# 3-Pyrrolyl-Oxindoles as Efficient Nucleophiles for Organocatalytic Asymmetric Synthesis of Structurally Diverse 3,3'-Disubstituted Oxindole Derivatives

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## Supporting Information

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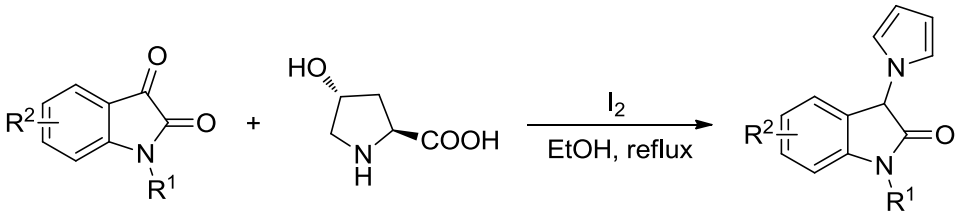
## 1. General remarks

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. $^{1}$H NMR and $^{13}$C NMR (300 and 75 MHz, respectively) 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 39.51 ppm). Melting points were recorded on a Buchi Melting Point B-545.

## 2. The synthesis of substrates 1

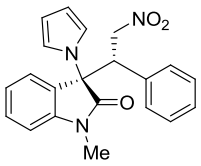
The procedure utilized in this paper was based on the method reported.[1]



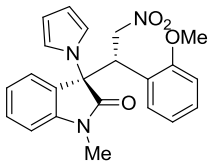

To isatin (10 mmol), hydroxyproline (10 mmol), and iodine (200 mg) was added ethanol (20 mL) and the mixture was heated under reflux for 1 h. Then the mixture was diluted with water (6 mL), extracted with dichloromethane (2×50mL), and the extract was washed with sodium thiosulfate solution (10%, 50 mL), saturated sodium bicarbonate (50 mL), and dried ($Na_2S0_4$). Pure product was isolated by silica gel column chromatography eluting with ethyl acetate/hexane (30/70).

## 3. General procedure for the synthesis of compounds 3a-y

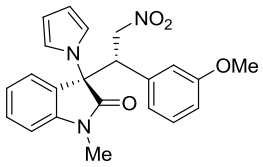
In an ordinary vial equipped with a magnetic stirring bar, the compounds **1** (0.1 mmol, 1.0 equiv), compounds **2** (0.15 mmol, 1.5 equiv) and catalyst **D** (5 mol %) were dissolved in 2 mL of DCM, and then the mixture was stirred at 0 $^{o}$C for indicated time. After completion of the reaction, as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1～3/1).



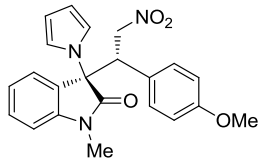

**(*R*)-1-methyl-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3a):** White solid; 35.1 mg, 97% yield; 87:13 dr, 94% ee; $[\alpha]_D^{20}$ = +150.9 (*c* 1.83, $CHCl_3$); mp 133.5-134.6 ℃; The ee was determined by HPLC (Chiralpak OJ-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 8.9 min, $t_{major}$ = 16.6 min); $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$(major diastereomer) 2.74 (s, 3H), 4.69 (dd, *J* = 3.0 Hz, 12.9 Hz, 1H), 4.80 (dd, *J* = 3.0 Hz, 12.0 Hz, 1H), 5.05 (t, *J* = 12.0 Hz, 1H), 6.28-6.29 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.77-6.80 (m, 2H), 7.03-7.08 (m, 2H), 7.11-7.14 (m, 3H), 7.26-7.29 (m, 1H), 7.42-7.49 (m，2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 25.9, 50.5, 68.4, 74.7, 109.3, 110.0, 119.3, 122.7, 123.5, 126.1, 128.0, 128.6, 128.9, 131.1, 131.6, 144.5, 172.3; HRMS (ESI-TOF) calcd. for $C_{21}H_{19}N_3NaO_3$ $[M + Na]^+$ 384.1319; found: 384.1314.



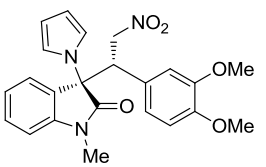
**(*R*)-3-((*S*)-1-(2-methoxyphenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl) indolin-2-one (3b)**: White solid; 35.6 mg, 91% yield; 71:29 dr, 93% ee; $[\alpha]_D^{20}$ = +131.4 (*c* 1.25, $CHCl_3$); mp 195.9-197.4 ℃; the ee was determined by HPLC (Chiralpak AD-H, EtOH /hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 8.8 min, $t_{major}$ = 9.3 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 3.10 (s, 3H), 3.61 (s, 3H), 4.71 (dd, *J* = 2.7 Hz, 13.5 Hz, 1H), 5.39-5.48 (m, 1H), 5.57 (dd, *J* = 2.7 Hz, 11.4 Hz, 1H), 6.28 (m, 2H), 6.44-6.50 (m, 2H), 6.75-6.80 (m, 1H), 6.92-6.97 (m, 1H), 7.01-7.12 (m, 2H), 7.16-7.26 (m, 3H), 7.51 (d, *J* = 7.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.2, 41.0, 54.9, 68.7, 74.6, 107.8, 109.8, 110.4, 118.9, 120.0, 121.2, 122.2, 124.5, 126.8, 127.5, 129.4 129.5, 141.7, 156.9, 172.3; HRMS (ESI-TOF) calcd. for $C_{22}H_{21}N_3NaO_4$ $[M + Na]^+$ 414.1424; found: 414.1432.



**(*R*)-3-((*S*)-1-(3-methoxyphenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3c):** White solid; 37.6 mg, 96%yield; 88:12 dr, 94% ee; $[\alpha]_D^{20}$ = +113.2 (*c* 1.98, $CHCl_3$); mp 149.5-150.7 ℃; The ee was determined by HPLC (Chiralpak OJ-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 13.9 min, $t_{major}$ = 19.8 min); $^1$H NMR (300 MHz, $CDCl_3$): *δ*(major diastereomer) 2.77 (s, 3H), 3.55 (s, 3H), 4.68 (dd, *J* = 3.0 Hz, 12.6 Hz, 1H), 4.77 (dd, *J* = 2.7 Hz, 11.7 Hz, 1H), 5.03 (t, *J* = 12.3 Hz, 1H), 6.24-6.28 (m, 3H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.95-7.01 (m, 1H), 7.11-7.13 (m, 2H), 7.24-7.29 (m, 1H), 7.42-7.48 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ*(major diastereomer) 25.9, 50.4, 55.0, 68.2, 74.8, 109.3, 110.0, 113.2, 115.0, 119.2, 121.6, 122.6, 123.6, 126.1, 129.0, 131.0, 133.1, 144.6, 159.0, 172.2; HRMS (ESI-TOF) calcd. for $C_{22}H_{21}N_3NaO_4$ $[M + Na]^+$ 414.1424; found: 414.1425.

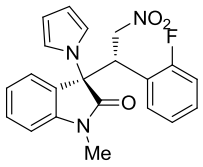


**(*R*)-3-((*S*)-1-(4-methoxyphenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3d):** White solid; 38.0 mg, 97%yield; 82:18 dr, 91% ee; $[\alpha]_D^{20}$ = +126.9 (*c* 1.58, $CHCl_3$); mp 100.5-101.7 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 17.2 min, $t_{major}$ = 15.8 min); $^1$H NMR (300 MHz, $CDCl_3$):*δ* (major diastereomer) 2.78 (s, 3H), 3.69 (s, 3H), 4.67 (dd, *J* = 3.0 Hz, 8.7 Hz, 1H), 4.75 (dd, *J* = 3.0 Hz, 12.0 Hz, 1H), 5.00 (t, *J* = 12.0 Hz, 1H), 6.27-6.29 (m, 2H), 6.57-6.62 (m, 2H), 6.67-6.72 (m, 3H), 7.10-7.13 (m, 2H), 7.24-7.29 (m, 1H), 7.42-7.48 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ* (major diastereomer) 26.0, 49.8, 55.1, 68.4, 75.0, 109.3, 110.0, 113.4, 119.2, 122.6, 123.1, 123.4, 123.6, 124.2, 126.1, 130.0, 131.0, 144.5, 159.5, 172.4; HRMS (ESI-TOF) calcd. for $C_{22}H_{21}N_3NaO_4$ $[M + Na]^+$ 414.1424; found: 414.1429.

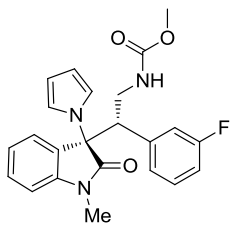


**(*R*)-3-((*S*)-1-(3,4-dimethoxyphenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3e):** White solid; 39.6 mg, 94%yield; 88:12 dr, 94% ee; $[\alpha]_D^{20}$ = +151.3 (*c* 2.00, $CHCl_3$); mp 157.7-158.7 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 30/70, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 7.8 min, $t_{major}$ = 8.8 min); $^1$H NMR (300 MHz, $CDCl_3$):*δ* (major diastereomer) 2.78 (s, 3H), 3.52 (s, 3H), 3.76 (s, 3H), 4.65-4.76 (m, 2H), 4.98 (t, *J* = 11.4 Hz, 1H), 6.10 (d, *J* = 1.8 Hz, 1H), 6.26-6.28 (m,

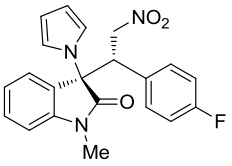
2H), 6.47-6.50 (m, 1H), 6.57-6.61 (m, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 7.09-7.11 (m, 2H), 7.26-7.28 (m, 1H), 7.41-7.48 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (major diastereomer) 26.0, 50.0, 55.4, 55.6, 68.3, 75.0, 109.4, 109.9, 110.4, 110.6, 119.2, 122.3, 122.5, 123.7, 123.8, 126.0, 131.0, 144.7, 148.1, 148.8, 172.4; HRMS (ESI-TOF) calcd. for $C_{23}H_{23}N_3NaO_5$ $[M + Na]^+$ 444.1530; found: 444.1538.



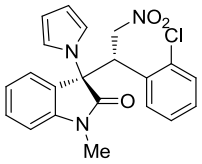
**(*R*)-3-((*S*)-1-(2-fluorophenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl) indolin-2-one (3f):** White solid; 36.9 mg, 97%yield; 96:4 dr, 79% ee; $[\alpha]_D^{20}$ = +147.5 (*c* 1.40, $CHCl_3$); mp 94.9-96.3 ℃; the ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 22.9 min, $t_{major}$ = 12.3 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$(major diastereomer) 2.84 (s, 3H), 4.78-4.85 (m, 1H), 5.04-5.15 (m, 2H), 6.27 (br s, 2H), 6.50-6.56 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.80-6.98 (m, 2H), 7.05-7.16 (m, 3H), 7.22-7.26 (m, 1H), 7.40-7.49 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 26.1, 43.8, 67.6, 74.3, 109.2, 109.9, 115.9 (d, *J* = 23.2 Hz, 1C), 119.6, 122.7, 123.4, 123.7 (d, *J* = 3.7 Hz, 1C), 124.2 (d, *J* = 3.5 Hz, 1C), 126.7, 129.6, 130.4 (d, *J* = 8.7 Hz, 1C), 131.2, 144.3, 161.1 (d, *J* = 249.0 Hz, 1C), 172.1; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}FN_3NaO_3$ $[M + Na]^+$ 402.1224; found: 402.1232.



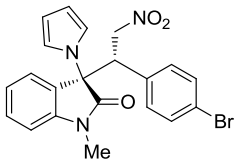
**Methyl-((*S*)-2-(3-fluorophenyl)-2-((*R*)-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)ethyl)carbamate (3g):** White solid; 39.4 mg, 97% yield; 89:11 dr, 94% ee; $[\alpha]_D^{20}$ = +113.1 (*c* 1.85, $CHCl_3$); mp 184.3-186.0 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 8.5 min, $t_{major}$ = 11.1 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.73 (s, 3H), 3.56 (s, 3H), 3.67-3.70 (m, 1H), 3.75-3.78 (m, 1H), 4.08-4.13 (m, 1H), 4.42 (brs, 1H), 6.25-6.26 (m, 2H), 6.40 (d, *J* = 10.2 Hz, 1H), 6.61-6.68 (m, 2H), 6.79-6.85 (m, 1H), 6.99-7.10 (m, 3H), 7.22-7.27 (m, 1H), 7.39-7.44 (m, 1H), 7.65 (d, *J* = 7.2 Hz, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 25.8, 40.1, 51.4, 52.1, 69.0, 108.9, 109.4, 114.8 (d, J = 20.8 Hz, 1C), 115.9 (d, J = 21.9 Hz, 1C), 119.4, 122.6, 124.1, 125.4, 126.7, 129.2 (d, J = 7.9 Hz, 1C), 130.7, 137.1, 144.4, 156.7, 162.0 (d, J = 244.8 Hz, 1C), 173.0; HRMS (ESI-TOF) calcd. for $C_{23}H_{22}FN_3NaO_3$ $[M + Na]^+$ 430.1537; found: 430.1547.



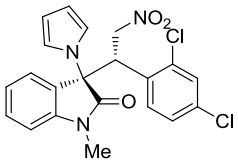
**(*R*)-3-((*S*)-1-(4-fluorophenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl) indolin-2-one (3h):** White solid; 36.4 mg, 96%yield; 87:13 dr, 94% ee; $[\alpha]_D^{20}$ = +194.3 (*c* 1.73, $CHCl_3$); mp 157.5-158.8 ℃; the ee was determined by HPLC (Chiralpak OJ-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 10.4 min, $t_{major}$ = 18.2 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$(major diastereomer) 2.78 (s, 3H), 4.67 (dd, *J* = 2.7 Hz, 12.6 Hz, 1H), 4.79 (dd, *J* = 2.7 Hz, 12.0 Hz, 1H), 5.00 (t, *J* = 12.3 Hz, 1H), 6.28-6.29 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.72-6.81 (m, 4H), 7.09-7.12 (m, 2H), 7.22-7.30 (m, 1H), 7.43-7.49 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 26.0, 49.7, 68.2, 74.7, 109.4, 110.1, 115.1 (d, *J* = 21.4 Hz, 1C), 119.2, 122.8, 123.3, 126.1, 127.4 (d, *J* = 3.2 Hz, 1C), 130.6 130.7, 131.2, 144.4, 162.5 (d, *J* = 246.9 Hz, 1C), 172.2; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}FN_3NaO_3$ $[M + Na]^+$ 402.1224; found: 402.1223.



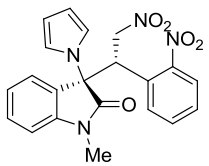
**(*R*)-3-((*S*)-1-(2-chlorophenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl) indolin-2-one (3i):** White solid; 37.2 mg, 94% yield; 87:13 dr, 97% ee; $[\alpha]_D^{20}$ = +96.3 (*c* 1.70, $CHCl_3$); mp 153.7-155.4 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 12.1 min, $t_{major}$ = 9.1 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.93 (s, 3H), 4.89 (t, *J* = 12.3 Hz, 1H), 5.17 (dd, *J* = 3.3 Hz, 12.9 Hz, 1H), 5.37 (dd, *J* = 3.3 Hz, 11.7 Hz, 1H), 6.22-6.30 (m, 3H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.90-6.95 (m, 1H), 7.09-7.22 (m, 5H), 7.33-7.36 (m, 1H), 7.46-7.51 (m, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.2, 45.0, 67.1, 75.7, 109.4, 109.7, 119.8, 122.8, 123.7, 124.6, 126.5, 126.6, 128.0, 129.7, 130.1, 131.2, 136.5, 144.3, 171.9; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}ClN_3NaO_3$ $[M + Na]^+$ 418.0929; found: 418.0933.



**(*R*)-3-((*S*)-1-(4-bromophenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3j):** White solid; 42.2 mg, 96% yield; 86:14 dr, 95% ee; $[\alpha]_D^{20}$ = +134.9 (*c* 1.57, $CHCl_3$); mp 132.6-133.8 ℃; the ee was determined by HPLC (Chiralpak OJ-H, ethanol /hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 11.9 min, $t_{major}$ = 20.2 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.80 (s, 3H), 4.66 (dd, *J* = 3.0 Hz, 12.9 Hz, 1H), 4.77 (dd, *J* = 3.0 Hz, 12.0 Hz, 1H), 5.00 (t, *J* = 12.3 Hz, 1H), 6.27-6.30 (m, 2H), 6.66-6.73 (m, 3H), 7.09-7.13 (m, 2H), 7.19-7.30 (m, 3H), 7.43-7.49 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.0, 49.9, 67.9, 74.5, 109.5, 110.1, 119.1, 122.8, 123.1, 123.3, 126.1, 130.3, 130.5,130.8 131.2, 144.4, 172.0; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}BrN_3NaO_3$ $[M + Na]^+$ 462.0424; found: 462.0420.

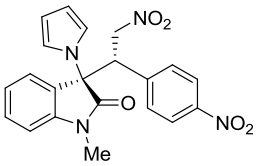


**(*R*)-3-((*S*)-1-(2,4-dichlorophenyl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3k):** White solid; 40.3 mg, 94%yield; 83:17 dr, 99% ee; $[\alpha]_D^{20}$ = +62.0 (*c* 1.27, $CHCl_3$); mp 168.6-169.9 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 12.9 min, $t_{major}$ = 8.2 min); $^1$H NMR (300 MHz, $CDCl_3$):*δ*(major diastereomer) 2.97 (s, 3H), 4.85 (t, *J* = 12.3 Hz, 1H), 5.14 (dd, *J* = 3.3 Hz, 12.9 Hz, 1H), 5.29 (dd, *J* = 3.3 Hz, 11.7 Hz, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 6.25-6.27 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.91-6.95 (m, 1H), 7.11-7.18 (m, 4H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.49-7.50 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ*(major diastereomer) 26.3, 44.8, 66.8, 75.5, 109.5, 109.9, 119.7, 122.9, 123.5, 126.5, 126.9, 128.1, 128.9, 129.9, 131.3, 135.0, 137.4, 144.2, 171.7; HRMS (ESI-TOF) calcd. for $C_{21}H_{17}Cl_2N_3NaO_3$ $[M + Na]^+$ 452.0539; found: 452.0543.

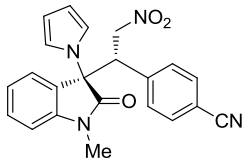


**(*R*)-1-methyl-3-((*S*)-2-nitro-1-(2-nitrophenyl)ethyl)-3-(1*H*-pyrrol-1-yl) indolin-2-one (3l):** White solid; 36.9 mg, 91% yield; 91:9 dr, 97% ee; $[\alpha]_D^{20}$ = -24.6 (*c* 1.85, $CHCl_3$); mp 208.6-209.7 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 11.4 min, $t_{major}$ = 7.7 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.91 (s, 3H), 5.00 (t, *J* = 11.4 Hz, 1H), 5.14 (dd, *J* = 3.6 Hz, 12.9Hz, 1H), 5.78 (dd, , *J* = 3.6 Hz, 11.4 Hz, 1H), 6.22-6.24 (m, 2H), 6.59 (d, *J* = 7.8 Hz,

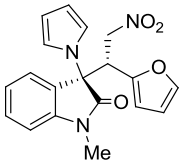
1H), 6.79 (d, *J* = 7.8 Hz, 1H), 7.05-7.07 (m, 2H), 7.20 (d, *J* = 4.2 Hz, 2H), 7.23-7.31(m, 1H), 7.37-7.50 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.2, 43.1, 67.2, 75.1, 109.5, 109.9, 119.7, 123.0, 123.5, 125.4, 126.3, 127.8, 128.6, 129.4, 131.4, 132.2, 144.1, 150.8, 171.8; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}N_4NaO_5$ $[M + Na]^+$ 429.1169; found: 429.1171.



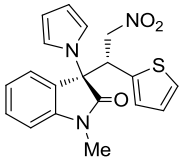

**(*R*)-1-methyl-3-((*S*)-2-nitro-1-(4-nitrophenyl)ethyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3m):** White solid; 39.8 mg, 98%yield; 84:16 dr, 95% ee; $[\alpha]_D^{20}$ = +129.3 (*c* 1.40, $CHCl_3$); mp 176.8.7-178.2 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 31.0 min, $t_{major}$ = 33.1 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$(major diastereomer) 2.80 (s, 3H), 4.68 (dd, *J* = 2.7 Hz, 12.9 Hz, 1H), 4.91 (dd, *J* = 2.7 Hz, 12.0 Hz, 1H), 5.07 (t, *J* = 12.6 Hz, 1H), 6.29-6.30 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.09-7.13 (m, 2H), 7.28-7.33 (m, 1H), 7.46-7.54 (m, 2H), 7.93 (d, *J* = 8.7 Hz, 2H);$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 26.1, 50.2, 67.7, 74.1, 109.7, 110.4, 119.1, 122.6, 123.1, 123.5, 126.1, 130.1, 131.6, 139.4, 144.2, 147.7, 171.7; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}N_4NaO_5$ $[M + Na]^+$ 429.1169; found: 429.1169.



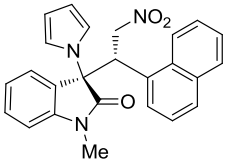

**4-((*S*)-1-((*R*)-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-nitroethyl)benzonitrile (3n):** White solid; 37.1 mg, 96% yield; 84:16 dr, 84% ee; $[\alpha]_D^{20}$ = +109.3 (*c* 1.88, $CHCl_3$); mp 161.4-162.3 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH /hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 9.5 min, $t_{major}$ = 8.4 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.79 (s, 3H), 4.67 (dd, *J* = 2.7 Hz, 13.2 Hz, 1H), 4.86 (dd, *J* = 2.7 Hz, 12.0 Hz, 1H), 5.04 (t, *J* = 12.6 Hz, 1H), 6.28-6.30 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.08-7.13 (m, 2H), 7.26-7.32 (m, 1H), 7.36-7.39 (m, 2H), 7.45-7.52 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.0, 50.4, 67.8, 74.0, 109.6, 110.3, 112.5, 118.0, 119.1, 123.0, 123.4, 126.1, 129.7, 131.5 131.7, 137.3, 144.2, 171.7; HRMS (ESI-TOF) calcd. for $C_{22}H_{18}N_4NaO_3$ $[M + Na]^+$ 409.1271; found: 409.1275.



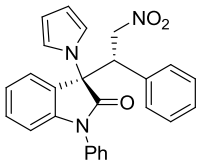

**(*R*)-3-((*S*)-1-(furan-2-yl)-2-nitroethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3o):** Brown oil; 34.1 mg, 97% yield; 71:29 dr, 78% ee, 17% ee; $[\alpha]_D^{20}$ = +123.2 (*c* 1.82, $CHCl_3$); the ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 14.2 min, $t_{major}$ = 15.7 min, minor diastereomer: $t_{minor}$ = 16.8 min, $t_{major}$ = 12.6 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$ (major + minor diastereomers) 2.99 (s, 2.1H), 3.19 (s, 0.9H), 4.39 (dd, *J* = 2.7 Hz, 13.5 Hz, 0.3H), 4.48 (dd, *J* = 2.4 Hz, 12.9 Hz, 0.7H), 4.87-4.91 (m, 0.3H), 4.96-5.01 (m, 1H), 5.07-5.15 (m, 0.7H), 5.76 (d, *J* = 3.3 Hz, 0.3H), 5.98 (d, *J* = 3.3 Hz, 0.7H), 6.09-6.11 (m, 0.7H), 6.16-6.18 (m, 0.3H), 6.21-6.23 (m, 0.6H), 6.25-6.26 (m, 1.4H), 6.74-6.81 (m, 1H), 7.02-7.10 (m, 3H), 7.20-7.24 (m, 1H), 7.35-7.42 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (major + minor diastereomers) 26.3, 26.5, 44.5, 44.7, 67.0, 67.2, 72.7, 72.9, 109.0, 109.1, 109.3, 109.6, 109.7, 110.1, 110.3, 110.9, 119.0, 119.1, 122.7, 123.3, 123.7, 125.4, 126.2, 130.6, 130.9, 142.3, 142.7, 143.0, 144.1, 146.4, 146.8, 172.1, 172.5; HRMS (ESI-TOF) calcd. for $C_{19}H_{17}N_3NaO_4$ $[M + Na]^+$ 347.1111; found: 347.1117.



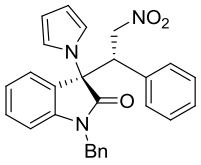
**(*R*)-1-methyl-3-((*S*)-2-nitro-1-(thiophen-2-yl)ethyl)-3-(1*H*-pyrrol-1-yl) indolin-2-one (3p):** White solid; 35.2 mg, 96%yield; 80:20 dr, 93% ee; $[\alpha]_D^{20}$ = +150.1 (*c* 1.08, $CHCl_3$); mp 114.7-116.3 ℃; the ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 7.8 min, $t_{major}$ = 6.4 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$(major diastereomer) 2.88 (s, 3H), 4.60 (dd, *J* = 2.7 Hz, 12.9 Hz, 1H), 4.92 (t, *J* = 12.3 Hz, 1H), 5.17 (dd, *J* = 2.7 Hz, 11.7 Hz, 1H), 6.27-6.28 (m, 2H), 6.69-6.78 (m, 3H), 7.03-7.09 (m, 3H), 7.26-7.31 (m, 1H), 7.46-7.52 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 26.1, 46.5, 68.0, 76.5, 109.4, 110.1, 119.1, 122.9, 124.5, 126.1, 126.2, 126.3, 128.8, 131.4, 134.1, 145.0, 172.2; HRMS (ESI-TOF) calcd. for $C_{19}H_{17}N_3NaO_3S$ $[M + Na]^+$ 390.0883; found: 390.0886.



**(*R*)-1-methyl-3-((*S*)-1-(naphthalen-1-yl)-2-nitroethyl)-3-(1*H*-pyrrol-1-yl )indolin-2-one (3q):** White solid; 38.7 mg, 94% yield; 83:17 dr, 98% ee; $[\alpha]_D^{20}$ = +40.3 (*c* 1.66, $CHCl_3$); mp 176.3-177.5 ℃; the ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 13.3 min, $t_{major}$ = 10.4 min); $^1$H NMR (300 MHz, $CDCl_3$):$\delta$(major diastereomer) 2.53 (s, 3H), 4.97-5.14 (m, 2H), 5.83 (dd, *J* = 3.6 Hz, 11.1 Hz, 1H), 6.32-6.33 (m, 2H), 6.40 (d, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.97-7.03 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.24-7.26 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.43-7.50 (m, 2H), 7.58-7.63 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 8.41 (d, *J* = 8.7 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 25.8, 43.2, 67.9, 76.4, 109.2, 109.9, 119.6, 122.6, 123.4, 123.9, 124.0, 124.7, 126.0, 126.6, 128.4, 128.6, 129.3, 131.1, 132.2, 133.6, 144.8, 172.0; HRMS (ESI-TOF) calcd. for $C_{25}H_{21}N_3NaO_3$ $[M + Na]^+$ 434.1475; found: 434.1480.

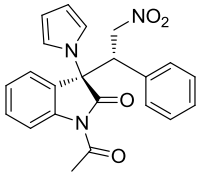


**(*R*)-3-((*S*)-2-nitro-1-phenylethyl)-1-phenyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3r):**Gray solid; 40.6 mg, 96% yield; 83:17 dr, 74% ee; $[\alpha]_D^{20}$ = +103.6 (*c* 1.33, $CHCl_3$); mp 115.7-116.9 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 16.1 min, $t_{major}$ = 50.6 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 4.72 (dd, *J* = 2.7 Hz, 12.6Hz, 1H), 4.92 (dd, *J* = 2.7 Hz, 12.0 Hz, 1H), 5.10 (t, *J* = 12.6 Hz, 1H), 6.33-6.35 (m, 2H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.60-6.64 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 7.05-7.15 (m, 3H), 7.20-7.22 (m, 2H), 7.29-7.38 (m, 4H), 7.38-7.61 (m, 2H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 50.9, 68.5, 74.8, 110.1, 110.5, 119.3, 123.1, 123.6, 126.2, 126.4, 128.3, 128.6, 128.7, 129.3 129.5, 131.0, 131.8, 132.8, 144.8, 171.6; HRMS (ESI-TOF) calcd. for $C_{26}H_{21}N_3NaO_3$ $[M + Na]^+$ 446.1475; found: 446.1459.

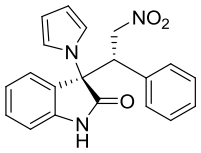


**(*R*)-1-benzyl-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3s):** White solid; 41.6 mg, 95%yield; 93:7 dr, 97% ee; $[\alpha]_D^{20}$ = +81.3 (*c* 1.26, $CHCl_3$); mp 137.2-138.9 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 10.1 min, $t_{major}$ = 13.6 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$(major diastereomer) 4.25 (d, *J* = 16.2 Hz, 1H), 4.69 (dd, *J* = 2.7 Hz, 12.6 Hz, 1H), 4.87 (d, *J* = 16.2 Hz, 1H), 4.95 (dd, *J* = 2.4 Hz, 12.0 Hz, 1H), 5.10 (t, *J* = 12.3 Hz, 1H), 6.30-6.32 (m,

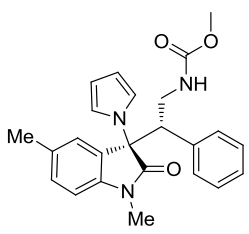
2H), 6.39 (d, *J* = 7.2 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 2H), 7.06-7.18 (m, 7H), 7.23-7.35 (m, 3H), 7.56 (d, *J* = 6.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 44.0, 50.4, 68.2, 75.4, 110.1, 110.8, 119.2, 122.8, 123.6, 126.2, 126.3, 127.3, 128.6, 128.7, 128.8, 129.6, 131.1, 132.0, 134.1, 143.9, 172.4; HRMS (ESI-TOF) calcd. for $C_{27}H_{23}N_3NaO_3$ $[M + Na]^+$ 460.1632; found: 460.1626.



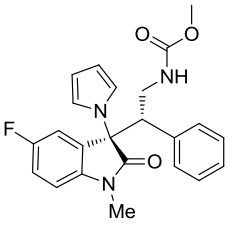
**(*R*)-1-acetyl-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3t):** White solid; 36.9 mg, 95% yield; 68:32 dr, 82% ee; $[\alpha]_D^{20}$ = +148.9 (*c* 1.88, $CHCl_3$); mp 187.3-188.6 ℃; the ee was determined by HPLC (ChiralpakAD-H, ethanol/hexane = 5/95, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 9.4 min, $t_{major}$ = 8.8 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (major diastereomer) 2.32 (s, 3H), 4.81 (dd, *J* = 2.4 Hz, 12.0 Hz,1H), 4.91 (dd, *J* = 2.4Hz, 11.7 Hz, 1H), 5.03 (t, *J* = 12.0 Hz, 1H), 6.28-6.33 (m, 2H), 6.72-6.76 (m, 2H), 7.01-7.06 (m, 2H), 7.08-7.13 (m, 2H), 7.17-7.20 (m, 1H), 7.24-7.30 (m, 1H), 7.40-7.47 (m, 1H), 7.51-7.56 (m, 1H), 8.08-8.11 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (major diastereomer) 26.0, 50.4, 68.8, 74.7, 110.6, 117.5, 119.4, 122.8, 124.0, 125.4, 128.5, 128.9, 129.3, 130.9, 131.5, 141.2, 169.7, 173.4; HRMS (ESI-TOF) calcd. for $C_{22}H_{19}N_3NaO_4$ $[M + Na]^+$412.1268; found: 412.1261.



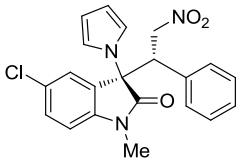
**(*R*)-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3u)**: White solid; 33.2 mg, 96% yield; 82:18 dr, 87% ee; $[\alpha]_D^{20}$ = +104.4 (*c* 1.08, $CHCl_3$); mp 108.7-110.1 ℃; the ee was determined by HPLC (ChiralpakOJ-H, ethanol/hexane = 15/85, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 13.3 min, $t_{major}$ = 28.2 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (major diastereomer) 4.70 (dd, *J* = 3.0 Hz, 12.6 Hz,1H), 4.80 (dd, *J* = 3.0Hz, 12.0 Hz, 1H), 5.06 (t, *J* = 12.0 Hz, 1H), 6.25-6.28 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 7.03-7.09 (m, 5H), 7.15-7.18 (m, 1H), 7.20-7.27 (m, 1H), 7.35-7.40 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 8.10 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (major diastereomer) 50.1, 68.6, 74.9, 110.1, 111.3, 119.2, 122.9, 124.0, 126.4, 128.3, 128.7, 129.1, 130.1, 131.1, 141.6, 174.3; HRMS (ESI-TOF) calcd. for $C_{20}H_{17}N_3NaO_3$ $[M + Na]^+$ 370.1162; found: 370.1157.



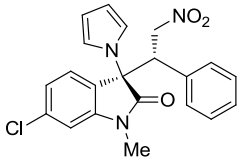
**Methyl((*S*)-2-((*R*)-1,5-dimethyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-phenylethyl)carbamate (3v):** White solid; 37.1 mg,92% yield; 84:16 dr, 86% ee; $[\alpha]_D^{20}$ = +75.0 (*c* 2.20, $CHCl_3$); mp 170.5-172.1 ℃; the ee was determined by HPLC (Chiralpak OD-H, ethanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 7.7 min, $t_{major}$ = 6.4 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (major diastereomer) 2.47 (s, 3H), 2.63 (s, 3H), 3.55 (s, 3H), 3.66-3.85 (m, 2H), 4.05-4.08 (m, 1H), 4.39 (brs, 1H), 6.19-6.25 (m, 2H), 6.46-6.53 (m, 1H), 6.75 (d, *J* = 6.9 Hz, 2H), 7.01-7.20 (m, 6H), 7.31-7.56 (m, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): $\delta$ (major diastereomer) 21.3, 25.7, 40.0, 51.5, 52.0, 69.4, 108.5, 108.8, 109.2, 119.5, 124.4, 127.8, 129.3, 129.9, 130.7, 132.0, 134.2, 142.1, 156.8, 173.1; HRMS (ESI-TOF) calcd. for $C_{24}H_{25}N_3NaO_3$ $[M + Na]^+$ 426.1788; found: 426.1785.



**Methyl((*S*)-2-((*R*)-5-fluoro-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-phenylethyl)carbamate (3w):** White solid; 38.2 mg,94% yield; 85:15 dr, 94% ee; $[\alpha]_D^{20}$ = +125.8 (*c* 1.72, $CHCl_3$); mp 174.2-175.6 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 10.1 min, $t_{major}$ = 13.7 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.66 (s, 3H), 3.56 (s, 3H), 3.61-3.69 (m, 1H), 3.76-3.90 (m, 1H), 4.11 (dd, *J* = 3.3 Hz, 10.5 Hz, 1H), 4.40 (brs, 1H), 6.26-6.28 (m, 2H), 6.49-6.54 (m,1H), 6.78 (d, *J* = 7.2 Hz, 2H), 7.03-7.16 (m, 6H), 7.42 (d, *J* = 6.0 Hz, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 25.8, 39.8, 51.4, 52.1, 69.6, 109.3 (d, *J* = 8.0 Hz, 1C), 109.5, 114.8 (d, *J* = 25.0 Hz, 1C), 116.9 (d, *J* = 23.0 Hz, 1C), 119.4, 125.9 (d, *J* = 7.3 Hz, 1C), 128.0, 129.2, 133.8, 140.5, 156.7, 157.0, 160.2, 172.9; HRMS (ESI-TOF) calcd. for $C_{23}H_{22}FN_3NaO_3$ $[M + Na]^+$ 430.1537; found: 430.1545.



**(*R*)-5-chloro-1-methyl-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl) indolin-2-one (3x)**: White solid; 37.9 mg, 94% yield; 84:16 dr, 94% ee; $[\alpha]_D^{20}$ = +94.3 (*c* 1.86, $CHCl_3$); mp 195.6-197.1 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 10.7 min, $t_{major}$ = 11.9 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.72 (s, 3H), 4.70 (dd, *J* = 3.0 Hz, 12.6 Hz, 1H), 4.79 (dd, *J* = 3.0 Hz, 11.7 Hz, 1H), 5.03 (t, *J* = 12.3 Hz, 1H), 6.29-6.30 (m, 2H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 7.07-7.17 (m, 5H), 7.40-7.44 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.0, 50.2, 68.4, 74.4, 109.6, 110.3, 119.1, 124.4, 126.3, 128.2, 128.5, 128.7, 128.8, 129.9, 131.0, 143.0, 171.9; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}ClN_3NaO_3$ $[M + Na]^+$ 418.0929; found: 418.0923.



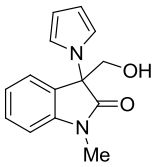
**(*R*)-6-chloro-1-methyl-3-((*S*)-2-nitro-1-phenylethyl)-3-(1*H*-pyrrol-1-yl) indolin-2-one (3y)**:White solid; 37.5 mg, 95% yield; 86:14 dr, 92% ee; $[\alpha]_D^{20}$ = +175.0 (*c* 1.76, $CHCl_3$); mp 128.5-129.8 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 7.1 min, $t_{major}$ = 6.0 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.72 (s, 3H), 4.68 (dd, *J* = 3.0 Hz, 12.6 Hz, 1H), 4.78 (dd, *J* = 3.0 Hz, 12.0 Hz, 1H), 5.01 (t, *J* = 12.3 Hz, 1H), 6.28-6.30 (m, 2H), 6.66 (d, *J* = 1.8 Hz, 1H), 6.79-6.82 (m, 2H), 6.99-7.18 (m, 5H), 7.22-7.26 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ (major diastereomer) 26.0, 50.3, 68.0, 74.4, 109.9, 110.2, 119.1, 121.9, 122.6, 125.1, 127.0, 128.2, 128.8, 131.3, 137.1, 145.7, 172.3; HRMS (ESI-TOF) calcd. for $C_{21}H_{18}ClN_3NaO_3$ $[M + Na]^+$ 418.0929; found: 418.0926.

## 4. The synthesis of compound 3a'-f', 11-15 and 17

### The synthesis of compound 3a'

In an ordinary vial equipped with a magnetic stirring bar, the compound **1a** (0.1 mmol, 1.0 equiv), paraformaldehyde **4** (0.3 mmol, 3.0 equiv) and catalyst (5 mol %) were dissolved in 2 mL of $CH_2Cl_2$, and then the mixture was stirred at 0 $^oC$ for indicated time. After completion of the reaction, as indicated by TLC, the product **3a'** were isolated by flash chromatography on silica gel

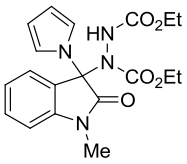
(petroleum ether/ethyl acetate = 3/1～1/1).



**3-(Hydroxymethyl)-1-methyl-3-(1*H*-pyrrol-1-yl)indolin-2-one (3a'):** White solid; 23.5 mg, 97%yield; 89% ee; $[\alpha]_D^{20}$ = +70.7 (*c* 1.20, $CHCl_3$); mp 181.9-183.2 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, $t_{minor}$ = 6.6 min, $t_{major}$ = 8.2 min); $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$3.15 (s, 3H), 4.06 (dd, *J* = 5.7 Hz, 10.2 Hz, 1H), 4.20 (dd, *J* = 5.1 Hz, 10.2 Hz, 1H), 5.41 (t, *J* = 5.1 Hz, 1H), 6.02-6.03 (m, 2H), 6.77-6.78 (m, 2H), 7.10-7.15 (m, 2H), 7.39-7.46 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$26.3, 64.3, 67.1, 108.2, 109.1, 119.0, 122.6, 125.2, 127.5, 129.9, 144.1, 173.4; HRMS (ESI-TOF) calcd. for $C_{14}H_{14}N_2NaO_2$ $[M + Na]^+$ 265.0947; found: 265.0958.

**The synthesis of compound 3b'**

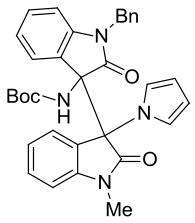
In an ordinary vial equipped with a magnetic stirring bar, the compound **1a** (0.1 mmol, 1.0 equiv), compound **5** (0.15 mmol, 1.5 equiv) and catalyst (10 mol %) were dissolved in 2 mL of $CH_2Cl_2$, and then the mixture was stirred at -20 $^o$C for indicated time. After completion of the reaction, as indicated by TLC, the product **3b'** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3/1).



**Diethyl 1-(1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)hydrazine-1,2-dicarboxylate (3b'):** White solid; 37.8 mg, 98%yield; 80% ee; $[\alpha]_D^{20}$ = +113.6 (*c* 1.35, $CHCl_3$); mp 181.3-182.7 ℃; The ee was determined by HPLC (Chiralpak OD-H, EtOH/hexane = 5/95, flow rate 1.0 mL/min, $\lambda$ = 254 nm, $t_{minor}$ = 8.5 min, $t_{major}$ = 9.7 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$1.07 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 3.23 (s, 3H), 4.03 (q, *J* = 7.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 6.17-6.19 (m, 2H), 6.45 (s, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 7.11-7.20 (m, 3H), 7.36-7.41 (m, 1H), 8.17 (d, *J* = 7.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$14.0, 14.4, 26.7, 62.1, 62.8, 77.6, 108.5, 110.0, 121.1, 122.9, 125.6, 127.0, 130.5, 143.7, 153.3, 156.2, 171.5; HRMS (ESI-TOF) calcd. for $C_{19}H_{22}N_4NaO_5$ $[M + Na]^+$ 409.1482; found: 409.1474.

**The synthesis of compound 3c'**

In an ordinary vial equipped with a magnetic stirring bar, the compound **1a** (0.1 mmol, 1.0 equiv), compound **6** (0.15 mmol, 1.5 equiv) and catalyst (5 mol %) were dissolved in 2 mL of $CH_2Cl_2$, and then the mixture was stirred at 0 $^o$C for indicated time. After completion of the reaction, as indicated by TLC, the product **3c'** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6/1~3/1).

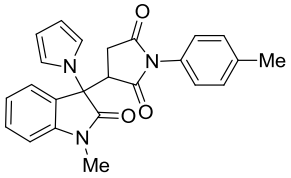


***tert*-Butyl(1-benzyl-1'-methyl-2,2'-dioxo-3'-(1*H*-pyrrol-1-yl)-[3,3'-biindolin]-3-yl)carbamate (3c'):** White solid; 51.0 mg, 93% yield; 81:19 dr, 95% ee; $[\alpha]_D^{20}$ = +93.5 (*c* 1.69, $CHCl_3$); mp 196.2-197.7 ℃; the ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexa-ne = 10/90, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 6.8 min, $t_{major}$ = 7.5min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (major diastereomer) 1.29 (s, 9H), 3.28(s, 3H), 4.38-4.50 (m, 2H), 5.97 (d, *J* = 7.5 Hz, 1H), 6.19-6.25 (m, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.69-6.75 (m, 1H), 6.88-6.95 (m, 4H), 7.15-7.20 (m, 4H), 7.22-7.26 (m, 1H), 7.31-7.39 (m, 2H), 8.14 (s,1H); $^{13}$CNMR (75 MHz, $CDCl_3$): $\delta$ (major diastereomer) 26.6, 28.1, 44.0, 64.4, 67.4, 80.2, 108.5, 108.7, 109.3, 121.6, 122.1, 122.3, 123.0, 125.4, 126.6, 127.2, 127.3, 128.5, 129.8, 131.1,

135.1, 144.2, 144.3, 154.4, 172.2, 173.8; HRMS (ESI-TOF) calcd. for $C_{33}H_{32}N_4NaO_4$ $[M + Na]^+$ 571.2316; found: 571.2308.

**The synthesis of compound 3d'**

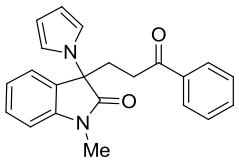
In an ordinary vial equipped with a magnetic stirring bar, the compound **1a** (0.1 mmol, 1.0 equiv), compound **7** (0.15 mmol, 1.5 equiv) and catalyst (20 mol %) were dissolved in 2 mL of $CH_2Cl_2$, and then the mixture was stirred at room temperature for indicated time. After completion of the reaction, as indicated by TLC, the product **3d'** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8/1~3/1).



**3-(1-Methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-1-(p-tolyl)pyrrolidine-2,5-dione (3d'):** White solid; 22.3 mg, 56%yield; 85:15 dr, 93% ee; $[\alpha]_D^{20}$ = -232.4 (*c* 1.10, $CHCl_3$); mp 208.3-209.5 ℃; The ee was determined by HPLC (Chiralpak OD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 11.1 min, $t_{major}$ = 17.8 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$(major diastereomer)2.30-2.31 (m, 1H), 2.36 (s, 3H), 2.91 (dd, *J* = 9.3 Hz, 18.3 Hz, 1H), 3.24 (s, 3H), 4.23 (dd, *J* = 5.1 Hz, 9.3 Hz, 1H), 6.23-6.25 (m, 2H), 6.96-6.99 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.19-7.25 (m, 3H), 7.41-7.49 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 21.1, 26.6, 30.8, 45.1, 65.5, 109.4, 109.5, 119.2, 122.8, 123.6, 124.6, 125.5, 126.0, 128.7, 129.7, 131.3, 138.8, 144.2, 172.2, 173.5, 173.6; HRMS (ESI-TOF) calcd. for $C_{24}H_{21}N_3NaO_3$ $[M + Na]^+$ 422.1475; found: 422.1475.

**The synthesis of compound 3e'**

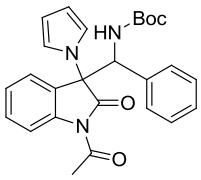
In an ordinary vial equipped with a magnetic stirring bar, the compound **1a** (0.1 mmol, 1.0 equiv), compound **8** (0.15 mmol, 1.5 equiv) and catalyst (20 mol %) were dissolved in 2 mL of $CH_2Cl_2$, and then the mixture was stirred at room temperature for indicated time. After completion of the reaction, as indicated by TLC, the product **3e'** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1~3/1).



**1-Methyl-3-(3-oxo-3-phenylpropyl)-3-(1*H*-pyrrol-1-yl)indolin-2-one (3e'):** White solid; 31.3 mg, 91%yield; 42% ee; $[\alpha]_D^{20}$ = -23.6 (*c* 0.88, $CHCl_3$); mp 131.5-132.9 ℃; The ee was determined by HPLC (Chiralpak OD-H, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, $\lambda$ = 254 nm, $t_{minor}$ = 8.7 min, $t_{major}$ = 11.4 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$2.74-2.84 (m, 4H), 3.26 (s, 3H), 6.19-6.21 (m, 2H), 6.85-6.87 (m, 2H), 6.93-6.95 (m, 1H), 7.13-7.18 (m, 1H), 7.39-7.44 (m, 4H), 7.51-7.56 (m, 1H), 7.80-7.82 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$26.5, 31.3, 32.4, 65.6, 108.9, 109.0, 118.9, 123.2, 124.9, 127.7, 127.9, 128.5, 130.2, 133.2, 136.3, 143.4, 174.2, 198.1; HRMS (ESI-TOF) calcd. for $C_{22}H_{20}N_2NaO_2$ $[M + Na]^+$ 367.1417; found: 367.1405.

**The synthesis of compound 3f'** [2]

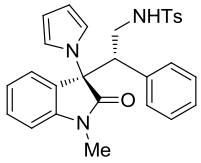
To a solution of compound **1d** (0.1 mmol, 1.0 equiv), compound **9** (0.15 mmol, 1.5 equiv), and catalyst (0.01 mmol, 10 mmol %) in toluene (2 mL) was added saturated $Na_2CO_3$ (0.1 mL). The reaction was stirred at indicated temperature forspecified time. The reaction was quenched by the addition of water. The water layer was extracted withethyl acetate three times. The combined organic layer was dried over sodium sulfate and concentrated.The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1) to give **3f'**.



***tert*-Butyl ((1-acetyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)(phenyl)methyl) carbamate (3f'):** White solid; 41.4 mg, 96%yield; 92:8 dr, 97% ee; $[\alpha]_D^{20}$ = -26.8 (*c* 1.20, $CHCl_3$); mp 92.5-93.6 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 5/95, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 9.0 min, $t_{major}$ = 12.3 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$(major diastereomer) 1.39 (s, 9H), 2.65 (s, 3H), 5.54 (d, *J* = 9.6 Hz, 1H), 5.94 (d, *J* = 9.9 Hz, 1H), 6.23-6.25 (m, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.91-6.98 (m, 3H), 7.11-7.20 (m, 4H), 7.33-7.39 (m, 1H), 8.09 (d, *J* = 8.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer)26.6, 28.2, 58.5, 69.2, 80.6, 109.6, 116.8, 119.5, 124.5, 125.2, 125.4, 127.2, 127.9, 128.3, 130.7, 135.0, 140.1, 154.6, 170.0, 174.8; HRMS (ESI-TOF) calcd. for $C_{26}H_{27}N_3NaO_4$ [M + Na]$^+$468.1894; found: 468.1883.

**The synthesis of compound 11**[3, 4]

To a suspension of compound **3a** (0.1 mmol, 1 equiv, 94% ee) and $NiCl_2$ (0.1 mmol, 1 equiv) in methanol (5 mL) was added $NaBH_4$ (1.2 mmol, 12 equiv) at 0 ℃ and the mixture was stirred at room temperature for 1 h, after which the mixture was quenched with sat. $NH_4Cl$ at 0 ℃ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine and dried over $Na_2SO_4$. After filtered, it was concentrated under vacuum to give the crude product **10**. Then the crude product **10** was dissolved in $CH_2Cl_2$ (5 mL) at 0 ℃ under an argon atmosphere flowed by adding of $Et_3N$ (0.1 mmol, 14 uL.).The resulting mixture was stirred at 0 ℃ for 10 min, then a solution of TsCl (0.15 mmol, 28.6 mg) in dry $CH_2Cl_2$ (1.0 mL) was added dropwise. The resulting solution was stirred at 0 ℃ for 30 min, then was allowed to warm to room temperature; stirring was then continued for about 4 h. The reaction mixture was concentrated under vacuum and purified with flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1~ 5/1) to afford **11**.

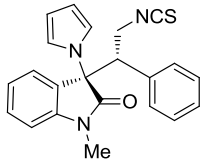


**4-Methyl-*N*-((*S*)-2-((*R*)-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-phenylethyl)benzenesulfonamide (11):** White solid; 44.2 mg, 91%yield; 87:13 dr, 94% ee; $[\alpha]_D^{20}$ = +135.0 (*c* 1.60, $CHCl_3$); mp 176.6-177.9 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, $\lambda$ = 254 nm, major diastereomer: $t_{minor}$ = 24.6 min, $t_{major}$ = 14.2 min); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$(major diastereomer) 2.47 (s, 3H), 2.62 (s, 3H), 3.40-3.59 (m, 2H), 3.90 (dd, *J* = 4.8 Hz, 10.5 Hz, 1H), 4.25 (dd, *J* = 4.5 Hz, 7.8 Hz, 1H), 6.20-6.21 (m, 2H), 6.54-6.59 (m, 3H), 6.90-6.91 (m, 2H), 6.96-7.01 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.14-7.19 (m, 1H), 7.26-7.31 (m, 2H), 7.33-7.39 (m, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.58-7.62 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$(major diastereomer) 21.5, 25.6, 41.6, 51.8, 69.0, 108.8, 109.3, 119.2, 122.3, 123.8, 126.6, 127.2, 127.9, 128.1, 129.1, 129.6, 130.5, 133.1, 136.6, 143.5, 144.3, 172.8; HRMS (ESI-TOF) calcd. for $C_{28}H_{27}N_3NaO_3S$ [M + Na]$^+$ 508.1665; found: 508.1652.

**The synthesis of compound 12**

To a suspension of compound **3a** (0.2 mmol, 1 equiv, 94% ee) and $NiCl_2$ (0.2 mmol, 1 equiv) in methanol (10 mL) was added $NaBH_4$ (2.4 mmol, 12 equiv) at 0 ℃ and the mixture was stirred at room temperature for 1 h, after which the mixture was quenched with sat. $NH_4Cl$ at 0 ℃ and extracted with $CH_2Cl_2$. The combined organic layers were washed with brine and dried over $Na_2SO_4$. After filtered, it was concentrated under vacuum to give the crude product **10**. The crude

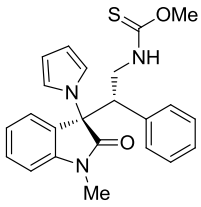
product **10** was dissolved in $CH_2Cl_2$ (15 mL) at 0 ℃. Then thiophosgene (0.79 mmol, 0.06 mL) was added and the resulting solution was stirred at 0 ℃ for 30 min. Then the mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was concentrated under vacuum and purified with flash chromatography on silica gel (petroleum ether/ethyl acetate = pure petroleum ether ~ 4/1) to afford compound **12**.




**(*R*)-3-((*S*)-2-isothiocyanato-1-phenylethyl)-1-methyl-3-(1*H*-pyrrol-1-yl) indolin-2-one (12):** White solid; 30.0 mg, 40% yield; 90:10 dr, 94% ee; $[\alpha]_D^{20}$ = +223.6 (*c* 0.85, $CHCl_3$); mp 117.3-118.8 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 6.4 min, $t_{major}$ = 5.9 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.72 (s, 3H), 3.82 (dd, *J* = 1.4 Hz, 11.7 Hz, 1H), 4.10-4.25 (m, 2H), 6.26-6.28 (m, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.75-6.79 (m, 2H), 7.06-7.11 (m, 4H), 7.14-7.21 (m, 1H), 7.23-7.26 (m, 1H), 7.39-7.45 (m, 1H), 7.47-7.50 (m, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 25.8, 44.5, 53.0, 68.7, 109.1, 109.7, 119.2, 122.5, 123.5, 126.4, 128.0, 128.4, 129.0, 130.0, 130.9, 132.7, 144.5, 172.5; HRMS (ESI-TOF) calcd. for $C_{22}H_{19}N_3NaOS$ $[M + Na]^+$ 396.1141; found: 396.1131.

**The synthesis of compound 13**[5]

To a solution of compound **12** (30.0 mg, 0.08 mmol, 1 equiv) in MeOH (10 ml) was added NaH (60% in oil, 9.6 mg, 0.24 mmol, 3.0 equiv) under ice cooling, followed by stirring at room temperature for 1 h. Then the reactionmixture was poured into ice water and extracted with ethyl acetate (3×10 mL). The organic layers were combined and washed with brine twice. Subsequently the combined organic layer was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to obtain compound **13**.

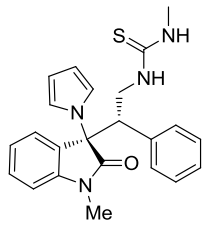



***O*-methyl ((*S*)-2-((*R*)-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-phenylethyl)carbamothioate (13):** White solid; 30.9 mg, 95%yield; 86:14 dr, 93% ee; $[\alpha]_D^{20}$ = +176.5 (*c* 1.45, $CHCl_3$); mp 171.1-172.5 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 8.1 min, $t_{major}$ = 12.9 min); $^1$H NMR (300 MHz, $CDCl_3$): *δ* (major diastereomer) 2.68 (s, 3H), 3.64-3.74 (m, 0.4H), 3.85 (s, 2H), 3.89-3.98 (m, 0.6H), 4.01 (s, 1H), 4.04-4.23 (m, 2H), 5.80 (br s, 1H), 6.26-6.28 (m, 2H), 6.58-6.64 (m, 1H), 6.71-6.78 (m, 2H), 7.02-7.18 (m, 5H), 7.23-7.28 (m, 1H), 7.38-7.43 (m, 1H), 7.72 (d, *J* = 7.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ* (major diastereomer) 25.7, 44.3, 50.8, 57.1, 69.2, 108.6, 108.8, 109.1, 109.4, 119.5, 122.5, 124.1, 125.3, 126.9, 127.9, 128.1, 129.2, 129.8, 130.6, 133.9, 144.5, 173.0, 191.2; HRMS (ESI-TOF) calcd. for $C_{23}H_{23}N_3NaO_2S$ $[M + Na]^+$ 428.1403; found: 428.1421.

**The synthesis of compound 14**

To an ice-cooled aqueous solution of methylamine (40percent w/w, 0.2ml) was added a solution of compound **12** (30.0 mg, 0.08 mmol, 1 equiv) in 1,4-dioxane (1.0ml). The coolant was removed and the reaction was stirred at ambient temperature for 2h. The reaction mixture was partitioned between ethyl acetate (20ml) and water (20ml). The aqueous phase was discarded and the organic phase washed with brine (2×10ml), and was dried over anhydrous sodium sulfate. The

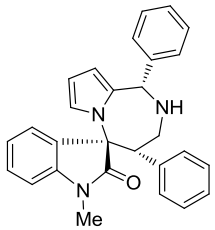
filtrate was concentrated under vacuum and purified by column chromatography on silica gel ($CH_2Cl_2$/MeOH = 20/1) to obtain compound **14**.



