

Supporting Information

for

Organocatalytic asymmetric Henry reaction of 1*H*-pyrrole-2,3-diones with bifunctional amine-thiourea catalysts bearing multiple hydrogen-bond donors

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General procedure, analytical data and spectra of all compounds, methods for conversion

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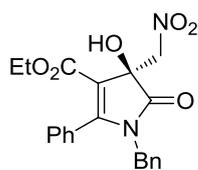
General methods

Reagents were purchased from commercial sources and were used as received unless otherwise mentioned. Reactions were monitored by TLC. ^1H NMR spectra were recorded on Bruker 300 (300 MHz) spectrophotometers. Chemical shifts (δ) are reported from the solvent resonance as the internal standard (CDCl_3 : δ 7.26, $\text{DMSO-}d_6$: δ 2.50). Data are given as follow: s (singlet), d (doublet), t (triplet), q (quadruple) or m (multiples), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl_3 at 77.20 ppm, $\text{DMSO-}d_6$ at 39.51 ppm). Mass spectra were recorded on Bruker micrOTOF-Q II mass spectrometer. HPLC data was acquired using a Shimadzu LC-20A with Daicel AD-H, Daicel OD- H, Daicel IC column.

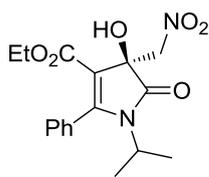
1*H*-Pyrrole-2,3-diones (**1a-s**) were prepared according to the reported procedures [1,2]. All reactions have been carried out with distilled and degassed solvents in oven-dried glassware. All the solvents were treated according to general methods. Column chromatography was performed using silica gel H.

General procedure for synthesis of compounds 4

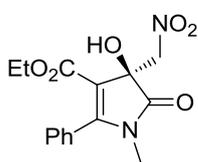
A solution of compounds **1** (0.2 mmol), compounds **2** (2 mmol) and catalyst **3e** (20 mol %) in THF was stirred at 30 °C for the indicated time. Then the reaction mixture was directly charged onto a silica gel column and purified through flash chromatography to furnish the corresponding products **4**.



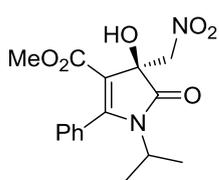
(*S*)-Ethyl 1-benzyl-4-hydroxy-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4a**). Light yellow oil; 48.3 mg, 61% yield; 61% ee; ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.40 (m, 1H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.22-7.13 (m, 3H), 7.08 (d, $J = 7.2$ Hz, 2H), 6.90-6.85 (m, 2H), 5.26 (d, $J = 13.0$ Hz, 1H), 5.09 (d, $J = 13.0$ Hz, 1H), 4.56 (s, 2H), 4.18 (s, 1H), 4.01-3.92 (m, 2H), 0.91 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.5, 162.7, 159.8, 135.5, 130.0, 128.5, 128.4, 128.3, 127.9, 127.6, 127.4, 107.4, 77.2, 74.0, 60.3, 44.6, 13.5; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 9.21$ min, $t_{\text{minor}} = 8.06$ min); $[\alpha]_{\text{D}}^{20} = +21.5$ (c 2.195, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 419.1214; found: 419.1206.



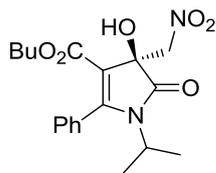
(*S*)-Ethyl 4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4b**). Light yellow oil; 48.0 mg, 69% yield; 71% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.49-7.45 (m, 3H), 7.30 (d, $J = 5.5$ Hz, 1H), 7.23 (d, $J = 6.1$ Hz, 1H), 5.19 (d, $J = 12.8$ Hz, 1H), 4.99 (d, $J = 12.8$ Hz, 1H), 4.00 – 3.89 (m, 3H), 3.63-3.54 (m, 1H), 1.37 (d, $J = 6.9$ Hz, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.5, 162.7, 161.0, 130.0, 129.4, 128.5, 128.3, 128.3, 127.5, 106.6, 77.5, 73.7, 60.2, 47.3, 19.9, 19.0, 13.5; HPLC (Chiralpak OD-H column, *i*-PrOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 7.56$ min, $t_{\text{minor}} = 6.27$ min); $[\alpha]_{\text{D}}^{20} = +18.0$ (*c* 2.200, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 371.1214; found: 371.1204.



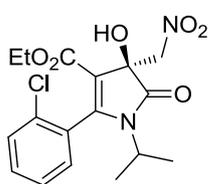
(*S*)-Ethyl 4-hydroxy-1-methyl-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4c**). Light yellow oil; 12.2 mg, 19% yield; 57% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.52-7.45 (m, 3H), 7.33-7.30 (m, 2H), 5.17 (d, $J = 12.8$ Hz, 1H), 5.04 (d, $J = 12.8$ Hz, 1H), 4.11-3.93 (m, 2H), 3.72 (s, 1H), 2.91 (s, 3H), 0.97 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.1, 162.8, 160.0, 130.5, 128.4, 128.4, 128.3, 106.5, 77.8, 74.0, 60.4, 28.0, 13.6; HPLC (Chiralpak OJ-H column, *i*-PrOH/*n*-hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 10.79$ min, $t_{\text{minor}} = 9.93$ min); $[\alpha]_{\text{D}}^{20} = +20.6$ (*c* 0.990, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 343.0901; found: 343.0897.



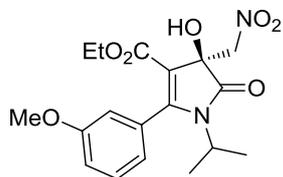
(*S*)-Methyl 4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4d**). Light yellow oil; 36.7 mg, 55% yield; 65% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.52-7.47 (m, 3H), 7.30 (d, $J = 3.6$ Hz, 1H), 7.24 (d, $J = 5.8$ Hz, 1H), 5.17 (d, $J = 12.8$ Hz, 1H), 4.99 (d, $J = 12.8$ Hz, 1H), 3.77 (s, 1H), 3.62-3.55 (m, 1H), 3.52 (s, 3H), 1.38 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.5, 163.0, 161.5, 130.2, 129.1, 128.7, 128.5, 128.2, 127.4, 106.2, 77.6, 73.7, 51.3, 47.4, 19.9, 19.0; HPLC (Chiralpak AD-H column, *i*-PrOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 16.06$ min, $t_{\text{minor}} = 14.68$ min); $[\alpha]_{\text{D}}^{20} = +21.5$ (*c* 2.195, CHCl_3); $[\alpha]_{\text{D}}^{20} = +2.4$ (*c* 2.150, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 357.1057; found: 357.1056.



(*S*)-Butyl 4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4e**). Colourless oil; 39.1 mg, 52% yield; 70% ee; $^1\text{H NMR}$ (300 MHz, DMSO) δ 7.52 (s, 3H), 7.38 (s, 1H), 7.10 (s, 1H), 6.75 (s, 1H), 5.13 (d, $J = 12.8$ Hz, 1H), 5.05 (d, $J = 12.8$ Hz, 1H), 3.80 (t, $J = 6.1$ Hz, 2H), 3.47-3.37 (m, 1H), 1.29 (d, $J = 6.8$ Hz, 3H), 1.22-1.14 (m, 5H), 0.99-0.89 (m, 2H), 0.72 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 176.3, 161.8, 159.4, 130.0, 129.7, 128.6 (d, $J = 6.6$ Hz), 127.8 (d, $J = 10.1$ Hz), 107.3, 77.7, 73.4, 62.9, 46.3, 29.9, 19.6, 19.0, 18.5, 13.5; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 6.16$ min, $t_{\text{minor}} = 5.22$ min); $[\alpha]_{\text{D}}^{20} = +11.3$ (c 1.995, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 399.1527; found: 399.1521.

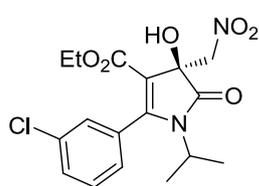


(*S*)-Ethyl 2-(2-chlorophenyl)-4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4f**). Light yellow oil; 40.5 mg, 53% yield; 54:46 dr, 73/60% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.52-7.38 (m, 3H), 7.29-7.26 (m, 1H), 5.12 (d, $J = 12.3$ Hz, 1H), 4.99 (d, $J = 12.3$ Hz, 1H), 3.98 (q, $J = 7.1$ Hz, 2H), 3.72 (s, 1H), 3.49-3.39 (m, 1H), 1.47 (d, $J = 6.9$ Hz, 3H), 1.32 (d, $J = 6.9$ Hz, 3H), 0.91 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.1, 162.3, 157.8, 133.2, 131.4, 129.8, 129.4, 129.1, 126.8, 107.6, 77.4, 73.9, 60.3, 47.9, 20.0, 19.3, 13.6; HPLC (Chiralpak AD-H column, *i*-PrOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm, $t_{\text{major}} = 16.63$ min, $t_{\text{minor}} = 15.88$ min; $t_{\text{major}} = 13.63$ min, $t_{\text{minor}} = 14.88$ min); $[\alpha]_{\text{D}}^{20} = +37.4$ (c 1.345, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 405.0824; found: 405.0819.



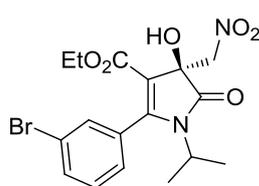
(*S*)-Ethyl 4-hydroxy-1-isopropyl-2-(3-methoxyphenyl)-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4g**). Light yellow oil; 55.2 mg, 73% yield; 71% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.42-7.35 (m, 1H), 7.04-7.00 (m, 1H), 6.88-6.74 (m, 2H), 5.16 (d, $J = 12.8$ Hz, 1H), 4.98 (d, $J = 12.8$ Hz, 1H), 4.00-3.94 (m, 2H), 3.83 (s, 3H), 3.72 (s, 1H), 3.64-3.55 (m, 1H), 1.38 (d, $J = 6.9$ Hz, 3H), 1.35 (d, $J = 6.9$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.4, 162.7, 160.8, 159.5 (d, $J = 8.2$ Hz), 130.5, 129.7 (d, $J = 11.3$ Hz), 120.1 (d, $J = 60.4$ Hz), 115.6 (d, $J = 17.1$ Hz), 113.5 (d, $J = 40.7$ Hz), 106.4, 77.6, 73.7, 60.2, 55.4, 47.4, 20.0,

19.1, 13.6. ¹³C NMR (100 MHz, DMSO, 60 °C) δ 176.6, 162.0, 159.7, 131.7, 130.4, 130.4, 120.4, 115.6, 114.1, 108.0, 78.1, 73.9, 59.5, 55.8, 46.8, 20.0, 19.5, 14.0; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, *t*_{major} = 7.87 min, *t*_{minor} = 6.55 min); [α]_D²⁰ = +14.8 (*c* 2.510, CHCl₃); HRMS (ESI-TOF) calcd for C₁₈H₂₂N₂NaO₇ [M + Na]⁺ 401.1319; found: 401.1313.



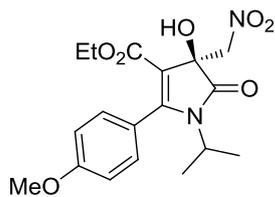
(*S*)-Ethyl 2-(3-chlorophenyl)-4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4h**).
Light yellow oil; 35.9 mg, 47% yield; 71% ee; ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.43 (m, 2H), 7.30 (d, *J* = 22.4 Hz, 1H),

7.17 (dd, *J* = 18.9, *J* = 7.3 Hz, 1H), 5.17 (d, *J* = 12.9 Hz, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 4.02-3.93 (m, 2H), 3.70 (d, *J* = 5.6 Hz, 1H), 3.62-3.53 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.36 (d, *J* = 6.9 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.2, 162.5, 159.2, 134.7 (d, *J* = 13.7 Hz), 131.0 (d, *J* = 3.9 Hz), 130.3 (d, *J* = 1.9 Hz), 129.9 (d, *J* = 13.7 Hz), 128.2 (d, *J* = 58.4 Hz), 126.1 (d, *J* = 56.8 Hz), 107.08, 77.5, 73.7, 60.4, 47.6, 20.0, 19.2 (d, *J* = 3.7 Hz), 13.6; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, *t*_{major} = 7.64 min, *t*_{minor} = 6.58 min); [α]_D²⁰ = +15.6 (*c* 1.985, CHCl₃); HRMS (ESI-TOF) calcd for C₁₇H₁₉ClN₂NaO₆ [M + Na]⁺ 405.0824; found: 405.0817.

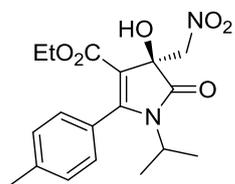


(*S*)-Ethyl 2-(3-bromophenyl)-4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4i**).
Light yellow oil; 37.5 mg, 44% yield; 70% ee; ¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.40-

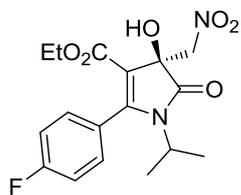
7.33 (m, 1H), 7.21 (dd, *J* = 21.2, *J* = 7.7 Hz, 1H), 5.18 (d, *J* = 13.0 Hz, 1H), 4.98 (d, *J* = 13.0 Hz, 1H), 4.03-3.92 (m, 2H), 3.86 (s, 1H), 3.62- 3.53 (m, 1H) 1.39 (d, *J* = 6.9 Hz, 3H), 1.35 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.6, 162.3, 158.9, 133.0 (d, *J* = 4.2 Hz), 131.3 (d, *J* = 5.3 Hz), 130.9 (d, *J* = 33.3 Hz), 130.0 (d, *J* = 11.9 Hz), 126.4 (d, *J* = 35.5 Hz), 122.3 (d, *J* = 11.8 Hz), 107.3, 77.2, 73.6, 60.2, 47.4, 19.8 (d, *J* = 5.0 Hz), 19.0 (d, *J* = 5.0 Hz), 13.4; HPLC (Chiralpak AD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, *t*_{major} = 8.24 min, *t*_{minor} = 7.59 min); [α]_D²⁰ = +10.8 (*c* 1.845, CHCl₃); HRMS (ESI-TOF) calcd for C₁₇H₁₉BrN₂NaO₆ [M + Na]⁺ 449.0319; found: 449.0305.



(*S*)-Ethyl 4-hydroxy-1-isopropyl-2-(4-methoxyphenyl)-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4j**). Light yellow oil; 46.1 mg, 61% yield; 72% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.26-7.18 (m, 2H), 6.99 (d, $J = 8.2$ Hz, 2H), 5.14 (d, $J = 12.6$ Hz, 1H), 4.98 (d, $J = 12.6$ Hz, 1H), 4.07-3.95 (m, 2H), 3.86 (s, 3H), 3.70- 3.61 (m, 2H), 1.39 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.4, 162.9, 161.3, 161.0, 130.2, 129.1, 121.0, 113.9, 106.3, 77.8, 73.7, 60.2, 55.3, 47.2, 19.9, 19.0, 13.8; HPLC (Chiralpak AD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 10.51$ min, $t_{\text{minor}} = 12.42$ min); $[\alpha]_{\text{D}}^{20} = +6.0$ (c 2.250, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaO}_7$ $[\text{M} + \text{Na}]^+$ 401.1319; found: 401.1311.

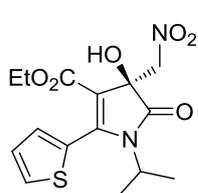


(*S*)-Ethyl 4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-2-(*p*-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4k**). Colourless oil; 46.3 mg, 64% yield; 69% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.29- 7.26 (m, 2H), 7.19-7.12 (m, 2H), 5.15 (d, $J = 12.7$ Hz, 1H), 4.98 (d, $J = 12.7$ Hz, 1H), 4.05-3.94 (m, 2H), 3.66- 3.57 (m, 2H), 2.42 (s, 3H), 1.38 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H), 0.97 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.4, 162.8, 161.6, 140.4, 129.2, 129.1, 128.4, 127.4, 126.2, 106.3, 77.7, 73.7, 60.2, 47.2, 21.5, 19.9, 19.0, 13.7; HPLC (Chiralpak OD-H column, *i*-PrOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 6.89$ min, $t_{\text{minor}} = 5.92$ min); $[\alpha]_{\text{D}}^{20} = +11.3$ (c 2.595, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 385.1370; found: 385.1363.

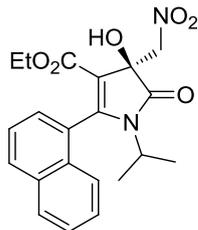


(*S*)-Ethyl 2-(4-fluorophenyl)-4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4l**). Light yellow oil; 53.4 mg, 73% yield; 70% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.30-7.15 (m, 4H), 5.17 (d, $J = 12.8$ Hz, 1H), 4.98 (d, $J = 12.8$ Hz, 1H), 4.04-3.93 (m, 2H), 3.78 (s, 1H), 3.60-3.54 (m, 1H), 1.38 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.35, 164.0 (d, $J = 204.4$ Hz), 162.0, 160.0, 130.7 (d, $J = 8.5$ Hz), 129.8 (d, $J = 8.6$ Hz), 125.2 (d, $J = 3.7$ Hz), 116.0 (d, $J = 9.7$ Hz), 115.7 (d, $J = 9.8$ Hz), 107.1, 77.6, 73.7, 60.3, 47.3, 20.0, 19.1, 13.6; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 6.24$ min, $t_{\text{minor}} =$

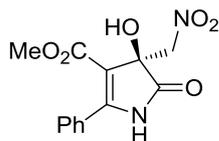
5.69 min); $[\alpha]_D^{20} = +12.4$ (*c* 1.320, CHCl₃); HRMS (ESI-TOF) calcd for C₁₇H₁₉FN₂NaO₆ [M + Na]⁺ 389.1119; found: 389.1114.



(*S*)-Ethyl 4-hydroxy-1-isopropyl-4-(nitromethyl)-5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4m**). Light yellow oil; 36.1 mg, 51% yield; 71% ee; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (dd, *J* = 4.2 Hz, *J* = 2.1 Hz, 1H), 7.17-7.14 (m, 2H), 5.13 (d, *J* = 12.9 Hz, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 4.09-4.00 (m, 2H), 3.77-3.70 (m, 1H), 3.52 (s, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.7, 162.6, 154.0, 130.3, 129.1 (d, *J* = 2.6 Hz), 127.7, 127.3 (d, *J* = 2.1 Hz), 109.5, 77.6, 73.8, 60.5, 47.5, 20.0, 19.1, 13.7; HPLC (Chiralpak AD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, *t*_{major} = 8.78 min, *t*_{minor} = 8.03 min); $[\alpha]_D^{20} = -3.9$ (*c* 1.000, CHCl₃); HRMS (ESI-TOF) calcd for C₁₅H₁₈N₂NaO₆S [M + Na]⁺ 377.0778; found: 377.0772.

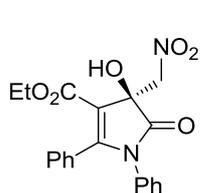


(*S*)-Ethyl 4-hydroxy-1-isopropyl-2-(naphthalen-1-yl)-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4n**). Light yellow oil; 59.7 mg, 75% yield; 53:47 dr, 51/49% ee; ¹H NMR (300 MHz, CDCl₃) δ 8.00- 7.92 (m, 2H), 7.75-7.72 (m, 1H), 7.58-7.53 (m, 3H), 7.37-7.35 (m, 1H), 5.25 (d, *J* = 12.9 Hz, 1H), 5.07 (d, *J* = 12.9 Hz, 1H), 3.85 (s, 1H), 3.82-3.72 (m, 2H), 3.37-3.33 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H), 0.53 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.4, 162.8, 160.1, 133.1, 130.4, 130.3, 128.6, 127.4, 127.0, 126.7, 126.4, 125.1, 124.1, 108.2, 77.5, 73.9, 60.0, 47.7, 20.0, 19.1, 13.1; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 3/97, flow rate 1.0 mL/min, λ = 254 nm, *t*_{major} = 14.89 min, *t*_{minor} = 11.64 min; *t*_{major} = 17.12 min, *t*_{minor} = 13.33 min); $[\alpha]_D^{20} = +6.0$ (*c* 1.955, CHCl₃); HRMS (ESI-TOF) calcd for C₂₁H₂₂N₂NaO₆ [M + Na]⁺ 421.1370; found: 421.1358.

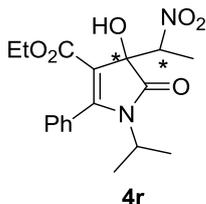


(*S*)-Methyl 4-hydroxy-4-(nitromethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4o**). Light yellow oil; 23.9 mg, 41% yield; 48% ee; ¹H NMR (300 MHz, CDCl₃) δ 8.10 (s, 1H), 7.56-7.43 (m, 5H), 5.14 (d, *J* = 12.9 Hz, 1H), 4.98 (d, *J* = 12.9 Hz, 1H), 3.94 (s, 1H), 3.67 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.2, 163.3, 156.2, 131.7, 128.6, 128.5, 128.4, 105.2, 77.5, 75.3, 51.6; HPLC (Chiralpak AD-H column,

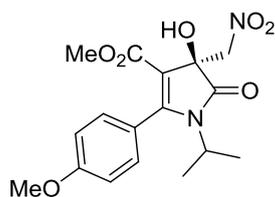
i-PrOH/*n*-hexane = 20/80, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 10.15$ min, $t_{\text{minor}} = 9.29$ min); $[\alpha]_{\text{D}}^{20} = +12.0$ (c 1.135, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 315.0588; found: 315.0584.



(*S*)-Ethyl 4-hydroxy-4-(nitromethyl)-5-oxo-1,2-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4p**). Light yellow oil; 32.1 mg, 42% yield; 29% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.30-7.22 (m, 6H), 7.18 -7.15 (m, 2H), 7.05-7.02 (m, 2H), 5.29 (d, $J = 13.0$ Hz, 1H), 5.12 (d, $J = 13.0$ Hz, 1H), 4.09 (m, 2H), 3.76 (s, 1H), 1.03 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 174.3, 163.1, 159.6, 133.1, 130.2, 129.2, 129.1, 128.4, 128.2, 127.8, 127.7, 106.7, 78.0, 74.2, 60.7, 13.7; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 9.95$ min, $t_{\text{minor}} = 8.77$ min); $[\alpha]_{\text{D}}^{20} = +8.7$ (c 1.645, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 405.1057; found: 405.1045.

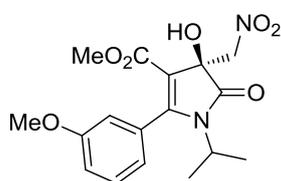


Ethyl 4-hydroxy-1-isopropyl-4-(1-nitroethyl)-5-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4q**). Light yellow oil; 16.7 mg, 23% yield; 94:6 dr, 22% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.50-7.44 (m, 3H), 7.26 -7.20 (m, 2H), 5.37 (q, $J = 7.0$ Hz, 1H), 3.98-3.91 (m, 2H), 3.80 (s, 1H), 3.60-3.50 (m, 1H), 1.87 (d, $J = 7.0$ Hz, 3H), 1.36 (d, $J = 0.9$ Hz, 3H), 1.34 (d, $J = 0.9$ Hz, 3H), 0.88 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 174.1, 163.0, 160.2, 130.0, 129.4, 128.6, 128.5, 128.3, 127.2, 106.7, 86.8, 75.2, 60.2, 47.2, 20.0, 19.0, 13.5, 12.6; HPLC (Chiralpak AD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 7.74$ min, $t_{\text{minor}} = 5.56$ min); $[\alpha]_{\text{D}}^{20} = -2.5$ (c 1.470, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 385.1370; found: 385.1373.



(*S*)-Methyl 4-hydroxy-1-isopropyl-2-(4-methoxyphenyl)-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (**4r**). Light yellow oil; 37.1 mg, 51% yield; 69% ee; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.26-7.17 (m, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 5.14 (d, $J = 12.7$ Hz, 1H), 4.97 (d, $J = 12.7$ Hz, 1H), 3.86 (s, 3H), 3.69 (s, 1H), 3.68-3.60 (m, 1H), 3.56 (s, 3H), 1.38 (d, $J = 6.9$ Hz, 3H), 1.34 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 175.5, 163.2, 161.7, 161.0, 130.1, 129.1, 120.8, 114.0, 106.1, 77.7, 73.7, 55.3, 51.3, 47.2, 19.9, 19.0; HPLC (Chiralpak

AD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{major}} = 10.22$ min, $t_{\text{minor}} = 12.03$ min); $[\alpha]_{\text{D}}^{20} = +8.2$ (c 1.780, CHCl_3); HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_7$ $[\text{M} + \text{Na}]^+$ 387.1163; found: 387.1159.



(*S*)-Methyl 4-hydroxy-1-isopropyl-2-(3-methoxyphenyl)-4-(nitromethyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate

(**4s**). Light yellow oil; 51.7 mg, 71% yield; 58% ee; $^1\text{H NMR}$

(**300 MHz, CDCl_3**) δ 7.40-7.37 (m, 1H), 7.05-7.01 (m, 1H),

6.88-6.74 (m, 2H), 5.16 (d, $J = 12.8$ Hz, 1H), 4.98 (d, $J = 12.8$ Hz, 1H), 3.84 (s, 3H),

3.67 (s, 1H), 3.62-3.53 (m, 4H), 1.36 (t, $J = 7.6$ Hz, 6H). $^{13}\text{C NMR}$ (**75 MHz, CDCl_3**)

δ 175.4, 163.0, 161.2, 159.6 (d, $J = 9.4$ Hz), 130.3, 129.9 (d, $J = 11.7$ Hz), 120.0 (d, $J = 57.2$ Hz),

115.7 (d, $J = 16.0$ Hz), 113.4 (d, $J = 36.5$ Hz), 106.1, 77.6, 73.7, 55.4,

51.4, 47.4, 19.9, 19.1 $^{13}\text{C NMR}$ (**101 MHz, DMSO, 60 °C**) δ 176.6, 162.4, 159.9,

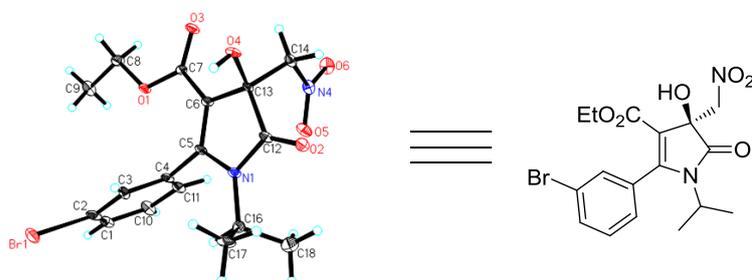
159.6, 131.5, 130.5, 120.4, 115.7, 114.0, 107.7, 78.2, 73.9, 55.8, 51.1, 46.8, 20.0,

19.5; HPLC (Chiralpak OD-H column, EtOH/*n*-hexane = 10/90, flow rate 1.0 mL/min,

$\lambda = 254$ nm, $t_{\text{major}} = 7.86$ min, $t_{\text{minor}} = 7.19$ min); $[\alpha]_{\text{D}}^{20} = +16.4$ (c 1.340, CHCl_3);

HRMS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_7$ $[\text{M} + \text{Na}]^+$ 387.1163; found: 387.1130.

Crystal data for **4i**



Crystal data and structure refinement for **4i**: (CDCC number: CCDC 1435541)

Identification code mo_zm12_0m

Empirical formula $\text{C}_{17}\text{H}_{19}\text{BrN}_2\text{O}_6$

Formula weight 427.25

Temperature 100(2) K

Wavelength 0.71073 Å

Crystal system, space group Triclinic, P 1

Unit cell dimensions $a = 9.380(4)$ Å $\alpha = 94.969(6)$ deg.

$b = 9.756(4)$ Å $\beta = 90.378(6)$ deg.

$c = 10.518(5)$ Å $\gamma = 103.743(6)$ deg.

Volume $931.1(7)$ Å³

Z, Calculated density 2, 1.524 Mg/m³

Absorption coefficient 2.243 mm⁻¹

F(000) 436

Crystal size $0.74 \times 0.26 \times 0.05$ mm

Theta range for data collection 1.94 to 28.35 deg.

