Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# Synthesis of a Series of Novel Chiral Lewis Base Catalysts and Application in Promoting Asymmetric Hydrosilylation of *β*-Enamino Esters

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## Supporting Information

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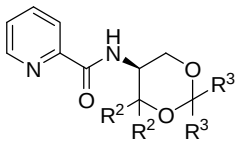
# 1. General information

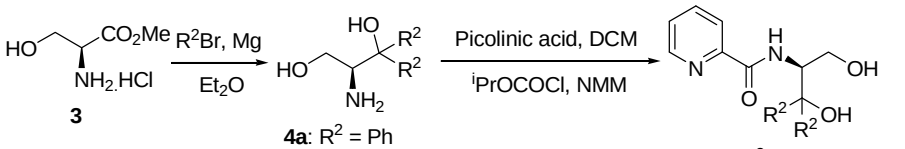
All starting materials were of the highest commercially available grade and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography (FC) was performed using silica gel HG/T2354-92. $^{1}H$ NMR and $^{13}C$ NMR (300 and 75 MHz, respectively) spectra were recorded in $CDCl_3$. $^{1}H$ NMR chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, $\delta$ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet ), coupling constants (Hz) and integration. $^{13}C$ NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, $\delta$ 77.0 ppm). All enantiomeric ratios have been controlled by co-injections of the pure sample with the racemic compounds.

# 2. Preparation and characterization of catalysts (2a-2g)



**2a**: $R^2$ = Ph, $R^3$ = H
**2b**: $R^2$ = *p*-$FC_6H_4$, $R^3$ = H
**2c**: $R^2$=*p*-$MeOC_6H_4$, $R^3$=H
**2d**: $R^2$ =*p*-$MeC_6H_4$, $R^3$=H
**2e**: $R^2$ =Ph, $R^3$ = Me
**2f**: $R^2$ = Bn, $R^3$ = H
**2g**: $R^2$ = Cy, $R^3$ = H

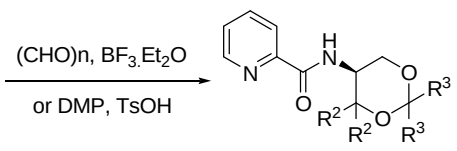
## (1) Preparation and characterization of catalysts (2a-2f):



**3**

**4a**: $R^2$ = Ph
**4b**: $R^2$ = *p*-$FC_6H_4$
**4c**: $R^2$ = *p*-$MeOC_6H_4$
**4d**: $R^2$ = *p*-$MeC_6H_4$
**4e**: $R^2$ = Bn

**12a**: $R^2$ = Ph
**12b**: $R^2$ = *p*-$FC_6H_4$
**12c**: $R^2$ = *p*-$MeOC_6H_4$
**12d**: $R^2$ = *p*-$MeC_6H_4$
**12e**: $R^2$ = Bn



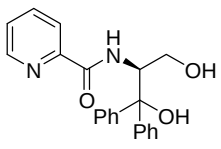
**2a**: $R^2$ = Ph, $R^3$ = H
**2b**: $R^2$ = *p*-$FC_6H_4$, $R^3$ = H
**2c**: $R^2$=*p*-$MeOC_6H_4$, $R^3$=H
**2d**: $R^2$ =*p*-$MeC_6H_4$, $R^3$=H
**2e**: $R^2$ =Ph, $R^3$ = Me
**2f**: $R^2$ = Bn, $R^3$ = H

General procedure for synthesis of **4a-4e**:

Compounds **4a-4e** were synthesized according to the literature method.[1] To a stirred suspension of (*S*)-methyl 2-amino-3-hydroxypropanoate hydrochloride **3** (3.0 g, 19.28 mmol) in $Et_2O$ (80 mL) was added dropwise Grignard reagent [prepared from Mg (3.28 g, 134.97 mmol) and appropriate bromide (136.88 mmol) in $Et_2O$ (100 mL)] at 10 °C. After stirring for overnight, only sufficient water was added to ensure that the magnaesium salt was converted into a coarse granular structure without forming an aqueous phase. The mixture was then filtered, and washed with DCM (3 × 100 mL), dried over anhydrous $Na_2SO_4$. Concentration in vacuo gave a residue, which was purified on silica gel column [PET: EA = 1:1, then MeOH: DCM = 1: 10] to give the product. Yield: 88 % for **4a** (4.12 g, white solid); 66 % for **4b** (3.55 g, colorless oil); 87 % for **4c** (5.08 g, white solid); 84 % for **4d** (4.4 g, yellow oil); 81 % for **4e** (4.25 g, colorless oil).

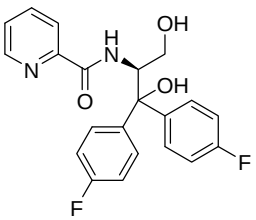
General procedure for synthesis of **12a-12e**:

A 250 mL three-necked flask is charged with picolinic acid (1.83 g, 14.87 mmol) and the flask is flushed with nitrogen. It is dissolved in DCM (80 mL) and *N*-methylmorpholine (1.82 mL). The reaction mixture was cooled to -15 °C, then isobutylchloroformate (2.14 g, 1.0 eq) was added dropwise over 10 min. The reaction mixture was stirred at this temperature for 1 hour. Then a solution of compound **4** (15.66 mmol) in DCM (50 mL) and NMM (2.5 mL) was added dropwise to the above reaction mixture at -10 °C. The reaction mixture was allowed to warm to room temperature, and stirred for an additional hour. The reaction mixture was diluted with DCM (100 mL), washed with 1N HCl (100 mL), $H_2O$ (100 mL), brine and dried over anhydrous $Na_2SO_4$. Solvent was removed in vacuo and the residue was purified on silica gel column [PET: EA = 3:1] to give the pure product.

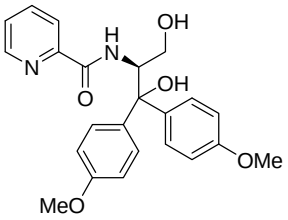



**(*S*)-*N*-(1,3-dihydroxy-1,1-diphenylpropan-2-yl)picolinamide (12a)**: white solid, yield 85%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.50 (brs, 1H), 3.86 (d, $J$ = 10.9 Hz, 1H), 3.99 (d, $J$ = 11.5 Hz, 1H), 4.88 (s, 1H), 5.16 (dt, $J_1$ = 2.7 Hz, $J_2$ = 8.8 Hz, 1H), 7.10 (t, $J$ = 7.2 Hz, 1H), 7.20-7.25 (m, 3H), 7.32-7.37 (m, 3H), 7.52-7.59 (m, 4H), 7.78 (td, $J_1$ = 1.5 Hz, $J_2$ = 7.7 Hz, 1H), 8.11 (d, $J$ = 7.7 Hz, 1H), 8.46 (d, $J$

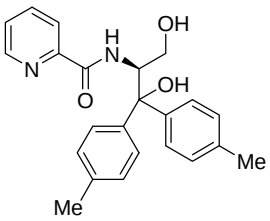
= 4.7 Hz, 1H), 8.83 (d, *J* = 9.1 Hz, 1H).



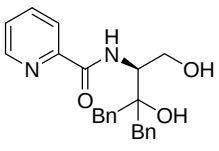
**(*S*)-*N*-(1,1-bis(4-fluorophenyl)-1,3-dihydroxypropan-2-yl) picolinamide (12b)**: white solid, yield 86%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.67 (t, *J* = 4.9 Hz, 1H), 3.84-3.90 (m, 1H), 3.96-3.99 (m, 1H), 5.06-5.09 (m, 1H), 5.17 (s, 1H), 6.86-6.92 (m, 2H), 7.01-7.07 (m, 1H), 7.34-7.39 (m, 1H), 7.45-7.55 (m, 4H), 7.79 (td, $J_1$ = 1.6 Hz, $J_2$ = 7.7 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 8.44 (d, J = 4.1 Hz), 8.81 (d, *J* = 8.8 Hz, 1H).



**(*S*)-*N*-(1,3-dihydroxy-1,1-bis(4-methoxyphenyl)propan-2-yl) picolinamide (12c)**: white solid, yield 88%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 5.58 (t, *J* = 5.0 Hz, 1H), 3.68 (s, 3H), 3.78 (s, 3H), 3.84-3.88 (m, 1H), 3.93-3.98 (m, 1H), 4.72 (s, 1H), 5.04-5.07 (m, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.34-7.38 (m, 1H), 7.43 (t, *J* = 8.8 Hz), 7.79 (td, $J_1$ = 1.5 Hz, $J_2$ = 7.7 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.46 (d, *J* = 4.6 Hz, 1H), 8.82 (d, *J* = 8.7 Hz, 1H).

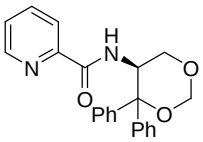


**(*S*)-*N*-(1,3-dihydroxy-1,1-dip-tolylpropan-2-yl)picolinamide (12d)**: white solid, yield 79%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.19 (s, 3H), 2.30 (s, 3H), 2.73-2.77 (m, 1H), 3.81-3.87 (m, 1H), 3.92-3.98 (m, 1H), 4.80 (s, 1H), 5.08-5.13 (m, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.30-7.35 (m, 1H), 7.37-7.44 (m, 4H), 7.76 (td, $J_1$ = 1.6 Hz, $J_2$ = 8.5 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.42 (d, *J* = 4.7 Hz, 1H), 8.82 (d, *J* = 8.5 Hz, 1H).



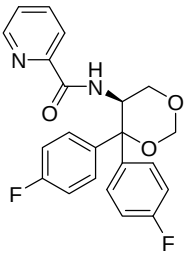
**(*S*)-*N*-(3-benzyl-1,3-dihydroxy-4-phenylbutan-2-yl)picolinamide (12e)**: colorless oil, yield 76%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.82 (d, *J* = 14.1 Hz, 1H), 2.90 (d, *J* = 14.0, 1H), 2.97 (d, *J* = 14.0, 1H), 3.12 (d, *J* = 14.1, 1H), 3.71 (s, 1H), 3.96-4.07 (m, 2H), 4.06-4.17 (m, 1H), 4.26 (brs, 1H), 7.09-7.36 (m, 11H), 7.74 (td, $J_1$ = 1.6 Hz, $J_2$ = 8.5 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.43 (d, *J* = 4.3 Hz, 1H), 8.69 (d, *J* = 8.2 Hz, 1H).

Synthesis and characterization of **2a-2f**:



**(*S*)-*N*-(4,4-diphenyl-1,3-dioxan-5-yl)picolinamide (2a)**:

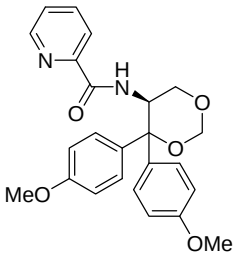
Compound **12a** (3.60 g, 10.33 mmol) was dissolved in EA (100 mL). Then, dimethoxymethane (2.1 mL, 2eq.) and $BF_3.Et_2O$ (4.2 mL, 3eq.) was added to the solution. The reaction mixture was refluxed for 6 hours. The reaction mixture was cooled to room temperature and quenched with saturated $NaHCO_3$ (100 mL), $H_2O$ (50 mL). The mixture was extracted with EA (100 mL × 3), washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified on silica gel column [PET: EA = 3:1] to give a colorless oil, which solidified under high vacuum, **2a** (2.30 g), yield 62 %. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.04 (d, $J$ = 11.4 Hz, 1H), 4.21 (d, $J$ = 11.4 Hz, 1H), 5.01 (d, $J$ = 6.4 Hz, 1H), 5.18 (d, $J$ = 6.4 Hz, 1H), 5.37 (d, $J$ = 9.7 Hz, 1H), 6.93-6.98 (m, 1H), 7.09-7.14 (m, 2H), 7.20-7.27 (m, 2H), 7.35-7.46 (m, 4H), 7.63 (td, $J_1$ = 1.7 Hz, $J_2$ = 7.7 Hz, 1H), 7.97 (d, $J$ = 7.8 Hz, 1H), 8.42-8.44 (m, 1H), 8.87 (d, $J$ = 9.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 47.9, 67.5, 81.7, 89.1, 121.7, 124.4, 125.7, 126.4, 126.6, 127.4, 127.6, 128.9, 136.7, 140.9, 143.6, 147.8, 149.0, 163.2. ESI-HR MS exact mass calcd. for $(C_{22}H_{20}N_2NaO_3)^+$ requires m/z 383.1366, found m/z 383.1375.



**(*S*)-*N*-(4,4-bis(4-fluorophenyl)-1,3-dioxan-5-yl)picolinamide** (**2b**):

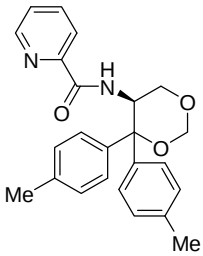
Compound **12b** (3.84 g, 10.0 mmol) was dissolved in THF (60 mL). Then, $(CHO)_n$ (6.06 g, 20 eq.) and $BF_3.Et_2O$ (4.8 mL) was added to the solution, and the reaction mixture was heated to reflux overnight. THF was removed in vacuum, the residue was dissolved in DCM (100 mL), and washed with saturated $NaHCO_3$ (80 mL), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified on silica gel [PET: EA = 4:1] to give a colorless oil, which solidified in vacuum, **2b** (1.80 g), yield 45 %. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.00 (d, $J$ = 11.4 Hz, 1H), 4.16 (d, $J$ = 11.5 Hz, 1H), 4.91 (d, $J$ = 6.5 Hz, 1H), 5.13 (d, $J$ = 6.4 Hz, 1H), 5.28 (d, $J$ = 9.7 Hz, 1H), 6.74-6.80 (m, 2H), 7.02-7.08 (m, 2H), 7.23-7.48 (m, 5H), 7.62-7.68 (m, 1H), 7.95 (d, $J$ = 7.7 Hz, 1H), 8.41-8.43 (m, 1H), 8.84 (d, $J$ = 9.7 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 47.7, 67.6 (d, $J$ = 10.6 Hz, 1C), 81.2, 89.0, 114.5 (d, $J$ = 21.3 Hz, 2C), 116.0 (d, $J$ = 21.3 Hz, 2C), 121.8, 125.9, 126.3 (d, $J$ = 8.0

Hz, 2C), 128.4 (d, $J$ = 7.9 Hz, 2C), 136.6 (d, $J$ = 3.2 Hz, 1C), 136.9, 139.4 (d, $J$ = 2.6 Hz, 1C), 147.9, 148.8, 161.1 (d, $J$ = 244.1 Hz, 1C), 161.8 (d, $J$ = 246.4 Hz, 1C), 163.1. ESI-HR MS exact mass calcd. for $(C_{22}H_{18}F_2N_2NaO_3)^+$ requires m/z 419.1178, found m/z 419.1186.




**(*S*)-*N*-(4,4-bis(4-methoxyphenyl)-1,3-dioxan-5-yl)picolinamide** (**2c**):

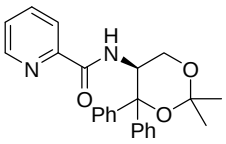
Compound **12c** (3.00 g, 7.34 mmol) was dissolved in THF (60 mL). Then, $(CHO)_n$ (4.45 g, 20 eq.) and $BF_3.Et_2O$ (3 mL) was added to the solution, and the reaction mixture was heated to reflux for 4 hours. THF was removed in vacuo, the residue was dissolved in DCM (100 mL), and washed with saturated $NaHCO_3$ (80 mL), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified on silica gel [PET : EA = 4:1] to give a colorless oil, which solidified under high vacuum, **2c** (1.8 g), 58 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.61 (s, 3H), 3.80 (s, 3H), 4.0 (d, $J$ = 11.2 Hz, 1H), 4.20 (d, $J$ = 11.2 Hz, 1H), 5.00 (d, $J$ = 6.4 Hz, 1H), 5.14 (d, $J$ = 6.4 Hz, 1H), 5.22 (d, $J$ = 9.7 Hz, 1H), 6.64 (d, $J$ = 8.9 Hz, 2H), 6.92 (d, $J$ = 8.9 Hz, 2H), 7.28 (d, $J$ = 8.9 Hz, 2H), 7.32-7.37 (m, 1H), 7.42 (d, $J$ = 8.8 Hz, 2H), 7.74 (td, $J_1$ = 1.7 Hz, $J_2$ = 7.7 Hz, 1H), 8.00 (d, $J$ = 7.8 Hz, 1H), 8.50-8.52 (m, 1H), 8.83 (d, $J$ = 9.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 47.8, 54.6, 54.8, 67.4, 81.2, 88.8, 112.8, 114.1, 121.6, 125.5, 125.7, 127.7, 133.0, 136.3, 136.7, 147.8, 148.9, 157.6, 158.4, 163.1. ESI-HR MS exact mass calcd. for $(C_{24}H_{24}N_2NaO_5)^+$ requires m/z 443.1577, found m/z 443.1578.




**(*S*)-*N*-(4,4-dip-tolyl-1,3-dioxan-5-yl)picolinamide** (**2d**):

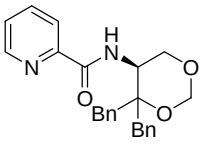
Compound **12d** (2.70 g, 7.17 mmol) was dissolved in EA (50 mL). Then, dimethoxymethane (1.46 mL, 2eq) and $BF_3.Et_2O$ (2.44 mL, 2.5eq.) was added to the solution, and the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was washed with saturated $NaHCO_3$ (50 ml), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified on silica gel column [PET: EA = 5:1] to give a colorless oil, which solidified under high vacuum, **2d** (0.94 g), 34 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.10 (s, 3H), 2.32 (s, 3H), 4.02 (d, $J$ = 11.4 Hz, 1H), 4.21 (d, $J$ = 11.5 Hz,

1H), 5.03 (d, $J$ = 6.4 Hz, 1H), 5.16 (d, $J$ = 6.4 Hz, 1H), 5.29 (d, $J$ = 9.6 Hz, 1H), 6.92 (d, $J$ = 8.0 Hz, 2H), 7.20 (d, $J$ = 8.0 Hz, 2H), 7.26-7.33 (m, 3H), 7.40 (d, $J$ = 8.2 Hz, 2H), 7.71 (td, $J_1$ = 1.6 Hz, $J_2$ = 7.7 Hz, 1H), 7.80 (d, $J$ = 7.8 Hz, 1H), 8.49-8.50 (m, 1H), 8.85 (d, $J$ = 9.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 20.7, 20.9, 48.0, 67.6, 81.7, 89.1, 121.8, 124.3, 125.8, 126.5, 128.5, 129.7, 135.8, 136.8, 137.1, 138.2, 141.1, 148.0, 149.3, 163.3. ESI-HR MS exact mass calcd. for $(C_{24}H_{24}N_2NaO_3)^+$ requires m/z 411.1679, found m/z 411.1682.



**(*S*)-*N*-(2,2-dimethyl-4,4-diphenyl-1,3-dioxan-5-yl)picolinamide** (**2e**):

To a solution of compound **12a** (0.17 g, 0.5 mmol) in DCM (5 mL) were added DMP (0.26 g, 2.5 mmol) and *p*-TsOH.$H_2O$ (10 mg, 0.05 mmol) at 0 $^o$C. After stirring at room temperature for 12 hours, the mixture was poured into saturated $NaHCO_3$ (10 mL) and extracted with DCM (15 mL × 3), washed with water and brine, dried over anhydrous $Na_2SO_4$. Concentration in vacuo gave a residue, which was purified on silica gel column [PET: EA = 4:1] to give a white solid **2e** (0.10 g), 51 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.97 (s, 3H), 1.66 (s, 3H), 3.92 (dd, $J_1$ = 2.3 Hz, $J_2$ = 11.9 Hz, 1H), 4.49 (dd, $J_1$ = 1.1 Hz, $J_2$ = 11.9 Hz, 1H), 5.25 (d, $J$ = 9.6 Hz, 1H), 6.88-6.93 (m, 1H), 7.02-7.08 (m, 2H), 7.19-7.32 (m, 7H), 7.47-7.50 (m, 2H), 7.67 (td, $J_1$ = 1.7 Hz, $J_2$ = 7.7 Hz, 1H), 7.91 (d, $J$ = 7.8 Hz, 1H), 8.44-8.46 (m, 1H), 8.65 (d, $J$ = 9.5 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 23.7, 31.0, 46.4, 61.8, 79.7, 100.0, 121.8, 124.9, 125.7, 126.2, 127.1, 127.3, 127.5, 128.2, 136.8, 144.3, 145.4, 148.0, 149.3, 163.0. ESI-HR MS exact mass calcd. for $(C_{24}H_{24}N_2NaO_3)^+$ requires m/z 411.1679, found m/z 411.1690.

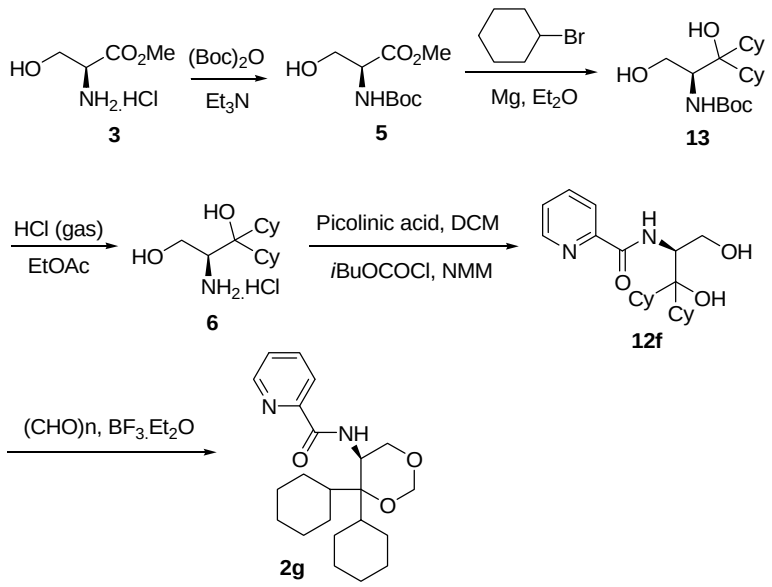


**(S)-N-(4,4-dibenzyl-1,3-dioxan-5-yl)picolinamide (2f)**:

Compound **12e** (2.32 g 6.16 mmol) was dissolved in EA (100 mL). Then, dimethoxymethane (1.25 mL, 2eq.) and $BF_3$.$Et_2O$ (2.1 mL, 2.5eq) was added to the solution, and the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was washed with saturated $NaHCO_3$ (30 mL), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified on silica gel column [PET: EA = 4:1] to give a colorless oil, which solidified under high vacuum, **12e** (1.07 g), 45 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.88 (d, $J$ =

14.5 Hz, 1H), 3.09 (dd, $J$ = 14.7 Hz, 34.5 Hz, 2H), 3.33 (d, $J$ = 14.6 Hz, 1H), 3.88 (dd, $J_1$ = 5.2 Hz, $J_2$ = 11.5 Hz, 1H), 4.25 (dd, $J_1$ = 2.8 Hz, $J_2$ = 11.5 Hz, 1H), 4.33-4.40 (m, 1H), 5.20 (dd, $J_1$ = 6.60 Hz, $J_2$ = 17.8 Hz, 2H), 7.22-7.35 (m, 10H), 7.41-7.46 (m, 1H), 7.85 (td, $J_1$ = 1.6 Hz, $J_2$ = 7.7 Hz, 1H), 8.19-8.22 (m, 1H), 8.58-8.59 (m, 1H), 8.73 (d, $J$ = 9.9 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 37.3, 38.5, 47.4, 66.3, 78.5, 87.5, 122.1, 126.2, 126.3, 126.5, 127.9, 128.1, 130.5, 139.7, 135.8, 136.1, 137.2, 148.1, 149.3, 163.6. ESI-HR MS exact mass calcd. for $(C_{24}H_{24}N_2NaO_3)^+$ requires m/z 411.1679, found m/z 411.1685.

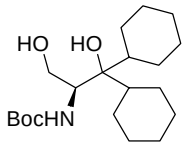
**(2) Preparation and characterization of catalyst 2g:**




Methyl *L*-serinate hydrochloride **3** (11.89 g, 76.42 mmol) was suspended in THF (150 mL), Then $Et_3N$ (16.62 g, 164.3 mmol) was added. The resulting white suspension was cooled to 0 $^oC$ and a solution of $(Boc)_2O$ (16.66 g, 76.37 mmol) in THF (75 mL) was added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for 12 hours. The solvent was removed in vacuo, and the residue partitioned between $Et_2O$ (100 mL) and $H_2O$ (100 mL). The aqueous phase was extracted with $Et_2O$ (60 mL × 2), and the organic phase was washed with 1*N* HCl (60 mL), saturated $NaHCO_3$ (60 mL) and brine (100 mL), dried over anhydrous $Na_2SO_4$. Solvent was removed to afford *N*-(Boc)-*L*-serine methyl ester **(5**) as a colorless oil, 15.90 g, 95 % yield.

To a stirred suspension of Grignard reagent [prepared from Mg (5.08 g, 209 mmol) and 1-bromocyclohexane (35.55 g, 218.05 mmol) in $Et_2O$ (150 mL)] was added dropwise to a

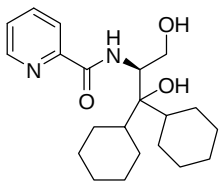
solution of *N*-(Boc)-*L*-serine methyl ester **5** (6.55 g, 29.87 mmol) in $Et_2O$ (80 mL) at -10 °C. After stirring overnight, the resulting mixture was quenched with saturated $NH_4Cl$ (100 mL) and $H_2O$ (100 mL). The mixture was extracted with EtOAc (3 × 100 mL), and washed with brine, dried over anhydrous $Na_2SO_4$. Concentration in vacuo gave a residue, which was purified on silica gel column [PET: EA = 10:1] to give (*S*)-tert-butyl 1,1-dicyclohexyl-1,3-dihydroxypropan-2-ylcarbamate (**13**) as a white solid, 6.16 g, 58 % yield.




**(*S*)-tert-butyl 1,1-dicyclohexyl-1,3-dihydroxypropan-2-ylcarbamate (13)**: white solid, yield 58 %, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.07-1.25 (m, 10H), 1.46 (s, 9H), 1.65-1.80 (m, 12H), 2.45-2.48 (m, 1H), 2.63 (brs, 1H), 3.78-3.97 (m, 3H), 5.39 (d, $J$ = 7.1 Hz, 1H).

The white solid **13** (6.16 g) was dissolved in ethyl acetate, and cooled to 0 °C. Then hydrogen chloride (gas) was bubbled in the solution for 2 hours. The product was filtered, washed with ethyl acetate, gave a white solid **6**, 3.52 g, 70 % yield.

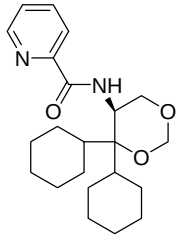
A 100 mL of three-necked flask was charged with picolinic acid (0.92 g, 7.44 mmol) and the flask was flushed with nitrogen. Then DCM (25 mL) and *N*-methylmorpholine (1.0 mL) were introduced in the flask to dissolve the material. The reaction mixture was cooled to -15 °C, then 1.15 mL of isobutylchloroformate (1.2 eq.) was added dropwise over 5 min. The reaction mixture was stirred at this temperature for 1 hour. Then a solution of compound **6** (2.50 g, 8.56 mmol) in DCM (40 mL) and NMM (2.2 mL) was added dropwise to the above reaction mixture at -10 °C. The reaction mixture was allowed to warm to room temperature, and stirred for one additional hour. The reaction mixture was diluted with DCM (50 mL), washed with 1*N* HCl (50 mL), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. Solvent was removed in vaccuo, and the residue was purified on silica gel [PET: EA = 3:1] to give a white solid **12f**, 2.40 g, 90 % yield.




**(*S*)-*N*-(1,1-dicyclohexyl-1,3-dihydroxypropan-2-yl)picolinamide (12f)**: white solid, yield 90 %, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.01-1.25 (m, 10H), 1.55-1.91 (m, 12H), 2.66 (s, 1H), 3.07 (brs, 1H), 3.93-4.08 (m, 2H), 4.37-4.40 (m, 1H), 7.40-7.45 (m, 1H), 7.84 (td, $J_1$ = 1.6 Hz, $J_2$ = 7.7 Hz,

1H), 8.18 (d, $J$ = 7.8 Hz, 1H), 8.59 (d, $J$ = 4.0 Hz, 1H), 8.85 (d, $J$ = 8.2 Hz, 1H).

Compound **12f** (0.36 g, 1 mmol) was dissolved in THF (20 mL). Then, $(CHO)_n$ (0.6 g, 20eq.) and $BF_3.Et_2O$ (0.5 mL) was added to the solution, and the reaction mixture was heated to reflux for overnight. THF was removed in vacuo. The residue was dissolved in DCM (100 mL) and washed with saturated $NaHCO_3$ (30 mL), $H_2O$ (50 mL), brine and dried over anhydrous $Na_2SO_4$. The Solvent was removed in vaccuo, and the residue was purified on silica gel [PET: EA = 6:1] to give a colorless oil, solidified under high vacuum, **2g** (0.32 g), 86 % yield.




**(*S*)-N-(4,4-dicyclohexyl-1,3-dioxan-5-yl)picolinamide (2g)**: white solid, 86%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.81-1.36 (m, 11H), 1.52 (m, 11H), 2.30-2.37 (m, 1H), 3.74 (dd, $J_1$ = 2.4 Hz, $J_2$ = 11.8 Hz, 1H), 4.24-4.30 (m, 2H), 4.88 (d, $J$ = 6.5 Hz, 1H), 5.00 (d, $J$ = 6.5 Hz, 1H), 7.39-7.44 (m, 1H), 7.83 (td, $J_1$ = 1.6 Hz, $J_2$ = 7.7 Hz, 1H), 8.17 (d, $J$ = 7.8 Hz, 1H), 8.60-8.61 (m, 1H), 8.97 (d, $J$ = 10.0 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 26.7, 26.9, 27.3, 27.5, 27.8, 28.1, 28.6, 29.2, 40.8, 46.1, 46.5, 67.2, 79.6, 87.6, 122.0, 126.0, 137.1, 148.3, 149.7, 163.3. ESI-HR MS exact mass calcd. for $(C_{22}H_{32}N_2NaO_3)^+$ requires m/z 395.2305, found m/z 395.2314.

## 3. Asymmetric hydrosilylation of $\beta$-enamino esters:

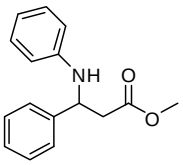
$\beta$-Enamino esters **7a-m**, **7o** and **7y**[2], **7r**[3], **7t**[4], **7q**[5], **7n**, **7p**, **7s**, **7u-7x** [6] were prepared from the corresponding $\beta$-keto esters according to the literatures.

**General procedure:**

A solution of trichlorosilane dissolved in $(ClCH_2)_2$ (1/4, v/v, 0.3 mL, 2.0 equiv.) was added to a solution of the catalyst (10 mol %) and the corresponding $\beta$-enamino ester (0.3 mmol) in dry 1,2-dichloroethane (3 mL) at -10 $^o$C. The reaction mixture was stirred at -10 $^o$C for 10 hours. Then the reaction was quenched with saturated aqueous solution of $NaHCO_3$ (1 mL). The mixture was filtered through a pad of celite, washed with DCM (70 mL), and dried

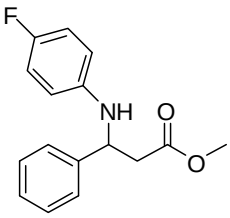
over anhydrous $Na_2SO_4$. The solution was filtered and the solvent was removed in vacuum. The residue was subjected to flash chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as the eluent to afford the pure product. The ee values were determined using established HPLC techniques with chiral stationary phases.

The corresponding racemates were prepared using DMF as the catalyst.



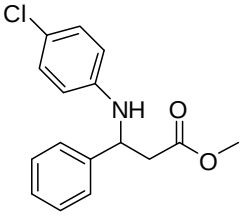

**methyl 3-phenyl-3-(phenylamino)propanoate (8a):**

White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.80-2.86 (m, 2H), 3.65 (s, 3H), 4.58 (brs, 1H), 4.83 (t, $J$= 6.7 Hz, 1H), 6.56 (d, $J$= 7.7 Hz, 2H), 6.67 (t, $J$= 7.3 Hz, 1H), 7.10 (dd, $J_1$ = 7.5 Hz, $J_2$ = 8.3 Hz, 2H), 7.22-7.39 (m, 5H). HPLC analysis: 94 % ee, Chiralcel AD-H (hexane/iPrOH = 80/20, 1.0 mL/min), $t_{r\text{-minor}}$ = 11.7 min, $t_{r\text{-major}}$ = 10.1 min. $[\alpha]_D^{20}$ = +1.4 (*c* 0.9, $CHCl_3$).



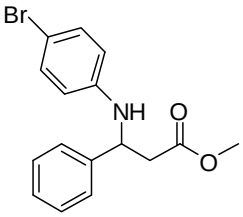

**methyl 3-(4-fluorophenylamino)-3-phenylpropanoate (8b):**

Colorless oil, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.74-2.88 (m, 2H), 3.66 (s, 3H), 4.50 (brs, 1H), 4.75-4.80 (m, 1H), 6.47-6.52 (m, 2H), 6.78-6.84 (m, 2H), 7.26-7.38 (m, 5H). HPLC analysis: 93 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 12.9 min, $t_{r\text{-major}}$ = 10.9 min. $[\alpha]_D^{20}$ = -12.1 (*c* 0.474, $CHCl_3$).




**methyl 3-(4-chlorophenylamino)-3-phenylpropanoate (8c)**

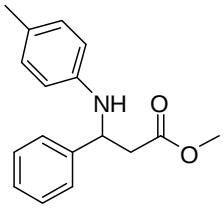
White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.73-2.88 (m, 2H), 3.66 (s, 3H), 4.62 (s, 1H), 4.75-4.80 (m, 1H), 6.46-6.50 (m, 2H), 7.04 (dd, $J_1$ = 2.1 Hz, $J_2$ = 6.7 Hz, 2H), 7.24-7.34 (m, 5H). HPLC analysis: 91 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 14.7 min, $t_{r\text{-major}}$ = 12.2 min. $[\alpha]_D^{20}$ = +8.8 (*c* 0.49, $CHCl_3$).




**methyl 3-(4-bromophenylamino)-3-phenylpropanoate (8d)**

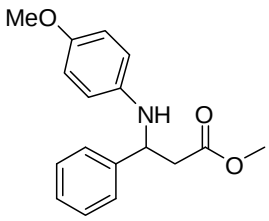
White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.73-2.88 (m, 2H), 3.66 (s, 3H), 4.62 (s, 1H), 4.75-4.79 (m, 1H), 6.41-6.45 (m, 2H),

7.15-7.34 (m, 7H). HPLC analysis: 92 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 16.0 min, $t_{r\text{-major}}$ = 13.3 min. $[\alpha]_D^{20}$ = +15.1 (*c* 0.666, $CHCl_3$).



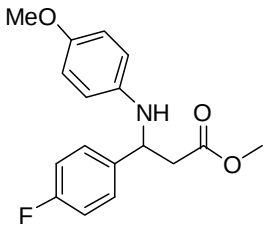

**methyl 3-phenyl-3-(p-tolylamino)propanoate (8e)**

White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.21 (s, 3H), 2.76-2.86 (m, 2H), 3.66 (s, 3H), 4.10 (brs, 1H), 4.83 (t, *J* = 6.8 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 7.23-7.40 (m, 5H). HPLC analysis: 98 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 7.2 min, $t_{r\text{-major}}$ = 6.3 min. $[\alpha]_D^{20}$ = +5.1 (*c* 0.666, $CHCl_3$).



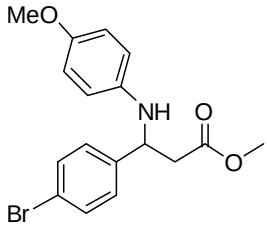

**methyl 3-(4-methoxyphenylamino)-3-phenylpropanoate (8f)**

White solid, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.80-2.82 (m, 2H), 3.66 (s, 3H), 3.70 (s, 3H), 4.31 (brs, 1H), 4.83 (t, *J* = 6.7 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 2H), 6.68-6.72 (m, 2H), 7.23-7.39 (m, 5H). HPLC analysis: 94 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 20.0 min, $t_{r\text{-major}}$ = 17.4 min. $[\alpha]_D^{20}$ = +9.1 (*c* 0.496, $CHCl_3$).




**methyl 3-(4-fluorophenyl)-3-(4-methoxyphenylamino)propanoate (5g)**

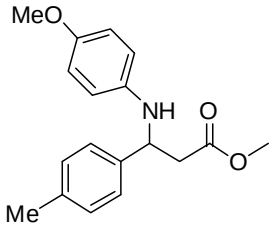
White solid, 98 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.79 (d, *J* = 6.7 Hz, 2H), 3.66 (s, 3H), 3.71 (s, 3H), 4.35 (brs, 1H), 4.75 (t, *J* = 6.6 Hz, 1H), 6.50-6.53 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 7.27-7.37 (m, 2H). HPLC analysis: 88 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 24.6 min, $t_{r\text{-major}}$ = 20.2 min. $[\alpha]_D^{20}$ = -7.0 (*c* 0.8, $CHCl_3$).




**methyl 3-(4-bromophenyl)-3-(4-methoxyphenylamino) propanoate (8h)**

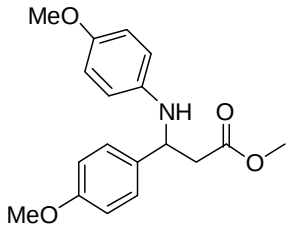
White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.78 (d, *J* = 6.6 Hz, 2H), 3.67 (s, 3H), 3.71 (s, 3H), 4.25 (brs, 1H), 4.72 (t, *J* = 6.6 Hz, 1H), 6.51 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.44(d, *J* = 8.3 Hz, 2H). HPLC analysis: 92 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min),

$t_{r\text{-minor}}$ = 23.7 min, $t_{r\text{-major}}$ = 21.2 min. $[\alpha]_D^{20}$ = +22.1 (*c* 1.2, $CHCl_3$).