**1-Methyl-3-((*S*)-2-((*R*)-1-methyl-2-oxo-3-(1*H*-pyrrol-1-yl)indolin-3-yl)-2-phenylethyl)thiourea (14):** White solid; 22.0 mg, 68% yield; 97:3 dr, 97% ee; $[\alpha]_D^{20}$ = +114.7 (*c* 1.20, $CHCl_3$); mp 104.3-105.6 ℃; the ee was determined by HPLC (Chiralpak AD-H, ethanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 10.4 min, $t_{major}$ = 13.3 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.68 (s, 3H), 2.72 (s, 3H), 4.01-4.14 (m, 3H), 5.29 (brs,1H), 5.75 (brs, 1H), 6.25-6.28 (m, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 2H), 6.99-7.05 (m, 2H), 7.07-7.11 (m, 1H), 7.20-7.26 (m, 3H), 7.35-7.45 (m, 1H), 7.73 (d, *J* = 7.5 Hz, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 25.7, 30.4, 44.2, 52.0, 69.2, 108.9, 109.5, 119.6, 122.6, 123.7, 127.0, 127.9, 128.0, 129.1, 130.7, 134.3, 144.5, 173.0, 182.4; HRMS (ESI-TOF) calcd. for $C_{23}H_{24}N_4NaOS$ $[M + Na]^+$ 427.1563; found: 427.1555.

**The synthesis of compound 15**[3]

To a solution of anhydrous $MgSO_4$ (0.5 g) and compound **10** (123.0 mg, 0.37 mmol, 1.0 equiv, 99% ee) in $CH_2Cl_2$ (8 mL) was added benzaldehyde (91 μL, 0.89 mmol, 2.4 equiv) at room temperature and the mixture was stirred at room temperature for 1 h. The mixture was then cooled to 0 °C and TFA (51 μL, 0.75 mmol) was slowly added. After stirred at room temperature for 2 days, the mixture was neutralized with sat. $NaHCO_3$ at 0 ℃ and then filtered over celite. The filtrate was extracted with $CH_2Cl_2$and the combinedorganic layers were washed with brine and dried over $Na_2SO_4$. After filtered and concentrated under vacuum, the crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 15/1~3/1).

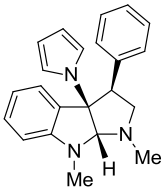


**(1'*S*,3*R*,4'*S*)-1-methyl-1',4'-diphenyl-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrrolo[1,2-a][1,4]diazepin]-2-one (15):** White solid; 149.5 mg, 96%yield; >99:1 dr, >99% ee; $[\alpha]_D^{20}$ = -247.6 (*c* 2.55, $CHCl_3$); mp 232.3-234.6 ℃; The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, *λ* = 254 nm, major diastereomer: $t_{minor}$ = 46.3 min, $t_{major}$ = 8.8 min); $^1$H NMR (300 MHz, $CDCl_3$): *δ*2.21 (br s, 1H), 2.69 (s, 3H), 3.35 (dd, *J* = 2.7 Hz, 13.8 Hz, 1H), 3.75 (dd, *J* = 12.3 Hz, 13.8 Hz, 1H), 3.88 (dd, *J* = 2.7 Hz, 11.7 Hz, 1H), 5.40-5.45 (m, 1H), 5.50 (s, 1H), 5.91-6.93 (m, 1H), 6.43-6.45 (m, 1H), 6.60-6.62 (m, 3H), 6.98-7.03 (m, 2H), 7.01-7.04 (m, 1H), 7.05-7.10 (m, 1H), 7.32-7.37 (m, 2H), 7.40-7.45 (m, 2H), 7.51-7.53 (m, 2H), 7.86 (d, *J* = 7.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): *δ*25.7, 51.4, 54.2, 62.4, 73.4, 107.2, 108.5, 111.1, 122.6, 122.8, 125.7, 127.4, 127.5, 127.8, 128.3, 128.4, 129.5, 137.2, 138.7, 142.5, 143.0, 174.2; HRMS (ESI-TOF) calcd. for $C_{28}H_{26}N_3O$ $[M + H]^+$ 420.2070; found: 420.2060.

**The synthesis of compound 17** [6]

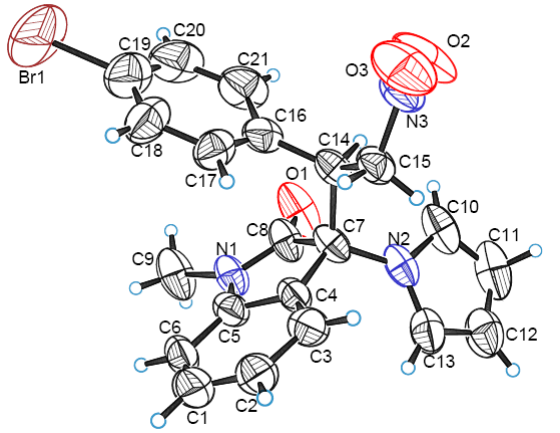
To a solution compound **10** (198.8 mg, 0.6 mmol, 1.0 equiv) in $CH_2Cl_2$ (20 mL) at 0 ℃, under an argon atmosphere, was added DIEA (0.46 mL, 2.8 mmol, 4.5 equiv), chloromethyl formate (0.19 mL, 2.4 mmol, 4.0 equiv), and DMAP (30.5 mg, 0.24 mmol, 40 mol %). After the addition, the reaction was allowed to warm to room temperature and stirred about 3 h. Then, the reaction was quenched with a saturated aqueous sodium bicarbonate solution and extracted with $CH_2Cl_2$ three times. The combined organic layers were dried over $Na_2SO_4$, filtered, and

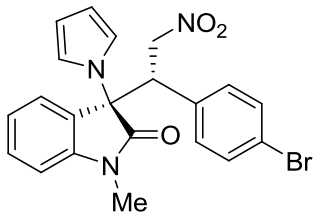
concentrated in vacuo to give the compound **16** (white solid, 197.4 mg, 88.3% yield). The compound **16** was dissolved in 20 mL of dry THF and $LiAlH_4$ (380 mg, 10 mmol, 20 equiv) was added at 0 ℃. The resulting mixture was heated to reflux for 3 h and then cooled to 0 ℃. Ethyl acetate (100 mL) and saturated aqueous $NaHCO_3$ (50 mL) were added. The aqueous layer was separated and extracted with ethyl acetate three times. The combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to obtain compound **17** (white solid, 39.4 mg, 22 % yield).




**(3*S*,3a*R*,8a*R*)-1,8-dimethyl-3-phenyl-3a-(1*H*-pyrrol-1-yl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (17):** White solid; 39.4 mg, 22% yield; >99:1 dr, >99% ee; $[\alpha]_D^{20}$ = +46.3 (*c* 1.97, $CHCl_3$); mp 116.9-118.2 ℃; the ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 1/99, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: $t_{minor}$ = 5.5 min, $t_{major}$ = 4.8 min); $^1$H NMR (300 MHz, $CDCl_3$): δ (major diastereomer) 2.82 (s, 3H), 3.07 (s, 3H), 3.27 (d, *J* = 8.1 Hz, 2H), 3.78 (t, *J* = 7.5 Hz 1H), 4.85 (s,1H), 5.95-5.98 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.59-6.65 (m,2H), 6.77-6.83 (m, 1H), 7.04-7.07 (m, 2H), 7.16-7.29 (m,4H), 7.38 (d, *J* = 7.5 Hz, 1H); $^{13}$CNMR (75 MHz, $CDCl_3$): δ (major diastereomer) 34.7, 39.8, 55.6, 59.1, 77.9, 97.2, 107.7, 107.9, 117.5, 119.6, 125.3, 127.0, 127.9, 128.5, 129.4, 129.8, 136.9, 150.7; HRMS (ESI-TOF) calcd. for $C_{22}H_{24}N_3$ $[M + H]^+$ 330.1965; found: 330.1977.

## 5. X-ray crystal data for compound 3j




Compound **3j**

| | |
|---|---|
| Identification code | **3j** |
| Empirical formula | $C_{21}H_{19}BrN_3O_3$ |
| Formula weight | 441.30 |
| Temperature/K | 291(2) |
| Crystal system | monoclinic |
| Space group | C2 |
| a/Å | 19.7543(7) |
| b/Å | 6.8067(3) |
| c/Å | 15.8605(4) |
| α/° | 90 |
| β/° | 98.736(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 2107.89(13) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.391 |
| m/mm$^{-1}$ | 2.871 |
| F(000) | 900.0 |
| Crystal size/mm$^3$ | 0.36 × 0.26 × 0.25 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection | 9.058 to 139.27° |
| Index ranges | $-14 \le h \le 23$, $-7 \le k \le 2$, $-19 \le l \le 17$ |
| Reflections collected | 4694 |
| Independent reflections | 2537[R(int) = 0.0244] |
| Data/restraints/parameters | 2537/20/255 |
| Goodness-of-fit on F$^2$ | 1.091 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0839, $wR_2$ = 0.2122 |
| Final R indexes [all data] | $R_1$ = 0.1060, $wR_2$ = 0.2290 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.81/-0.66 |
| Flack parameter | -0.02(2) |

## 6. Reference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[3] J.-Q. Weng, Q.-M. Deng, L. Wu, K. Xu, H. Wu, R.-R. Liu, J.-R. Gao and Y.-X. Jia, *Org. Lett.*, 2014**, 16**, 776.

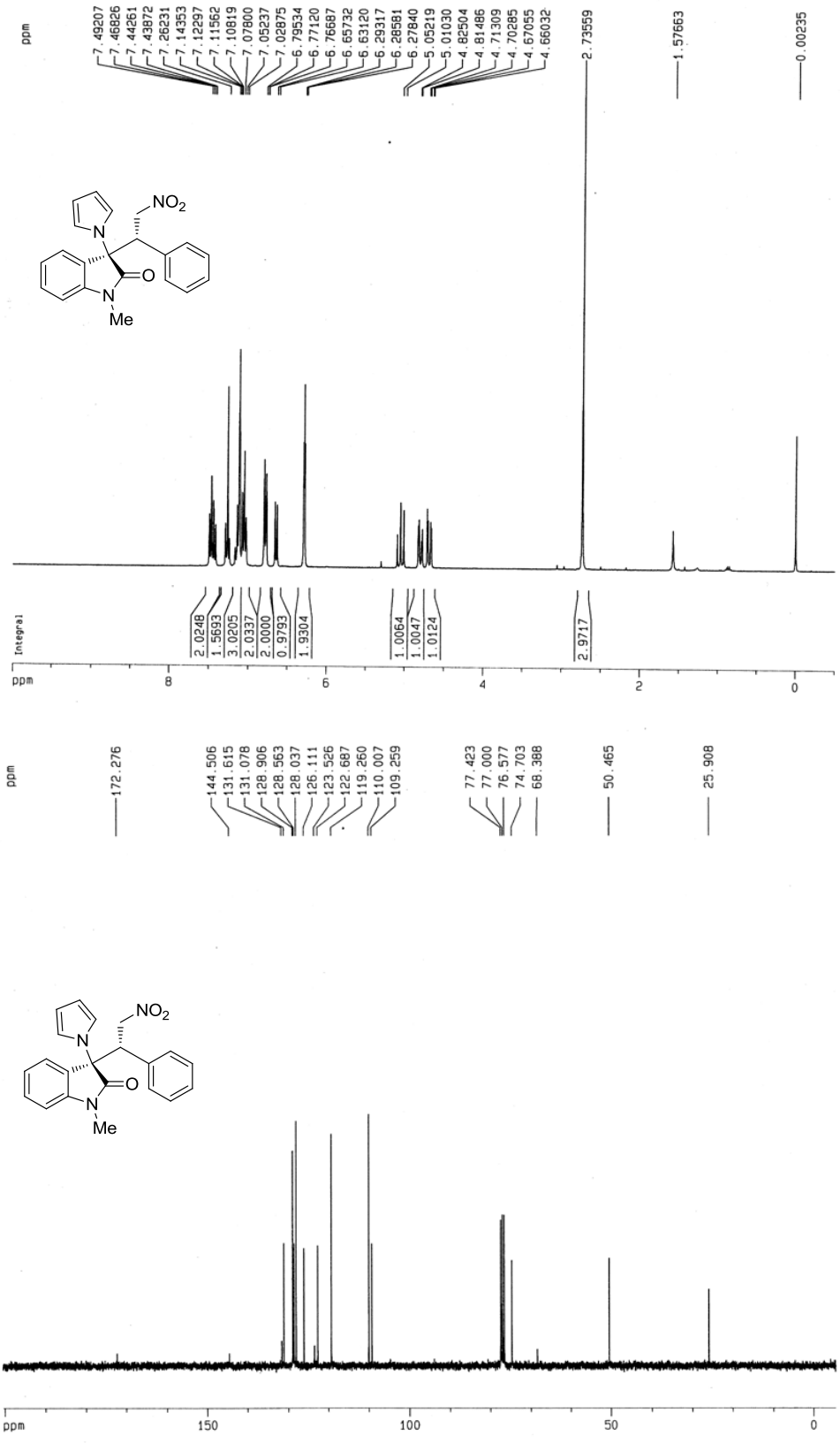
[4] X.-L. Liu, Z.-J. Wu, X.-L. Du, X.-M. Zhang and W.-C. Yuan, *J. Org. Chem*., 2011, **76**, 4008.

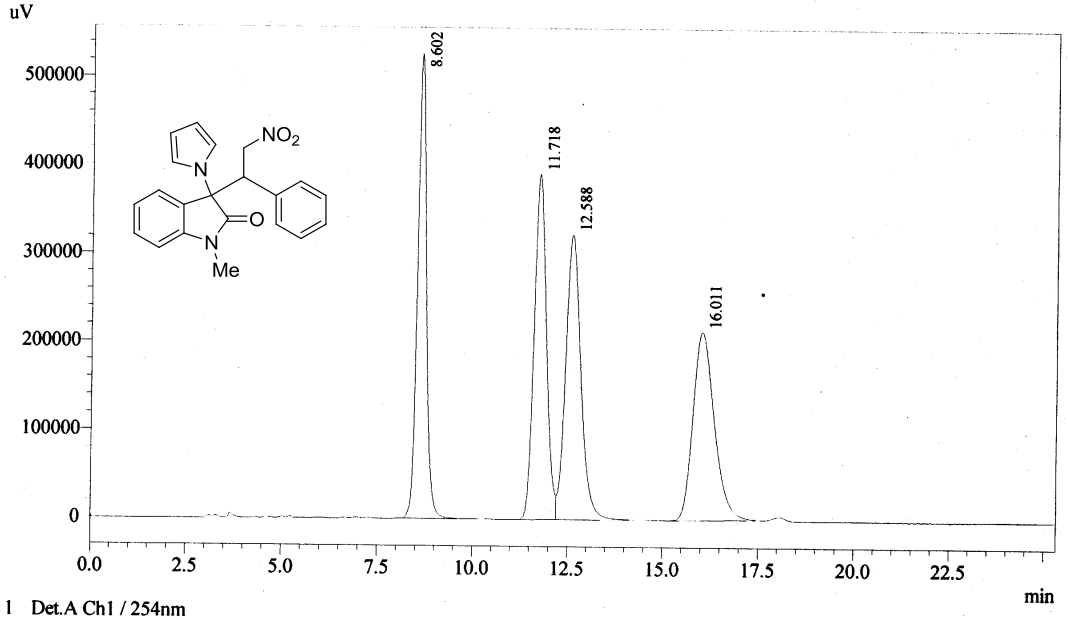
[5] R. Tokuyama, Y. Takahashi, Y. Tomita, M. Tsubouchi, N. Iwsaki, N. Kado, E. Okezaki and O. Nagata, *Chem. Pharm. Bull.*, 2001**, 49**, 361.

[6] M. Retini, G. Bergonzini and P. Melchiorre, *Chem. Commun.*, 2012, **48**, 3336.

**7. The copies of $^{1}$H NMR, $^{13}$C NMR and HPLC spectra for compounds 3a-y, 3a'-f', 11-15 and 17.**

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3a**

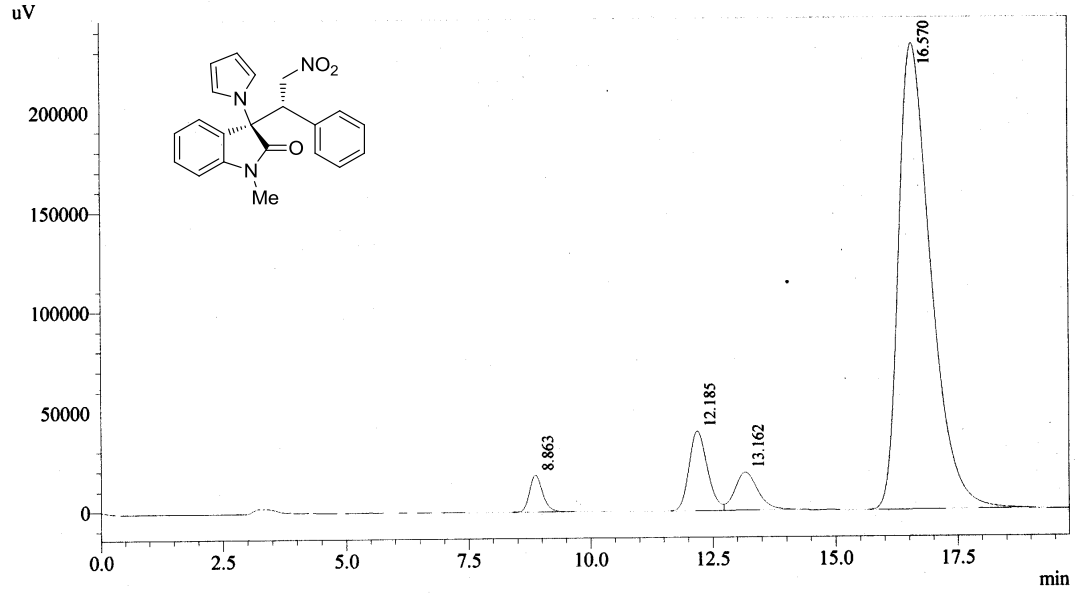





1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.602 | 8546091 | 526732 | 24.652 | 36.253 |
| 2 | 11.718 | 8800775 | 390733 | 25.387 | 26.893 |
| 3 | 12.588 | 9018730 | 322724 | 26.016 | 22.212 |
| 4 | 16.011 | 8300850 | 212737 | 23.945 | 14.642 |
| Total | | 34666446 | 1452926 | 100.000 | 100.000 |

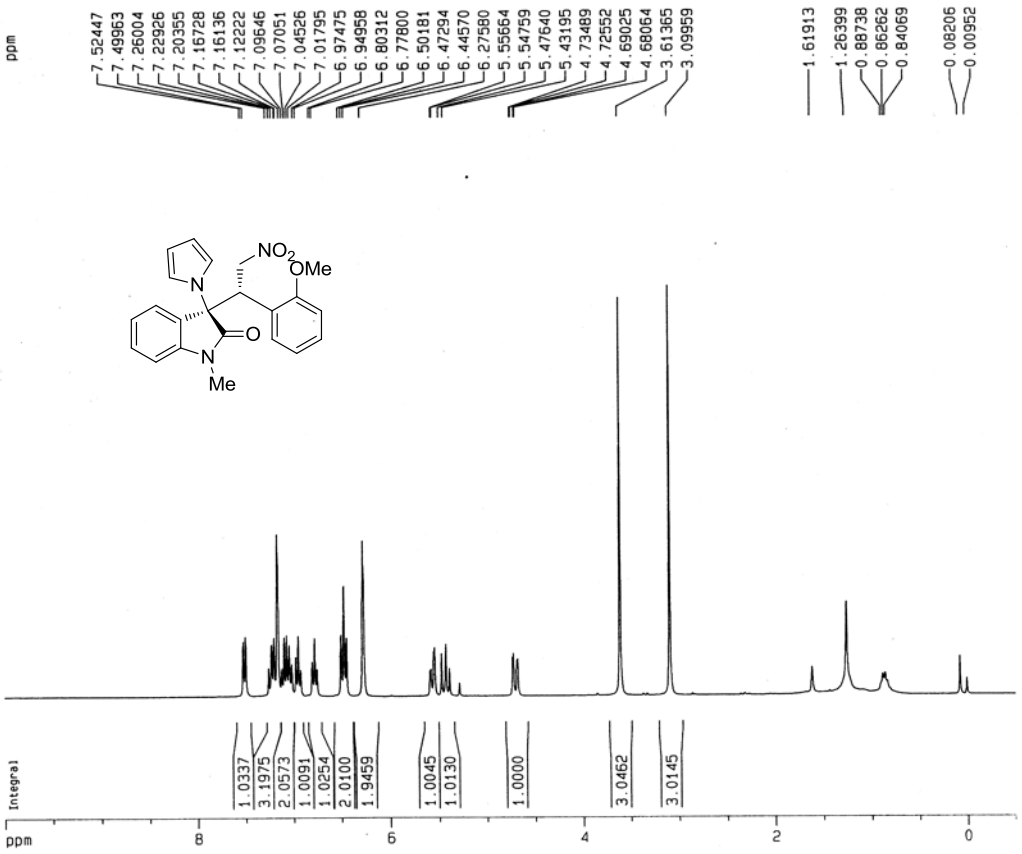


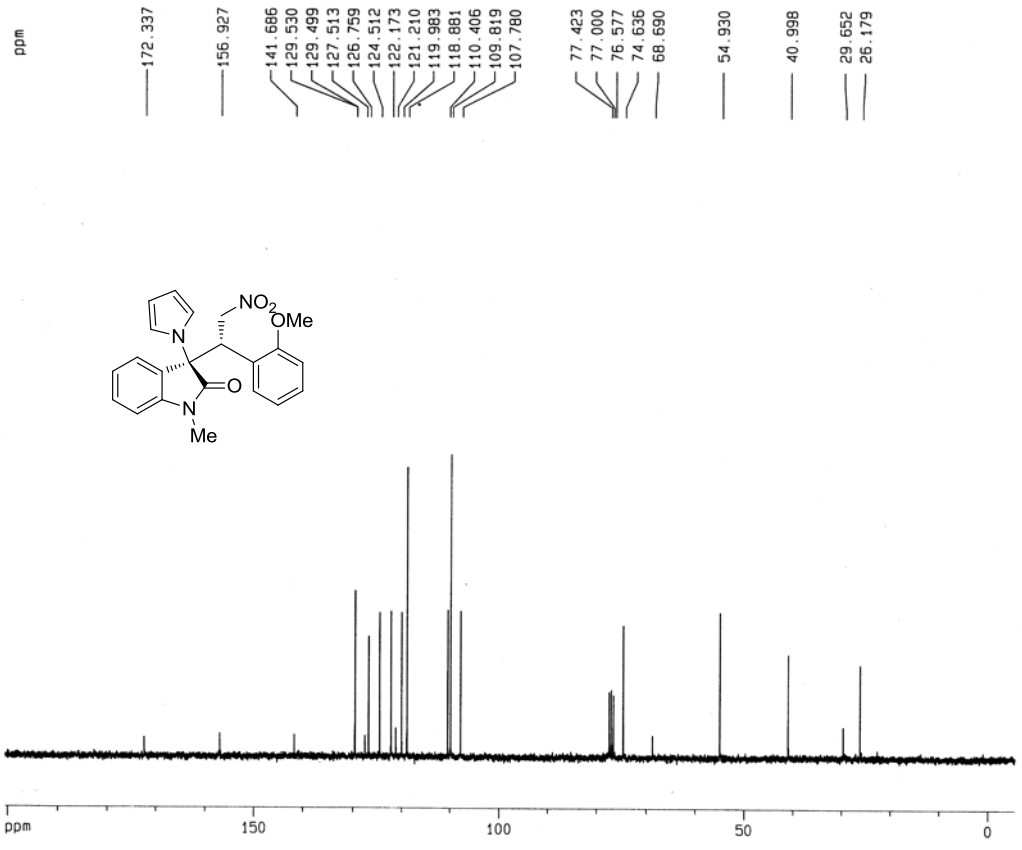

1 Det.A Ch1 / 254nm

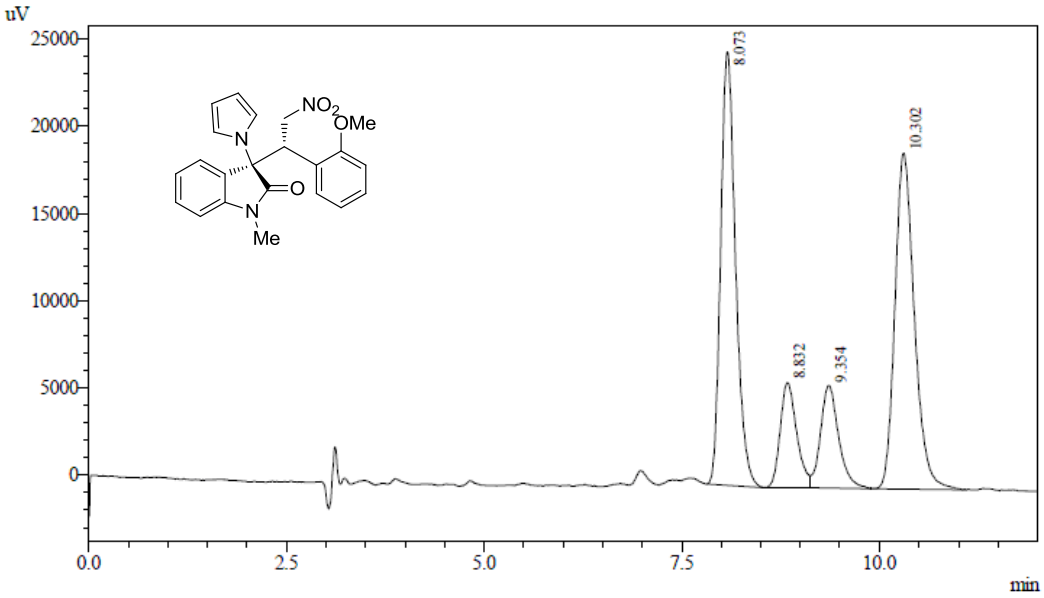
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.863 | 347477 | 18512 | 2.733 | 5.954 |
| 2 | 12.185 | 1040626 | 39961 | 8.186 | 12.852 |
| 3 | 13.162 | 606479 | 18896 | 4.771 | 6.077 |
| 4 | 16.570 | 10717281 | 233567 | 84.309 | 75.117 |
| Total | | 12711864 | 310936 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3b**



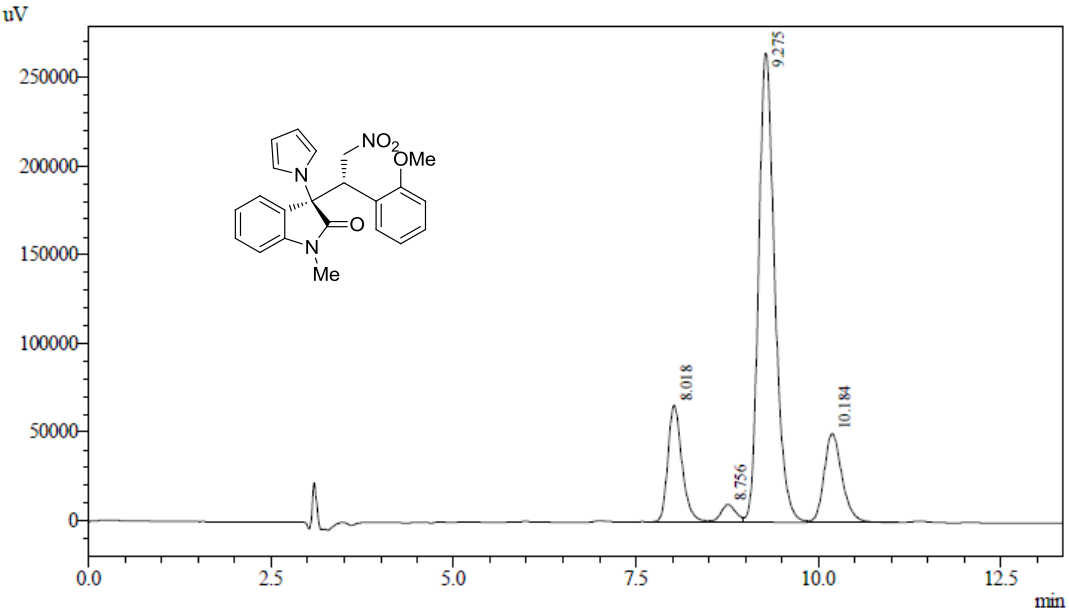






1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.073 | 324233 | 24851 | 38.820 | 44.373 |
| 2 | 8.832 | 87792 | 6031 | 10.511 | 10.768 |
| 3 | 9.354 | 93996 | 5880 | 11.254 | 10.499 |
| 4 | 10.302 | 329206 | 19243 | 39.415 | 34.359 |
| Total | | 835227 | 56005 | 100.000 | 100.000 |

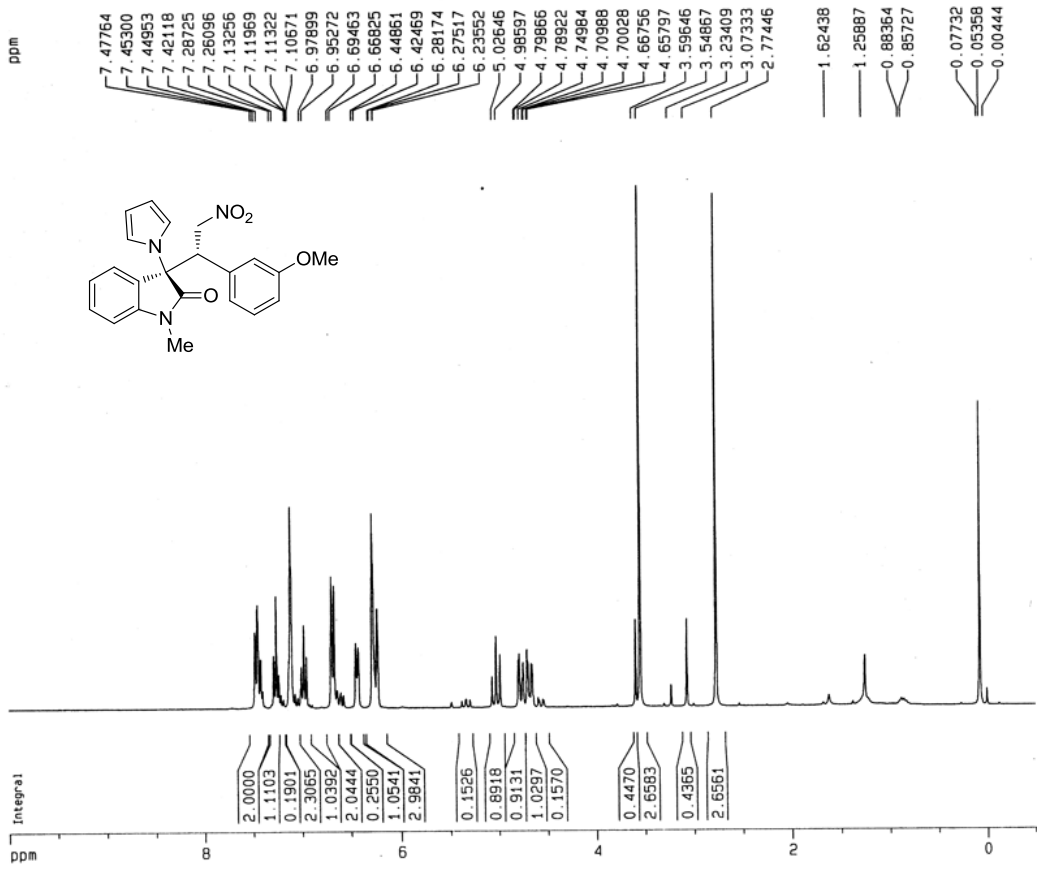


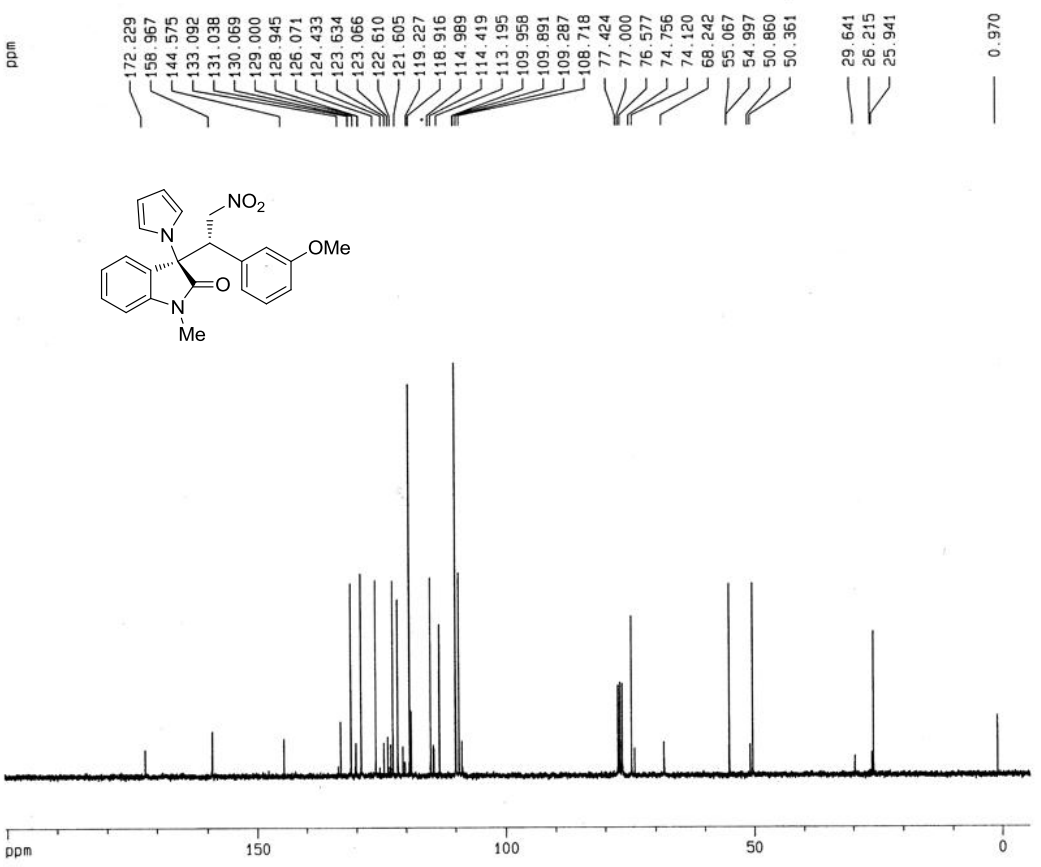

1 Det.A Ch1 / 220nm

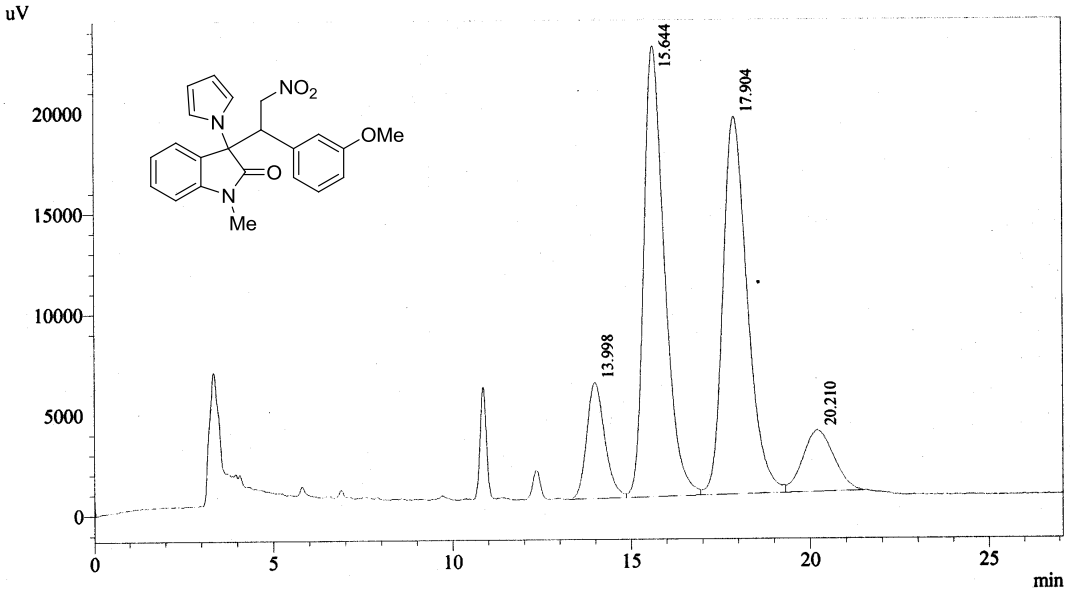
Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.018 | 883325 | 65932 | 14.825 | 16.890 |
| 2 | 8.756 | 141851 | 9861 | 2.381 | 2.526 |
| 3 | 9.275 | 4073851 | 264385 | 68.373 | 67.730 |
| 4 | 10.184 | 859284 | 50173 | 14.422 | 12.853 |
| Total | | 5958311 | 390350 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3c**



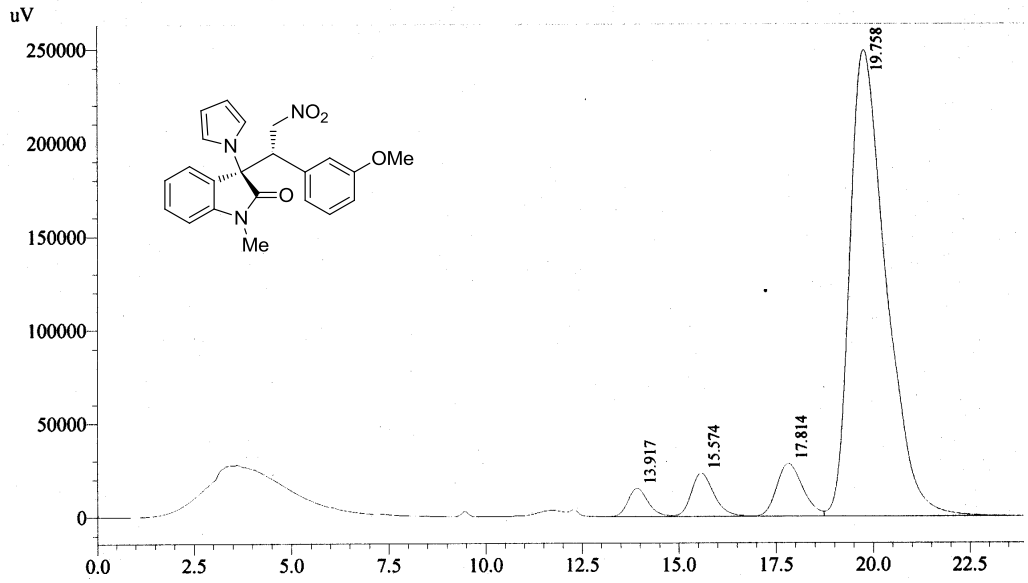






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.998 | 203208 | 5764 | 9.307 | 11.536 |
| 2 | 15.644 | 907160 | 22387 | 41.548 | 44.801 |
| 3 | 17.904 | 889765 | 18749 | 40.752 | 37.522 |
| 4 | 20.210 | 183253 | 3069 | 8.393 | 6.141 |
| Total | | 2183386 | 49969 | 100.000 | 100.000 |

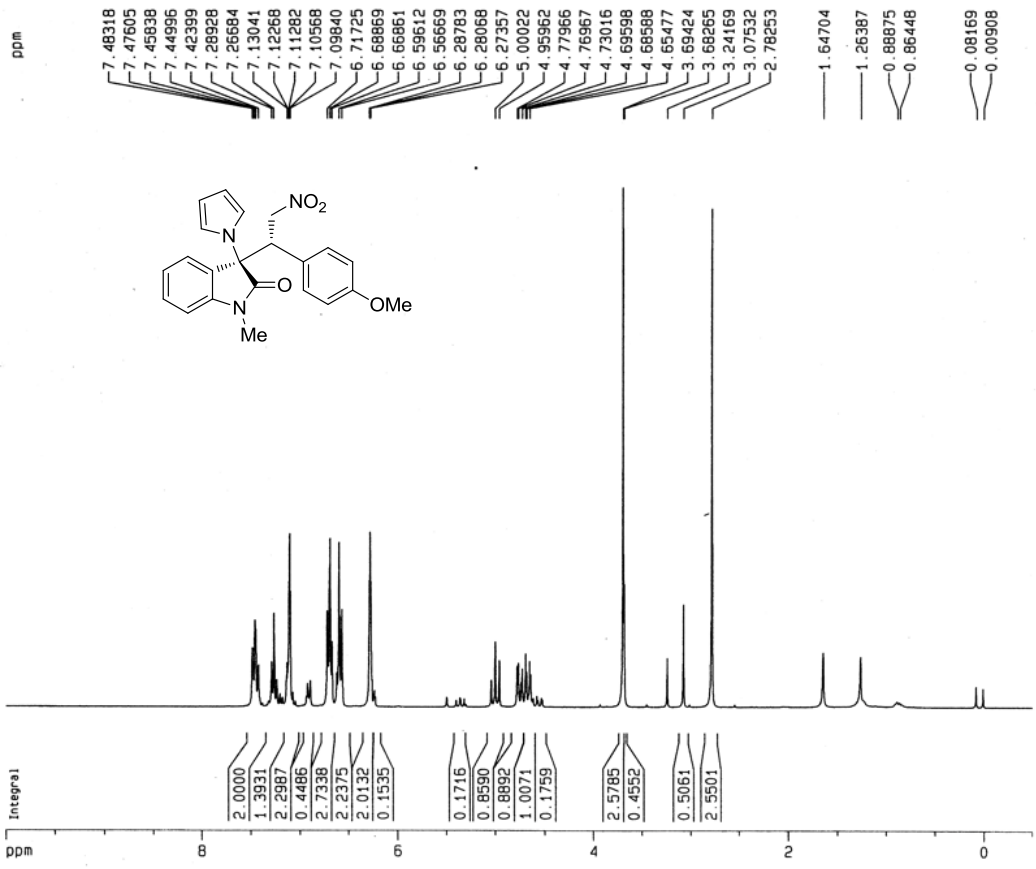


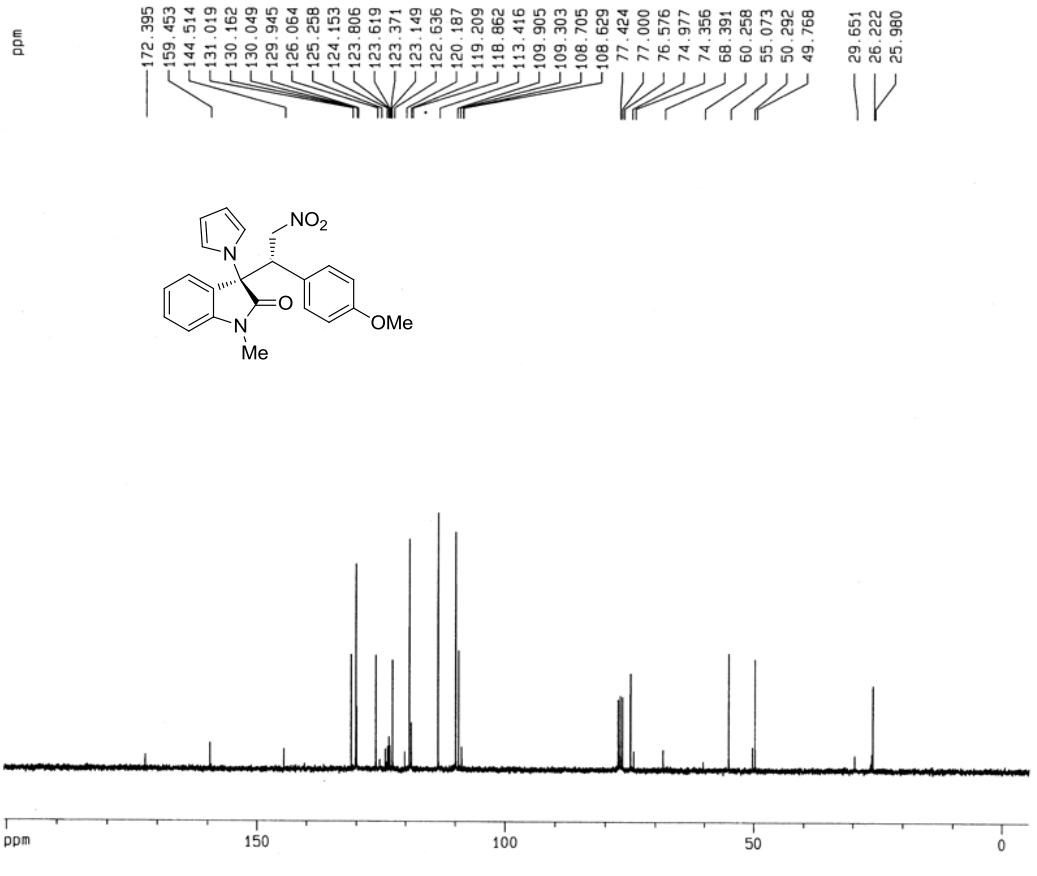

1 Det.A Ch1 / 254nm

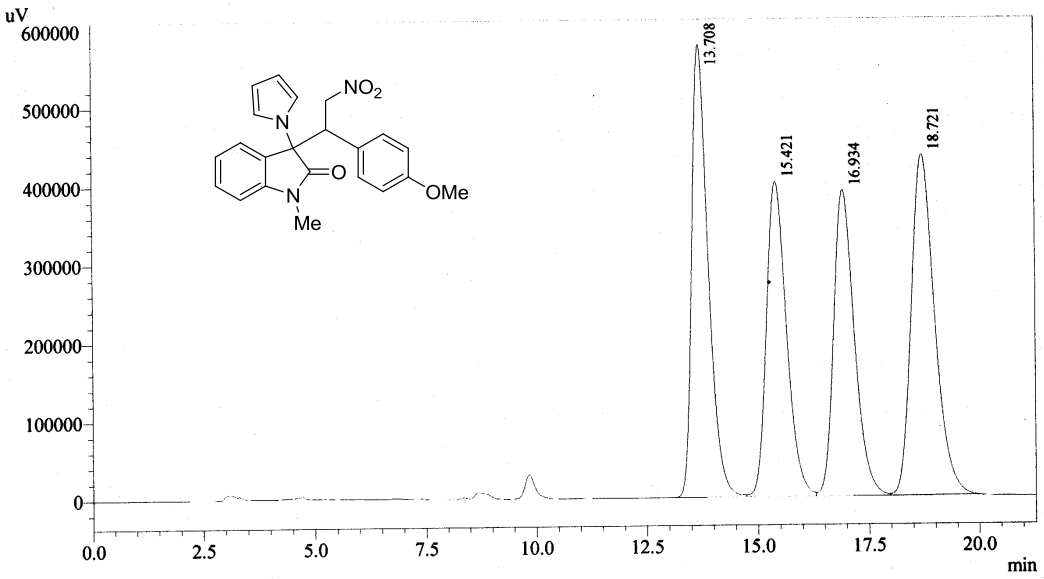
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.917 | 542329 | 15037 | 2.860 | 4.765 |
| 2 | 15.574 | 937187 | 23089 | 4.942 | 7.317 |
| 3 | 17.814 | 1314531 | 28227 | 6.932 | 8.945 |
| 4 | 19.758 | 16167834 | 249197 | 85.265 | 78.972 |
| Total | | 18961880 | 315550 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3d**



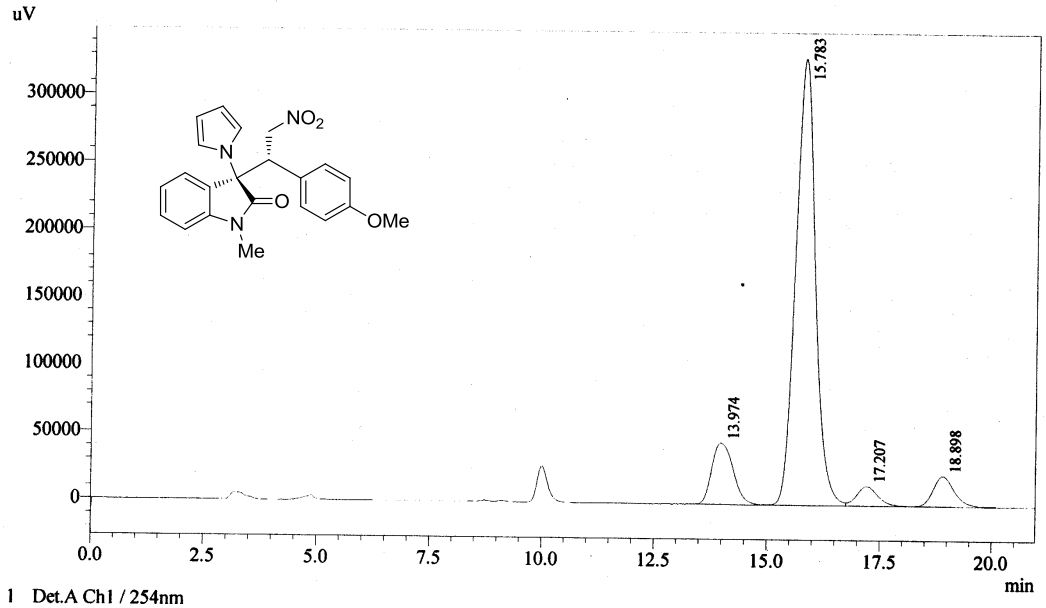






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.708 | 14860838 | 578864 | 26.456 | 32.014 |
| 2 | 15.421 | 12643749 | 402695 | 22.509 | 22.271 |
| 3 | 16.934 | 12637131 | 391059 | 22.497 | 21.627 |
| 4 | 18.721 | 16030322 | 435562 | 28.538 | 24.088 |
| Total | | 56172040 | 1808180 | 100.000 | 100.000 |

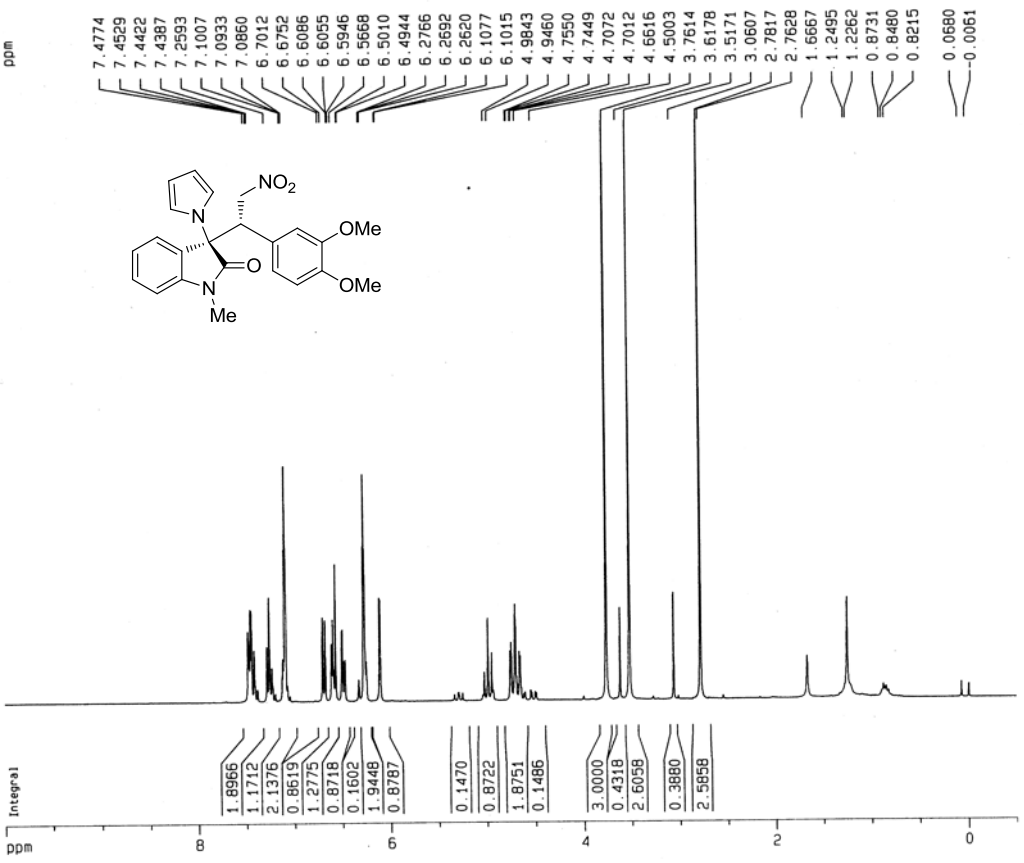


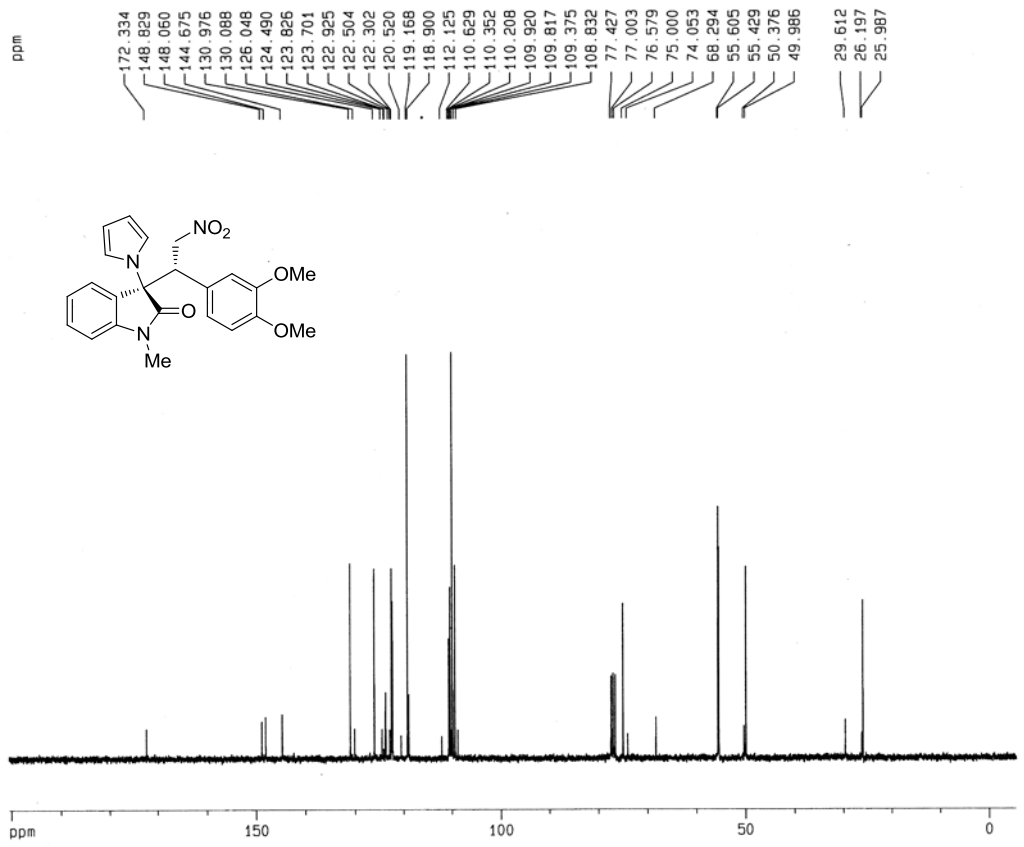

1 Det.A Ch1 / 254nm

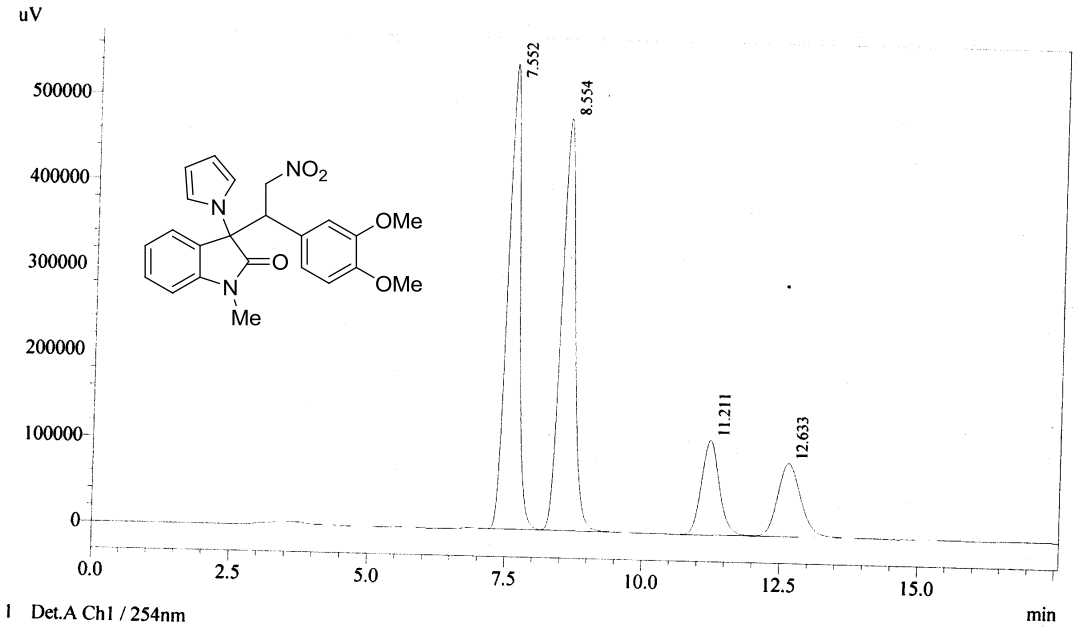
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.974 | 1495403 | 45327 | 11.739 | 10.977 |
| 2 | 15.783 | 10028357 | 330842 | 78.725 | 80.121 |
| 3 | 17.207 | 473388 | 14421 | 3.716 | 3.492 |
| 4 | 18.898 | 741278 | 22337 | 5.819 | 5.409 |
| Total | | 12738426 | 412926 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3e**