Limiting indices $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-13 \leq l \leq 14$

Reflections collected / unique $11667 / 8465$ [$R(\text{int}) = 0.0527$]

Completeness to theta = 28.35 98.4 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.8961 and 0.2876

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters $8465 / 27 / 476$

Goodness-of-fit on F^2 1.004

Final R indices [$I > 2\sigma(I)$] $R1 = 0.0742$, $wR2 = 0.1870$

R indices (all data) $R1 = 0.1035$, $wR2 = 0.2053$

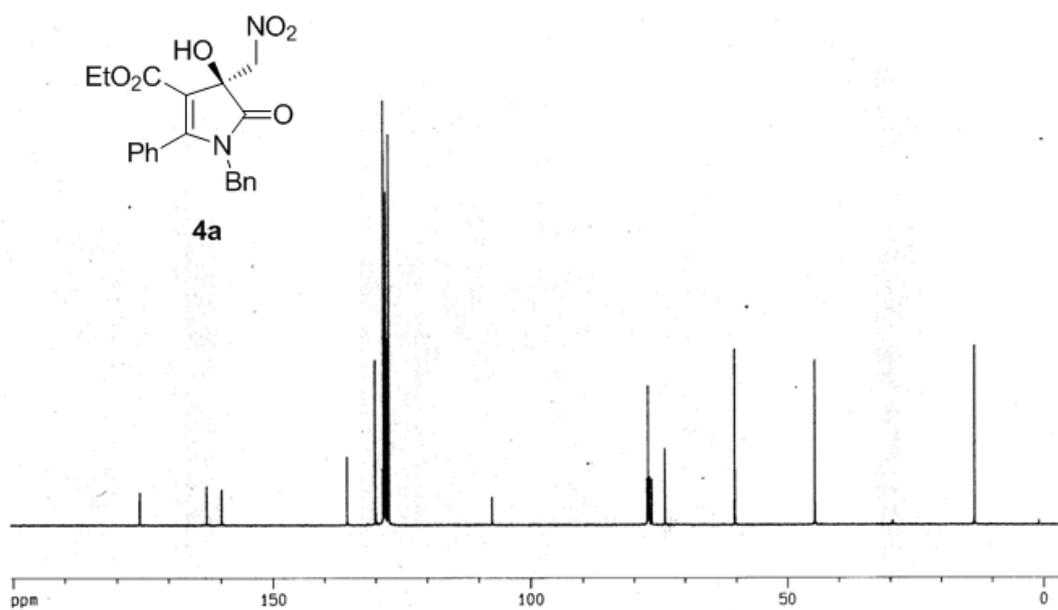
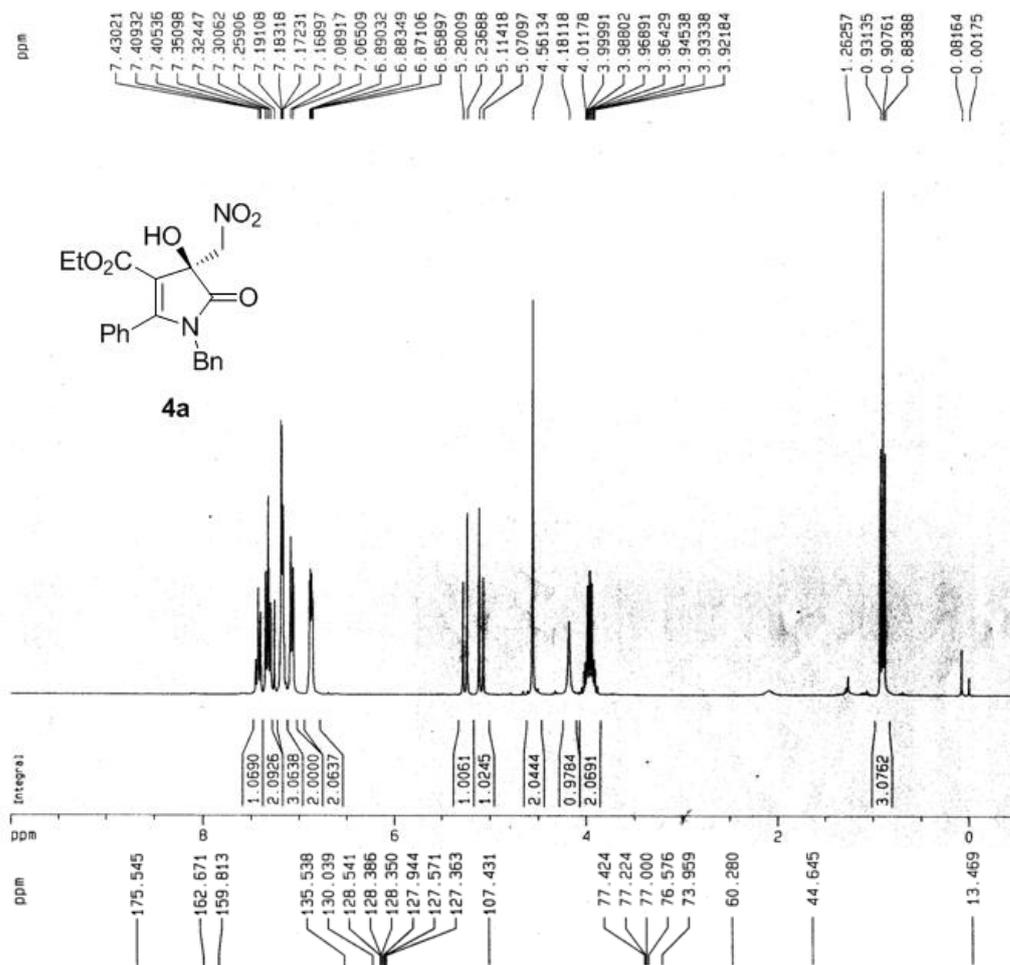
Absolute structure parameter 0.054 (13)

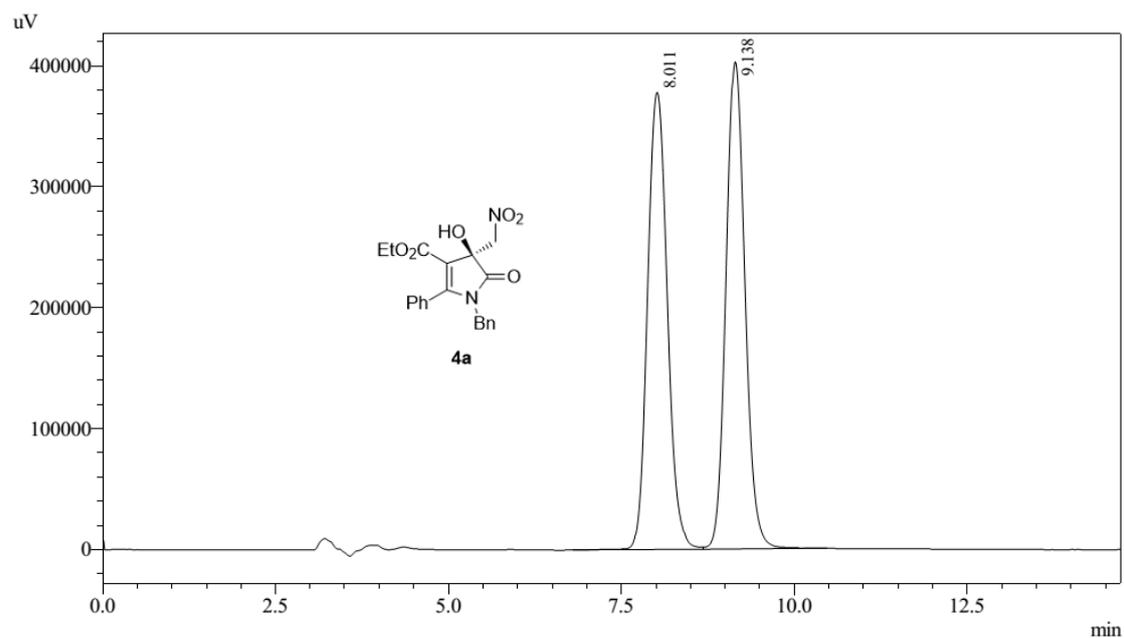
Largest diff. peak and hole 2.249 and -1.301 e.Å⁻³

References

1. Sano, T.; Horiguchi, Y.; Toda, J.; Imafuku, K.; Tsuda, Y. *Chem. Pharm. Bull.* **1984**, *32*, 497-503. doi.org/10.1248/cpb.32.497
2. Zheng, H.-J.; Chen, W.-B.; Wu, Z.-J.; Deng, J.-G.; Lin, W.-Q.; Yuan, W.-C.; Zhang, X.-M. *Chem. - Eur. J.* **2008**, *14*, 9864-9867. doi: 10.1002/chem.200801582

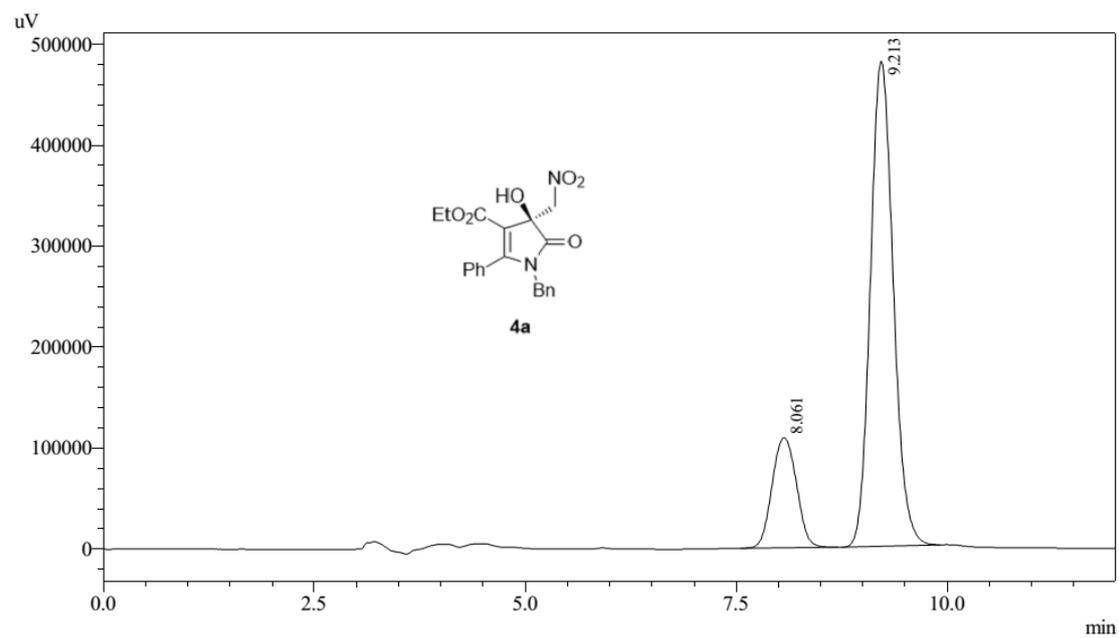
Copies of NMR and HPLC Spectra for compounds 4





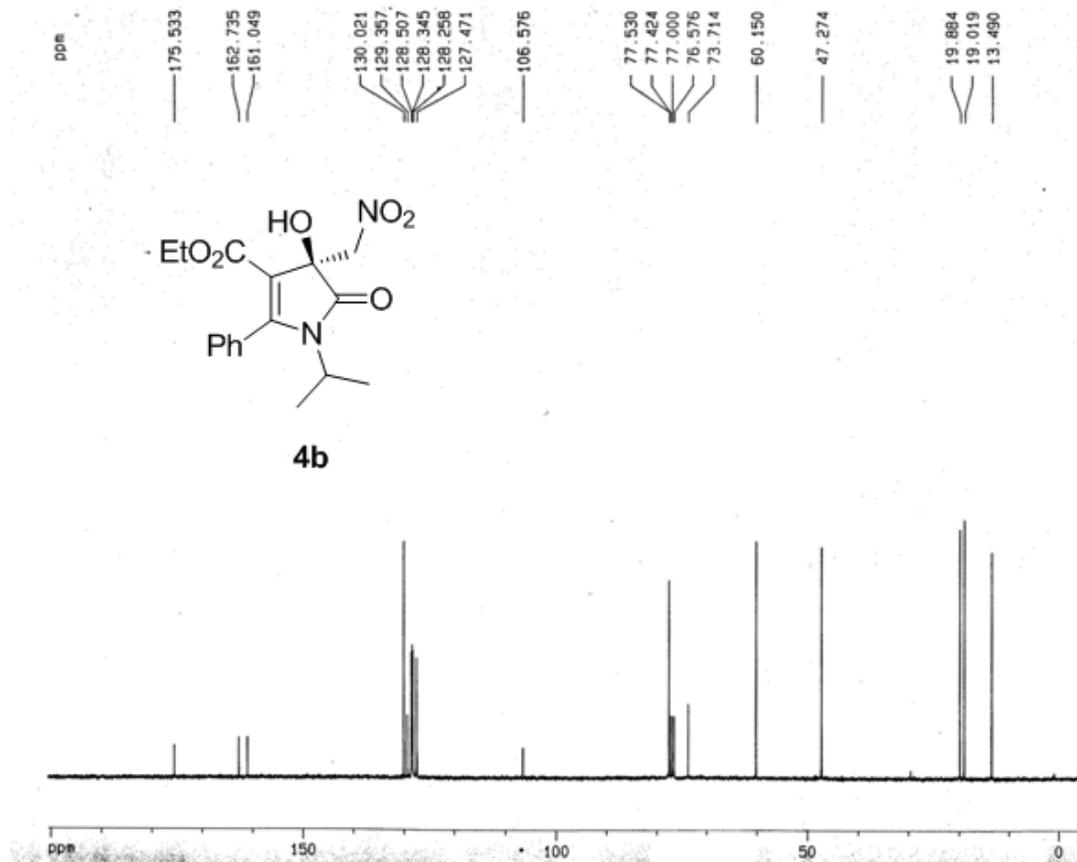
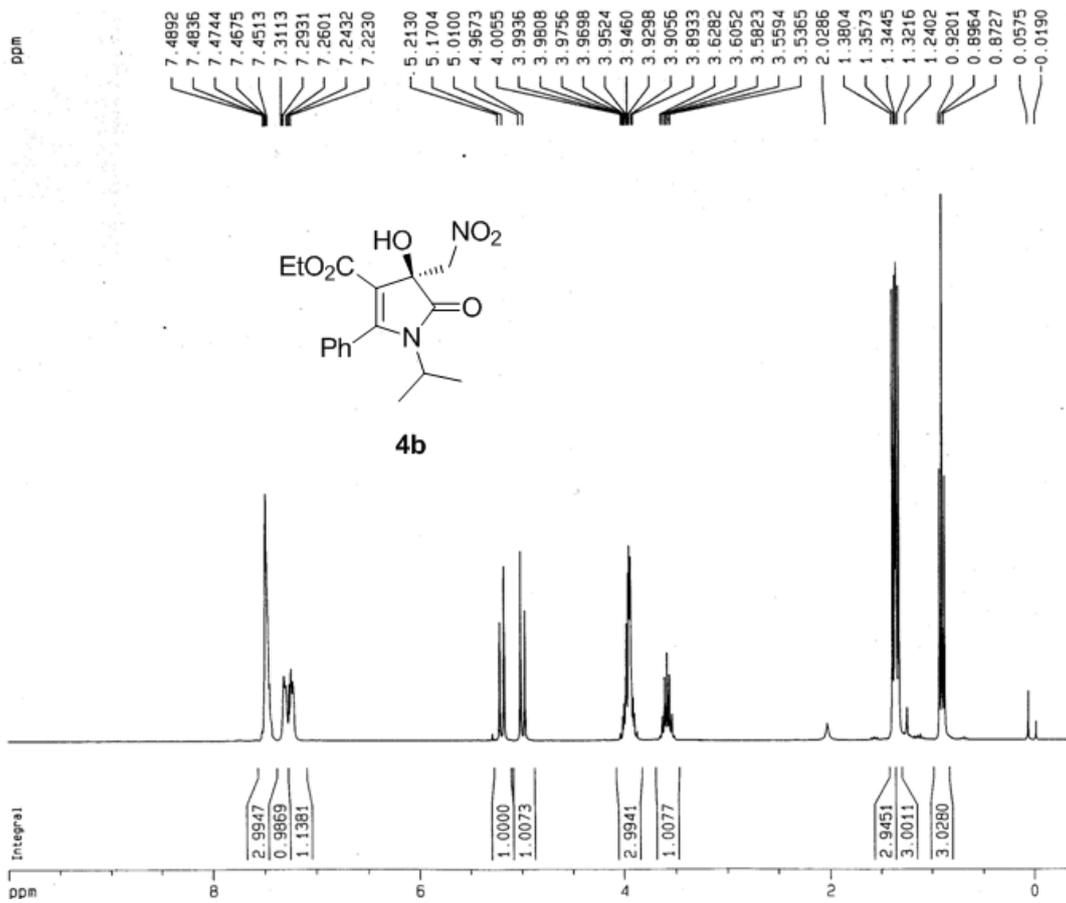
Detector A Ch1 254nm

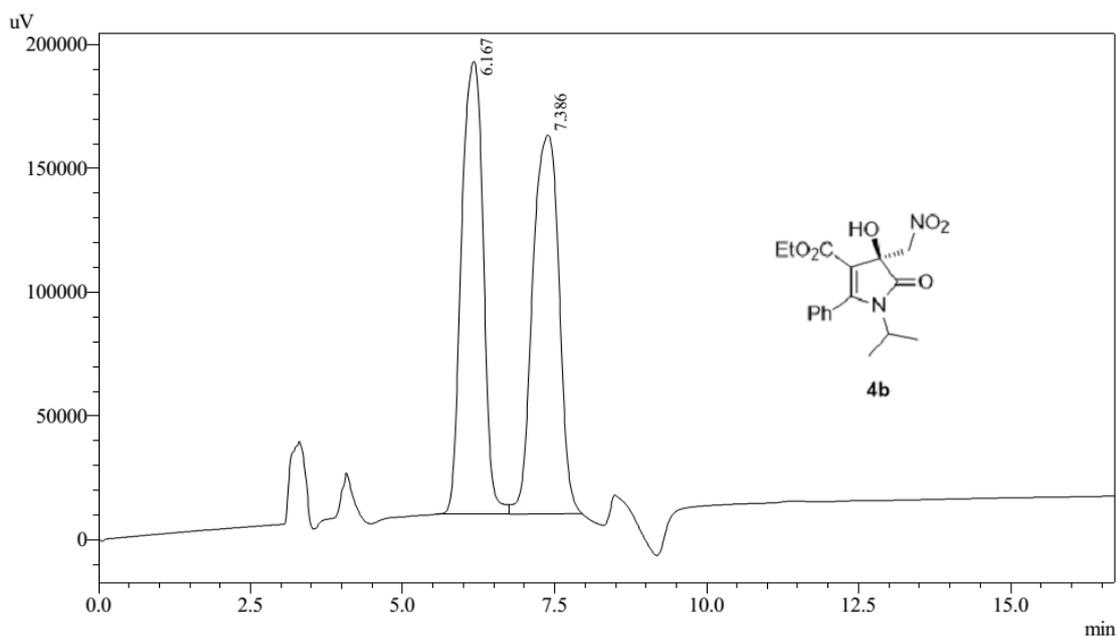
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Total		15249144	781599	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.061	2187534	109009	19.457	18.480
2	9.213	9055527	480864	80.543	81.520
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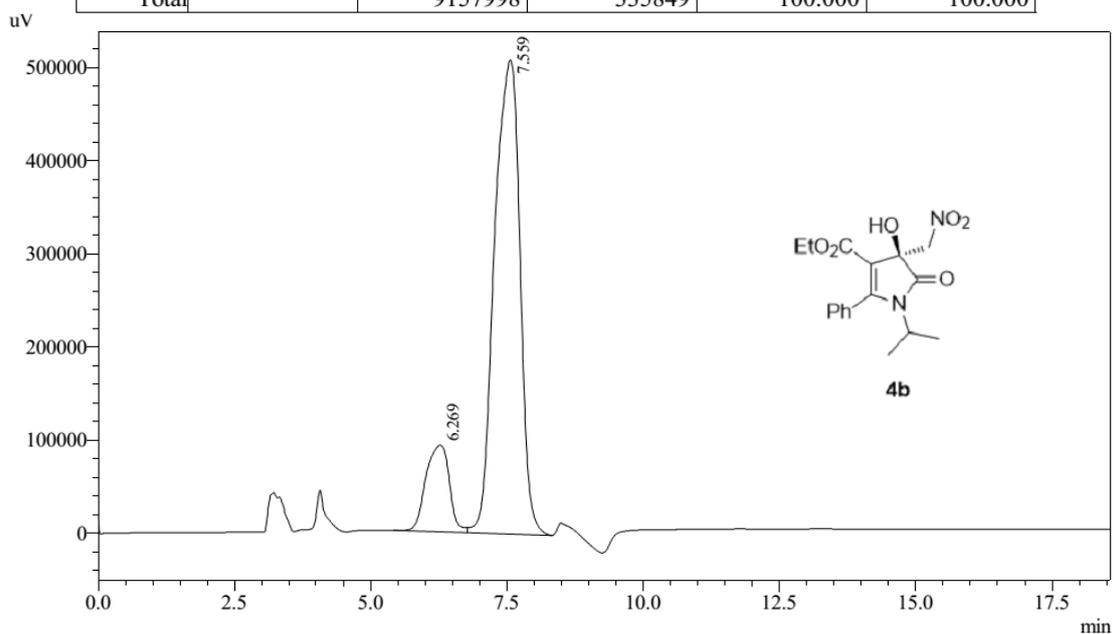




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

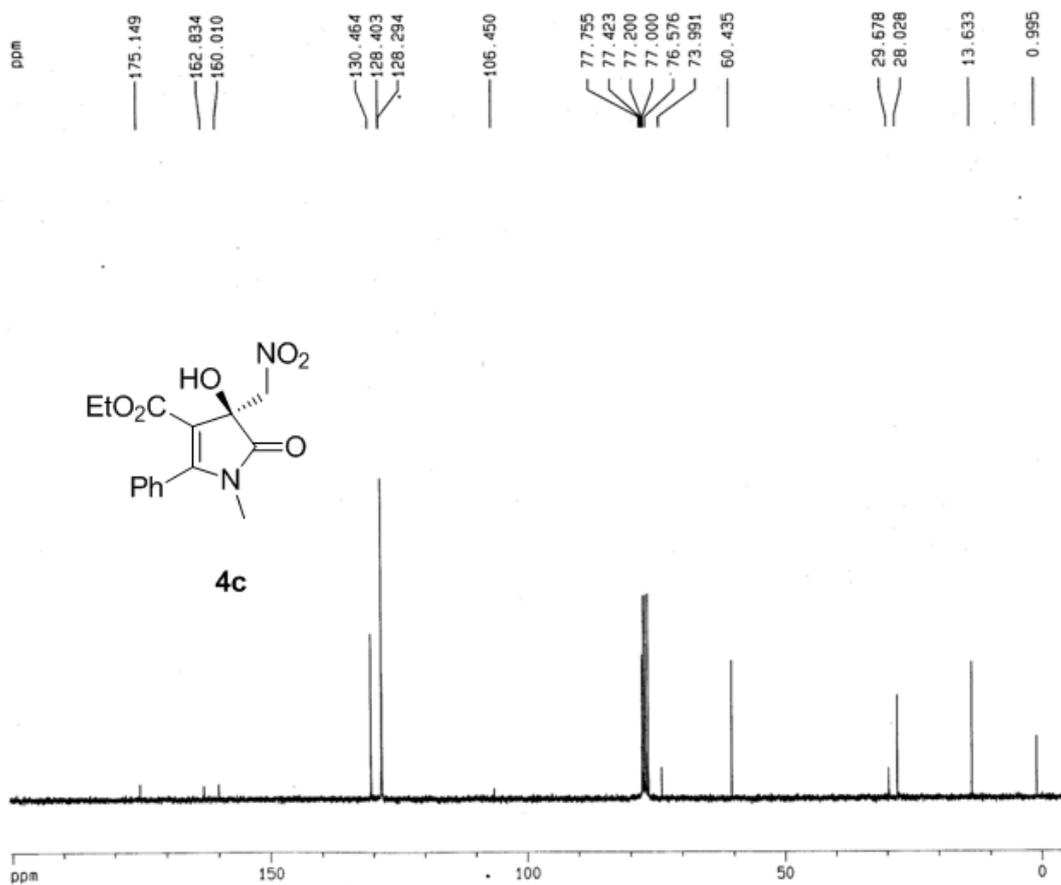
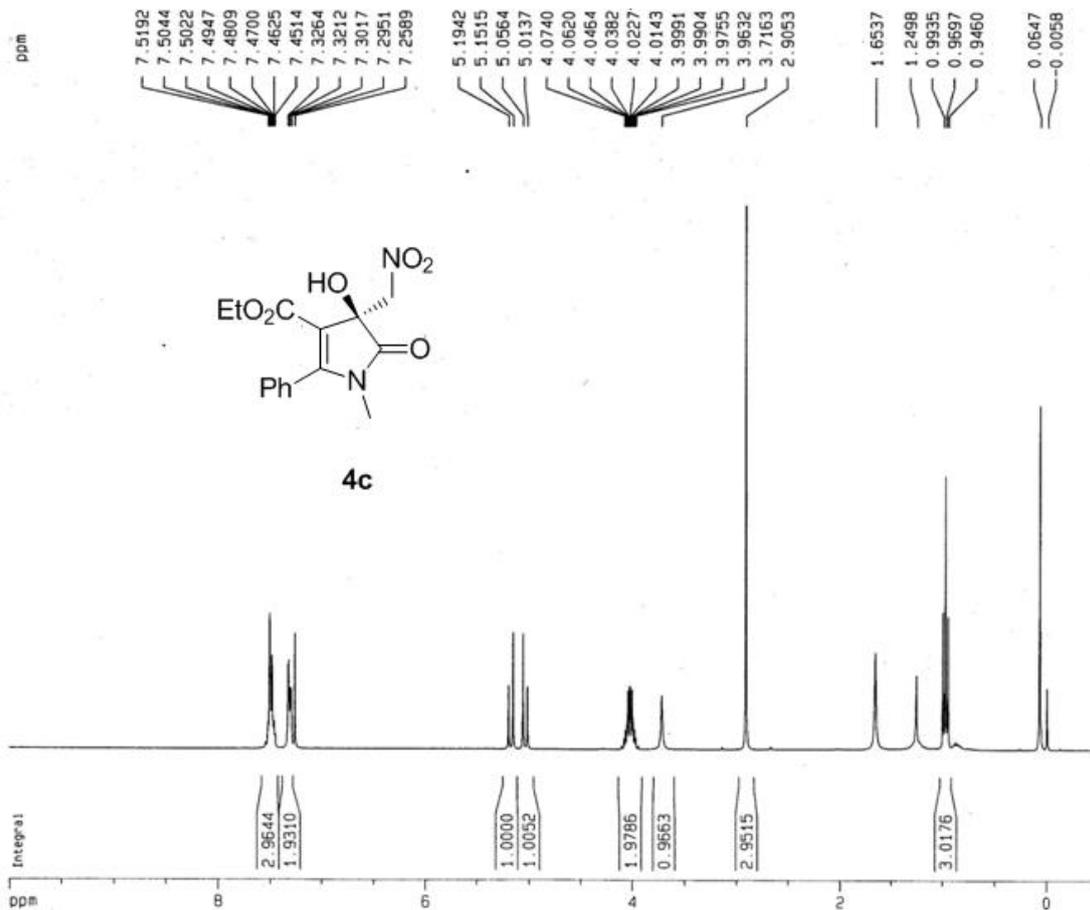
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.167	4547674	182845	49.658	54.443
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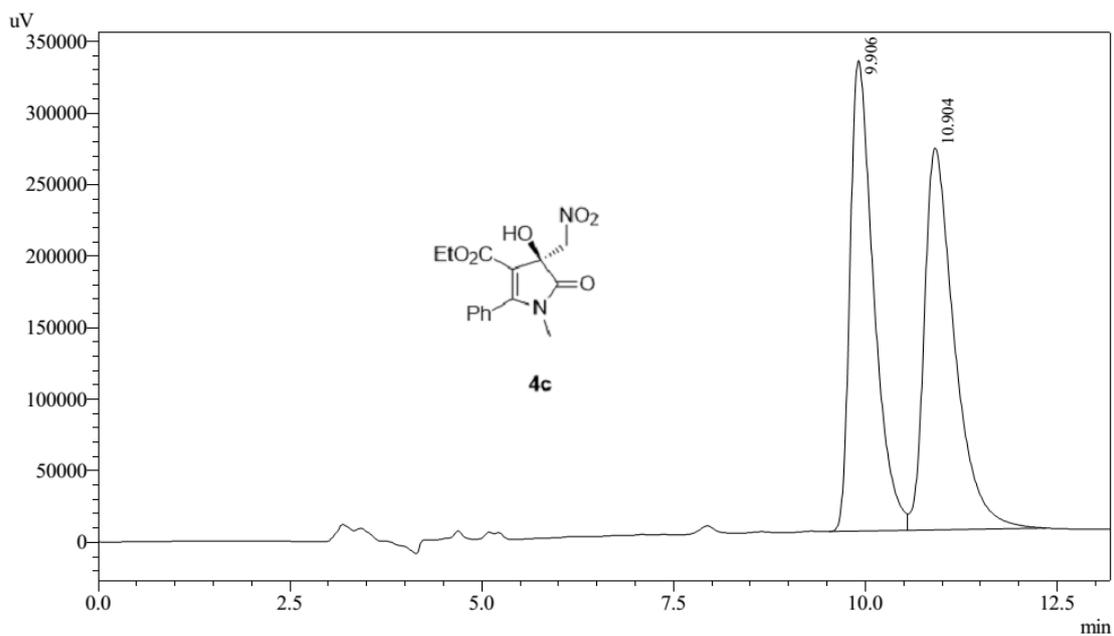