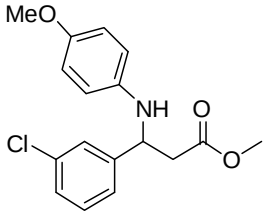

**methyl 3-(4-methoxyphenylamino)-3-p-tolyl propanoate (8i)**

White solid, 98 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.33 (s, 3H), 2.80 (d, *J* = 6.8 Hz, 2H), 3.67 (s, 3H), 3.71 (s, 3H), 4.55 (brs, 1H), 4.74 (t, *J* = 6.7 Hz, 1H), 6.53-6.57 (m, 2H), 6.69-6.74 (m, 2H), 7.13-7.27 (m, 4H). HPLC analysis: 95 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 16.7 min, $t_{r\text{-major}}$ = 1 4.3 min. $[\alpha]_D^{20}$ = +22.9 (*c* 0.49, $CHCl_3$).



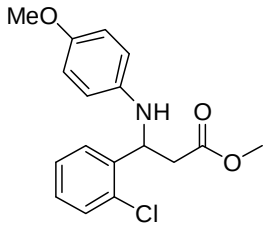

**methyl 3-(4-methoxyphenyl)-3-(4-methoxyphenyl amino) propanoate (8j)**

White solid, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.79 (d, *J* = 6.5 Hz, 2H), 3.66 (s, 3H), 3.71 (s, 3H), 3.79 (s, 3H), 4.15 (brs, 1H), 4.73 (t, *J* = 6.7 Hz, 1H), 6.55 (d, *J* = 8.9 Hz, 2H), 6.70-6.73 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H). HPLC analysis: 94 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 37.0 min, $t_{r\text{-major}}$ = 34.7 min. $[\alpha]_D^{20}$ = +19.7 (*c* 0.94, $CHCl_3$).




**methyl 3-(3-chlorophenyl)-3-(4-methoxyphenyl amino)propanoate (8k)**

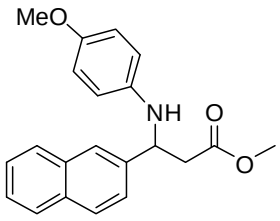
White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.76-2.81 (m, 2H), 3.66 (s, 3H), 3.70 (s, 3H), 4.31 (brs, 1H), 4.73 (t, *J* = 6.6 Hz, 1H), 6.50 (d, *J* = 8.8 Hz, 2H), 6.68-6.74 (m, 2H), 7.19-7.38 (m, 4H). HPLC analysis: 94 % ee, Chiralcel OD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 22.2 min, $t_{r\text{-major}}$ = 20.0 min. $[\alpha]_D^{20}$ = +2.7(*c* 0.96, $CHCl_3$).




**methyl 3-(2-chlorophenyl)-3-(4-methoxyphenyl amino)propanoate (8l)**

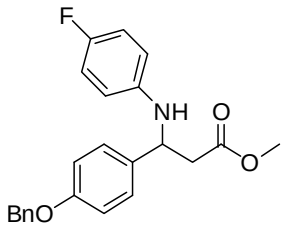
White solid, 98 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.71 (dd, $J_1$ = 8.5 Hz, $J_2$ = 15.0 Hz, 1H), 2.93 (dd, $J_1$ = 4.0 Hz, $J_2$ = 15.0 Hz, 1H), 3.66 (s, 3H), 3.69 (s, 3H), 4.62 (brs, 1H), 5.15 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.5 Hz, 1H), 6.47 (d, *J* = 8.8

Hz, 2H), 6.69 (d, $J$ = 8.9 Hz, 2H), 7.36-7.45 (m, 4H). HPLC analysis: 80 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 17.8 min, $t_{r\text{-major}}$ = 16.2 min. $[\alpha]_D^{20}$ = -50.3 ($c$ 0.52, $CHCl_3$).



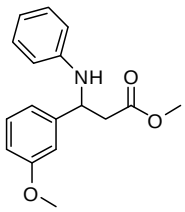

**methyl 3-(4-methoxyphenylamino)-3-(naphthalen-2-yl) propanoate (8m)**

White solid, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.89-2.94 (m, 2H), 3.67 (s, 3H), 3.69 (s, 3H), 4.43 (brs, 1H), 4.95 (t, $J$ = 6.8 Hz, 1H), 6.59-6.73 (m, 4H), 7.44-7.54 (m, 3H), 7.82-7.86 (m, 4H). HPLC analysis: 96 % ee, Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{r\text{-minor}}$ = 23.7 min, $t_{r\text{-major}}$ = 25.1 min. $[\alpha]_D^{20}$ = +23.7 ($c$ 0.38, $CHCl_3$).



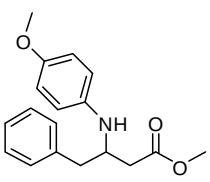

**methyl 3-(4-(benzyloxy)phenyl)-3-(4-fluorophenyl amino) propanoate (8n)**

White solid, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.80 (d, $J$ = 6.7 Hz, 2H), 3.67 (s, 3H), 4.45 (brs, 1H), 4.46 (t, $J$ = 6.7 Hz, 1H), 5.04 (s, 2H), 6.49-6.53 (m, 2H), 6.80-6.97 (m, 4H), 7.27-7.45 (m, 7H). HPLC analysis: 95 % ee, Chiralcel AS-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{r\text{-minor}}$ = 24.2min, $t_{r\text{-major}}$ = 17.6 min. $[\alpha]_D^{20}$ = +1.7 ($c$ 0.65, $CHCl_3$).




**methyl 3-(3-methoxyphenyl)-3-(phenylamino)propanoate (8o)**

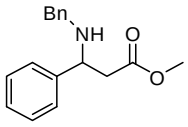
White solid, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.80-2.83 (m, 2H), 3.66 (s, 3H), 3.78 (s, 3H), 4.54 (s, 1H), 4.80-4.84 (m, 1H), 6.57-6.60 (m, 2H), 6.66-6.71 (m, 1H), 6.78-6.81 (m, 1H), 6.94-6.99 (m, 2H), 7.09-7.14 (m, 2H), 7.22-7.28 (m, 1H). HPLC analysis: 92 % ee, Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{r\text{-minor}}$ = 9.7 min, $t_{r\text{-major}}$ = 9.0 min. ESI-HR MS exact mass calcd. for $(C_{17}H_{20}NO_3)^+$ requires m/z 286.1438, found m/z 286.1438.




**methyl 3-(4-methoxyphenylamino)-4-phenylbutanoate (8p)**

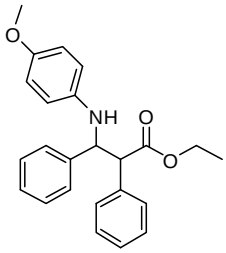
Colorless oil, 96 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.41-2.55 (m,

2H), 2.84 (dd, $J_1$ = 7.16 Hz, $J_2$ = 13.6 Hz, 1H), 2.96 (dd, $J_1$ = 5.12 Hz, $J_2$ = 13.6 Hz, 1H), 3.56 (brs, 1H), 3.65 (s, 3H), 3.75 (m, 3H), 4.04 (dd, $J_1$ = 6.03 Hz, $J_2$ = 12.2 Hz, 1H), 6.50 (d, $J$ = 8.9 Hz, 2H), 6.82 (d, $J$ = 8.9 Hz, 2H),7.17-7.33 (m, 5H). HPLC analysis: 45 % ee, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 14.9 min, $t_{r\text{-major}}$ = 16.8 min.



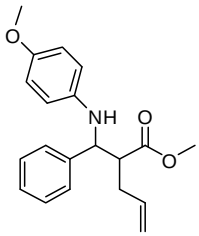

**methyl 3-(benzylamino)-3-phenylpropanoate (8q)**

Colorless oil, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.02-2.05 (m, 2H), 2.60-2.78 (m, 2H), 3.52-3.56 (m, 1H), 3.64 (s, 3H), 3.69 (s, 1H), 4.12 (dd, $J_1$ = 5.2 Hz, $J_2$ = 8.7 Hz, 1H), 7.21-7.37 (m, 10H). HPLC analysis: 82 % ee, Chiralcel OD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t_{r\text{-minor}}$ = 9.2 min, $t_{r\text{-major}}$ = 6.0 min. $[\alpha]_D^{20}$ = +26.7 ($c$ 0.68, $CHCl_3$).



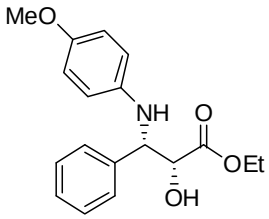

**ethyl 3-(4-methoxyphenylamino)-2,3-diphenylpropanoate(8r)**

White solid, 97 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.96 (t, $J$ = 7.1 Hz, 3H), 3.64-3.67 (m, 4H), 3.83-3.91 (m, 3H), 4.86 (d, $J$ = 10.0Hz, 1H), 6.34 (d, $J$ = 8.5 Hz, 2H), 6.58 (d, $J$ = 8.9 Hz, 2H), 7.24-7.46 (m, 6H), 7.48-7.49 (m, 4H). HPLC analysis: 34 % ee, 21: 1 dr, Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{r\text{-minor}}$ = 14.9 min, $t_{r\text{-major}}$ = 9.5 min. $[\alpha]_D^{20}$ = -21.0 ($c$ 0.48, $CHCl_3$).



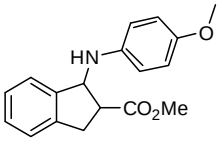

**methyl 2-((4-methoxyphenylamino)(phenyl)methyl) pent-4-enoate (8s)**

Colorless oil, 90 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.22-2.29 (m, 1H), 2.43-2.53 (m, 1H), 2.82-2.93 (m, 1H), 3.56-3.59 (m, 3H), 3.68-3.69 (m, 3H), 4.52 (d, $J$ = 6.9 Hz, 1.39H), 4.59 (d, $J$ = 5.9 Hz, 0.43H), 5.01-5.05 (m, 1.5H), 5.08-5.10 (m, 0.5H), 5.68-5.77 (m, 1H), 6.48- 6.52 (m, 2H), 6.66-6.70 (m, 2H), 7.22-7.32 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 31.9, 34.4, 51.5, 51.6, 52.2, 52.6, 55.6, 59.8, 60.0, 114.6, 114.7, 114.9, 117.0, 117.4, 126.6, 126.9, 127.3, 127.4, 128.4, 128.5, 134.7, 135.3, 140.7, 140.9, 141.1, 141.3, 151.9, 152.2, 173.5, 174.4. HPLC analysis: 90 % ee, 3.2: 1 dr, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 11.1 min, $t_{r\text{-major}}$ = 10.5 min. $[\alpha]_D^{20}$ = +9.8 ($c$ 1.24, $CHCl_3$). ESI-HR MS exact mass calcd. for $(C_{20}H_{23}NNaO_3)^+$ requires m/z 348.1570, found m/z 348.1573.



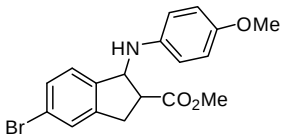

**methyl 2-hydroxy-3-(4-methoxyphenylamino)-3-phenyl propanoate**

White solid, 82 % yield (two steps). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.29 (t, $J$= 7.1 Hz, 3H), 3.44 (brs, 2H), 3.68 (s, 3H), 4.24 (q, $J$= 7.1 Hz, 2H), 4.47 (d, $J$= 2.7 Hz, 1H), 4.85 (d, $J$= 2.7 Hz, 1H), 6.52-6.71 (m, 4H), 7.22-7.39 (m, 5H). HPLC analysis: 90 % ee, 91:9 dr, Chiralcel AD-H (hexane/iPrOH = 90/10, 1.0 mL/min), $t$ = 20.4, 27.7, 28.8, 46.7 min. $[\alpha]_D^{20}$ = -1.0 ($c$ 0.72, $CHCl_3$).



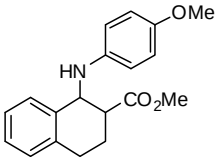

**methyl 1-(4-methoxyphenylamino)-2,3-dihydro-1H- indene-2-carboxylate (8u)**

White solid, 98 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.12 (dd, $J_1$ = 8.4 Hz, $J_2$ = 16.3 Hz, 1H), 3.40-3.46 (m, 1H), 3.48 (s, 3H), 3.62-3.69 (m, 1H), 3.76 (s, 3H), 3.82 (s, 1H), 5.30 (d, $J$= 7.5 Hz, 1H), 6.69-6.81 (m, 4H), 7.21-7.31(m, 4H). HPLC analysis: 95 % ee, > 99: 1 dr, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{\text{r-minor}}$ = 14.4 min, $t_{\text{r-major}}$ = 29.0 min. $[\alpha]_D^{20}$ = -28.5 ($c$ 1.06, $CHCl_3$).




**methyl 5-bromo-1-(4-methoxyphenylamino)-2,3-dihydro-1H-indene-2-carboxylate (8v)**

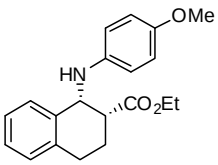
Colorless oil, 95 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.10 (dd, $J_1$ = 8.4 Hz, $J_2$ = 16.6 Hz, 1H),3.39 (dd, $J_1$ = 5.8 Hz, $J_2$ = 16.6 Hz, 1H), 3.48 (s, 3H), 3.62-3.69 (m, 1H), 3.76 (s, 3H), 3.82 (s, 1H), 5.22 (d, $J$= 7.5 Hz, 1H), 6.67-6.81 (m, 4H), 7.15 (d, $J$= 8.06 Hz, 1H), 7.32 (d, $J$= 8.07 Hz, 1H), 7.39 (s, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 33.5, 48.2, 51.5, 55.6, 61.2, 114.7, 115.2, 122.1, 125.8, 127.9, 130.2, 140.9, 141.8, 143.2, 152.5, 173.1. HPLC analysis: 96 % ee, >99:1 dr, Chiralcel AD-H (hexane/iPrOH = 85/15, 1.0 mL/min), $t_{\text{r-minor}}$ = 8.5 min, $t_{\text{r-major}}$ = 14.2 min. $[\alpha]_D^{20}$ = +7.7 ($c$ 1.06, $CHCl_3$). ESI-HR MS exact mass calcd. for $(C_{18}H_{19}BrNO_3)^+$ requires m/z 376.0543, found m/z 376.0546.




**methyl 1-(4-methoxyphenylamino)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (8w)**

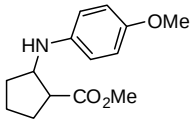
Colorless oil, 95 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.06-2.23 (m,

2H), 2.74-2.85 (m, 1H), 2.90-3.06 (m, 2H), 3.63 (s, 3H), 3.71-3.77 (m, 4H), 4.96 (d, $J$= 4.4 Hz, 1H), 6.70-6.81 (m, 4H), 7.08-7.26 (m, 4H). HPLC analysis: 92 % ee, >99:1 dr, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 12.1 min, $t_{r\text{-major}}$ = 15.6 min. $[\alpha]_D^{20}$ = +128.0 ($c$ 0.14, $CHCl_3$).




**(1*R*,2*R*)-ethyl 1-(4-methoxyphenylamino)-1,2,3,4-tetrahydronaphthalene -2-carboxylate (8x)**

Colorless oil, 98 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.18 (t, $J$= 7.1 Hz, 3H), 2.02-2.20 (m, 2H), 2.71-3.0 (m, 3H), 3.68(s, 1H), 3.74 (s, 3H), 3.95-4.14 (m, 2H), 4.93 (d, $J$= 4.4 Hz, 1H), 6.70-6.77 (m, 4H), 7.06-7.24 (m, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 14.1, 21.0, 27.7, 44.7, 54.6, 55.6, 60.4, 114.6, 115.6, 126.1, 127.1, 128.2, 128.8, 135.1, 137.7, 141.7, 152.3, 173.2. HPLC analysis: 90 % ee, >99:1 dr, Chiralcel AD-H (hexane/iPrOH = 70/30, 1.0 mL/min), $t_{r\text{-minor}}$ = 5.4 min, $t_{r\text{-major}}$ = 6.5 min. $[\alpha]_D^{20}$ = +204.0 ($c$ 0.226, $CHCl_3$). ESI-HR MS exact mass calcd. for $(C_{20}H_{24}NO_3)^+$ ($M+H^+$) requires m/z 326.1751, found m/z 326.1738; $(C_{20}H_{23}NNaO_3)^+$ ($M+Na^+$) requires m/z 348.1570, found m/z 348.1559.




**methyl 2-(4-methoxyphenylamino)cyclopentanecarboxylate (8y)**

Colorless oil, 95 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.63-2.10 (m, 6H), 3.06 (dd, $J_1$ = 7.4 Hz, $J_2$ = 15.4 Hz, 1H), 3.52 (s, 3H), 3.73 (s, 3H), 3.76 (br s, 1H), 4.02 (dd, $J_1$ = 6.5 Hz, $J_2$ = 13.3 Hz, 1H), 6.58 (d, $J$= 8.9 Hz, 2H), 6.75 (d, $J$= 8.9 Hz, 2H). HPLC analysis: 18 % ee, >99:1 dr, Chiralcel AD-H (hexane/iPrOH = 95/5, 1.0 mL/min), $t_{r\text{-minor}}$ = 11.2 min, $t_{r\text{-major}}$ = 8.9 min. $[\alpha]_D^{20}$ = +15.0 ($c$ 0.144, $CHCl_3$).

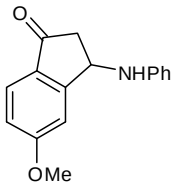
## 4. Preparation and Characterization of compound 9, 10 and 11

### 4.1 Synthesis of chiral 3-aminoindan-1-one derivative 9

The chiral product **8o** (0.95 g, 3.33 mmol) obtained above was hydrolyzed by LiOH (2 eq.) in THF/MeOH/$H_2O$ (2/2/1) at room temperature. The mixture was adjusted to pH ~ 3-4 with 3N HCl, and extracted with DCM (20 mL × 3). The organic phase was washed with brine and

dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the acid was subjected to the next step without further purification.

The acid was treated with PPA (20 mL) at 110 $^oC$ for 0.5 hour and the reaction mixture was poured into ice water (50 mL) and then neutralized with $K_2CO_3$ to pH = 8. Extracted of the mixture with EtOAc (2×60 mL) followed by chromatography (PET: EA = 6: 1) afforded 5-methoxy-3-(phenylamino)-2,3-dihydro-1H-inden-1-one **9** (0.48 g, 57 %) as a solid.




**5-methoxy-3-(phenylamino)-2,3-dihydro-1H-inden-1-one (9)**

White solid, 57 % yield (two steps). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 2.45 (dd, $J_1$ = 3.2 Hz, $J_2$ = 18.7 Hz, 1H), 3.10 (dd, $J_1$ = 6.8 Hz, $J_2$ = 18.7 Hz, 1H), 3.84 (s, 3H), 4.21 (d, $J$ = 5.7 Hz, 1H), 5.05 (s, 1H), 6.70 (d, $J$ = 7.7 Hz, 2H), 6.77 (t, $J$ = 7.3 Hz, 1H), 6.96 (dd, $J_1$ = 2.1 Hz, $J_2$ = 8.5 Hz, 1H), 7.10 (d, $J$ = 1.9 Hz, 1H), 7.18-7.26 (m, 2H), 7.63 (d, $J$ = 8.5Hz, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 45.3, 51.2, 55.5, 108.7, 113.2, 116.9, 118.1, 124.8, 129.3, 129.8, 146.8, 157.5, 165.4, 201.8. HPLC analysis: 90 % ee, Chiralcel AD-H (hexane/iPrOH = 70/30, 1.0 mL/min), $t_{r\text{-minor}}$ = 9.4 min, $t_{r\text{-major}}$ = 8.5 min. $[\alpha]_D^{20}$ = -222.1 (*c* 1.4, $CHCl_3$). ESI-HR MS exact mass calcd. for $(C_{16}H_{15}NNaO_2)^+$ requires m/z 276.0995, found m/z 276.0997.

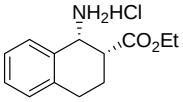
### 4.2 Synthesis of compounds 11[7] and 12

Na (100 mg, 4.34 mmol) was dissolved in dry EtOH (10 mL). Compound **8x** (150 mg) was added to the solution and the mixture was refluxed for 5 minutes. The reaction mixture was adjusted to pH = 8. Then EtOH was removed, the residue was extracted with EA. The organic layer was washed with brine, dried over anhydrous $Na_2SO_4$. The solvent was removed and the residue was purified on FC (PET: EA = 20:1) to give the diastereoisomer mixture (**8x**:**10** = 1:5).

**Data for diastereoisomer mixture:** Colorless oil. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.16-1.37(m, 8H), 2.10-2.12 (m, 3H), 2.85-2.93 (m, 4H), 3.70 (brs, 1H), 3.74 (s, 3H), 3.75 (s, 0.9H), 4.03-4.15(m, 2.6H), 4.91 (d, $J$ = 7.1 Hz, 1H), 4.94 (d, $J$ = 5.2 Hz, 0.2H), 6.62-6.79 (m, 5H), 7.11-7.43 (m, 5.3H).

To a solution of compound **8x** (0.69 g, 2.12 mmol) in MeCN/$H_2O$ (4:1, 25 mL) was added ceric ammonium nitrate (4.65 g, 8.48 mmol) at room temperature, and the reaction mixture

was stirred for 1 hour. The reaction was quenched with 10% aqueous NaOH and adjusted to pH = 9 to give a mass. The mass was filtered through a pad of celite, washed with DCM. The solution was extracted with DCM. The organic phase was washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed and the residue was purified on FC (PET: EA=2:1 to DCM: MeOH=30:1) to give a brown oil, which was dissolved in EA/$Et_2O$= 1:2. Hydrogen Chloride was bubbled in the solution for 5 minutes. White solid precipitated. The solid was collected by filtration and washed with $Et_2O$, dried under reduced pressure to give the product **11** (0.41 g, 76 % yield).




**(1*R*,2*R*)-ethyl 1-amino-1,2,3,4-tetrahydronaphthalene-2-carboxylate hydrochloride (11):** white solid, 76 % yield. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.20 (t, $J$= 7.1 Hz, 3H), 2.09-2.14 (m, 2H), 2.79-2.84 (m, 2H), 3.20-3.23 (m, 1H), 4.10-4.17 (m, 2H), 4.65 (s, 1H), 7.15-7.25 (m, 3H), 7.54 (d, $J$= 6.8 Hz, 1H), 8.58 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 13.9, 20.1, 27.1, 41.6, 48.7, 60.9, 126.0, 128.5, 129.1, 129.3, 131.8, 136.5, 171.5. $[\alpha]_D^{20}$ = +35.0 (*c* 0.15, EtOH).

References:

1. (*a*) M. P. Sibi, J. X. Chen and G. R. Cook, *Tetrahedron Lett.* 1999, **40**, 3301; (*b*) S. Rajaram and M. S. Sigman, *Org. Lett.* 2005, **7**, 5473.

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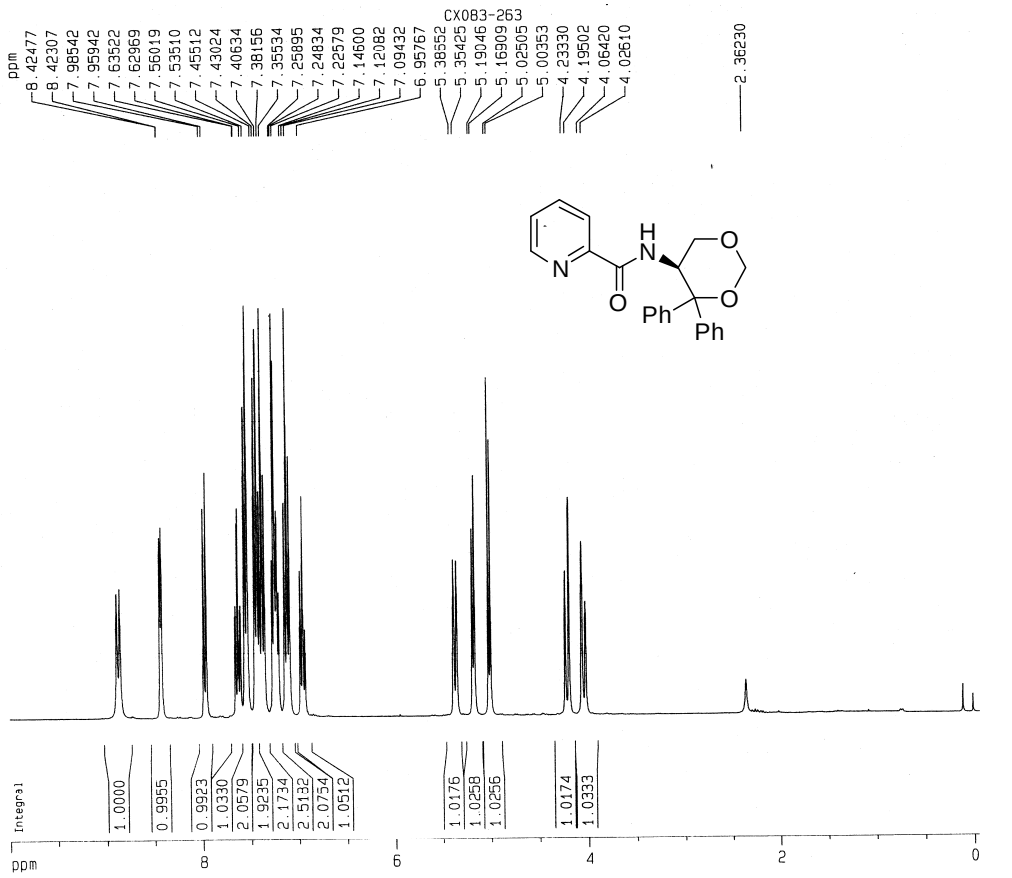
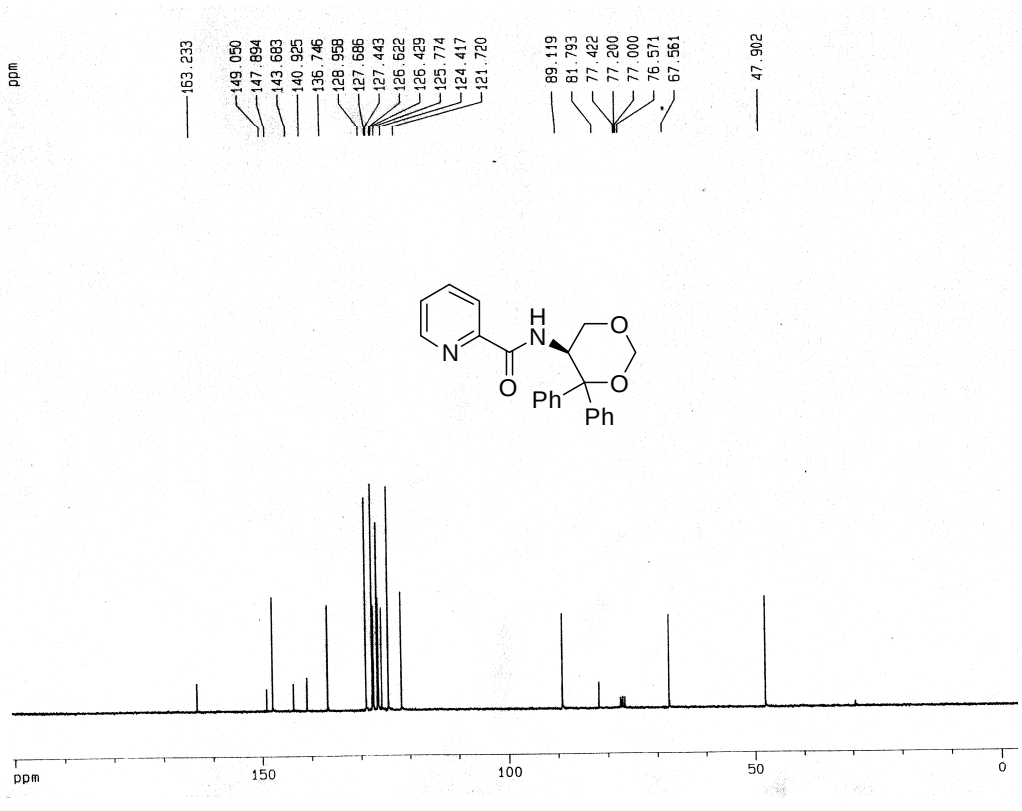
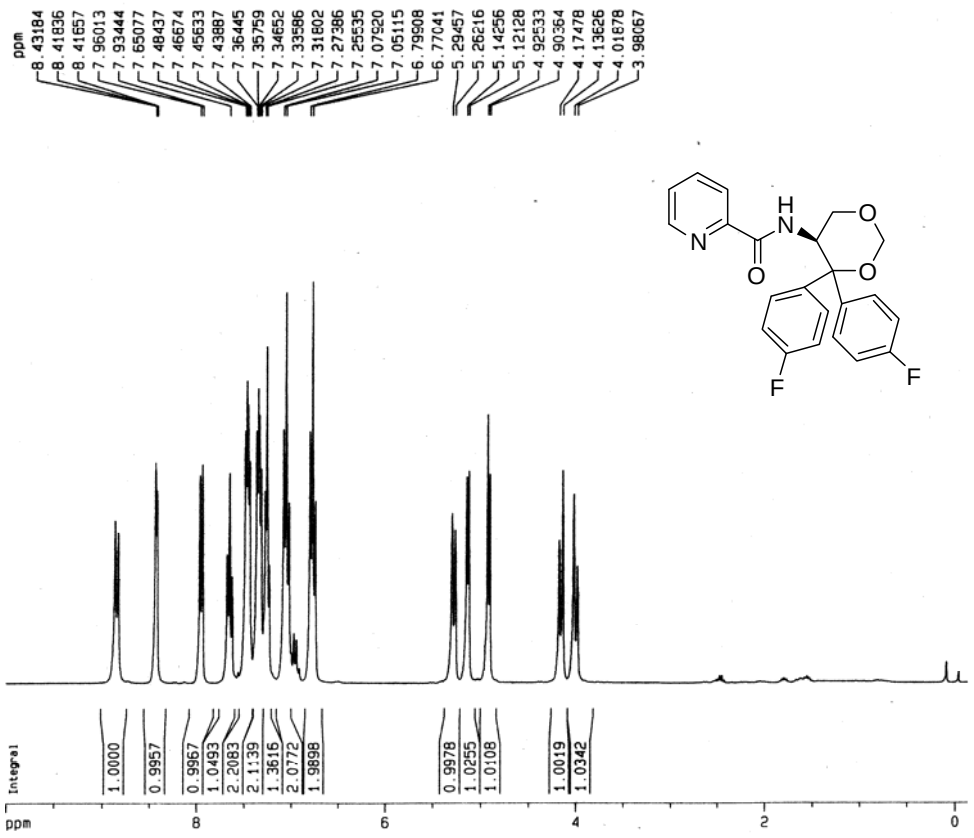
# $^{1}$H-NMR and $^{13}$C-NMR Spectra



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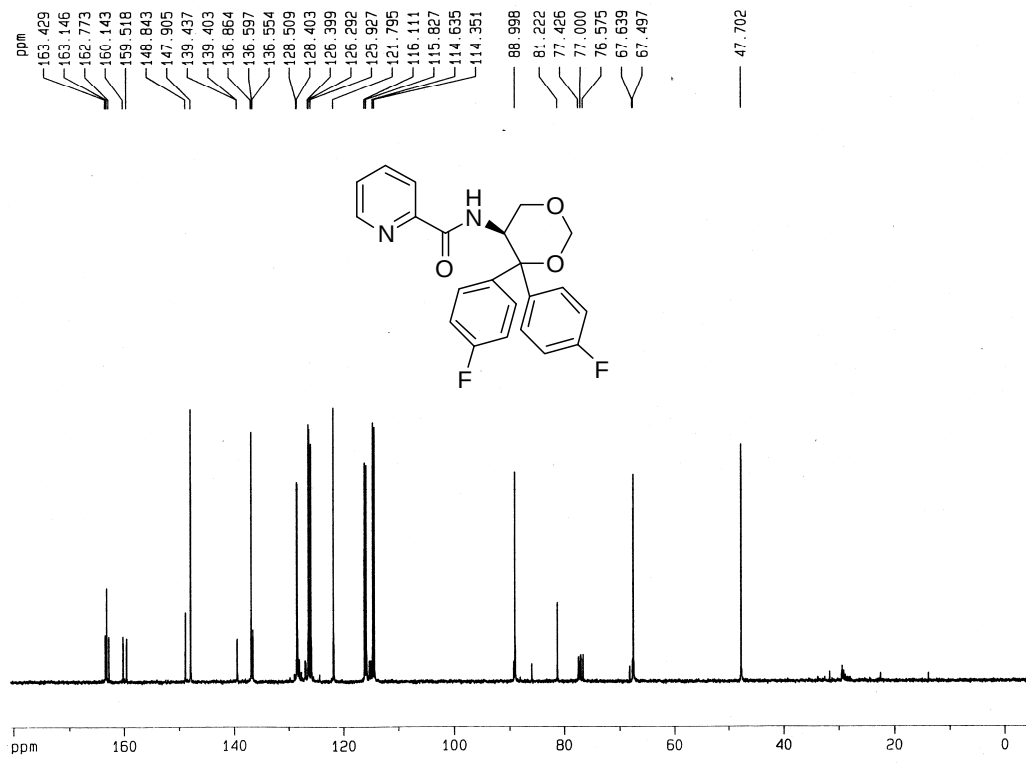