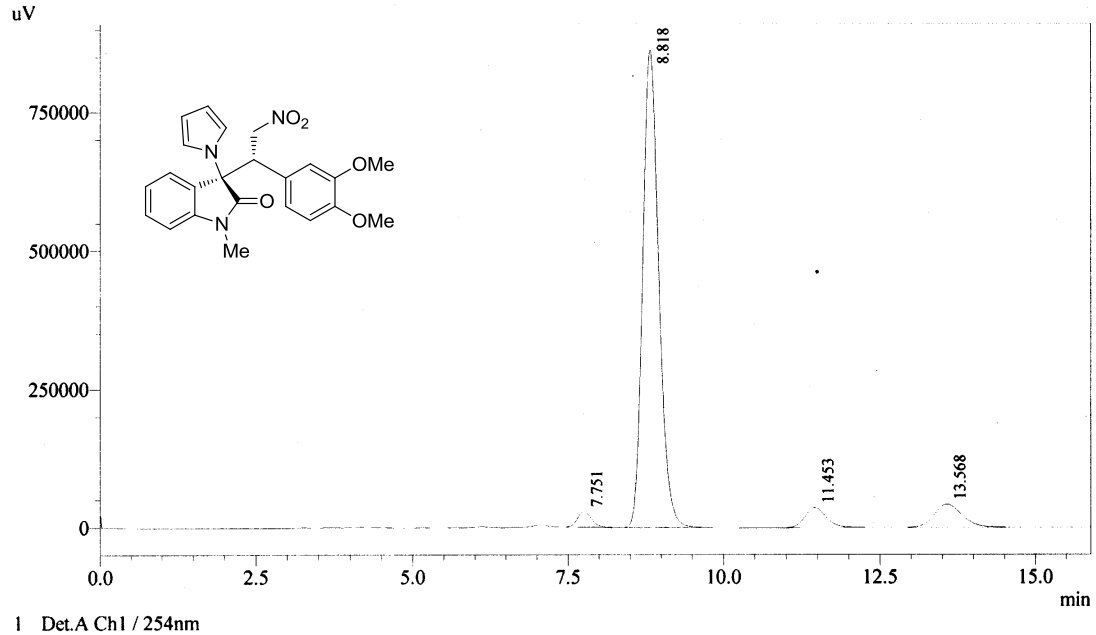





Detector A Ch1 254nm

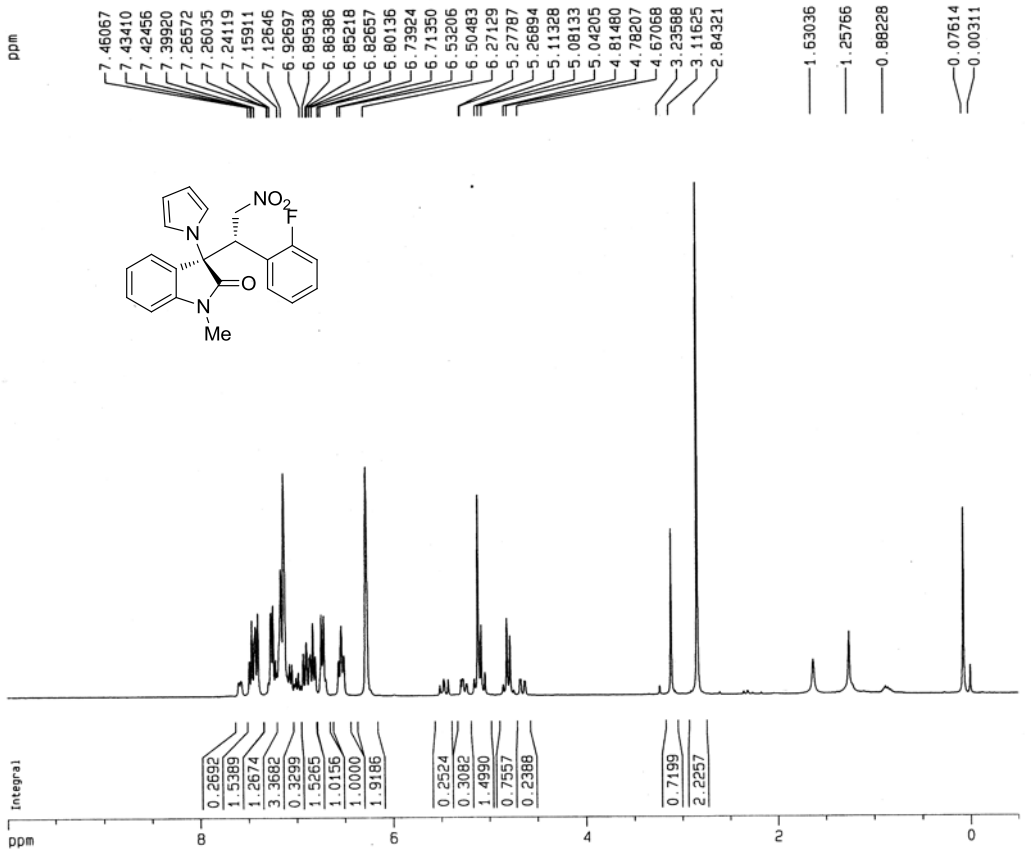
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.552 | 8501096 | 542985 | 38.659 | 44.548 |
| 2 | 8.554 | 8527621 | 480477 | 38.780 | 39.420 |
| 3 | 11.211 | 2491229 | 110279 | 11.329 | 9.048 |
| 4 | 12.633 | 2469766 | 85137 | 11.231 | 6.985 |
| Total | | 21989712 | 1218878 | 100.000 | 100.000 |

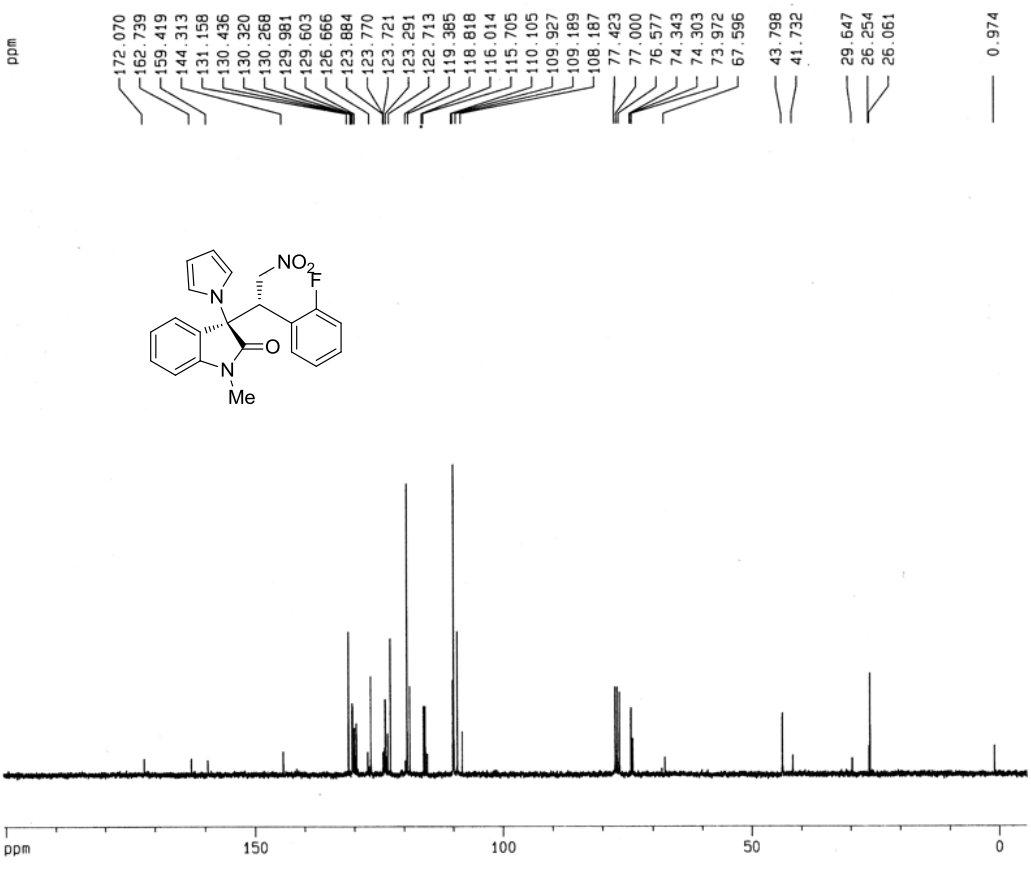


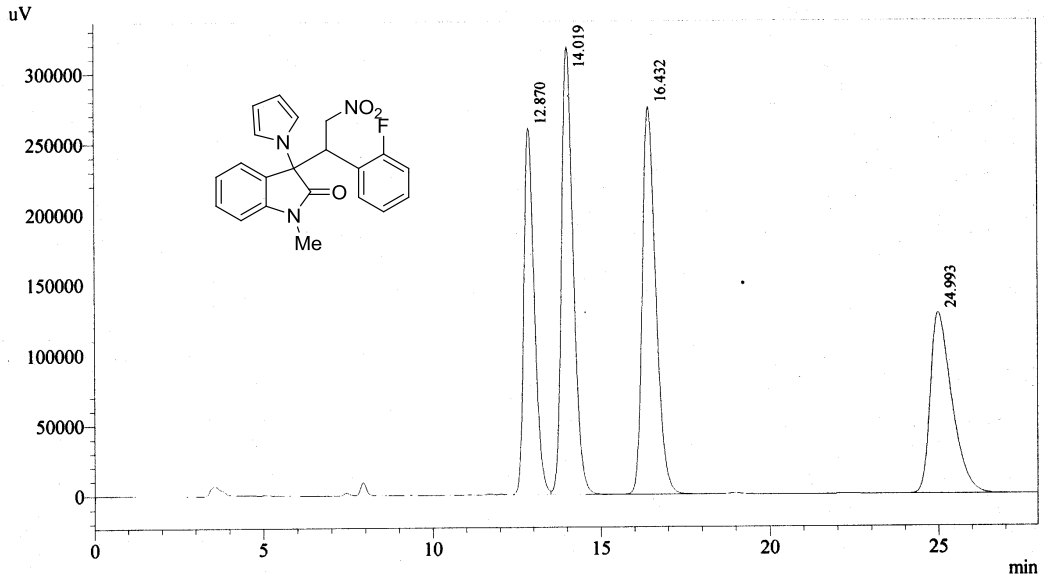

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.751 | 452971 | 28560 | 2.499 | 2.946 |
| 2 | 8.818 | 15467394 | 862319 | 85.342 | 88.950 |
| 3 | 11.453 | 864223 | 36480 | 4.768 | 3.763 |
| 4 | 13.568 | 1339530 | 42079 | 7.391 | 4.341 |
| Total | | 18124118 | 969438 | 100.000 | 100.000 |

## $^{1}$H NMR, $^{13}$C NMR and HPLC of 3f



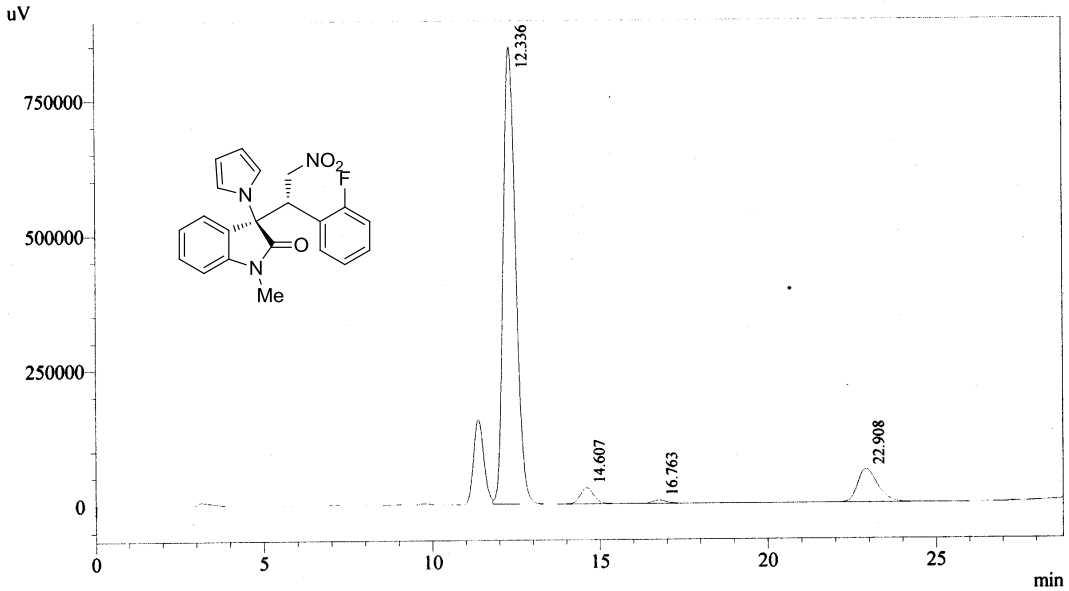






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.870 | 5649423 | 260529 | 21.061 | 26.495 |
| 2 | 14.019 | 7722543 | 318546 | 28.790 | 32.396 |
| 3 | 16.432 | 7666790 | 275604 | 28.582 | 28.028 |
| 4 | 24.993 | 5784890 | 128620 | 21.566 | 13.080 |
| Total | | 26823646 | 983298 | 100.000 | 100.000 |

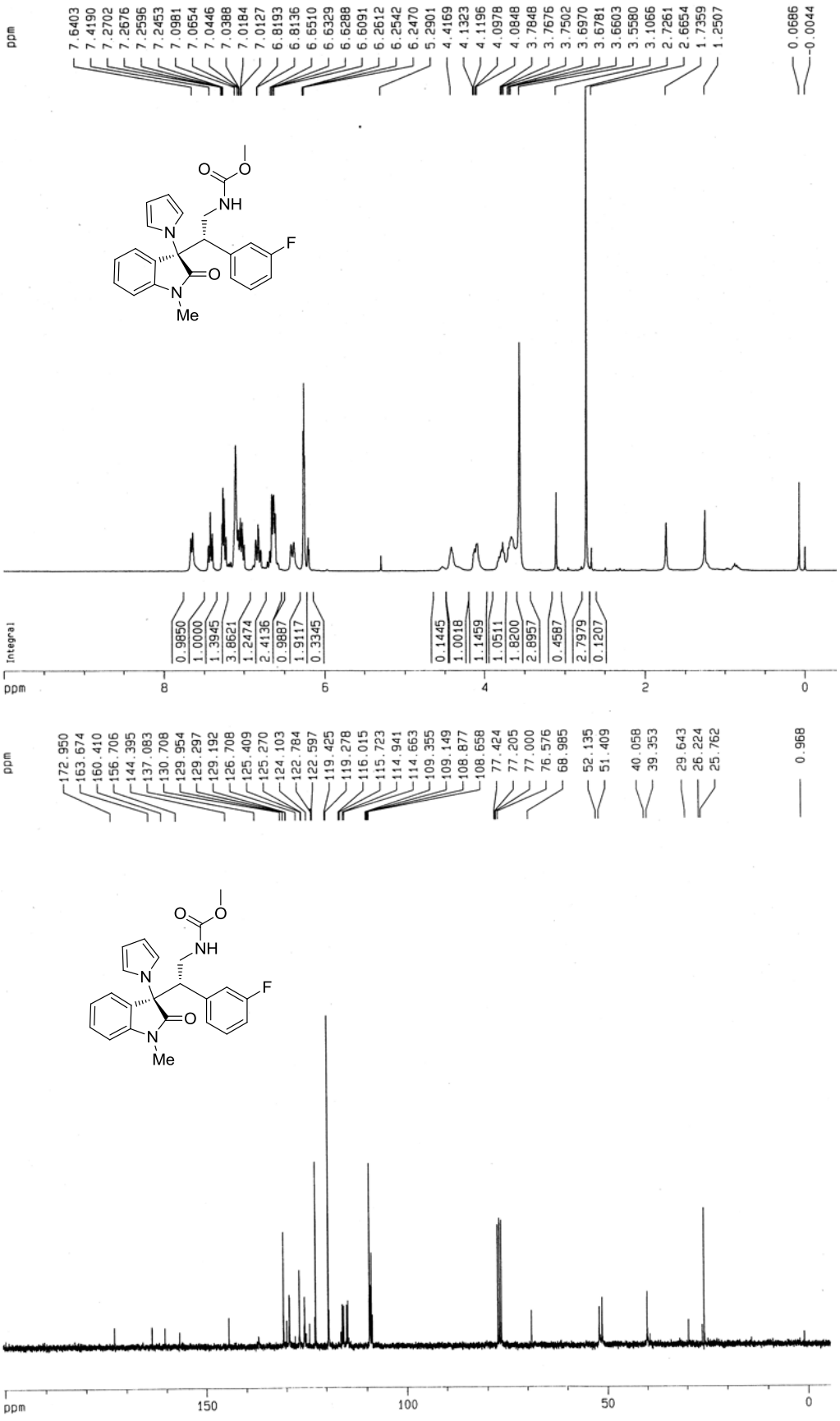


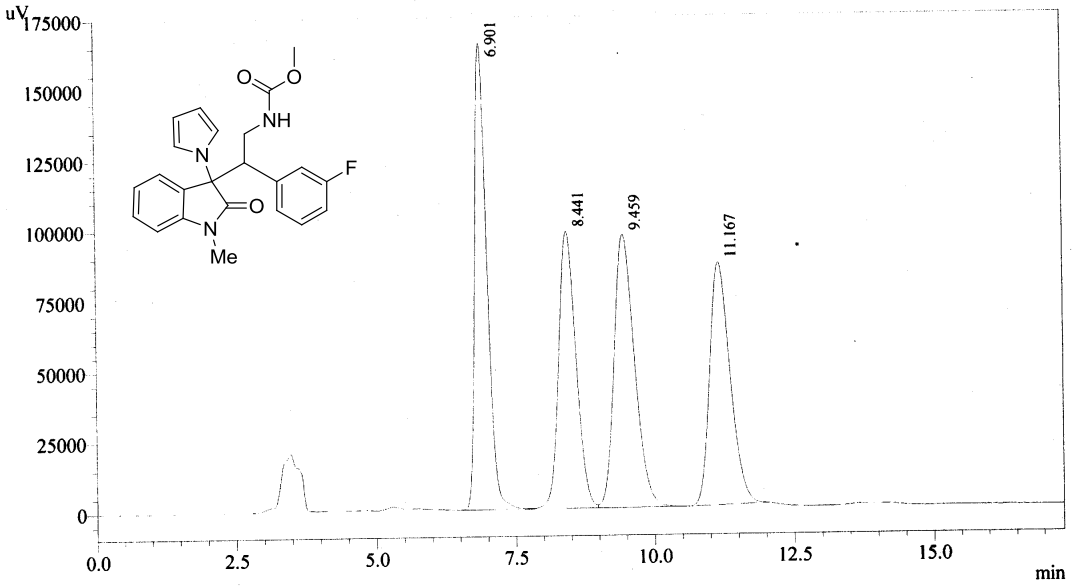

1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.336 | 21832399 | 846700 | 85.888 | 89.651 |
| 2 | 14.607 | 843243 | 29717 | 3.317 | 3.147 |
| 3 | 16.763 | 177535 | 6317 | 0.698 | 0.669 |
| 4 | 22.908 | 2566320 | 61708 | 10.096 | 6.534 |
| Total | | 25419498 | 944443 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3g**

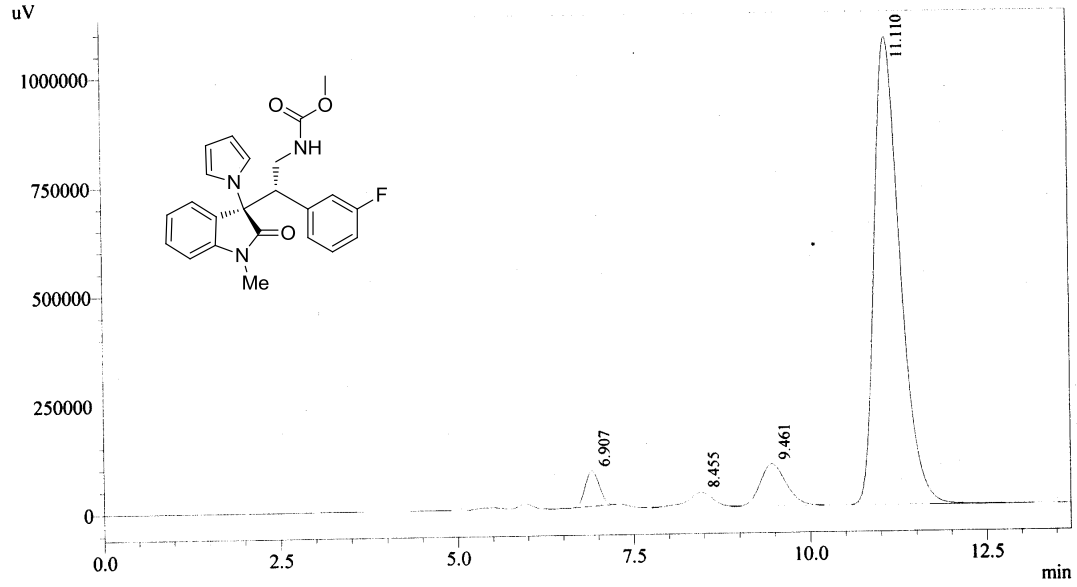





1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.901 | 2507343 | 165521 | 26.948 | 37.077 |
| 2 | 8.441 | 2130254 | 98179 | 22.895 | 21.992 |
| 3 | 9.459 | 2476713 | 96791 | 26.619 | 21.681 |
| 4 | 11.167 | 2190147 | 85936 | 23.539 | 19.250 |
| Total | | 9304458 | 446428 | 100.000 | 100.000 |

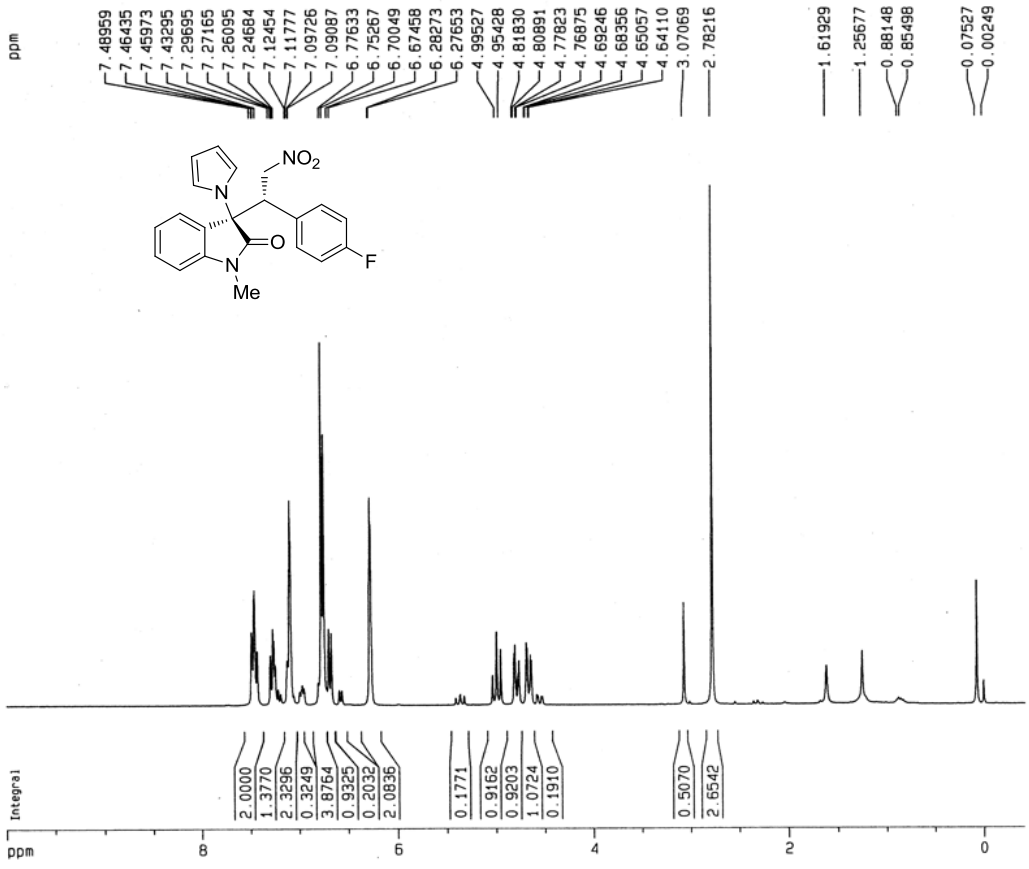


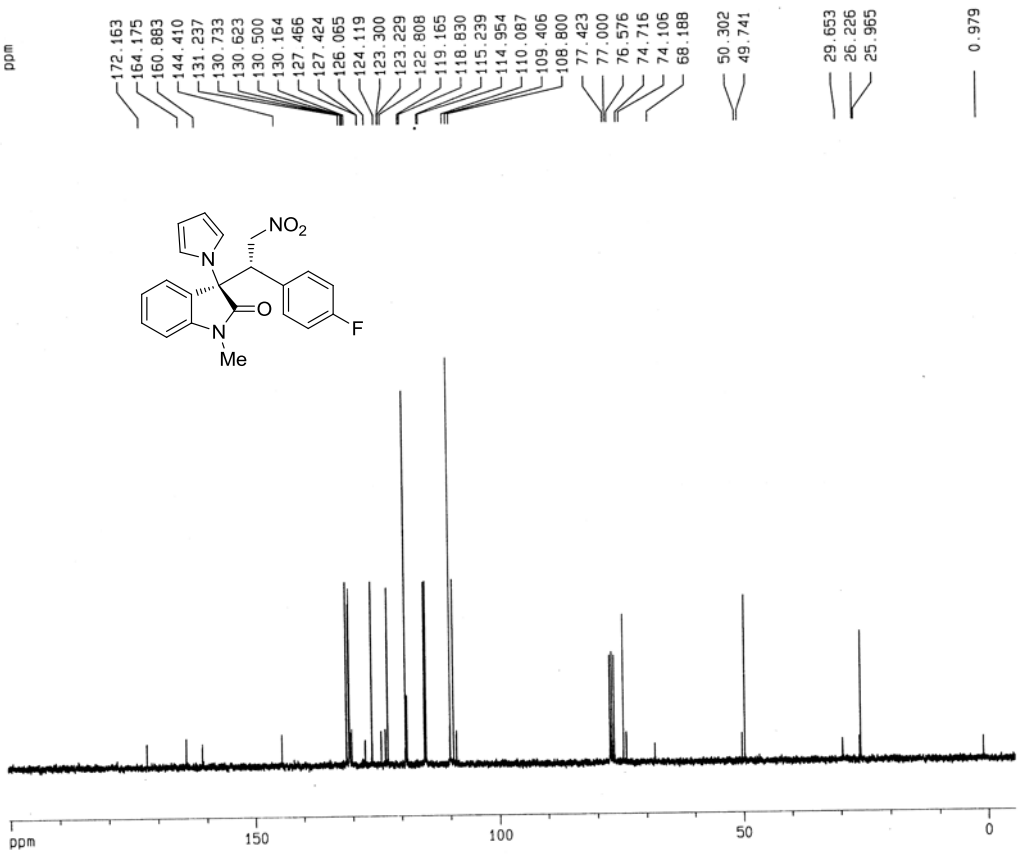

1 Det.A Ch1 / 254nm

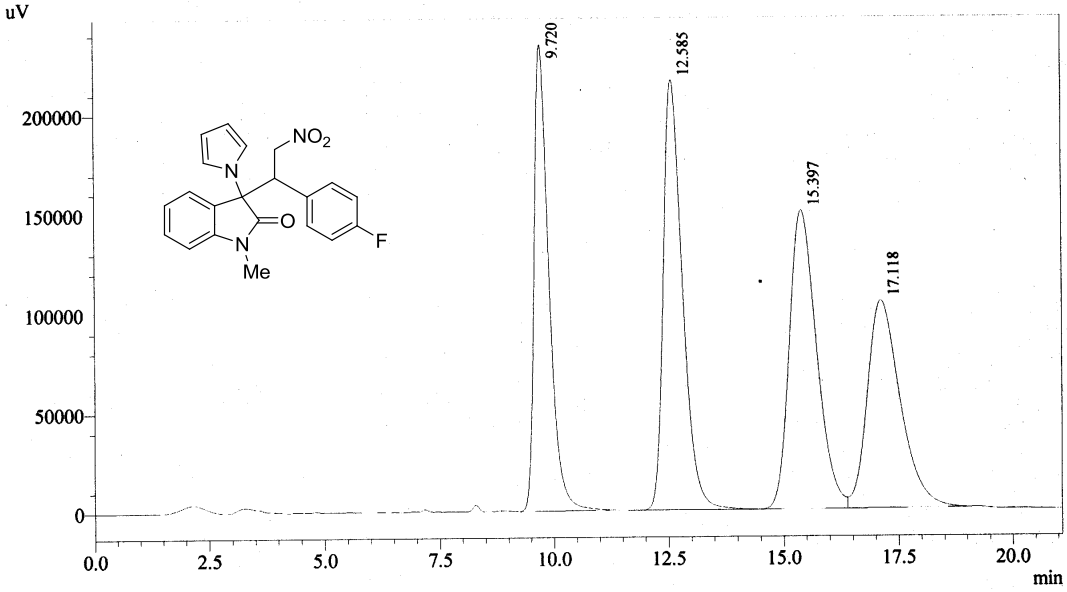
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.907 | 1135711 | 80662 | 3.588 | 6.287 |
| 2 | 8.455 | 810122 | 33162 | 2.559 | 2.585 |
| 3 | 9.461 | 2442655 | 95368 | 7.717 | 7.433 |
| 4 | 11.110 | 27265454 | 1073870 | 86.136 | 83.696 |
| Total | | 31653941 | 1283062 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3h**



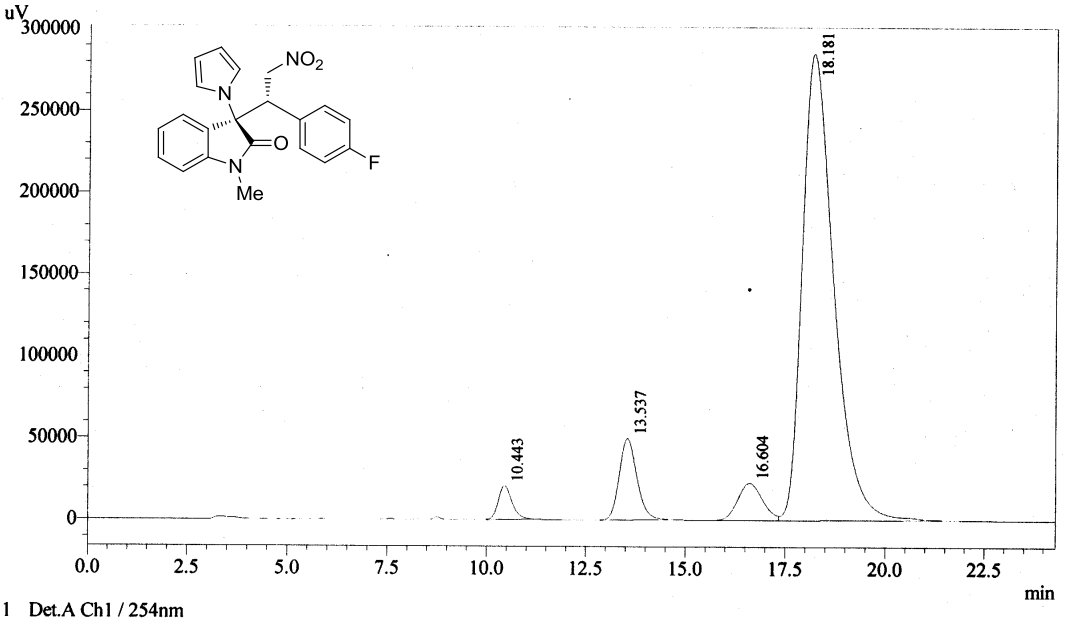






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.720 | 5249671 | 234780 | 22.912 | 33.266 |
| 2 | 12.585 | 6277113 | 216424 | 27.396 | 30.665 |
| 3 | 15.397 | 6179545 | 150261 | 26.970 | 21.290 |
| 4 | 17.118 | 5206069 | 104306 | 22.722 | 14.779 |
| Total | | 22912398 | 705771 | 100.000 | 100.000 |



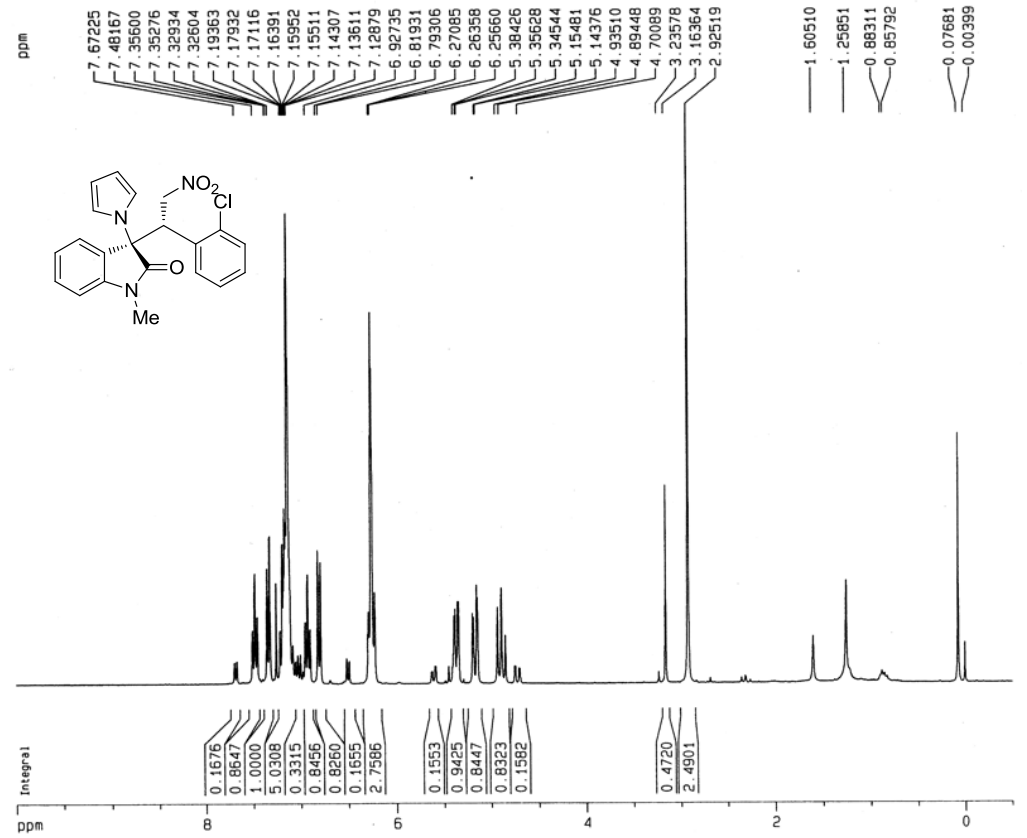

1 Det.A Ch1 / 254nm

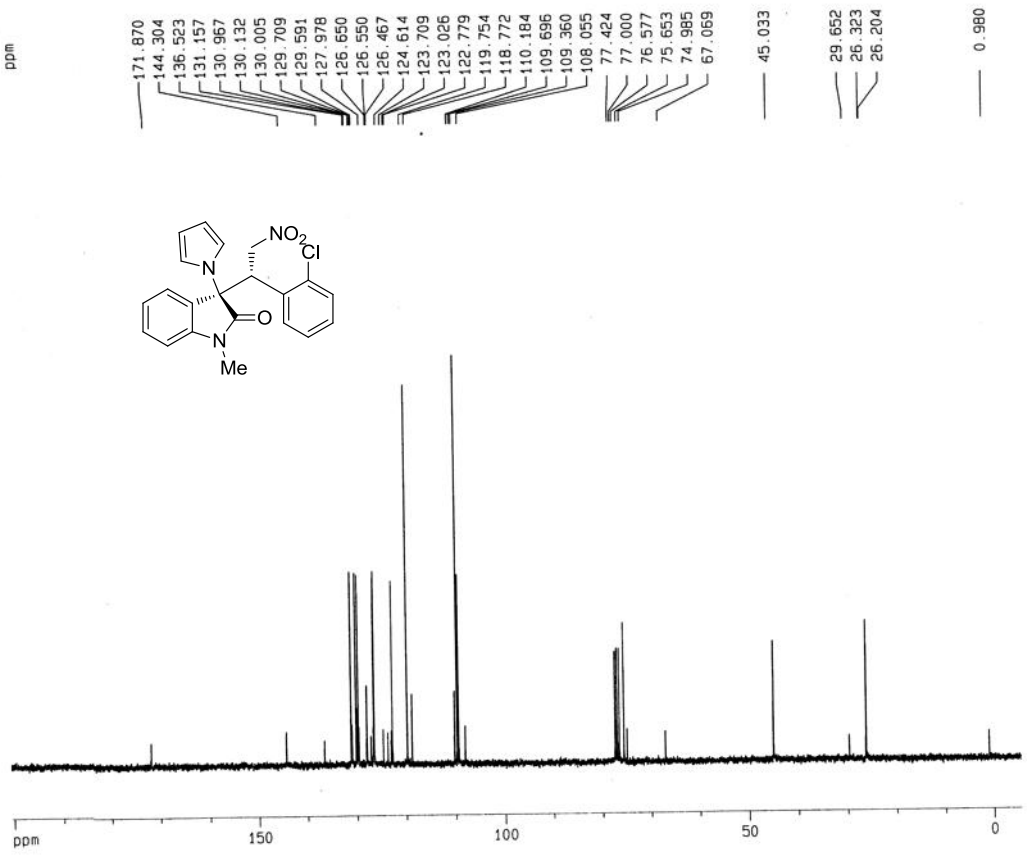
Detector A Ch1 254nm

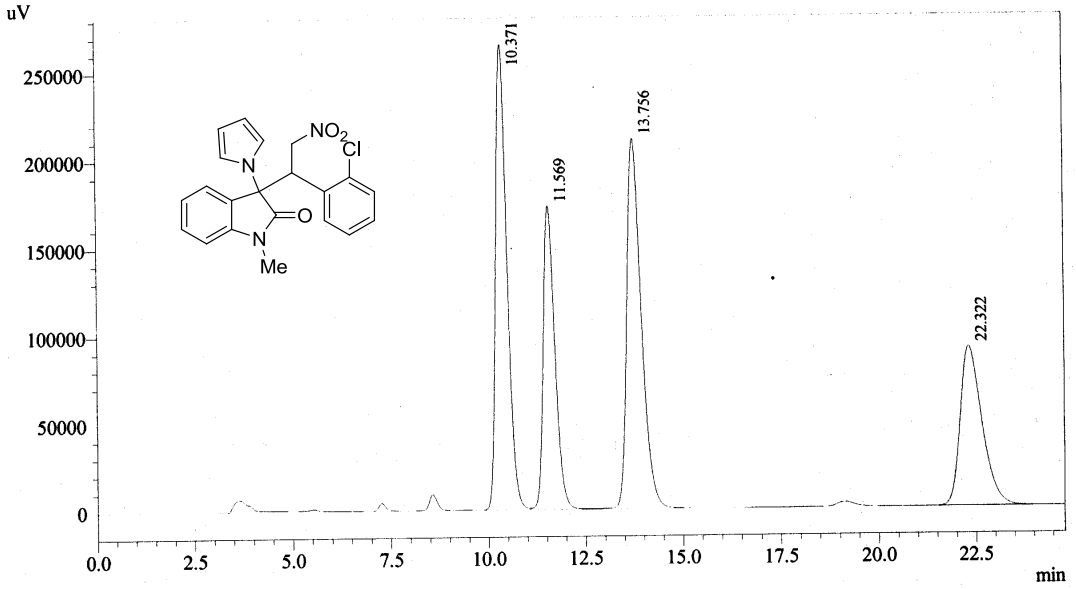
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.443 | 489079 | 20508 | 2.621 | 5.419 |
| 2 | 13.537 | 1532304 | 49729 | 8.211 | 13.140 |
| 3 | 16.604 | 981746 | 22726 | 5.261 | 6.005 |
| 4 | 18.181 | 15658773 | 285501 | 83.908 | 75.437 |
| Total | | 18661902 | 378463 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3i**



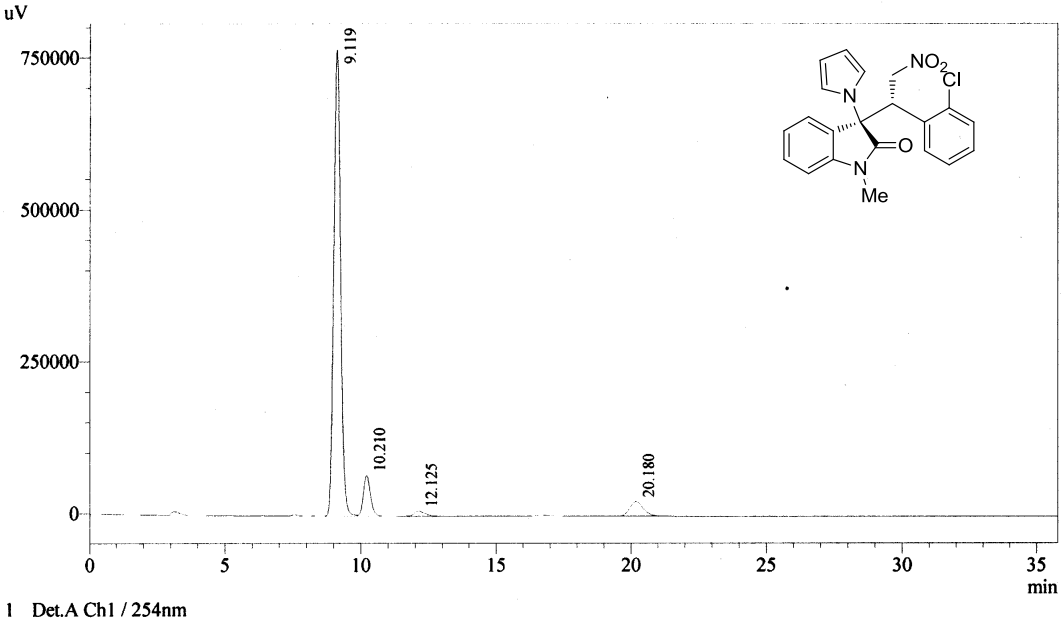






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.371 | 5365781 | 265913 | 29.843 | 35.874 |
| 2 | 11.569 | 3585705 | 173089 | 19.943 | 23.351 |
| 3 | 13.756 | 5453350 | 211013 | 30.330 | 28.468 |
| 4 | 22.322 | 3575041 | 91220 | 19.884 | 12.306 |
| Total | | 17979878 | 741234 | 100.000 | 100.000 |



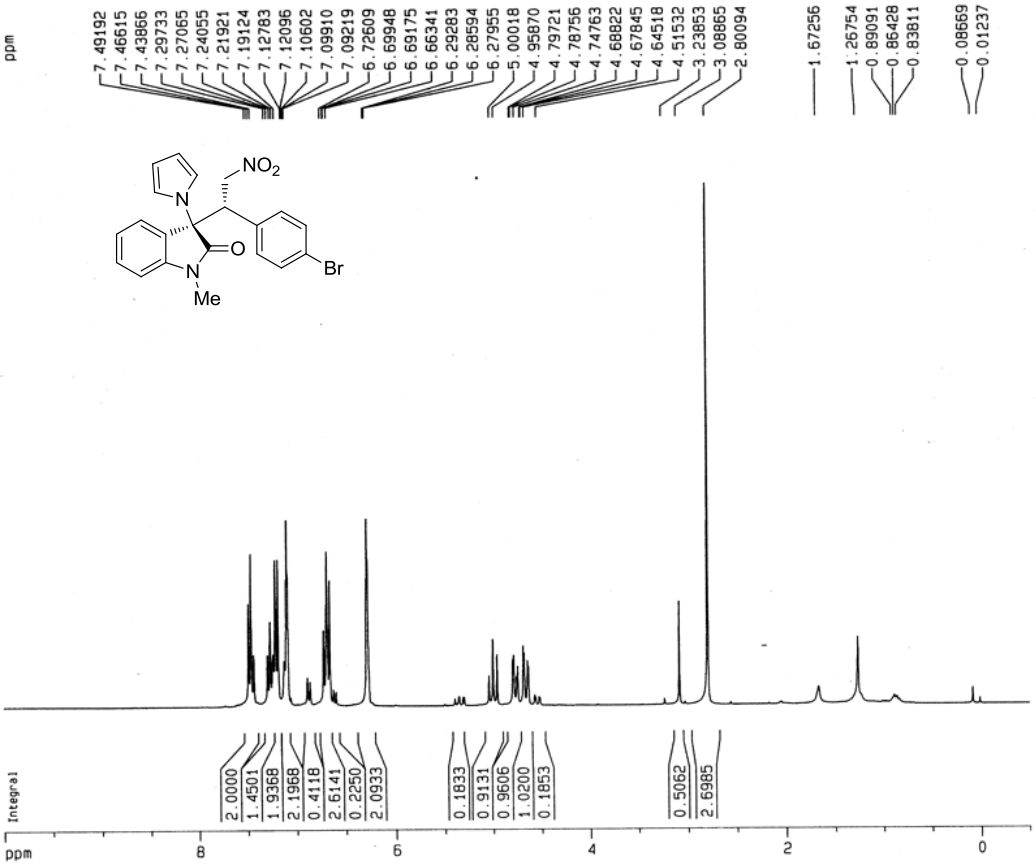

1 Det.A Ch1 / 254nm

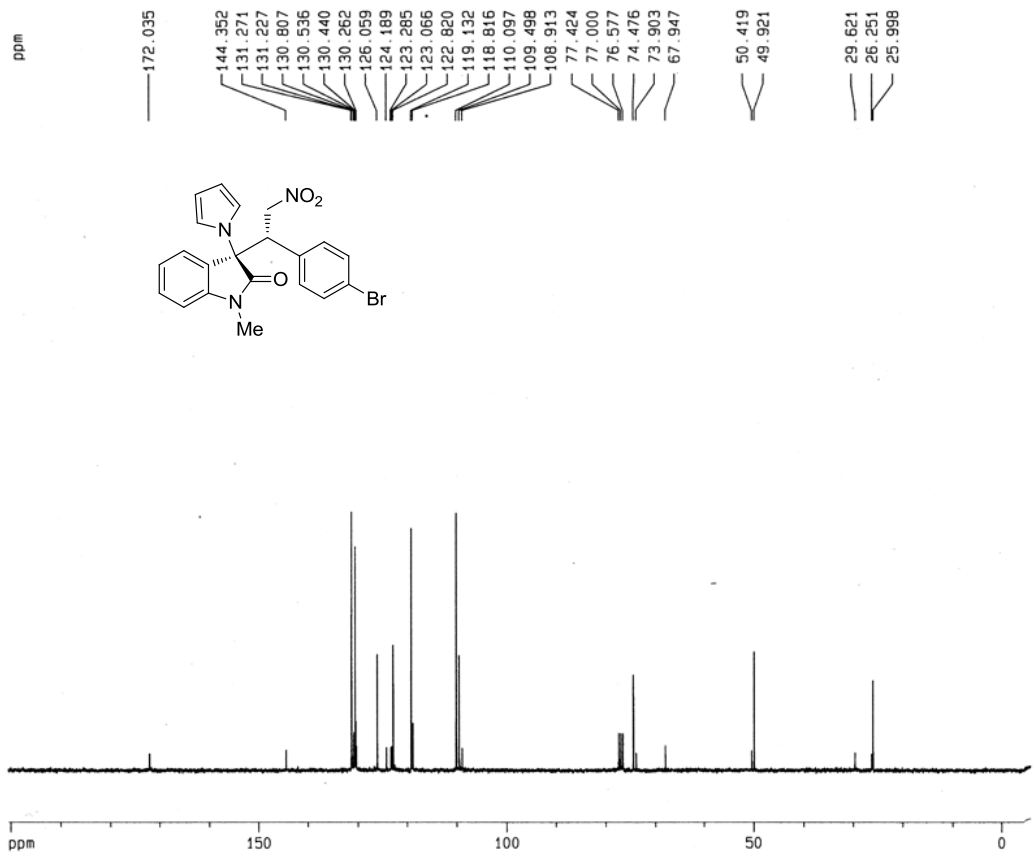
Detector A Ch1 254nm

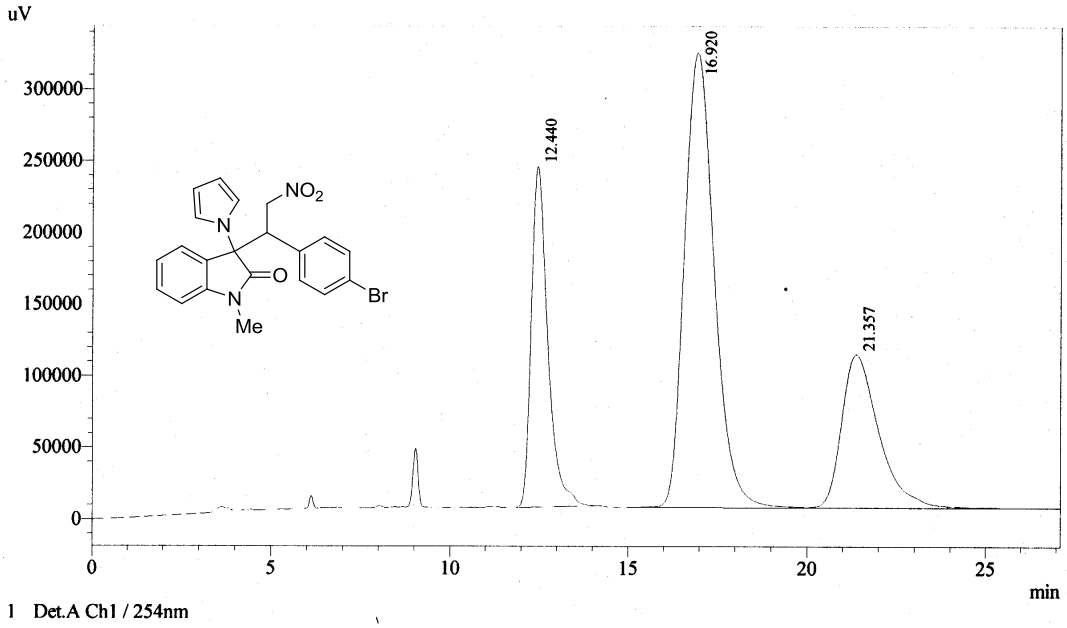
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.119 | 13402558 | 767418 | 85.443 | 88.574 |
| 2 | 10.210 | 1215219 | 66848 | 7.747 | 7.715 |
| 3 | 12.125 | 227323 | 8220 | 1.449 | 0.949 |
| 4 | 20.180 | 840924 | 23927 | 5.361 | 2.762 |
| Total | | 15686024 | 866413 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3j**



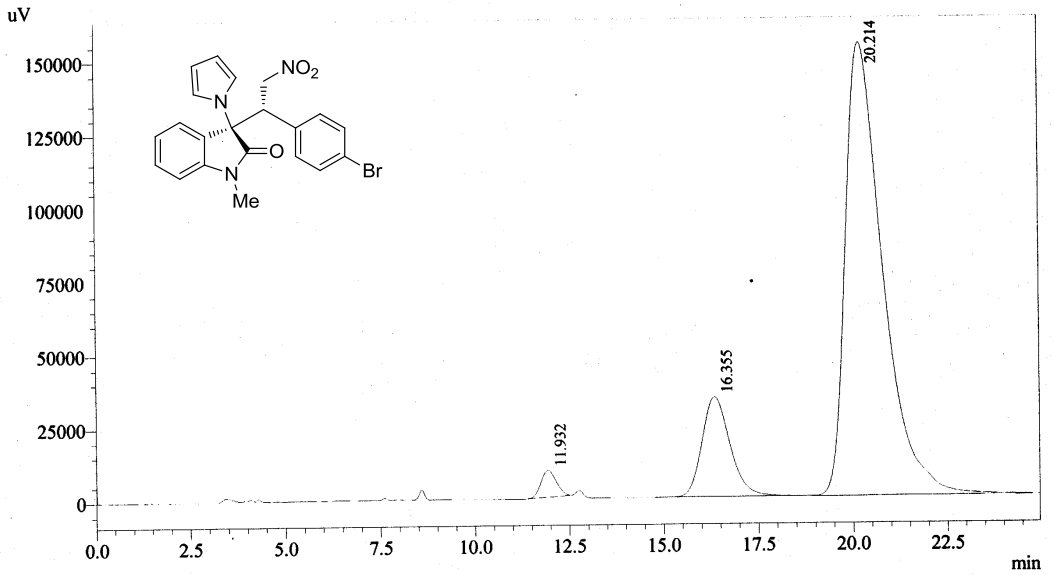






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.440 | 7656709 | 237478 | 22.656 | 35.878 |
| 2 | 16.920 | 18414955 | 317344 | 54.489 | 47.944 |
| 3 | 21.357 | 7723758 | 107089 | 22.854 | 16.179 |
| Total | | 33795422 | 661911 | 100.000 | 100.000 |

