

# Highly Enantioselective hydrosilylation of N-(1,2-diarylethylidene) arylamines

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## Supporting Information

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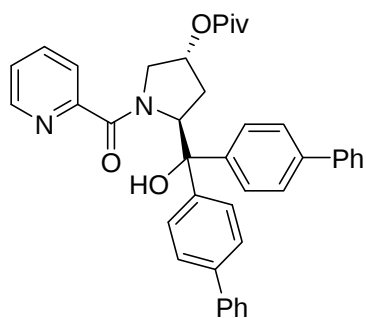
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## 1. General Methods.

All starting materials were of the highest commercially available grade and used without further purification. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography (FC) was performed using silica gel HG/T2354-92.  $^1\text{H}$  and  $^{13}\text{C}$  NMR (300 and 75 MHz, respectively) spectra were recorded in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ( $\text{CDCl}_3$ ,  $\delta$  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.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ( $\text{CDCl}_3$ ,  $\delta$  77.0 ppm). ESI HRMS spectra were recorded on BioTOF Q. HPLC analysis was performed on Waters-Breeze (2487 Dual  $\lambda$  Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AD and OJ columns were purchased from Daicel Chemical Industries (Hong Kong, China). Chiralpak OD column (Sino-chiral® OD) was purchased from Funsea Technology Inc. (Beijing, China). Optical rotations were measured on a Perkin-Elmer 341 Polarimeter at  $\lambda$  = 589 nm (c g/100 mL). All enantiomeric ratios have been controlled by coinjections of the pure sample with the racemic substrates.

## 2. Synthesis and characterization of chiral Lewis base catalysts 1a-1h

Chiral Lewis base catalyst **1a** was synthesized according to the literature procedure.<sup>1</sup> Catalyst **1b** was synthesized according to the literature procedure.<sup>2</sup> Catalysts **1c-1h** were synthesized according to the literature procedure.<sup>3</sup>



**(3R,5S)-5-(hydroxydi(p-phenyl)phenylmethyl)-1-picolinoyl-pyrrolidine-3-yl pivalate (1h):** White solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.13

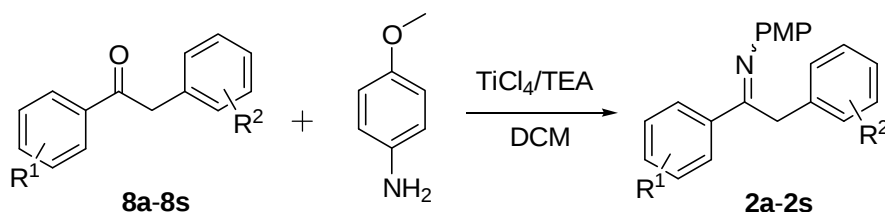
(s, 9H), 2.34 (br s, 1H), 2.56 (br s, 1H), 3.22 (br s, 1H), 3.82 (br s, 1H), 4.98 (br s, 1H), 5.79 (br s, 1H), 6.18 (br s, 1H), 7.26-7.63 (m, 22H), 8.47 (br s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.9, 35.6, 38.5, 56.3, 64.8, 124.8, 126.5, 126.6, 126.9, 127.0, 127.2, 127.3, 127.6, 127.8, 128.7,

128.7, 136.7, 139.9, 140.1, 140.4, 140.5, 143.9, 153.3, 177.9.  $[\alpha]_{\text{D}}^{20}$  = +2.9 (c 1.01  $\text{CHCl}_3$ ). HRMS (ESI)

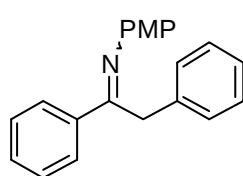
Calcd. For  $\text{C}_{40}\text{H}_{38}\text{N}_2\text{NaO}_4$   $[\text{M}+\text{Na}]^+$ : 633.2723; Found: 633.2724.

### 3. General procedure for the preparation of N-(1,2-diphenylethylidene)-4-methoxyanilines 2a-2s

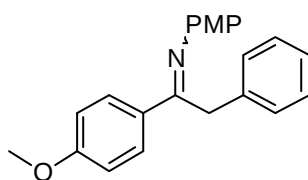
1,2-diarylethanones **8a-8s** were prepared according to the literature procedure.<sup>4</sup> N-(1,2-diphenylethylidene)-4-methoxyanilines **2a-2s** were synthesized from **8a-8s** according to literature methods.<sup>5</sup>



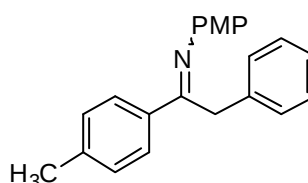
4-Methoxyaniline (27 mmol) and Et<sub>3</sub>N (27 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) in the atmosphere of N<sub>2</sub>. The mixture was cooled by an ice-salt bath. A solution of TiCl<sub>4</sub> (1.0 mL, 9 mmol) was introduced via syringe to the rapidly stirred mixture. After stirring for 30 min, the ice bath was removed, and stirring continued until the mixture reached room-temperature. Then 1,2-diarylethanone (9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added via syringe. The temperature of the solution was raised to 40°C and stirring was continued for 5 h. The solvent was evaporated and the residue was subjected to chromatography and subsequent recrystallization to afford **2a-2s**.



**N-(1,2-diphenylethylidene)-4-methoxyaniline (2a):** Yellow solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.79 (s, 3H), 4.12 (s, 2H), 6.78-6.80 (m, 2H), 6.86-6.89 (m, 2H), 7.08-7.10 (m, 2H), 7.13-7.28 (m, 3H), 7.33-7.40 (m, 3H), 7.91-7.94 (m, 2H).

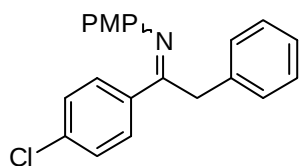


**4-methoxy-N-(1-(4-methoxyphenyl)-2-phenylethylidene)aniline (2b):** Yellow solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.79 (s, 3H), 3.82 (s, 3H), 4.09 (s, 2H), 6.78 (dd, *J* = 2.1 Hz, *J* = 6.6 Hz, 2H), 6.79-6.88 (m, 4H), 7.09 (d, *J* = 6.9 Hz, 2H), 7.16-7.26 (m, 3H), 7.89 (d, *J* = 9.0 Hz, 2H).

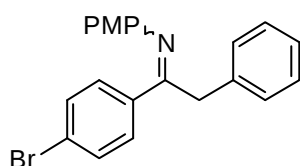


**4-methoxy-N-(2-phenyl-1-p-tolylyethylidene)aniline (2c):** Yellow solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.37 (s, 3H), 3.79 (s, 3H), 4.12 (s, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.17-7.26

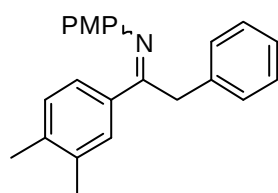
(m, 5H), 7.85 (d,  $J$  = 8.1 Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 35.9, 55.4, 113.7, 114.2, 120.4, 122.2, 126.1, 127.9, 128.1, 128.3, 128.4, 128.6, 129.0, 129.2, 135.8, 137.5, 140.4, 144.3, 155.9, 166.2.



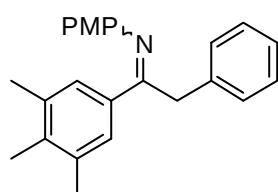
**N-(1-(4-chlorophenyl)-2-phenylethylidene)-4-methoxyaniline (2d):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.79 (s, 3H), 4.10 (s, 2H), 6.78-6.81 (s,m, 2H), 6.86-6.92 (m, 2H), 7.07 (d,  $J$  = 6.9 Hz, 2H), 7.14-7.24 (m, 3H), 7.29-7.35 (m, 2H), 7.82-7.87 (m, 2H).



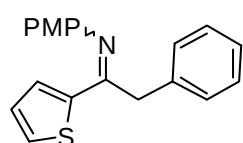
**N-(1-(4-bromophenyl)-2-phenylethylidene)-4-methoxyaniline (2e):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.79 (s, 3H), 4.40 (s, 2H), 6.78-6.81 (m, 2H), 6.86-6.89 (m, 2H), 7.07 (d,  $J$  = 6.9 Hz, 2H), 7.17-7.46 (m, 3H), 7.48 (d,  $J$  = 8.7 Hz, 2H), 7.79 (d,  $J$  = 8.7 Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  35.8, 55.4, 133.8, 114.3, 120.3, 124.8, 126.4, 128.2, 128.7, 129.6, 131.2, 131.5, 136.9, 137.3, 143.8, 156.2, 165.3.



**N-(1-(3,4-dimethylphenyl)-2-phenylethylidene)-4-methoxyaniline (2f):** Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.28 (s, 3H), 2.29 (s, 3H), 3.79 (s, 3H), 4.12 (s, 2H), 6.79-6.82 (m, 2H), 6.87-6.90 (m, 2H), 7.11-7.16 (m, 3H), 7.19-7.24 (m, 3H), 7.59 (dd,  $J$  = 7.8 Hz,  $J$  = 1.5 Hz, 1H), 7.84 (s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.7, 19.8, 35.8, 55.3, 114.1, 120.4, 125.6, 126.1, 128.3, 128.5, 128.8, 129.5, 136.1, 136.6, 137.5, 139.2, 144.4, 155.9, 166.5.

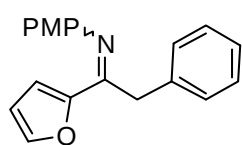


**4-methoxy-N-(2-phenyl-1-(3,4,5-trimethylphenyl)ethylidene)aniline (2g):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.19 (s, 3H), 2.30 (s, 6H), 3.79 (s, 3H), 4.11 (s, 2H), 6.78 (d,  $J$  = 8.7 Hz, 2H), 6.87 (d,  $J$  = 8.7 Hz, 2H), 7.10-7.18 (m, 3H), 7.22 (d,  $J$  = 7.5 Hz, 2H), 7.60 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.5, 20.7, 35.8, 55.3, 114.1, 120.4, 126.0, 127.0, 128.3, 128.5, 135.4, 136.3, 137.6, 137.8, 144.5, 155.8, 166.8.

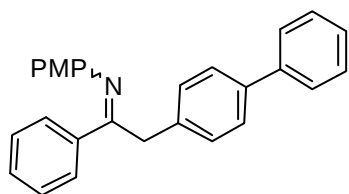


**4-methoxy-N-(2-phenyl-1-(thiophen-2-yl)ethylidene)aniline (2h):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.78 (s, 3H), 4.09 (s, 2H), 6.79-6.84 (m, 4H),

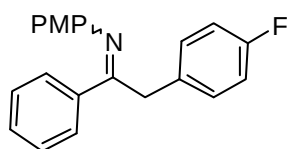
6.98-6.99 (m, 1H), 7.15 (d,  $J = 7.2$  Hz, 2H), 7.19-7.29 (m, 3H), 7.39 (d,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  36.5, 55.4, 114.1, 121.0, 126.4, 127.5, 128.2, 128.5, 128.6, 129.4, 129.6, 137.2, 143.1, 145.8, 156.2, 161.3.



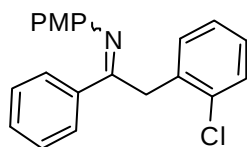
**N-(1-(furan-2-yl)-2-phenylethylidene)-4-methoxyaniline (2i):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.78 (s, 3H), 3.99 (s, 2H), 6.43-6.45 (m, 1H), 6.44-6.81 (m, 5H), 7.10 (d,  $J = 6.9$  Hz, 2H), 7.17-7.24 (m, 3H), 7.52 (s, 1H).



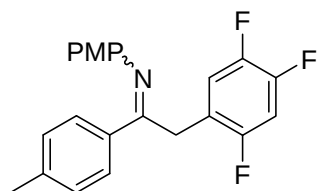
**N-(2-(biphenyl-4-yl)-1-phenylethylidene)-4-methoxyaniline (2j):** Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.82 (s, 3H), 4.20 (s, 2H), 6.68-6.94 (m, 4H), 7.20 (d,  $J = 7.8$  Hz, 2H), 7.35-7.62 (m, 14H), 7.98-7.99 (m, 2H).



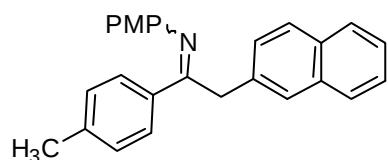
**N-(2-(4-fluorophenyl)-1-phenylethylidene)-4-methoxyaniline (2k):** Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.81 (s, 3H), 4.10 (s, 2H), 6.77-6.81 (m, 2H), 6.89 (d,  $J = 2.7$  Hz, 2H), 6.91 (d,  $J = 2.7$  Hz, 2H), 7.05 (d,  $J = 3.0$  Hz, 2H), 7.39-7.41 (m, 3H), 7.91-7.94 (m, 2H).



**N-(2-(2-chlorophenyl)-1-phenylethylidene)-4-methoxyaniline (2l):** Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.78 (s, 3H), 4.24 (s, 2H), 6.84-6.92 (m, 4H), 7.14-7.13 (m, 3H), 7.36-7.40 (m, 4H), 7.94-7.96 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  33.6, 55.2, 113.6, 113.9, 114.2, 120.2, 121.3, 121.9, 126.8, 127.4, 127.6, 127.7, 128.1, 128.2, 128.4, 128.5, 129.3, 129.6, 130.2, 133.5, 135.1, 138.0, 143.9, 156.1, 165.6.

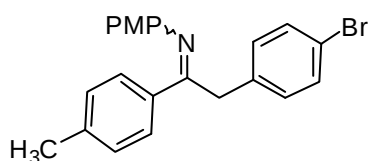


**4-methoxy-N-(1-p-tolyl-2-(2,4,5-trifluorophenyl)ethylidene)aniline (2m):** Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H), 3.80 (s, 3H), 4.04 (s, 2H), 6.75-6.91 (m, 6H), 7.20 (d,  $J = 8.1$  Hz, 2H), 7.78 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.2, 21.3, 28.0, 55.2, 55.4, 105.4 (dd,  $J = 83.1$  Hz,  $J = 63.7$  Hz), 113.4, 114.3, 114.4, 117.6 (dd,  $J = 21.0$  Hz,  $J = 78.4$  Hz, 1C), 119.0, 120.2, 122.1, 127.4, 127.6, 127.9, 128.9, 129.2, 135.0, 140.9, 143.9, 156.2, 164.7.



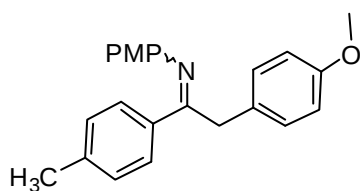
**4-methoxy-N-(2-(naphthalen-2-yl)-1-p-tolylethylidene) aniline (2n):**

Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.36 (s, 3H), 3.79 (s, 3H), 4.29 (s, 2H), 6.88 (s, 4H), 7.18 (d,  $J = 8.1$  Hz, 2H), 7.25-7.28 (m, 1H), 7.43-7.46 (m, 2H), 7.56 (s, 1H), 7.72-7.81 (m, 3H), 7.92 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 36.1, 55.4, 113.8, 114.2, 120.5, 122.3, 125.5, 125.9, 126.0, 126.7, 126.8, 127.5, 127.8, 127.9, 128.1, 128.2, 128.6, 129.1, 131.9, 133.5, 135.1, 135.8, 140.4, 144.4, 156.0, 166.1.



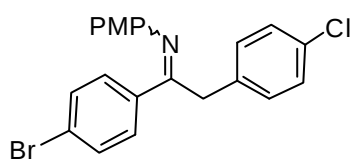
**N-(2-(4-bromophenyl)-1-p-tolylethylidene)-4-methoxyaniline (2o):**

Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H), 3.79 (s, 3H), 4.04 (s, 2H), 6.76 (d,  $J = 8.7$  Hz, 2H), 6.86-6.89 (m, 2H), 6.96 (d,  $J = 8.4$  Hz, 2H), 7.18 (d,  $J = 8.1$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 7.81 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 35.3, 55.2, 55.4, 113.8, 114.3, 120.1, 120.3, 122.2, 127.9, 128.0, 128.7, 129.1, 130.0, 130.9, 131.5, 131.6, 135.5, 136.5, 140.7, 144.2, 156.1, 165.7.



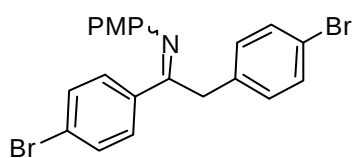
**4-methoxy-N-(2-(4-methoxyphenyl)-1-p-tolylethylidene)aniline (2p):**

Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.36 (s, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 4.03 (s, 2H), 6.75-6.79 (m, 4H), 6.85-6.88 (m, 2H), 7.00 (d,  $J = 8.7$  Hz, 2H), 7.17 (d,  $J = 8.1$  Hz, 2H), 7.83 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 35.0, 55.1, 55.4, 113.7, 113.9, 114.0, 114.2, 120.5, 122.3, 127.9, 128.1, 128.6, 129.0, 129.3, 129.4, 130.2, 135.9, 140.4, 144.4, 155.9, 157.9, 166.6.



**N-(1-(4-bromophenyl)-2-(4-chlorophenyl)ethylidene)-4-methoxyaniline (2q):**

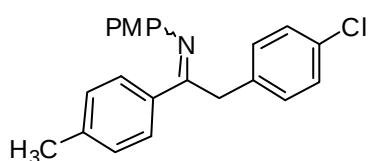
Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.79 (s, 3H), 4.05 (s, 2H), 6.74-6.77 (m, 2H), 6.86-6.89 (m, 2H), 6.98 (d,  $J = 8.4$  Hz, 2H), 7.20 (d,  $J = 8.4$  Hz, 2H), 7.49 (d,  $J = 8.7$  Hz, 2H), 7.76 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  35.1, 55.4, 113.9, 114.4, 120.3, 122.1, 125.0, 128.7, 128.9, 129.5, 129.6, 130.5, 131.3, 131.6, 132.3, 135.4, 137.1, 143.7, 156.3, 164.8.



**N-(1,2-bis(4-bromophenyl)ethylidene)-4-methoxyaniline (2r):**

Yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.79 (s, 3H), 4.03 (s, 2H), 6.75 (d,  $J$

= 8.7 Hz, 2H), 6.88 (d,  $J$  = 8.7 Hz, 2H), 6.93 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.49 (d,  $J$  = 8.7 Hz, 2H), 7.76 (d,  $J$  = 8.4 Hz, 2H).



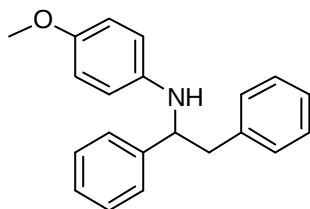
**N-(2-(4-chlorophenyl)-1-p-tolylolethylidene)-4-methoxyaniline (2s):**

Light yellow solid,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H), 3.80 (s, 3H), 4.07 (s, 2H), 6.77 (d,  $J$  = 8.4 Hz, 2H), 6.87-6.89 (m, 2H), 7.02 (d,  $J$  = 8.4 Hz, 2H), 7.18-7.21 (m, 4H), 7.82 (d,  $J$  = 8.1 Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 35.2, 55.4, 113.7, 144.2, 120.3, 122.2, 127.9, 128.5, 128.7, 129.1, 129.6, 135.5, 135.9, 140.6, 144.2, 156.0, 165.8.

#### 4. General procedure for the catalytic asymmetric hydrosilylation of N-(1,2-diphenylethylidene)-methoxyanilines 2a-2s

A solution of trichlorosilane (41  $\mu\text{L}$ , 0.4 mmol, 2.0 equiv.) in 120  $\mu\text{L}$  of  $\text{CH}_2\text{Cl}_2$  was added to a stirred solution of the corresponding N-(1,2-diarylethylidene)- methoxyaniline (0.2 mmol) and the catalyst (0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) at  $-10^\circ\text{C}$ . The mixture was stirred at the same temperature until the reaction was completed. Then the reaction was quenched with a saturated aqueous solution of  $\text{NaHCO}_3$  and extracted with EtOAc. The combined extracts was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvents were evaporated. Purification by column chromatography (silica gel, Petroleum ether/ Ethyl acetate = 20:1) afforded the pure product. The e.e. values were determined using established HPLC techniques with chiral stationary phases.

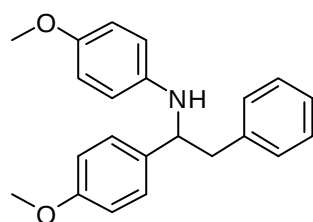
**Racemates:** All of the racemic products were prepared by using DMF (0.1equiv.) as a catalyst and trichlorosilane as hydrosilylation reagent and their chiral HPLC retention time data were compared just prior to authentic samples with enantiomeric excess.



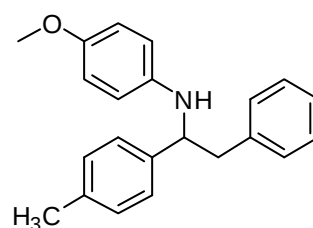
**N-(1,2-diphenylethyl)-4-methoxyaniline (3a):** Liquid, yield 99%, 98% ee,

$[\alpha]_{\text{D}}^{20} = +57$  ( $c$  = 0.23,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.18 (dd,  $J$  = 8.1 Hz,  $J$  = 13.8 Hz, 1H), 3.29 (dd,  $J$  = 5.7 Hz,  $J$  = 13.8 Hz, 1H), 3.80 (s, 3H), 4.03-4.07 (br s, 1H), 4.2 (dd,  $J$  = 5.7 Hz,  $J$  = 8.1 Hz, 1H), 6.62 (d,  $J$  = 6.6 Hz,  $J$  = 2.1 Hz, 2H), 6.84 (d,  $J$  = 6.7 Hz,  $J$  = 2.1 Hz, 2H), 7.29-7.31 (m, 2H), 7.38-7.50 (m, 8H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  45.0, 55.4, 59.9, 114.5, 114.7, 126.3, 126.5, 126.8, 128.3, 128.4, 128.5, 129.0, 137.7, 141.4, 143.5, 151.9. HRMS (ESI) Calcd. For  $\text{C}_{21}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$ : 304.1696; Found: 304.1691. HPLC

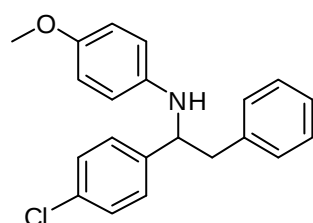
conditions: Chiralcel AD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 6.41 min,  $tr_{minor}$  = 5.93 min.



**4-methoxy-N-(1-(4-methoxyphenyl)-2-phenylethyl)aniline (3b):** Liquid, yield 97%, 97% ee,  $[\alpha]_D^{20}$  = +34.1 (c 1.695 CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.97-3.04 (m, 1H), 3.10-3.14 (m, 1H), 3.69 (s, 3H), 3.81 (s, 3H), 3.87 (br s, 1H), 4.47-4.51 (m, 1H), 6.45 (d,  $J$  = 8.7 Hz, 2H), 6.68 (d,  $J$  = 8.7 Hz, 2H), 6.87 (d,  $J$  = 8.4 Hz, 2H), 7.15 (d,  $J$  = 6.6 Hz, 2H), 7.25-7.32 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  45.3, 55.2, 55.6, 59.4, 113.8, 114.5, 114.9, 126.6, 127.5, 128.4, 129.2, 135.6, 137.9, 141.5, 151.9, 158.5. HRMS (ESI) Calcd. For C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 334.1802; Found: 334.1792. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 8.87 min,  $tr_{minor}$  = 7.42 min.

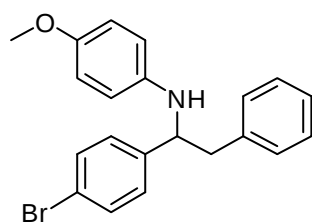


**4-methoxy-N-(2-phenyl-1-p-tolylolethyl)aniline (3c):** White solid, yield 99%, 96% ee,  $[\alpha]_D^{20}$  = +39.8 (c = 1.29, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.36 (s, 3H), 2.99 (dd,  $J$  = 13.8 Hz,  $J$  = 8.4 Hz, 1H), 3.14 (dd,  $J$  = 13.8 Hz,  $J$  = 5.4 Hz, 1H), 3.68 (s, 3H), 3.85 (br s, 1H), 4.51 (dd,  $J$  = 8.4 Hz,  $J$  = 5.4 Hz, 1H), 6.44 (d,  $J$  = 8.7 Hz, 2H), 6.65-6.69 (m, 2H), 7.13-7.19 (m, 4H), 7.24-7.33 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  21.1, 45.3, 55.6, 59.7, 114.5, 114.8, 126.3, 128.5, 129.1, 129.2, 136.5, 137.9, 140.6, 141.6, 151.9. HRMS (ESI) Calcd. For C<sub>22</sub>H<sub>24</sub>NO [M+H]<sup>+</sup>: 318.1852; Found: 318.1849. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 7.42 min,  $tr_{minor}$  = 5.89 min.

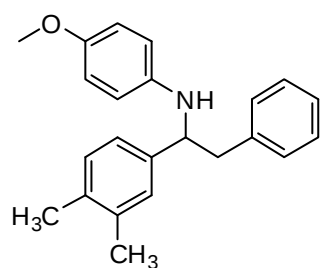


**N-(1-(4-chlorophenyl)-2-phenylethyl)-4-methoxyaniline (3d):** Liquid, yield 99%, 97% ee,  $[\alpha]_D^{20}$  = +44.6 (c = 1.11, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.01 (dd,  $J$  = 13.8,  $J$  = 8.1 Hz, 1H), 3.10 (dd,  $J$  = 13.8 Hz,  $J$  = 5.7 Hz, 1H), 3.70 (s, 3H), 3.85 (br s, 1H), 4.51 (dd,  $J$  = 8.1 Hz,  $J$  = 5.7 Hz, 1H), 6.42 (d,  $J$  = 8.7 Hz, 2H), 6.66-6.70 (m, 2H), 7.13-7.15 (m, 2H), 7.24-7.35 (m, 7H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  45.1, 55.6, 59.4, 114.6, 114.9, 126.8, 127.9, 128.6, 128.6, 129.2, 132.5, 137.3, 141.1, 142.2, 152.1. HRMS (ESI) Calcd. For C<sub>21</sub>H<sub>20</sub>ClNNaO [M+Na]<sup>+</sup>: 360.1126; Found: 360.1121. HPLC conditions:

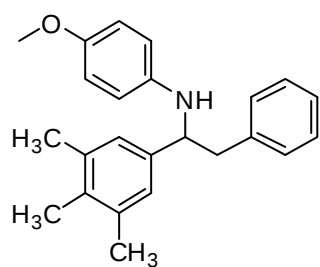
Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 8.47 min,  $tr_{minor}$  = 6.19 min.



**N-(1-(4-bromophenyl)-2-phenylethyl)-4-methoxyaniline (3e):** Liquid, yield 97%, 96% ee,  $[\alpha]_D^{20} = +34.1$  ( $c = 1.51$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.98 (dd,  $J = 13.8$  Hz,  $J = 8.1$  Hz, 1H), 3.09 (dd,  $J = 13.8$  Hz,  $J = 5.7$  Hz, 1H), 3.69 (s, 3H), 3.89 (br s, 1H), 4.46-4.50 (m, 1H), 6.40 (d,  $J = 12.9$ , 2H), 6.66-6.69 (d,  $J = 8.7$ , 2H), 7.13 (d,  $J = 7.5$ , 2H), 7.20-7.33 (m, 5H), 7.44 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  45.1, 55.6, 59.4, 114.5, 114.8, 120.6, 126.8, 128.2, 128.6, 129.1, 131.6, 137.2, 141.0, 142.7, 152.1. HRMS (ESI) Calcd. For  $\text{C}_{21}\text{H}_{20}\text{BrNNaO}$   $[\text{M}+\text{Na}]^+$ : 404.0620; Found: 404.0610. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 13.48 min,  $tr_{minor}$  = 8.29 min.

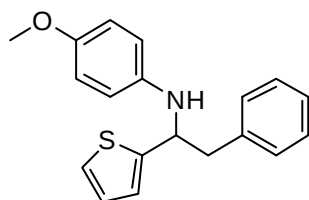


**N-(1-(3,4-dimethylphenyl)-2-phenylethyl)-4-methoxyaniline (3f):** White solid, yield 99%, 97% ee,  $[\alpha]_D^{20} = +34.7$  ( $c = 1.282$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.29 (s, 6H), 2.99 (dd,  $J = 13.8$  Hz,  $J = 8.7$  Hz, 1H), 3.17 (dd,  $J = 13.8$  Hz,  $J = 5.1$  Hz, 1H), 3.71 (s, 3H), 3.88 (br s, 1H), 4.50 (dd,  $J = 8.7$  Hz,  $J = 5.1$  Hz, 1H), 6.48 (d,  $J = 8.7$  Hz, 2H), 6.71 (d,  $J = 8.7$  Hz, 2H), 7.13-7.23 (m, 5H), 7.26-7.36 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.4, 19.9, 45.3, 55.6, 59.7, 114.5, 114.8, 123.7, 126.5, 127.6, 128.5, 129.1, 129.7, 135.1, 136.6, 138.0, 141.2, 141.7, 151.9. HRMS (ESI) Calcd. For  $\text{C}_{23}\text{H}_{26}\text{NO}$   $[\text{M}+\text{H}]^+$ : 332.2009; Found: 332.2008. HPLC conditions: Chiralpak OJ-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 11.49 min,  $tr_{minor}$  = 9.79 min.



**4-methoxy-N-(2-phenyl-1-(3,4,5-trimethylphenyl)ethyl)aniline (3g):** White solid, yield 99%, 96% ee,  $[\alpha]_D^{20} = +31.2$  ( $c = 1.39$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.21 (s, 3H), 2.33 (s, 6H), 2.97 (dd,  $J = 14.1$  Hz,  $J = 9.3$  Hz, 1H), 3.19 (dd,  $J = 14.1$  Hz,  $J = 4.8$  Hz, 1H), 3.72 (s, 3H), 3.91 (br s, 1H), 4.46 (dd,  $J = 9.3$  Hz,  $J = 4.8$  Hz, 1H), 6.49 (d,  $J = 8.7$  Hz, 2H), 6.71 (d,  $J = 8.7$  Hz, 2H), 7.08 (s, 2H), 7.24-7.38 (m, 5H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.1, 20.7, 45.4, 55.6,

59.8, 114.5, 114.8, 125.5, 126.5, 128.5, 129.0, 133.6, 136.5, 138.2, 140.7, 141.9, 151.8. HRMS (ESI) Calcd. For  $C_{24}H_{28}NO$   $[M+H]^+$ : 346.2165; Found: 346.2163. HPLC conditions: Chiralpak OJ-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 9.24 min,  $tr_{minor}$  = 8.32 min.



**4-methoxy-N-(2-phenyl-1-(thiophen-2-yl)ethyl)aniline (3h):** Liquid, yield

97%, 93% ee,  $[\alpha]_D^{20}$  = +33.7 (c = 1.39,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):

$\delta$  3.18 (d,  $J$  = 6.84 Hz, 2H), 3.70 (s, 3H), 3.89 (br s, 1H), 4.80-4.85 (m, 1H),

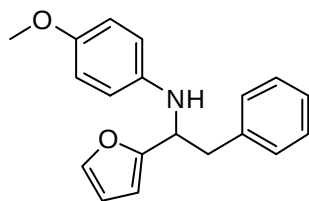
6.54 (d,  $J$  = 8.7 Hz, 2H), 6.71 (d,  $J$  = 8.7 Hz, 2H), 6.86 (d,  $J$  = 3.3Hz, 1H),

6.91-6.94 (m, 1H), 7.15-7.19 (m, 3H), 7.24-7.32 (m, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  45.3, 55.6, 56.4,

114.6, 115.2, 123.7, 123.8, 126.7, 126.8, 128.5, 129.2, 137.4, 141.1. 148.9, 152.4. HRMS (ESI) Calcd. For

$C_{19}H_{20}NOS$   $[M+H]^+$ : 310.1260; Found: 310.1250. HPLC conditions: Chiralpak OD-H column, i-PrOH/

hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 9.98 min,  $tr_{minor}$  = 7.29 min.



**N-(1-(furan-2-yl)-2-phenylethyl)-4-methoxyaniline (3i):** Black liquid, yield

97%, 69% ee,  $[\alpha]_D^{20}$  = -20.2 (c = 1.16,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):

$\delta$  3.20 (d,  $J$  = 6.6 Hz, 2H), 3.5 (br s, 1H), 3.73 (s, 3H), 4.66-4.71 (m, 1H),

6.04 (d,  $J$  = 3.3 Hz, 1H), 6.26-6.27 (m, 1H), 6.56-6.59 (m, 2H), 6.75 (d,  $J$  =

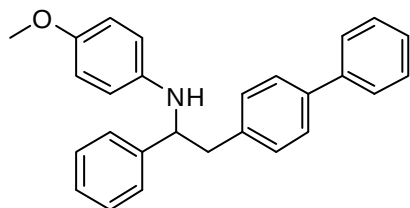
8.7 Hz, 2H), 7.06-7.09 (m, 2H), 7.24-7.27 (m, 3H), 7.39 (dd,  $J$  = 1.8 Hz,  $J$  = 0.6 Hz, 1H).  $^{13}C$  NMR (75

MHz,  $CDCl_3$ ):  $\delta$  40.9, 54.2, 55.6, 106.7, 110.2, 114.7, 115.3, 126.6, 128.3, 129.2, 137.4, 140.9, 141.3,

152.5, 155.4. HRMS (ESI) Calcd. For  $C_{19}H_{20}NO_2$   $[M+H]^+$ : 294.1489; Found: 294.1493. HPLC conditions:

Chiralcel AD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  =

7.52 min,  $tr_{minor}$  = 6.46 min.



**N-(2-(biphenyl-4-yl)-1-phenylethyl)-4-methoxyaniline (3j):**

Liquid, yield 95%, 98% ee,  $[\alpha]_D^{20}$  = +58.3 (c = 1.44,  $CHCl_3$ ).  $^1H$

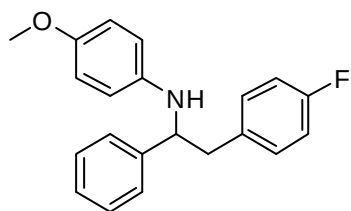
NMR (300 MHz,  $CDCl_3$ ):  $\delta$  3.07 (dd,  $J$  = 13.8 Hz,  $J$  = 8.1 Hz, 1H),

3.19 (dd,  $J$  = 13.8,  $J$  = 5.4 Hz, 1H), 3.70 (s, 3H), 3.79 (br s, 1H),

4.59 (dd,  $J$  = 8.1 Hz,  $J$  = 5.4 Hz, 1H), 6.47 (d,  $J$  = 8.7 Hz, 2H), 6.69 (d,  $J$  = 8.7 Hz, 2H), 7.22-7.26 (m, 3H),

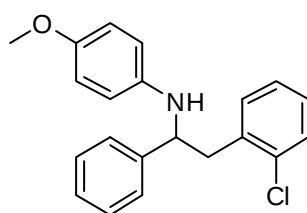
7.32-7.40(m, 5H), 7.44-7.48 (m, 2H) 7.54 (d,  $J$  = 8.1 Hz, 2H), 7.61 (d,  $J$  = 7.2 Hz, 2H).  $^{13}C$  NMR (75 MHz,

CDCl<sub>3</sub>):  $\delta$  44.8, 55.6, 59.9, 114.6, 114.9, 126.5, 126.9, 127.0, 127.2, 128.6, 128.7, 129.6, 136.9, 139.5, 140.7, 141.5, 143.6, 152.1. HRMS (ESI) Calcd. For C<sub>27</sub>H<sub>25</sub>NNaO [M+Na]<sup>+</sup>: 402.1828; Found: 402.1833. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 17.85 min,  $tr_{minor}$  = 54.55 min.



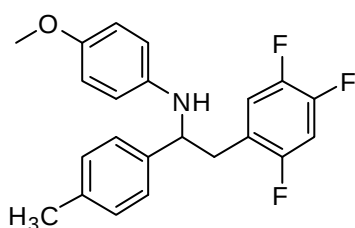
**N-(2-(4-fluorophenyl)-1-phenylethyl)-4-methoxyaniline (3k):** Liquid, yield 95%, 98% ee,  $[\alpha]_D^{20}$  = +41.2 ( $c$  = 1.22, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.98-3.13 (m, 2H), 3.69 (s, 3H), 3.86 (brs, 1H), 4.48-4.52 (m, 1H), 6.44-6.47 (m, 2H), 6.67-6.70 (m, 2H), 6.93-6.99 (m, 2H), 7.04-7.09

(m, 2H), 7.26-7.32 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  44.2, 55.6, 60.1, 114.6, 114.8, 115.2 (d,  $J$  = 21.1 Hz, 2C), 126.4, 127.0, 128.5, 130.6 (d,  $J$  = 7.8 Hz, 2C), 133.3 (d,  $J$  = 3.3 Hz, 1C), 141.3, 143.2, 152.0, 161.6 (d,  $J$  = 243.7 Hz, 1C). HRMS (ESI) Calcd. For C<sub>21</sub>H<sub>21</sub>FNO [M+H]<sup>+</sup>: 322.1602; Found: 322.1606. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 11.60 min,  $tr_{minor}$  = 6.64 min.



**N-(2-(2-chlorophenyl)-1-phenylethyl)-4-methoxyaniline (3l):** Liquid, yield 98%, 95% ee,  $[\alpha]_D^{20}$  = +44 ( $c$  = 1.32, CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) :  $\delta$  3.19 (d,  $J$  = 7.2 Hz, 2H), 3.70 (s, 3H) 4.10 (brs, 1H), 4.63-4.67 (m, 1H), 6.46 (d,  $J$  = 8.7 Hz, 2H) 6.67 (d,  $J$  = 8.7 Hz, 2H), 7.12-7.19 (m, 3H),

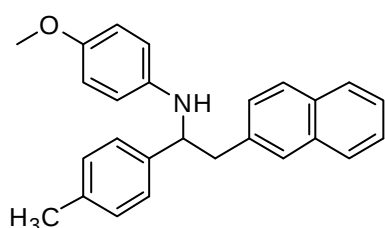
7.25-7.40 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  42.9, 55.7, 58.8, 114.7, 114.8, 126.3, 126.7, 127.1, 128.1, 128.6, 129.7, 131.3, 134.3, 135.9, 141.4, 143.6, 152.0. HRMS (ESI) Calcd. For C<sub>21</sub>H<sub>20</sub>ClNNO [M+Na]<sup>+</sup>: 360.1126; Found: 360.1134. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major}$  = 6.65 min,  $tr_{minor}$  = 4.86 min.



**4-methoxy-N-(1-p-tolyl-2-(2,4,5-trifluorophenyl)ethyl)aniline (3m):**

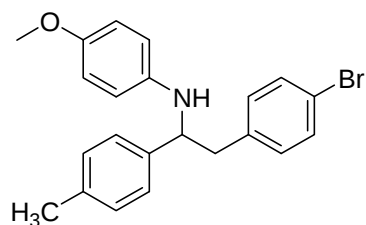
Liquid, yield 87%, 98% ee,  $[\alpha]_D^{20}$  = +16.3 ( $c$  = 1.48, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) :  $\delta$  2.23 (s, 3H), 2.93-2.99 (m, 1H), 3.06-3.13 (m, 1H), 3.45 (brs, 1H), 3.69 (s, 3H), 4.46-4.51 (m, 1H), 6.48 (d,  $J$  = 8.7 Hz, 2H), 6.69 (d,  $J$  = 8.7 Hz, 2H), 6.79-6.94 (m, 2H), 7.12 (d,  $J$  = 7.8 Hz, 2H), 7.18 (d,  $J$  = 8.1 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  21.0, 37.4, 55.5, 58.9, 105.2 (dd,  $J$  = 20.6 Hz,  $J$  = 28.7 Hz, 1C), 114.7, 114.8, 118.8

(dd,  $J = 6.1$  Hz,  $J = 18.8$  Hz, 1C), 121.7 (m, 1C), 126.2, 129.3, 136.9, 139.6, 141.1, 146.5 (octet,  $J = 243.0$  Hz,  $J = 12.2$  Hz,  $J = 3.6$  Hz, 1C), 148.7 (octet,  $J = 248.4$  Hz,  $J = 12.5$  Hz,  $J = 3.4$  Hz, 1C), 152.2, 156.2 (octet,  $J = 241.8$  Hz,  $J = 11.8$  Hz,  $J = 2.5$  Hz, 1C). HRMS (ESI) Calcd. For  $C_{22}H_{20}F_3NNaO$   $[M+Na]^+$ : 394.1389; Found: 394.1400. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major} = 7.34$  min,  $tr_{minor} = 5.63$  min



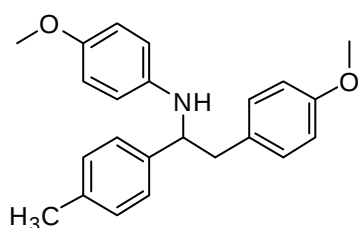
**4-methoxy-N-(2-(naphthalen-2-yl)-1-p-tolylethyl)aniline (3n):**

Liquid, yield 92%, 97% ee,  $[\alpha]_D^{20} = +80$  ( $c = 1.36$ ,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  2.38 (s, 3H), 3.18 (dd,  $J = 13.8$  Hz,  $J = 8.4$  Hz, 1H), 3.32 (dd,  $J = 13.8$  Hz,  $J = 5.4$  Hz, 1H), 3.69 (s, 3H), 3.93 (brs, 1H), 4.65 (dd,  $J = 8.4$  Hz,  $J = 5.4$  Hz), 6.46 (d,  $J = 8.7$  Hz, 2H), 6.68 (d,  $J = 8.7$  Hz, 2H), 7.17 (d,  $J = 7.8$  Hz, 2H), 7.26-7.31 (m, 3H), 7.46-7.53 (m, 2H), 7.65 (s, 1H), 7.77-7.86 (m, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  21.0, 45.4, 55.6, 59.6, 114.6, 114.9, 125.5, 126.0, 126.4, 127.4, 127.5, 127.6, 127.8, 128.1, 129.3, 132.3, 133.4, 135.5, 136.5, 140.7, 141.6, 152.0. HRMS (ESI) Calcd. For  $C_{26}H_{26}NO$   $[M+H]^+$ : 368.2009; Found: 368.2010. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 30/70, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major} = 7.45$  min,  $tr_{minor} = 6.07$  min



**N-(2-(4-bromophenyl)-1-p-tolylethyl)-4-methoxyaniline (3o):**

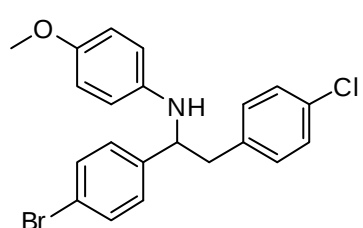
Liquid, yield 99%, 97% ee,  $[\alpha]_D^{20} = +47.4$  ( $c = 1.50$ ,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  2.35 (s, 3H), 2.96-3.10 (m, 2H), 3.45 (br s, 1H), 3.70 (s, 3H), 4.46-4.51 (m, 1H), 6.45-6.48 (m, 2H), 6.69 (d,  $J = 8.7$  Hz, 2H), 6.99 (d,  $J = 8.4$  Hz, 2H), 7.13 (d,  $J = 7.8$  Hz, 2H), 7.19 (d,  $J = 8.1$  Hz, 2H), 7.340 (d,  $J = 8.4$  Hz, 2H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  21.0, 44.3, 55.6, 59.6, 114.6, 114.9, 120.4, 126.4, 129.2, 130.9, 131.4, 136.7, 136.9, 139.9, 141.2, 152.1. HRMS (ESI) Calcd. For  $C_{22}H_{22}BrNNaO$   $[M+Na]^+$ : 418.0777; Found: 418.0780. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 30/70, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{major} = 7.79$  min,  $tr_{minor} = 5.29$  min.



