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AgOAc/Quinine-Derived Aminophosphine Complex as Efficient Catalyst for Diastereo- and Enantioselective 1,3-Dipolar Cycloaddition of *α,β*-Unsaturated 7-Azaindoline Amides and Azomethine Ylides

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Supporting Information

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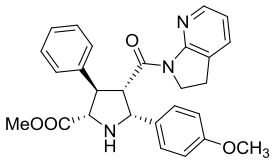
1. General information.

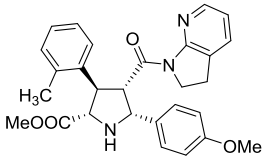
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm, DMSO-d_6 at 39.52 ppm). The ee were determined by chiral HPLC analysis. HRMS was recorded on Bruker Q TOF. Optical rotations were measured with a Perkin-Elmer-341 polarimeter. Melting points were recorded on a Büchi Melting Point B-545.

2. General procedure for the synthesis of compounds 3 in Table 2 and Table 3.

Under Ar atmosphere, AgOAc (1.7 mg, 0.01 mmol) and ligand **B** (7.3 mg, 0.012 mmol) were dissolved in toluene (2.0 mL) in a flame dried glass tube, and stirred at room temperature for 30 min. Then, azomethine ylides **2** (0.15 mmol) and Cs_2CO_3 (3.25 mg, 0.01mmol) were added, the mixture was further stirred at 0 ℃ for 15 min before the addition of *α,β*-unsaturated 7-azaindoline amides **1** (0.10 mmol). Once starting material **1** was consumed (monitored by TLC), the mixture was concentrated and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 to 4:1) on silica gel to afford the corresponding product **3**.

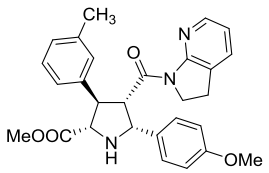


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (3aa). White solid; 44.8 mg, 98% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -68.9 (*c* 1.00, CH_2Cl_2); mp 163.5-164.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 10.69 min, t_{minor} = 17.24 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.19 (d, *J* = 4.4 Hz, 1H), 7.59-7.50 (m, 1H), 7.37-7.25 (m, 4H), 7.23-7.14 (m, 1H), 7.02-6.90 (m, 3H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.26 (t, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 9.5 Hz, 1H), 4.12 (t, *J* = 10.0 Hz, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 3H), 3.64-3.54 (m, 4H), 3.43 (s, 1H), 3.28-3.14 (m, 1H), 2.85-2.69 (m, 1H), 2.67-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.8, 158.2, 155.0, 145.7, 140.4, 134.0, 133.8, 128.5, 128.2, 127.9, 126.7, 126.6, 118.3, 112.8, 66.4, 62.2, 57.1, 55.0, 51.7, 50.1, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_4$ $[M + H]^+$ 458.2074; found: 458.2081.

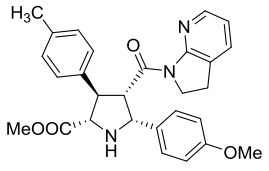


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(o-tolyl)pyrrolidine-2-carboxylate (3ba). White solid; 46.2 mg, 98% yield; >20:1 dr, 98% ee; $[\alpha]_D^{20}$ = -24.2 (*c* 1.00, CH_2Cl_2); mp 154.0-155.3 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.35 min, t_{minor} = 13.14 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.24-8.15 (m, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.22-7.13 (m, 1H), 7.13-7.02 (m, 2H), 7.01-6.89 (m, 3H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.25 (t, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 9.5 Hz, 1H), 4.42 (t, *J* = 10.0 Hz, 1H), 3.98 (d, *J* = 10.0 Hz, 1H), 3.81-3.63 (m, 4H), 3.63-3.51 (m, 4H), 3.27-3.12 (m, 1H), 2.84-2.67 (m, 1H), 2.65-2.51 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.5, 169.1, 158.3, 155.0, 145.7, 138.9, 136.9, 134.0, 133.6, 130.1, 128.2, 126.6, 126.3, 126.2, 118.3, 112.7, 66.9, 62.3, 58.1, 55.0, 51.8, 45.5, 45.3, 23.4, 19.4; HRMS (ESI-TOF) calcd. for

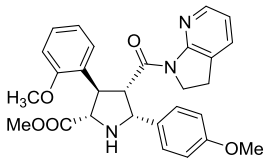
$C_{28}H_{30}N_3O_4$ $[M + H]^+$ 472.2231; found: 472.2225.



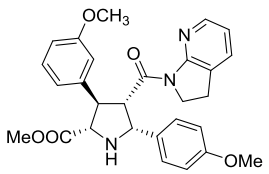
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(m-tolyl)pyrrolidine-2-carboxylate (3ca). White solid; 46.5 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -73.3 (*c* 1.00, CH_2Cl_2); mp 52.0-53.3 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.17 min, t_{minor} = 13.93 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.24-8.10 (m, 1H), 7.59-7.46 (m, 1H), 7.21-7.06 (m, 3H), 7.06-6.86 (m, 4H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.22 (t, *J* = 9.6 Hz, 1H), 4.92 (d, *J* = 9.4 Hz, 1H), 4.16-3.92 (m, 2H), 3.66 (s, 3H), 3.62-3.52 (m, 4H), 3.42 (s, 1H), 3.27-3.09 (m, 1H), 2.87-2.67 (m, 1H), 2.68-2.51 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.9, 158.2, 155.0, 145.7, 140.4, 137.4, 134.0, 133.8, 128.6, 128.4, 128.2, 127.4, 126.6, 125.0, 118.3, 112.7, 66.4, 62.3, 57.1, 55.0, 51.7, 50.1, 45.5, 23.4, 21.1; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_4$ $[M + H]^+$ 472.2231; found: 472.2229.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(p-tolyl)pyrrolidine-2-carboxylate (3da). White solid; 46.2 mg, 98% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -17.6 (*c* 1.00, CH_2Cl_2); mp 48.8-49.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.66 min, t_{minor} = 14.93 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.23-8.15 (m, 1H), 7.60-7.50 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02-6.89 (m, 3H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.22 (t, *J* = 9.7 Hz, 1H), 4.92 (d, *J* = 9.5 Hz, 1H), 4.07 (t, *J* = 10.0 Hz, 1H), 3.97 (d, *J* = 10.1 Hz, 1H), 3.66 (s, 3H), 3.64-3.54 (m, 4H), 3.42 (s, 1H), 3.28-3.14 (m, 1H), 2.85-2.70 (m, 1H), 2.68-2.51 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.8, 158.2, 155.0, 145.7, 137.3, 135.7, 133.9, 133.8, 129.0, 128.2, 127.7, 126.5, 118.3, 112.7, 66.3, 62.16, 57.1, 55.0, 51.6, 49.8, 45.5, 23.3, 20.6; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_4$ $[M + H]^+$ 472.2231; found: 472.2213.

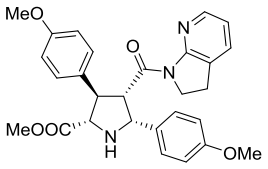


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-(2-methoxyphenyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ea). White solid; 48.1 mg, 99% yield; >20:1 dr, 99% ee; $[\alpha]_D^{20}$ = -29.8 (*c* 1.00, CH_2Cl_2); mp 54.3-56.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.55 min, t_{minor} = 18.46 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.13 (d, *J* = 4.5 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.31-7.24 (m, 1H), 7.23-7.15 (m, 1H), 7.03-6.84 (m, 5H), 6.66 (d, *J* = 8.6 Hz, 2H), 5.59 (t, *J* = 8.8 Hz, 1H), 4.80 (d, *J* = 9.1 Hz, 1H), 4.28 (t, *J* = 9.0 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.64-3.55 (m, 4H), 3.31-3.12 (m, 2H), 2.84-2.67 (m, 1H), 2.61-2.45 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.6, 170.2, 158.2, 157.6, 155.1, 145.5, 133.8, 132.9, 128.5, 128.4, 128.1, 127.9, 126.5, 120.5, 118.1, 112.7, 111.3, 65.0, 63.2, 55.4, 55.0, 54.3, 51.6, 46.7, 45.5, 23.3; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_5$ $[M + H]^+$ 488.2180; found: 488.2183.

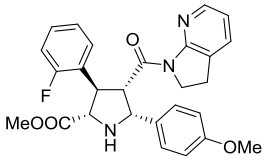


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-(3-methoxyphenyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3fa). White solid; 47.8 mg, 98% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -47.2 (*c* 1.00, CH_2Cl_2); mp 145.4-147.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate

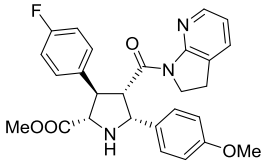
1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.39 min, t_{minor} = 41.62 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.22-8.16 (m, 1H), 7.59-7.51 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.02-6.87 (m, 4H), 6.85 (s, 1H), 6.81-6.73 (m, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 5.27 (t, *J* = 9.6 Hz, 1H), 4.91 (d, *J* = 9.5 Hz, 1H), 4.09 (t, *J* = 9.9 Hz, 1H), 4.00 (d, *J* = 10.2 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.65-3.56 (m, 4H), 3.53-3.41 (m, 1H), 3.28-3.15 (m, 1H), 2.85-2.70 (m, 1H), 2.67-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.9, 159.2, 158.2, 155.0, 145.7, 142.0, 134.0, 133.7, 129.5, 128.2, 126.6, 120.0, 118.3, 114.0, 112.7, 111.7, 66.2, 62.3, 56.8, 55.0, 54.9, 51.7, 50.1, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_5$ $[M + H]^+$ 488.2180; found: 488.2166.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3,5-bis(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ga). White solid; 48.2 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -30.9 (*c* 1.00, CH_2Cl_2); mp 45.4-46.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 10.78min, t_{minor} = 20.55 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (d, *J* = 4.9 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.98-6.87 (m, 3H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.16 (t, *J* = 9.7 Hz, 1H), 4.89 (d, *J* = 9.5 Hz, 1H), 4.03 (t, *J* = 10.0 Hz, 1H), 3.94 (d, *J* = 10.2 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H), 3.61-3.50 (m, 4H), 3.45-3.35 (m, 1H), 3.24-3.10 (m, 1H), 2.82-2.66 (m, 1H), 2.64-2.48 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.8, 158.2, 158.0, 155.0, 145.7, 134.0, 133.8, 132.1, 128.9, 128.2, 126.5, 118.3, 113.9, 112.7, 66.3, 62.1, 57.1, 55.0, 54.9, 51.7, 49.3, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_5$ $[M + H]^+$ 488.2180; found: 488.2171.

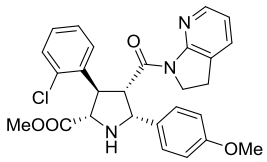


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-(2-fluorophenyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ha). White solid; 47.1 mg, 99% yield; >20:1 dr, 90% ee; $[\alpha]_D^{20}$ = -54.4 (*c* 1.00, CH_2Cl_2); mp 54.2-56.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH /hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.88 min, t_{minor} = 11.54 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.22-8.14 (m, 1H), 7.59-7.51 (m, 1H), 7.49-7.39 (m, 1H), 7.31-7.20 (m, 1H), 7.20-7.07 (m, 2H), 7.03-6.91 (m, 3H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.41 (t, *J* = 9.7 Hz, 1H), 4.93 (d, *J* = 9.4 Hz, 1H), 4.32 (t, *J* = 10.0 Hz, 1H), 3.99 (d, *J* = 10.2 Hz, 1H), 3.66 (s, 3H), 3.64-3.54 (m, 4H), 3.48 (s, 1H), 3.28-3.14 (m, 1H), 2.85-2.69 (m, 1H), 2.65-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 168.8, 160.8 (*J* = 243.4 Hz, 1C), 158.3, 155.0, 145.7, 134.0, 133.2, 129.7 (*J* = 4.6 Hz, 1C), 128.7 (*J* = 8.5 Hz, 1C), 128.2, 127.0 (*J* = 13.4 Hz, 1C), 126.6, 124.6 (*J* = 3.1 Hz, 1C), 118.4, 115.5 (*J* = 22.2 Hz, 1C), 112.7, 65.3, 62.3, 55.5, 55.0, 51.8, 45.5, 44.3, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}FN_3O_4$ $[M + H]^+$ 476.1980; found: 476.1970.

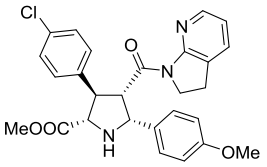


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-(4-fluorophenyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ia). White solid; 47.1 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -33.5 (*c* 1.00, CH_2Cl_2); mp 51.7-52.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.21 min, t_{minor} = 11.84 min); ^{1}H NMR (300 MHz, DMSO) δ 8.19 (d, *J* = 4.4 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.41-7.30 (m, 2H), 7.11 (t, *J* = 8.8 Hz, 2H), 7.02-6.89 (m, 3H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.19 (t, *J* = 9.7 Hz, 1H), 4.94 (d, *J* = 9.5 Hz, 1H), 4.10 (t, *J* = 10.1 Hz, 1H), 4.02 (d, *J* = 10.3 Hz, 1H), 3.70-3.53 (m, 8H), 3.27-3.12 (m, 1H), 2.85-2.69

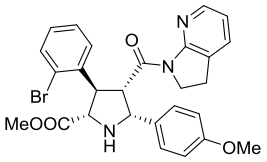
(m, 1H), 2.66-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.7, 161.1 (J = 241.0 Hz, 1C), 158.3, 155.0, 145.7, 136.5, 136.5, 133.9 (J = 23.9 Hz, 1C), 129.8 (J = 8.0 Hz, 1C), 128.3, 126.6, 118.4, 115.2 (J = 21.0 Hz, 1C), 112.7, 66.2, 62.1, 57.3, 55.0, 51.7, 49.4, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}FN_3O_4$ $[M + H]^+$ 476.1980; found: 476.1961.



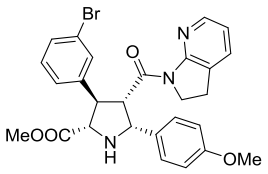
Methyl (2*S*,3*R*,4*S*,5*R*)-3-(2-chlorophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ja). White solid; 48.6 mg, 99% yield; >20:1 dr, 88% ee; $[\alpha]_D^{20}$ = -22.7 (*c* 1.00, CH_2Cl_2); mp 45.8-47.2 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.78 min, t_{minor} = 11.10 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18-8.10 (m, 1H), 7.64-7.55 (m, 1H), 7.55-7.47 (m, 1H), 7.44-7.36 (m, 1H), 7.36-7.29 (m, 1H), 7.28-7.19 (m, 1H), 7.03-6.90 (m, 3H), 6.67 (d, J = 8.6 Hz, 2H), 5.46 (t, J = 8.9 Hz, 1H), 4.91 (d, J = 9.1 Hz, 1H), 4.58 (t, J = 9.1 Hz, 1H), 3.96 (d, J = 9.5 Hz, 1H), 3.71-3.53 (m, 7H), 3.32-3.09 (m, 2H), 2.83-2.67 (m, 1H), 2.61-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 169.2, 158.4, 154.9, 145.6, 138.2, 133.9 (2C), 132.7, 129.5, 128.9, 128.3, 128.1, 127.6, 126.5, 118.3, 112.8, 66.2, 63.0, 56.4, 55.0, 51.9, 47.4, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}ClN_3O_4$ $[M + H]^+$ 492.1685; found: 492.1673.



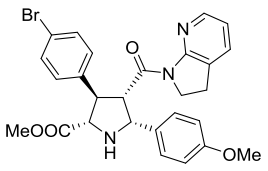
Methyl (2*S*,3*R*,4*S*,5*R*)-3-(4-chlorophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ka). White solid; 48.7 mg, 99% yield; >20:1 dr, 93% ee; $[\alpha]_D^{20}$ = -16.2 (*c* 1.00, CH_2Cl_2); mp 50.9-52.5 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.22 min, t_{minor} = 11.72 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, J = 3.8 Hz, 1H), 7.78-7.47 (m, 1H), 7.34 (s, 4H), 7.08-6.82 (m, 3H), 6.67 (d, J = 8.7 Hz, 2H), 5.20 (t, J = 9.6 Hz, 1H), 4.94 (d, J = 9.2 Hz, 1H), 4.22-3.94 (m, 2H), 3.66 (s, 3H), 3.64-3.52 (m, 4H), 3.42 (s, 1H), 3.29-3.12 (m, 1H), 2.89-2.68 (m, 1H), 2.69-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 168.6, 158.3, 155.0, 145.7, 139.4, 134.0, 133.7, 131.3, 129.9, 128.4, 128.2, 126.6, 118.4, 112.7, 66.0, 62.1, 57.2, 55.0, 51.7, 49.5, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}ClN_3O_4$ $[M + H]^+$ 492.1685; found: 492.1705.



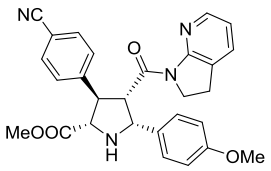
Methyl (2*S*,3*R*,4*S*,5*R*)-3-(2-bromophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3la). White solid; 53.0 mg, 99% yield; >20:1 dr, 91% ee; $[\alpha]_D^{20}$ = -5.3 (*c* 1.00, CH_2Cl_2); mp 55.1-56.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.62 min, t_{minor} = 14.48 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18-8.08 (m, 1H), 7.65-7.55 (m, 2H), 7.54-7.47 (m, 1H), 7.45-7.35 (m, 1H), 7.21-7.10 (m, 1H), 7.04-6.90 (m, 3H), 6.66 (d, J = 8.7 Hz, 2H), 5.43 (t, J = 8.6 Hz, 1H), 4.90 (d, J = 8.9 Hz, 1H), 4.57 (t, J = 8.8 Hz, 1H), 3.94 (d, J = 9.2 Hz, 1H), 3.72-3.55 (m, 7H), 3.32-3.15 (m, 2H), 2.84-2.67 (m, 1H), 2.61-2.50 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 169.2, 158.4, 154.9, 145.6, 140.2, 133.9, 132.7, 132.5, 128.9, 128.6, 128.2, 128.1, 126.5, 125.1, 118.3, 112.7, 66.5, 63.1, 56.7, 55.0, 51.9, 50.1, 45.5, 23.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}BrN_3O_4$ $[M + H]^+$ 536.1179; found: 536.1186.



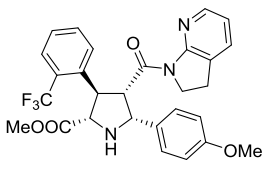
Methyl (2*S*,3*R*,4*S*,5*R*)-3-(3-bromophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ma). White solid; 52.5 mg, 98% yield; >20:1 dr, 87% ee; $[\alpha]_D^{20}$ = -36.5 (*c* 1.00, CH_2Cl_2); mp 49.7-50.4 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.92 min, t_{minor} = 10.22 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.19 (d, *J* = 4.4 Hz, 1H), 7.58-7.49 (m, 2H), 7.43-7.32 (m, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.02-6.95 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.25-5.11 (m, 1H), 4.94 (d, *J* = 9.5 Hz, 1H), 4.15-4.02 (m, 2H), 3.73-3.53 (m, 8H), 3.26-3.13 (m, 1H), 2.84-2.68 (m, 1H), 2.65-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 168.5, 158.3, 154.9, 145.7, 143.3, 134.0, 133.5, 130.8, 130.7, 129.7, 128.3, 127.2, 126.6, 121.7, 118.4, 112.7, 65.7, 62.1, 57.2, 55.0, 51.8, 49.7, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}BrN_3O_4$ $[M + H]^+$ 536.1179; found: 536.1174.



Methyl (2*S*,3*R*,4*S*,5*R*)-3-(4-bromophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3na). White solid; 52.6 mg, 98% yield; >20:1 dr, 92% ee; $[\alpha]_D^{20}$ = -11.3 (*c* 1.00, CH_2Cl_2); mp 58.7-60.2 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.53 min, t_{minor} = 12.03 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, *J* = 5.0 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.02-6.97 (m, 1H), 6.97-6.89 (m, 2H), 6.67 (d, *J* = 8.3 Hz, 2H), 5.19 (t, *J* = 9.5 Hz, 1H), 4.94 (d, *J* = 9.3 Hz, 1H), 4.14-3.95 (m, 2H), 3.66 (s, 3H), 3.64-3.53 (m, 4H), 3.42 (s, 1H), 3.29-3.13 (m, 1H), 2.86-2.69 (m, 1H), 2.67-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 168.6, 158.3, 154.9, 145.7, 139.9, 134.0, 133.7, 131.3, 130.3, 128.2, 126.6, 119.8, 118.4, 112.7, 66.0, 62.1, 57.2, 55.0, 51.7, 49.5, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}BrN_3O_4$ $[M + H]^+$ 536.1179; found: 536.1199.

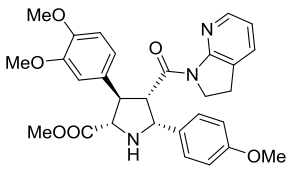


Methyl (2*S*,3*R*,4*S*,5*R*)-3-(4-cyanophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-c arboxylate (3oa). White solid; 47.7 mg, 99% yield; >20:1 dr, 82% ee; $[\alpha]_D^{20}$ = -9.9 (*c* 1.00, CH_2Cl_2); mp 113.8-115.2 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH /hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 11.74 min, t_{minor} = 17.95 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.22-8.14 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 3H), 7.03-6.96 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.22 (t, *J* = 9.4 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.23-4.07 (m, 2H), 3.80-3.63 (m, 4H), 3.64-3.54 (m, 4H), 3.27-3.13 (m, 1H), 2.85-2.70 (m, 1H), 2.66-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 168.4, 158.3, 154.9, 146.4, 145.7, 134.1, 133.3, 132.4, 129.2, 128.3, 126.6, 118.8, 118.5, 112.7, 109.6, 65.6, 62.1, 57.2, 55.0, 51.8, 50.0, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{28}H_{27}N_4O_4$ $[M + H]^+$ 483.2027; found: 483.2014.

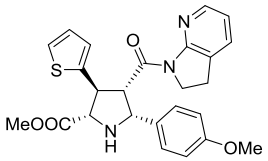


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(2-(trifluoromethyl)phenyl)pyrrolidine-2-carboxylate (3pa). White solid; 52.0 mg, 99% yield; >20:1 dr, 86% ee; $[\alpha]_D^{20}$ = -49.5 (*c* 1.00, CH_2Cl_2); mp 50.4-52.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate

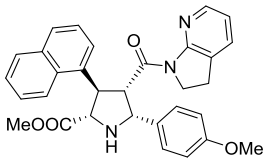
1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.27 min, t_{minor} = 10.37 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03-7.97 (m, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.49-7.39 (m, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.88 (dd, *J* = 7.3, 5.1 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 5.53-5.43 (m, 1H), 4.90 (d, *J* = 8.5 Hz, 1H), 4.43-4.33 (m, 1H), 4.02 (d, *J* = 8.3 Hz, 1H), 3.68-3.60 (m, 3H), 3.61-3.52 (m, 4H), 3.35-3.14 (m, 2H), 2.78-2.61 (m, 1H), 2.47-2.35 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.5, 169.9, 158.4, 154.9, 145.3, 141.2, 133.9, 133.2, 130.9, 129.5, 128.0, 127.6 (q, *J* = 28.5 Hz, 1C), 127.2, 126.5, 125.7 (q, *J* = 5.5 Hz, 1C), 124.4 (q, *J* = 272.4 Hz, 1C),118.3, 112.7, 68.5, 64.7, 57.7, 55.0, 51.7, 47.9, 45.6, 23.3; HRMS (ESI-TOF) calcd. for $C_{28}H_{27}F_3N_3O_4$ $[M + H]^+$ 526.1948; found: 526.1954.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-(3,4-dimethoxyphenyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3qa). White solid; 50.1 mg, 97% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -18.4 (*c* 1.00, CH_2Cl_2); mp 46.9-48.1 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 11.17 min, t_{minor} = 24.44 min); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.23-8.16 (m, 1H), 7.59-7.52 (m, 1H), 7.03-6.92 (m, 3H), 6.91-6.80 (m, 3H), 6.68 (d, *J* = 8.7 Hz, 2H), 5.28 (t, *J* = 9.5 Hz, 1H), 4.91 (d, *J* = 9.4 Hz, 1H), 4.09-3.92 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 3.67 (s, 3H), 3.65-3.56 (m, 4H), 3.39 (s, 1H), 3.29-3.15 (m, 1H), 2.87-2.72 (m, 1H), 2.69-2.53 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.6, 169.0, 158.2, 155.0, 148.5, 147.6, 145.7, 134.0, 133.9, 132.7, 128.2, 126.6, 119.5, 118.3, 112.7, 111.9 (2C), 66.4, 62.2, 56.8, 55.5, 55.4, 55.0, 51.7, 49.9, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{29}H_{32}N_3O_6$ $[M + H]^+$ 518.2286; found: 518.2268.

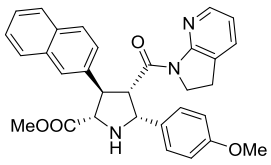


Methyl (2*S*,3*S*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(thiophen-2-yl)pyrrolidine-2-carboxylate (3ra). White solid; 44.9 mg, 97% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -67.4 (*c* 1.00, CH_2Cl_2); mp 129.4-130.6 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 10.74 min, t_{minor} = 15.89 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.24-8.16 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.36-7.29 (m, 1H), 7.04-6.97 (m, 1H), 6.96-6.86 (m, 4H), 6.67 (d, *J* = 8.5 Hz, 2H), 5.22 (t, *J* = 9.9 Hz, 1H), 4.90 (d, *J* = 9.6 Hz, 1H), 4.42 (t, *J* = 10.1 Hz, 1H), 3.97 (d, *J* = 10.0 Hz, 1H), 3.75-3.61 (m, 7H), 3.59 (s, 1H), 3.30-3.16 (m, 1H), 2.91-2.74 (m, 1H), 2.72-2.55 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 168.3, 158.3, 154.9, 145.8, 143.4, 134.1, 133.7, 128.2, 127.0, 126.6, 124.7, 124.2, 118.4, 112.7, 66.7, 61.8, 57.7, 55.0, 51.9, 45.5, 44.8, 23.4; HRMS (ESI-TOF) calcd. for $C_{25}H_{26}N_3O_4S$ $[M + H]^+$ 464.1639; found: 464.1639.

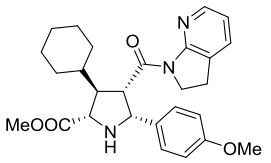


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(naphthalen-1-yl)pyrrolidine-2-carboxylate (3sa): White solid; 49.6 mg, 98% yield; >20:1 dr, 97% ee; $[\alpha]_D^{20}$ = +32.0 (*c* 1.00, CH_2Cl_2); mp 62.5-63.4 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.96 min, t_{minor} = 16.74 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.29-8.21 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 4.5 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.61-7.45 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.99-6.92 (m, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 5.50 (t, *J* = 9.3 Hz, 1H), 5.11-4.96 (m, 2H), 4.14 (d, *J* = 9.4 Hz, 1H), 3.67 (s, 3H), 3.61-3.46 (m, 2H), 3.42 (s, 3H), 3.30-3.15 (m, 1H), 2.80-2.64 (m, 1H), 2.61-2.52 (m, 1H);

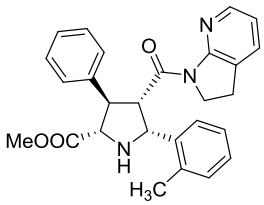
^{13}C NMR (100 MHz, DMSO-d_6) δ 173.6, 169.3, 158.3, 154.9, 145.6, 137.2, 133.9, 133.5, 133.4, 132.0, 128.6, 128.3, 127.0, 126.5, 125.9, 125.7, 125.6, 124.2, 123.4, 118.3, 112.7, 67.3, 62.8, 57.6, 55.0, 51.7, 45.5, 44.9, 23.2; HRMS (ESI-TOF) calcd. for $C_{31}H_{30}N_3O_4$ [M + H]$^+$ 508.2231; found: 508.2224.



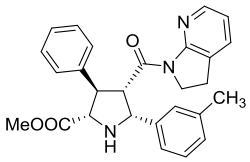
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-(naphthalen-2-yl)pyrrolidine-2-carboxylate (3ta). White solid; 49.1 mg, 97% yield; >20:1 dr, 94% ee; $[\alpha]_D^{20}$ = -1.2 (*c* 1.00, CH_2Cl_2); mp 104.8-106.5 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 9.38 min, t_{minor} = 16.57 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20 (d, *J* = 4.6 Hz, 1H), 7.91-7.78 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.50-7.40 (m, 2H), 7.03-6.93 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 2H), 5.34 (t, *J* = 9.7 Hz, 1H), 5.02 (d, *J* = 9.5 Hz, 1H), 4.29 (t, *J* = 10.0 Hz, 1H), 4.18 (d, *J* = 10.1 Hz, 1H), 3.67 (s, 3H), 3.64-3.45 (m, 5H), 3.29-3.15 (m, 1H), 2.81-2.66 (m, 1H), 2.65-2.51 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.8, 158.3, 155.0, 145.7, 138.0, 133.9, 133.8, 133.0, 132.0, 128.2, 128.0, 127.6, 127.4, 126.6, 126.5, 126.2, 126.1, 125.6, 118.3, 112.7, 66.2, 62.3, 57.4, 55.0, 51.7, 50.5, 45.5, 23.3; HRMS (ESI-TOF) calcd. for $C_{31}H_{30}N_3O_4$ [M + H]$^+$ 508.2231; found: 508.2212.



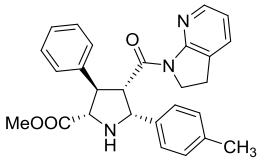
Methyl (2*S*,3*S*,4*S*,5*R*)-3-cyclohexyl-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)pyrrolidine-2-carboxylate (3ua). White solid; 44.9 mg, 97% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -14.6 (*c* 1.00, CH_2Cl_2); mp 34.5-36.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.84 min, t_{minor} = 13.30 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18-8.10 (m, 1H), 7.53-7.47 (m, 1H), 6.94 (dd, *J* = 7.3, 5.1 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 5.27-5.13 (m, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 3.75-3.68 (m, 3H), 3.67-3.56 (m, 5H), 3.30-3.07 (m, 2H), 2.94-2.68 (m, 2H), 2.48-2.35 (m, 1H), 1.79-1.38 (m, 6H), 1.22-0.90 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.0, 171.4, 158.1, 155.2, 145.4, 133.8, 132.2, 128.0, 126.5, 118.1, 112.4, 64.1, 63.1, 55.0, 51.8, 51.6, 51.1, 45.6, 31.2, 30.2, 26.1, 26.0, 23.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{34}N_3O_4$ [M + H]$^+$ 464.2544; found: 464.2556.



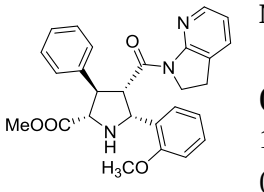
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenyl-5-(o-tolyl)pyrrolidine-2-carboxylate (3ab). White solid; 43.6 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -13.6 (*c* 1.00, CH_2Cl_2); mp 41.8-43.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.92 min, t_{minor} = 13.70 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.08-8.01 (m, 1H), 7.44 (m, 1H), 7.41-7.29 (m, 5H), 7.27-7.19 (m, 1H), 7.17-7.08 (m, 1H), 7.06-6.97 (m, 1H), 6.93-6.85 (m, 1H), 6.79 (d, *J* = 7.3 Hz, 1H), 5.53-5.43 (m, 1H), 5.06 (d, *J* = 9.0 Hz, 1H), 4.20-4.10 (m, 1H), 3.98 (d, *J* = 9.1 Hz, 1H), 3.65 (s, 3H), 3.63-3.53 (m, 1H), 3.34-3.19 (m, 2H), 2.75-2.60 (m, 1H), 2.45-2.29 (m, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 170.1, 154.9, 145.4, 141.6, 138.1, 135.2, 133.7, 129.2, 128.6, 127.8, 127.0, 126.7 (2C), 126.4, 125.1, 118.2, 67.1, 60.4, 55.7, 52.0, 51.8, 45.8, 23.3, 18.6; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_3$ [M + H]$^+$ 442.2125; found: 442.2135.



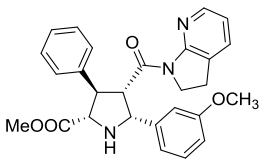
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenyl-5-(m-tolyl)pyrrolidine-2-carboxylate (3ac). White solid; 43.2 mg, 98% yield; >20:1 dr, 93% ee; $[\alpha]_D^{20}$ = -29.6 (*c* 1.00, CH_2Cl_2); mp 49.0-50.7 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.21 min, t_{minor} = 8.88 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.23-8.16 (m, 1H), 7.58-7.50 (m, 1H), 7.39-7.25 (m, 4H), 7.24-7.15 (m, 1H), 7.06-6.84 (m, 4H), 6.69 (s, 1H), 5.33 (t, *J* = 9.6 Hz, 1H), 4.88 (d, *J* = 9.6 Hz, 1H), 4.13 (t, *J* = 9.8 Hz, 1H), 4.02 (d, *J* = 10.0 Hz, 1H), 3.61 (s, 3H), 3.60-3.50 (m, 1H), 3.45 (s, 1H), 3.22-3.07 (m, 1H), 2.82-2.65 (m, 1H), 2.49-2.38 (m, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 169.0, 155.1, 145.7, 141.4, 140.6, 136.1, 133.9, 128.5, 128.0, 127.9, 127.4, 127.2, 126.7, 126.5, 124.2, 118.2, 66.5, 63.0, 57.0, 51.7, 50.2, 45.5, 23.3, 20.9; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_3$ $[M + H]^+$ 442.2125; found: 442.2139.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenyl-5-(p-tolyl)pyrrolidine-2-carboxylate (3ad). White solid; 43.3 mg, 98% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -59.8 (*c* 1.00, CH_2Cl_2); mp 53.1-54.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 13.24 min, t_{minor} = 17.13 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.19 (d, *J* = 4.5 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.38-7.23 (m, 4H), 7.22-7.13 (m, 1H), 7.01-6.87 (m, 5H), 5.29 (t, *J* = 9.7 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.13 (t, *J* = 10.0 Hz, 1H), 4.03 (d, *J* = 10.2 Hz, 1H), 3.70-3.51 (m, 5H), 3.24-3.10 (m, 1H), 2.82-2.66 (m, 1H), 2.62-2.47 (m, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.8, 155.0, 145.7, 140.4, 138.8, 135.9, 133.9, 128.5, 128.0, 127.9, 127.1, 126.7, 126.6, 118.3, 66.4, 62.6, 57.1, 51.7, 50.2, 45.5, 23.3, 20.6; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_3$ $[M + H]^+$ 442.2125; found: 442.2127.

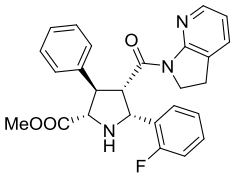


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(2-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (3ae). White solid; 45.1 mg, 99% yield; >20:1 dr, 94% ee; $[\alpha]_D^{20}$ = +14.0 (*c* 1.00, CH_2Cl_2); mp 50.8-52.0 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.17 min, t_{minor} = 9.60 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (d, *J* = 4.8 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.36-7.25 (m, 4H), 7.24-7.16 (m, 1H), 7.16-7.08 (m, 1H), 6.99-6.91 (m, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 5.58 (t, *J* = 9.1 Hz, 1H), 5.23 (d, *J* = 9.0 Hz, 1H), 4.12-3.94 (m, 2H), 3.75-3.48 (m, 5H), 3.31-3.20 (m, 1H), 3.16 (s, 3H), 2.85-2.69 (m, 1H), 2.68-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 169.3, 155.8, 155.4, 145.6, 140.4, 133.5, 129.4, 128.7, 128.5, 127.8, 126.7, 126.2, 119.5, 117.8, 109.2, 66.6, 56.7, 55.6, 54.2, 51.7, 50.8, 45.6, 23.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_4$ $[M + H]^+$ 458.2074; found: 458.2072.

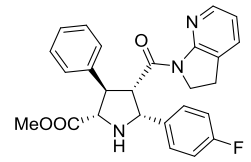


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(3-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (3af). White solid; 45.3 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -43.2 (*c* 1.00, CH_2Cl_2); mp 109.3-110.5 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.78 min, t_{minor} = 11.70 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, *J* = 4.7 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.37-7.24 (m, 4H), 7.23-7.14 (m, 1H), 7.09-6.93 (m, 2H), 6.74-6.66 (m,

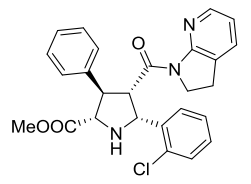
2H), 6.58 (d, *J* = 7.5 Hz, 1H), 5.30 (t, *J* = 9.7 Hz, 1H), 4.97 (d, *J* = 9.6 Hz, 1H), 4.12 (t, *J* = 10.0 Hz, 1H), 4.03 (d, *J* = 10.2 Hz, 1H), 3.67-3.52 (m, 8H), 3.26-3.11 (m, 1H), 2.86-2.70 (m, 1H), 2.68-2.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.6, 158.5, 155.0, 145.8, 143.7, 140.3, 134.0, 128.4, 128.3, 127.9, 126.7, 126.5, 119.2, 118.3, 112.8, 112.5, 66.4, 62.6, 57.0, 54.6, 51.7, 50.0, 45.5, 23.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_4$ [M + H]$^+$ 458.2074; found: 458.2076.



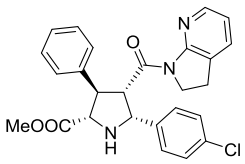
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(2-fluorophenyl)-3-phenylpyrrolidine-2-carboxylate (3ag). White solid; 44.0 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -16.5 (*c* 1.00, CH_2Cl_2); mp 48.7-49.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.93 min, t_{minor} = 11.13 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20-8.11 (m, 1H), 7.79-7.68 (m, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.38-7.25 (m, 4H), 7.24-7.09 (m, 3H), 7.00-6.92 (m, 1H), 6.88-6.77 (m, 1H), 5.51 (t, *J* = 9.5 Hz, 1H), 5.28 (d, *J* = 9.1 Hz, 1H), 4.19-4.00 (m, 2H), 3.75 (s, 1H), 3.71-3.56 (m, 4H), 3.35-3.23 (m, 1H), 2.87-2.73 (m, 1H), 2.72-2.57 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.5, 168.4, 159.4 (*J* = 243.2 Hz, 1C), 155.1, 145.7, 139.9, 133.9, 130.2 (*J* = 3.9 Hz, 1C), 129.2 (*J* = 12.8 Hz, 1C), 128.6 (*J* = 8.4 Hz, 1C), 128.5, 127.9, 126.8, 126.2, 123.7 (*J* = 3.1 Hz, 1C), 118.2, 114.1 (*J* = 46.1 Hz, 1C), 66.3, 56.1, 55.2 (*J* = 3.4 Hz, 1C), 51.7, 49.8, 45.6, 23.3; HRMS (ESI-TOF) calcd. for $C_{26}H_{25}FN_3O_3$ [M + H]$^+$ 446.1874; found: 446.1863.



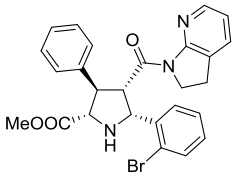
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-fluorophenyl)-3-phenylpyrrolidine-2-carboxylate (3ah). White solid; 44.1 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -27.2 (*c* 1.00, CH_2Cl_2); mp 52.6-53.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.66 min, t_{minor} = 11.21 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.24-8.18 (m, 1H), 7.61-7.53 (m, 1H), 7.35-7.23 (m, 4H), 7.22-7.14 (m, 1H), 7.14-7.05 (m, 2H), 7.03-6.90 (m, 3H), 5.26 (t, *J* = 9.9 Hz, 1H), 5.03 (d, *J* = 9.7 Hz, 1H), 4.13 (t, *J* = 10.2 Hz, 1H), 4.04 (d, *J* = 10.2 Hz, 1H), 3.78-3.51 (m, 5H), 3.27-3.13 (m, 1H), 2.88-2.72 (m, 1H), 2.72-2.57 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.4, 161.2 (*J* = 241.0 Hz, 1C), 154.9, 145.9, 140.1, 138.4, 138.4, 134.1, 129.1 (*J* = 8.0 Hz, 1C), 128.5, 127.9, 126.6 (*J* = 18.7 Hz, 1C), 118.4, 114.0 (*J* = 21.0 Hz, 1C), 66.2, 61.6, 56.9, 51.7, 49.6, 45.4, 23.3; HRMS (ESI-TOF) calcd. for $C_{26}H_{25}FN_3O_3$ [M + H]$^+$ 446.1874; found: 446.1867.



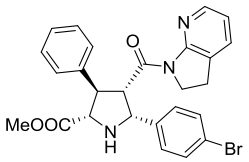
Methyl (2*S*,3*R*,4*S*,5*R*)-5-(2-chlorophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenylpyrrolidine-2-carboxylate (3ai). White solid; 45.2 mg, 98% yield; >20:1 dr, 93% ee; $[\alpha]_D^{20}$ = +27.2 (*c* 1.00, CH_2Cl_2); mp 46.3-47.6 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.65 min, t_{minor} = 10.20 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (d, *J* = 4.6 Hz, 1H), 7.93-7.83 (m, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.38-7.25 (m, 5H), 7.23-7.08 (m, 3H), 6.98-6.90 (m, 1H), 5.75 (t, *J* = 9.4 Hz, 1H), 5.36-5.25 (m, 1H), 4.14 (t, *J* = 9.8 Hz, 1H), 4.08-3.98 (m, 1H), 3.81 (s, 1H), 3.69-3.55 (m, 4H), 3.41-3.26 (m, 1H), 2.86-2.55 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.6, 155.3, 145.6, 139.8, 139.6, 133.9, 131.7, 130.6, 128.5, 128.4, 128.2, 127.8, 126.9, 126.4, 126.3, 118.2, 66.5, 58.8, 54.8, 51.7, 50.3, 45.6, 23.3; HRMS (ESI-TOF) calcd. for $C_{26}H_{25}ClN_3O_3$ [M + H]$^+$ 462.1579; found: 462.1564.



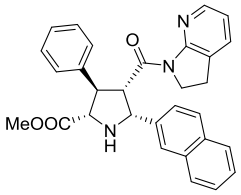
Methyl (2*S*,3*R*,4*S*,5*R*)-5-(4-chlorophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenylpyrrolidine-2-carboxylate (3aj). White solid; 45.6 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -74.9 (*c* 1.00, CH_2Cl_2); mp 138.8-139.4 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.00 min, t_{minor} = 9.50 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.25-8.17 (m, 1H), 7.62-7.54 (m, 1H), 7.33-7.23 (m, 4H), 7.23-7.14 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.01 (m, 1H), 5.27 (t, *J* = 9.8 Hz, 1H), 5.03 (d, *J* = 9.3 Hz, 1H), 4.16-3.98 (m, 2H), 3.73 (s, 1H), 3.68-3.55 (m, 4H), 3.28-3.15 (m, 1H), 2.89-2.74 (m, 1H), 2.74-2.59 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.2, 154.9, 145.8, 141.5, 139.9, 134.2, 131.4, 129.1, 128.5, 127.9, 127.3, 126.8, 126.6, 118.5, 66.2, 61.6, 56.9, 51.7, 49.5, 45.5, 23.3; HRMS (ESI-TOF) calcd. For $C_{26}H_{25}ClN_3O_3$ $[M + H]^+$ 462.1579; found: 462.1586.



Methyl (2*S*,3*R*,4*S*,5*R*)-5-(2-bromophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenylpyrrolidine-2-carboxylate (3ak). White solid; 49.0 mg, 97% yield; >20:1 dr, 93% ee; $[\alpha]_D^{20}$ = +50.6 (*c* 1.00, CH_2Cl_2); mp 49.0-50.4 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.95 min, t_{minor} = 10.29 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (d, *J* = 5.0 Hz, 1H), 7.89-7.80 (m, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.40-7.24 (m, 6H), 7.23-7.15 (m, 1H), 7.12-7.04 (m, 1H), 6.98-6.88 (m, 1H), 5.78 (t, *J* = 9.3 Hz, 1H), 5.27-5.16 (m, 1H), 4.14 (t, *J* = 9.6 Hz, 1H), 4.07-3.96 (m, 1H), 3.90-3.75 (m, 1H), 3.69-3.54 (m, 4H), 3.36-3.28 (m, 1H), 2.84-2.70 (m, 1H), 2.69-2.54 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.4, 168.7, 155.3, 145.7, 141.0, 139.9, 133.8, 131.5, 130.8, 128.8, 128.6, 127.8, 127.0, 126.9, 126.4, 122.4, 118.2, 66.6, 61.7, 54.6, 51.7, 50.5, 45.7, 23.3; HRMS (ESI-TOF) calcd. for $C_{26}H_{25}BrN_3O_3$ $[M + H]^+$ 506.1074; found: 506.1085.

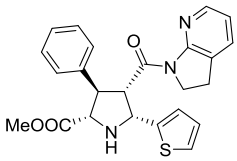


Methyl (2*S*,3*R*,4*S*,5*R*)-5-(4-bromophenyl)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenylpyrrolidine-2-carboxylate (3al). White solid; 50.1 mg, 99% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -103.4 (*c* 1.00, CH_2Cl_2); mp 128.9-130.2 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 10.98 min, t_{minor} = 12.31 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.26-8.14 (m, 1H), 7.64-7.53 (m, 1H), 7.39-7.22 (m, 6H), 7.22-7.11 (m, 1H), 7.09-6.94 (m, 3H), 5.27 (t, *J* = 9.7 Hz, 1H), 5.02 (d, *J* = 9.5 Hz, 1H), 4.18-3.98 (m, 2H), 3.95-3.72 (m, 1H), 3.72-3.54 (m, 4H), 3.30-3.15 (m, 1H), 2.91-2.74 (m, 1H), 2.74-2.56 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.2, 154.9, 145.8, 141.9, 139.9, 134.2, 130.2, 129.4, 128.5, 127.9, 126.8, 126.6, 119.9, 118.5, 66.2, 61.6, 56.8, 51.7, 49.5, 45.5, 23.3; HRMS (ESI-TOF) calcd. for $C_{26}H_{25}BrN_3O_3$ $[M + H]^+$ 506.1074; found: 506.1089.

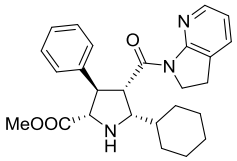


Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(naphthalen-2-yl)-3-phenylpyrrolidine-2-carboxylate (3am). White solid; 46.7 mg, 98% yield; >20:1 dr, 94% ee; $[\alpha]_D^{20}$ = -75.3 (*c* 1.00, CH_2Cl_2); mp 66.5-67.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.16 min, t_{minor} = 9.35 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.29-8.22 (m, 1H), 7.84-7.77 (m, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.62-7.55 (m, 1H), 7.51-7.46 (m,

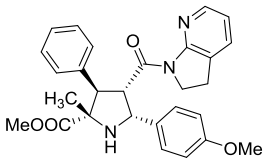
1H), 7.46-7.39 (m, 3H), 7.39-7.25 (m, 5H), 7.24-7.16 (m, 1H), 7.05-6.97 (m, 1H) 5.41 (t, *J* = 9.8 Hz, 1H), 5.15 (d, *J* = 9.6 Hz, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 4.11 (d, *J* = 10.2 Hz, 1H), 3.82 (s, 1H), 3.65 (s, 3H), 3.55-3.42 (m, 1H), 3.04-2.91 (m, 1H), 2.70-2.54 (m, 1H), 2.23-2.07 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 168.7, 155.0, 145.9, 140.3, 139.6, 134.0, 132.3 (2C), 128.5, 128.0, 127.5, 127.4, 126.8, 126.7, 126.5, 125.9, 125.8, 125.7, 125.6, 118.4, 66.4, 62.7, 56.9, 51.7, 49.9, 45.4, 23.2; HRMS (ESI-TOF) calcd. for $C_{30}H_{28}N_3O_3$ [M + H]$^+$ 478.2125; found: 478.2118.



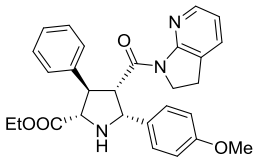
Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenyl-5-(thiophen-2-yl)pyrrolidine-2-carboxylate (3an). White solid; 42.4 mg, 98% yield; >20:1 dr, 96% ee; $[\alpha]_D^{20}$ = -3.4 (*c* 1.00, CH_2Cl_2); mp 46.5-47.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 8.61 min, t_{minor} = 12.29 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, *J* = 4.3 Hz, 1H), 7.64-7.57 (m, 1H), 7.34-7.22 (m, 5H), 7.21-7.13 (m, 1H), 7.05-6.96 (m, 1H), 6.83-6.76 (m, 1H), 6.47 (d, *J* = 3.1 Hz, 1H), 5.34 (d, *J* = 8.8 Hz, 1H), 5.17 (t, *J* = 10.0 Hz, 1H), 4.12 (t, *J* = 10.5 Hz, 1H), 4.01 (d, *J* = 10.2 Hz, 1H), 3.93 (s, 1H), 3.78-3.64 (m, 1H), 3.59 (s, 3H), 3.46-3.37 (m, 1H), 2.95-2.70 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 167.8, 155.1, 147.5, 145.9, 139.9, 134.2, 128.4, 128.1, 126.7, 126.6, 126.3, 124.6, 123.2, 118.4, 65.8, 57.6, 57.2, 51.7, 49.1, 45.6, 23.4; HRMS (ESI-TOF) calcd. for $C_{24}H_{24}N_3O_3S$ [M + H]$^+$ 434.1533; found: 434.1528.



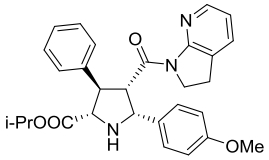
Methyl (2*S*,3*R*,4*S*,5*S*)-5-cyclohexyl-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-3-phenylpyrrolidine-2-carboxylate (3ao). White solid; 12.6 mg, 29% yield; >20:1 dr, 93% ee; $[\alpha]_D^{20}$ = +7.8 (*c* 1.00, CH_2Cl_2); mp 116.9-117.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.38 min, t_{minor} = 7.48 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.96 (d, *J* = 4.9 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.30-7.20 (m, 4H), 7.20-7.09 (m, 1H), 6.95-6.86 (m, 1H), 5.23-5.13 (m, 1H), 4.03-3.81 (m, 2H), 3.80-3.63 (m, 2H), 3.57 (s, 3H), 3.47 (t, *J* = 7.4 Hz, 1H), 3.14 (s, 1H), 2.95 (t, *J* = 8.4 Hz, 2H), 2.04-1.89 (m, 1H), 1.72-1.59 (m, 1H), 1.56-1.43 (m, 2H), 1.36 (d, *J* = 8.8 Hz, 2H), 1.18-0.82 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 171.5, 155.1, 145.6, 141.7, 134.1, 128.3, 127.6, 126.6, 126.5, 118.3, 67.6, 66.6, 53.9, 53.7, 51.6, 45.7, 39.4, 31.0, 29.5, 26.0, 25.8, 25.7, 23.4; HRMS (ESI-TOF) calcd. for $C_{26}H_{31}N_3O_3$ [M + H]$^+$ 434.2438; found: 434.2429.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-2-methyl-3,5-diphenylpyrrolidine-2-carboxylate (3ap). White solid; 14.1 mg, 30% yield; >20:1 dr, 90% ee; $[\alpha]_D^{20}$ = -31.8 (*c* 1.00, CH_2Cl_2); mp 50.2-51.5 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 5.86 min, t_{minor} = 7.57 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.30 (d, *J* = 4.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.32-7.24 (m, 2H), 7.24-7.15 (m, 3H), 7.04 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.76-5.65 (m, 1H), 4.95 (d, *J* = 9.9 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.64-3.52 (m, 1H), 3.35 (s, 1H), 3.19-3.06 (m, 1H), 2.89-2.73 (m, 1H), 2.73-2.56 (m, 1H), 1.12 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) δ 175.2, 168.8, 158.3, 155.2, 146.0, 138.1, 134.2, 134.1, 128.3, 128.2, 126.7, 126.6, 118.3, 112.8, 67.5, 59.8, 55.0, 52.4, 52.1, 52.0, 45.4, 23.4, 20.3; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_4$ [M + H]$^+$ 472.2236; found: 472.2234.



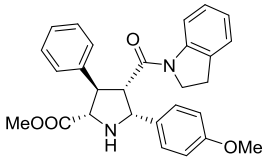
Ethyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (3aq). White solid; 46.1 mg, 98% yield; >20:1 dr, 94% ee; $[\alpha]_D^{20}$ = -31.6 (*c* 1.00, CH_2Cl_2); mp 39.4-41.2 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 9.88 min, t_{minor} = 15.41 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20 (d, *J* = 4.7 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.36-7.24 (m, 4H), 7.23-7.15 (m, 1H), 7.03-6.91 (m, 3H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.26 (t, *J* = 9.8 Hz, 1H), 4.95 (d, *J* = 9.5 Hz, 1H), 4.18-3.94 (m, 4H), 3.73-3.53 (m, 5H), 3.28-3.13 (m, 1H), 2.85-2.69 (m, 1H), 2.67-2.51 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 168.8, 158.2, 155.0, 145.7, 140.4, 134.0, 133.7, 128.4, 128.2, 128.0, 126.6, 126.5, 118.3, 112.7, 66.5, 62.2, 60.2, 57.1, 55.0, 50.4, 45.5, 23.3, 14.0; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}N_3O_4$ $[M + H]^+$ 472.2231; found: 472.2235.



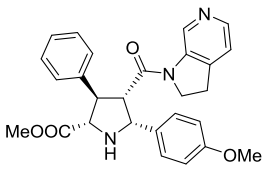
Isopropyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (3ar). White solid; 48.0 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -12.2 (*c* 1.00, CH_2Cl_2); mp 39.9-40.7 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.67 min, t_{minor} = 11.86 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20 (d, *J* = 4.6 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.36-7.24 (m, 4H), 7.22-7.14 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 3H), 6.69 (d, *J* = 8.2 Hz, 2H), 5.26 (t, *J* = 9.8 Hz, 1H), 5.00-4.84 (m, 2H), 4.05 (t, *J* = 10.2 Hz, 1H), 3.92 (d, *J* = 10.3 Hz, 1H), 3.76-3.51 (m, 5H), 3.27-3.12 (m, 1H), 2.84-2.68 (m, 1H), 2.66-2.52 (m, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.02 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.5, 168.9, 158.3, 155.0, 145.8, 140.4, 134.0, 133.8, 128.4, 128.2, 128.1, 126.7, 126.6, 118.4, 112.8, 67.7, 66.8, 62.4, 57.3, 55.0, 50.9, 45.5, 23.4, 21.5 (2C); HRMS (ESI-TOF) calcd. for $C_{29}H_{32}N_3O_4$ $[M + H]^+$ 486.2387; found: 486.2387.

3. General procedure for the synthesis of compounds 4′-6′.

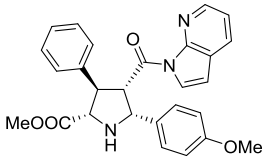
Under Ar atmosphere, AgOAc (1.7 mg, 0.01 mmol) and ligand **B** (7.3 mg, 0.012 mmol) were dissolved in toluene (2.0 mL) in a flame dried glass tube, and stirred at room temperature for 30 min. Then, imino ester **2a** (0.15 mmol) and Cs_2CO_3 (3.25 mg, 0.01mmol) were added, the mixture was further stirred at 0 ℃ for 15 min before the addition of corresponding *α,β*-unsaturated amides (0.10 mmol). Once starting material (*α,β*-unsaturated amides) was consumed (monitored by TLC), the mixture was concentrated and the residue was purified by column chromatography (petroleum ether/ethyl acetate 8:1 to 1:1) on silica gel to afford the corresponding product **4-6**.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(indoline-1-carbonyl)-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (4'). White solid; 34.1 mg, 75% yield; >20:1 dr, 67% ee; $[\alpha]_D^{20}$ = -37.2 (*c* 1.00, CH_2Cl_2); mp 45.1-46.9 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.50 min, t_{minor} = 7.48 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.47-7.25 (m, 6H), 7.25-7.15 (m, 1H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92-6.82 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 4.91 (d, *J* = 8.7 Hz, 1H), 4.12-3.92 (m, 4H), 3.87 (t, *J* = 8.6 Hz, 1H), 3.77-3.52 (m, 7H), 3.07-2.77 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 168.5, 158.3, 142.5, 140.4, 133.1, 131.6, 128.7, 128.5, 128.0, 126.8, 126.7, 124.5, 123.2, 116.1, 113.0, 66.7, 62.5, 57.1, 54.9, 51.8, 51.4, 47.5, 27.2; HRMS (ESI-TOF) calcd. for $C_{28}H_{29}N_2O_4$ $[M + H]^+$ 457.2122; found: 457.2130.



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*c*]pyridine-1-carbonyl)-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (5'). White solid; 36.9 mg, 81% yield; >20:1 dr, 37% ee; $[\alpha]_D^{20}$ = -32.2 (*c* 1.00, CH_2Cl_2); mp 38.3-40.1 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 7.72 min, t_{minor} = 17.28 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.81 (s, 1H), 8.09 (d, *J* = 4.5 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.36-7.26 (m, 4H), 7.25-7.14 (m, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 4.92 (d, *J* = 8.7 Hz, 1H), 4.10-3.92 (m, 4H), 3.88 (t, *J* = 8.7 Hz, 1H), 3.70-3.56 (m, 7H), 3.13-2.83 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 168.9, 158.3, 144.1, 141.0, 140.3, 139.9, 136.6, 132.9, 128.6, 128.5, 128.0, 126.8, 120.2, 113.0, 66.8, 62.5, 56.9, 54.9, 51.8, 51.2, 46.9, 27.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{28}N_3O_4$ $[M + H]^+$ 458.2074; found: 458.2071.



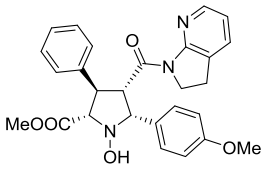
Methyl (2*S*,3*R*,4*S*,5*R*)-5-(4-methoxyphenyl)-3-phenyl-4-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)pyrrolidine-2-carboxylate (6'). White solid; 44.5 mg, 98% yield; >20:1 dr, 27% ee; $[\alpha]_D^{20}$ = -35.8 (*c* 1.00, CH_2Cl_2); mp 154.1-155.3 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 4.98 min, t_{minor} = 5.99 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.55-8.49 (m, 1H), 8.07-7.99 (m, 1H), 7.50 (d, *J* = 4.1 Hz, 1H), 7.43-7.25 (m, 5H), 7.23-7.15 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.63-6.52 (m, 3H), 5.77-5.63 (m, 1H), 5.22 (d, *J* = 9.6 Hz, 1H), 4.26-4.08 (m, 2H), 3.78 (s, 1H), 3.63 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 168.5, 158.2, 146.6, 144.0, 139.4, 133.3, 130.1, 128.6, 128.0, 127.9, 127.0, 125.2, 123.5, 119.2, 112.9, 106.2, 66.1, 62.2, 58.4, 54.9, 51.8, 50.0; HRMS (ESI-TOF) calcd. for $C_{27}H_{26}N_3O_4$ $[M + H]^+$ 456.1918; found: 456.1907.

4. Procedure for the scale-up experiment.

Under Ar atmosphere, AgOAc (41.7 mg, 0.25 mmol) and ligand **B** (183.5 mg, 0.30 mmol) were dissolved in toluene (50.0 mL) in a flame dried glass tube, and stirred at room temperature for 30 min. Then, azomethine ylide **2a** (3.75 mmol, 1.5 equiv) and Cs_2CO_3 (0.25 mmol, 0.1 equiv) were added, the mixture was further stirred at 0 ℃ for 15 min before the addition of *α,β*-unsaturated amide **1a** (2.50 mmol, 1.0 equiv). Once starting material **1a** was consumed (monitored by TLC), the mixture was concentrated and the residue was purified by column chromatography (petroleum ether/ethyl acetate 6:1 to 3:1) on silica gel to afford the corresponding product **3aa** as a white solid; 1121 mg, 98% yield, >20:1 dr and 95% ee.

5. Synthesis of products 10-12.

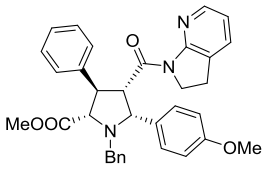
The compound **10** was synthesized according to the literature procedures.[1,2] The solution of compound **3aa** (45.6 mg, 0.1 mmol) in dichloromethane (2 mL) was stirred at 0 ^{o}C in a sealed tube. Subsequently, *m*-CPBA (19.0 mg, 0.11 mmol) was added to the above solution. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of Na_2CO_3 aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate 8:1 to 5:1) to obtain compound **10** (white solid, 37.5 mg, 79 % yield).



Methyl (2*S*,3*R*,4*S*,5*R*)-4-(2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)-1-hydroxy-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2-carboxylate (10). White solid; 37.5 mg, 79% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = -13.7 (*c* 1.00, CH_2Cl_2); mp 48.5-49.8 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 4.78 min, t_{minor} = 10.06 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (s, 1H), 8.18 (d, *J* = 4.4 Hz, 1H), 7.50-7.42 (m, 1H), 7.38-7.27 (m, 4H), 7.27-7.17 (m, 1H), 7.00-6.91 (m, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 5.48-5.30 (m, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 4.38-4.27 (m, 1H), 3.90 (d, *J* = 11.5 Hz, 1H), 3.65 (s, 3H), 3.63-3.48 (m, 4H), 3.24-3.09 (m, 1H), 2.77-2.59 (m, 1H), 2.40-2.22 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.6, 168.6, 158.5, 154.8, 145.5, 139.6, 133.8, 131.0, 129.5, 128.7, 127.8, 127.1, 126.5, 118.4, 112.4, 74.9, 72.3, 55.1, 52.5, 51.7, 45.6, 45.0, 23.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{27}N_3NaO_5$ $[M + Na]^+$ 496.1843; found: 496.1851.

