Supporting Information

Short Enantioselective Total Synthesis of (-)-Rhazinilam using a Gold(I)-Catalyzed Cyclization

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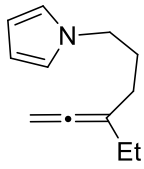
I. General information.

All non-aqueous reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF and CH_2Cl_2). All reagents and solvents were of commercial quality and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel (Merck 60 F_{254}). The developed chromatogram was visualized by UV absorbance. Flash column chromatography was performed using 40-63 mesh silica gel. Purifications have been performed on a CombiFlash Companion TS Chromatography system, unless otherwise stated. Nuclear magnetic resonance spectra (^1H, ^{13}C) were recorded on either Brucker AV 500 or AV 300 spectrometers. Chemical shifts are reported in parts per million relative to an internal standard of residual chloroform (δ = 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR) or dimethylsulfoxyde (δ = 2.50 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR). IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer and are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS-ESI) were obtained on a LCT Waters equipment. Optical rotations were determined on a JASCO P-1010 polarimeter. Data are reported as follows: $[\alpha]_D^{temp}$ (*c* in g/100 mL, solvent). HPLC was performed on a Waters 2695 Separations Module equipped with a diode array UV detector. Data are reported as follows: column type, eluent, flow rate, retention time (t_r).

II. Experimental Procedures.

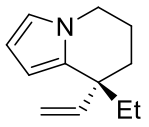
1-(4-ethylhexa-4,5-dienyl)-1*H*-pyrrole (3).



Magnesium turnings (1.29 g, 53.2 mmol, 5 equiv.) were placed in a dry three-necked flask equipped with a reflux condenser and an addition funnel. The system was then conditioned under argon and freshly distilled and degassed tetrahydrofurane was added (15 mL). The solution was warmed to 50 °C and the magnesium was activated by adding few drops of dibromoethane under vigorous stirring. Then a solution of 1-(3-bromopropyl)-1*H*-pyrrole (2.0 g, 10.6 mmol, 1 equiv.) in dry and degassed THF was added dropwise over 2 hours. The stirring was then pursued for 3 hours at 50 °C and the reaction mixture was allowed to reach room temperature. In a separated shlenck tube filled with argon was added sequentially CuCN (76 mg, 0.85 mmol, 8 mol %), LiBr (146 mg, 1.7 mmol, 16 mol %), and dry THF (50 mL). This solution was cooled to -78 °C and pent-2-yn-1-yl methanesulfonate (1.38 g, 8.48 mmol, 0.8 equiv.) was added. The Grignard solution was then added dropwise at -78 °C over the mesylate solution. The solution was then allowed to reach room temperature overnight. The solvent was then removed under vacuum carefully, cause of the volatility of the product. Finally, the crude mixture was purified over silica gel column chromatography (gradient from 100 % pentane to 98:2 pentane:Et_2O) to afford the pure compound as a colorless oil (1.48 g, 0.844 mmol, 99 %).

^{1}**H NMR (CDCl$_3$, 300 MHz)** δ 6.65 (t, *J* = 2.1 Hz, 2H), 6.14 (t, *J* = 2.1 Hz, 2H), 4.74 (d, *J* = 3.5 Hz, 1H), 4.75 (d, *J* = 3.5 Hz, 1H), 3.90 (m, 2H), 1.97-1.89 (m, 6H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}**C NMR (CDCl$_3$, 75 MHz)** δ 205.4 (C_q), 120.7 (CH), 108.0 (CH), 104.2 (C_q), 77.0 (CH_2), 49.1 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 25.4 (CH_2), 12.3 (CH_3); **IR (neat)** ν_{max}: 3101, 2965, 2932, 1955, 1702, 1499, 1447, 1281, 1088, 846 cm^{-1}; **HRMS (APPI)**: calcd for $C_{12}H_{18}N$ $[M + H]^+$ 176.1434, found 176.1429.

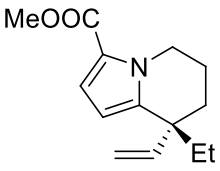
(*R*)-8-ethyl-8-vinyl-5,6,7,8-tetrahydroindolizine (4).



1-(4-ethylhexa-4,5-dien-1-yl)-1*H*-pyrrole (175 mg, 1.0 mmol, 1 equiv.) and [(*R*)-3,5-*t*Bu-MeO-BIPHEP-$(AuCl)_2$] (81 mg, 0.05 mmol, 5 mol %) were placed in a Schlenk tube filled with argon. Mesitylene (10 mL) was then added, and after 5 minutes stirring, silver trifluoromethanesulfonate (25.7 mg, 0.1 mmol, 10 mol %) was added in one portion. The reaction mixture was stirred for 20 hours and was directly purified using a silica gel column chromatography (elution with 100 % pentane to remove mesitylene, then 98:2 pentane:Et_2O) affording the product as a clear colorless oil (156 mg, 0.89 mmol, 89 %).

^{1}**H NMR (CDCl$_3$, 500 MHz)** δ 6.51 (brs, 1H), 6.15 (d, *J* = 3.4 Hz, 1H), 5.91 (d, *J* = 3.5 Hz, 1H), 5.85 (dd, *J* = 10.5 and 17.2 Hz, 1H), 5.00 (dd, *J* = 1.6 and 10.5 Hz, 1H), 4.74 (dd, *J* = 1.6 and 17.2 Hz, 1H), 3.94 (dddd, *J* = 12.0, 5.5, 4.0 and 0.8 Hz, 1H), 3.82 (ddd, *J* = 4.9, 11.9 and 10.5 Hz, 1H), 2.03-1.94 (m, 1H), 1.91-1.85 (m, 1H), 1.77-1.72 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}**C NMR (CDCl$_3$, 75 MHz)** δ 146.1 (CH), 134.1 (C_q), 118.7 (CH), 113.2 (CH_2), 107.4 (CH), 104.8 (CH), 45.5 (CH_2), 42.6 (C_q), 34.1 (CH_2), 30.5 (CH_2), 20.1 (CH_2), 8.8 (CH_3); **IR (neat)** ν_{max}: 3085, 2940, 2875, 1955, 1634, 485, 1235, 915, 750, 719 cm^{-1}; **HRMS (APPI)**: calcd for $C_{12}H_{18}N$ $[M + H]^+$ 176.1434, found 176.1429; **$[\alpha]_D^{24}$** = + 8.2 (c 1.0, $CHCl_3$).

(*R*)-methyl 8-ethyl-8-vinyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (5).

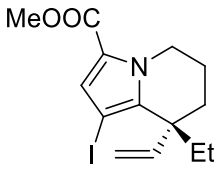


To a solution of (*R*)-8-ethyl-8-vinyl-5,6,7,8-tetrahydroindolizine (156 mg, 0.89 mmol, 1 equiv.) in dry dichloromethane (9 mL) was added trichloromethylacetylchloride (109 μL, 0.98 mmol, 1.1 equiv.), the solution slowly turned to yellow and after 1 hours stirring, the dichloromethane was removed under vacuum. The crude mixture was then

solubilized in dry methanol (1 mL) and sodium methanolate in methanol (8.9 mL, 0.3 M, 2.67 mmol, 3 equiv.) was then added slowly. After 1 hour stirring, water (20 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 three times (3 × 10 mL). The organic phase was dried over magnesium sulfate and the volatiles were removed. The crude mixture was purified over silica gel chromatography (gradient from 100 to 98 % heptane:EtOAc) affording the product as a clear oil (195 mg, 0.836 mmol, 94 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96 (d, *J* = 4.0 Hz, 1H), 5.97 (d, *J* = 4.0 Hz, 1H), 5.83 (dd, *J* = 10.4 and 17.2 Hz, 1H), 5.04 (d, *J* = 10.5 Hz, 1H), 4.72 (d, *J* = 17.2 Hz, 1H), 4.58 (dt, *J* = 13.8 and 4.4 Hz, 1H), 4.00 (td, *J* = 6.6 and 13.8 Hz, 1H), 3.78 (s, 3H), 2.00-1.94 (m, 2H), 1.78-1.67 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.9 (C_q), 145.4 (CH), 141.8 (C_q), 120.7 (C_q), 117.6 (CH), 114.0 (CH_2), 106.7 (CH), 50.9 (CH_3), 45.7 (CH_2), 43.3 (C_q), 33.9 (CH_2), 29.1 (CH_2), 19.7 (CH_2), 8.6 (CH_3); **IR (neat)** ν_{max}: 2939, 2879, 1696, 1232, 1103, 916 cm^{-1}; **HRMS (ESI)**: calcd for $C_{14}H_{20}NO_2$ $[M + H]^+$ 234.1494, found 234.1499; **$[\alpha]_D^{24}$** = - 34.9 (c 1.0, $CHCl_3$); **HPLC** Analysis: [CHIRALPAK ® OJH , 15°C, 1% *i*PrOH/ *n*-heptane, 0.8 mL/min, retention times: 5.2 min (minor) and 5.9 min (major)].