**4-methoxy-N-(2-(4-methoxyphenyl)-1-p-tolylethyl)aniline (3p):**

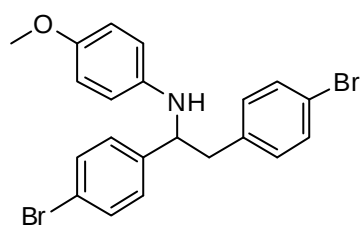
Liquid, yield 98%, 96% ee,  $[\alpha]_D^{20} = +25.2$  ( $c = 1.39$ ,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  2.36 (s, 3H), 2.95 (dd,  $J = 8.1$  Hz,  $J = 13.8$  Hz,

1H), 3.08 (dd,  $J = 5.4$  Hz,  $J = 13.8$  Hz, 1H), 3.52 (br s, 1H), 3.69 (s, 3H), 3.81 (s, 3H), 4.47 (dd,  $J = 5.4$  Hz,  $J = 8.1$  Hz, 1H), 6.45 (d,  $J = 8.7$  Hz, 2H), 6.68 (d,  $J = 8.7$  Hz, 2H), 6.85 (d,  $J = 8.7$  Hz, 2H), 7.08 (d,  $J = 8.7$  Hz, 2H), 7.15 (d,  $J = 7.8$  Hz, 2H), 7.25 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.1, 44.3, 55.1, 55.6, 59.8, 113.9, 114.6, 114.8, 126.4, 129.2, 129.9, 130.1, 136.4, 140.7, 141.7, 151.9, 158.3. HRMS (ESI) Calcd. For  $\text{C}_{23}\text{H}_{26}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 348.1958; Found: 348.1958. HPLC conditions: Chiralcel AD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{\text{major}} = 7.51$  min,  $tr_{\text{minor}} = 6.97$  min.



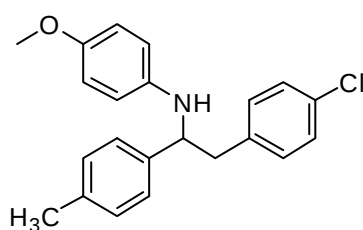
**N-(1-(4-bromophenyl)-2-(4-chlorophenyl)ethyl)-4-methoxyaniline**

**(3q):** Liquid, yield 99%, 97% ee,  $[\alpha]_{\text{D}}^{20} = +48.9$  ( $c = 1.67$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.99-3.05 (m, 2H), 3.69 (s, 3H), 3.83 (br s, 1H), 4.43-4.49 (m, 1H), 6.40-6.44 (m, 2H), 6.66-6.69 (m, 2H), 7.02 (d,  $J = 8.4$  Hz, 2H), 7.16 (d,  $J = 8.4$  Hz, 2H), 7.25 (m, 2H), 7.43 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  44.2, 55.6, 59.4, 114.7, 114.9, 120.8, 128.3, 128.6, 130.5, 131.6, 132.6, 135.7, 140.8, 142.2, 152.3. HRMS (ESI) Calcd. For  $\text{C}_{21}\text{H}_{19}\text{BrClNNaO}$   $[\text{M}+\text{Na}]^+$ : 438.0231; Found: 438.0238. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{\text{major}} = 17.32$  min,  $tr_{\text{minor}} = 7.23$  min.



**N-(1,2-bis(4-bromophenyl)ethyl)-4-methoxyaniline (3r):** Liquid, yield

95%, 93% ee,  $[\alpha]_{\text{D}}^{20} = +25.5$  ( $c = 1.68$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.99 (d,  $J = 6.3$  Hz, 2H), 3.49 (br s, 1H), 3.69 (s, 3H), 4.43-4.47 (m, 1H), 6.40 (d,  $J = 8.7$  Hz, 2H), 6.7 (d,  $J = 8.7$  Hz, 2H), 6.95 (d,  $J = 8.4$  Hz, 2H), 7.15 (d,  $J = 8.4$  Hz, 2H), 7.38-7.43 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  44.2, 55.6, 59.3, 114.7, 114.9, 120.7, 120.8, 128.3, 130.9, 131.6, 131.7, 136.2, 140.8, 142.2, 152.3. HRMS (ESI) Calcd. For  $\text{C}_{21}\text{H}_{19}\text{Br}_2\text{NNaO}$   $[\text{M}+\text{Na}]^+$ : 481.9726, Found: 481.9717. HPLC conditions: Chiralpak OD-H column, i-PrOH/ hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $tr_{\text{major}} = 17.09$  min,  $tr_{\text{minor}} = 7.03$  min.

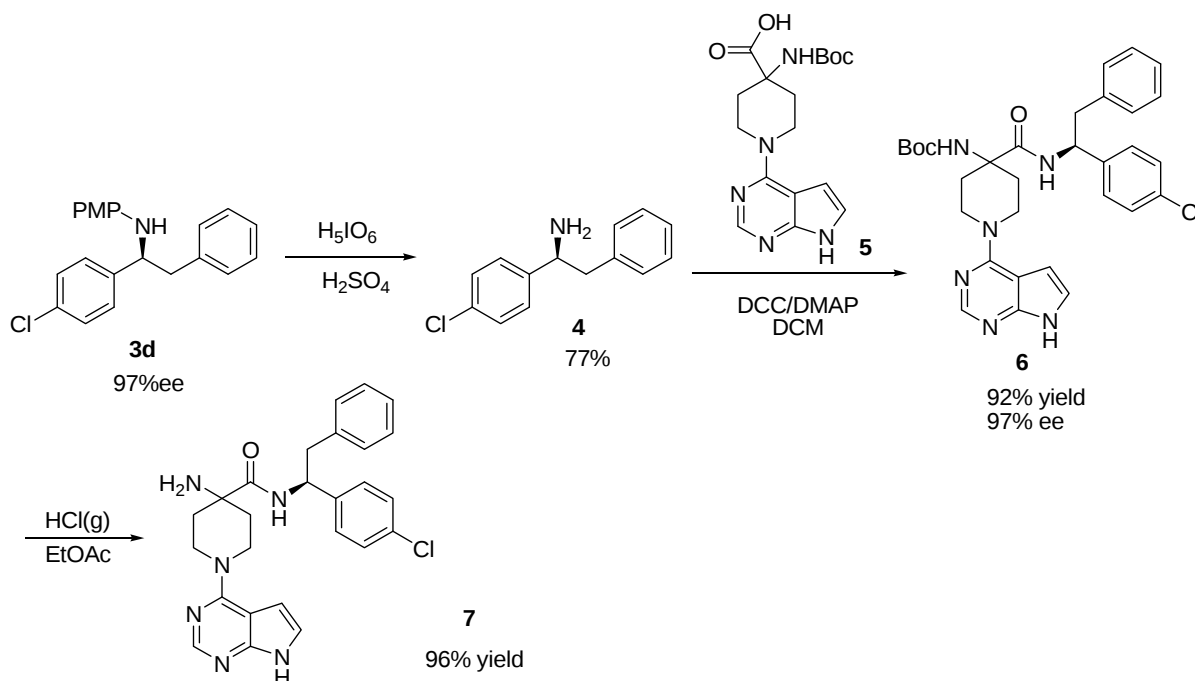


**N-(2-(4-chlorophenyl)-1-p-tolyethyl)-4-methoxyaniline (3s):** Liquid,

yield 97%, 97% ee,  $[\alpha]_{\text{D}}^{20} = +46.0$  ( $c = 0.27$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.34 (s, 3H), 3.07 (d,  $J = 6.3$  Hz, 2H), 3.69 (s, 3H), 3.82

(br s, 1H), 4.45-4.50 (m, 1H), 6.49 (d,  $J = 8.4$  Hz, 2H), 6.68 (d,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 7.8$  Hz, 2H), 7.12 (d,  $J = 7.8$  Hz, 2H). 7.17-7.25 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.6, 43.9, 55.2, 59.2, 114.3, 114.5, 125.9, 128.1, 128.8, 130.1, 131.9, 135.9, 136.2, 139.7, 140.9, 151.7. HRMS (ESI) Calcd. For  $\text{C}_{22}\text{H}_{23}\text{ClNO}$   $[\text{M}+\text{Na}]^+$ : 352.1463; Found: 352.1468. HPLC condition: Chiralpak OD-H column, i-PrOH/hexane: 20/80, flow rate 1.0 mL/min, UV detection at 254 nm,  $t_{r\text{major}} = 11.06\text{min}$ ,  $t_{r\text{minor}} = 6.16\text{ min}$ .

## 5. Synthesis of (S)-4-amino-N-(1-(4-chlorophenyl)-2-phenylethyl)-1-(7H-pyrrolo[2,3-d]pyrimidin-4-yl)piperidine-4-carboxamide (7)



### (S)-1-(4-chlorophenyl)-2-phenylethanamine (4)

To a solution of **3d** (0.97 g, 2.8 mmol) in  $\text{MeCN}/\text{H}_2\text{O}$  (20 mL, 1:1) were added  $\text{H}_5\text{IO}_6$  (0.66 g, 2.8 mmol) and 1 M aqueous  $\text{H}_2\text{SO}_4$  (4.2 mL). The mixture was stirred for 16 h at rt and washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The resulting aqueous phase was subsequently brought to pH 10.5 through addition of 5 M aqueous  $\text{KOH}$  and extracted with  $\text{EtOAc}$  ( $4 \times 20$  mL). The combined organic layers were dried ( $\text{MgSO}_4$ ) and concentrated to afford **4** (0.52 g). Liquid, yield 77%;  $[\alpha]_{\text{D}}^{20} = +118.8$  ( $c = 1.02$ ,  $\text{MeOH}/0.1\text{N HCl}$ : 50/50), lit<sup>6</sup>:  $[\alpha]_{\text{D}}^{20} = -117.0$  ( $c = 1.02$ ,  $\text{MeOH}/0.1\text{N HCl}$ : 50/50, 77 % ee,  $R$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.53 (br s, 2H), 2.81 (dd,  $J = 13.2$  Hz,  $J = 8.7$  Hz, 1H), 2.97 (dd,  $J = 13.2$  Hz,  $J = 5.1$  Hz, 1H), 4.19 (dd,  $J = 8.7$  Hz,  $J = 5.1$  Hz, 1H), 7.14-7.17 (m, 2H), 7.20-7.32 (m, 7H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  46.4, 56.9, 126.4, 127.8, 128.4, 129.2, 132.5, 138.5, 143.9.

**4-(tert-butoxycarbonylamino)-1-(7H-pyrrolo[2,3-d]pyrimidin-4-yl)piperidine-4-carboxylic acid (5)**

Compound **5** was prepared according to the literature method.<sup>7</sup> White solid, yield 92%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  1.38 (s, 9H), 1.85-1.92 (m, 2H), 1.98-2.06 (m, 2H), 3.44-3.51 (m, 2H), 4.27-4.31 (m, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.28 (br s, 1H), 8.13 (s, 1H), 11.6 (s, 1H).

**(S)-tert-butyl 4-(1-(4-chlorophenyl)-2-phenylethylcarbamoyl)-1-(7H-pyrrolo[2,3-d]pyrimidin-4-yl)piperidine-4-ylcarbamate (6)**

Compound **5** (2.13 g, 5.89 mmol), compound **4** (1.36 g, 5.86 mmol) and DMAP (10 mg) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL). A solution of cyclohexylcarbodiimide (1.58 g, 7.66 mmol) in dichloromethane was added dropwise. After the addition, the mixture was stirred at room temperature for 24 h. The mixture was filtered, the filtrate was evaporated and subjected to chromatography to give 3.09 g of the desired compound **6**. White solid, yield 92%.  $[\alpha]_D^{20} = -13.9$  (*c* = 1.32, DMSO). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  1.36 (s, 9H), 1.56-1.58 (m, 2H), 1.76-1.78 (m, 2H), 3.01-3.03 (m, 2H), 3.55-3.58 (m, 2H), 3.65-3.69 (m, 1H), 4.07 (d, *J* = 13.2 Hz, 2H), 5.09-5.14 (m, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 6.96 (s, 1H), 7.15-7.22 (m, 6H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.13 (s, 1H), 11.68 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  28.2, 41.1, 41.5, 41.8, 53.1, 57.1, 78.4, 101.0, 102.0, 121.3, 126.2, 127.9, 128.0, 128.6, 129.3, 131.2, 138.6, 142.4, 150.7, 151.9, 154.4, 156.2, 172.8. HPLC condition: Chiralpak AD-H column, i-PrOH/ hexane: 30/70, flow rate 1.0 mL/min, UV detection at 254 nm, *tr*<sub>major</sub> = 10.09 min, *tr*<sub>minor</sub> = 15.96 min.

**(S)-4-amino-N-(1-(4-chlorophenyl)-2-phenylethyl)-1-(7H-pyrrolo[2,3-d]pyrimidin-4-yl)piperidine-4-carboxamide (7)**

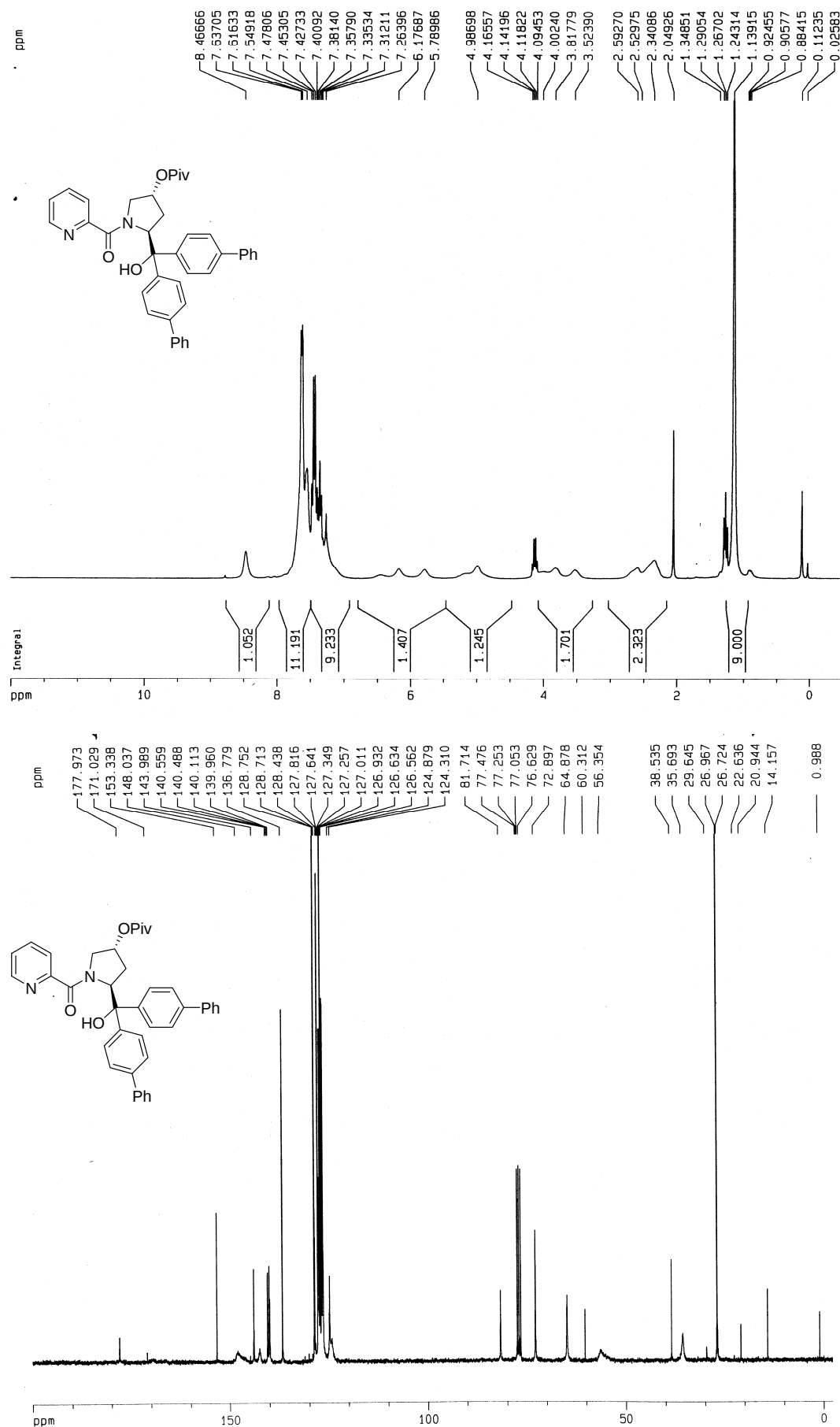
Compound **6** (0.80 g, 1.39 mmol) was charged in a 50 mL round-bottom flask. A solution of EtOAc (15 mL) saturated with HCl (gas) was added. The mixture was stirred at room temperature until **5** disappeared completely monitored by TLC. The volatiles were removed under vacuum. The residue was diluted with EtOAc (20 mL), H<sub>2</sub>O (5 mL) and Na<sub>2</sub>CO<sub>3</sub> (1.50 g) were added. The mixture was stirred at room temperature for 0.5 h. the organic phase was separated. The aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum and subjected to chromatography to give 0.63 g of the desired compound **7**. White solid, yield 96%.  $[\alpha]_D^{20} = -40.0$  (*c* = 0.18, CHCl<sub>3</sub>). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$  1.23-1.27 (m,

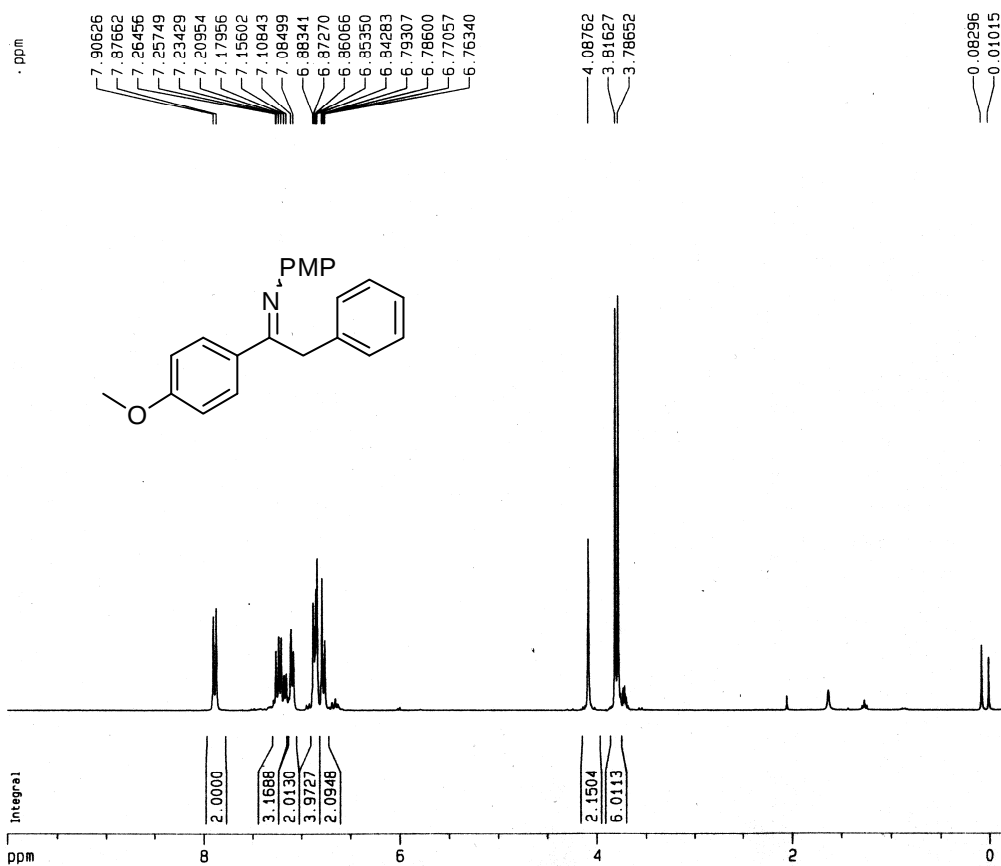
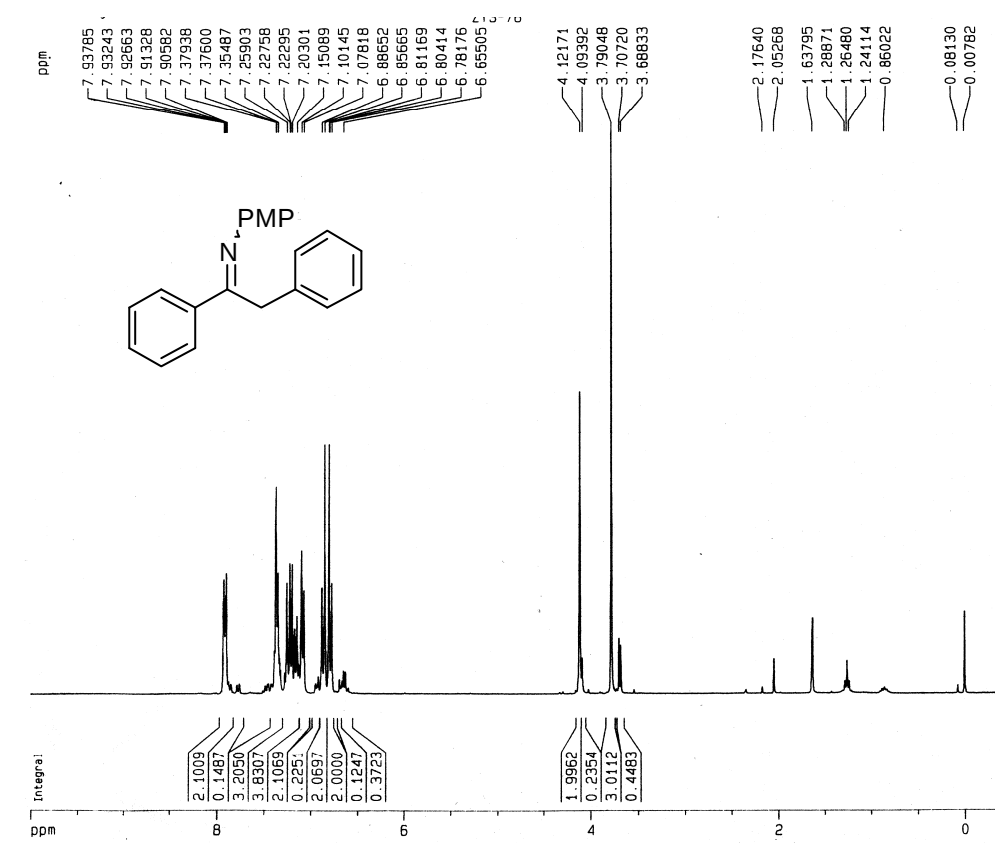
2H), 1.74-1.85 (m, 2H), 2.25 (br s, 2H), 3.01-3.03 (m, 2H), 3.47-3.55 (m, 2H), 4.15-4.25 (m, 2H), 5.02-5.05 (m, 1H), 6.53 (d,  $J = 2.4$  Hz, 1H), 7.14-7.24 (m, 6H), 7.34-7.37 (m, 4H), 8.11 (s, 1H), 8.44 (d,  $J = 8.4$  Hz, 1H), 11.6 (s, 1H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz):  $\delta$  34.1, 34.2, 41.1, 41.3, 41.8, 53.3, 55.6, 100.9, 102.0, 121.1, 126.2, 128.0, 128.1, 128.5, 129.3, 131.3, 138.3, 142.3, 150.7, 151.9, 156.1, 175.9. HRMS (ESI) Calcd. For  $\text{C}_{26}\text{H}_{28}\text{ClN}_6\text{O}$   $[\text{M}+\text{H}]^+$ : 475.2008; Found: 475.2022.

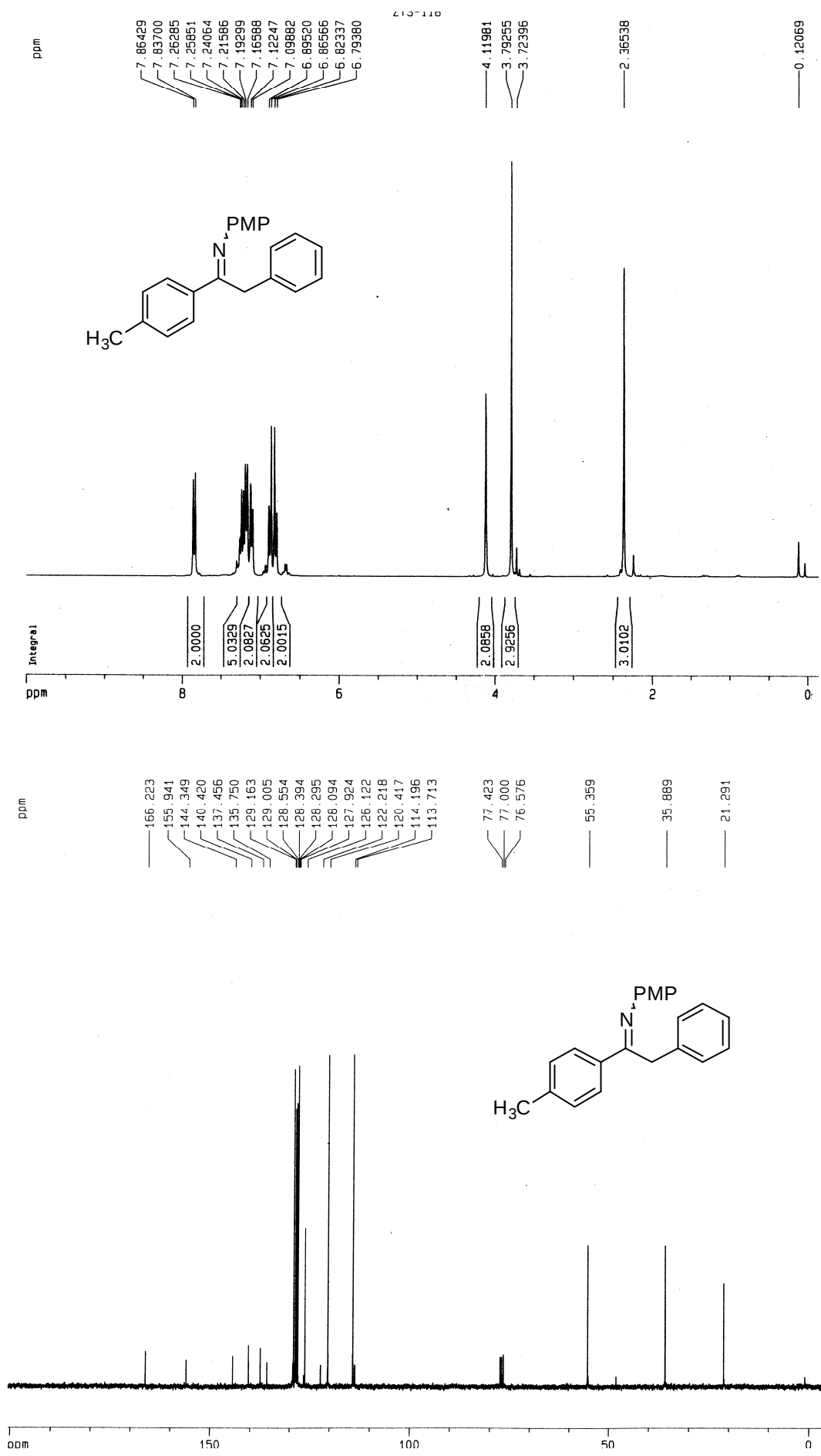
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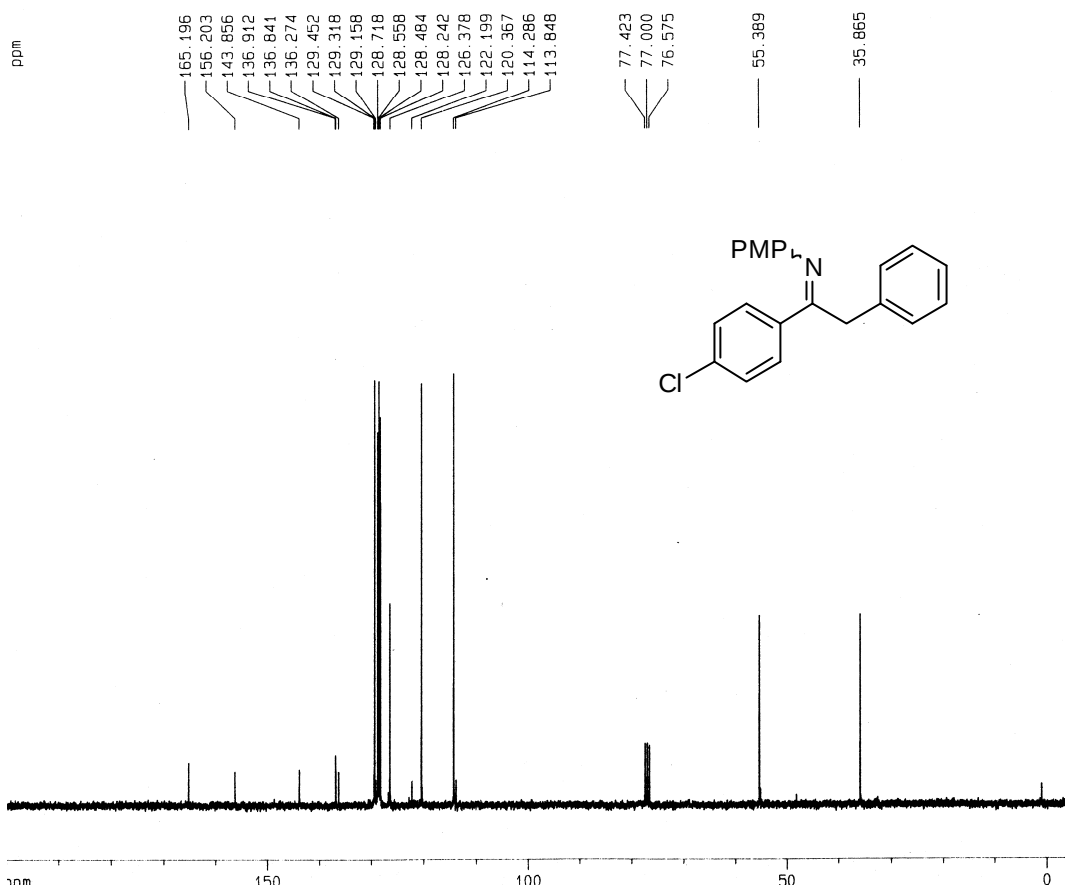
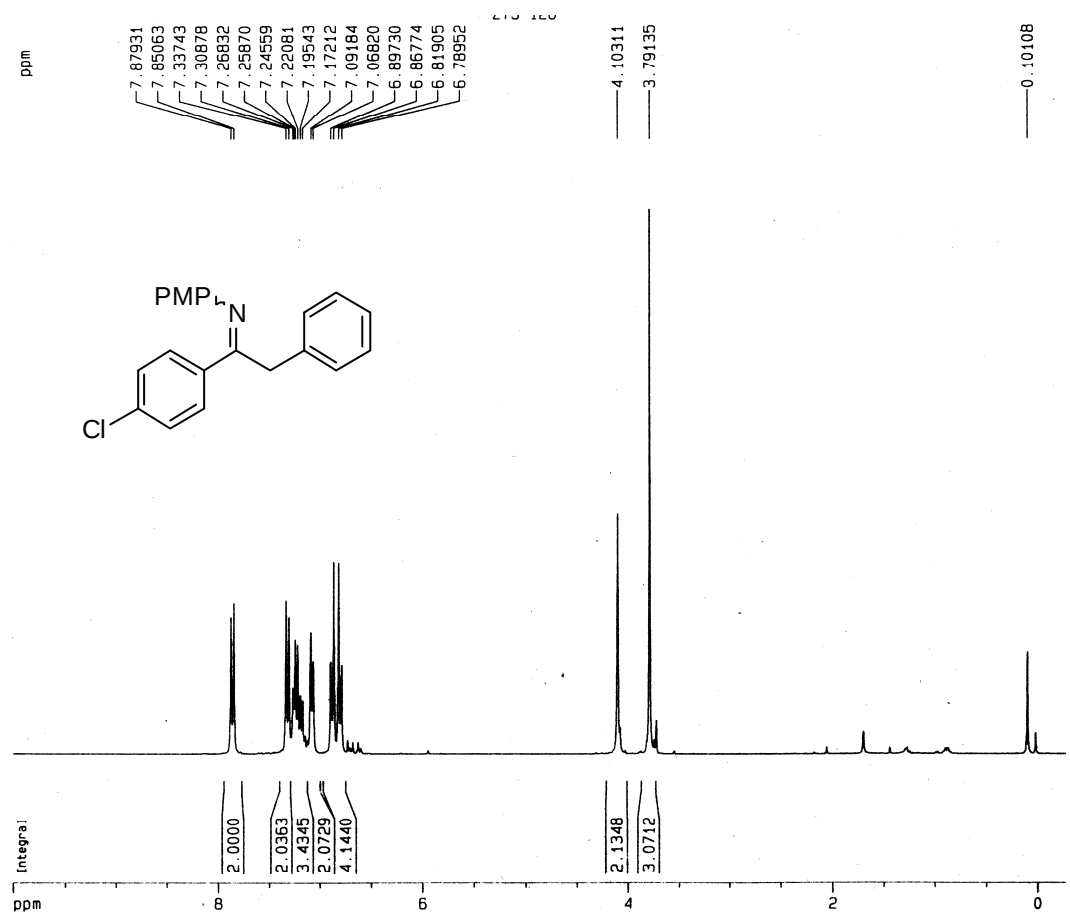
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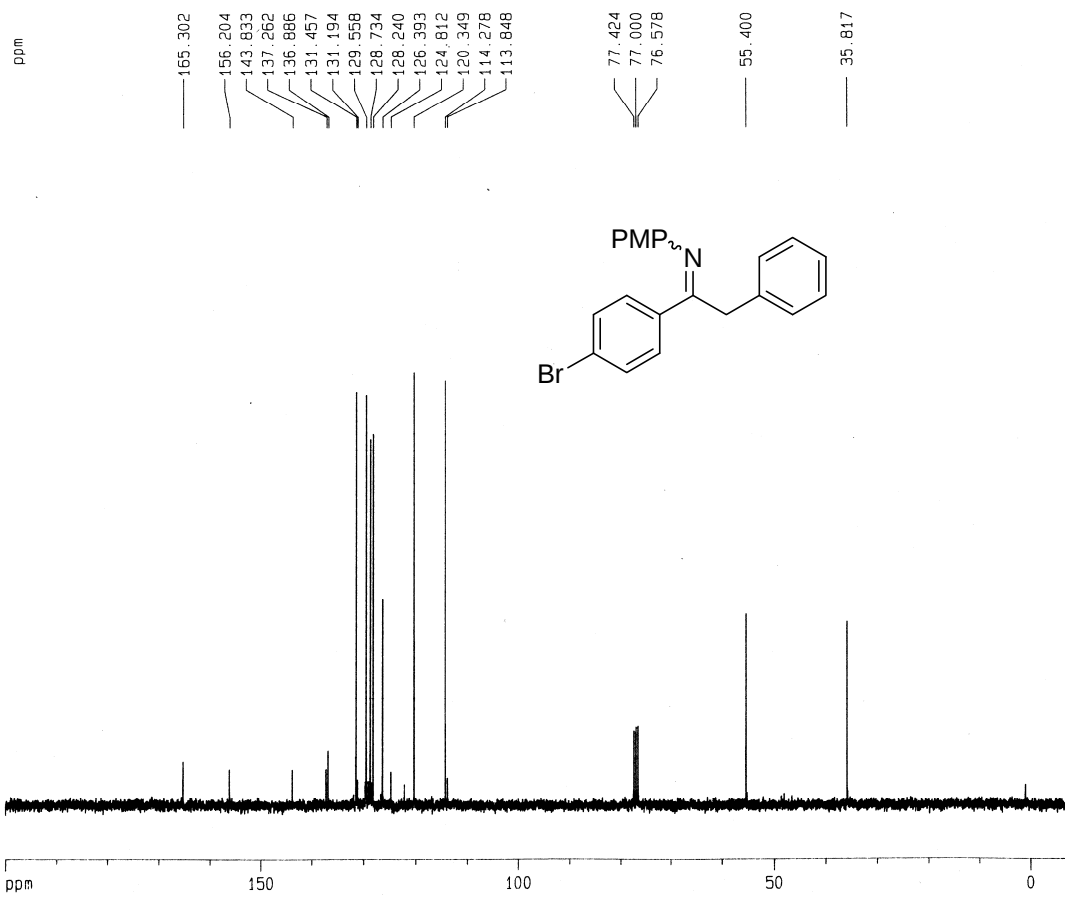
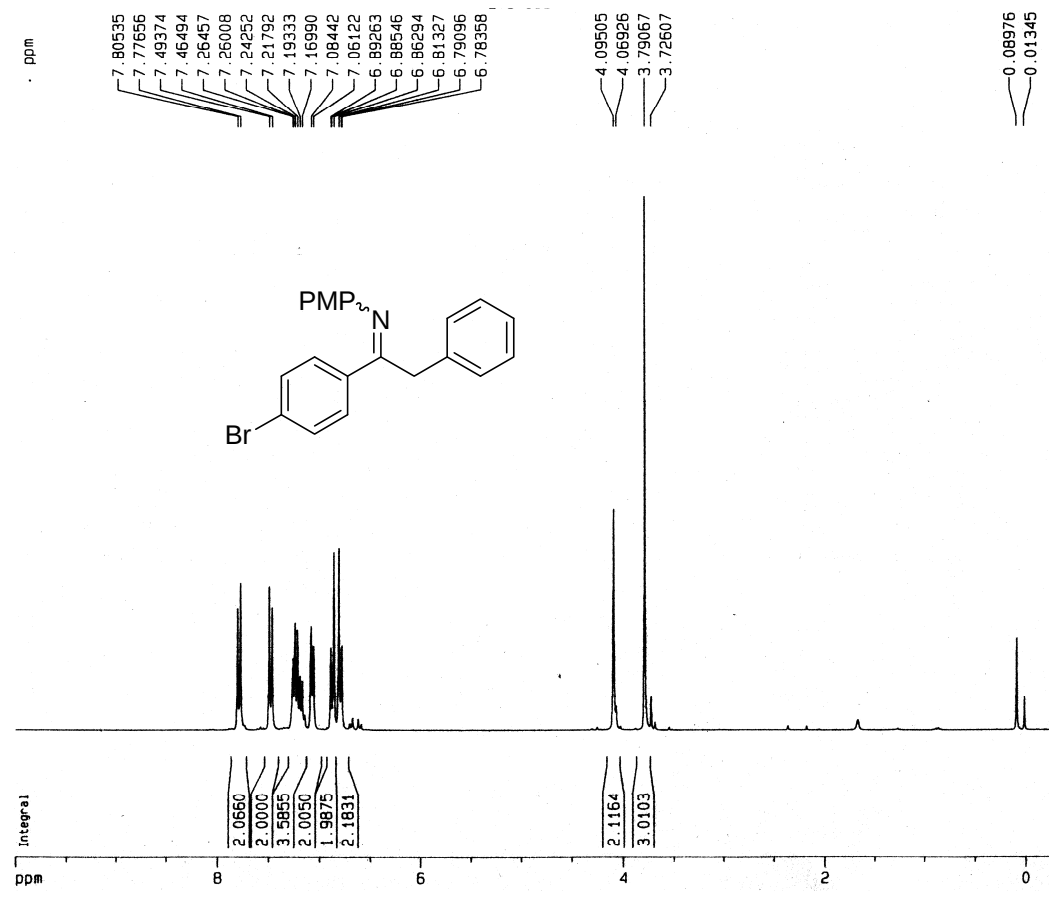
## 6. The Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR Spectra

