Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Organocatalytic Enantioselective Pyrazol-3-one Addition to Maleimides: Reactivity and Stereochemical Course

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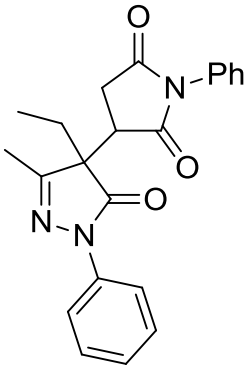
Supporting Information

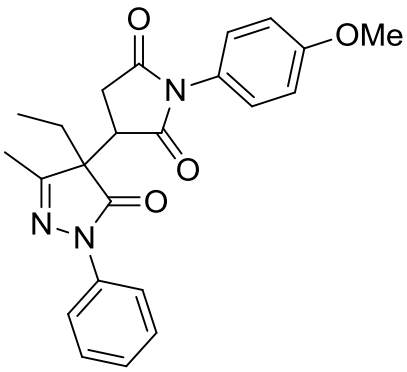
NMR spectra and HPLC traces

General methods.

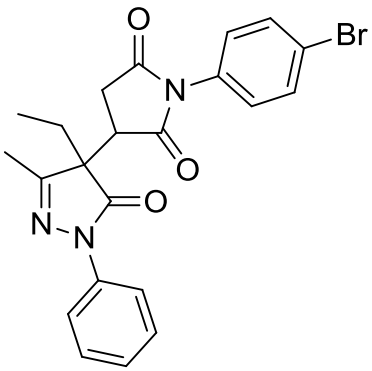
Chemicals and solvents were either purchased *puriss p.A.* from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL) followed by heating or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating. Flash chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm), ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian AS 400. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and the coupling constants *J* are given in Hz. The spectra were recorded in $CDCl_3$ as solvent at room temperature. TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR, $CDCl_3$ was used as internal standard (δ = 77.0 ppm) for ^{13}C NMR. High-resolution mass spectra were recorded on a Bruker MicrOTOF spectrometer.



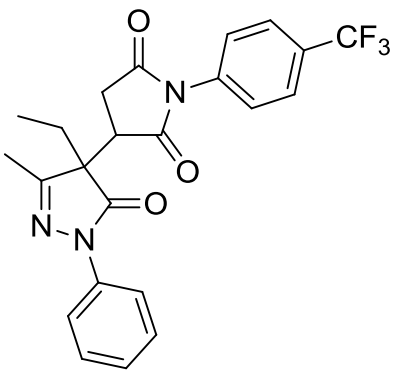
3a: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.86 (d, J=7.7Hz, 2H), 7.45-7.35 (m, 5H), 7.25-7.15 (m, 3H), 3.37 (dd, J=5.7Hz, J'=9.6Hz, 1H), 3.23 (dd, J=5.7Hz, J'=18.3Hz, 1H), 2.96 (dd, J=9.6Hz, J'=18.3Hz, 1H), 2.21 (s, 3H), 2.11 (q, J=7.4Hz, 2H), 0.83 (t, J=7.4Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.8, 175.1, 174.3, 161.8, 138.7, 132.7, 130.5, 130.3, 130.2, 127.6, 126.9, 120.5, 60.0, 44.6, 31.6, 28.2, 15.8, 9.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{22}H_{22}N_3O_3$) requires 376.1656, found 376.1659. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 220 nm, 1.0 mL/min): t_R= 13.1, 17.7 min. $[\alpha]_D^{25}$ = -40.3 (c=0.8, $CHCl_3$, ee=80%,).



3b: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.85, (d**, J=7.7Hz, 2H), 7.42-7.38 (n, 2H), 7.24-7.18 **(m**, 1H), 7.08**, (d**, J=8.7Hz, 2H), 6.91**, (d**, J=8.9Hz, 2H), 3.79 (s, 3H), 3.34 (dd, J=5.6Hz, J'=9.3Hz, 1H), 3.30-3.15 (m, 1H), 2.93 (dd, J=9.3Hz, J'=18.0Hz, 1H), 2.19 (s, 3H), 2.15-2.05 (m, 2H), 0.82 (t, J=7.3Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.1, 175.5, 174.4, 161.9, 161.0, 138.8, 130.3, 129.3, 129.0, 128.9, 126.9, 120.5, 116.0, 115.9, 115.9, 60.0, 56.9, 44.6, 31.5, 28.2, 15.9, 9.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_4$) requires 406.1761, found 406.1769. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): t_R= 21.9, 31.4 min.

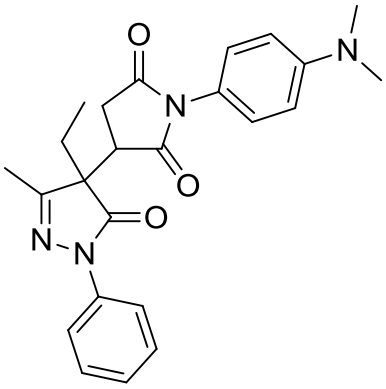


3c: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.85, (d**, J=8.6Hz, 2H), 7.53**, (d**, J=8.7Hz, 2H), 7.43-7.37 (m, 2H), 7.25-7.18 (m, 1H), 7.07**, (d**, J=8.7Hz, 2H), 3.40-3.20 (m, 2H), 2.96 (dd, J=9.0Hz, J'=17.7Hz, 1H), 2.20 (s, 3H), 2.13-2.00 (m, 2H), 0.83 (t, J=7.4Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 138.8, 133.8, 130.4, 129.2, 127.0, 120.5, 59.8, 44.8, 31.5, 28.3, 15.8, 9.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{22}H_{21}BrN_3O_3$) requires 454.0761, found 454.0766. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): t_R= 13.1, 18.4 min.

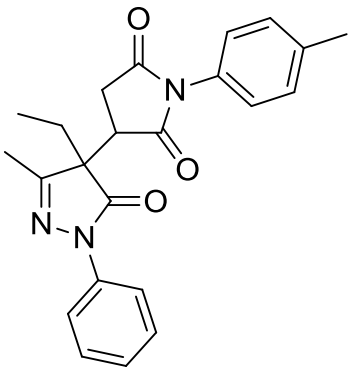


3d: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95, (d**, J=8.5Hz, 2H), 7.84**, (d**, J=8.6Hz, 2H), 7.37-7.23 (m, 4H), 7.23-7.17 (m, 1H), 3.43-3.33 (m, 2H), 2.99 (dd, J=10.5Hz, J'=19.2Hz, 1H), 2.21 (s, 3H), 2.13-2.00 (m, 2H), 0.83 (t, J=7.4Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):**

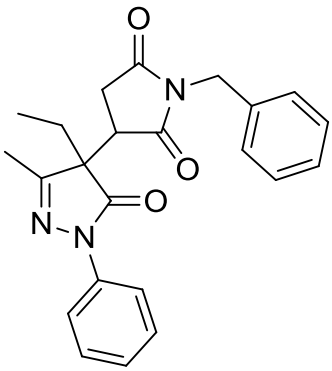
175.3, 174.7, 174.2, 161.9, 138.5, 135.6, 130.2, 130.1, 128.3, 127.8, 127.6 (m, CF3), 126.9, 120.3, 59.5, 44.7, 31.3, 28.2, 15.6, 9.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{21}F_3N_3O_3$) requires 444.1530, found 444.1523. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): t_R= 12.0, 16.0 min.



3e: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.85 (d, J=7.7Hz, 2H), 7.40 (t, J=7.7Hz, 2H), 7.23-7.18 (m, 1H), 7.00 (d, J=9.1Hz, 2H), 3.33 (dd, J=5.6Hz, J'=9.3Hz, 1H), 3.11-3.01 (m, 1H), 3.00-2.85 (m, 1H), 2.93 (s, 6H), 2.18 (s, 3H), 2.17-2.00 (m, 2H), 0.81 (t, J=7.4Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.4, 175.9, 174.5, 161.9, 151.9, 138.8, 130.3, 128.3, 126.9, 120.6, 113.8, 60.4, 44.5, 41.8, 31.6, 28.2, 16.0, 9.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{26}H_{33}N_4O_3$) requires 449.2547 found 449.2558. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 85:15, λ= 254 nm, 1.0 mL/min): t_R= 44.4, 63.7 min.

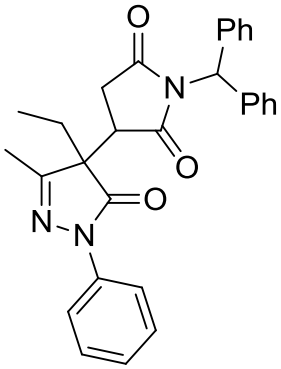


3f: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.86 (d**, J=7.8Hz, 2H), 7.42-7.36 (m, 2H), 7.22-7.18 **(m**, 2H), 7.04**, (d**, J=8.1Hz, 2H), , 3.34 (dd, J=5.5Hz, J'=9.4Hz, 1H), 3.22-3.12 (m, 1H), 2.93 (dd, J=9.4Hz, J'=18.1Hz, 1H), 2.33 (s, 3H), 2.18 (s, 3H), 2.12-2.08 (m, 2H), 0.81 (t, J=7.5Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.0, 175.4, 174.4, 162.0, 140.3, 138.8, 131.3, 131.2, 130.3, 127.9, 127.5, 127.5, 126.9, 120.5, 60.0, 44.7, 31.6, 28.2, 22.6, 15.9, 9.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_3$) requires 390.1812 found 390.1817. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): t_R= 14.0, 19.5 min.

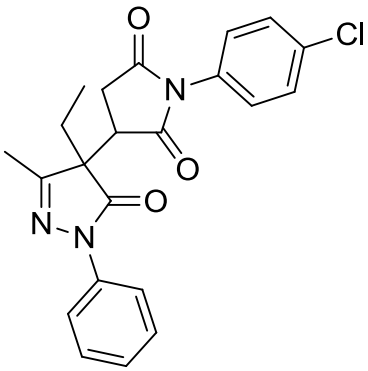


3g: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.90-7.80 (m, 4H), 7.45-7.10, (m**, 2H), 7.00-6.95 (m, 2H), 3.40-3.30 (m, 1H), 3.25-3.20 (m, 1H), 2.90-2.75 (m, 2H), 2.00 (s, 3H), 2.00-1.95 (m, 1H), 1.95 (s, 3H), 1.92-1.70 (m, 2H), 0.80-0.75 (m, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.2, 176.0, 175.4, 174.5, 174.3, 162.4, 160.3, 139.0, 138.6, 130.3,1130.3, 130.2, 130.0, 129.9, 129.9, 129.7, 129.6, 129.4, 129.3, 129.0, 126.9, 126.0, 61.4, 60.4, 60.0, 59.6, 44.5, 44.1, 32.4, 31.1, 28.5, 27.3, 16.1

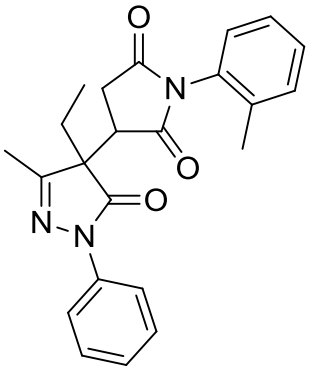
15.6, 9.6, 9.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_3$) requires 390.1812 found 390.1807. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 85:15, λ= 254 nm, 1.0 mL/min): t_R= 14.0.5, 17.0, 21.4, 28.4 min.



3h: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.90-7.80 (m, 4H), 7.44-7.16, (m**, 22H), 7.13-7.06 (m, 2H), 7.01-6.94 (m, 2H), 6.54 (s, 1H), 6.47 (s, 1H), 3.42-3.10 (m, 3H), 2.87-2.76 (m, 2H), 2.42-2.35 (m, 1H), 2.04 (s, 3H), 1.95 (s, 3H), 3.25-3.20 (m, 1H), 2.90-2.75 (m, 2H), 2.00 (s, 3H), 2.10-1.90 (m, 4H), 2.00-1.95 (m, 1H), 1.95 (s, 3H), 0.77 (m, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 176.2, 176.0, 175.4, 174.6, 174.3, 162.4, 160.3, 138.7, 138.6, 138.2, 130.4, 130.3, 130.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.4, 129.2, 129.0, 126.9, 126.8, 120.5, 120.2, 61.4, 60.4, 60.0, 59.6, 44.5, 44.1, 32.4, 31.1, 28.5, 27.3, 16.1, 15.7, 9.6, 9.5**. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_3$) requires 390.1812 found 390.1807. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 95:5, λ= 254 nm, 1.0 mL/min): 15.9, 16.7, 20.9, 22.1 min

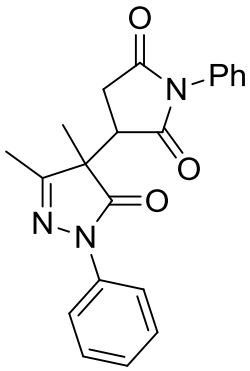


3i: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.85 (d, J=7.7Hz, 2H), 7.45-7.35 (m, 3H), 7.23-7.18 (m,2H), 7.13 (d, J=8.6Hz, 2H), 3.39-3.24 (m, 2H), 2.96 (dd, J=9.1Hz, J'=18.3Hz, 1H), 2.20 (s, 3H), 2.18-2.04 (m, 2H), 0.83 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.6, 174.9, 174.3, 161.9, 147.6, 144.7, 138.7, 137.8, 136.0, 130.8, 130.7, 130.4, 130.3, 128.9, 127.0, 59.8, 44.8, 32.3, 31.5, 28.3, 15.8, 9.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{22}H_{21}ClN_3O_3$) requires 410.1266 found 410.1275. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): t_R= 24.6, 39.3 min.

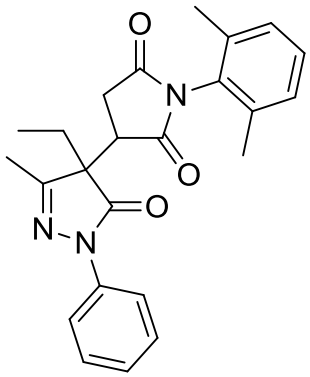


3j: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.90-7.85 (m, 4H), 7.45-7.35, (m**, 4H), 7.30-7.15 (m, 8H), 7.02-6.96 (m, 1H), 6.88-6.84 (m, 1H), 3.75 (dd, J=5.4Hz, J'=18.0Hz, 1H), 3.43-3.34 (m, 2H), 3.25-3.16 (m, 1H), 3.05-2.93 (m, 2H), 2.24 (s, 3H), 2.21 (s, 3H), 2.15-2.05 (m, 1H), 2.11 (s, 3H), 1.95-1.85 (m, 1H), 1.77 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.8, 175.6, 175.5, 175.2, 174.4, 174.3, 162.6, 161.9, 139.0, 137.3, 132.6, 132.5, 131.9, 131.1, 131.0, 130.3, 130.2, 129.2, 129.0, 128.5,

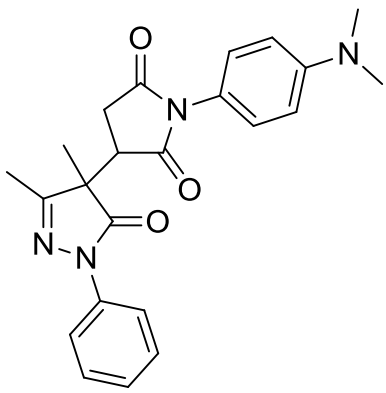
128.2, 127.0, 126.7, 120.5, 120.3, 60.2, 59.0, 45.4, 44.8, 31.9, 31.1, 28.8, 28.3, 19.1, 18.9, 16.0, 15.6, 9.5, 9.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_3$) requires 390.1812 found 390.1801. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): 24.3, 38.1 min.



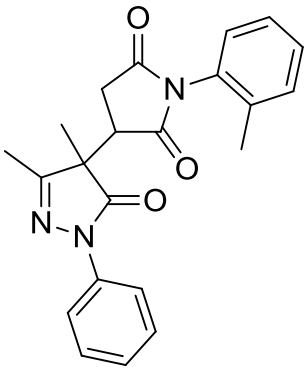
3m: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.83 (d, J=7.6Hz, 2H), 7.45-7.35 (m, 5H), 7.25-7.15 (m, 3H), 3.35 (dd, J=5.8Hz, J'=9.7Hz, 1H), 3.23-3.18 (m, 1H), 2.96 (dd, J=9.7Hz, J'=18.1Hz, 1H), 2.23 (s, 3H), 1.56 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.6, 174.8, 174.7, 163.0, 138.6, 132.4, 130.2, 130.0, 129.9, 127.3, 126.5, 120.0, 54.4, 44.5, 31.3, 20.7, 15.3. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{21}H_{20}N_3O_3$) requires 362.1499, found 362.1489. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): t_R= 16.9, 19.3 min.



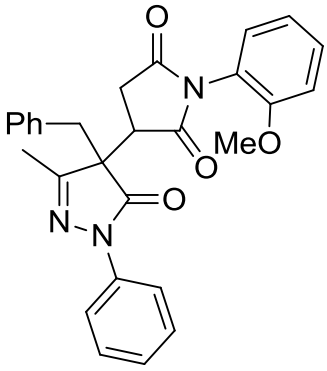
3l: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.90-7.85 (m, 4H), 7.42-7.35, (m**, 4H), 7.25-7.00 (m, 8H), 3.62 (dd, J=5.6Hz, J'=18.5Hz, 1H), 3.50-3.30 (m, 3H), 3.07-2.90 (m, 3H), 2.64 (dd, J=6.5Hz, J'=18.5Hz, 1H), 2.50-2.40 (m, 1H), 2.24 (s, 3H), 2.20 (s, 3H), 2.19 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.00-1.85 (m, 1H), 1.84 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.4, 175.3, 175.1, 174.7, 174.5 174.3, 162.6, 160.2, 139.0, 137.6, 137.4, 136.7, 136.7, 131.3, 131.2, 130.9, 130.4, 130.2, 130.2, 130.0, 129.9, 129.9, 129.7, 126.9, 126.7, 120.5, 120.3, 61.2, 58.9, 45.4, 44.9, 32.7, 31.1, 28.9, 27.3, 22.0, 19.4, 19.2, 19.1, 19.0, 16.4, 15.6, 9.6, 9.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{25}H_{28}N_3O_3$) requires 418.2125 found 418.2121. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): 16.8, 21.6 min.



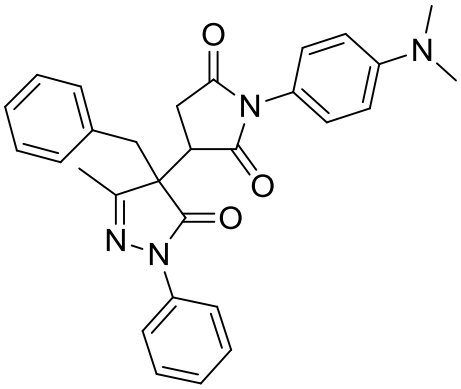
3n: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.86 (d, J=8.7Hz, 2H), 7.42-7.36 (m, 2H), 7.22-7.17 **(m**, 1H), 7.01 **(d**, J=8.9Hz, 2H), 6.69 (d, J=8.9Hz, 2H), 3.31 (dd, J=5.7Hz, J'=9.2Hz, 1H), 3.08-2.08 (m, 2H), 2.94 (s, 6H), 2.20 (s, 3H),1.61 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.5, 175.8, 175.2, 163.3, 152.0, 139.0, 130.3, 128.7, 128.3, 126.7, 121.1, 120.5, 113.9, 113.8, 55.1, 44.6, 41.9, 31.7, 21.0, 15.8.. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{25}N_4O_3$) requires 405.1921 found 405.1919. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 85:15, λ= 254 nm, 1.0 mL/min): t_R= 60.9, 65.8 min.



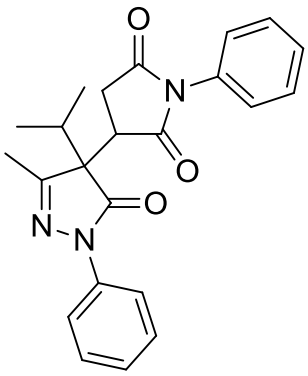
3o: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.90-7.80 (m, 4H), 7.45-7.15, (m, 12H), 7.01-6.99 (m, 1H), 6.89-6.86 (m, 1H), 3.73 (dd, J=5.2Hz, J'=18.1Hz, 1H), 3.40-3.30 (m, 2H), 3.22-3.12 (m, 1H), 3.05-2.95 (m, 2H), 2.27 (s, 3H), 2.24 (s, 3H), 2.12 (s, 3H), 1.90 (s, 3H), 1.63 (s, 3H), 1.53 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.7, 175.4, 175.1, 164.0, 139.2, 137.4, 136.8, 132.7, 132.6, 131.9, 131.1, 131.0, 130.5, 130.4, 130.2, 129.3, 129.0, 128.5, 128.2, 126.9, 126.7, 120.5, 120.3, 53.7, 46.6, 44.9, 31.9, 31.2, 21.6, 21.1, 19,1, 18.9, 15.7, 15.3. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{22}H_{22}N_3O_3$) requires 376.1656 found 376.1661. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): 21.4, 28.0 min.



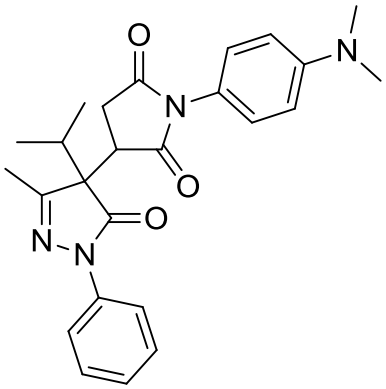
3p: White scum(mixture of diastereomers). **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.61-7.53 (m, 4H), 7.45-7.30, (m**, 6H), 7.20-7.10 (m, 14H), 7.06-6.96 (m, 4H), 3.80 (s, 3H), 3.75-3.70 (m, 1H), 3.64 (s, 3H), 3.60-3.50 (m, 3H), 3.42-3.35 (m, 2H), 3.06-2.96 (m, 3H), 2.85-2.75 (m,1H), 2.29 (s, 3H), 2.25 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.2, 176.0, 174.9, 174.8, 174.2, 174.1, 161.0, 156.0, 138.5, 135.2, 135.0, 132.5, 132.5, 130.7, 130.6, 130.5, 130.4, 130.2, 129.9, 129.9, 129.1, 129.0, 127.1, 127.0, 122.4, 121.5, 121.1, 121.0, 62.1, 61.5, 57.3, 56.9, 44.4, 44.1, 41.0, 40.8, 32.4, 32.3, 16.8, 16.6. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{28}H_{26}N_3O_4$) requires 468.1918 found 468.1921. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 80:20, λ= 254 nm, 1.0 mL/min): 23.2, 27.8 min.



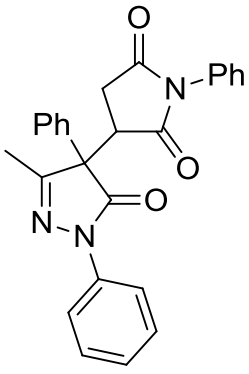
3q: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.53 (d, J=8.7Hz, 2H), 7.36-7.28 (m, 2H), 7.21-7.00 **(m**, 8H), 6.72 (d, J=9.0Hz, 2H), 3.58 (d, J=13.1Hz, 1H), 3.53-3.48 (m, 1H), 3.38 (d, J=13.1Hz, 1H), 3.05-2.91 (m, 2H), 2.96 (s, 6H), 2.23 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.7, 175.7, 174.3, 161.0, 152.1, 128.5, 135.1, 130.7, 130.3, 130.0, 129.2, 128.4, 127.2, 121.2, 113.9, 61.7, 44.2, 41.9, 41.0, 32.1, 16.9. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{29}H_{29}N_4O_3$) requires 481.2234 found 481.2228.



3r: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.84 (d, J=7.6Hz, 2H), 7.50-7.30 (m, 5H), 7.20-7.14 **(m**, 3H), 3.62 (dd, J=7.5Hz, J'=7.5Hz, 1H), 3.00-2.90 (m, 2H) 2.64-2.54 (m, 1H), 2.20 (s, 3H), 1.14 (d, J=6.5Hz, 3H), 1.04 (d, J=7.3Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.3, 175.4, 174.6, 161.7, 138.9, 133.0,130.8, 130.5, 130.4, 127.8, 127.1, 120.7, 62.9, 42.2, 32.9, 31.9, 19.1, 17.8, 17.5. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{23}H_{24}N_3O_3$) requires 390.1812 found 390.1819. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): t_R= 15.6, 29.3 min.

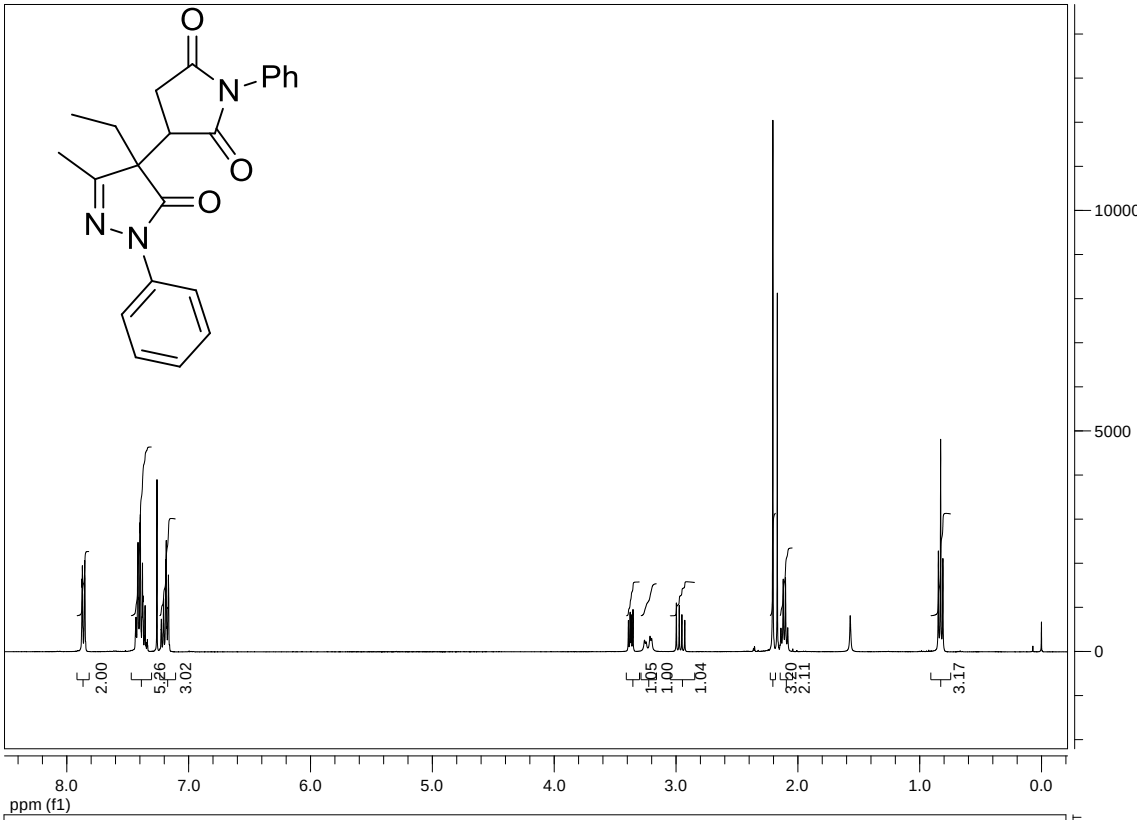


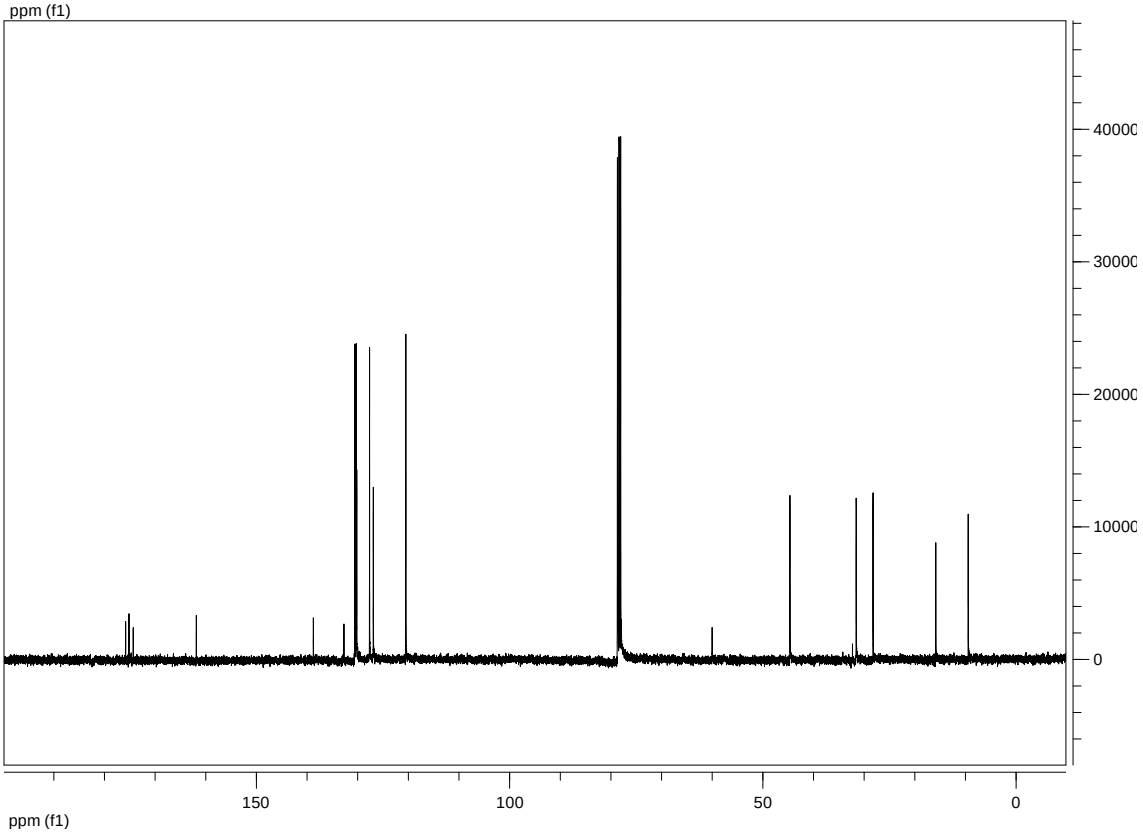
3s: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.84 (d, J=8.8Hz, 2H), 7.42-7.36 (m, 2H), 7.22-7.17 **(m**, 1H), 7.01 **(d**, J=8.8Hz, 2H), 6.69 (d, J=8.9Hz, 2H), 3.60 (dd, J=6.9Hz, J'=8.5Hz, 1H), 2.98-2.80 (m, 2H), 2.94 (s, 6H), 2.66-2.56 (m, 1H), 2.17 (s, 3H), 1.17 (d, J=6.3Hz, 3H), 0.99 (d, J=7.0Hz, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 176.8, 176.0, 174.6, 161.8, 152.1, 138.9, 130.5, 130.4, 128.5, 127.1, 121.3, 120.7, 114.0, 113.9, 63.1, 42.0, 41.9, 32.7, 31.9, 19.2, 17.8, 17.4. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{25}H_{29}N_4O_3$) requires 433.2234 found 433.2240. **HPLC** (Chiralpak IA, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): t_R= 28.8, 62.6 min.