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.269	2800755	93113	14.524	15.451
2	7.559	16483100	509522	85.476	84.549
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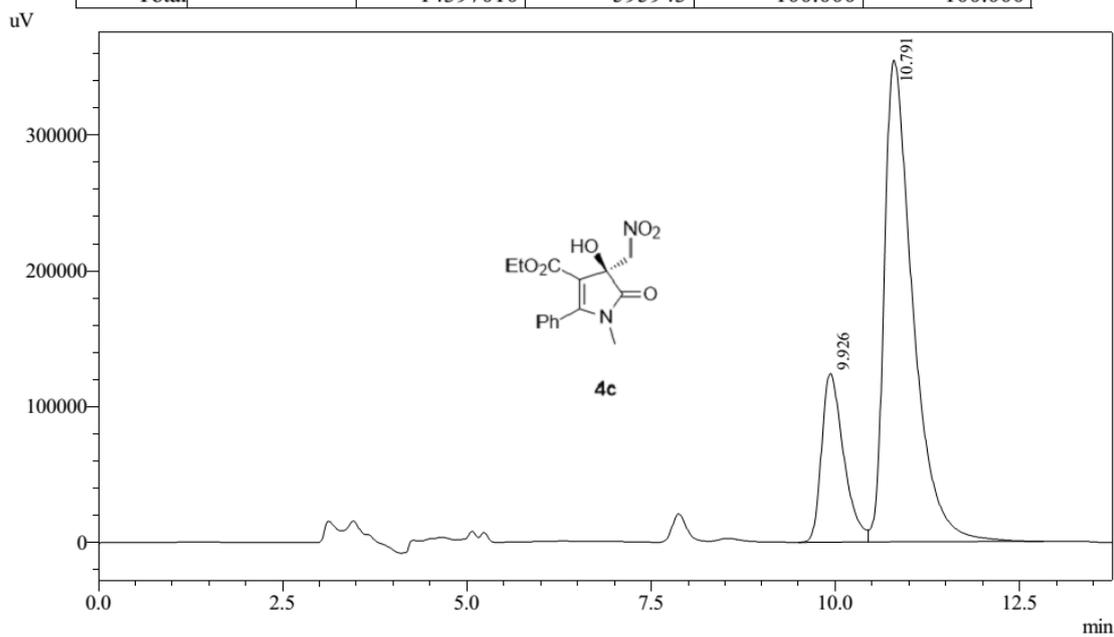




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

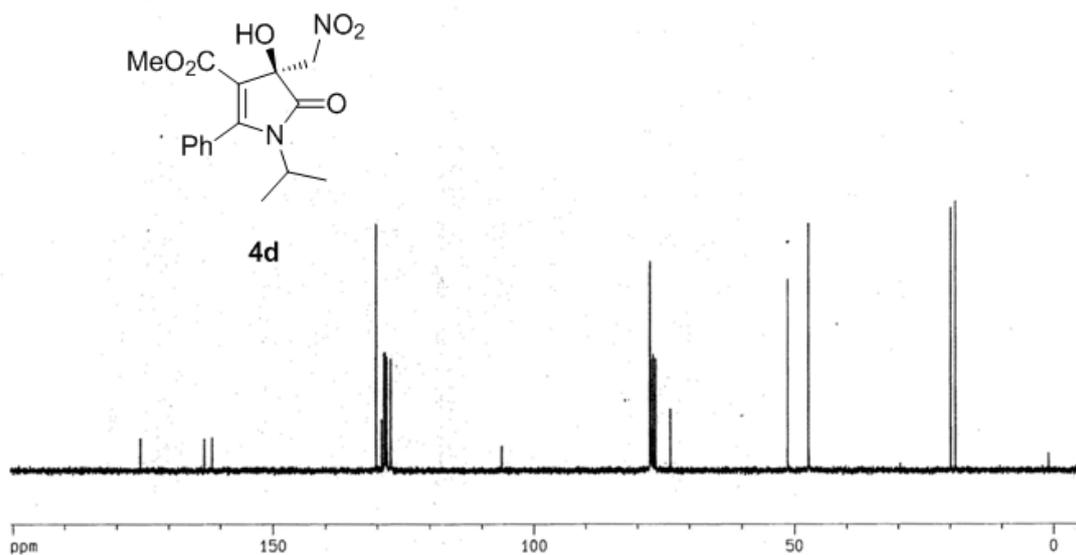
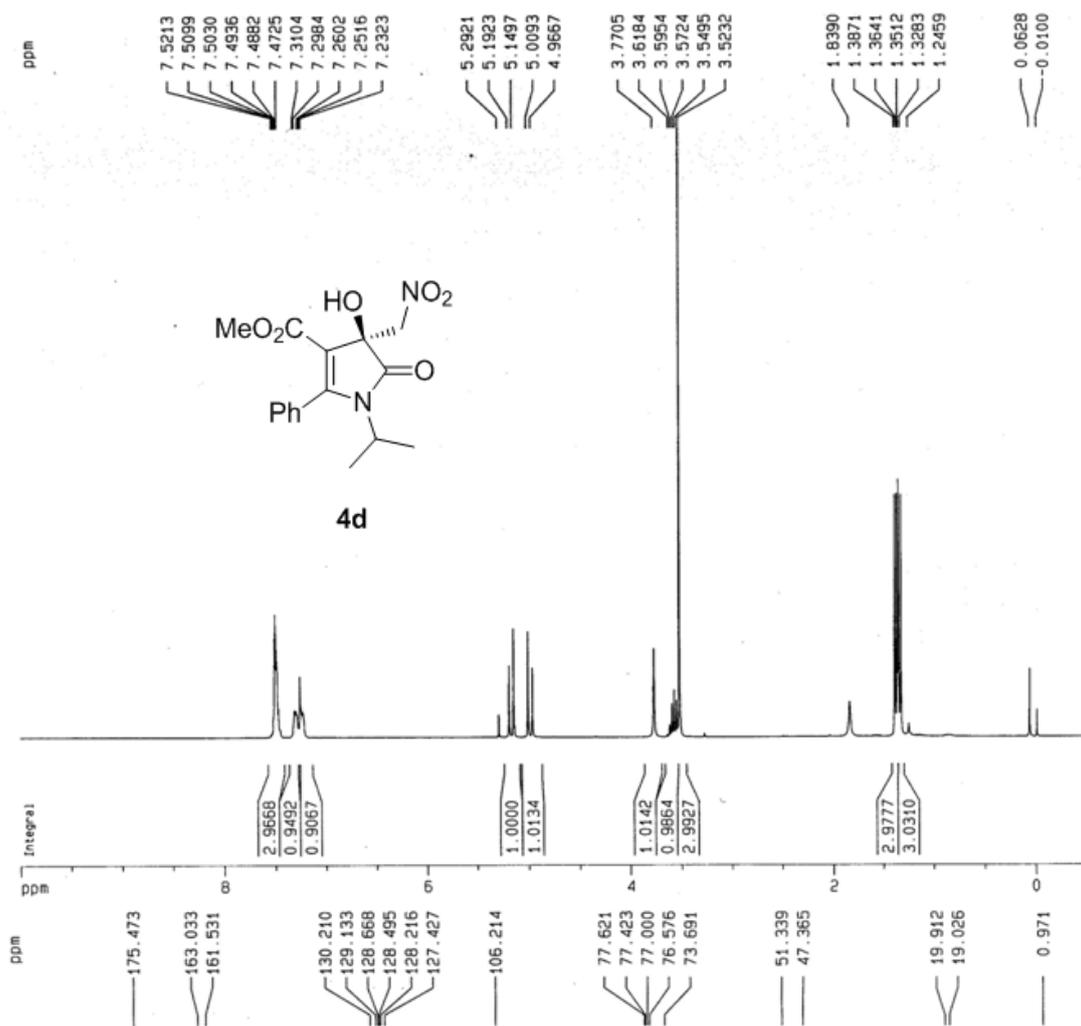
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1	9.906	7095968	329036	49.288	55.213
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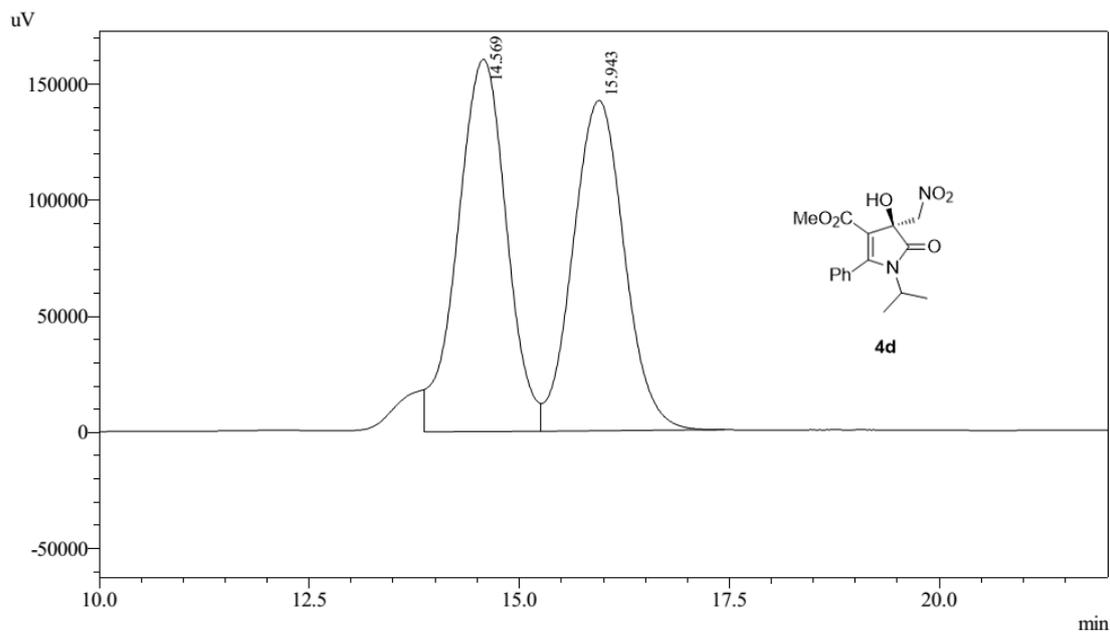


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.926	2594358	124350	21.323	25.938
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Total		12167057	479416	100.000	100.000

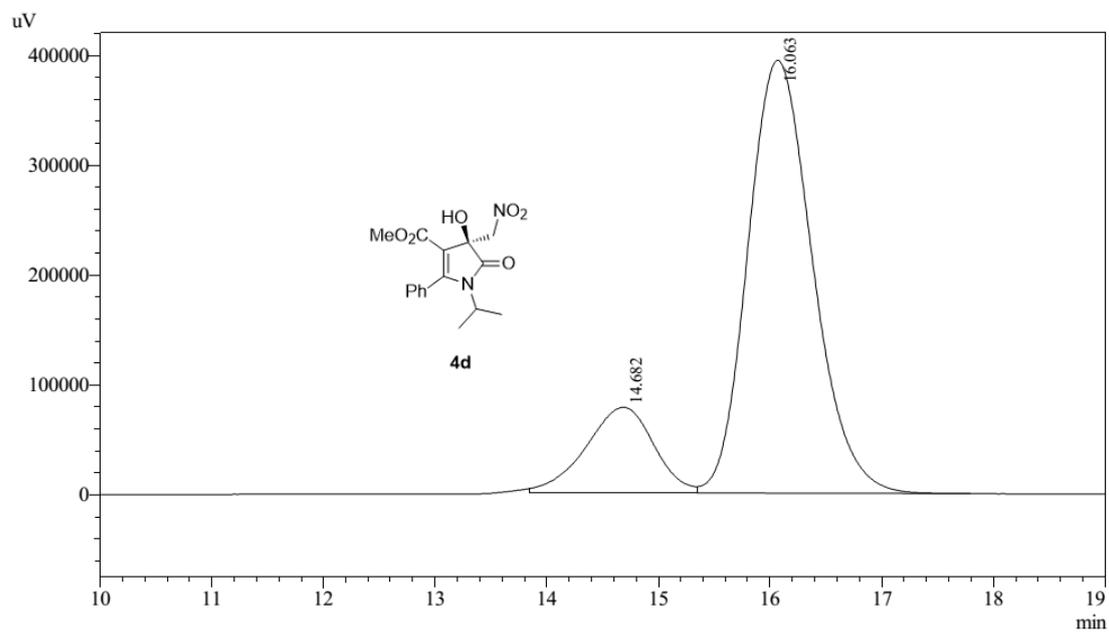




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

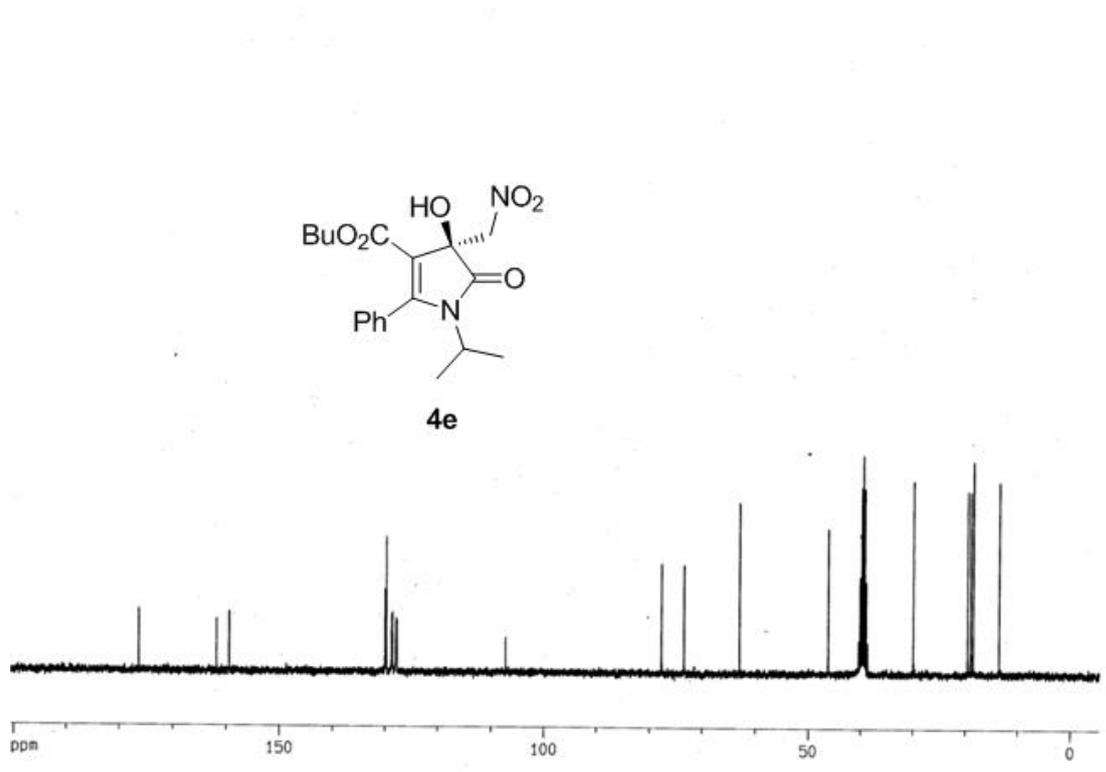
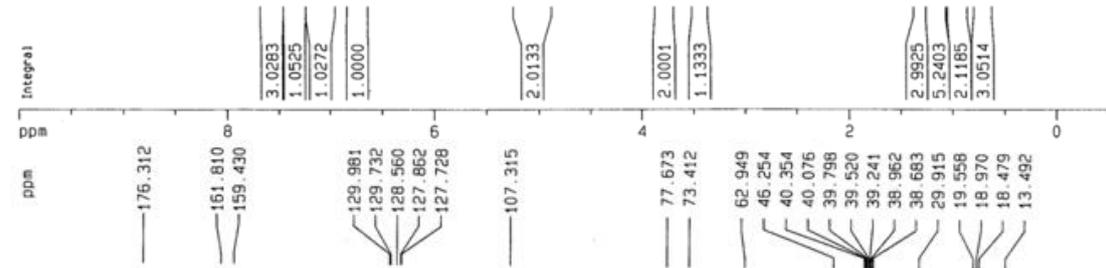
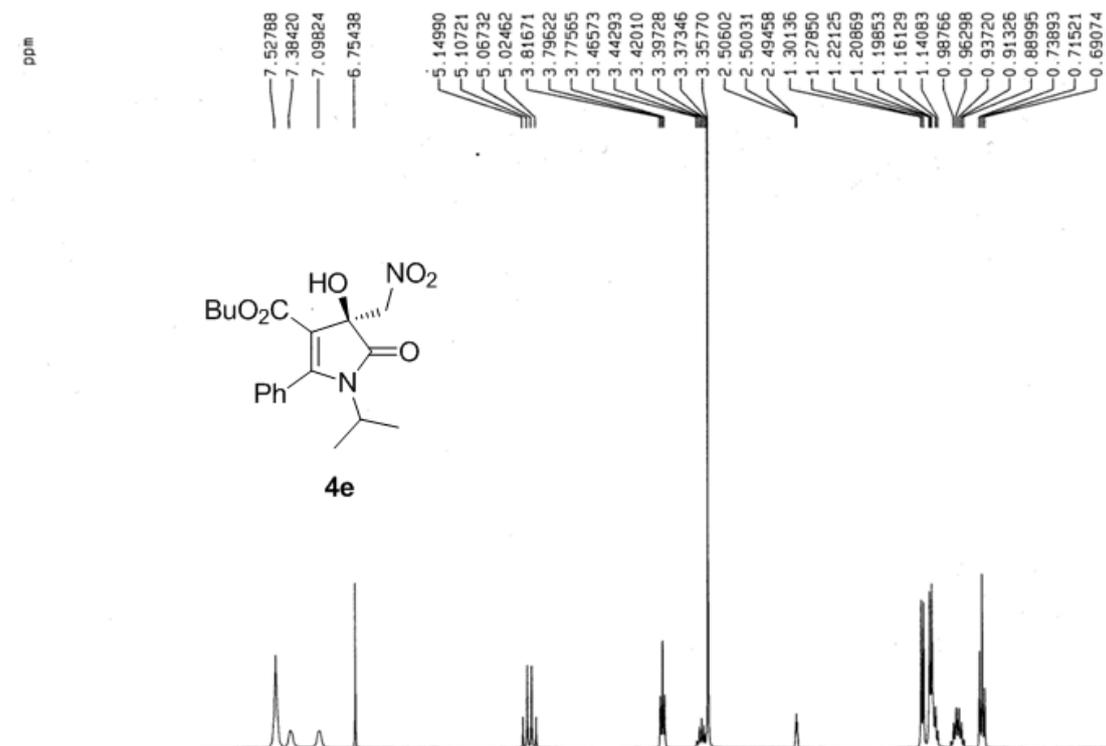
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.569	6483423	160396	51.700	52.976
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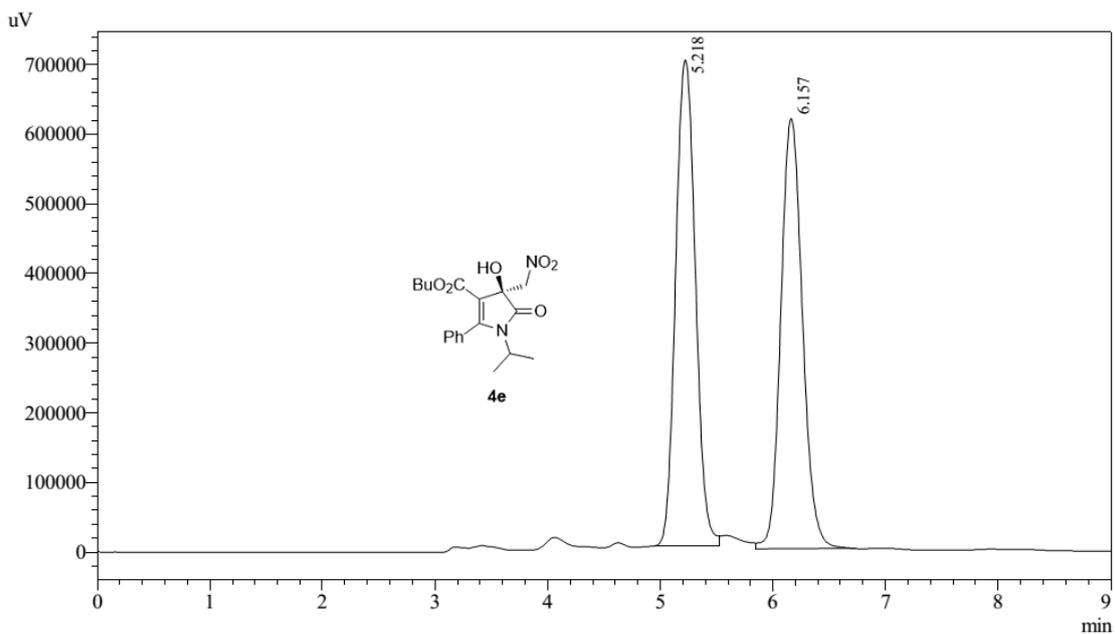


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.682	3317243	78064	17.290	16.527
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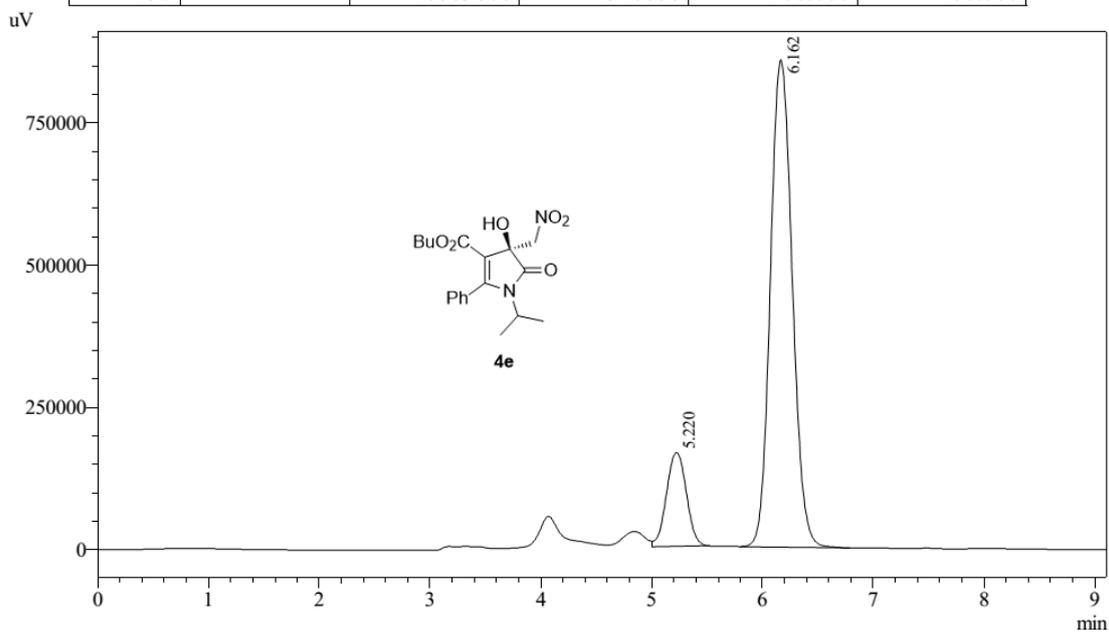




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

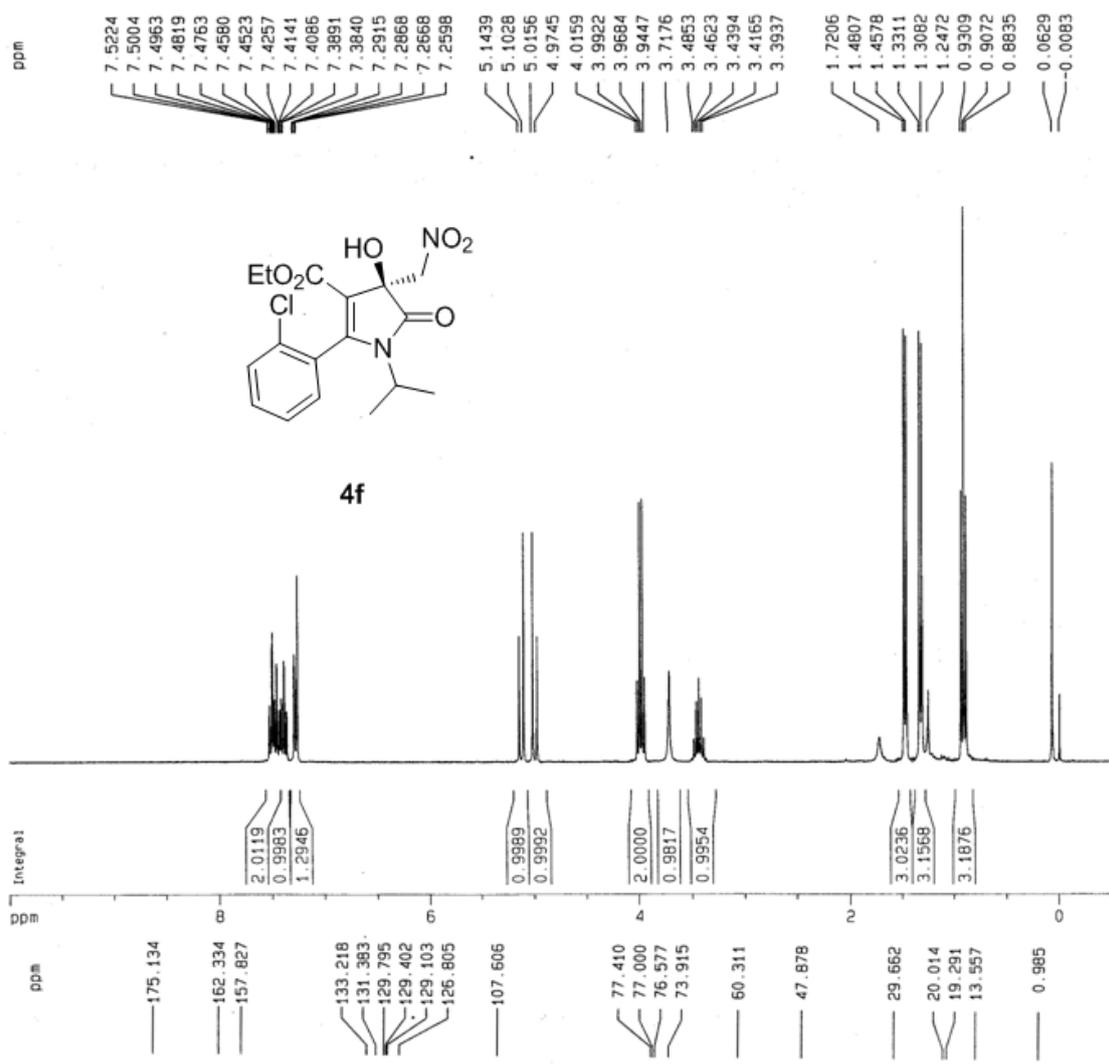
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.218	8514398	698407	50.772	53.043
2	6.157	8255408	618271	49.228	46.957
Total		16769806	1316678	100.000	100.000

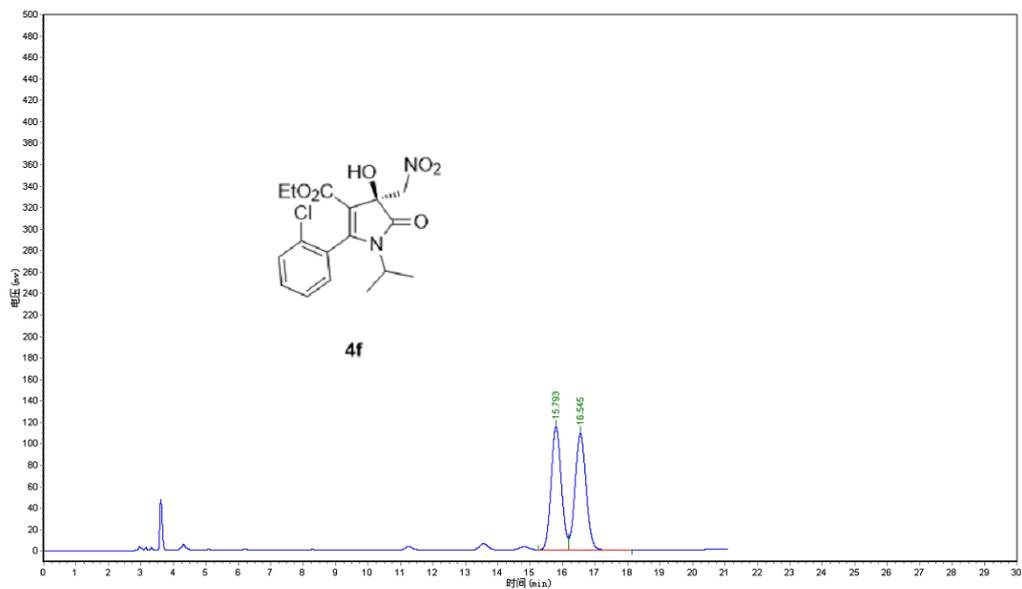


1 Det.A Ch1 / 254nm

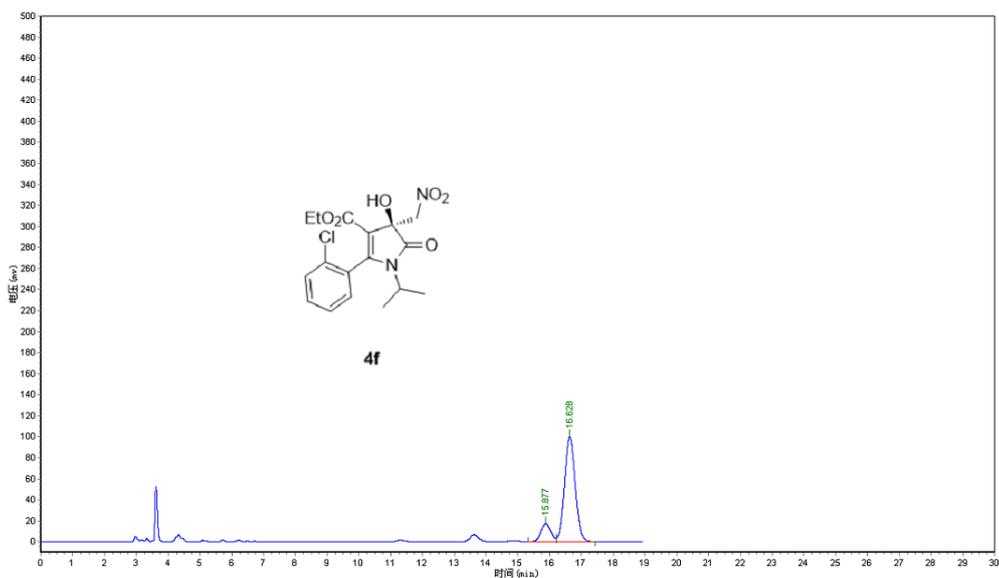
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.220	2065178	164749	14.971	16.119
2	6.162	11729794	857350	85.029	83.881
Total		13794972	1022099	100.000	100.000