Synthesis of products 11

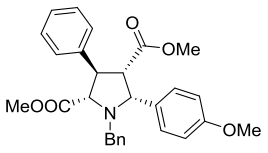
The solution of compound **3aa** (45.7 mg, 0.1 mmol) in THF (2 mL) was stirred at room temperature in a reaction tube. Subsequently, K_2CO_3 (0.2 mmol, 2.0 equiv) and BnBr (0.2 mmol, 2.0 equiv) were added, and then stirred at room temperature for 12 h. After the **3aa** was consumed completely, remove the solvent under reduced pressure. The corresponding derivative **11** were obtained by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) as a white solid (54.5 mg, 99% yield).



Methyl (2*S*,3*R*,4*S*,5*R*)-1-benzyl-5-(4-methoxyphenyl)-3-phenyl-4-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carbonyl)pyrrolidine-2-carboxylate (11). White solid; 54.5 mg, 99% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = +16.3 (*c* 1.00, CH_2Cl_2); mp 58.1-59.6 ℃; The ee was determined by HPLC (Chiralpak IC-H, EtOH/hexane = 50/50, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 6.18 min, t_{minor} = 31.23 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, *J* = 4.6 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.31-7.11 (m, 10H), 7.05-6.93 (m, 3H), 6.70 (d, *J* = 8.6 Hz, 2H), 5.18 (t, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.5 Hz, 1H), 4.34 (t, *J* = 10.7 Hz, 1H), 3.79-3.50 (m, 7H), 3.22 (s, 3H), 3.17-3.05 (m, 1H), 2.81-2.65 (m, 1H), 2.56-2.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 168.2, 158.5, 154.9, 145.7, 139.3, 136.6, 134.0, 132.0, 129.2, 128.5, 127.8, 127.0, 126.9, 126.6, 118.4, 112.7, 71.3, 67.5, 55.9, 55.0, 54.5, 51.3, 49.0, 45.5, 23.4; HRMS (ESI-TOF) calcd. for $C_{34}H_{34}N_3O_4$ $[M + H]^+$ 548.2544; found: 548.2543.

Synthesis of products 12

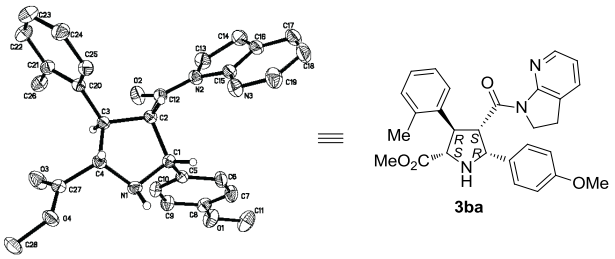
The compound **12** was synthesized according to the literature procedures.[3] The solution of compound **11** (54.7 mg, 0.1 mmol) was dissolved in 2 M HCl/MeOH (2 mL) at 90 ^{o}C for 48 hours in a sealed tube. After cooled down to room temperature, the reaction mixture was neutralized by Na_2CO_3 aq., and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 10:1 to 8:1) to afford the desired product **12** as a white solid (34.2 mg, 74% yield).



Dimethyl (2*S*,3*R*,4*S*,5*R*)-1-benzyl-5-(4-methoxyphenyl)-3-phenylpyrrolidine-2,4-dicarboxylate (12). White solid; 34.2 mg, 74% yield; >20:1 dr, 95% ee; $[\alpha]_D^{20}$ = +33.1 (*c* 1.00, CH_2Cl_2); mp 113.0-114.3 ℃; The ee was determined by HPLC (Chiralpak IC-H,

i-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: t_{major} = 21.25 min, t_{minor} = 26.86 min); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.30-7.12 (m, 10H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.43 (d, *J* = 10.4 Hz, 1H), 3.92 (t, *J* = 10.6 Hz, 1H), 3.82 (d, *J* = 13.9 Hz, 1H), 3.74 (s, 3H), 3.71-3.61 (m, 2H), 3.58 (d, *J* = 10.3 Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 170.7, 158.6, 138.2, 136.8, 132.0, 129.3, 129.1, 128.6, 127.8 (2C), 127.3, 127.0, 113.2, 72.0, 68.1, 56.5, 55.0, 54.7, 51.3, 51.1, 49.8; HRMS (ESI-TOF) calcd. for $C_{28}H_{30}NO_5$ $[M + H]^+$ 460.2118; found: 460.2114.

6. X-ray crystal data for compound 3ba.



Crystal data and structure refinement for **3ba (**CCDC 1894102**)**

Identification code	**3ba**
Empirical formula	$C_{28}H_{29}N_3O_4$
Formula weight	471.54
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.8070(3)
b/Å	15.9924(5)
c/Å	10.5193(4)
α/°	90
β/°	109.003(4)
γ/°	90
Volume/Å^3	1241.80(8)
Z	2
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	0.688
F(000)	500.0
Crystal size/mm^3	0.16 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.89 to 141.788
Index ranges	$-9 \le h \le 9$, $-19 \le k \le 19$, $-9 \le l \le 12$
Reflections collected	12385
Independent reflections	4763 [R_{int} = 0.0288, R_{sigma} = 0.0337]
Data/restraints/parameters	4763/1/324
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1007

Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.1060
Largest diff. peak/hole / e Å^{-3}	0.13/-0.14
Flack parameter	-0.20(12)

Reference

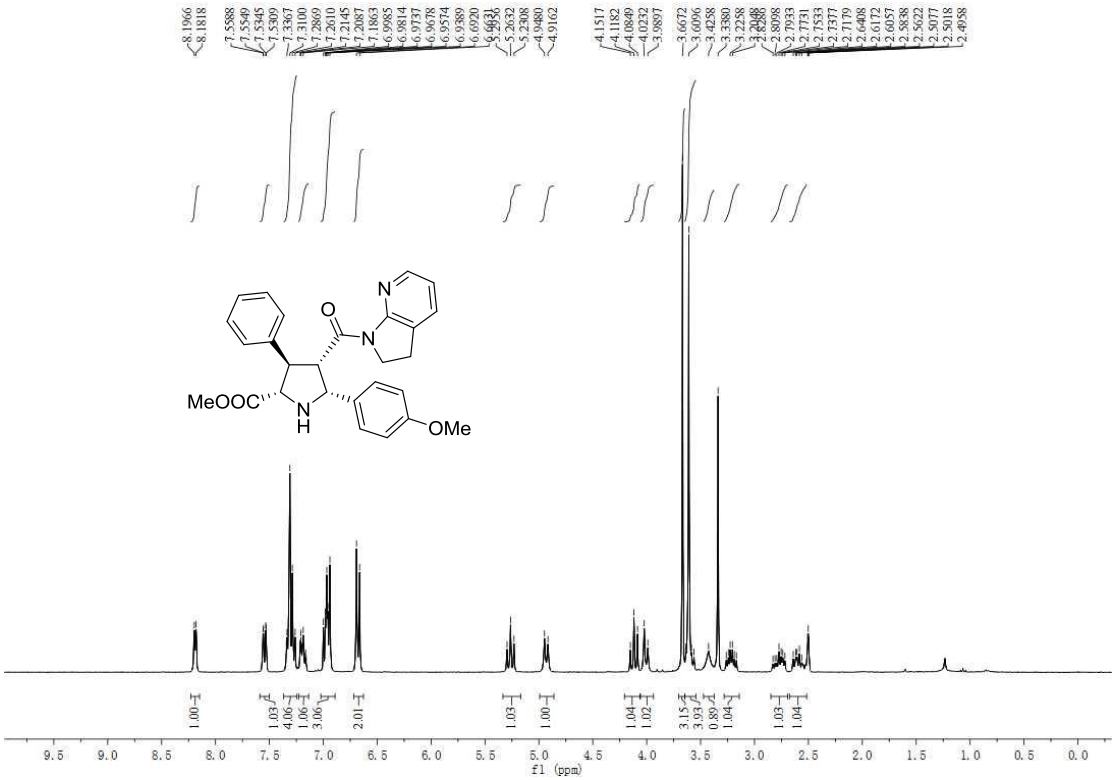
[1] S. Xu, Z.-M. Zhang, B. Xu, B. Liu, Y.-Y. Liu, and J.-L. Zhang, *J. Am. Chem. Soc*., 2018, **140**, 2272.

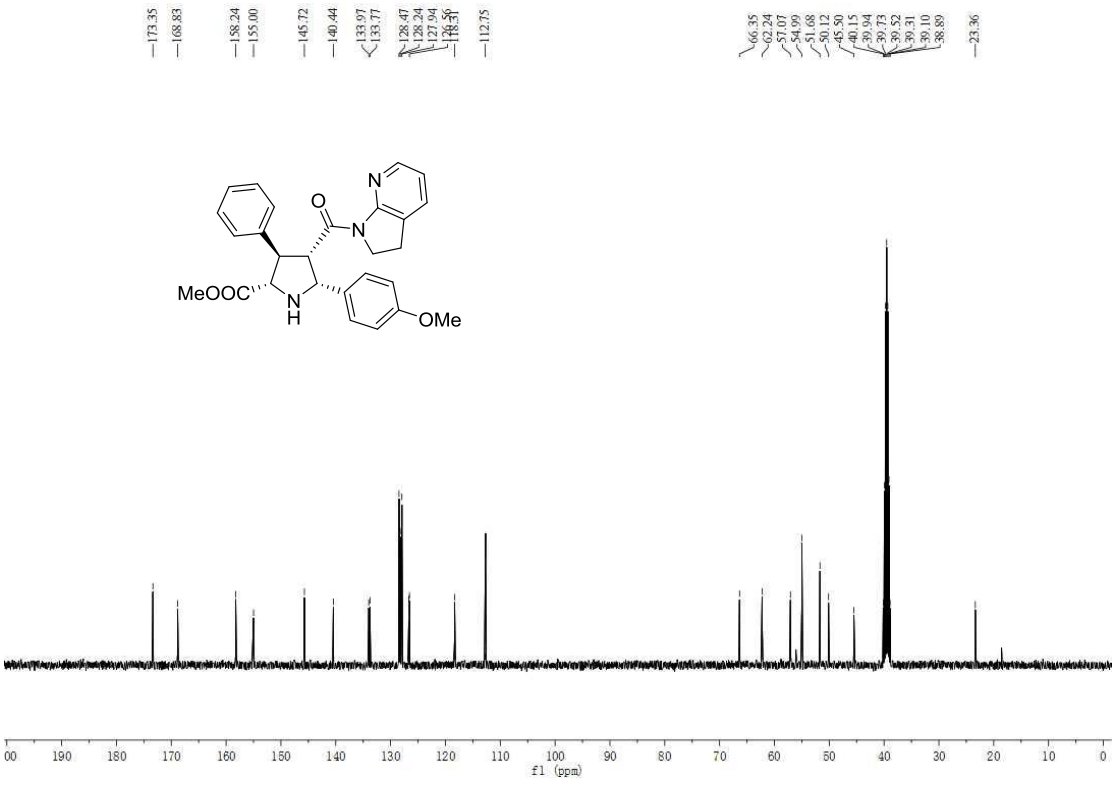
[2] Y. Yuan, Z.-J. Zheng, F. Ye, J.-H. Ma, Z. Xu, X.-F. Bai, L. Li, and L.-W. Xu, *Org. Chem. Front.*, 2018, **5**, 2759.

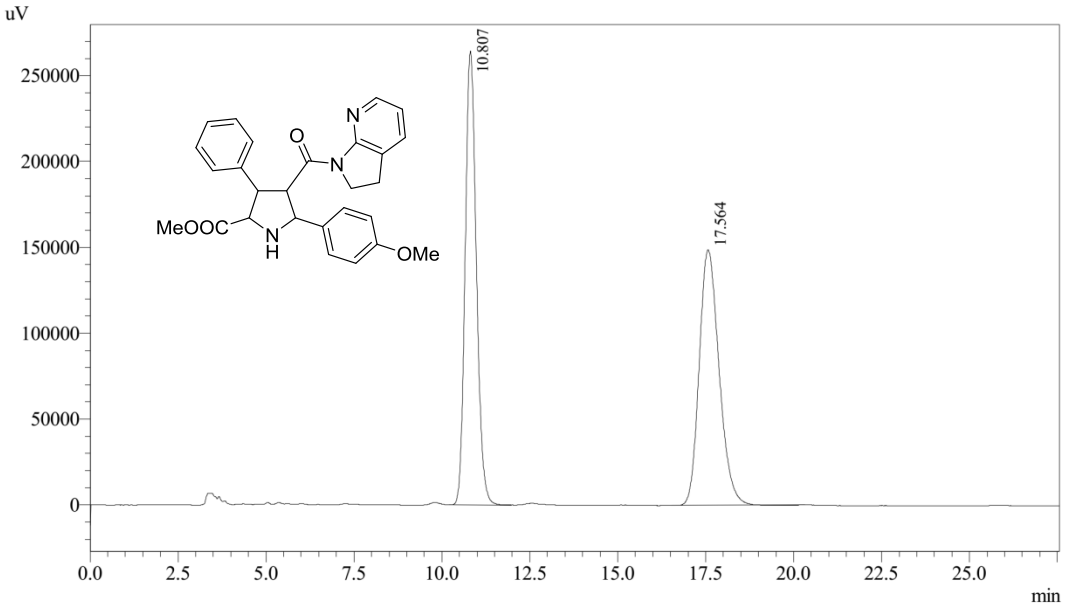
[3] (a) Z. Sun, K. Weidner, N. Kumagai and M. Shibasaki, *Chem. Eur. J*., 2015, **21**, 17574; (b) Z. Liu, T. Takeuchi, R. Pluta, F. A. Arteaga, N. Kumagai and M. Shibasaki, *Org. Lett*., 2017, **19**, 710; (c) M. Zhang, N. Kumagai and M. Shibasaki, *Chem. Eur. J*., 2017, **23**, 12450; (d) B. Sun, P. V. Balaji, N. Kumagai, and M. Shibasaki, *J. Am. Chem. Soc*., 2017, **139**, 8295; (e) B. Sun, R. Pluta, N. Kumagai, and M. Shibasaki, *Org. Lett.*, 2018, **20**, 526; (f) Z. Sun, B. Sun, N. Kumagai, and M. Shibasaki, *Org. Lett*., 2018, **20**, 3070.

7. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3, 4'-6' and 10-12.

^{1}H NMR, ^{13}C NMR and HPLC of 3aa



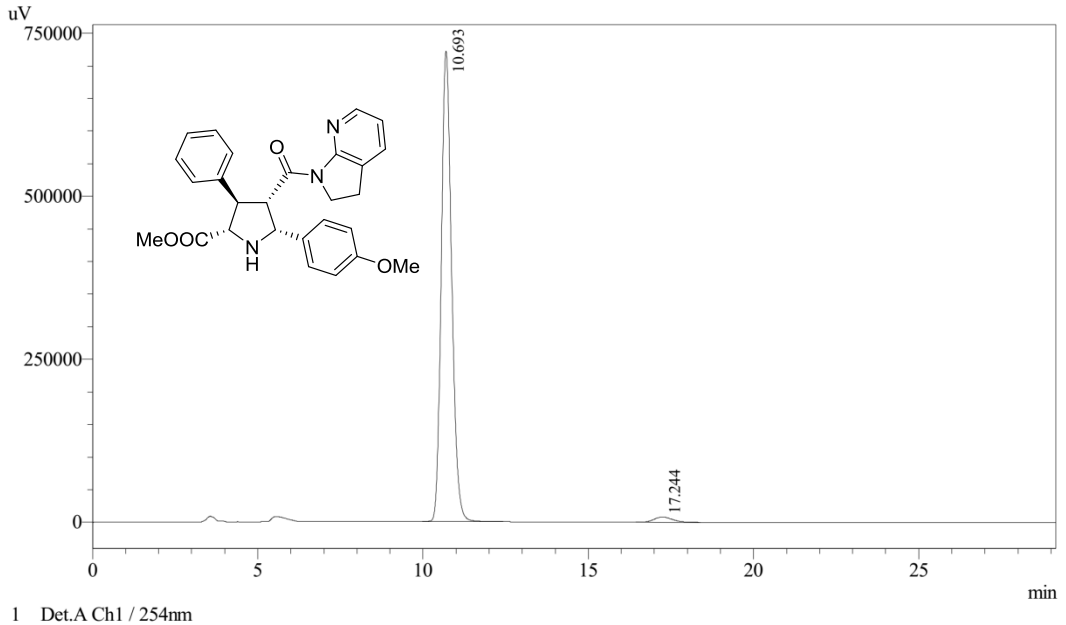




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.807	5857824	264278	50.062	63.967
2	17.564	5843420	148866	49.938	36.033
Total		11701244	413144	100.000	100.000

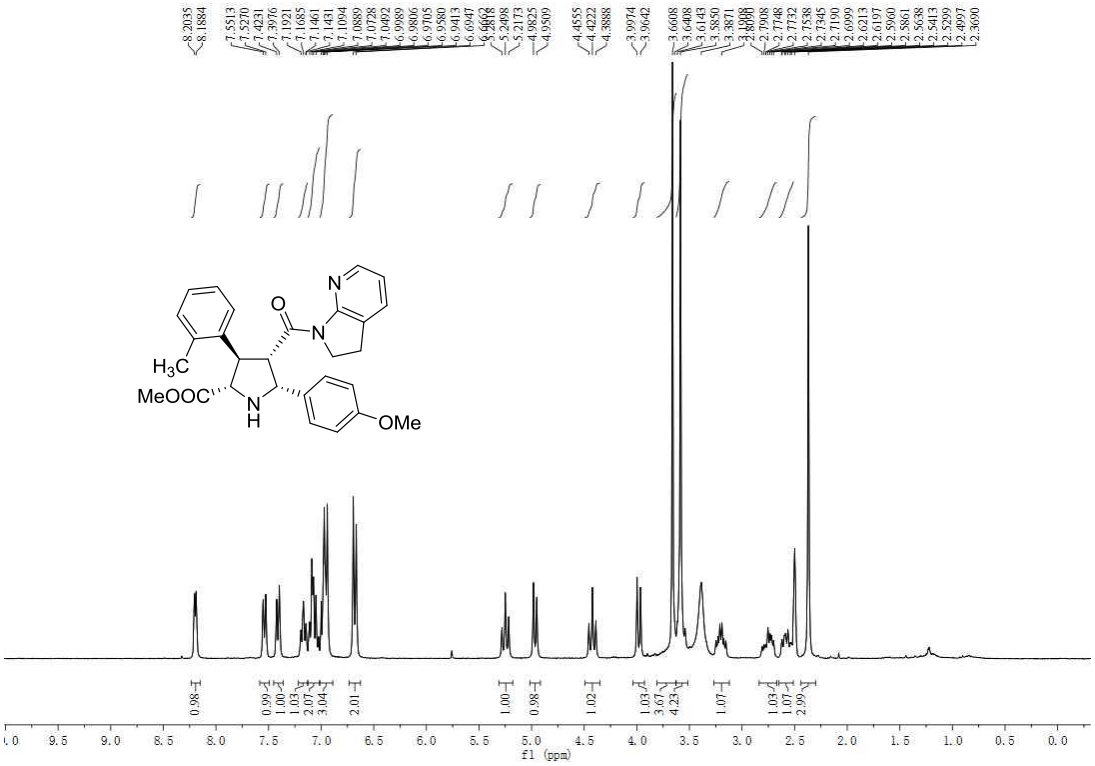


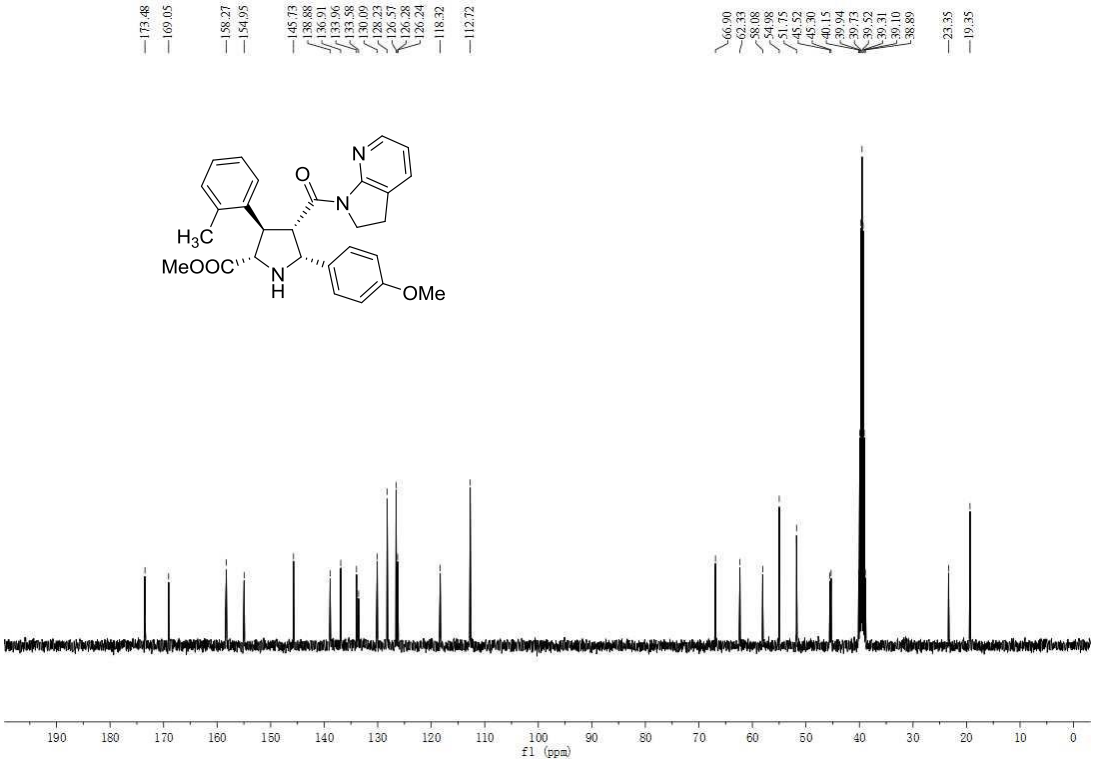
1 Det.A Ch1 / 254nm

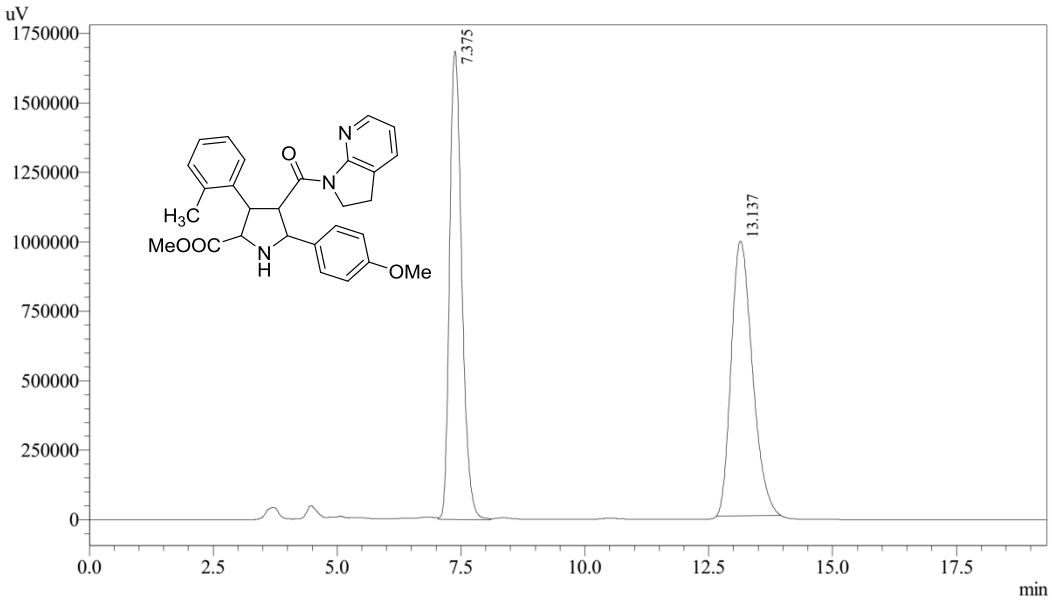
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.693	15813777	721512	98.034	98.883
2	17.244	317065	8150	1.966	1.117
Total		16130842	729662	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ba



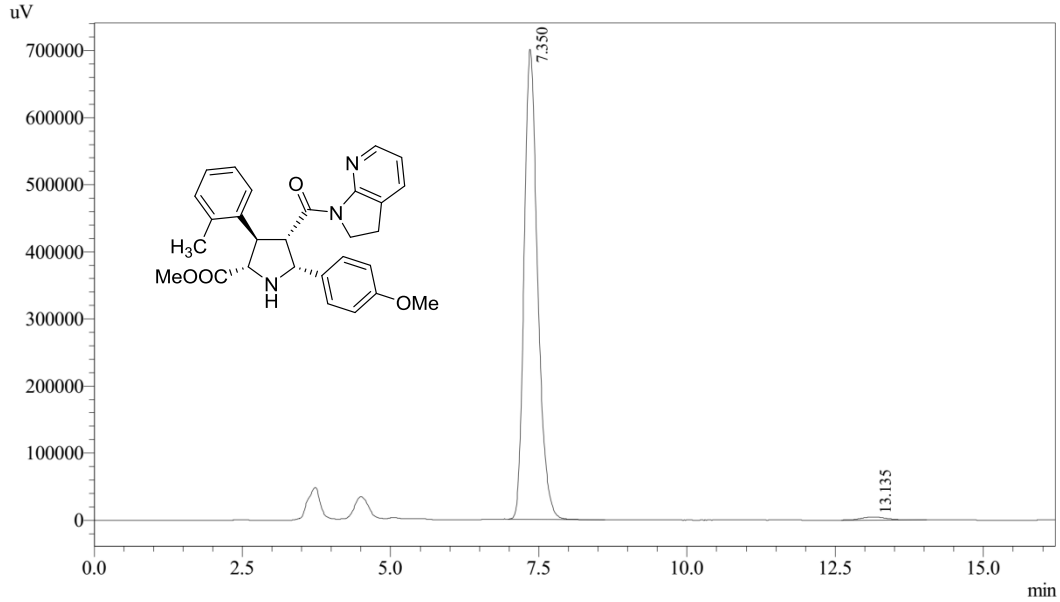




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.375	28948191	1685660	49.526	63.038
2	13.137	29501731	988391	50.474	36.962
Total		58449922	2674051	100.000	100.000

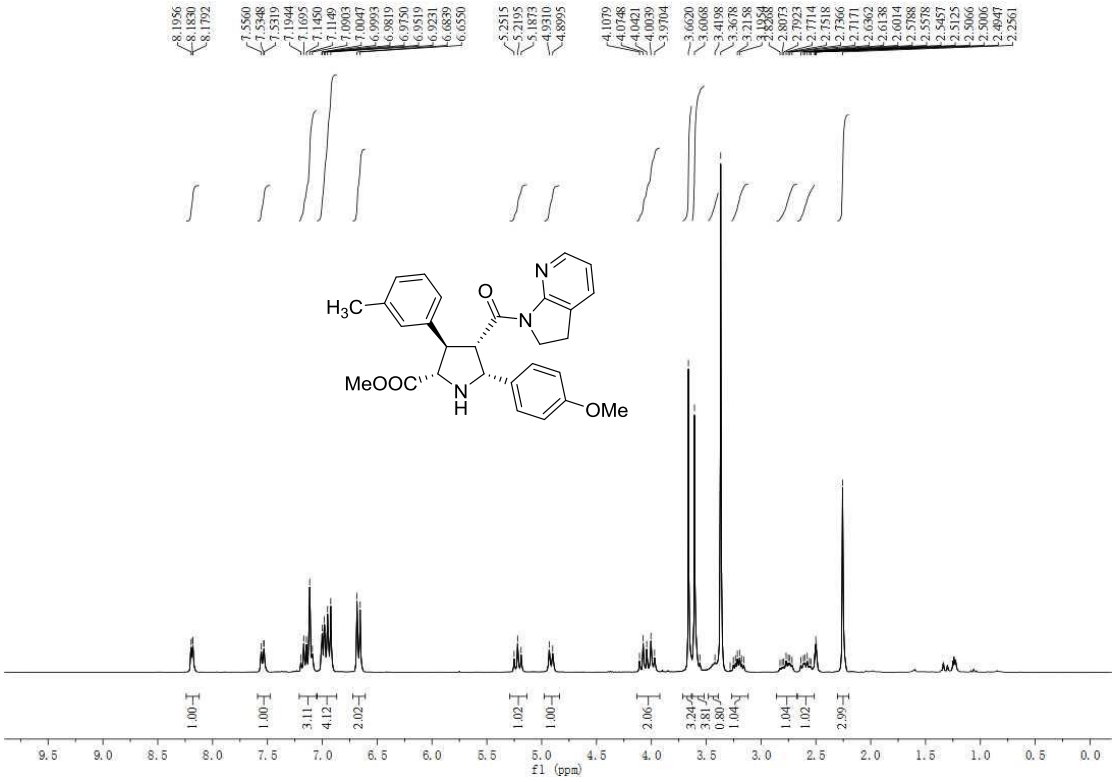


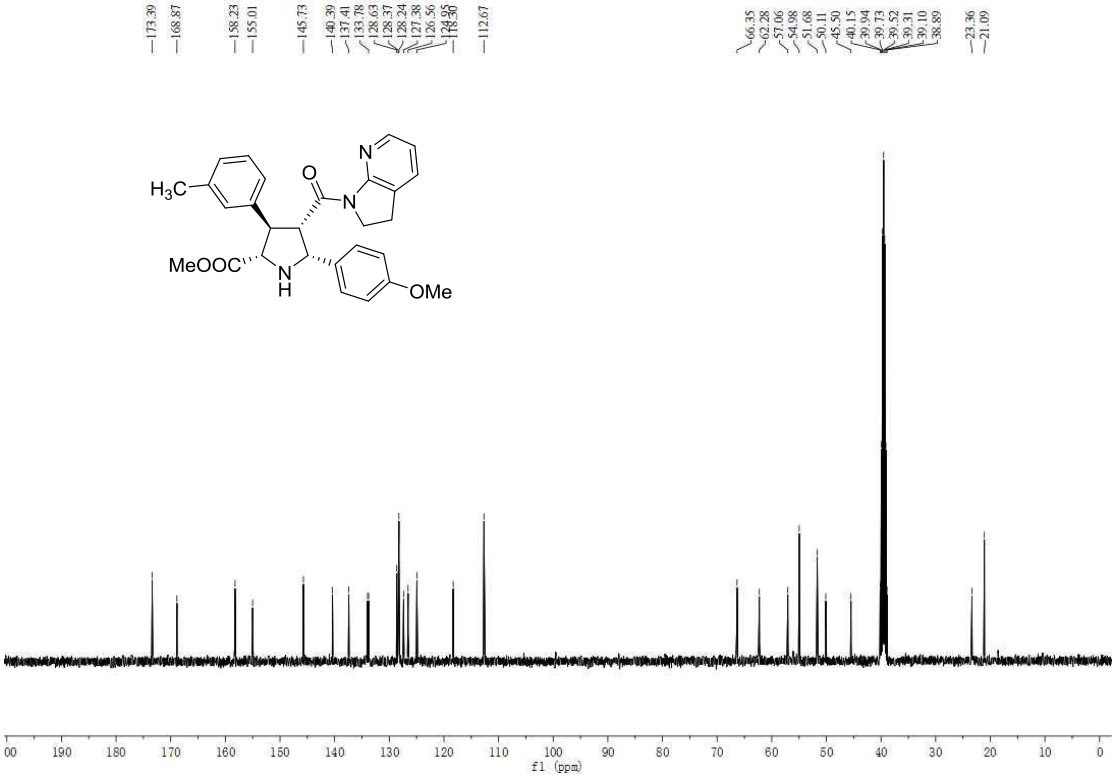
1 Det.A Ch1 / 254nm

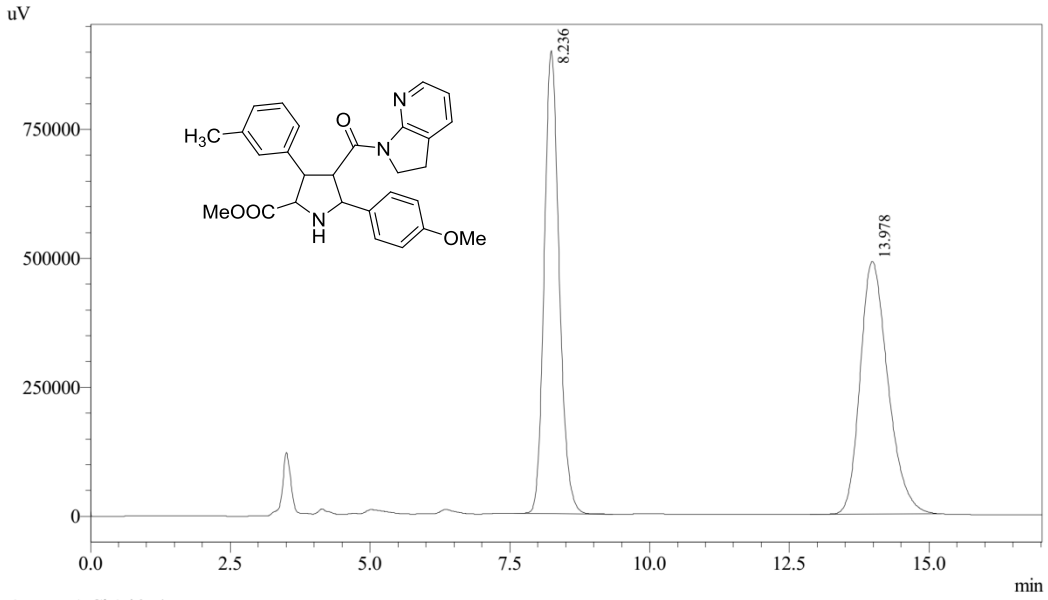
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.350	11096278	700318	98.751	99.337
2	13.135	140387	4673	1.249	0.663
Total		11236665	704991	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ca



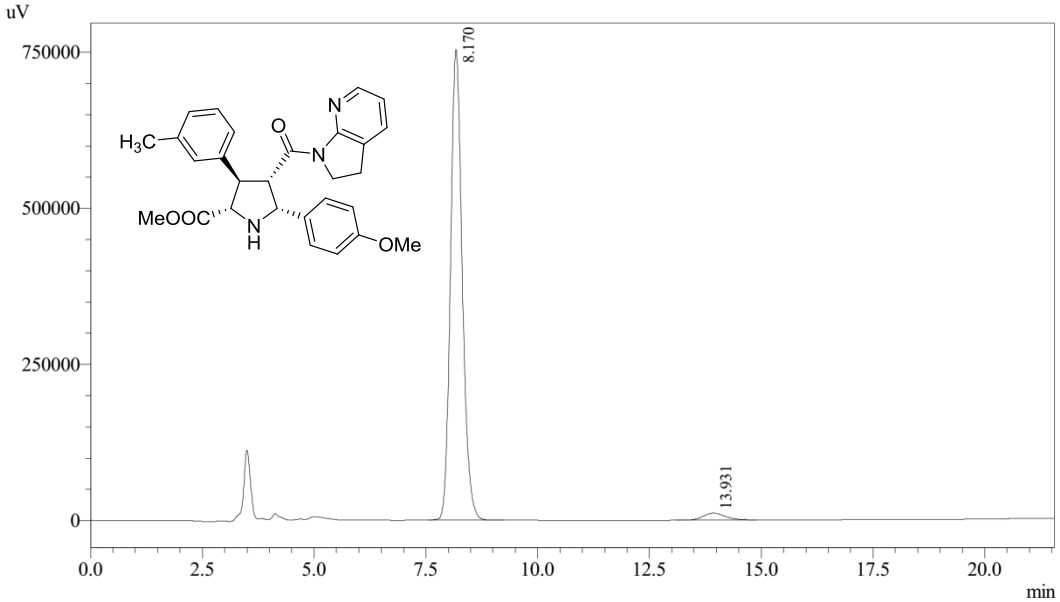




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.236	16739348	898033	49.601	64.711
2	13.978	17008750	489730	50.399	35.289
Total		33748098	1387763	100.000	100.000

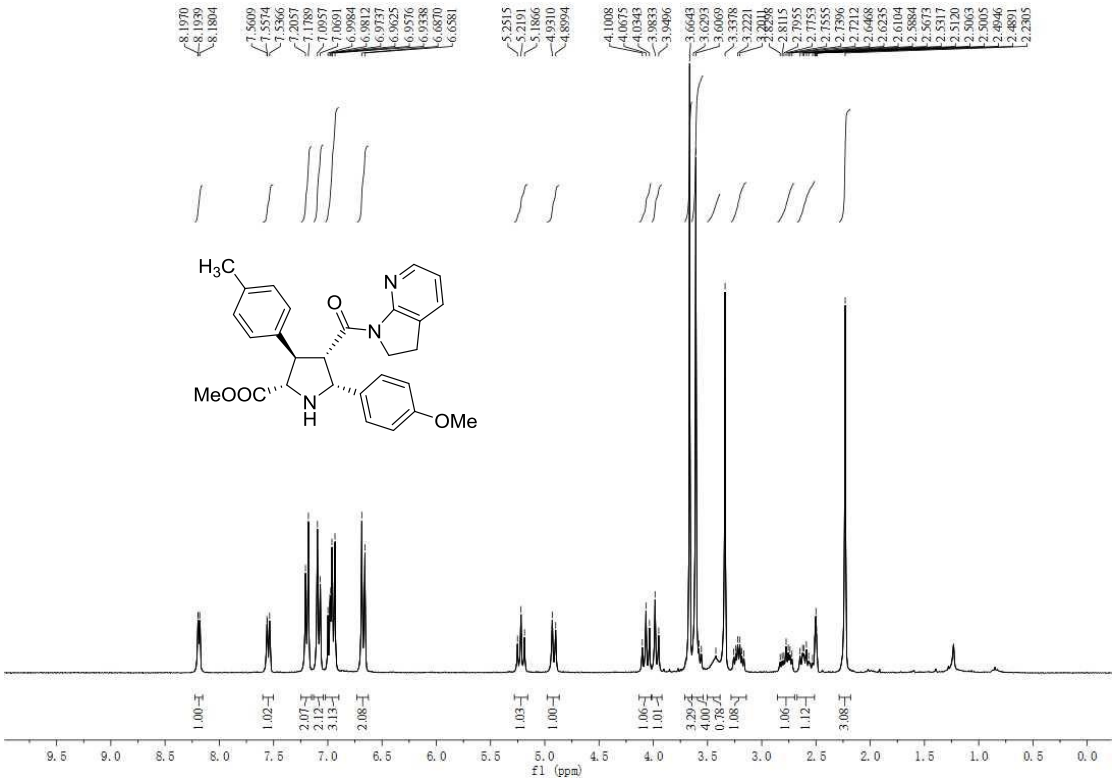


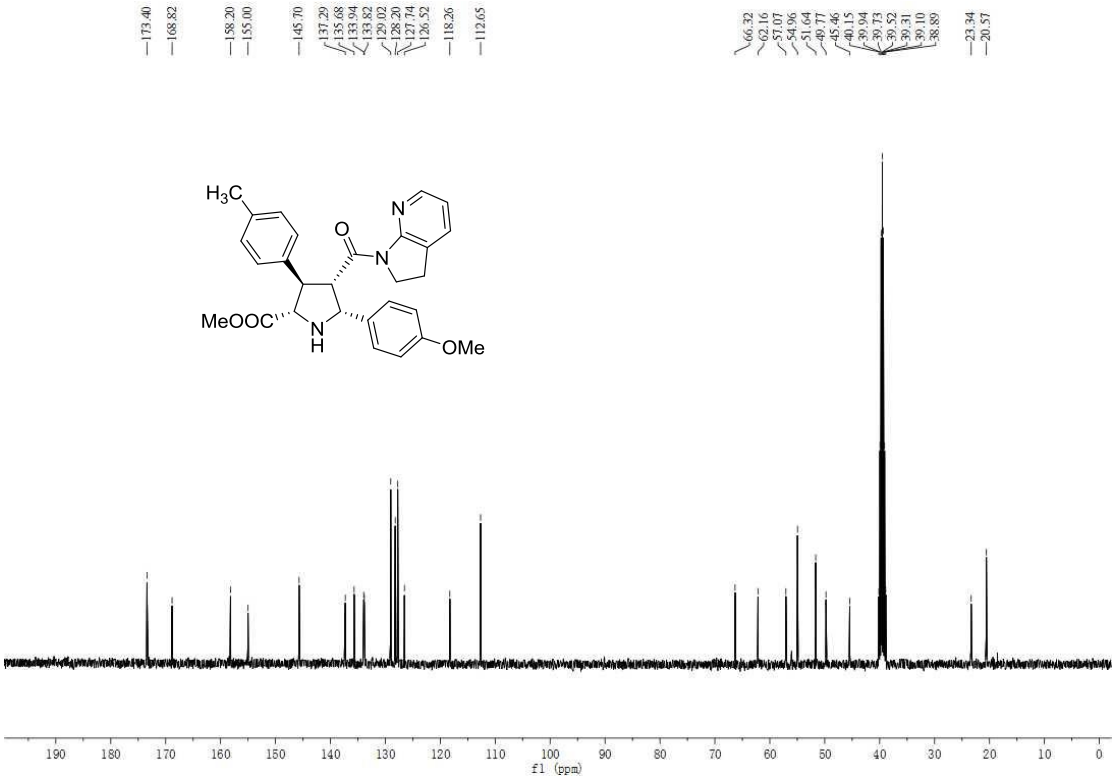
1 Det.A Ch1 / 254nm

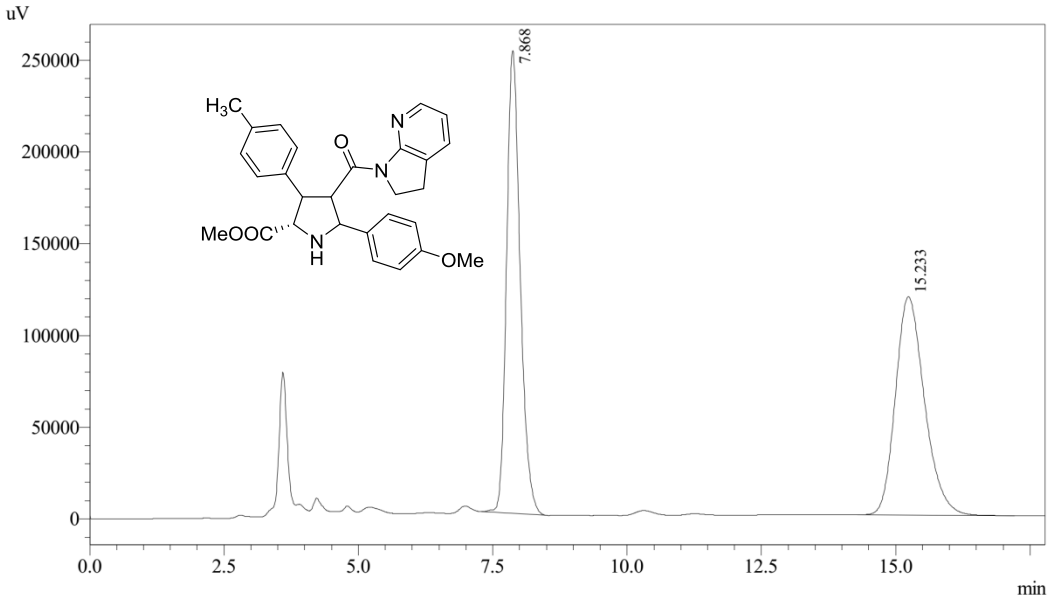
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.170	13780566	753549	97.312	98.548
2	13.931	380676	11099	2.688	1.452
Total		14161242	764648	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3da



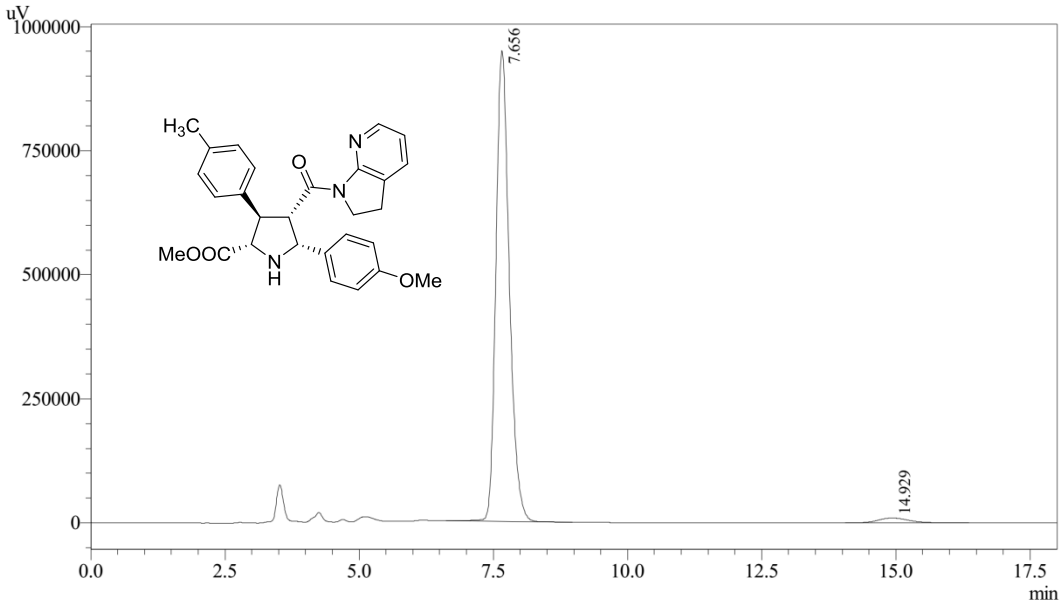




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.868	4464634	252257	49.926	67.961
2	15.233	4477886	118922	50.074	32.039
Total		8942520	371179	100.000	100.000

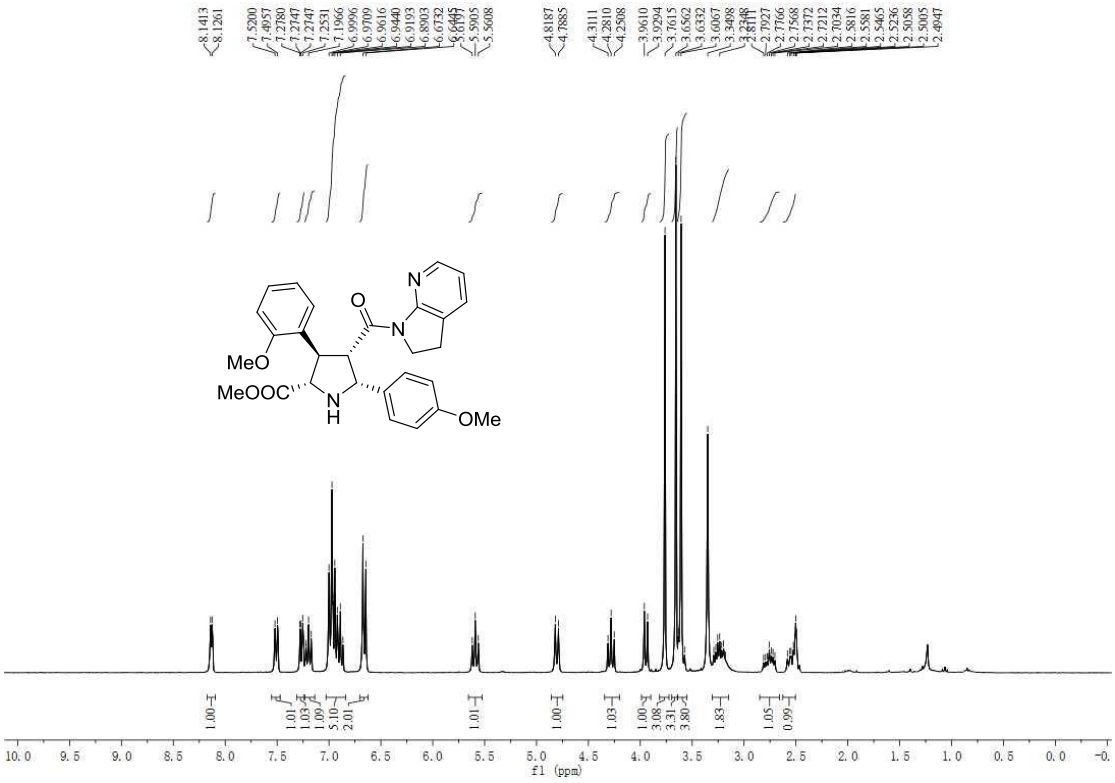


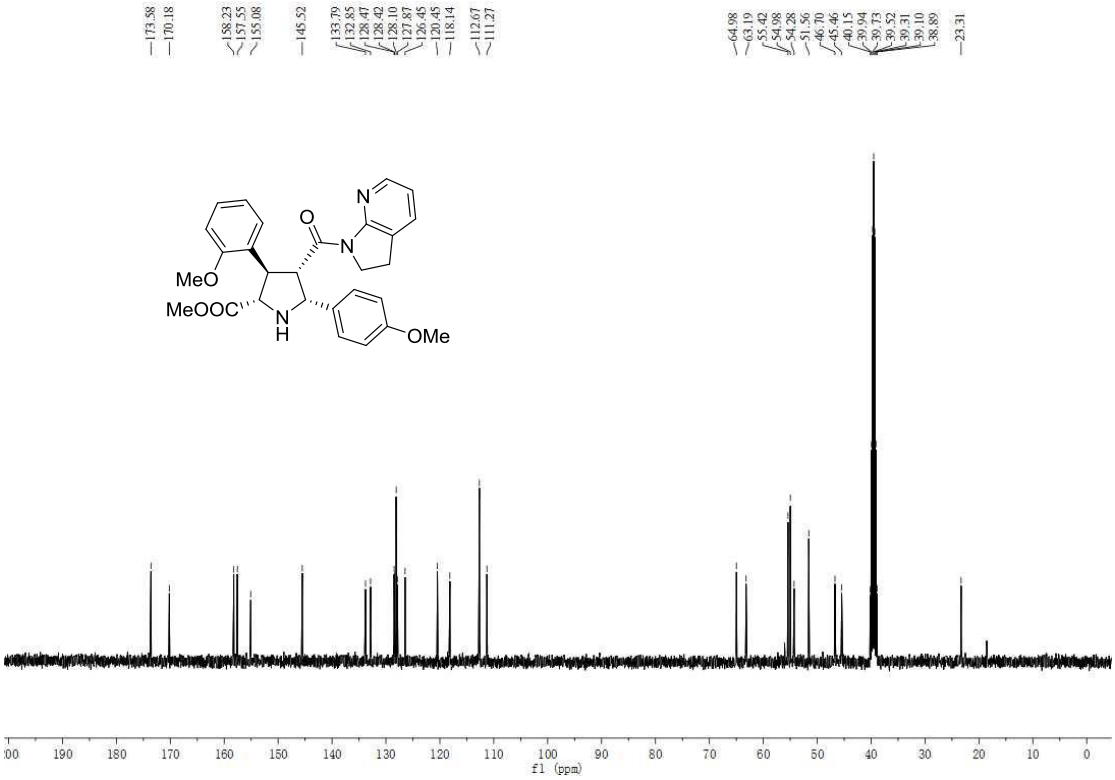
1 Det.A Ch1 / 254nm

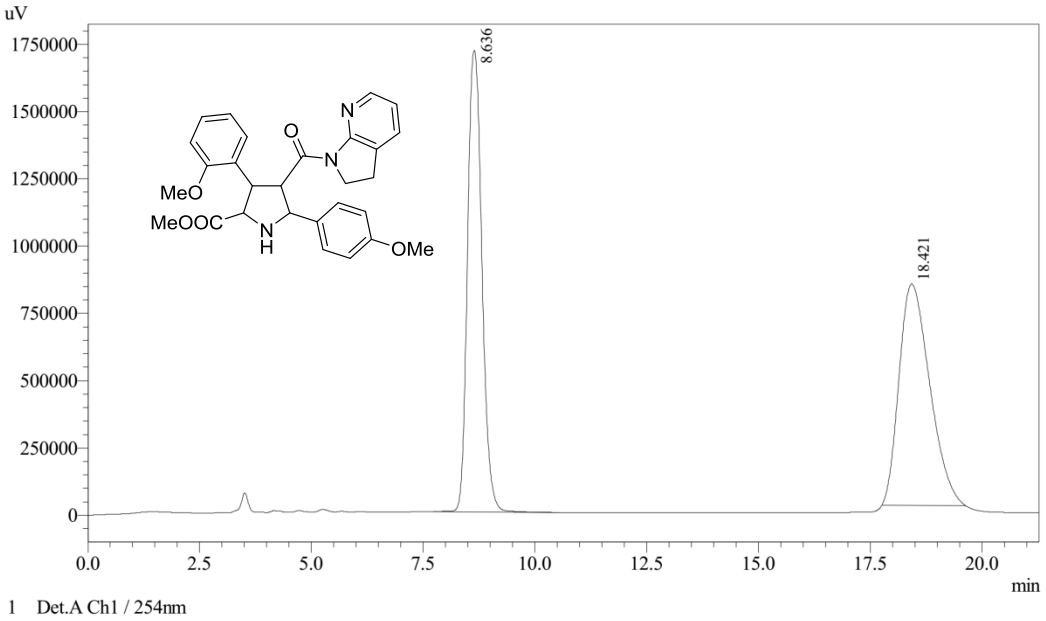
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.656	16496601	948829	97.668	98.963
2	14.929	393873	9944	2.332	1.037
Total		16890474	958773	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ea



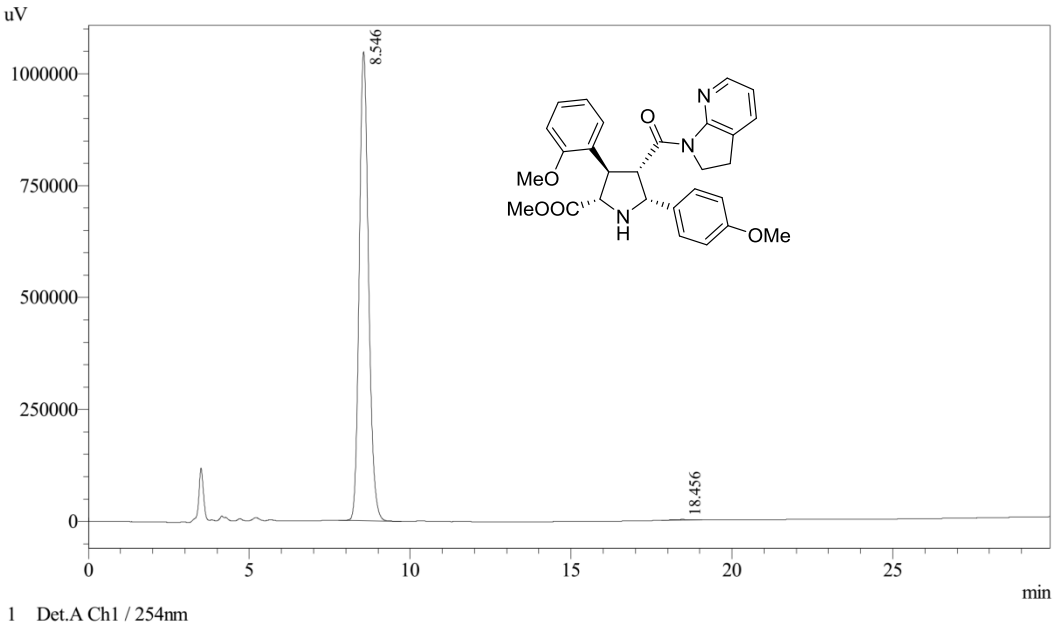




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.636	38430274	1714742	49.428	67.588
2	18.421	39319929	822310	50.572	32.412
Total		77750204	2537052	100.000	100.000

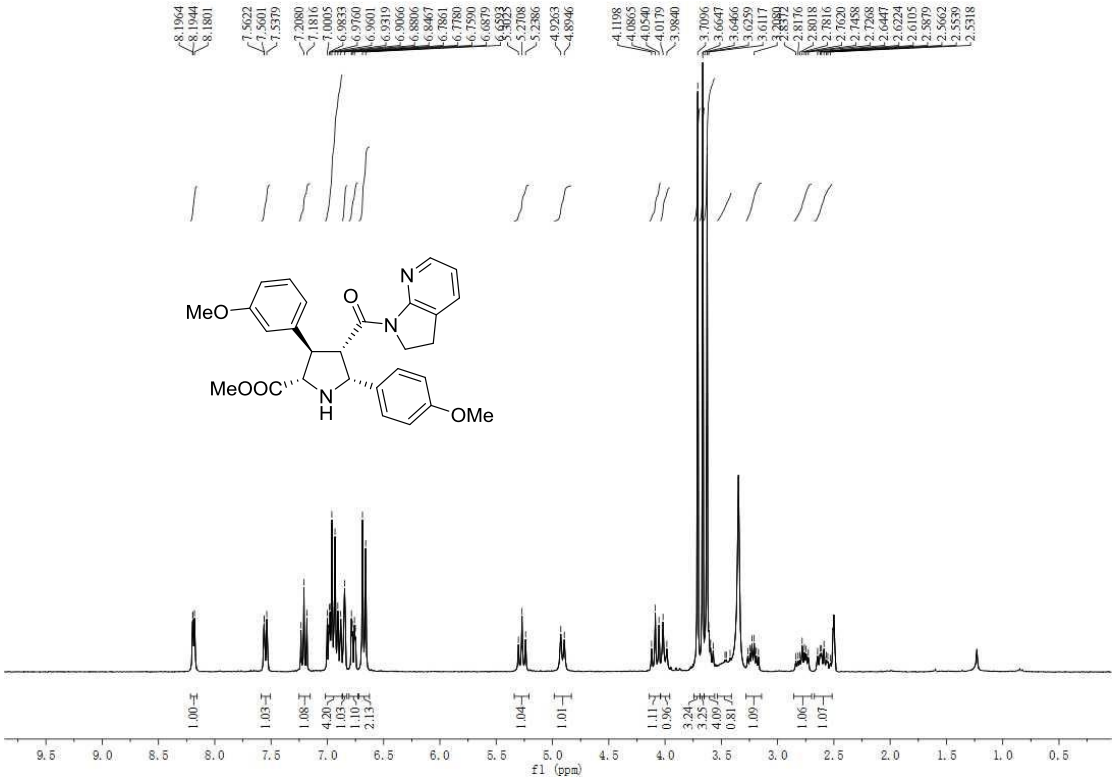


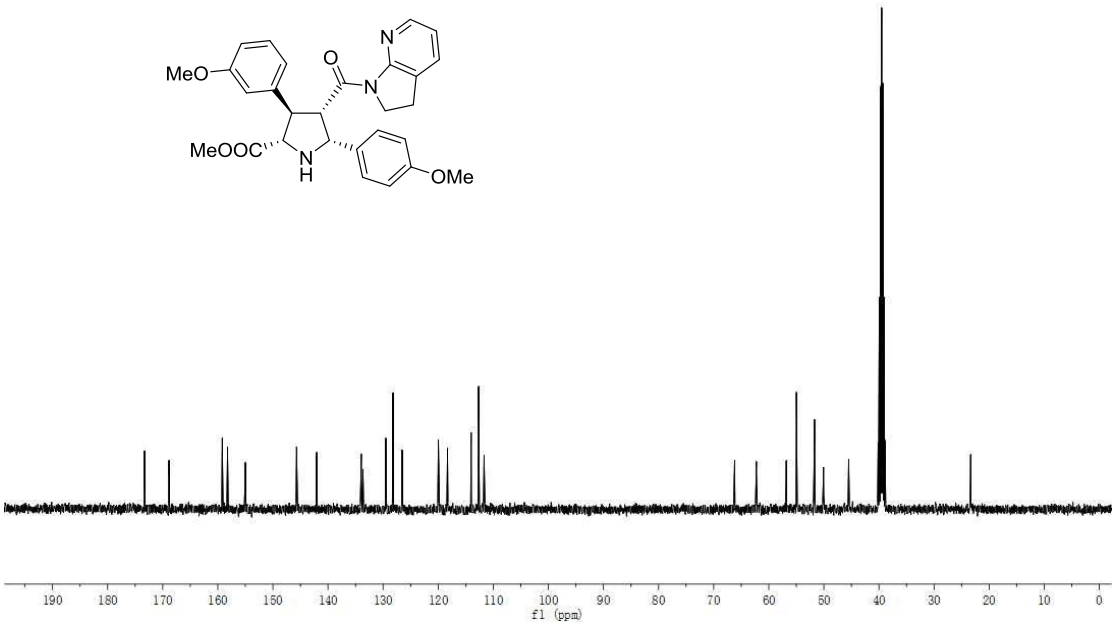
1 Det.A Ch1 / 254nm

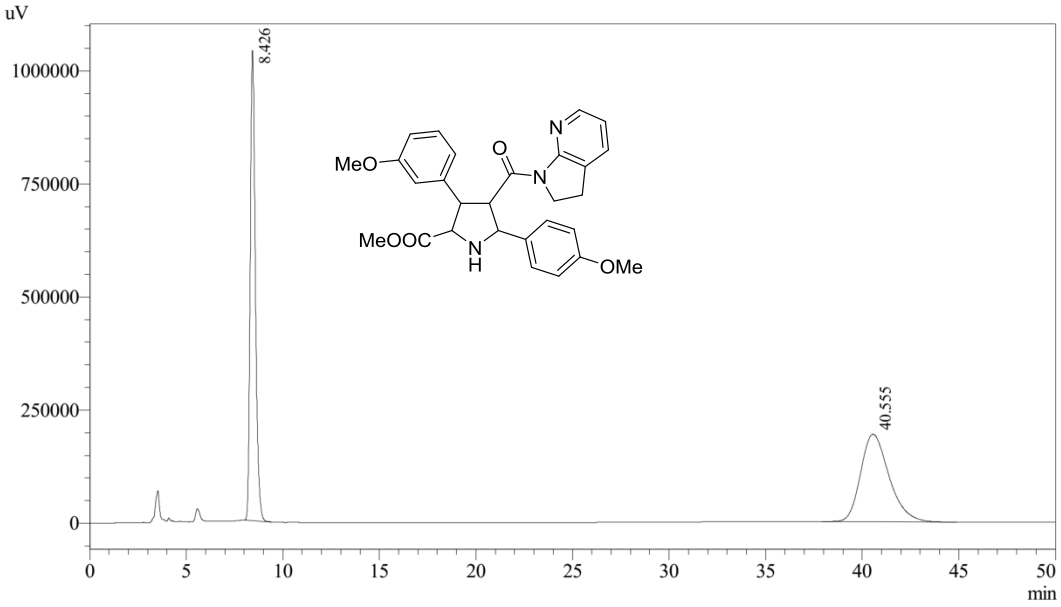
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.546	21032095	1047607	99.713	99.858
2	18.456	60637	1489	0.287	0.142
Total		21092732	1049096	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3fa