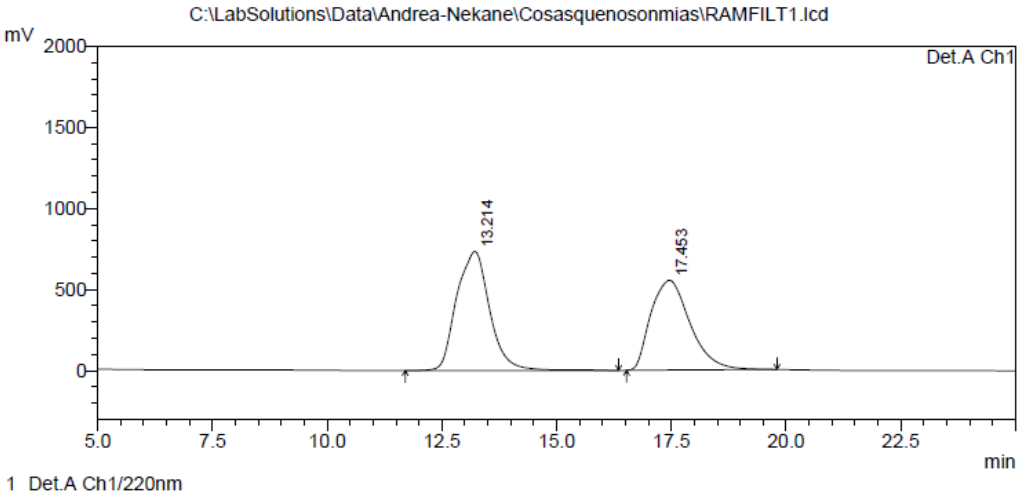


3t: White scum. **^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm):** 7.93 (d, J=7.7Hz, 2H), 7.48-7.10 (m, 13H), 3.99 (dd, J=4.7Hz, J'=9.5Hz, 1H), 3.36 (dd, J=4.7Hz, J'=18.5Hz, 1H), 2.92 (dd, J=9.5Hz, J'=18.5Hz, 1H), 2.20 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):** 175.9, 175.4, 174.2, 162.7, 138.9, 135.6, 132.9, 131.3, 131.2 130.7, 130.6, 130.5, 130.4, 130.4, 130.2, 128.3, 127.9, 127.8, 127.7, 127.1, 120.8, 63.5, 44.2, 32.9, 15.8. **HRMS (ESI):** calcd. for $[M+H]^+$ ($C_{29}H_{29}N_4O_3$) requires 481.2234 found 481.2228. **HPLC** (Chiralpak IB, *n*-hexane: *i*-PrOH= 90:10, λ= 254 nm, 1.0 mL/min): t_R= 47.6, 65.4 min.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



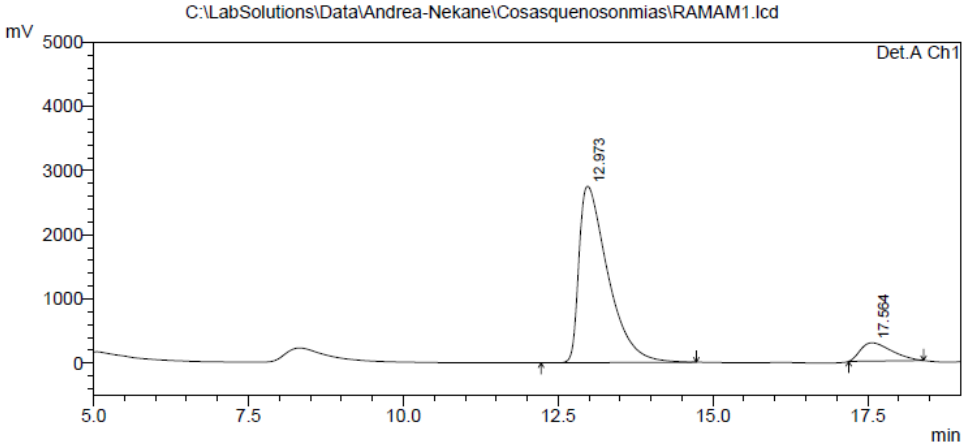




PeakTable

Detector A Ch1 220nm

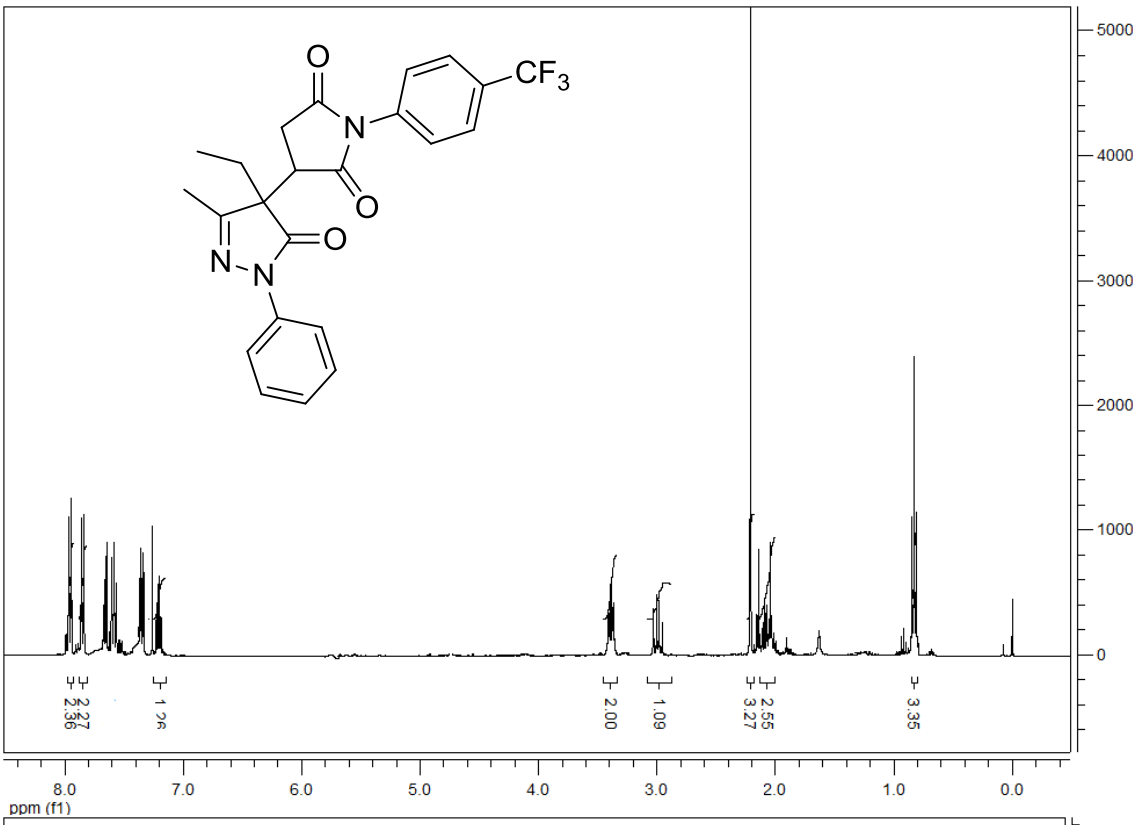
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.214	36748969	733839	52.772	57.018
2	17.453	32888425	553185	47.228	42.982
Total		69637394	1287024	100.000	100.000

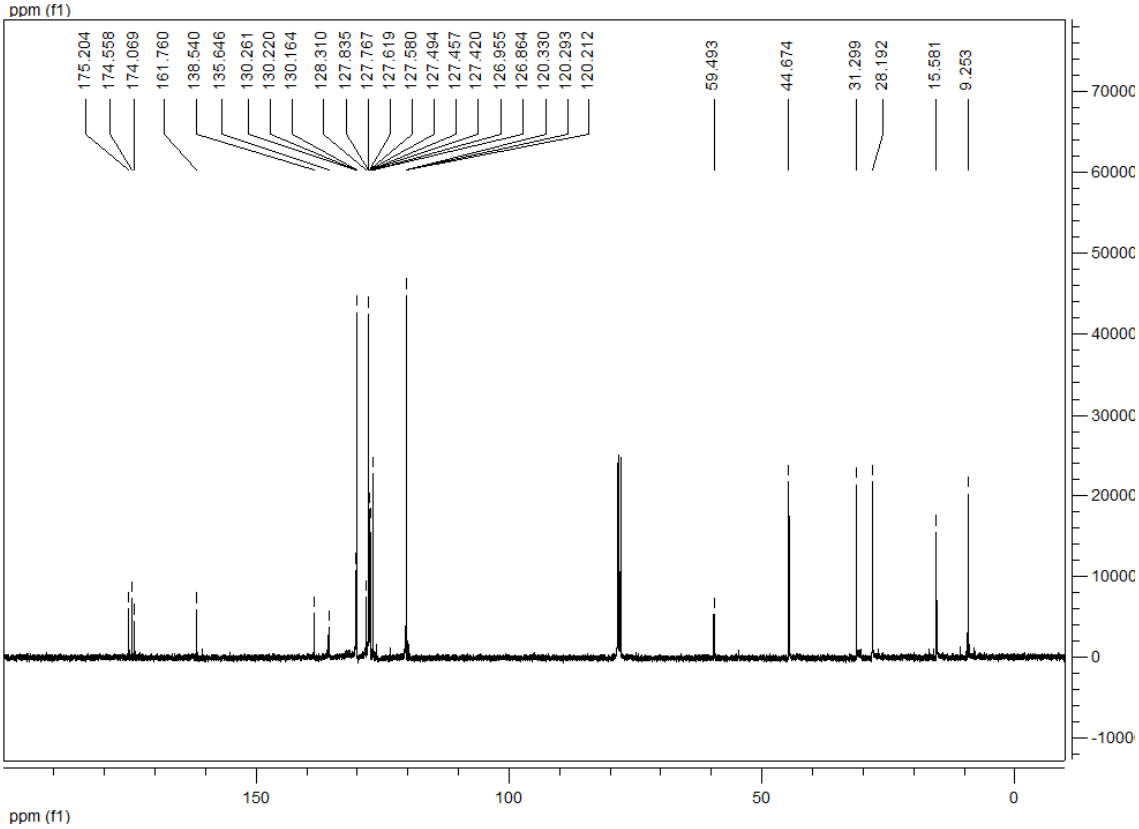


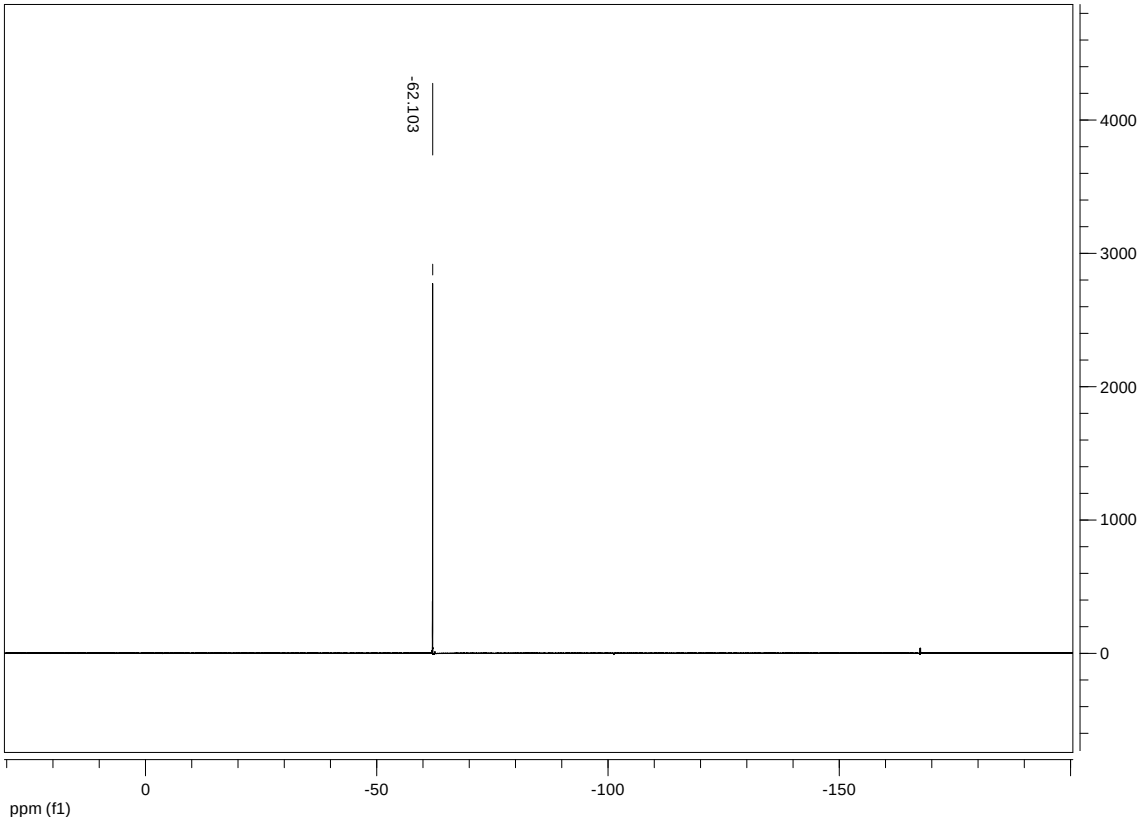
PeakTable

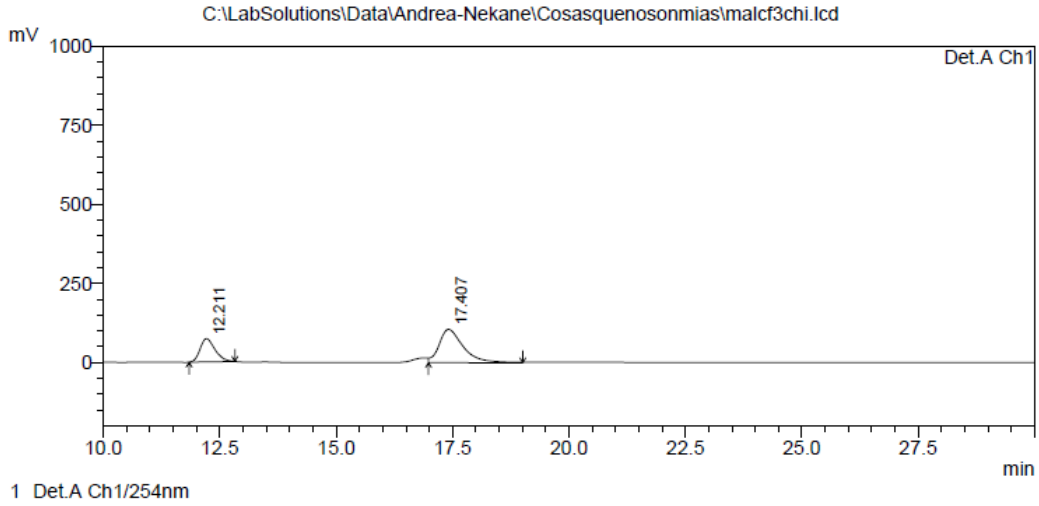
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.973	89352867	2751833	89.976	90.622
2	17.564	9954968	284777	10.024	9.378
Total		99307835	3036610	100.000	100.000





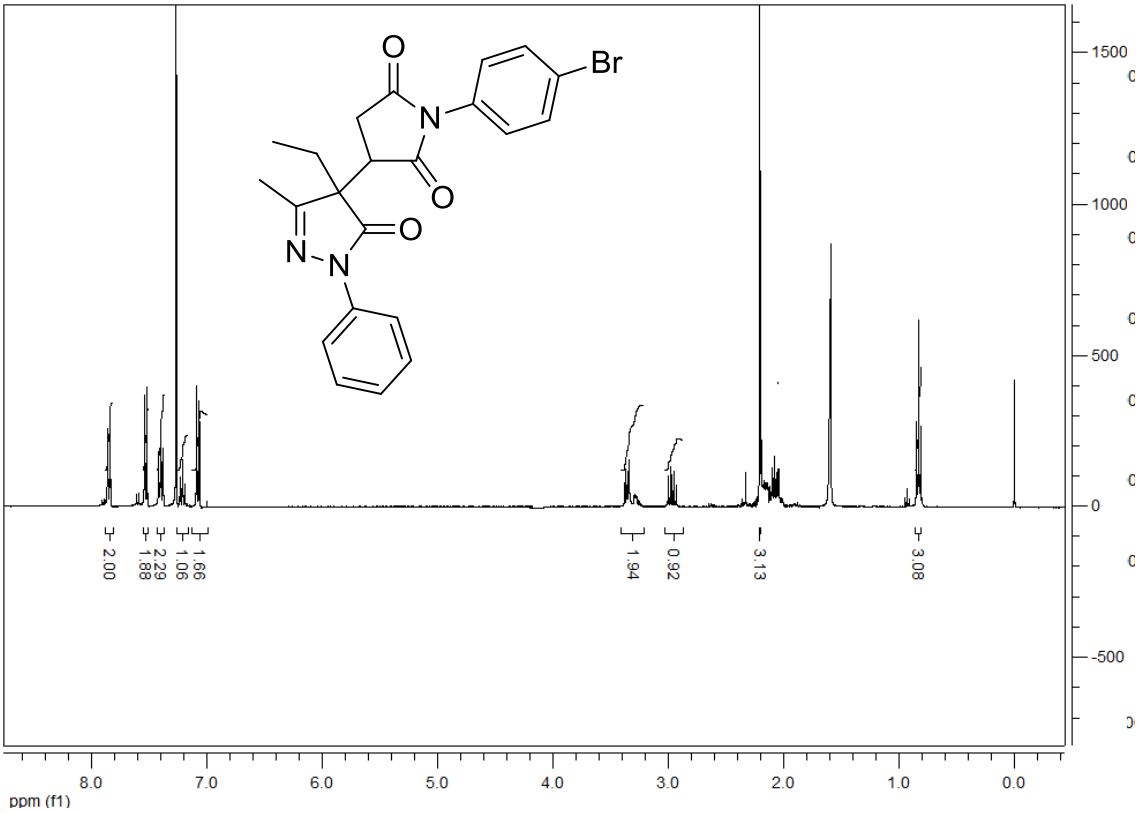


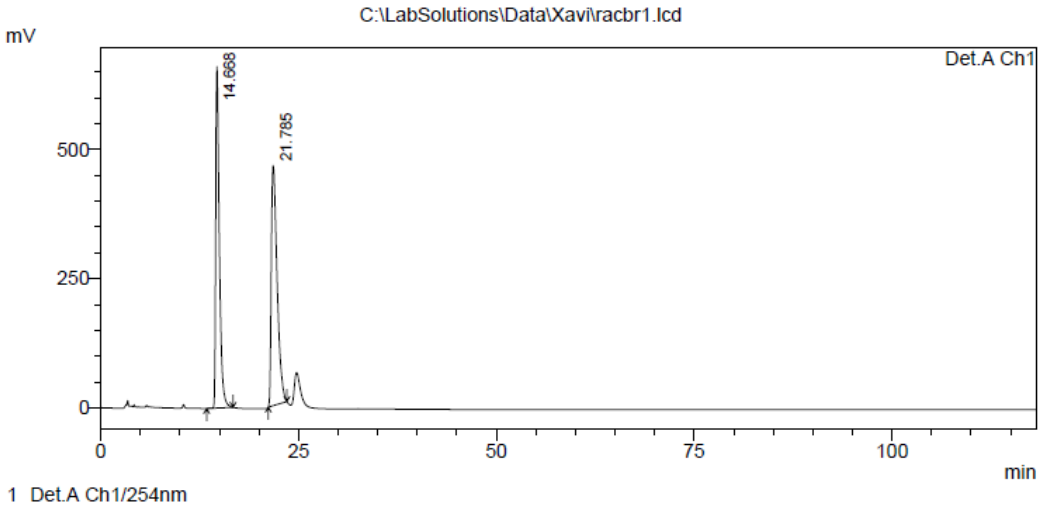


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.211	1635543	73395	29.798	41.007
2	17.407	3853310	105588	70.202	58.993
Total		5488853	178983	100.000	100.000



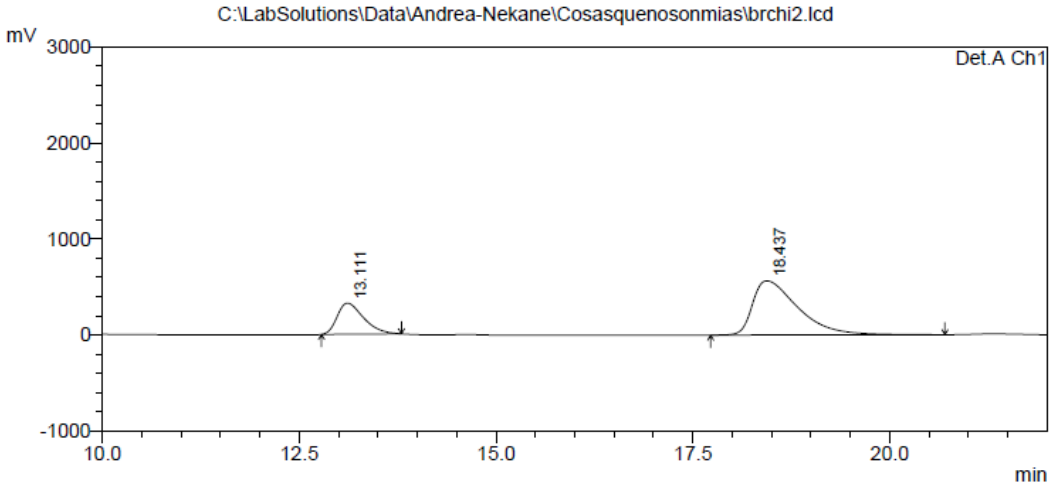


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.668	21176223	660245	47.134	58.688
2	21.785	23751506	464763	52.866	41.312
Total		44927729	1125008	100.000	100.000