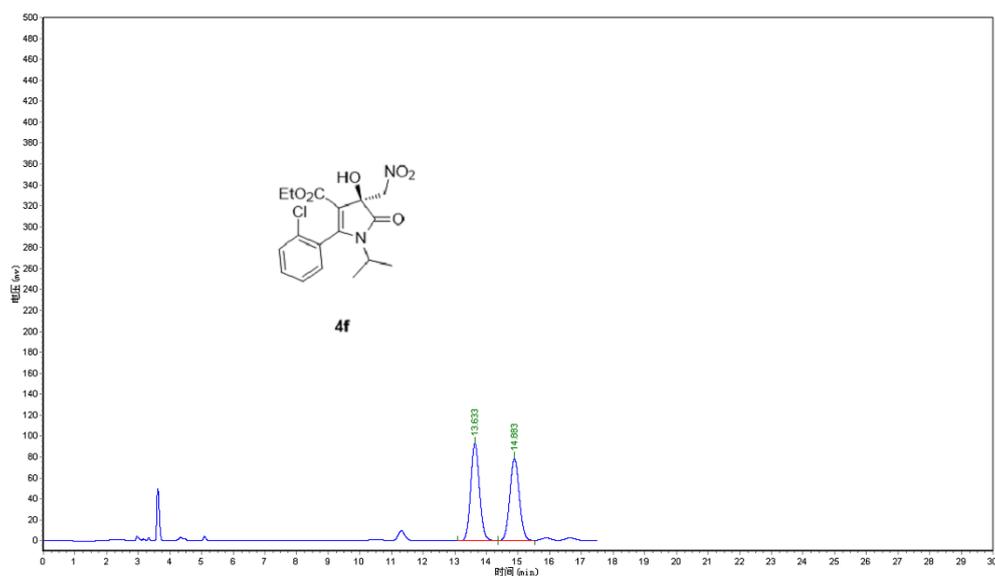




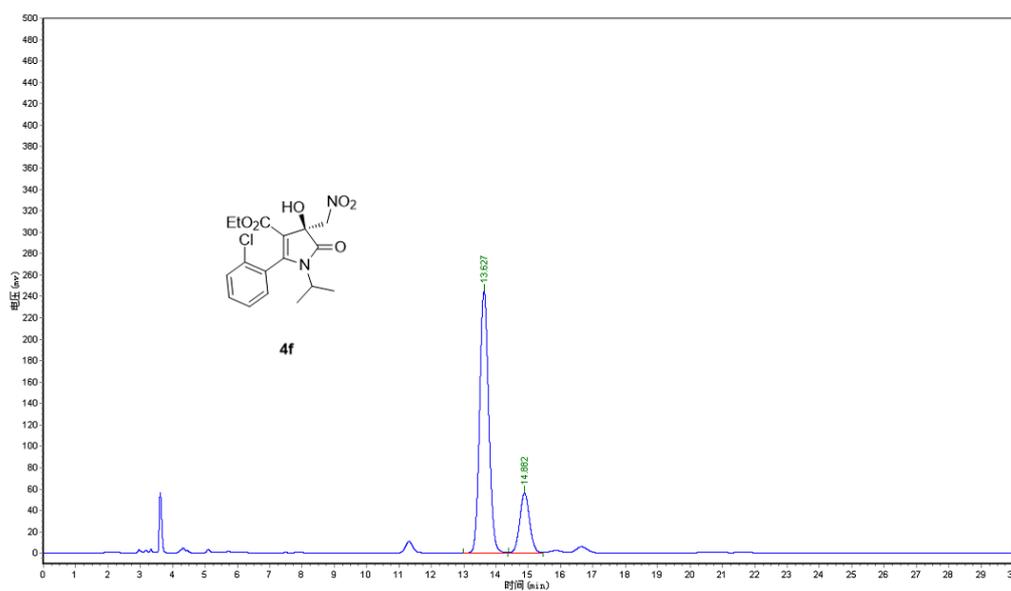
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.793	2526267	114312	49.797	51.276
2	16.545	2546849	108624	50.203	48.724
Total		5073116	222936	100.000	100.000



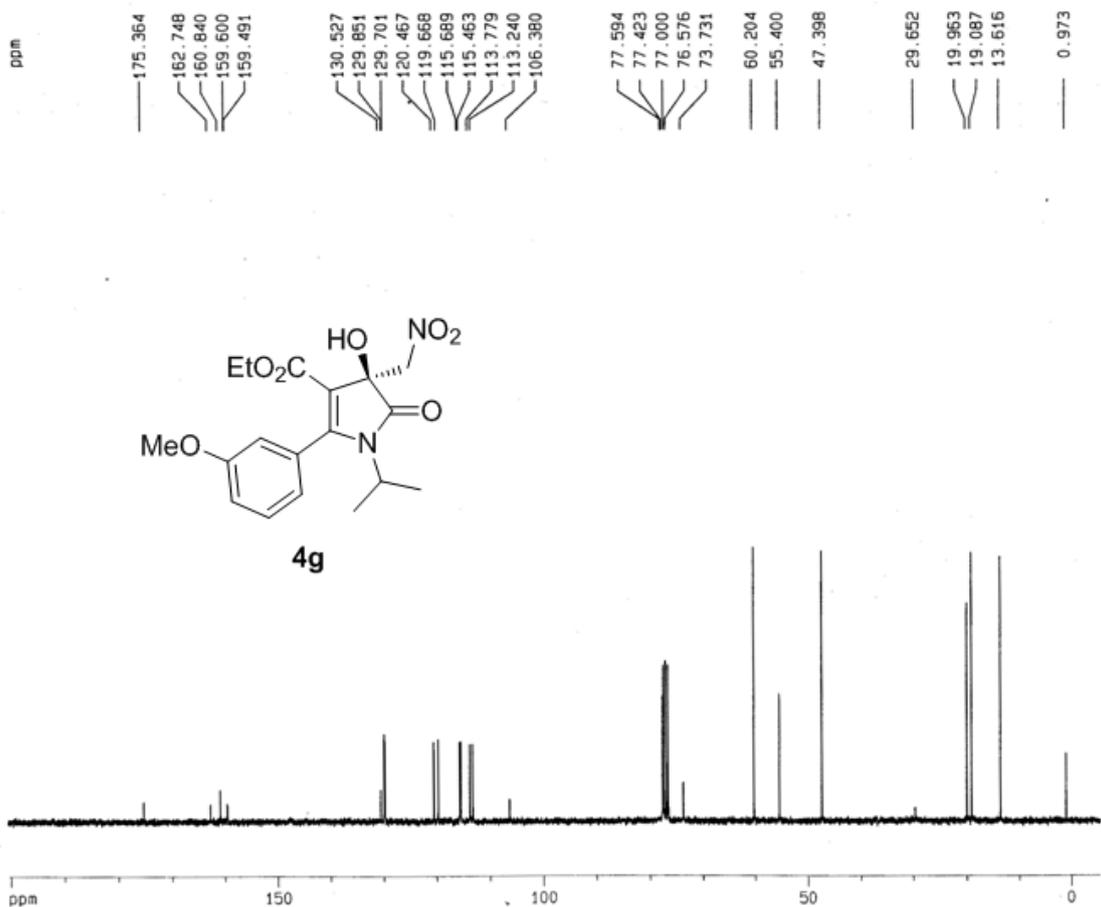
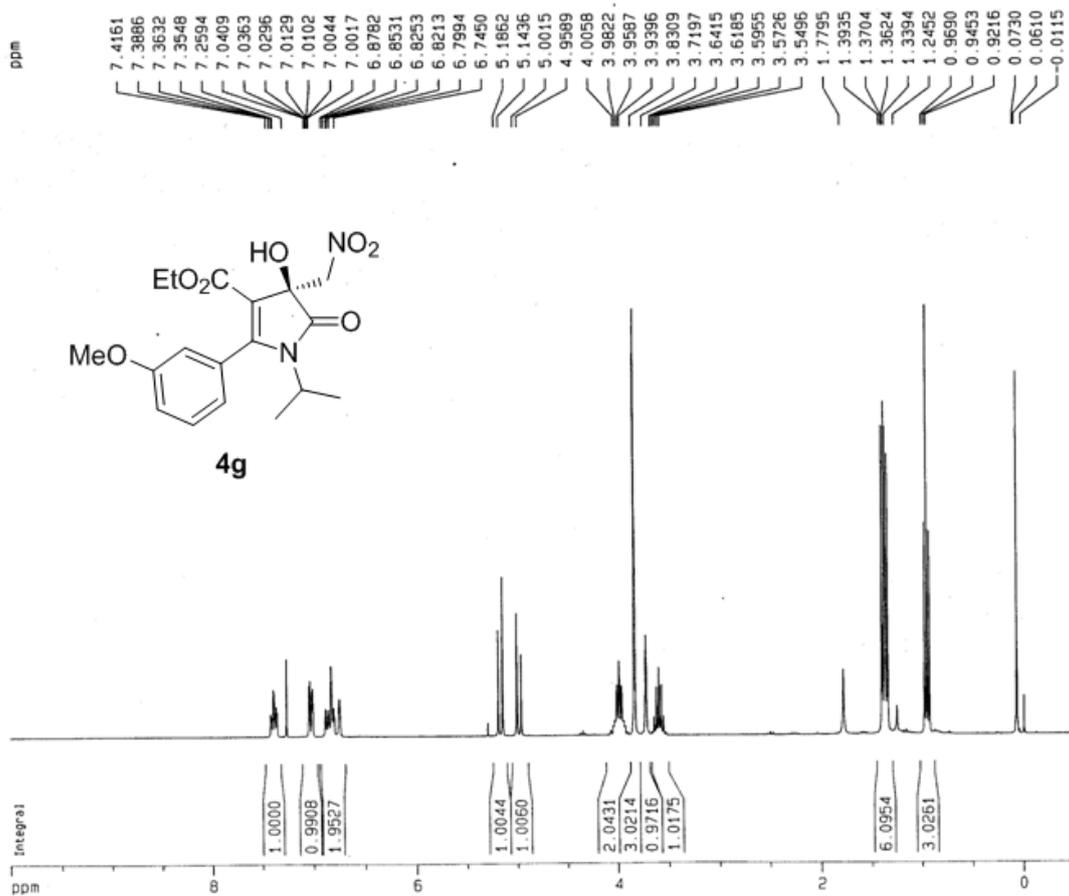
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.877	369338	17009	13.662	14.572
2	16.628	2334019	99716	86.338	85.428
Total		2703357	116725	100.000	100.000

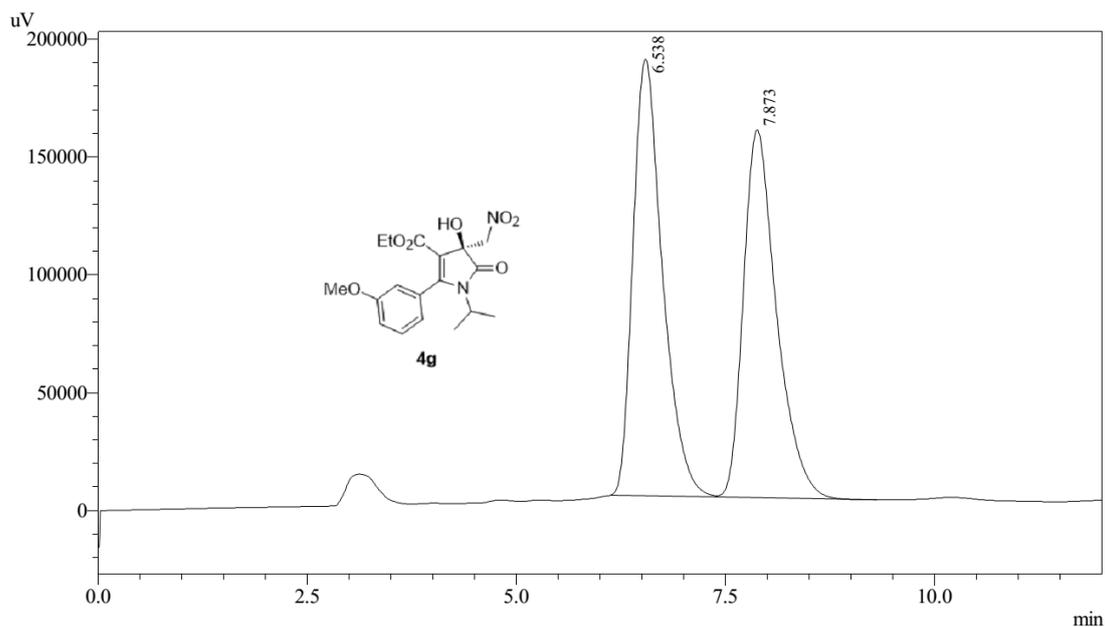


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.633	1790298	92735	52.005	54.220
2	14.883	1652242	78301	47.995	45.780
Total		3442540	171036	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.627	4764456	244531	80.111	81.390
2	14.882	1182840	55913	19.889	18.610
Total		5947296	300444	100.000	100.000

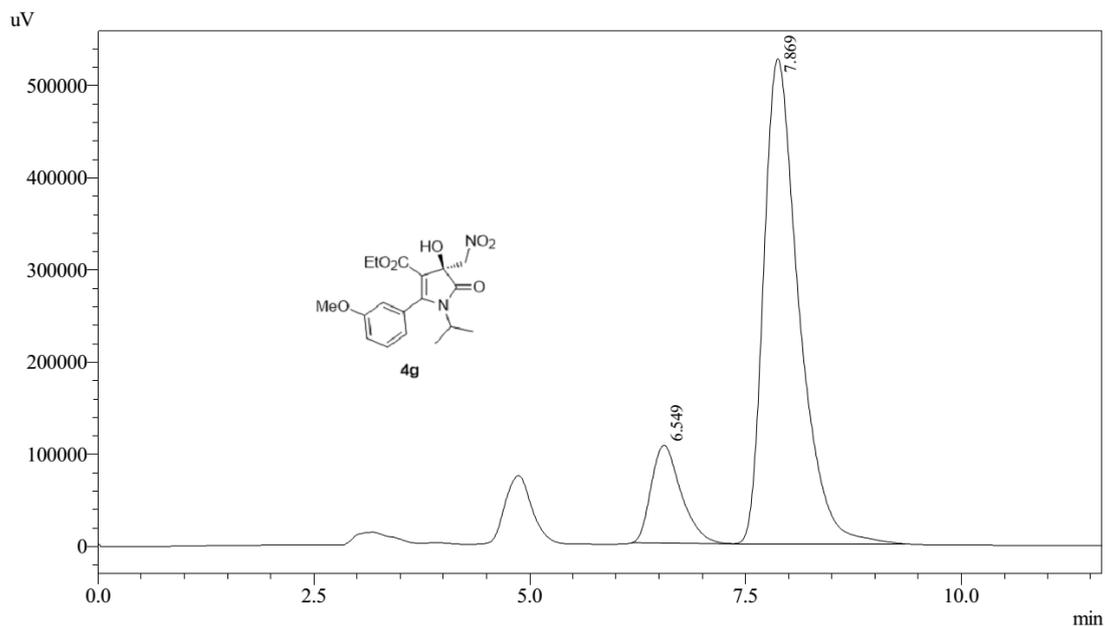




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

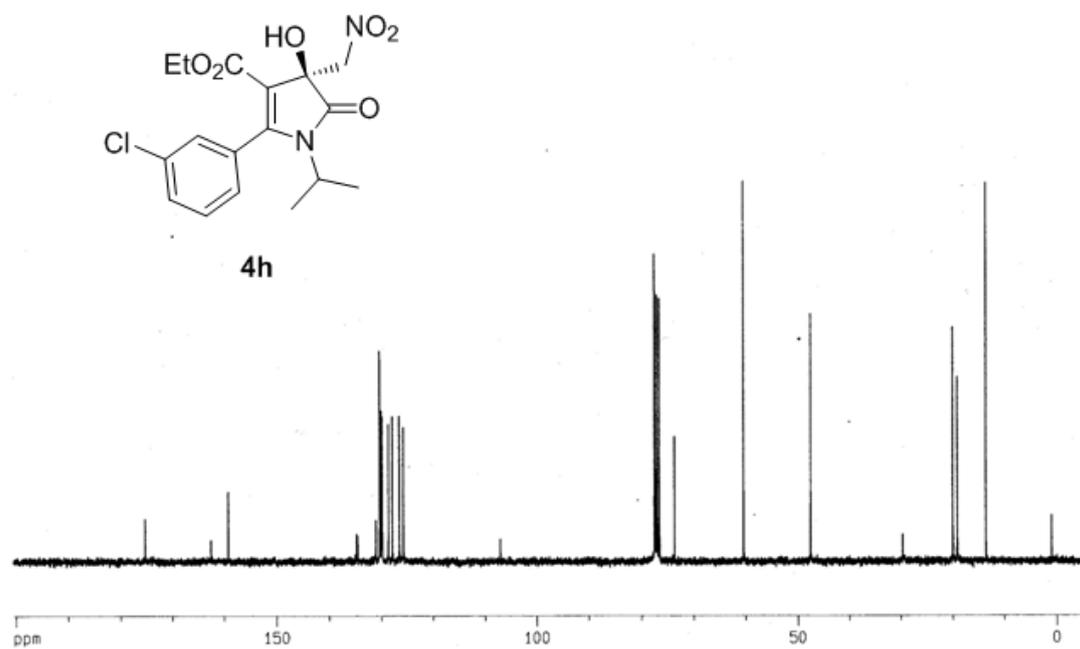
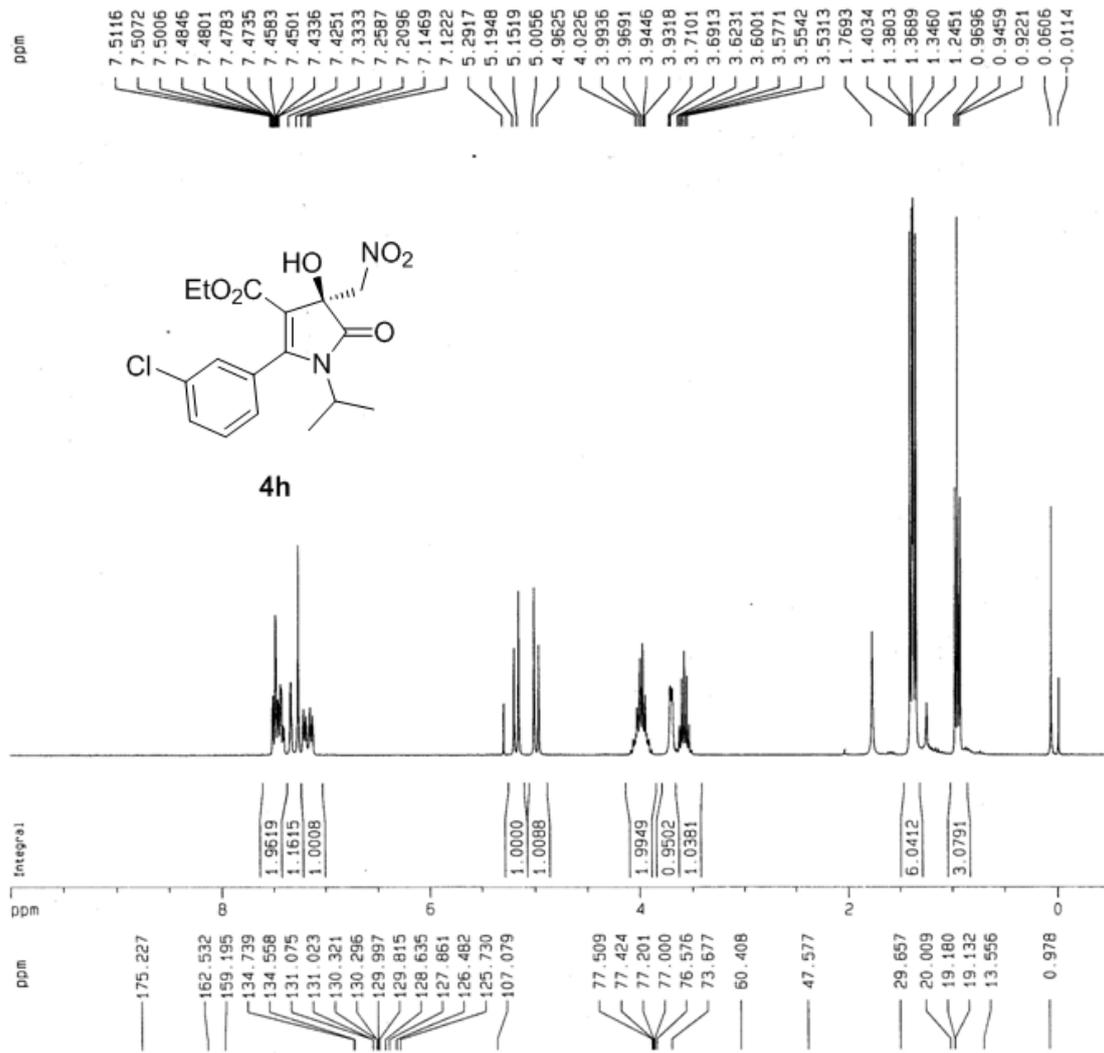
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.538	4554844	185183	51.450	54.287
2	7.873	4298119	155938	48.550	45.713
Total		8852963	341122	100.000	100.000

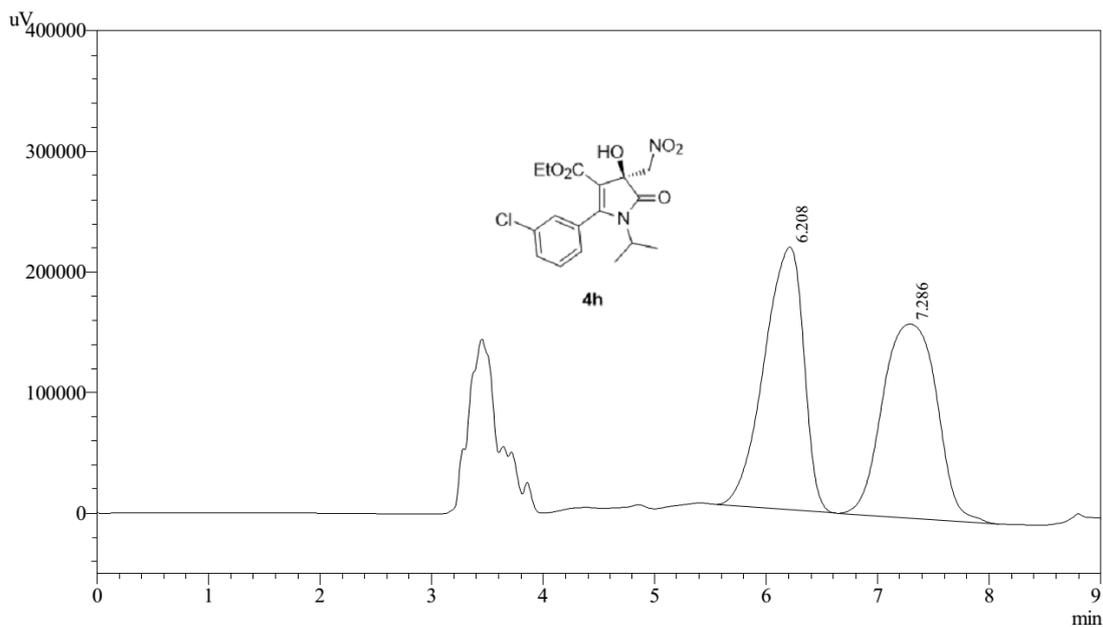


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.549	2558160	105999	14.672	16.761
2	7.869	14877166	526411	85.328	83.239
Total		17435326	632409	100.000	100.000

