60 (s, 3H), 2.38 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 145.4, 138.5, 137.9, 136.9, 135.0, 128.9, 128.2, 128.0, 126.0, 125.2, 121.9, 120.5, 118.8, 116.3, 107.1, 65.0, 57.1, 56.8, 51.7, 32.6, 26.5, 21.5. HRMS (ESI+) Calcd. For $C_{24}H_{27}N_2O_2^+$ ([M+H]$^+$): 375.2067, found: 375.2069. IR (thin film) *v* (cm^{-1}) 3335, 2924, 2863, 1730, 1606, 1453, 1241, 1131, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IC, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.20 and 9.78 min.

Methyl (6*S*,7*S*,9*R*)-9-(3-methoxyphenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3j)



Yield (61%); 16:1 dr; white solid; m.p. 122-124 ℃; $[\alpha]^{30}_D$ = 80.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 1H), 7.16 – 7.12 (m, 1H), 7.10 – 7.05 (m, 3H), 6.93 (d, *J* = 7.0 Hz, 1H), 6.86 – 6.82 (m, 1H), 6.37 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.22 (s, 1H), 5.76 (s, 1H), 5.18 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.09 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.58 (s, 6H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 159.6, 147.1, 138.4, 136.9, 134.9, 129.3, 126.0, 125.1, 121.9, 120.5, 120.2, 118.7, 116.4, 113.6, 112.7, 107.1, 65.0, 57.0, 56.7, 55.2, 51.7, 32.6, 26.4. HRMS (ESI+) Calcd. For $C_{24}H_{27}N_2O_3^+$ ($[M+H]^+$): 391.2016, found: 391.2019. IR (thin film) *v* (cm^{-1}) 3339, 2933, 2865, 1730, 1602, 1455, 1244, 1152, 1045, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.87 and 6.67 min.

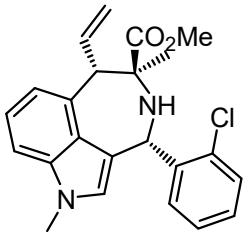
Methyl (6*S*,7*S*,9*R*)-2,7-dimethyl-9-(*o*-tolyl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3k)



Yield (63%); 11:1 dr; white solid; m.p. 88-90 ℃; $[\alpha]^{30}_D$ = 138.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.22 – 7.19 (m, 3H), 7.18 – 7.13 (m, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.35 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.06 (s, 1H), 5.98 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.10 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.62 – 4.30 (m, 1H), 3.62 (s, 3H), 3.58 (s, 3H), 2.48 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 143.2, 138.1, 137.1, 135.1, 130.1, 128.4, 127.0, 126.2, 125.5, 125.2, 120.0, 120.5, 119.4, 118.6, 116.5, 107.2, 65.5, 60.4, 56.1, 51.7, 32.6, 25.5, 19.5. HRMS (ESI+) Calcd. For $C_{24}H_{27}N_2O_2^+$ ($[M+H]^+$): 375.2067, found: 375.2068. IR (thin film) *v* (cm^{-1}) 3358, 2919, 2850, 1733, 1633, 1454, 1241, 1114, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 4.24 and 5.37 min.

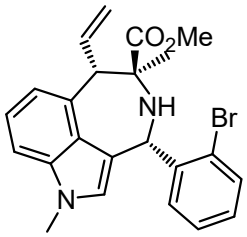
Methyl (6*S*,7*S*,9*R*)-9-(2-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino

[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3l)



Yield (66%); 15:1 dr; white solid; m.p. 148-150 °C; $[\alpha]^{30}_D$ = 83.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 1H), 7.44 – 7.40 (m, 1H), 7.29 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.44 – 6.30 (m, 1H), 6.35 (s, 1H), 6.18 (brs, 1H), 5.22 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.14 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.47 (d, *J* = 9.6 Hz, 1H), 3.64 (s, 3H), 3.61 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 143.0, 137.9, 136.9, 134.7, 132.9, 130.3, 129.2, 128.2, 127.2, 125.3, 122.0, 119.5, 118.7, 116.8, 107.3, 65.4, 56.2, 52.6, 51.8, 32.7, 25.7. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1518; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1496. IR (thin film) *v* (cm^{-1}) 3334, 2925, 2853, 1724, 1633, 1451, 1250, 1119, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.05 and 6.01 min.

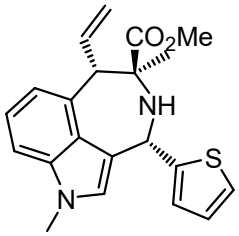
Methyl (6*S*,7*S*,9*R*)-9-(2-bromophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3m)



Yield (64%); 15:1 dr; white solid; m.p. 162-164 °C; $[\alpha]^{30}_D$ = 70.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 1H), 7.58 – 7.55 (m, 1H), 7.35 – 7.28 (m, 1H), 7.20 – 7.14 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.44 – 6.34 (m, 1H), 6.33 (s, 1H), 6.20 (s, 1H), 5.23 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.44 (d, *J* = 9.6 Hz, 1H), 3.65 (s, 3H), 3.61 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 144.9, 138.1, 136.9, 134.7, 132.3, 130.6, 128.6, 127.8, 125.5, 125.2, 123.3, 122.0, 119.2, 118.8, 116.6, 107.2, 65.2, 56.0, 55.0, 51.8, 32.7, 26.0.

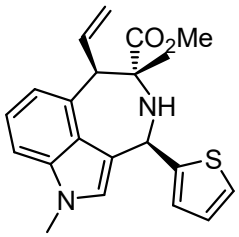
HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{78.9183}BrN_2O_2^+$ ([M+H]$^+$): 439.1016, found: 439.1017; $C_{23}H_{24}{}^{80.9163}BrN_2O_2^+$ ([M+H]$^+$): 441.0996, found: 441.1000. IR (thin film) ν (cm^{-1}) 3334, 3071, 2926, 1729, 1633, 1456, 1246, 1134, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.01 and 5.78 min.

Methyl (6*S*,7*S*,9*S*)-2,7-dimethyl-9-(thiophen-2-yl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*S*)-3n)



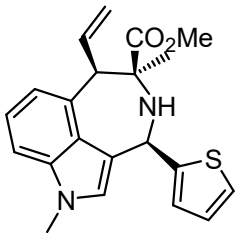
Yield (58%); 14:1 dr; white solid; m.p. 56-58 ℃; $[\alpha]^{30}_D$ = 83.4 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 1H), 7.18 – 7.16 (m, 1H), 7.16 – 7.12 (m, 1H), 7.11 – 7.07 (m, 1H), 7.03 – 6.99 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 6.38 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.22 (s, 1H), 5.20 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.11 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 150.1, 138.3, 137.0, 134.8, 126.2, 126.0, 124.5, 124.4, 124.0, 121.9, 119.4, 118.9, 116.4, 107.2, 64.8, 56.9, 52.5, 51.7, 32.7, 26.5. HRMS (ESI+) Calcd. For $C_{21}H_{23}N_2O_2S^+$ ([M+H]$^+$): 367.1475, found: 367.1472. IR (thin film) ν (cm^{-1}) 3342, 3065, 2945, 1730, 1606, 1454, 1238, 1125, 750. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.65 and 7.80 min.

Methyl (6*R*,7*R*,9*R*)-2,7-dimethyl-9-(thiophen-2-yl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*R*)-3n)



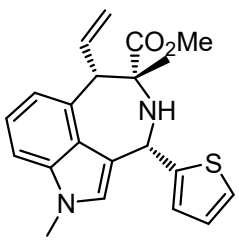
Yield (60%); 14:1 dr; white solid; m.p. 56-58 °C; $[\alpha]^{30}_D$ = -86.1 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{21}H_{23}N_2O_2S^+$ ($[M+H]^+$): 367.1475, found: 367.1473. IR (thin film) *v* (cm^{-1}) 3340, 3061, 2945, 1730, 1606, 1452, 1238, 1125, 744. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.65 and 7.80 min.

Methyl (6*R*,7*S*,9*R*)-2,7-dimethyl-9-(thiophen-2-yl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*R*)-3n)



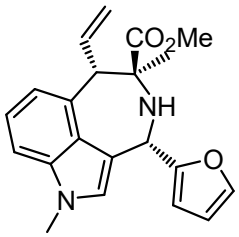
Yield (45%); 10:1 dr; white solid; m.p. 54-56 °C; $[\alpha]^{30}_D$ = - 93.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 1H), 7.19 – 7.09 (m, 3H), 7.05 – 6.87 (m, 2H), 6.51 (s, 1H), 6.43 – 6.27 (m, 1H), 5.75 (s, 1H), 5.04 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.92 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.14 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 150.07, 140.87, 137.1, 132.8, 126.8, 125.7, 124.9, 124.2, 124.1, 121.7, 121.2, 119.8, 114.3, 107.4, 64.8, 60.0, 52.6, 51.8, 32.8, 20.7. HRMS (ESI+) Calcd. For $C_{21}H_{23}N_2O_2S^+$ ($[M+H]^+$): 367.1475, found: 367.1472. IR (thin film) *v* (cm^{-1}) 3340, 3065, 2944, 1729, 1605, 1454, 1240, 1125, 750. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 280 nm); t_r = 6.01 and 17.97 min.

Methyl (6*S*,7*R*,9*S*)-2,7-dimethyl-9-(thiophen-2-yl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*S*)-3n)



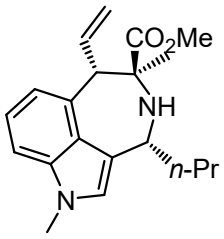
Yield (52%); 10:1 dr; white solid; m.p. 54-56 ℃; $[\alpha]^{30}_D$ = 96.0 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{21}H_{23}N_2O_2S^+$ ($[M+H]^+$): 367.1475, found: 367.1473. IR (thin film) *v* (cm^{-1}) 3340, 3060, 2944, 1730, 1606, 1452, 1238, 1125, 741. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 280 nm); t_r = 6.01 and 17.97 min.

Methyl (6*S*,7*S*,9*S*)-2,7-dimethyl-(furan-2-yl)-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*S*)-3o)



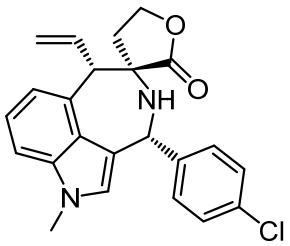
Yield (55%); 10:1 dr; white solid; m.p. 76-78 ℃; $[\alpha]^{30}_D$ = 110.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.26 – 7.25 (m, 1H), 7.20 – 7.04 (m, 2H), 6.96 – 6.85 (m, 1H), 6.48 (s, 1H), 6.42 – 6.30 (m, 2H), 6.20 (ddd, *J* = 17.2, 10.0, 8.6 Hz, 1H), 5.56 (s, 1H), 5.29 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.09 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.09 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 3.50 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 156.3, 141.7, 137.5, 137.1, 133.0, 125.3, 125.2, 121.7, 120.0, 118.7, 118.4, 110.1, 107.8, 106.3, 66.0, 59.0, 51.8, 49.7, 32.8, 20.1. HRMS (ESI+) Calcd. For $C_{21}H_{23}N_2O_3^+$ ($[M+H]^+$): 351.1703, found: 351.1699. IR (thin film) *v* (cm^{-1}) 3342, 3117, 2925, 1736, 1585, 1455, 1373, 1247, 1148, 750. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.62 and 13.82 min.

Methyl (6*S*,7*S*,9*R*)-2,7-dimethyl-9-propyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3p)



Yield (44%); 11:1 dr; white solid; m.p. 68-70 °C; $[\alpha]^{30}_D$ = 71.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 6.85 – 6.81 (m, 1H), 6.69 (s, 1H), 6.31 – 6.16 (m, 1H), 5.23 (s, 1H), 5.21 – 5.17 (m, 1H), 4.76 – 4.68 (m, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 1.95 – 1.85 (m, 1H), 1.67 – 1.61 (m, 1H), 1.50 – 1.41 (m, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 136.8, 135.7, 134.3, 127.3, 122.5, 122.1, 121.6, 118.5, 117.3), 107.5, 66.6, 52.5, 51.5, 49.8, 37.6, 32.7, 21.5, 19.1, 14.2. HRMS (ESI+) Calcd. For $C_{20}H_{27}N_2O_2^+$ ($[M+H]^+$): 327.2067, found: 327.2064. IR (thin film) *v* (cm^{-1}) 3345, 2926, 2867, 1735, 1673, 1495, 1231, 1146, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.39 and 6.18 min.

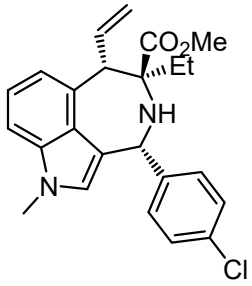
(6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-2-methyl-6-vinyl-2,4',5',6,8,9-hexahydro-2'*H*-spiro[azepino[3,4,5-*cd*]indole-7,3'-furan]-2'-one ((6*S*,7*S*,9*R*)-3q)



Yield (62%); 10:1 dr; white solid; m.p. 134-136 °C; $[\alpha]^{30}_D$ = 63.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.17 (m, 2H), 6.93 – 6.87 (m, 1H), 6.76 (ddd, *J* = 17.2, 10.4, 4.4 Hz, 1H), 5.95 (s, 1H), 5.84 (s, 1H), 5.35 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.90 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.12 – 4.02 (m, 1H), 3.86 – 3.78 (m, 1H), 3.64 (s, 3H), 2.37 – 2.19 (m, 1H), 1.95 – 1.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 142.5, 137.6, 137.3, 132.9, 132.0, 129.7, 128.3, 127.4, 126.5, 122.4, 120.8, 119.2, 117.6, 108.4, 65.7, 65.3, 55.9, 52.8, 39.6, 32.7, 29.8. HRMS (ESI+) Calcd. For $C_{23}H_{22}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 393.1364, found: 393.1365; $C_{23}H_{22}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 395.1334, found: 395.1335. IR (thin film) *v* (cm^{-1}) 3357, 2922, 2851, 1727, 1632, 1514, 1246, 1123, 811. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 9.19 and 11.26 min.

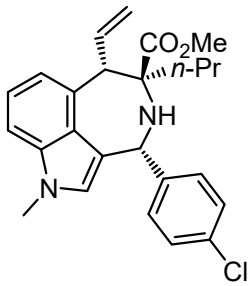
Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-7-ethyl-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino

[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3r)



Yield (66%); 20:1 dr; white solid; m.p. 114-116 °C; $[\alpha]^{30}_{D}$ = 103.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.13 (m, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.48 – 6.36 (m, 1H), 6.21 (s, 1H), 5.68 (s, 1H), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.20 (d, *J* = 9.6 Hz, 1H), 3.60 (s, 3H), 3.55 (s, 3H), 2.01 – 1.90 (m, 1H), 1.75 – 1.68 (m, 1H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 145.1, 139.8, 136.9, 135.4, 133.0, 129.8, 128.5, 126.4, 124.1, 121.9, 119.6, 118.4, 114.9, 106.8, 67.7, 57.6, 56.1, 51.4, 33.8, 32.7, 8.6. HRMS (ESI+) Calcd. For $C_{24}H_{26}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 409.1677, found: 409.1672; $C_{24}H_{26}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 411.1647, found: 411.1657. IR (thin film) *v* (cm^{-1}) 3339, 2943, 2878, 1729, 1632, 1487, 1224, 1137, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.40 and 7.37 min.

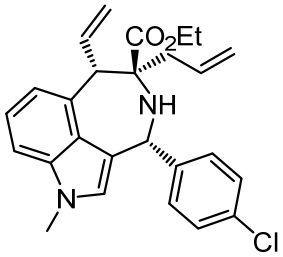
Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-7-propyl-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3s)



Yield (63%); 20:1 dr; white solid; m.p. 138-140 °C; $[\alpha]^{30}_{D}$ = 107.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.37 – 7.29 (m, 2H), 7.18 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.48 – 6.36 (m, 1H), 6.20 (s, 1H), 5.69 (s, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.19 (d, *J* = 9.6 Hz, 1H), 3.60 (s, 3H), 3.53 (s, 3H), 1.91 (dd, *J* = 12.8, 4.8 Hz, 1H), 1.60 (dd, *J* = 25.2, 4.8 Hz, 1H), 1.52 – 1.40 (m, 1H), 1.31 – 1.24 (m, 1H), 0.89 (t, *J*

= 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 145.1, 139.8, 136.9, 135.4, 133.0, 129.8, 128.5, 126.4, 124.1, 121.9, 119.6, 118.5, 115.0, 106.8, 67.3, 57.5, 56.7, 51.4, 43.2, 32.7, 17.4, 14.2. HRMS (ESI+) Calcd. For $C_{25}H_{28}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 423.1834, found: 423.1835; $C_{25}H_{28}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 425.1804, found: 425.1807. IR (thin film) *v* (cm^{-1}) 3340, 2944, 2877, 1729, 1593, 1455, 1241, 1082, 752. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.24 and 6.89 min.

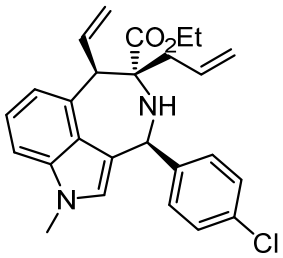
Ethyl (6*S*,7*S*,9*R*)-7-allyl-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3t)



Yield (66%); 20:1 dr; white solid; m.p. 54-56 °C; $[\alpha]^{30}_D$ = 74.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.48 – 6.38 (m, 1H), 6.21 (s, 1H), 5.78 (s, 1H), 5.85 – 5.70 (m, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.16 – 5.12 (m, 2H), 5.05 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.17 (d, *J* = 9.6 Hz, 1H), 4.02 – 3.94 (m, 2H), 3.59 (s, 3H), 2.67 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.43 (dd, *J* = 13.6, 8.4 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 145.2, 139.6, 136.9, 135.2, 132.9, 132.4, 129.8 128.5, 126.4, 124.2, 121.8, 119.8, 119.4, 118.4, 115.6, 106.9, 66.5, 60.3, 57.2, 44.6, 32.7, 14.0. HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 435.1834, found: 435.1824; $C_{26}H_{28}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 437.1804, found: 437.1806. IR (thin film) *v* (cm^{-1}) 3334, , 2931, 2862, 1726, 1634, 1487, 1204, 1138, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.99 and 8.53 min.

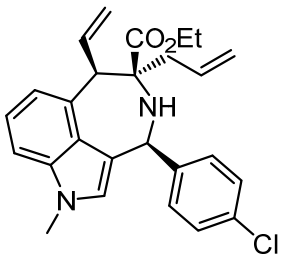
Ethyl (6*R*,7*R*,9*S*)-7-allyl-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino

[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*S*)-3t)



Yield (60%); 19:1 dr; white solid; m.p. 54-56 °C; $[\alpha]^{30}_D$ = -72.4 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 435.1834, found: 435.1829; $C_{26}H_{28}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 437.1804, found: 437.1811. IR (thin film) *v* (cm^{-1}) 3344, 2926, 2855, 1729, 1635, 1487, 1215, 1162, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.99 and 8.53 min.

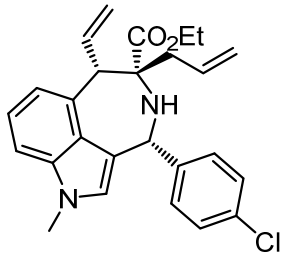
Ethyl (6*R*,7*S*,9*S*)-7-allyl-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-3t)



Yield (60%); 20:1 dr; white solid; m.p. 140-142 °C; $[\alpha]^{30}_D$ = -79.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.11 (m, 2H), 6.97 (d, *J* = 6.0 Hz, 1H), 6.45 – 6.28 (m, 1H), 6.24 (s, 1H), 5.87 – 5.67 (m, 1H), 5.37 (s, 1H), 5.14 – 5.09 (m, 1H), 5.14 – 5.08 (m, 1H), 5.03 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.92 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.26 – 4.18 (m, 2H), 4.17 (d, *J* = 8.8 Hz, 1H), 3.63 (s, 3H), 3.10 (dd, *J* = 15.2, 6.4 Hz, 1H), 2.52 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 144.3, 140.8, 137.0, 133.5, 133.1, 132.8, 129.9, 128.5, 126.5, 124.6, 121.7, 121.0, 119.8, 118.2, 114.4, 107.5, 68.1, 61.6, 60.1, 55.8, 37.9, 32.7, 14.3. HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 435.1834, found: 435.1830; $C_{26}H_{28}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 437.1804, found: 437.1808. IR (thin film) *v* (cm^{-1}) 3335, 2925, 2855, 1726, 1634, 1487, 1204, 1138, 748. The product was analyzed by HPLC to determine the

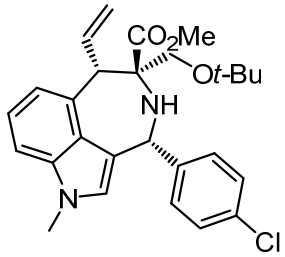
enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.55 and 8.68 min.

Ethyl (6*S*,7*R*,9*R*)-7-allyl-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*R*)-3t)



Yield (62%); 20:1 dr; white solid; m.p. 140-142 °C; $[\alpha]^{30}_D$ = 79.6 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 435.1834, found: 435.1832; $C_{26}H_{28}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 437.1804, found: 437.1807. IR (thin film) *v* (cm^{-1}) 3348, 2976, 2872, 1728, 1635, 1469, 1215, 1159, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.55 and 8.68 min.

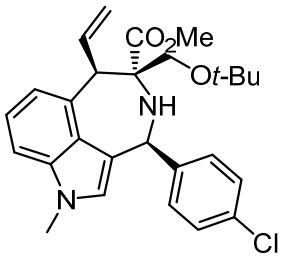
Methyl (6*S*,7*R*,9*R*)-7-(*tert*-butoxymethyl)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetra-hydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*R*)-3u)



Yield (65%); 20:1 dr; white solid; m.p. 148-150 °C; $[\alpha]^{30}_D$ = 51.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.09 (m, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.45 – 6.33 (m, 1H), 6.22 (s, 1H), 5.85 (s, 1H), 5.17 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.99 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.23 (d, *J* = 9.2 Hz, 1H), 3.59 (s, 1H), 3.51(s, 1H), 3.63 – 3.56 (m, 1H), 3.53 – 3.45 (m, 1H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 145.5, 139.8, 136.9, 135.1, 132.8, 129.9, 128.4, 126.7, 124.1, 121.8, 119.5, 118.4, 115.0, 106.9, 73.2, 68.2, 67.6,

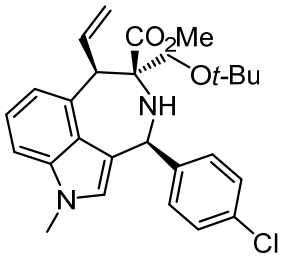
57.5, 55.6, 51.4, 32.7, 27.4. HRMS (ESI+) Calcd. For $C_{27}H_{32}{}^{34.9689}ClN_2O_3^+$ ([M+H]$^+$): 467.2096, found: 467.2097; $C_{27}H_{32}{}^{36.9659}ClN_2O_3^+$ ([M+H]$^+$): 469.2066, found: 469.2061. IR (thin film) ν (cm^{-1}) 3334, 2973, 2873, 1743, 1604, 1487, 1196, 1090, 746. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.38 and 6.64 min.

Methyl (6*R*,7*S*,9*S*)-7-(*tert*-butoxymethyl)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetra-hydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-3u)



Yield (61%); 20:1 dr; white solid; m.p. 148-150 ℃; $[\alpha]^{30}_D$ = -55.0 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{27}H_{32}{}^{34.9689}ClN_2O_3^+$ ([M+H]$^+$): 467.2096, found: 467.2103; $C_{27}H_{32}{}^{36.9659}ClN_2O_3^+$ ([M+H]$^+$): 469.2066, found: 469.2067. IR (thin film) ν (cm^{-1}) 3333, 2973, 2875, 1743, 1630, 1488, 1197, 1091, 747. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.38 and 6.64 min.

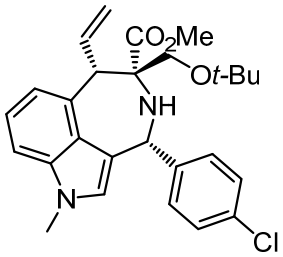
Methyl (6*R*,7*R*,9*S*)-7-(*tert*-butoxymethyl)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetra-hydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*S*)-3u)



Yield (60%); 20:1 dr; white solid; m.p. 178-180 ℃; $[\alpha]^{30}_D$ = -81.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.05 (m, 2H), 6.93 (d, *J* = 6.4 Hz, 1H), 6.40 – 6.30 (m, 1H), 6.23 (s, 1H), 5.38 (s, 1H), 5.04 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.90 (dd, *J* =

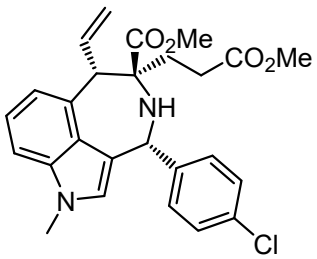
10.4, 2.0 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.66 (d, *J* = 9.2 Hz, 1H), 3.62 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 144.6, 140.8, 137.1, 132.9, 132.7, 130.1, 128., 126.5, 124.7, 121.6, 120.7, 120.2, 114.1, 107.4, 72.9, 69.6, 62.5, 57.2, 55.6, 52.3, 32.7, 27.5. HRMS (ESI+) Calcd. For $C_{27}H_{32}{}^{34.9689}ClN_2O_3^+$ ([M+H]$^+$): 467.2096, found: 467.2095; $C_{27}H_{32}{}^{36.9659}ClN_2O_3^+$ ([M+H]$^+$): 469.2066, found: 469.2076. IR (thin film) *v* (cm^{-1}) 3341, 2975, 2879, 1739, 1631, 1473, 1221, 1092, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 4.01 and 10.64 min.

Methyl (6*S*,7*S*,9*R*)-7-(*tert*-butoxymethyl)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetra-hydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3u)



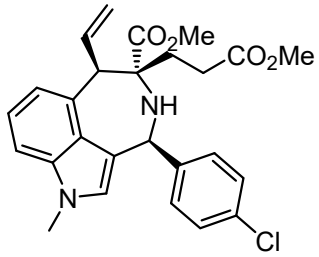
Yield (62%); 19:1 dr; white solid; m.p. 178-180 °C; $[\alpha]^{30}_D$ = 84.8 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{27}H_{32}{}^{34.9689}ClN_2O_3^+$ ([M+H]$^+$): 467.2096, found: 467.2092; $C_{27}H_{32}{}^{36.9659}ClN_2O_3^+$ ([M+H]$^+$): 469.2066, found: 469.2068. IR (thin film) *v* (cm^{-1}) 3342, 2973, 2885, 1741, 1631, 1487, 1236, 1090, 747. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 4.01 and 10.64 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-7-(3-methoxy-3-oxopropyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3v)



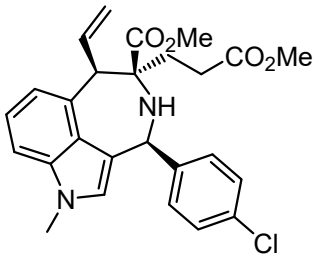
Yield (58%); 20:1 dr; yellow liquid; $[\alpha]^{30}_D$ = 72.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.30 (m, 2H), 7.17 – 7.12 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.46 – 6.31 (m, 1H), 6.19 (s, 1H), 5.78 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.09 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.26 (d, *J* = 8.4 Hz, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 3.55 (s, 3H), 2.52 – 2.32 (m, 2H), 2.22 (ddd, *J* = 13.6, 10.4, 6.4 Hz, 1H), 2.03 (ddd, *J* = 10.4, 6.4, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.4, 134.4, 133.0, 129.7, 128.5, 126.1, 122.0, 119.3, 116.4, 107.2, 67.2, 56.8, 56.3, 51.7, 32.7, 29.1. HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_4^+$ ($[M+H]^+$): 467.1732, found: 467.1722; $C_{26}H_{28}{}^{36.9659}ClN_2O_4^+$ ($[M+H]^+$): 469.1702, found: 469.1709. IR (thin film) *v* (cm^{-1}) 3357, 2924, 2852, 1736, 1591, 1453, 1202, 1086, 752. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.04 and 9.56 min.

Methyl (6*R*,7*R*,9*S*)-9-(4-chlorophenyl)-7-(3-methoxy-3-oxopropyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*S*)-3v)



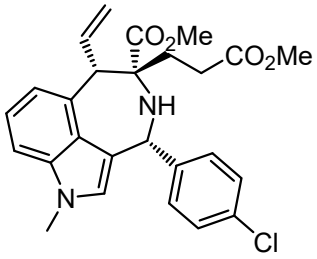
Yield (52%); 19:1 dr; yellow liquid; $[\alpha]^{30}_D$ = -73.4 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_4^+$ ($[M+H]^+$): 467.1732, found: 467.1735; $C_{26}H_{28}{}^{36.9659}ClN_2O_4^+$ ($[M+H]^+$): 469.1702, found: 469.1707. IR (thin film) *v* (cm^{-1}) 3356, 2924, 2852, 1735, 1592, 1488, 1201, 1085, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.04 and 9.56 min.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-7-(3-methoxy-3-oxopropyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-3v)



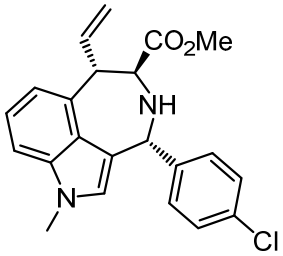
Yield (54%); 20:1 dr; white solid; m.p. 68-70 °C; $[\alpha]^{30}_D$ = -225.4 (*c* 0.50, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.09 (m, 2H), 6.96 – 6.92 (m, 1H), 6.40 – 6.26 (m, 1H), 6.21 (s, 1H), 5.22 (s, 1H), 5.02 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.93 (dd, *J* = 10.4, 2.0 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H), 2.62 – 2.52 (m, 1H), 2.50 – 2.39 (m, 1H), 2.23 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 173.2, 143.9, 140.6, 137.0, 133.2, 132.4, 129.8, 128.6, 126.6, 124.6, 121.9, 120.9, 119.7, 114.6, 107.6, 67.9, 60.1, 55.6, 52.7, 51.7, 32.7, 29.8, 28.6. HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_4^+$ ($[M+H]^+$): 467.1732, found: 467.1729; $C_{26}H_{28}{}^{36.9659}ClN_2O_4^+$ ($[M+H]^+$): 469.1702, found: 469.1702. IR (thin film) *v* (cm^{-1}) 3347, 2949, 2852, 1735, 1589, 1457, 1171, 1085, 754. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.53 and 10.34 min.

Methyl (6*S*,7*R*,9*R*)-9-(4-chlorophenyl)-7-(3-methoxy-3-oxopropyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*R*)-3v)



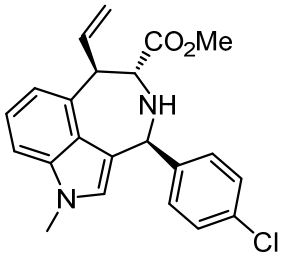
Yield (55%); 18:1 dr; white solid; m.p. 68-70 °C; $[\alpha]^{30}_D$ = 222.5 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_4^+$ ($[M+H]^+$): 467.1732, found: 467.1742; $C_{26}H_{28}{}^{36.9659}ClN_2O_4^+$ ($[M+H]^+$): 469.1702, found: 469.1709. IR (thin film) *v* (cm^{-1}) 3357, 2949, 2854, 1735, 1591, 1485, 1240, 1083, 753. The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak AD-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.53 and 10.34 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*S*,7*S*,9*R*)-3w)



Yield (54%); 9:1 dr; white solid; m.p. 168-170 °C; $[\alpha]^{30}_D$ = 83.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.22 – 7.18 (m, 2H), 7.11 – 7.04 (m, 1H), 6.22 (s, 1H), 5.92 (ddd, *J* = 17.2, 10.4, 9.2 Hz, 1H), 5.25 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.19 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.14 (s, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 143.2, 138.5, 137.4, 133.1, 133.0, 129.3, 128.6, 126.5, 124.8, 121.5, 120.8, 120.5, 117.8, 107.9, 67.2, 61.9, 55.8 51.5, 32.8. HRMS (ESI+) Calcd. For $C_{22}H_{22}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 381.1364, found: 381.1360; $C_{22}H_{22}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 383.1334, found: 383.1333. IR (thin film) *v* (cm^{-1}) 3306, 2946, 2854, 1739, 1601, 1451, 1164, 1090, 744. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.90 and 14.91 min.

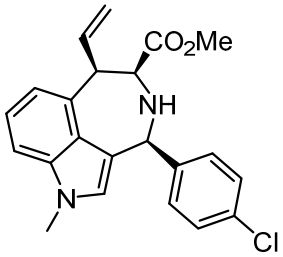
Methyl (6*R*,7*R*,9*S*)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*S*)-3w)



Yield (55%); 10:1 dr; white solid; m.p. 168-170 °C; $[\alpha]^{30}_D$ = -86.2 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{22}H_{22}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 381.1364, found: 381.1363; $C_{22}H_{22}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 383.1334, found: 383.1332. IR (thin film) *v* (cm^{-1}) 3306, 2945, 2854, 1740, 1601, 1451, 1164, 1092, 744. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee

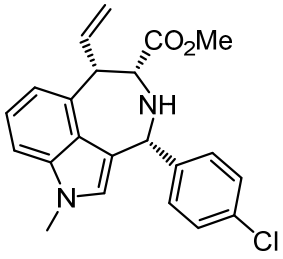
(Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.90 and 14.91 min.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*] indole-7-carboxylate ((6*R*,7*S*,9*S*)-3w)



Yield (52%); 10:1 dr; white solid; m.p. 166-168 ℃; $[\alpha]^{30}_D$ = 83.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.34 – 7.27 (m, 2H), 7.22 – 7.10 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.29 (ddd, *J* = 17.2, 10.0, 8.8 Hz, 1H), 6.21 (s, 1H), 5.11 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.07 (s, 1H), 5.02 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.36 (d, *J* = 8.8 Hz, 1H), 4.22 (d, *J* = 1.8 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 143.6, 139.4, 137.5, 134.2, 133.2, 129.7, 128.5, 126.7, 124.4, 121.6, 120.5, 119.9, 115.2, 107.3, 65.3, 63.2, 54.5, 52.5, 32.7. HRMS (ESI+) Calcd. For $C_{22}H_{22}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 381.1364, found: 381.1364; $C_{22}H_{22}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 383.1334, found: 383.1333. IR (thin film) *v* (cm^{-1}) 3305, 2945, 2854, 1740, 1601, 1452, 1164, 1091, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.87 and 6.67 min.

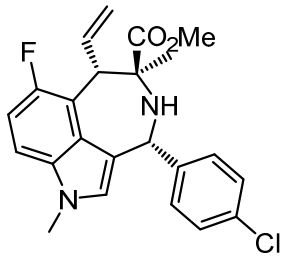
Methyl (6*S*,7*R*,9*R*)-9-(4-chlorophenyl)-2-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*R*)-3w)



Yield (56%); 10:1 dr; white solid; m.p. 166-168 ℃; $[\alpha]^{30}_D$ = -86.2 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{22}H_{22}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 381.1364, found: 381.1362; $C_{22}H_{22}{}^{36.9659}ClN_2O_2^+$

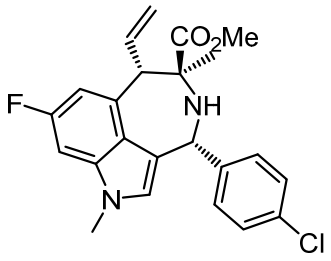
([M+H]$^+$): 383.1334, found: 383.1334. IR (thin film) ν (cm^{-1}) 3305, 2946, 2854, 1739, 1602, 1452, 1164, 1092, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.90 and 14.91 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-5-fluoro-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3x)



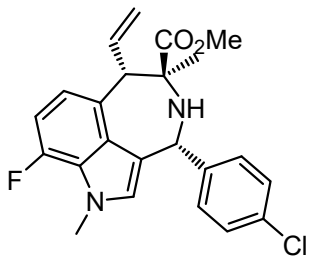
Yield (63%); 14:1 dr; white solid; m.p. 202-204 °C; $[\alpha]^{30}_D$ = 106.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.39 – 7.28 (m, 2H), 7.01 – 6.89 (m, 2H), 6.36 – 6.25 (m, 1H), 6.24 (s, 1H), 5.63 (s, 1H), 5.26 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.39 (d, *J* = 9.2 Hz, 1H), 3.57 (s, 3H), 3.55 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 154.81 (d, *J* = 234.0 Hz), 145.0, 137.4, 133.16 (d, *J* = 13.8 Hz), 129.9, 128.5, 128.0, 124.2, 120.41 (d, *J* = 16.2 Hz), 118.3, 116.5, 110.3, 110.0, 107.45 (d, *J* = 10.2 Hz), 63.5, 57.6, 51.8, 50.2, 32.8, 29.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.0. HRMS (ESI+) Calcd. For $C_{23}H_{23}{}^{34.9689}ClFN_2O_2^+$ ([M+H]$^+$): 413.1427, found: 413.1425; $C_{23}H_{23}{}^{36.9659}ClFN_2O_2^+$ ([M+H]$^+$): 415.1397, found: 415.1406. IR (thin film) ν (cm^{-1}) 3329, 2920, 2849, 1720, 1583, 1484, 1250, 1132, 783. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.00 and 8.00 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-6-fluoro-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3y)



Yield (60%); 9:1 dr; white solid; m.p. 122-124 °C; $[\alpha]^{30}_D$ = 99.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.31 (m, 2H), 6.88 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.72 (dd, *J* = 10.4, 2.0 Hz, 1H), 6.35 (s, 1H), 6.34 – 6.24 (m, 1H), 5.68 (s, 1H), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.28 (d, *J* = 9.6 Hz, 1H), 3.94 (s, 3H), 3.61 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 160.29 (d, *J* = 240.0 Hz), 143.1, 137.3, 137.02 (d, *J* = 9.2 Hz), 133.2, 132.50 (d, *J* = 12.8 Hz), 129.4, 128.6, 120.39 (d, *J* = 3.6 Hz), 117.7, 117.4, 108.6, 108.3, 92.69 (d, *J* = 27.2 Hz), 65.6, 64.8, 56.5, 56.3, 51.9, 26.2. ^{19}F NMR δ -119.5. HRMS (ESI+) Calcd. For $C_{23}H_{23}{}^{34.9689}ClFN_2O_2^+$ ($[M+H]^+$): 413.1427, found: 413.1417; $C_{23}H_{23}{}^{36.9659}ClFN_2O_2^+$ ($[M+H]^+$): 415.1397, found: 415.1399. IR (thin film) *v* (cm^{-1}) 3341, 2931, 2854, 1733, 1618, 1489, 1237, 1093, 770. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.93 and 8.56 min.

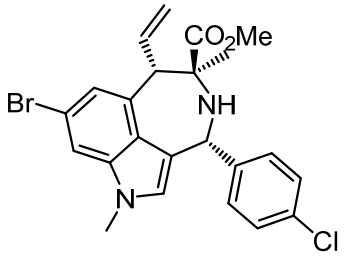
Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-7-fluoro-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3z)



Yield (54%); 11:1 dr; white solid; m.p. 104-106 °C; $[\alpha]^{30}_D$ = 91.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 6.81 – 6.77 (m, 1H), 6.77 – 6.75 (m, 1H), 6.36 – 6.25 (m, 1H), 6.08 (s, 1H), 5.77 (s, 1H), 5.17 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.12 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.32 (d, *J* = 9.6 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 149.0 (d, *J* = 242.4 Hz), 143.6, 137.9, 133.0, 130.4, 130.3, 129.4, 128.6, 127.6, 124.7 (d, *J* =

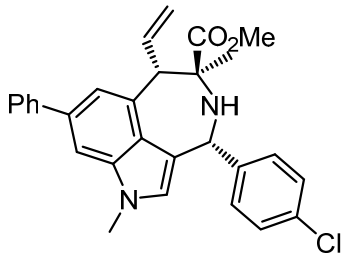
10.4 Hz), 121.0, 118.9 (d, J = 6.4 Hz), 116.8, 107.3 (d, J = 17.9 Hz), 65.0, 56.1, 55.8, 51.8, 35.5, 35.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.5. HRMS (ESI+) Calcd. For $C_{23}H_{23}{}^{34.9689}ClFN_2O_2^+$ ($[M+H]^+$): 413.1427, found: 413.1421; $C_{23}H_{23}{}^{36.9659}ClFN_2O_2^+$ ($[M+H]^+$): 415.1397, found: 415.1407. IR (thin film) v (cm^{-1}) 3357, 2949, 2854, 1735, 1591, 1485, 1240, 1083, 753. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.05 and 5.46 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-4-bromo-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3A)



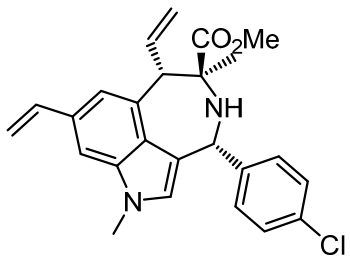
Yield (63%); 12:1 dr; white solid; m.p. 176-178 ℃; $[\alpha]^{30}_D$ = 48.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.24 – 7.22 (m, 1H), 7.07 – 7.04 (m, 1H), 6.36 – 7.24 (m, 1H), 6.14 (s, 1H), 5.71 (s, 1H), 5.20 (dd, J = 17.2 Hz, 1.6 Hz, 1H), 5.12 (dd, J = 10.4, 1.6 Hz, 1H), 4.21 (d, J = 9.6 Hz, 1H), 3.58 (s, 3H), 3.55 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 143.9, 137.8, 137.7, 136.7, 133.1, 129.5, 128.6, 126.6, 123.6, 122.2, 119.9, 117.0, 115.5, 110.2, 64.5, 56.7, 56.2, 51.8, 32.7, 27.0. HRMS (ESI+) Calcd. For $C_{23}H_{23}{}^{34.9689}Cl^{78.9183}BrN_2O_2^+$ ($[M+H]^+$): 473.0626, found: 473.0630; $C_{23}H_{23}{}^{36.9659}Cl^{78.9183}BrN_2O_2^+$ ($[M+H]^+$): 475.0596, found: 475.0601; $C_{23}H_{23}{}^{36.9659}Cl^{80.9163}BrN_2O_2^+$ ($[M+H]^+$): 477.0576, found: 477.0570. IR (thin film) v (cm^{-1}) 3354, 2921, 2851, 1731, 1632, 1487, 1239, 1039, 788. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.21 and 7.40 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-4-phenyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3B)



Yield (56%); 20:1 dr; white solid; m.p. 186-188 °C; $[\alpha]^{30}_D$ = 29.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.49 – 7.41 (m, 4H), 7.37 – 7.30 (m, 3H), 7.29 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 7.21 (s, 1H), 6.46 – 6.35 (m, 1H), 6.20 (s, 1H), 5.81 (s, 1H), 5.23 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.12 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.37 (d, *J* = 9.6 Hz, 1H), 3.64 (s, 3H), 3.60 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 144.2, 142.5, 138.4, 137.5, 135.6, 135.1, 132.9, 129.6, 128.6, 128.5, 127.4, 126.67, 126.5, 124.2, 119.7, 119.1, 116.6, 105.8, 64.8, 57.2, 56.6, 51.8, 32.78, 27.0. HRMS (ESI+) Calcd. For $C_{29}H_{28}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 471.1834, found: 471.1827; $C_{29}H_{28}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 473.1804, found: 473.1806. IR (thin film) *v* (cm^{-1}) 3341, 2927, 2854, 1730, 1597, 1486, 1238, 1091, 763. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak ID, *i*-propanol /hexane = 5/95, flow rate 1.0 mL/min, λ = 230 nm); t_r = 7.93 and 10.55 min.

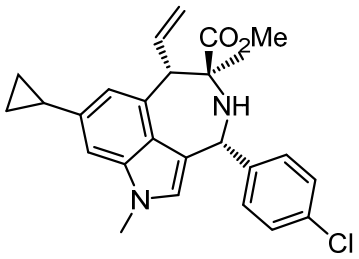
Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-4,6-divinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3C)



Yield (64%); 18:1 dr; white solid; m.p. 186-188 °C; $[\alpha]^{30}_D$ = 29.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.08 (d, *J* = 11.2 Hz, 2H), 6.81 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.42 – 6.30 (m, 1H), 6.16 (s, 1H), 5.80 – 5.72 (m, 1H), 5.76 (s, 1H), 5.24 – 5.14 (m, 2H), 5.11 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 3.58 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 144.2, 138.3, 137.9, 137.2, 134.8, 132.9, 131.9, 129.5, 128.5, 126.8,

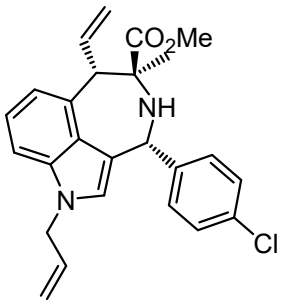
124.8, 119.8, 117.6, 116.6, 111.7, 105.4, 64.7, 57.0, 56.4, 51.8, 32.7, 26.9. HRMS (ESI+) Calcd. For $C_{25}H_{26}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 421.1677, found: 421.1679; $C_{25}H_{26}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 423.1647, found: 423.1651. IR (thin film) ν (cm^{-1}) 3330, 2974, 2925, 1722, 1625, 1485, 1249, 1133, 782. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IC, *i*-propanol /hexane = 5/95, flow rate 1.0 mL/min, λ = 280 nm); t_r = 8.07 and 10.42 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-4-cyclopropyl-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3D)



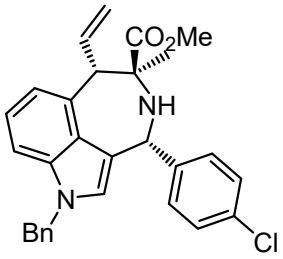
Yield (61%); 13:1 dr; white solid; m.p. 166-168 ℃; $[\alpha]^{30}_D$ = 66.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 2H), 6.74 (d, *J* = 10.4 Hz, 2H), 6.04 – 6.28 (m, 1H), 6.07 (s, 1H), 5.74 (s, 1H), 5.23 – 5.16 (m, 1H), 5.13 – 5.07 (m, 1H), 4.27 (d, *J* = 9.6 Hz, 1H), 3.58 (s, 3H), 3.54 (s, 3H), 2.06 – 1.97 (m, 1H), 1.42 (s, 3H), 0.98 – 0.91 (m, 2H), 0.77 – 0.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 144.2, 138.4, 138.0, 137.3, 134.4, 132.8, 129.5, 128.4, 125.4, 123.2, 119.7, 118.1, 116.4, 103.7, 64.8, 56.5, 51.7, 32.5, 26.7, 15.9, 9.1, 9.0. HRMS (ESI+) Calcd. For $C_{26}H_{28}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 435.1834, found: 435.1832; $C_{26}H_{28}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 437.1804, found: 437.1810. IR (thin film) ν (cm^{-1}) 3340, 2930, 2857, 1731, 1617, 1488, 1239, 1093, 779. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IC, *i*-propanol /hexane = 5/95, flow rate 1.0 mL/min, λ = 230 nm); t_r = 8.10 and 10.74 min.

Methyl (6*S*,7*S*,9*R*)-2-allyl-9-(4-chlorophenyl)-7-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3E)



Yield (63%); 10:1 dr; white solid; m.p. 118-120 °C; $[\alpha]^{30}_D$ = 67.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 7.18 – 7.07 (m, 2H), 6.93 (d, *J* = 6.4 Hz, 1H), 6.40 – 6.30 (m, 1H), 6.19 (s, 1H), 5.94 – 5.83 (m, 1H), 5.81 (s, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.03 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.60 – 4.46 (m, 2H), 4.40 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 143.8, 138.0, 136.4, 134.8, 133.3, 132.9, 129.5, 128.5, 125.4, 124.8, 122.1, 120.8, 118.9, 117.3, 116.7, 107.6, 65.2, 56.2, 51.7, 48.8, 29.7, 25.9. HRMS (ESI+) Calcd. For $C_{25}H_{26}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 421.1677, found: 421.1673; $C_{25}H_{26}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 423.1647, found: 423.1659. IR (thin film) *v* (cm^{-1}) 3336, 2924, 2853, 1730, 1600, 1487, 1240, 1092, 747. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.13 and 6.60 min.

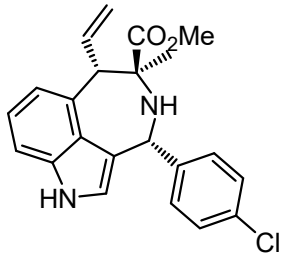
Methyl (6*S*,7*S*,9*R*)-2-benzyl-9-(4-chlorophenyl)-7-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3F)



Yield (61%); 15:1 dr; white solid; m.p. 88°C-90 °C; $[\alpha]^{30}_D$ = 70.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.12 – 7.05 (m, 2H), 7.04 – 7.00 (m, 2H), 6.93 (d, *J* = 6.8 Hz, 1H), 6.42 – 6.30 (m, 1H), 6.25 (s, 1H), 5.84 (s, 1H), 5.25 – 5.19 (m, 1H), 5.19 – 5.11 (m, 2H), 5.11 – 5.04 (m, 1H), 4.43 (d, *J* = 9.6 Hz, 1H), 3.60 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 143.7, 137.8, 137.4, 136.7, 134.8, 132.9, 129.4, 128.5,

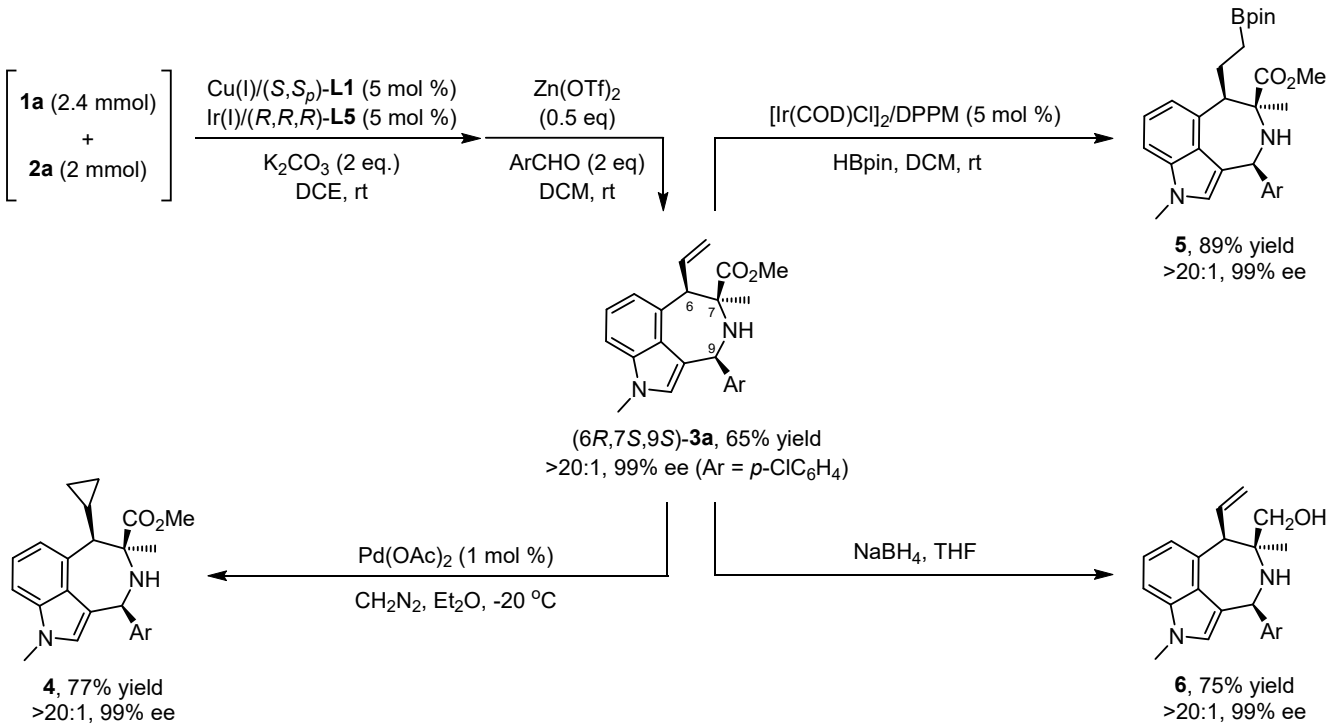
128.5, 127.5 126.6, 125.6, 125.2, 122.3, 121.2, 119.0, 116.8, 107.8, 65.3, 56.2, 51.7, 50.0, 29.4, 25.7. HRMS (ESI+) Calcd. For $C_{29}H_{28}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 471.1834, found: 471.1837; $C_{29}H_{28}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 473.1804, found: 473.1814. IR (thin film) ν (cm^{-1}) 3339, 2928, 2869, 1731, 1600, 1488, 1240, 1091, 740. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IC, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.65 and 8.32 min.

Methyl (6*S*,7*S*,9*R*)-9-(4-chlorophenyl)-7-methyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*R*)-3G)

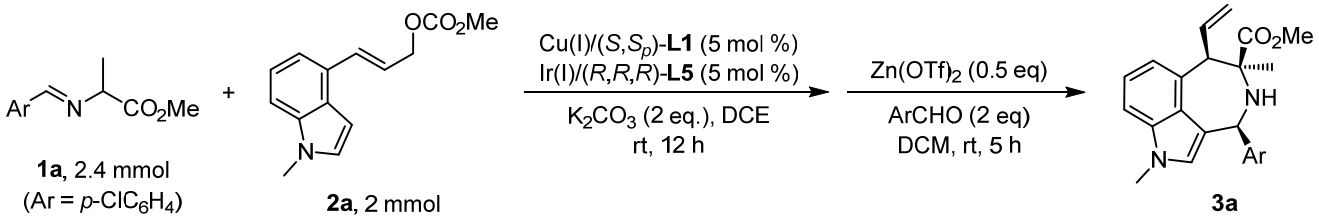


Yield (66%); 11:1 dr; white solid; m.p. 158-160 ℃; $[\alpha]^{30}_D$ = 40.6 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.56 – 7.50 (m, 2H), 7.38 – 7.32 (m, 2H), 7.19 – 7.07 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.33 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 6.15 (s, 1H), 5.45 (s, 1H), 5.37 – 5.23 (m, 1H), 5.19 – 5.03 (m, 1H), 4.08 (d, *J* = 7.6 Hz, 1H), 3.77 – 3.72 (m, 1H), 3.37 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 142.9, 137.7, 136.4, 133.5, 133.0, 129.8, 128.6, 125.2, 122.4, 121.6, 121.1, 120.3, 118.5, 109.5, 66.3, 57.9, 56.1, 51.8, 23.6. HRMS (ESI+) Calcd. For $C_{22}H_{22}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 381.1364, found: 381.1363; $C_{22}H_{22}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 383.1334, found: 383.1343. IR (thin film) ν (cm^{-1}) 3396, 2926, 2852, 1726, 1619, 1487, 1240, 1092, 749. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.90 and 14.91 min.

4. Scale-Up Experiment and Synthetic Transformation

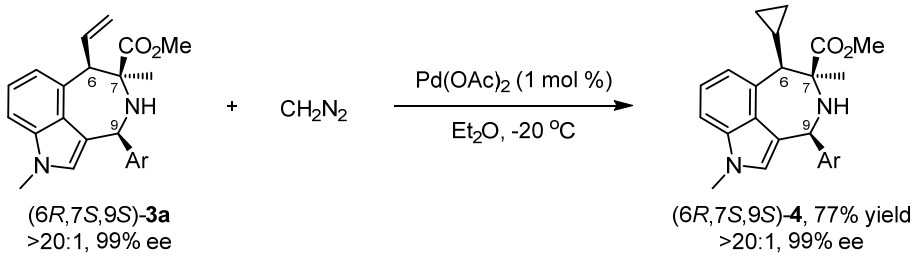


Scheme S1 Scale-Up Experiment and Synthetic Transformation



A flame dried Schlenk tube **A** was cooled to room temperature and filled with N_2. To this flask were added $[Ir(COD)Cl]_2$ (0.05 mmol), (*R*,*R*,*R*)-**L5** (0.10 mmol), degassed THF (4 mL) and degassed *n*-propylamine (1 mL). The reaction mixture was heated at 50 ºC for 30 min and then the volatile solvents were removed under vacuum to gain a pale-yellow solid. Meanwhile, $Cu(MeCN)_4BF_4$ (0.10 mmol) and (S,S_p)-^{i}Pr-Phosferrox-**L1** (0.11 mmol) were dissolved in 15.0 mL of DCE in a Schlenk tube **B**, and stirred at room temperature for about 40 min. Then, aldimine ester **1** (2.4 mmol), 4-indolyl allylic carbonate **2** (2.0 mmol) and K_2CO_3 (4.0 mmol) were added into the Schlenk tube **A** and filled with N_2. The Cu/**L1** complex solution was then transferred from the Schlenk tube **B** to the Schlenk

tube **A** *via* syringe. Finally, the reaction mixture was continuously stirred at room temperature under N_2 atmosphere. Once starting material was consumed (monitored by TLC), the residue was separated by flash column chromatography to give the crude product. The crude product was dissolved in dichloromethane and two equivalent of *para*-chlorobenzaldehyde and $Zn(OTf)_2$ (50 mol%) were added. Once starting material was consumed (monitored by TLC), the reaction was quenched with 1 mol of HCl solution (5 mL). The layers were separated, and the aqueous layer was extracted with DCM (5 mL x 3). The combined organic components were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtration and evaporated in vacuum. After evaporation of the solvent under vacuum, the crude mixture was flushed with short silica gel plug to remove the metal complex and the diastereoselectivity was determined with ^1H NMR analysis. Then, the whole residue was further purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess.



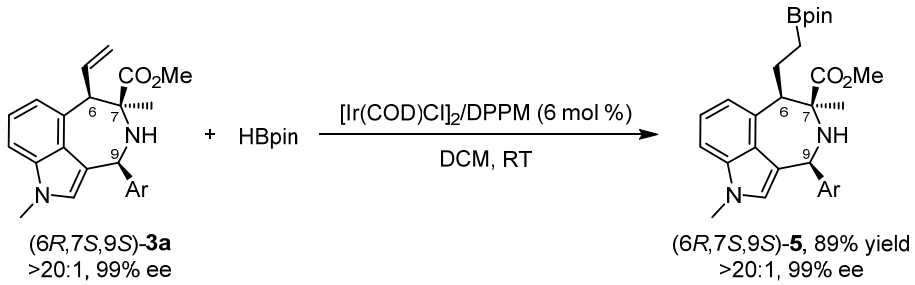
(6*R*,7*S*,9*S*)-**3a**
>20:1, 99% ee

(6*R*,7*S*,9*S*)-**4**, 77% yield
>20:1, 99% ee

Fresh prepared diazomethane solution (0.5 M in Et_2O, 2 mL) and (6*R*,7*S*,9*S*)-**3a** (78.8 mg, 0.2 mmol) were added into a Schlenk tube. Under a positive nitrogen pressure, the reaction was cooled to -20 °C, and $Pd(OAc)_2$ (1.5 mg, 1 mol %) was added in one portion with gas evolution. After stirring for 1 hour in -20 °C, the reaction was moved to room temperature and stirred overnight. While the reaction was partly completed, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (PE/EA = 6/1) to afford the product (6*R*,7*S*,9*S*)-**4**.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-6-cyclopropyl-2,7-dimethyl-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-4): Yield (77%); >20:1 dr; white solid; m.p. 180-182 ℃; $[\alpha]^{30}_D$ = -53.0 (*c* 0.50, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.36

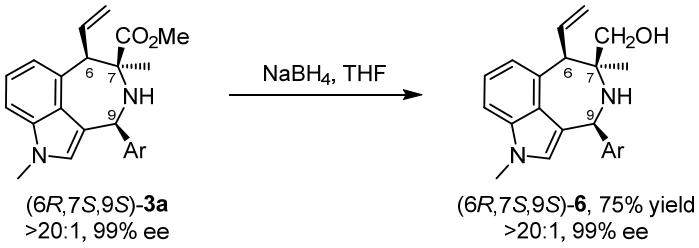
– 7.30 (m, 2H), 7.21 – 7.11 (m, 2H), 6.89 (dd, J = 5.6, 2.4 Hz, 1H), 6.22 (s, 1H), 5.31 (s, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 2.74 (d, J = 9.6 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.58 (s, 3H), 0.57 – 0.44 (m, 1H), 0.36 – 0.28 (m, 2H), 0.26 – 0.16 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 144.6, 136.8, 135.0, 133.0, 130.0, 128.5, 126.4, 124.6, 121.4, 120.6, 119.9, 107.4, 64.1, 59.3, 56.2, 52.2, 32.7, 21.6, 15.9, 6.1, 3.8. HRMS (ESI+) Calcd. For $C_{24}H_{26}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 409.1677, found: 409.1667; $C_{24}H_{26}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 411.1647, found: 411.1653. IR (thin film) ν (cm^{-1}) 3340, 2946, 2856, 1730, 1599, 1455, 1245, 1089, 748. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol /hexane = 5/95, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.22 and 6.87 min.



To a solution of $[Ir(COD)Cl]_2$ (4.0 mg, 3 mol %) and bis(diphenylphosphino)methane (DPPM, 4.6 mg, 6 mol %) in anhydrous DCM (2 mL) was added (6*R*,7*S*,9*S*)-**3a** (78.8 g, 0.2 mmol) in one portion under a positive argon pressure. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (HBpin, 58 μL, 0.4 mmol) was added at room temperature and the resulting solution was stirred overnight. The reaction mixture was quenched with MeOH (1 mL) and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (PE/EA = 3/1, with 1% MeOH) to afford the product (6*R*,7*S*,9*S*)-**5**.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6,7,8,9-tetrahydro-2*H*-azepino[3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*S*)-5): Yield (89%); >20:1 dr; white solid; m.p. 114-116 °C; $[\alpha]^{30}_D$ = -52.0 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.34 – 7.30 (m, 2H), 7.16 – 7.07 (m, 2H), 6.96 – 6.90 (m, 1H), 6.18 (s, 1H), 5.28 (s, 1H), 3.80 (s, 3H), 3.61 (s, 3H), 3.36 (dd, J = 9.6, 3.2 Hz, 1H), 2.08 – 1.83 (m, 1H), 1.65

– 1.60 (m, 1H), 1.55 (s, 3H), 1.20 (d, J = 2.4 Hz, 12H), 0.71 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 144.6, 137.1, 134.1, 132.9, 130.1, 128.4, 126.3, 124.6, 121.7, 120.9, 119.7, 107.3, 82.7, 64.6, 56.6, 56.3, 52.8, 32.6, 29.4, 28.3, 24.8, 21.7. HRMS (ESI+) Calcd. For $C_{29}H_{37}B^{34.9689}ClN_2O_4^+$ ([M+H]$^+$): 523.2529, found: 523.2534; $C_{29}H_{37}B^{36.9659}ClN_2O_4^+$ ([M+H]$^+$): 525.2499, found: 525.2502. IR (thin film) v (cm^{-1}) 3373, 2978, 2935, 1728, 1583, 1454, 1374, 1244, 1146, 1091, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.26 and 6.09 min.

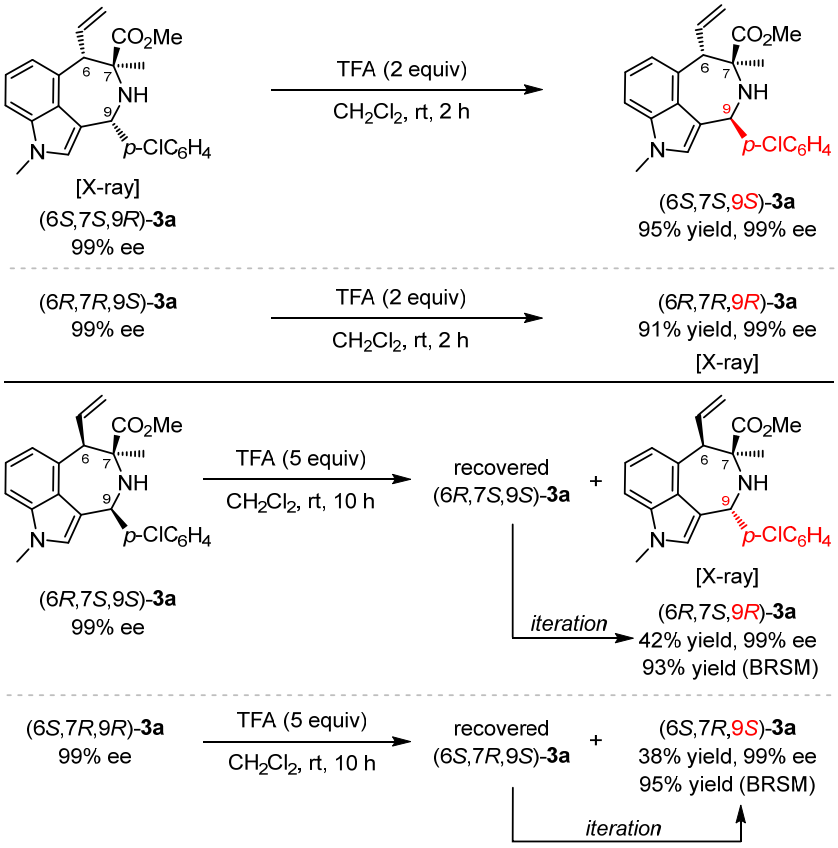


Under nitrogen atmosphere, to a solution of (6*R*,7*S*,9*S*)-**3a** (78.8 mg, 0.2 mmol) in anhydrous THF (2 mL) was added $NaBH_4$ (1.0 mmol), the reaction was then moved into room temperature and continuously stirred until 3a complete consumption of starting material (detected by TLC). The reaction mixture was quenched with H_2O, extracted with EA (× 3) and filtered through celite to remove the colloid. The organic layer was combined, washed with brine, dried over Na_2SO_4 before evaporation. Then the residue was purified by a flash column chromatography (EA/PE=1:2) to afford the product (6*R*,7*S*,9*S*)-**6**.

Methyl (6*R*,7*S*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indol-7-yl)methanol ((6*R*,7*S*,9*S*)-6): Yield (75%); >20:1 dr; white solid; m.p. 82-84 °C; $[\alpha]^{30}_D$ = -54.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.21 – 7.11 (m, 2H), 6.91 (dd, J = 6.0, 2.0 Hz, 1H), 6.26 (s, 1H), 6.17 (ddd, J = 17.2, 10.4, 8.4 Hz, 1H), 5.19 (s, 1H), 5.06 (dd, J = 10.4, 1.6 Hz, 1H), 4.94 (dd, J = 17.2, 1.6 Hz, 1H), 3.67 (d, J = 8.4 Hz, 1H), 3.64 (s, 3H), 3.53 (d, J = 10.4 Hz, 1H), 3.37 (d, J = 10.4 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.3, 136.9, 134.2, 133.0, 129.7, 128.6, 126.5, 125.7, 121.9, 120.9, 120.1,

116.9, 107.3, 69.7, 59.3, 58.4, 56.7, 32.7, 19.7. HRMS (ESI+) Calcd. For $C_{22}H_{24}{}^{34.9689}ClN_2O^+$ ($[M+H]^+$): 367.1572, found: 367.1568; $C_{22}H_{24}{}^{36.9659}ClN_2O^+$ ($[M+H]^+$): 369.1542, found: 369.1550. IR (thin film) ν (cm^{-1}) 3700, 3369, 2923, 2851, 1728, 1581, 1457, 1375, 1086, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 5.30 and 6.35 min.

5. TFA-Promoted C9-Epimerization of 6,9-*cis*-3a to Access Another Four Stereoisomers 6,9-*trans*-3a



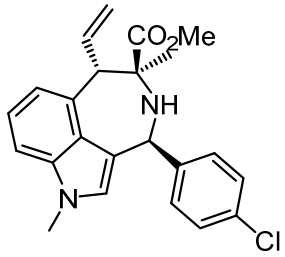
Scheme S2. TFA-Promoted C9-Epimerization of 6,9-*cis*-**3a** to Access Another Four Stereoisomers 6,9-*trans*-**3a**

General Reaction Procedure A for (6*S*,7*S*,9*R*)-**3a** and (6*R*,7*R*,9*S*)-**3a**: Under air atmosphere, to a solution of (6*S*,7*S*,9*R*)-**3a** or (6*R*,7*R*,9*S*)-**3a** (78.8 mg, 0.2 mmol) in DCM (2 mL) was added TFA (0.4 mmol), the reaction was continuously stirred until complete consumption of starting material (detected by TLC). The reaction mixture was quenched with $NaHCO_3$ (aq), extracted with DCM (× 3). The

organic layer was combined, washed with brine, dried over Na_2SO_4 before evaporation. Then the residue was purified by a column chromatography to afford the product (6*S*,7*S*,9*S*)-**3a** or (6*R*,7*R*,9*R*)-**3a**.

General Reaction Procedure B for (6*R*,7*S*,9*S*)-**3a** and (6*S*,7*R*,9*R*)-**3a**: under air atmosphere, to a solution of (6*R*,7*S*,9*S*)-**3a** or (6*S*,7*R*,9*R*)-**3a** (78.8 mg, 0.2 mmol) in DCM (2 mL) was added TFA (1.0 mmol), the reaction was continuously stirred until complete consumption of starting material (detected by TLC). The reaction mixture was quenched with $NaHCO_3$(aq), extracted with DCM (× 3). The organic layer was combined, washed with brine, dried over Na_2SO_4 before evaporation. Then the residue was purified by a column chromatography to afford the product (6*R*,7*S*,9*R*)-**3a** or (6*S*,7*R*,9*S*)-**3a** with the starting material being recovered.

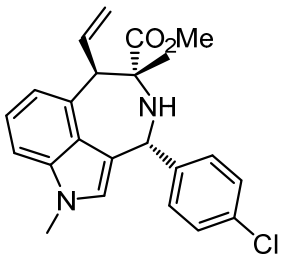
Methyl (6*S*,7*S*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*S*,9*S*)-3a)



Following **General Reaction Procedure A:** Yield (95%); >20:1 dr; white solid; m.p. 138-140 °C; $[\alpha]^{30}_D$ = 62.2 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.08 (m, 2H), 6.95 – 6.89 (m, 1H), 6.32 (ddd, *J* = 17.2, 10.4, 7.8 Hz, 1H), 6.04 (s, 1H), 5.45 (s, 1H), 5.29 (dd, *J* = 17.2, 1.6, 1H), 5.09 (dd, *J* = 10.4, 1.6, 1H), 4.08 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 3.37 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 143.1, 137.7, 137.2, 133.6, 133.0, 129.8, 128.7, 125.9, 125.5, 121.9, 120.1, 119.8, 118.5, 107.6, 66.3, 57.9, 56.1, 51.7, 32.7, 23.4. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1511; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1497. IR (thin film) *v* (cm^{-1}) 3337, 3049, 2947, 1730, 1597, 1487, 1246, 1088, 748. The product was analyzed by HPLC to determine the

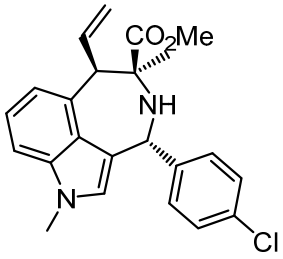
enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.62 and 7.30 min.

Methyl (6*R*,7*R*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*R*,9*R*)-3a)



Following **General Reaction Procedure A:** Yield (91%); >20:1 dr; white solid; m.p. 138-140 °C; $[\alpha]^{30}_D$ = -60.7 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ($[M+H]^+$): 395.1521, found: 395.1520; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ($[M+H]^+$): 397.1491, found: 397.1497. IR (thin film) *v* (cm^{-1}) 3333, 3068, 2929, 1728, 1577, 1486, 1245, 1090, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak IE, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.62 and 7.30 min.

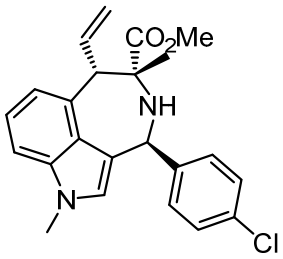
Methyl (6*R*,7*S*,9*R*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*R*,7*S*,9*R*)-3a)



Following **General Reaction Procedure B:** Yield (93% BRSM); >20:1 dr; white solid; m.p. 130-132 °C; $[\alpha]^{30}_D$ = -96.8 (*c* 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.98-6.92 (m, 1H), 6.26 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 6.06 (s, 1H), 5.65 (s, 1H), 5.04 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.83 (dd, *J* = 17.2, 1.6 Hz, 1H), 3.99 (d, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 142.6, 140.0, 137.3, 132.7, 132.2, 129.2, 128.5, 126.3, 125.6, 122.4, 121.6, 120.6, 116.8, 108.3, 67.6, 58.4,

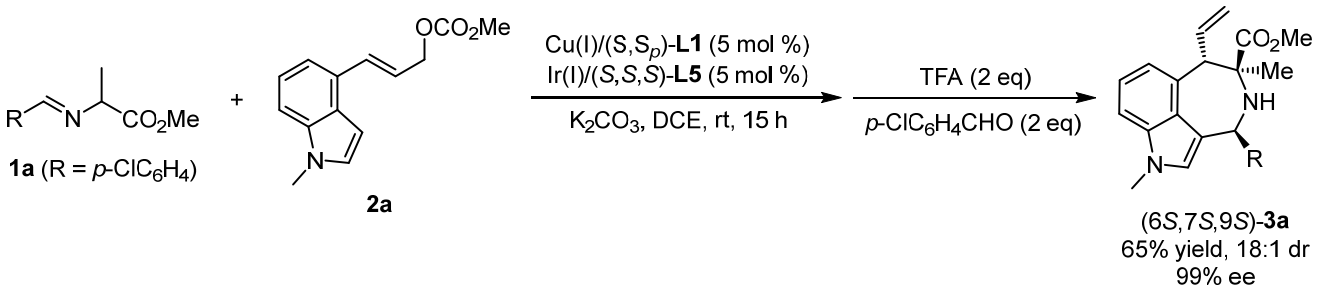
55.5, 52.2 32.7, 28.4. HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 395.1521, found: 395.1518; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 397.1491, found: 397.1495. IR (thin film) ν (cm^{-1}) 3343, 3047, 2929, 1727, 1576, 1486, 1246, 1089, 745. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 7.91 and 8.90 min.

Methyl (6*S*,7*R*,9*S*)-9-(4-chlorophenyl)-2,7-dimethyl-6-vinyl-6,7,8,9-tetrahydro-2*H*-azepino [3,4,5-*cd*]indole-7-carboxylate ((6*S*,7*R*,9*S*)-3a)



Following **General Reaction Procedure B:** Yield (95% BRSM); >20:1 dr; white solid; m.p. 130-132 °C; $[\alpha]^{30}_D$ = 93.0 (*c* 0.50, CH_2Cl_2); HRMS (ESI+) Calcd. For $C_{23}H_{24}{}^{34.9689}ClN_2O_2^+$ ([M+H]$^+$): 395.1521, found: 395.1517; $C_{23}H_{24}{}^{36.9659}ClN_2O_2^+$ ([M+H]$^+$): 397.1491, found: 397.1494. IR (thin film) ν (cm^{-1}) 3340, 3063, 2944, 1729, 1593, 1483, 1241, 1082, 751. The product was analyzed by HPLC to determine the enantiomeric excess: >99% ee (Chiralpak AD-H, *i*-propanol /hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 6.62 and 7.30 min.

6. One-pot allylation/cyclization/epimerization with TFA as the cyclization promoter



A flame dried Schlenk tube **A** was cooled to room temperature and filled with N_2. To this flask were added $[Ir(COD)Cl]_2$ (0.005 mmol), (*S,S,S*)-**L5** (0.010 mmol), degassed THF (0.5 mL) and degassed *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 ºC for 30 min and then the volatile solvents were removed under vacuum to gain a pale-yellow solid. Meanwhile, $Cu(MeCN)_4BF_4$ (0.01 mmol) and (S,S_p)-^{i}Pr-Phosferrox-**L1** (0.011 mmol) were dissolved in 1.0 mL of DCE in a Schlenk tube **B**, and stirred at room temperature for about 40 min. Then, aldimine ester **1a** (0.30 mmol), 4-indolyl allylic carbonate **2a** (0.20 mmol) and K_2CO_3 (0.40 mmol) were added into the Schlenk tube **A** and filled with N_2. The Cu/**L1** complex solution was then transferred from the Schlenk tube **B** to the Schlenk tube **A** *via* syringe. Finally, the reaction mixture was continuously stirred at room temperature under N_2 atmosphere. Once 4-indolyl allylic carbonate was consumed (monitored by TLC), two equivalents of the *p*-ClC_6H_4CHO and TFA (200 mol%) were added. When the generated allylation intermediate in first step was consumed (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution. The layers were separated, and the aqueous layer was extracted with DCM (5 mL x 3). The combined organic components were washed with saturated brine (5 mL), dried over anhydrous Na_2SO_4, filtration and evaporated in vacuum. After evaporation of the solvent under vacuum, the crude mixture was flushed with short silica gel plug to remove the metal complex and the diastereoselectivity was determined with ^1H NMR analysis. Then, the whole residue was further purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess.

7. References

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8. X-ray Structures of (6*S*,7*S*,9*R*)-3a, (6*R*,7*R*,9*R*)-3a, and (6*R*,7*S*,9*R*)-3a

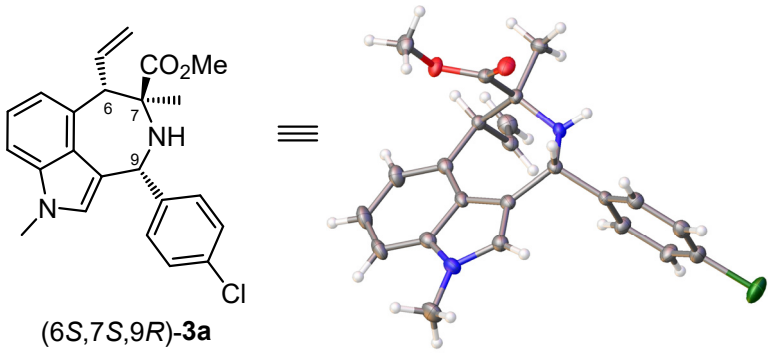


Figure S1. X-ray structure of (6*S*,7*S*,9*R*)-**3a**

Crystal data for (6*S*,7*S*,9*R*)-**3a**: $C_{23}H_{23}ClN_2O_2$, M_r = 394.88, T = 296 K, monoclinic, space group $P12_11$, a = 9.606(10), b = 7.933(10), c = 13.748(10) Å, β = 101.1060(10) °, V = 1028.1(19) Å^3, Z = 2, 8054 unique reflections, final R_1 = 0.0431 and wR_2 = 0.1141 for 8320 observed [I>2σ(I)] reflections, Flack χ = -0.012(8). CCDC 2090369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

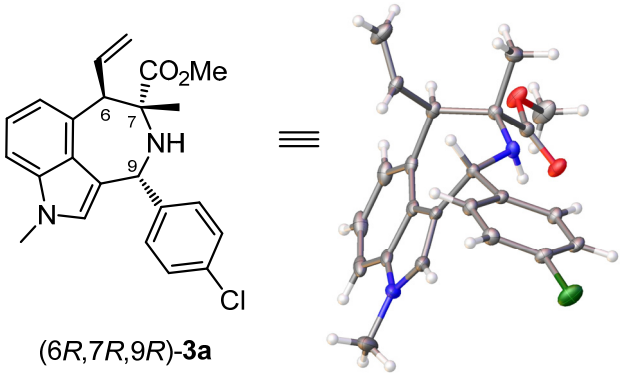
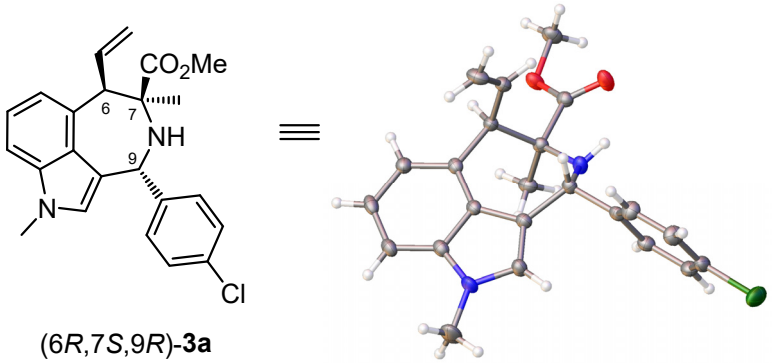


Figure S2. X-ray structure of (6*R*,7*R*,9*R*)-**3a**

Crystal data for (6*R*,7*R*,9*R*)-**3a**: $C_{23}H_{23}ClN_2O_2$, M_r = 394.88, T = 296 K, orthorhombic, space group $P2_12_12_1$, a = 9.119(5), b = 17.378(10), c = 50.209(3) Å, V = 7956.7(8) Å^3, Z = 16, 3930 unique reflections, final R_1 = 0.0342 and wR_2 = 0.0902 for 4034 observed [I>2σ(I)] reflections, Flack χ = 0.013(3). CCDC 2090370 contains the supplementary crystallographic data for this paper. These data

can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



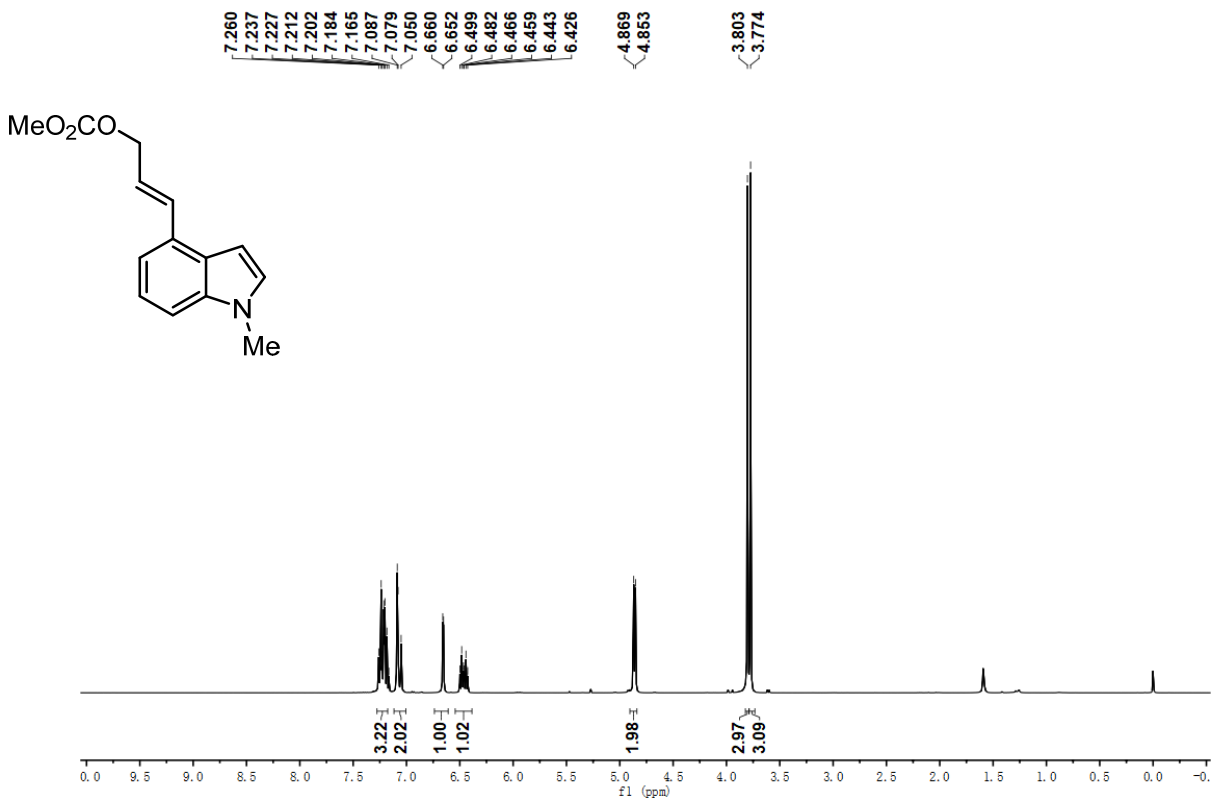
(6*R*,7*S*,9*R*)-**3a**

Figure S3. X-ray structure of (6*R*,7*S*,9*R*)-**3a**

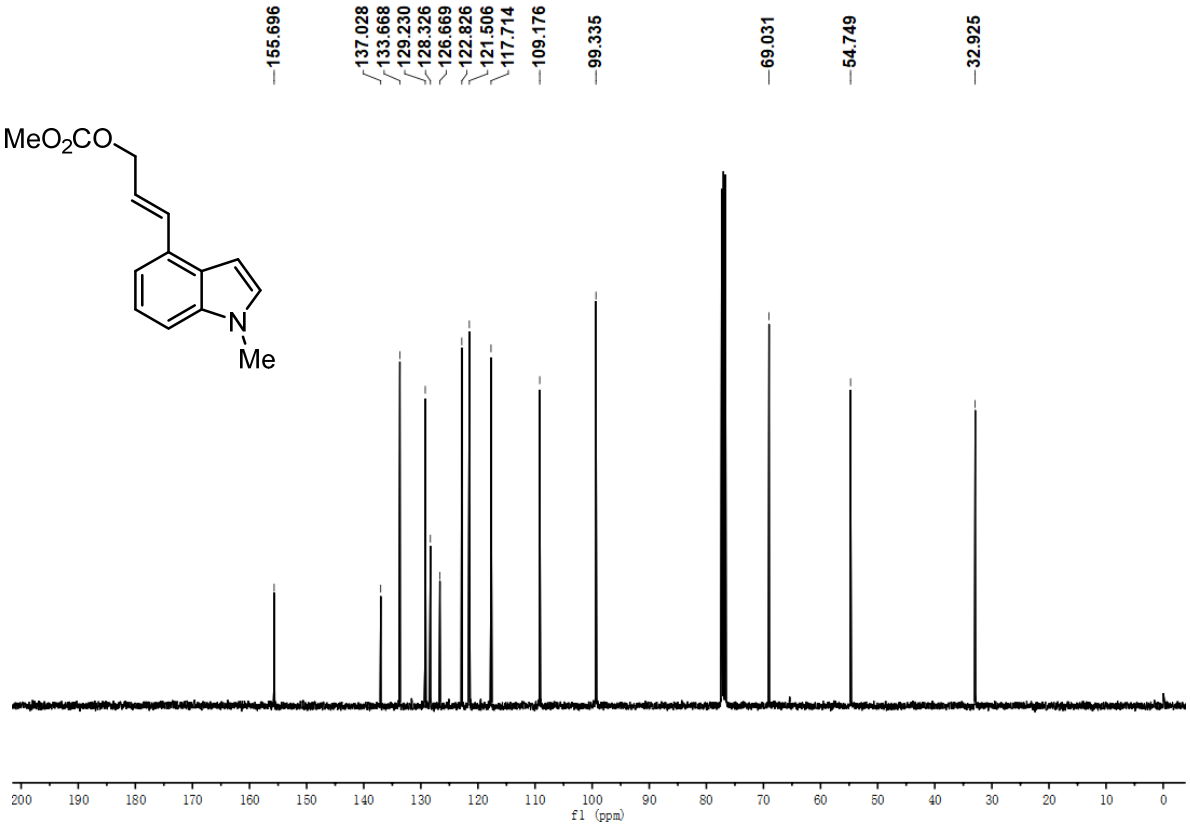
Crystal data for (6*R*,7*S*,9*R*)-**3a**: $C_{23}H_{23}ClN_2O_2$, M_r = 394.88, T = 296 K, orthorhombic, space group $P2_12_12_1$, a = 9.299(10), b = 18.085(2), c = 24.744(2) Å, V = 4161.3(7) Å^3, Z = 4, 8054 unique reflections, final R_1 = 0.0431 and wR_2 = 0.1141 for 8320 observed [I>2σ(I)] reflections, Flack χ = -0.004(6). CCDC 2090371 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

9. NMR and HPLC Spectra

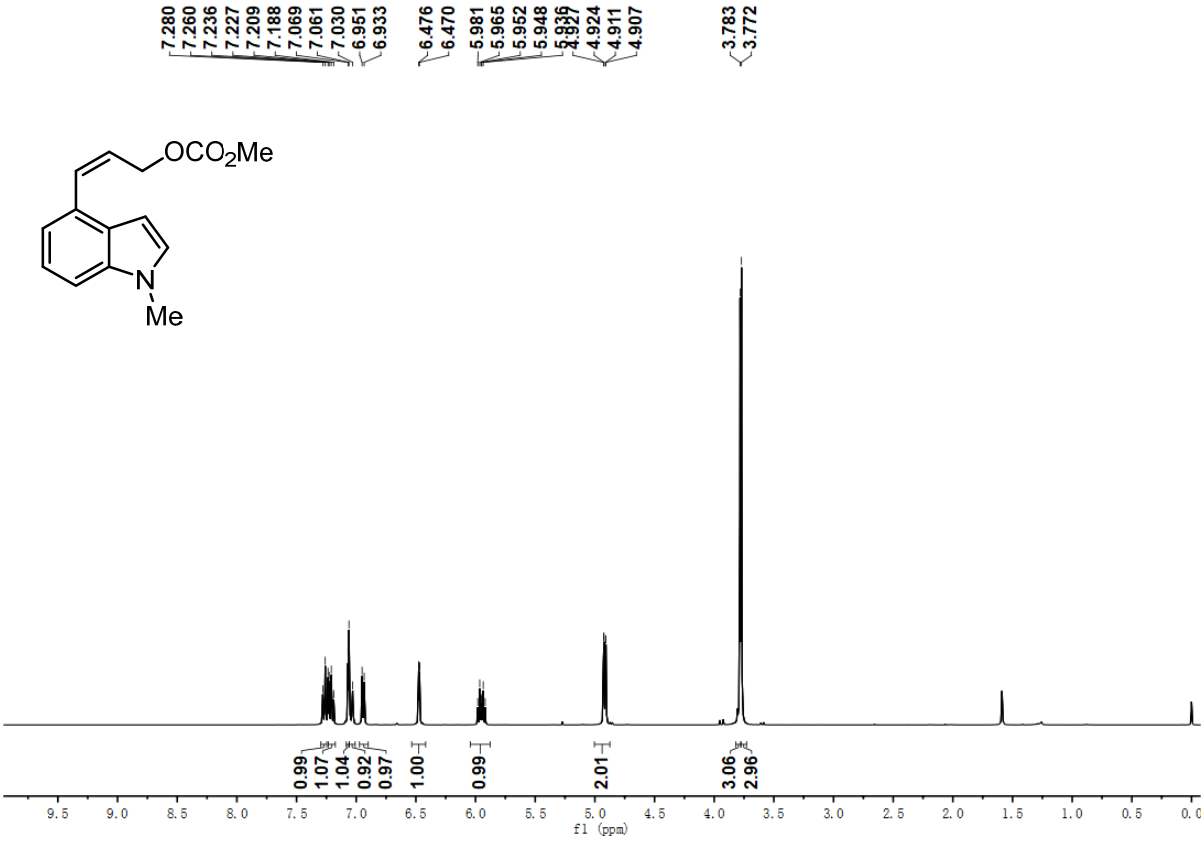
^{1}H NMR (400 MHz) of (*E*)-**2a** in $CDCl_3$



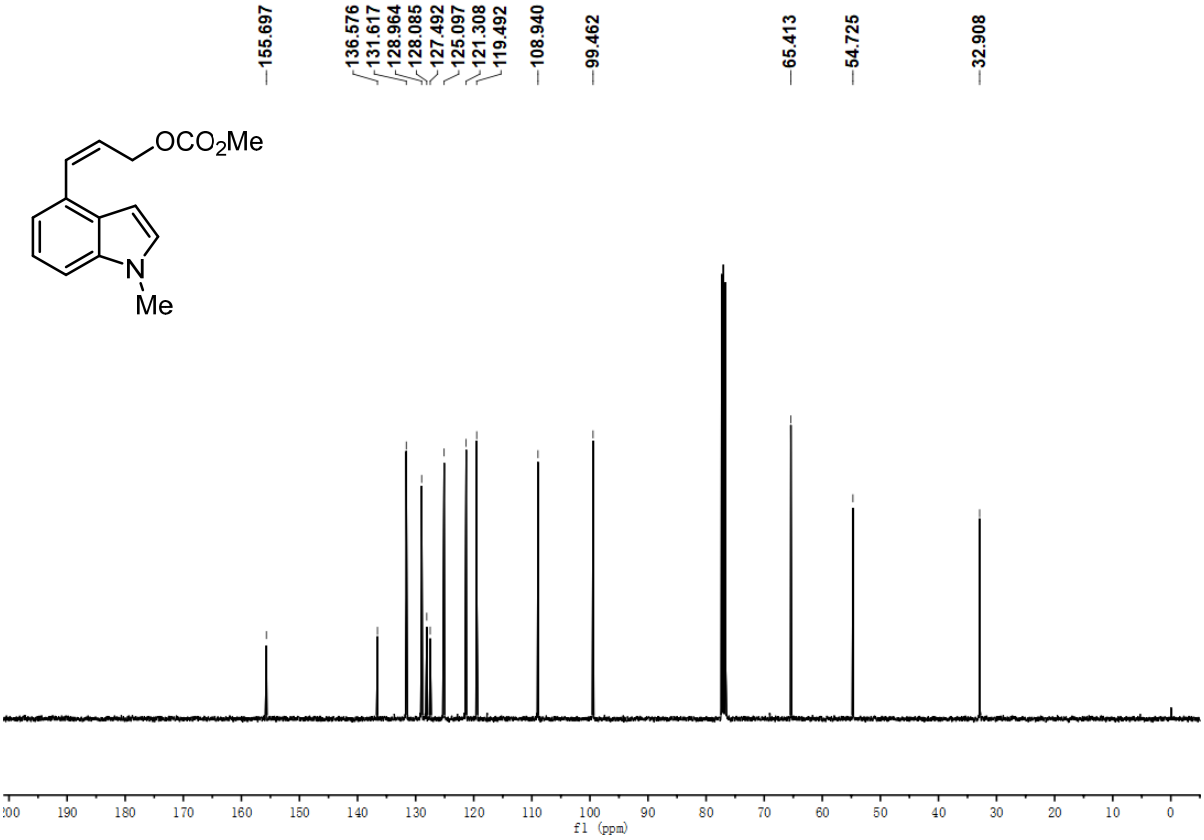
^{13}C NMR (101 MHz) of (*E*)-**2a** in $CDCl_3$



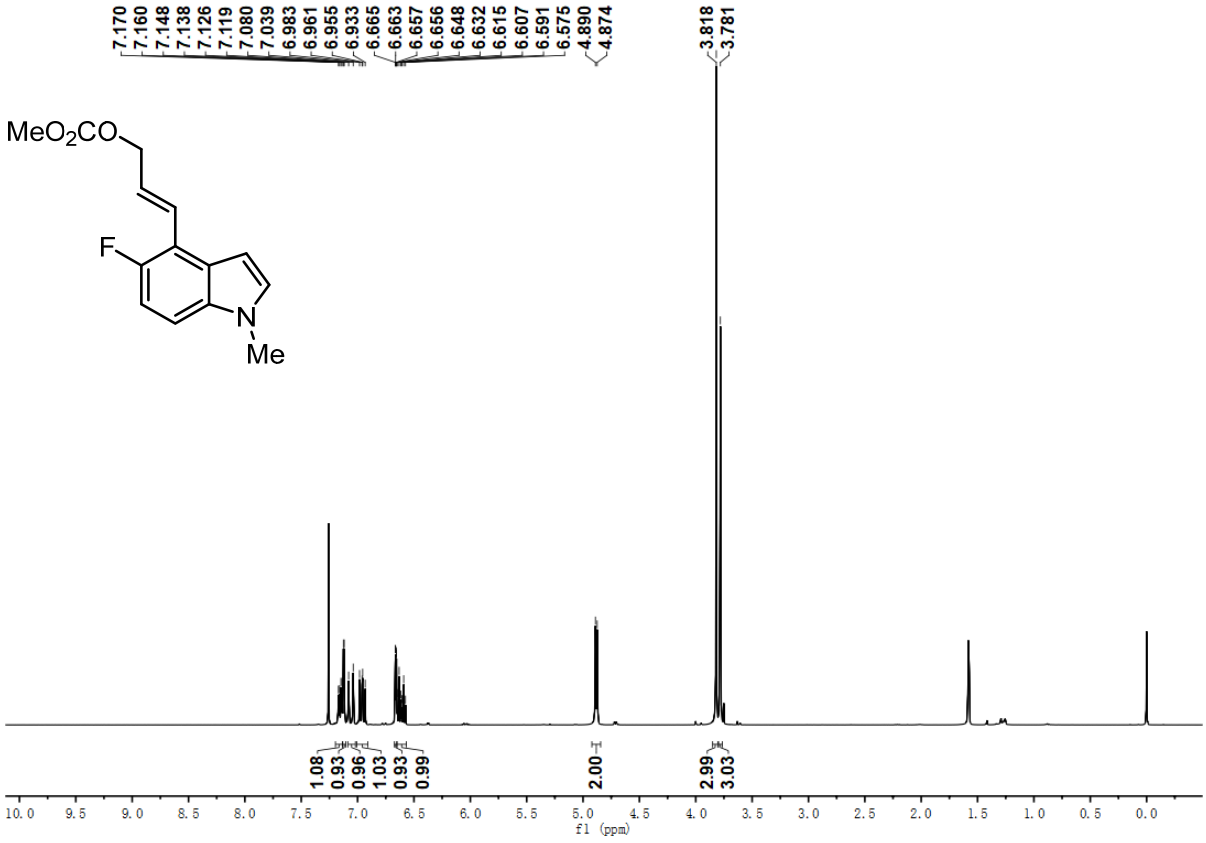
^{1}H NMR (400 MHz) of (*Z*)-**2a'** in $CDCl_3$



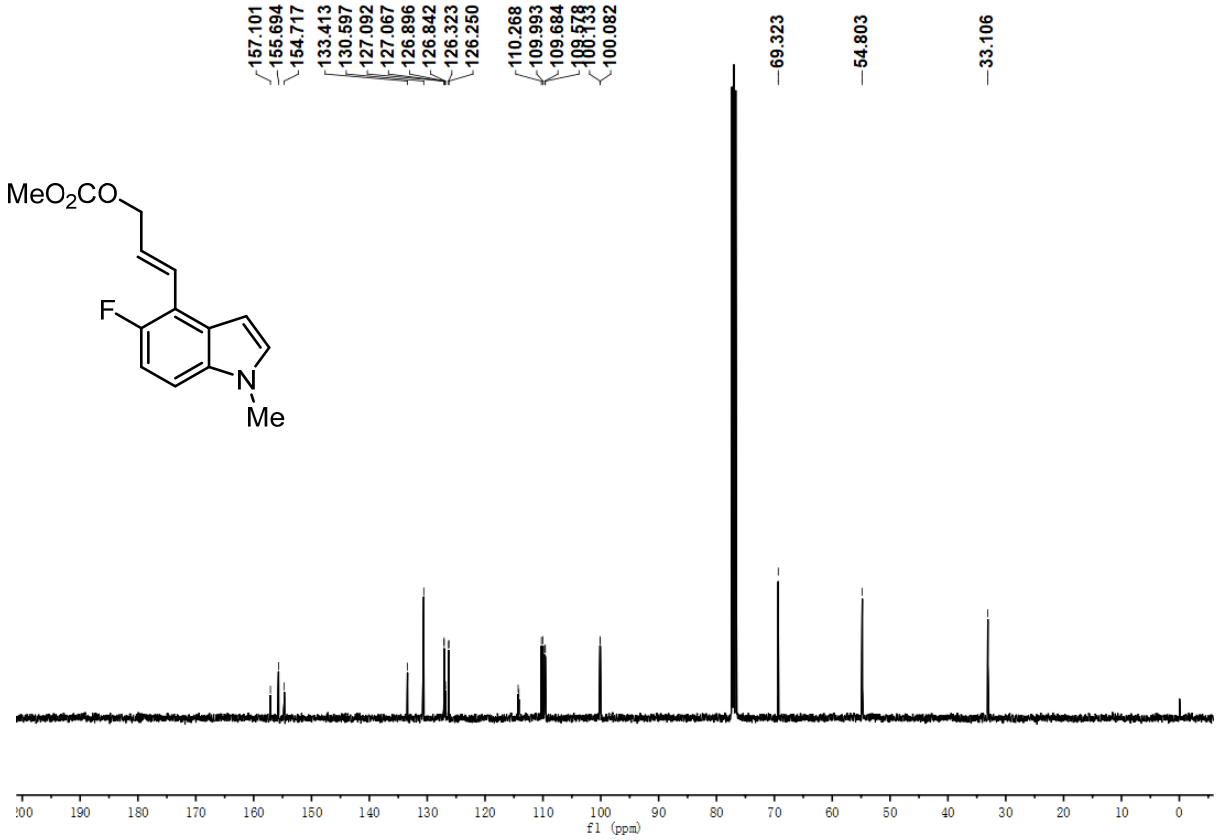
^{13}C NMR (400 MHz) of (*Z*)-**2a'** in $CDCl_3$