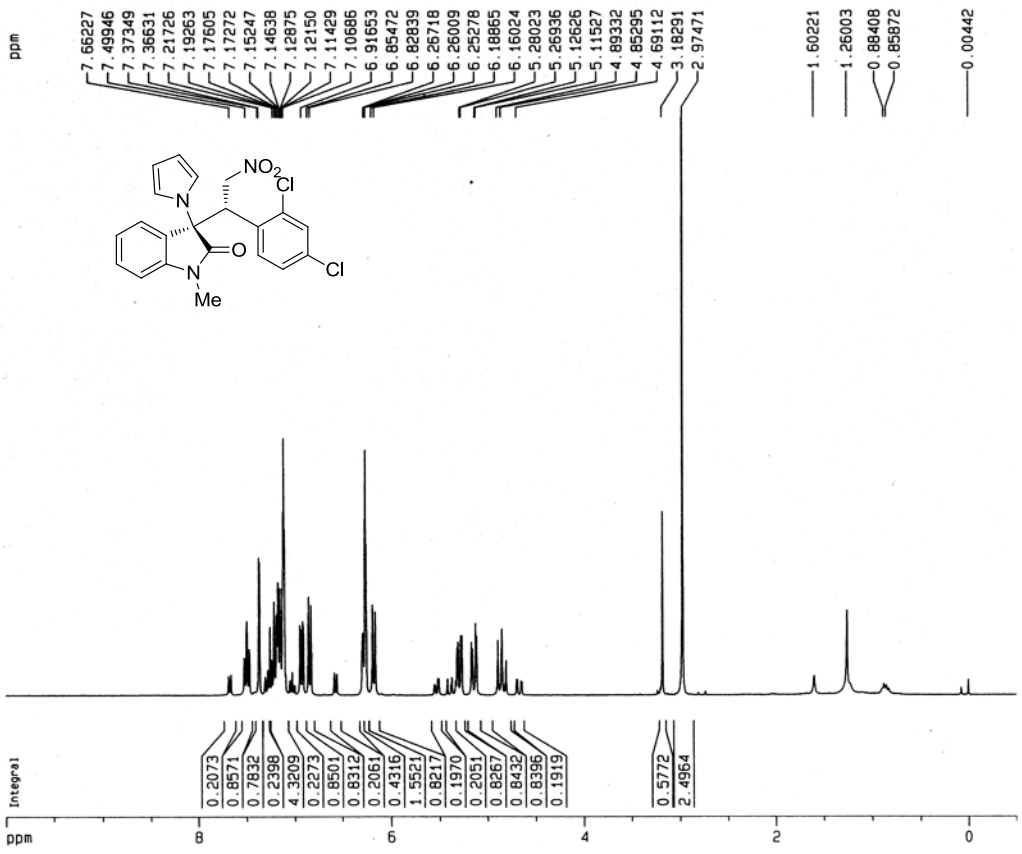


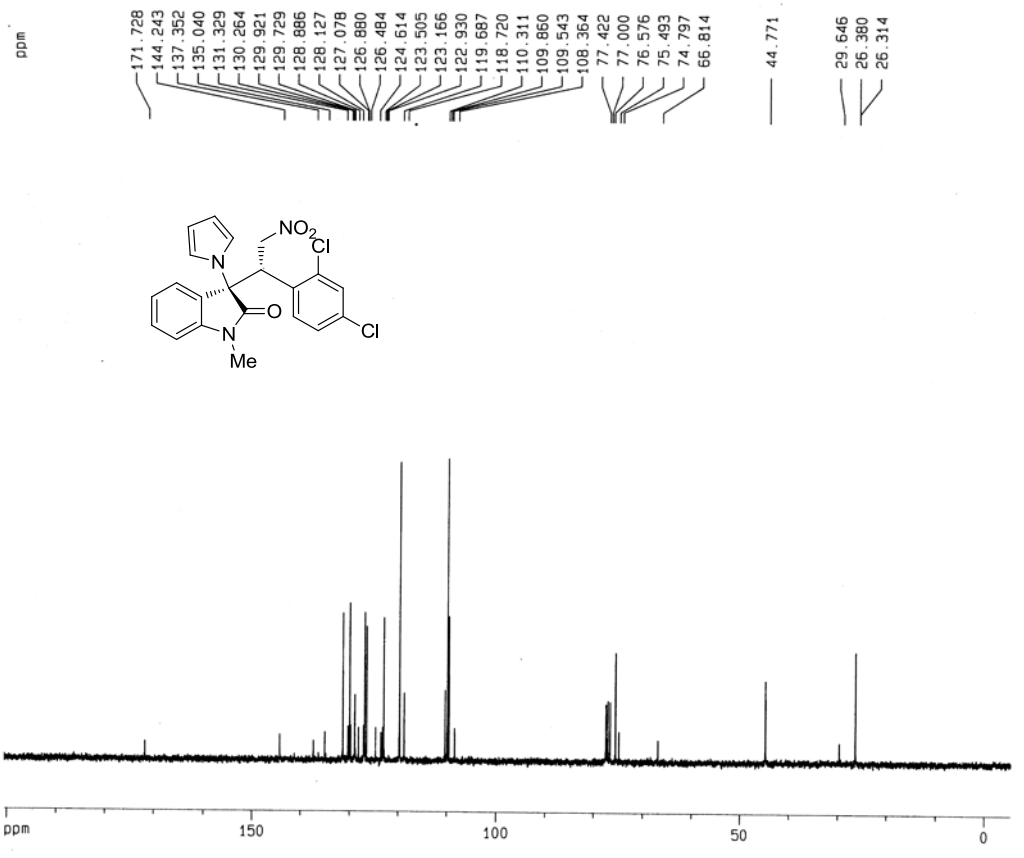

1 Det.A Ch1 / 254nm

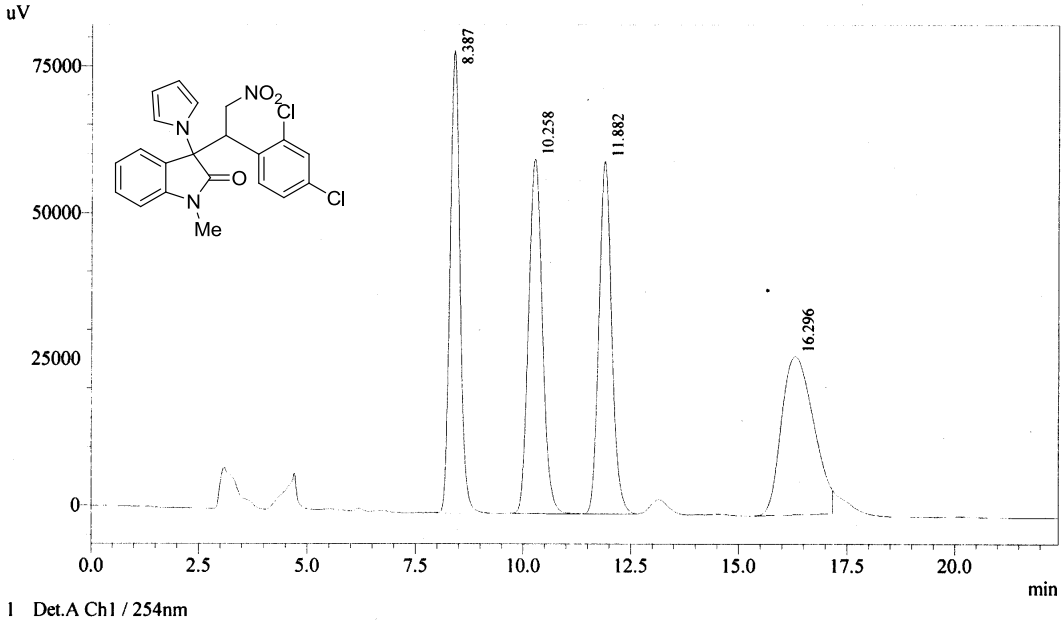
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.932 | 256722 | 9073 | 2.044 | 4.592 |
| 2 | 16.355 | 1745547 | 34021 | 13.899 | 17.218 |
| 3 | 20.214 | 10556369 | 154491 | 84.057 | 78.190 |
| Total | | 12558638 | 197585 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3k**



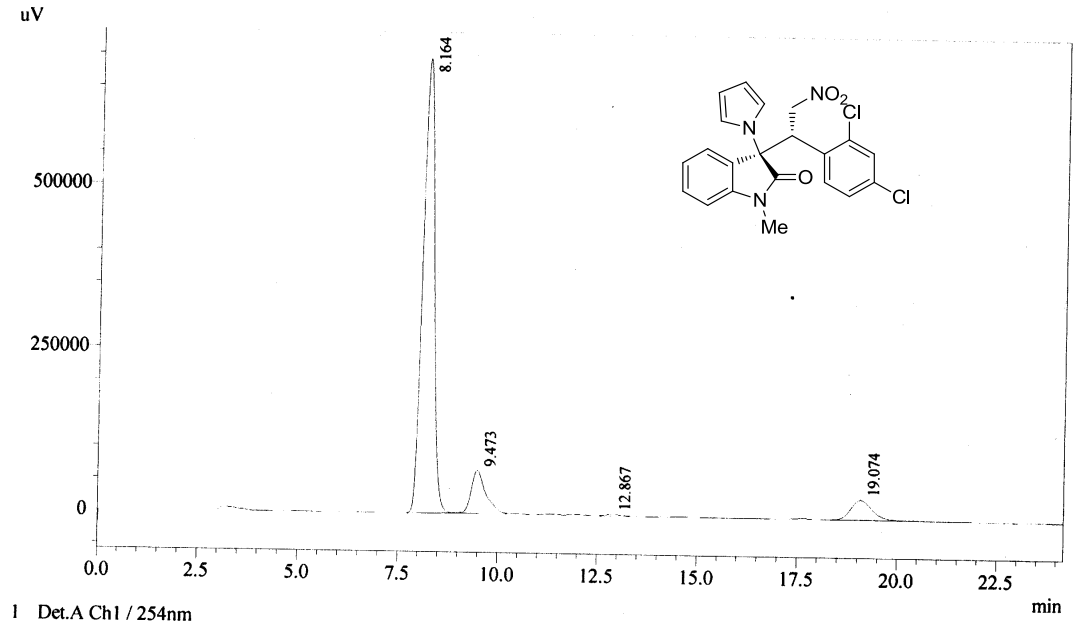






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.387 | 1267767 | 79028 | 23.983 | 34.845 |
| 2 | 10.258 | 1360140 | 60526 | 25.730 | 26.687 |
| 3 | 11.882 | 1252951 | 60189 | 23.702 | 26.538 |
| 4 | 16.296 | 1405300 | 27057 | 26.585 | 11.930 |
| Total | | 5286158 | 226801 | 100.000 | 100.000 |



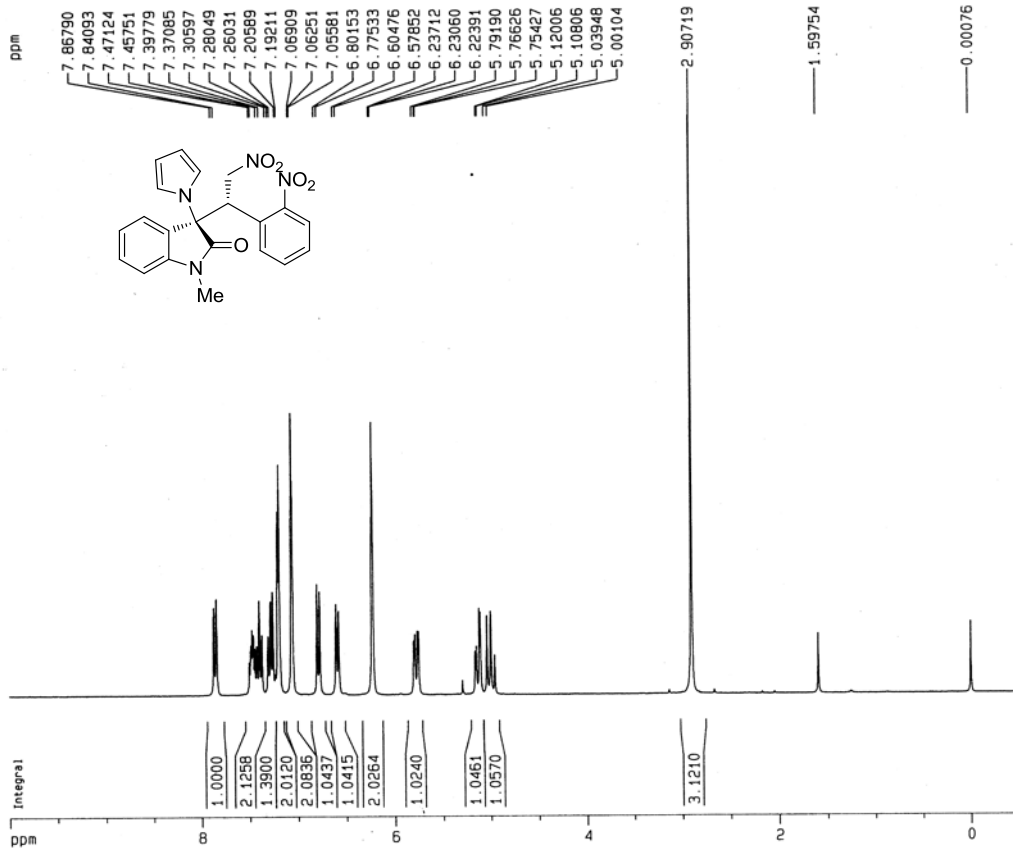

1 Det.A Ch1 / 254nm

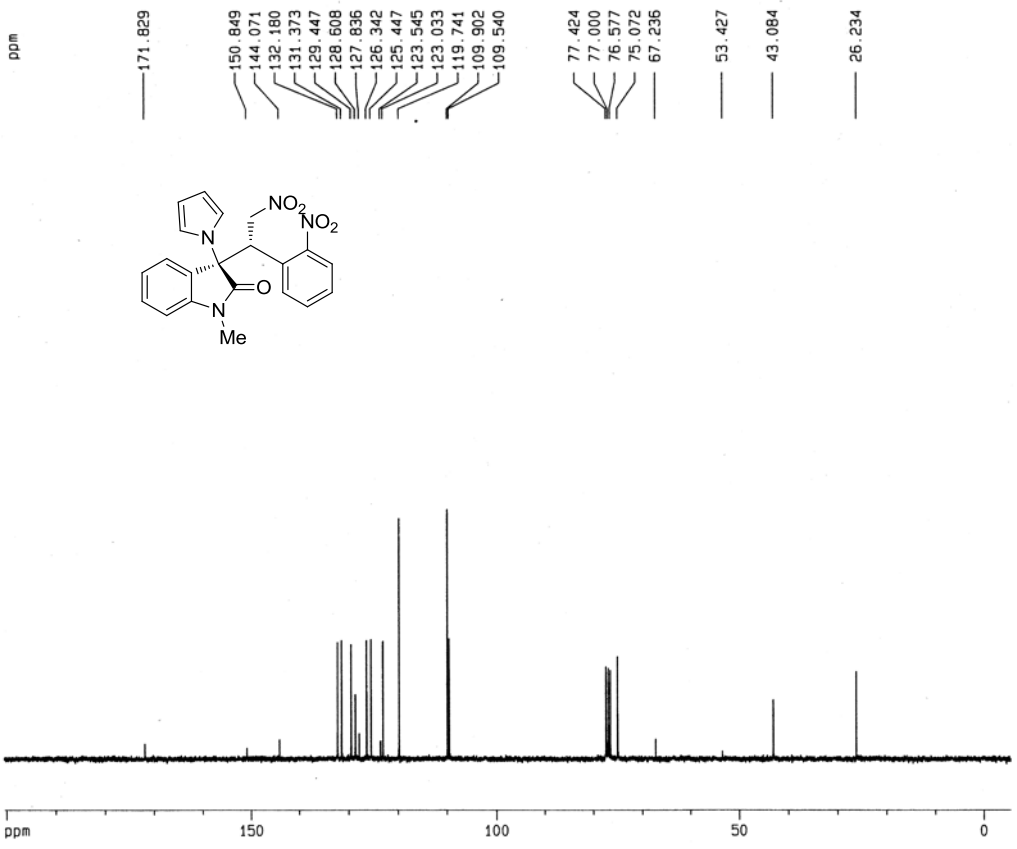
Detector A Ch1 254nm

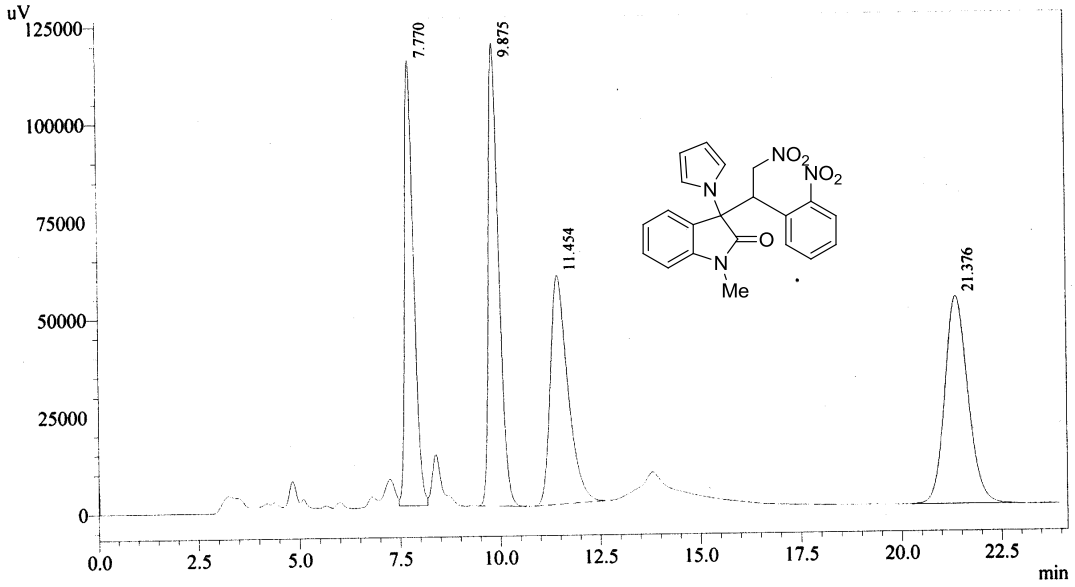
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.164 | 13909318 | 696445 | 83.026 | 87.559 |
| 2 | 9.473 | 1648930 | 65927 | 9.843 | 8.289 |
| 3 | 12.867 | 67853 | 2507 | 0.405 | 0.315 |
| 4 | 19.074 | 1126834 | 30520 | 6.726 | 3.837 |
| Total | | 16752934 | 795399 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3l**



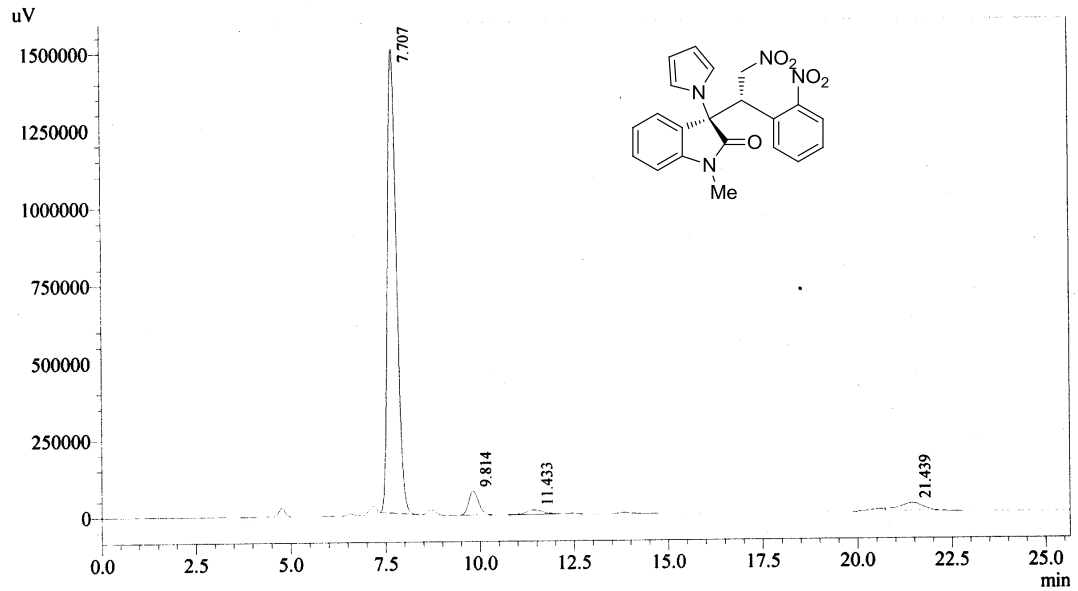






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.770 | 1787871 | 114349 | 22.716 | 33.134 |
| 2 | 9.875 | 2131975 | 118728 | 27.088 | 34.403 |
| 3 | 11.454 | 1797105 | 58784 | 22.834 | 17.033 |
| 4 | 21.376 | 2153461 | 53253 | 27.361 | 15.431 |
| Total | | 7870412 | 345115 | 100.000 | 100.000 |

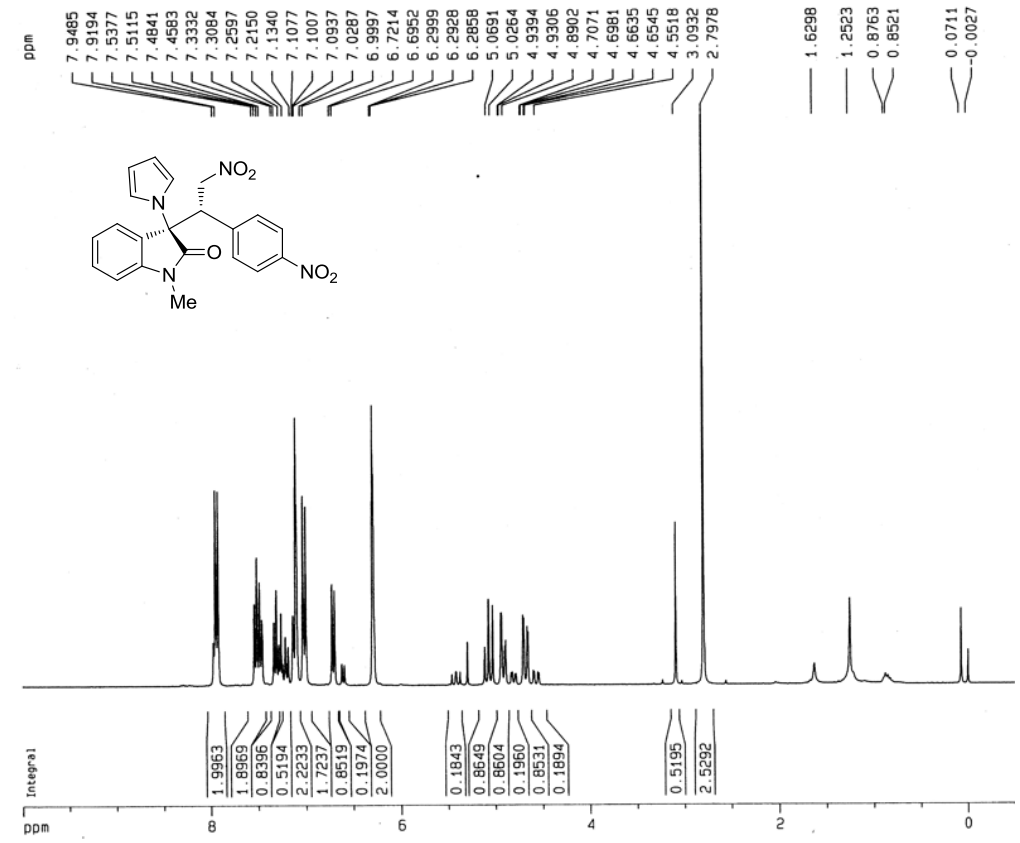


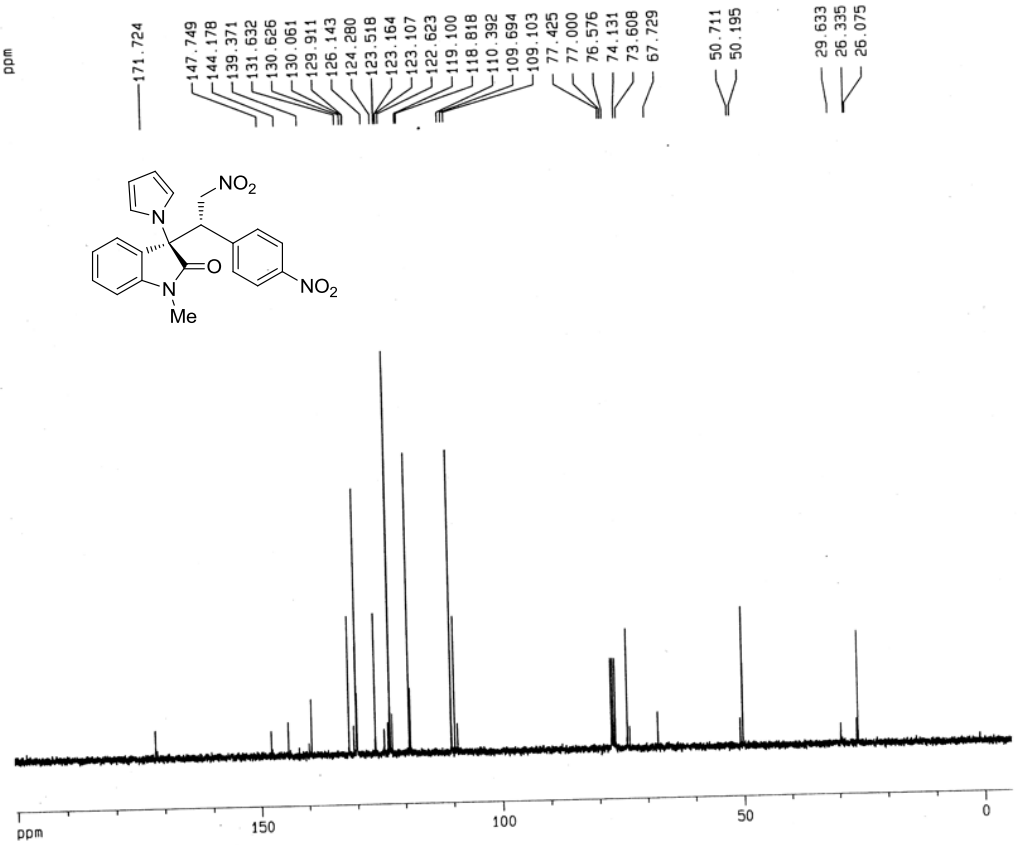

1 Det.A Ch1 / 254nm

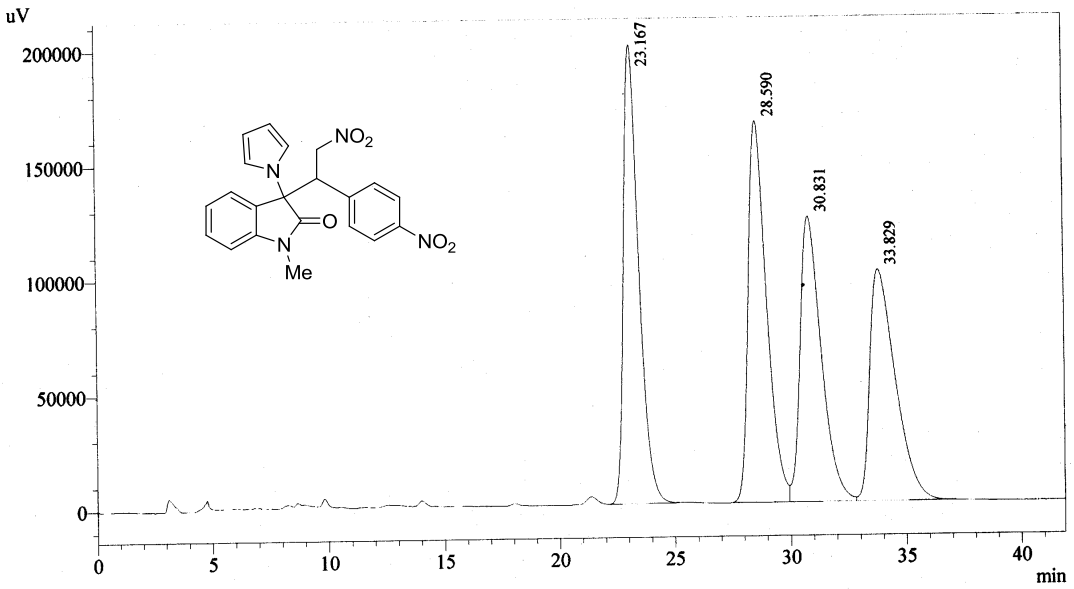
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.707 | 24754711 | 1500652 | 89.355 | 92.826 |
| 2 | 9.814 | 1396917 | 76772 | 5.042 | 4.749 |
| 3 | 11.433 | 432993 | 14137 | 1.563 | 0.874 |
| 4 | 21.439 | 1119138 | 25066 | 4.040 | 1.551 |
| Total | | 27703759 | 1616627 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3m**



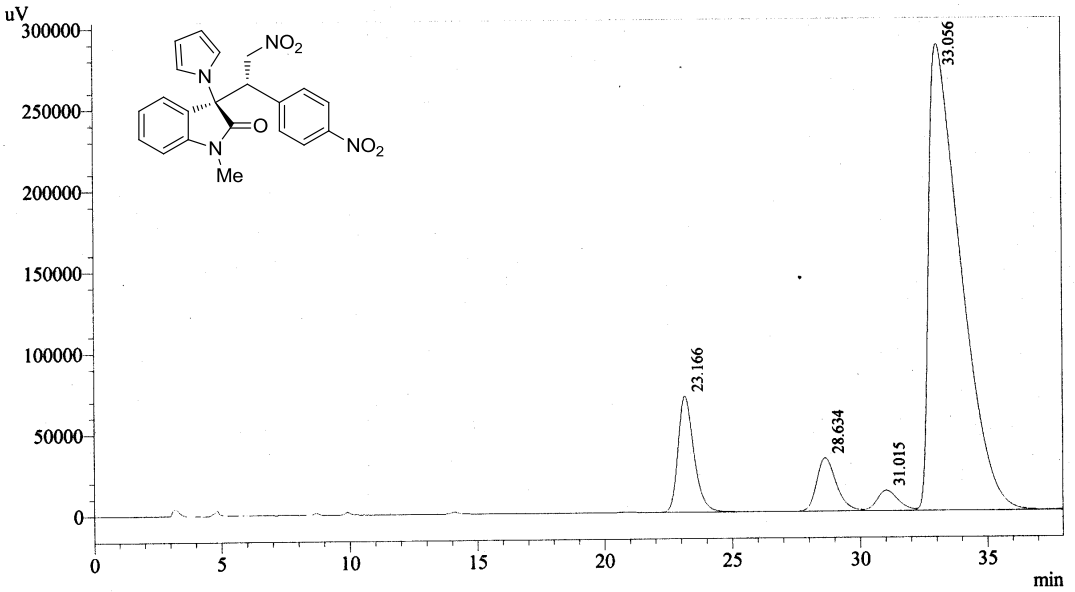






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 23.167 | 9194784 | 200197 | 27.026 | 33.826 |
| 2 | 28.590 | 9176509 | 166331 | 26.973 | 28.104 |
| 3 | 30.831 | 7873051 | 124400 | 23.141 | 21.019 |
| 4 | 33.829 | 7777254 | 100910 | 22.860 | 17.050 |
| Total | | 34021598 | 591838 | 100.000 | 100.000 |

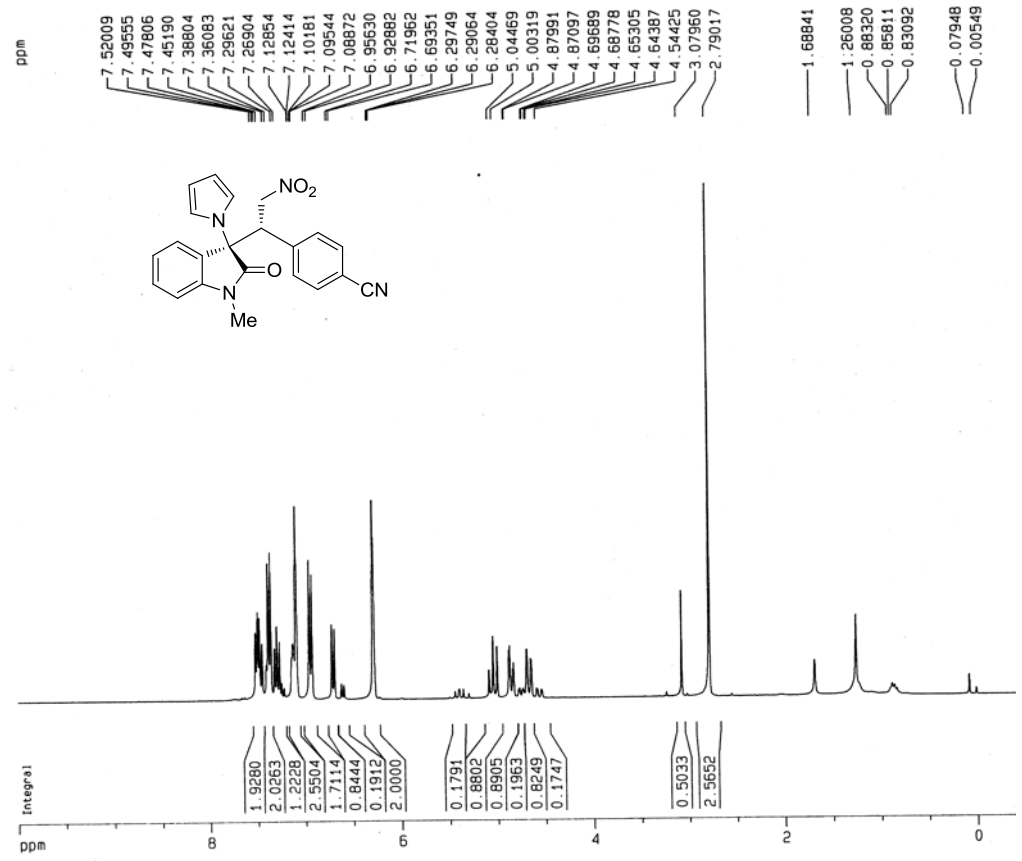


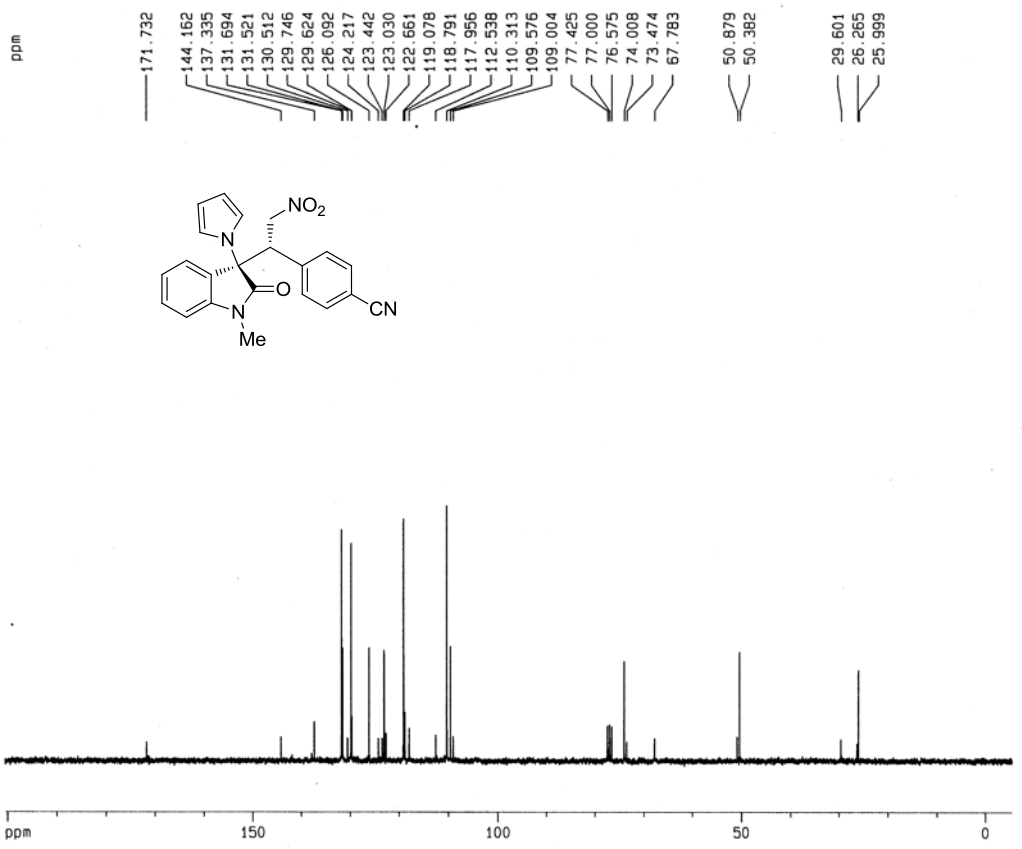

1 Det.A Ch1 / 254nm

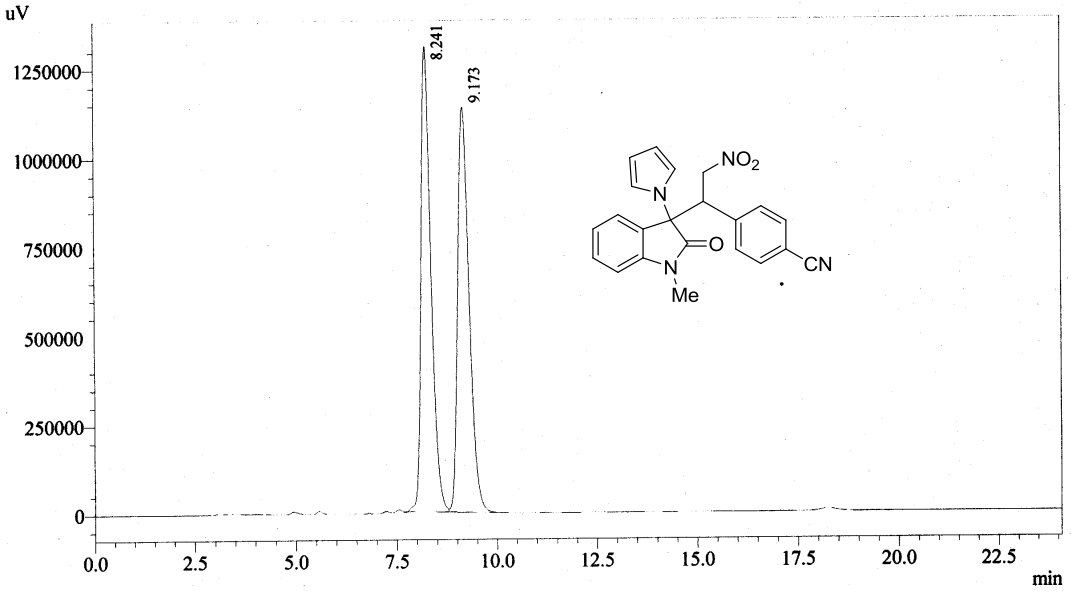
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 23.166 | 3095943 | 71621 | 10.078 | 17.711 |
| 2 | 28.634 | 1740569 | 32779 | 5.666 | 8.106 |
| 3 | 31.015 | 712940 | 12486 | 2.321 | 3.088 |
| 4 | 33.056 | 25170357 | 287492 | 81.935 | 71.095 |
| Total | | 30719809 | 404379 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3n**



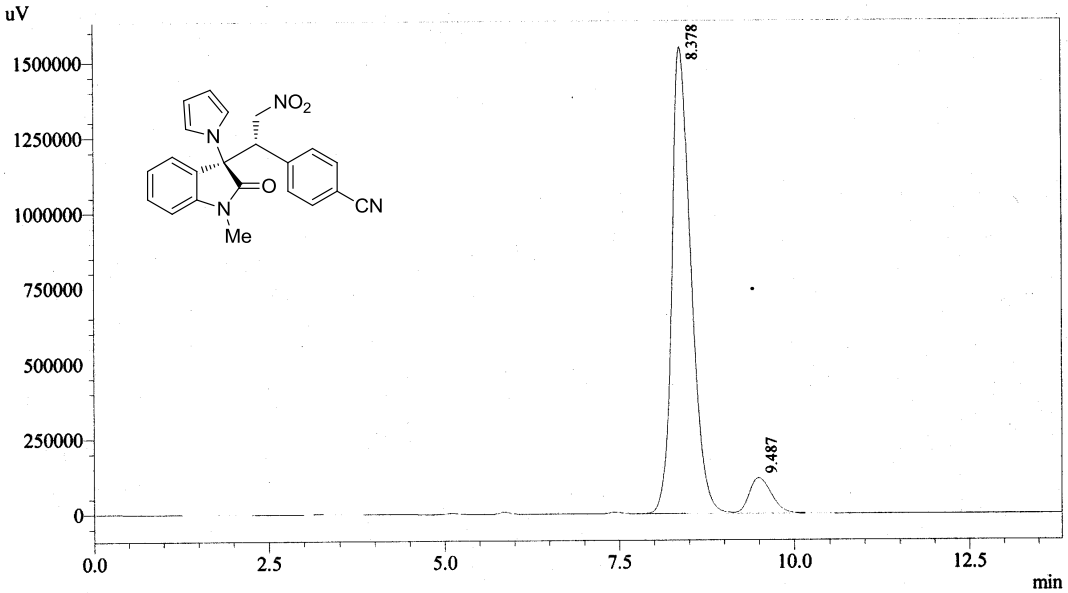






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.241 | 22517543 | 1307536 | 49.912 | 53.463 |
| 2 | 9.173 | 22596929 | 1138159 | 50.088 | 46.537 |
| Total | | 45114472 | 2445695 | 100.000 | 100.000 |

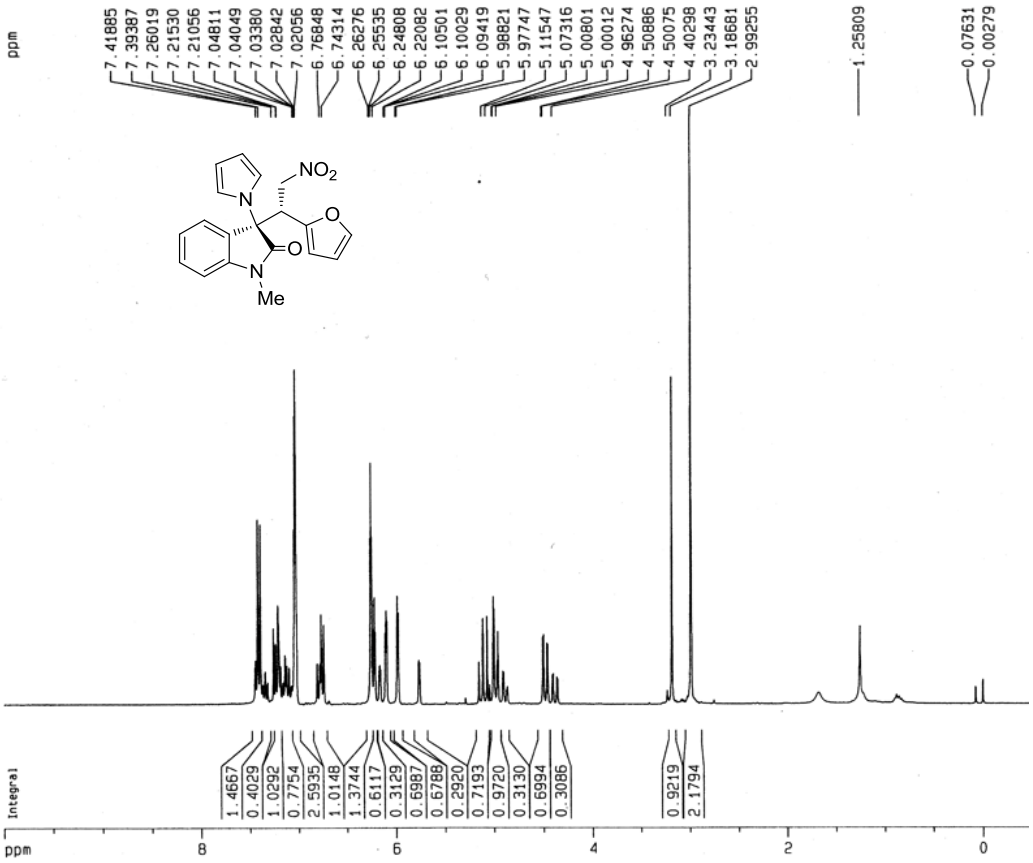


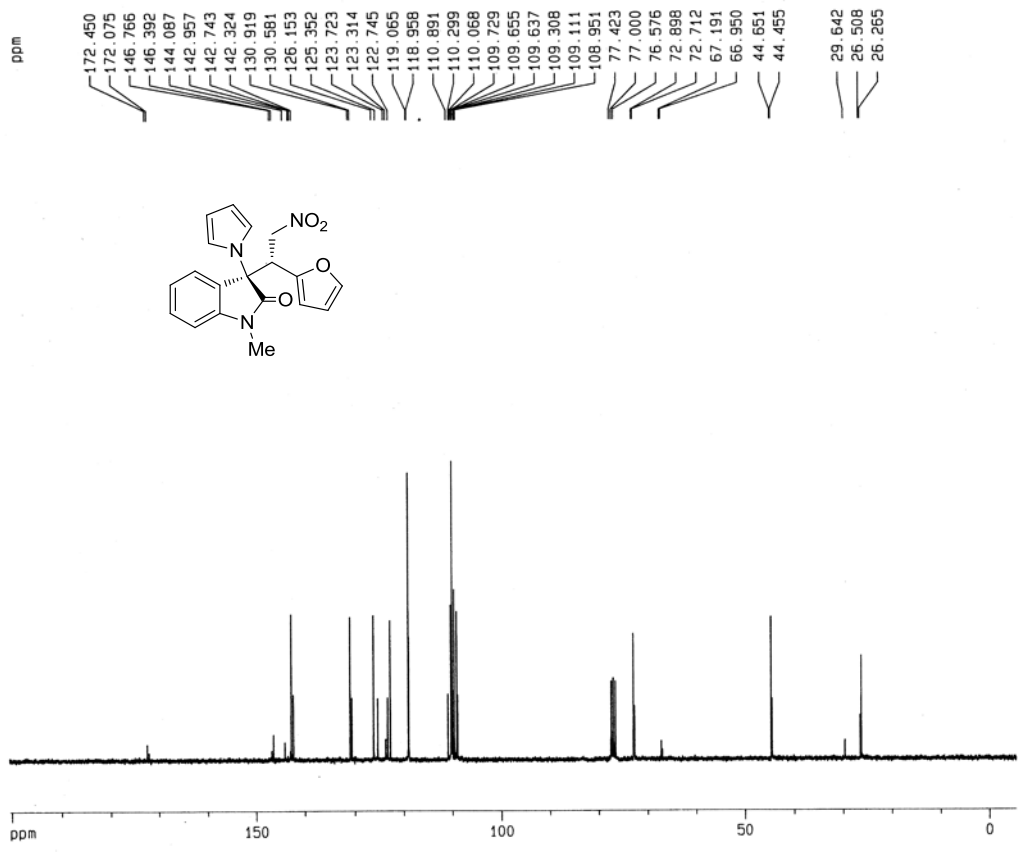

1 Det.A Ch1 / 254nm

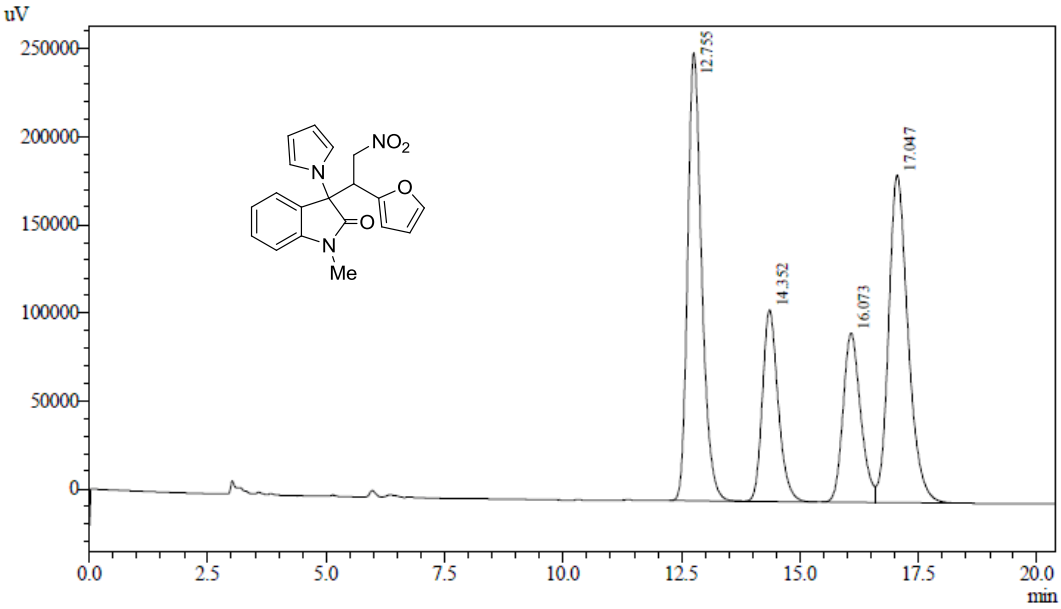
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.378 | 29360196 | 1549936 | 91.866 | 92.910 |
| 2 | 9.487 | 2599706 | 118271 | 8.134 | 7.090 |
| Total | | 31959902 | 1668207 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3o**



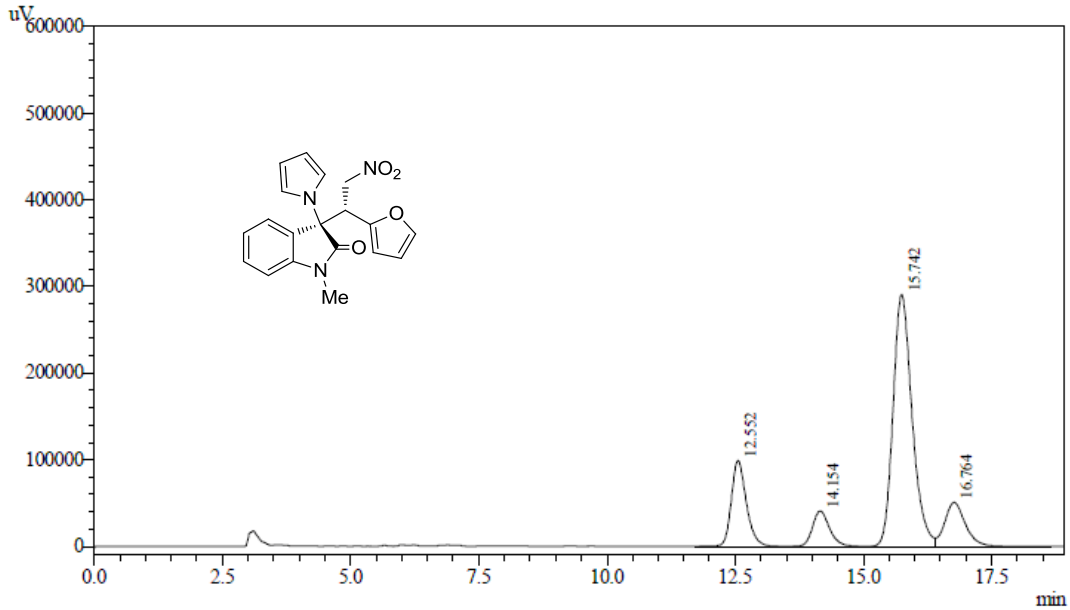






1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.755 | 5248797 | 254489 | 33.699 | 39.426 |
| 2 | 14.352 | 2518392 | 108864 | 16.169 | 16.865 |
| 3 | 16.073 | 2491635 | 96116 | 15.997 | 14.891 |
| 4 | 17.047 | 5316575 | 186017 | 34.134 | 28.818 |
| Total | | 15575400 | 645487 | 100.000 | 100.000 |

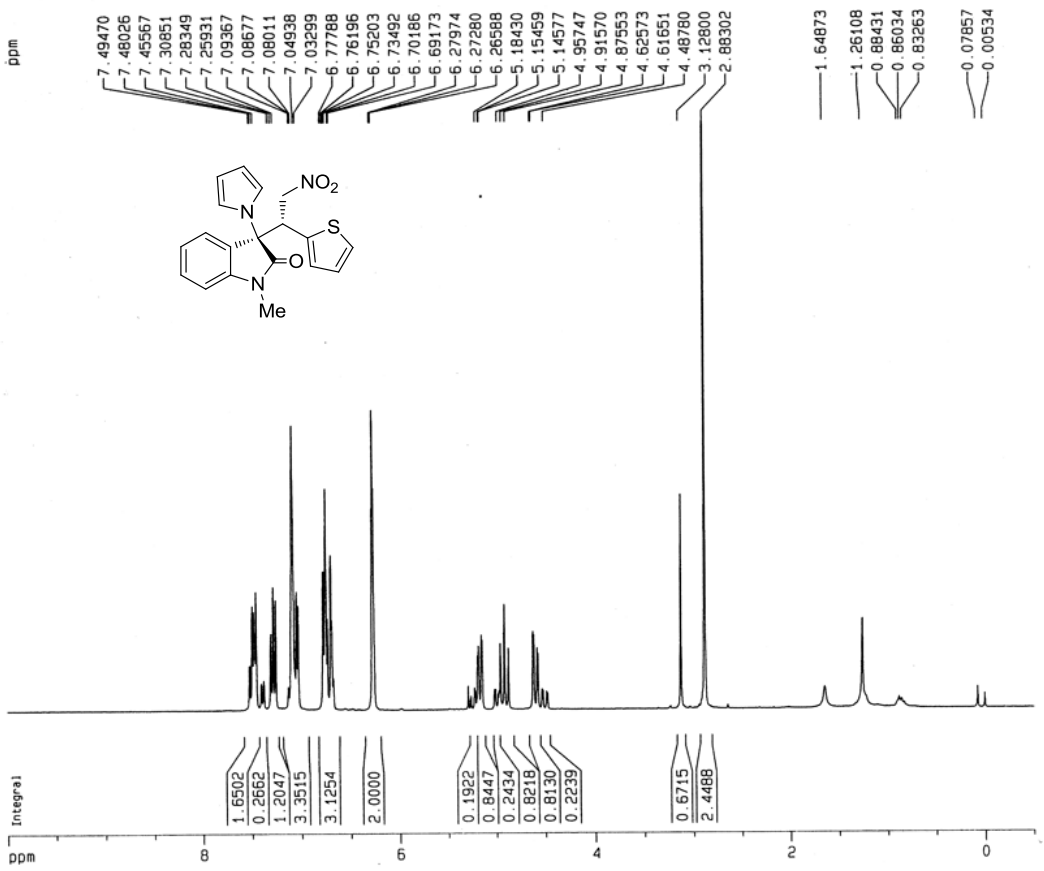


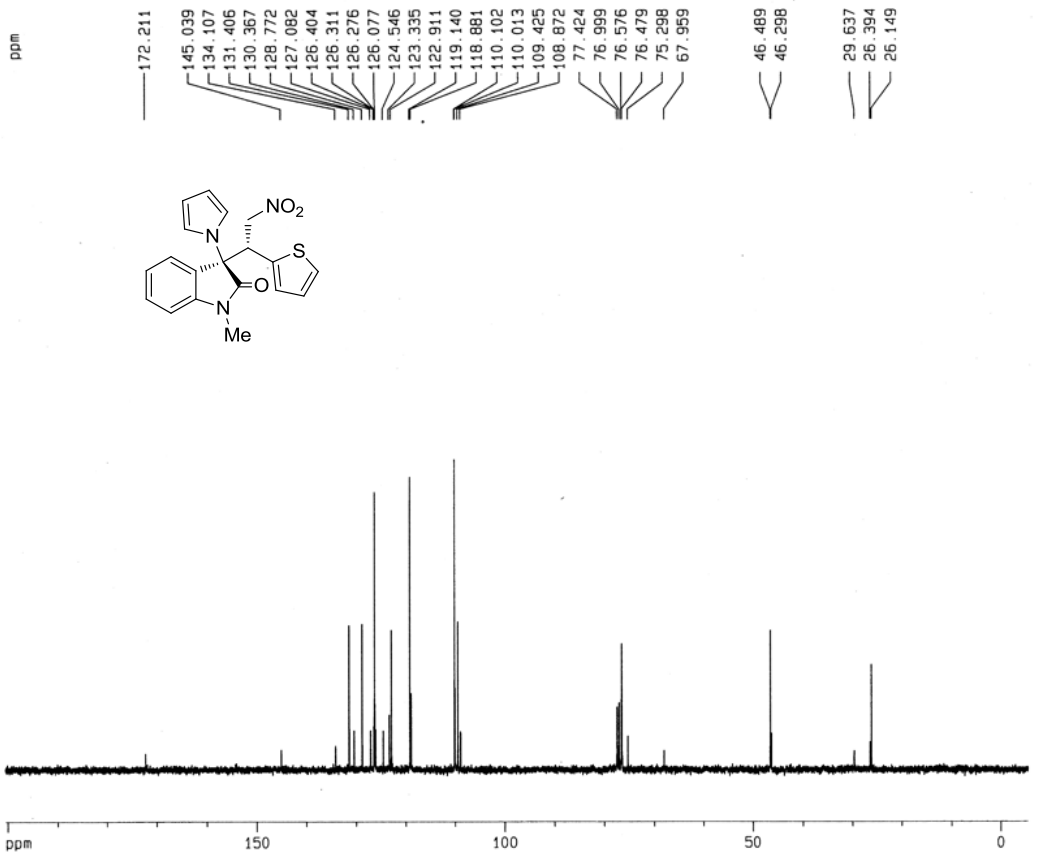

1 Det.A Ch1 / 220nm

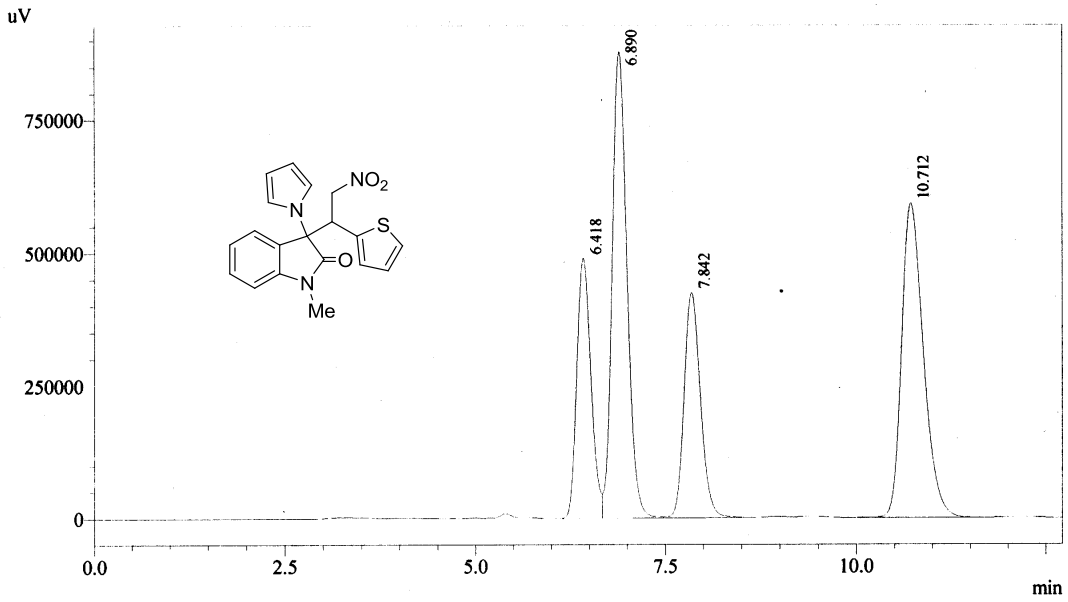
Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.552 | 2018085 | 98940 | 16.977 | 20.571 |
| 2 | 14.154 | 938532 | 40937 | 7.895 | 8.511 |
| 3 | 15.742 | 7509472 | 290462 | 63.172 | 60.390 |
| 4 | 16.764 | 1421340 | 50636 | 11.957 | 10.528 |
| Total | | 11887429 | 480976 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3p**