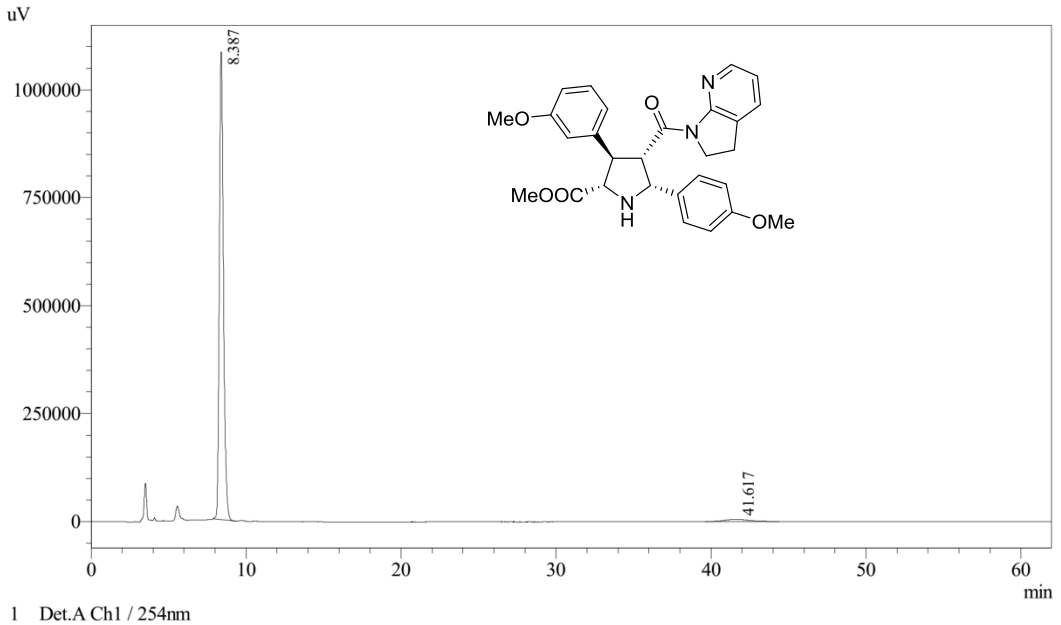




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.426	19241473	1039270	49.212	84.299
2	40.555	19857507	193564	50.788	15.701
Total		39098980	1232835	100.000	100.000

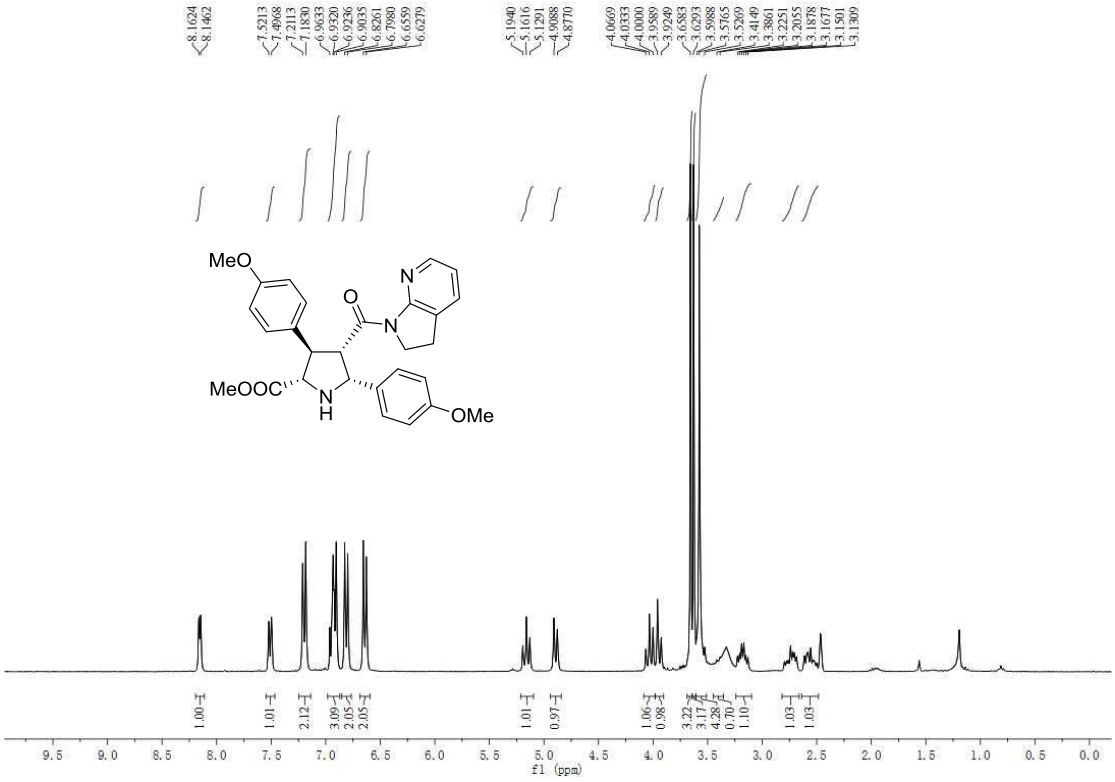


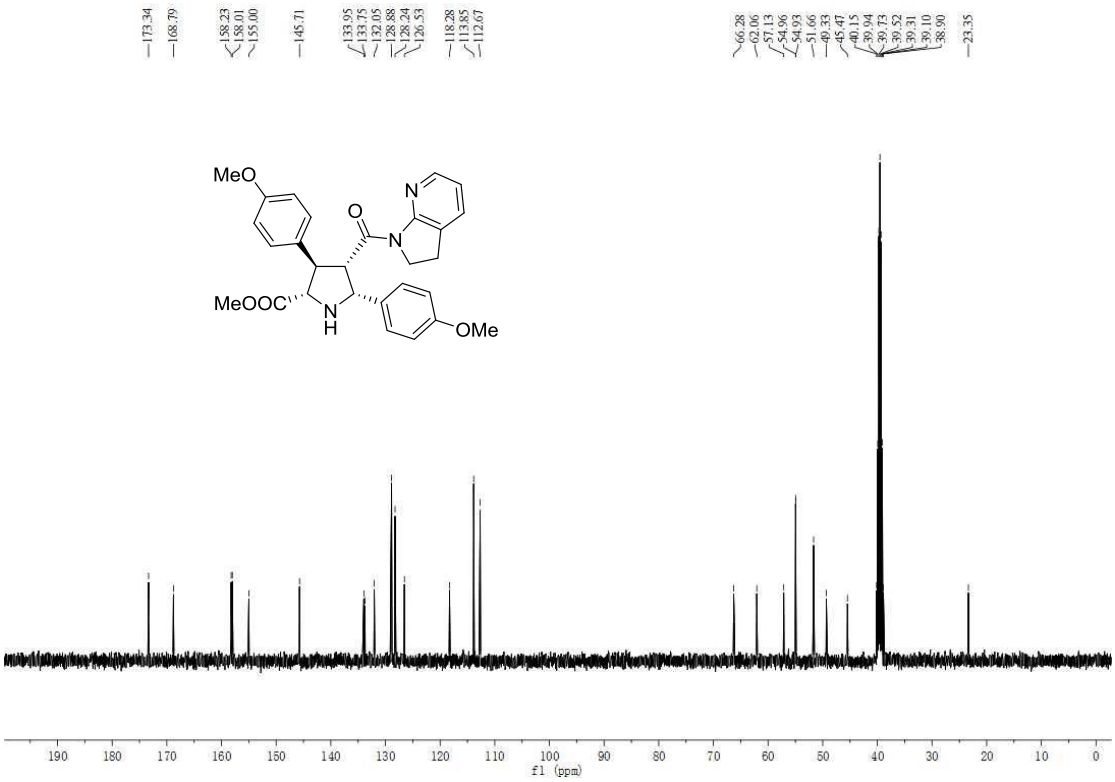
1 Det.A Ch1 / 254nm

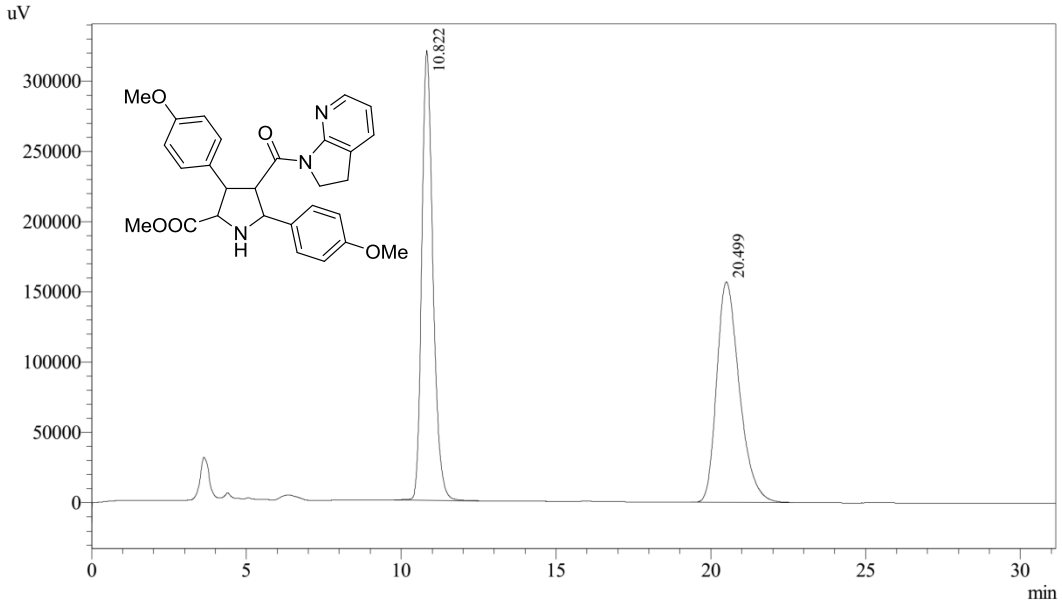
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.387	19987077	1083225	97.356	99.542
2	41.617	542726	4988	2.644	0.458
Total		20529803	1088212	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ga



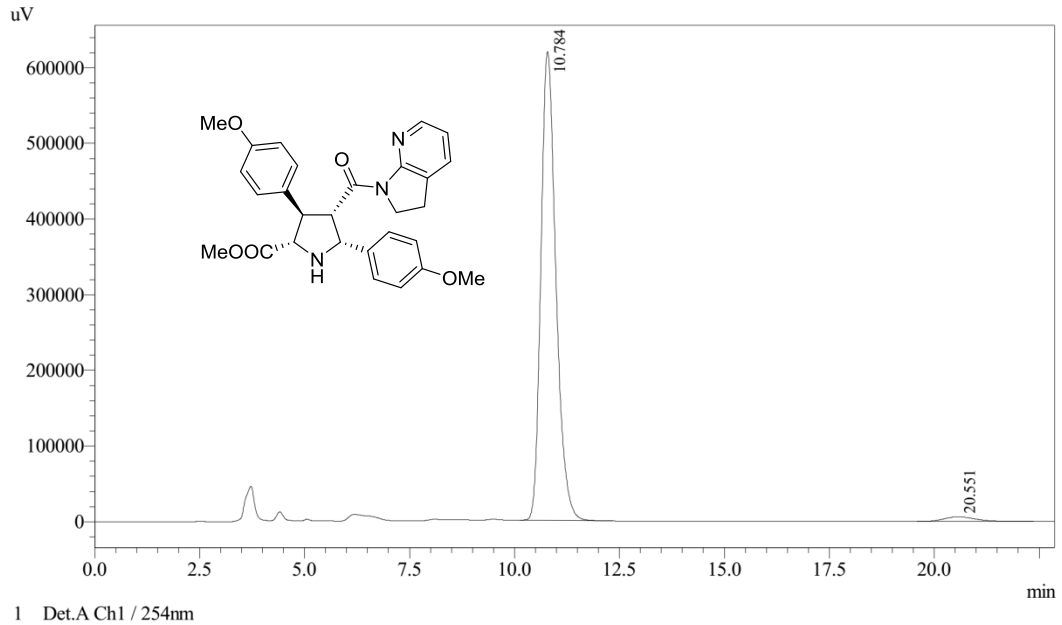




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.822	8024084	319875	50.043	67.104
2	20.499	8010391	156812	49.957	32.896
Total		16034475	476687	100.000	100.000

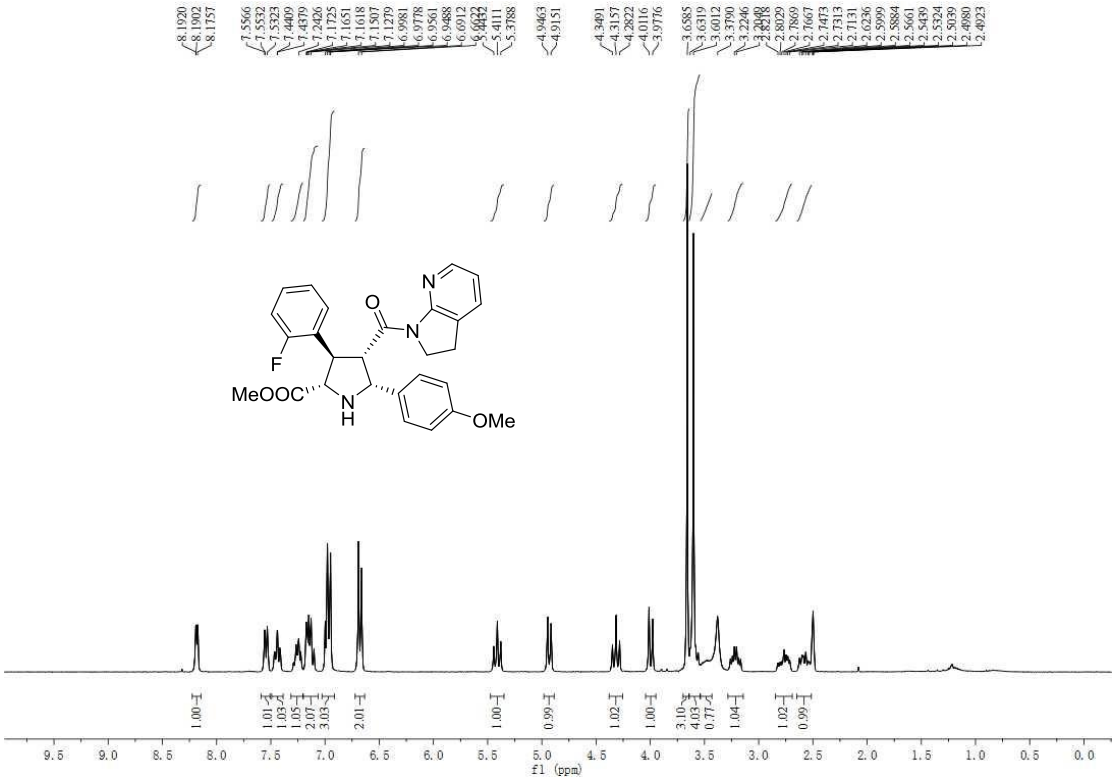


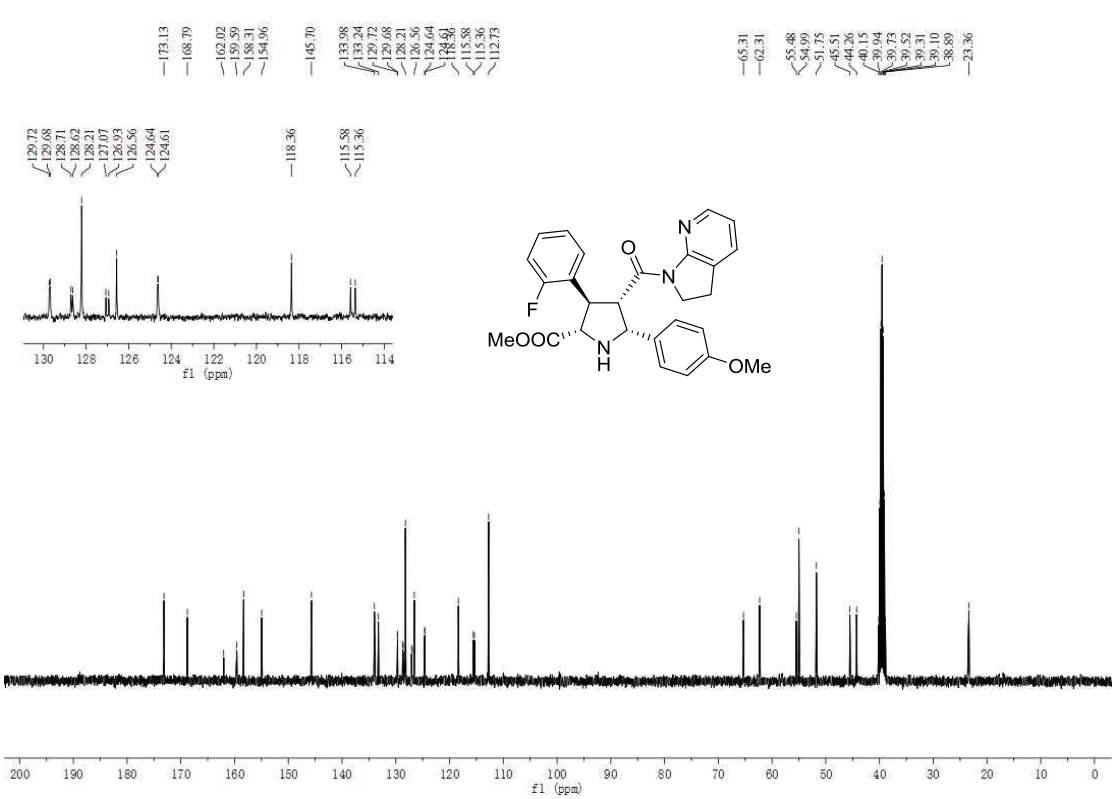
1 Det.A Ch1 / 254nm

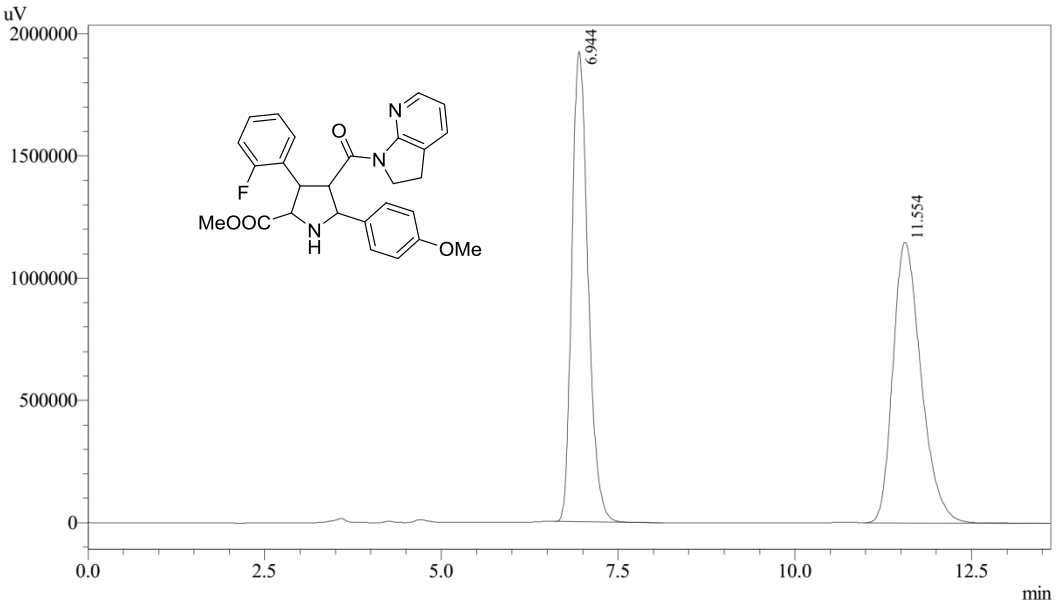
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.784	15396452	619295	97.887	98.994
2	20.551	332287	6292	2.113	1.006
Total		15728739	625587	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ha



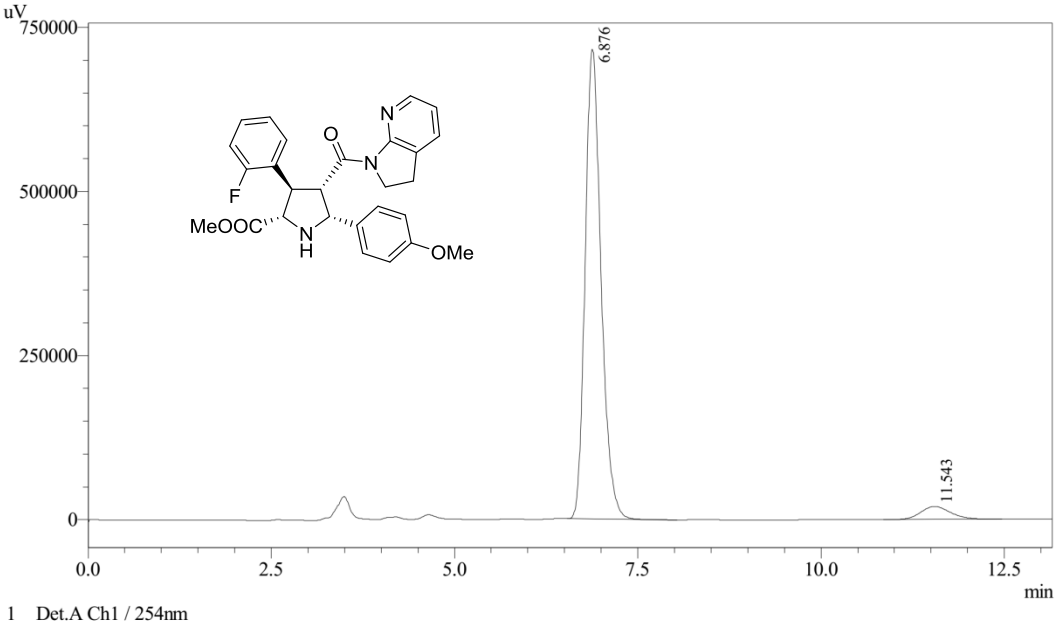




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.944	30700262	1923467	49.077	62.641
2	11.554	31854900	1147157	50.923	37.359
Total		62555162	3070623	100.000	100.000

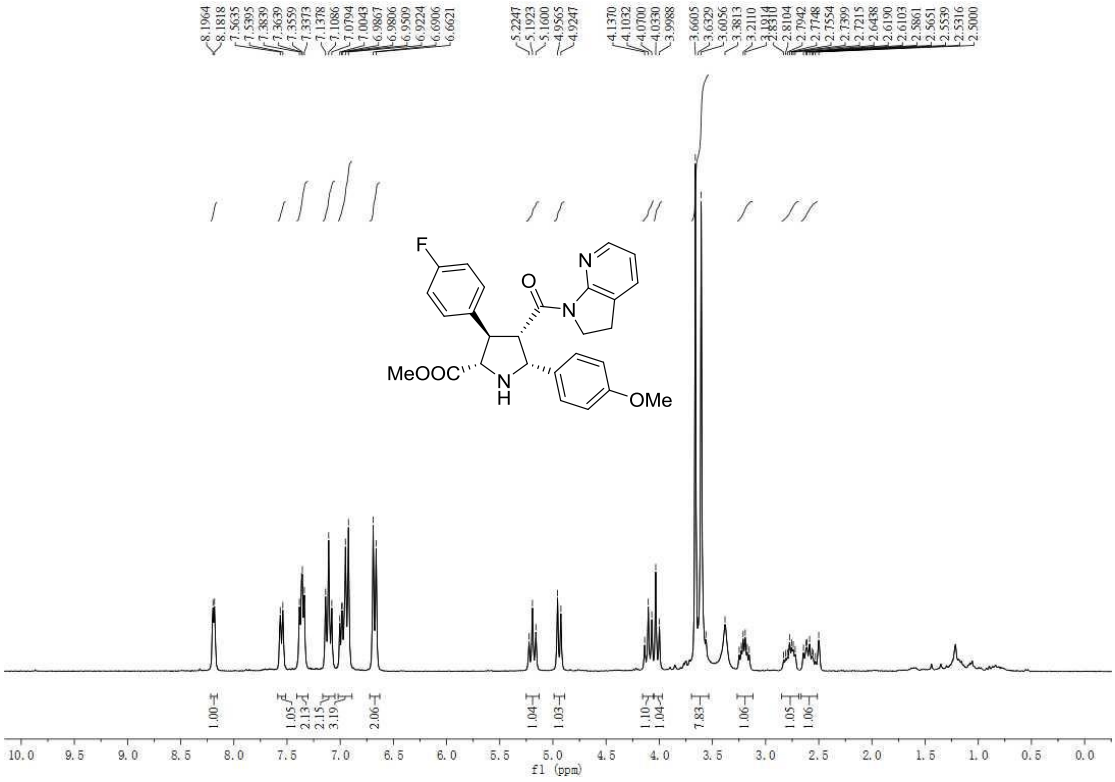


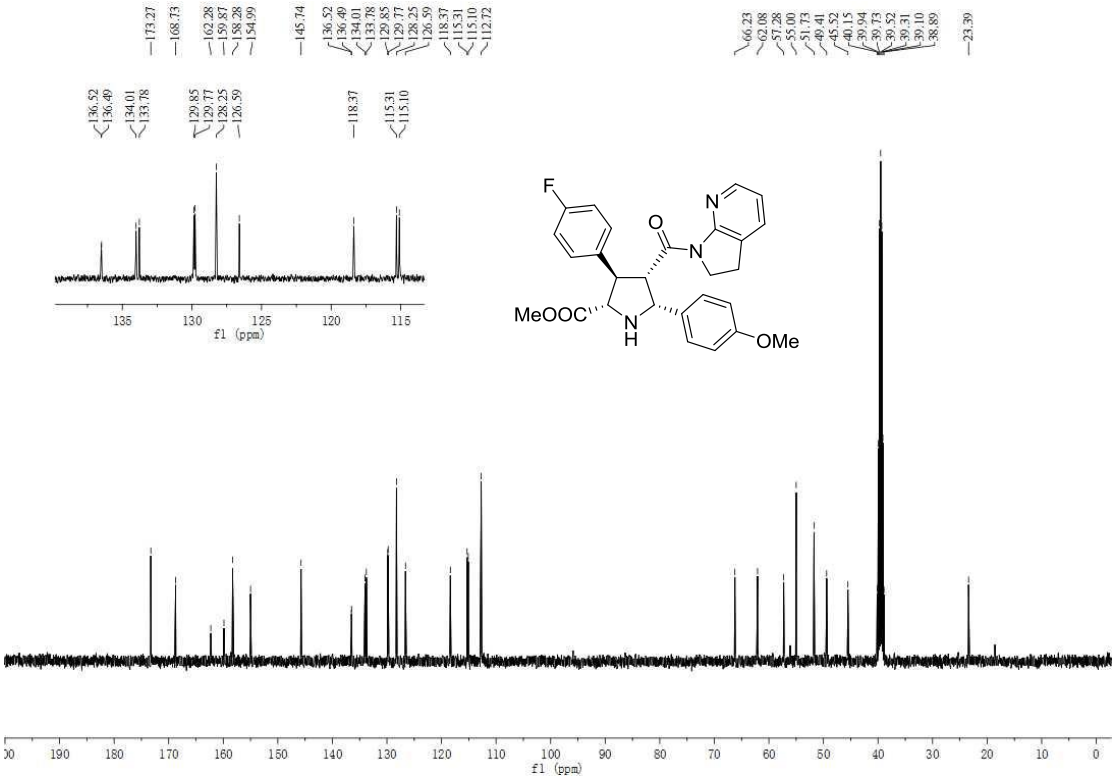
1 Det.A Ch1 / 254nm

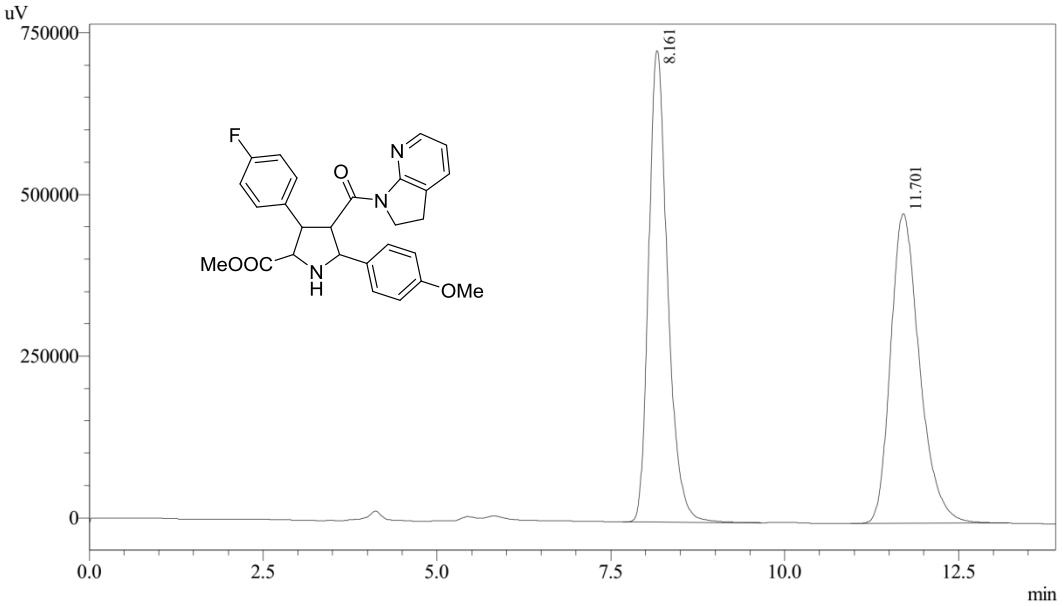
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.876	10843561	715142	95.042	97.309
2	11.543	565628	19775	4.958	2.691
Total		11409189	734916	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ia



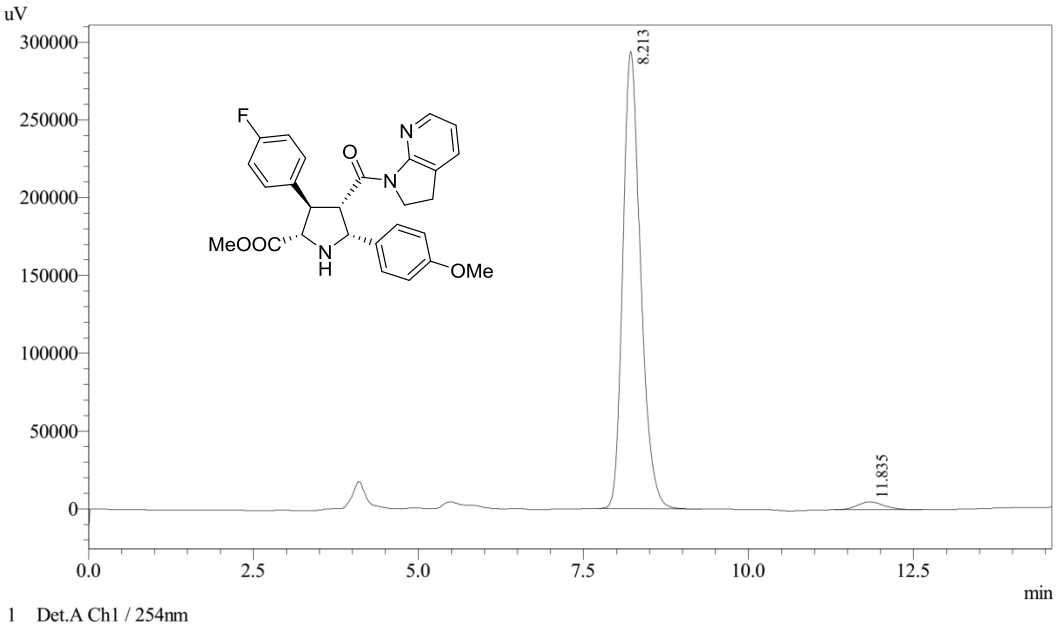




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.161	13878576	729028	49.913	60.350
2	11.701	13927093	478972	50.087	39.650
Total		27805669	1208000	100.000	100.000

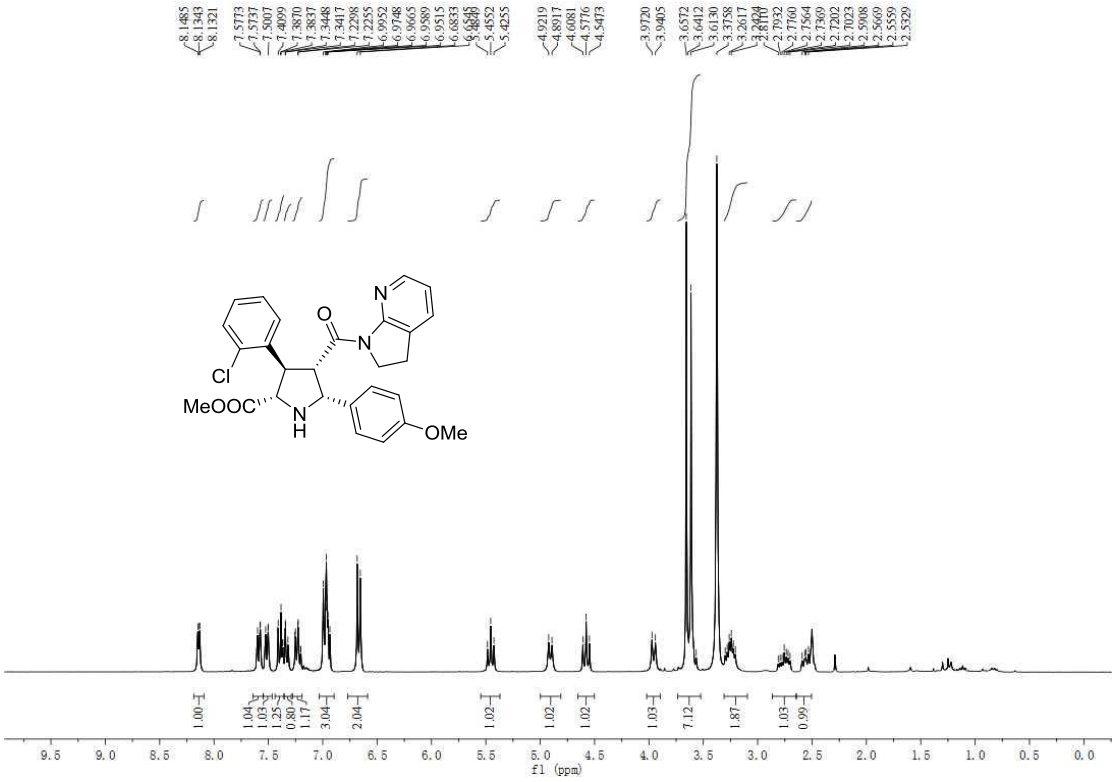


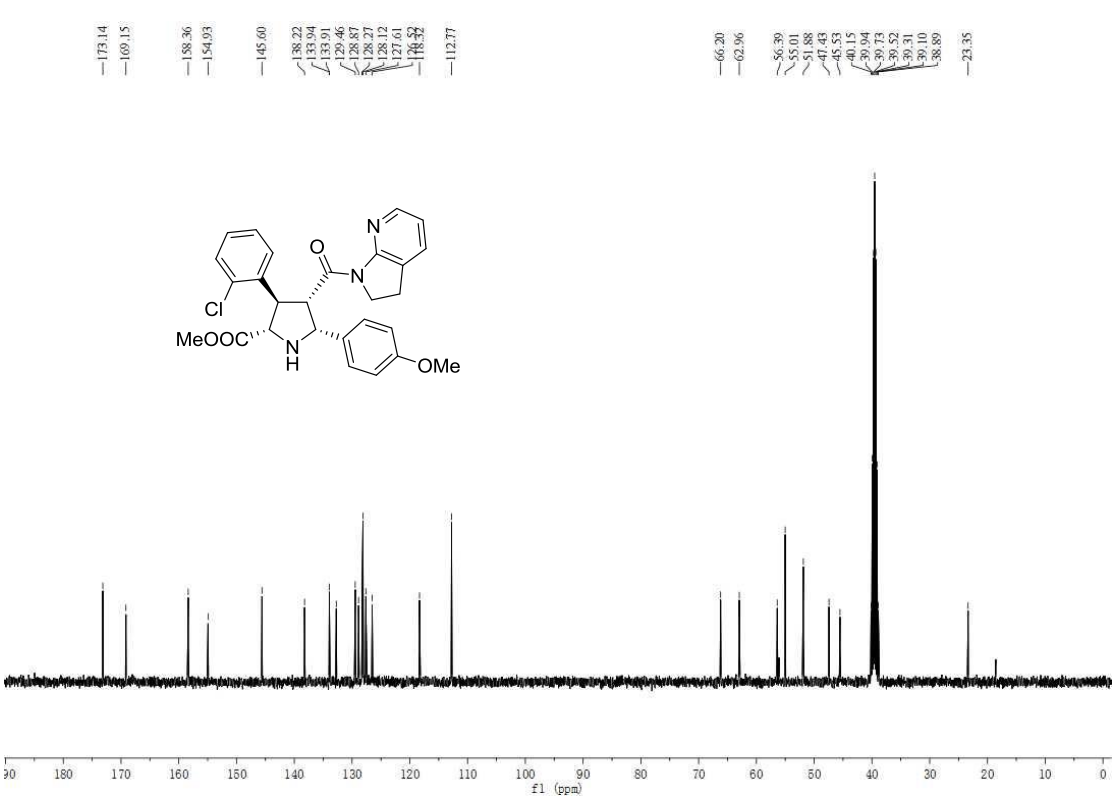
1 Det.A Ch1 / 254nm

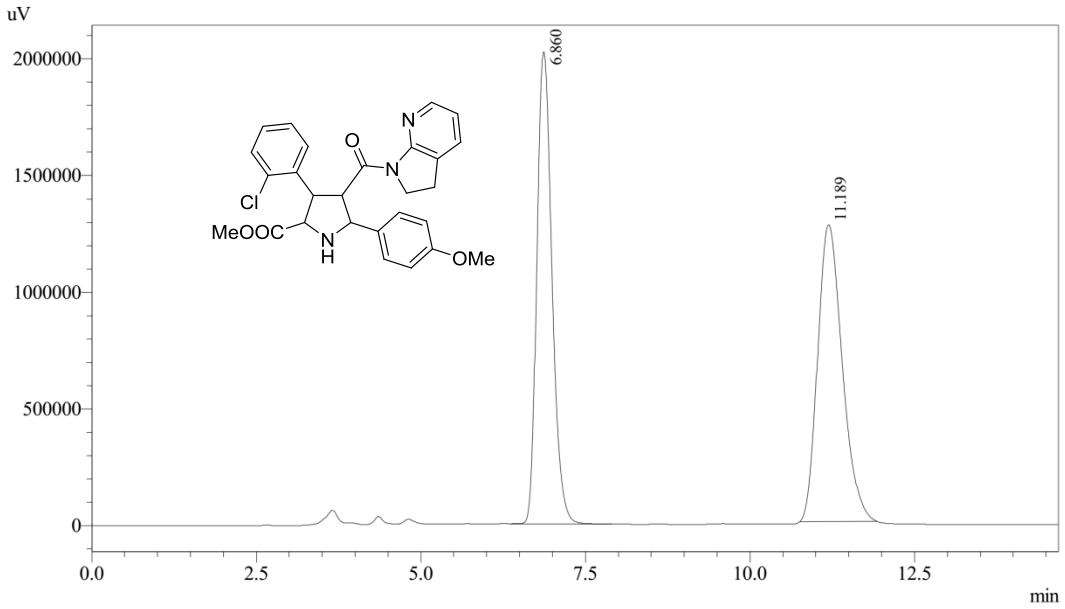
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.213	5524883	293859	97.474	98.319
2	11.835	143166	5025	2.526	1.681
Total		5668049	298884	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ja



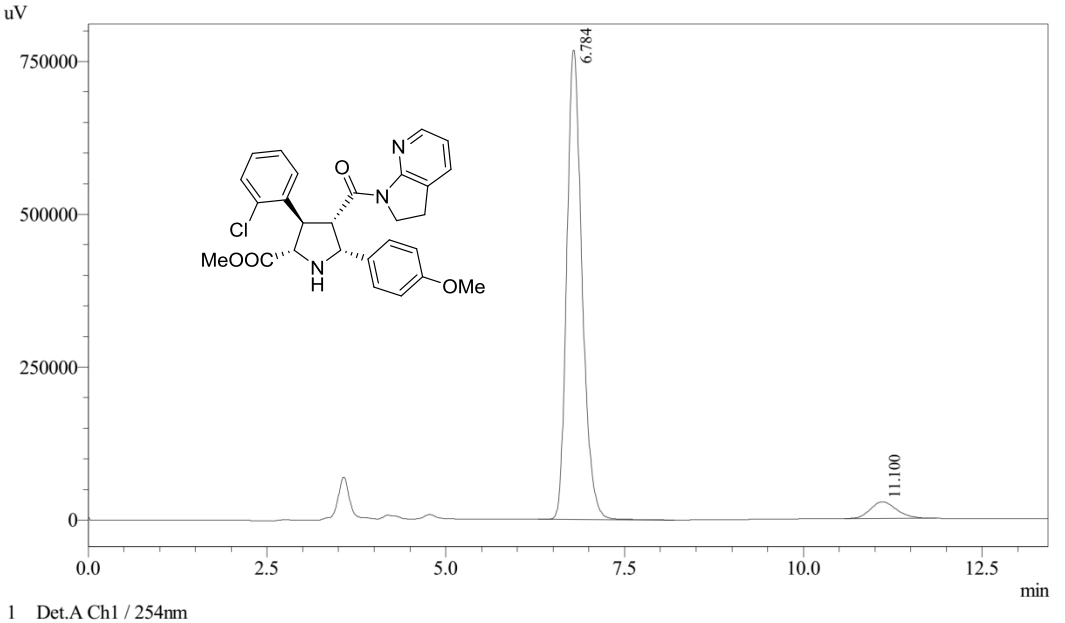




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.860	32358925	2023639	49.381	61.369
2	11.189	33170664	1273871	50.619	38.631
Total		65529589	3297510	100.000	100.000

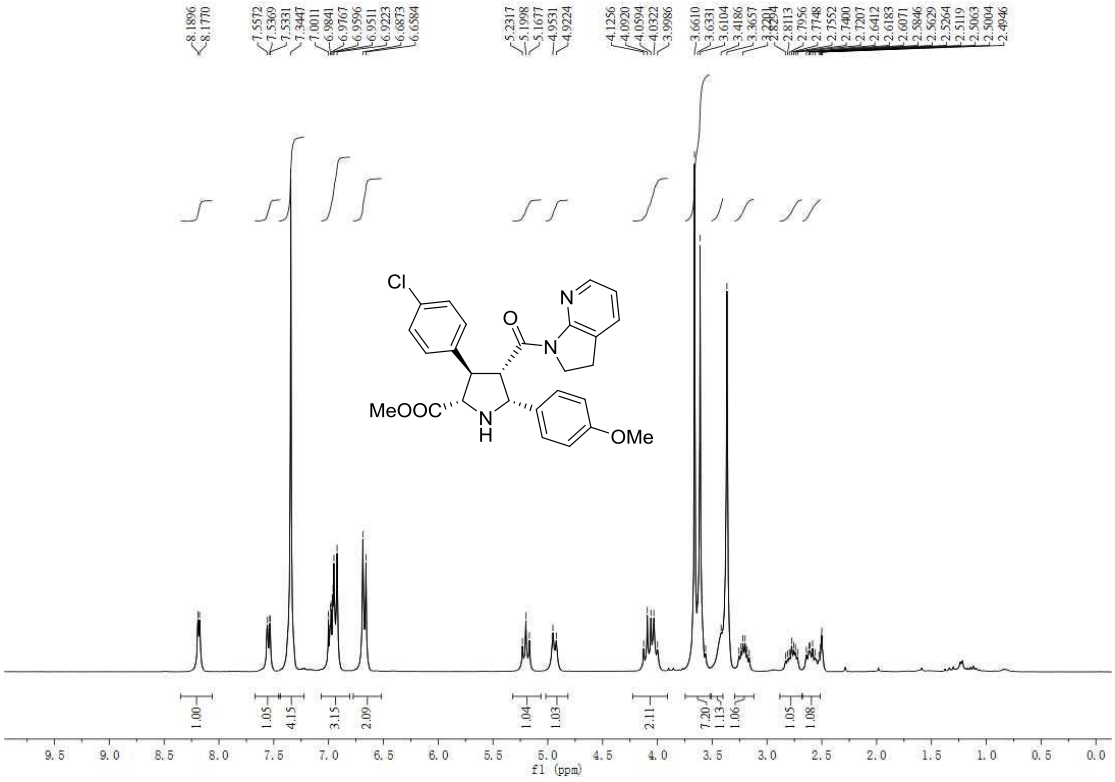


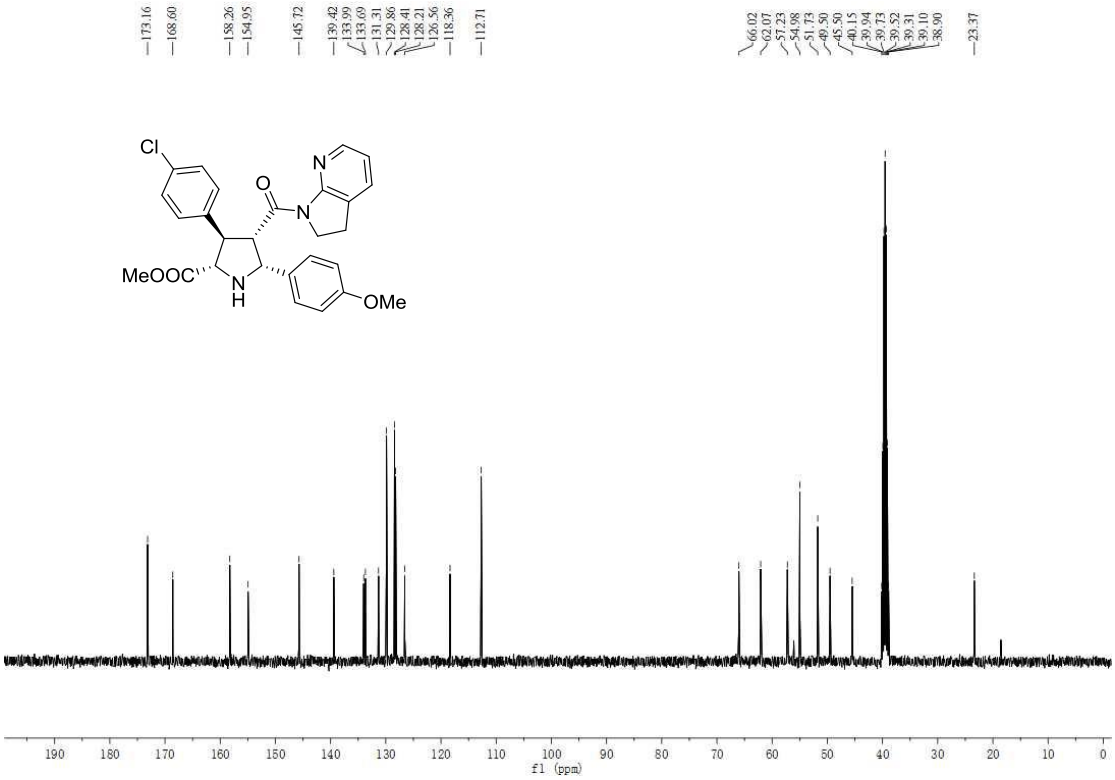
1 Det.A Ch1 / 254nm

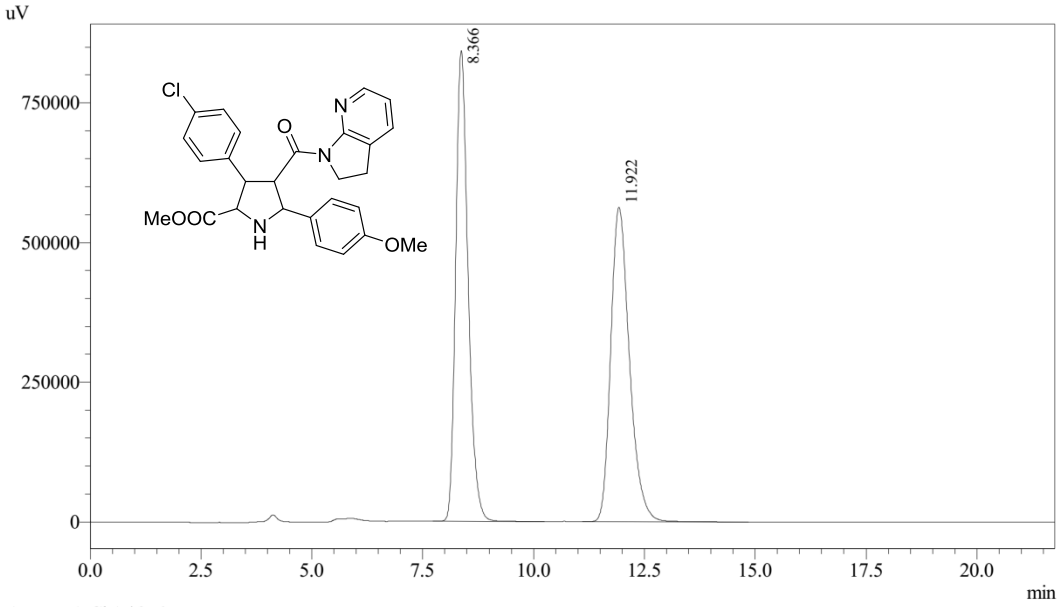
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.784	11446762	767317	94.237	96.575
2	11.100	700035	27214	5.763	3.425
Total		12146797	794531	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ka



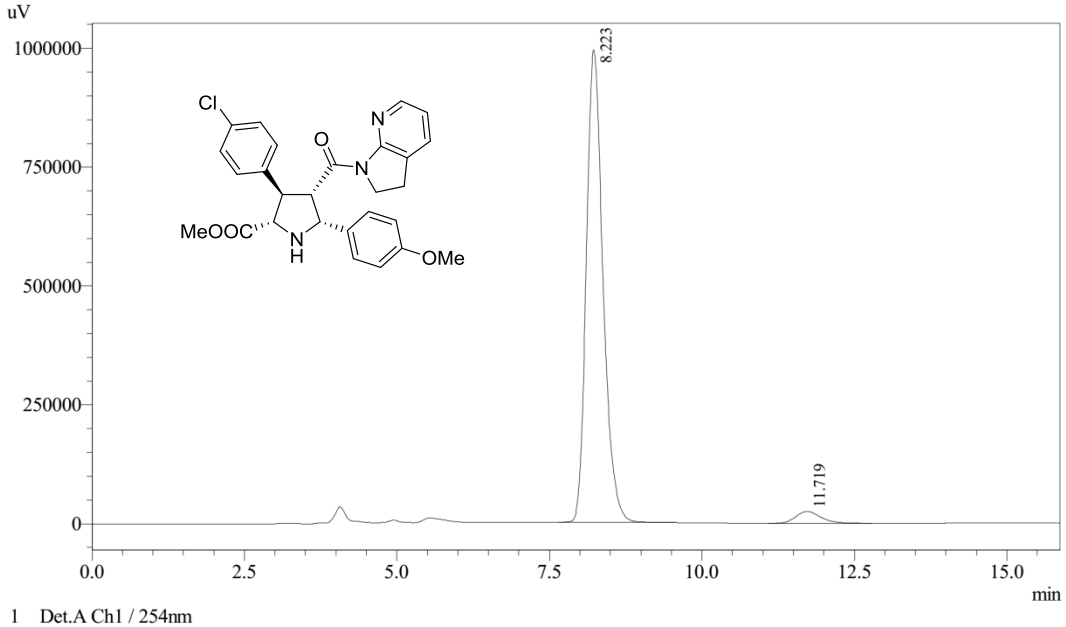




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.366	16437331	842754	49.850	59.946
2	11.922	16536134	563102	50.150	40.054
Total		32973465	1405855	100.000	100.000

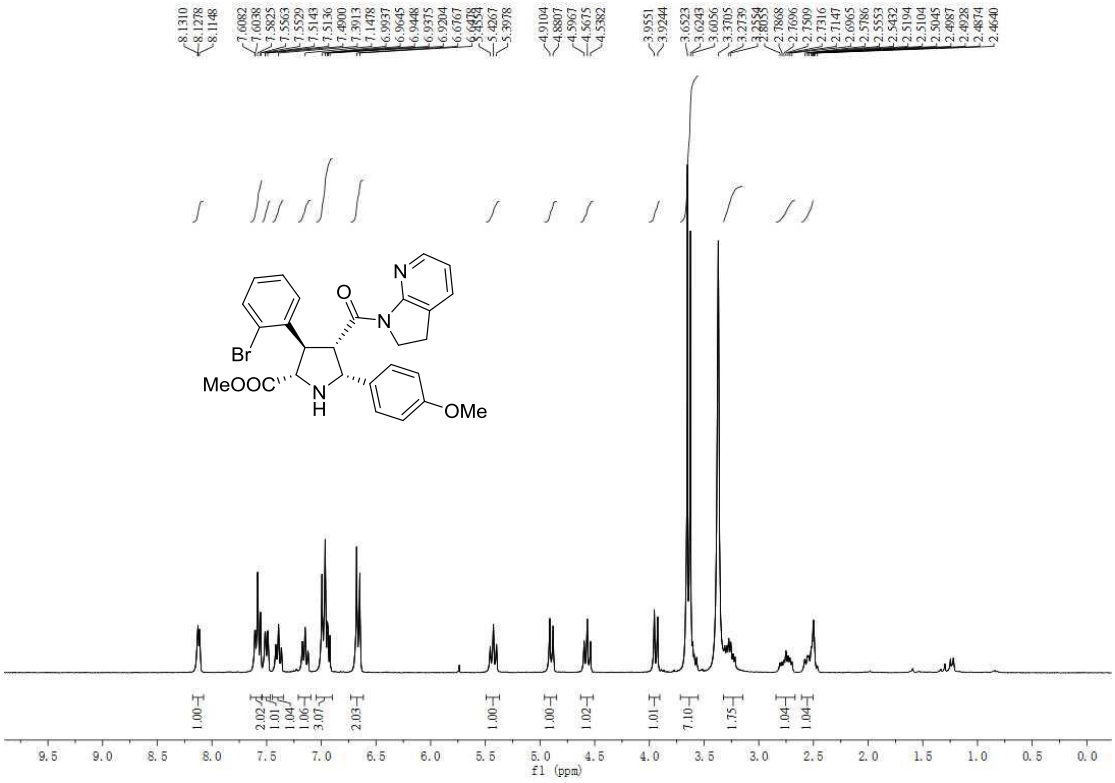


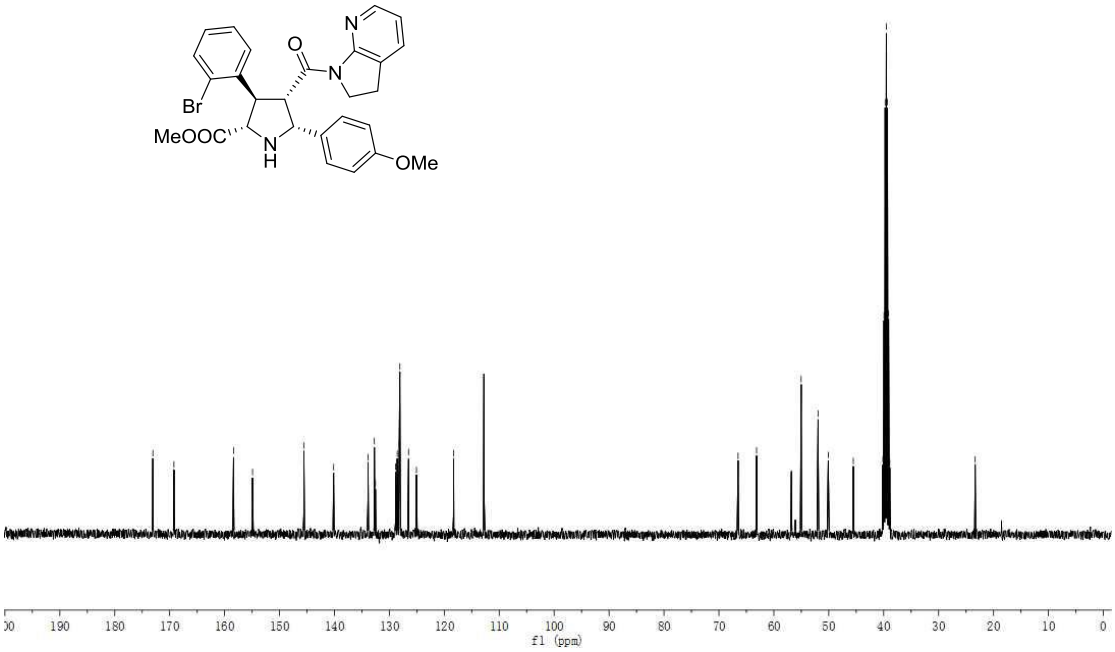
1 Det.A Ch1 / 254nm

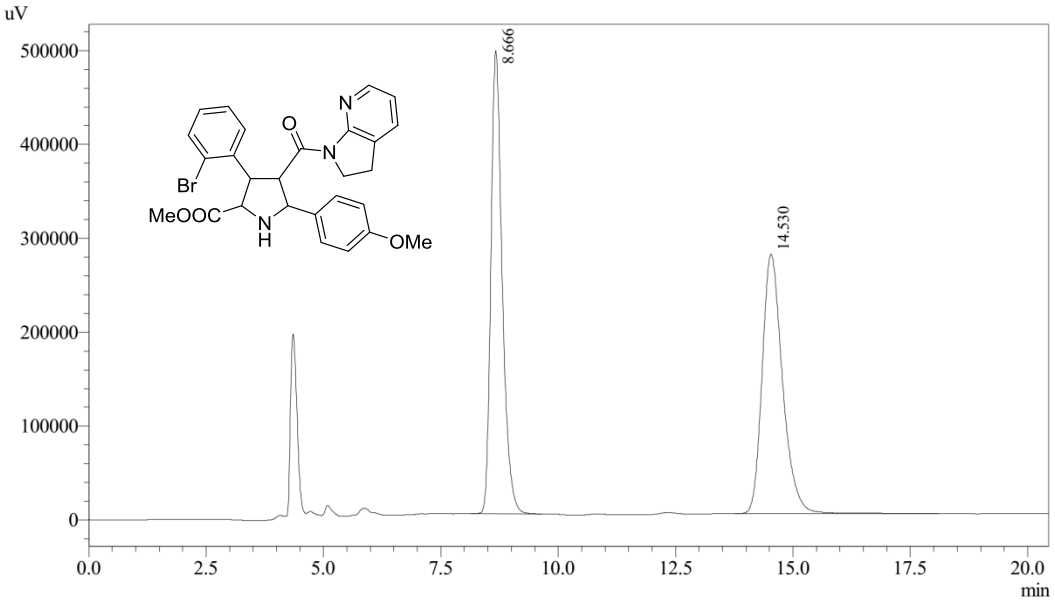
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.223	18931558	993781	96.422	97.577
2	11.719	702499	24681	3.578	2.423
Total		19634056	1018461	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3la



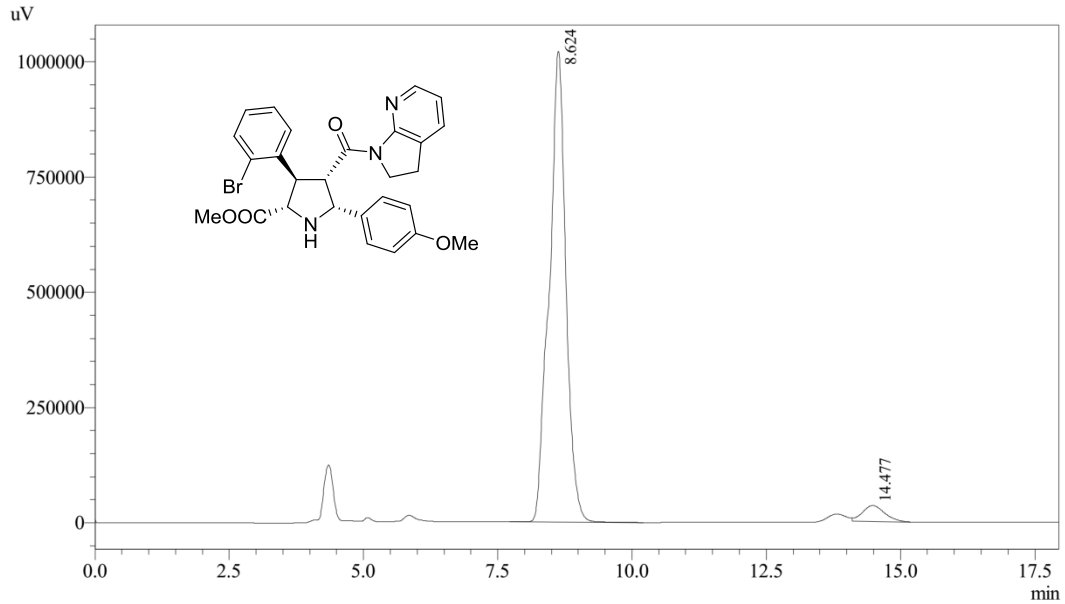




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.666	8258707	493081	49.610	64.084
2	14.530	8388530	276350	50.390	35.916
Total		16647237	769431	100.000	100.000