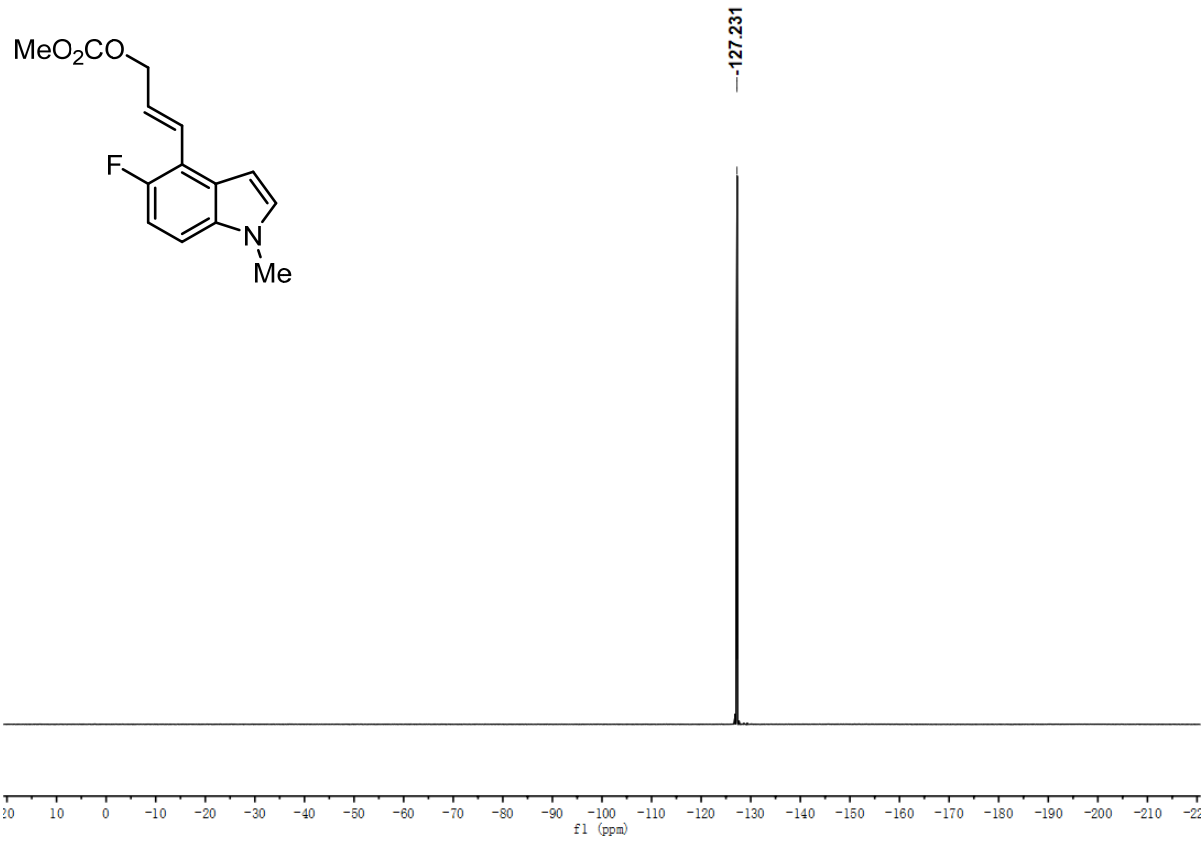
^{1}H NMR (400 MHz) of **2x** in $CDCl_3$



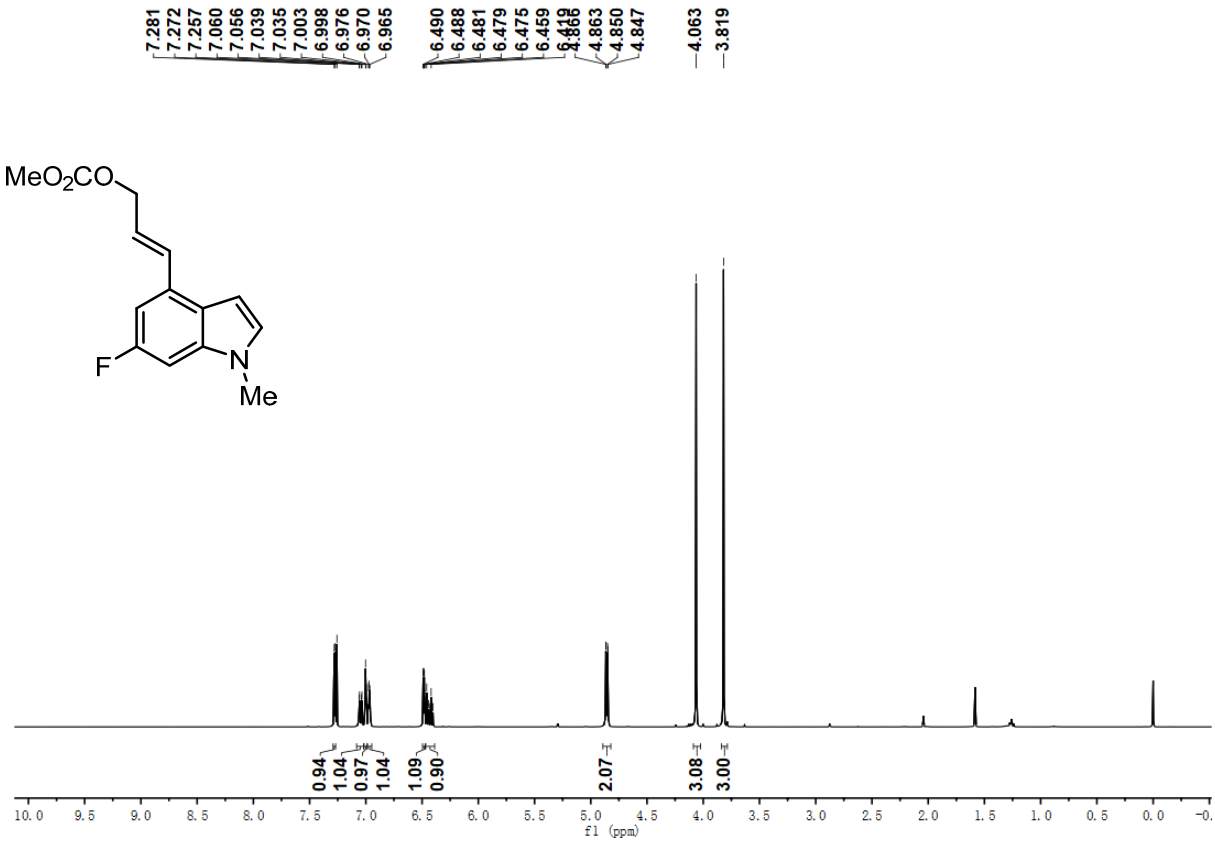
^{13}C NMR (101 MHz) of **2x** in $CDCl_3$



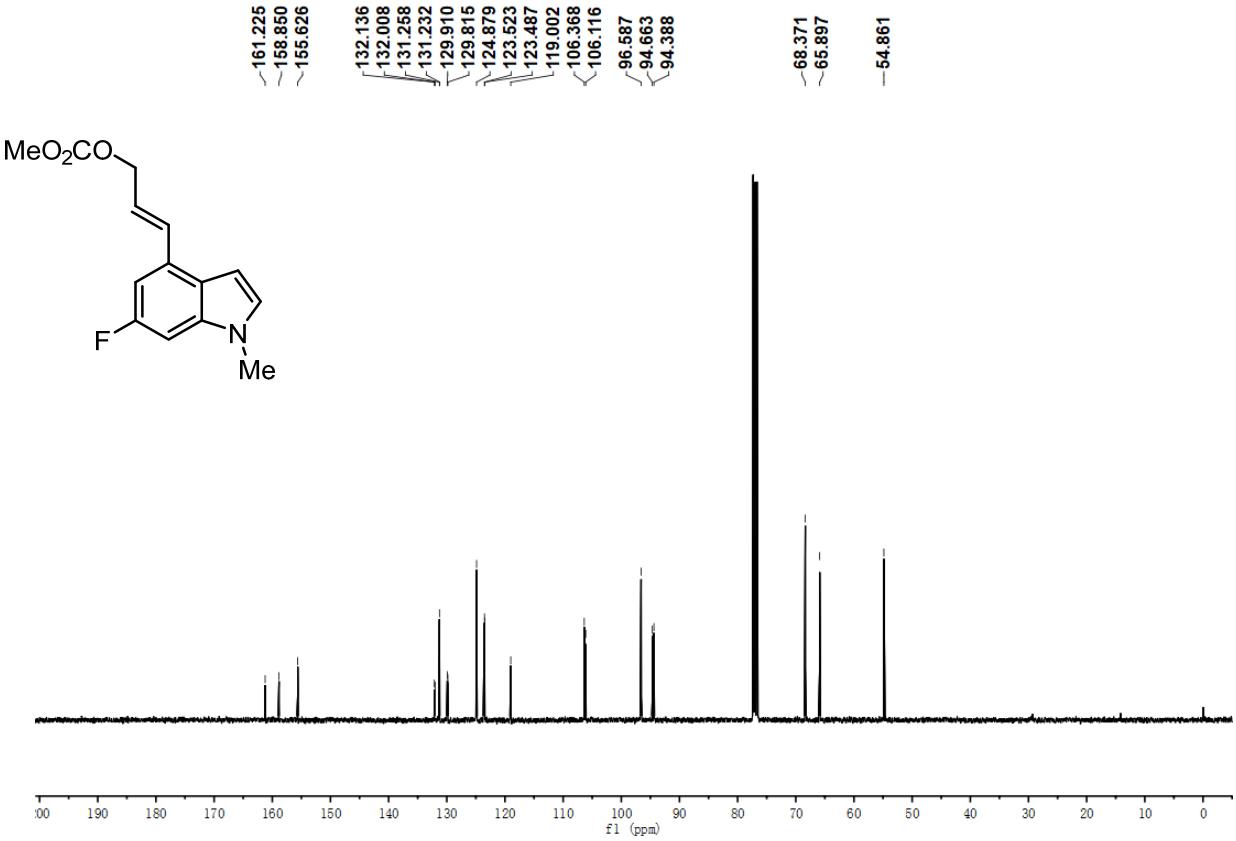
^{19}F NMR (376 MHz) of **2x** in $CDCl_3$



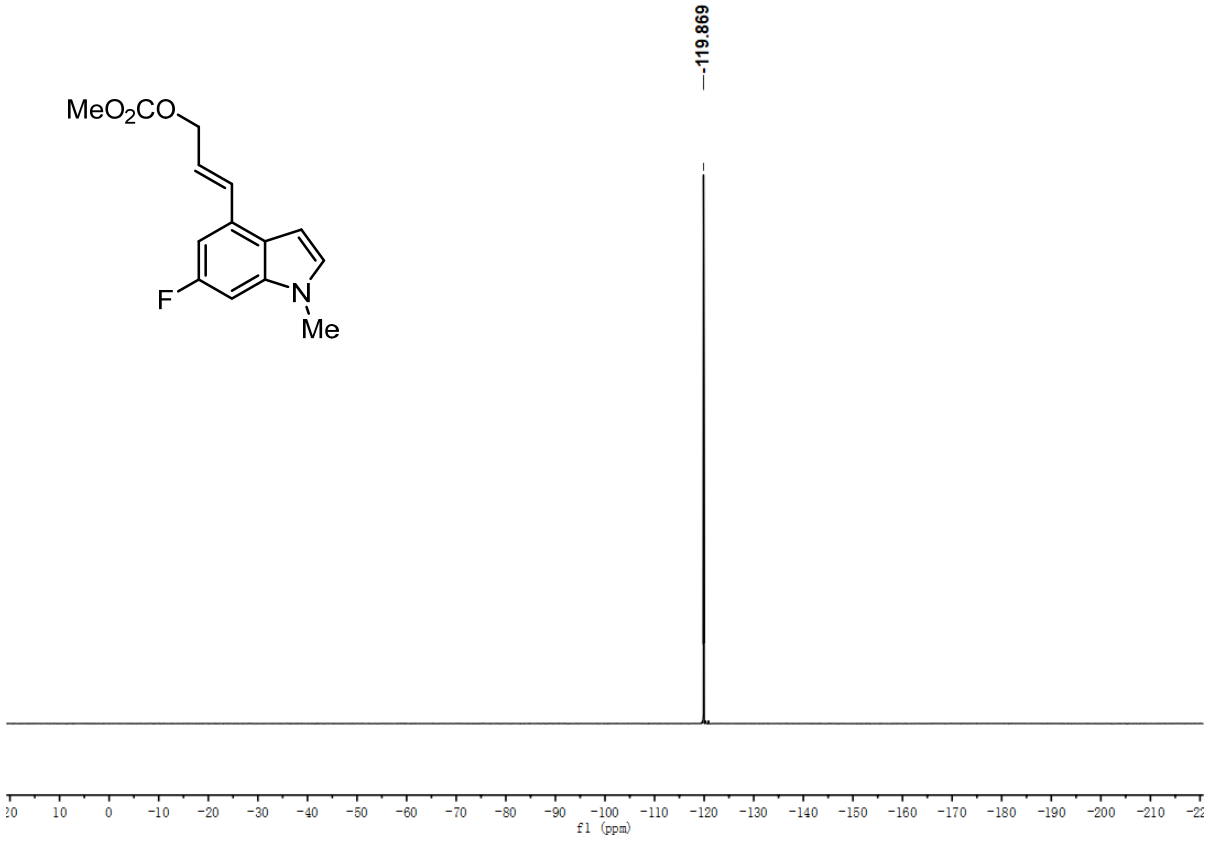
^{1}H NMR (400 MHz) of **2y** in $CDCl_3$



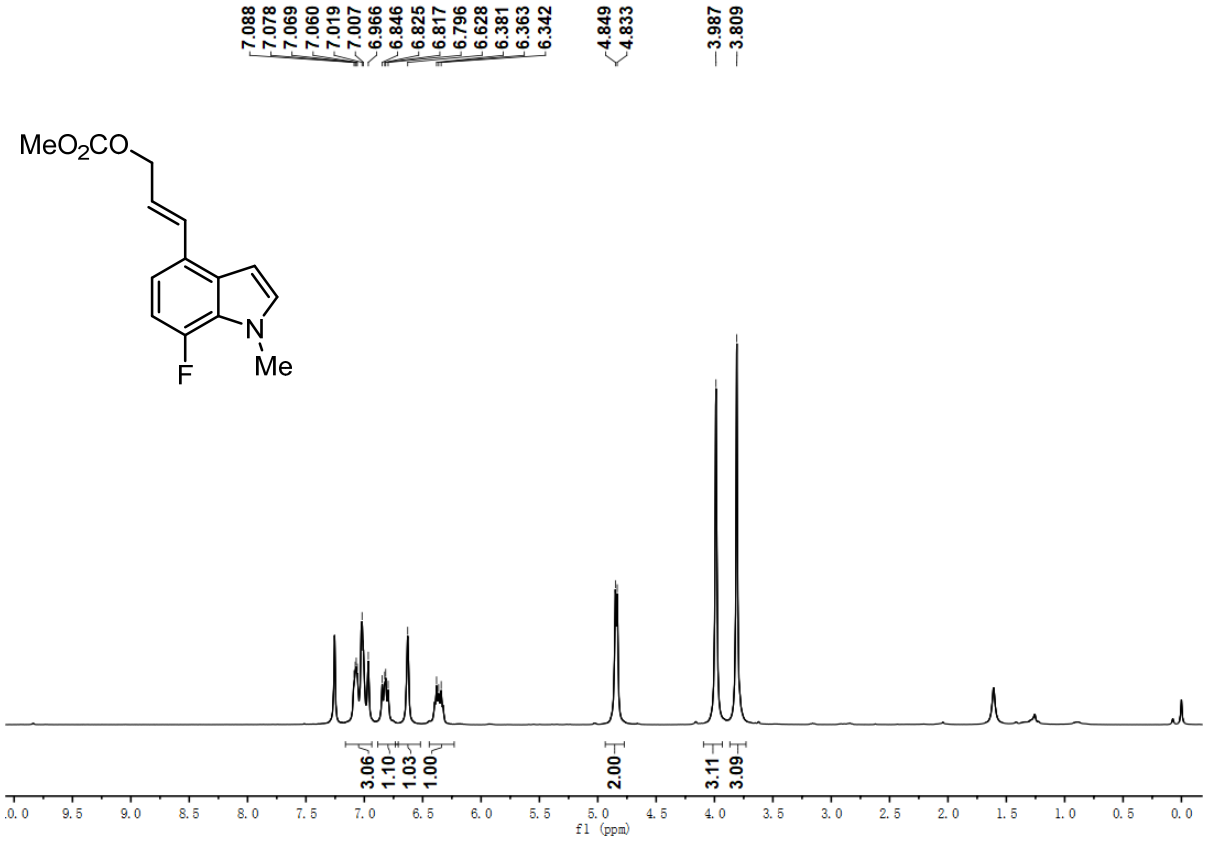
^{13}C NMR (101 MHz) of **2y** in $CDCl_3$



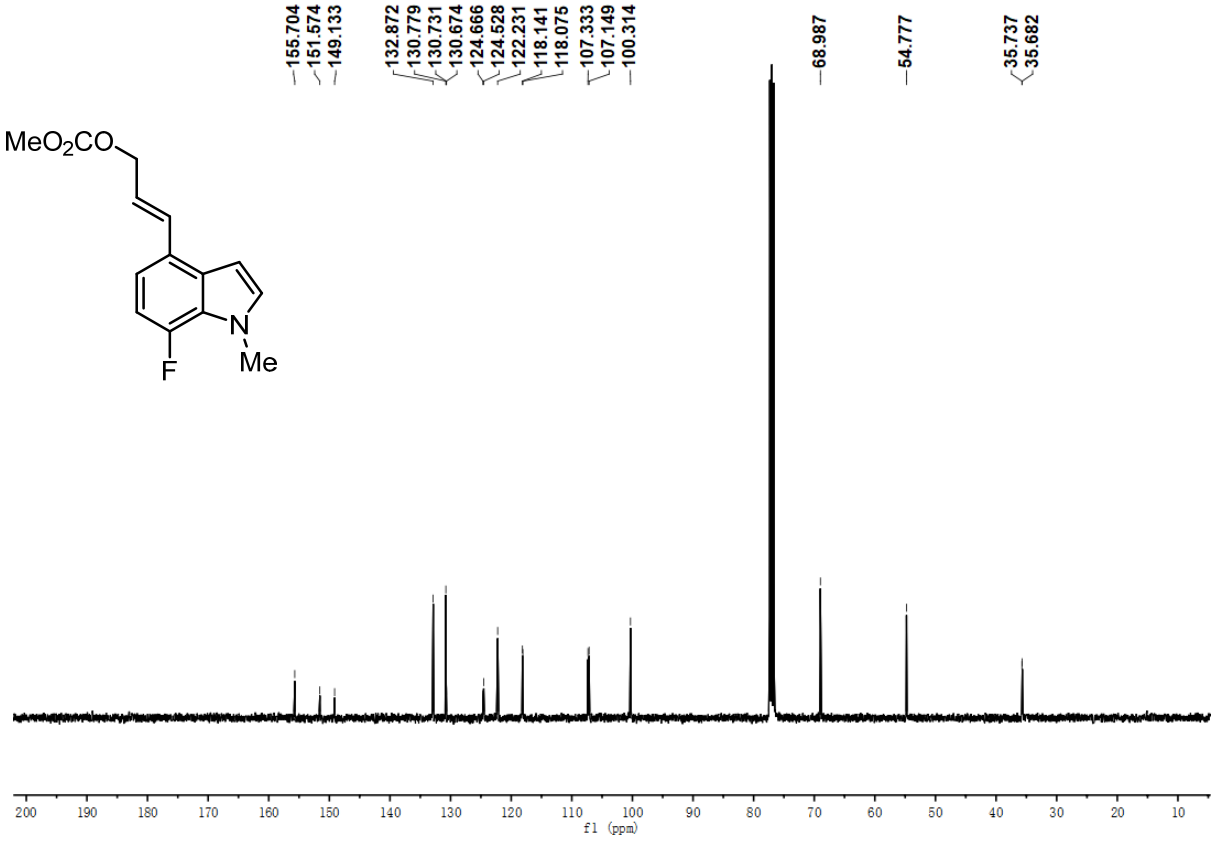
^{19}F NMR (376 MHz) of **2y** in $CDCl_3$



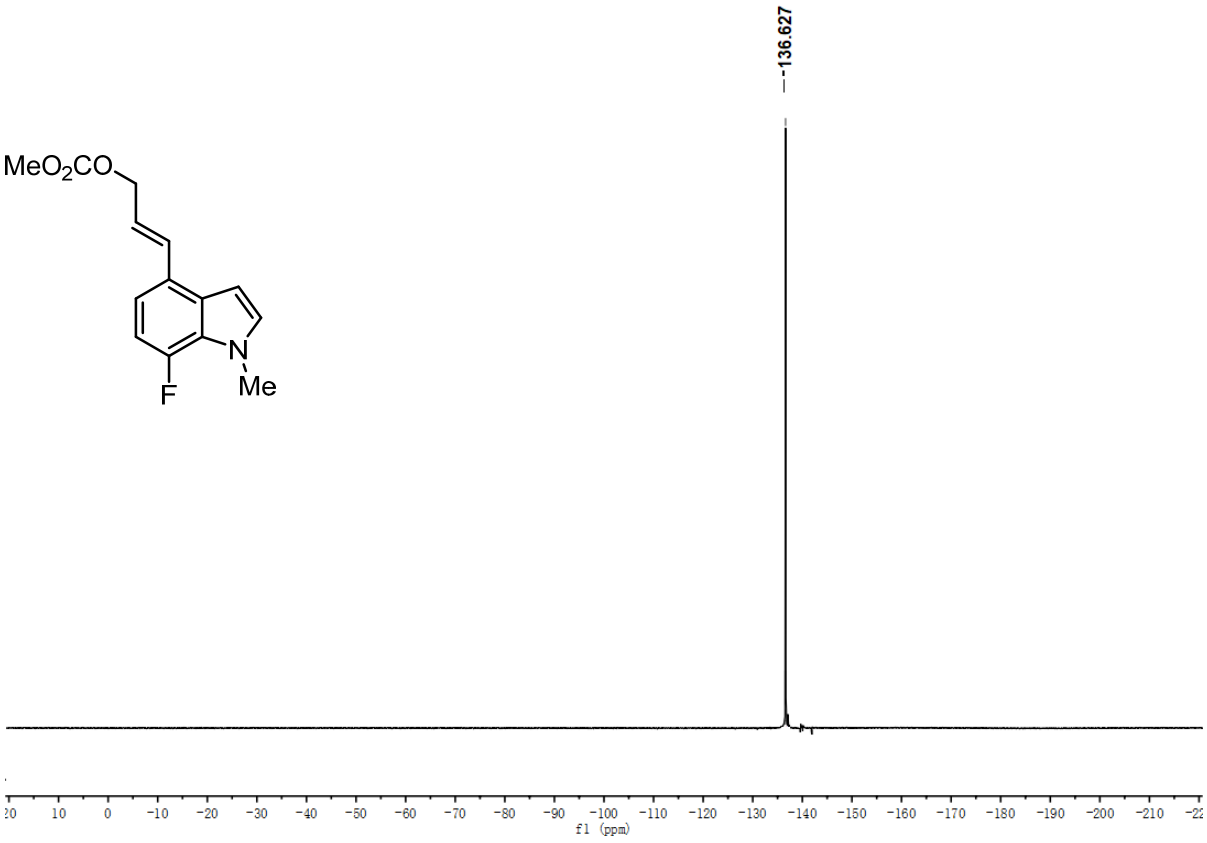
^{1}H NMR (400 MHz) of **2z** in $CDCl_3$



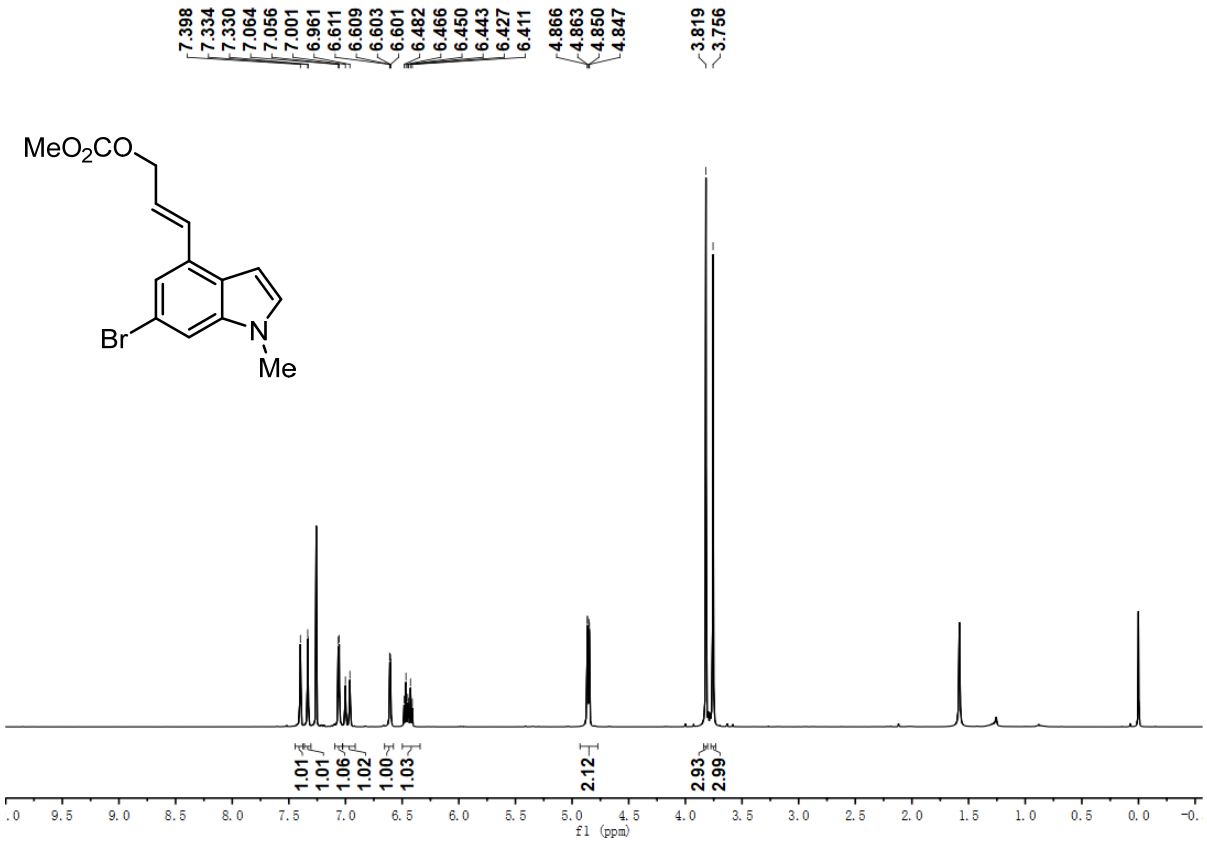
^{13}C NMR (101 MHz) of **2z** in $CDCl_3$



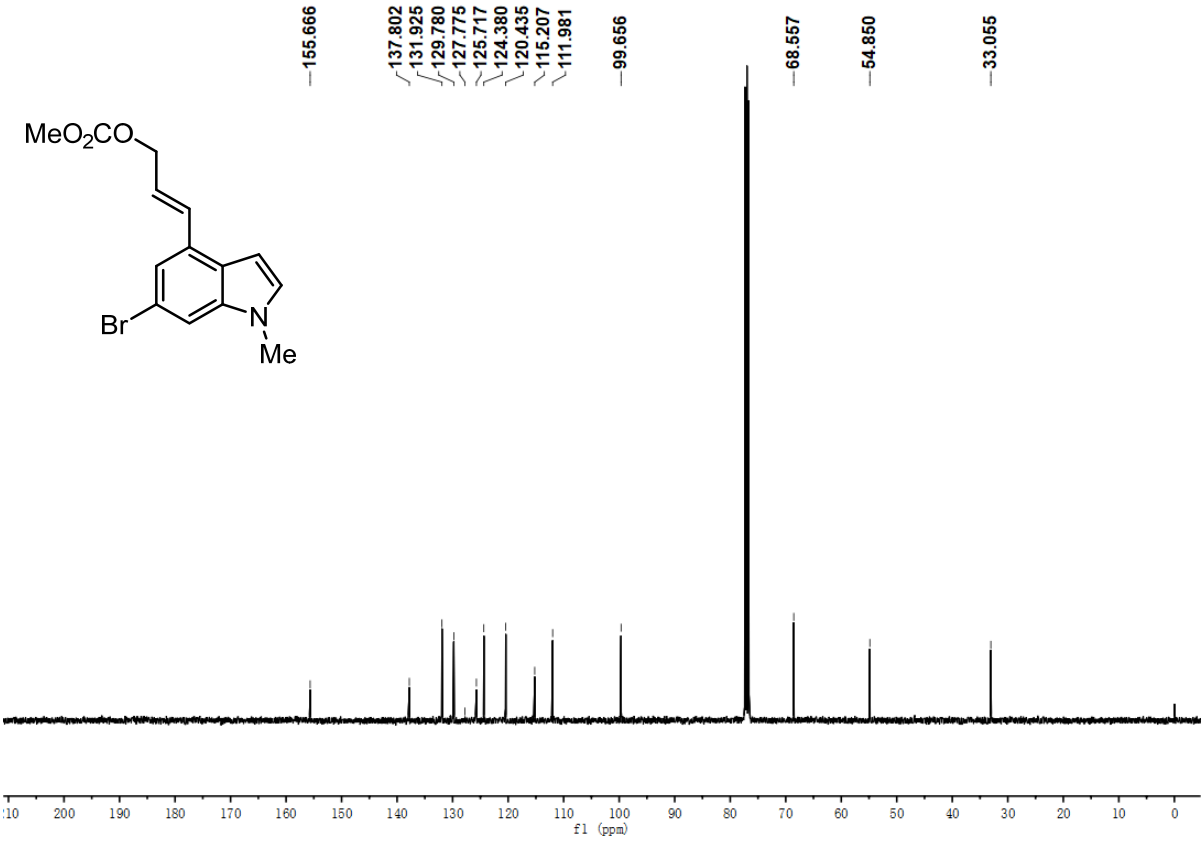
^{19}F NMR (376 MHz) of **2z** in $CDCl_3$



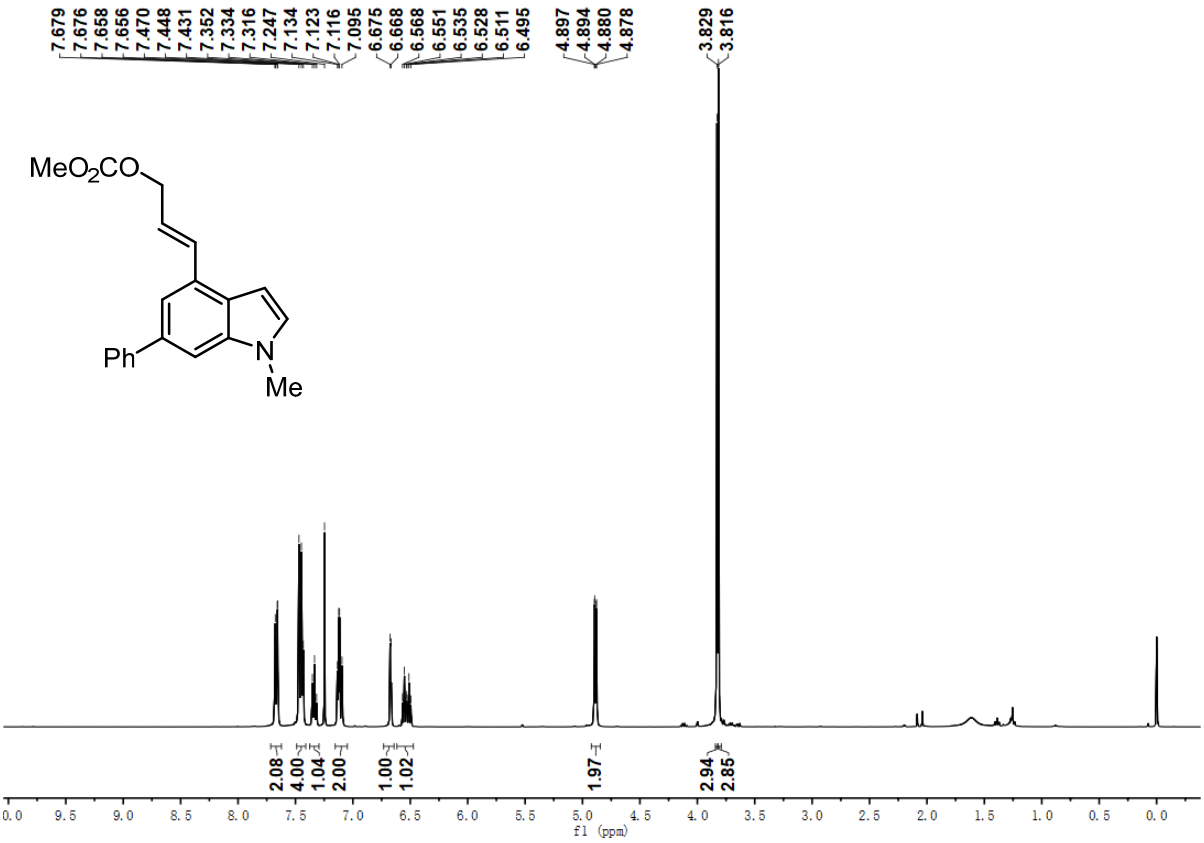
^{1}H NMR (400 MHz) of **2A** in $CDCl_3$



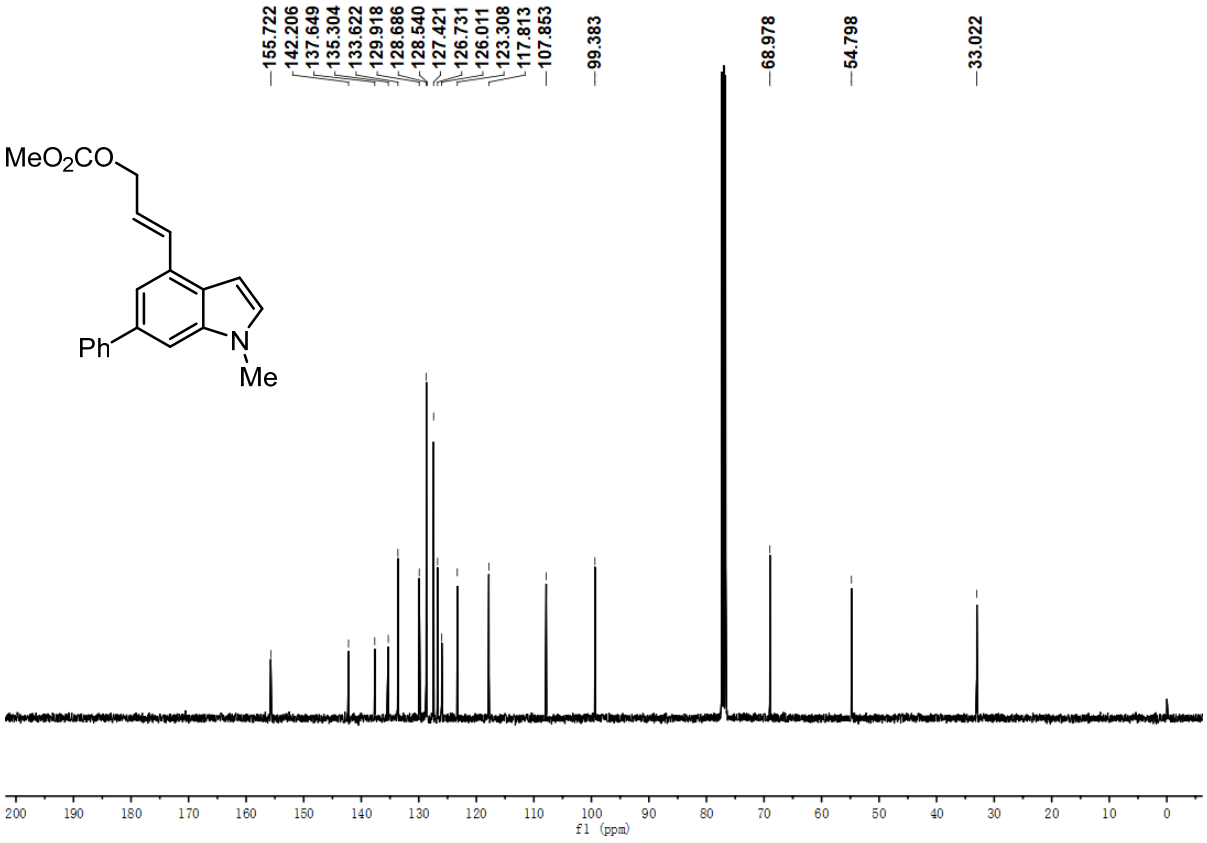
^{13}C NMR (101 MHz) of **2A** in $CDCl_3$



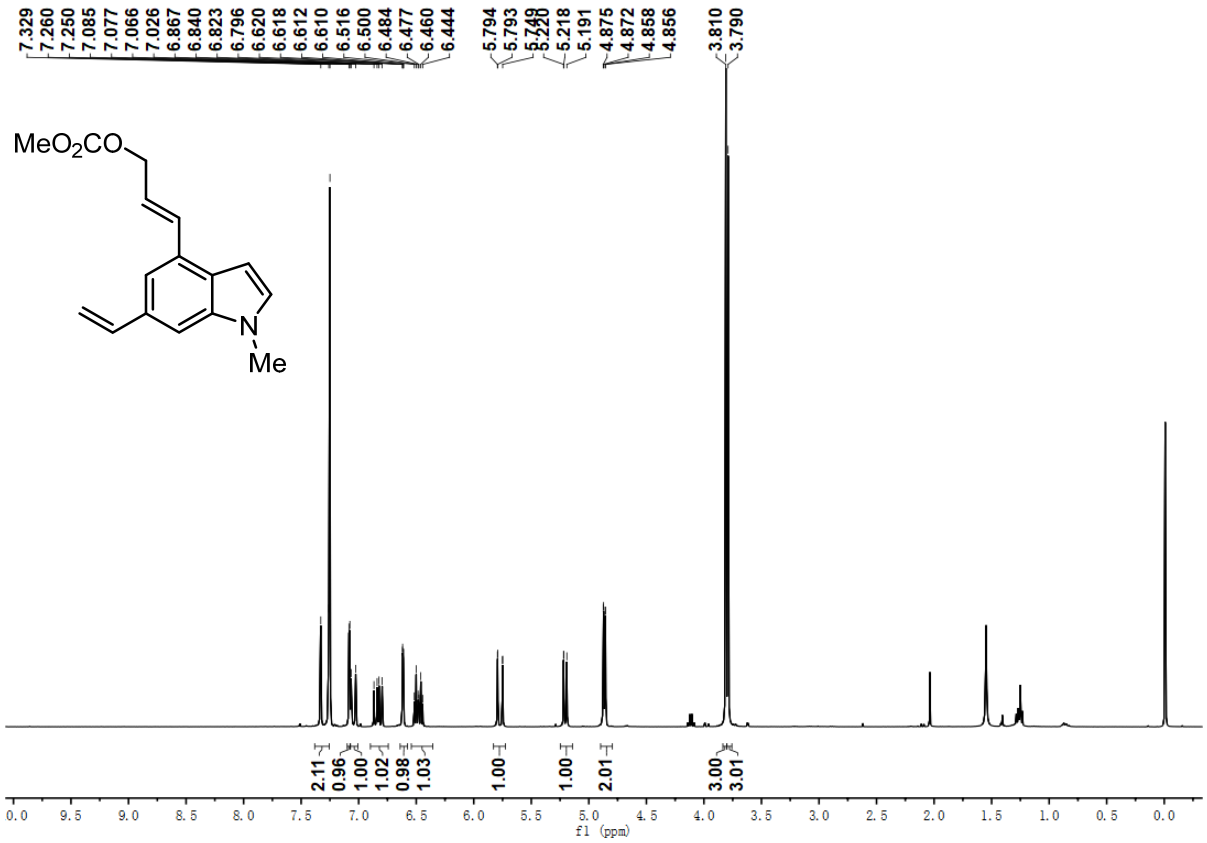
^{1}H NMR (400 MHz) of **2B** in $CDCl_3$



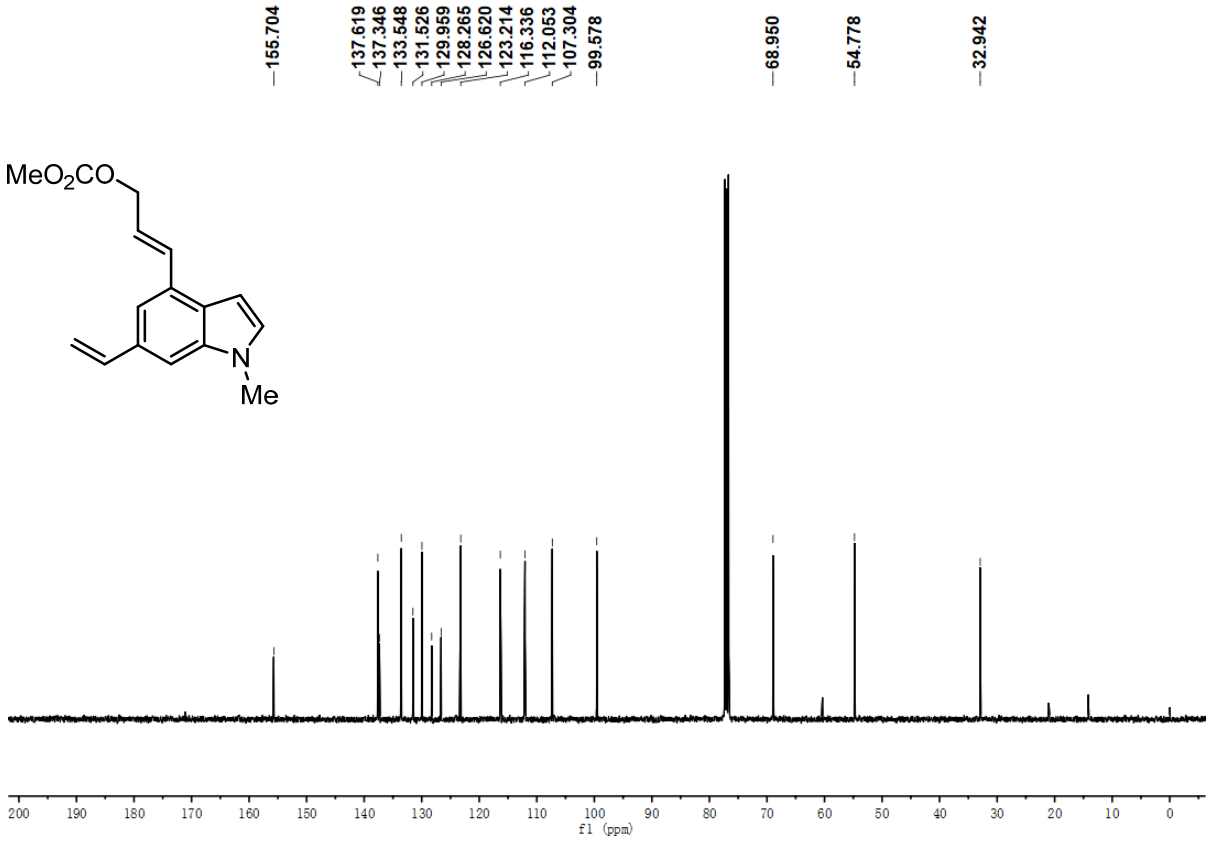
^{13}C NMR (101 MHz) of **2B** in $CDCl_3$



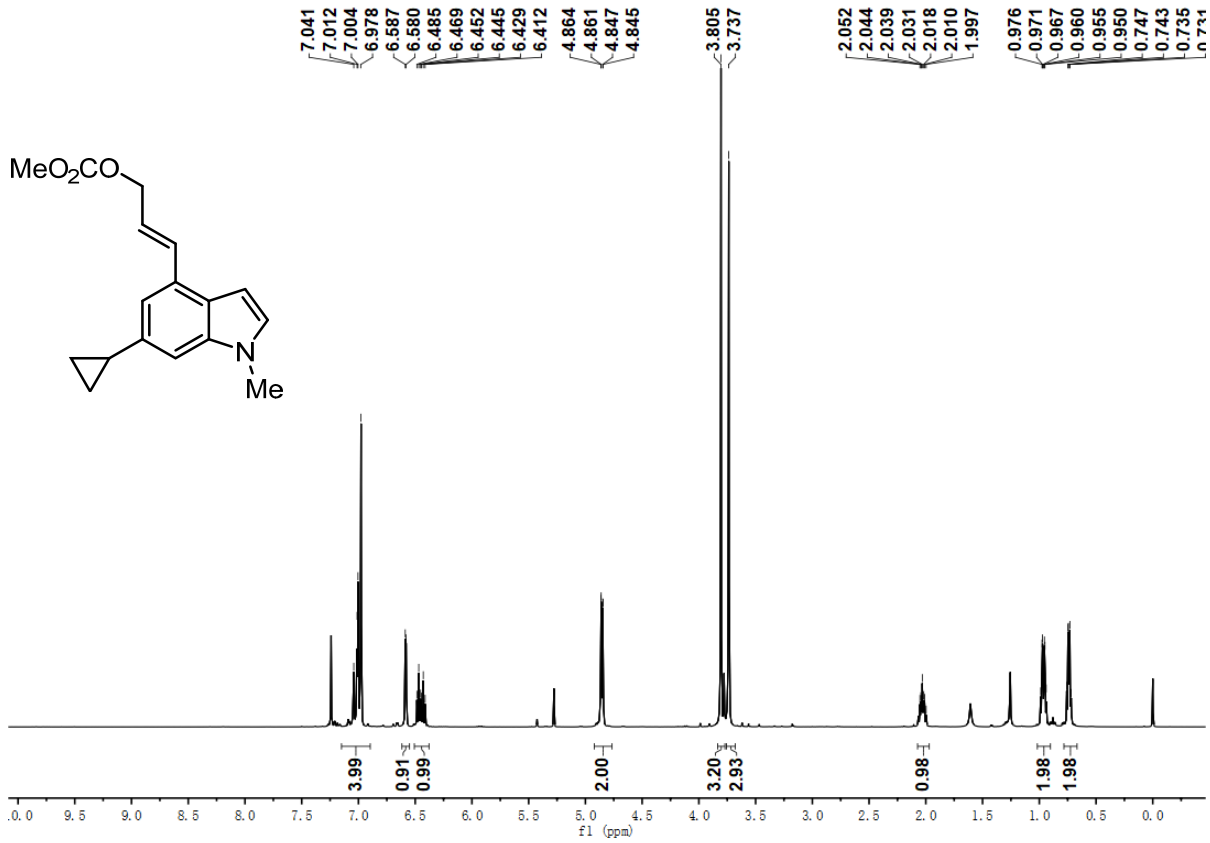
^{1}H NMR (400 MHz) of **2C** in $CDCl_3$



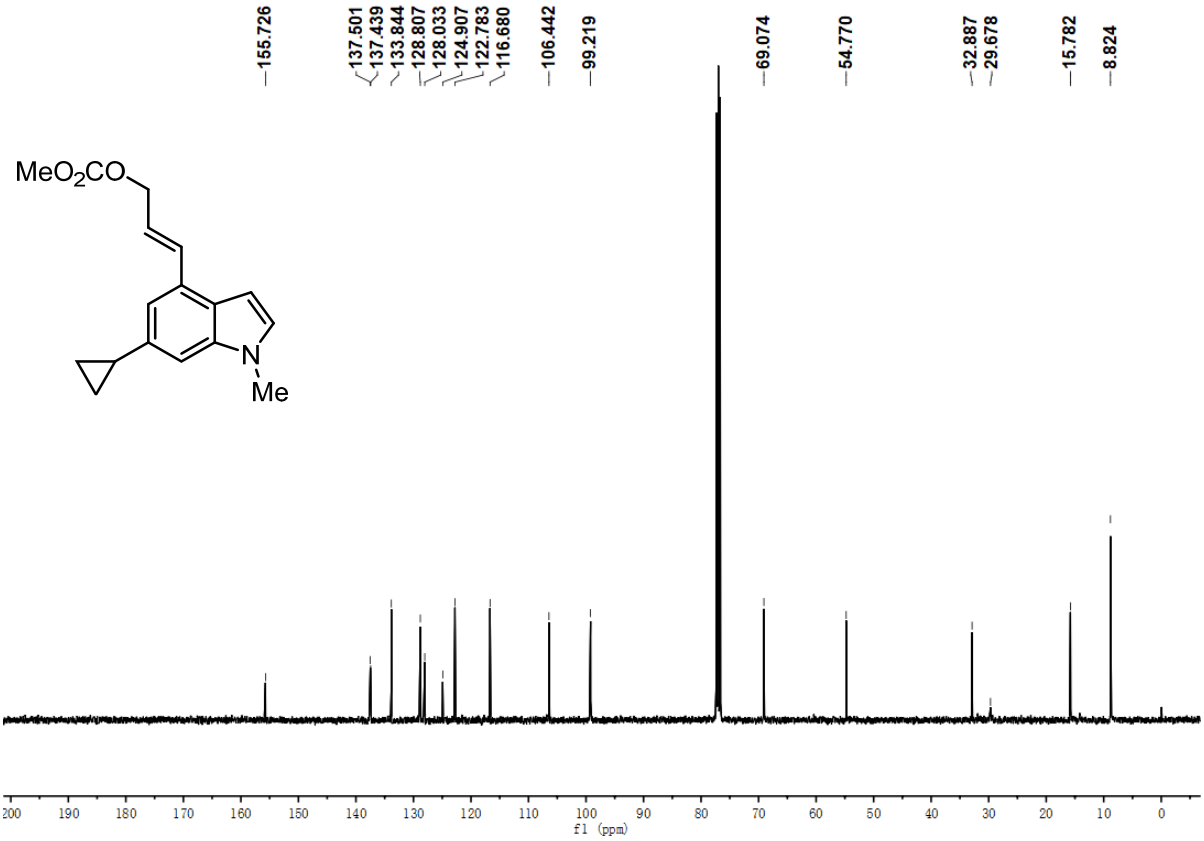
^{13}C NMR (101 MHz) of **2C** in $CDCl_3$



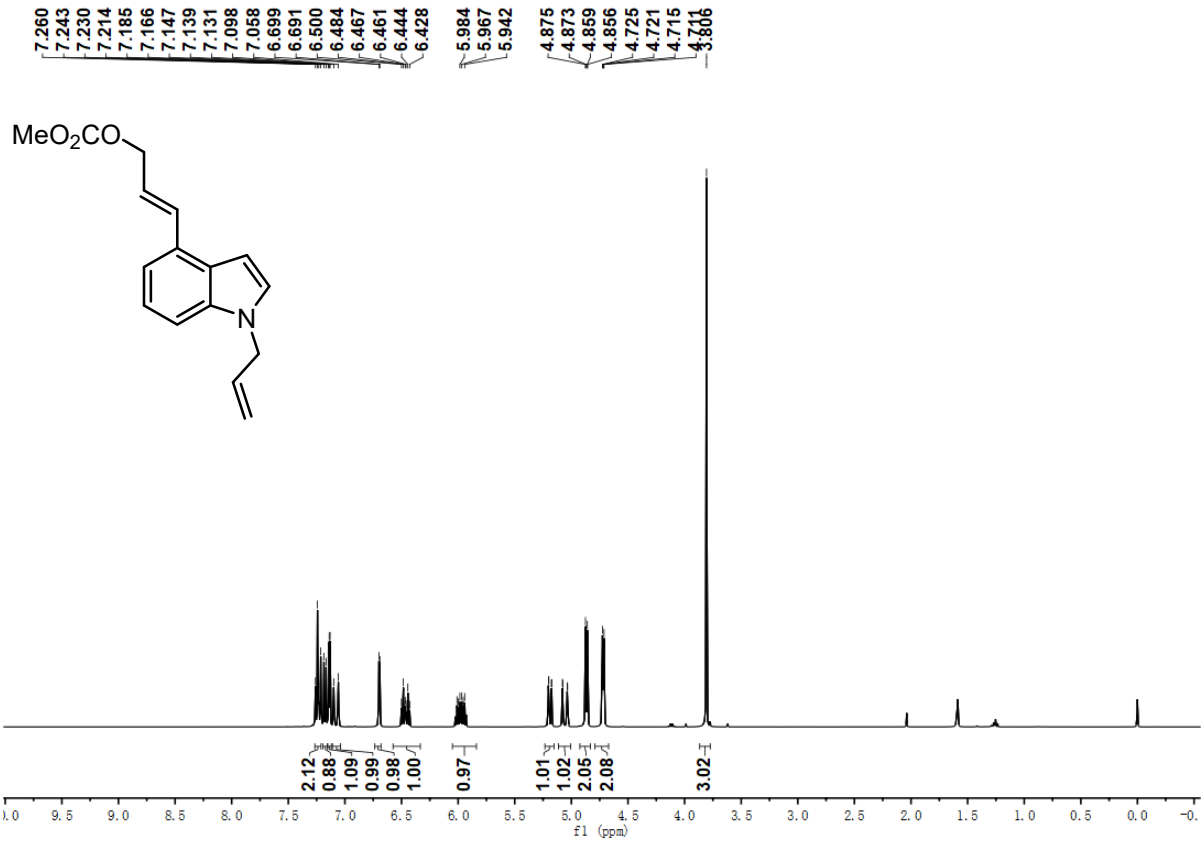
^{1}H NMR (400 MHz) of **2D** in $CDCl_3$



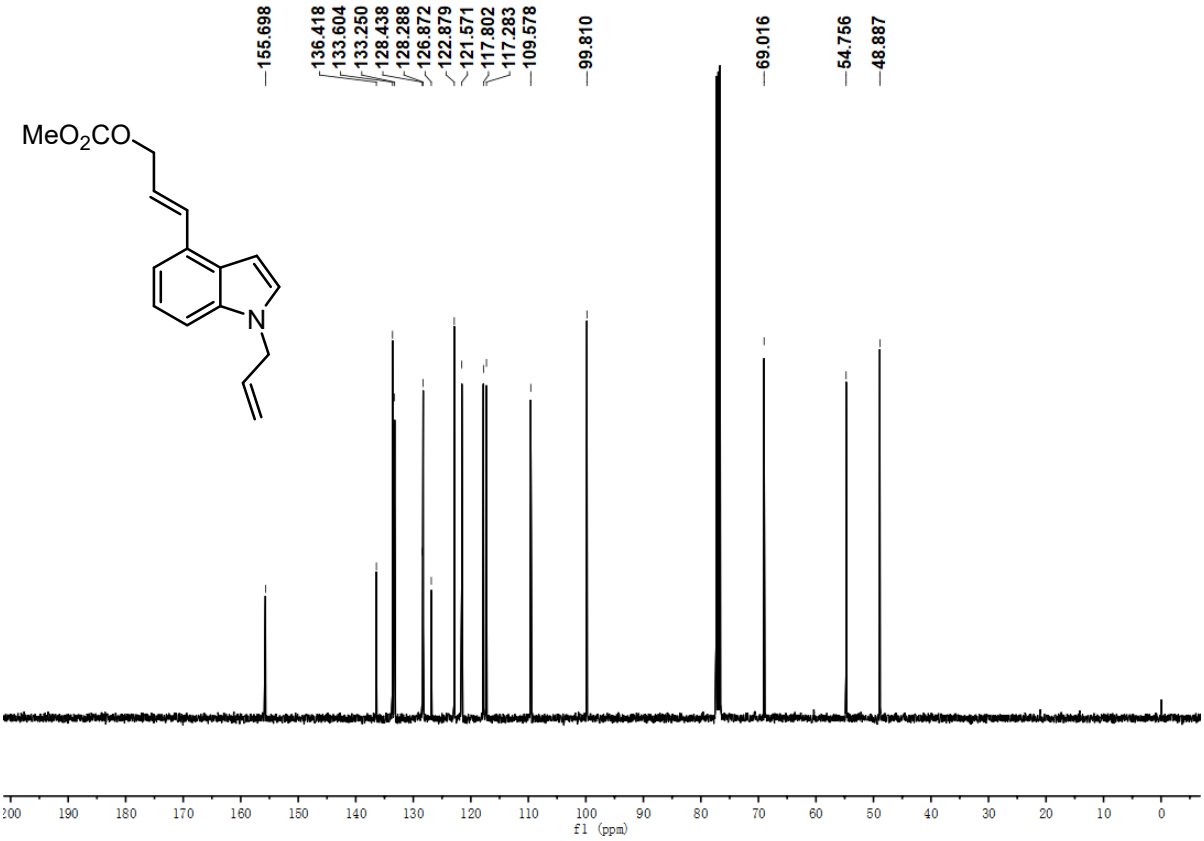
^{13}C NMR (101 MHz) of **2D** in $CDCl_3$



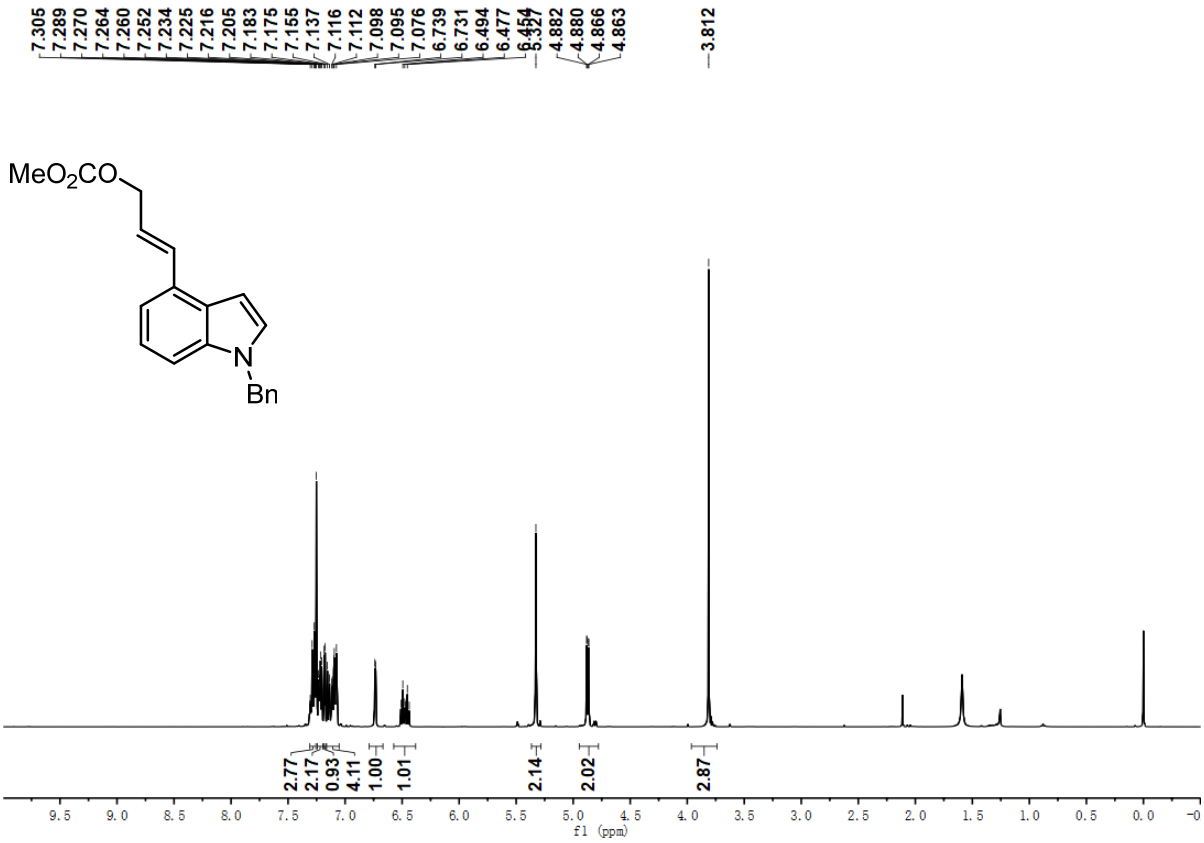
^{1}H NMR (400 MHz) of **2E** in $CDCl_3$



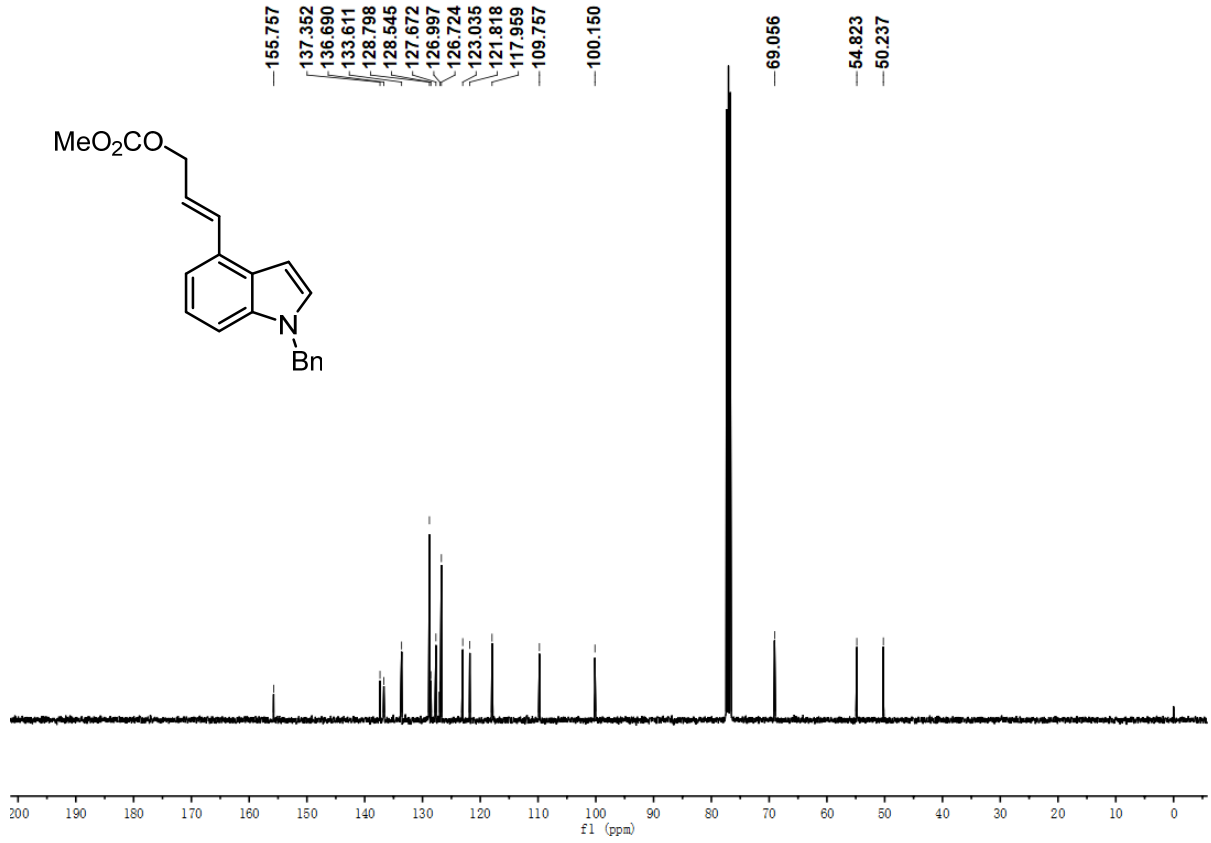
^{13}C NMR (101 MHz) of **2E** in $CDCl_3$



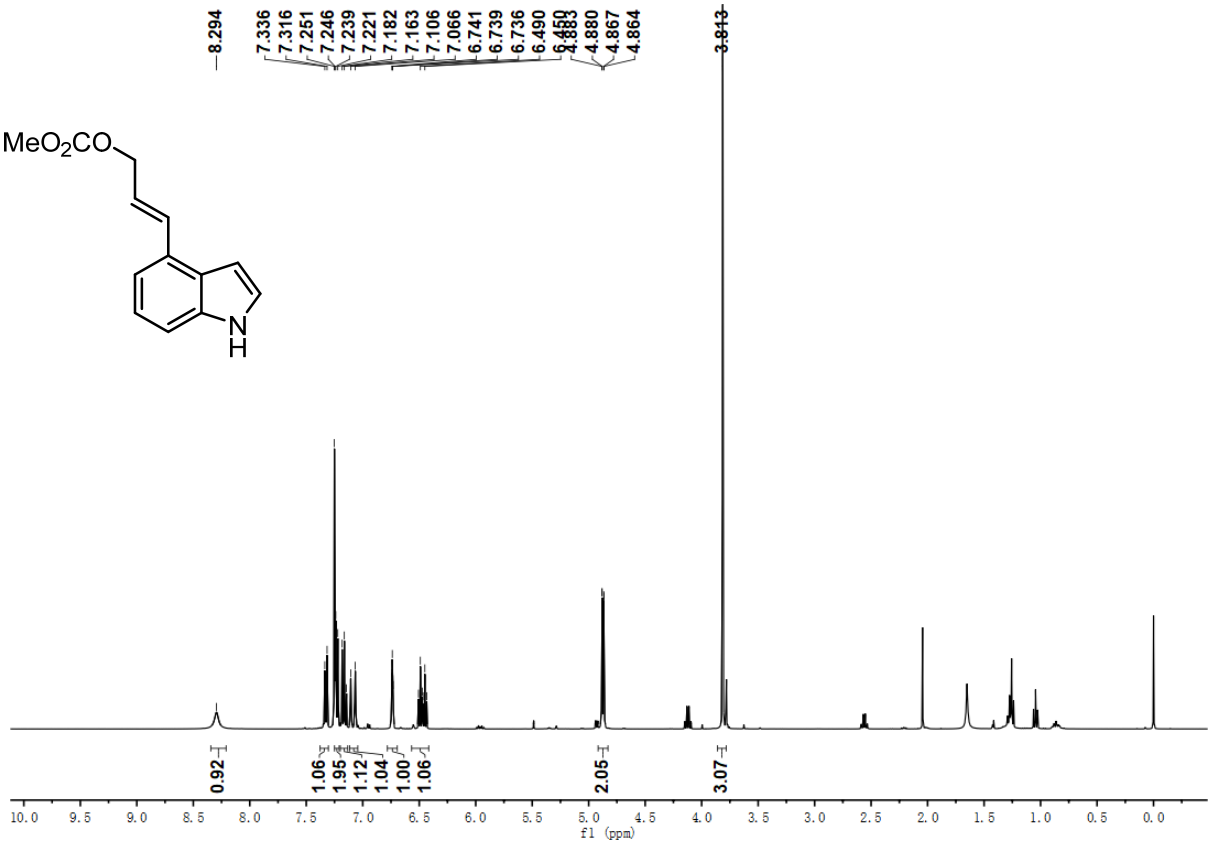
^{1}H NMR (400 MHz) of **2F** in $CDCl_3$



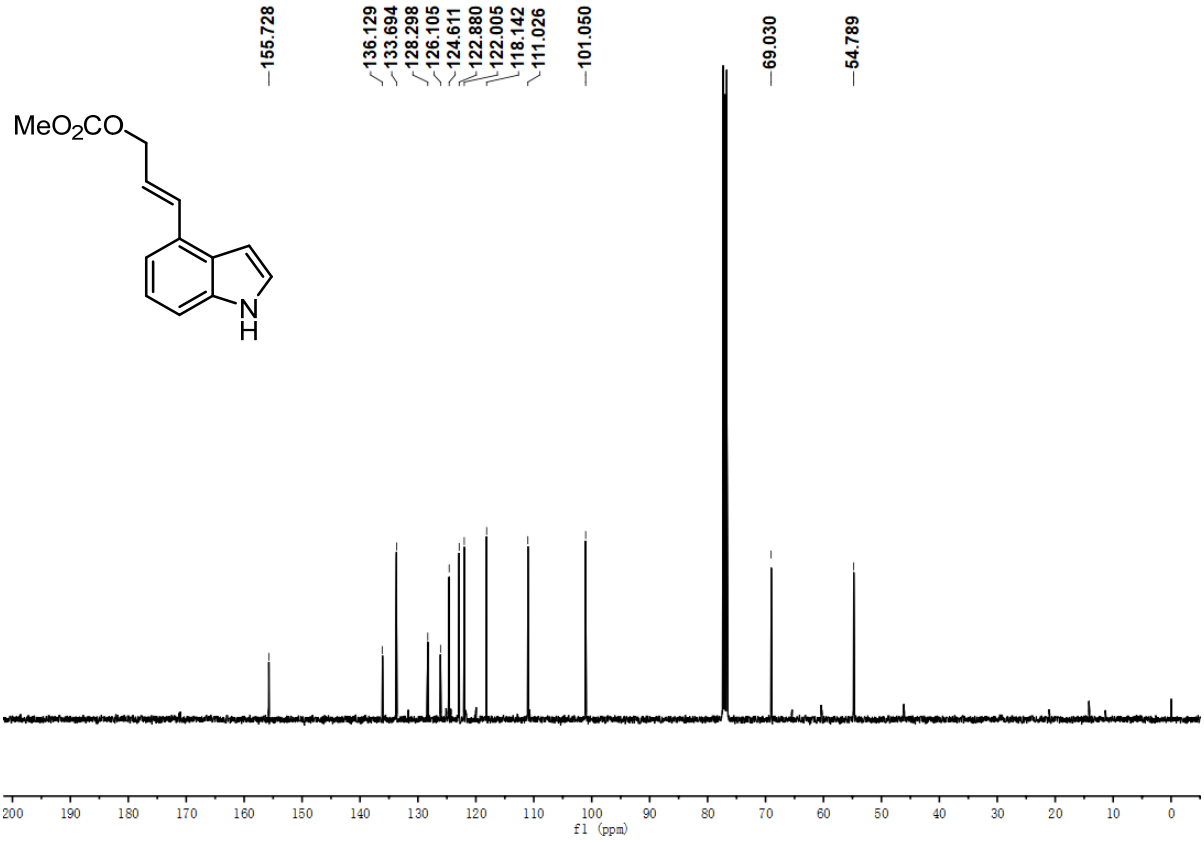
^{13}C NMR (101 MHz) of **2F** in $CDCl_3$



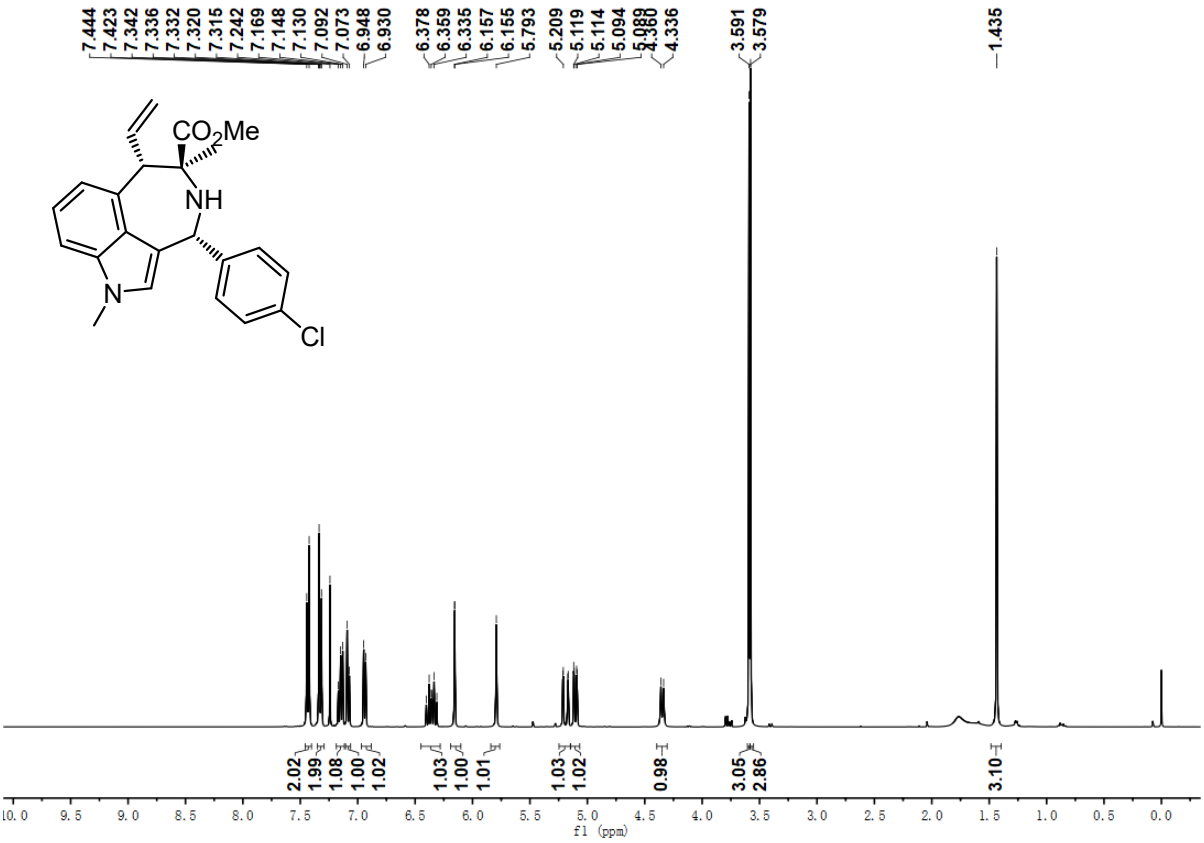
^{1}H NMR (400 MHz) of **2G** in $CDCl_3$



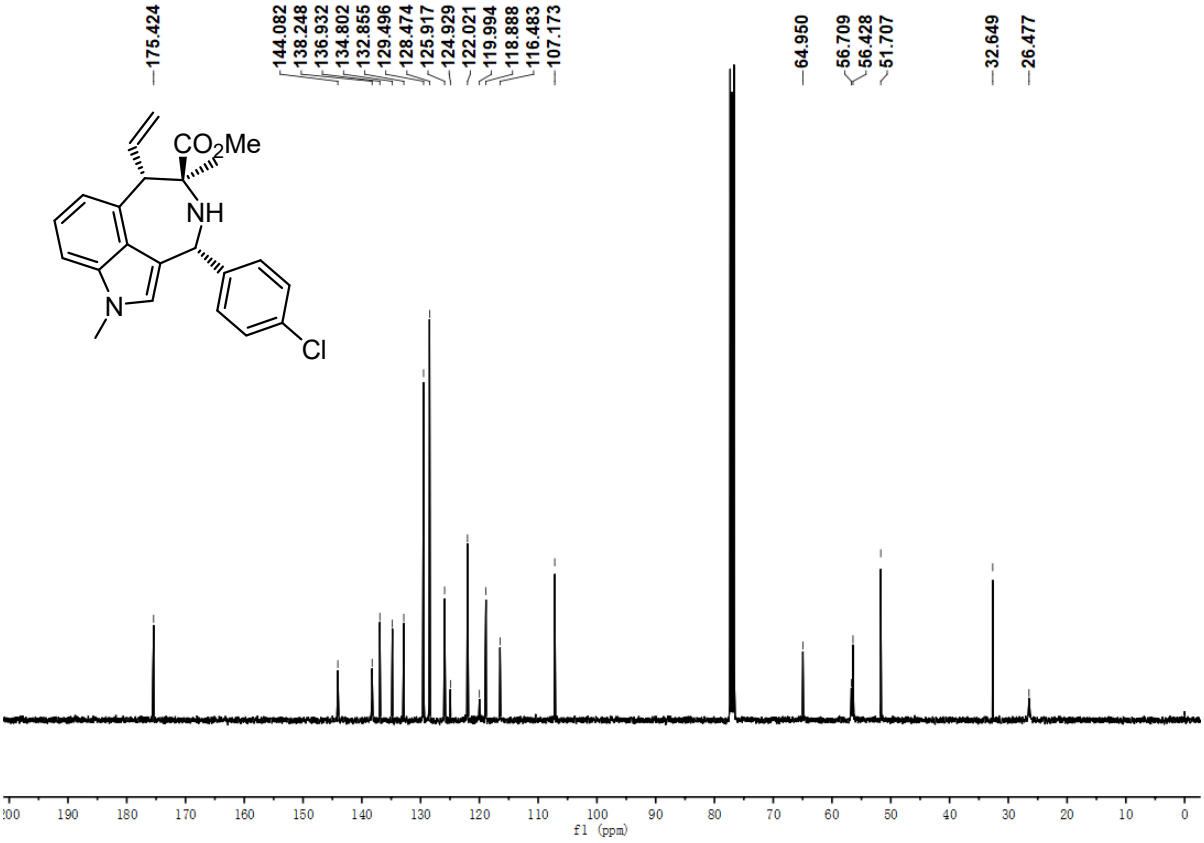
^{13}C NMR (101 MHz) of **2G** in $CDCl_3$



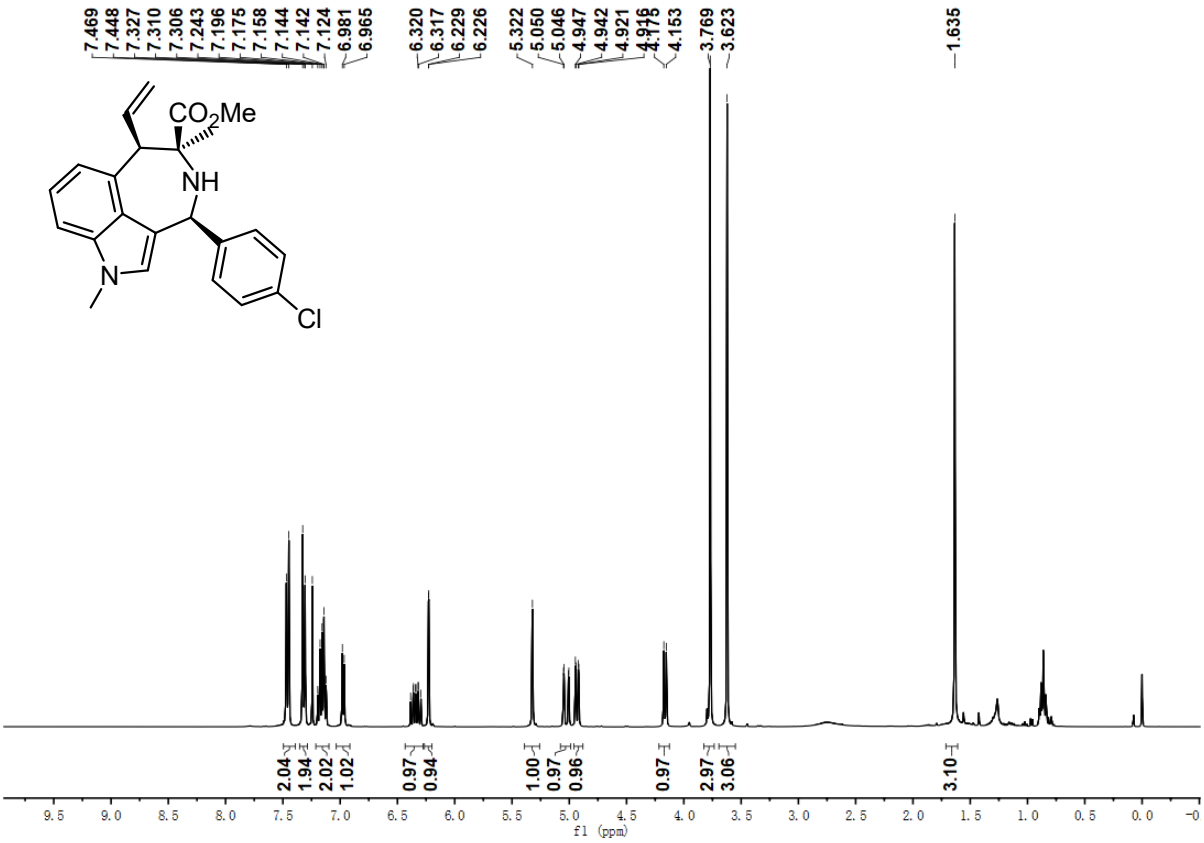
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3a** in $CDCl_3$



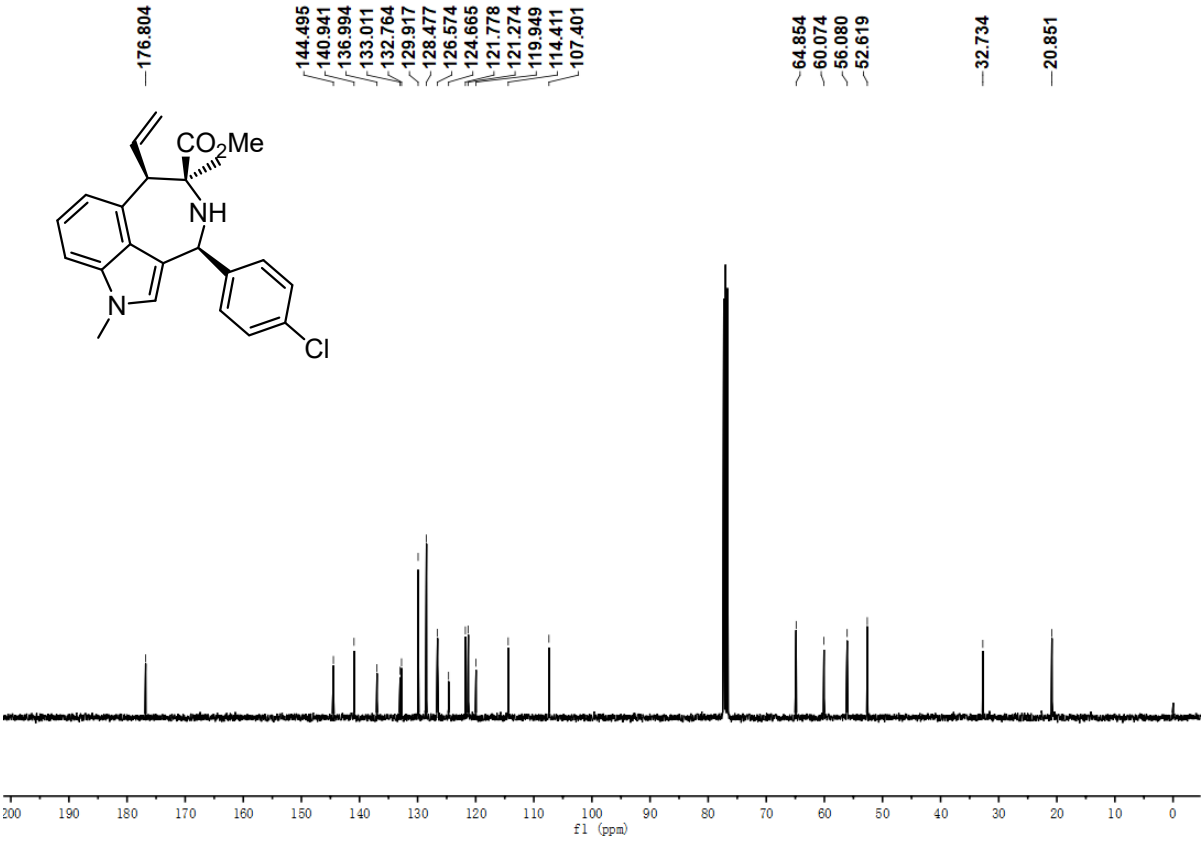
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3a** in $CDCl_3$



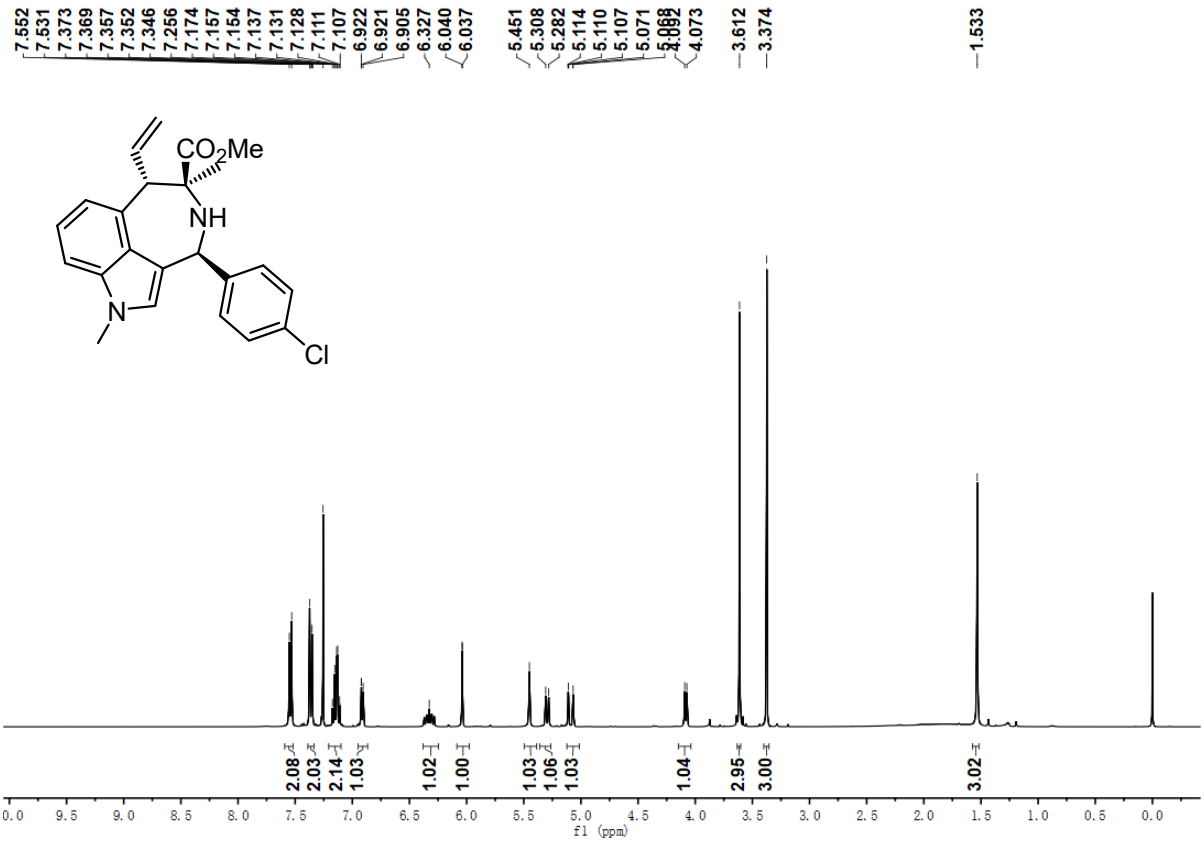
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**3a** in $CDCl_3$



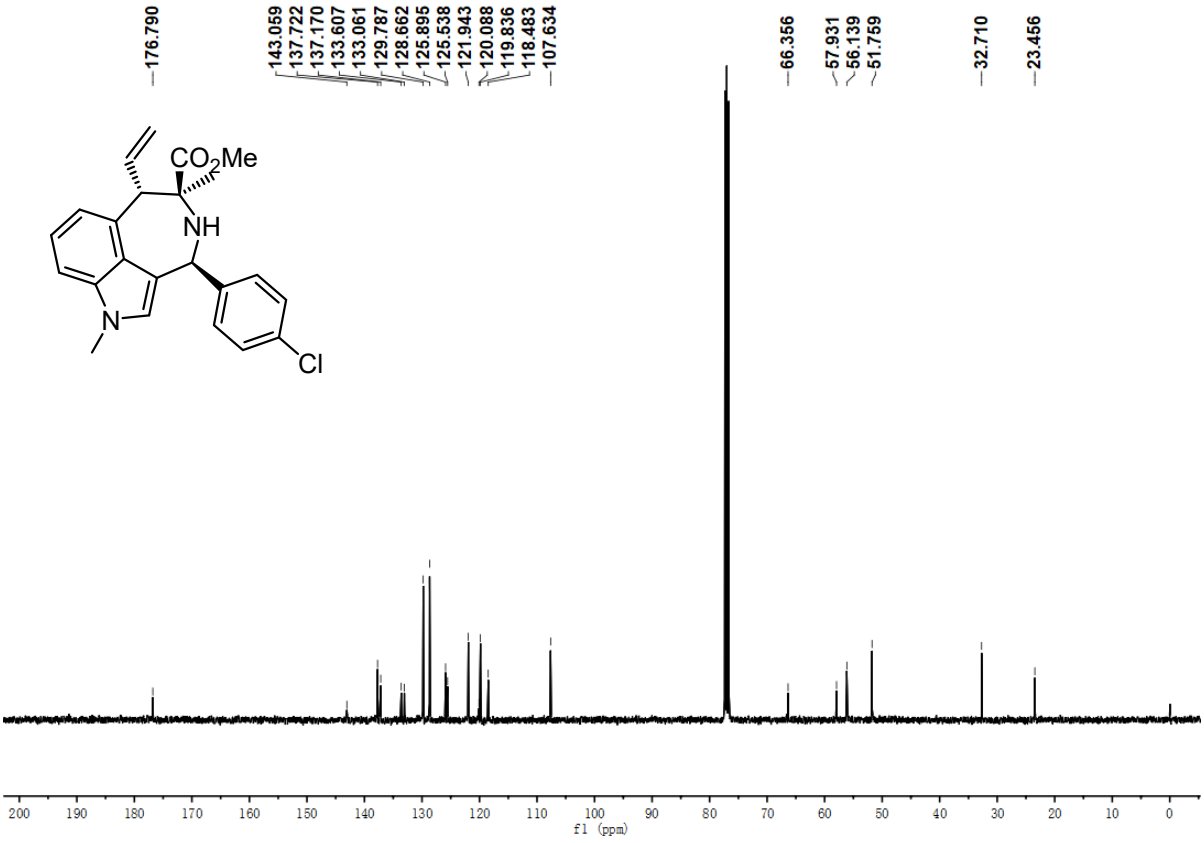
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**3a** in $CDCl_3$



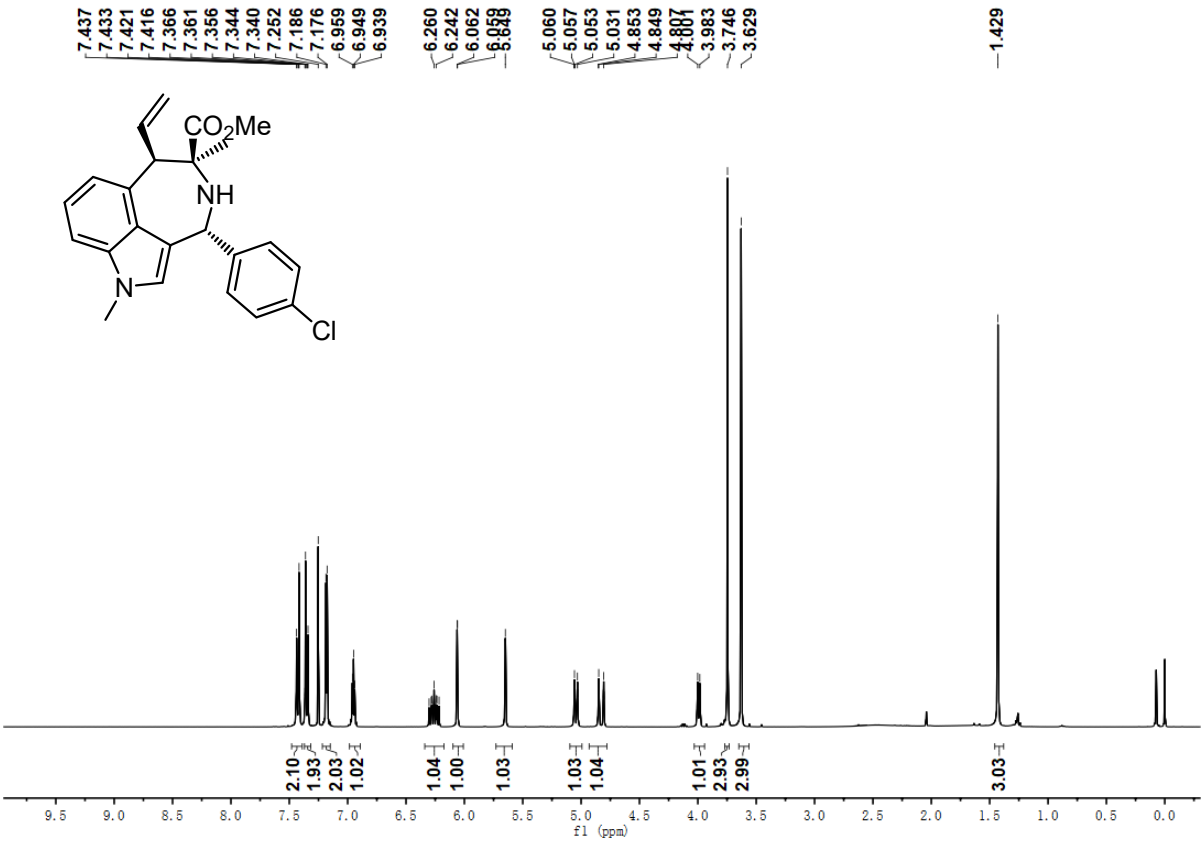
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*S*)-**3a** in $CDCl_3$



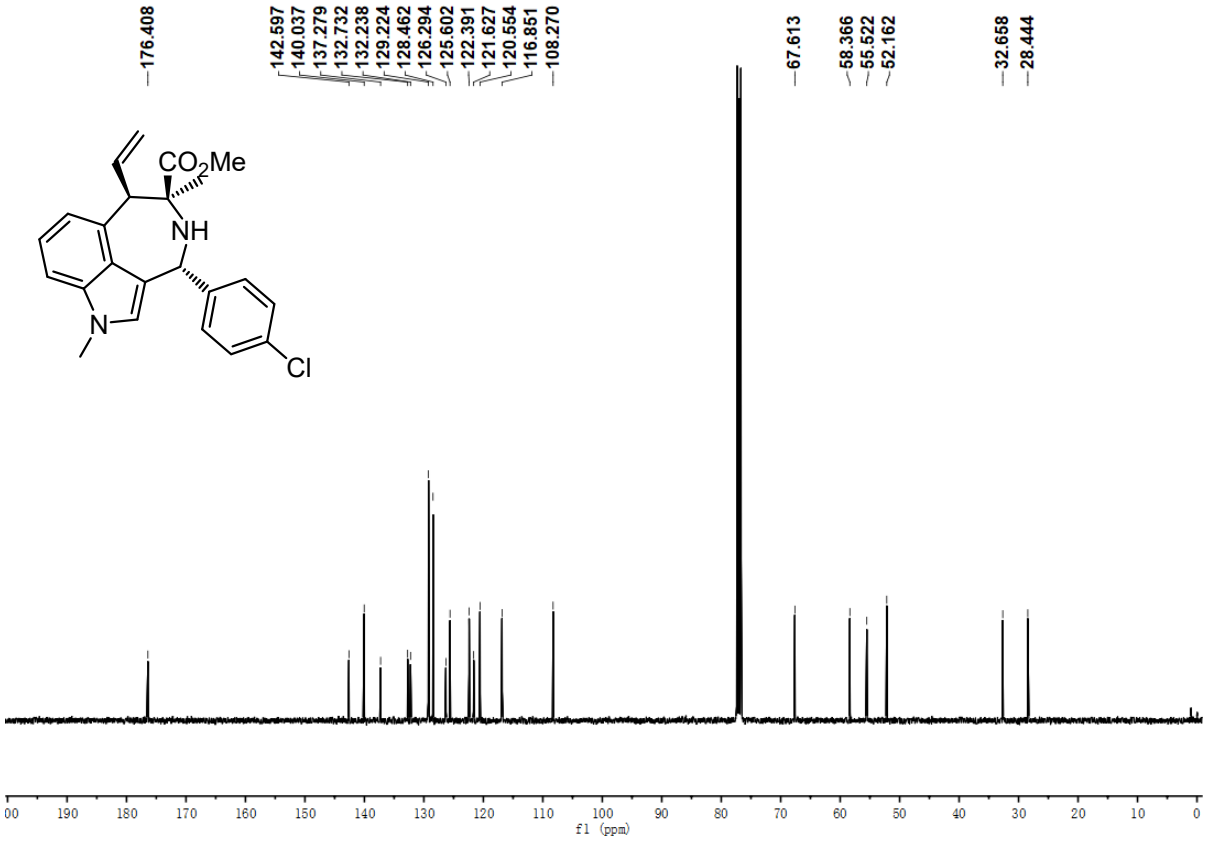
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*S*)-**3a** in $CDCl_3$



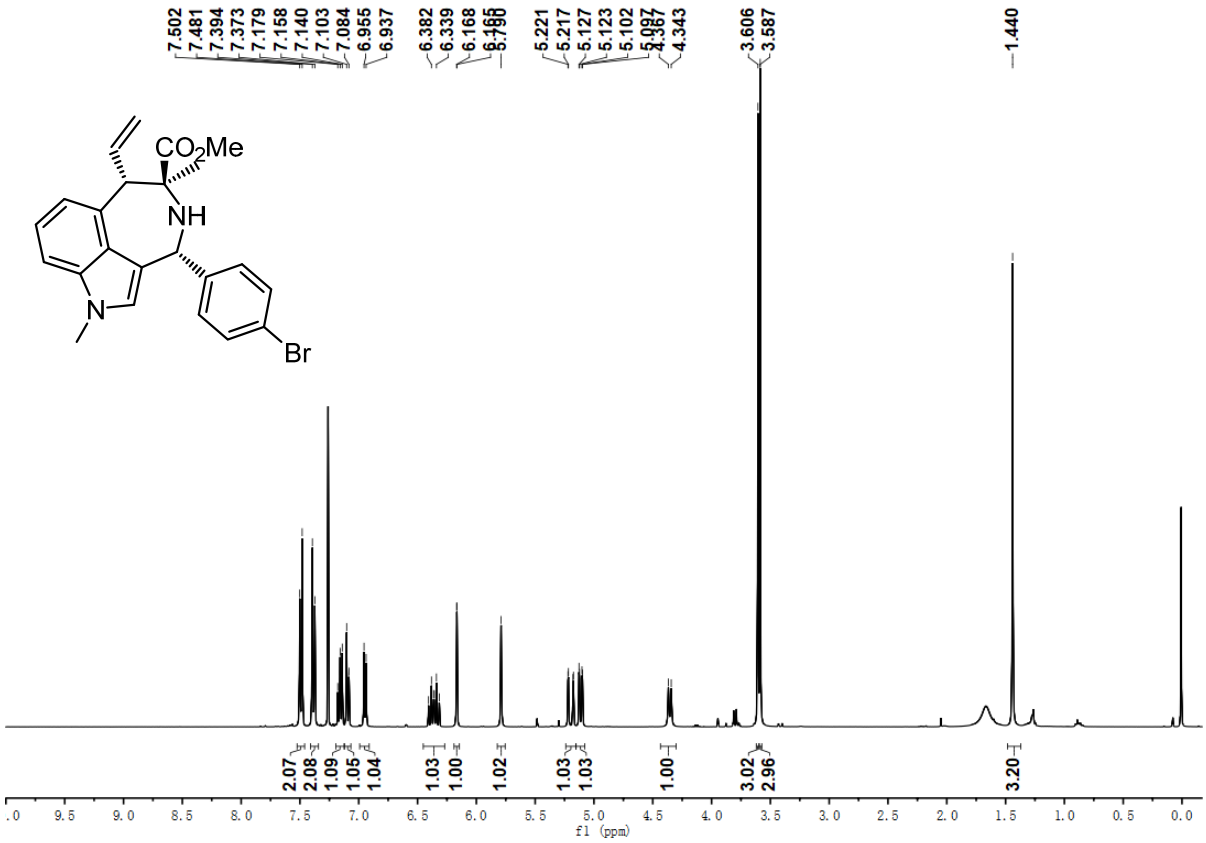
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*R*)-**3a** in $CDCl_3$



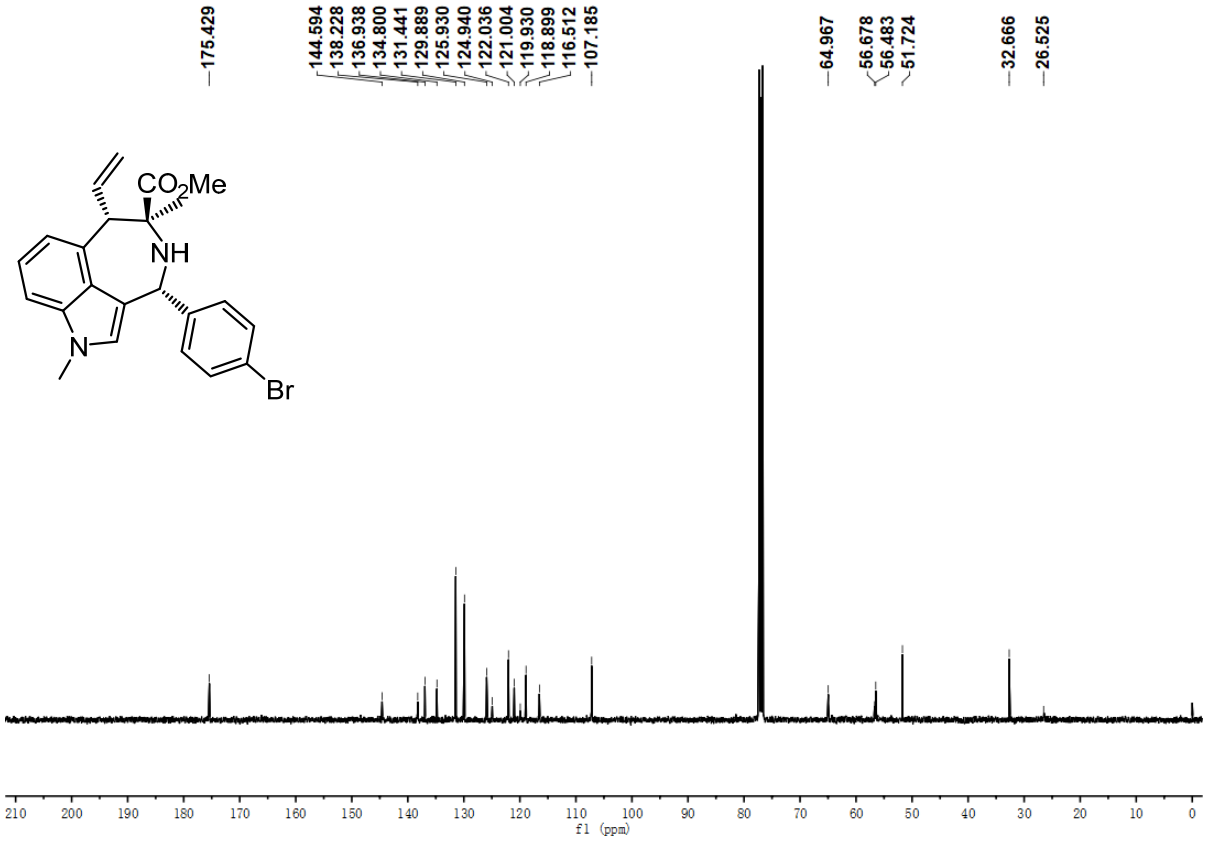
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*R*)-**3a** in $CDCl_3$