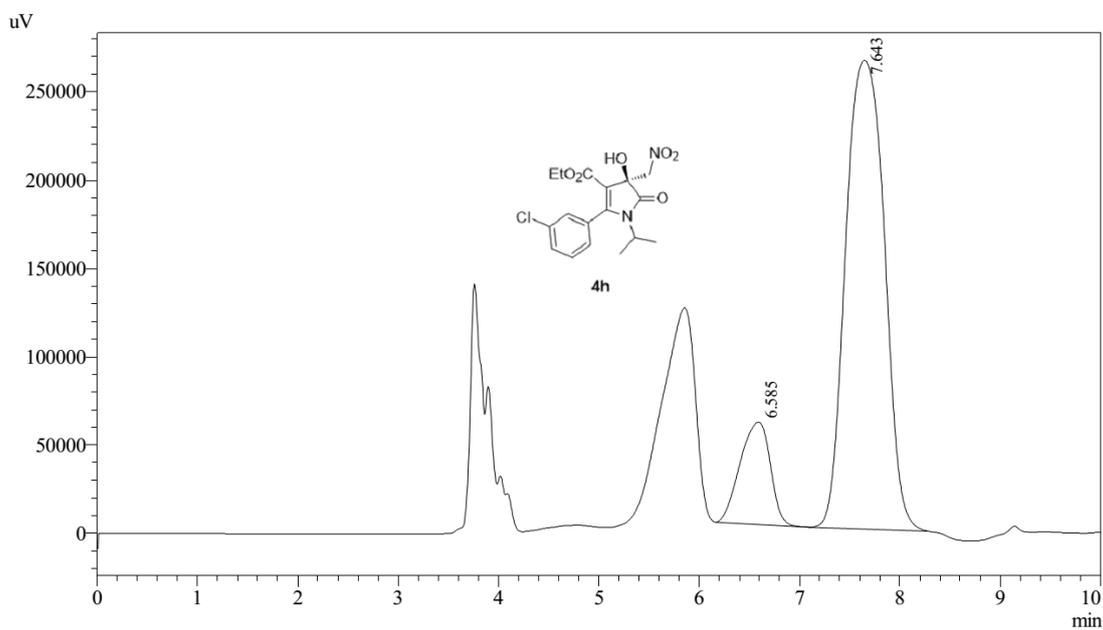




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

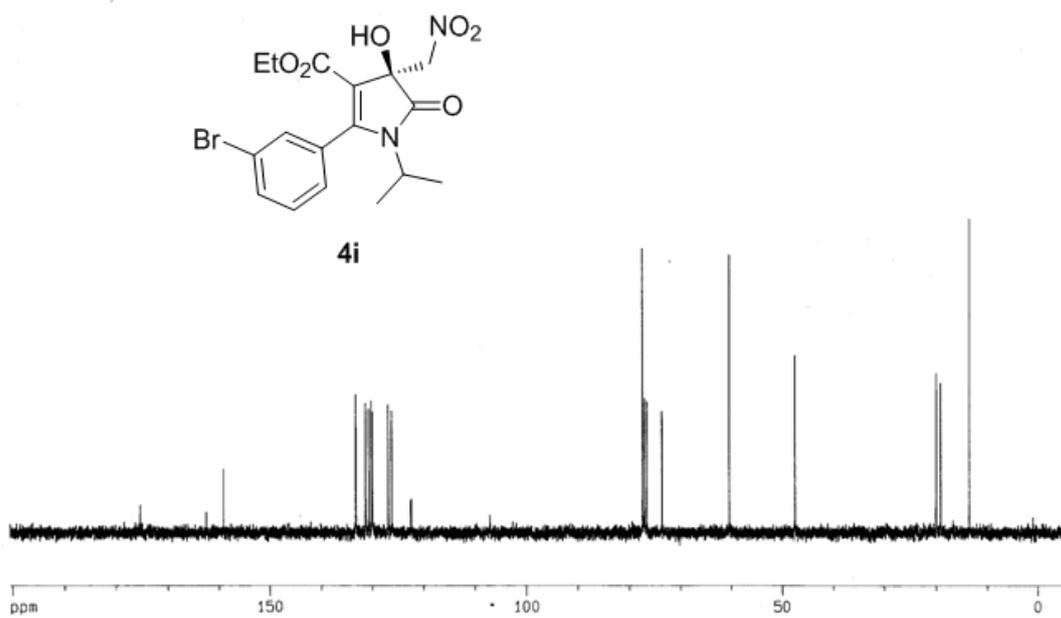
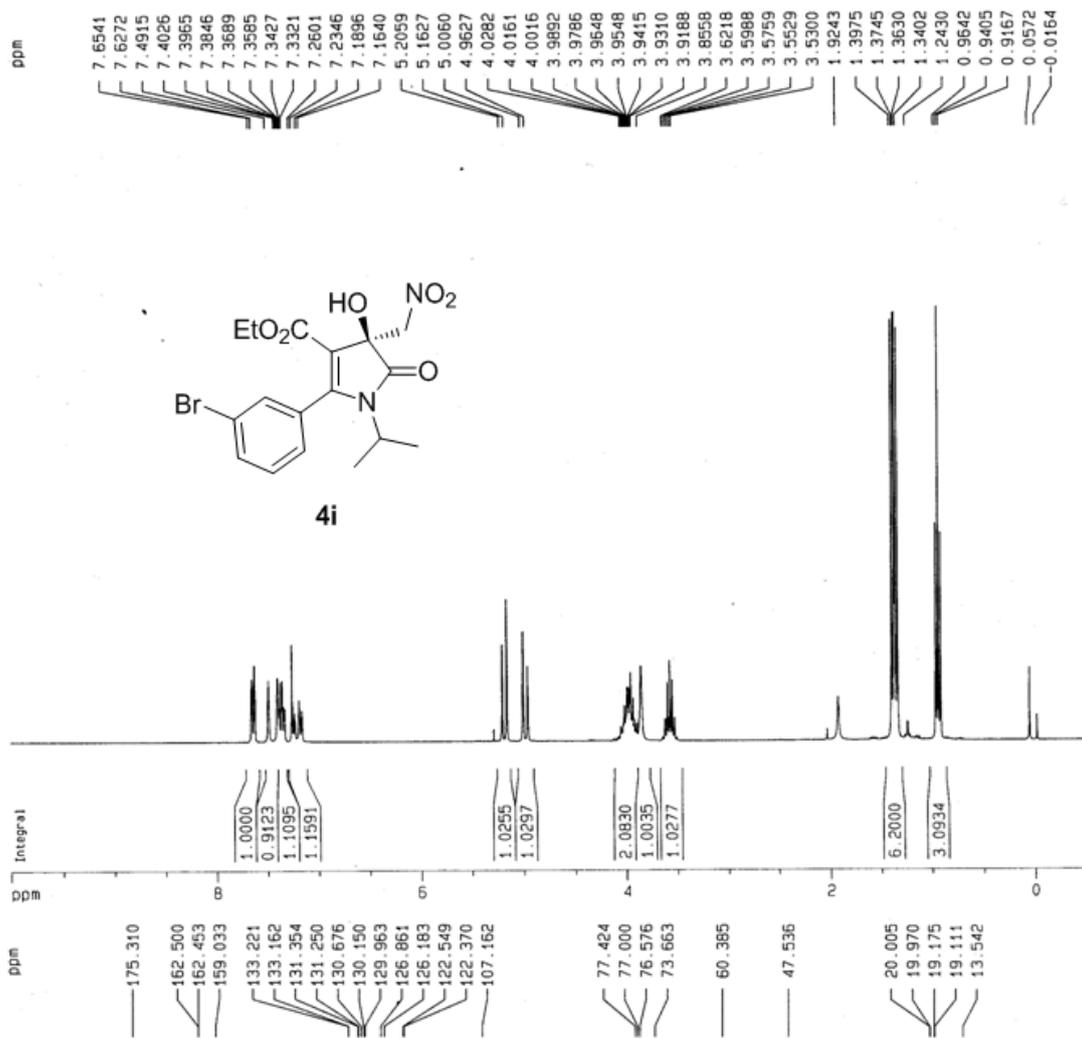
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.208	5371811	217766	49.720	57.499
2	7.286	5432274	160962	50.280	42.501
Total		10804085	378728	100.000	100.000

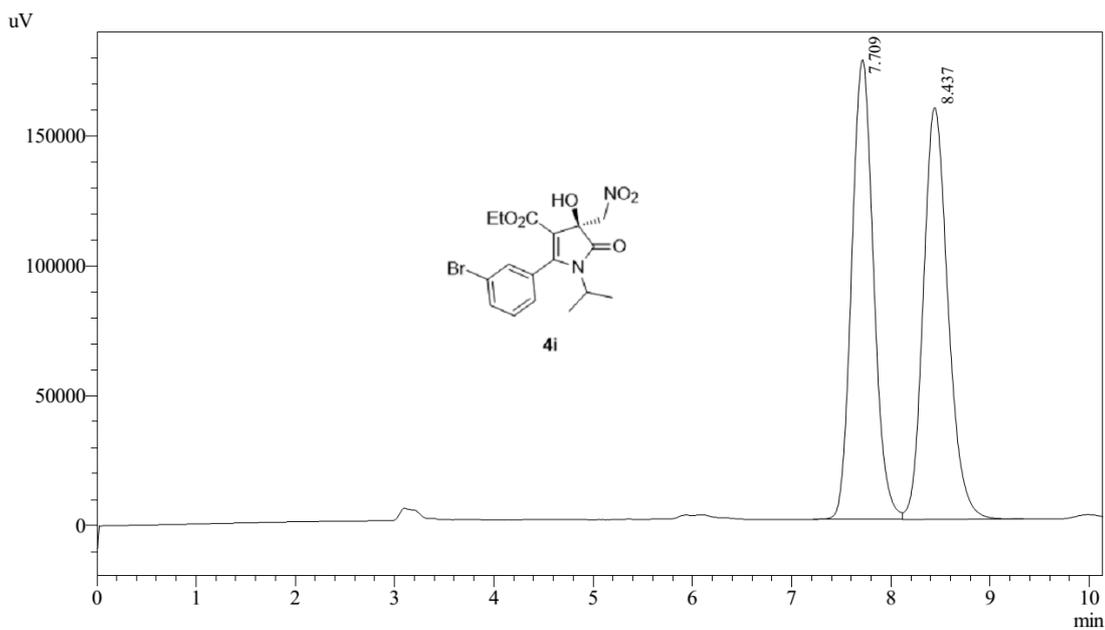


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.585	1206559	57942	14.471	17.923
2	7.643	7131150	265347	85.529	82.077
Total		8337709	323288	100.000	100.000

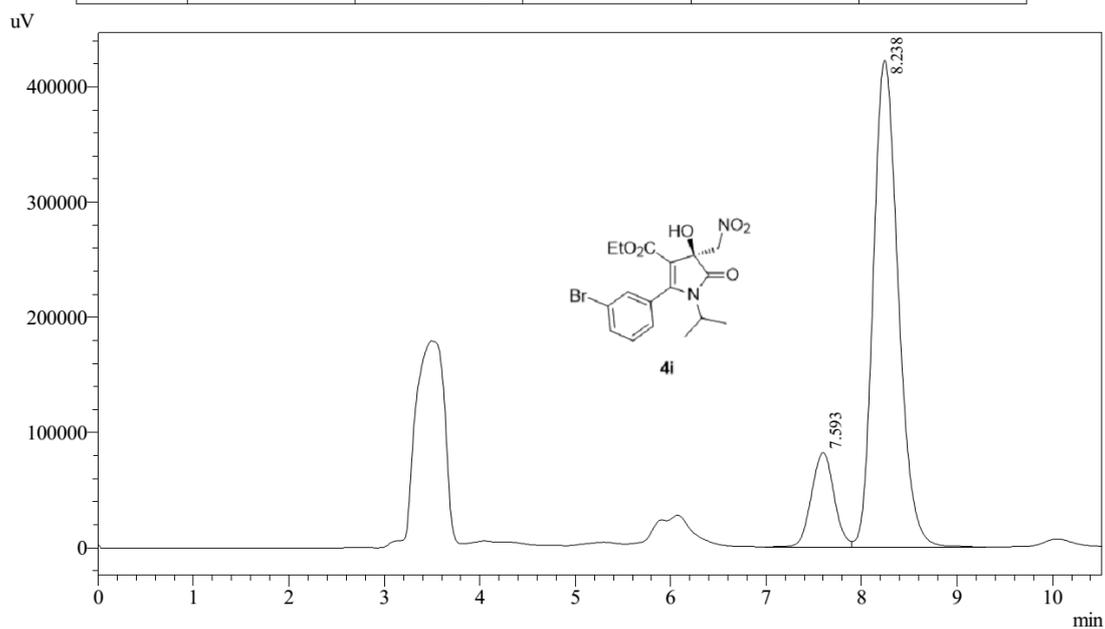




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

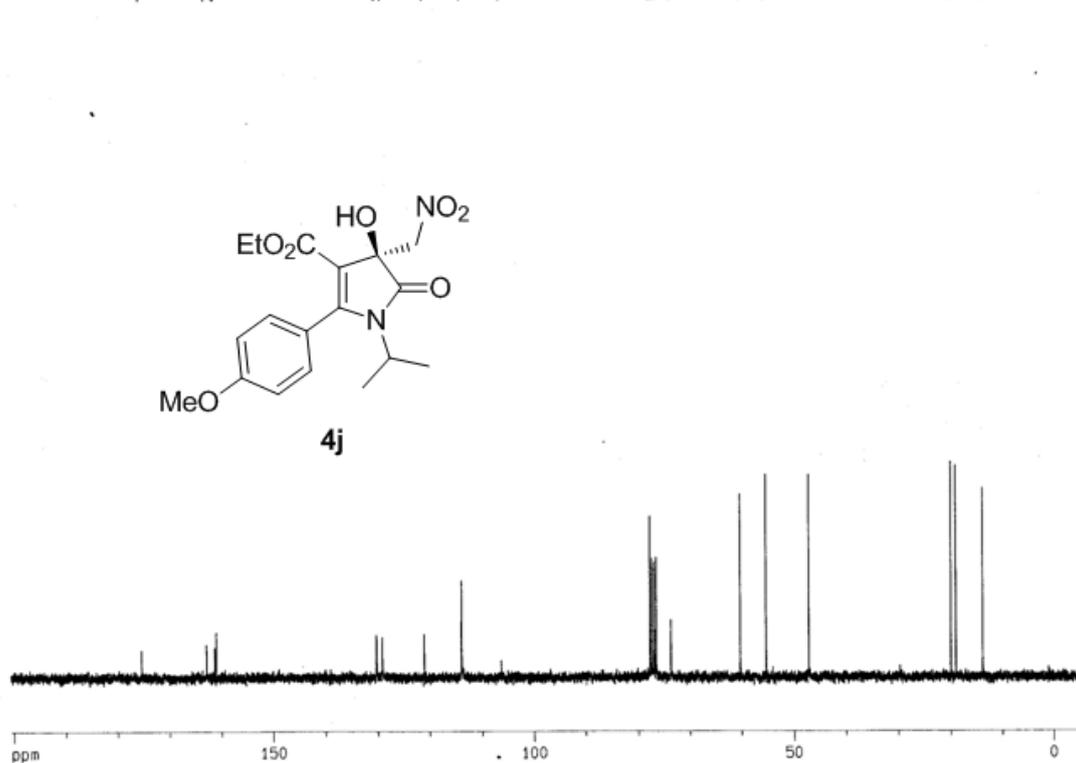
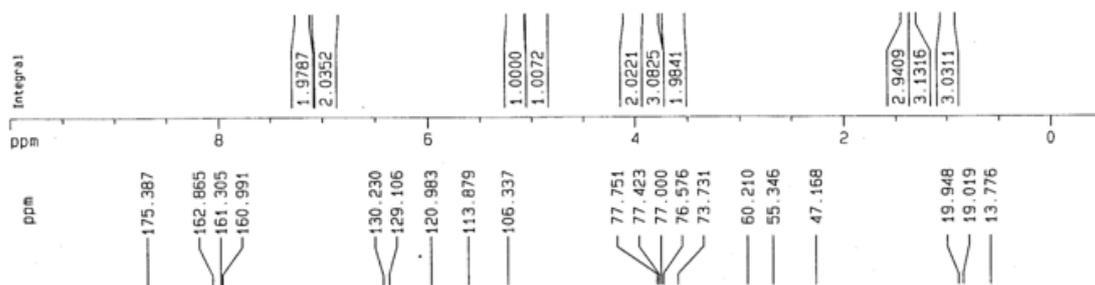
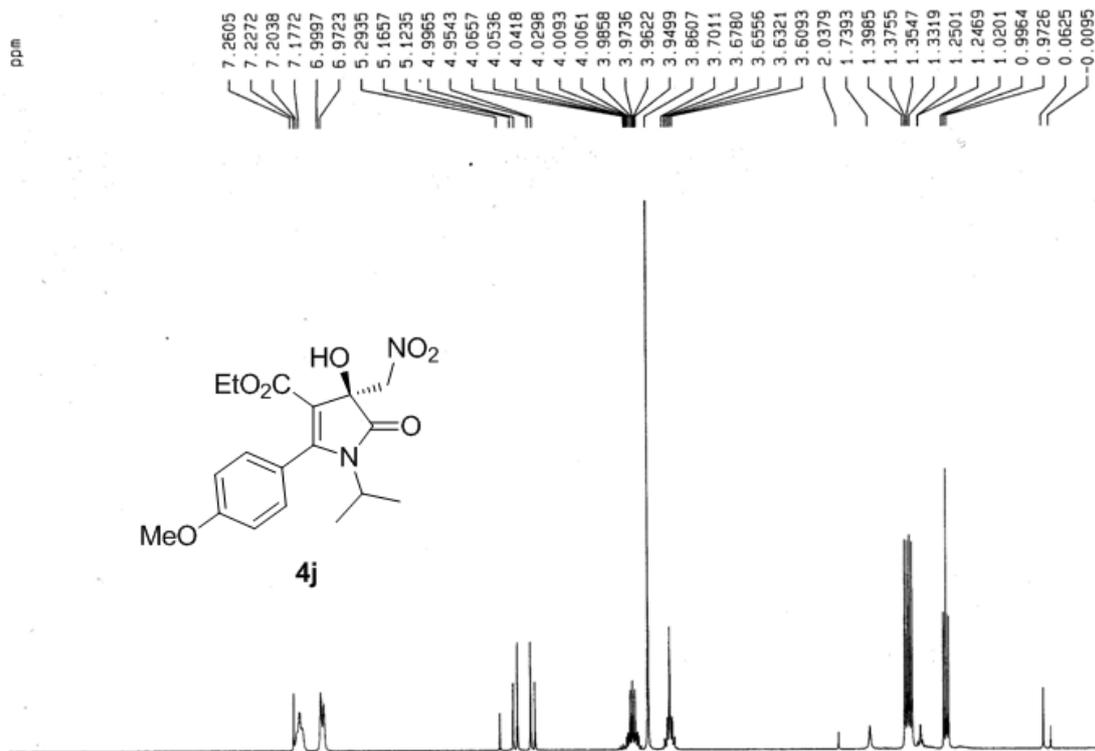
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.709	2709797	176841	49.728	52.725
2	8.437	2739413	158559	50.272	47.275
Total		5449210	335399	100.000	100.000

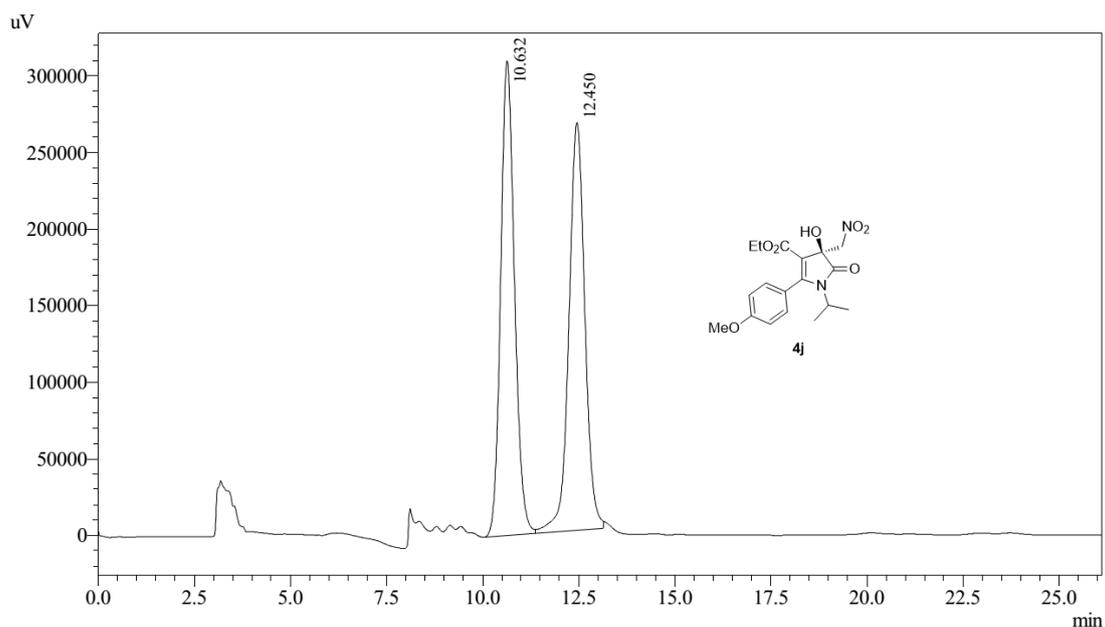


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.593	1352217	81845	14.994	16.228
2	8.238	7665886	422488	85.006	83.772
Total		9018103	504333	100.000	100.000

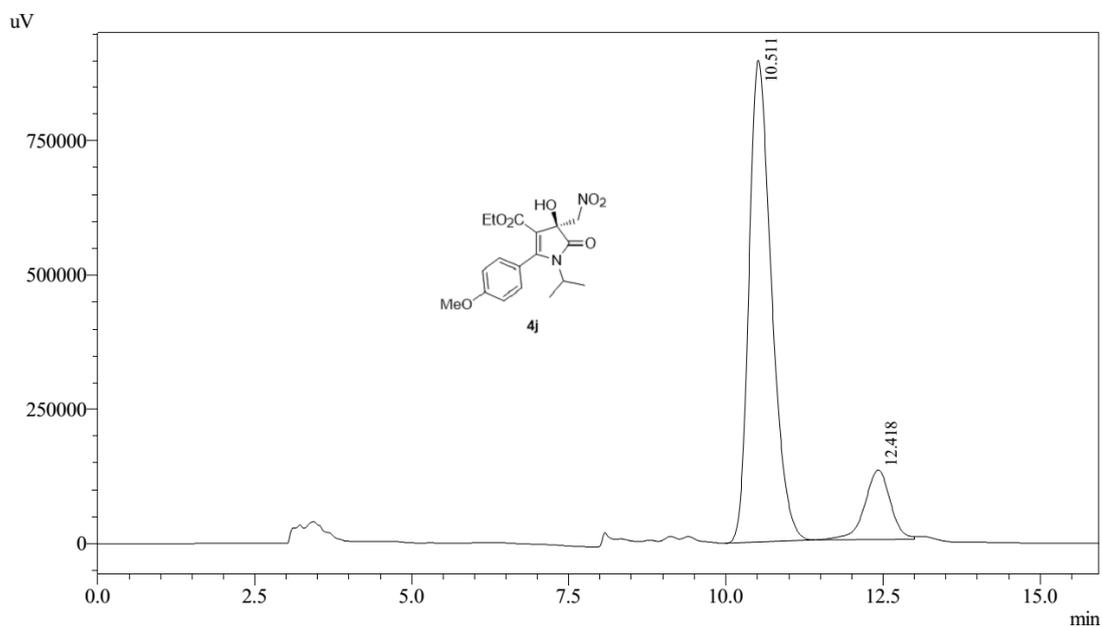




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

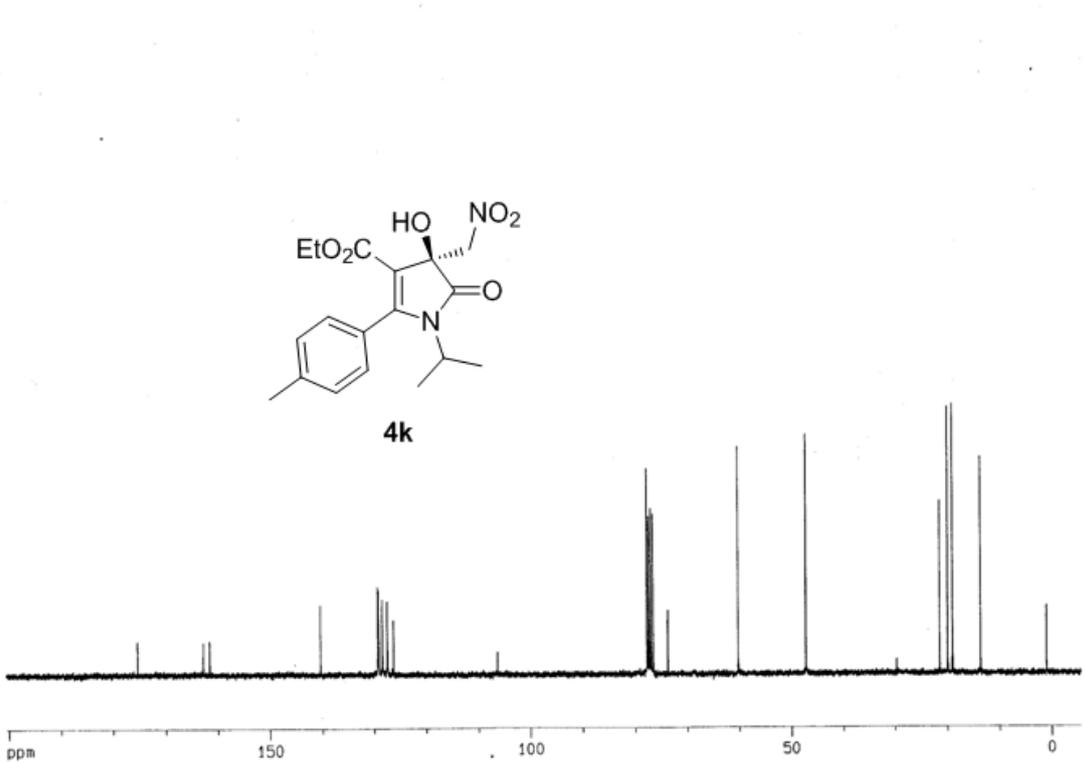
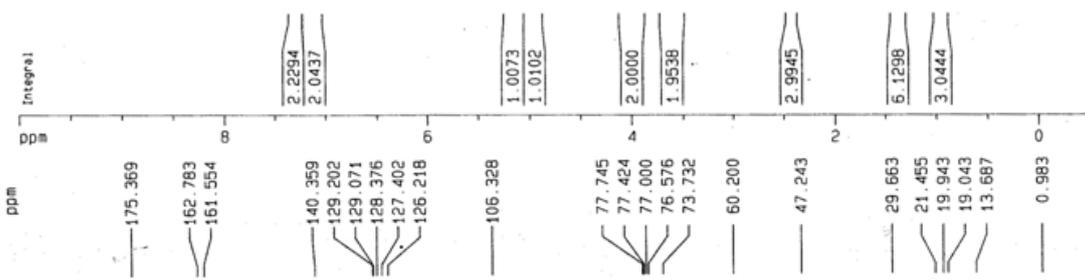
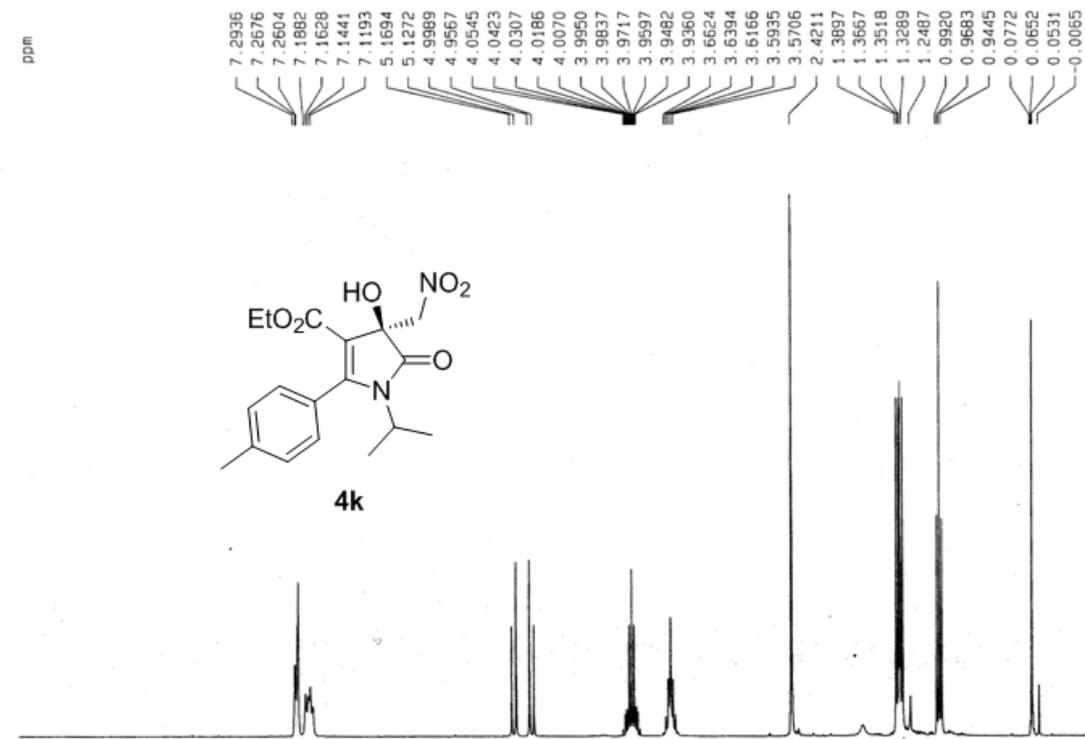
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.632	7754028	310076	50.194	53.785
2	12.450	7694145	266436	49.806	46.215
Total		15448173	576511	100.000	100.000

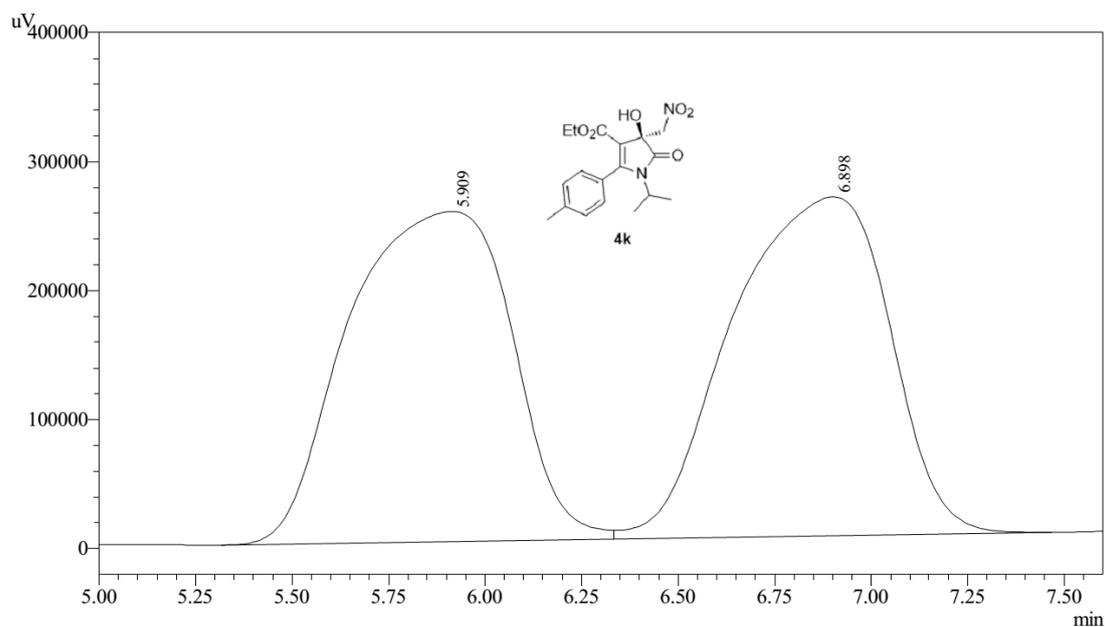


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

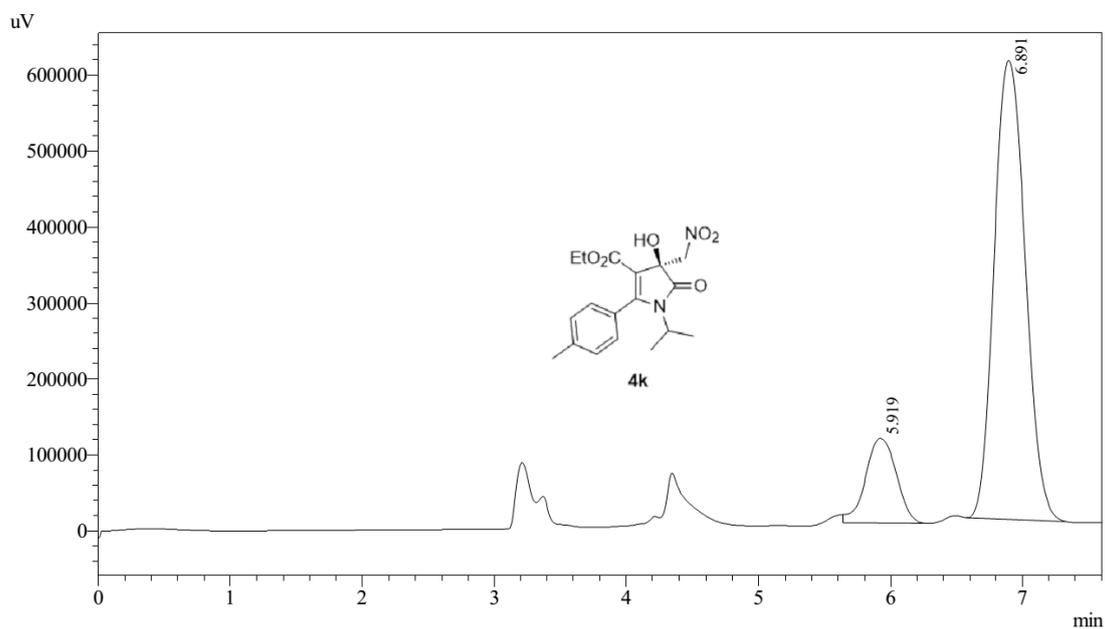
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.511	22399812	897656	85.775	87.356
2	12.418	3714925	129932	14.225	12.644
Total		26114737	1027588	100.000	100.000





