

Supporting Information for

**Direct Synthesis of Chiral 1,2,3,4-Tetrahydropyrrolo[1,2-a]pyrazines  
via a Catalytic Asymmetric Intramolecular Aza-Friedel-Crafts  
Reaction**

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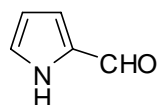
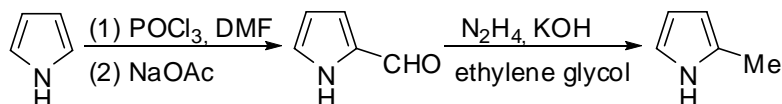
General considerations .....	S2
Experimental section.....	S3- S19
References.....	S19
X-ray data.....	S20- S29
Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR and chiral HPLC Spectra for all products.....	S30- S83

**General Considerations:** All reactions were carried out with magnetic stirring and in screw-cap test tubes, which were dried under a high temperature hot gun or oven. Molecular Sieves (4Å, both powder and ball) were dried with high temperature hot gun under high vacuum before use. All aldehydes were purified either according to the standard procedure in the book of 'Purification of Laboratory Chemicals' (fifth edition) or by flash column chromatography and were used freshly. Chloroform was purified by passing through a silica gel column and then dried with molecular sieves (4Å). Anhydrous toluene, benzene, dichloromethane, and acetonitrile were refluxed and distilled from CaH<sub>2</sub>. Anhydrous THF and ether were freshly distilled from sodium and benzophenone before use. Chiral BINOL was purchased from commercial sources and used without further purification. Substituted BINOL phosphoric acid was prepared from chiral BINOL according to the known literature procedures.<sup>[1]</sup> Phenylphosphinic acid was purchased from commercial sources and used without further purification. Flash column chromatography was performed with silica gel (200-300 mesh). Enantiomeric excess (ee) was determined using a Shimadzu LC-10AT vp plus HPLC with a single pump and UV detection monitored at 254 nm. Column conditions are reported in the experimental section below. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Varian 300 MHz instrument with chemical shifts reported relative to Tetramethylsilane (TMS). The HRMS data were measured on a Thermo MAT95XP mass spectrometer (EI). Compounds described in the literature were characterized by comparing their <sup>1</sup>H NMR and <sup>13</sup>C NMR to the reported values. The IR spectra were measured on a Nicolet/Nexus 670 FT-IR spectrometer. The optical rotation data were recorded on a Perkin Elmer Model 341 Polarimeter.

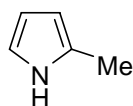
## Experimental section:

### The preparation of pyrrole derivatives:

#### 1. The preparation of 2-methylpyrrole:

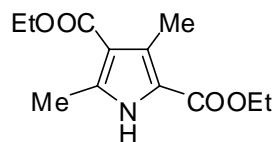
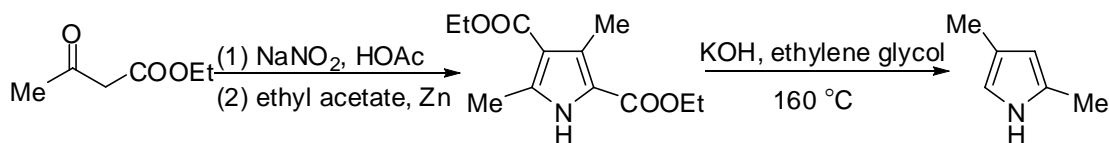


**1H-pyrrole-2-carbaldehyde** This compound was prepared according to the literature <sup>[2]</sup>. <sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 10.18(s, 1H) 9.50(br s, 1H), 7.16-7.14(m, 1H), 7.00-6.98(m, 1H), 6.36-6.33(m, 1H).

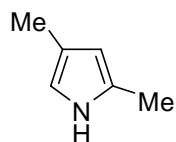


**2-methylpyrrole** This compound was prepared according to the literature <sup>[3]</sup>. <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ(ppm): 7.88(br s, 1H), 6.69-6.67(m, 1H), 6.17-6.14(m, 1H), 5.95-5.94(m, 1H), 2.33(s, 1H).