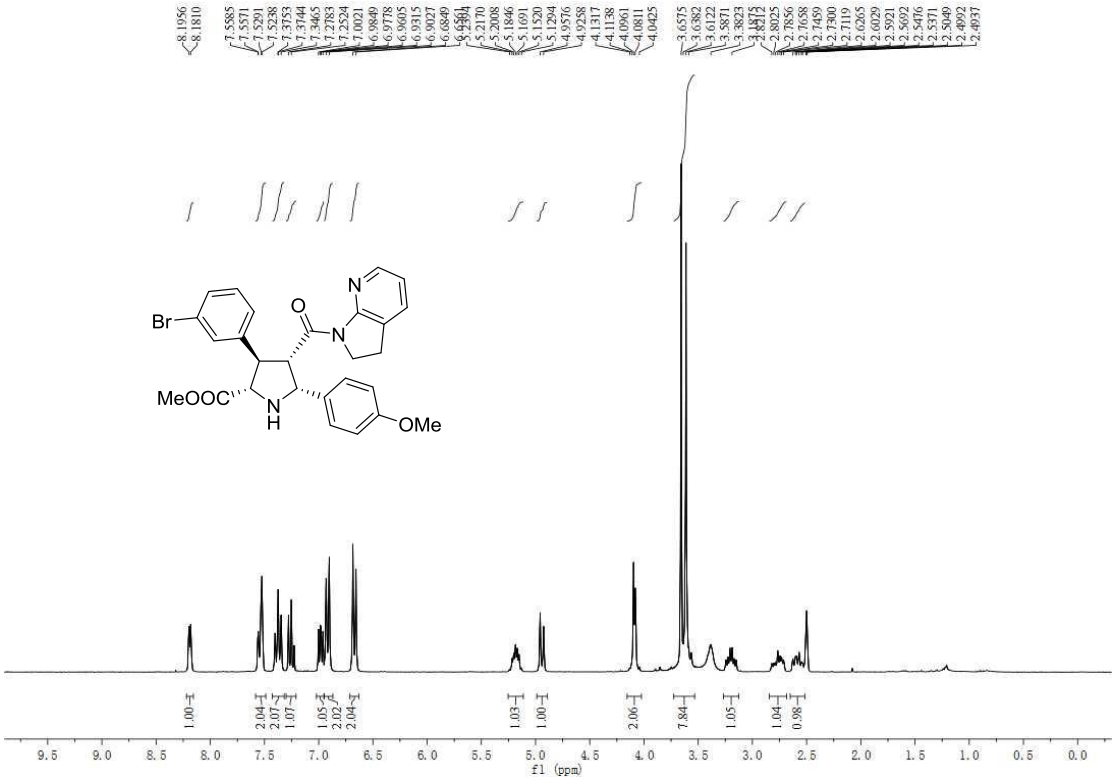


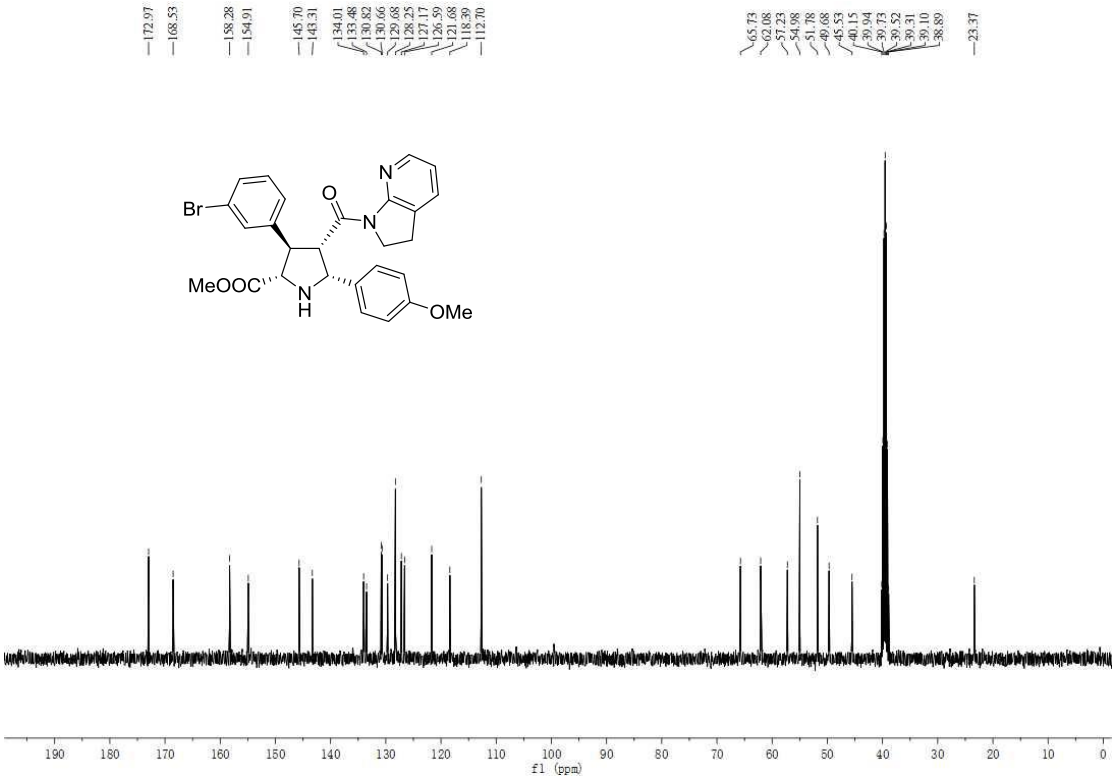
1 Det.A Ch1 / 254nm

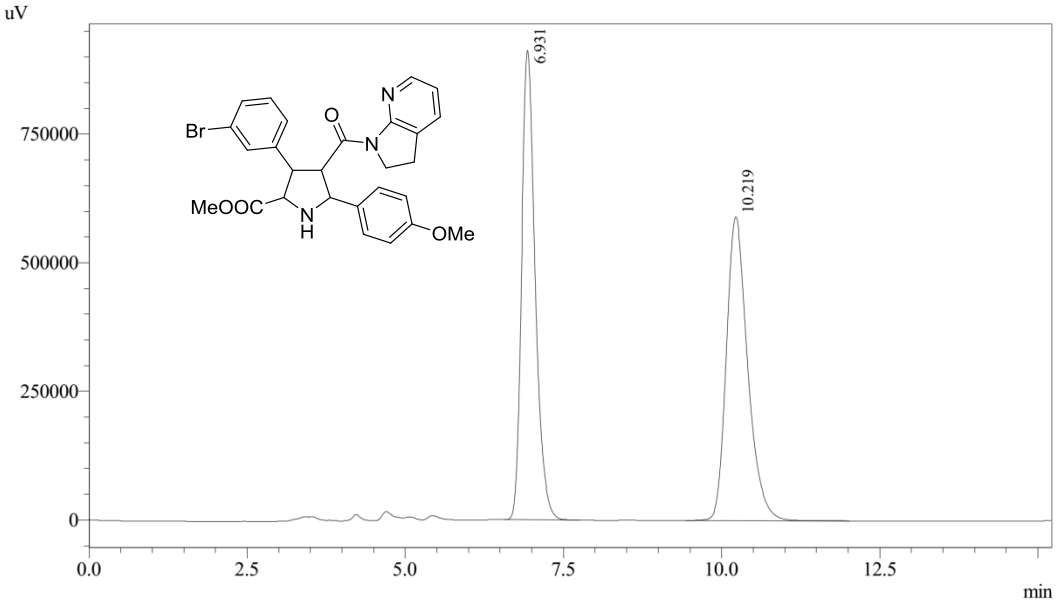
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.624	22125678	1020907	95.609	96.698
2	14.477	1016148	34857	4.391	3.302
Total		23141826	1055765	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ma



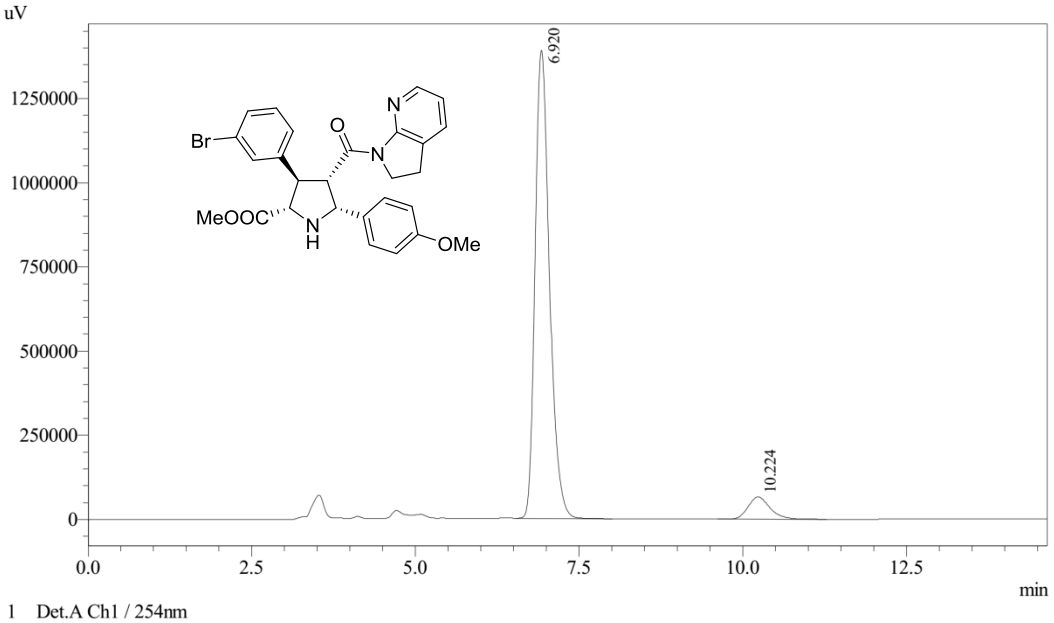




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.931	13653775	912655	49.592	60.723
2	10.219	13878217	590329	50.408	39.277
Total		27531992	1502984	100.000	100.000

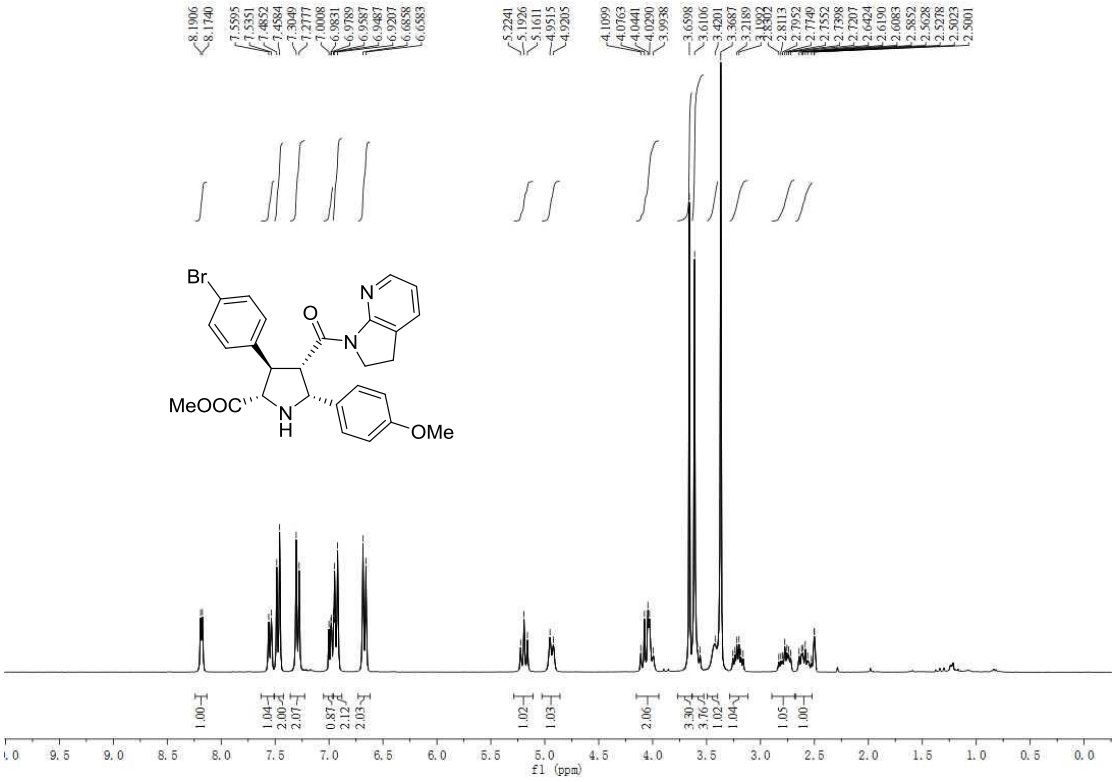


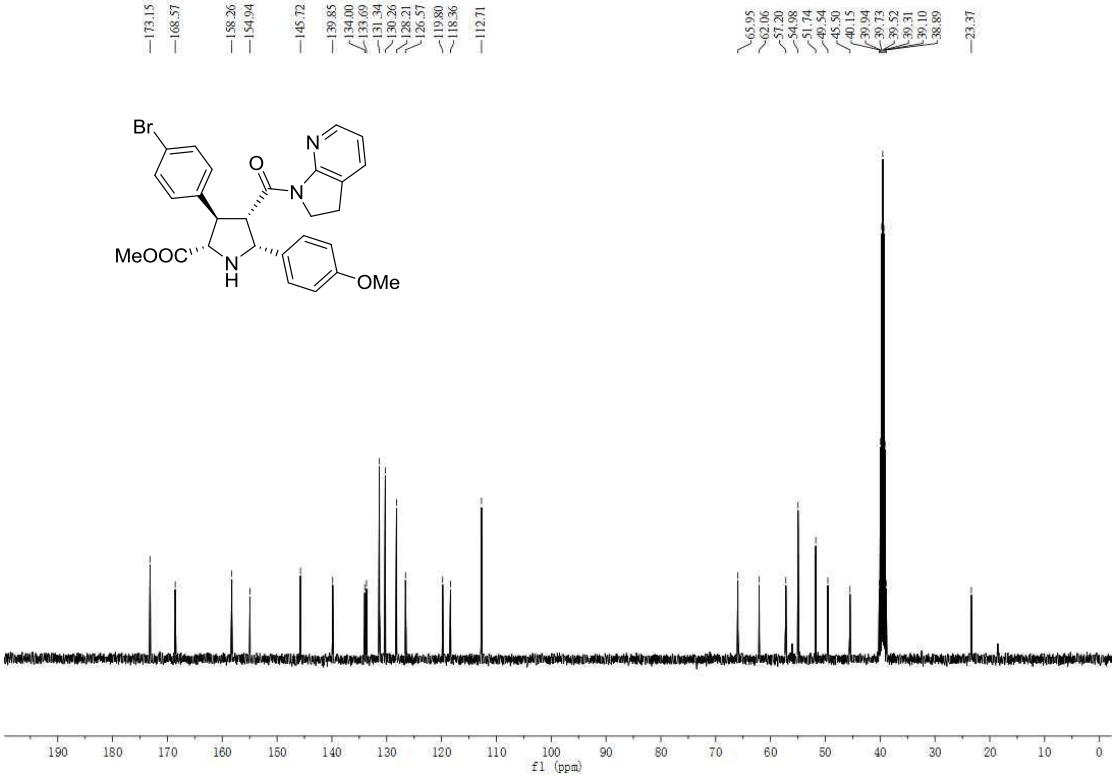
1 Det.A Ch1 / 254nm

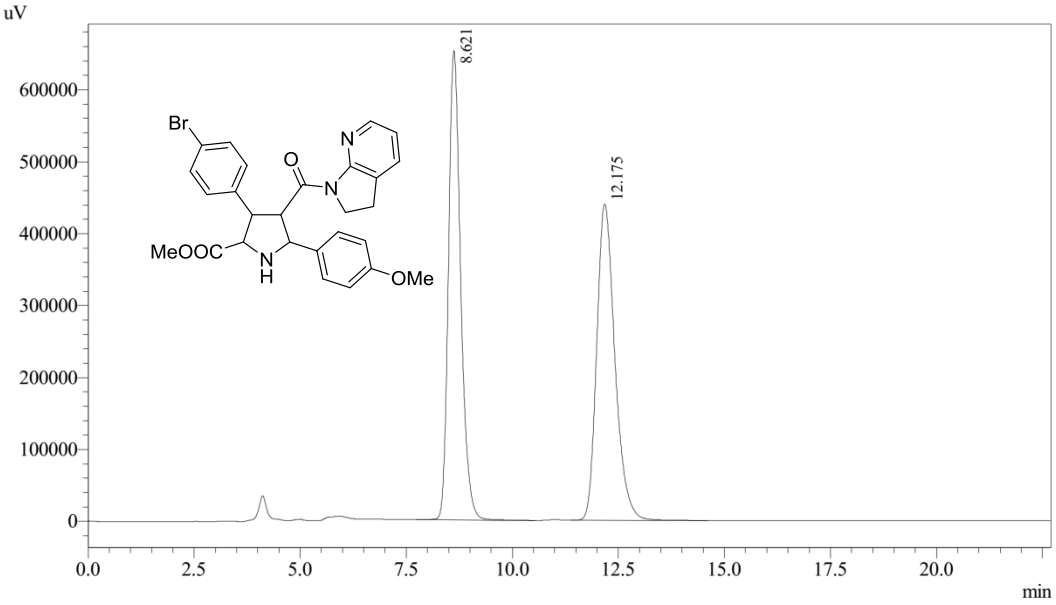
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.920	21326997	1390306	93.280	95.467
2	10.224	1536442	66018	6.720	4.533
Total		22863439	1456324	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3na



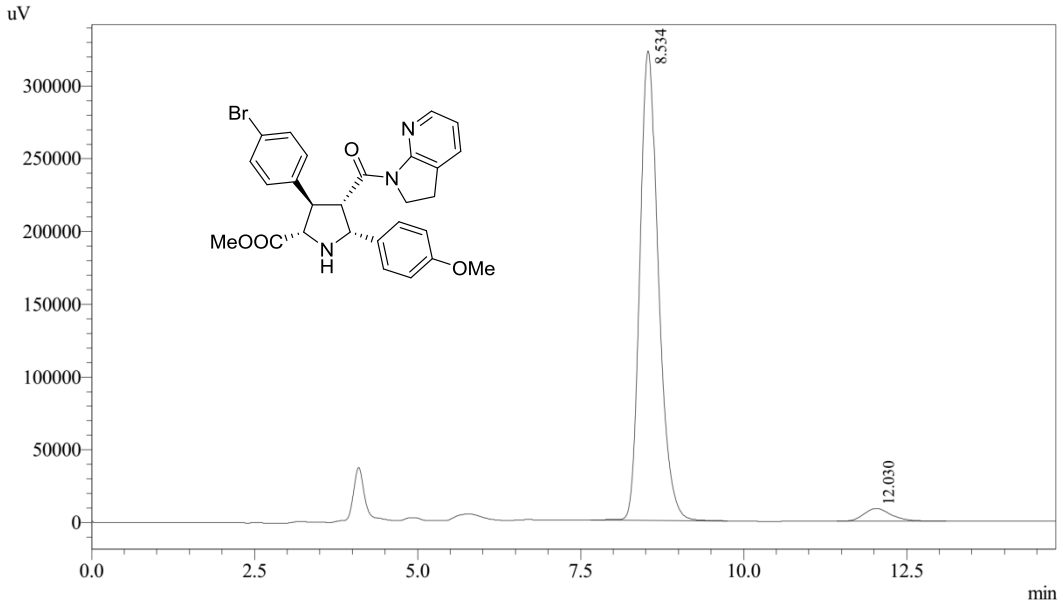




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.621	13114720	652820	50.044	59.759
2	12.175	13091423	439599	49.956	40.241
Total		26206144	1092419	100.000	100.000

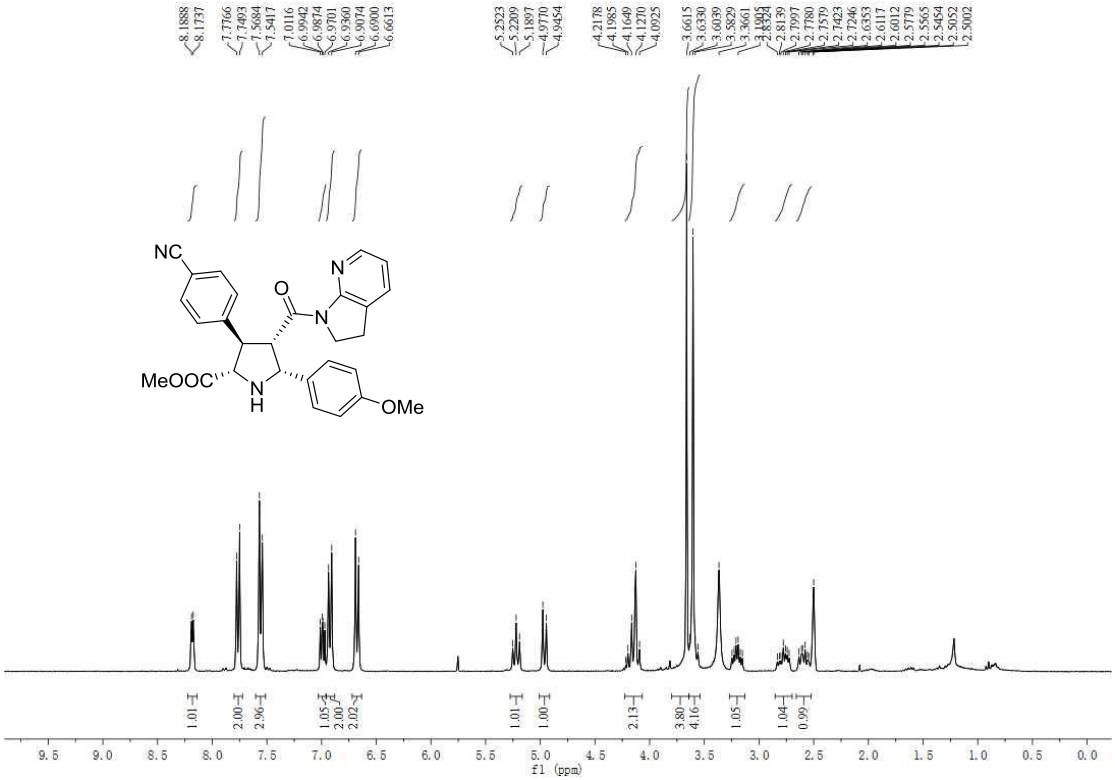


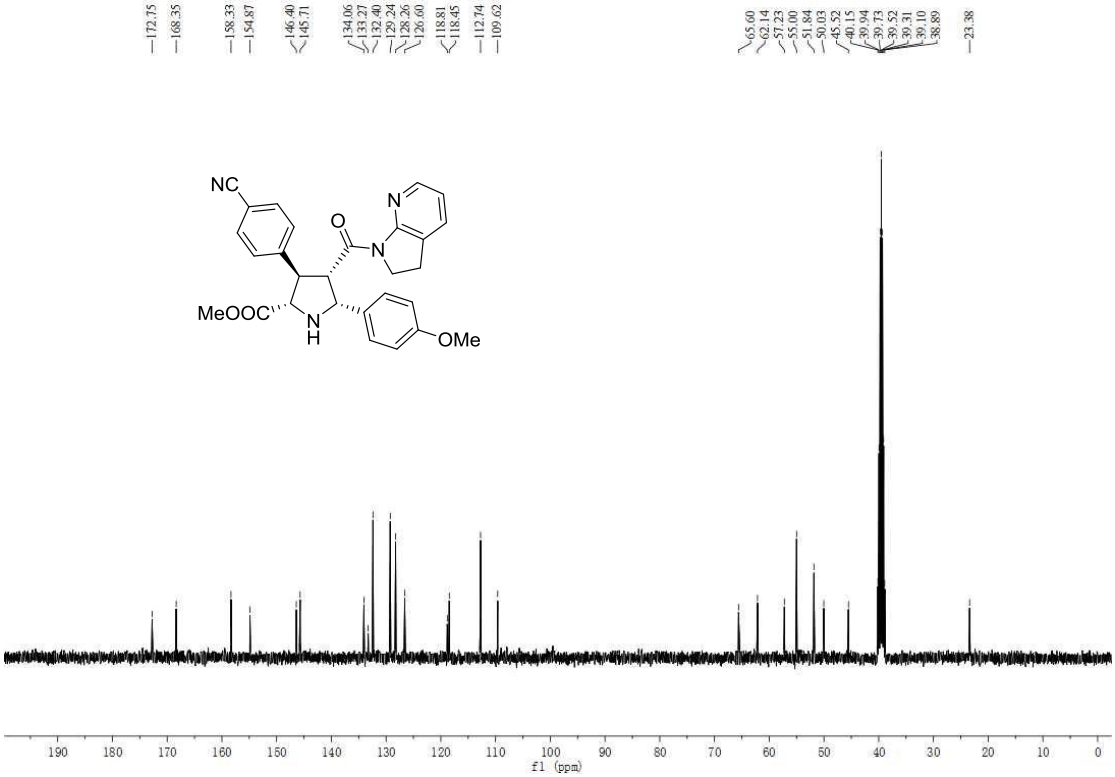
1 Det.A Ch1 / 254nm

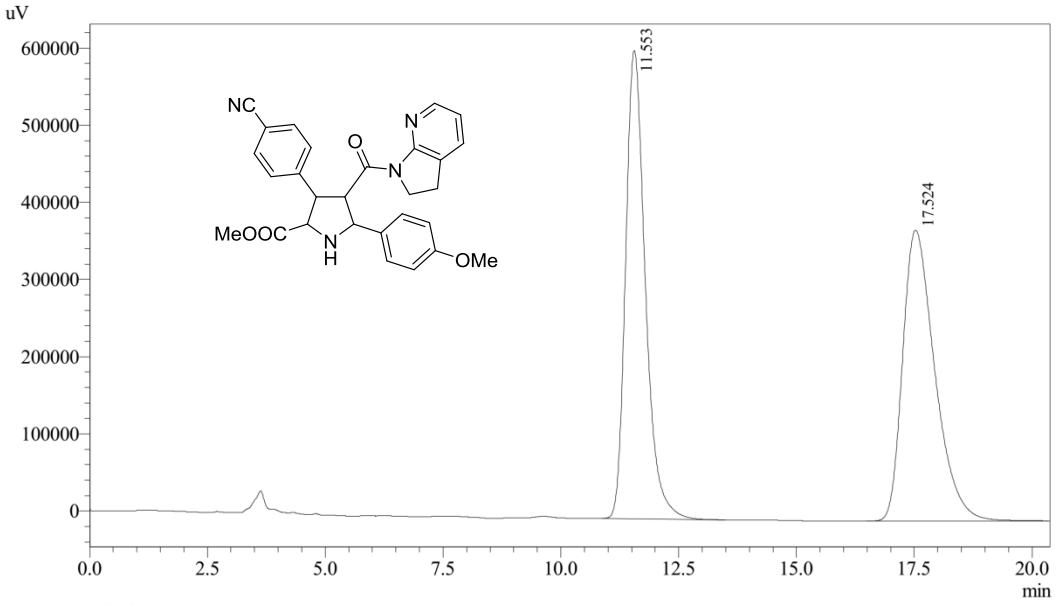
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.534	6319944	322351	96.142	97.366
2	12.030	253601	8720	3.858	2.634
Total		6573545	331071	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3oa



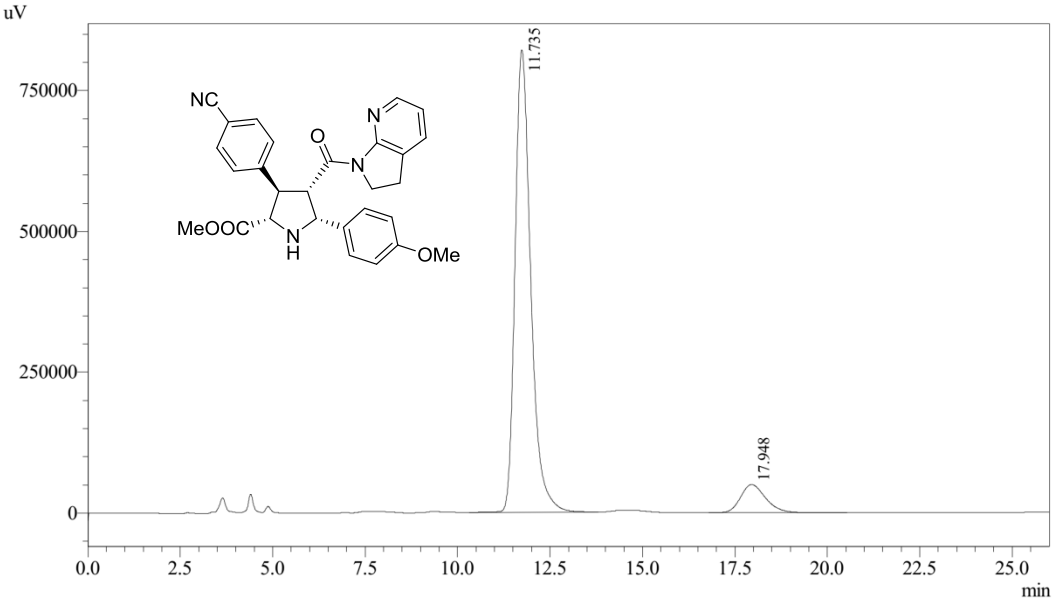




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.553	17609009	606833	49.602	61.694
2	17.524	17891381	376792	50.398	38.306
Total		35500390	983625	100.000	100.000

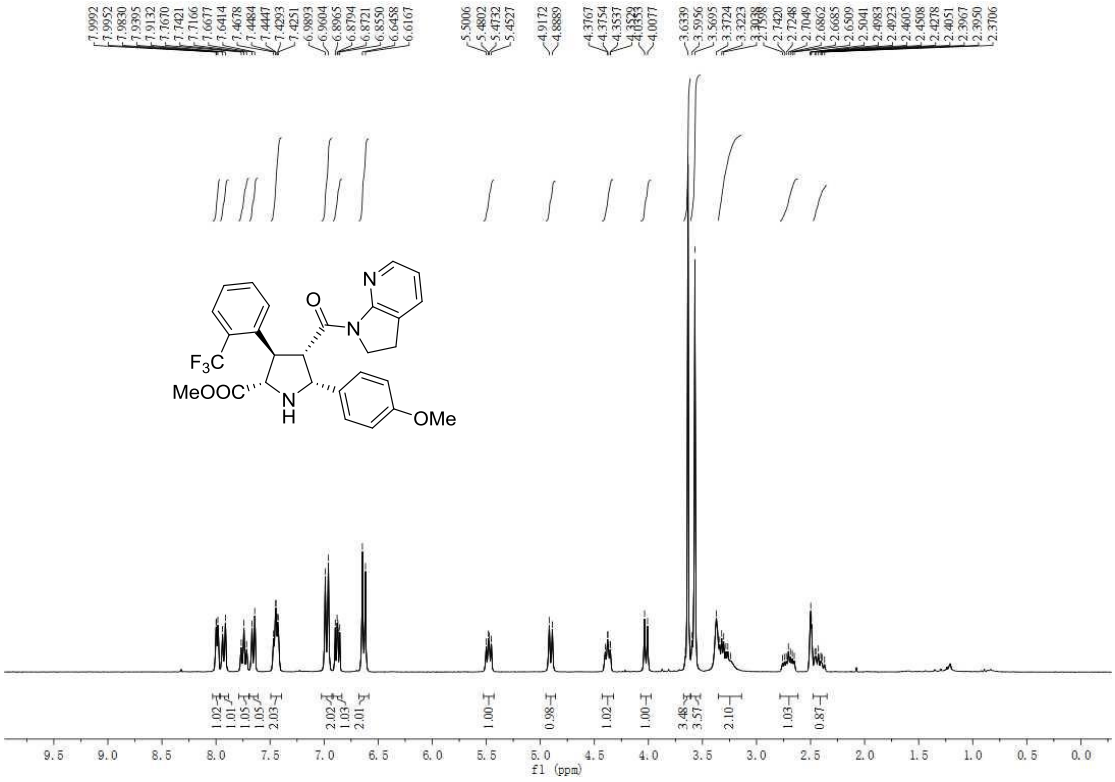


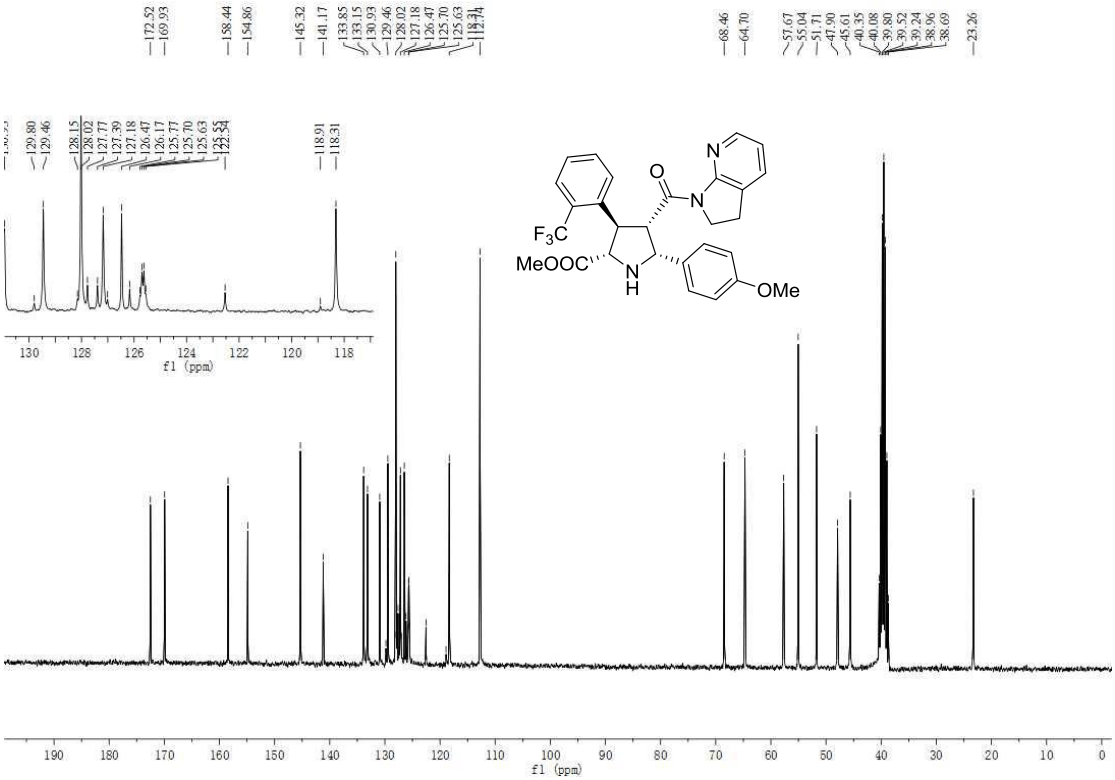
1 Det.A Ch1 / 254nm

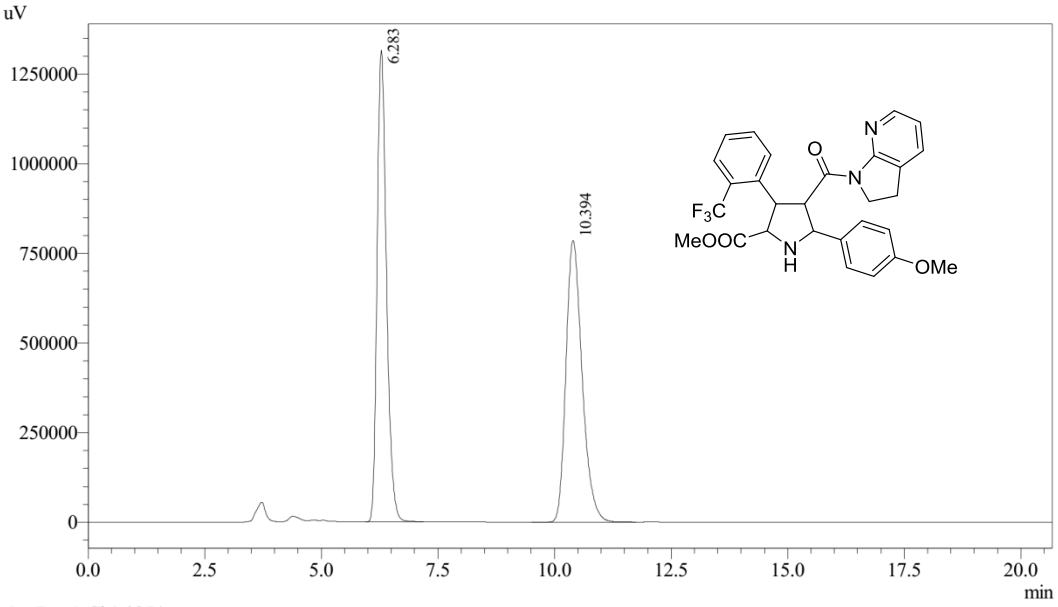
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.735	24181087	820323	91.077	94.255
2	17.948	2369153	50003	8.923	5.745
Total		26550240	870326	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3pa



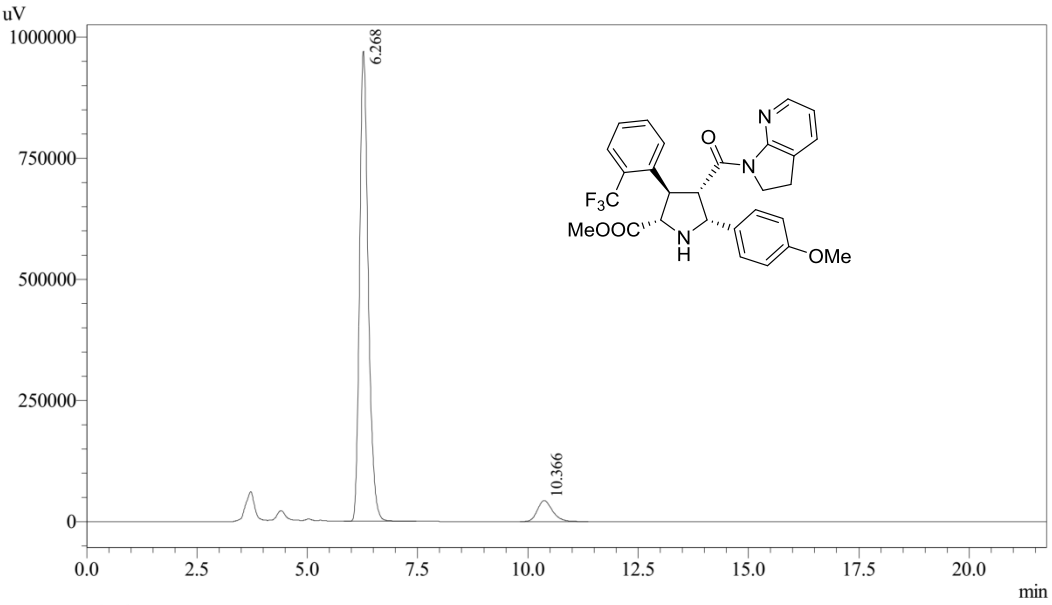




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.283	18411370	1315113	49.319	62.582
2	10.394	18920027	786301	50.681	37.418
Total		37331397	2101414	100.000	100.000

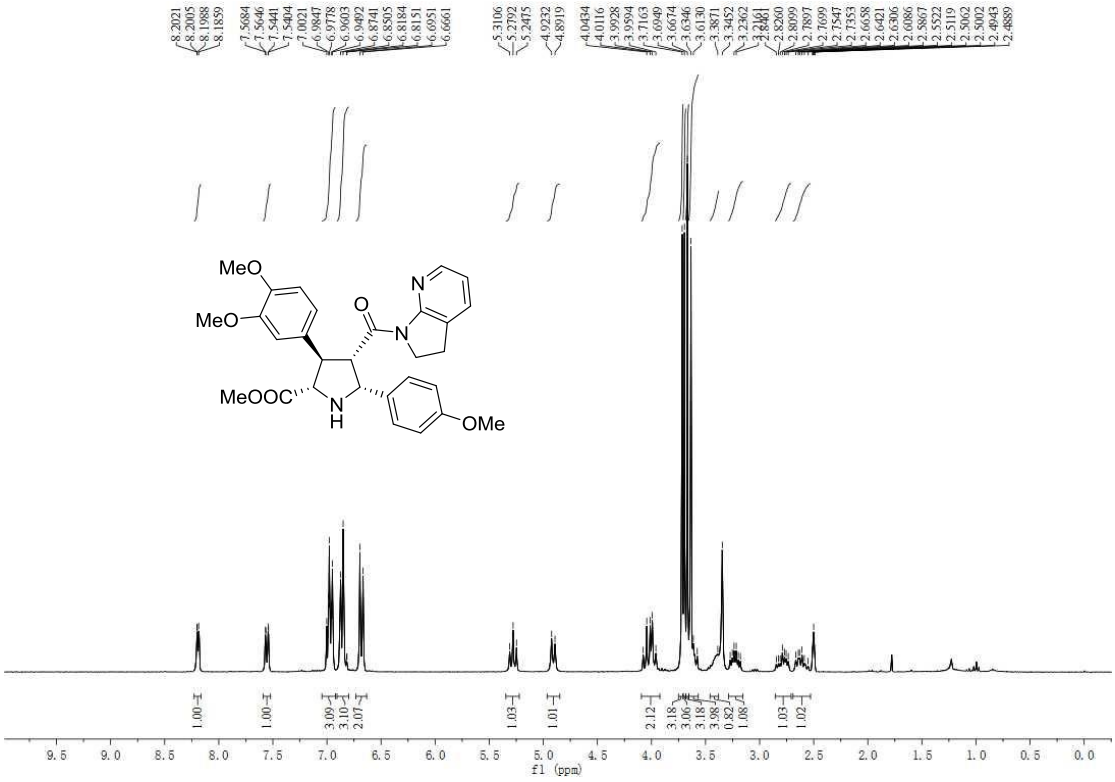


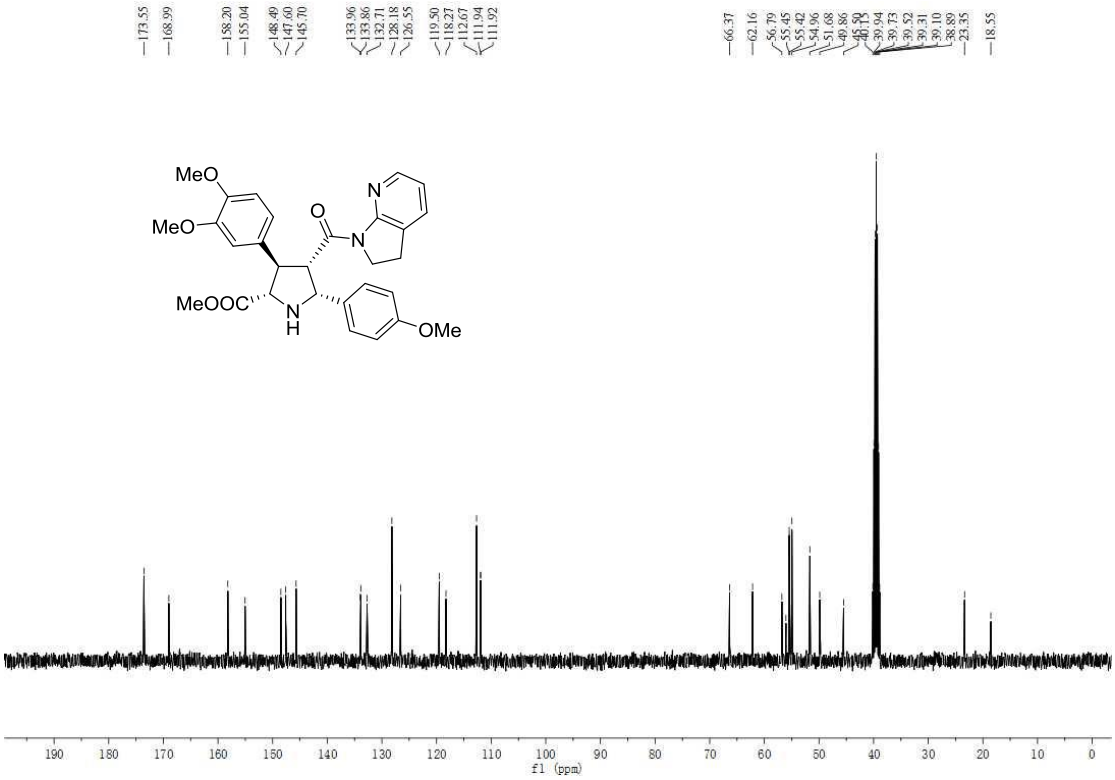
1 Det.A Ch1 / 254nm

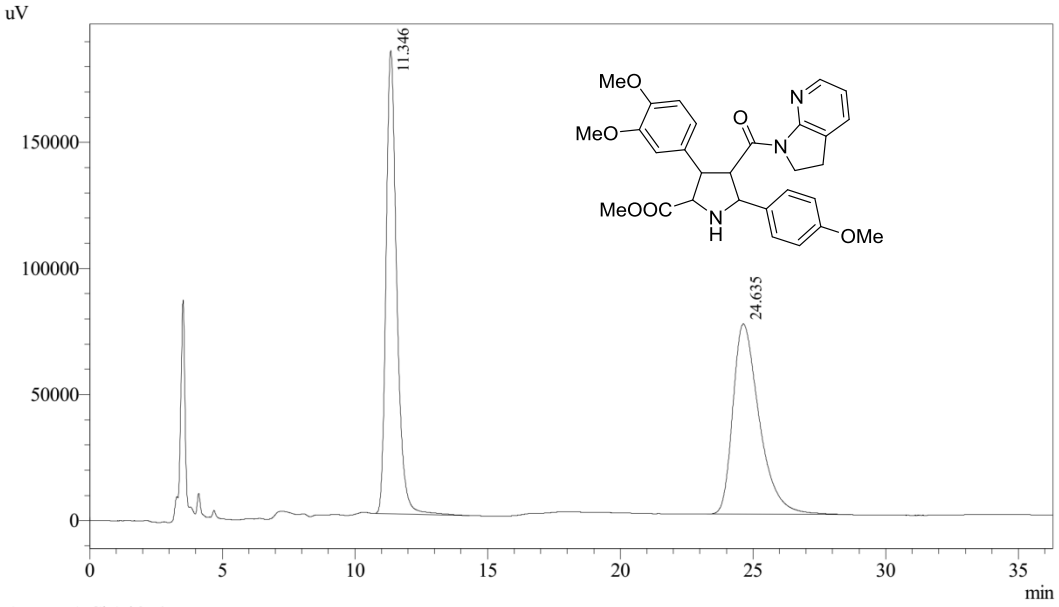
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.268	13310374	969961	92.837	95.731
2	10.366	1026919	43254	7.163	4.269
Total		14337293	1013215	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3qa



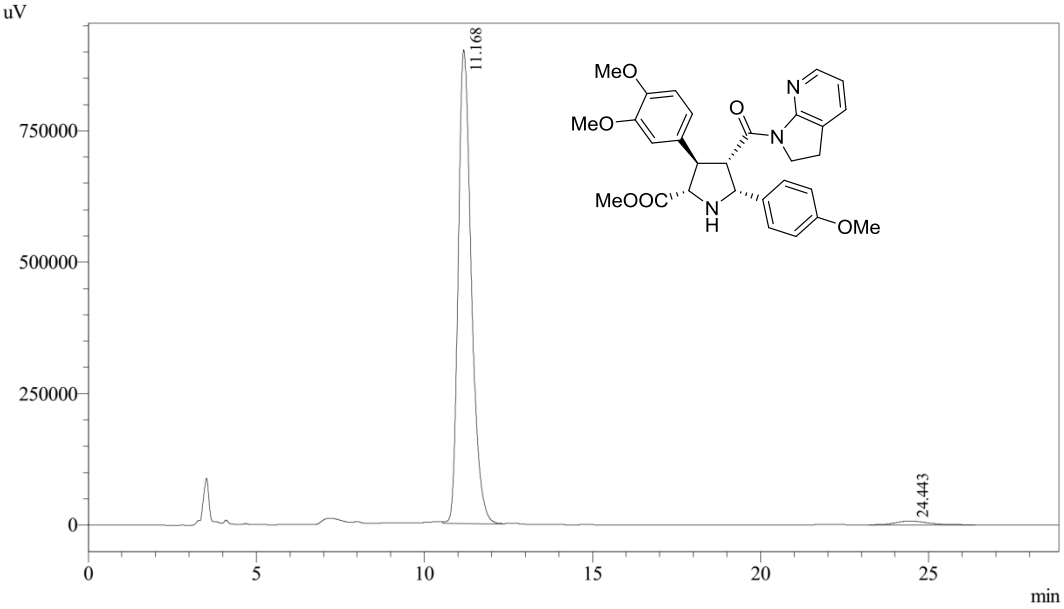




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.346	5156440	183876	49.544	70.889
2	24.635	5251445	75511	50.456	29.111
Total		10407885	259386	100.000	100.000

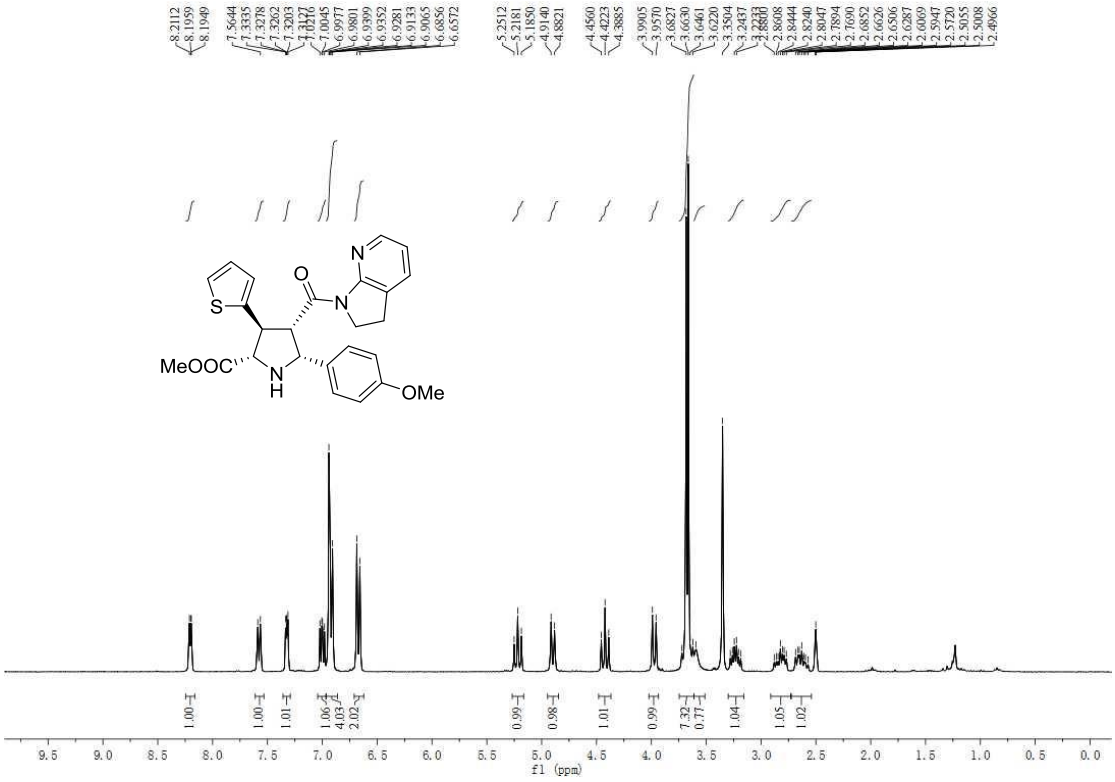


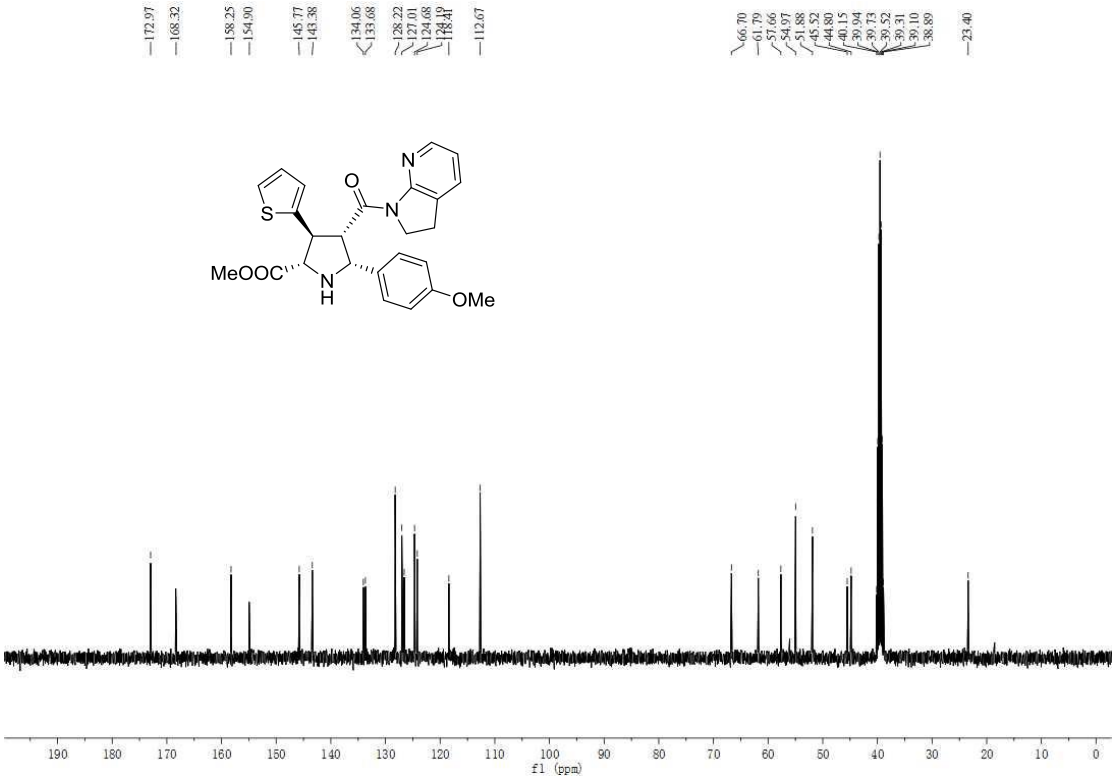
1 Det.A Ch1 / 254nm

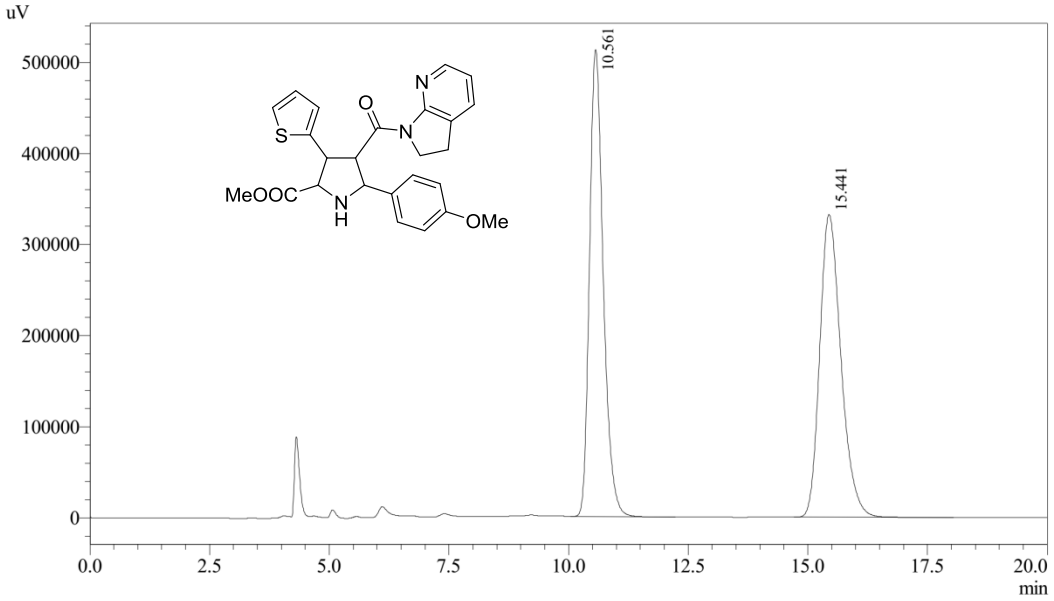
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.168	24487000	900893	98.156	99.221
2	24.443	460021	7070	1.844	0.779
Total		24947021	907964	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ra



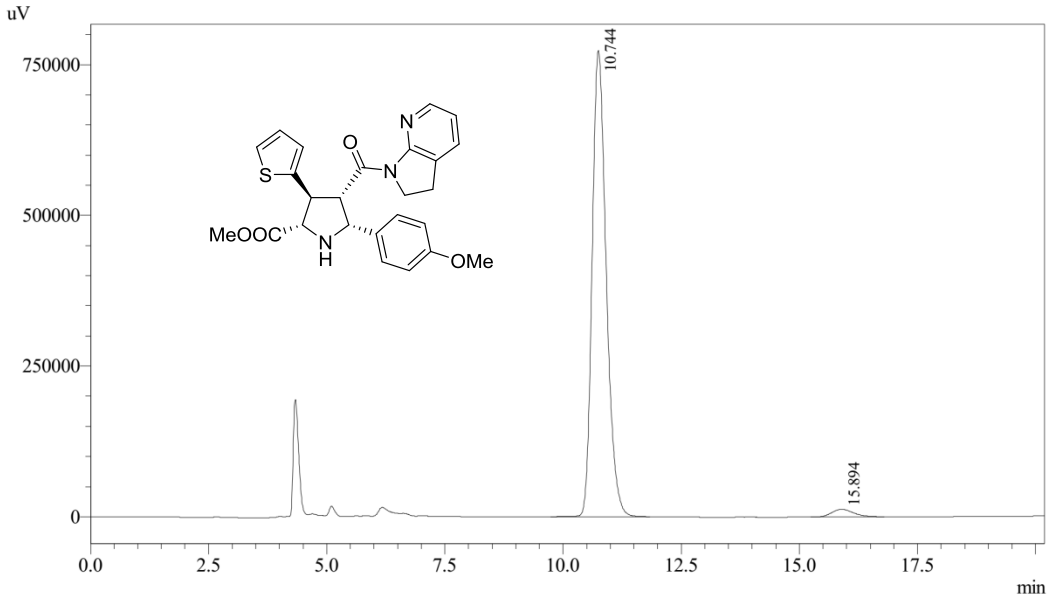




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.561	10221951	512362	49.867	60.670
2	15.441	10276405	332146	50.133	39.330
Total		20498356	844507	100.000	100.000

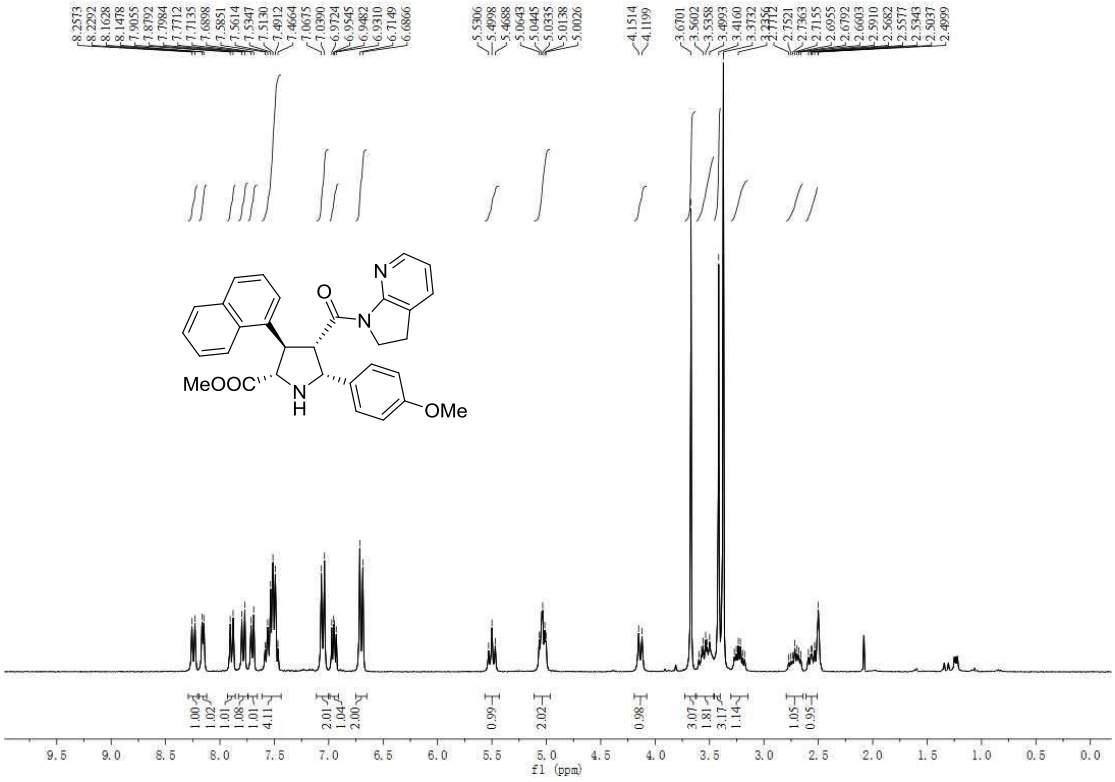


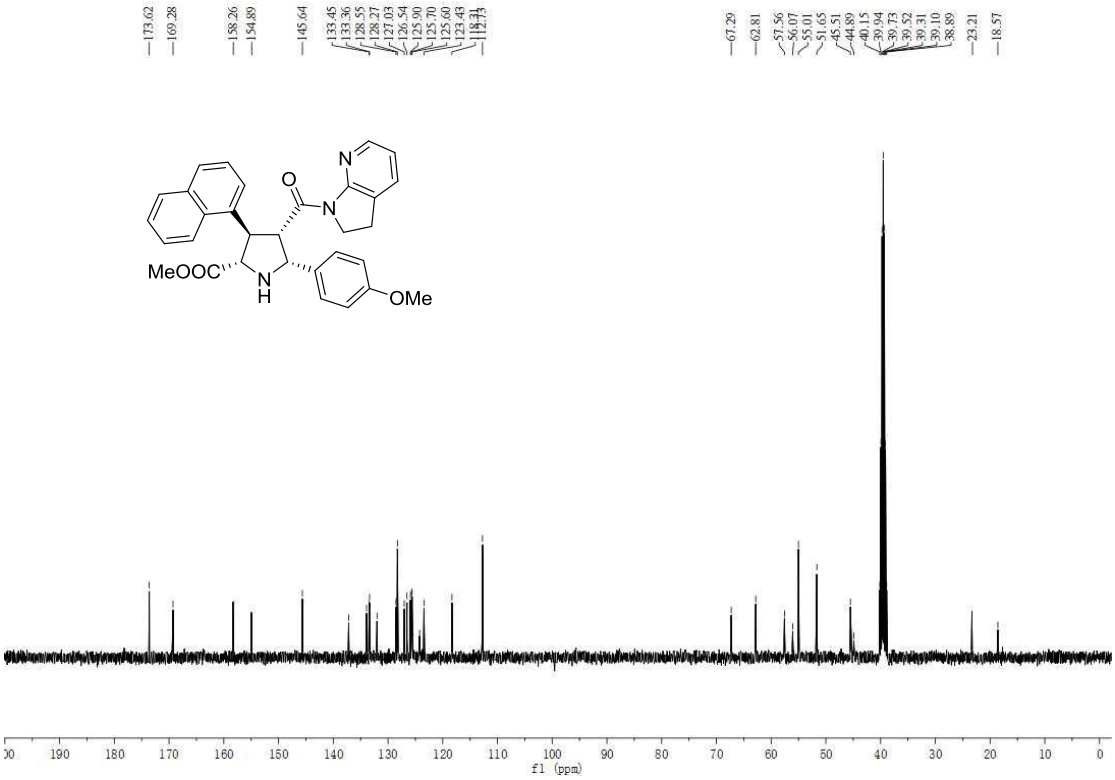
1 Det.A Ch1 / 254nm

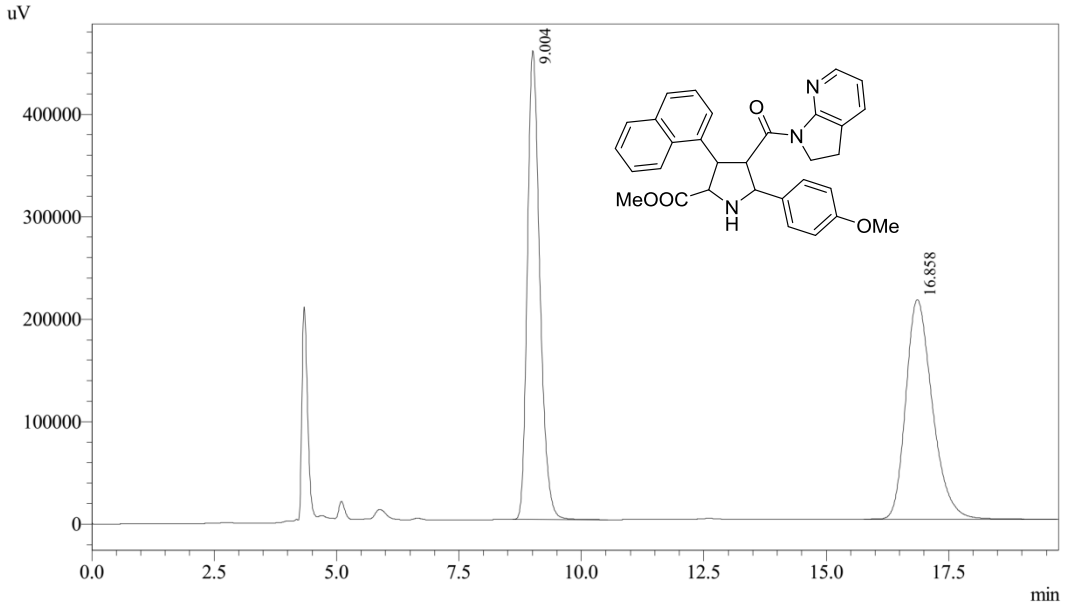
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.744	16021191	773188	97.503	98.373
2	15.894	410243	12790	2.497	1.627
Total		16431434	785979	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3sa