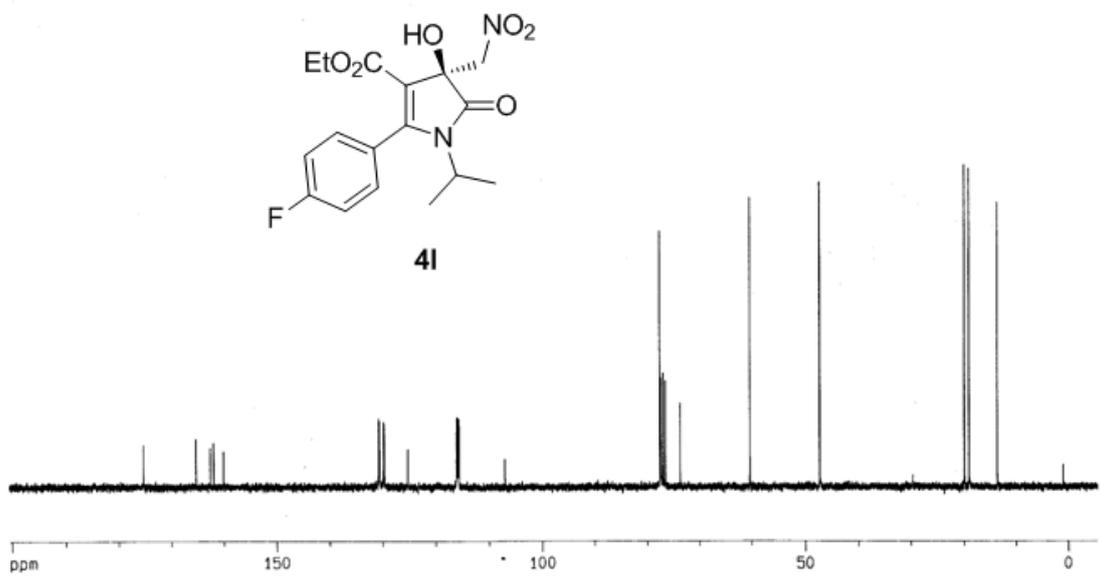
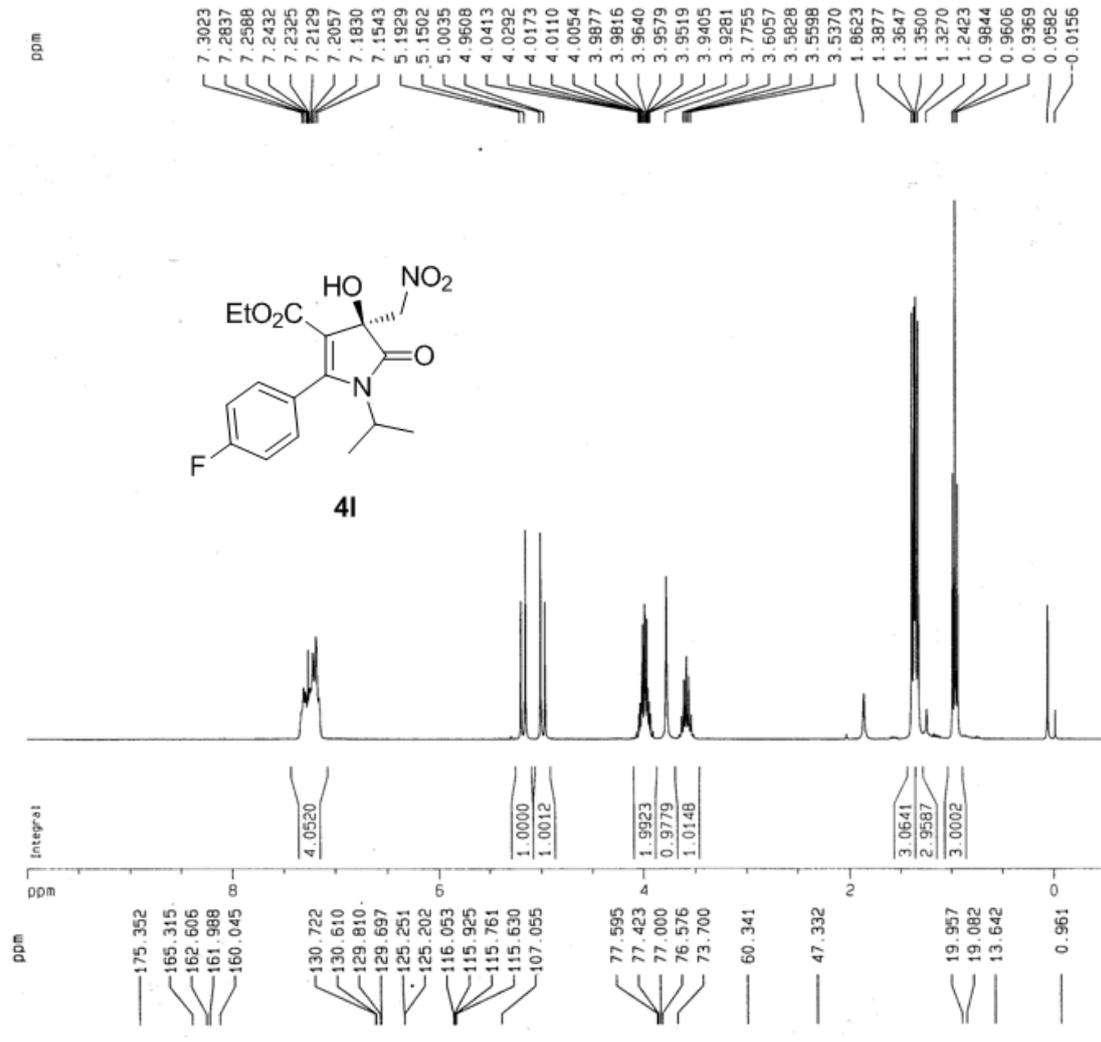
Detector A Ch1 254nm

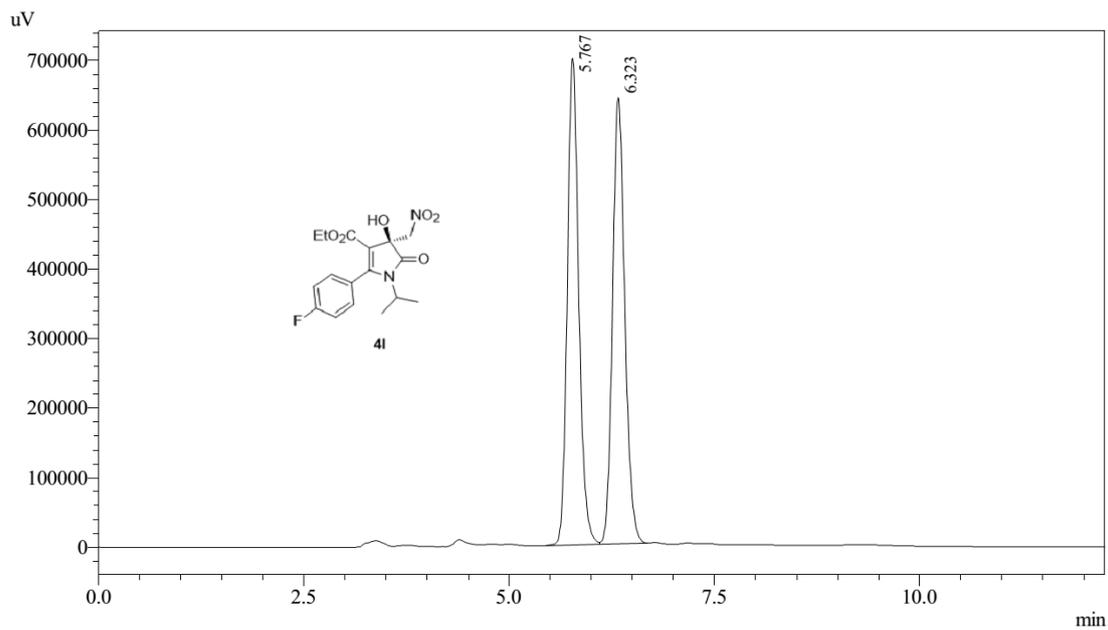
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.909	7536771	255969	50.169	49.344
2	6.898	7486076	262778	49.831	50.656
Total		15022846	518747	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.919	1808477	111332	15.474	15.557
2	6.891	9878533	604292	84.526	84.443
Total		11687010	715624	100.000	100.000

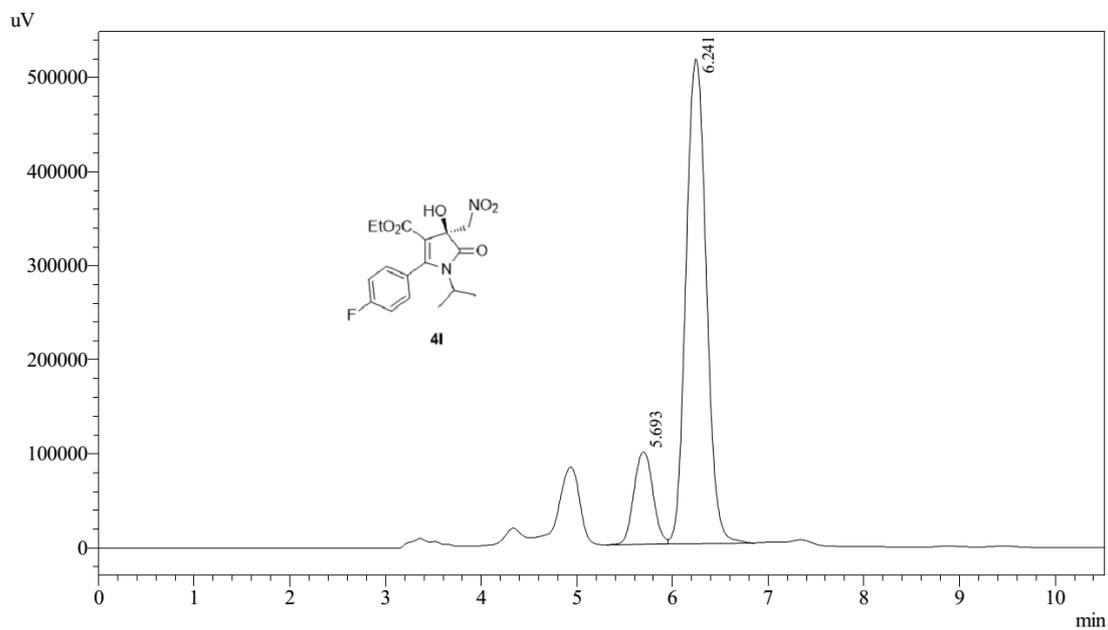




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

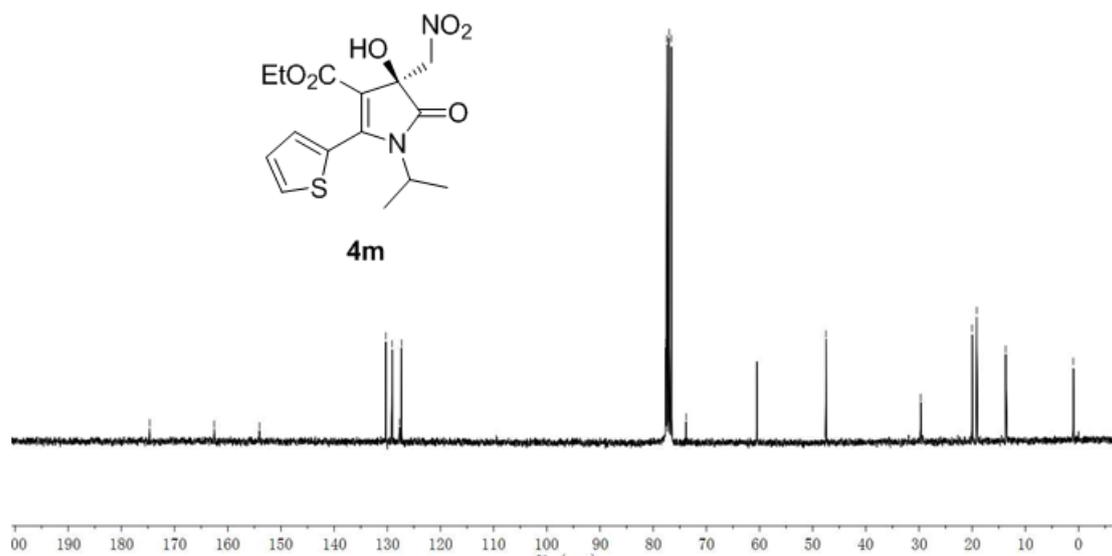
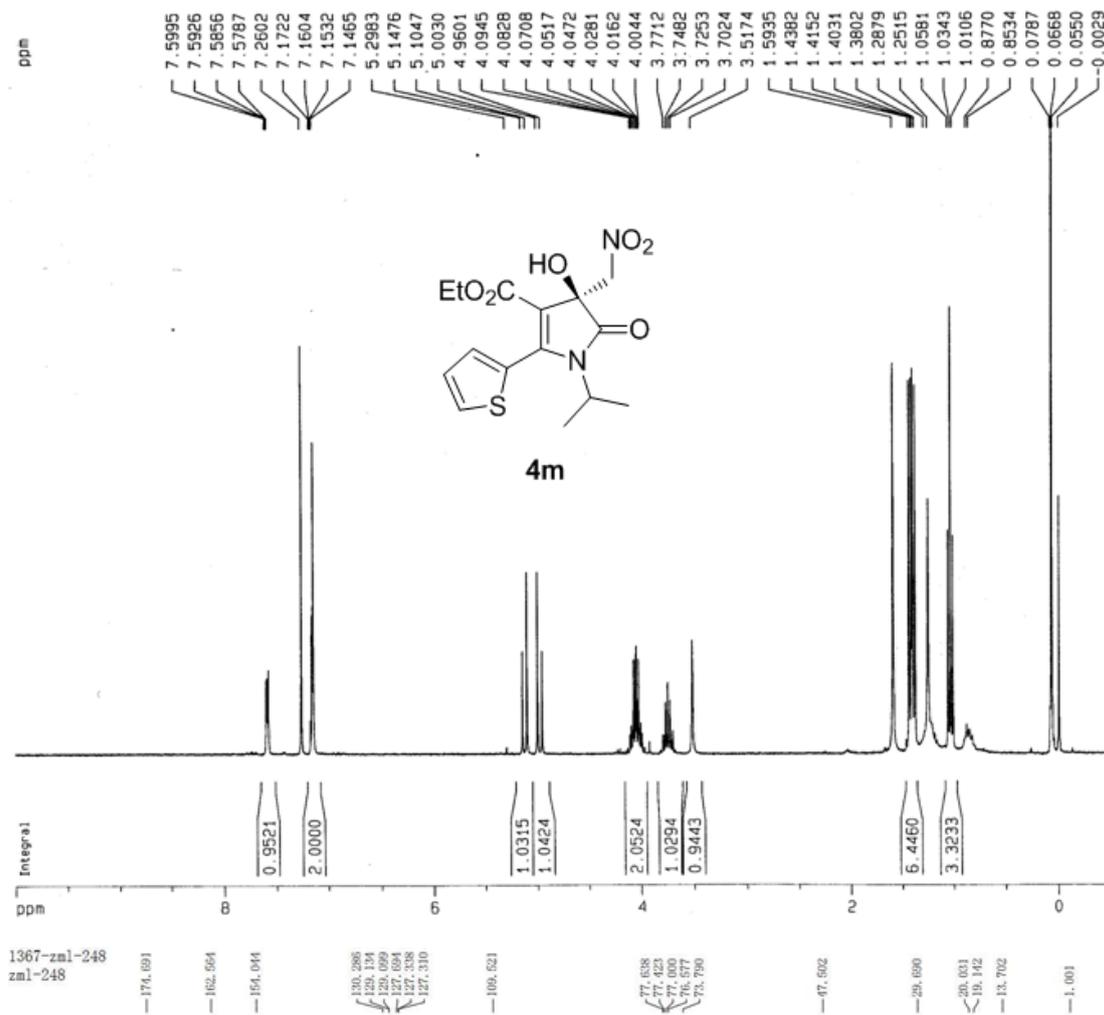
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.767	6796590	700281	50.453	52.174
2	6.323	6674490	641919	49.547	47.826
Total		13471080	1342200	100.000	100.000

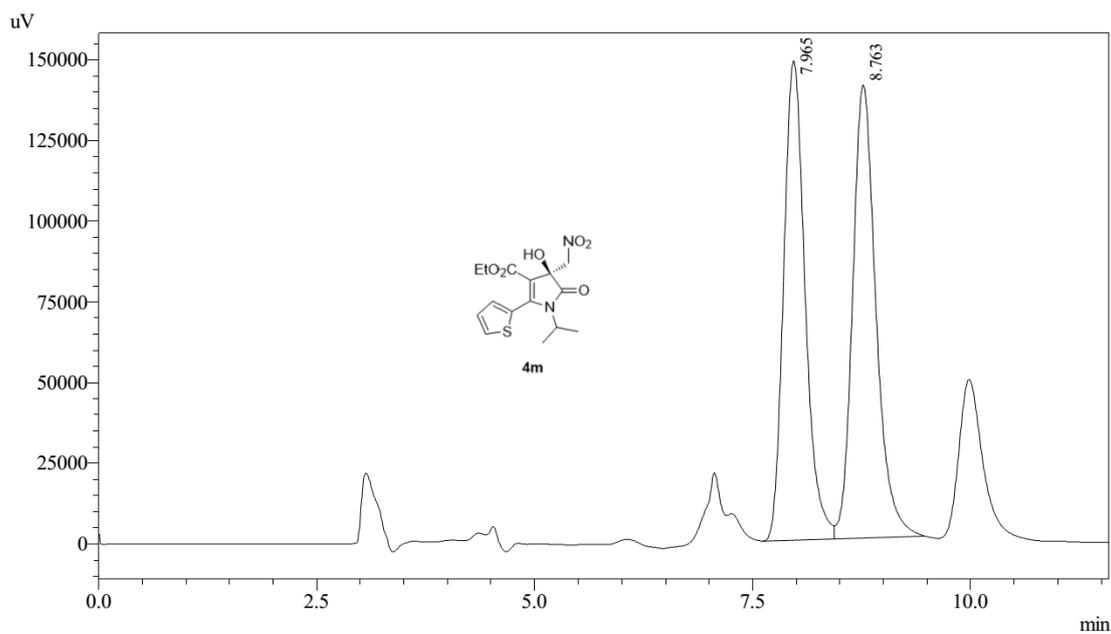


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.693	1367967	98399	15.242	16.038
2	6.241	7606727	515125	84.758	83.962
Total		8974694	613524	100.000	100.000

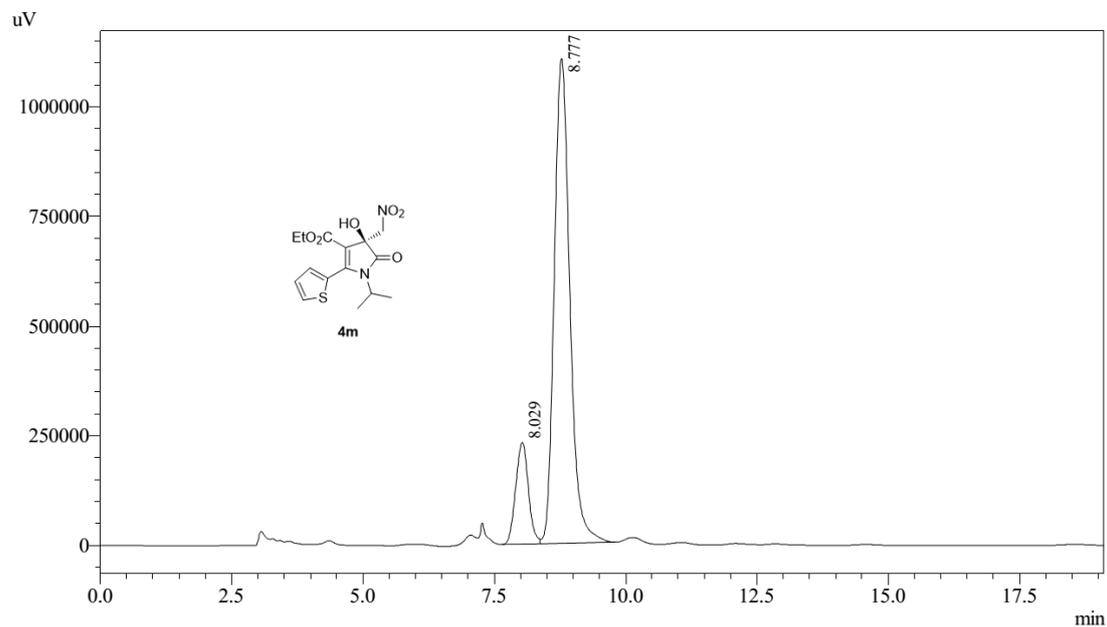




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

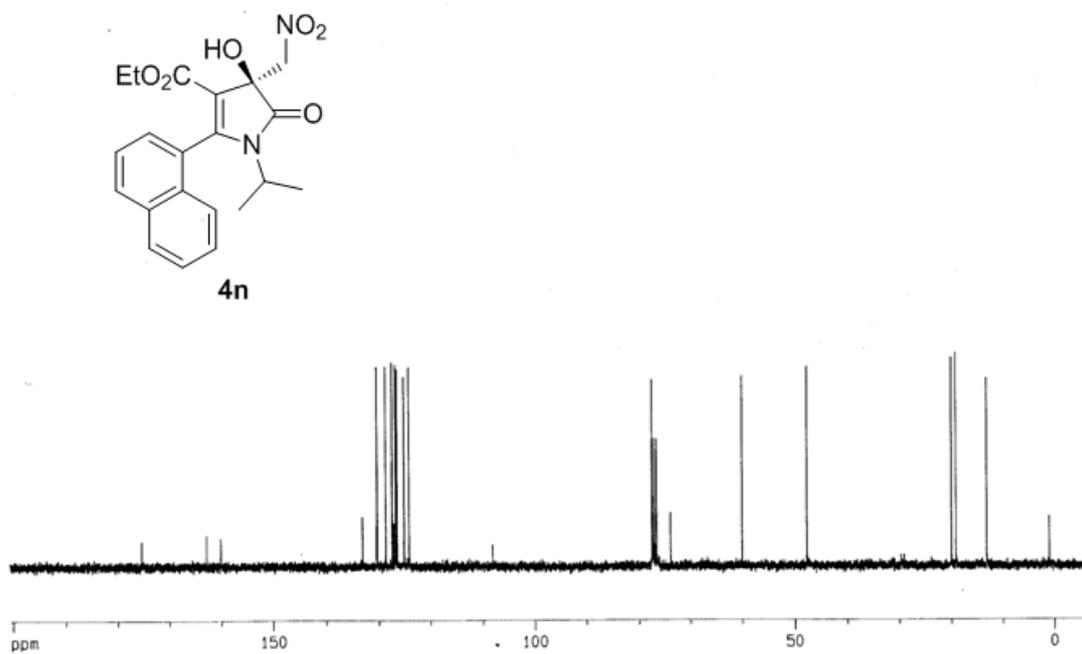
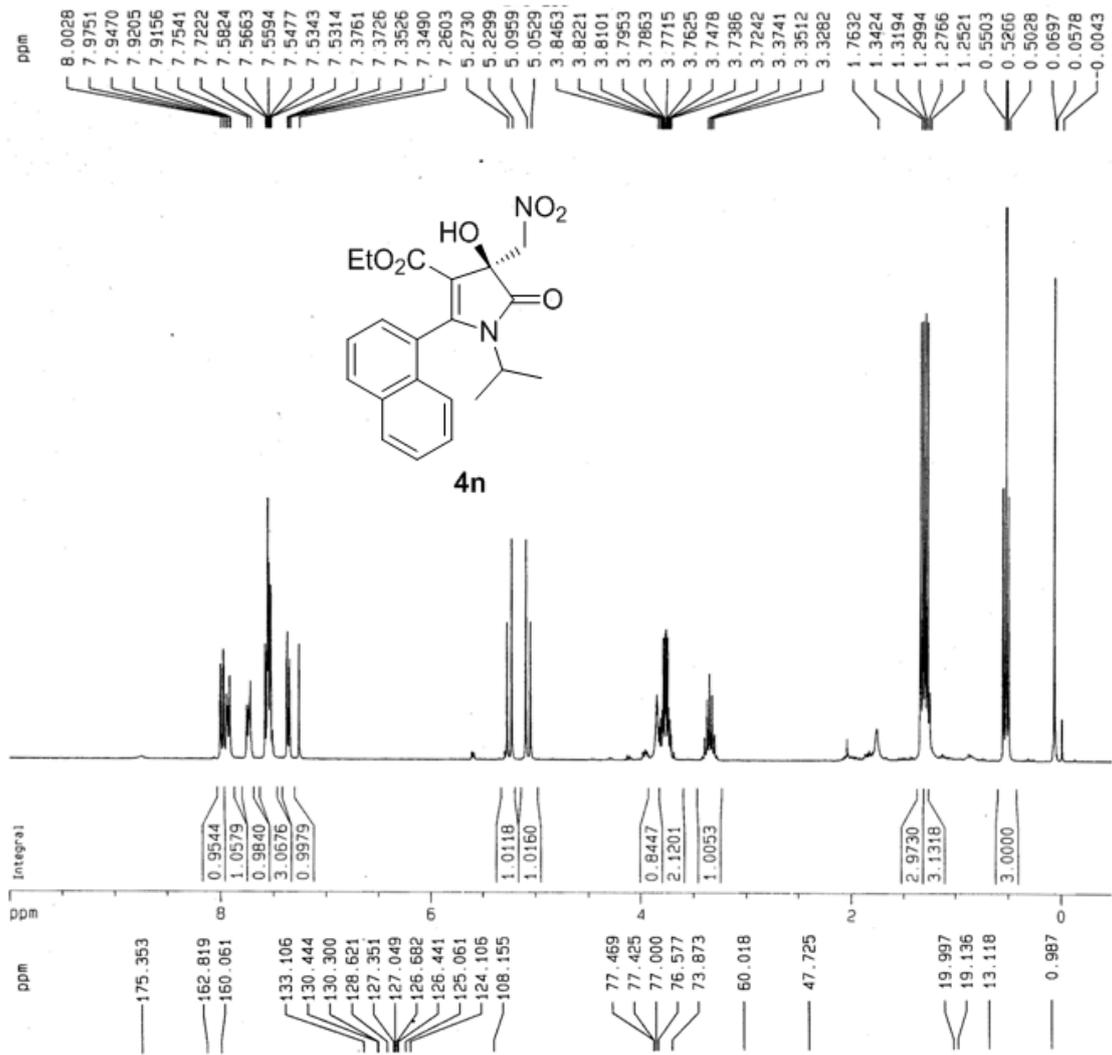
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.965	2533357	148632	49.230	51.413
2	8.763	2612614	140462	50.770	48.587
Total		5145971	289094	100.000	100.000

