Novel bifunctional chiral thiourea catalyzed highly enantioselective aza-Henry reaction

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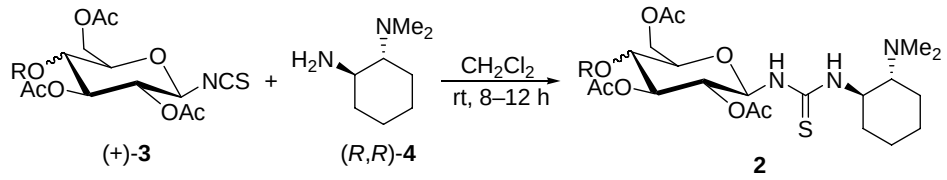
1. Experimental Section

General information

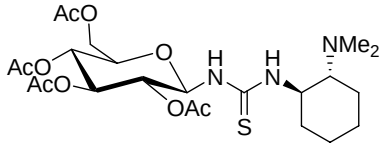
Flame-dried (under vacuum) glassware was used for all reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. NMR spectra were acquired on either a Bruker AMX-300 or Varian 400 MHz instrumental. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.1 ($CDCl_3$). Specific rotations were measured on a Perkin-Elmer 341MC polarimeter. Enantiomeric excesses were determined on a HP-1100 instrument (chiral column; mobile phase: Hexane/*i*-PrOH). Elemental analyses were conducted on a Yanaco CHN Corder MT-3 automatic analyzer. Melting points were determined on a T-4 melting point apparatus. All temperatures were uncorrected. Glucosyl isothiocyanate 3,[1] (*R*,*R*)-*N*,*N*-Dimethyl cyclohexane-1,2-diamine 4[2] and *N*-protected imines[3] were prepared according to the literature procedure.

Preparation of the title chiral thiourea compound



(+)-**3** (*R*,*R*)-**4** **2**

To a solution of (1*R*,2*R*)-N,N-dimethylcyclohexane-1,2-diamine (1.10 g, 7.7 mmol) in methylene chloride (10 mL) was added dropwise a solution of the corresponding sugar-derived isothiocyanate (7.0 mmol) in methylene chloride (25 mL) under a nitrogen atmosphere. The resulting mixture was stirred at room temperature until total consumption of the isothiocyanate (monitored by TLC). After removal of solvent, the residue was purified through column chromatography on silica gel (200–300 mesh, eluted with ethyl acetate / petroleum ether: 1/2) to give the thiourea catalyst as a white solid.



(+)-**2a**: 79% yield, m.p 105–106 °C, $[\alpha]_D^{20}$ +18.0 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95–1.24 (m, 5 H, 2 CH_2 and one proton of CH_2), 1.61–1.83 (m, 3 H, CH_2 and one proton of CH_2), 1.95 (s, 3 H, $COCH_3$), 1.97 (s, 3 H, $COCH_3$), 1.99 (s, 3 H, $COCH_3$), 2.02 (s, 3 H, $COCH_3$), 2.11–2.50 (m, 3 H, 3 NCH), 2.16 (s, 6 H, 2 NCH_3), 3.77–3.81 (m, 1 H, OCH), 4.02–4.07 (m, 1 H, OCH), 4.28 (dd, 1 H, *J* = 9.3, 4.2 Hz, OCH), 4.91 (t, 1 H, *J* = 9.6 Hz, OCH), 5.01 (t, 1 H, *J* = 9.6 Hz, OCH), 5.25–5.31 (m, 1 H, OCH), 5.70 (br. s, 1 H, NH), 6.65 (br. s, 1

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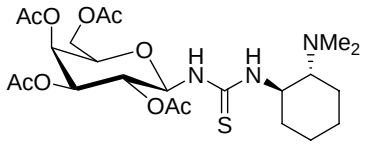
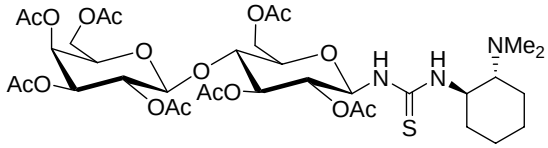
H, NH). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ = 20.58, 20.73, 21.61, 24.49, 24.90, 32.65, 33.95, 39.95, 55.80, 61.76, 66.81, 68.31, 71.04, 73.06, 73.29, 76.72, 77.15, 77.57, 82.90, 100.00, 169.60, 169.83, 170.60, 170.96, 183.48. IR (KBr): ν 3358, 2938, 1754, 1541, 1370, 1228, 1038, 908, 758, 600 cm^{-1}. HMS (ESI) *m/z* calc'd for $C_{23}H_{37}N_3O_9S$ $[M+H]^+$: 532.2323, found 532.2320.



(+)-**2b**: 67% yield, m.p 94–95 °C, $[\alpha]_D^{20}$ +22.9 (c 1.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96–1.28 (m, 5 H, 2 CH_2 and one proton of CH_2), 1.62–1.83 (m, 3 H, CH_2 and one proton of CH_2), 1.92 (s, 3 H, $COCH_3$), 1.97 (s, 3 H, $COCH_3$), 2.01 (s, 3 H, $COCH_3$), 2.08 (s, 3 H, $COCH_3$), 2.17 (s, 6 H, 2 NCH_3), 2.34–2.41 (m, 2 H, 2 NCH), 3.58–3.59 (m, 1 H, NCH), 3.98–4.07 (m, 3 H, OCH), 5.05–5.14 (m, 2 H, 2 OCH), 5.38 (d, 1 H, 1.6 Hz, OCH), 5.63 (br. s, 1 H, NH), 6.69 (br. s, 1 H, NH). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ 19.54, 19.61, 19.69, 19.81, 20.66, 23.57, 23.99, 31.66, 38.90, 54.81, 60.10, 65.70, 66.37, 70.12, 71.10, 75.88, 76.31, 76.73, 82.30, 168.77, 168.99, 169.38, 170.16, 182.38. IR (KBr): ν 3360, 2936, 1751, 1541, 1370, 1228, 1050, 954, 915, 761, 600 cm^{-1}. HRMS (ESI) *m/z* calc'd for $C_{23}H_{37}N_3O_9S$ $[M+H]^+$: 532.2323, found 532.2333.



(–)-**2c**: 64% yield, m.p 118–120 °C, $[\alpha]_D^{20}$ –1.12 (c 0.98, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10–1.20 (m, 4 H, 2 CH_2), 1.60–1.81 (m, 4 H, 2 CH_2), 1.89 (s, 3 H, $COCH_3$), 1.97 (s, 9 H, 3 $COCH_3$), 1.99 (s, 3 H, $COCH_3$), 2.04 (s, 3 H, $COCH_3$), 2.08 (s, 3 H, $COCH_3$), 2.15 (s, 6 H, 2 NCH_3), 2.28–2.40 (m, 2 H, 2 NCH), 3.69–3.84 (m, 4 H), 3.99–4.12 (m, 4 H, OCH), 4.38 (d, 1 H, *J* = 11.6 Hz), 4.42 (d, 1 H, *J* = 11.6 Hz), 4.81 (t, 1 H, *J* = 9.6 Hz), 5.03 (dd, 1 H, *J* = 8.0, 10.4 Hz), 5.22–5.28 (m, 2 H, OCH and NH), 5.59 (br. s, 1 H, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 20.36, 20.47, 20.60, 20.67, 20.76, 21.64, 24.43, 24.86, 32.53, 39.85, 55.71, 60.83, 62.08, 66.68, 68.99, 70.54, 70.93, 71.25, 72.85, 74.16, 75.99, 76.84, 77.27, 77.47, 77.70, 82.54, 100.58, 168.82, 169.31, 169.89, 170.02, 170.21, 170.86, 183.45. IR (KBr): ν 3362, 2938, 1754, 1541, 1370, 1229, 1047, 952, 904, 759, 602 cm^{-1}. HRMS *m/z* (ESI) calc'd for $C_{35}H_{53}N_3O_{17}S$ $[M+H]^+$: 820.3169, found 820.3168.

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General Procedure for the 2 catalyzed enantioselective aza-Henry reaction

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To A solution of imine (0.5 mmol), thiourea catalyst (40 mg, 0.075 mmol) in methylene chloride was added nitromethane (270 μL, 5 mmol) in one portion at the temperature as depicted in the text. The resulting mixture was stirred at the same temperature and monitored by TLC. The solution was concentrated and purified by column chromatography on silica gel (200–300 mesh, eluted with ethyl acetate / petroleum ether: 1/12) to furnish the desired products as white solid. Enantiomeric excess was determined by chiral HPLC analysis.

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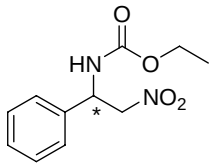

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Ethyl 2-nitro-1-phenylethylcarbamate: White solid, m.p 118–120 °C, $[\alpha]_D^{20}$ –19.4 (c 1.32, $CHCl_3$), 85.8% ee. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, 3 H, *J* = 7.2 Hz, CH_3), 4.14 (q, 2 H, *J* = 7.2 Hz, CH_2), 4.69–4.75 (m, 1 H, CH), 4.85 (br. s, 1 H, NH), 5.40–5.44 (m, 2 H, CH_2), 7.29–7.42 (m, 5 Haorm). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 15.36 (minor) and 17.55 min (major).

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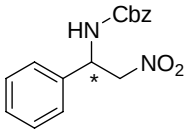
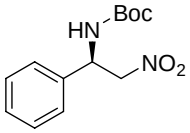
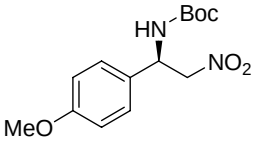


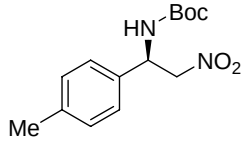
Benzyl 2-nitro-1-phenylethylcarbamate: White solid, m.p 104–105 °C, $[\alpha]_D^{20}$ –8.36 (c 1.46, $CHCl_3$), 87.3% ee. ^1H NMR (300 MHz, $CDCl_3$): δ 4.71 (dd, 1 H, *J* = 12.3 and 6.3 Hz, CH), 4.86 (br. s, 1 H, NH), 5.12 (s, 2 H, CH_2), 5.45 (dd, *J* = 13.2 and 6.6 Hz, one proton of CH_2), 5.62 (br. s, 1 H, one proton of CH_2), 7.29-7.41 (m, 10 Haorm). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm); *R*t = 24.19 (major) and 31.91 min (minor).



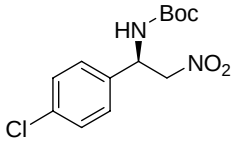
tert-Butyl (*R*)-2-nitro-1-phenylethylcarbamate (**6a**): White solid, m.p 105–106 °C, $[\alpha]_D^{20}$ –22.5 (c 0.99, $CHCl_3$), 99.7% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^{t}Bu), 4.70 (dd, 1 H, *J* = 12.0, 4.8 Hz, CH), 4.84 (br. s, 1 H, NH), 5.28 (br. s, 1 H, one proton of CH_2), 5.38 (d, *J* = 4.8 Hz, 1 H, one proton of CH_2), 7.30–7.40 (m, 5 Haorm). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm); *R*t = 9.98 (major) and 12.38 min (minor).



tert-Butyl (*R*)-1-(4-methoxyphenyl)-2-nitroethylcarbamate (**6b**): White solid, m.p 150–151 °C, $[\alpha]_D^{20}$ –34.9 (c 1.00, $CHCl_3$), 93.6% ee. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, ^{t}Bu), 3.80 (s, 3 H, OCH_3), 4.66 (dd, 1 H, *J* = 12.4, 6.0 Hz, CH), 4.84 (br. s, 1 H, NH), 5.17 (m, 1 H, one proton of CH_2), 5.32 (d, 1 H, *J* =6.0 Hz, one proton of CH_2), 6.89 (d, 2 Harom, *J* = 8.4 Hz), 7.22 (d, 2 Harom, *J* = 8.4 Hz). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm); *R*t = 14.80 (minor) and 15.44 min (major).



tert-Butyl (*R*)-1-(4-methylphenyl)-2-nitroethylcarbamate (**6c**): White solid, m.p 106–107 °C, $[\alpha]_D^{20}$ –23.2 (c 0.98, $CHCl_3$), 82.6% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^{t}Bu), 2.34 (s, 3 H, CH_3), 4.67 (dd, 1 H, *J* = 12.4, 5.6 Hz, CH), 4.84 (br. s, 1 H, NH), 5.22–5.34 (m, 2 H, CH_2), 7.18 (s, 4 Harom). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm); *R*t = 9.86 (major) and 10.54 min (minor).



tert-Butyl (*R*)-1-(4-chlorophenyl)-2-nitroethylcarbamate (**6d**): White solid, m.p 139–140 °C, $[\alpha]_D^{20}$ –26.9 (c 0.52, $CHCl_3$), 99.3% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^{t}Bu), 4.69 (dd, 1 H, *J* = 12.8, 4.8 Hz, CH), 4.84 (br. s, 1 H, NH), 5.33 (m, 2 H, CH_2), 7.25 (d, 2 Harom, *J* = 8.4 Hz), 7.36 (d, 2 Harom, *J* = 8.4 Hz). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm); *R*t = 13.33 (minor) and 18.71 min (major).

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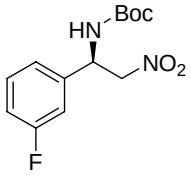
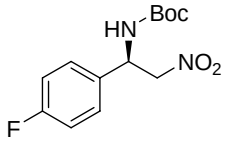
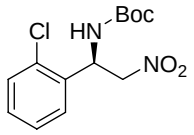


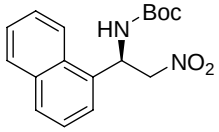
tert-Butyl (*R*)-1-(3-fluorophenyl)-2-nitroethylcarbamate (**6e**): White solid, m.p 109–110 °C, $[\alpha]_D^{20}$ –12.9 (c 1.08, $CHCl_3$), 99.8% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^tBu), 4.70 (d, 1 H, *J* = 10.8 Hz, CH), 4.83 (br. s, 1 H, NH), 5.37 (s, 2 H, CH_2), 7.02–7.05 (m, 2 Harom), 7.09 (d, 1 Harom, *J* = 7.6 Hz), 7.33–7.39 (m, 1 Harom). Elemental analysis (%) calcd for $C_{13}H_{17}FN_2O_2$: C 54.92, H 6.03, N 9.85; Found: C 54.74, H 5.91, N 9.77. HPLC analysis: AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 7.16 (minor) and 8.20 min (major).



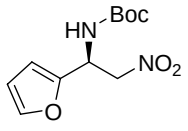
tert-Butyl (*R*)-1-(4-fluorophenyl)-2-nitroethylcarbamate (**6f**): White solid, m.p 122–123 °C, $[\alpha]_D^{20}$ –19.3 (c 1.00, $CHCl_3$), 99.5% ee. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^tBu), 4.66–4.69 (m, 1 H, CH), 4.84 (br. s, 1 H, NH), 5.28–5.34 (m, 2 H, CH_2), 7.05–7.09 (m, 2 Harom), 7.28–7.31 (m, 2 Harom). Elemental analysis (%) calcd for $C_{13}H_{17}FN_2O_2$: C 54.92, H 6.03, N 9.85; Found: C 54.83, H 5.88, N 9.72. HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, wavelength = 254 nm): flow rate 1.0 mL/min, *R*t = 9.83 (major) and 10.81 min (minor).



tert-Butyl (*R*)-1-(2-chlorophenyl)-2-nitroethylcarbamate (**6g**): White solid, m.p 106–107 °C, $[\alpha]_D^{20}$ –2.03 (c 1.04, $CHCl_3$), 92.2% ee. ^1H NMR (300 MHz, $CDCl_3$): δ 1.43 (s, 9 H, ^tBu), 4.78–4.87 (m, 2 H, CH and NH), 5.71–5.75 (m, 2 H, CH_2), 7.28–7.42 (m, 4 Harom). Elemental analysis (%) calcd for $C_{13}H_{17}ClN_2O_2$: C 51.92, H 5.70, N 9.31; Found: C 51.79, H 5.56, N 9.15. HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 90:10, flow rate = 0.8 mL/min, wavelength = 254 nm): *R*t = 12.05 (major) and 18.75 min (minor).



tert-Butyl (*R*)-1-(1-naphthyl)-2-nitroethylcarbamate (**6h**): White solid, m.p 176–177 °C, $[\alpha]_D^{20}$ –5.99 (c 1.02, $CHCl_3$), 99.8% ee. ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^tBu), 4.90 (d, 2 H, *J* = 7.6 Hz, CH_2), 5.28 (br. s, 1 H, NH), 6.24–6.31 (m, 1 H, CH), 7.45–7.47 (m, 2 Harom), 7.53–7.65 (m, 2 Harom), 7.84–7.92 (m, 2 Harom), 8.12 (d, 1 Harom, *J* = 8.4 Hz). HPLC analysis: AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 7.71 (minor) and 10.66 min (major).



tert-Butyl (*R*)-1-(1-furyl)-2-nitroethylcarbamate (**6i**): White solid, m.p 59–60 °C, $[\alpha]_D^{20}$ –25.0 (c 1.10, $CHCl_3$), 99.7% ee. ^1H NMR (300 MHz, $CDCl_3$): δ 1.46 (s, 9 H, ^tBu), 4.73 (dd, 1 H, *J* = 12.9, 6.0 Hz, CH), 4.85 (br. s, 1 H, NH), 5.28 (br. s, 1 H, one proton of CH_2), 5.43–5.50 (m, 1 H, one proton of CH_2), 6.31–6.36 (m, 2 Harom), 7.38 (m, 1 Harom). HPLC analysis (Chiralpak AD-

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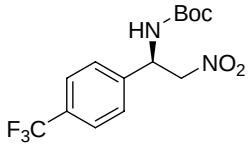
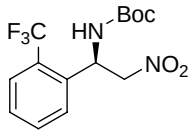
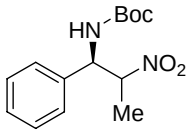
H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 9.70 (major) and 17.48 min (minor).