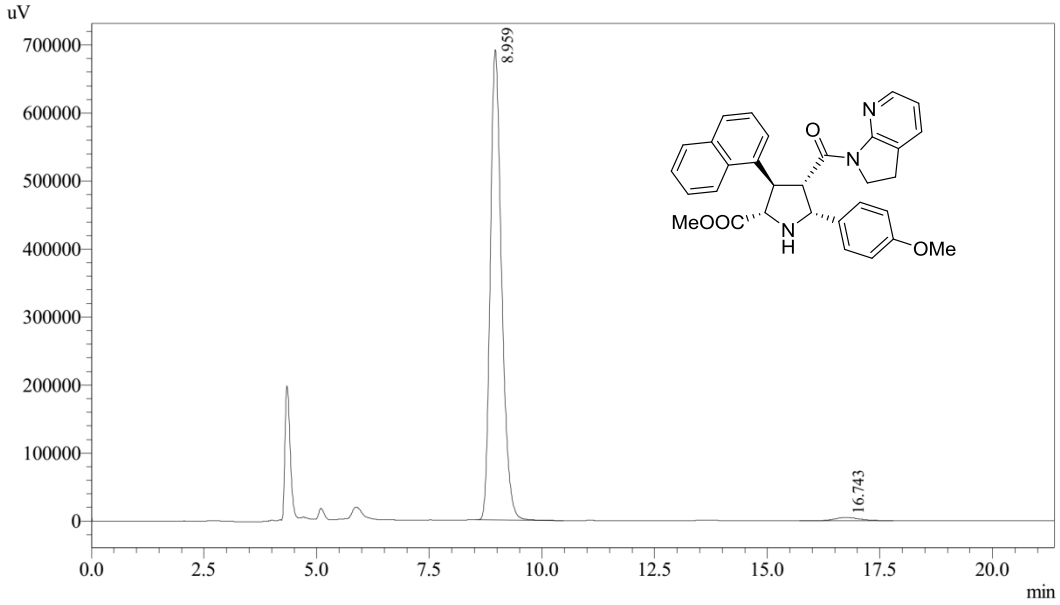




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.004	8101679	457626	49.998	68.124
2	16.858	8102417	214126	50.002	31.876
Total		16204096	671752	100.000	100.000

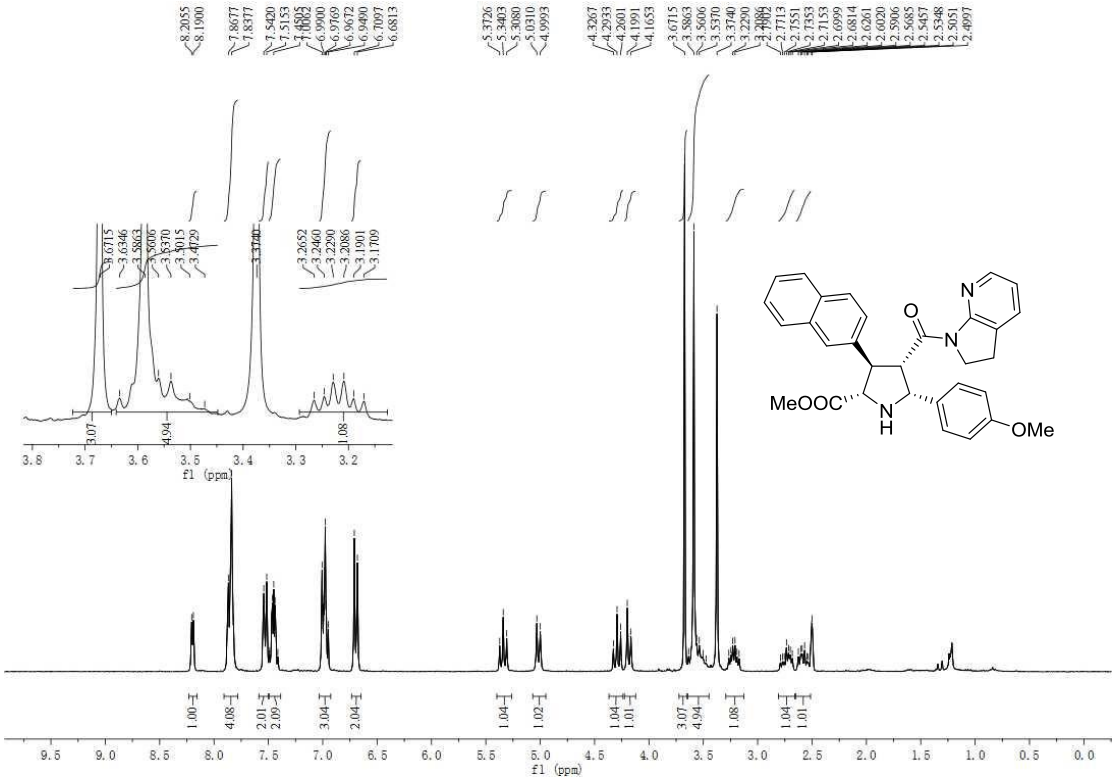


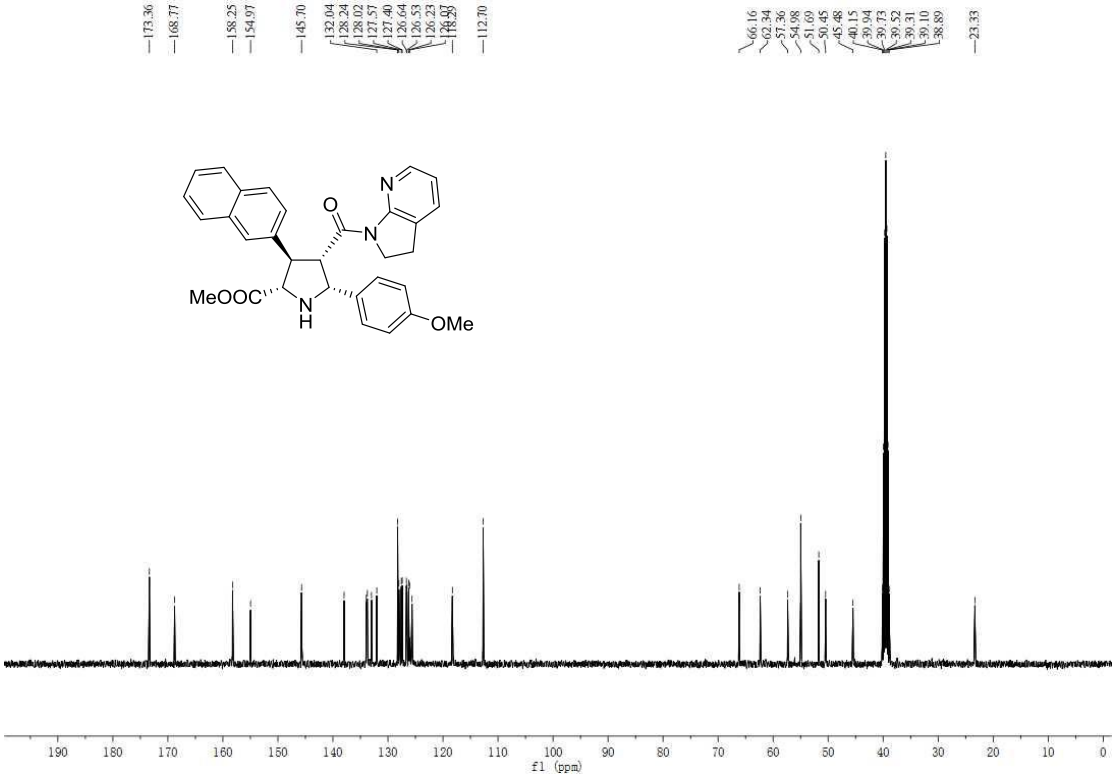
1 Det.A Ch1 / 254nm

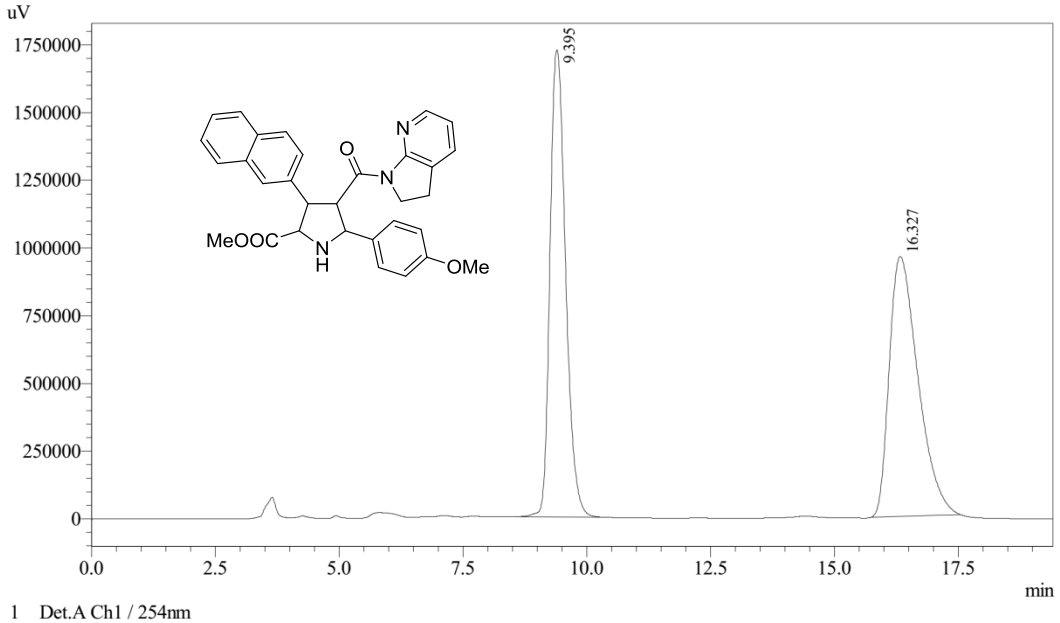
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.959	12144645	691144	98.483	99.313
2	16.743	187026	4782	1.517	0.687
Total		12331671	695926	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ta



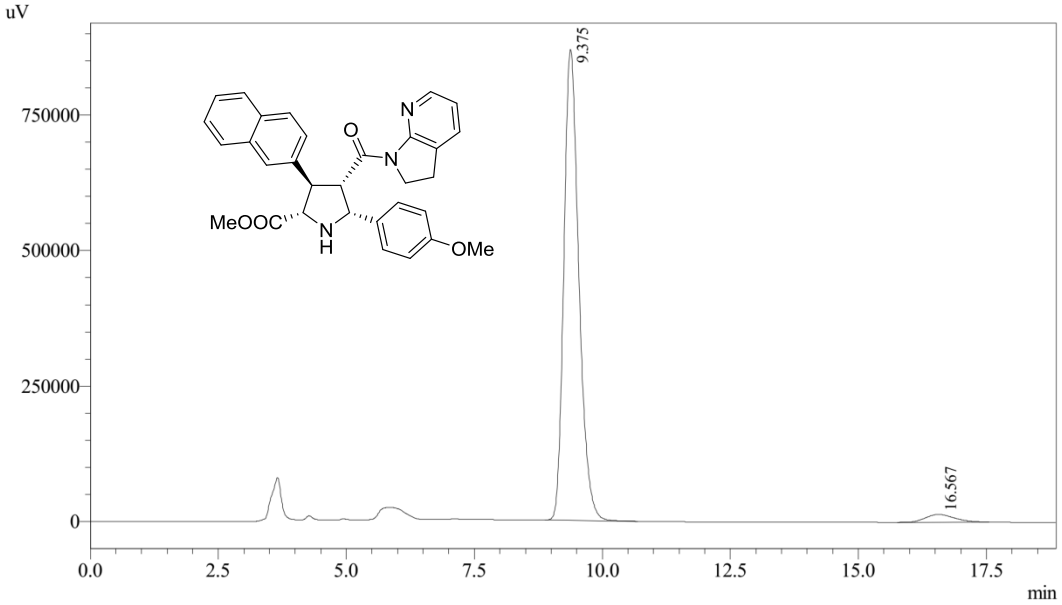




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.395	37822725	1724529	49.359	64.246
2	16.327	38804797	959735	50.641	35.754
Total		76627523	2684264	100.000	100.000

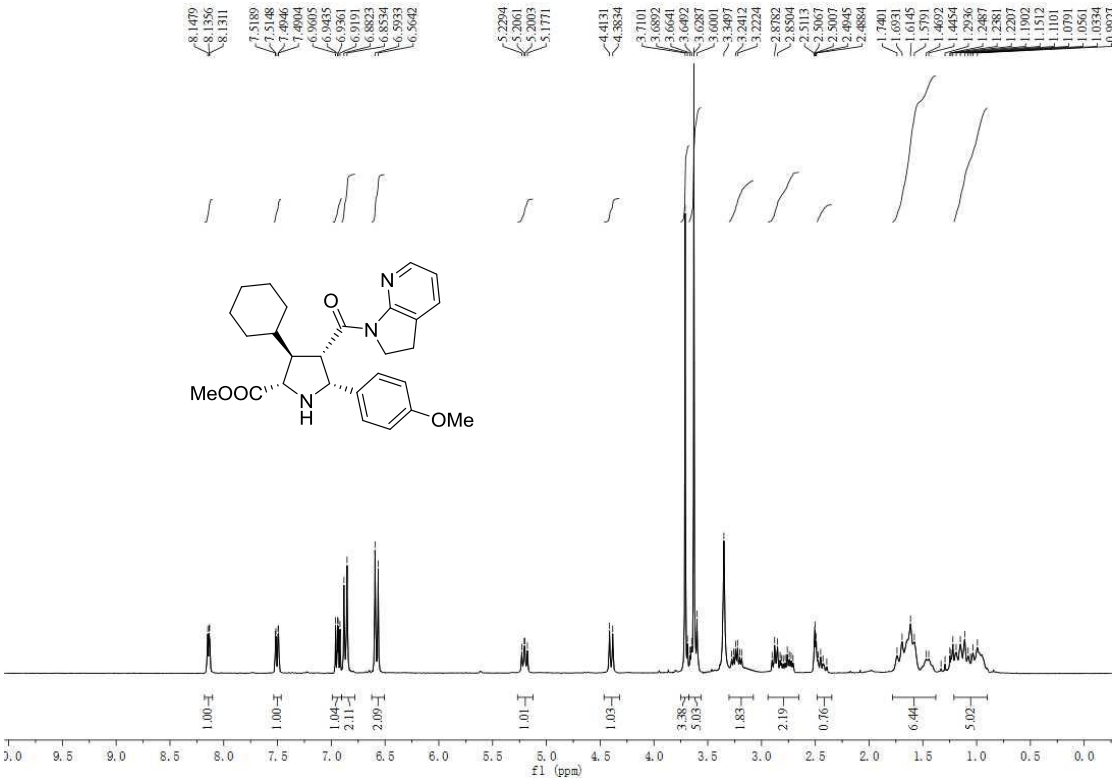


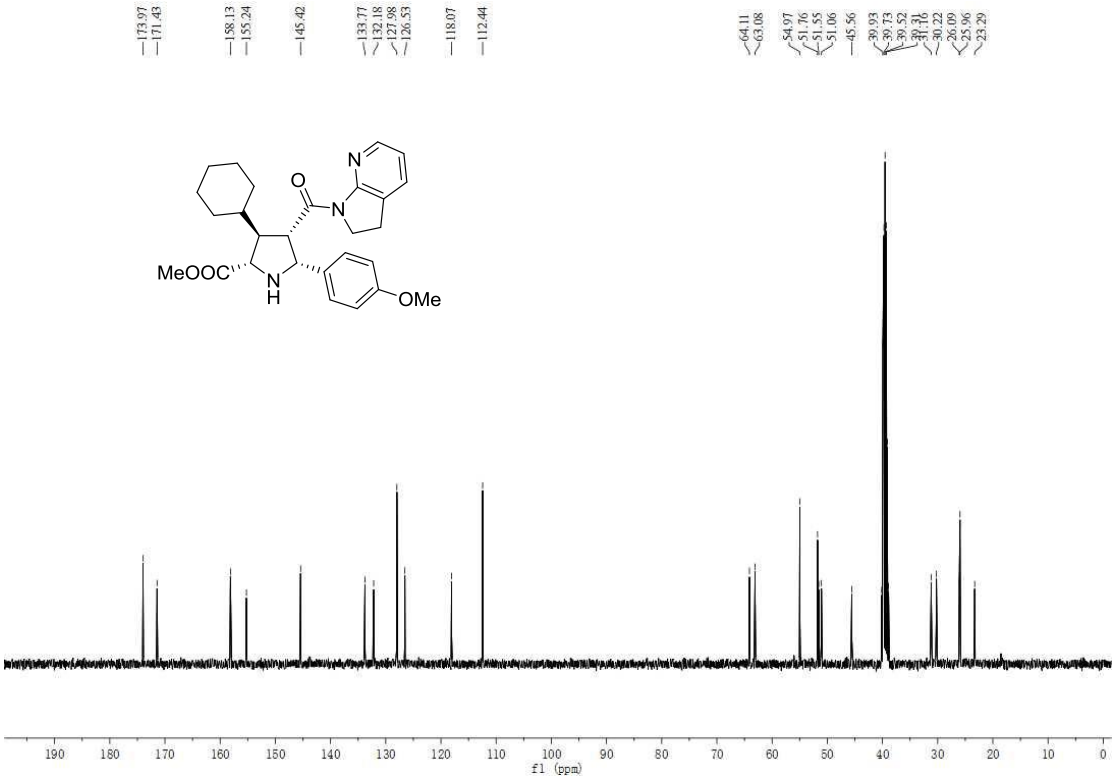
1 Det.A Ch1 / 254nm

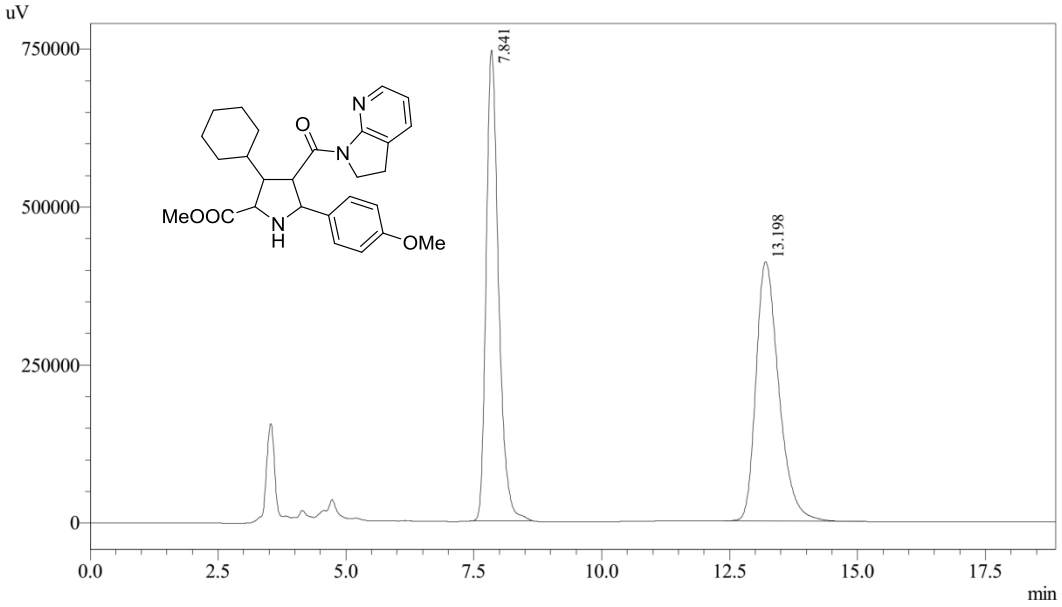
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.375	17638562	868237	96.893	98.378
2	16.567	565600	14314	3.107	1.622
Total		18204163	882552	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ua



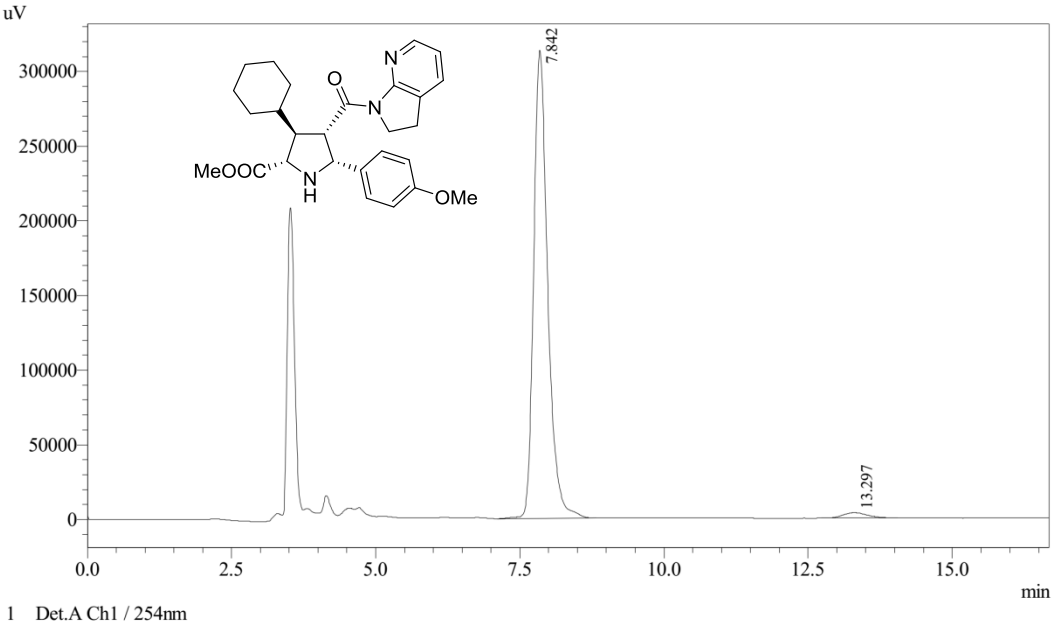




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.841	12560647	745174	49.624	64.489
2	13.198	12751189	410326	50.376	35.511
Total		25311836	1155500	100.000	100.000

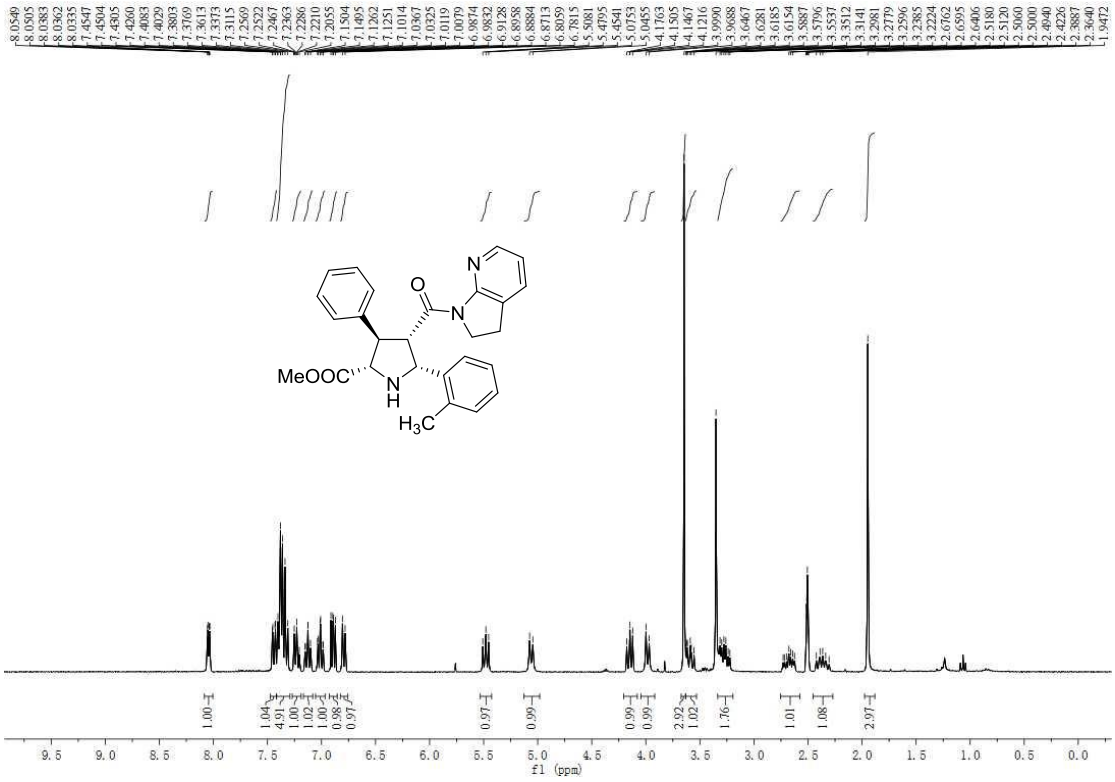


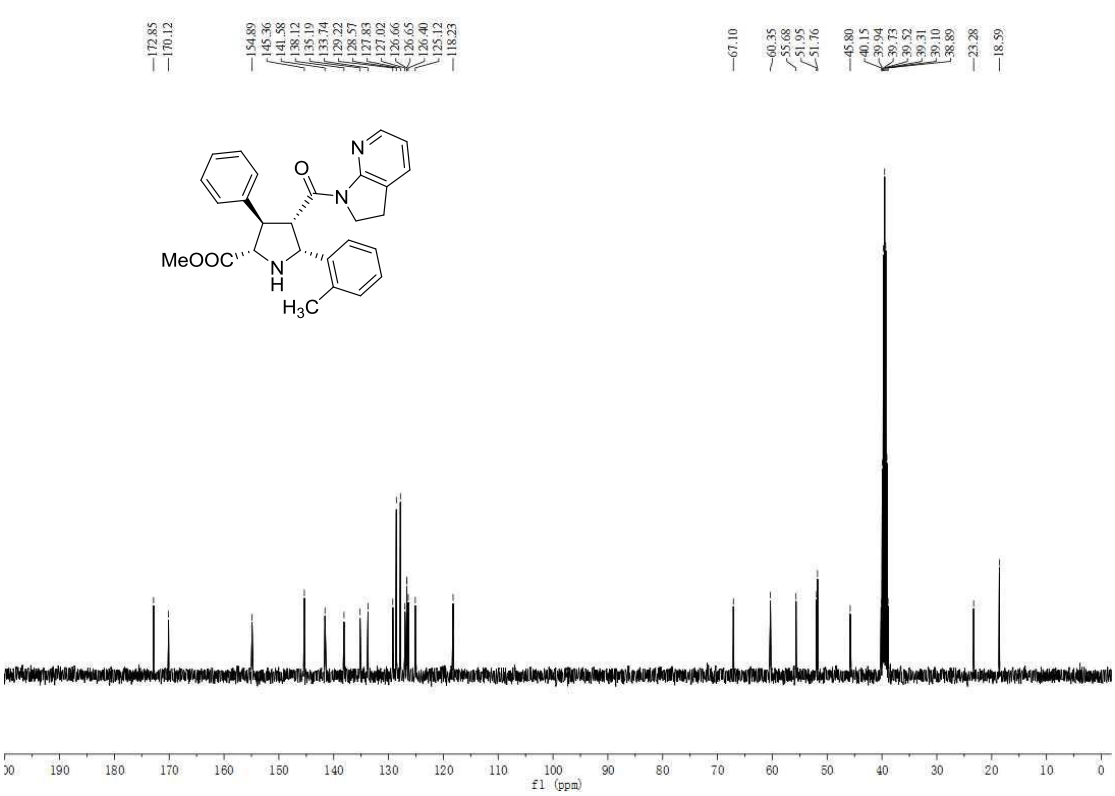
1 Det.A Ch1 / 254nm

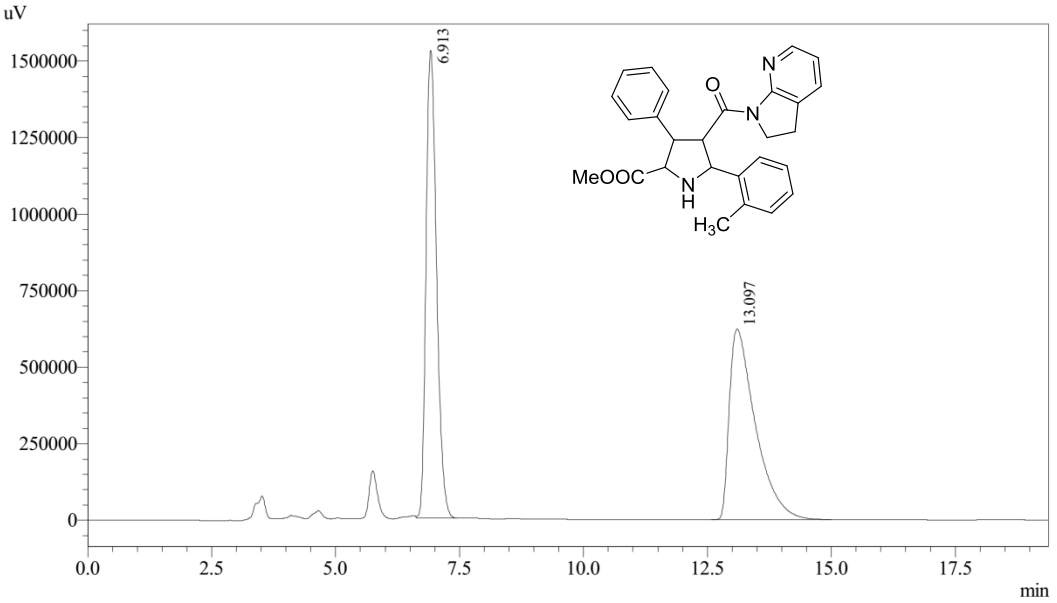
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.842	5307179	313464	98.012	98.858
2	13.297	107635	3622	1.988	1.142
Total		5414814	317086	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ab



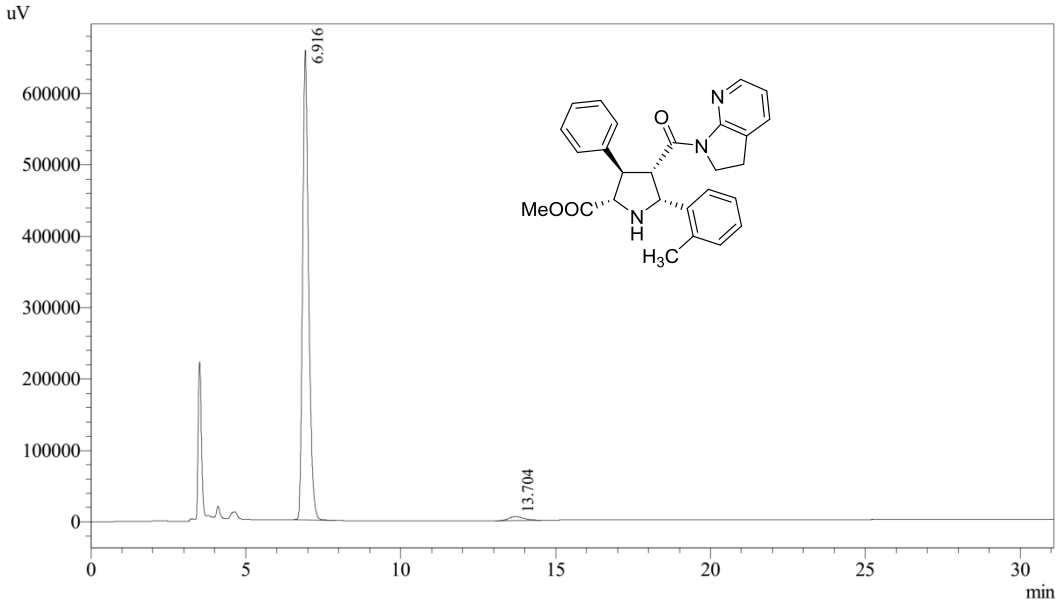




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.913	22508517	1527615	49.703	71.048
2	13.097	22777499	622513	50.297	28.952
Total		45286015	2150128	100.000	100.000

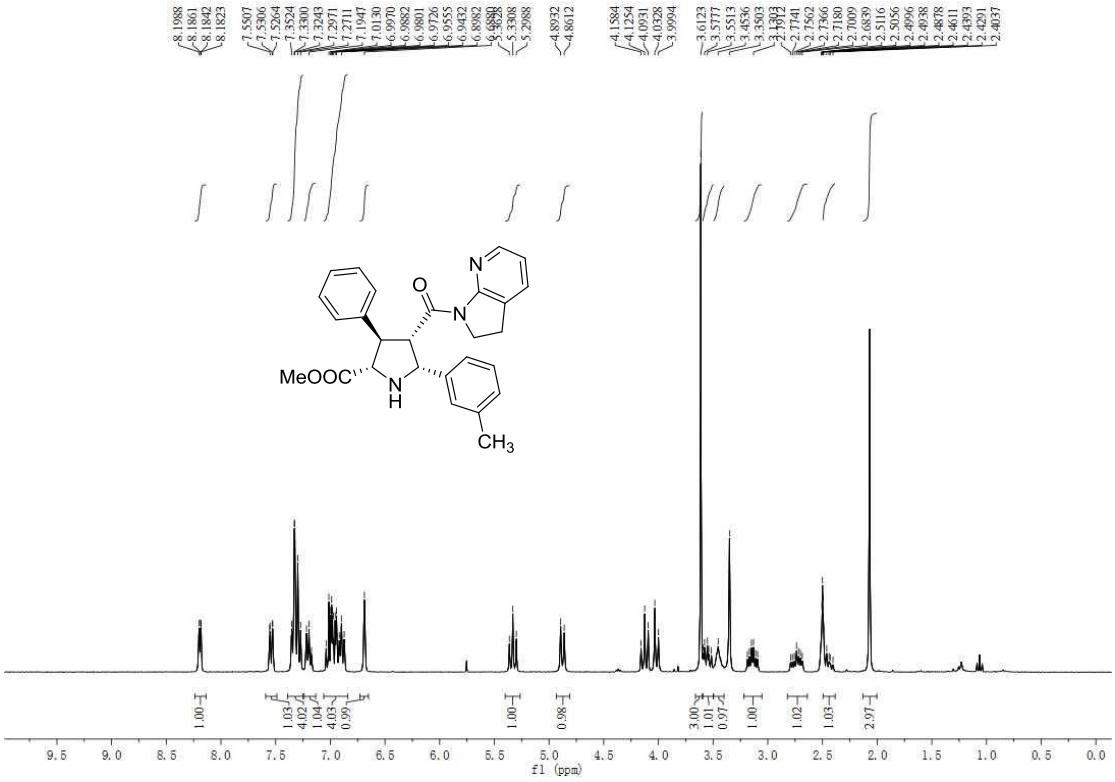


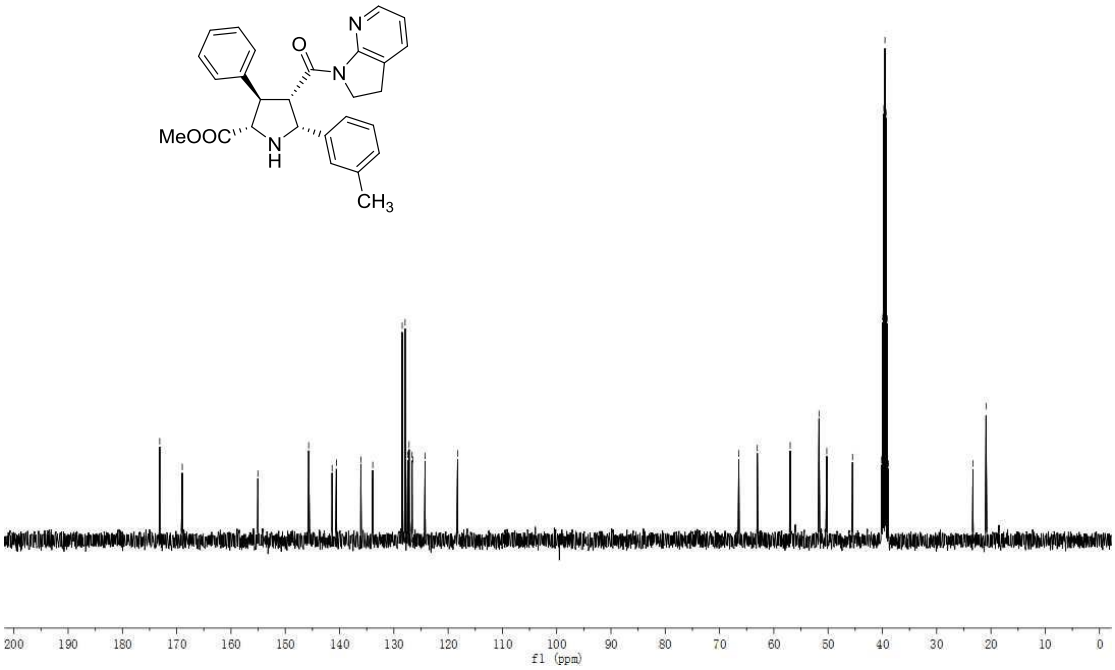
1 Det.A Ch1 / 254nm

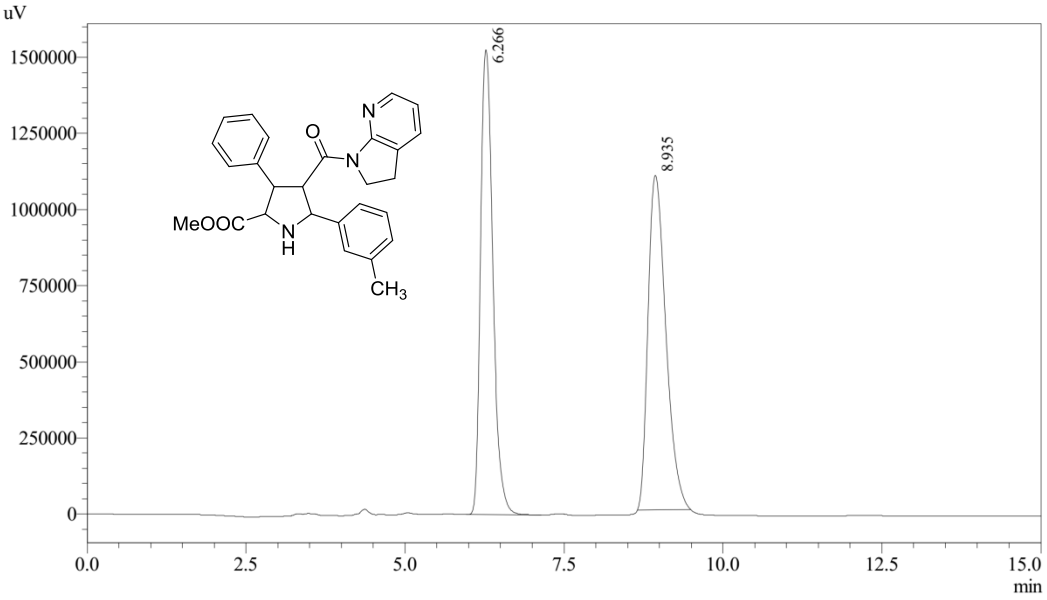
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.916	8871803	657439	97.981	99.185
2	13.704	182816	5401	2.019	0.815
Total		9054619	662841	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ac



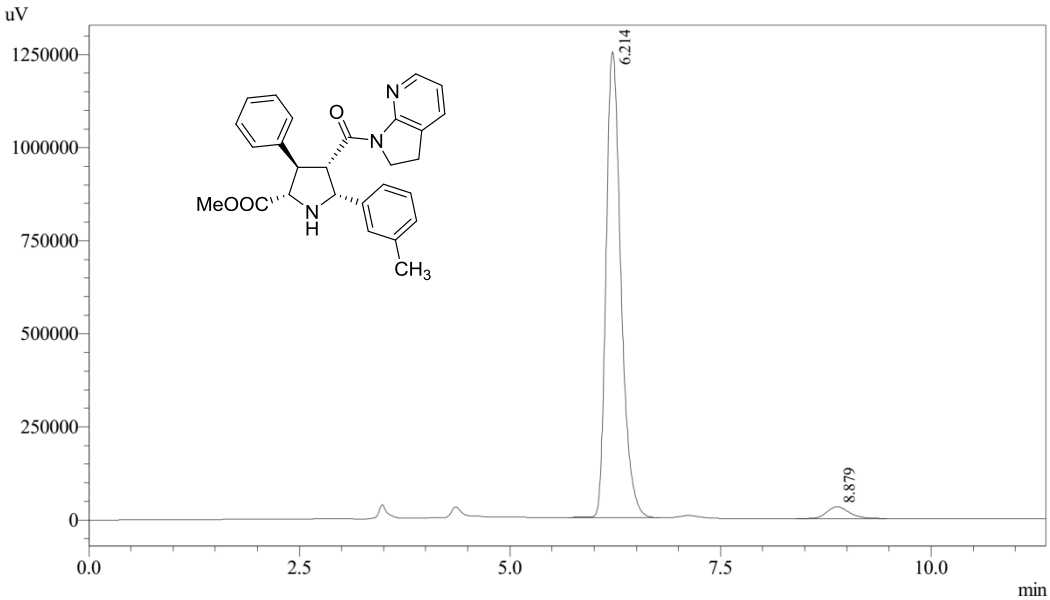




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.266	20719781	1526770	49.311	58.131
2	8.935	21298432	1099655	50.689	41.869
Total		42018212	2626425	100.000	100.000

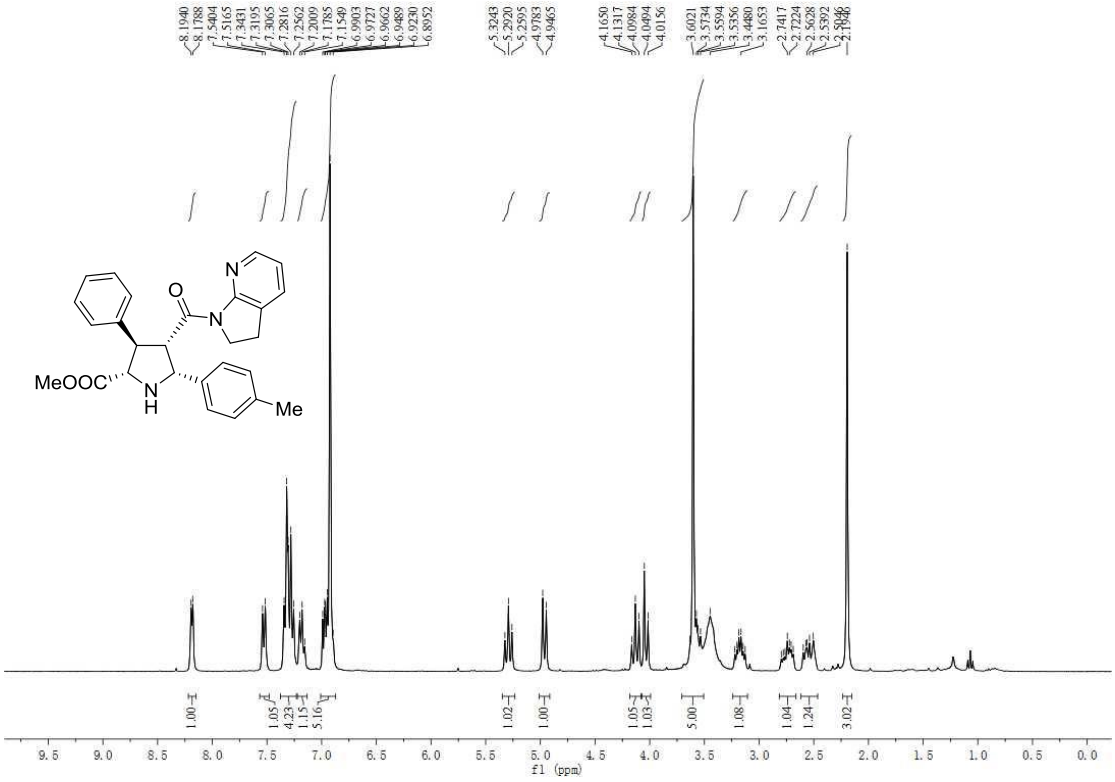


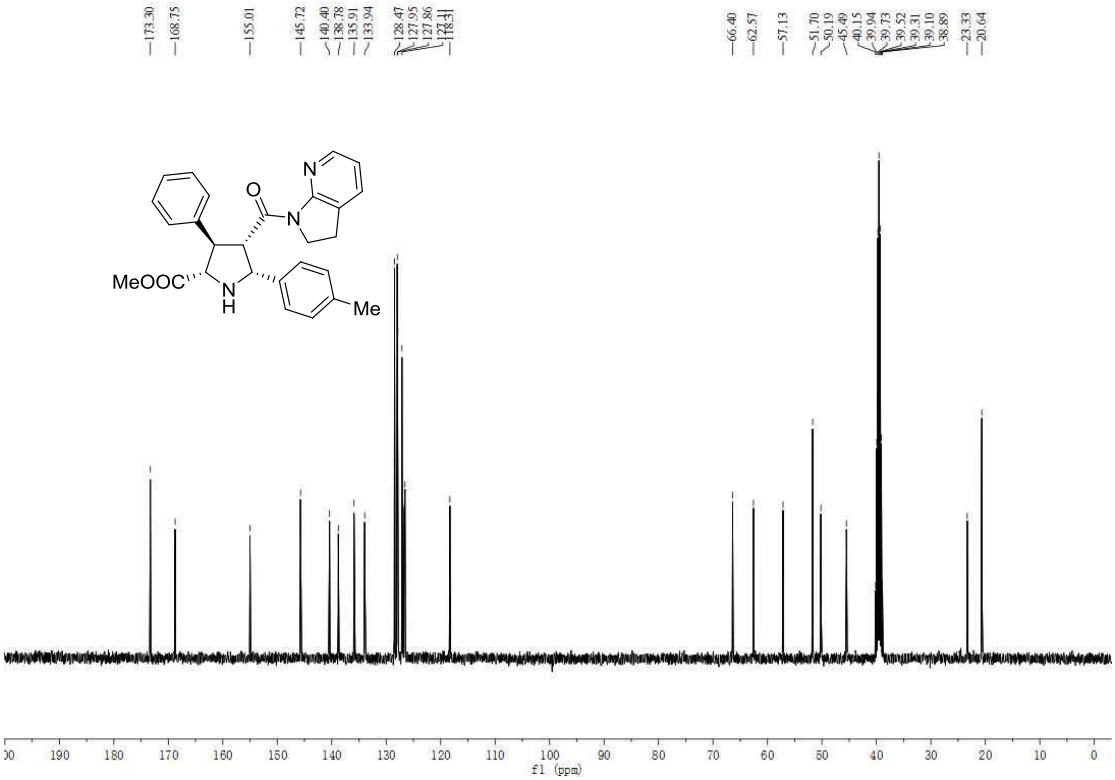
1 Det.A Ch1 / 254nm

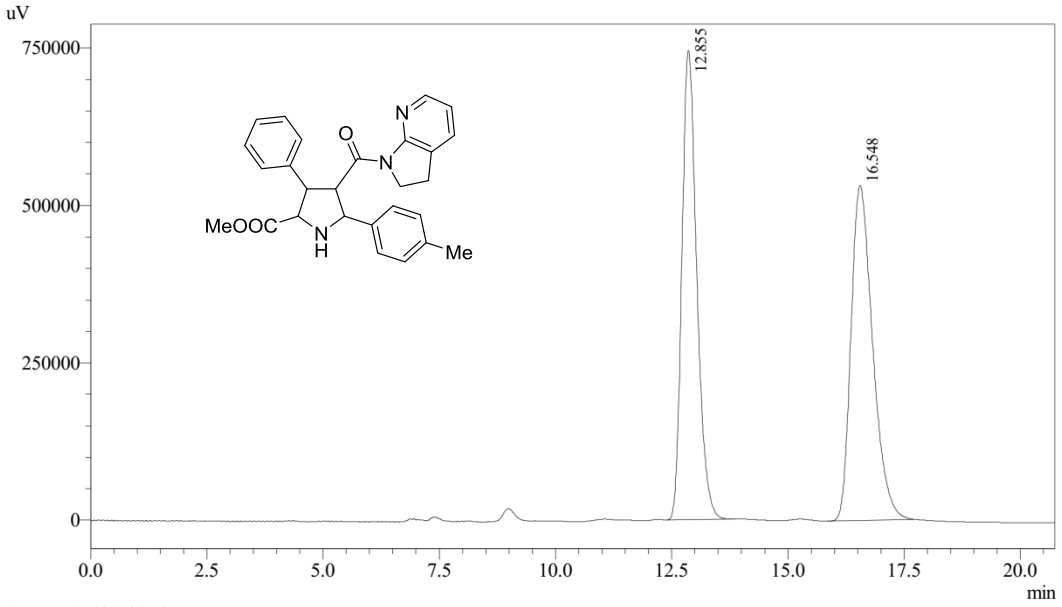
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.214	15350926	1251309	96.377	97.543
2	8.879	577075	31520	3.623	2.457
Total		15928001	1282829	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ad



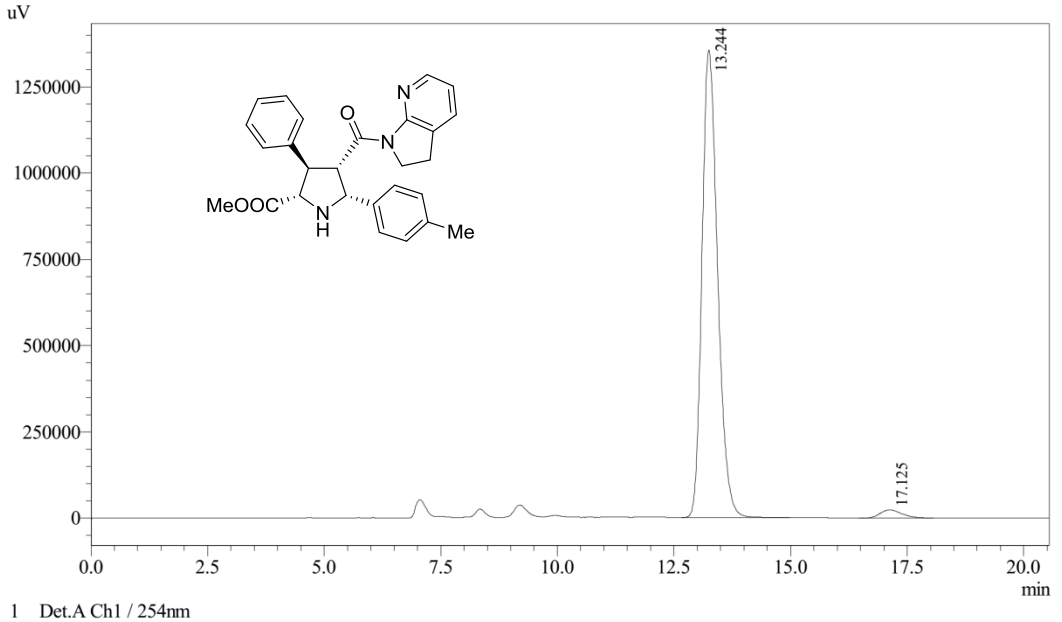




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.855	16609249	744944	49.088	58.337
2	16.548	17226199	532032	50.912	41.663
Total		33835448	1276976	100.000	100.000

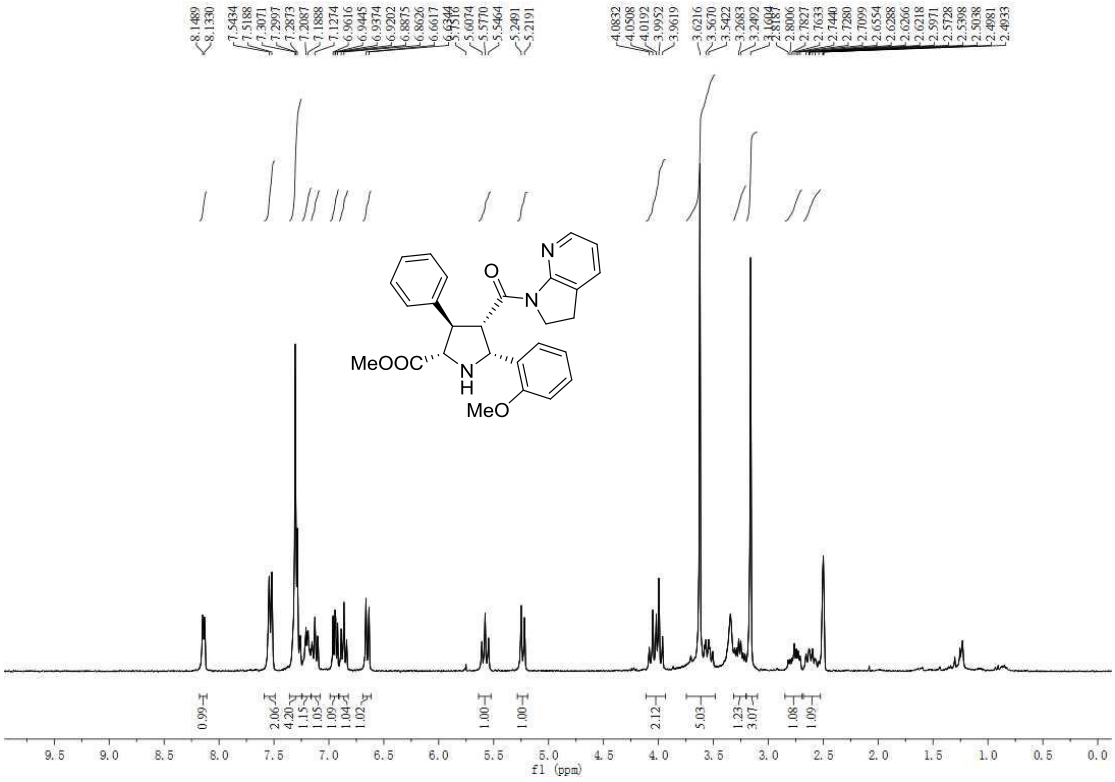


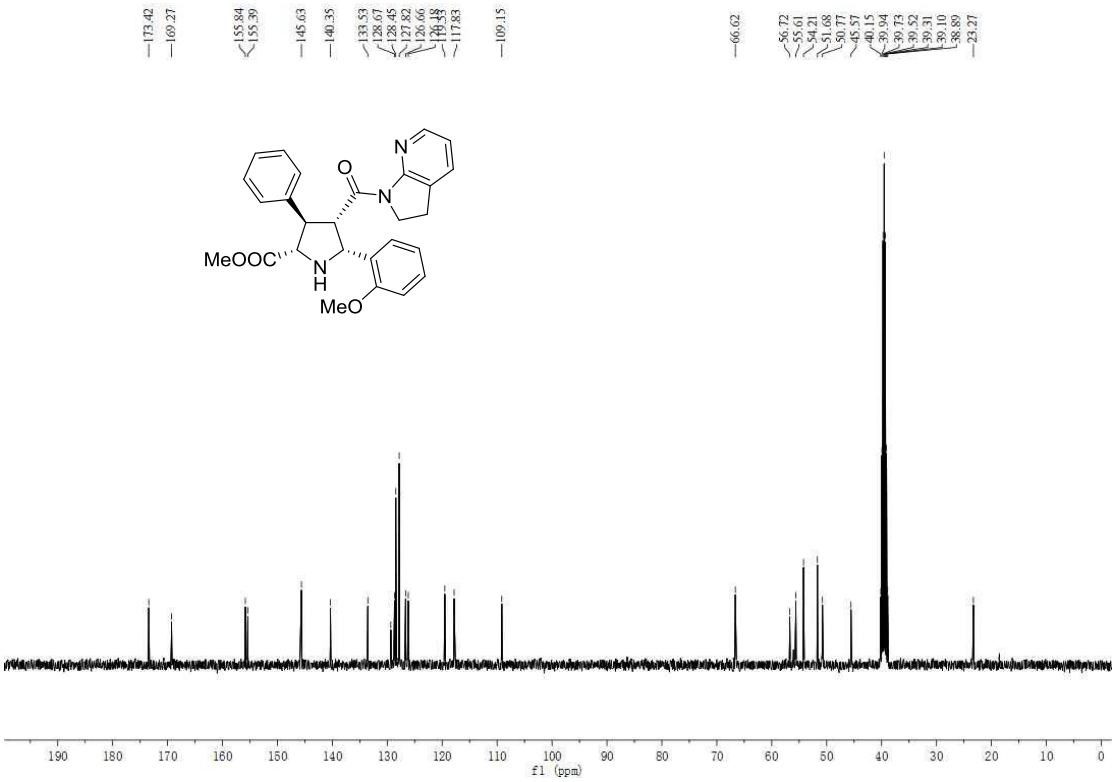
1 Det.A Ch1 / 254nm

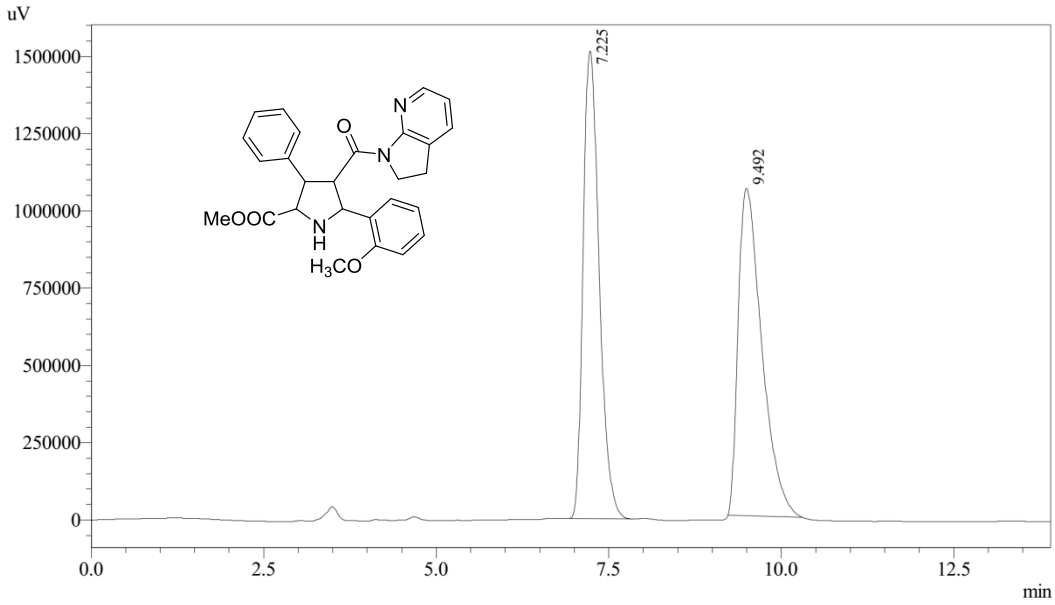
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.244	31537511	1355214	97.600	98.285
2	17.125	775593	23647	2.400	1.715
Total		32313105	1378861	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ae



