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Supporting Information

Reaction Control in the Organocatalytic Asymmetric One Pot, Three-component Reaction of Aldehydes, Diethyl α-Aminomalonate and Nitroalkenes: toward Diversity-oriented Synthesis

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Table of Contents

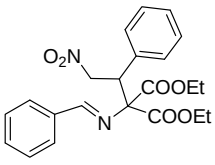
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. Optical rotations were measured at 589 nm at 20 °C. TLC was performed on glass-backed silica plates. Enantiomeric excess was determined by HPLC analysis on Chiralpak or Chiralcel OD, AD or IC columns. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). The chiral thiourea or urea catalysts were prepared according to the literature procedures.[1]

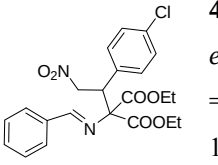
[1] a) B.-J. Li, L. Jiang, M. Liu, Y.-C. Chen, L.-S. Ding, Y. Wu, *Synlett* **2005**, 603; b) Y. Zhang, Y.-K. Liu, T.-R. Kang, Z.-K. Hu, Y.-C. Chen, *J. Am. Chem. Soc*. **2008**, *130*, 2456; c) M. S. Taylor, E. N. Jacobsen, *J. Am. Chem. Soc*. **2004**, *126*, 10558.

2. General procedure for the one pot, three-component Michael addition

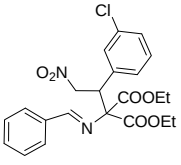
To a stirred mixture of aldehyde **6** (0.1 mmol) and 4 Å MS (80 mg) in toluene (0.8 mL) was added diethyl α-aminomalonate **7** (18.0 mg, 0.1 mmol,) at 0 °C. The mixture was stirred for 2 h and then nitroalkenes **3** (0.12 mmol) and catalyst **1b** (4.0 mg, 0.01 mmol) were added. After the stated reaction time, product **4** was isolated by FC on silica gel eluted with EtOAc/petroleum ether. The enantiomeric excess was determined by HPLC analysis on chiral column.



4a 93% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +199.0 (*c* = 0.99 in $CHCl_3$); 96% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.51 min, t (major) = 8.45 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 7.87-7.85 (m, 2H), 7.54-7.47 (m, 3H), 7.41-7.39 (m, 2H), 7.26-7.23 (m, 3H), 5.33 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.16 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.58 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.36-4.22 (m, 2H), 4.06-3.81 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 167.3, 166.7, 131.9, 129.5, 129.2, 128.8, 128.6, 128.3, 128.2, 127.1, 78.7, 77.2, 62.7, 62.0, 48.8, 13.9, 13.7 ppm; ESI-HRMS: calcd. for $C_{22}H_{24}N_2O_6$+H 413.1713, found 413.1709.

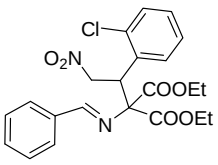


4b 87% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +116.7 (*c* = 1.83 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.60 min, t (major) = 10.60 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.86-7.83 (m, 2H), 7.58-7.48 (m, 2H), 7.43-7.21 (m, 5H), 5.31 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.10 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.56 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.38-4.22 (m, 2H), 4.09-4.00 (m, 1H), 3.97-3.87 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 167.1, 166.5, 135.8, 134.7, 134.3, 132.1, 130.8, 128.81, 128.77, 128.6, 78.5, 77.0, 62.9, 62.2, 48.2, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+Na 469.1142, found 469.1144.

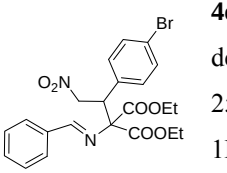


4c 93% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +95.5 (*c* = 0.61 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.87 min, t (major) = 8.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H),

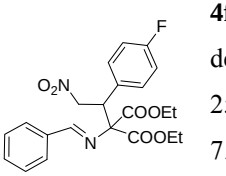
7.87-7.83 (m, 2H), 7.56-7.48 (m, 3H), 7.41-7.29 (m, 3H), 7.24-7.17 (m, 1H), 5.30 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.11 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.55 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.36-4.22 (m, 2H), 4.07-3.91 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4, 167.1, 166.5, 138.3, 135.8, 134.0, 132.1, 130.1, 129.7, 128.9, 128.8, 128.5, 127.4, 78.3, 77.0, 62.9, 62.3, 48.4, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+Na 469.1142, found 469.1145.



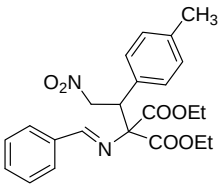
4d 80% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +110.2 (*c* = 1.80 in $CHCl_3$); 94% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.90 min, t (major) = 8.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 7.87-7.84 (m, 2H), 7.71-7.69 (m, 1H), 7.54-7.48 (m, 3H), 7.35-7.32 (m, 1H),7.20-7.15 (m, 2H), 5.35 (dd, *J* = 22.8, 3.6 Hz, 2H), 5.13 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.37-4.25 (m, 2H), 4.12-4.04 (m, 1H), 3.94-3.86 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3, 167.1, 166.6, 135.8, 135.3, 134.6, 132.0, 129.6, 129.5, 129.2, 128.8, 127.2, 78.7, 77.1, 62.9, 62.3, 43.2, 13.9, 13.6 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+Na 469.1142, found 469.1133.



4e 84% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +89.8 (*c* = 6.40 in $CHCl_3$); 96% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.97 min, t (major) = 11.71 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1H), 7.85-7.83 (m, 2H), 7.56-7.48 (m, 3H), 7.39-7.37 (m, 2H), 7.31-7.29 (m, 2H), 5.30 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.10 (dd, *J* = 13.6, 10.4 Hz, 1H), 4.54 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.36-4.22 (m, 2H), 4.09-4.01 (m, 1H), 3.97-3.89 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 167.1, 166.5, 135.8, 135.2, 132.1, 131.6, 131.2, 128.82, 128.7, 122.5, 78.4, 77.0, 62.9, 62.2, 48.2, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}BrN_2O_6$+Na 513.0637, found 513.0632.

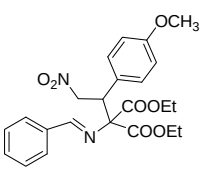


4f 83% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +57.1 (*c* = 0.61 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.29 min, t (major) = 8.92 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.86-7.8-7. 4 (m, 2H), 7.5648 (m, 3H), 7.42-7.38 (m, 2H), 6.97-6.92 (m, 2H), 5.31 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.10 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.57 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.37-4.22 (m, 2H), 4.08-4.00 (m, 1H), 3.96-3.88 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4, 167.2, 166.6, 164.2, 160.9, 135.8, 132.1, 131.3, 131.1, 128.82, 128.77, 127.0, 115.5, 115.2, 78.7, 77.0, 62.8, 62.2, 48.1, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}FN_2O_6$+Na 453.1438, found 453.1432.

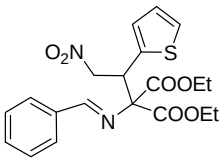


4g 95% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +124.4 (*c* = 1.39 in $CHCl_3$); 96% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.13 min, t (major) = 7.10 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.87-7.84 (m, 2H), 7.55-7.44 (m, 3H), 7.28-7.26 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.31 (dd, *J* =13.6, 3.6 Hz, 1H), 5.13 (dd, *J* = 13.6, 10.4 Hz, 1H), 4.54 (dd, *J* = 10.4, 3.6 Hz,

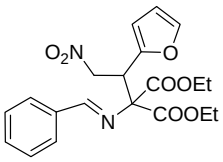
1H), 4.36-4.21 (m, 2H), 4.08-3.87 (m, 2H), 2.26 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 167.4, 166.7, 137.9, 136.0, 133.0, 131.9, 129.3, 129.1, 128.8, 78.7, 77.3, 62.6, 62.0, 48.5, 21.0, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{23}H_{26}N_2O_6$+Na 449.1689, found 449.1683.



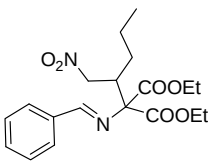
4h 83% yield; R_f = 0.4 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +130.1 (*c* = 1.43 in $CHCl_3$); 95% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 7.00 min, t (major) = 10.13 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.87-7.84 (m, 2H), 7.53-7.48 (m, 3H), 7.33-7.31 (m, 2H), 6.78-6.76 (m, 2H), 5.29 (dd, *J* =13.2, 3.6 Hz, 1H), 5.11 (dd, *J* = 12.8, 10.4 Hz, 1H), 4.53 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.36-4.21 (m, 2H), 4.08-3.88 (m, 2H), 3.74 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 167.4, 166.7, 159.3, 135.9, 131.9, 130.5, 128.7, 127.9, 113.7, 78.8, 77.2, 62.7, 62.0, 55.0, 48.1, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{23}H_{26}N_2O_7$+Na 465.1638, found 465.1632.



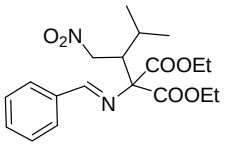
4i 90% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +93.86 (*c* = 0.23 in $CHCl_3$); 96% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.03 min, t (major) = 9.85 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7. 89 (d, *J* = 6.8 Hz, 2H), 7.55-7.48 (m, 3H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.89-6.87 (m, 1H), 5.27 (dd, *J* = 12.8, 3.2 Hz, 1H), 5.07-4.95 (m, 2H), 4.36-4.25 (m, 2H), 4.14-4.03 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 167.0, 166.4, 137.6, 135.8, 132.0, 128.9, 128.7, 128.3, 126.6, 126.0, 79.3, 76.8, 62.8, 62.3, 45.3, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{20}H_{22}N_2O_6S$+Na 441.1096, found 441.1092.



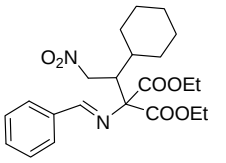
4j 89% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +99.7 (*c* = 0.65 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.77 min, t (major) = 8.22 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.80-7.78 (m, 2H), 7.51-7.43 (m, 3H), 7.31-7.30 (m, 1H), 6.32 (d, *J* = 3.6 Hz, 1H), 6.27 (m, 1H), 5.18 (dd, *J* = 13.6, 3.6 Hz, 1H), 5.07 (dd, *J* = 13.6, 10.0 Hz, 1H), 4.81 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.32-4.18 (m, 2H), 4.17-4.09 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 167.1, 166.7, 149.7, 142.3, 135.8, 131.9, 128.8, 128.7, 110.6, 109.5, 76.6, 76.0, 62.7, 62.3, 43.5, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{20}H_{22}N_2O_7$+Na 425.1325, found 425.1319.



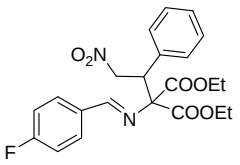
4k 56% yield; R_f = 0.4 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +27.4 (*c* = 1.00 in $CHCl_3$); 97% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.61 min, t (major) = 6.66 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.77-7.74 (m, 2H), 7.50-7.41 (m, 3H), 4.92 (dd, *J* = 14.4, 4.8 Hz, 1H), 4.42 (dd, *J* = 14.4, 5.6 Hz, 1H), 4.31-4.23 (m, 4H), 3.43-3.37 (m, 1H), 1.63-1.54 (m, 2H), 1.52-1.35 (m, 2H), 1.33-1.22 (m, 6H), (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 166.5, 135.8, 131.8, 128.8, 128.7, 78.2, 77.0, 62.4, 62.2, 43.0, 32.4, 20.4, 14.0, 13.9 ppm; ESI-HRMS: calcd. for $C_{19}H_{26}N_2O_6$+Na 401.1689, found 401.1683.



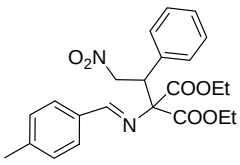
4l 60% yield; R_f= 0.7 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +28.0 (*c* = 1.15 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 4.76 min, t (major) = 5.42 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 7.76-7.75 (m, 2H), 7.50-7.42 (m, 3H), 4.90 (dd, *J* = 15.2, 4.0 Hz, 1H), 4.54 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.36-4.18 (m, 4H), 3.55-3.52 (m, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.1, 167.9, 166.6, 136.0, 131.7, 128.7, 78.3, 73.5, 62.5, 62.1, 46.7, 28.9, 22.5, 17.5, 14.0, 13.8 ppm; ESI-HRMS: calcd. for $C_{19}H_{26}N_2O_6$+H 379.1869, found 379.1760.



4m 48% yield; R_f= 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +27.9 (*c* = 1.36 in $CHCl_3$); 98% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 4.54 min, t (major) = 4.95 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 7.76-7.73 (m, 2H), 7.50-7.42 (m, 3H), 4.88 (dd, *J* = 14.8, 4.0 Hz, 1H), 4.61 (dd, *J* = 14.8, 6.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.26-4.18 (m, 2H), 349-3.46 (m, 1H), 1.78-1.58 (m, 10 H), 1.34-1.24 (m, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.1, 166.3, 136.0, 131.7, 128.7, 78.3, 74.3, 62.4, 62.1, 47.2, 39.6, 32.7, 28.1, 27.0, 26.5, 26.1, 14.0, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{30}N_2O_6$+H 419.2182, found 419.2183.

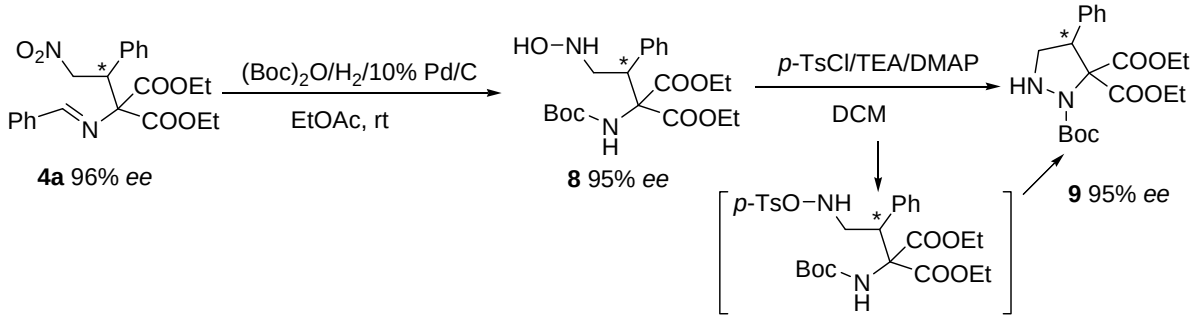


4n 93% yield; R_f= 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +153.1 (*c* = 1.38 in $CHCl_3$); 96% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.71 min, t (major) = 11.87 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.88-7.84 (m, 2H), 7.39-7.37 (m, 2H), 7.26-7.22 (m, 3H), 7.20-7.16 (m, 2H), 5.31 (dd, *J* =13.2, 3.6 Hz, 1H), 5.13 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.58 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.36-4.22 (m, 2H), 4.06-3.86 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 167.3, 166.8, 162.6, 136.1, 132.3, 130.9, 130.7, 129.4, 128.4, 128.3, 116.2, 115.8, 78.6, 62.8, 62.1, 48.7, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}FN_2O_6$+H 431.1618, found 431.1606.



4o 86% yield; R_f= 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +168.6 (*c* = 1.15 in $CHCl_3$); 97% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.69 min, t (major) = 8.87 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.41-7.39 (m, 2H), 7.32-7.16 (m, 5H), 5.32 (dd, *J* = 13.2, 3.2 Hz, 1H), 5.15 (dd, *J* = 13.2, 10.4 Hz, 1H), 4.56 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.33-4.22 (m, 2H), 4.03- 3.96 (m, 1H), 3.91- 3.87 (m, 1H), 2.44 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 167.5, 166.8, 142.5, 136.2, 133.5, 129.5, 128.8, 128.3, 128.2, 127.0, 78.8, 62.6, 62.0, 48.8, 30.0, 21.6, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{23}H_{26}N_2O_6$+H 427.1869, found 427.1856.

Transformations of the Michael addition product 4a



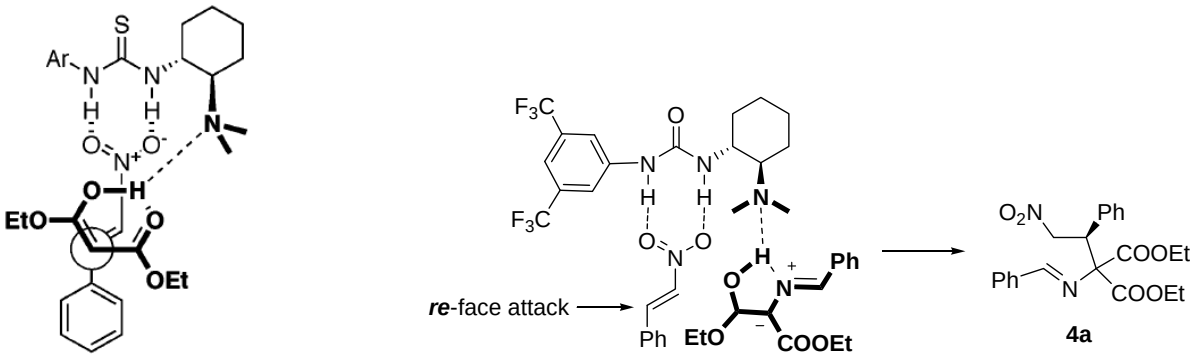
4a 96% *ee* **8** 95% *ee* **9** 95% *ee*

To a solution of compound **4a** (98 mg, 0.24 mmol) and $(Boc)_2O$ (63 mg, 0.29 mmol) in ethyl acetate (3 mL) was added 10% Pd/C (10 mg, 10%). The resulting suspension was hydrogenated at atmospheres for 12 h. The catalyst was filtered, washed with ethyl acetate (5 mL) and the filtrate was concentrated. Flash chromatography of the residue on silica gel with EtOAc/petroleum ether (1:10) as eluents yielded compound **8** (86 mg, 89%) as a colorless oil. *The hydroxylamine structure was obtained and could not be easily converted to the corresponding amine compound.* $[\alpha]_D^{20}$ = +86.0 (*c* = 1.12 in $CHCl_3$); 95% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t (major) = 12.14 min, t (minor) = 14.54 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.42 (m, 2H), 7.30-7.22 (m, 3H), 4.28 (dd, *J* = 14.4, 8.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.10 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.03-3.93 (m, 2H), 3.66 (dd, *J* = 14.8, 5.6 Hz, 1H), 31.43 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.4, 169.5, 155.6, 137.1, 129.6, 128.3, 127.8, 81.5, 68.5, 62.8, 62.4, 51.5, 47.8, 29.7, 28.2, 13.9, 13.8 ppm; ESI-HRMS: calcd. for $C_{20}H_{30}N_2O_7$+H 411.2131, found 411.2183.

To a solution of compound **8** (72 mg, 0.18 mmol) in DCM was added TEA (50 μL, 0.36 mmol), DMAP (3 mg, 0.018 mmol) and TsCl (41 mg, 0.22 mmol) at rt. 2 h later the solution was refluxed for 24 h. The solution was washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to yield compound **9** (64 mg, 90%) as a colorless oil (*The similar amination reactions have been well studied*).[2] $[\alpha]_D^{20}$ = +79.8 (*c* = 0.93 in $CHCl_3$); 95% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t (minor) = 19.61 min, t (major) = 31.74 min]; ^{1}H NMR (400 MHz, $CDCl_3$): 7.33-7.30 (m, 3H), 7.29-7.19 (m, 2H), 4.40 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.33-4.22 (m, 3H), 3.88 (m, 1H), 3.67-3.59 (m, 2H), 1.49 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.8, 166.3, 155.7, 137.5, 128.4, 128.1, 127.7, 80.8, 62.3, 62.0, 53.9, 51.0, 29.6, 28.2, 13.8, 13.4 ppm; ESI-HRMS: calcd. for $C_{20}H_{28}N_2O_6$+Na 415.1845, found 415.1847.

[2] For a spotlight, see: E. Bodio, *Synlett* **2008**, 1744.

Since we have not been able to obtain some crystals suitable for X-ray analysis from the Michael addition products or their derivatives to determine their absolute configuration despite a great deal of efforts, we proposed a plausible catalytic mechanism based on the concerted activation mode by Takemoto et al.[3] As illustrated in the following scheme, the chiral Michael adduct **4a** with *R*-configuration might be obtained.

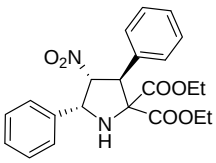


Catalytic mode observed by Takemoto **Proposed catalytic mode in this Michael addition**

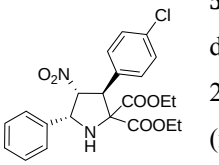
[3] T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, *J. Am. Chem. Soc.* **2005**, *127*, 119.

3. General procedure for the one pot, three-component [3 + 2] cycloaddition

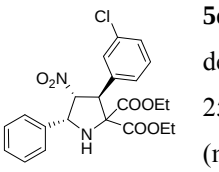
To a stirred mixture of aldehyde **6** (0.1 mmol) and 4 Å MS (80 mg) in MTBE (0.8 mL) was added diethyl α-aminomalonate **7** (18 mg, 0.1 mmol) at 0 °C. The mixture was stirred for 2 h and cooled to −20°C. Then nitroalkene **3** (0.12 mmol) and catalyst **1l** (12.4 mg, 0.02 mmol) were added. After 72 h, product **5** was isolated by FC on silica gel eluted with EtOAc/petroleum ether. The enantiomeric excess was determined by HPLC analysis on chiral column.



5b 73% yield; R_f = 0.4 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +96.1 (*c* = 0.81 in $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 9.31 min, t (minor) = 12.28 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43-7.29 (m, 10H), 5.63-5.49 (m, 2H), 5.15 (d, *J* = 8.8 Hz, 1H), 4.43-4.25 (m, 2H), 3.94-3.84 (m, 1H), 3.59-3.48 (m, 1H), 3.24 (d, *J* = 6.6 Hz, 1H), 1.30 (t, *J* = 9.5 Hz, 3H), 0.79 (t, *J* = 9.5 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0, 168.5, 136.6, 135.1, 128.7, 128.6, 128.4, 128.2, 127.1, 93.7, 76.0, 64.6, 62.1, 62.0, 52.0, 13.9, 13.3 ppm; ESI-HRMS: calcd. for $C_{22}H_{24}N_2O_6$+H 413.1713, found 413.1709.

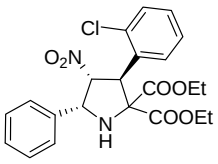


5c 79% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +28.3 (*c* = 0.76 in $CHCl_3$); 89% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 9.99 min, t (minor) = 14.37 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.28 (m, 9H), 5.59 (t, *J* = 8.0 Hz, 1H), 5.49 (dd, *J* = 8.4, 5.6 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.42-4.25 (m, 2H), 4.00-3.92 (m, 1H), 3.67-3.59 (m, 1H), 3.23 (d, *J* = 5.6 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0, 168.4, 136.6, 134.3, 133.4, 130.0, 128.9, 128.8, 128.5, 127.2, 93.1, 75.7, 64.1, 62.3, 62.2, 51.2, 14.0, 13.4 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+Na 447.1323, found 447.1315.

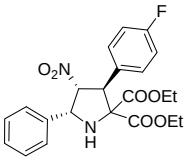


5d 79% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +30.0 (*c* = 0.76 in $CHCl_3$); 90% *ee*, determined by HPLC analysis [Daicel chiralcel OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 8.69 min, t (minor) = 12.23 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.25 (m, 9H), 5.59 (t, *J* = 8.0 Hz, 1 H), 5.50 (dd, *J* = 8.0, 5.6 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.42-4.26 (m, 2H), 4.00-3.92 (m, 1H), 3.71-3.63 (m, 1H), 3.23 (d, *J* = 5.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J*

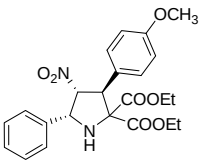
= 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.9, 168.3, 136.9, 136.5, 134.5, 129.9, 128.9, 128.8, 128.5, 127.2, 126.9, 93.1, 75.7, 64.2, 62.3, 62.2, 51.4, 14.0, 13.4 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+H 447.1323, found 447.1315.



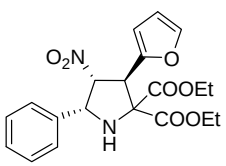
5e 69% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +16.8 (*c* = 0.84 in $CHCl_3$); 84% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 20.09 min, t (minor) = 27.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.32 (m, 7H), 7.27-7.25 (m, 2H), 5.71 (d, *J* = 4.8 Hz, 1H), 5.55 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.46 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.39-4.28 (m, 2H), 4.02-3.94 (m, H), 3.75-3.67 (m, 1H), 3.34 (d, *J* = 4.8 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.4, 168.1, 135.9, 135.3, 133.9, 130.2,129.4, 129.0, 128.5, 127.1, 95.1, 75.9, 65.6, 62.4, 62.2, 50.0, 14.0, 13.3 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+H 447.1323, found 447.1310.



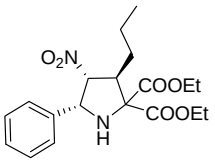
5f 73% yield; R_f = 0.4 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +38.2 (*c* = 1.44 in $CHCl_3$); 86% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 220 nm, t (major) = 7.11 min, t (minor) = 9.76 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.31 (m, 7H), 7.06-7.00 (m, 2H), 5.59 (t, *J* = 7.6 Hz, 1H), 5.49 (dd, *J* = 8.0, 5.2 Hz, 1H), 5.11 (d, *J* = 7.6 Hz, 1H), 4.42-4.25 (m, 2H), 4.00-3.92 (m, 1H), 3.66-3.57 (m, 1H), 3.22 (d, *J* = 5.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 168.5, 165.0, 160.1, 136.6, 130.7, 130.6, 130.4, 130.3, 128.9, 128.5, 127.2, 115.8, 115.3, 93.4, 75.7, 64.1, 62.2, 62.1, 51.1, 14.0, 13.4 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}FN_2O_6$+H 431.1618, found 431.1613.



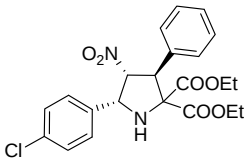
5g 75% yield; R_f = 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +38.1 (*c* = 1.53 in $CHCl_3$); 91% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 10.65 min, t (major) = 16.04 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.24 (m, 7H), 6.87-6.83 (m, 2H), 5.58 (t, *J* = 8.0 Hz, 1H), 5.49 (dd, *J* = 7.6, 3.6 Hz, 1H), 5.07 (d, *J* = 6.8 Hz, 1H), 4.41-4.25 (m, 2H), 3.98-3.90 (m, 1H), 3.78 (s, 3H), 3.65-3.57 (m, 1H), 3.21 (s, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.3, 168.6, 159.5, 136.7, 129.7, 128.8, 128.4, 127.2, 126.9, 114.0, 93.8, 75.8, 64.2, 62.1, 62.0, 55.3, 51.4, 14.0, 13.6 ppm; ESI-HRMS: calcd. for $C_{23}H_{26}N_2O_7$+H 443.1818, found 443.1809.



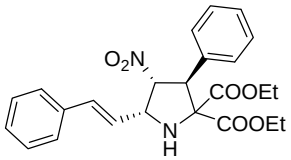
5h 77% yield; R_f = 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +24.0 (*c* = 1.38 in $CHCl_3$); 91% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 12.99 min, t (major) = 16.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.38 (m, 2H), 7.36-7.30 (m, 4H), 6.40 (d, *J* = 3.6 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.60 (dd, *J* = 8.4, 7.2 Hz, 1H), 5.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 5.22 (d, *J* = 6.8 Hz, 1H), 4.42-4.26 (m, 2H), 4.12-4.04 (m, 1H), 3.88-3.80 (m, 1H), 3.22 (d, *J* = 4.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.6, 168.1, 148.0, 142.6, 136.4, 128.8, 128.4, 127.3, 110.9, 110.0, 91.3, 74.1, 63.9, 62.6, 62.3, 48.3, 14.0, 13.6 ppm; ESI-HRMS: calcd. for $C_{20}H_{22}N_2O_7$+H 403.1505, found 403.1489.



5i 62% yield; R_f= 0.6 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +36.2 (*c* = 0.80 in $CHCl_3$); 60% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 220 nm, t (minor) = 8.30 min, t (major) = 13.47 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 5H), 5.29 (dd, *J* = 8.4, 5.2 Hz, 1H), 5.05 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.39-4.24 (m, 4H), 3.73-3.68 (m, 1H), 3. 00 (d, *J* = 5.6 Hz, 1H), 1.83-1.78 (m, 1H), 1.41-1.24 (m, 10H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 168.7, 136.5, 128.6, 128.2, 127.3, 94.5, 74.1, 63.7, 62.0, 48.1, 32.1, 21.0, 14.1, 14.0, 13.8 ppm; ESI-HRMS: calcd. for $C_{19}H_{26}N_2O_6$+H 379.1869, found 379.1867.

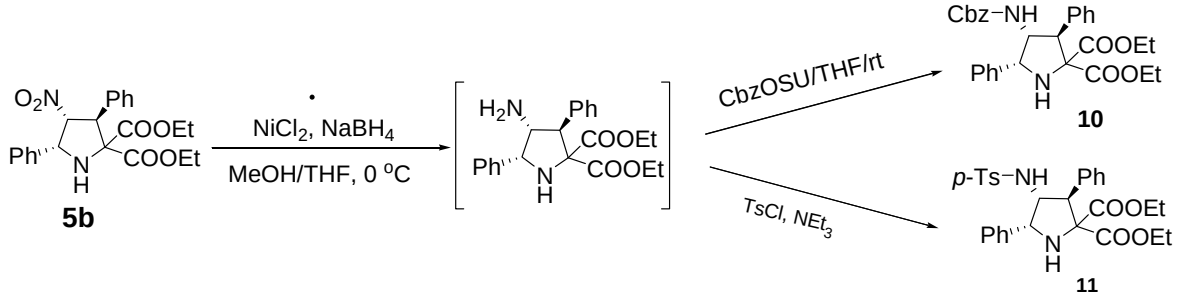


5j 90% yield; R_f= 0.5 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +25.9 (*c* = 0.91 in $CHCl_3$); 86% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 8.46 min, t (major) = 11.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.28 (m, 9H), 5.59 (t, *J* = 8.0 Hz, 1H), 5.48 (dd, *J* = 8.0, 5.2 Hz, 1H), 5.13 (d, *J* = 7.2 Hz, 1H), 4.42-4.25 (m, 2H), 3.94-3.86 (m, 1H), 3.57-3.50 (m, 1H), 3.21 (d, *J* = 5.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 168.4, 135.2, 134.9, 134.6, 128.7, 128.6, 128.3, 93.6, 75.8, 63.7, 62.2, 62.0, 51.9, 14.0, 13.3 ppm; ESI-HRMS: calcd. for $C_{22}H_{23}ClN_2O_6$+H 447.1323, found 447.1313.



5k 90% yield; R_f = 0.4 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{20}$ = +32.9 (*c* = 1.10 in $CHCl_3$); 86% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 9.50 min, t (major) = 13.76 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 10H), 6.76 (d, *J* = 15.2 Hz, 1 H), 6.03 (q, *J* = 7.2 Hz, 1H), 5.50 (t, *J* = 7.2 Hz, 1H), 5.12 (d, *J* = 4.0 Hz, 1H), 4.94 (td, *J* = 7.2, 0.8 Hz, 1H), 4.40-4.22 (m, 2H), 3.89-3.81 (m, 1H), 3.53-3.45 (m, 1H), 2.81 (bs, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 168.9, 135.9, 135.2, 135.1, 128.7, 128.6, 128.5, 128.3, 128.2, 126.8, 123.8, 92.7, 76.1, 62.7, 62.3, 62.0, 52.3, 13.9, 13.3 ppm; ESI-HRMS: calcd. for $C_{24}H_{26}N_2O_6$+H 439.1869, found 439.1858.

Transformations of the [3 + 2] cycloaddition product 5b

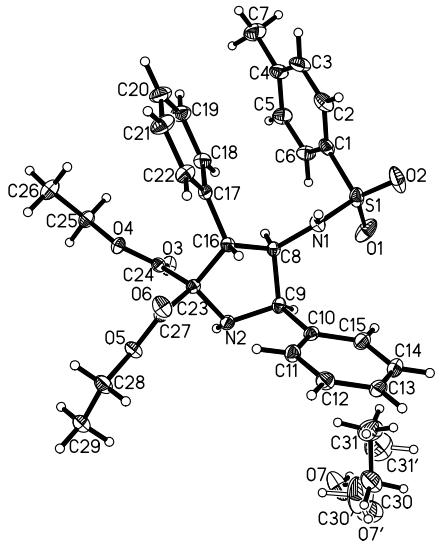


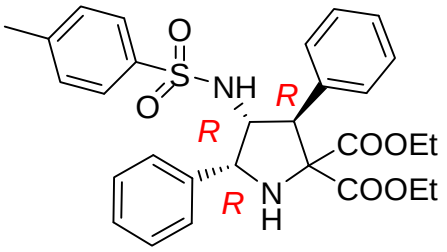
A 25 mL round-bottom flask containing $NiCl_2 \cdot 6H_2O$ (94 mg, 0.4 mmol), CH_3OH (1 mL), THF (0.5 mL) and compound **5b** (42 mg, 0.1 mmol, 99% *ee* after recrystallization) was sonicated to effect complete solution. Then solid $NaBH_4$ (30 mg, 0.8 mmol) was added (***CAUTION: frothing***) at 0 ℃ over 15 min. After completion monitored by TLC, the reaction mixture was diluted with H_2O (10 mL) and EtOAc (5 mL), filtered through Celite. The solid was thoroughly washed with EtOAC (10 mL). The organic layer was separated, dried over Na_2SO_4, and removed under reduced pressure to give the crude amine product, which can be used without purification.

The residue was dissolved in dry THF (1.0 mL), and to this solution was added CbzOSU (30 mg, 0.12 mmol) at room temperature. The resulting mixture was stirred overnight. After concentration, the residue was purified by column chromatography to give compound **10** as a white solid **(**43 mg, 84% yield for two steps**)**. R_f= 0.5 (petroleum ether/EtOAc = 4:1); $[\alpha]_D^{20}$= +57.9 (*c* = 2.55 in $CHCl_3$); 99% *ee*, determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 220 nm, t (minor) = 15.42 min, t (major) = 20.51 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.24 (m, 13H), 7.13-7.11 (m, 2H), 5.08 (t, *J* = 6.4 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.91-4.81 (m, 2H), 4.59 (d, *J* = 9.6 Hz, 1H), 4.37-4.18 (m, 2H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.92-3.84 (m, 1H), 3.58-3.50 (m, 1H), 3.37 (d, *J* = 5.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.2, 170.4, 155.6, 139.8, 136.5, 128.8, 128.3, 128.2, 127.9, 127.7, 127.5, 75.1, 66.4, 62.4, 61.9, 61.7, 58.1, 53.5, 14.0, 13.3 ppm; ESI-HRMS: calcd. for $C_{30}H_{32}N_2O_6$+H 517.2339, found 517.2386.

Compound **11** was prepared in a similar procedure as **10**. Crystals of **11** suitable for X-ray analysis were fortunately obtained from its ethanol solution, incorporating an ethanol molecule in the crystals. Therefore, the absolute structure of the corresponding dipolar cycloaddition product **5b** could be determined as (*3R*, *4R*, *5R*), in *endo*-selectivity.

Crystal data and structure refinement for enantiopoure 11



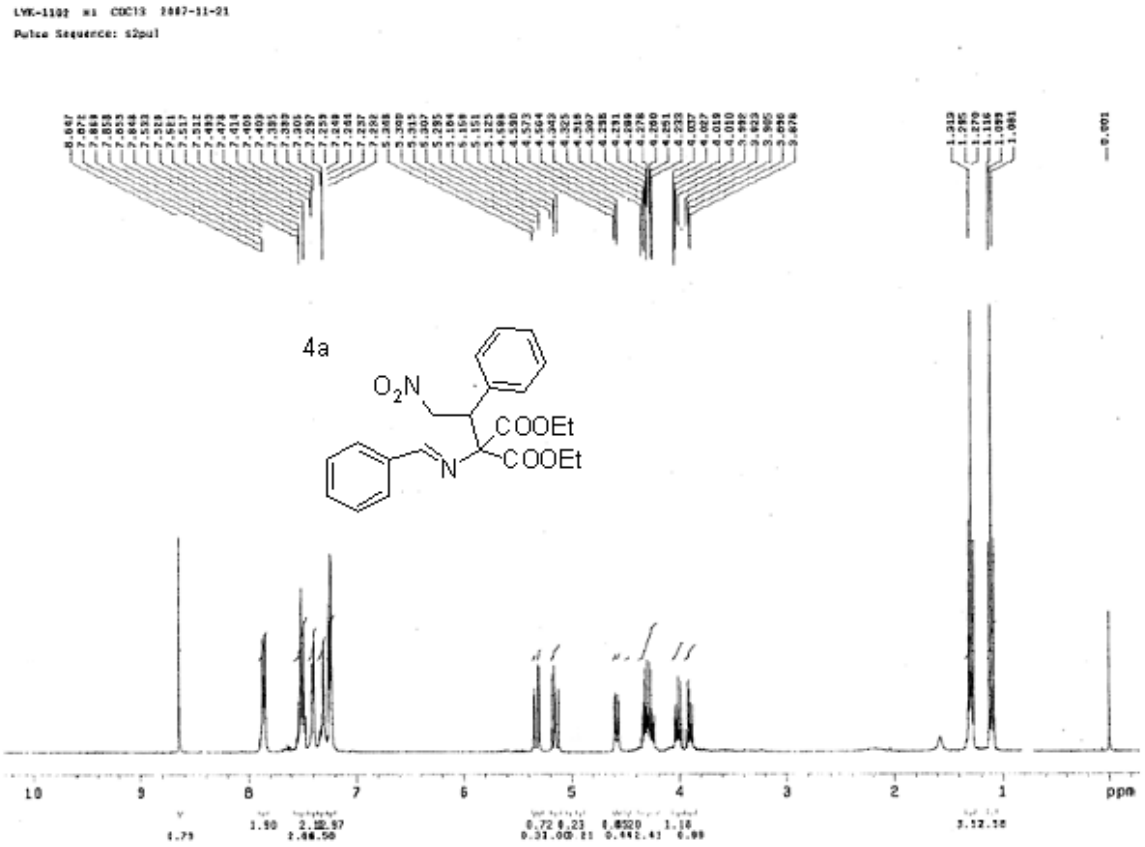


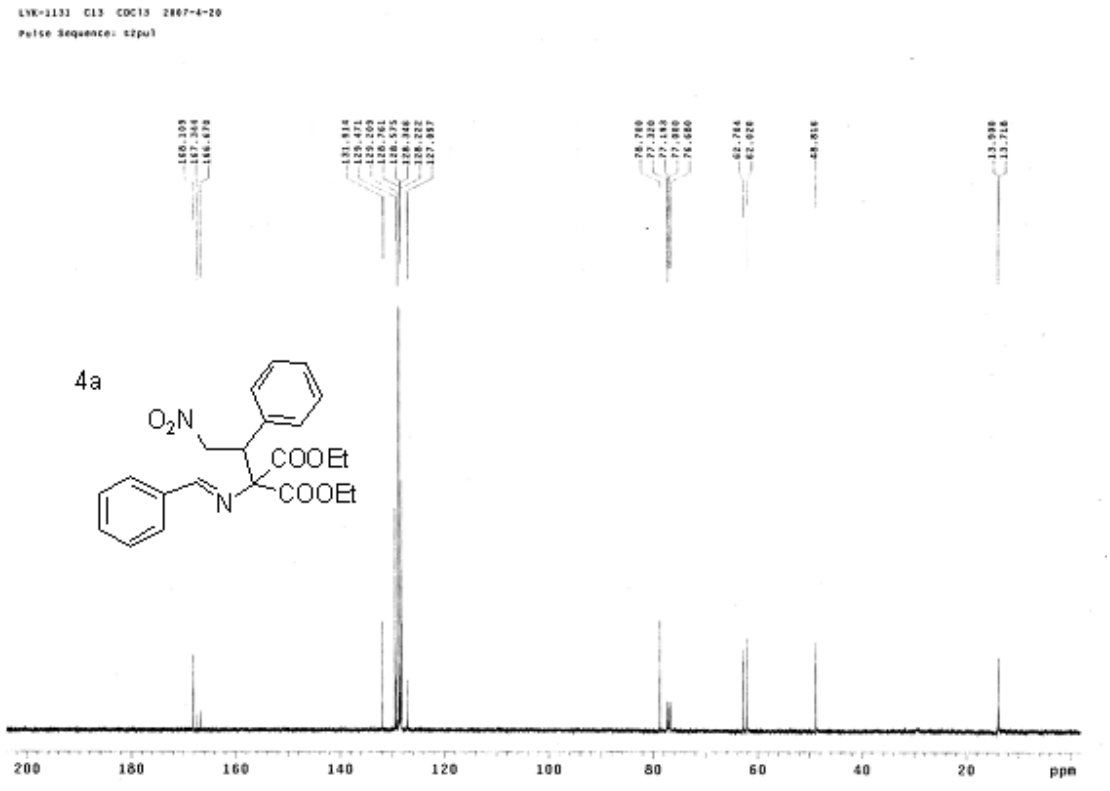
11

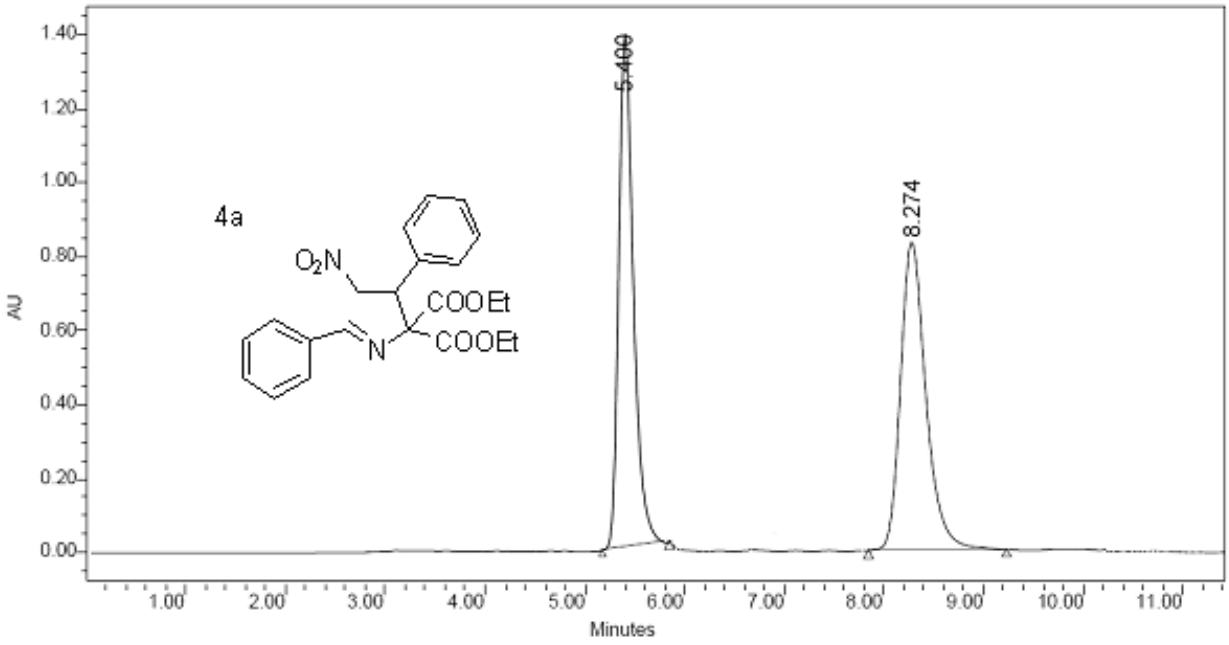
Identification code	**11**
Empirical formula	C31 H38 N2 O7 S [**5b** ($C_{29}H_{32}N_2O_6S$) + C_2H_5OH]
Formula weight	582.69
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 11.844(2) A alpha = 90 deg.

	b = 12.413(3) A beta = 90 deg.
	c = 20.850(4) A gamma = 90 deg.
Volume	3065.4(11) A^3
Z, Calculated density	4, 1.263 Mg/m^3
Absorption coefficient	0.154 mm^-1
F(000)	1240
Crystal size	0.24 x 0.22 x 0.20 mm
Theta range for data collection	1.95 to 27.87 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -27<=l<=27
Reflections collected / unique	38040 / 7319 [R(int) = 0.0451]
Completeness to theta = 27.87	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9699 and 0.9640
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7319 / 43 / 413
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0934
R indices (all data)	R1 = 0.0468, wR2 = 0.0962
Absolute structure parameter	-0.01(6)
Largest diff. peak and hole	0.178 and -0.363 e.A^-3