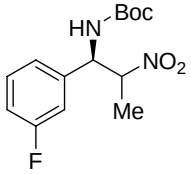
tert-Butyl (*R*)-1-(4-trifluorophenyl)-2-nitroethylcarbamate (**6j**): White solid, m.p 152–153 °C, $[\alpha]_D^{20}$ –12.07 (c 0.82, $CHCl_3$), 94.1% ee. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 9 H, ^{t}Bu), 4.71–4.76 (m, 1 H, CH), 4.86 (br. s, 1 H, NH), 5.42 (s, 2 H, CH_2), 7.45 (d, 2 Harom, *J* = 8.4 Hz), 7.65 (d, 2 Harom, *J* = 8.4 Hz). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 6.70 (minor) and 8.67 min (major).



tert-Butyl (*R*)-1-(2-trifluorophenyl)-2-nitroethylcarbamate (**6k**): White solid, m.p 75–76 °C, $[\alpha]_D^{20}$ –5.0 (c 0.7, $CHCl_3$), 95.8% ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (s, 9 H, ^{t}Bu), 4.76 (s, 2H, CH_2), 5.55(d, 1 H, *J* = 6.4 Hz, NH), 5.77 (q, *J* = 6.4 Hz,, CH), 7.47 (t, 1 Harom, *J* = 7.6 Hz), 7.52 (d, 1 Harom, *J* = 7.6 Hz), 7.60 (t, 1 Harom, *J* = 7.6 Hz), 7.72 (d, 1Harm, *J* = 7.6 Hz). Elemental analysis (%) calcd for $C_{14}H_{17}F_3N_2O_2$: C 50.30, H 5.13, N 8.38; Found: C 50.17, H 5.02, N 8.21. HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 5.75 (major) and 6.58 min (minor).



tert-Butyl (1*R*)-2-nitro-1-phenylpropylcarbamate (**7a**): White solid, m.p 178–180 °C, $[\alpha]_D^{20}$ –16.0 (c 0.1, $CHCl_3$), dr (*syn*/*anti*): 9.3/1, 97.0% ee (*syn*), 61.2% ee (*anti*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 9 H, ^{t}Bu), 1.52 (d, 3 H, *J* = 6.9 Hz, CH_3), 4.90–4.93 (m, 1 H, CH), 5.16–5.21 (m, 1 H, CH), 5.30 (br. s, 1 H, NH), 7.22–7.24 (m, 2 Harom), 7.33–7.37 (m, 3 Harom). HPLC anlysis (Chiralpak AD-H column, Hexane:2-Propanol = 90:10, flow rate = 0.8 mL/min, wavelength = 254 nm): *R*t = 12.07 (minor of *syn*-isomer) and 13.80 min (major of *syn*-isomer); *R*t = 16.54 (major of *anti*-isomer) and 20.87 min (minor of *anti*-isomer).



tert-Butyl (1*R*)-1-(3-fluorophenyl)-2-nitropropylcarbamate (**7b**): White solid, m.p 134–136 °C, $[\alpha]_D^{20}$ –13.95 (c 0.70, $CHCl_3$), dr (*syn*/*anti*): 1.2/1, 95.3% ee (*anti*), *syn*-isomer is inseparable under this condition. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 9 H, ^{t}Bu), 1.53 (d, 1.36 H, *J* = 6.4 Hz, CH_3 of *anti*-isomer), 1.59 (d, 1.65 H, CH_3 of *syn*-isomer), 4.88–4.96 (m, 1 H, CH), 5.08–5.12 (m, 0.54 H, CH of *syn*-isomer), 5.17–5.21 (m, 0.46 H, CH of *anti*-isomer), 5.31–5.35 (m, 0.53 H, NH of *syn*-isomer), 5.61–5.64 (m, 0.44 H, NH of *anti*-isomer), 6.94–7.05 (m, 3 Harom), 7.31–7.36 (m, 1 Harom). HPLC analysis (Chiralpak AD-H column, Hexane:2-Propanol = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm): *R*t = 17.87 (minor of *anti*-isomer) and 20.26 min (major of *anti*-isomer).

References

[1] a) X. J. Deng, Q. H. Wan, Fine Chemicals **2005**, 22, 307–310 (in Chinese). b) J. X. Yu, F. M. Liu, W. J. Lu, Y. P. Li, L. L. Tian, Y. T. Liu, *Chem. J. Chin. Univ.* **1999**, *20*, 1233–1237 (in Chinese).

[2] M. Kaik, J. Gawroński, *Tetrahedron: Asymmetry* **2003**, *14*, 1559–1563.

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[3] A. G. Wenzel, E. N. Jacobsen, J. Am. Chem. Soc. 2002, 124, 12964–12965.

2. Copies of ^{1}H and ^{13}C NMR Spectra

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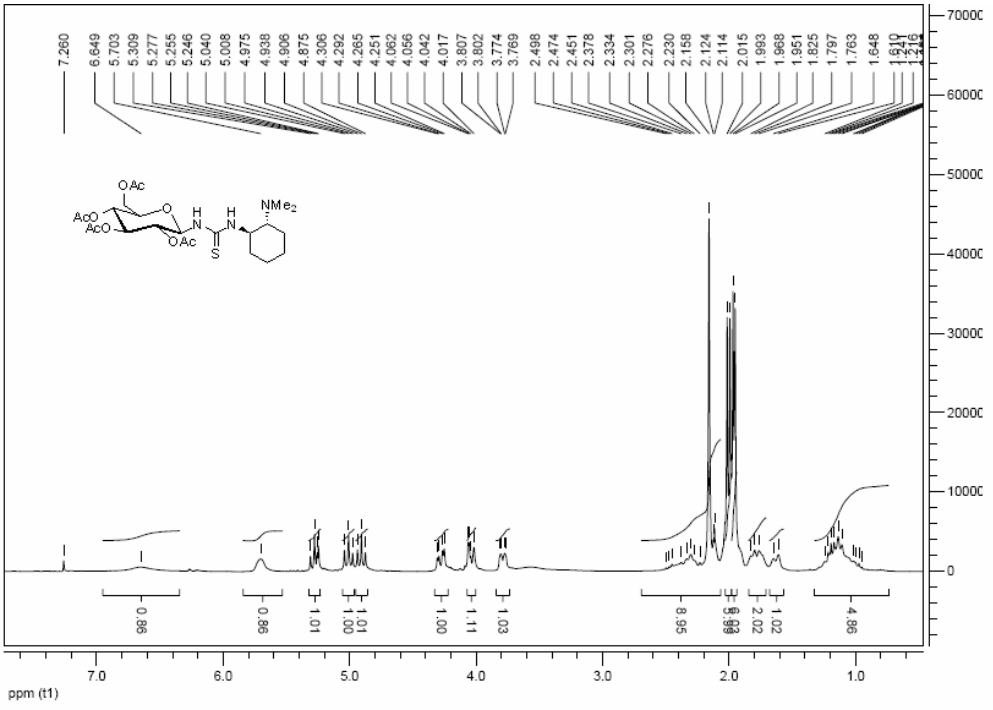