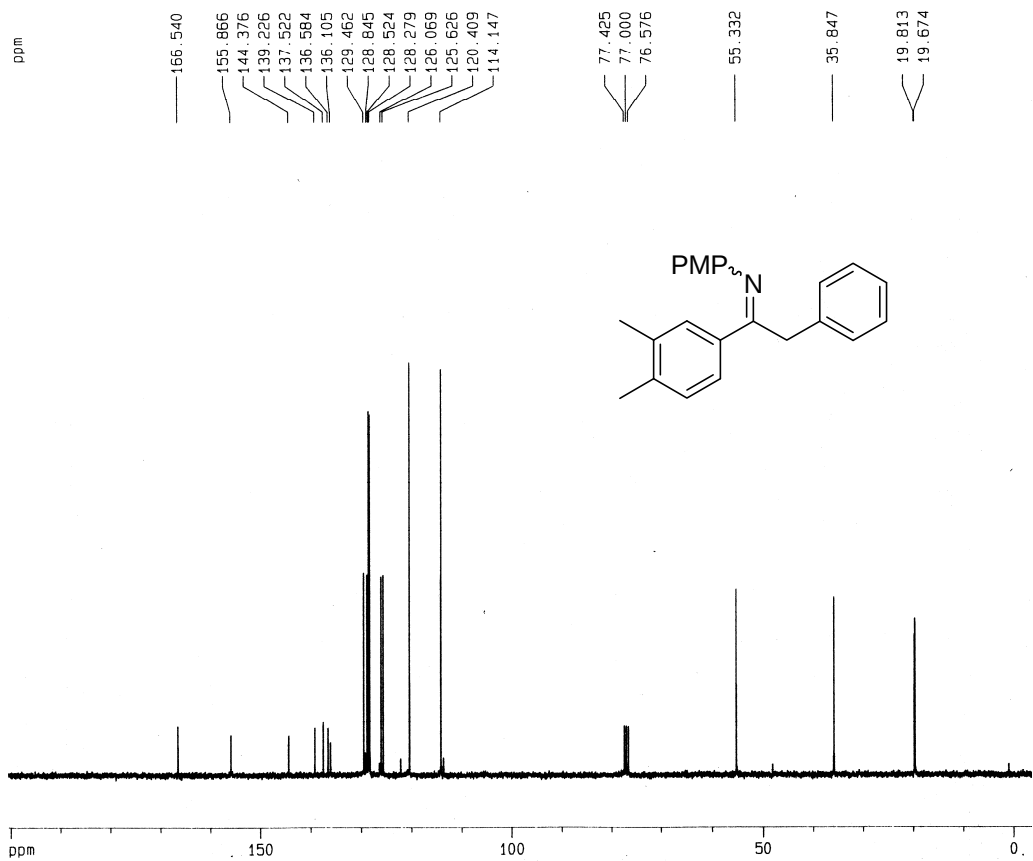
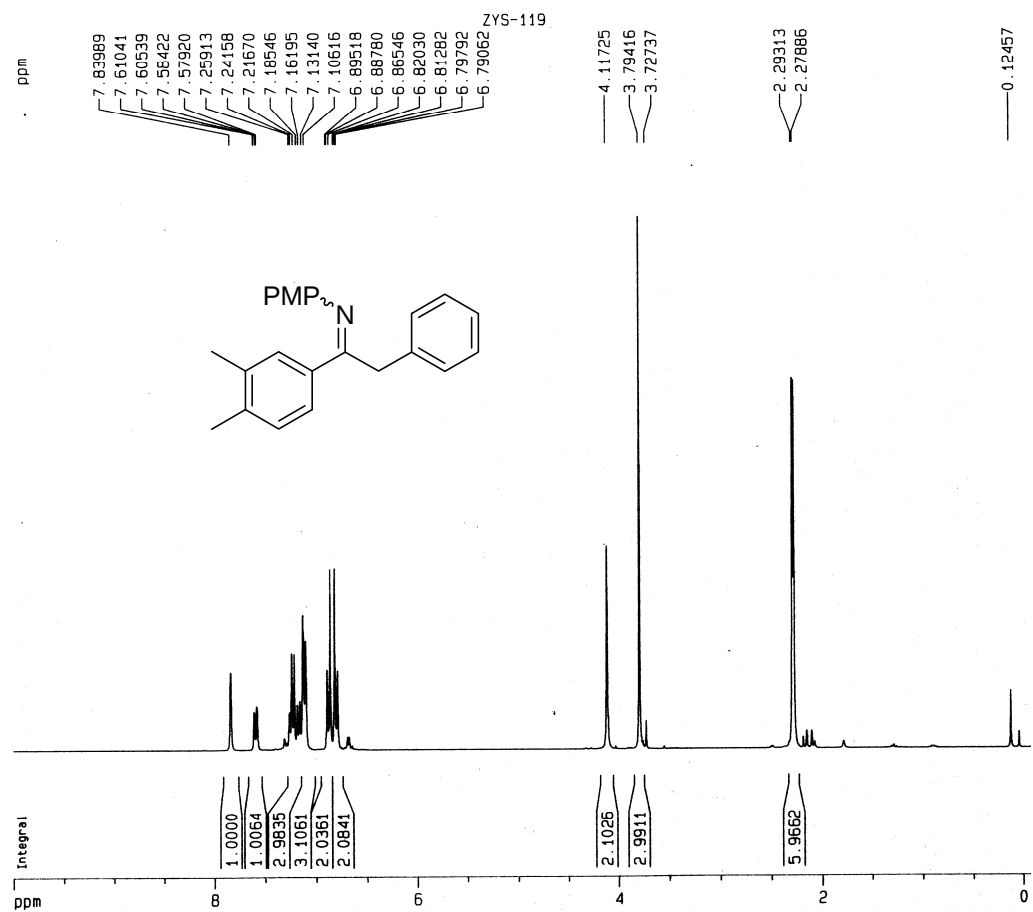


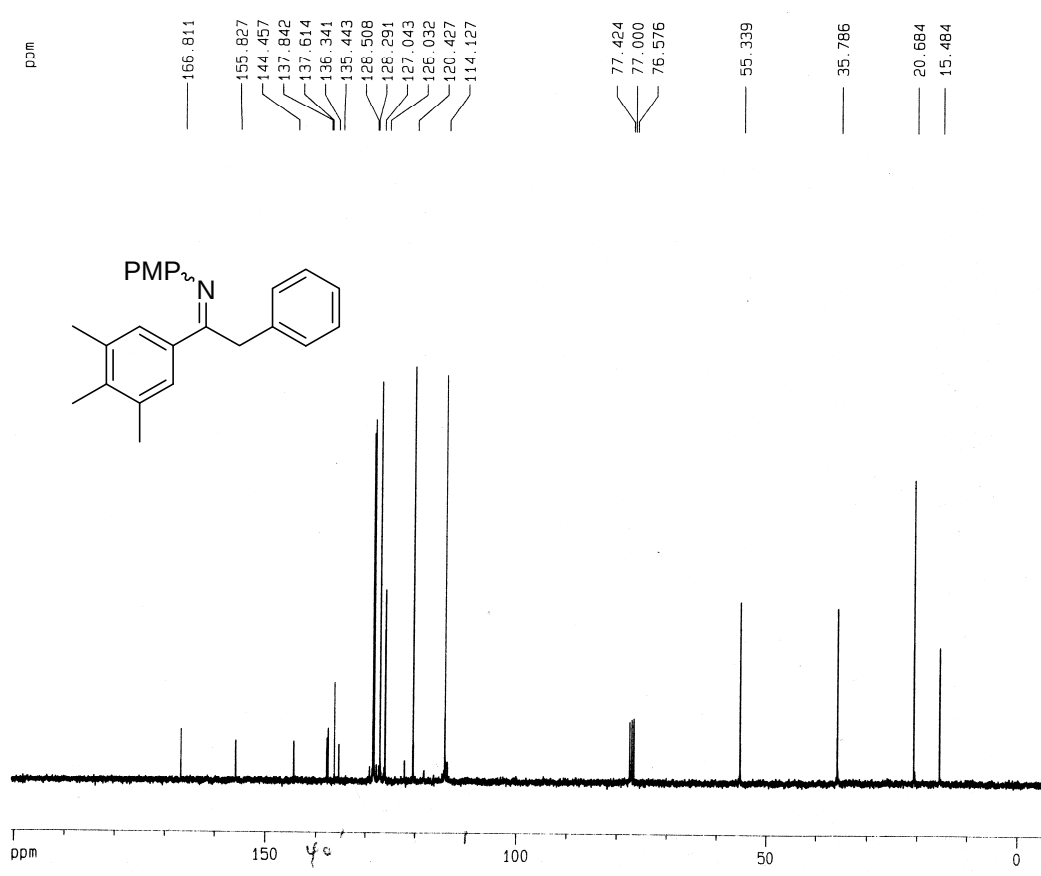
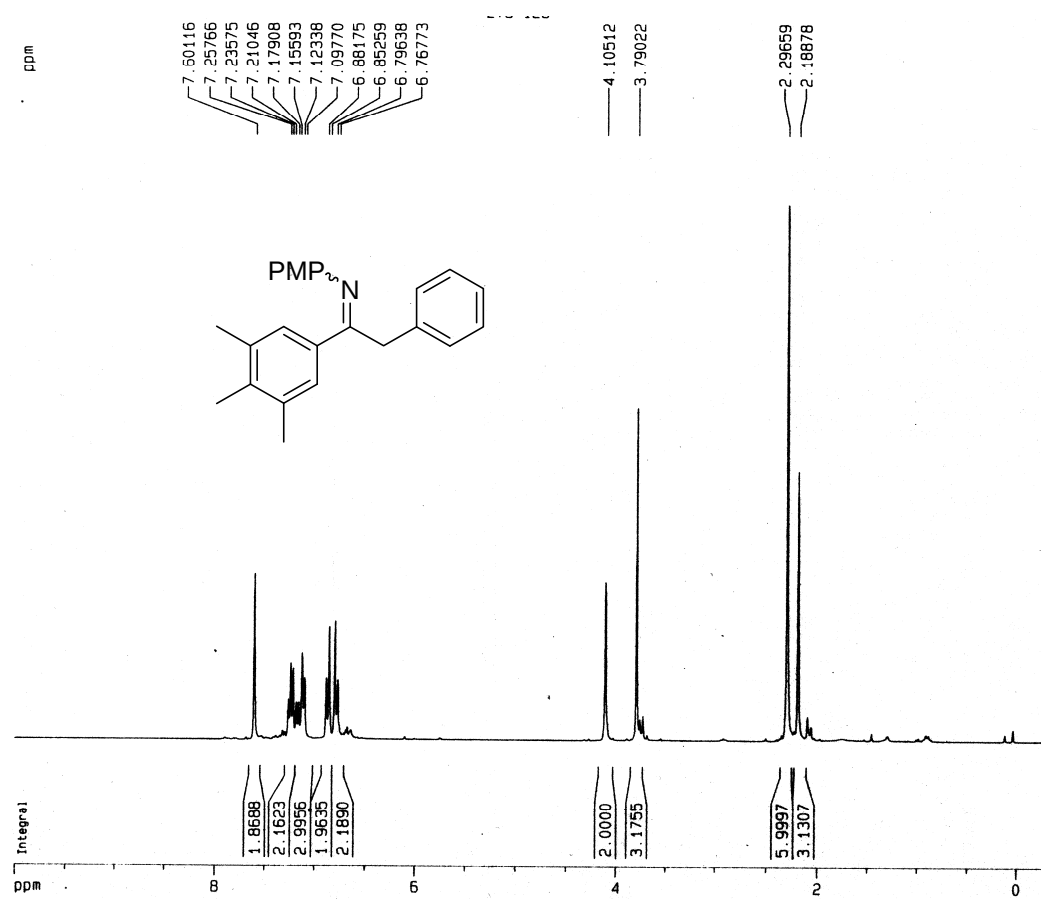


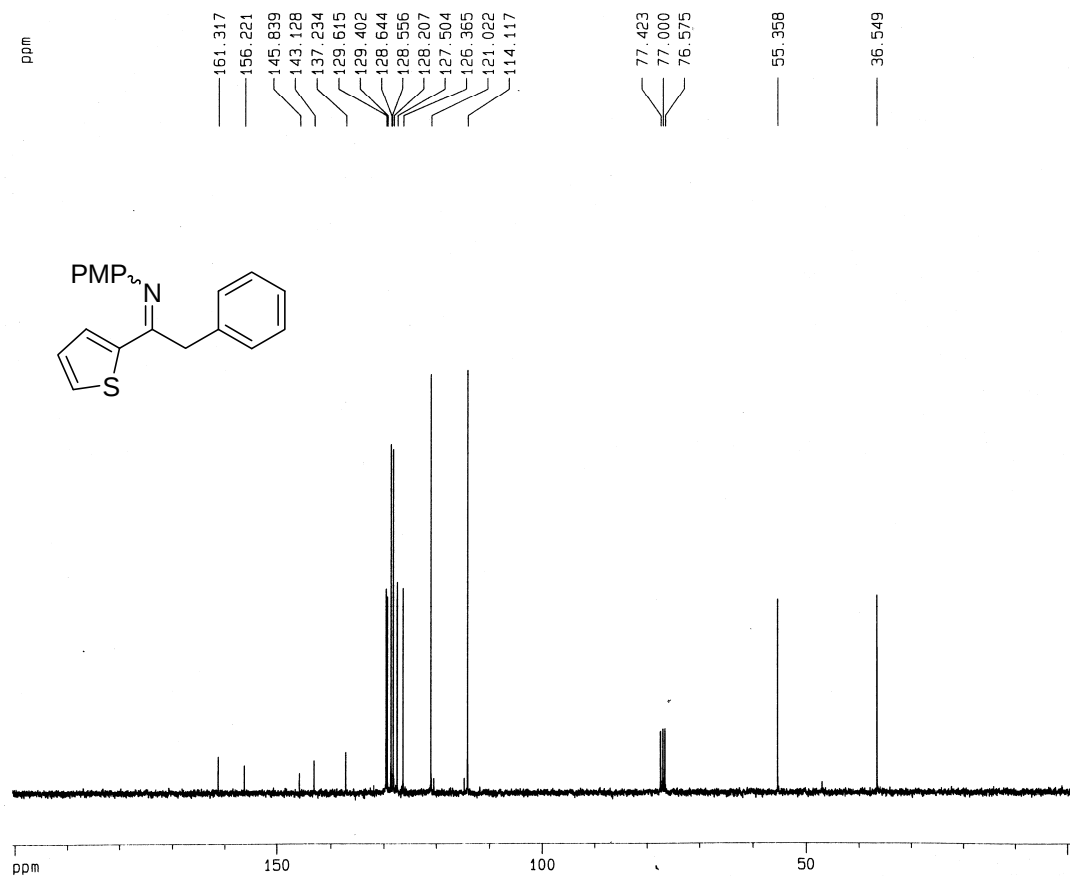
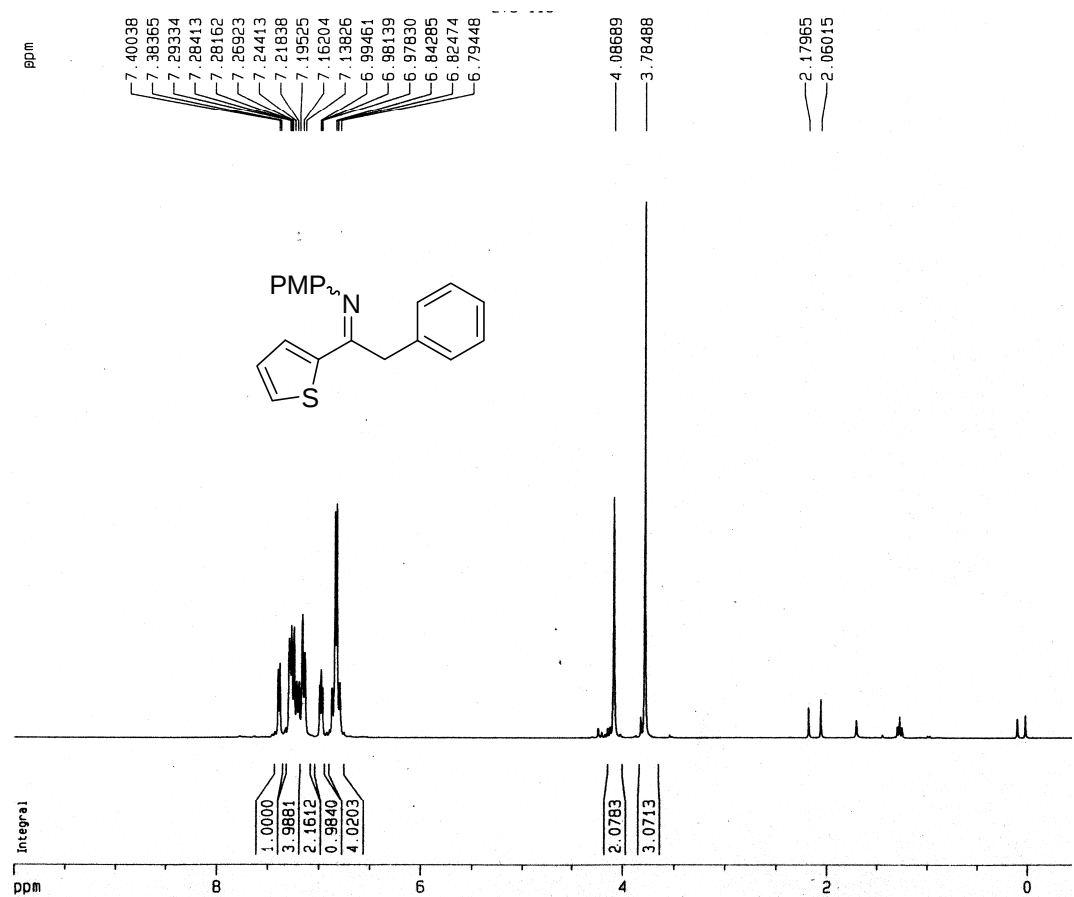


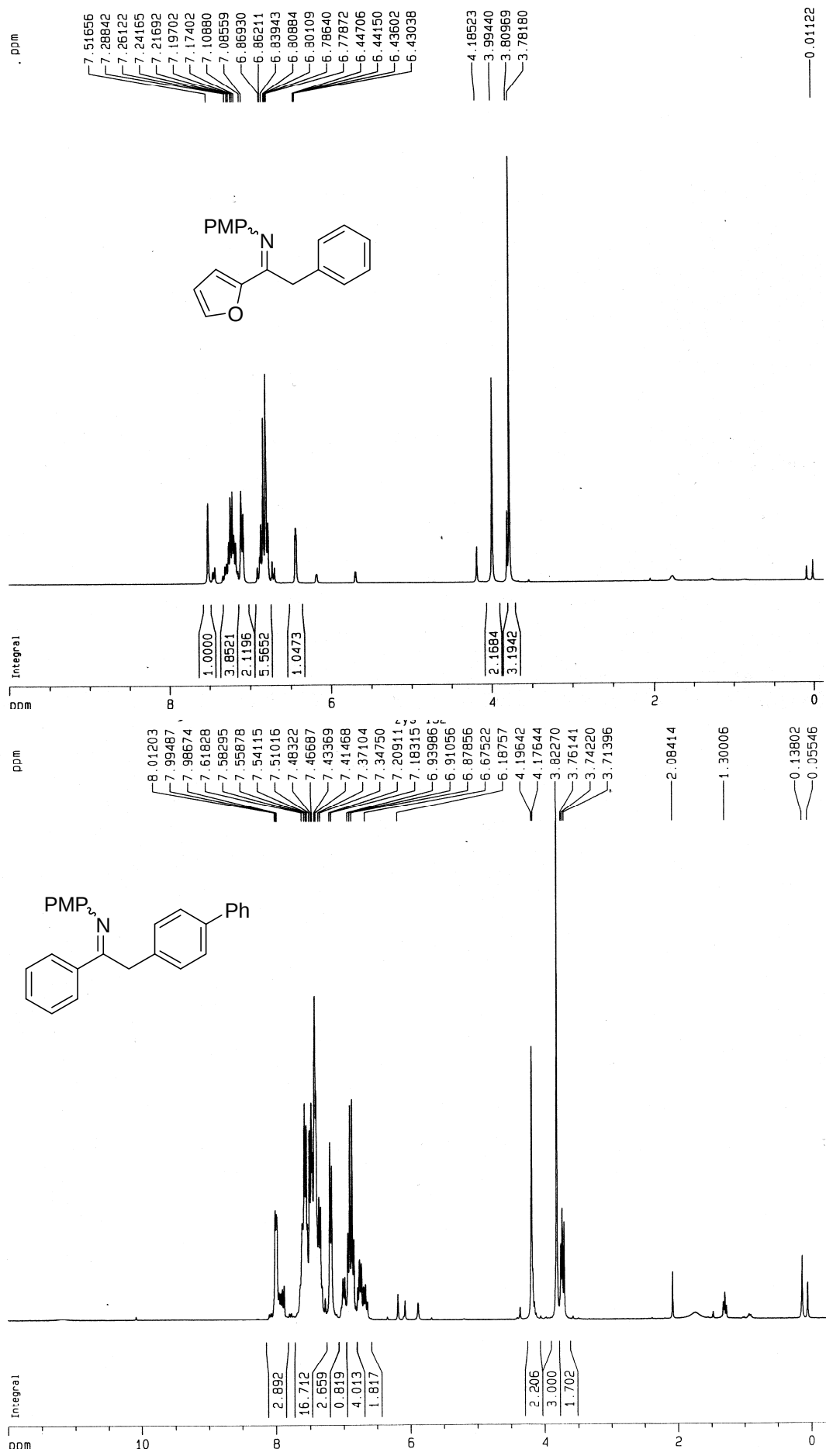


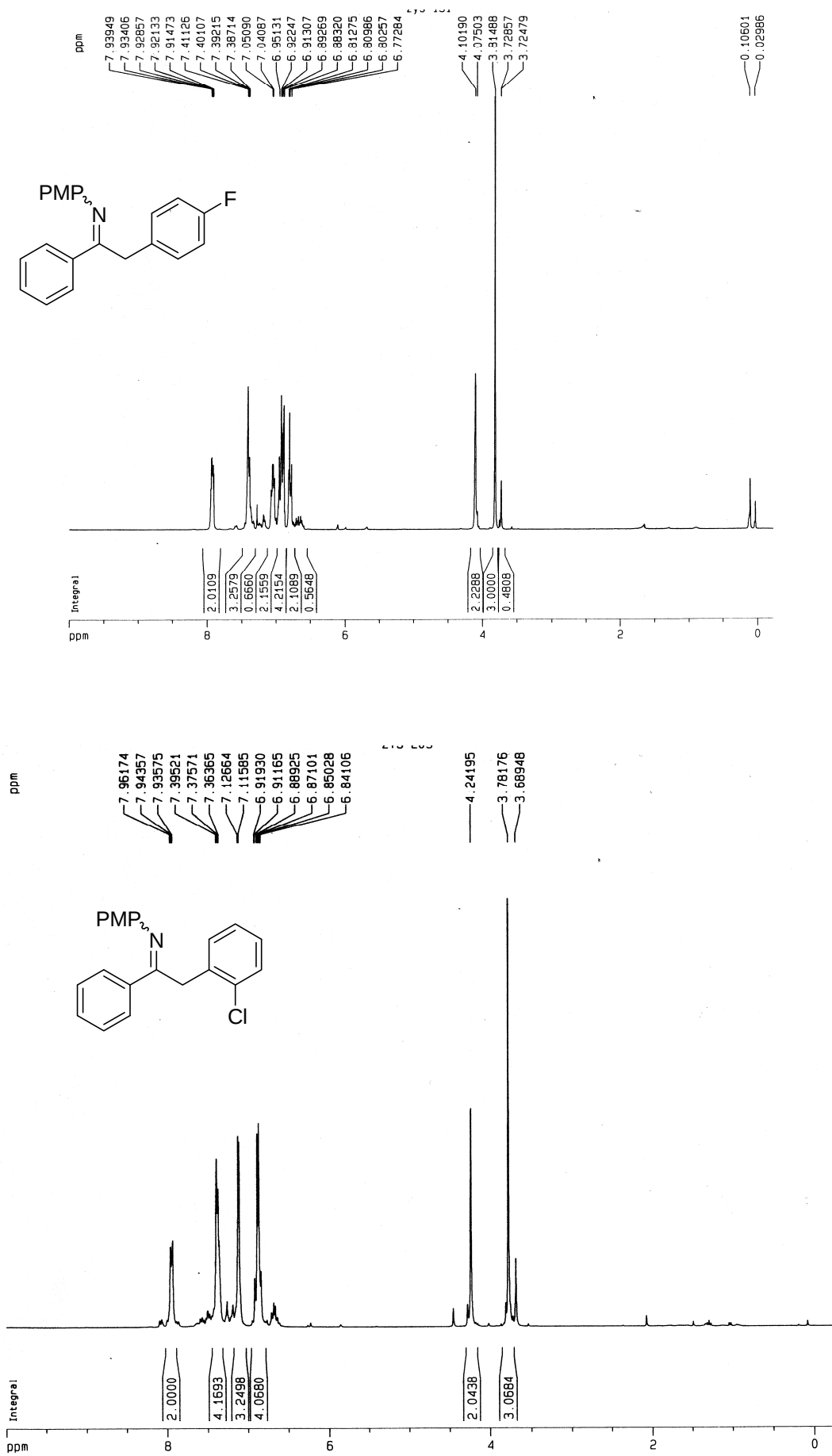


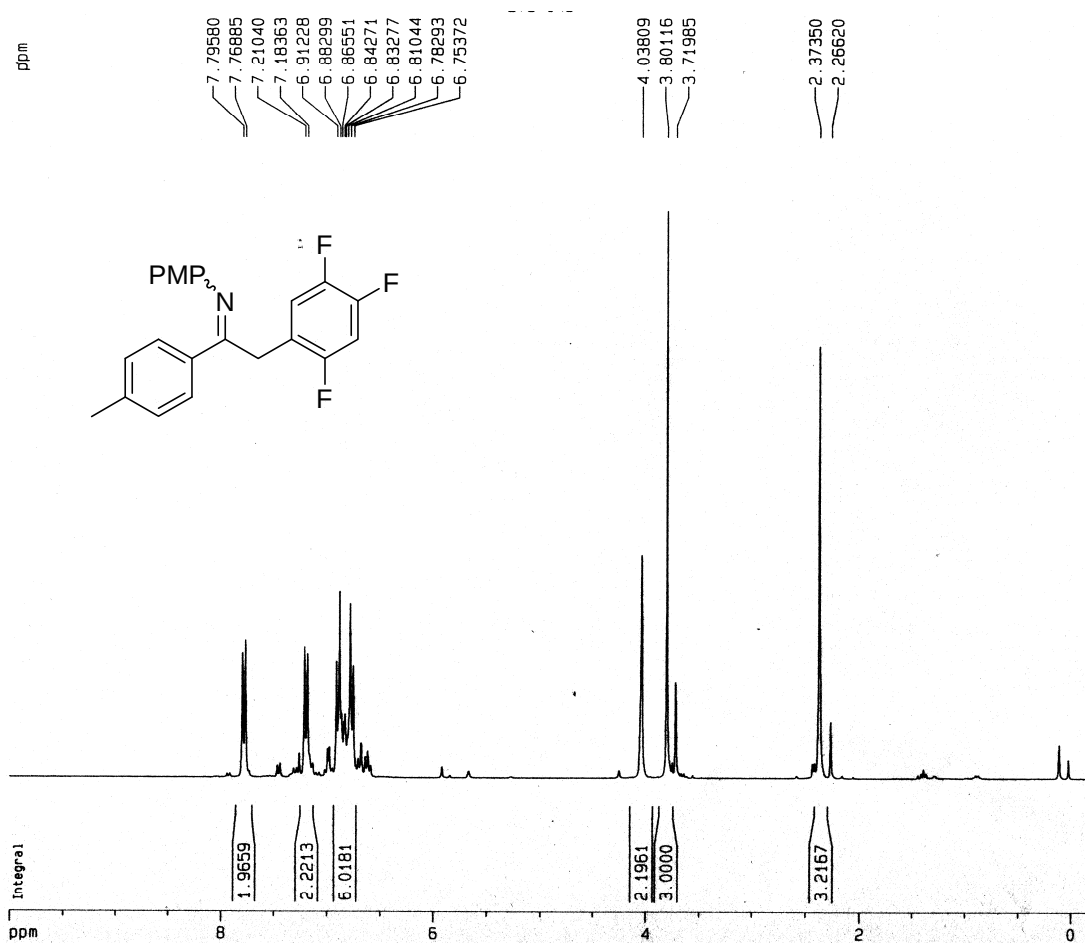
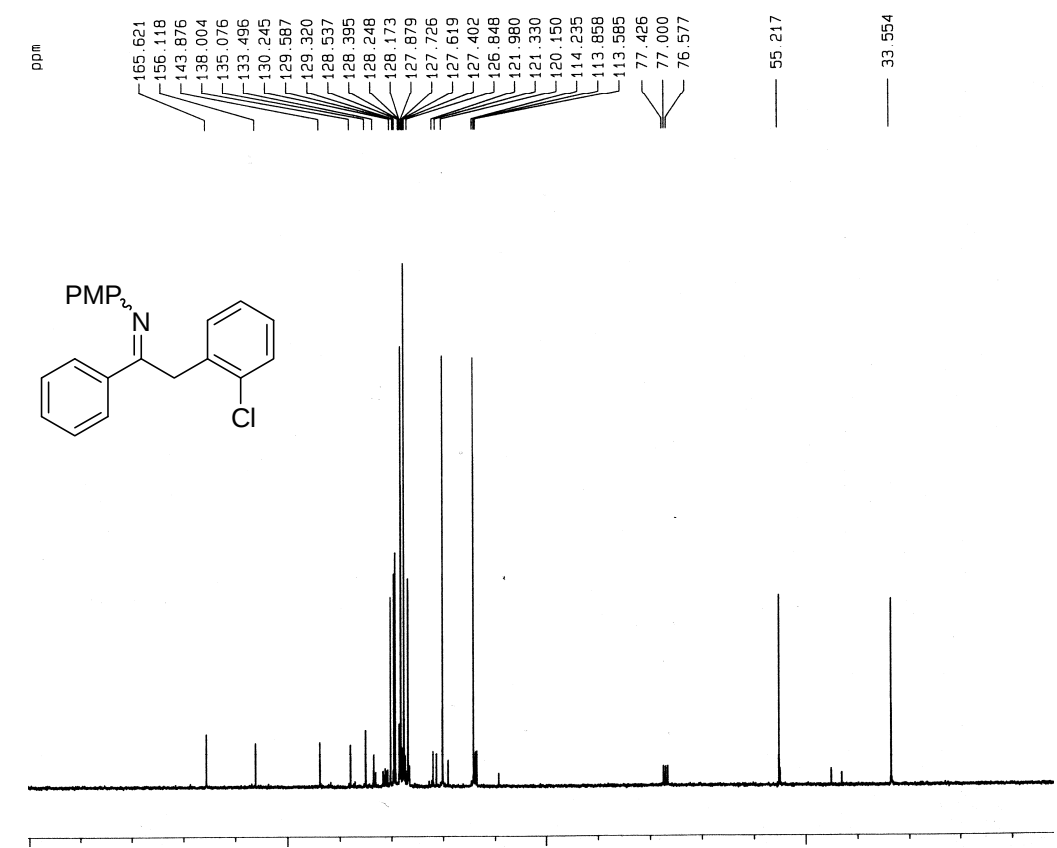


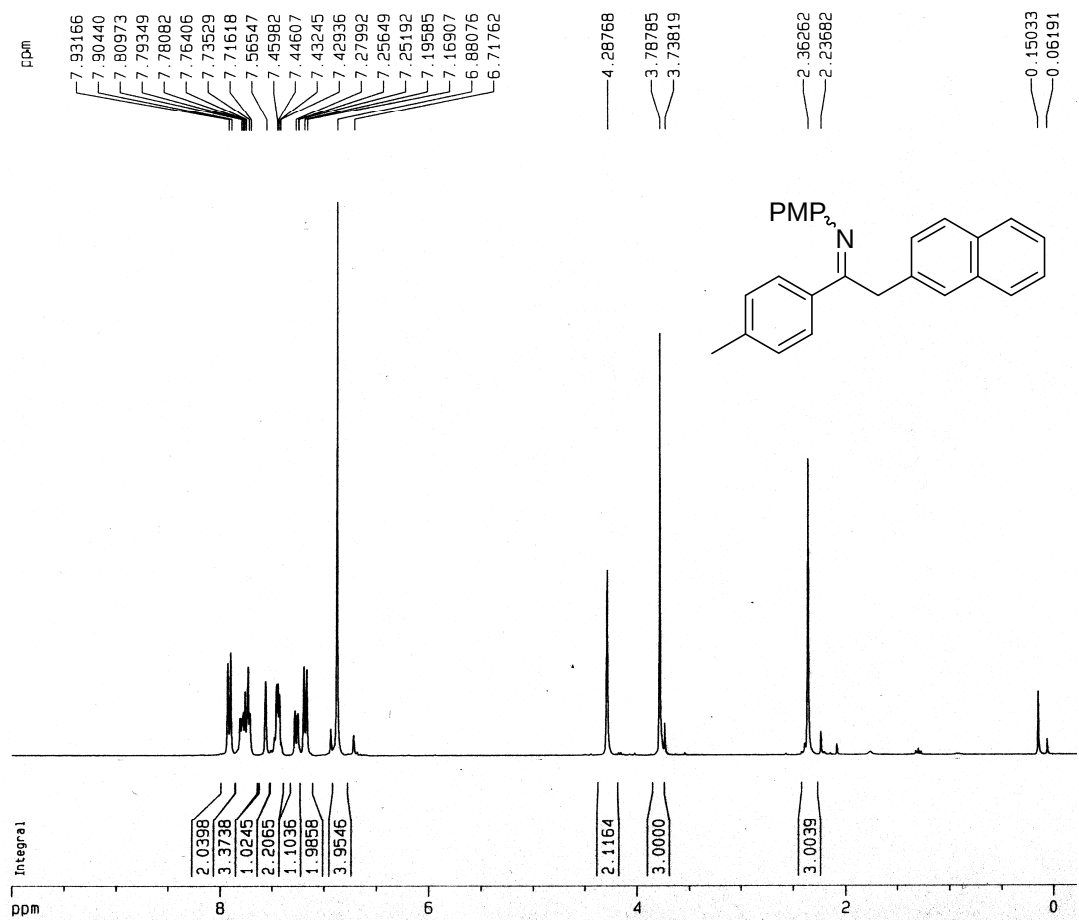
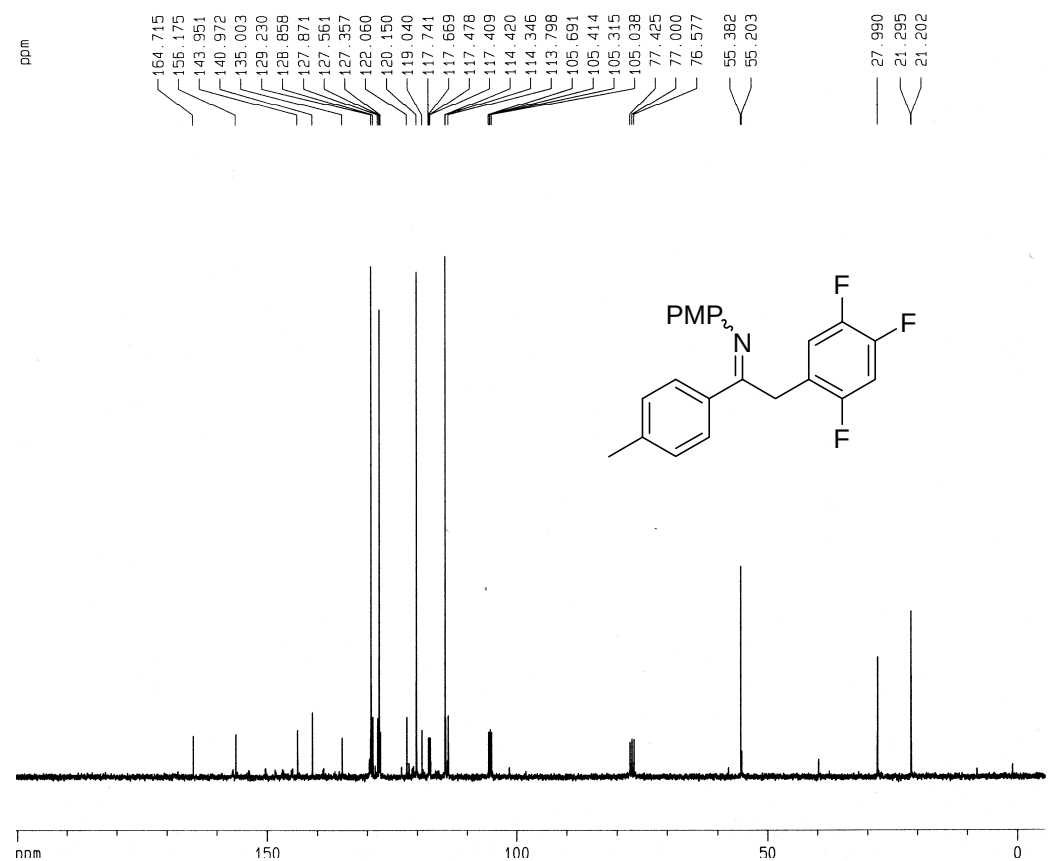


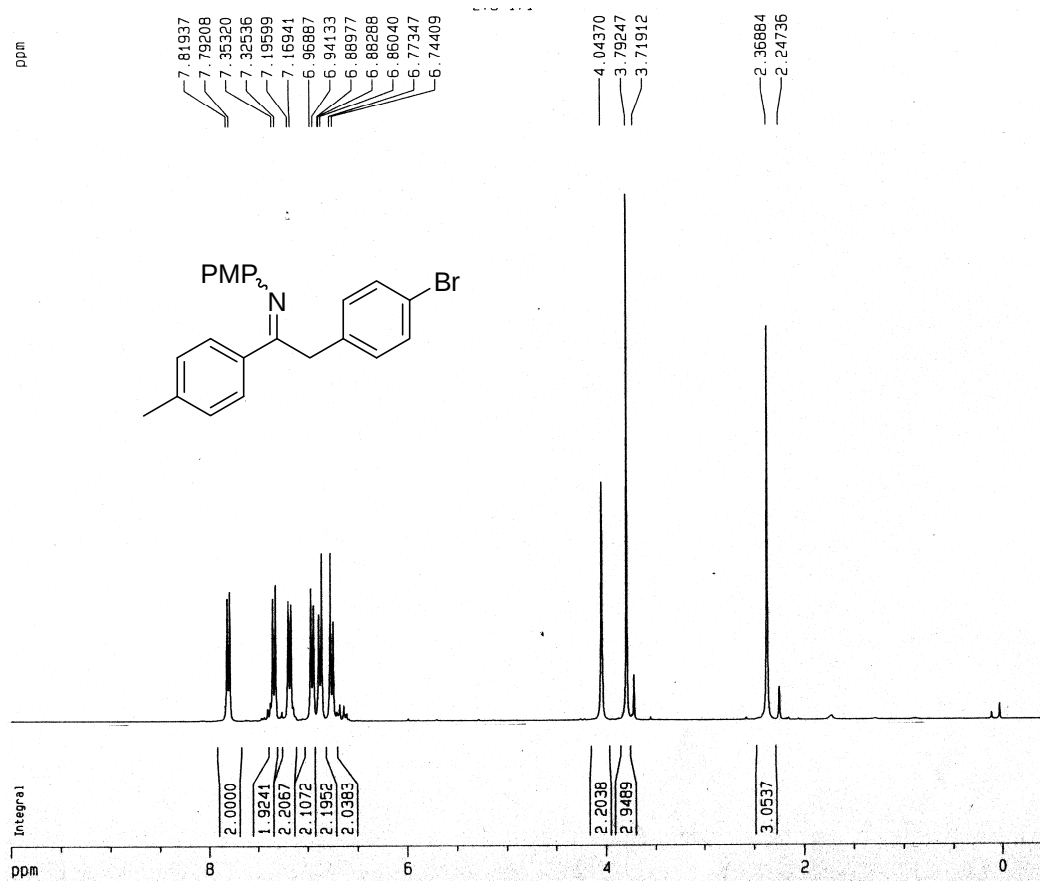
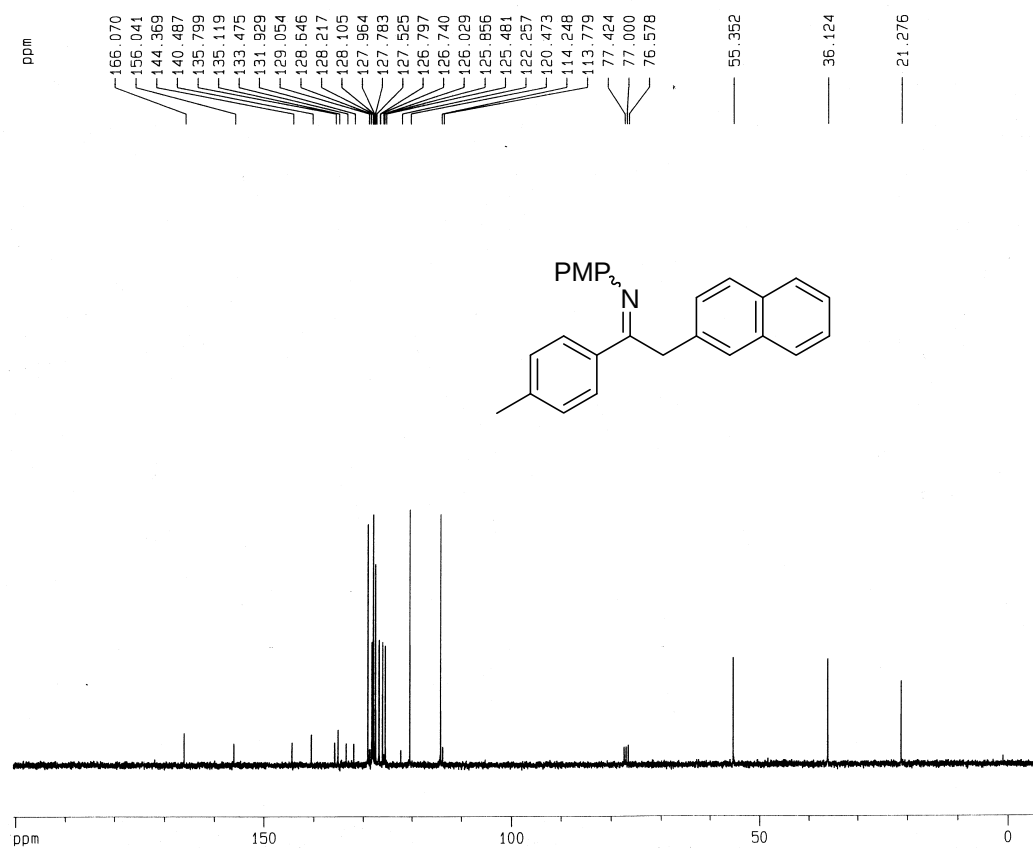