NMR and HPLC spectra







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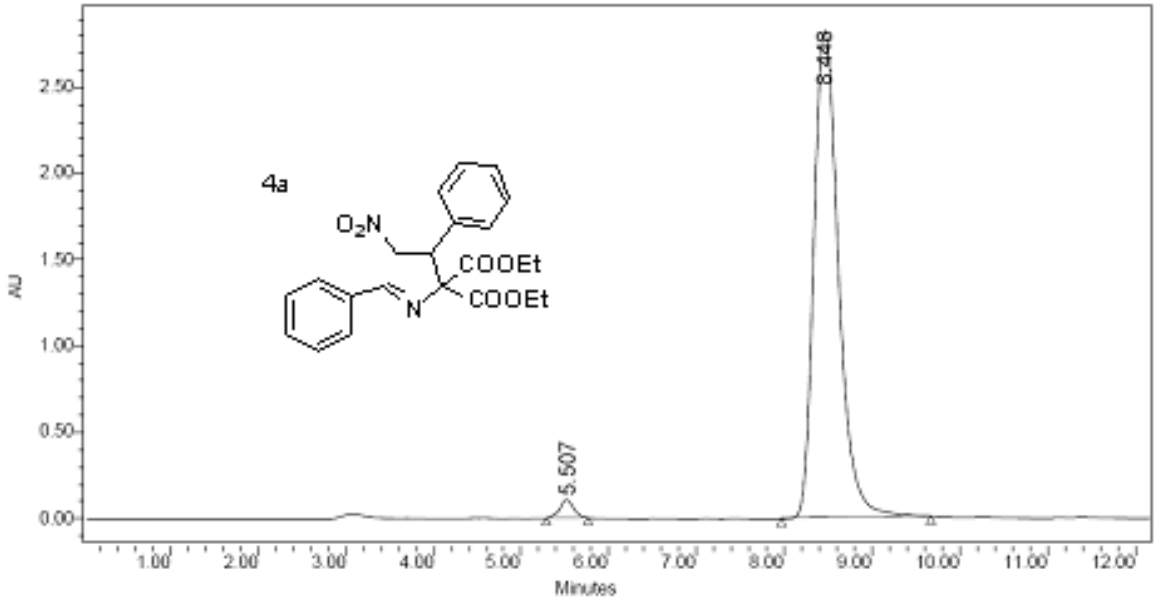

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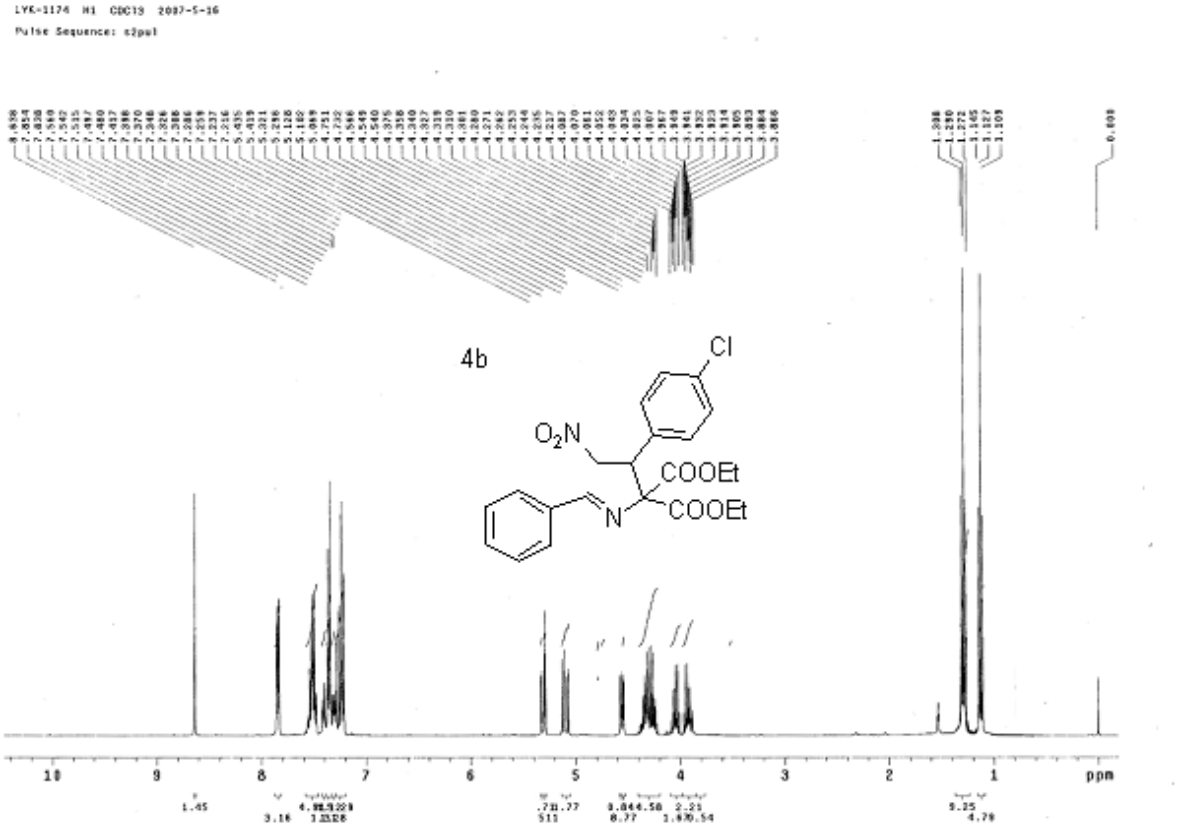

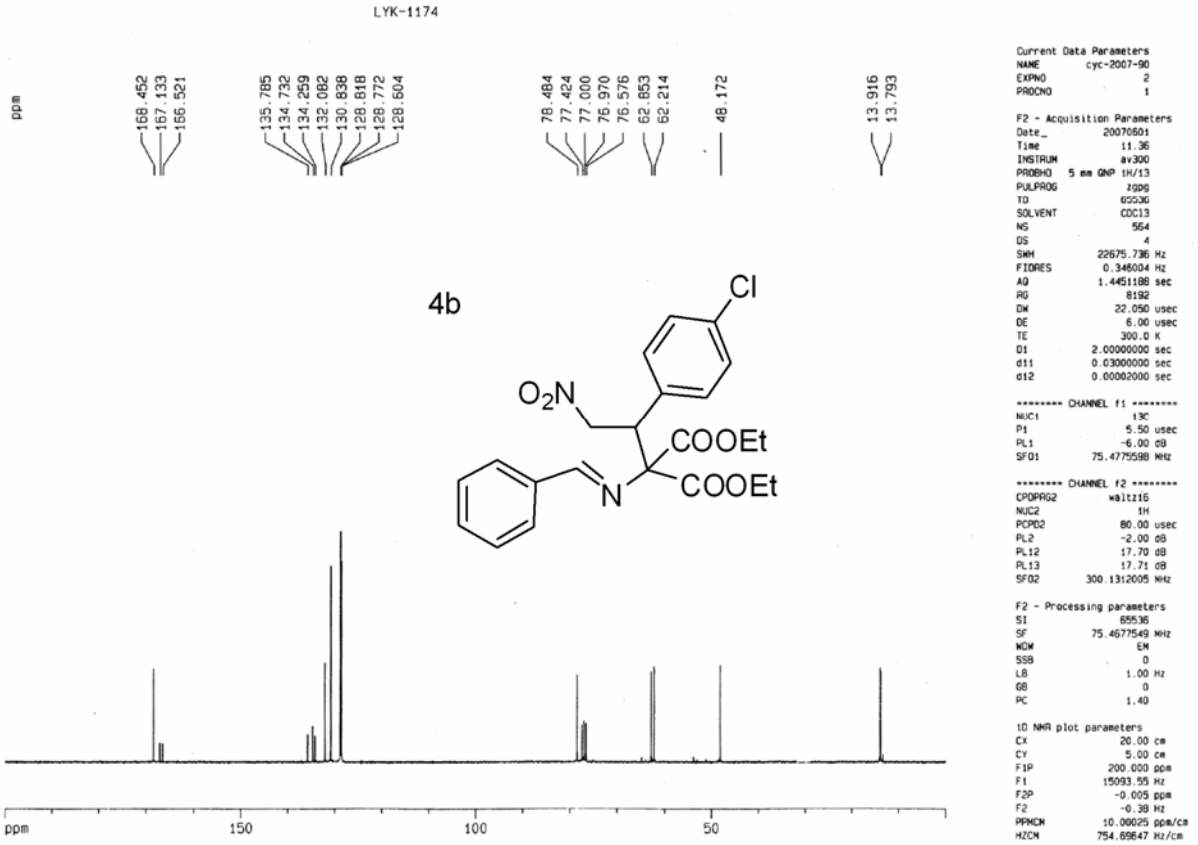


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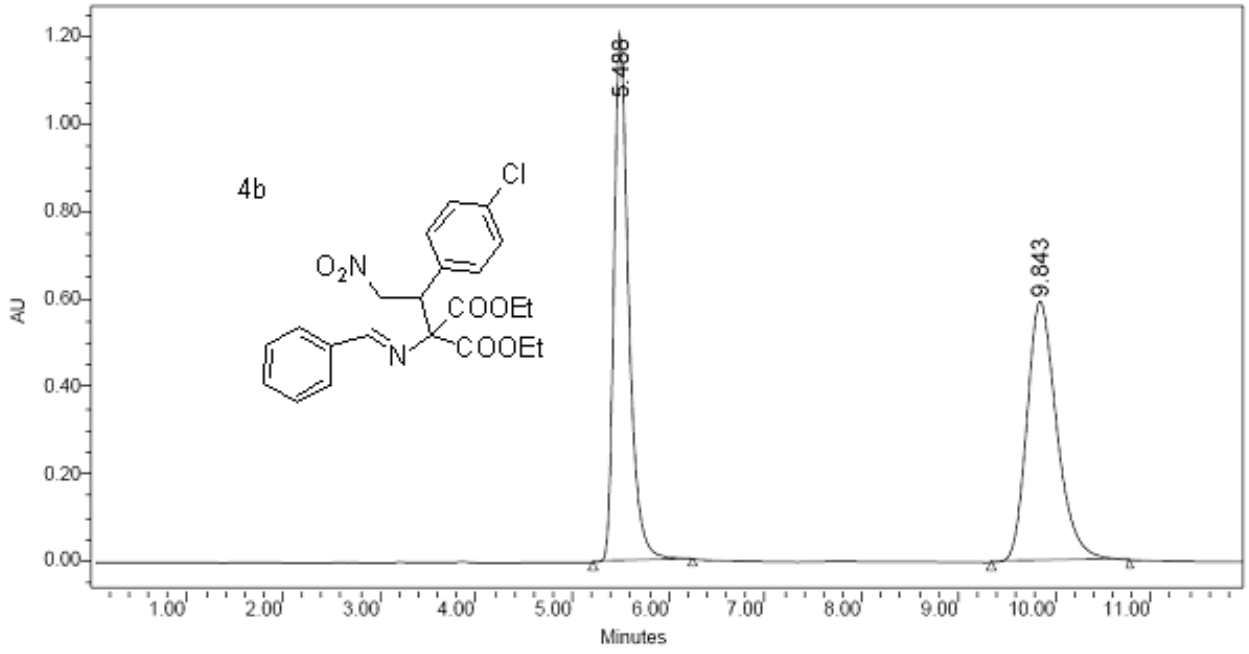

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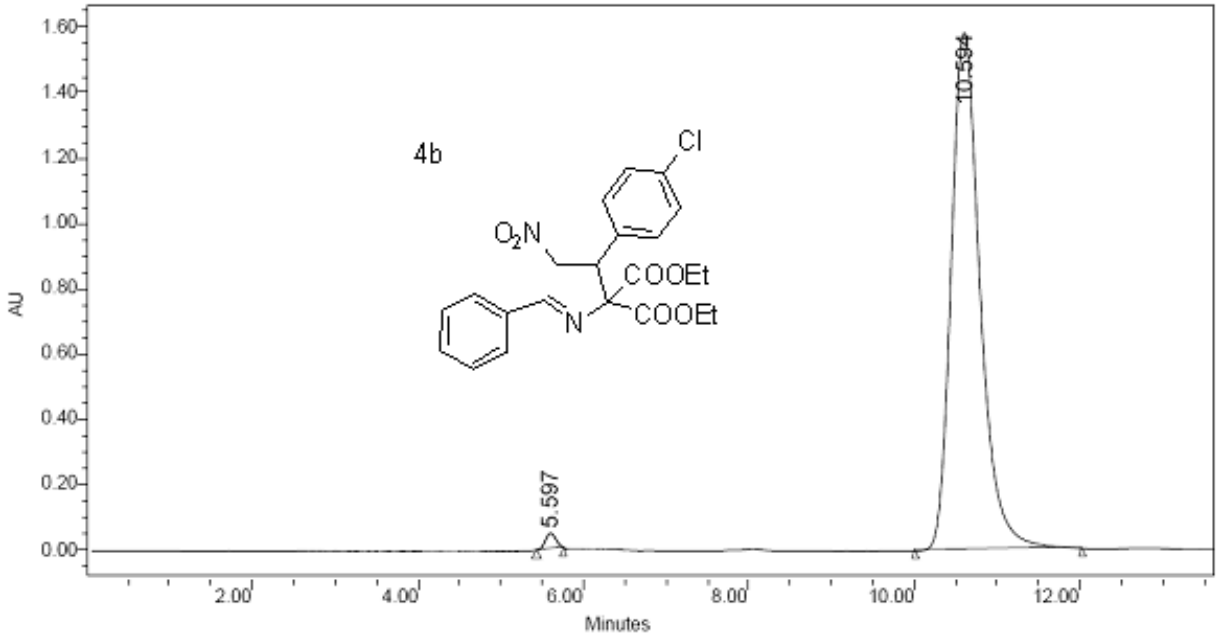

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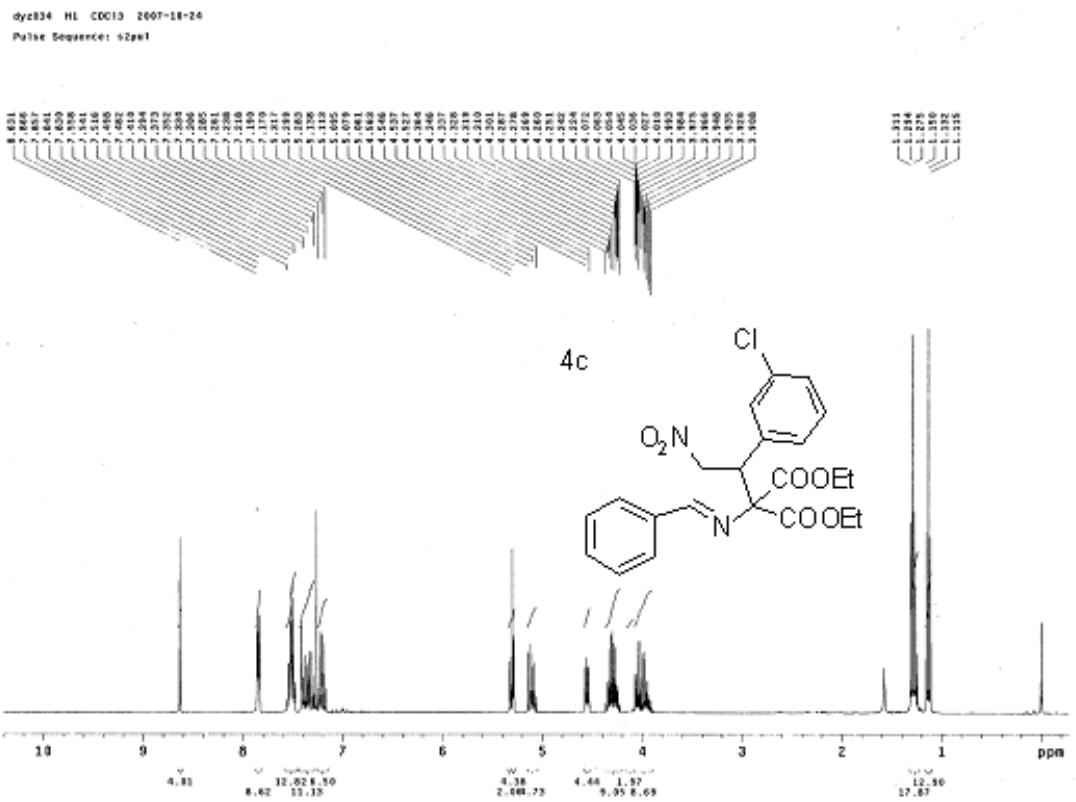

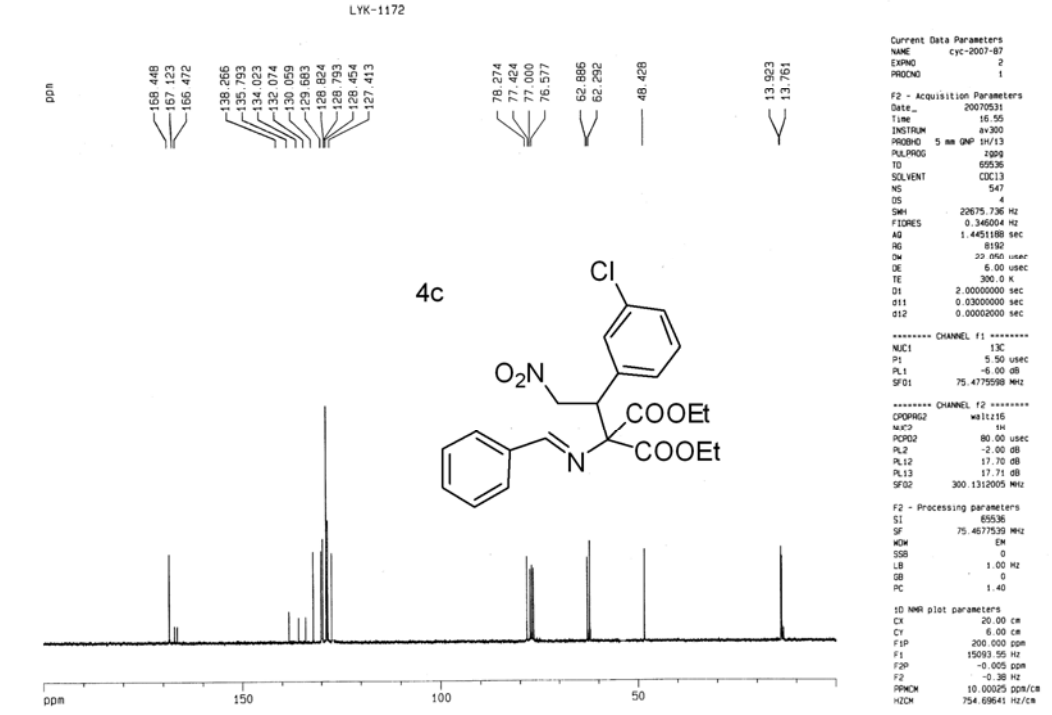

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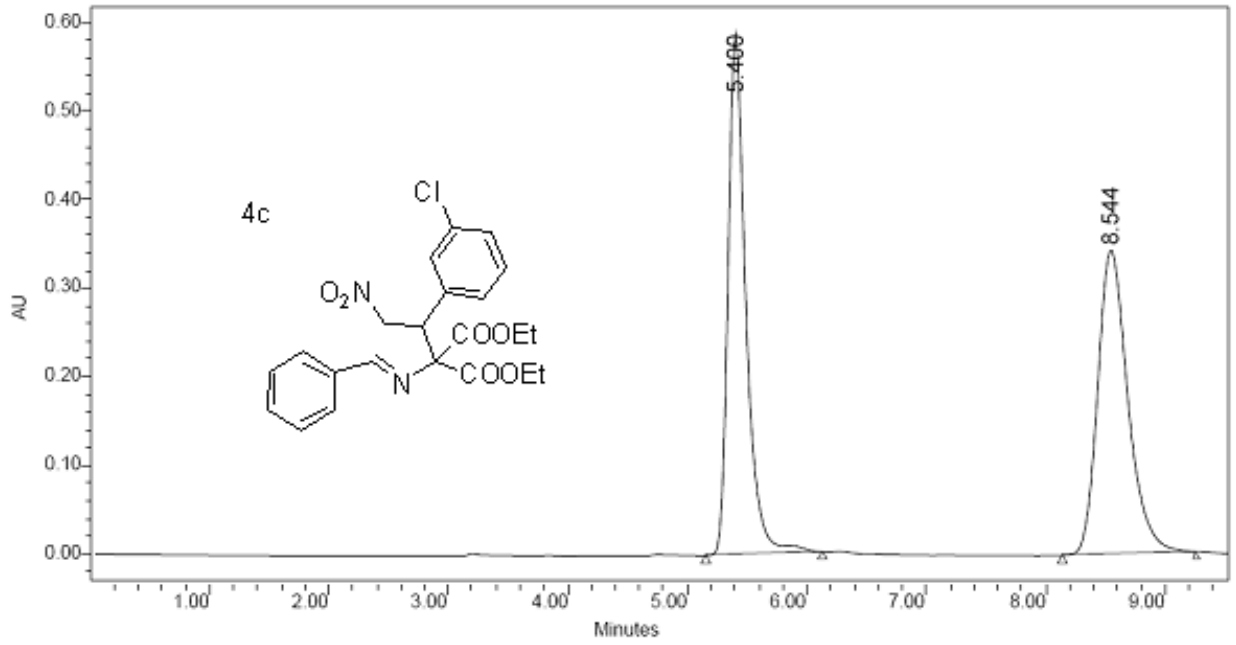

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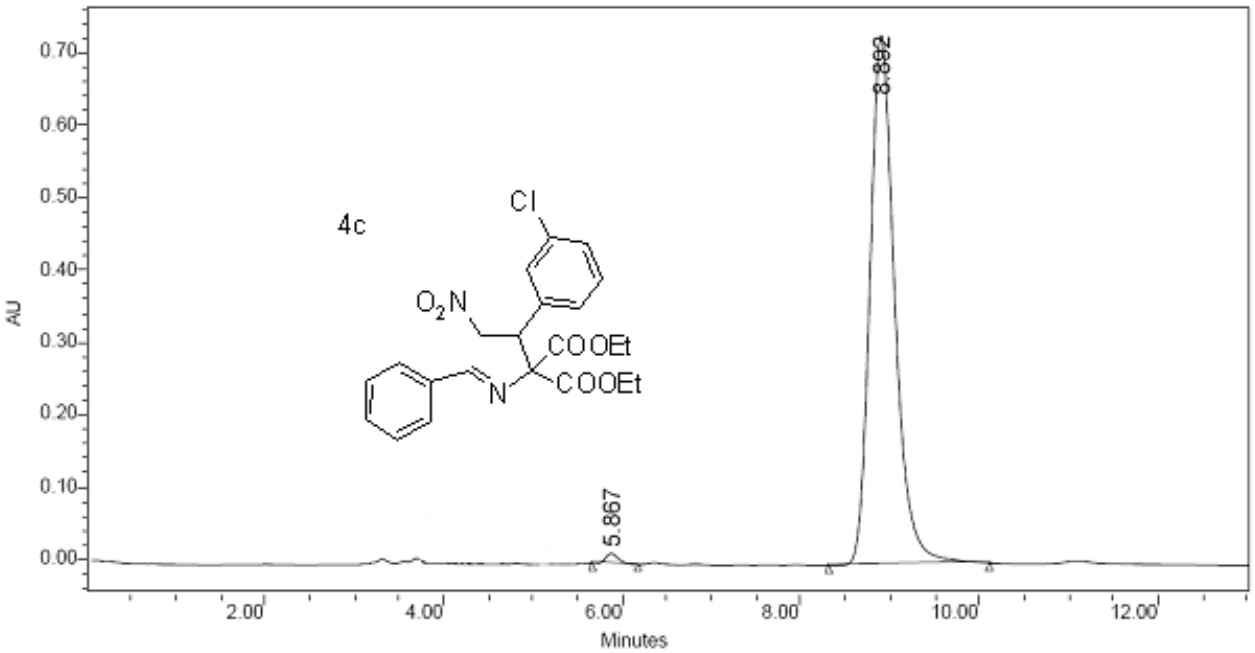

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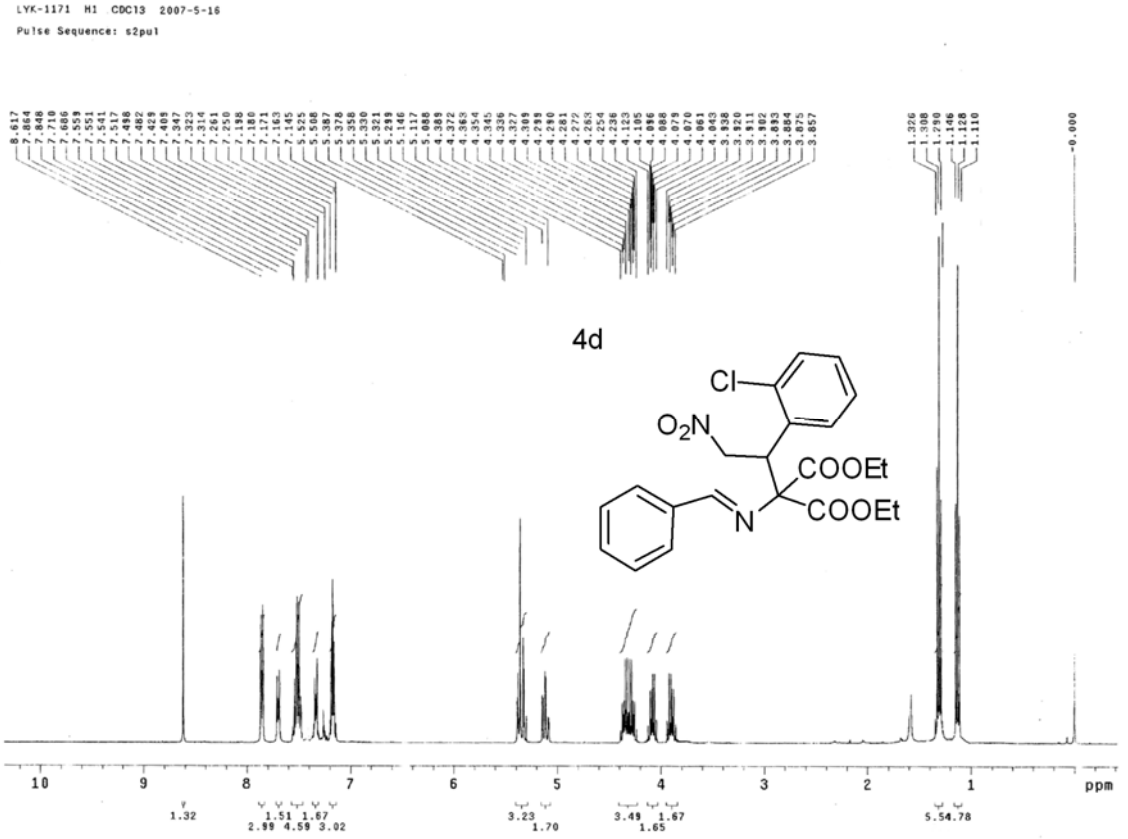
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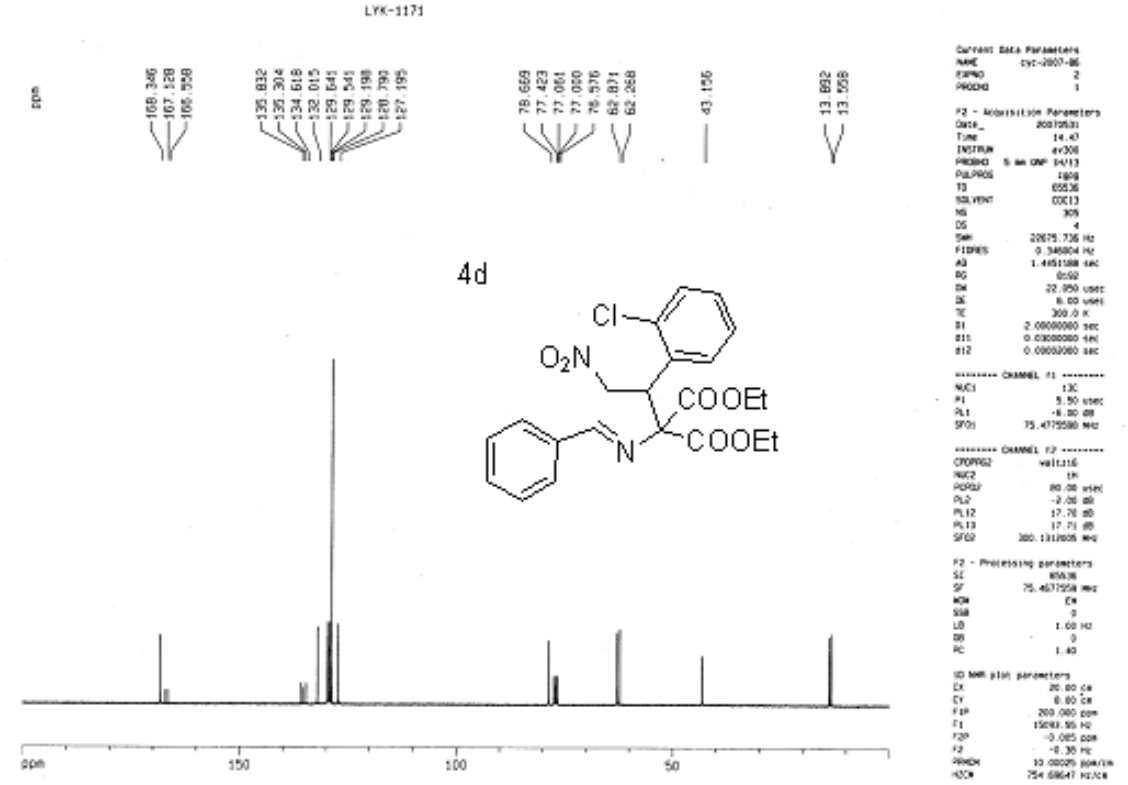
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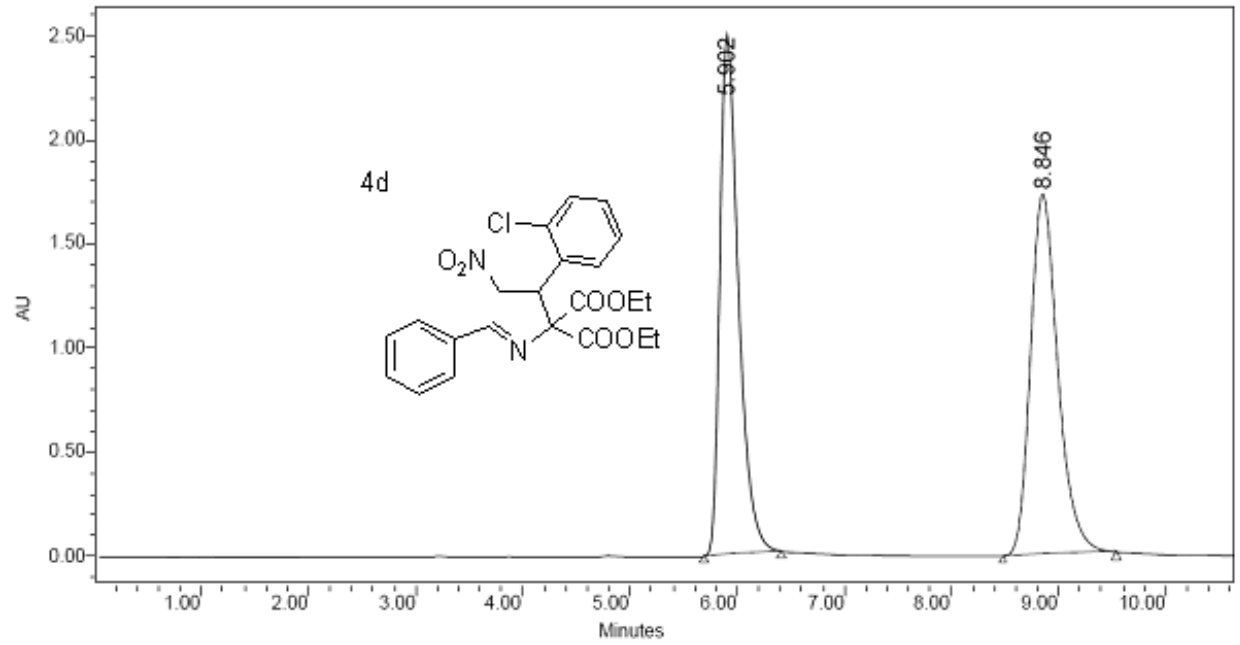

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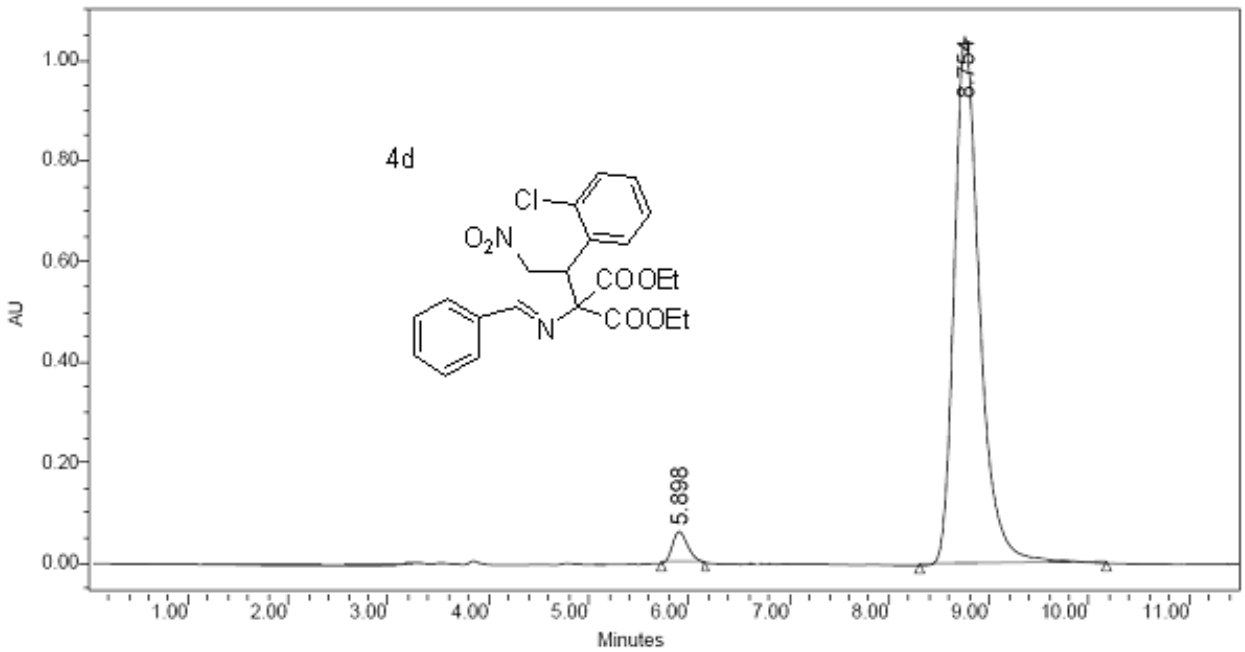

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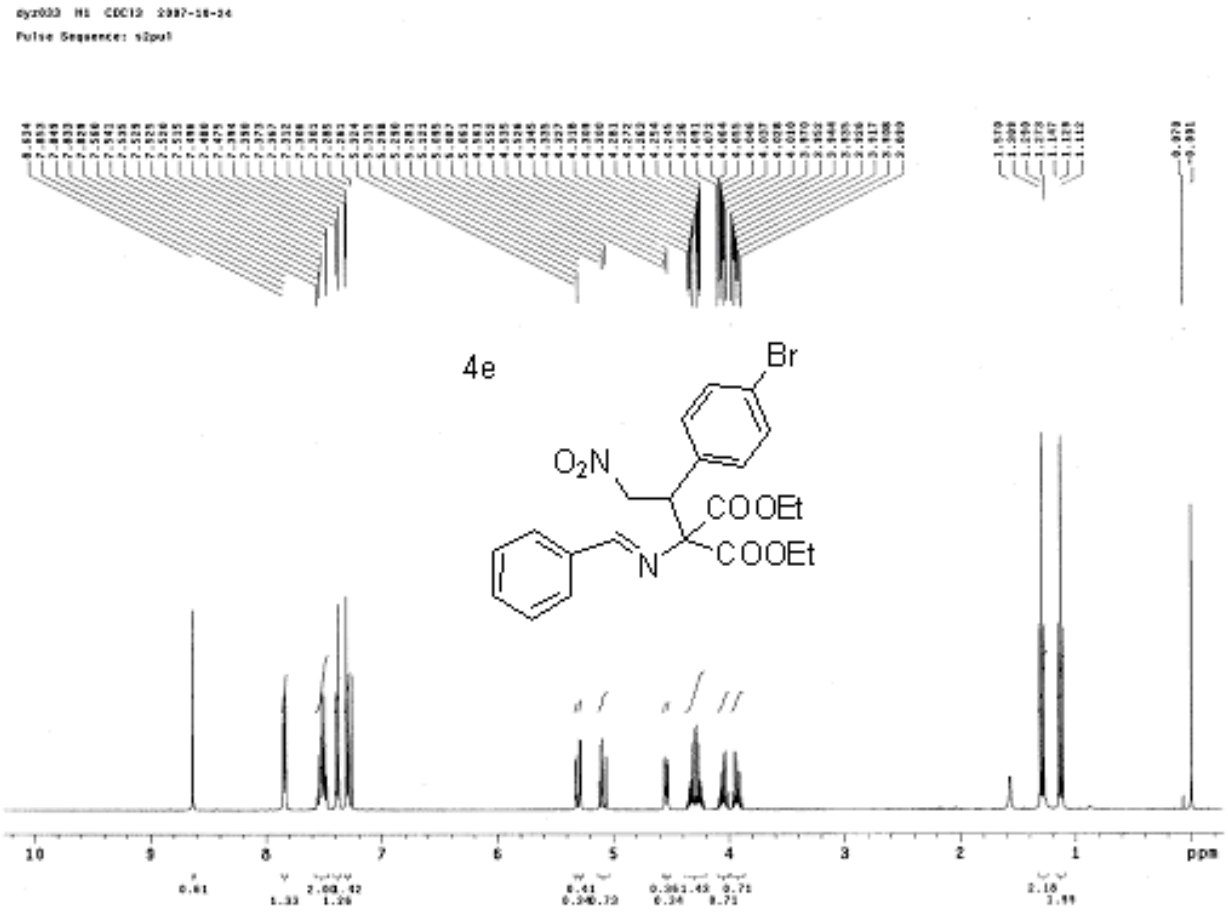
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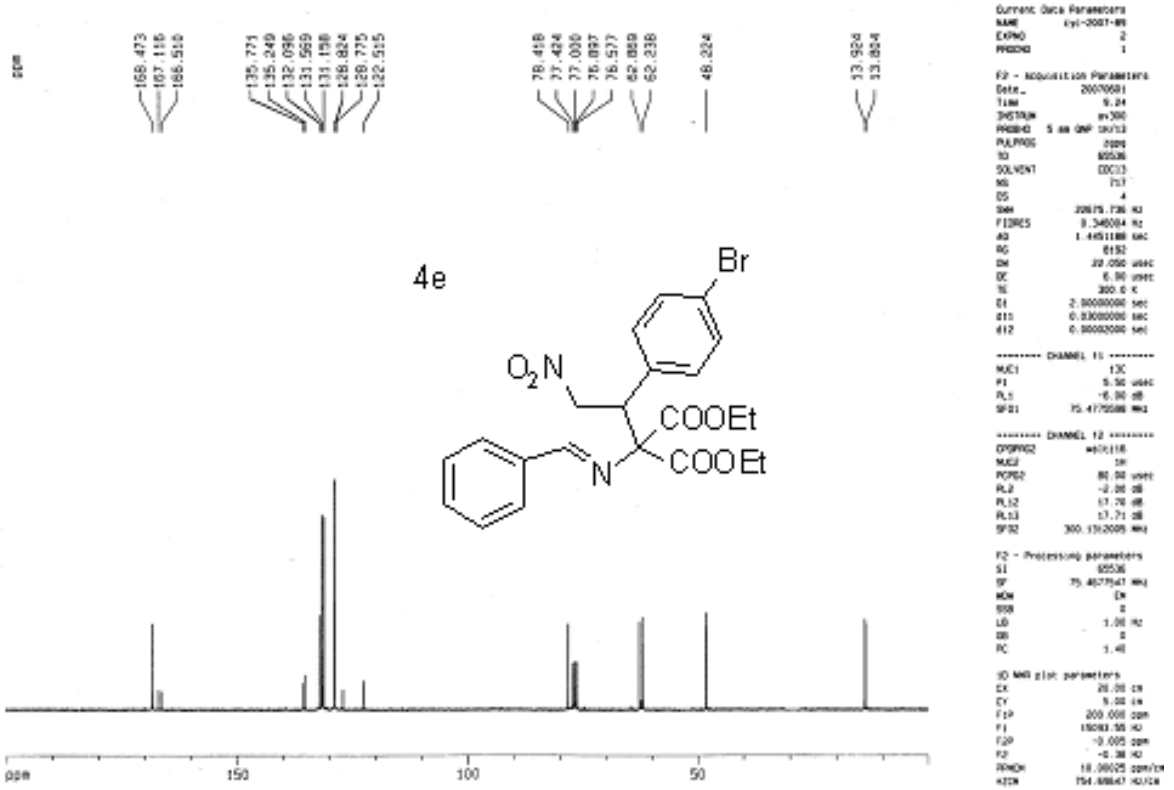
LYK-1176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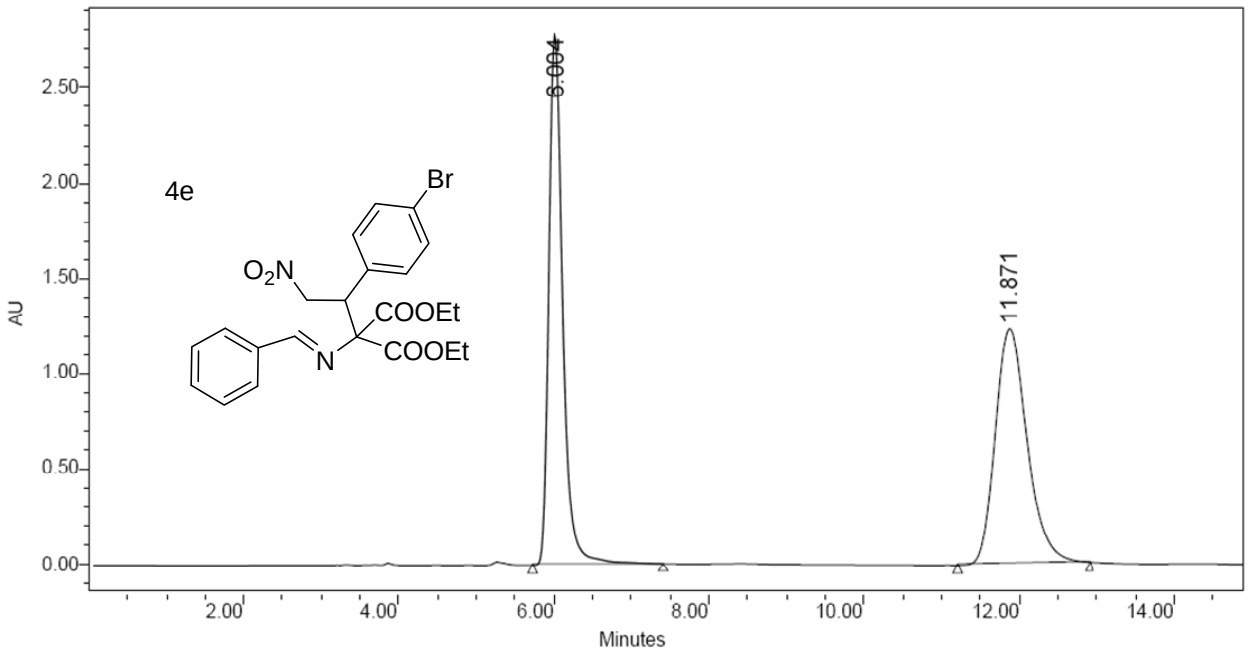