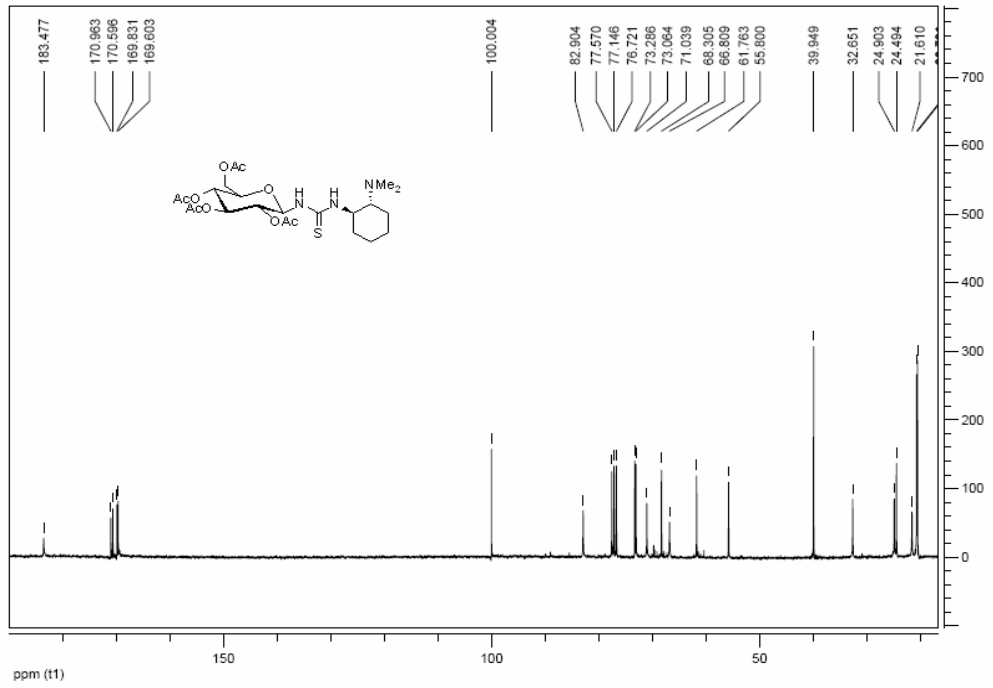

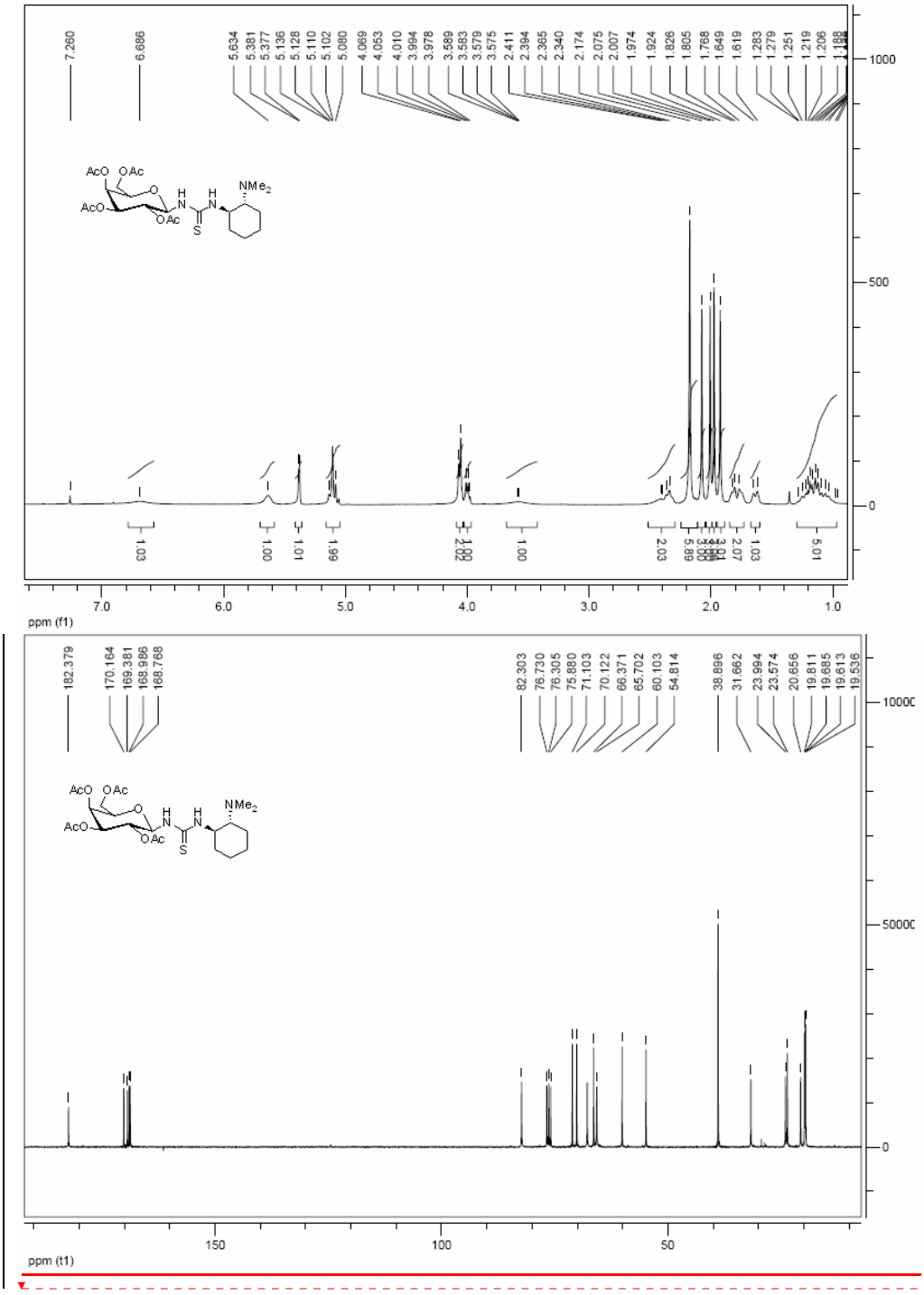
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1.251
1.219
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AcO
OAc
AcO
OAc
H
N
H
N
S
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500
0
1.03
1.00
1.01
1.99
2.00
1.00
2.03
5.01
7.0
6.0
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4.0
3.0
2.0
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54.814
38.896
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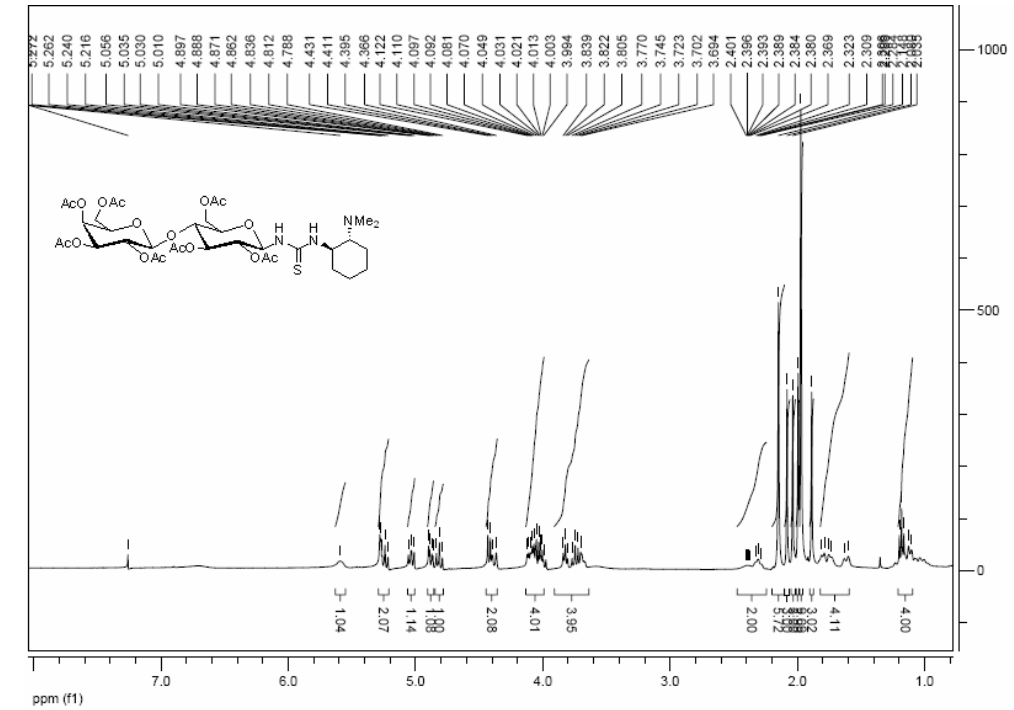
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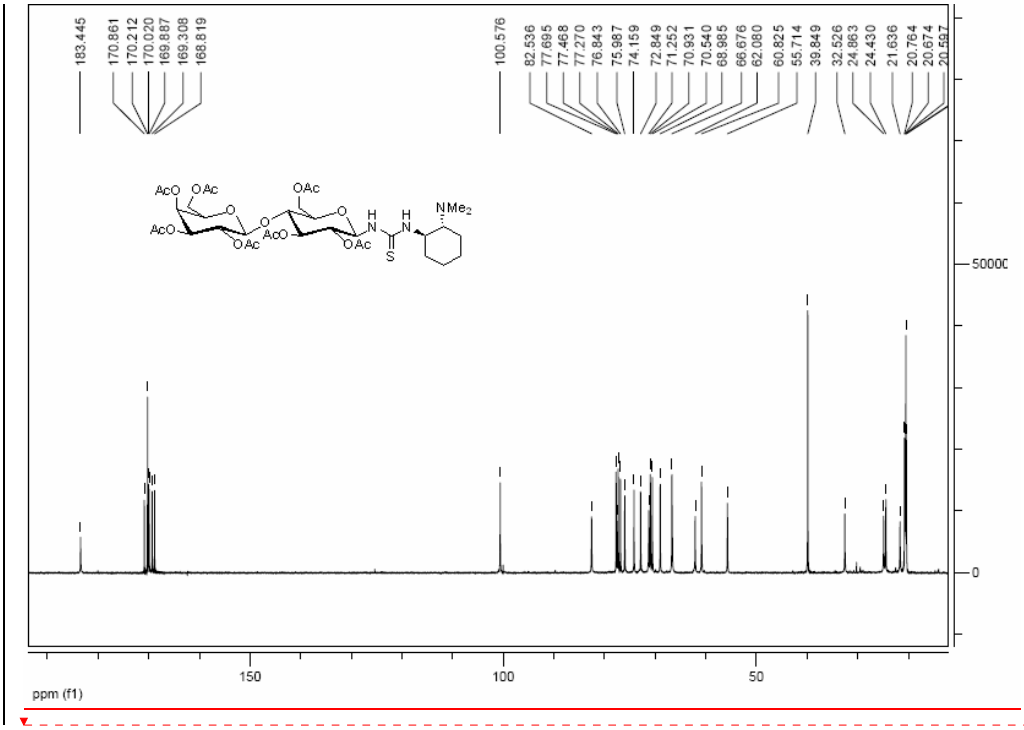
S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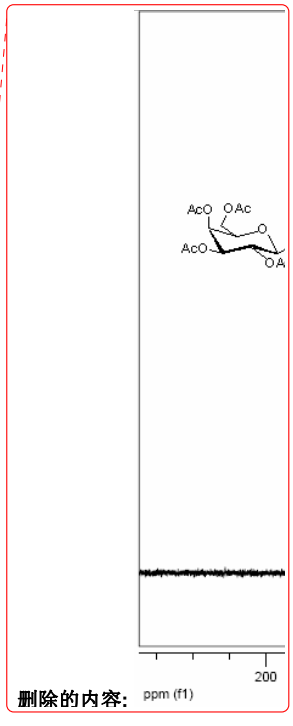
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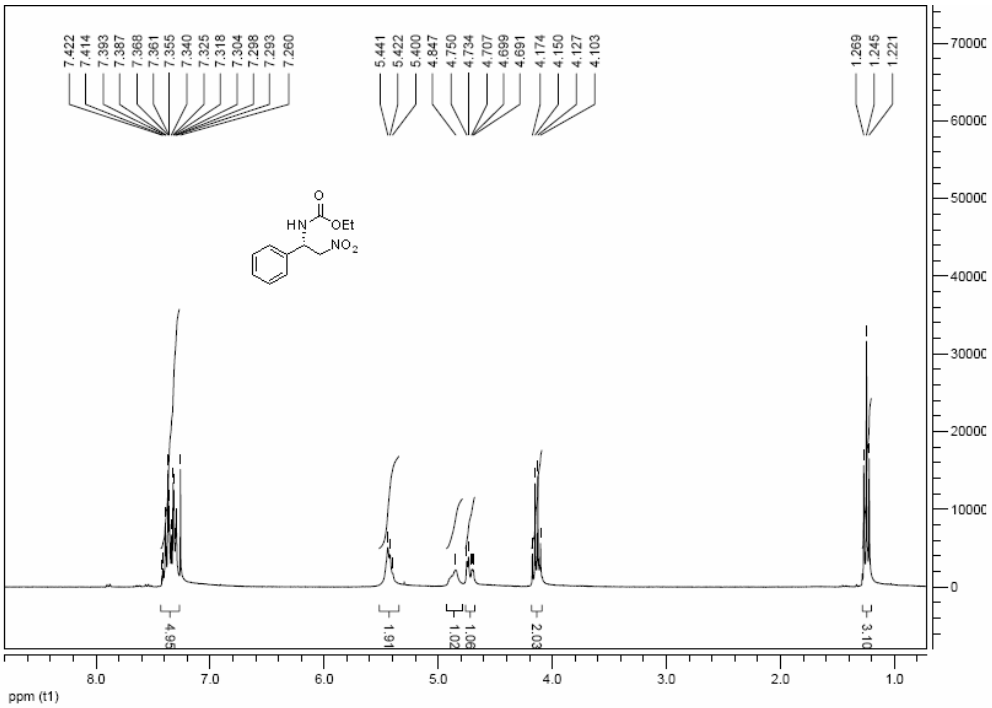
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4.150
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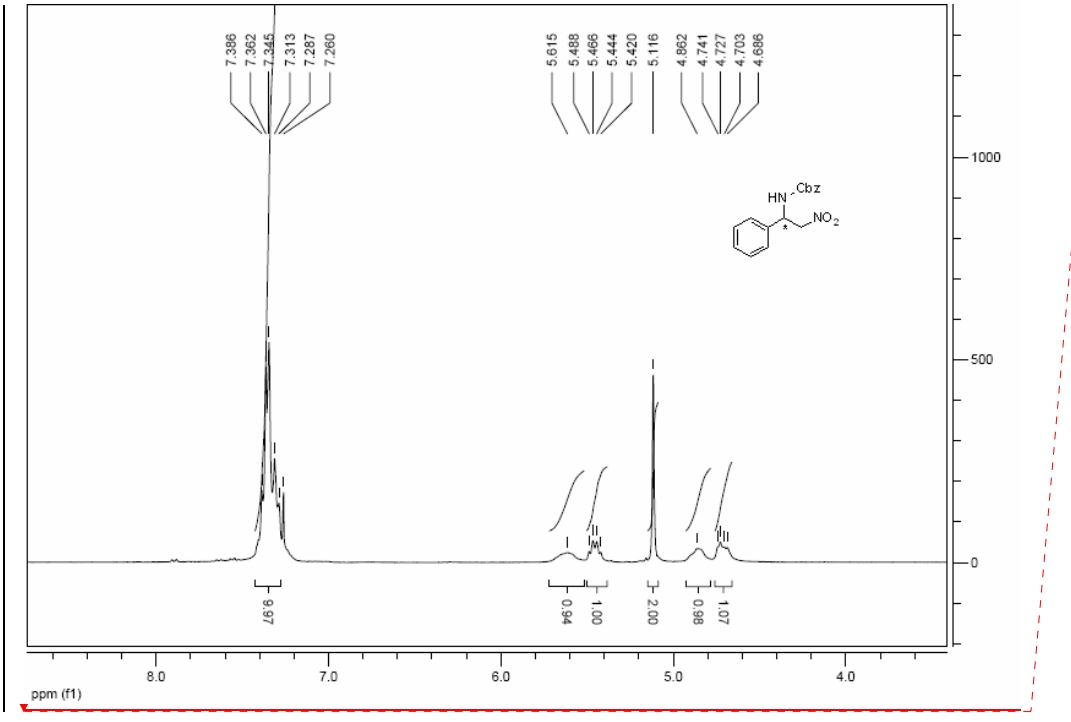
ppm (t1)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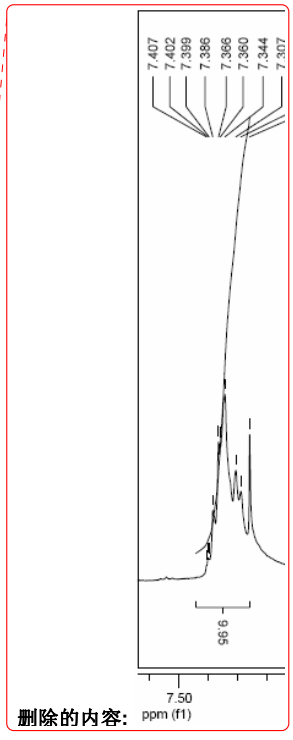
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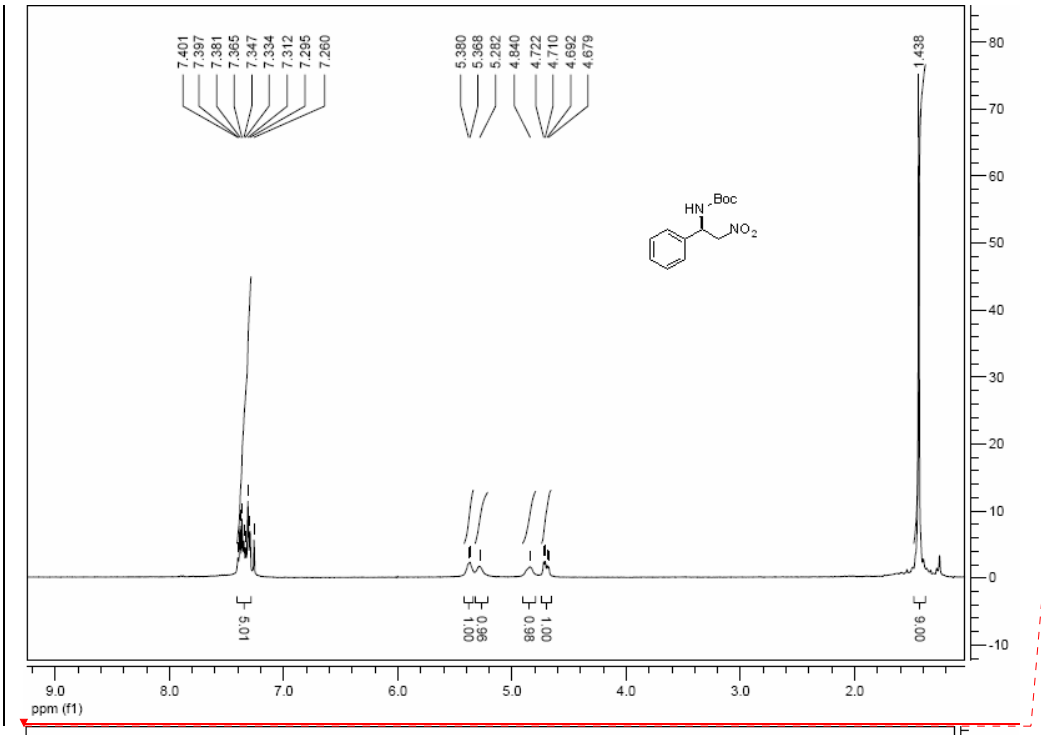
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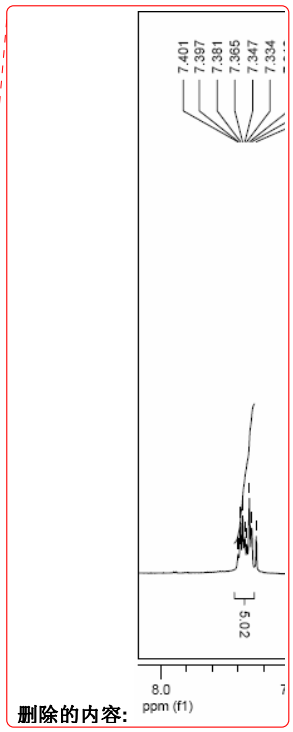
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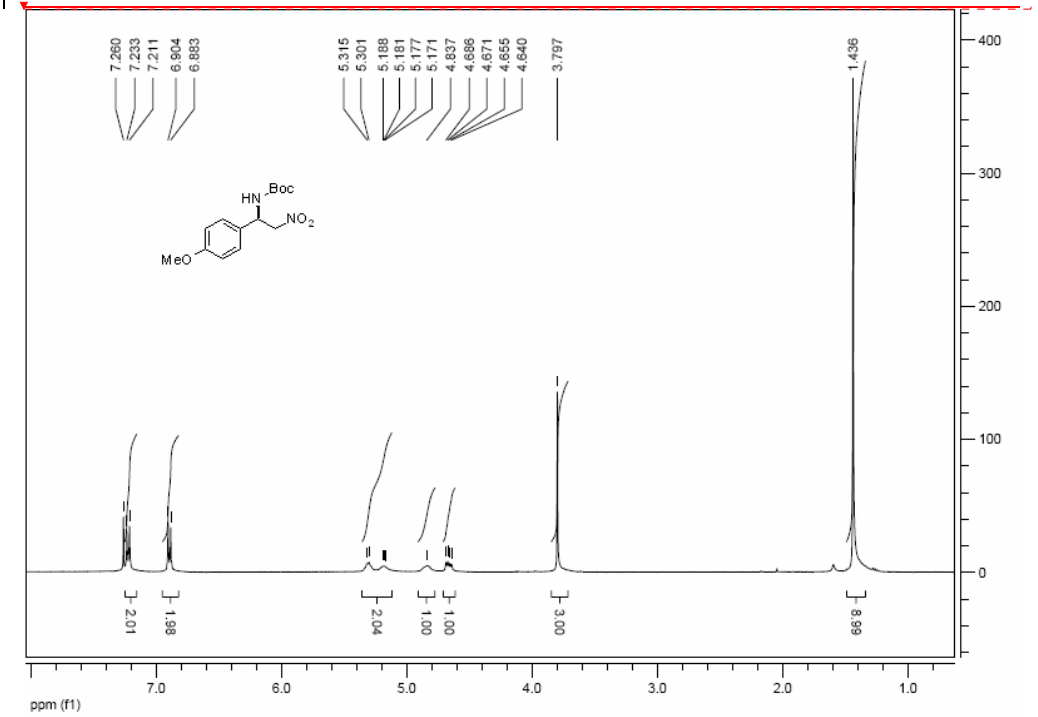
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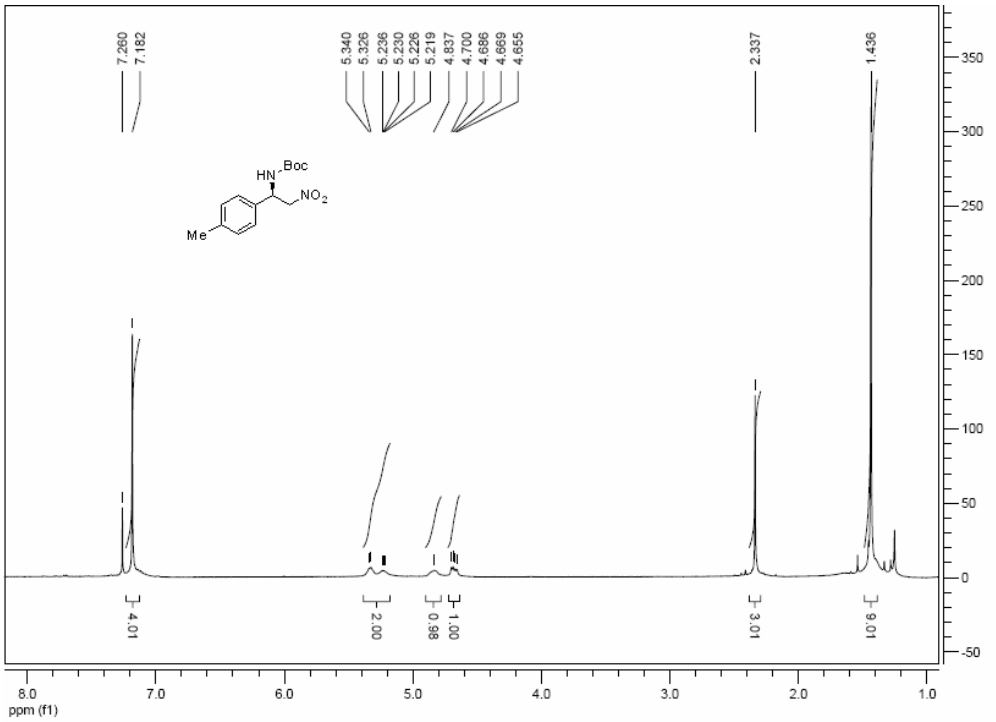
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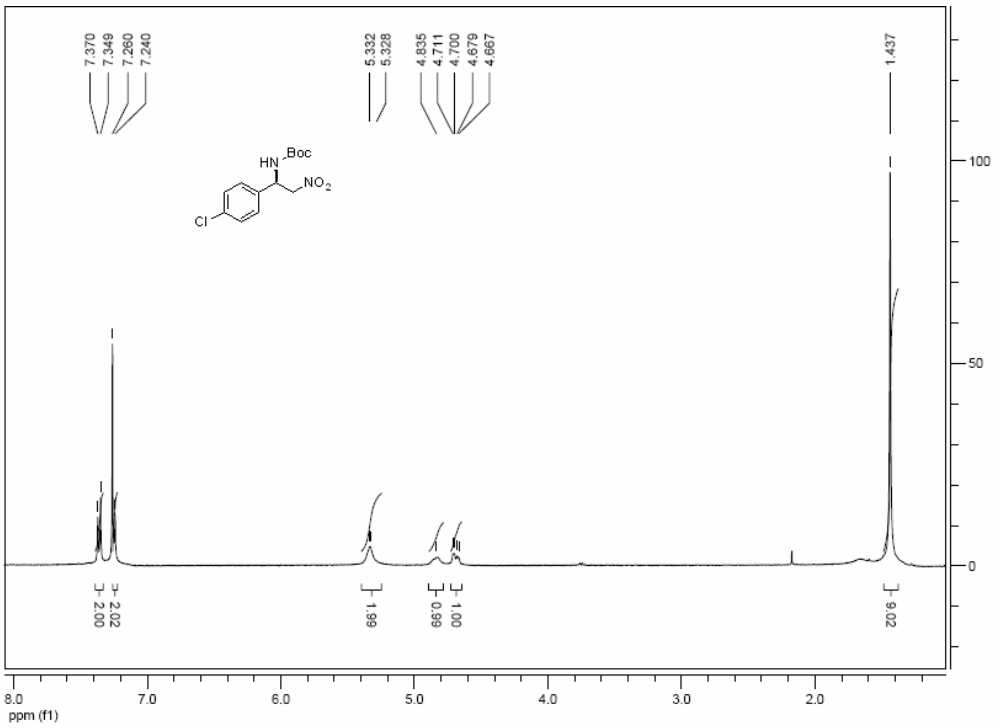
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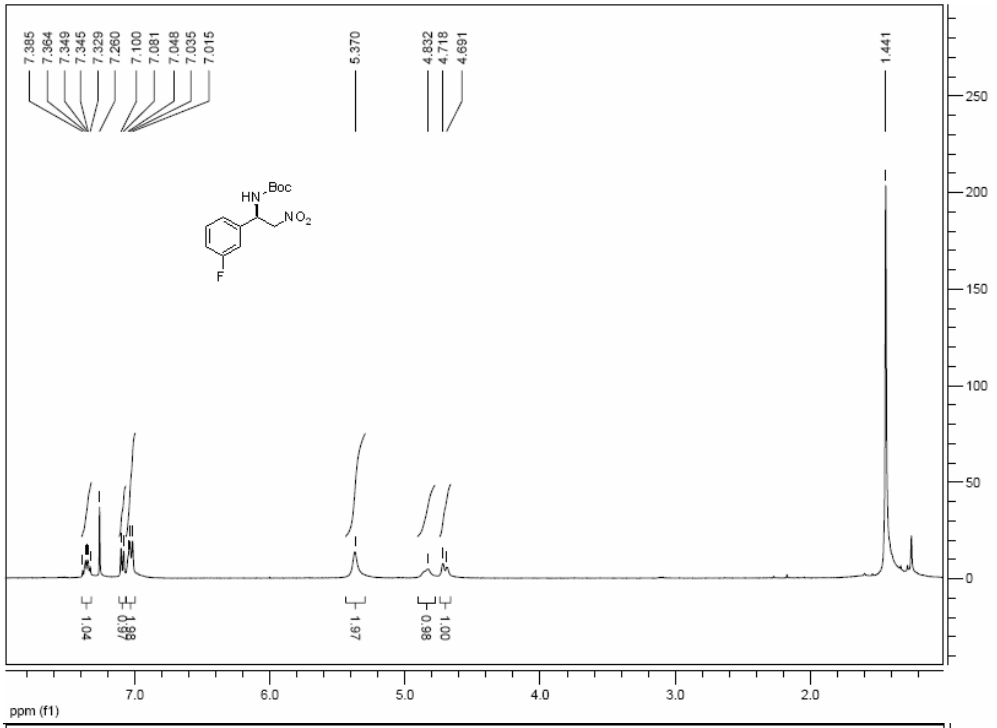
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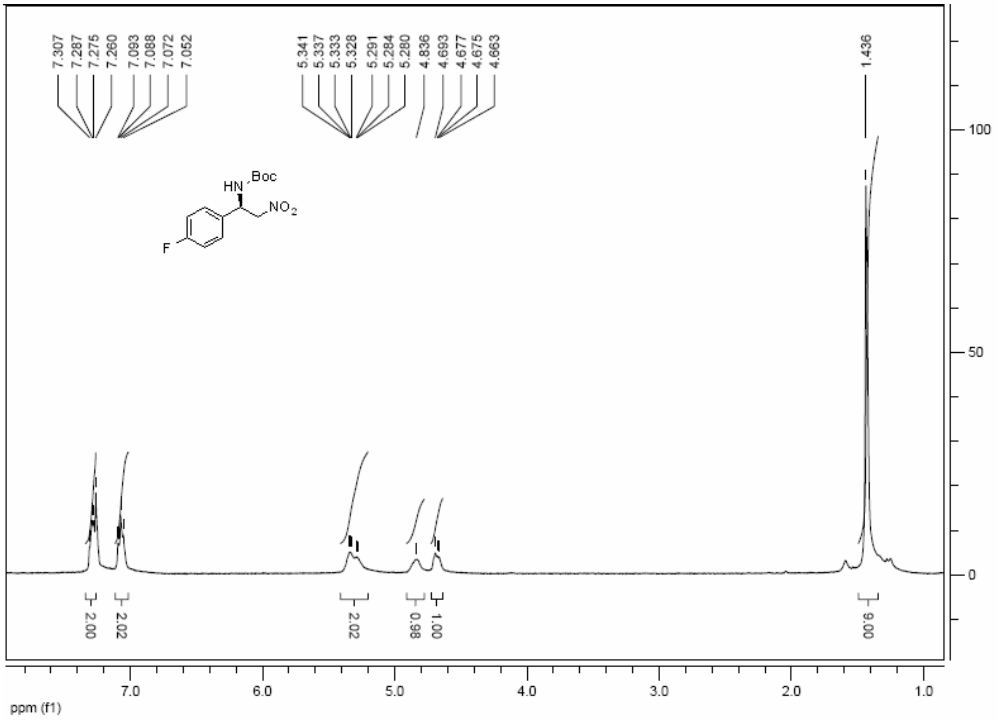
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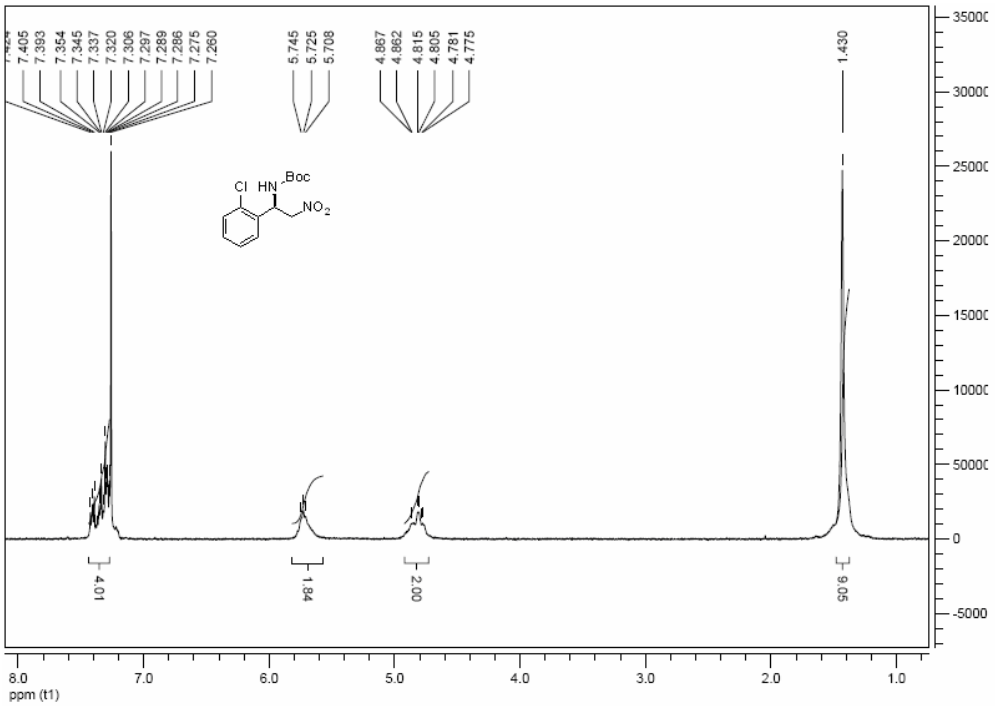
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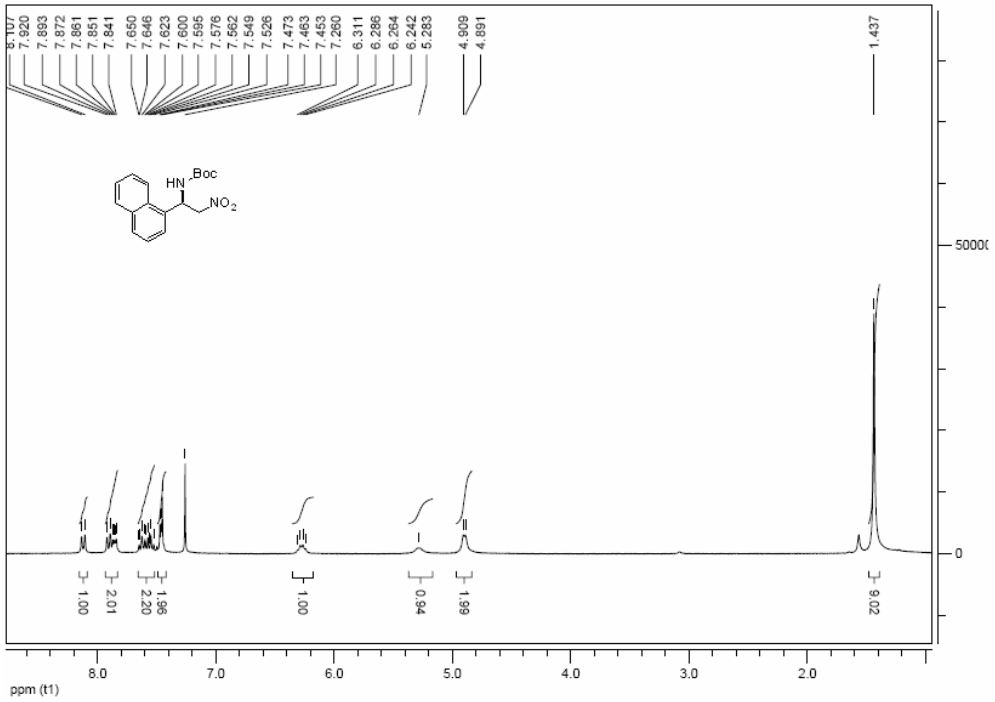
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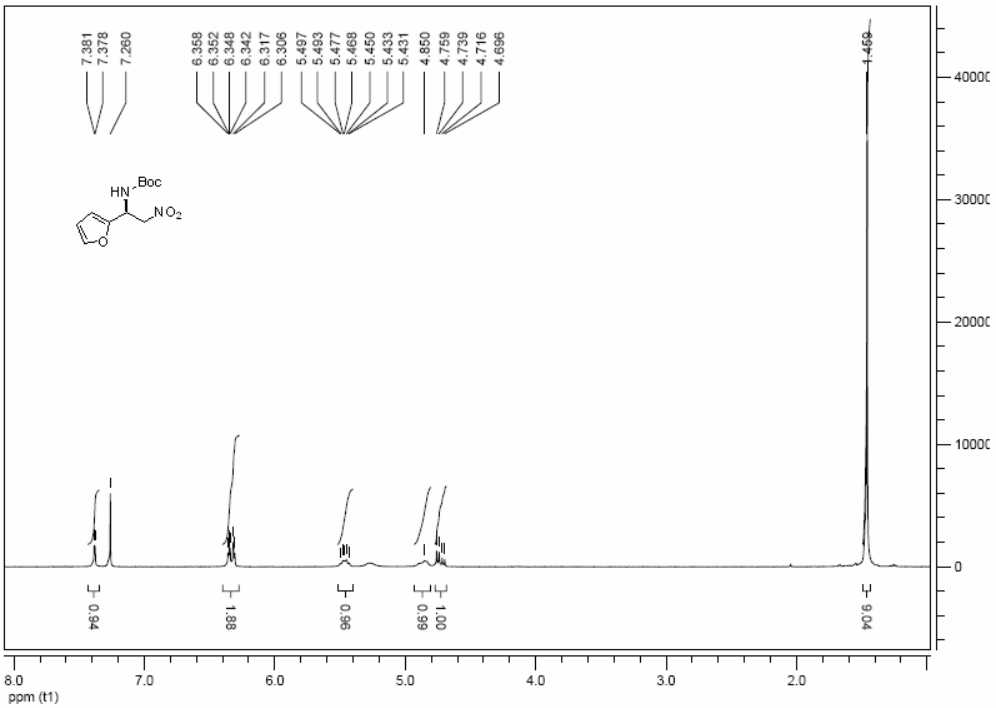
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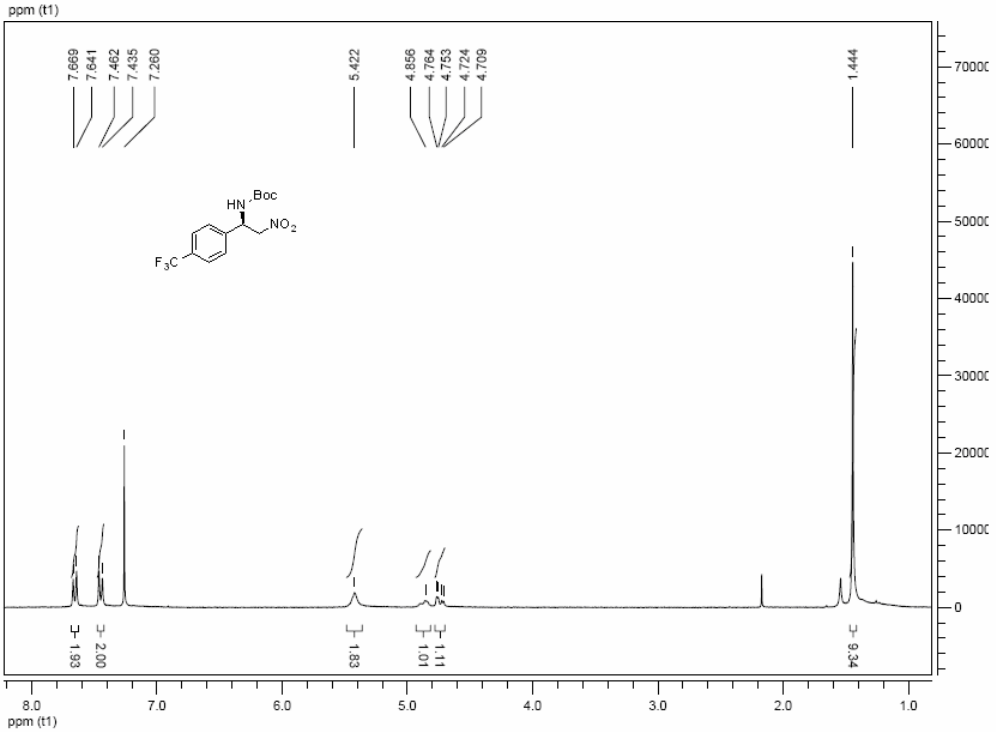
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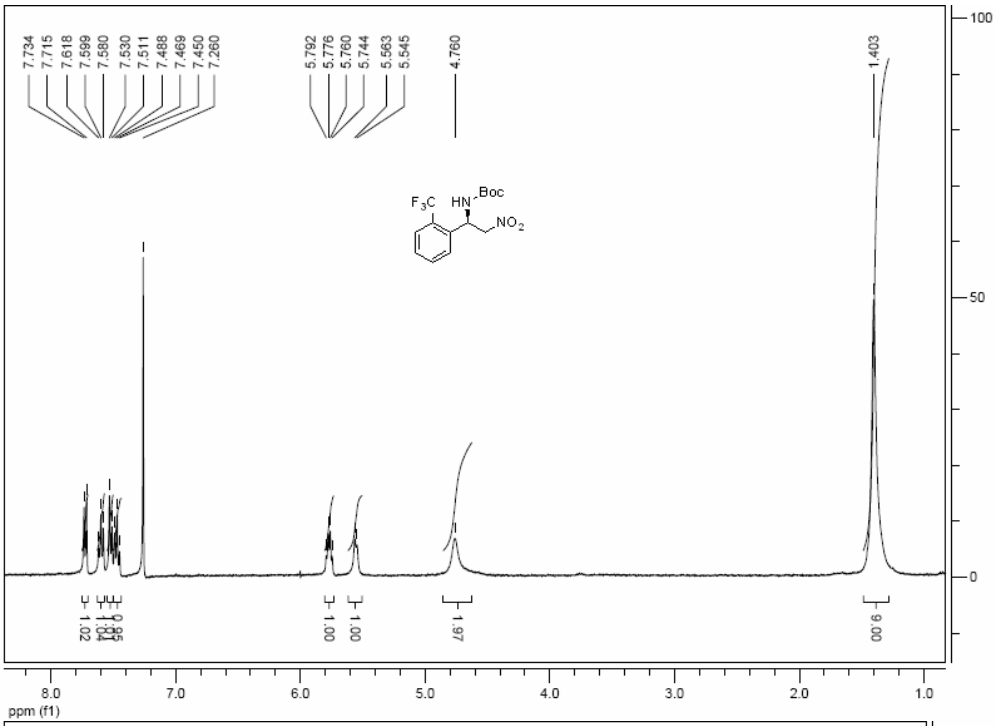
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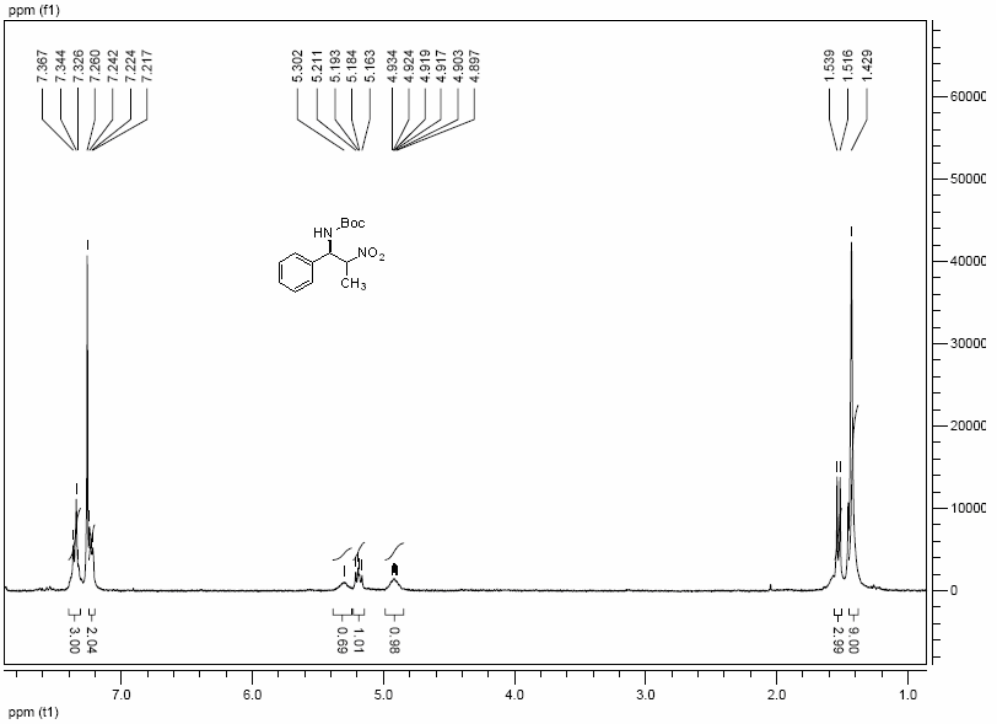
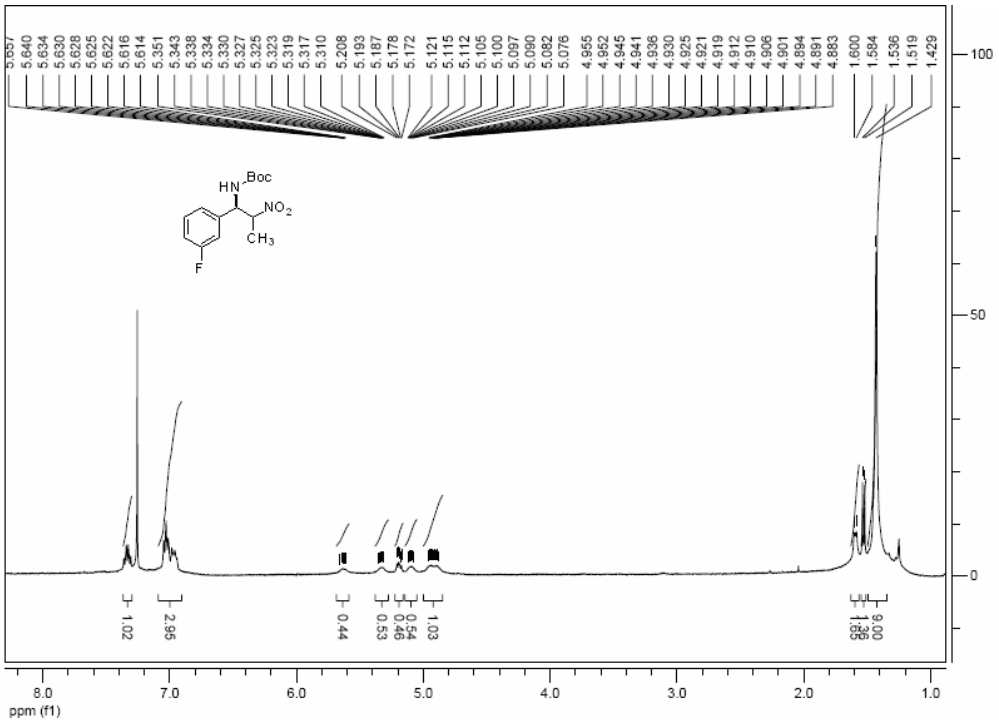
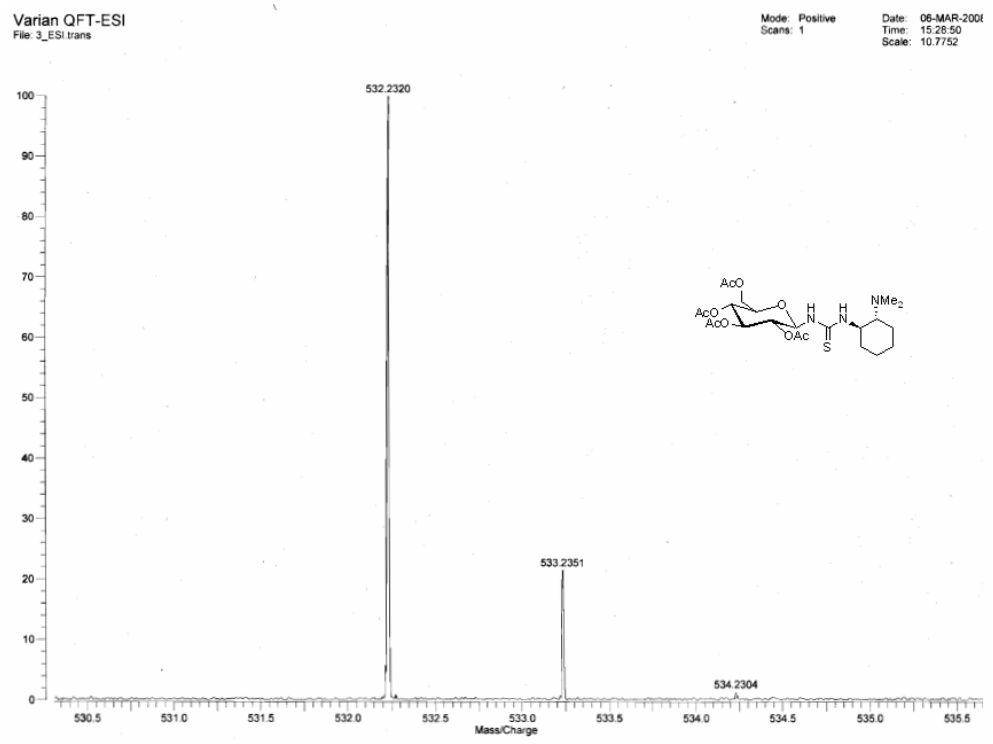
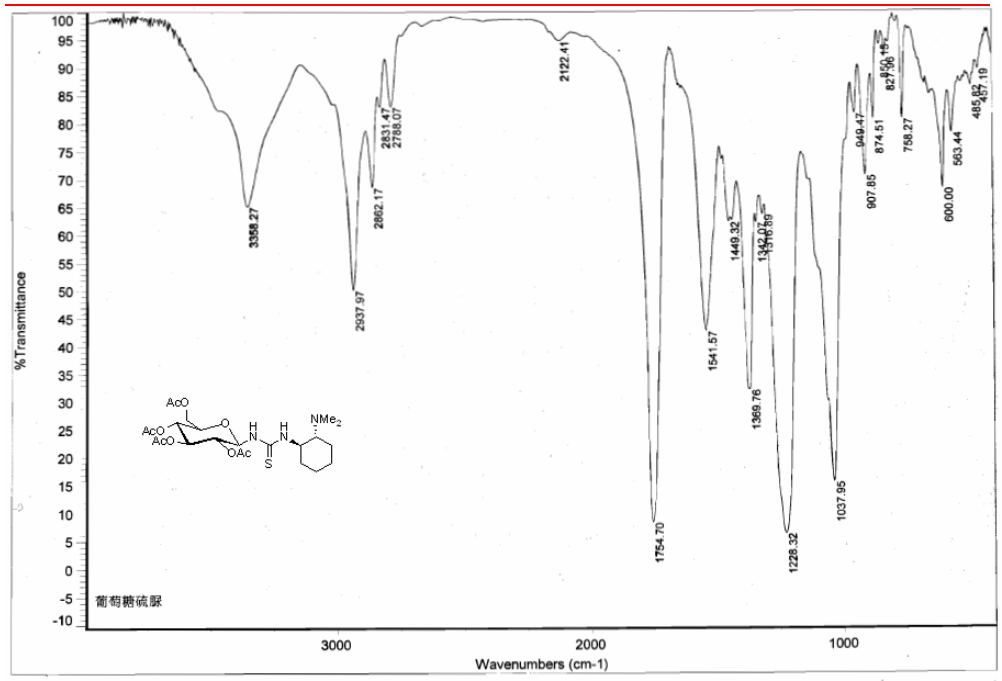
7.580
7.530
7.511
7.488
7.469
7.450
7.260
5.792
5.776
5.760
5.744
5.563
5.545
4.760
1.403
F3C
HN
Boc
NO2
1.02
0.86
1.00
1.00
1.97
9.00
ppm (f1)