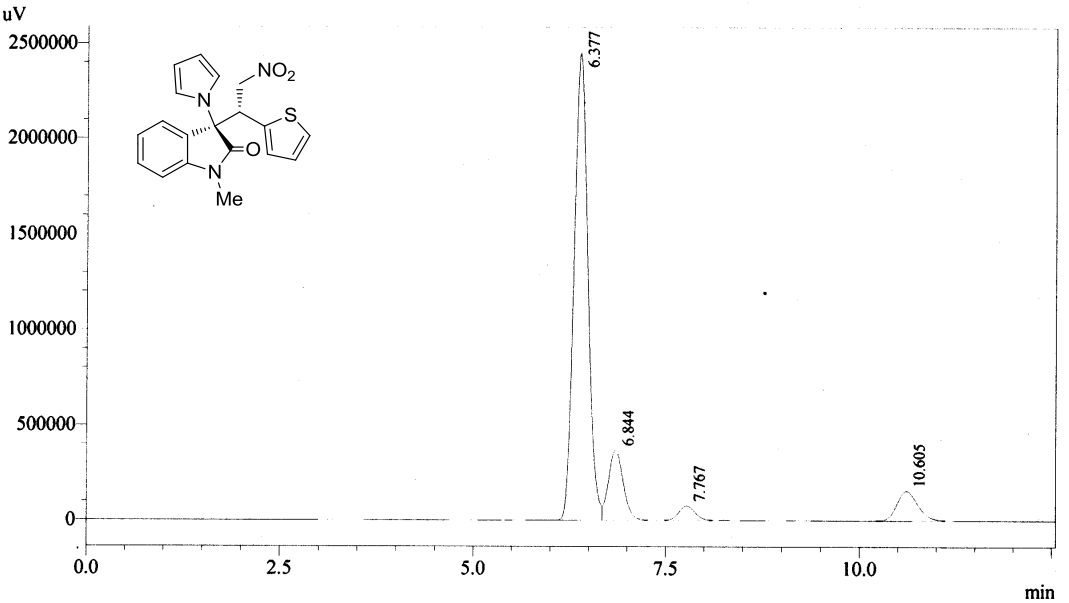






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.418 | 6367988 | 489587 | 17.520 | 20.549 |
| 2 | 6.890 | 11882020 | 877825 | 32.691 | 36.845 |
| 3 | 7.842 | 6329951 | 423364 | 17.416 | 17.770 |
| 4 | 10.712 | 11766513 | 591724 | 32.373 | 24.836 |
| Total | | 36346473 | 2382501 | 100.000 | 100.000 |



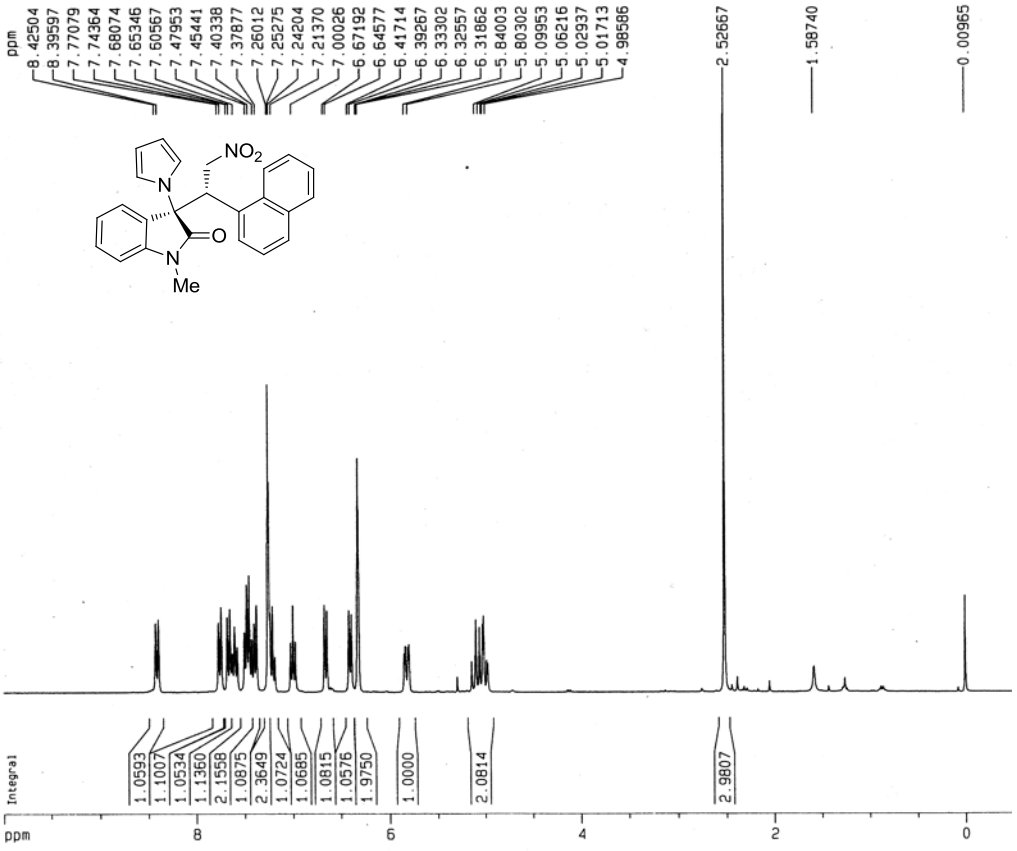

1 Det.A Ch1 / 254nm

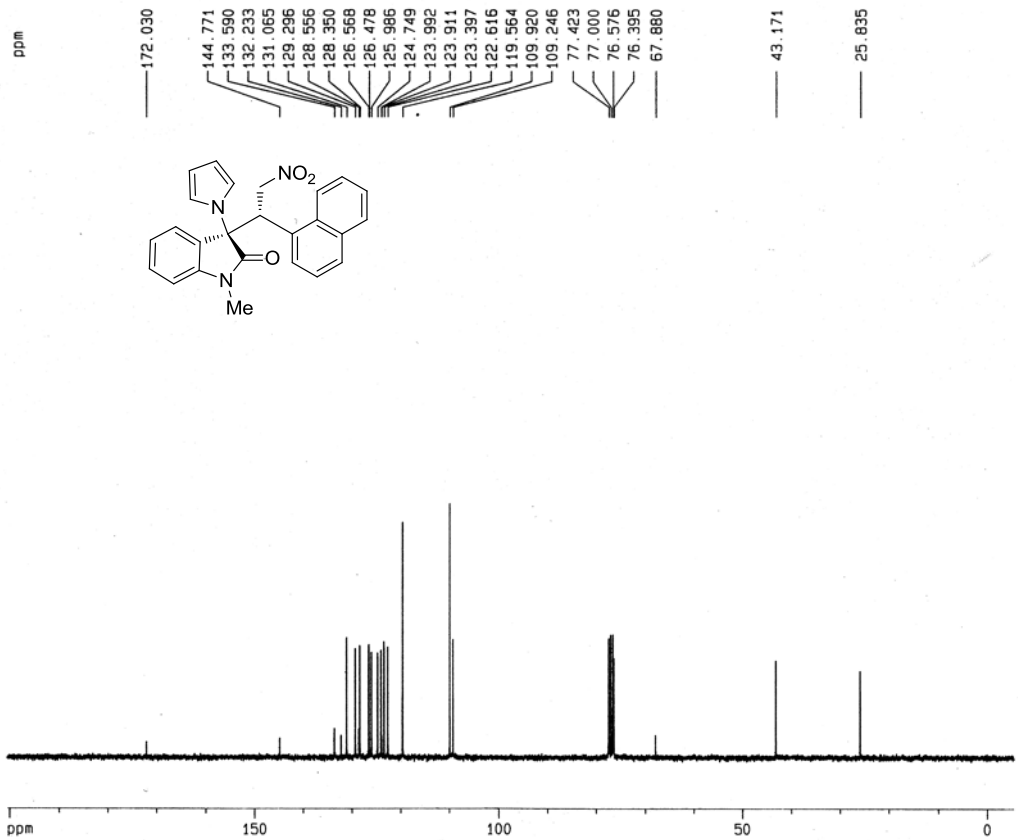
Detector A Ch1 254nm

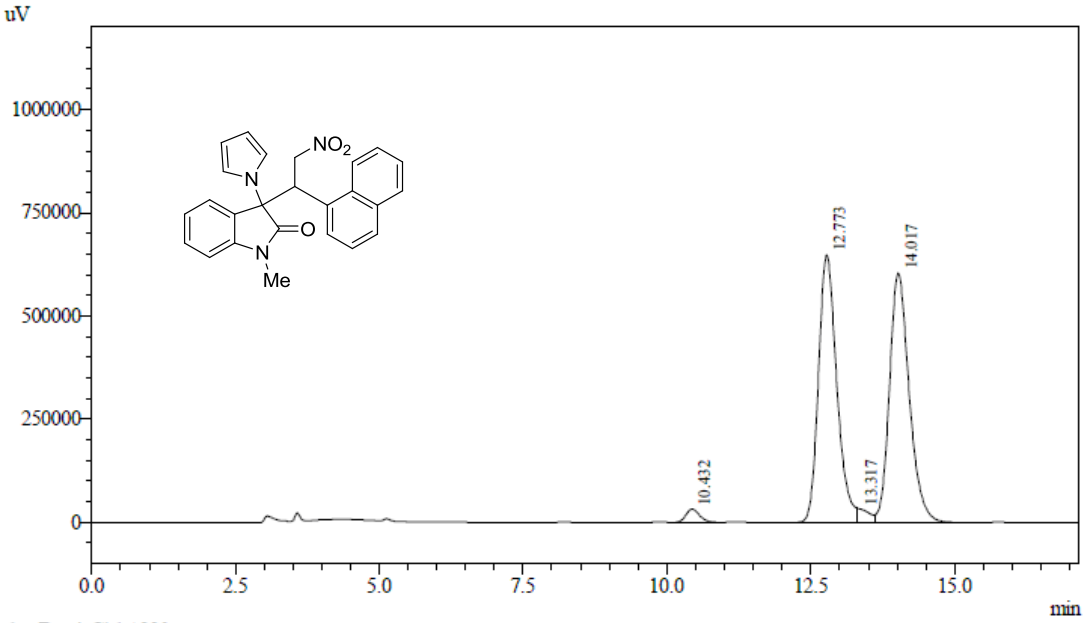
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.377 | 30602678 | 2449265 | 77.372 | 80.305 |
| 2 | 6.844 | 4920673 | 370384 | 12.441 | 12.144 |
| 3 | 7.767 | 1085134 | 75320 | 2.744 | 2.470 |
| 4 | 10.605 | 2944421 | 154966 | 7.444 | 5.081 |
| Total | | 39552906 | 3049935 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3q**



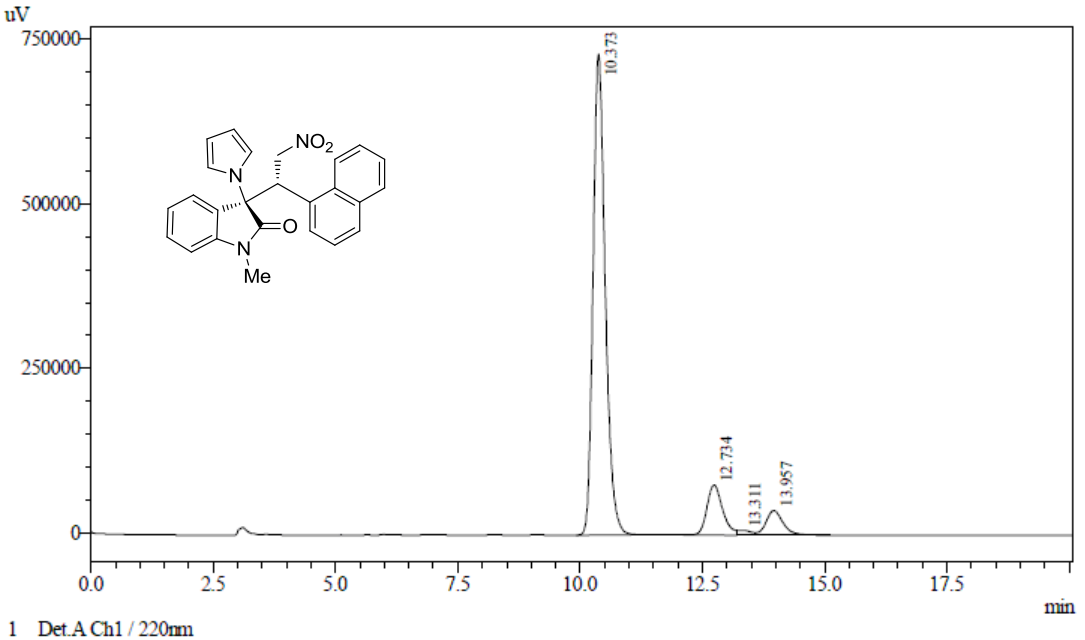






1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.432 | 531209 | 32092 | 1.784 | 2.439 |
| 2 | 12.773 | 14345300 | 647089 | 48.190 | 49.172 |
| 3 | 13.317 | 465841 | 33801 | 1.565 | 2.568 |
| 4 | 14.017 | 14425647 | 602999 | 48.460 | 45.821 |
| Total | | 29767996 | 1315981 | 100.000 | 100.000 |

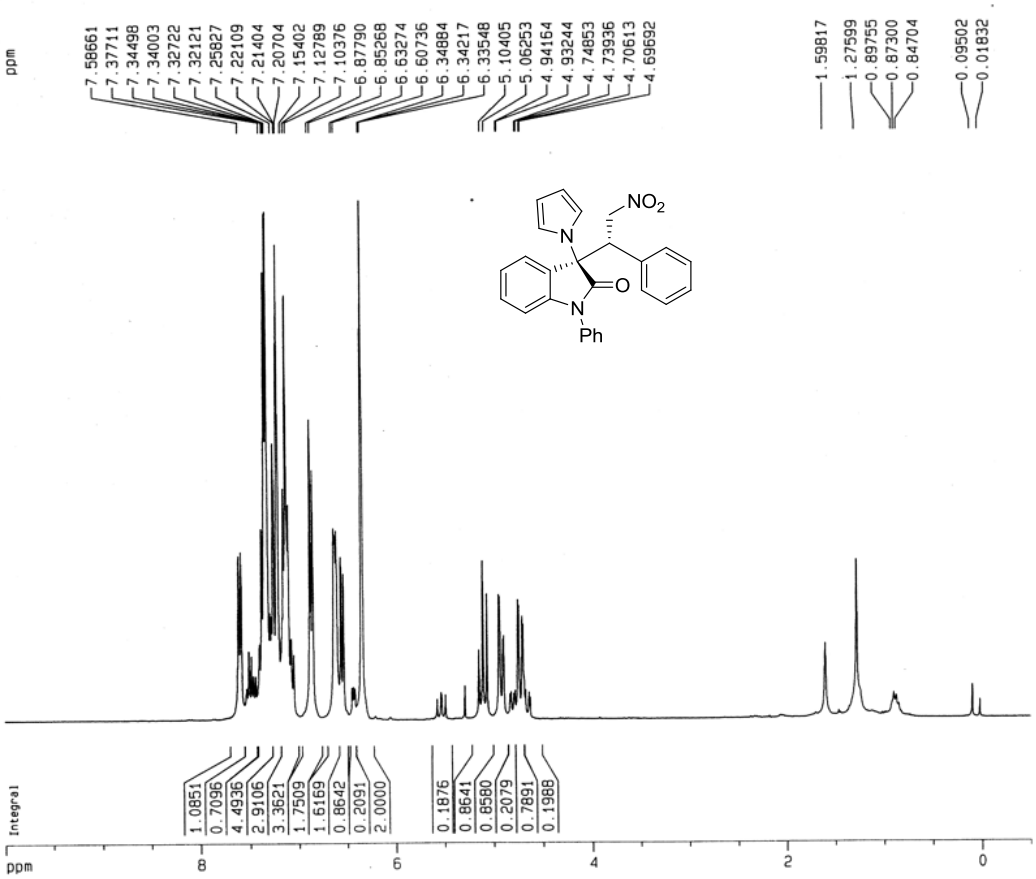


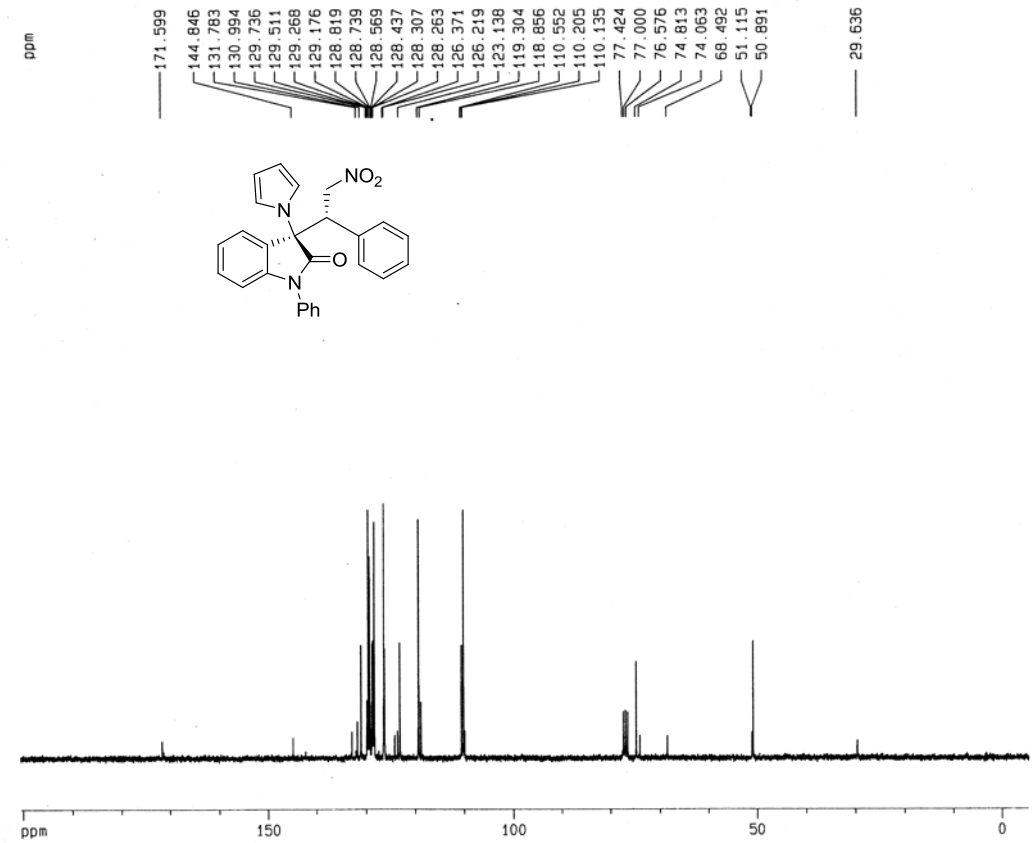

1 Det.A Ch1 / 220nm

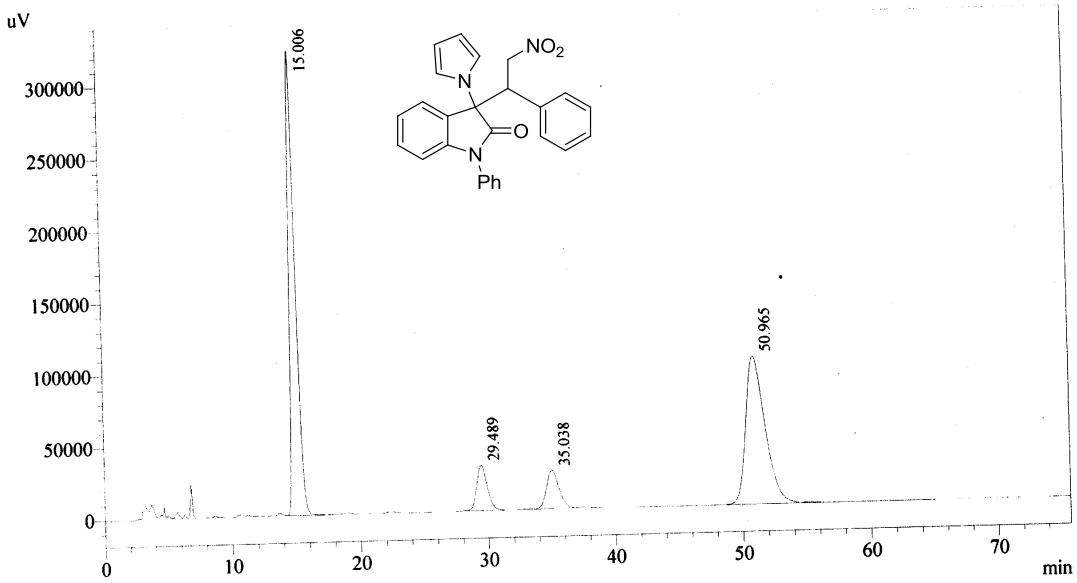
Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.373 | 12621876 | 730285 | 82.229 | 85.810 |
| 2 | 12.734 | 1694140 | 76083 | 11.037 | 8.940 |
| 3 | 13.311 | 132601 | 7481 | 0.864 | 0.879 |
| 4 | 13.957 | 901059 | 37196 | 5.870 | 4.371 |
| Total | | 15349676 | 851045 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3r**



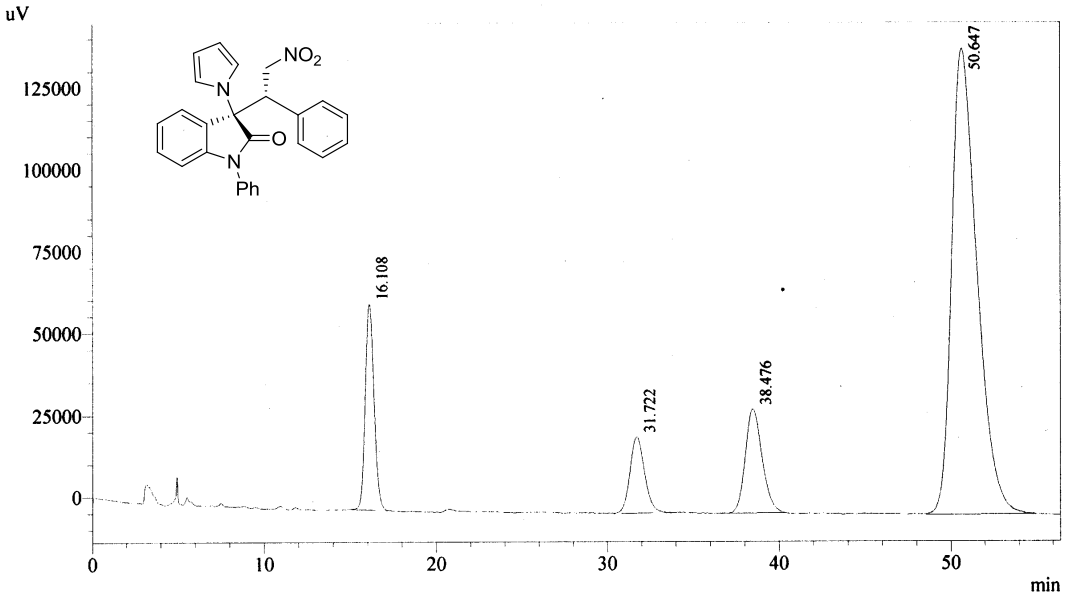






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 15.006 | 10727541 | 322317 | 42.663 | 66.743 |
| 2 | 29.489 | 1806453 | 31426 | 7.184 | 6.508 |
| 3 | 35.038 | 1779445 | 26403 | 7.077 | 5.467 |
| 4 | 50.965 | 10831389 | 102776 | 43.076 | 21.282 |
| Total | | 25144829 | 482921 | 100.000 | 100.000 |



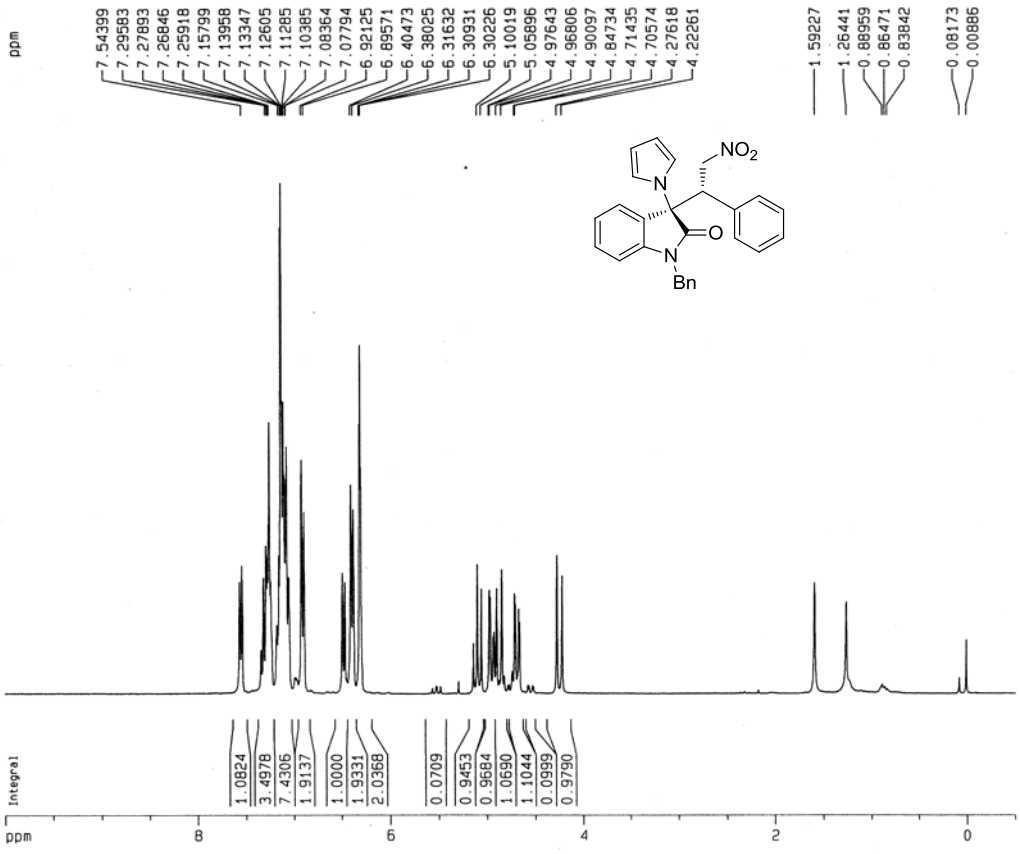

1 Det.A Ch1 / 254nm

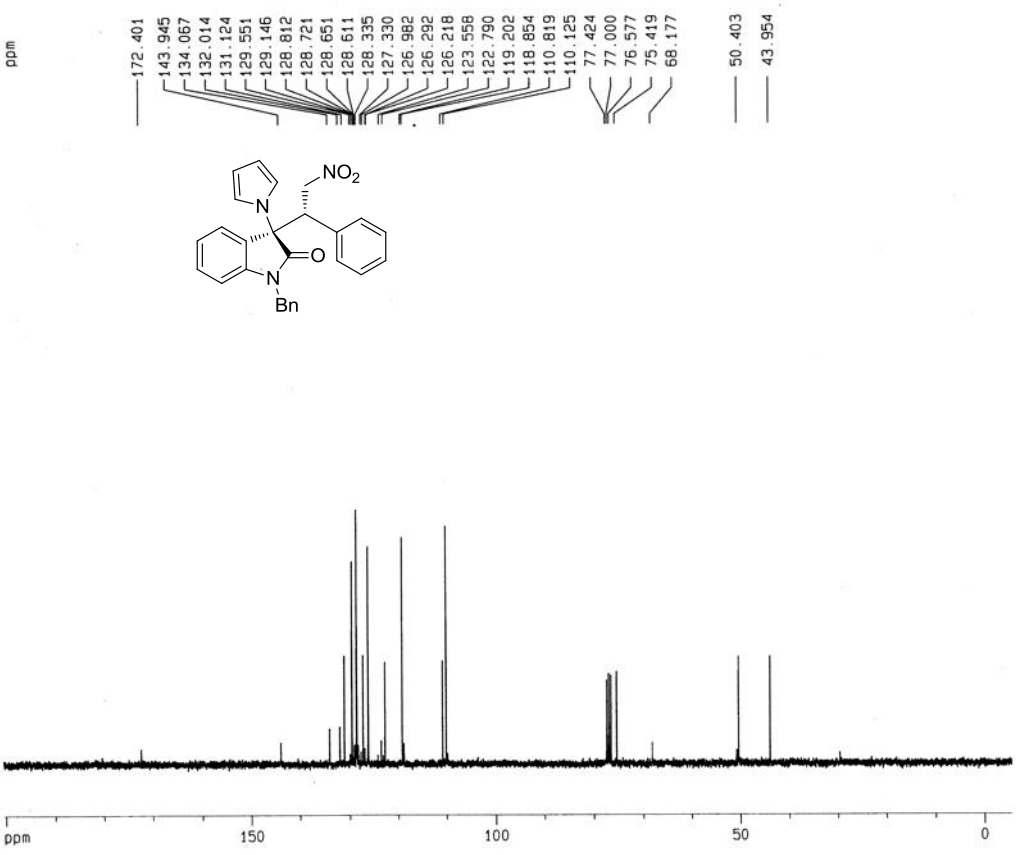
Detector A Ch1 254nm

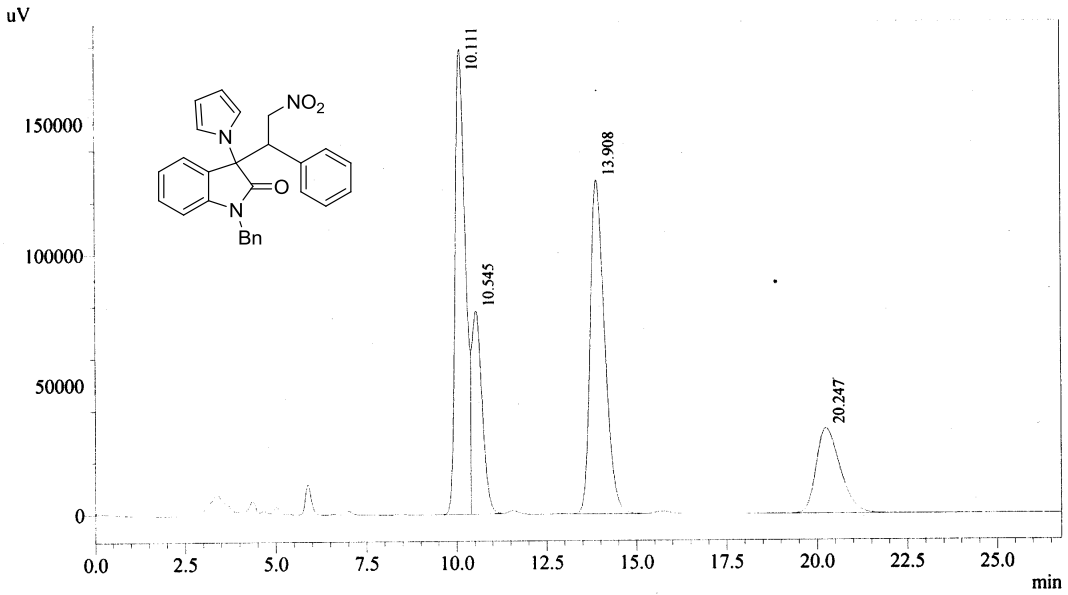
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 16.108 | 2236509 | 62787 | 10.927 | 24.126 |
| 2 | 31.722 | 1384731 | 23350 | 6.766 | 8.972 |
| 3 | 38.476 | 2165991 | 31834 | 10.583 | 12.232 |
| 4 | 50.647 | 14679676 | 142273 | 71.724 | 54.669 |
| Total | | 20466907 | 260243 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3s**



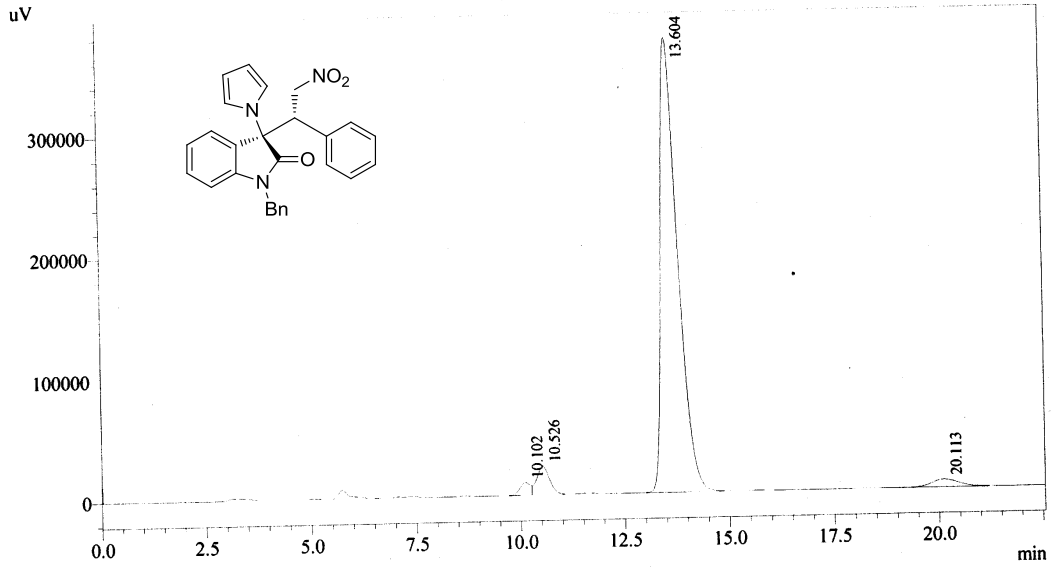






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.111 | 3557505 | 178801 | 34.828 | 42.810 |
| 2 | 10.545 | 1550107 | 77983 | 15.176 | 18.671 |
| 3 | 13.908 | 3589722 | 128090 | 35.144 | 30.668 |
| 4 | 20.247 | 1517112 | 32787 | 14.853 | 7.850 |
| Total | | 10214446 | 417660 | 100.000 | 100.000 |

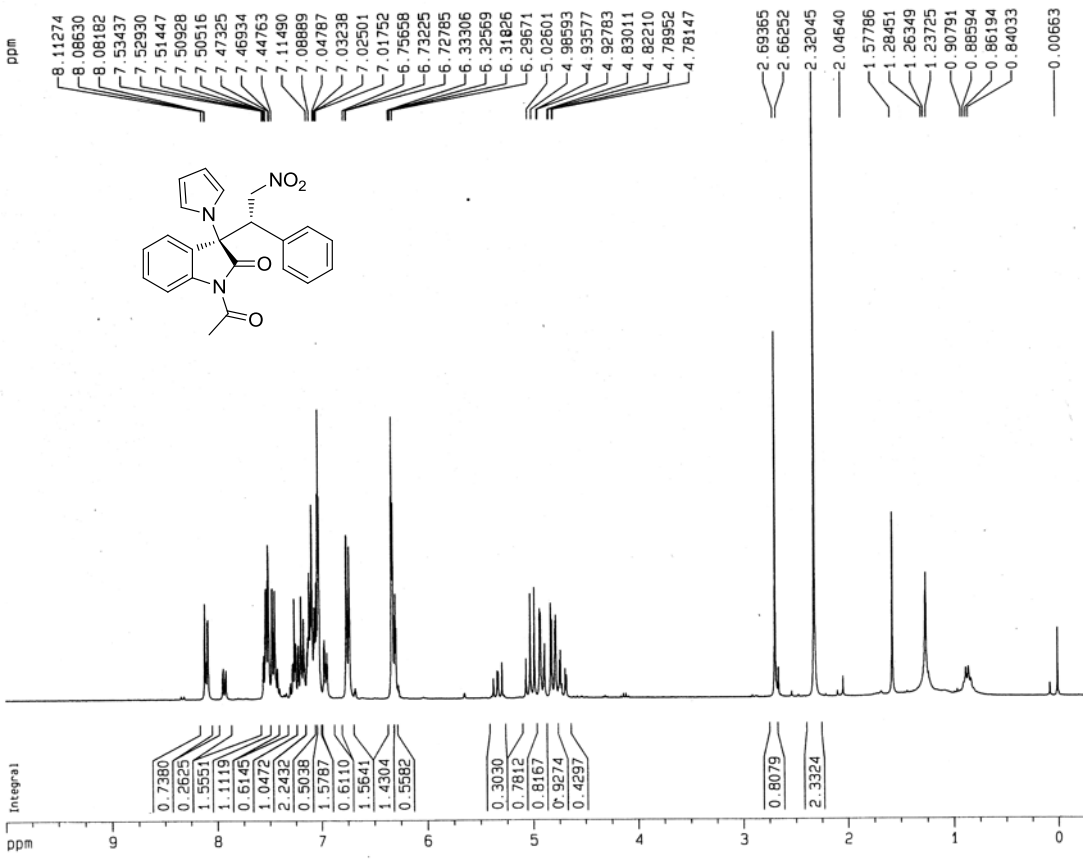


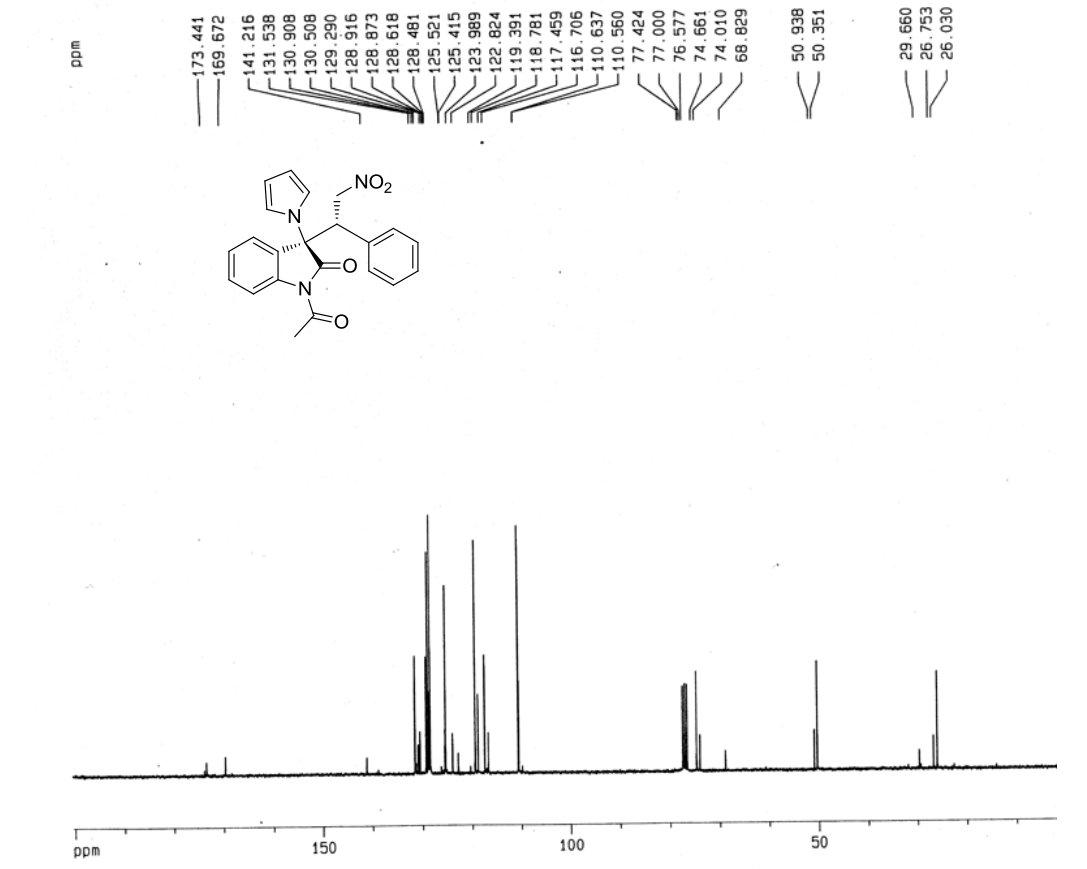

1 Det.A Ch1 / 254nm

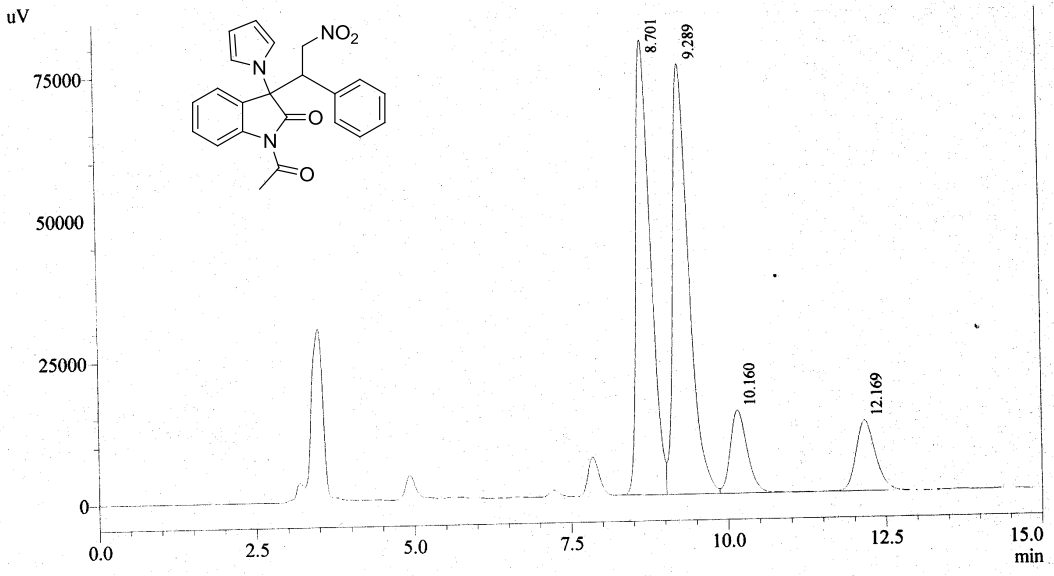
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.102 | 181292 | 10377 | 1.561 | 2.501 |
| 2 | 10.526 | 501570 | 23516 | 4.317 | 5.667 |
| 3 | 13.604 | 10640183 | 374740 | 91.588 | 90.304 |
| 4 | 20.113 | 294348 | 6341 | 2.534 | 1.528 |
| Total | | 11617393 | 414973 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3t**



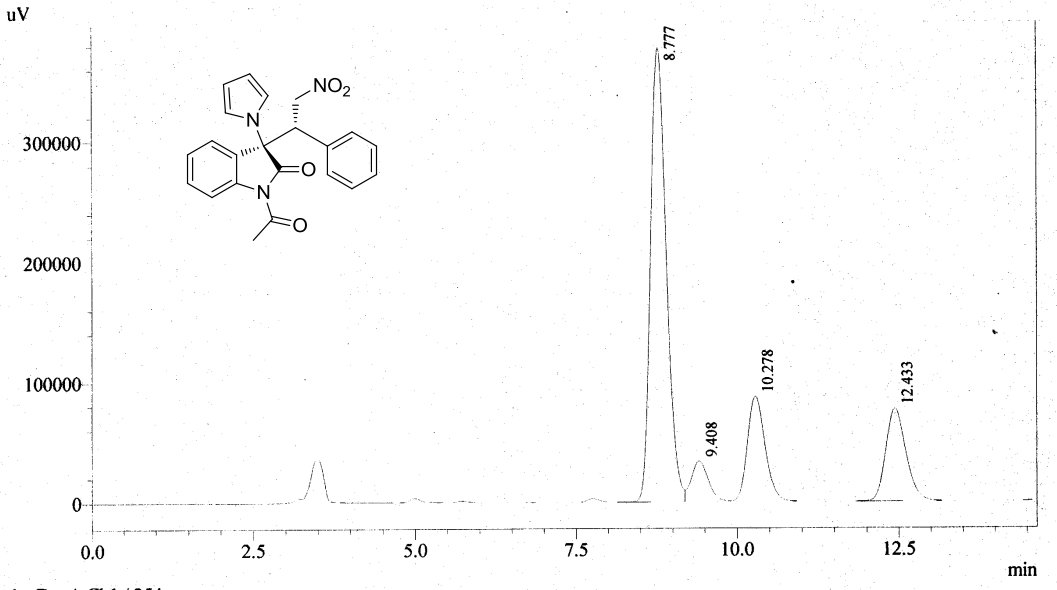






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.701 | 1283115 | 80000 | 40.594 | 43.773 |
| 2 | 9.289 | 1344969 | 75749 | 42.550 | 41.447 |
| 3 | 10.160 | 268602 | 14609 | 8.498 | 7.994 |
| 4 | 12.169 | 264197 | 12405 | 8.358 | 6.787 |
| Total | | 3160884 | 182763 | 100.000 | 100.000 |



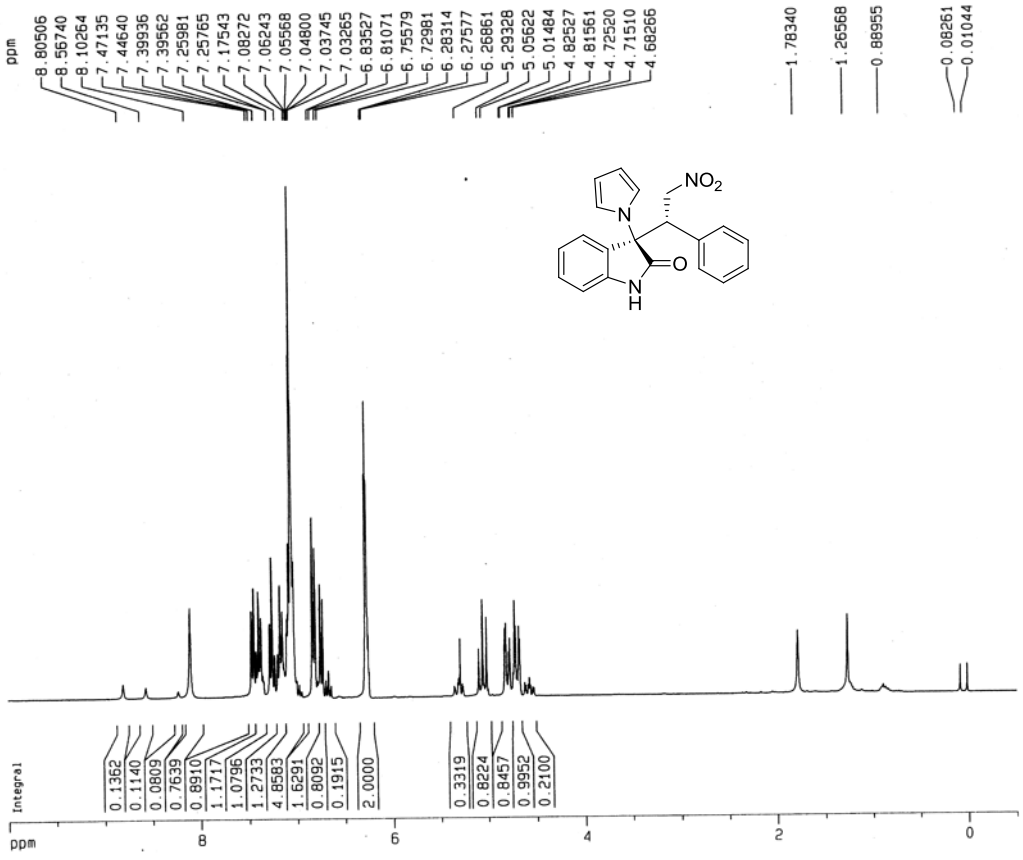

1 Det.A Ch1 / 254nm

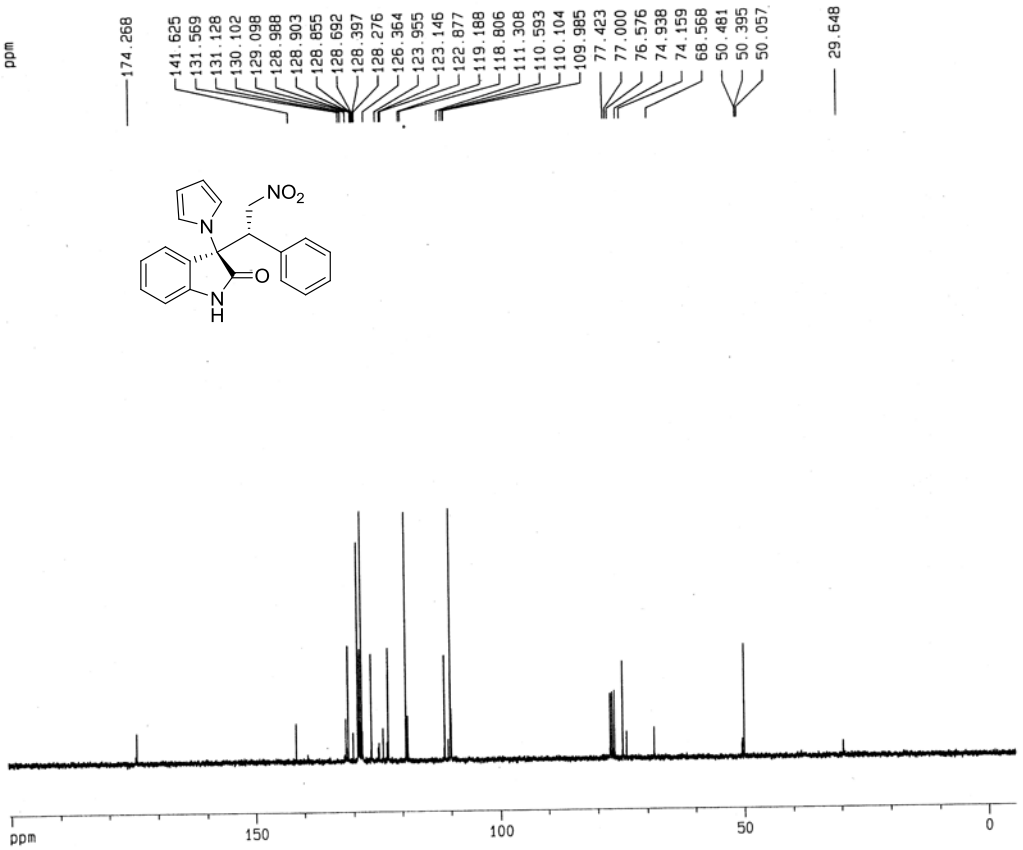
Detector A Ch1 254nm

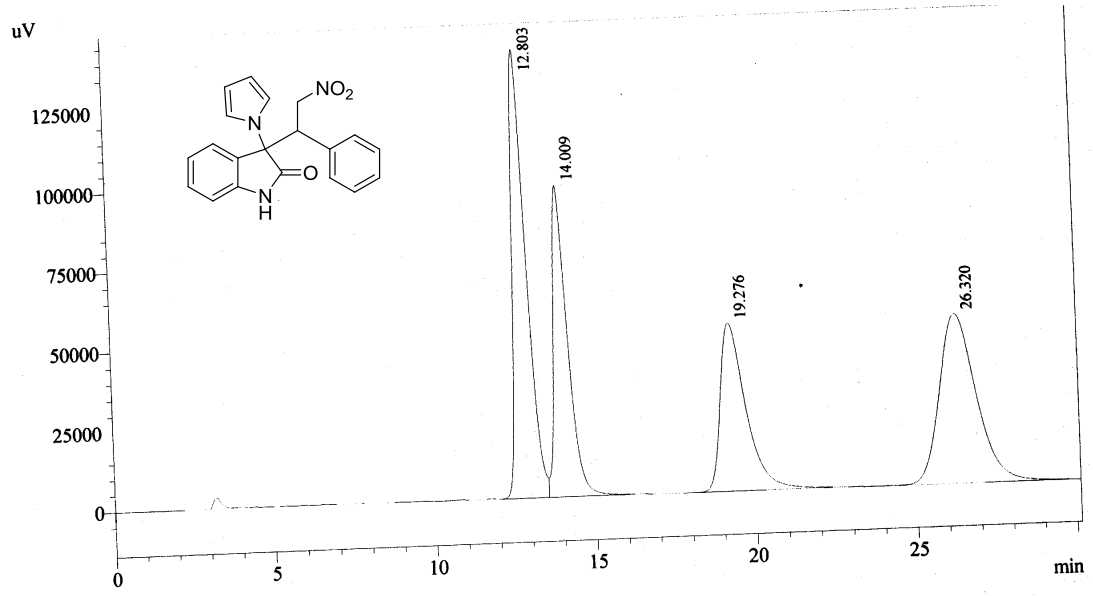
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.777 | 6431963 | 377894 | 61.900 | 65.578 |
| 2 | 9.408 | 616771 | 33715 | 5.936 | 5.851 |
| 3 | 10.278 | 1664156 | 87486 | 16.015 | 15.182 |
| 4 | 12.433 | 1678072 | 77159 | 16.149 | 13.390 |
| Total | | 10390963 | 576254 | 100.000 | 100.000 |

1

**H NMR, $^{13}$C NMR and HPLC of 3u**



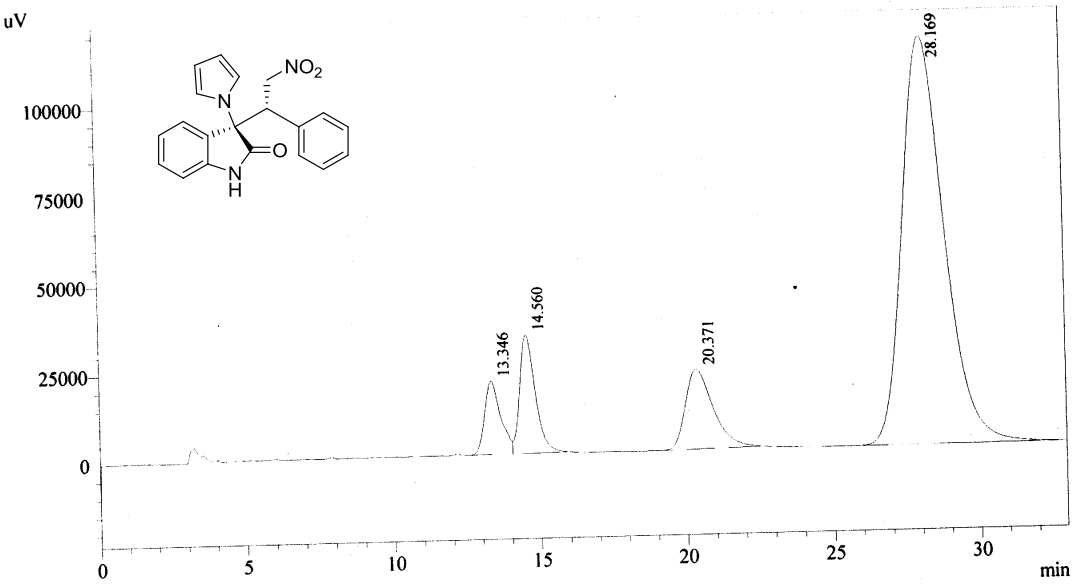






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.803 | 4228510 | 140940 | 29.239 | 40.897 |
| 2 | 14.009 | 3041711 | 97819 | 21.033 | 28.384 |
| 3 | 19.276 | 2923780 | 52711 | 20.217 | 15.295 |
| 4 | 26.320 | 4267930 | 53155 | 29.511 | 15.424 |
| Total | | 14461931 | 344625 | 100.000 | 100.000 |