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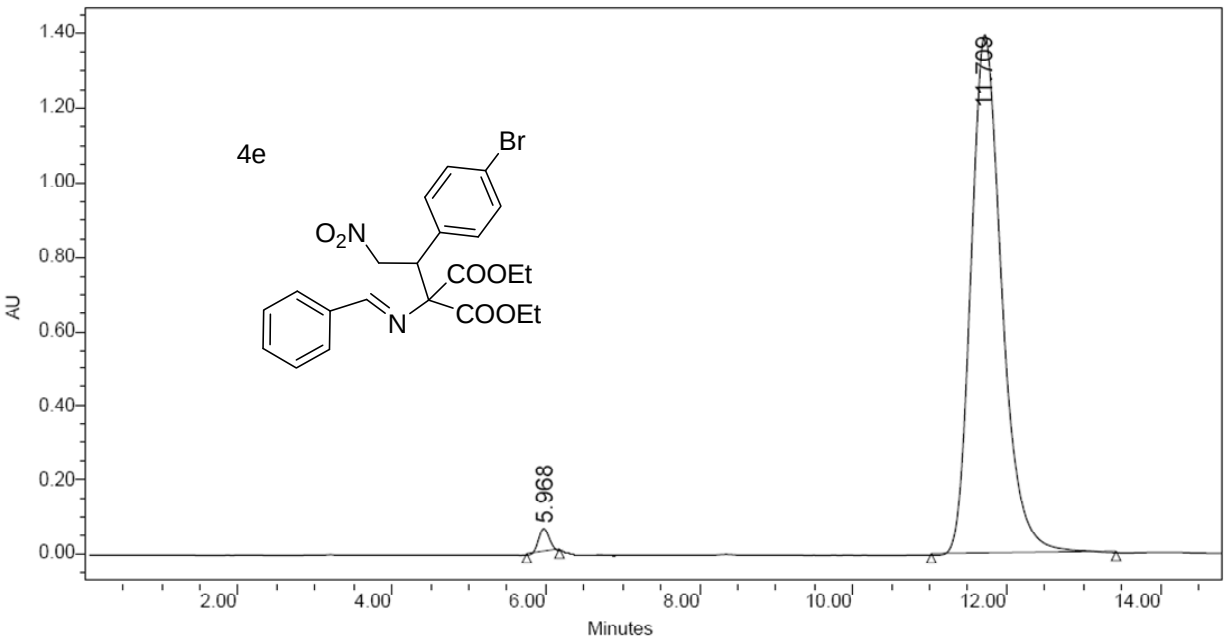
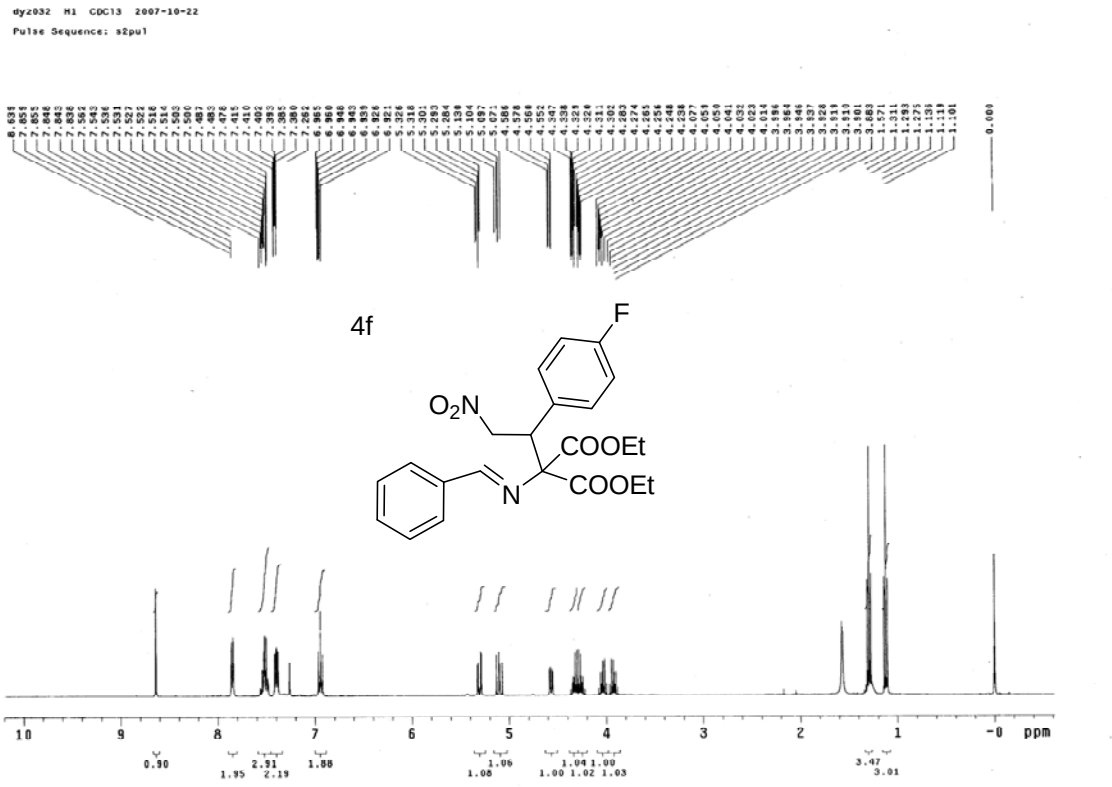
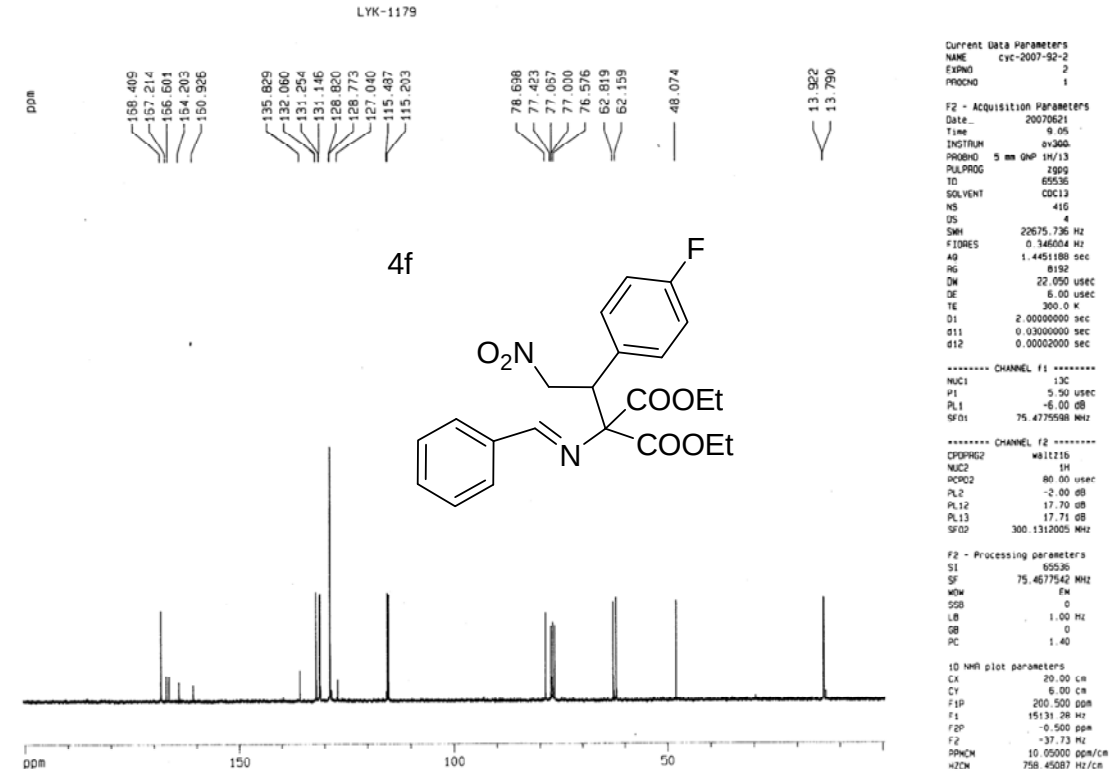
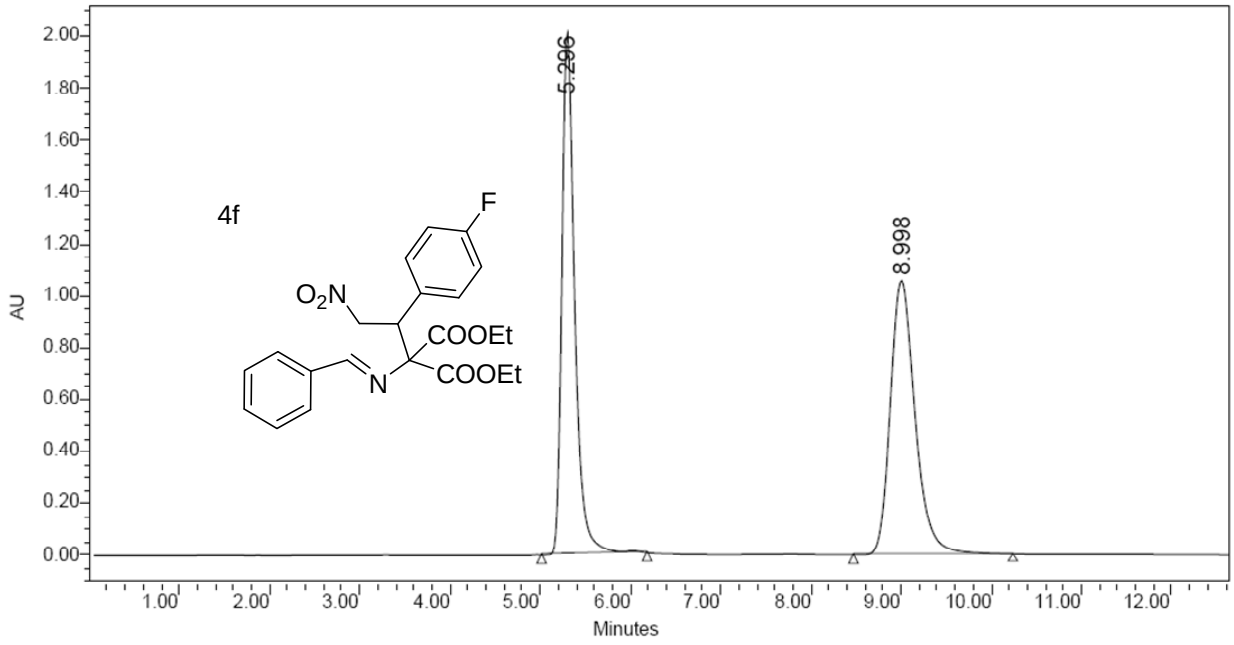
1	6.004	34475834	49.50	2773649	69.24
2	11.871	35174333	50.50	1232386	30.76



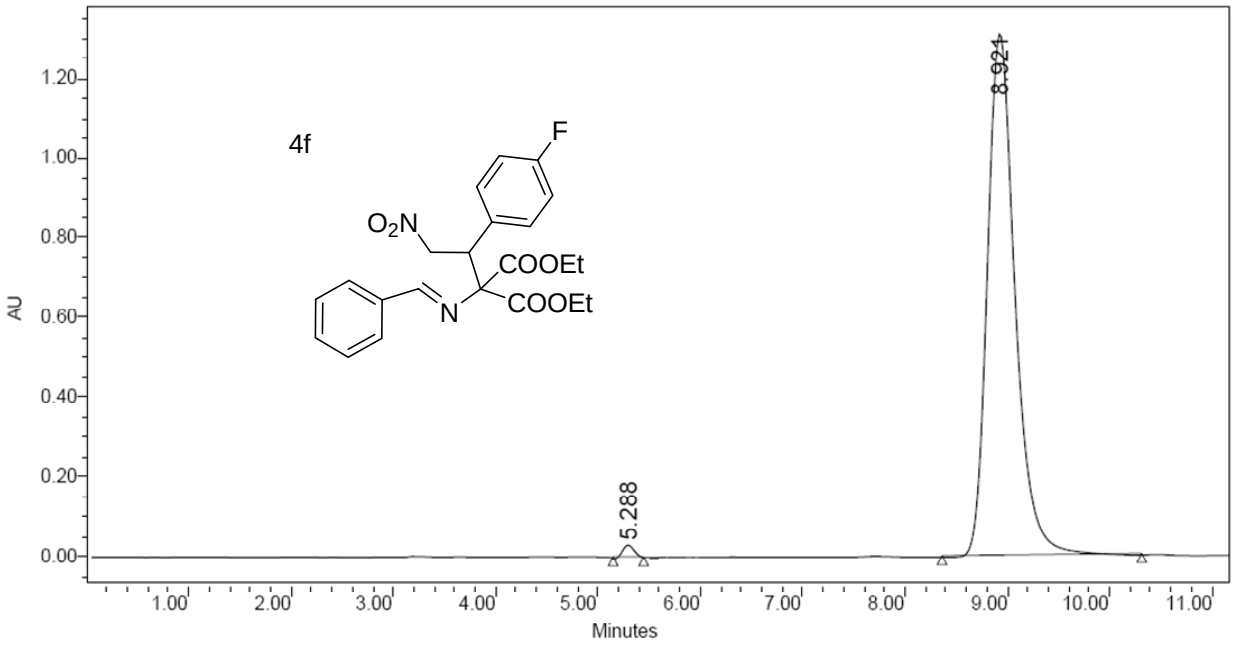
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.968	653089	1.64	66090	4.52
2	11.709	39115139	98.36	1395836	95.48


dyz032 H1 CDCl3 2007-10-22
Pulse Sequence: s2pul
4f
F
O2N
COOEt
COOEt
N
ppm

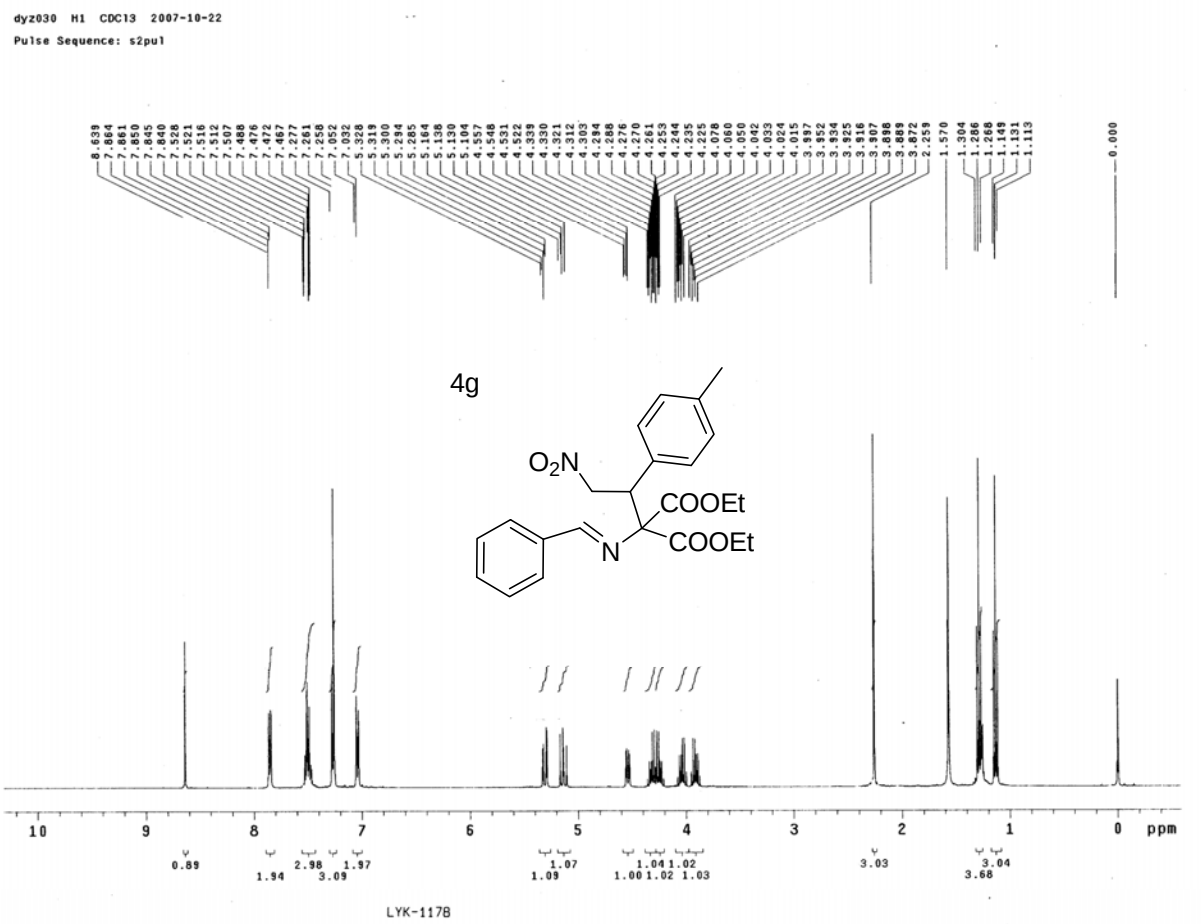

LYK-1179
ppm
4f
F
O2N
COOEt
COOEt
N
ppm

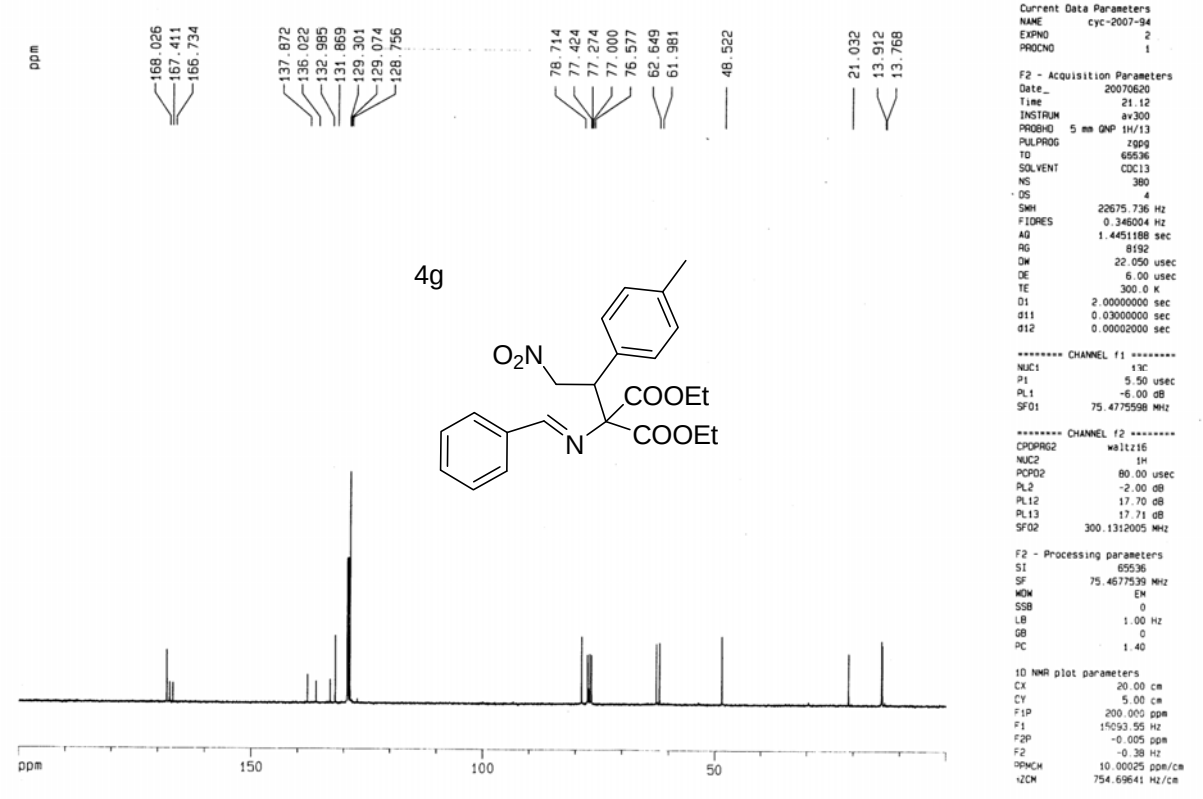


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.296	20044936	49.74	2012599	65.55
2	8.998	20256299	50.26	1057955	34.45



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.288	272322	1.09	33714	2.51
2	8.921	24738611	98.91	1311358	97.49





Current Data Parameters
NAME cyc-2007-94
EXPNO 2
PROCNO 1

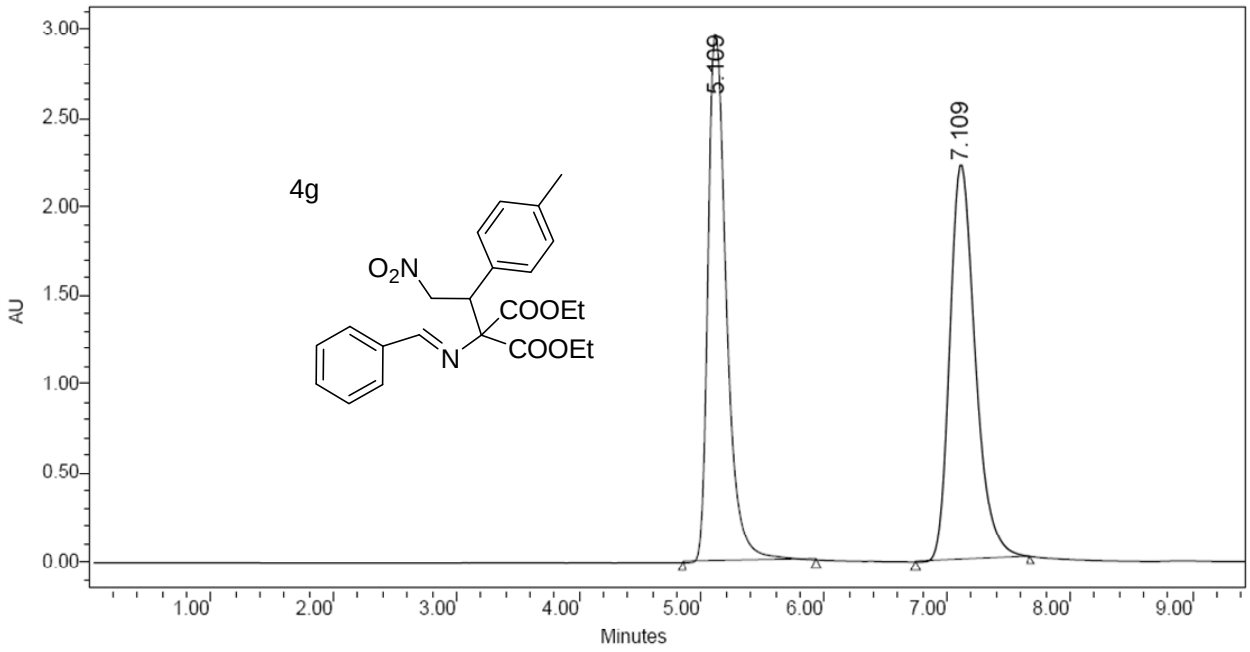
F2 - Acquisition Parameters
Date_ 20070620
Time 21.12
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 380
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SF01 75.4775598 MHz

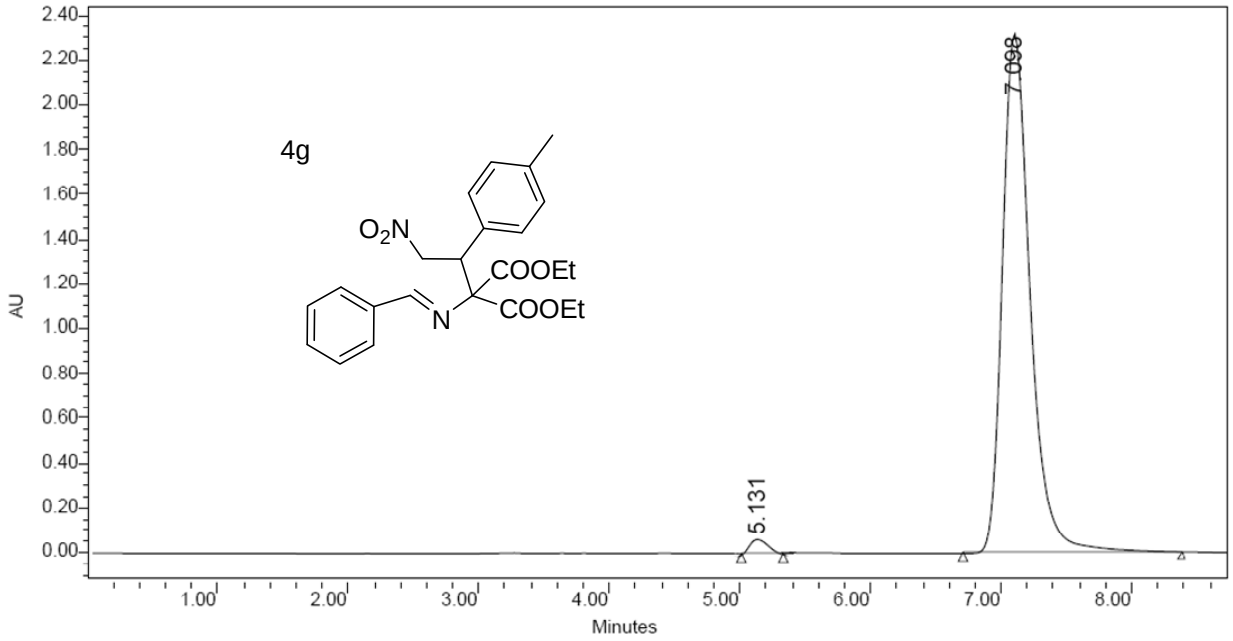
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677539 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

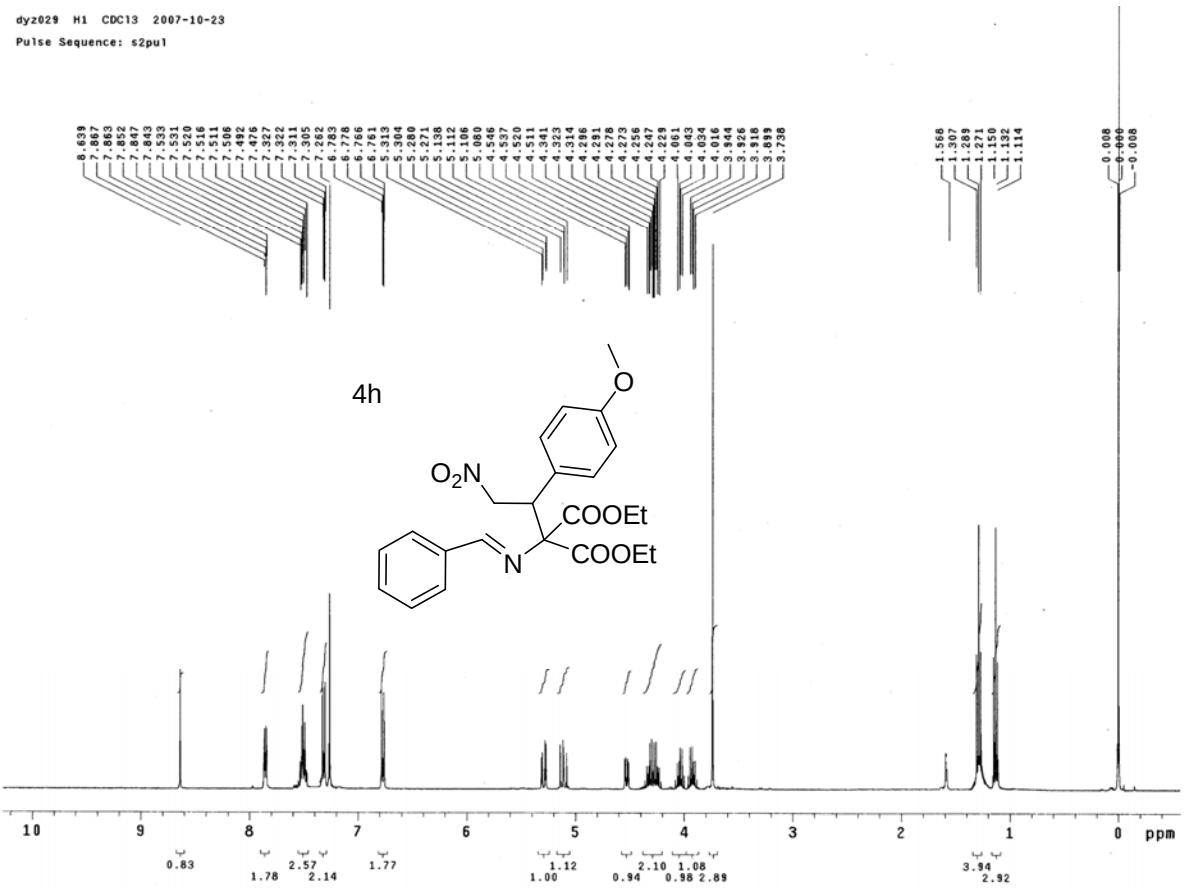
1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -0.005 ppm
F2 -0.38 Hz
PPMCM 10.00025 ppm/cm
HZCM 754.69641 Hz/cm

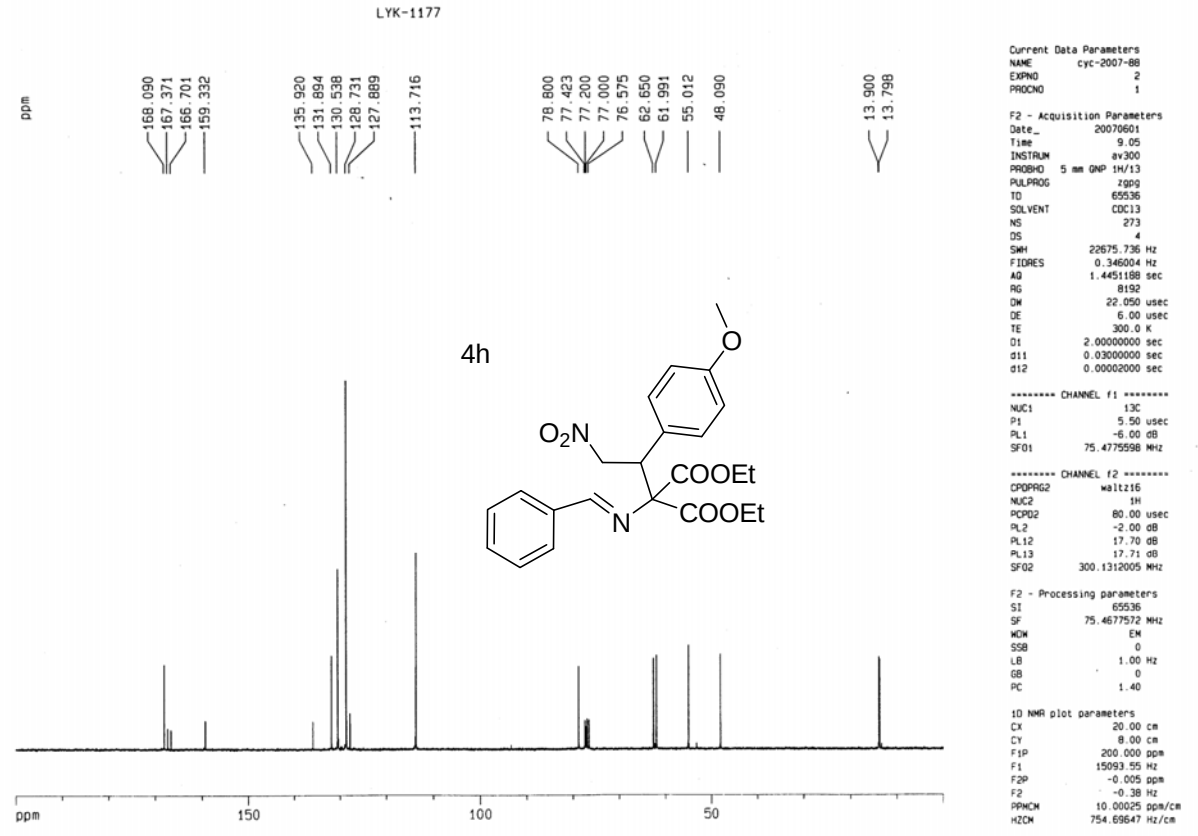


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.109	31186160	49.25	3000680	57.34
2	7.109	32131185	50.75	2232727	42.66



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.131	660321	1.88	67129	2.82
2	7.098	34426483	98.12	2317271	97.18





Current Data Parameters
NAME cyc-2007-88
EXPNO 2
PROCNO 1

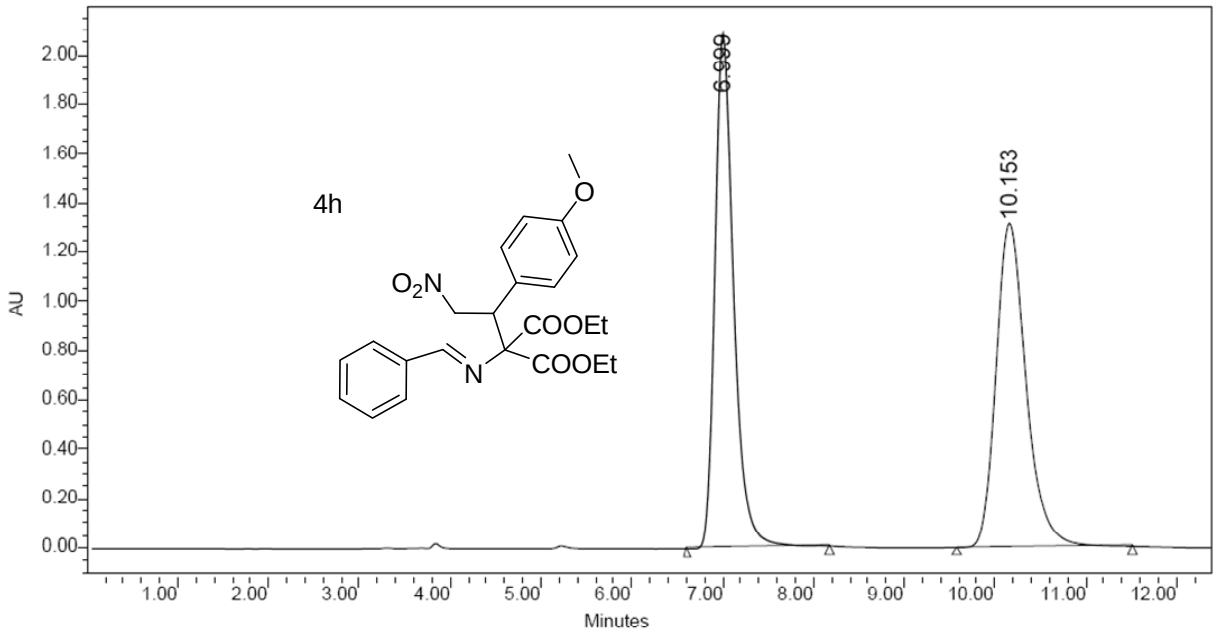
F2 - Acquisition Parameters
Date_ 20070601
Time 9.05
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 273
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SF01 75.4775598 MHz

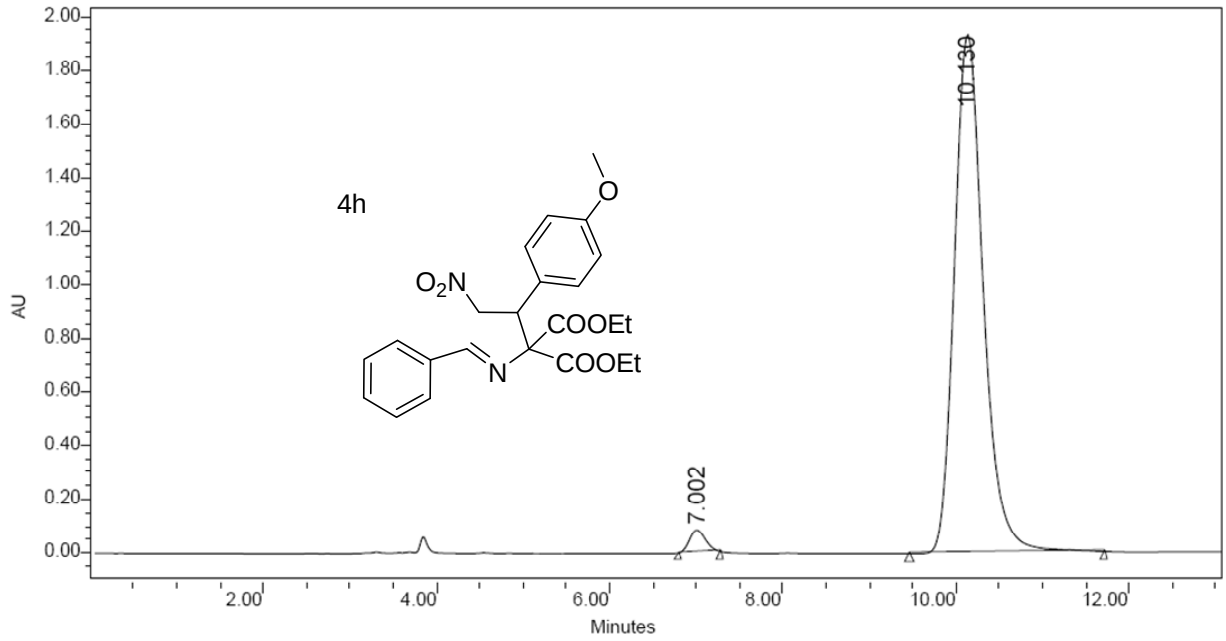
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -0.005 ppm
F2 -0.38 Hz
PPMCM 10.00025 ppm/cm
HZCM 754.69647 Hz/cm



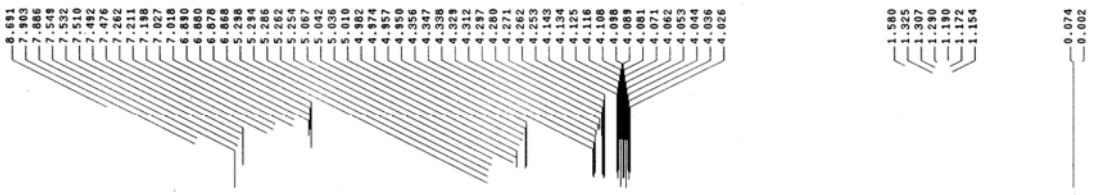
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.999	30032240	49.77	2083754	61.30
2	10.153	30307835	50.23	1315284	38.70



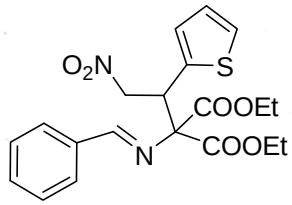
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.002	1083278	2.35	83555	4.15
2	10.130	45097620	97.65	1931185	95.85