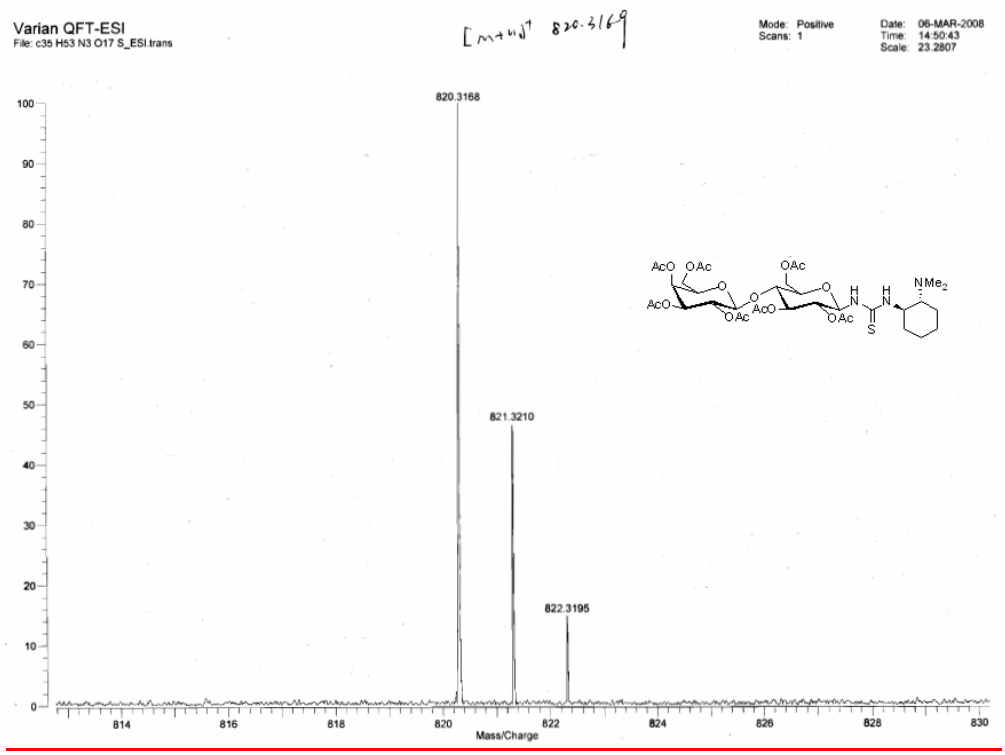

7.367
7.344
7.326
7.260
7.242
7.224
7.217
5.302
5.211
5.193
5.184
5.163
4.934
4.924
4.919
4.917
4.903
4.897
1.539
1.516
1.429
HN
Boc
NO2
CH3
3.00
2.04
0.69
1.01
0.98
2.99
9.00
ppm (f1)