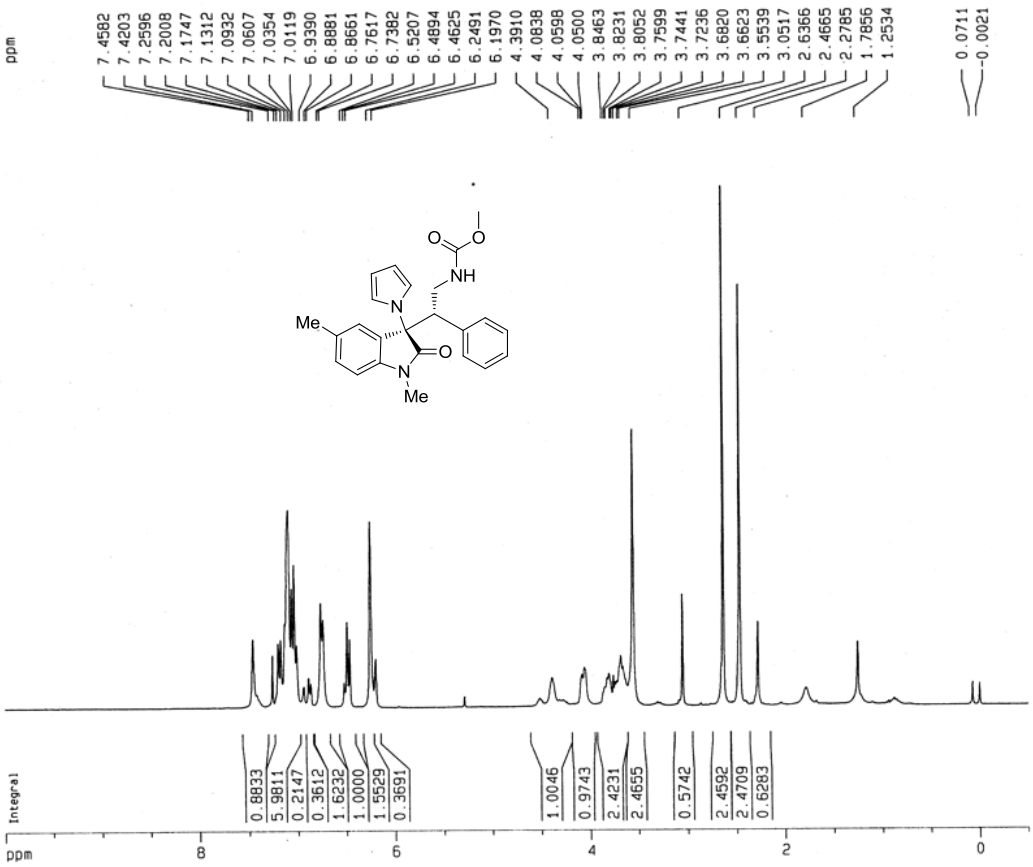


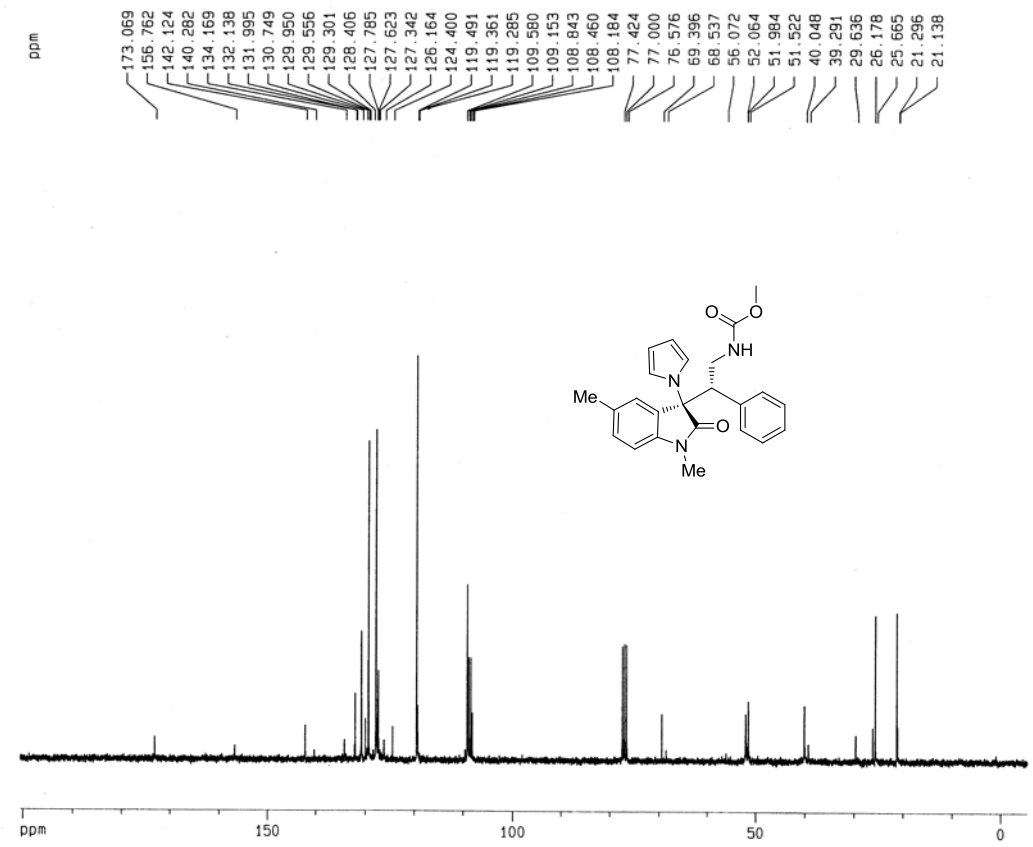

1 Det.A Ch1 / 254nm

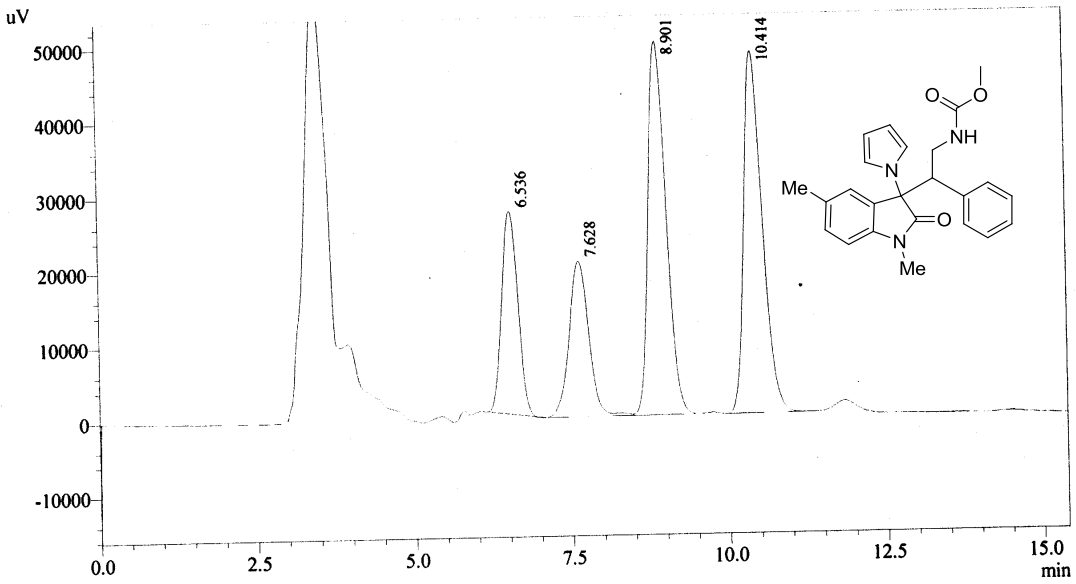
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.346 | 797376 | 20660 | 5.342 | 10.810 |
| 2 | 14.560 | 1233092 | 33160 | 8.261 | 17.349 |
| 3 | 20.371 | 1487082 | 22493 | 9.962 | 11.768 |
| 4 | 28.169 | 11409519 | 114817 | 76.435 | 60.073 |
| Total | | 14927068 | 191129 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3v**



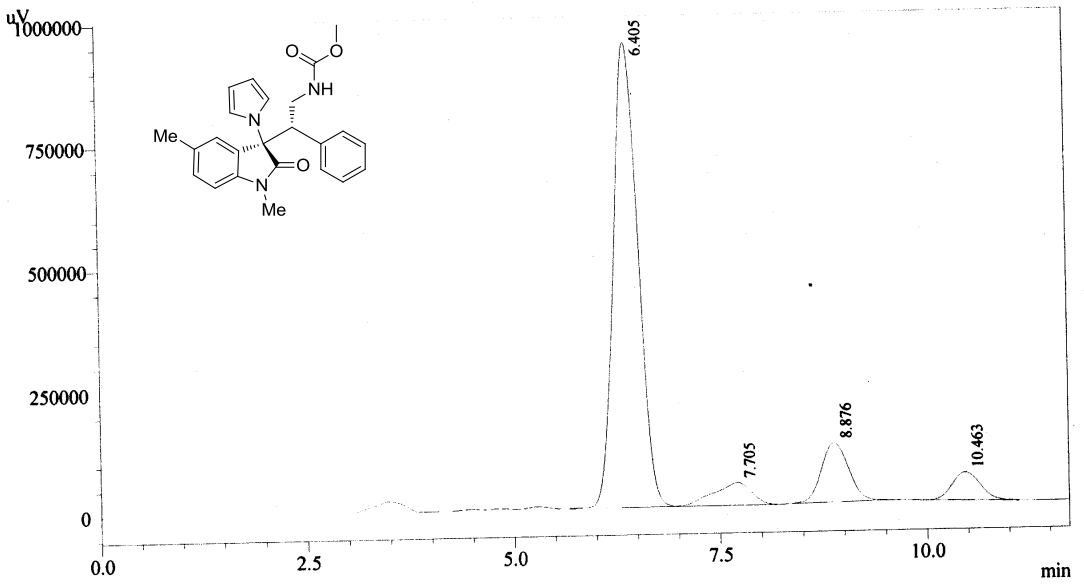






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.536 | 482899 | 27167 | 16.607 | 18.548 |
| 2 | 7.628 | 452755 | 20831 | 15.571 | 14.223 |
| 3 | 8.901 | 989212 | 49979 | 34.020 | 34.124 |
| 4 | 10.414 | 982905 | 48488 | 33.803 | 33.106 |
| Total | | 2907771 | 146466 | 100.000 | 100.000 |

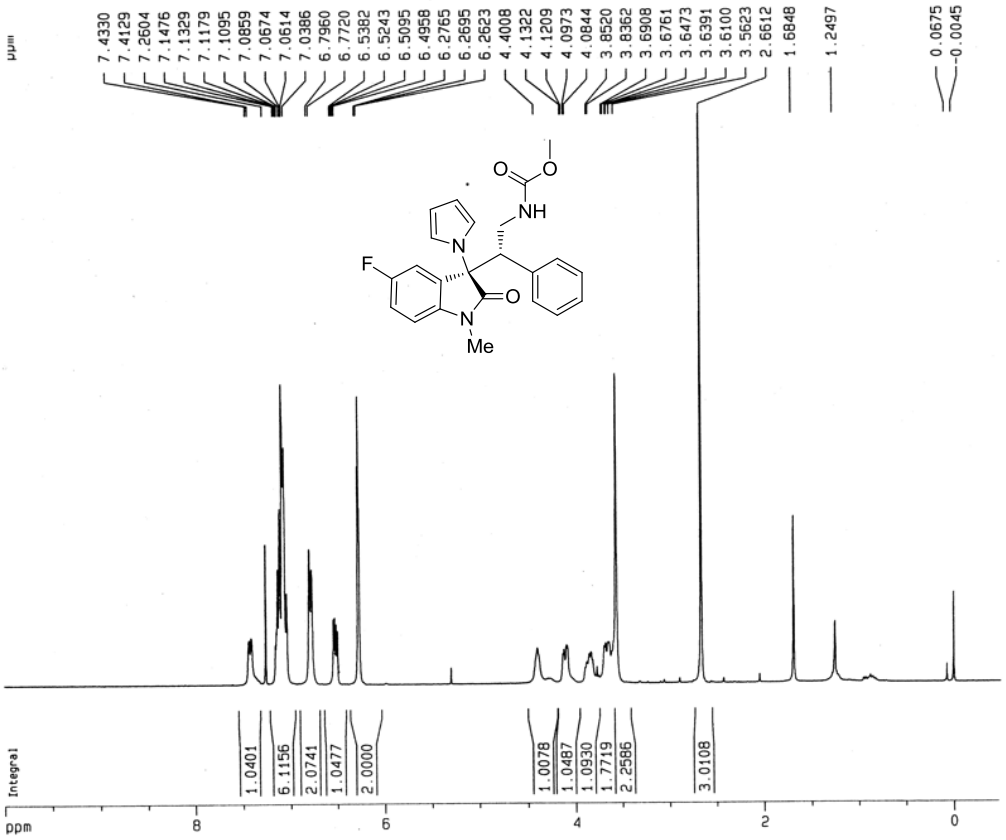


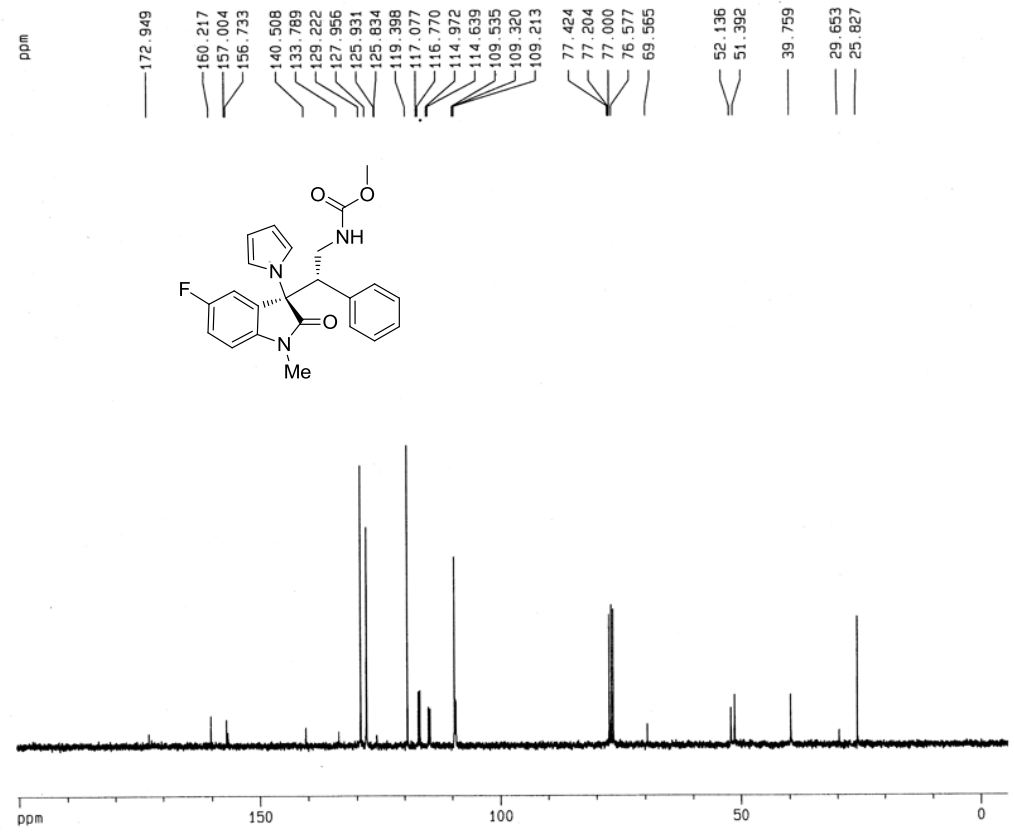

1 Det.A Ch1 / 254nm

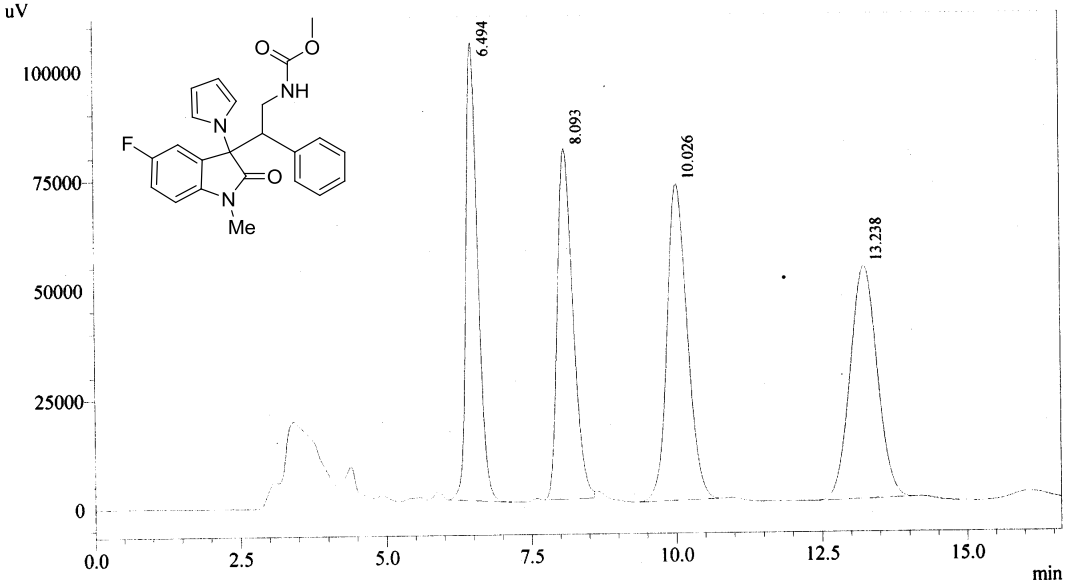
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.405 | 19597590 | 947547 | 77.822 | 80.856 |
| 2 | 7.705 | 1464208 | 46314 | 5.814 | 3.952 |
| 3 | 8.876 | 2767552 | 120920 | 10.990 | 10.318 |
| 4 | 10.463 | 1353374 | 57110 | 5.374 | 4.873 |
| Total | | 25182725 | 1171890 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3w**



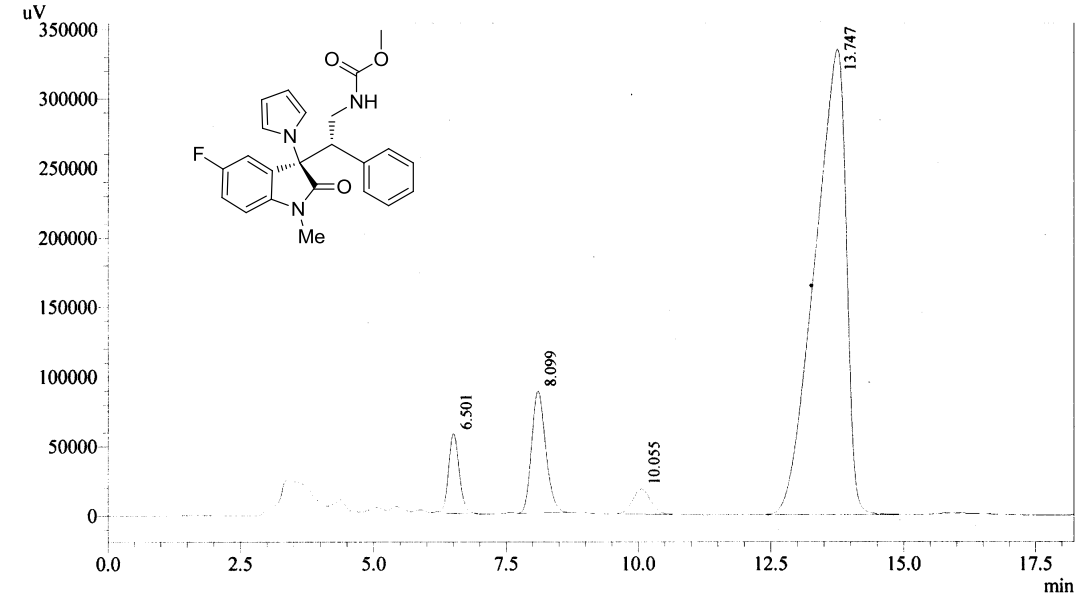






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.494 | 1478068 | 104690 | 22.852 | 33.743 |
| 2 | 8.093 | 1506408 | 80005 | 23.290 | 25.787 |
| 3 | 10.026 | 1754042 | 72366 | 27.119 | 23.325 |
| 4 | 13.238 | 1729402 | 53196 | 26.738 | 17.146 |
| Total | | 6467920 | 310257 | 100.000 | 100.000 |

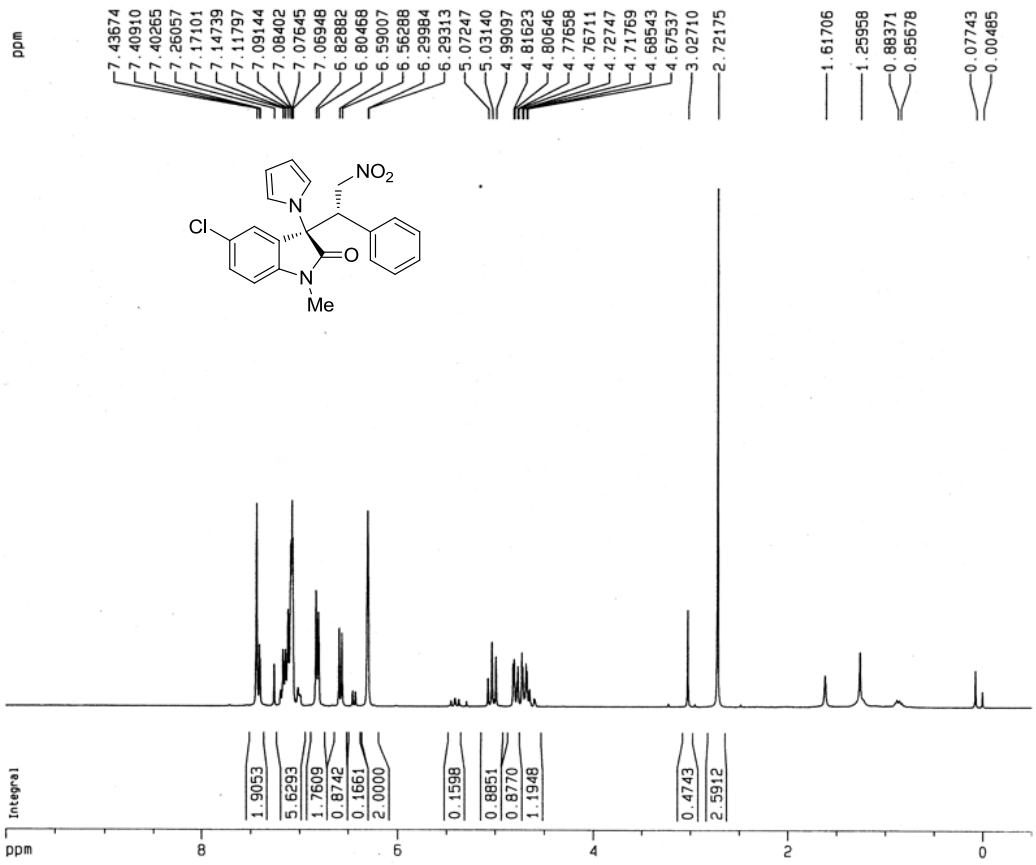


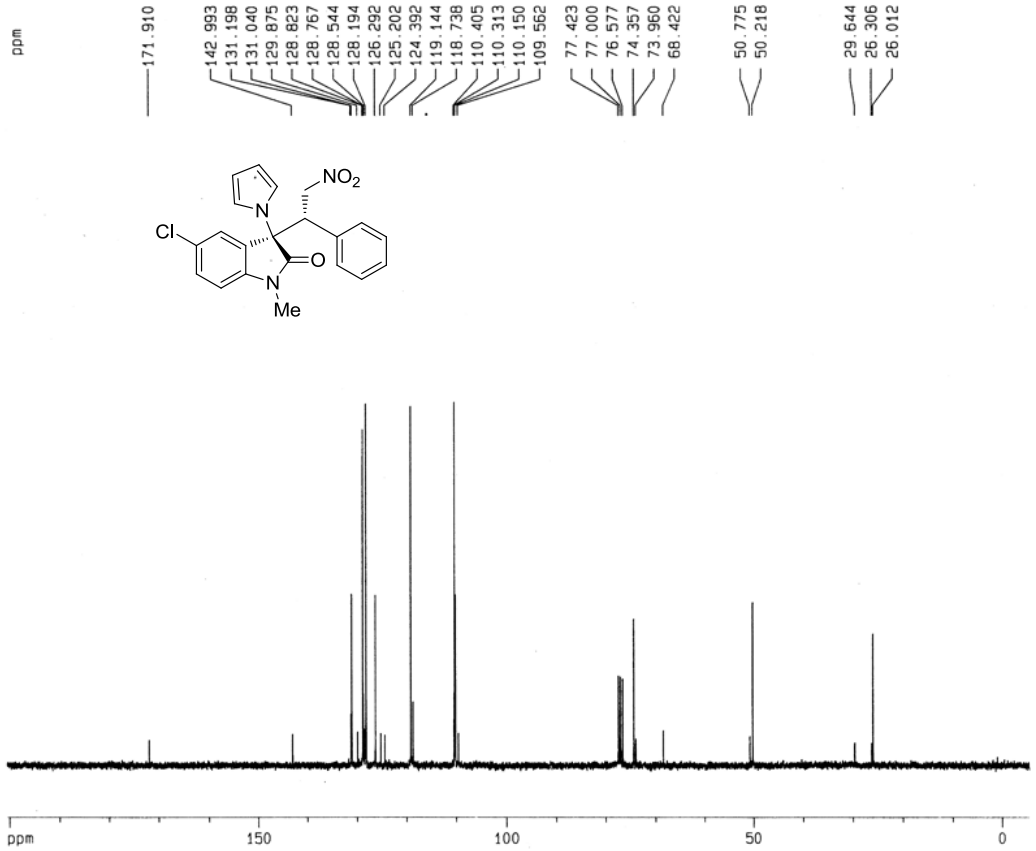

1 Det.A Ch1 / 254nm

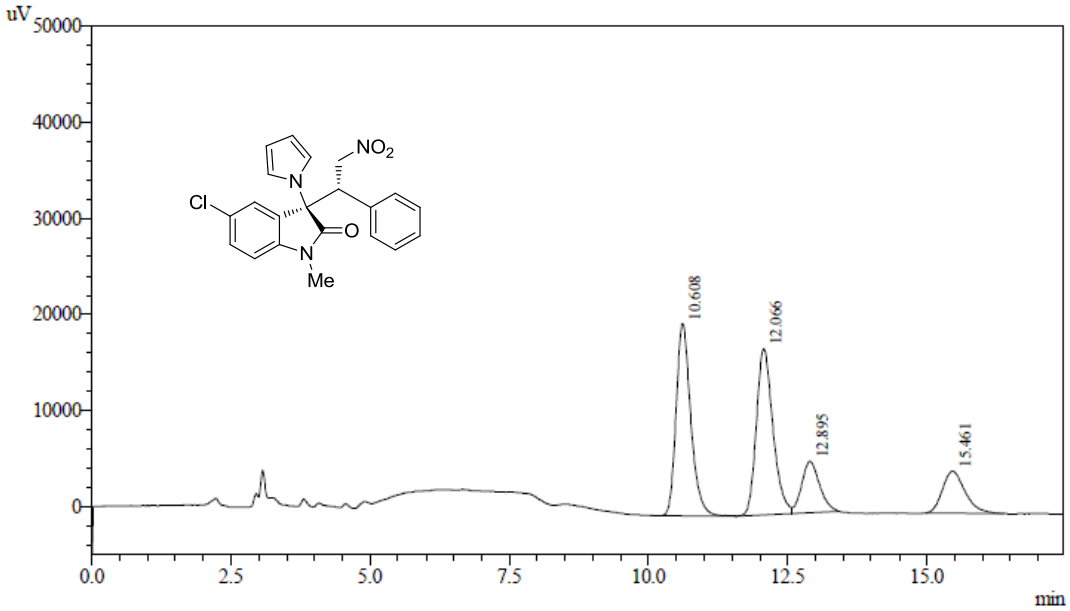
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.501 | 812058 | 57562 | 4.881 | 11.551 |
| 2 | 8.099 | 1639157 | 87836 | 9.852 | 17.626 |
| 3 | 10.055 | 424201 | 17894 | 2.550 | 3.591 |
| 4 | 13.747 | 13761896 | 335050 | 82.717 | 67.233 |
| Total | | 16637313 | 498342 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3x**



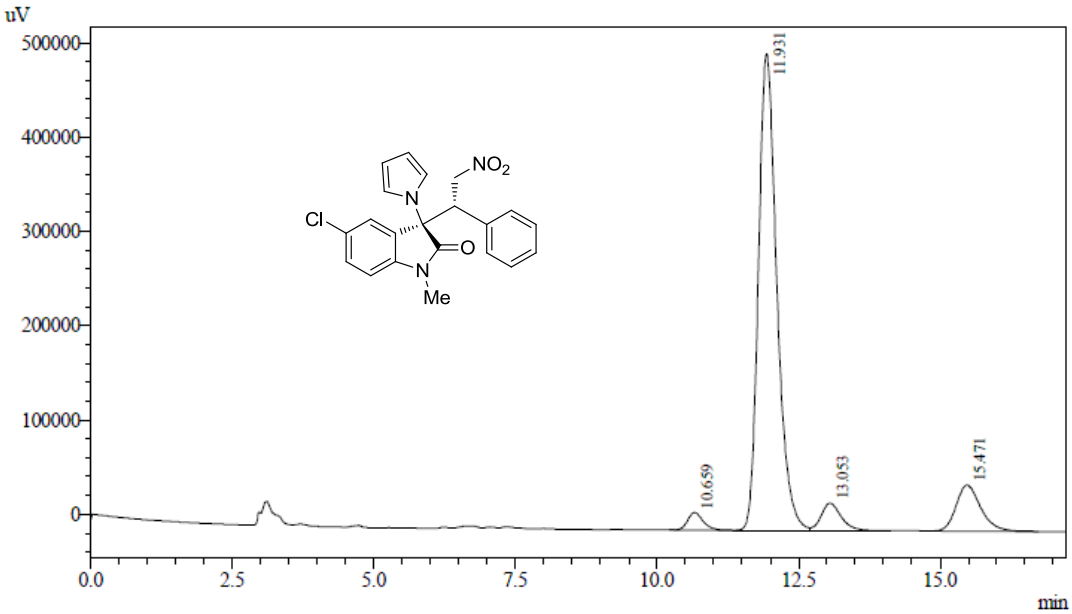






1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.608 | 367447 | 20025 | 37.874 | 42.563 |
| 2 | 12.066 | 358880 | 17299 | 36.991 | 36.769 |
| 3 | 12.895 | 119233 | 5321 | 12.290 | 11.309 |
| 4 | 15.461 | 124629 | 4403 | 12.846 | 9.359 |
| Total | | 970189 | 47047 | 100.000 | 100.000 |

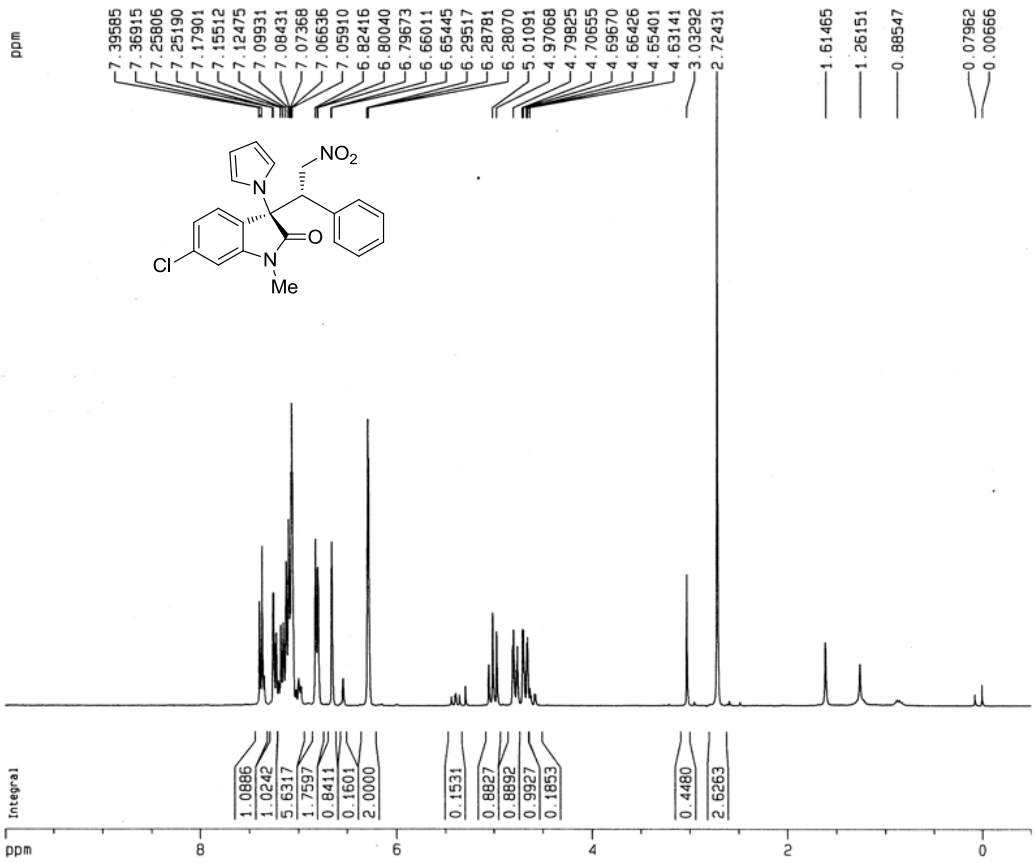


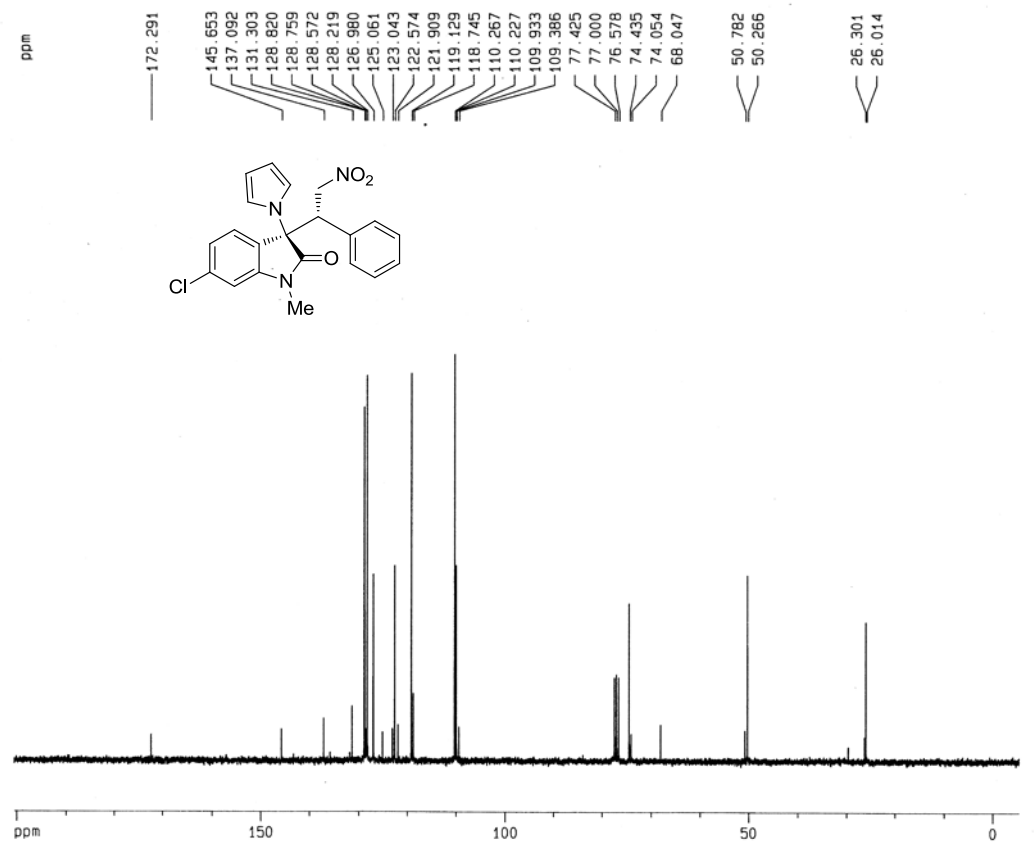

1 Det.A Ch1 / 220nm

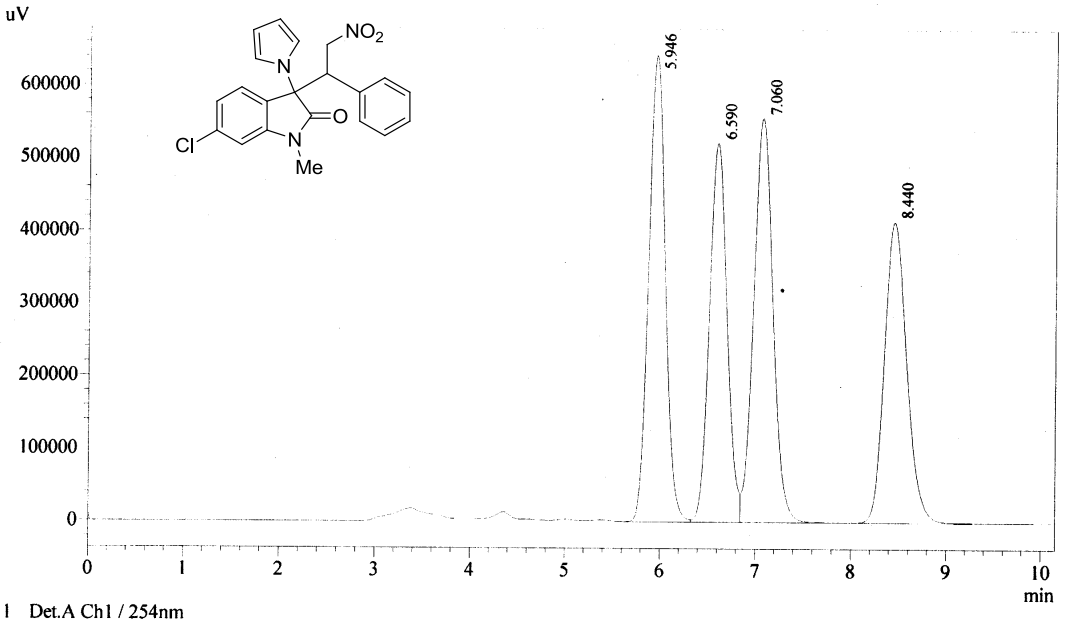
Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.659 | 355832 | 18625 | 2.549 | 3.093 |
| 2 | 11.931 | 11411099 | 505513 | 81.737 | 83.954 |
| 3 | 13.053 | 717651 | 29140 | 5.140 | 4.839 |
| 4 | 15.471 | 1476160 | 48854 | 10.574 | 8.114 |
| Total | | 13960742 | 602133 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3y**



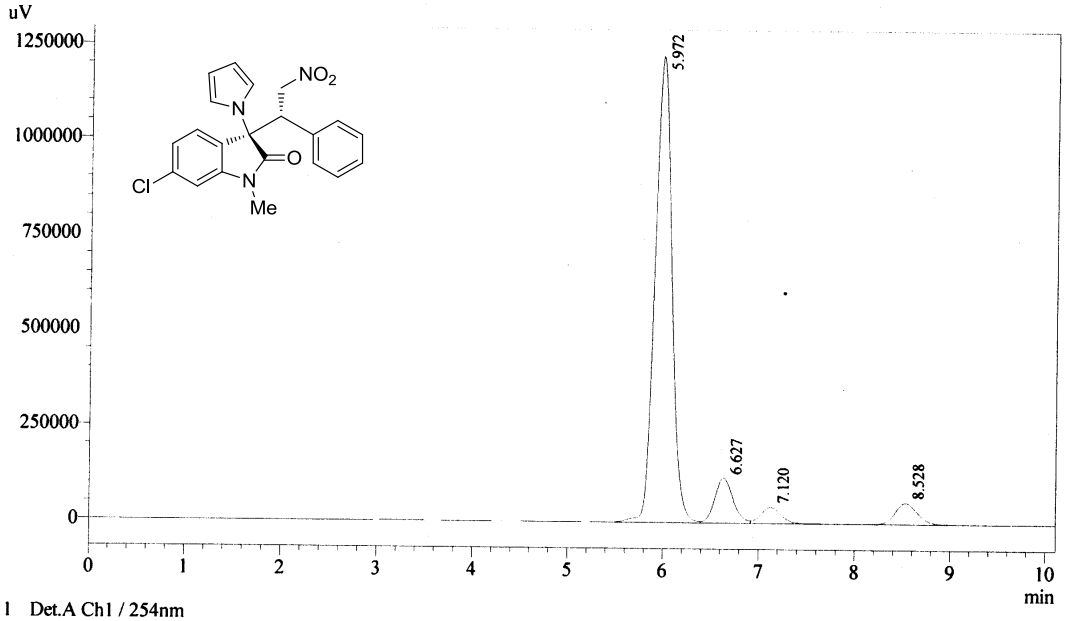






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.946 | 7805235 | 642211 | 26.894 | 30.106 |
| 2 | 6.590 | 6690047 | 520900 | 23.051 | 24.419 |
| 3 | 7.060 | 7788690 | 555686 | 26.837 | 26.050 |
| 4 | 8.440 | 6738692 | 414351 | 23.219 | 19.424 |
| Total | | 29022664 | 2133148 | 100.000 | 100.000 |



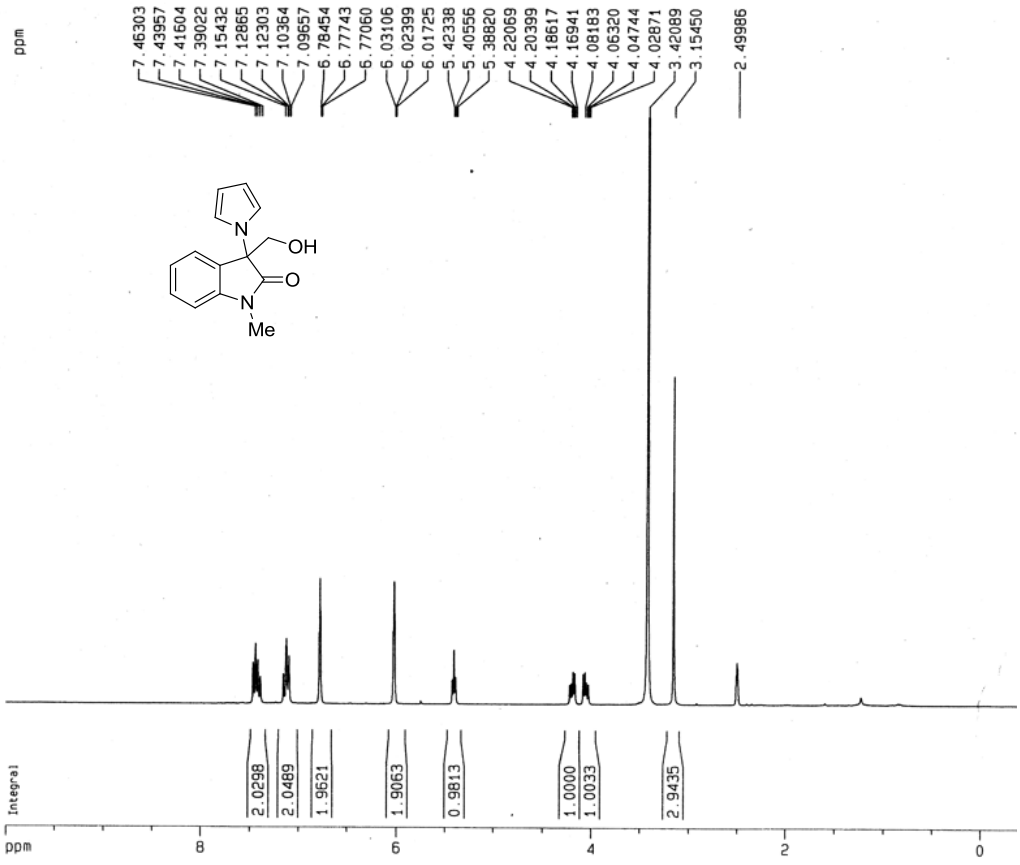

1 Det.A Ch1 / 254nm

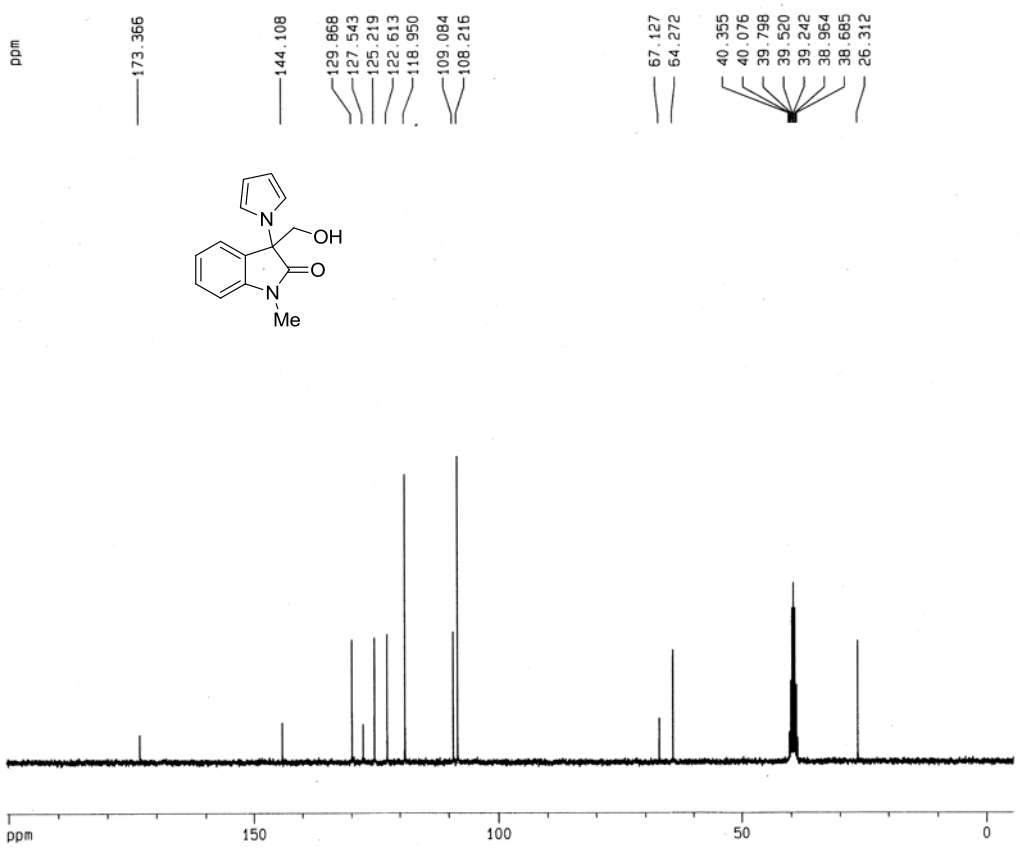
Detector A Ch1 254nm

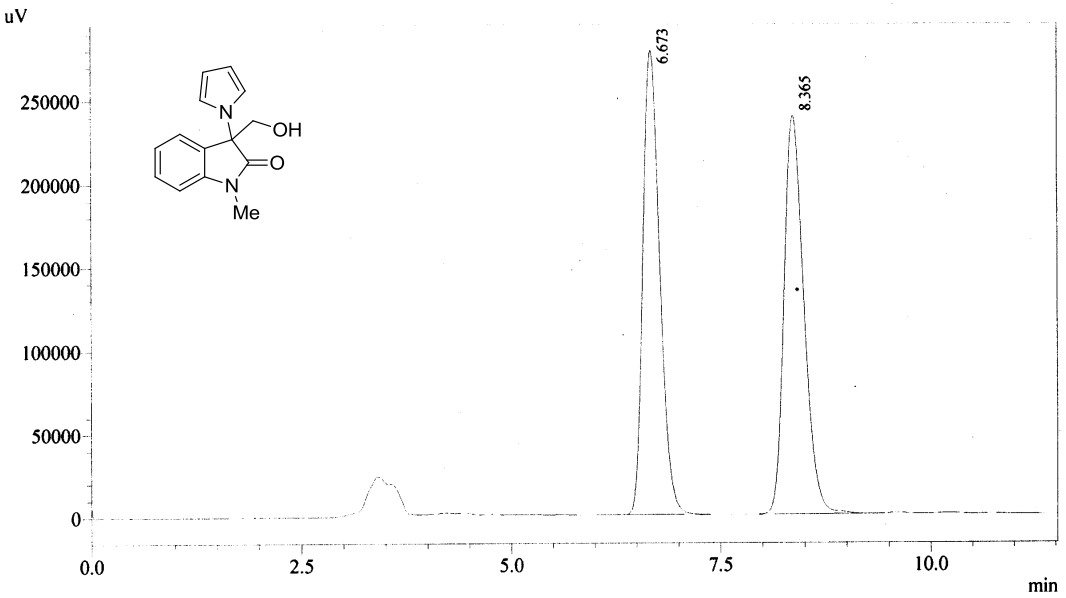
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.972 | 15037242 | 1224823 | 82.937 | 84.995 |
| 2 | 6.627 | 1563524 | 117851 | 8.624 | 8.178 |
| 3 | 7.120 | 621537 | 42478 | 3.428 | 2.948 |
| 4 | 8.528 | 908511 | 55899 | 5.011 | 3.879 |
| Total | | 18130814 | 1441051 | 100.000 | 100.000 |

1

## H NMR, $^{13}$C NMR and HPLC of 3a'



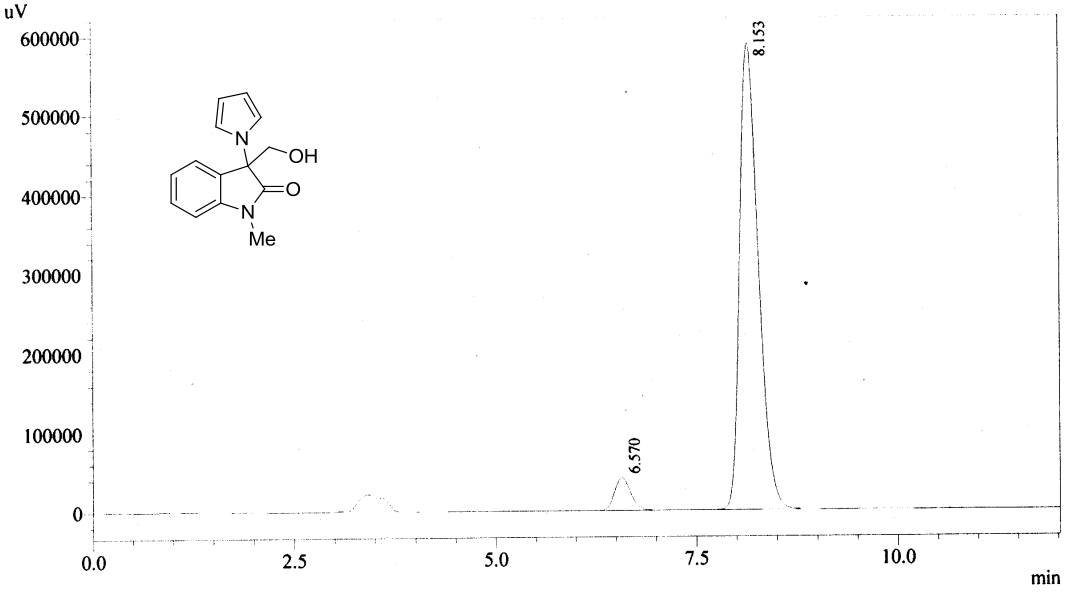






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.673 | 3901245 | 278751 | 49.875 | 53.858 |
| 2 | 8.365 | 3920767 | 238813 | 50.125 | 46.142 |
| Total | | 7822012 | 517564 | 100.000 | 100.000 |

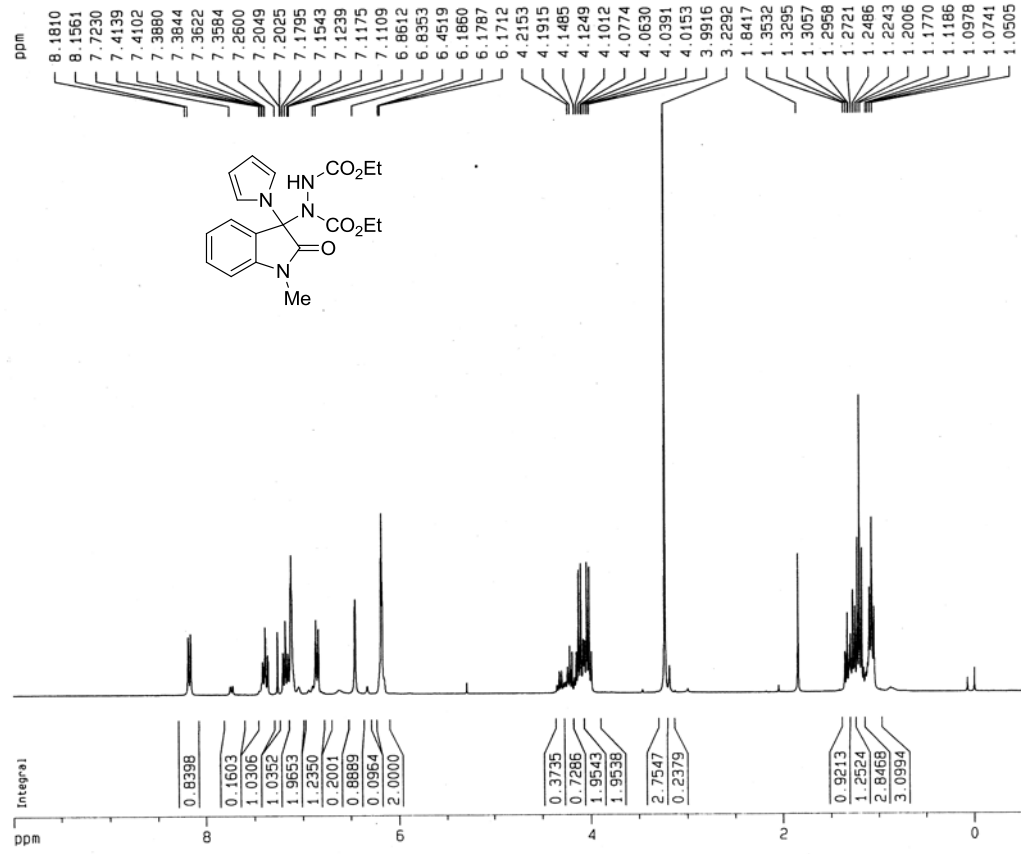


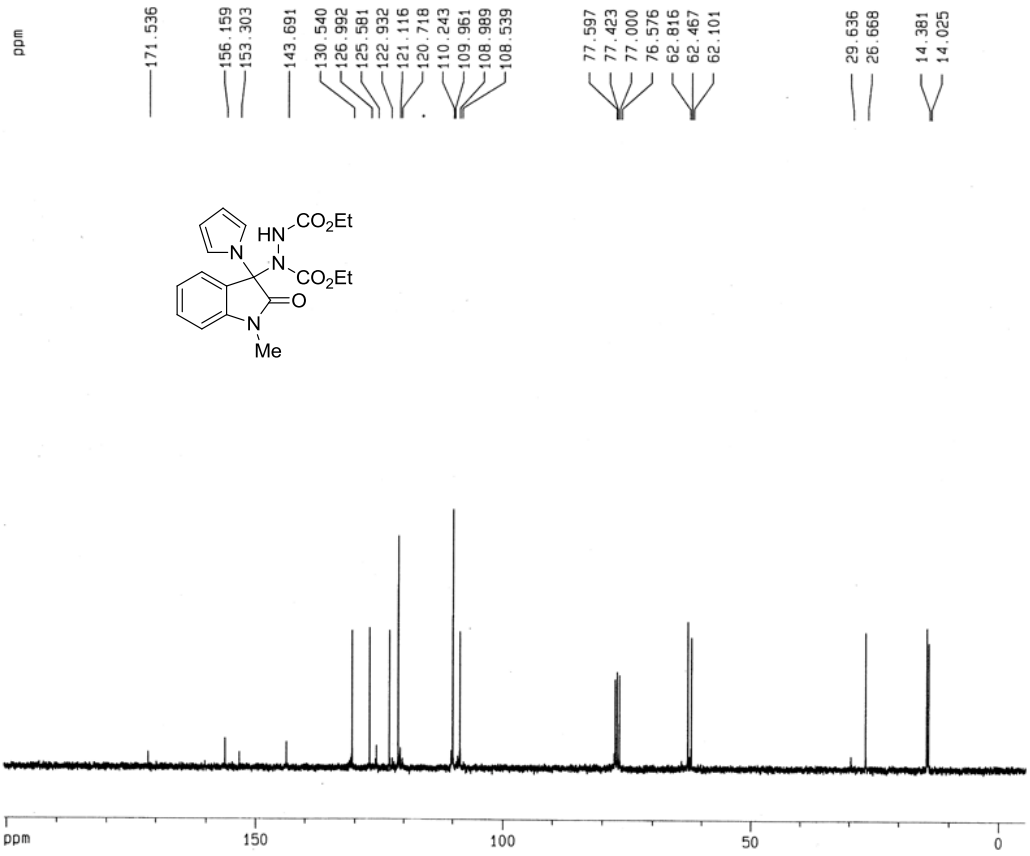

1 Det.A Ch1 / 254nm

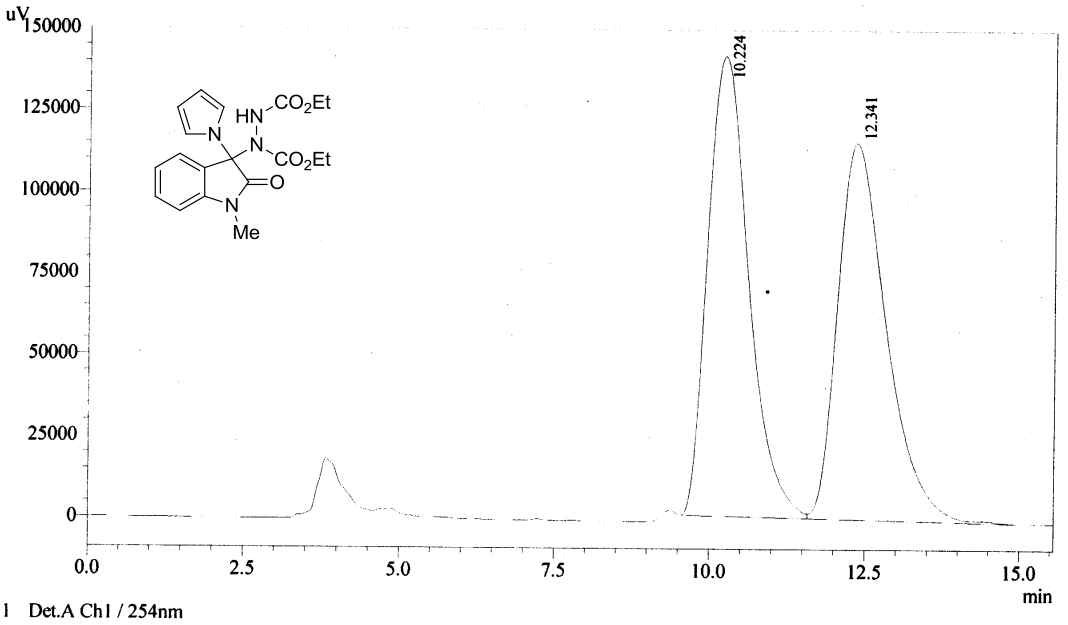
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.570 | 577276 | 41262 | 5.746 | 6.552 |
| 2 | 8.153 | 9469397 | 588467 | 94.254 | 93.448 |
| Total | | 10046673 | 629729 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3b'**