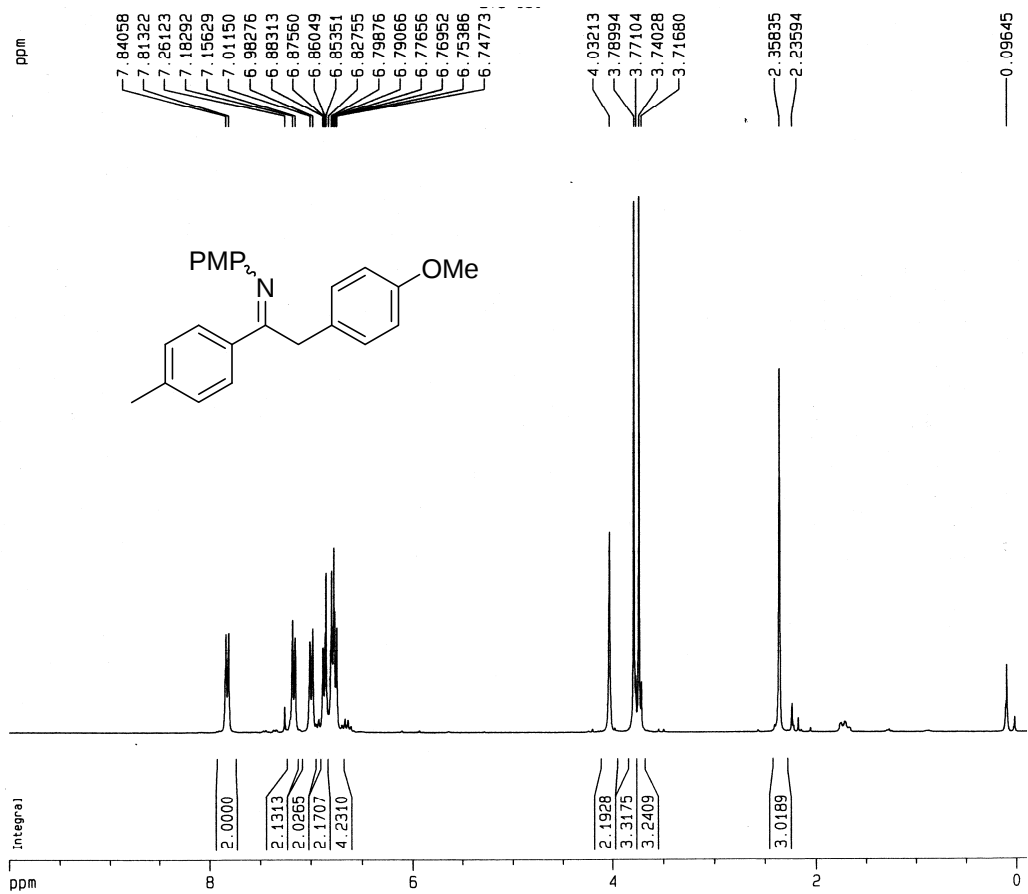
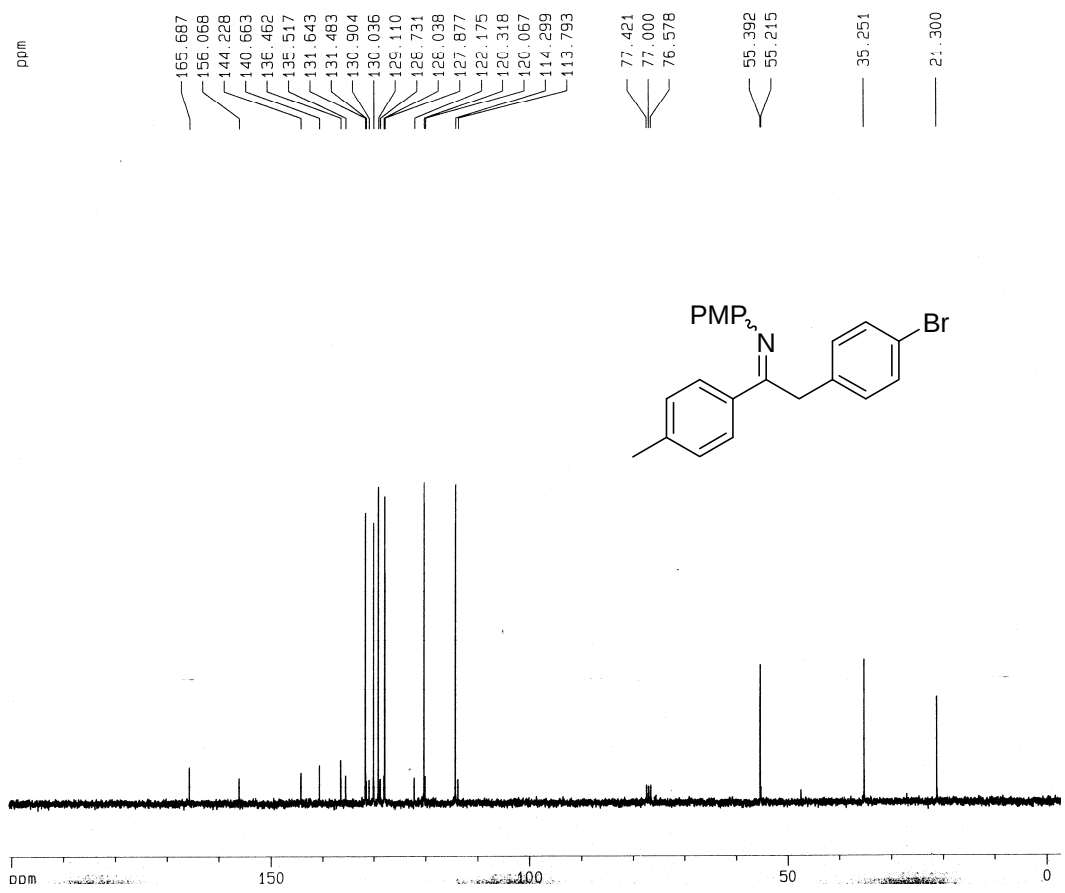


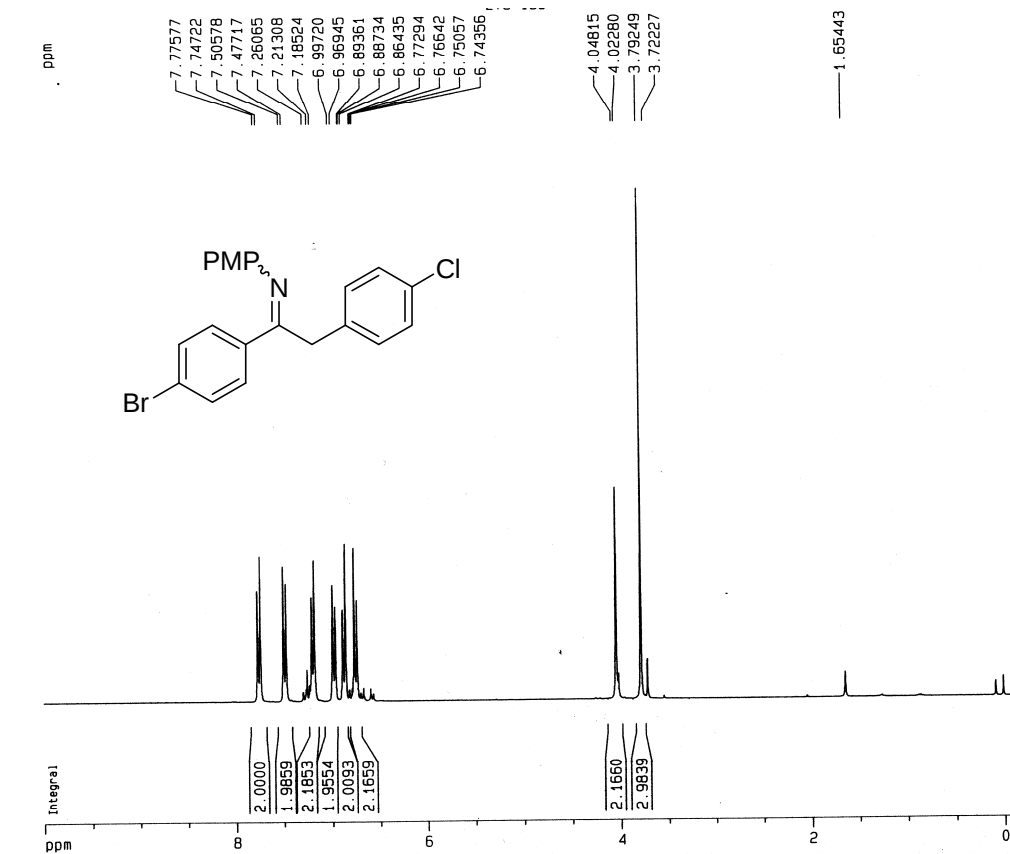


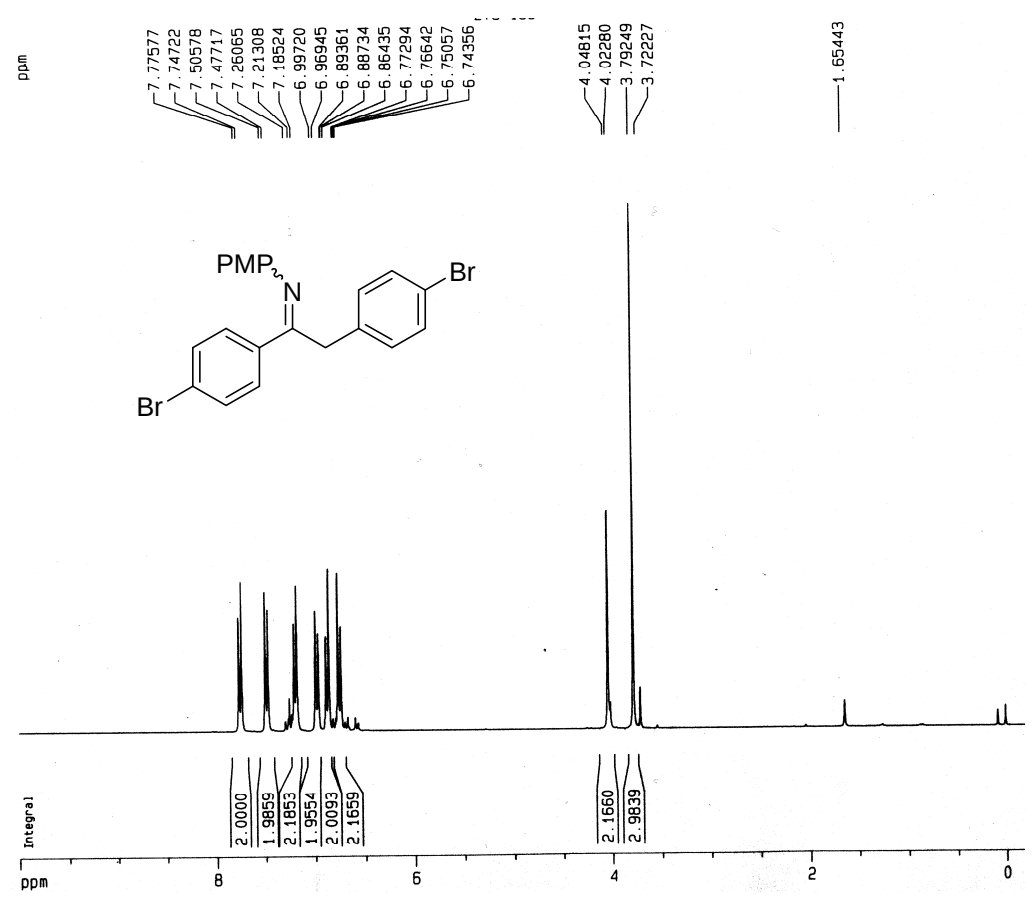
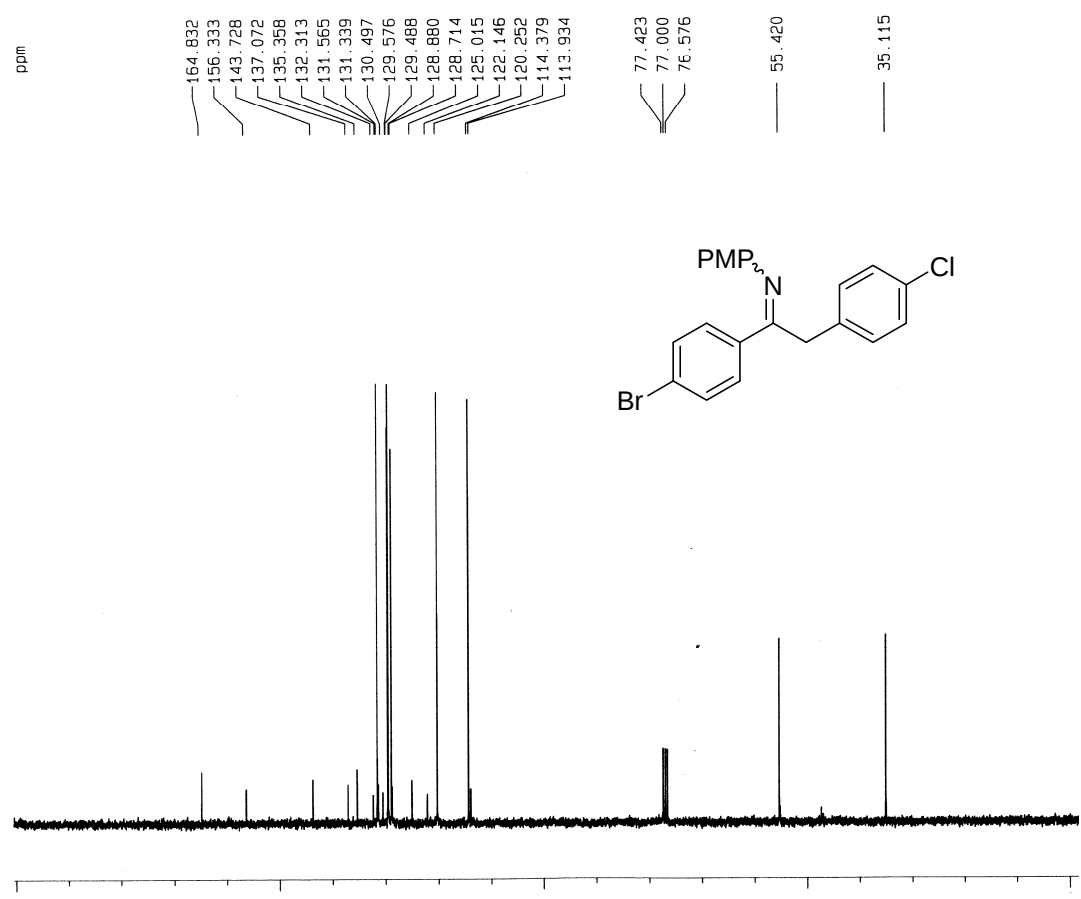


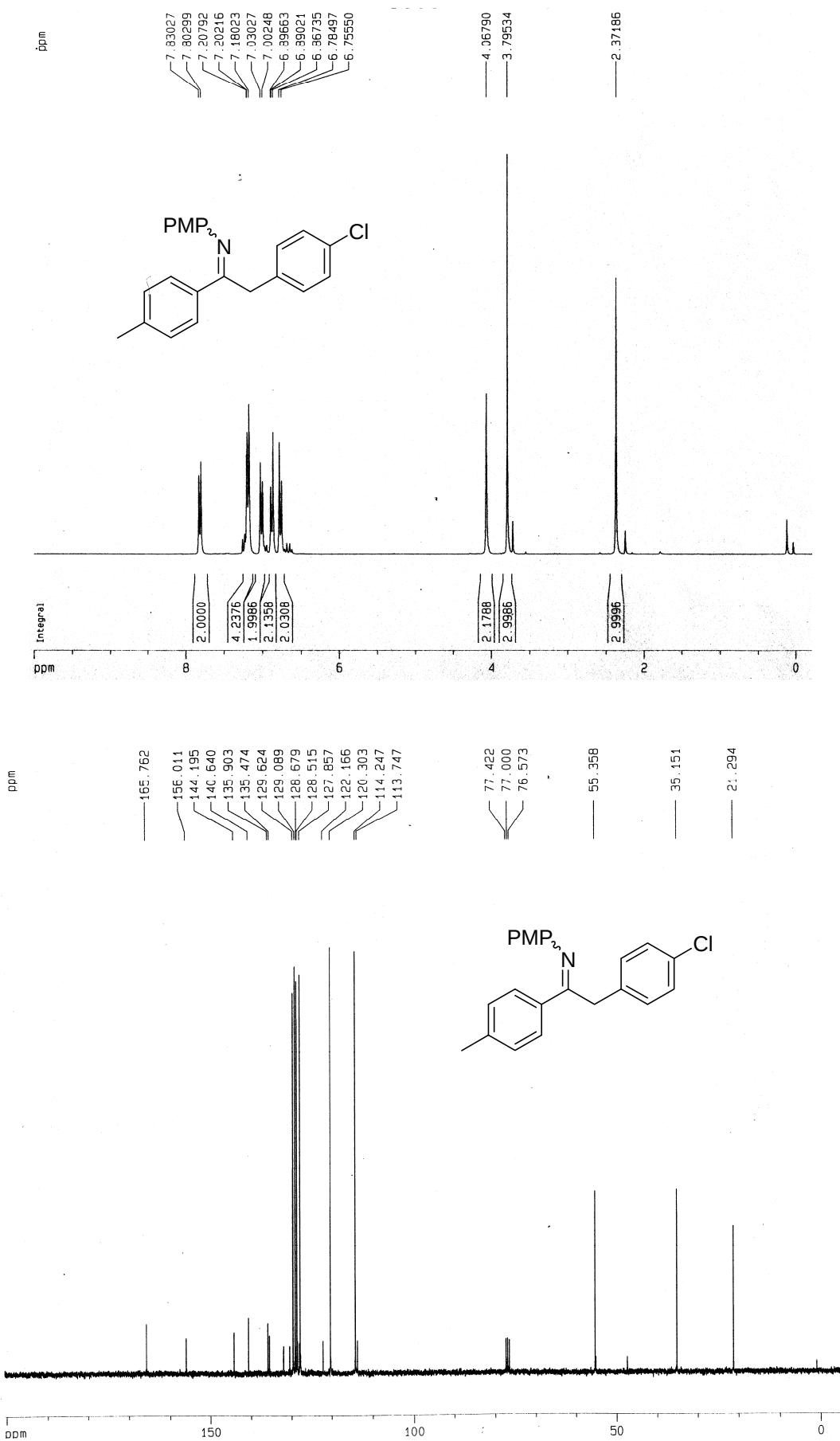


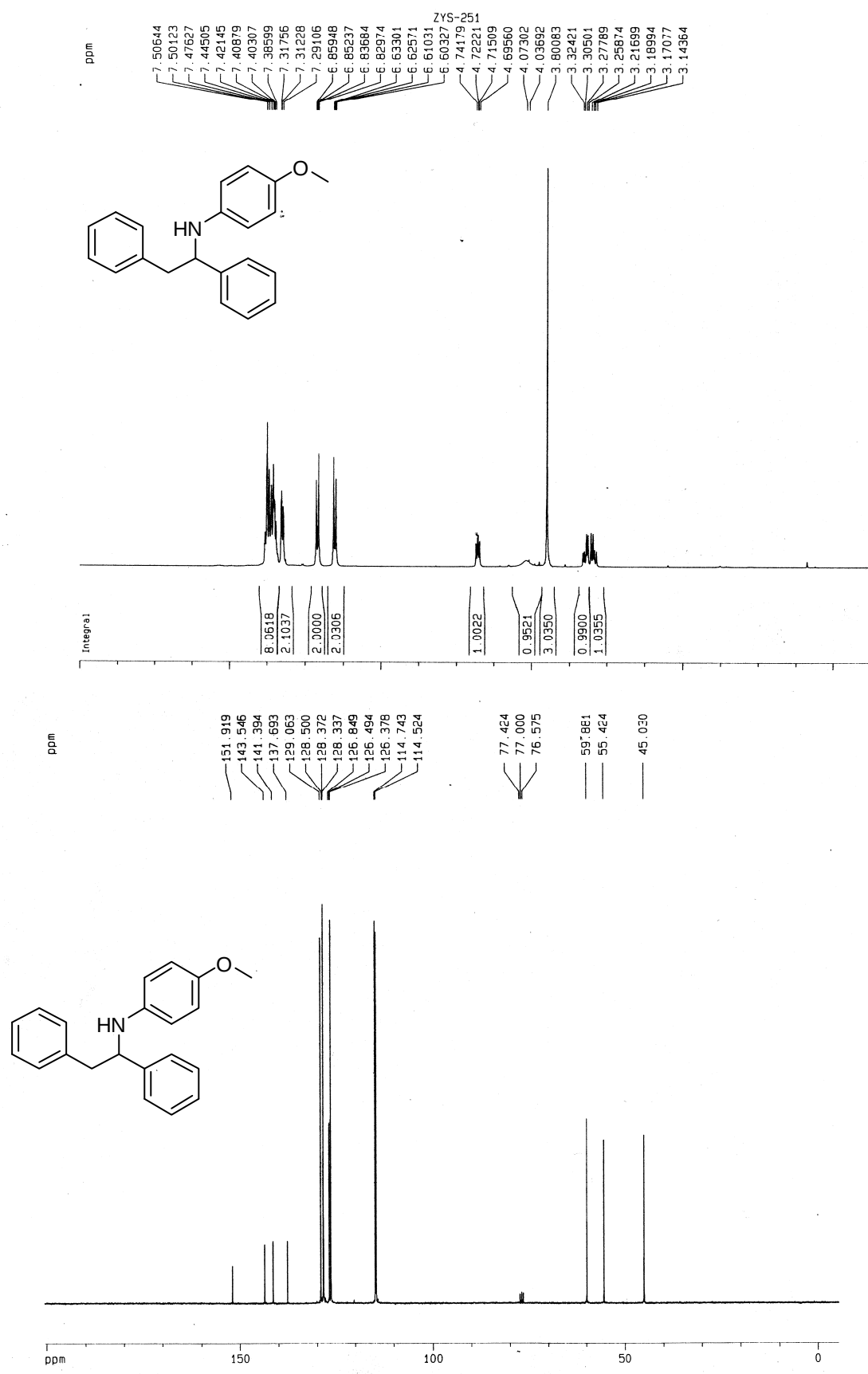




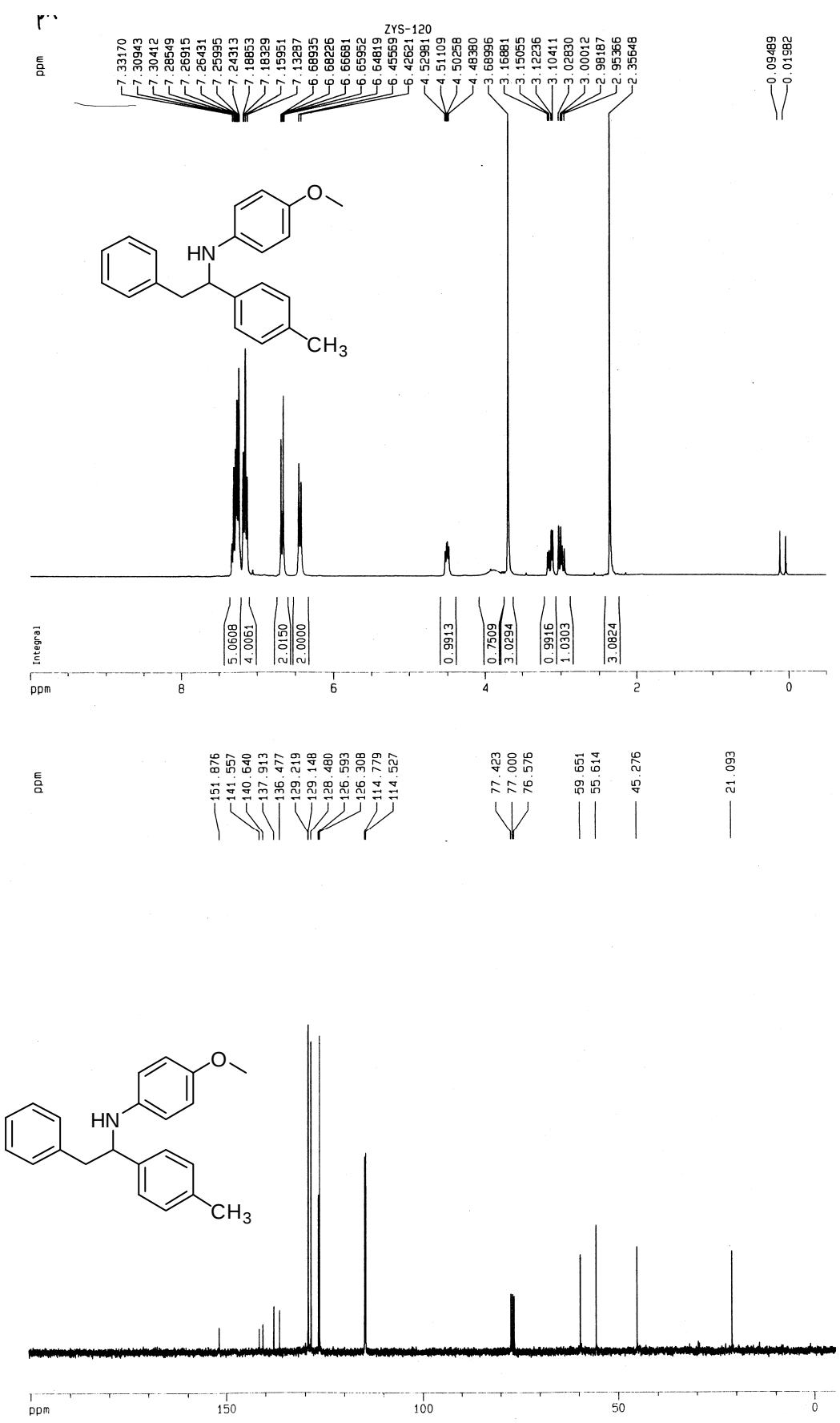


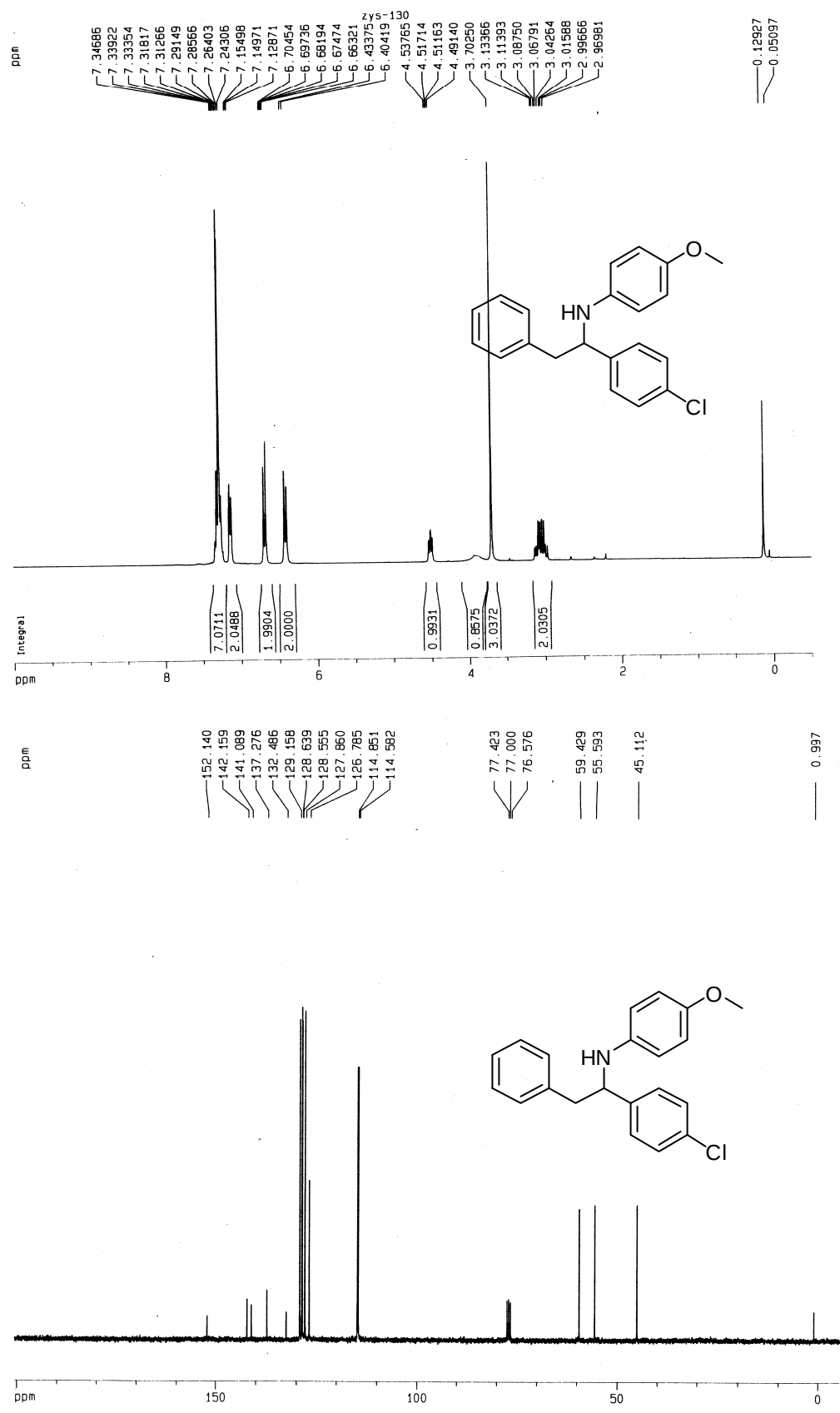


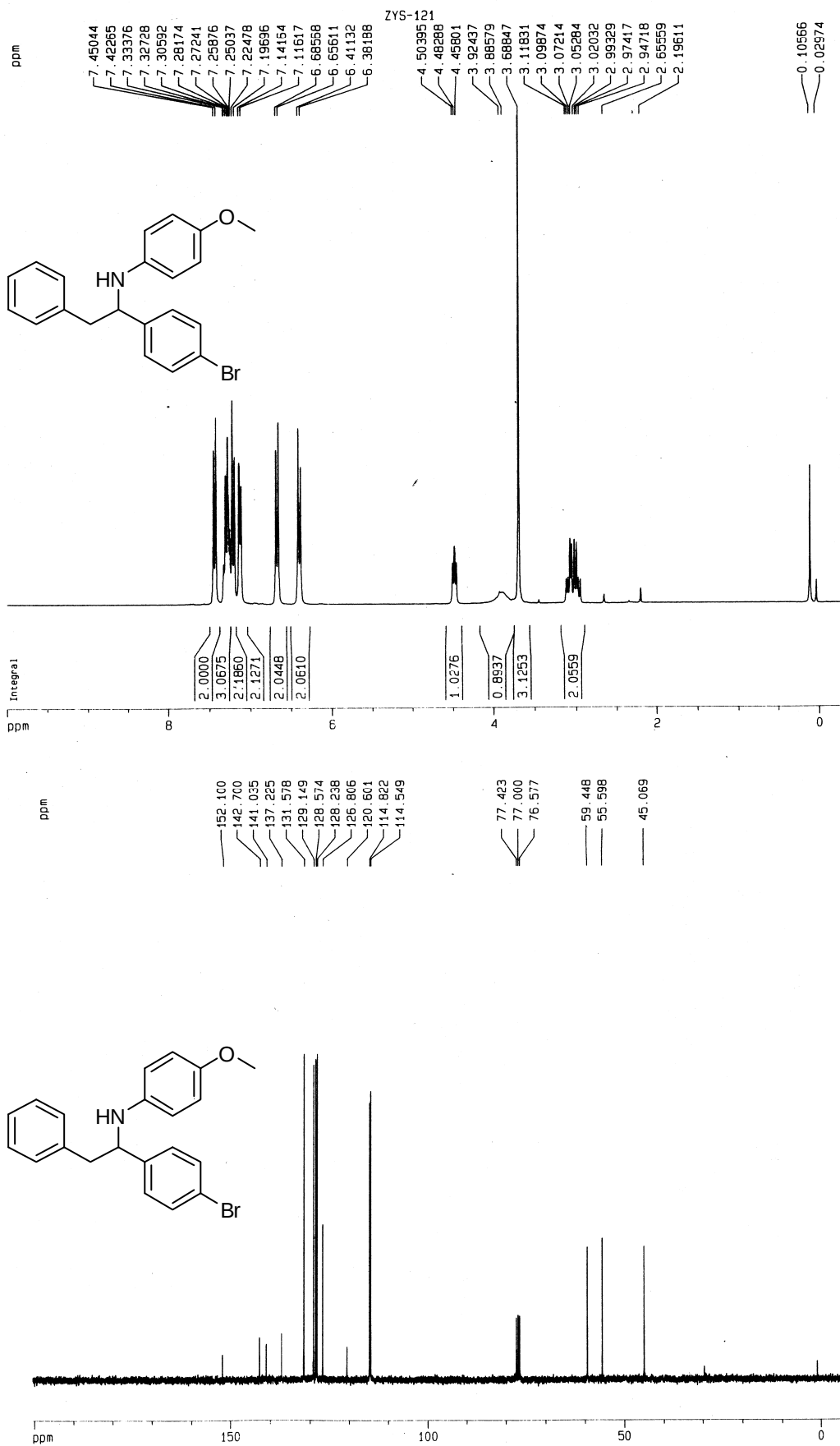


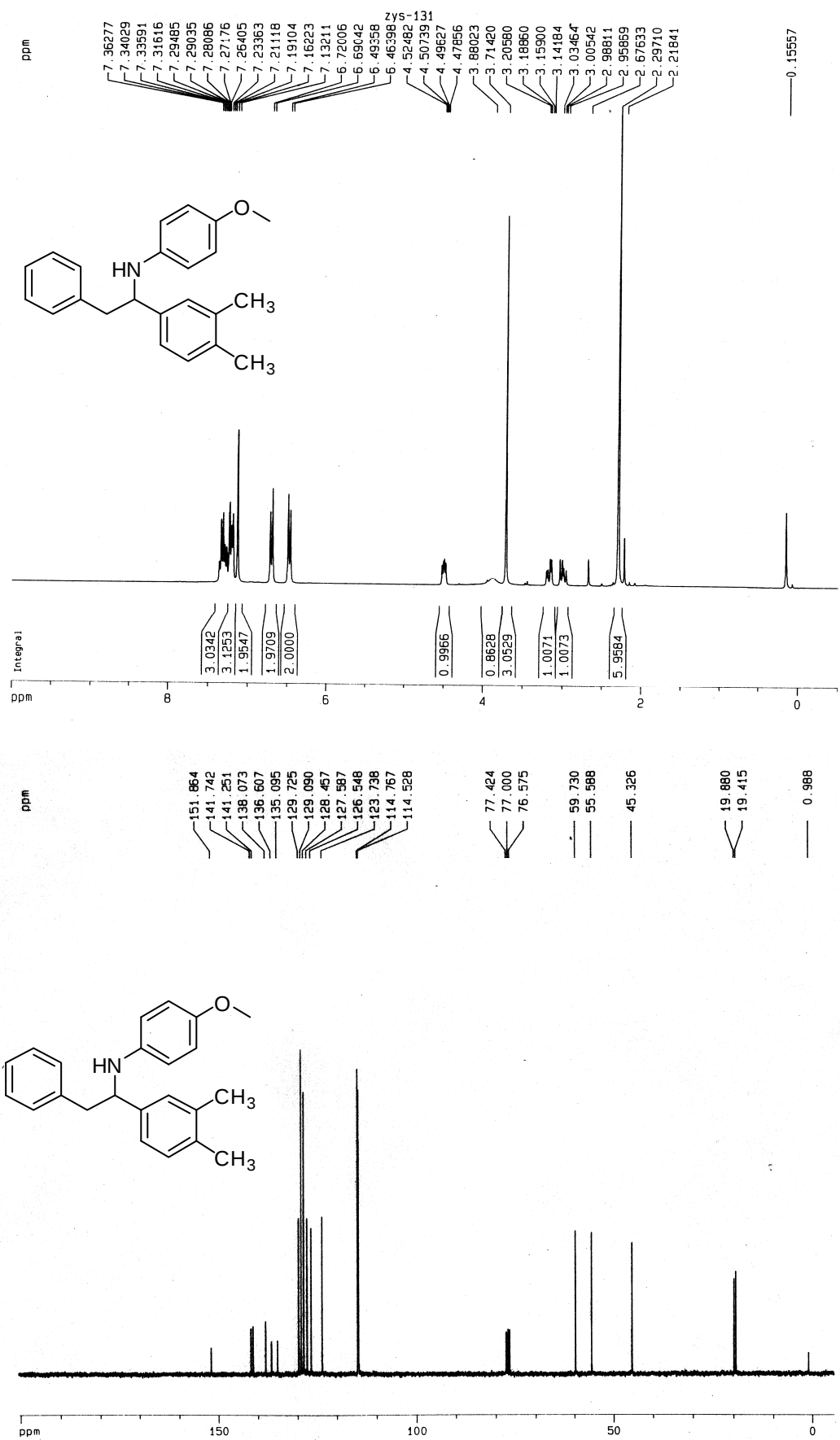


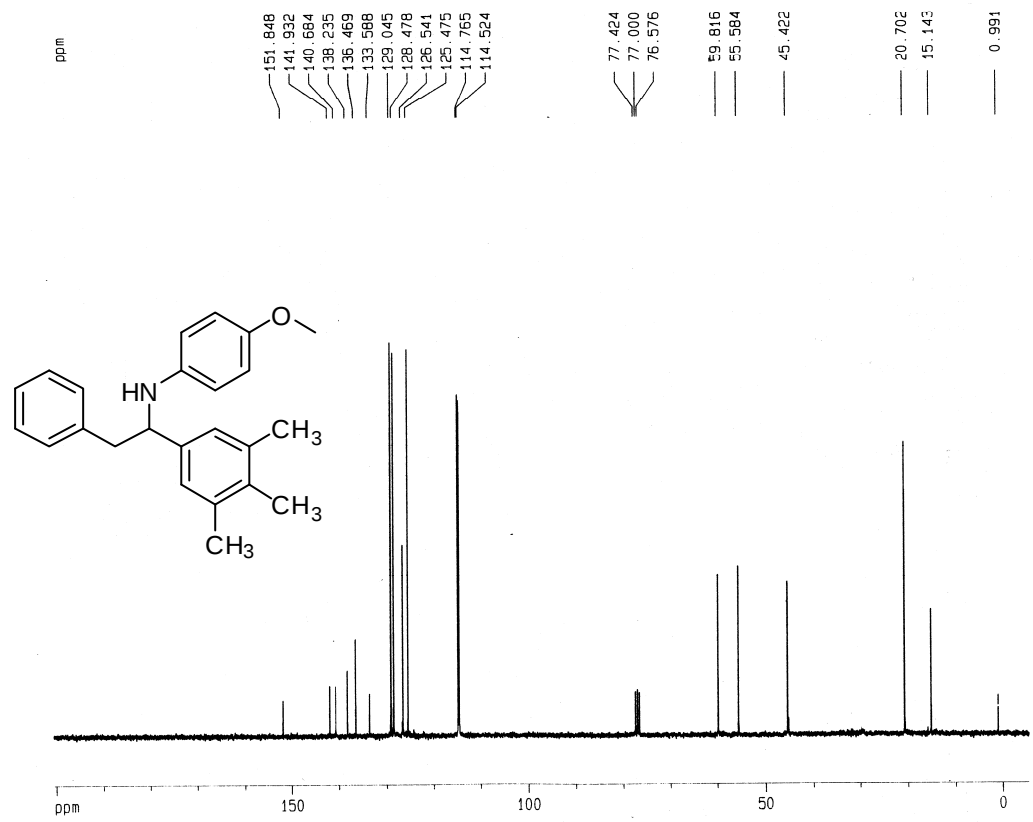
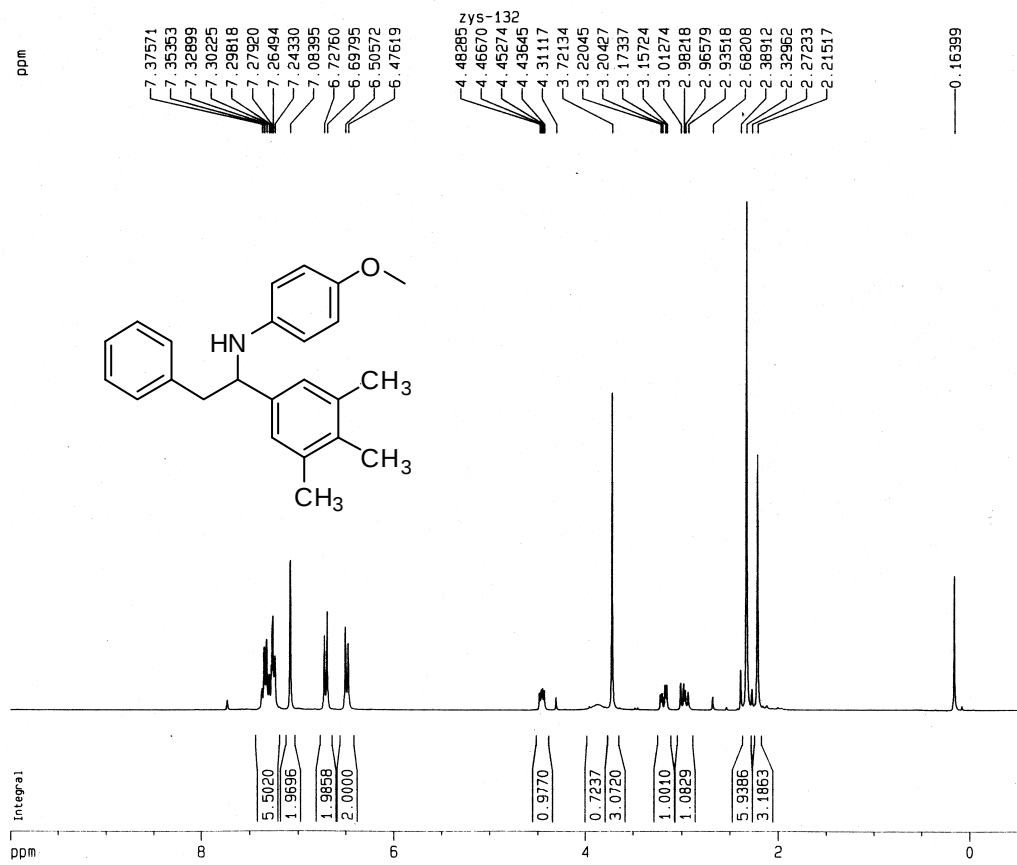