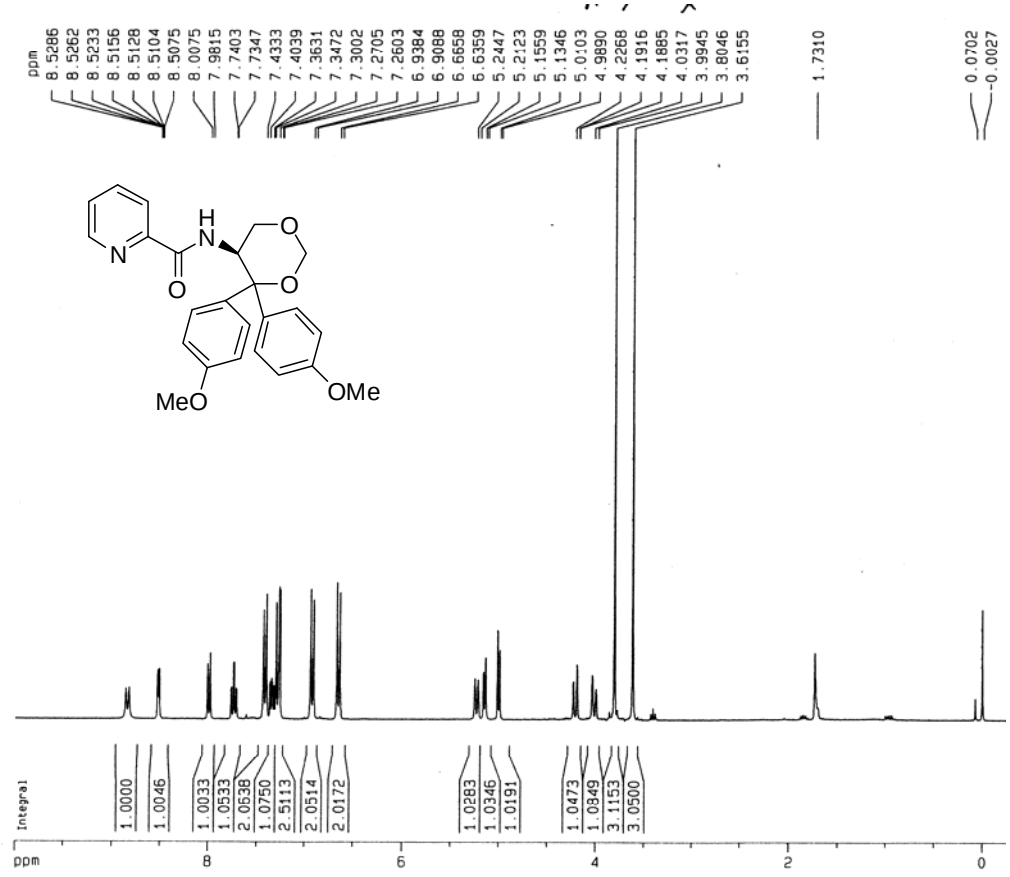


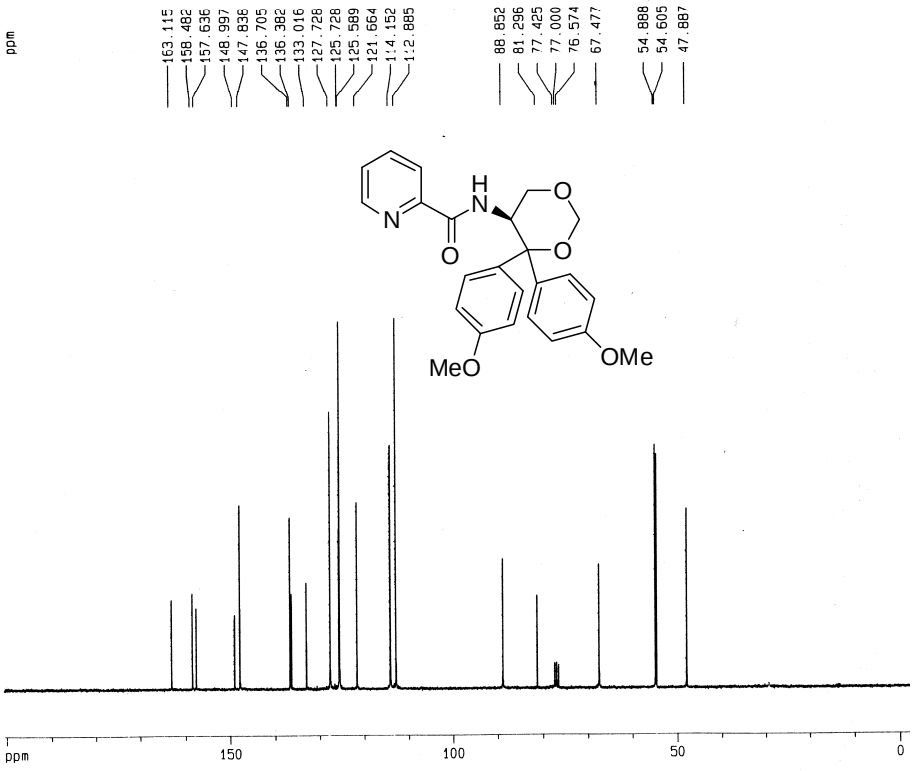

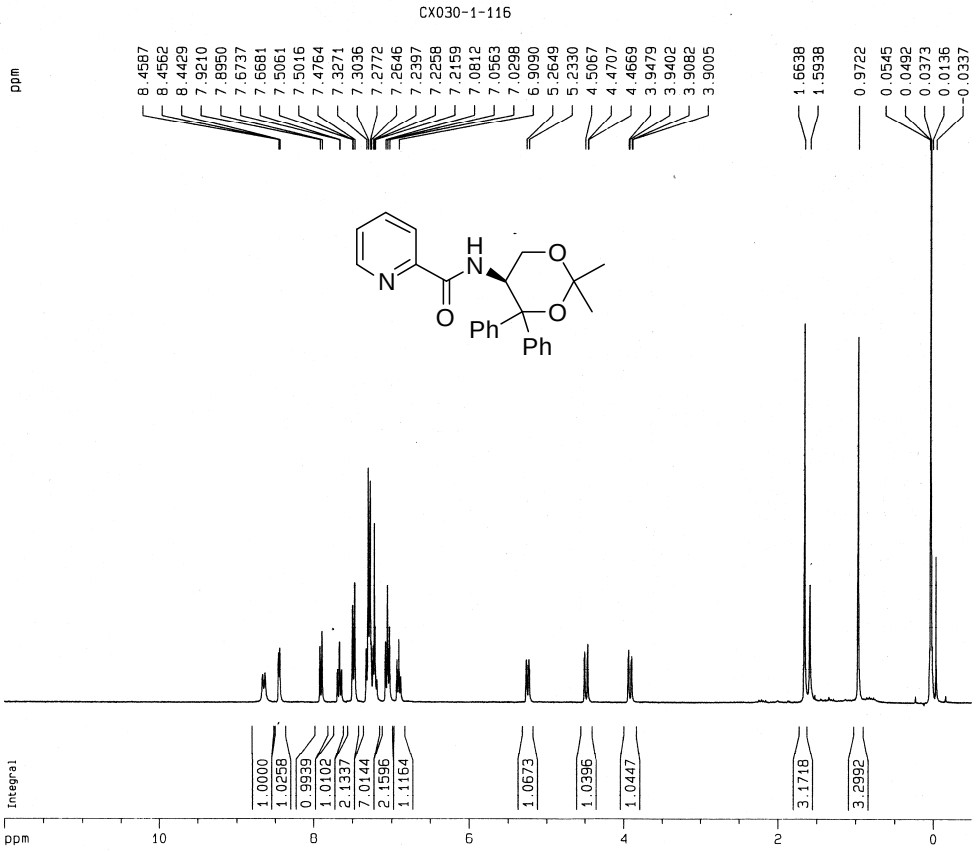


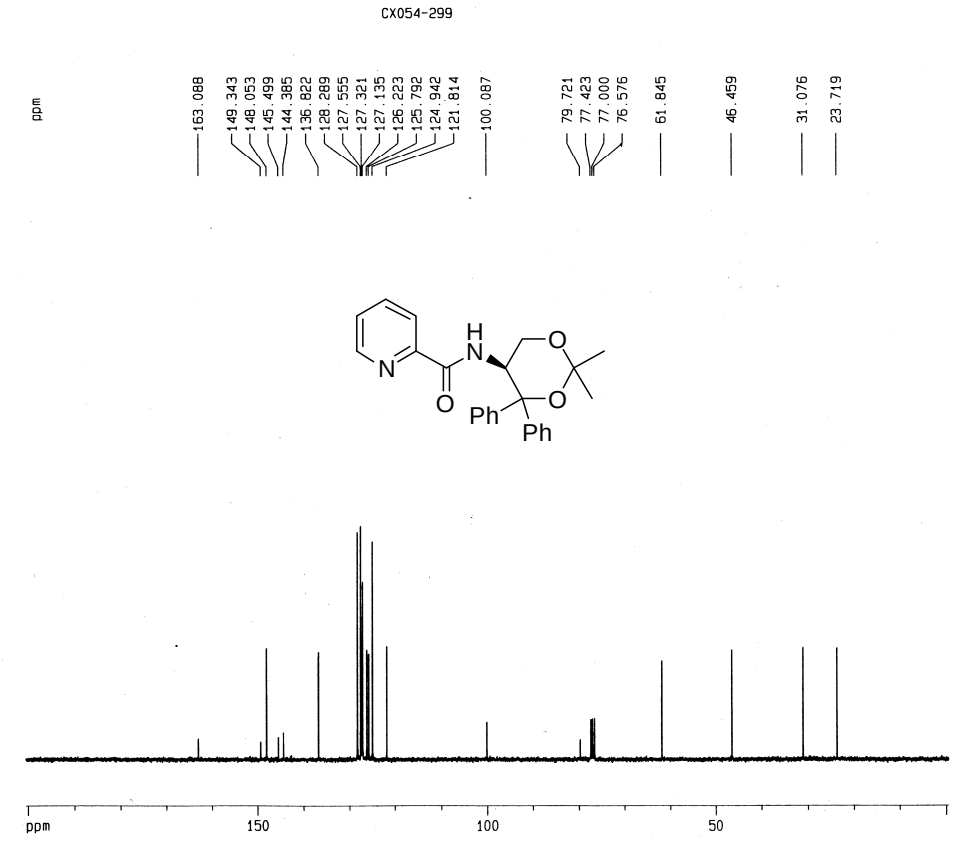

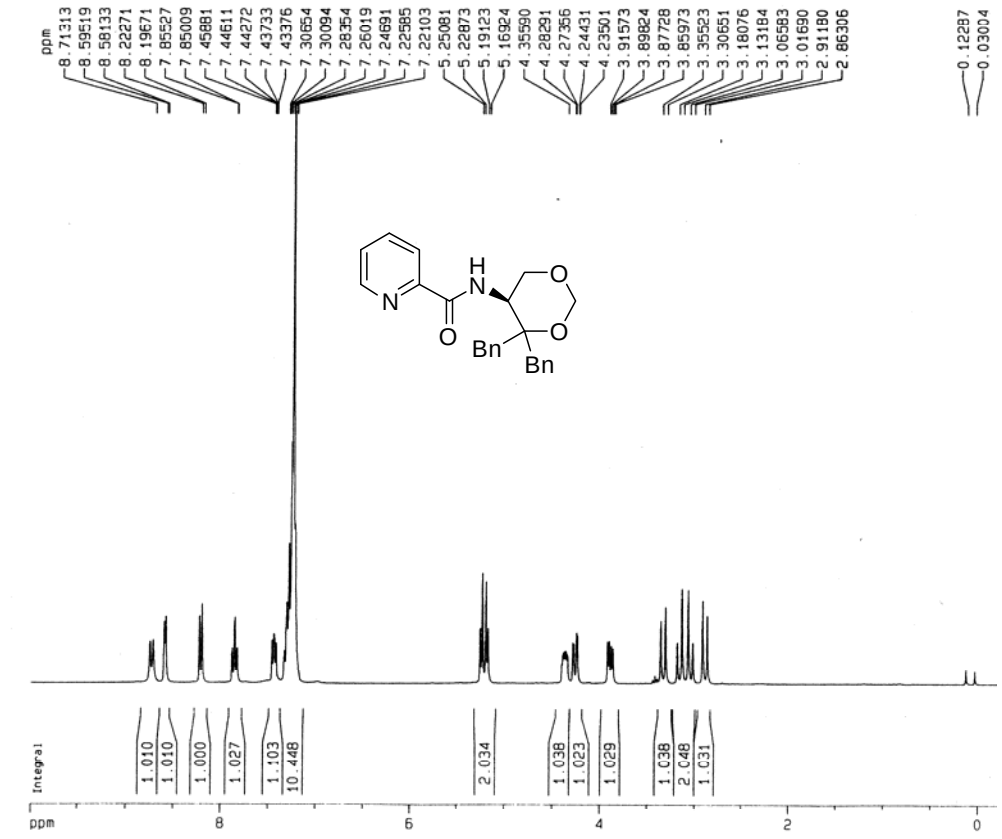
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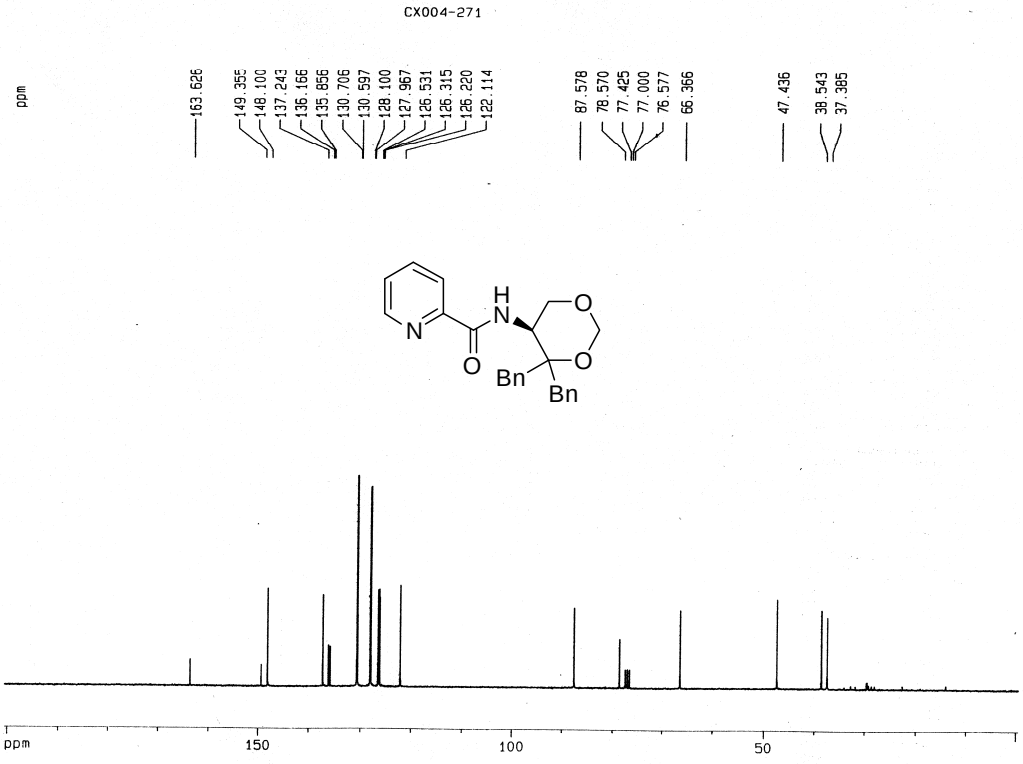
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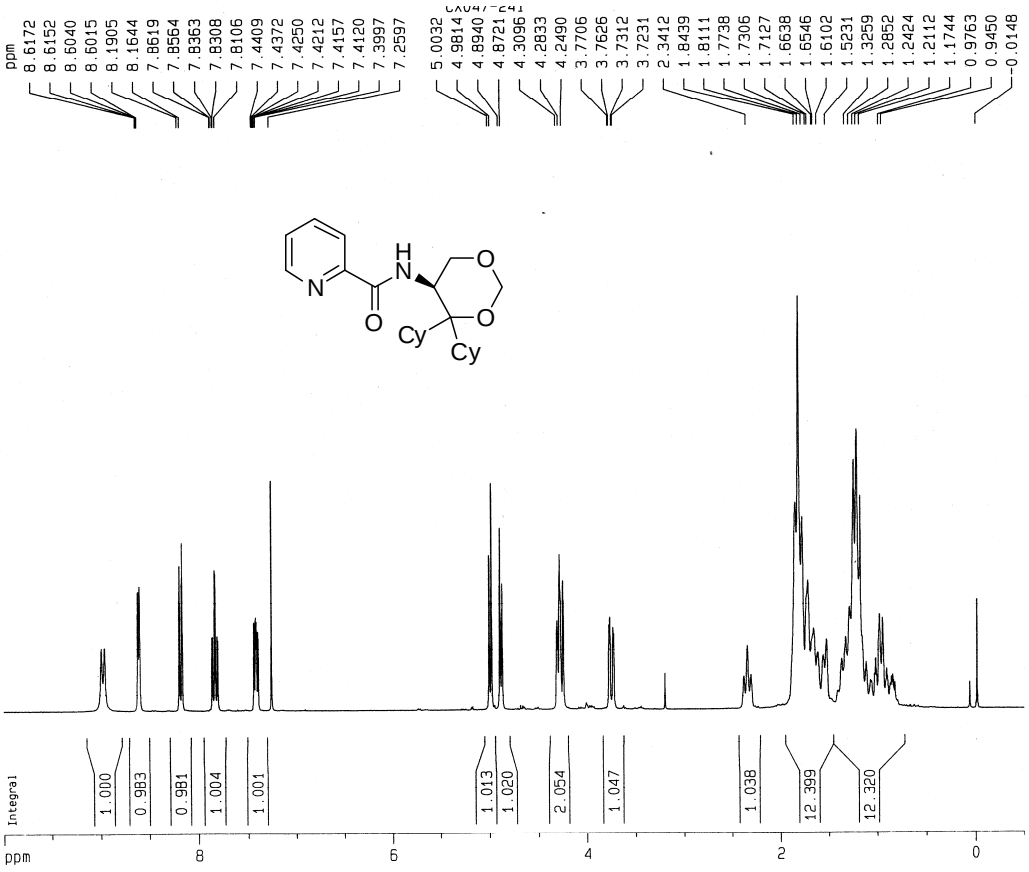
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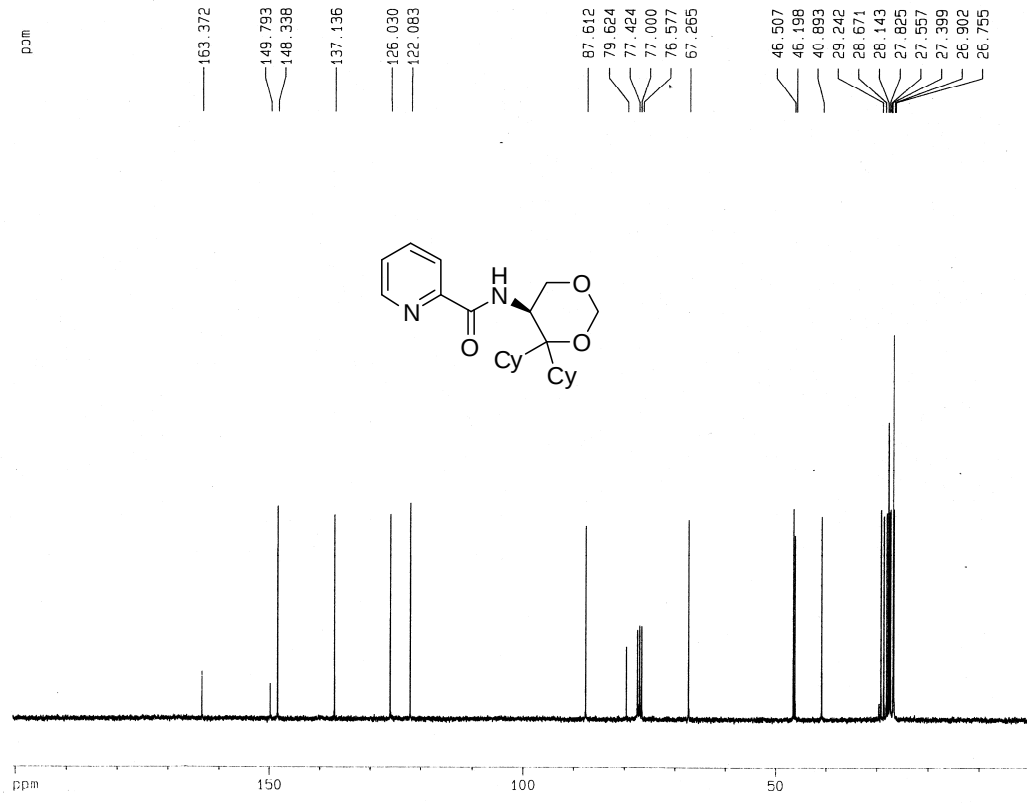
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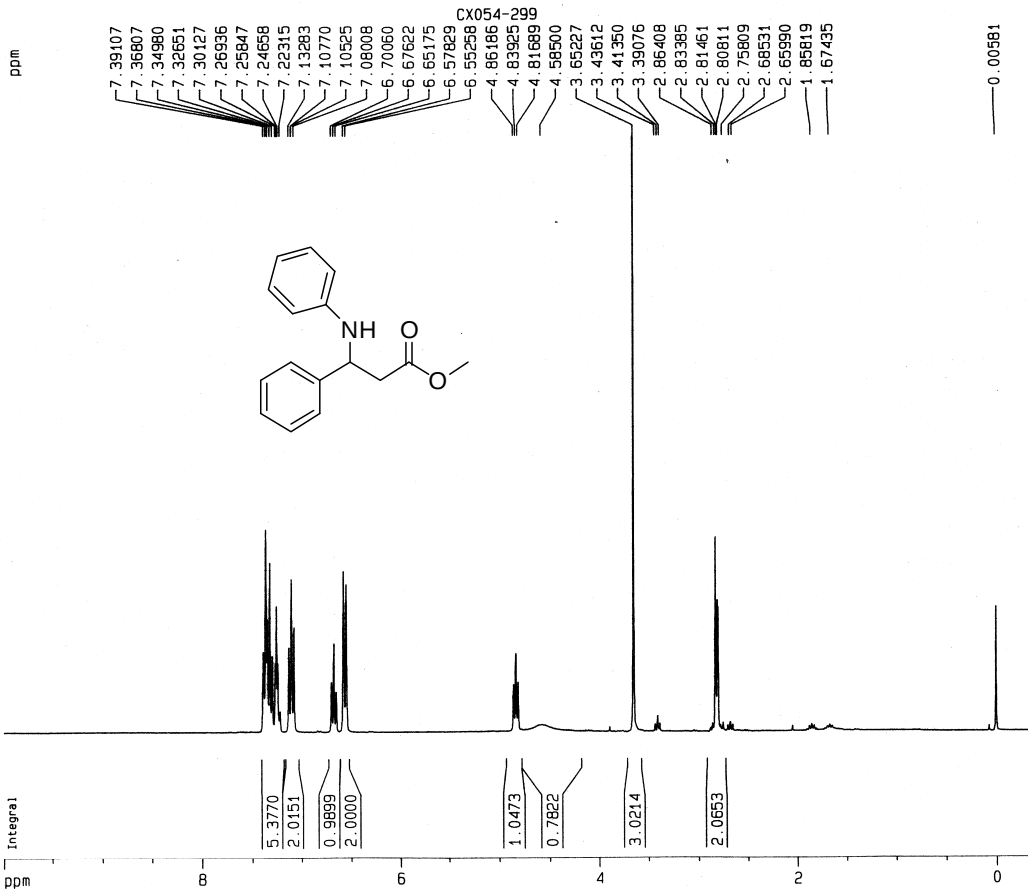