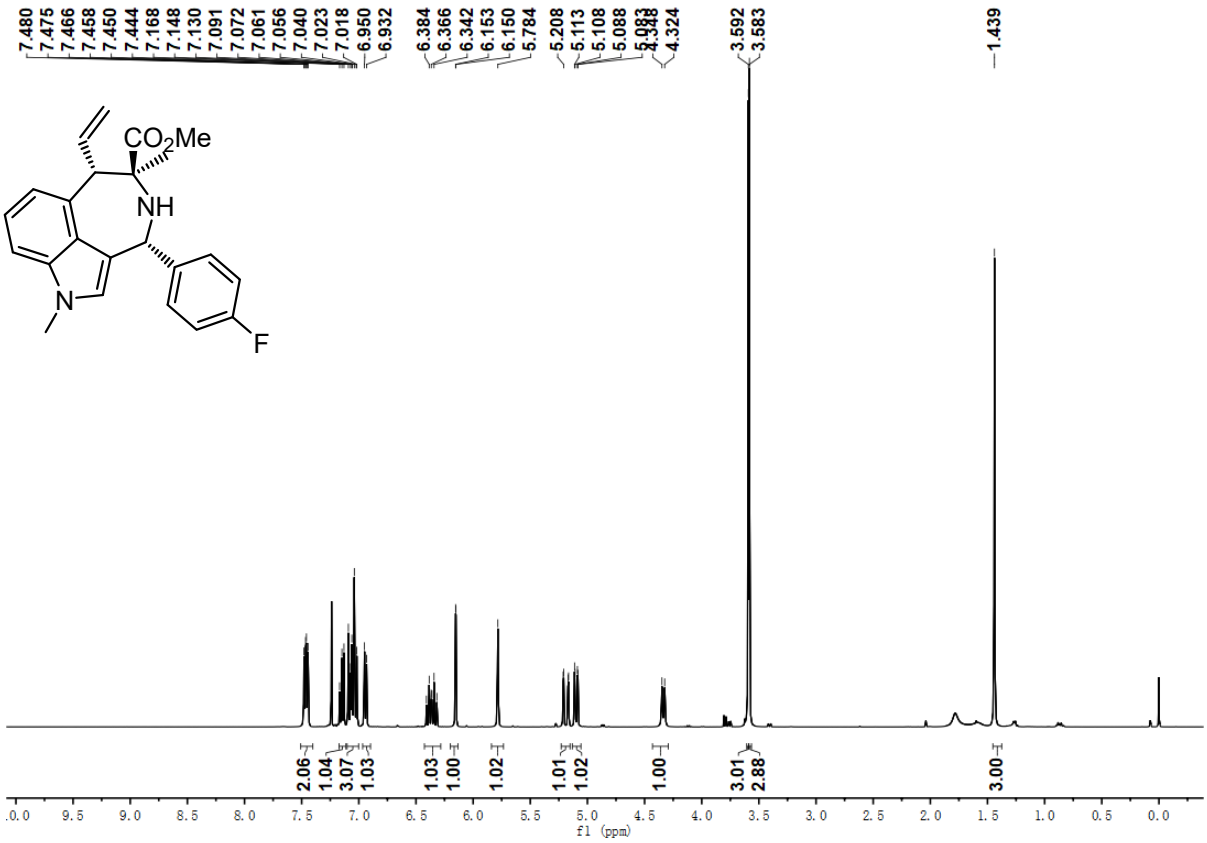
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3b** in $CDCl_3$



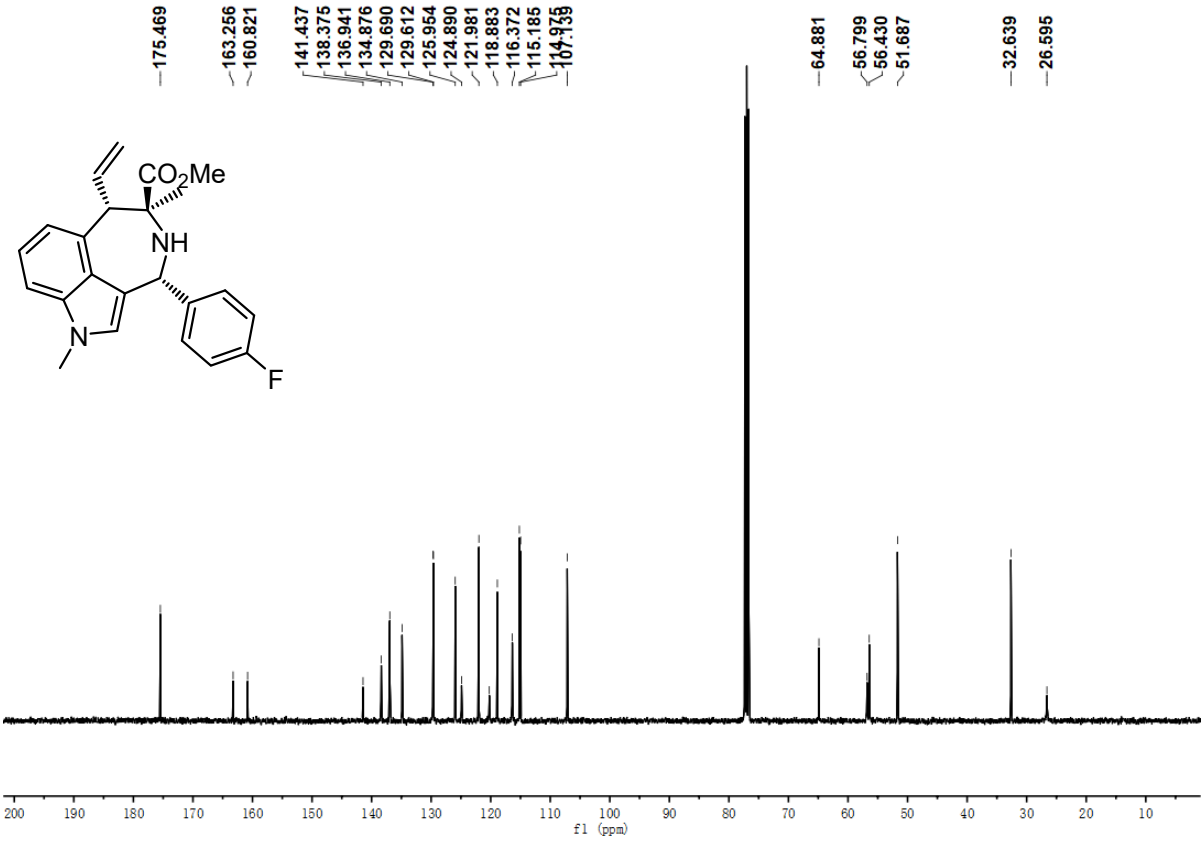
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3b** in $CDCl_3$



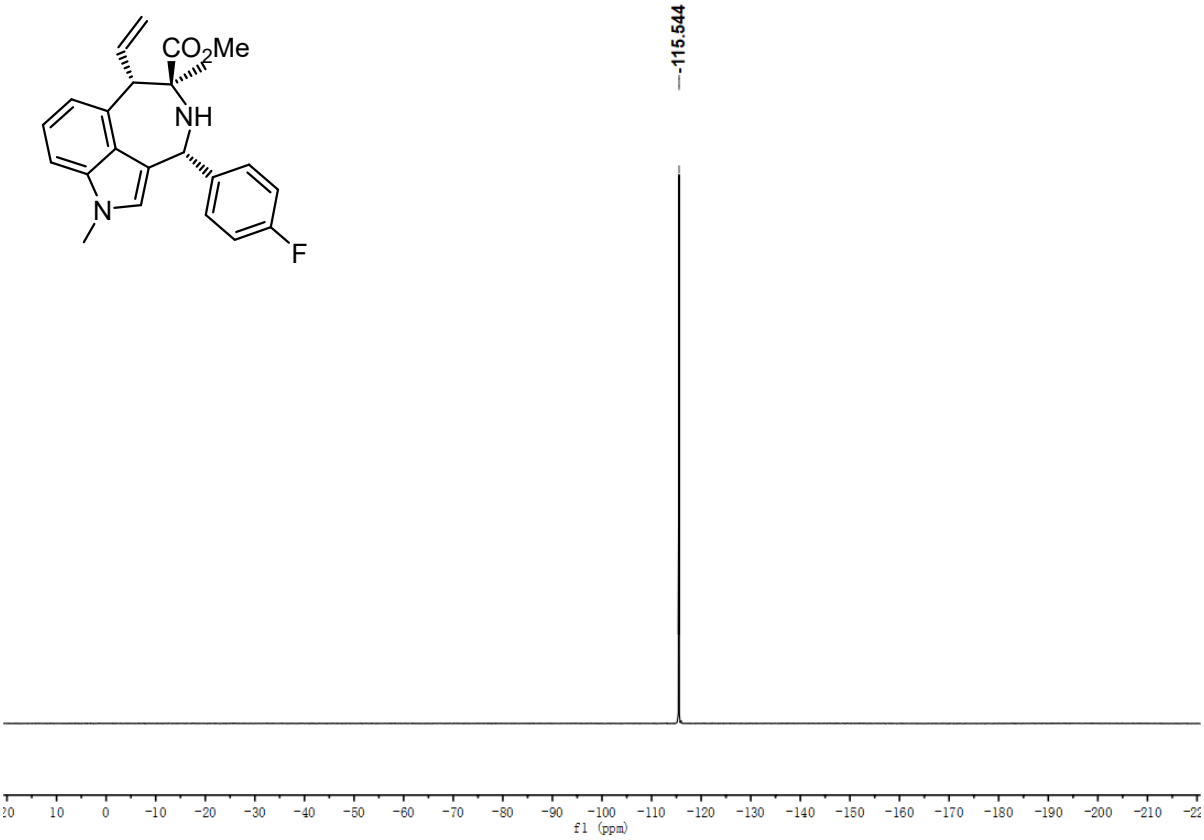
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3c** in $CDCl_3$



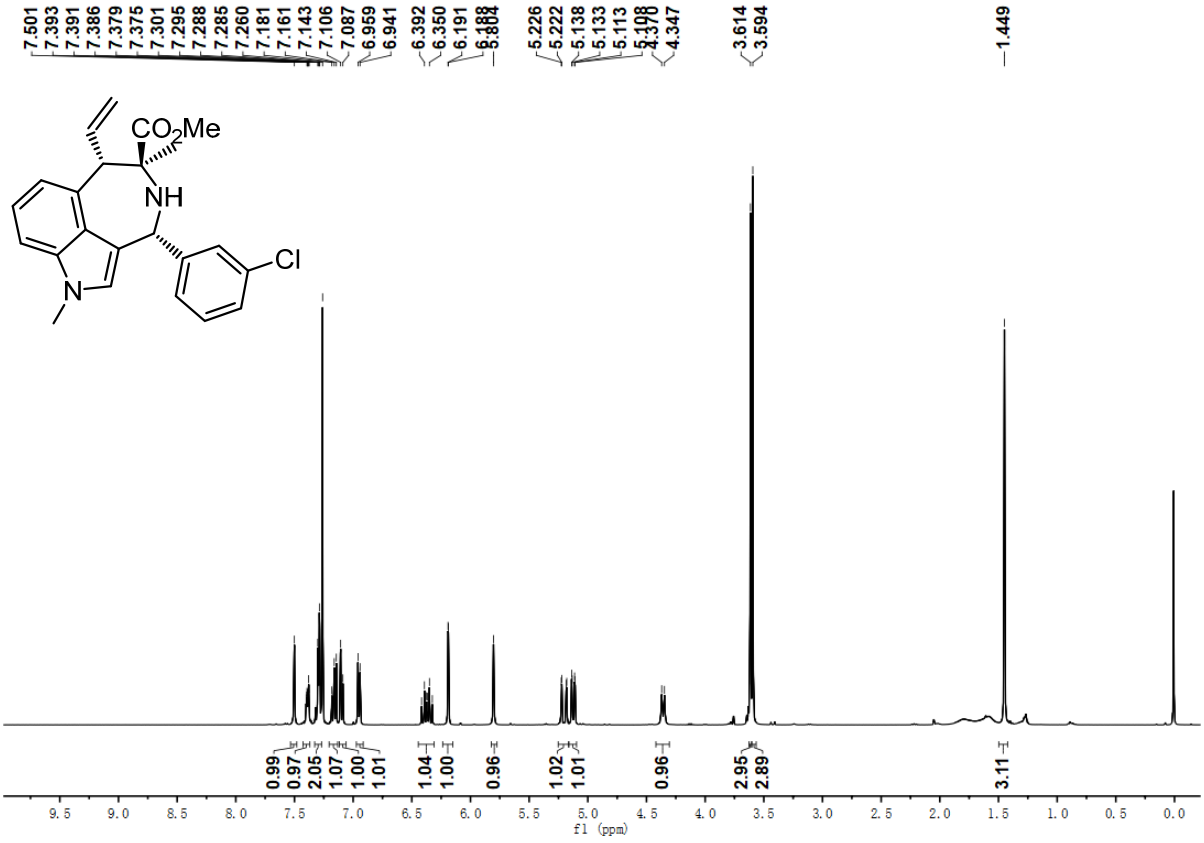
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3c** in $CDCl_3$



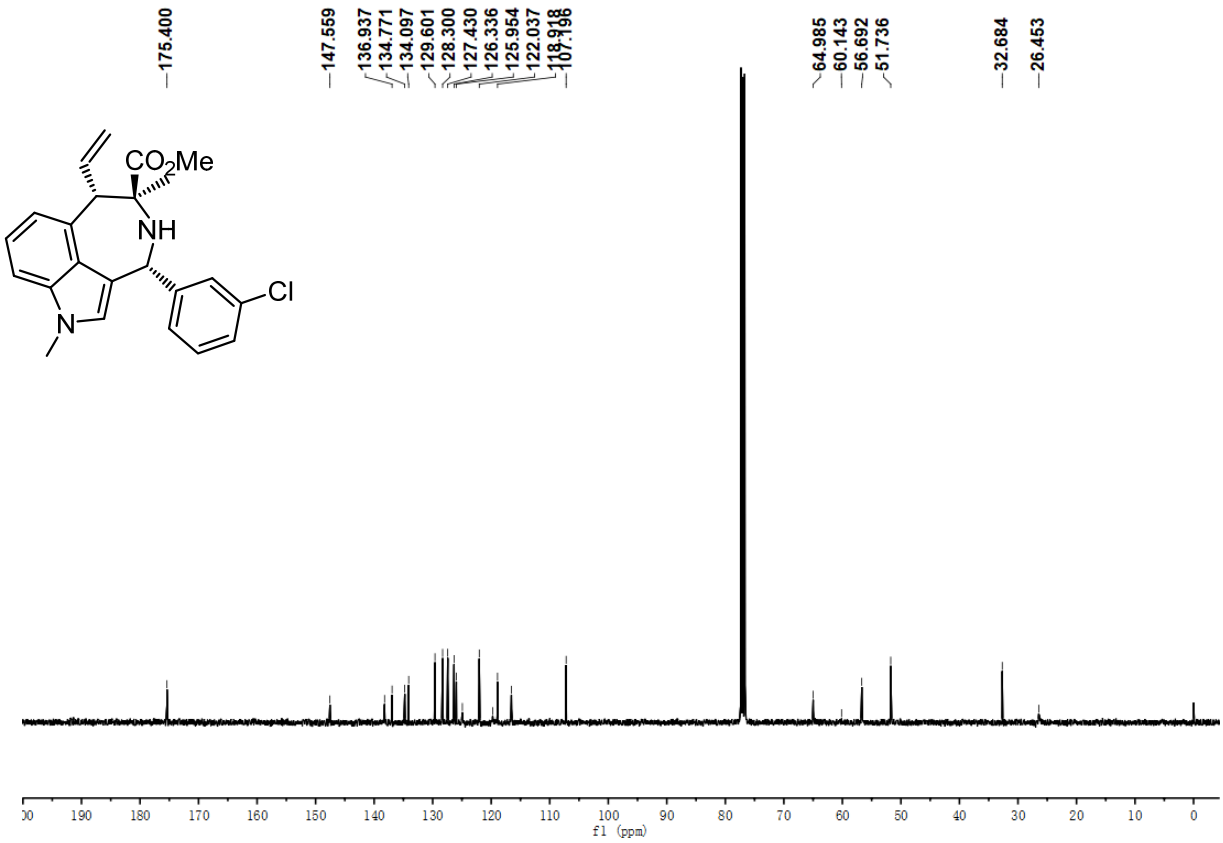
^{19}F NMR (376 MHz) of (6*S*,7*S*,9*R*)-**3c** in $CDCl_3$



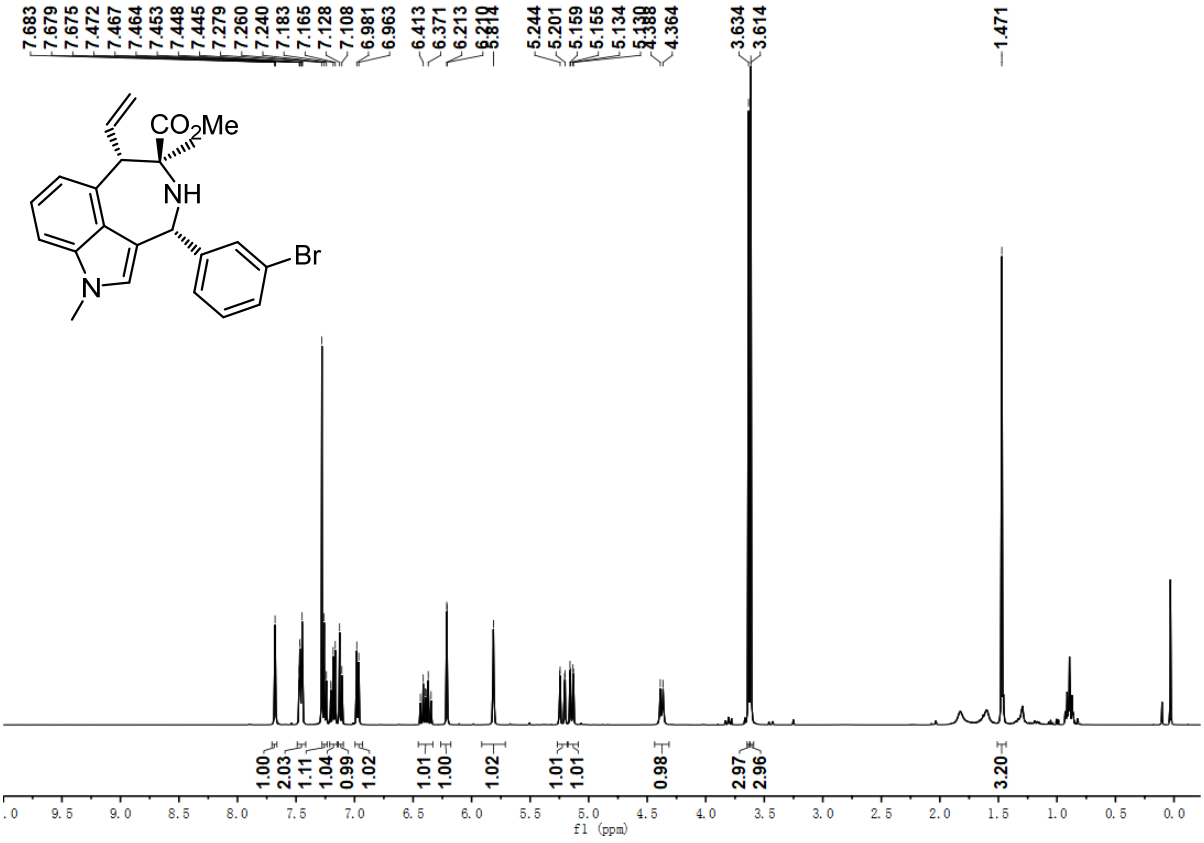
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3d** in $CDCl_3$



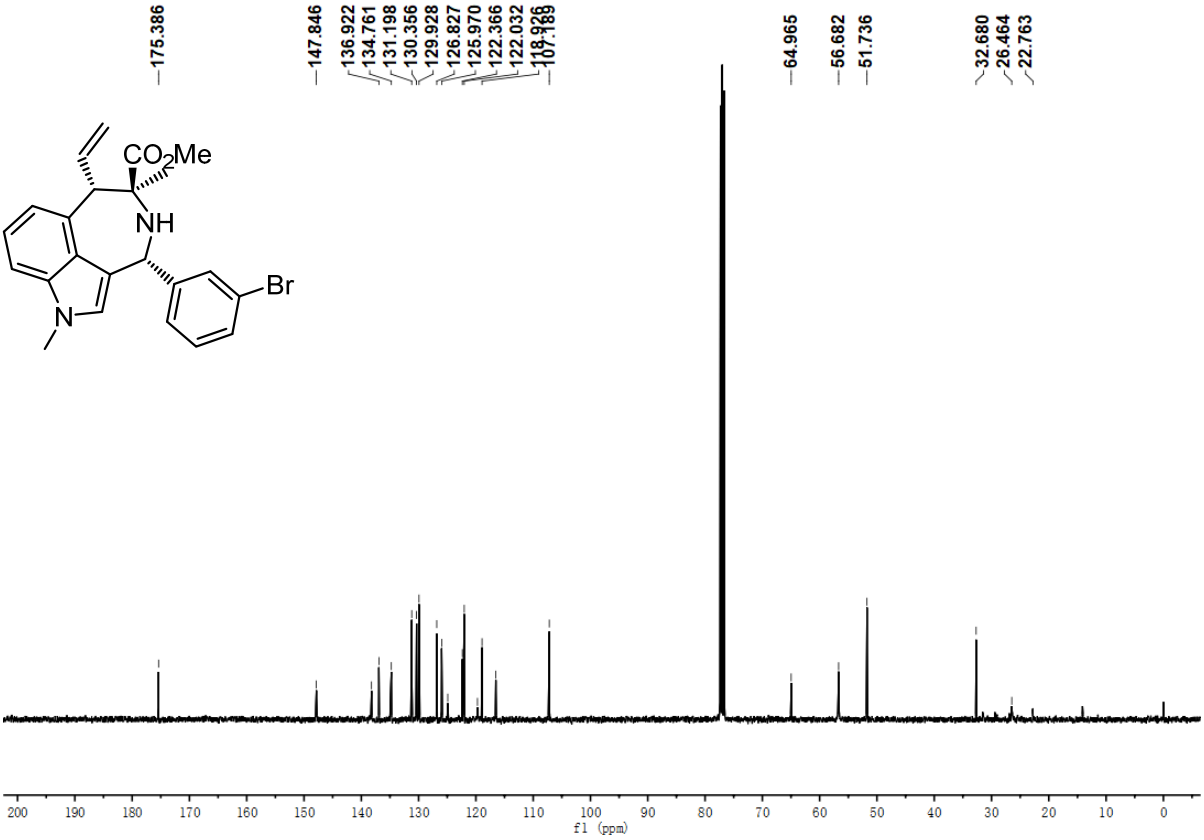
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3d** in $CDCl_3$



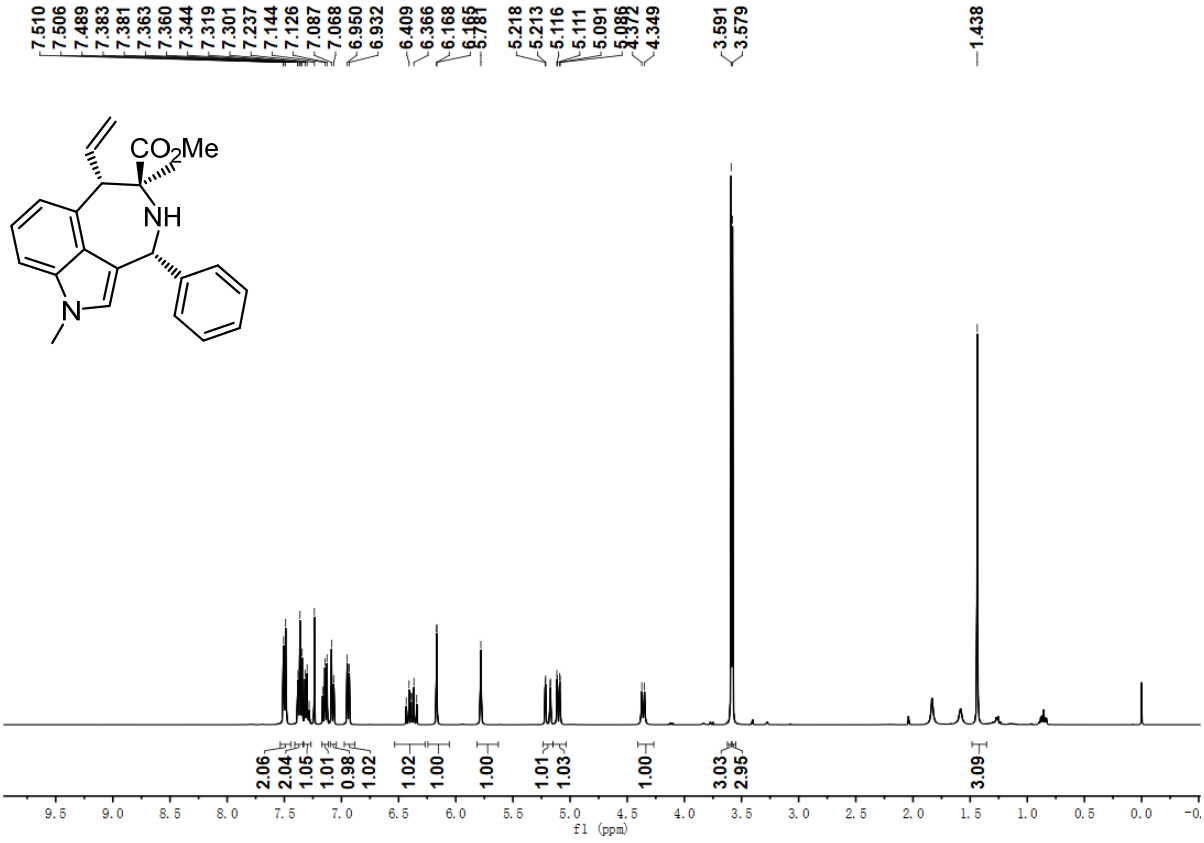
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3e** in $CDCl_3$



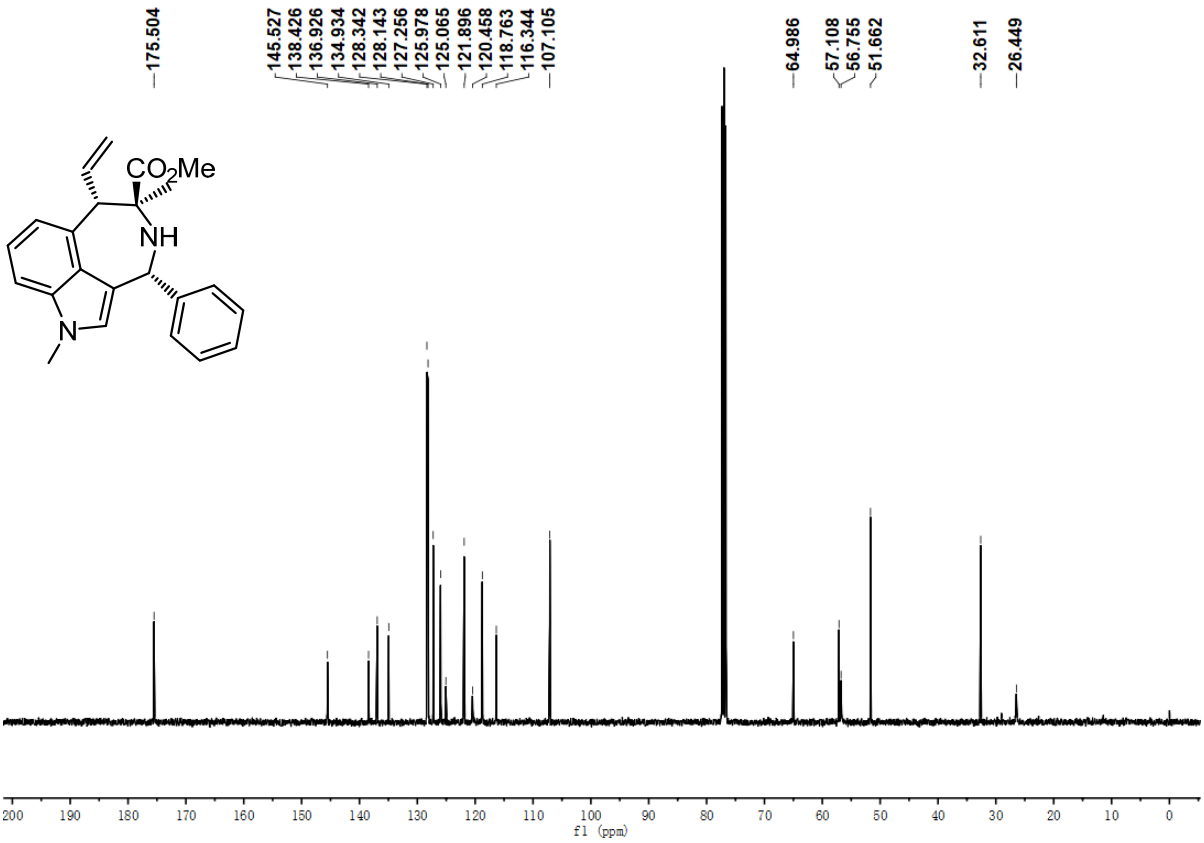
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3e** in $CDCl_3$



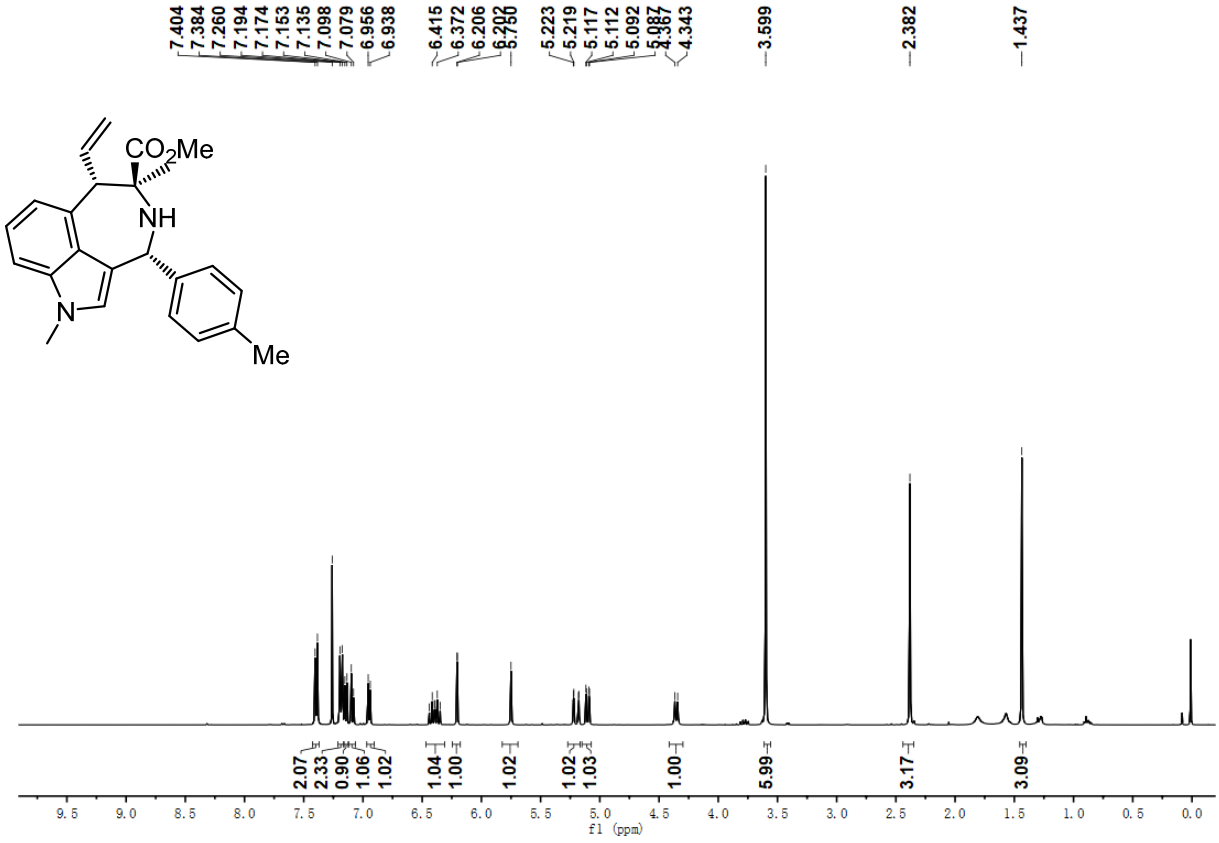
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3f** in $CDCl_3$



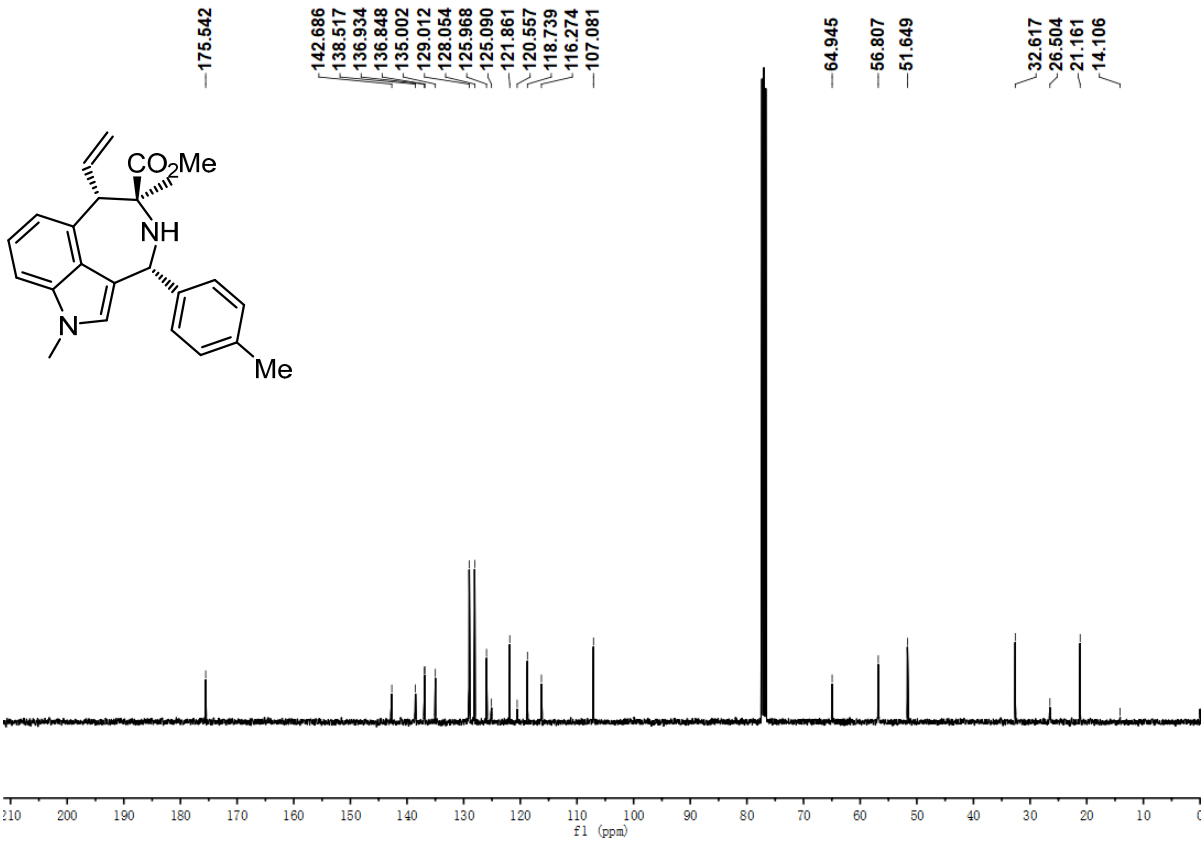
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3f** in $CDCl_3$



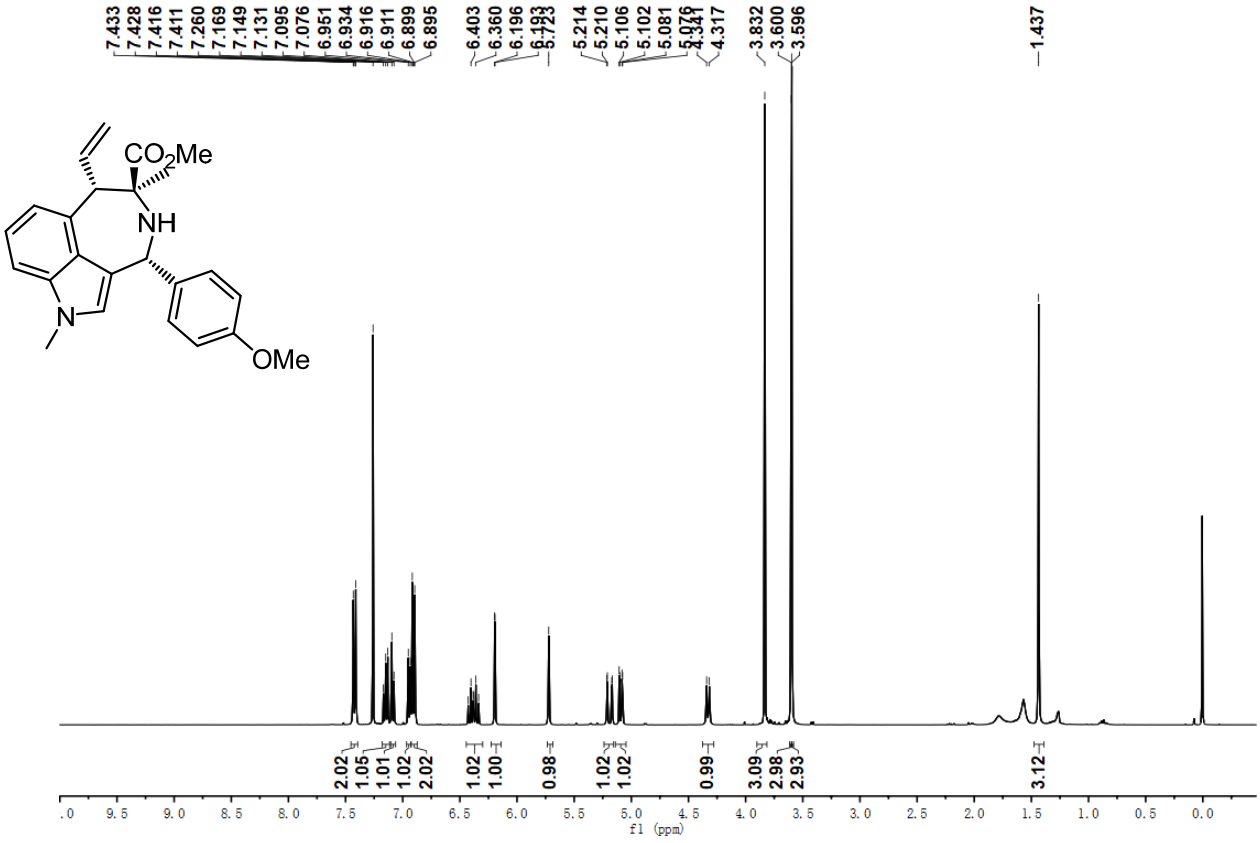
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3g** in $CDCl_3$



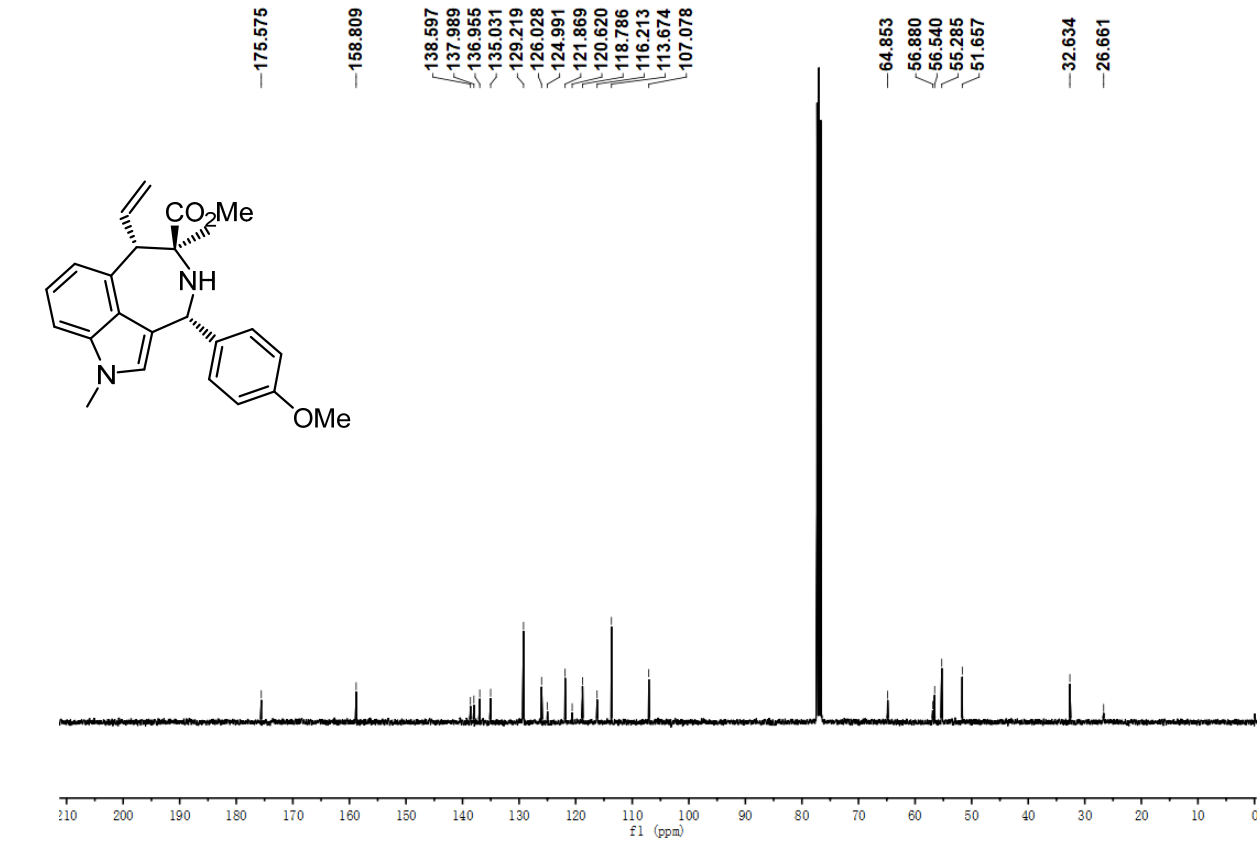
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3g** in $CDCl_3$



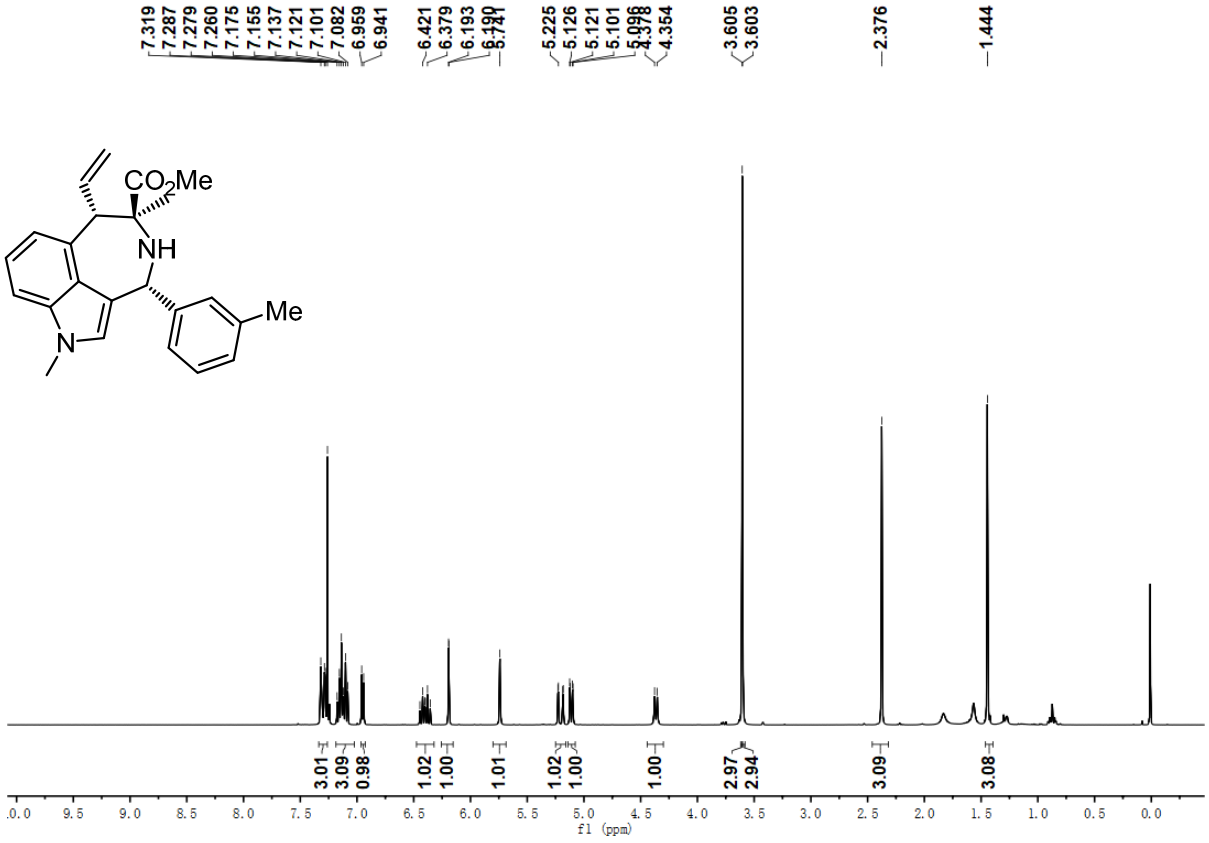
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3h** in $CDCl_3$



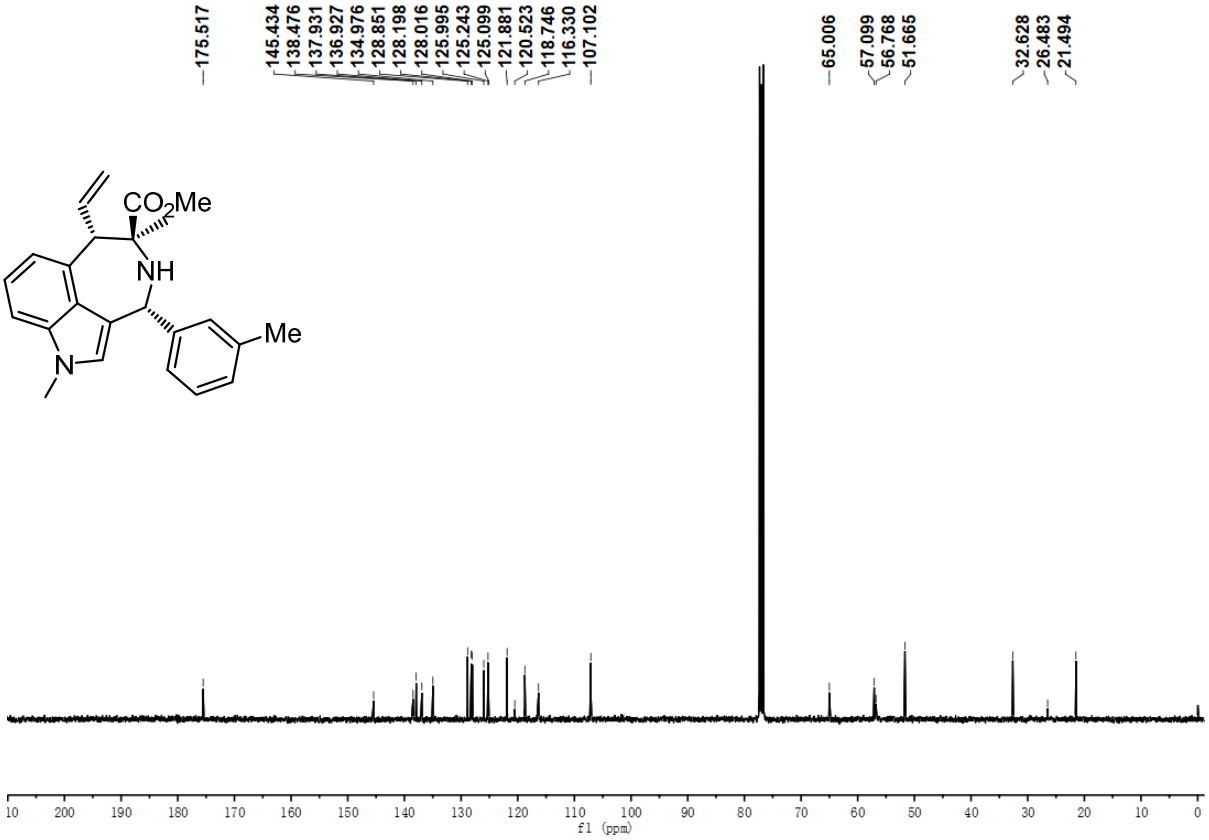
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3h** in $CDCl_3$



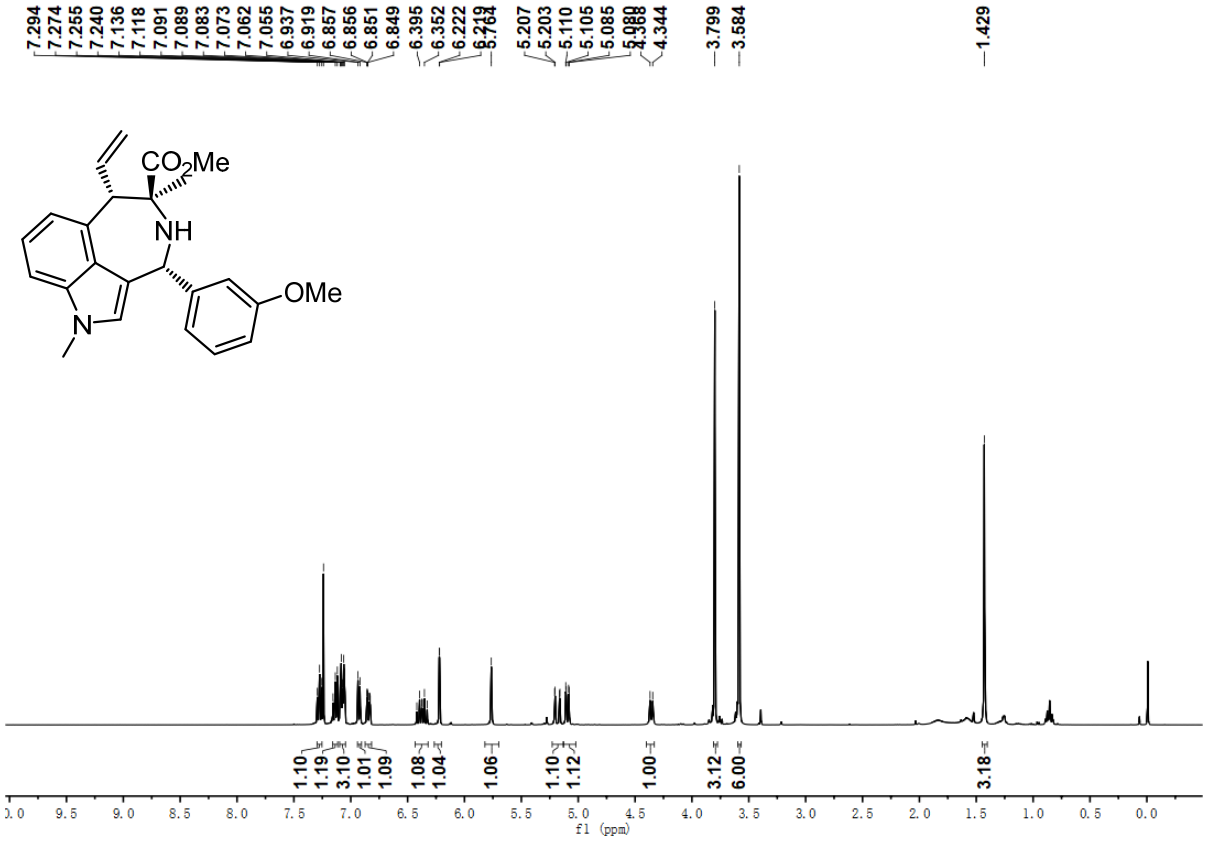
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3i** in $CDCl_3$



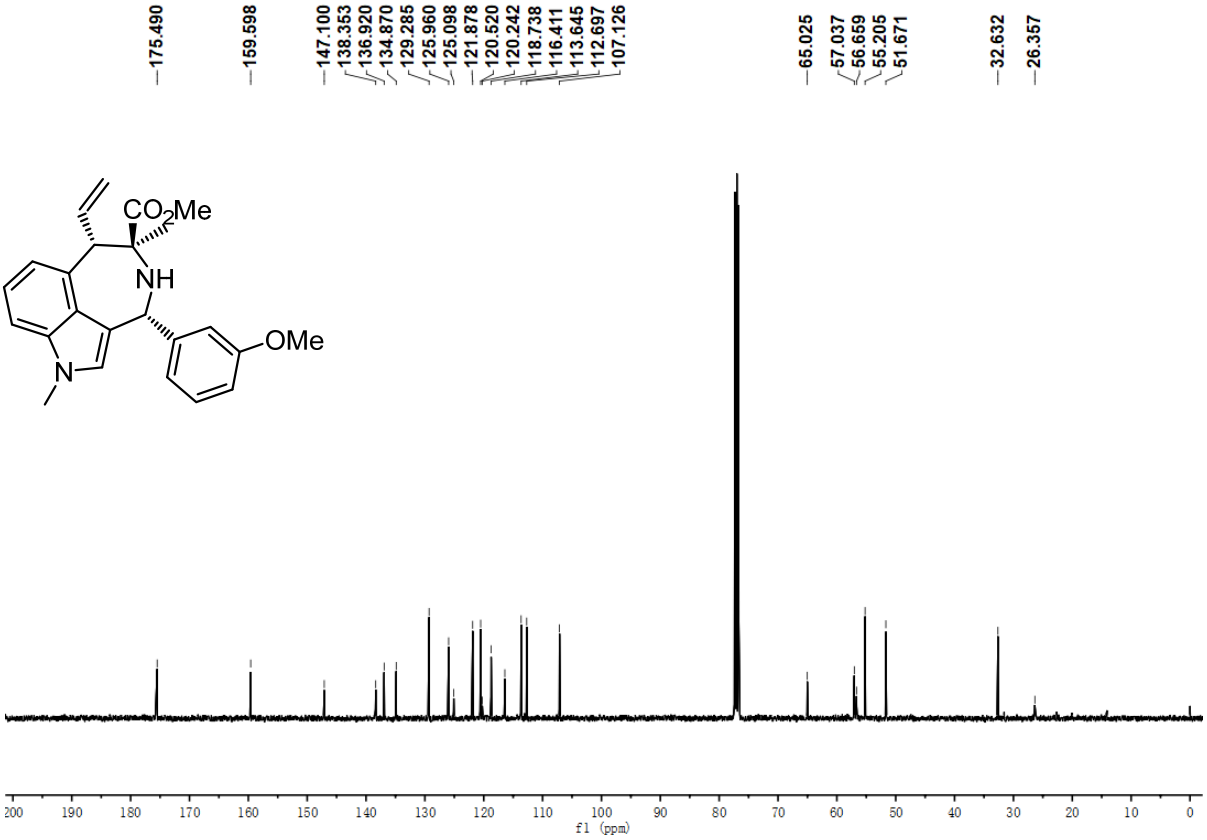
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3i** in $CDCl_3$



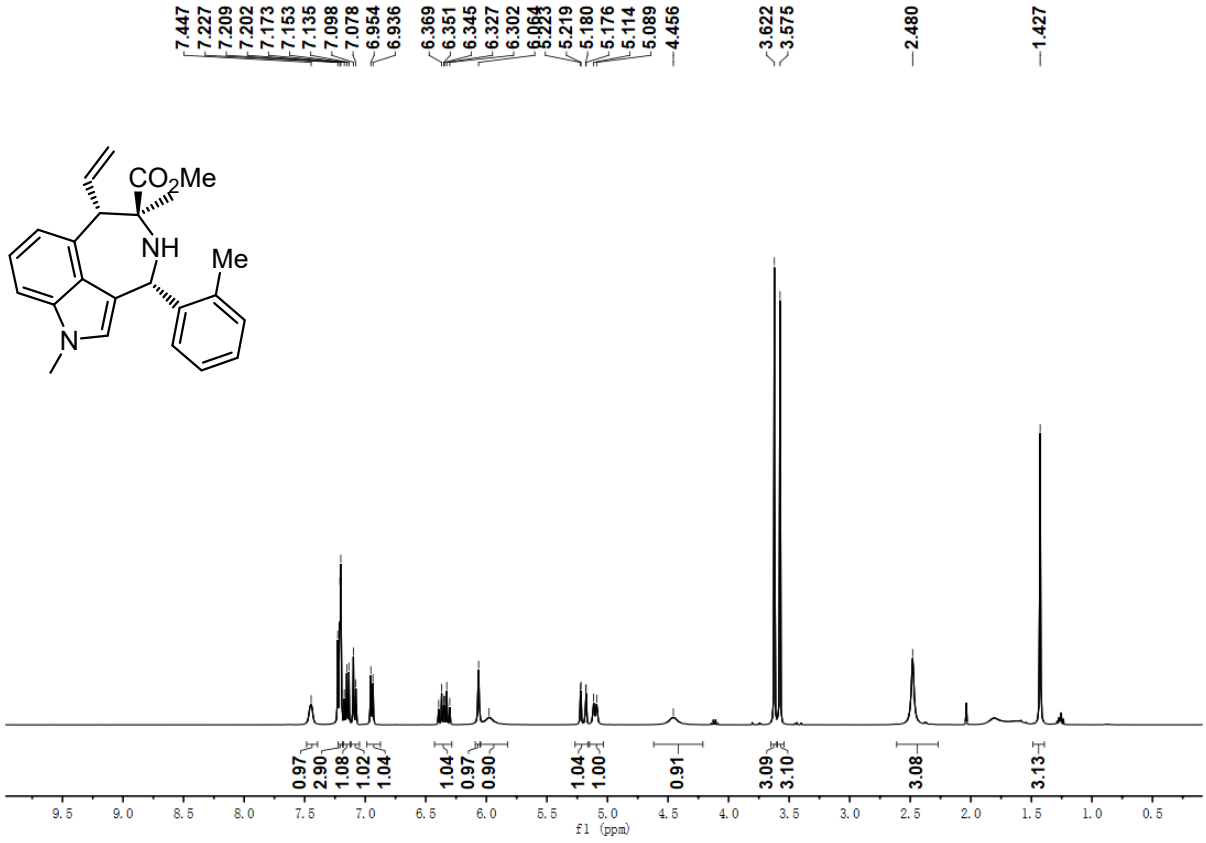
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3j** in $CDCl_3$



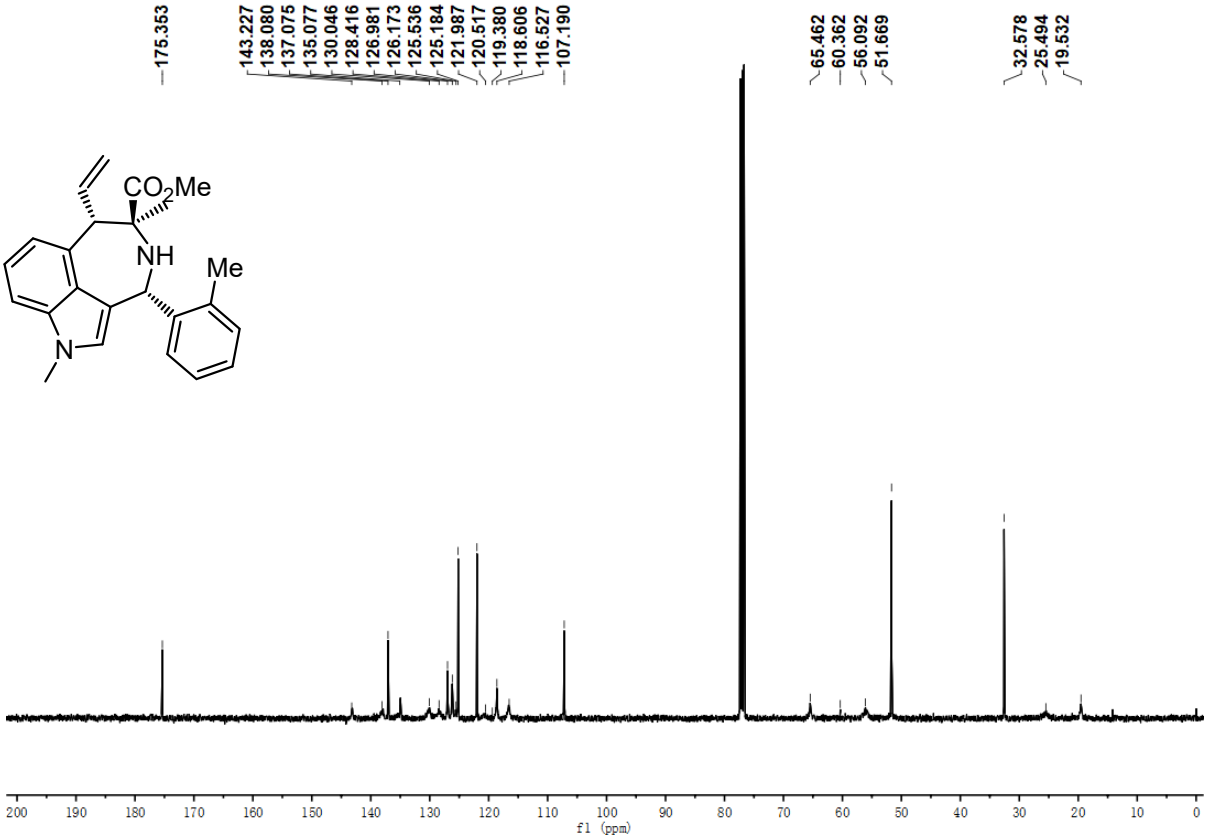
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3j** in $CDCl_3$



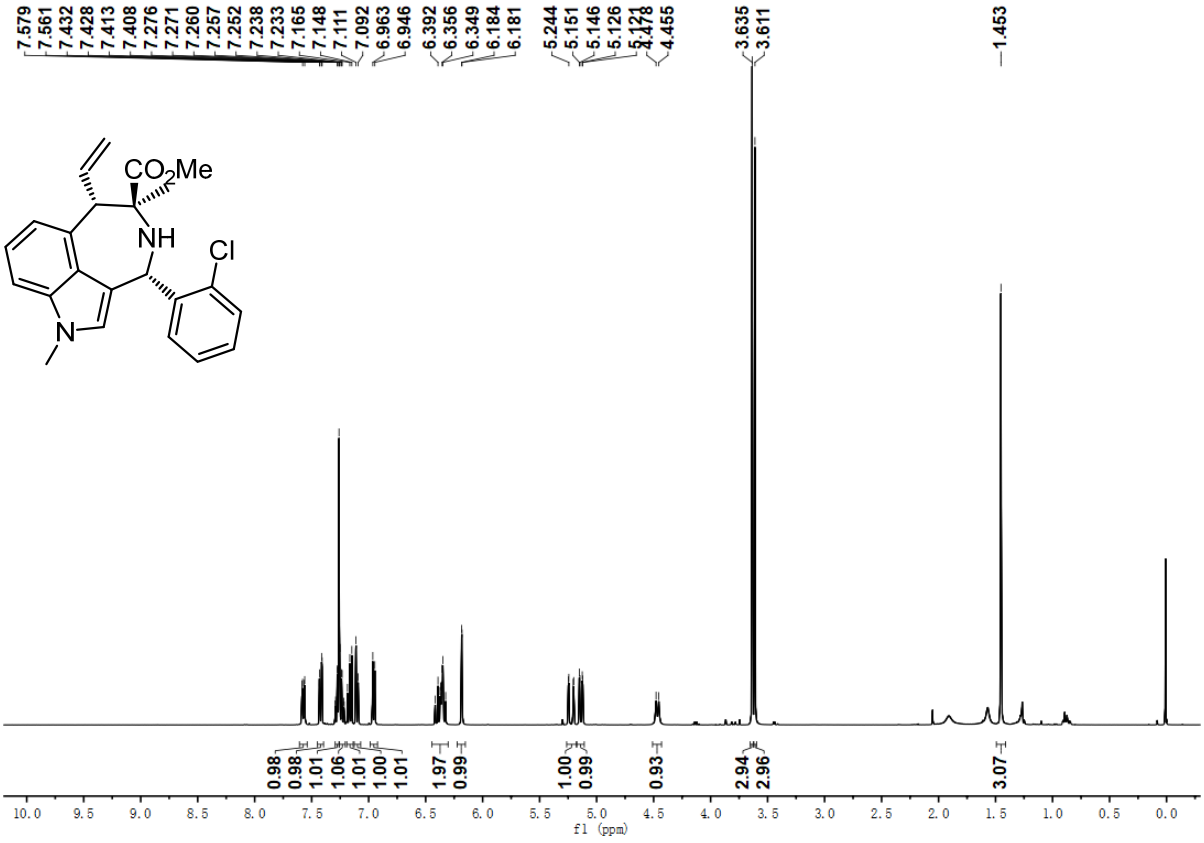
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3k** in $CDCl_3$



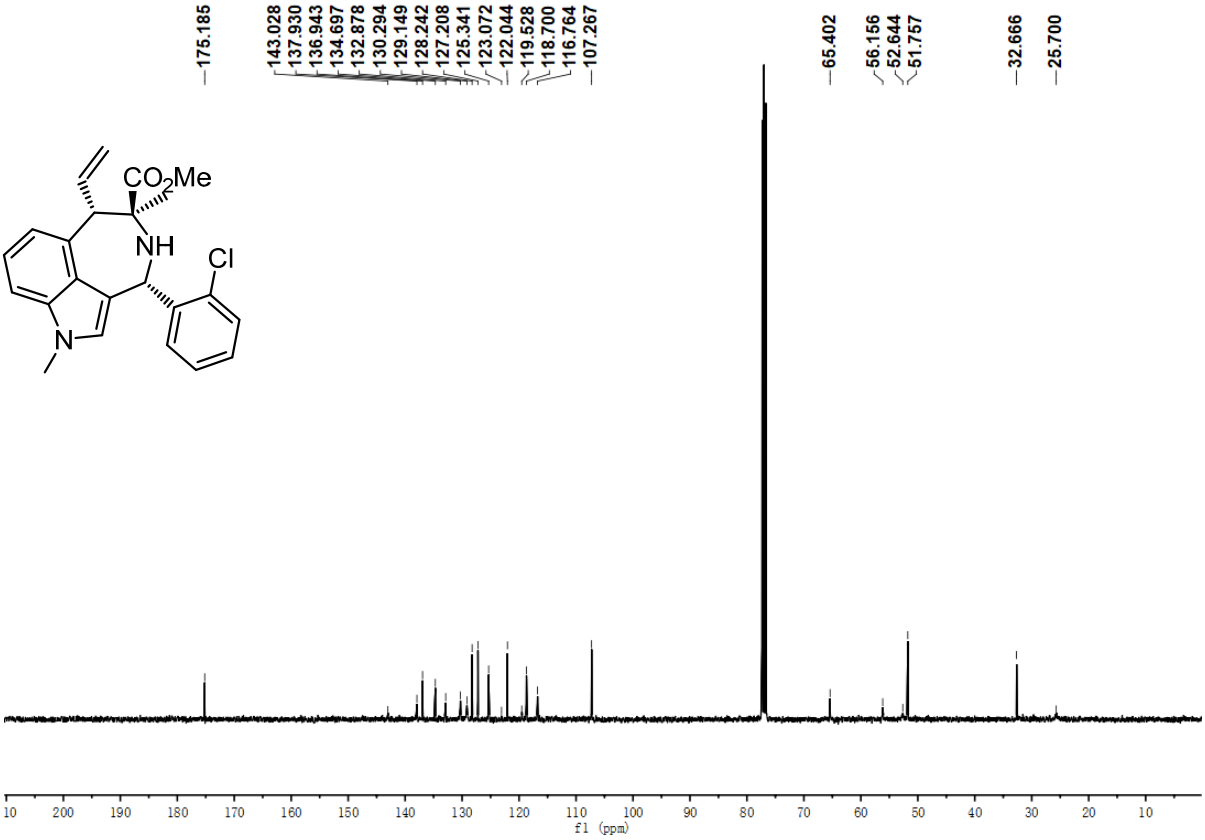
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3k** in $CDCl_3$



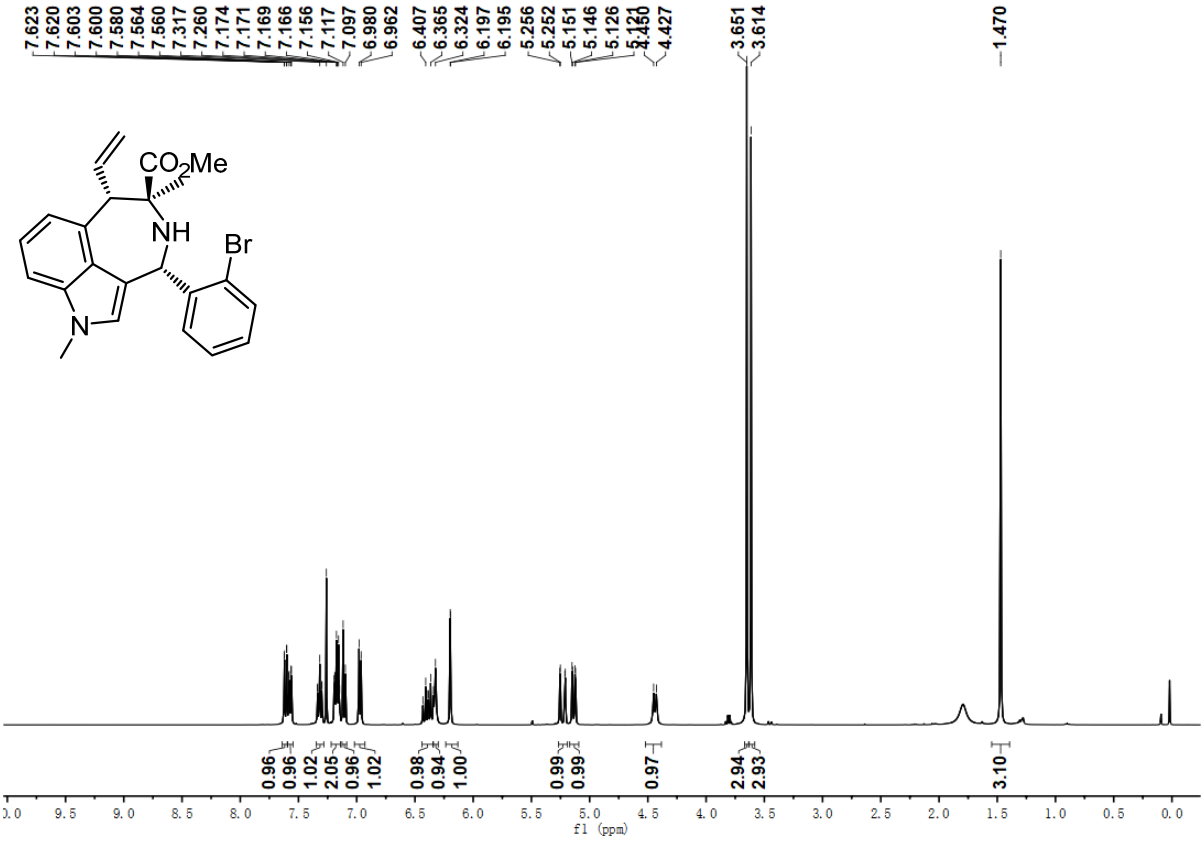
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3l** in $CDCl_3$



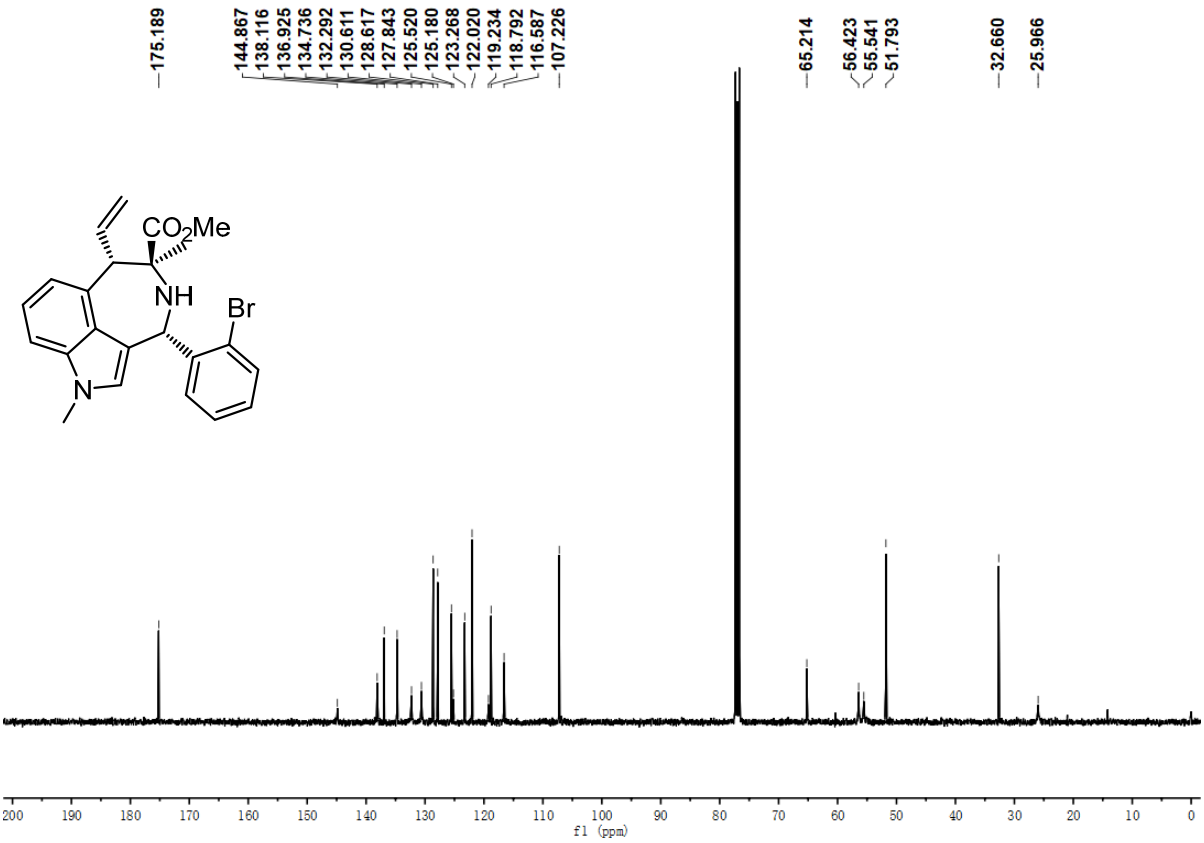
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3l** in $CDCl_3$



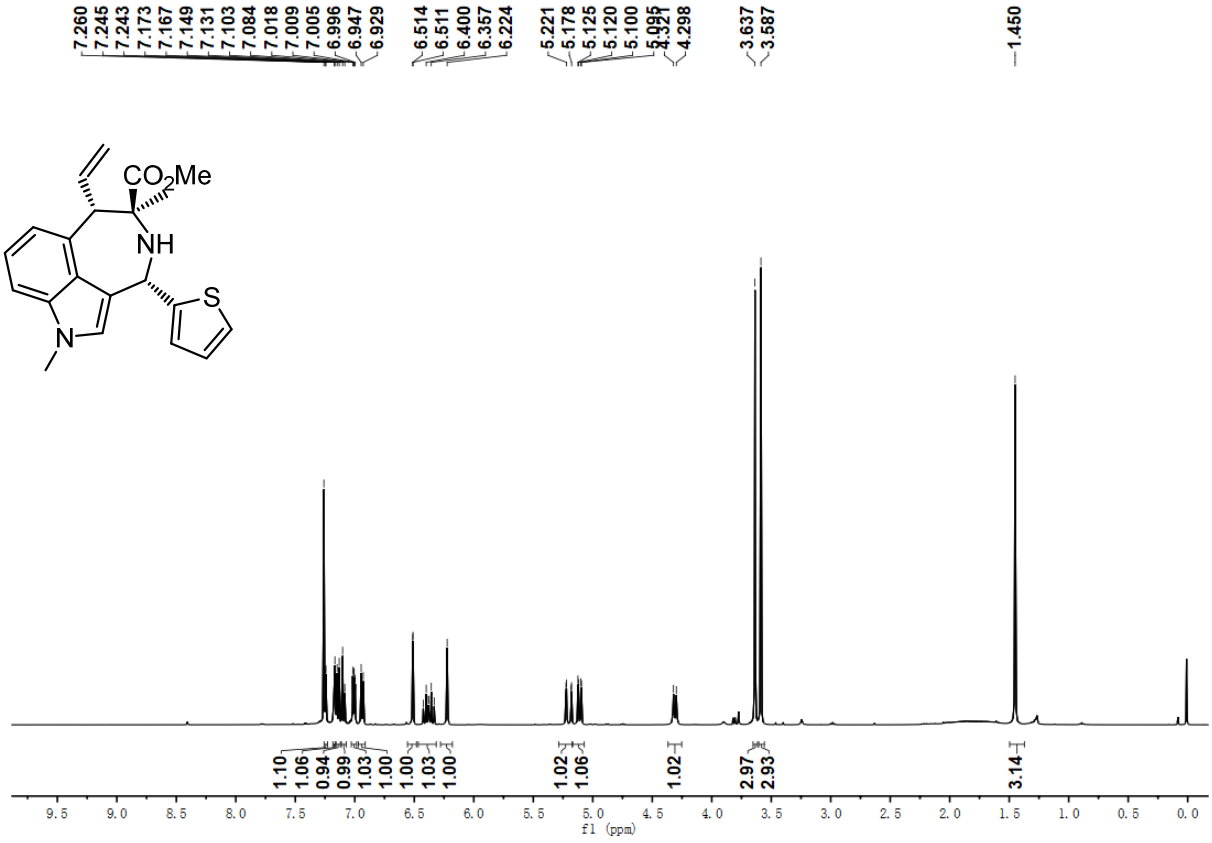
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3m** in $CDCl_3$



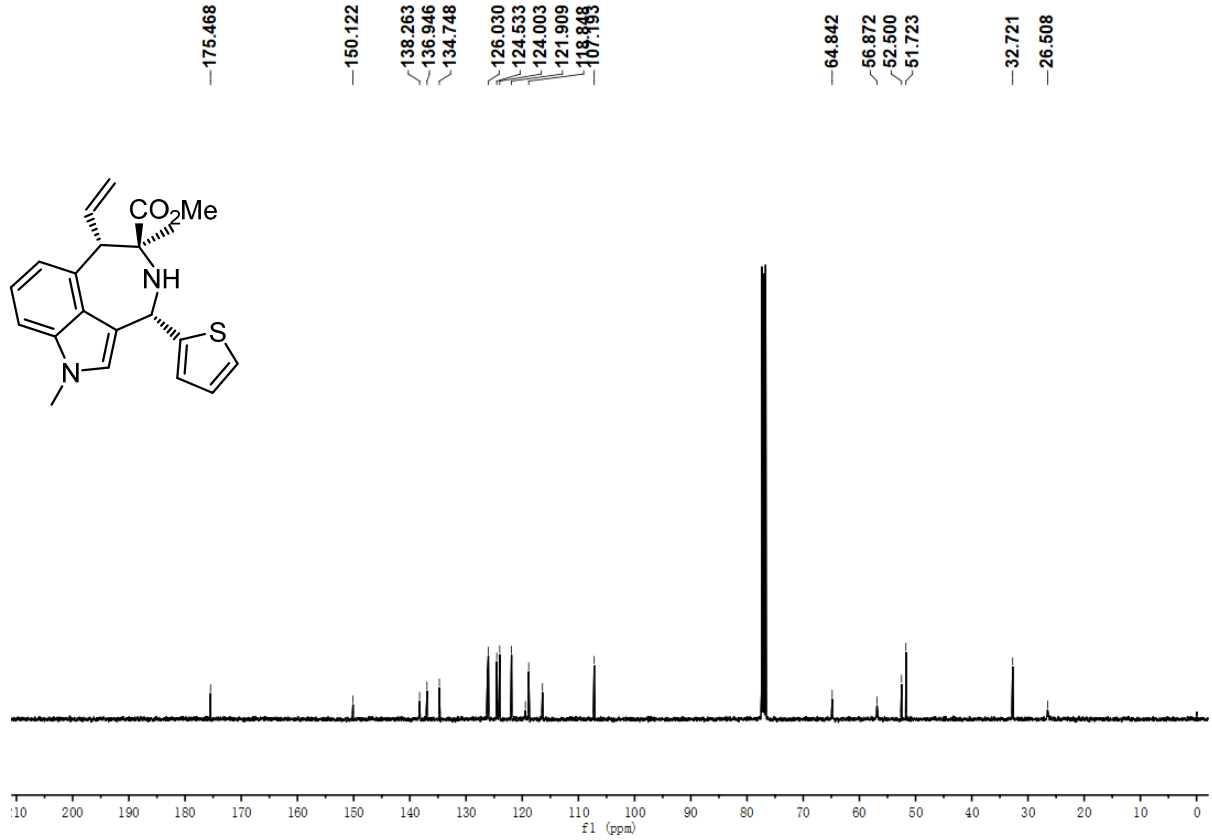
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3m** in $CDCl_3$



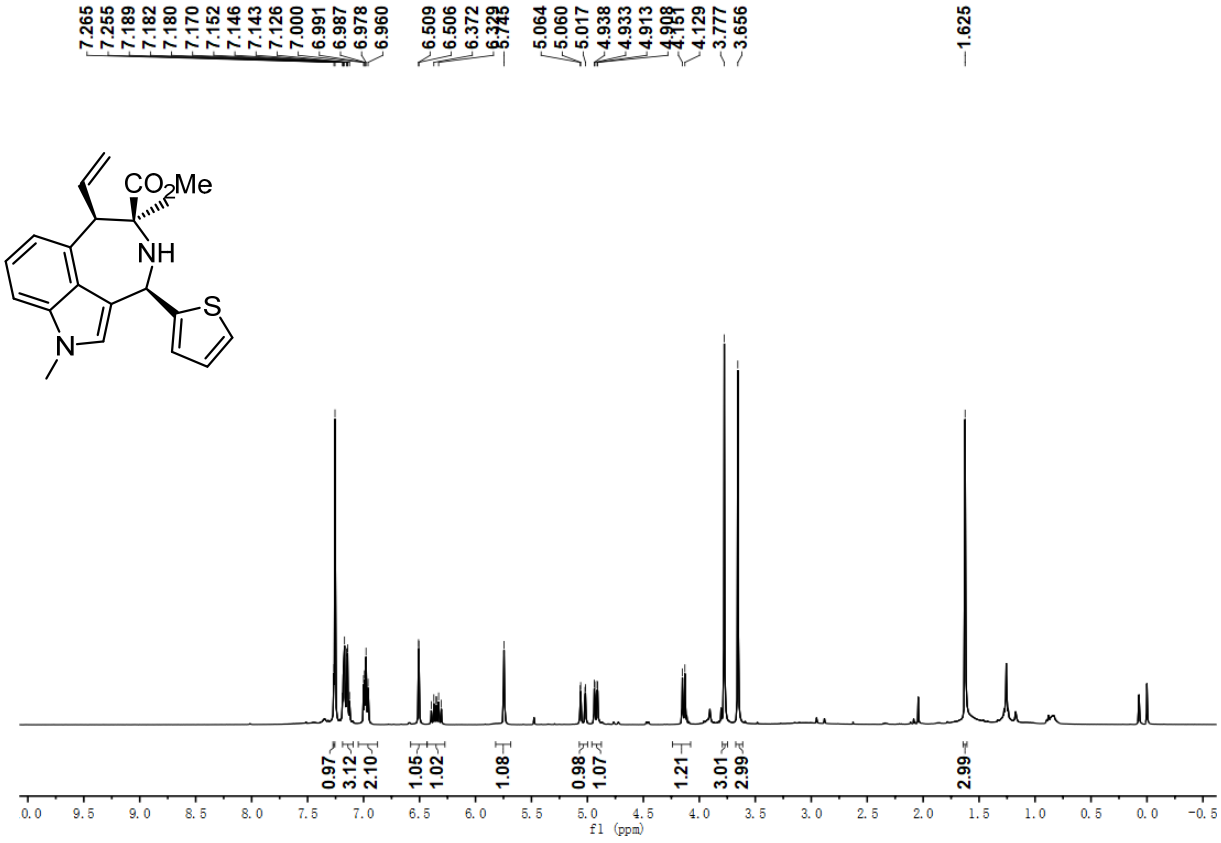
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3n** in $CDCl_3$



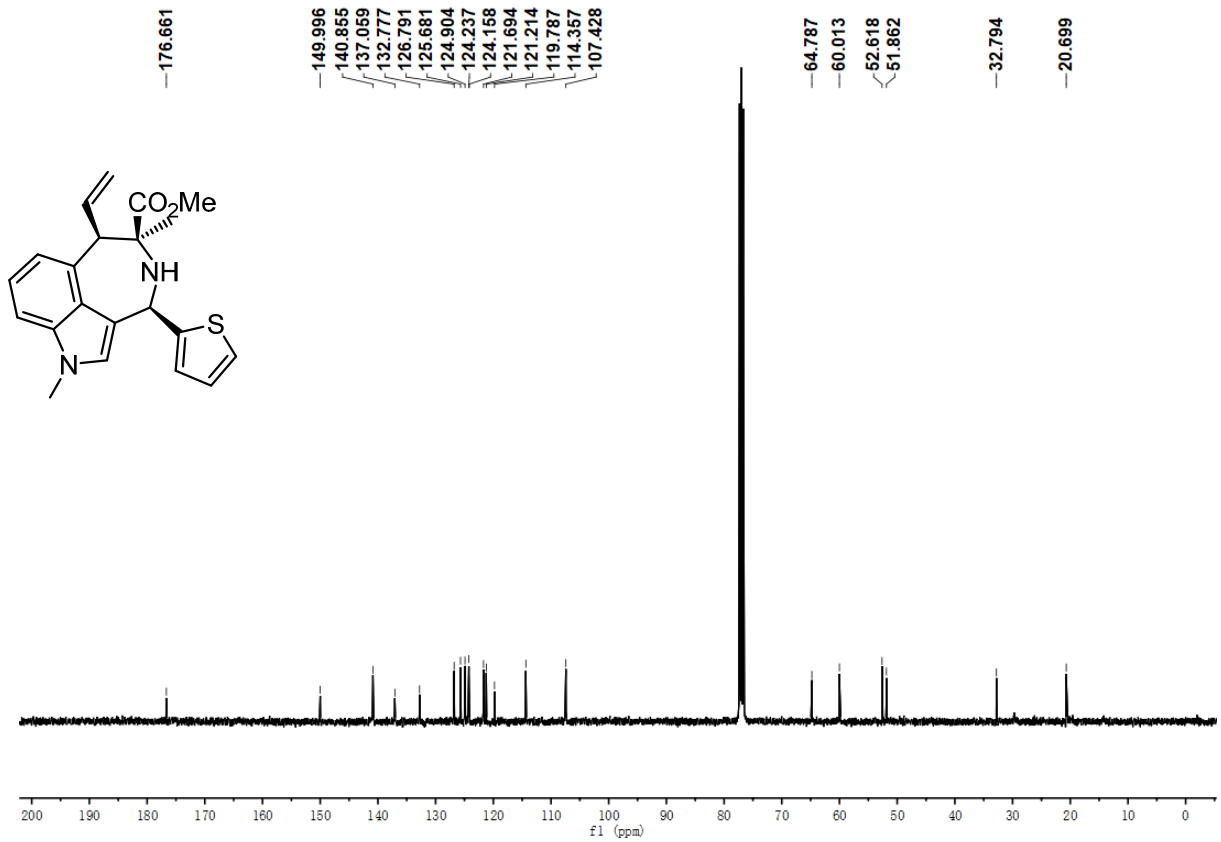
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3n** in $CDCl_3$



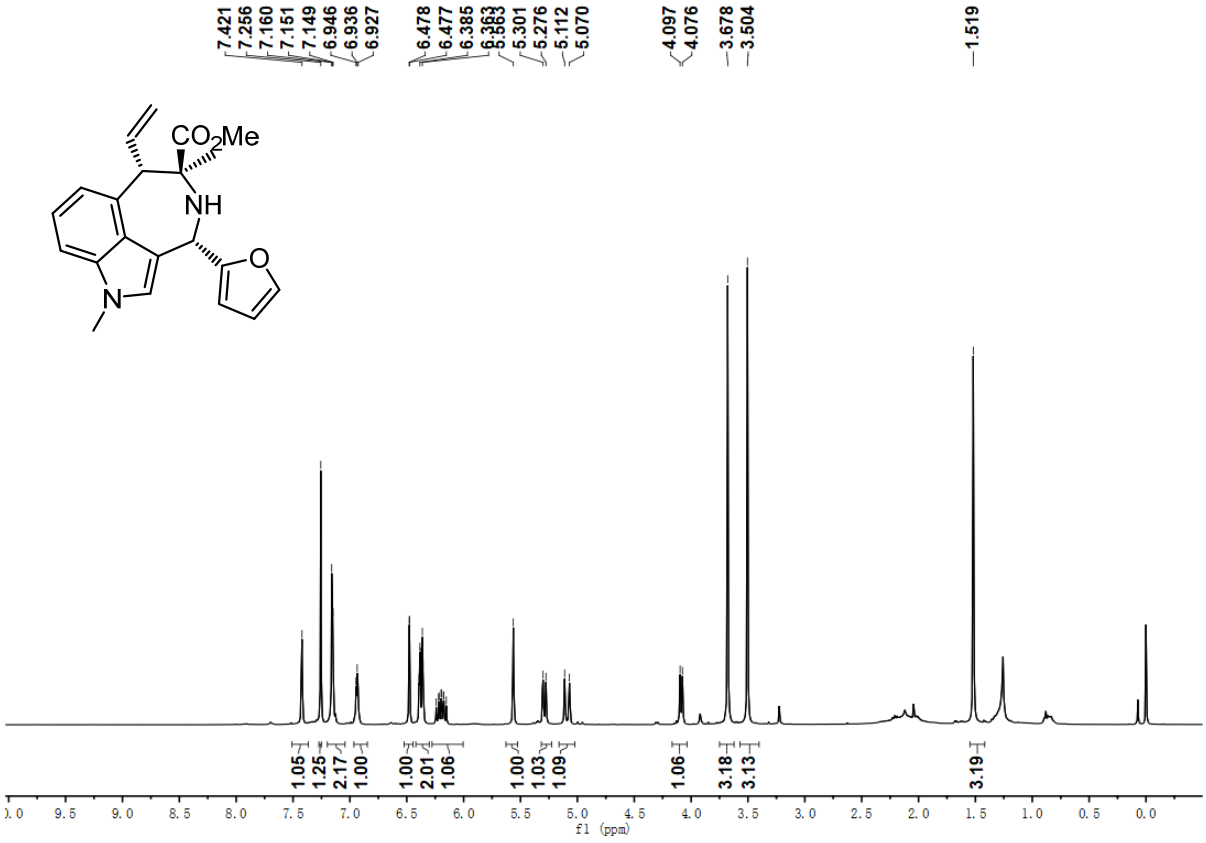
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*R*)-**3n** in $CDCl_3$



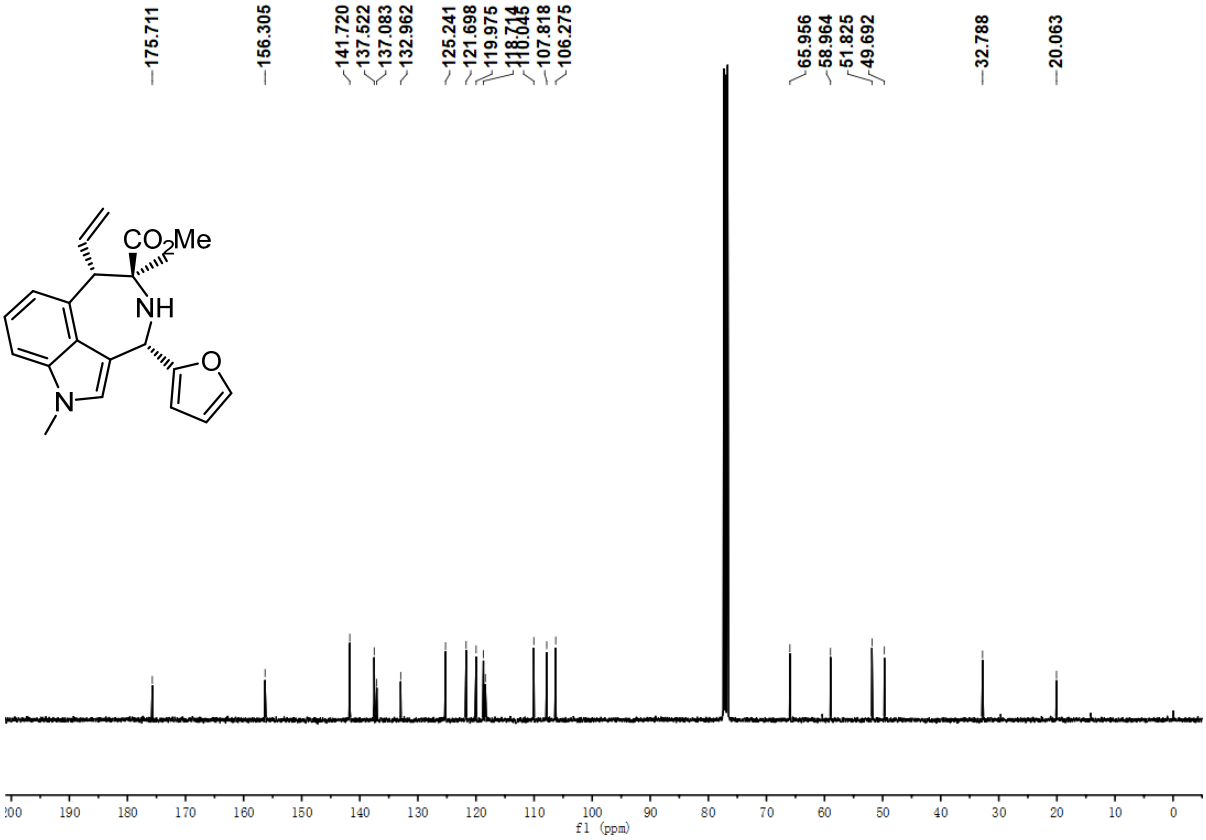
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*R*)-**3n** in $CDCl_3$



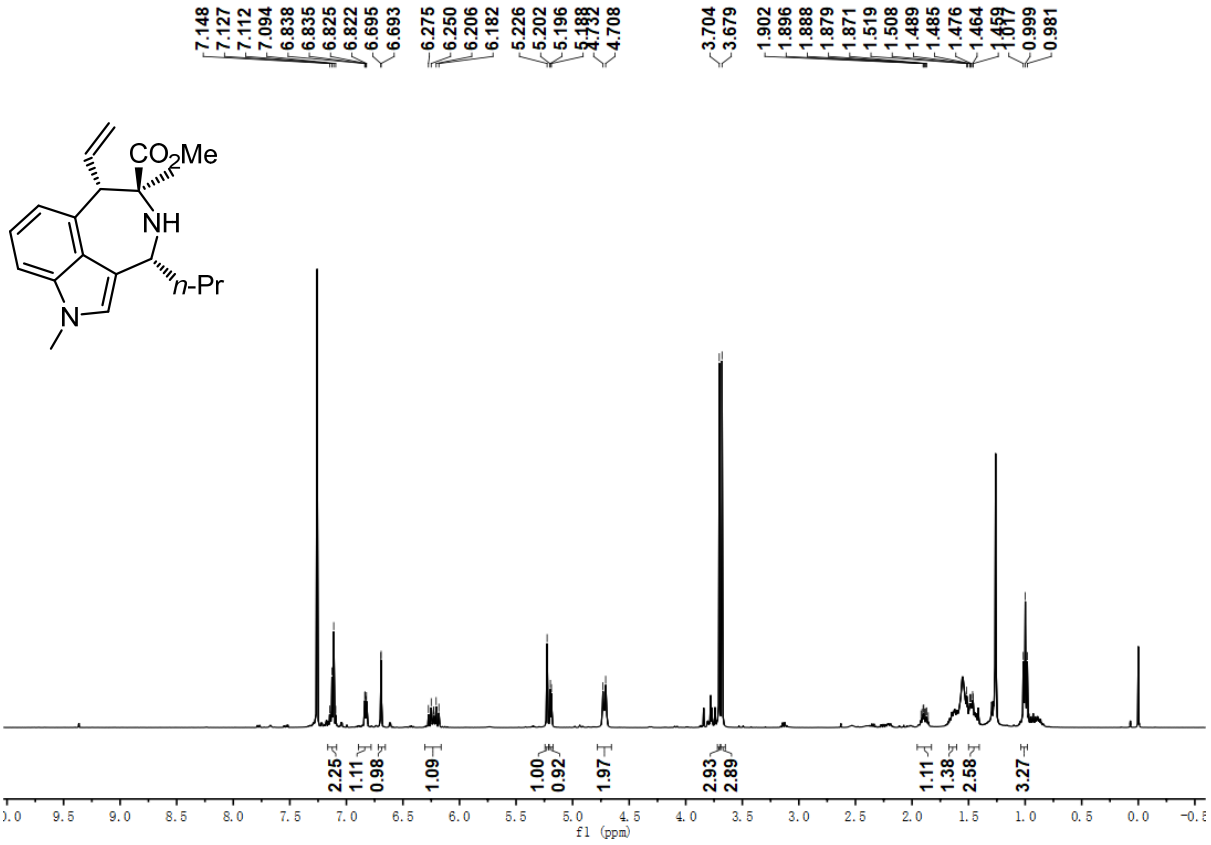
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3o** in $CDCl_3$



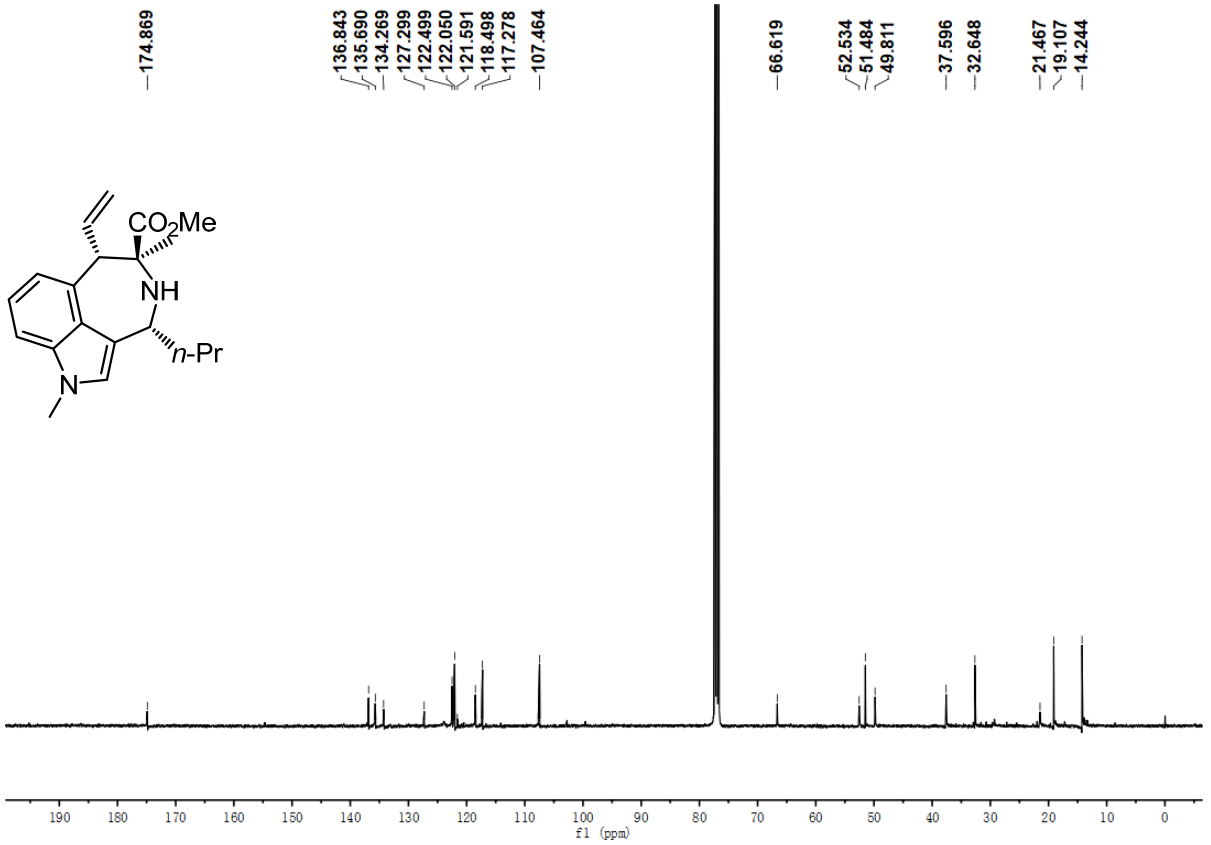
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3o** in $CDCl_3$