#### 2. The preparation of 2,4-dimethylpyrrole:

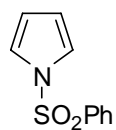
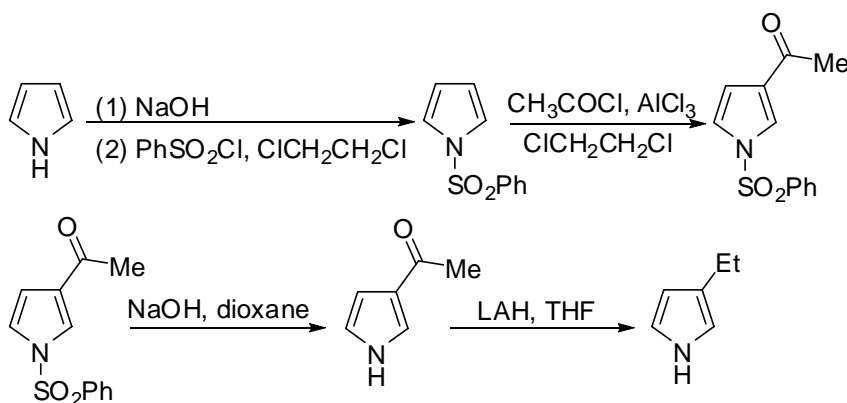


**diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate** This compound was prepared according to the literature <sup>[4]</sup>. The product was used in next step without further purification. <sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 9.19(br s, 1H), 4.36-4.25(m, 4H), 2.56(s, 3H), 2.52(s, 3H), 1.40-1.34(m, 6H).

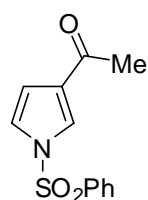


**2,4-dimethylpyrrole** A mixture of diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate (3.00g, 14 mmol) and potassium hydroxide (4.06 g, 72mmol) in ethylene glycol (10 ml) was heated to reflux for 4 h at 160 °C. The result solution was extracted with chloroform, dried with anhydrous sodium sulfate and then concentrated to give the crude product. The crude product was distilled in vacuum to give the pure product (0.96g, 10 mmol, 81% yield). The <sup>1</sup>H NMR data are identical to the data in the literature <sup>[5]</sup>. <sup>1</sup>H NMR (300 MHz CDCl<sub>3</sub>) δ(ppm): 7.63(br s, 1H), 6.47(s, 1H), 5.85(s, 1H), 2.32(s, 1H), 2.20(s, 1H).

3. The preparation of 3-ethylpyrrole:

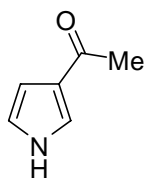


**1-phenylsulfonylpyrrole** This compound was prepared according to the literature <sup>[6]</sup>. <sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 7.86-7.83(m, 2H), 7.60-7.45(m, 3H), 7.17-7.16(m, 2H), 6.30-6.29(m, 2H).



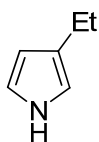
**3-acetyl-1-phenylsulfonylpyrrole** This compound was prepared according to the literature. <sup>[7]</sup> <sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 7.92-7.89(m, 2H),

7.72-7.71(m, 1H), 7.68-7.52(m, 3H), 7.15-7.13(m, 1H), 6.69-6.67(m, 1H), 2.41(s, 3H).



**3-acetylpyrrole** This compound was prepared according to the literature.<sup>[8]</sup>

<sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 9.96(br s, 1H), 7.43(t, *J* = 1.5 Hz, 1H), 6.77(t, *J* = 2.4 Hz, 1H), 6.63-6.62(m, 1H), 2.44(s, 3H).

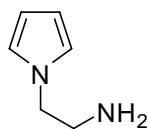


**3-ethylpyrrole** To a suspension of LiAlH<sub>4</sub> (2.00 g, 53 mmol) in dry THF (30ml) was added dropwise with 3-acetylpyrrole (2.93 g, 27 mmol) at 0 °C with stirring. Then the mixture was heated to reflux overnight. The reaction was quenched with saturated solution of sodium sulfate. The insoluble solid was filtrated off, and washed with dichloromethane. Then the solution was concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography (silica gel, eluent: petroleum ether / ethyl acetate= 8:1) to yield the product, colorless oil (2.38 g, 94% yield). The <sup>1</sup>H NMR data are identical to the data in the literature.<sup>[9]</sup> <sup>1</sup>H NMR(300 MHz CDCl<sub>3</sub>) δ(ppm): 7.98(br s, 1H), 6.82(m, 1H), 6.68(s, 1H), 6.29-6.26(m, 1H), 2.71(q, *J* = 6.0 Hz, 2H), 1.39(t, *J* = 6.0 Hz, 3H).