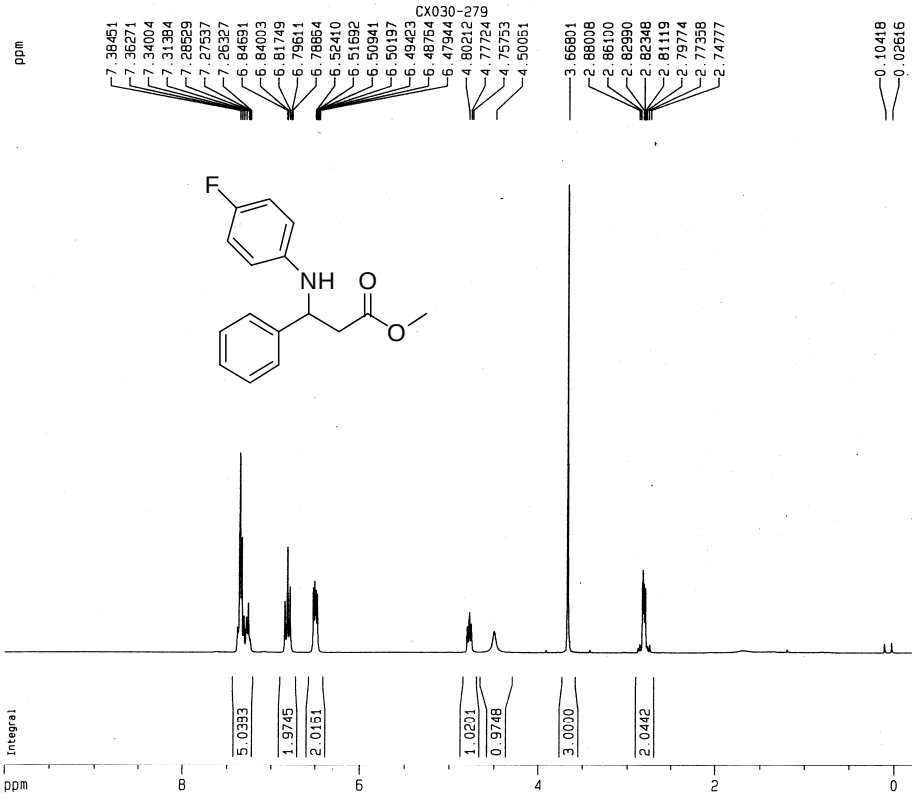

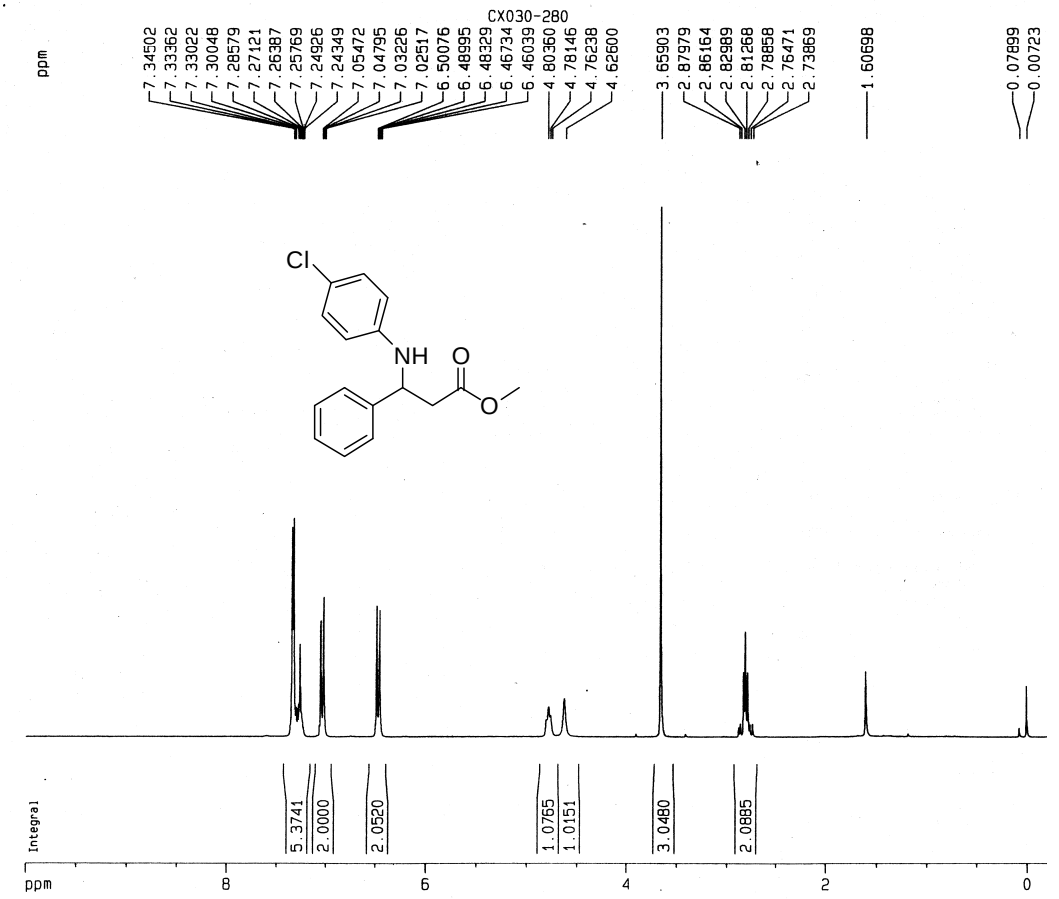
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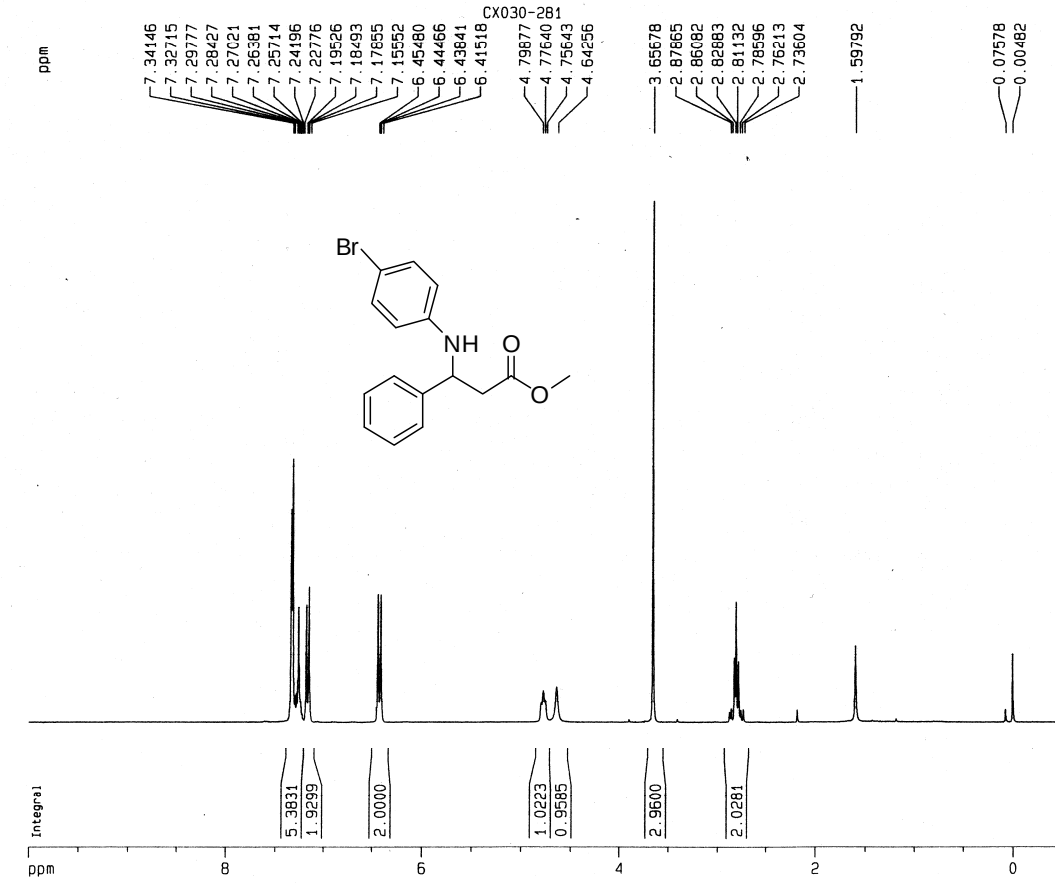
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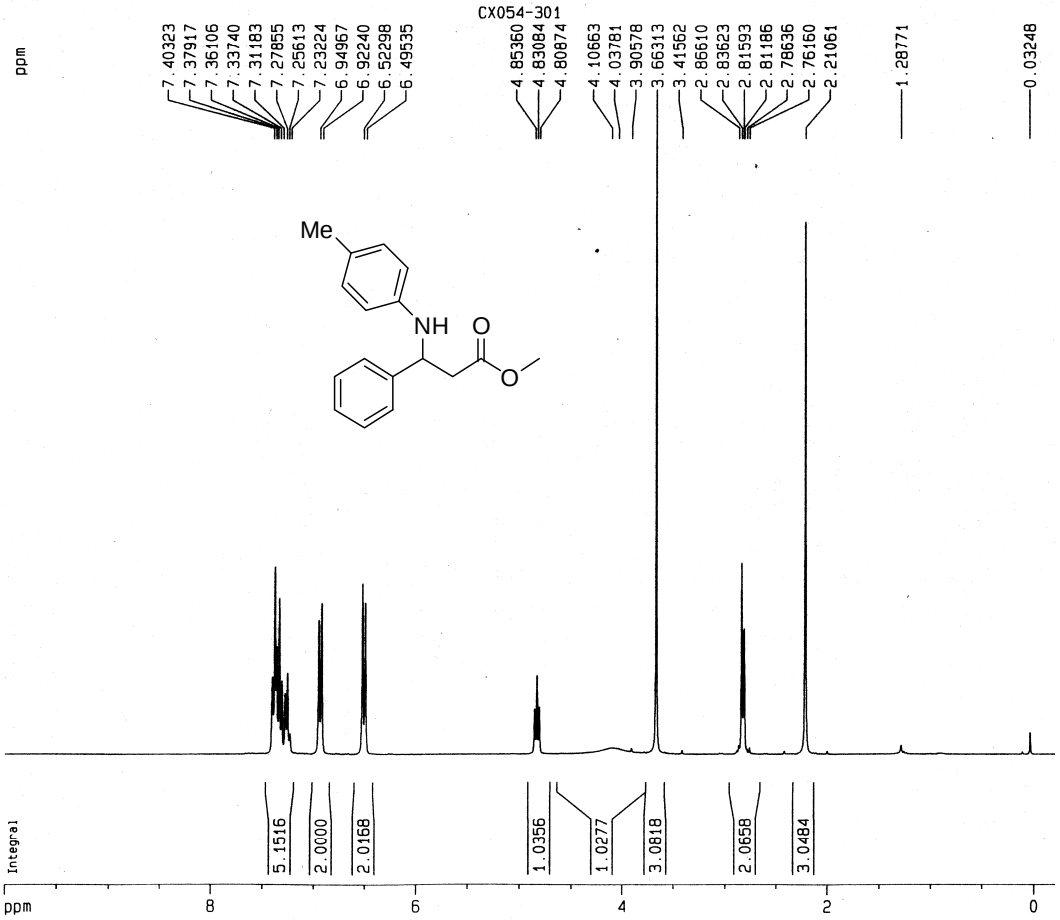
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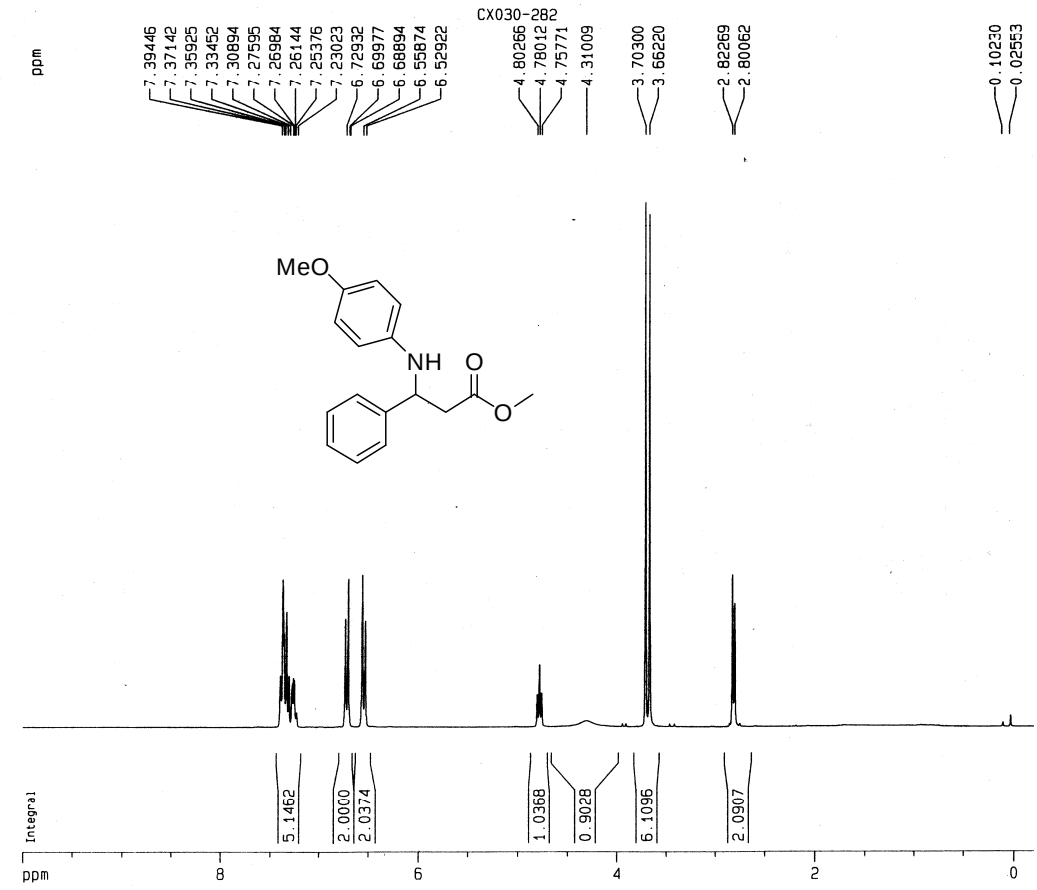
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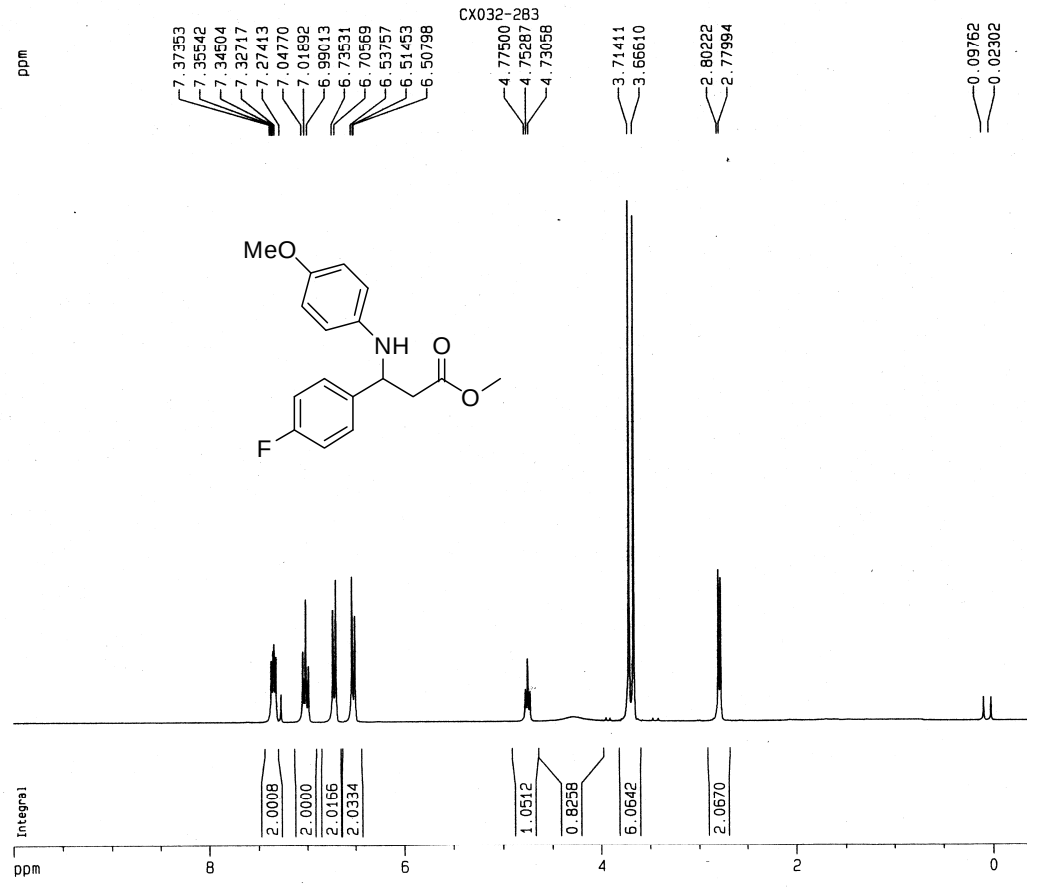
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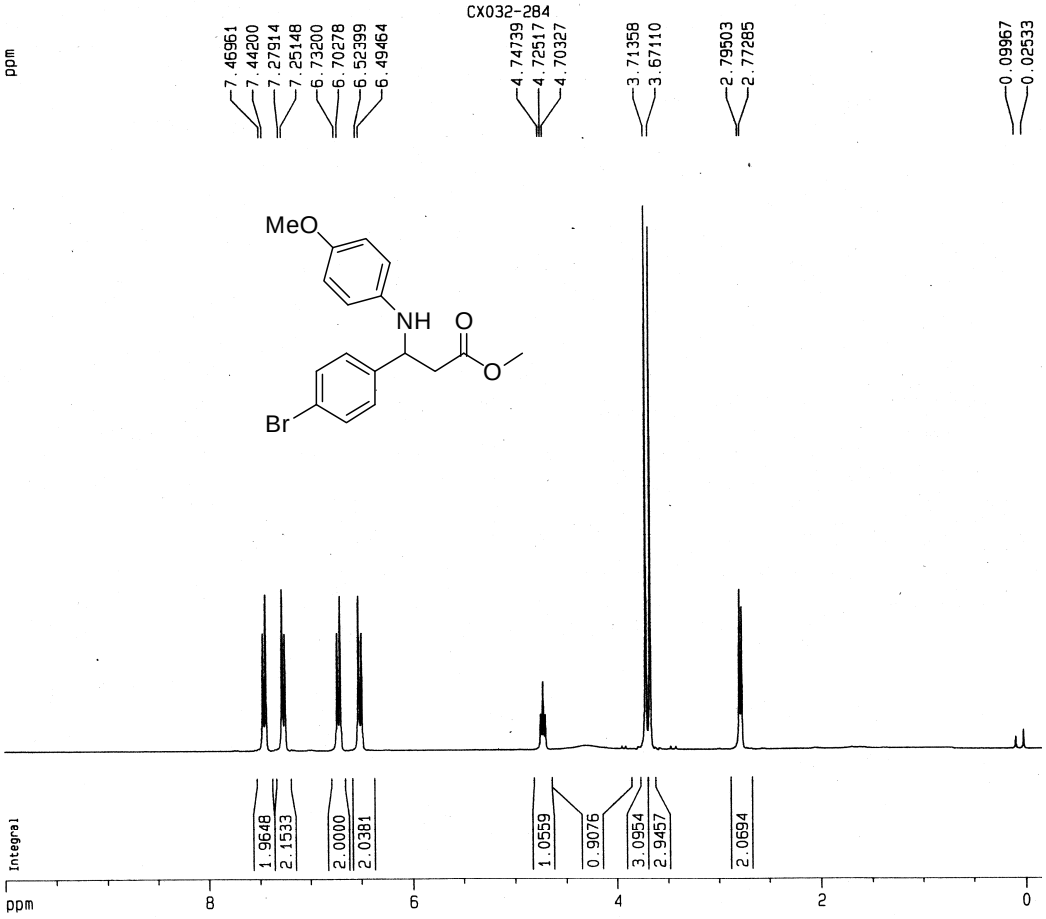
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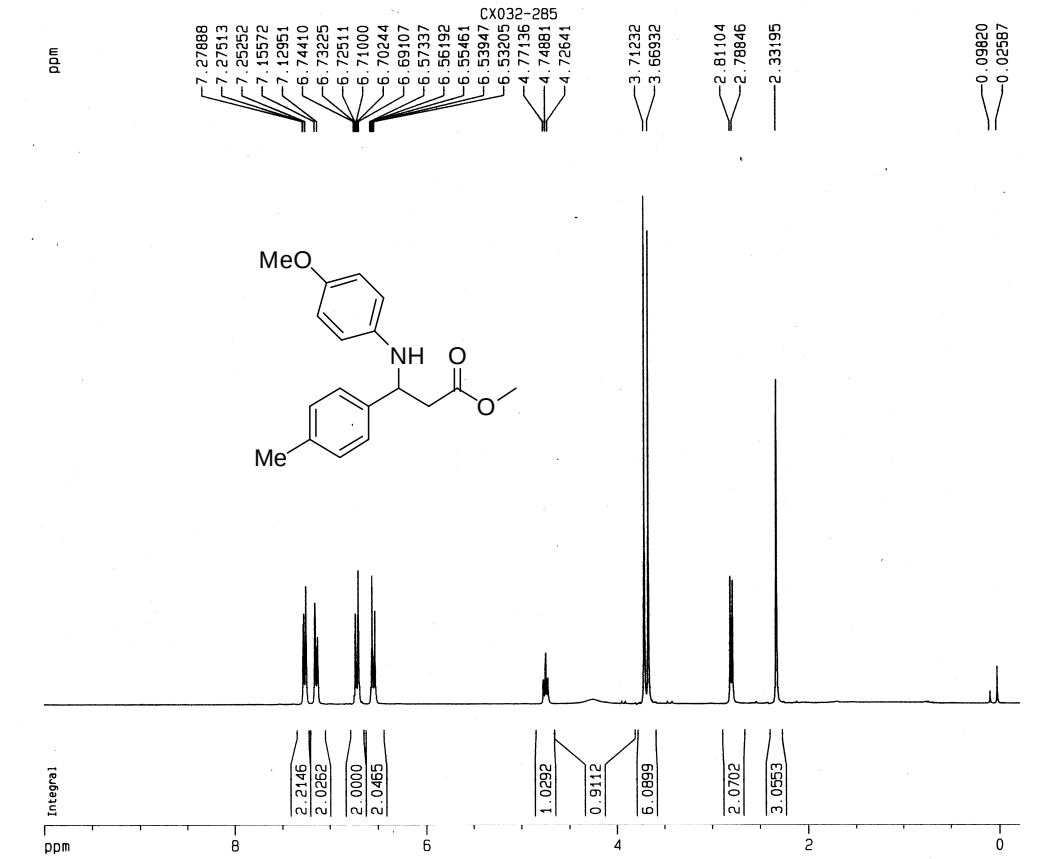
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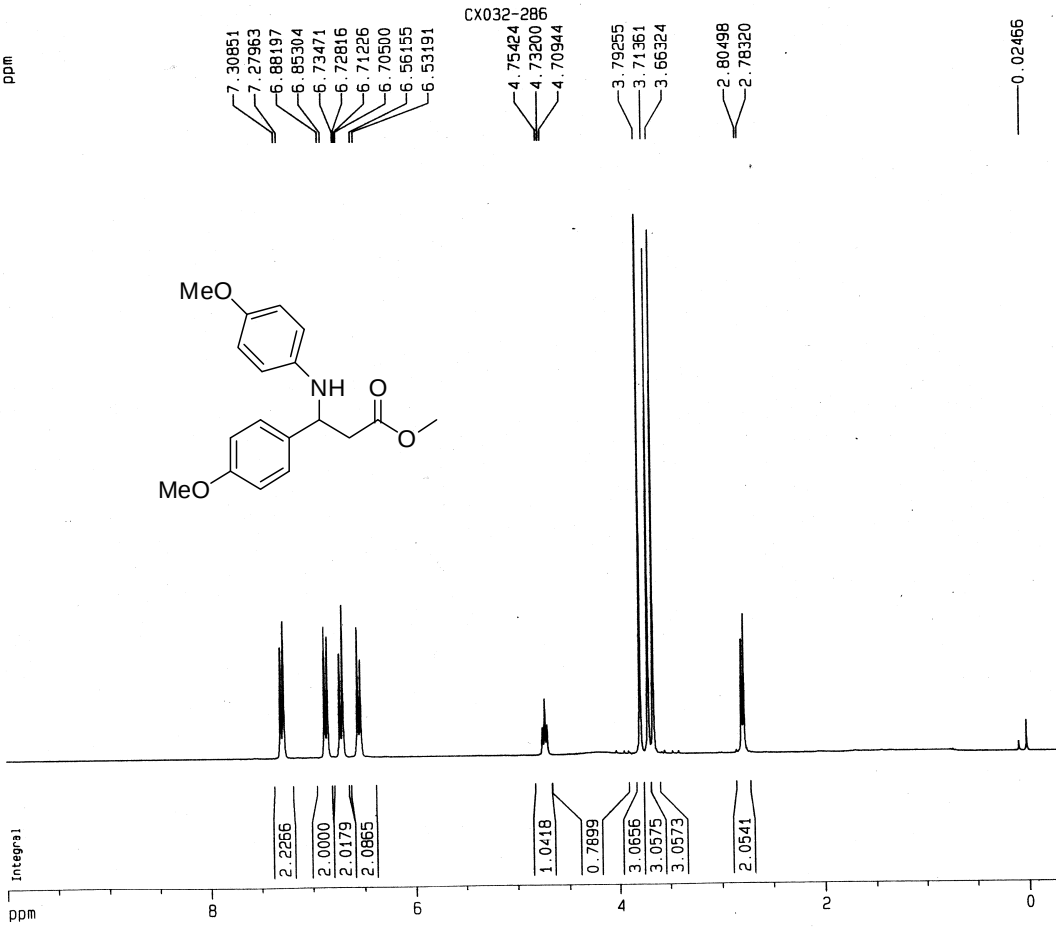
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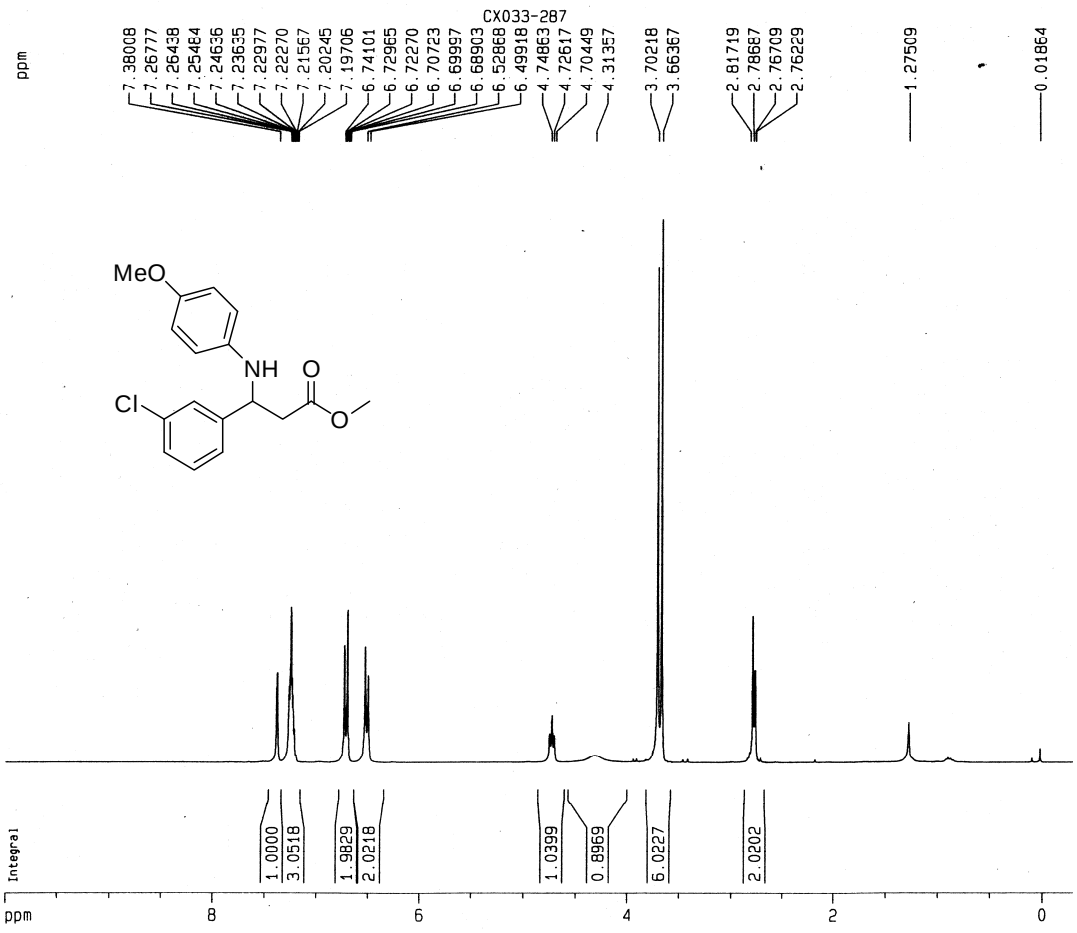
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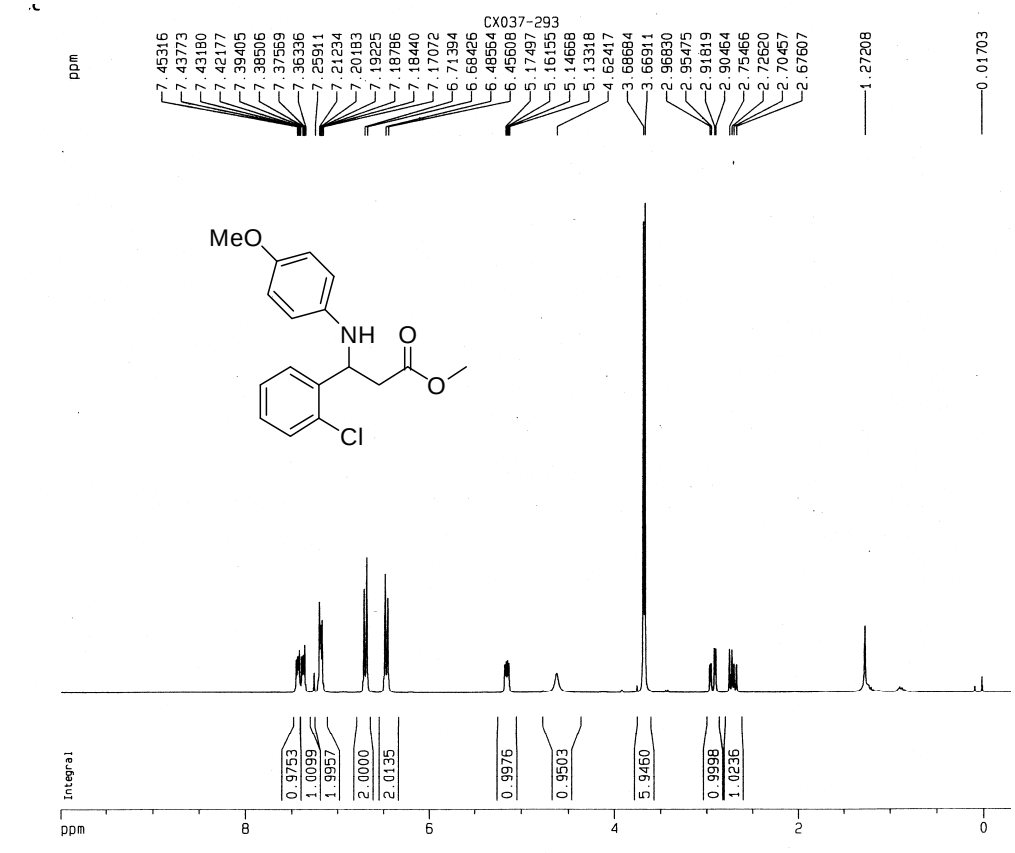
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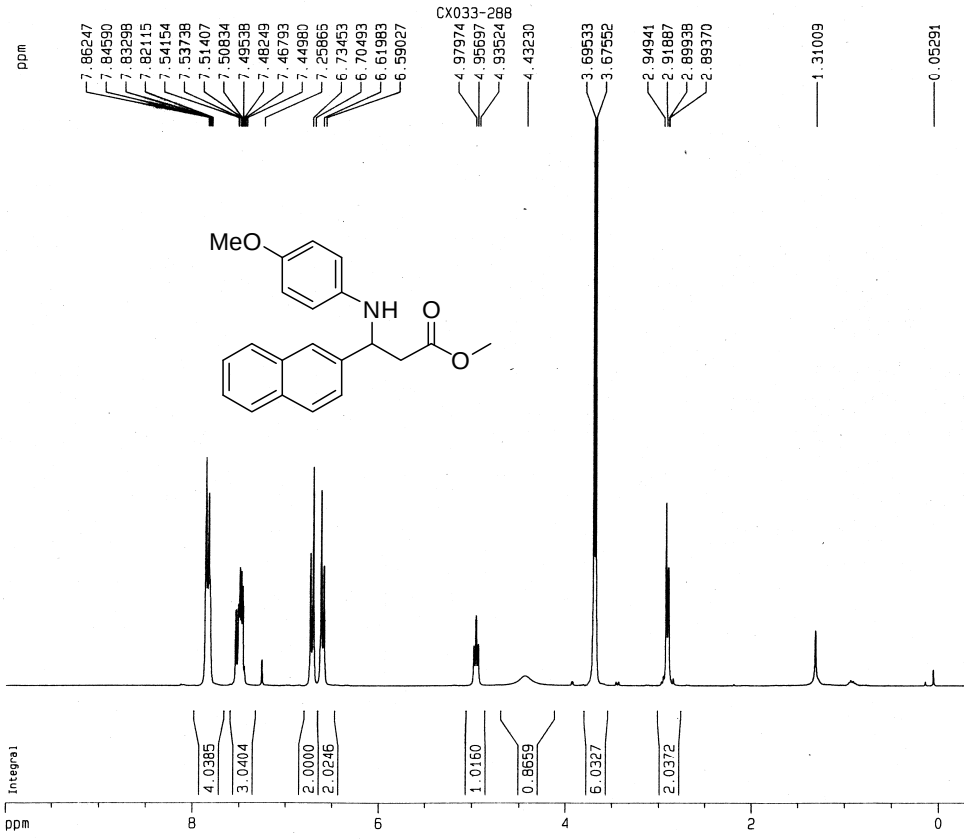
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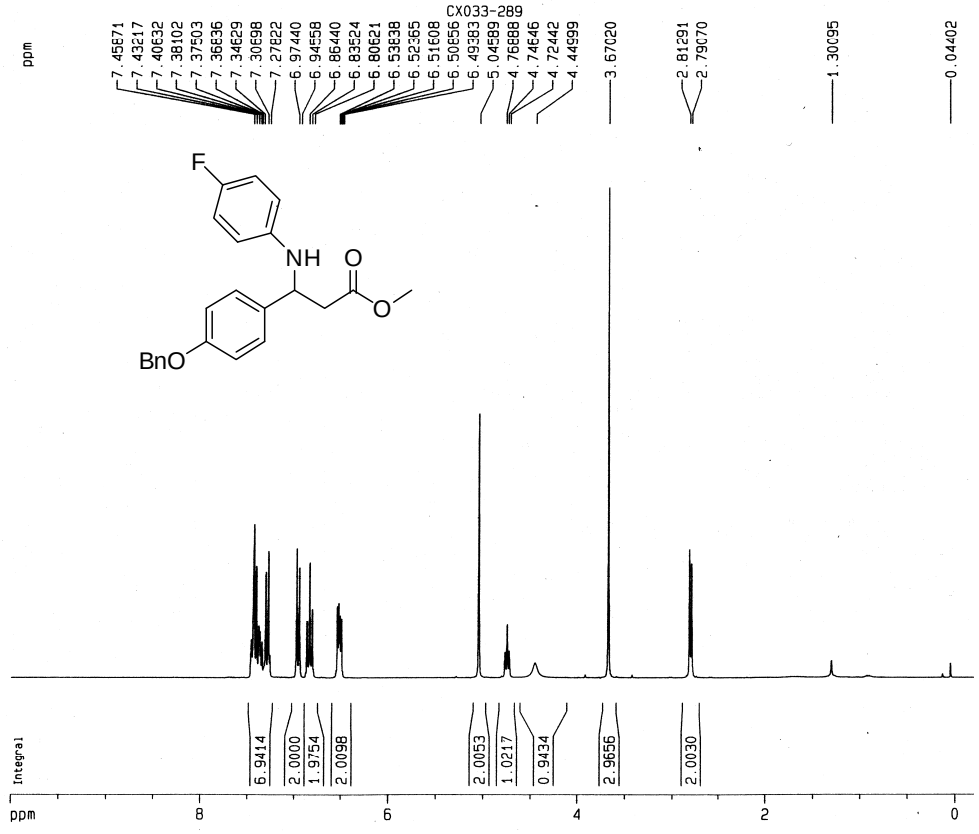
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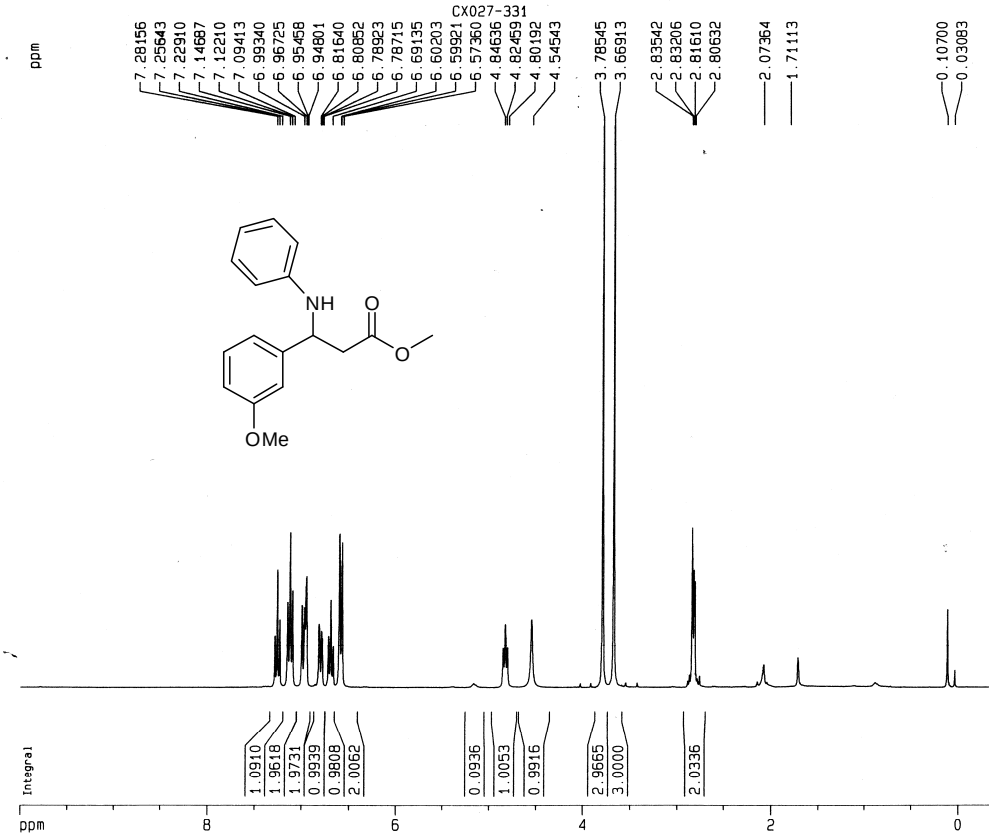


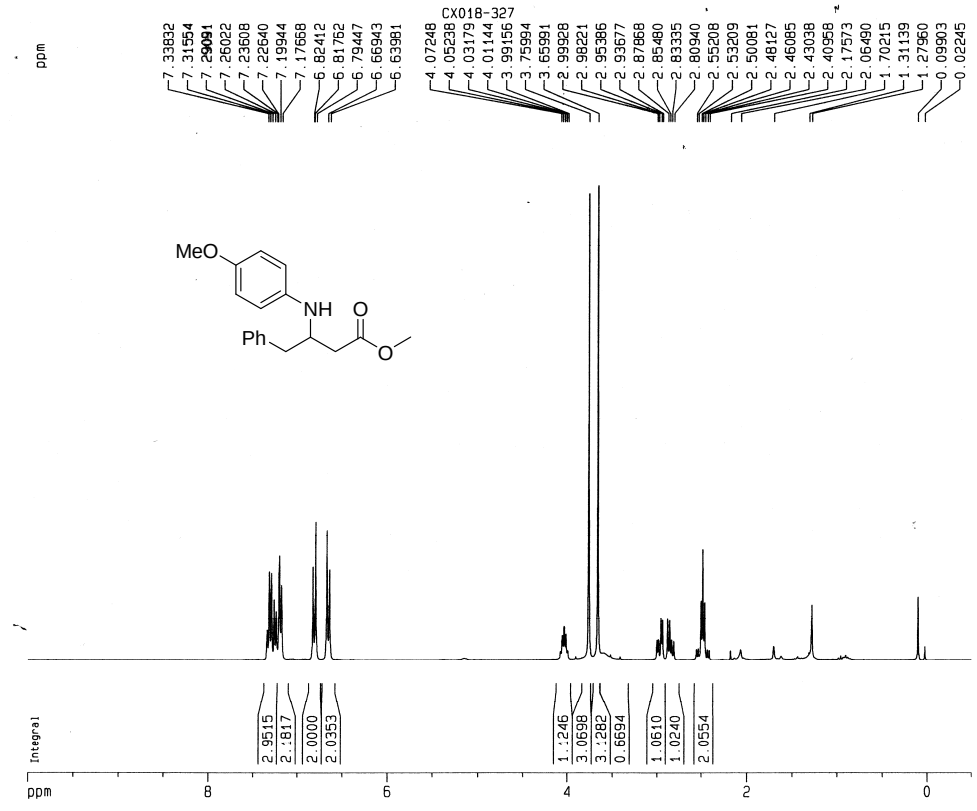

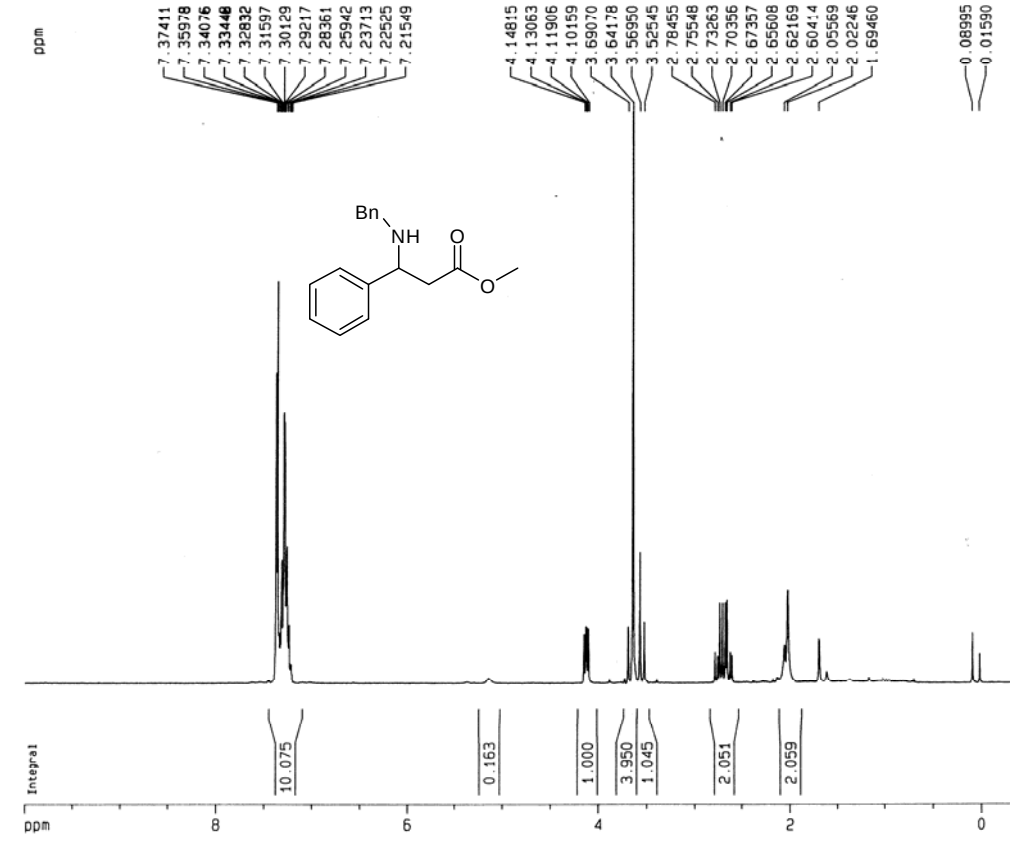
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7.22525
7.21549
4.14815
4.13063
4.11906
4.10159
3.69070
3.64178
3.56950
3.52545
2.78455
2.75548
2.73263
2.70356
2.67357
2.65608
2.62169
2.60414
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2.02246
1.69460
0.08995
0.01590
Bn
NH
O
O
Integral
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2.059
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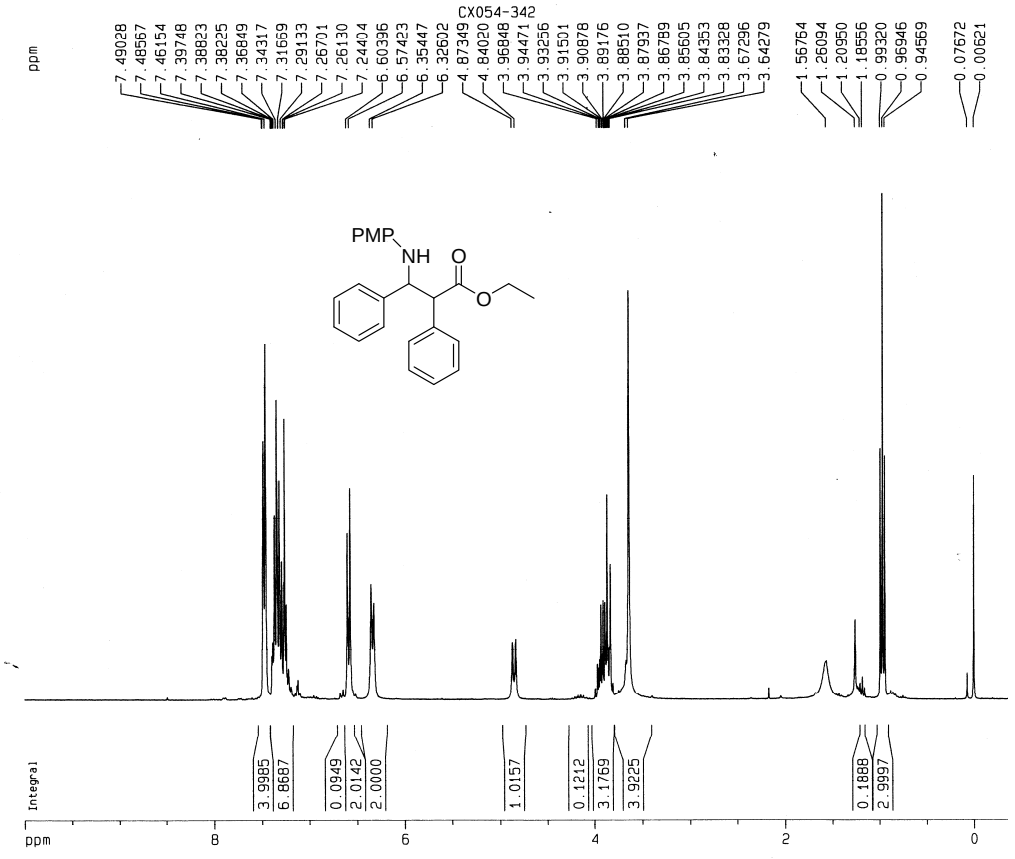
2
0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7.26701
7.26130
7.24404
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6.35447
6.32602
4.87349
4.84020
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3.87937
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3.85605
3.84353
3.83328
3.67296
3.64279
1.56764
1.26094
1.20950
1.18556
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PMP
NH
O
O
Integral
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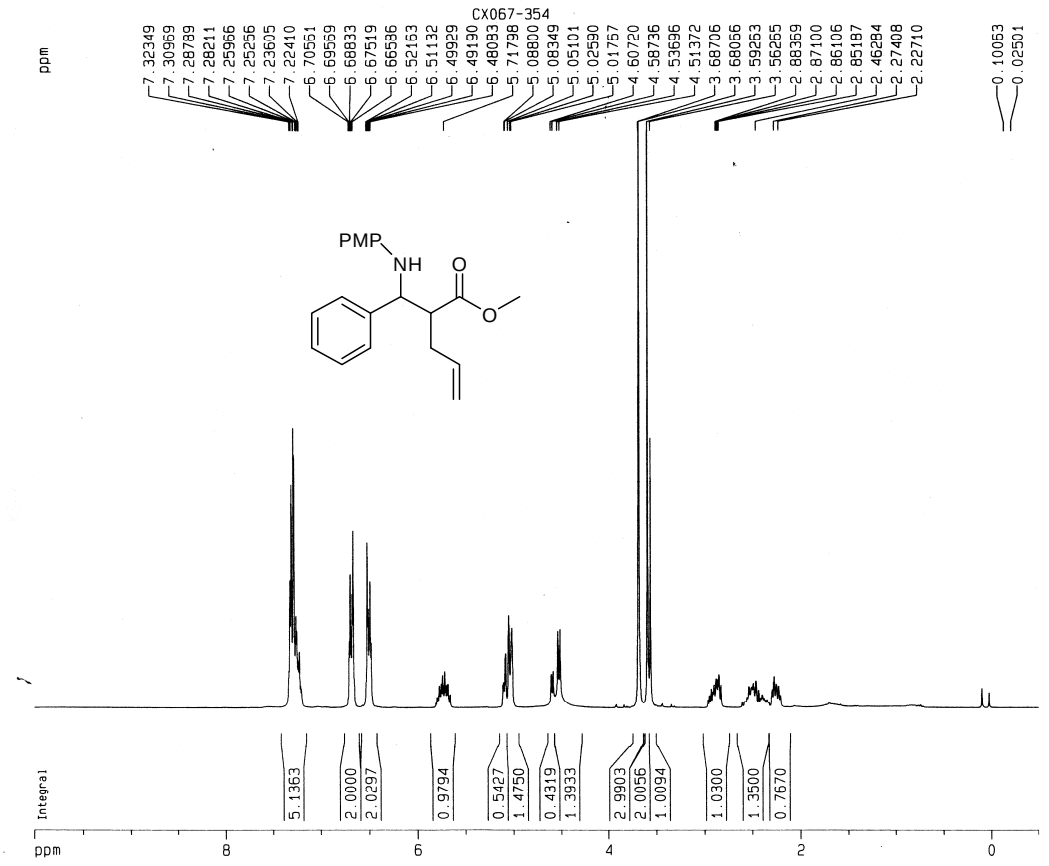
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6.67519
6.66536
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6.49929
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6.48093
5.71796
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5.02590
5.01757
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4.53696
4.51372
3.68706
3.68056
3.59253
3.56265
2.88359
2.87100
2.86106
2.85187
2.46284
2.27408
2.22710
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0.02501
PMP
NH
O
O
Integral
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2
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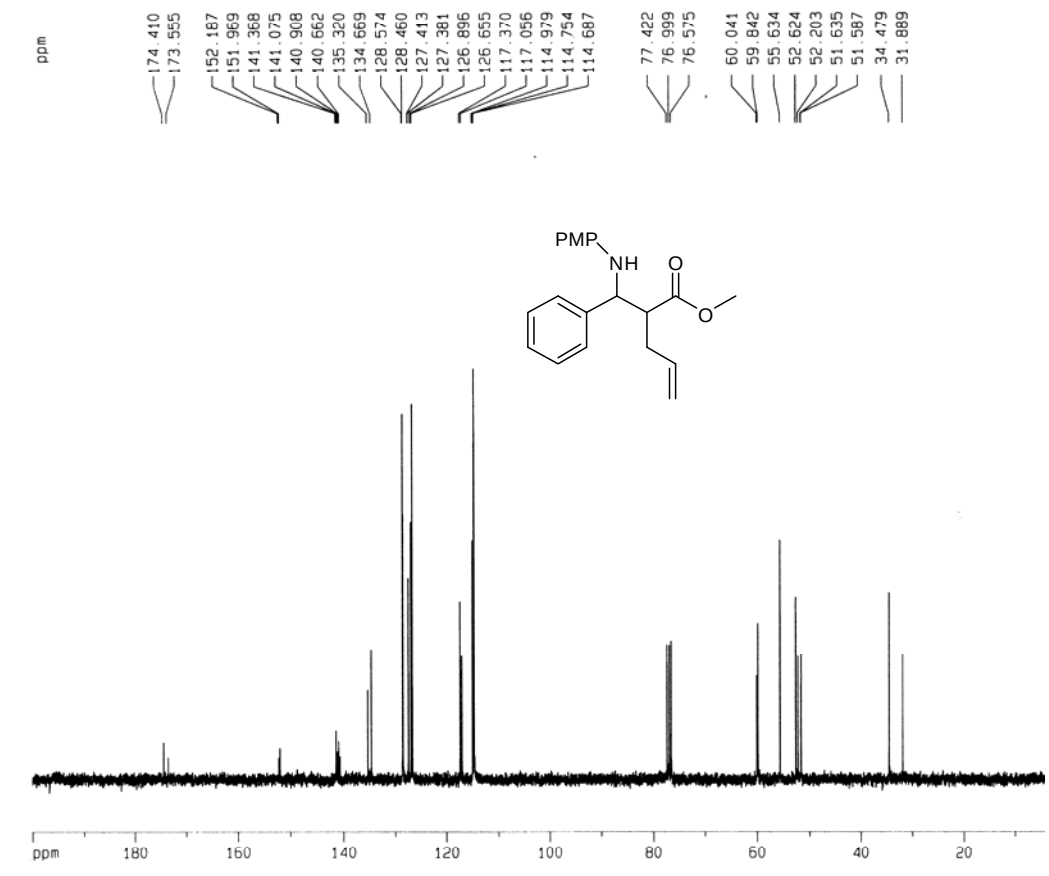
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126.896
126.655
117.370
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114.979
114.754
114.687
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76.999
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60.041
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55.634
52.624
52.203
51.635
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PMP
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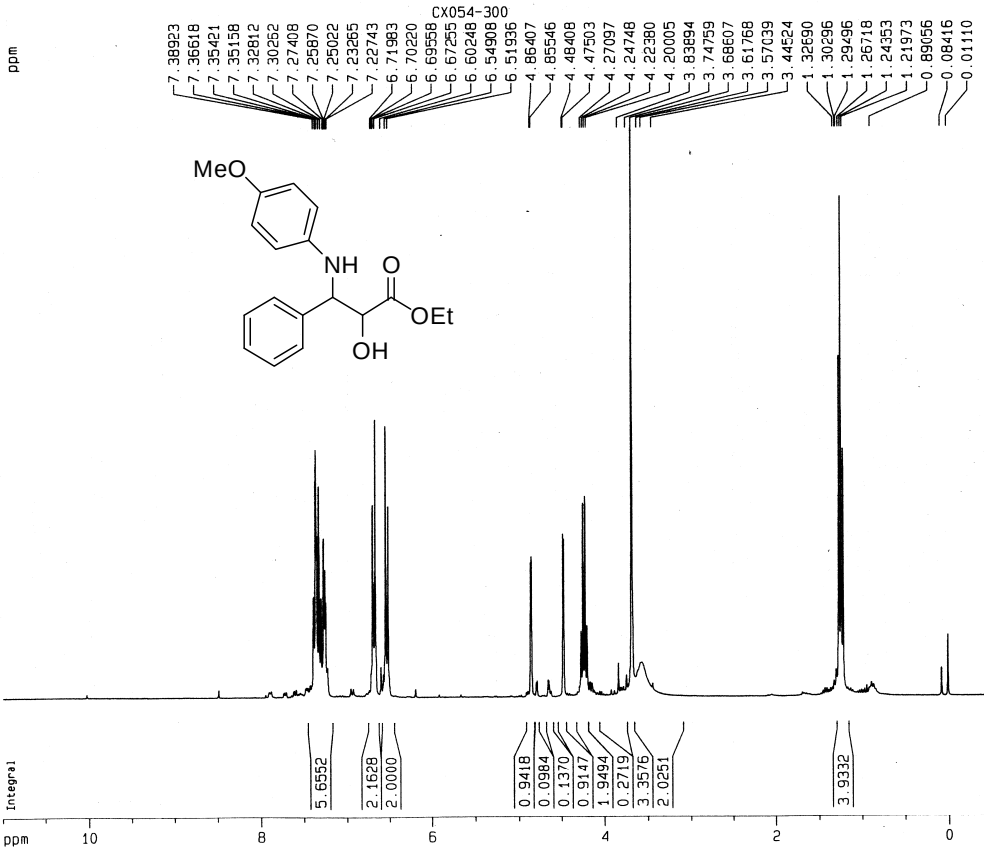
80
60
40
20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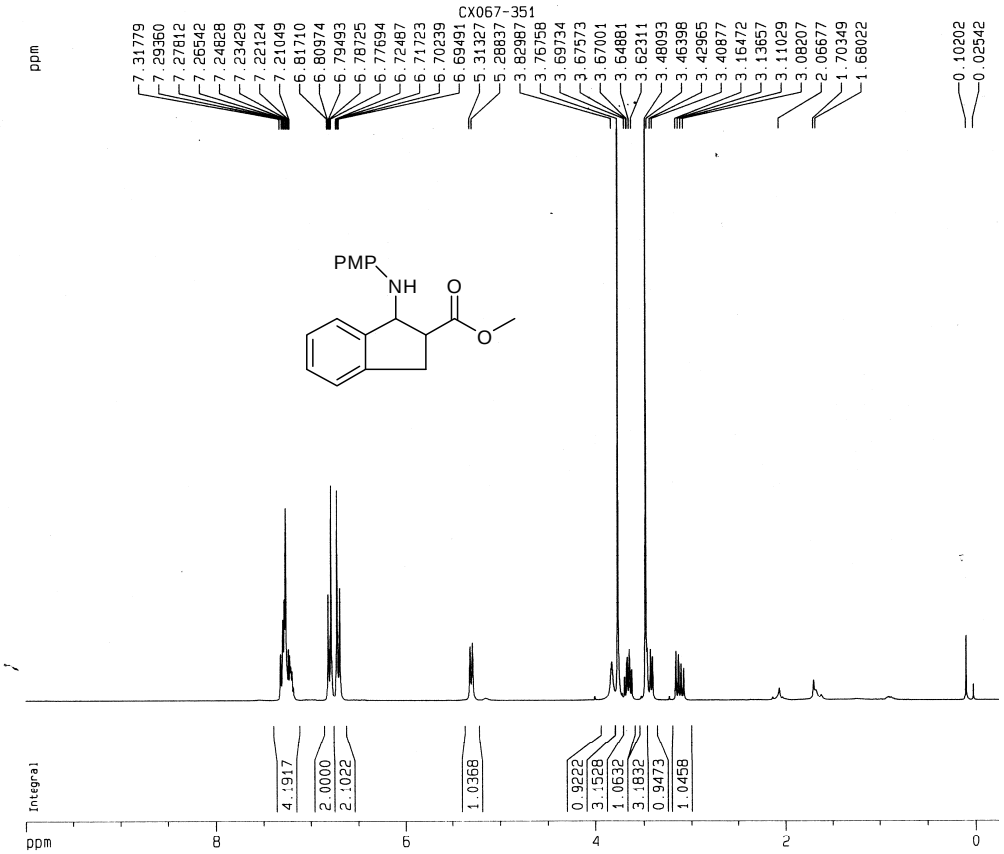
ppm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PMP
NH
O
O
Integral
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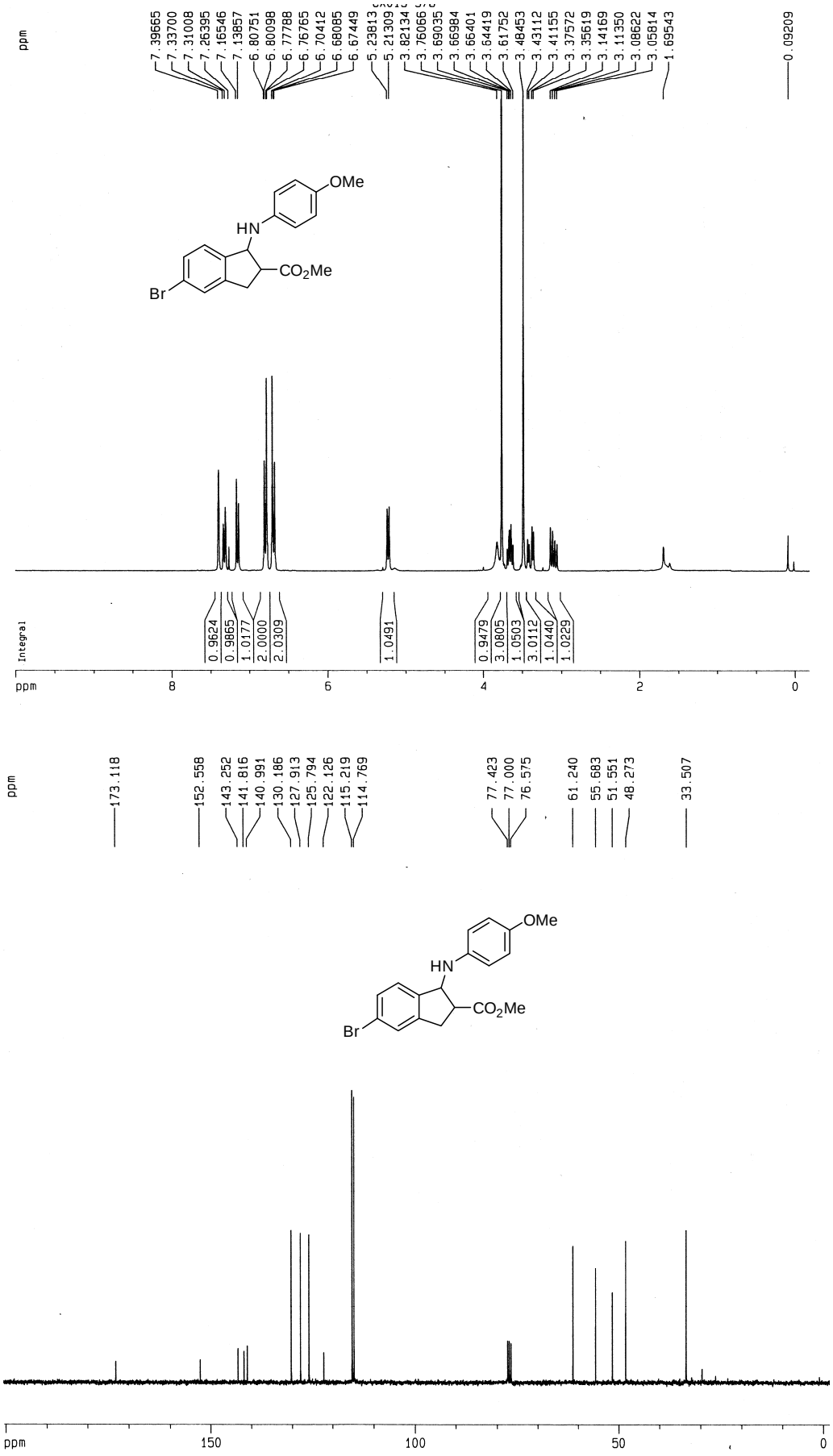
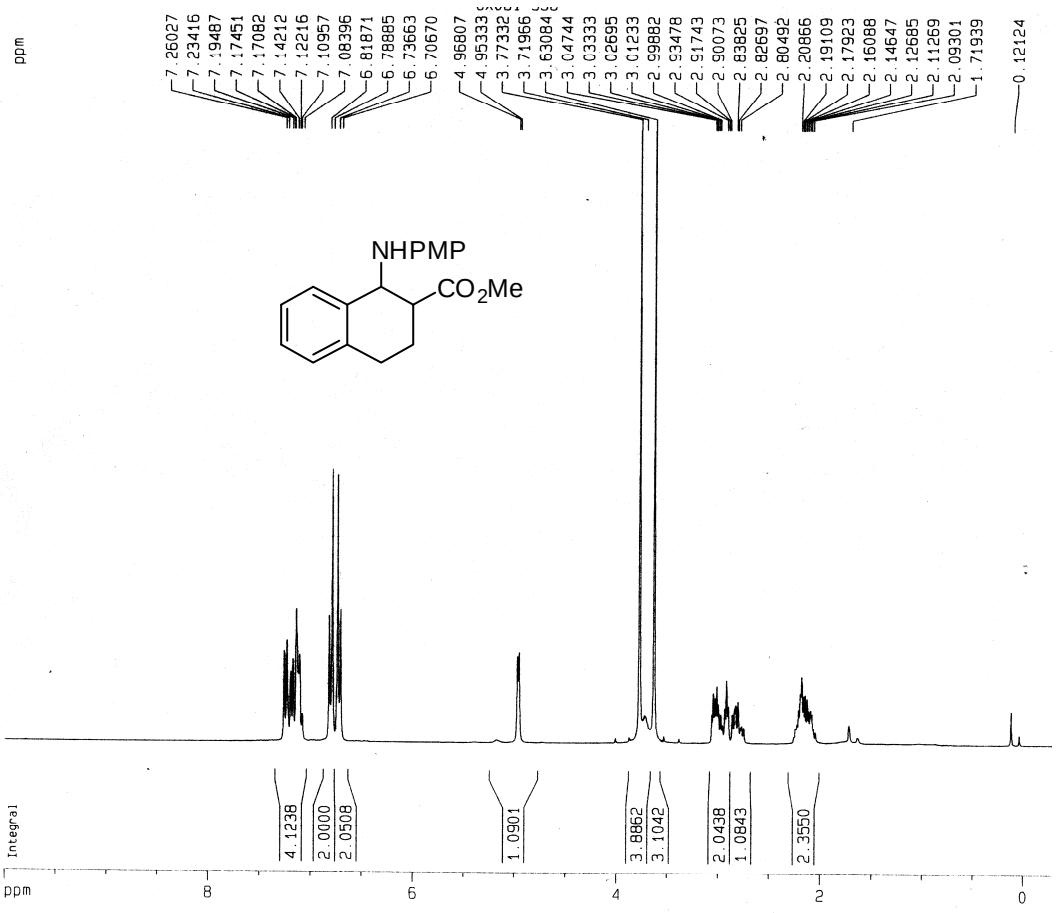
ppm