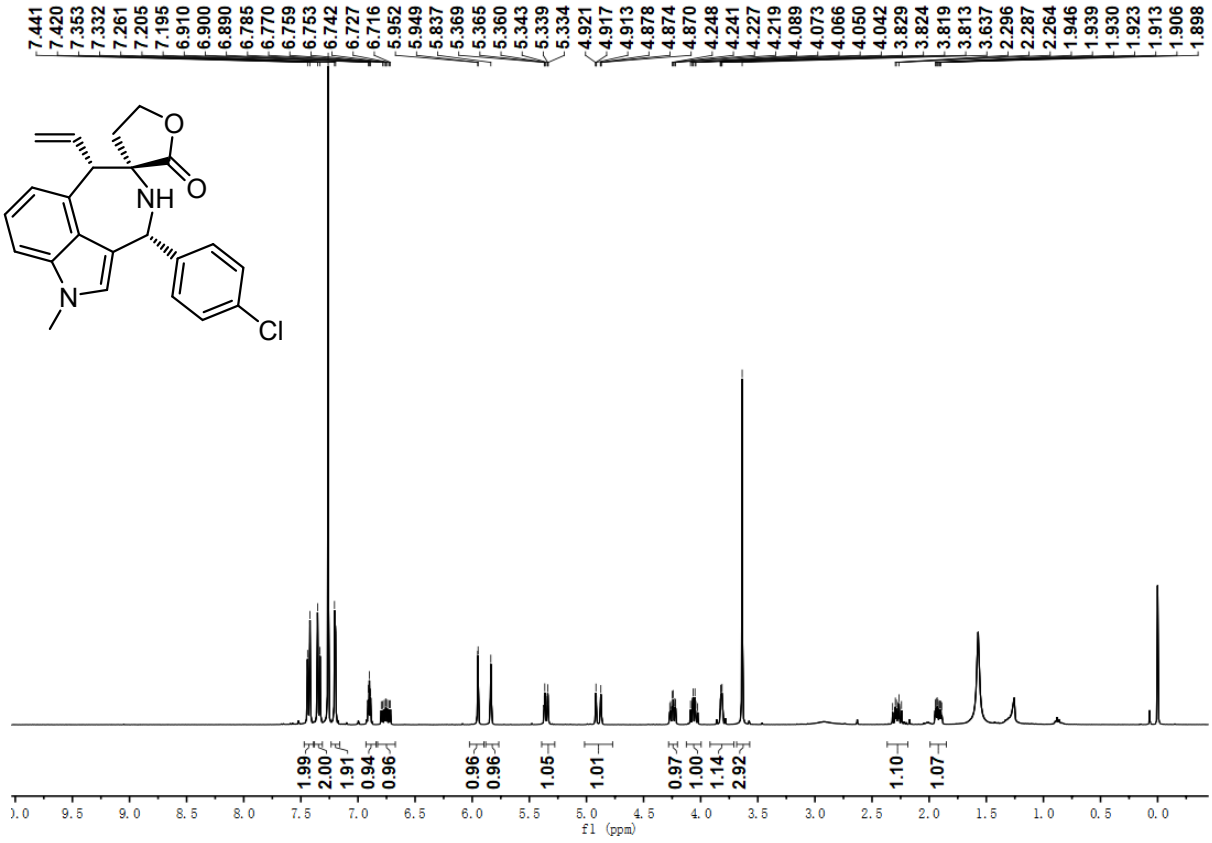
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3p** in $CDCl_3$



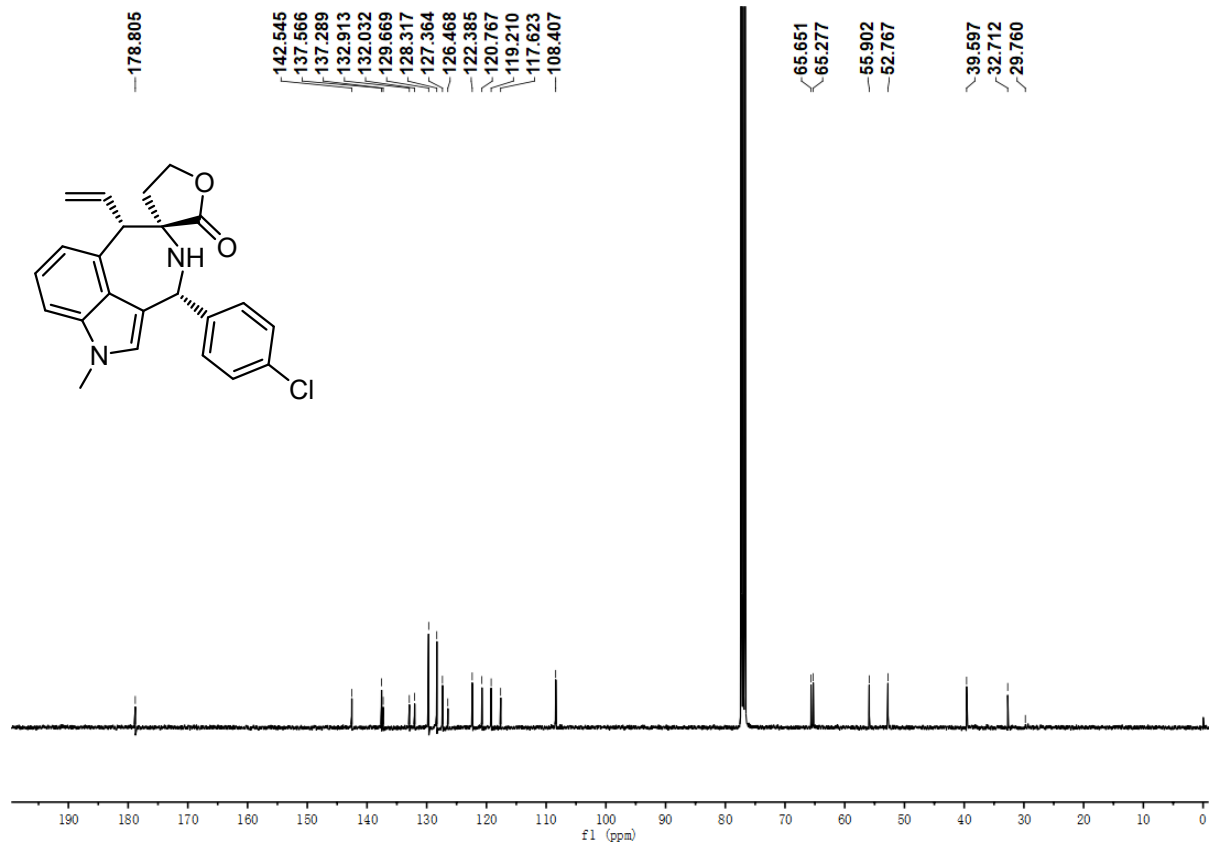
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3p** in $CDCl_3$



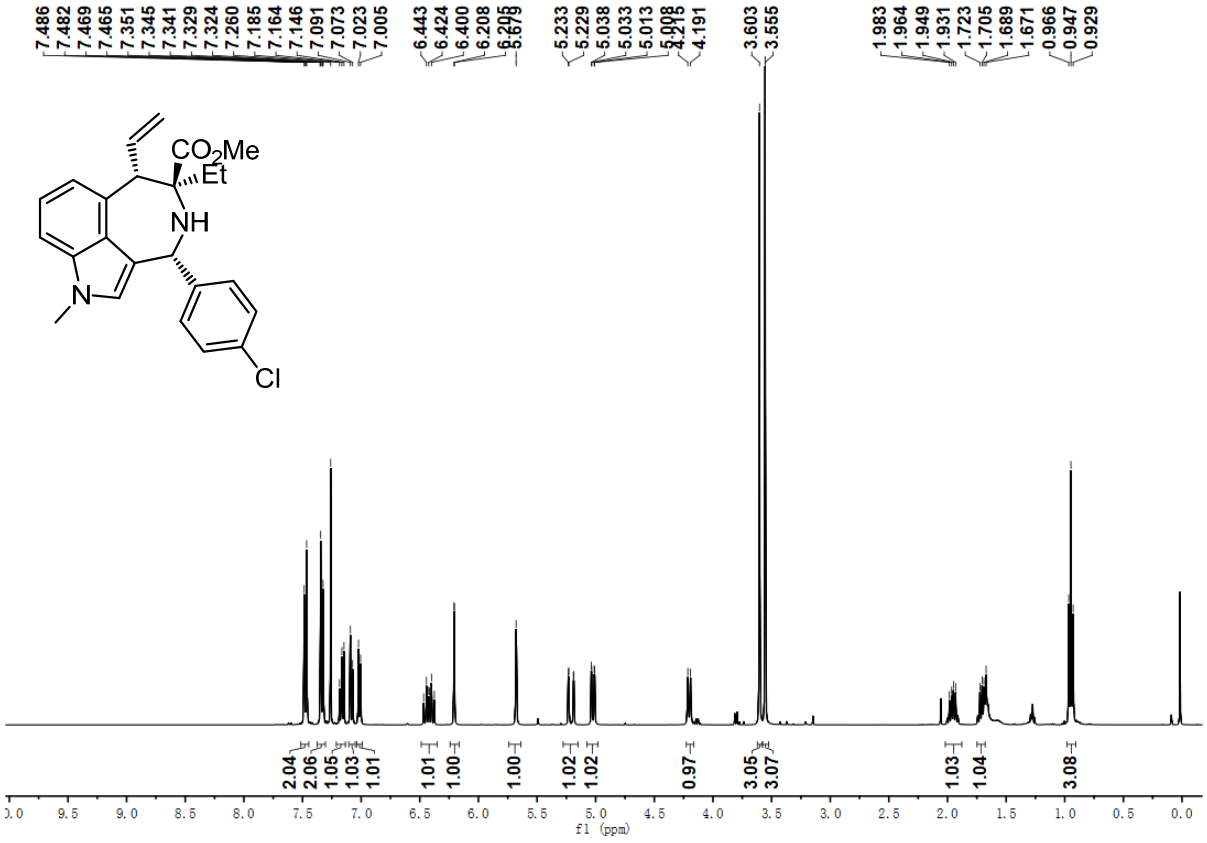
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3q** in $CDCl_3$



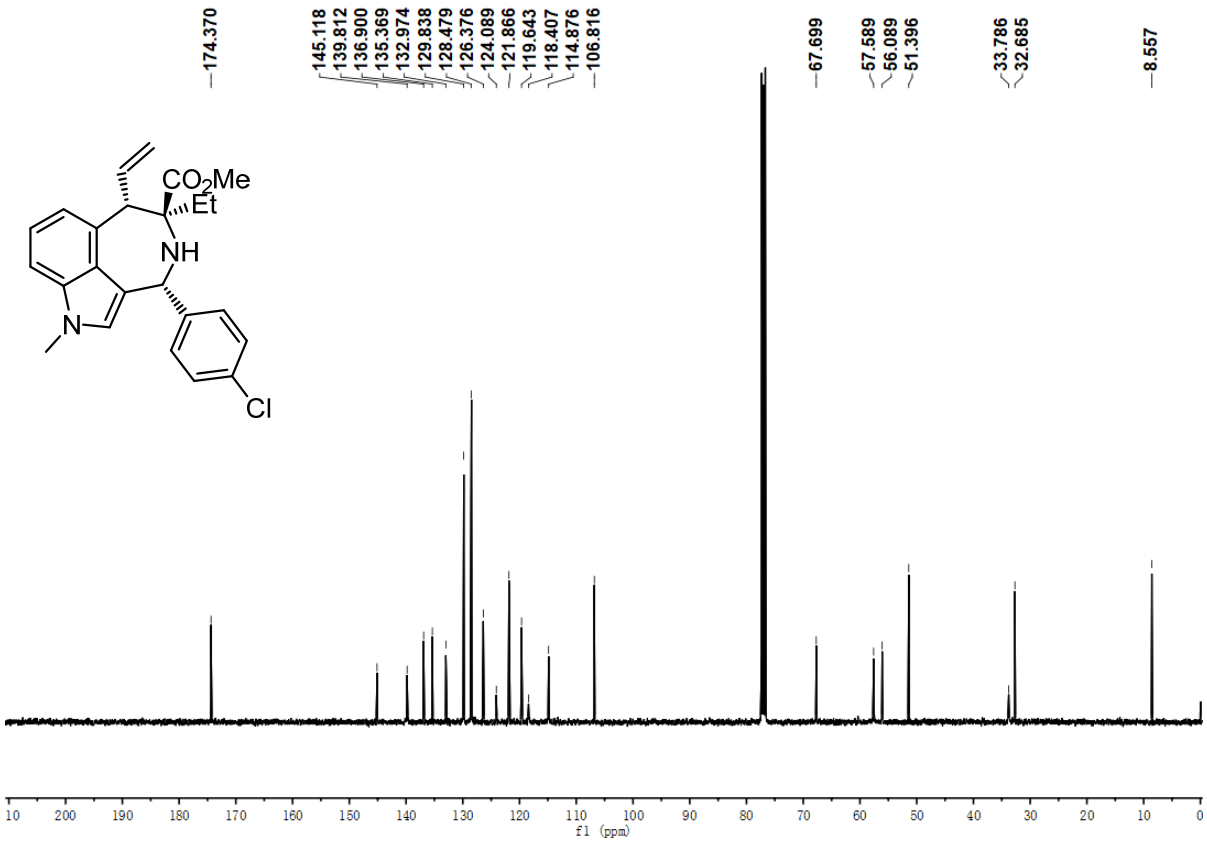
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3q** in $CDCl_3$



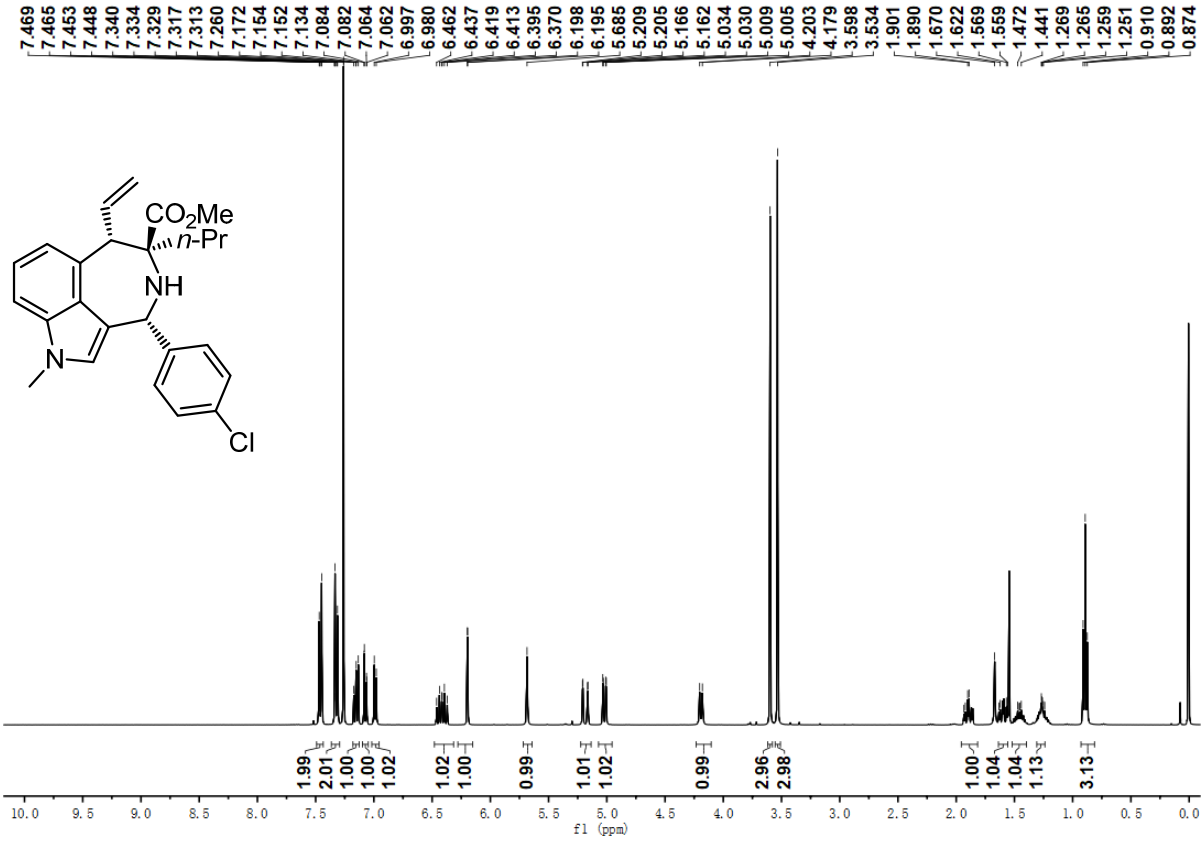
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3r** in $CDCl_3$



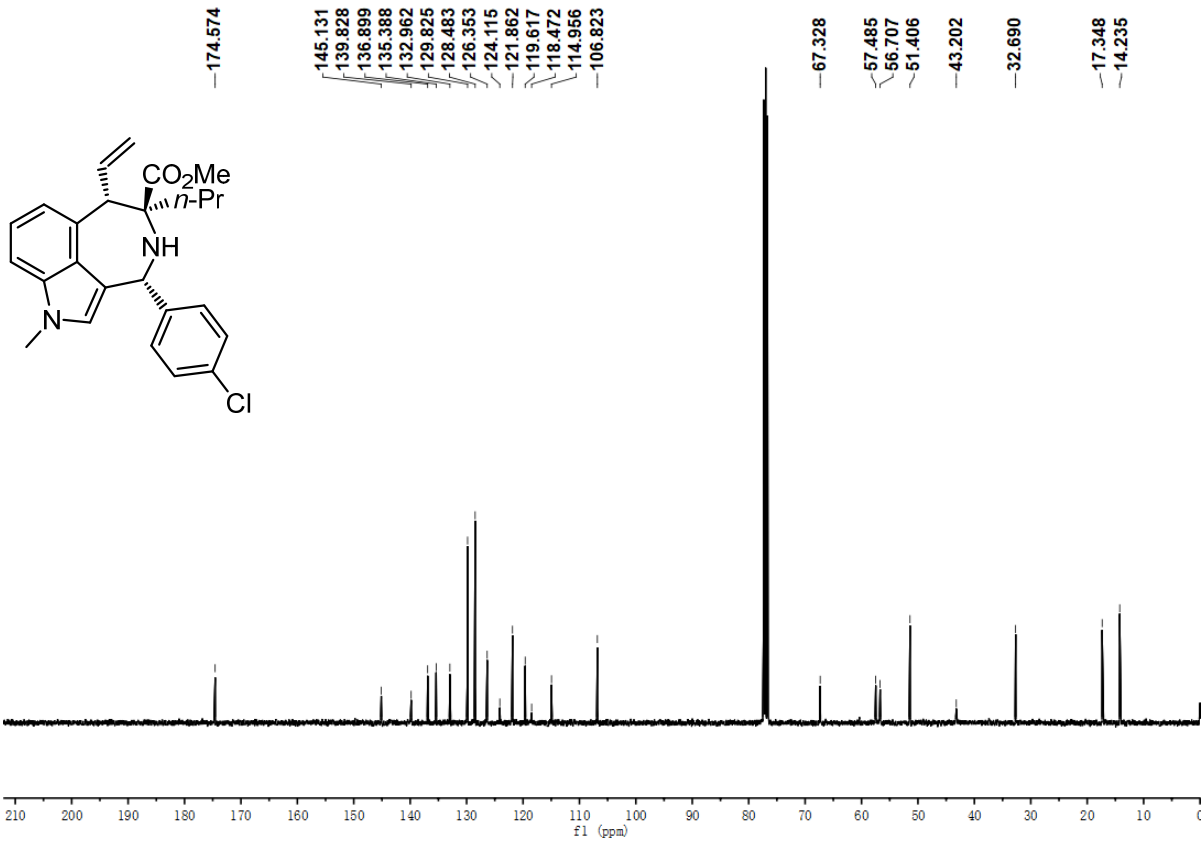
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3r** in $CDCl_3$



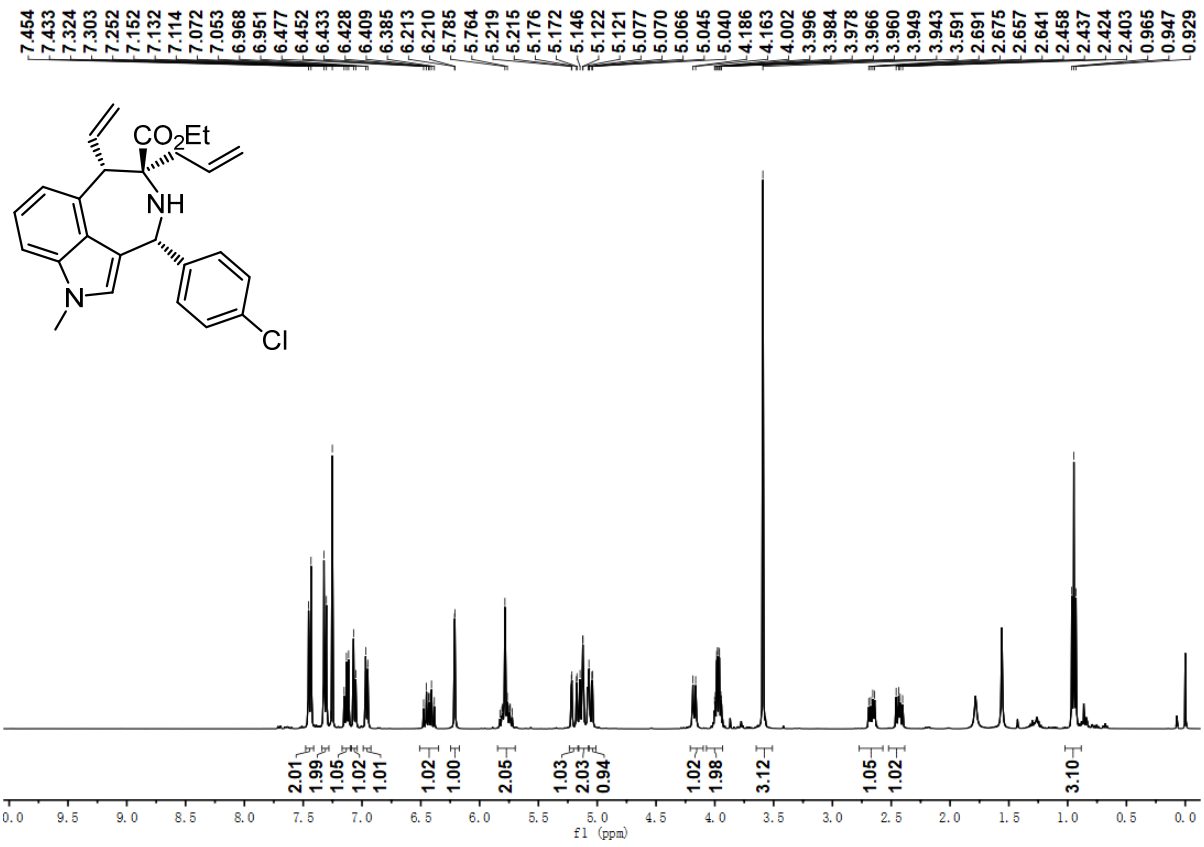
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3s** in $CDCl_3$



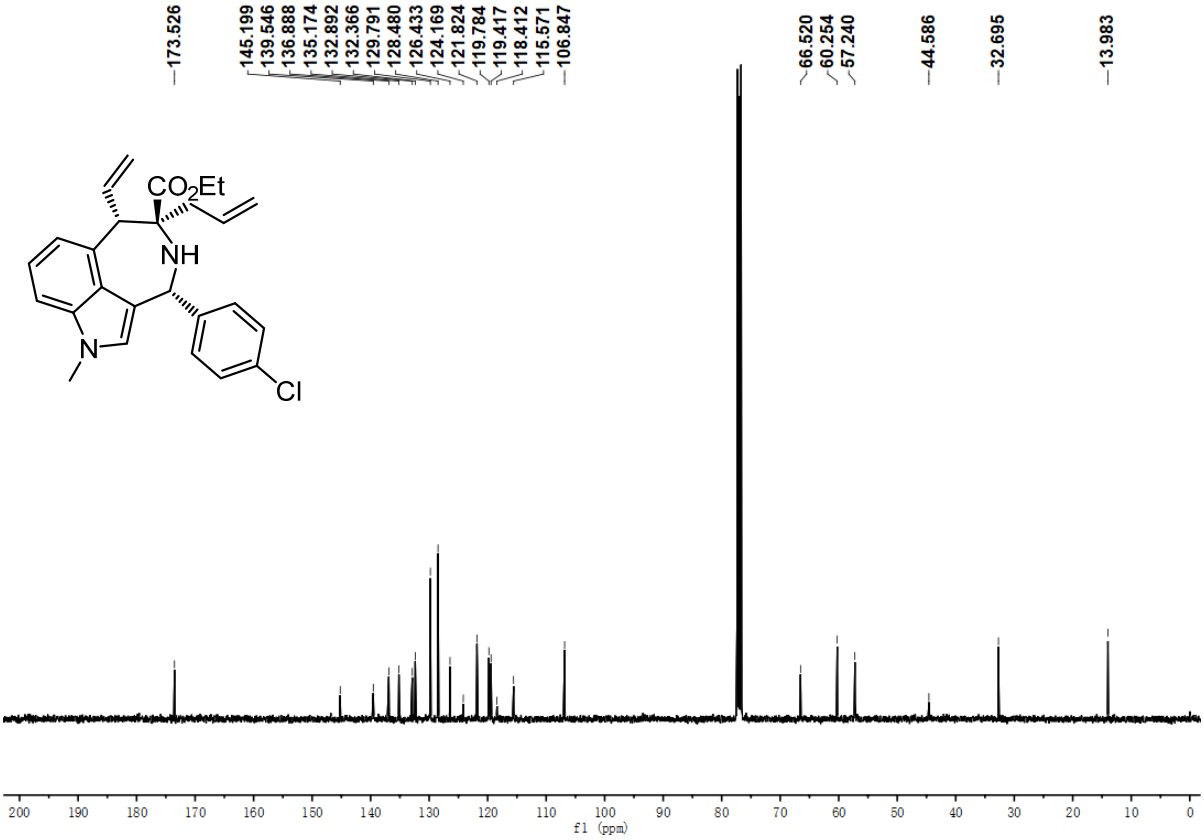
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3s** in $CDCl_3$



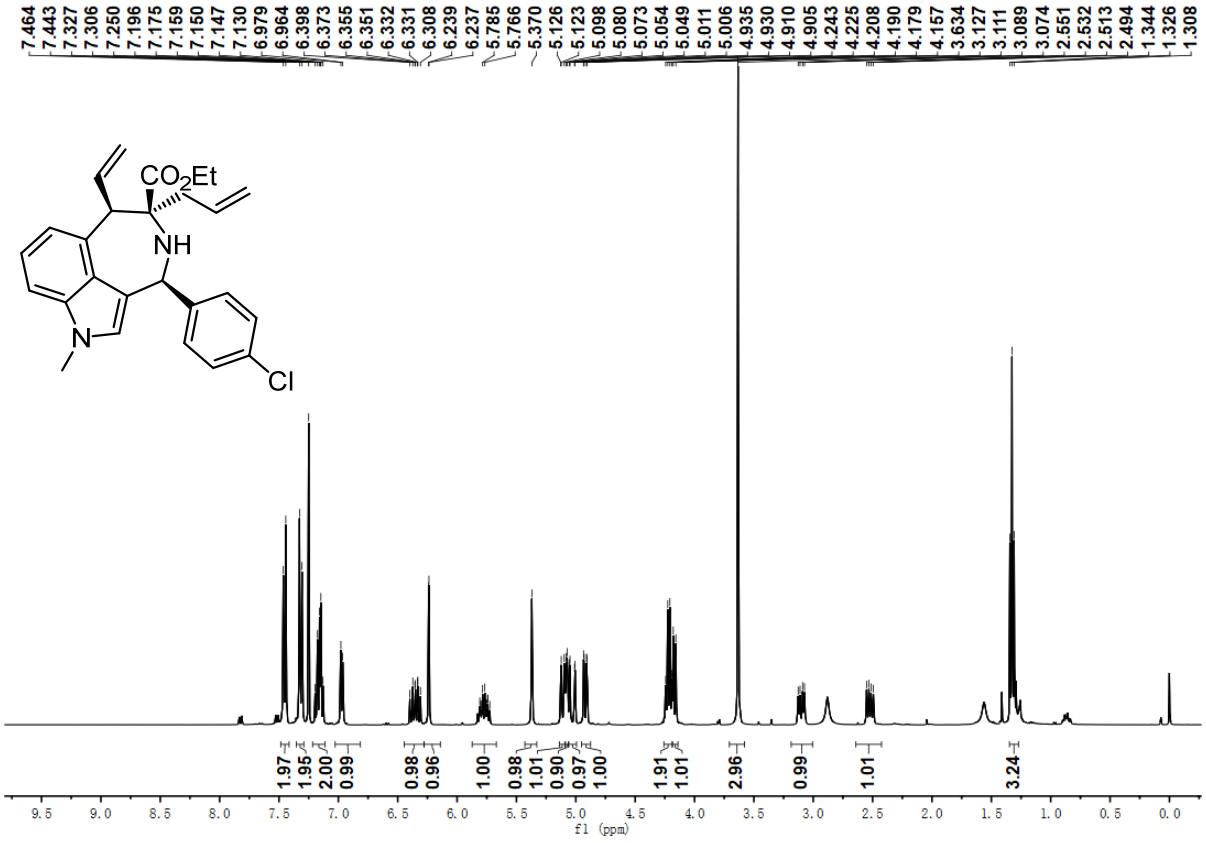
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3t** in $CDCl_3$



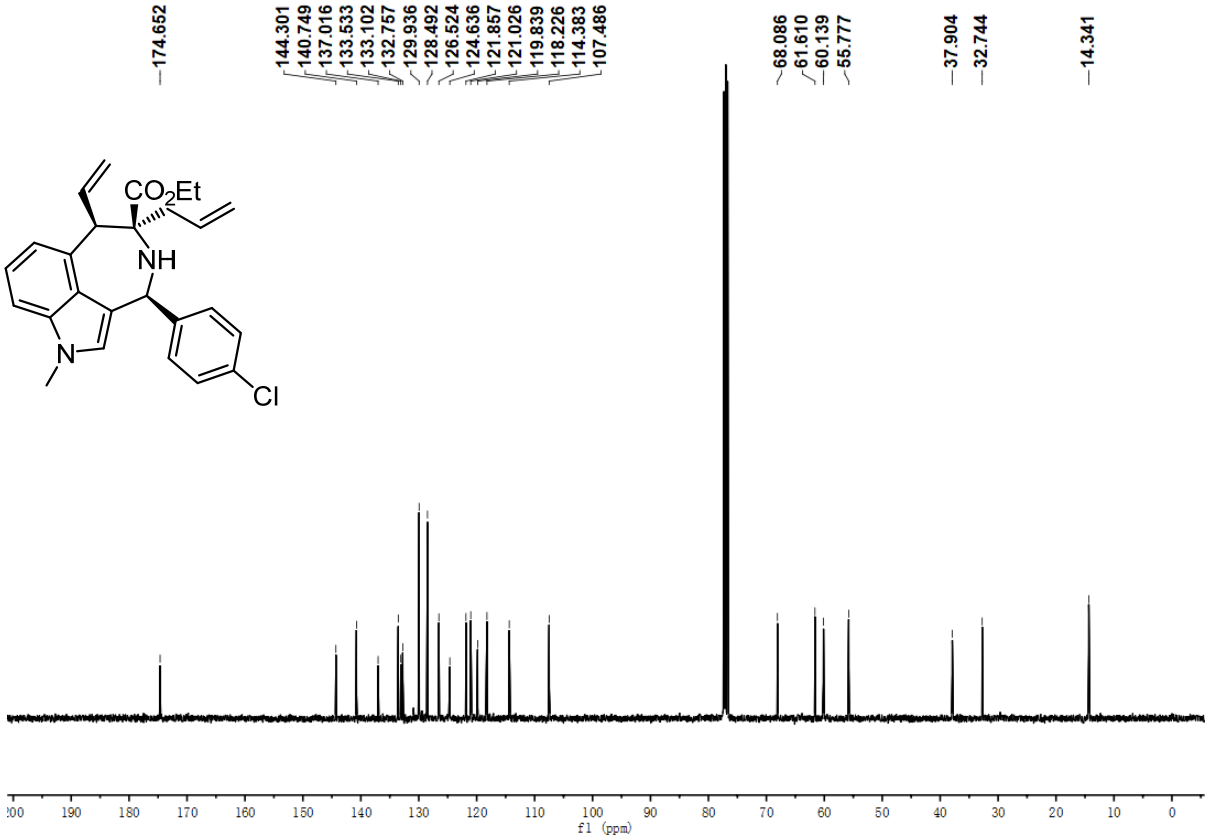
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3t** in $CDCl_3$



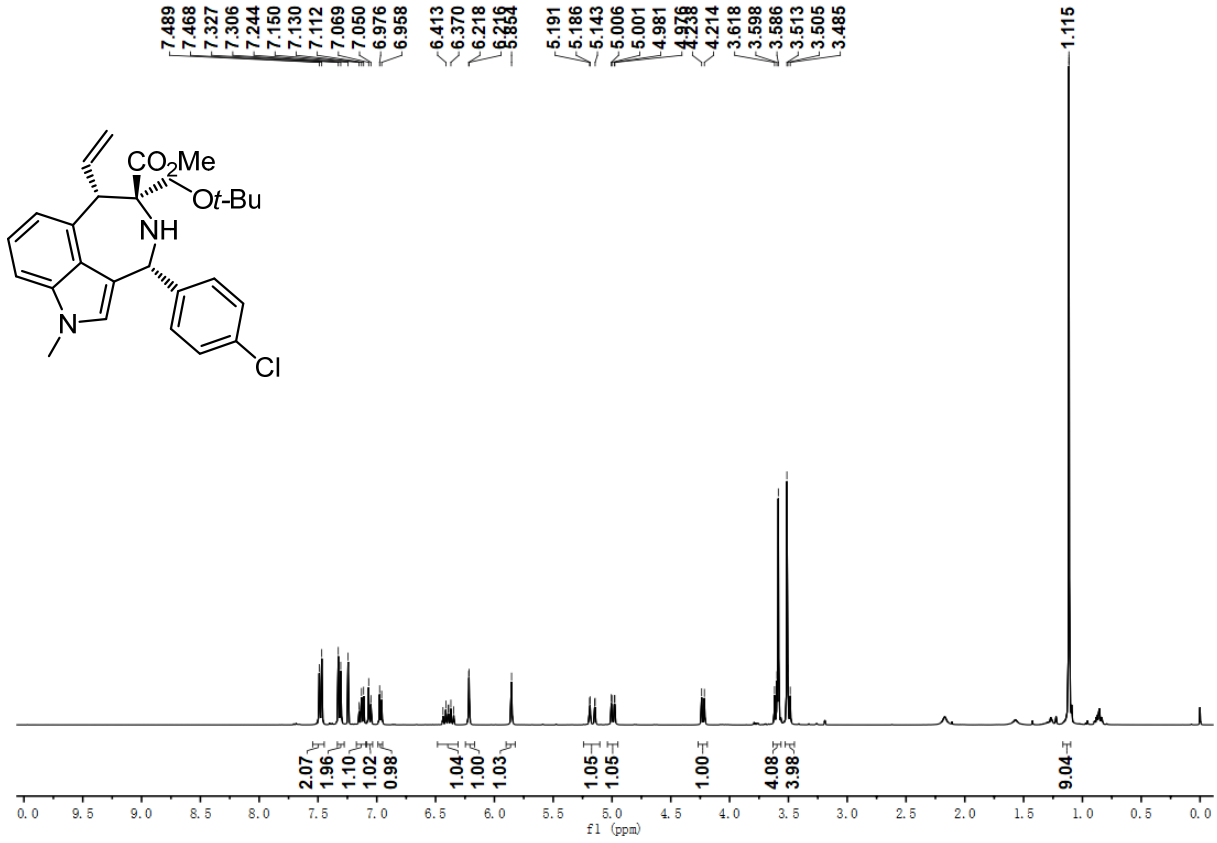
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**3t** in $CDCl_3$



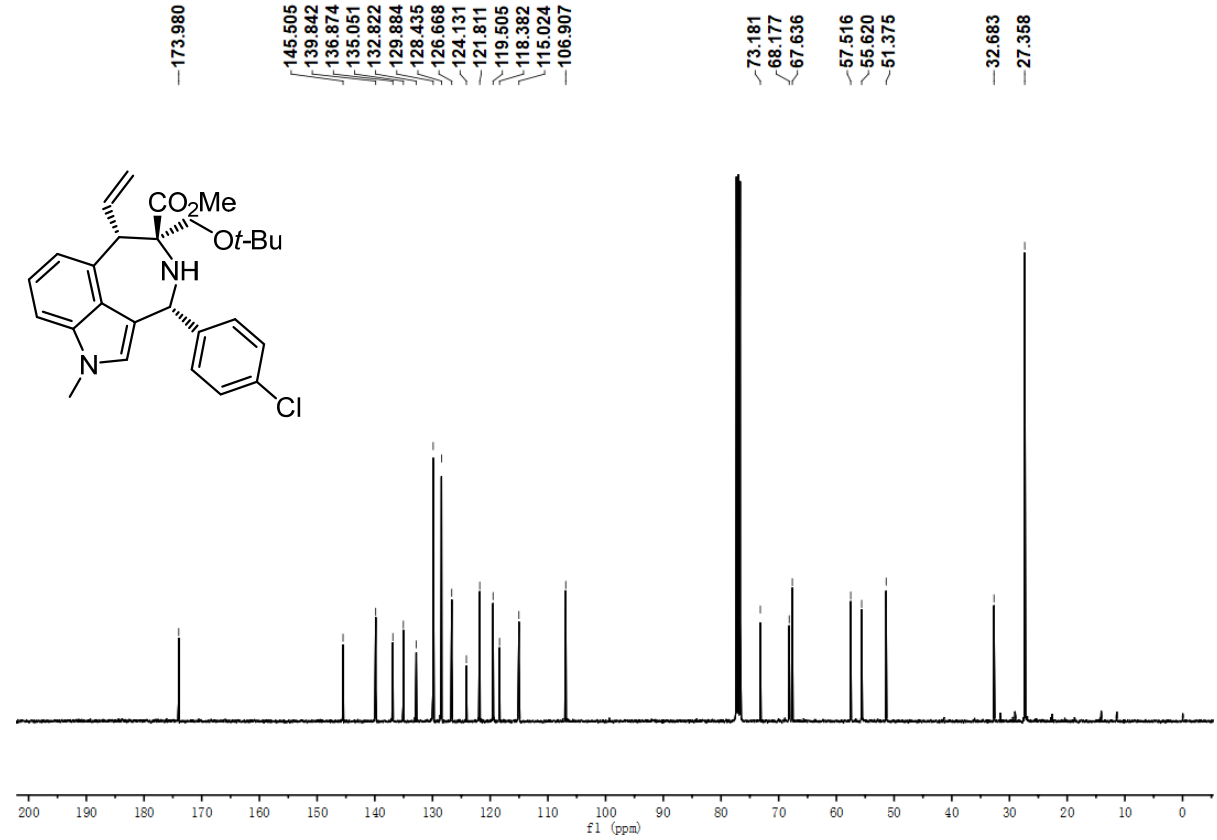
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**3t** in $CDCl_3$



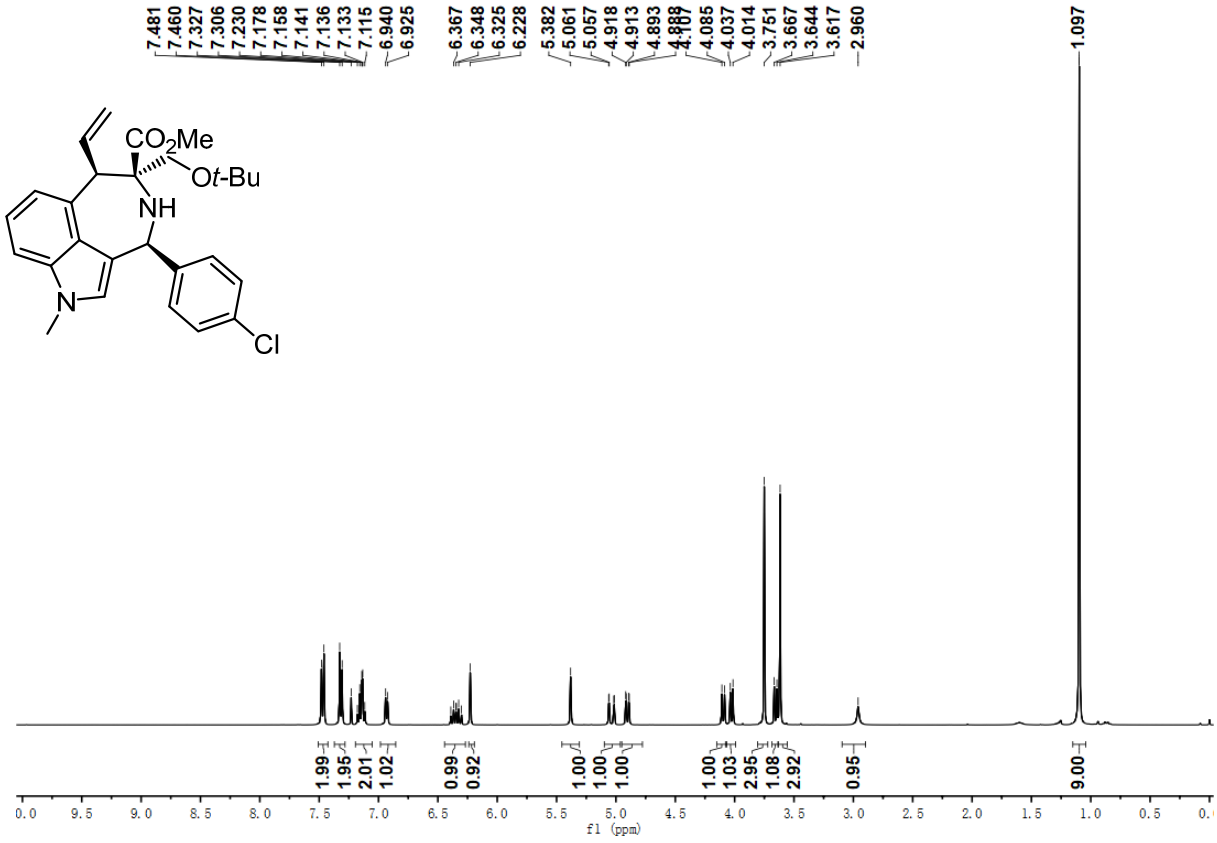
^{1}H NMR (400 MHz) of (6*S*,7*R*,9*R*)-**3u** in $CDCl_3$



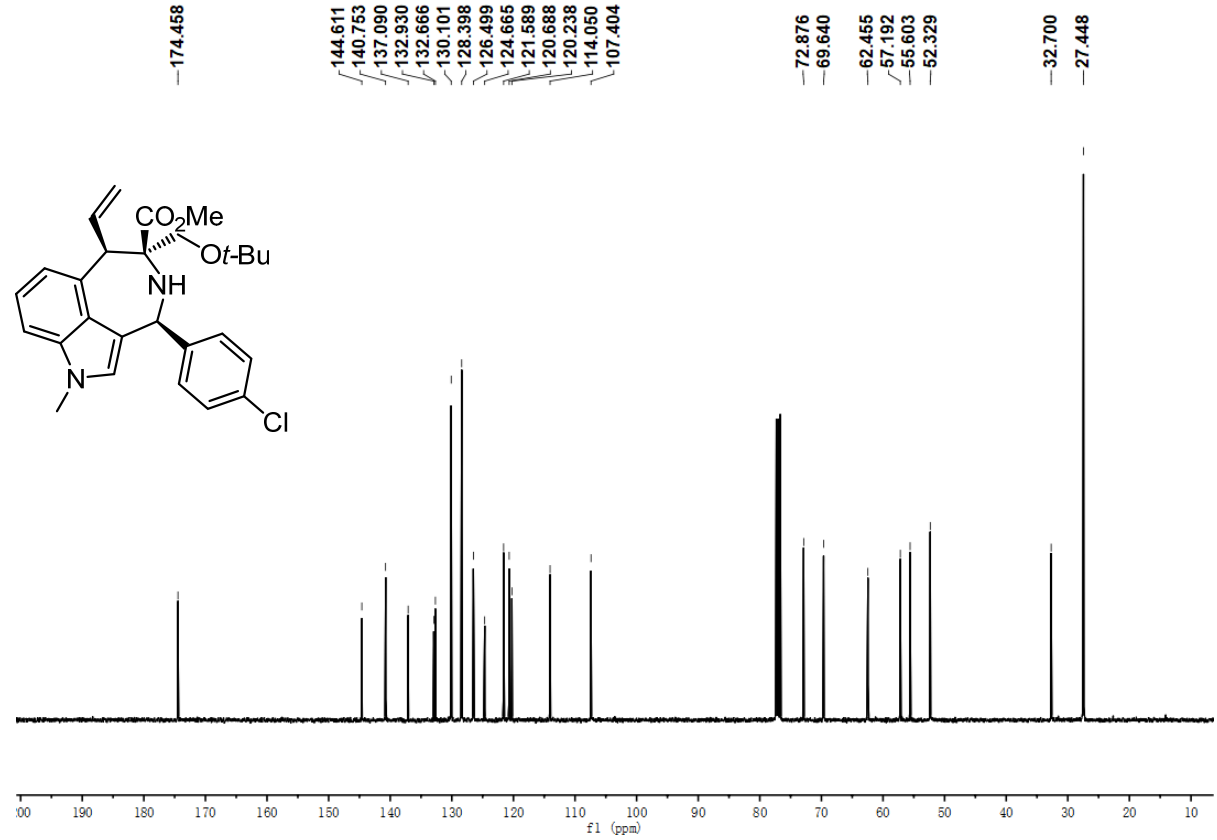
^{13}C NMR (101 MHz) of (6*S*,7*R*,9*R*)-**3u** in $CDCl_3$



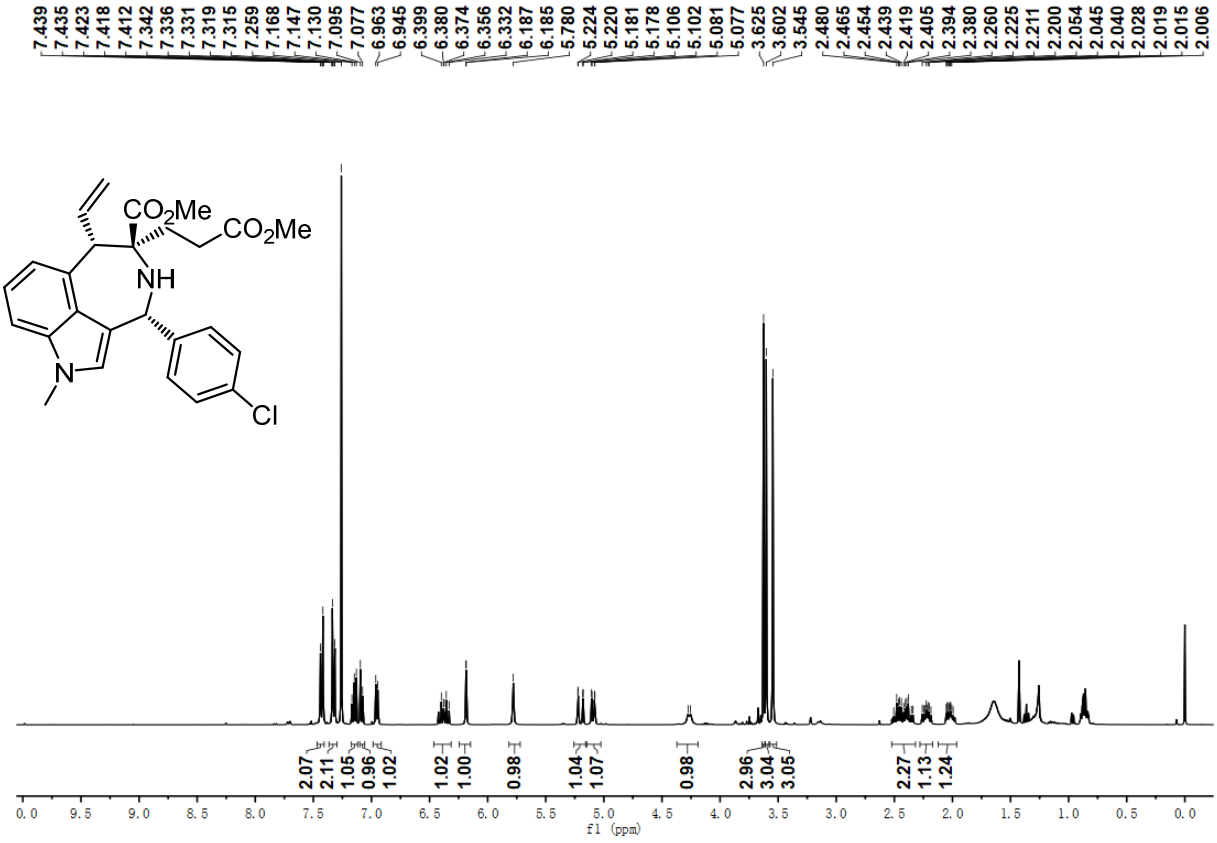
^{1}H NMR (400 MHz) of (6*R*,7*R*,9*S*)-**3u** in $CDCl_3$



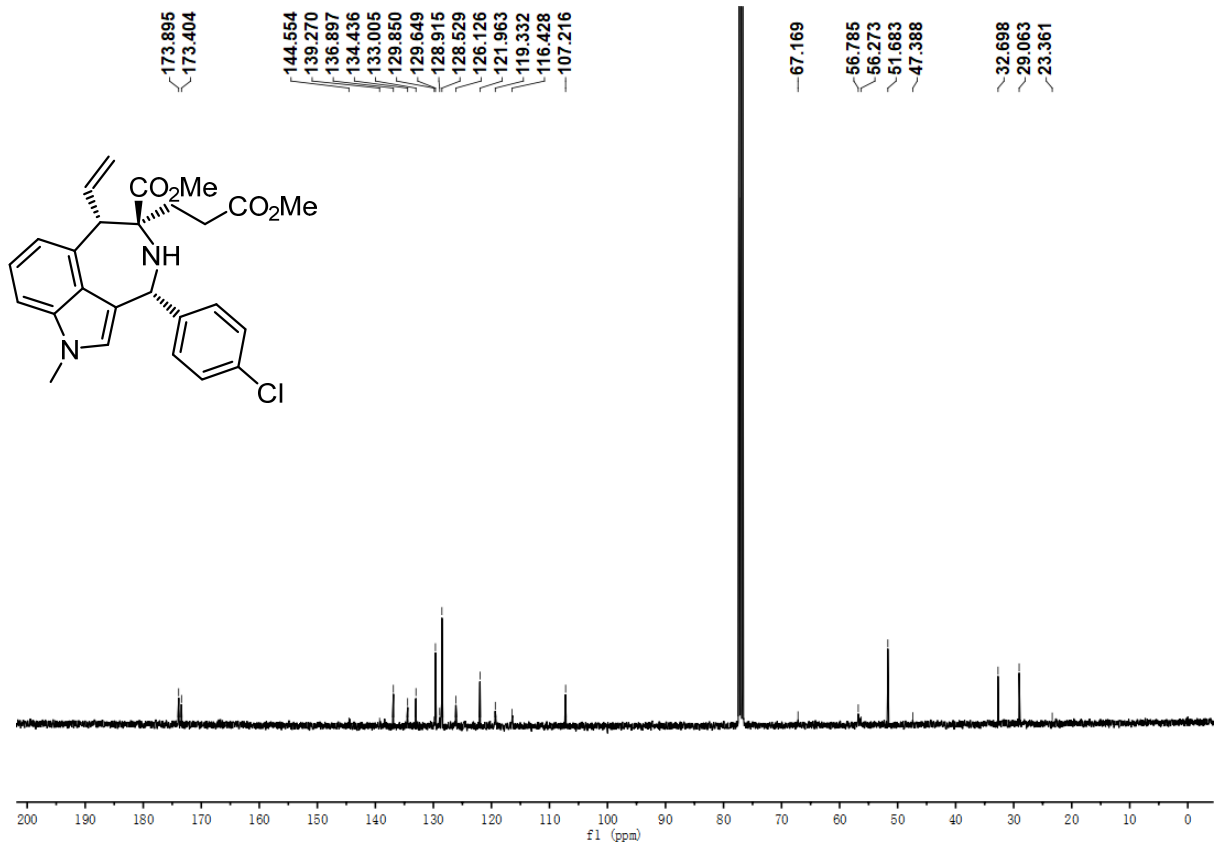
^{13}C NMR (101 MHz) of (6*R*,7*R*,9*S*)-**3u** in $CDCl_3$



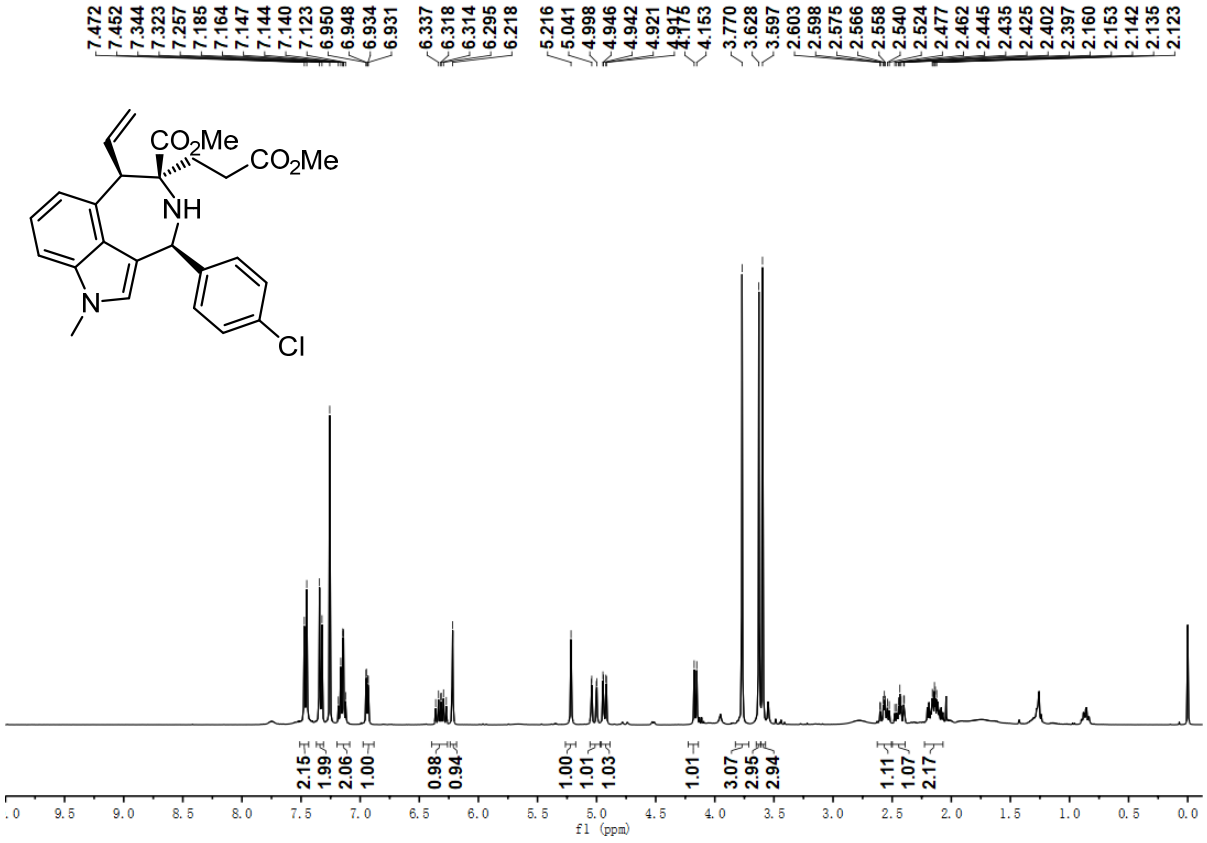
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3v** in $CDCl_3$



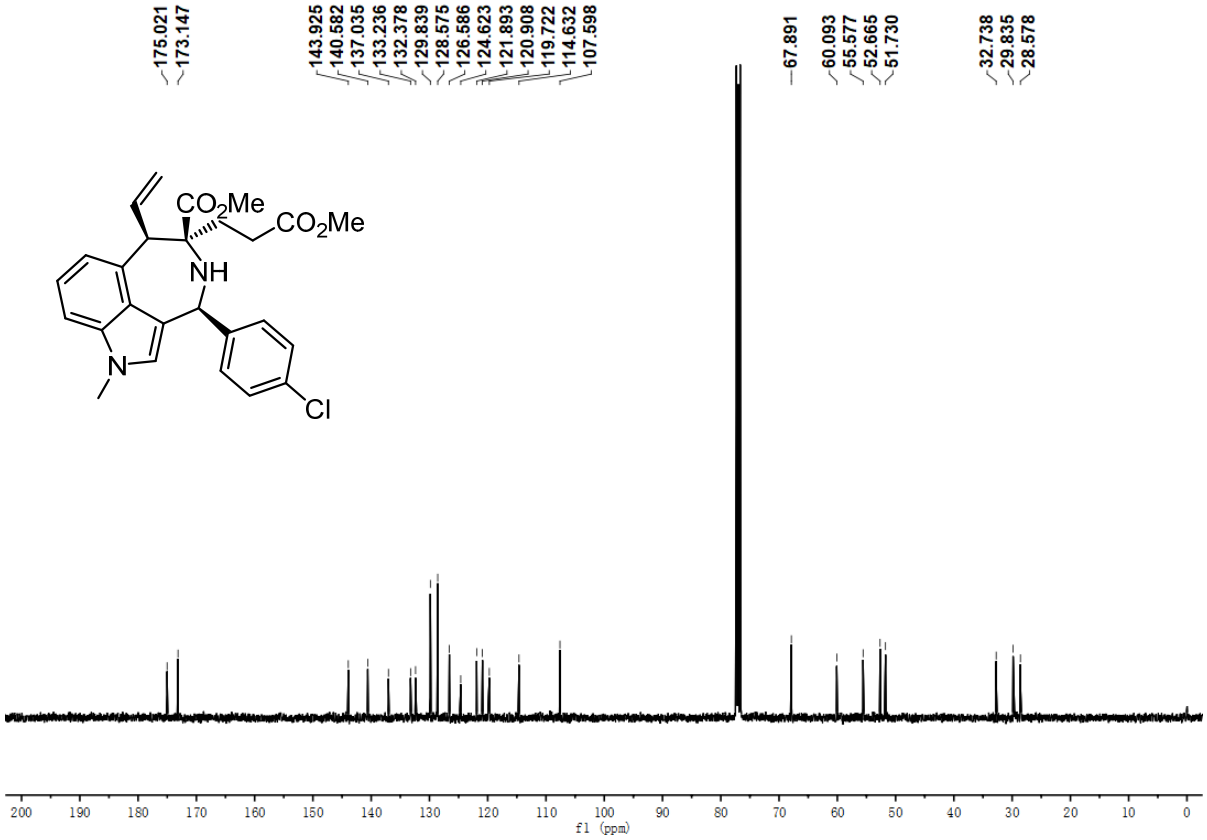
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3v** in $CDCl_3$



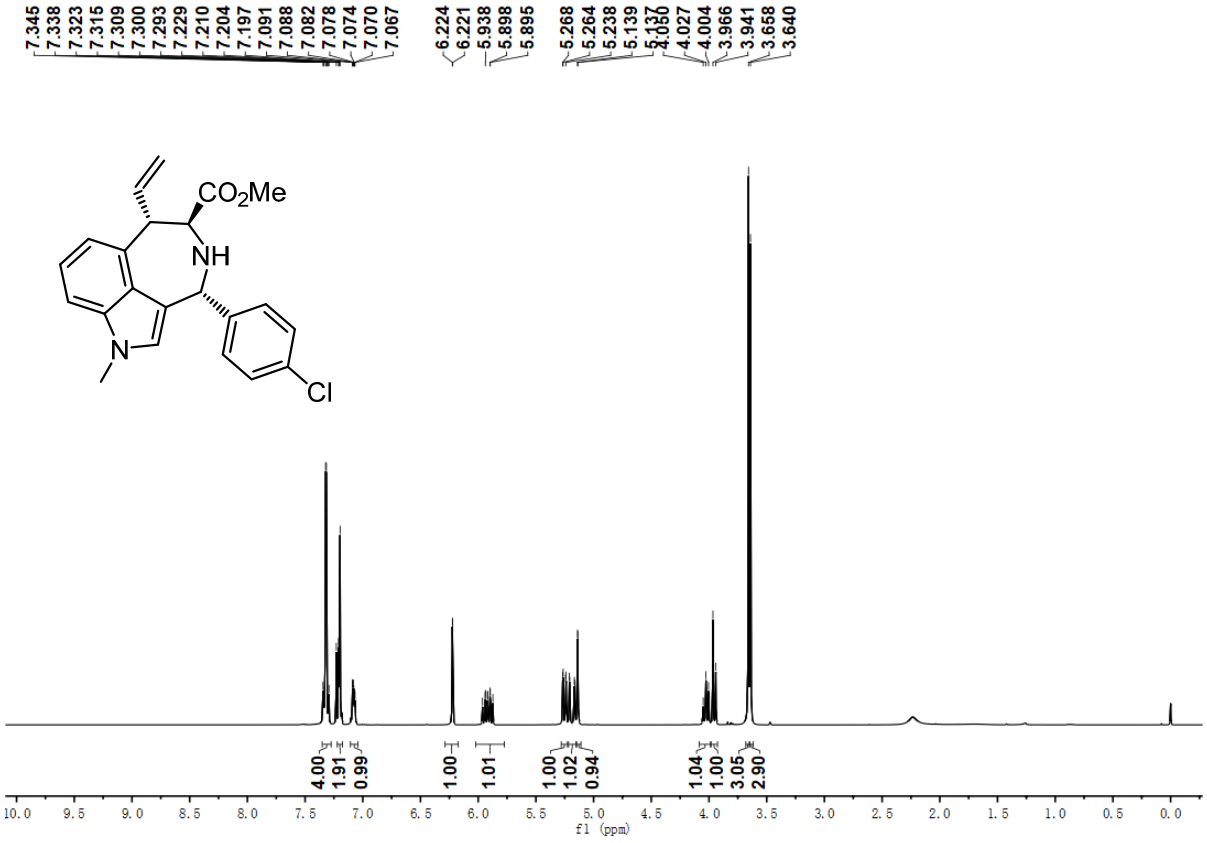
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**3v** in $CDCl_3$



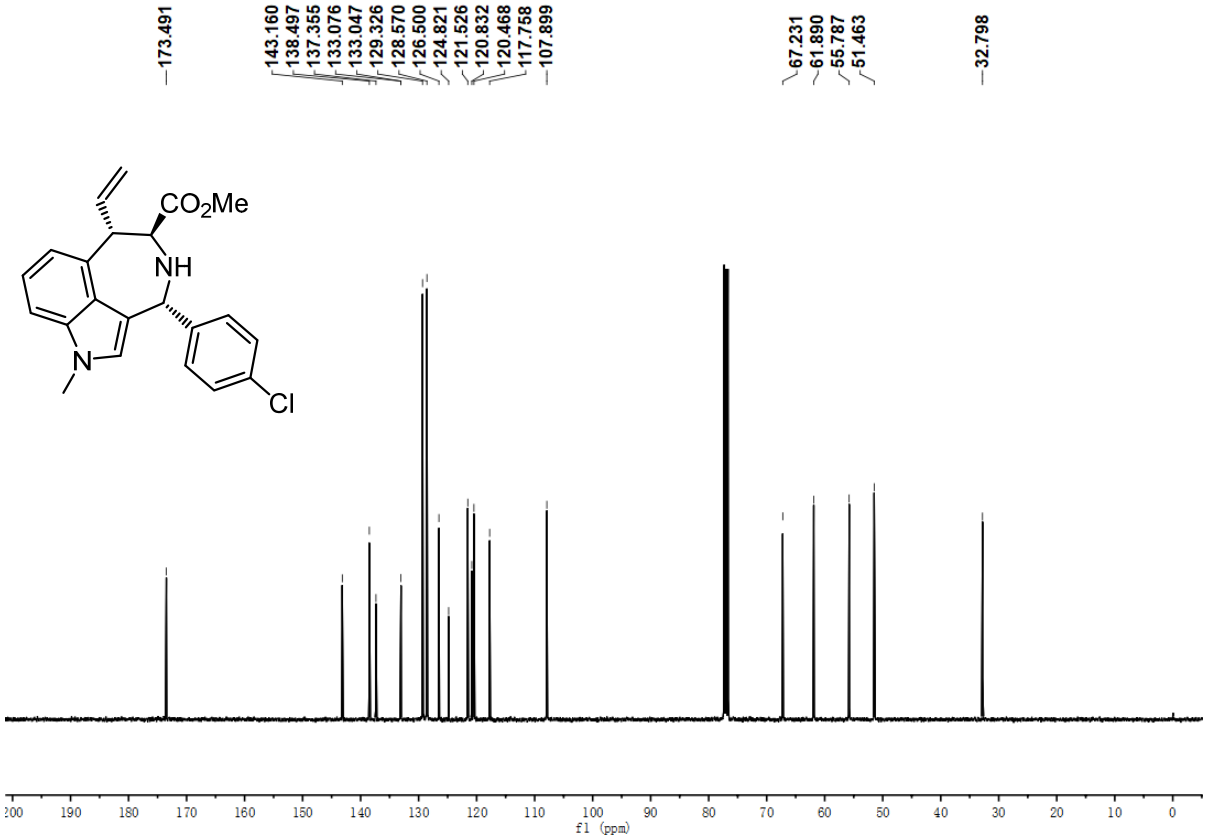
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**3v** in $CDCl_3$



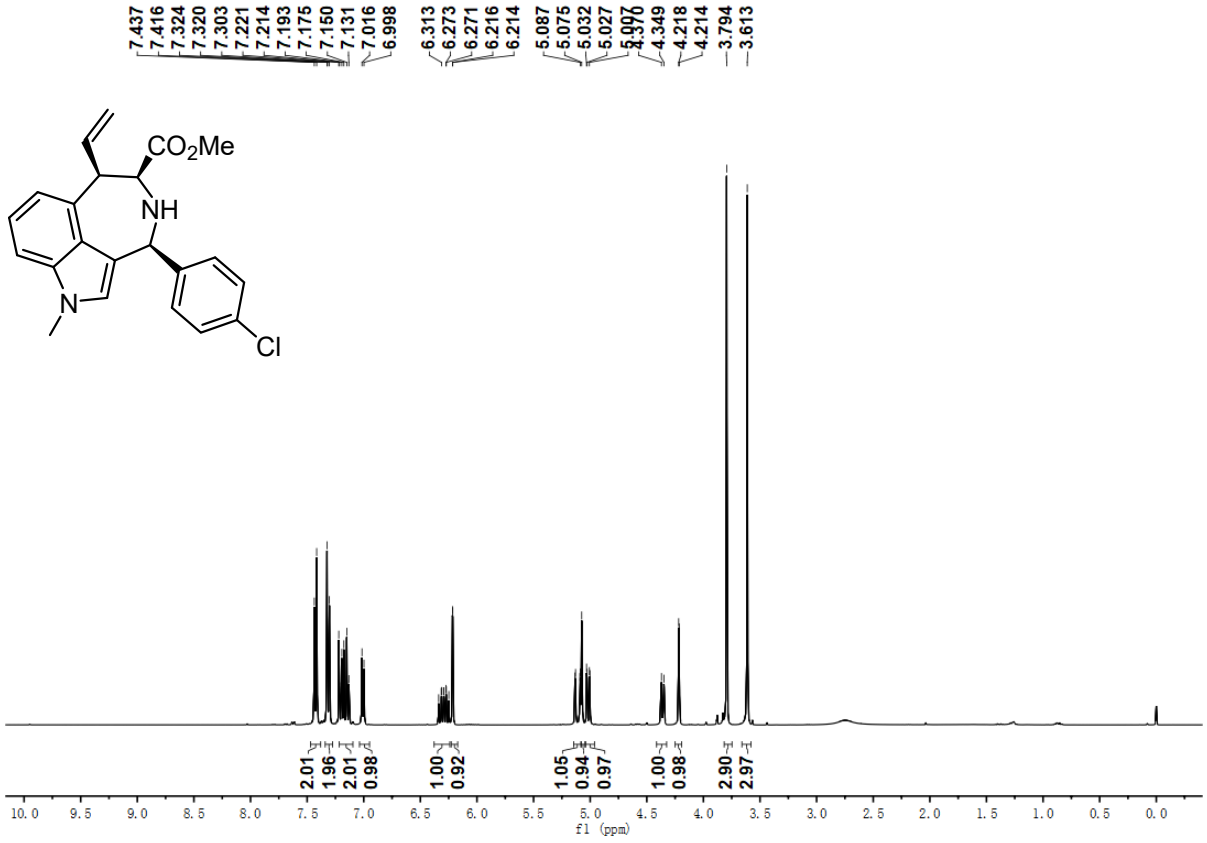
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3w** in $CDCl_3$



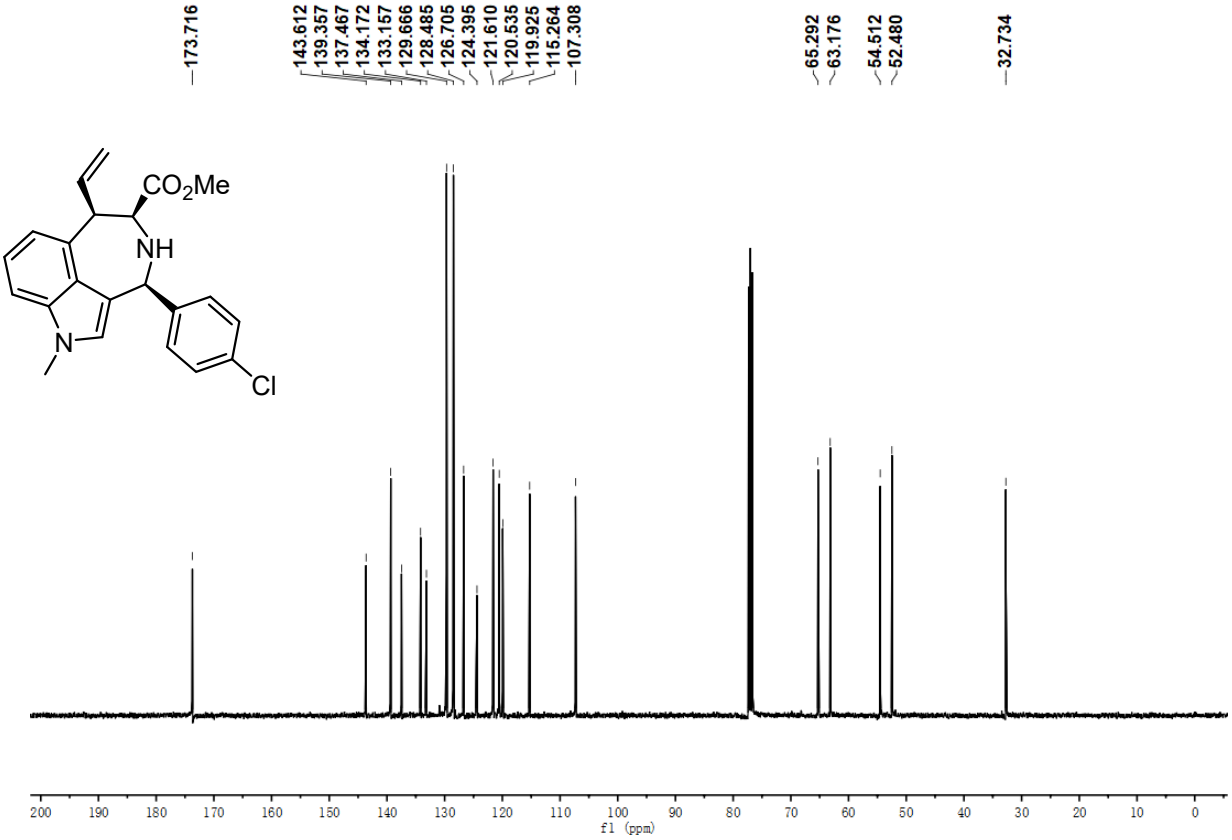
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3w** in $CDCl_3$



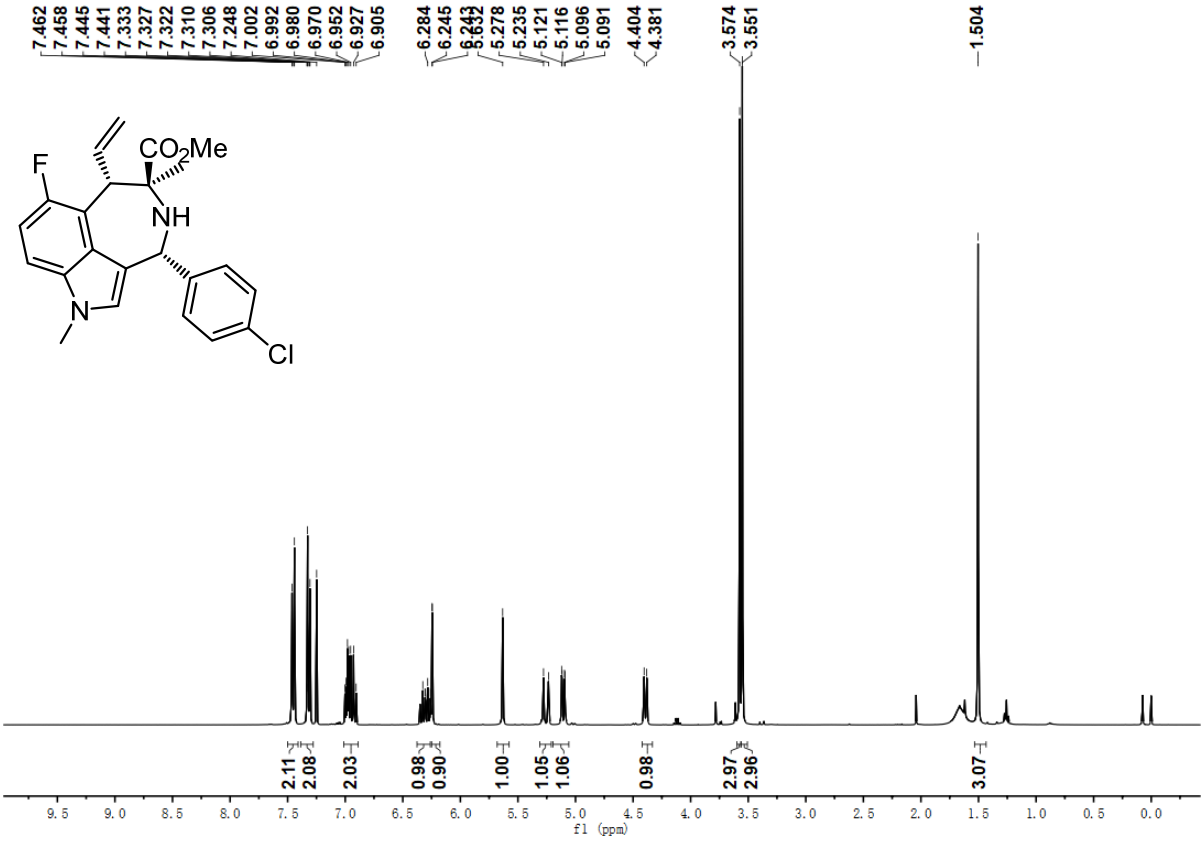
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**3w** in $CDCl_3$



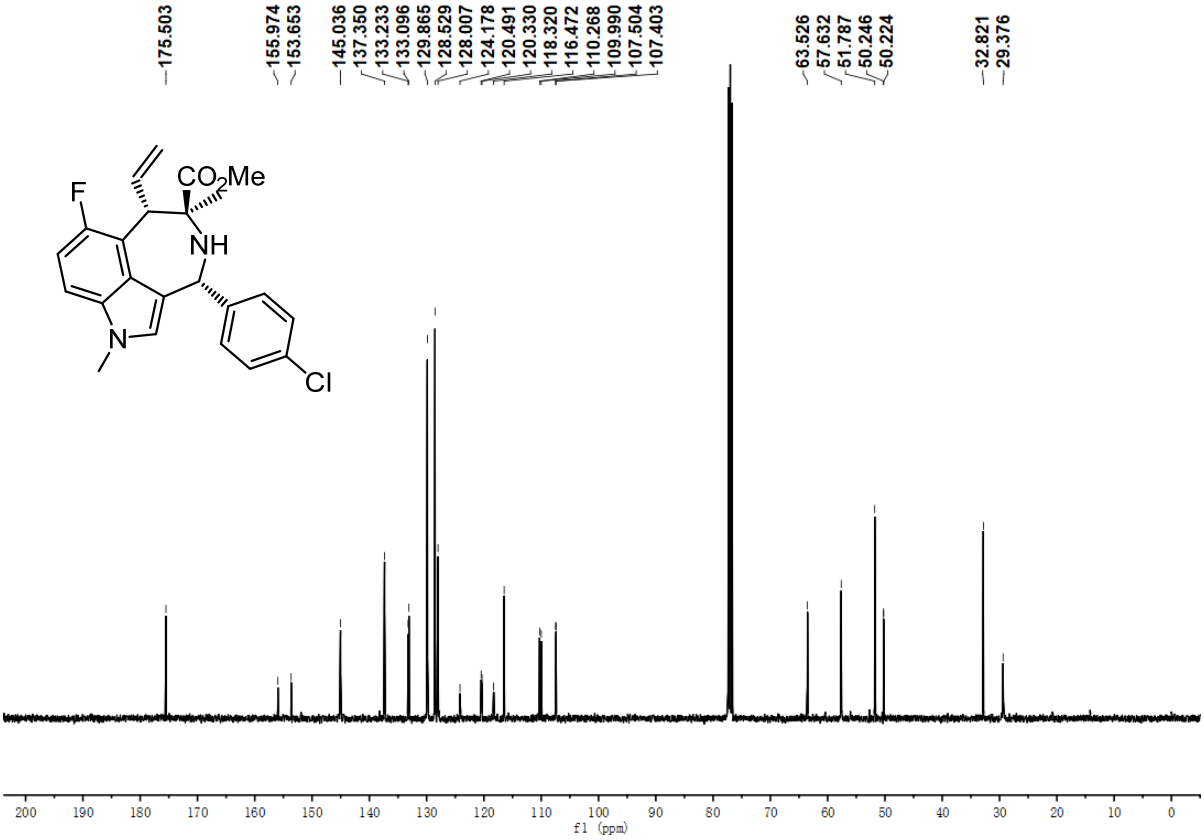
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**3w** in $CDCl_3$



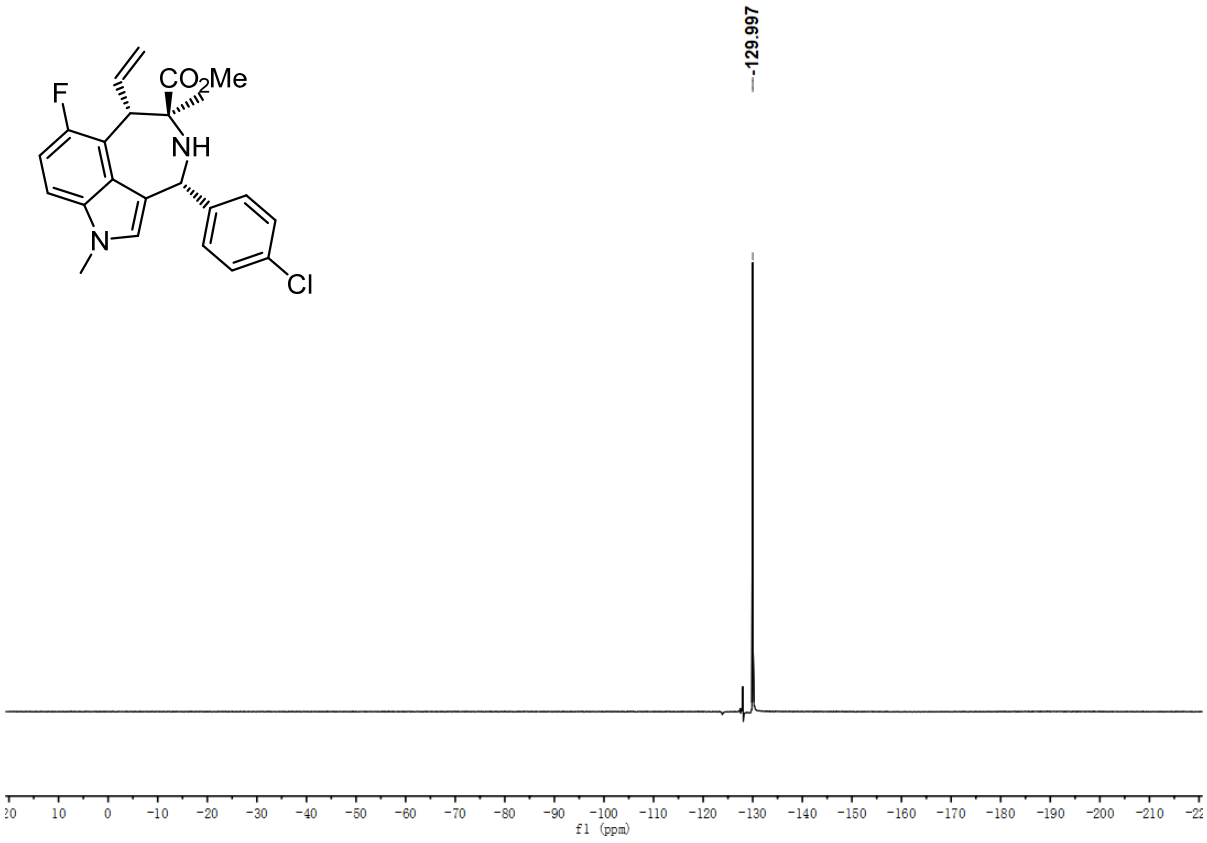
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3x** in $CDCl_3$



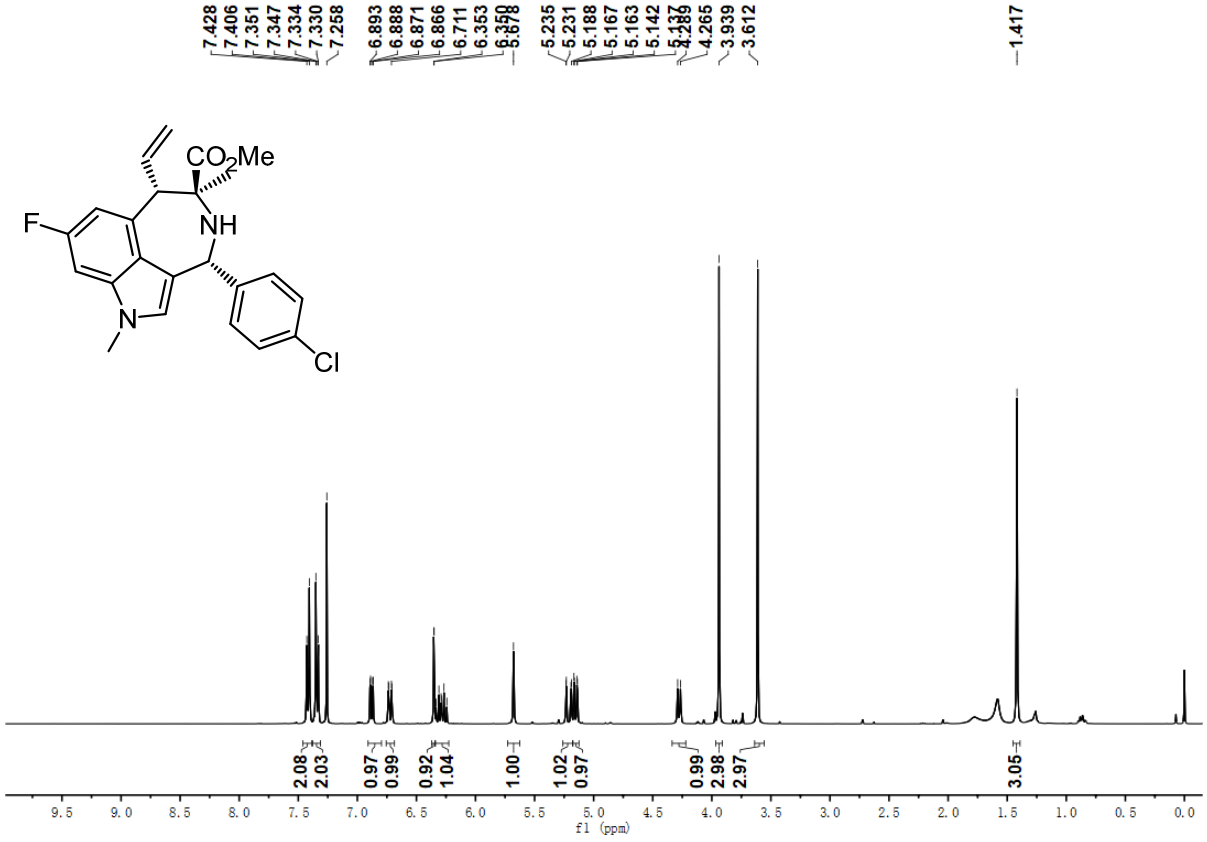
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3x** in $CDCl_3$



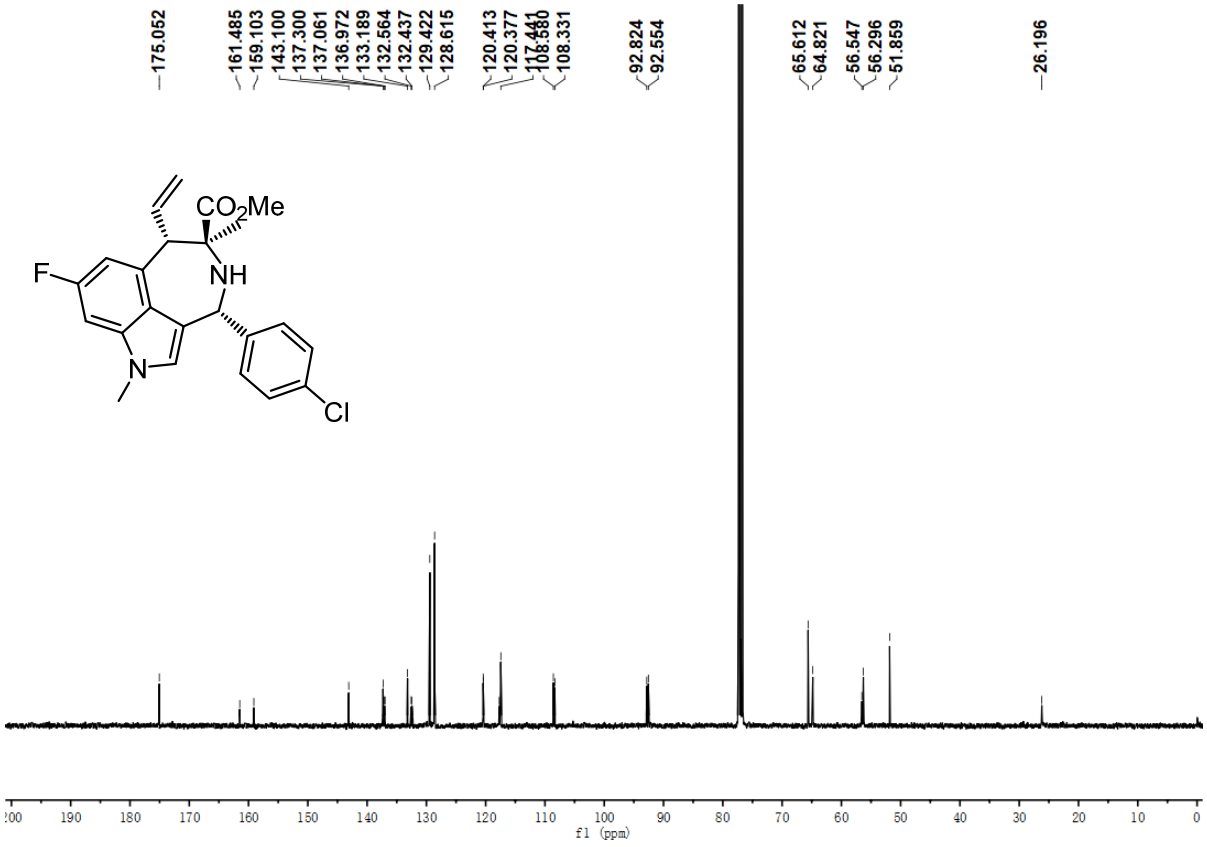
^{19}F NMR (376 MHz) of (6*S*,7*S*,9*R*)-**3x** in $CDCl_3$



^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3y** in $CDCl_3$

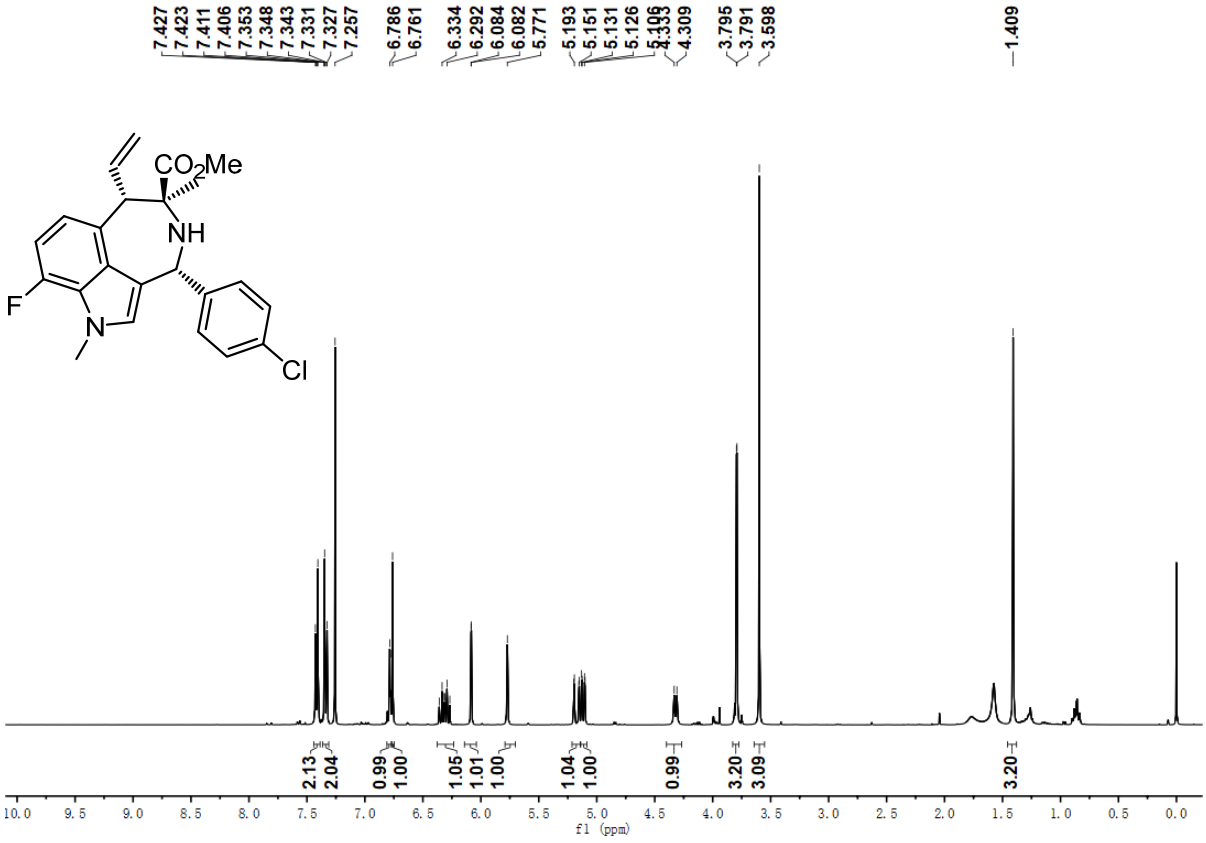


^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3y** in $CDCl_3$

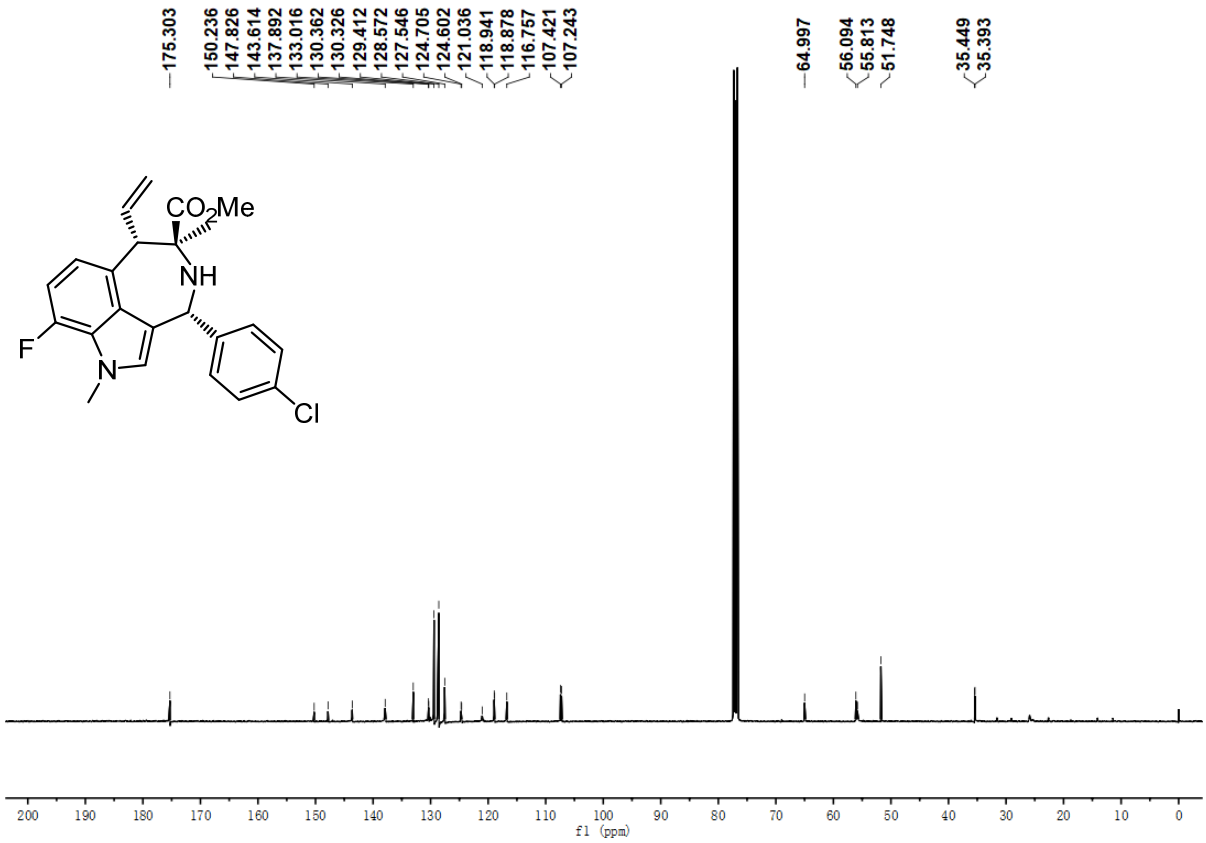


^{19}F NMR (376 MHz) of (6*S*,7*S*,9*R*)-**3y** in $CDCl_3$

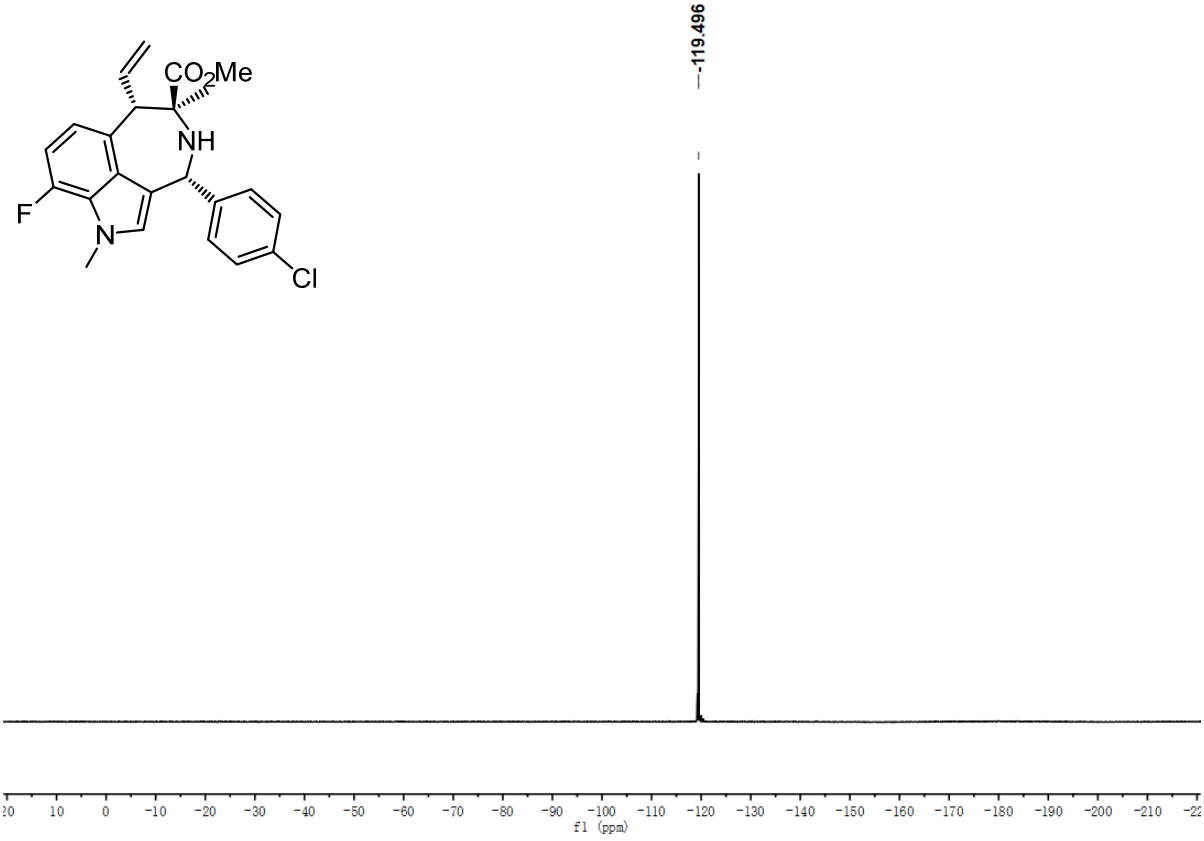
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3z** in $CDCl_3$