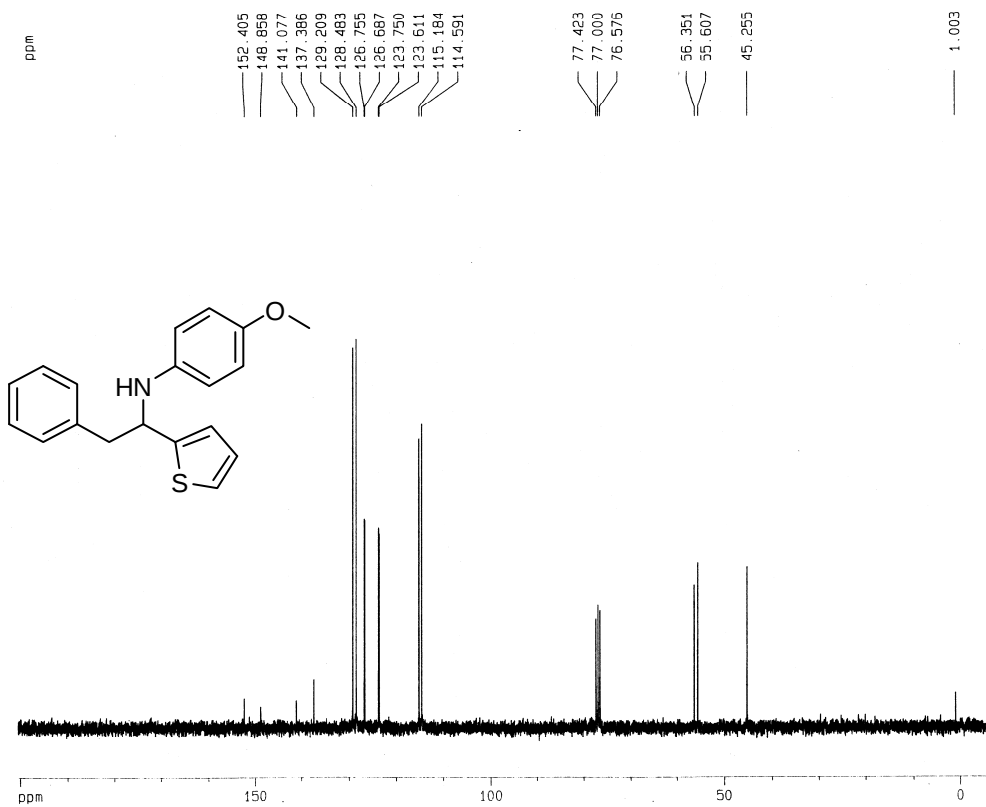
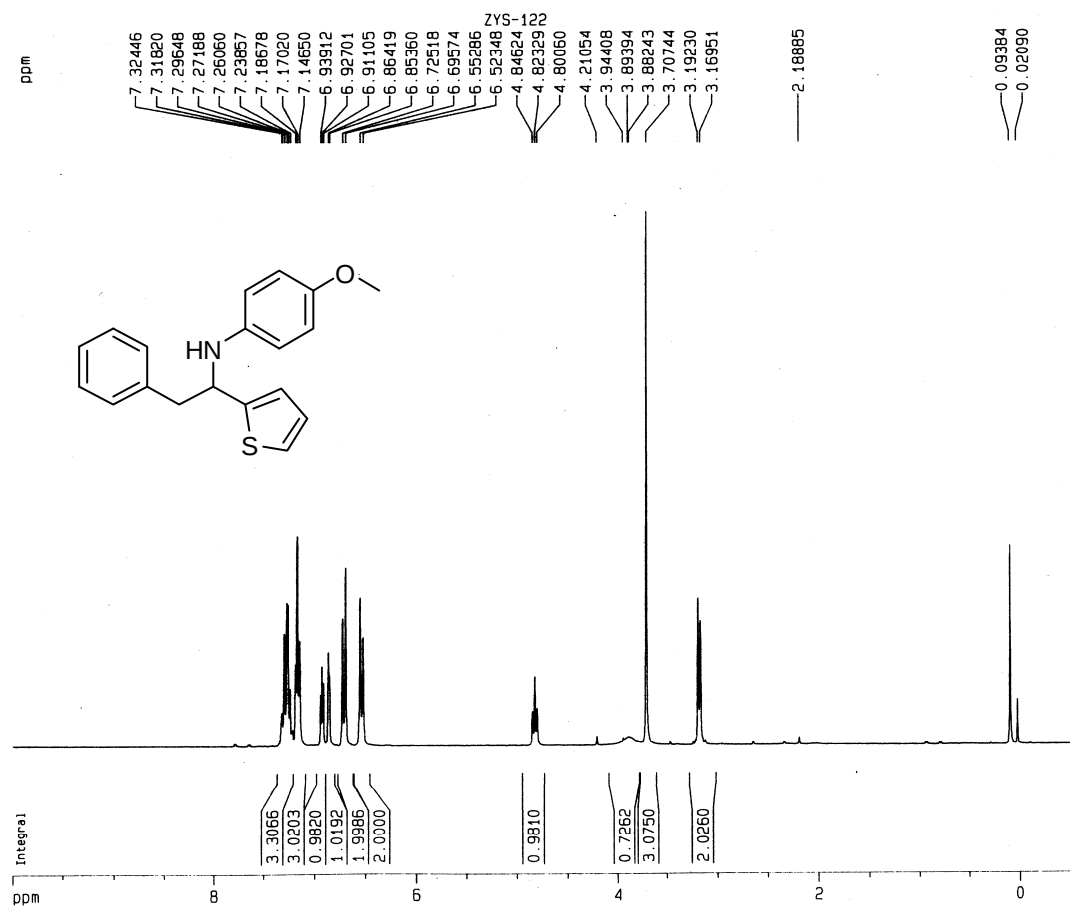


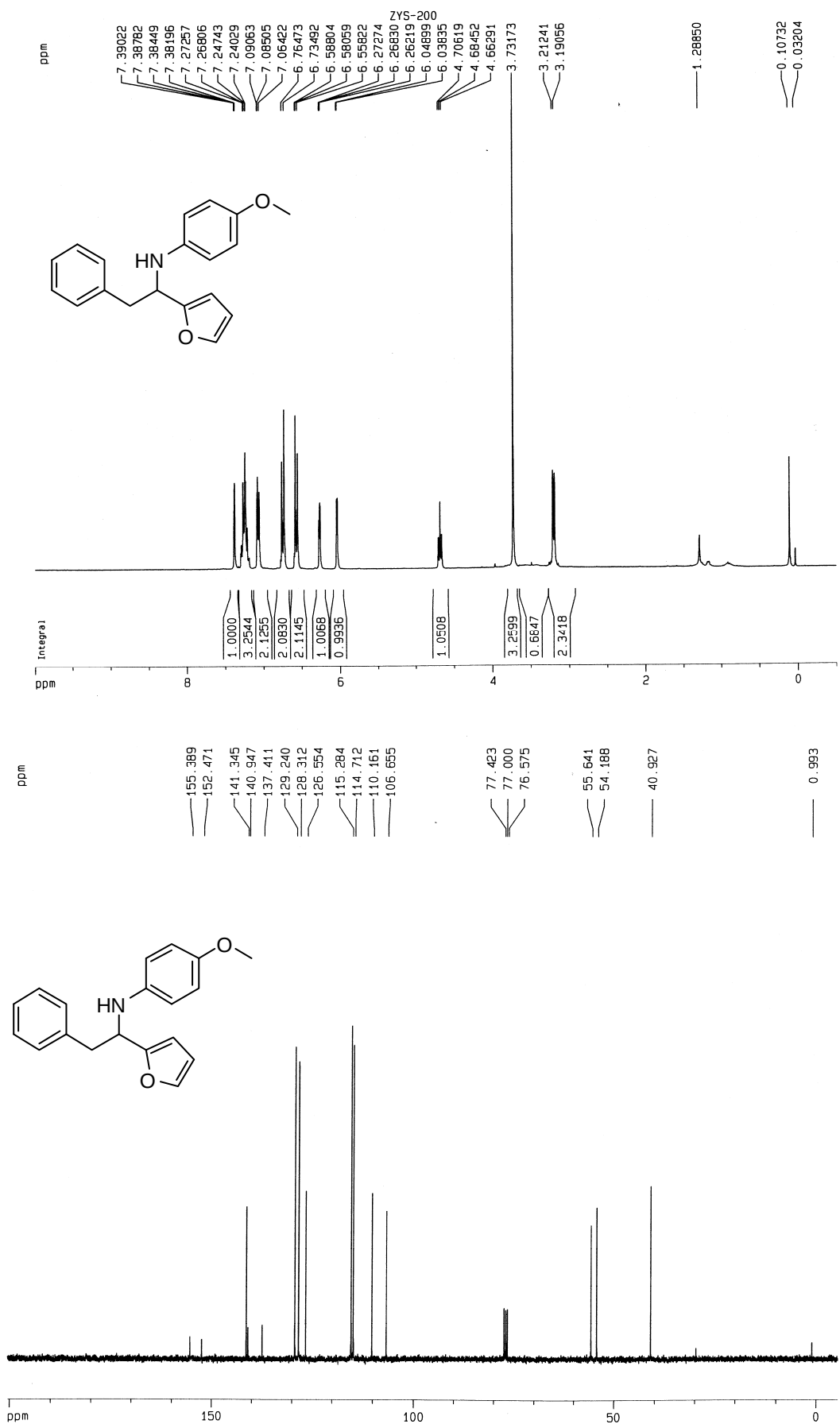


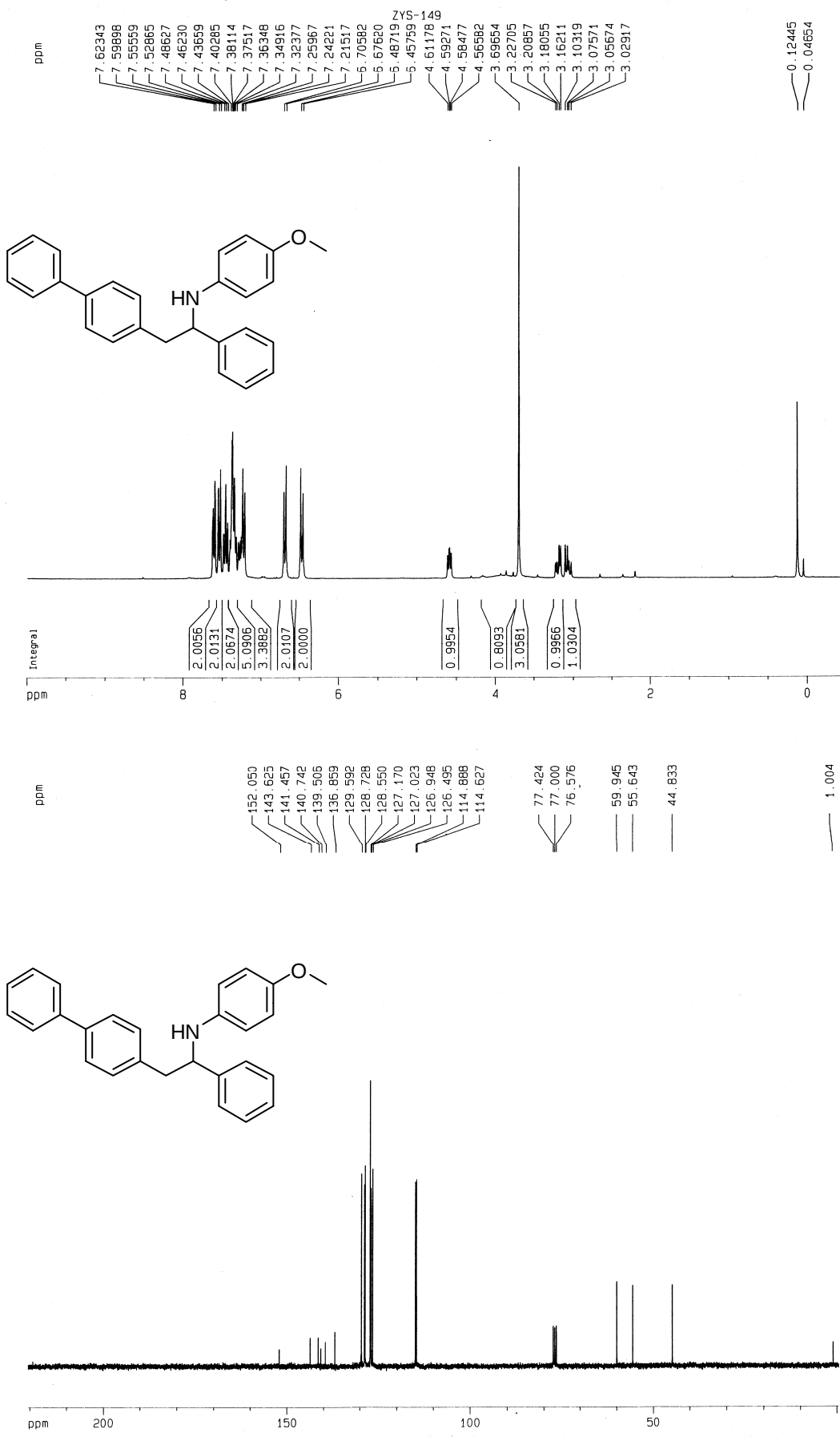


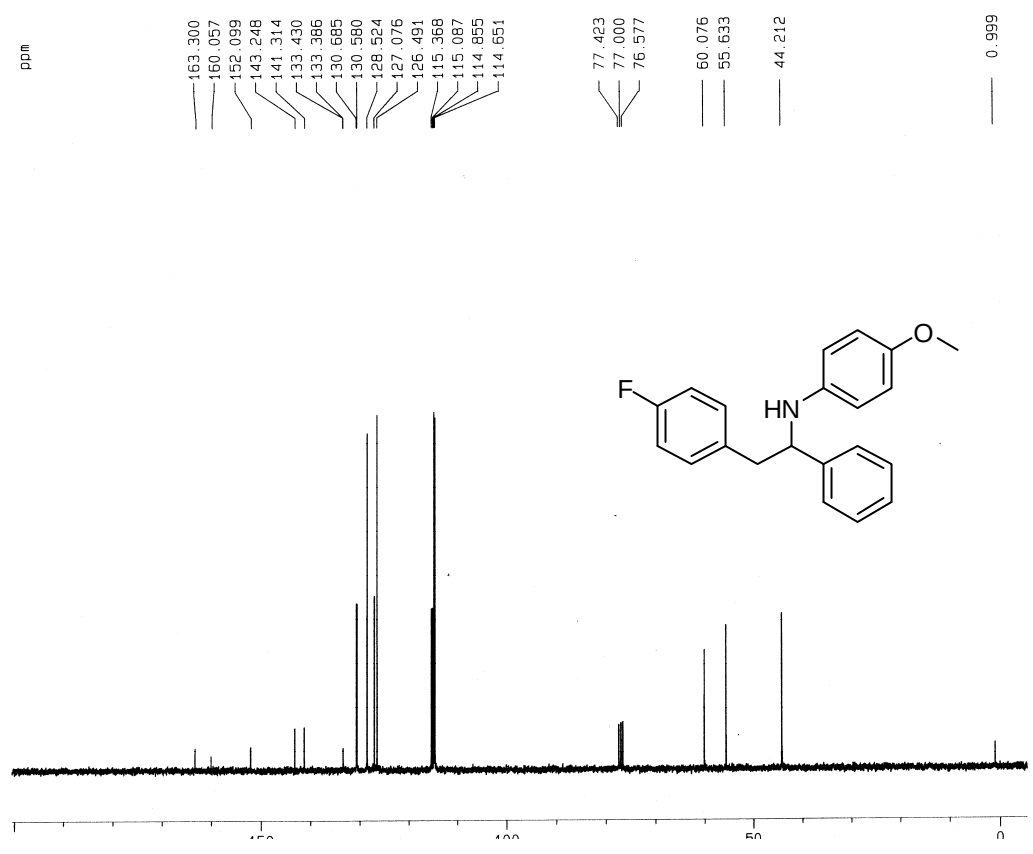
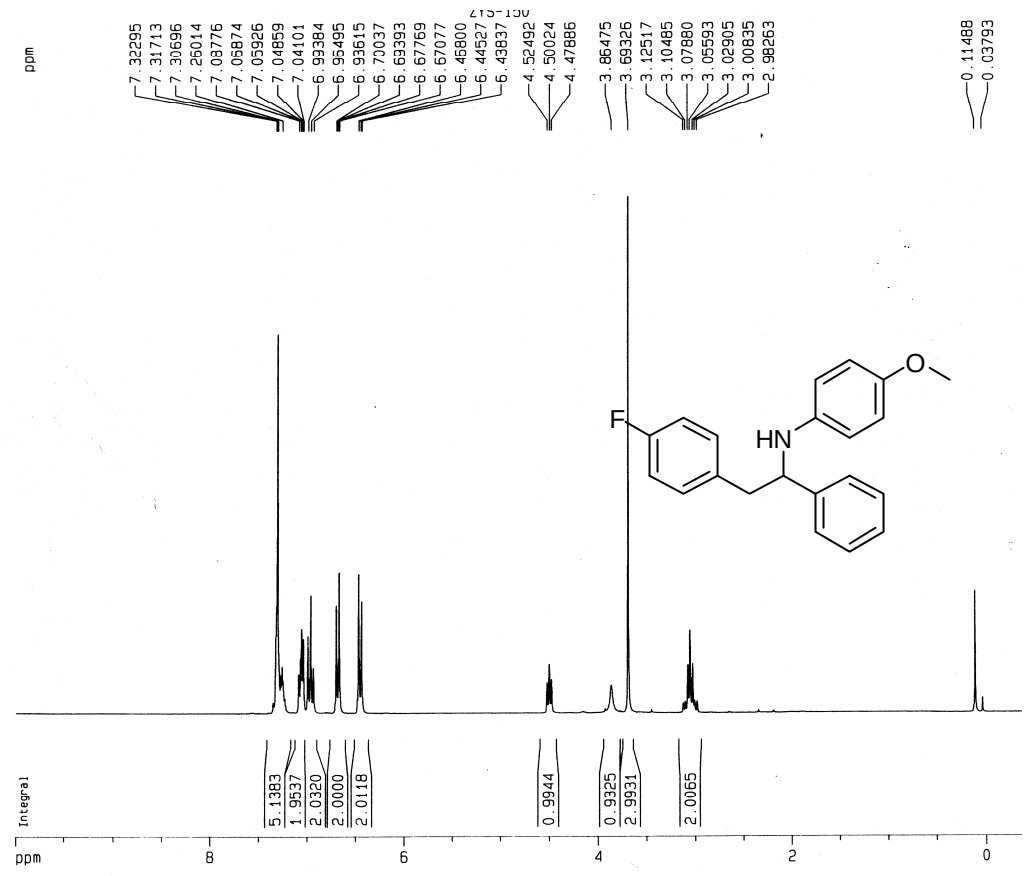


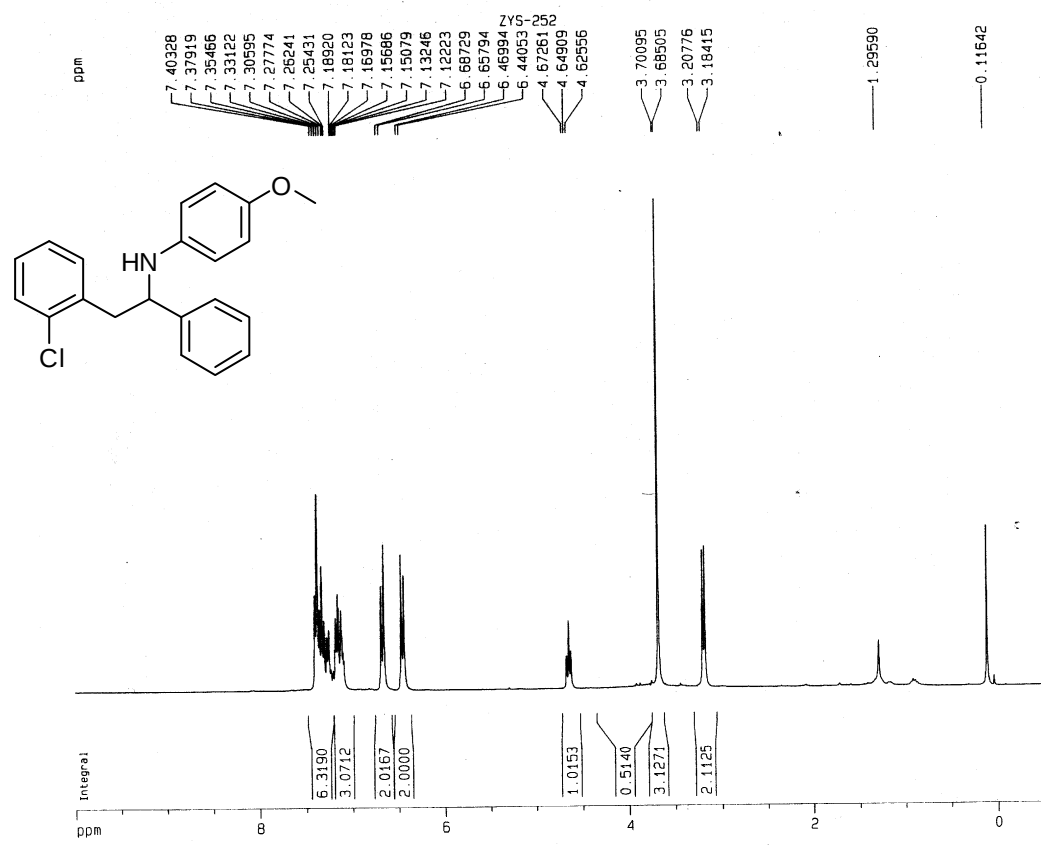




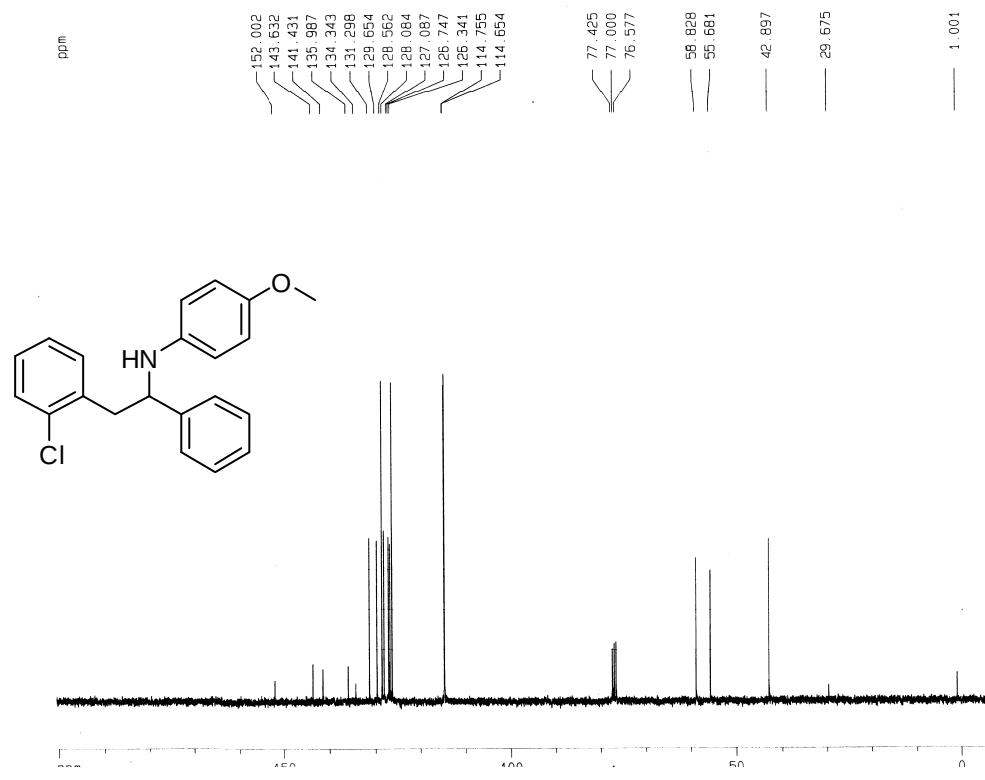


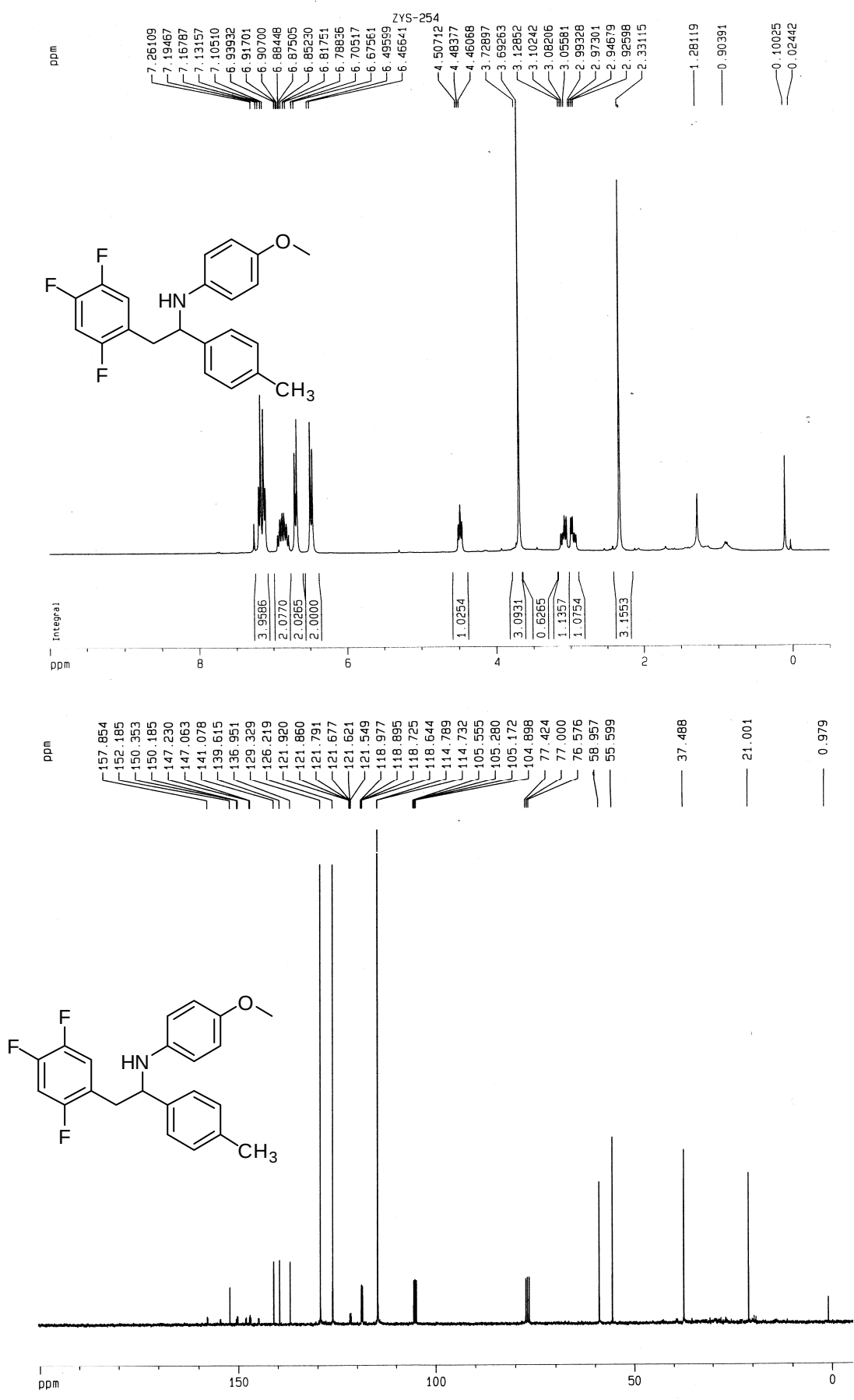


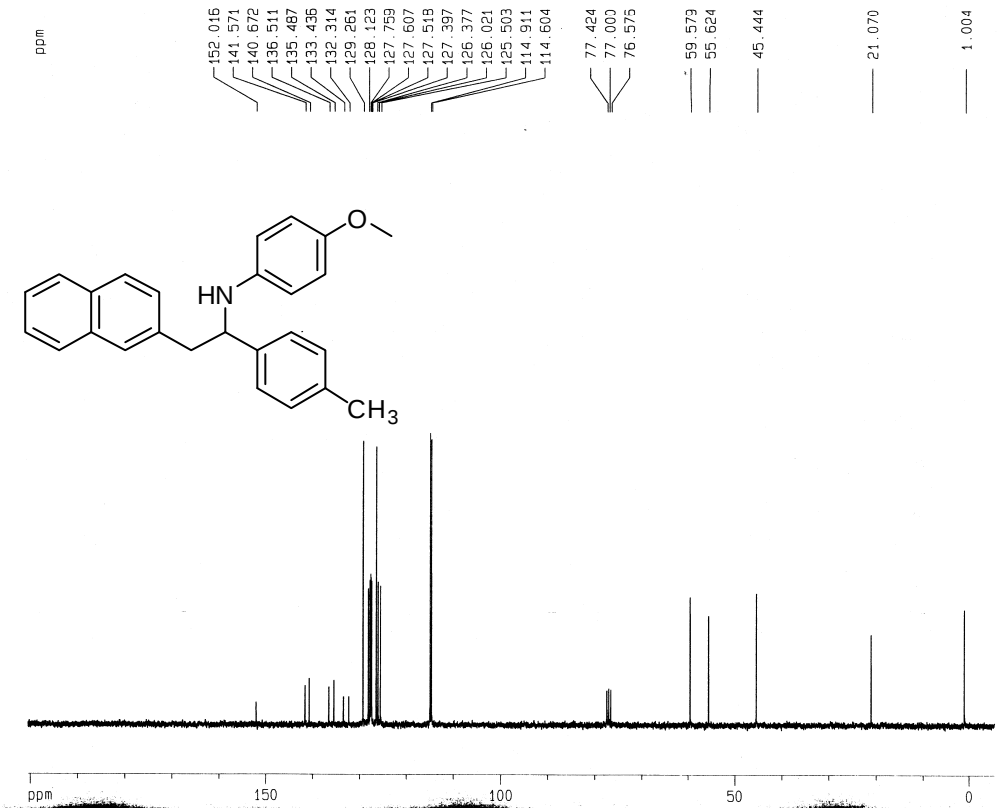
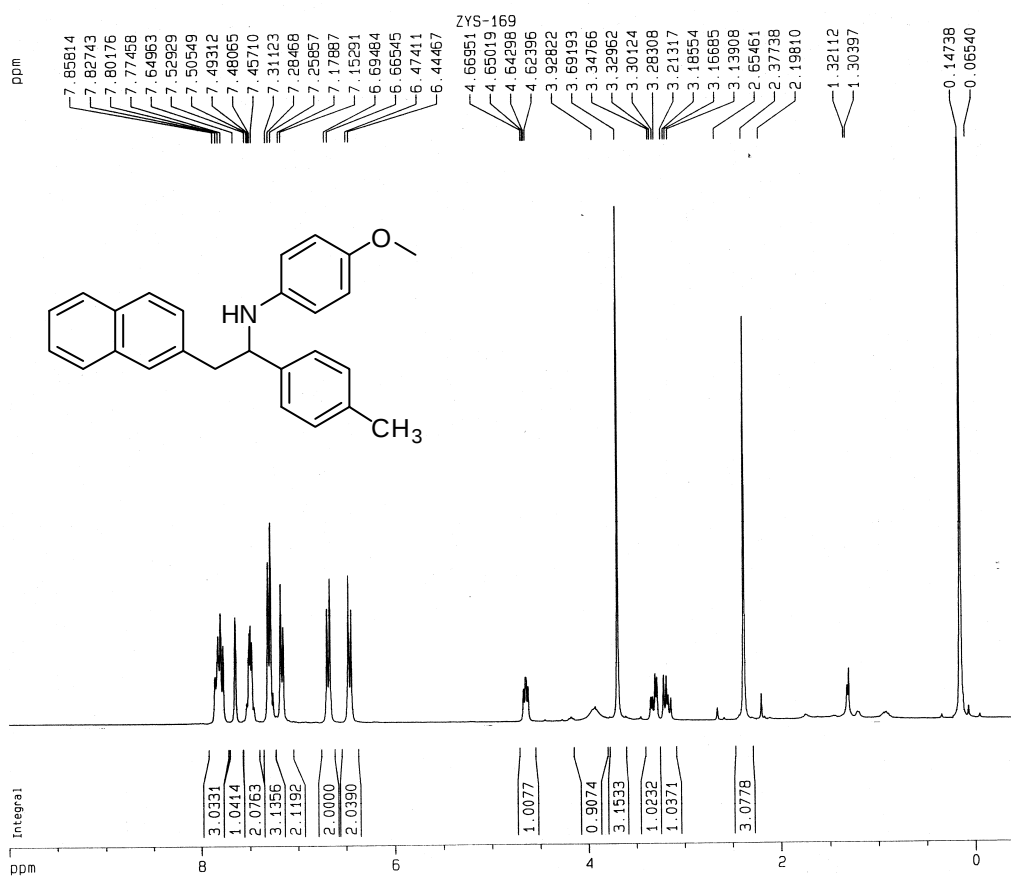


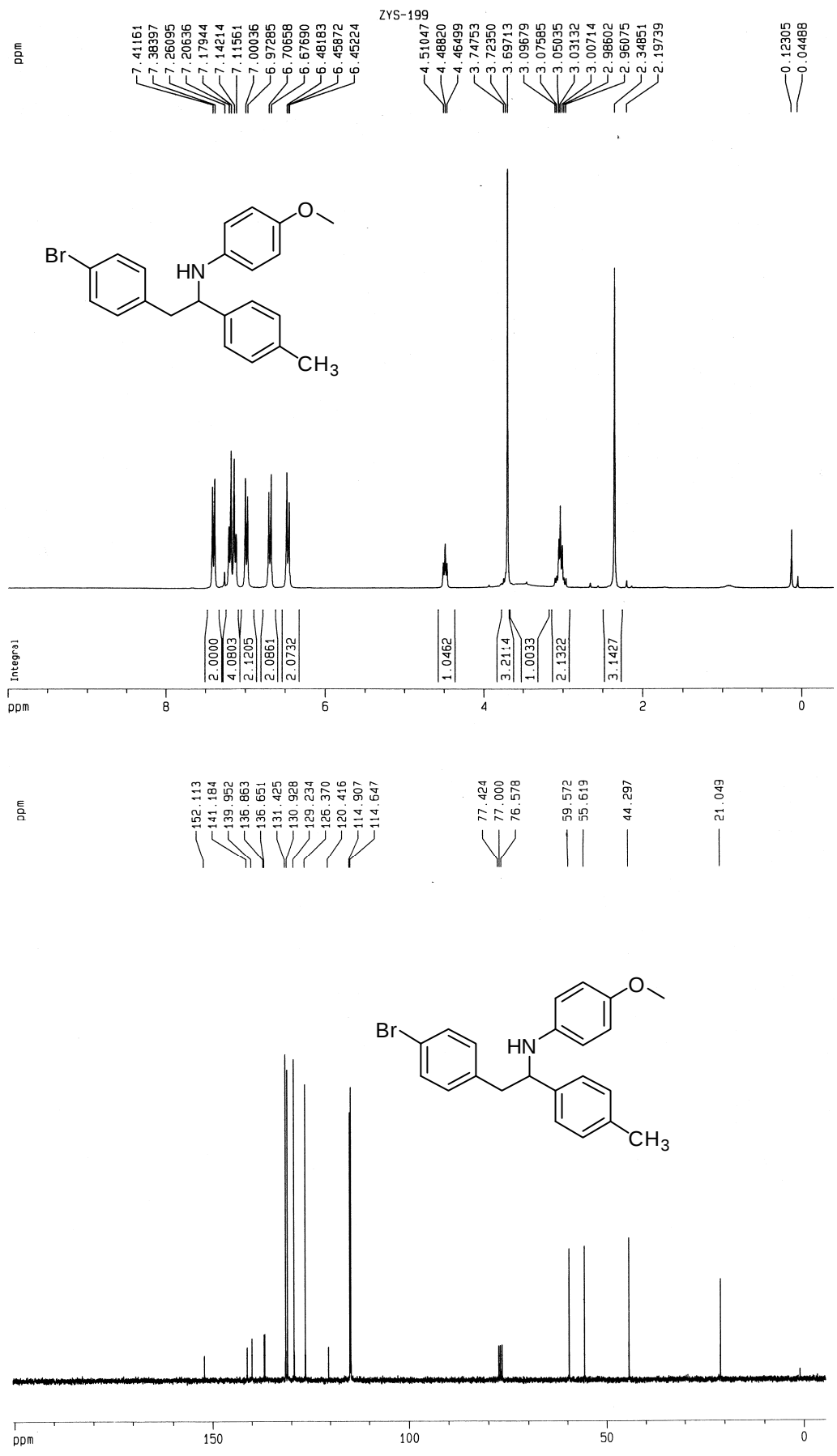


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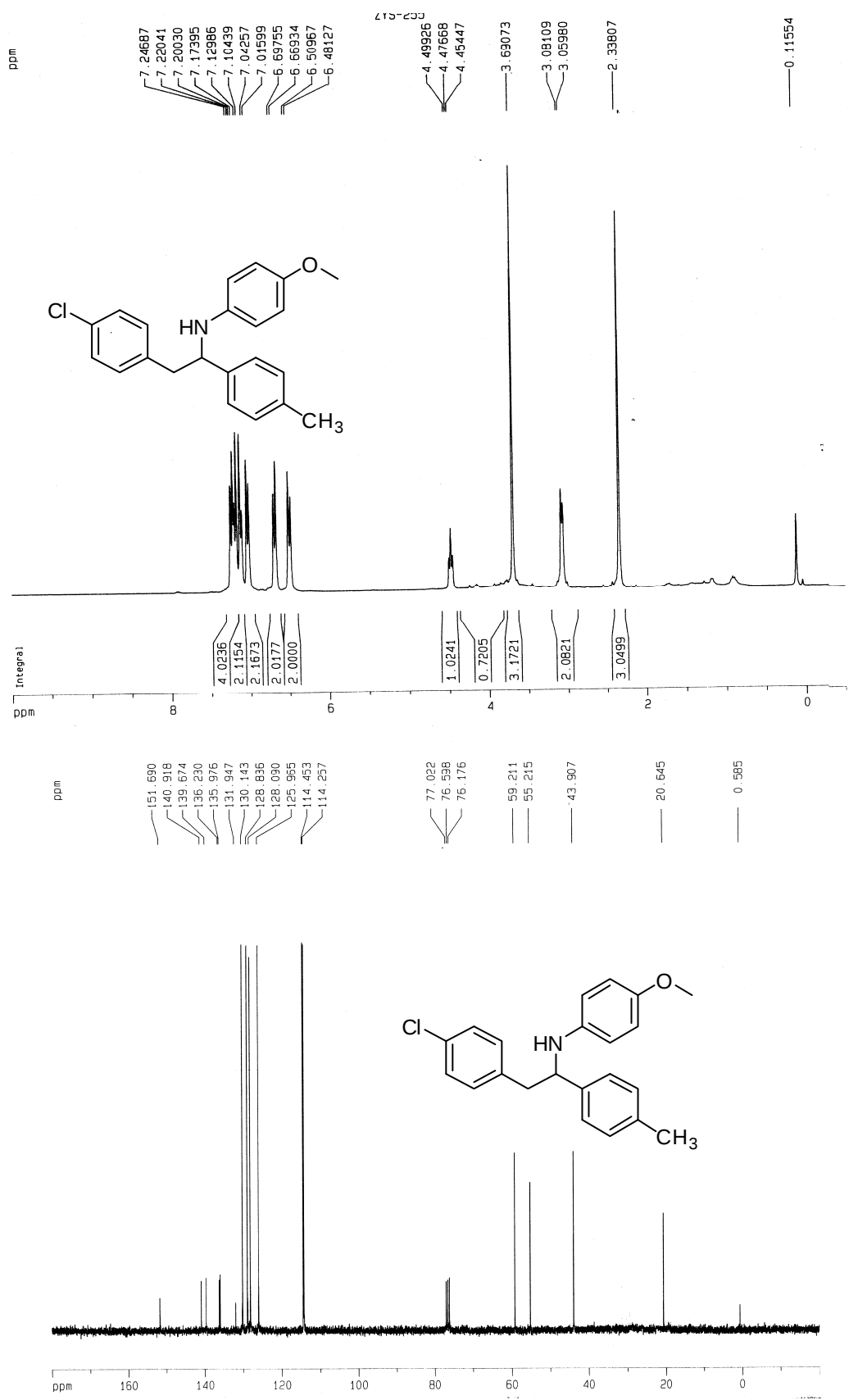