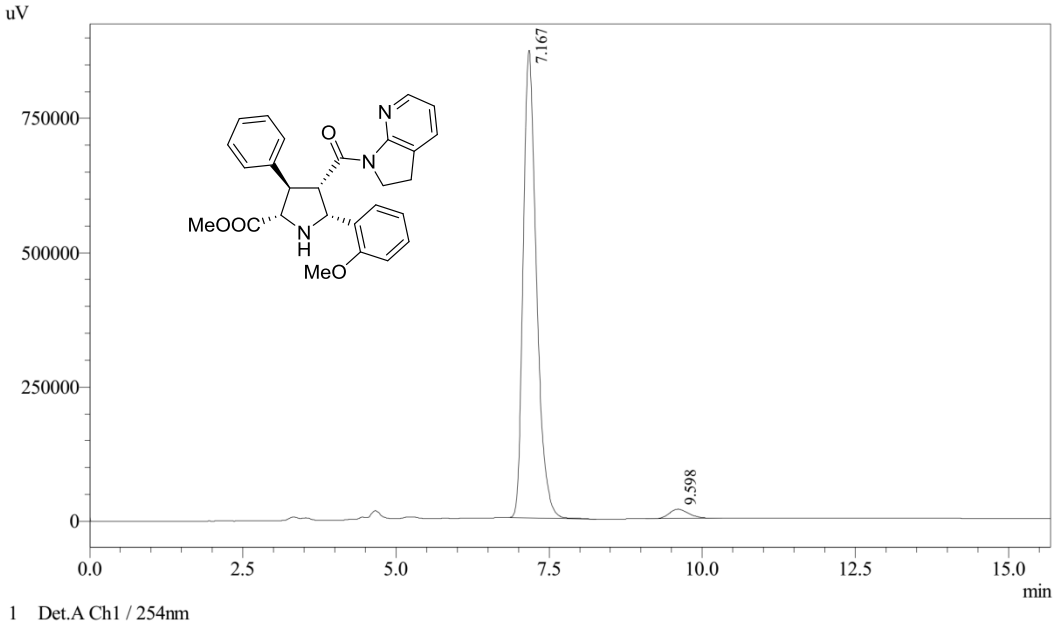




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.225	24563555	1513111	49.280	58.797
2	9.492	25281051	1060337	50.720	41.203
Total		49844606	2573448	100.000	100.000

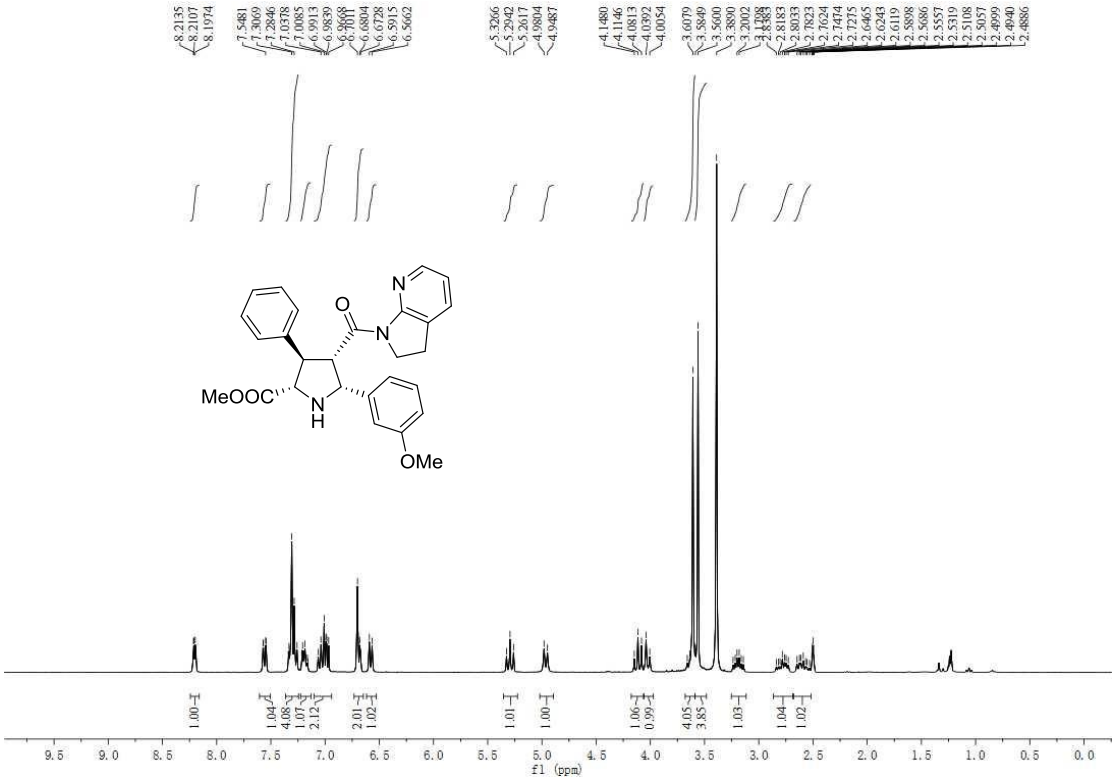


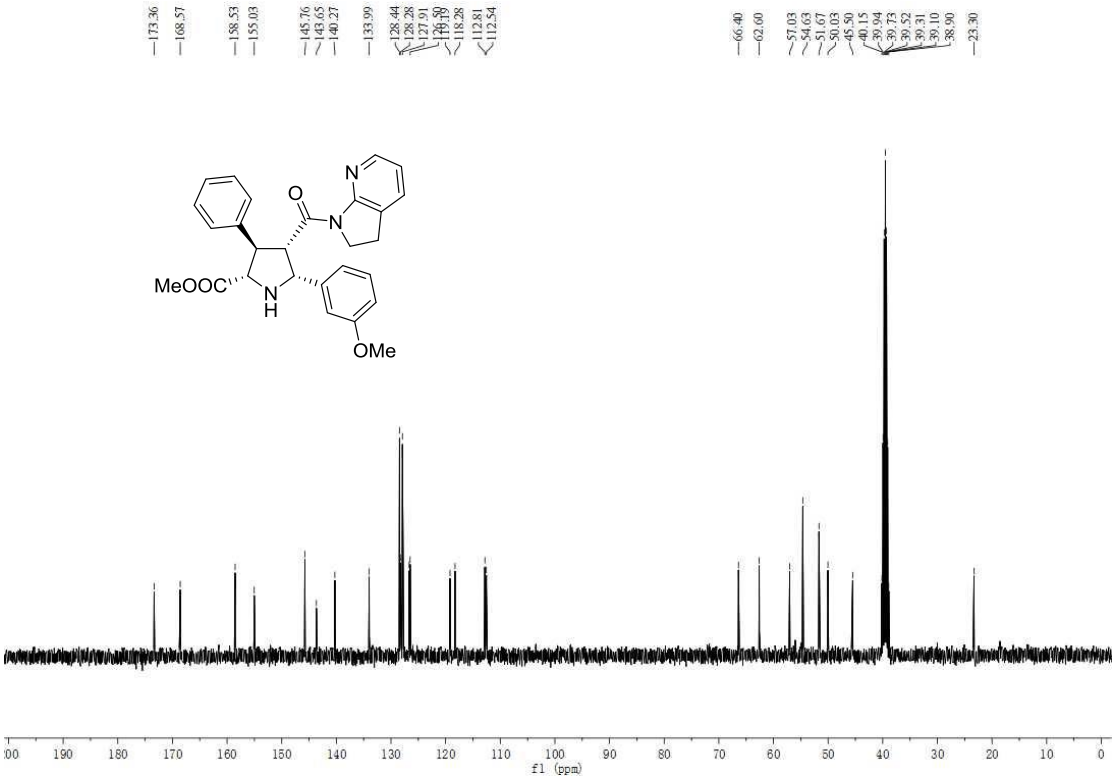
1 Det.A Ch1 / 254nm

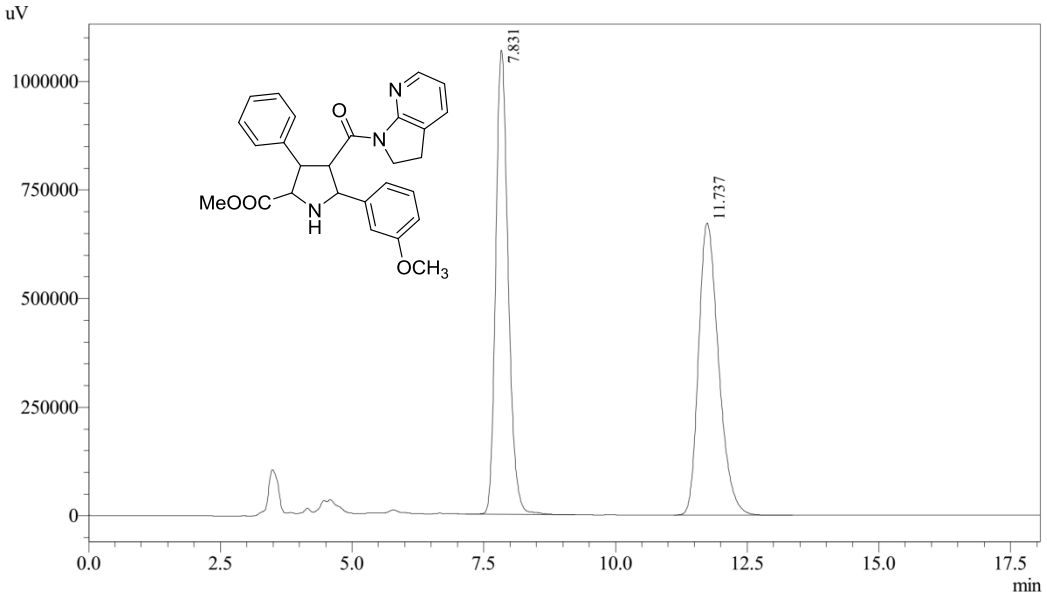
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.167	13141301	870453	97.085	98.026
2	9.598	394549	17525	2.915	1.974
Total		13535849	887978	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3af



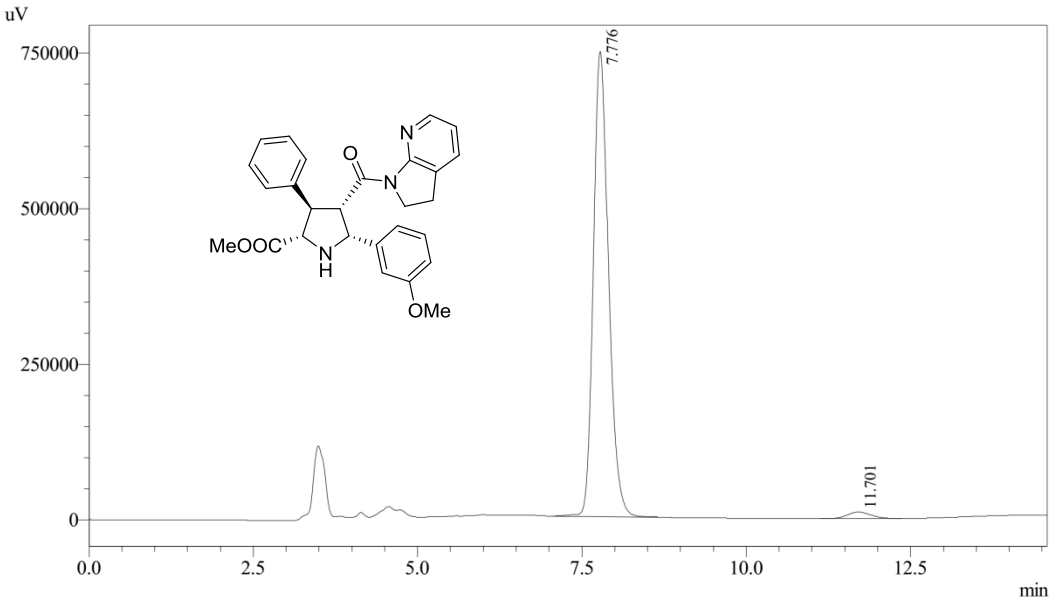




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.831	17589448	1068638	49.677	61.386
2	11.737	17818202	672221	50.323	38.614
Total		35407650	1740859	100.000	100.000

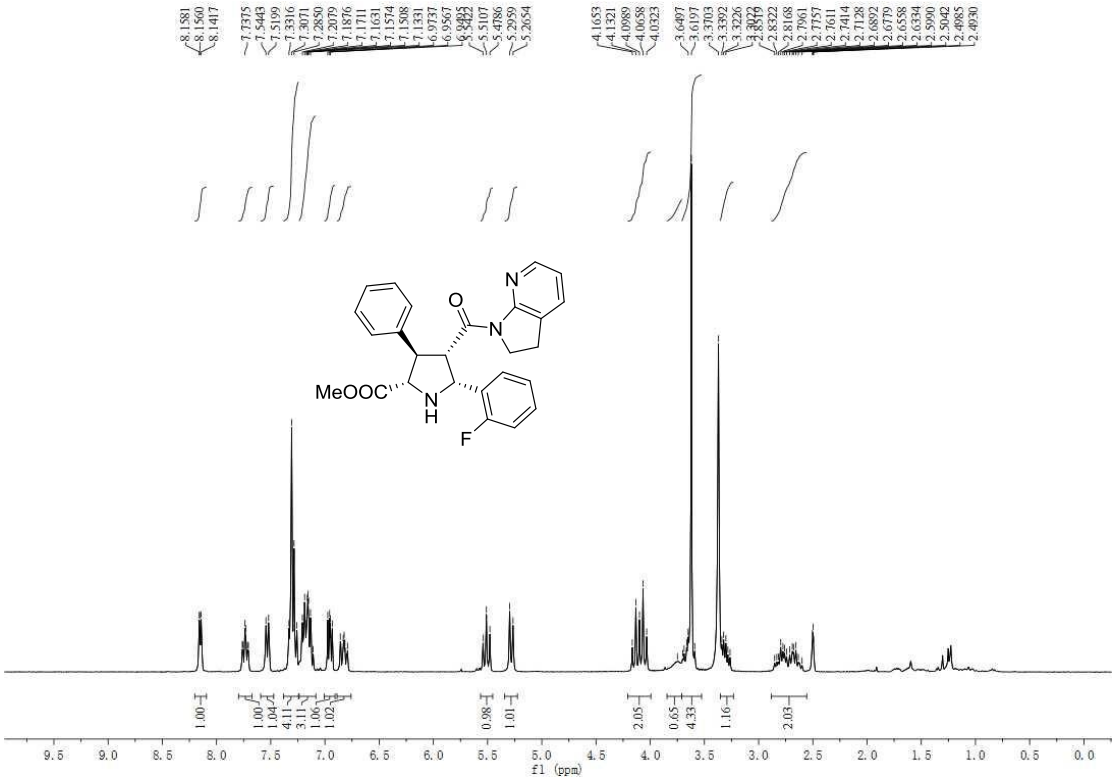


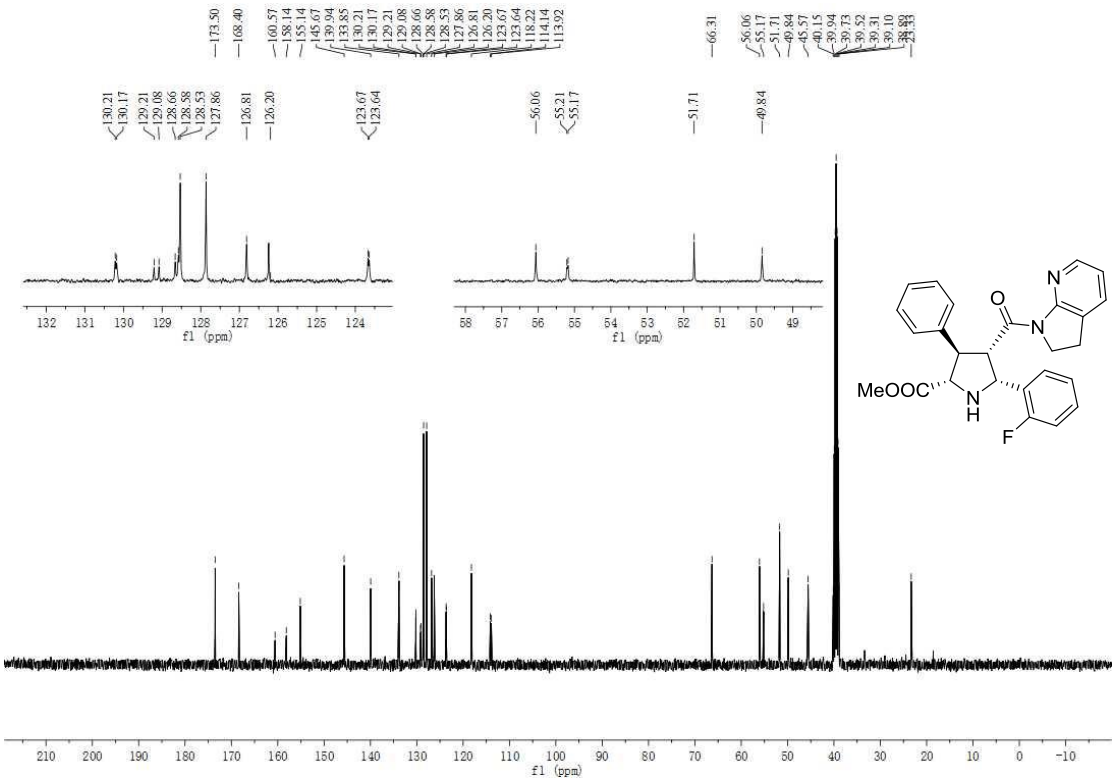
1 Det.A Ch1 / 254nm

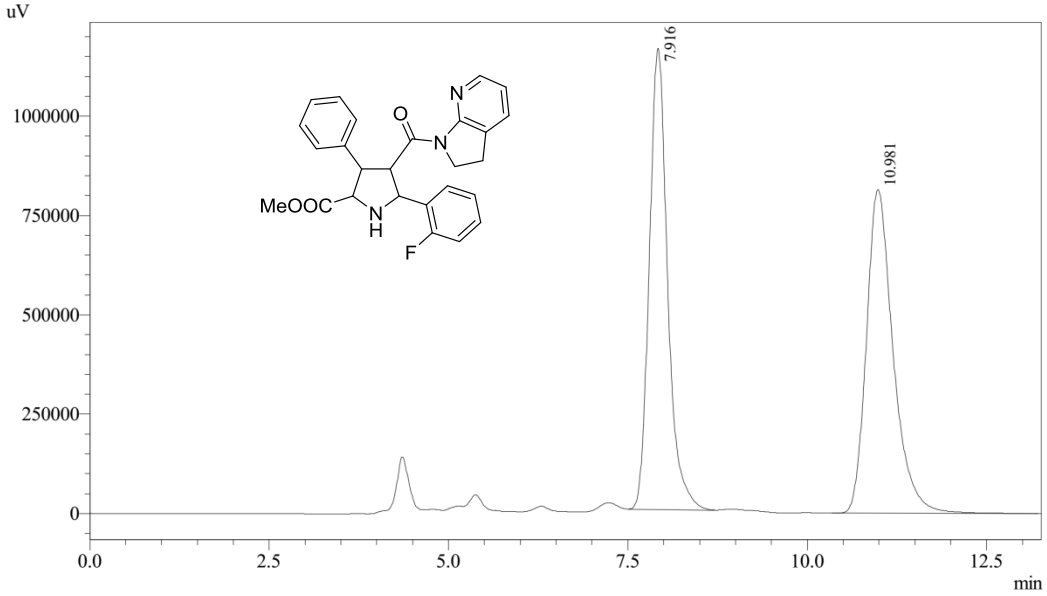
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.776	12000656	747187	97.904	98.628
2	11.701	256953	10392	2.096	1.372
Total		12257609	757579	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ag



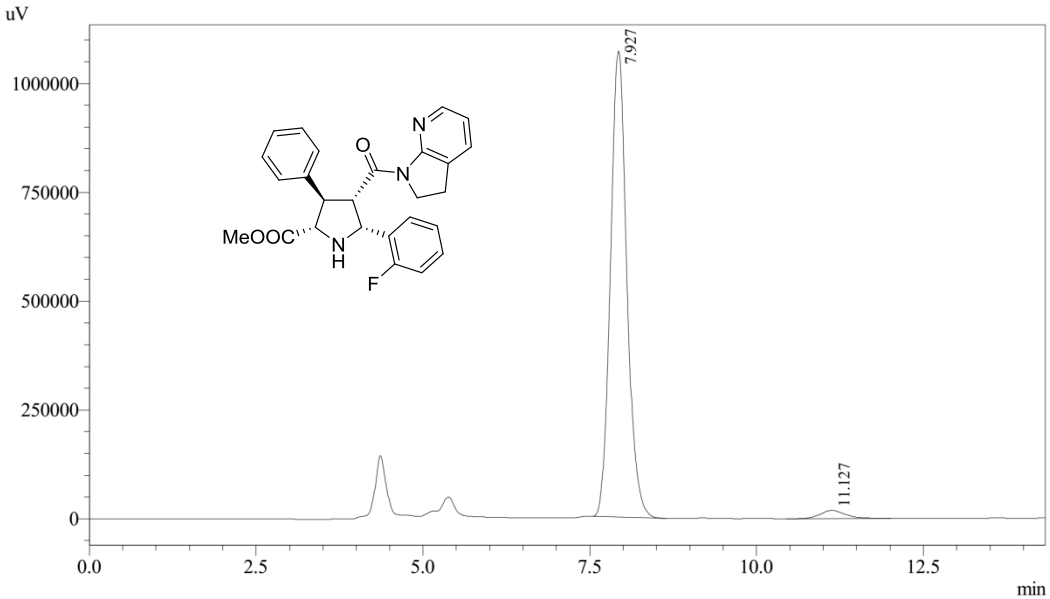




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.916	20550127	1160302	49.320	58.732
2	10.981	21117041	815294	50.680	41.268
Total		41667168	1975596	100.000	100.000

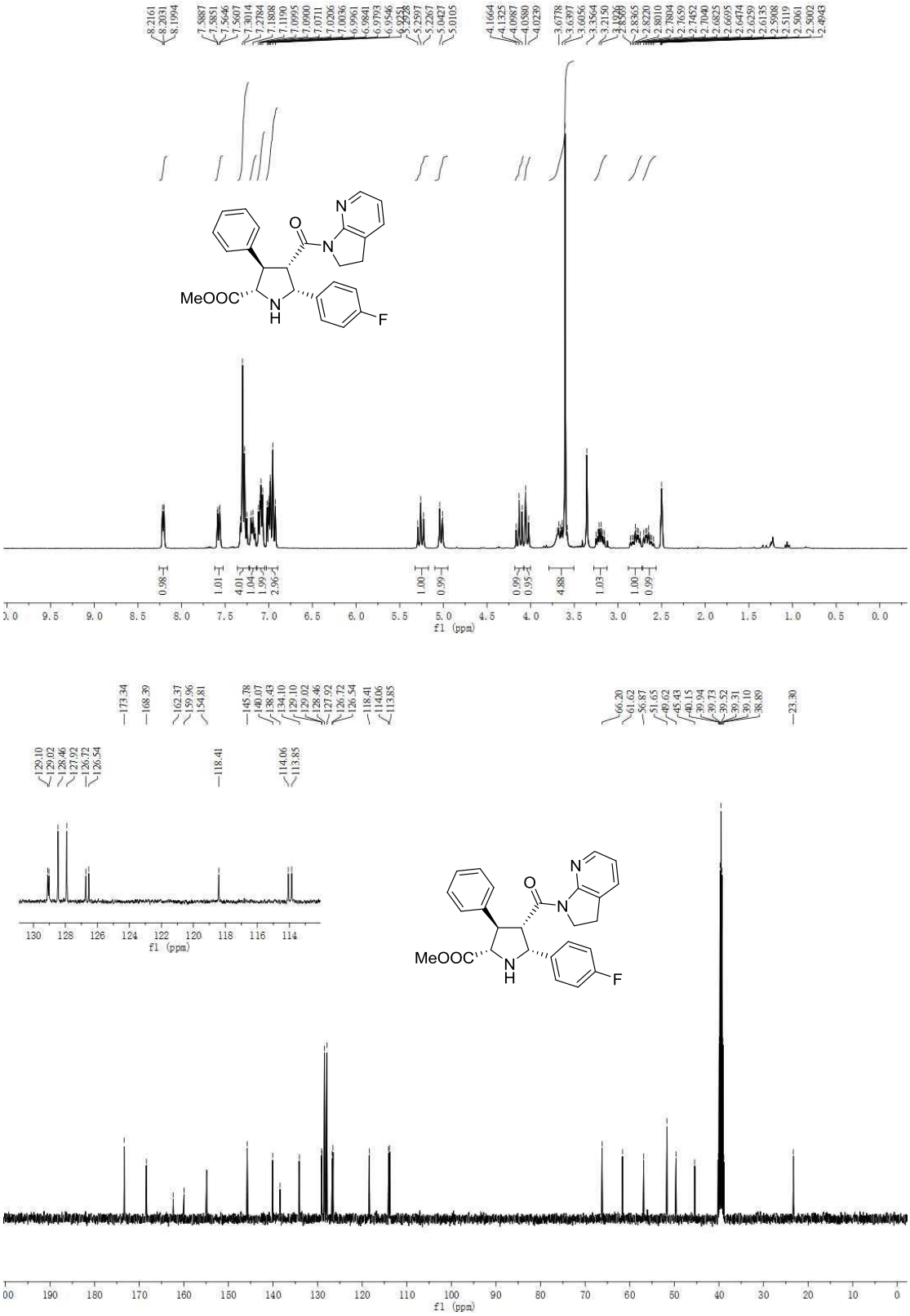


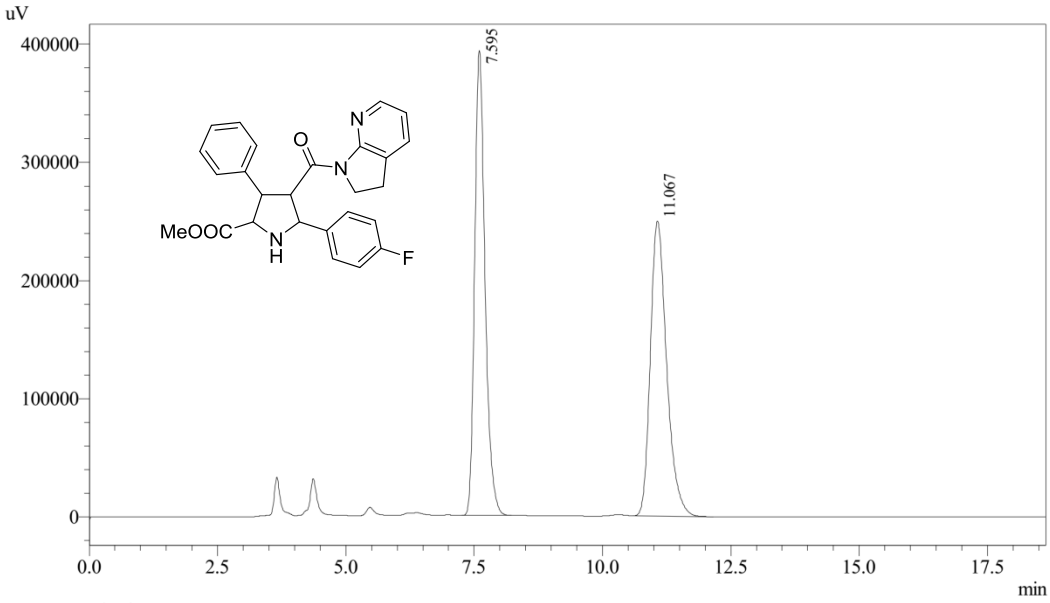
1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.927	18289958	1070471	97.382	98.286
2	11.127	491661	18664	2.618	1.714
Total		18781620	1089136	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ah

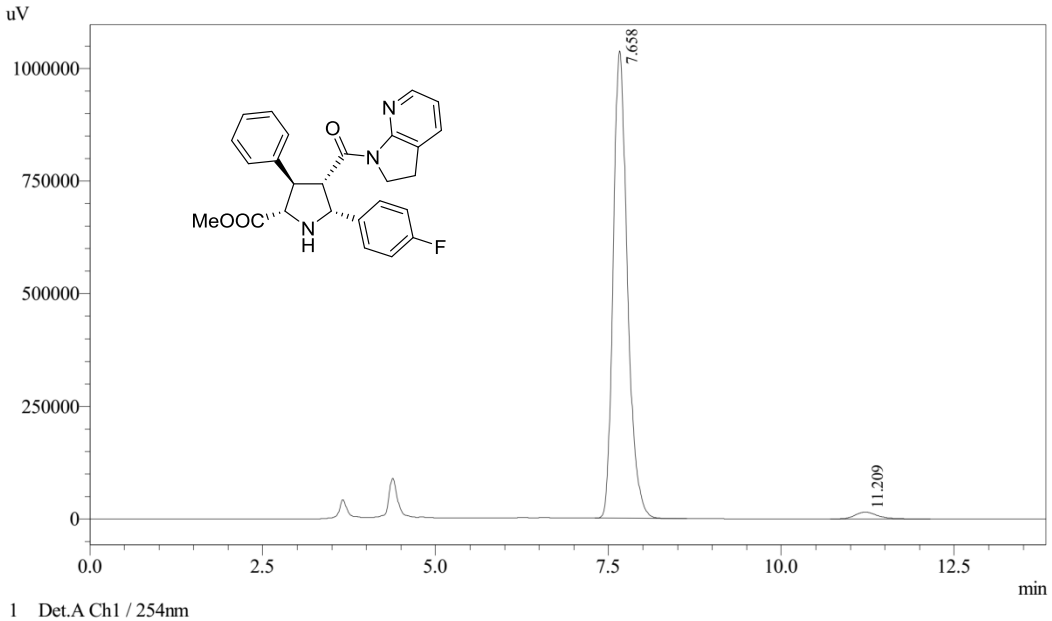




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.595	5502580	393260	49.959	61.168
2	11.067	5511643	249655	50.041	38.832
Total		11014223	642915	100.000	100.000

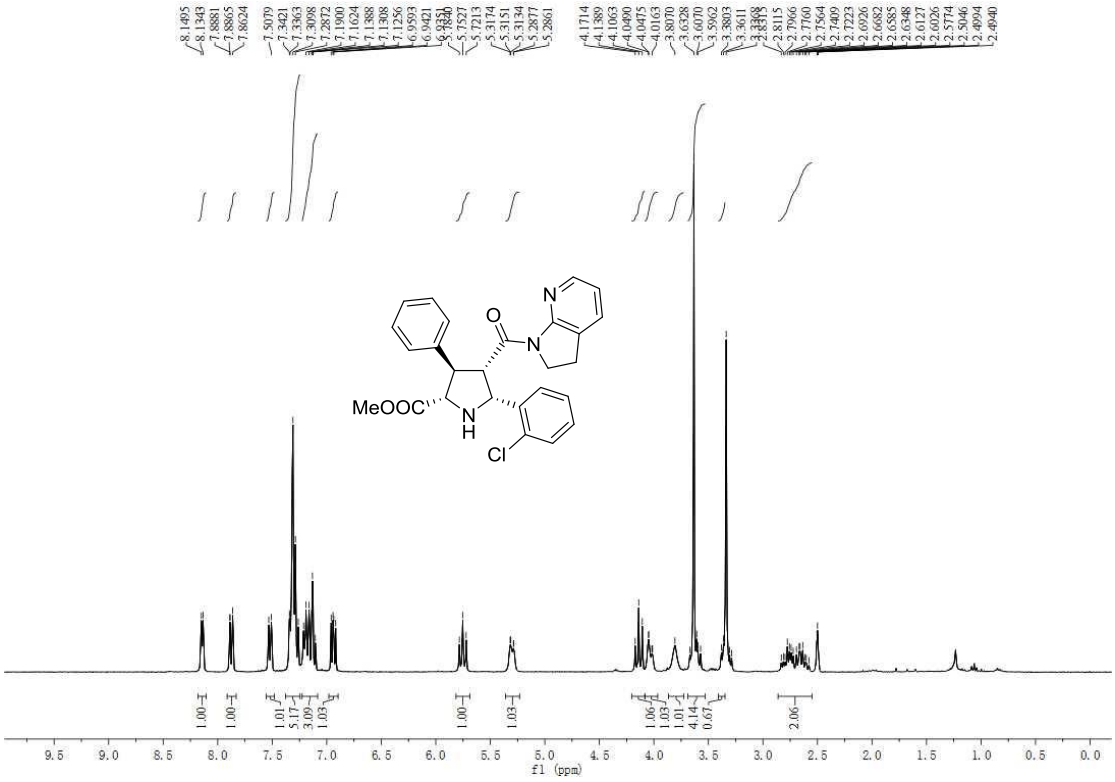


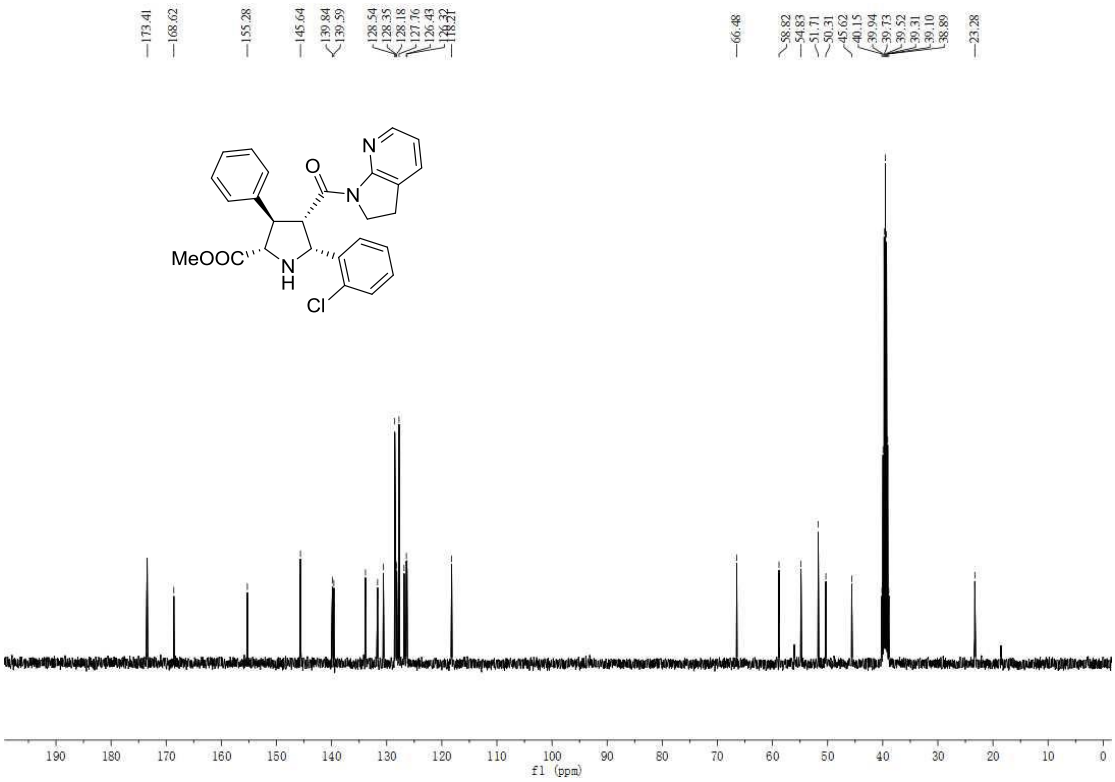
1 Det.A Ch1 / 254nm

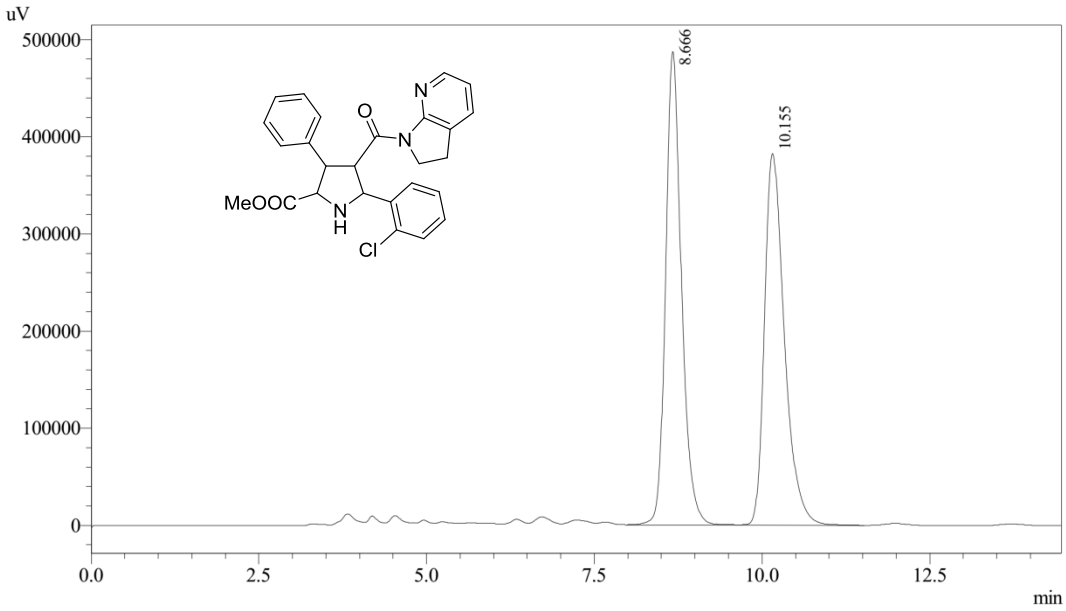
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.658	14907709	1037813	97.768	98.561
2	11.209	340325	15155	2.232	1.439
Total		15248034	1052968	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ai



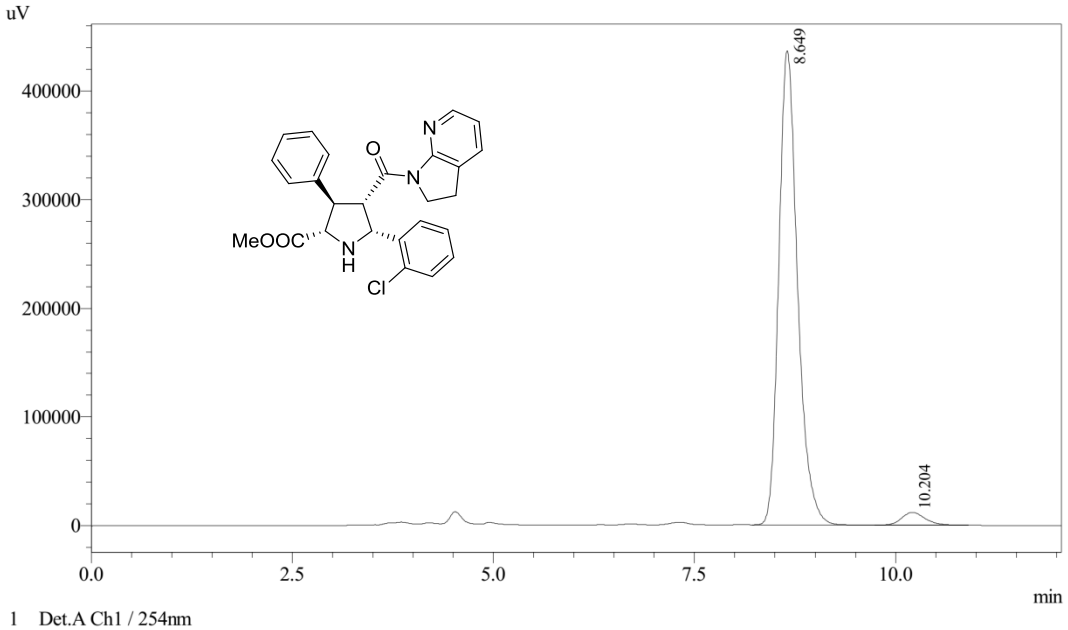




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.666	8037178	486867	50.427	56.016
2	10.155	7901172	382296	49.573	43.984
Total		15938351	869162	100.000	100.000

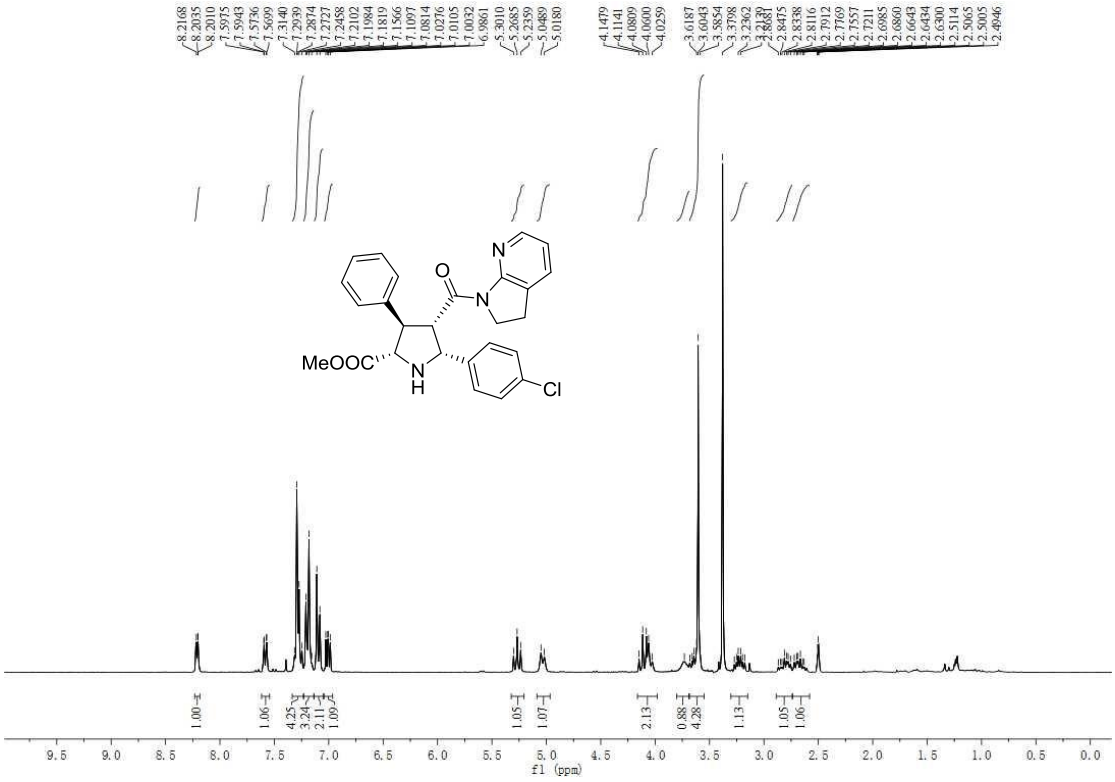


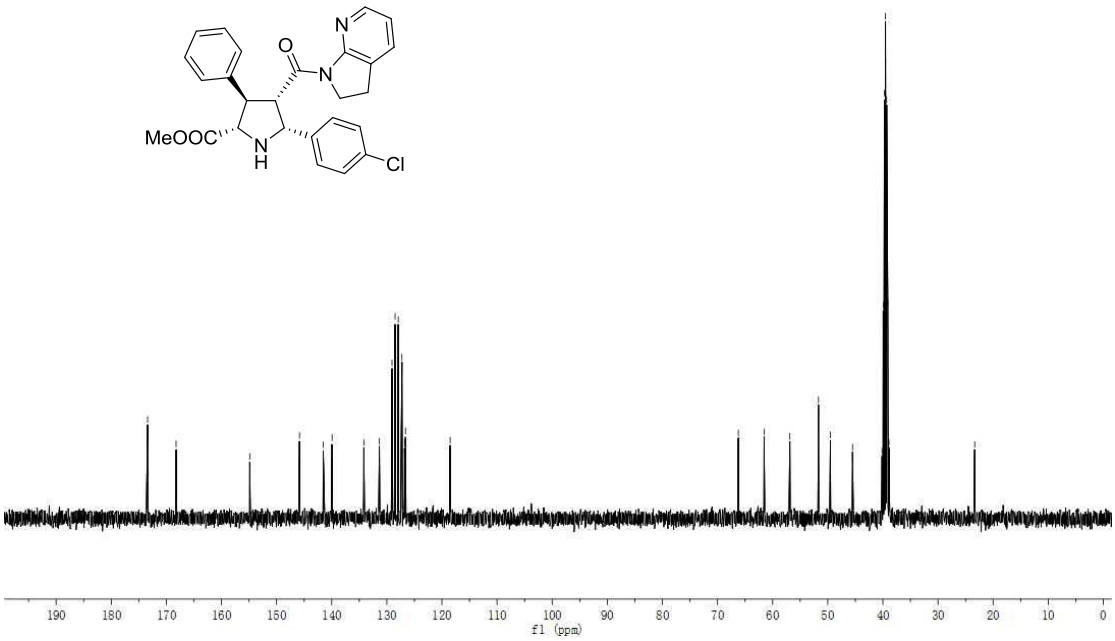
1 Det.A Ch1 / 254nm

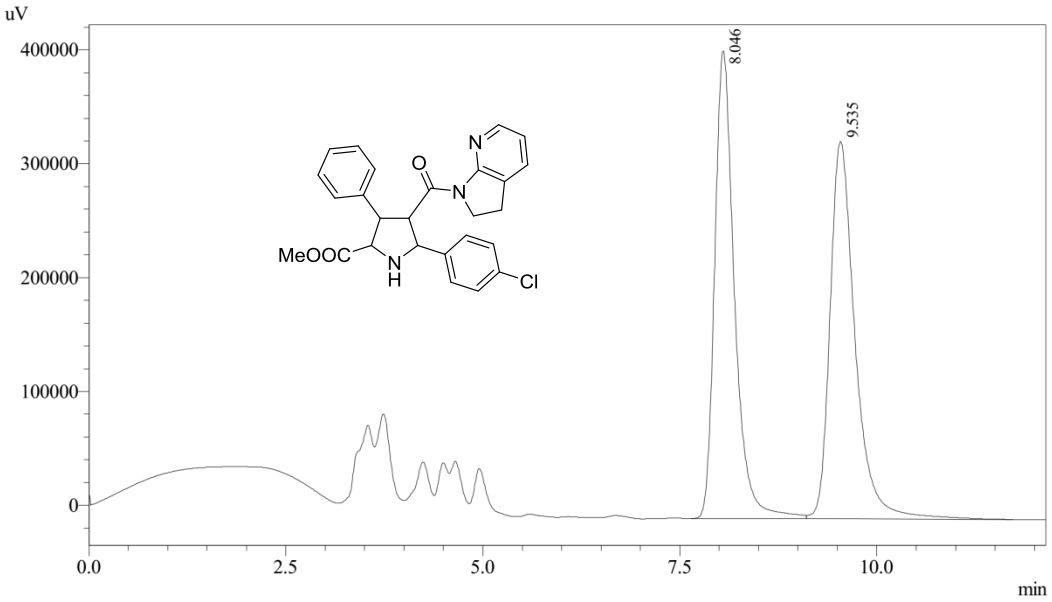
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.649	7096391	436390	96.691	97.358
2	10.204	242838	11843	3.309	2.642
Total		7339229	448233	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3aj



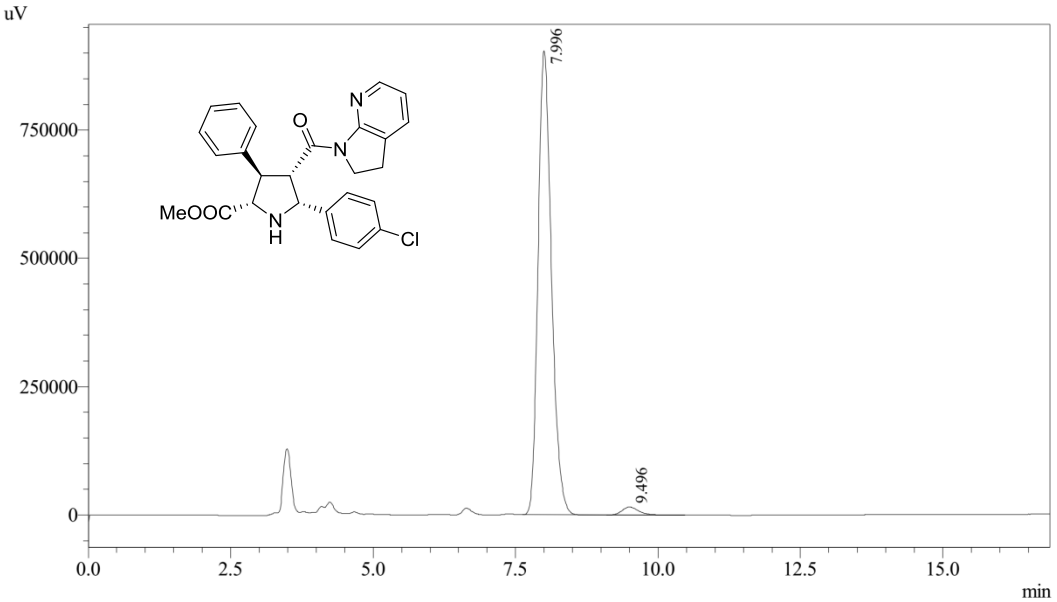




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.046	7181366	410815	49.389	55.337
2	9.535	7359082	331574	50.611	44.663
Total		14540448	742389	100.000	100.000

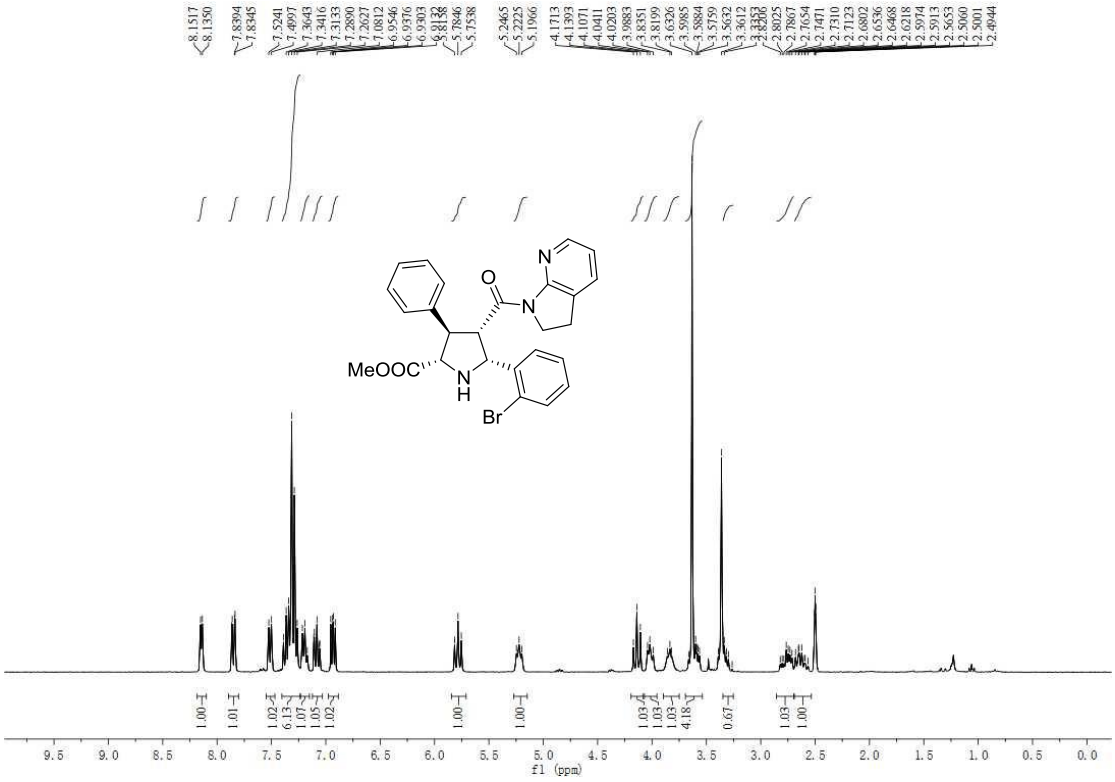


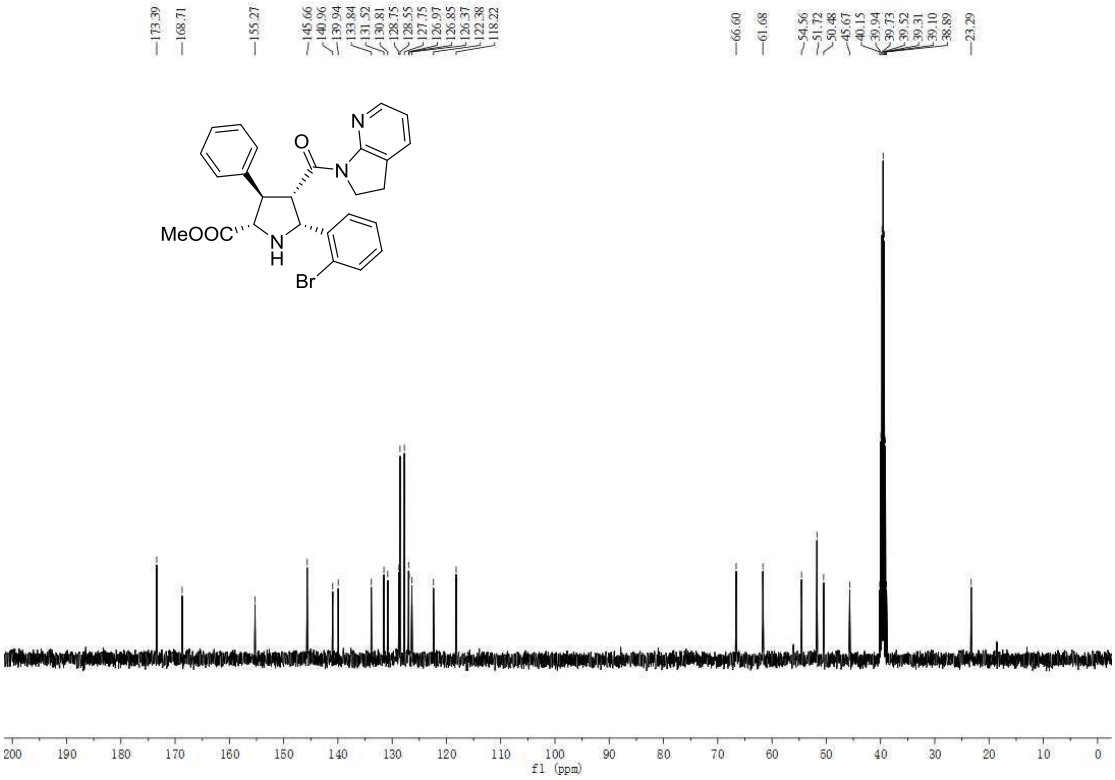
1 Det.A Ch1 / 254nm

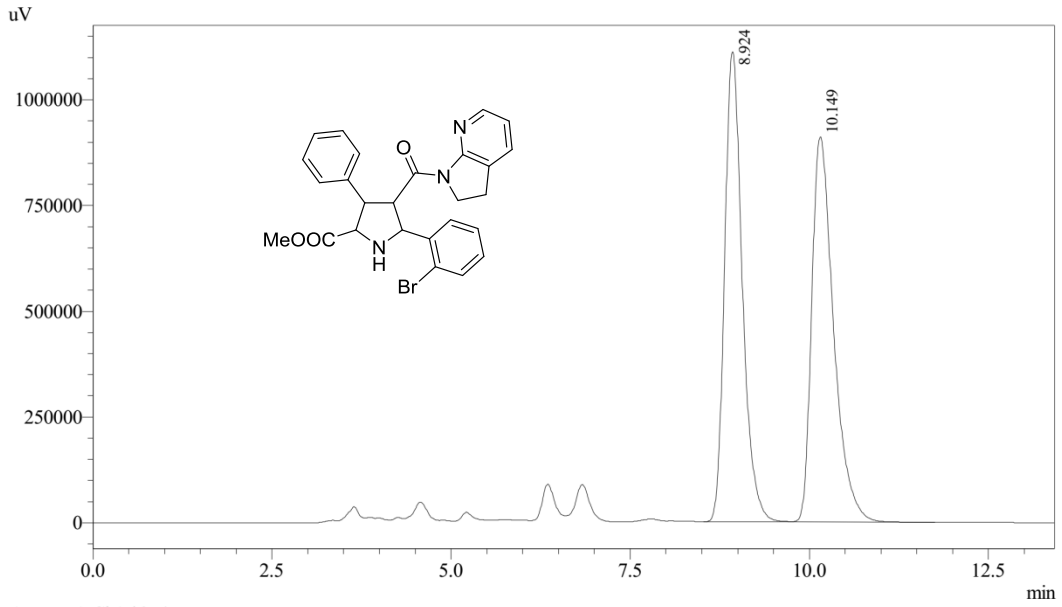
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.996	14784721	904068	97.893	98.309
2	9.496	318171	15554	2.107	1.691
Total		15102892	919622	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ak



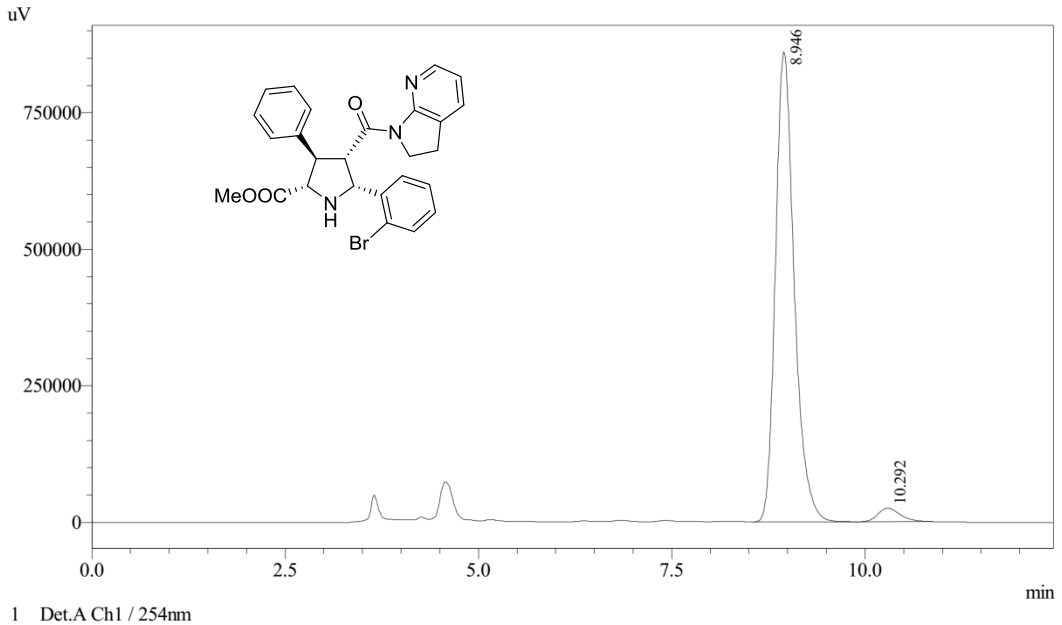




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.924	19101692	1111187	49.698	54.959
2	10.149	19334220	910644	50.302	45.041
Total		38435911	2021832	100.000	100.000