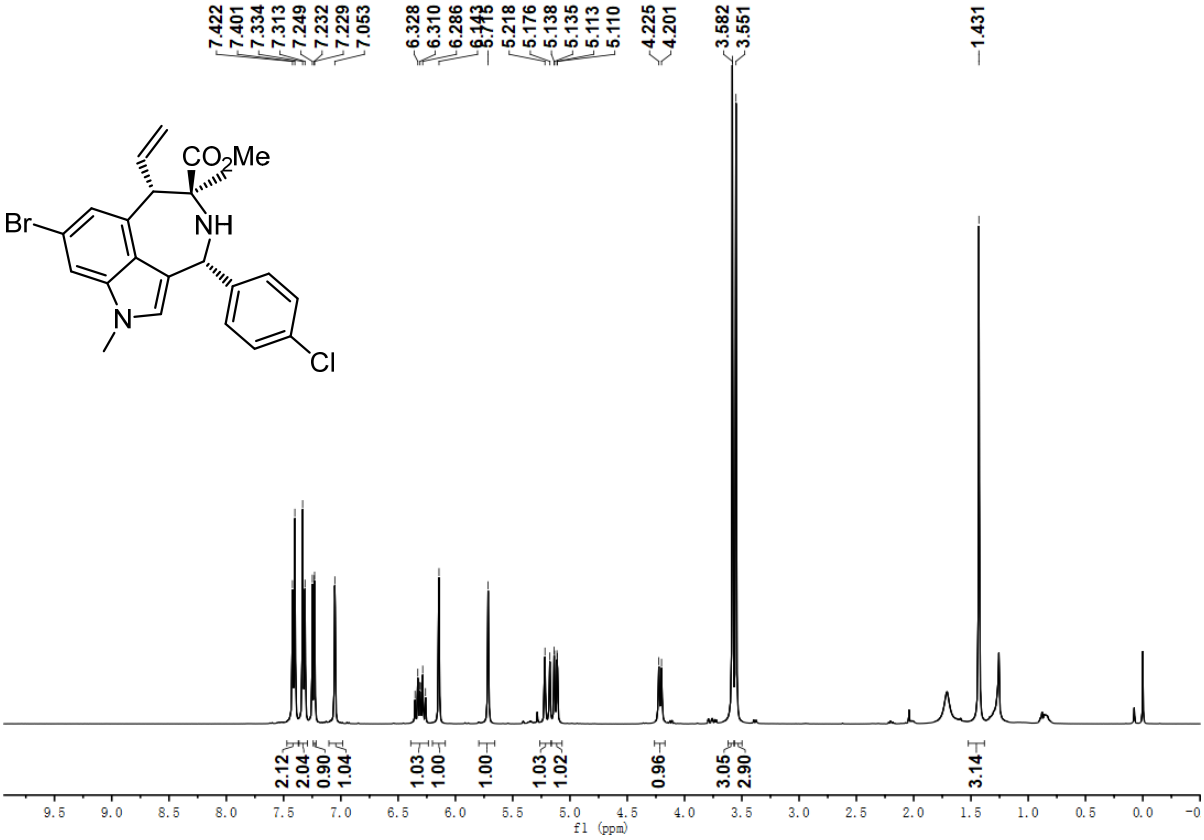
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3z** in $CDCl_3$



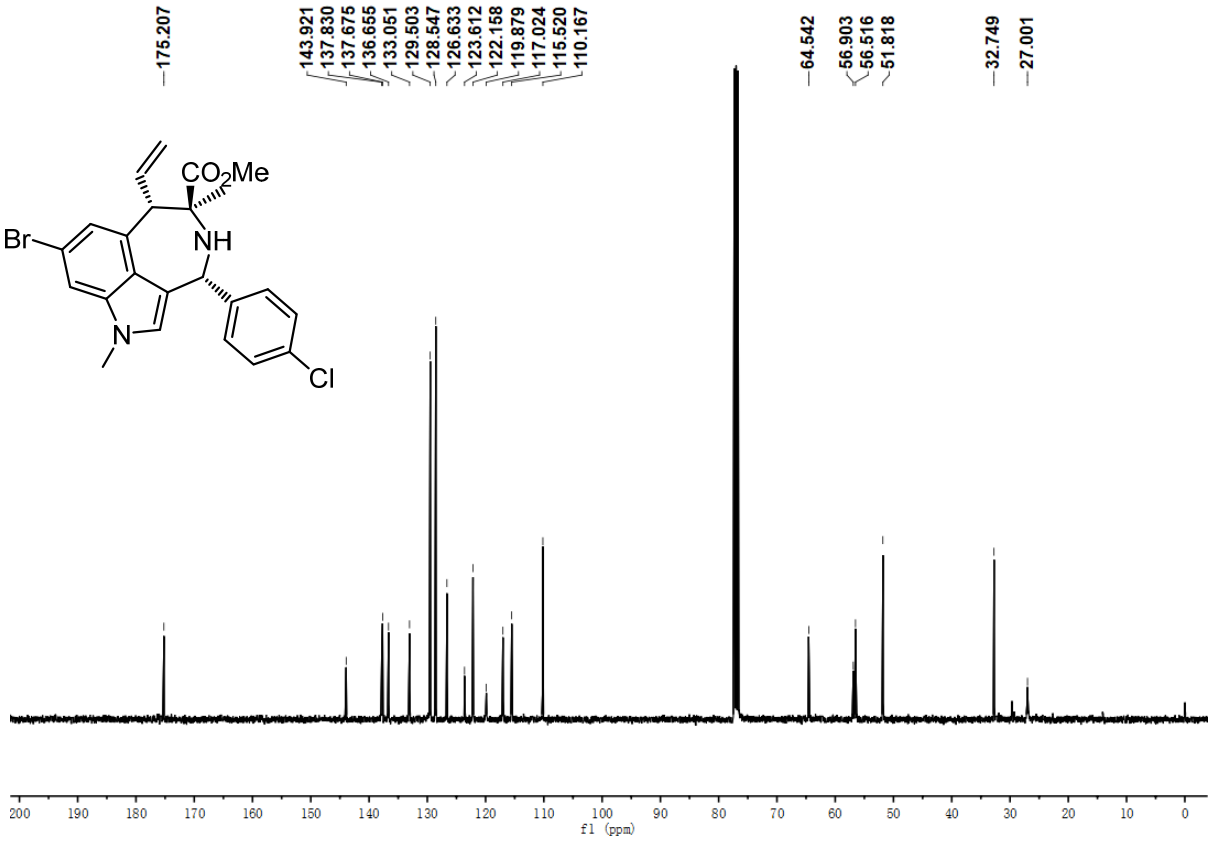
^{19}F NMR (376 MHz) of (6*S*,7*S*,9*R*)-**3z** in $CDCl_3$



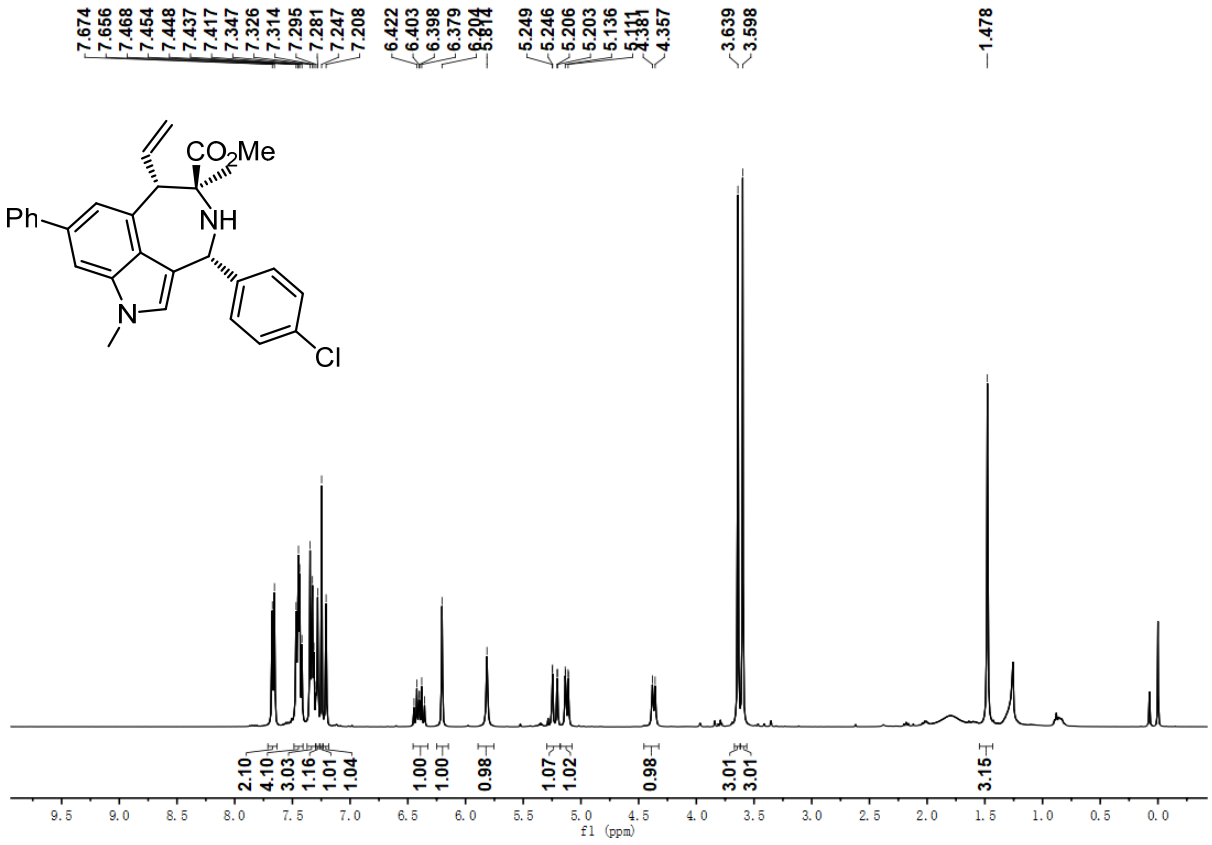
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3A** in $CDCl_3$



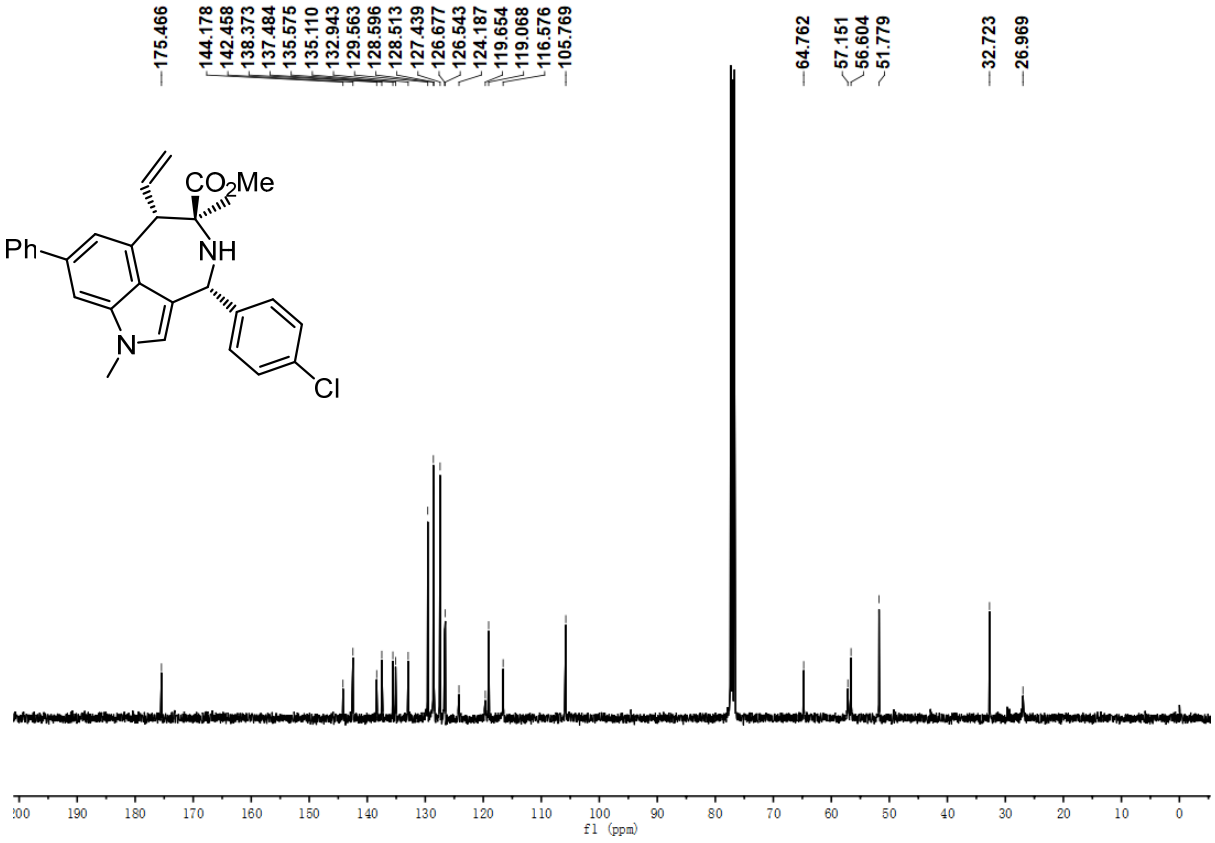
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3A** in $CDCl_3$



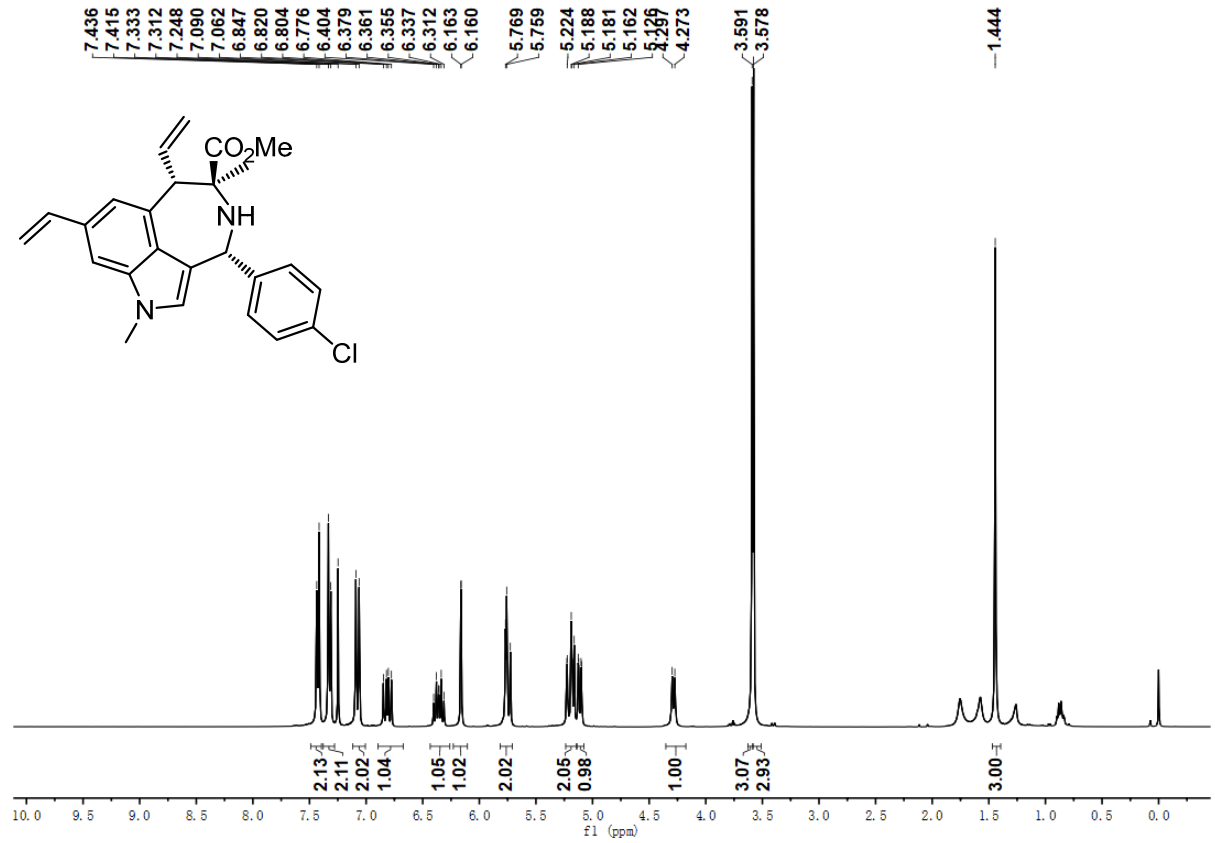
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3B** in $CDCl_3$



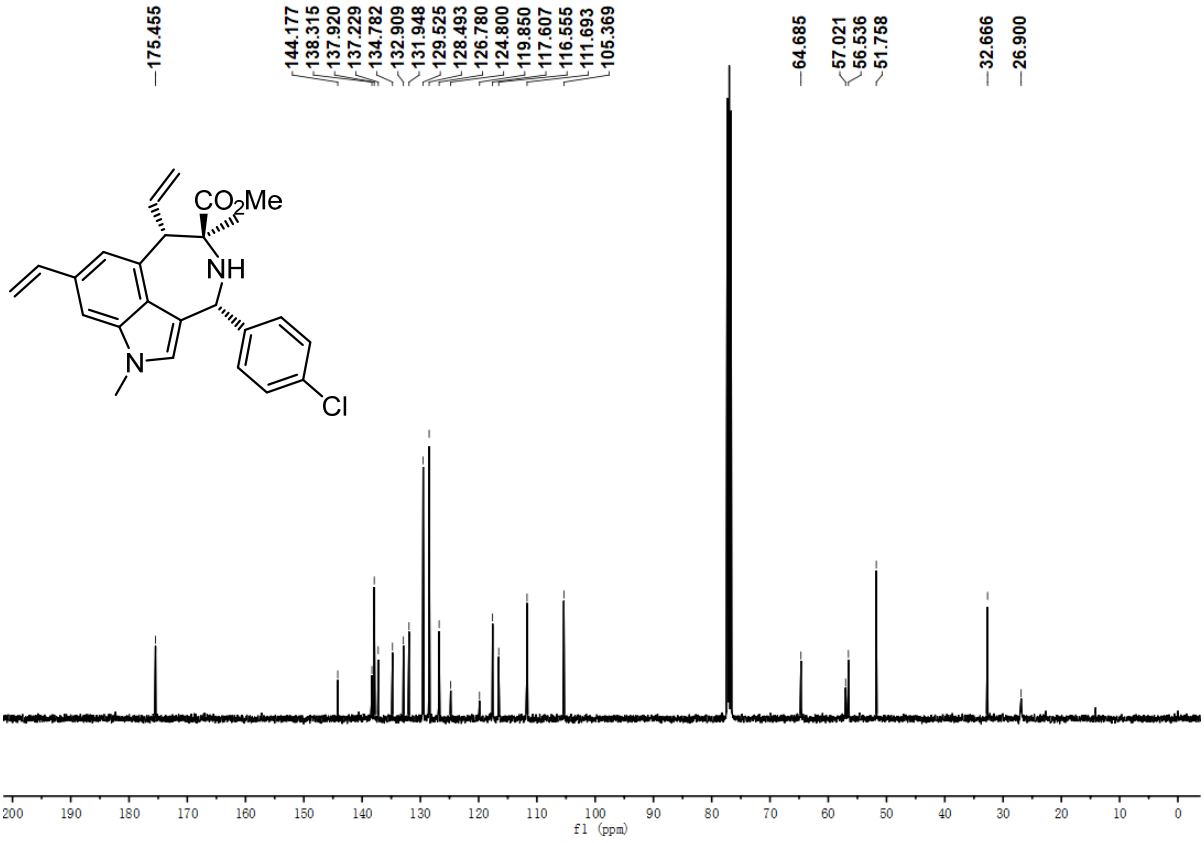
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3B** in $CDCl_3$



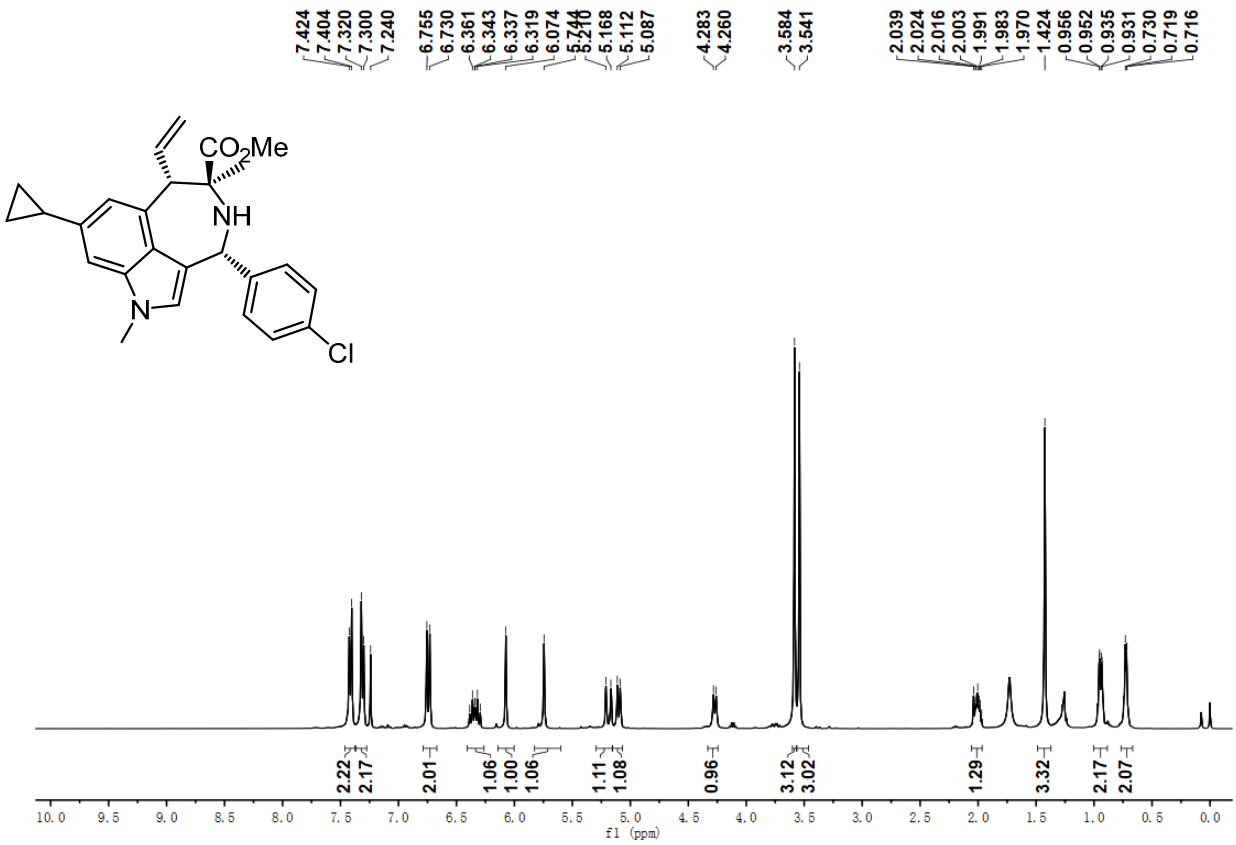
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3C** in $CDCl_3$



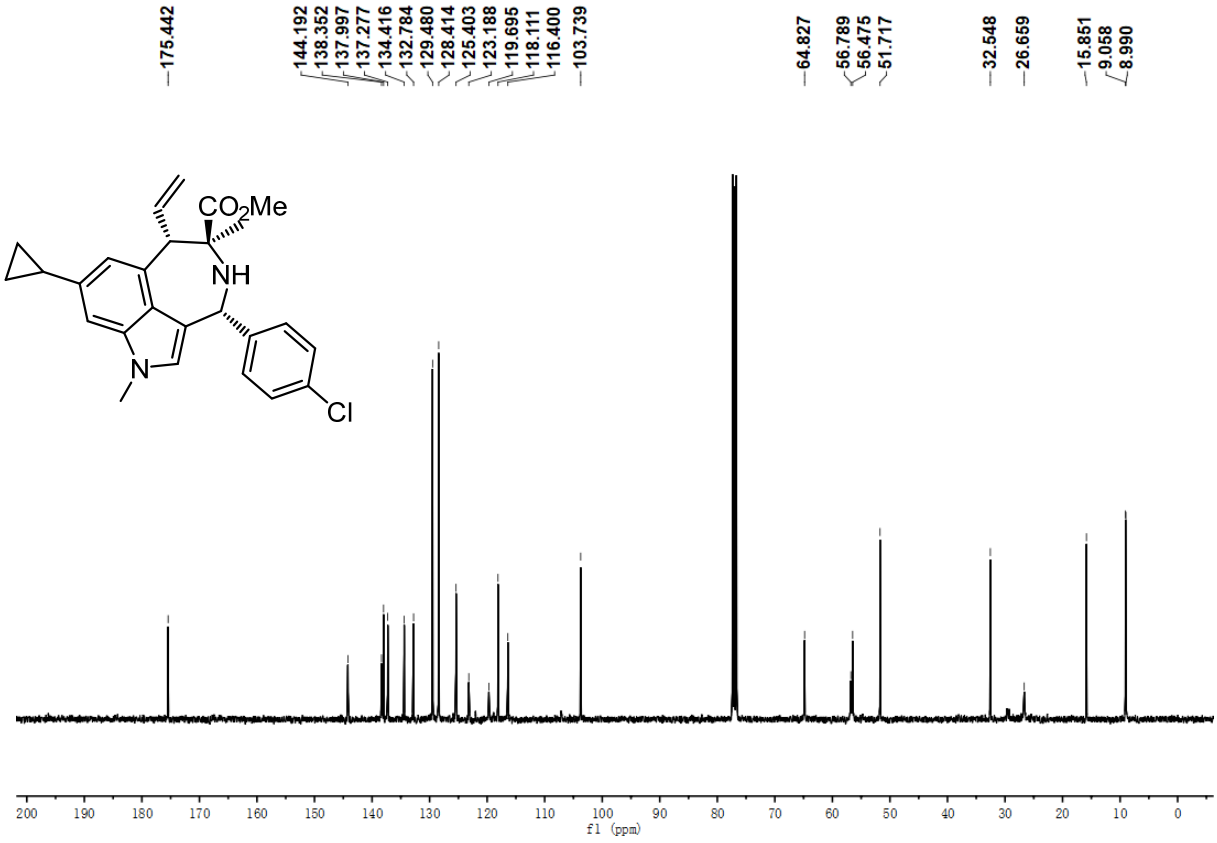
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3C** in $CDCl_3$



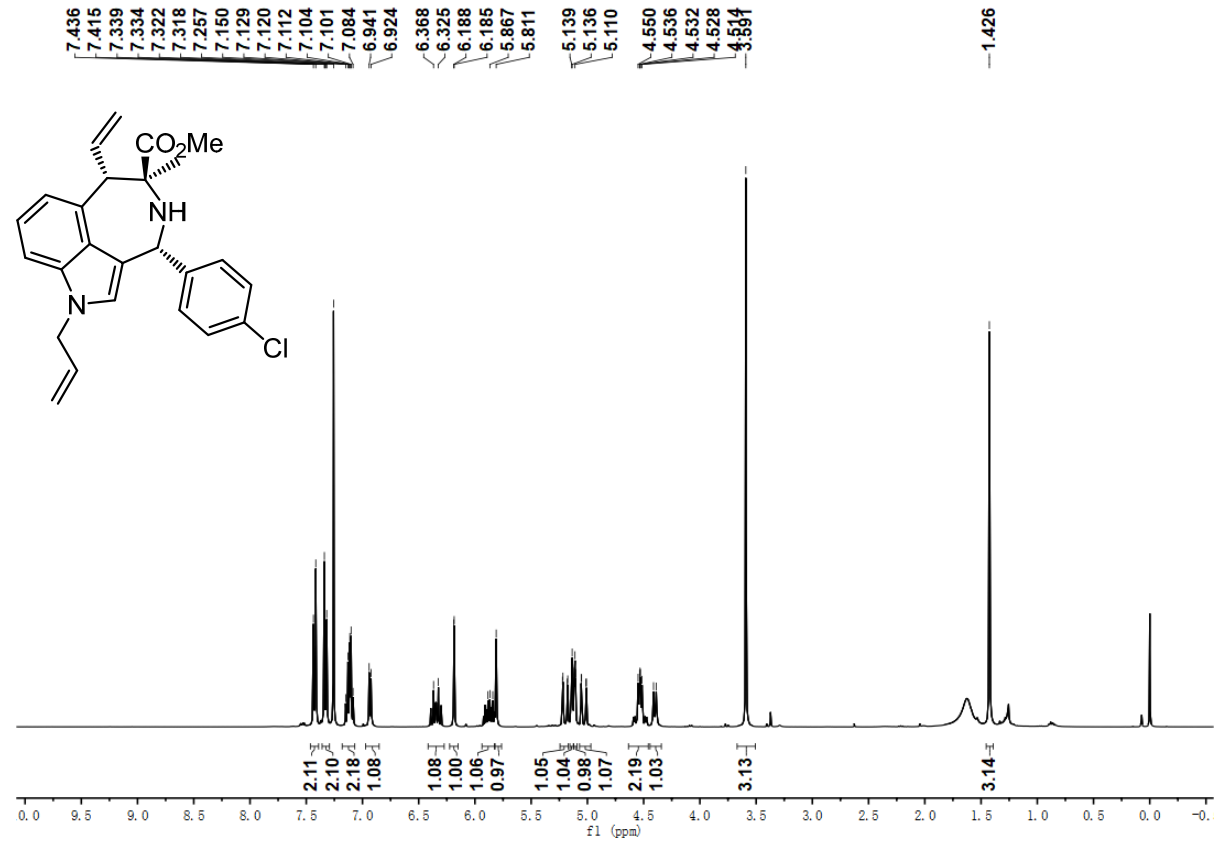
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3D** in $CDCl_3$



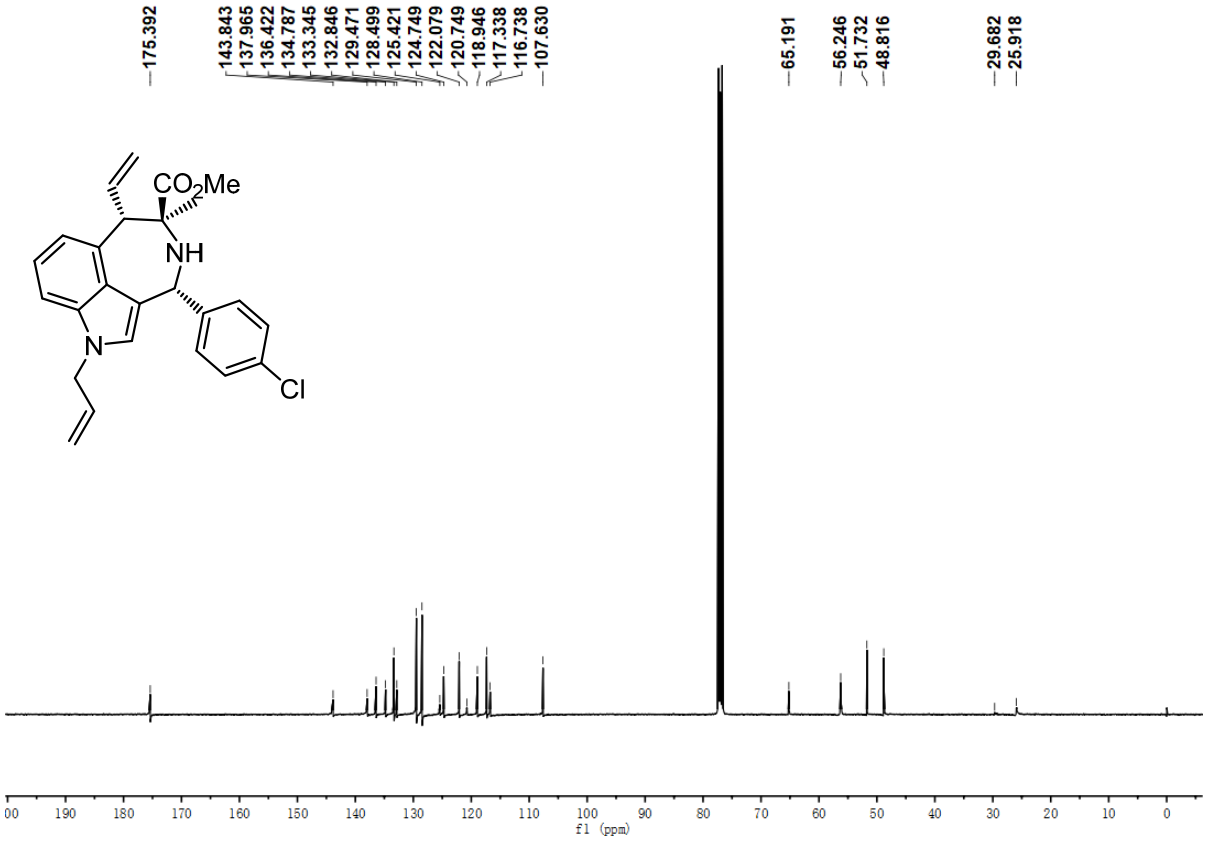
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3D** in $CDCl_3$



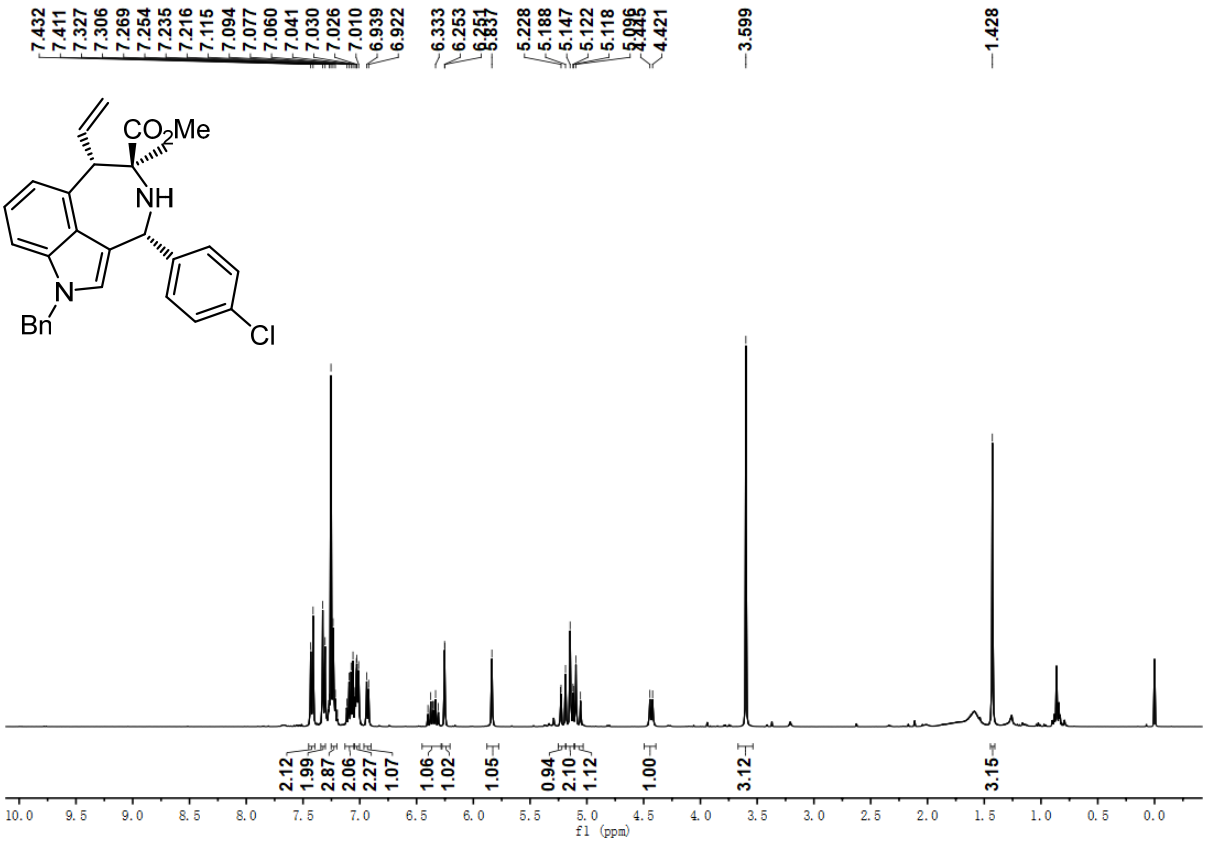
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3E** in $CDCl_3$



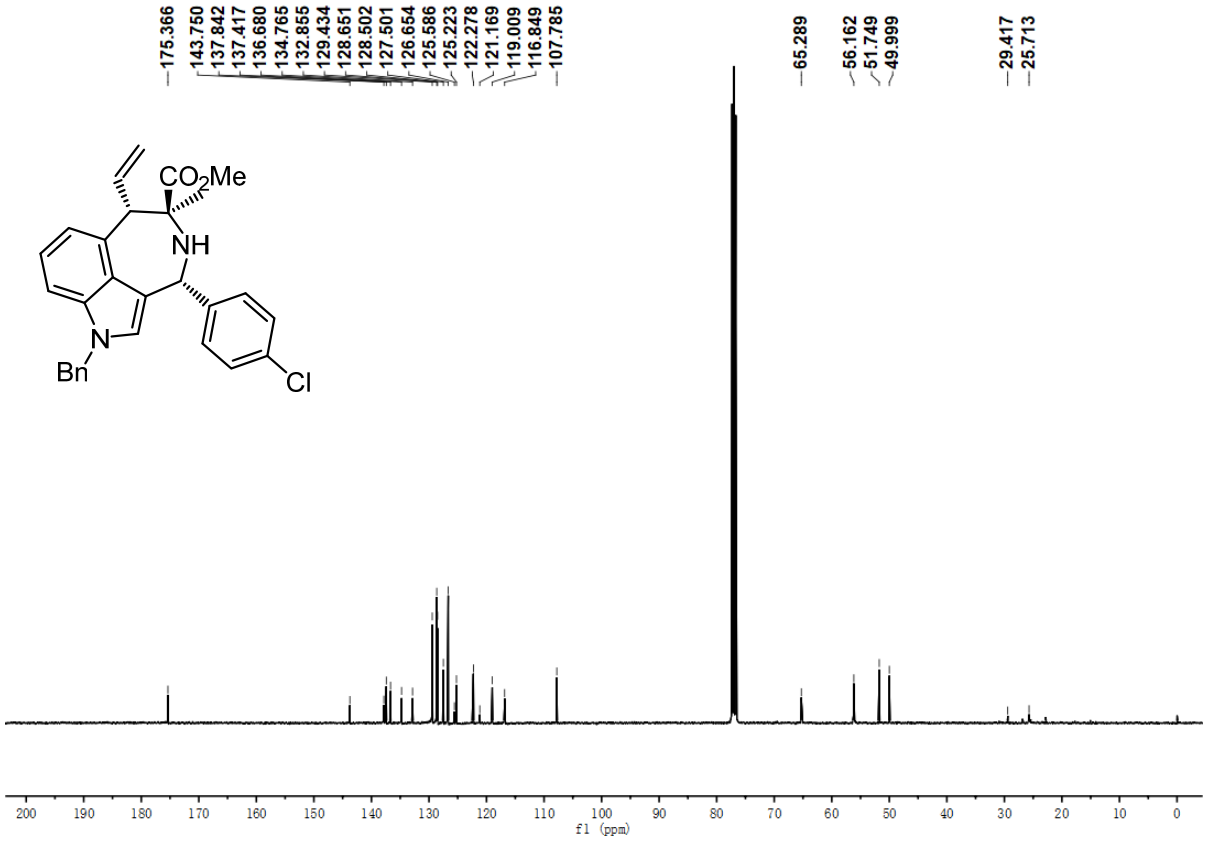
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3E** in $CDCl_3$



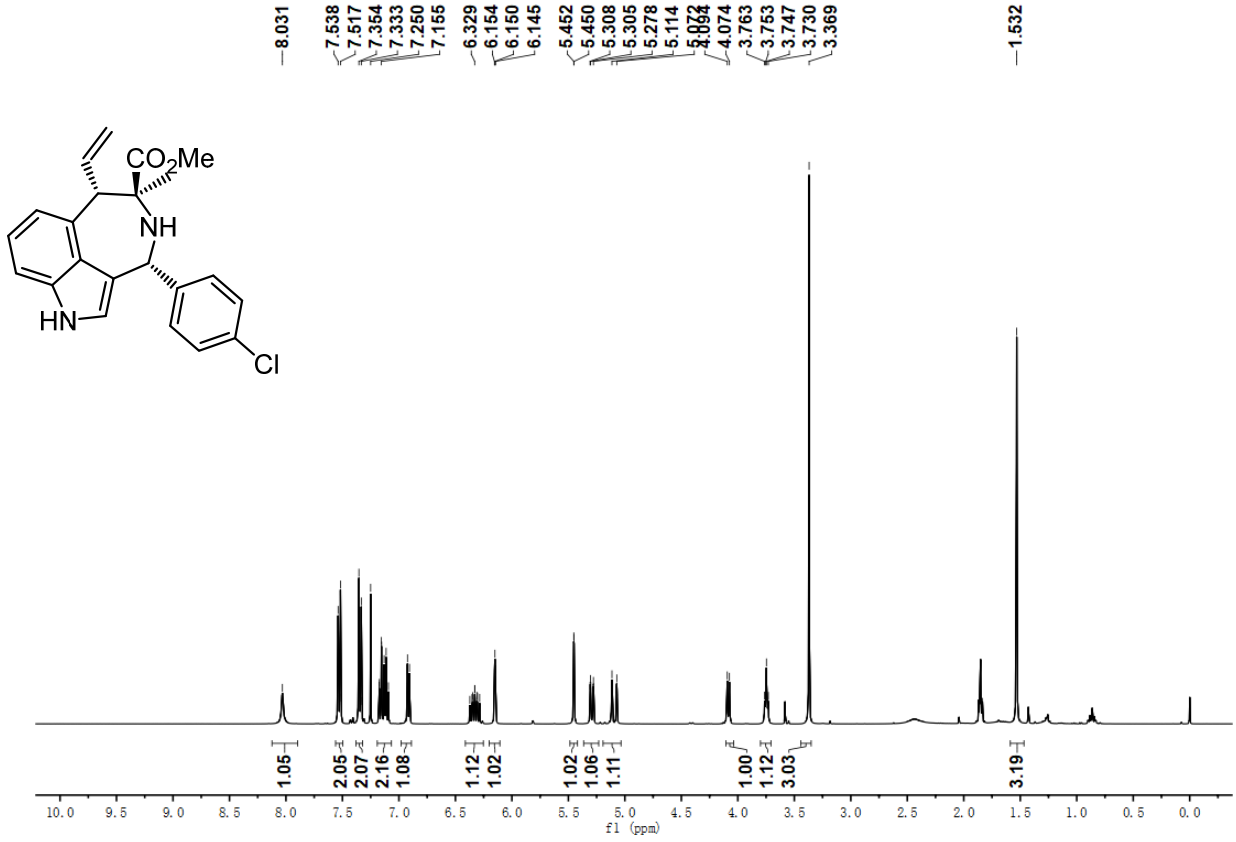
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3F** in $CDCl_3$



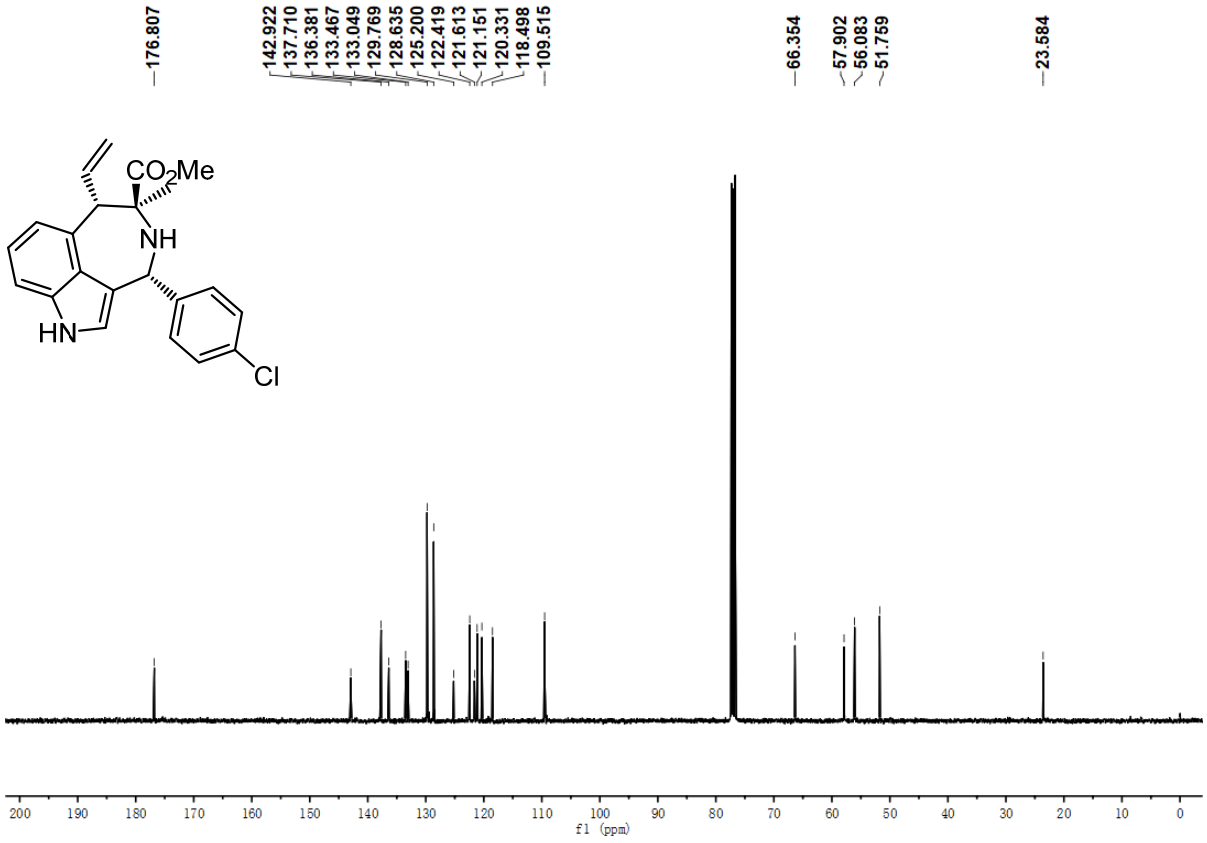
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3F** in $CDCl_3$



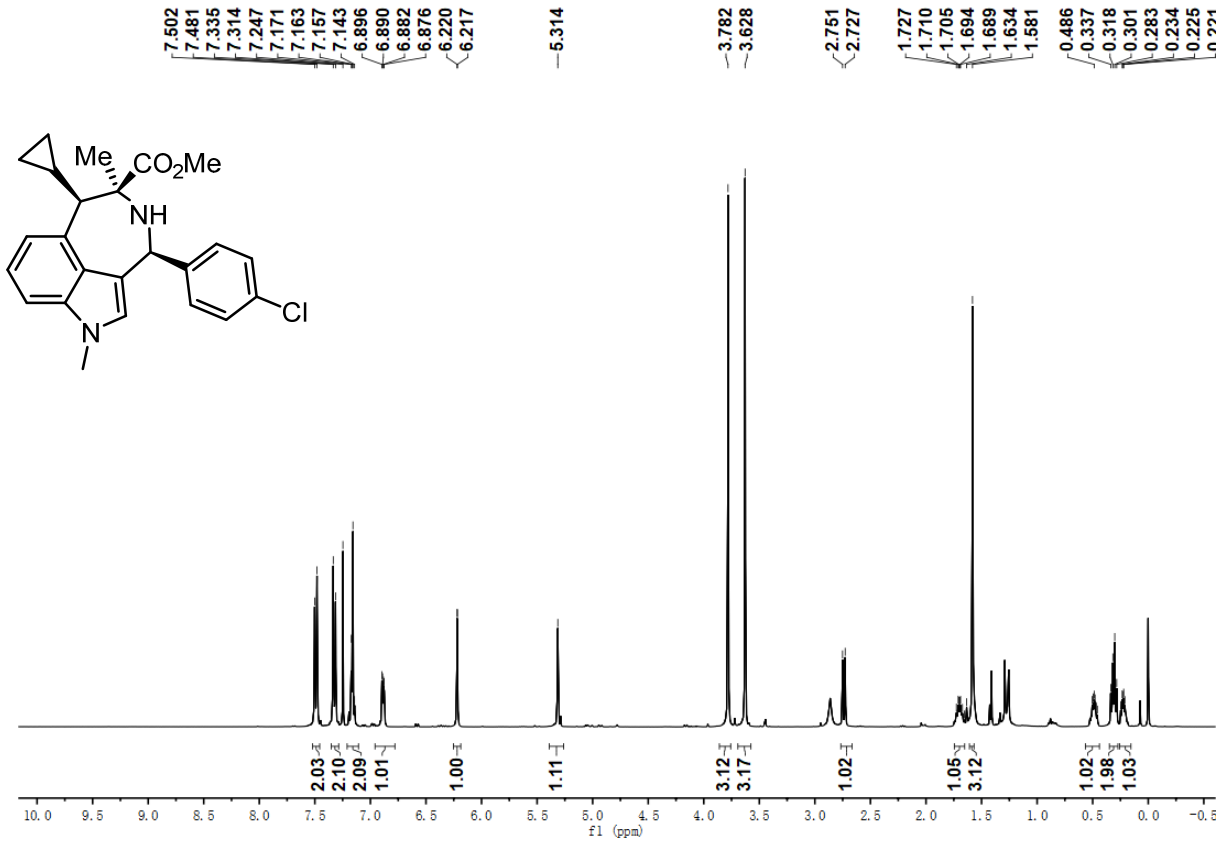
^{1}H NMR (400 MHz) of (6*S*,7*S*,9*R*)-**3G** in $CDCl_3$



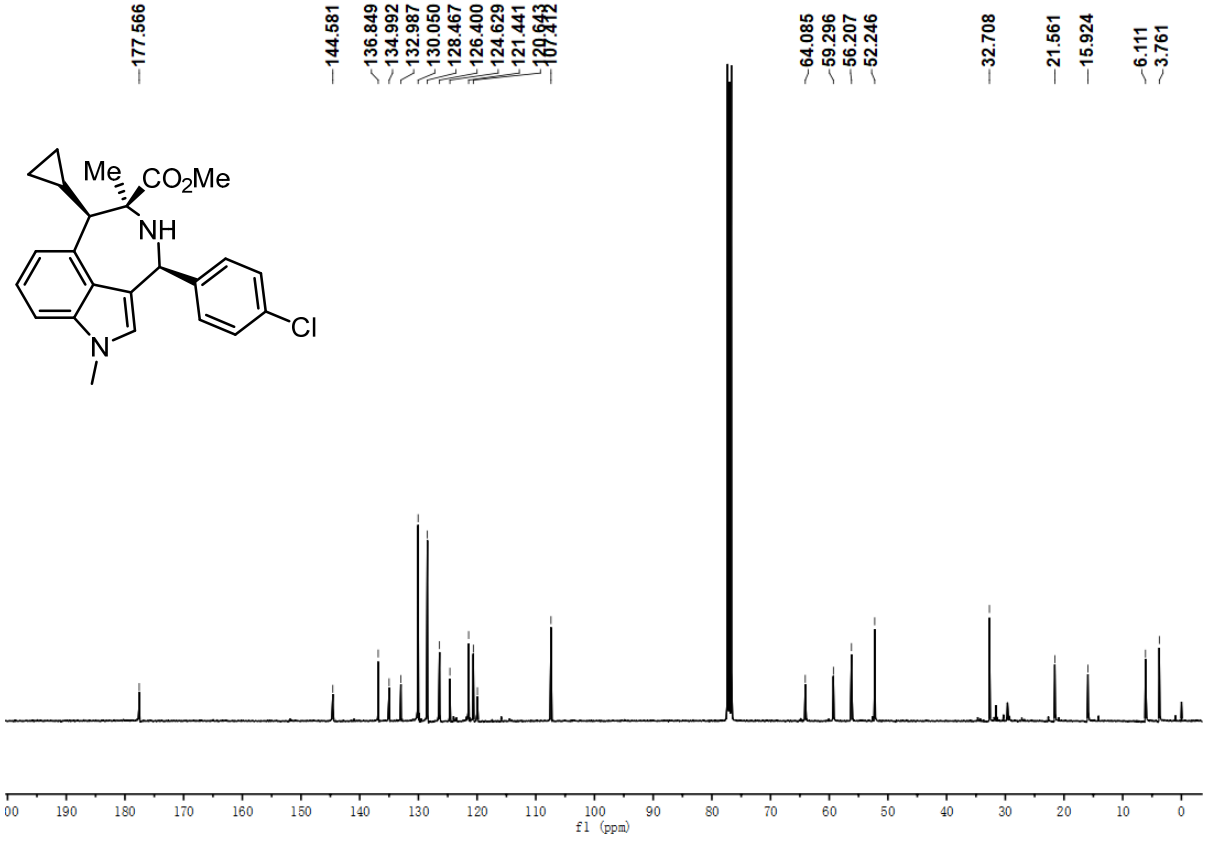
^{13}C NMR (101 MHz) of (6*S*,7*S*,9*R*)-**3G** in $CDCl_3$



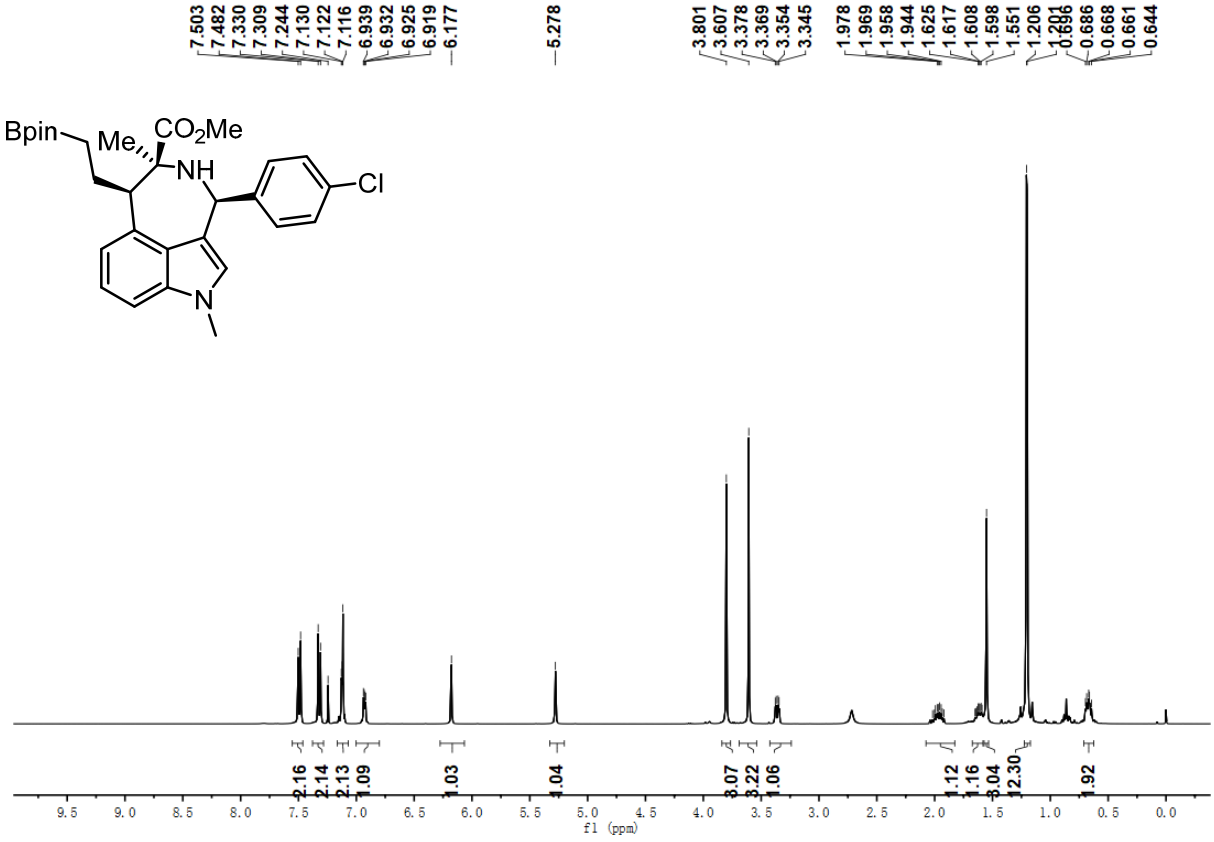
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**4** in $CDCl_3$



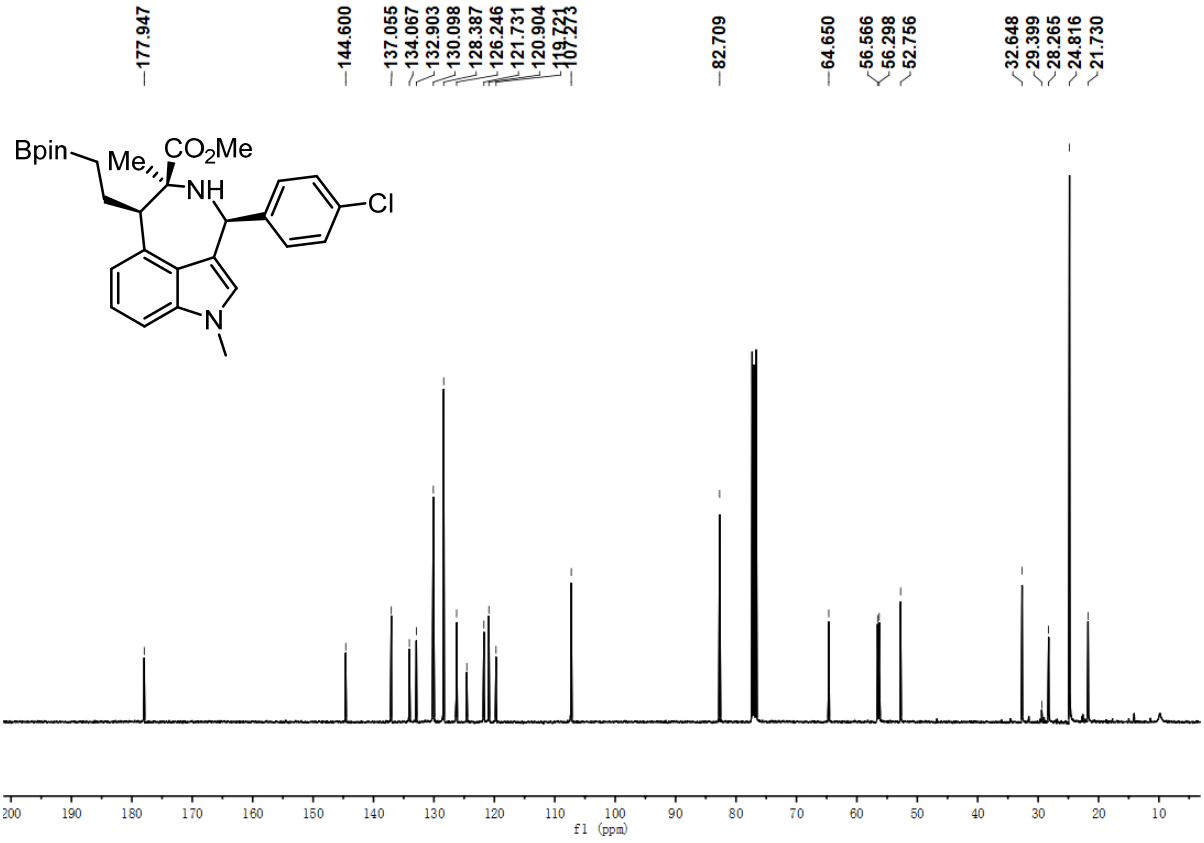
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**4** in $CDCl_3$



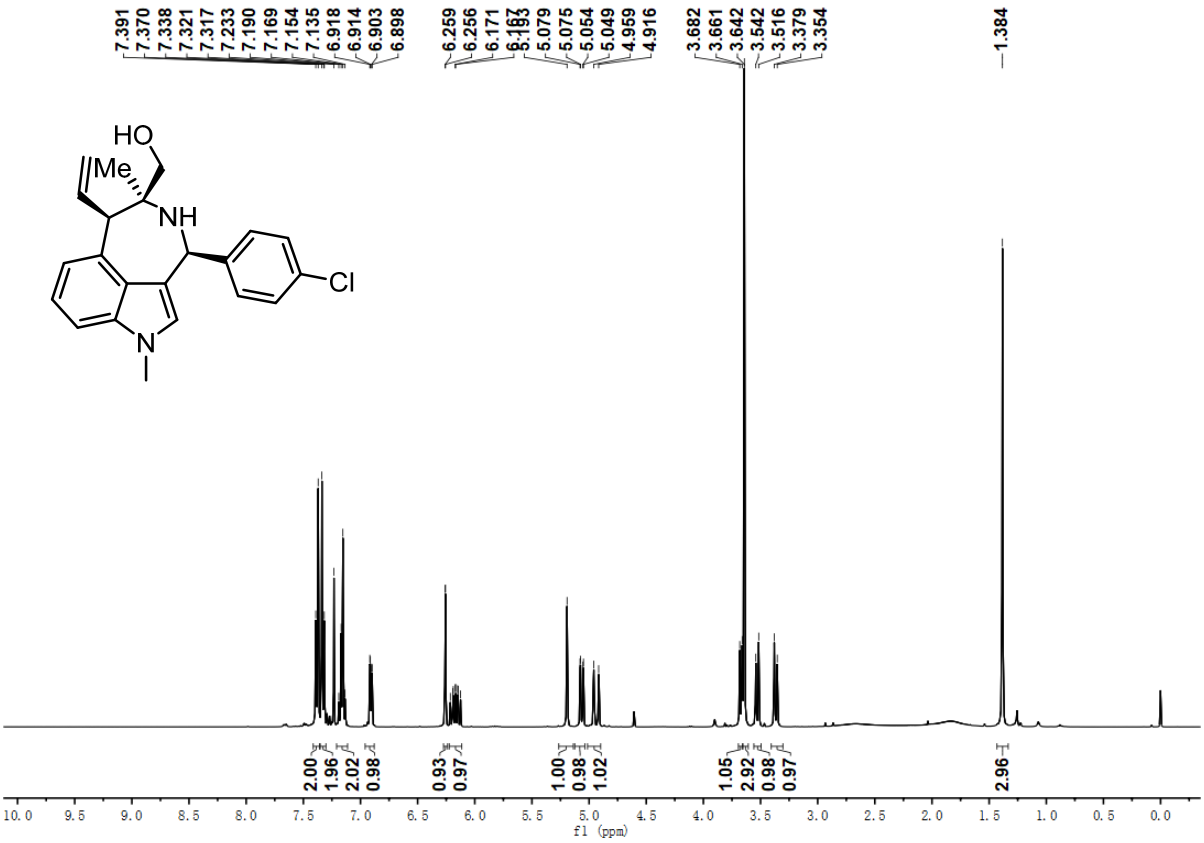
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**5** in $CDCl_3$



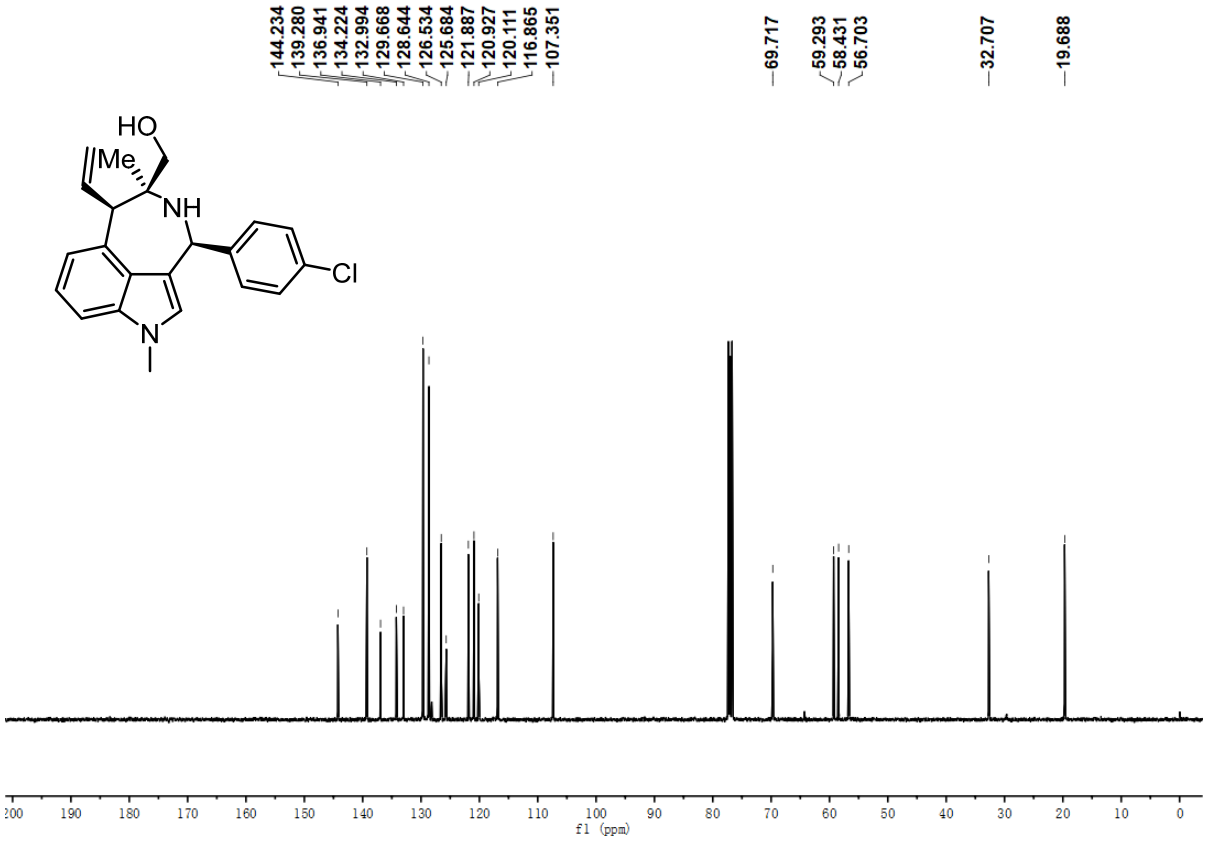
^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**5** in $CDCl_3$



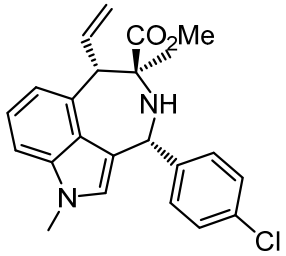
^{1}H NMR (400 MHz) of (6*R*,7*S*,9*S*)-**6** in $CDCl_3$

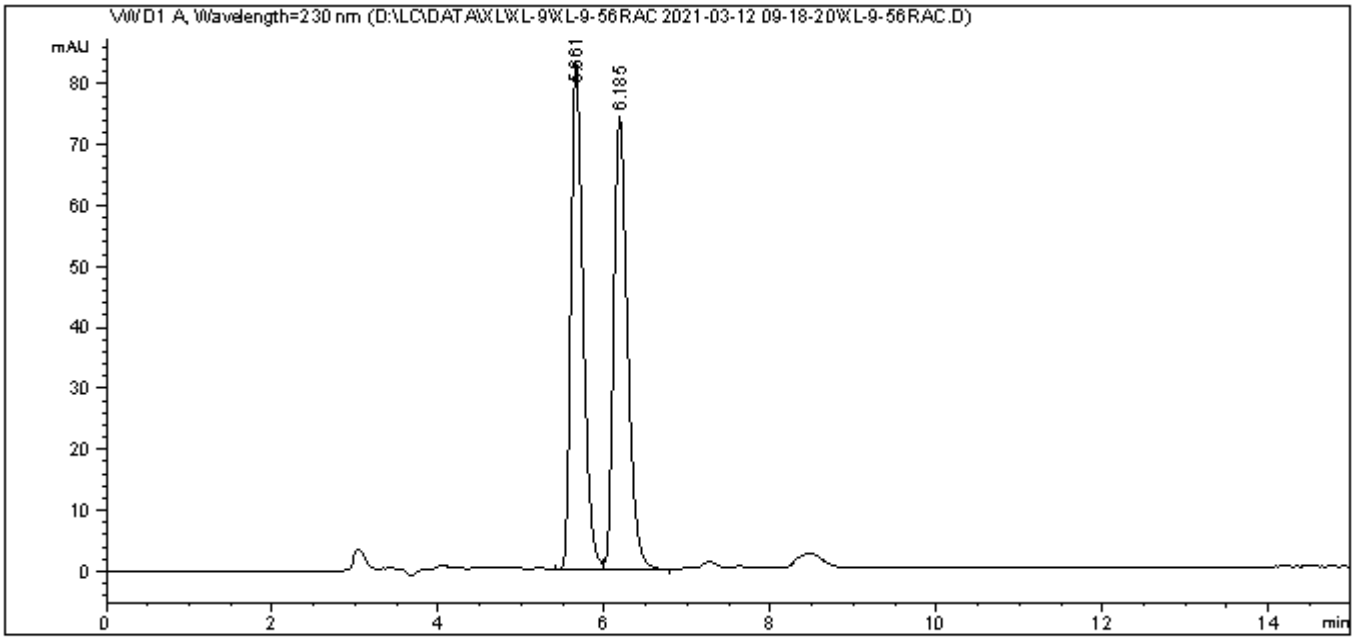


^{13}C NMR (101 MHz) of (6*R*,7*S*,9*S*)-**6** in $CDCl_3$



HPLC chromatogram of compound (*rac*)-3a [(6*S*,7*S*,9*R*)-3a + (6*R*,7*R*,9*S*)-3a]



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=====================================================================
                        Area Percent Report
=====================================================================

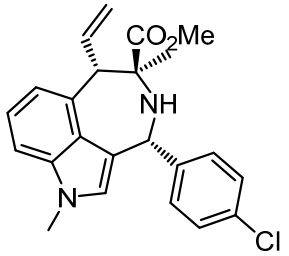
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

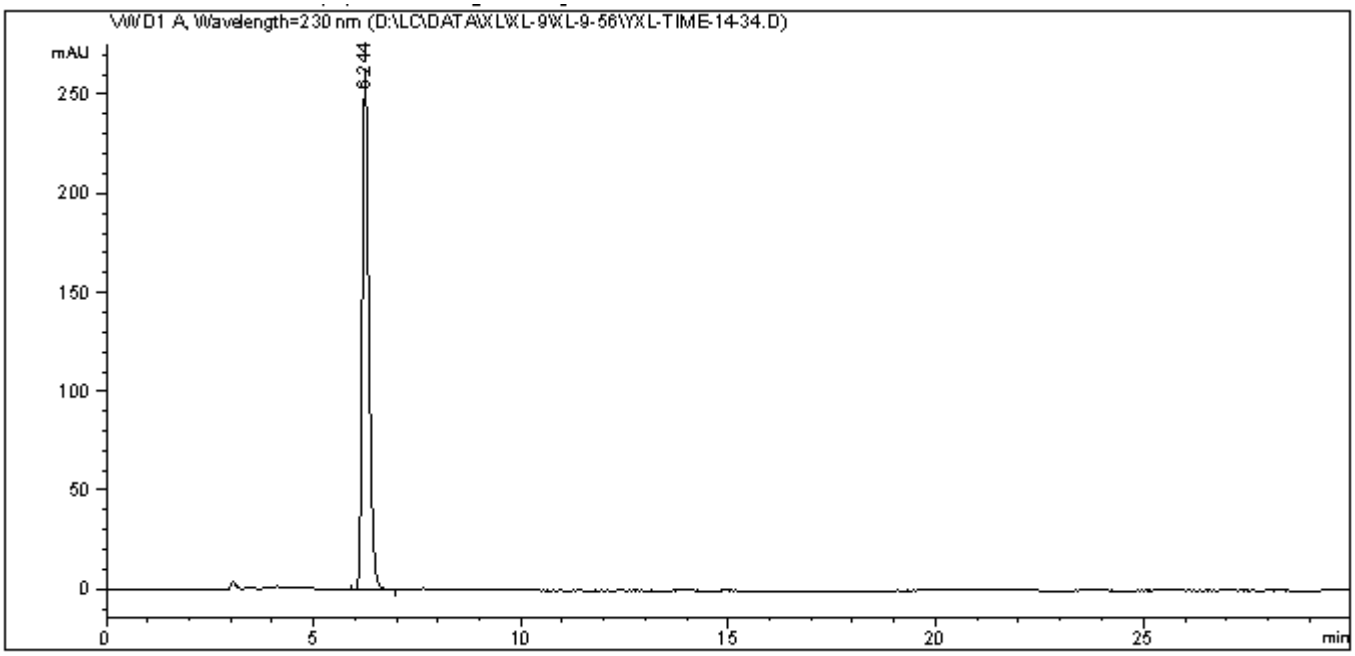

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.661 BV    0.1559  851.66162   83.12485  50.0017
   2   6.185 VB    0.1745  851.60272   74.30883  49.9983

Totals :                  1703.26434  157.43368
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.244 BB    0.1728 2980.98779  263.30911 100.0000

Totals :                  2980.98779  263.30911

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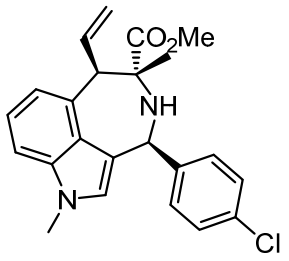
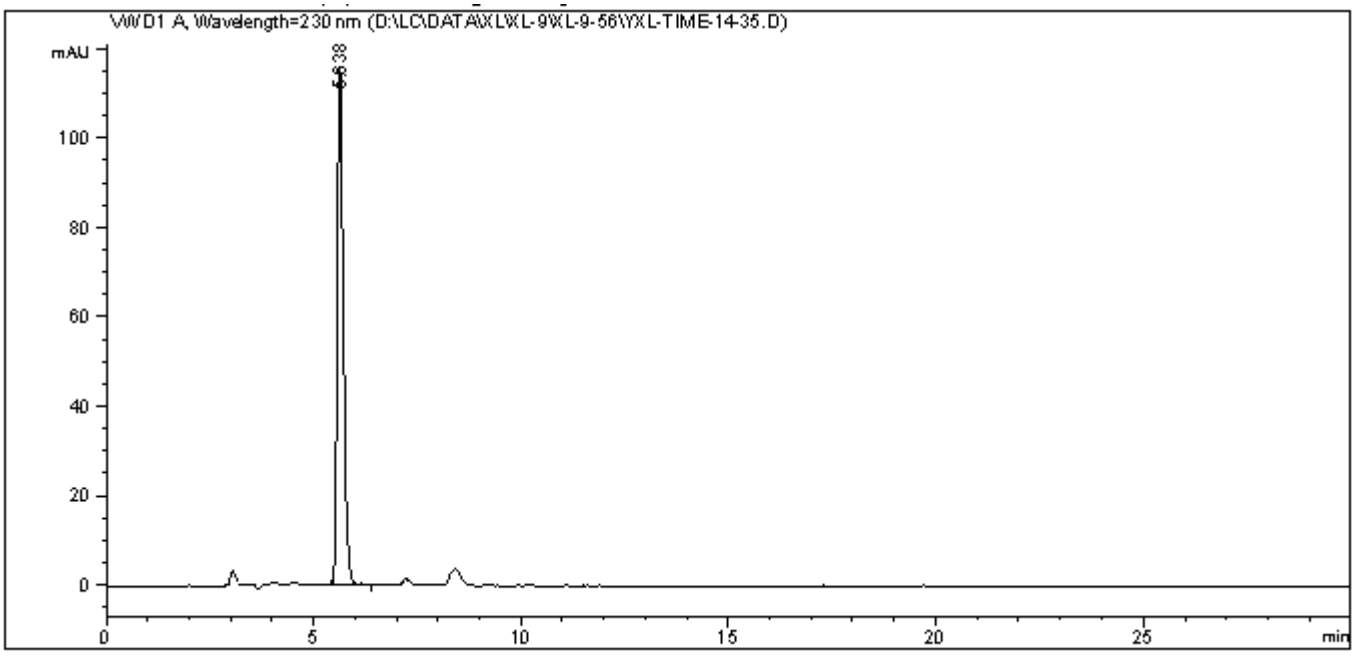
HPLC chromatogram of compound (6*R*,7*R*,9*S*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.638 BV R  0.1552 1176.58679  115.58137 100.0000

Totals :                  1176.58679  115.58137

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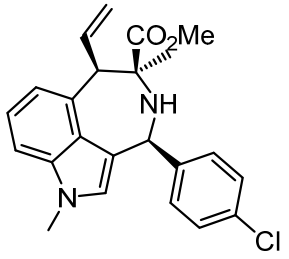
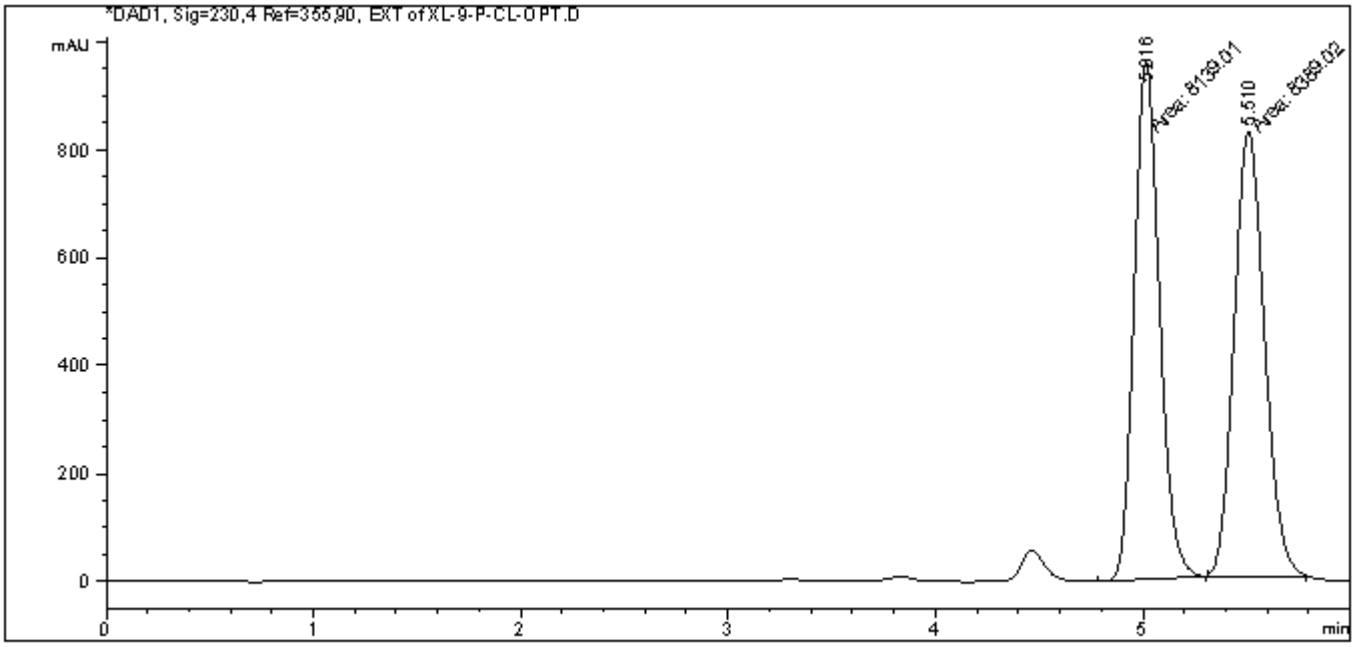
HPLC chromatogram of compound (*rac*)-3a [(*6R,7S,9S*)-3a + (6*S*,7*R*,9*R*)-3a]



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.016 MM    0.1414 8139.00537  959.13647  49.2437
   2   5.510 MM    0.1697 8389.01758  824.11896  50.7563

Totals :                  1.65280e4  1783.25543


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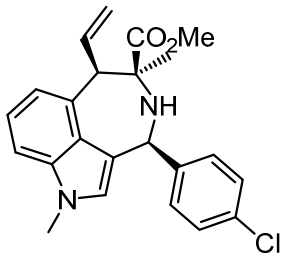
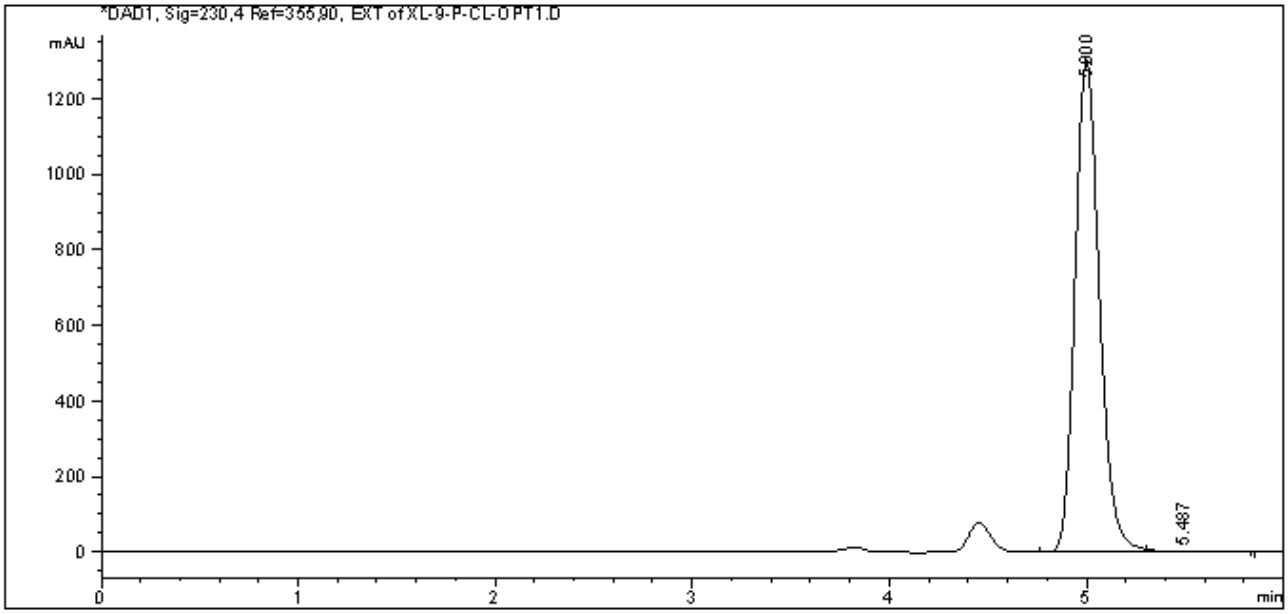
HPLC chromatogram of compound (*6R,7S,9S*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.000 BV R  0.1324 1.12364e4  1305.22974  99.6927
   2   5.487 VB E  0.1570   34.63268    3.23317   0.3073

Totals :                  1.12710e4  1308.46291

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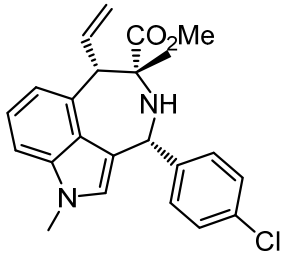
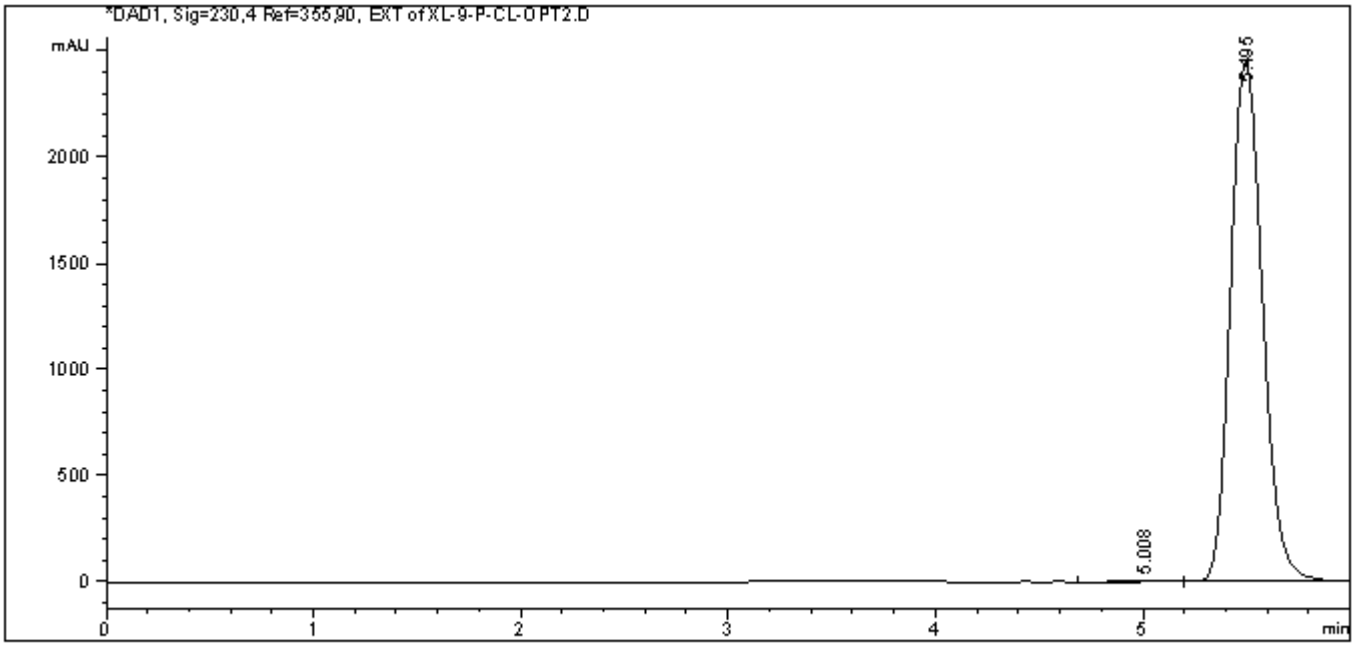
HPLC chromatogram of compound (6*S*,7*R*,9*R*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.008 BV    0.1321   73.13862    8.52303   0.2756
   2   5.495 VB    0.1682 2.64668e4  2447.50879  99.7244

Totals :                  2.65400e4  2456.03182


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                        *** End of Report ***
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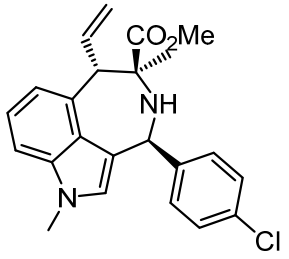
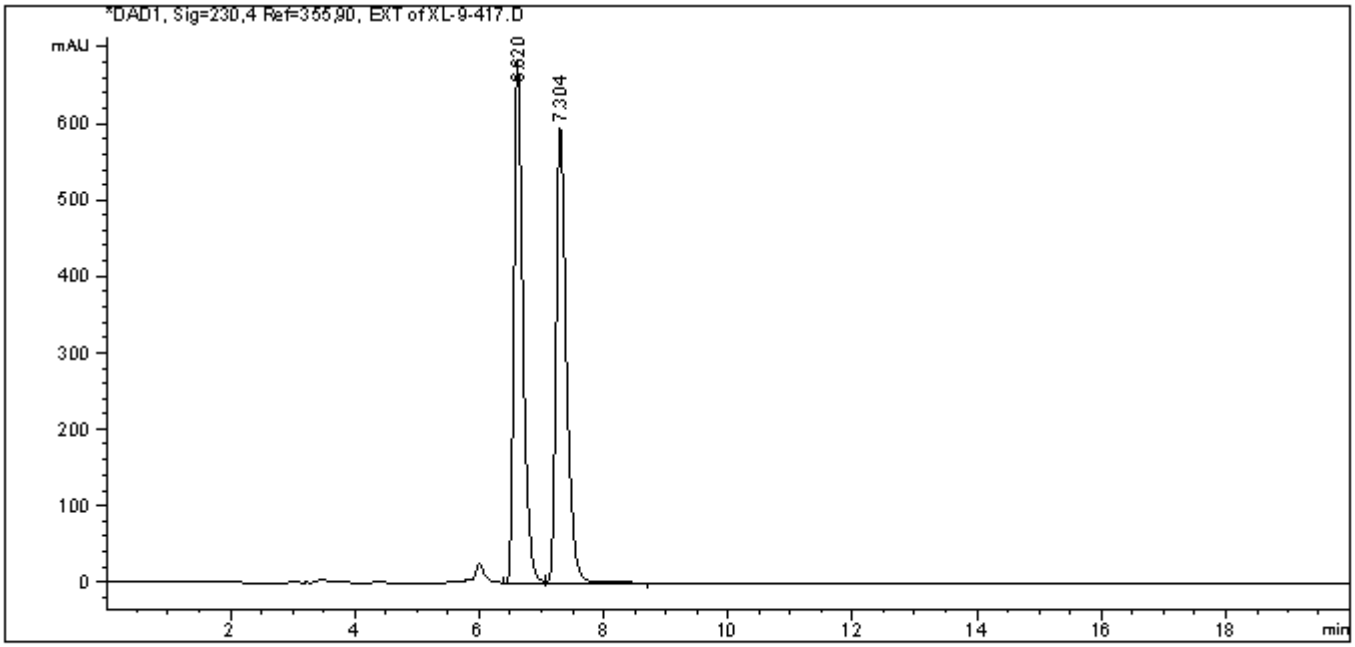
HPLC chromatogram of compound (*rac*)-3a [(6*S*,7*S*,9*S*)-3a + (6*R*,7*R*,9*R*)-3a]



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.620 BV    0.1490 6832.64551  681.40723  50.0163
   2   7.304 VB    0.1719 6828.19971  594.87445  49.9837

Totals :                  1.36608e4  1276.28168


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                        *** End of Report ***
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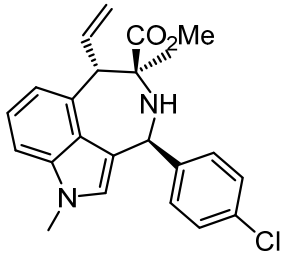
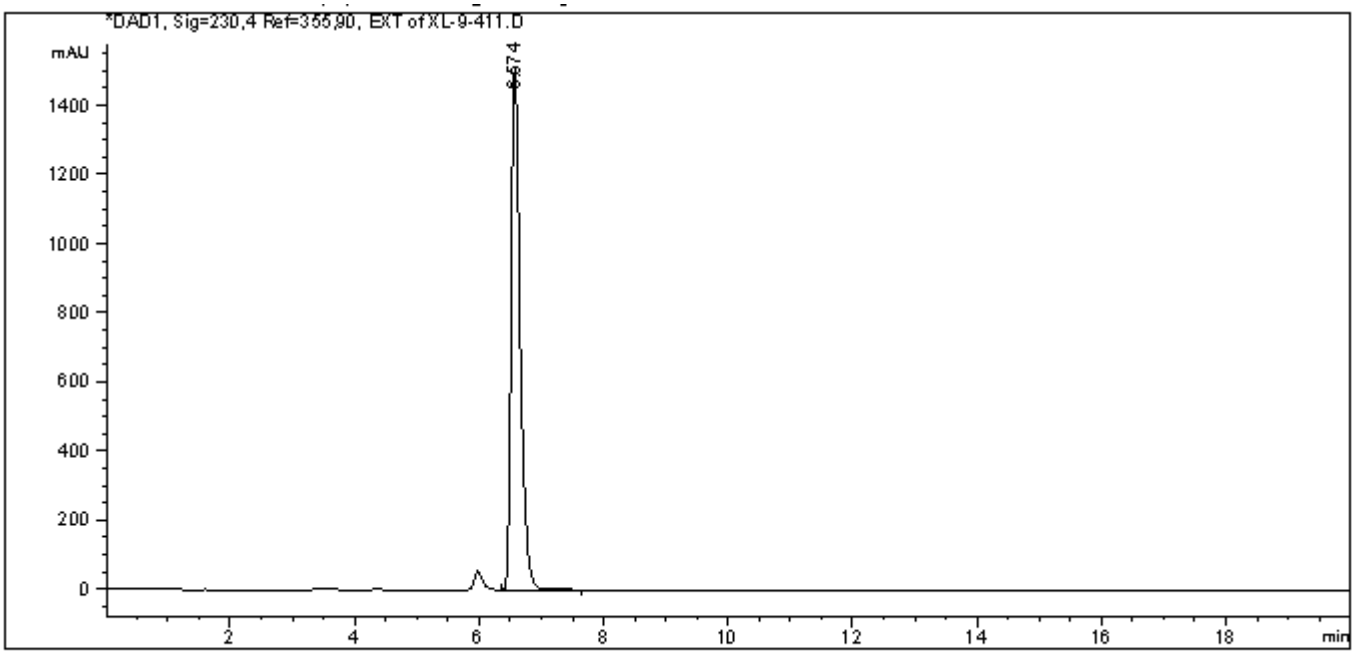
HPLC chromatogram of compound (6*S*,7*S*,9*S*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.574 BB    0.1508 1.51093e4  1508.81506 100.0000

Totals :                  1.51093e4  1508.81506

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                        *** End of Report ***
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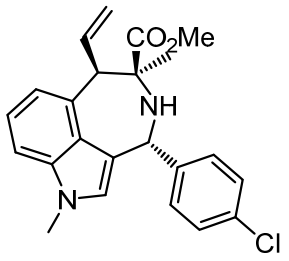
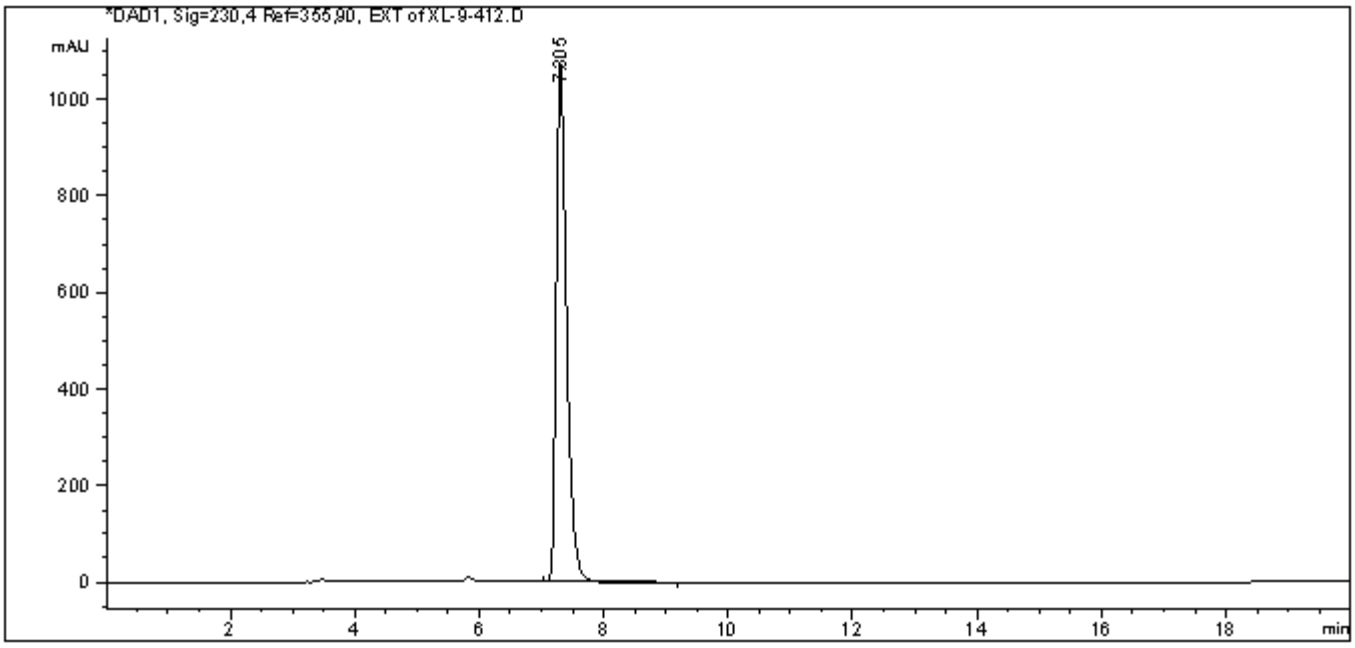
HPLC chromatogram of compound (6*R*,7*R*,9*R*)-3a



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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.305 BB    0.1726 1.2379le4  1073.22412 100.0000

Totals :                  1.2379le4  1073.22412


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                        *** End of Report ***
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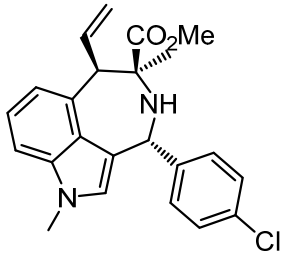
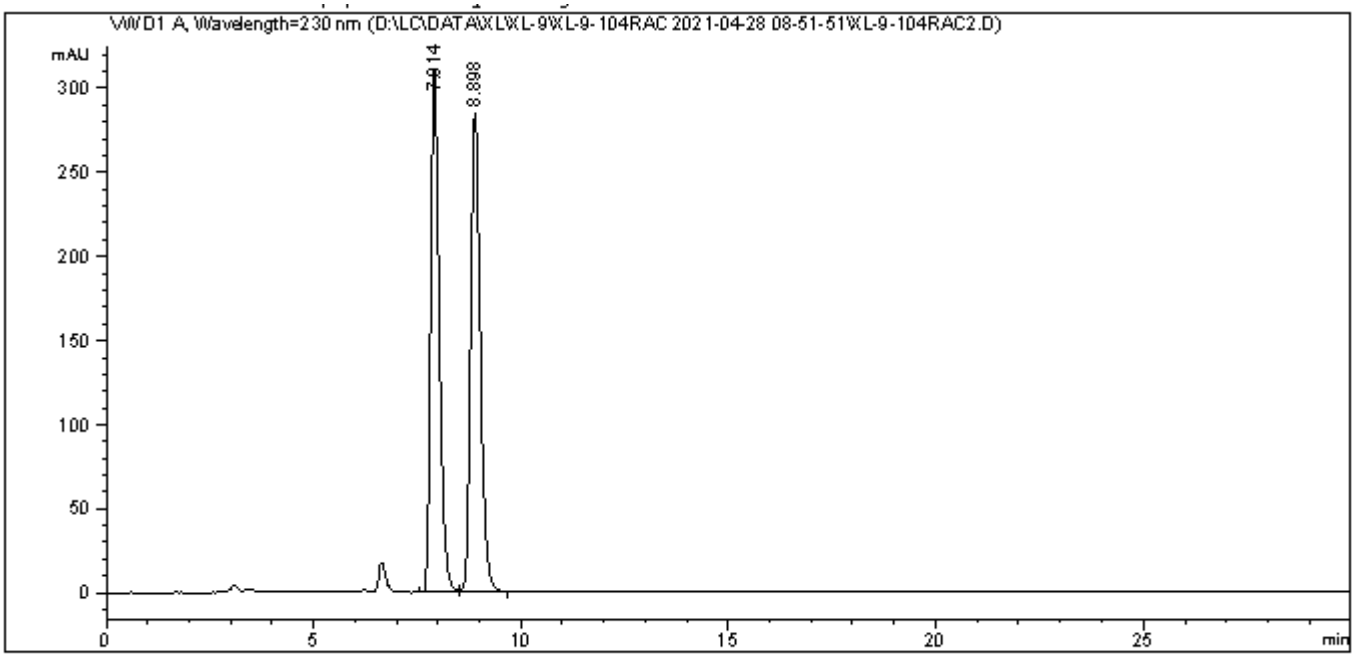
HPLC chromatogram of compound (*rac*)-3a [(6*R*,7*S*,9*R*)-3a + (6*S*,7*R*,9*S*)-3a]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.914 BV    0.2262 4582.09277  310.17975  49.7308
   2   8.898 VB    0.2492 4631.70898  285.21521  50.2692

Totals :                  9213.80176  595.39496


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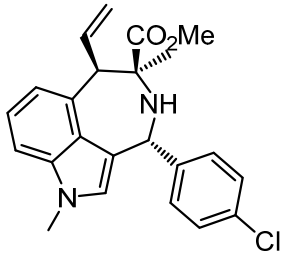
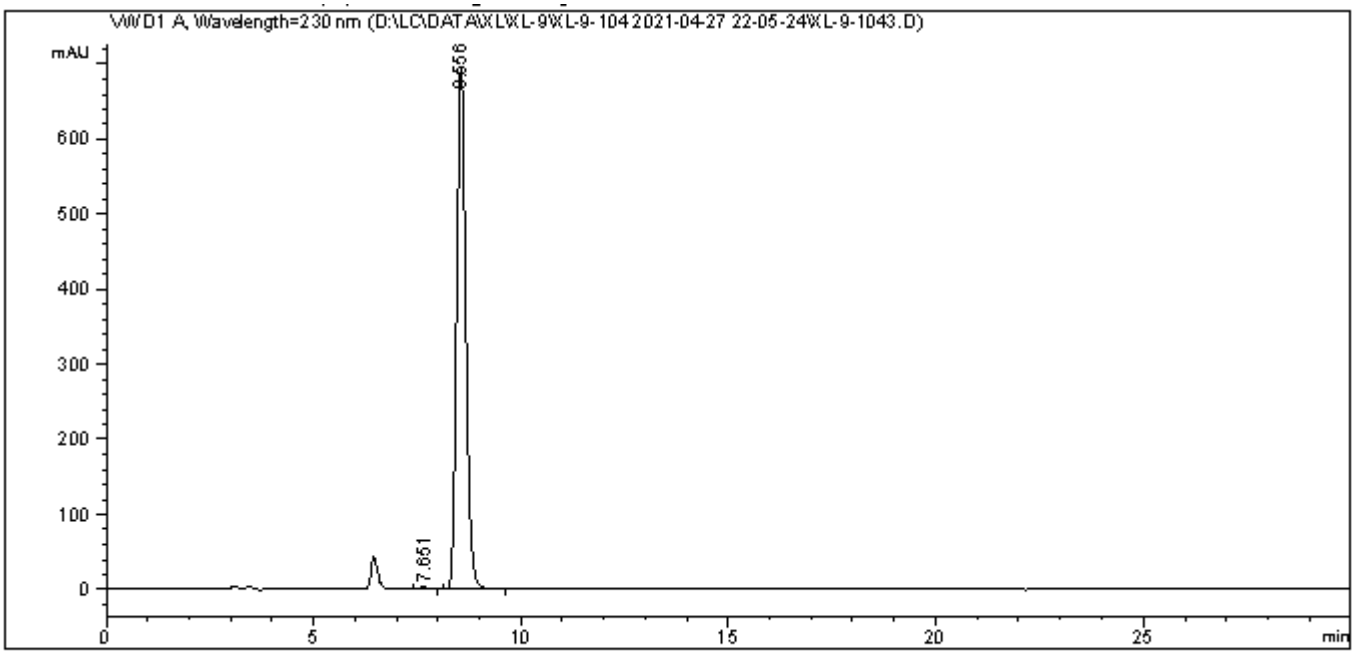
HPLC chromatogram of compound (6*R*,7*S*,9*R*)-3a