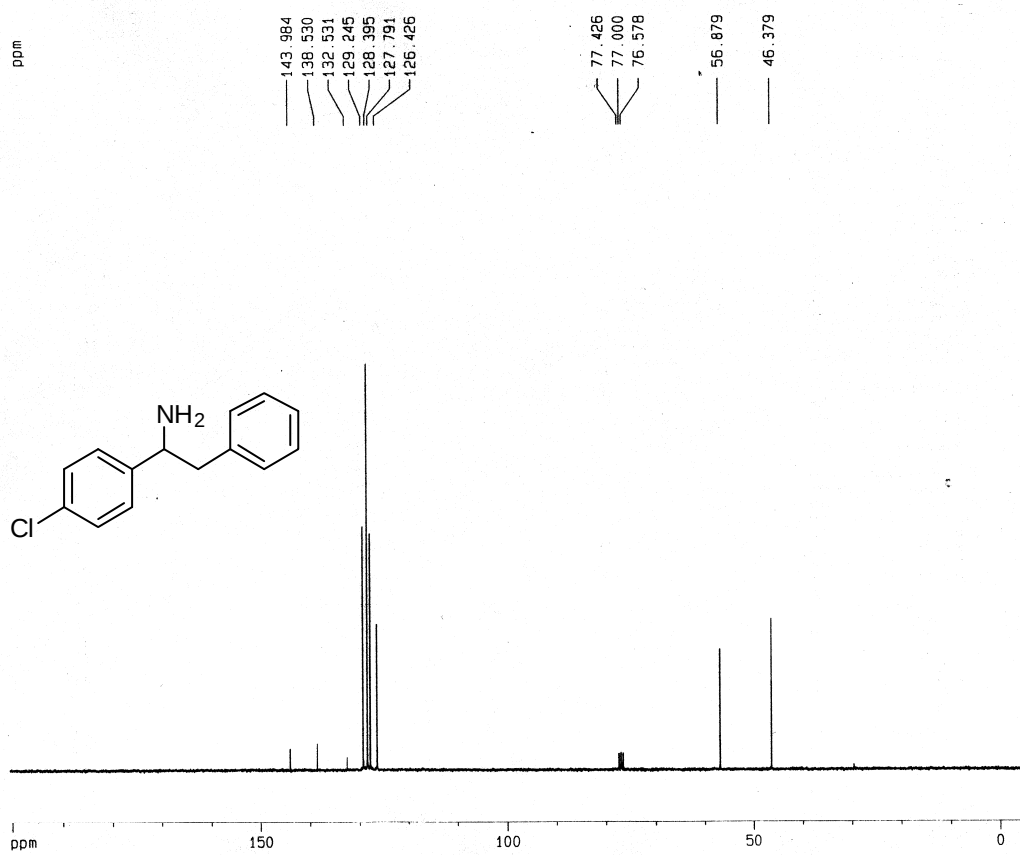
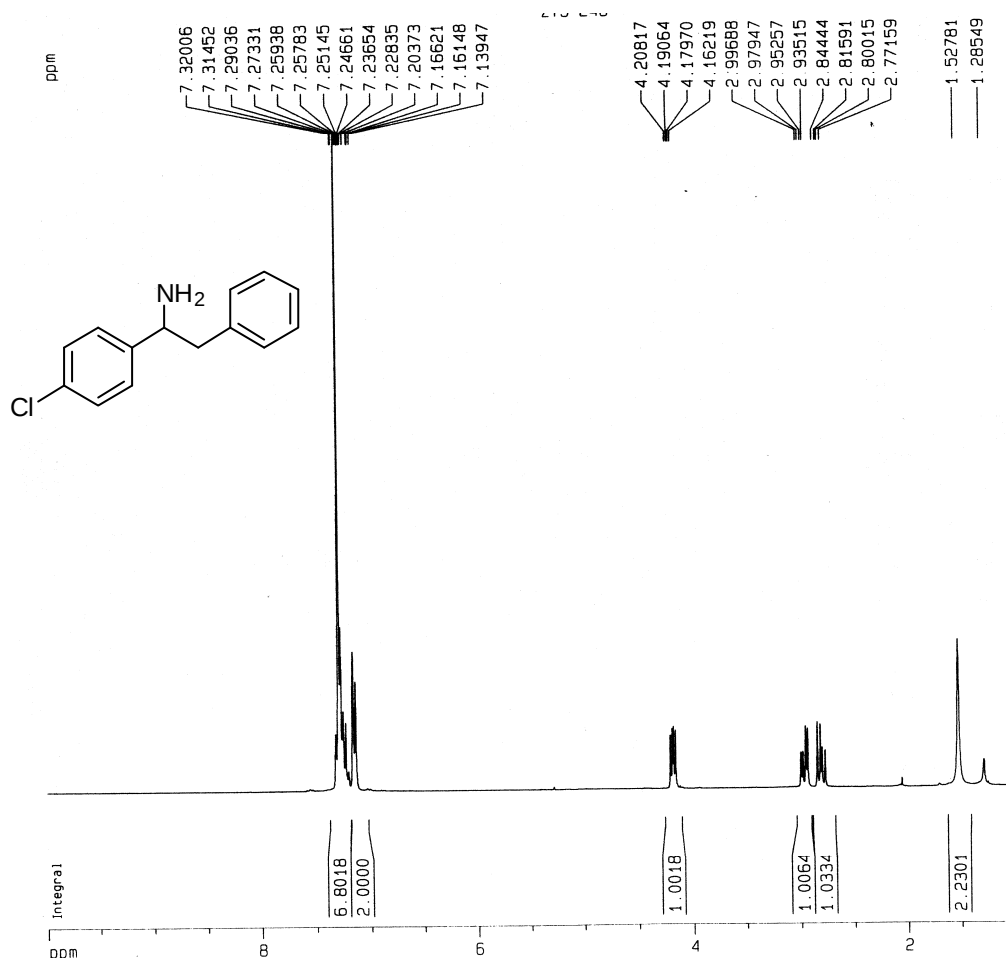


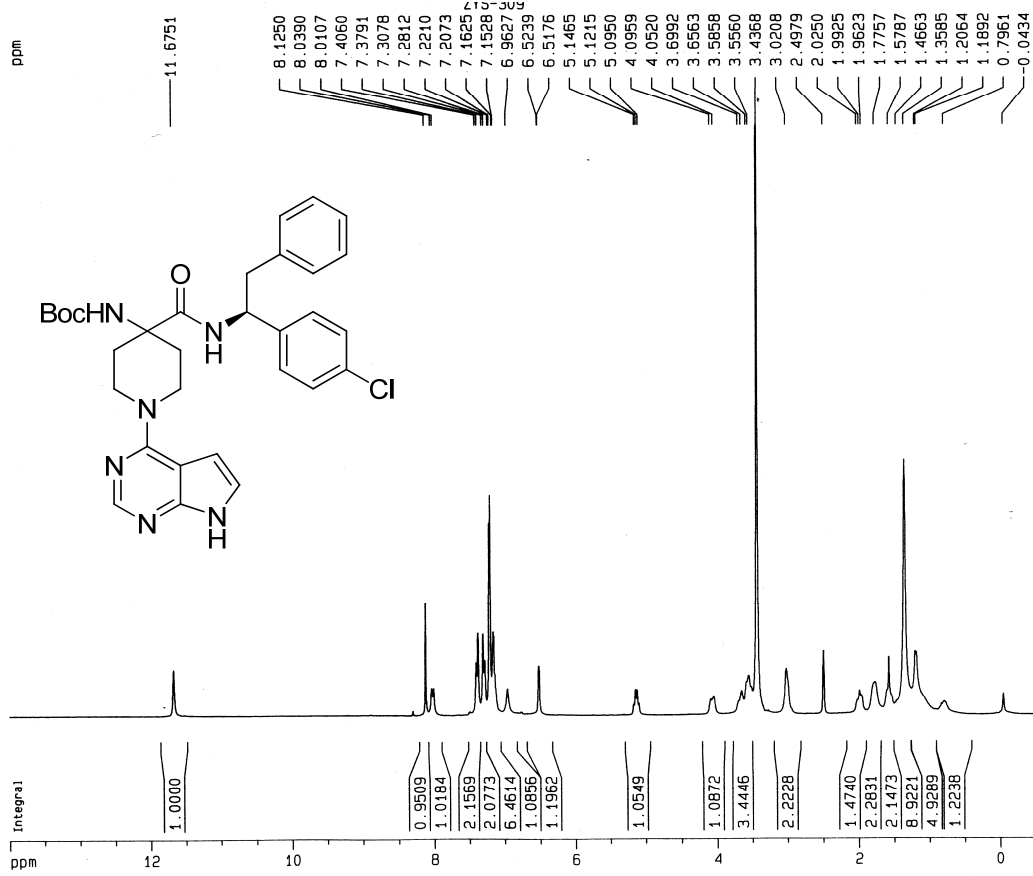
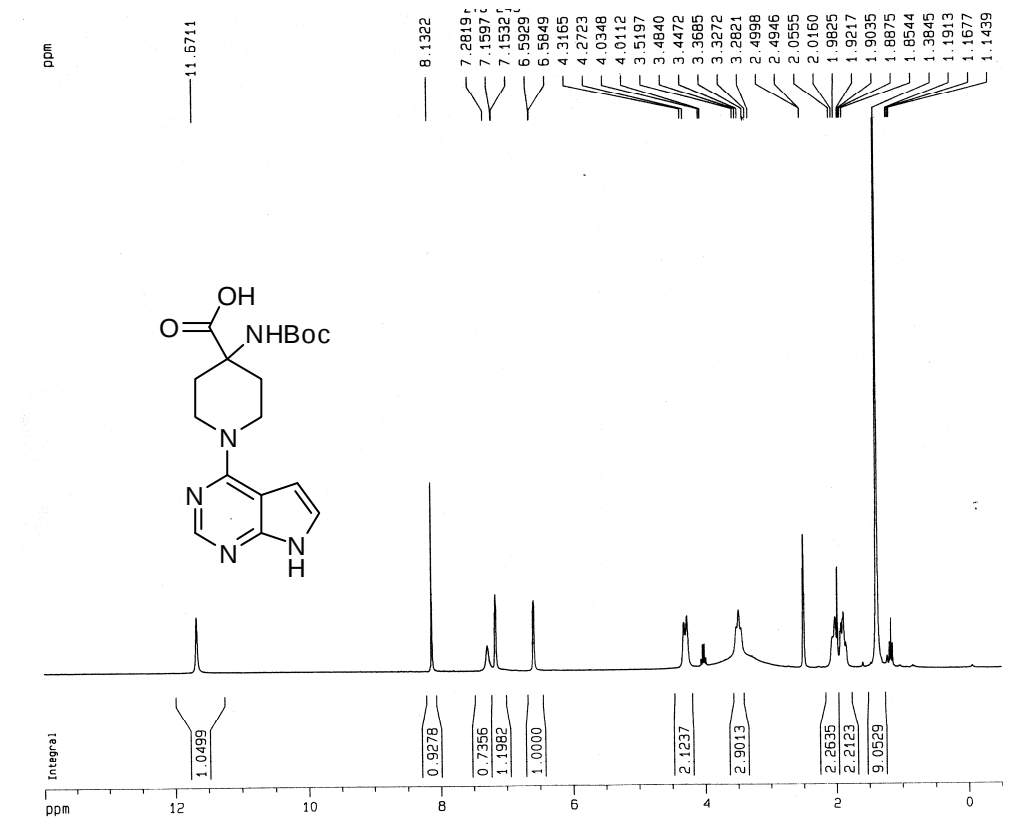


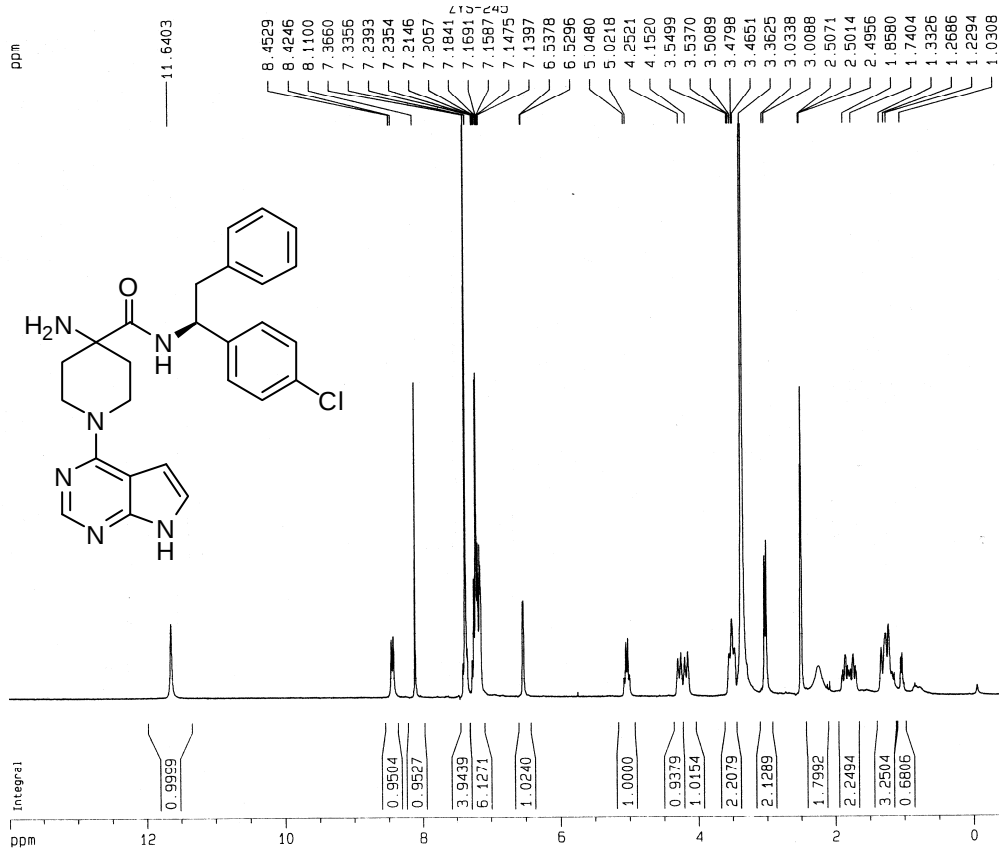
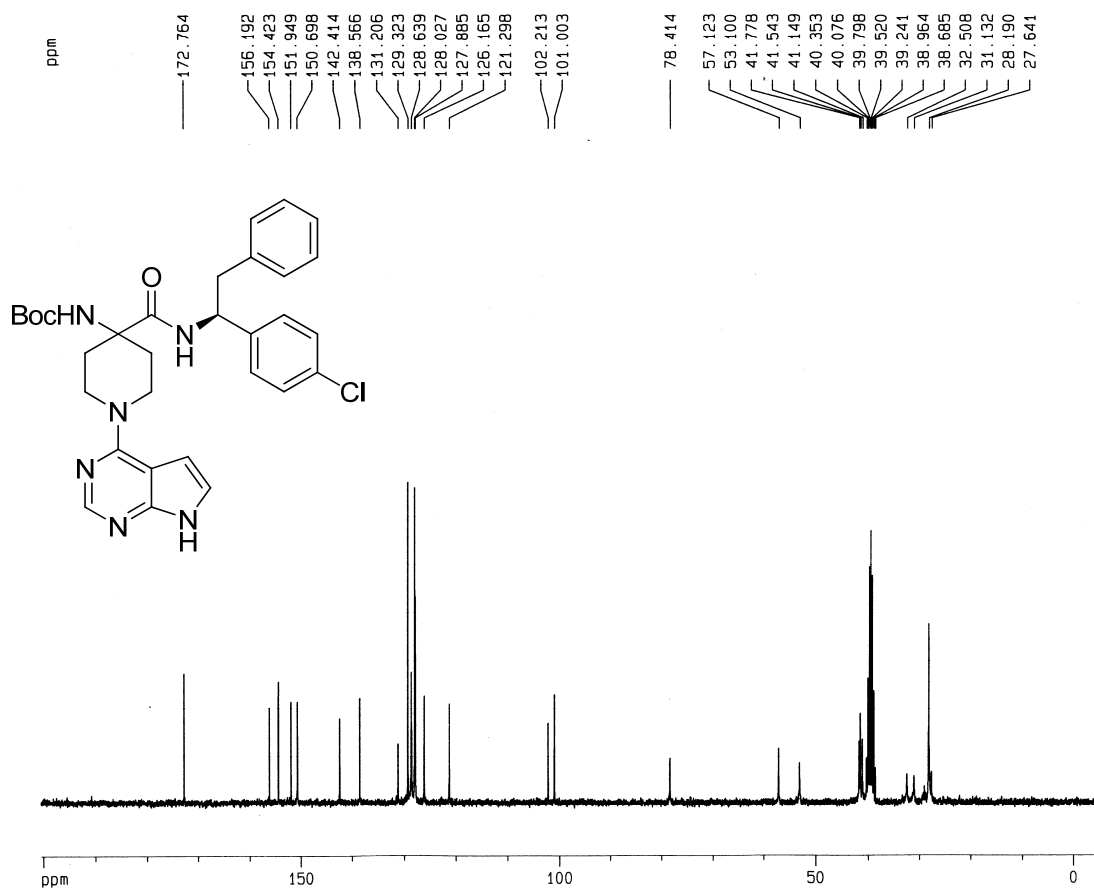


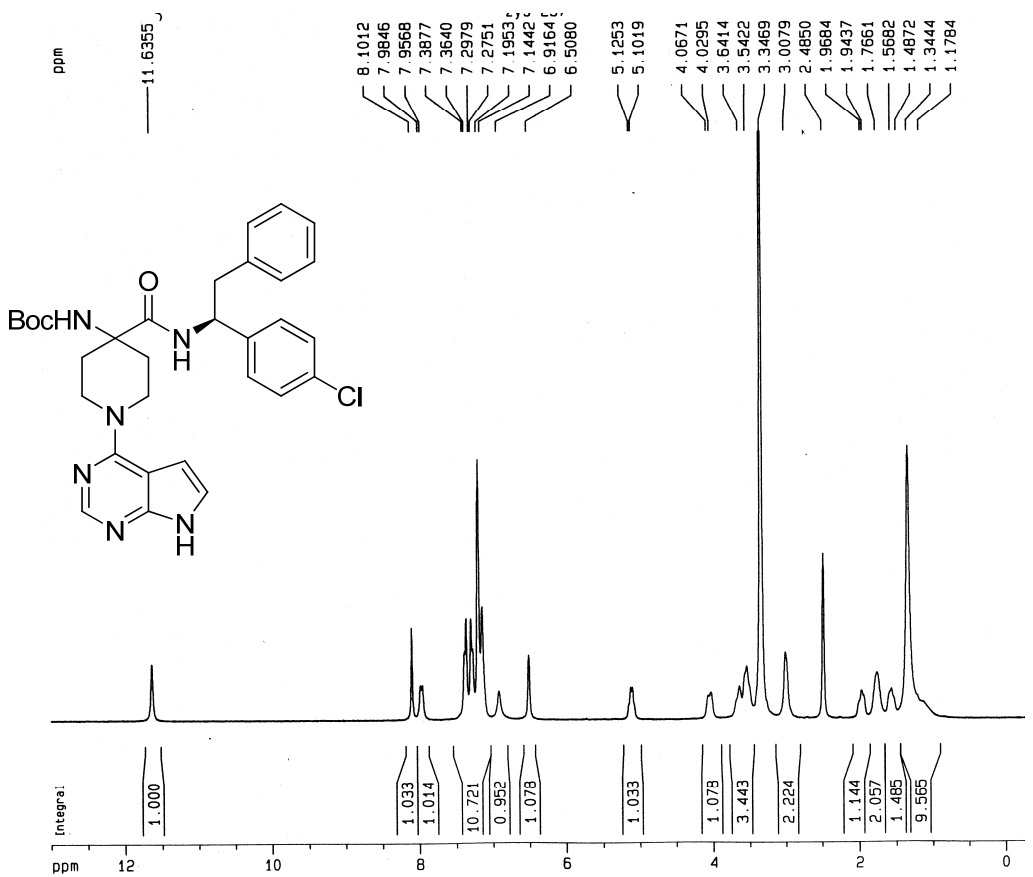
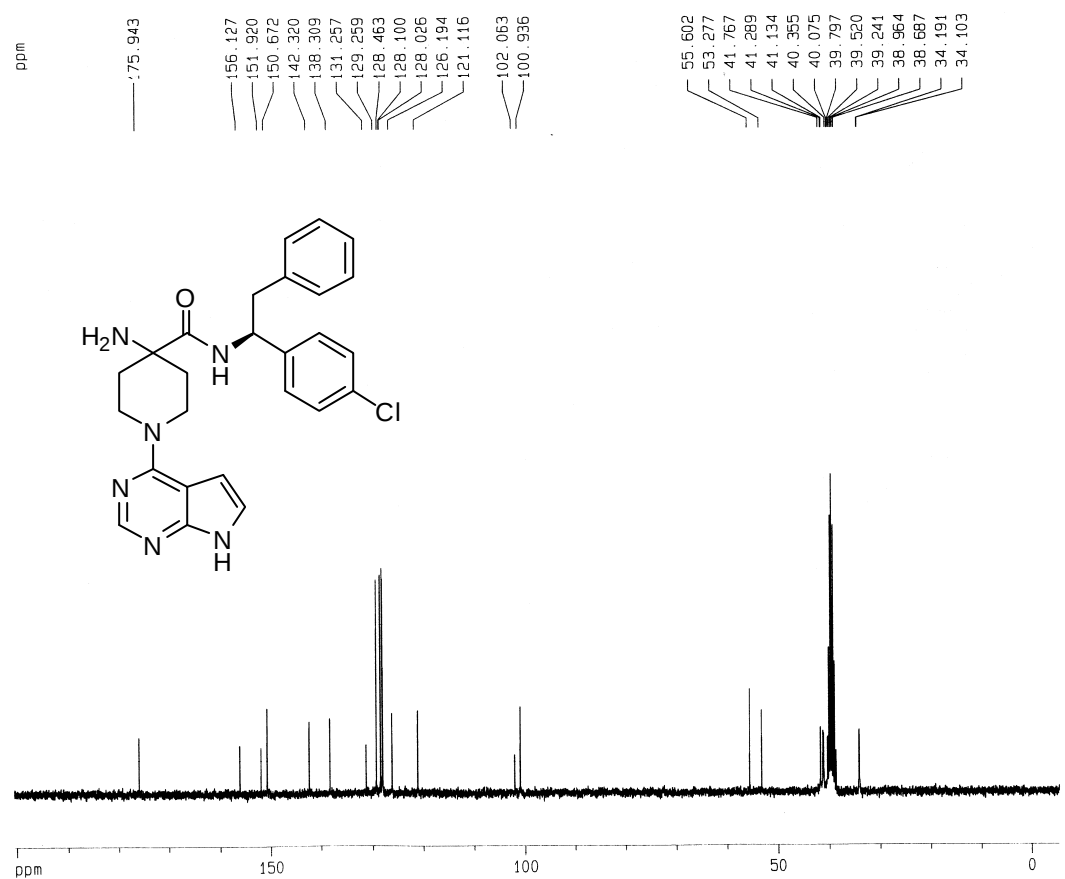




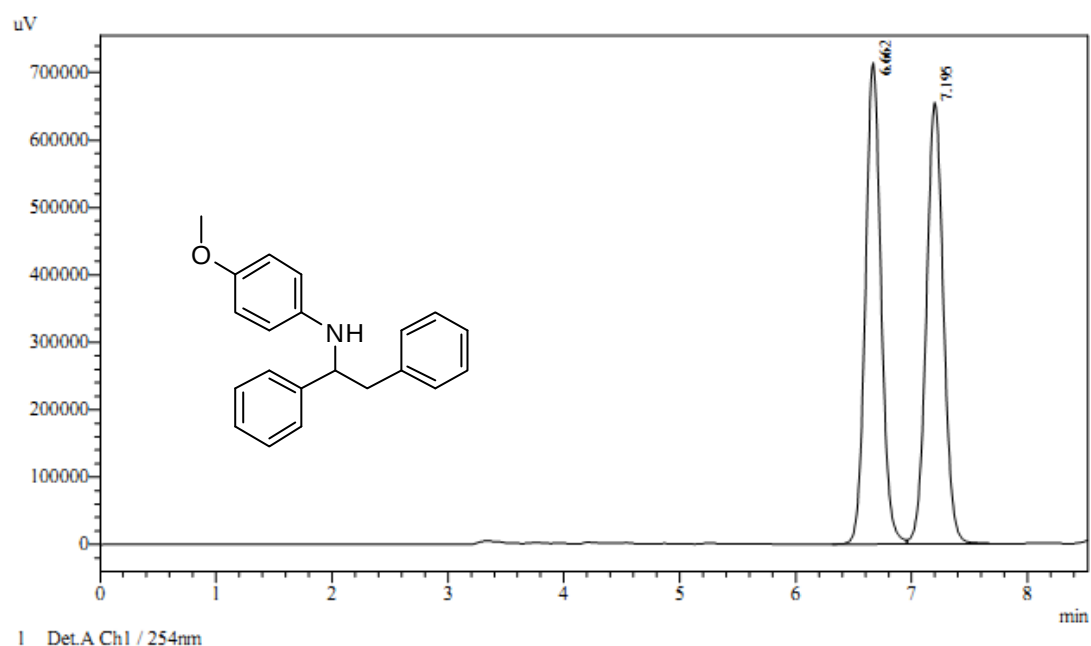






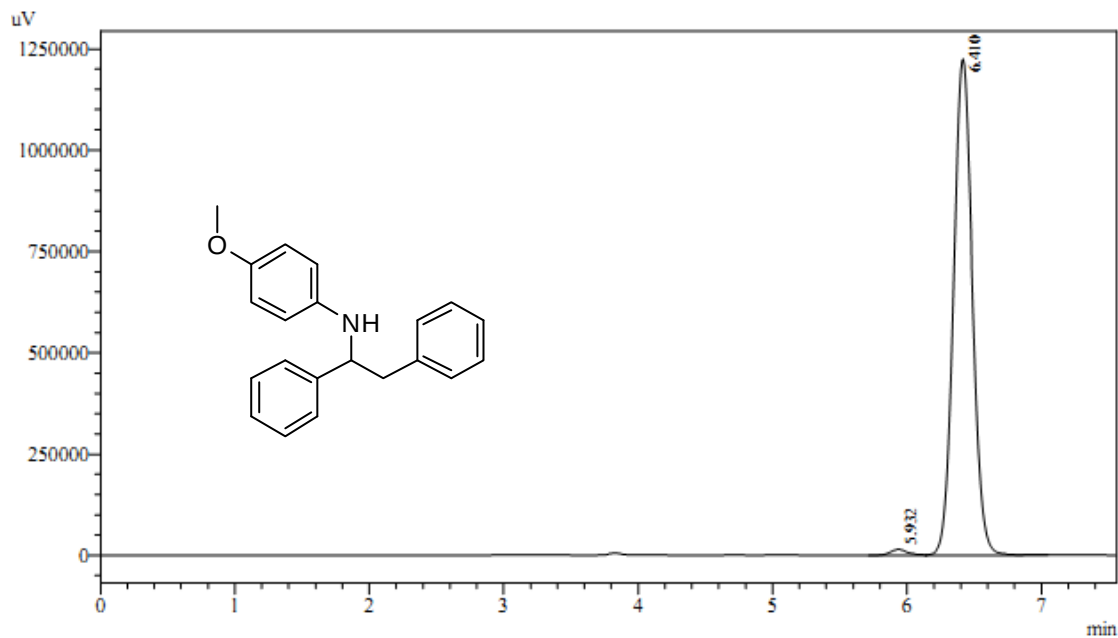


## 7. The Copies of HPLC Spectra



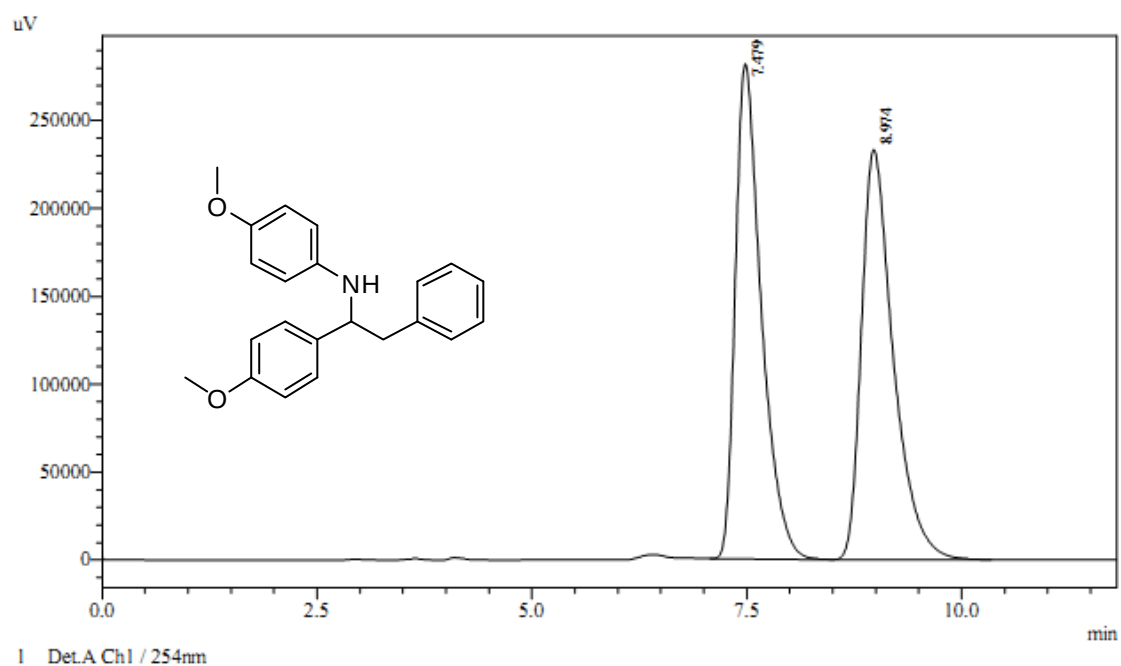
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.662     | 6673066  | 714291  | 49.971  | 52.180   |
| 2     | 7.195     | 6680835  | 654619  | 50.029  | 47.820   |
| Total |           | 13353901 | 1368910 | 100.000 | 100.000  |



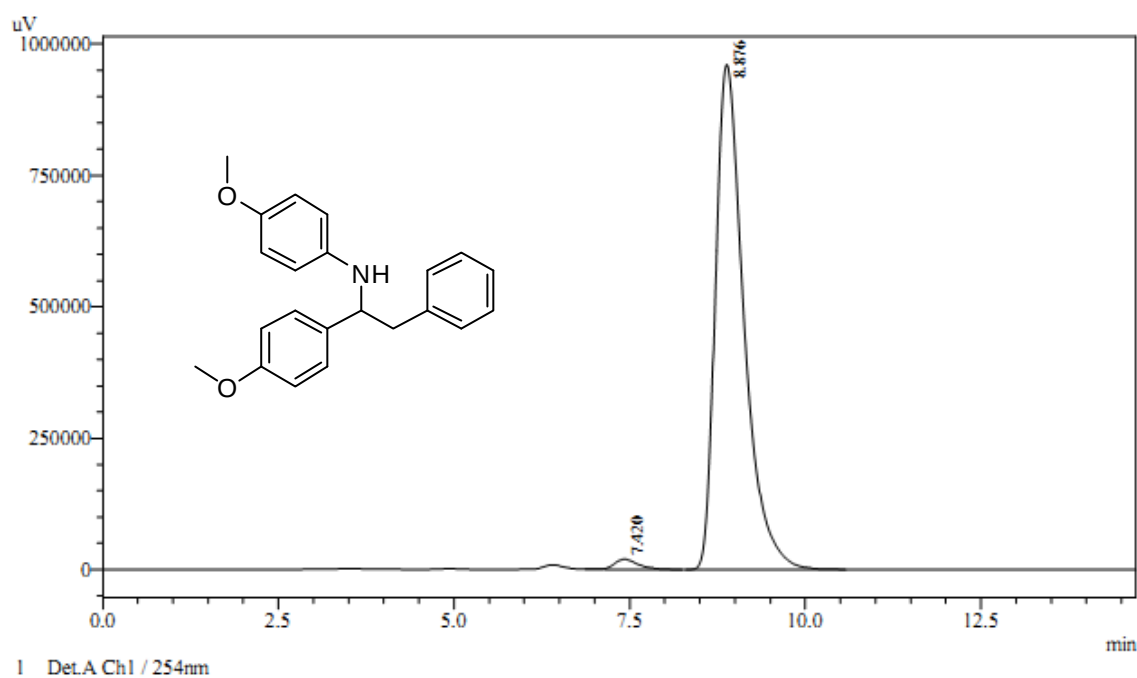
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.932     | 138186   | 15057   | 1.147   | 1.214    |
| 2     | 6.410     | 11908392 | 1225044 | 98.853  | 98.786   |
| Total |           | 12046578 | 1240102 | 100.000 | 100.000  |



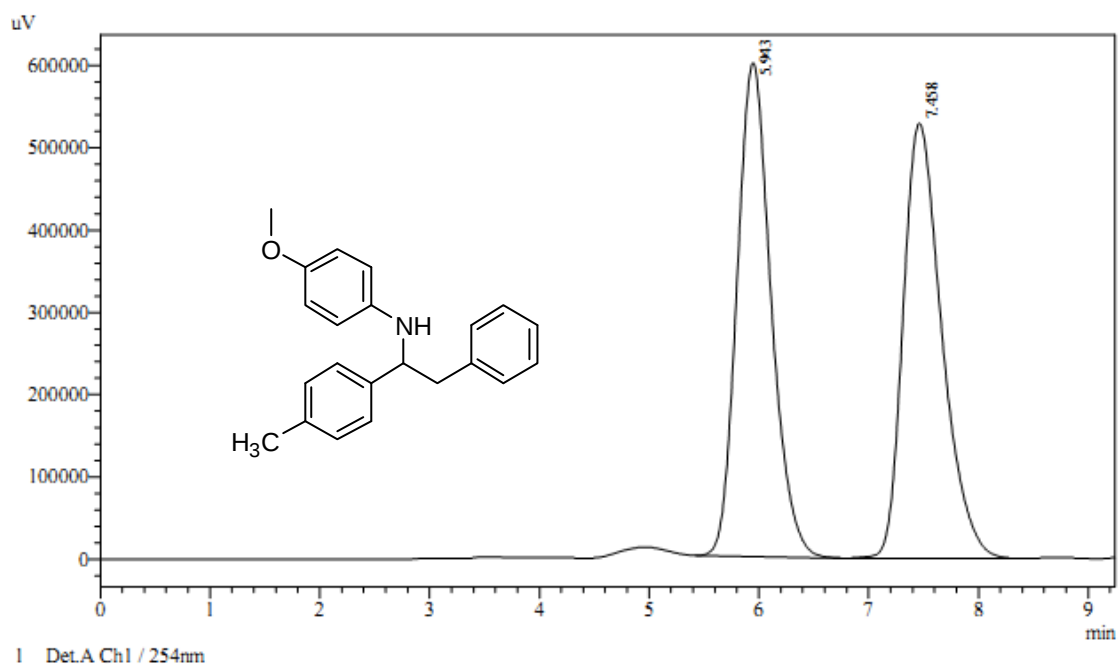
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 7.479     | 5944247  | 281933 | 49.697  | 54.723   |
| 2     | 8.974     | 6016651  | 233266 | 50.303  | 45.277   |
| Total |           | 11960898 | 515199 | 100.000 | 100.000  |



Detector A Ch1 254nm

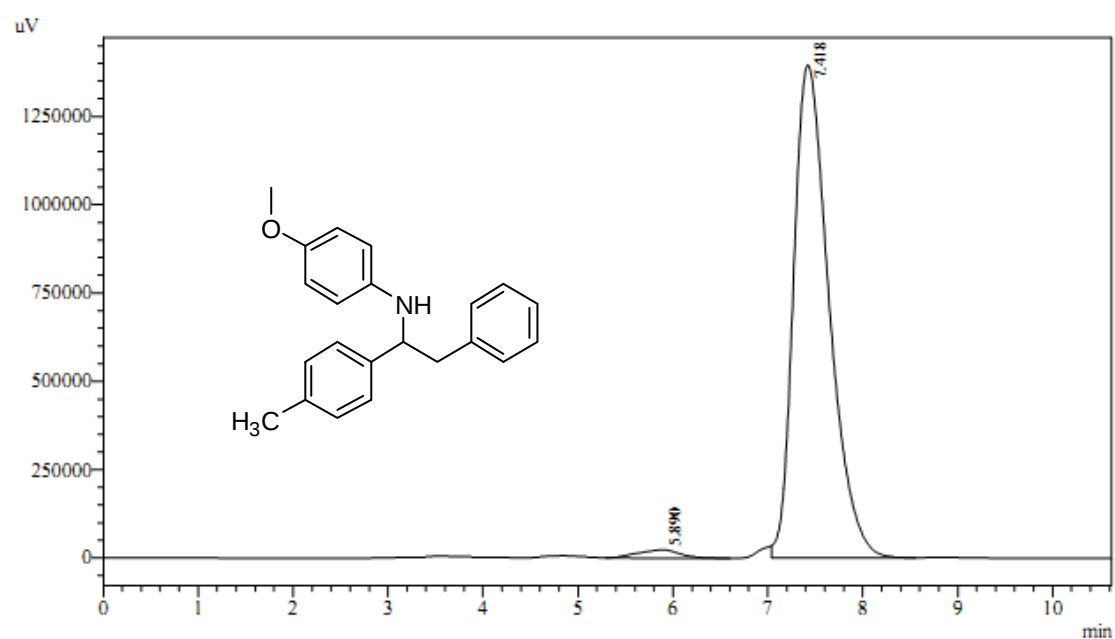
| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 7.420     | 443590   | 19255  | 1.610   | 1.966    |
| 2     | 8.876     | 27110840 | 960359 | 98.390  | 98.034   |
| Total |           | 27554429 | 979614 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

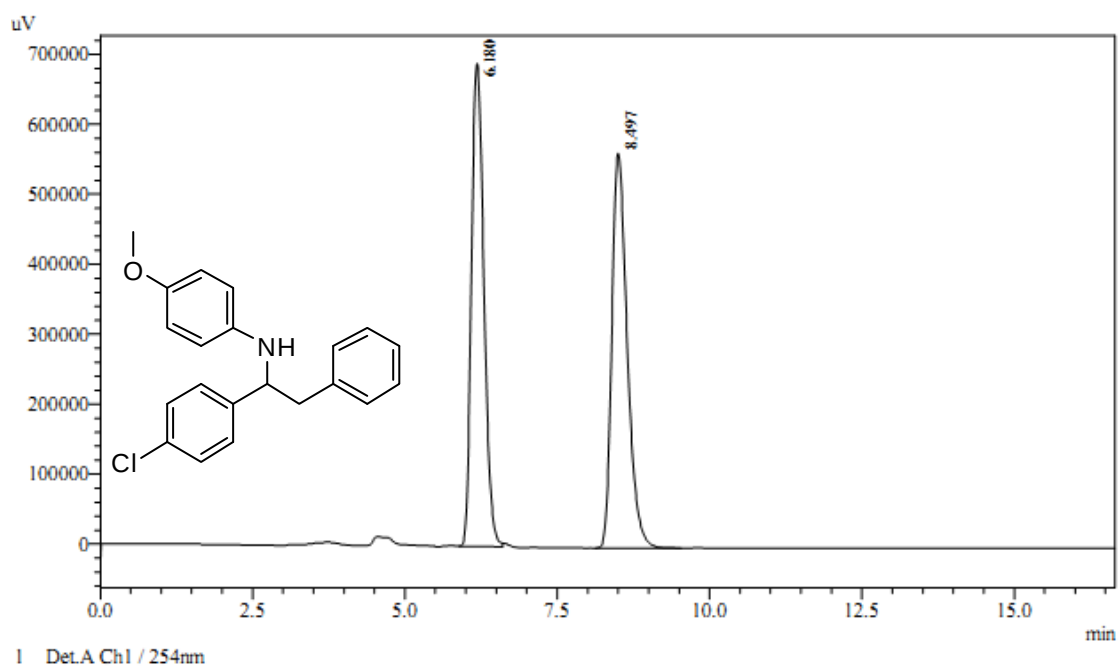
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.943     | 12927223 | 600378  | 49.980  | 53.185   |
| 2     | 7.458     | 12937703 | 528474  | 50.020  | 46.815   |
| Total |           | 25864925 | 1128851 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