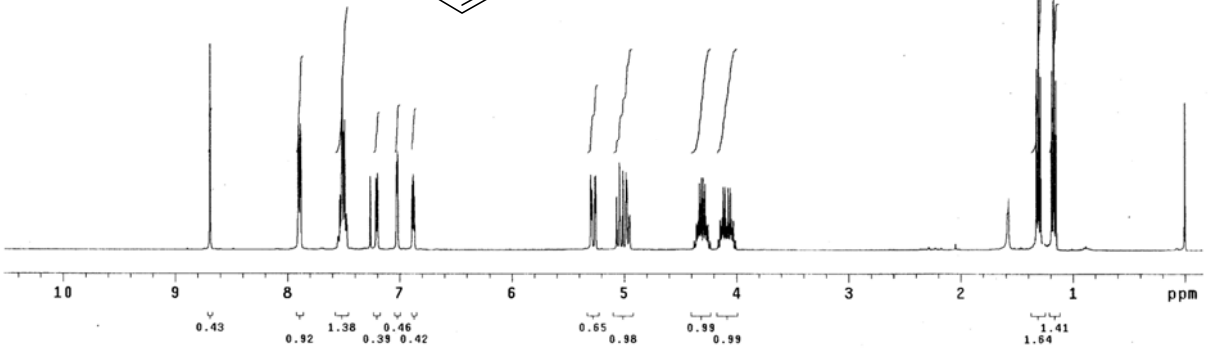
Dyz035-CDCL3-H1-2007-10-25

Pulse Sequence: s2pul

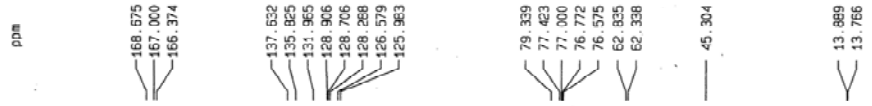


4i

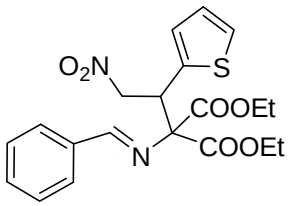


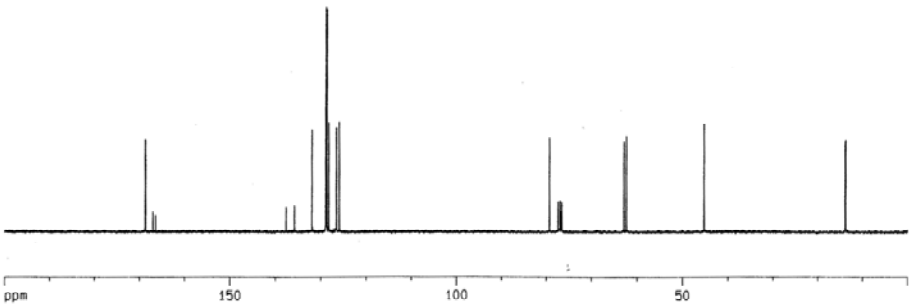


LYK-1175



4i



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Current Data Parameters
NAME          cyc-2007-05
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20070531
Time              14.35
INSTRUM           av300
PROBHD  5 mm QNP 1H/13
PULPROG           zgpg
TD                65536
SOLVENT           CDCl3
NS                  160
DS                   -4
SWH           22675.736 Hz
FIDRES        0.345004 Hz
AQ            1.4451188 sec
RG                8192
DW              22.050 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                5.50 usec
PL1               +6.00 dB
SFO1         75.4775598 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2              -2.00 dB
PL12             17.70 dB
PL13             17.71 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                65536
SF           75.4677576 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
CY                5.00 cm
F1P             200.000 ppm
F1             15093.55 Hz
F2P              -0.005 ppm
F2               -0.38 Hz
PPMCM         10.00025 ppm/cm
HZCM         754.69647 Hz/cm
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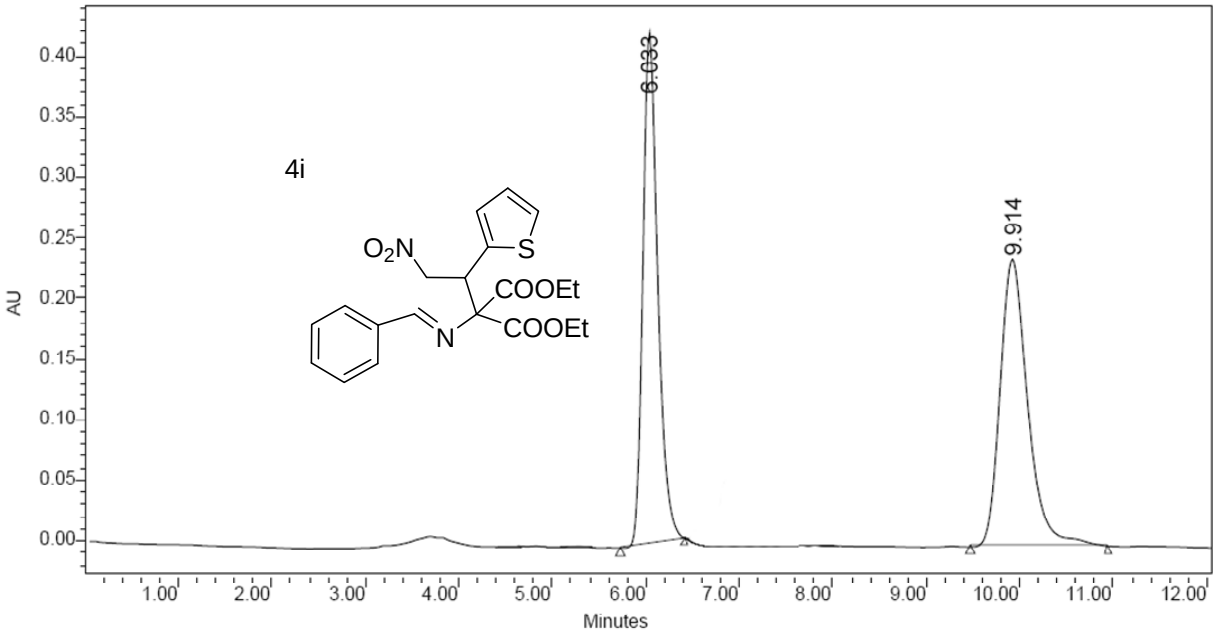
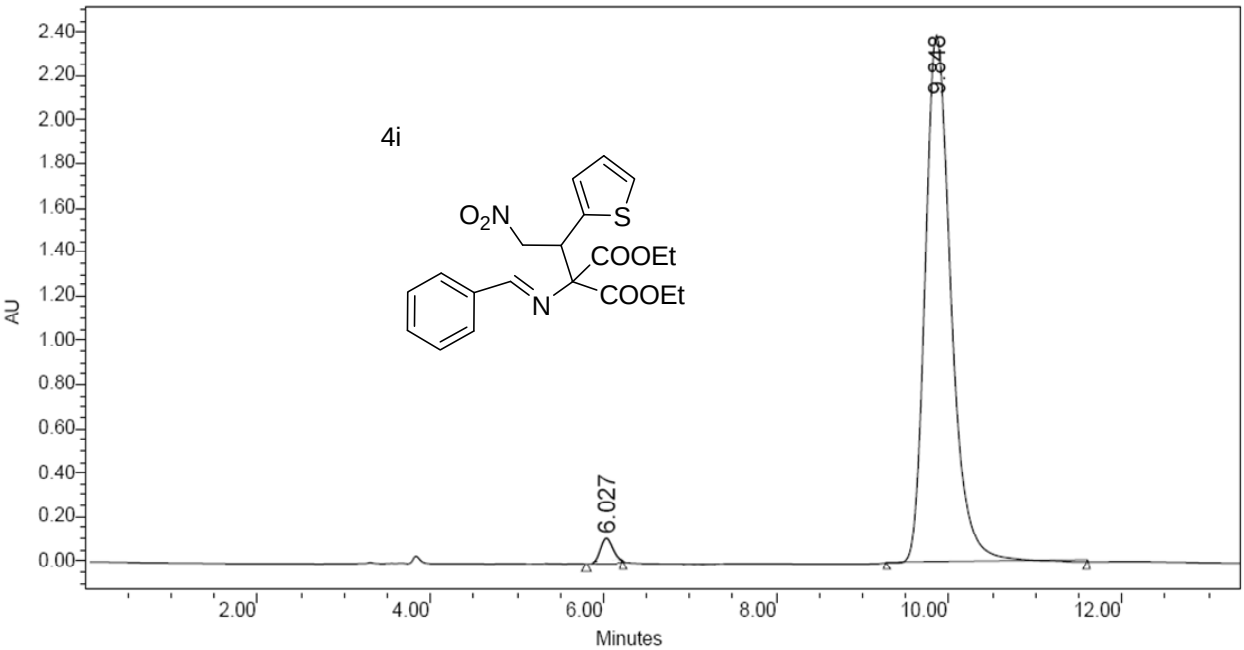
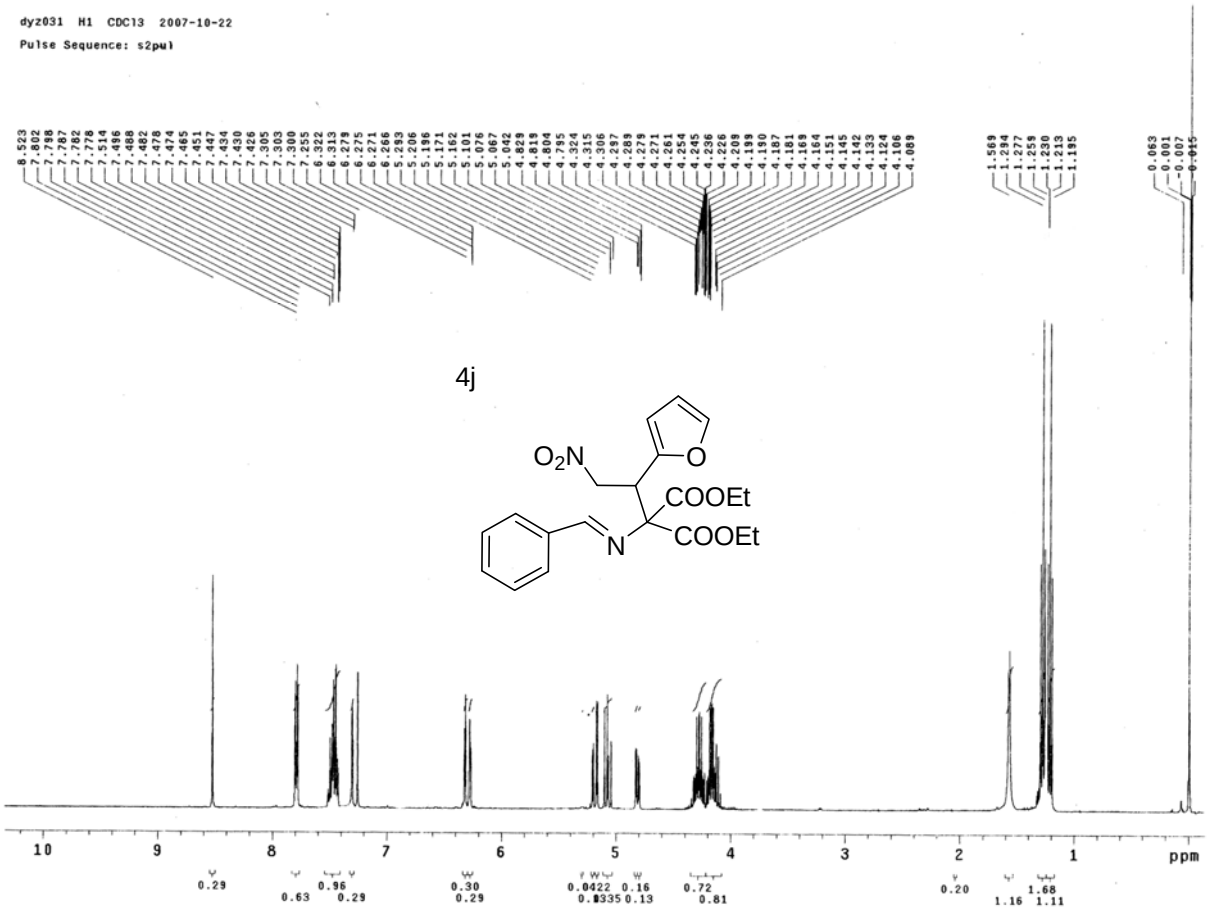
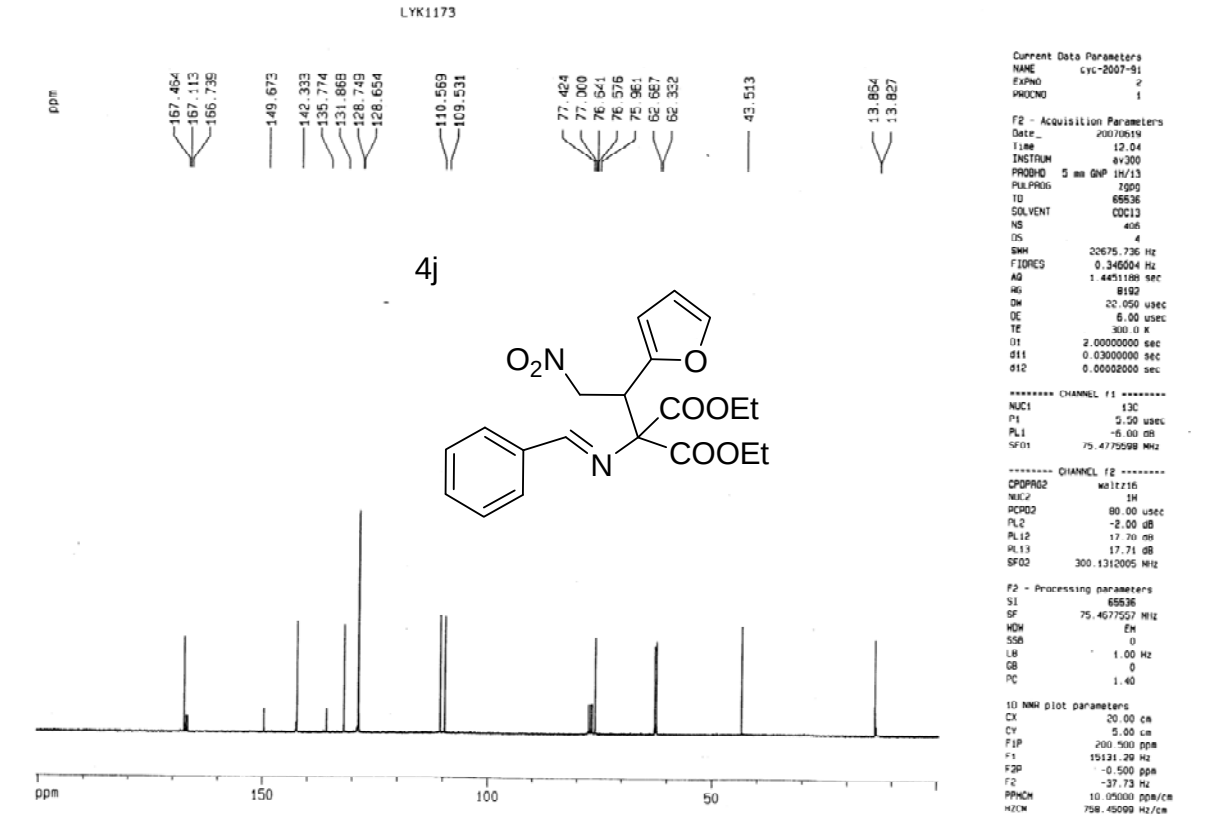


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.033	4666399	48.79	420996	63.98
2	9.914	4897633	51.21	237040	36.02



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.027	1077316	2.12	107172	4.29
2	9.848	49816698	97.88	2389654	95.71





Current Data Parameters
NAME cyc-2007-91
EXPNO 2
PROCNO 1

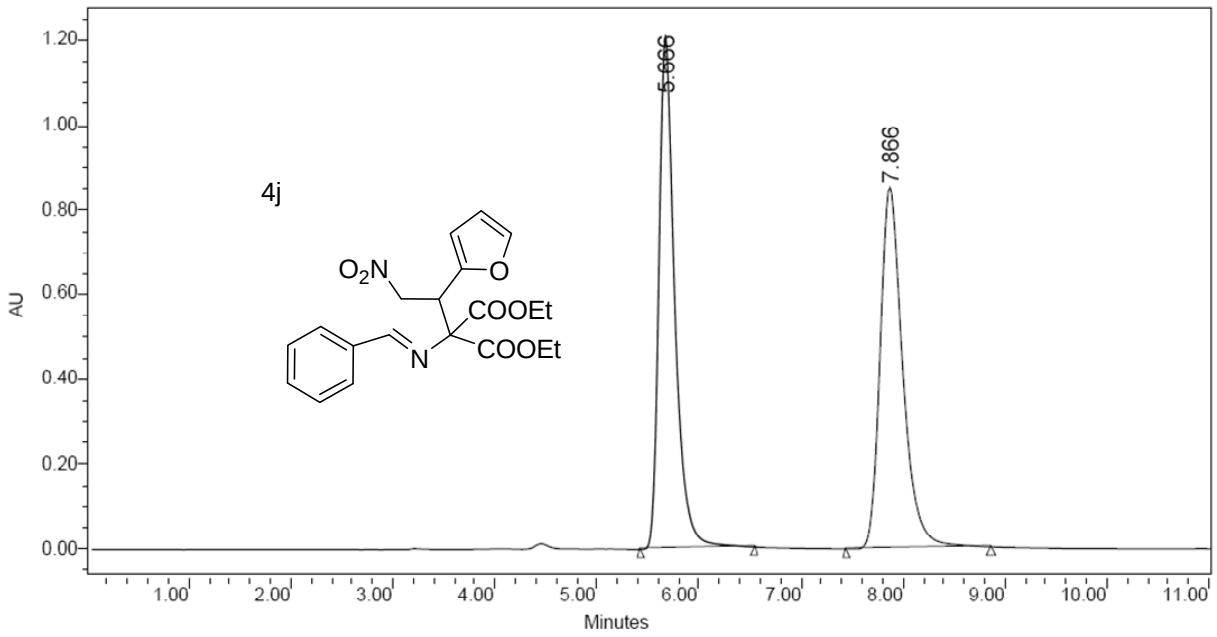
F2 - Acquisition Parameters
Date_ 20070619
Time 12.04
INSTRUM av300
PROBHD 5 mm GNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 406
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz

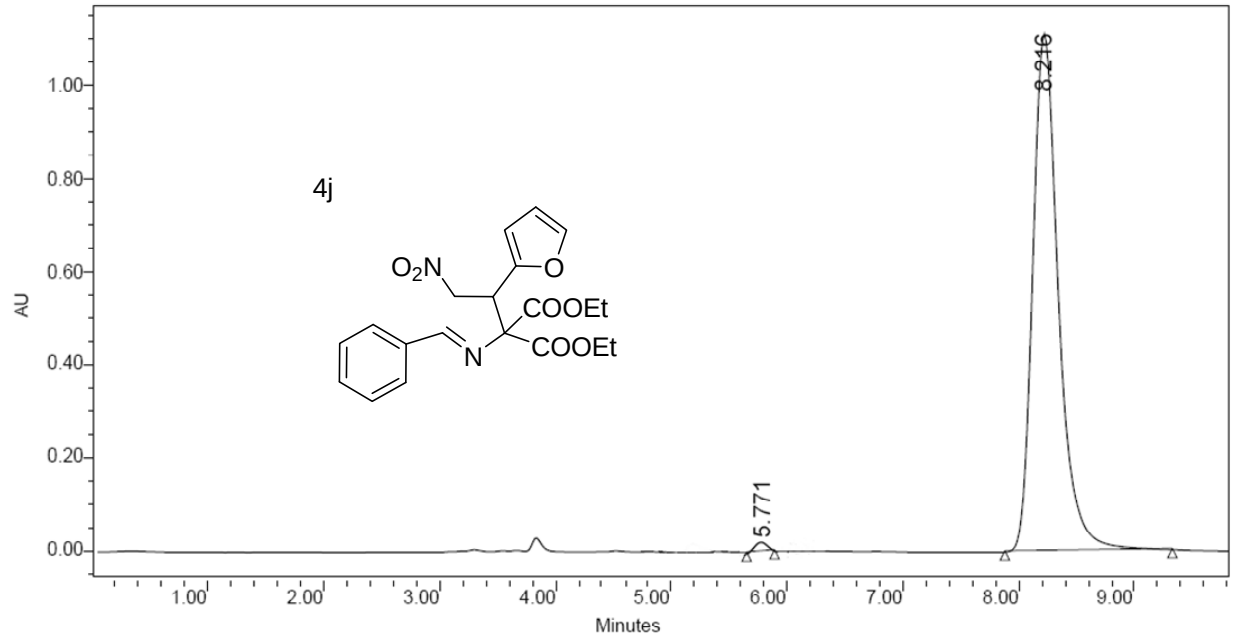
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677557 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

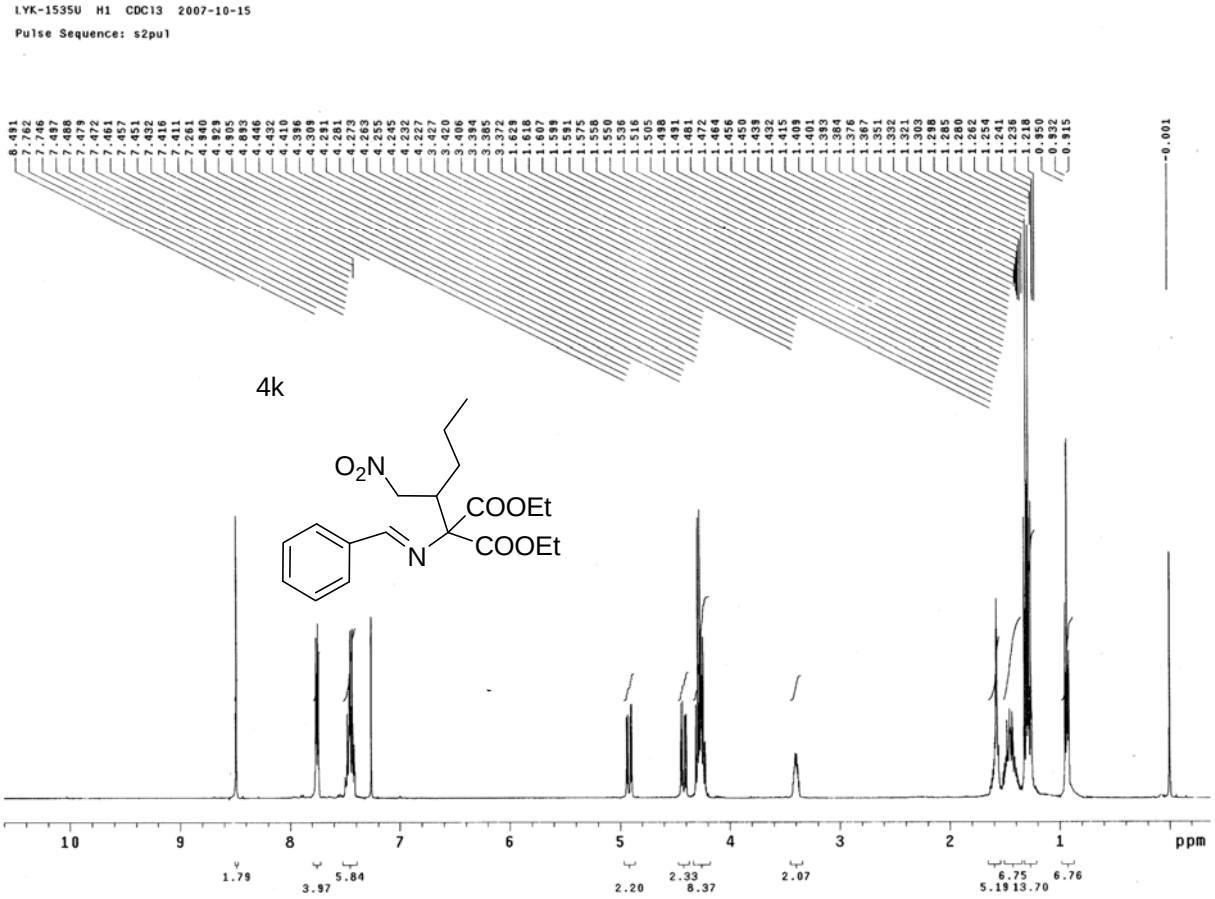
1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 200.500 ppm
F1 15131.29 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCM 10.05000 ppm/cm
HZCM 758.45099 Hz/cm



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.666	13065431	49.87	1209456	58.68
2	7.866	13132082	50.13	851547	41.32



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.771	178668	1.03	22613	1.99
2	8.216	17200896	98.97	1111971	98.01


LYK-1535U H1 CDCl3 2007-10-15
Pulse Sequence: s2pul
4k
O2N
COOEt
COOEt
N
ppm
1.79
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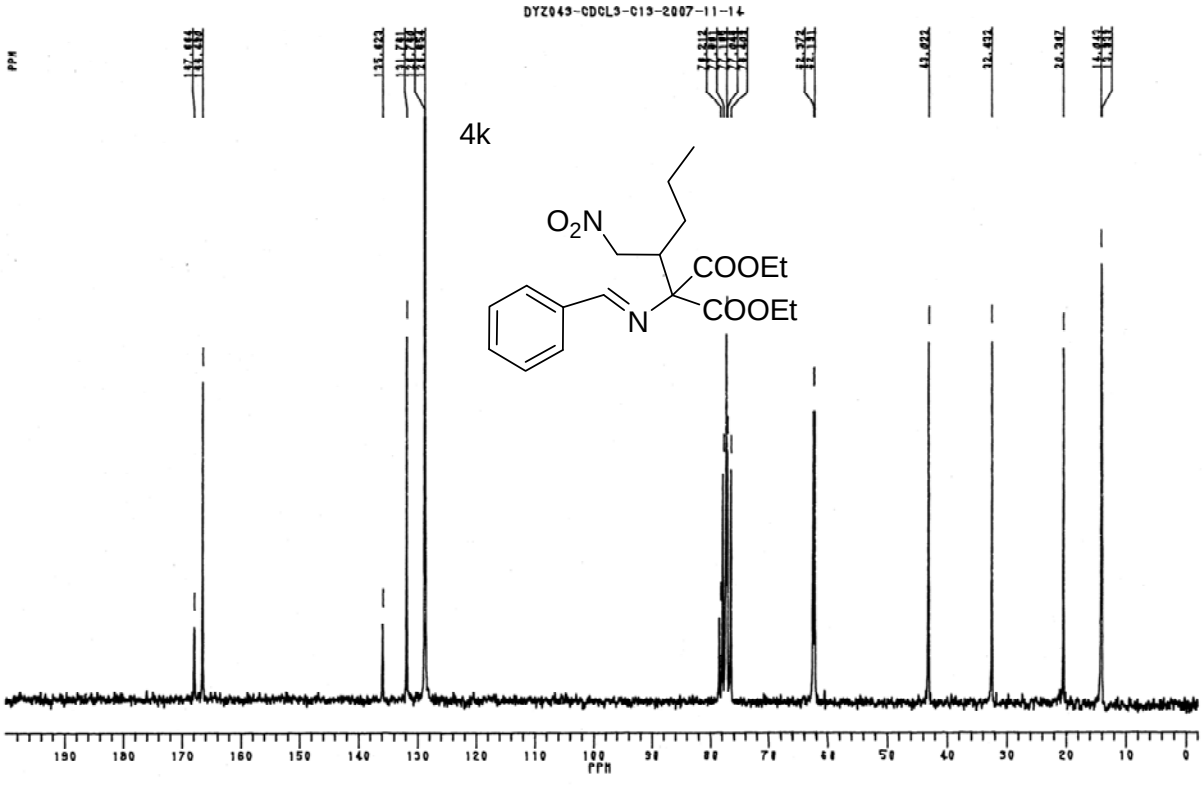
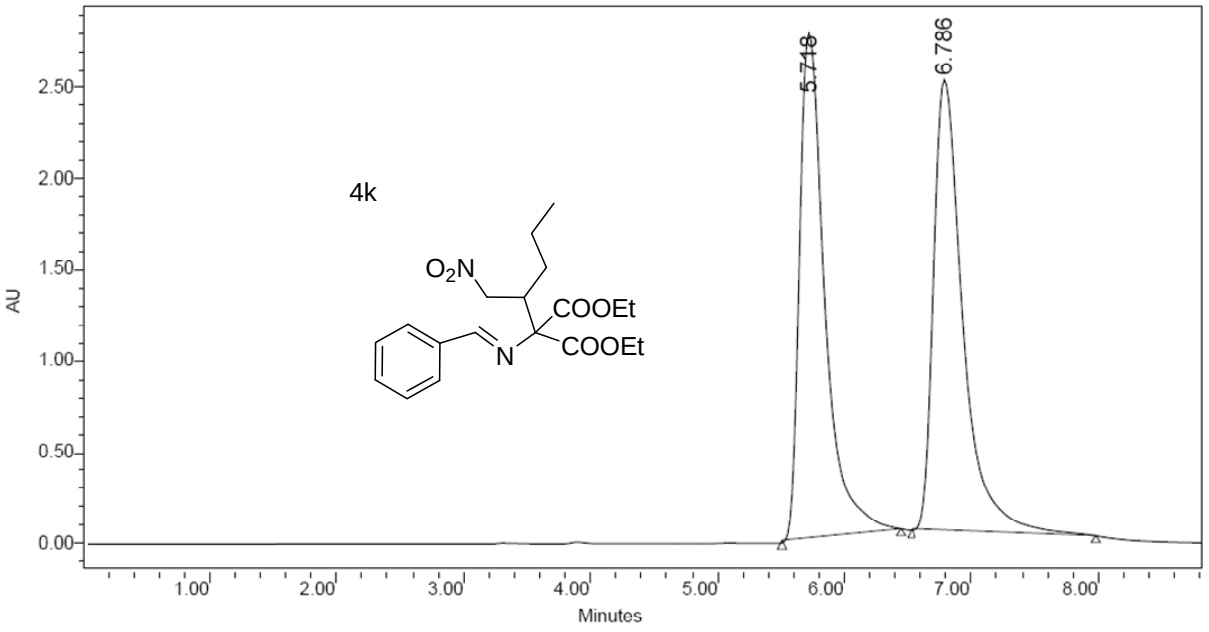
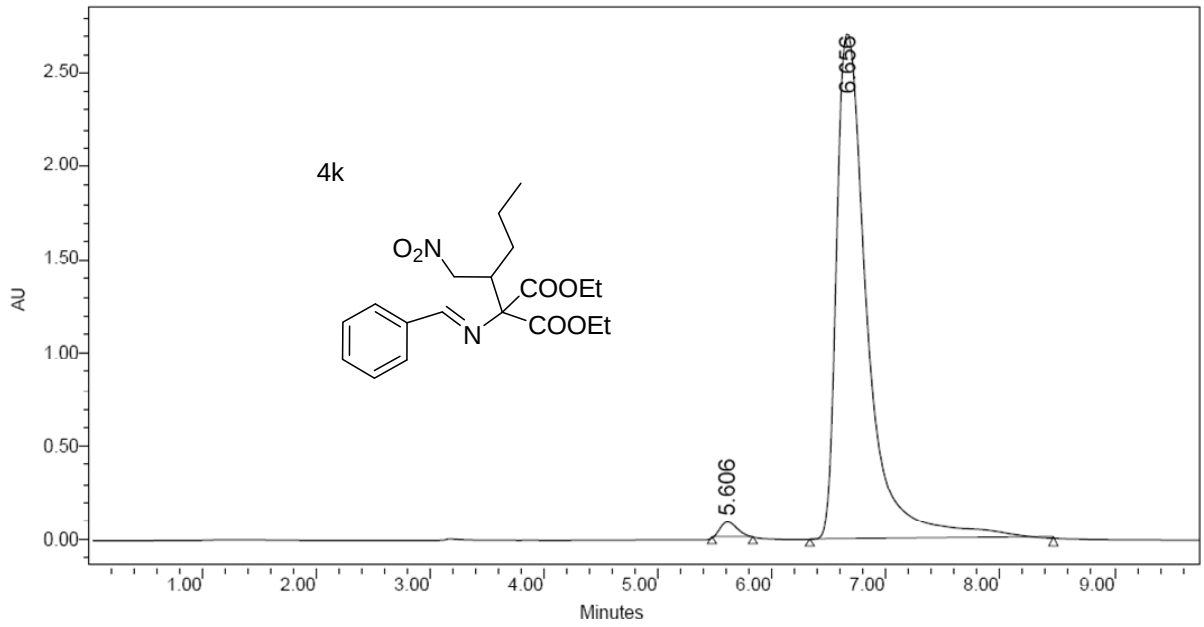
5.84
2.20
2.33
8.37
2.07
6.75
5.19
13.70
6.76

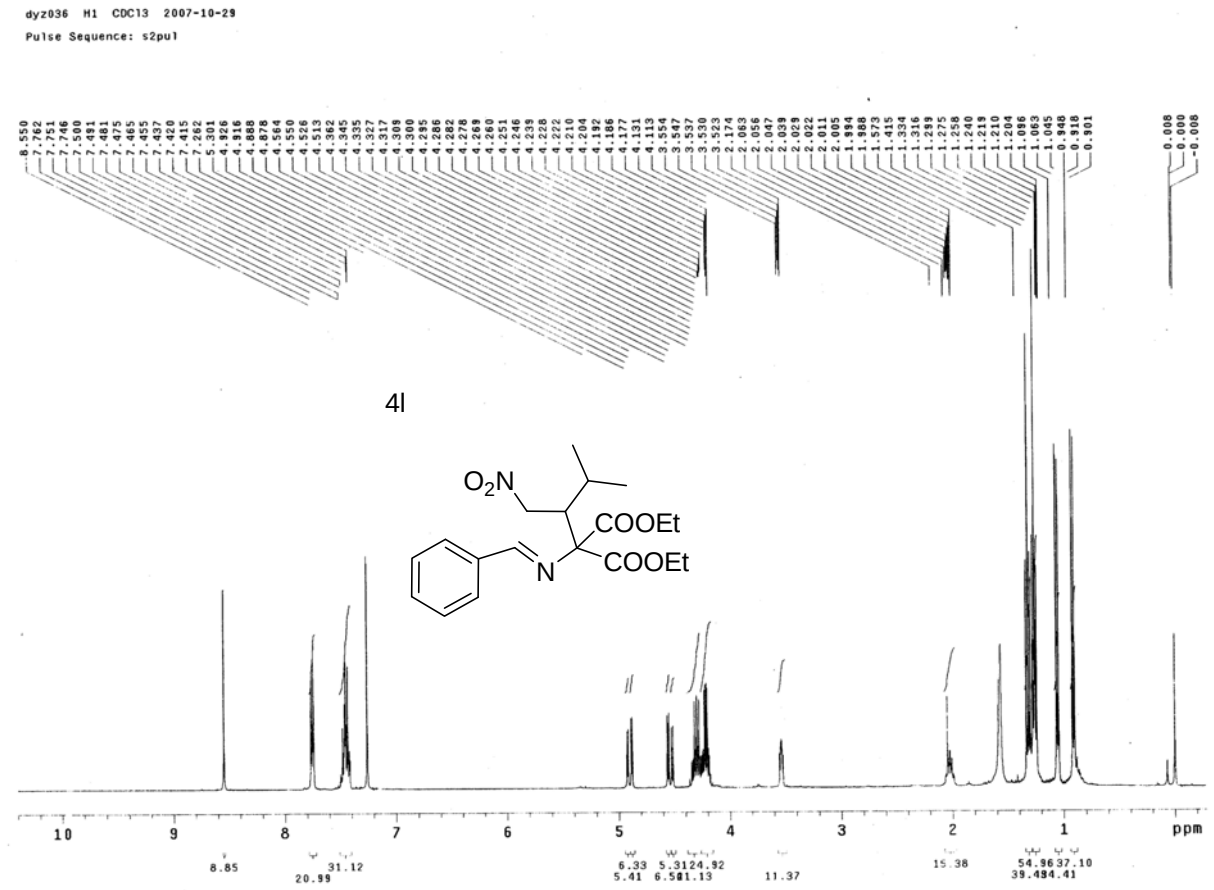

DYZ043-CDCL3-C13-2007-11-14
PPM
4k
O2N
COOEt
COOEt
N
PPM

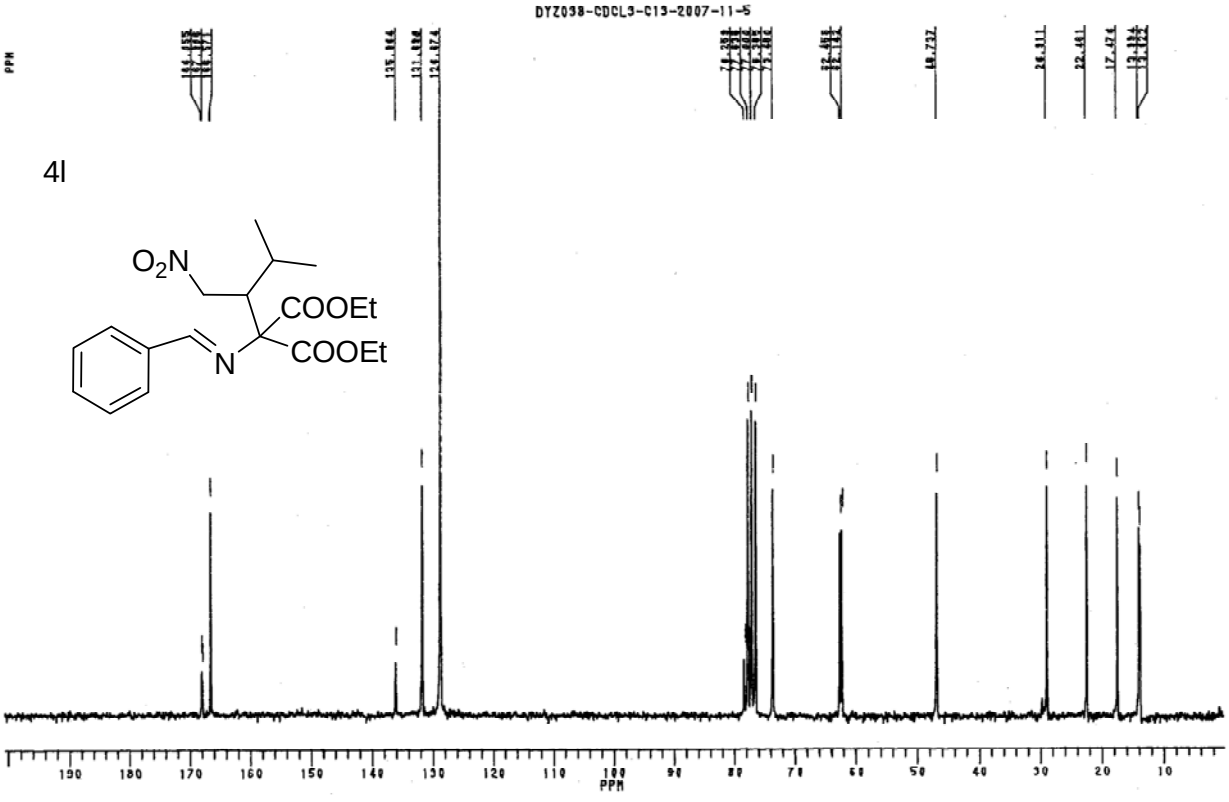


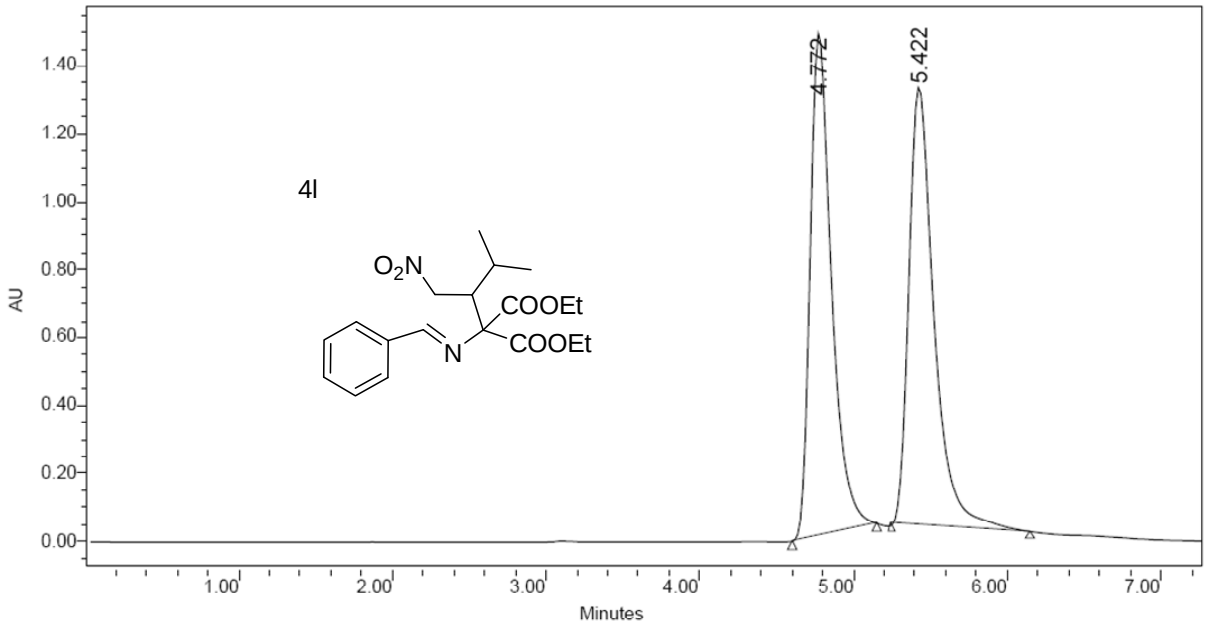
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.718	38585412	49.07	2776712	52.85
2	6.786	40049019	50.93	2477253	47.15



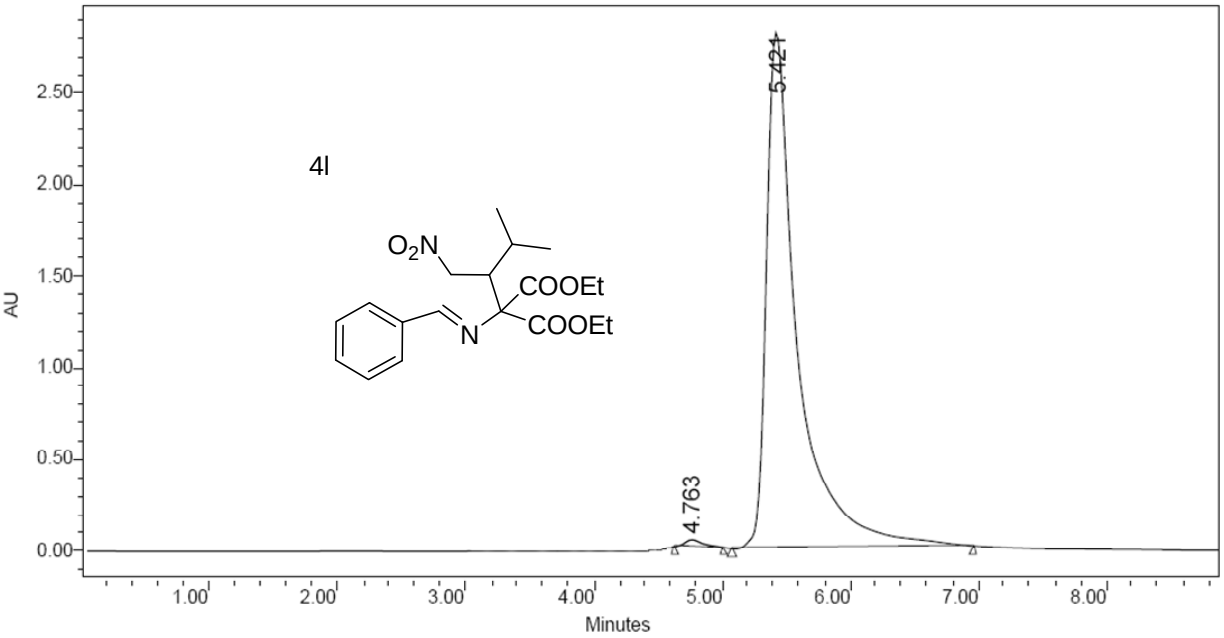
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.606	799788	1.54	78724	2.82
2	6.656	51072365	98.46	2711041	97.18


dyz036 H1 CDCl3 2007-10-29
Pulse Sequence: s2pul
4l
O2N
COOEt
COOEt
N
ppm

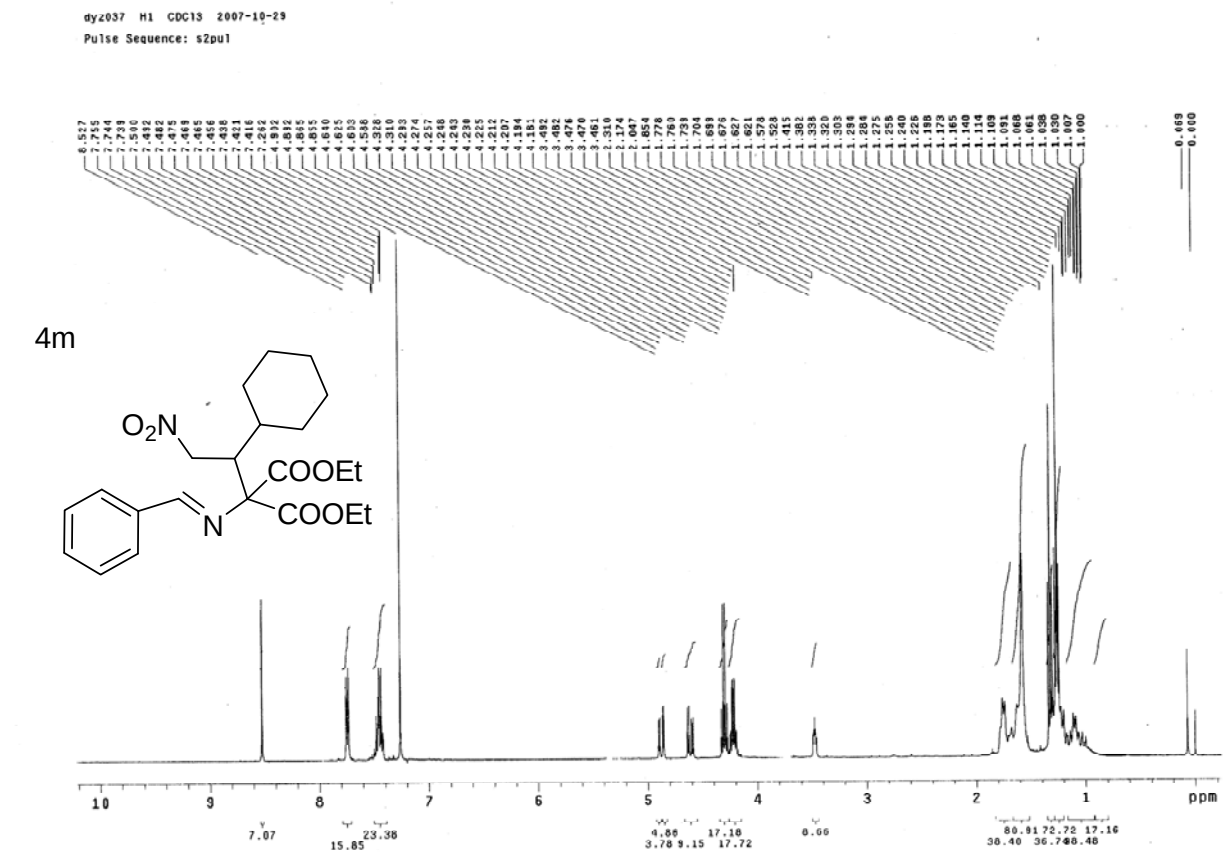

DYZ038-CDCL3-C13-2007-11-5
4l
O2N
COOEt
COOEt
N
PPM

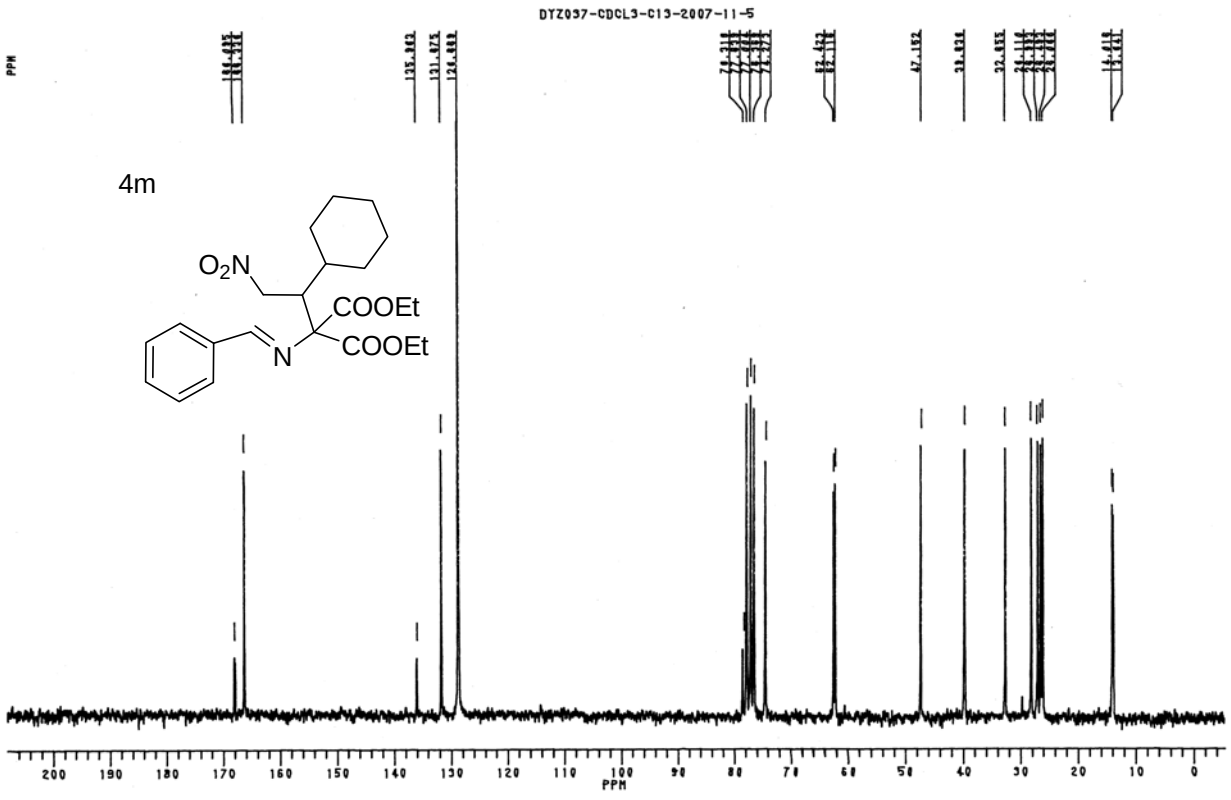


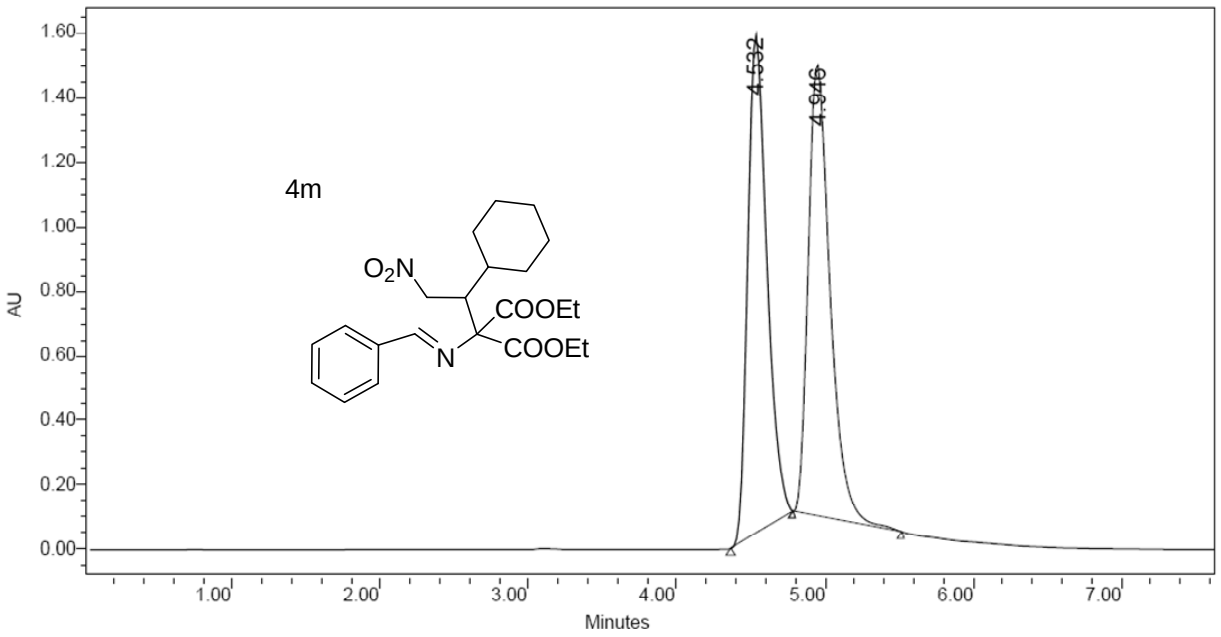
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	4.772	14264475	49.17	1481644	53.39
2	5.422	14744570	50.83	1293355	46.61