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.651 BB    0.2013   29.84655    2.29325   0.2797
   2   8.556 BV R  0.2360 1.064lle4   692.69025  99.7203

Totals :                  1.06709e4   694.98350


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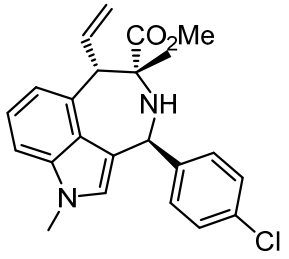
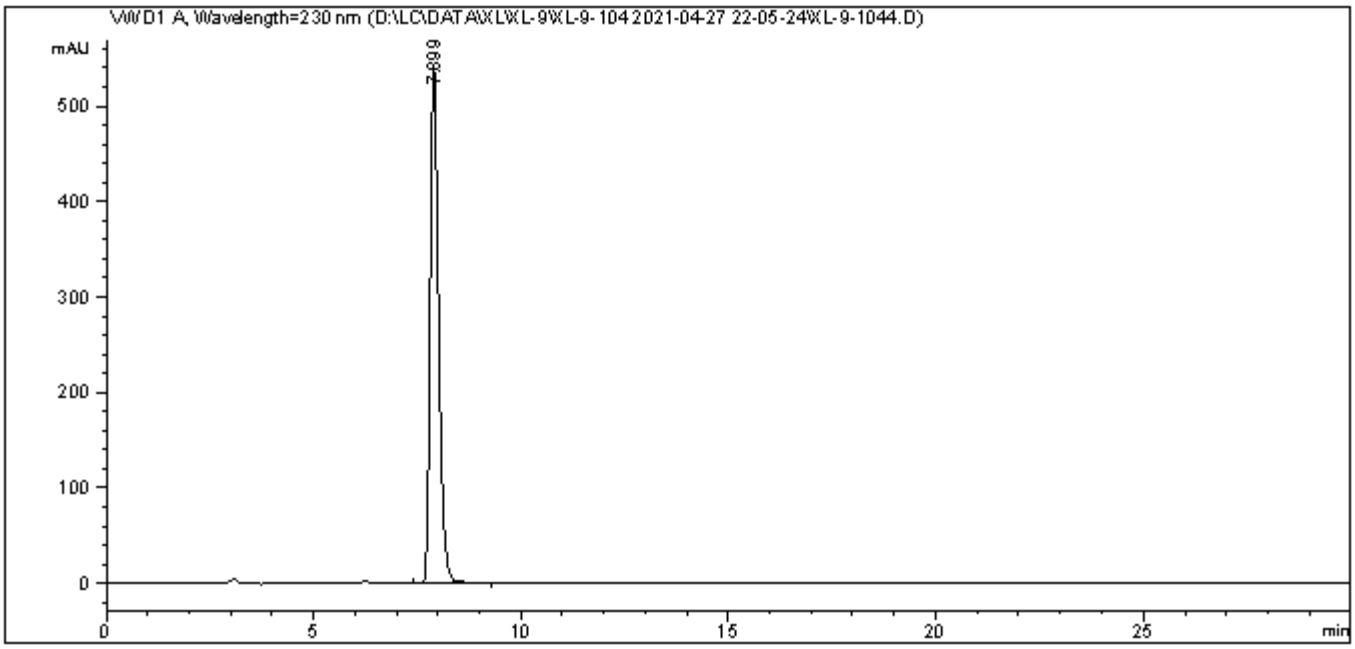
                        *** End of Report ***
```

HPLC chromatogram of compound (6*S*,7*R*,9*S*)-3a



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

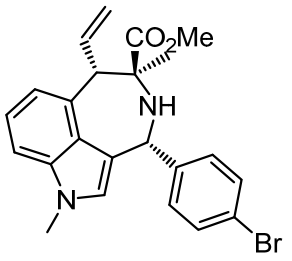

Signal 1: VWD1 A, Wavelength=230 nm

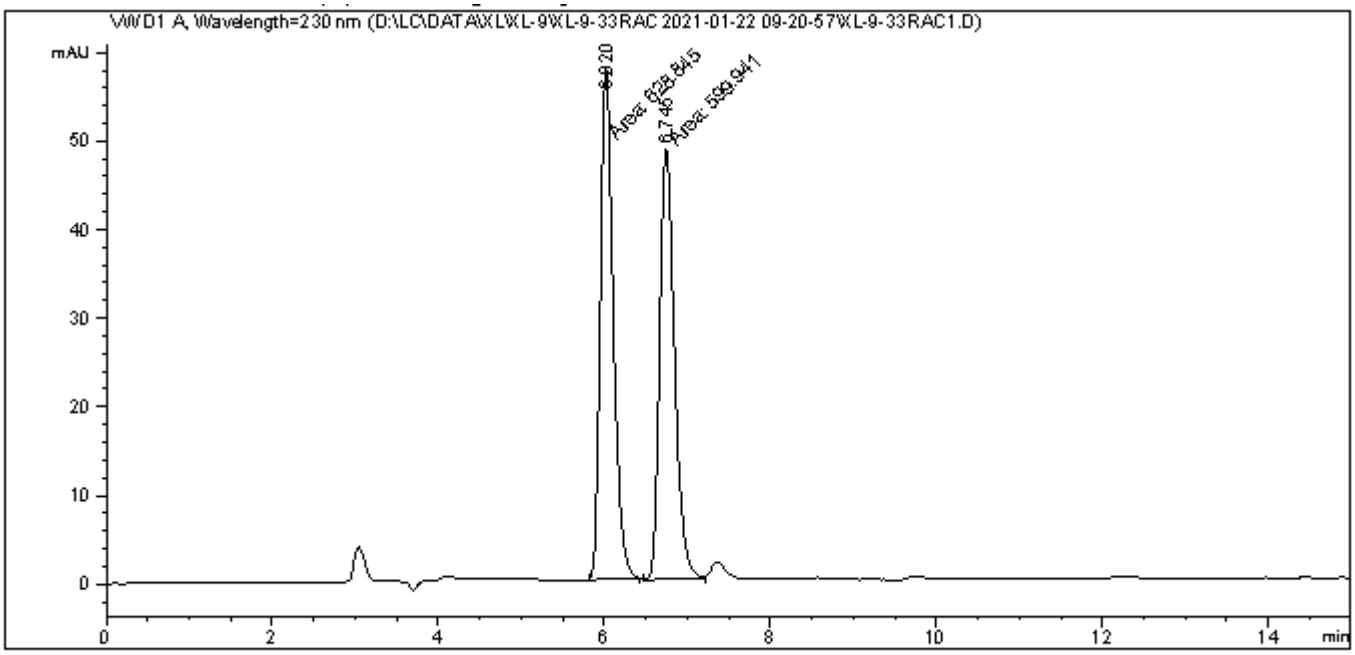
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.899 VV R  0.2209 7844.21289  543.11774 100.0000

Totals :                  7844.21289  543.11774


=====================================================================
                        *** End of Report ***
```

HPLC chromatogram of compound (*rac*)-3b [(6*S*,7*S*,9*R*)-3b + (6*R*,7*R*,9*S*)-3b]



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================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

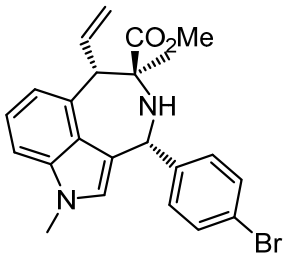

Signal 1: VWD1 A, Wavelength=230 nm

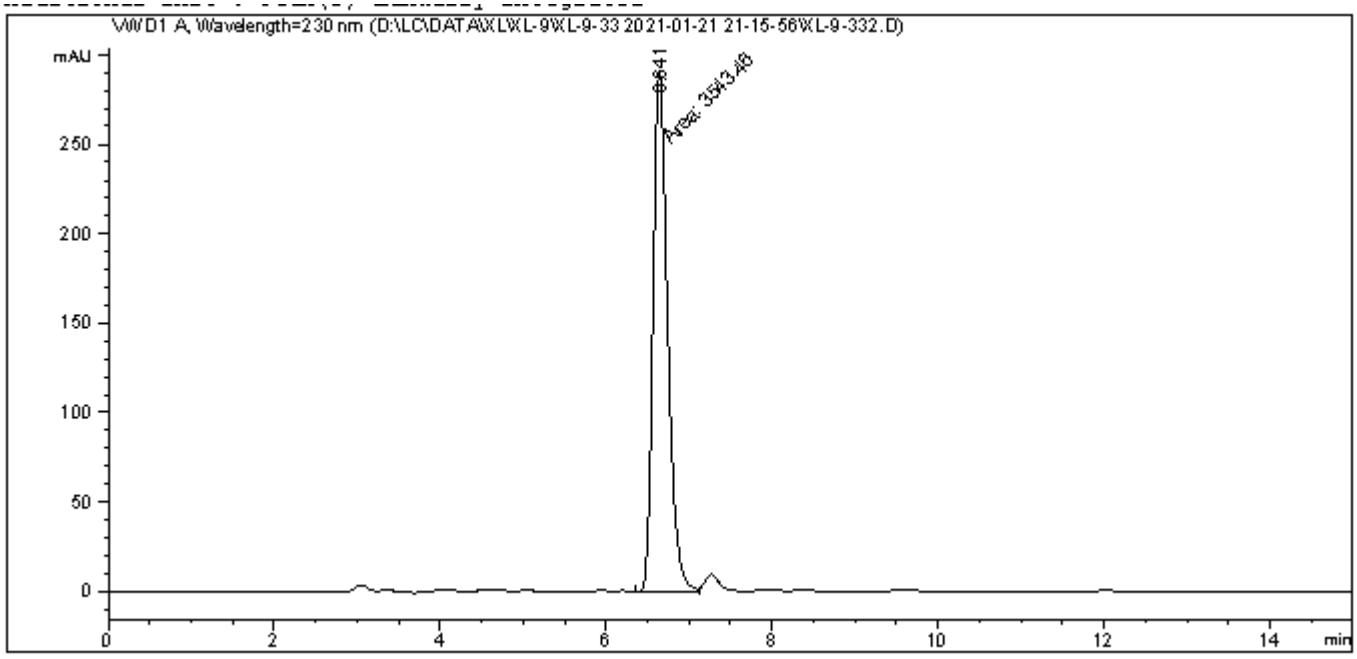
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.020 MM    0.1817  628.84509   57.68770  51.1761
   2   6.745 MM    0.2057  599.94086   48.60559  48.8239

Totals :                  1228.78595  106.29329


================================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3b



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.641 MF    0.2036 3543.45850  290.00925 100.0000

Totals :                  3543.45850  290.00925


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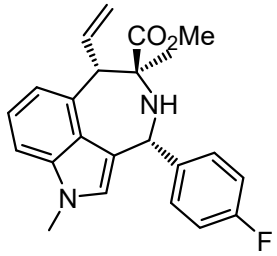
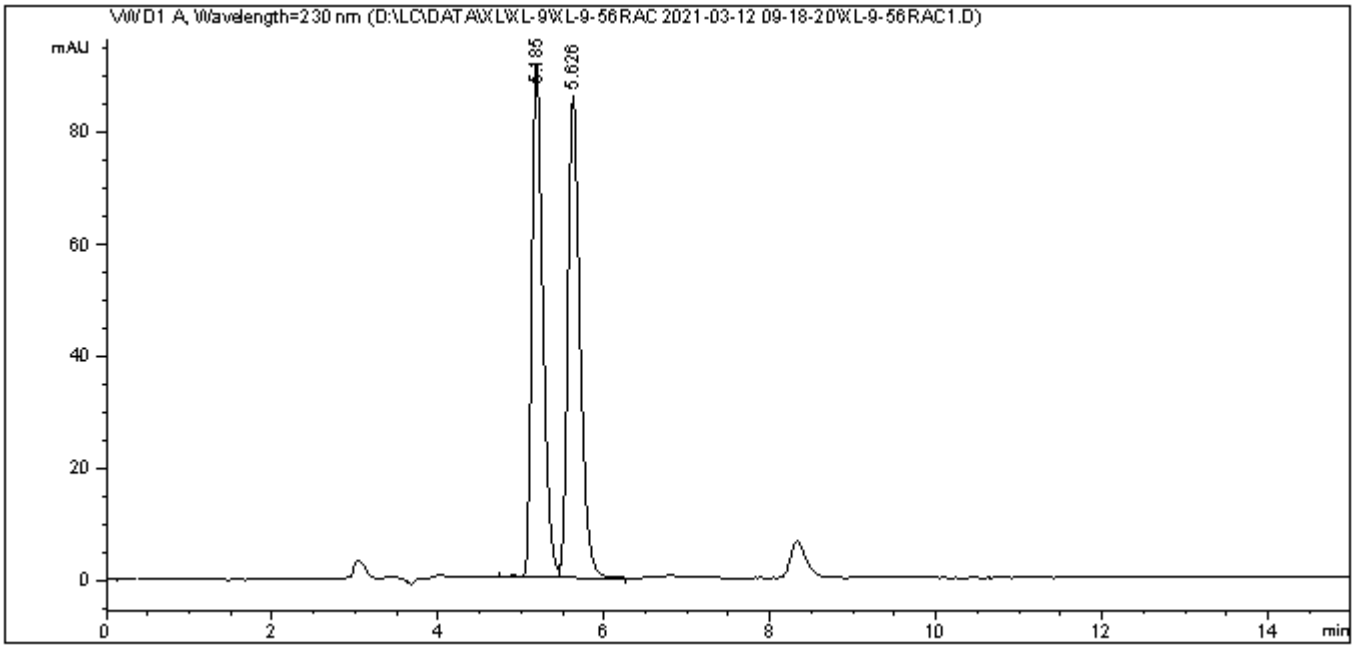
                        *** End of Report ***
```

HPLC chromatogram of compound (*rac*)-3c [(6*S*,7*S*,9*R*)-3c + (6*R*,7*R*,9*S*)-3c]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.185 VV R  0.1431  860.56982   91.63569  49.2944
   2   5.626 VB    0.1562  885.20770   86.19644  50.7056

Totals :                  1745.77753  177.83213


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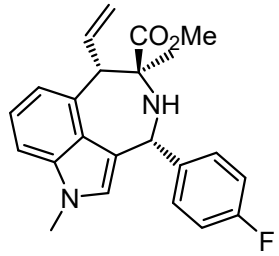
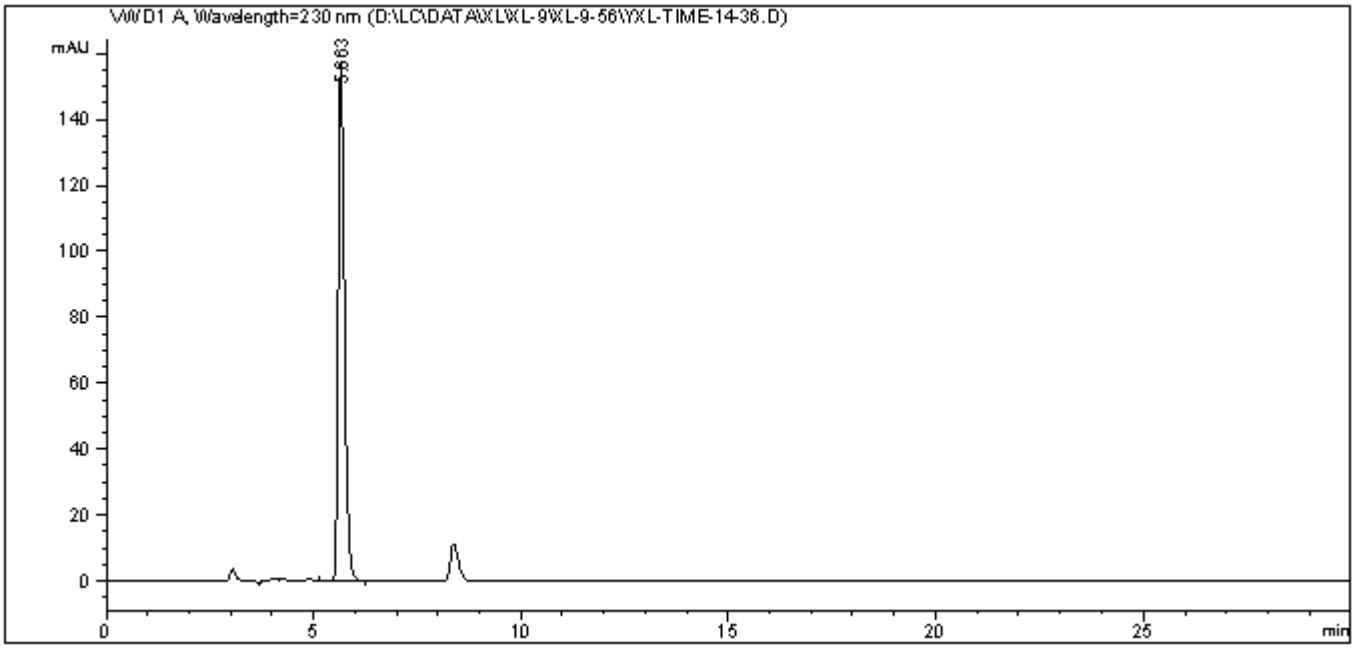
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3c



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

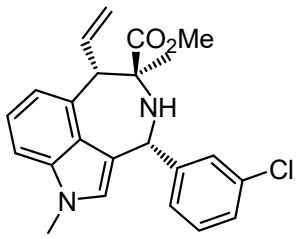

Signal 1: VWD1 A, Wavelength=230 nm

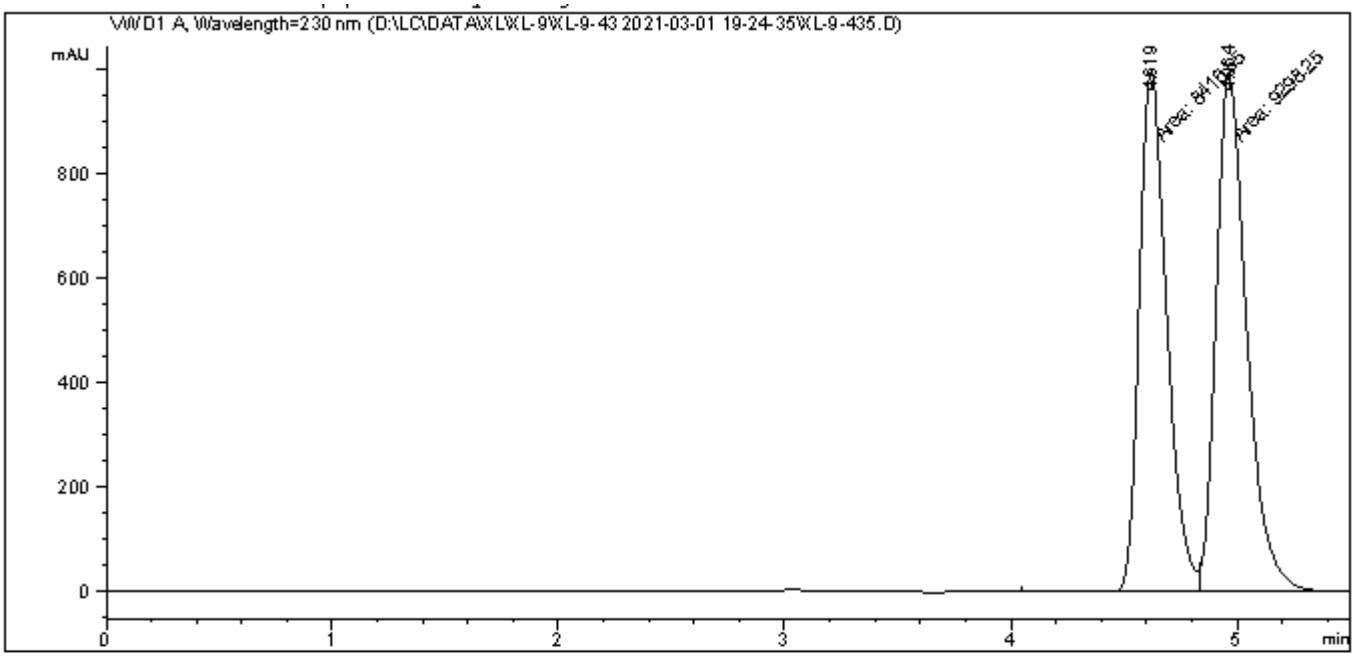
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.663 VV R  0.1572 1622.17908  156.64230 100.0000

Totals :                  1622.17908  156.64230


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3d [(6*S*,7*S*,9*R*)-3d + (6*R*,7*R*,9*S*)-3d]



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=====================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

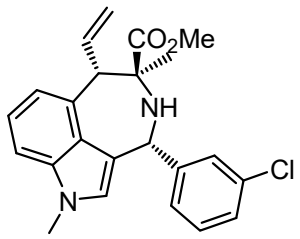

Signal 1: VWD1 A, Wavelength=230 nm

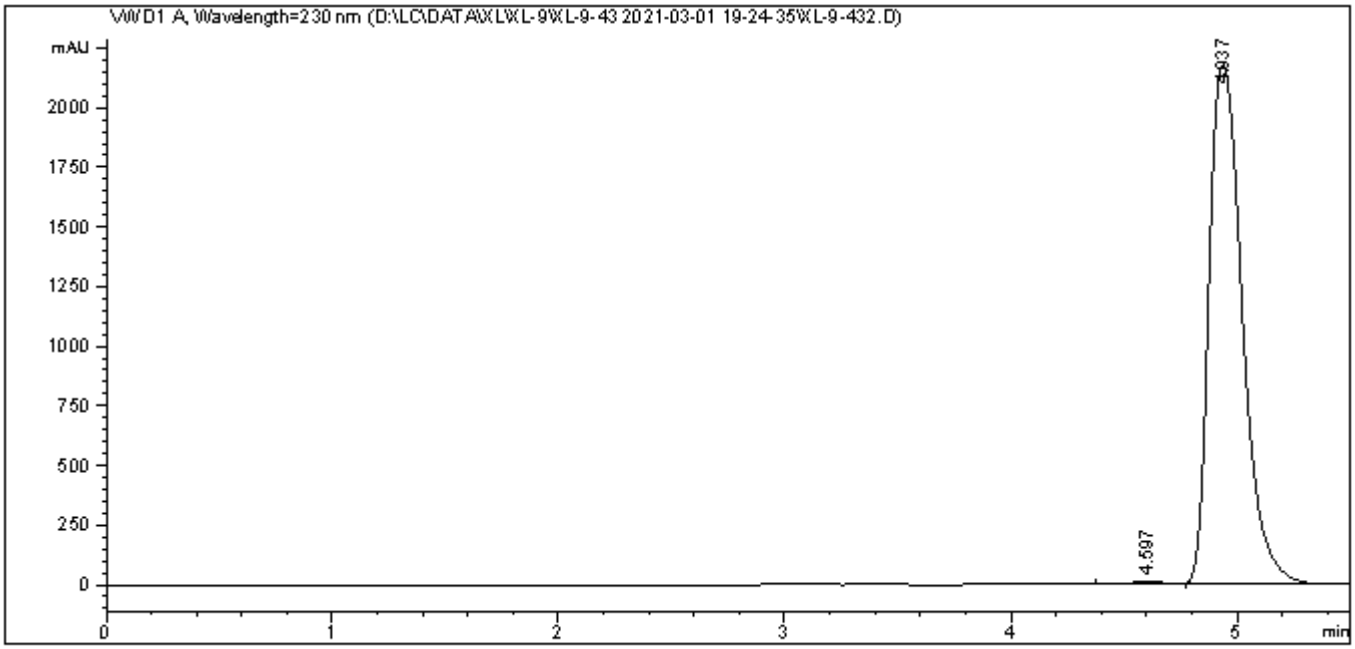
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.619 MF    0.1409 8416.55469  995.77808  47.5114
   2   4.964 FM    0.1568 9298.24512  988.02466  52.4886

Totals :                  1.77148e4  1983.80273


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3d



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

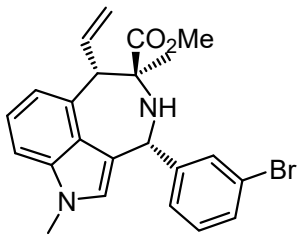

Signal 1: VWD1 A, Wavelength=230 nm

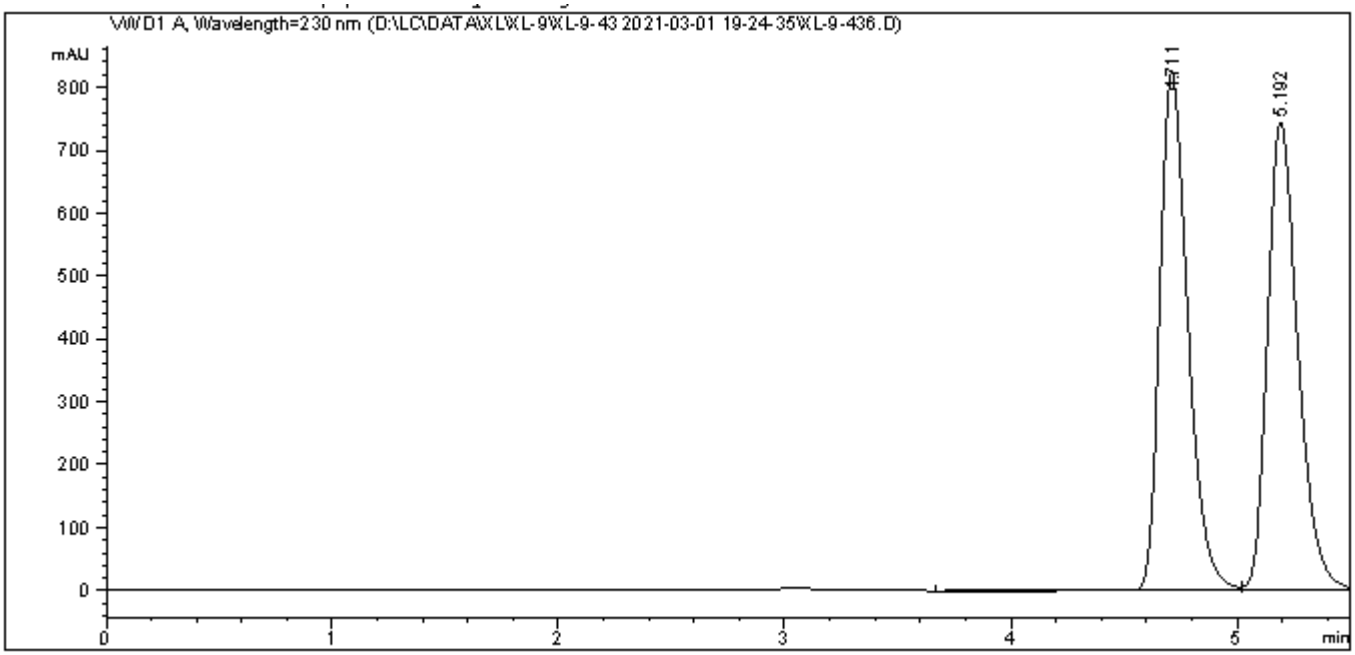
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.597 BV E  0.1264  133.61182   16.27563   0.5954
   2   4.937 VV R  0.1615 2.23072e4  2181.15747  99.4046

Totals :                  2.24408e4  2197.43310


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3e [(6*S*,7*S*,9*R*)-3e + (6*R*,7*R*,9*S*)-3e]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1   4.711 VV R  0.1332 7163.95410  826.07642  50.6553
   2   5.192 VB    0.1428 6978.61475  744.65002  49.3447

Totals :                  1.41426e4  1570.72644


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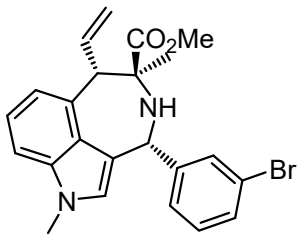
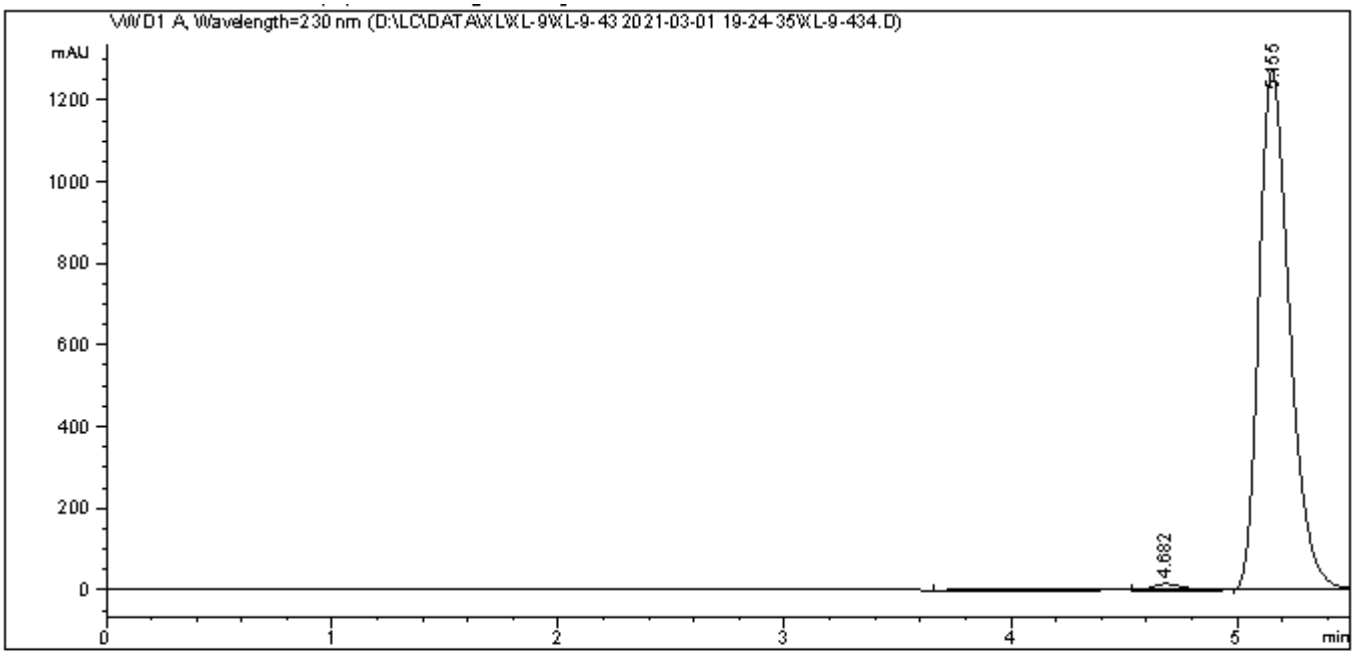
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3e



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

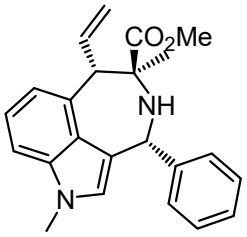

Signal 1: VWD1 A, Wavelength=230 nm

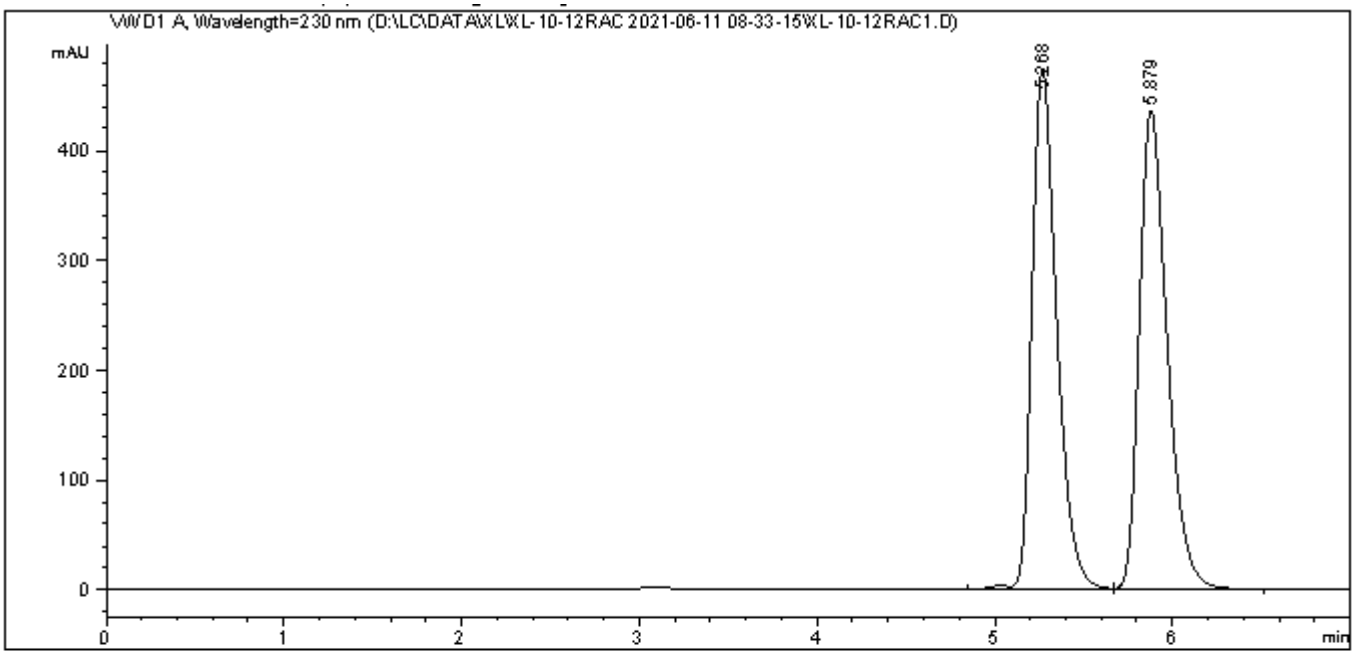
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.682 VV E  0.1444  147.38219   15.10049   1.2086
   2   5.155 VV R  0.1445 1.20471e4  1275.94910  98.7914

Totals :                  1.21945e4  1291.04959


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3f [(6*S*,7*S*,9*R*)-3f + (6*R*,7*R*,9*S*)-3f]



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=====================================================================
                        Area Percent Report
=====================================================================

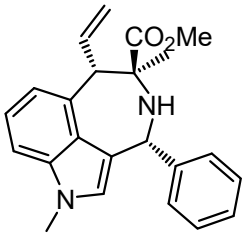
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

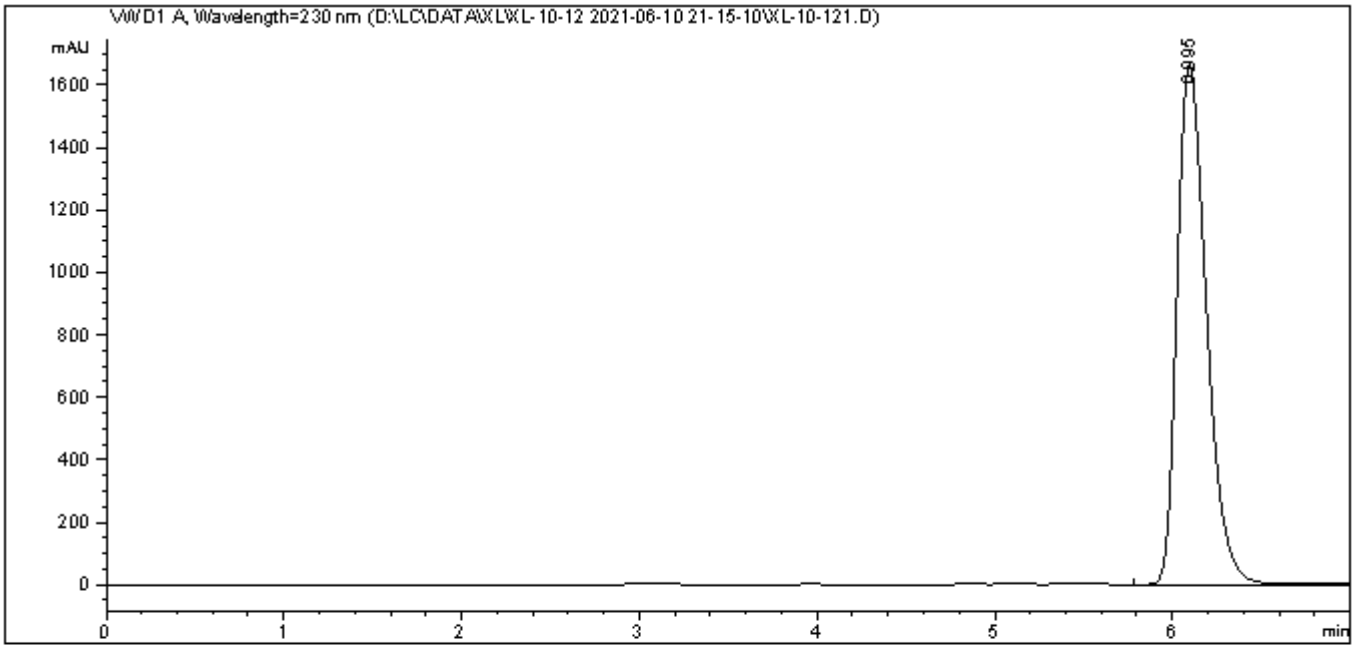

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.268 VB R  0.1471 4571.70117  473.17191  49.2114
   2   5.879 BB    0.1641 4718.22266  436.12241  50.7886

Totals :                  9289.92383  909.29431
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3f



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

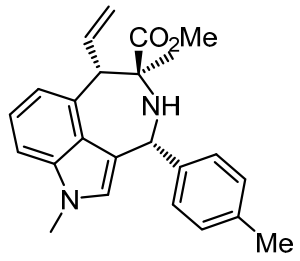

Signal 1: VWD1 A, Wavelength=230 nm

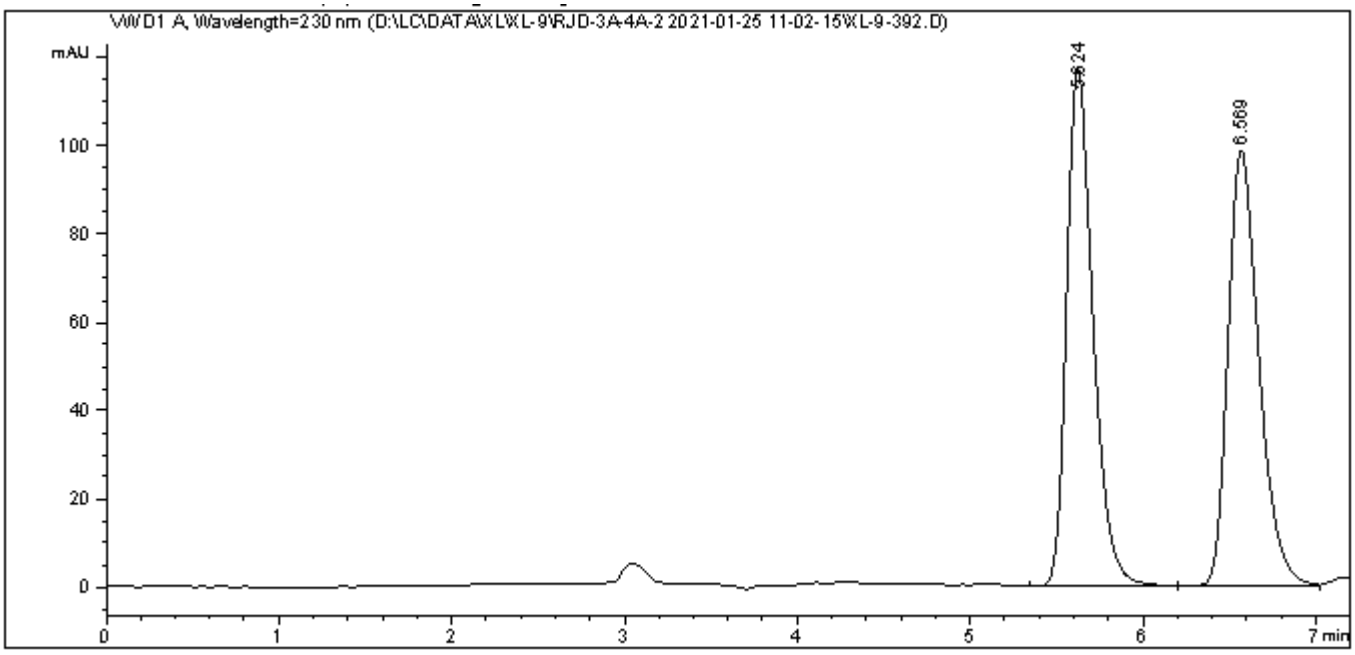
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.095 BV R  0.1772 1.90697e4  1666.02026 100.0000

Totals :                  1.90697e4  1666.02026

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3g [(6*S*,7*S*,9*R*)-3g + (6*R*,7*R*,9*S*)-3g]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.624 BB    0.1615 1241.98657  117.14567  50.2863
   2   6.569 BV    0.1902 1227.84534   98.76231  49.7137

Totals :                  2469.83191  215.90798


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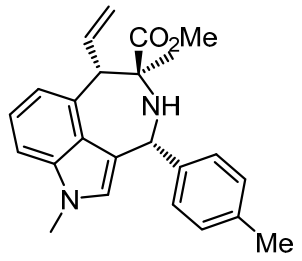
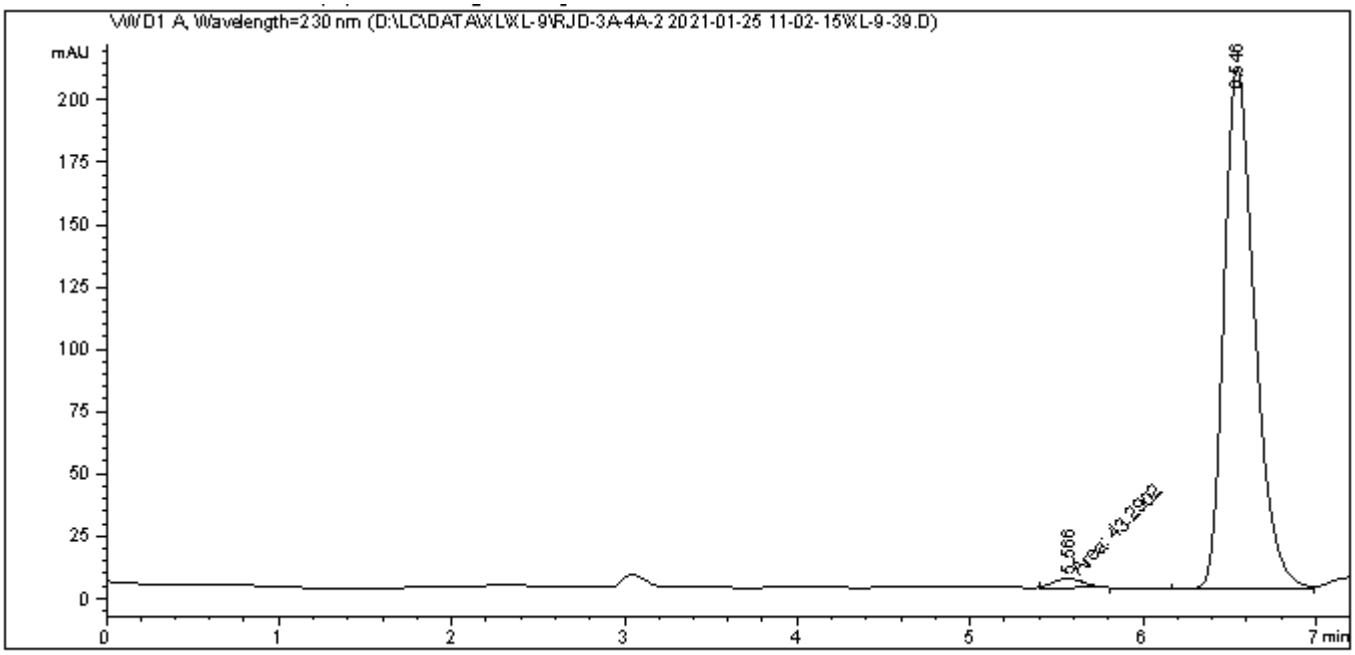
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3g



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=====================================================================
                        Area Percent Report
=====================================================================

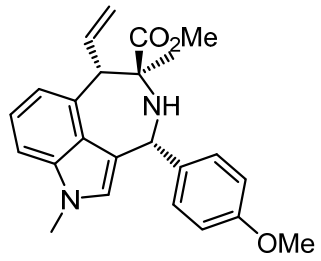
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

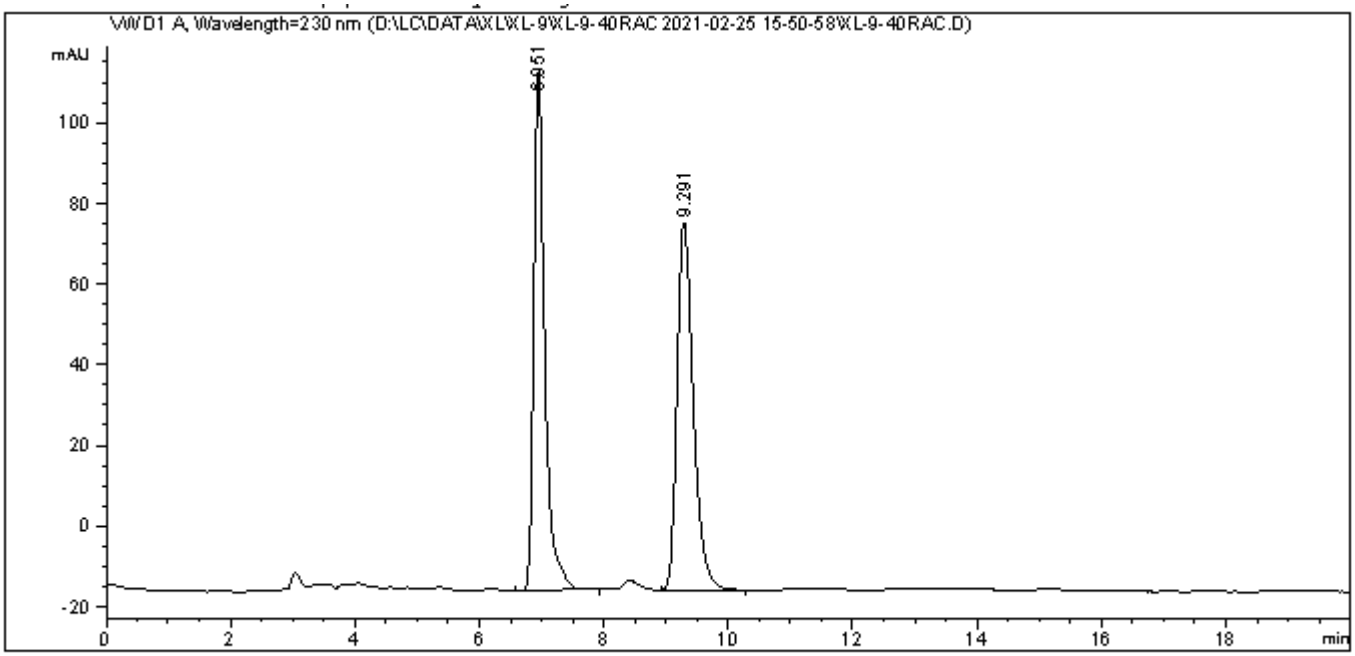

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.566 MM    0.2026   43.29018    3.56189   1.6553
   2   6.546 BV    0.1891 2571.99097  208.43007  98.3447

Totals :                  2615.28115  211.99196
```

HPLC chromatogram of compound (*rac*)-3h [(6*S*,7*S*,9*R*)-3h + (6*R*,7*R*,9*S*)-3h]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

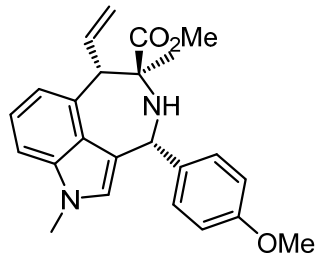

Signal 1: VWD1 A, Wavelength=230 nm

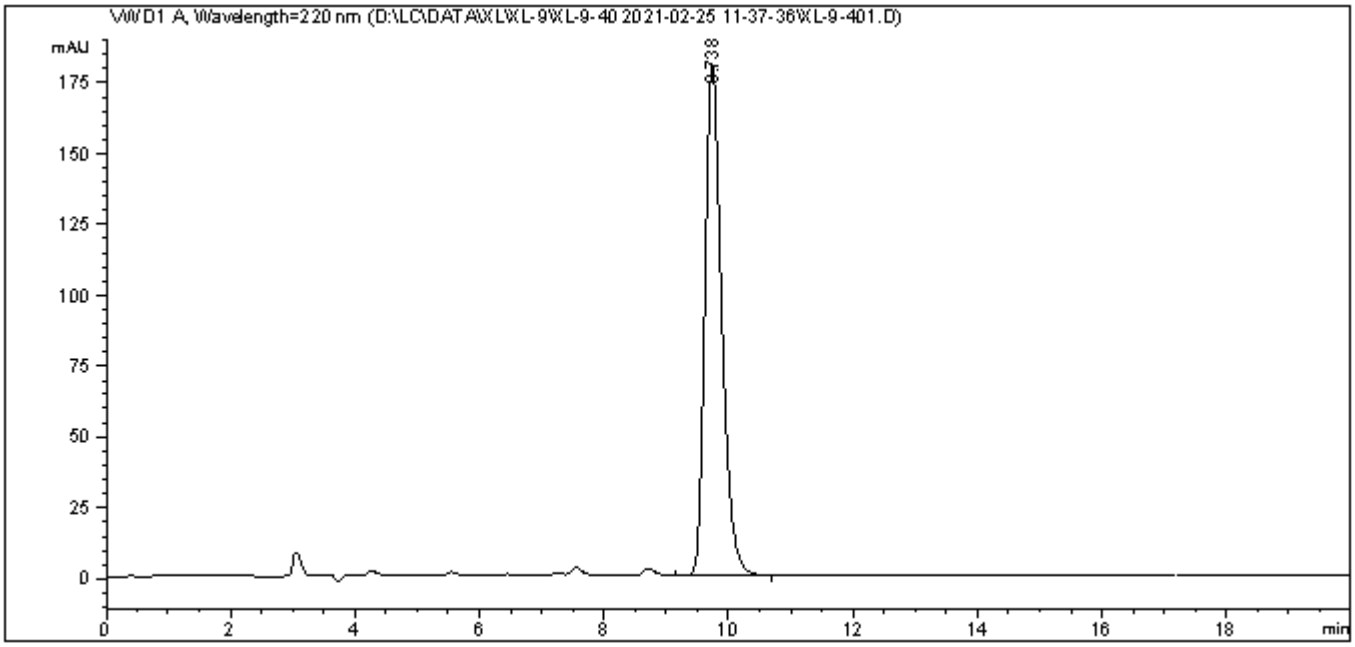
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.951 VV R  0.1824 1577.71741  128.63957  48.7474
   2   9.291 BV R  0.2781 1658.79736   91.02004  51.2526

Totals :                  3236.51477  219.65961

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3h






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

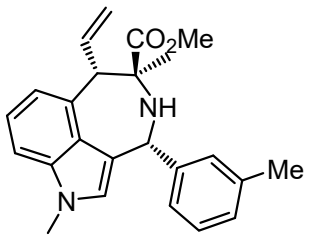

Signal 1: VWD1 A, Wavelength=220 nm

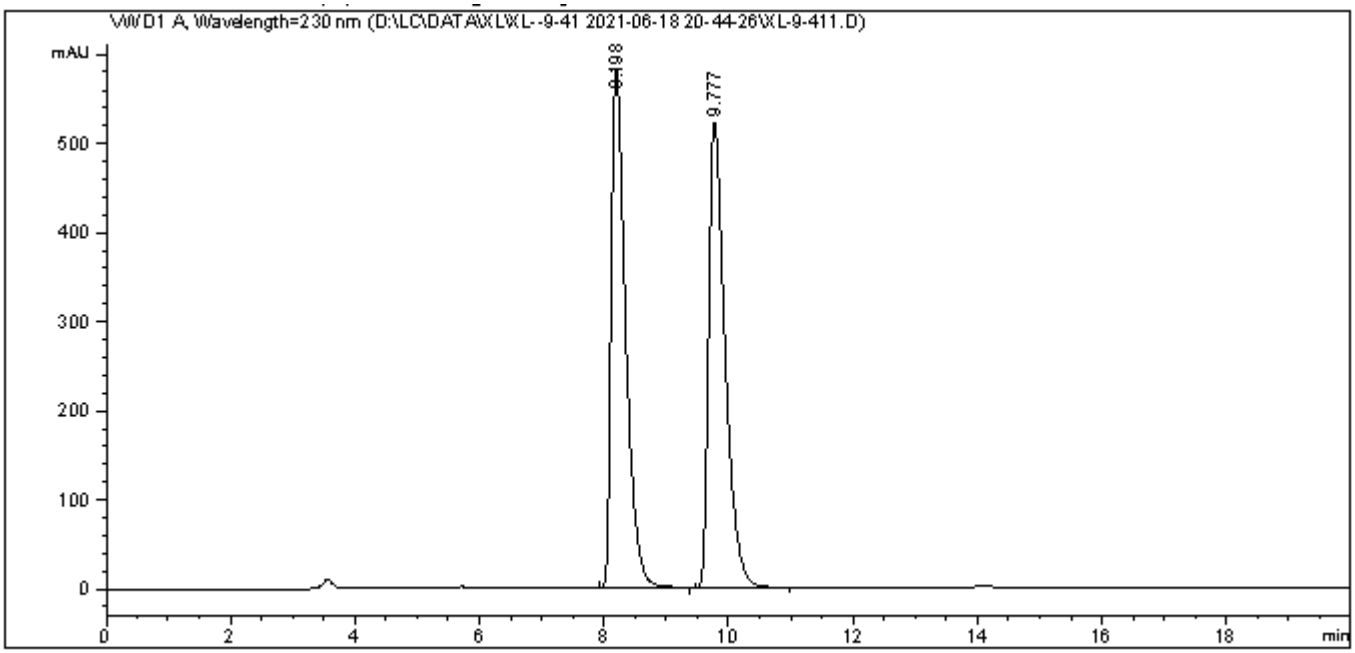
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.738 BB    0.2860 3391.60840  180.65225 100.0000

Totals :                  3391.60840  180.65225


=====================================================================
                        *** End of Report ***
```

HPLC chromatogram of compound (*rac*)-3i [(6*S*,7*S*,9*R*)-3i + (6*R*,7*R*,9*S*)-3i]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

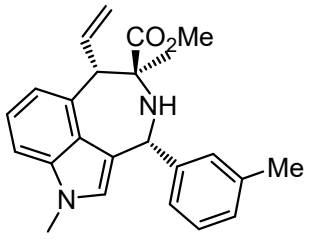

Signal 1: VWD1 A, Wavelength=230 nm

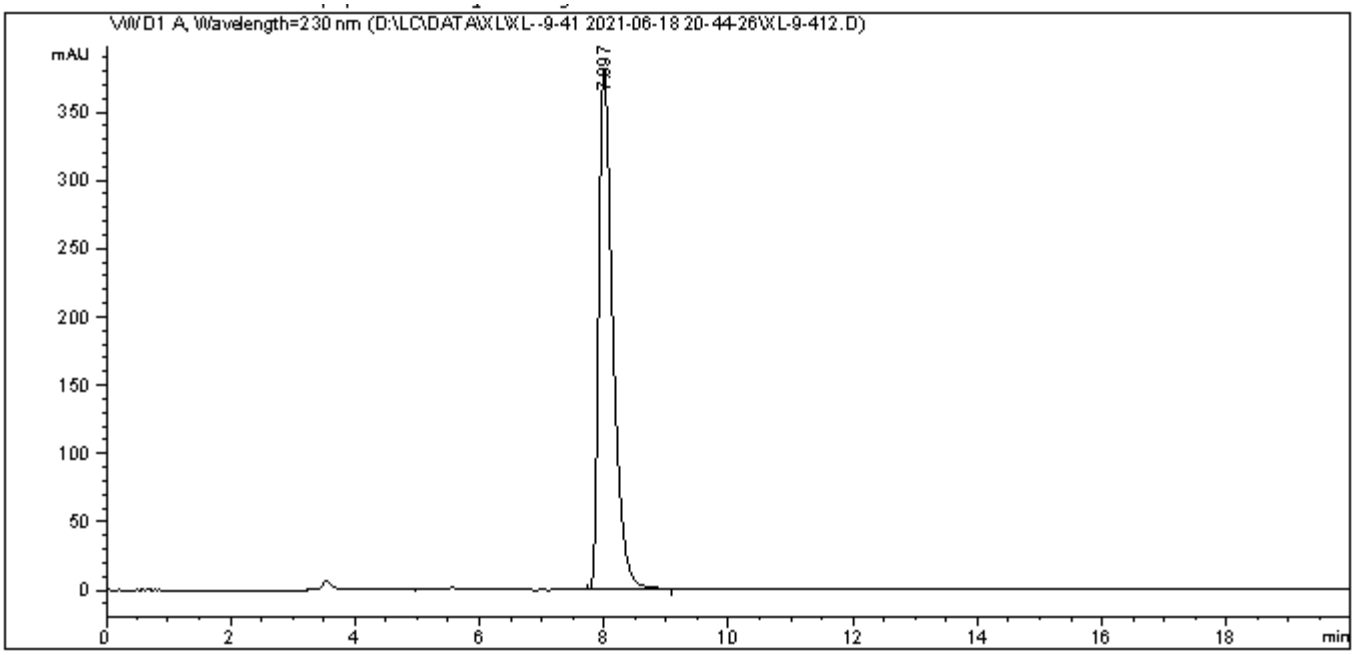
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1   8.198 VB    0.2425 9419.24414  582.71033  49.4766
   2   9.777 BB    0.2771 9618.53418  523.12152  50.5234

Totals :                  1.90378e4  1105.83185


=====================================================================
                        *** End of Report ***
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3i






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

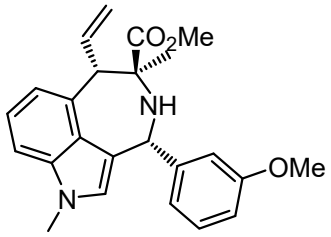

Signal 1: VWD1 A, Wavelength=230 nm

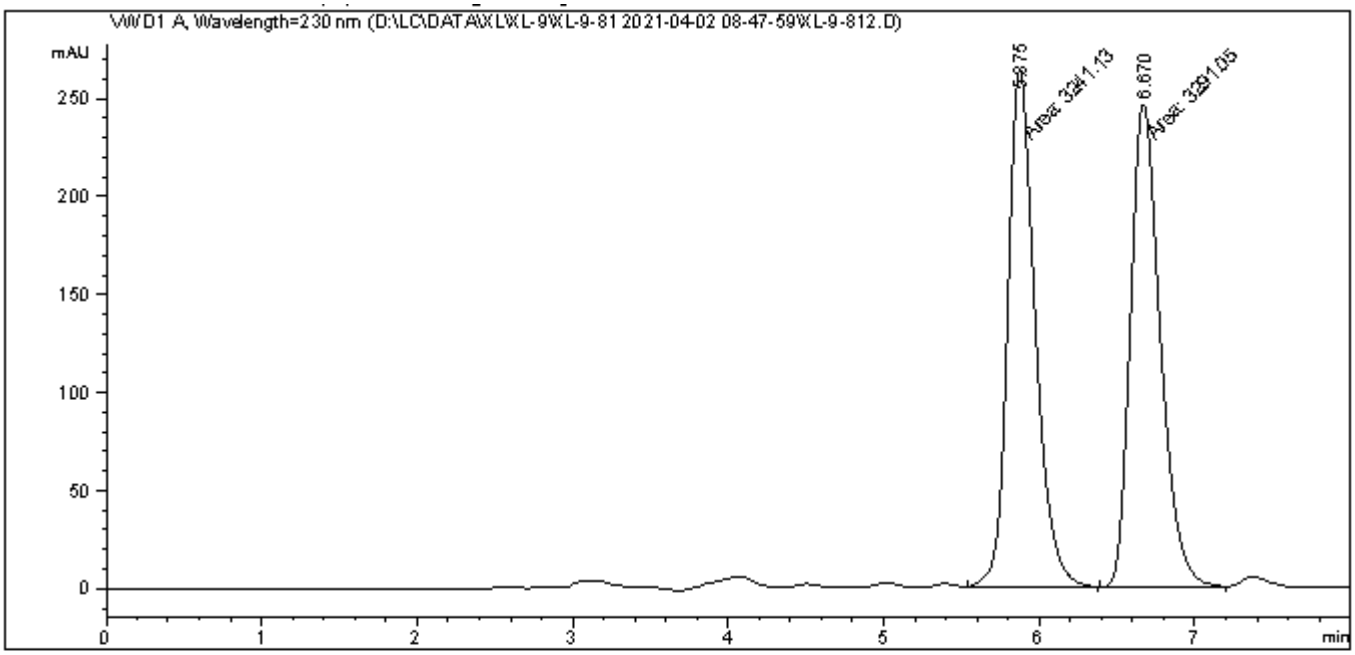
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.997 VB    0.2409 6045.53955  379.98526 100.0000

Totals :                  6045.53955  379.98526


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3j [(6*S*,7*S*,9*R*)-3j + (6*R*,7*R*,9*S*)-3j]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

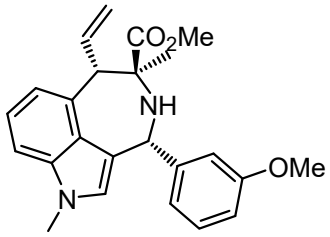

Signal 1: VWD1 A, Wavelength=230 nm

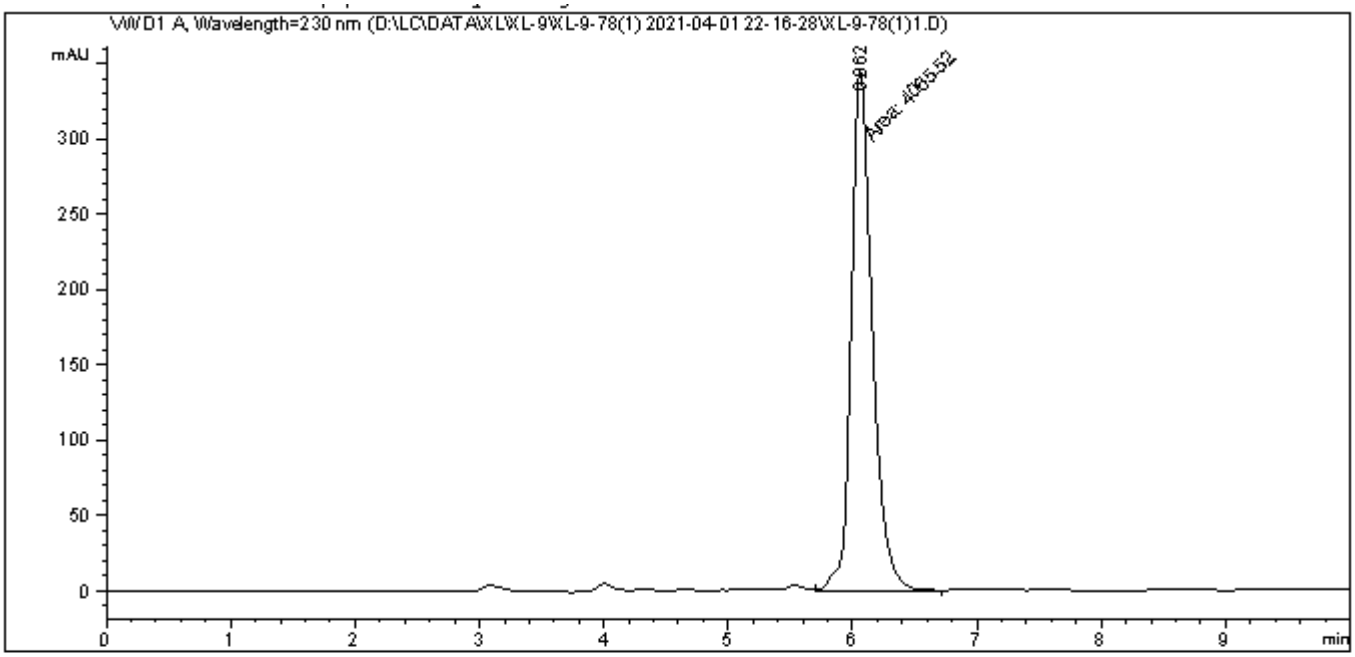
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.875 MM    0.2043 3241.12695  264.36353  49.6179
   2   6.670 MF    0.2224 3291.05005  246.64017  50.3821

Totals :                  6532.17700  511.00369

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3j






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

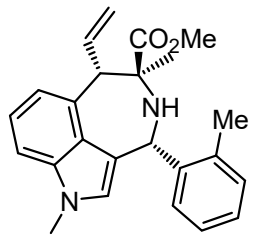

Signal 1: VWD1 A, Wavelength=230 nm

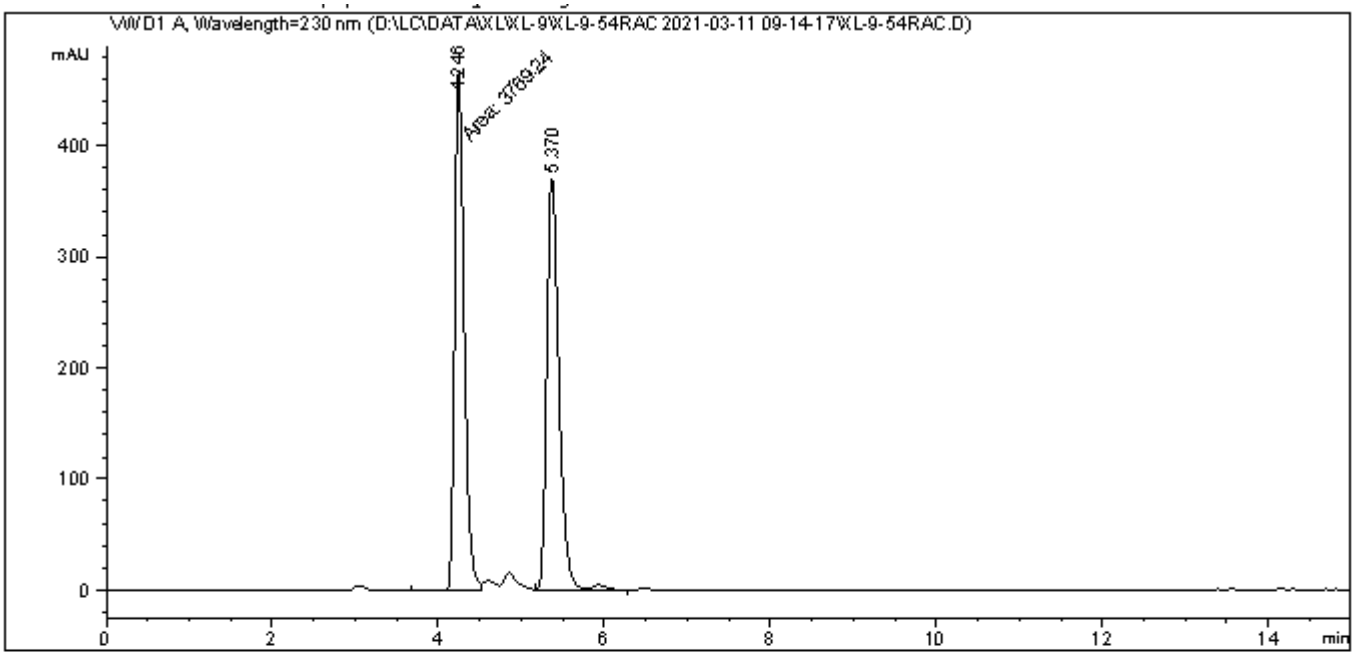
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.062 FM    0.1965 4065.51904  344.76599 100.0000

Totals :                  4065.51904  344.76599

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3k [(6*S*,7*S*,9*R*)-3k + (6*R*,7*R*,9*S*)-3k]






```
=====================================================================
                        Area Percent Report
=====================================================================

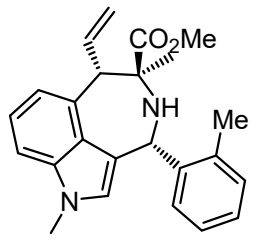
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

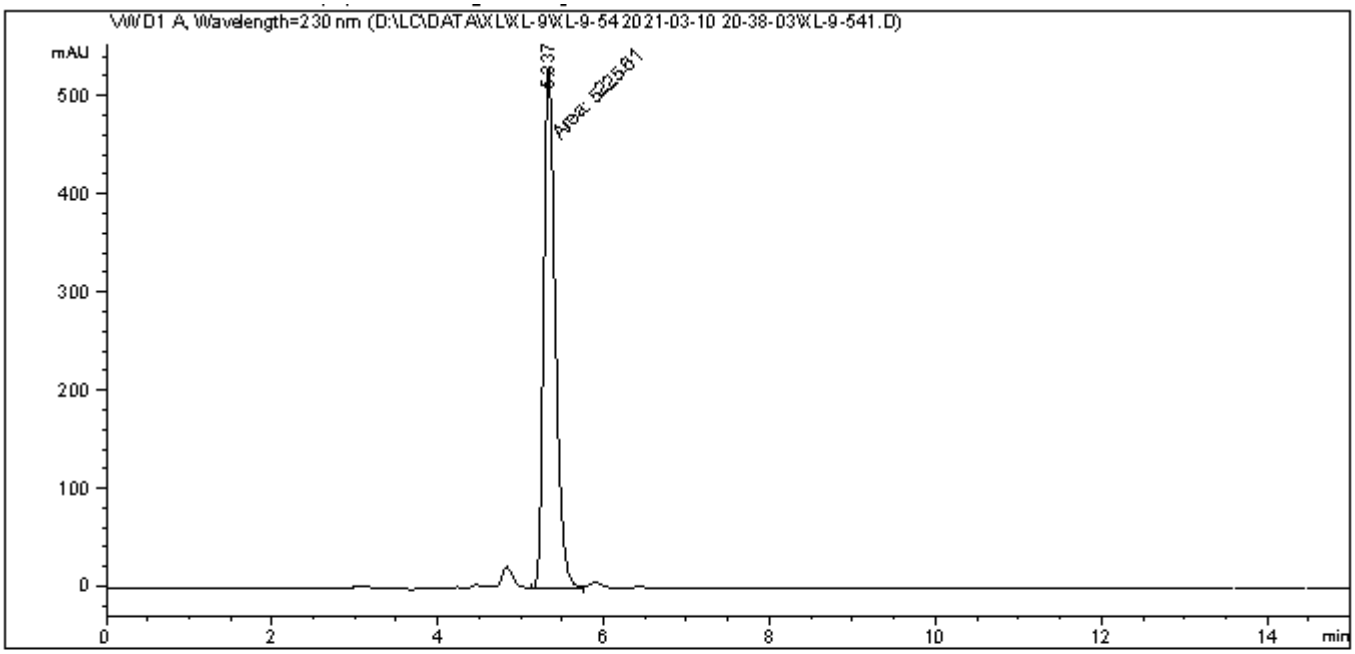

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.246 MF    0.1343 3769.24243  467.69119  49.9879
   2   5.370 BV R  0.1521 3771.07007  370.63354  50.0121

Totals :                  7540.31250  838.32474
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3k






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

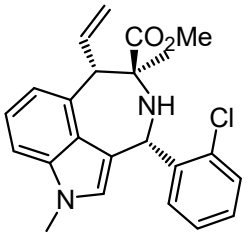

Signal 1: VWD1 A, Wavelength=230 nm

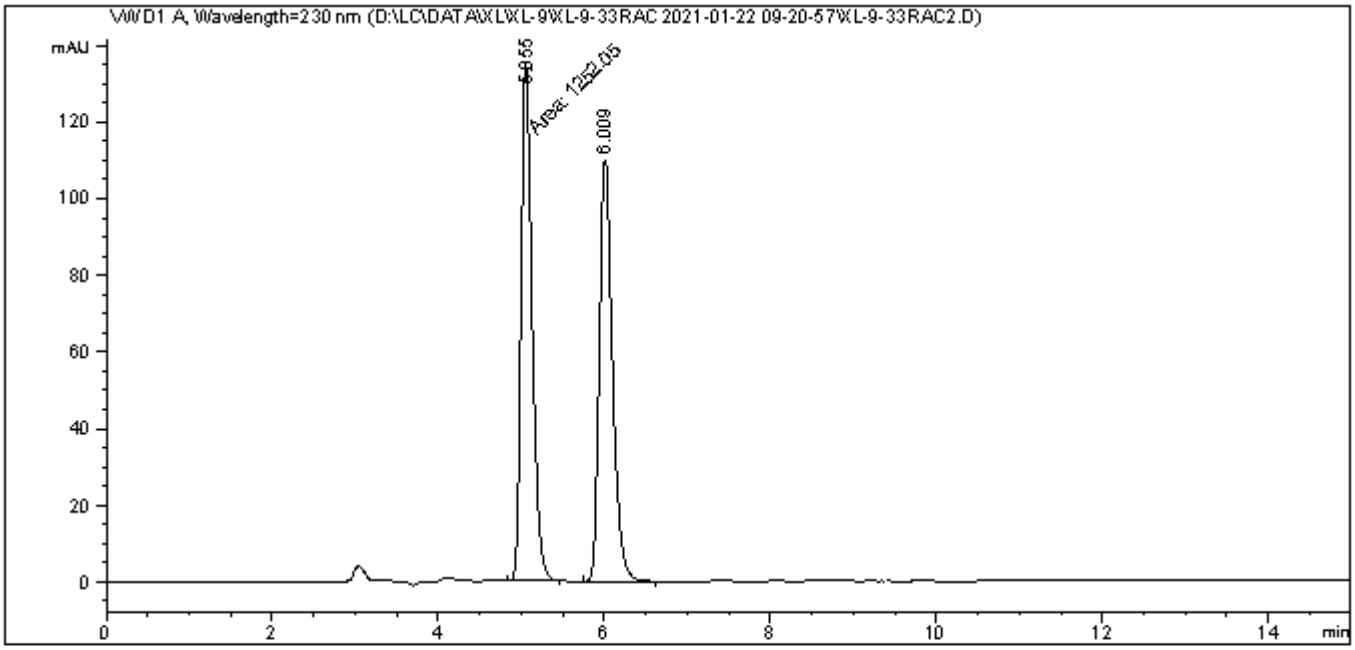
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.337 MF    0.1644 5225.61182  529.67822 100.0000

Totals :                  5225.61182  529.67822

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3l [(6*S*,7*S*,9*R*)-3l + (6*R*,7*R*,9*S*)-3l]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

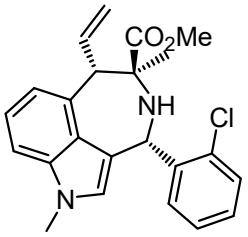

Signal 1: VWD1 A, Wavelength=230 nm

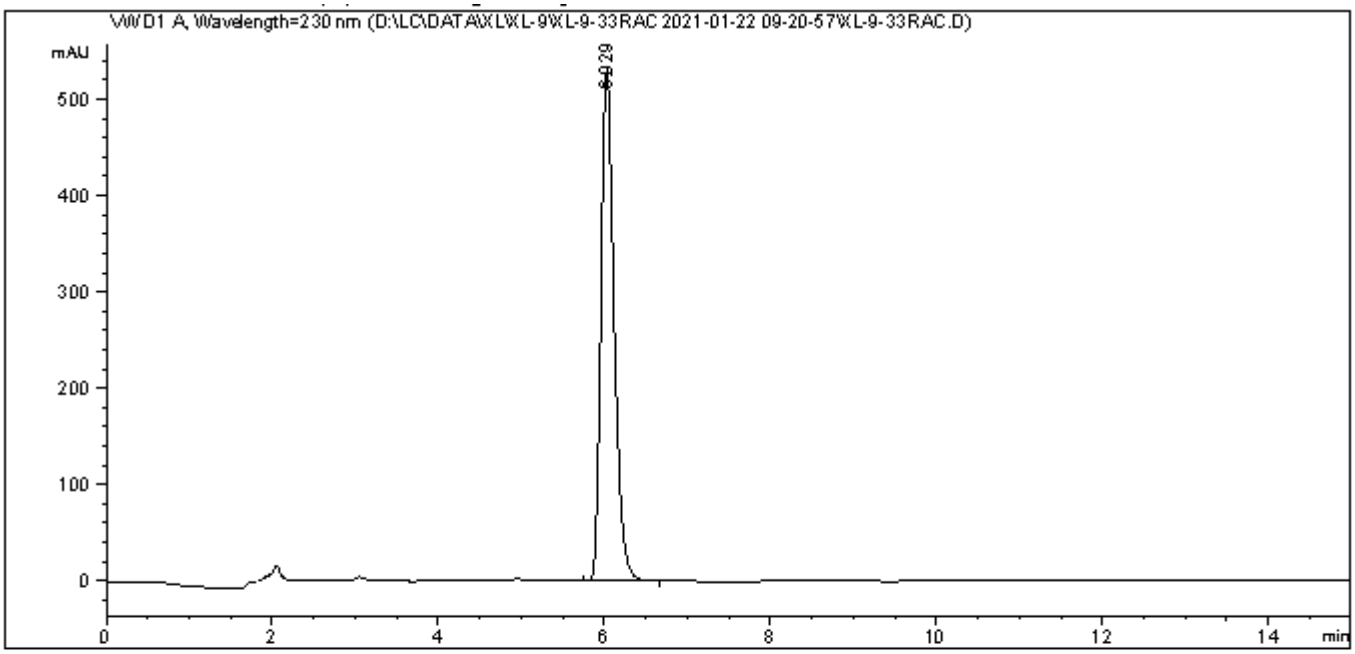
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.055 MM    0.1549 1252.05444  134.75844  50.8594
   2   6.009 BB    0.1676 1209.74036  110.03841  49.1406

Totals :                  2461.79480  244.79685


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3l






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

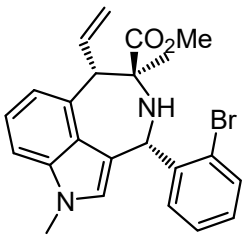

Signal 1: VWD1 A, Wavelength=230 nm

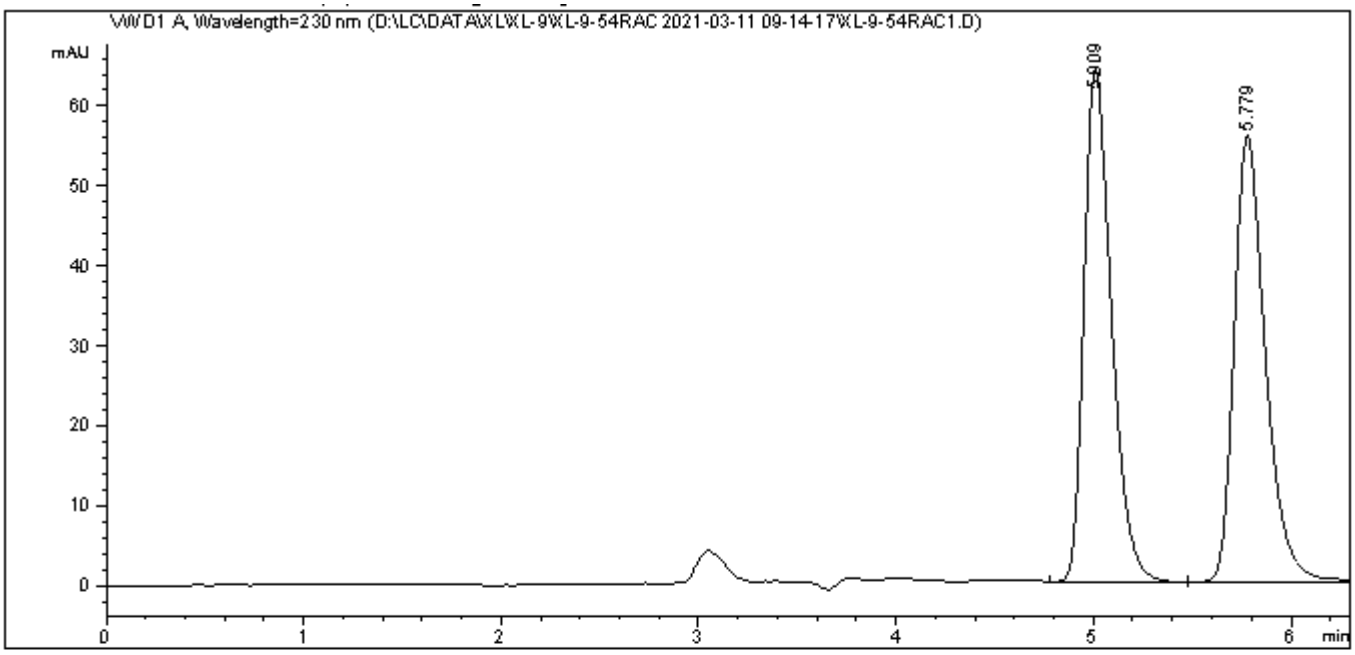
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.029 BB    0.1685 5890.53418  531.89130 100.0000

Totals :                  5890.53418  531.89130

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3m [(6*S*,7*S*,9*R*)-3m + (6*R*,7*R*,9*S*)-3m]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

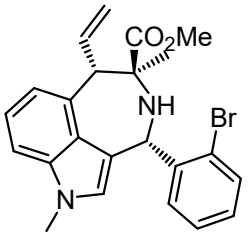

Signal 1: VWD1 A, Wavelength=230 nm

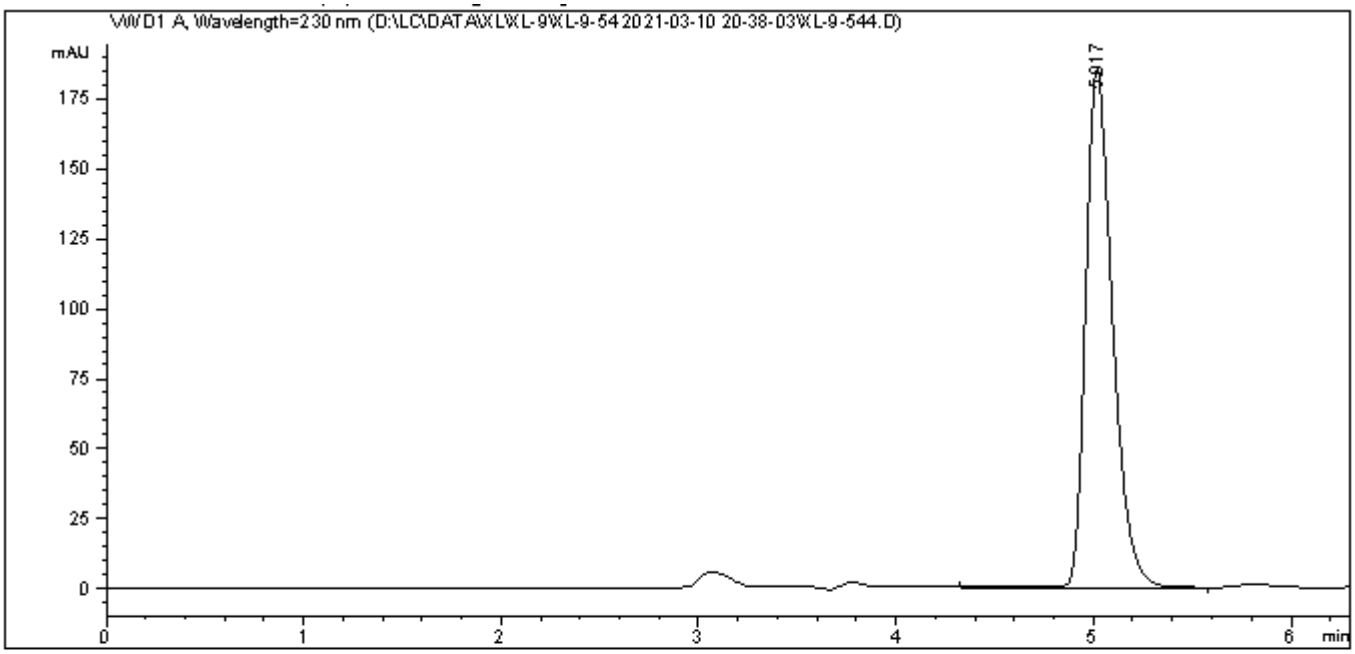
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1   5.009 BB    0.1477  620.11047   64.15859  50.2034
   2   5.779 BV R  0.1664  615.08685   55.84666  49.7966

Totals :                  1235.19733  120.00525


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3m






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

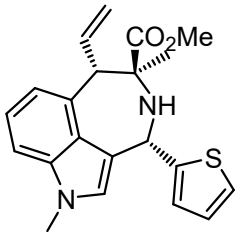

Signal 1: VWD1 A, Wavelength=230 nm

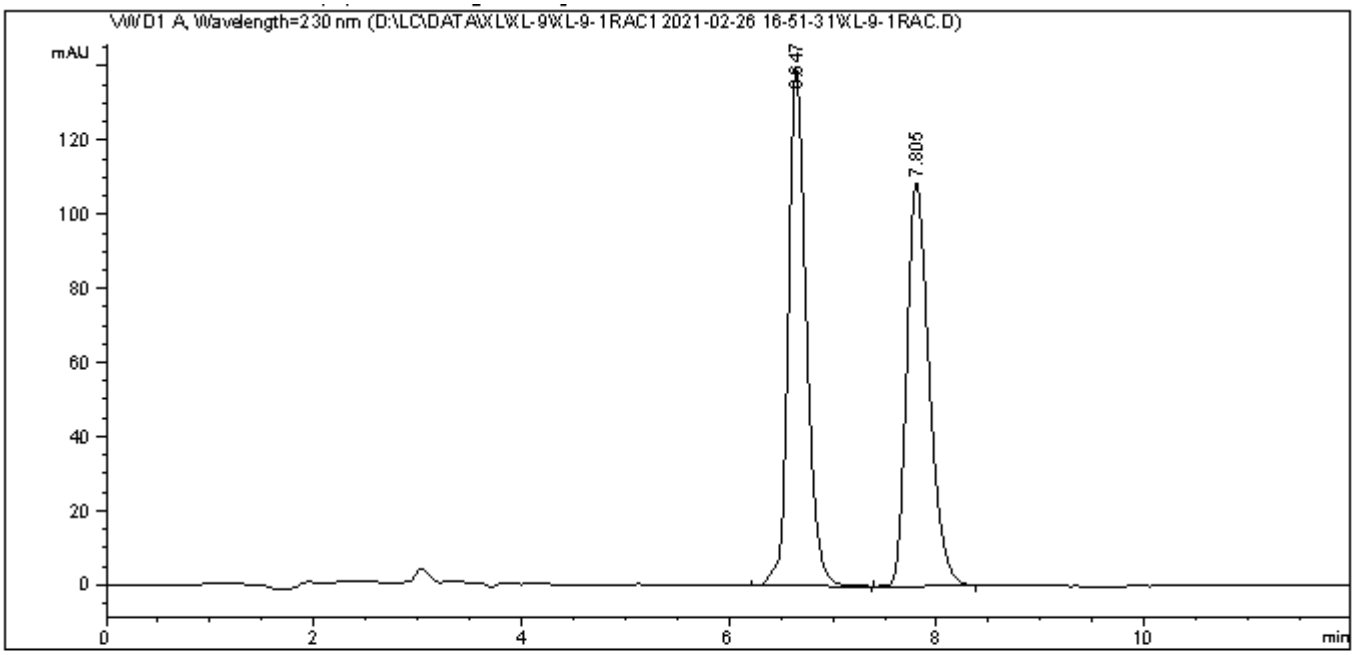
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.017 VB R  0.1439 1752.58997  185.26711 100.0000

Totals :                  1752.58997  185.26711


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3n [(6*S*,7*S*,9*S*)-3n + (6*R*,7*R*,9*R*)-3n]






```
=====================================================================
                        Area Percent Report
=====================================================================

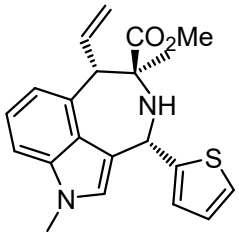
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

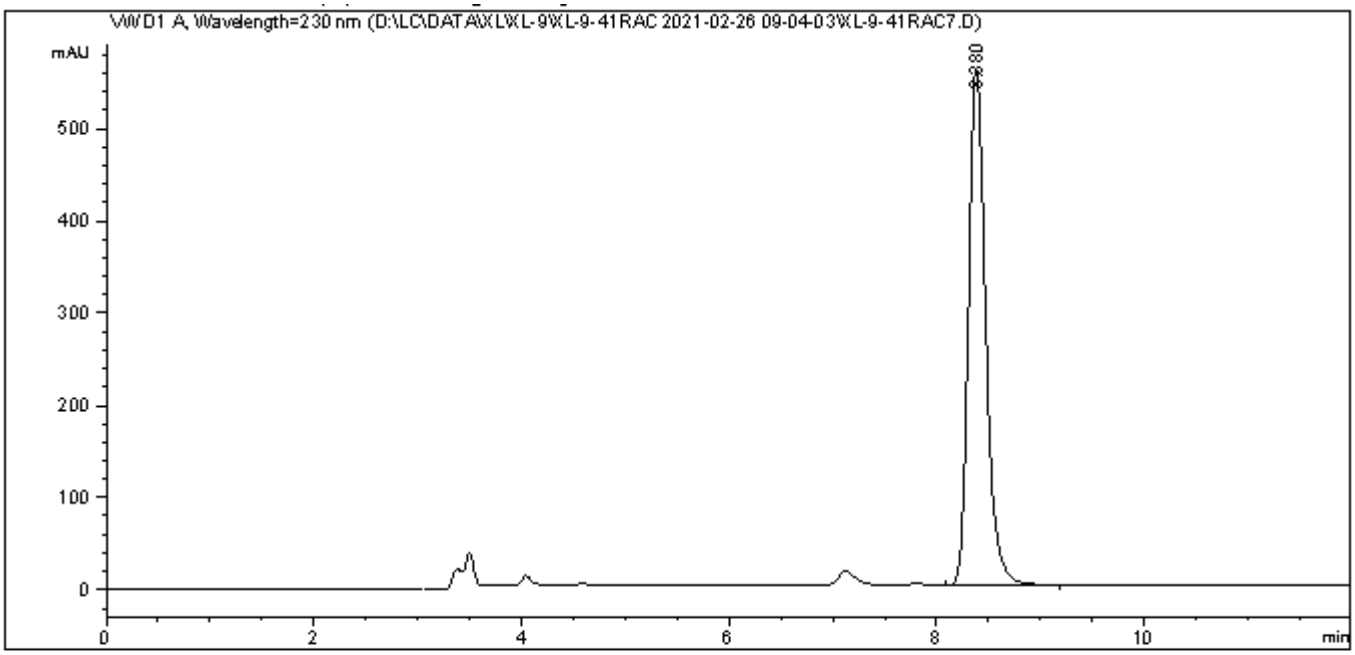

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.647 BB    0.1830 1683.97693  139.59908  50.6914
   2   7.805 BB    0.2292 1638.04297  108.97227  49.3086

Totals :                  3322.01990  248.57135
```

HPLC chromatogram of compound (6*S*,7*S*,9*S*)-3n






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

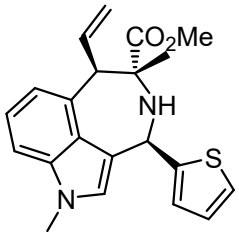

Signal 1: VWD1 A, Wavelength=230 nm

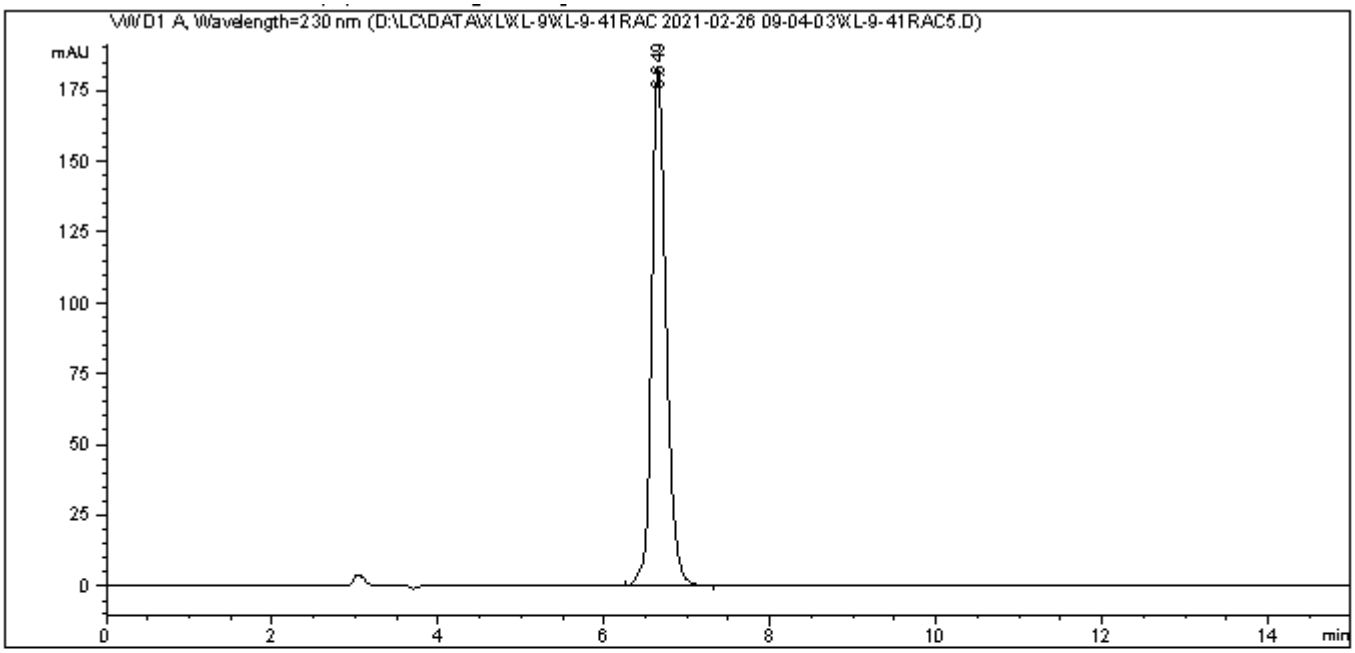
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   8.380 VB    0.1779 6436.46240  559.68188 100.0000

Totals :                  6436.46240  559.68188

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*R*,9*R*)-3n






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

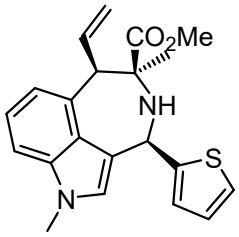

Signal 1: VWD1 A, Wavelength=230 nm

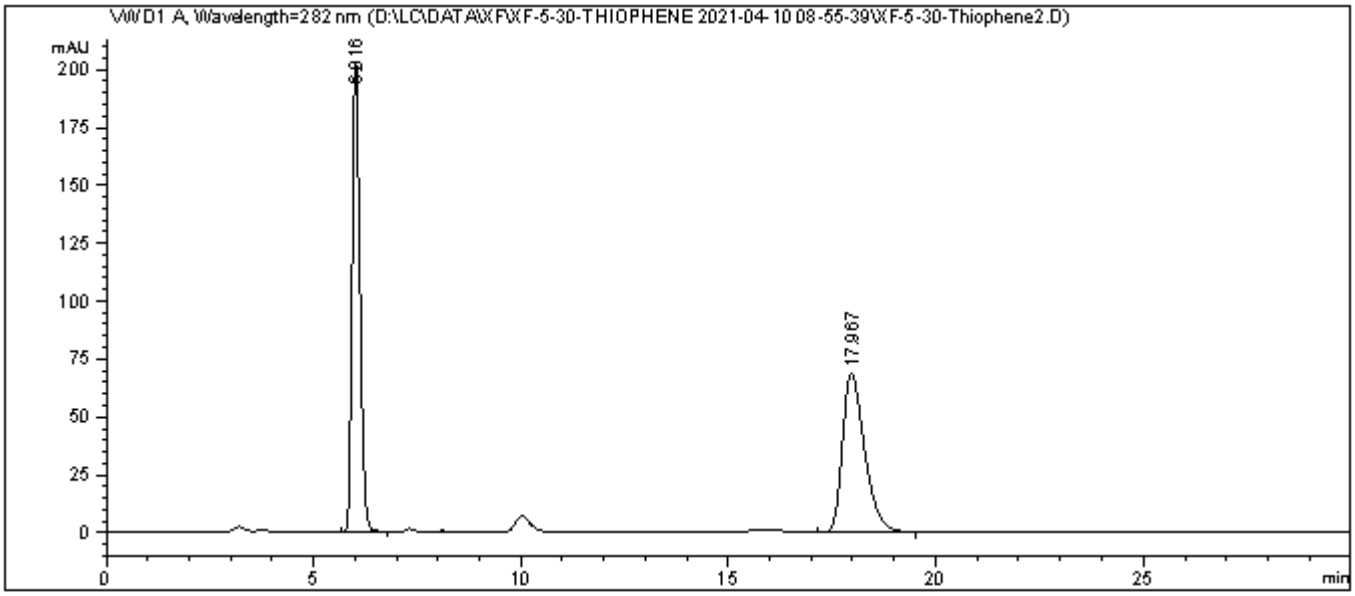
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.649 BB    0.1838 2214.52295  182.50430 100.0000

Totals :                  2214.52295  182.50430

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3n [(6*R*,7*S*,9*R*)-3n + (6*S*,7*R*,9*S*)-3n]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

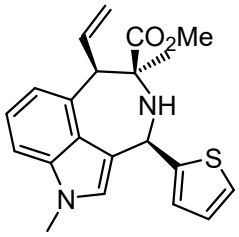

Signal 1: VWD1 A, Wavelength=282 nm

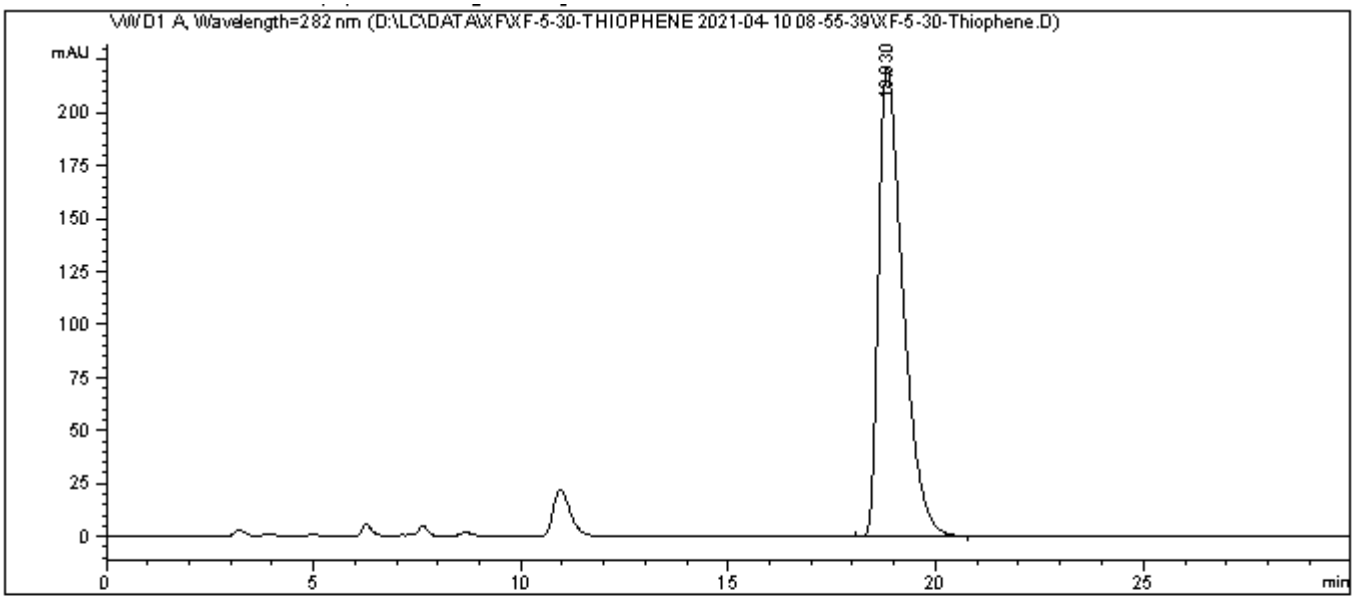
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.016 BV    0.2020 2656.27197  203.26733  50.8831
   2  17.967 VV R  0.5646 2564.07178   68.76900  49.1169