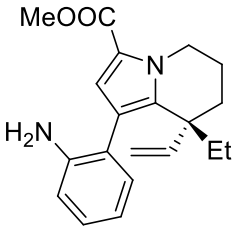
(*R*)-methyl 8-ethyl-1-iodo-8-vinyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (6).



To a solution of **5** (169 mg, 0.725 mmol, 1 equiv.) in dry chloroform (20 mL) at 0 °C was added sequentially silver trifluoroacetate (192 mg, 0.87 mmol, 1.2 equiv.) and iodine (221 mg, 0.87 mmol, 1.2 equiv.). After 1 hour stirring the reaction mixture was quenched by adding a saturated solution of sodium bisulfite (5 mL). The aqueous phase was then extracted by CH_2Cl_2 three times (3 × 10 mL). The crude mixture was purified over silica gel chromatography (gradient from 100 % to 98 % heptane:EtOAc) affording the product as a clear oil (195 mg, 0.543 mmol, 75 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (s, 1H), 5.81 (dd, *J* = 10.5 and 17.3 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.73-4.66 (m, 2H), 4.00-3.89 (m, 1H), 3.78 (s, 3H), 2.53 (sex, *J* = 7.1 Hz, 1H), 1.93-1.83 (m, 3H), 1.70-1.60 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.8 (C_q), 142.5 (CH), 138.5 (C_q), 126.9 (CH), 125.3 (C_q), 122.9 (C_q), 114 .5 (CH_2), 59.9 (C_q), 51.2 (CH_3), 46.7 (CH_2), 44.4 (C_q), 30.7 (CH_2), 30.6 (CH_2), 19.5 (CH_2), 8.4 (CH_3); **IR (neat)** ν_{max}: 2948, 2875, 1700, 1509, 1435, 1347, 1233, 1203, 912, 759 cm^{-1}; **HRMS (ESI)**: calcd for $C_{14}H_{19}INO_2$ $[M + H]^+$ 360.0460, found 360.0467; **$[\alpha]_D^{24}$** = -16.5 (c 1.0, $CHCl_3$).

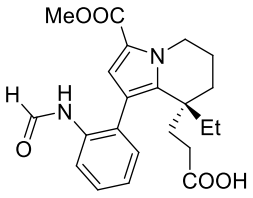
(*R*)-methyl 1-(2-aminophenyl)-8-ethyl-8-vinyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (7).



$Pd(OAc)_2$ (0.8 mg, 0.0035 mmol, 2.5 mol %), SPhos (2.9 mg, 0.007 mmol, 5 mol %) and K_3PO_4 (59 mg, 0.28 mmol, 2.0 equiv.) were placed in a Shlenck tube filled with argon. DMSO (200 µL) was added and the solution was stirred 20 minutes. In a separated flask, a solution of **6** (50 mg, 0.139 mmol, 1.0 equiv.) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (36.6 mg, 0.17 mmol, 1.2 equiv.) in DMSO (300 µL) was prepared. The palladium solution was then poured in an oil bath pre-heated at 120 °C and the substrate solution was added quickly, DMSO (100 µL) was used to rinse the flask and added again on the catalyst solution. After 4 hours stirring, ethyl acetate (10 mL) and saturated aqueous solution of $NaHCO_3$ (10 mL) were added. The aqueous phase was extracted three times by ethyl acetate (3 × 10 mL), and the combined organic phases were washed three times with water (3 × 10 mL), then with brine (10 mL). After drying over magnesium sulfate, the volatiles were removed under vacuum. Subsequent purification over silica gel chromatography (gradient from 100 % heptane to 70:30 heptane:Ethyl acetate) afforded the product as a visquous oil (34 mg, 0.105 mmol, 75 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.14-7.05 (m, 2H), 6.90 (brs, 1H), 6.70-6.63 (m, 2H), 5.86 (dd, *J* = 10.7 and 17.4 Hz, 1H), 5.08-5.02 (m, 1H), 4.77 (dd, *J* = 17.4 and 0.8 Hz, 1H), 4.71-4.66 (m, 1H), 4.14-4.09 (m, 1H), 3.79 (s, 3H), 3.63 (brs, 2H), 2.10-2.04 (m, 1H), 1.97-1.91 (m, 1H), 1.80 (ddd, *J* = 3.0 and 11.6 and 13 .4 Hz, 1H), 1.72-1.68 (m, 2H), 1.52 (sex, *J* = 7.4 Hz, 1H), 0.71 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 161.8 (C_q), 145.3 (C_q), 144.8 (bs, CH), 132.4 (CH), 128.4 (CH), 123.1 (C_q), 121.0 (C_q), 120.4 (CH), 118.5 (C_q), 117.5 (CH), 115.0 (CH), 113.7 (bs, CH), 50.9 (CH_3), 46.2 (CH_2), 44.0 (C_q), 31.0 (bs, CH_2), 29.3 (bs, CH_2), 19.4 (CH_2), 8.6 (CH_3); **IR (neat)** ν_{max}: 3439, 3356, 3078, 2945, 2870, 1682, 1618, 1458, 1218, 1087, 921, 752 cm^{-1}; **HRMS (ESI)**: calcd for $C_{20}H_{25}N_2O_2$ $[M + H]^+$ 325.1916, found 325.1909.

(*R*)-3-(8-ethyl-1-(2-formamidophenyl)-3-(methoxycarbonyl)-5,6,7,8-tetrahydroindolizin-8-yl)propanoic acid (8).

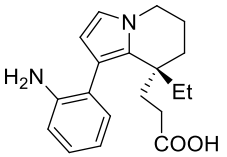


To a solution of **7** (34 mg, 0.095 mmol, 1.0 equiv.) in toluene (0.5 mL) was added sequentially $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol %), 1,1'-*bis*(diphenylphosphino)ferrocene (dppf) (10.5 mg, 0.019 mmol, 20 mol %), formic acid (7.2 μL, 0.19 mmol, 2.0 equiv.) and phenyl formate (13.9 mg, 0.114 mmol, 1.2 equiv.). The reaction mixture was then heated at 90 °C for 20 hours. Then HCl 1M was added and the aqueous phase were extracted three times with dichloromethane (3 × 10 mL). After drying the organic phases over magnesium sulfate, the volatiles were removed under vacuum. Subsequent purification over silica gel chromatography (gradient from 100 % heptane to 100/99/1:heptane/EtOAc/AcOH) afforded the product as a visquous oil (36 mg, 0.0904 mmol, 95 %).

At room temperature, the product exists as a mixture of conformers, so NMR experiments were done at 383 K. See spectra for more information.

^{1}H NMR (DMSO D_6, 500 MHz) δ 11.30 (brs, 1H), 8.31 (brs, 1H), 8.09 (brs, 1H), 8.05-7.95 (brs, 1H), 7.30 (td, *J* = 7.8 and 1.9 Hz, 1H), 7.19 (dd, *J* = 1.6 and 7.8 Hz, 1H), 7.07 (dd, *J* = 6.6 and 7.8 Hz, 1H), 6.70 (s, 1H), 4.34 (dd, *J* = 5.3 and 6.6 Hz, 2H), 3.76 (s, 3H), 2.19-2.13 (m, 1H), 2.05-2.02 (m, 1H), 1.97-1.90 (m, 2H), 1.76-1.71 (m, 2H), 1.68-1.63 (m, 2H), 1.53 (dd, *J* = 7.8 and 14 .1 Hz, 1H), 1.36 (dd, *J* = 7.8 and 14 .1 Hz, 1H), 0.73 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (DMSO D_6, 125 MHz)** δ 173.0 (C_q), 160.0 (C_q), 159.7 (C_q), 139.0 (C_q), 135.9 (C_q), 130.7 (CH), 127.3 (CH), 122.3 (CH), 119.5 (C_q), 119.3 (CH), 49.8 (CH_3), 44.7 (CH_2), 34.7 (CH_2), 32.0 (CH_2), 29.2 (CH_2), 27.9 (CH_2), 19.6 (CH_2), 8.0 (CH_3); **IR** (neat) ν_{max}: 3330, 2949, 2879, 1695, 1690, 1655, 1582, 1435, 1252, 1148, 1087, 758, 727 cm^{-1}; **HRMS (ESI)**: calcd for $C_{22}H_{27}N_2O_5$ $[M + H]^+$ 399.1920, found 399.1933; **$[\alpha]_D^{24}$** = -10.2 (c 1.0, $CHCl_3$).