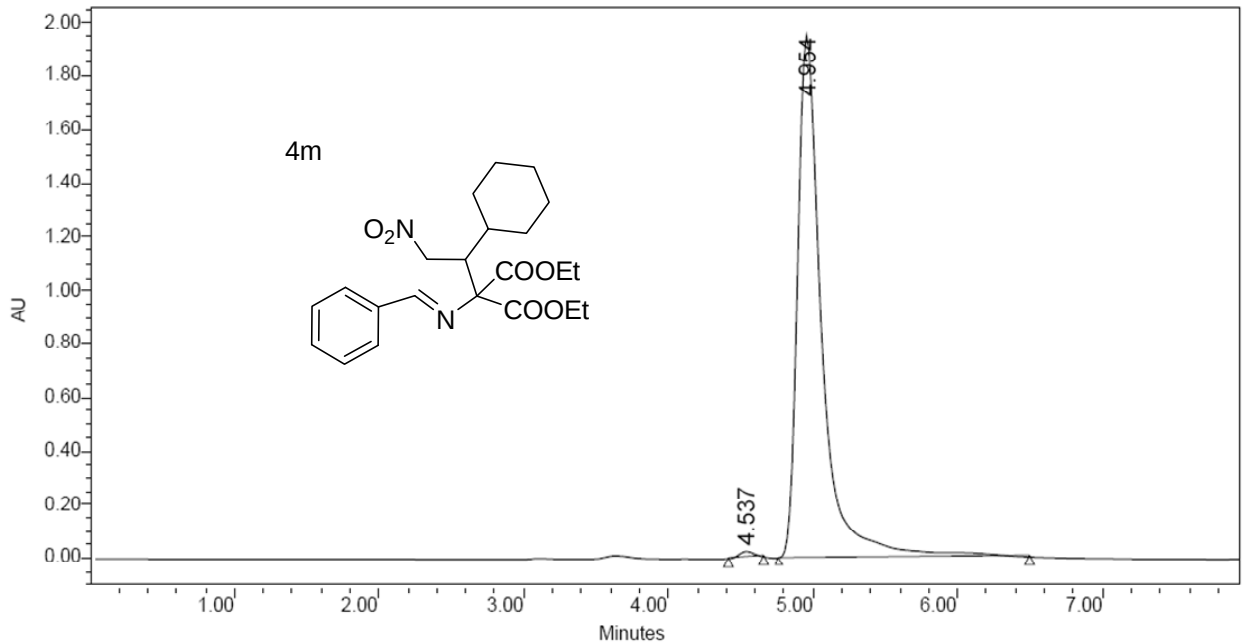
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	4.763	387059	0.80	39226	1.37
2	5.421	48008700	99.20	2816114	98.63


dyz037 H1 CDCl3 2007-10-29
Pulse Sequence: s2pul
4m
O_2N
COOEt
COOEt
N
ppm

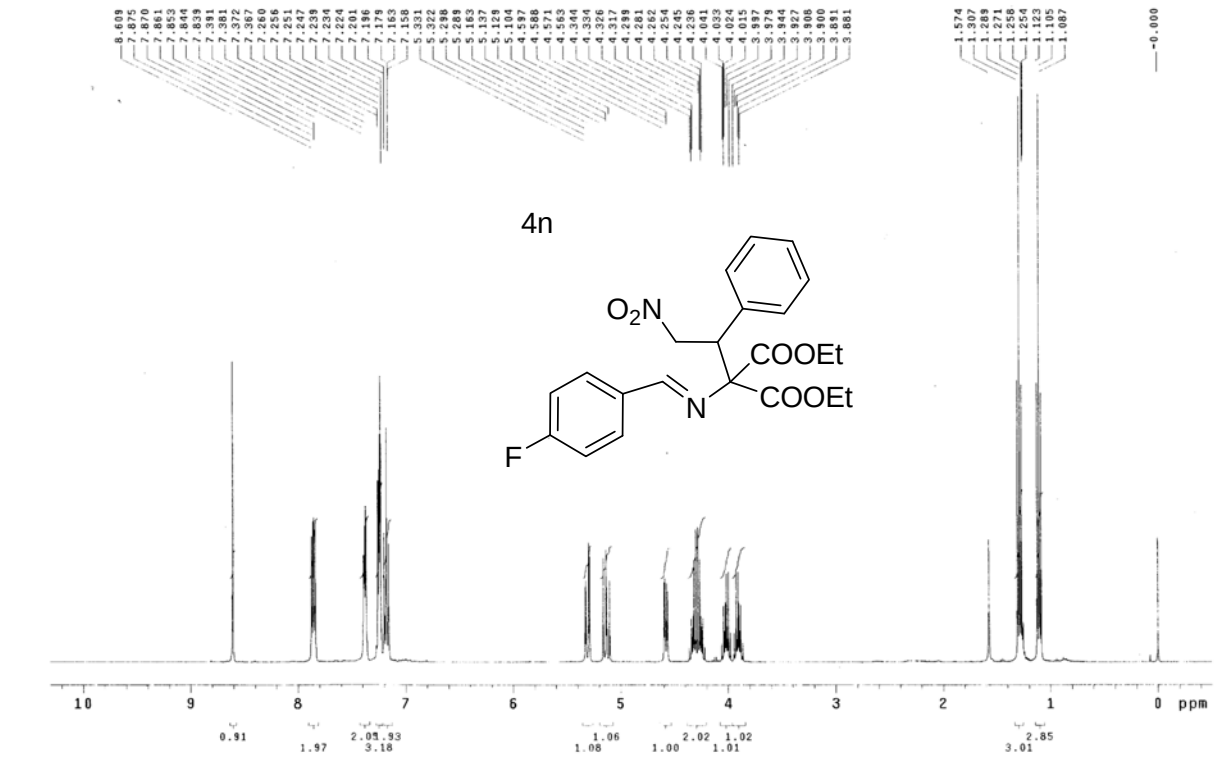

DYZ037-CDCL3-C13-2007-11-5
PPM
4m
O_2N
COOEt
COOEt
N



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	4.532	14048308	49.39	1545859	52.42
2	4.946	14392656	50.61	1403294	47.58



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	4.537	178011	0.77	24320	1.23
2	4.954	22928123	99.23	1951029	98.77


4n
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COOEt
COOEt
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F
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9
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7
6
5
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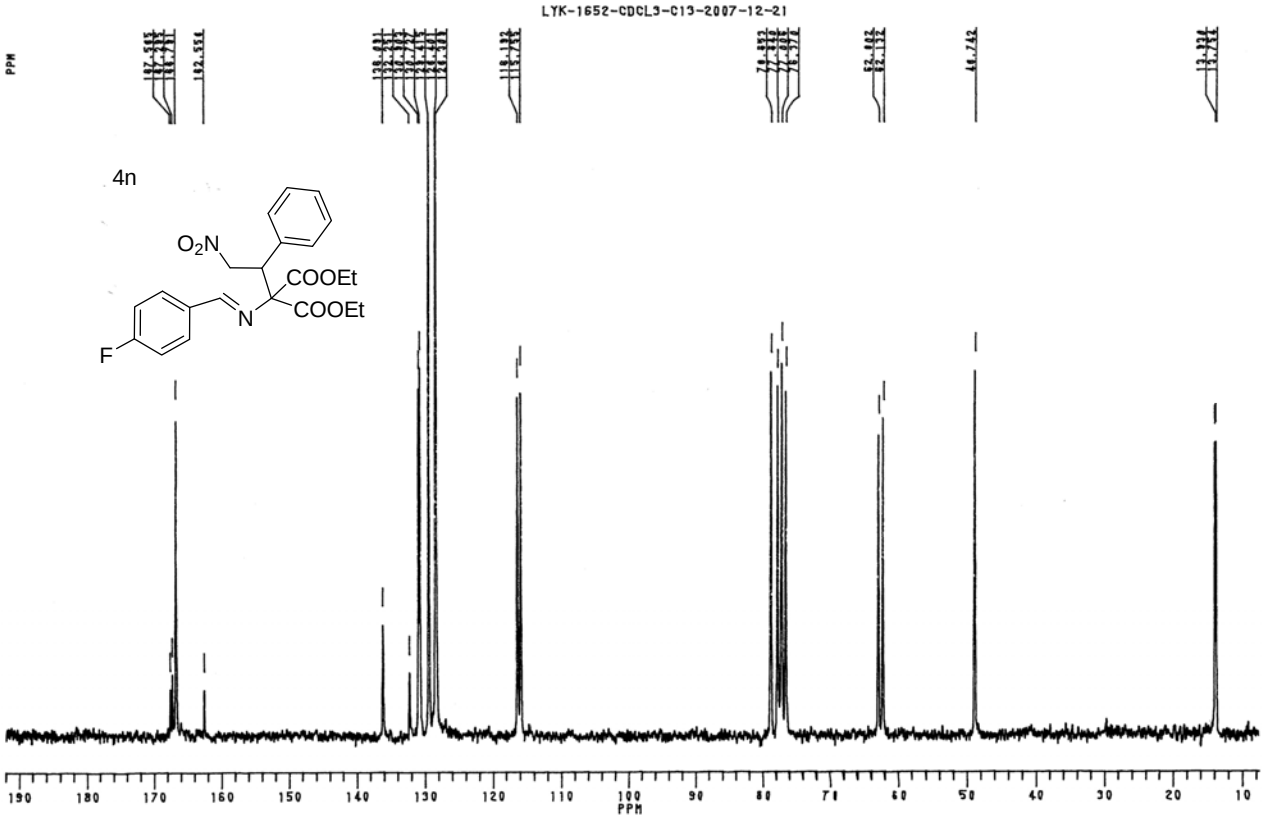
3
2
1
0 ppm


LYK-1652-CDCL3-C13-2007-12-21
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COOEt
COOEt
N
F
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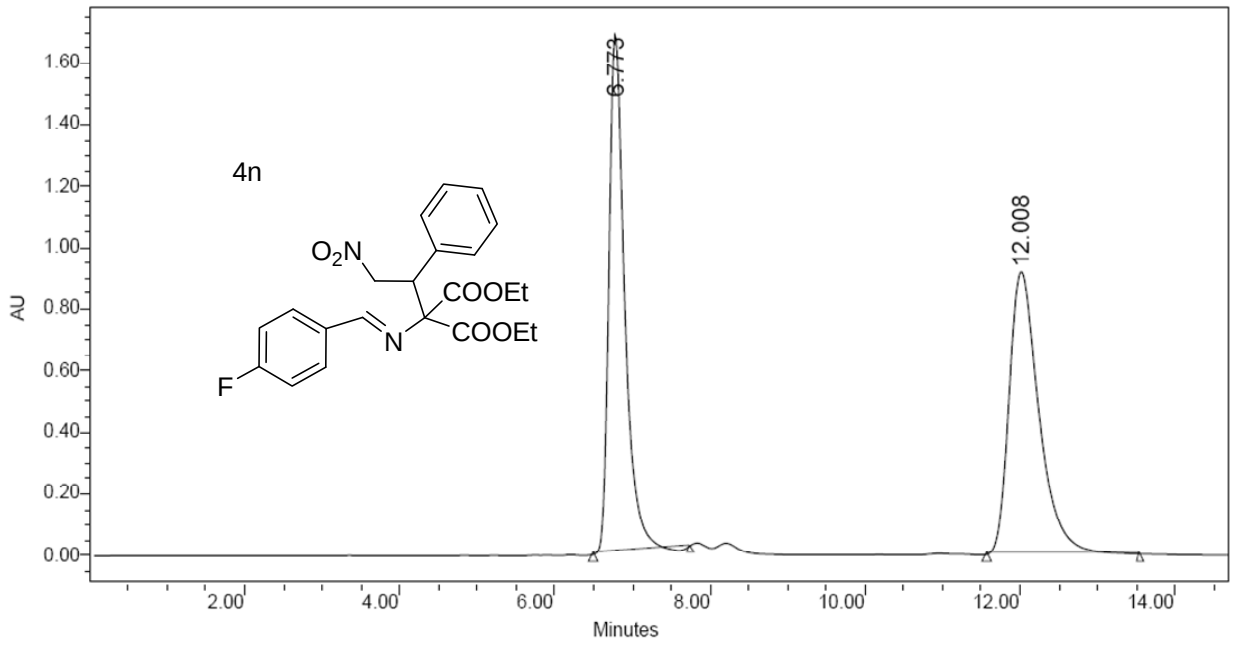
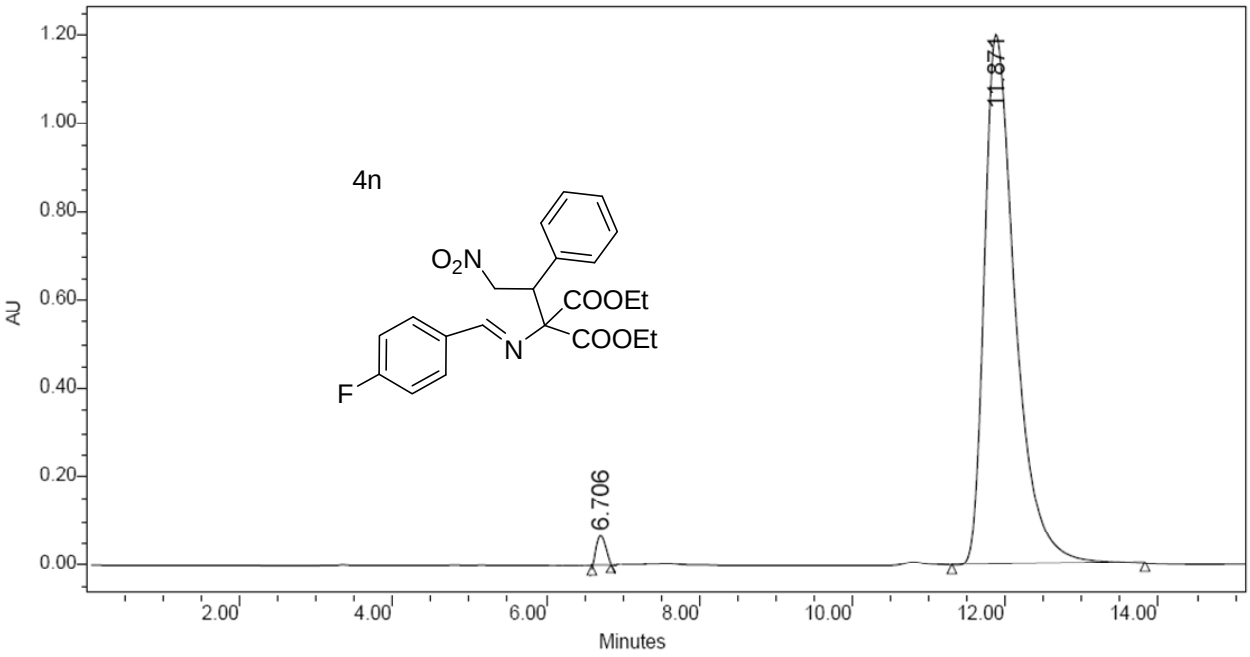
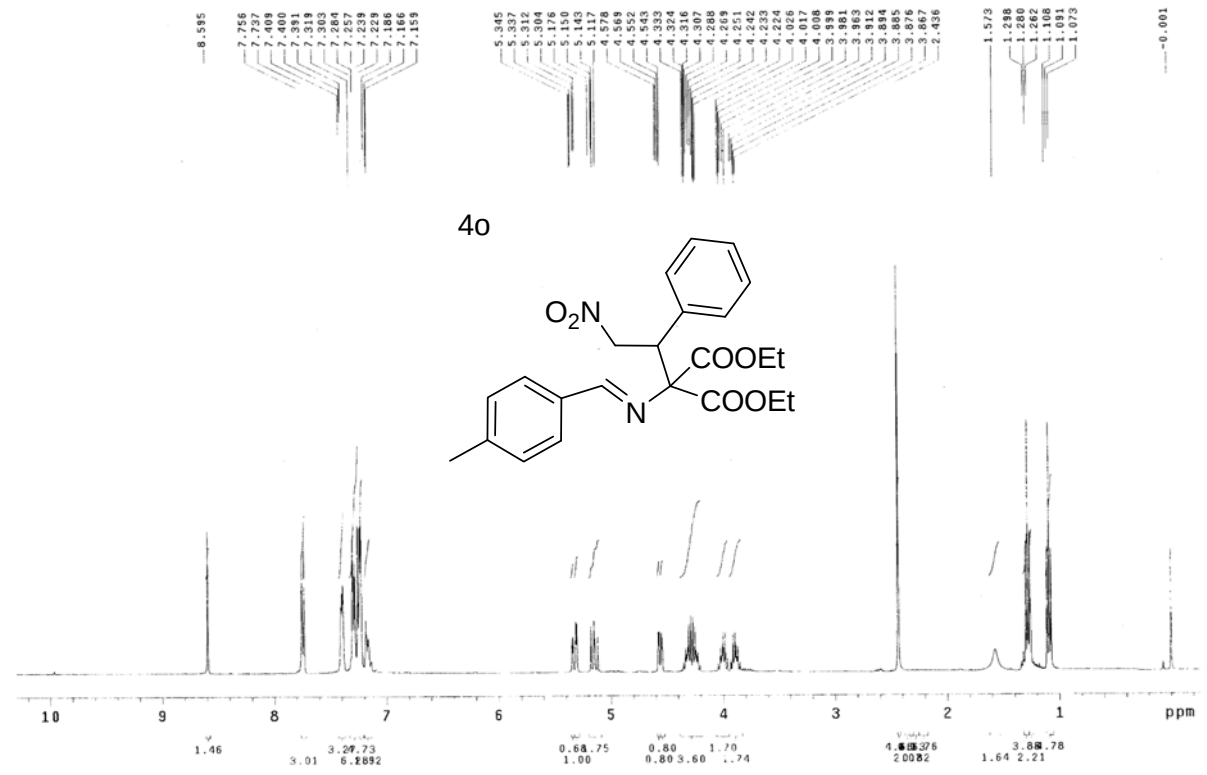
10
PPM

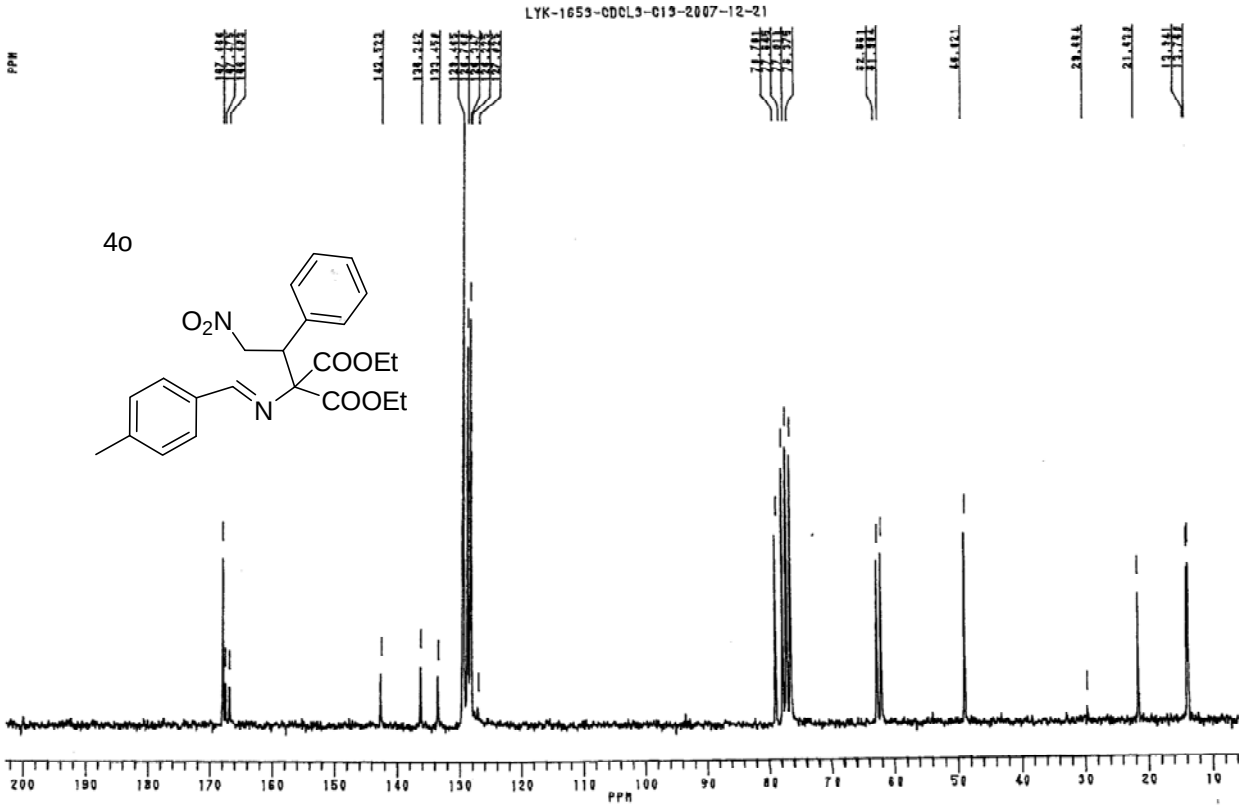


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.773	23931980	49.32	1682872	64.74
2	12.008	24593458	50.68	916412	35.26



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.706	609620	1.77	69756	5.49
2	11.871	33840379	98.23	1201126	94.51


4o
O_2N
COOEt
COOEt
N
ppm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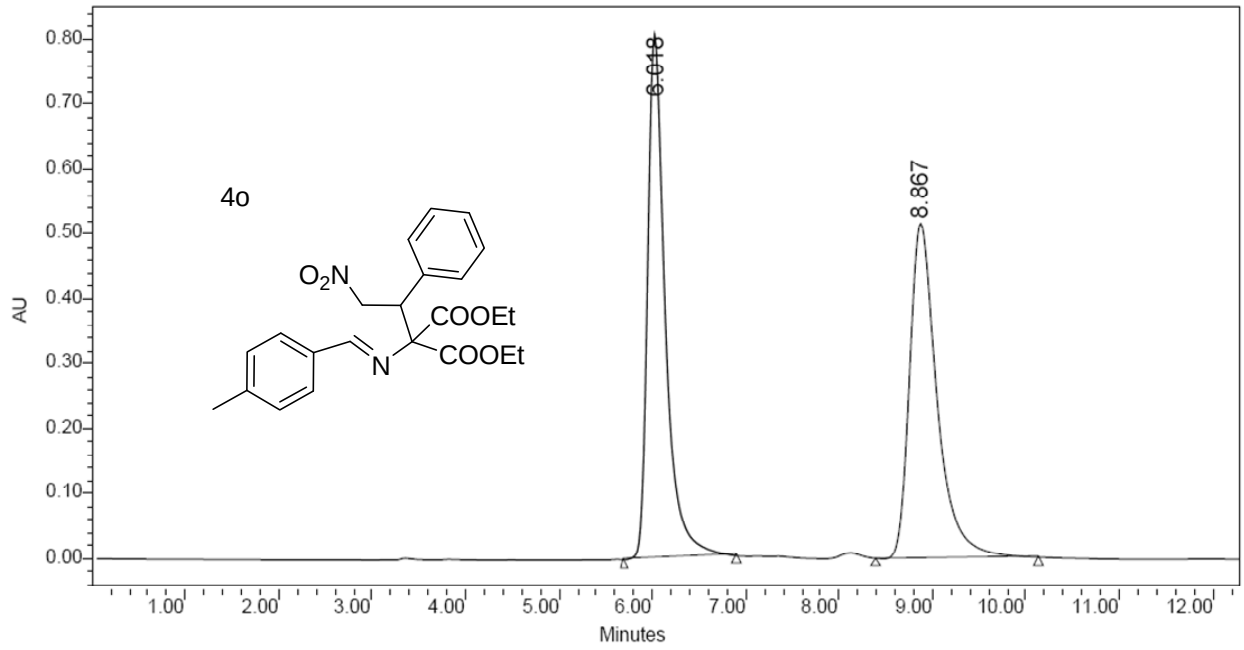
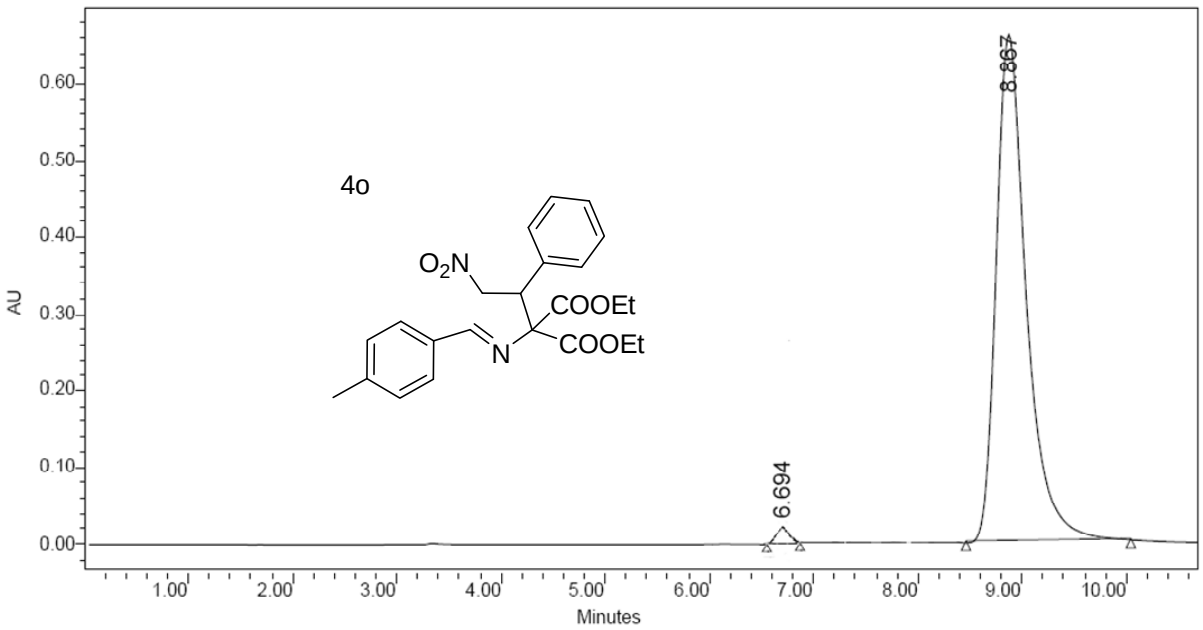
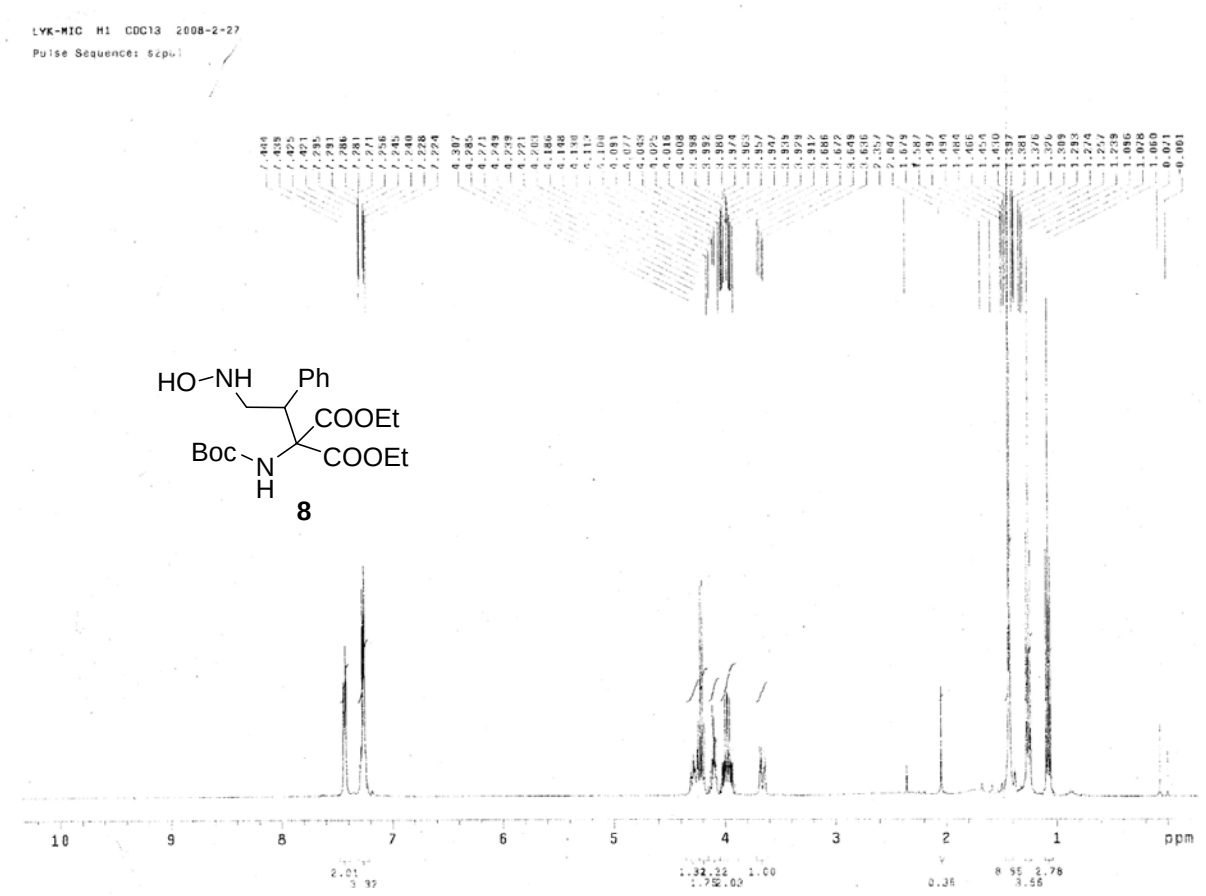
O_2N
COOEt
COOEt
N
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.018	10652941	50.22	806607	61.01
2	8.867	10557558	49.78	515472	38.99



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.694	197702	1.46	51427	7.22
2	8.867	13358292	98.54	660539	92.78


LYK-MIC H1 CDCl3 2008-2-27
HO–NH
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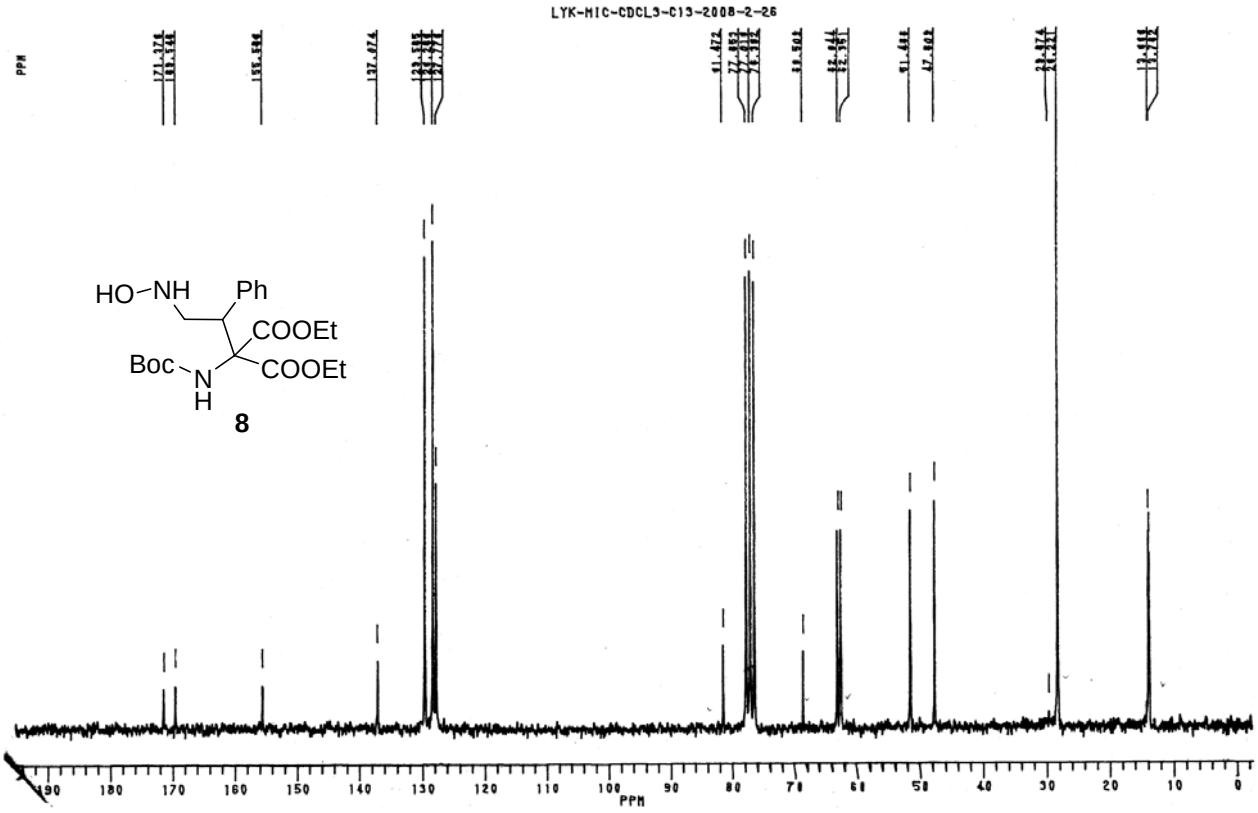
COOEt
Boc
N
H
COOEt
8
10
9
8
7
6
5
4
3
2
1
ppm


LYK-MIC-CDCL3-C13-2008-2-26
PPM
HO–NH
Ph
COOEt
Boc
N
H
COOEt
8
190
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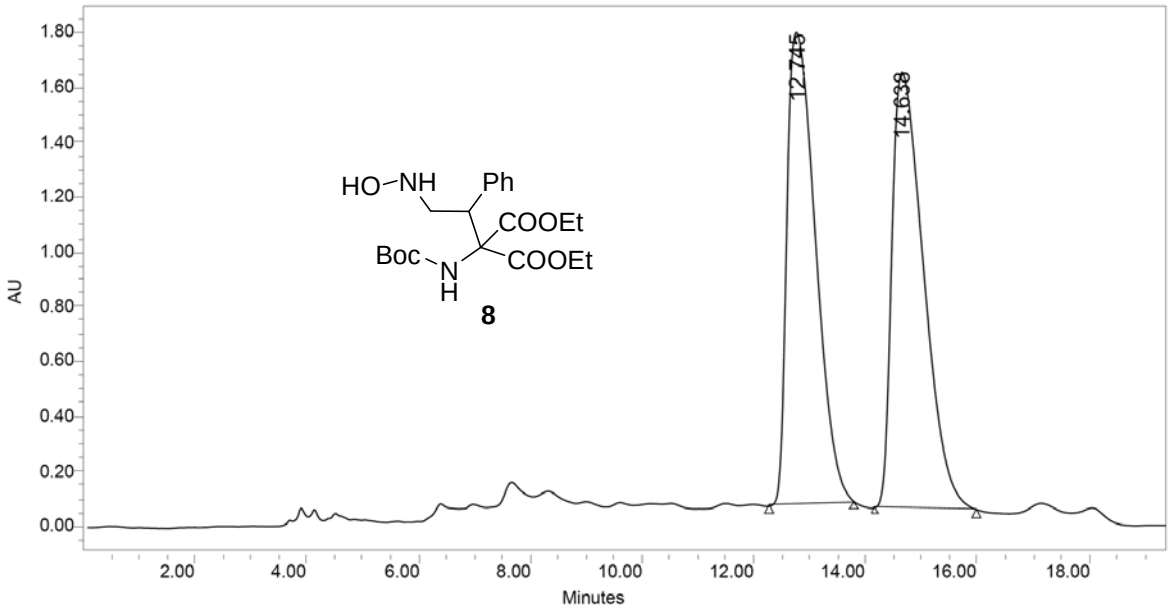
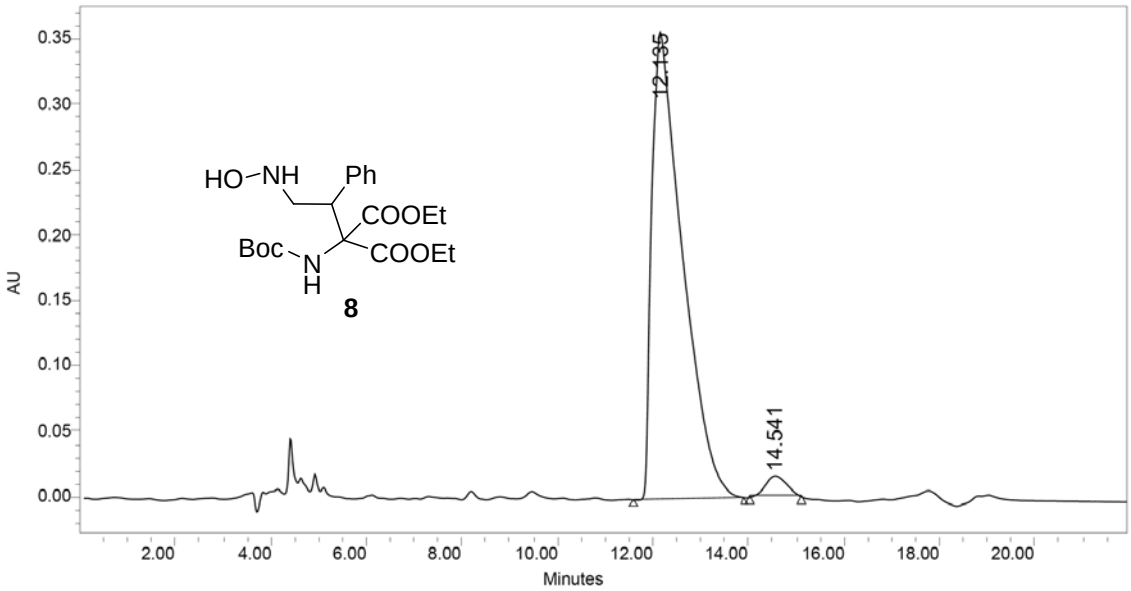
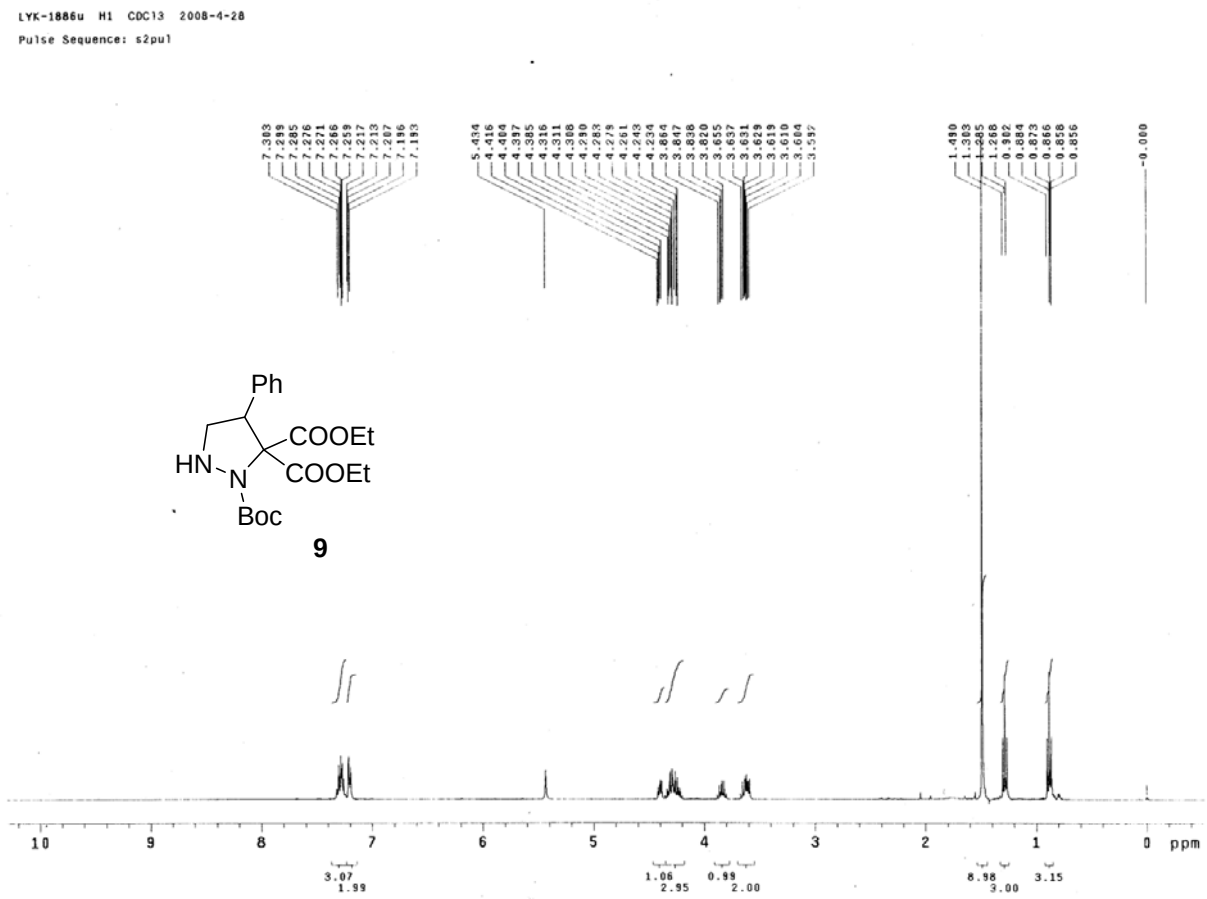
10
0
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.745	61202258	49.44	1722993	52.01
2	14.638	62594077	50.56	1589896	47.99