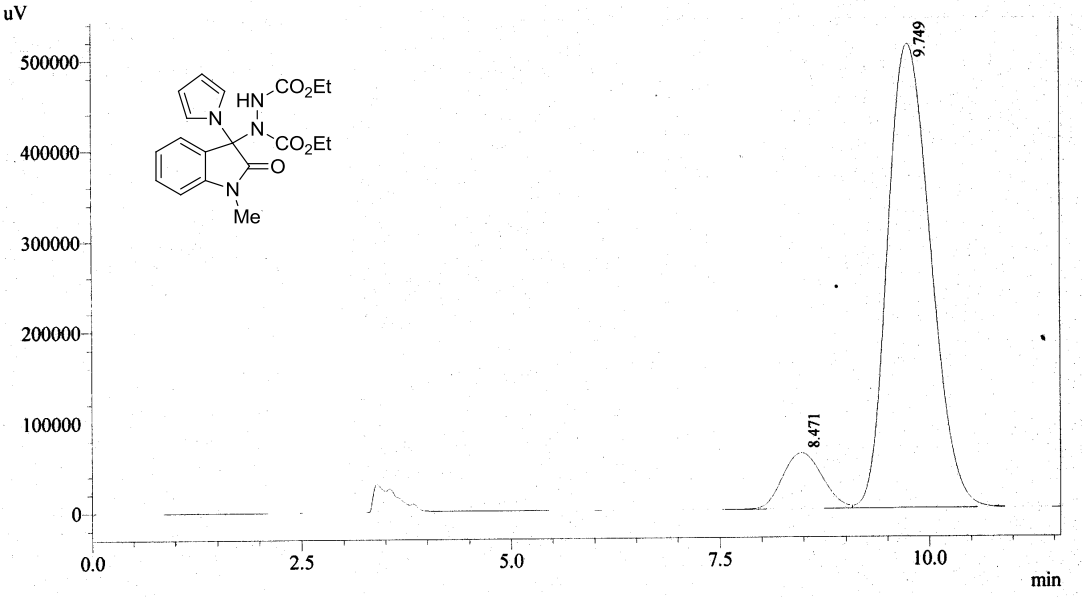






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.224 | 6468481 | 141157 | 50.682 | 55.015 |
| 2 | 12.341 | 6294364 | 115421 | 49.318 | 44.985 |
| Total | | 12762845 | 256577 | 100.000 | 100.000 |

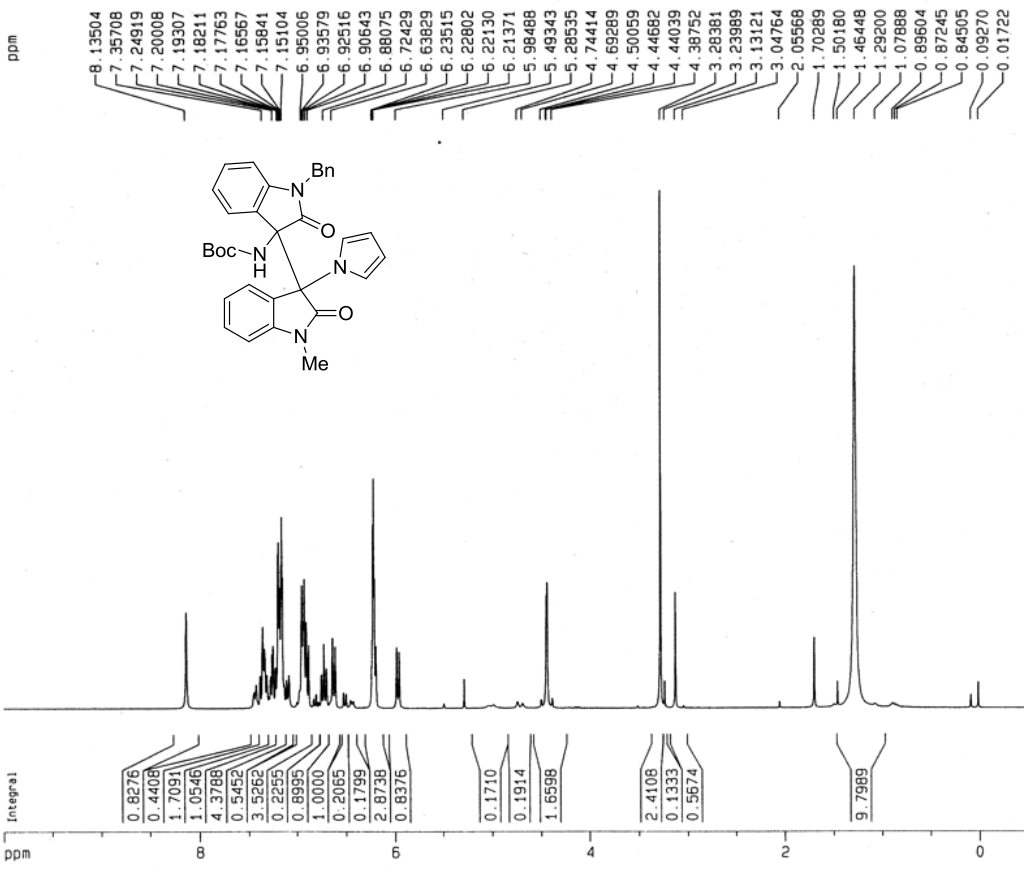


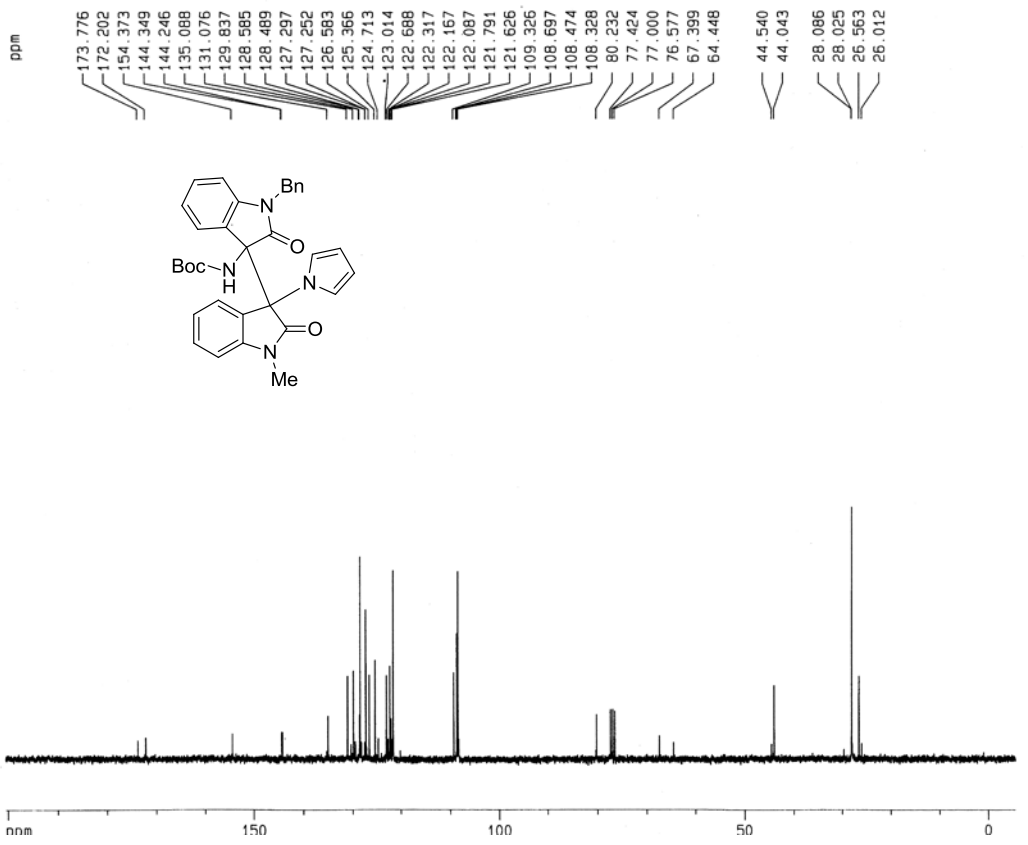

1 Det.A Ch1 / 254nm

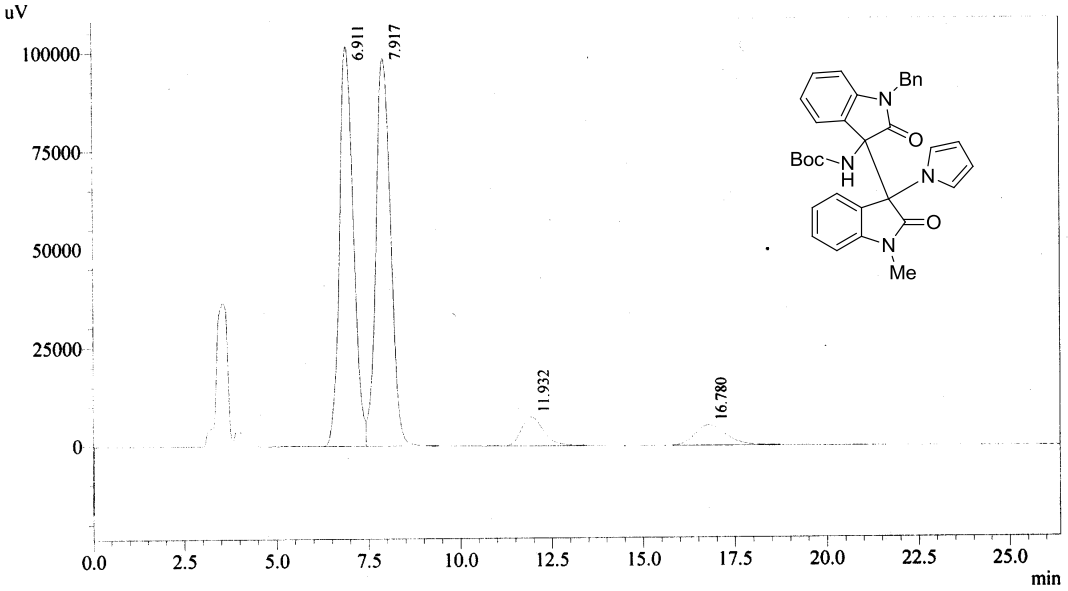
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.471 | 2030520 | 62205 | 9.931 | 10.808 |
| 2 | 9.749 | 18416550 | 513366 | 90.069 | 89.192 |
| Total | | 20447070 | 575571 | 100.000 | 100.000 |

## $^{1}$H NMR, $^{13}$C NMR and HPLC of 3c'



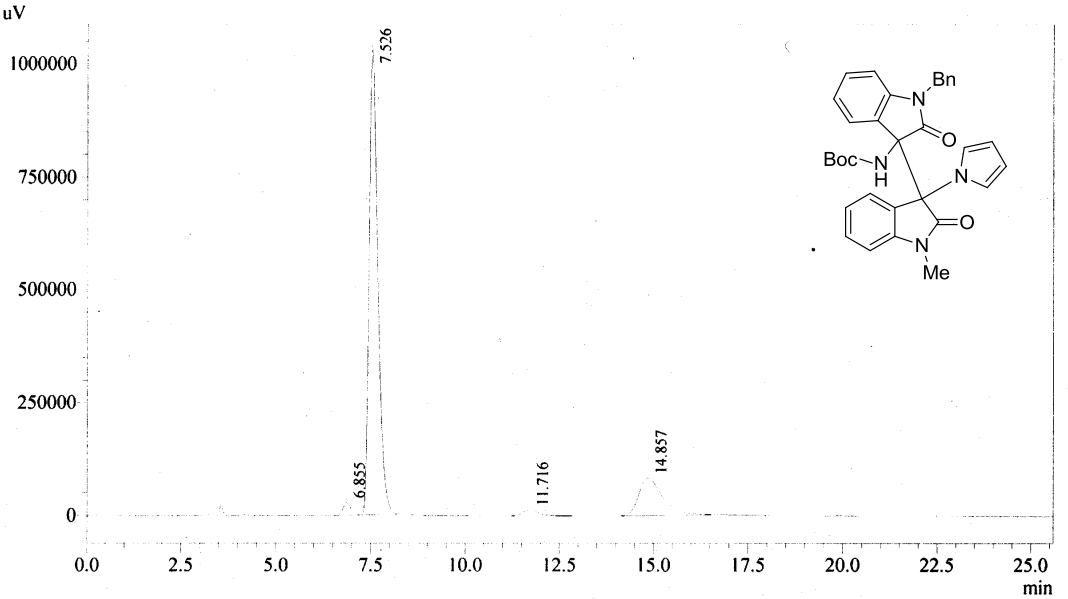






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.911 | 2684373 | 101755 | 44.163 | 47.765 |
| 2 | 7.917 | 2764108 | 98607 | 45.475 | 46.287 |
| 3 | 11.932 | 316712 | 7447 | 5.211 | 3.496 |
| 4 | 16.780 | 313098 | 5223 | 5.151 | 2.452 |
| Total | | 6078291 | 213032 | 100.000 | 100.000 |

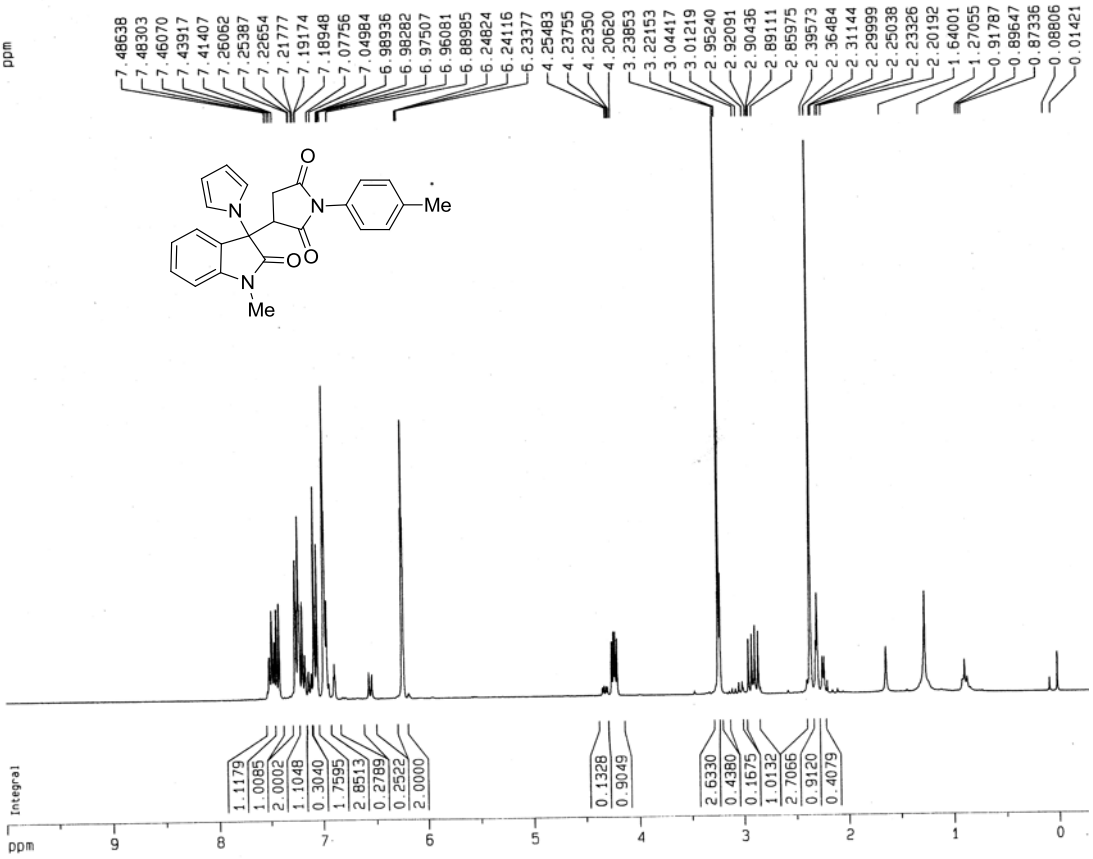


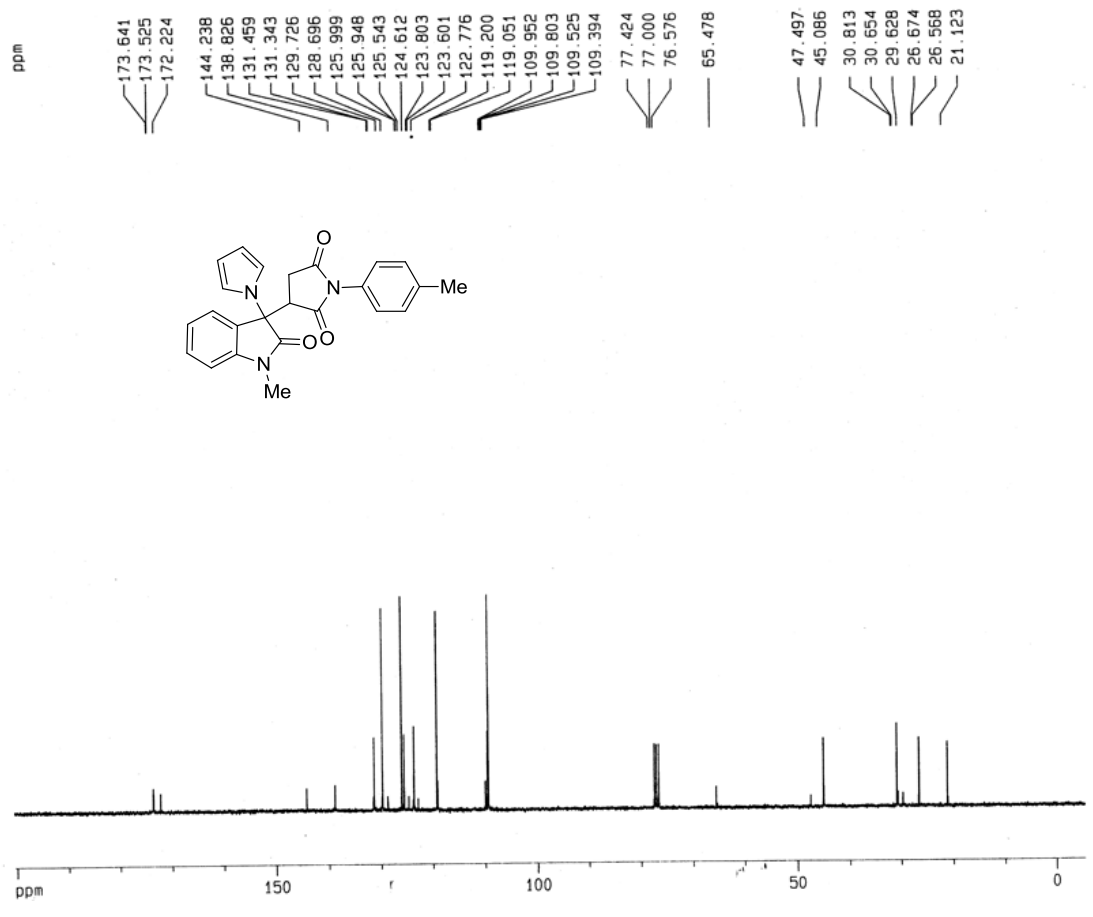

1 Det.A Ch1 / 254nm

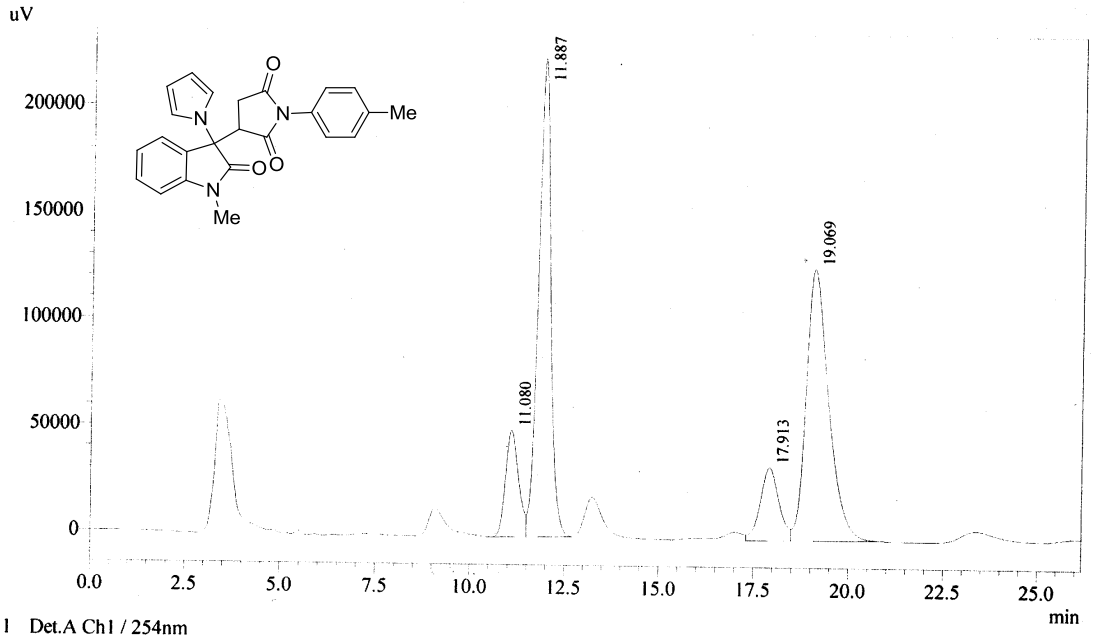
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.855 | 411292 | 28779 | 1.969 | 2.496 |
| 2 | 7.526 | 16493956 | 1029506 | 78.952 | 89.293 |
| 3 | 11.716 | 395443 | 12488 | 1.893 | 1.083 |
| 4 | 14.857 | 3590440 | 82182 | 17.186 | 7.128 |
| Total | | 20891131 | 1152955 | 100.000 | 100.000 |

## $^{1}$H NMR, $^{13}$C NMR and HPLC of 3d'



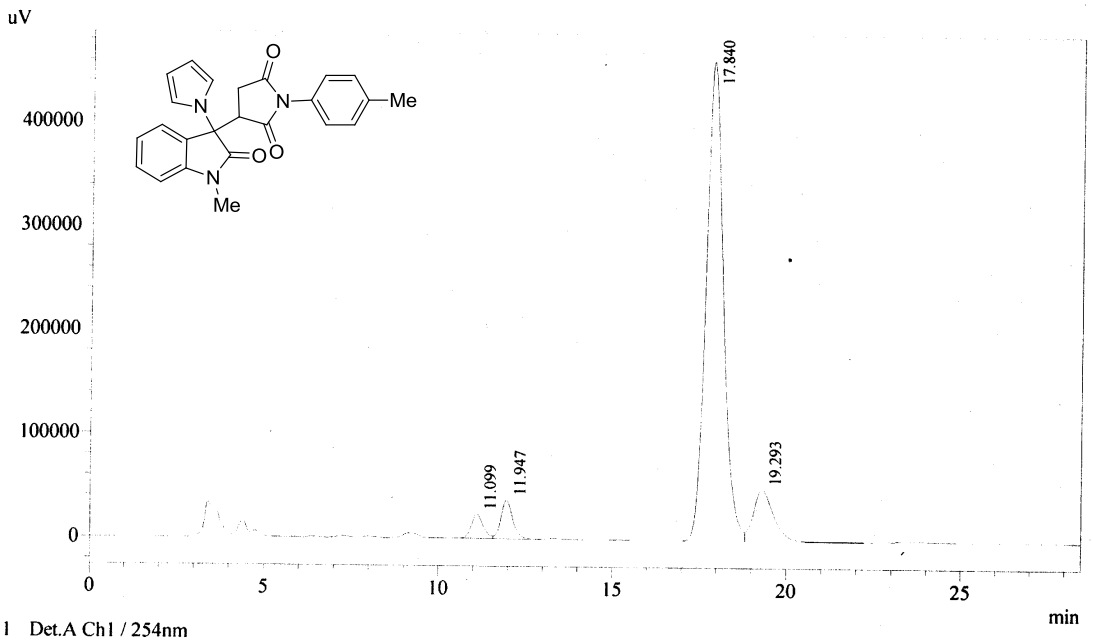






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.080 | 1203575 | 49994 | 9.470 | 11.473 |
| 2 | 11.887 | 5107863 | 224453 | 40.188 | 51.508 |
| 3 | 17.913 | 1170757 | 34019 | 9.211 | 7.807 |
| 4 | 19.069 | 5227672 | 127295 | 41.131 | 29.212 |
| Total | | 12709867 | 435761 | 100.000 | 100.000 |



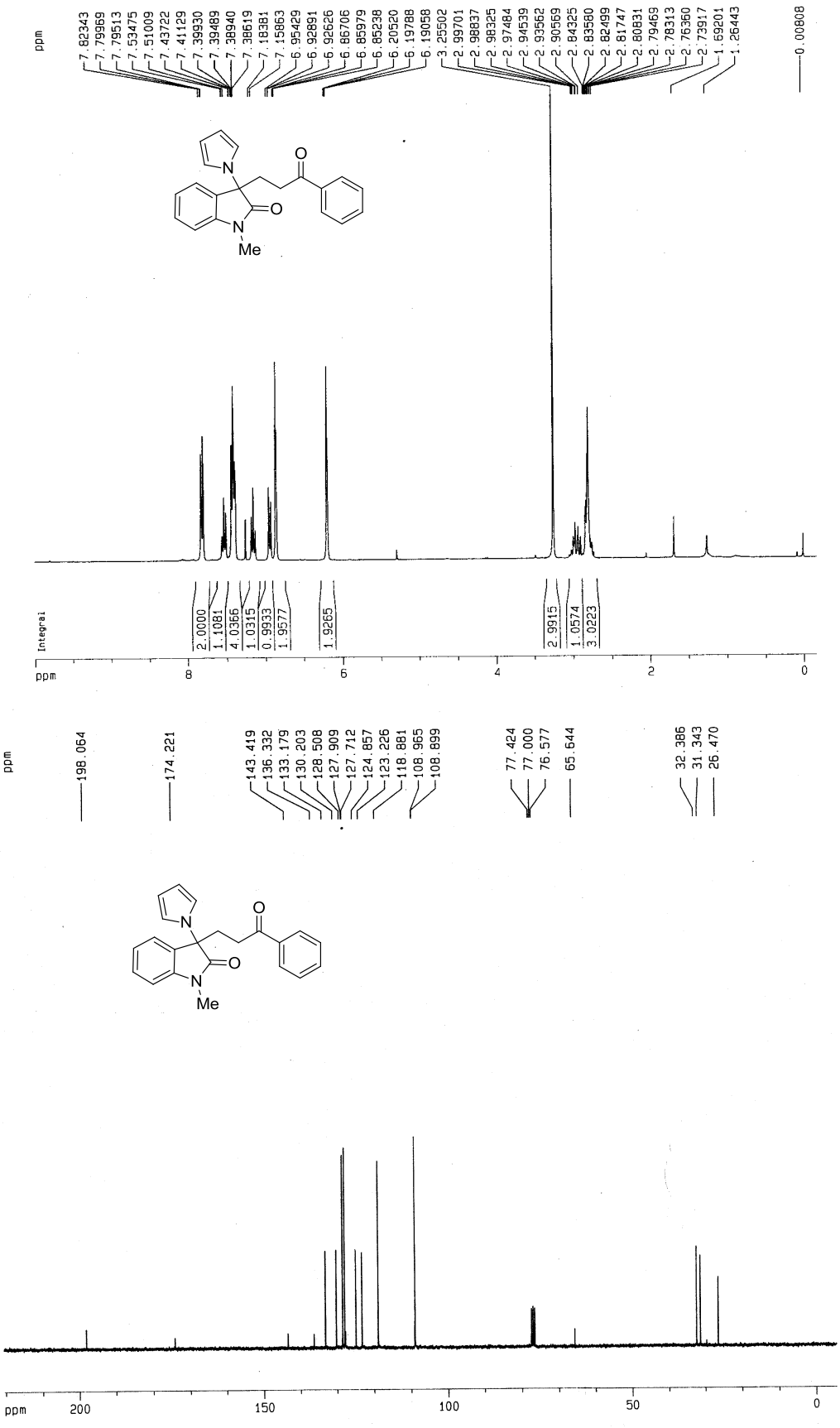

1 Det.A Ch1 / 254nm

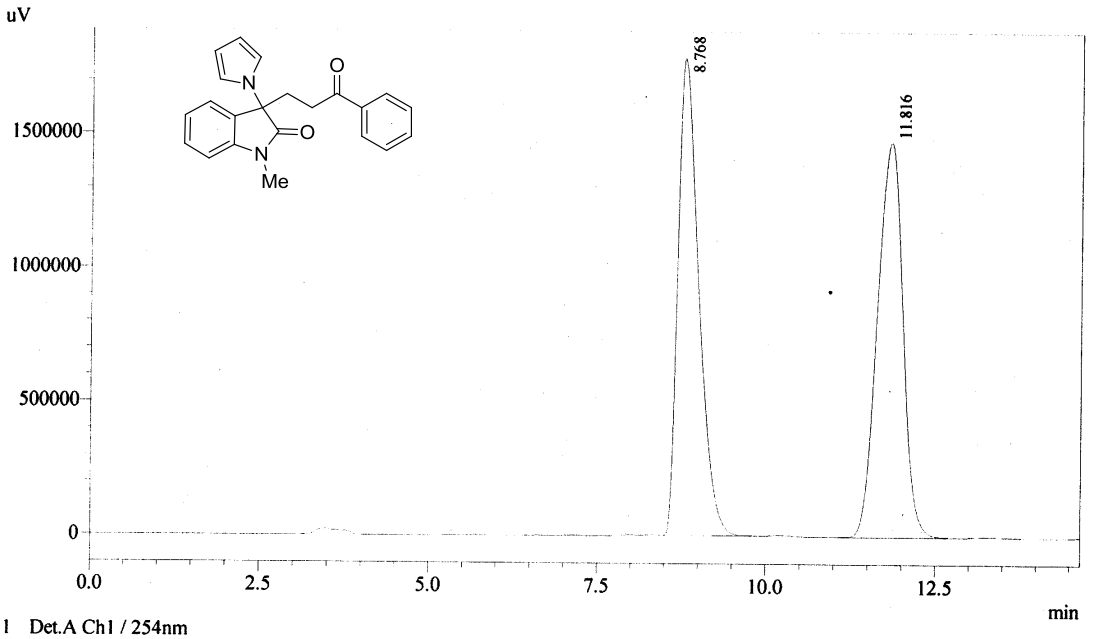
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.099 | 546884 | 23151 | 2.835 | 4.052 |
| 2 | 11.947 | 866921 | 37190 | 4.494 | 6.510 |
| 3 | 17.840 | 15900153 | 461514 | 82.429 | 80.782 |
| 4 | 19.293 | 1975510 | 49456 | 10.241 | 8.657 |
| Total | | 19289467 | 571311 | 100.000 | 100.000 |

1

## H NMR, $^{13}$C NMR and HPLC of 3e'

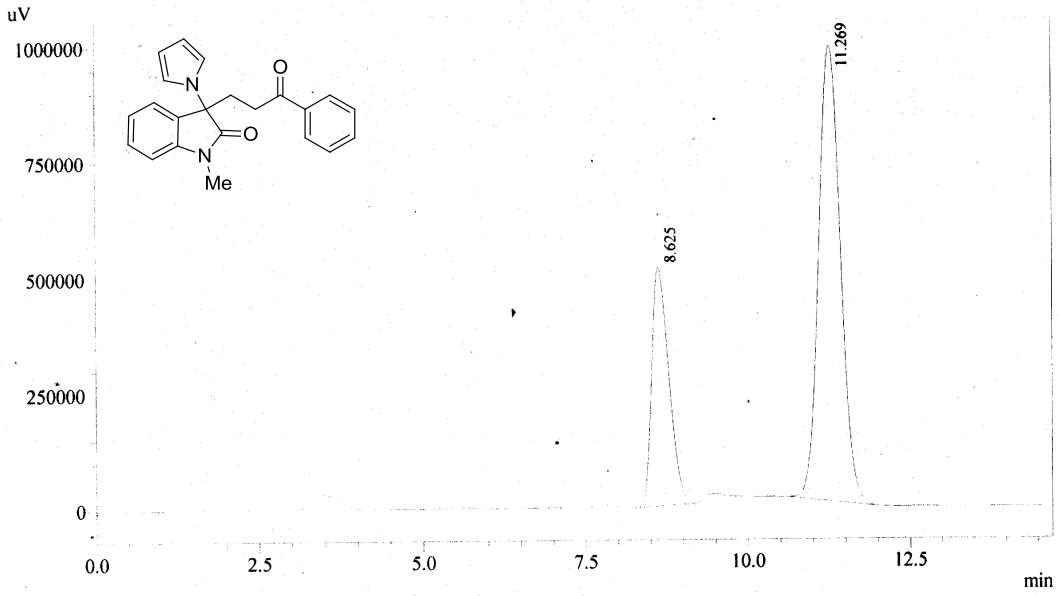





1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.768 | 38301678 | 1784389 | 49.774 | 54.748 |
| 2 | 11.816 | 38649838 | 1474895 | 50.226 | 45.252 |
| Total | | 76951516 | 3259284 | 100.000 | 100.000 |

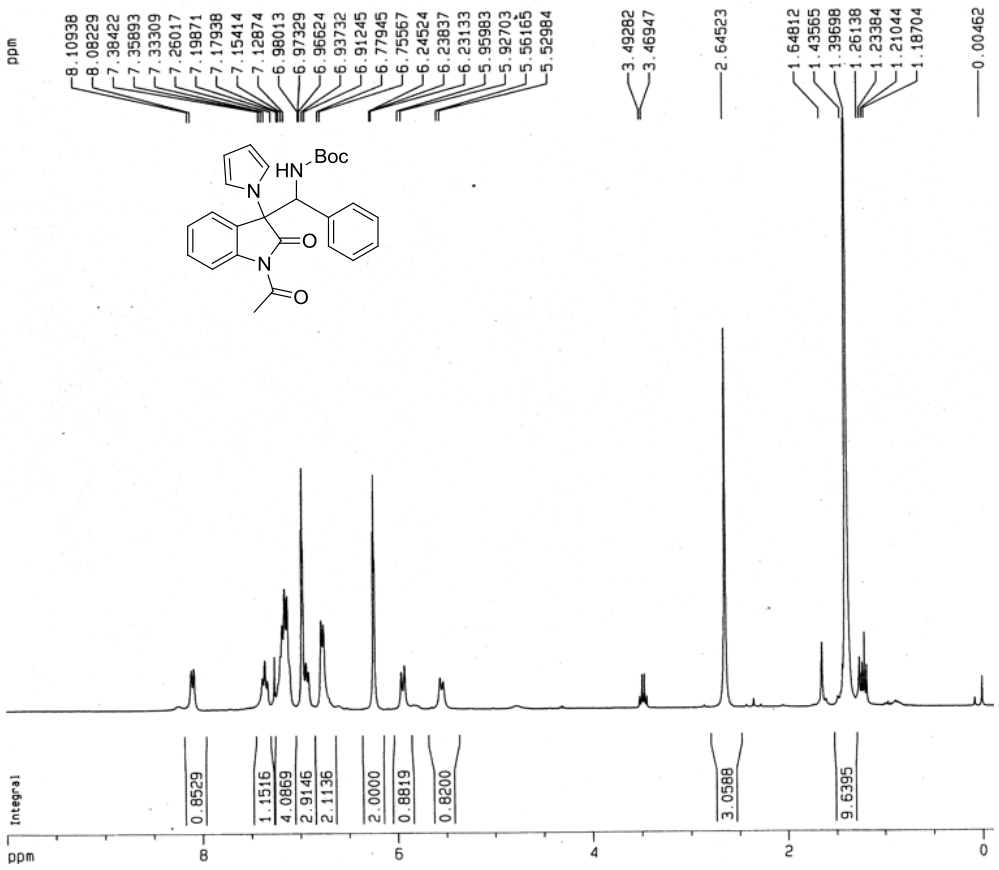


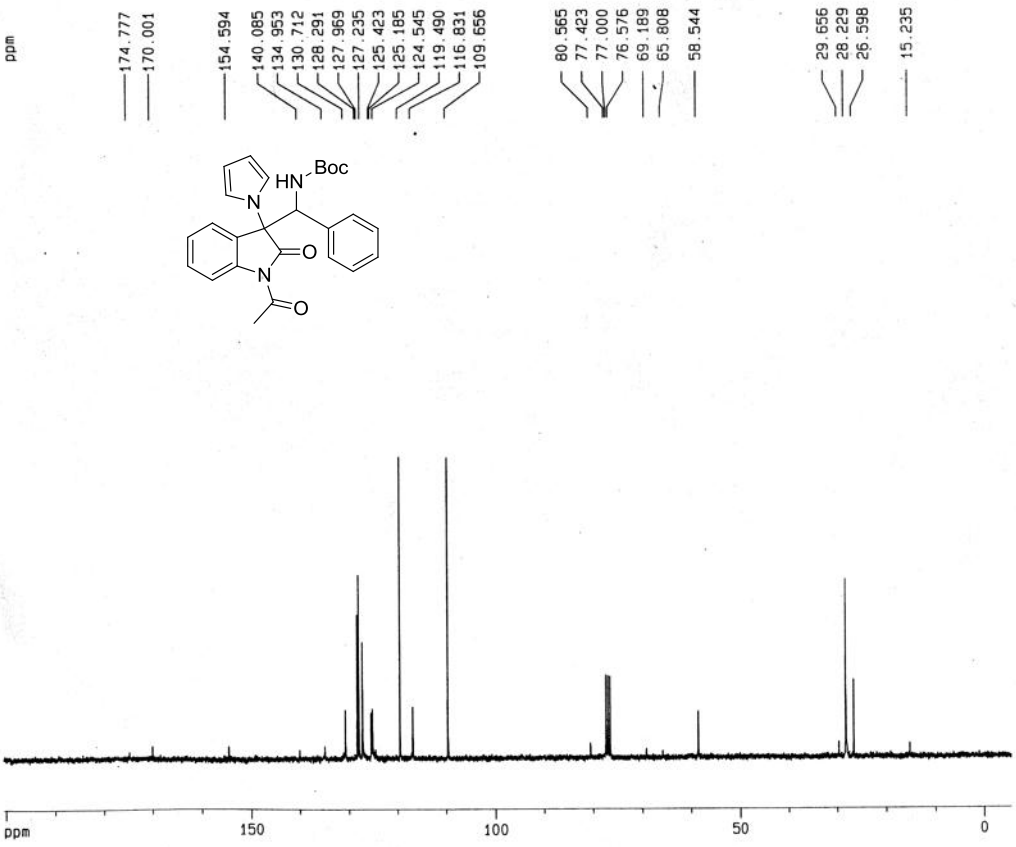

1 Det.A Ch1 / 254nm

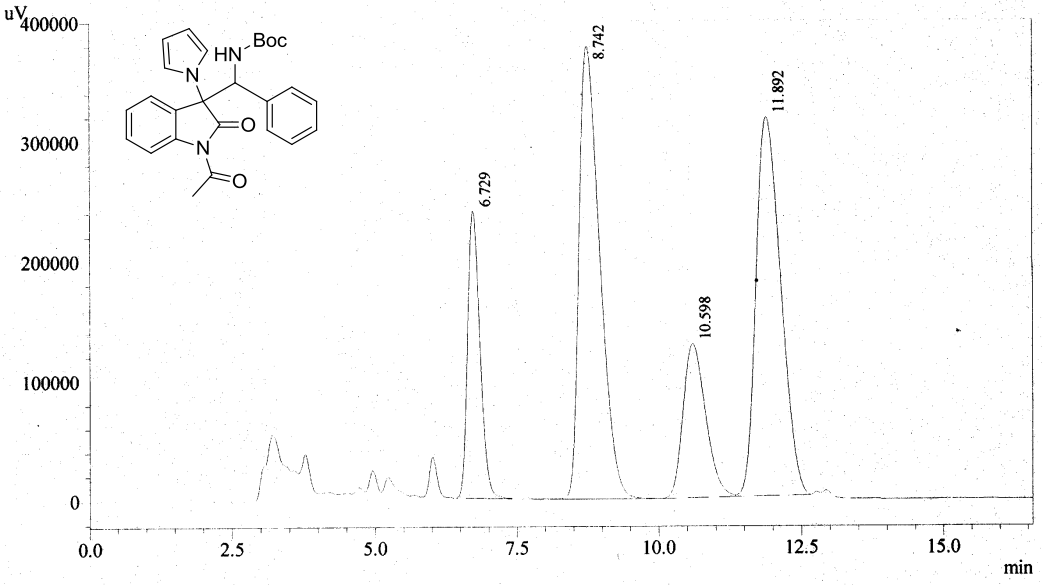
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.625 | 9458261 | 515402 | 29.224 | 34.390 |
| 2 | 11.269 | 22906446 | 983282 | 70.776 | 65.610 |
| Total | | 32364707 | 1498684 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 3f'**



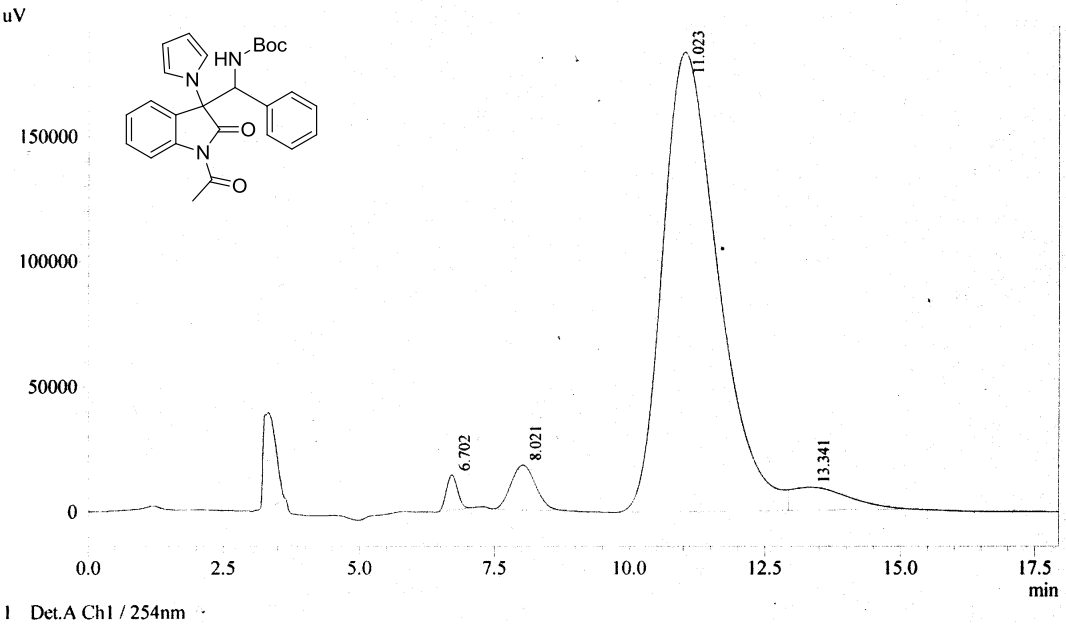






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.729 | 3644442 | 240113 | 13.802 | 22.574 |
| 2 | 8.742 | 9645447 | 378412 | 36.528 | 35.576 |
| 3 | 10.598 | 3562232 | 128705 | 13.491 | 12.100 |
| 4 | 11.892 | 9553289 | 316451 | 36.179 | 29.751 |
| Total | | 26405411 | 1063680 | 100.000 | 100.000 |

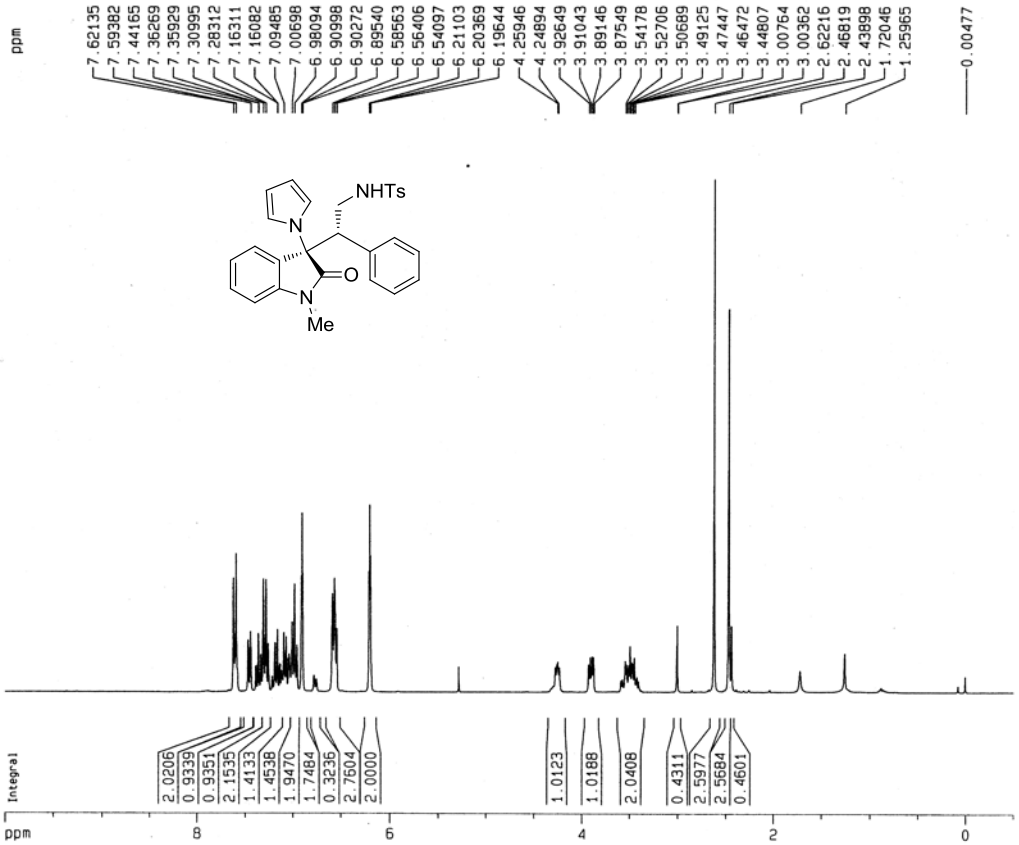


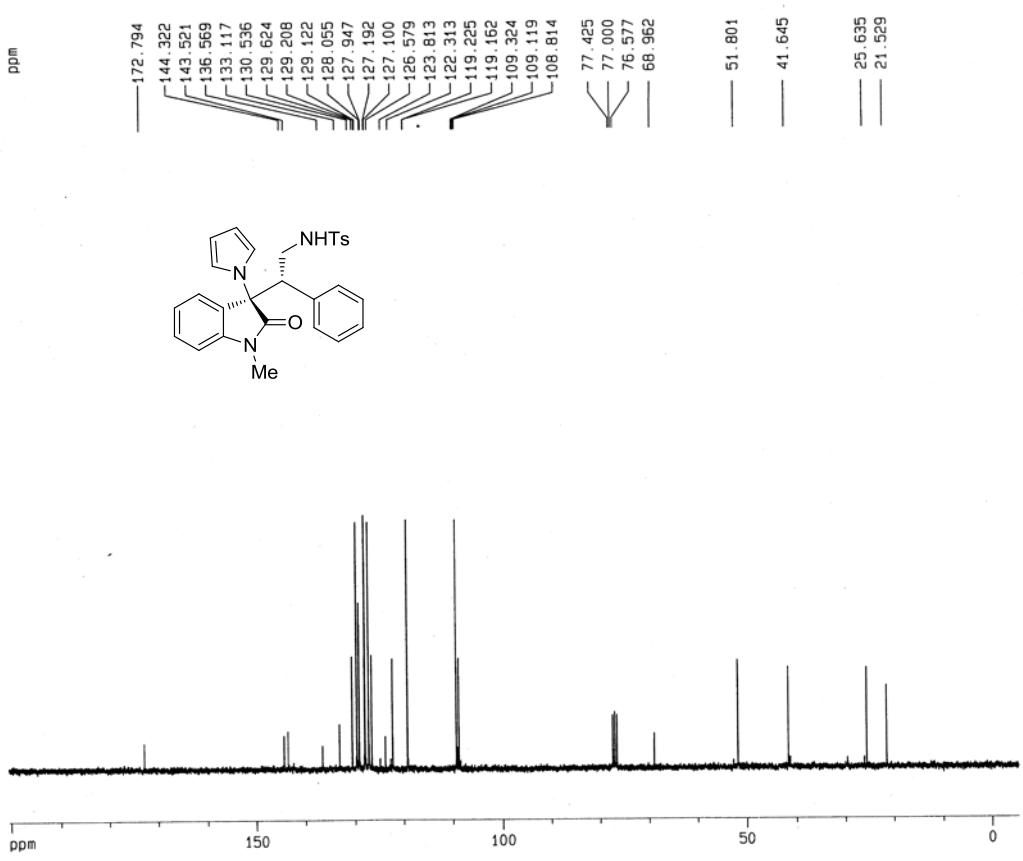

1 Det.A Ch1 / 254nm

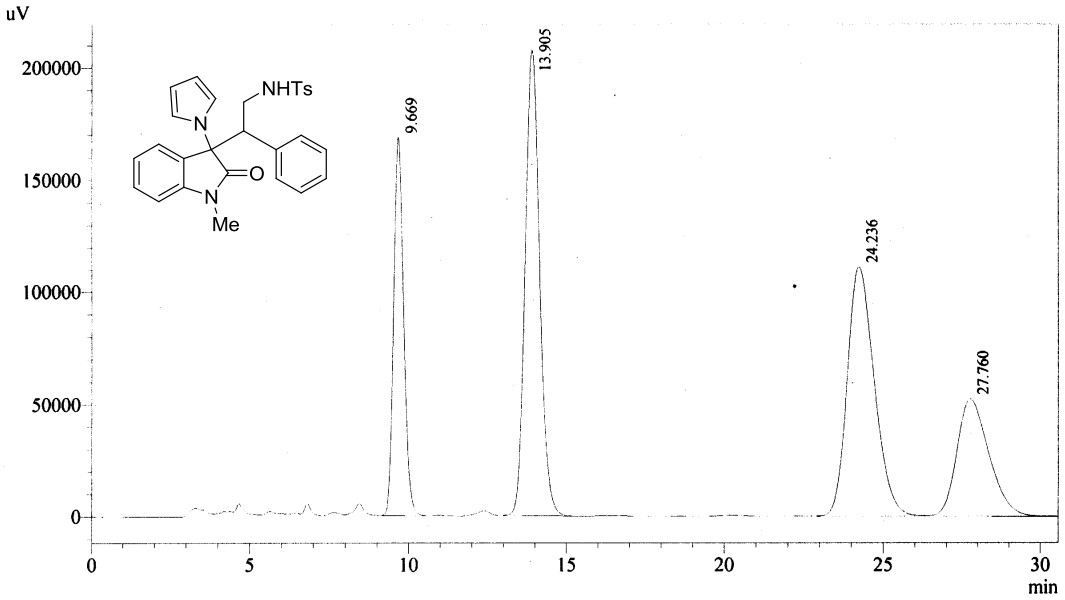
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.702 | 203091 | 14009 | 1.405 | 6.242 |
| 2 | 8.021 | 575045 | 17903 | 3.979 | 7.977 |
| 3 | 11.023 | 13020419 | 183472 | 90.099 | 81.746 |
| 4 | 13.341 | 652608 | 9058 | 4.516 | 4.036 |
| Total | | 14451163 | 224442 | 100.000 | 100.000 |

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



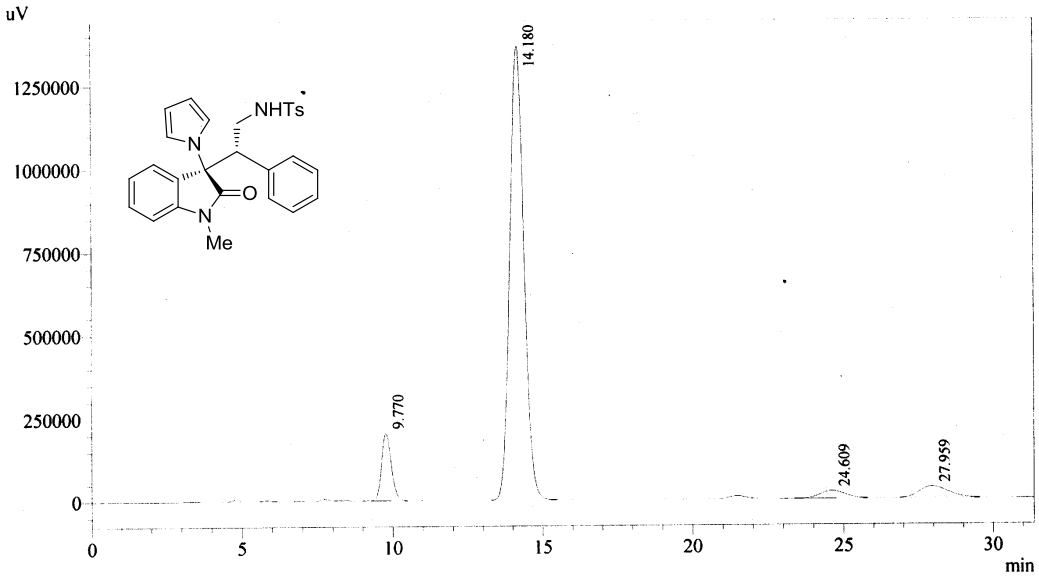






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.669 | 3703232 | 168407 | 17.912 | 31.205 |
| 2 | 13.905 | 6656897 | 207615 | 32.199 | 38.470 |
| 3 | 24.236 | 6596292 | 111188 | 31.906 | 20.602 |
| 4 | 27.760 | 3717769 | 52476 | 17.983 | 9.723 |
| Total | | 20674190 | 539687 | 100.000 | 100.000 |