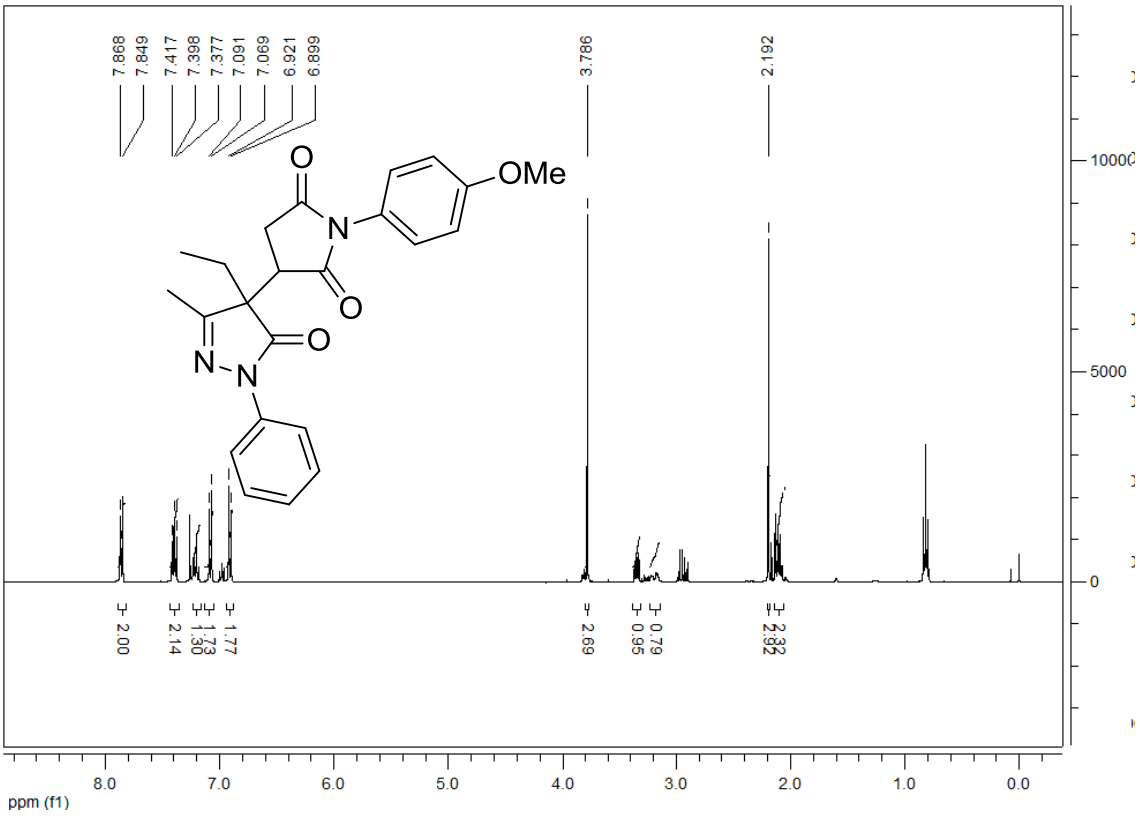


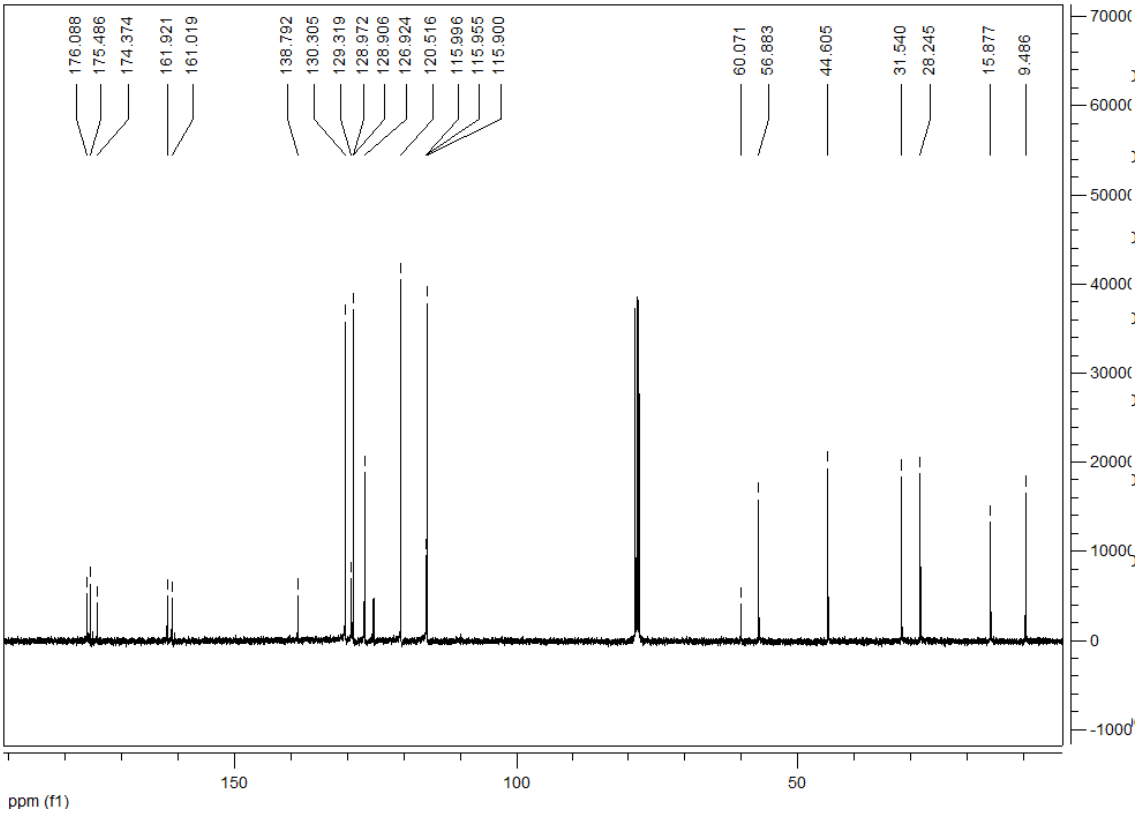
1 Det.A Ch1/254nm

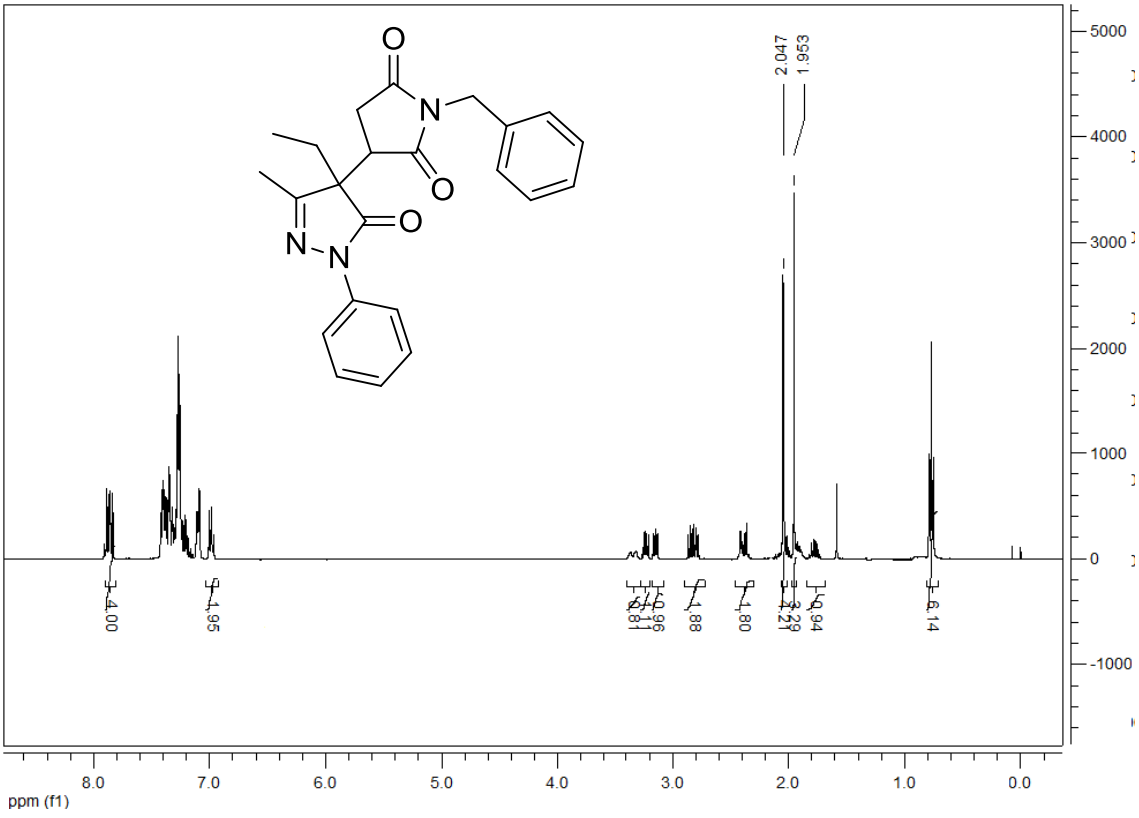
PeakTable

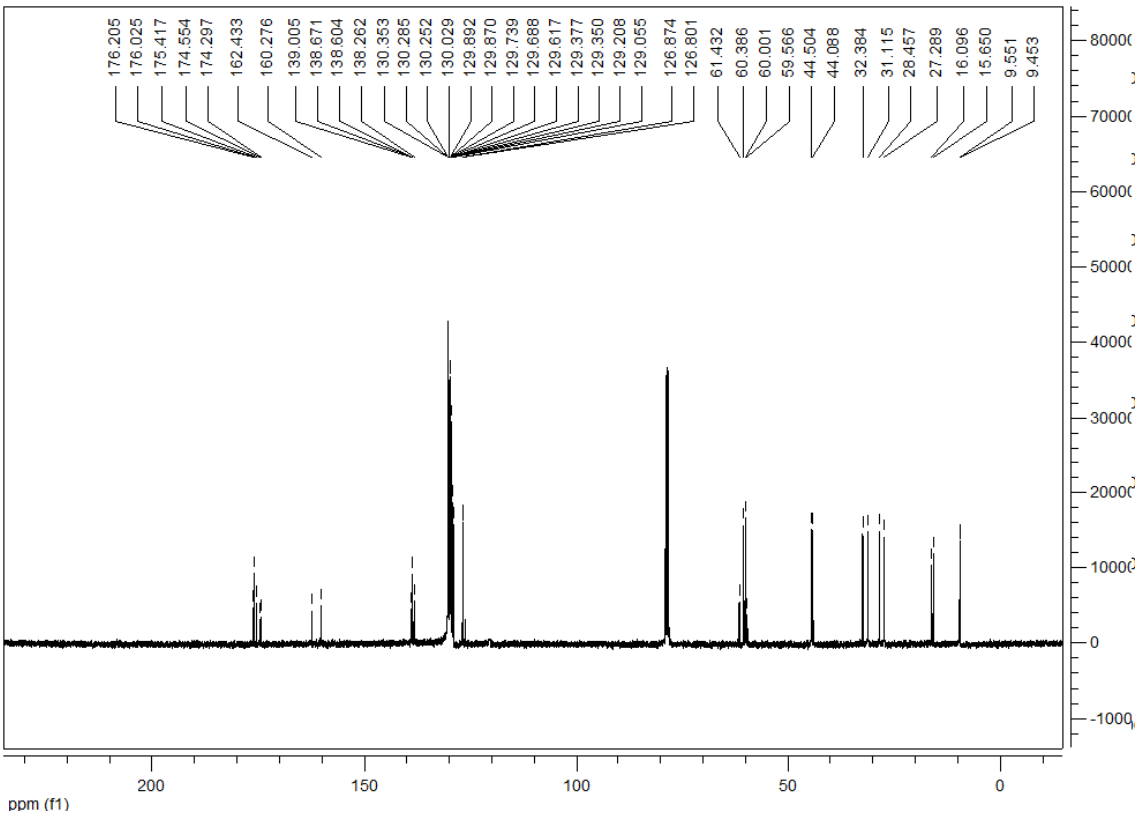
Detector A Ch1 254nm

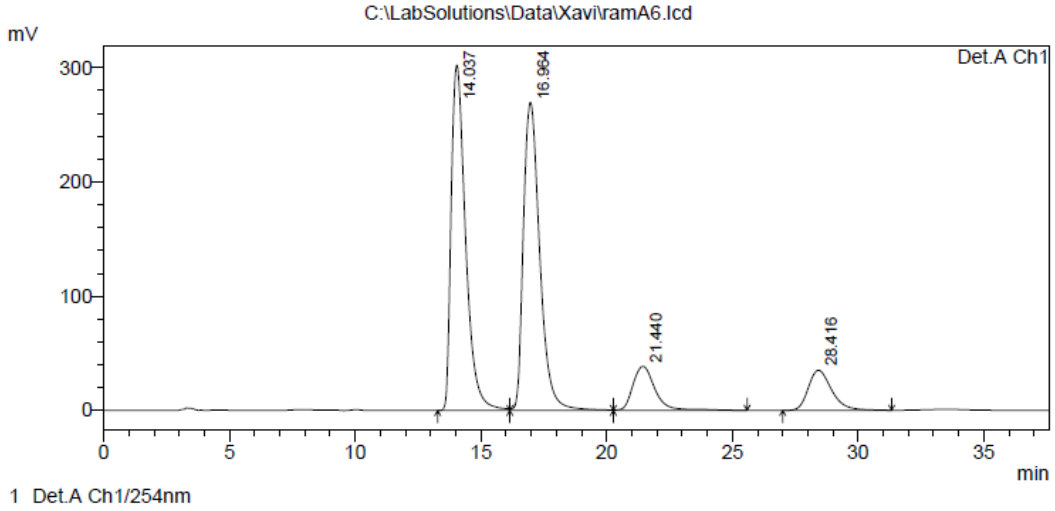
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.111	7559723	323932	25.089	36.441
2	18.437	22571737	564998	74.911	63.559
Total		30131460	888931	100.000	100.000







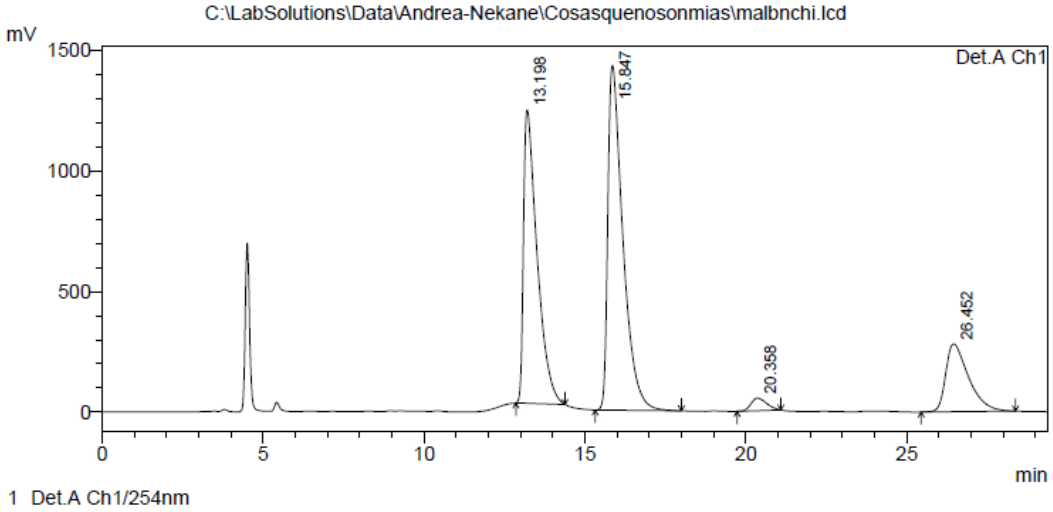




PeakTable

Detector A Ch1 254nm

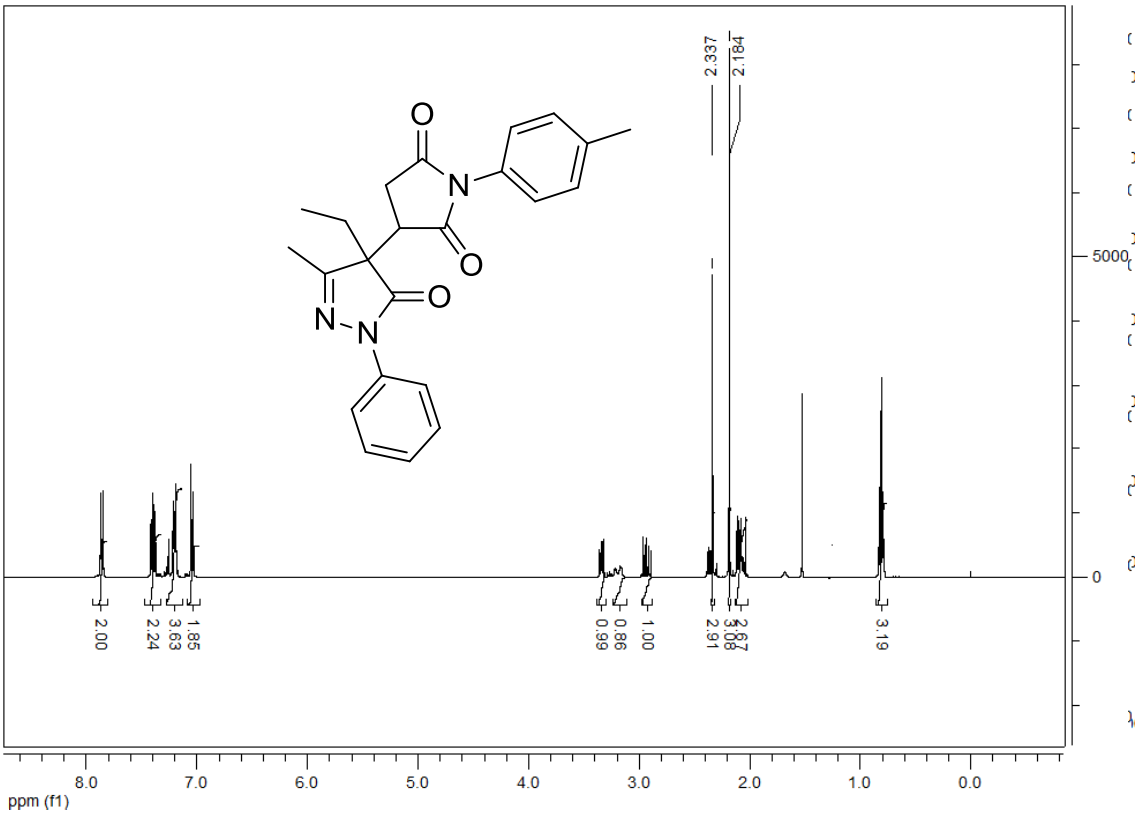
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.037	12044752	302301	41.699	46.818
2	16.964	12206446	269638	42.259	41.760
3	21.440	2367373	38604	8.196	5.979
4	28.416	2266405	35149	7.846	5.444
Total		28884977	645692	100.000	100.000

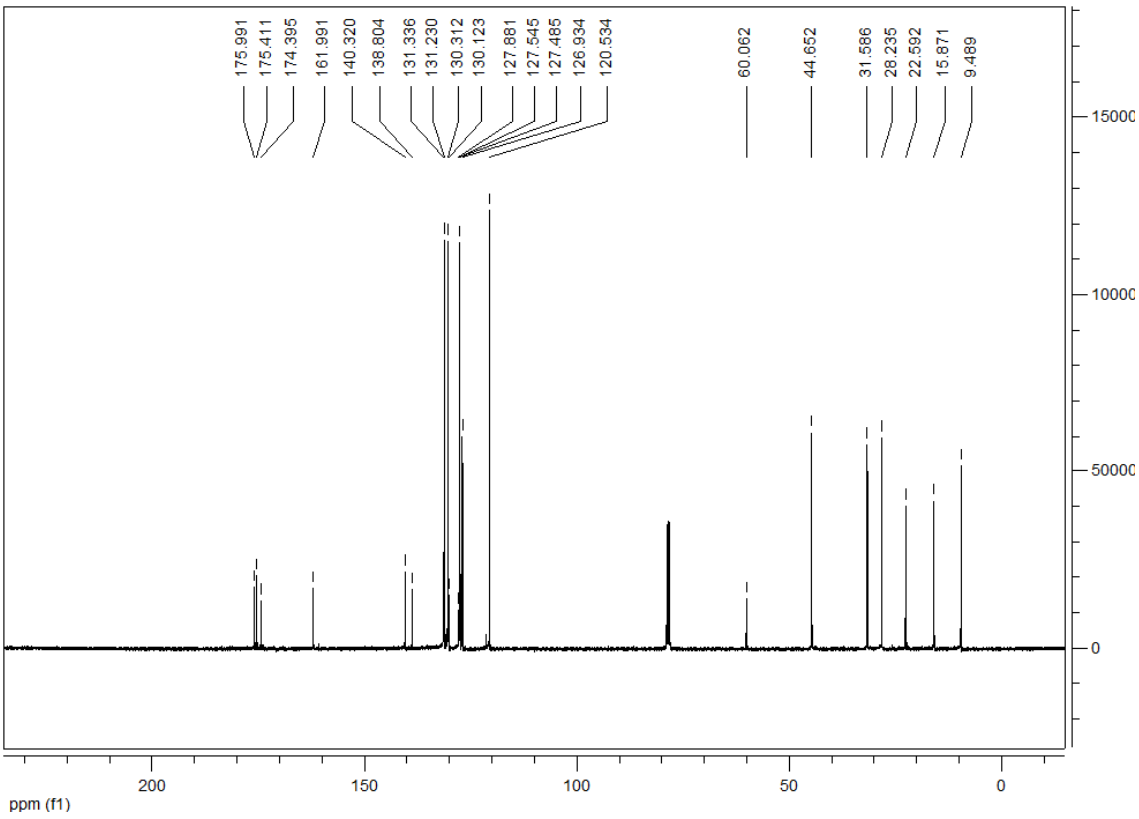


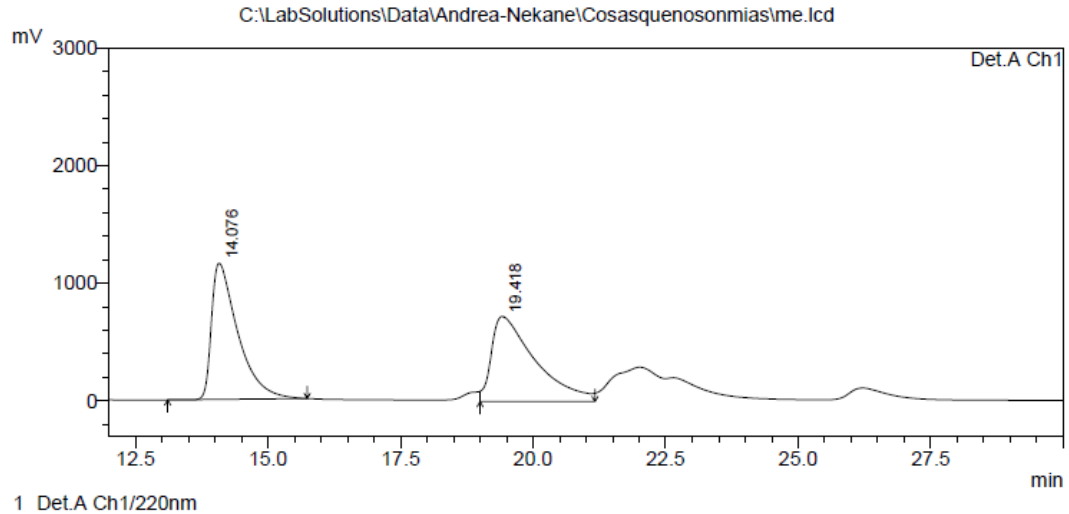
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.198	35654004	1217810	36.472	40.827
2	15.847	46453292	1431639	47.519	47.996
3	20.358	1767226	52167	1.808	1.749
4	26.452	13881988	281223	14.201	9.428
Total		97756510	2982839	100.000	100.000





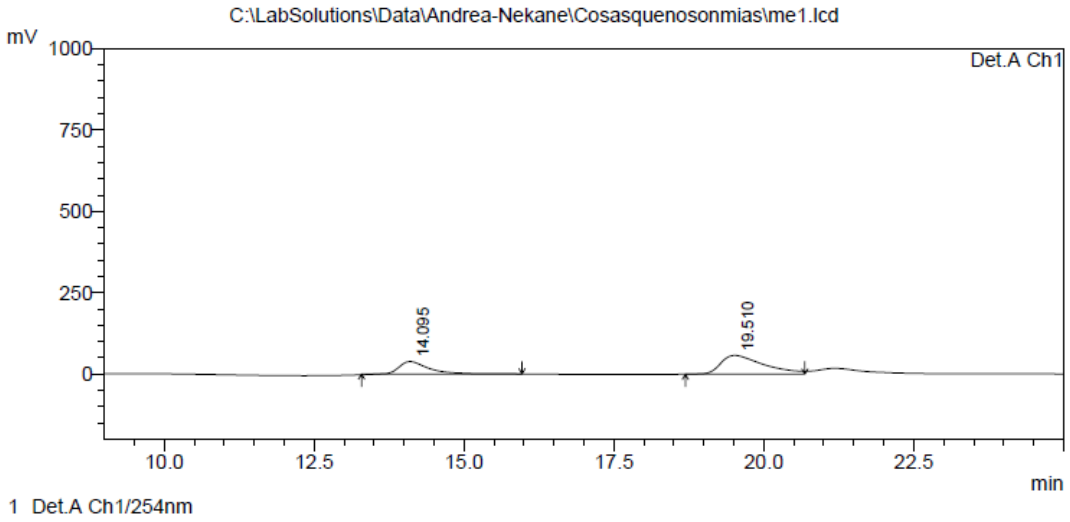


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.076	39992827	1158690	49.005	61.519
2	19.418	41616955	724784	50.995	38.481
Total		81609783	1883473	100.000	100.000

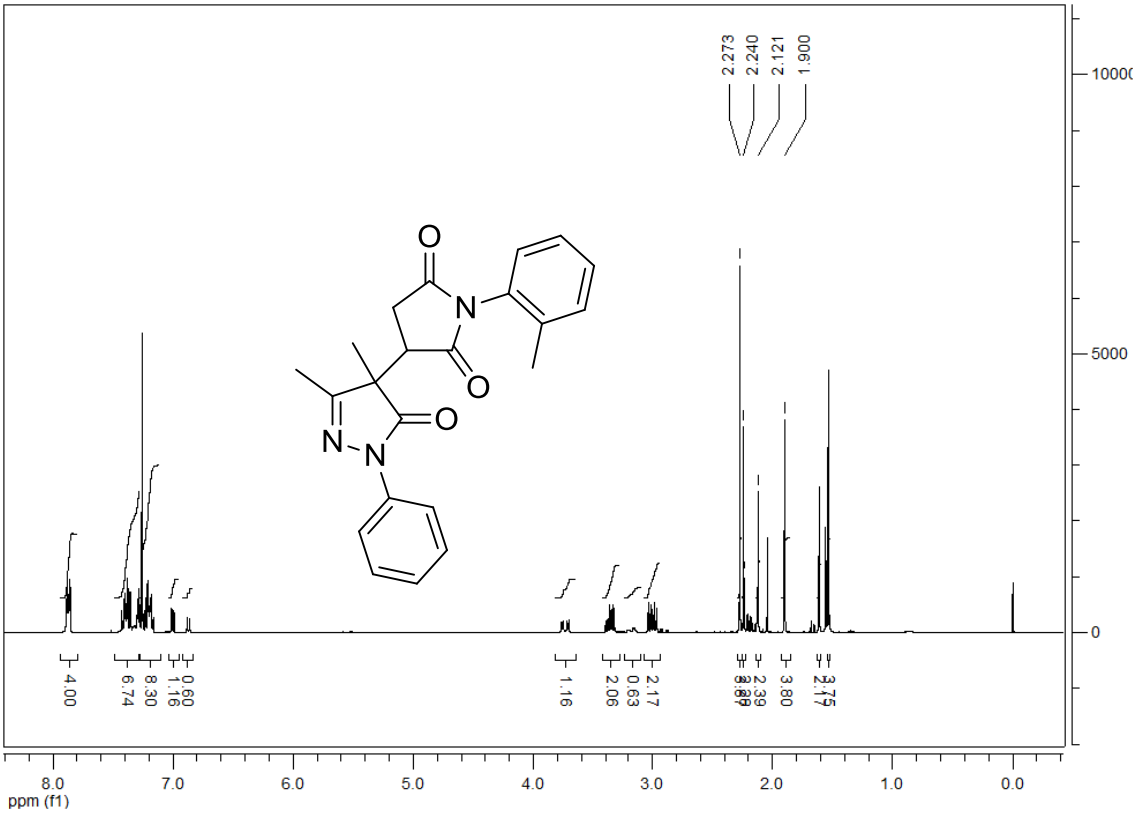


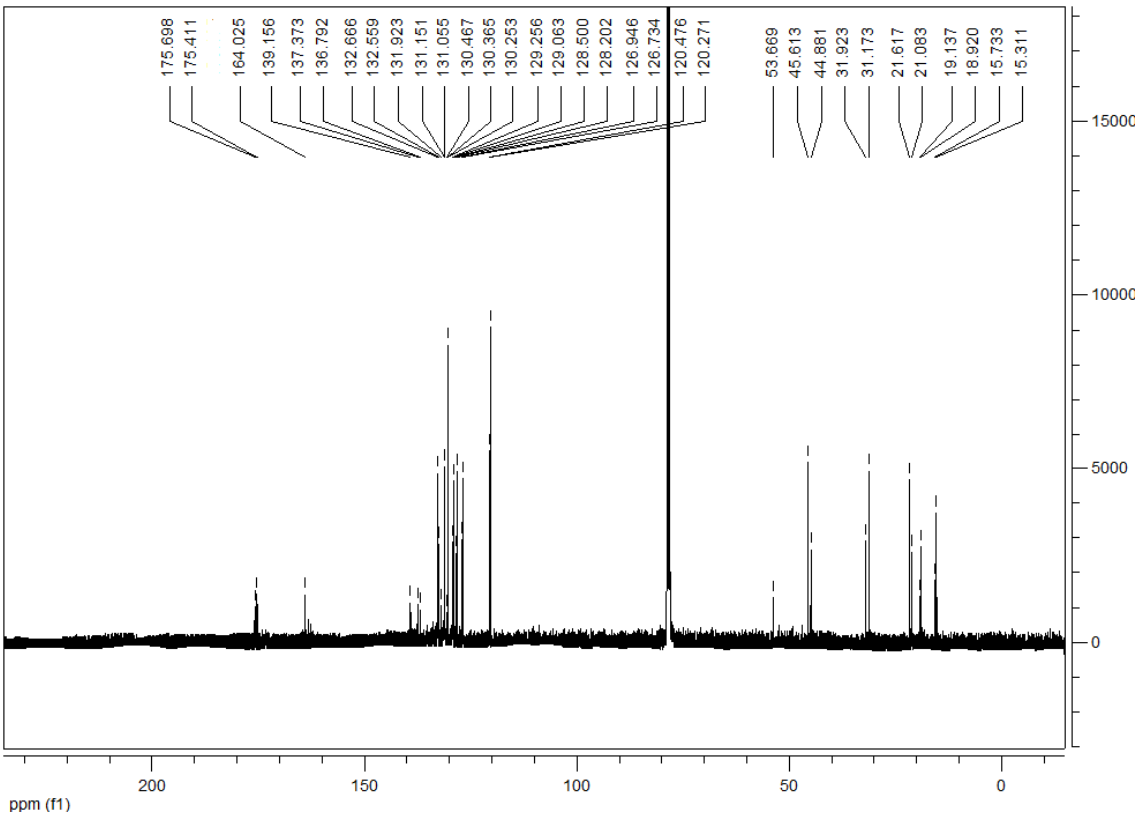
1 Det.A Ch1/254nm

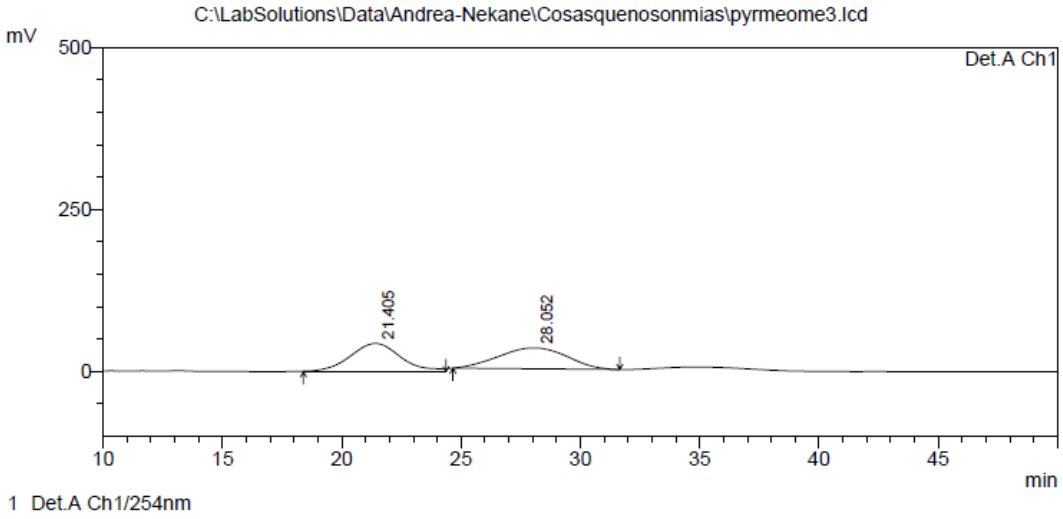
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.095	1296660	38181	30.669	39.765
2	19.510	2931226	57834	69.331	60.235
Total		4227886	96015	100.000	100.000