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.135	15927653	96.92	356412	95.66
2	14.541	505871	3.08	16175	4.34


LYK-1886u H1 CDCl3 2008-4-28
Pulse Sequence: s2pul
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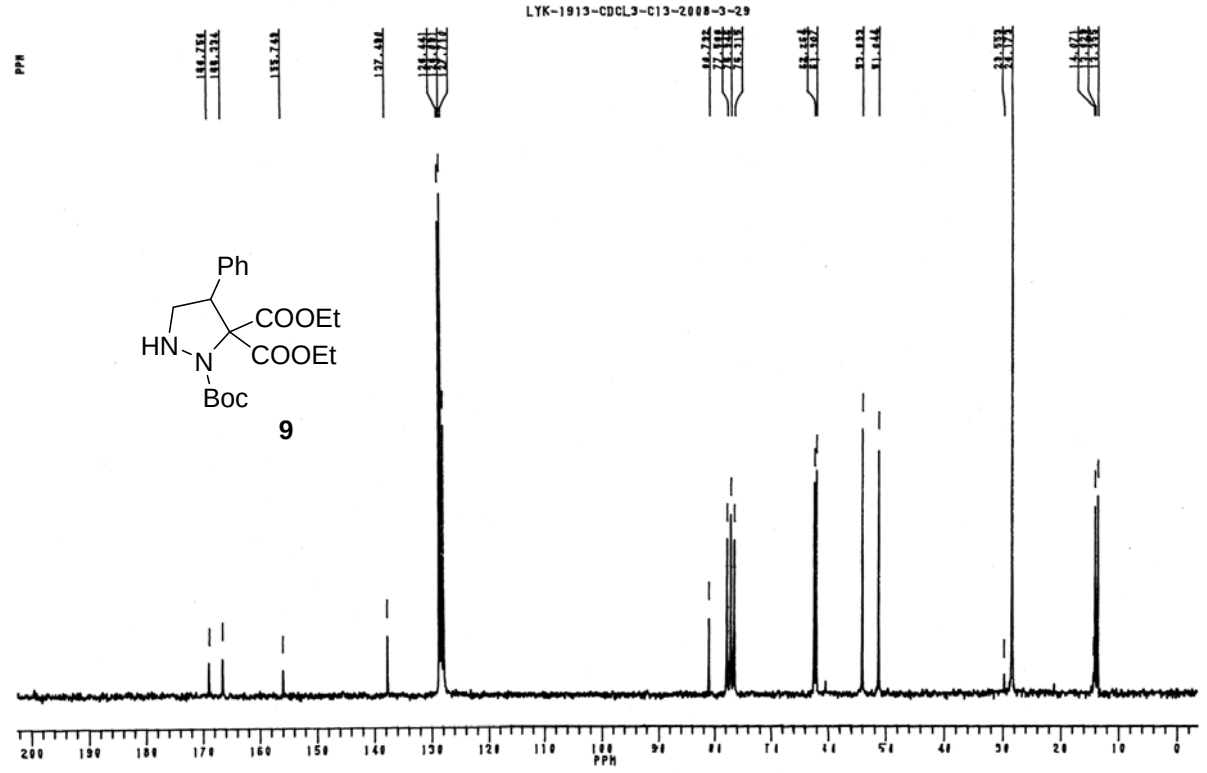
COOEt
HN
N
Boc
9
ppm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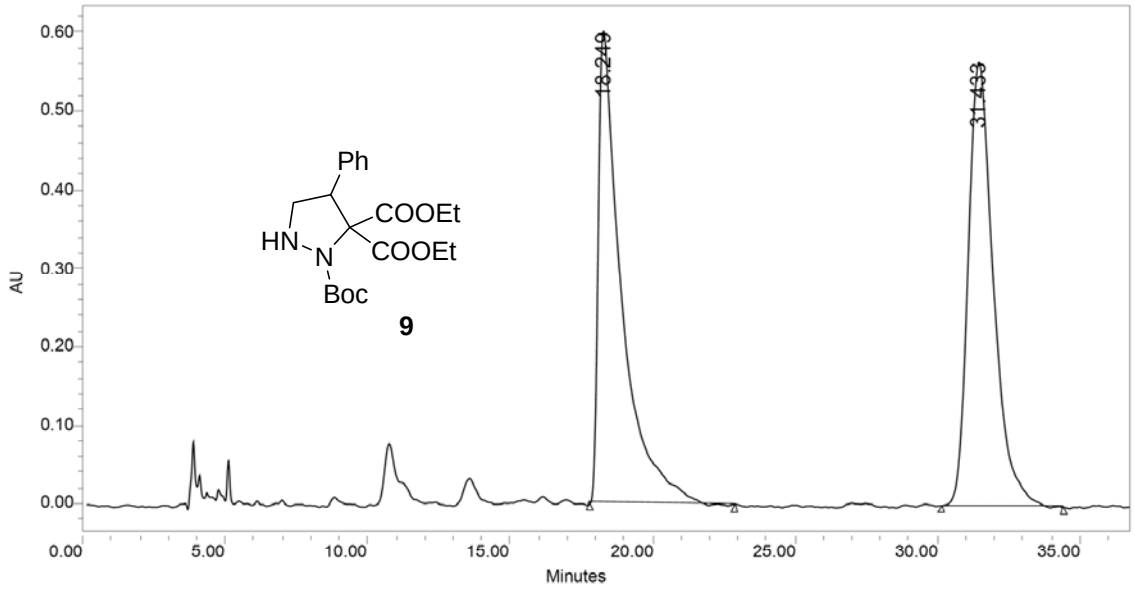
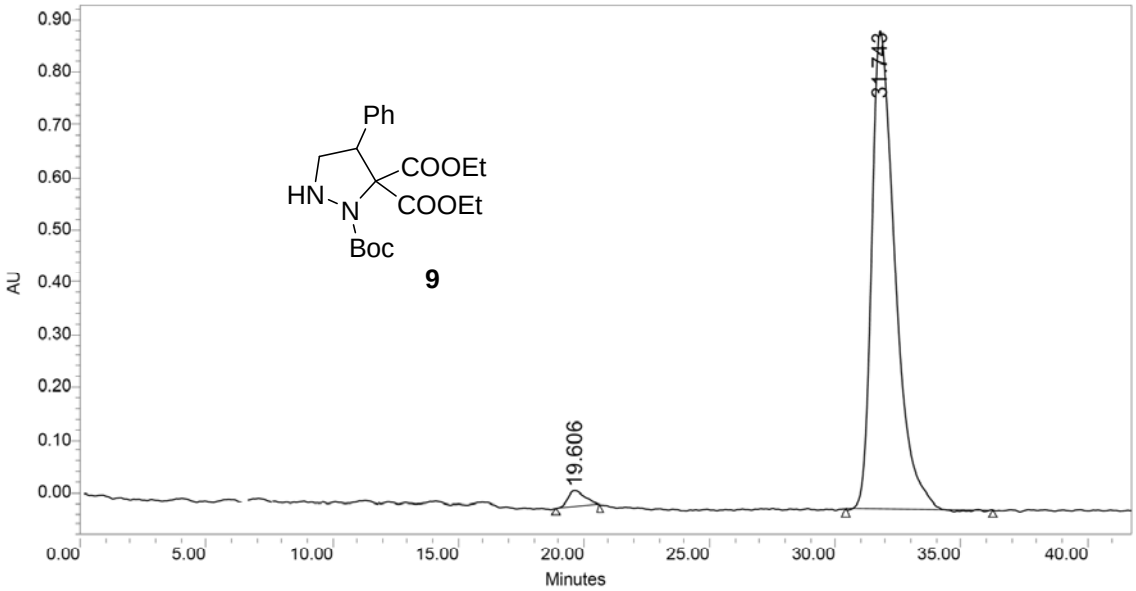
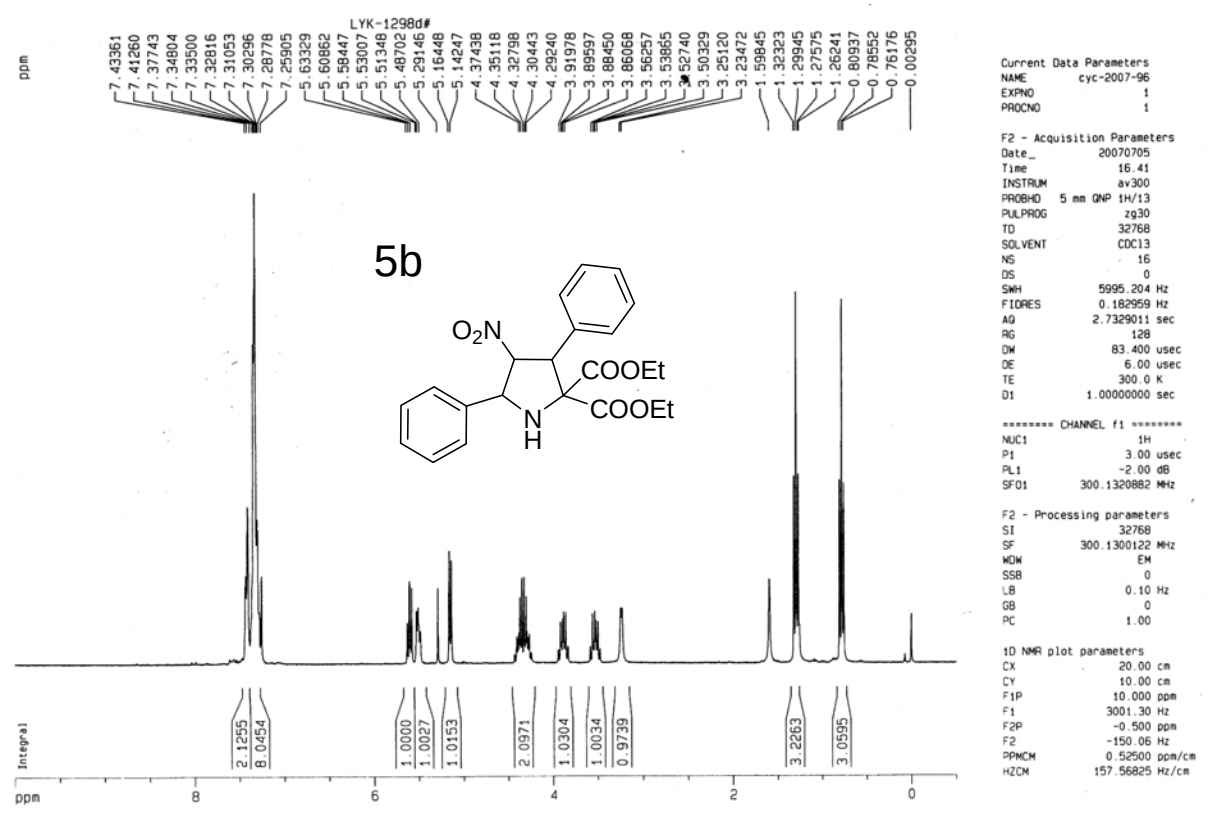
PPM
Ph
COOEt
COOEt
HN
N
Boc
9



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	18.249	34163802	49.47	599773	51.50
2	31.433	34890523	50.53	564826	48.50



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	19.606	1520097	2.51	31180	3.31
2	31.743	59141644	97.49	910614	96.69



Current Data Parameters
NAME cyc-2007-96
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070705
Time 16.41
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
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F2P -0.500 ppm
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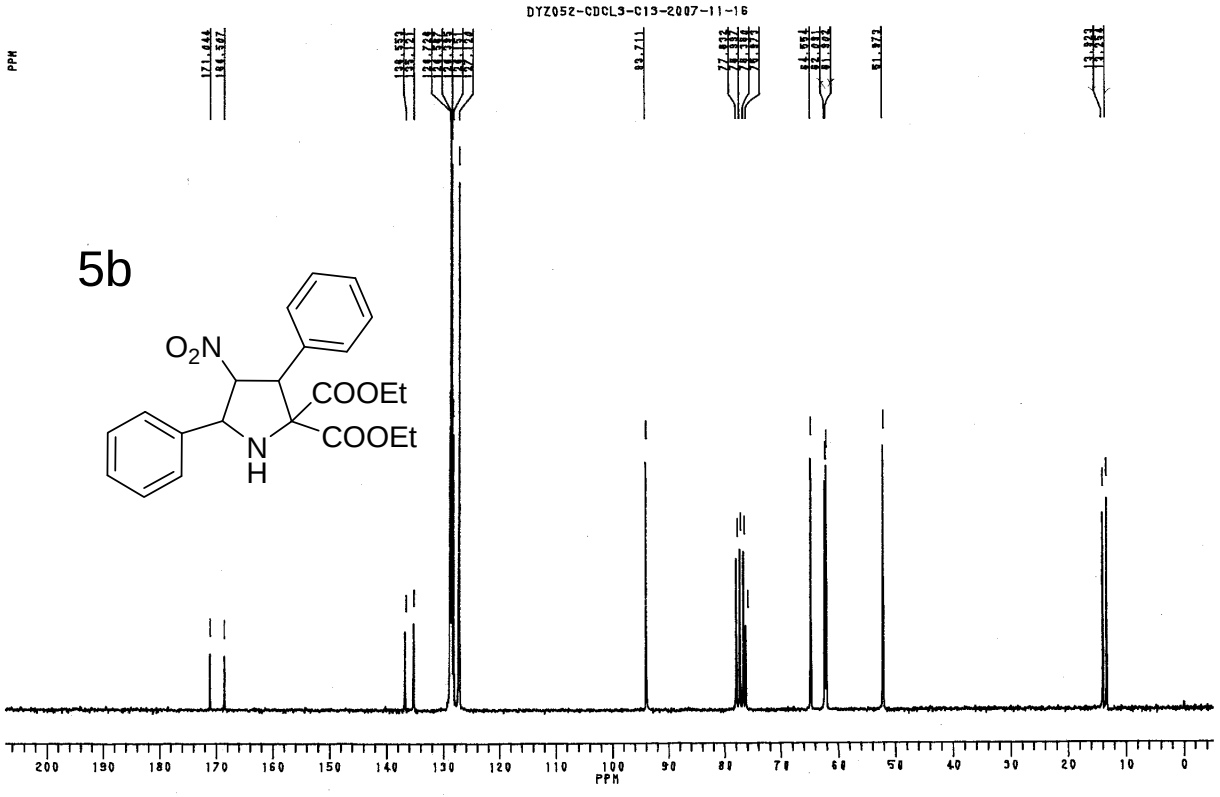
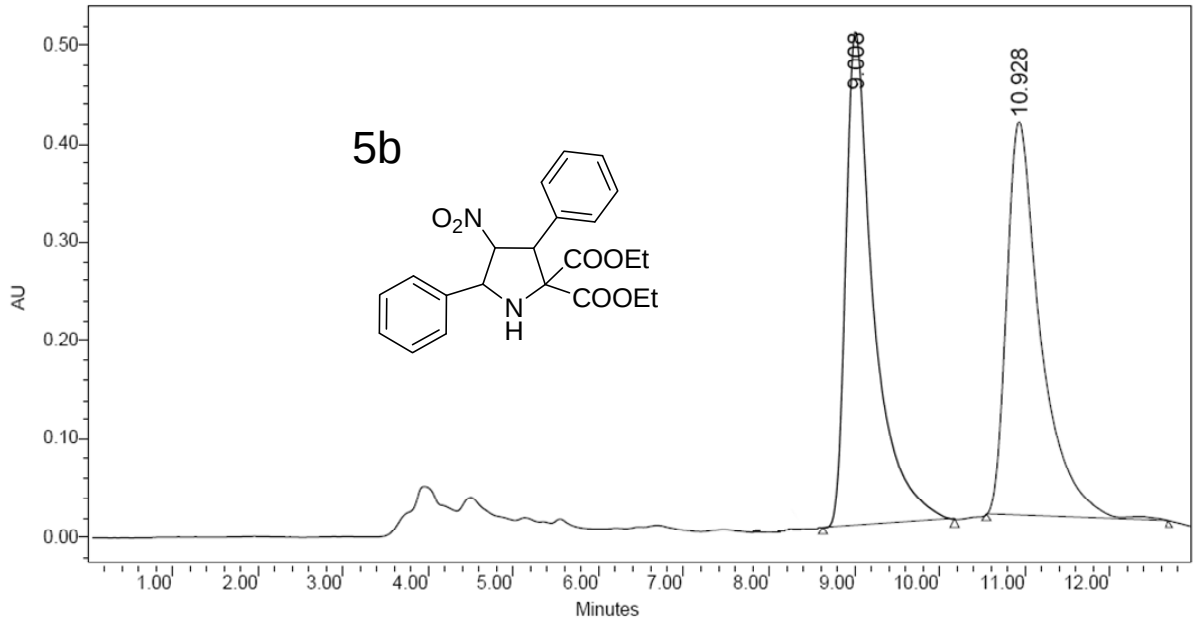
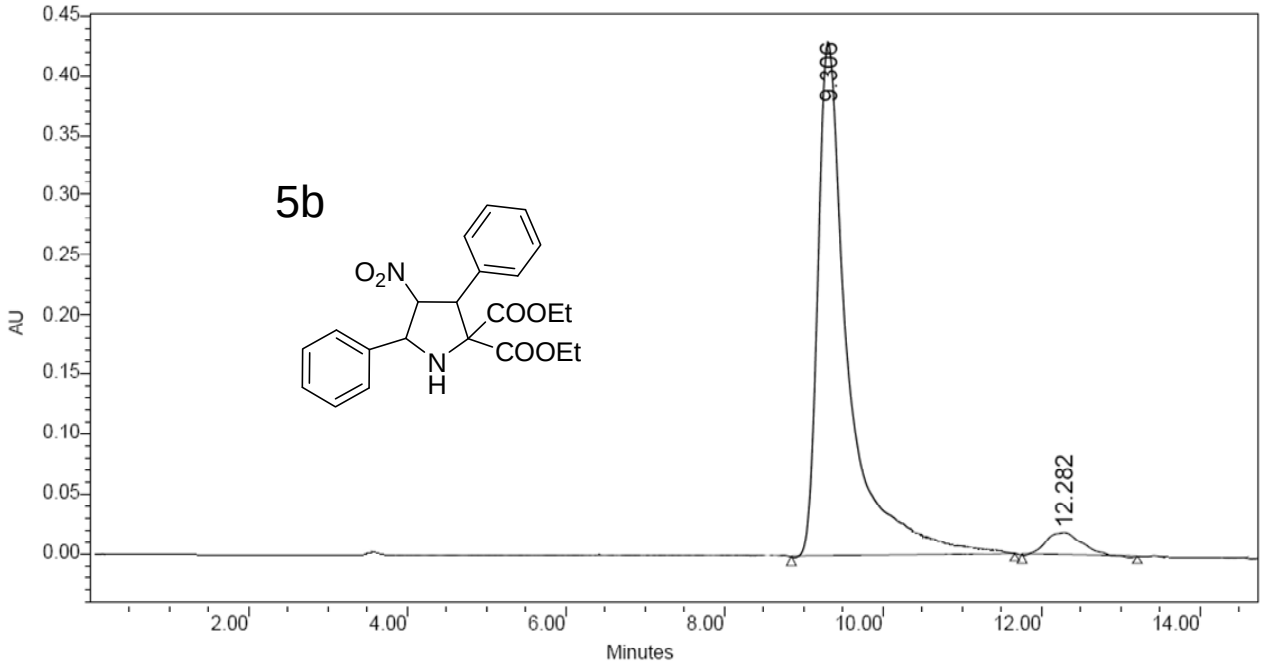
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm

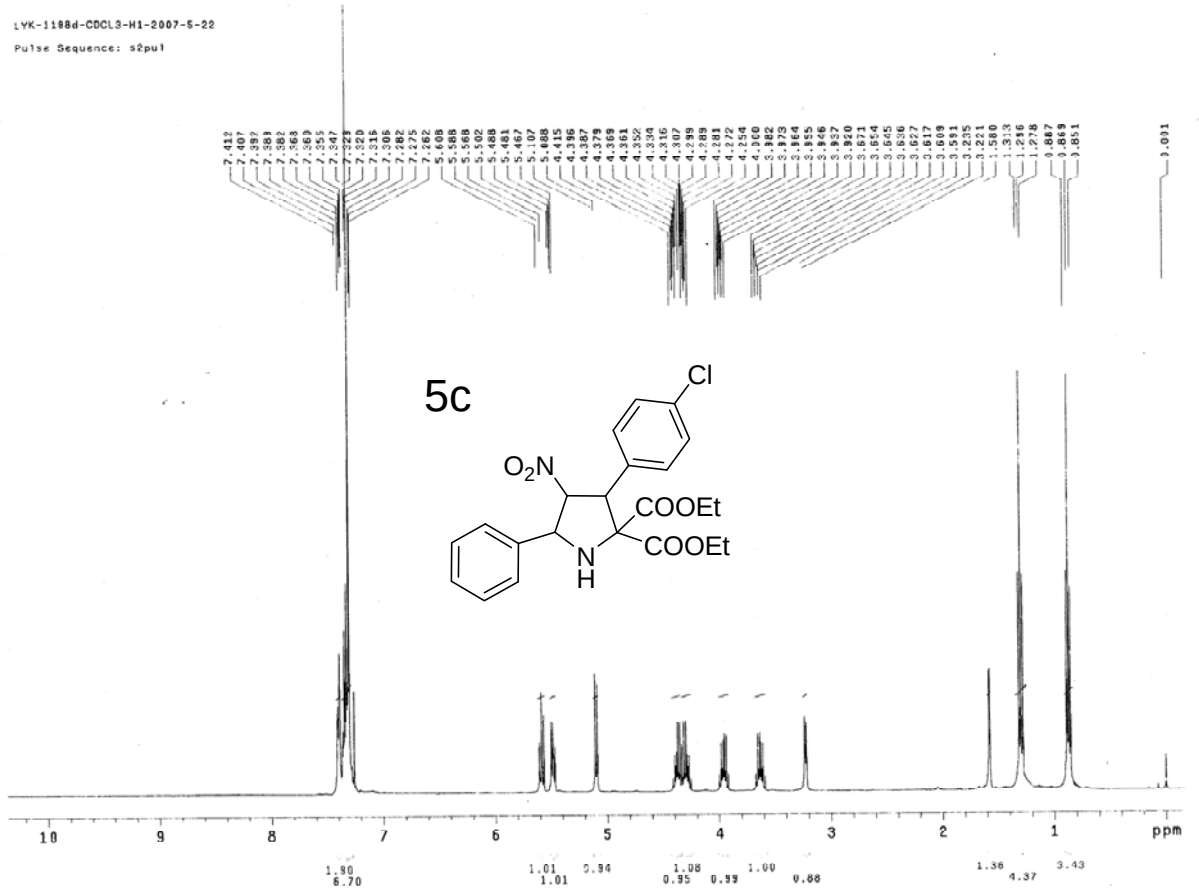




	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.008	11463359	50.67	502086	55.61
2	10.928	11161825	49.33	400809	44.39



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.306	12508168	95.04	430782	95.62
2	12.282	652496	4.96	19754	4.38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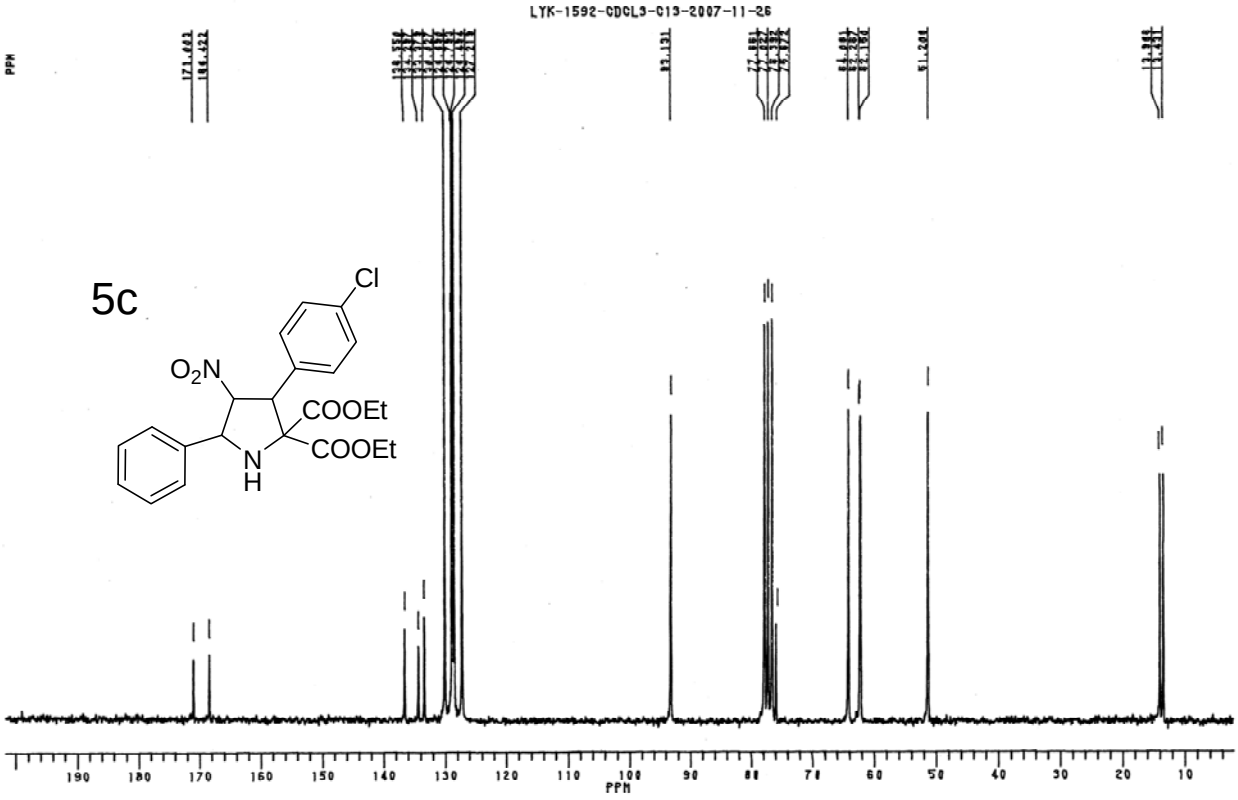
COOEt
COOEt
N
H
ppm


LYK-1592-CDCL3-C13-2007-11-26
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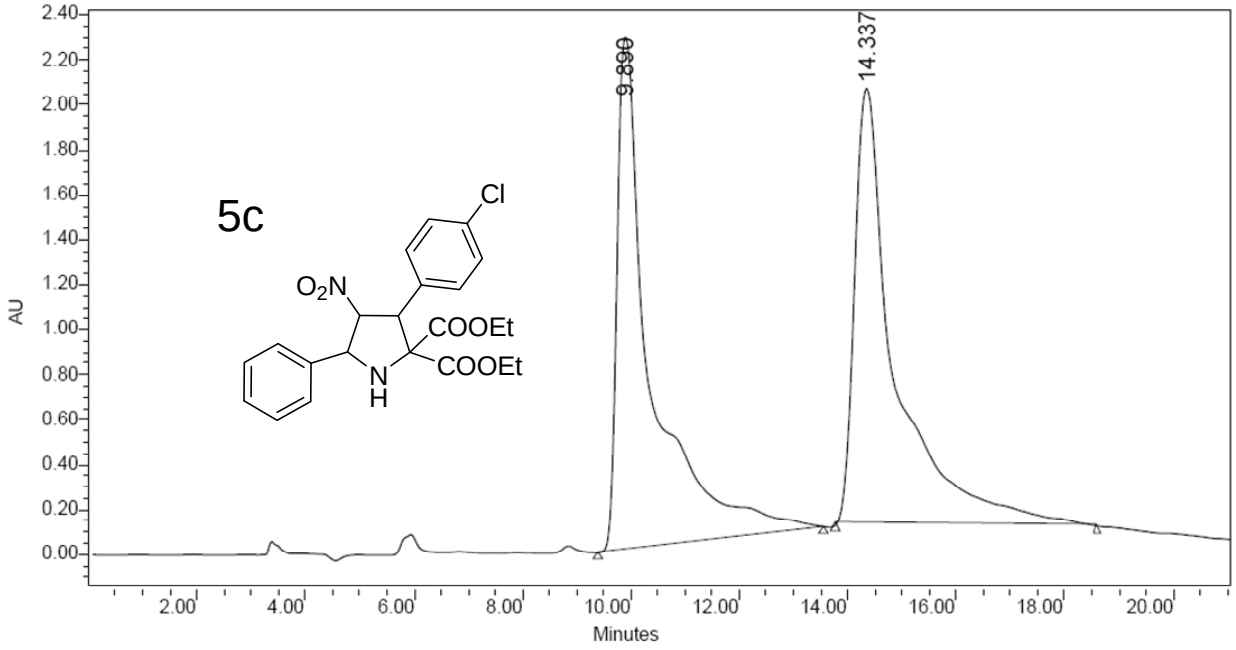
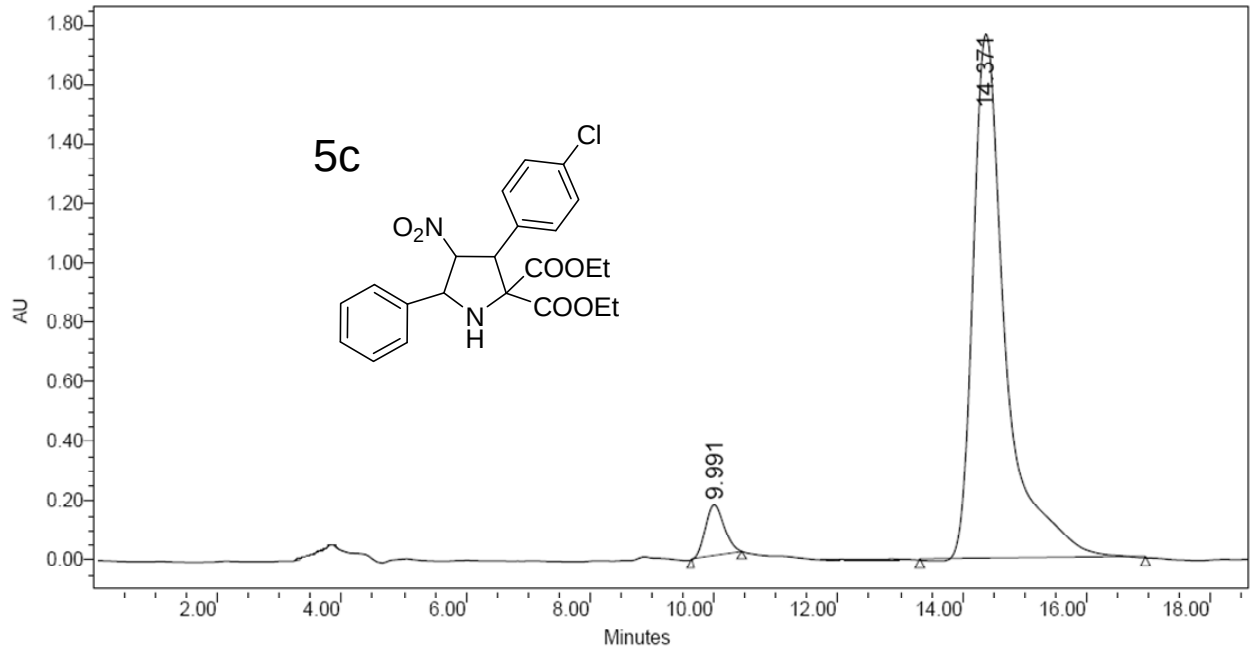
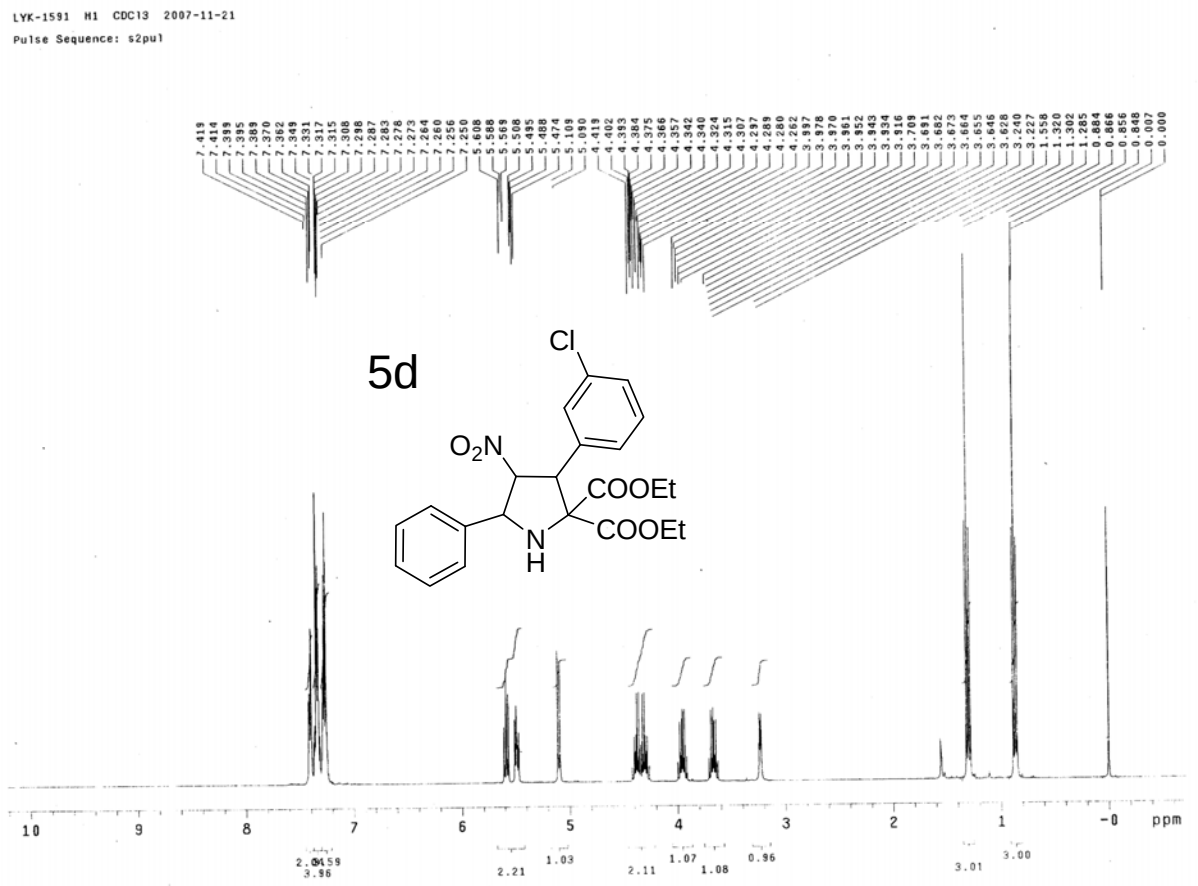
N
H



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.890	100797944	49.73	2278708	54.06
2	14.337	101893587	50.27	1936346	45.94



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.991	3679014	5.37	173954	8.95
2	14.371	64806680	94.63	1769168	91.05


LYK-1591 H1 CDCl3 2007-11-21
Pulse Sequence: s2pul
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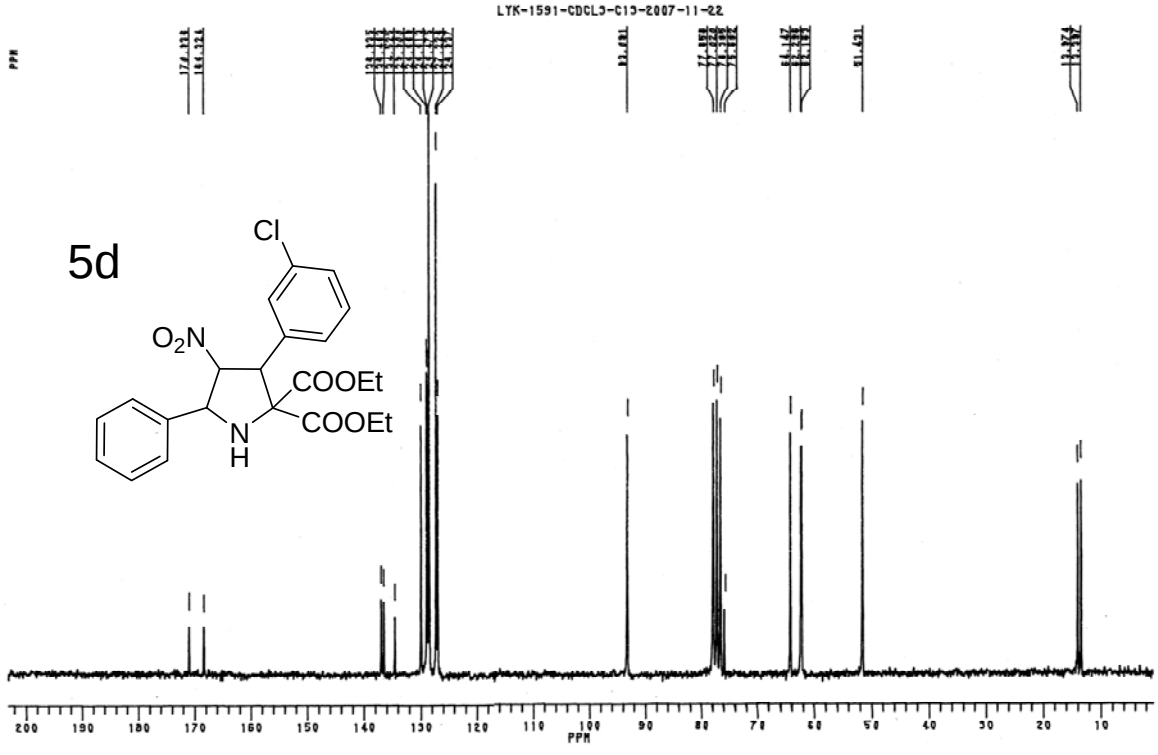
COOEt
COOEt
N
H
ppm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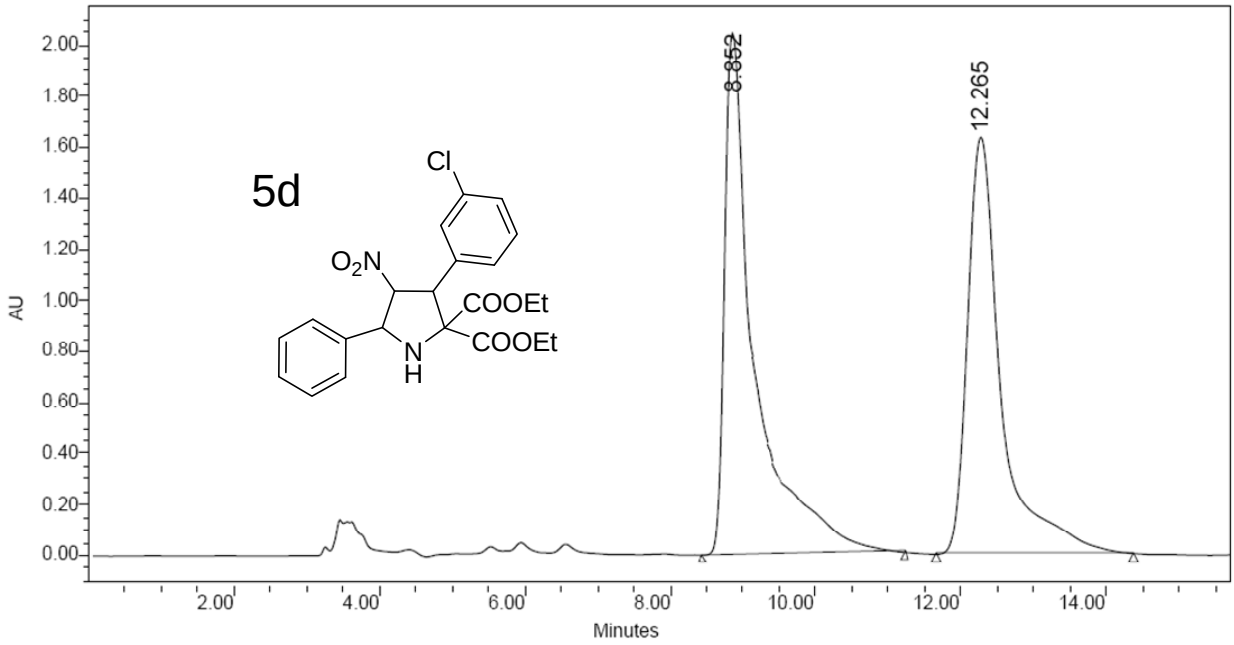
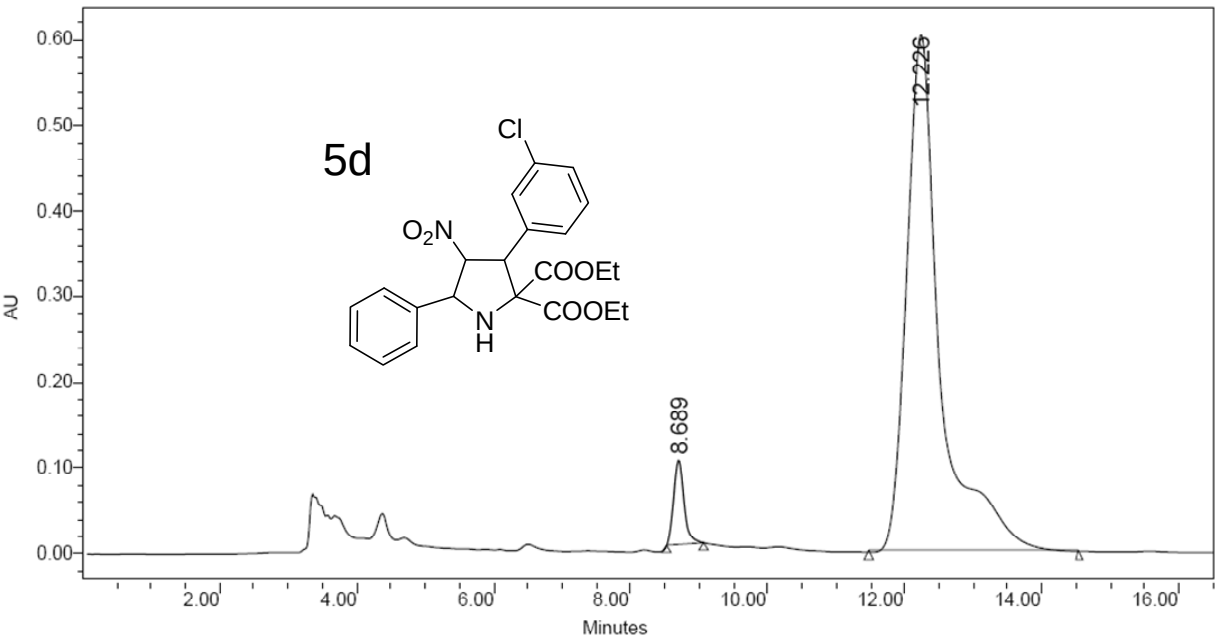
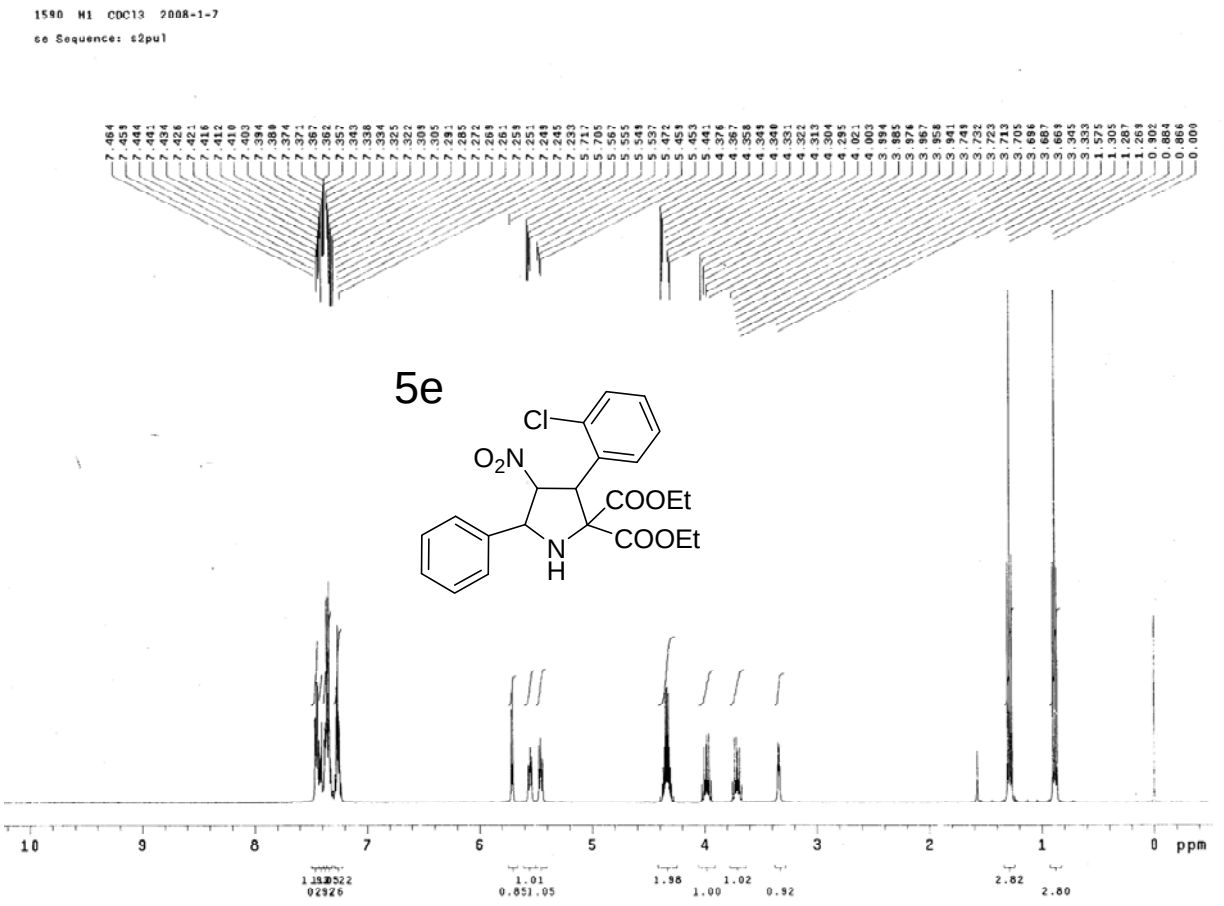
COOEt
COOEt
N
H
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.852	52903135	50.10	1992535	54.95
2	12.265	52700197	49.90	1633437	45.05