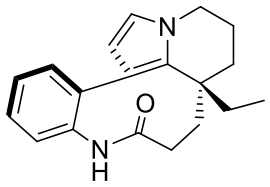
(*R*)-3-(1-(2-aminophenyl)-8-ethyl-5,6,7,8-tetrahydroindolizin-8-yl)propanoic acid (9).



To a solution of **8** (59 mg, 0.15 mmol, 1 equiv.) in methanol (7.5 mL) and water (2.5 mL) was added sodium hydroxide (590 mg, 14.8 mmol, 100 equiv.). The reaction media was heated at 50 °C for 4 hours before to let it rise room temperature, the solution was then acidified to pH 1 with HCl 6 M (2.6 mL) and warmed again at 50 °C for 4 hours. Then the reaction media was allowed to reach room temperature again. Brine (15 mL) was added, and the aqueous phase was extracted twice with CH_2Cl_2 (2 × 15 mL) and twice with AcOEt (2 × 15 mL), the combined organic phases were dried over $MgSO_4$, and the volatiles were removed under vacuum. The residue was solubilized in MeOH (7.5 mL) and water (2.5 mL) and KOH (99 mg, 85 %w/w, 1.5 mmol, 10 equiv.) was added. The solution was heated at 50 °C for 1 hour. Finally, the reaction was cooled to room temperature and the reaction mixture was diluted with water (5 mL) and the pH was corrected to 4-5 with 1 M HCl. Brine was added (15 mL) and the aqueous phase was

extracted three times with CH_2Cl_2 (3 × 20 mL) and three times by ethyl acetate (3 × 20 mL). The organic phases were dried over magnesium sulfate and the volatiles were removed under vacuum. This product was used without purification in the next step.

(*R*)-(-)-Rhazinilam (1).



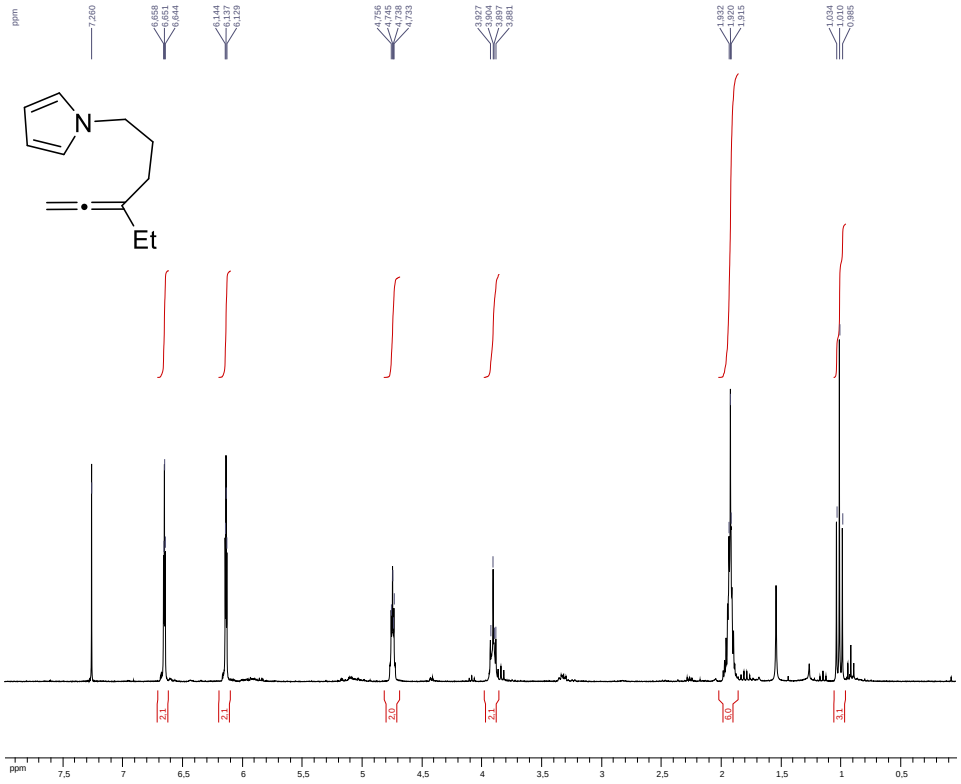
To a solution of crude **9** (0.15 mmol) in dry CH_2Cl_2 (15 mL) was added sequentially NEt_3 (83 μL, 0.6 mmol, 4.0 equiv.), 1-hydroxybenzotriazole hydrate (30.4 mg, 0.225 mmol, 1.5 equiv.) and (3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (43.2 mg, 0.225 mmol, 1.5 equiv.). After 2.5h stirring, HCl 1M (10 mL) was added, and the aqueous phase was extracted four times with CH_2Cl_2 (4 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were removed under vacuum. Subsequent purification over silica gel chromatography (gradient from 100 % heptane to 70:30 heptane:EtOAc) afforded the product as a white solid (19.7 mg, 0.067 mmol, 45 % over two steps).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43 (dd, *J* = 1.8 and 7.3 Hz, 1H), 7.34 (td, *J* = 7.5 and 2.0 Hz, 1H), 7.30 (td, *J* = 7.3 and 1.5 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.63 (brs, 1H), 6.51 (d, *J* = 2.7 Hz, 1H), 5.75 (d, *J* = 2.7 Hz, 1H), 4.01 (dd, *J* = 5.6 and 12.0 Hz, 1H), 3.79 (dt, *J* = 4.8 and 12.1 Hz, 1H), 2.49-2.35 (m, 2H), 2.24 (qdd, *J* = 13.0 and 5.3 and 2.7 Hz, 1H), 1.95 (dd, *J* = 7.9 and 13.8 Hz, 1H), 1.89-1.83 (m, 1H), 1.72 (td, *J* = 13.5 and 3.1 Hz, 1H), 1.54 (dt, *J* = 13.0 and 3.1 Hz, 1H), 1.50-1.43 (m, 2H), 1.28-1.21 (m, 1H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 177.5 (C_q), 140.5 (C_q), 138.2 (C_q), 131.6 (CH), 130.7 (C_q), 128.1 (CH), 127.4 (CH), 127.0 (CH), 119.3 (CH), 117.4 (C_q), 109.7 (CH), 46.2 (CH_2), 39.0 (C_q), 36.7 (CH_2), 33.2 (CH_2), 30.2 (CH_2), 28.2 (CH_2), 19.6 (CH_2), 8.3 (CH_3); **IR** (neat) ν_{max}: 3168, 3046, 2955, 2875, 1666, 1601, 1500, 1396, 756, 732, 701 cm^{-1}; **HRMS (ESI)**: calcd for $C_{19}H_{23}N_2O$ $[M + H]^+$ 295.1805, found 295.1806; **HPLC** Analysis: [CHIRALPAK ® IC, 25°C, 15% *i*PrOH/ *n*-heptane, 1.0 mL/min, 250 nm, retention times: 21.3 min (major) and 27.8 min (minor)].

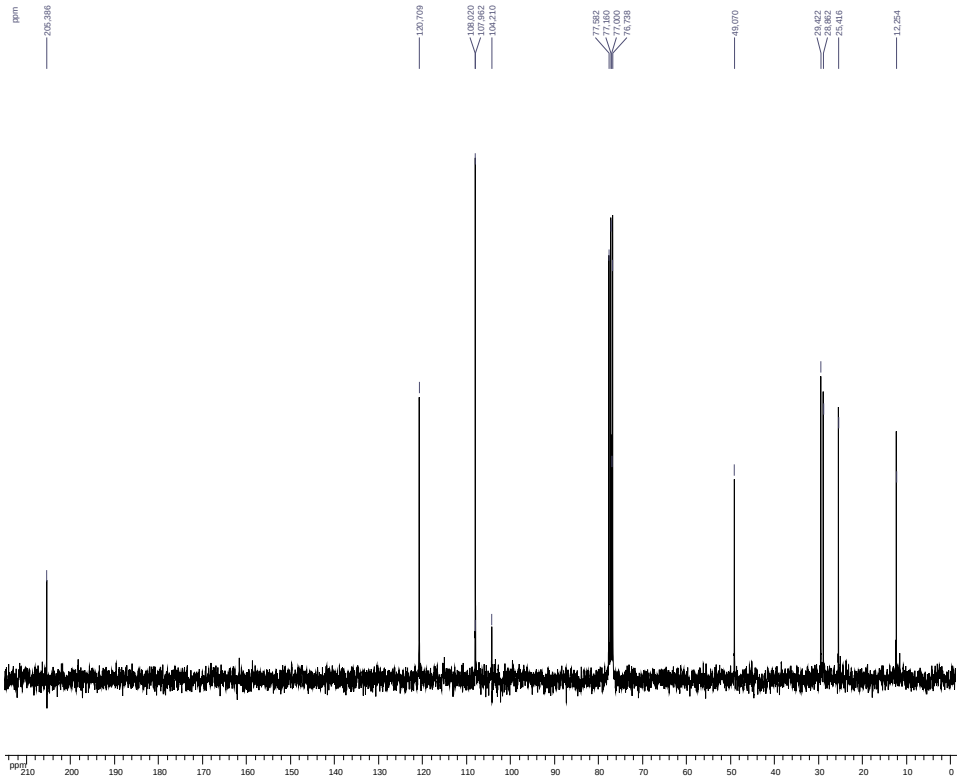
III. NMR Spectra (^{1}H NMR and ^{13}C NMR)

III.1. Compound (3).