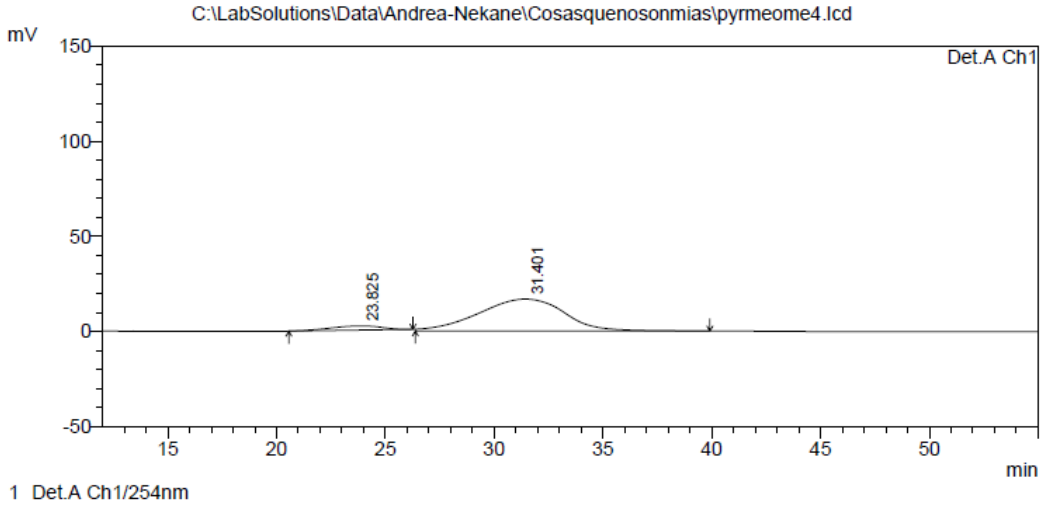




PeakTable

Detector A Ch1 254nm

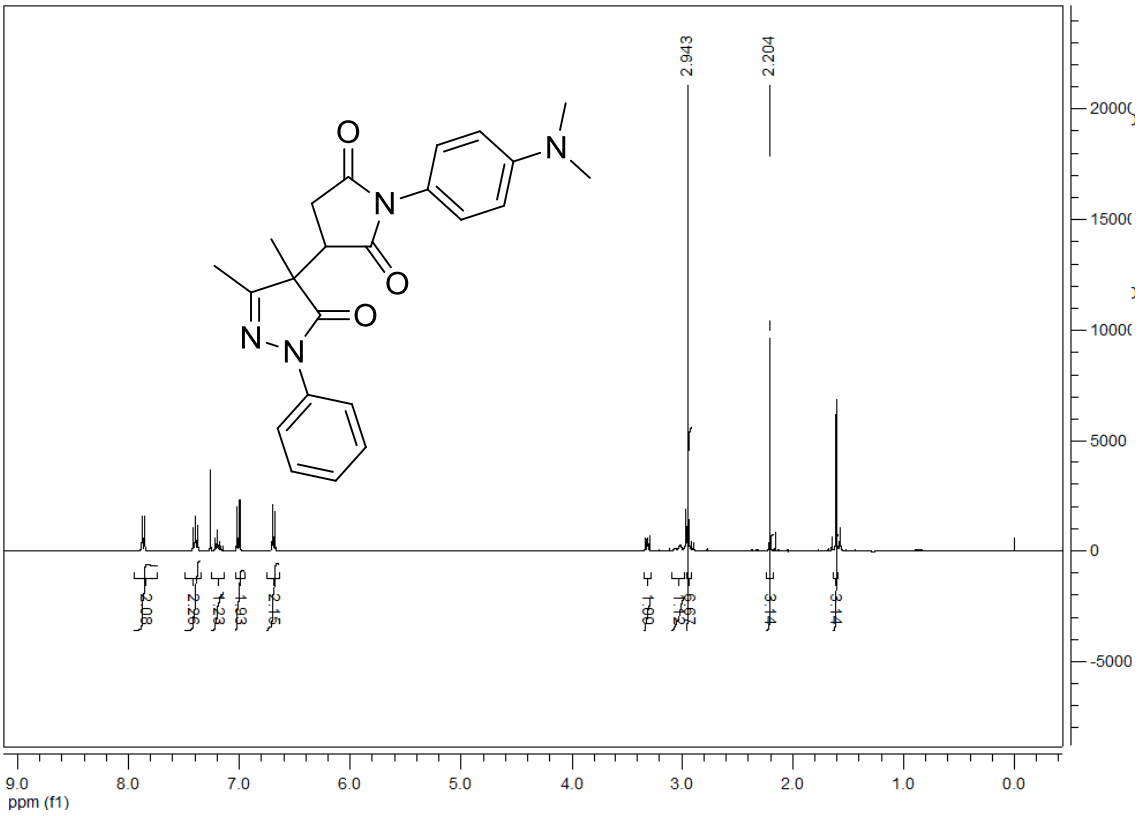
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.405	6523932	43767	50.311	57.537
2	28.052	6443167	32300	49.689	42.463
Total		12967099	76067	100.000	100.000

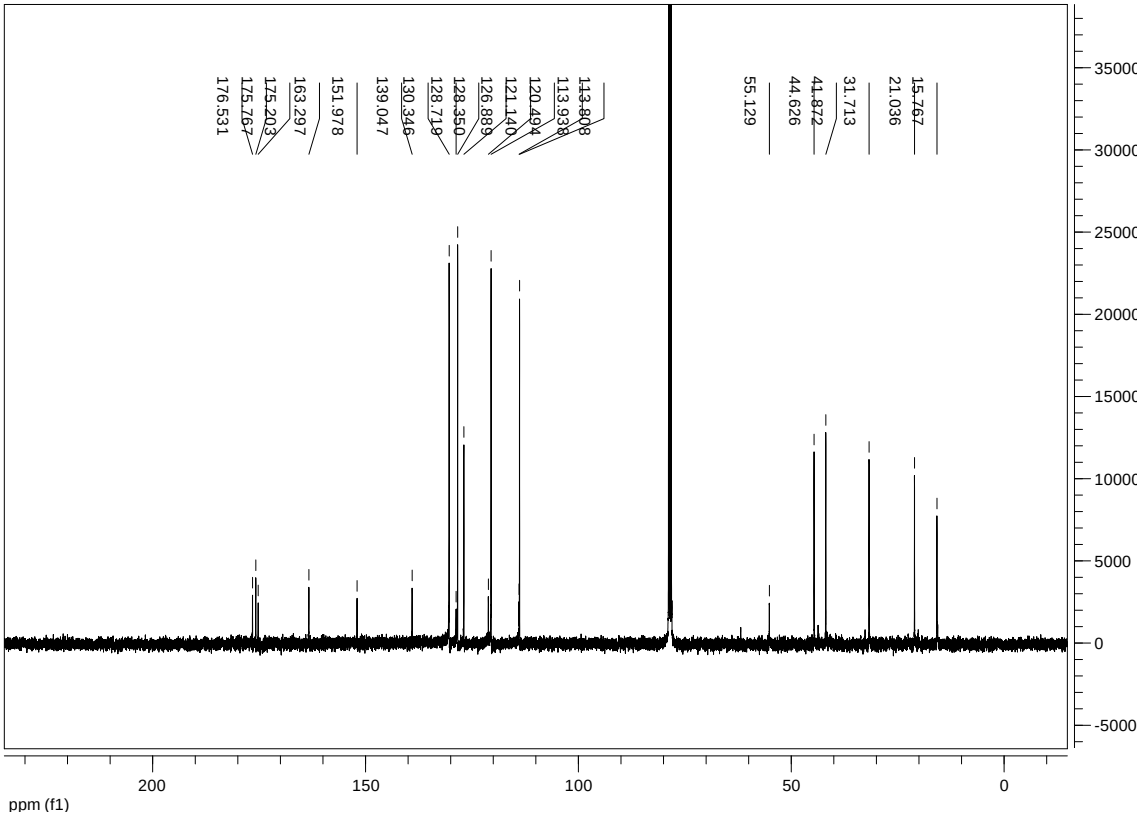


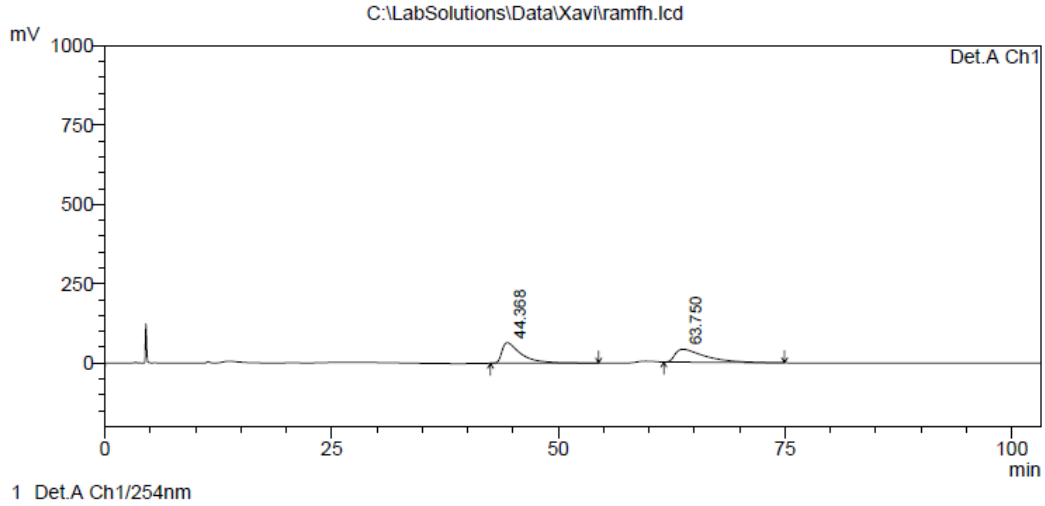
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.825	352340	2214	7.048	11.648
2	31.401	4646752	16797	92.952	88.352
Total		4999093	19011	100.000	100.000



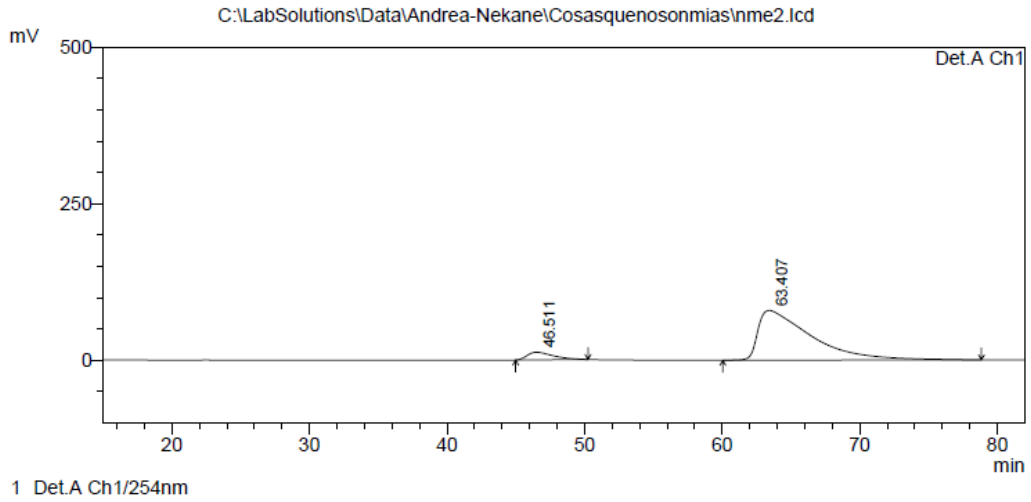




PeakTable

Detector A Ch1 254nm

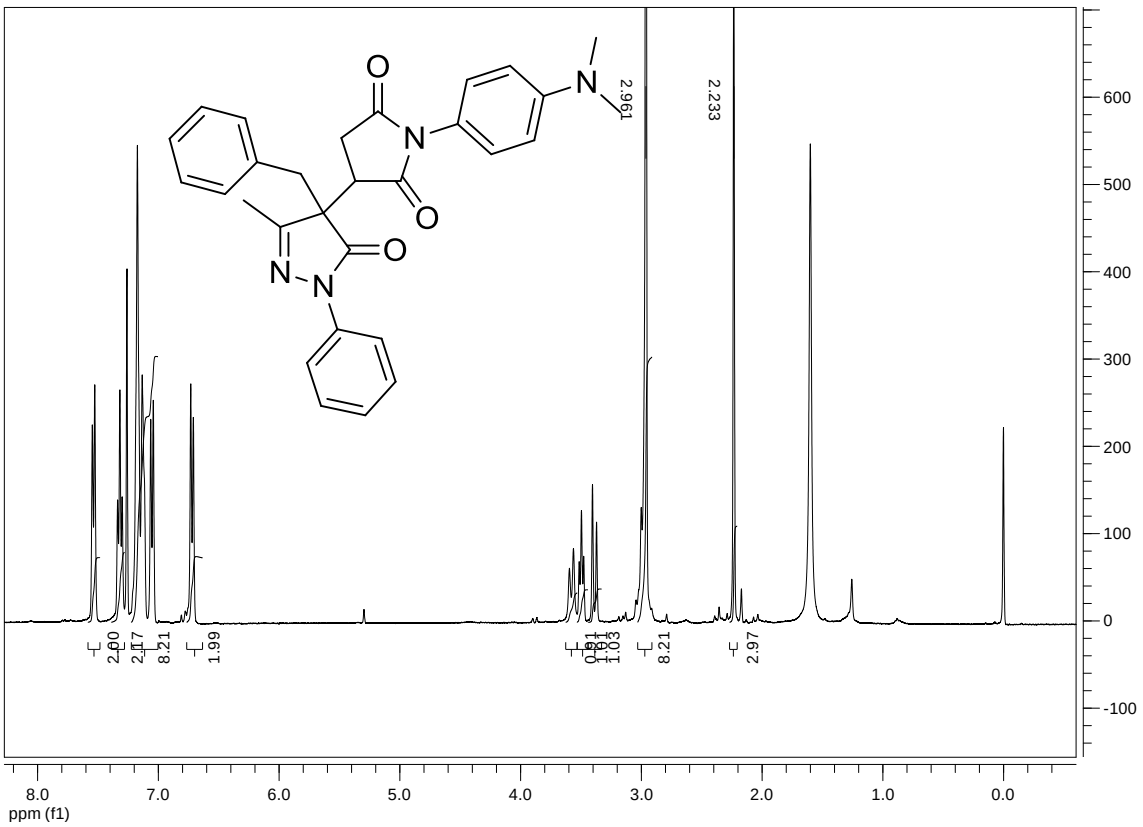
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.368	9477439	64616	50.339	61.380
2	63.750	9349672	40656	49.661	38.620
Total		18827111	105272	100.000	100.000

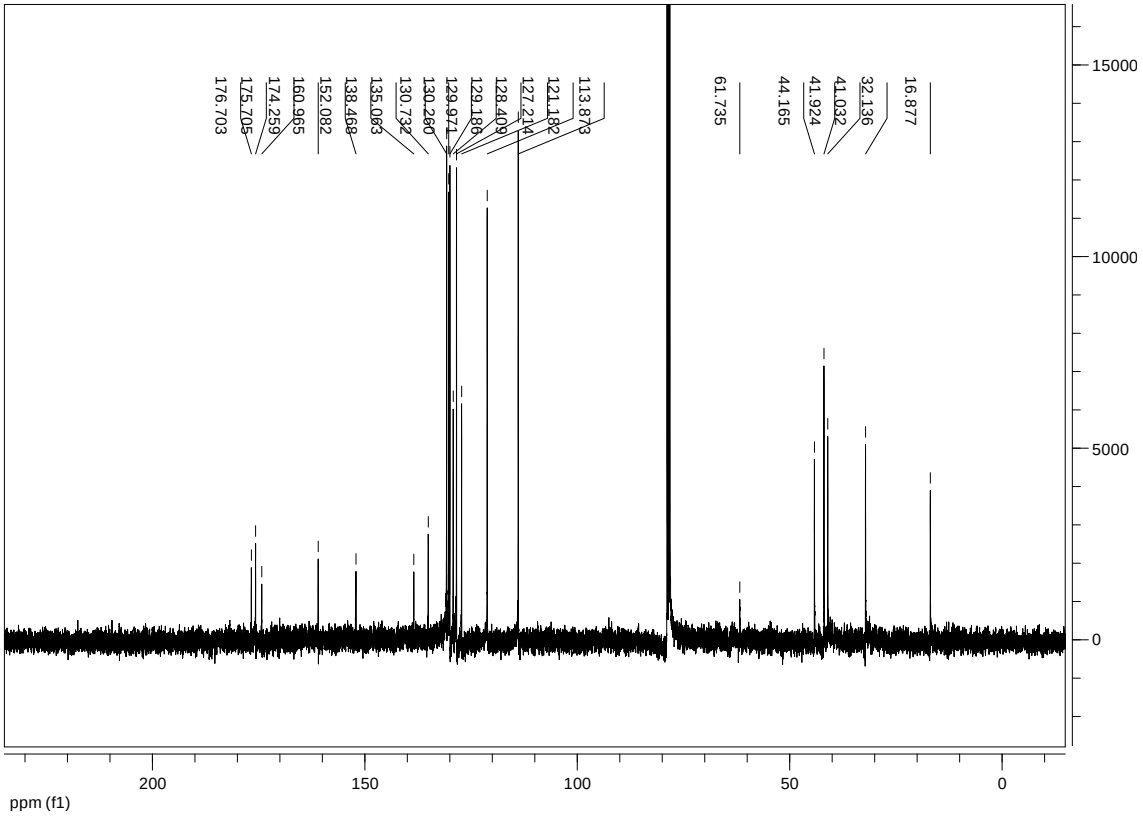


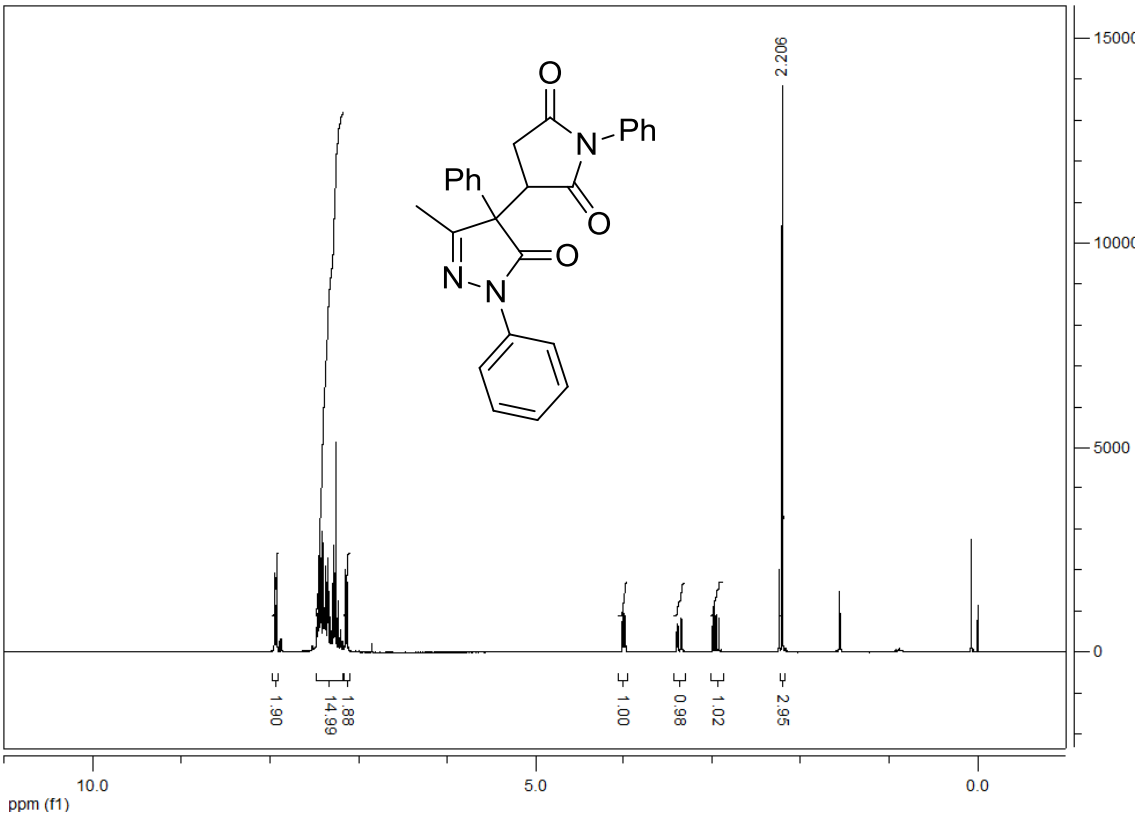
PeakTable

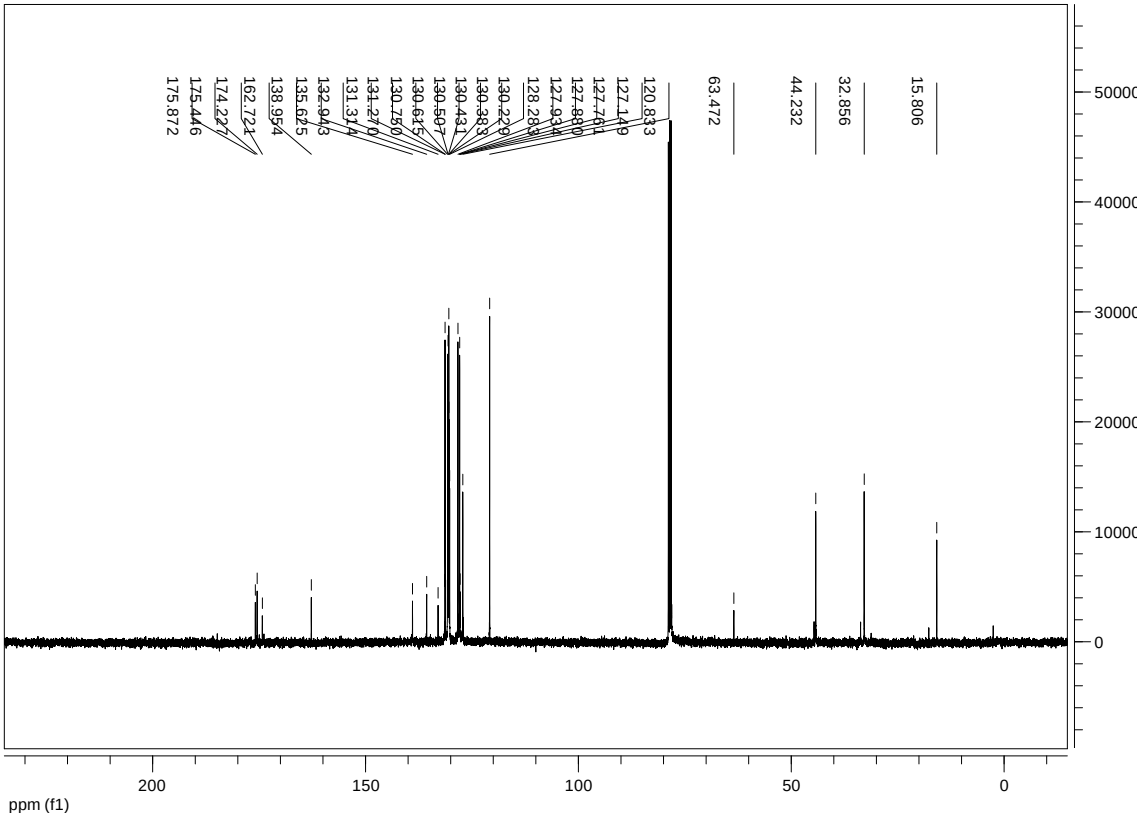
Detector A Ch1 254nm

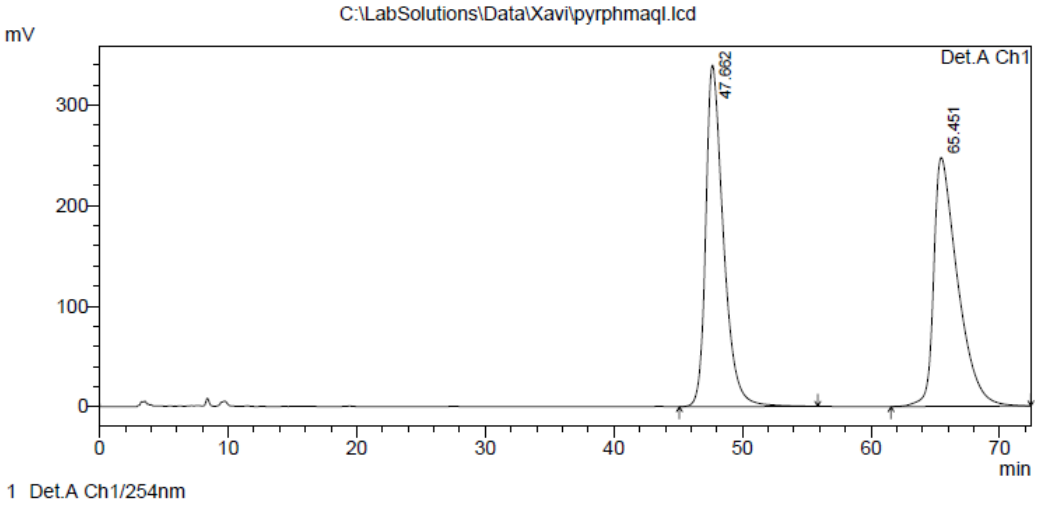
Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.511	1609386	12203	7.049	13.312
2	63.407	21223216	79466	92.951	86.688
Total		22832602	91669	100.000	100.000









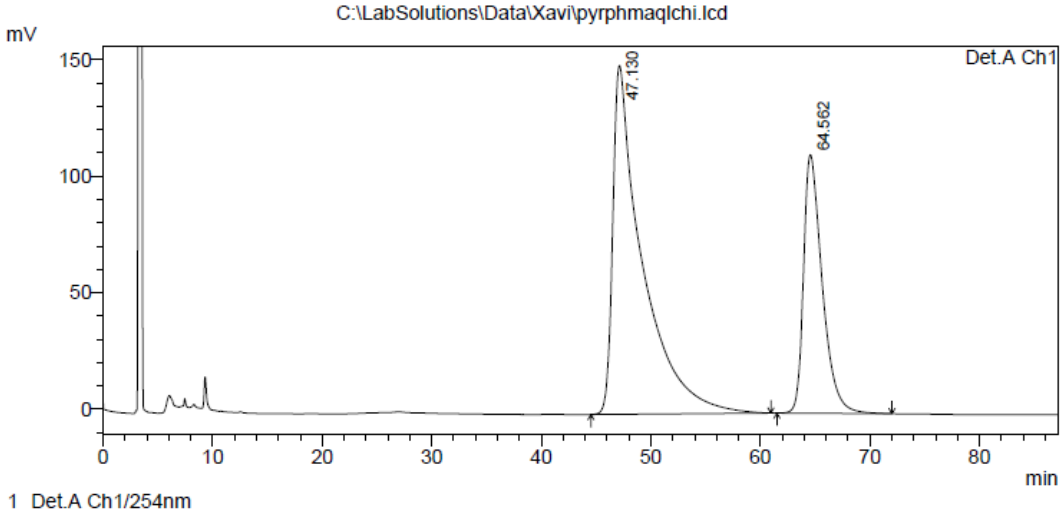


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

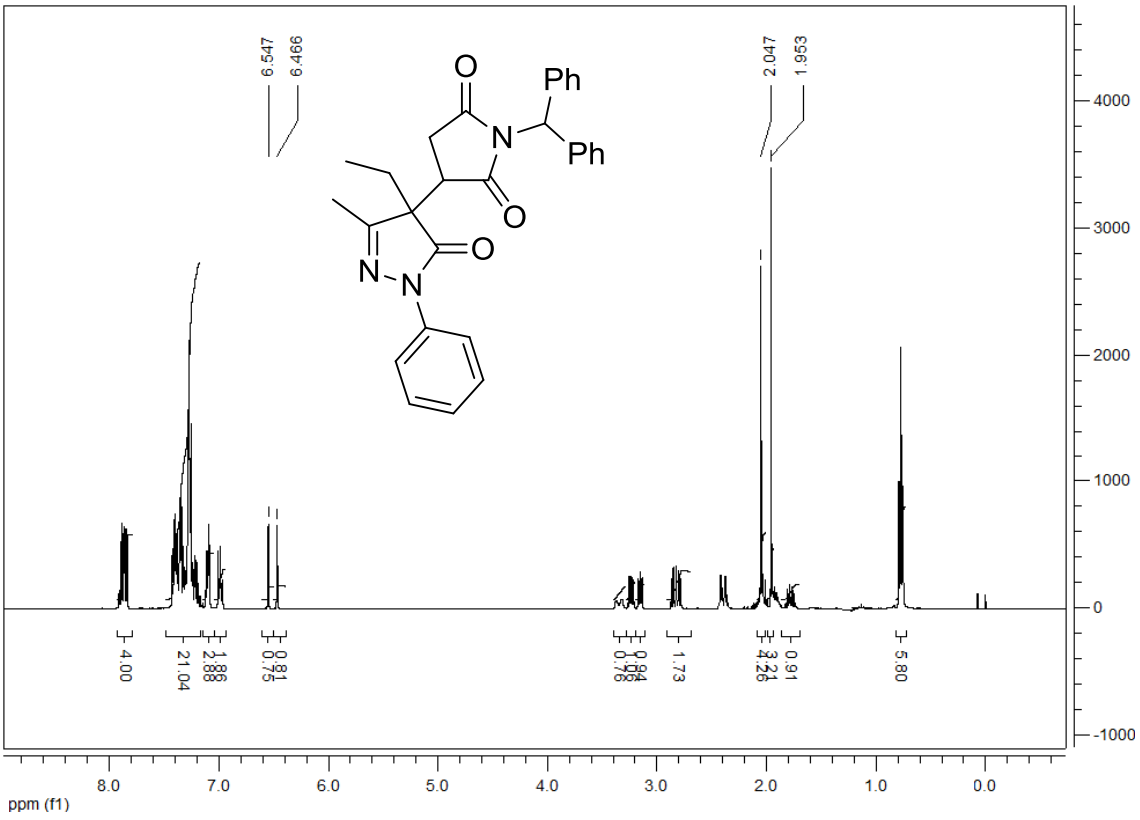
Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.662	32419825	339650	50.252	57.836
2	65.451	32094643	247611	49.748	42.164
Total		64514468	587261	100.000	100.000