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.689	1057017	4.86	98965	14.08
2	12.226	20684425	95.14	603928	85.92


1590 H1 CDCl3 2008-1-7
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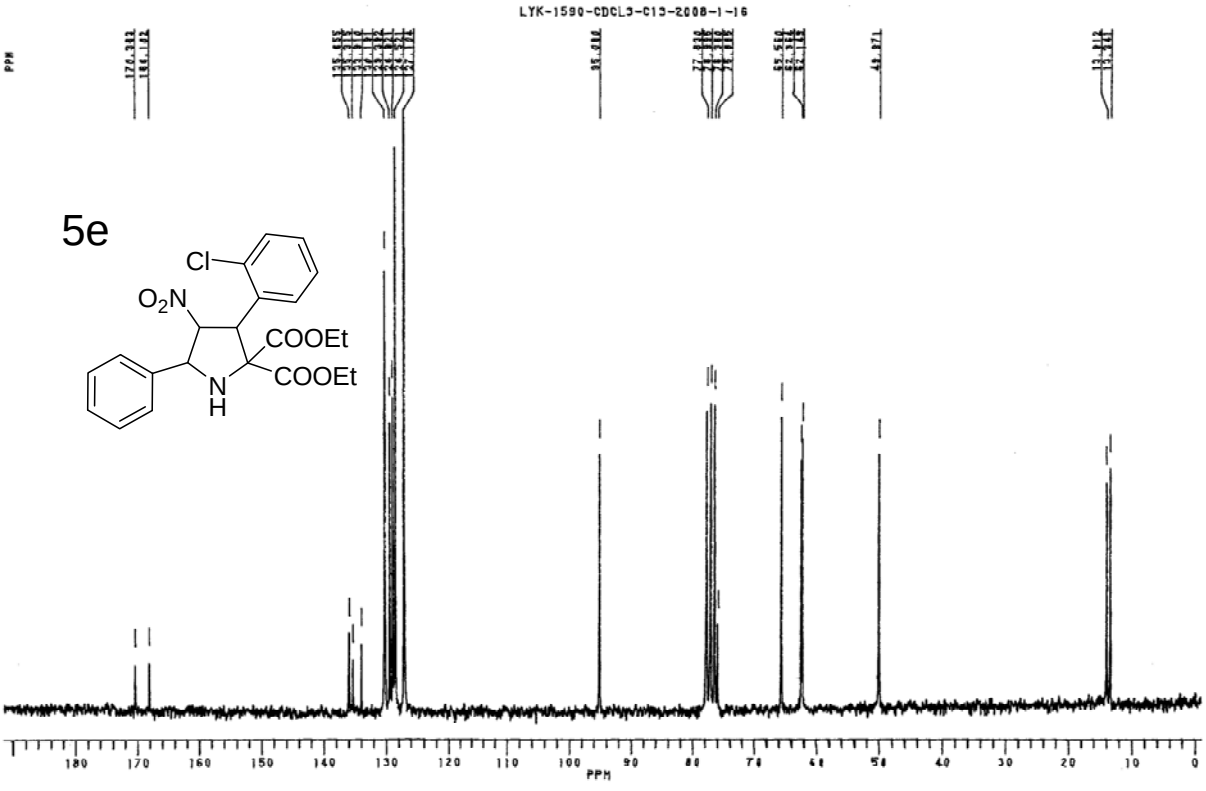
Cl
O2N
COOEt
COOEt
N
H
ppm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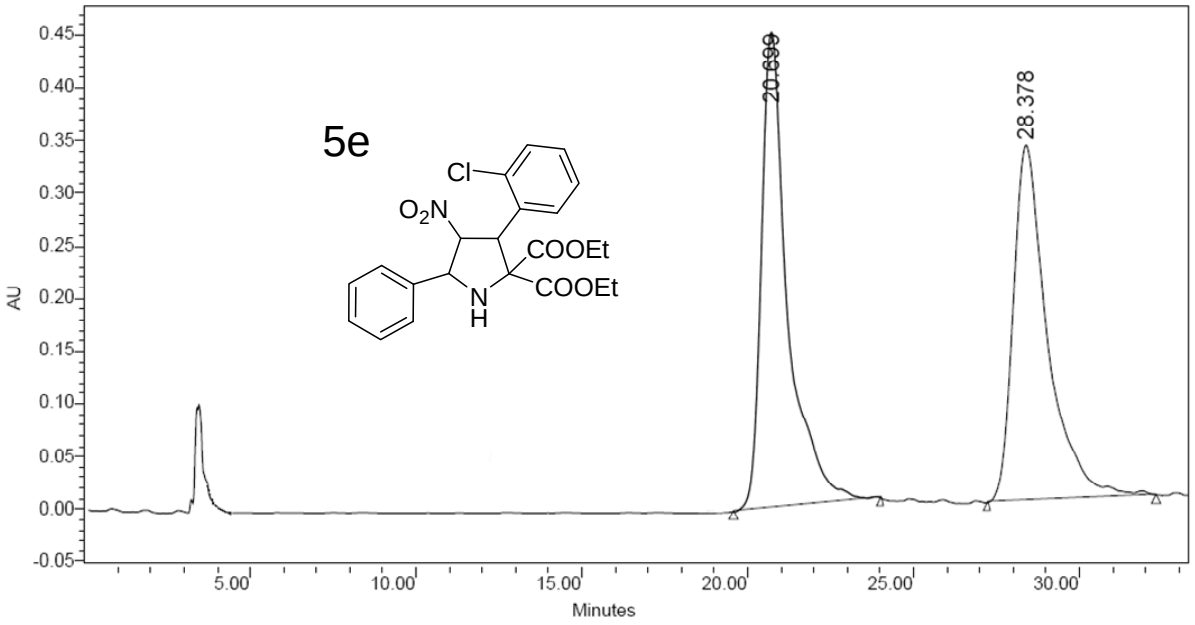
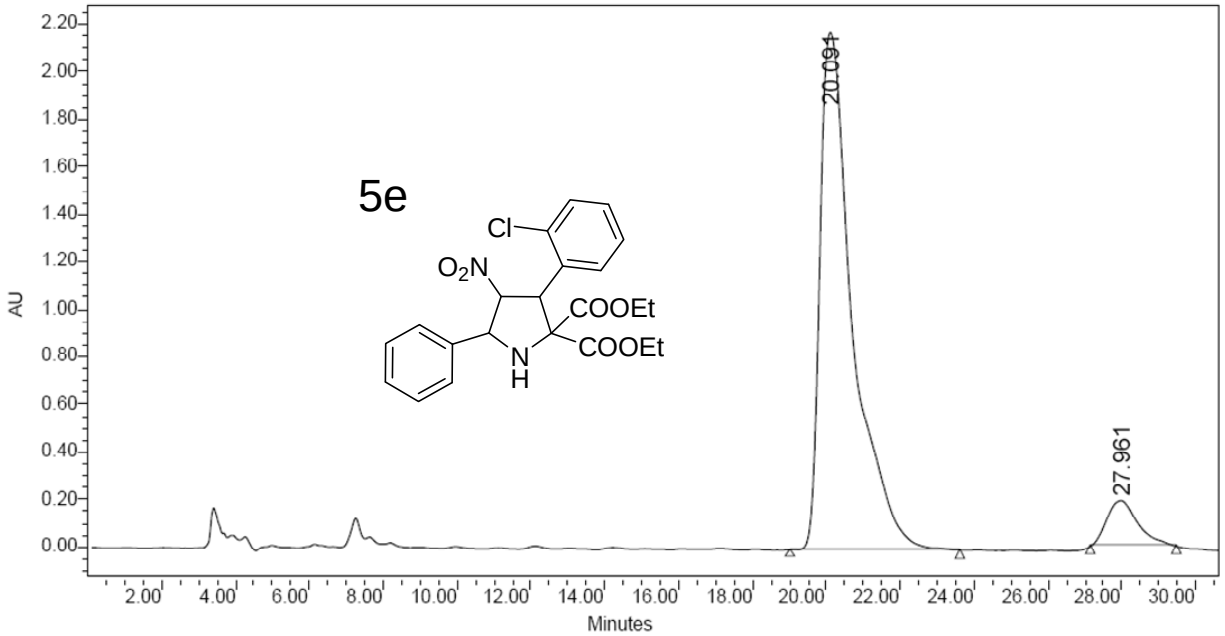
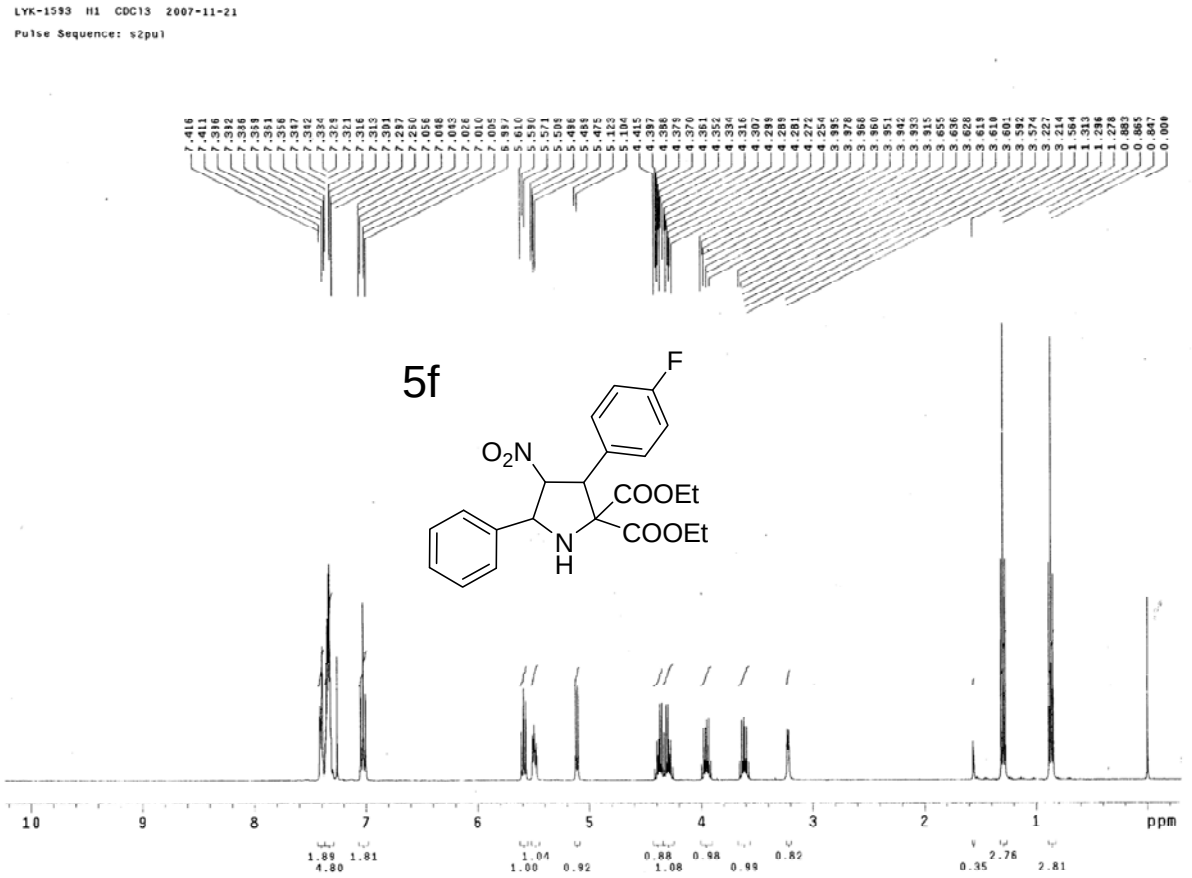
N
H
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	20.699	25141342	50.79	451633	57.22
2	28.378	24355064	49.21	337710	42.78



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	20.091	133130893	92.13	2175475	91.92
2	27.961	11368740	7.87	191196	8.08


LYK-1593 H1 CDCl3 2007-11-21
Pulse Sequence: s2pul
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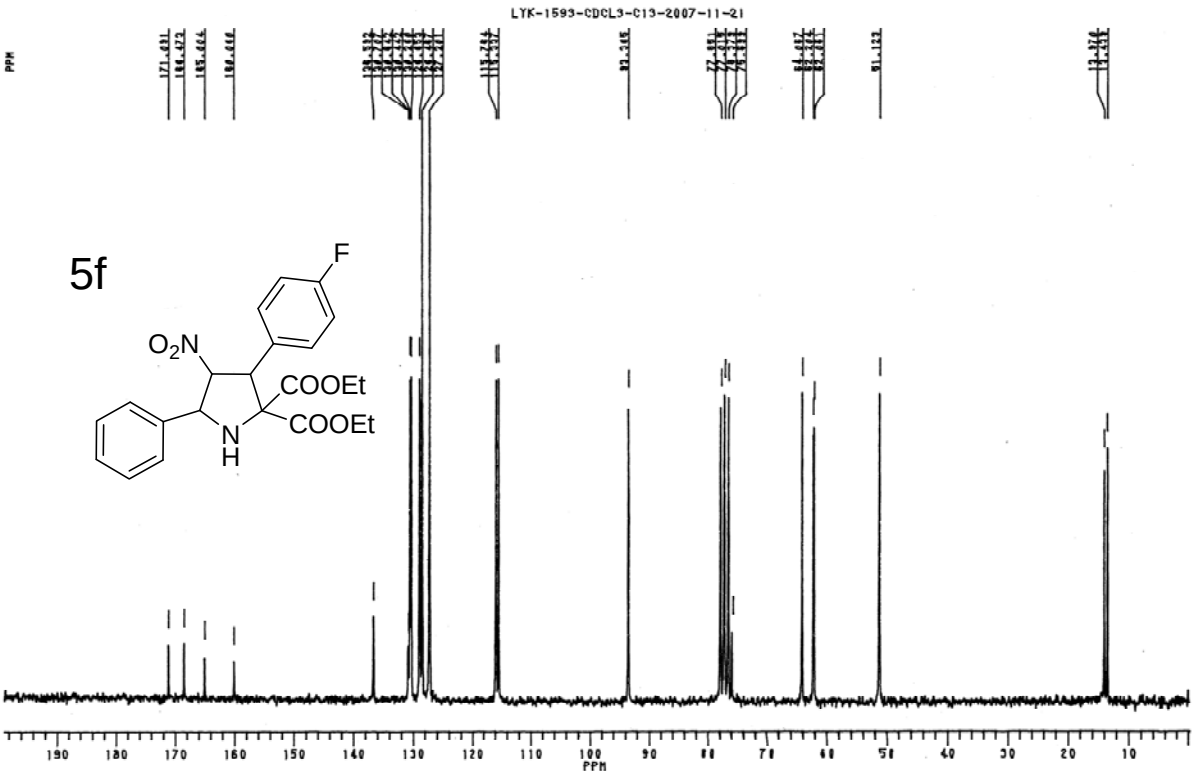
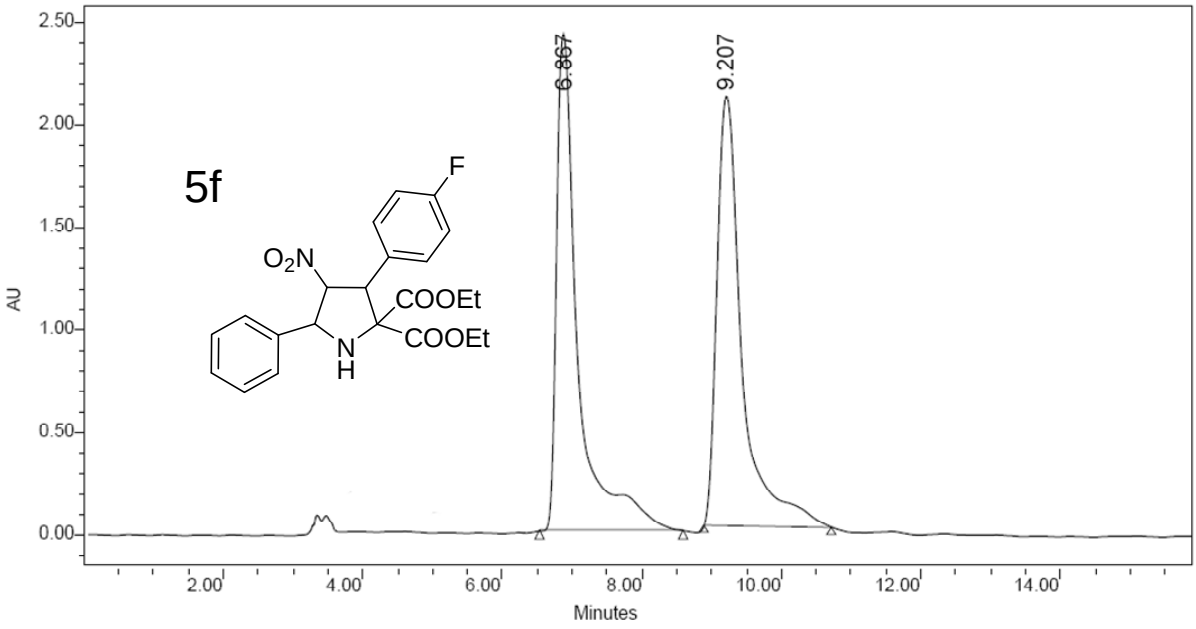
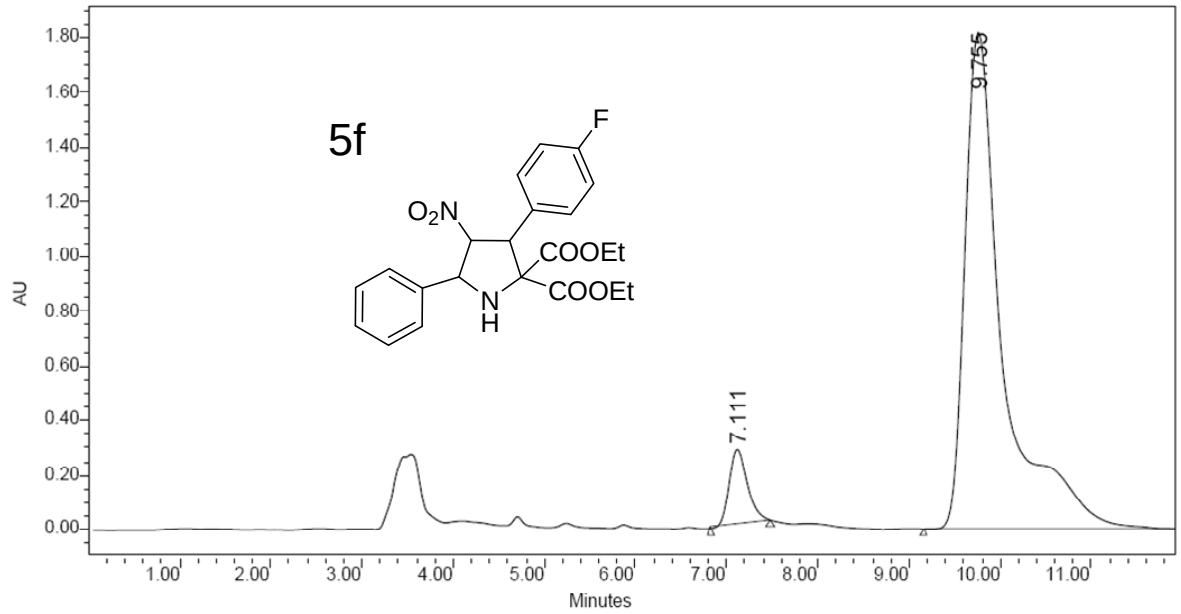
O2N
COOEt
COOEt
N
H
ppm

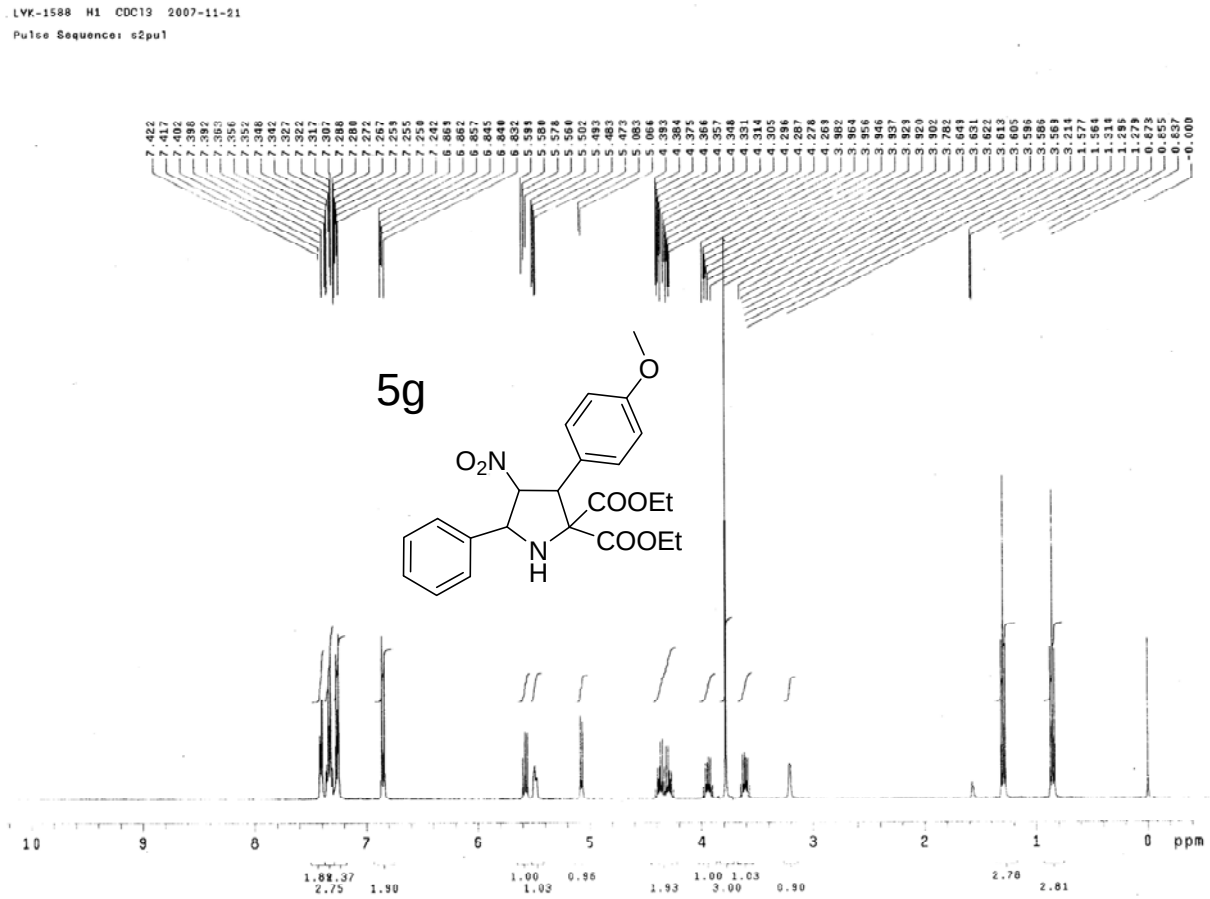

LYK-1593-CDCL3-C13-2007-11-21
PPM
5f
F
O2N
COOEt
COOEt
N
H
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.867	52036659	49.61	2431676	53.59
2	9.207	52853085	50.39	2105465	46.41



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	7.111	3909557	6.93	277034	13.23
2	9.755	52467161	93.07	1816392	86.77


LVK-1588 H1 CDCl3 2007-11-21
Pulse Sequence: s2pul
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O2N
COOEt
COOEt
N
H
10
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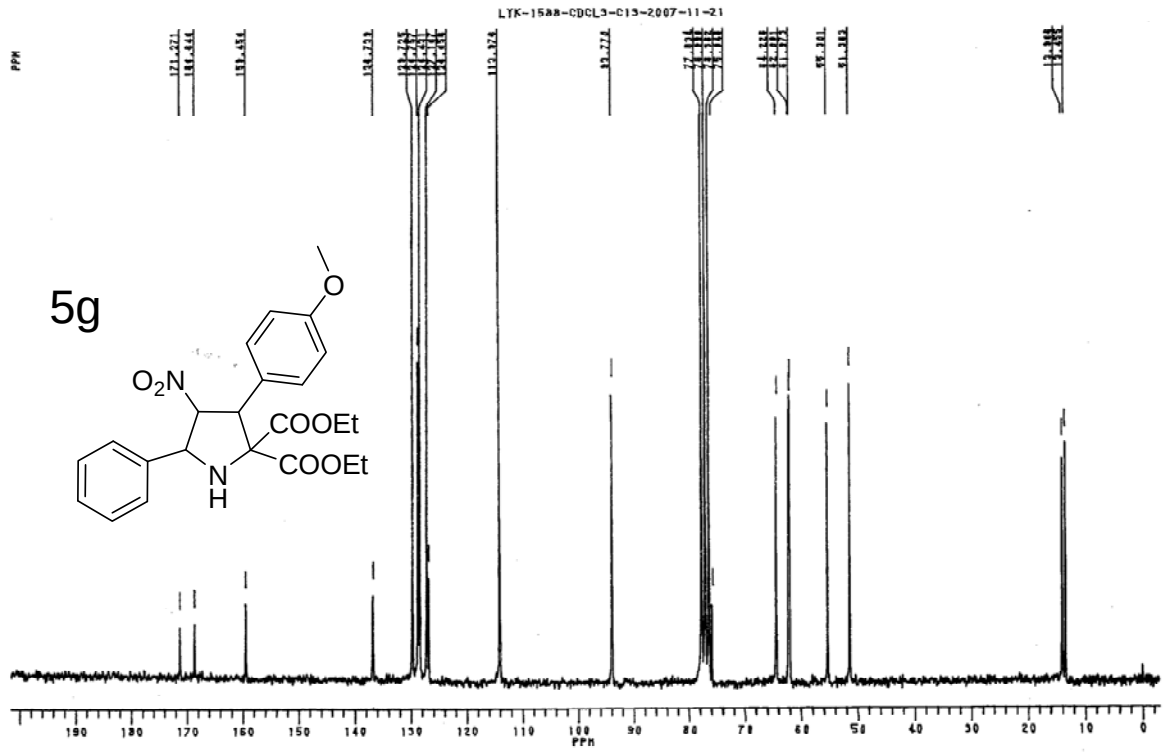
6
5
4
3
2
1
0 ppm


LVK-15aa-CDCL3-C13-2007-11-21
PPM
5g
O
O2N
COOEt
COOEt
N
H
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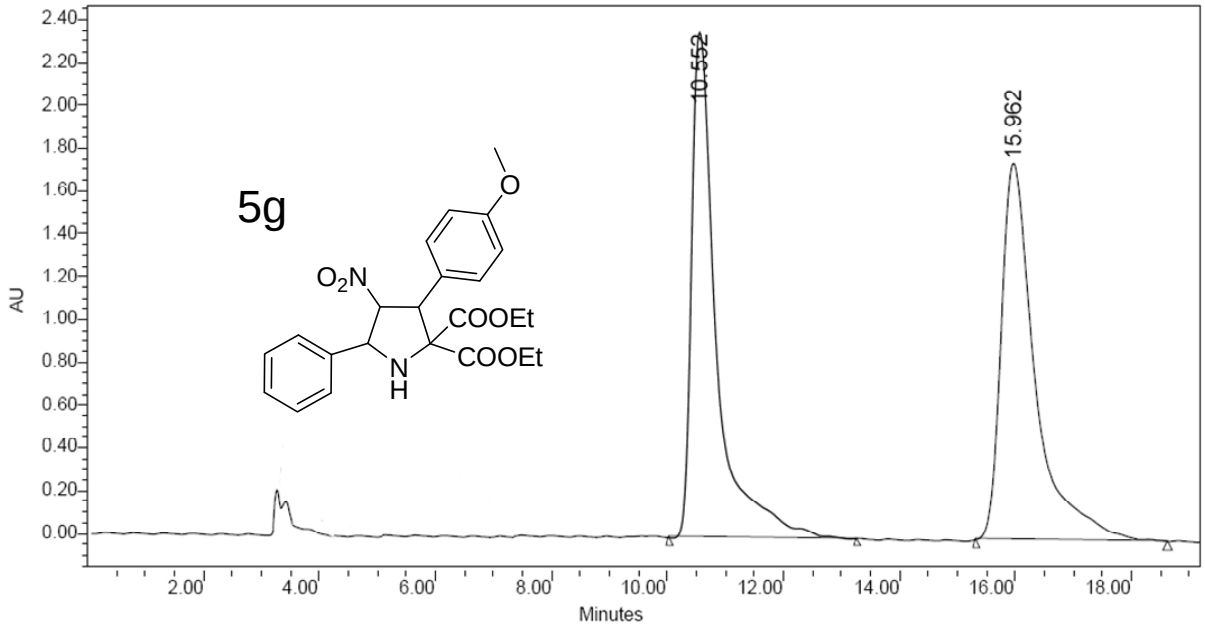
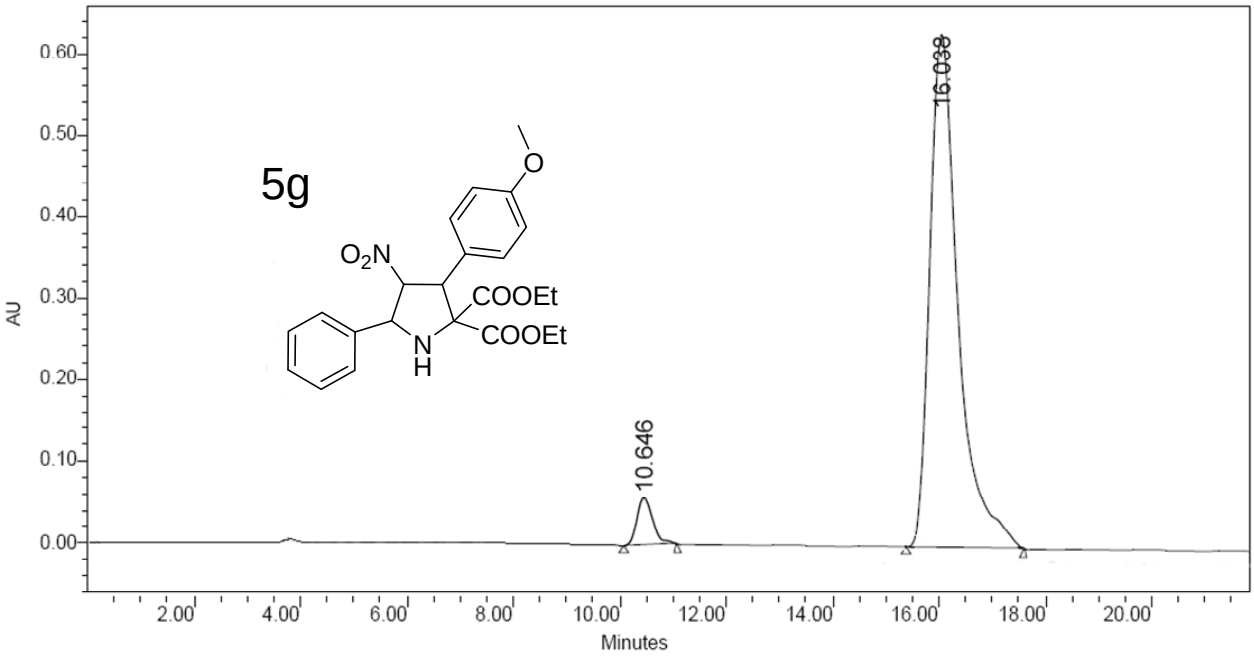
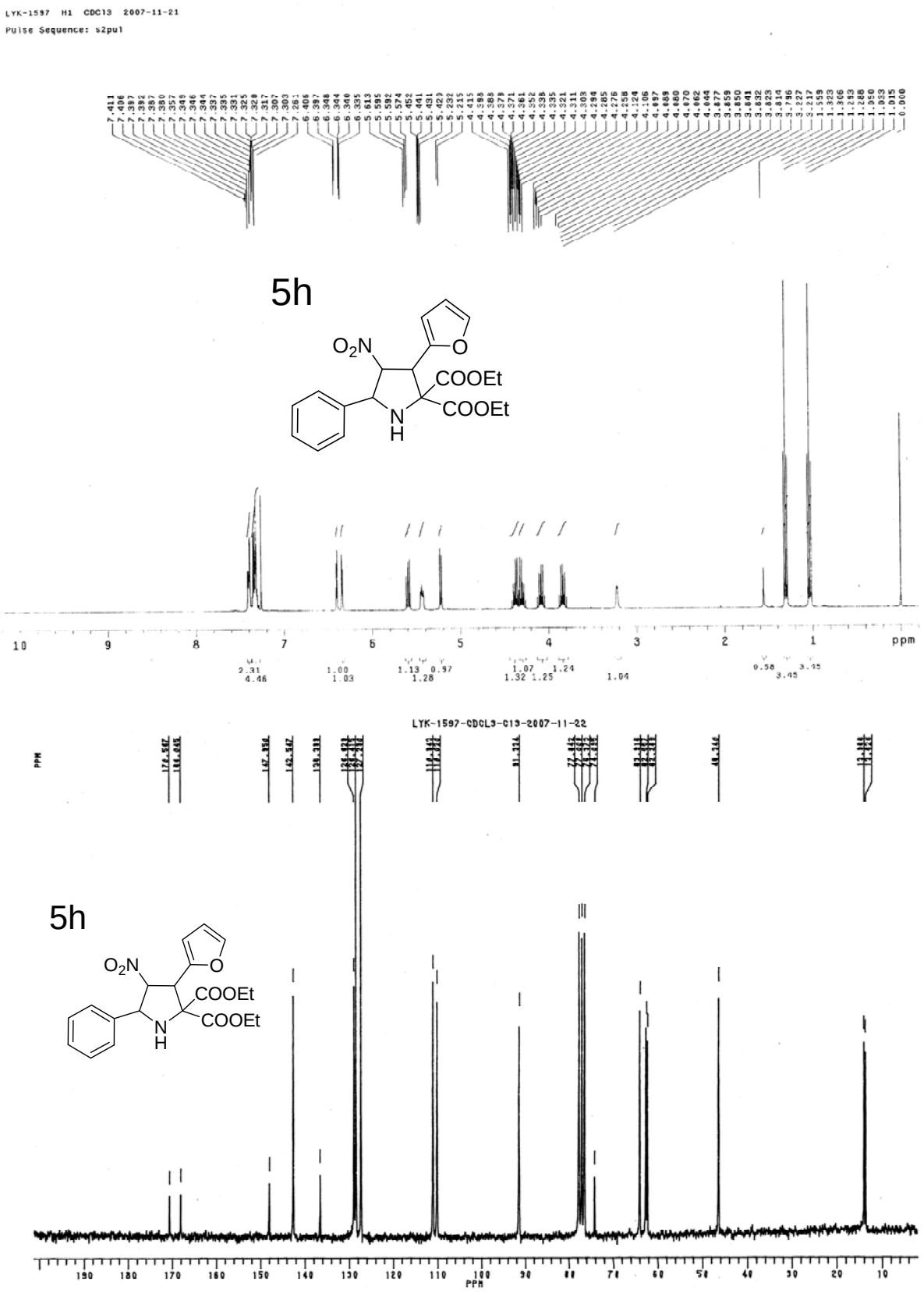
PPM

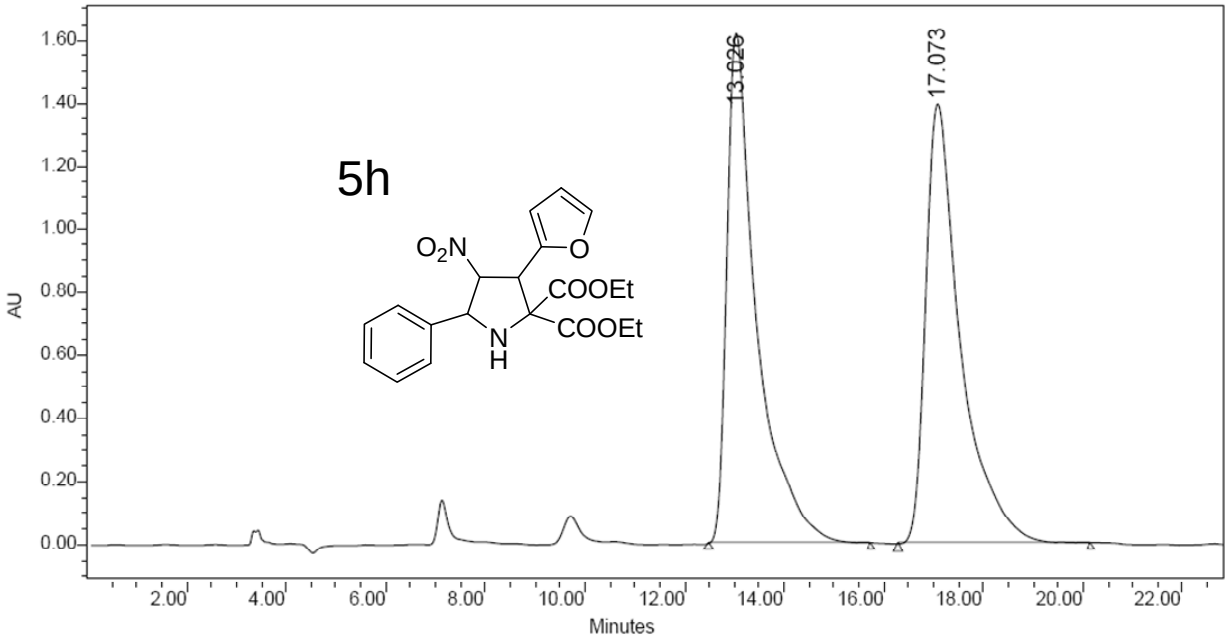


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	10.552	70740785	49.52	2359688	57.30
2	15.962	72112643	50.48	1758587	42.70

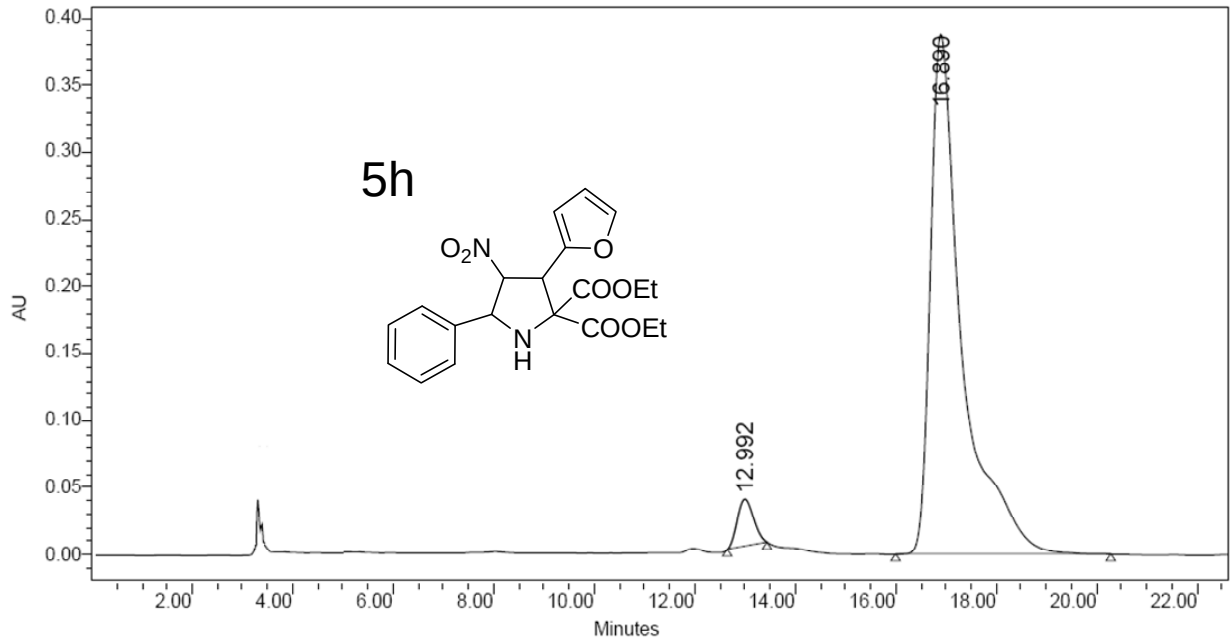


	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	10.646	1221996	4.50	57756	8.21
2	16.038	25955264	95.50	645836	91.79