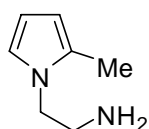
### General Procedure for Synthesis of 1-(2-aminoethyl) pyrroles

To a solution of previously prepared pyrrole (10 mmol) in MeCN (30 ml) was added sodium hydroxide (2.00 g, 50 mmol) powder and tetrabutylammonium hydrogen sulfate (TBAS) (0.17 g, 0.5 mmol). After the solution was stirred at room temperature for 30min, 2-chloroethylamine hydrochloride (1.39 g, 12 mmol) was added. Then the reaction mixture was refluxed for 24h. The mixture was poured into water (100 mL), then extracted with ether, dried under MgSO<sub>4</sub> and concentrated under reduced pressure to give a crude product. The product was purified by flash chromatography

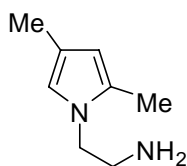
(silica gel, eluent: dichloromethane / methanol) to give pure product.



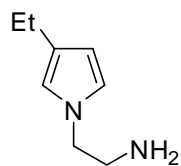
**1-(2-aminoethyl)pyrrole** 0.94g (Flash column chromatography eluent, dichloromethane : methanol= 10/1 ), 86% yield, yellow oil. The  $^1\text{H}$  NMR spectrum of the product matched the literature data.<sup>[10]</sup>  $^1\text{H}$  NMR(300 MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 6.68 (t,  $J = 2.1\text{Hz}$ , 2H), 6.14 (t,  $J = 2.1\text{ Hz}$ , 2H), 3.88 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.97(t,  $J = 6.0\text{ Hz}$ , 2H), 1.67(br s, 2H);  $^{13}\text{C}$  NMR(75MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 121.0, 108.6, 52.9, 43.5.



**1-(2-aminoethyl)-2-methylpyrrole** 1.10g, (Flash column chromatography eluent, dichloromethane : methanol= 10/1 ), 73% yield, yellow oil; The  $^1\text{H}$  NMR spectrum of the product matched the literature data<sup>[11]</sup>.  $^1\text{H}$  NMR(300MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 6.61 (t,  $J = 1.8\text{ Hz}$ , 2H), 6.07 (t,  $J = 3.0\text{ Hz}$ , 1H), 5.90-5.88 (m, 1 H), 3.86 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.97(t,  $J = 6.0\text{ Hz}$ , 2H), 2.26(s, 3H), 1.23(br s, 2H);  $^{13}\text{C}$  NMR(75MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 128.6, 120.5, 120.3, 107.1, 49.9, 43.3, 12.5.



**1-(2-aminoethyl)-2,4-dimethylpyrrole** 0.60g (Flash column chromatography eluent, dichloromethane : methanol= 10/1 ), 50% yield, yellow oil;  $^1\text{H}$  NMR(300 MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 6.37 (s, 1H), 5.73 (s 1H), 3.80 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.97(t,  $J = 6.0\text{ Hz}$ , 2H), 2.20(s, 3H), 2.07(s, 3H), 1.42(br s, 2H);  $^{13}\text{C}$  NMR(75MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 128.1, 118.2, 117.8, 108.6, 49.7, 43.3, 12.4, 12.2; IR(KBr)  $\nu$ : 3449, 2918, 1655, 1638, 1627, 1561, 1544, 1476, 1385, 1107, 708, 562  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_8\text{H}_{14}\text{N}_2$  ( $[\text{M}^+]$ ) 138.1152, found 138.1153.