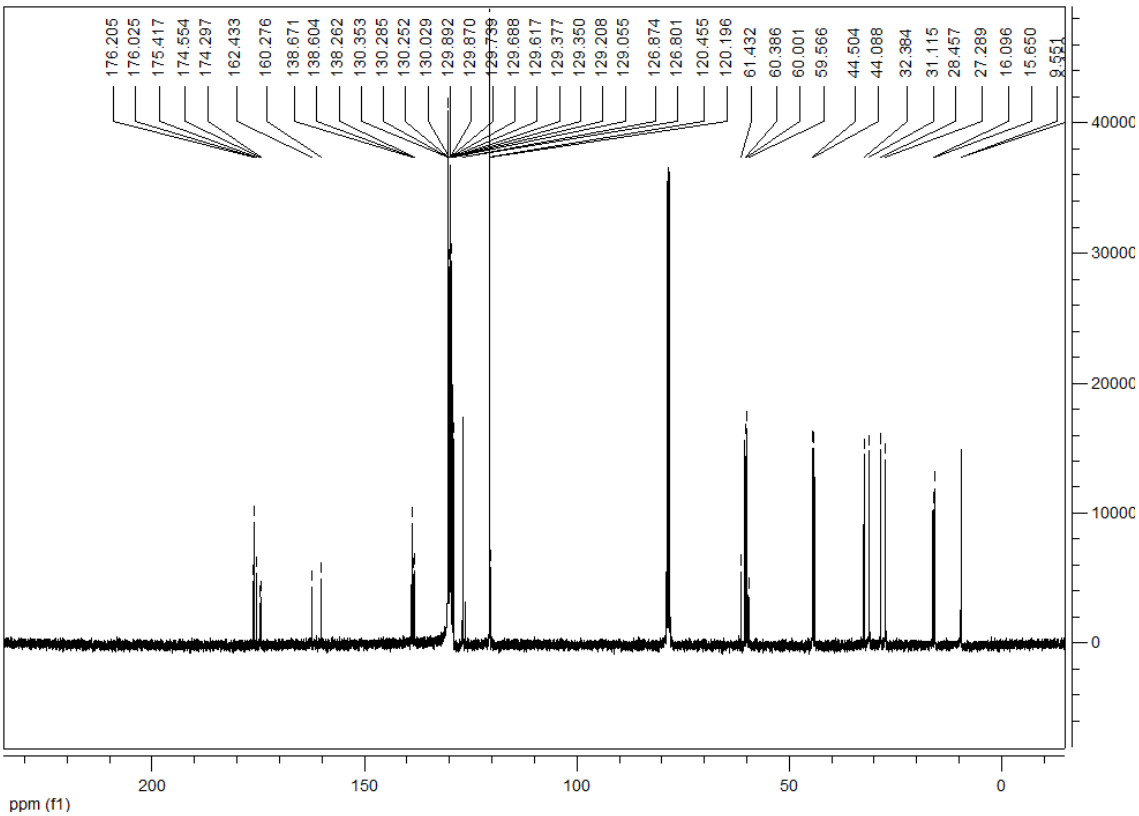


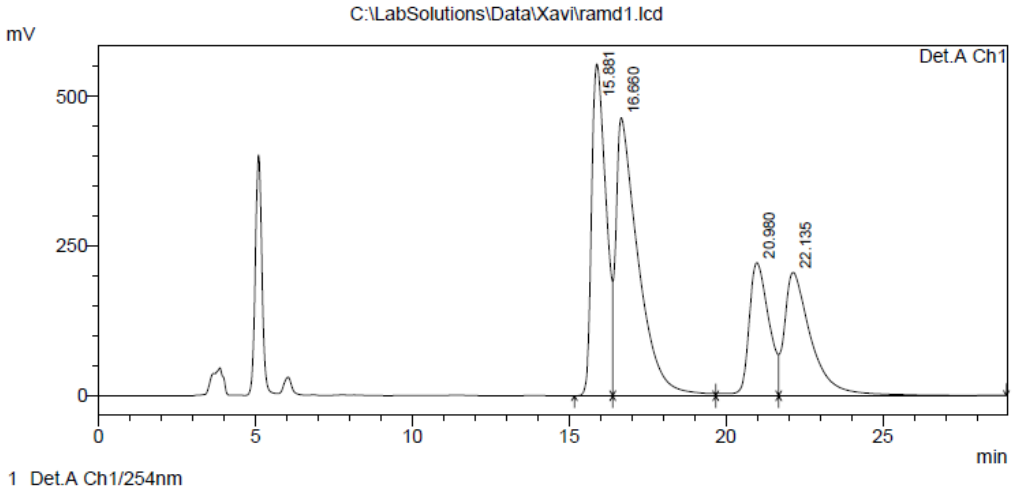
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.130	28005472	149669	68.002	57.433
2	64.562	13178126	110930	31.998	42.567
Total		41183598	260599	100.000	100.000





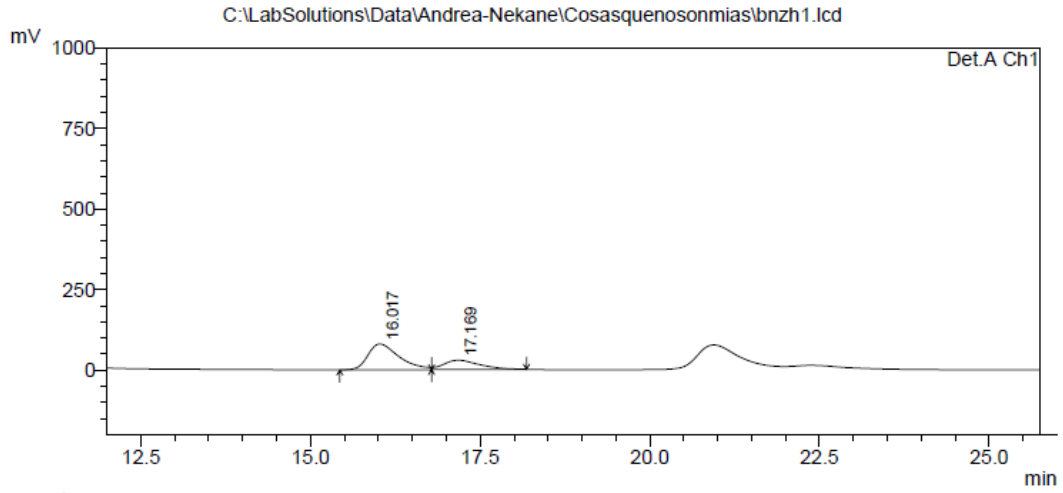


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.881	17582746	554065	28.117	38.304
2	16.660	22985449	464114	36.757	32.085
3	20.980	9775313	222276	15.632	15.366
4	22.135	12190292	206048	19.494	14.245
Total		62533800	1446503	100.000	100.000

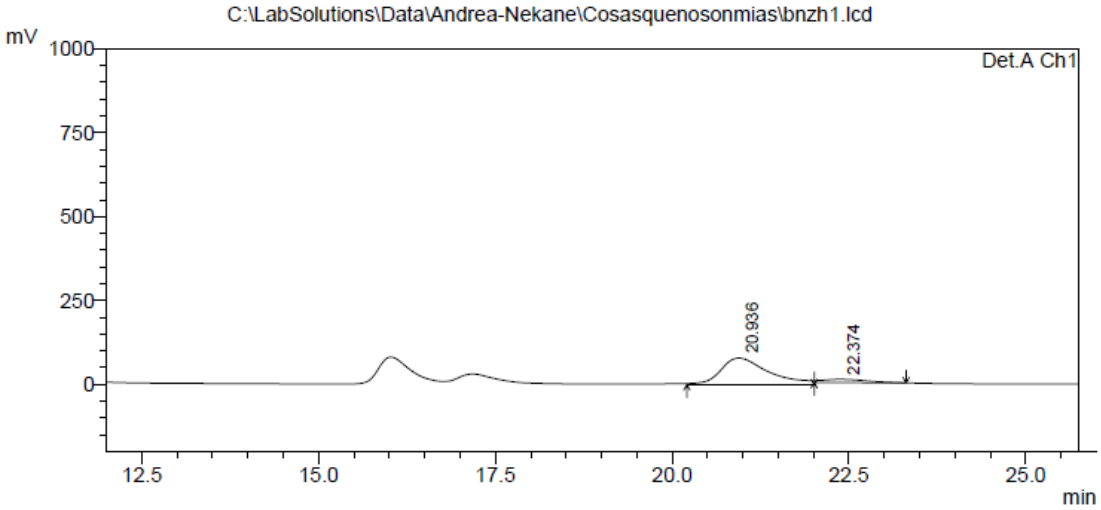


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.017	2593874	80523	71.125	73.702
2	17.169	1053051	28732	28.875	26.298
Total		3646926	109256	100.000	100.000

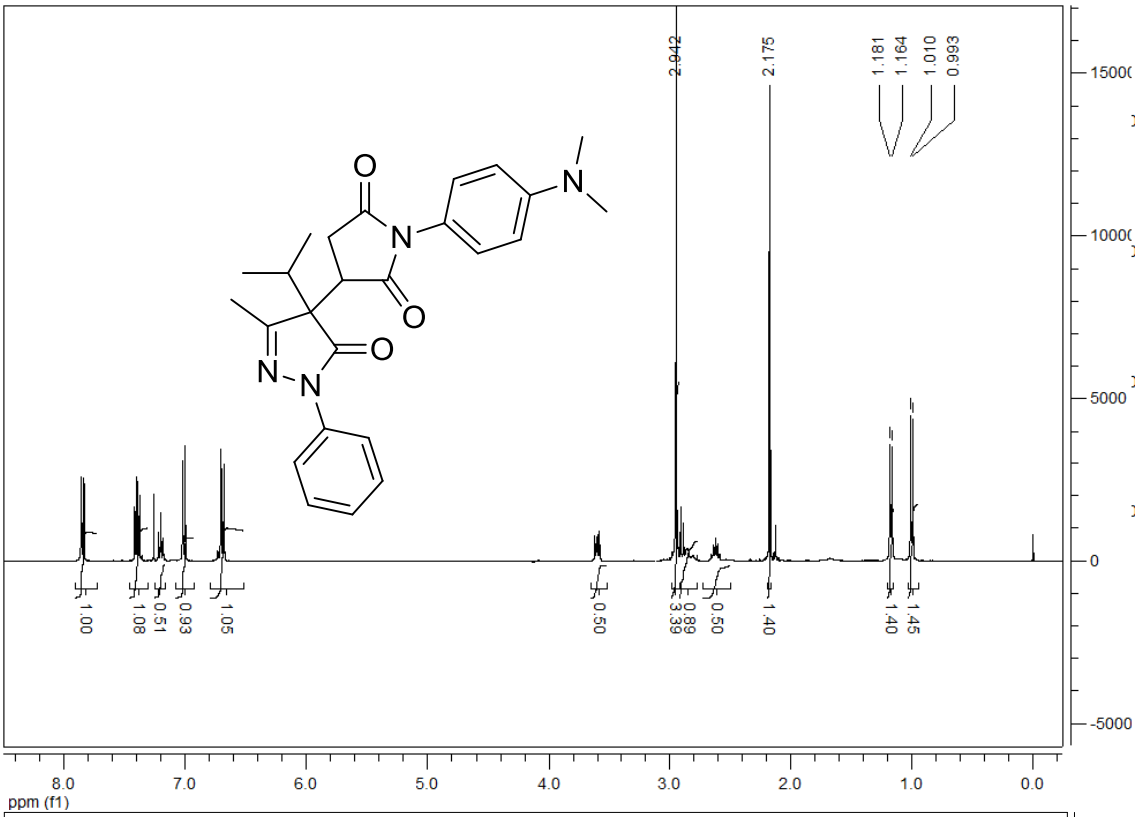


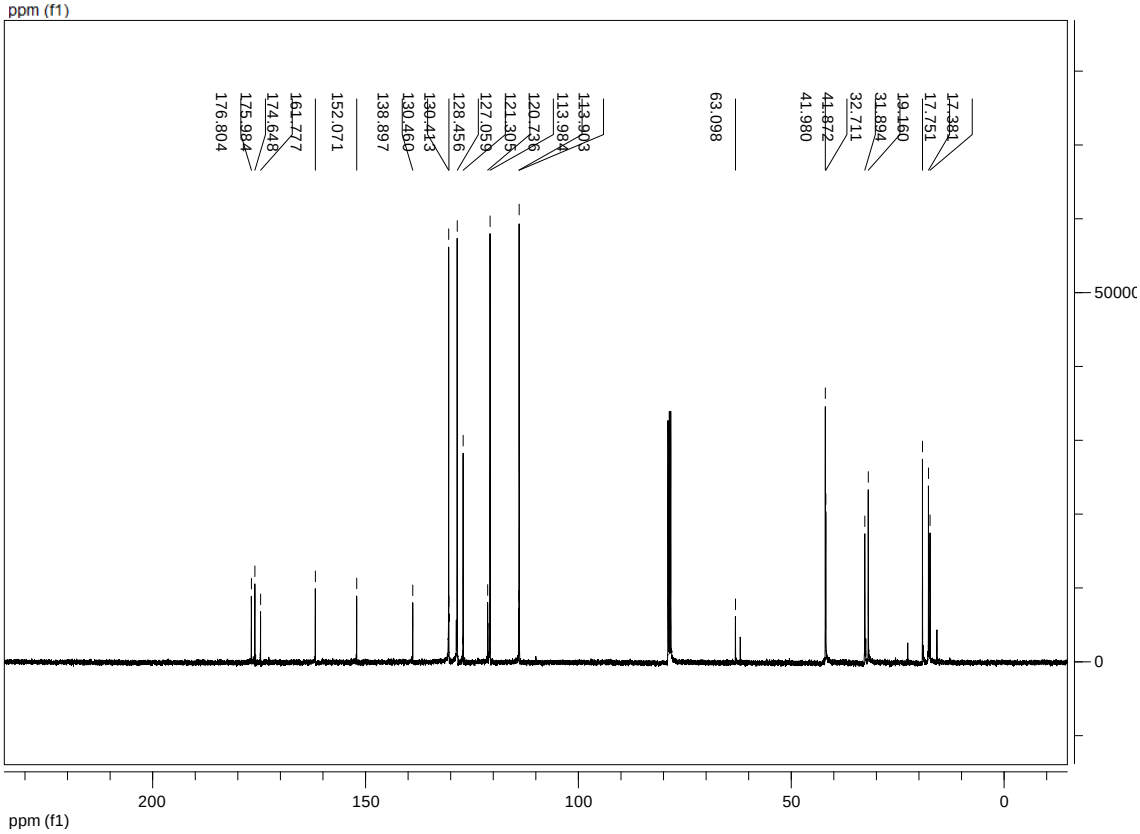
1 Det.A Ch1/254nm

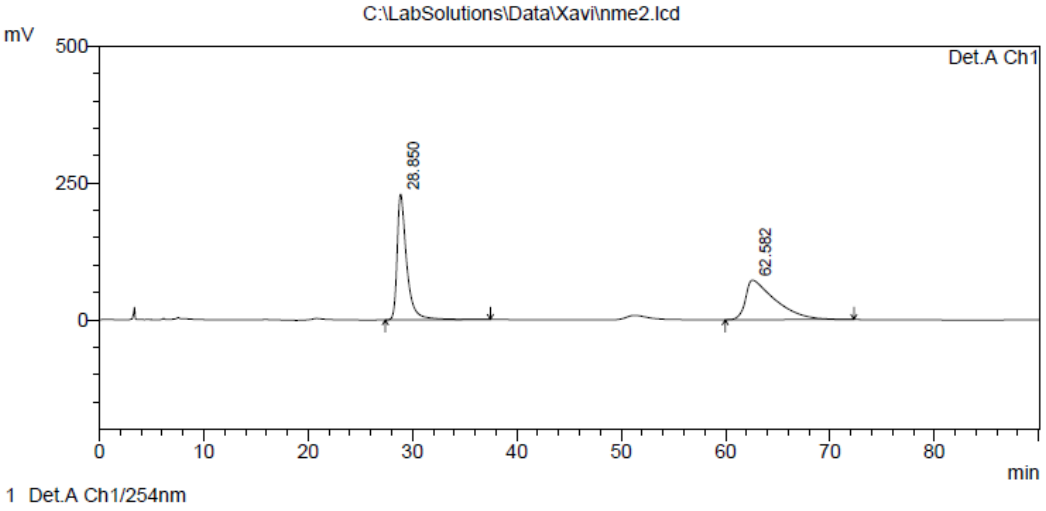
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.936	3756451	79625	89.581	88.708
2	22.374	436907	10136	10.419	11.292
Total		4193358	89761	100.000	100.000



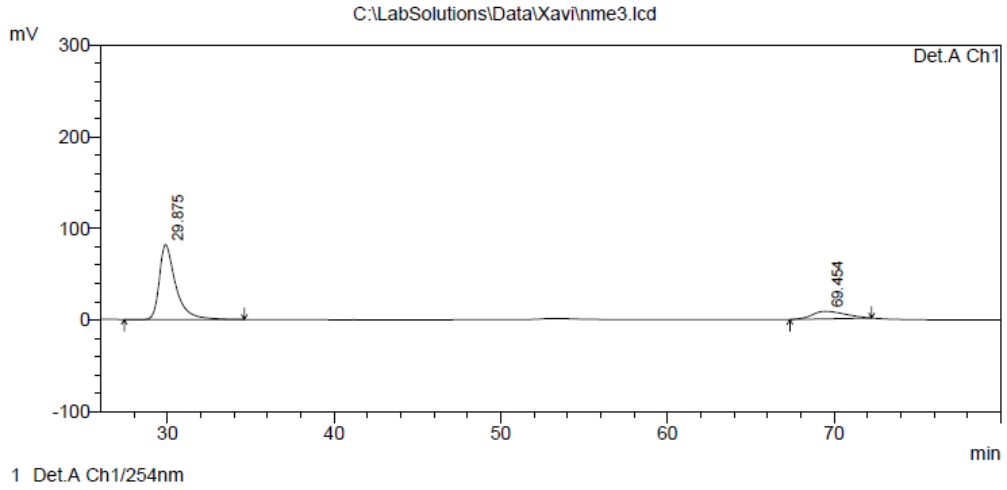




PeakTable

Detector A Ch1 254nm

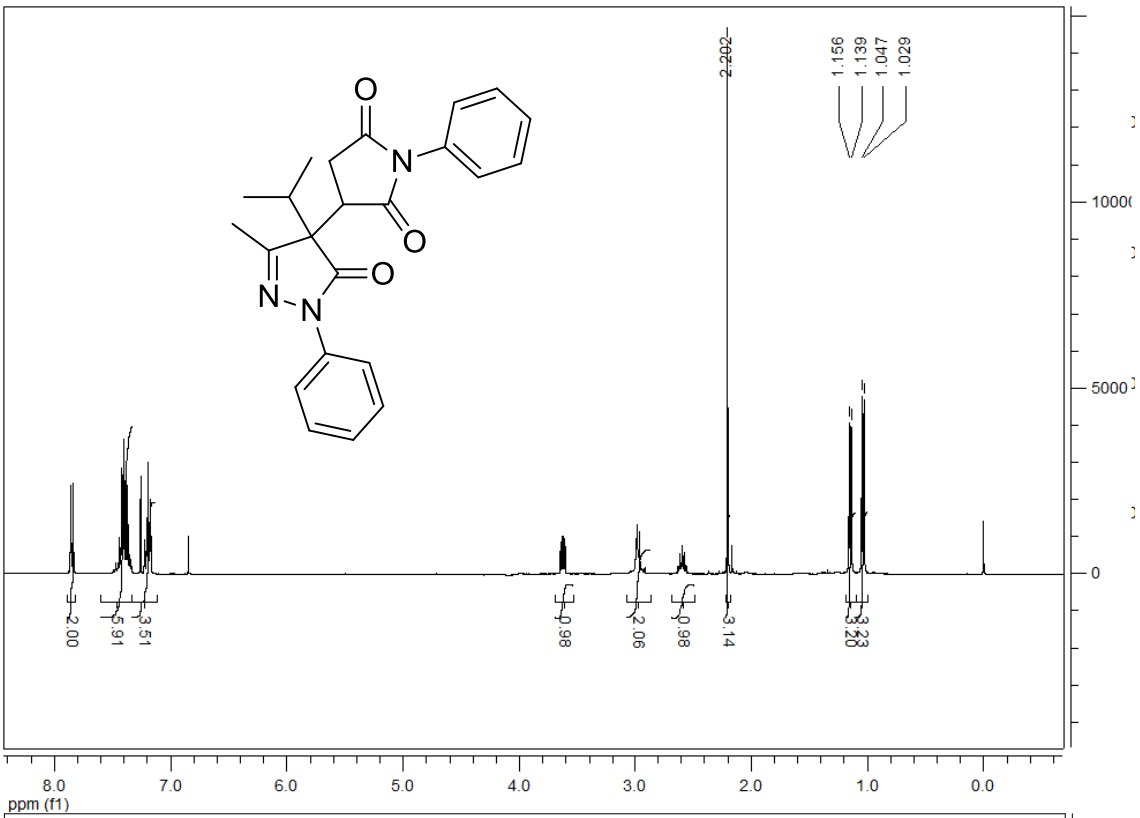
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.850	14655156	229552	50.608	76.062
2	62.582	14302851	72244	49.392	23.938
Total		28958007	301797	100.000	100.000

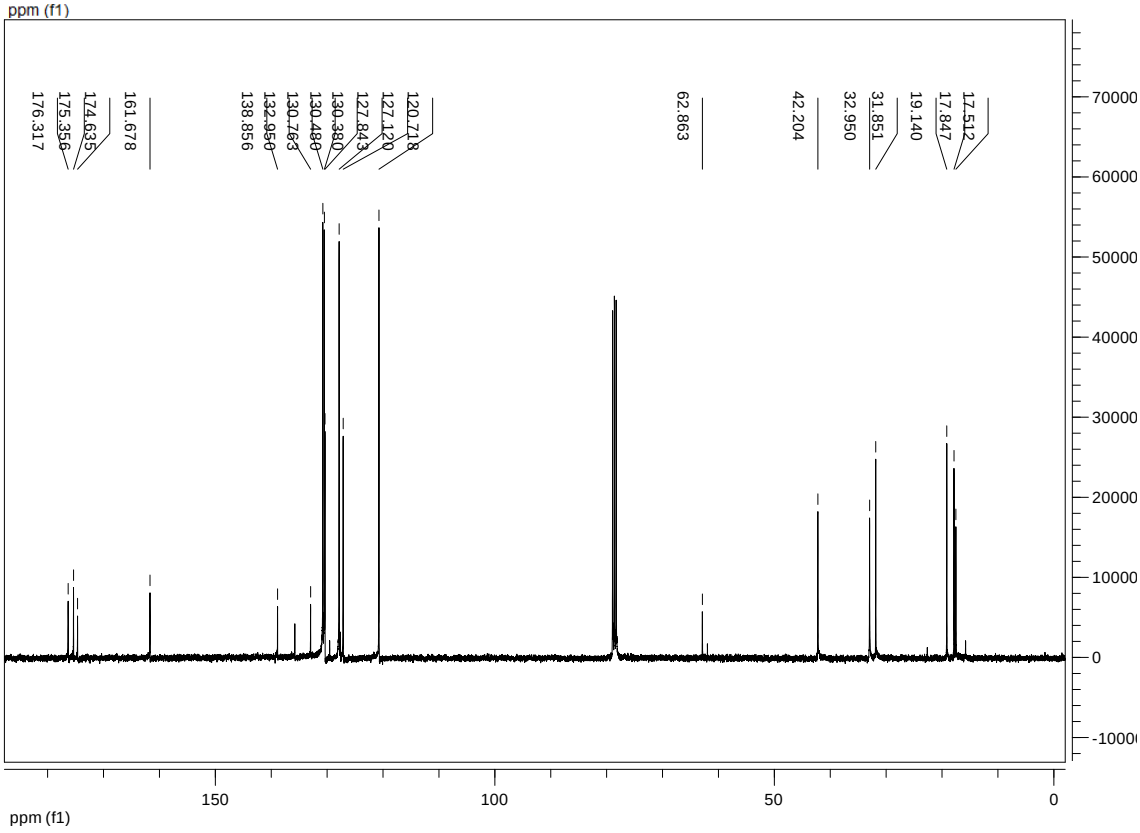


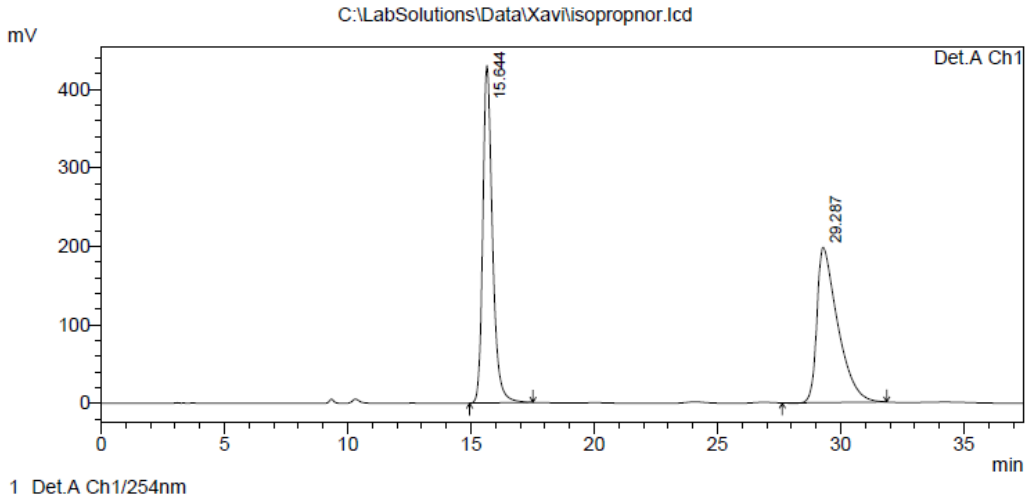
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.875	5579747	81623	83.007	90.732
2	69.454	1142298	8338	16.993	9.268
Total		6722045	89960	100.000	100.000





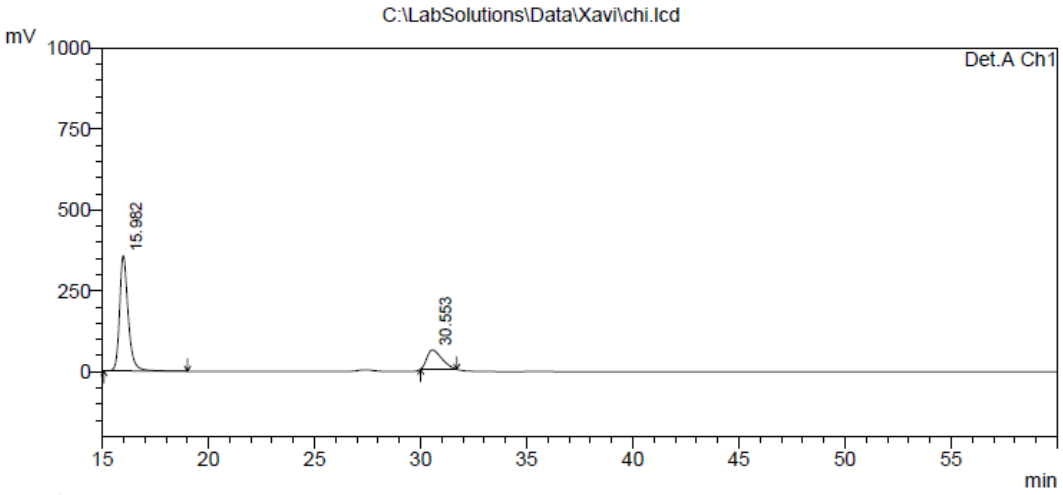


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.644	11704188	429765	50.231	68.487
2	29.287	11596542	197746	49.769	31.513
Total		23300730	627511	100.000	100.000