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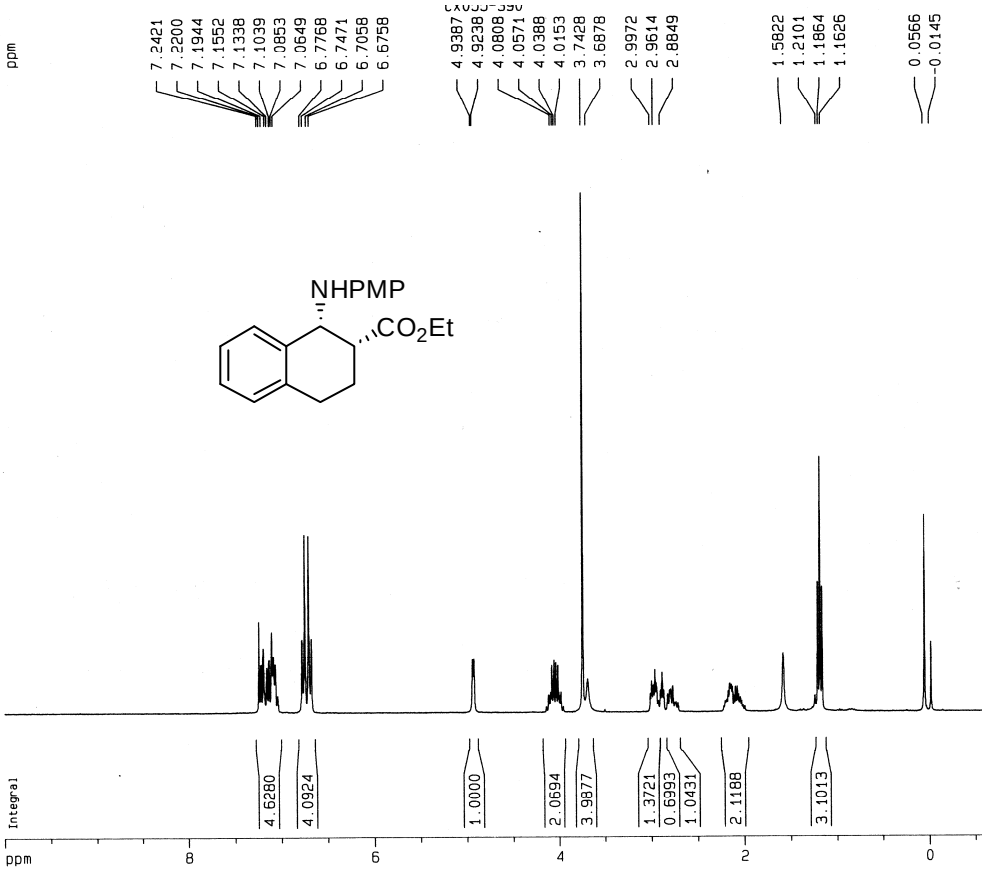
1.0843
2.3550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CO2Et
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Integral
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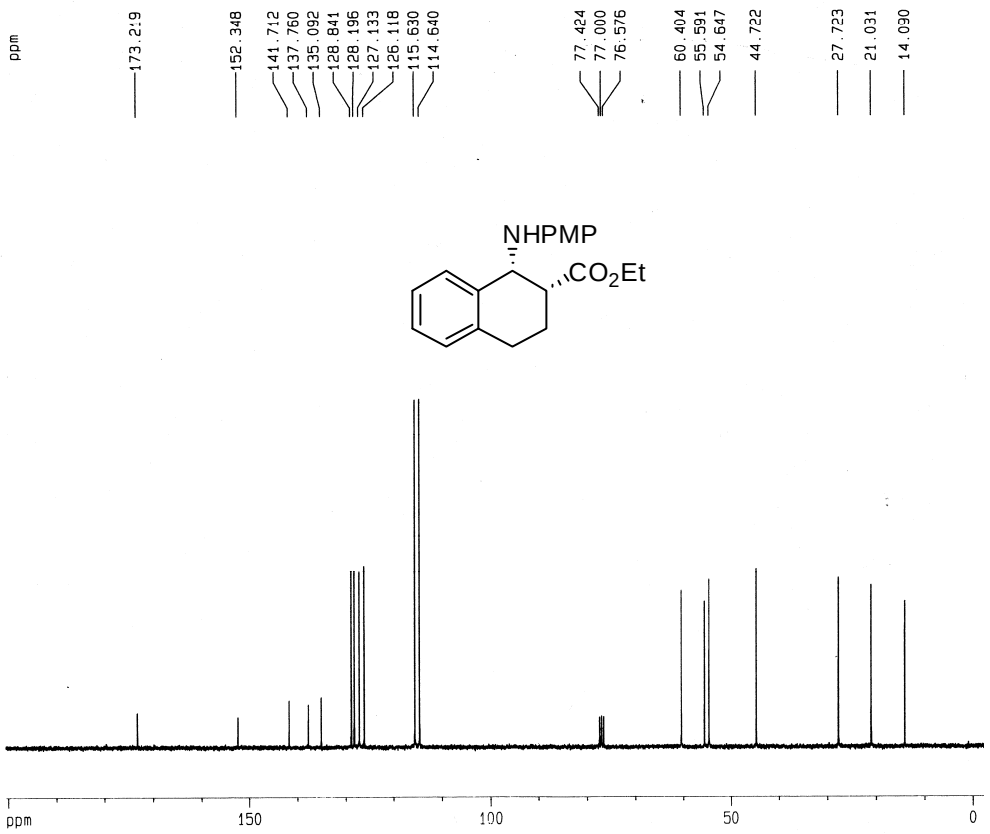
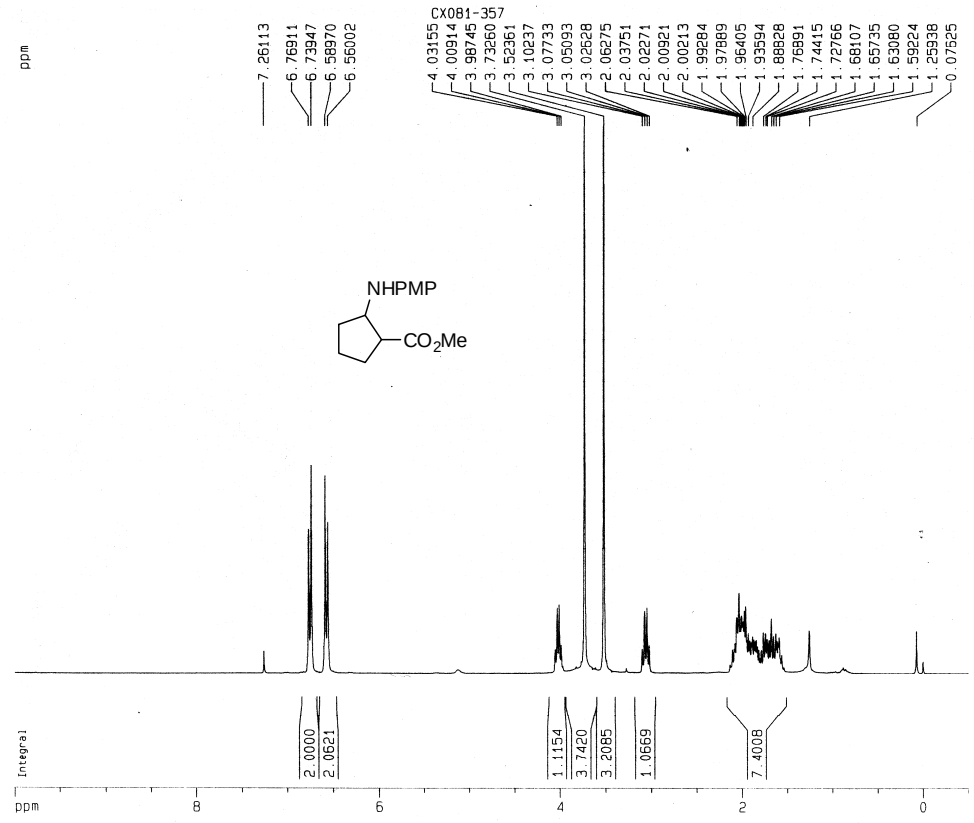
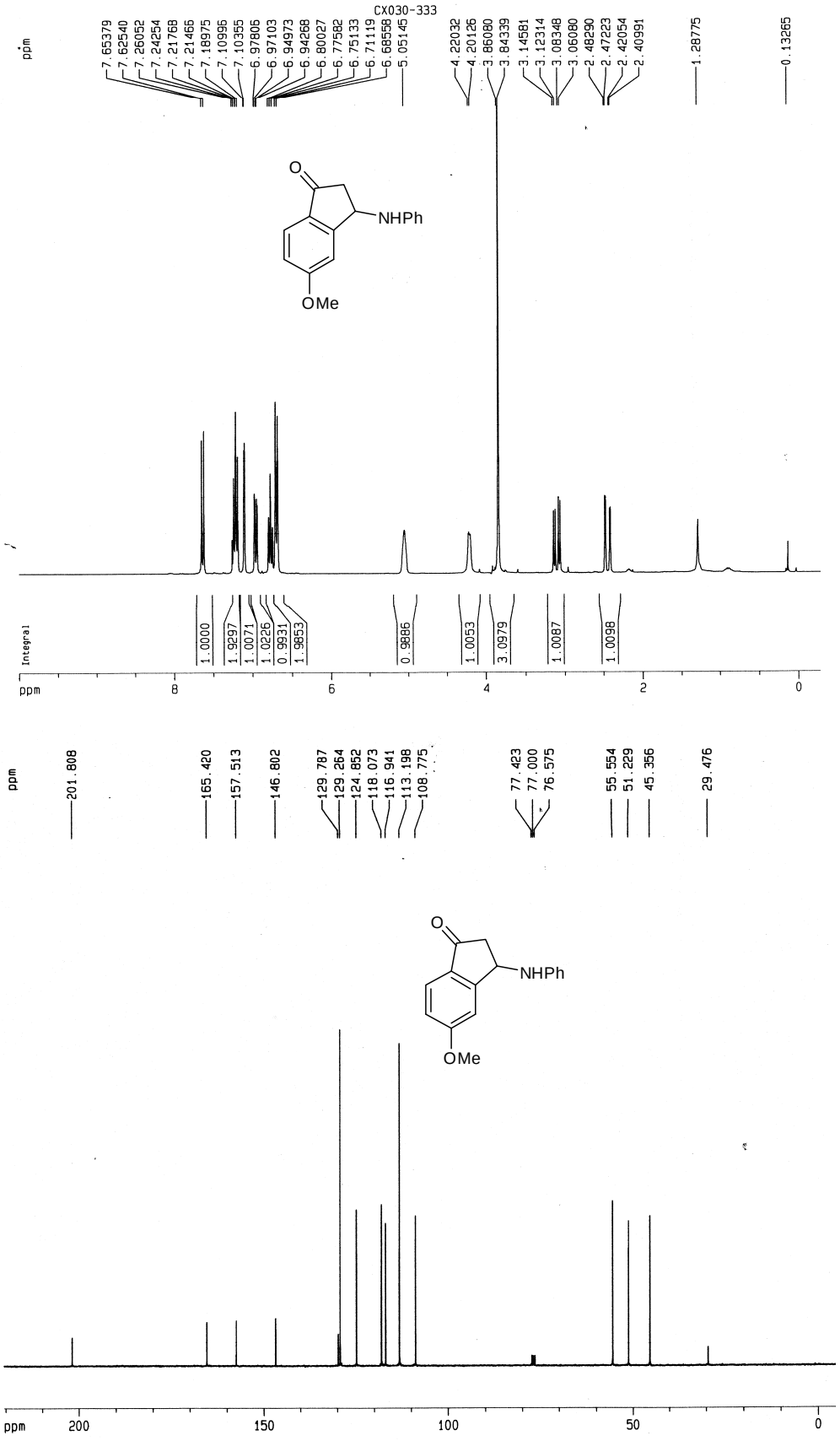
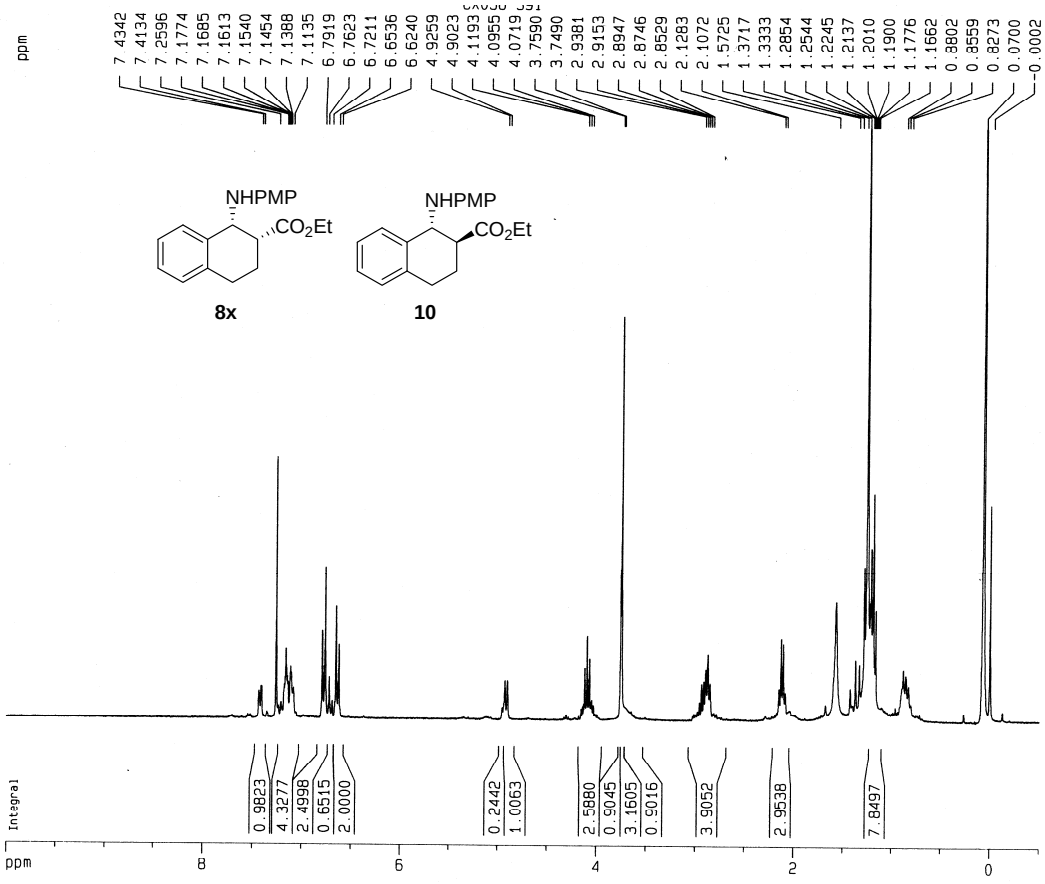
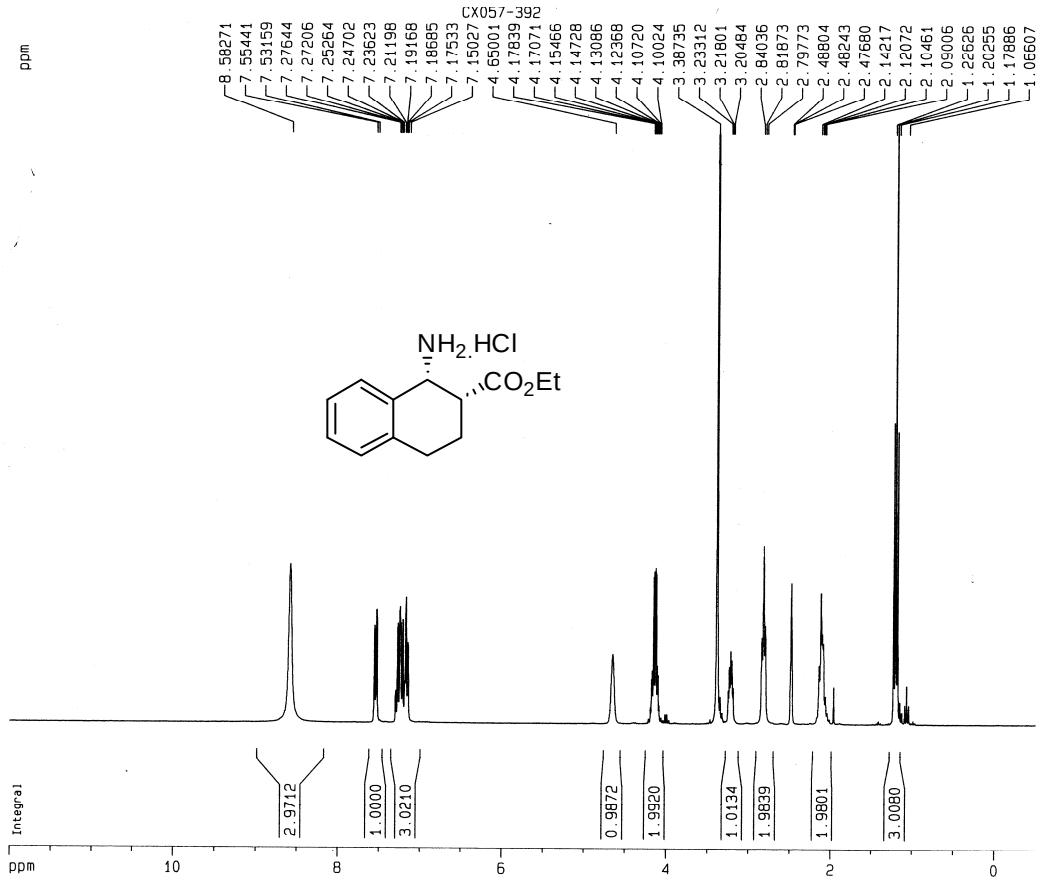
3.1013

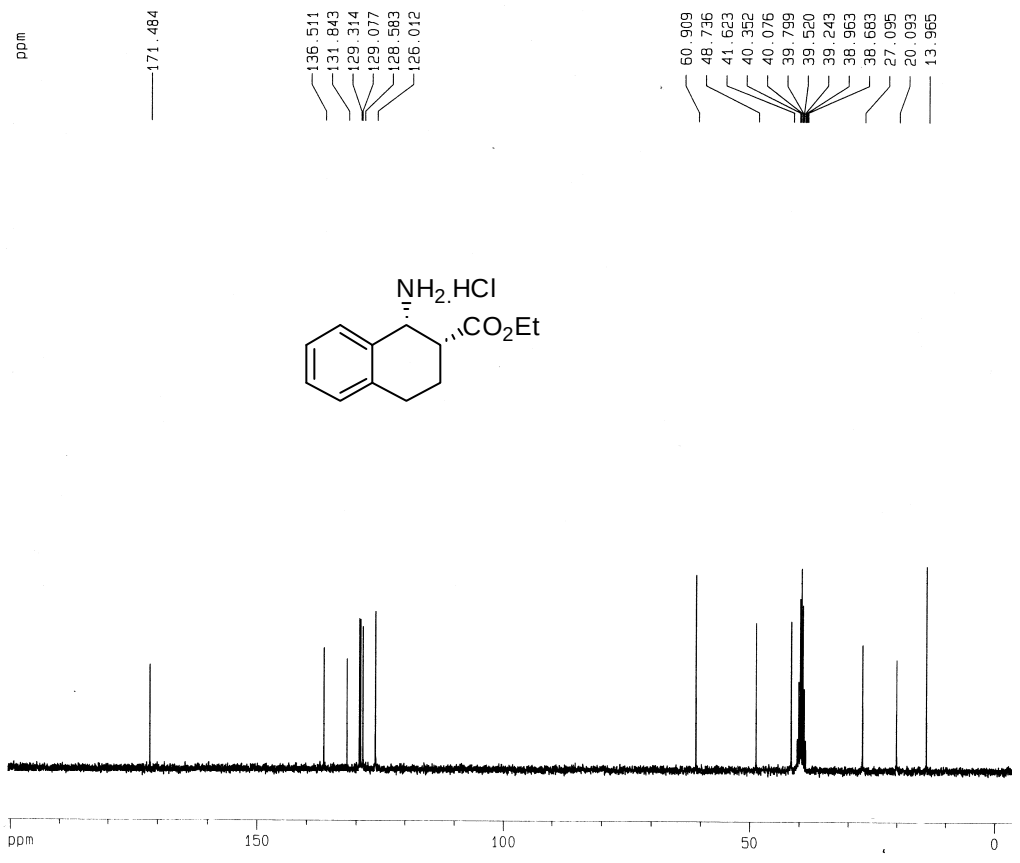


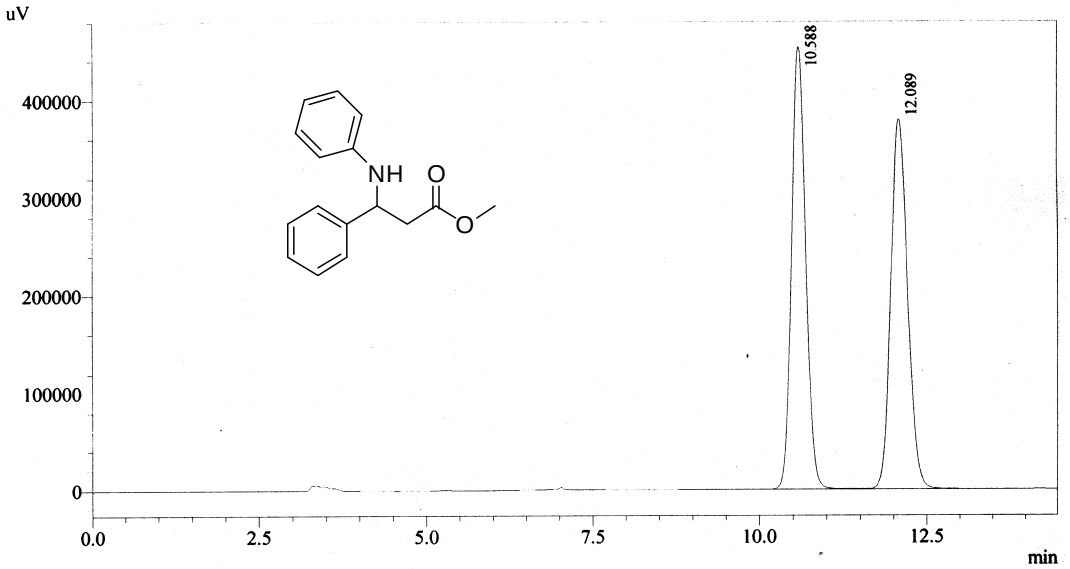






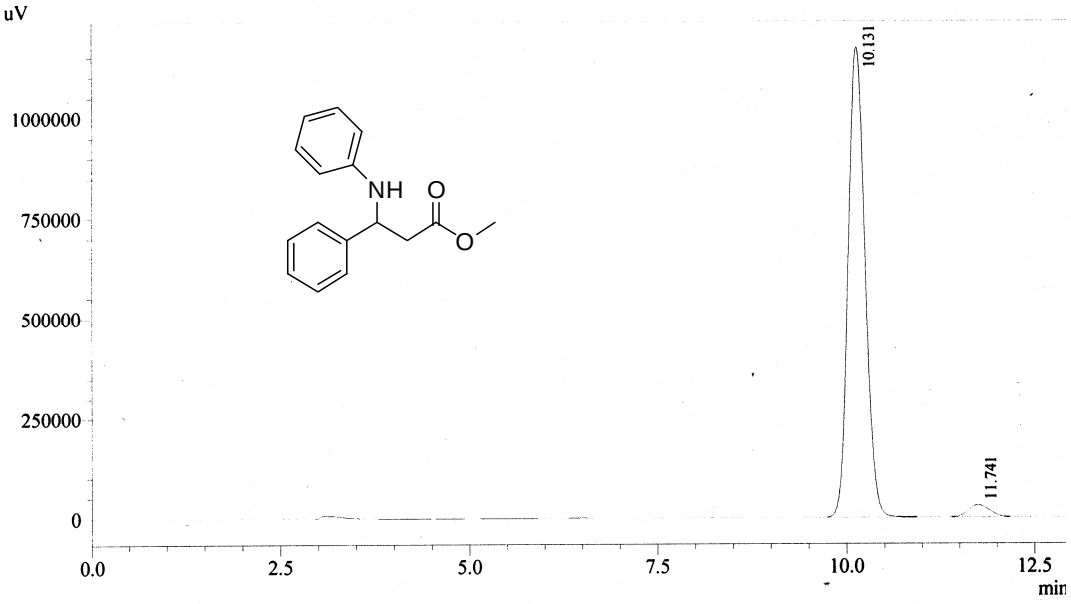
# HPLC spectra




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

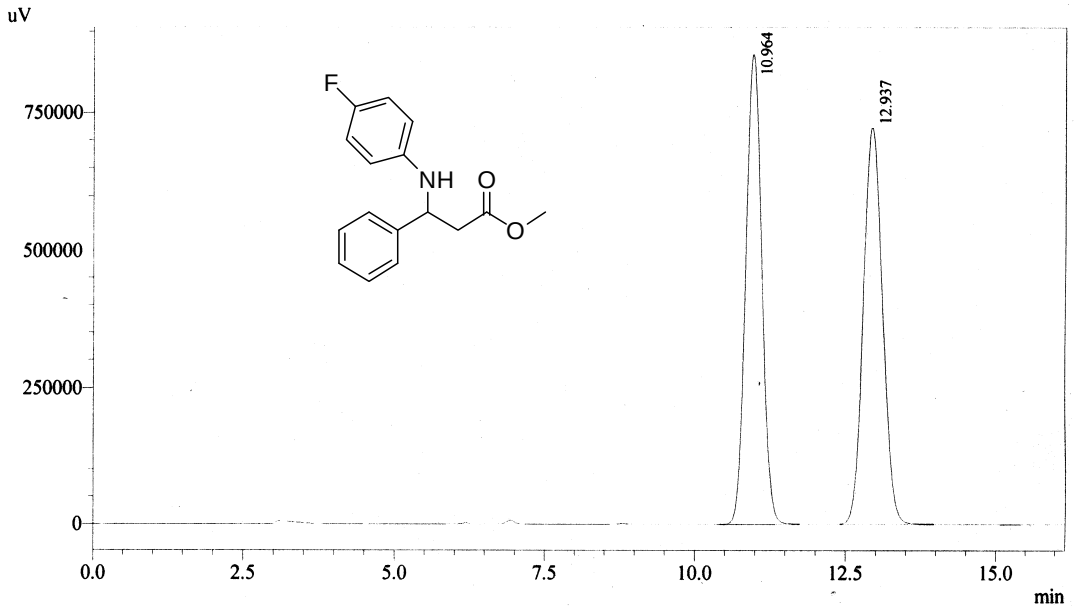
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.588 | 6636691 | 454078 | 49.966 | 54.533 |
| 2 | 12.089 | 6645783 | 378585 | 50.034 | 45.467 |
| Total | | 13282473 | 832663 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