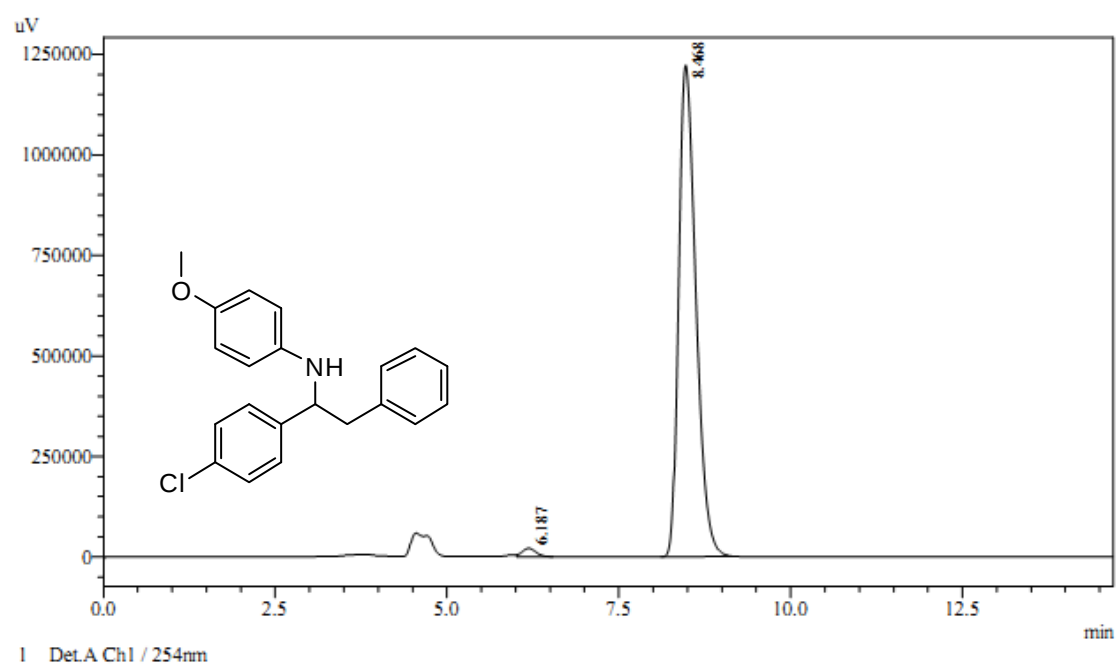
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.890     | 695414   | 22871   | 1.885   | 1.614    |
| 2     | 7.418     | 36190860 | 1394189 | 98.115  | 98.386   |
| Total |           | 36886274 | 1417060 | 100.000 | 100.000  |



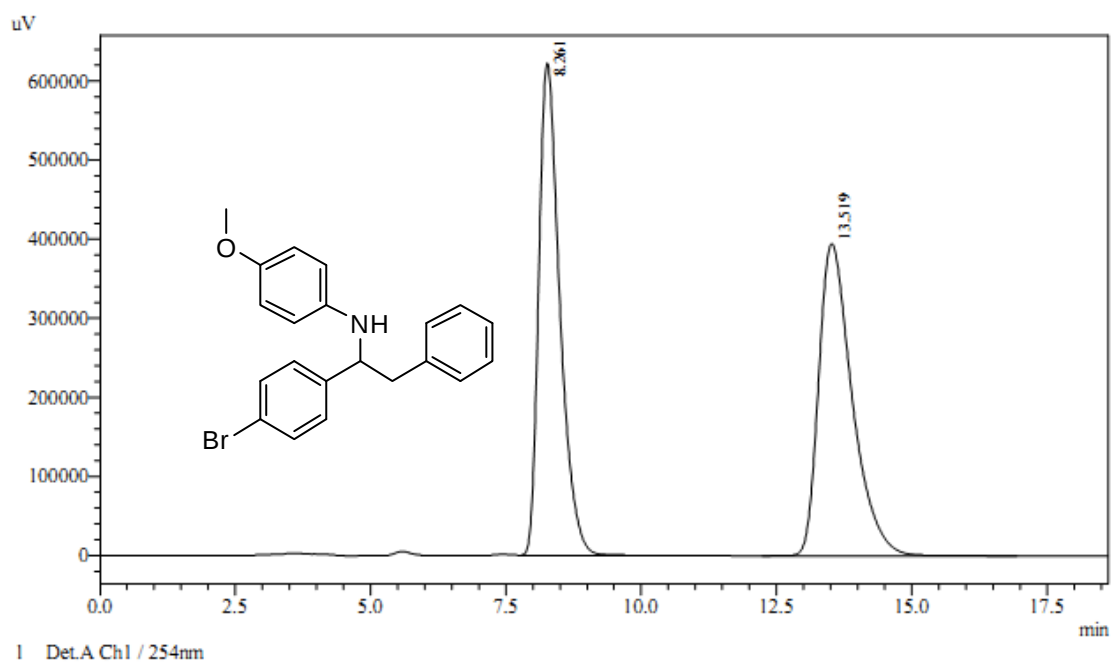
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.180     | 9813871  | 690325  | 49.758  | 55.022   |
| 2     | 8.497     | 9909246  | 564319  | 50.242  | 44.978   |
| Total |           | 19723118 | 1254644 | 100.000 | 100.000  |



Detector A Ch1 254nm

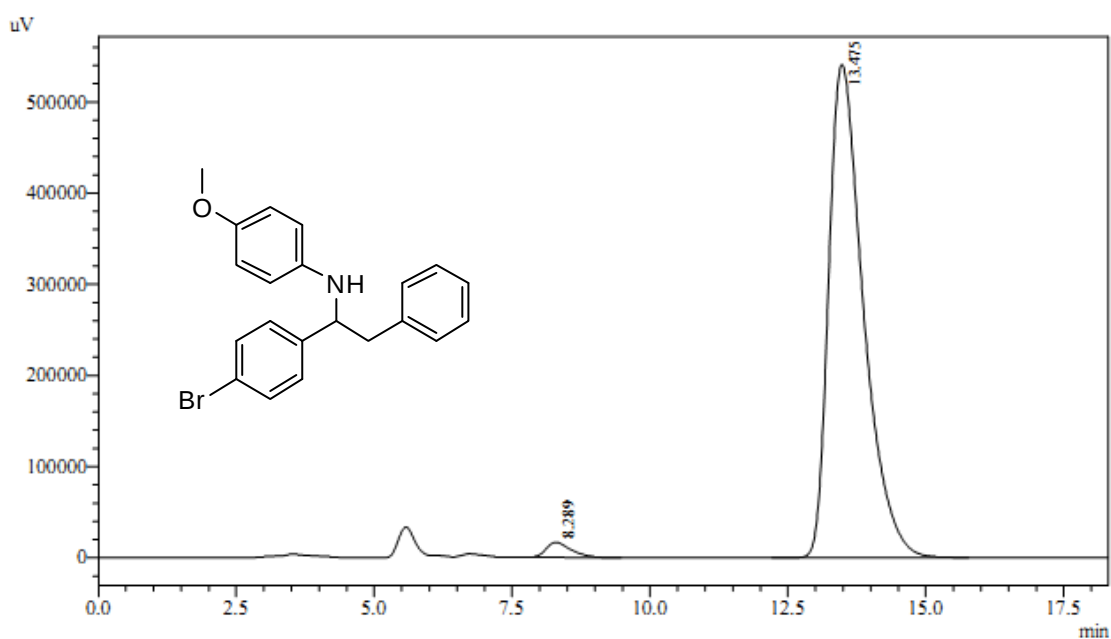
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.187     | 289982   | 20707   | 1.336   | 1.665    |
| 2     | 8.468     | 21421497 | 1223114 | 98.664  | 98.335   |
| Total |           | 21711480 | 1243820 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

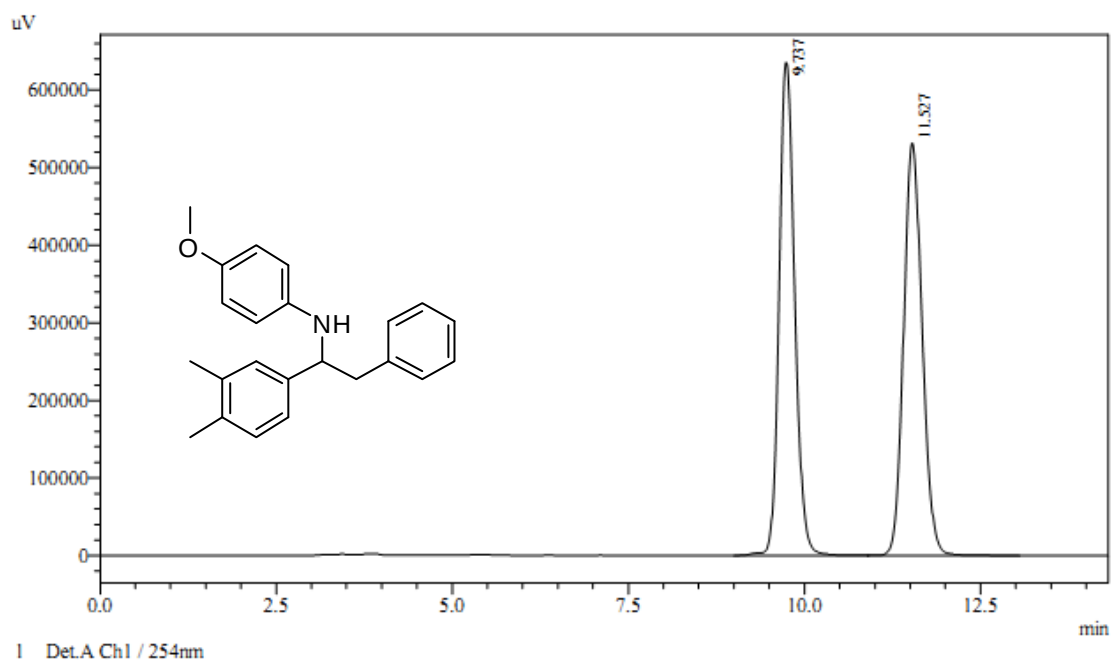
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 8.261     | 16792798 | 622594  | 49.690  | 61.202   |
| 2     | 13.519    | 17002241 | 394682  | 50.310  | 38.798   |
| Total |           | 33795039 | 1017275 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

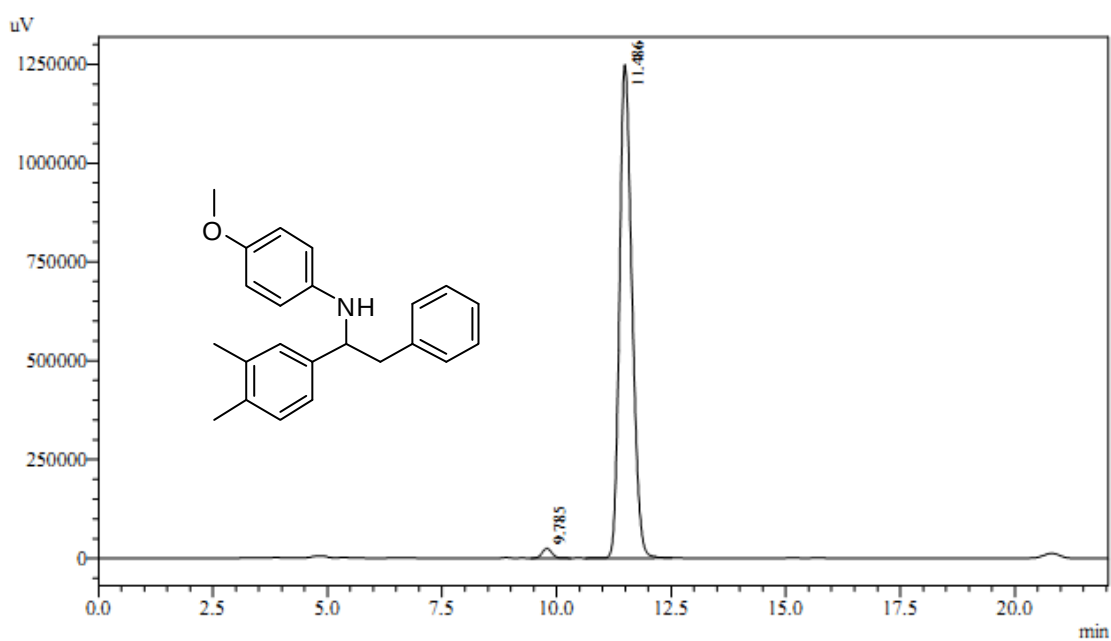
| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 8.289     | 527899   | 16795  | 2.184   | 3.010    |
| 2     | 13.475    | 23646516 | 541161 | 97.816  | 96.990   |
| Total |           | 24174415 | 557956 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

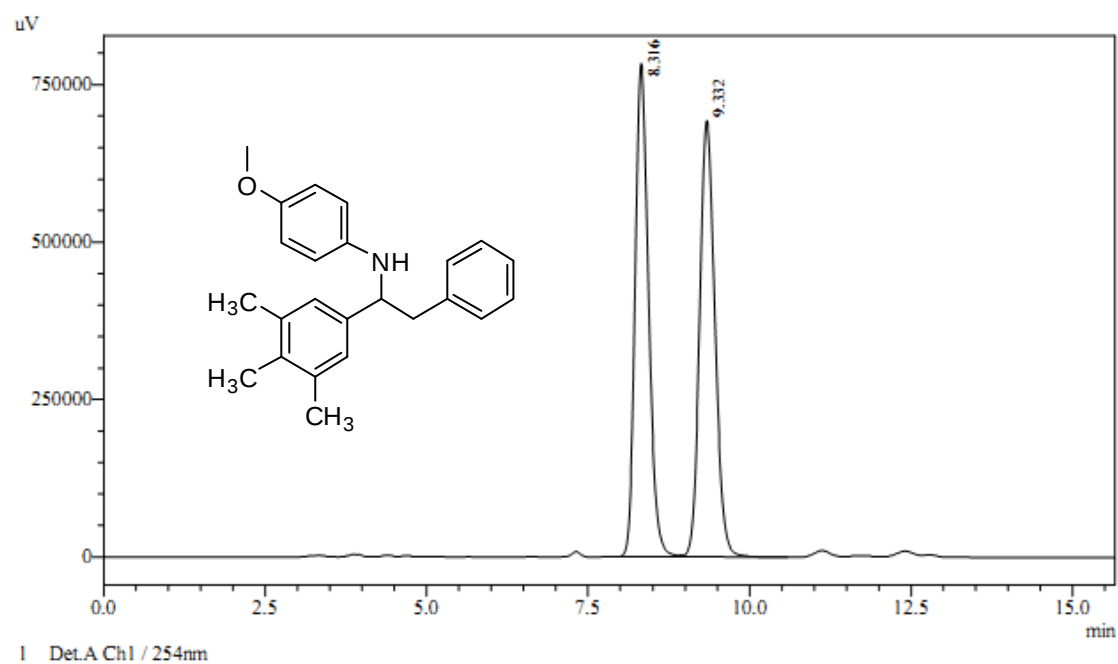
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 9.737     | 9766325  | 635734  | 50.028  | 54.456   |
| 2     | 11.527    | 9755565  | 531688  | 49.972  | 45.544   |
| Total |           | 19521891 | 1167421 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

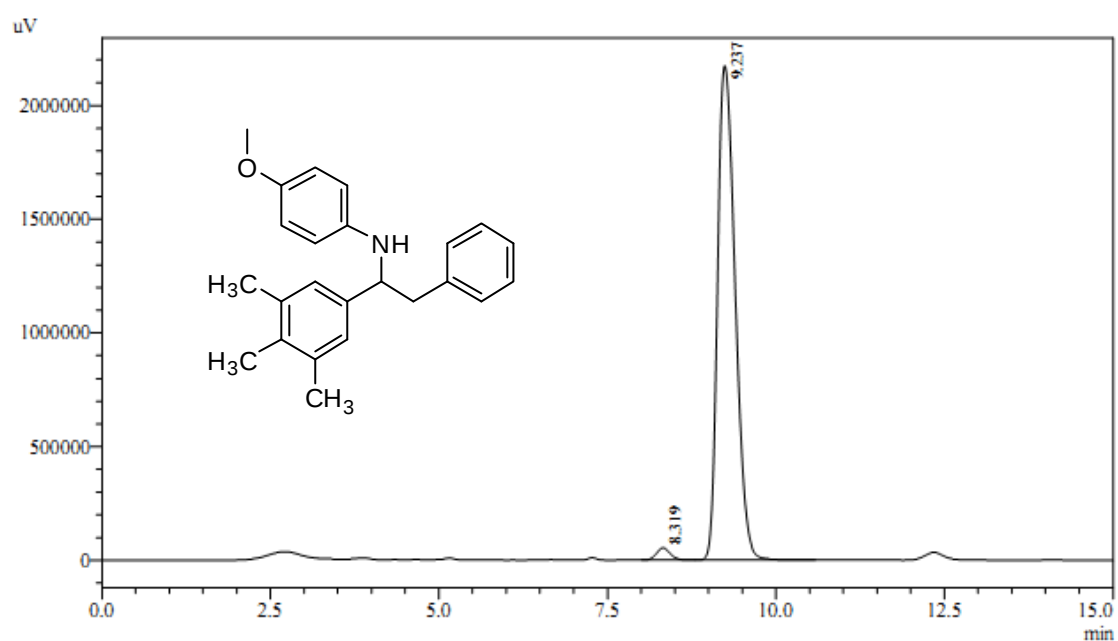
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 9.785     | 369740   | 24797   | 1.538   | 1.947    |
| 2     | 11.486    | 23668817 | 1248640 | 98.462  | 98.053   |
| Total |           | 24038557 | 1273437 | 100.000 | 100.000  |



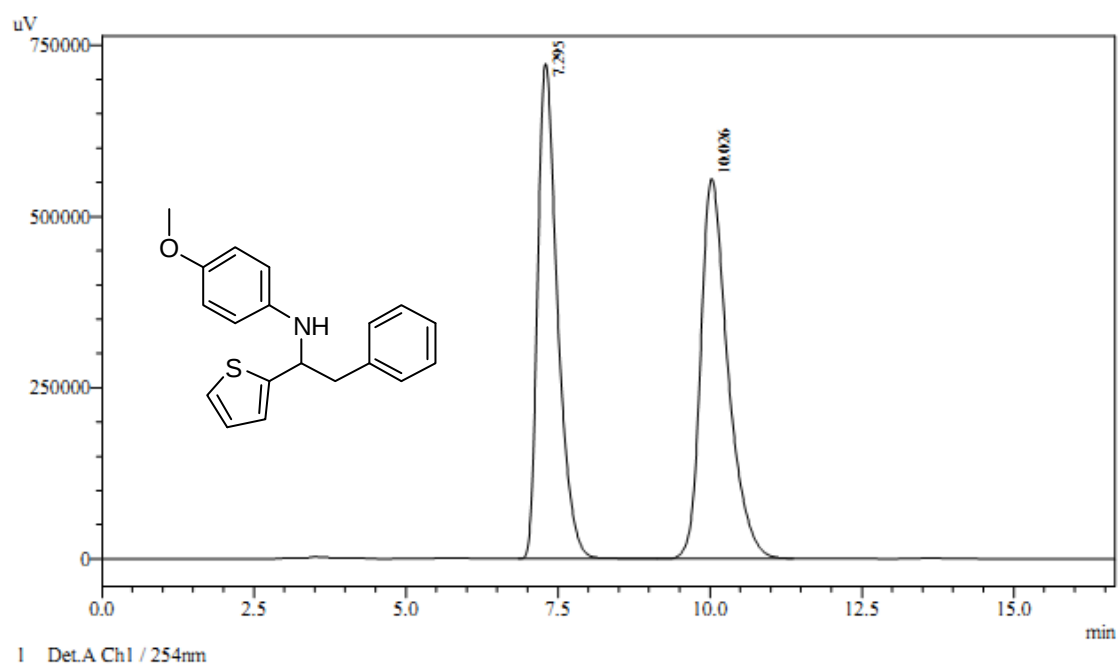
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 8.316     | 11311095 | 783579  | 49.794  | 53.057   |
| 2     | 9.332     | 11404465 | 693282  | 50.206  | 46.943   |
| Total |           | 22715560 | 1476861 | 100.000 | 100.000  |



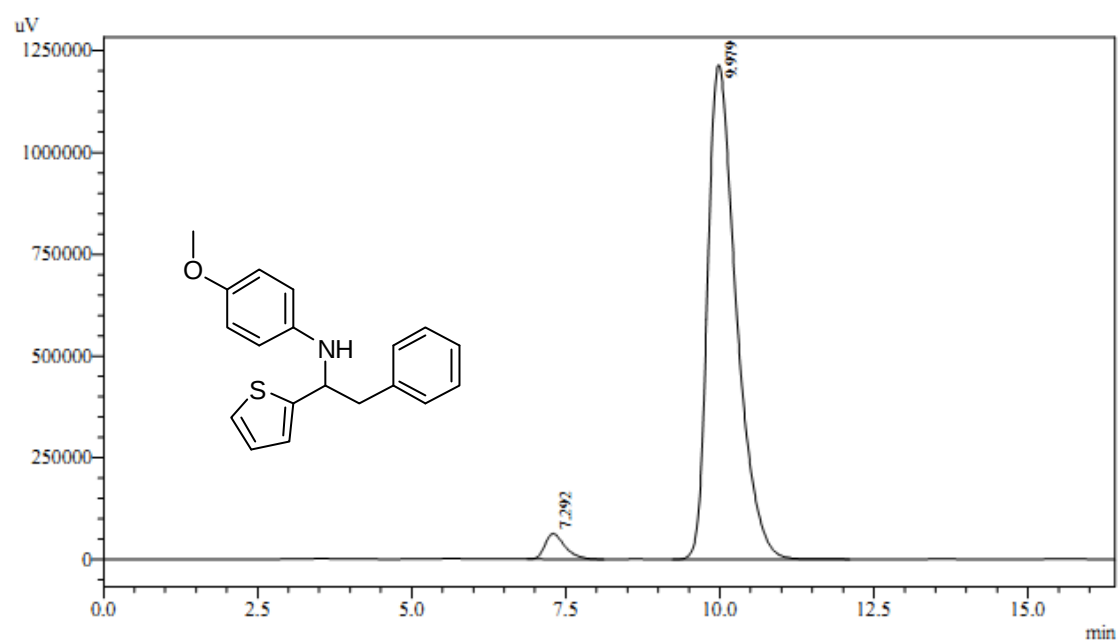
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 8.319     | 761641   | 53641   | 1.906   | 2.407    |
| 2     | 9.237     | 39192979 | 2174664 | 98.094  | 97.593   |
| Total |           | 39954619 | 2228305 | 100.000 | 100.000  |



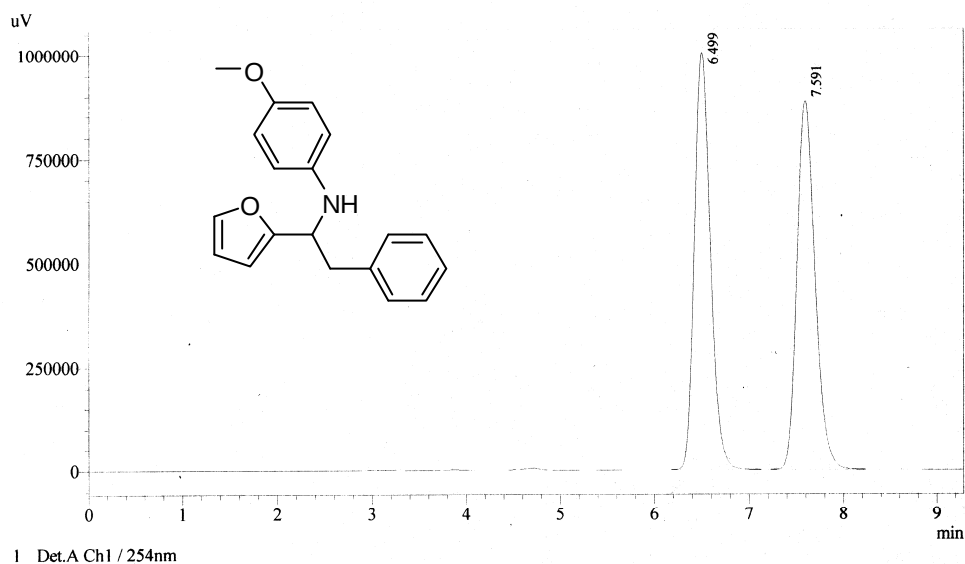
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 7.295     | 16428597 | 722735  | 48.814  | 56.589   |
| 2     | 10.026    | 17226902 | 554431  | 51.186  | 43.411   |
| Total |           | 33655499 | 1277166 | 100.000 | 100.000  |

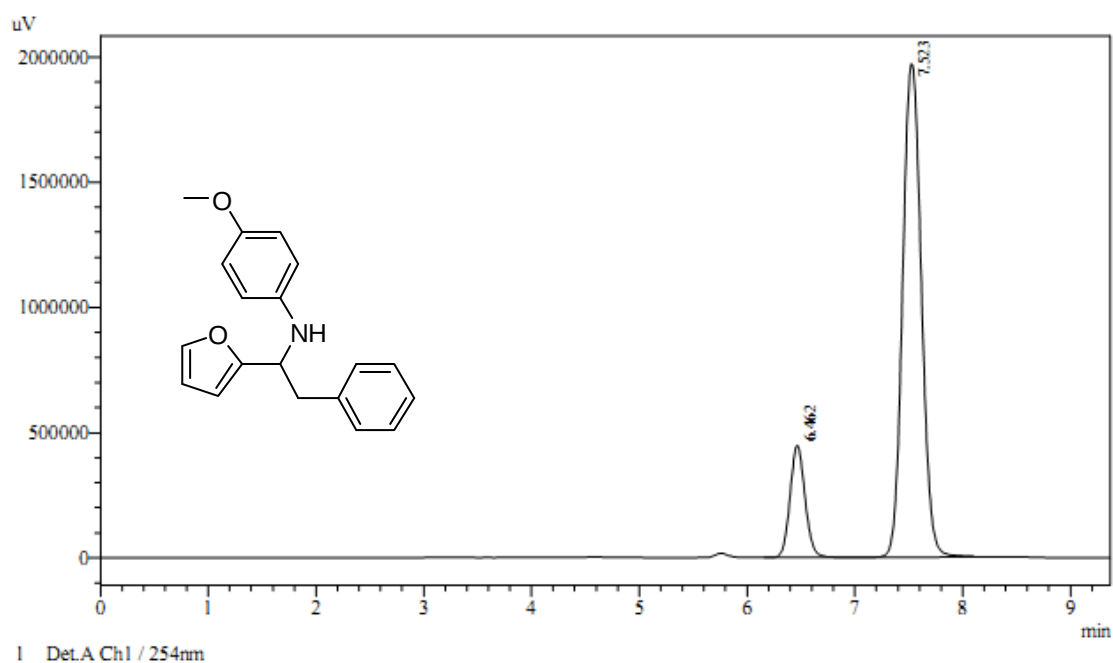


Detector A Ch1 254nm

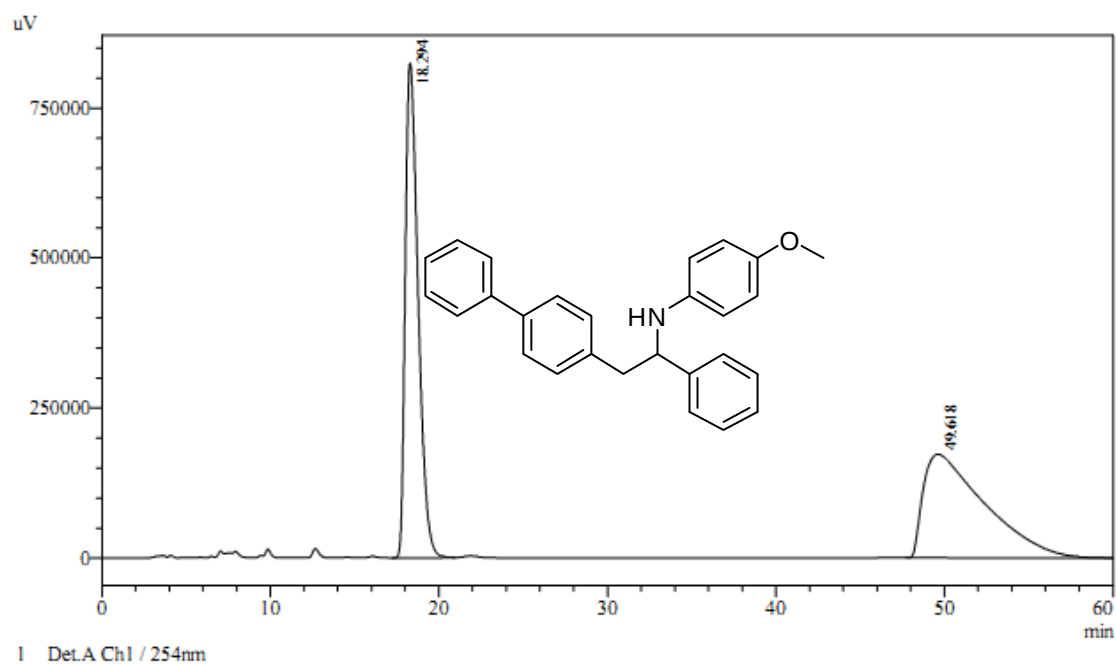
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 7.292     | 1422626  | 62570   | 3.497   | 4.896    |
| 2     | 9.979     | 39256707 | 1215527 | 96.503  | 95.104   |
| Total |           | 40679333 | 1278097 | 100.000 | 100.000  |



| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.499     | 11830787 | 1004570 | 49.884  | 53.126   |
| 2     | 7.591     | 11885573 | 886353  | 50.116  | 46.874   |
| Total |           | 23716360 | 1890923 | 100.000 | 100.000  |

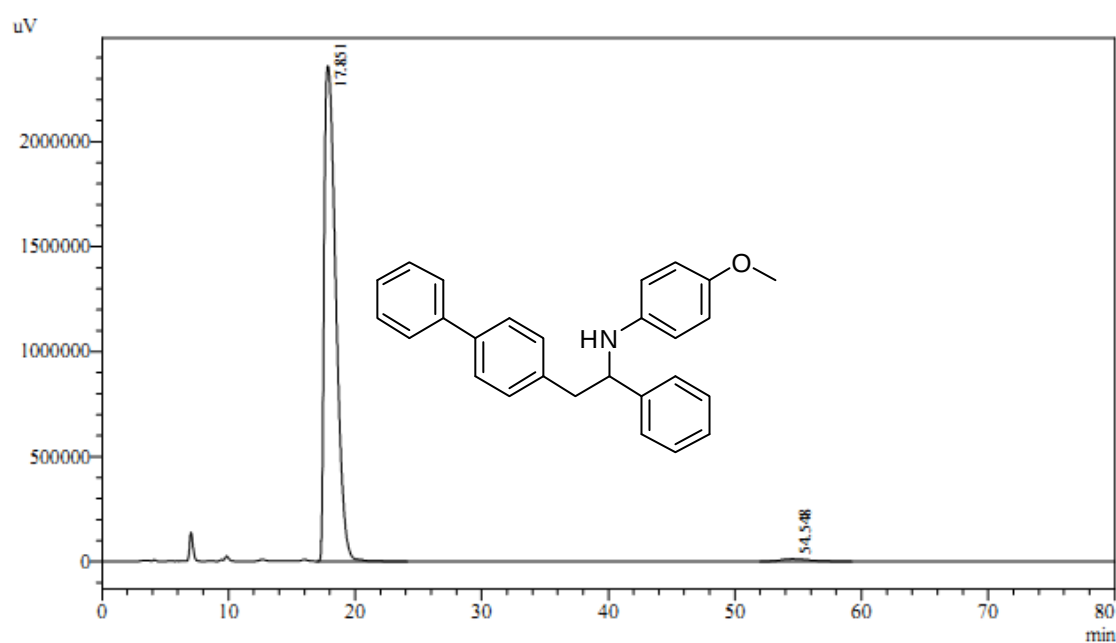


| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.462     | 4364130  | 448340  | 15.484  | 18.523   |
| 2     | 7.523     | 23820271 | 1972159 | 84.516  | 81.477   |
| Total |           | 28184401 | 2420500 | 100.000 | 100.000  |



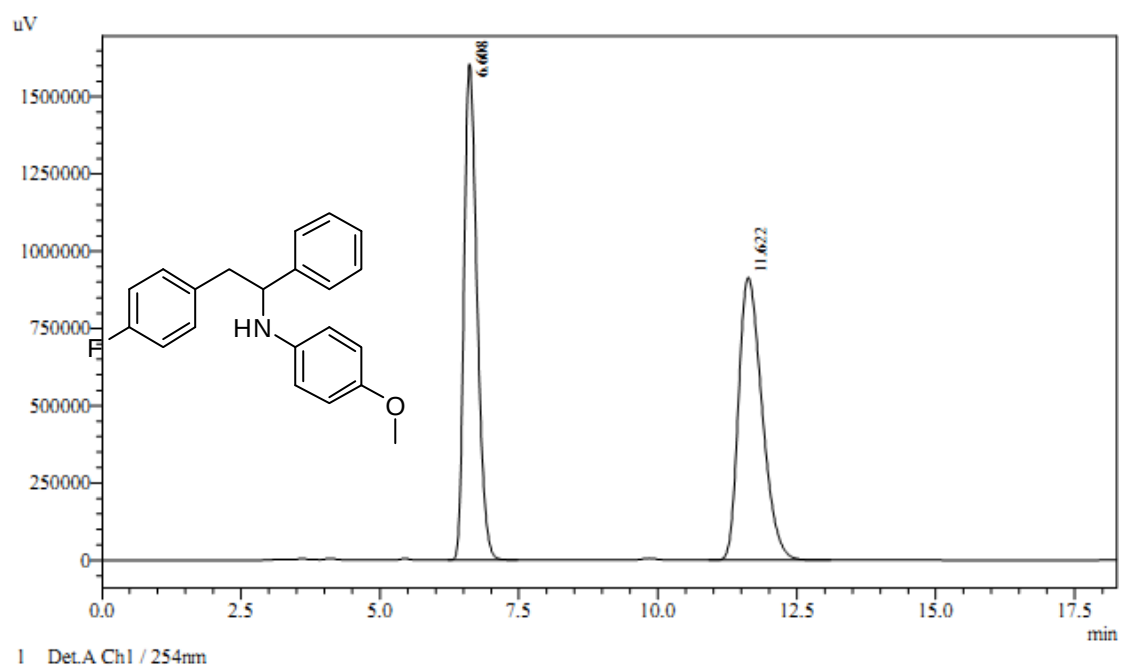
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 18.294    | 43766500 | 824860 | 49.951  | 82.686   |
| 2     | 49.618    | 43851808 | 172716 | 50.049  | 17.314   |
| Total |           | 87618308 | 997576 | 100.000 | 100.000  |



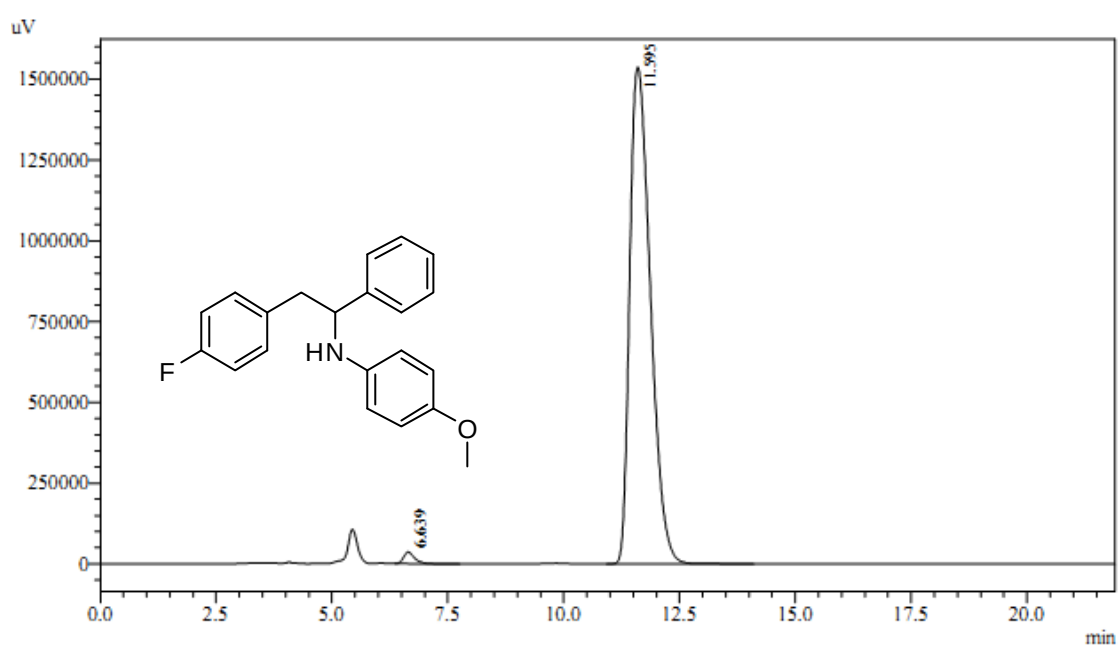
Detector A Ch1 254nm

| Peak# | Ret. Time | Area      | Height  | Area %  | Height % |
|-------|-----------|-----------|---------|---------|----------|
| 1     | 17.851    | 151235283 | 2362669 | 98.773  | 99.499   |
| 2     | 54.548    | 1878947   | 11906   | 1.227   | 0.501    |
| Total |           | 153114229 | 2374575 | 100.000 | 100.000  |



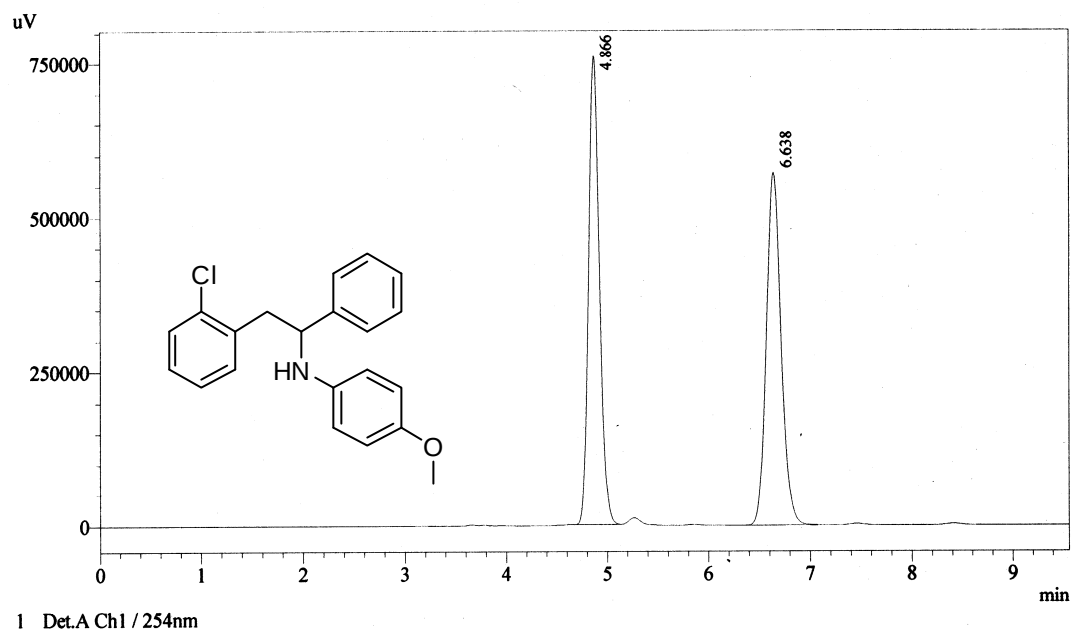
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.608     | 26175517 | 1606199 | 49.316  | 63.707   |
| 2     | 11.622    | 26901145 | 915029  | 50.684  | 36.293   |
| Total |           | 53076661 | 2521228 | 100.000 | 100.000  |



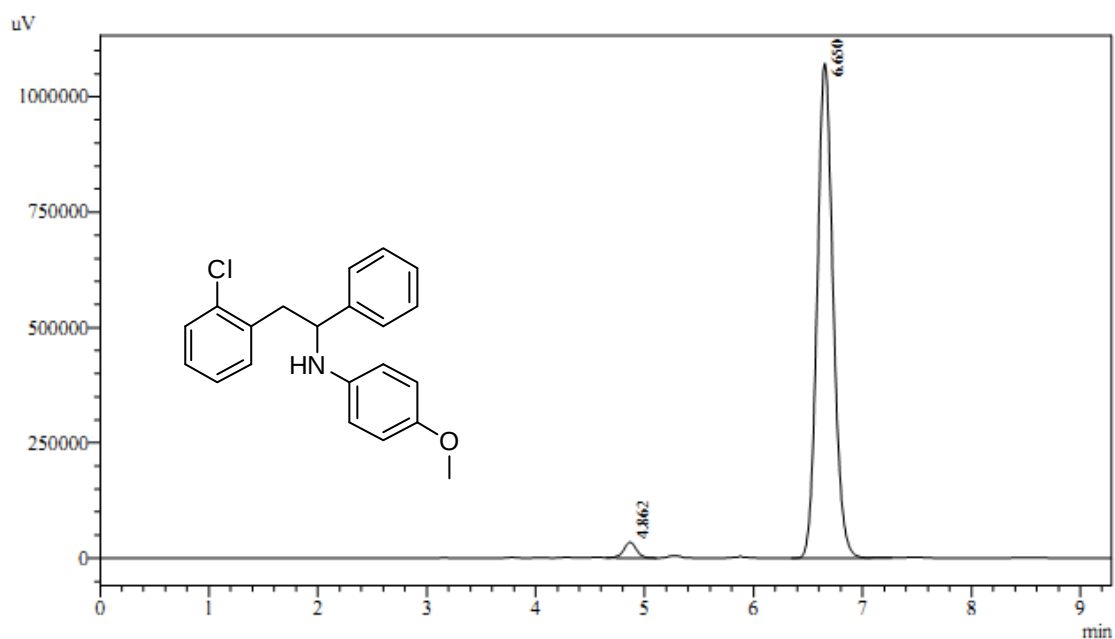
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.639     | 602260   | 36002   | 1.247   | 2.287    |
| 2     | 11.595    | 47698091 | 1538024 | 98.753  | 97.713   |
| Total |           | 48300351 | 1574026 | 100.000 | 100.000  |