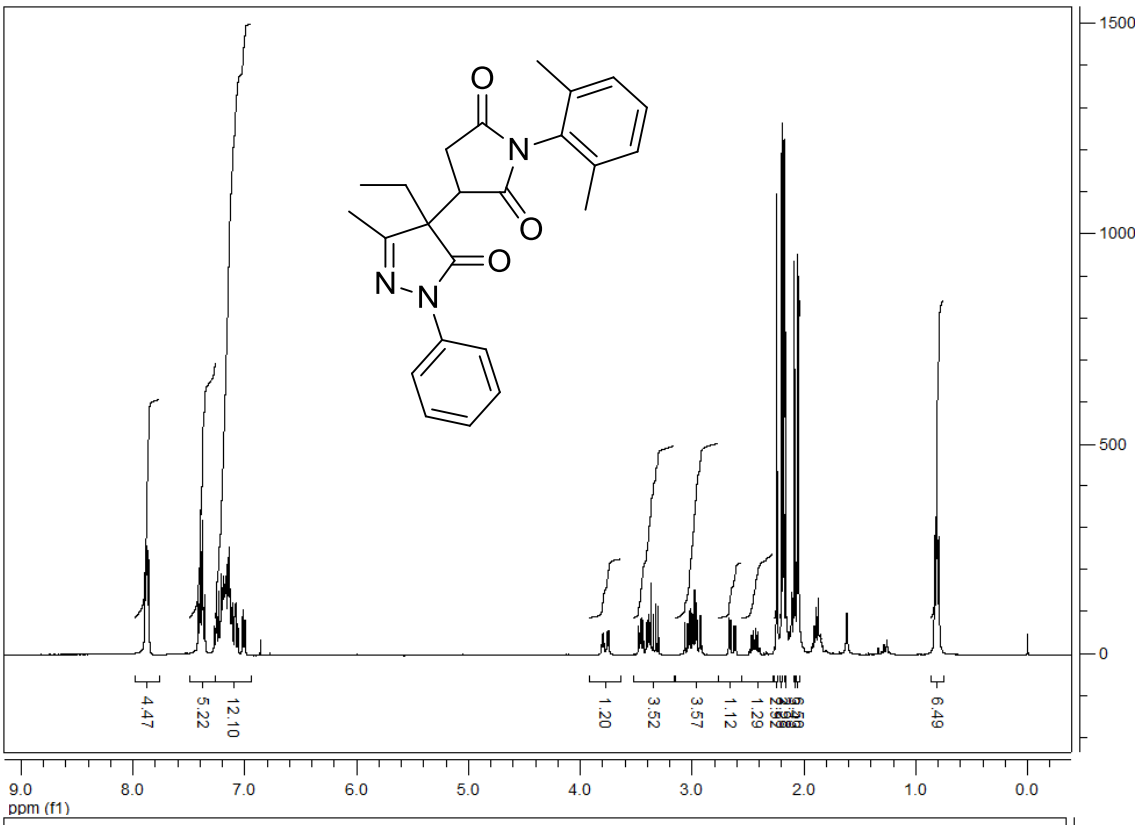


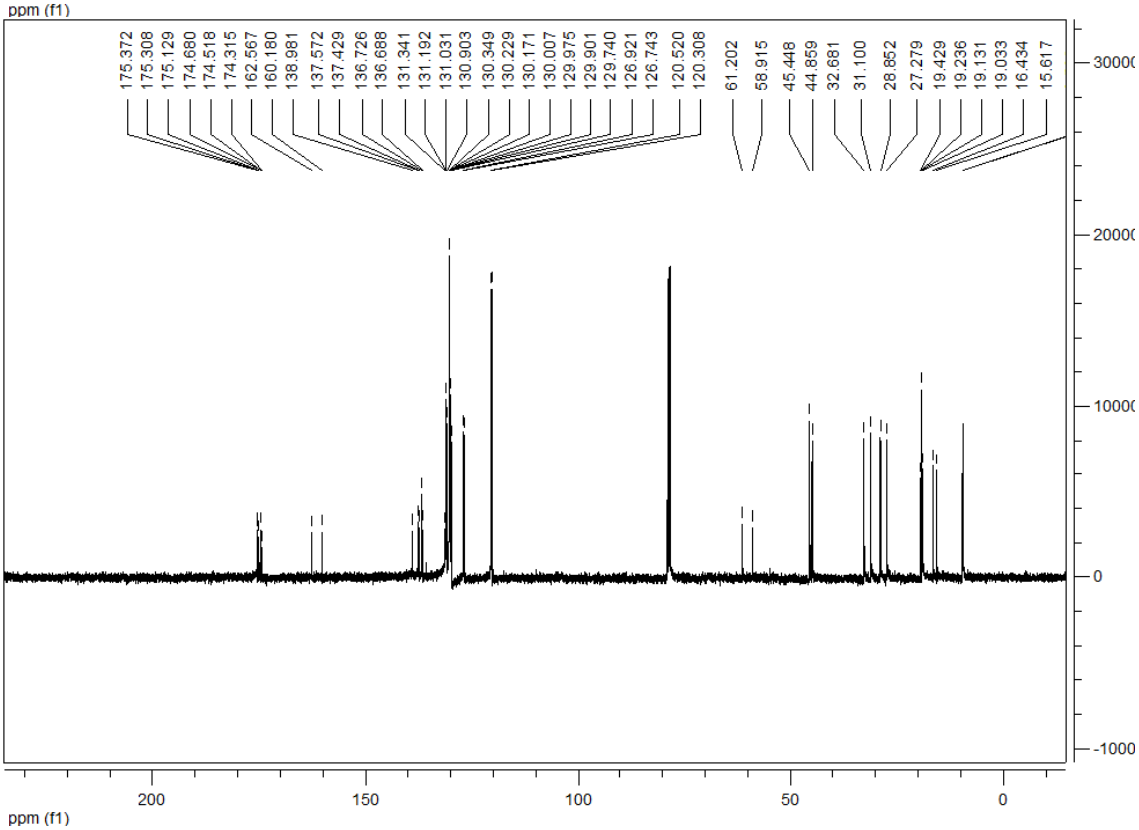
1 Det.A Ch1/254nm

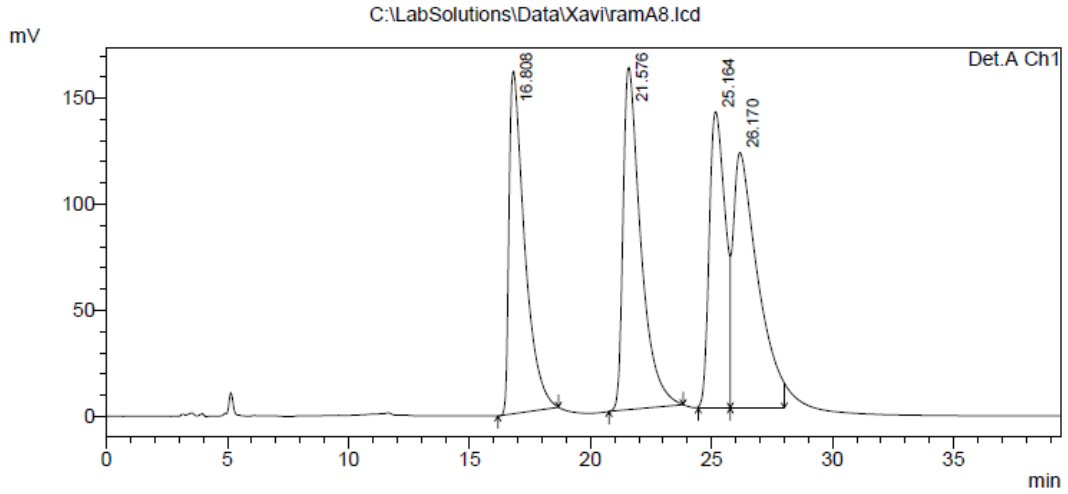
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.982	9989188	356373	77.520	85.726
2	30.553	2896693	59339	22.480	14.274
Total		12885882	415711	100.000	100.000





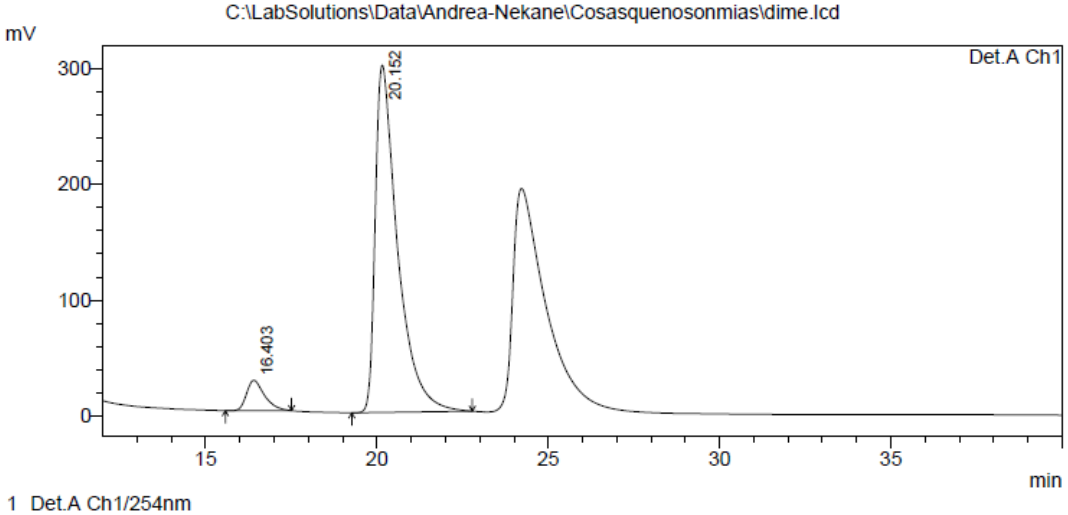


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.808	7239731	161541	23.813	27.709
2	21.576	8249617	161437	27.134	27.691
3	25.164	6386705	139618	21.007	23.949
4	26.170	8526910	120388	28.046	20.650
Total		30402962	582984	100.000	100.000

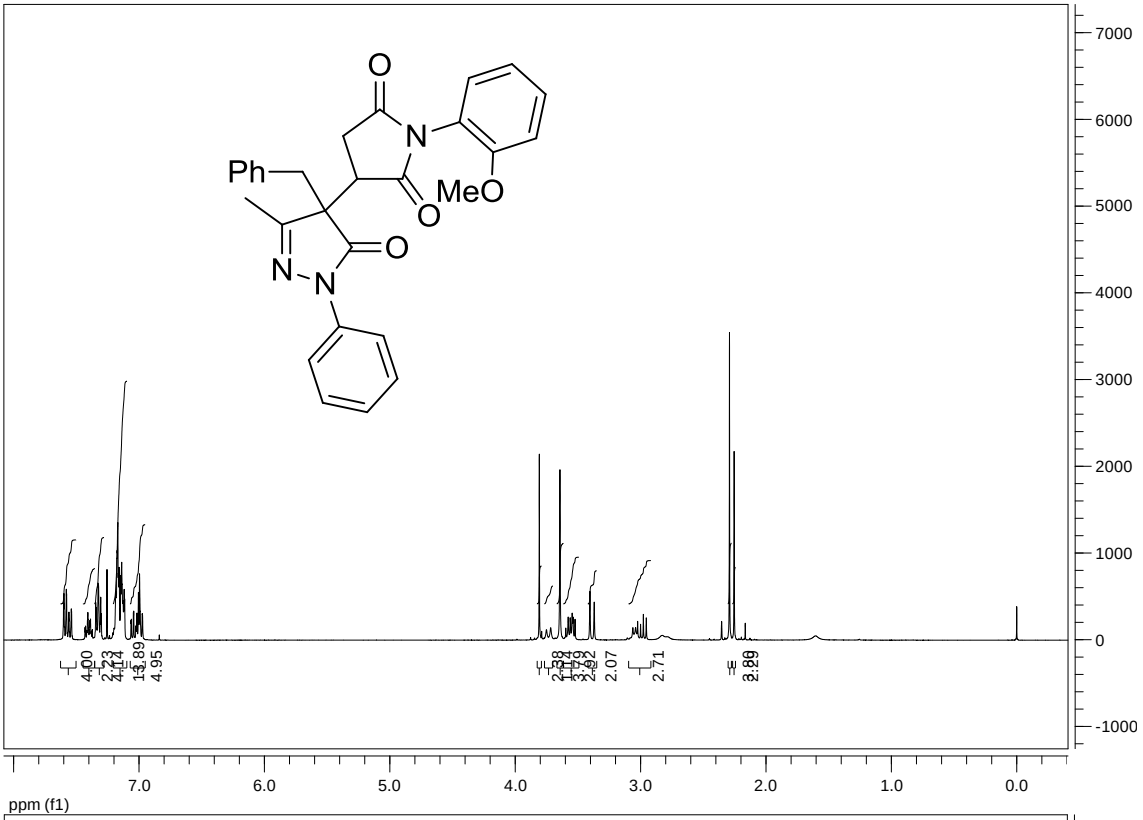


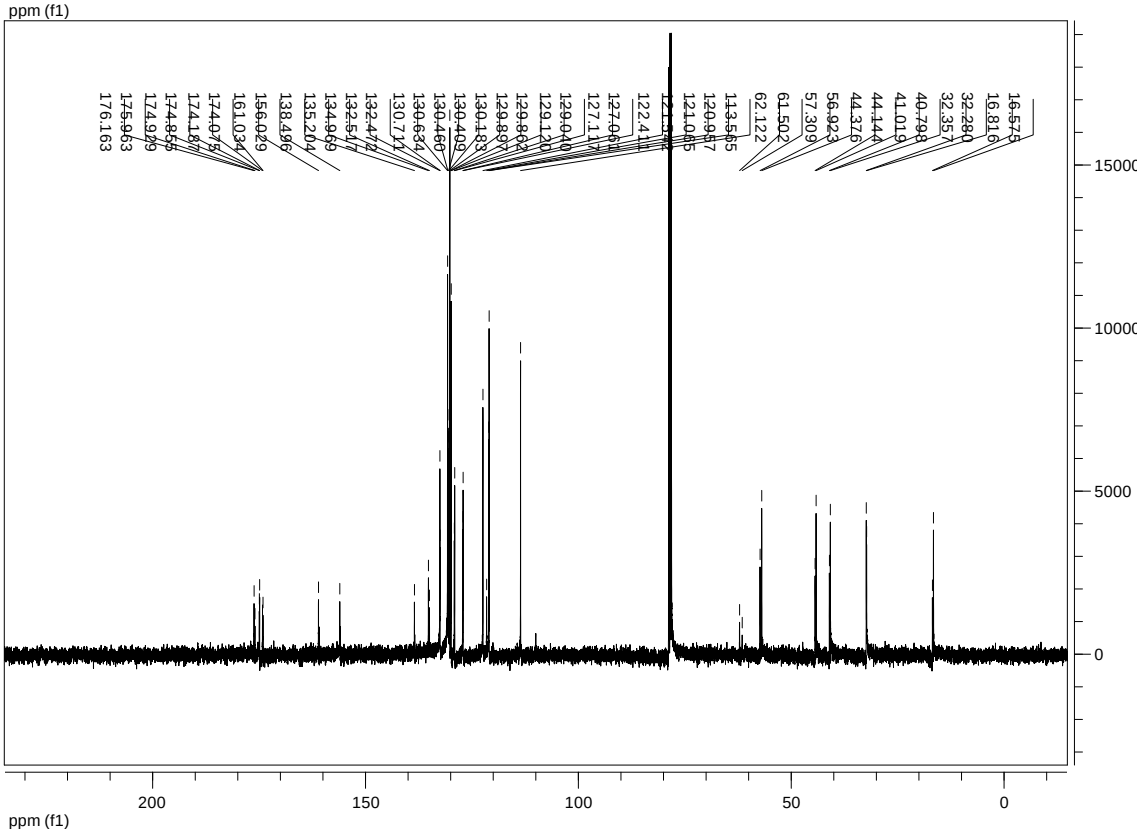
1 Det.A Ch1/254nm

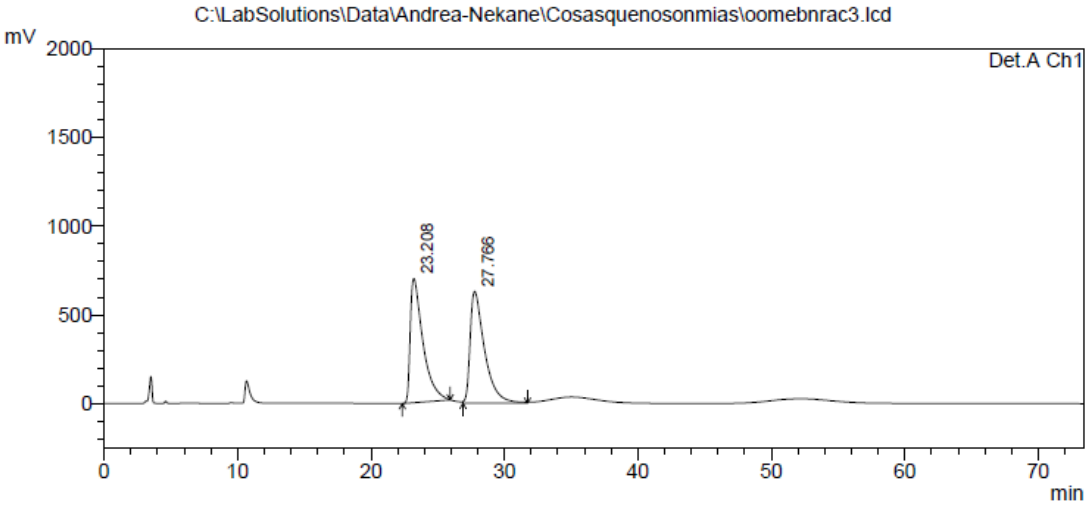
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.403	954558	26306	6.568	8.073
2	20.152	13577810	299534	93.432	91.927
Total		14532368	325840	100.000	100.000



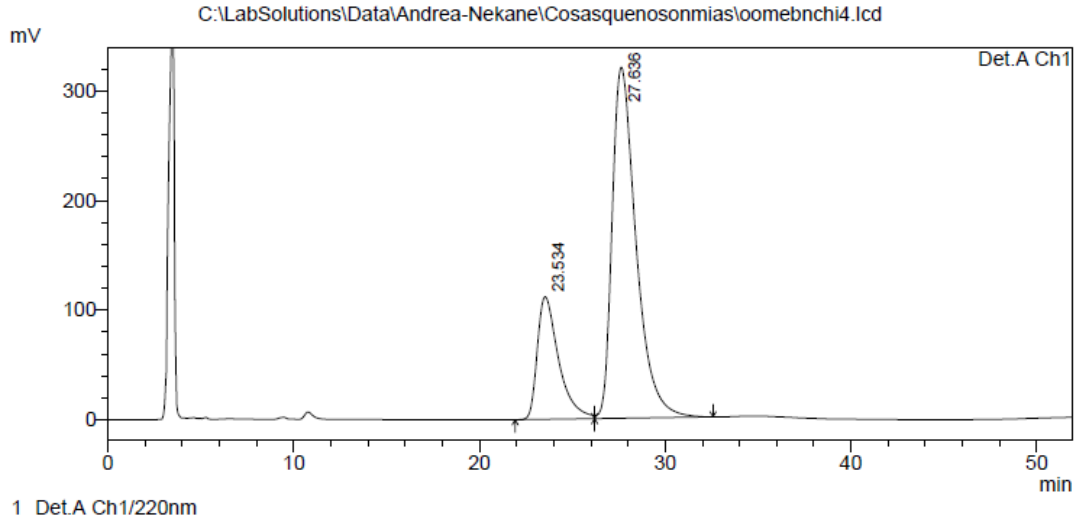




PeakTable

Detector A Ch1 220nm

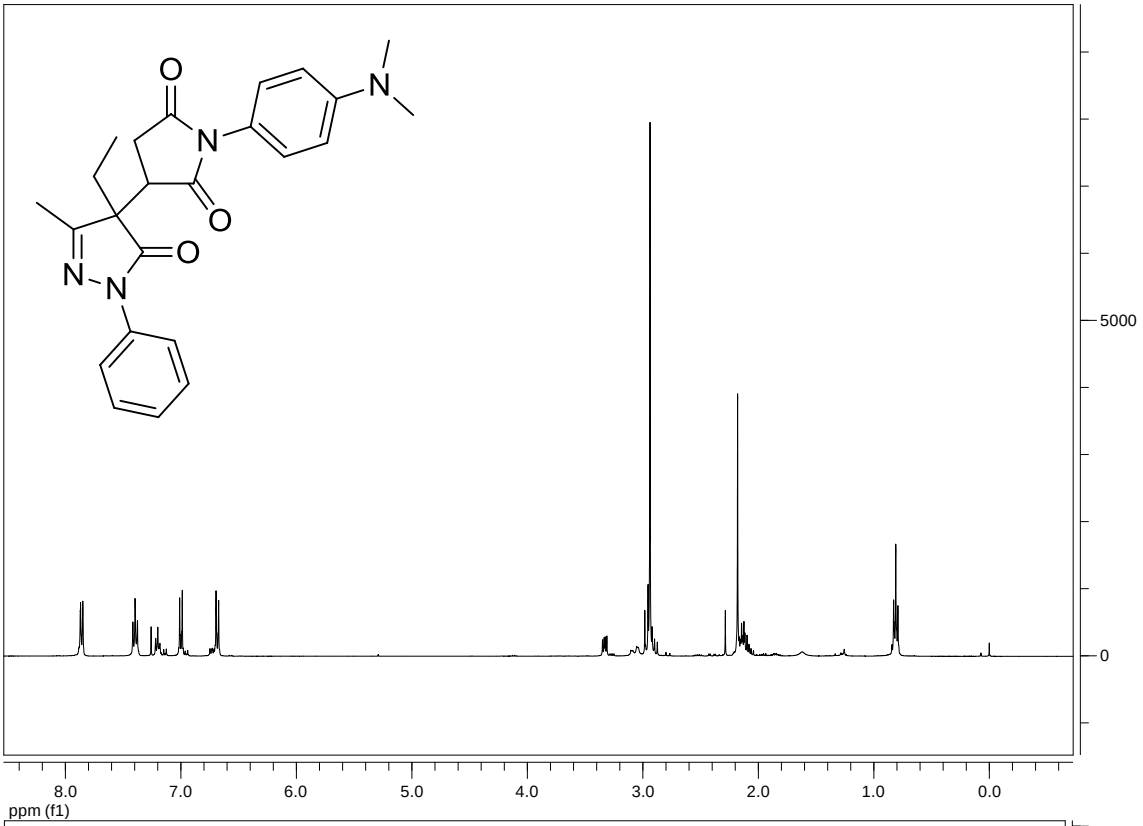
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.208	46256545	699593	49.244	52.555
2	27.766	47677123	631571	50.756	47.445
Total		93933668	1331164	100.000	100.000

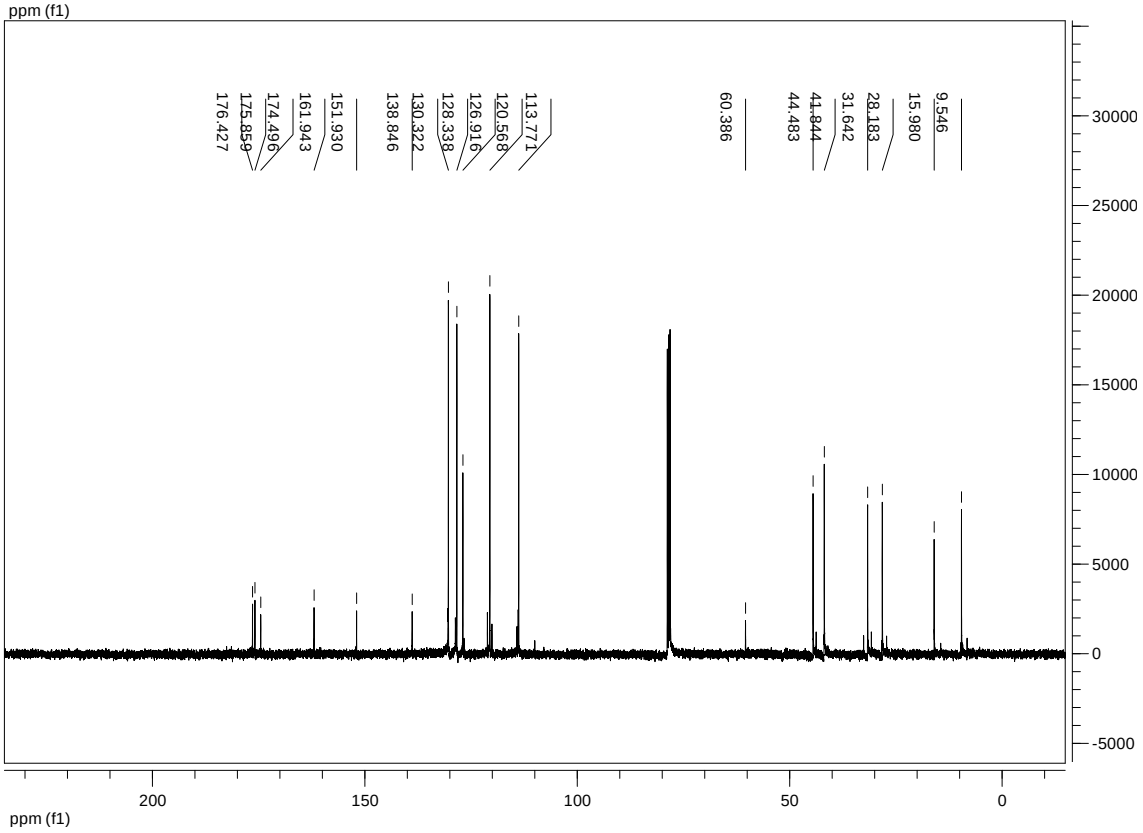


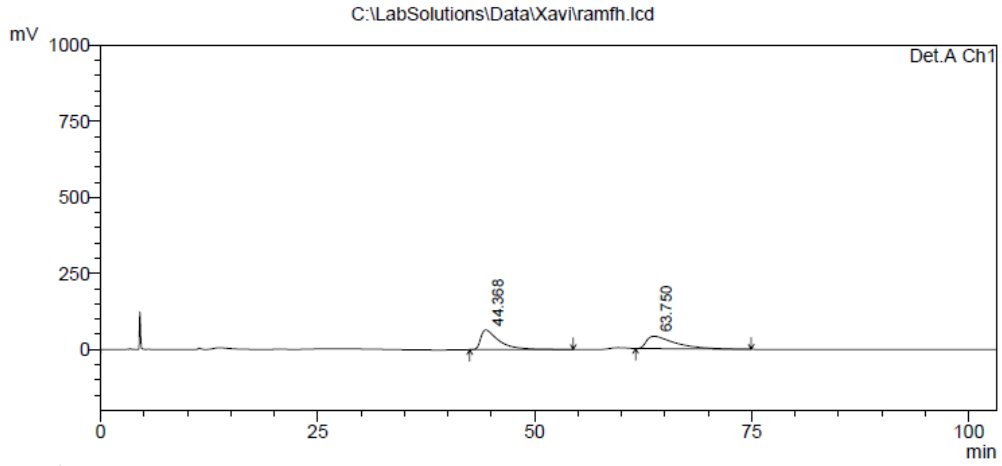
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.534	8932399	111872	23.741	25.889
2	27.636	28691246	320253	76.259	74.111
Total		37623645	432125	100.000	100.000





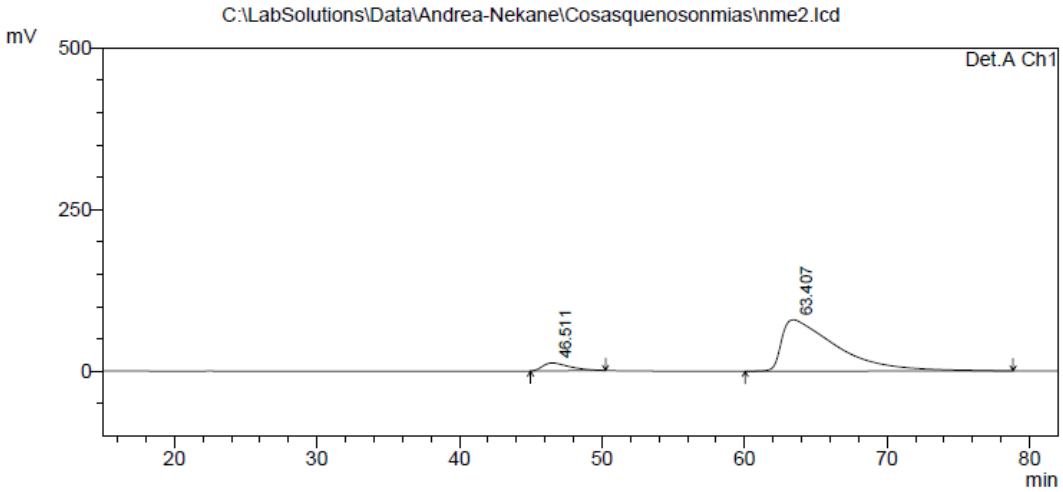


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.368	9477439	64616	50.339	61.380
2	63.750	9349672	40656	49.661	38.620
Total		18827111	105272	100.000	100.000