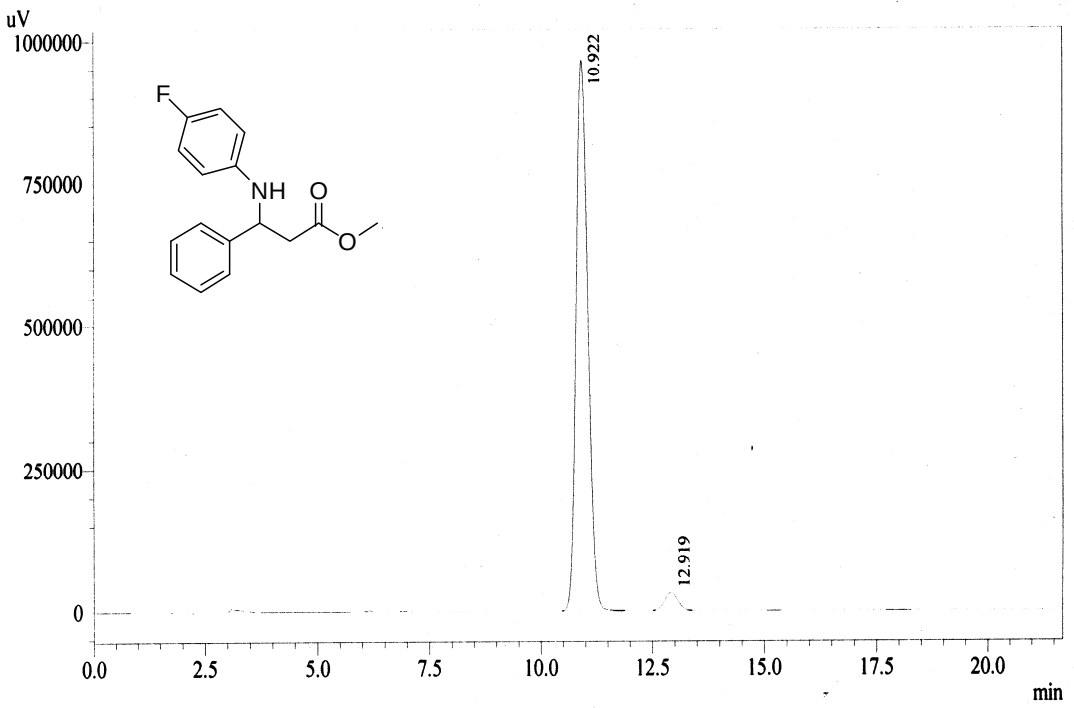
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.131 | 18195109 | 1174666 | 96.756 | 97.483 |
| 2 | 11.741 | 610039 | 30333 | 3.244 | 2.517 |
| Total | | 18805148 | 1204998 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

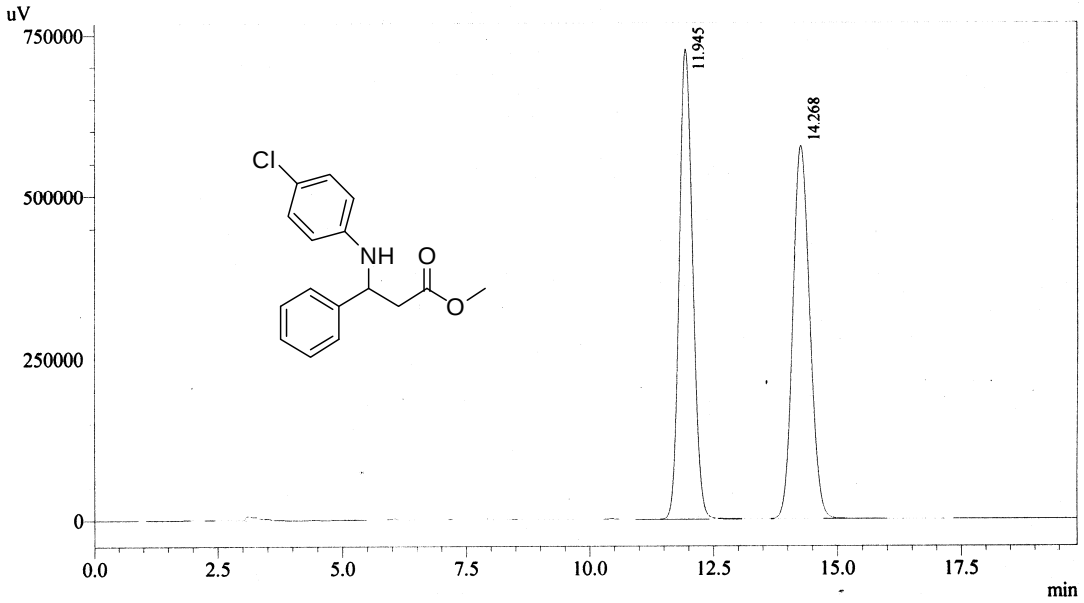
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.964 | 15900610 | 859347 | 49.709 | 54.329 |
| 2 | 12.937 | 16086947 | 722389 | 50.291 | 45.671 |
| Total | | 31987557 | 1581736 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

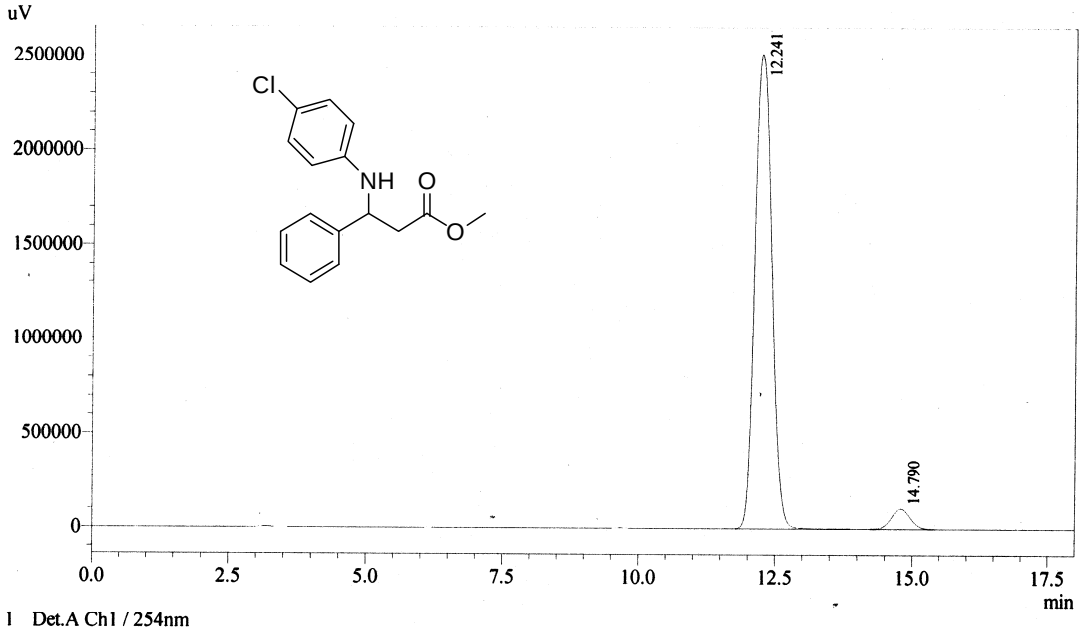
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.922 | 17690920 | 964645 | 96.402 | 96.829 |
| 2 | 12.919 | 660271 | 31596 | 3.598 | 3.171 |
| Total | | 18351191 | 996241 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

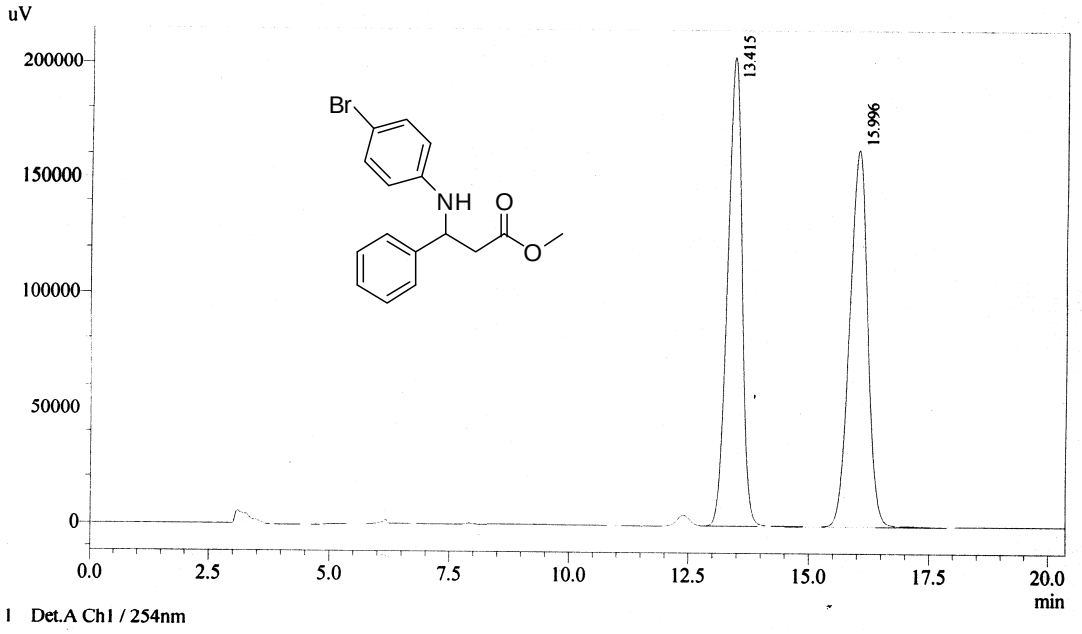
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 11.945 | 13693904 | 726641 | 50.071 | 55.803 |
| 2 | 14.268 | 13654948 | 575504 | 49.929 | 44.197 |
| Total | | 27348852 | 1302145 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

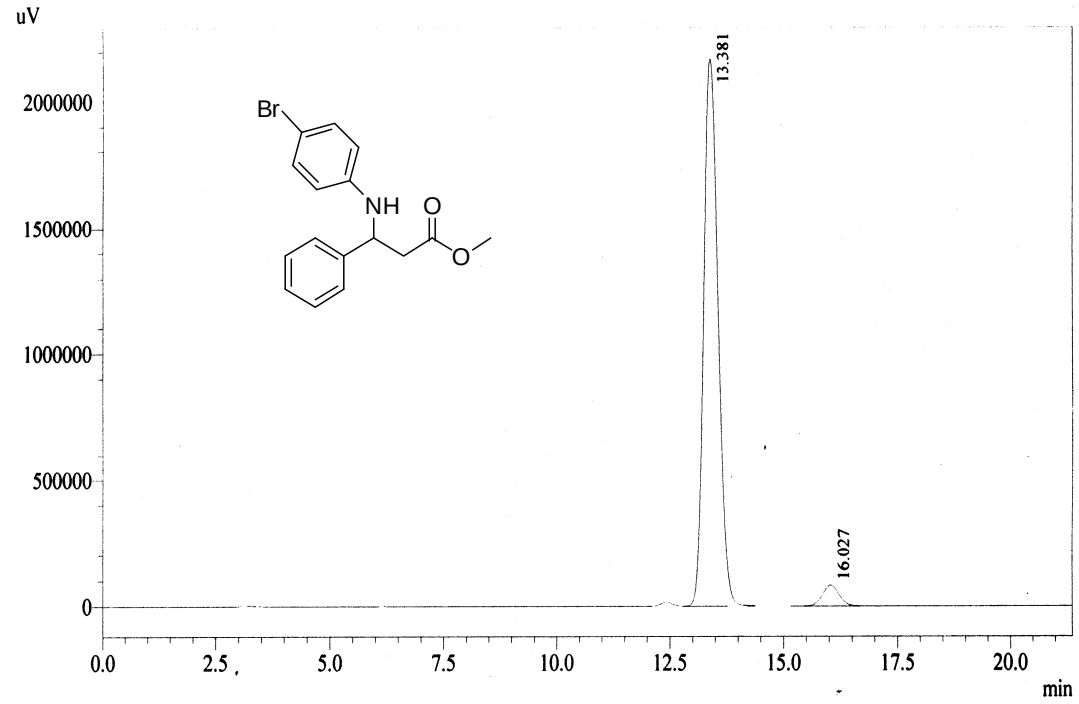
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.241 | 54646771 | 2515675 | 95.489 | 95.949 |
| 2 | 14.790 | 2581426 | 106220 | 4.511 | 4.051 |
| Total | | 57228197 | 2621896 | 100.000 | 100.000 |



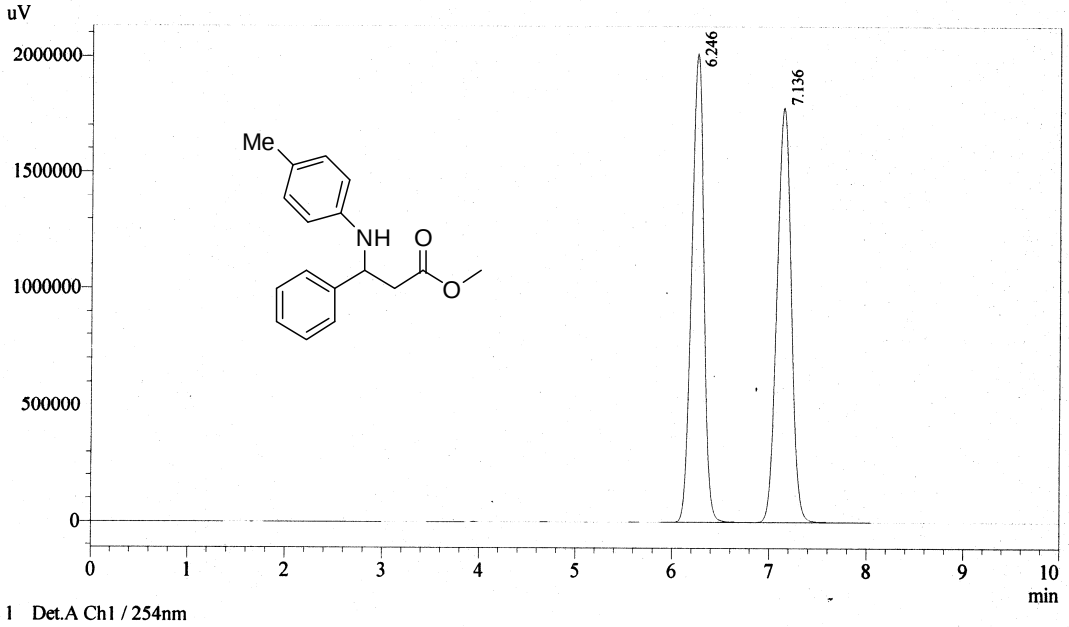

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.415 | 4240998 | 203538 | 49.866 | 55.540 |
| 2 | 15.996 | 4263835 | 162935 | 50.134 | 44.460 |
| Total | | 8504833 | 366472 | 100.000 | 100.000 |




Detector A Ch1 254nm

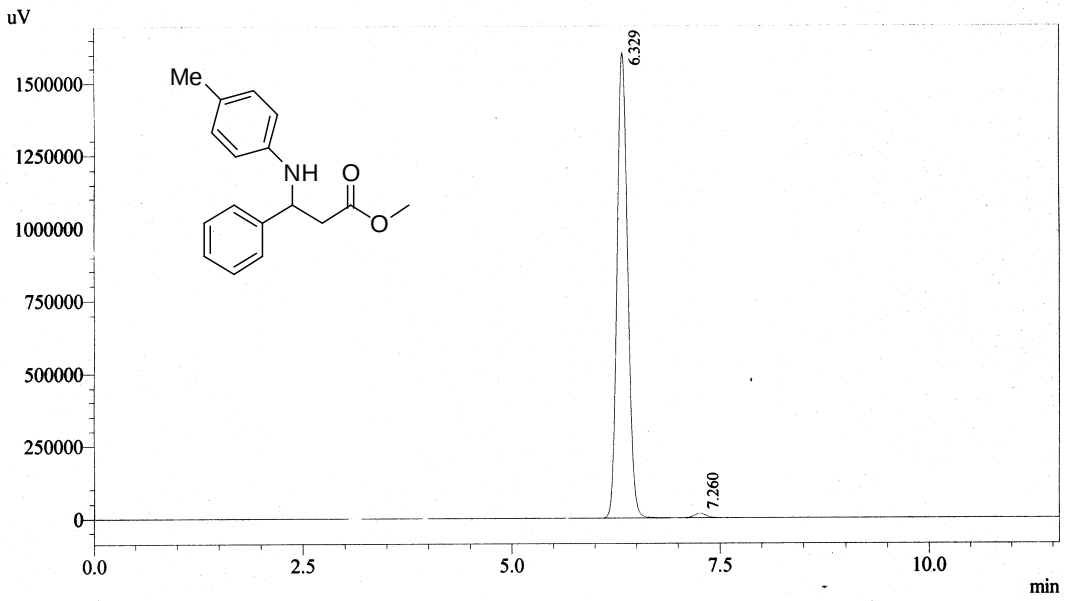
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 13.381 | 47504282 | 2172382 | 95.830 | 96.418 |
| 2 | 16.027 | 2067052 | 80716 | 4.170 | 3.582 |
| Total | | 49571334 | 2253097 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

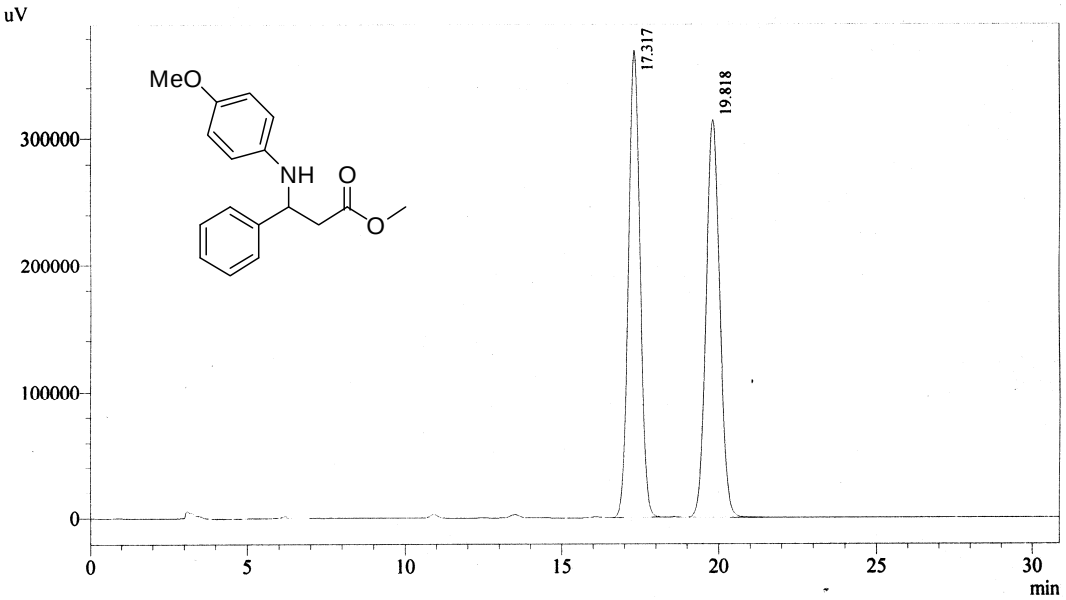
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.246 | 17690005 | 2014413 | 49.378 | 53.111 |
| 2 | 7.136 | 18135389 | 1778419 | 50.622 | 46.889 |
| Total | | 35825394 | 3792833 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

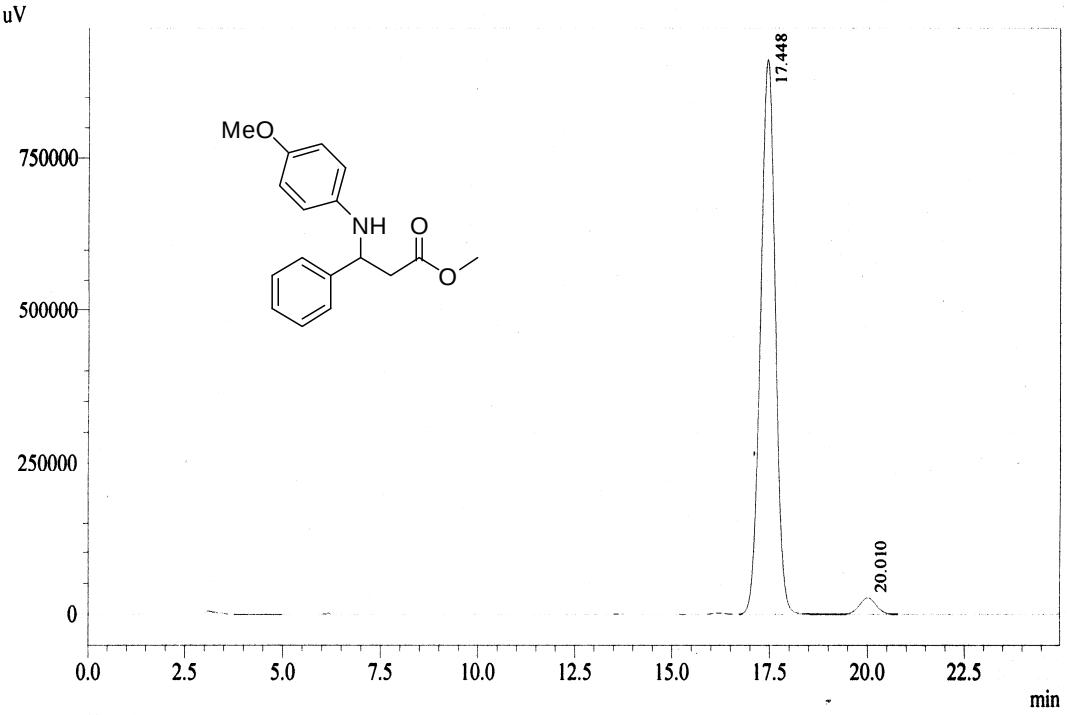
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.329 | 14230125 | 1605661 | 98.853 | 99.042 |
| 2 | 7.260 | 165142 | 15532 | 1.147 | 0.958 |
| Total | | 14395268 | 1621193 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

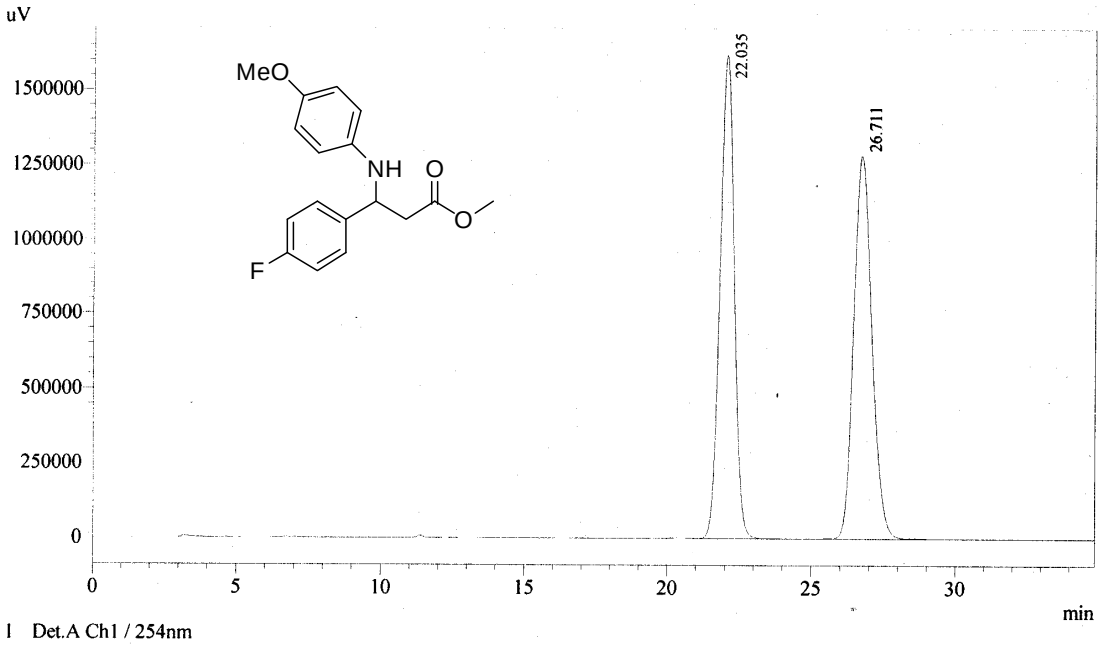
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 17.317 | 9498378 | 369620 | 49.915 | 54.044 |
| 2 | 19.818 | 9530698 | 314303 | 50.085 | 45.956 |
| Total | | 19029076 | 683923 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

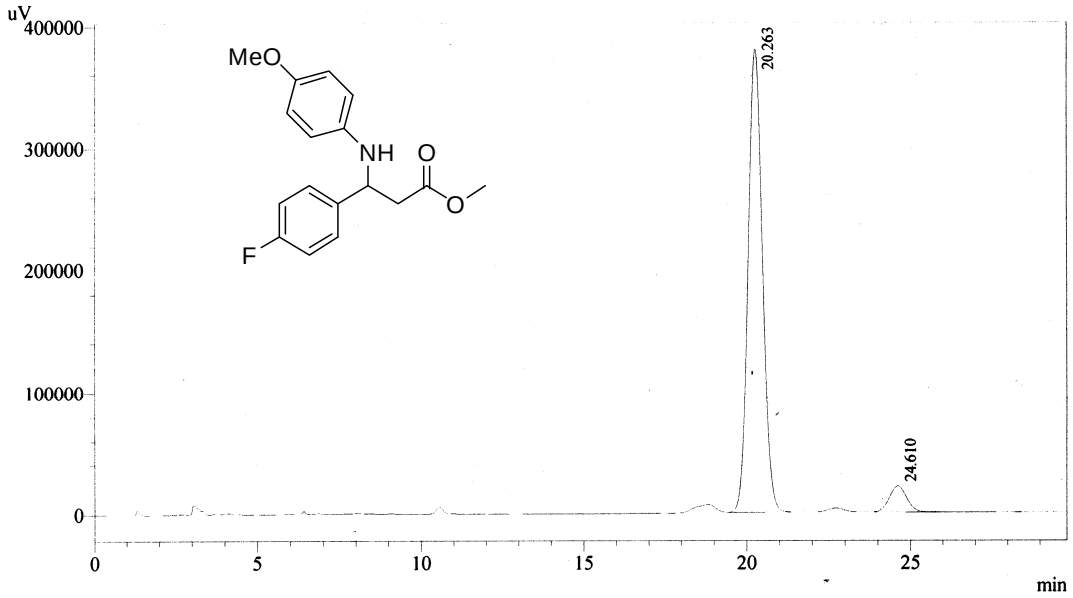
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 17.448 | 23978800 | 914605 | 96.689 | 97.165 |
| 2 | 20.010 | 821076 | 26686 | 3.311 | 2.835 |
| Total | | 24799876 | 941291 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

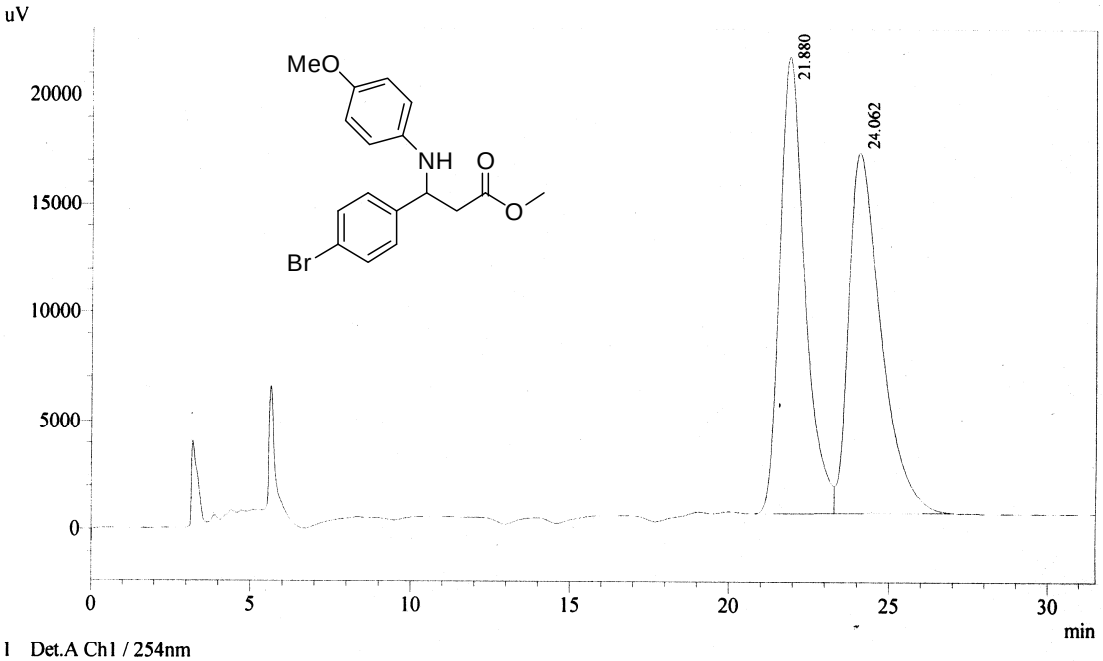
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 22.035 | 55402128 | 1616565 | 49.584 | 55.764 |
| 2 | 26.711 | 56332846 | 1282375 | 50.416 | 44.236 |
| Total | | 111734974 | 2898940 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

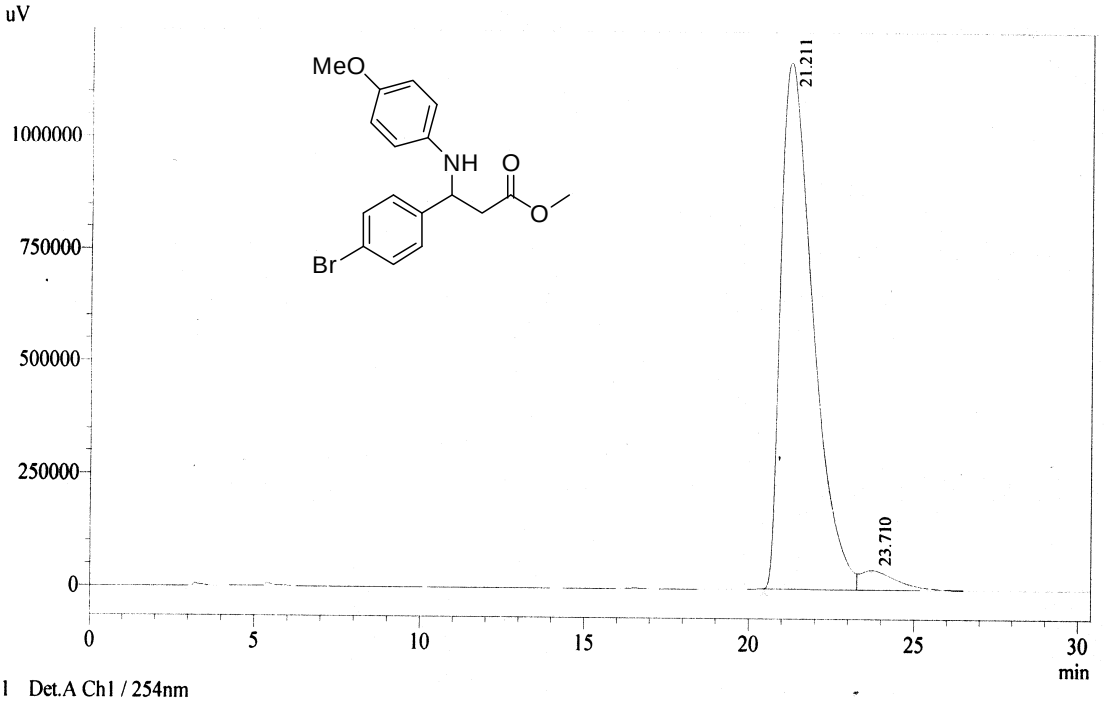
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 20.263 | 11555737 | 379991 | 93.721 | 94.790 |
| 2 | 24.610 | 774179 | 20886 | 6.279 | 5.210 |
| Total | | 12329917 | 400877 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

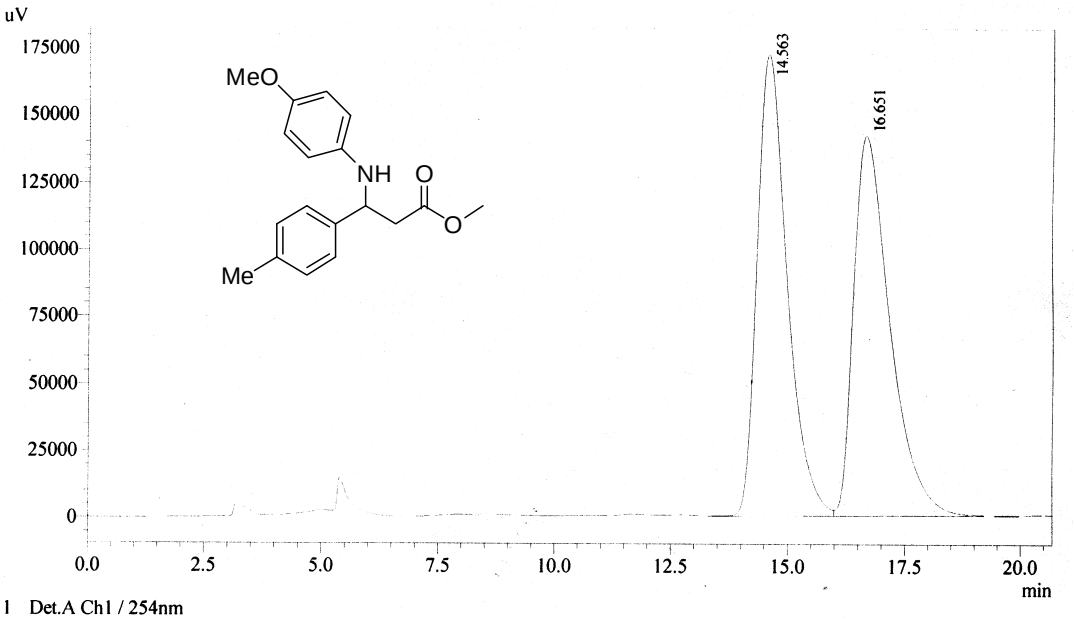
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 21.880 | 1154857 | 21064 | 49.632 | 55.896 |
| 2 | 24.062 | 1171962 | 16620 | 50.368 | 44.104 |
| Total | | 2326820 | 37684 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

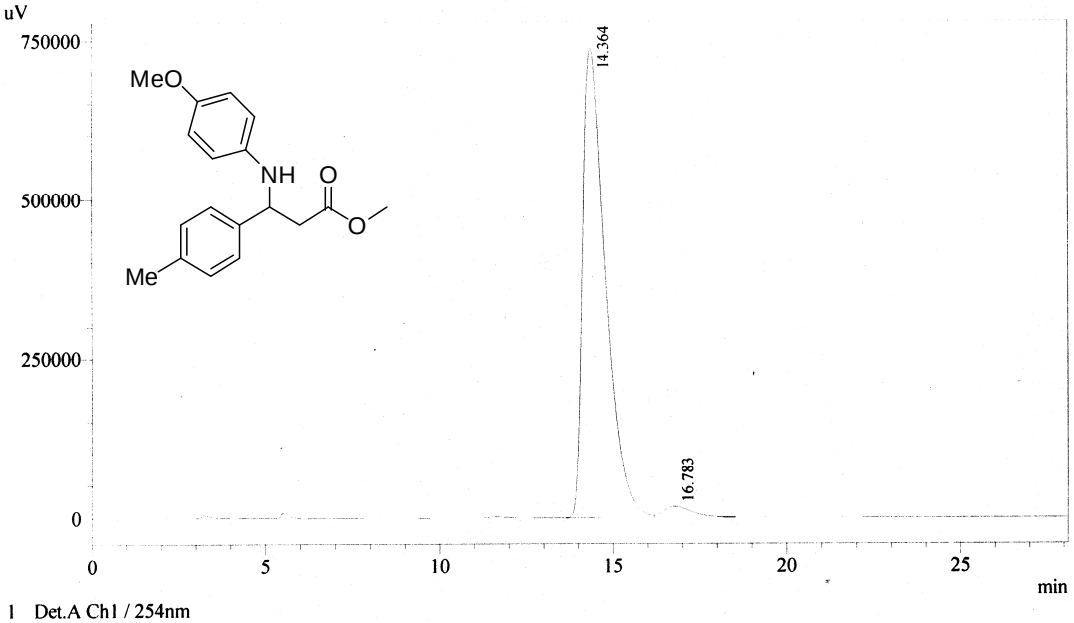
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 21.211 | 79207018 | 1170981 | 95.993 | 96.507 |
| 2 | 23.710 | 3306495 | 42381 | 4.007 | 3.493 |
| Total | | 82513513 | 1213362 | 100.000 | 100.000 |



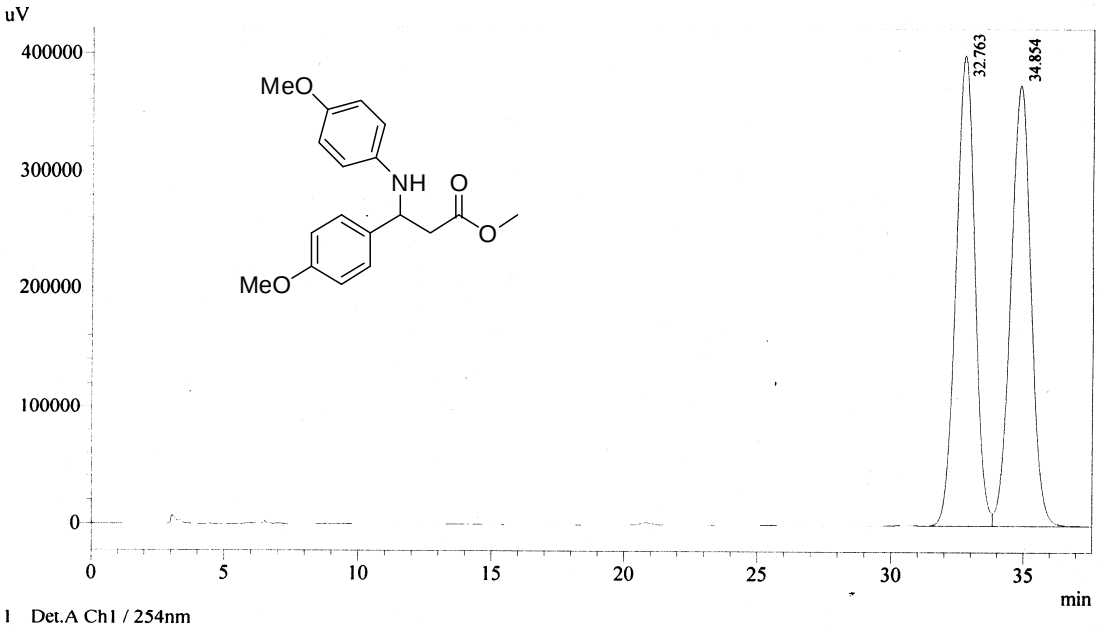

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.563 | 7685697 | 172080 | 49.954 | 54.889 |
| 2 | 16.651 | 7699705 | 141428 | 50.046 | 45.111 |
| Total | | 15385402 | 313508 | 100.000 | 100.000 |