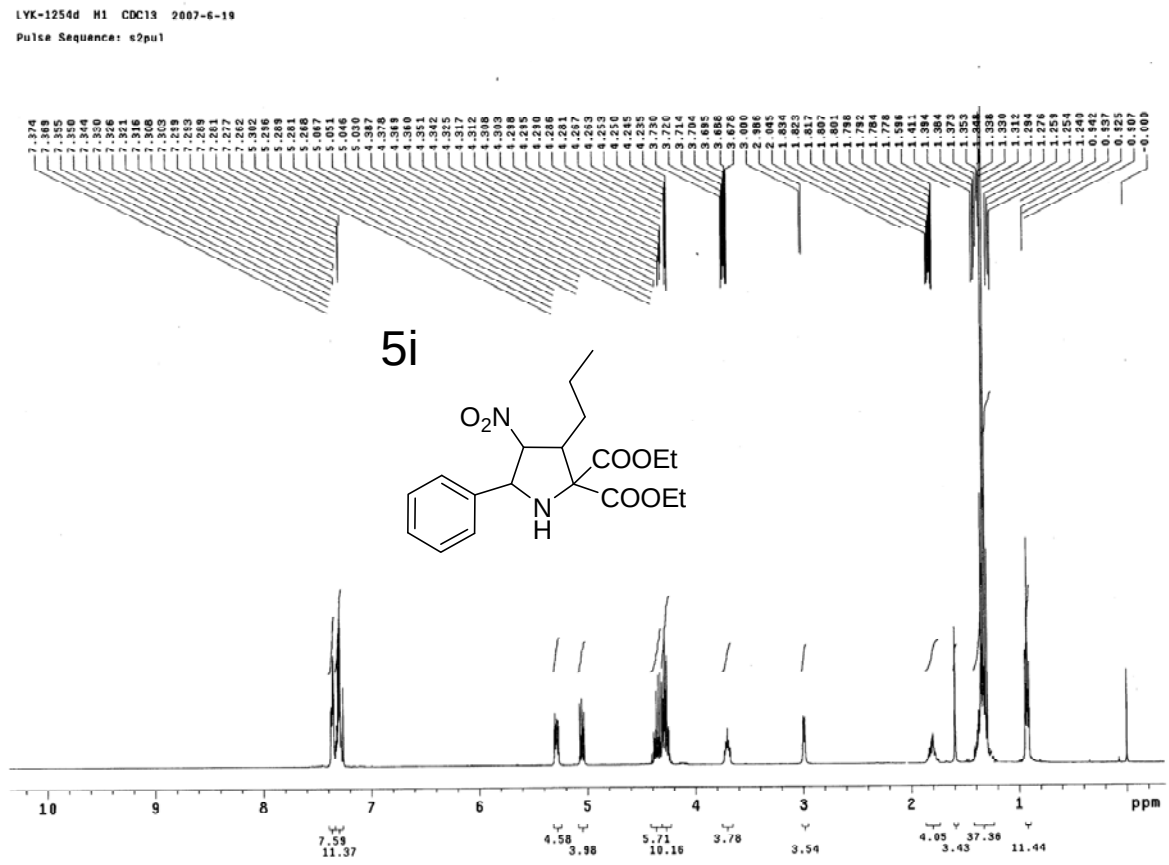

LYK-1597 H1 CDCl3 2007-11-21
Pulse Sequence: s2pul
5h
O2N
O
COOEt
COOEt
N
H
ppm
LYK-1597-CDCL3-C13-2007-11-22
PPM
5h
O2N
O
COOEt
COOEt
N
H
PPM

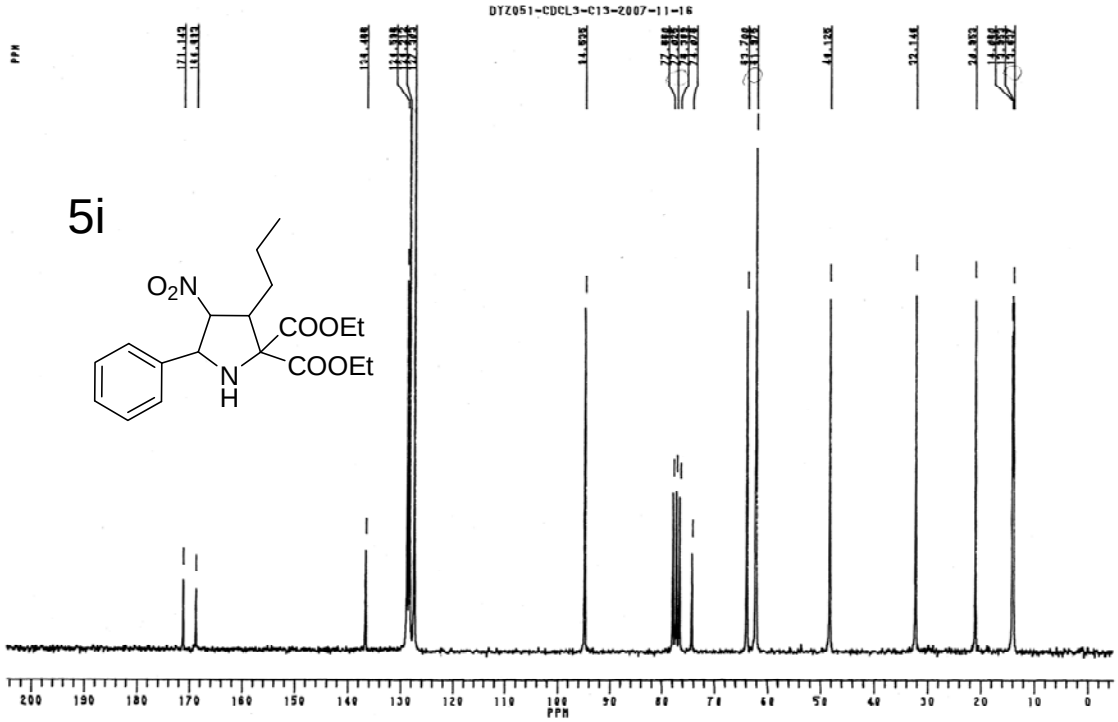


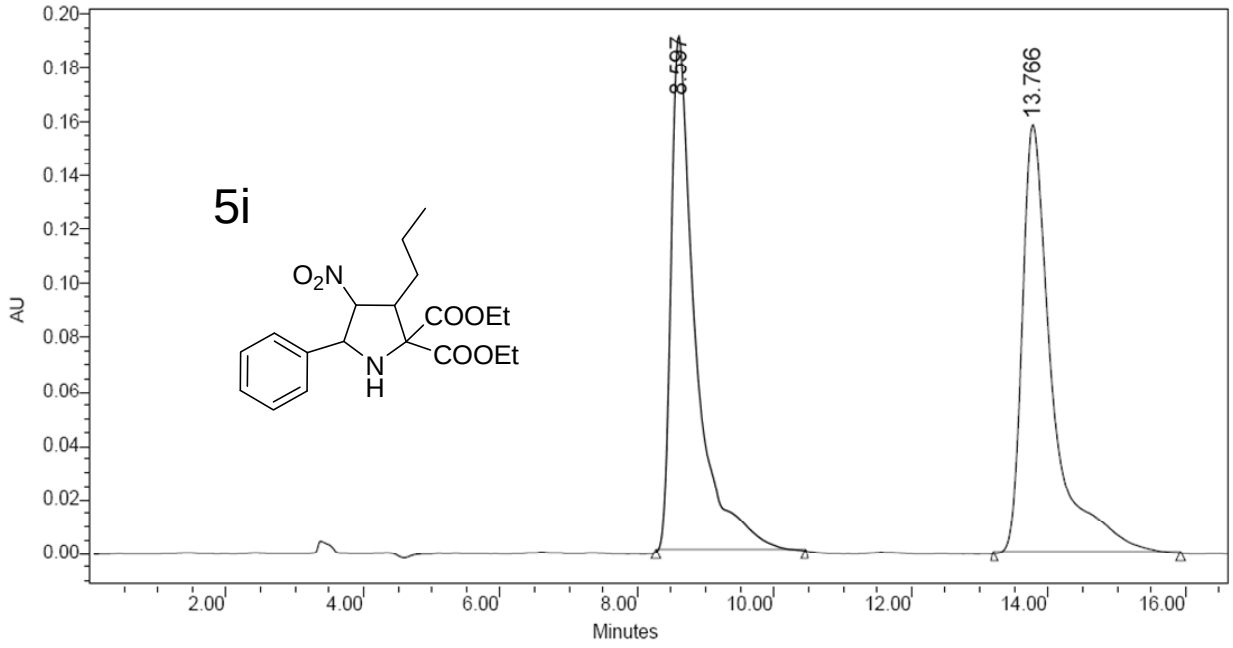
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	13.026	67134853	49.78	1614526	53.70
2	17.073	67727719	50.22	1392259	46.30



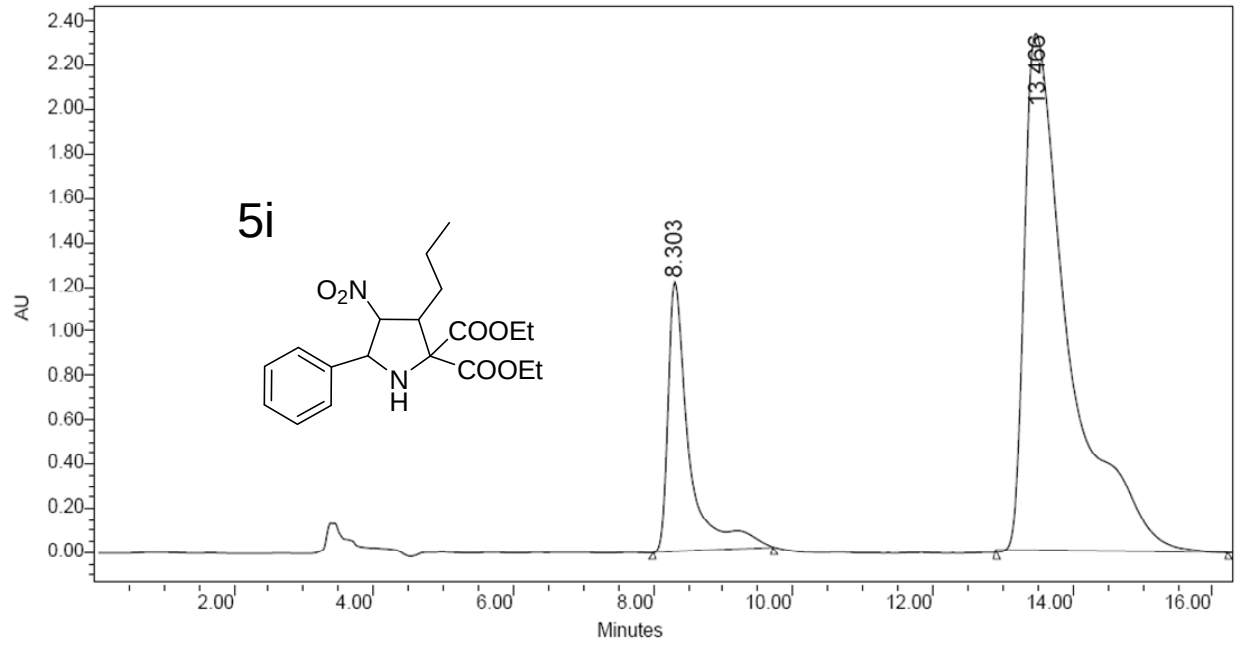
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.992	792897	4.47	35089	8.31
2	16.890	16936550	95.53	387076	91.69


LYK-1254d H1 CDCl3 2007-6-19
Pulse Sequence: s2pul
5i
O2N
COOEt
COOEt
N
H
ppm
7.59
11.37
4.58
3.98
5.71
10.16
3.78
3.54
4.05
3.43
37.36
11.44

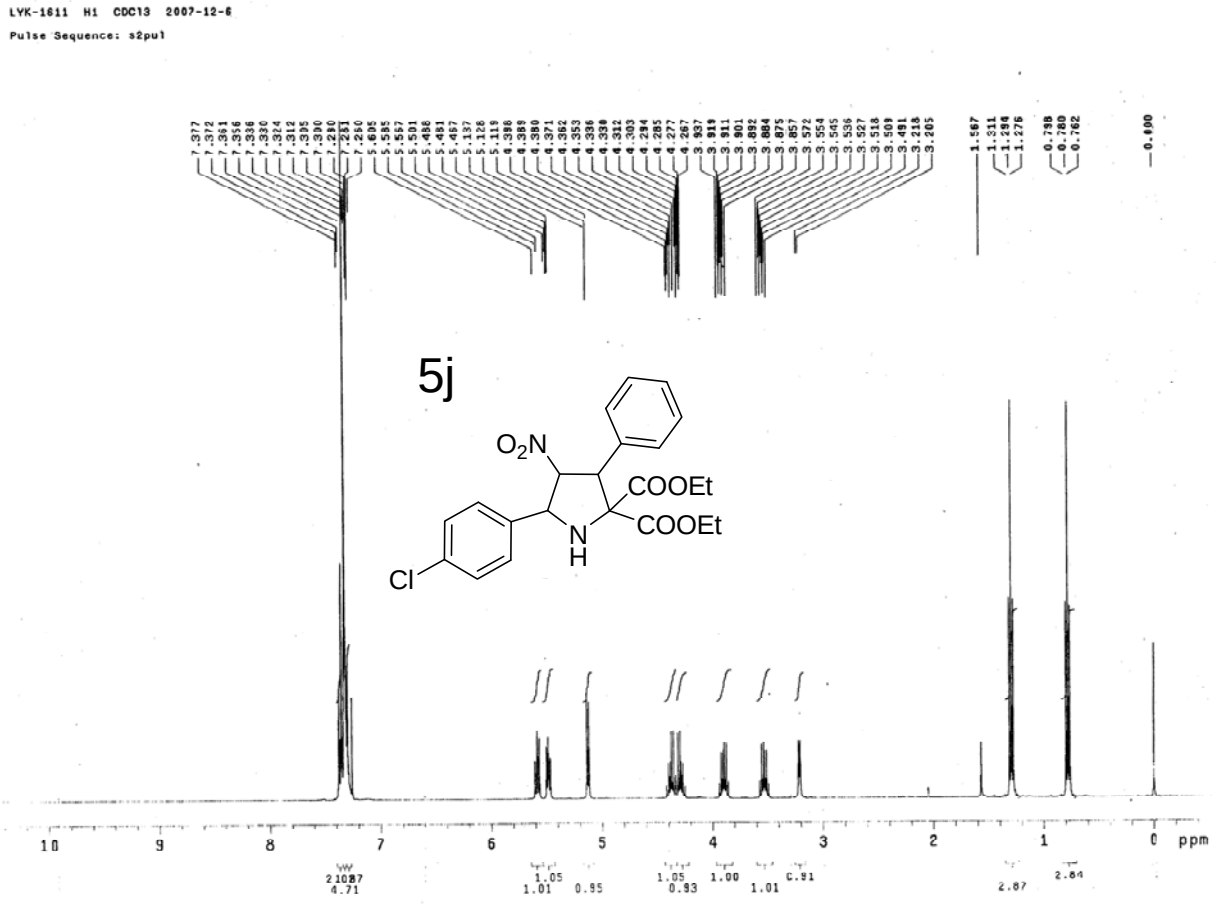

DTZ051-CDCL3-C13-2007-11-16
PPM
5i
O2N
COOEt
COOEt
N
H

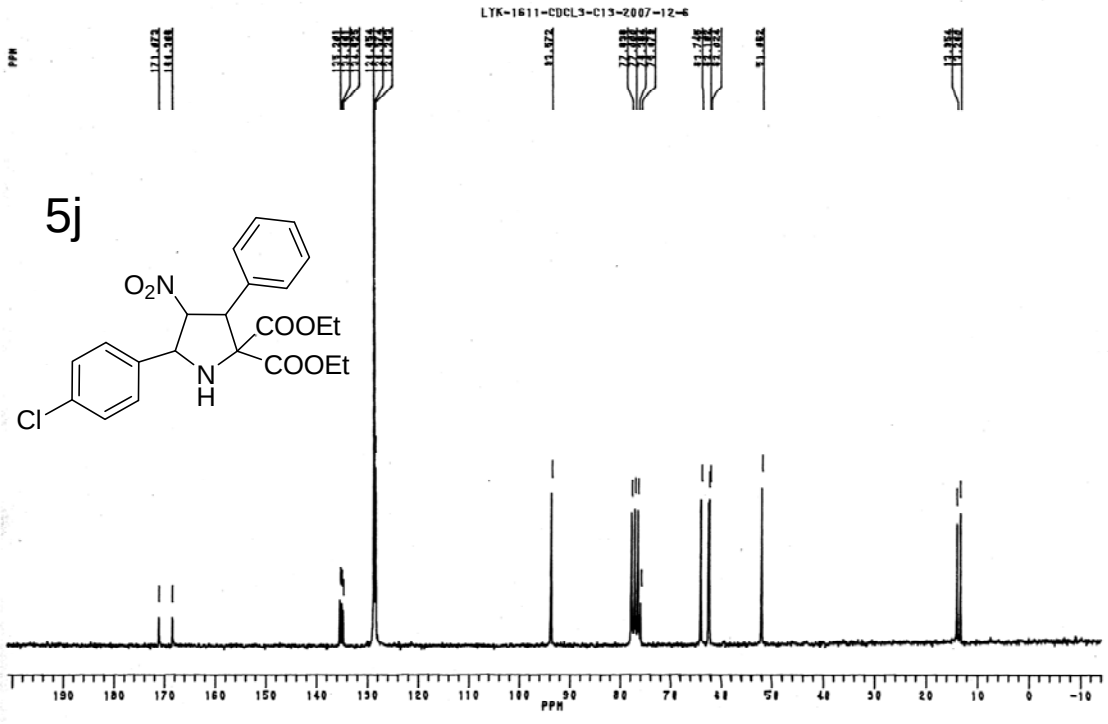


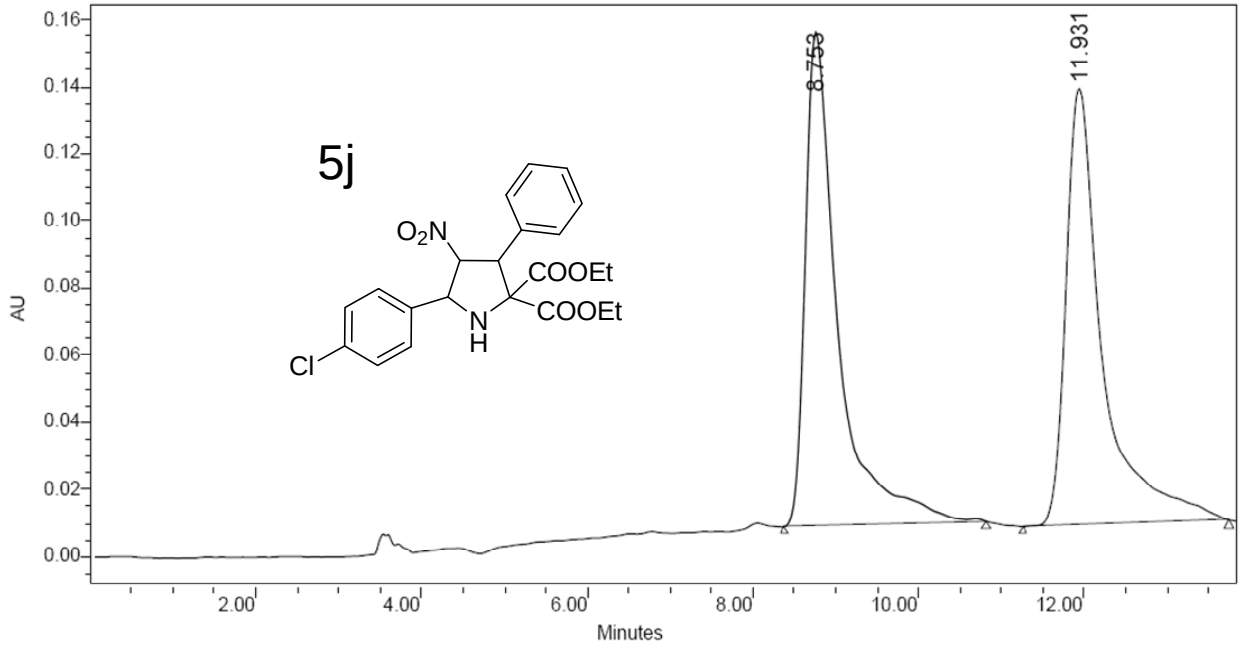
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.597	4776313	49.46	190793	54.51
2	13.766	4880211	50.54	159225	45.49



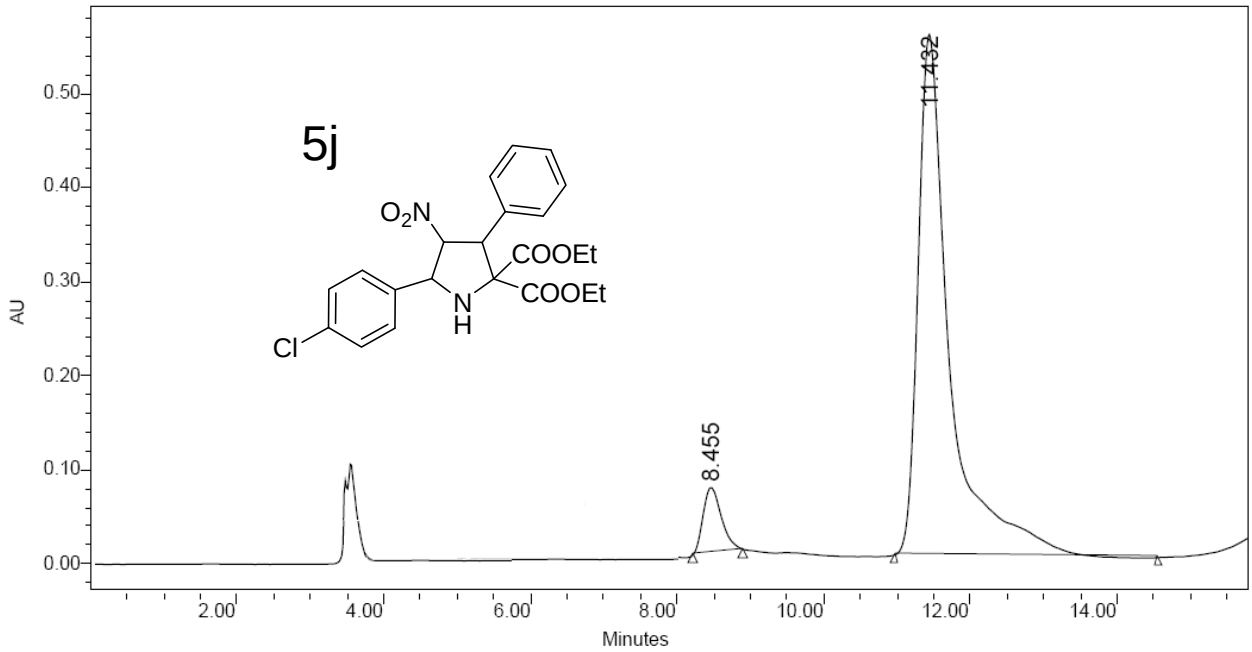
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.303	25724187	19.92	1218325	34.26
2	13.466	103441285	80.08	2338216	65.74


LYK-1611 H1 CDCl3 2007-12-6
Pulse Sequence: s2pul
5j
O2N
COOEt
COOEt
N
H
Cl
ppm

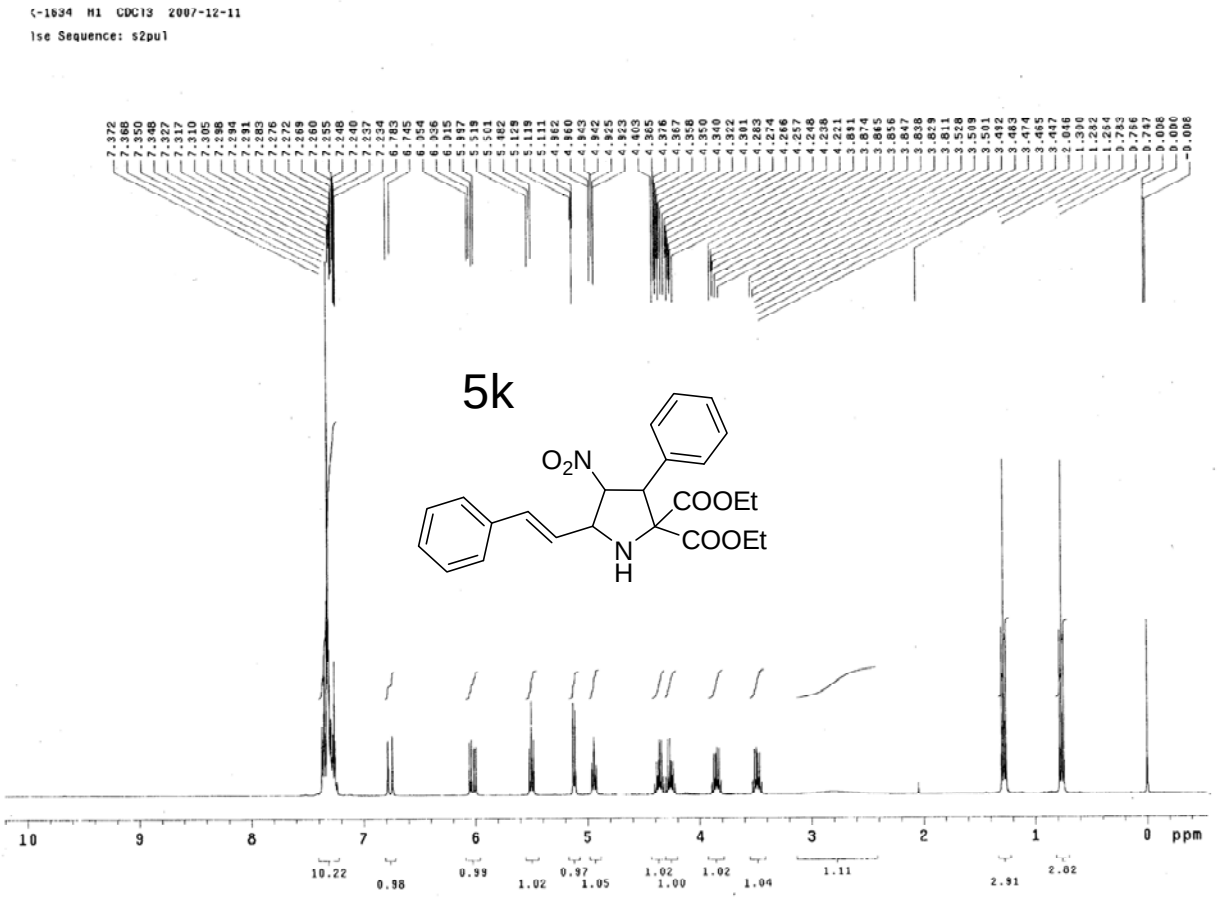

LYK-1611-CDCL3-C13-2007-12-6
5j
O2N
COOEt
COOEt
N
H
Cl
PPM

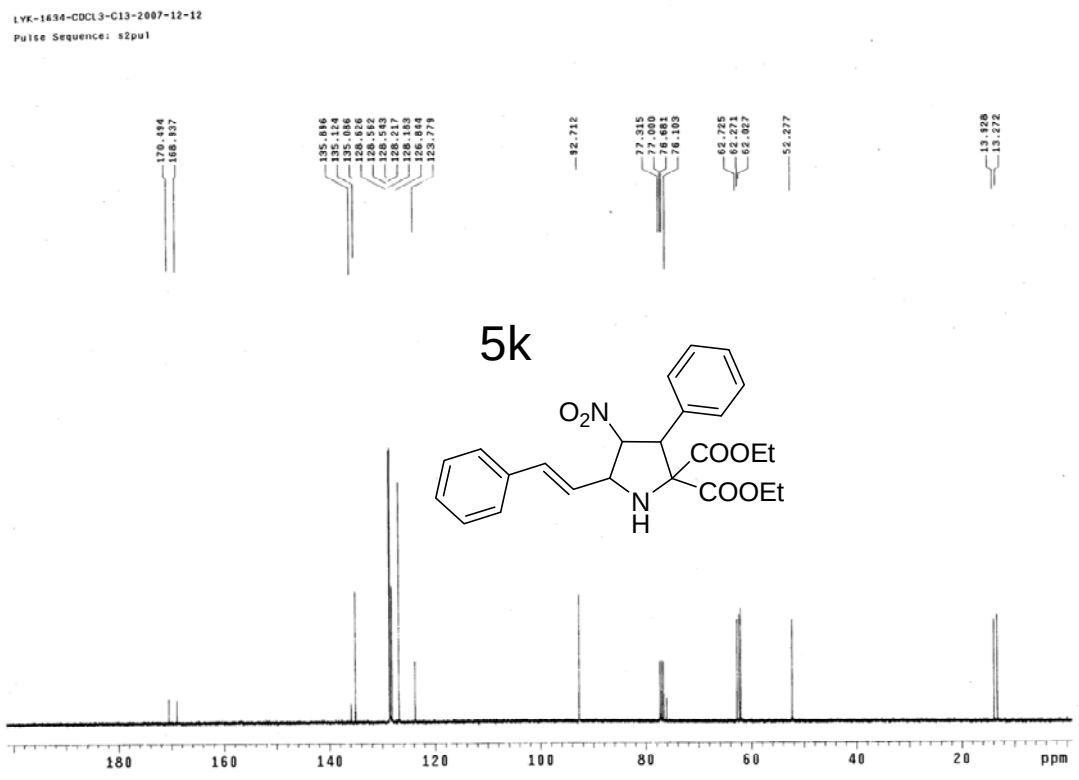


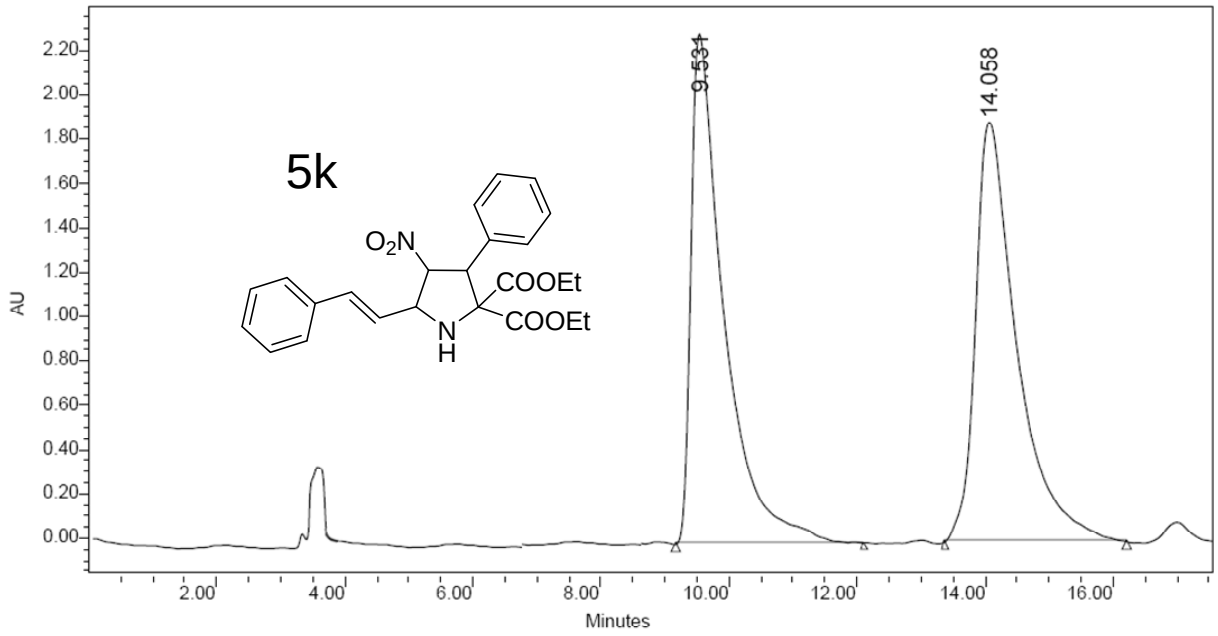
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.753	4036921	50.21	146725	53.03
2	11.931	4003401	49.79	129962	46.97



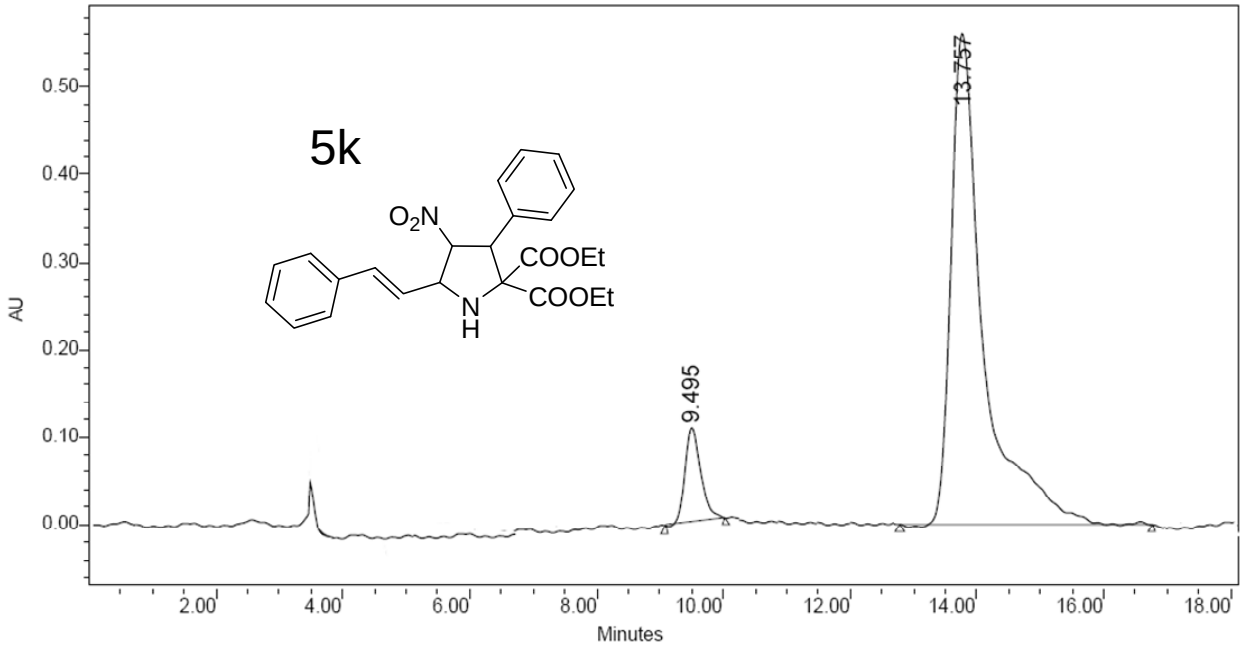
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.455	1201173	6.70	69110	11.09
2	11.432	16736688	93.30	553793	88.91


5k
O_2N
COOEt
COOEt
N
H
10
9
8
7
6
5
4
3
2
1
0
ppm
10.22
0.98
0.99
1.02
0.97
1.05
1.02
1.00
1.02
1.04
1.11
2.91
2.02

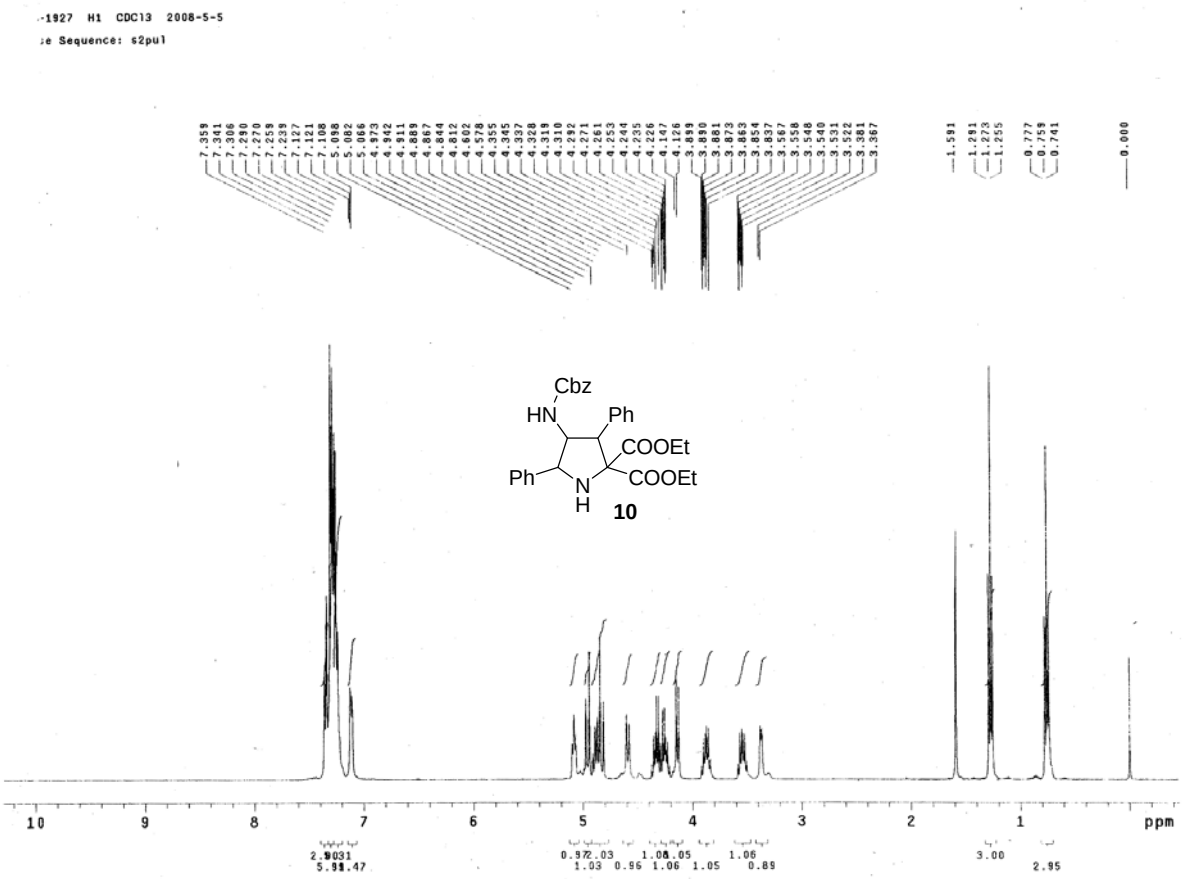

5k
O_2N
COOEt
COOEt
N
H
180
160
140
120
100
80
60
40
20
ppm

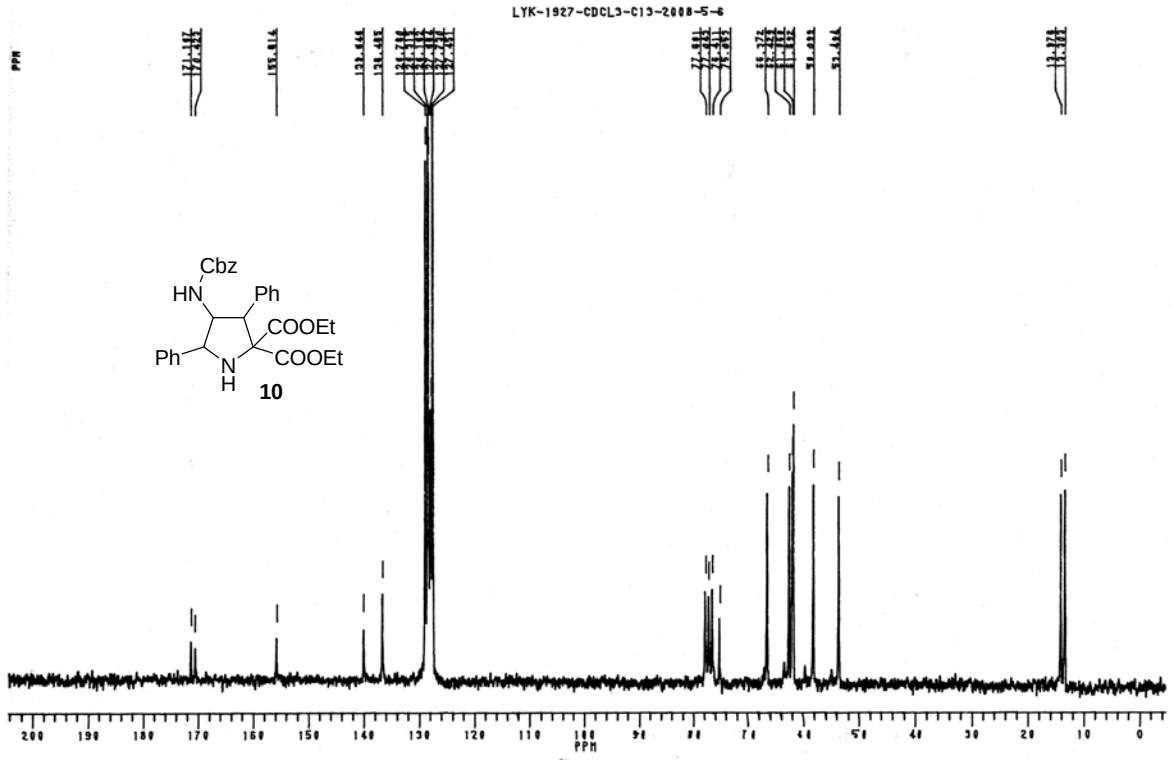


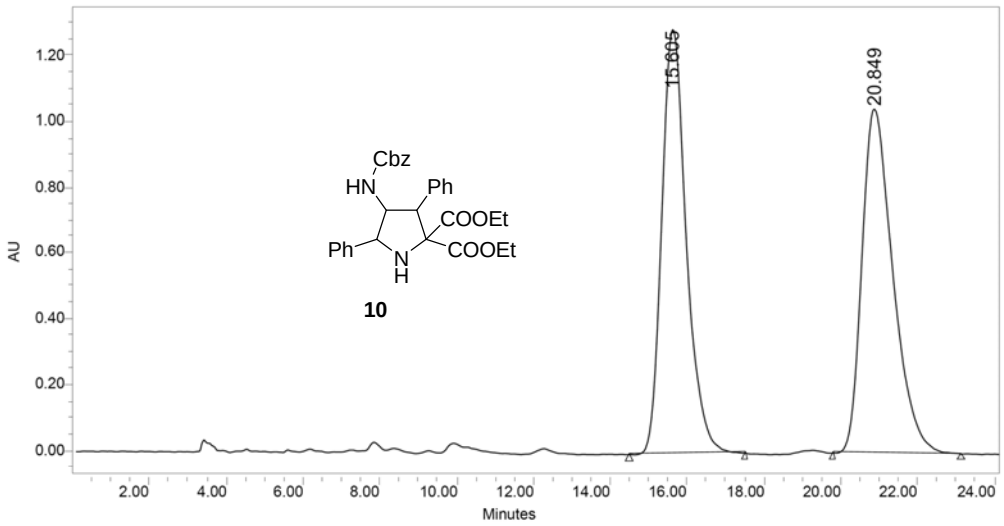
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.531	82054569	49.17	2295146	54.85
2	14.058	84822039	50.83	1889221	45.15



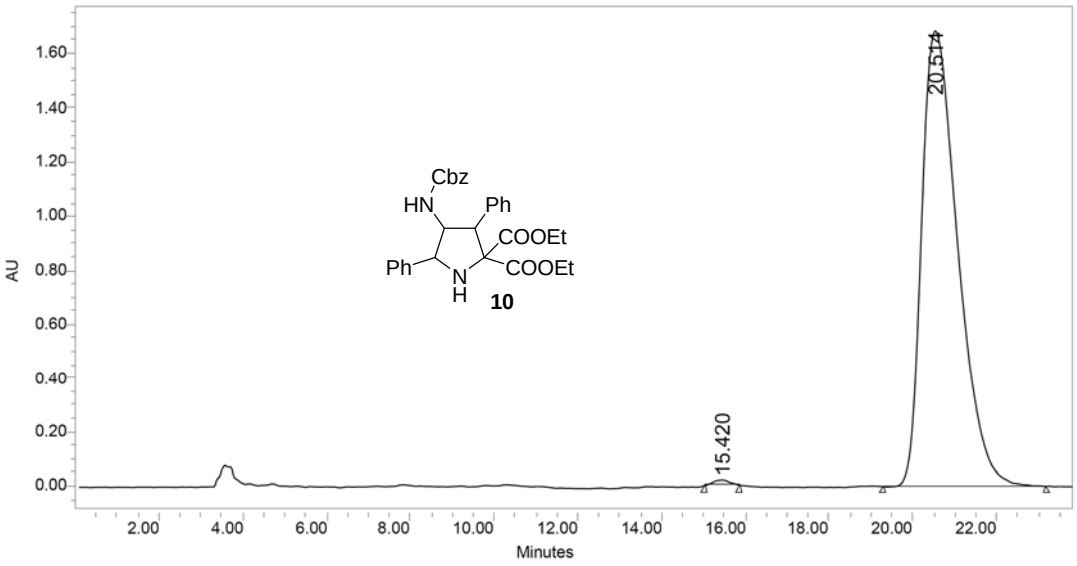
	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	9.495	1910085	8.69	108616	16.20
2	13.757	20081311	91.31	561706	83.80


Cbz
HN
Ph
COOEt
Ph
N
H
COOEt
10
ppm


Cbz
HN
Ph
COOEt
Ph
N
H
COOEt
10
PPM



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	15.605	57256702	49.38	1288137	55.24
2	20.849	58683473	50.62	1043899	44.76



	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	15.420	552010	0.54	19882	1.17
2	20.514	100747124	99.46	1683626	98.83