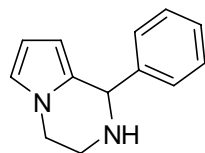


**1-(2-aminoethyl)-3-ethylpyrrole** 0.96 g(Flash column

chromatography eluent, dichloromethane : methanol= 10/1 ), 70% yield, yellow oil;  
 $^1\text{H}$  NMR( 300 MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 6.58(t,  $J = 2.4$  Hz, 1H), 6.46(s, 1H), 6.02(t,  $J = 2.1$  Hz, 1H), 3.86 (t,  $J = 6.0$  Hz, 2H), 3.00 (t,  $J = 6.0$  Hz, 2H), 2.51 (q,  $J = 7.8$  Hz, 2H), 1.32(br s, 2H), 1.21(t,  $J = 7.8$  Hz, 3H);  $^{13}\text{C}$  NMR(75 MHz  $\text{CDCl}_3$ )  $\delta$ (ppm): 126.1, 120.8, 117.7, 108.2, 50.0, 43.7, 20.5, 15.7; IR(KBr)  $\nu$ :3448, 1654, 1647, 1637, 1073, 602, 581  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_8\text{H}_{14}\text{N}_2$  ( $[\text{M}^+]$ ) 138.1152, found 138.1153.

**Typical procedure for the catalytic asymmetric intramolecular aza-Friedel-Crafts reaction of *N*-aminoethylpyrrole and aldehydes:**

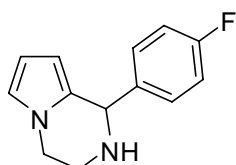
To a flame-dried reaction tube charged with 4Å molecular sieves (50 mg, pre-activated with a high temperature hot gun) was added chiral phosphoric acid **PA1e** (7.5 mg, 0.01mmol), freshly distilled THF (1.0 mL) and benzaldehyde (**2a**) (0.1 mmol, 10.6 mg) successively at room temperature. The mixture was stirred for 5 min and *N*-aminoethyl pyrrole (**1a**) (0.1 mmol, 11.0 mg) was added via a syringe. The reaction mixture was stirred at 25 °C until the starting materials were consumed, determined by TLC analysis. The crude product was purified directly by column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the desired product **3a**.



**1-phenyl-1, 2, 3, 4-tetrahydropyrrolo[1, 2-a]pyrazine (3a)**, 18.0

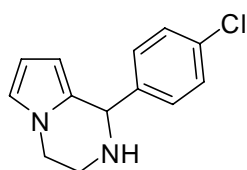
mg, (Flash column chromatography eluent, ethyl acetate), white solid: mp 96-98 °C;  $[\alpha]_D^{20} = +32.7$  ( $c = 0.32$ ,  $\text{CHCl}_3$ ); 91% yield, 94% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 98/2, 0.6 mL/min),  $t_{\text{r-major}}$  26.9 min,  $t_{\text{r-minor}}$  31.6 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.43-7.31(m, 5H), 6.62 (t,  $J = 2.1$ Hz, 1H), 6.14-6.12 (m,

1H), 5.58-5.57 (m, 1H), 5.10(s, 1H) 4.15-3.97(m, 2H), 3.42-3.24(m, 2H), 1.96(br s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ(ppm): 143.1, 130.8, 128.6, 128.5, 127.9, 119.3, 107.9, 105.1, 59.5, 45.8, 43.5; IR(KBr) v: 3230, 3251, 2928, 1654, 1631, 1449, 1381, 1296, 726, 703 cm<sup>-1</sup>; HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub> ([M<sup>+</sup>]) 198.1152, found 198.1148.



**1-(4-fluorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3b)**

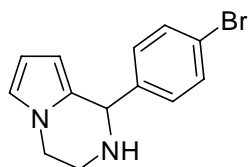
20.3 mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 100-102 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +29.4 (c = 0.27, CHCl<sub>3</sub>); 94% yield, 91% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 98/2, 0.6 mL/min), *t*<sub>r-major</sub> 24.7 min, *t*<sub>r-minor</sub> 35.0 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm): 7.42-7.36 (m, 2H), 7.07-7.00 (m, 2H), 6.62-6.61 (m, 1H), 6.13-6.11 (m, 1H), 5.55-5.43 (m, 1H), 5.08 (s, 1H), 4.14-3.96 (m, 2H), 3.41-3.23 (m, 2H), 1.89 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 162.5 (d, *J* = 245.1 Hz), 138.9, 130.7, 130.10 (d, *J* = 7.1 Hz, 2C), 119.4, 115.3 (d, *J* = 21.6 Hz, 2C), 108.0, 105.1, 58.8, 45.7, 43.5; IR(KBr) v: 3433, 3251, 3107, 2922, 2819, 1603, 1509, 1297, 1224, 1084, 840, .86, 710 cm<sup>-1</sup>; HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>12</sub>FN<sub>2</sub> ([M<sup>+</sup>]) 216.1057, found 216.1060.