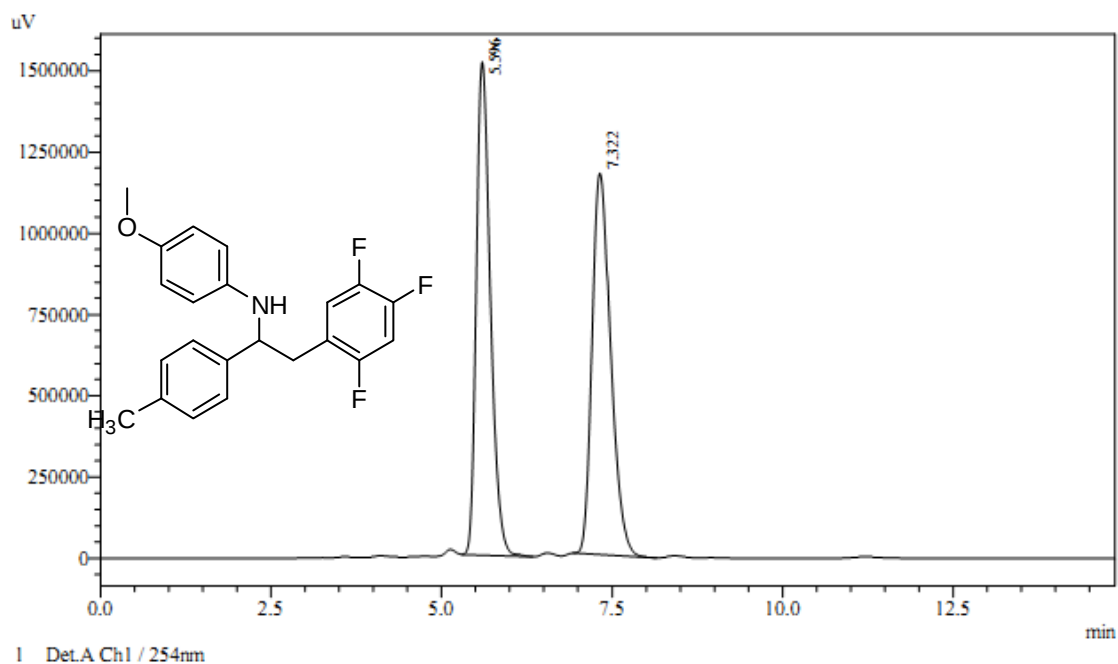
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 4.866     | 5665786  | 758882  | 49.647  | 57.020   |
| 2     | 6.638     | 5746448  | 572033  | 50.353  | 42.980   |
| Total | .         | 11412234 | 1330915 | 100.000 | 100.000  |



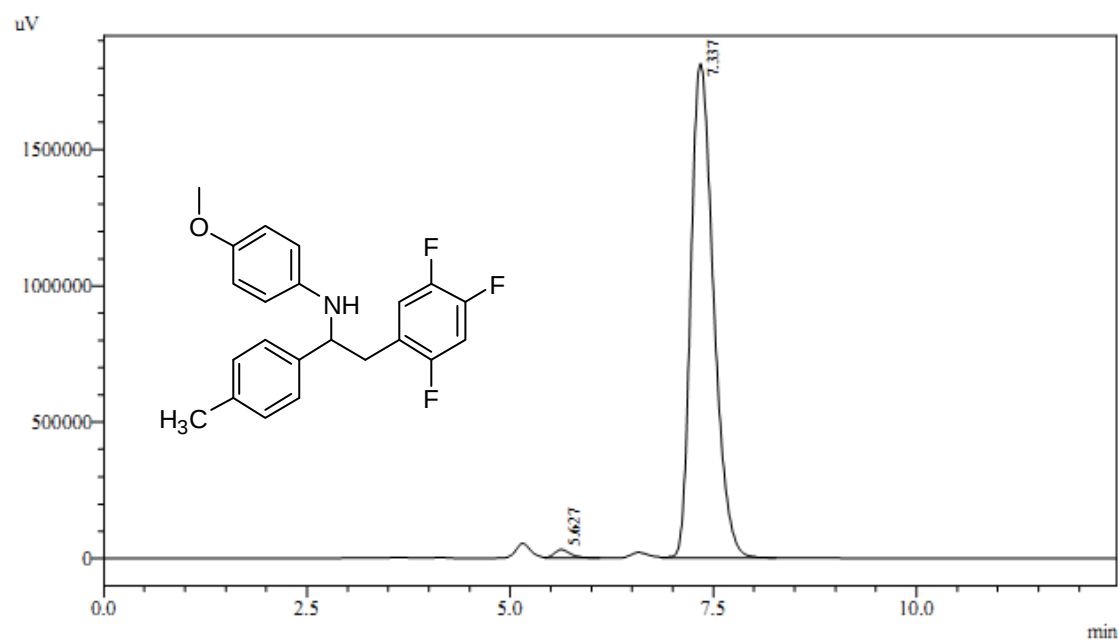
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 4.862     | 273413   | 33983   | 2.439   | 3.071    |
| 2     | 6.650     | 10935151 | 1072628 | 97.561  | 96.929   |
| Total |           | 11208564 | 1106611 | 100.000 | 100.000  |



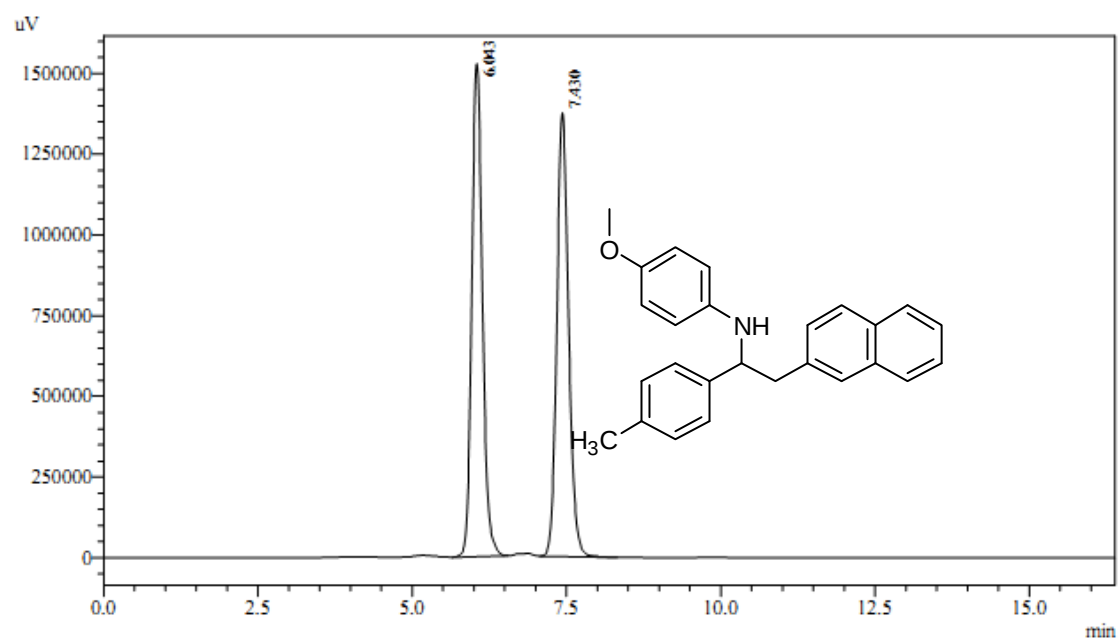
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.596     | 21788342 | 1516961 | 49.941  | 56.385   |
| 2     | 7.322     | 21839937 | 1173380 | 50.059  | 43.615   |
| Total |           | 43628278 | 2690342 | 100.000 | 100.000  |



Detector A Ch1 254nm

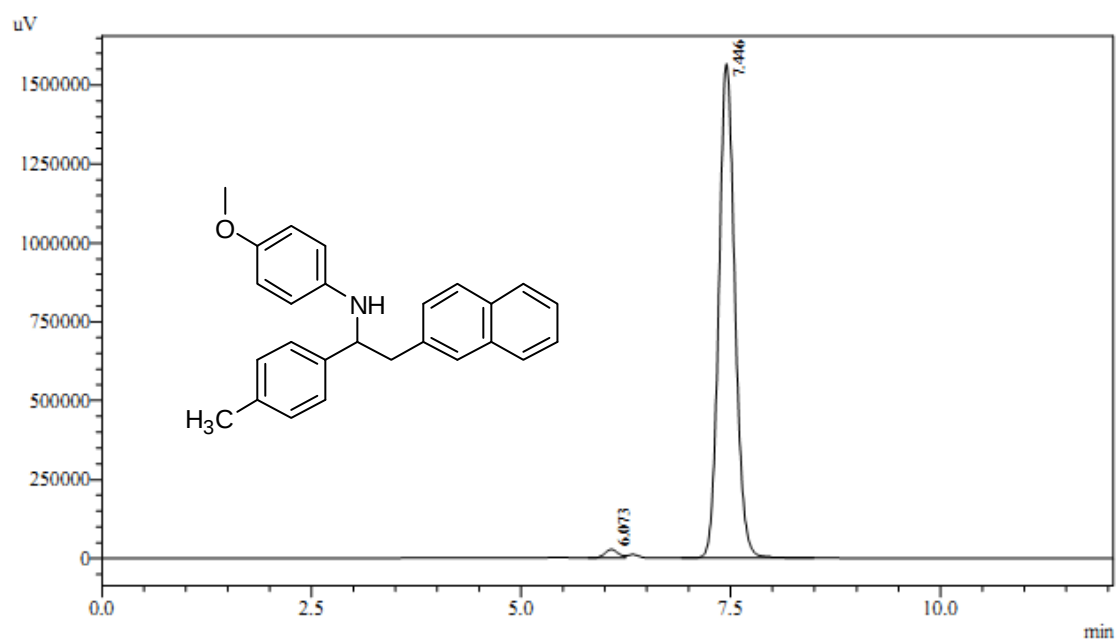
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.627     | 437855   | 31358   | 1.231   | 1.700    |
| 2     | 7.337     | 35130603 | 1813650 | 98.769  | 98.300   |
| Total |           | 35568459 | 1845007 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

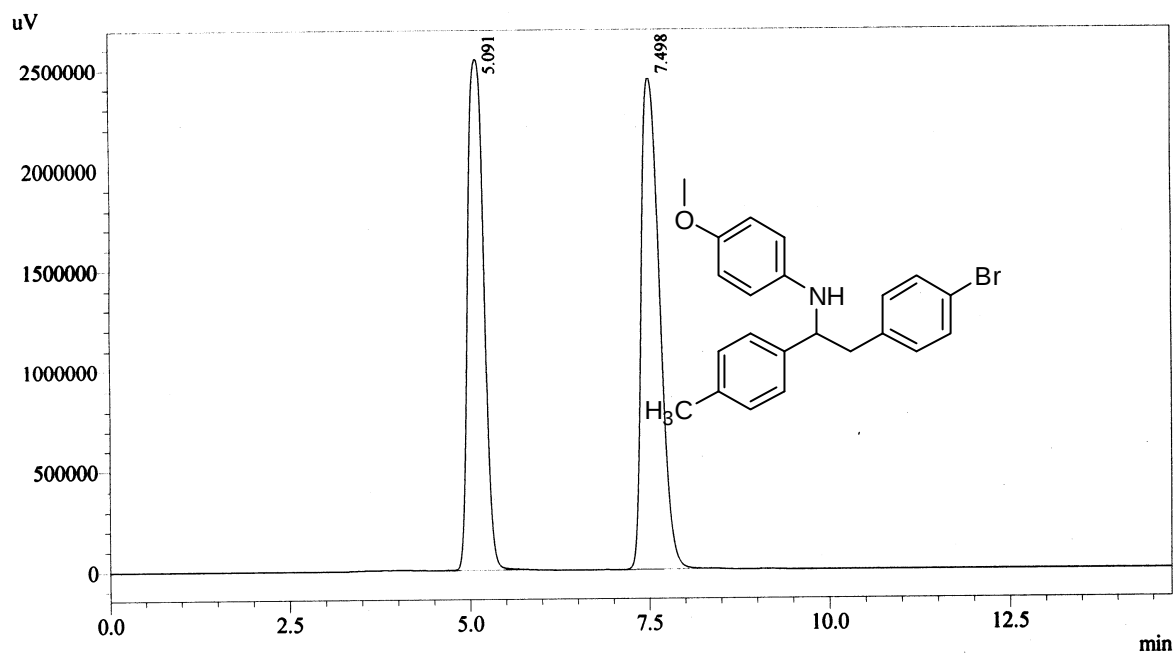
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.043     | 18368831 | 1527088 | 50.237  | 52.641   |
| 2     | 7.430     | 18195604 | 1373850 | 49.763  | 47.359   |
| Total |           | 36564435 | 2900938 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

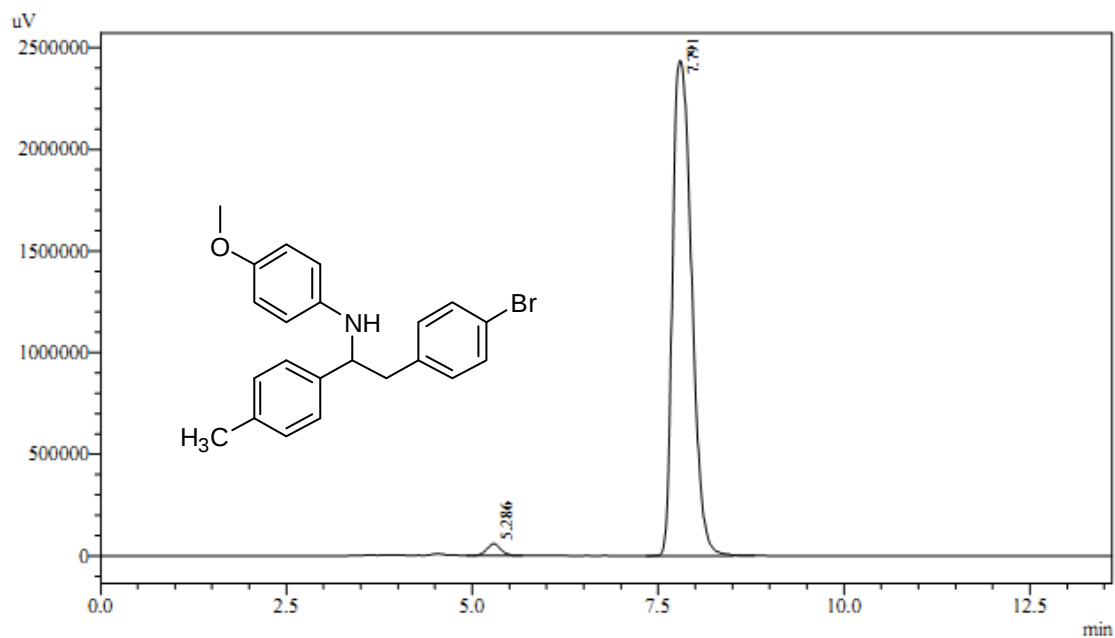
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.073     | 310775   | 27252   | 1.466   | 1.709    |
| 2     | 7.446     | 20892918 | 1567496 | 98.534  | 98.291   |
| Total |           | 21203694 | 1594749 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

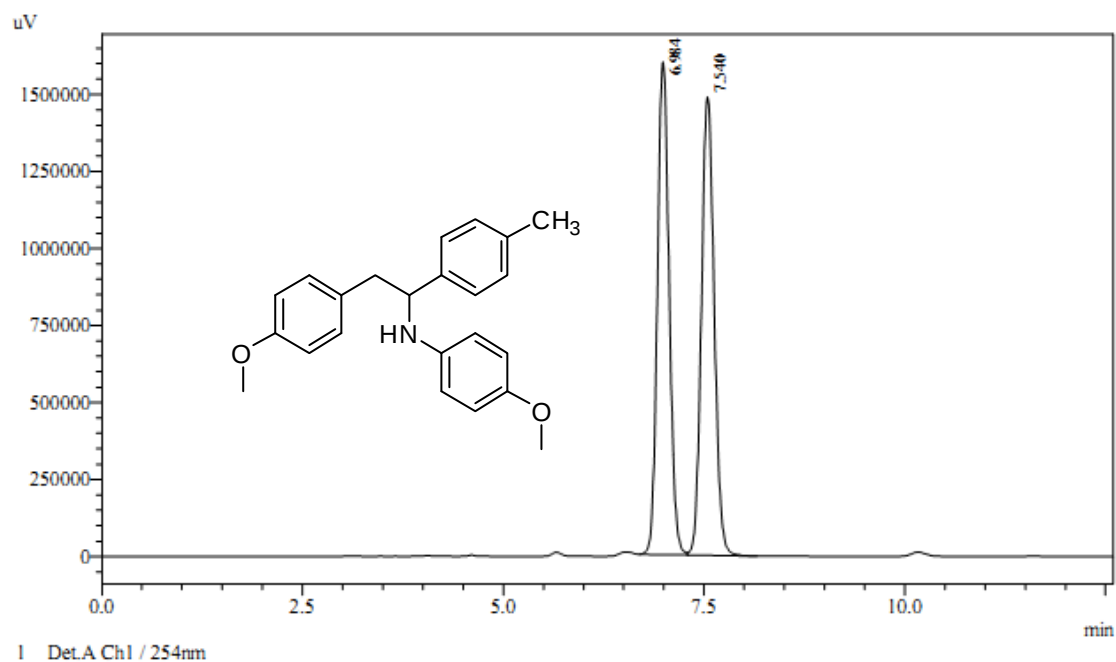
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.091     | 39623773 | 2544849 | 47.841  | 50.987   |
| 2     | 7.498     | 43199584 | 2446349 | 52.159  | 49.013   |
| Total |           | 82823357 | 4991198 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

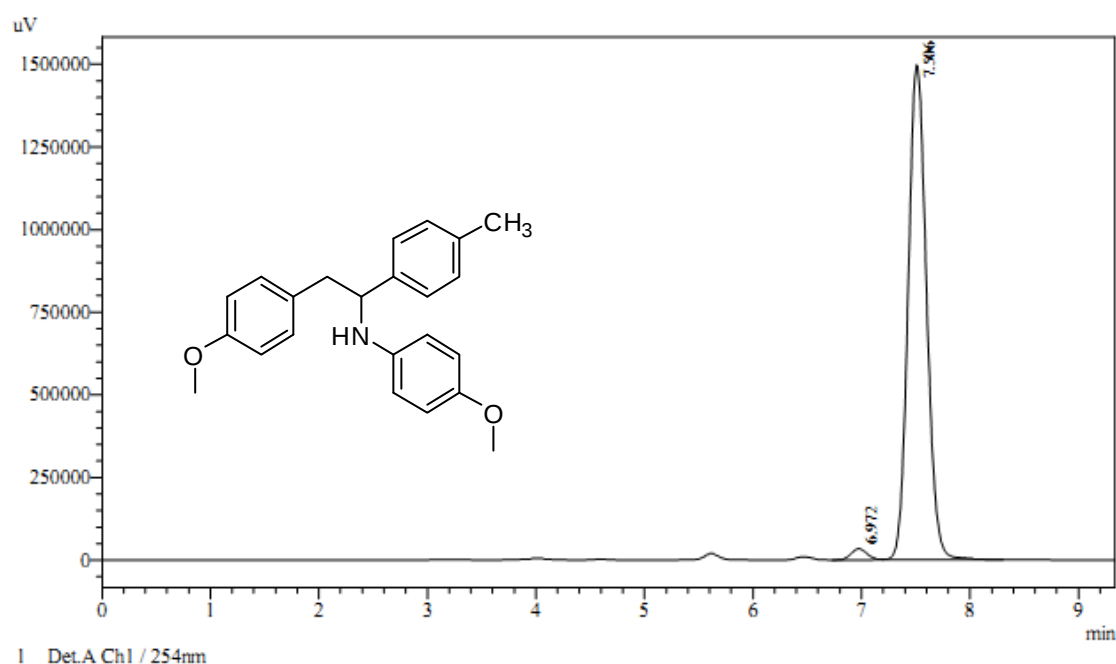
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 5.286     | 771141   | 58163   | 1.744   | 2.332    |
| 2     | 7.791     | 43456895 | 2435750 | 98.256  | 97.668   |
| Total |           | 44228036 | 2493912 | 100.000 | 100.000  |



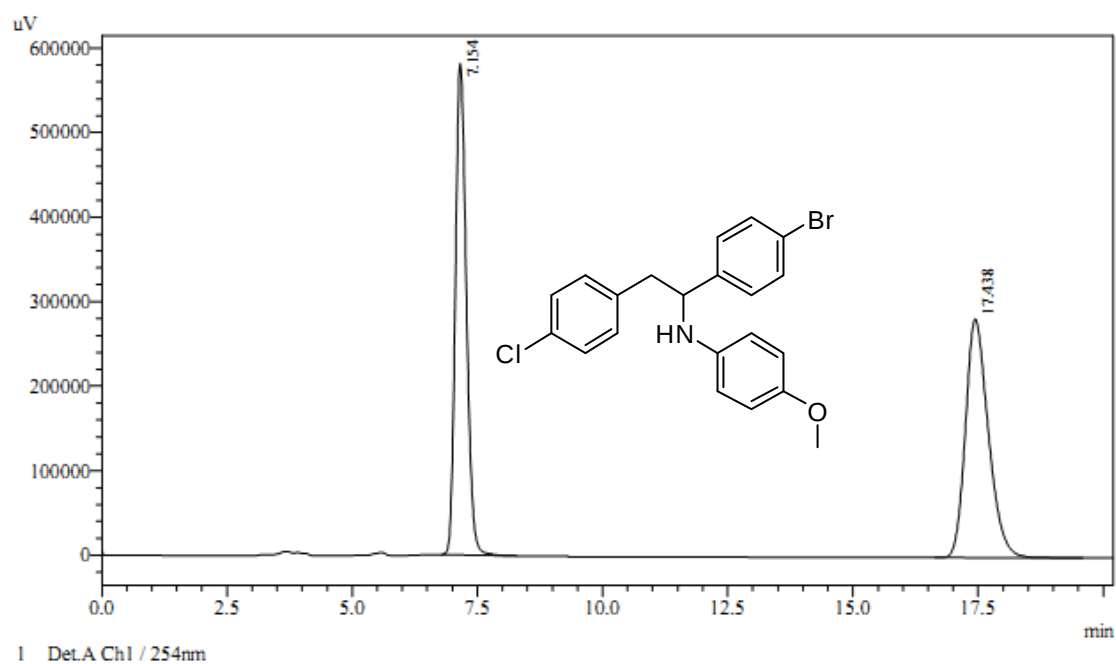
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.984     | 16263891 | 1599776 | 49.667  | 51.815   |
| 2     | 7.540     | 16481790 | 1487729 | 50.333  | 48.185   |
| Total |           | 32745681 | 3087505 | 100.000 | 100.000  |



Detector A Ch1 254nm

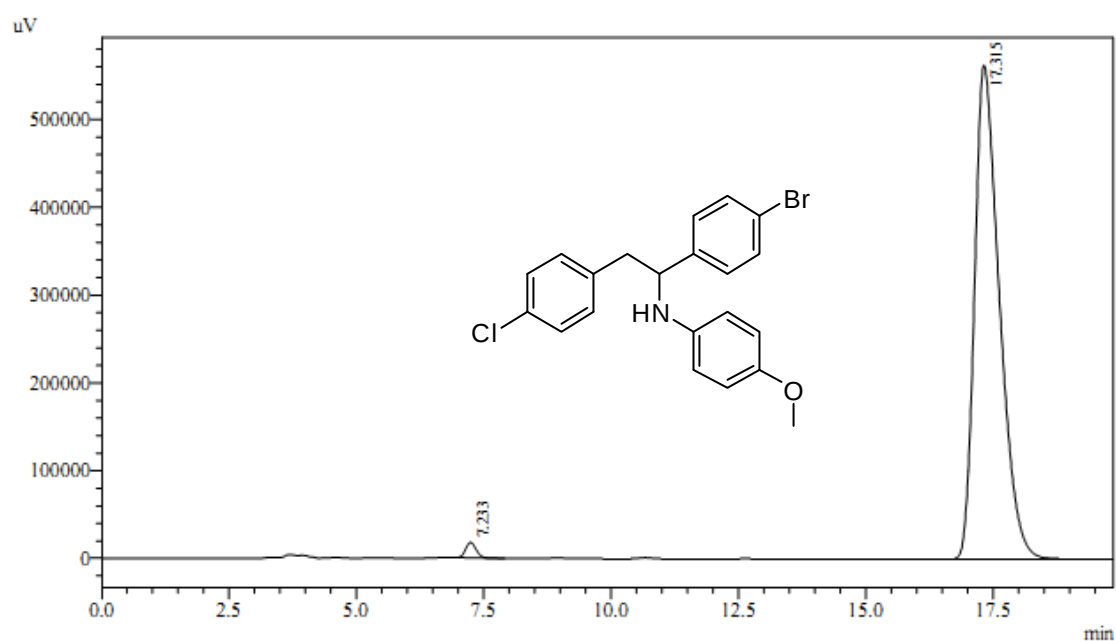
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.972     | 354668   | 34444   | 1.971   | 2.248    |
| 2     | 7.506     | 17642115 | 1497863 | 98.029  | 97.752   |
| Total |           | 17996783 | 1532308 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

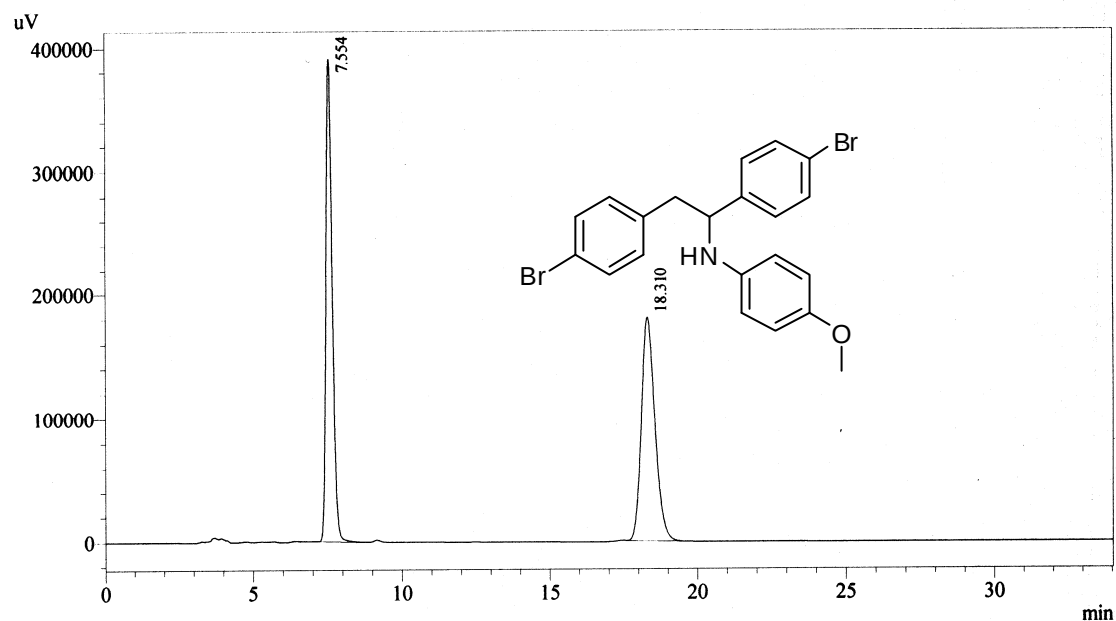
| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 7.154     | 8869258  | 581367 | 49.648  | 67.310   |
| 2     | 17.438    | 8994958  | 282348 | 50.352  | 32.690   |
| Total |           | 17864216 | 863714 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

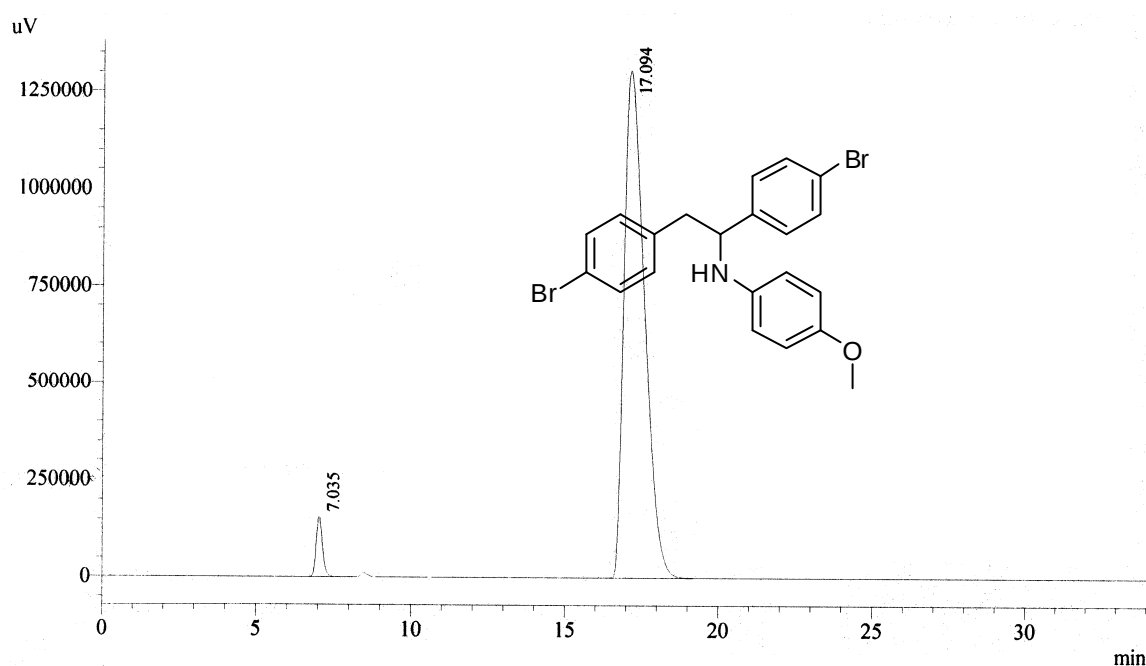
| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 7.233     | 258971   | 17759  | 1.341   | 3.057    |
| 2     | 17.315    | 19059215 | 563110 | 98.659  | 96.943   |
| Total |           | 19318186 | 580869 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

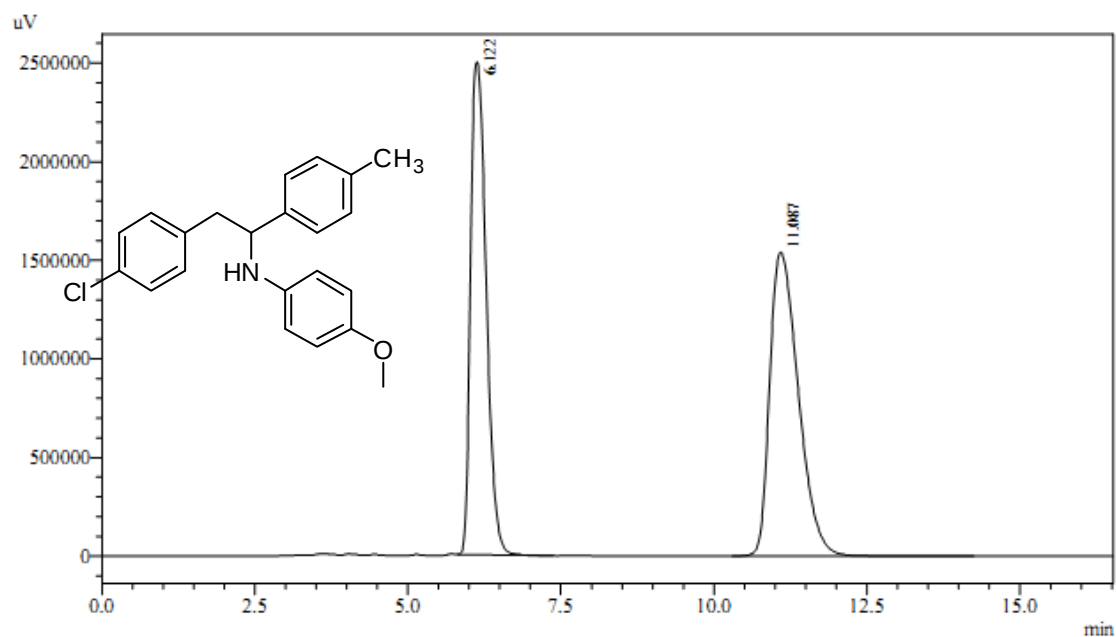
| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 7.554     | 5753928  | 390847 | 49.923  | 68.425   |
| 2     | 18.310    | 5771574  | 180361 | 50.077  | 31.575   |
| Total |           | 11525502 | 571209 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

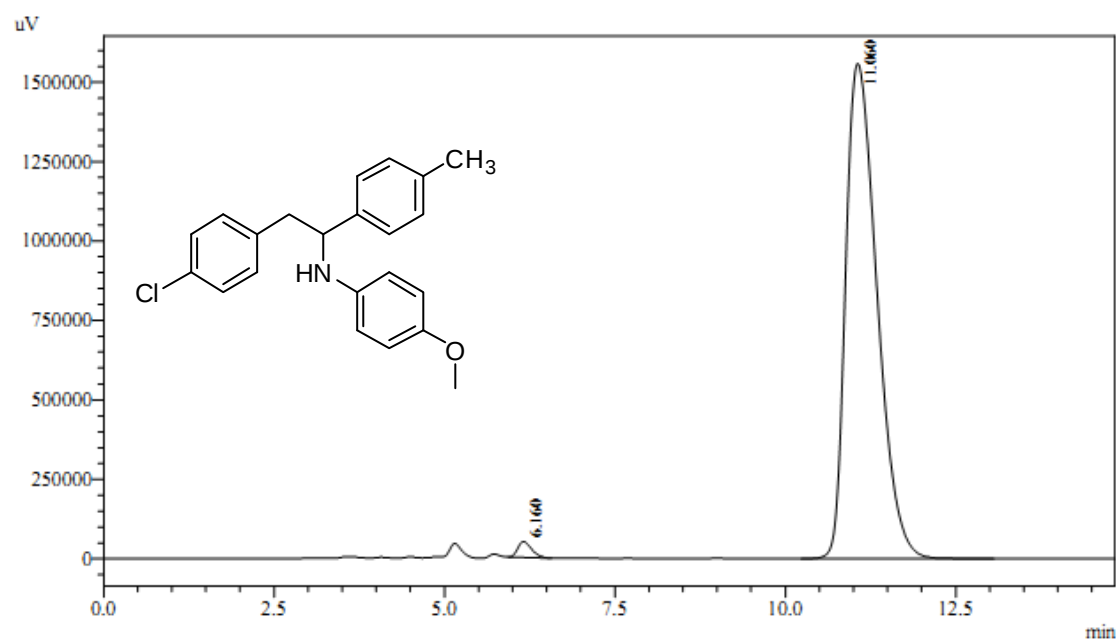
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 7.035     | 2207359  | 157522  | 3.517   | 10.759   |
| 2     | 17.094    | 60558244 | 1306592 | 96.483  | 89.241   |
| Total |           | 62765603 | 1464114 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

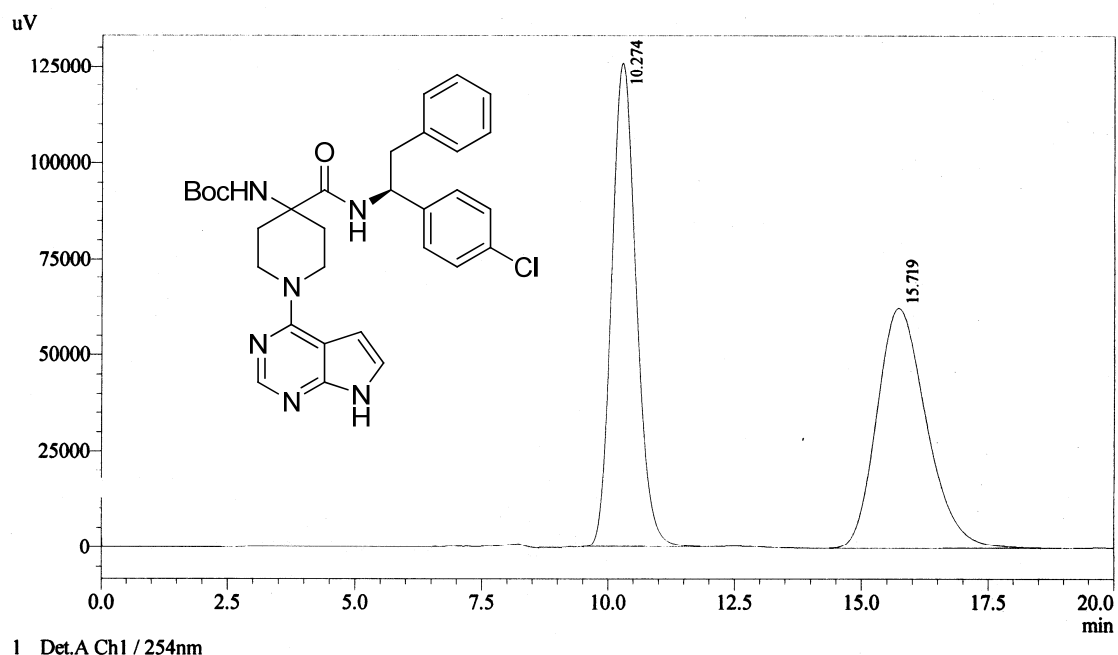
| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.122     | 44601028 | 2499967 | 47.126  | 61.880   |
| 2     | 11.087    | 50041736 | 1540066 | 52.874  | 38.120   |
| Total |           | 94642764 | 4040034 | 100.000 | 100.000  |



1 Det.A Ch1 / 254nm

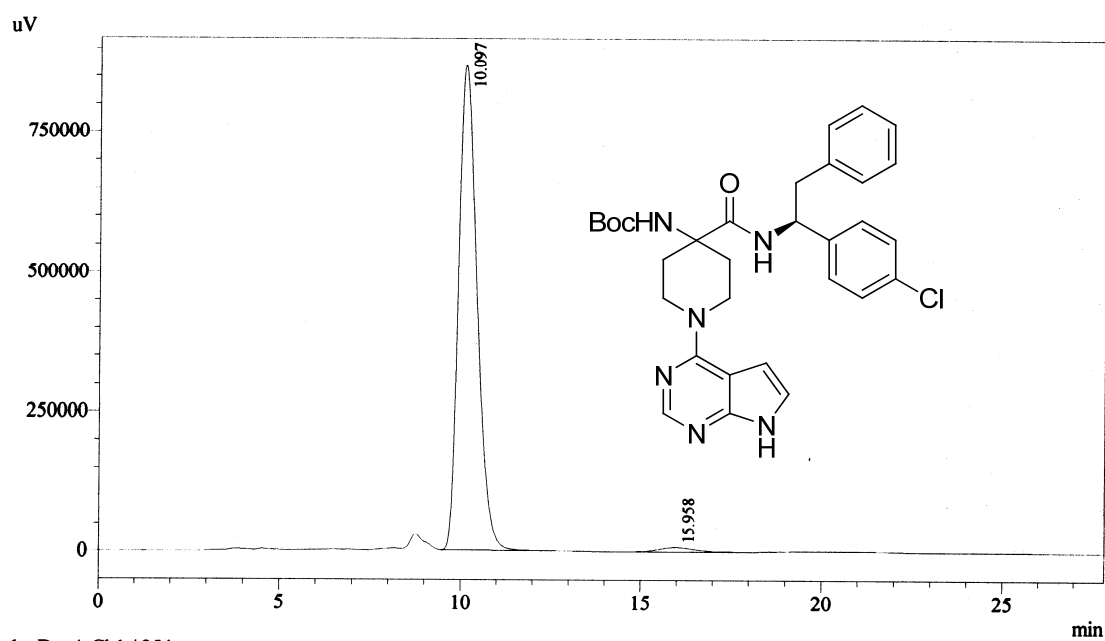
Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 6.160     | 729341   | 50667   | 1.439   | 3.148    |
| 2     | 11.060    | 49951270 | 1558603 | 98.561  | 96.852   |
| Total |           | 50680611 | 1609270 | 100.000 | 100.000  |



Detector A Ch1 254nm

| Peak# | Ret. Time | Area    | Height | Area %  | Height % |
|-------|-----------|---------|--------|---------|----------|
| 1     | 10.274    | 4254295 | 125832 | 50.009  | 66.866   |
| 2     | 15.719    | 4252782 | 62354  | 49.991  | 33.134   |
| Total |           | 8507077 | 188186 | 100.000 | 100.000  |



Detector A Ch1 254nm

| Peak# | Ret. Time | Area     | Height | Area %  | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1     | 10.097    | 31013971 | 868405 | 98.314  | 99.109   |
| 2     | 15.958    | 531952   | 7808   | 1.686   | 0.891    |
| Total |           | 31545923 | 876213 | 100.000 | 100.000  |