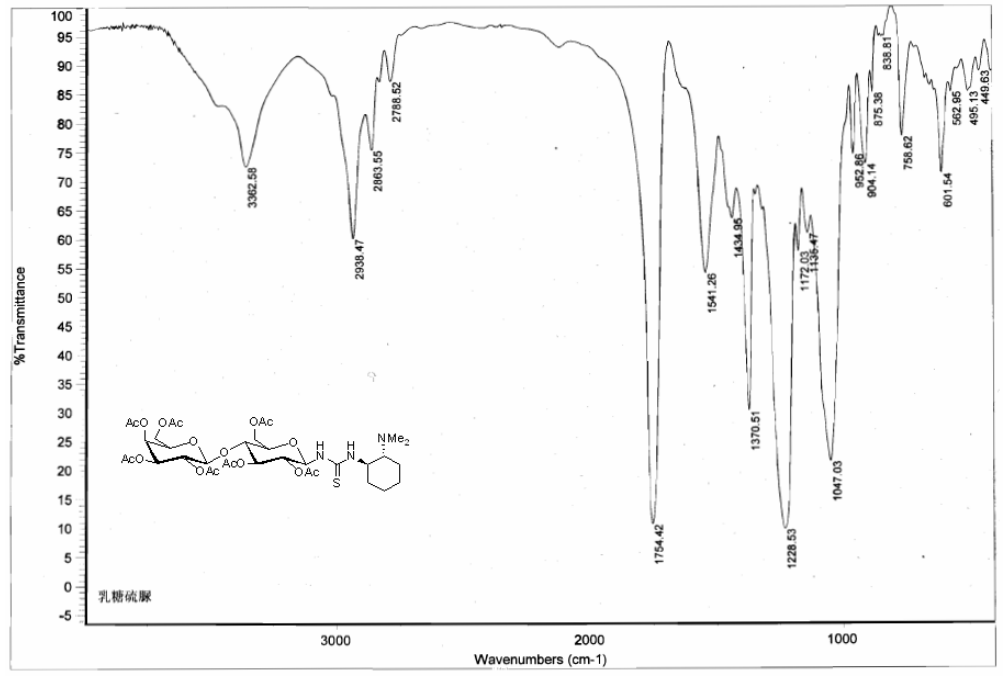

5.657
5.640
5.634
5.630
5.628
5.625
5.622
5.616
5.614
5.351
5.343
5.338
5.334
5.330
5.327
5.325
5.323
5.319
5.317
5.310
5.208
5.193
5.187
5.178
5.172
5.121
5.115
5.112
5.105
5.100
5.097
5.090
5.082
5.076
4.955
4.952
4.945
4.941
4.936
4.930
4.925
4.921
4.919
4.912
4.910
4.906
4.901
4.894
4.891
4.883
1.600
1.584
1.536
1.519
1.429
HN
Boc
NO2
CH3
F
100
50
0
1.02
2.95
0.44
0.53
0.54
0.46
1.03
3.36
3.65
9.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

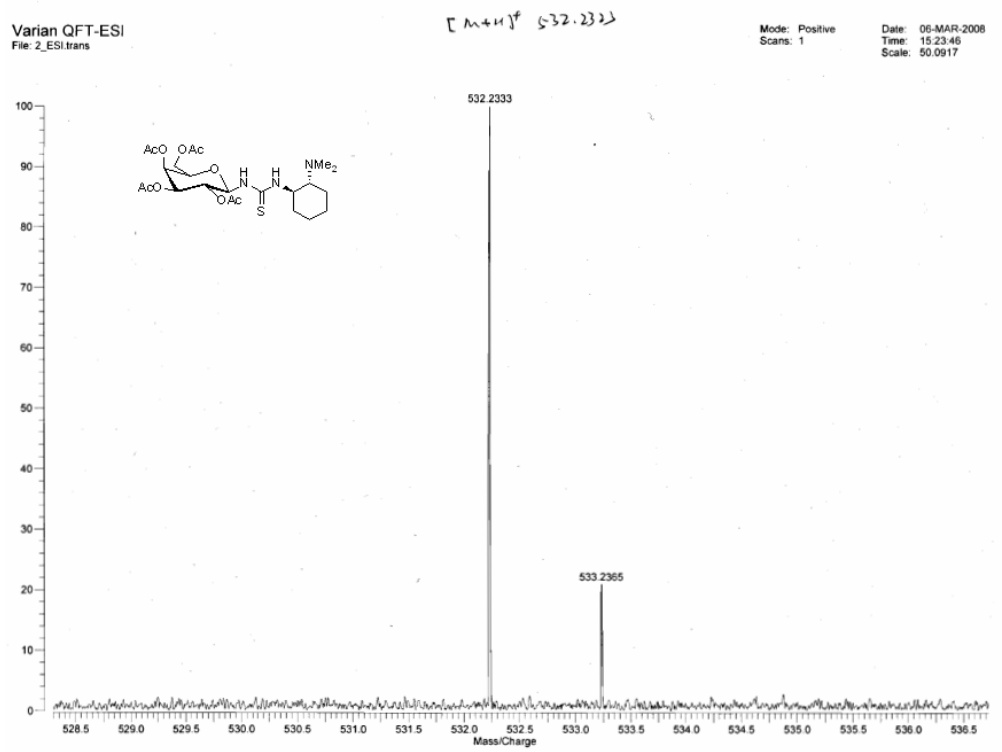
3. HRMS and IR spectra of the prepared thiourea catalysts 2**a-c**

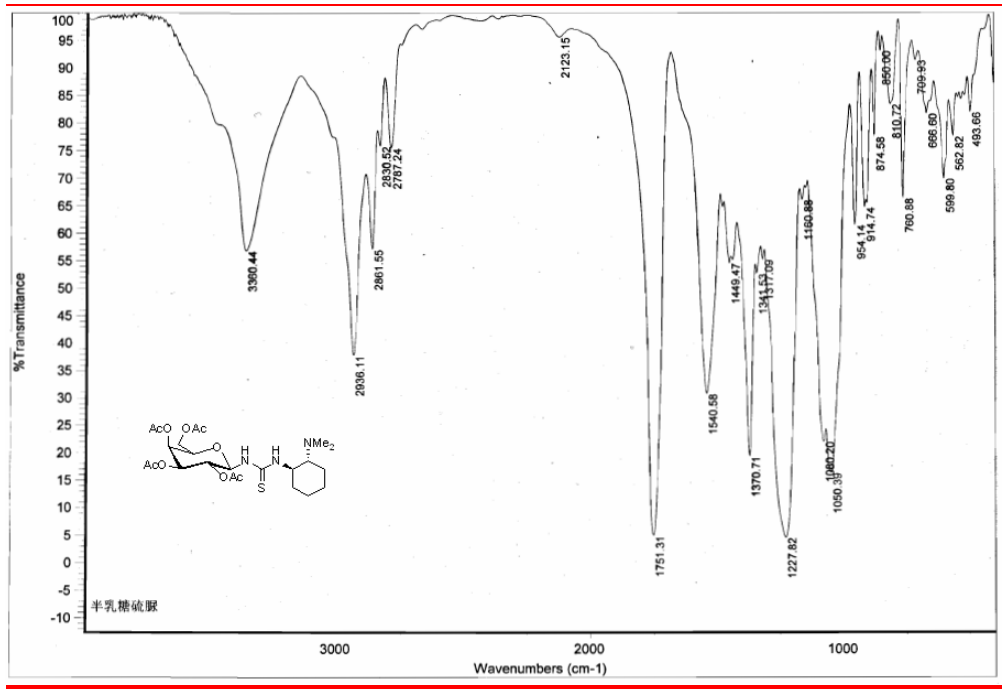





Varian QFT-ESI
File: c35 H53 N3 O17 S_ESI.trans
[M+H]+ 820.3169
Mode: Positive
Scans: 1
Date: 06-MAR-2008
Time: 14:50:43
Scale: 23.2807
820.3168
821.3210
822.3195
Mass/Charge


%Transmittance
3362.58
2938.47
2863.55
2788.52
1754.42
1541.26
1434.96
1370.51
1228.53
1172.03
1138.47
1047.03
962.86
904.14
875.38
838.81
758.62
601.54
562.96
495.13
449.63
乳糖硫脲
Wavenumbers (cm-1)

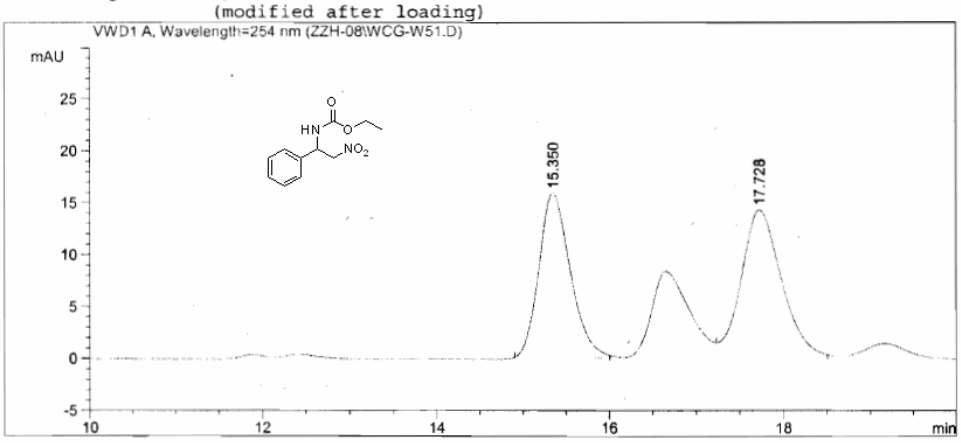

Varian QFT-ESI
File: 2_ESI.trans
[M+H]+ 532.2333
Mode: Positive
Scans: 1
Date: 06-MAR-2008
Time: 15:23:46
Scale: 50.0917
532.2333
533.2365
Mass/Charge


%Transmittance
Wavenumbers (cm-1)
3300.44
2936.11
2861.55
2830.52
2787.24
2123.15
1751.31
1540.58
1449.47
1370.71
1341.53
1317.09
1227.82
1160.88
1080.20
1050.39
954.14
914.74
874.58
850.00
810.72
700.88
666.60
599.80
562.82
493.66
半乳糖硫脲

4. Copies of HPLC data

删除的内容: 3

```
==================================================================================
Injection Date  : 1/23/2008 8:29:14 PM
Sample Name     :                              Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 8:30:15 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 8:51:53 PM
                  (modified after loading)
```




```
==================================================================================
                          Area Percent Report
==================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

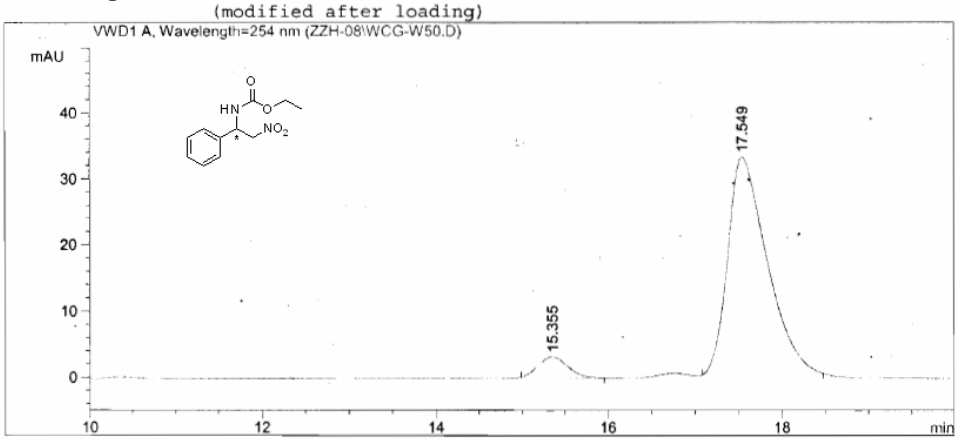

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  15.350 BB    0.3858  404.92535   15.90762  47.4117
   2  17.728 VB    0.4826  449.13760   14.08690  52.5883

Totals :                  854.06296   29.99452

 Results obtained with enhanced integrator!
==================================================================================
                          *** End of Report ***
```

```
Injection Date  : 1/23/2008 8:05:10 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 7:57:18 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 8:30:15 PM
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

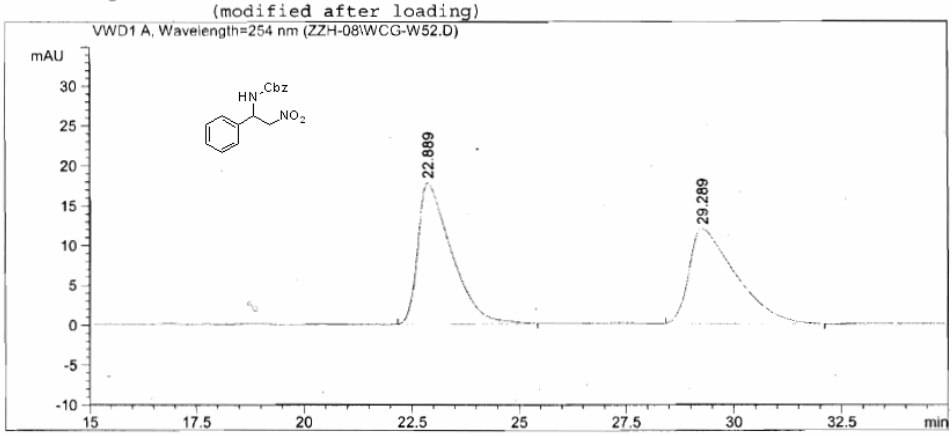
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.355 BB    0.3753   80.00152    3.27492   7.1186
   2  17.549 BB    0.4698 1043.82983   32.97514  92.8814

Totals :                  1123.83135   36.25006

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

```
Injection Date  : 1/23/2008 11:10:40 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 10:19:34 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 11:46:55 PM
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

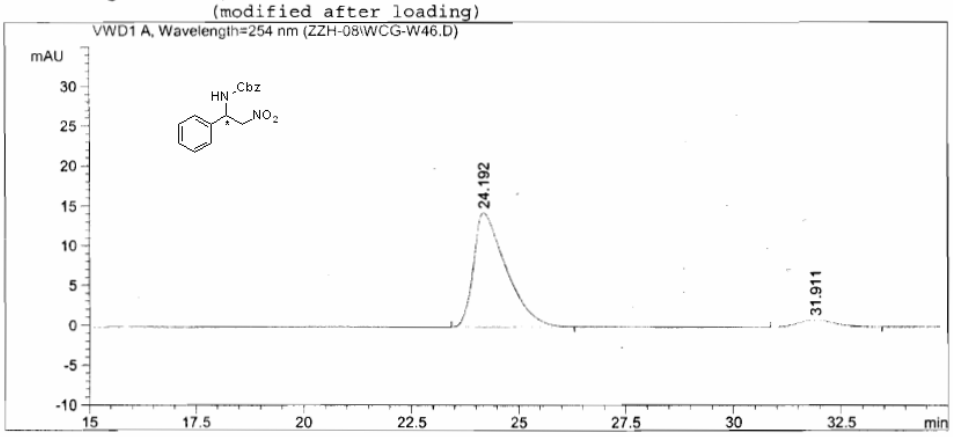
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  22.889 BB    0.7888  963.70654   17.72125  52.0823
   2  29.289 BP    1.0560  886.64777   11.85567  47.9177

Totals :                  1850.35431   29.57692

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 1/23/2008 10:28:06 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 10:19:34 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/23/2008 11:07:45 PM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

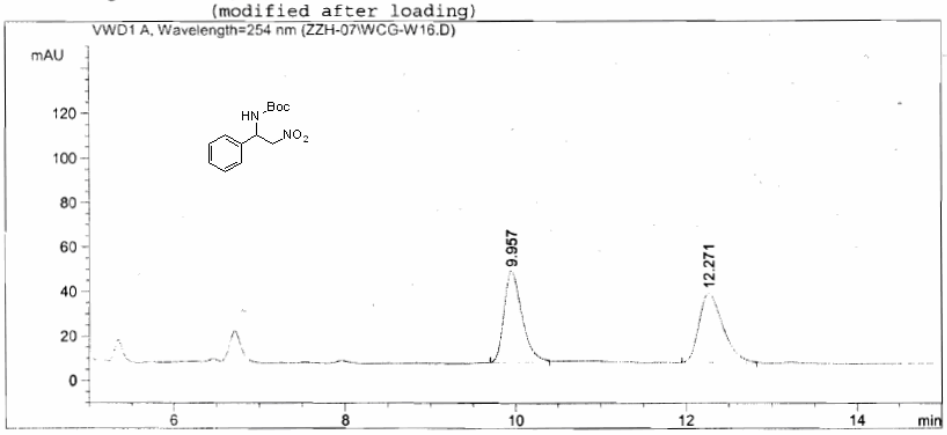
Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  24.192 BB    0.7757  764.91492   14.36156  93.6386
   2  31.911 BB    0.7460   51.96542 8.56183e-1   6.3614

Totals :                  816.88034   15.21774

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

85/15 1.0ml/min 254nm

```
==================================================================
Injection Date  : 12/11/2007 12:04:45 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/11/2007 11:56:47 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/11/2007 12:21:17 PM
                  (modified after loading)
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

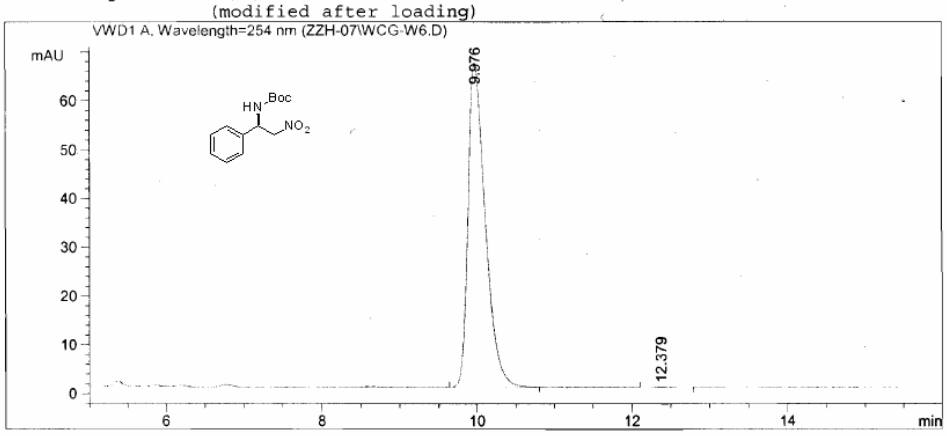
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.957 BB    0.2273  606.04120   41.10975  50.1366
   2  12.271 BB    0.2954  602.73999   31.17706  49.8634

Totals :                  1208.78119   72.28681

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```

85:15 1ml/min 254nm