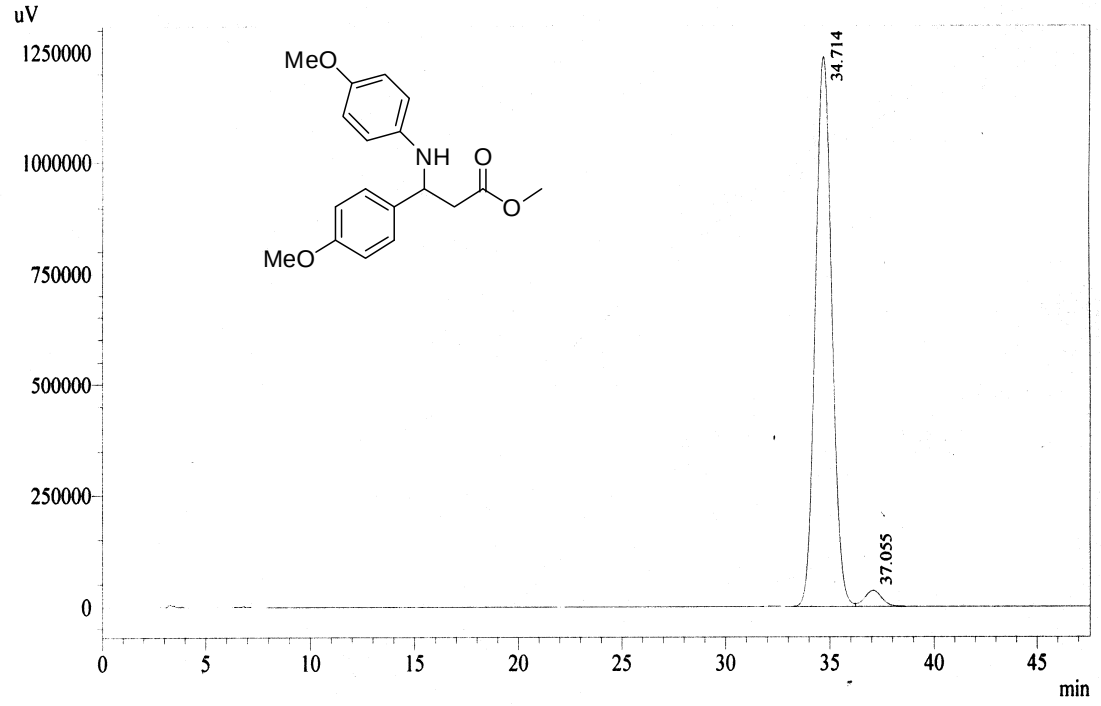

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.364 | 33587507 | 737772 | 97.229 | 97.721 |
| 2 | 16.783 | 957153 | 17204 | 2.771 | 2.279 |
| Total | | 34544660 | 754976 | 100.000 | 100.000 |



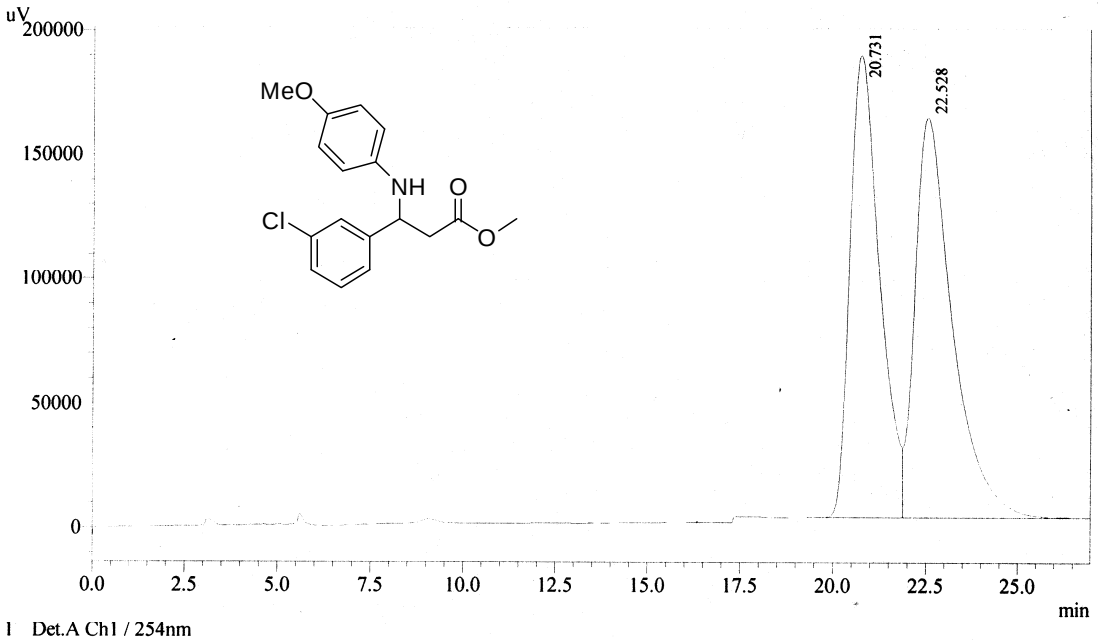

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 32.763 | 19837455 | 399756 | 49.877 | 51.684 |
| 2 | 34.854 | 19935306 | 373711 | 50.123 | 48.316 |
| Total | | 39772761 | 773468 | 100.000 | 100.000 |



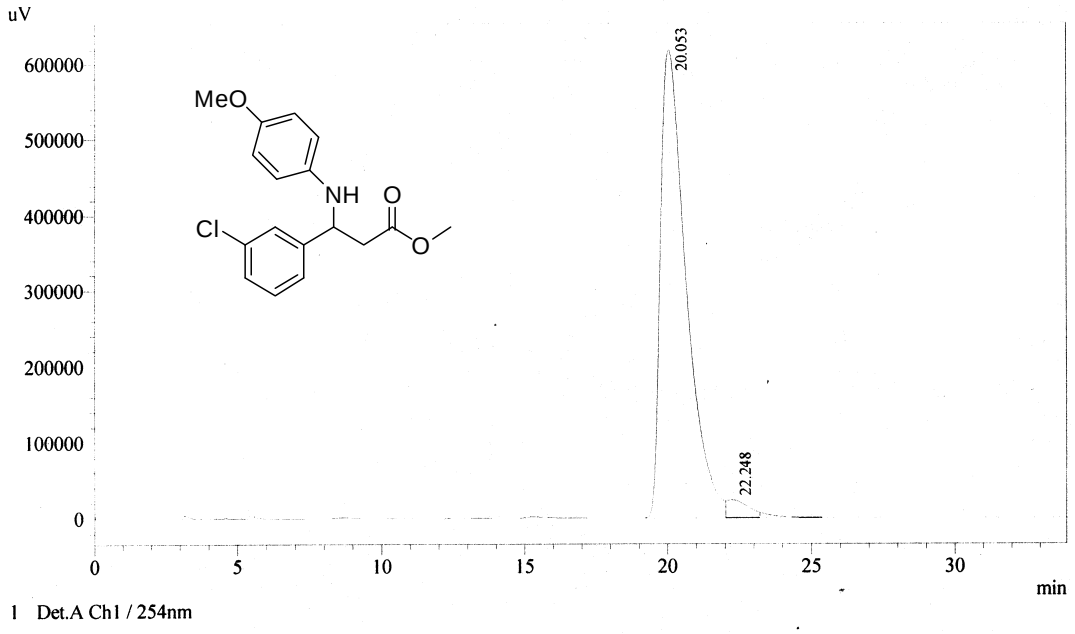

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 34.714 | 67921423 | 1239430 | 97.091 | 97.232 |
| 2 | 37.055 | 2035347 | 35283 | 2.909 | 2.768 |
| Total | | 69956771 | 1274713 | 100.000 | 100.000 |



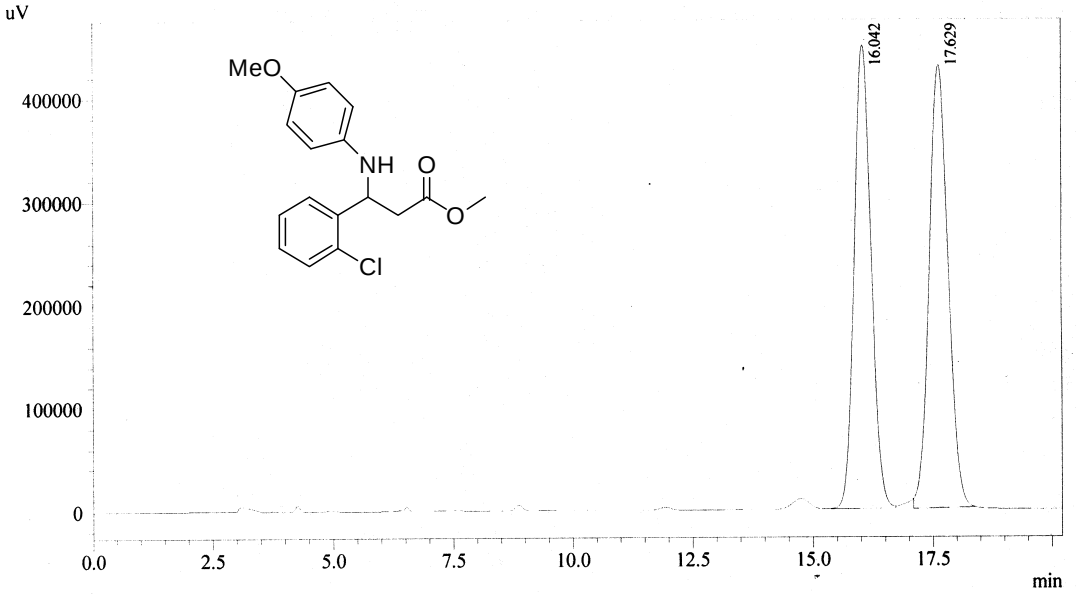

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 20.731 | 10339848 | 185936 | 47.644 | 53.603 |
| 2 | 22.528 | 11362387 | 160939 | 52.356 | 46.397 |
| Total | | 21702235 | 346875 | 100.000 | 100.000 |




Detector A Ch1 254nm

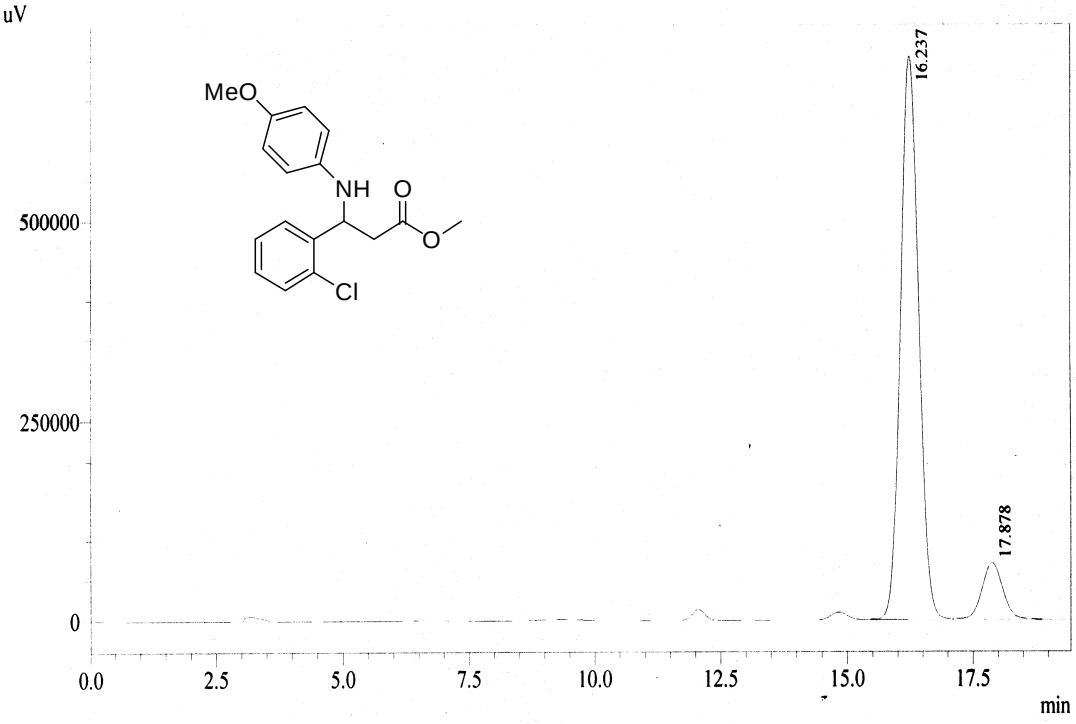
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 20.053 | 38749496 | 619084 | 97.032 | 96.450 |
| 2 | 22.248 | 1185230 | 22787 | 2.968 | 3.550 |
| Total | | 39934726 | 641871 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

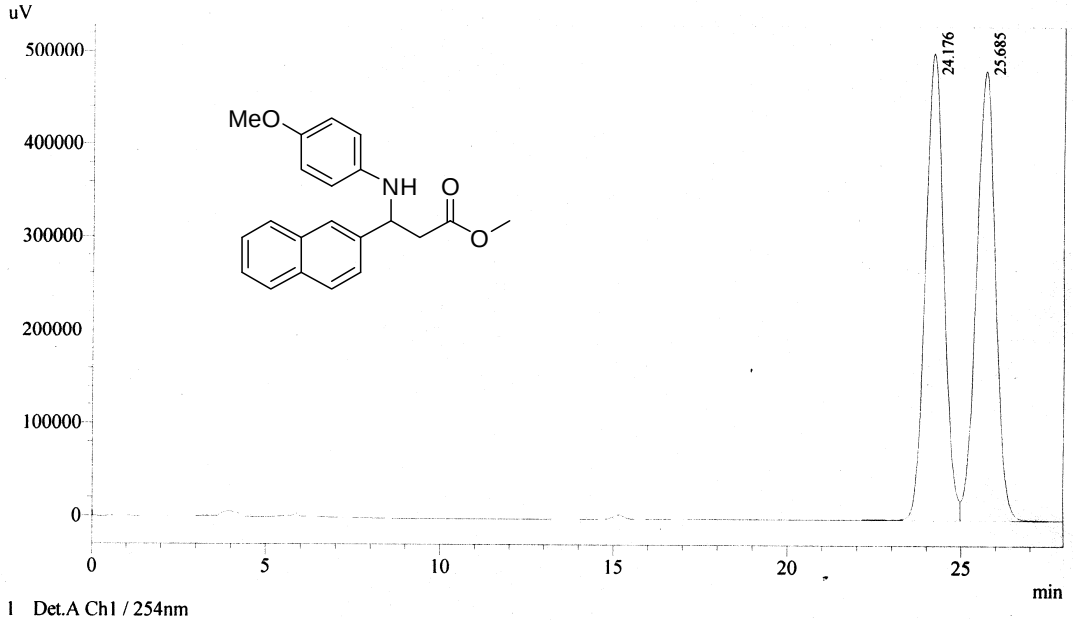
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 16.042 | 10981541 | 448959 | 48.088 | 51.174 |
| 2 | 17.629 | 11854866 | 428359 | 51.912 | 48.826 |
| Total | | 22836406 | 877317 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

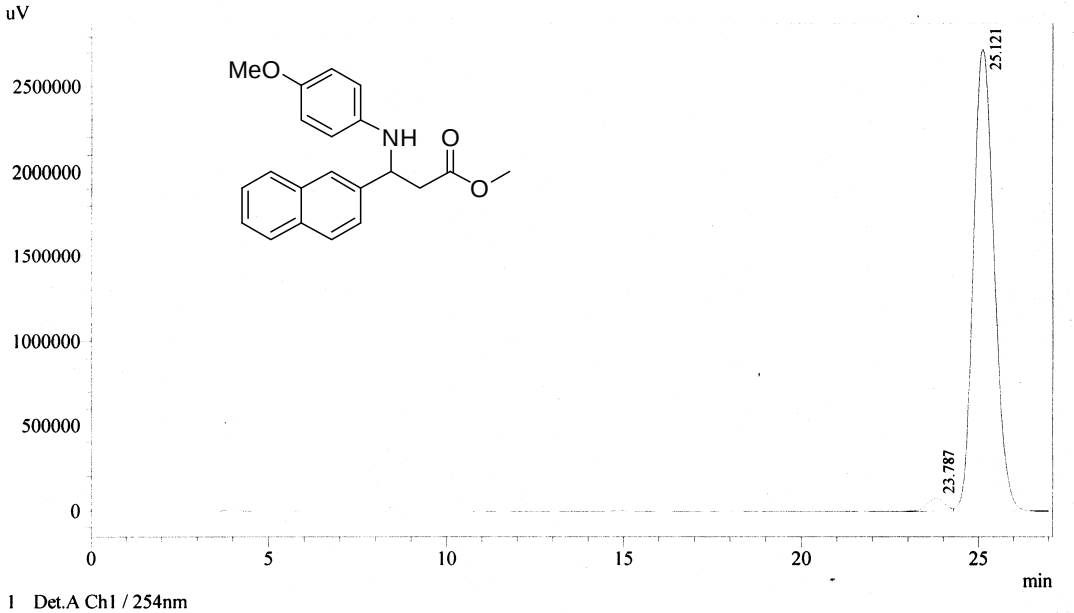
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 16.237 | 17666891 | 703269 | 89.733 | 90.996 |
| 2 | 17.878 | 2021493 | 69585 | 10.267 | 9.004 |
| Total | | 19688384 | 772854 | 100.000 | 100.000 |



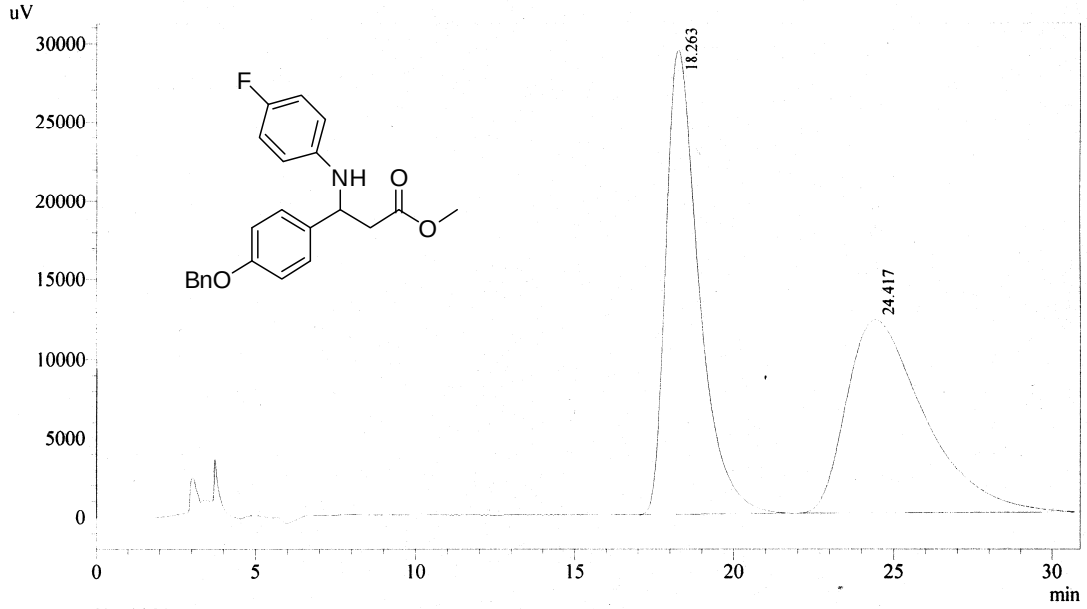

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 24.176 | 18643982 | 502494 | 49.981 | 51.005 |
| 2 | 25.685 | 18657890 | 482684 | 50.019 | 48.995 |
| Total | | 37301872 | 985179 | 100.000 | 100.000 |




Detector A Ch1 254nm

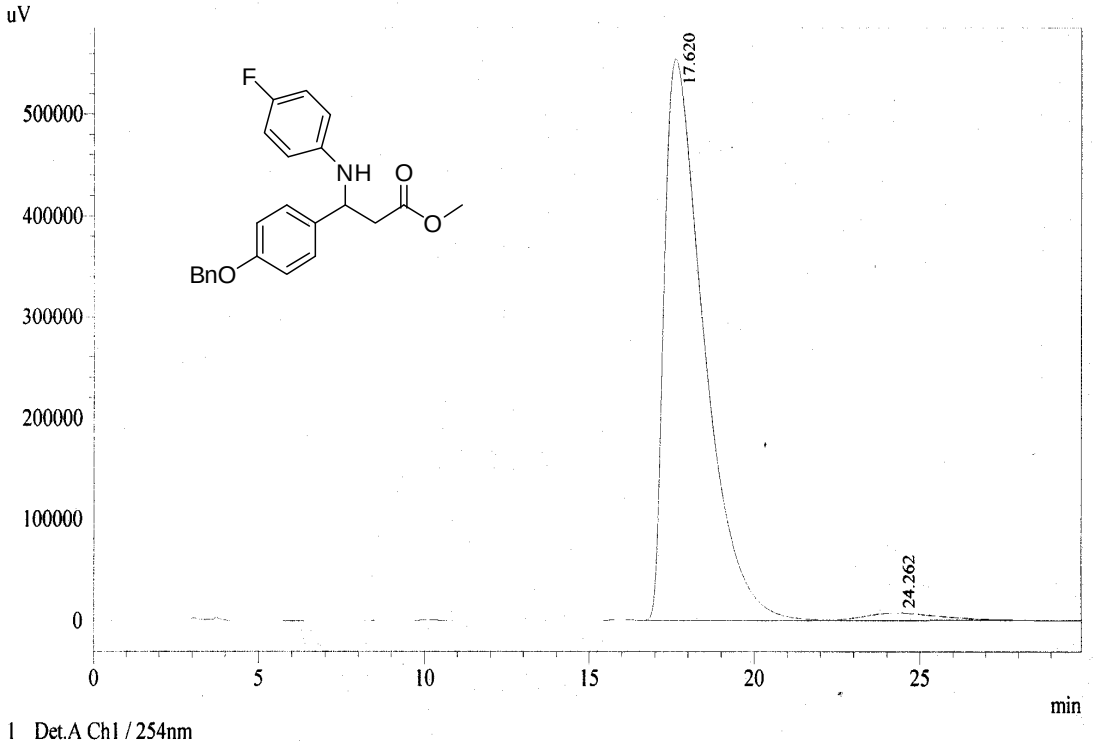
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 23.787 | 2605458 | 75855 | 2.278 | 2.709 |
| 2 | 25.121 | 111751808 | 2724234 | 97.722 | 97.291 |
| Total | | 114357266 | 2800089 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

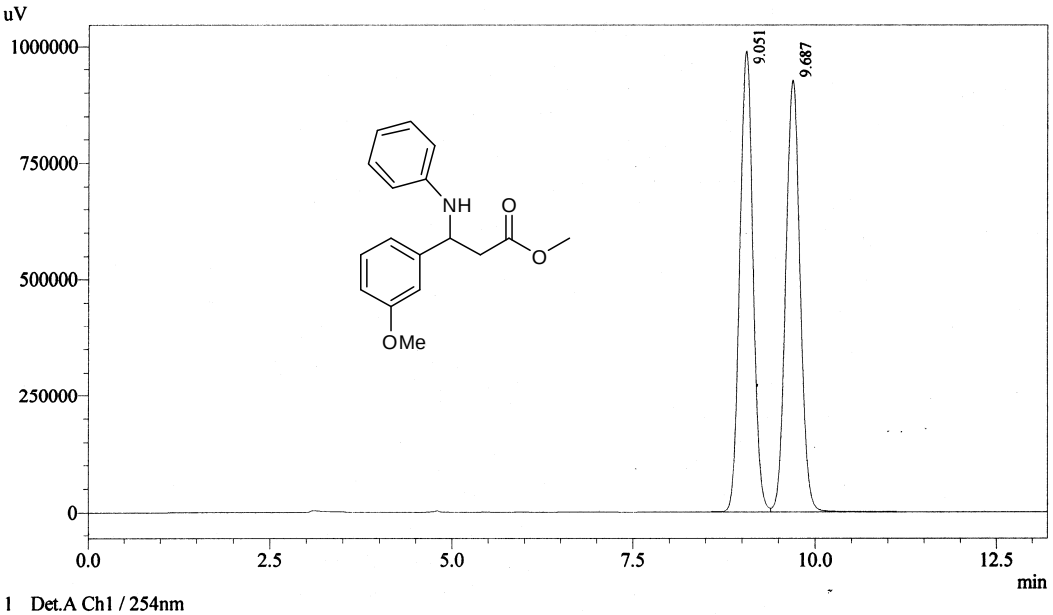
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 18.263 | 2119915 | 29398 | 50.573 | 70.625 |
| 2 | 24.417 | 2071890 | 12228 | 49.427 | 29.375 |
| Total | | 4191805 | 41626 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

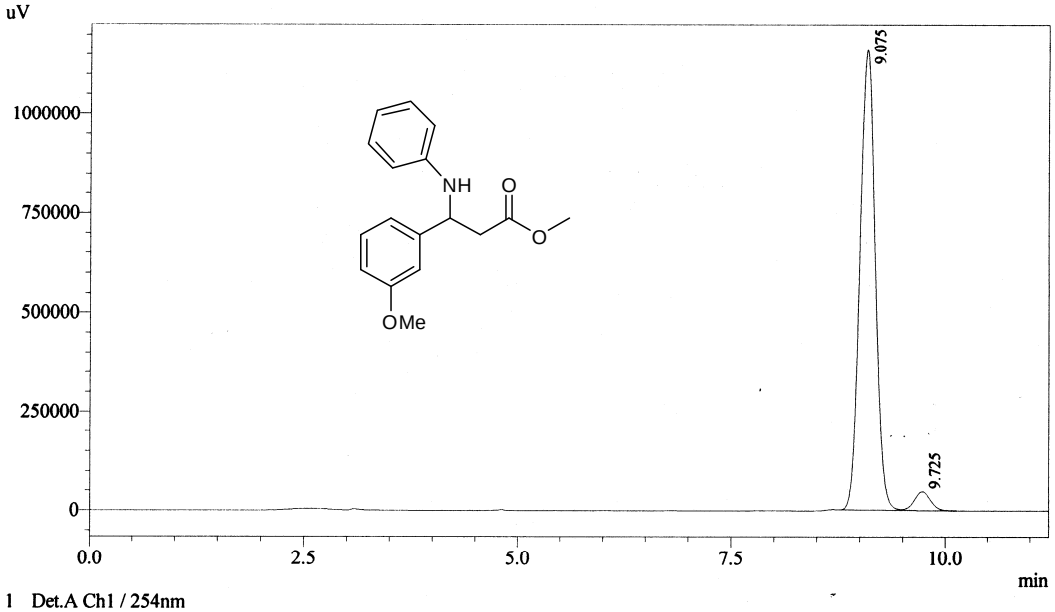
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 17.620 | 46369885 | 554169 | 97.557 | 98.719 |
| 2 | 24.262 | 1161231 | 7190 | 2.443 | 1.281 |
| Total | | 47531116 | 561359 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

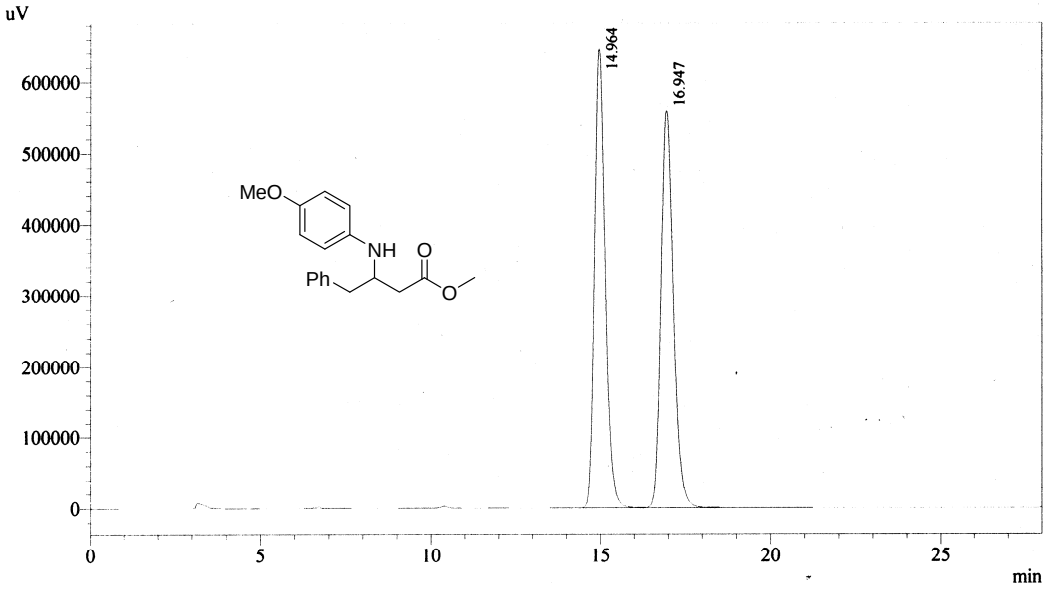
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.051 | 12537403 | 989712 | 49.640 | 51.650 |
| 2 | 9.687 | 12718998 | 926494 | 50.360 | 48.350 |
| Total | | 25256400 | 1916206 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

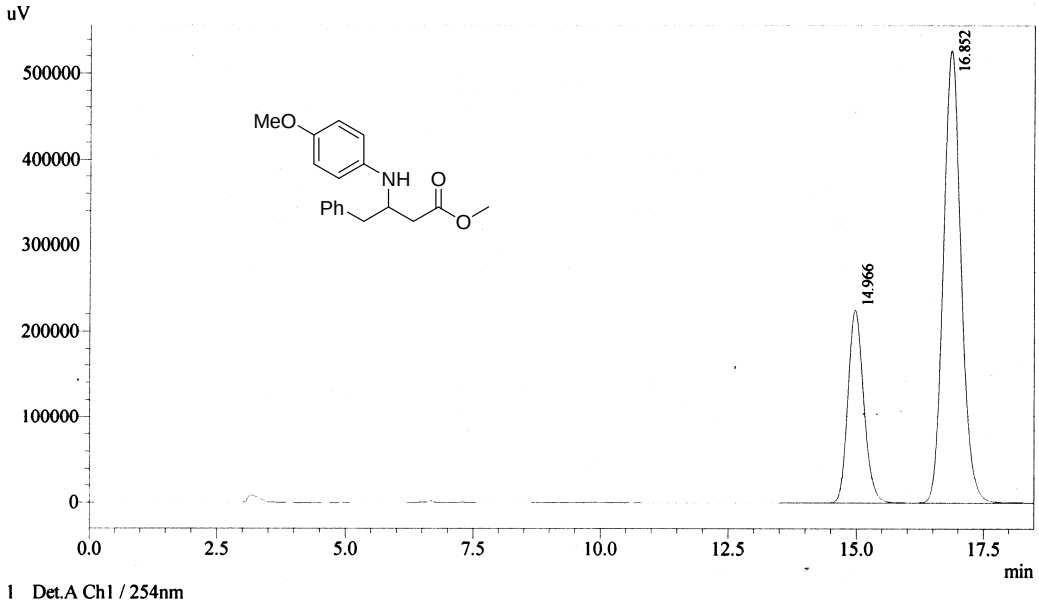
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.075 | 14478062 | 1160076 | 95.866 | 96.076 |
| 2 | 9.725 | 624328 | 47380 | 4.134 | 3.924 |
| Total | | 15102390 | 1207455 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

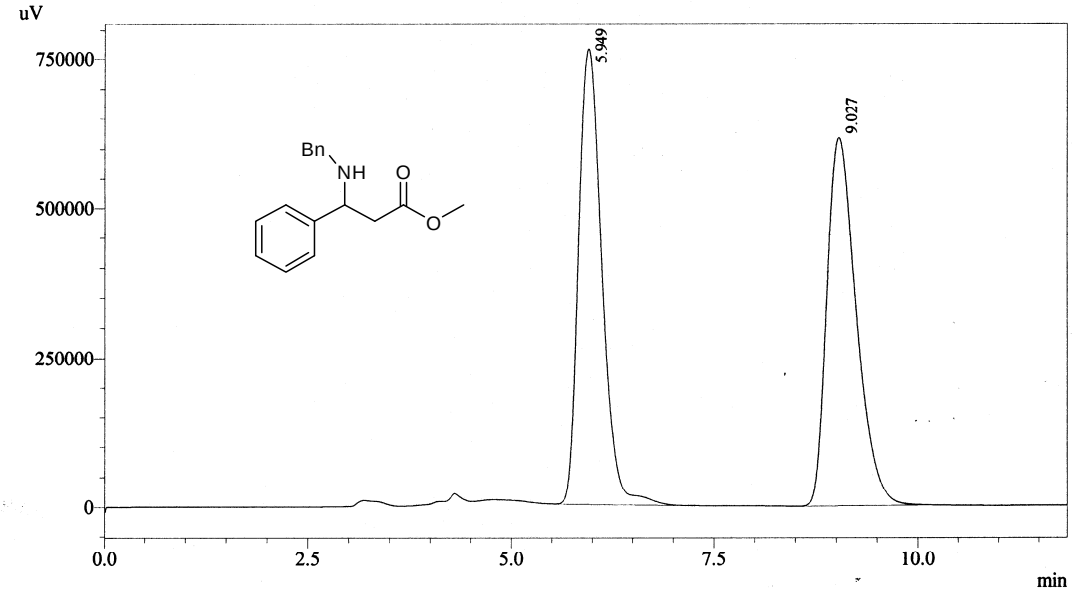
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.964 | 14146139 | 645790 | 49.875 | 53.570 |
| 2 | 16.947 | 14217008 | 559710 | 50.125 | 46.430 |
| Total | | 28363147 | 1205500 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

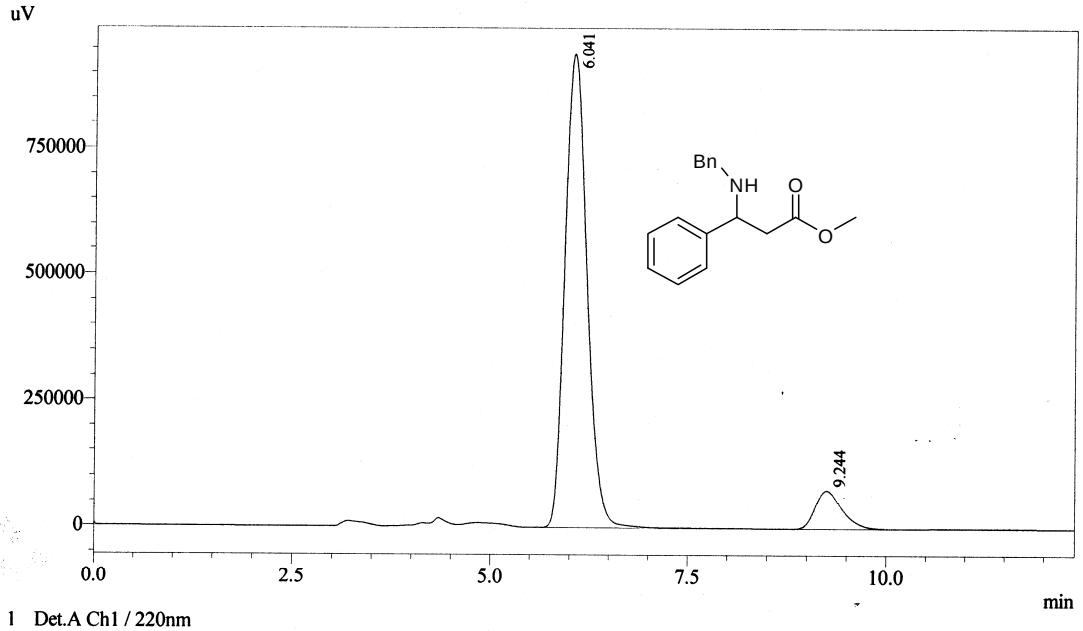
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.966 | 4843846 | 224833 | 27.375 | 29.907 |
| 2 | 16.852 | 12850326 | 526932 | 72.625 | 70.093 |
| Total | | 17694171 | 751766 | 100.000 | 100.000 |




1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

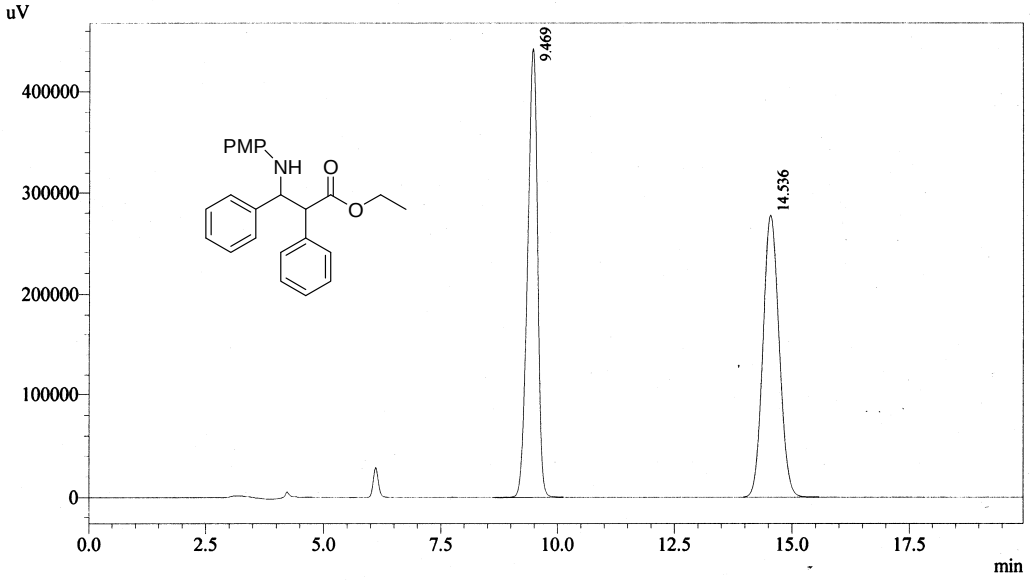
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.949 | 15311394 | 761973 | 49.735 | 55.279 |
| 2 | 9.027 | 15474786 | 616441 | 50.265 | 44.721 |
| Total | | 30786180 | 1378414 | 100.000 | 100.000 |