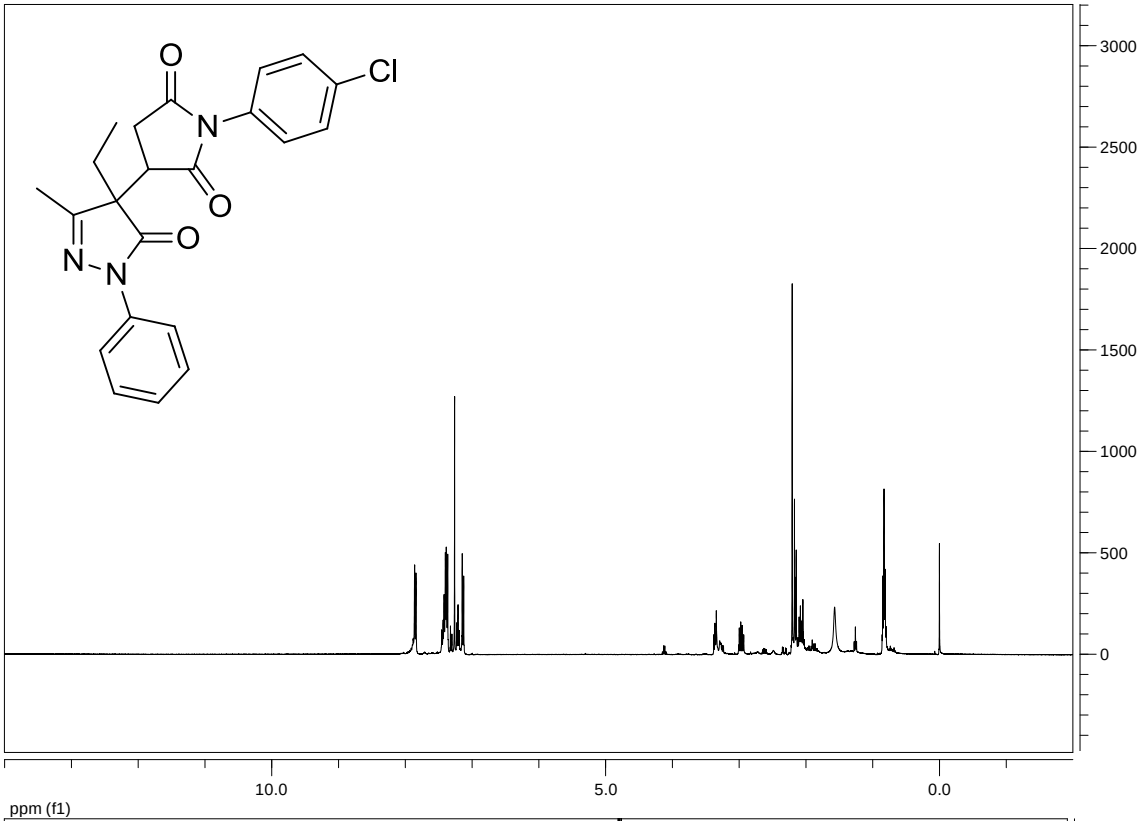


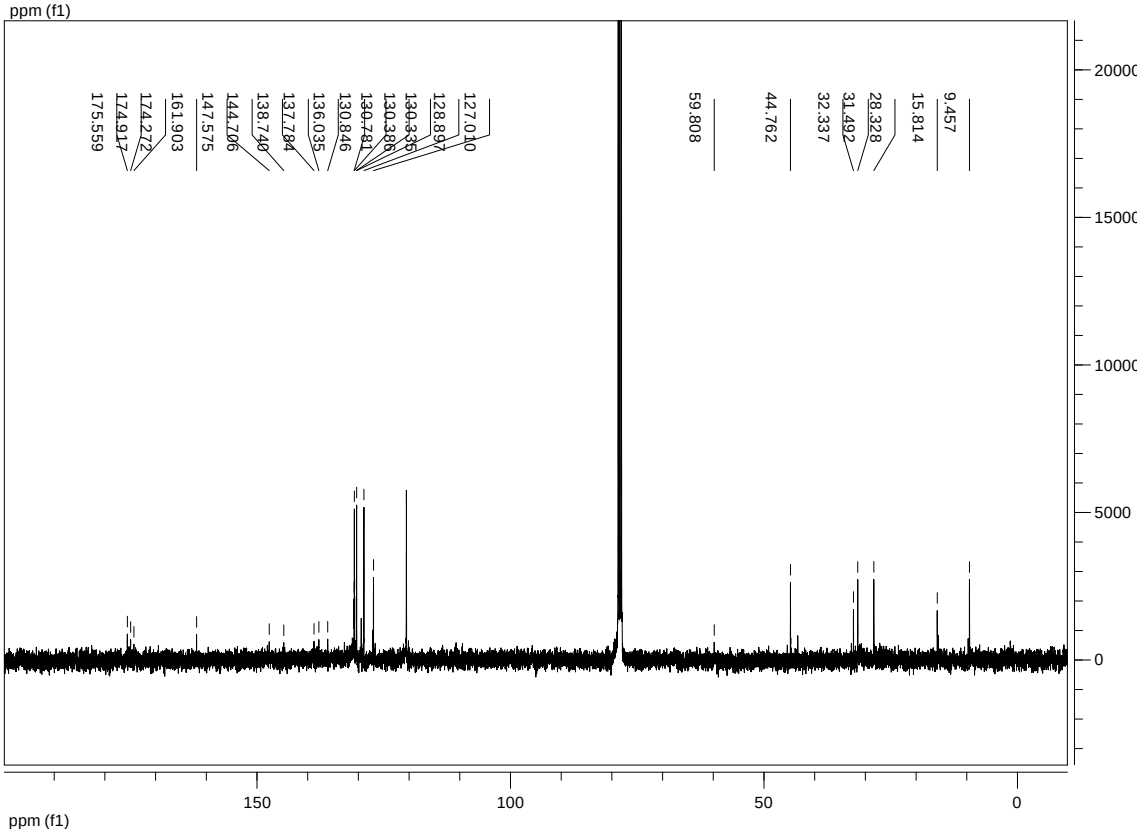
1 Det.A Ch1/254nm

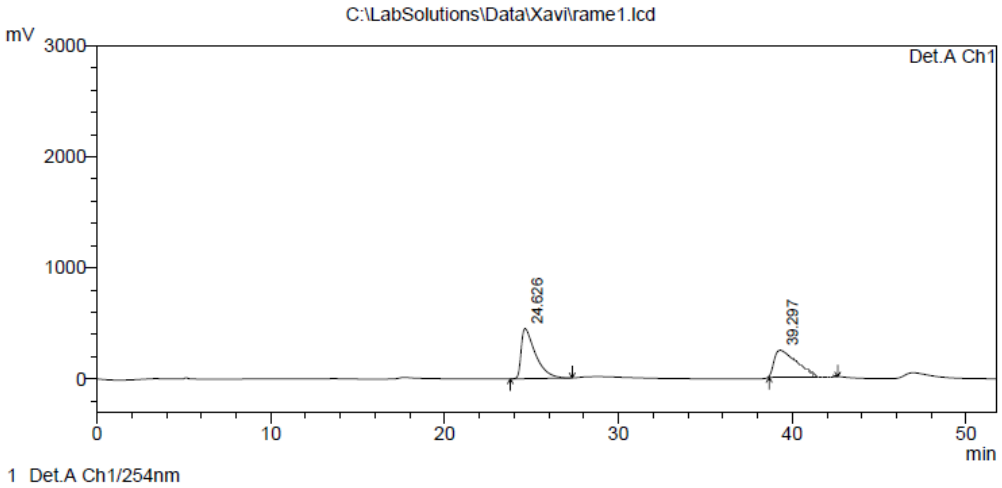
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.511	1609386	12203	7.049	13.312
2	63.407	21223216	79466	92.951	86.688
Total		22832602	91669	100.000	100.000



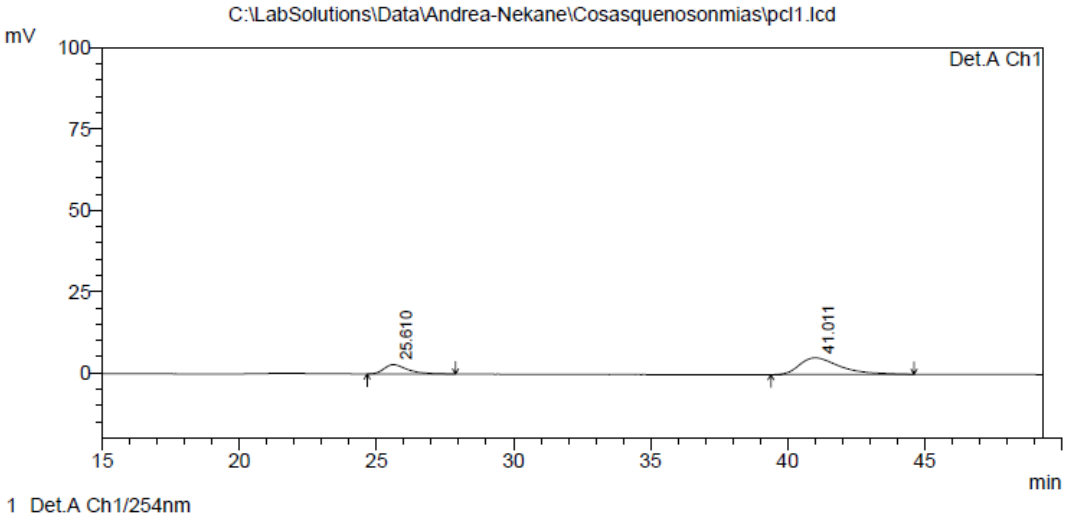




PeakTable

Detector A Ch1 254nm

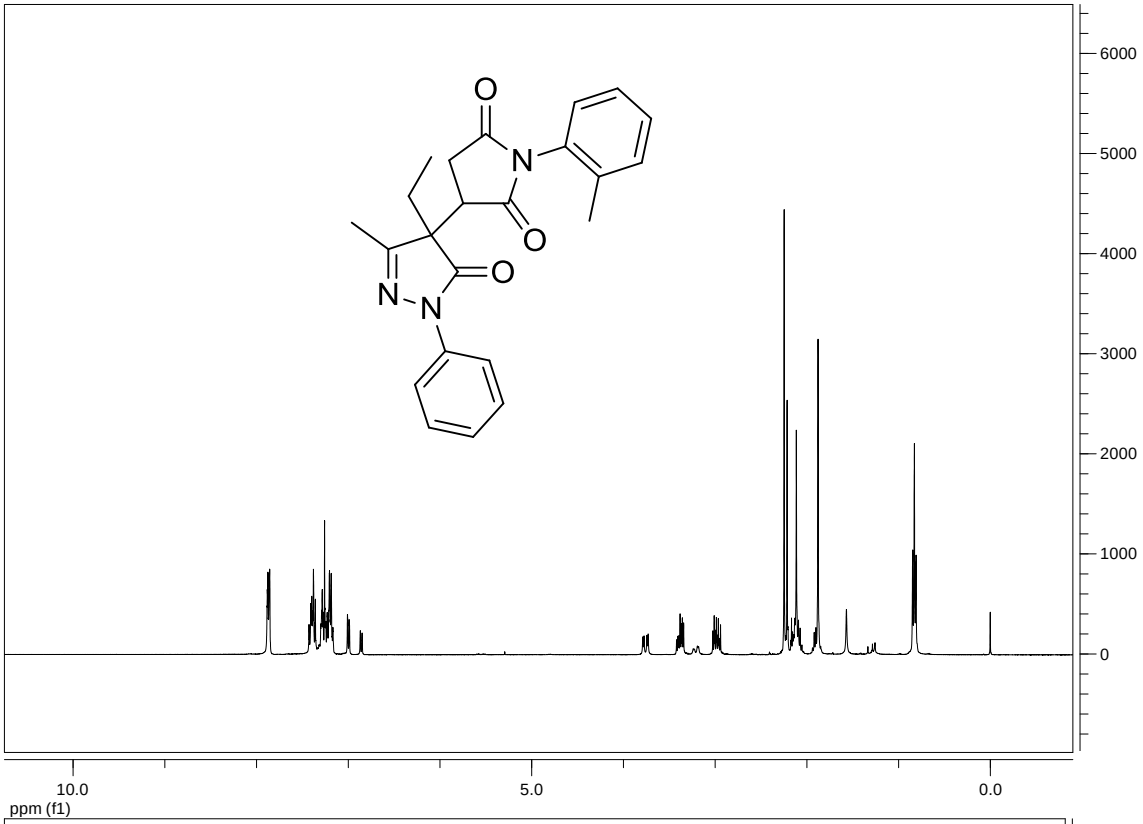
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.626	25688099	451157	47.823	64.962
2	39.297	28027247	243340	52.177	35.038
Total		53715346	694497	100.000	100.000

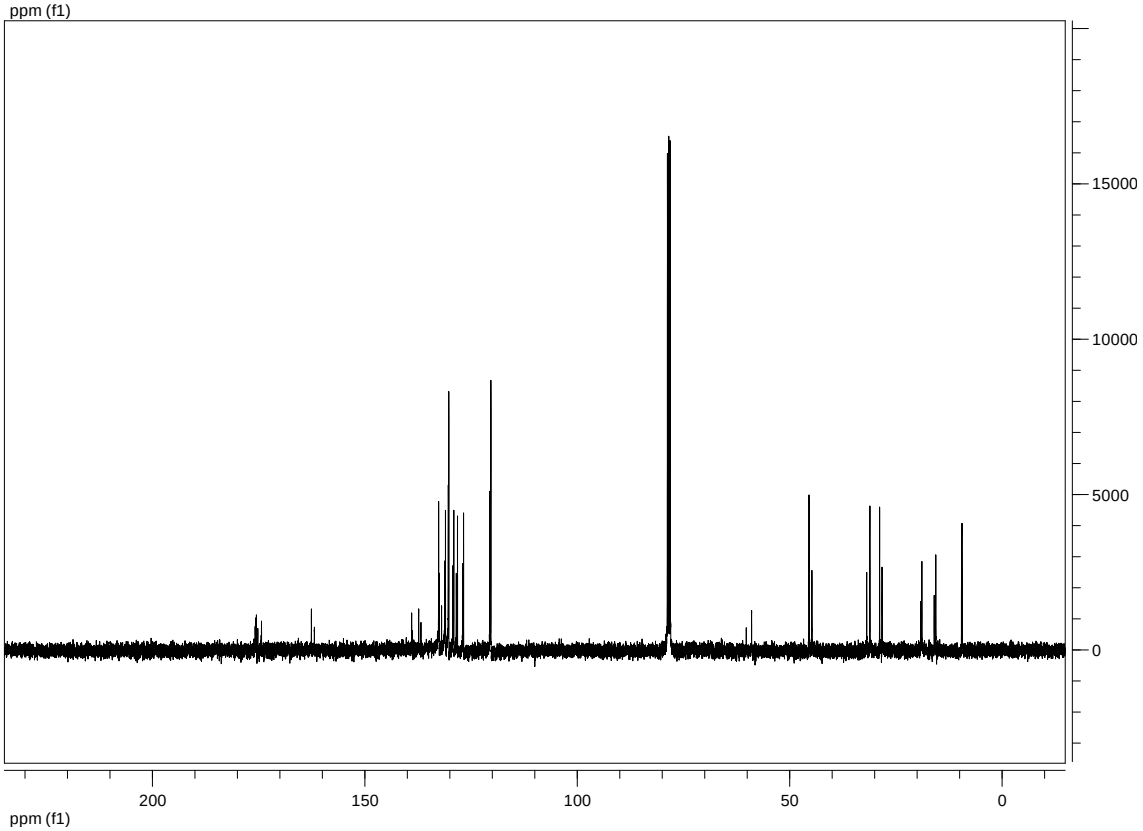


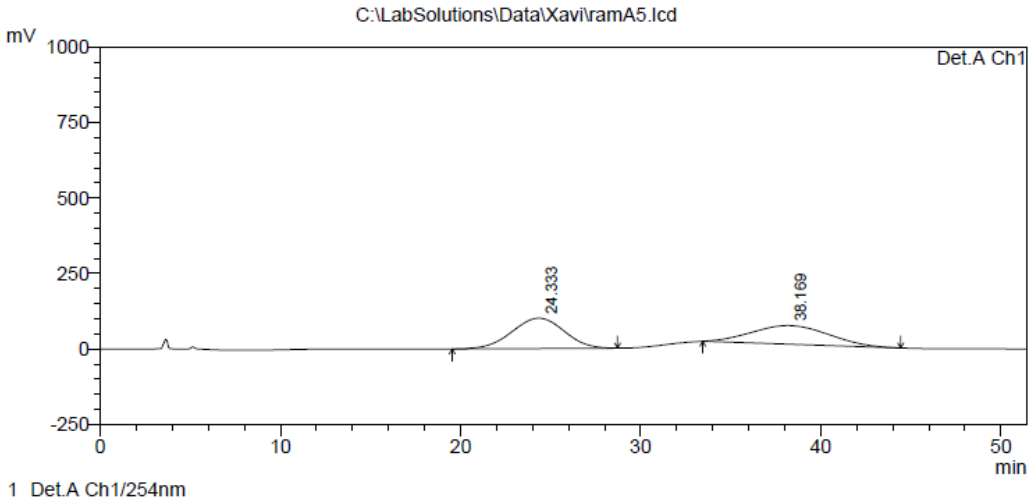
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.610	169433	2865	24.413	35.859
2	41.011	524583	5124	75.587	64.141
Total		694016	7989	100.000	100.000





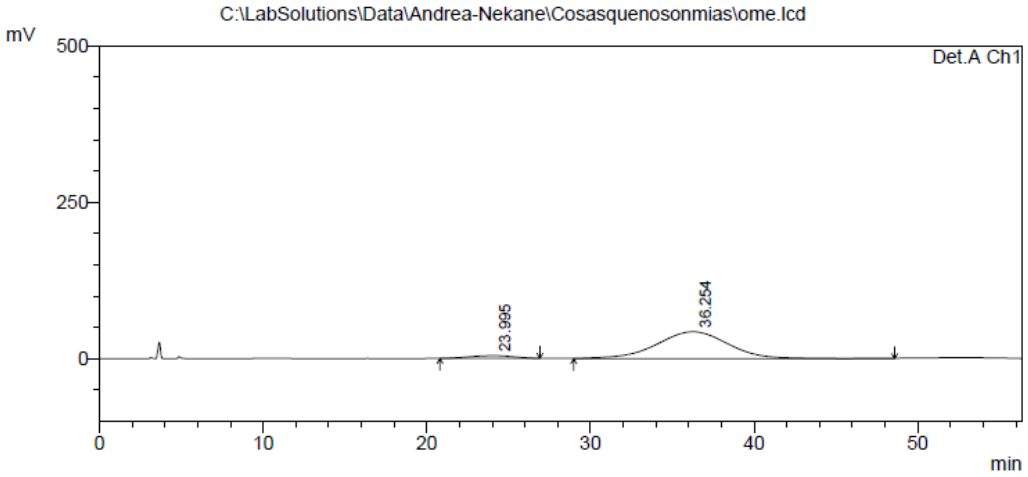


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.333	20404987	100821	52.676	62.123
2	38.169	18331612	61471	47.324	37.877
Total		38736599	162291	100.000	100.000

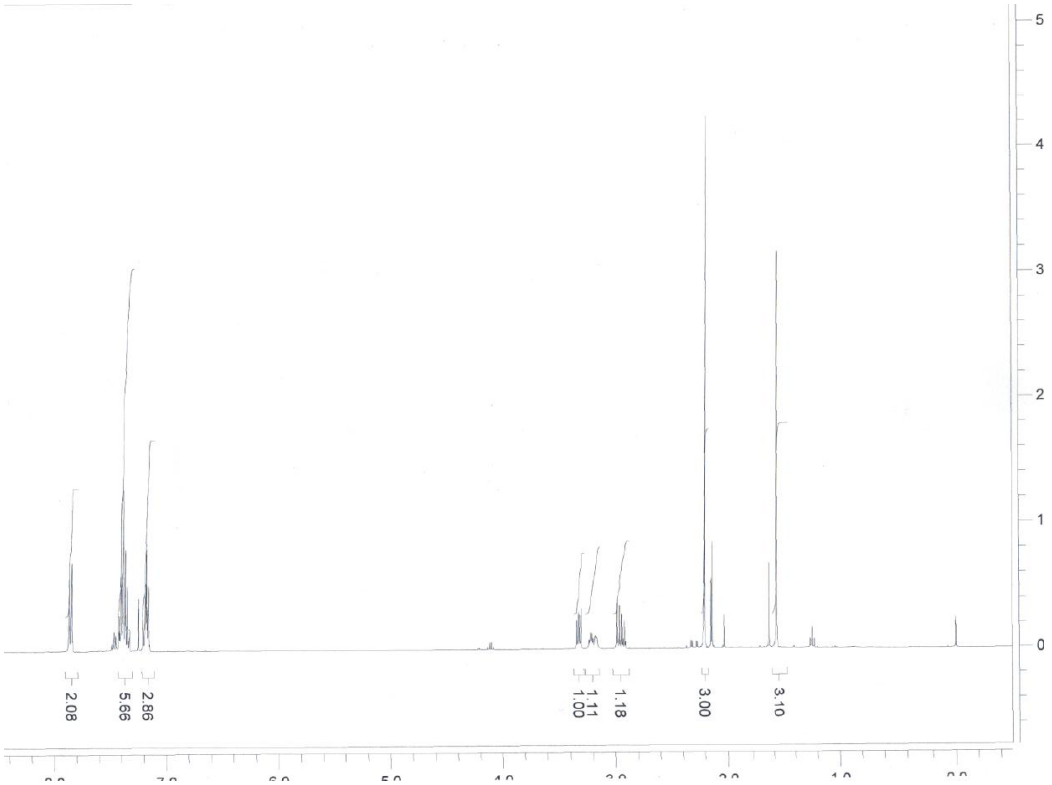


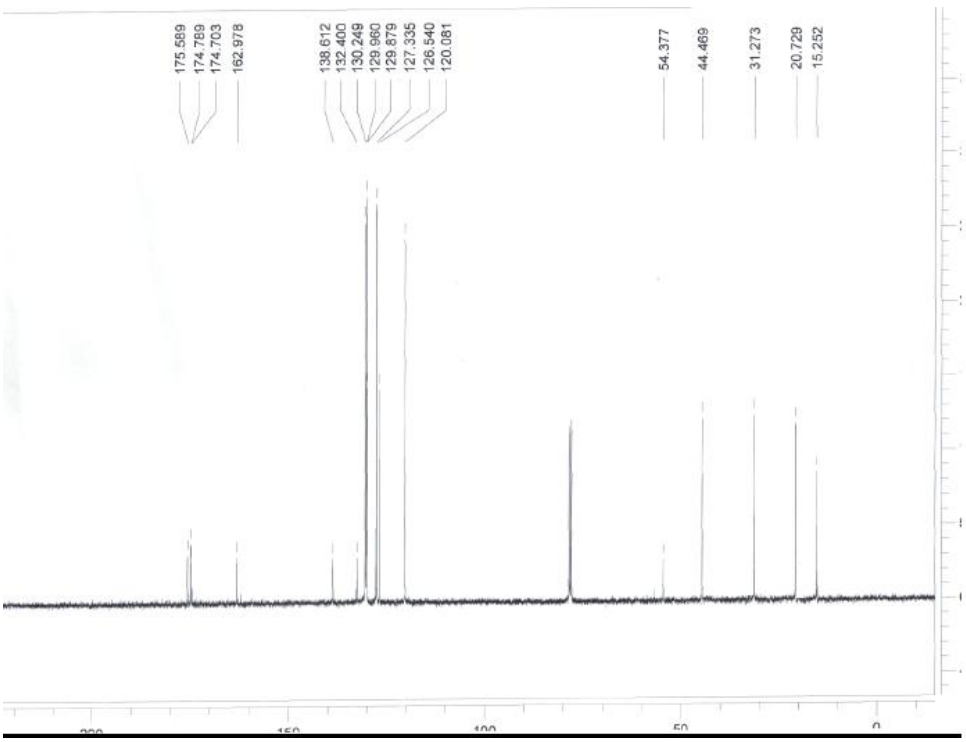
1 Det.A Ch1/254nm

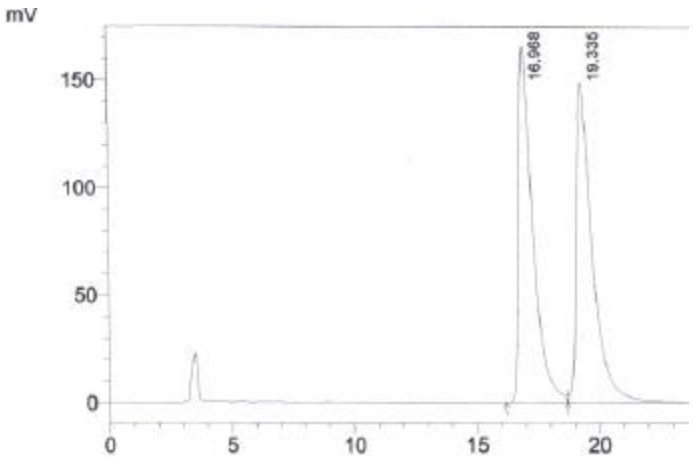
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.995	787207	4379	5.556	9.213
2	36.254	13381402	43153	94.444	90.787
Total		14168609	47532	100.000	100.000



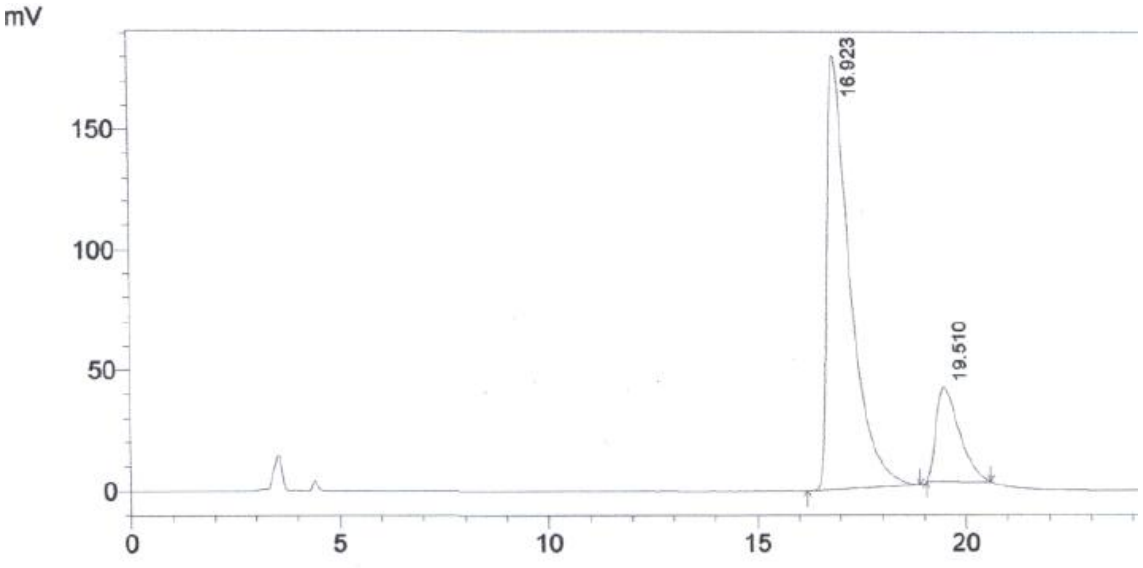




1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.968	6558371	165579	49.174	52.629
2	19.335	6778752	149036	50.826	47.371
Total		13337123	314614	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.923	6901348	180223	81.850	82.102
2	19.510	1530362	39287	18.150	17.898
Total		8431710	219510	100.000	100.000

Calculated energies and cartesian coordinates for the conformations of compound 3a. The uncorrected total energies reported in table 4 is highlighted in yellow, whereas the ZPE corrected free energy is highlighted in green All the values are in Hartree. Table 4 reports the energy differences in kcal/mol.