**1-(4-chlorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3c)**

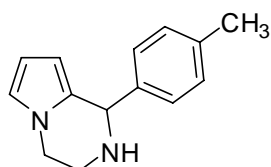
20.2 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +12.5 (c = 0.02, CHCl<sub>3</sub>); 87% yield, 90% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 80/20, 0.6 mL/min), *t*<sub>r-major</sub> 10.4 min, *t*<sub>r-minor</sub> 12.1 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.37-7.29 (m, 4H), 6.61 (s, 1H), 6.12 (t, *J* = 2.7Hz, 1H), 5.54 (t, *J* = 1.8 Hz, 1H), 5.07 (s, 1H), 4.13-3.96 (m, 2H), 3.39-3.22 (m, 2H), 2.20 (br s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 141.6, 133.6, 130.3, 129.9(2C), 128.7(2C),

119.4, 108.0, 105.2, 58.8, 45.7, 43.4; IR(KBr)  $\nu$ : 3431, 2955, 2926, 1634, 1592, 1486, 1409, 1091, 731  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{ClN}_2$  ( $[\text{M}^+]$ ) 232.0762, found 232.0757.



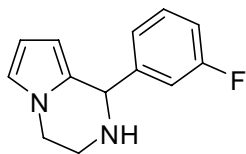
**1-(4-bromophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine(3d)**

20.7mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_{\text{D}}^{20} = +6.3$  ( $c = 0.30$ ,  $\text{CHCl}_3$ ); 77% yield, 90% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 80/20, 0.6 mL/min),  $t_{\text{r-major}}$  11.8 min,  $t_{\text{r-minor}}$  14.0 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.48 (d,  $J=8.4$  Hz, 2H), 7.30 (d,  $J = 8.4\text{Hz}$ , 2H), 6.62 (t,  $J = 1.8$  Hz, 1H), 6.14-6.12 (m, 1H), 5.56-5.54 (m, 1H), 5.06 (s, 1H), 4.14-3.96 (m, 2H), 3.39-3.21 (m, 2H), 2.07 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 142.1, 131.7, 130.3(2C), 121.8, 119.5, 108.0, 105.2, 58.8, 45.7, 43.4; IR(KBr)  $\nu$ : 3435, 2947, 2921, 1636, 1587, 1483, 1441, 1329, 1290, 1100, 1071, 1011, 708  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{BrN}_2$  ( $[\text{M}^+]$ ) 275.0178, found 276.0248.



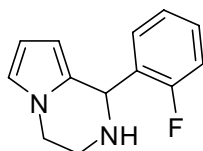
**1-p-tolyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3e)**

21.2mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 50-52°C;  $[\alpha]_{\text{D}}^{20} = +9.6$  ( $c = 0.28$ ,  $\text{CHCl}_3$ ); 84% yield, 90% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 98/2, 0.6 mL/min),  $t_{\text{r-major}}$  26.5 min,  $t_{\text{r-minor}}$  34.3 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.32 (d,  $J = 7.8\text{Hz}$ , 2H), 7.19 (d,  $J = 7.8\text{Hz}$ , 2H), 6.65-6.64 (m, 1H), 6.17-6.15 (m, 1H), 5.60-5.59 (m, 1H), 5.09 (s, 1H), 4.16-3.98 (m, 2H), 3.43-3.25 (m, 2H), 2.41 (s, 3H), 2.01 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 140.1, 137.6, 131.1, 129.3 (2C), 128.5 (2C), 119.1, 107.9, 105.0, 59.1, 45.8, 43.6, 21.6; IR(KBr)  $\nu$ : 3430, 2918, 1647, 1637, 1437, 1380, 1271, 1161, 1110, 1062, 711, 567  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_2$  ( $[\text{M}^+]$ ) 212.1308, found 212.1308.