^{1}H NMR ($CDCl_3$, 300 MHz):

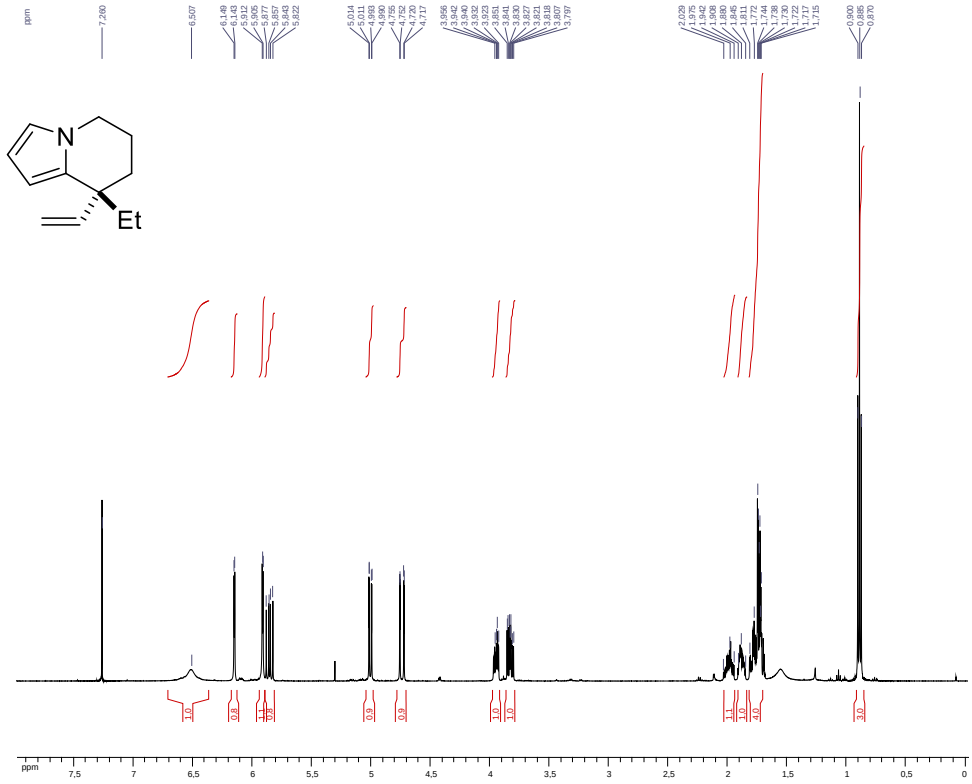


^{13}C NMR ($CDCl_3$, 75 MHz):

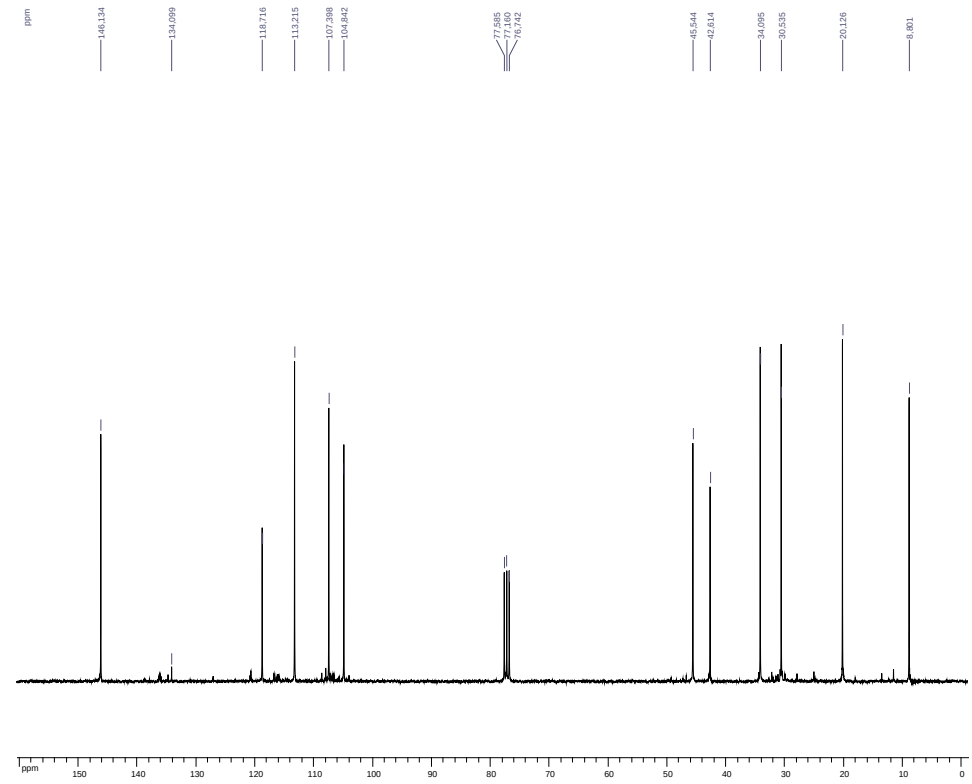


III.2. Compound (4).

^{1}H NMR ($CDCl_3$, 500 MHz):

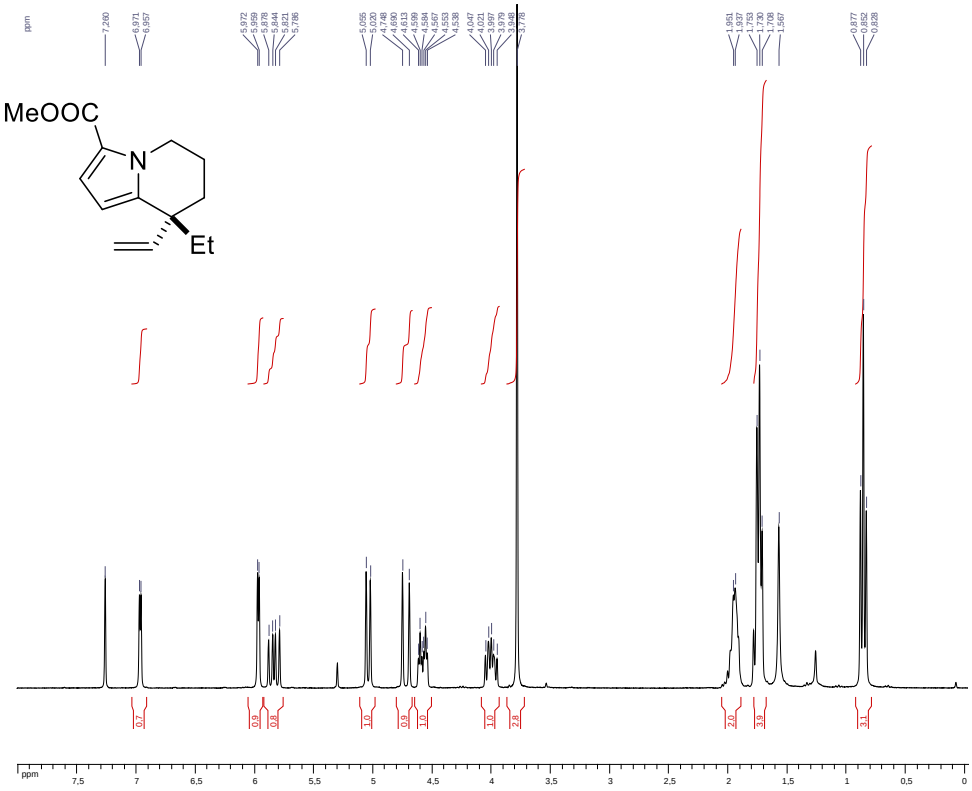


^{13}C NMR ($CDCl_3$, 75 MHz):