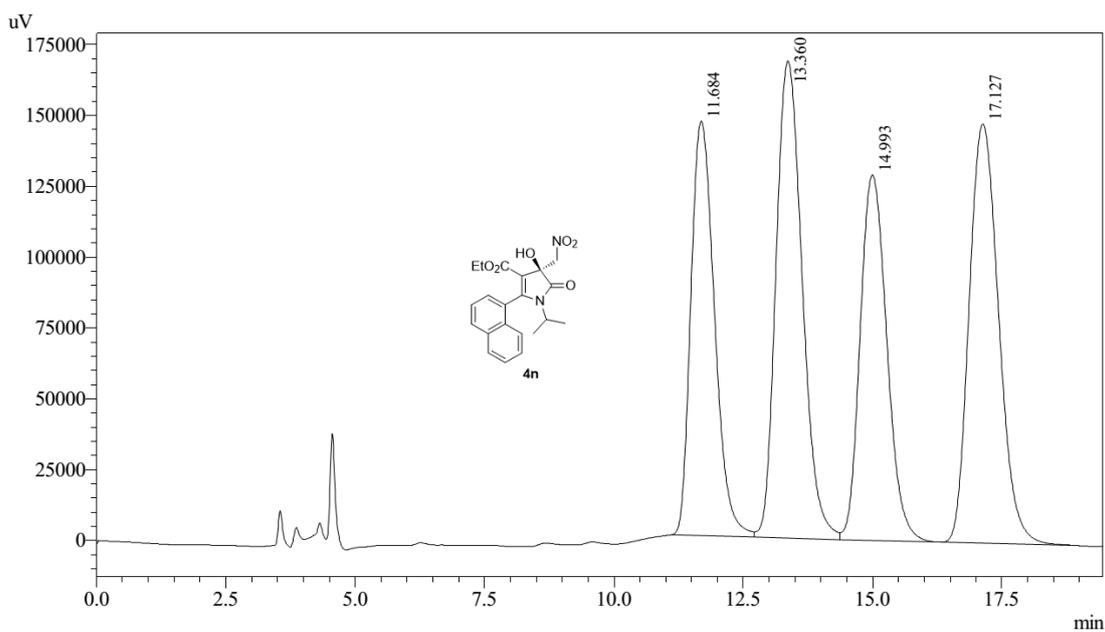


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.029	3921129	231770	14.682	17.338
2	8.777	22785352	1105014	85.318	82.662
Total		26706480	1336784	100.000	100.000

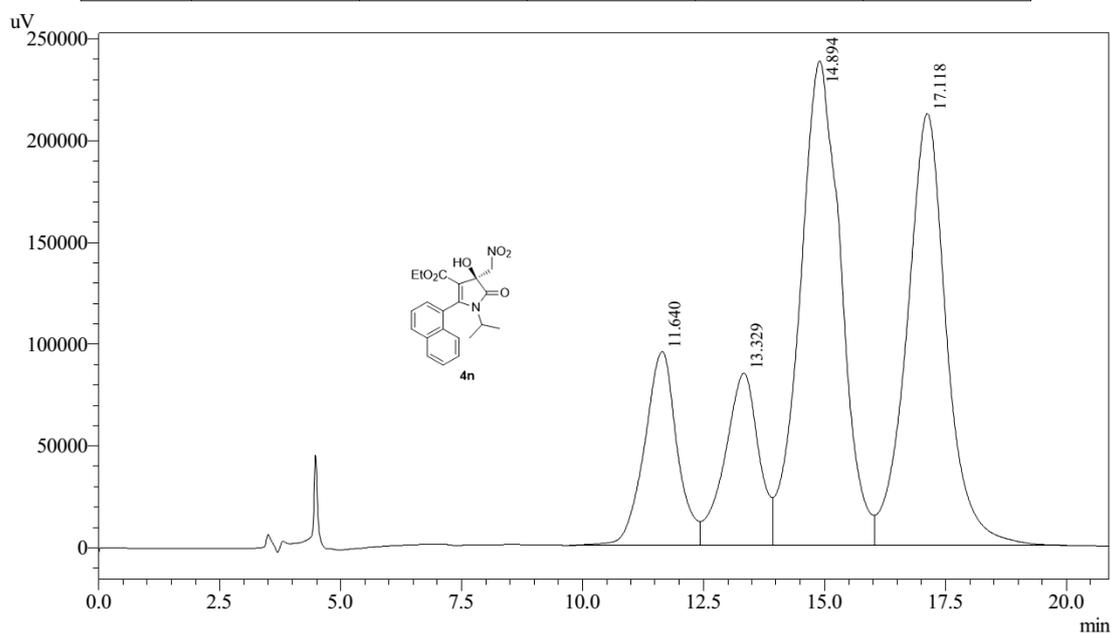




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

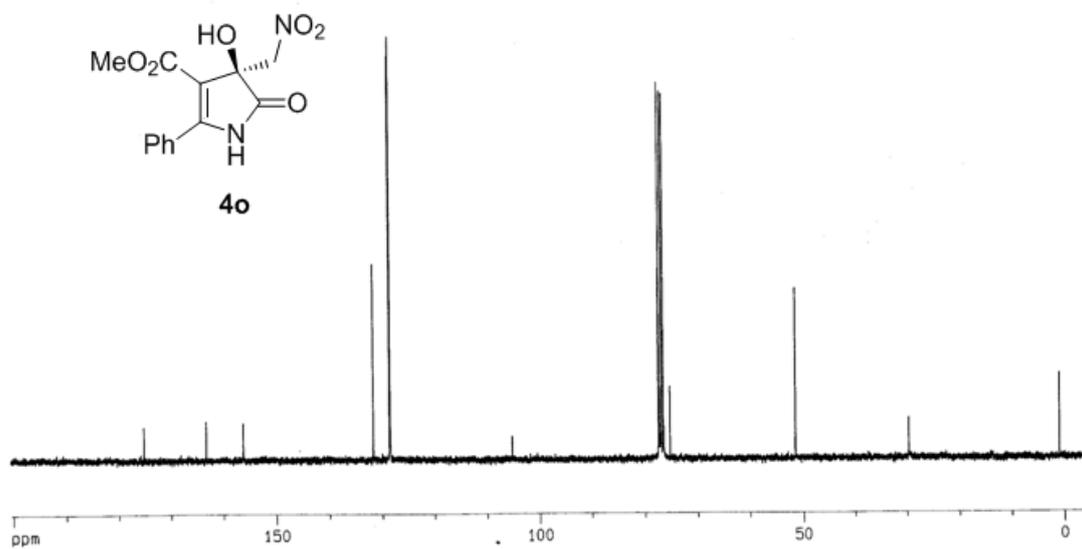
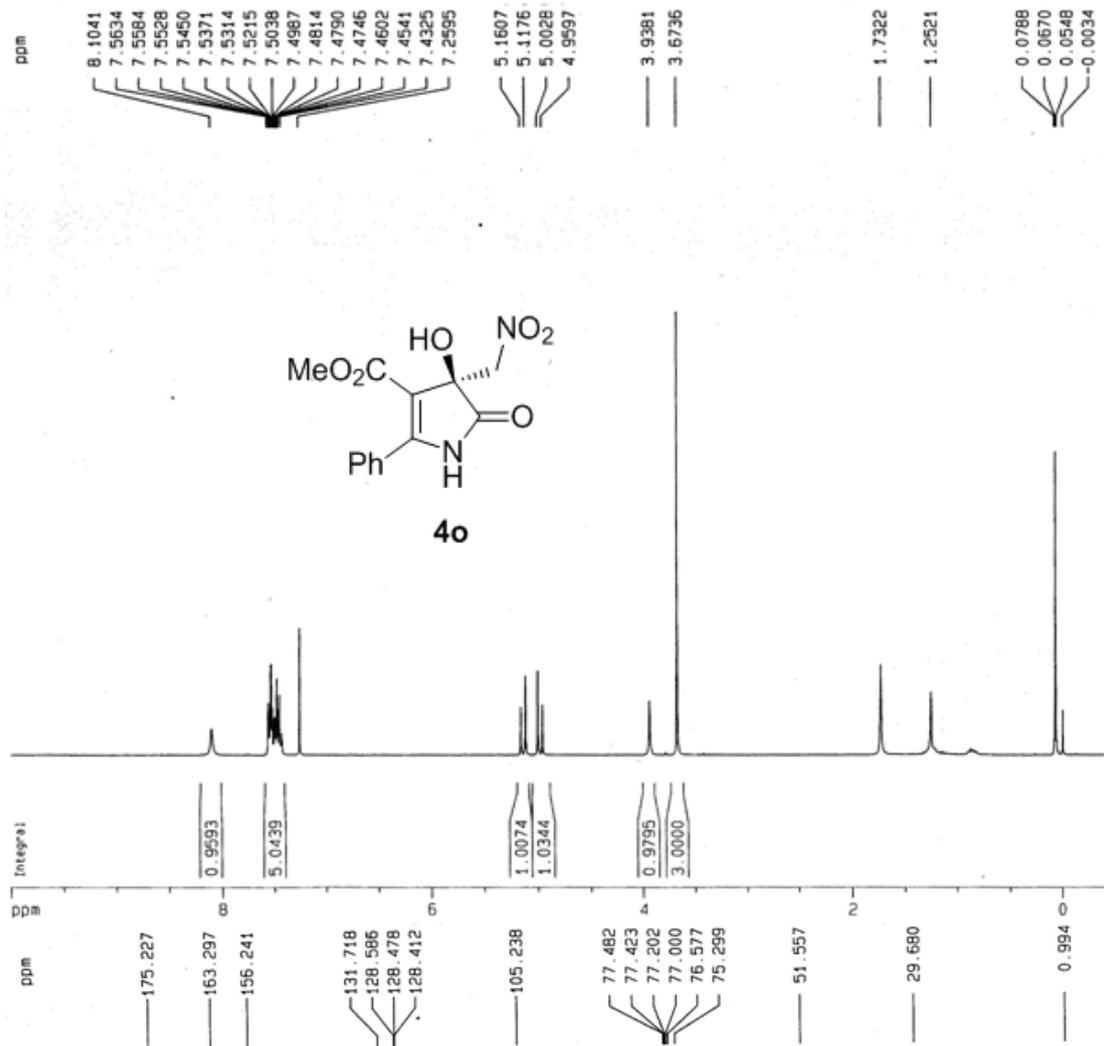
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.684	4639600	146291	22.025	24.735
2	13.360	5941227	168315	28.204	28.459
3	14.993	4628557	128940	21.972	21.801
4	17.127	5856135	147890	27.800	25.005
Total		21065518	591435	100.000	100.000

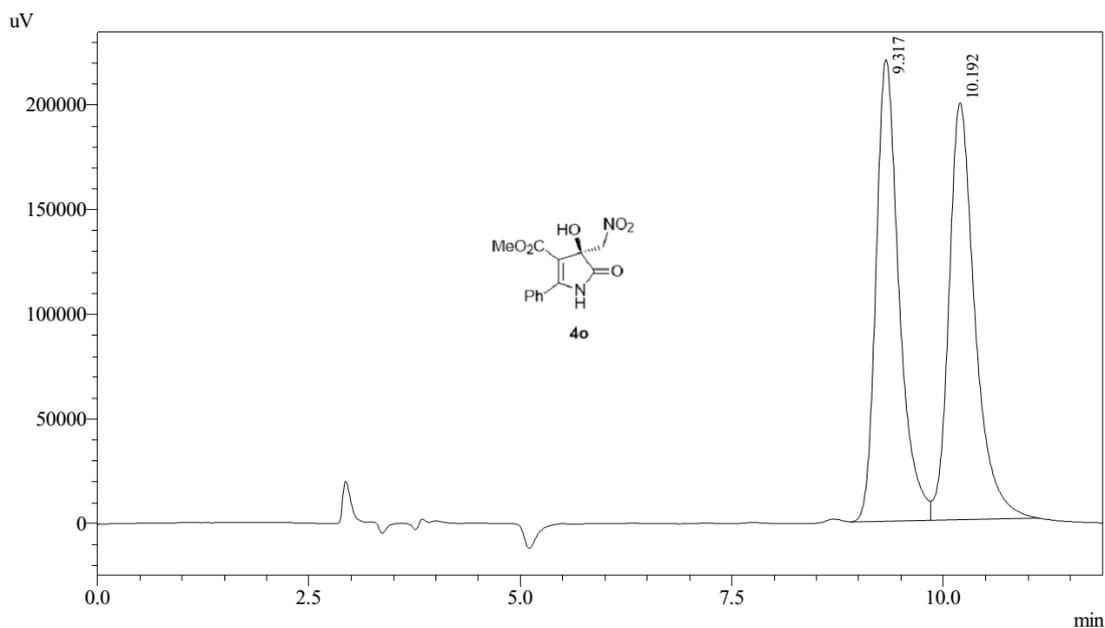


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.640	4484018	95360	12.930	15.121
2	13.329	4128815	84797	11.906	13.446
3	14.894	13942374	238210	40.203	37.771
4	17.118	12124412	212296	34.961	33.662
Total		34679618	630662	100.000	100.000

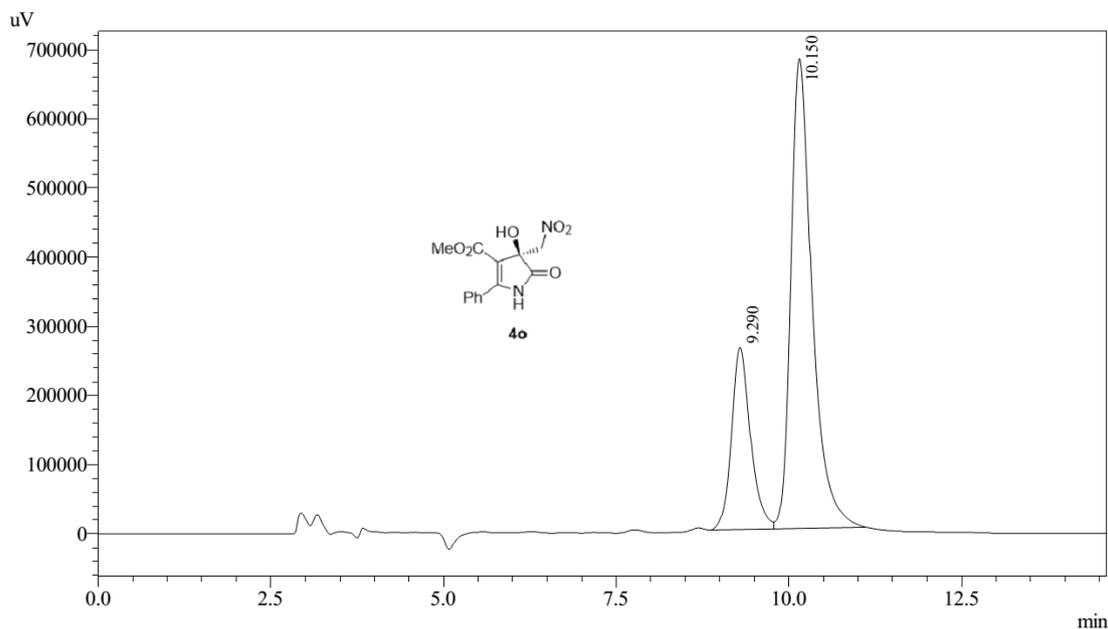




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

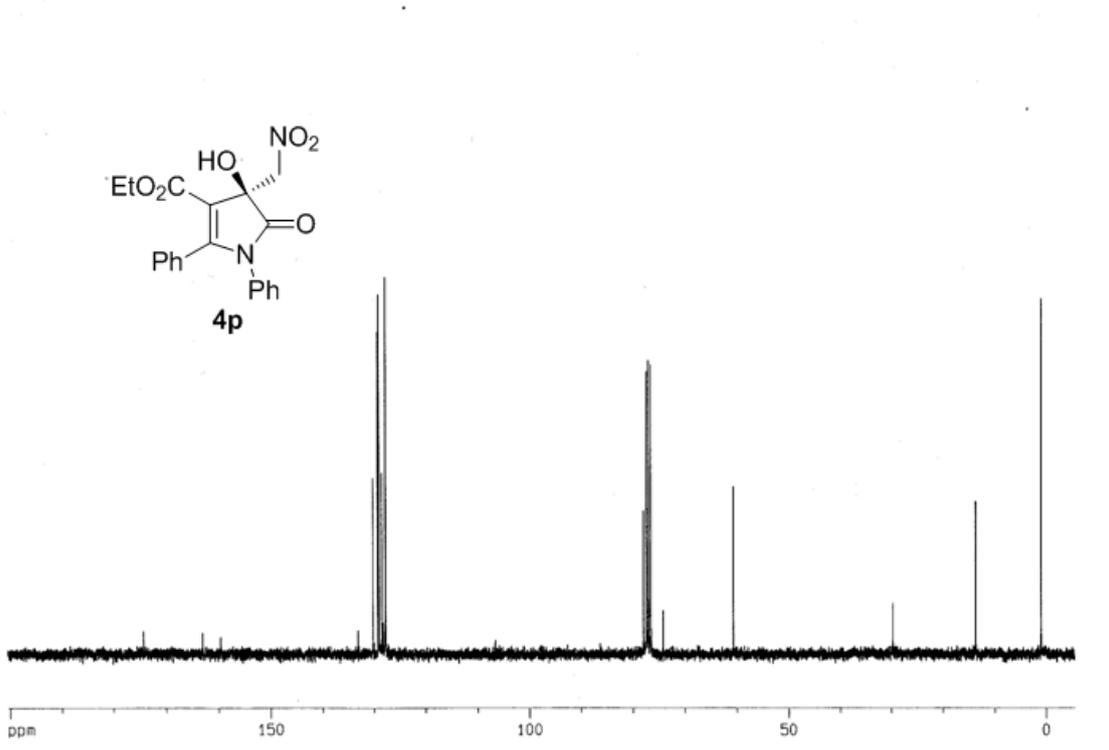
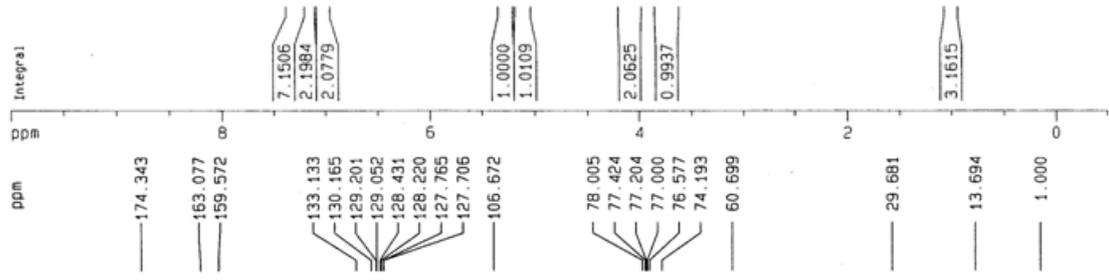
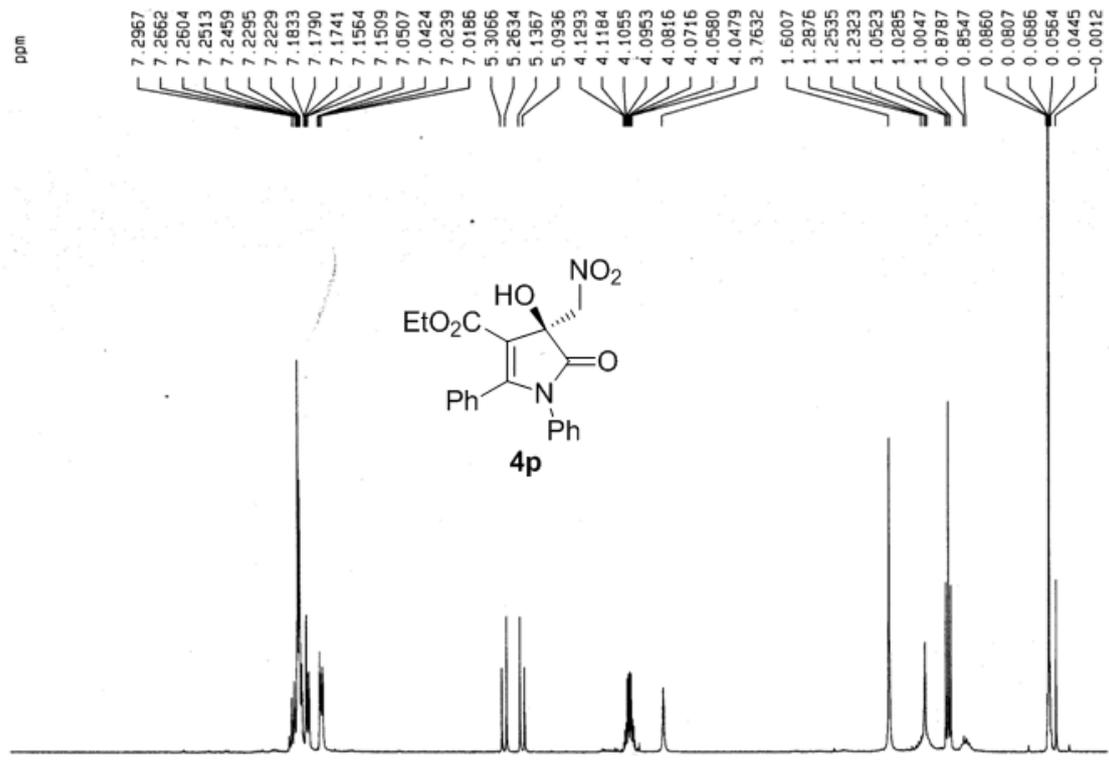
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.317	4168487	220420	49.448	52.539
2	10.192	4261578	199119	50.552	47.461
Total		8430065	419538	100.000	100.000

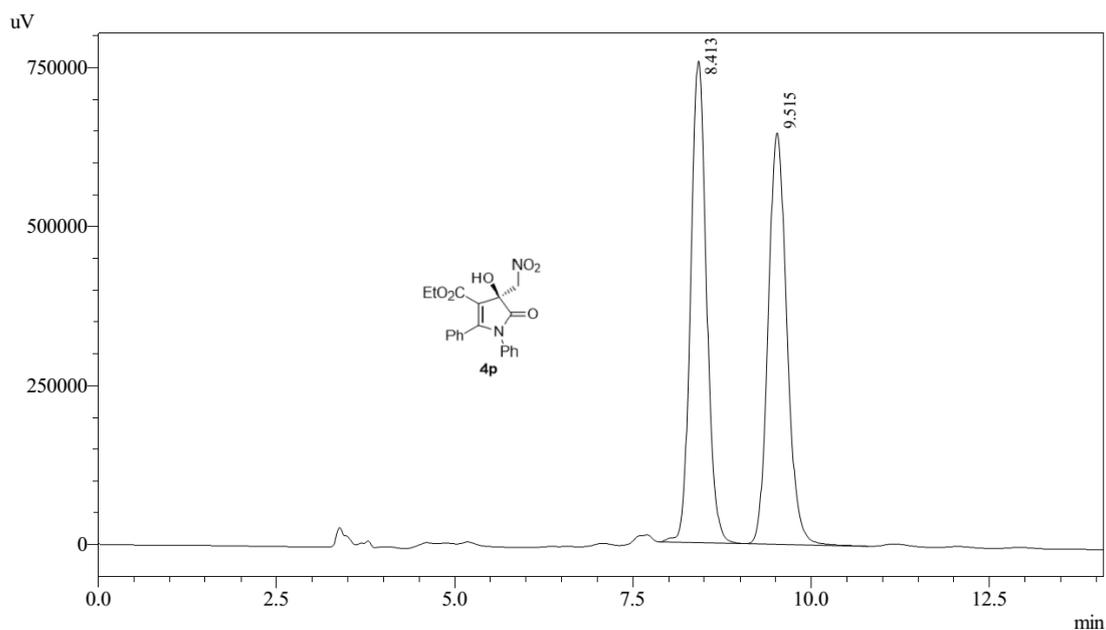


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.290	5072251	263148	25.759	27.946
2	10.150	14619258	678475	74.241	72.054
Total		19691508	941624	100.000	100.000

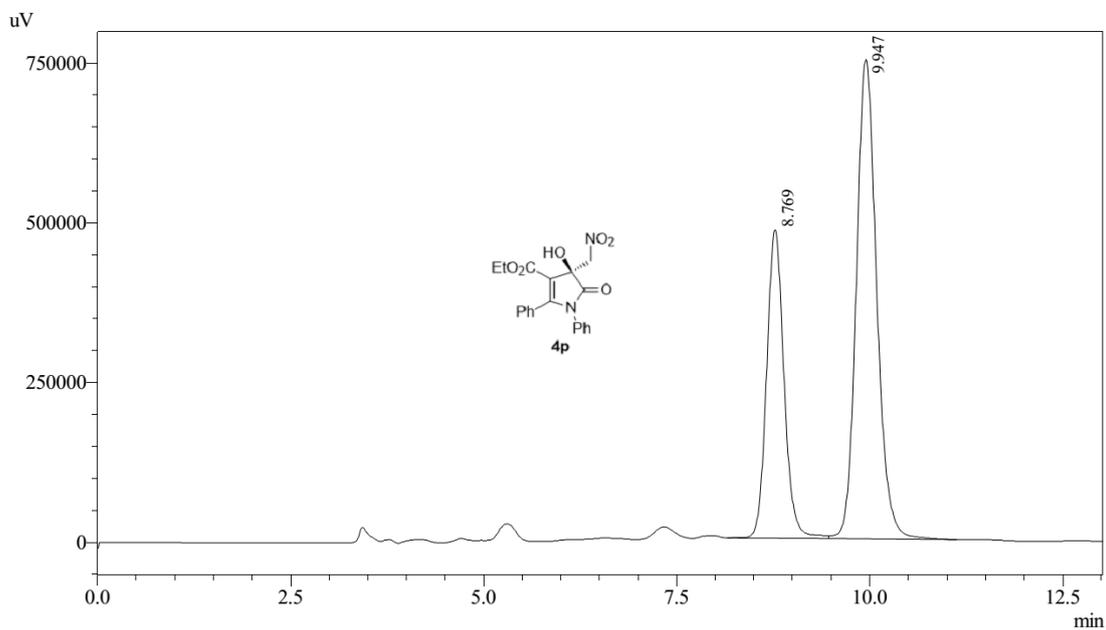




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

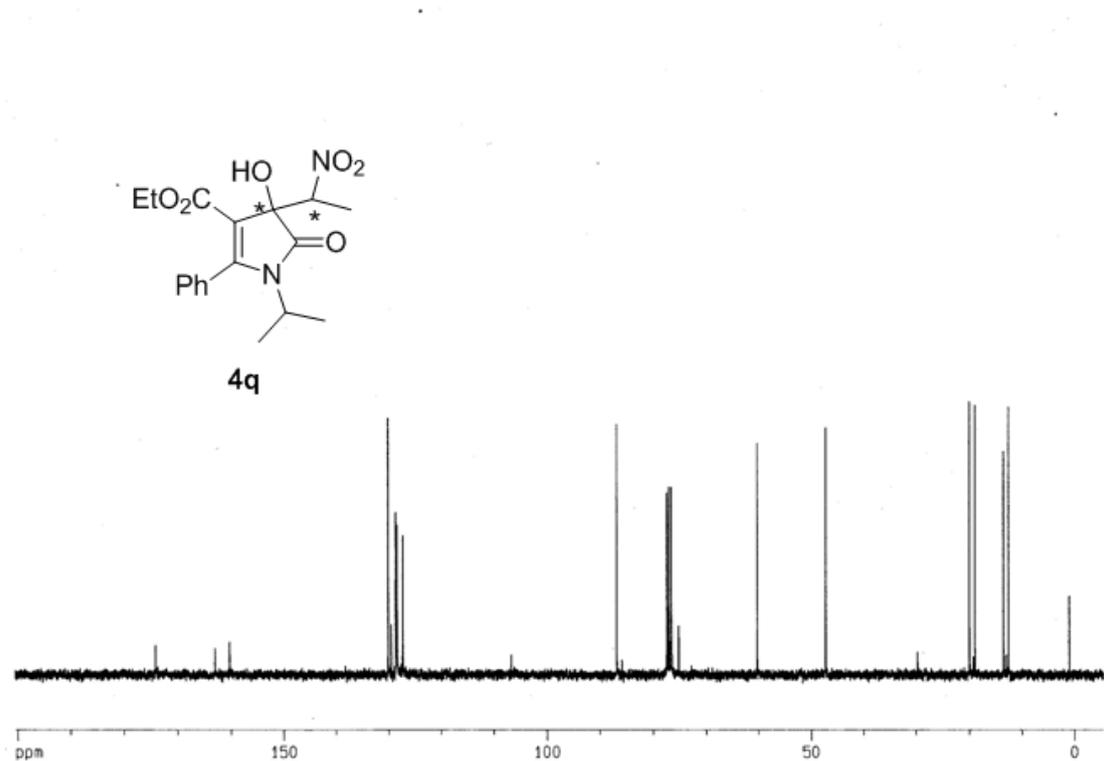
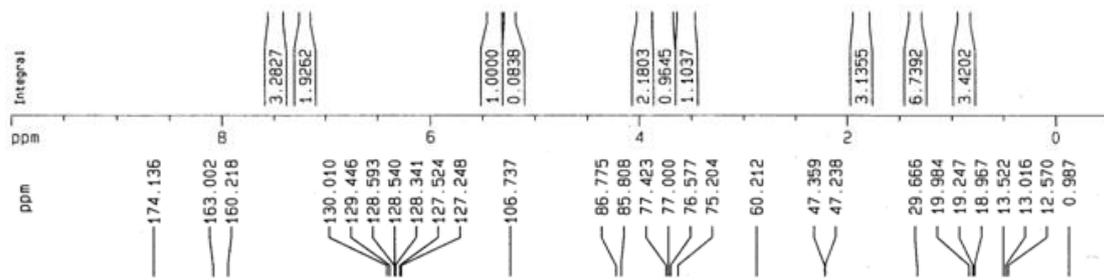
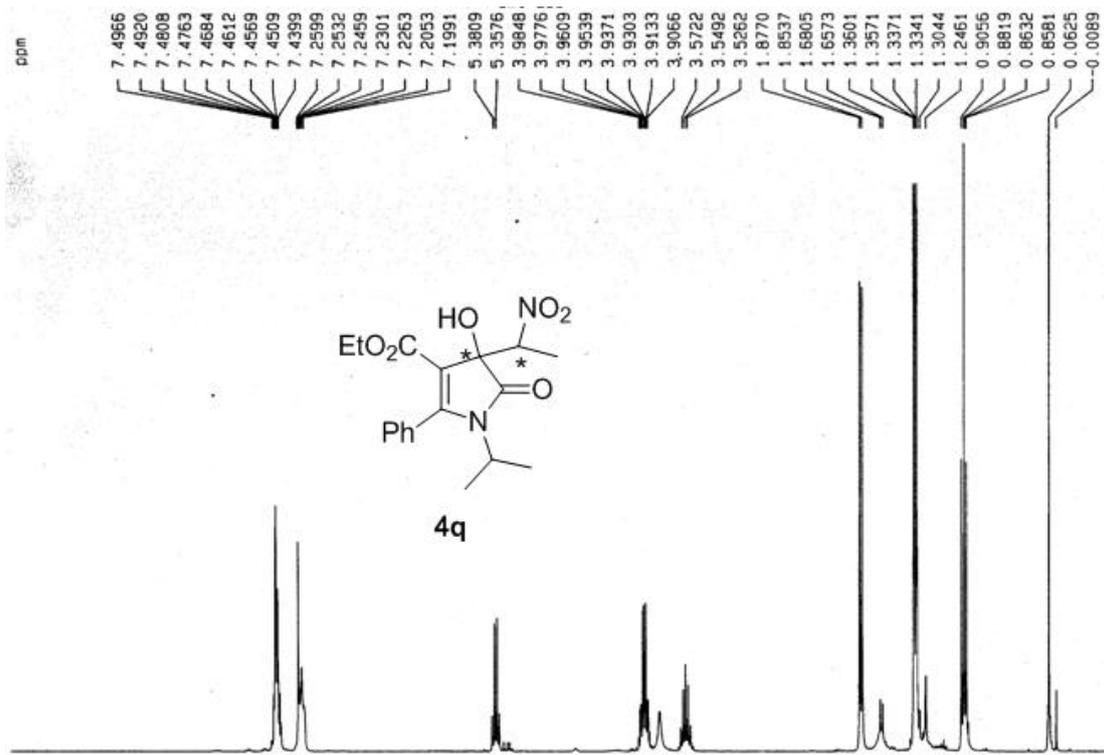
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.413	11754086	757832	49.938	53.951
2	9.515	11783436	646823	50.062	46.049
Total		23537523	1404654	100.000	100.000