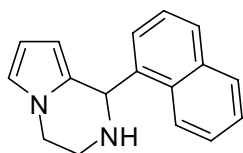
**1-(3-fluorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

(**3f**) 20.0mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 80-82°C;  $[\alpha]_D^{20} = +20.7$  (c = 0.40, CHCl<sub>3</sub>); 92% yield, 91% ee; HPLC analysis: Chiralcel AS-H (hexanes/iPrOH = 98/2, 0.6 mL/min),  $t_{r\text{-minor}}$  24.7 min,  $t_{r\text{-major}}$  28.6 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 7.36-7.28 (m, 1H), 7.22-7.13 (m, 2H), 7.04-6.97 (m, 1H), 6.62 (s, 1H), 6.15-6.13 (m, 1H), 5.60-5.59 (m, 1H), 5.11 (s, 1H), 4.14-3.97 (m, 2H), 3.40-3.22 (m, 2H), 2.10 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 163.0 (d,  $J = 245.2$  Hz), 145.6 (d,  $J = 6.6$  Hz), 130.1, 130.0, 124.2, 119.4, 115.4 (d,  $J = 21.3$  Hz), 114.9 (d,  $J = 22.2$  Hz), 108.0, 105.2, 58.8, 45.7, 43.3; IR(KBr) ν: 3248, 3309, 3087, 2956, 2918, 2839, 2807, 1612, 1588, 1484, 1499, 1291, 1263, 1135, 1079, 752, 727 cm<sup>-1</sup>; HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>12</sub>FN<sub>2</sub> ([M<sup>+</sup>]) 216.1057, found 216.1056.



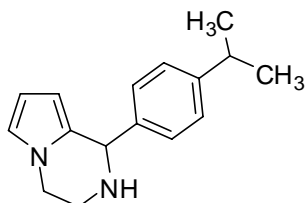
**1-(2-fluorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3g)**

20.9mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{20} = +28.7$  (c = 0.42, CHCl<sub>3</sub>); 93% yield, 91% ee; HPLC analysis: Chiralcel AS-H (hexanes/iPrOH = 98/2, 0.6 mL/min),  $t_{r\text{-minor}}$  21.0 min,  $t_{r\text{-major}}$  23.8 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.34-7.24 (m, 2H), 7.12-7.05 (m, 2H), 6.63-6.52 (m, 1H), 6.15 (dd,  $J = 3.6, 2.7$  Hz, 1H), 5.64-5.63 (m, 1H), 5.50 (s, 1H), 4.12-3.97 (m, 2H), 3.41-3.21 (m, 2H), 2.13 (br s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 161.0 (d,  $J = 246.3$  Hz), 130.2, 130.1 (d,  $J = 18.7$  Hz), 129.5 (d,  $J = 8.3$  Hz), 129.1, 124.3, 119.3, 115.7 (d,  $J = 21.7$  Hz), 108.0, 104.9, 52.2, 45.7, 43.0; IR(KBr) ν: 3437, 2916, 1634, 1486, 1447, 1438, 1070, 708, 560 cm<sup>-1</sup>; HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>12</sub>FN<sub>2</sub> ([M<sup>+</sup>]) 216.1057, found 216.1053.



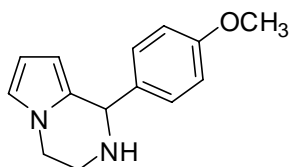
**1-(naphthalen-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

**(3h)** 22.6 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{20} = +7.9$  ( $c = 0.37$ ,  $\text{CHCl}_3$ ); 91% yield, 90% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 98/2, 0.6 mL/min),  $t_{r\text{-minor}}$  34.8 min,  $t_{r\text{-major}}$  41.8 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.22 (d,  $J = 9.1\text{Hz}$ , 1H), 7.92-7.89 (m, 1H), 7.83 (d,  $J = 7.8\text{ Hz}$ , 1H), 7.54-7.40 (m, 4H), 6.69-6.68 (m, 1H), 6.16-6.13 (m, 1H), 5.89 (s, 1H), 5.59-5.58 (m, 1H), 4.22-4.03 (m, 2H), 3.44-3.26 (m, 2H), 2.17 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 138.5, 134.3, 131.7, 130.2, 129.0, 128.6, 126.4, 126.3, 125.8, 125.5, 124.2, 119.2, 108.1, 105.2, 56.1, 45.9, 43.3; IR(KBr)  $\nu$ : 3431, 2916, 1635, 1384, 1269, 1107, 1075, 705, 563  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_2$  ( $[\text{M}^+]$ ) 248.1308, found 248.1309.