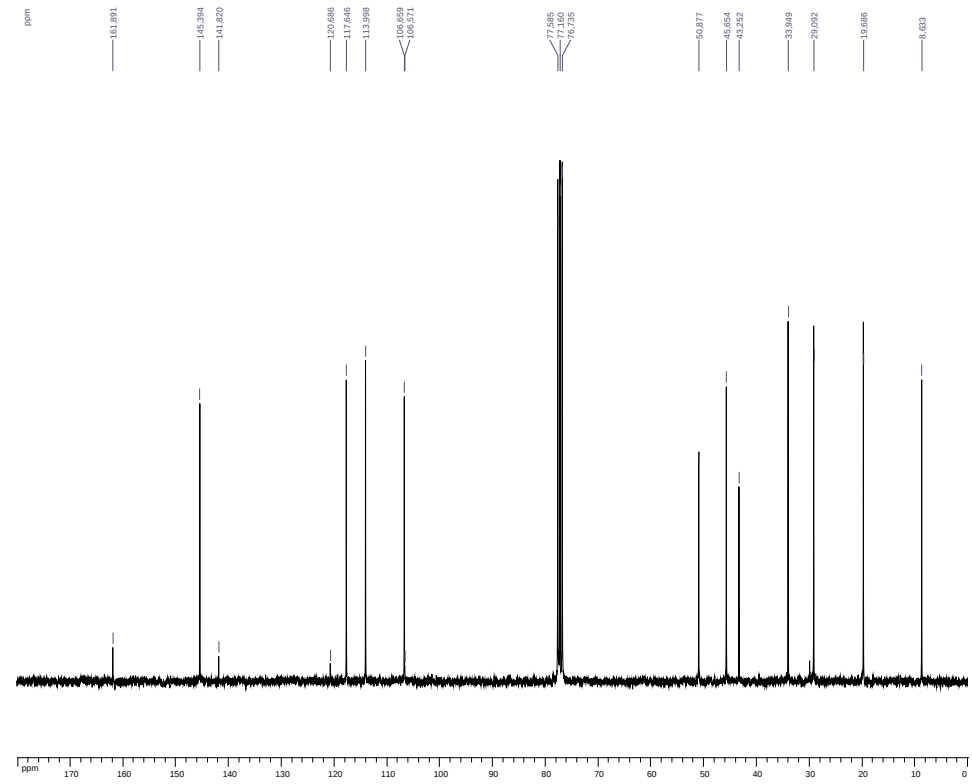


III.3. Compound (5).

^{1}H NMR ($CDCl_3$, 500 MHz):

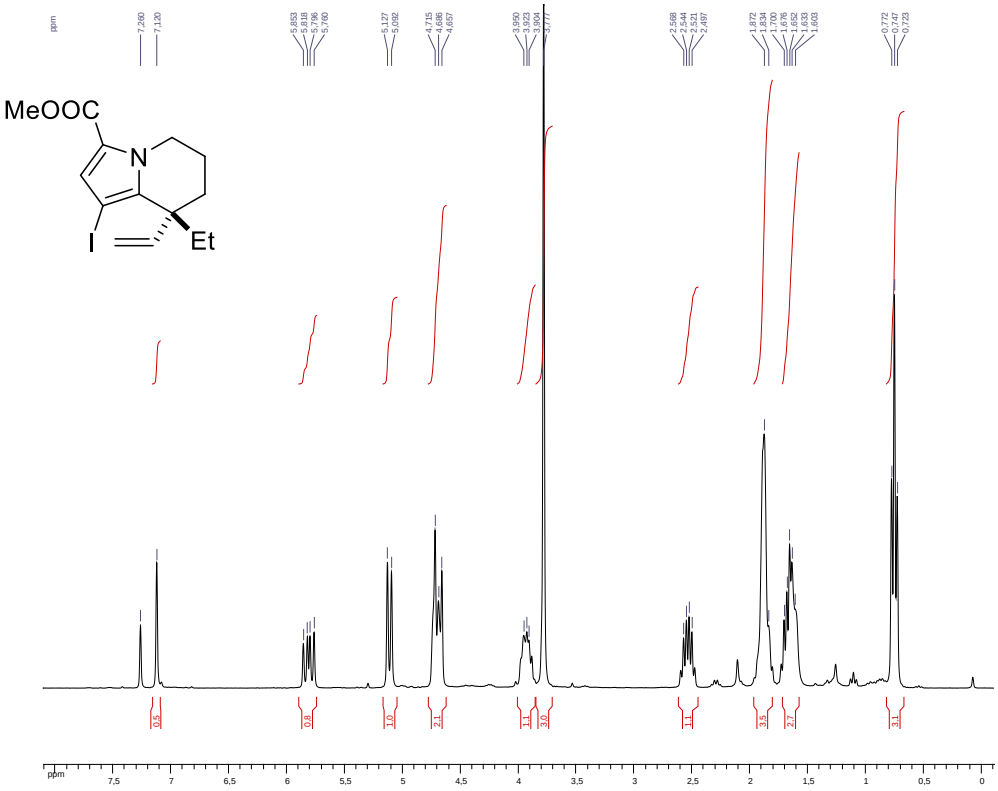


^{13}C NMR ($CDCl_3$, 75 MHz):

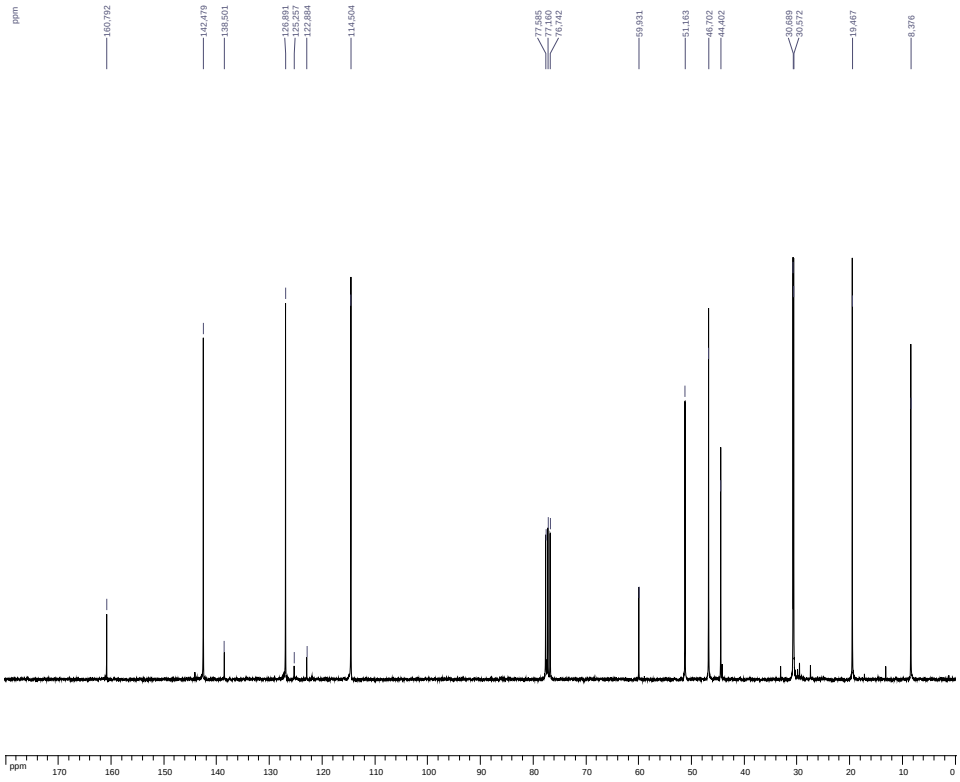


III.4. Compound (6).