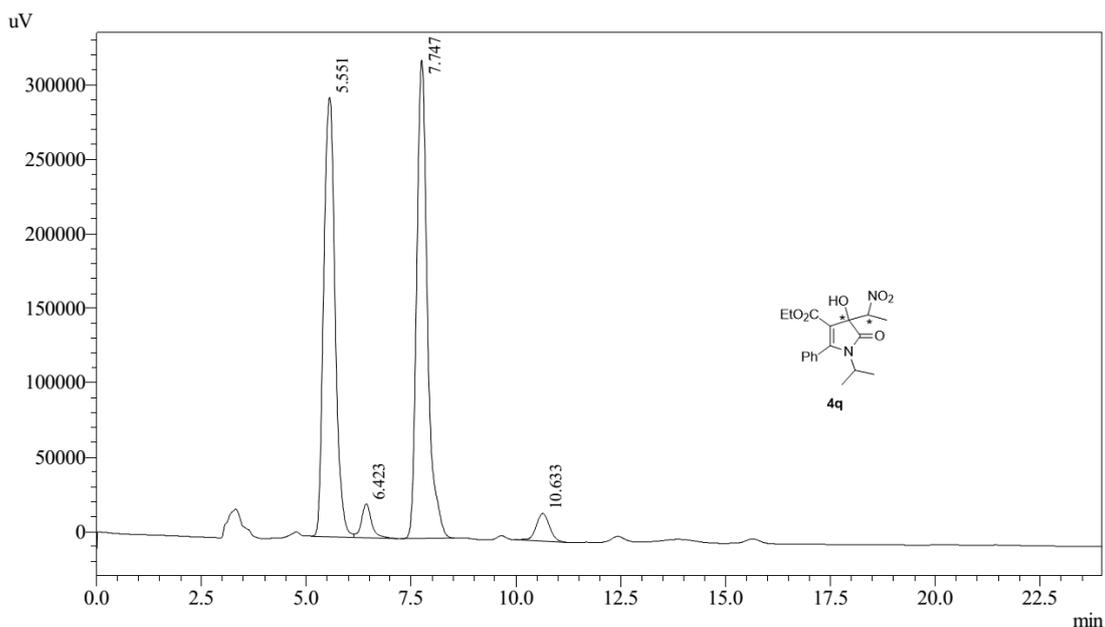


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.769	7540260	482303	35.341	39.120
2	9.947	13795492	750573	64.659	60.880
Total		21335753	1232876	100.000	100.000

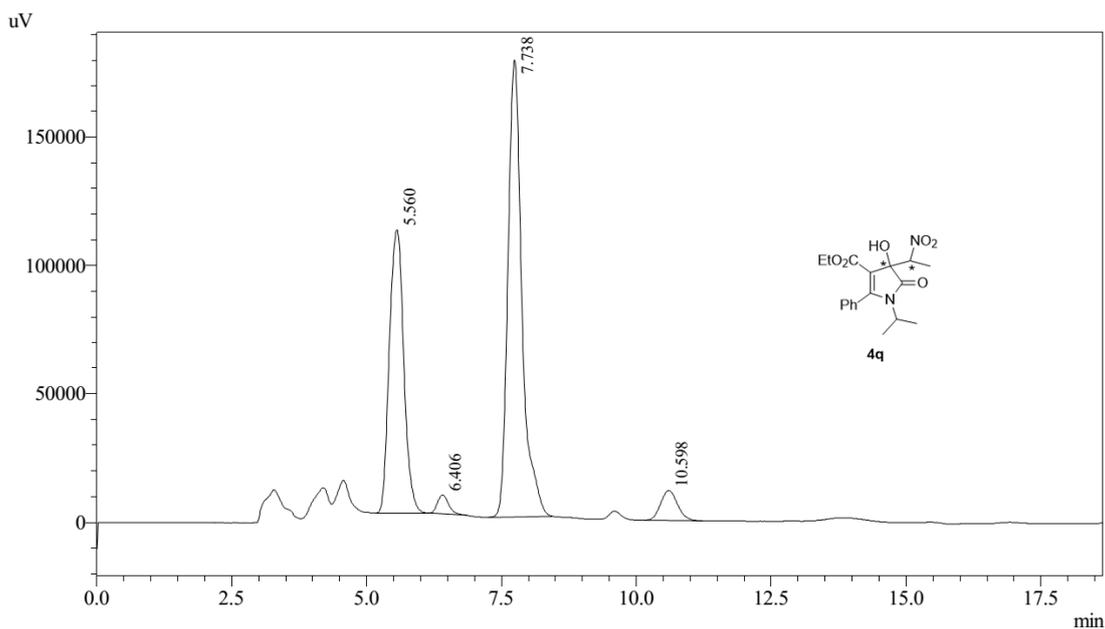




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

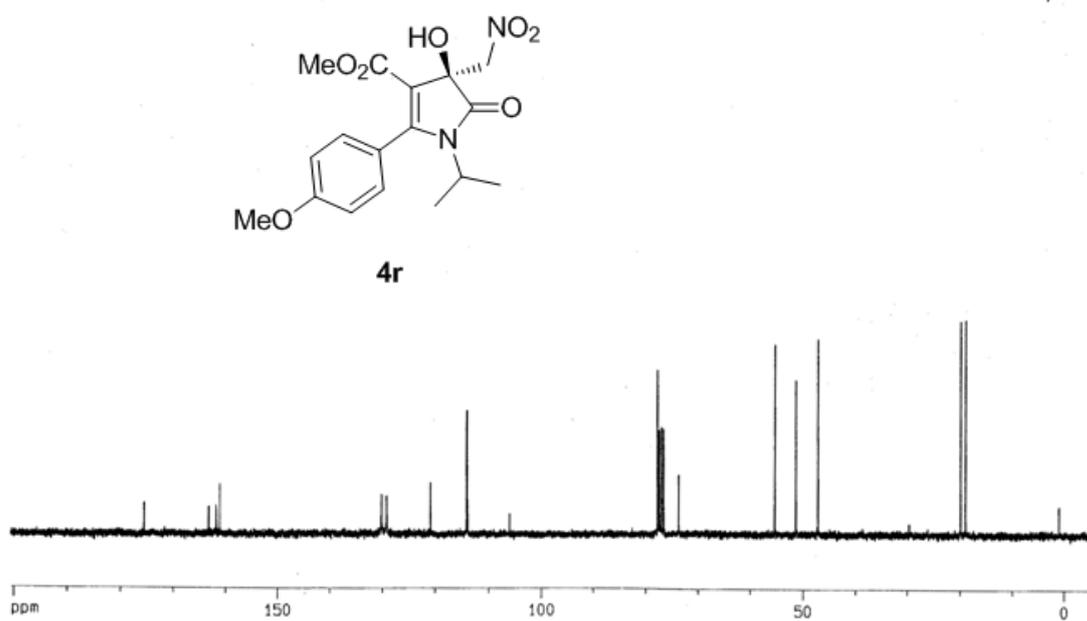
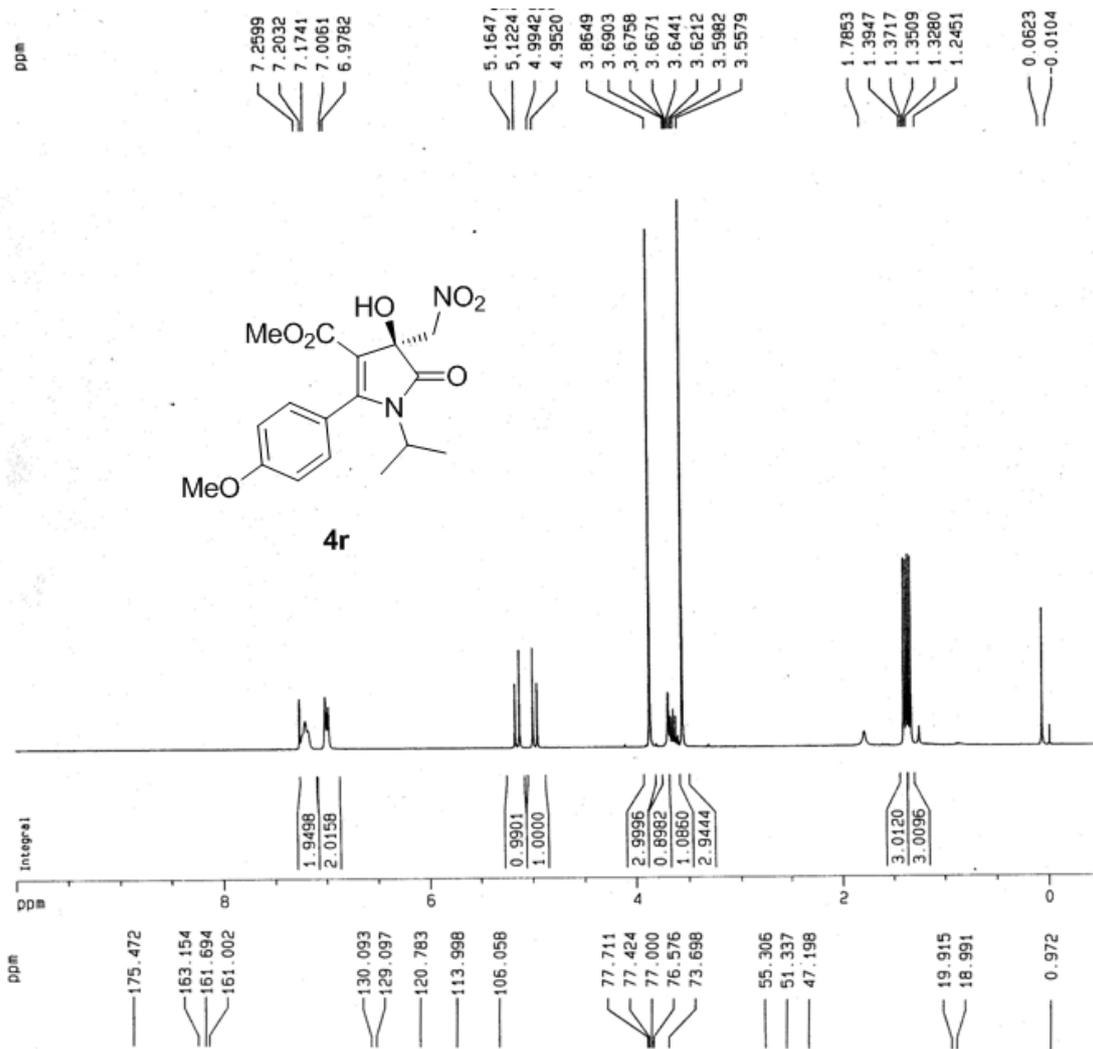
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.551	5557076	294892	46.076	44.861
2	6.423	373667	22666	3.098	3.448
3	7.747	5714429	321167	47.381	48.858
4	10.633	415383	18628	3.444	2.834
Total		12060555	657353	100.000	100.000

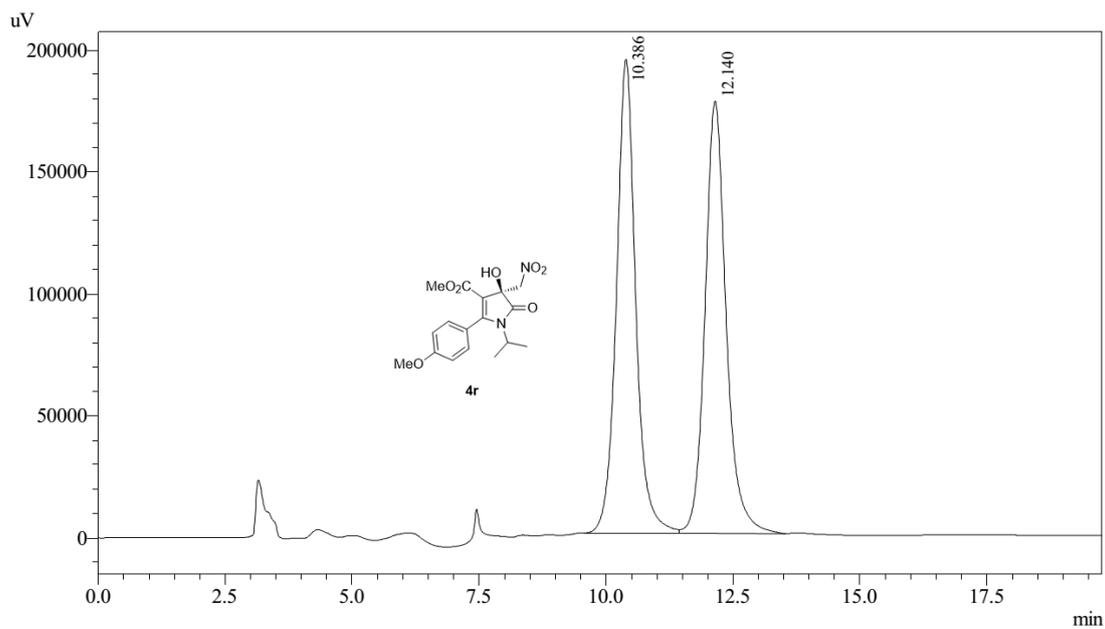


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.560	2044644	110373	36.488	35.905
2	6.406	105826	7392	1.889	2.405
3	7.738	3199376	177966	57.095	57.893
4	10.598	253724	11674	4.528	3.798
Total		5603570	307405	100.000	100.000

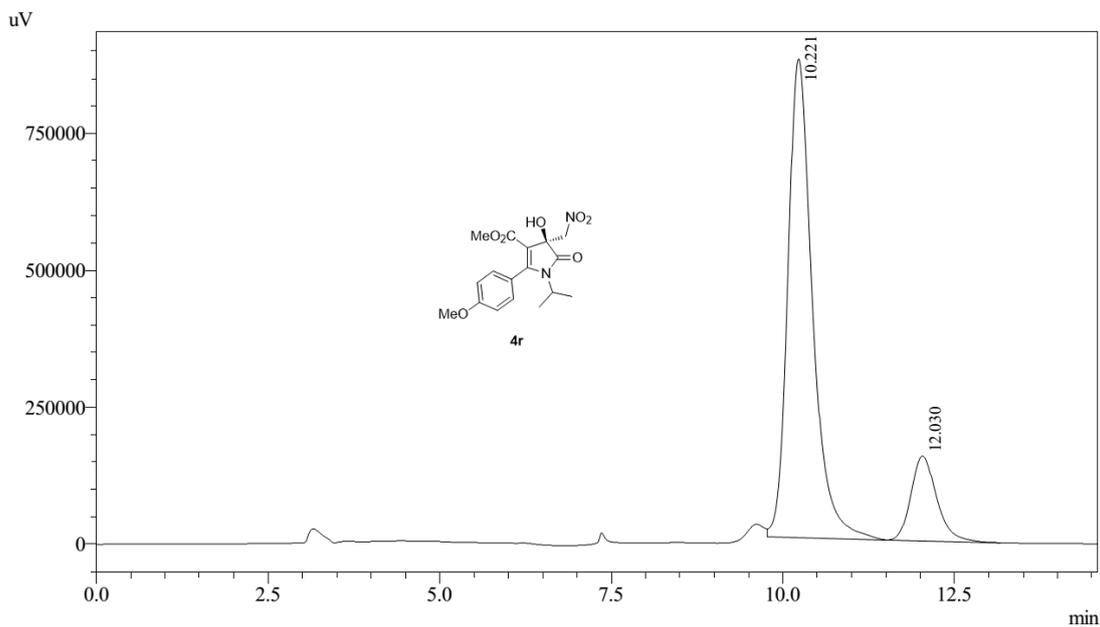




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

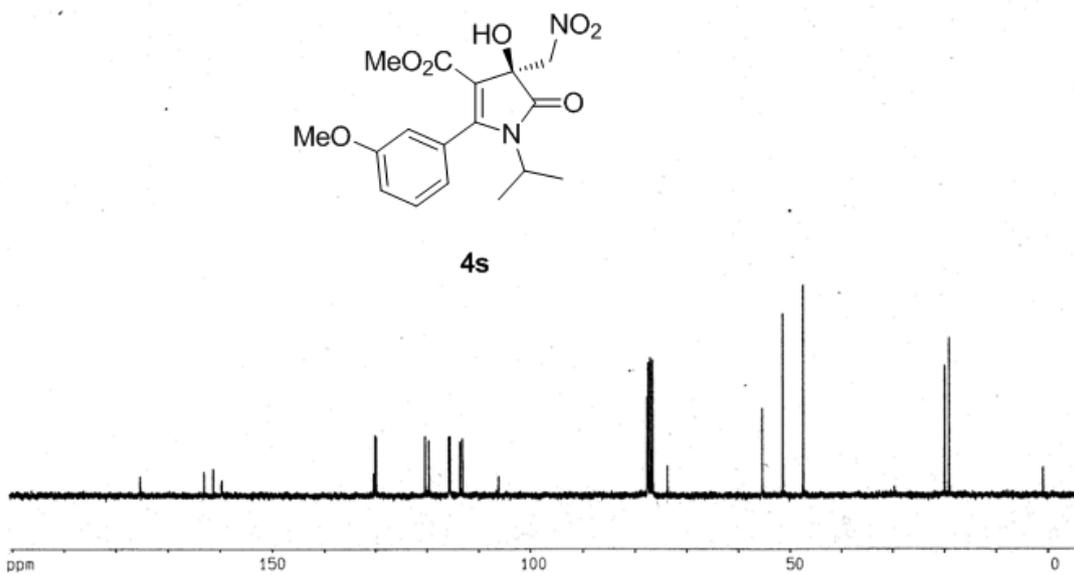
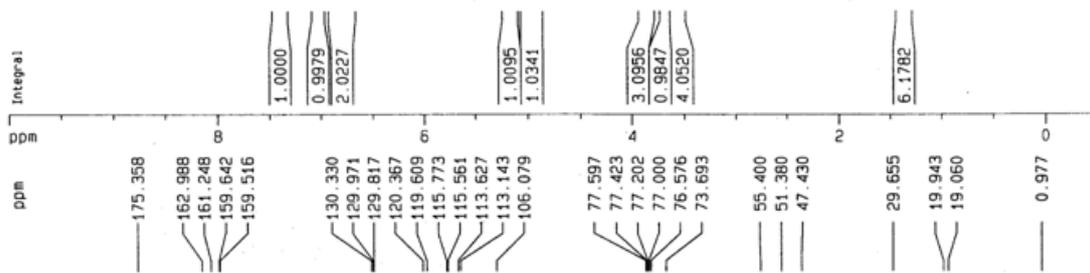
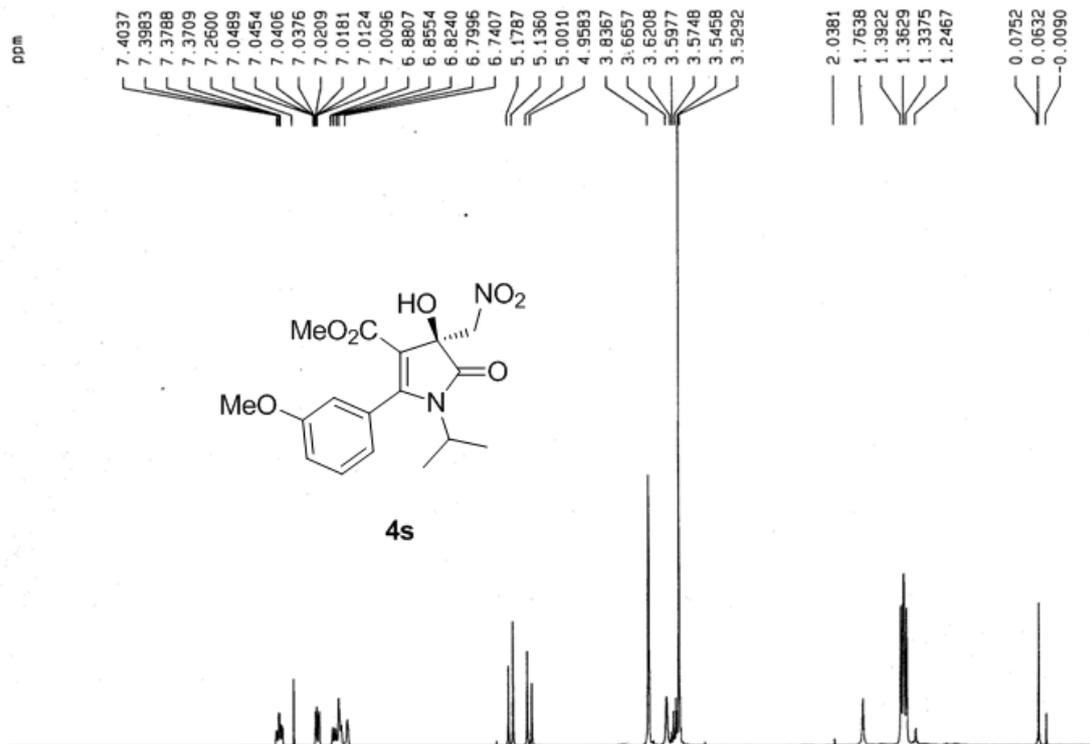
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.386	5122338	194251	49.979	52.291
2	12.140	5126683	177233	50.021	47.709
Total		10249021	371485	100.000	100.000

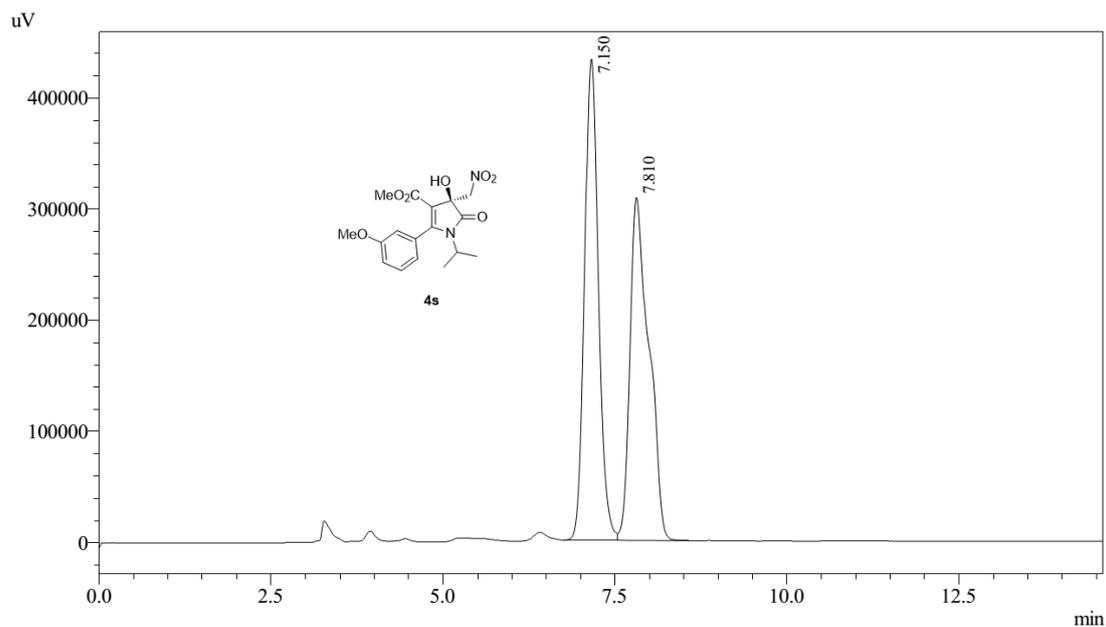


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

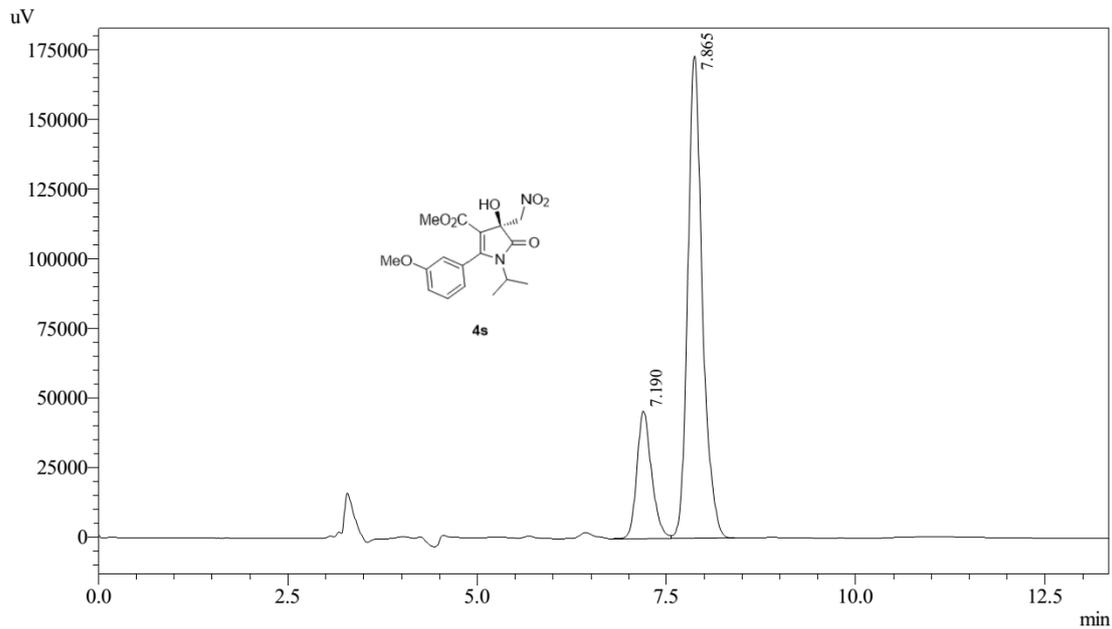
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.221	21797879	873916	84.357	84.965
2	12.030	4042184	154645	15.643	15.035
Total		25840063	1028560	100.000	100.000





Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.150	6076688	432784	50.611	58.372
2	7.810	5929991	308639	49.389	41.628
Total		12006678	741422	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.190	621115	45812	21.023	20.918
2	7.865	2333303	173194	78.977	79.082
Total		2954418	219005	100.000	100.000