```
==========================================================================
Injection Date  : 11/2/2007 8:59:40 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 8:29:50 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 9:18:44 PM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

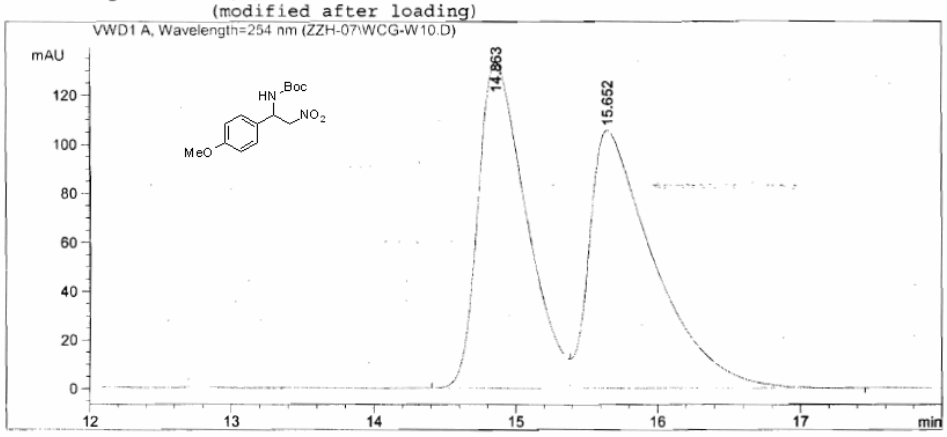
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.976 BB    0.2374 1035.50940   66.36609  99.8391
   2  12.379 BB    0.2375    1.66853 9.21245e-2   0.1609

Totals :                  1037.17793   66.45821

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

85:15 1ml/min 254nm

```
Injection Date  : 11/2/2007 7:34:59 PM
Sample Name     :                              Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 5:31:35 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 8:00:02 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

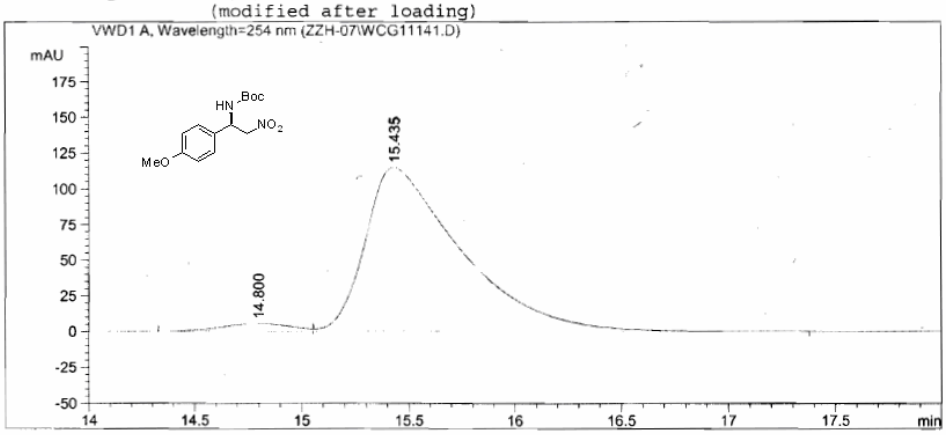
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.863 BV    0.3605 3142.76050  132.83284  48.6219
   2  15.652 VB    0.4558 3320.90723  105.16181  51.3781

Totals :                  6463.66772  237.99465

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

```
==================================================================
Injection Date  : 11/14/2007 12:30:35 PM
Sample Name     :                              Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/14/2007 11:47:09 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/3/2007 7:30:05 PM
                  (modified after loading)
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

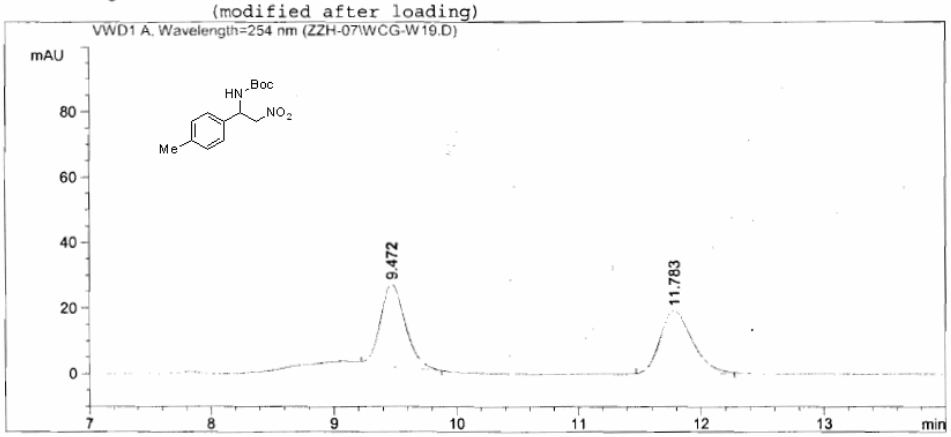
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.800 BV    0.3465  119.28725    5.43144   3.2204
   2  15.435 VB    0.4459 3584.78418  114.77058  96.7796

Totals :                  3704.07143  120.20203

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

85/15 1.0ml/min 254nm

```
Injection Date  : 12/11/2007 4:28:12 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/11/2007 4:25:03 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/11/2007 5:06:07 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.472 BP    0.2191  362.29755   25.35271  50.3635
   2  11.783 BB    0.2829  357.06735   19.29562  49.6365

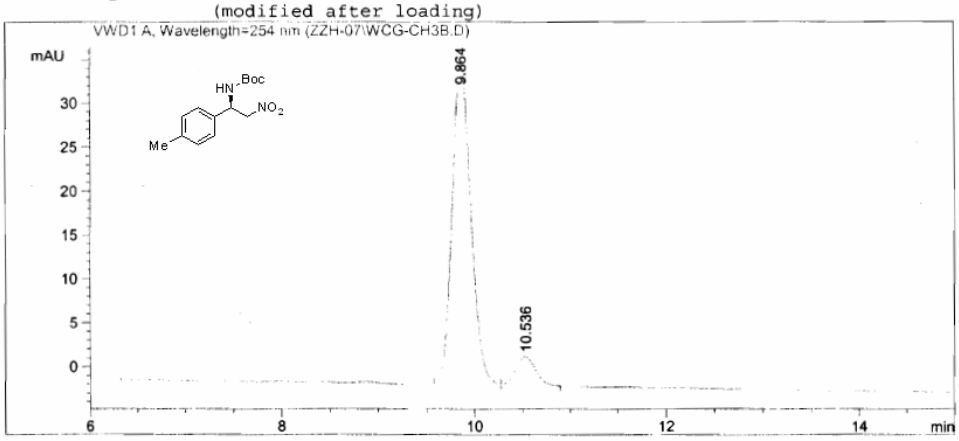
Totals :                   719.36490   44.64833

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

AD-H 85:15 1ml/min

```
================================================================================
Injection Date  : 8/7/2007 10:18:26 AM
Sample Name     :                                    Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 8/7/2007 9:51:19 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 8/7/2007 12:52:53 PM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

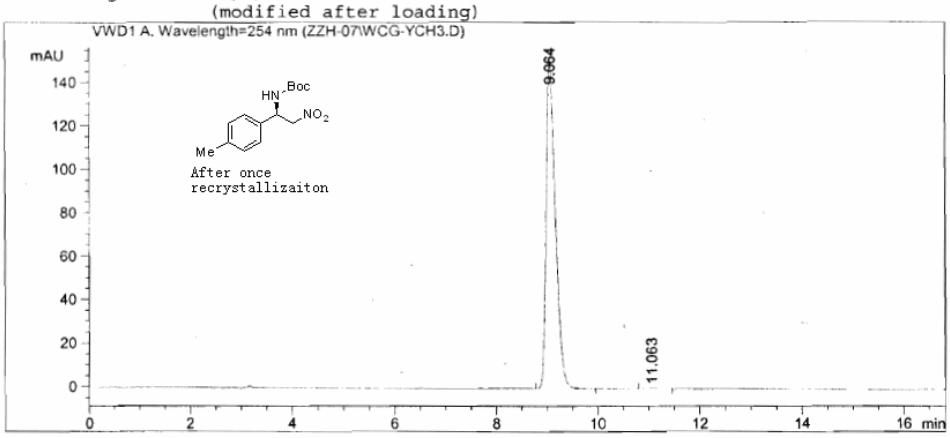
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.864 BB    0.2125  503.13983   36.65794  91.2961
   2  10.536 BB    0.2223   47.96773    3.32277   8.7039

Totals :                   551.10756   39.98071

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

85:15

```
==========================================================================
Injection Date  : 10/23/2007 4:06:30 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/23/2007 3:45:05 PM by gp-248
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 9:34:47 AM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
.

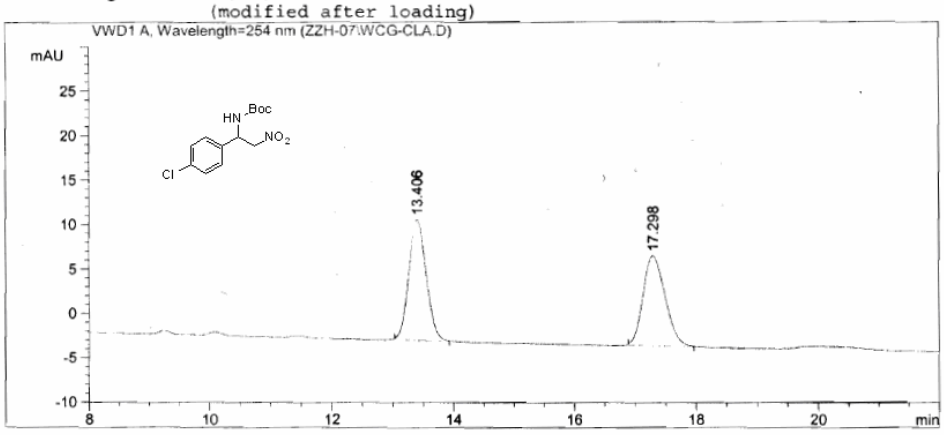
Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.064 BB    0.1968 1925.23254  149.49438  99.8328
   2  11.063 PP    0.2235    3.22391 2.12600e-1   0.1672

Totals :                  1928.45645  149.70698

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

```
Injection Date  : 7/27/2007 9:27:32 AM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 7/27/2007 9:04:35 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/11/2007 4:16:12 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  13.406 BB    0.3112  270.62241   13.57241  51.5353
   2  17.298 BB    0.3927  254.49770   10.11122  48.4647

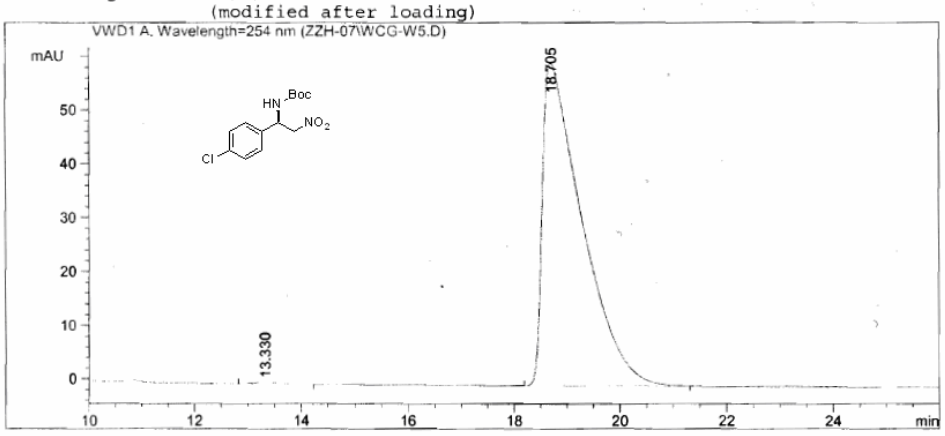
Totals :                   525.12010   23.68363

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

90:10 1ml/min 254nm

```
================================================================================
Injection Date  : 11/2/2007 3:28:27 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 3:00:38 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 3:58:02 PM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

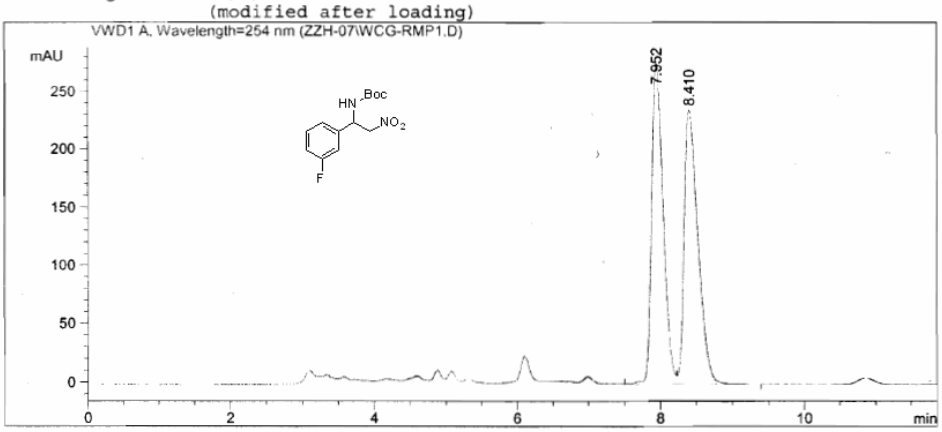

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.330 BB    0.4144   11.49326 3.34113e-1   0.3671
   2  18.705 BB    0.7345 3118.92236   60.00627  99.6329

Totals :                  3130.41563   60.34038

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

```
==========================================================================
Injection Date  : 10/19/2007 5:23:03 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/19/2007 4:07:49 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 9:34:47 AM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

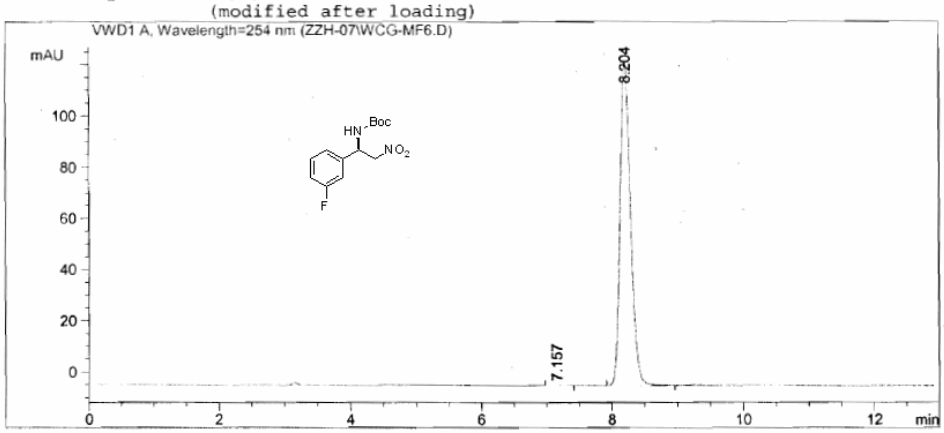
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.952 VV    0.1707 3075.99731  276.12070  49.7711.
   2   8.410 VB    0.2004 3104.28564  235.40923  50.2289

Totals :                  6180.28296  511.52992

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

85:15 1.0ml/min 254nm

```
==========================================================================
Injection Date  : 10/23/2007 11:02:35 AM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/23/2007 9:19:39 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 11/2/2007 9:32:50 AM
                  (modified after loading)
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

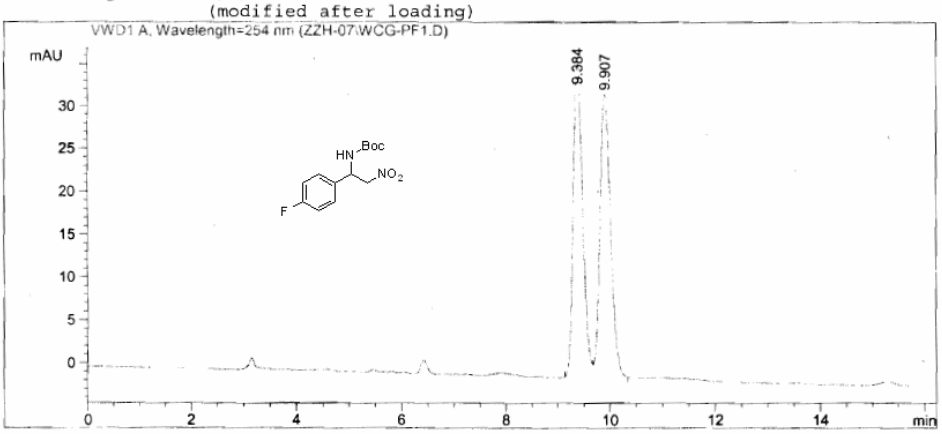
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   7.157 BP    0.1443    1.44160 1.57939e-1   0.1029
   2   8.204 BB    0.1732 1399.89563  126.05016  99.8971

Totals :                  1401.33723  126.20809

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

AD-H 85:15 1ml/min

```
==================================================================
Injection Date  : 9/3/2007 10:09:36 AM
Sample Name     :                              Location : Vial 1
Acq. Operator   :
Method          : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 9/3/2007 9:55:08 AM
                  (modified after loading)
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

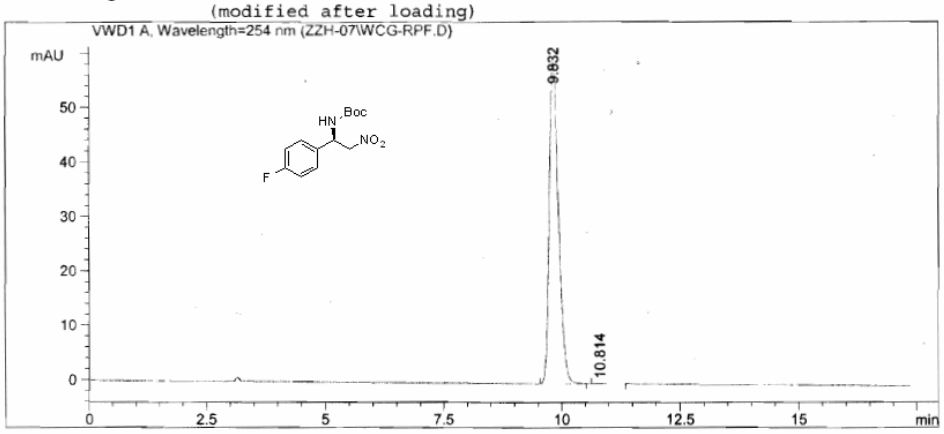

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   9.384 BV    0.1960  466.46371   36.77612  49.8463
   2   9.907 VB    0.2194  469.33945   33.07088  50.1537

Totals :                   935.80316   69.84700

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

```
Injection Date  : 10/19/2007 4:20:20 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/19/2007 4:07:49 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/19/2007 4:47:19 PM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

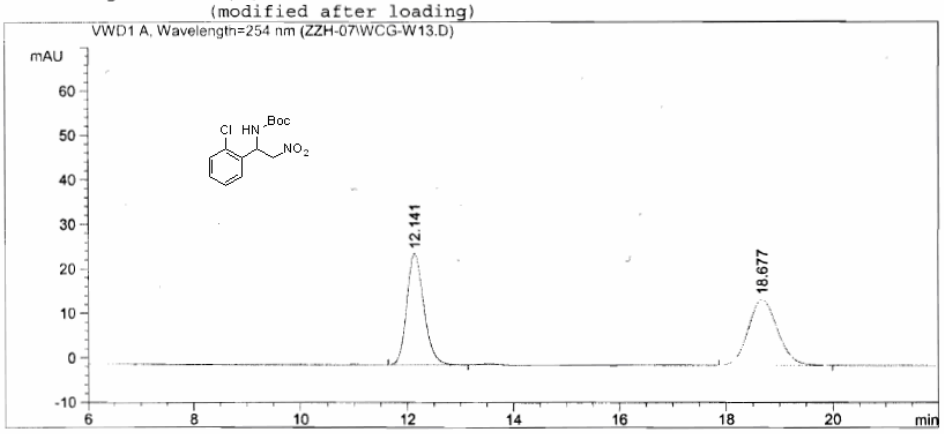
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.832 BB    0.2114  811.17676   58.99923  99.7421
   2  10.814 BP    0.2148    2.09776 1.23122e-1   0.2579

Totals :                  813.27452   59.12235

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