1 Det.A Ch1 / 220nm

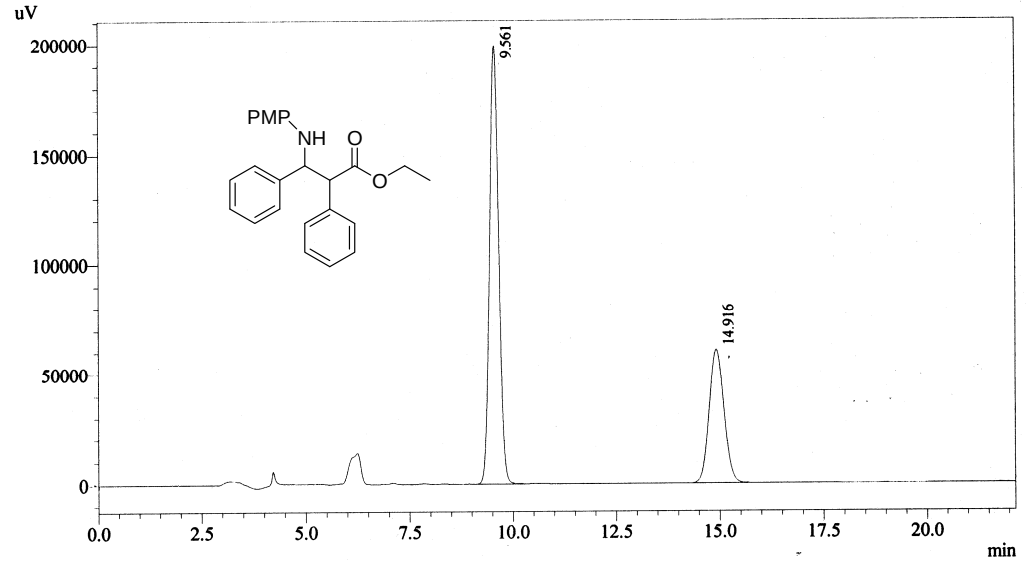
Detector A Ch1 220nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.041 | 18321042 | 940843 | 90.984 | 92.467 |
| 2 | 9.244 | 1815527 | 76644 | 9.016 | 7.533 |
| Total | | 20136570 | 1017487 | 100.000 | 100.000 |



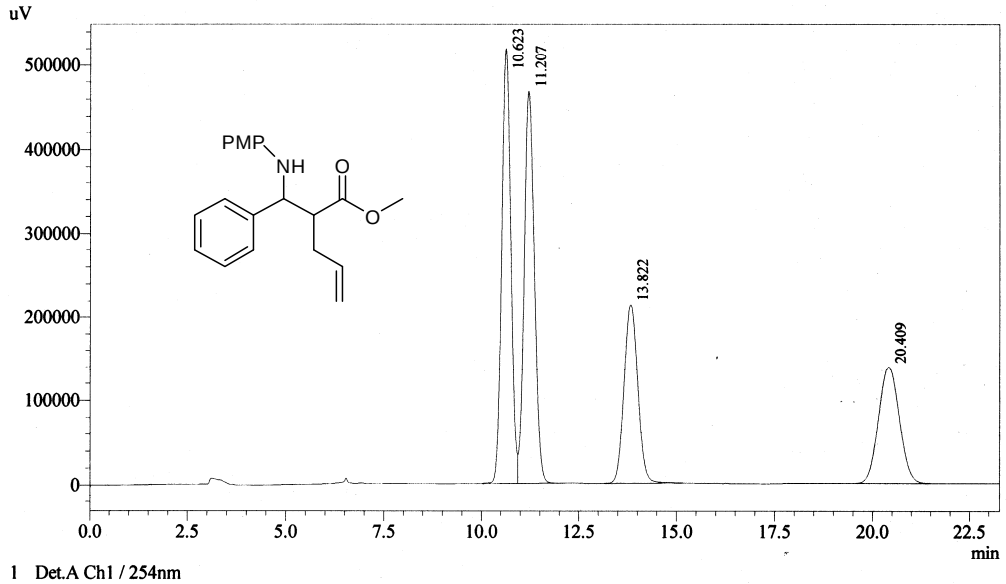

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.469 | 6602585 | 442734 | 49.901 | 61.454 |
| 2 | 14.536 | 6628656 | 277696 | 50.099 | 38.546 |
| Total | | 13231241 | 720431 | 100.000 | 100.000 |




Detector A Ch1 254nm

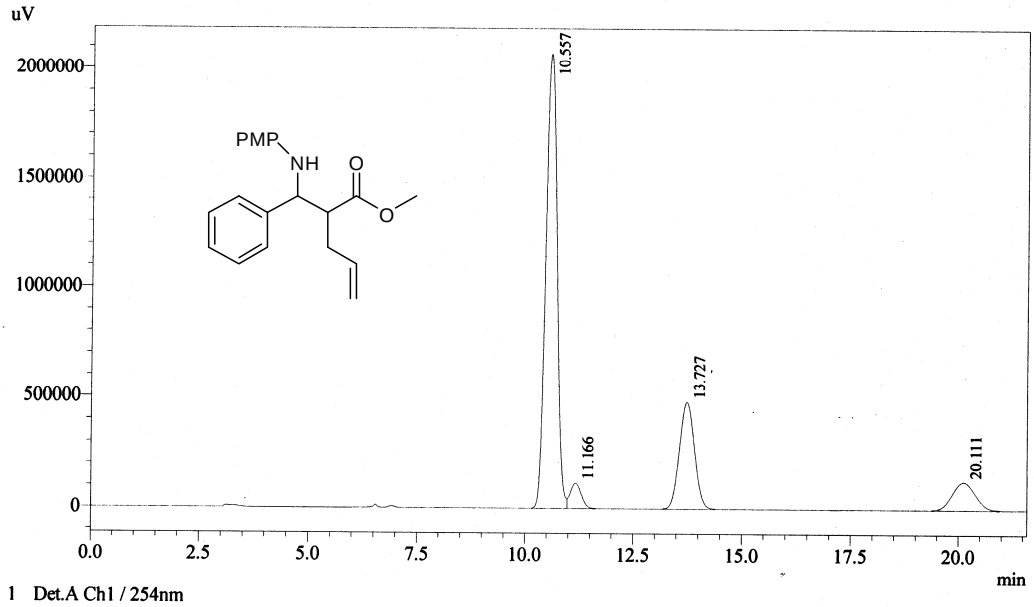
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 9.561 | 3064025 | 199320 | 67.130 | 76.671 |
| 2 | 14.916 | 1500269 | 60649 | 32.870 | 23.329 |
| Total | | 4564294 | 259969 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

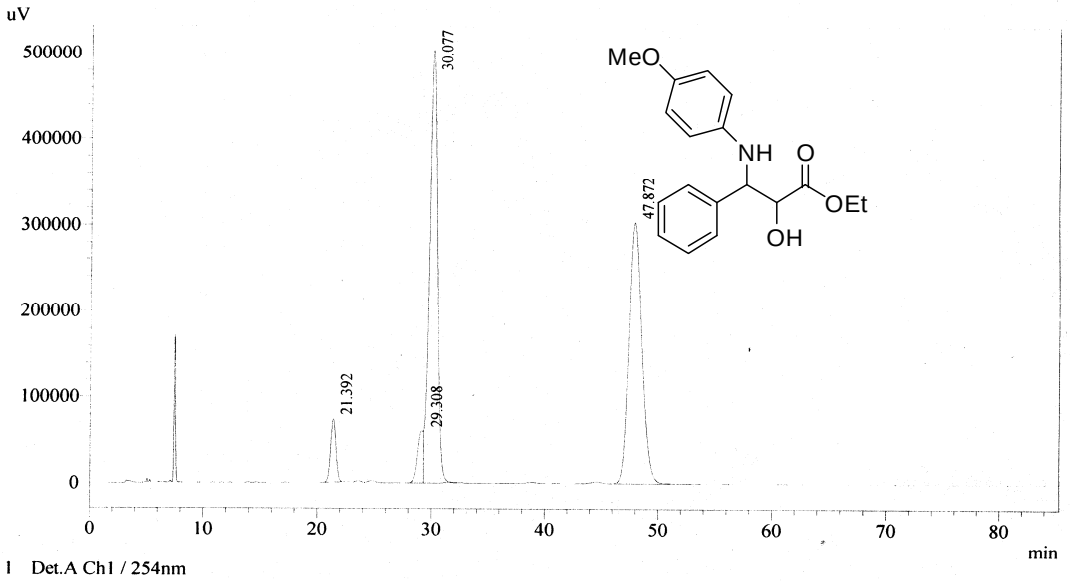
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.623 | 8441302 | 517930 | 30.937 | 38.761 |
| 2 | 11.207 | 8496396 | 467343 | 31.139 | 34.976 |
| 3 | 13.822 | 5204214 | 213155 | 19.073 | 15.952 |
| 4 | 20.409 | 5143469 | 137770 | 18.851 | 10.311 |
| Total | | 27285381 | 1336199 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

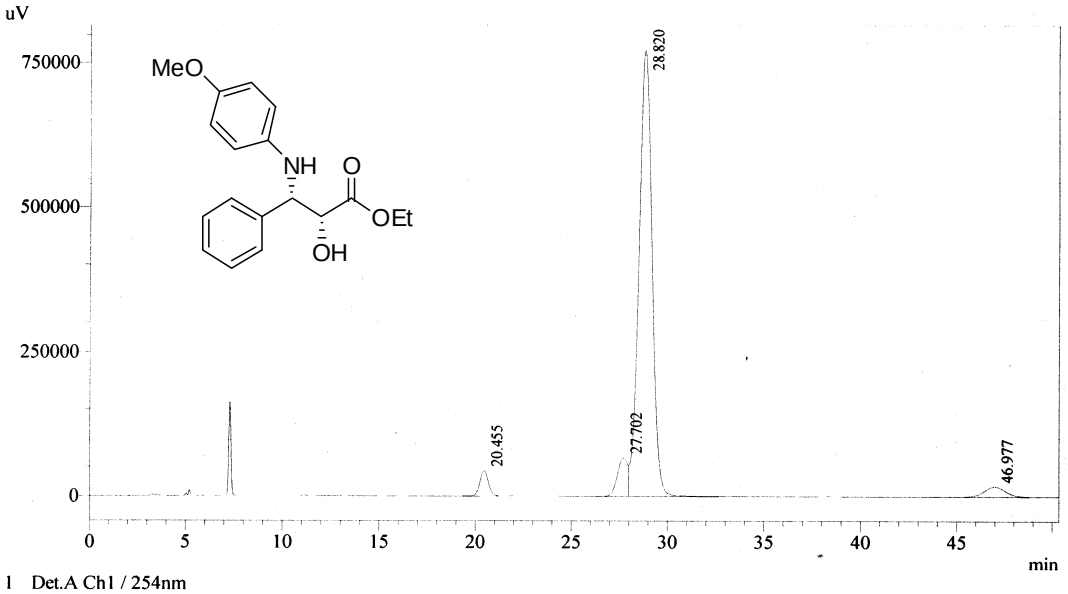
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.557 | 37425737 | 2070945 | 66.912 | 74.156 |
| 2 | 11.166 | 2035919 | 114192 | 3.640 | 4.089 |
| 3 | 13.727 | 11691153 | 480718 | 20.902 | 17.213 |
| 4 | 20.111 | 4779988 | 126845 | 8.546 | 4.542 |
| Total | | 55932797 | 2792700 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

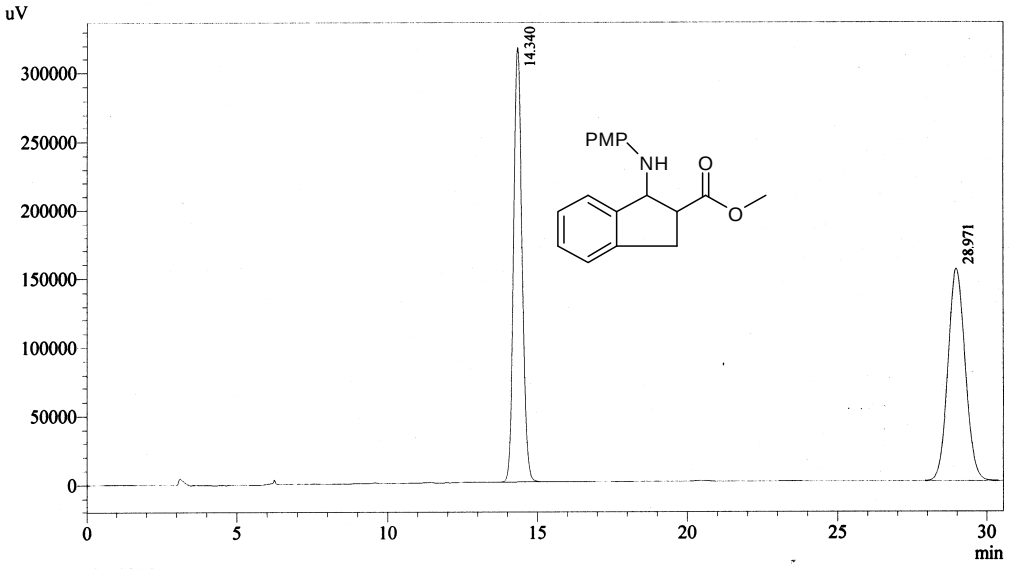
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 21.392 | 2377050 | 73537 | 4.526 | 7.825 |
| 2 | 29.308 | 2098982 | 60233 | 3.996 | 6.409 |
| 3 | 30.077 | 24333273 | 502886 | 46.329 | 53.509 |
| 4 | 47.872 | 23713760 | 303167 | 45.149 | 32.258 |
| Total | | 52523065 | 939823 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

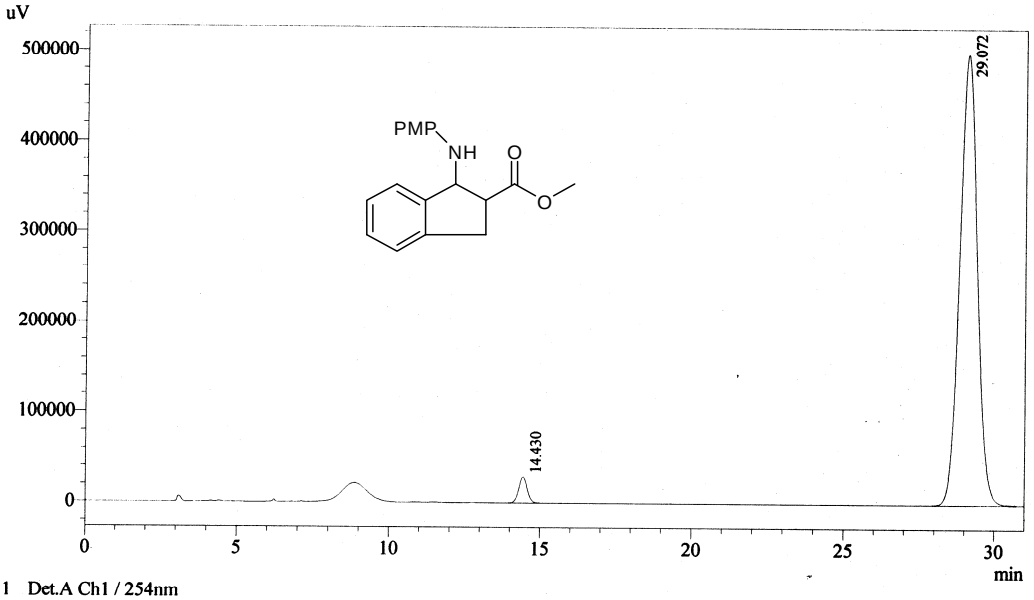
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 20.455 | 1332984 | 42972 | 3.194 | 4.776 |
| 2 | 27.702 | 2375428 | 65360 | 5.691 | 7.265 |
| 3 | 28.820 | 36635480 | 773796 | 87.777 | 86.008 |
| 4 | 46.977 | 1392986 | 17547 | 3.338 | 1.950 |
| Total | | 41736879 | 899675 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

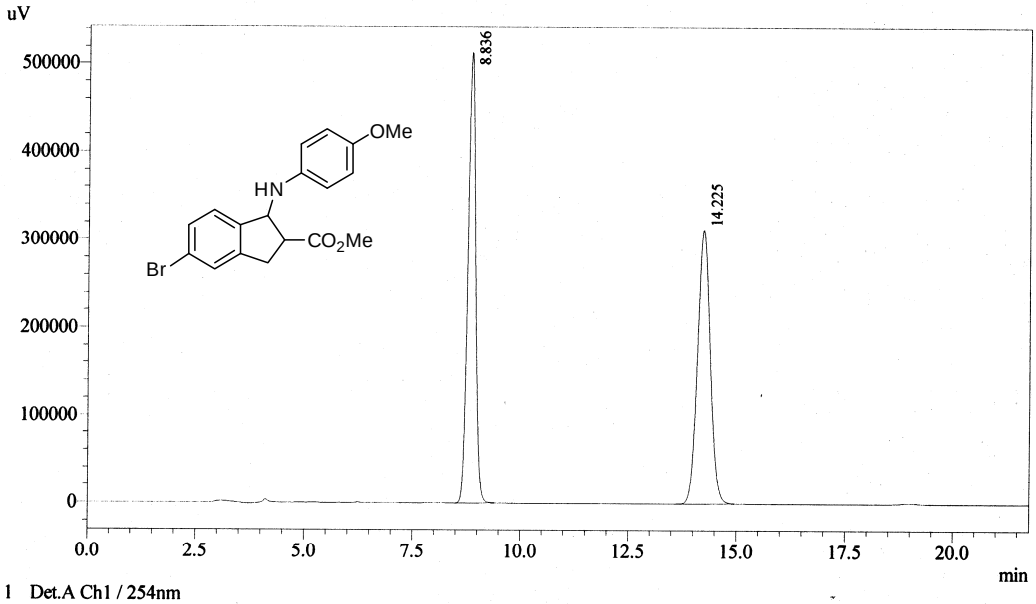
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.340 | 6237457 | 316769 | 49.932 | 67.264 |
| 2 | 28.971 | 6254440 | 154163 | 50.068 | 32.736 |
| Total | | 12491898 | 470932 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

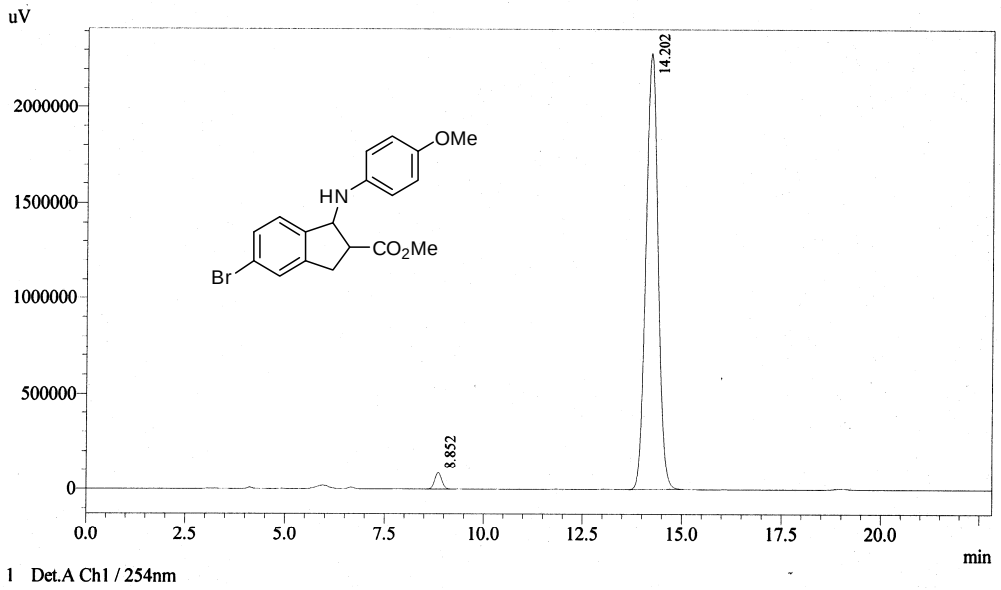
Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 14.430 | 567901 | 28758 | 2.711 | 5.449 |
| 2 | 29.072 | 20383380 | 499003 | 97.289 | 94.551 |
| Total | | 20951281 | 527761 | 100.000 | 100.000 |



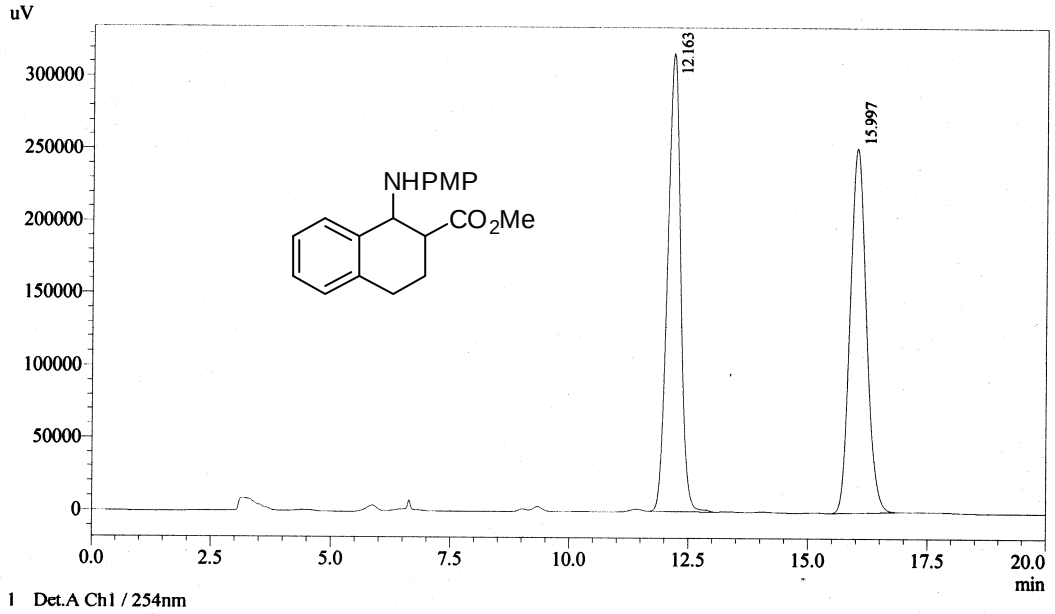

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.836 | 6406080 | 514073 | 50.002 | 62.208 |
| 2 | 14.225 | 6405547 | 312300 | 49.998 | 37.792 |
| Total | | 12811627 | 826373 | 100.000 | 100.000 |



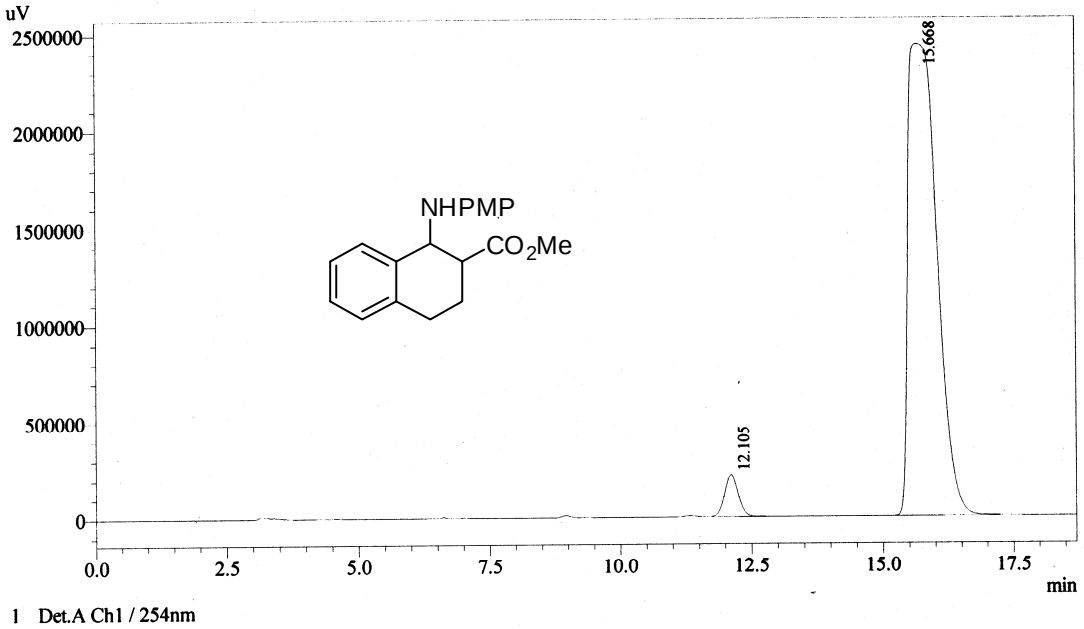

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.852 | 1081455 | 86593 | 2.176 | 3.650 |
| 2 | 14.202 | 48608686 | 2285823 | 97.824 | 96.350 |
| Total | | 49690141 | 2372416 | 100.000 | 100.000 |



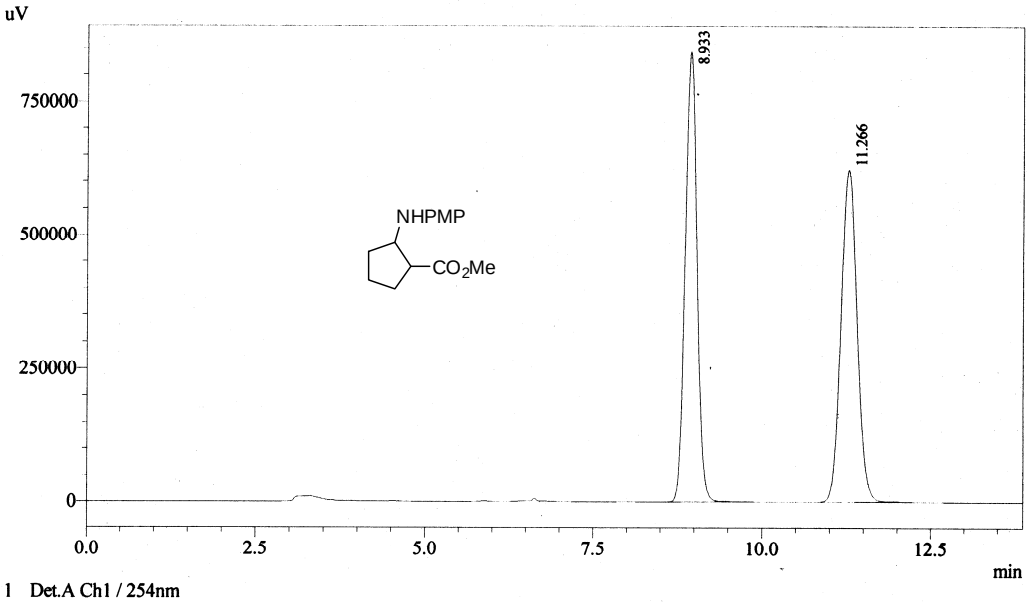

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.163 | 6003646 | 316749 | 50.211 | 55.711 |
| 2 | 15.997 | 5953144 | 251813 | 49.789 | 44.289 |
| Total | | 11956790 | 568562 | 100.000 | 100.000 |




Detector A Ch1 254nm

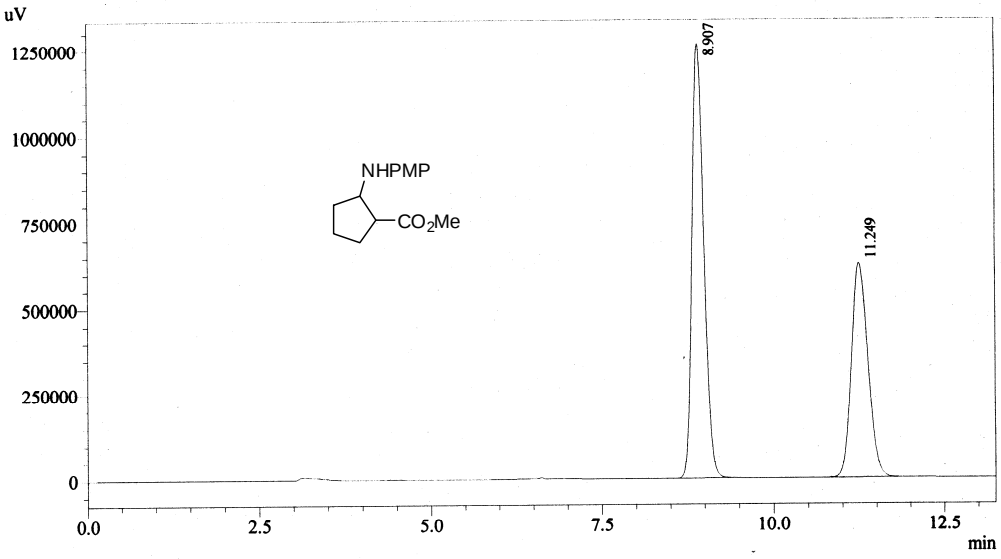
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 12.105 | 3955889 | 217123 | 4.072 | 8.185 |
| 2 | 15.668 | 93198282 | 2435488 | 95.928 | 91.815 |
| Total | | 97154170 | 2652611 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

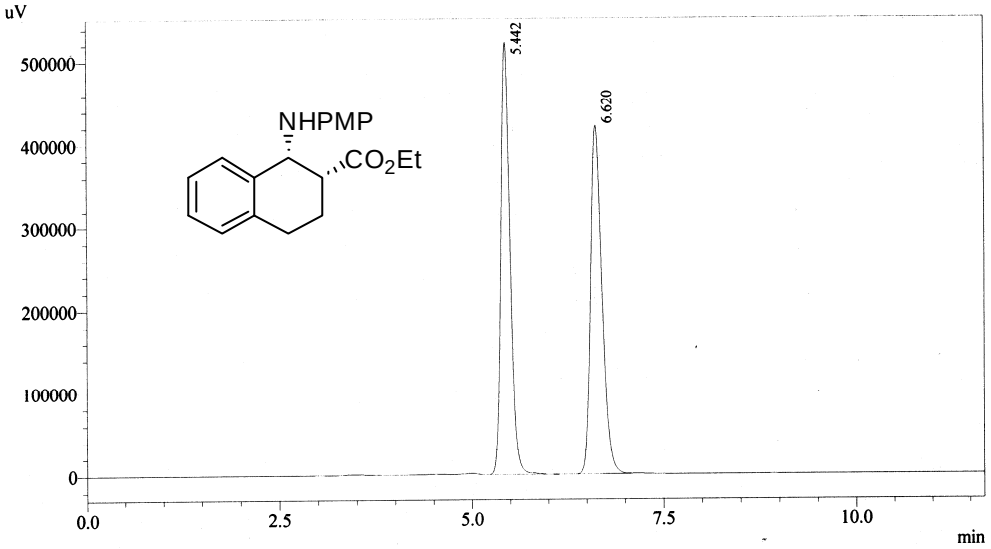
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.933 | 10223322 | 844448 | 49.784 | 57.544 |
| 2 | 11.266 | 10311844 | 623044 | 50.216 | 42.456 |
| Total | | 20535167 | 1467492 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

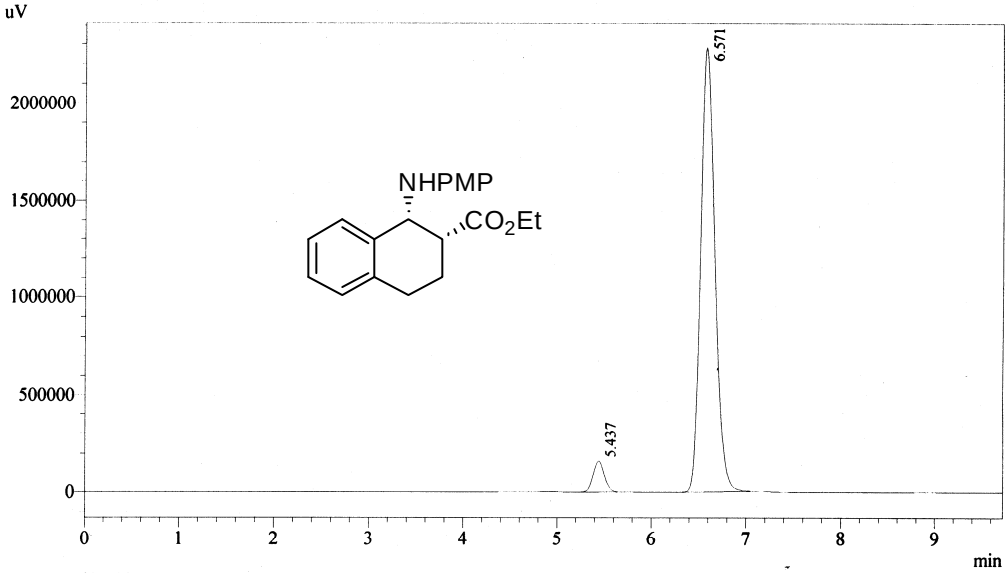
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.907 | 15225734 | 1263897 | 59.108 | 66.892 |
| 2 | 11.249 | 10533580 | 625561 | 40.892 | 33.108 |
| Total | | 25759314 | 1889457 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

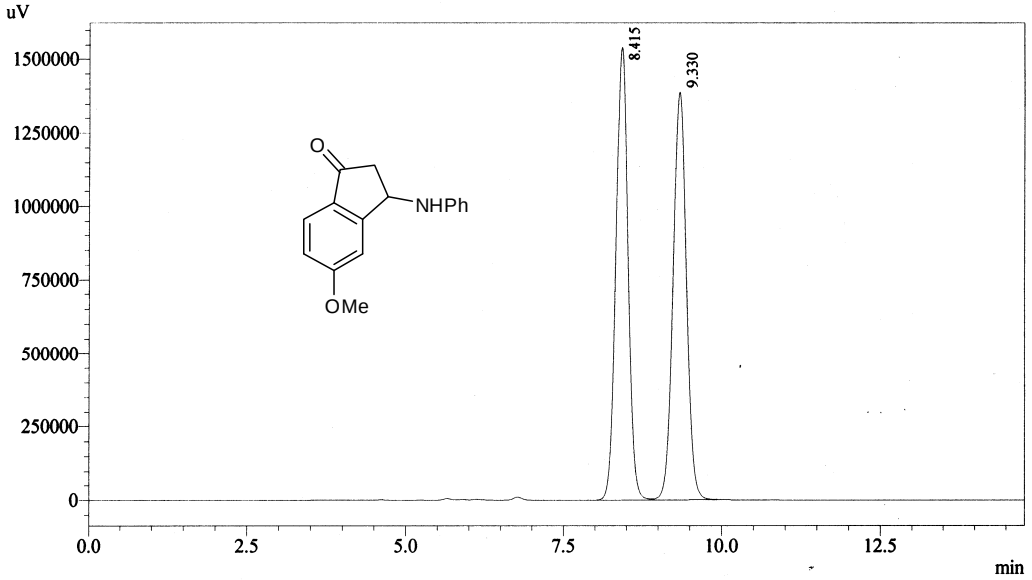
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.442 | 4350542 | 522356 | 49.906 | 55.342 |
| 2 | 6.620 | 4366869 | 421507 | 50.094 | 44.658 |
| Total | | 8717410 | 943863 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

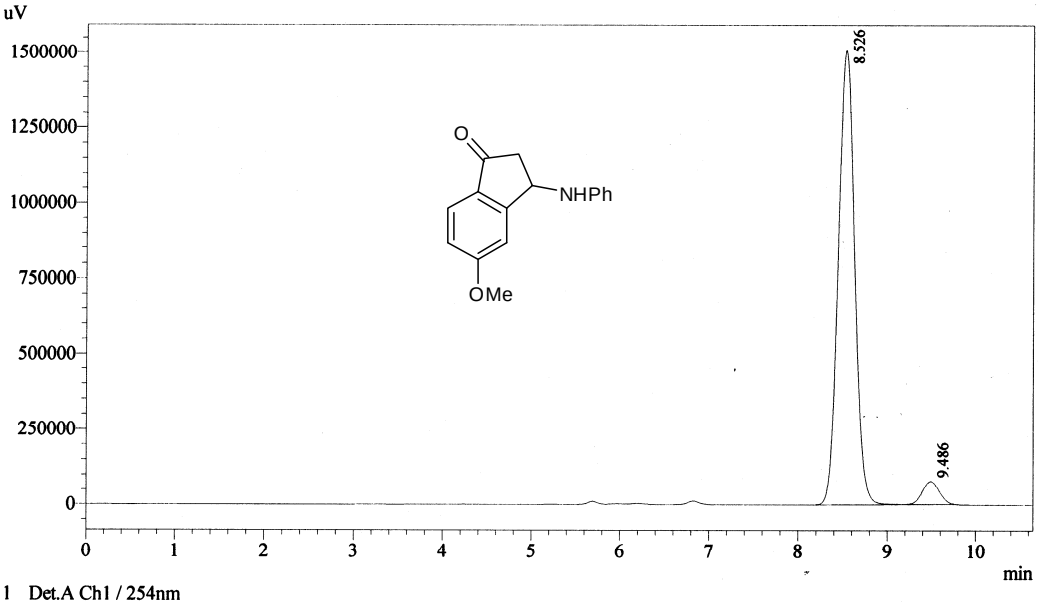
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.437 | 1332162 | 161639 | 5.283 | 6.616 |
| 2 | 6.571 | 23885560 | 2281583 | 94.717 | 93.384 |
| Total | | 25217722 | 2443222 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.415 | 20497554 | 1539177 | 49.887 | 52.563 |
| 2 | 9.330 | 20590186 | 1389089 | 50.113 | 47.437 |
| Total | | 41087741 | 2928266 | 100.000 | 100.000 |




1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 8.526 | 19254032 | 1507841 | 94.863 | 95.082 |
| 2 | 9.486 | 1042640 | 77999 | 5.137 | 4.918 |
| Total | | 20296671 | 1585840 | 100.000 | 100.000 |