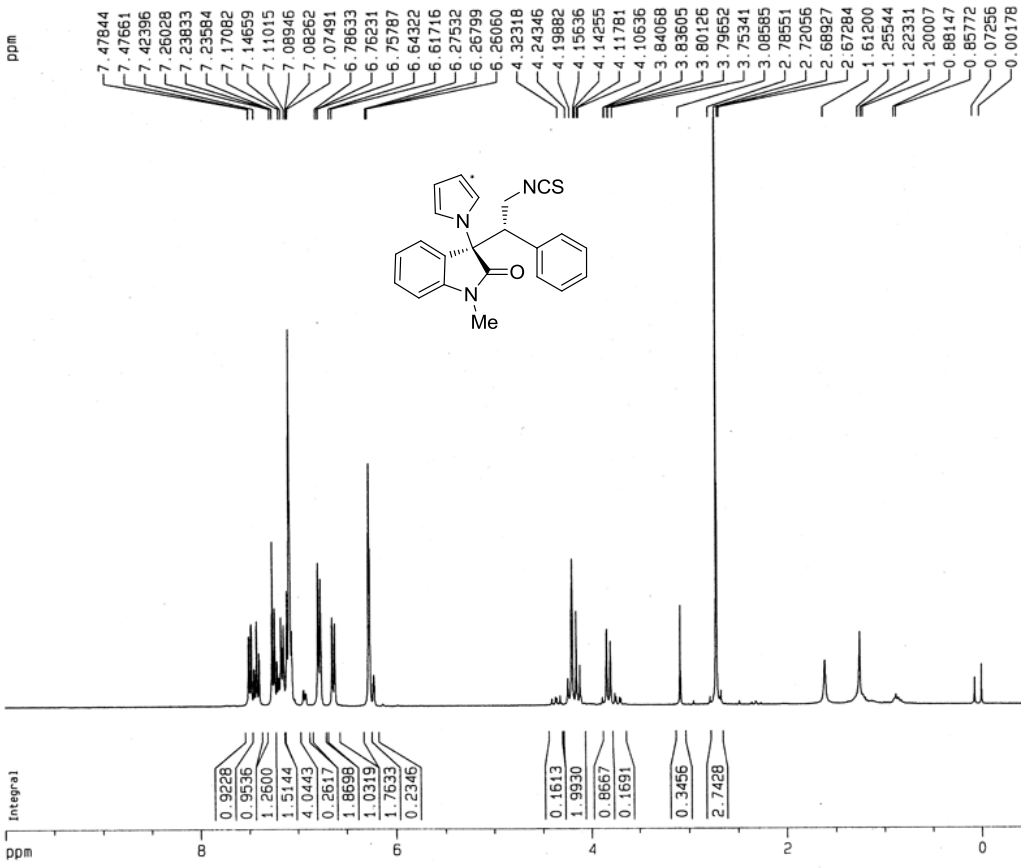


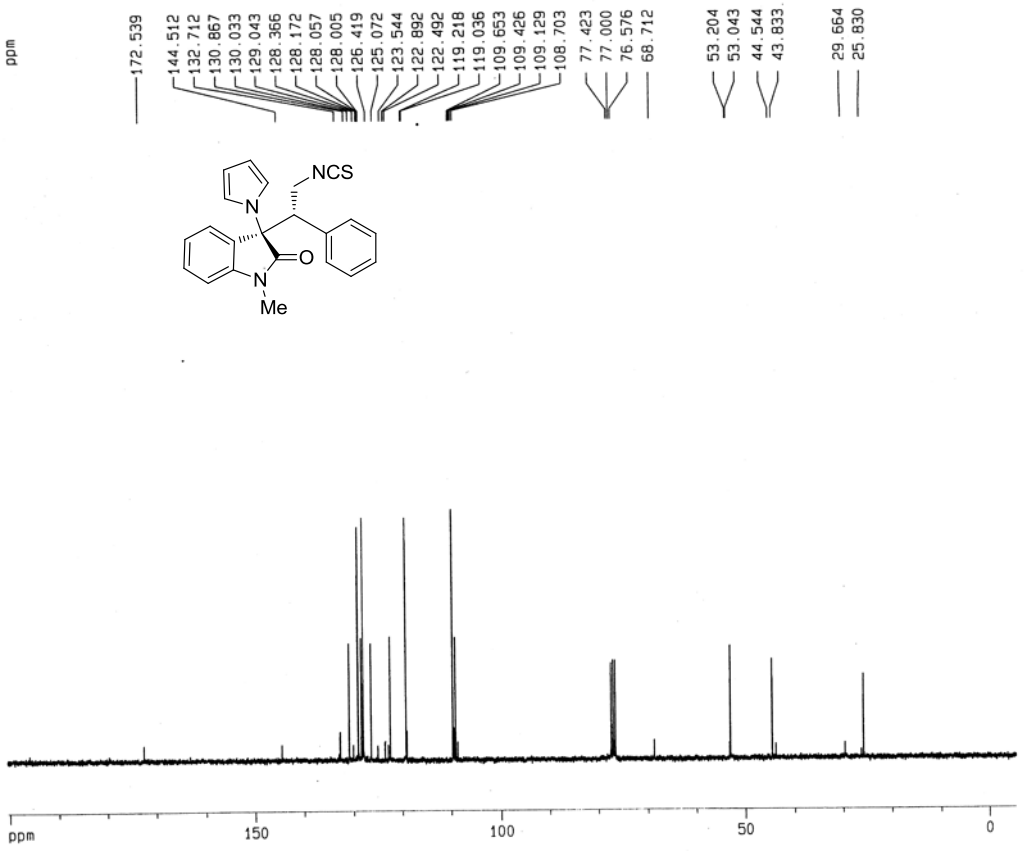

1 Det.A Ch1 / 254nm

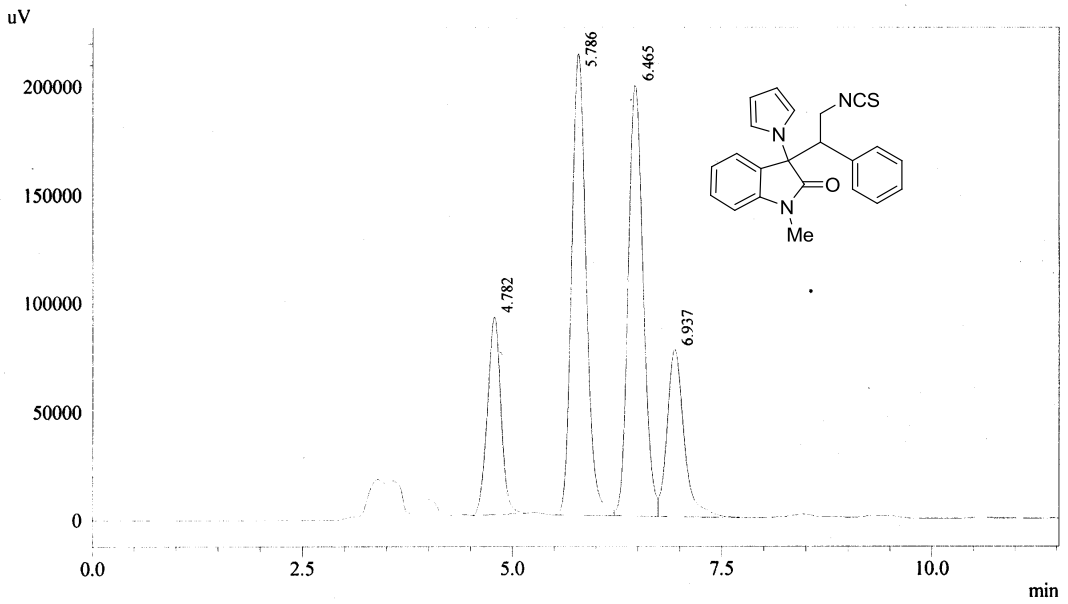
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.770 | 4537076 | 204432 | 8.501 | 12.551 |
| 2 | 14.180 | 45023982 | 1365971 | 84.365 | 83.864 |
| 3 | 24.609 | 1373502 | 23404 | 2.574 | 1.437 |
| 4 | 27.959 | 2433484 | 34986 | 4.560 | 2.148 |
| Total | | 53368044 | 1628793 | 100.000 | 100.000 |

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



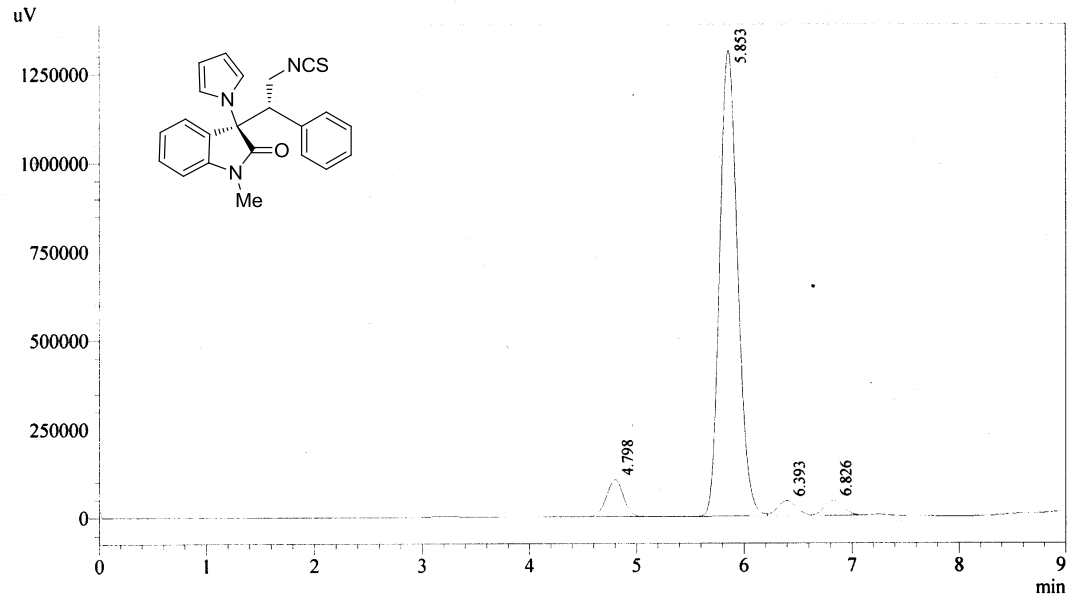






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 4.782 | 1029451 | 91055 | 14.296 | 15.693 |
| 2 | 5.786 | 2591256 | 213080 | 35.984 | 36.723 |
| 3 | 6.465 | 2490958 | 198902 | 34.591 | 34.279 |
| 4 | 6.937 | 1089534 | 77203 | 15.130 | 13.305 |
| Total | | 7201200 | 580239 | 100.000 | 100.000 |

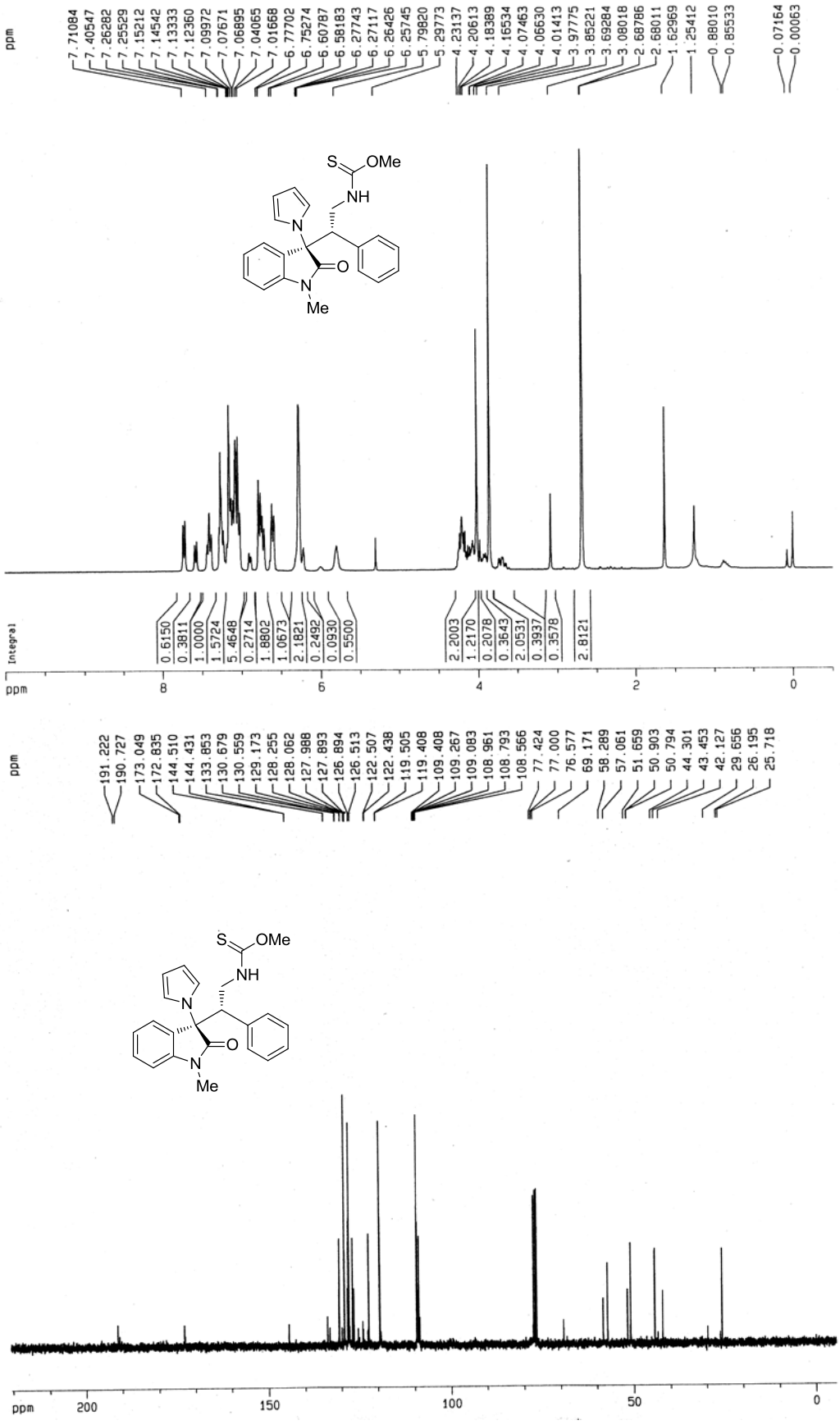


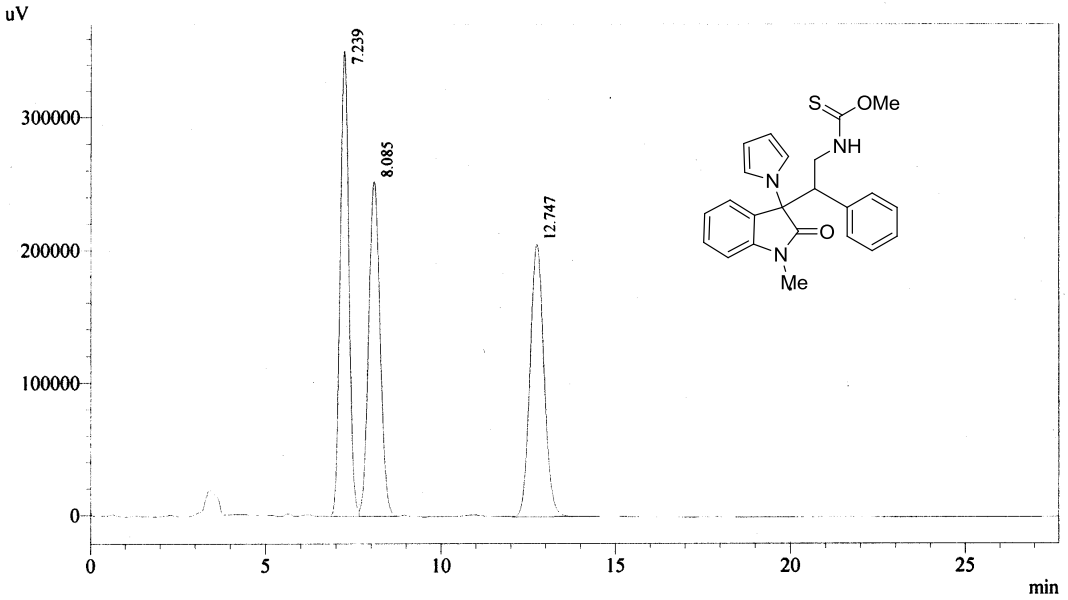

1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 4.798 | 1144238 | 104863 | 6.580 | 6.975 |
| 2 | 5.853 | 15227414 | 1313936 | 87.563 | 87.393 |
| 3 | 6.393 | 507656 | 42340 | 2.919 | 2.816 |
| 4 | 6.826 | 510958 | 42348 | 2.938 | 2.817 |
| Total | | 17390265 | 1503486 | 100.000 | 100.000 |

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

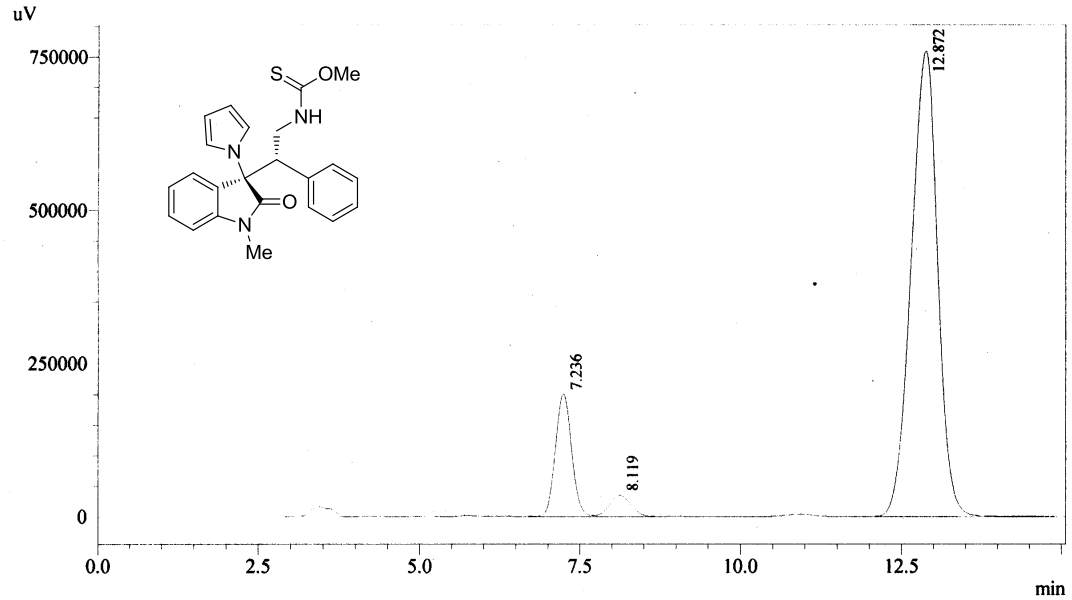





1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.239 | 6054777 | 351873 | 34.458 | 43.416 |
| 2 | 8.085 | 5770638 | 252788 | 32.841 | 31.190 |
| 3 | 12.747 | 5745852 | 205804 | 32.700 | 25.393 |
| Total | | 17571267 | 810465 | 100.000 | 100.000 |

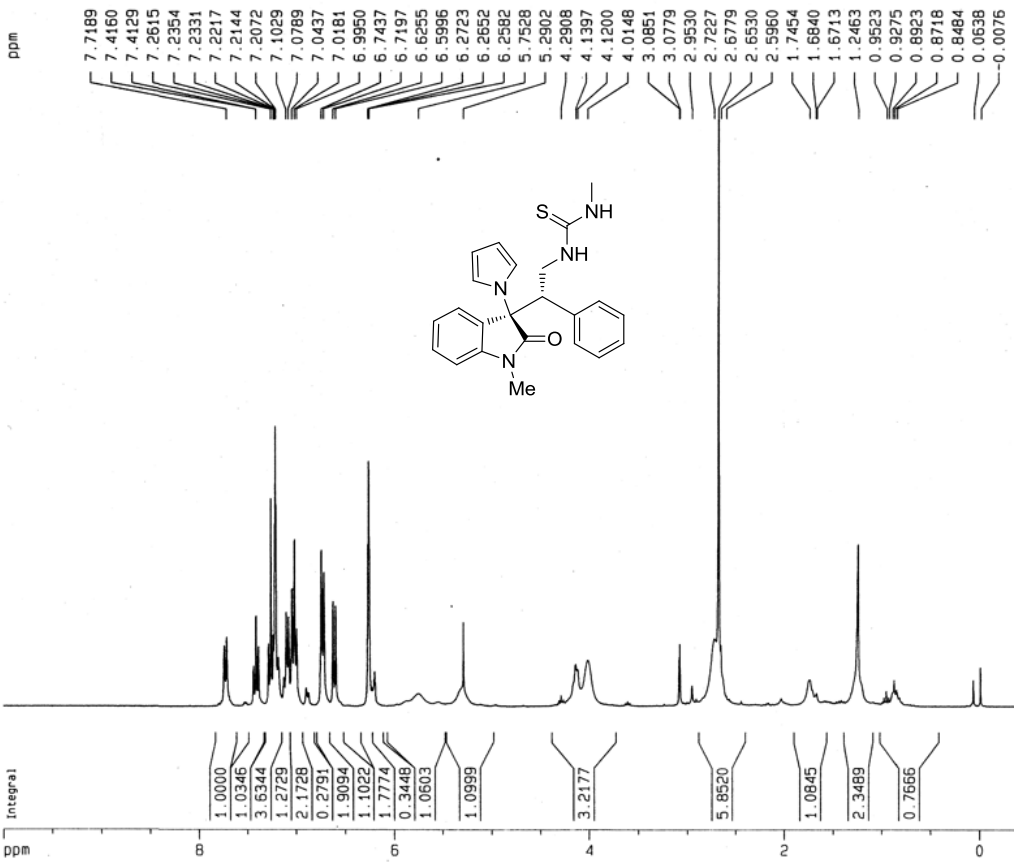


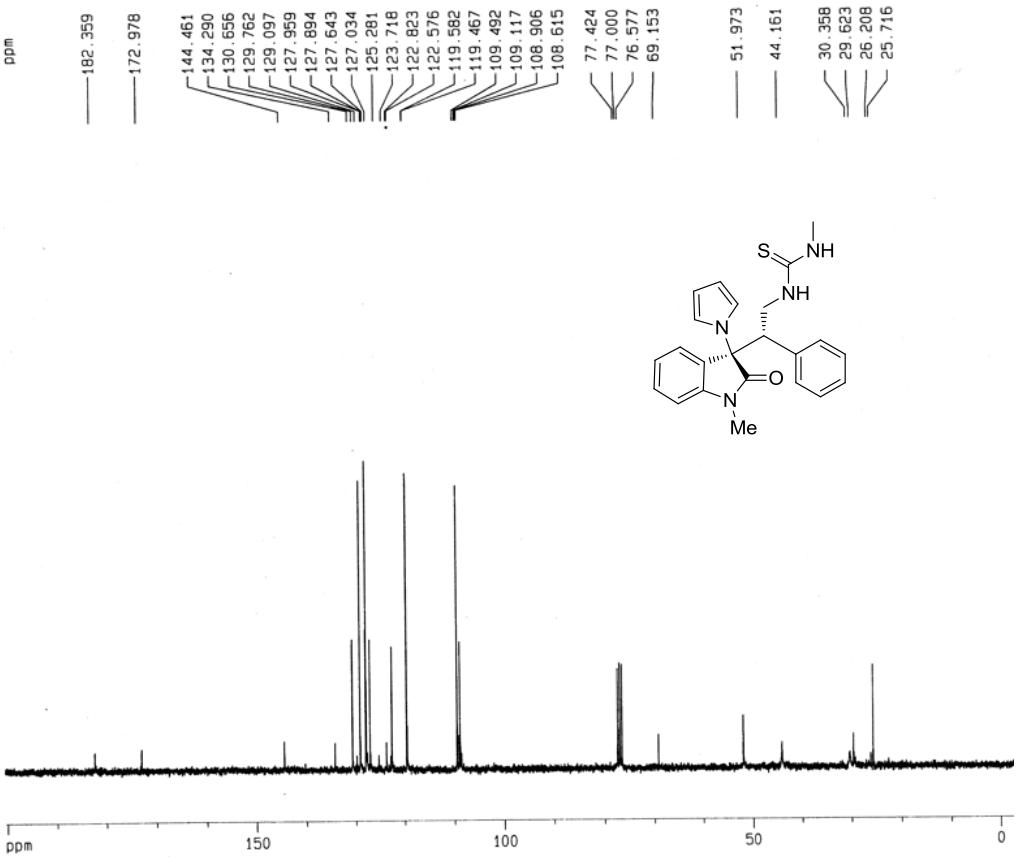

1 Det.A Ch1 / 254nm

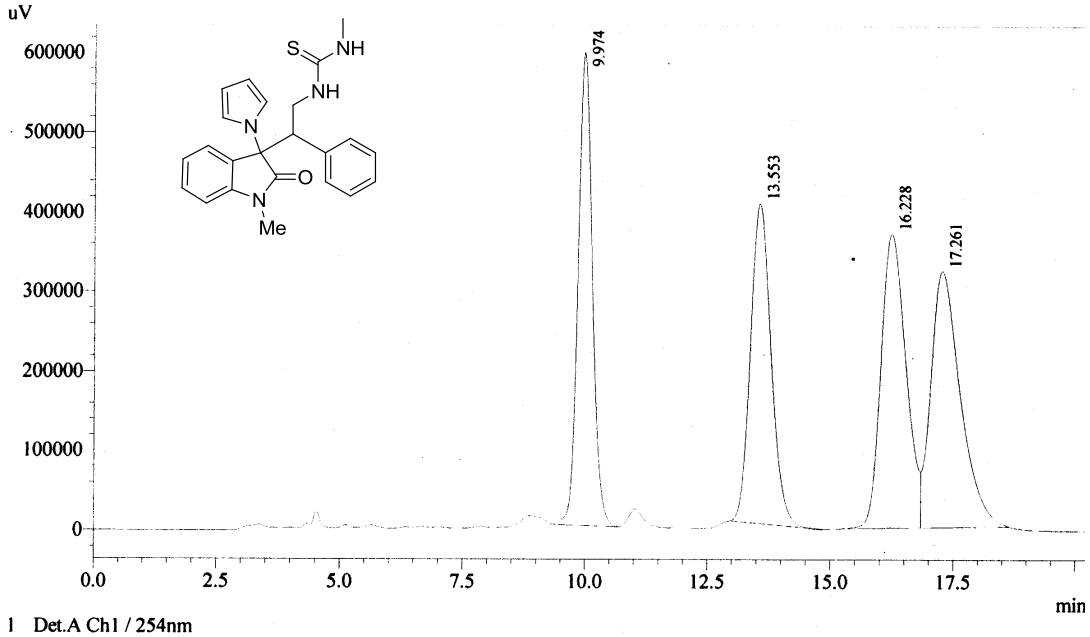
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 7.236 | 3533367 | 200799 | 13.520 | 20.170 |
| 2 | 8.119 | 803215 | 34591 | 3.073 | 3.475 |
| 3 | 12.872 | 21798732 | 760162 | 83.407 | 76.356 |
| Total | | 26135314 | 995552 | 100.000 | 100.000 |

**$^{1}$H NMR, $^{13}$C NMR and HPLC of 14**



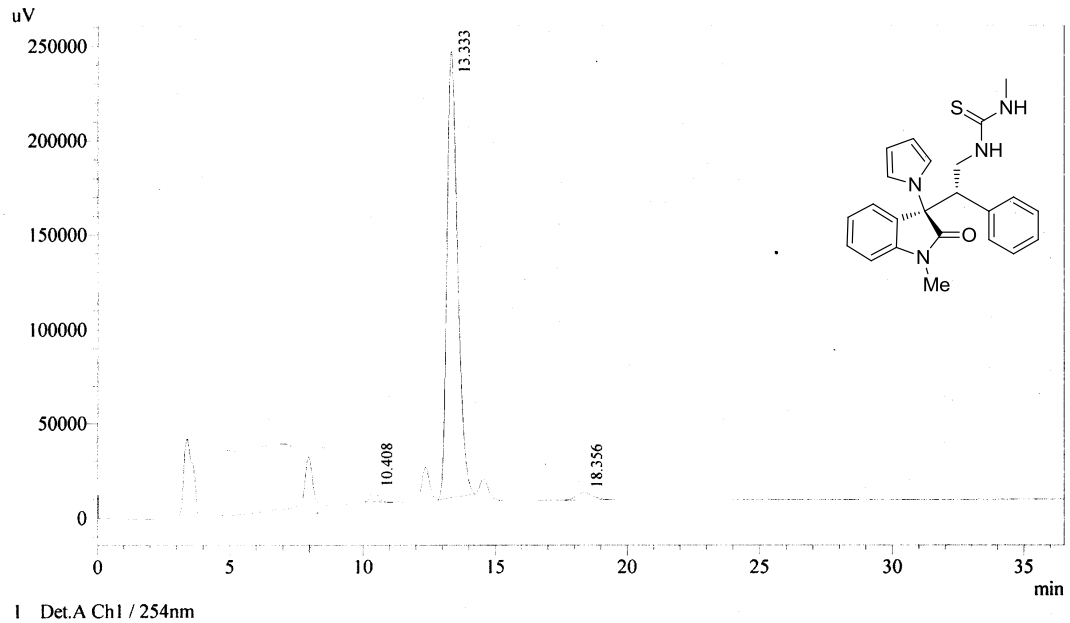






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.974 | 12087349 | 595088 | 23.995 | 35.247 |
| 2 | 13.553 | 11737150 | 402543 | 23.300 | 23.843 |
| 3 | 16.228 | 13022607 | 369373 | 25.852 | 21.878 |
| 4 | 17.261 | 13526313 | 321325 | 26.852 | 19.032 |
| Total | | 50373420 | 1688330 | 100.000 | 100.000 |

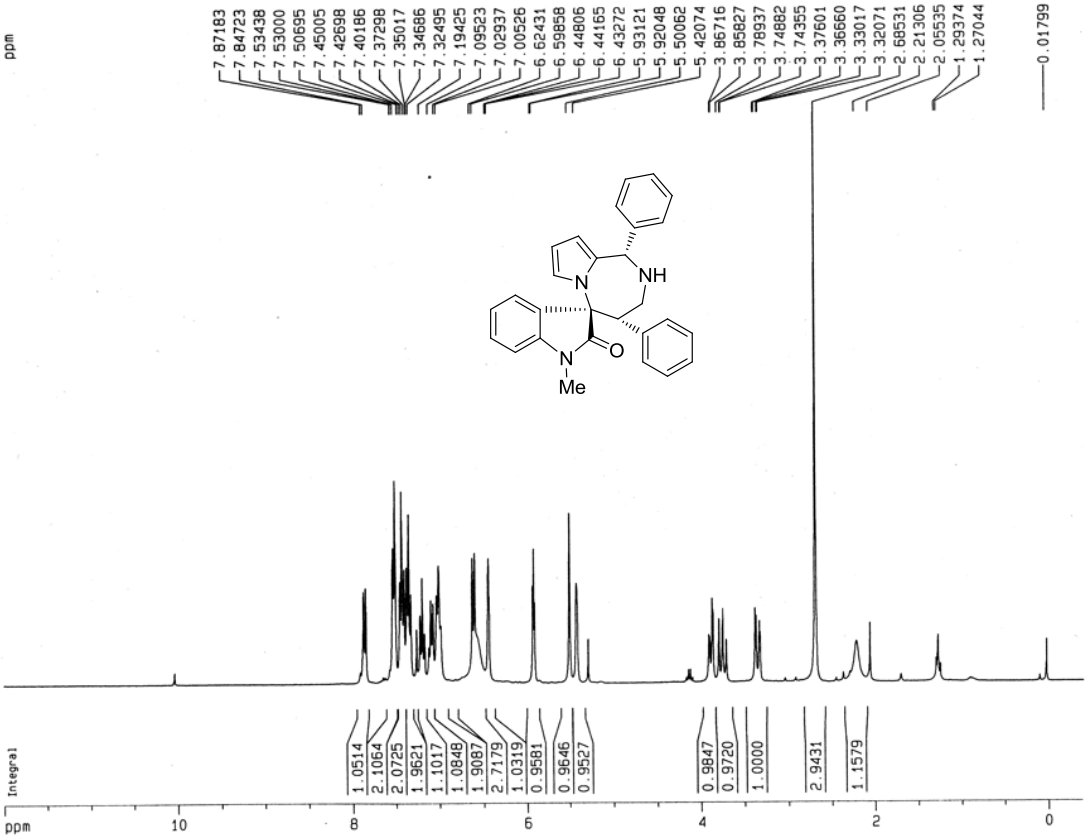


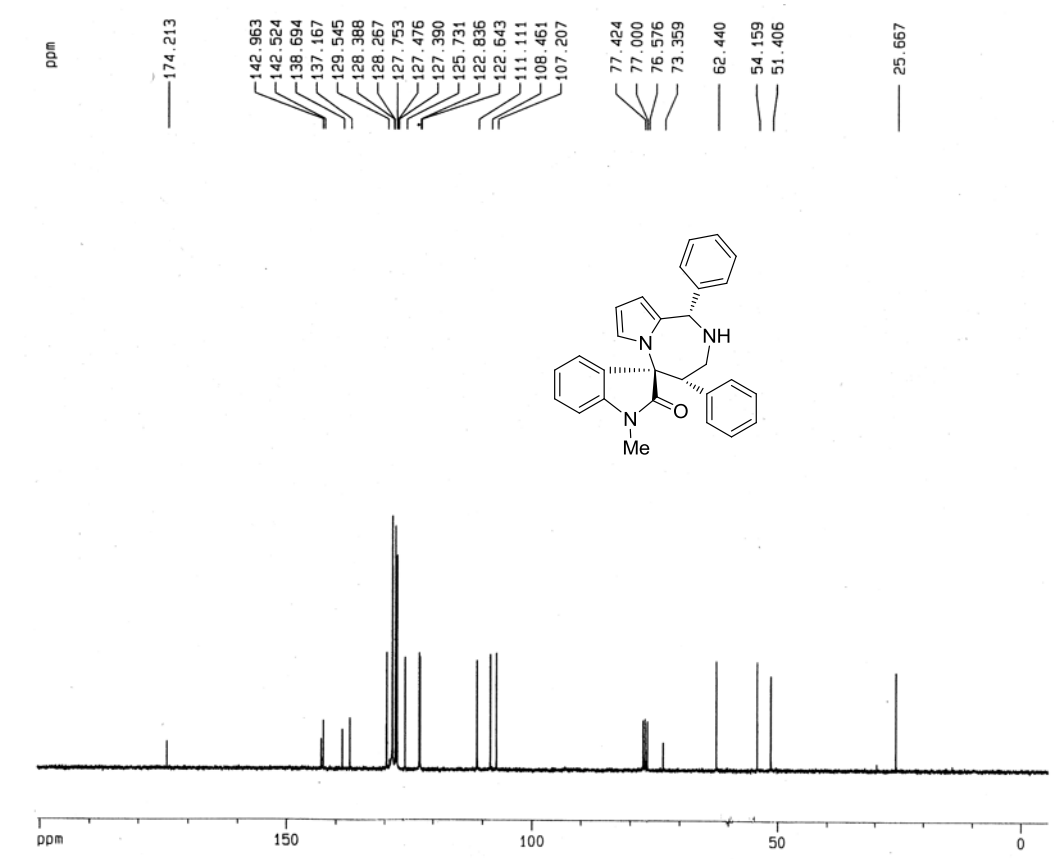

1 Det.A Ch1 / 254nm

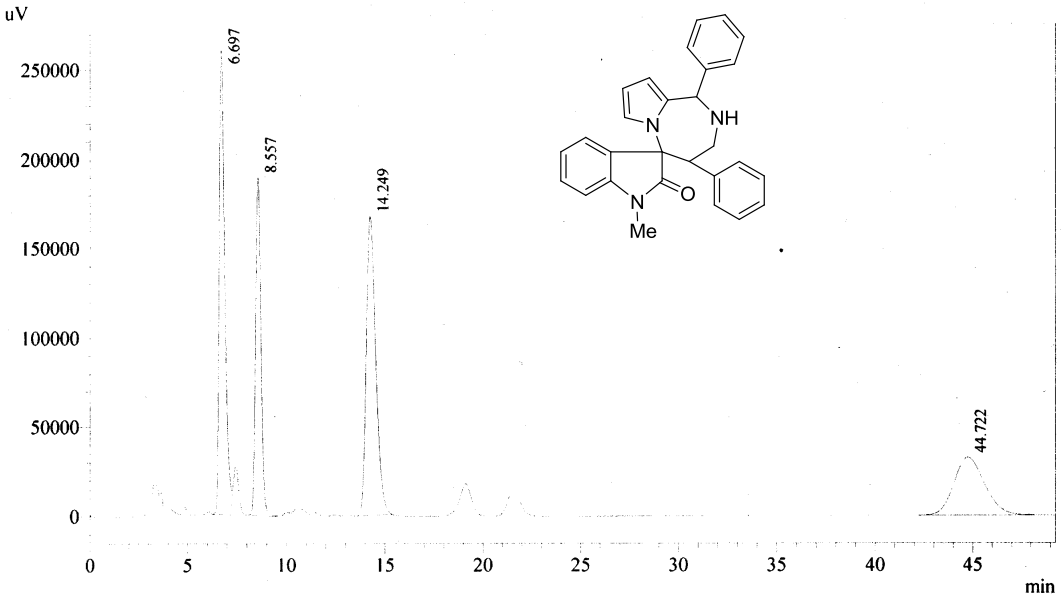
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.408 | 116470 | 5784 | 1.680 | 2.349 |
| 2 | 13.333 | 6643861 | 236416 | 95.806 | 96.019 |
| 3 | 18.356 | 174365 | 4018 | 2.514 | 1.632 |
| Total | | 6934696 | 246218 | 100.000 | 100.000 |

## $^{1}$H NMR, $^{13}$C NMR and HPLC of 15



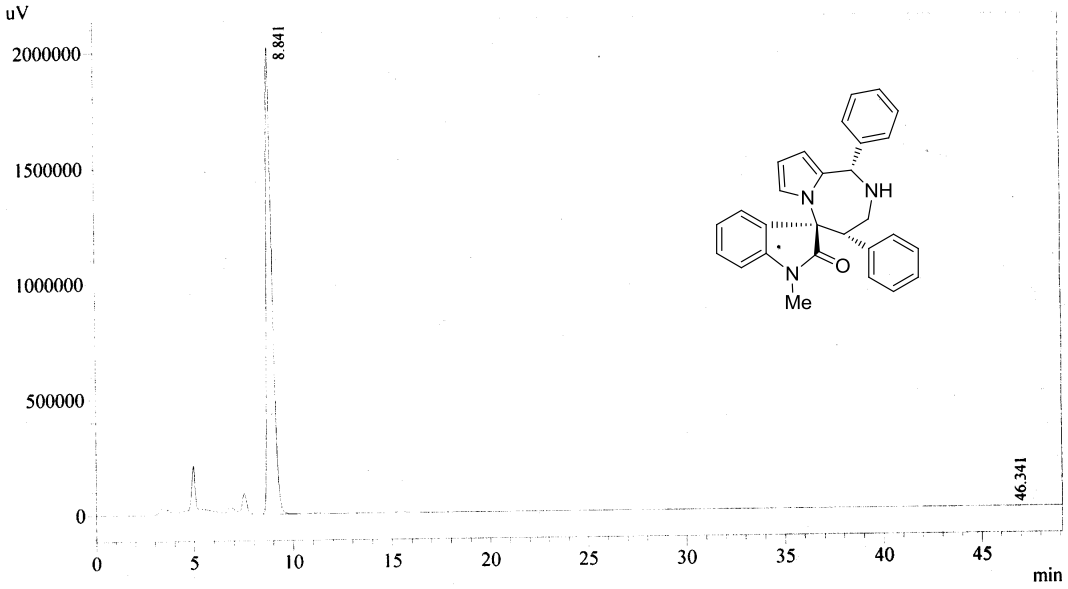






1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

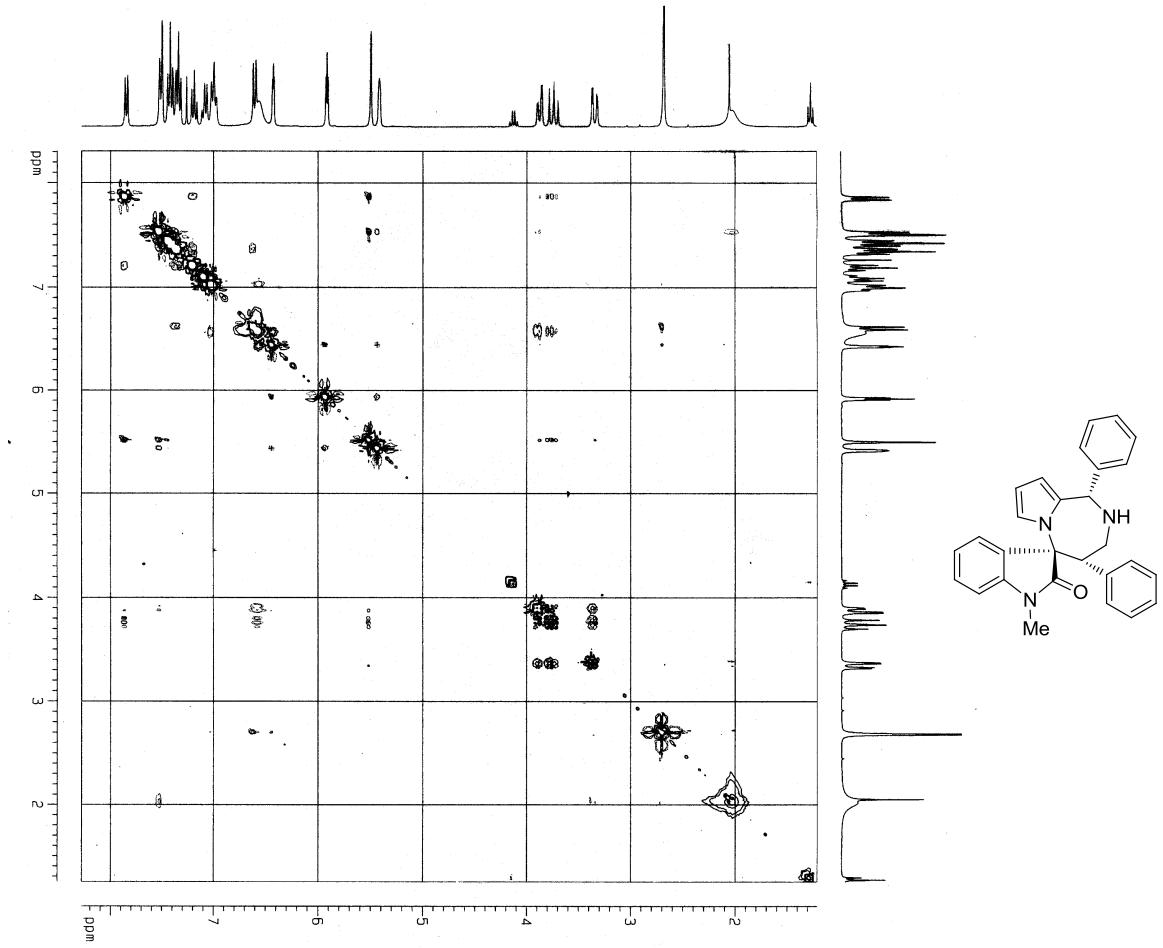
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.697 | 5146541 | 260273 | 28.874 | 40.066 |
| 2 | 8.557 | 3537788 | 189538 | 19.848 | 29.177 |
| 3 | 14.249 | 5605730 | 167607 | 31.450 | 25.801 |
| 4 | 44.722 | 3534017 | 32186 | 19.827 | 4.955 |
| Total | | 17824076 | 649603 | 100.000 | 100.000 |



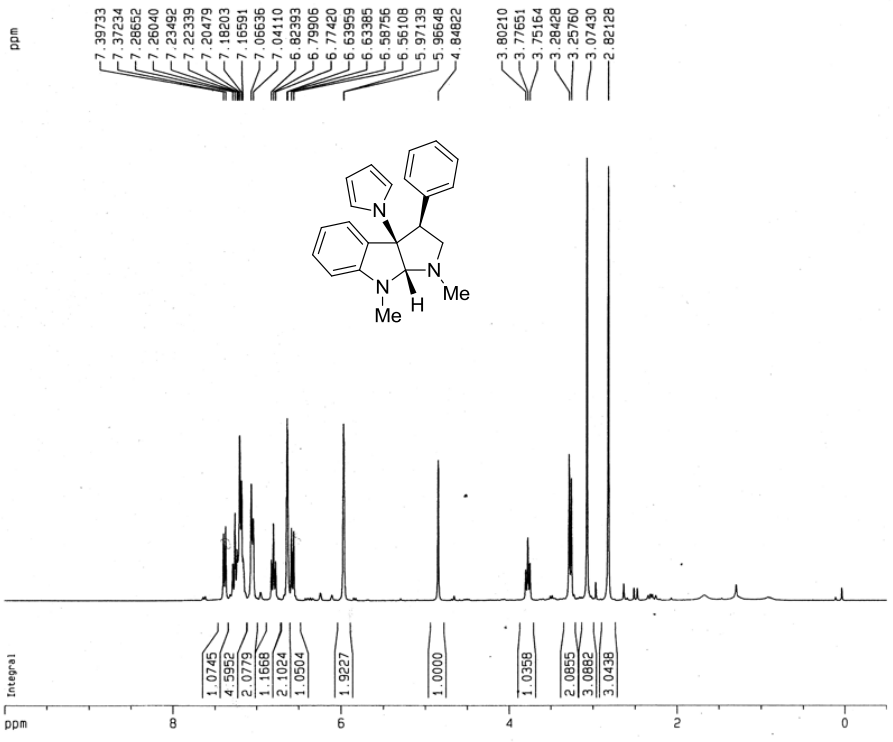

1 Det.A Ch1 / 254nm

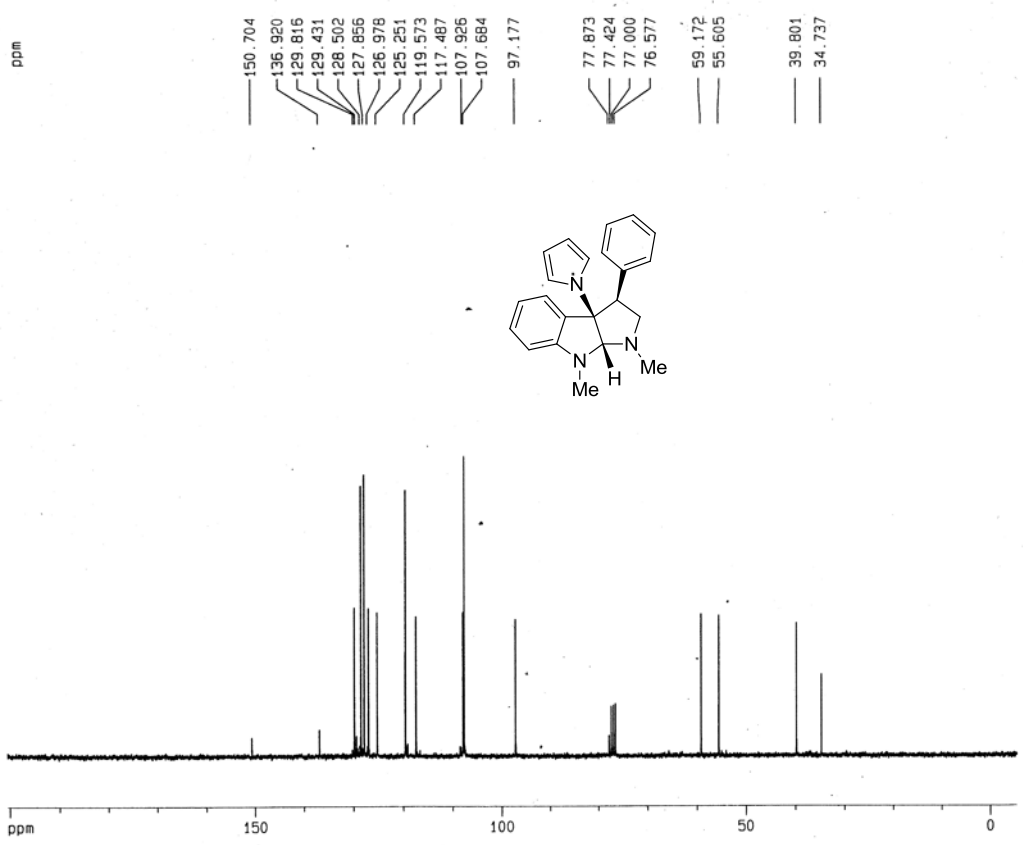
Detector A Ch1 254nm

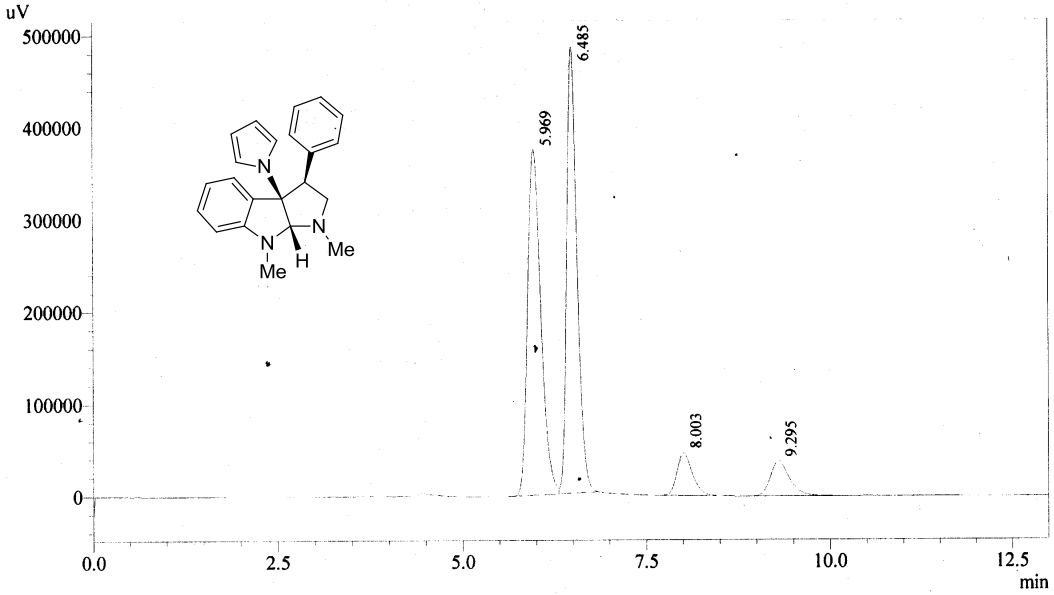
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.841 | 40402291 | 2019565 | 99.943 | 99.985 |
| 2 | 46.341 | 22954 | 311 | 0.057 | 0.015 |
| Total | | 40425245 | 2019876 | 100.000 | 100.000 |




**$^{1}$H NMR, $^{13}$C NMR and HPLC of 17**



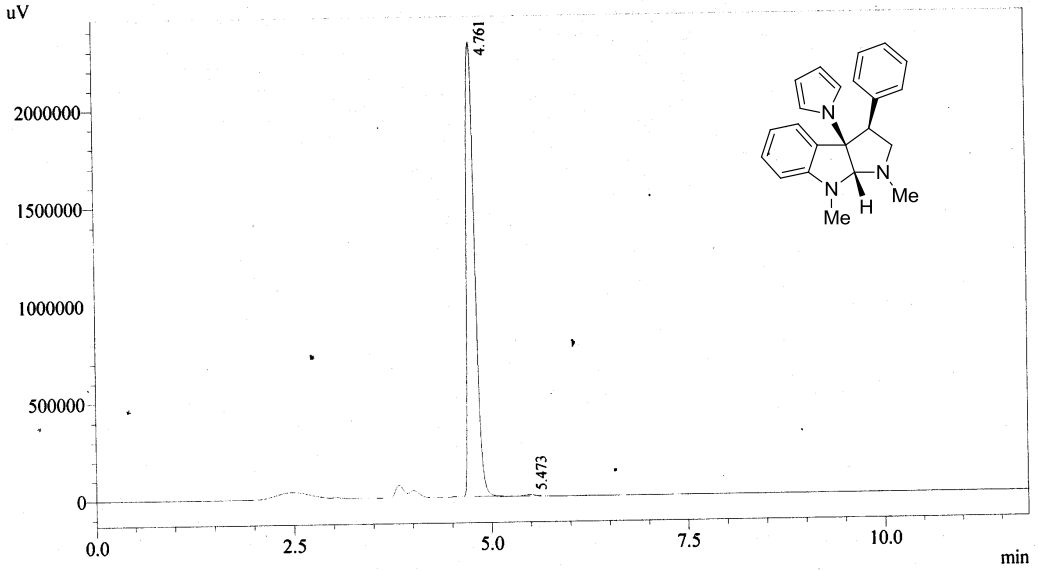



I Det.A Ch1 / 254nm

Detector A Ch1 254nm

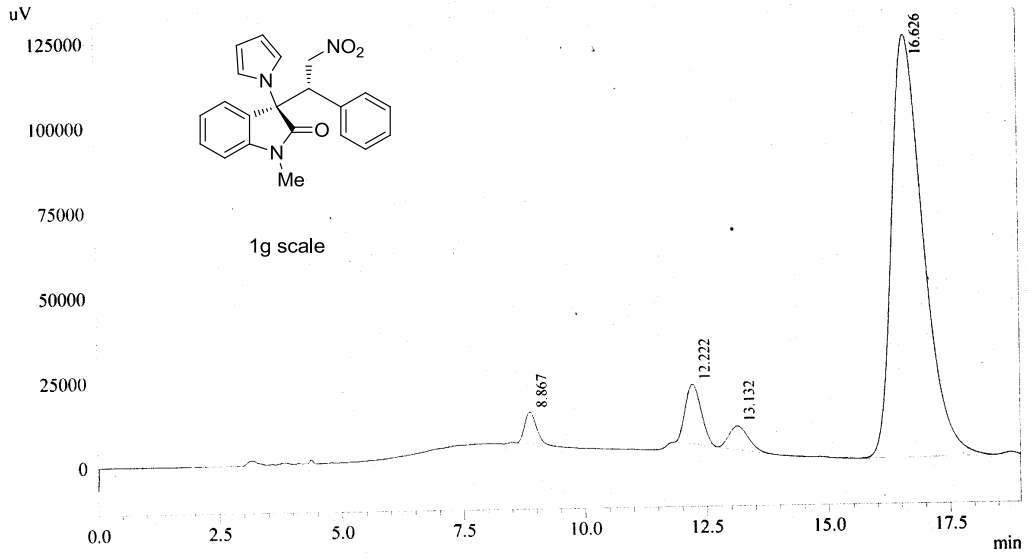
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.969 | 4719465 | 374481 | 43.710 | 39.736 |
| 2 | 6.485 | 4715422 | 483791 | 43.672 | 51.335 |
| 3 | 8.003 | 671397 | 46090 | 6.218 | 4.891 |
| 4 | 9.295 | 690988 | 38066 | 6.400 | 4.039 |
| Total | | 10797271 | 942428 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 4.761 | 17025861 | 2327705 | 99.570 | 99.623 |
| 2 | 5.473 | 73607 | 8813 | 0.430 | 0.377 |
| Total | | 17099468 | 2336518 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.867 | 162591 | 9410 | 2.544 | 5.937 |
| 2 | 12.222 | 400063 | 17645 | 6.259 | 11.132 |
| 3 | 13.132 | 191001 | 6903 | 2.988 | 4.355 |
| 4 | 16.626 | 5637742 | 124540 | 88.208 | 78.575 |
| Total | | 6391398 | 158497 | 100.000 | 100.000 |