^{1}H NMR ($CDCl_3$, 300 MHz):

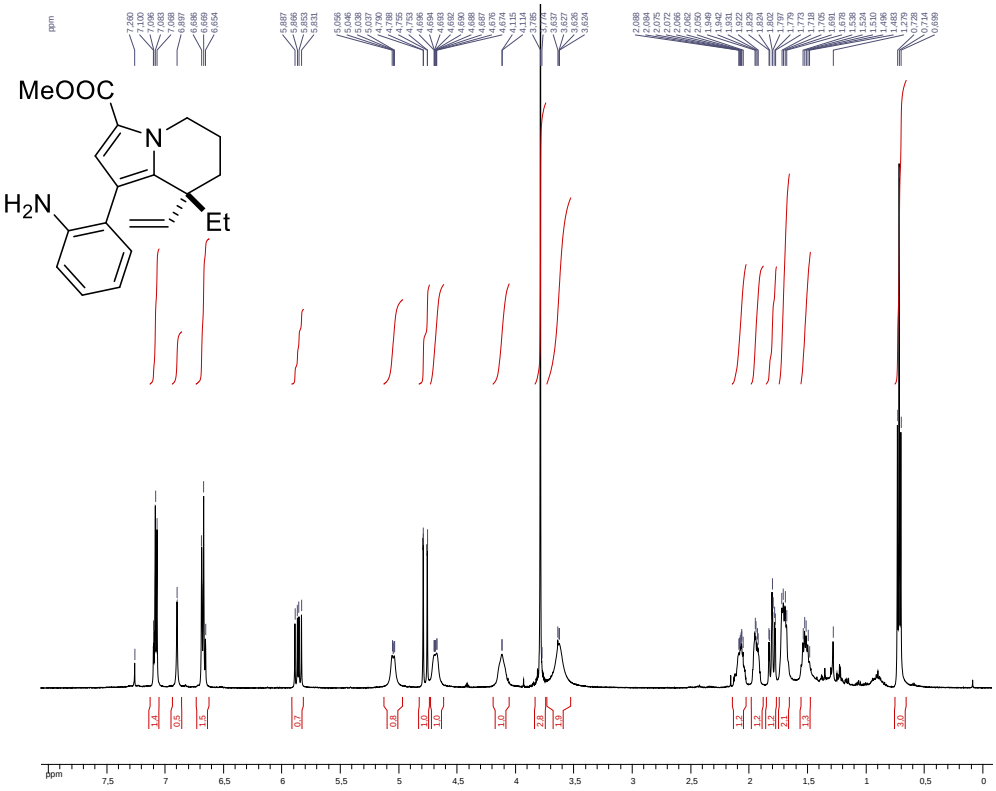


^{13}C NMR ($CDCl_3$, 75 MHz):

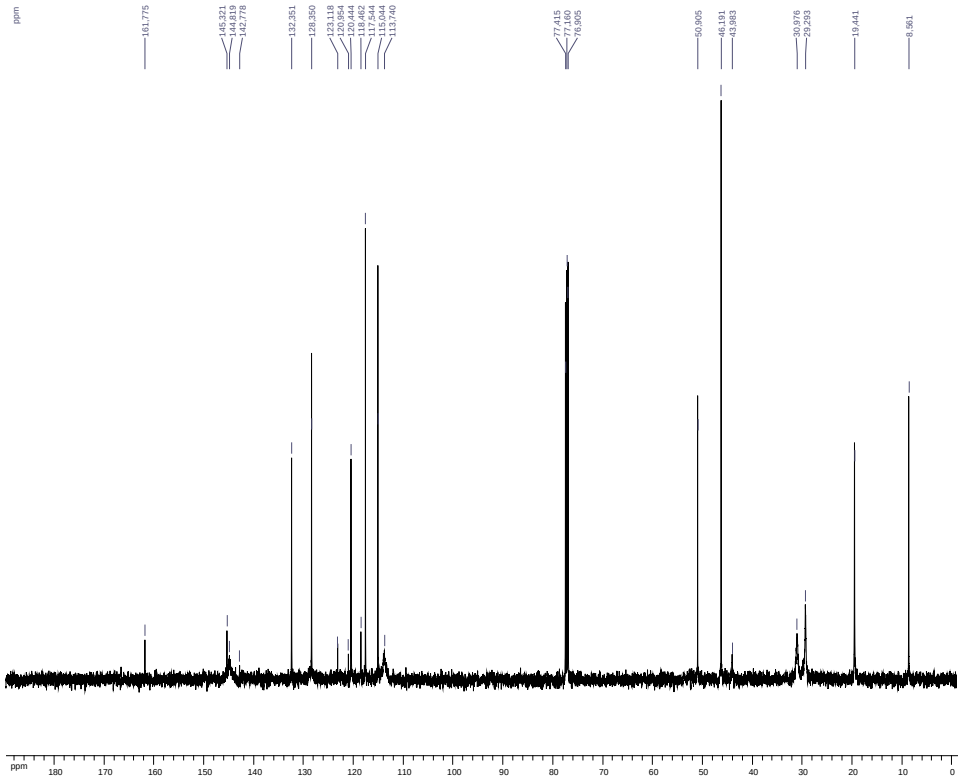


III.5. Compound (7).

^{1}H NMR ($CDCl_3$, 500 MHz):



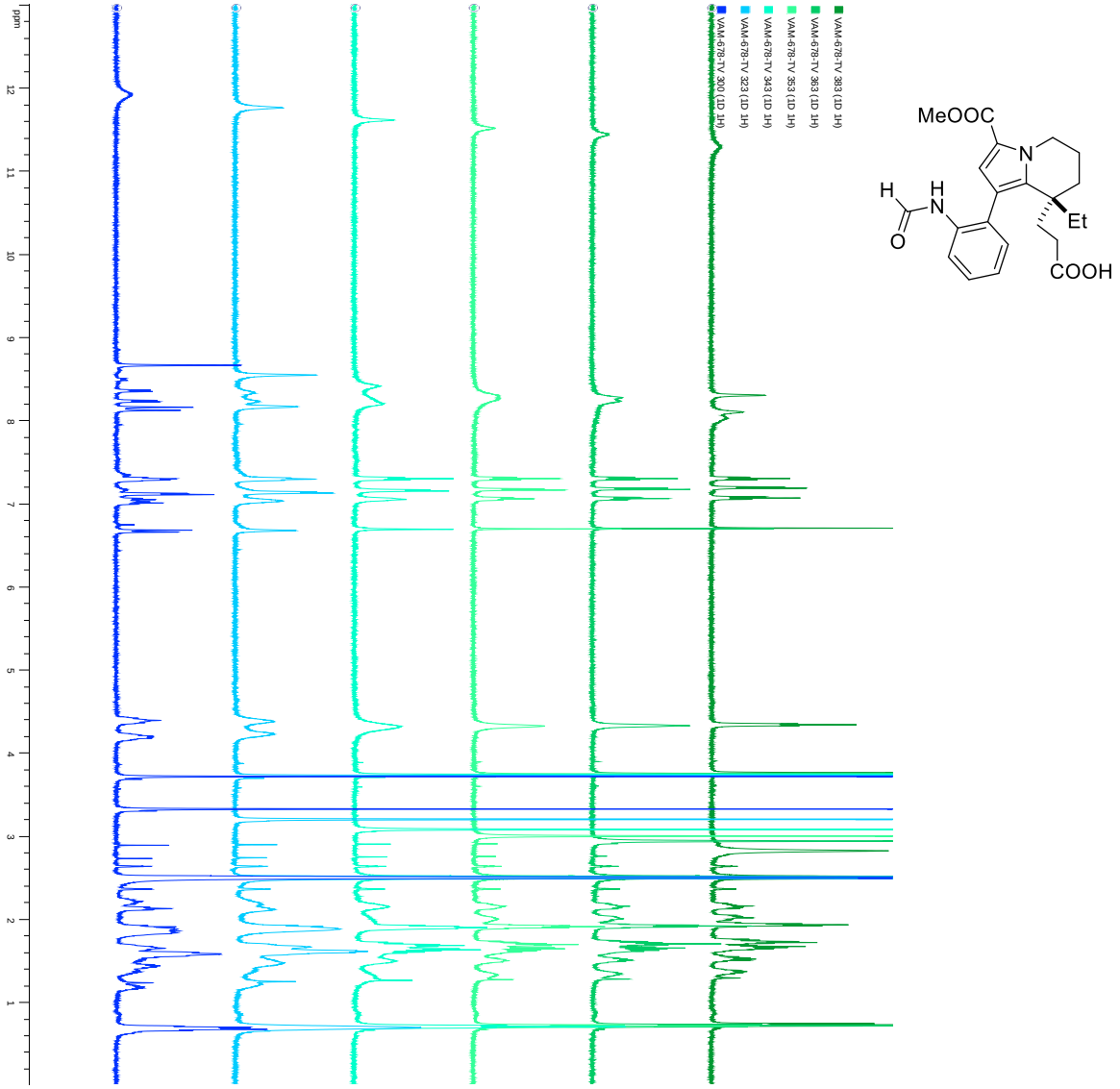
^{13}C NMR ($CDCl_3$, 125 MHz):