Totals :                  5220.34375  272.03633

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*R*)-3n






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

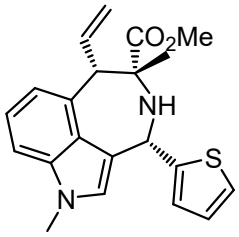

Signal 1: VWD1 A, Wavelength=282 nm

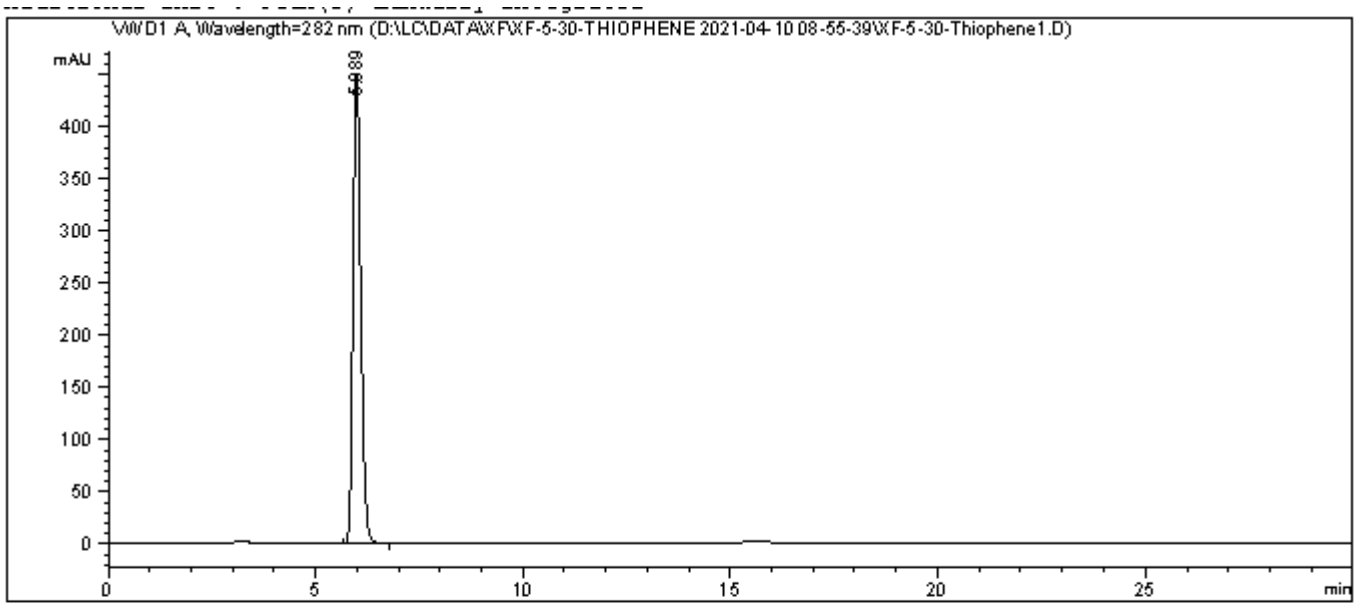
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.830 VV R  0.6116 9057.90527  221.89972 100.0000

Totals :                  9057.90527  221.89972

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*R*,9*S*)-3n



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

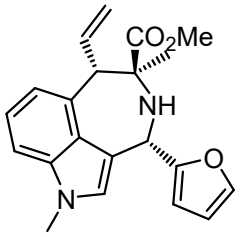

Signal 1: VWD1 A, Wavelength=282 nm

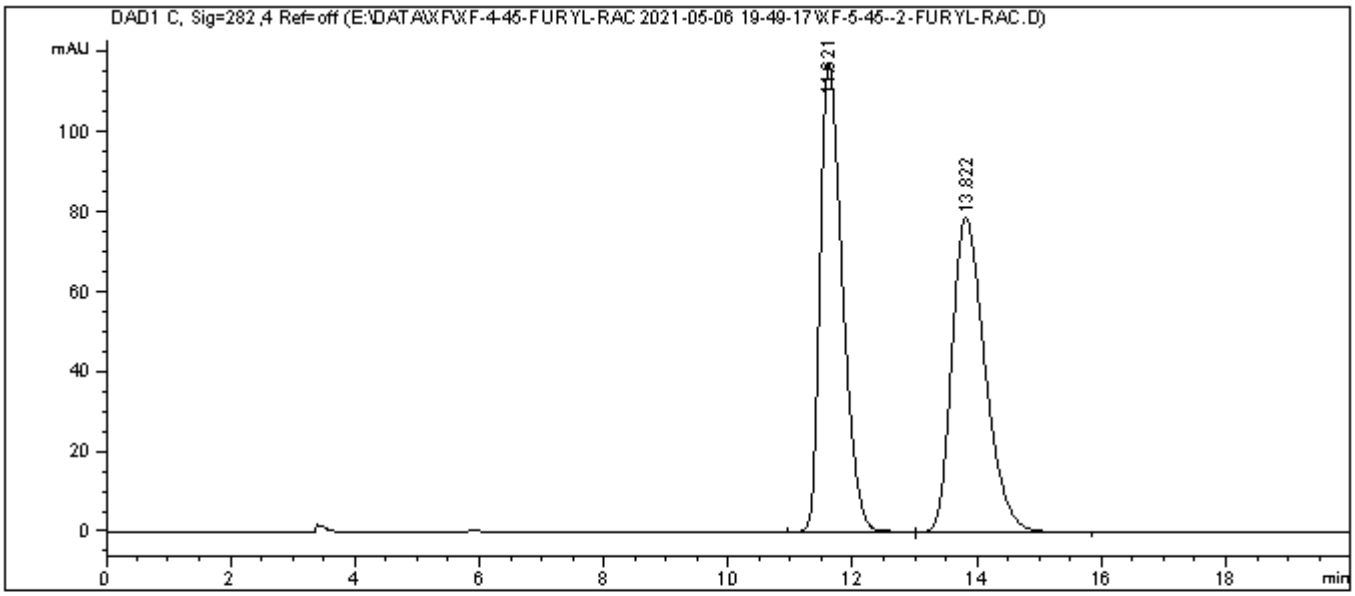
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.989 BB    0.1996 5855.35010  450.72839 100.0000

Totals :                  5855.35010  450.72839

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3o [(6*S*,7*S*,9*S*)-3o + (6*R*,7*R*,9*R*)-3o]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

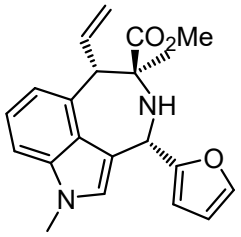

Signal 1: DAD1 C, Sig=282,4 Ref=off

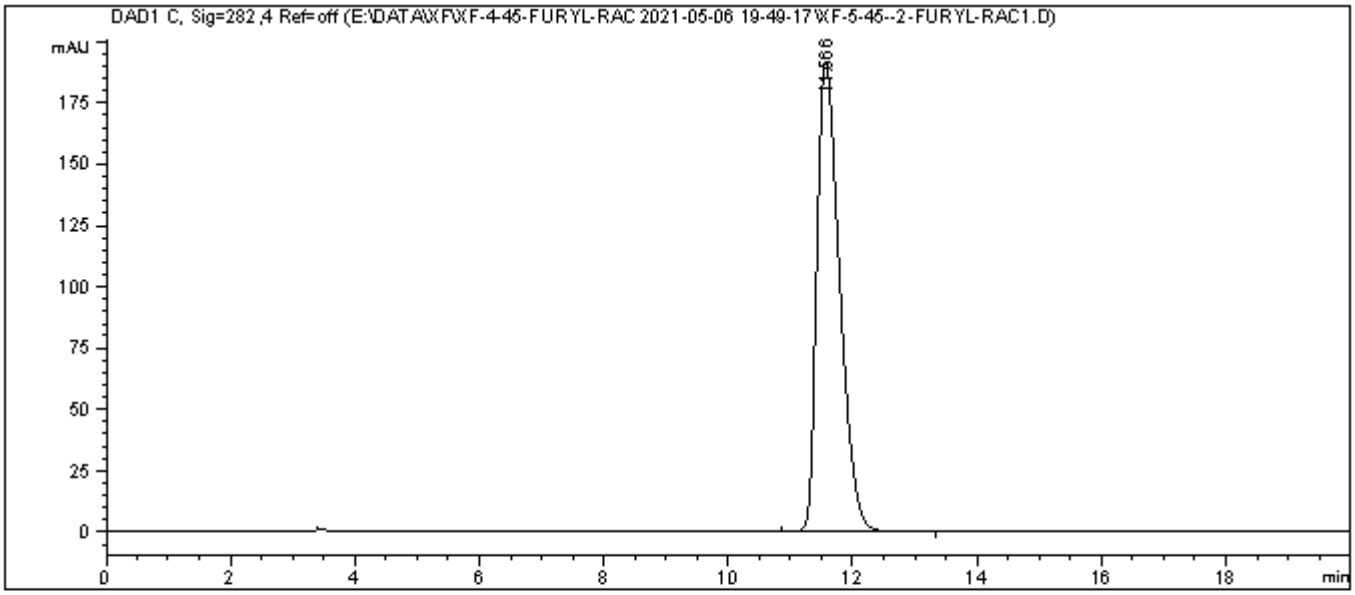
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.621 BB    0.3836 2941.39404  117.68037  50.2827
   2  13.822 BB    0.5707 2908.32202   78.77827  49.7173

Totals :                  5849.71606  196.45865

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*S*)-3o



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

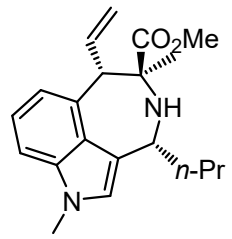

Signal 1: DAD1 C, Sig=282,4 Ref=off

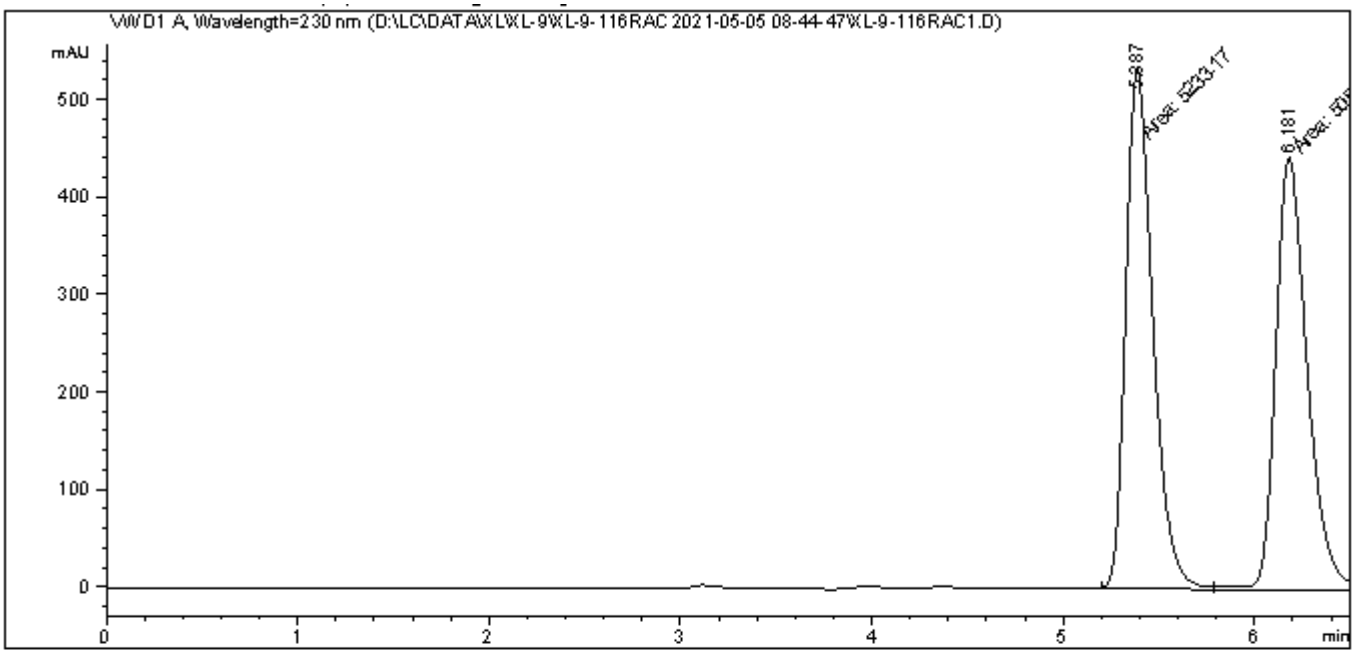
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.566 BB    0.3954 4885.49365  191.63930 100.0000

Totals :                  4885.49365  191.63930

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3p [(6*S*,7*S*,9*R*)-3p + (6*R*,7*R*,9*S*)-3p]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

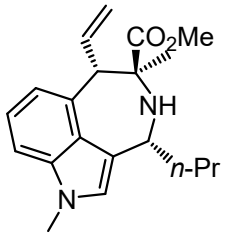

Signal 1: VWD1 A, Wavelength=230 nm

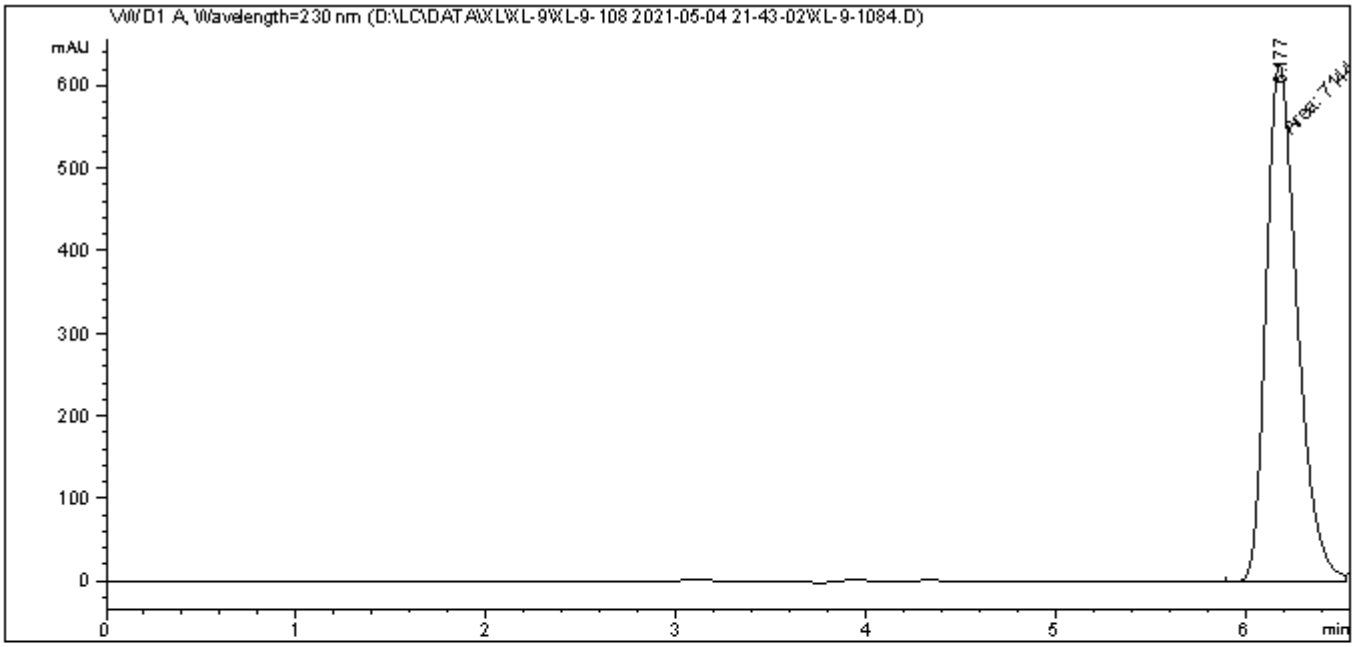
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.387 MF    0.1636 5233.17432  532.99854  50.8655
   2   6.181 FM    0.1900 5055.08105  443.37534  49.1345

Totals :                  1.02883e4   976.37387


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3p



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

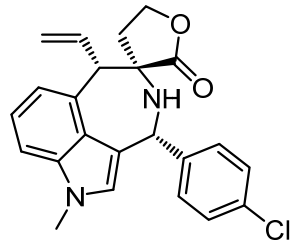

Signal 1: VWD1 A, Wavelength=230 nm

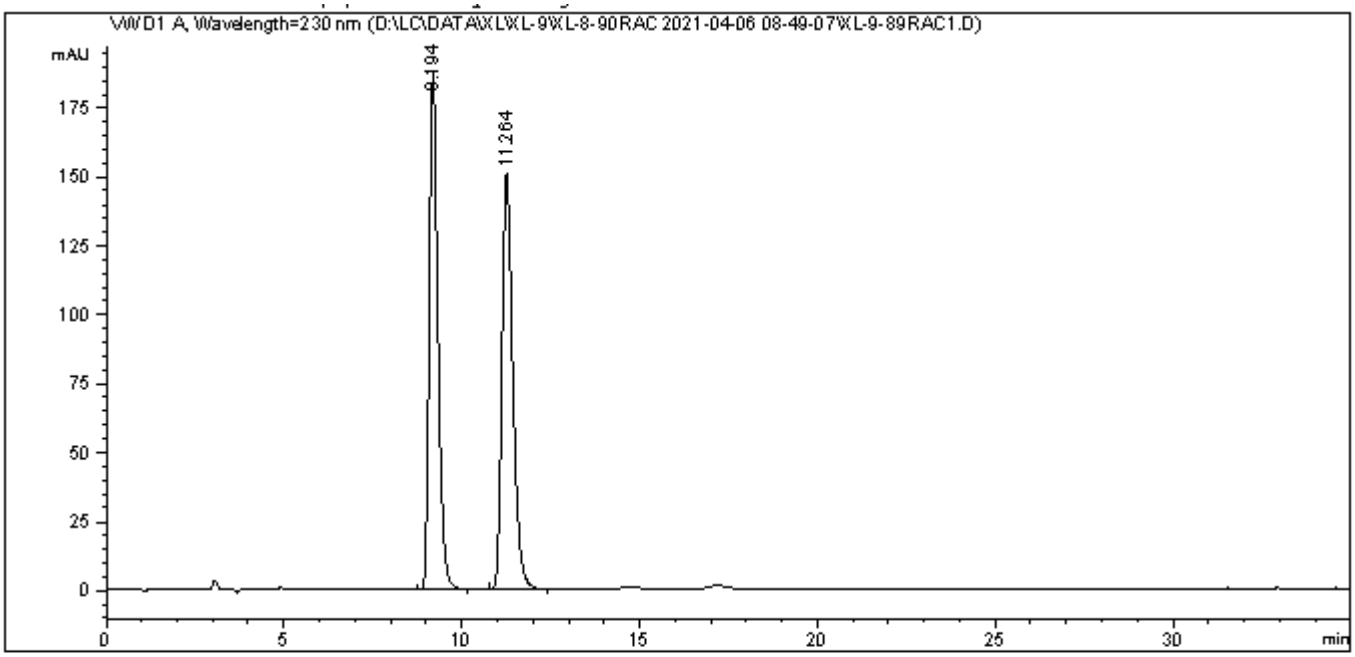
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.177 MF    0.1899 7144.43945  627.18958 100.0000

Totals :                  7144.43945  627.18958

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3q [(6*S*,7*S*,9*R*)-3q + (6*R*,7*R*,9*S*)-3q]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

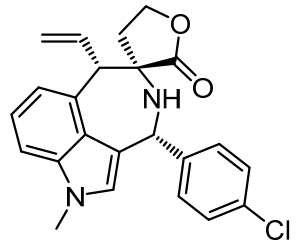

Signal 1: VWD1 A, Wavelength=230 nm

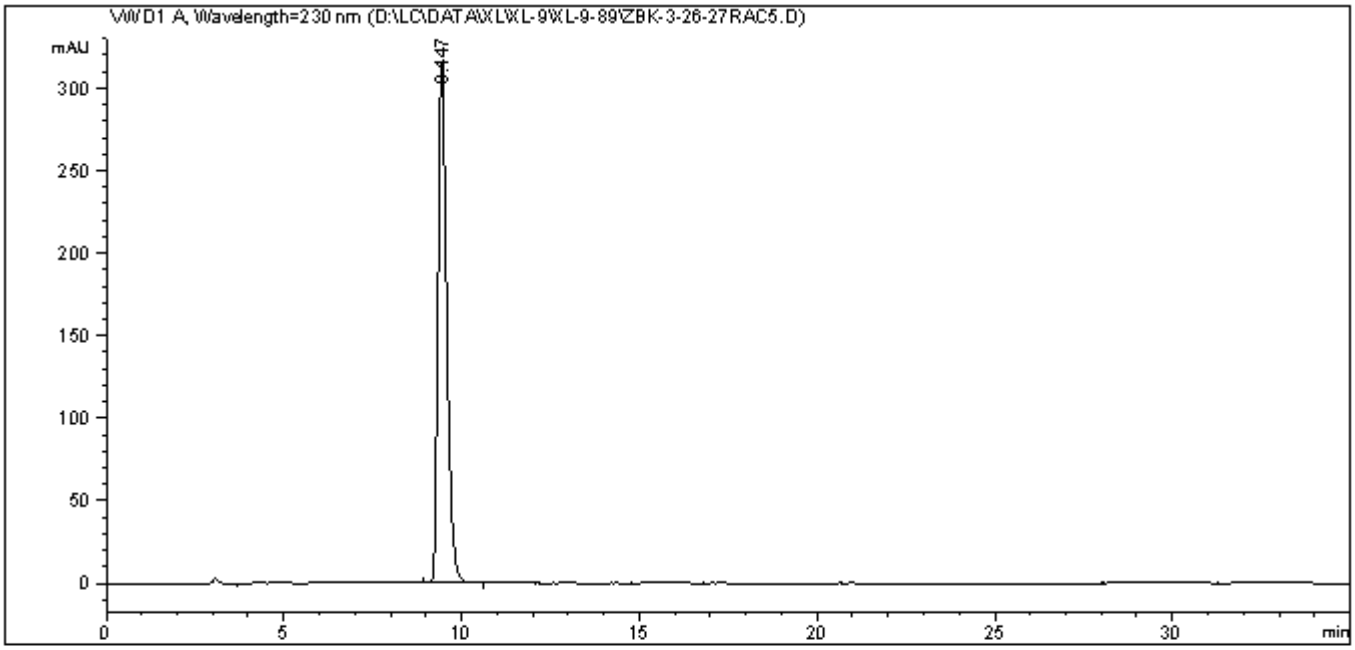
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.194 BB    0.2588 3206.79517  187.93295  50.0065
   2  11.264 BV R  0.3254 3205.96338  150.66389  49.9935

Totals :                  6412.75854  338.59685

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3q






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

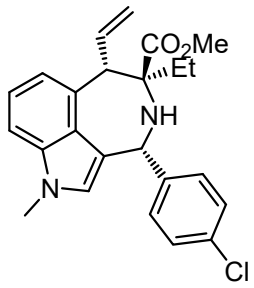

Signal 1: VWD1 A, Wavelength=230 nm

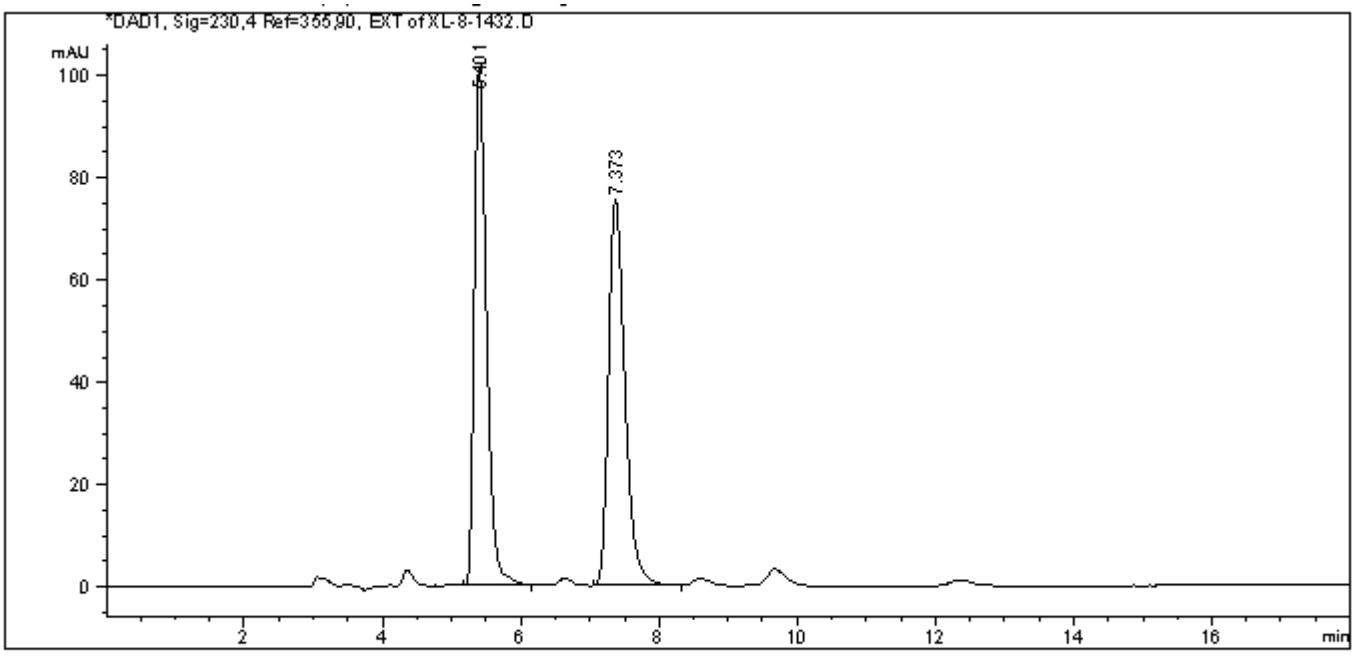
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.447 VV R  0.2616 5400.13086  314.33347 100.0000

Totals :                  5400.13086  314.33347

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3r [(6*S*,7*S*,9*R*)-3r + (6*R*,7*R*,9*S*)-3r]



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==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

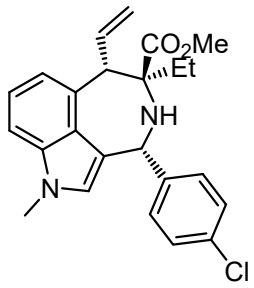

Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

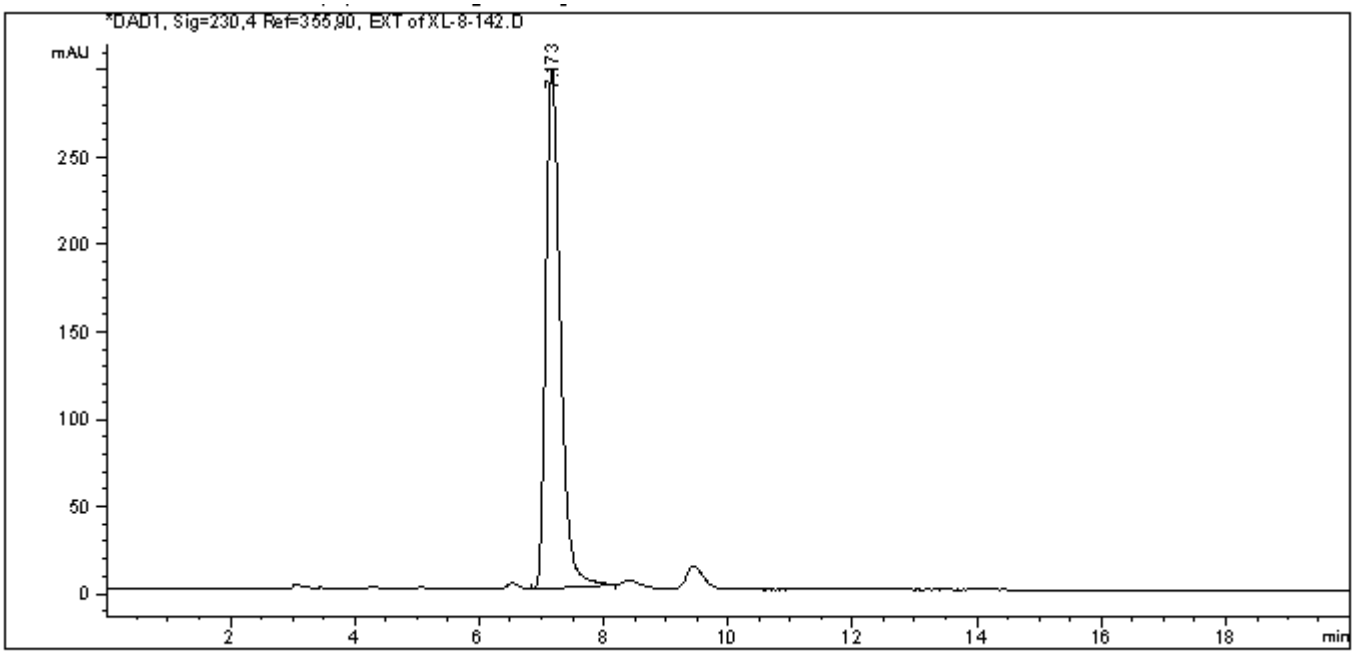
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.401 BB    0.1914 1238.24109  100.71017  49.7037
   2   7.373 BB    0.2539 1253.00439   75.40665  50.2963

Totals :                  2491.24548  176.11681


==================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3r






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

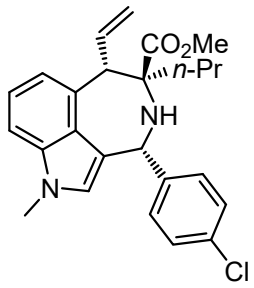

Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

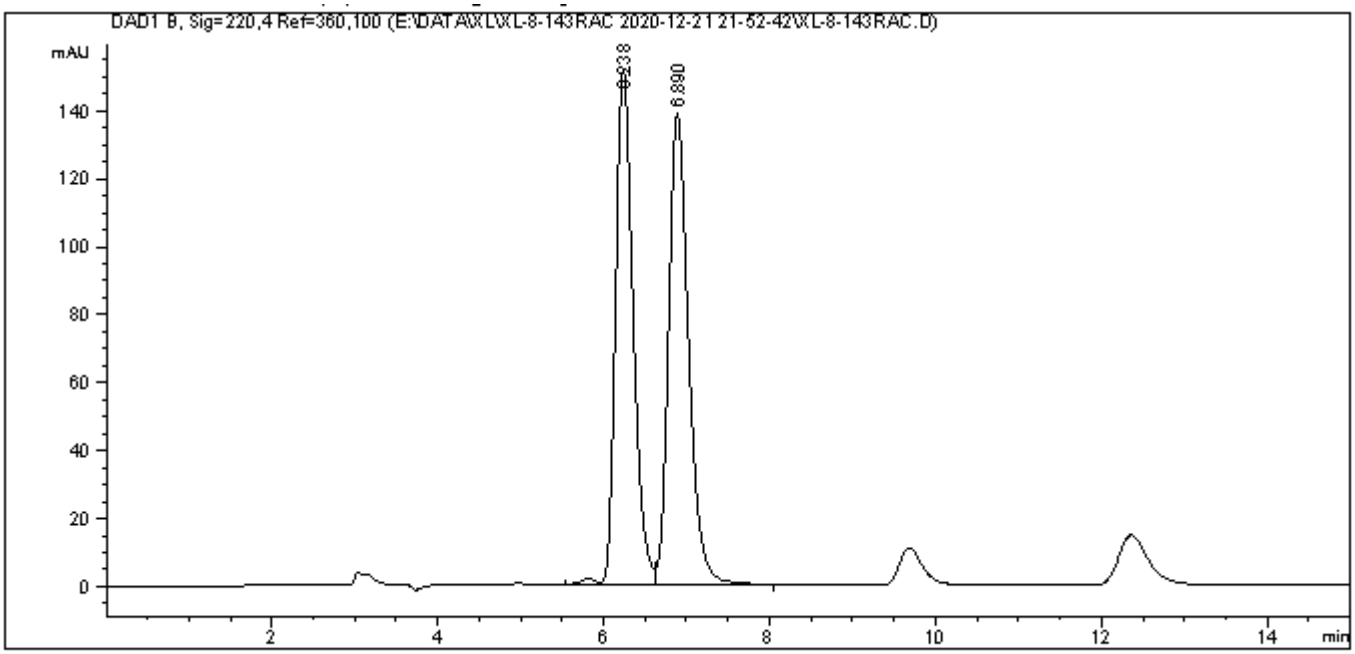
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.173 BB    0.2467 4804.78516  297.09149 100.0000

Totals :                  4804.78516  297.09149


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3s [(6*S*,7*S*,9*R*)-3s +(6*R*,7*R*,9*S*)-3s]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

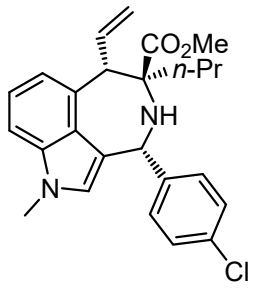

Signal 1: DAD1 B, Sig=220,4 Ref=360,100

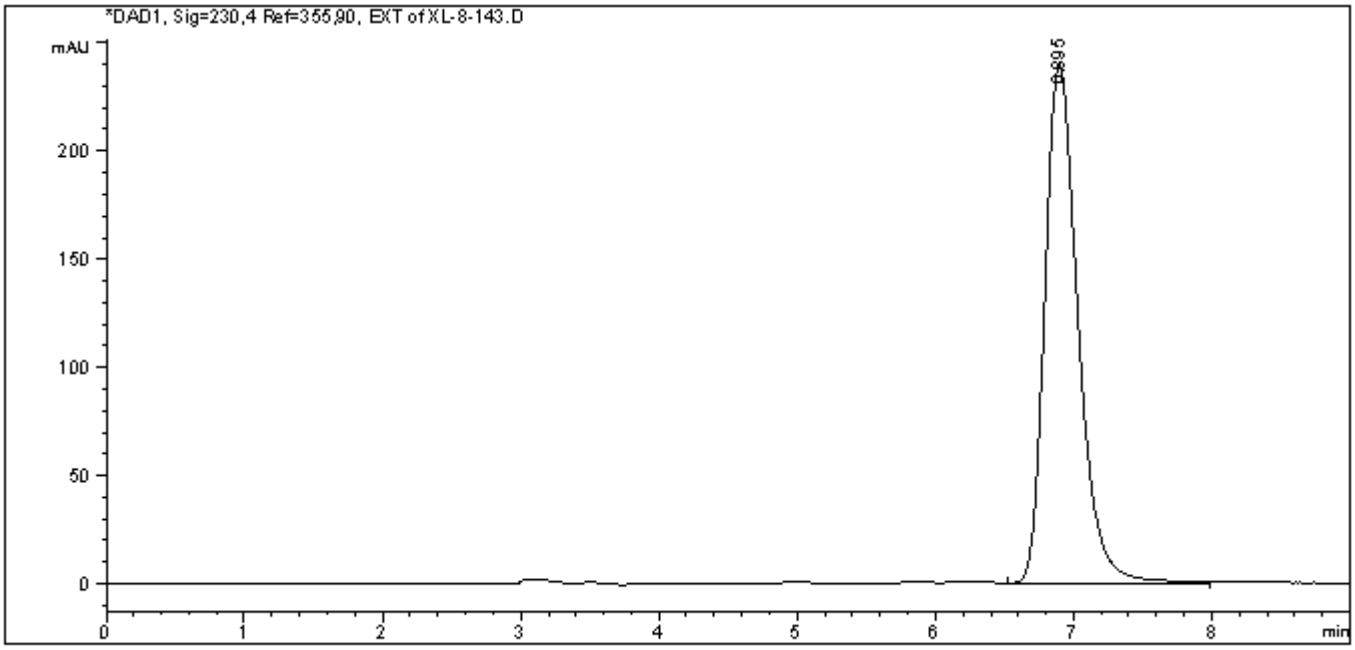
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.238 VV R  0.2251 2248.14502  151.63770  49.0974
   2   6.890 VB    0.2570 2330.80713  138.73984  50.9026

Totals :                  4578.95215  290.37753


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3s






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

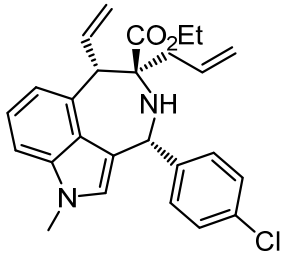

Signal 1: DAD1, Sig=230,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

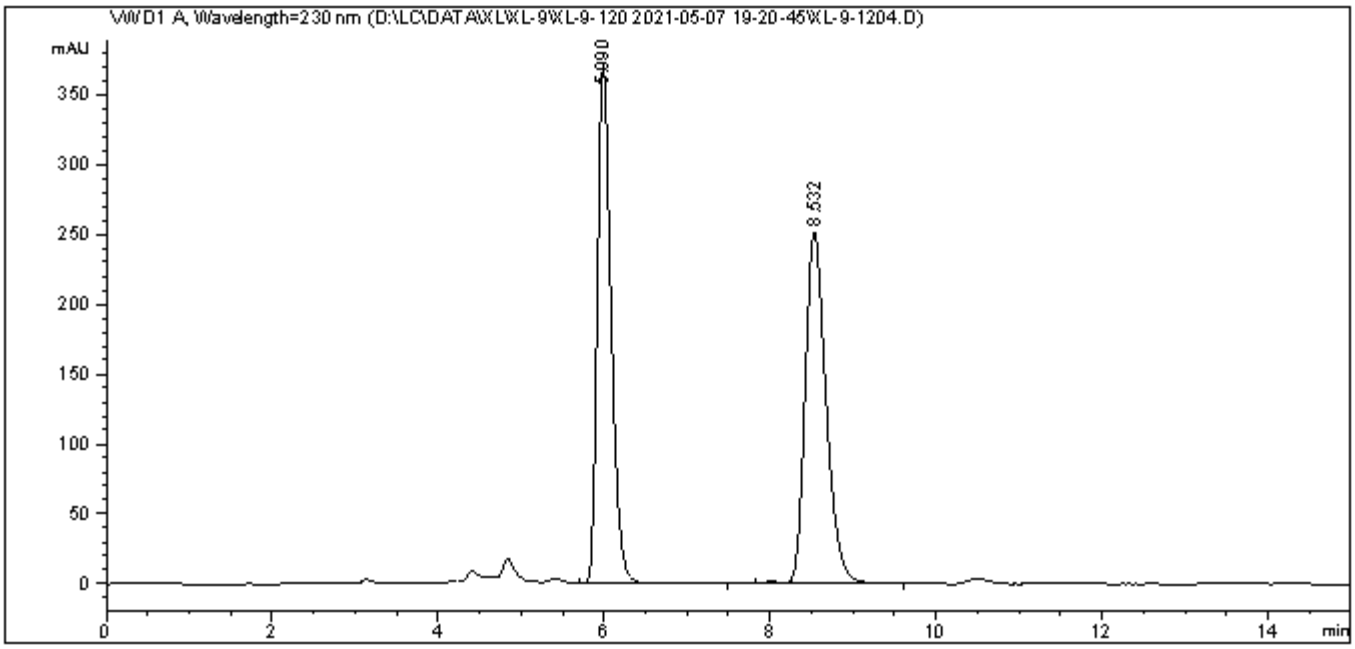
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.895 BB    0.2549 3985.82813  239.86305 100.0000

Totals :                  3985.82813  239.86305


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3t [(6*S*,7*S*,9*R*)-3t + (6*R*,7*R*,9*S*)-3t]






```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

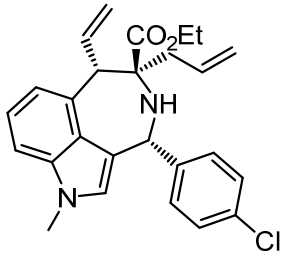

Signal 1: VWD1 A, Wavelength=230 nm

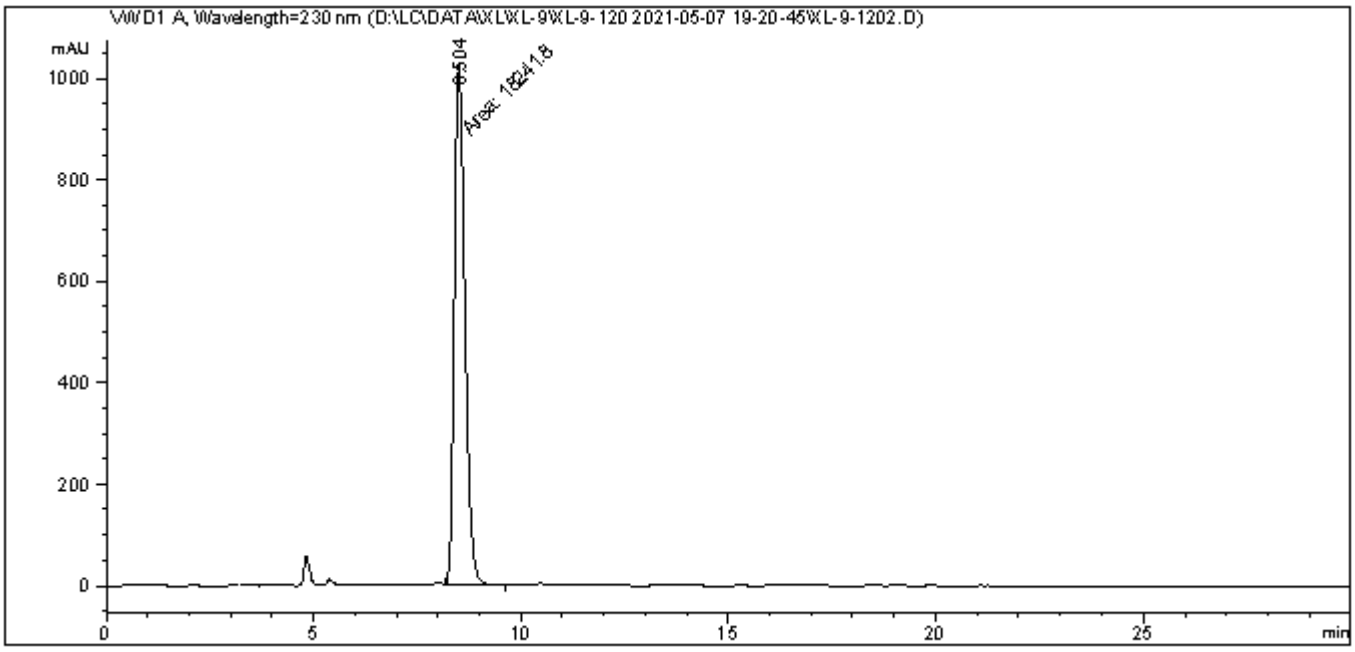
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.990 BV R  0.1779 4311.48926  370.79184  49.4068
   2   8.532 VV R  0.2686 4415.01416  251.88193  50.5932

Totals :                  8726.50342  622.67377


==================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3t



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

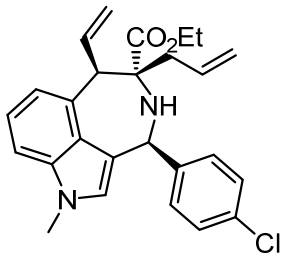

Signal 1: VWD1 A, Wavelength=230 nm

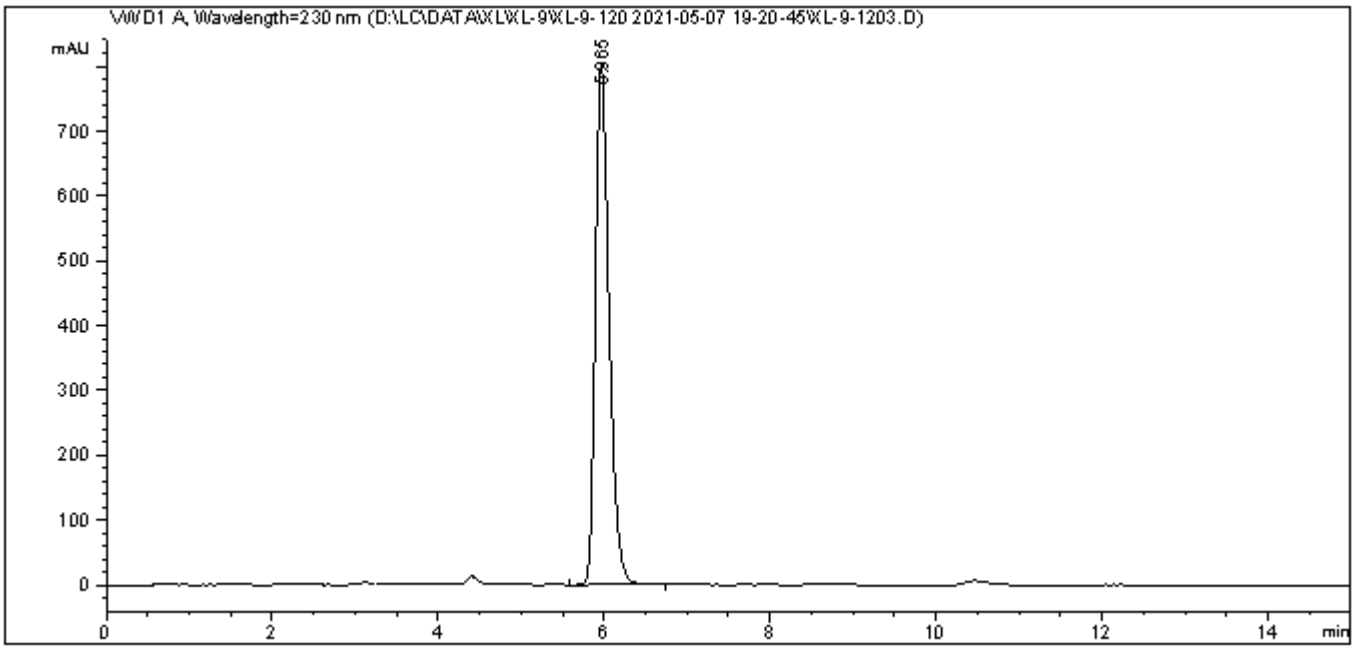
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.504 FM    0.2964 1.82418e4  1025.91406 100.0000

Totals :                  1.82418e4  1025.91406

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*R*,9*S*)-3t






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

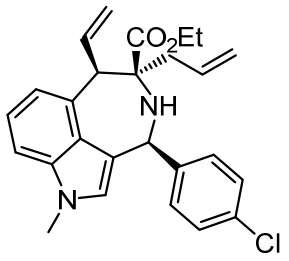

Signal 1: VWD1 A, Wavelength=230 nm

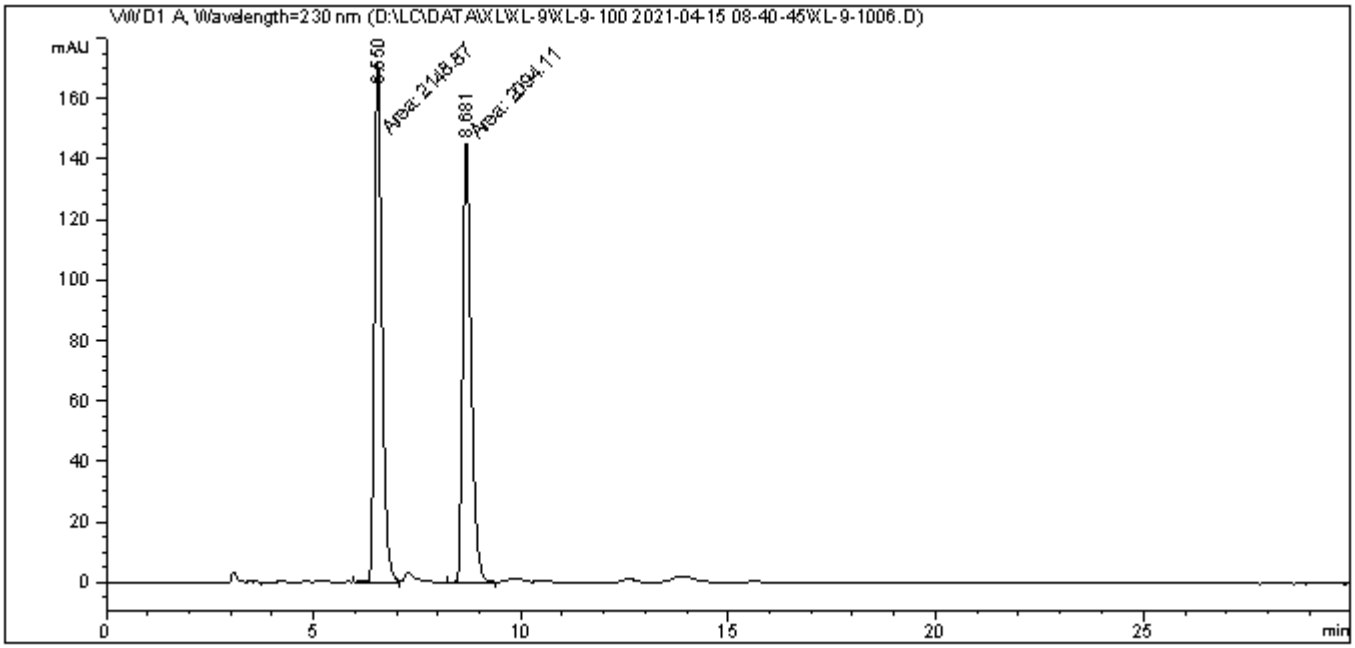
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.965 BB    0.1773 9275.46875  801.03607 100.0000

Totals :                  9275.46875  801.03607

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3t [(6*R*,7*S*,9*S*)-3t + (6*S*,7*R*,9*R*)-3t]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

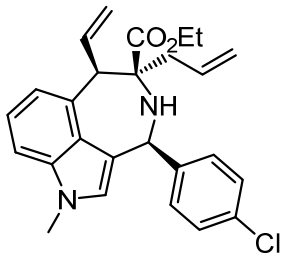

Signal 1: VWD1 A, Wavelength=230 nm

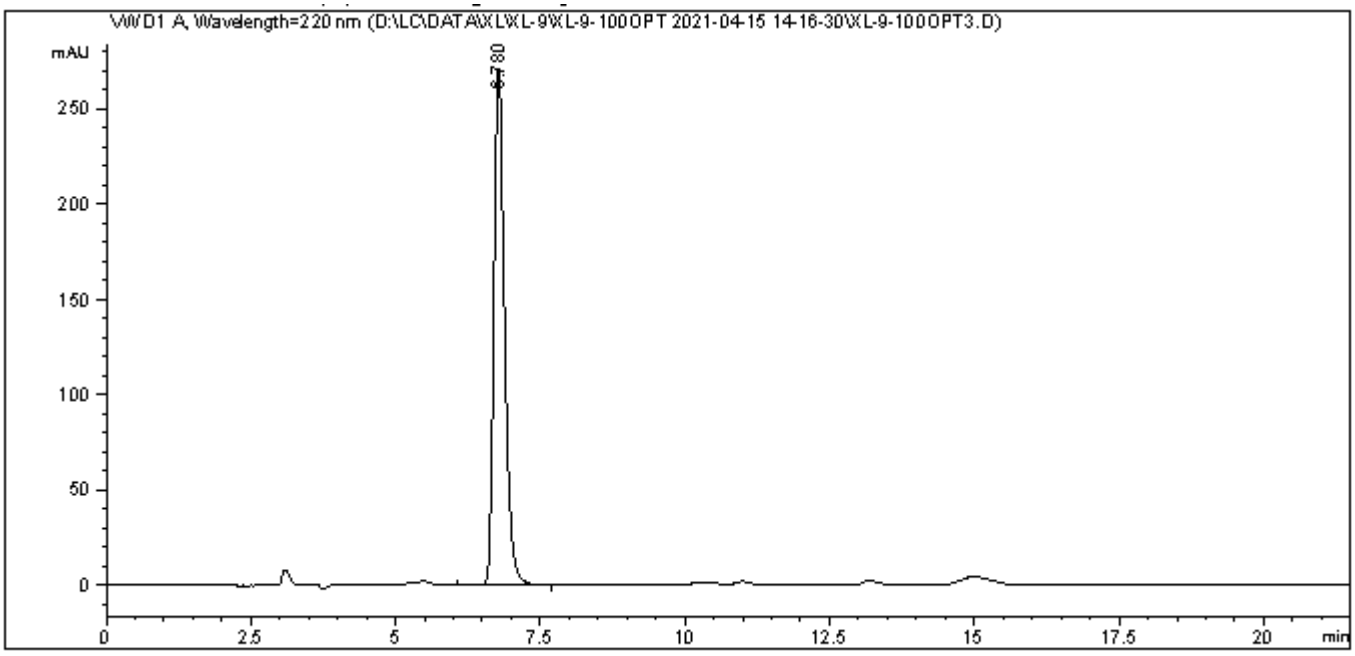
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.550 MF    0.2089 2148.87085  171.40378  50.6454
   2   8.681 MF    0.2398 2094.10596  145.52927  49.3546

Totals :                  4242.97681  316.93304


=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-3t






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

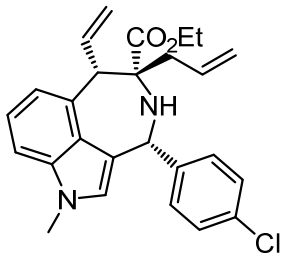

Signal 1: VWD1 A, Wavelength=220 nm

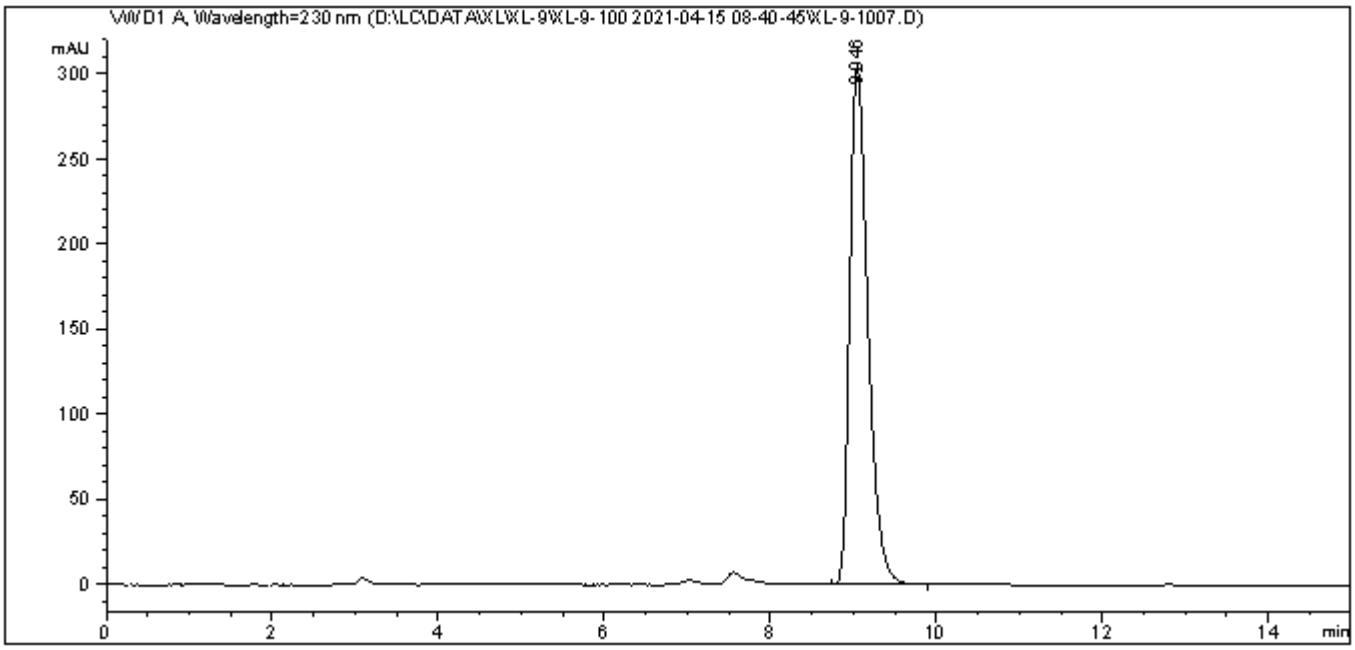
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.780 VV R  0.1968 3523.16943  271.00604 100.0000

Totals :                  3523.16943  271.00604


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*R*,9*R*)-3t



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

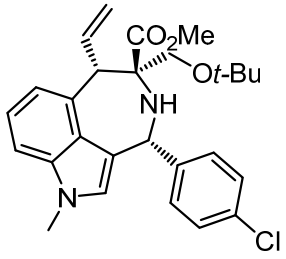

Signal 1: VWD1 A, Wavelength=230 nm

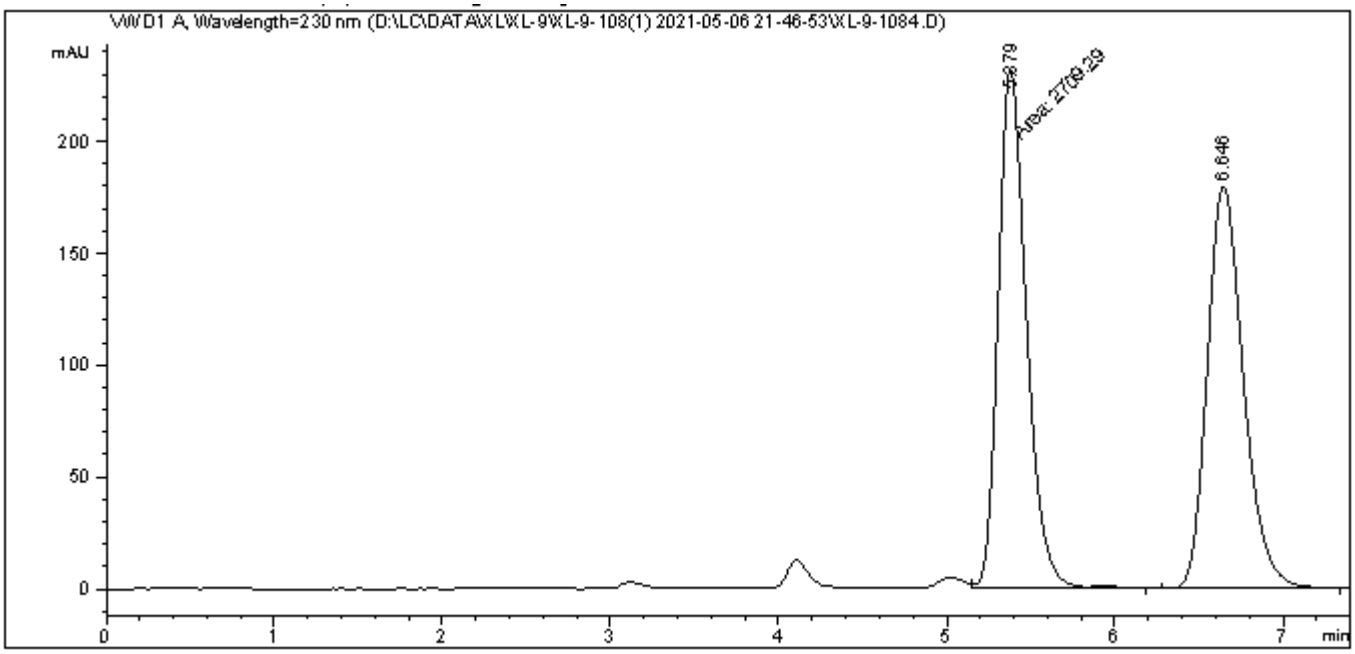
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.046 BB    0.2299 4604.00391  305.11819 100.0000

Totals :                  4604.00391  305.11819

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3u [(6*S*,7*R*,9*R*)-3u + (6*R*,7*S*,9*S*)-3u]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

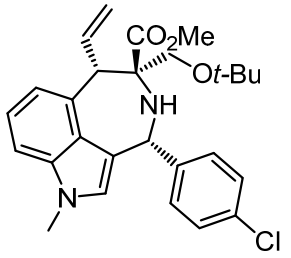

Signal 1: VWD1 A, Wavelength=230 nm

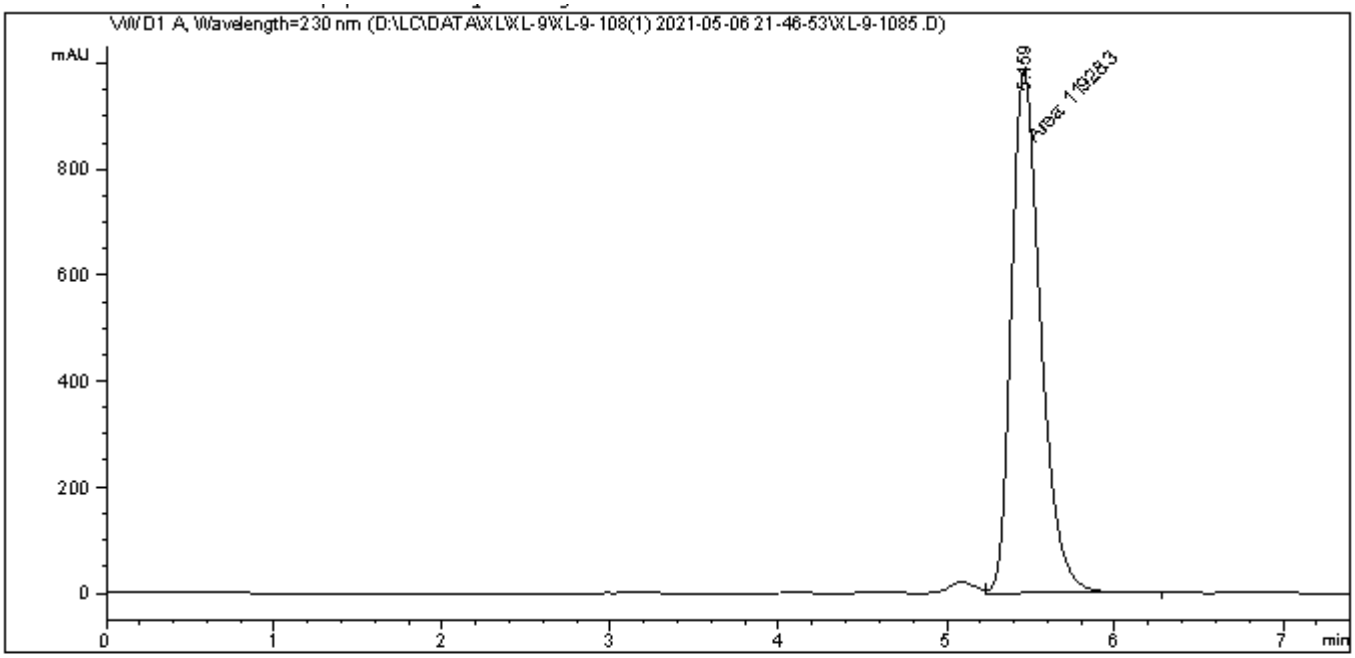
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.379 FM    0.1945 2709.29346  232.11978  50.2130
   2   6.646 BV    0.2283 2686.31079  179.72554  49.7870

Totals :                  5395.60425  411.84532


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*R*,9*R*)-3u



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

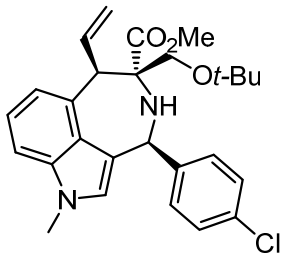

Signal 1: VWD1 A, Wavelength=230 nm

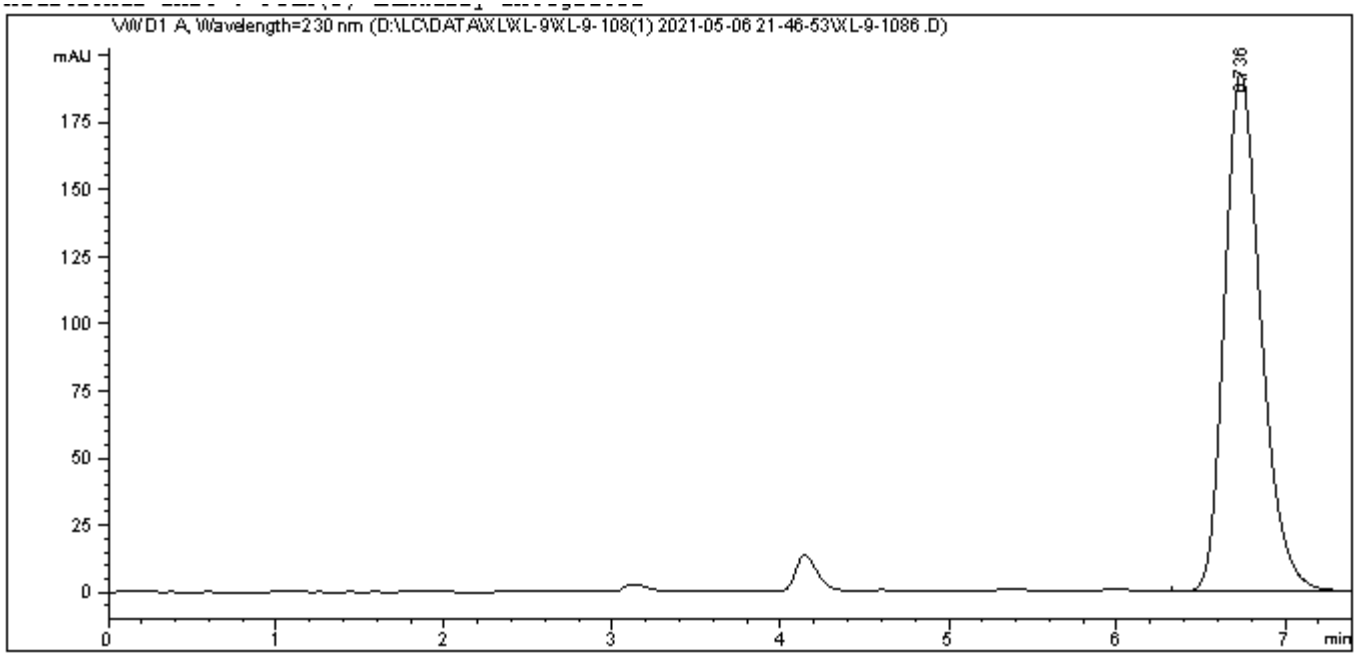
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.459 FM    0.2019 1.19283e4   984.55157 100.0000

Totals :                  1.19283e4   984.55157


=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-3u



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

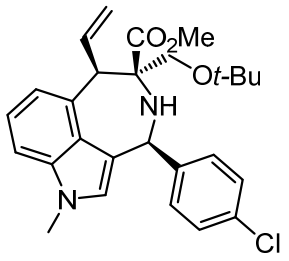

Signal 1: VWD1 A, Wavelength=230 nm

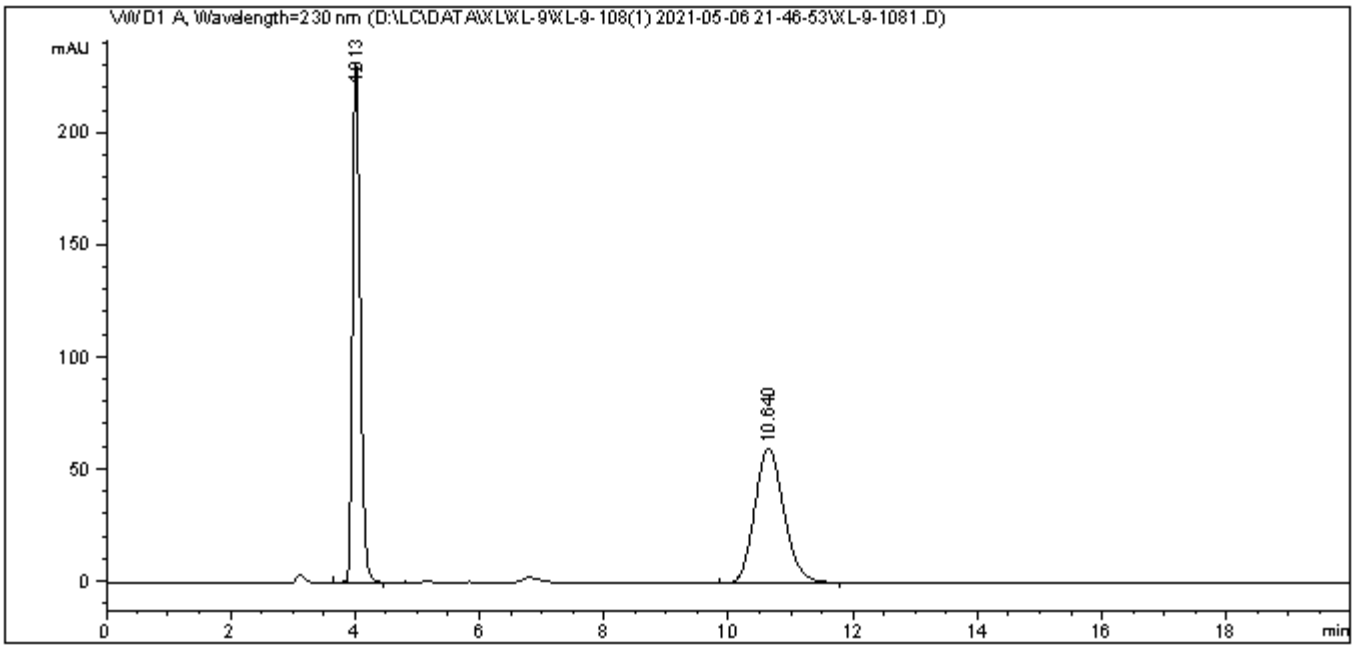
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.736 BV    0.2310 2906.13525  192.97833 100.0000

Totals :                  2906.13525  192.97833


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3u [(6*R*,7*R*,9*S*)-3u + (6*S*,7*S*,9*R*)-3u]



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=====================================================================
                        Area Percent Report
=====================================================================

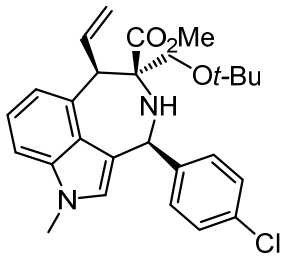
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

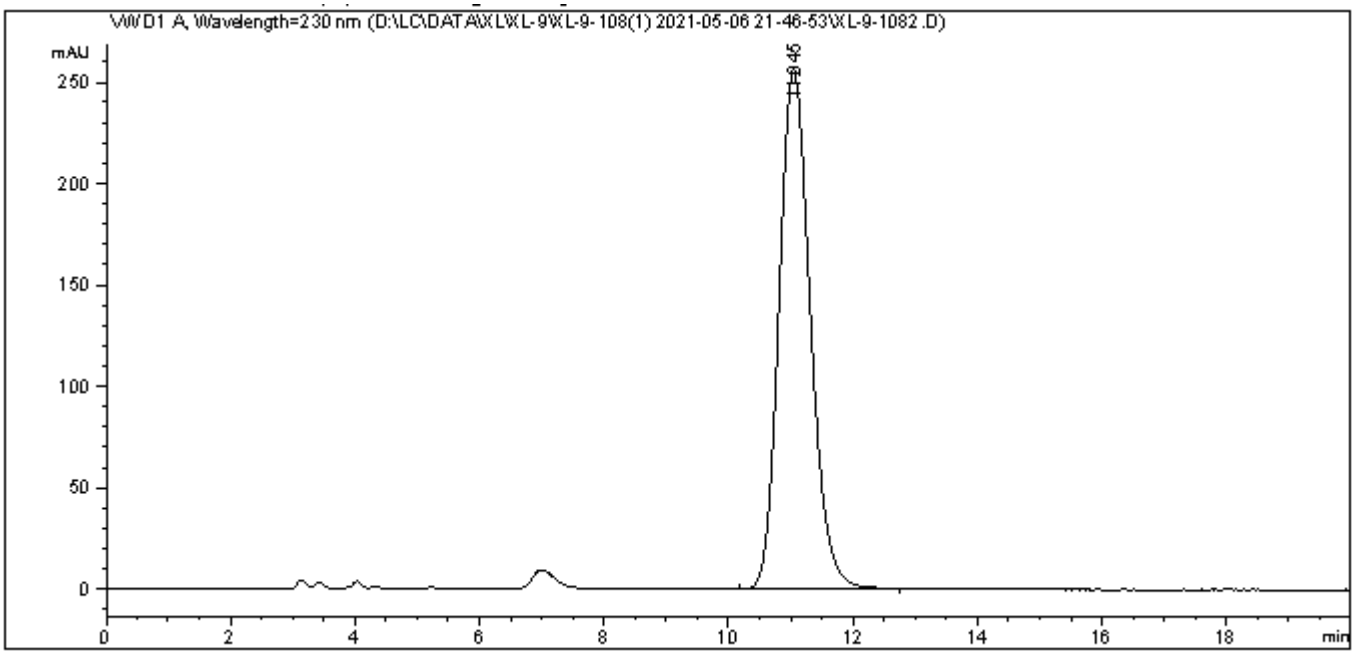

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.013 BB    0.1326 1990.22046  230.88676  50.2550
   2  10.640 BB    0.5021 1970.02393   60.28826  49.7450

Totals :                  3960.24438  291.17502
```

HPLC chromatogram of compound (6*R*,7*R*,9*S*)-3u






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

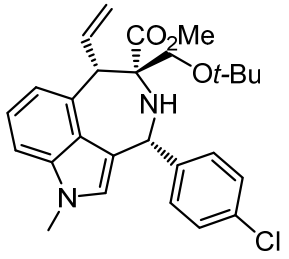

Signal 1: VWD1 A, Wavelength=230 nm

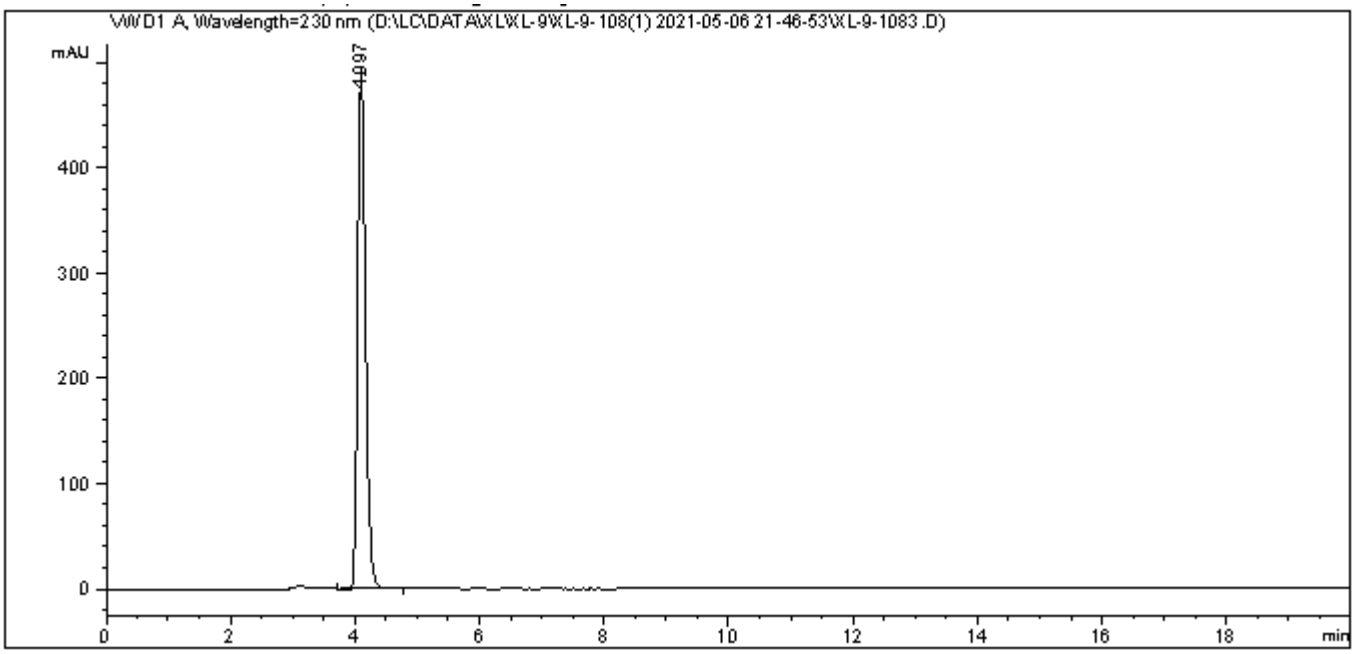
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.045 BV R  0.5389 8926.01563  256.23291 100.0000

Totals :                  8926.01563  256.23291


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3u



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

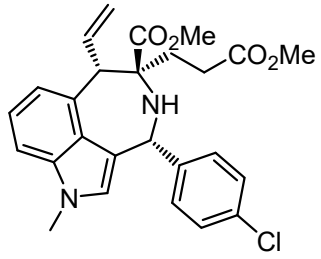

Signal 1: VWD1 A, Wavelength=230 nm

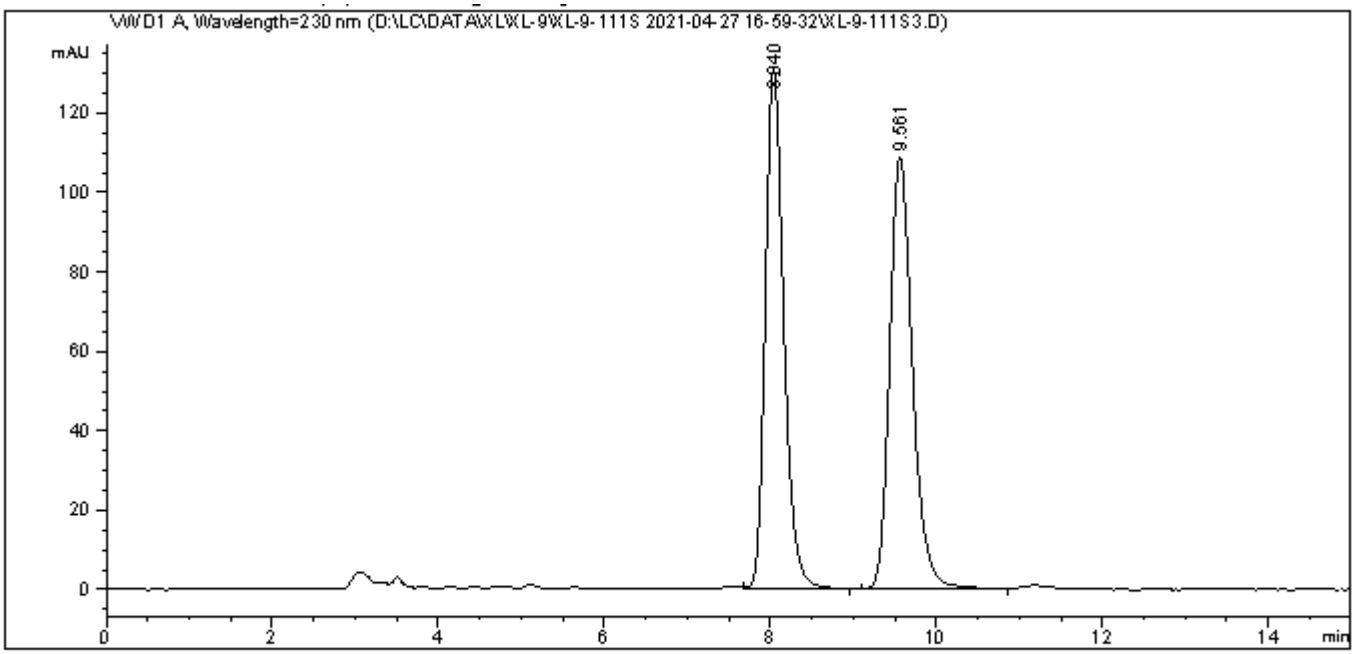
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.097 VV R  0.1364 4349.53662  493.10995 100.0000

Totals :                  4349.53662  493.10995


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3v [(6*S*,7*S*,9*R*)-3v + (6*S*,7*S*,9*R*)-3v]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

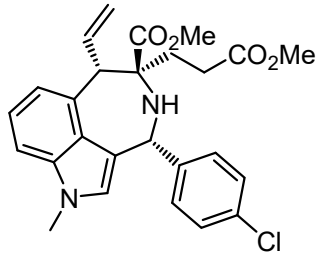

Signal 1: VWD1 A, Wavelength=230 nm

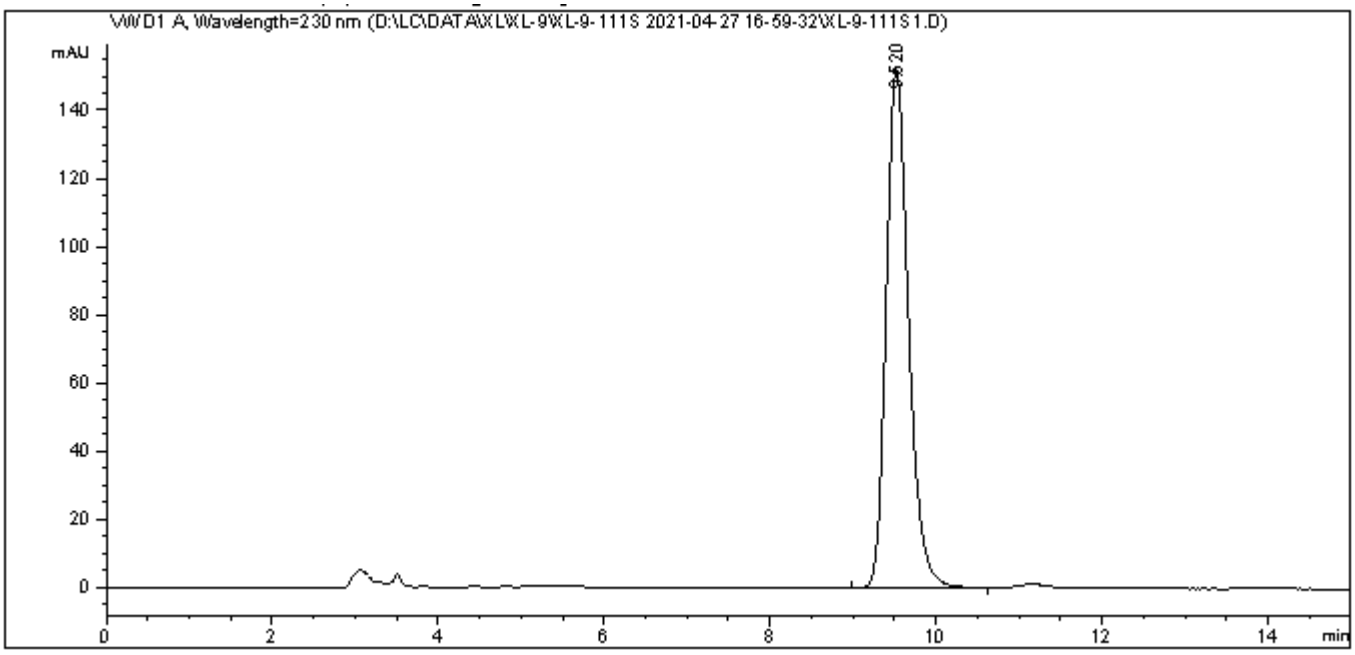
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.040 BV R  0.2354 2016.88623  130.64432  49.3566
   2   9.561 BV R  0.2903 2069.46729  108.81210  50.6434

Totals :                  4086.35352  239.45641

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3v



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

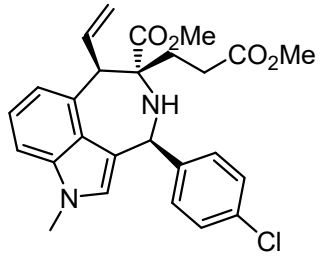

Signal 1: VWD1 A, Wavelength=230 nm

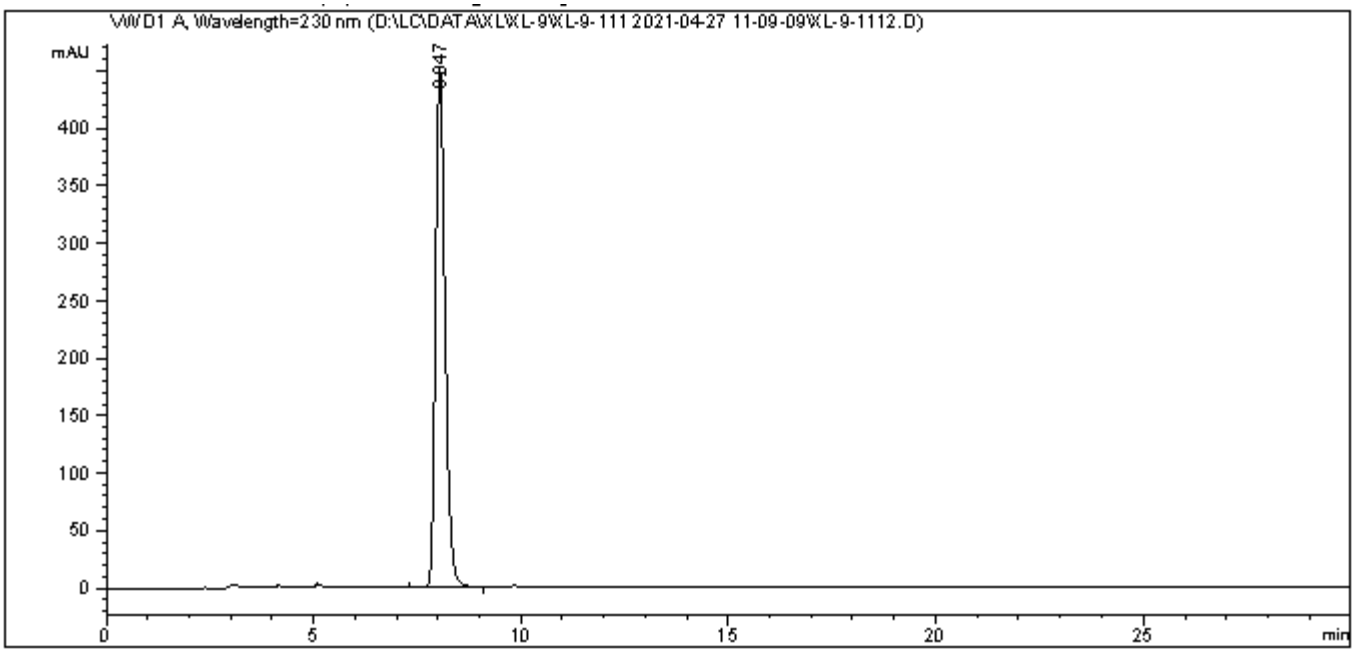
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.520 VB R  0.2847 2842.49683  152.31169 100.0000

Totals :                  2842.49683  152.31169


=====================================================================
```

HPLC chromatogram of compound (6*R*,7*R*,9*S*)-3v



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

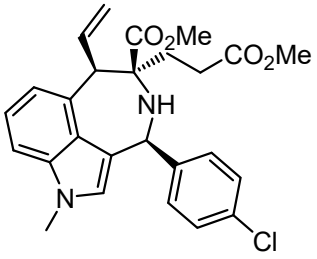

Signal 1: VWD1 A, Wavelength=230 nm

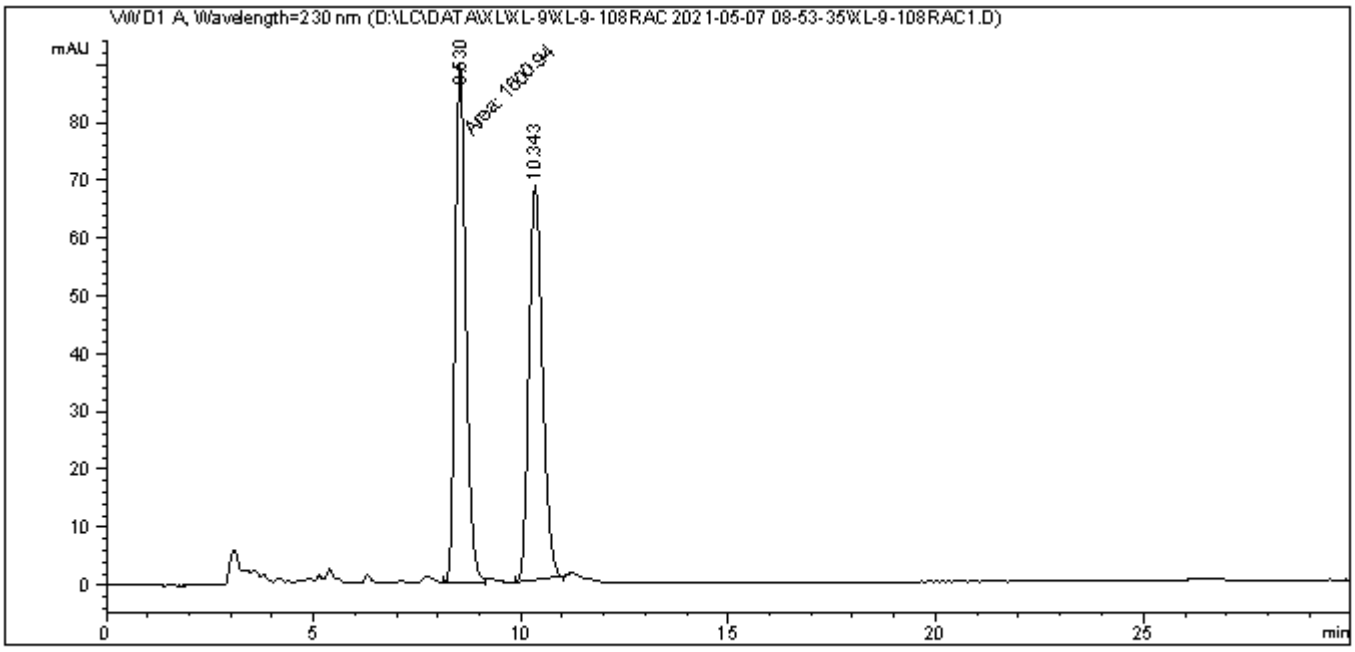
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.047 VV R  0.2471 7303.34668  451.09256 100.0000

Totals :                  7303.34668  451.09256


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3v [(6*R*,7*S*,9*S*)-3v + (6*S*,7*R*,9*R*)-3v]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

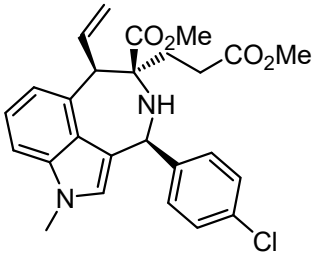

Signal 1: VWD1 A, Wavelength=230 nm

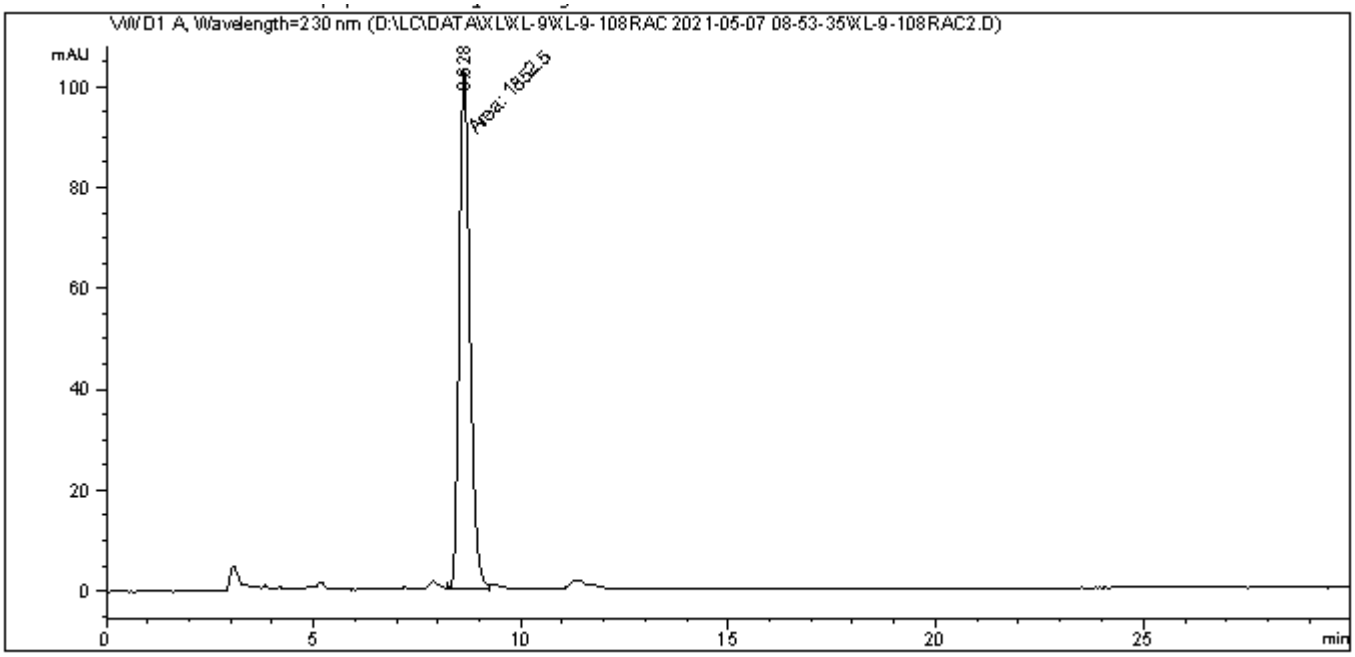
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.530 MF    0.2982 1600.94043   89.48106  50.7714
   2  10.343 BB    0.3530 1552.29163   68.18536  49.2286

Totals :                  3153.23206  157.66641

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-3v



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

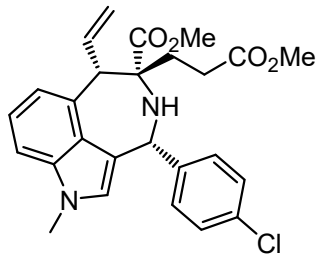

Signal 1: VWD1 A, Wavelength=230 nm

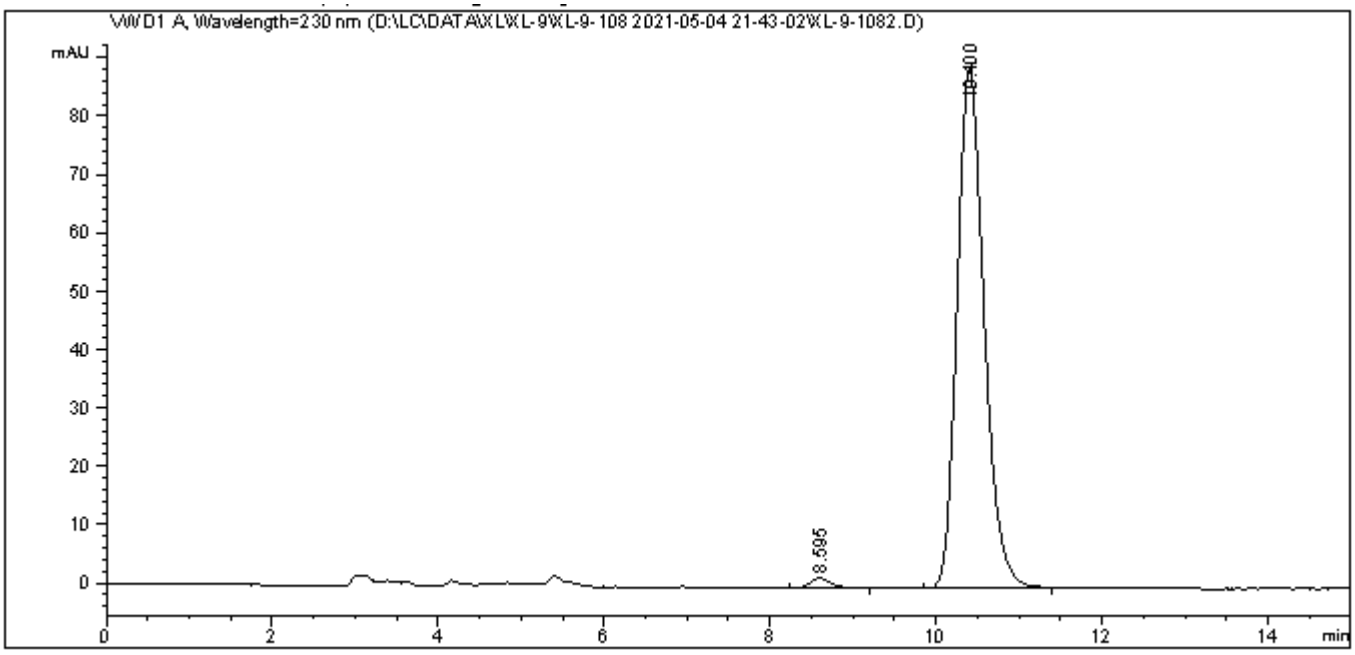
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.628 MF    0.3011 1852.50439  102.54133 100.0000

Totals :                  1852.50439  102.54133


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*R*,9*R*)-3v






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

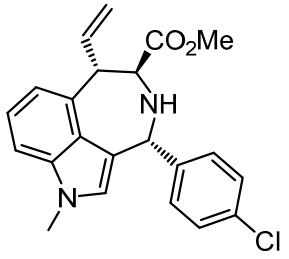

Signal 1: VWD1 A, Wavelength=230 nm

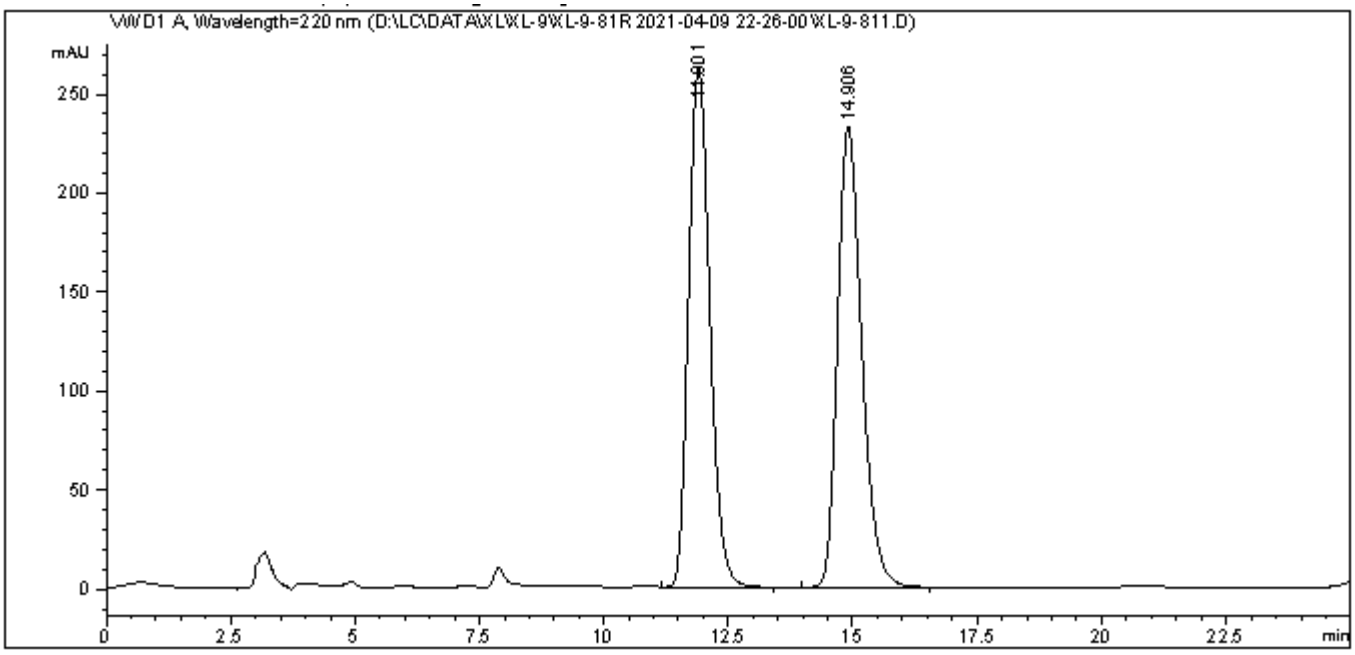
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.595 BV R  0.2541   32.58307    1.74613   1.5923
   2  10.400 BV R  0.3459 2013.67163   88.85639  98.4077

Totals :                  2046.25470   90.60252

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3w [(6*S*,7*S*,9*R*)-3w + (6*R*,7*R*,9*S*)-3w]






```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

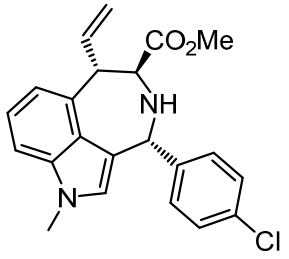

Signal 1: VWD1 A, Wavelength=220 nm

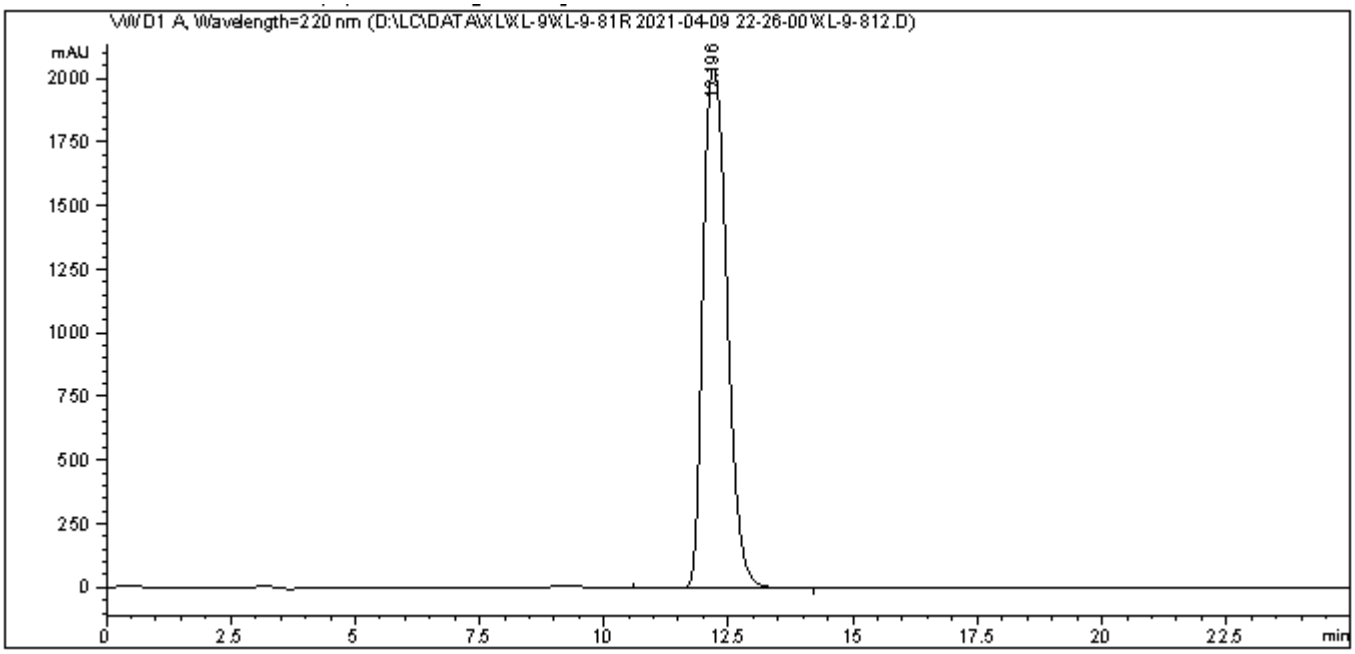
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.901 BB    0.4645 7769.15869  261.50870  49.6805
   2  14.906 BV R  0.5193 7869.07617  232.98563  50.3195