```
================================================================================
Injection Date  : 12/3/2007 8:32:21 PM
Sample Name     :                                    Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/3/2007 8:32:58 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/3/2007 8:55:28 PM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

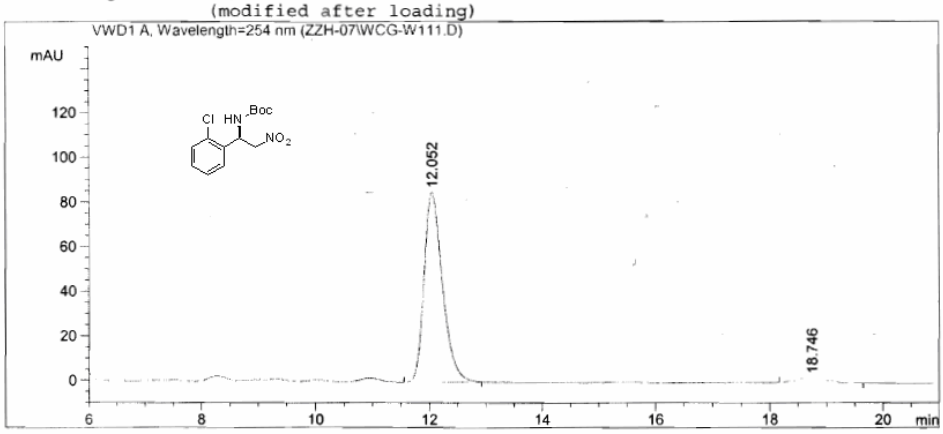

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.141 BB    0.3423  558.80823   25.00049  49.8704
   2  18.677 BB    0.5879  561.71271   14.81680  50.1296

Totals :                  1120.52094   39.81729

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

```
Injection Date  : 12/3/2007 8:10:18 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/3/2007 8:11:37 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/3/2007 8:36:16 PM
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

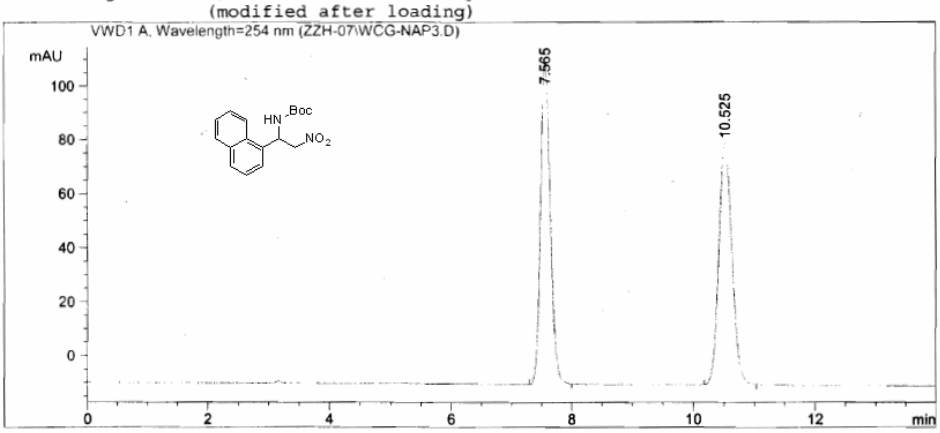
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.052 VB    0.3436 1922.47290   85.09743  96.0741
   2  18.746 BP    0.5581   78.55857    2.16071   3.9259

Totals :                  2001.03147   87.25814

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

```
Injection Date  : 9/13/2007 10:50:46 AM
Sample Name     :                                  Location : Vial 1
Acq. Operator   : odb1
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 9/13/2007 10:51:39 AM by odb1
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 9/13/2007 11:05:54 AM by odb1
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

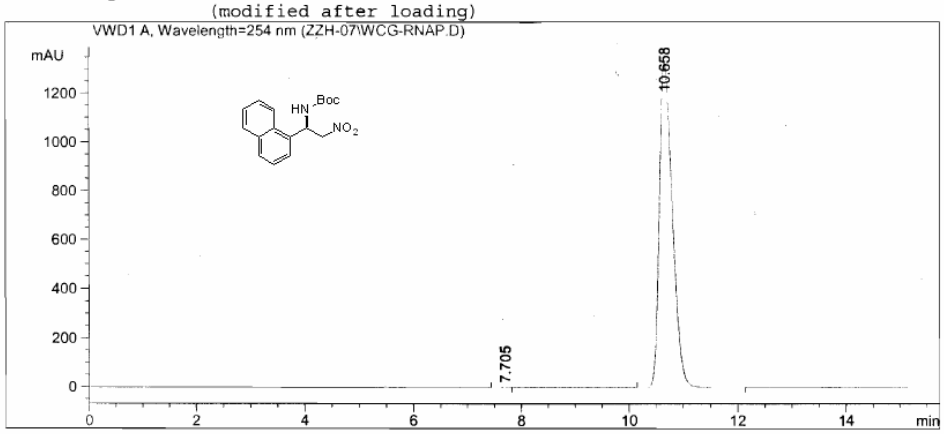
Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.565 BB    0.1734 1337.14441  118.95836  49.9567
   2  10.525 BB    0.2330 1339.46472   89.42050  50.0433

Totals :                  2676.60913  208.37886

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

```
================================================================================
Injection Date  : 10/19/2007 5:02:16 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/19/2007 4:07:49 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/19/2007 4:47:19 PM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

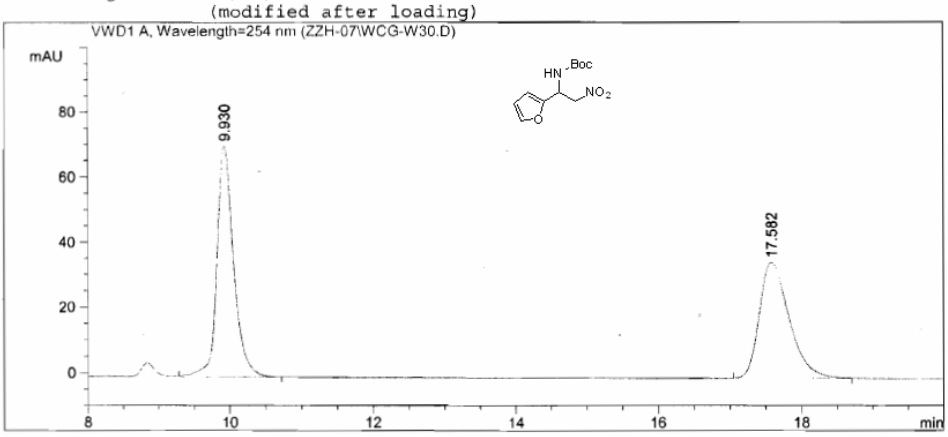

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   7.705 VV    0.1756   17.93740    1.55216   0.0809
   2  10.658 BB    0.2573 2.21505e4  1327.29712  99.9191

Totals :                  2.21684e4  1328.84928

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

```
================================================================================
Injection Date  : 12/21/2007 10:46:06 AM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/21/2007 10:39:34 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/21/2007 11:14:59 AM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

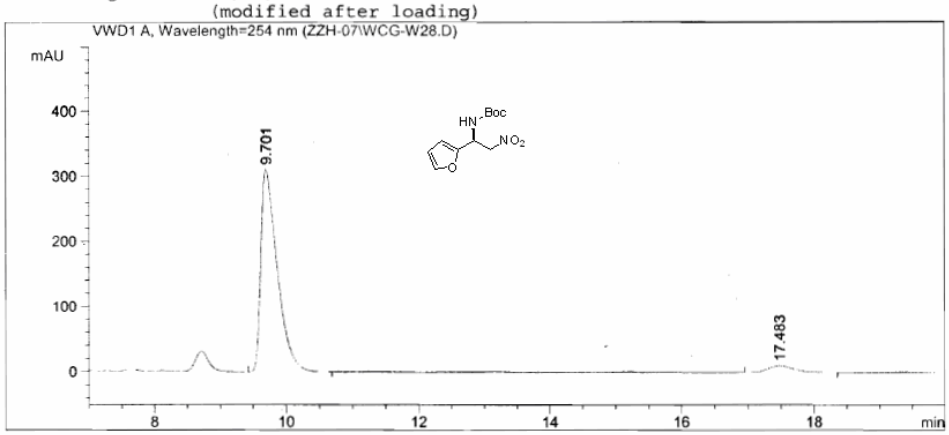

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.930 BB    0.2421 1151.12183   70.80299  52.9841
   2  17.582 BB    0.4421 1021.45673   35.33159  47.0159

Totals :                  2172.57855  106.13458

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

```
Injection Date  : 12/21/2007 10:16:24 AM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/21/2007 10:10:00 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/21/2007 10:39:34 AM
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.701 BB    0.2582 5327.55420  310.83191  94.9407
   2  17.483 BB    0.4214  283.90186   10.27302   5.0593

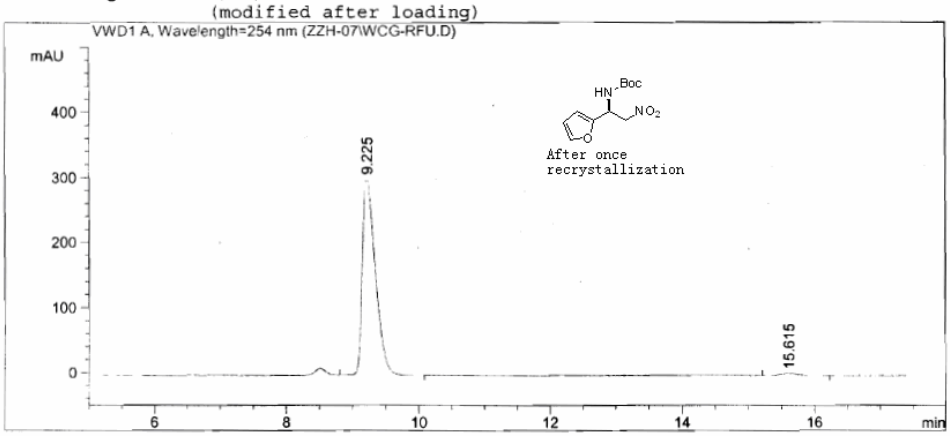
Totals :                  5611.45605  321.10493

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

85:15 1.0ml/min 254nm

```
==================================================================
Injection Date  : 10/23/2007 10:42:55 AM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 10/23/2007 9:19:39 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/26/2008 2:58:59 PM
                  (modified after loading)
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

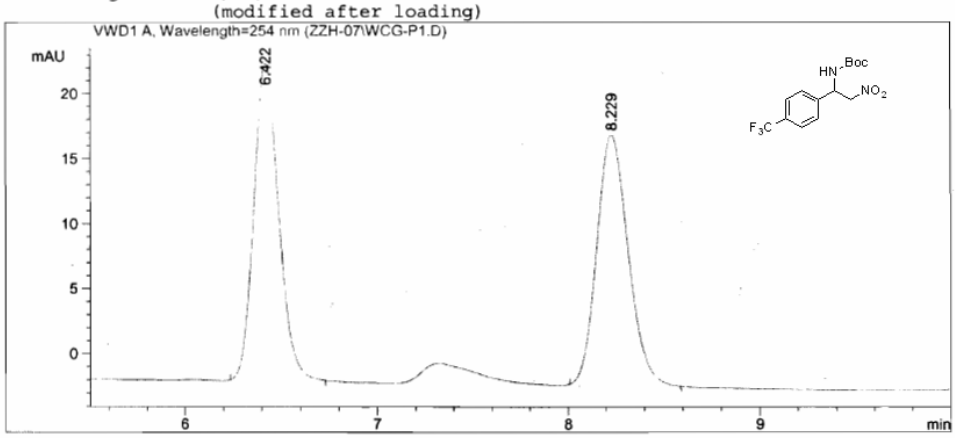

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   9.225 VB     0.2100 4157.97559  302.20551  98.5789
   2  15.615 PB     0.3197   59.93933    2.86634   1.4211

Totals :                  4217.91491  305.07185

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```

```
================================================================================
Injection Date  : 9/26/2007 10:10:52 AM
Sample Name     :                                    Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 9/26/2007 9:24:27 AM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 9/30/2007 11:32:25 AM
                  (modified after loading)
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

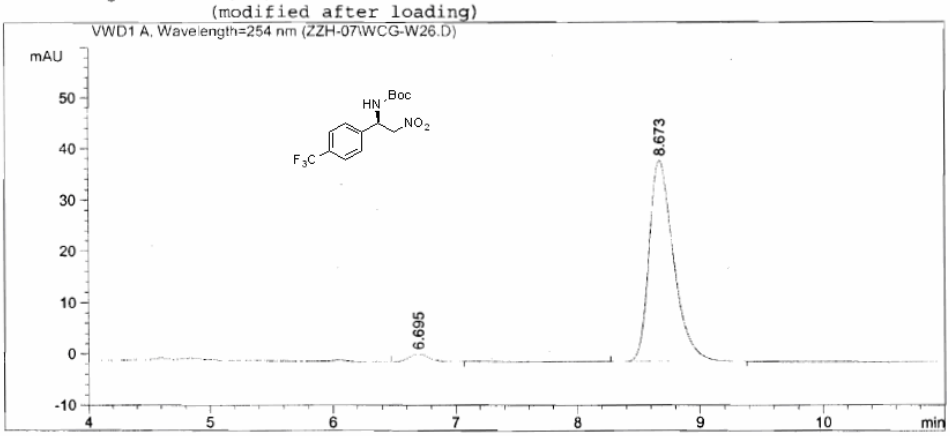

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.422 BB    0.1388  220.41510   24.41012  49.9246
   2   8.229 BB    0.1777  221.08081   19.24961  50.0754

Totals :                   441.49591   43.65973

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```

```
Injection Date  : 12/17/2007 5:01:48 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/17/2007 4:31:25 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 12/17/2007 5:16:11 PM
                  (modified after loading)
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

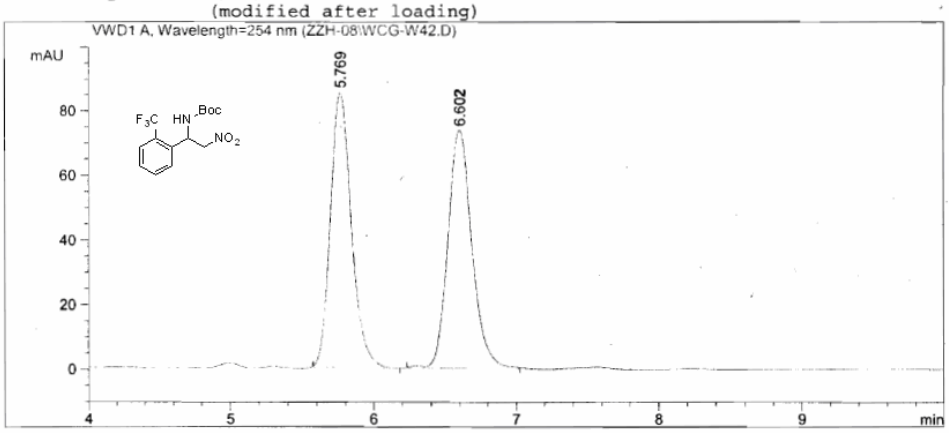
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.695 BB    0.1704   16.43554    1.47945   2.9379
   2   8.673 PB    0.2115  543.00146   39.09673  97.0621

Totals :                   559.43700   40.57618

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

```
Injection Date  : 1/17/2008 4:25:43 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/17/2008 4:12:21 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/18/2008 10:09:12 AM
                  (modified after loading)
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   5.769 BP    0.1560  863.83997   85.27428  49.7886
   2   6.602 BB    0.1817  871.17444   73.64616  50.2114

Totals :                  1735.01440  158.92043

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

```
Injection Date  : 1/17/2008 4:38:17 PM
Sample Name     :                                   Location : Vial 1
Acq. Operator   :
Acq. Method     : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/17/2008 4:12:21 PM
                  (modified after loading)
Analysis Method : D:\HPCHEM\1\METHODS\07-3.M
Last changed    : 1/18/2008 10:11:44 AM
                  (modified after loading)
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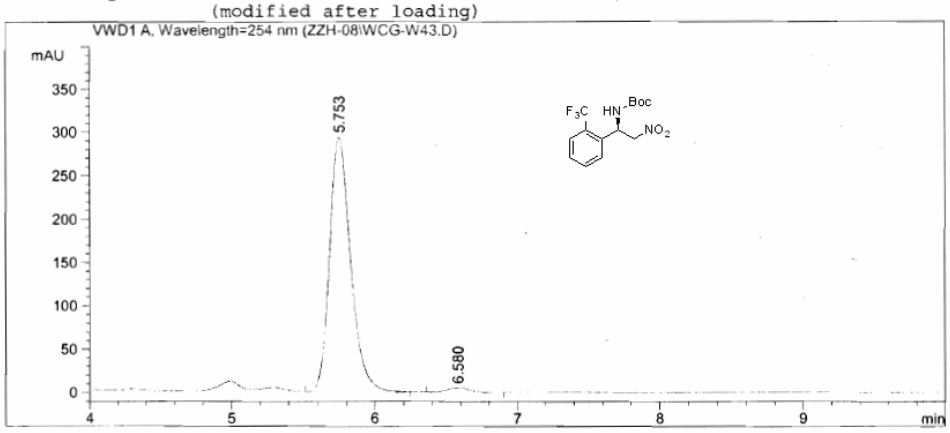


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   1   5.753 VB    0.1572 3003.73853  293.66443  97.9006
   2   6.580 BB    0.1827   64.41174    5.34794   2.0994

Totals :                  3068.15027  299.01237

 Results obtained with enhanced integrator!