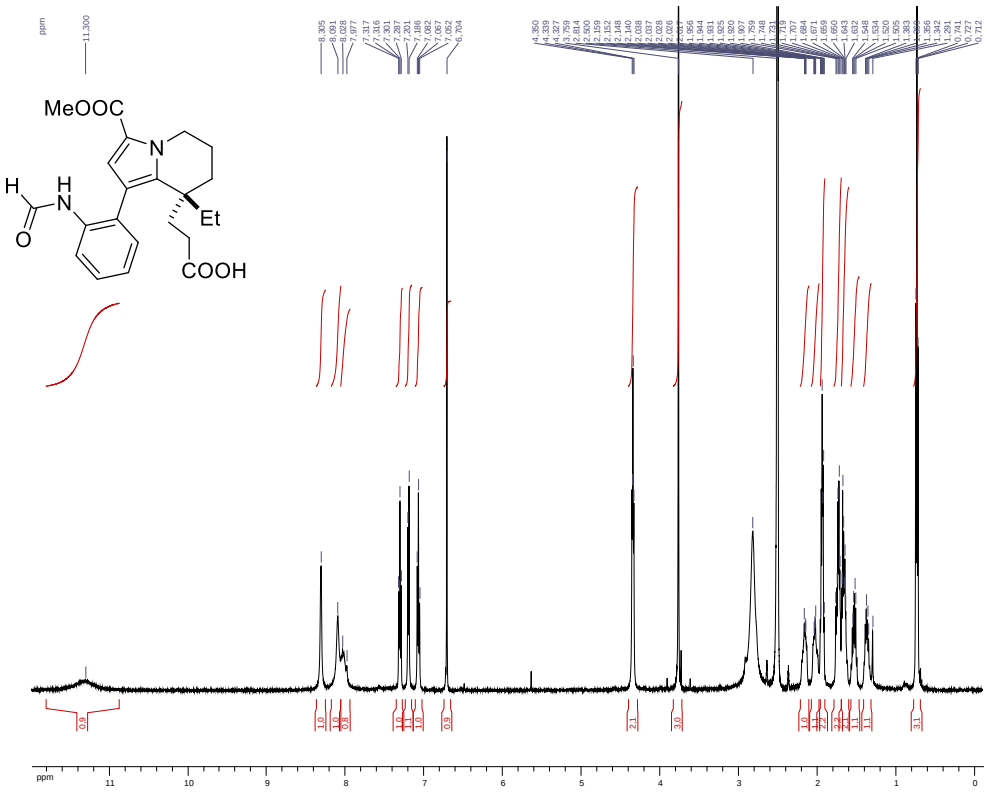
III.6. Compound (8).

NMR tube was subjected to temperature gradient from 300 K to 383 K:

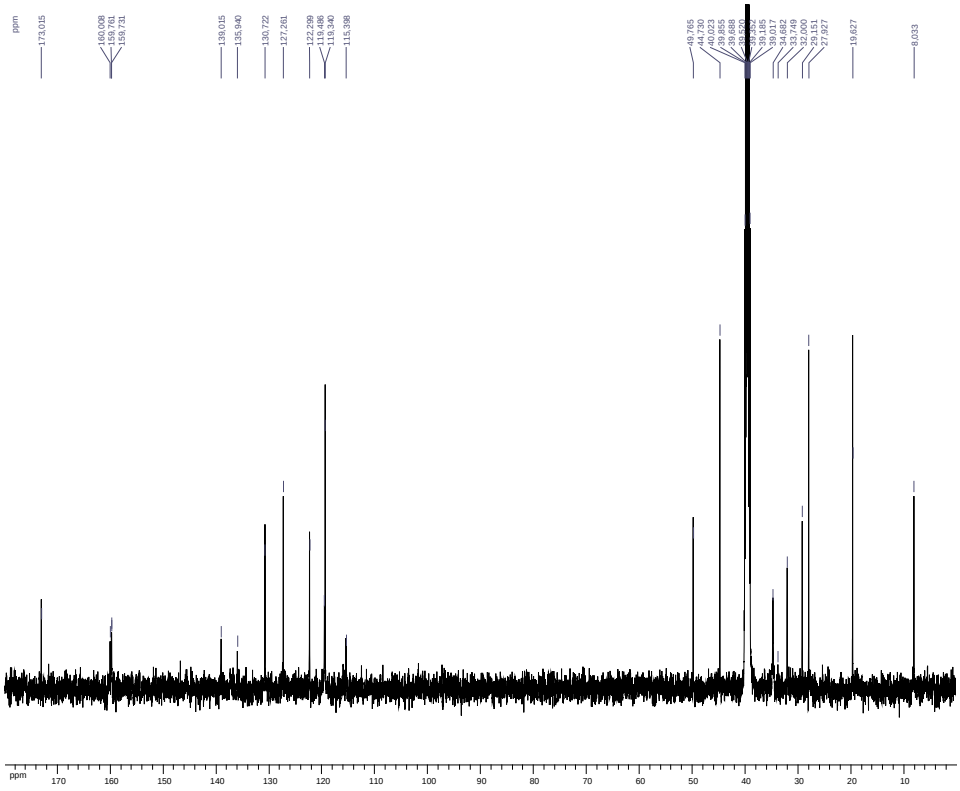
^{1}H NMR (DMSO D_6, 500 MHz):



^{1}H NMR (DMSO D_6, 500 MHz):

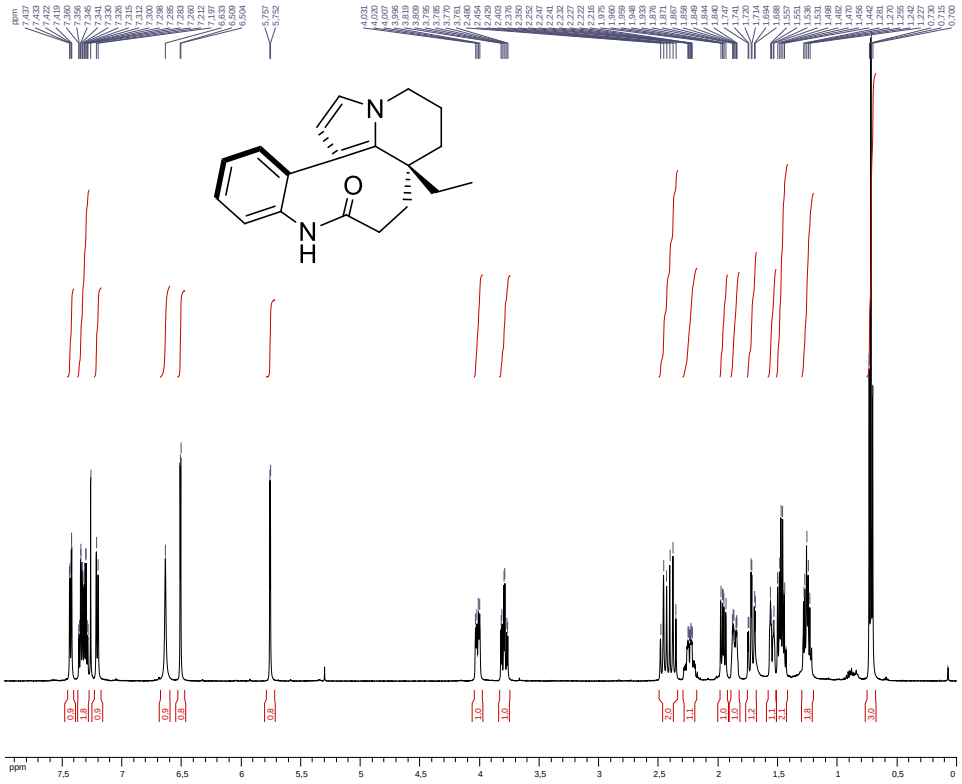


^{13}C NMR (DMSO D_6, 125 MHz):

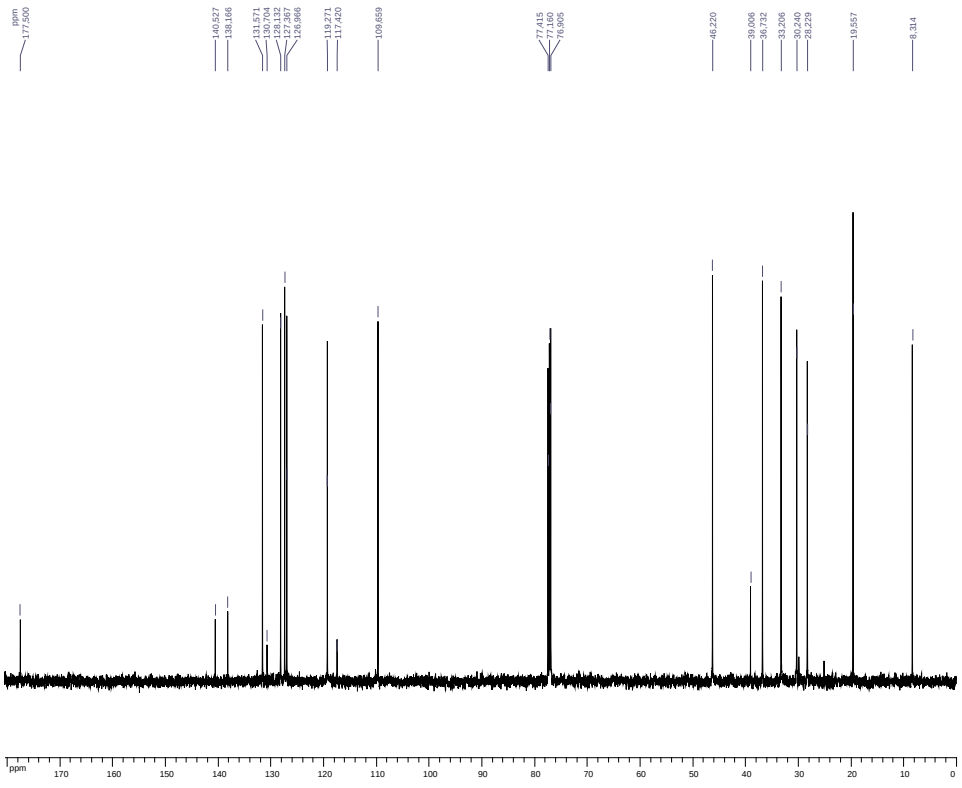


III.7. (-)-Rhazinilam (1).