Compound 3a Ground State conformation a

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.94260135 A.U. after 1 cycles
Imaginary frequencies: 0 (18.2)

Zero-point correction=	0.394211 (Hartree/Particle)
Thermal correction to Energy=	0.418772
Thermal correction to Enthalpy=	0.419716
Thermal correction to Gibbs Free Energy=	0.337653
Sum of electronic and zero-point Energies=	-1240.548391
Sum of electronic and thermal Energies=	-1240.523829
Sum of electronic and thermal Enthalpies=	-1240.522885
Sum of electronic and thermal Free Energies=	-1240.604948

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.300999	0.898119	-1.979254
2	8	0	2.364032	1.870986	-0.008494
3	8	0	2.249764	-2.607861	-1.045590
4	7	0	-2.674204	0.118394	0.199825
5	7	0	-1.971493	0.130569	1.415807
6	7	0	2.631976	-0.389626	-0.451271
7	6	0	-3.953129	-0.499334	0.158887
8	6	0	-4.475701	-1.070235	1.328418
9	1	0	-3.899553	-1.031005	2.243775
10	6	0	-5.728094	-1.679524	1.298284
11	1	0	-6.123654	-2.118728	2.210272
12	6	0	-6.469695	-1.728573	0.116935
13	1	0	-7.445606	-2.205355	0.099698
14	6	0	-5.941978	-1.157303	-1.041238
15	1	0	-6.506694	-1.186405	-1.969288
16	6	0	-4.690546	-0.542046	-1.034425
17	1	0	-4.285300	-0.099788	-1.933962
18	6	0	-1.973201	0.750460	-0.812705
19	6	0	-0.659225	1.236376	-0.173103
20	6	0	-0.845274	0.731567	1.242037
21	6	0	-0.584041	2.786460	-0.274968
22	1	0	0.371817	3.112889	0.141229
23	1	0	-0.565958	3.026529	-1.345296
24	6	0	-1.748323	3.530273	0.389013
25	1	0	-1.608428	4.610700	0.278552
26	1	0	-1.819095	3.314458	1.461074
27	1	0	-2.709447	3.274517	-0.070139
28	6	0	0.104530	0.908500	2.383732
29	1	0	-0.349825	0.527402	3.301602
30	1	0	0.362516	1.965014	2.519345
31	1	0	1.048384	0.376979	2.213501
32	6	0	0.503485	0.552729	-0.949095
33	1	0	0.481637	0.990062	-1.956204
34	6	0	0.422081	-0.979617	-1.063302
35	1	0	-0.189391	-1.426273	-0.269166
36	1	0	0.017458	-1.329614	-2.015645

37	6	0	1.845040	-1.480118	-0.883502
38	6	0	1.911044	0.814306	-0.398285
39	6	0	4.020299	-0.499123	-0.111425
40	6	0	4.457055	-1.563912	0.682678
41	1	0	3.749455	-2.306798	1.030465
42	6	0	5.809335	-1.670253	1.004855
43	1	0	6.147502	-2.501278	1.617293
44	6	0	6.721535	-0.718046	0.547669
45	6	0	6.276589	0.343815	-0.241441
46	1	0	6.979818	1.089391	-0.601482
47	6	0	4.928614	0.455838	-0.578401
48	1	0	4.581848	1.281955	-1.187417
49	1	0	7.773781	-0.803407	0.804279

##

Compound 3a Ground State conformation b

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.94272319 A.U. after 1 cycles
Imaginary frequencies: 0 (13.6)

Zero-point correction=	0.394389 (Hartree/Particle)
Thermal correction to Energy=	0.418797
Thermal correction to Enthalpy=	0.419741
Thermal correction to Gibbs Free Energy=	0.338232
Sum of electronic and zero-point Energies=	-1240.548334
Sum of electronic and thermal Energies=	-1240.523926
Sum of electronic and thermal Enthalpies=	-1240.522982
Sum of electronic and thermal Free Energies=	-1240.604491

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.268383	-0.410728	-1.917436
2	8	0	-1.128141	-0.391309	1.714531
3	8	0	-3.252954	-1.167082	-2.289858
4	7	0	2.176535	0.099008	0.177025
5	7	0	2.193829	-0.484940	1.456934
6	7	0	-2.396509	-0.506637	-0.229031
7	6	0	2.872313	1.321895	-0.018461
8	6	0	3.512445	1.923556	1.074936
9	1	0	3.462031	1.450054	2.046688
10	6	0	4.202211	3.120543	0.897397
11	1	0	4.693926	3.578165	1.751776
12	6	0	4.263691	3.729944	-0.356752
13	1	0	4.802785	4.663835	-0.488589
14	6	0	3.622856	3.125175	-1.438198
15	1	0	3.659880	3.586878	-2.421355
16	6	0	2.927090	1.926519	-1.283917
17	1	0	2.430428	1.463107	-2.124781
18	6	0	1.452399	-0.646862	-0.729423
19	6	0	0.957942	-1.882088	0.045431
20	6	0	1.495617	-1.563332	1.425859
21	6	0	1.625088	-3.161728	-0.542314
22	1	0	1.270391	-4.022837	0.039675
23	1	0	1.247045	-3.290917	-1.562485
24	6	0	3.157275	-3.148643	-0.576305
25	1	0	3.528488	-4.099204	-0.973416
26	1	0	3.590950	-3.009097	0.419496
27	1	0	3.534810	-2.350560	-1.223897

28	6	0	1.310519	-2.394532	2.652428
29	1	0	1.906215	-1.980719	3.469630
30	1	0	1.611489	-3.436233	2.485273
31	1	0	0.257240	-2.389355	2.955397
32	6	0	-0.589337	-2.044870	-0.013983
33	1	0	-0.834469	-2.929328	0.590036
34	6	0	-1.203453	-2.178413	-1.419020
35	1	0	-0.519277	-1.816119	-2.193052
36	1	0	-1.512392	-3.193539	-1.680704
37	6	0	-2.415631	-1.262870	-1.423085
38	6	0	-1.355931	-0.880462	0.626987
39	6	0	-3.351150	0.518005	0.075096
40	6	0	-3.696958	1.451058	-0.907017
41	1	0	-3.248334	1.392640	-1.891288
42	6	0	-4.629612	2.444075	-0.611654
43	1	0	-4.899547	3.166113	-1.377029
44	6	0	-5.208930	2.514889	0.656277
45	6	0	-4.854466	1.582223	1.632123
46	1	0	-5.299009	1.631239	2.622152
47	6	0	-3.930027	0.578497	1.346294
48	1	0	-3.649527	-0.142103	2.104882
49	1	0	-5.932130	3.293418	0.883018

##

Compound 3a Ground State conformation c

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.94175926 A.U. after 1 cycles
Imaginary frequencies: 0 (18.3)

Zero-point correction= 0.394520 (Hartree/Particle)
Thermal correction to Energy= 0.418902
Thermal correction to Enthalpy= 0.419846
Thermal correction to Gibbs Free Energy= 0.338364
Sum of electronic and zero-point Energies= -1240.547239
Sum of electronic and thermal Energies= -1240.522857
Sum of electronic and thermal Enthalpies= -1240.521913
Sum of electronic and thermal Free Energies= -1240.603395

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.334058	1.414772	-1.526762
2	8	0	2.323954	1.774883	0.528844
3	8	0	2.232805	-2.261016	-1.677721
4	7	0	-2.764507	0.052336	0.327772
5	7	0	-2.049801	-0.394565	1.449347
6	7	0	2.604096	-0.287396	-0.500147
7	6	0	-4.081042	-0.440762	0.119074
8	6	0	-4.620890	-1.357526	1.032910
9	1	0	-4.028664	-1.676071	1.880959
10	6	0	-5.911156	-1.845916	0.839735
11	1	0	-6.319264	-2.555975	1.554138
12	6	0	-6.674246	-1.433346	-0.253565
13	1	0	-7.679649	-1.818043	-0.399126
14	6	0	-6.129319	-0.520479	-1.156740
15	1	0	-6.710015	-0.188493	-2.013265
16	6	0	-4.840071	-0.018127	-0.983093
17	1	0	-4.421190	0.687030	-1.687316
18	6	0	-2.017686	0.915353	-0.457660

19	6	0	-0.684269	1.110935	0.288039
20	6	0	-0.882975	0.150763	1.443207
21	6	0	-0.605196	2.576409	0.831442
22	1	0	-1.518846	2.749747	1.414786
23	1	0	0.236608	2.633777	1.526146
24	6	0	-0.457373	3.670660	-0.230682
25	1	0	-0.553410	4.652487	0.245628
26	1	0	-1.221896	3.589879	-1.007987
27	1	0	0.530678	3.633479	-0.700294
28	6	0	0.098865	-0.141775	2.532408
29	1	0	-0.357422	-0.806741	3.269721
30	1	0	0.423806	0.778592	3.030982
31	1	0	1.003680	-0.622731	2.140630
32	6	0	0.459421	0.729658	-0.688906
33	1	0	0.399207	1.446829	-1.516453
34	6	0	0.395675	-0.699845	-1.255939
35	1	0	-0.223429	-1.370069	-0.646817
36	1	0	0.010946	-0.750560	-2.277353
37	6	0	1.822142	-1.222636	-1.213839
38	6	0	1.874743	0.850091	-0.116941
39	6	0	3.995783	-0.474090	-0.211396
40	6	0	4.445572	-1.713496	0.254292
41	1	0	3.745792	-2.529966	0.385589
42	6	0	5.800694	-1.893585	0.528000
43	1	0	6.148619	-2.859021	0.884268
44	6	0	6.703167	-0.844183	0.348763
45	6	0	6.245280	0.390925	-0.112673
46	1	0	6.940728	1.213218	-0.254934
47	6	0	4.894228	0.580746	-0.399212
48	1	0	4.537825	1.540477	-0.753164
49	1	0	7.757689	-0.988233	0.566822

##

Compound 3a Ground State conformation d

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.93990894 A.U. after 1 cycles
Imaginary frequencies: 0 (12.8)

Zero-point correction= 0.394589 (Hartree/Particle)
Thermal correction to Energy= 0.418936
Thermal correction to Enthalpy= 0.419880
Thermal correction to Gibbs Free Energy= 0.338303
Sum of electronic and zero-point Energies= -1240.545320
Sum of electronic and thermal Energies= -1240.520973
Sum of electronic and thermal Enthalpies= -1240.520029
Sum of electronic and thermal Free Energies= -1240.601606

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.249755	0.336078	-1.928292
2	8	0	1.015043	0.245440	1.680507
3	8	0	3.300178	0.962145	-2.246732
4	7	0	-2.290540	-0.030867	0.132883
5	7	0	-2.295167	0.577446	1.398109
6	7	0	2.354689	0.324787	-0.217595
7	6	0	-3.061355	-1.209480	-0.055989
8	6	0	-3.768683	-1.741746	1.031779
9	1	0	-3.710639	-1.251257	1.994650

10	6	0	-4.533967	-2.892832	0.860143
11	1	0	-5.077297	-3.297218	1.710089
12	6	0	-4.605103	-3.523962	-0.382688
13	1	0	-5.203148	-4.421887	-0.510107
14	6	0	-3.897368	-2.987902	-1.458686
15	1	0	-3.941089	-3.467503	-2.432955
16	6	0	-3.125246	-1.836239	-1.310008
17	1	0	-2.575857	-1.426712	-2.146062
18	6	0	-1.471239	0.625895	-0.759036
19	6	0	-0.933677	1.861933	-0.007719
20	6	0	-1.524666	1.606770	1.368724
21	6	0	-1.582137	3.103644	-0.705704
22	1	0	-1.421653	2.978426	-1.782900
23	1	0	-2.666666	3.041013	-0.552334
24	6	0	-1.084613	4.488495	-0.276722
25	1	0	-1.642854	5.257616	-0.821459
26	1	0	-0.024120	4.637086	-0.506572
27	1	0	-1.226631	4.677959	0.791395
28	6	0	-1.304788	2.405970	2.612697
29	1	0	-1.850549	1.941106	3.437313
30	1	0	-1.646717	3.441745	2.506029
31	1	0	-0.239961	2.424607	2.870235
32	6	0	0.617163	1.944467	-0.040935
33	1	0	0.908031	2.807457	0.571769
34	6	0	1.264580	2.046872	-1.433267
35	1	0	0.585045	1.703309	-2.219303
36	1	0	1.616106	3.048080	-1.695455
37	6	0	2.440884	1.086023	-1.405236
38	6	0	1.303728	0.736353	0.608371
39	6	0	3.254485	-0.742164	0.107135
40	6	0	3.591415	-1.681788	-0.871830
41	1	0	3.177426	-1.596771	-1.869216
42	6	0	4.470724	-2.716235	-0.555840
43	1	0	4.733978	-3.443350	-1.318765
44	6	0	5.005451	-2.821612	0.729131
45	6	0	4.659987	-1.882080	1.701584
46	1	0	5.069844	-1.957745	2.704830
47	6	0	3.789086	-0.837291	1.395477
48	1	0	3.515242	-0.111157	2.151256
49	1	0	5.686949	-3.632225	0.971655

##

Compound 3a Ground State conformation e

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.93887705 A.U. after 1 cycles
Imaginary frequencies: 0 (14.4)

Zero-point correction= 0.394706 (Hartree/Particle)
Thermal correction to Energy= 0.418955
Thermal correction to Enthalpy= 0.419899
Thermal correction to Gibbs Free Energy= 0.338813
Sum of electronic and zero-point Energies= -1240.544171
Sum of electronic and thermal Energies= -1240.519922
Sum of electronic and thermal Enthalpies= -1240.518978
Sum of electronic and thermal Free Energies= -1240.600064

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	-1.379282	0.614380	-1.792372
2	8	0	1.134464	0.133841	1.742548
3	8	0	3.226122	1.171183	-2.216266
4	7	0	-2.284497	-0.033956	0.261189
5	7	0	-2.192192	0.375704	1.602742
6	7	0	2.385896	0.380048	-0.195350
7	6	0	-3.081746	-1.169519	-0.045198
8	6	0	-3.702238	-1.866732	1.001850
9	1	0	-3.558534	-1.532502	2.020988
10	6	0	-4.492754	-2.977891	0.718168
11	1	0	-4.967855	-3.510830	1.537561
12	6	0	-4.674738	-3.407339	-0.597288
13	1	0	-5.291825	-4.275199	-0.812235
14	6	0	-4.052734	-2.708843	-1.632216
15	1	0	-4.182829	-3.030622	-2.662115
16	6	0	-3.257648	-1.593187	-1.371628
17	1	0	-2.774488	-1.058367	-2.177046
18	6	0	-1.521936	0.748033	-0.581690
19	6	0	-0.915581	1.851080	0.305369
20	6	0	-1.398733	1.384163	1.669939
21	6	0	-1.638928	3.213313	0.017457
22	1	0	-2.694825	3.072076	0.280563
23	1	0	-1.243024	3.947855	0.731198
24	6	0	-1.563608	3.785574	-1.403376
25	1	0	-2.239810	4.644520	-1.476527
26	1	0	-1.866528	3.048754	-2.151856
27	1	0	-0.561096	4.139174	-1.658712
28	6	0	-1.106091	2.041793	2.978632
29	1	0	-1.679095	1.550804	3.768884
30	1	0	-1.367570	3.107144	2.962976
31	1	0	-0.040656	1.954718	3.216391
32	6	0	0.630706	1.956825	0.173243
33	1	0	0.945925	2.780767	0.829022
34	6	0	1.215622	2.159515	-1.237683
35	1	0	0.503330	1.862954	-2.012838
36	1	0	1.546016	3.179723	-1.445844
37	6	0	2.405132	1.221146	-1.329910
38	6	0	1.365873	0.712141	0.700379
39	6	0	3.319668	-0.686220	0.017390
40	6	0	3.634136	-1.547916	-1.037771
41	1	0	3.176054	-1.404942	-2.008856
42	6	0	4.549006	-2.579223	-0.831333
43	1	0	4.794903	-3.245538	-1.653279
44	6	0	5.141410	-2.758836	0.419589
45	6	0	4.818037	-1.897011	1.468659
46	1	0	5.272913	-2.030731	2.446099
47	6	0	3.911797	-0.855977	1.272490
48	1	0	3.655597	-0.190066	2.087563
49	1	0	5.850589	-3.566821	0.576290

##

Compound 3a Ground State conformation f

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.93447571 A.U. after 1 cycles
Imaginary frequencies: 0 (17.0)

Zero-point correction= 0.394339 (Hartree/Particle)
Thermal correction to Energy= 0.418816
Thermal correction to Enthalpy= 0.419760
Thermal correction to Gibbs Free Energy= 0.337813
Sum of electronic and zero-point Energies= -1240.540137

Sum of electronic and thermal Energies= -1240.515660
Sum of electronic and thermal Enthalpies= -1240.514716
Sum of electronic and thermal Free Energies= -1240.596662

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.313068	0.764837	-2.008910
2	8	0	2.348471	1.747864	0.266332
3	8	0	2.052907	-2.568518	-1.278664
4	7	0	-2.730790	0.207117	0.225968
5	7	0	-2.059377	0.350122	1.447839
6	7	0	2.524405	-0.447435	-0.442639
7	6	0	-3.989210	-0.454033	0.211782
8	6	0	-4.513725	-0.950877	1.413650
9	1	0	-3.954578	-0.823699	2.331543
10	6	0	-5.746645	-1.599479	1.411894
11	1	0	-6.144145	-1.980662	2.348770
12	6	0	-6.466362	-1.760603	0.227024
13	1	0	-7.427161	-2.267422	0.231836
14	6	0	-5.936625	-1.262473	-0.963494
15	1	0	-6.484570	-1.379320	-1.894683
16	6	0	-4.704452	-0.609801	-0.985498
17	1	0	-4.297502	-0.225841	-1.910617
18	6	0	-2.015788	0.746737	-0.825034
19	6	0	-0.734403	1.352780	-0.203556
20	6	0	-0.944274	0.967835	1.251962
21	6	0	-0.873569	2.886423	-0.483149
22	1	0	-1.054066	2.965972	-1.562681
23	1	0	-1.807839	3.205097	-0.001471
24	6	0	0.243340	3.853685	-0.082708
25	1	0	-0.075493	4.871352	-0.337364
26	1	0	1.179851	3.644983	-0.601222
27	1	0	0.458502	3.831061	0.988806
28	6	0	-0.059945	1.259649	2.424536
29	1	0	-0.508914	0.831959	3.324484
30	1	0	0.060426	2.339210	2.567932
31	1	0	0.947216	0.852572	2.295225
32	6	0	0.466739	0.654514	-0.913074
33	1	0	0.552012	1.129809	-1.899999
34	6	0	0.302828	-0.864887	-1.119876
35	1	0	-0.310698	-1.320764	-0.331626
36	1	0	-0.145846	-1.135848	-2.077129
37	6	0	1.697447	-1.447562	-0.996743
38	6	0	1.857487	0.776458	-0.269776
39	6	0	3.895177	-0.660695	-0.081985
40	6	0	4.258009	-1.825502	0.601113
41	1	0	3.506331	-2.565181	0.848848
42	6	0	5.593674	-2.033878	0.942148
43	1	0	5.873773	-2.942262	1.467897
44	6	0	6.562910	-1.084761	0.614385
45	6	0	6.191789	0.077317	-0.064007
46	1	0	6.939570	0.821463	-0.323114
47	6	0	4.861103	0.292381	-0.419061
48	1	0	4.572065	1.196029	-0.942209
49	1	0	7.601901	-1.249966	0.885339

##

Compound 3a Ground State conformation g

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.93112557 A.U. after 1 cycles
Imaginary frequencies: 0 (18.6)

Zero-point correction= 0.394471 (Hartree/Particle)
Thermal correction to Energy= 0.418808
Thermal correction to Enthalpy= 0.419752
Thermal correction to Gibbs Free Energy= 0.338266
Sum of electronic and zero-point Energies= -1240.536655
Sum of electronic and thermal Energies= -1240.512318
Sum of electronic and thermal Enthalpies= -1240.511374
Sum of electronic and thermal Free Energies= -1240.592859

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.990453	-1.132349	0.953385
2	8	0	-1.036548	-1.388657	-1.083968
3	8	0	-3.746039	2.256825	-0.374696
4	7	0	2.670735	0.158669	-0.037703
5	7	0	2.824257	1.501515	-0.396388
6	7	0	-2.636611	0.212349	-0.529451
7	6	0	3.812368	-0.686169	-0.043859
8	6	0	5.068425	-0.142169	-0.348518
9	1	0	5.152442	0.914477	-0.568022
10	6	0	6.190833	-0.967283	-0.369479
11	1	0	7.159561	-0.535546	-0.606999
12	6	0	6.079584	-2.330073	-0.089745
13	1	0	6.958458	-2.968382	-0.106669
14	6	0	4.825485	-2.862287	0.211251
15	1	0	4.721232	-3.921642	0.430090
16	6	0	3.688507	-2.055602	0.236186
17	1	0	2.719789	-2.471840	0.475505
18	6	0	1.387142	-0.115714	0.417176
19	6	0	0.575745	1.179571	0.180751
20	6	0	1.694416	2.105033	-0.267994
21	6	0	-0.118622	1.576367	1.505892
22	1	0	-0.725968	2.475193	1.350933
23	1	0	-0.804952	0.763520	1.768949
24	6	0	0.843641	1.813657	2.676811
25	1	0	0.281626	2.109878	3.568511
26	1	0	1.566590	2.608104	2.459126
27	1	0	1.401369	0.904932	2.923723
28	6	0	1.587015	3.563998	-0.583600
29	1	0	2.583646	3.965453	-0.783552
30	1	0	1.142390	4.122034	0.249593
31	1	0	0.960934	3.745056	-1.466110
32	6	0	-0.432277	0.991112	-1.019992
33	1	0	0.165795	0.831026	-1.921947
34	6	0	-1.441229	2.141898	-1.189302
35	1	0	-1.186921	3.077090	-0.689824
36	1	0	-1.597351	2.374977	-2.249610
37	6	0	-2.758304	1.608843	-0.638545
38	6	0	-1.346071	-0.239216	-0.882313
39	6	0	-3.725228	-0.654159	-0.183659
40	6	0	-4.552392	-0.318207	0.893255
41	1	0	-4.371607	0.592148	1.451318
42	6	0	-5.615667	-1.154463	1.229301
43	1	0	-6.258893	-0.889115	2.063621
44	6	0	-5.850740	-2.324374	0.505408
45	6	0	-5.017504	-2.654179	-0.564182
46	1	0	-5.191537	-3.563769	-1.132135

47	6	0	-3.956087	-1.821794	-0.918303
48	1	0	-3.304491	-2.081118	-1.742644
49	1	0	-6.677942	-2.975500	0.773925

##

Compound 3a Ground State conformation h

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.92748998 A.U. after 1 cycles
Imaginary frequencies: 0 (14.8)

Zero-point correction= 0.394606 (Hartree/Particle)
Thermal correction to Energy= 0.418873
Thermal correction to Enthalpy= 0.419818
Thermal correction to Gibbs Free Energy= 0.338318
Sum of electronic and zero-point Energies= -1240.532884
Sum of electronic and thermal Energies= -1240.508617
Sum of electronic and thermal Enthalpies= -1240.507672
Sum of electronic and thermal Free Energies= -1240.589172

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.194059	-0.968601	1.245216
2	8	0	-0.891580	-1.309580	-0.666222
3	8	0	-3.844063	2.211815	-0.528856
4	7	0	2.779569	0.222791	0.017908
5	7	0	2.918588	1.526258	-0.464368
6	7	0	-2.621492	0.231163	-0.466268
7	6	0	3.901458	-0.647229	-0.036045
8	6	0	5.123475	-0.159332	-0.522039
9	1	0	5.196131	0.872383	-0.841198
10	6	0	6.226768	-1.006936	-0.592892
11	1	0	7.168299	-0.617751	-0.971530
12	6	0	6.131169	-2.337983	-0.184492
13	1	0	6.995116	-2.994166	-0.240924
14	6	0	4.911545	-2.814816	0.296522
15	1	0	4.819047	-3.849027	0.617318
16	6	0	3.793788	-1.984840	0.374709
17	1	0	2.852850	-2.359080	0.752660
18	6	0	1.536547	0.007001	0.604986
19	6	0	0.726572	1.304329	0.352127
20	6	0	1.815007	2.160911	-0.280607
21	6	0	0.269253	1.896778	1.715726
22	1	0	1.172845	2.006045	2.329347
23	1	0	-0.097018	2.917612	1.552504
24	6	0	-0.771221	1.092367	2.503862
25	1	0	-0.933928	1.565069	3.478639
26	1	0	-0.435323	0.066252	2.665945
27	1	0	-1.739223	1.057399	1.994785
28	6	0	1.693564	3.593534	-0.694486
29	1	0	2.651508	3.937938	-1.091783
30	1	0	1.415525	4.232505	0.152909
31	1	0	0.927423	3.732284	-1.467165
32	6	0	-0.400635	1.094991	-0.732563
33	1	0	0.126902	0.945868	-1.681586
34	6	0	-1.424485	2.238937	-0.860215
35	1	0	-1.279023	3.066546	-0.163410
36	1	0	-1.442337	2.672841	-1.865762
37	6	0	-2.790856	1.618553	-0.596403

38	6	0	-1.273796	-0.166629	-0.592177
39	6	0	-3.709075	-0.685252	-0.282812
40	6	0	-4.710798	-0.386754	0.646693
41	1	0	-4.666290	0.534774	1.214076
42	6	0	-5.771382	-1.274200	0.822017
43	1	0	-6.550041	-1.037812	1.541758
44	6	0	-5.832190	-2.457315	0.084222
45	6	0	-4.826592	-2.748838	-0.838301
46	1	0	-4.864909	-3.667918	-1.416221
47	6	0	-3.765106	-1.865415	-1.031010
48	1	0	-2.981218	-2.095460	-1.741136
49	1	0	-6.658374	-3.148020	0.227826

##

Compound 3a Ground State conformation i

Method: B3LYP/6-31G(d) opt freq
SCF Done: E(RB3LYP) = -1240.92608683 A.U. after 1 cycles
Imaginary frequencies: 0 (13.8)

Zero-point correction= 0.394504 (Hartree/Particle)
Thermal correction to Energy= 0.418874
Thermal correction to Enthalpy= 0.419819
Thermal correction to Gibbs Free Energy= 0.338226
Sum of electronic and zero-point Energies= -1240.531583
Sum of electronic and thermal Energies= -1240.507212
Sum of electronic and thermal Enthalpies= -1240.506268
Sum of electronic and thermal Free Energies= -1240.587861

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.495388	-1.439468	0.975140
2	8	0	-1.506864	-1.074703	1.137924
3	8	0	-3.400515	1.666198	-2.029958
4	7	0	2.945022	0.145442	0.066213
5	7	0	2.900336	1.504735	-0.240492
6	7	0	-2.740350	0.088142	-0.447614
7	6	0	4.153112	-0.566689	-0.164801
8	6	0	5.246650	0.108880	-0.726752
9	1	0	5.154745	1.159025	-0.972015
10	6	0	6.436343	-0.576793	-0.960972
11	1	0	7.276699	-0.042570	-1.396462
12	6	0	6.553951	-1.930816	-0.643627
13	1	0	7.484133	-2.460519	-0.828780
14	6	0	5.461460	-2.594577	-0.085380
15	1	0	5.535946	-3.648695	0.168390
16	6	0	4.260827	-1.928219	0.158482
17	1	0	3.417880	-2.447358	0.592328
18	6	0	1.746450	-0.311961	0.595186
19	6	0	0.784262	0.907935	0.591124
20	6	0	1.726294	1.965999	0.020424
21	6	0	0.385855	1.188838	2.072493
22	1	0	0.098044	0.224531	2.500401
23	1	0	1.293034	1.510773	2.599856
24	6	0	-0.734947	2.204010	2.326247
25	1	0	-0.892768	2.302786	3.405709
26	1	0	-1.689582	1.881906	1.897168
27	1	0	-0.508154	3.202753	1.938901
28	6	0	1.494240	3.436586	-0.162473

29	1	0	2.418710	3.891485	-0.527259
30	1	0	1.223940	3.917924	0.784556
31	1	0	0.695771	3.656182	-0.877600
32	6	0	-0.409451	0.565483	-0.364744
33	1	0	-0.008907	-0.092863	-1.148510
34	6	0	-1.148119	1.711253	-1.078484
35	1	0	-1.228059	2.607285	-0.454841
36	1	0	-0.709475	2.007172	-2.033994
37	6	0	-2.562178	1.193063	-1.295350
38	6	0	-1.559637	-0.254485	0.253509
39	6	0	-3.983727	-0.605332	-0.284660
40	6	0	-5.179350	0.115969	-0.206739
41	1	0	-5.166324	1.196607	-0.276504
42	6	0	-6.385540	-0.567606	-0.059866
43	1	0	-7.313127	-0.004738	-0.005478
44	6	0	-6.403864	-1.960731	0.019638
45	6	0	-5.205630	-2.672865	-0.053460
46	1	0	-5.209361	-3.757374	0.008784
47	6	0	-3.994010	-2.002060	-0.210323
48	1	0	-3.064106	-2.555600	-0.260826
49	1	0	-7.346109	-2.488463	0.137763