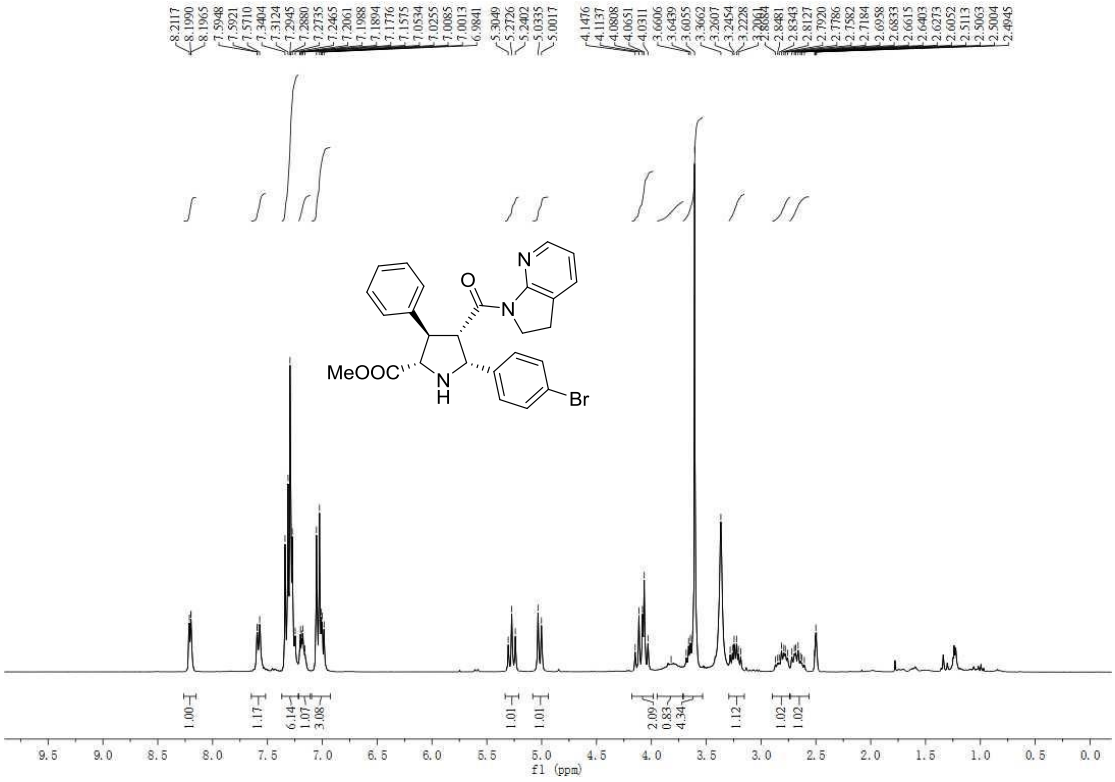


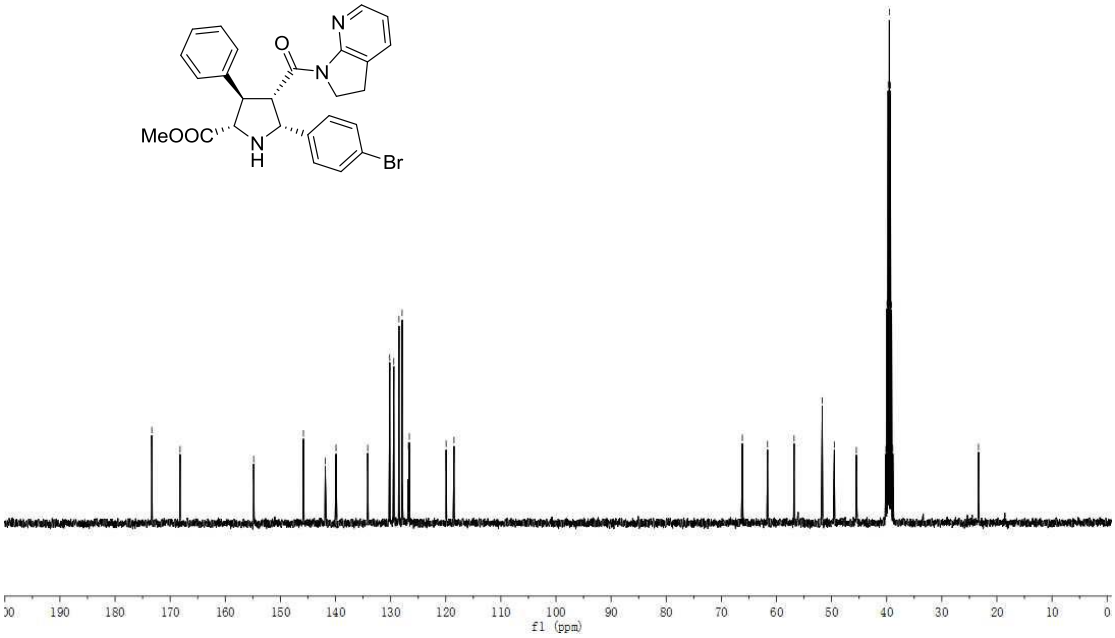
1 Det.A Ch1 / 254nm

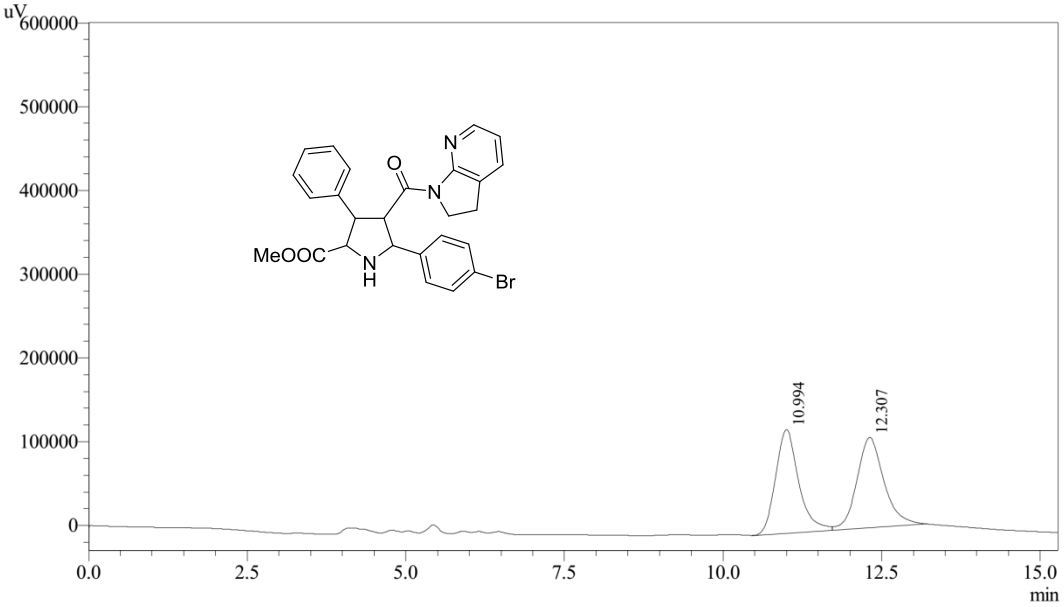
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.946	14590764	861114	96.658	97.183
2	10.292	504454	24958	3.342	2.817
Total		15095218	886072	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3al



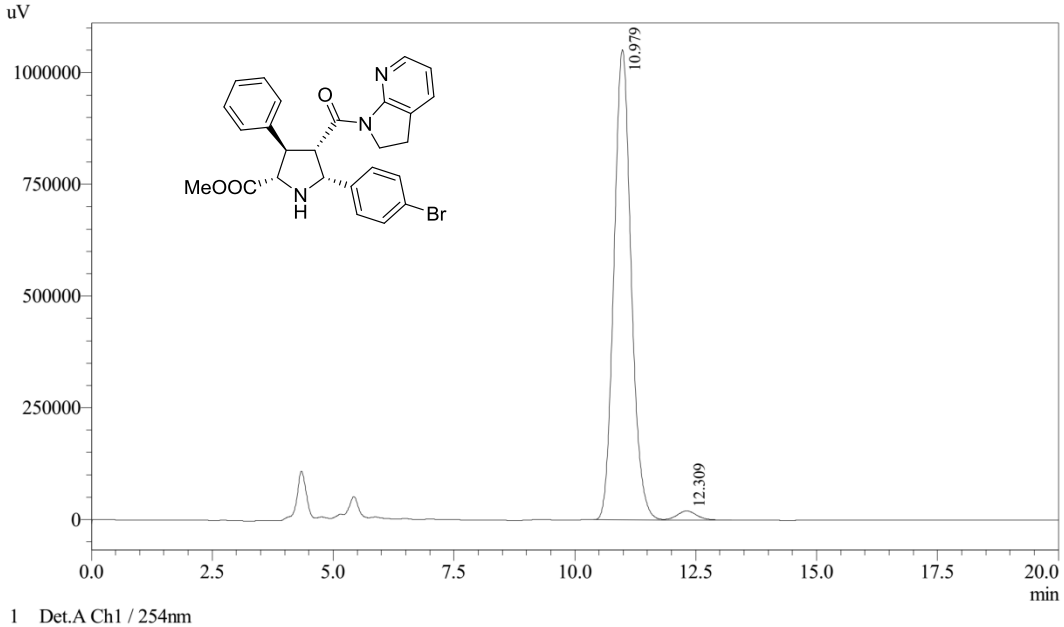




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.994	3137918	123615	49.442	53.416
2	12.307	3208771	107804	50.558	46.584
Total		6346689	231420	100.000	100.000

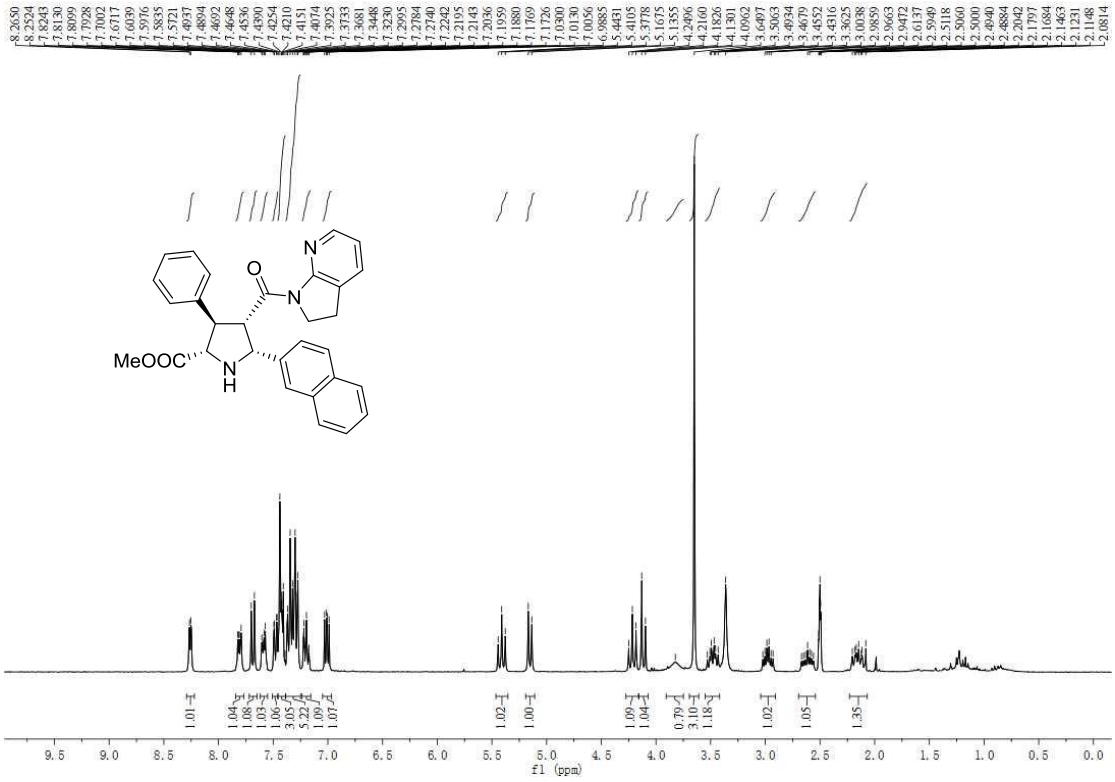


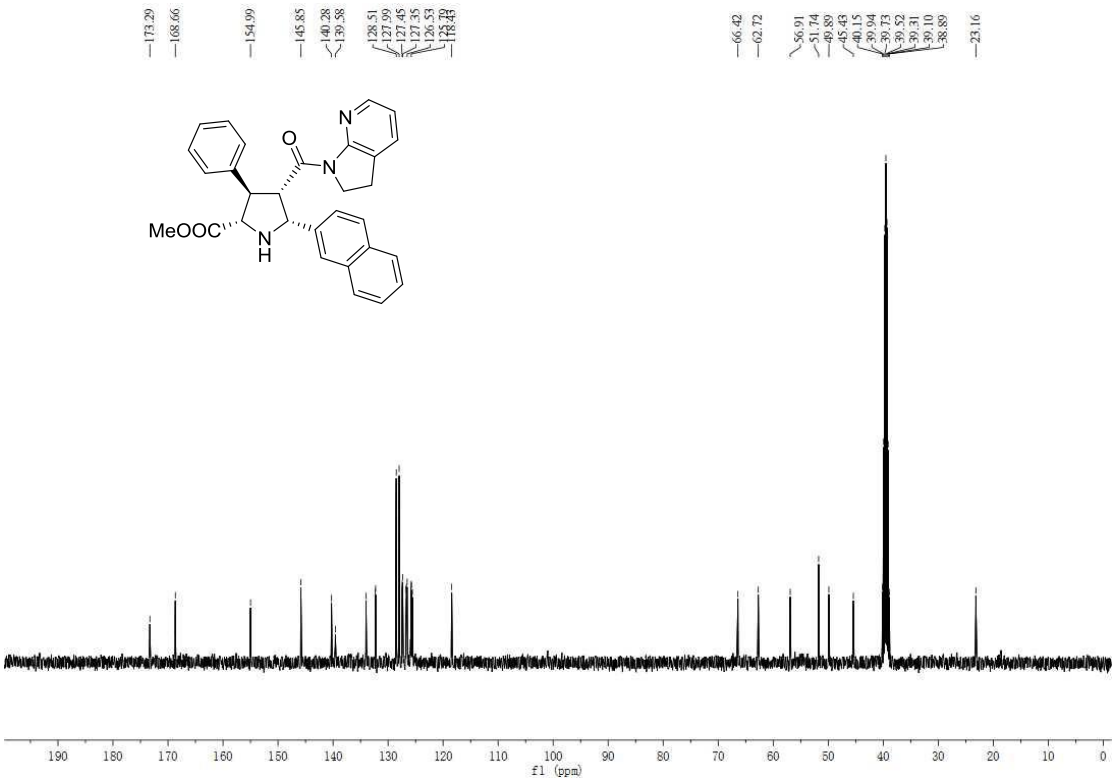
1 Det.A Ch1 / 254nm

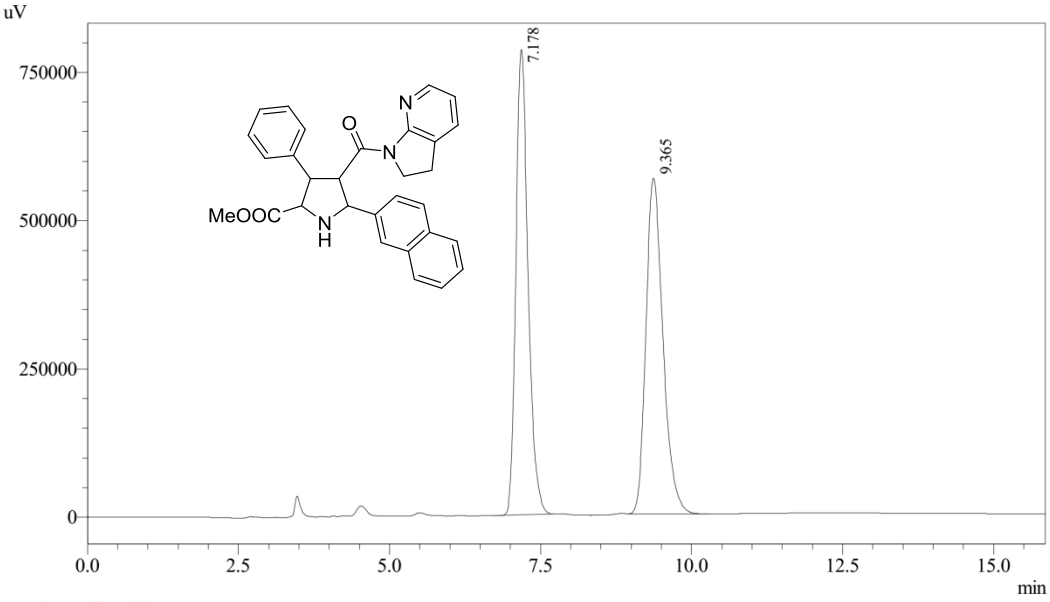
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.979	26022062	1052171	97.831	98.096
2	12.309	577029	20424	2.169	1.904
Total		26599090	1072595	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3am



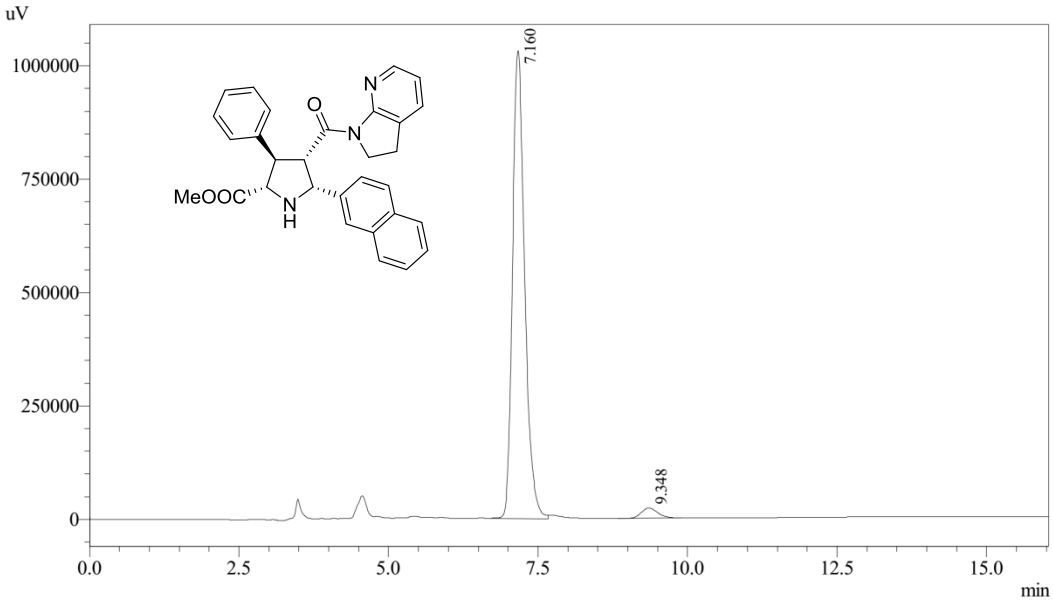




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.178	10989748	784754	49.737	58.111
2	9.365	11105844	565694	50.263	41.889
Total		22095592	1350448	100.000	100.000

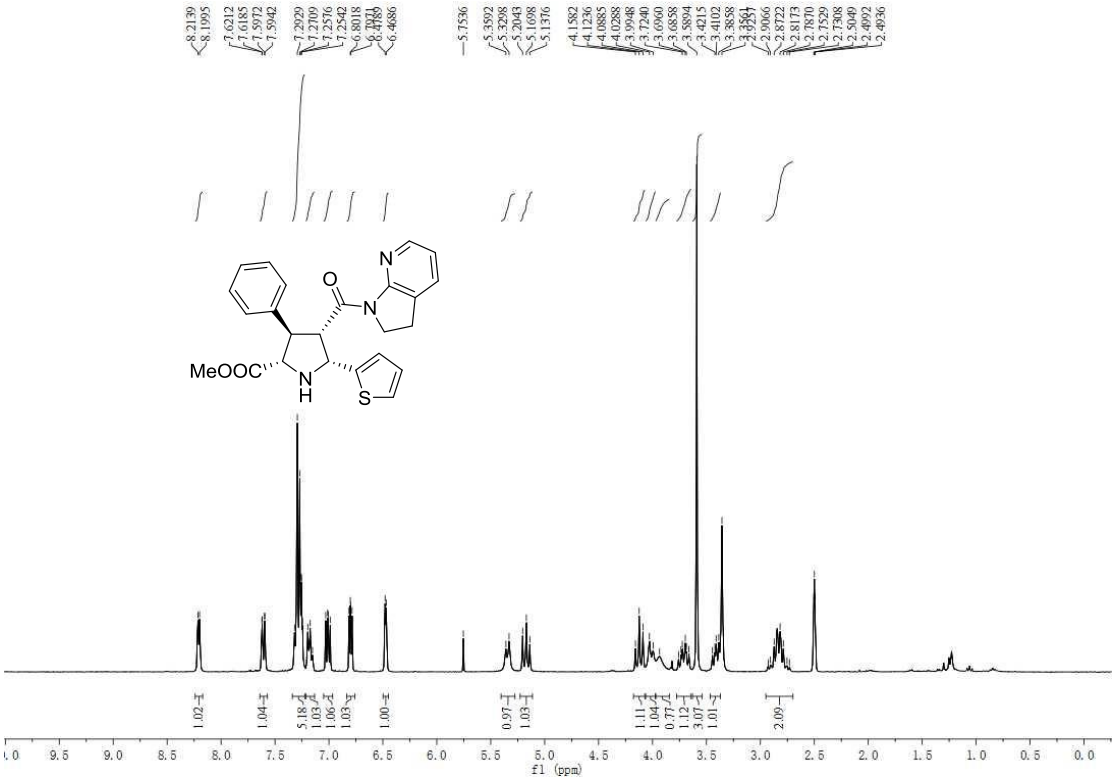


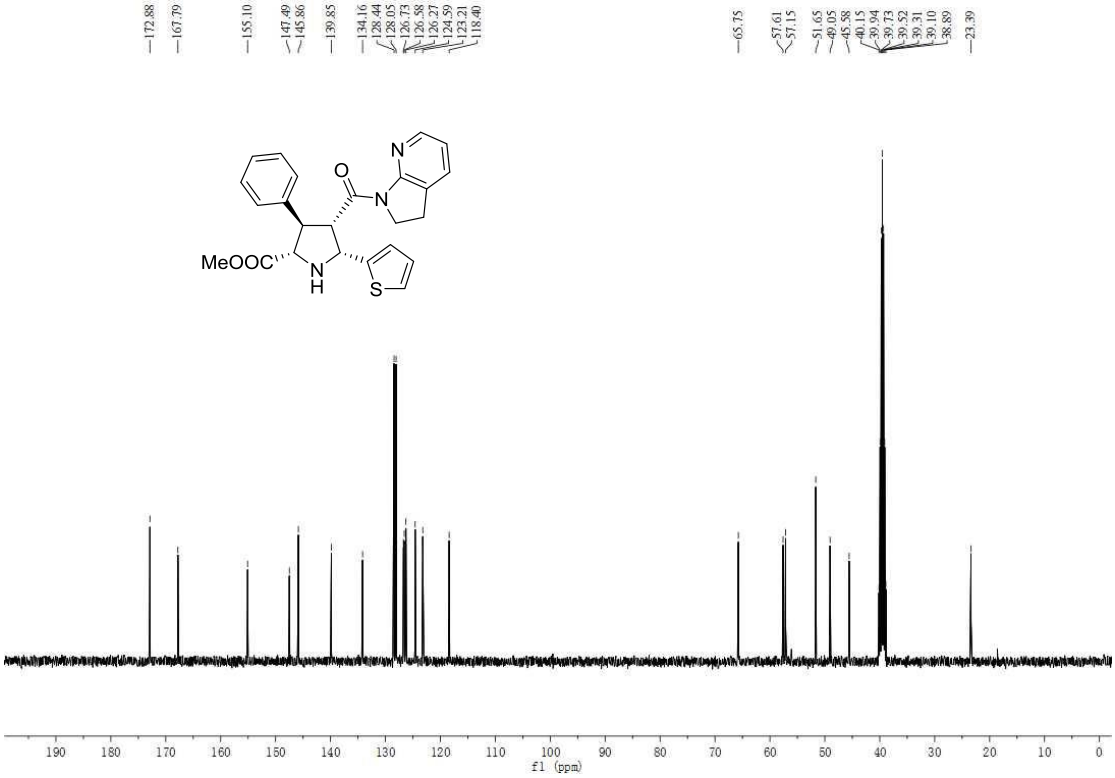
1 Det.A Ch1 / 254nm

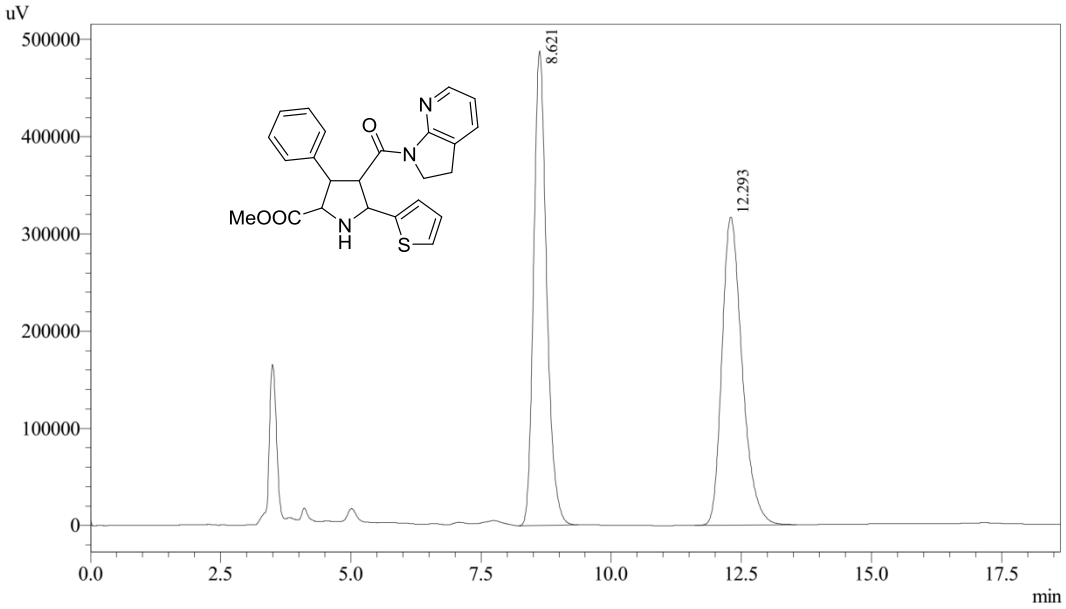
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.160	14600418	1031632	97.139	97.864
2	9.348	429973	22515	2.861	2.136
Total		15030391	1054147	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3an



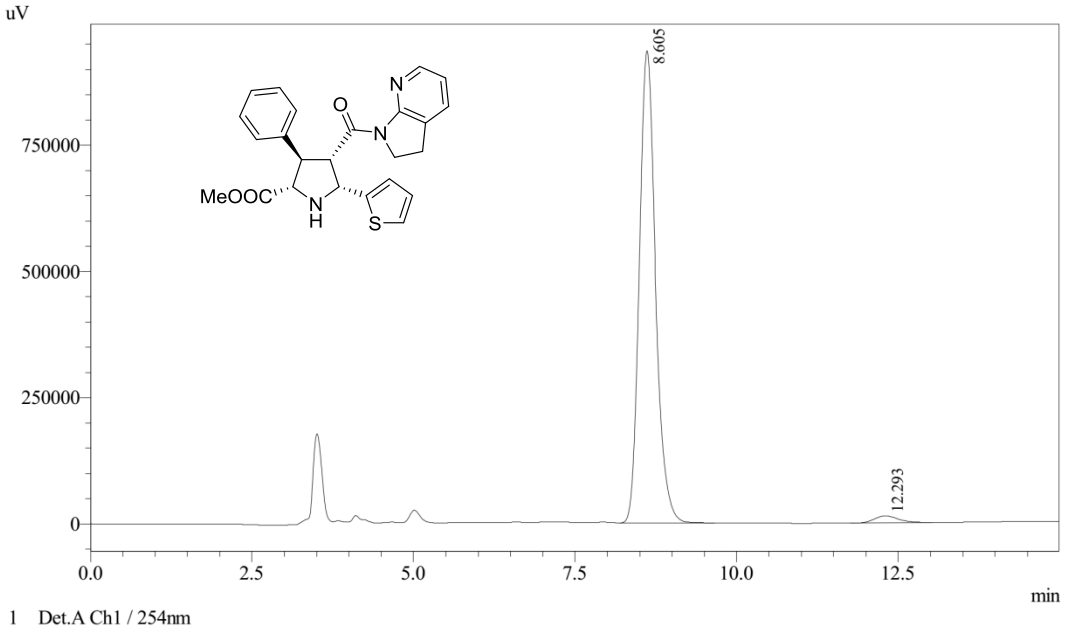




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.621	8476632	488366	49.725	60.654
2	12.293	8570378	316808	50.275	39.346
Total		17047010	805173	100.000	100.000

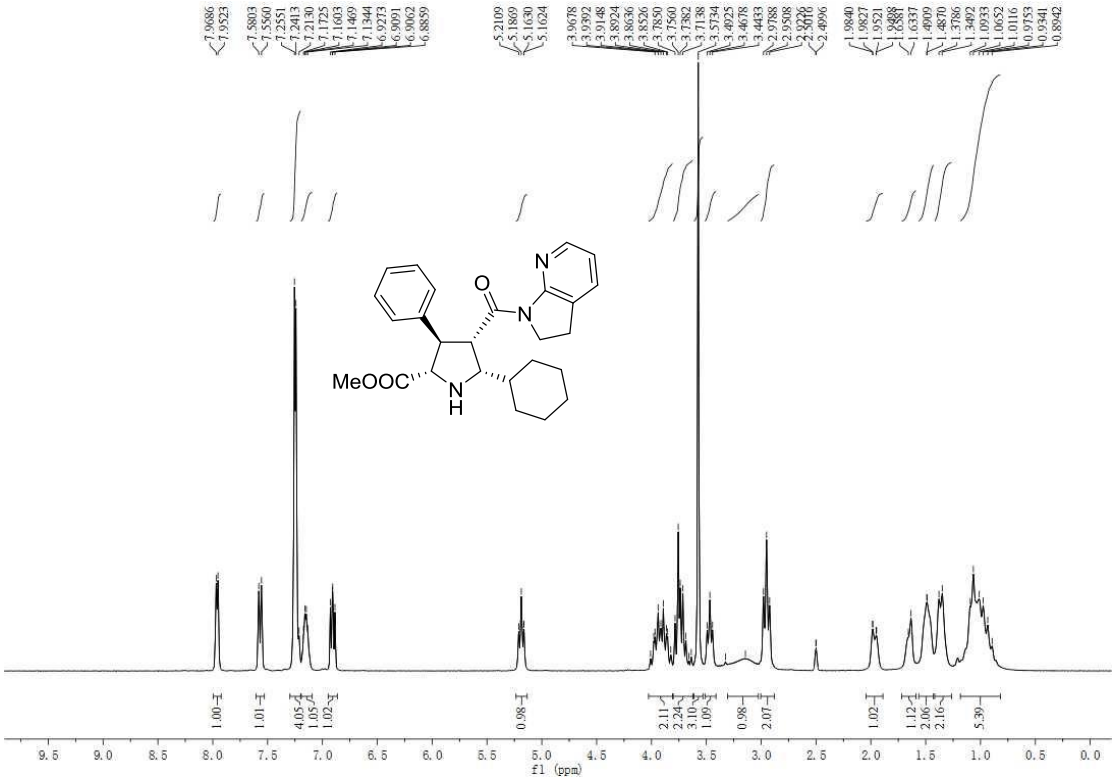


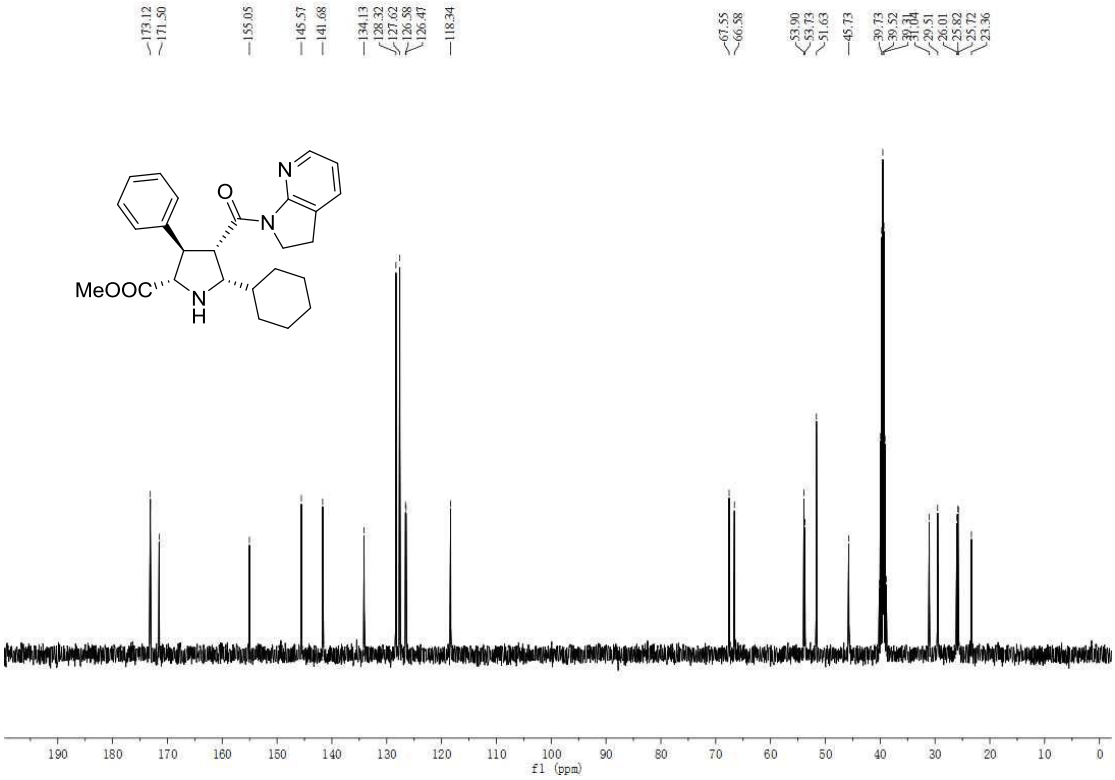
1 Det.A Ch1 / 254nm

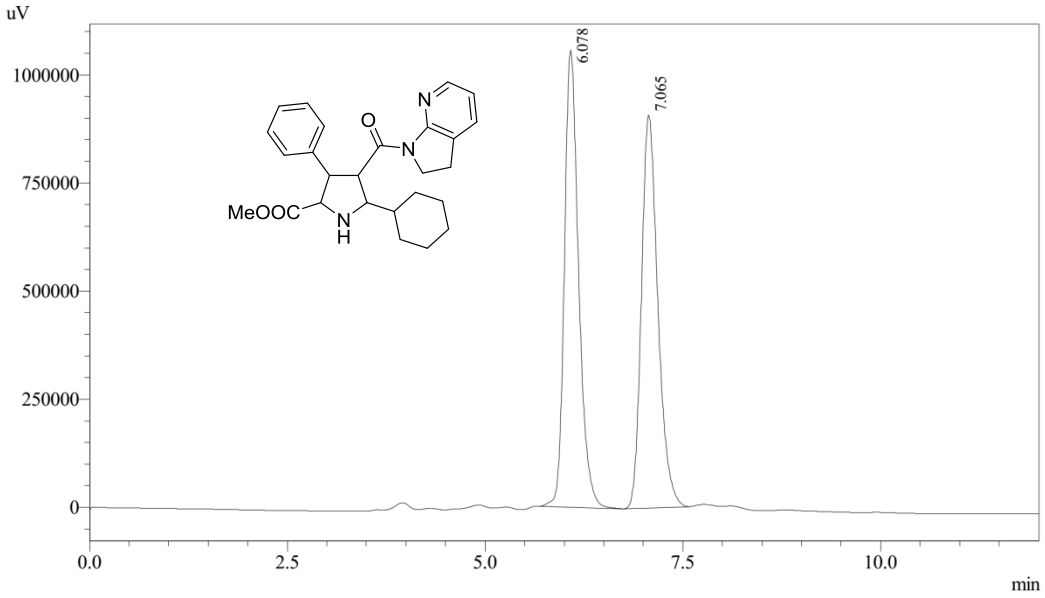
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.605	16435974	934674	97.823	98.534
2	12.293	365691	13902	2.177	1.466
Total		16801664	948577	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ao



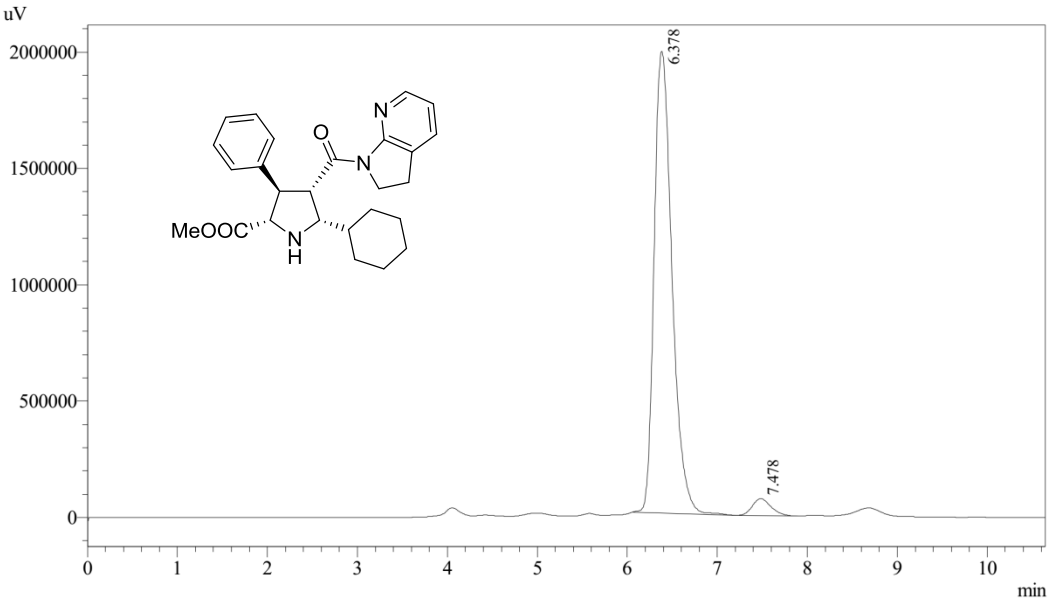




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.078	13245415	1056908	50.236	53.788
2	7.065	13121220	908049	49.764	46.212
Total		26366635	1964957	100.000	100.000

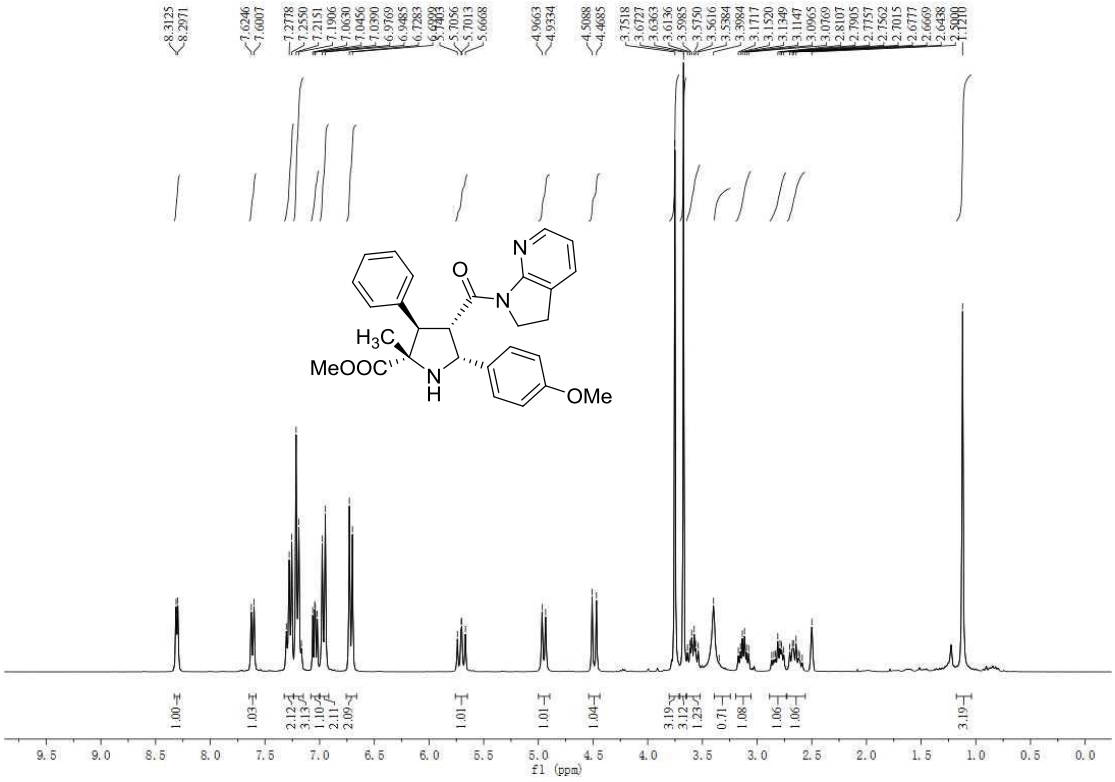


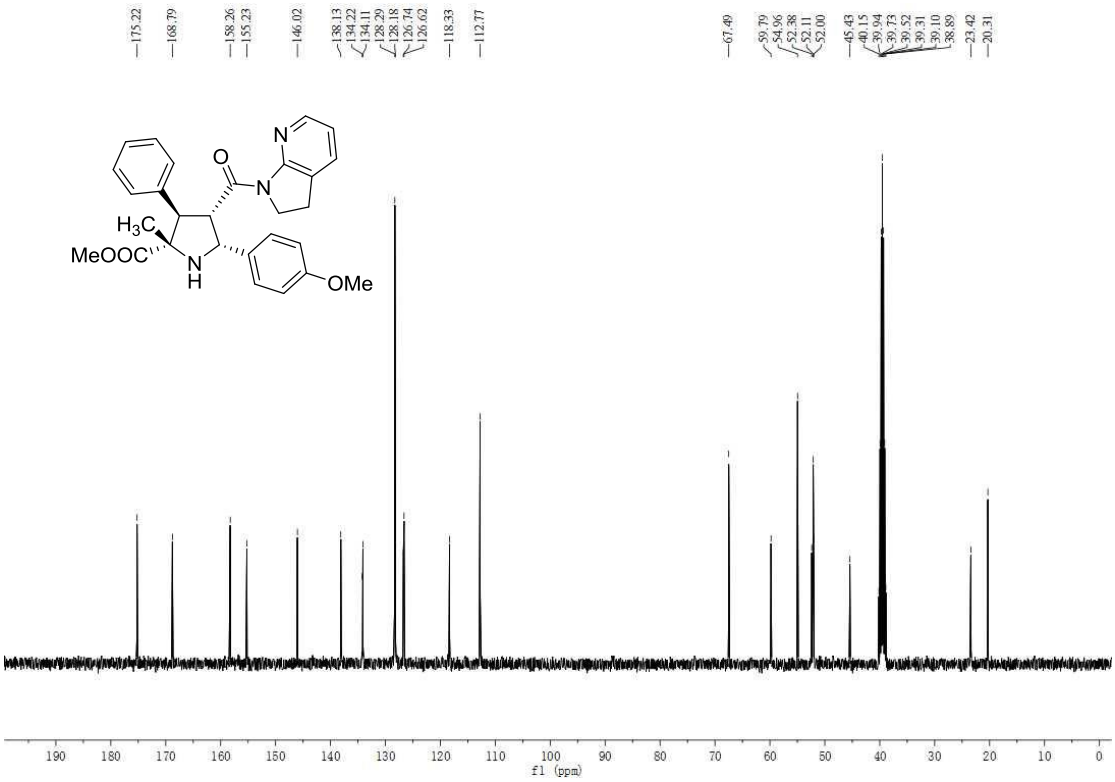
1 Det.A Ch1 / 254nm

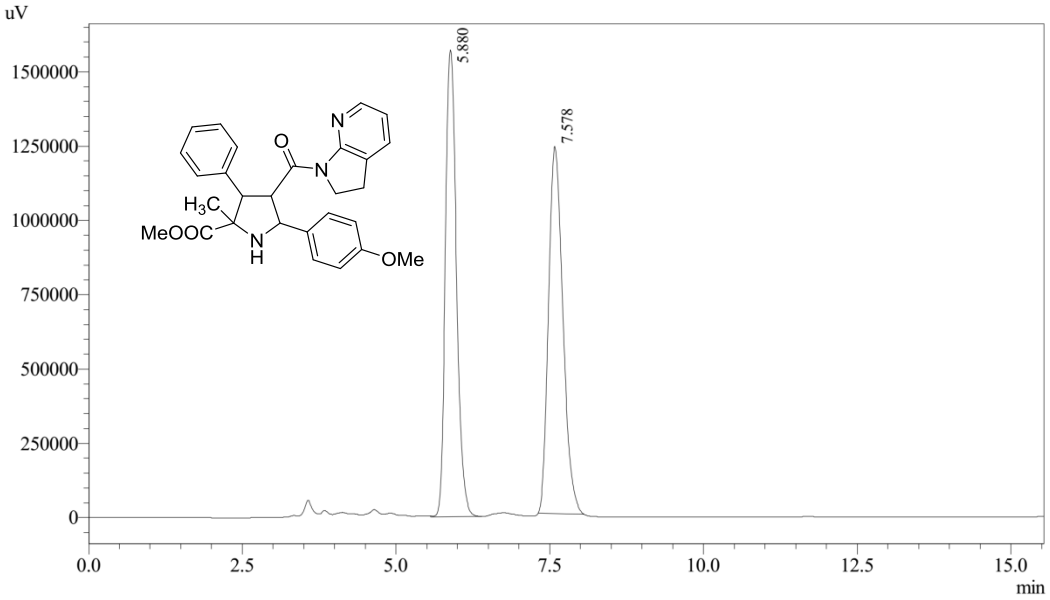
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.378	27332567	1984087	96.266	96.439
2	7.478	1060205	73264	3.734	3.561
Total		28392772	2057351	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ap



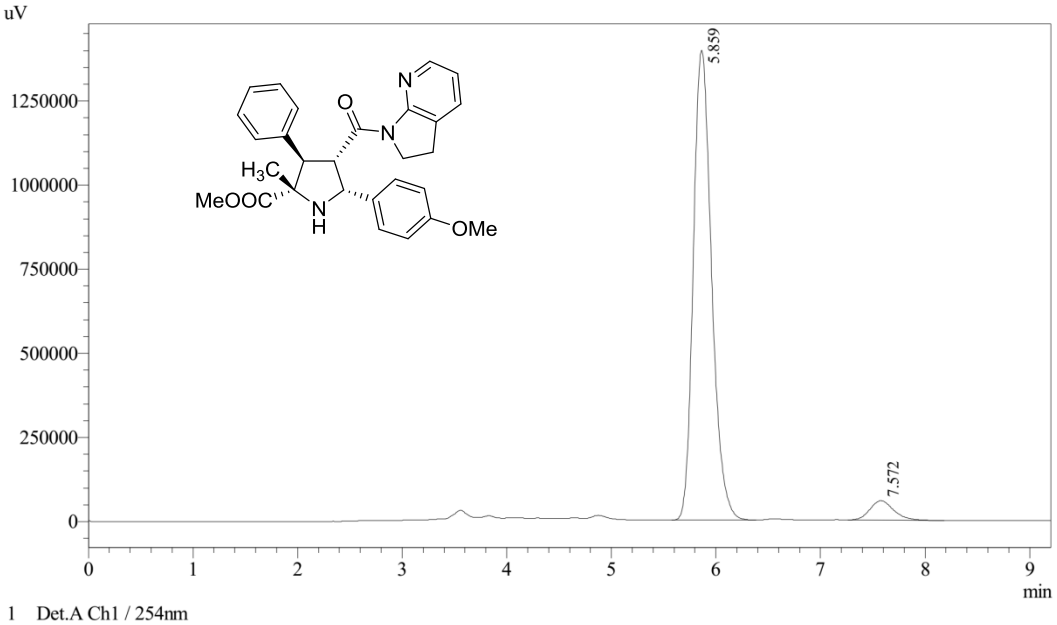




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.880	19670397	1569925	49.434	55.980
2	7.578	20120853	1234518	50.566	44.020
Total		39791250	2804443	100.000	100.000

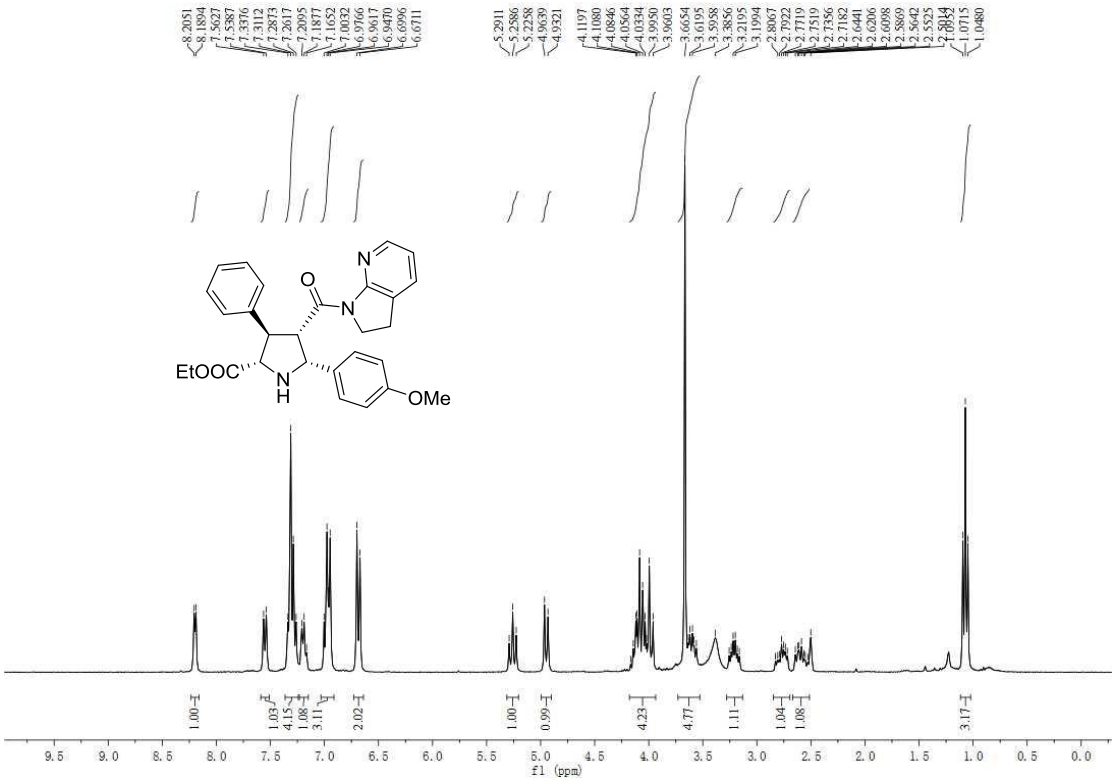


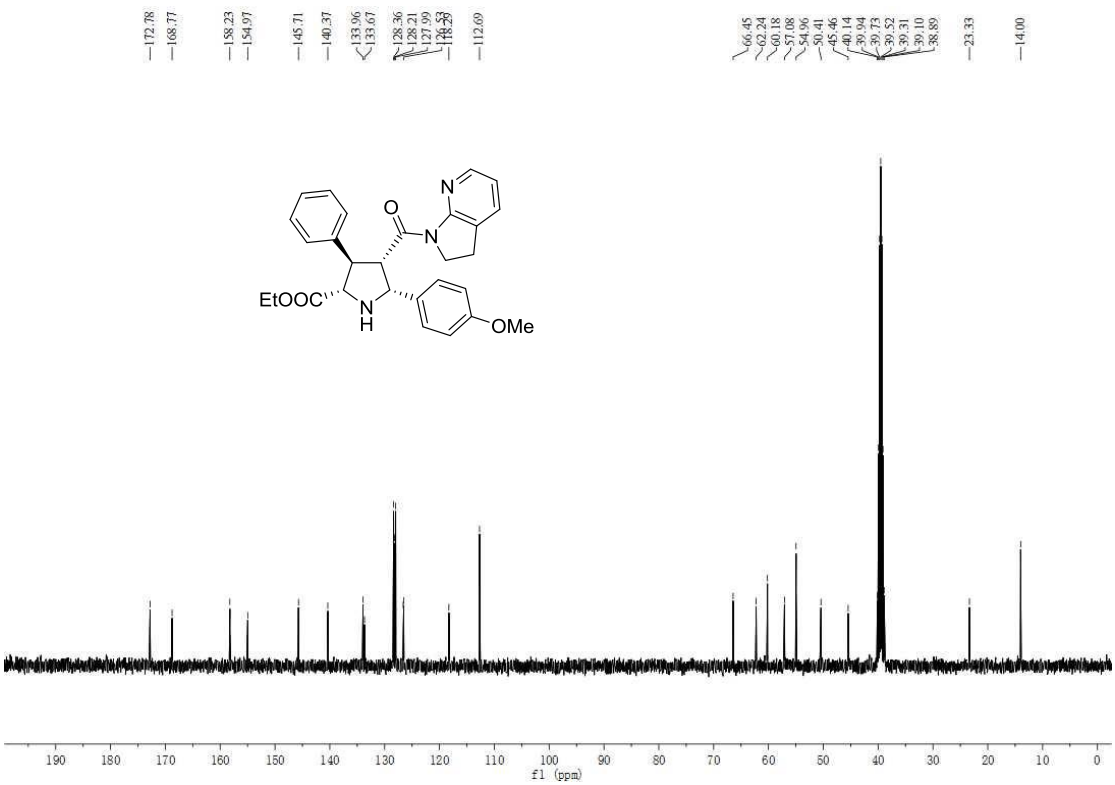
1 Det.A Ch1 / 254nm

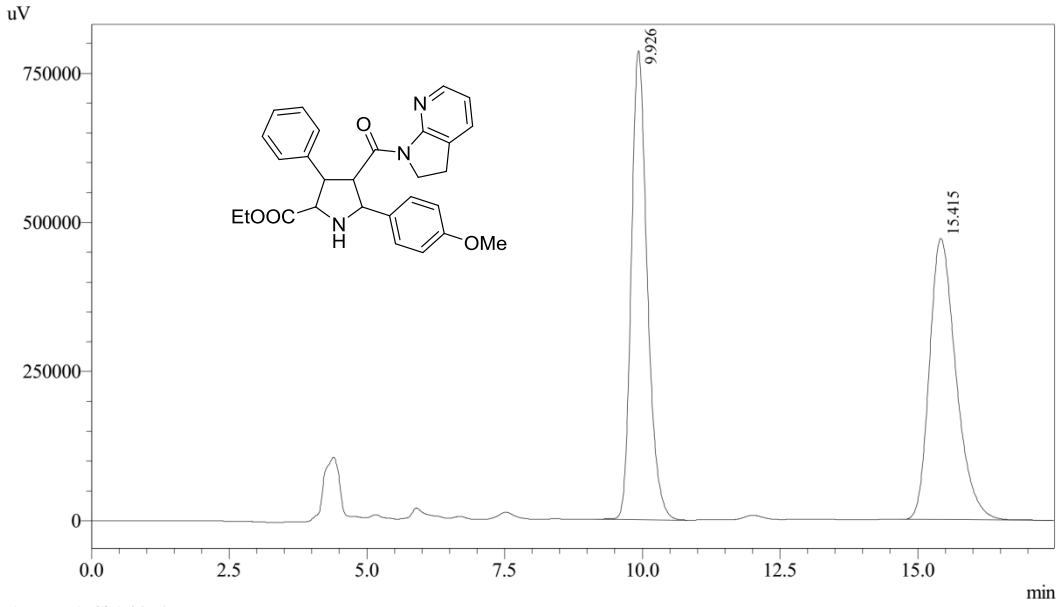
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.859	16984516	1396609	94.920	96.050
2	7.572	908921	57442	5.080	3.950
Total		17893437	1454051	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3aq



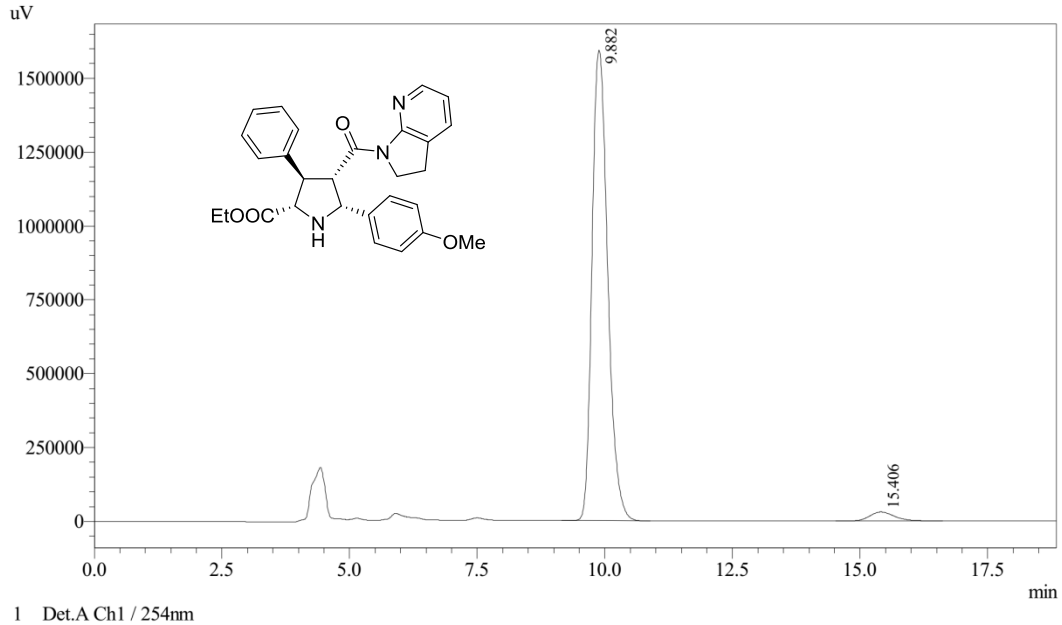




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.926	15862291	785582	50.124	62.514
2	15.415	15783512	471071	49.876	37.486
Total		31645803	1256653	100.000	100.000

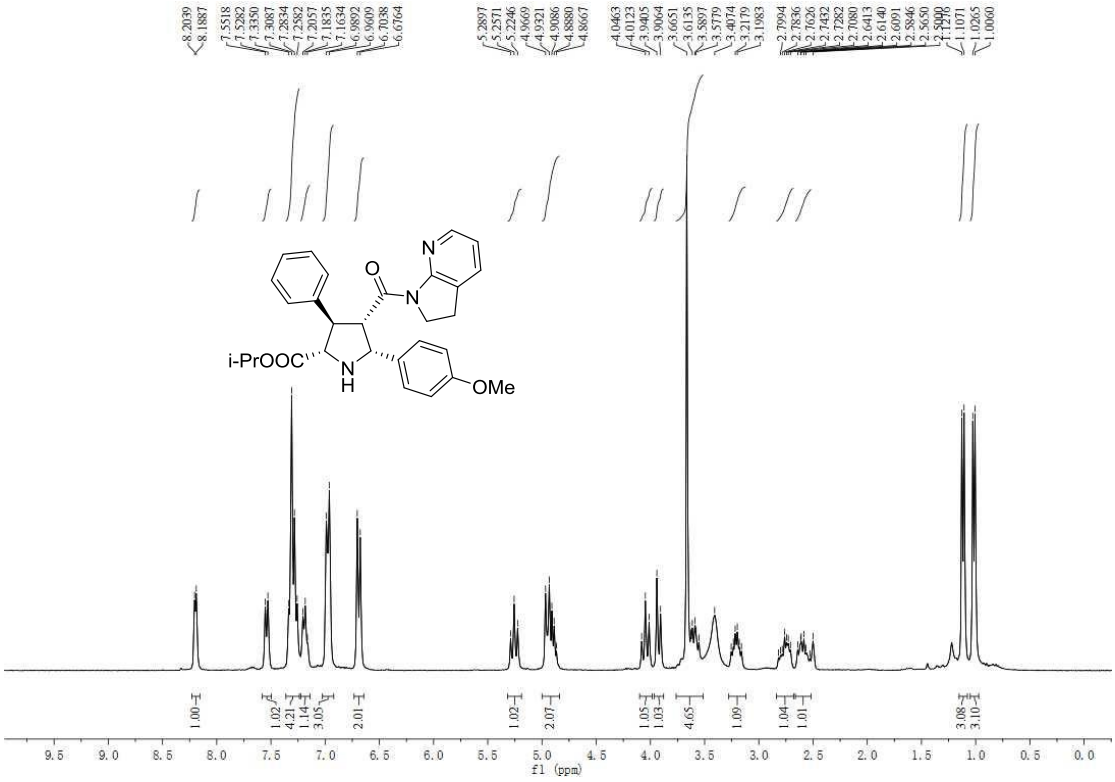


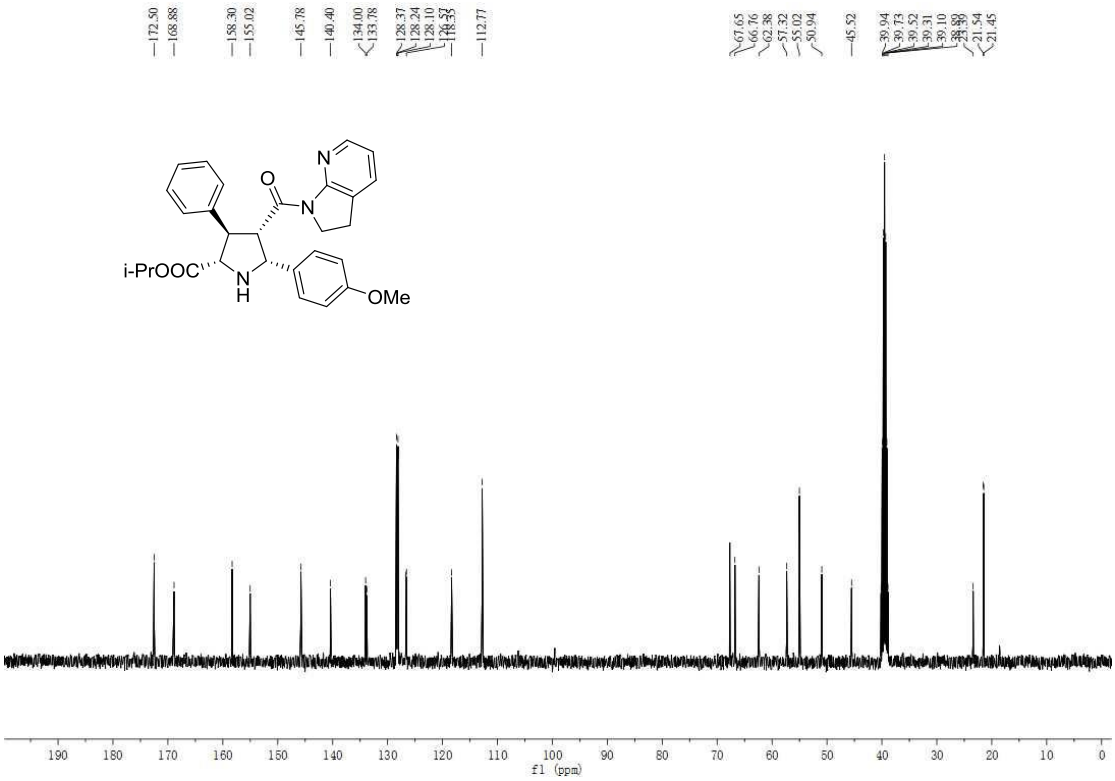
1 Det.A Ch1 / 254nm

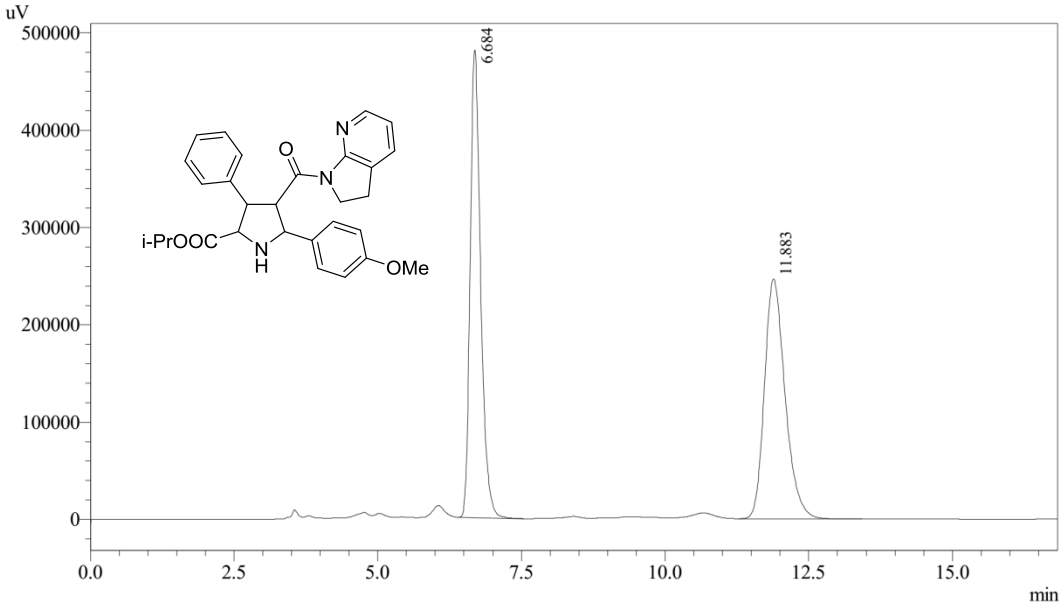
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.882	33999320	1592084	97.080	98.127
2	15.406	1022683	30386	2.920	1.873
Total		35022003	1622470	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 3ar