^{1}H NMR ($CDCl_3$, 500 MHz):

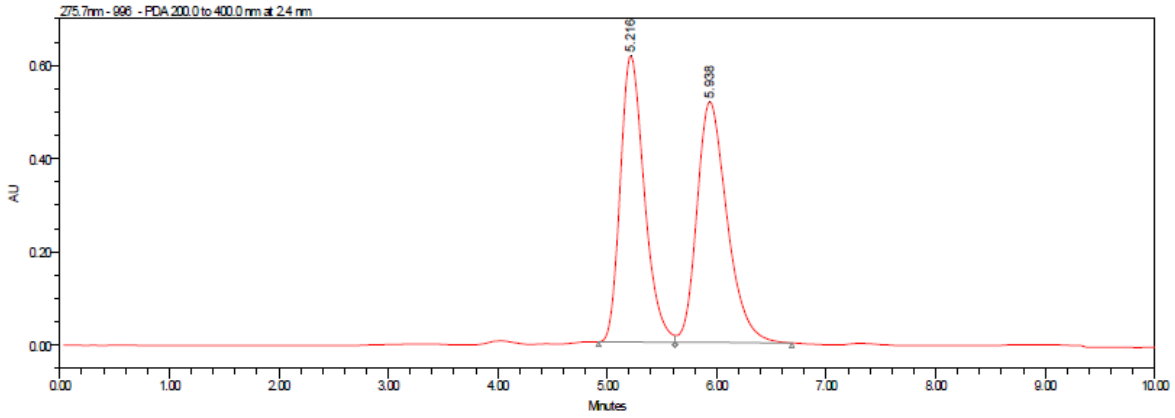


^{13}C NMR ($CDCl_3$, 125 MHz):

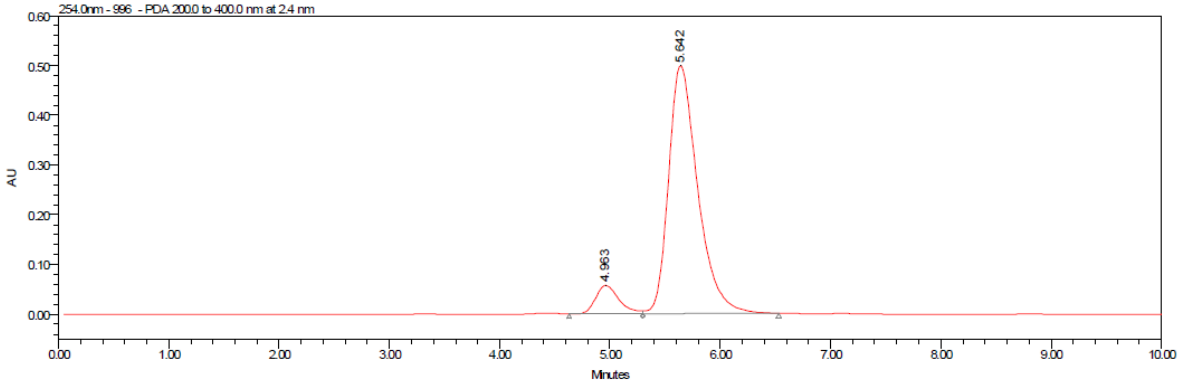


IV. HPLC Data.
IV.1. Compound (5).

Reaction on a 1 mmol scale. HPLC Analysis: [CHIRALPAK ® OJH , 15°C, 1% *i*PrOH/ *n*-heptane, 0.8 mL/min, retention times: 5.2 min (minor) and 5.9 min (major)].



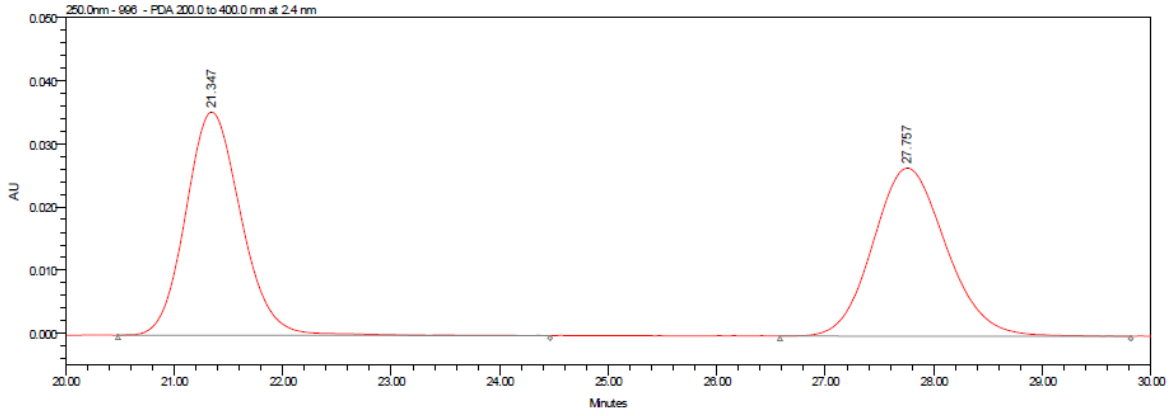
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	5.216	9363984	48.65
2	PDA 200.0 to 400.0 nm at 2.4 nm	5.938	9882906	51.35



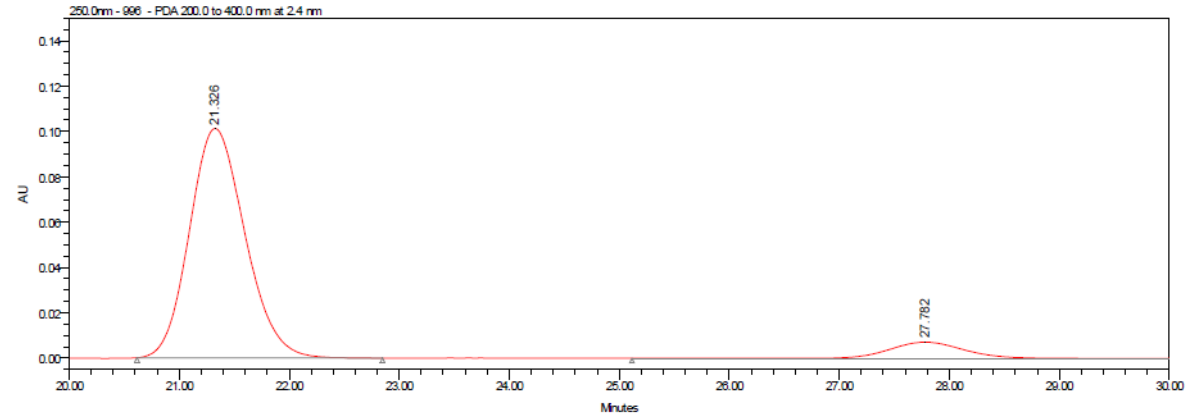
	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	4.963	845268	8.42
2	PDA 200.0 to 400.0 nm at 2.4 nm	5.642	9196458	91.58

IV.2. (-)-Rhazinilam (1).

HPLC Analysis: [CHIRALPAK ® IC, 25°C, 15% *i*PrOH/ *n*-heptane, 1.0 mL/min, 250 nm, retention times: 21.3 min (major) and 27.8 min (minor)].



	Channel Description	RT	Area	%Area
1	PDA200.0 to 400.0 nm at 2.4 nm	21.347	1250113	50.16
2	PDA200.0 to 400.0 nm at 2.4 nm	27.757	1241935	49.84



	Channel Description	RT	Area	%Area
1	PDA200.0 to 400.0 nm at 2.4 nm	21.326	3547223	91.32
2	PDA200.0 to 400.0 nm at 2.4 nm	27.782	337053	8.68