Totals :                  1.56382e4   494.49432


==================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3w



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

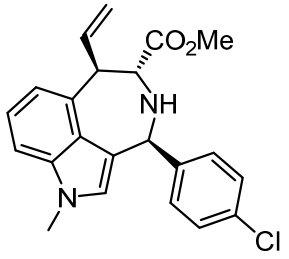

Signal 1: VWD1 A, Wavelength=220 nm

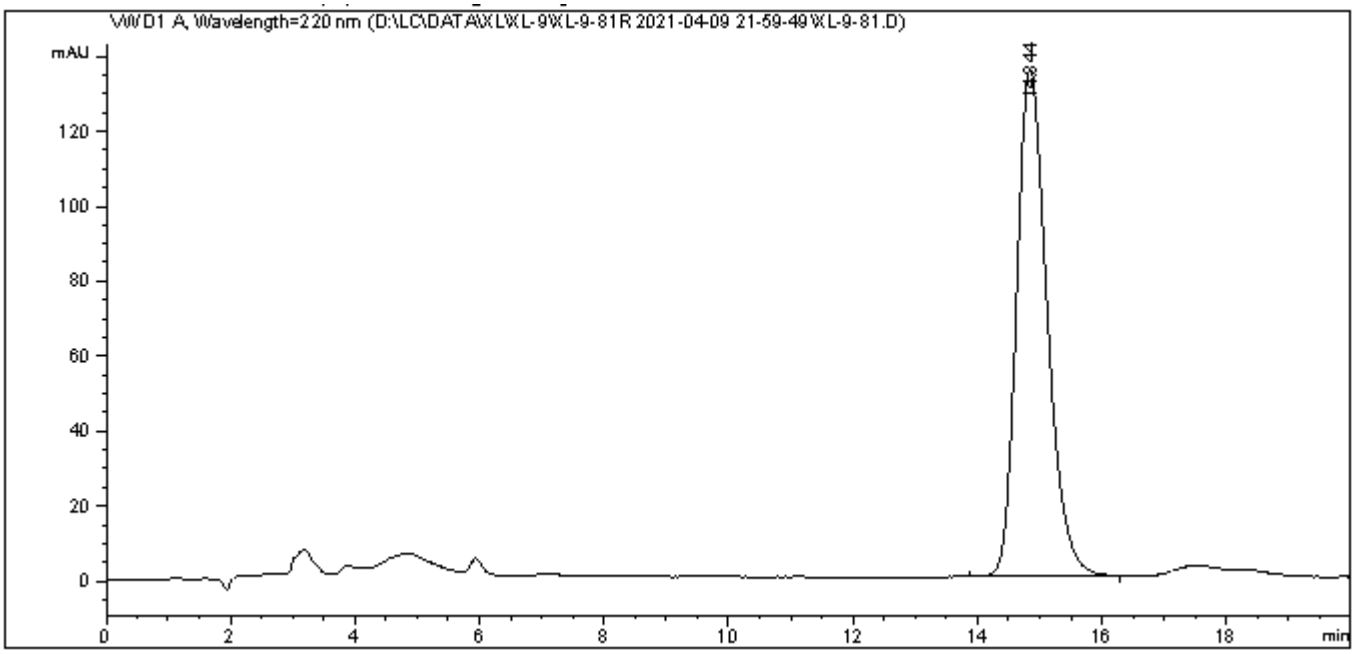
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.196 VB R  0.5359 6.8839le4  2039.37207 100.0000

Totals :                  6.8839le4  2039.37207


=====================================================================
```

HPLC chromatogram of compound (6*R*,7*R*,9*S*)-3w






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

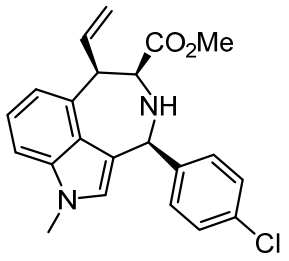

Signal 1: VWD1 A, Wavelength=220 nm

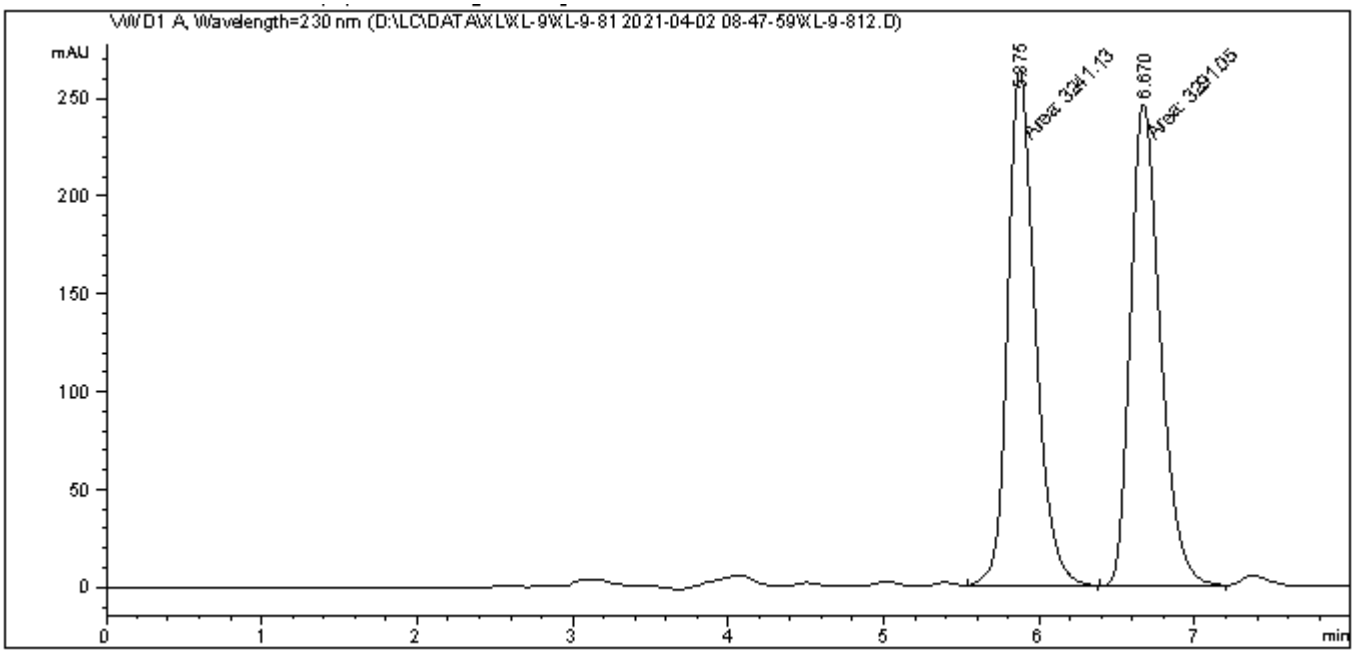
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.844 BB    0.5226 4607.84668  135.29094 100.0000

Totals :                  4607.84668  135.29094


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3w [(6*R*,7*S*,9*S*)-3w + (6*S*,7*R*,9*R*)-3w]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

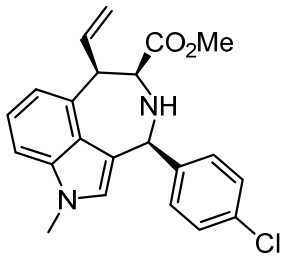

Signal 1: VWD1 A, Wavelength=230 nm

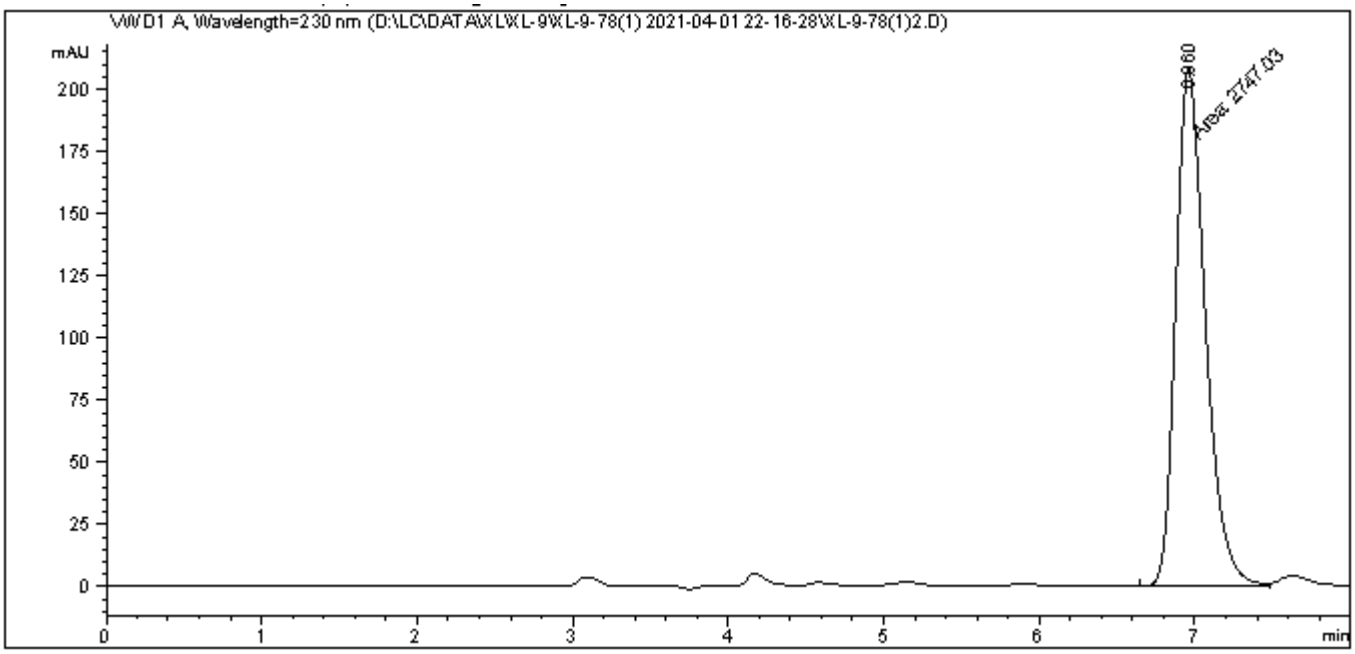
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.875 MM    0.2043 3241.12695  264.36353  49.6179
   2   6.670 MF    0.2224 3291.05005  246.64017  50.3821

Totals :                  6532.17700  511.00369

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-3w






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

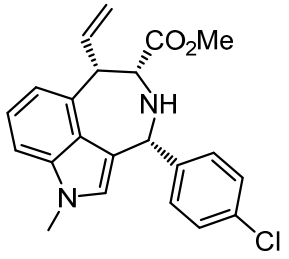

Signal 1: VWD1 A, Wavelength=230 nm

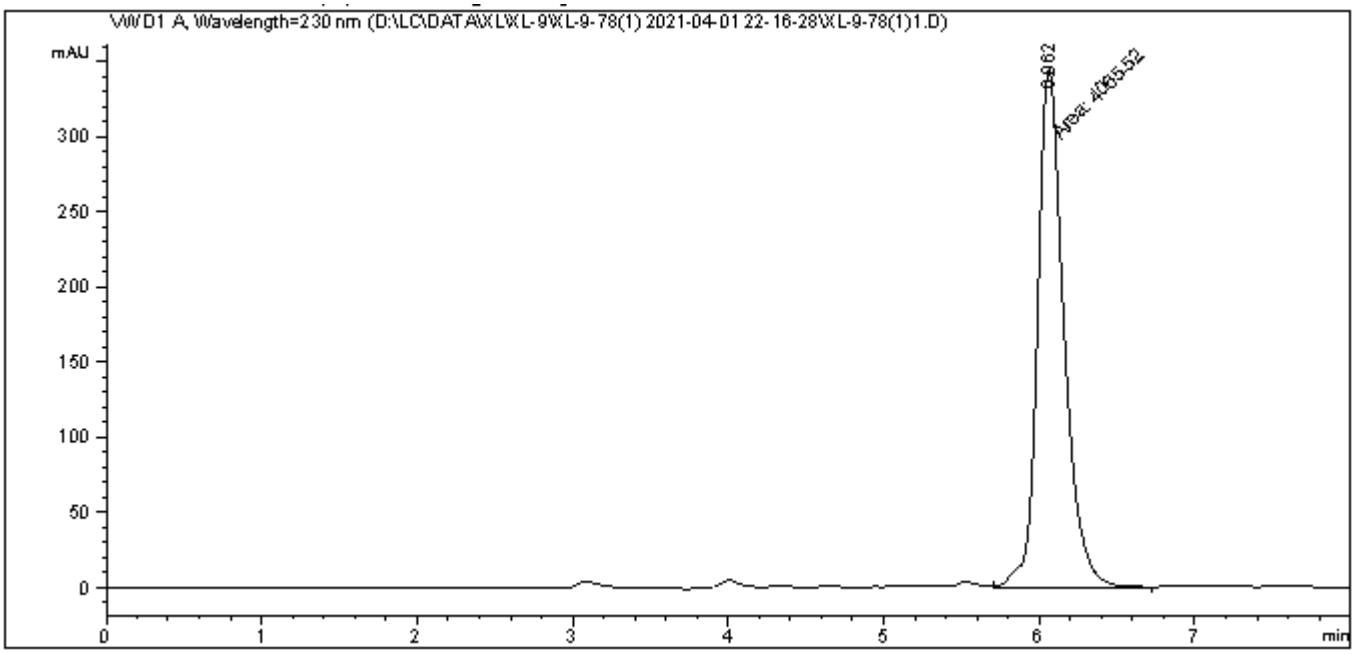
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.960 MF    0.2202 2747.03101  207.89195 100.0000

Totals :                  2747.03101  207.89195


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*R*,9*R*)-3w



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======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

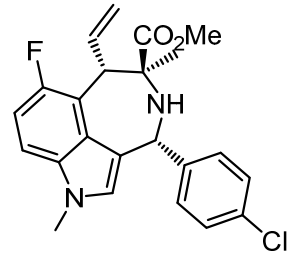

Signal 1: VWD1 A, Wavelength=230 nm

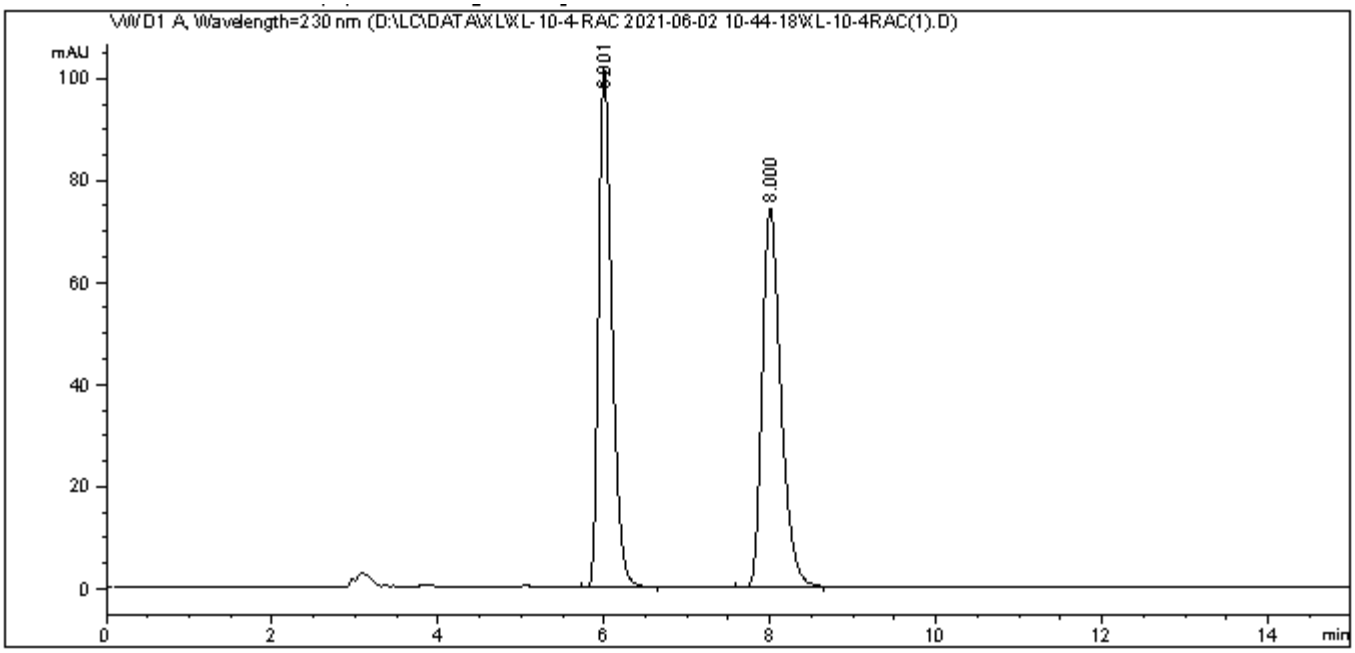
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.062 FM    0.1965 4065.51904  344.76599 100.0000

Totals :                  4065.51904  344.76599

======================================================================
```

HPLC chromatogram of compound (*rac*)-3x [(6*S*,7*S*,9*R*)-3x + (6*R*,7*R*,9*S*)-3x]






```
=====================================================================
                        Area Percent Report
=====================================================================

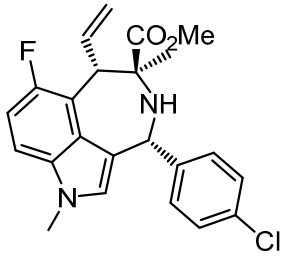
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

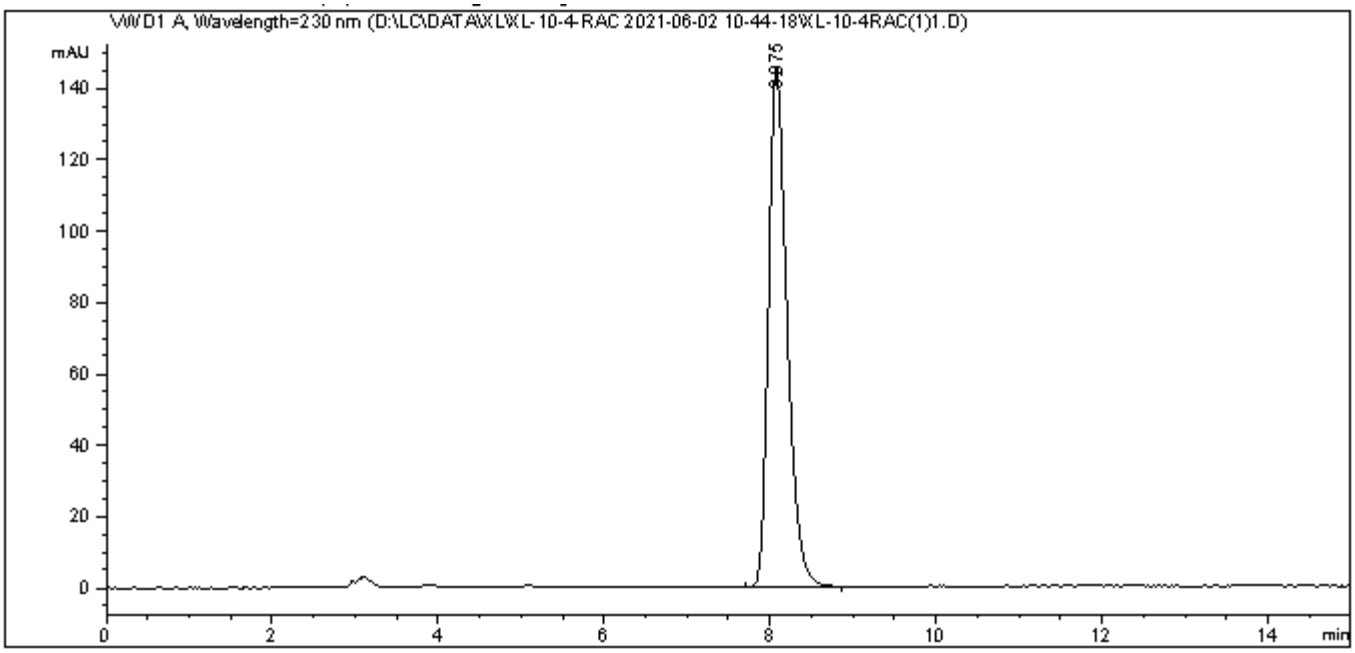

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.001 BV R  0.1705 1142.04541  101.54745  49.7489
   2   8.000 BB    0.2351 1153.57483   74.26209  50.2511

Totals :                  2295.62024  175.80955
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3x






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

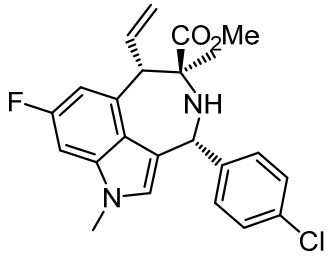

Signal 1: VWD1 A, Wavelength=230 nm

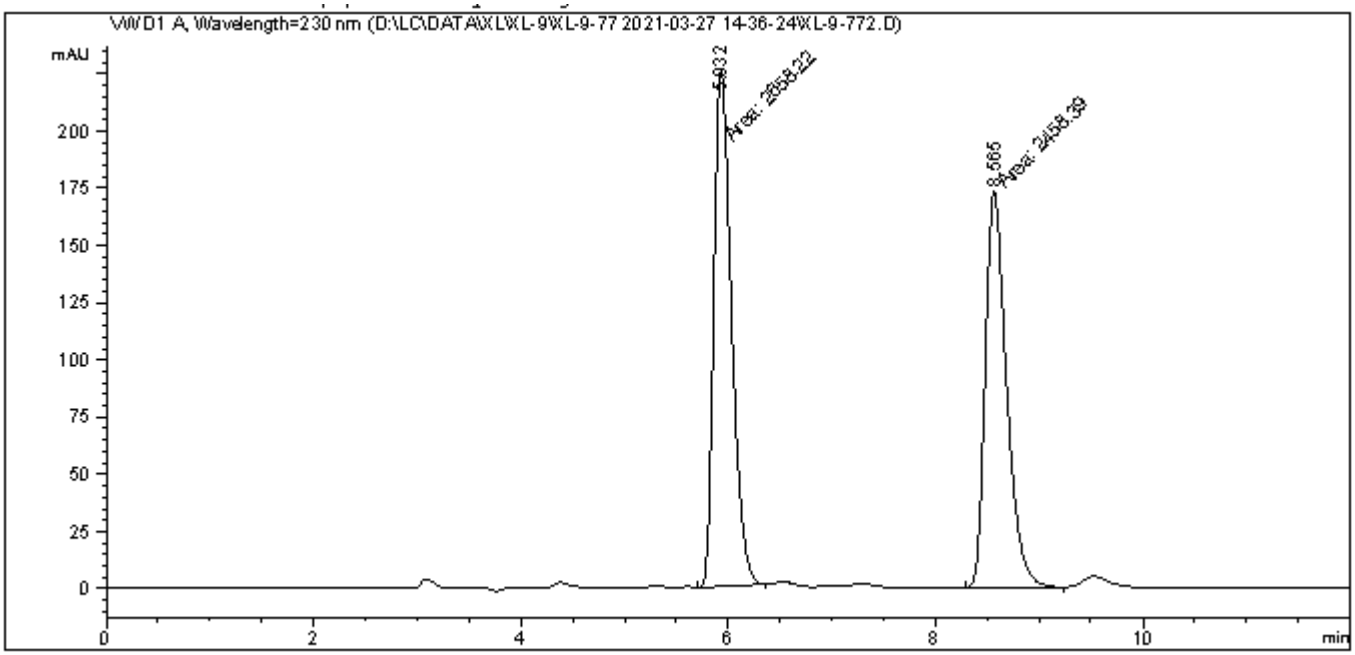
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.075 BB    0.2371 2261.91650  145.21368 100.0000

Totals :                  2261.91650  145.21368


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3y [(6*S*,7*S*,9*R*)-3y + (6*R*,7*R*,9*S*)-3y]






```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

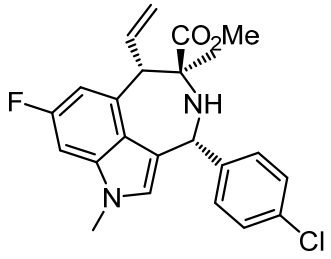

Signal 1: VWD1 A, Wavelength=230 nm

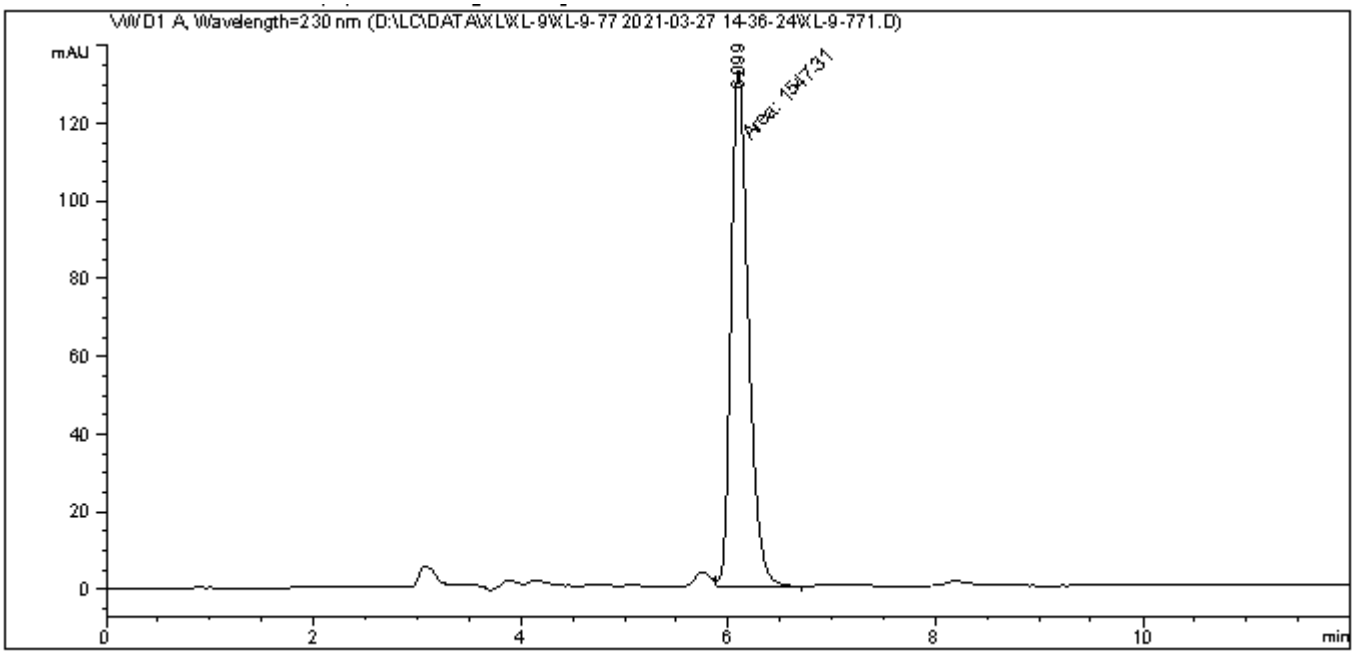
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.932 MM    0.1968 2658.22119  225.09253  51.9528
   2   8.565 MM    0.2370 2458.38574  172.90269  48.0472

Totals :                  5116.60693  397.99522


==================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3y






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

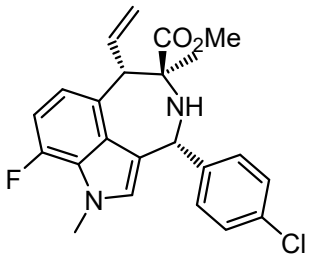

Signal 1: VWD1 A, Wavelength=230 nm

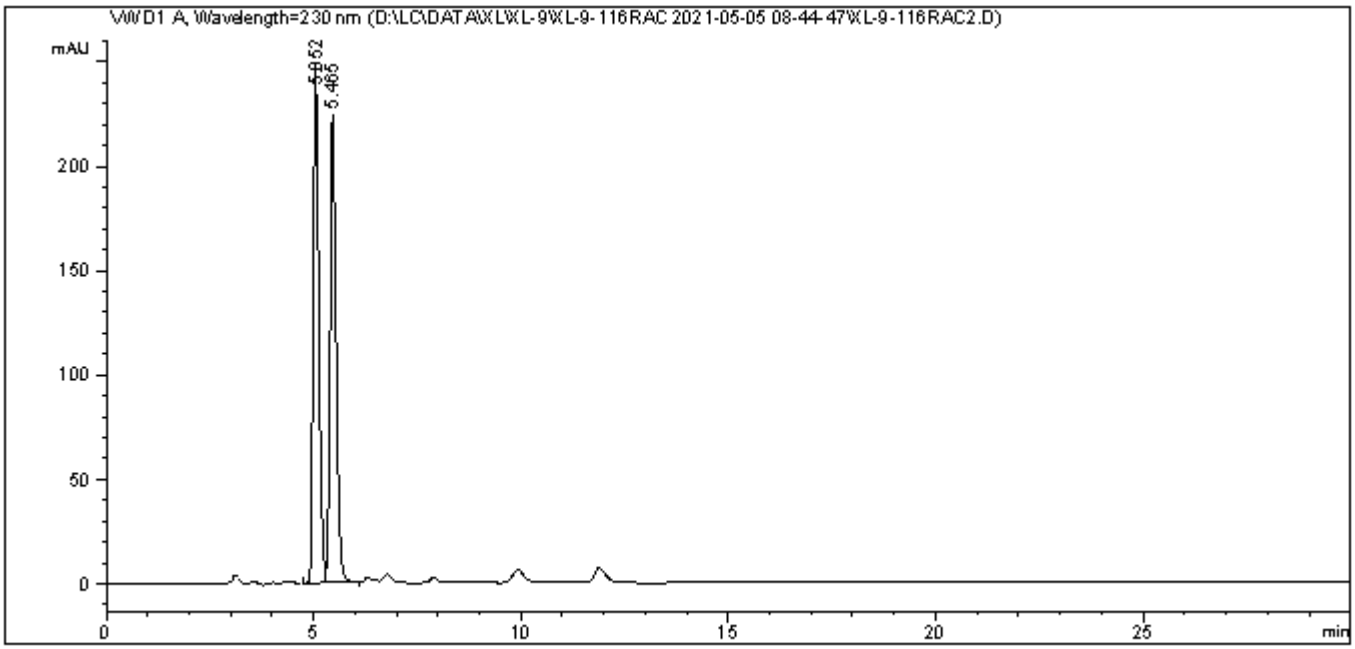
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.099 FM    0.1936 1547.30591  133.21687 100.0000

Totals :                  1547.30591  133.21687


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3z [(6*S*,7*S*,9*R*)-3z + (6*R*,7*R*,9*S*)-3z]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

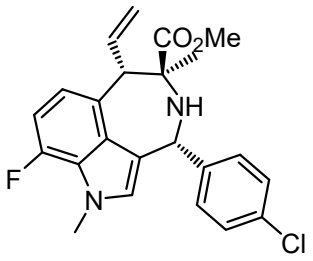

Signal 1: VWD1 A, Wavelength=230 nm

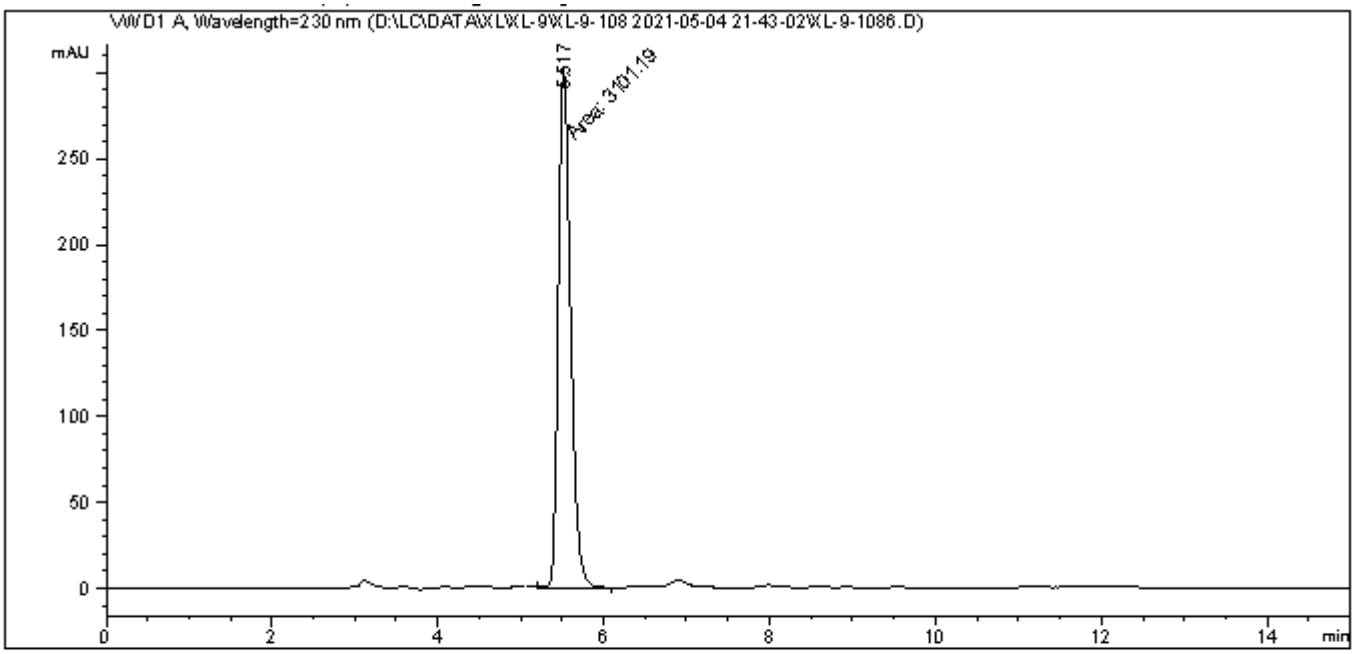
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.052 BV    0.1416 2296.94092  247.93579  50.0599
   2   5.465 VB    0.1553 2291.44458  224.77055  49.9401

Totals :                  4588.38550  472.70634


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3z






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

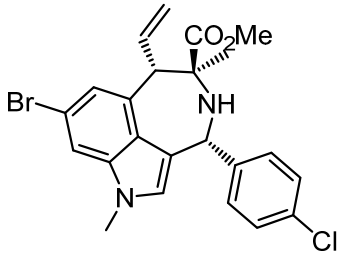

Signal 1: VWD1 A, Wavelength=230 nm

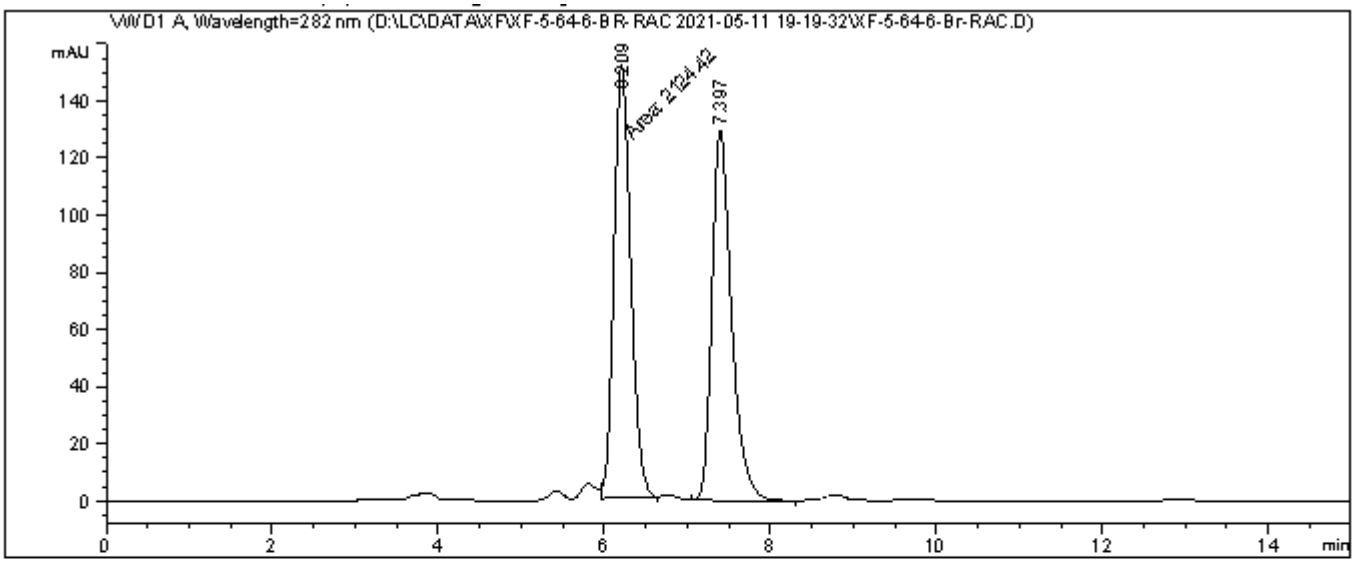
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.517 FM    0.1713 3101.19312  301.78656 100.0000

Totals :                  3101.19312  301.78656

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3A [(6*S*,7*S*,9*R*)-3A + (6*R*,7*R*,9*S*)-3A]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

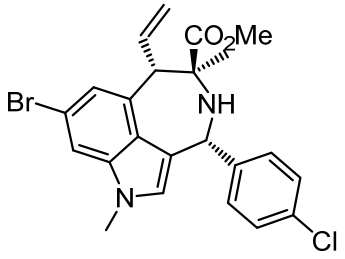

Signal 1: VWD1 A, Wavelength=282 nm

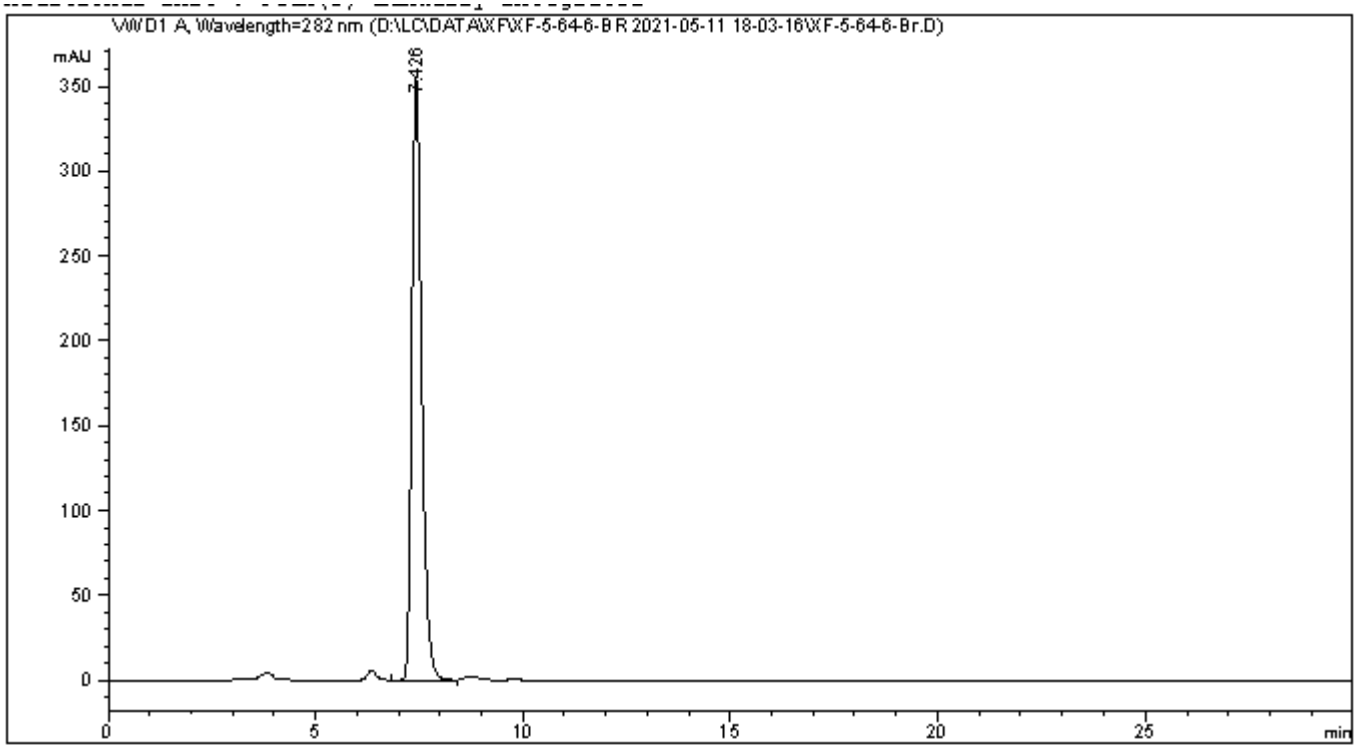
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.209 FM    0.2337 2124.41748  151.48035  50.0996
   2   7.397 BB    0.2491 2115.97437  129.36566  49.9004

Totals :                  4240.39185  280.84601


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3A






```
======================================================================
                        Area Percent Report
======================================================================

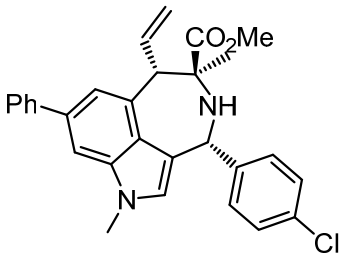
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

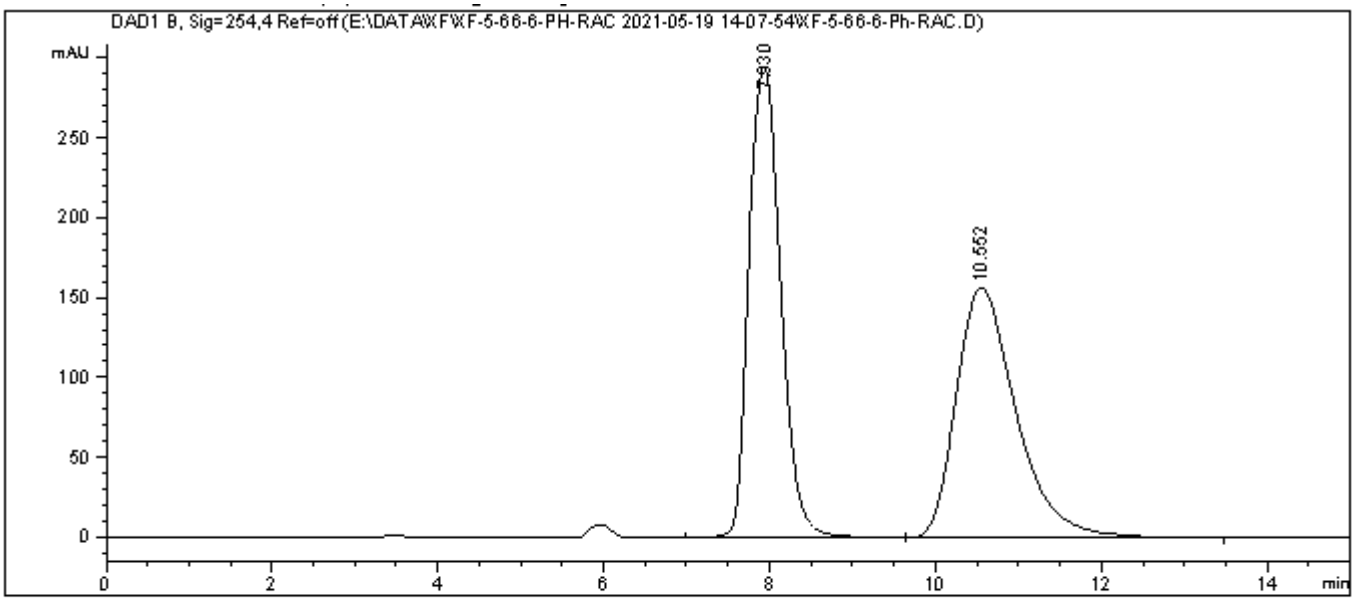

Signal 1: VWD1 A, Wavelength=282 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.426 VV R  0.2518 5845.20459  355.07141 100.0000

Totals :                  5845.20459  355.07141
```

HPLC chromatogram of compound (*rac*)-3B [(6*S*,7*S*,9*R*)-3B + (6*R*,7*R*,9*S*)-3B]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

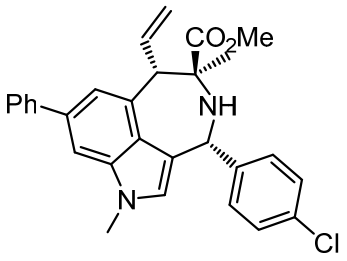

Signal 1: DAD1 B, Sig=254,4 Ref=off

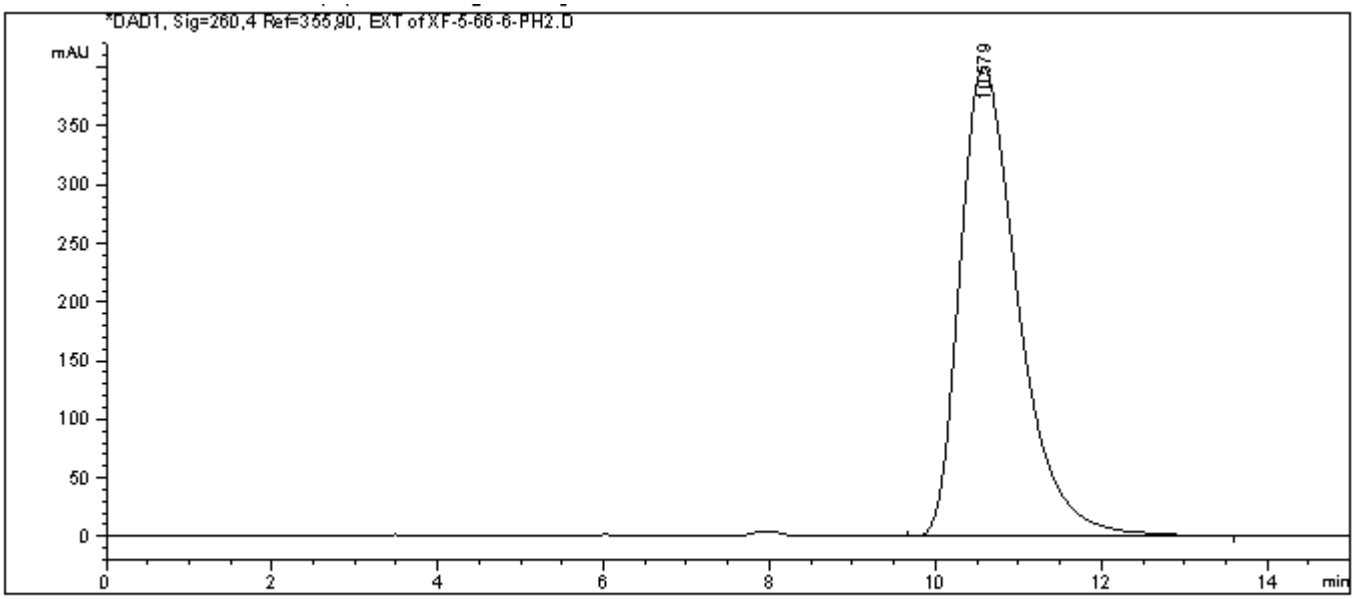
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.930 BB    0.4275 7867.33057  294.70032  50.1456
   2  10.552 BB    0.7660 7821.65430  156.24738  49.8544

Totals :                  1.56890e4   450.94769


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3B






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

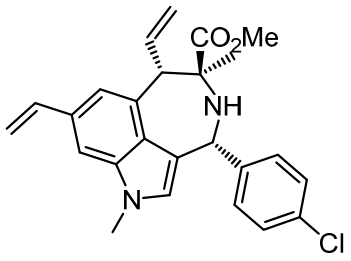

Signal 1: DAD1, Sig=260,4 Ref=355,90, EXT
 Signal has been modified after loading from rawdata file!

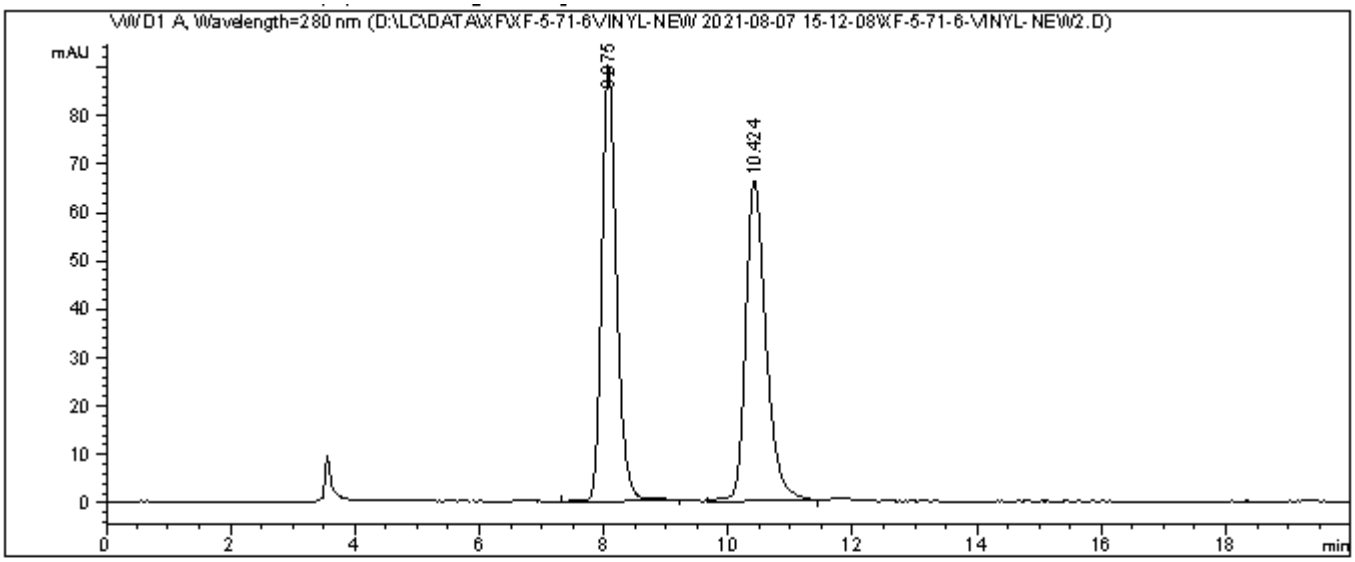
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.579 BB    0.7489 1.95010e4   399.89008 100.0000

Totals :                  1.95010e4   399.89008

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3C [(6*S*,7*S*,9*R*)-3C + (6*R*,7*R*,9*S*)-3C]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

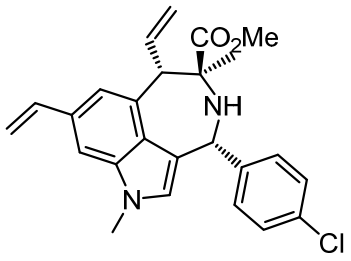

Signal 1: VWD1 A, Wavelength=280 nm

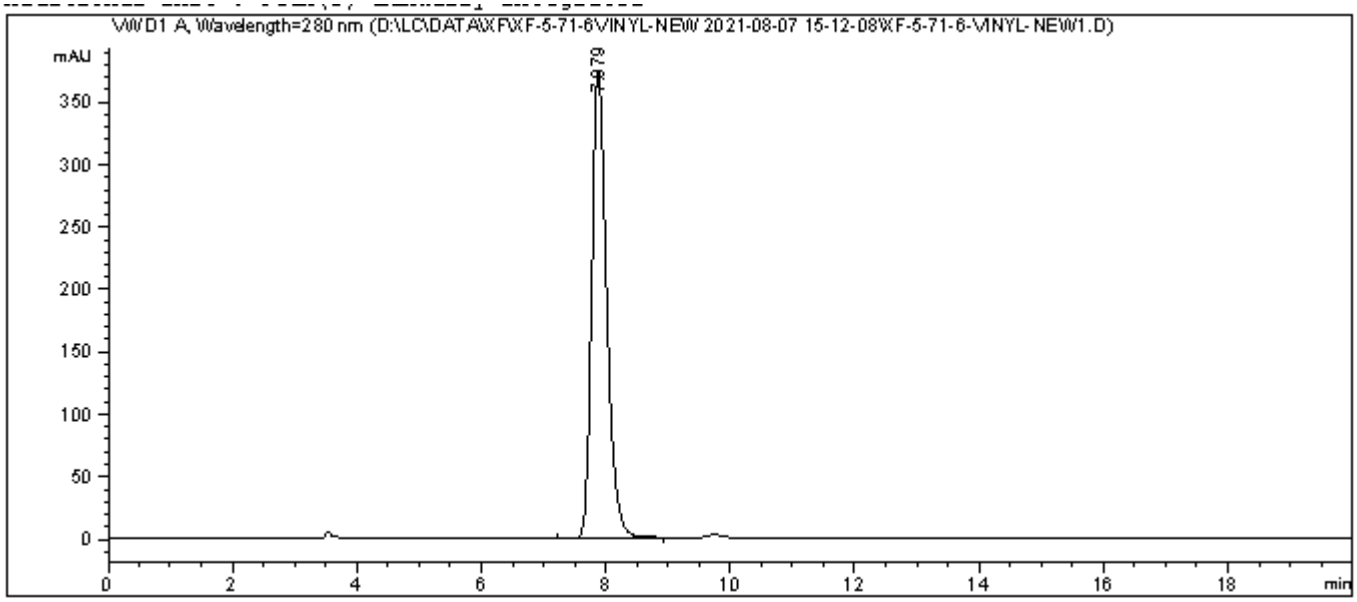
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.075 VV R  0.2523 1498.13367   90.04637  50.0669
   2  10.424 VV R  0.3431 1494.12988   65.91650  49.9331

Totals :                  2992.26355  155.96287


=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3C






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

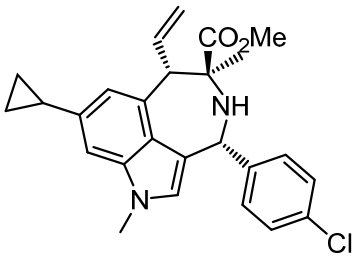

Signal 1: VWD1 A, Wavelength=280 nm

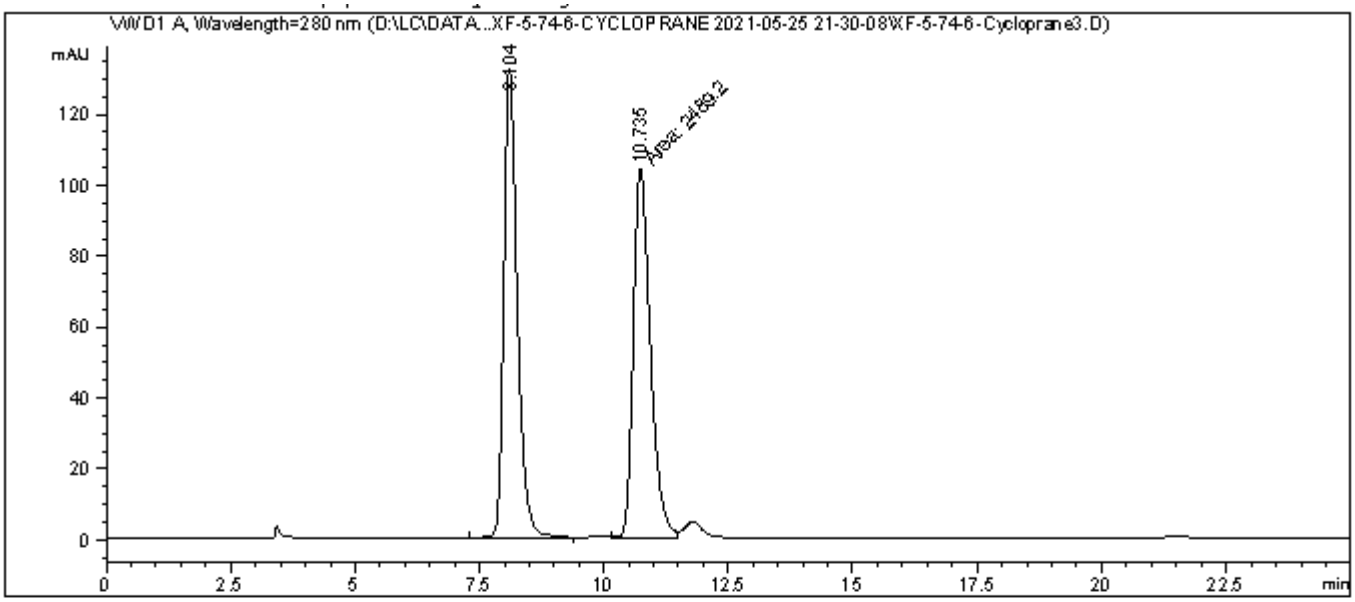
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.879 VB R  0.2531 6262.44287  374.99780 100.0000

Totals :                  6262.44287  374.99780

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3D [(6*S*,7*S*,9*R*)-3D + (6*R*,7*R*,9*S*)-3D]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

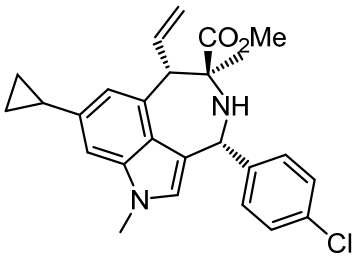

Signal 1: VWD1 A, Wavelength=280 nm

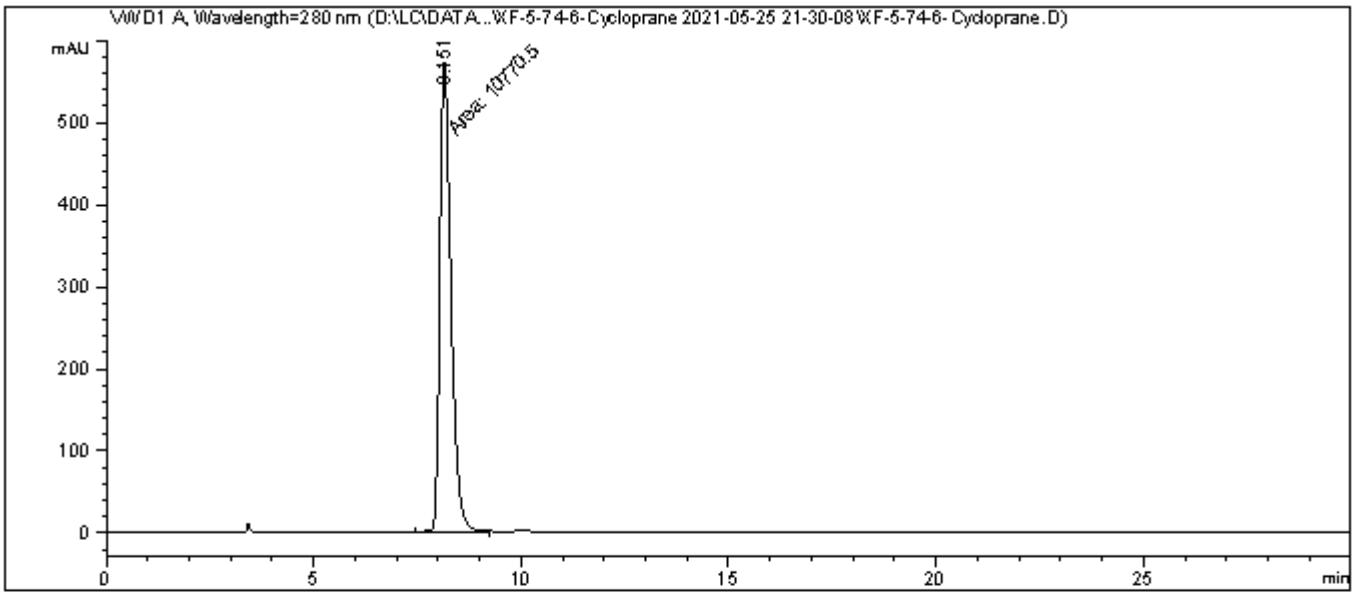
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.104 VV R  0.2869 2514.18677  132.51926  50.2497
   2  10.735 MF    0.3983 2489.20459  104.16281  49.7503

Totals :                  5003.39136  236.68207

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3D



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

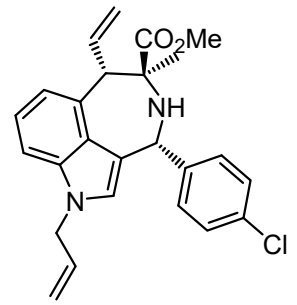

Signal 1: VWD1 A, Wavelength=280 nm

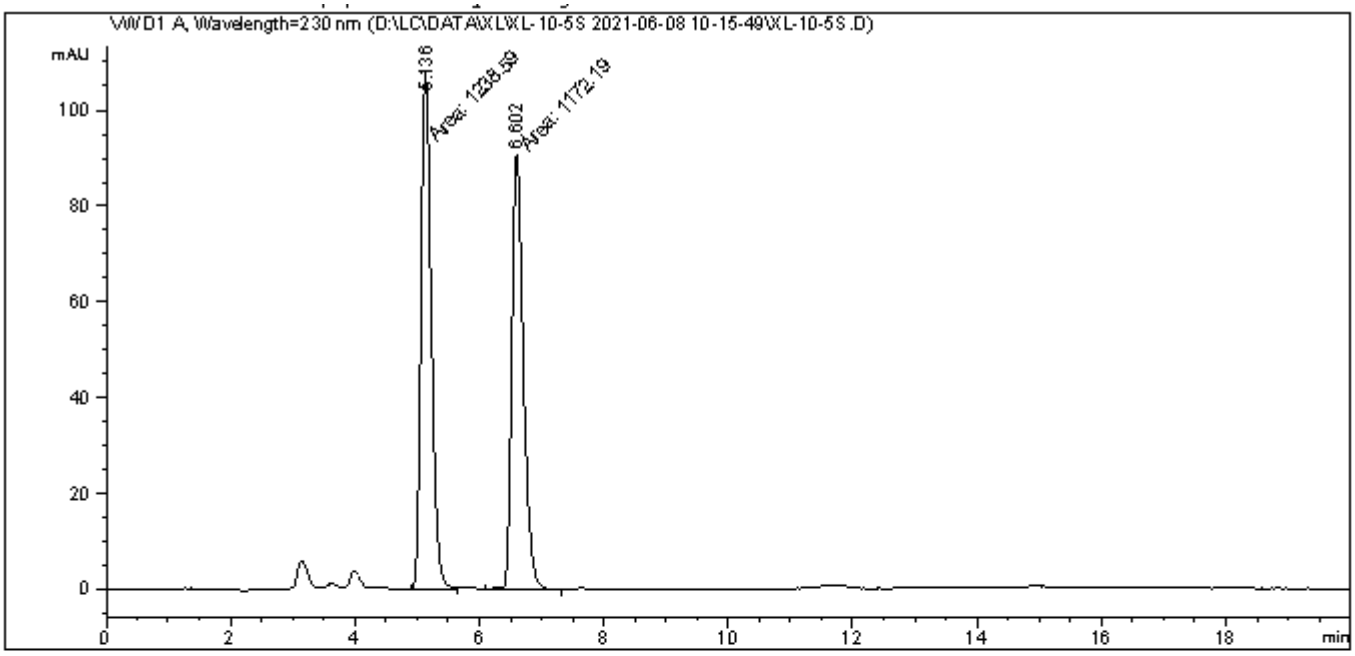
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.151 MF    0.3135 1.07705e4   572.66125 100.0000

Totals :                  1.07705e4   572.66125

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3E [(6*S*,7*S*,9*R*)-3E + (6*R*,7*R*,9*S*)-3E]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

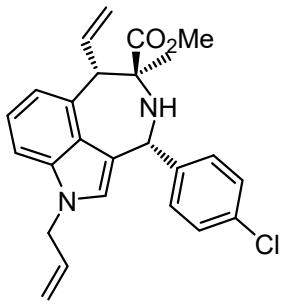

Signal 1: VWD1 A, Wavelength=230 nm

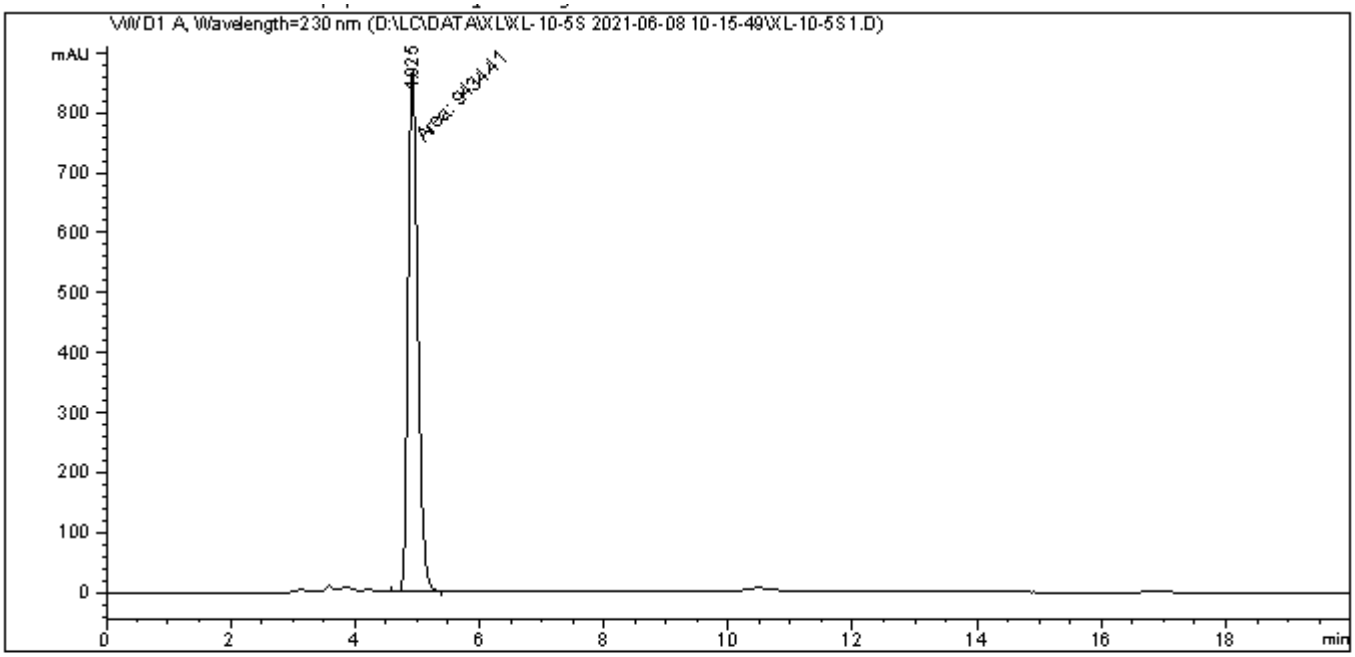
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.136 MM    0.1908 1238.59473  108.19269  51.3773
   2   6.602 MM    0.2147 1172.18835   91.00120  48.6227

Totals :                  2410.78308  199.19389

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3E






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

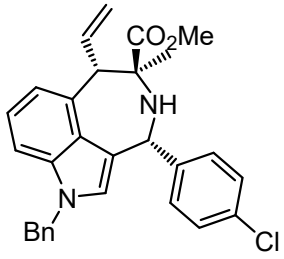

Signal 1: VWD1 A, Wavelength=230 nm

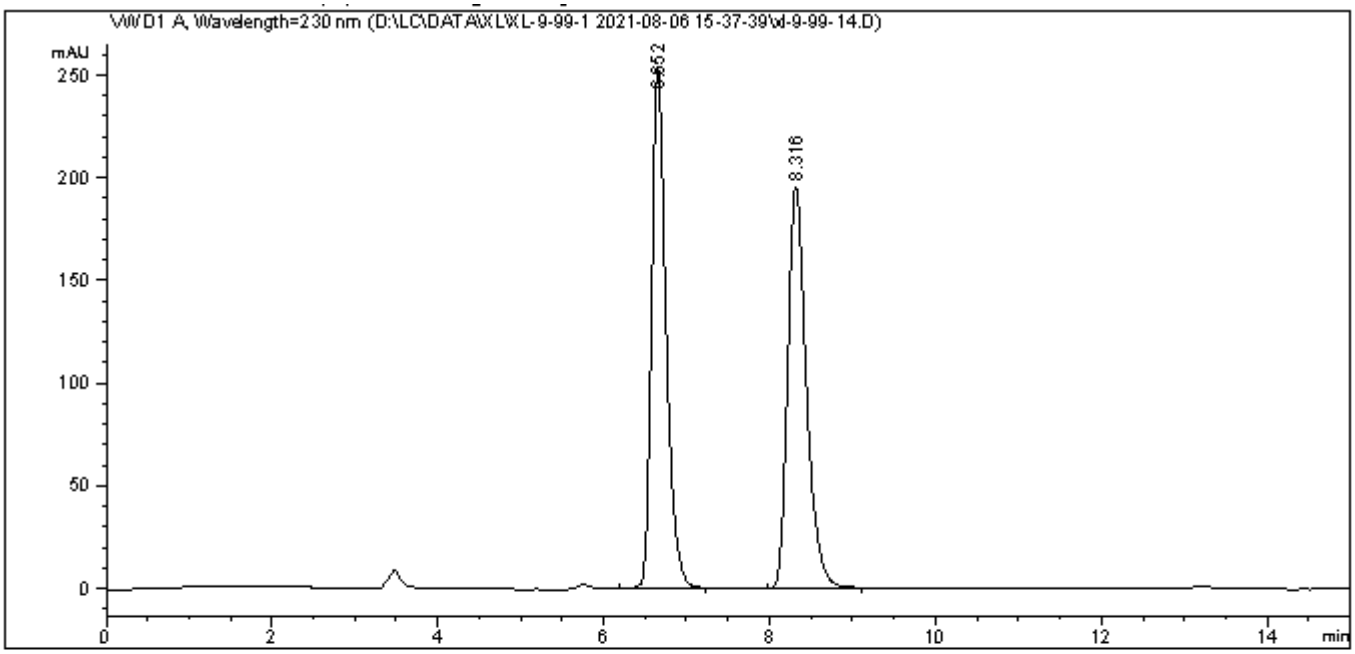
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1   4.925 MF    0.1810 9434.40723  868.95294 100.0000

Totals :                  9434.40723  868.95294

=====================================================================
```

HPLC chromatogram of compound (*rac*)-3F [(6*S*,7*S*,9*R*)-3F + (6*R*,7*R*,9*S*)-3F]



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=====================================================================
                        Area Percent Report
=====================================================================

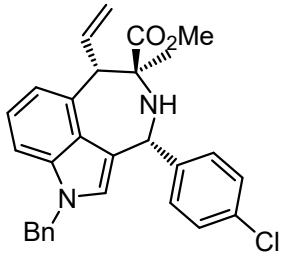
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

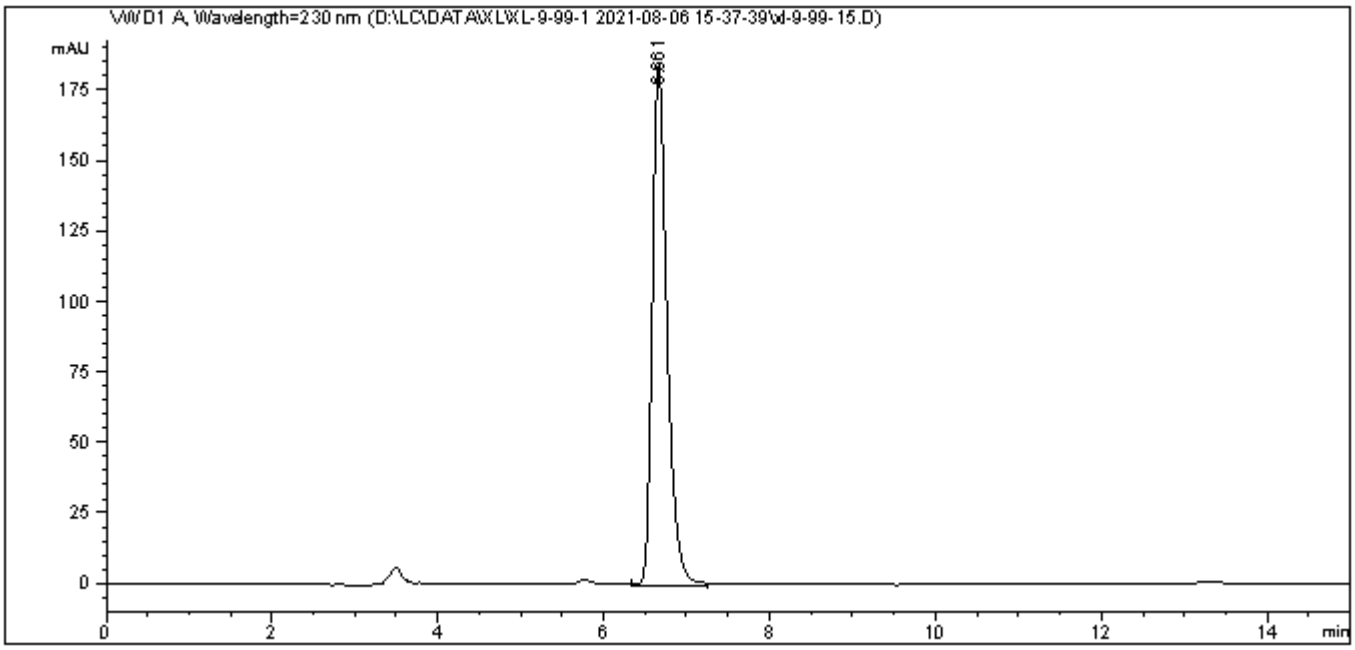

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.652 VB    0.1828 3079.36255  252.90845  50.2627
   2   8.316 VB    0.2359 3047.17554  195.32420  49.7373

Totals :                  6126.53809  448.23265
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3F



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

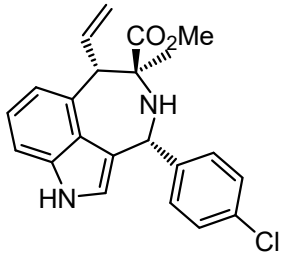

Signal 1: VWD1 A, Wavelength=230 nm

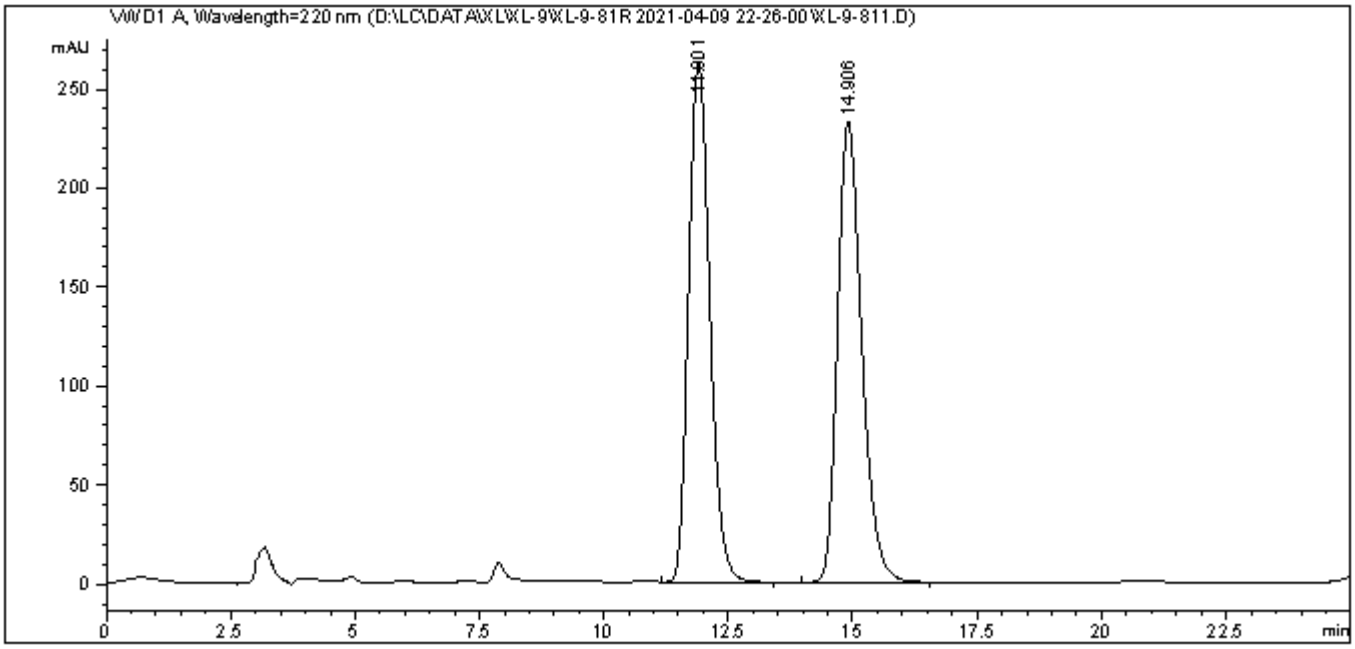
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.661 VB    0.1855 2264.36475  184.39798 100.0000

Totals :                  2264.36475  184.39798


=====================================================================
```

HPLC chromatogram of compound (*rac*)-3G [(6*S*,7*S*,9*R*)-3G + (6*R*,7*R*,9*S*)-3G]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

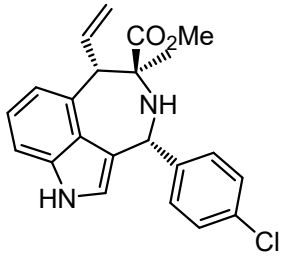

Signal 1: VWD1 A, Wavelength=220 nm

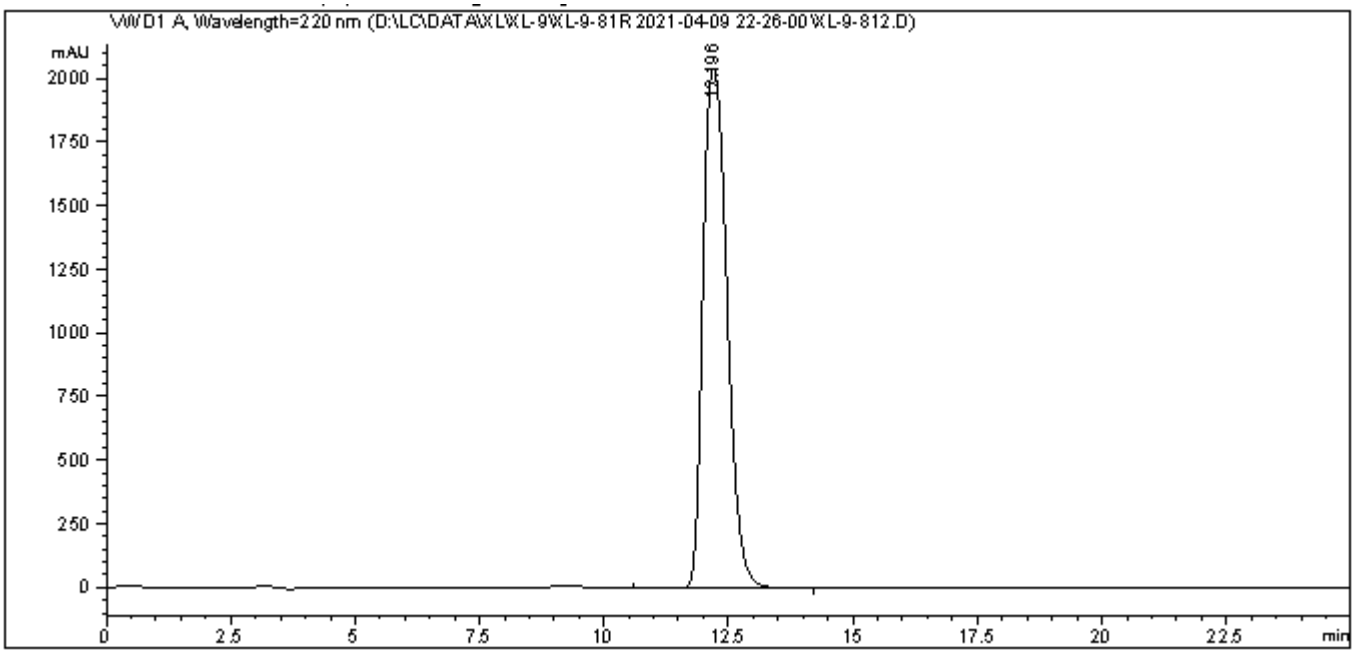
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.901 BB    0.4645 7769.15869  261.50870  49.6805
   2  14.906 BV R  0.5193 7869.07617  232.98563  50.3195

Totals :                  1.56382e4   494.49432

=====================================================================
```

HPLC chromatogram of compound (6*S*,7*S*,9*R*)-3G



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

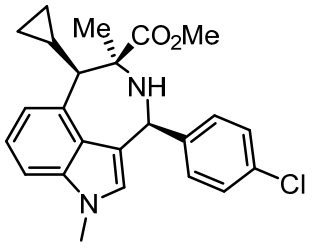

Signal 1: VWD1 A, Wavelength=220 nm

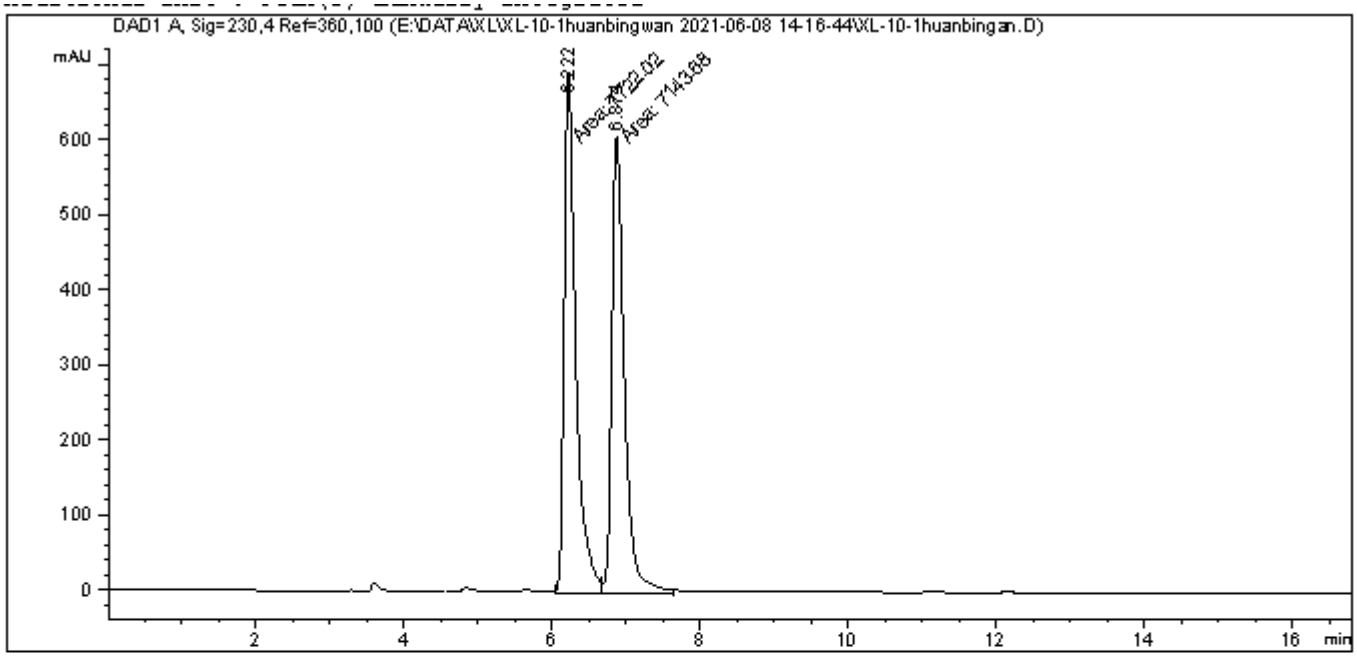
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.196 VB R  0.5359 6.8839le4  2039.37207 100.0000

Totals :                  6.8839le4  2039.37207


=====================================================================
```

HPLC chromatogram of compound (*rac*)-4 [(6*R*,7*S*,9*S*)-4 + (6*S*,7*R*,9*R*)-4]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

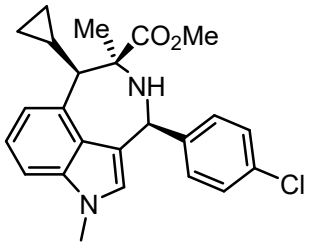

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

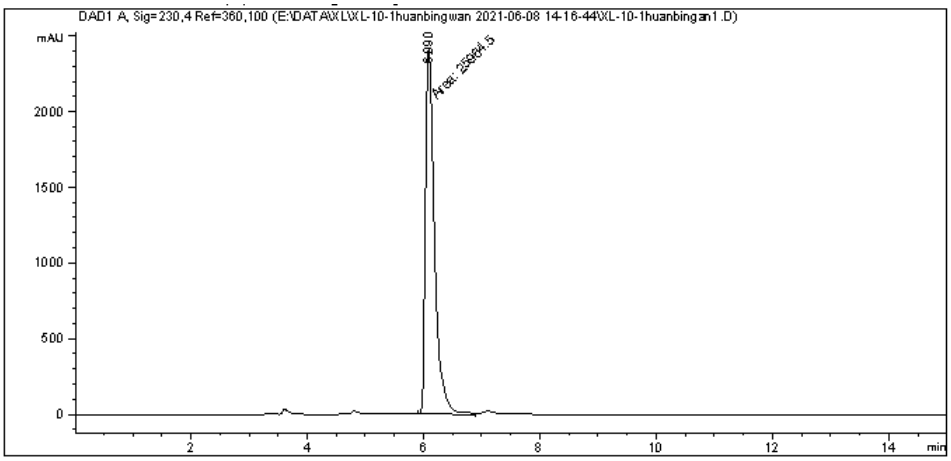
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.222 MF    0.1856 7722.01611  693.60529  51.9452
   2   6.874 FM    0.1955 7143.67578  609.05365  48.0548

Totals :                  1.48657e4  1302.65894

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-4



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

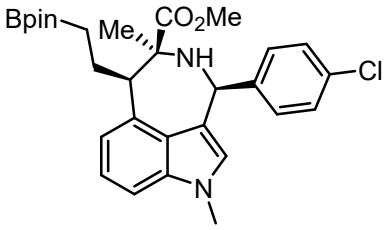

Signal 1: DAD1 A, Sig=230,4 Ref=360,100

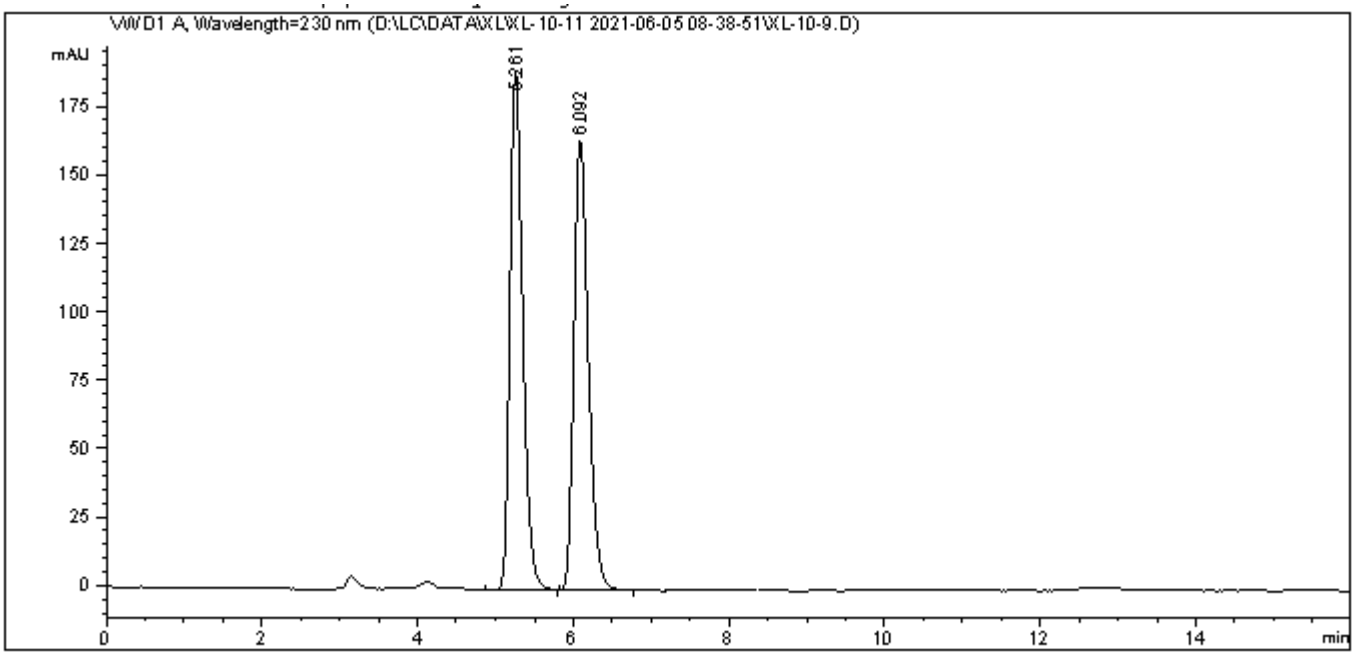
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.090 FM    0.1798 2.59645e4  2407.43652 100.0000

Totals :                  2.59645e4  2407.43652

=====================================================================
```

HPLC chromatogram of compound (*rac*)-5 [(6*R*,7*S*,9*S*)-5 + (6*S*,7*R*,9*R*)-5]






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

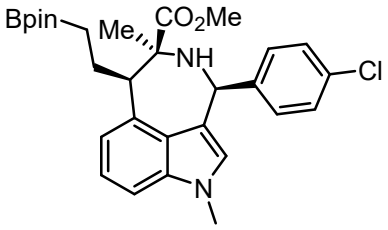

Signal 1: VWD1 A, Wavelength=230 nm

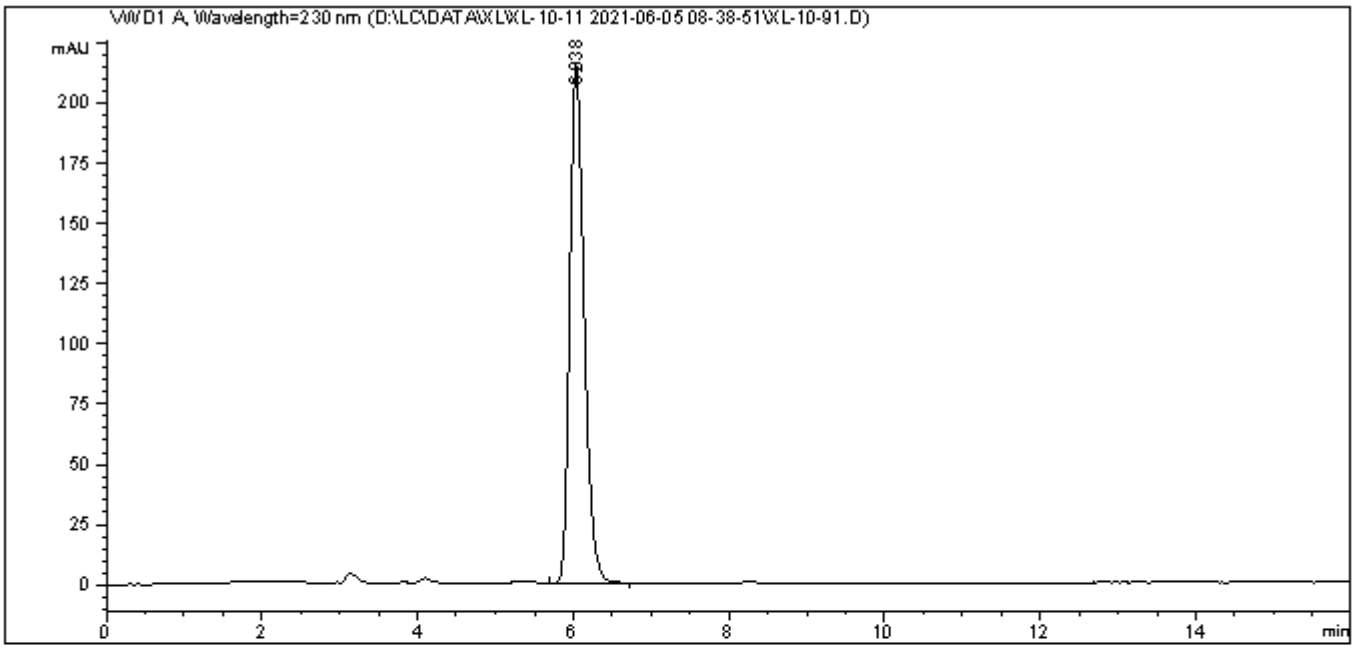
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1   5.261 VB R  0.1757 2168.16724  189.53319  50.5272
   2   6.092 BB    0.1991 2122.91846  164.01160  49.4728

Totals :                  4291.08569  353.54478


=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-5






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

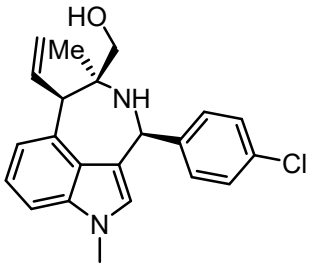

Signal 1: VWD1 A, Wavelength=230 nm

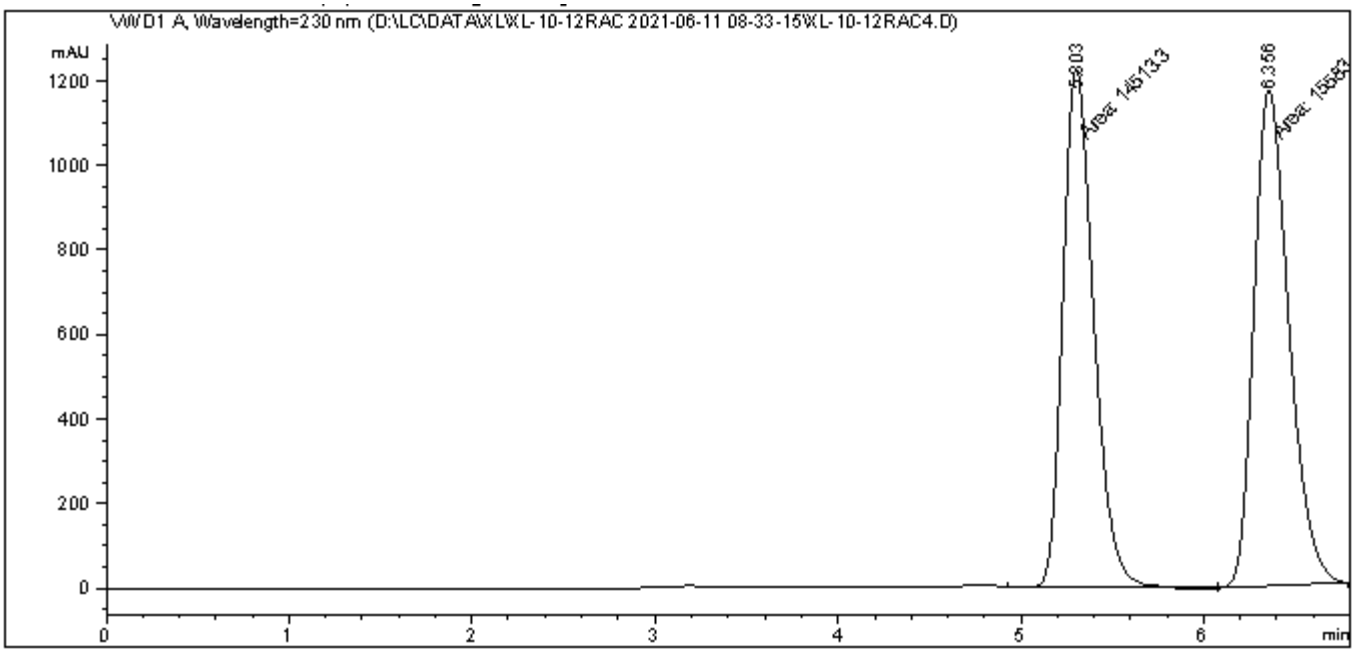
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.038 BB    0.1983 2766.15430  214.80917 100.0000

Totals :                  2766.15430  214.80917

=====================================================================
```

HPLC chromatogram of compound (*rac*)-6 [(6*R*,7*S*,9*S*)-6 + (6*S*,7*R*,9*R*)-6]



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

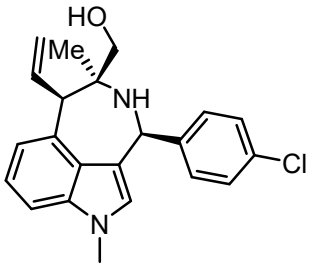

Signal 1: VWD1 A, Wavelength=230 nm

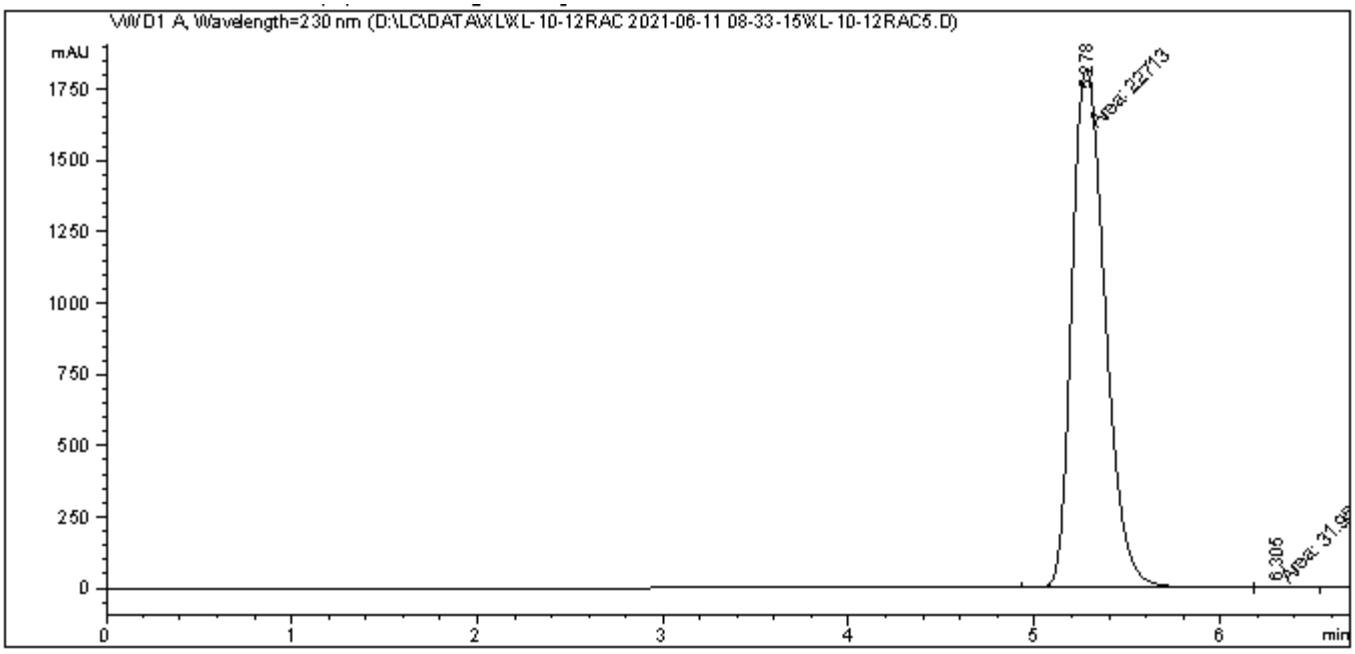
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.303 MM    0.1969 1.45133e4  1228.28394  48.2224
   2   6.356 MM    0.2214 1.55832e4  1172.85889  51.7776

Totals :                  3.00965e4  2401.14282

=====================================================================
```

HPLC chromatogram of compound (6*R*,7*S*,9*S*)-6






```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.278 MF    0.2079 2.27130e4  1821.03748  99.8595
   2   6.305 FM    0.1942   31.95740    2.74292   0.1405

Totals :                  2.27450e4  1823.78040

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```