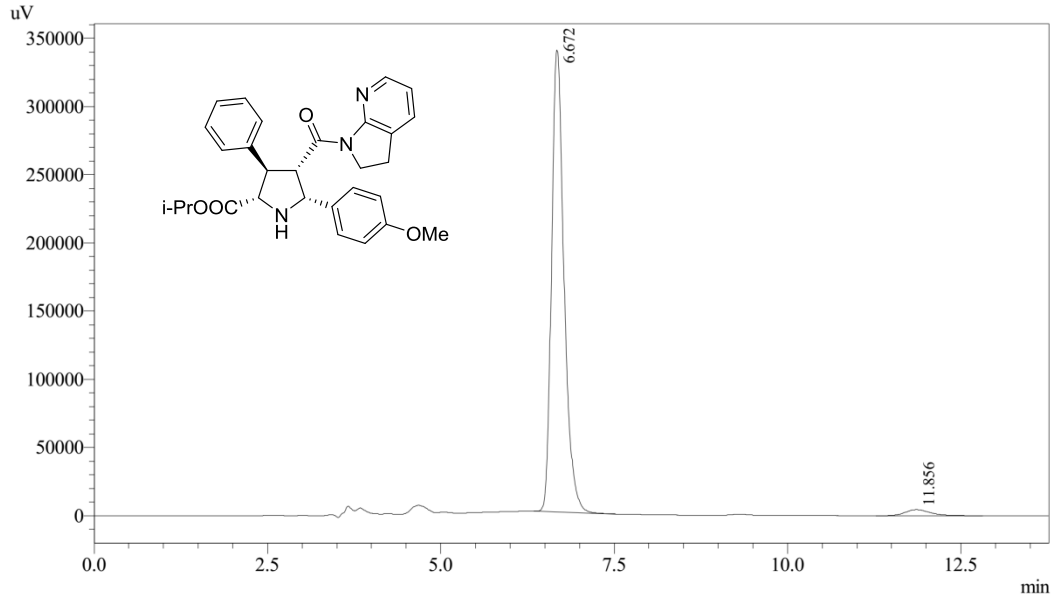




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.684	6100709	480580	49.760	66.111
2	11.883	6159515	246352	50.240	33.889
Total		12260224	726932	100.000	100.000

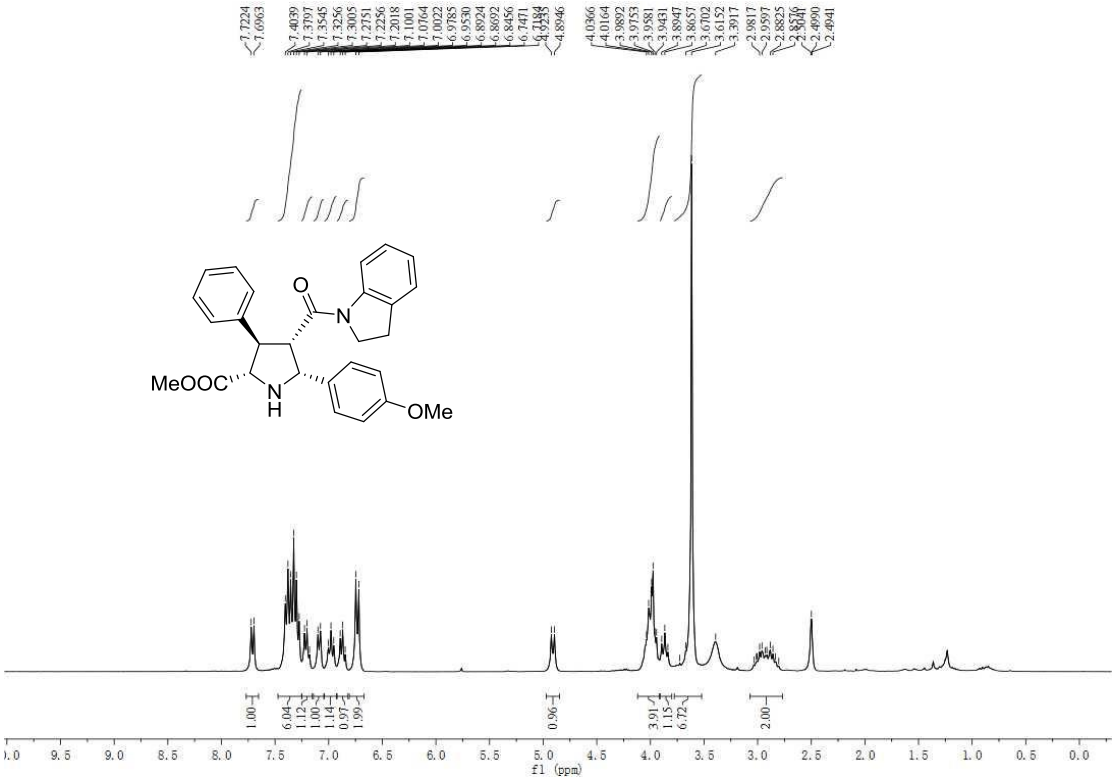


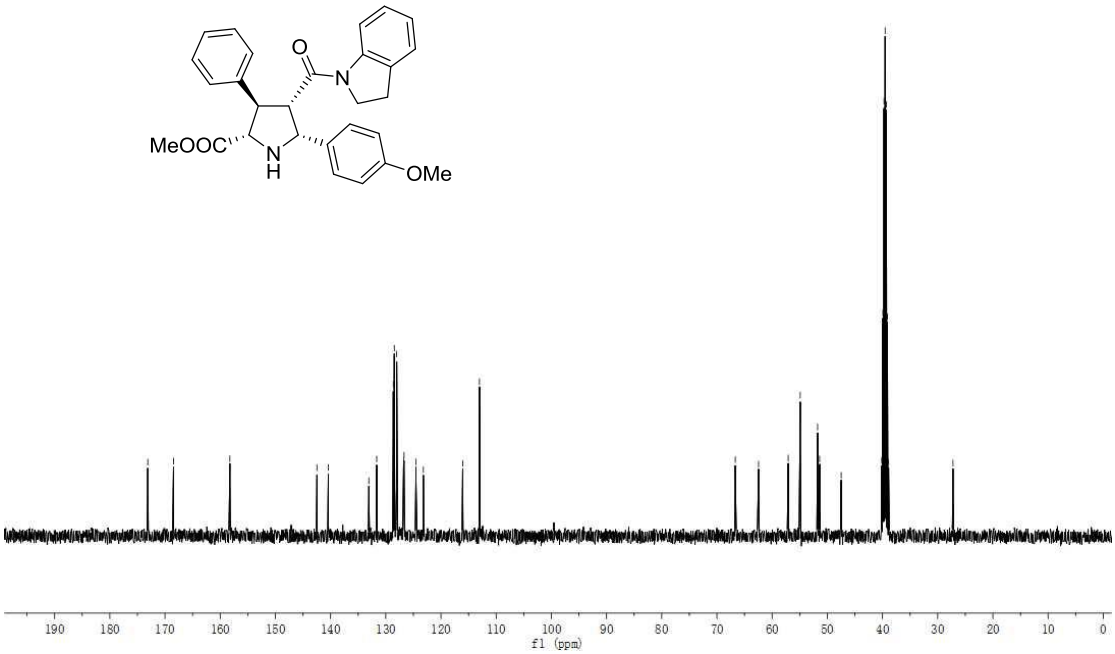
1 Det.A Ch1 / 254nm

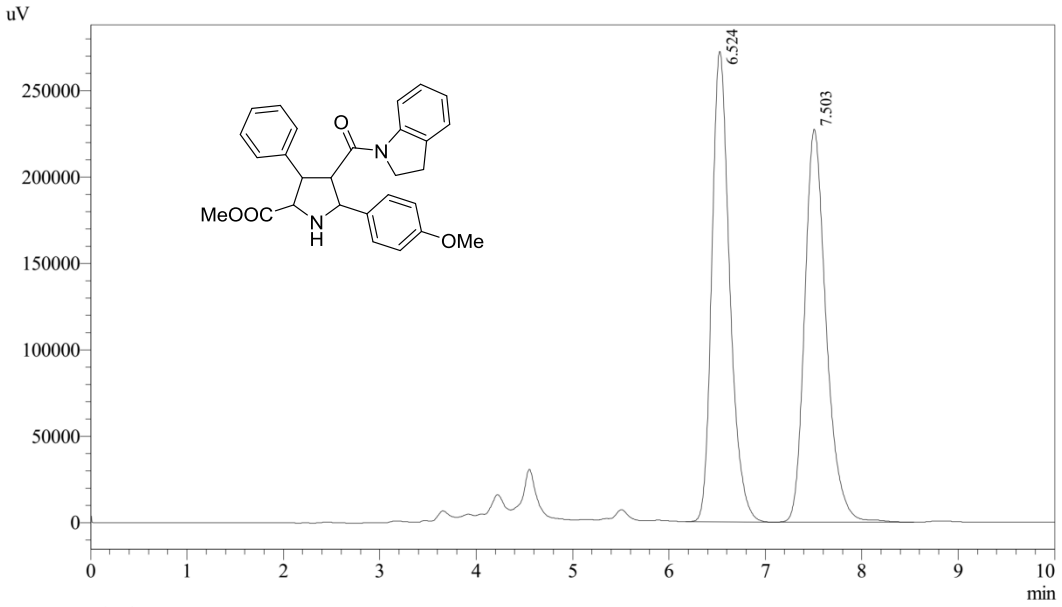
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.672	4238795	338780	97.441	98.710
2	11.856	111340	4429	2.559	1.290
Total		4350135	343208	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 4'



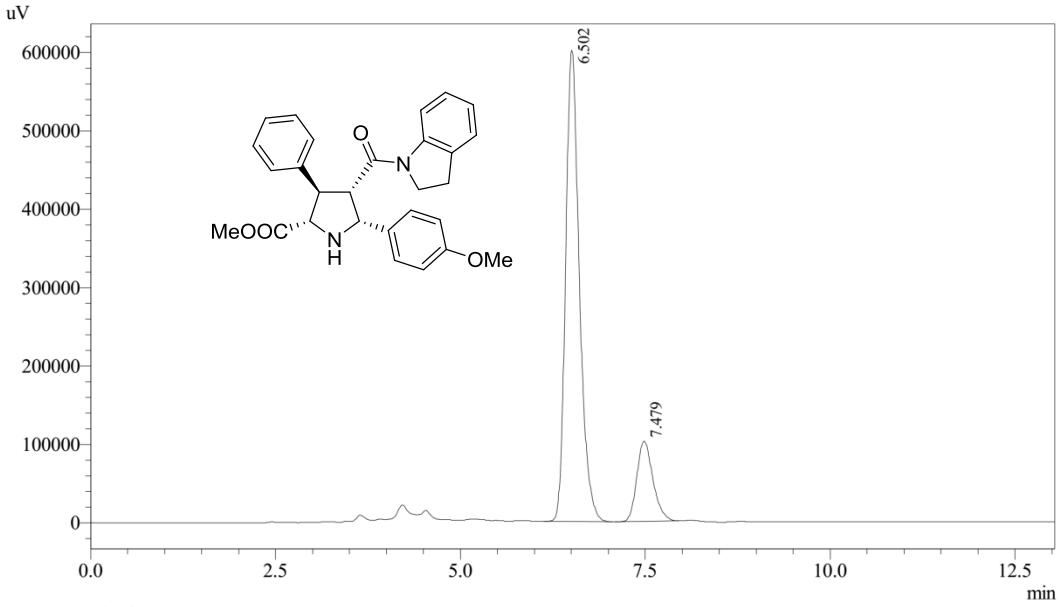




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.524	3509102	272270	49.754	54.467
2	7.503	3543775	227608	50.246	45.533
Total		7052877	499878	100.000	100.000

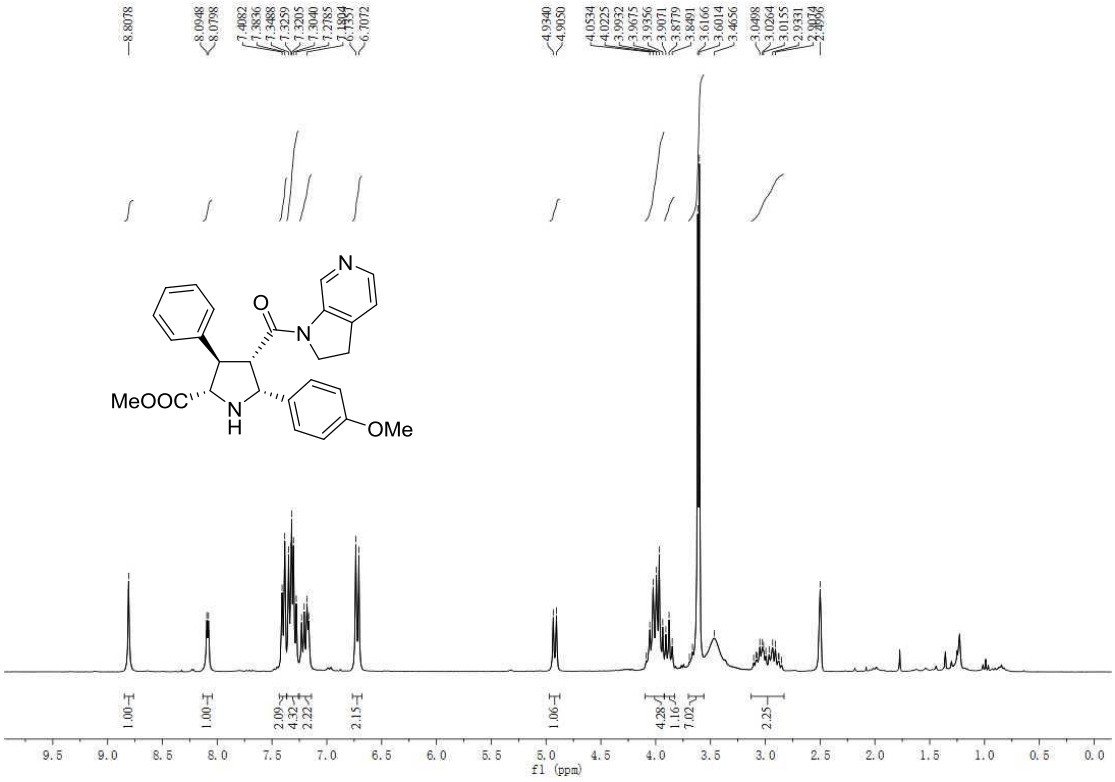


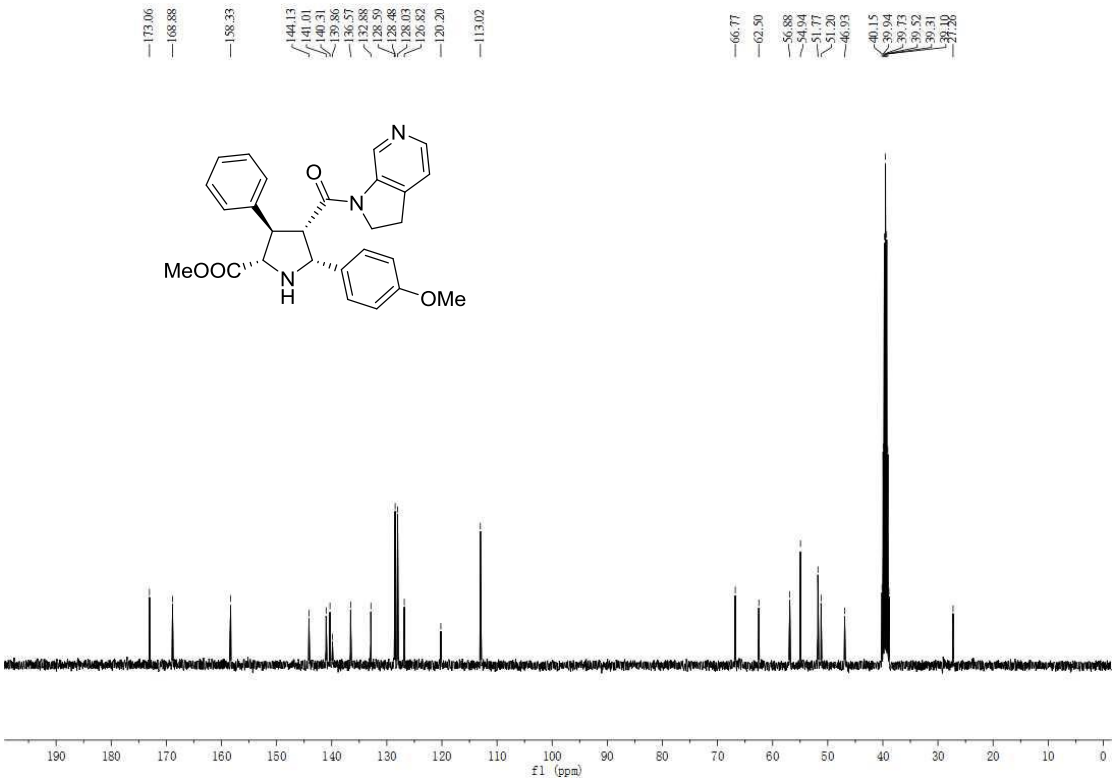
1 Det.A Ch1 / 254nm

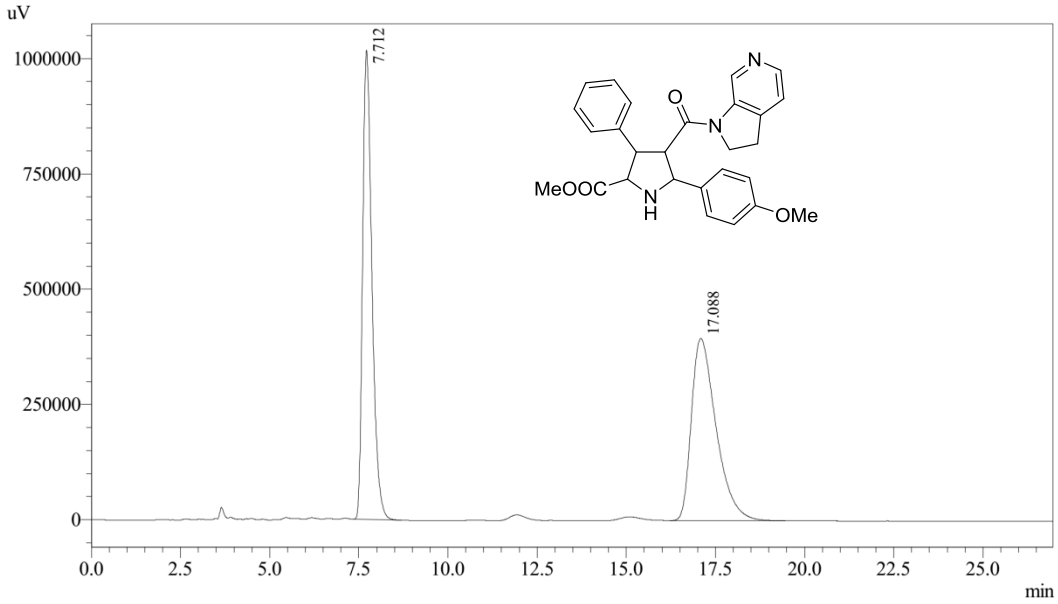
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.502	7804232	600854	83.319	85.414
2	7.479	1562475	102610	16.681	14.586
Total		9366707	703464	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 5'



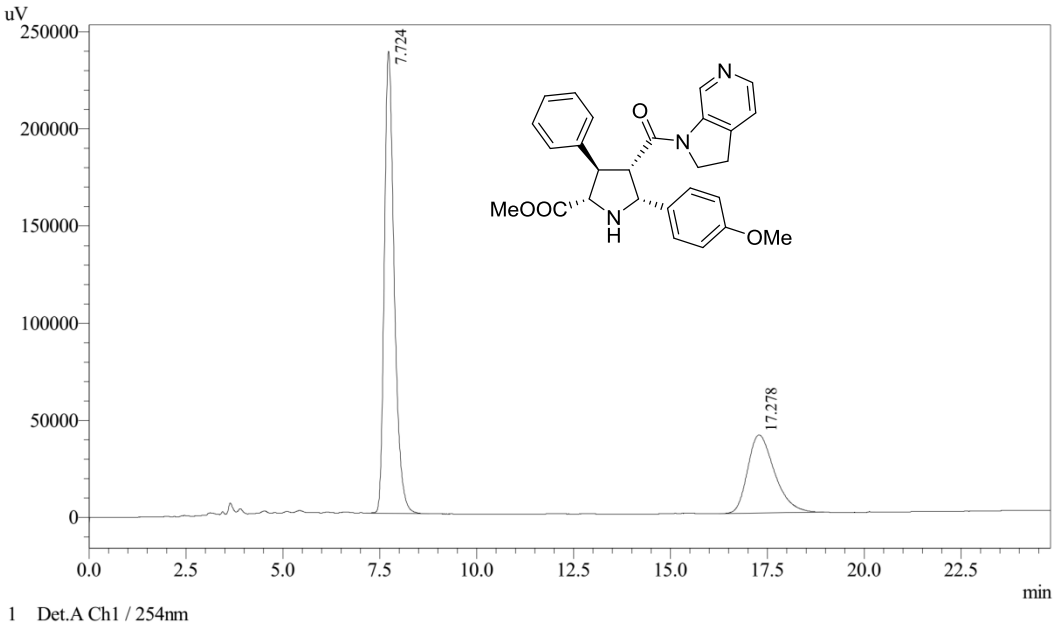




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.712	18511479	1018009	49.276	72.040
2	17.088	19055326	395104	50.724	27.960
Total		37566805	1413113	100.000	100.000

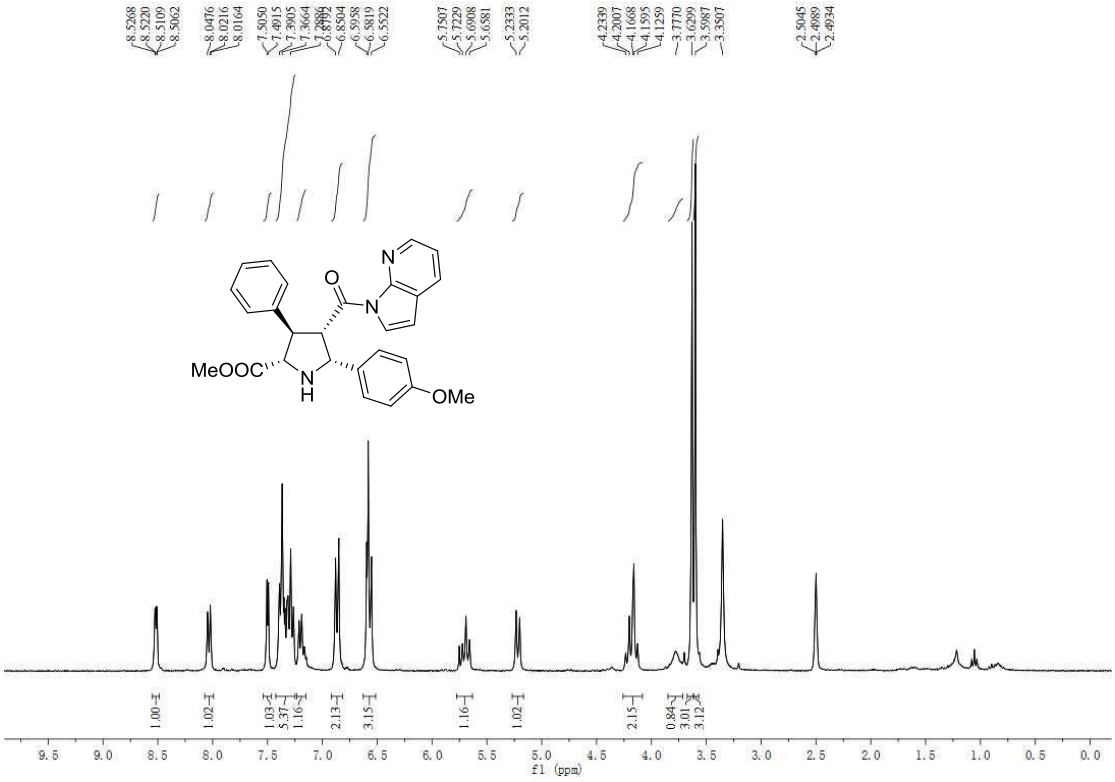


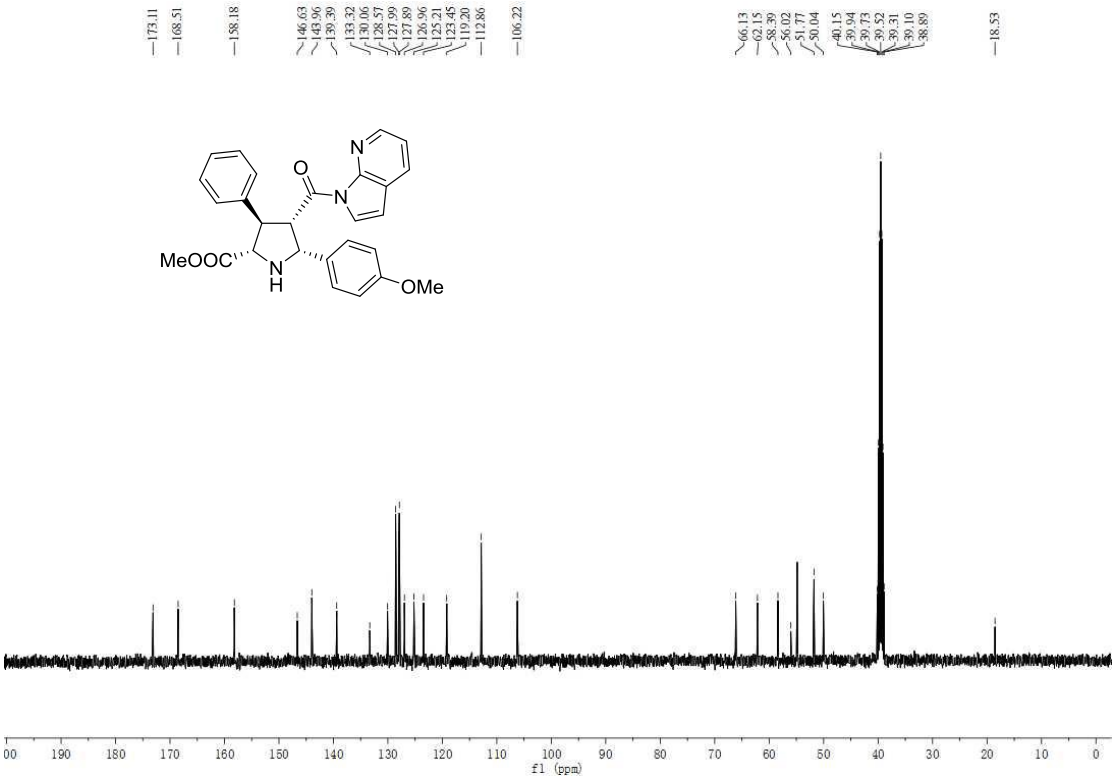
1 Det.A Ch1 / 254nm

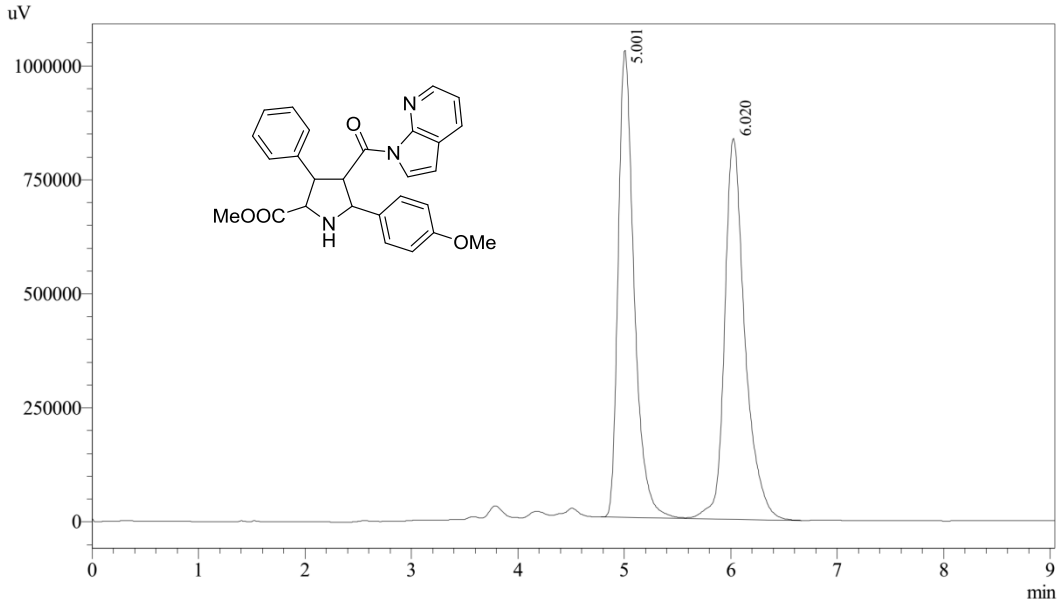
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.724	4226934	237754	68.434	85.518
2	17.278	1949739	40262	31.566	14.482
Total		6176673	278016	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 6'



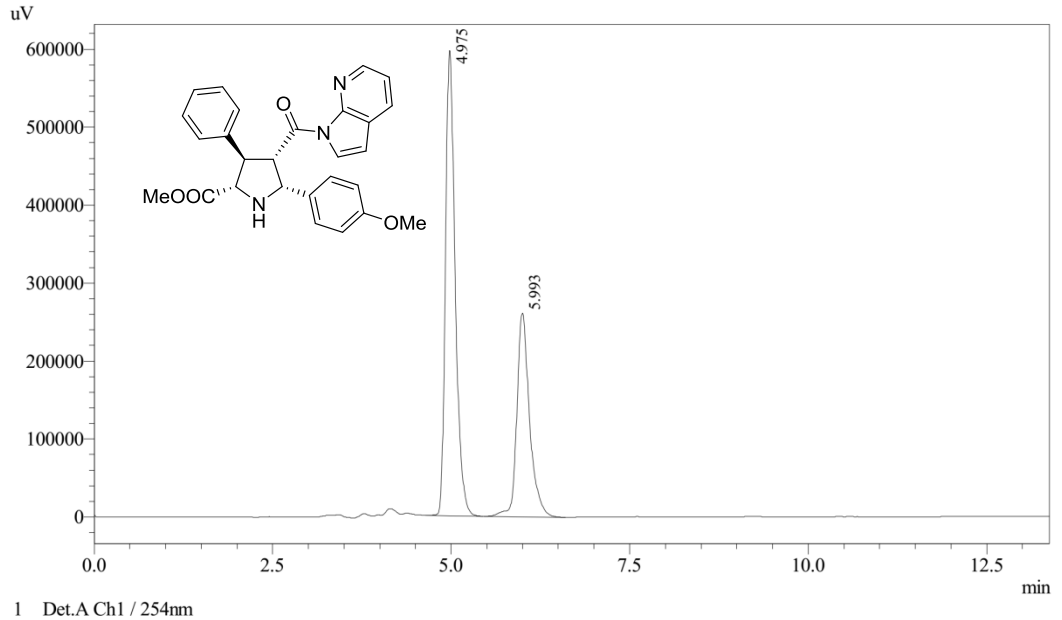




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.001	10656417	1023612	49.076	55.063
2	6.020	11057829	835367	50.924	44.937
Total		21714246	1858979	100.000	100.000

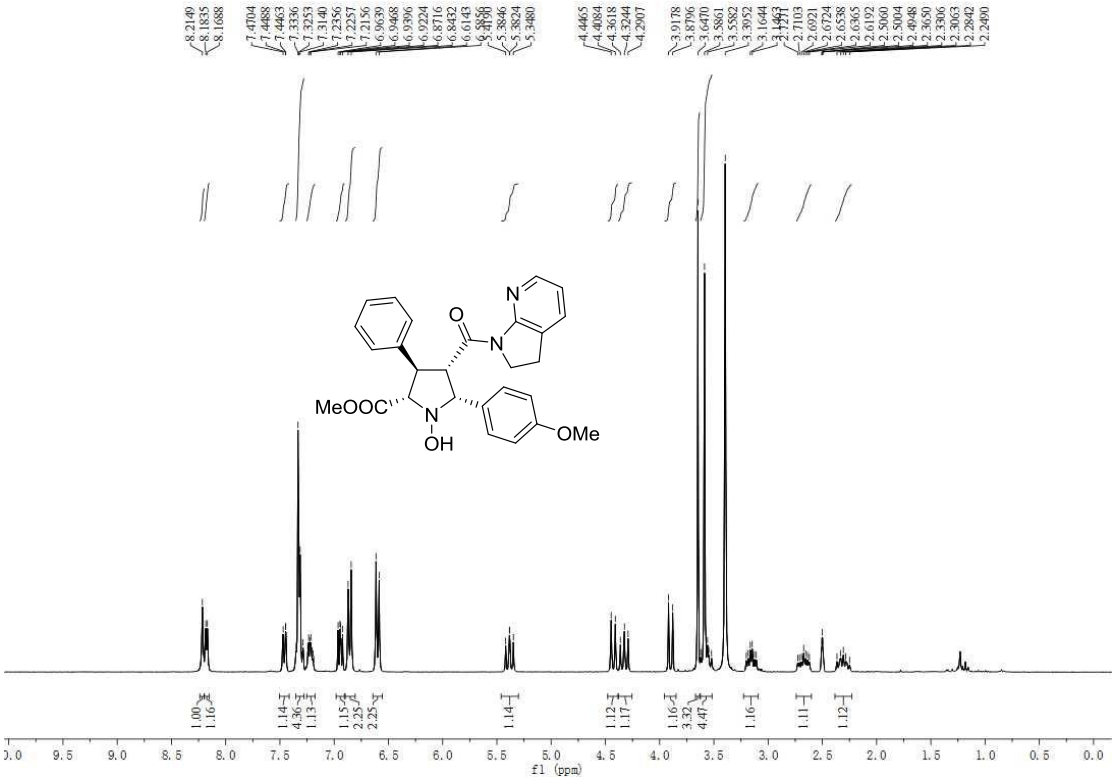


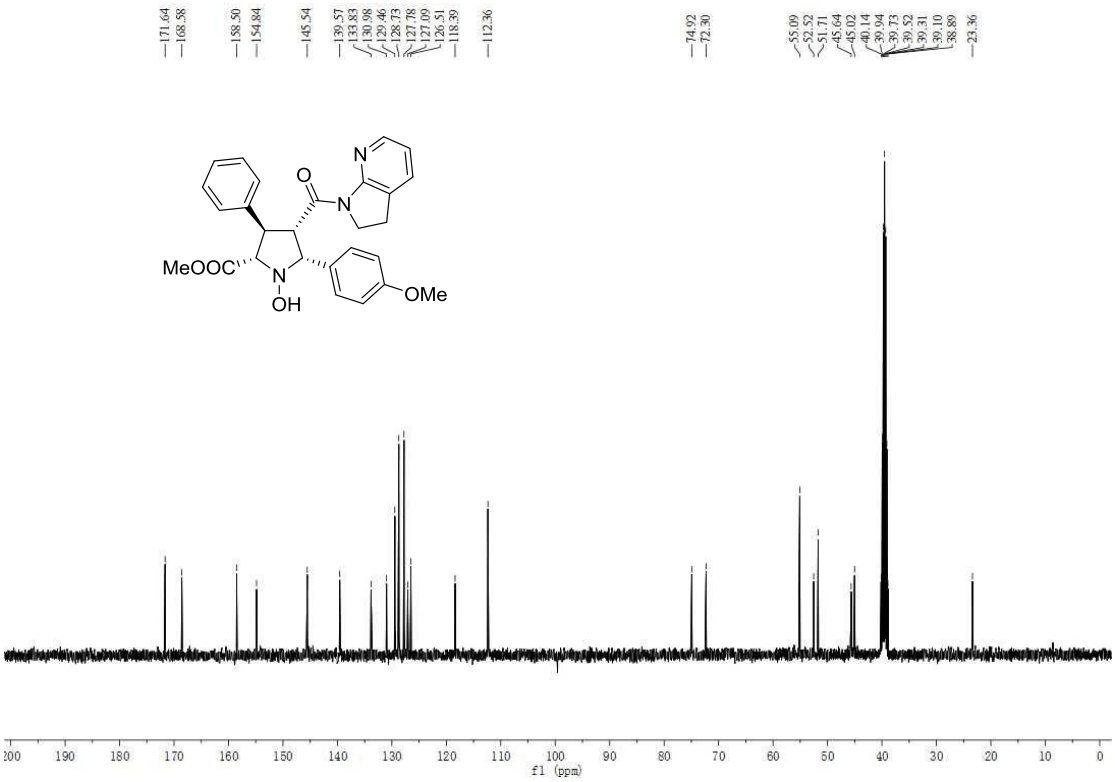
1 Det.A Ch1 / 254nm

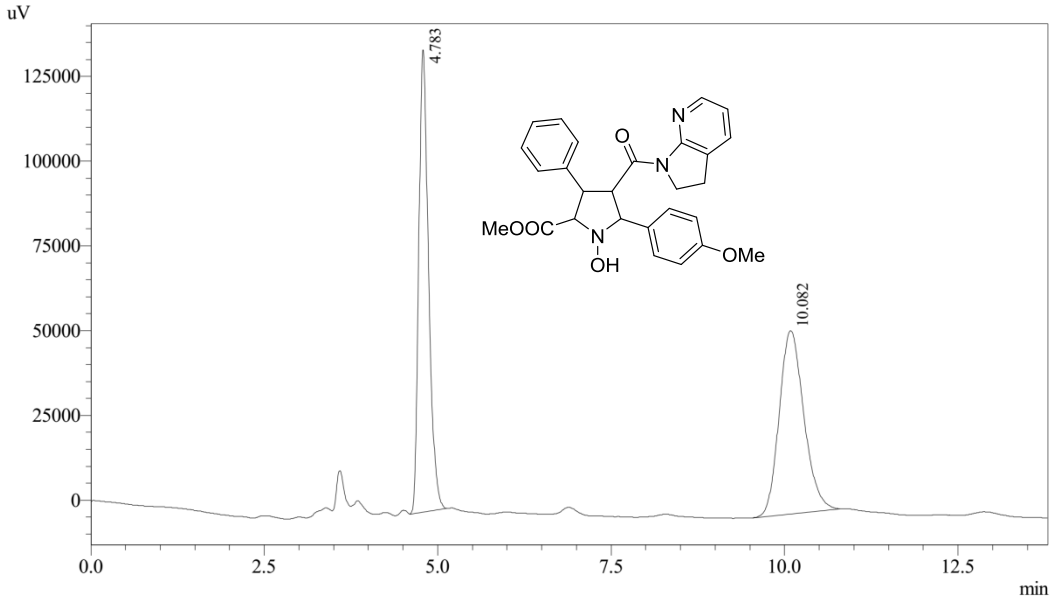
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.975	5628682	596700	63.394	69.528
2	5.993	3250152	261510	36.606	30.472
Total		8878833	858211	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 10



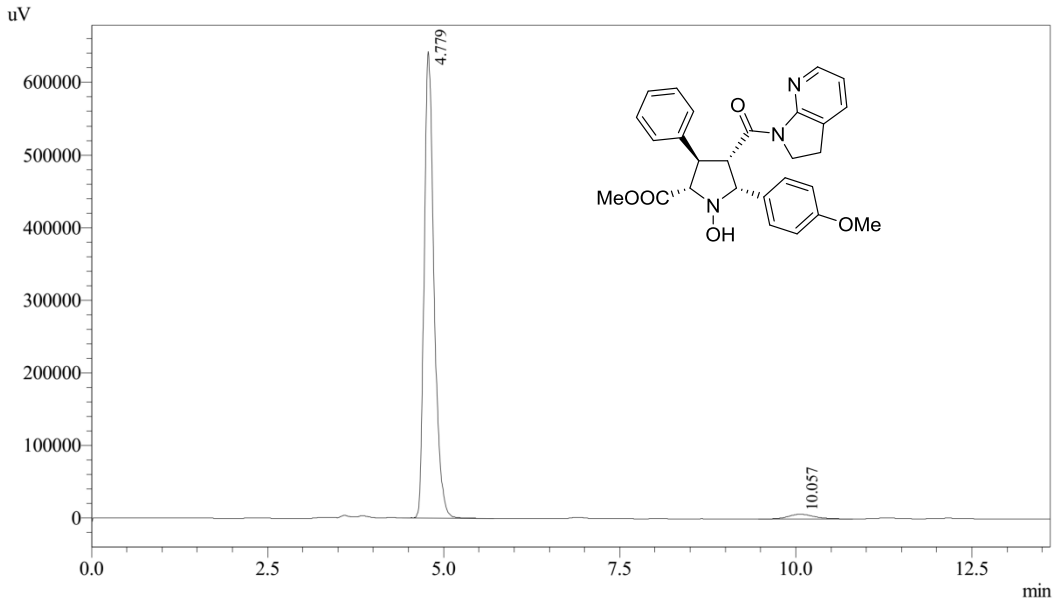




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.783	1340133	136309	50.044	71.607
2	10.082	1337751	54048	49.956	28.393
Total		2677884	190357	100.000	100.000

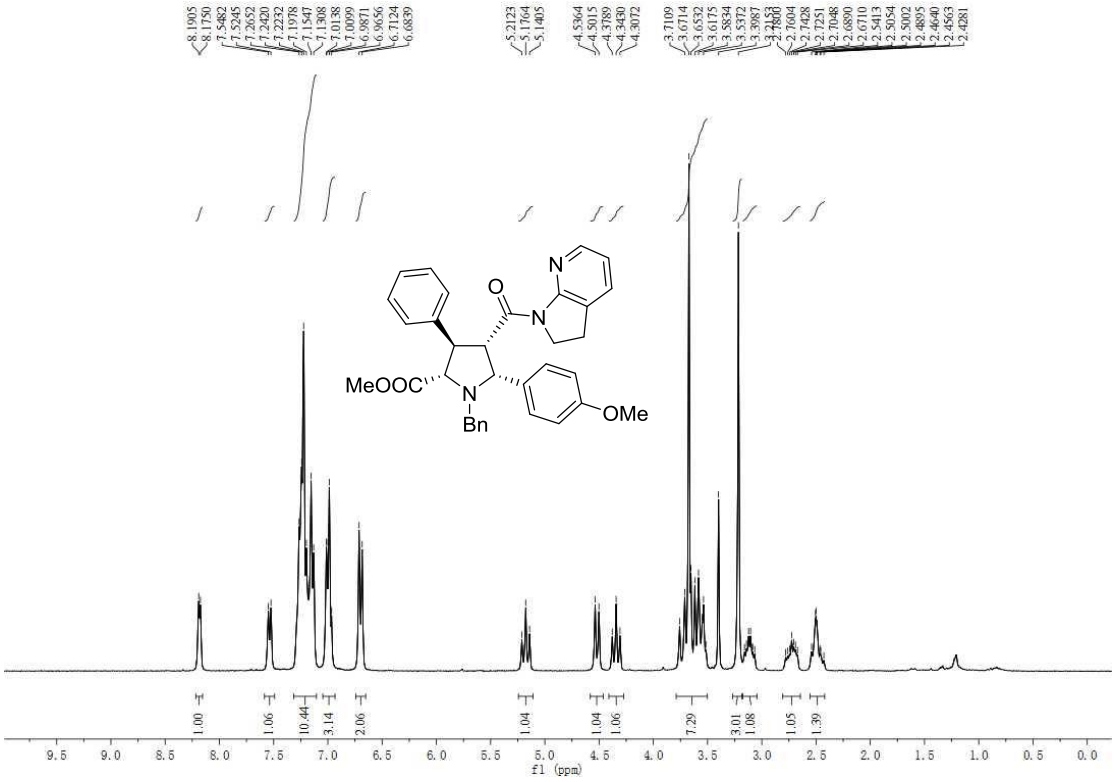


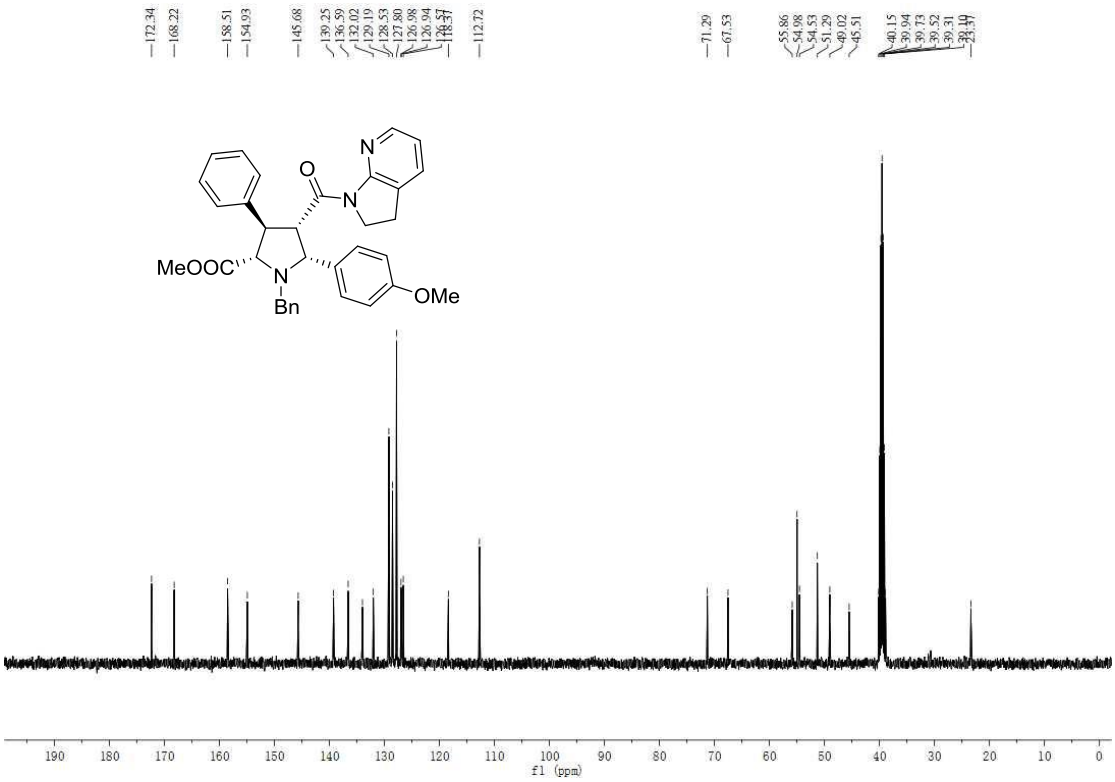
1 Det.A Ch1 / 254nm

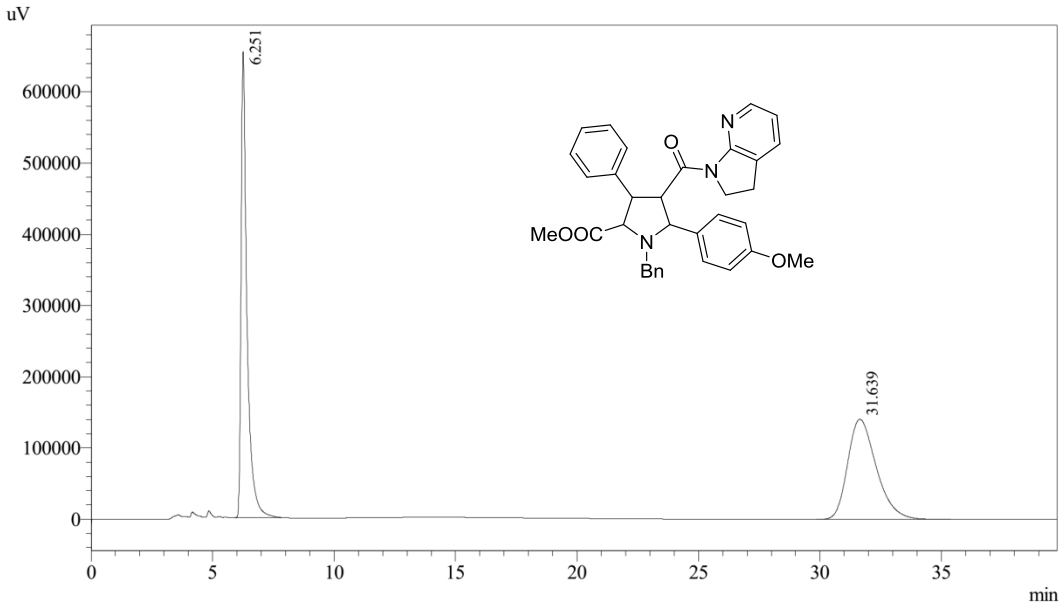
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.779	6280903	642772	97.484	99.007
2	10.057	162103	6449	2.516	0.993
Total		6443006	649221	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 11



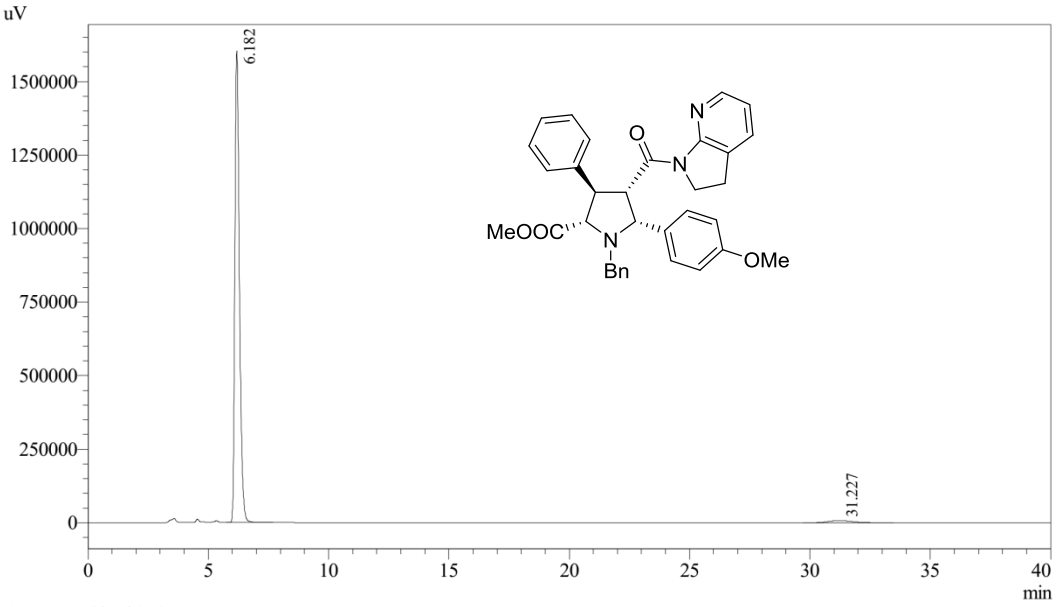




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.251	11051838	654513	48.989	82.324
2	31.639	11507940	140531	51.011	17.676
Total		22559778	795043	100.000	100.000

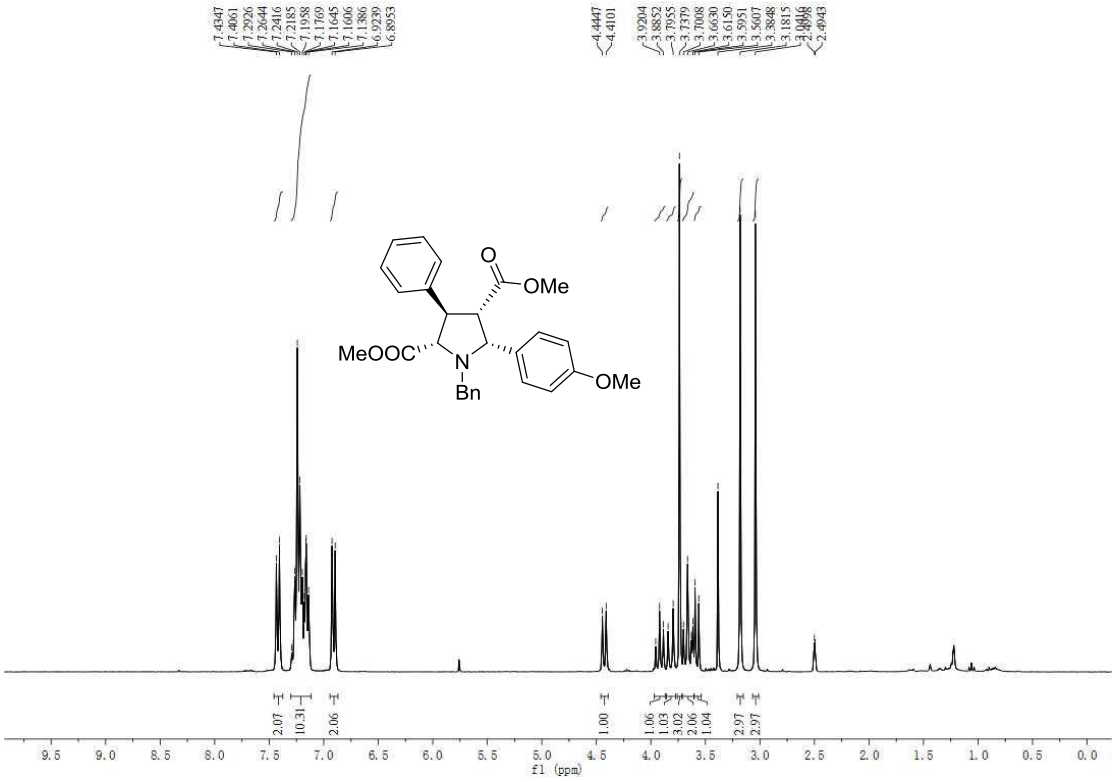


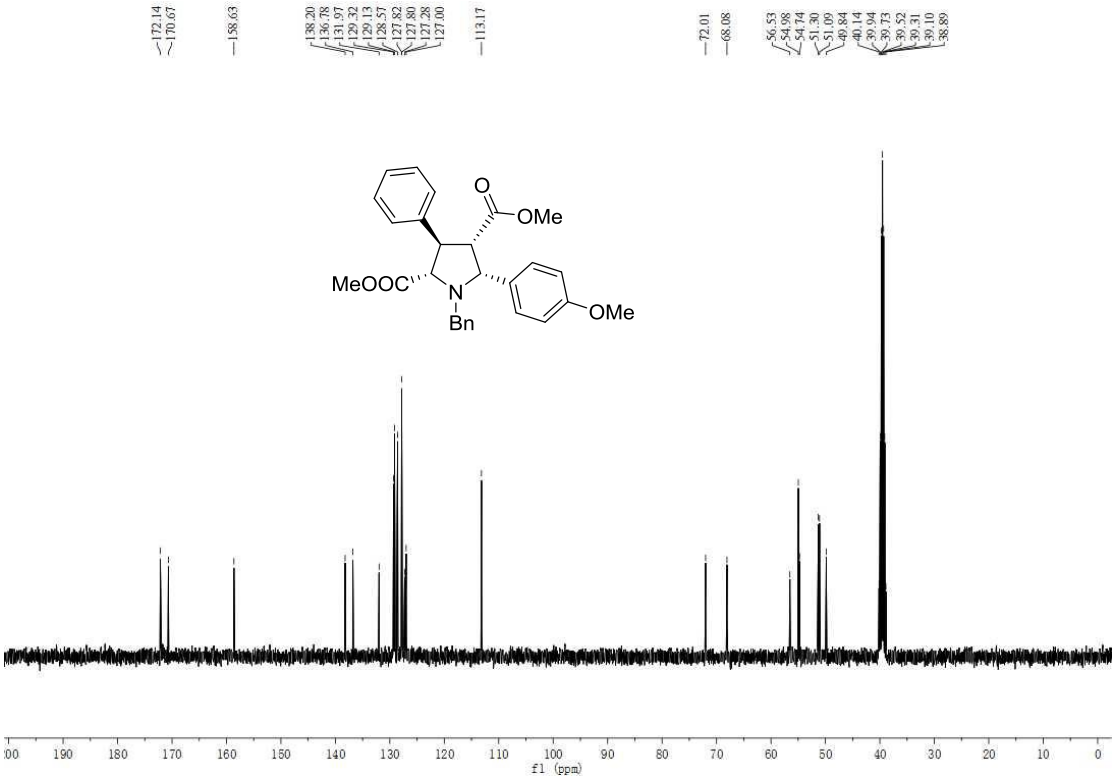
1 Det.A Ch1 / 254nm

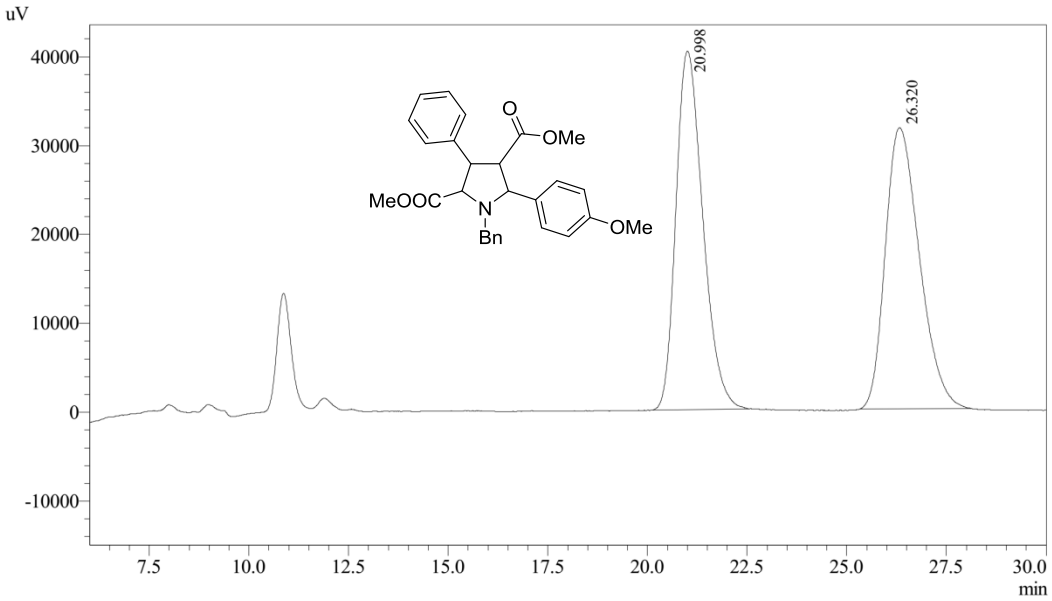
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.182	21135361	1603113	97.423	99.530
2	31.227	559166	7566	2.577	0.470
Total		21694527	1610679	100.000	100.000

^{1}H NMR, ^{13}C NMR and HPLC of 12



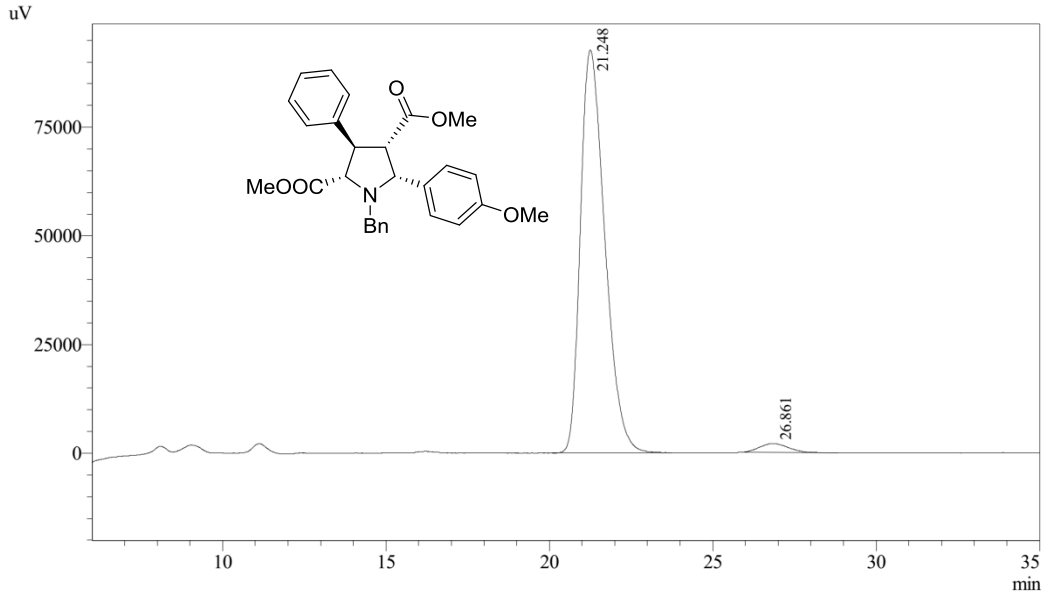




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.998	1891404	40322	50.078	56.047
2	26.320	1885545	31621	49.922	43.953
Total		3776949	71943	100.000	100.000



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.248	4819472	92671	97.432	97.818
2	26.861	127011	2067	2.568	2.182
Total		4946483	94738	100.000	100.000