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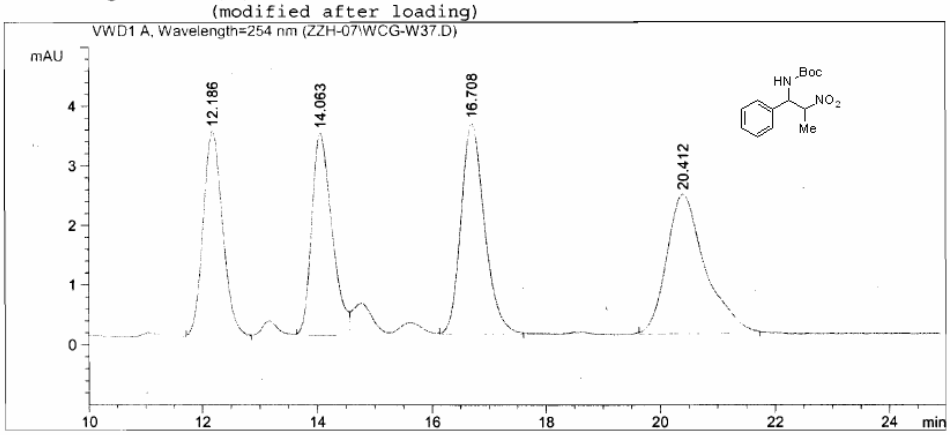


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   1  12.186 BB    0.3665   81.32866    3.43488  21.6654
   2  14.063 BV    0.3689   82.52700    3.38510  21.9847
   3  16.708 VB    0.4420  102.22213    3.53746  27.2313
   4  20.412 BB    0.6915  109.30671    2.33619  29.1186

Totals :                   375.38450   12.69362

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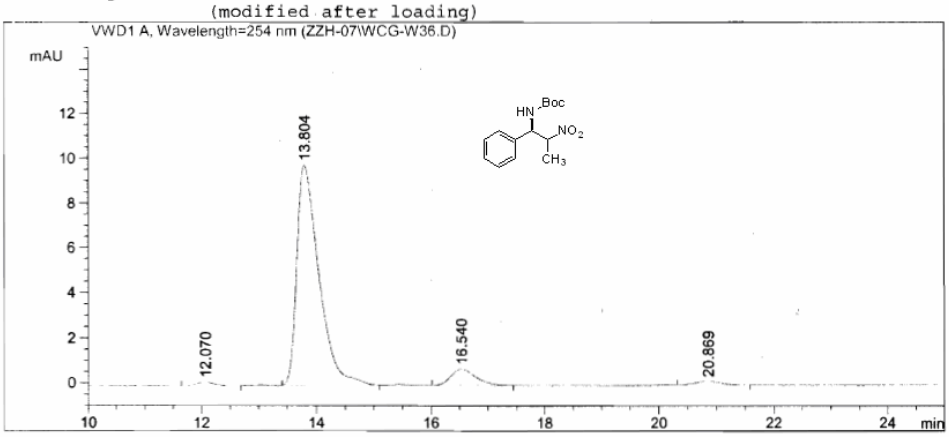


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
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   1  12.070 PP    0.2777    3.95289 1.73356e-1   1.3501
   2  13.804 PP    0.3952  260.48245    9.78025  88.9697
   3  16.540 PB    0.4328   22.84808 7.34546e-1   7.8039
   4  20.869 BB    0.4122    5.49321 1.62345e-1   1.8762

Totals :                  292.77663   10.85050

 Results obtained with enhanced integrator!
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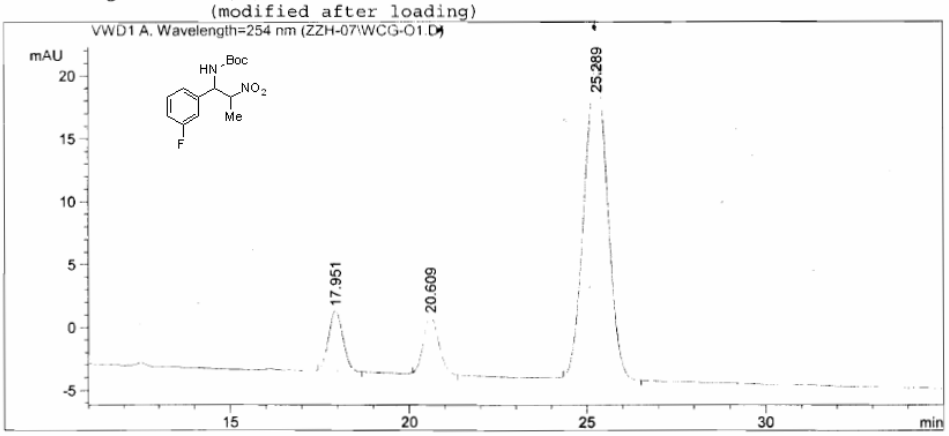


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  17.951 BB    0.4314  133.28291    4.78345   9.5496
   2  20.609 BB    0.4543  132.49855    4.47883   9.4934
   3  25.289 BB    0.7115 1129.90430   25.03554  80.9569

Totals :                  1395.68576   34.29783

 Results obtained with enhanced integrator!
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AD-H 254nm 1ml/min

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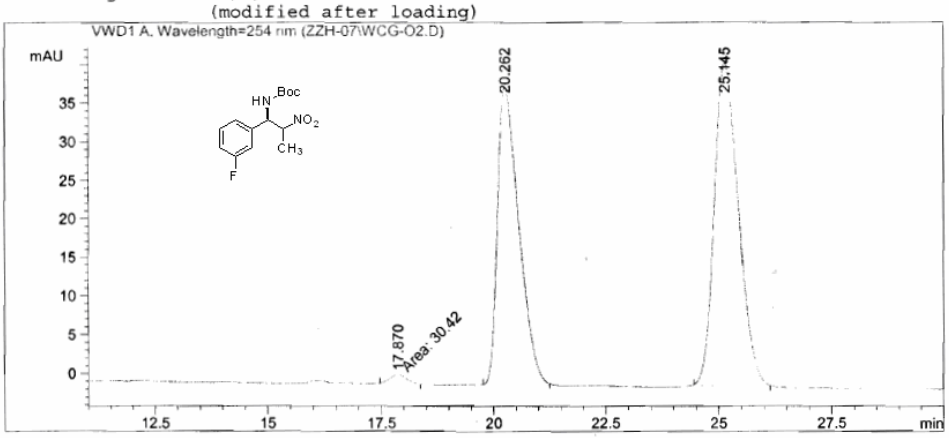


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Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  17.870 MM    0.4475   30.41999    1.13307   1.0662
   2  20.262 BB    0.4986 1272.59155   38.55871  44.6044
   3  25.145 BB    0.5787 1550.04895   41.75228  54.3293

Totals :                  2853.06049   81.44406

 Results obtained with enhanced integrator!
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Novel bifunctional chiral thiourea catalyzed highly enantioselective aza-Henry reaction†

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State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

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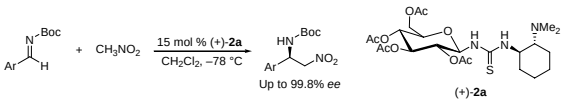
Received Date (will be automatically inserted after manuscript is accepted)

ABSTRACT



A novel bifunctional chiral thiourea organocatalyst bearing a glycosyl scaffold and a tertiary amino group was synthesized starting from readily available alpha-D-glucose. This thiourea was proven to be an effective organocatalyst for the asymmetric aza-Henry reaction between *N*-Boc imines and nitromethane. The corresponding adducts were obtained in good to excellent yields with excellent enantioselectivities (up to 99.8% ee). In addition, the reaction of nitroethane also proceeded smoothly with excellent enantioselectivity, albeit with low to good diastereoselectivities.

The nucleophilic addition of nitroalkanes to the C=N bond of imines, known as the aza-Henry (or nitro-Mannich) reaction, is a useful carbon-carbon bond-forming process in organic synthesis.[1] The resulting β-nitroamine derivatives can be readily transformed into valuable building blocks or biologically active compounds, such as vicinal diamines via reduction of the nitro group[2] and α-amino acids by means of the Nef reaction.[2g,3] As a result, much attention has been paid to the aza-Henry reaction, especially for the catalytic asymmetric version of this reaction, during the past several years.[4,5] In 1999, Shibasaki reported the first example of a catalytic asymmetric aza-Henry reaction using a heterobimetallic catalyst [YbK_3(binaphthoxide)$_3$], in which up to 91% ee was obtained.[4a] Thereafter, significant progress has been witnessed for chiral metallic catalyst promoted enantioselective aza-Henry reaction.[4] However, besides these metal-catalyzed variants, the organocatalytic version remainined unexplored until two reports of enantioselective organocatalytic aza-Henry reaction appeared in 2004. Takemoto has developed a bifunctional thiourea catalyst that resulted in moderate stereoselectivity in the addition of nitromethane to a variety of aromatic *N*-phosphinoyl imines,[5a] and Johnston has documented a chiral bisamidine triflate salt that provides up to 95% ee in the diastereo- and enantioselective addition of nitroethane to a range of *N*-Boc imines.[5f] Although only moderate ee values were observed for the thiourea **1a** catalyzed reaction between *N*-phosphinoyl imines and nitromethane,[5a] high stereoselectivity (up to 98% ee) was obtained when *N*-Boc imines were employed instead of *N*-phosphinoyl imines as the substrates.[5b] Using thiourea **1b**, Jacobsen developed another variation of the aza-Henry reaction of *N*-Boc imines, in which moderate de values and excellent ee values were attained.[5c] Most recently, Ricci[5d] and Schaus[5e] independently screened a variety of cinchona-based thiourea organocatalysts to catalyze the addition of nitromethane to acyl imines, in which satisfactory yields and enantiomeric excesses were provided. In addition, chiral proton catalysis,[5g] chiral urea catalysis [5h] and chiral phase-transfer catalysis[5f,j] based on quinine or cinchonidine derived quaternary ammonium salts effecting the asymmetric aza-Henry reaction have also

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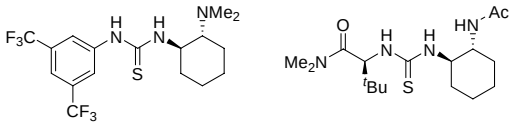
been described, and gave rise to good diastereo- and enantioselectivities. As aforementioned, bifunctional thioureas have proven to be an efficient type of organocatalyst for the asymmetric aza-Henry reaction. Therefore, the development of new bifunctional thiourea catalysts is still in great demand. Carbohydrates are in general very attractive scaffolds because of their availabilty and well dedined stereocenters. Hence, a novel type of bifunctional thiourea **2** bearing a saccharide-scaffold and a tertiary amino group was synthesized and employed as the catalyst in the asymmetric aza-Henry reaction. Herein, we report the discovery that thiourea **2a** efficiently promotes the aza-Henry reaction of nitromethane with *N*-Boc imines with excellent levels of enantioselectivity.

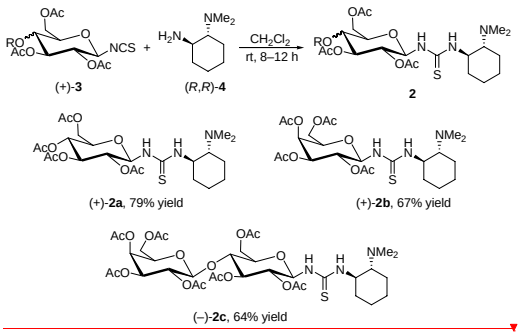
Figure 1 thiourea organocatalysts



1a **1b**

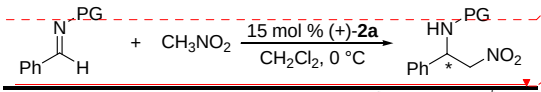
Starting from commercially available α-D-glucopyranose, glucosyl isothiocyanate **3** was prepared via acetylation, bromination and nucleophilic substitution reactions.[6] (*R*,*R*)-*N*,*N*-Dimethyl cyclohexane-1,2-diamine **4** was synthesized through mono amino-protection with phthalic anhydride, *N*,*N*-dimethylation and subsequently deprotection starting from (*R*,*R*)-cyclohexane-1,2-diamine.[7] Consequently, coupling of **3** and **4** afforded the desired bifunctional thiourea catalyst **2a** in good yield. Following the same procedure, thiourea catalysts **2b** and **2c** were also synthesized from galactose and lactose, respectively (in a yield of 67% for **2b** and 73% for **2c**).

Scheme 1 Synthesis of novel thiourea **2**



With these novel catalysts in hand, we initially screened several imines with different *N*-protecting groups (PG) in the presence of **2a** (15 mol %) and nitromethane in methylene chloride at 0 °C (Table 1).

Table 1 Enantioselective aza-Henry reaction of different imines with nitromethane



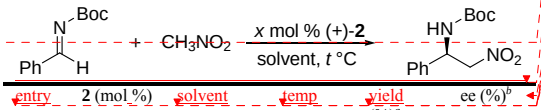
entry	PG	time (h)	yield (%)[a]	ee (%)[b]
1	Ts	4.5	79	8
2	$Ph_2P(S)$	48	Trace	
3	$Ph_2P(O)$	48	NR[lc]	
4	Boc	16	85	90
5	CO_2Et	24	77	85
6	CO_2Bn	24	71	86

[a] Yield of the isolated product after chromatography on silica gel. [b] Determined chiral HPLC analysis. [c] NR means no reaction occurred.

Among the imines examined, *N*-alkoxycarbonyliminines tended to provide the desired adducts with good enantioselectivities compared with other imines (Table 1, entries 1–6), and the best result was obtained for *N*-Boc imine in terms of chemical yield and enantiomeric excess (Table 1, entry 4, 95% yield, 90% ee). Although *N*-tosyl imine exhibited the best reactivity, an almost racemic product was attained (Table 1, entry 1). In the case of *N*-(thio)phosphinoyl imines, the reactions were quite sluggish even after a prolonged reaction time (Table 1, entries 2 and 3).

In further experiments, other factors, such as solvent, catalyst loading and reaction temperature, influencing the reaction were thoroughly investigated employing **2** as the catalyst and the reaction between *tert*-butyl benzylidenecarbamate and nitromethane as the model. The results are listed in Table 2.

Table 2 Optimization of the reaction conditions



entry	2 (mol %)	solvent	temp (°C)	yield (%)[a]	ee (%)[b]
1	**2a** (15)	CH_2Cl_2	0	85	90
2	**2a** (15)	MePh	0	87	85
3	**2a** (15)	THF	0	87	67
4	**2a** (15)	$CHCl_3$	0	90	80
5	**2a** (15)	MeOH	0	Trace	
6	**2a** (15)	MeCN	0	88	91
7	**2a** (10)	CH_2Cl_2	0	77	85
8	**2a** (20)	CH_2Cl_2	0	78	87
9	**2b** (15)	CH_2Cl_2	0	89	85
10	**2c** (15)	CH_2Cl_2	0	89	78
11	**2a** (15)	CH_2Cl_2	–40	87	93
12	**2a** (15)	CH_2Cl_2	–60	86	96
13	**2a** (15)	CH_2Cl_2	–78	86	>99

[a] Yield of the isolated product after chromatography on silica gel. [b] Determined chiral HPLC analysis.

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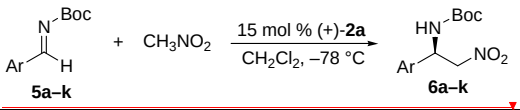
Solvent evaluation revealed that all the tested solvents except for methanol, which probably inhibits hydrogen-bonding interaction between nitromethane and the thiourea moiety of **2**, afforded the desired product in good yield and ee values (Table 2, entries 1–6). The best results were observed when methylene chloride and acetonitrile were used (Table 2, entries 1 and 6, 90% and 91% ee, respectively). Since acetonitrile has a relatively higher freezing point (–48 °C), it is not applicable for low temperature tests, therefore, we chose methylene chloride as the favourable solvent for this reaction. Although bifunctional thiourea catalysts **2b**,**c** can also promote this reaction, a moderate decrease in enantioselectivtiy was observed, which affords the desired adduct with 85% and 78% ee, respectively (Table 1, entries 9 and 10). Adjusting the catalyst loading demonstrated little influence on the ee value of the reaction. For example, the use of a more or less amount of thiourea organocatalyst resulted in only a slightly loss of stereo-control (Table 2, entry 8, 87% ee and entry 7, 85% ee). Moreover, the reaction temperature was found to be an essential factor to the enantioselectivity of this reaction. Generally, lowering the temperature improved the enantiomeric excess of the reaction (Table 2, entries 1, 11–13). It is worth noting that almost perfect enantio-control was realized with good chemical yield when the reaction was performed at –78 °C (Table 2, entry 11, >99% ee).

With the optimal reaction conditions in hand (15 mol % **2a** as the catalyst, at –78 °C in methylene chloride), we then investigated the scope and limitations of this asymmetric aza-Henry reaction. The results are summarized in Table 3.

Table 3 Chiral thiourea **2a** catalyzed asymmetric addition of nitromethane to *N*-Boc imines [a]



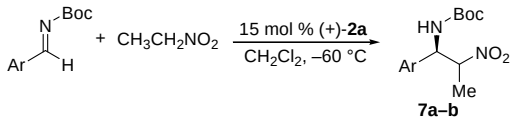
Entry	Ar group	6	Time (h)	Yield (%)[b,c]	ee (%)[c,d]
1	Ph (**5a**)	**a**	60	86	>99
2	4-MeOC$_6$H$_4$ (**5b**)	**b**	66	94	94
3	4-MeC$_6$H$_4$ (**5c**)	**c**	68	93(70)	83(>99)
4	4-ClC$_6$H$_4$ (**5d**)	**d**	60	93	>99
5	3-FC$_6$H$_4$ (**5e**)	**e**	39	87	>99
6	4-FC$_6$H$_4$ (**5f**)	**f**	65	91	>99
7	2-ClC$_6$H$_4$ (**5g**)	**g**	42	85	92
8	1-Naphthyl (**5h**)	**h**	65	95	>99
9	2-Furyl (**5i**)	**i**	62	86(69)	90(97)
10	4-F$_3$CC$_6$H$_4$ (**5j**)	**j**	64	85	94
11	2-F$_3$CC$_6$H$_4$ (**5k**)	**k**	61	84	96

[a] The absolute configurations of major isomer of the aza-Henry adducts **6** were assigned as *R* by comparison to the literature value of optical rotation in reference [5c,e,i,j], the others were. [b] Yield of the isolated product after chromatography on silica gel. [c] Data in parenthesis were obtained through a simple recrystallization from ethyl acetate/petroleum ether. [d] Determined chiral HPLC analysis.

As shown in Table 3, in all cases, the corresponding aza-Henry adducts were obtained in satisfactory chemical yields within acceptable reaction times. Excellent enantioselectivities can be obtained for the substrates bearing electron-withdrawing substituents (**5d**–**g**, **5j**,**k**) and imine derived from 1-naphthyl aldehyde, and in most cases, almost perfect enantio-control was realized. The reaction of the electron-donating methoxy group substituted imine (**5b**) also proceeded smoothly to afford the desired product in excellent stereoselectivity. Although, a slight decrease in ee value was observed for methyl substituted imine (**5c**) and electron-rich heteroaromatic aldehyde-dervied substrate (**5i**), the optical purity of the product can be significantly improved via a simple recrystallization (99.7% and 97.2% ee, respectively).

In addition, aza-Henry reactions with other nitro alkanes were preliminarily investigated. Nitroethane proved to be considerably less reactive under the standard conditions, but is underwent smooth reaction at an elevated temperature (–60 °C) to provide adducts **7** in excellent eantioselectivities with low to good diastereoselectivities. For example, benzadehyde-derived imine (**5a**) underwent reaction with excellent enantioselectivity (97.0% ee for *syn*-isomer) and provided products with synthetically useful levels of diastereoselectivity (*syn*/*anti* = 9.3/1). Although a low *syn*/*anti* ratio (1.2/1) was attained in the case of 3-fluorobenzaldehyde-based imine (**5e**), it was gratifying, high enantioselectivity was obtained for the separable *anti*-isomer. Reaction with the more sterically challenging 2-nitropropane did not proceed at all.

Scheme 2 Chiral thiourea **2a** catalyzed asymmetric addition of nitroethane to *N*-Boc imines



7a, Ar = Ph, 87% yield, *syn*/*anti*: 9.3:1, 97% ee (*syn*)
7b, Ar = 3-FC$_6$H$_4$, 90% yield, *syn*/*anti*: 1.2:1, 95% ee (*anti*),
syn isomer is inserperable under all the tested conditions

In conclusion, we have developed a readily available novel bifunctional chiral thiourea organocatalyst bearing a glycosyl scaffold and a tertiary amino group. The high effectiveness of this novel organocatalyst was demonstrated by catalysis of the aza-Henry reaction of nitromethane with *N*-Boc imines with excellent enantioselectivity. In addition, the reaction of nitroethane was also effective to provide the corresponding adducts with high enantioselectivities, albeit with low to good diastereoselectivities. Further investigation on the diastereoselective aza-Henry reaction and application of this novel catalyst in other asymmetric reactions are ongoing in our laboratory.

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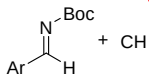

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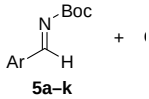

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Acknowledgment. We are grateful to the National Natural Science Foundation of China (No. 20472033, 20772058) for generous financial support for our programs.

Supporting Information Available: Experimental procedures, characterization of the catalyst and copies of ^{1}H NMR spectra, chiral HPLC spectra of the aza-Henry adducts. This material is available free of charge via the Internet at http://pubs.acs.org.

References

† Dedicated to professor Chuchi Tang on the occasion of his 70th birthday.

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