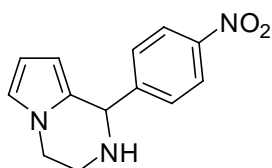
**1-(4-isopropylphenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

**azine (3i)** 21.1 mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 101-103  $^{\circ}\text{C}$ ;  $[\alpha]_D^{20} = +41.9$  ( $c = 0.45$ ,  $\text{CHCl}_3$ ); 88% yield, 87% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 90/10, 0.6 mL/min),  $t_{r\text{-major}}$  16.0 min,  $t_{r\text{-minor}}$  17.2 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.34 (d,  $J = 8.1\text{ Hz}$ , 2H), 7.22 (d,  $J = 8.1\text{ Hz}$ , 2H), 6.63 (t,  $J = 2.1\text{Hz}$ , 1H), 6.15-6.13 (m, 1H), 5.62-5.60 (m, 1H), 5.09 (s, 1H), 4.15-3.97 (m, 2H), 3.42-3.23 (m, 2H), 2.99-2.96 (m, 1H), 1.94 (br s, 1H), 1.29 (d,  $J = 6.9\text{ Hz}$ , 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 148.5, 140.4, 131.0, 128.4(2C), 126.6(2C), 119.2, 107.9, 105.0, 59.2, 45.8, 43.5, 34.2, 24.5(2C); IR(KBr)  $\nu$ : 3430, 3255, 3095, 2955, 2830, 2818, 1634, 1508, 1455, 1369, 1331, 1297, 1111, 1078, 1052, 958, 888, 838, 717  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_2$  ( $[\text{M}^+]$ ) 240.1621, found 240.1615.



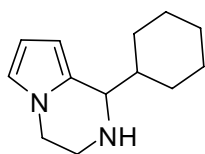
**1-(4-methoxyphenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

**ine (3j)** 18.4 mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 75-77 °C;  $[\alpha]_D^{20} = +23.1$  ( $c = 0.30$ ,  $\text{CHCl}_3$ ); 81% yield, 83% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 90/10, 0.6 mL/min),  $t_{r\text{-major}}$  20.2 min,  $t_{r\text{-minor}}$  26.6 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.32 (d,  $J = 8.7$  Hz, 2H), 6.87 (d,  $J = 8.4$  Hz, 2H), 6.59 (s, 1H), 6.12-6.10 (m, 1H), 5.56-5.54 (m, 1H), 5.04 (s, 1H), 4.13-3.95 (m, 2H), 3.82 (s, 3H), 3.40-3.22 (m, 2H), 1.87 (br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 159.3, 135.3, 131.2, 129.6(2C), 119.2, 114.0(2C), 107.9, 105.0, 58.9, 55.6, 45.8, 43.6; IR(KBr)  $\nu$ : 3431, 2916, 1629, 1448, 1385, 1159, 1109, 1071, 876, 711, 562  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}$  ( $[\text{M}^+]$ ) 228.1257, found 228.1252.



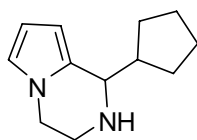
**1-(4-nitrophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

**(3k)** 19.9mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 94-96 °C;  $[\alpha]_D^{20} = -2.3$  ( $c = 0.13$ ,  $\text{CHCl}_3$ ); 82% yield, 84% ee; HPLC analysis: Chiralcel AD-H (hexanes/*i*PrOH = 90/10, 0.6 mL/min),  $t_{r\text{-major}}$  33.7 min,  $t_{r\text{-minor}}$  35.5 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.18 (d,  $J = 9.0$  Hz, 2H), 7.59 (d,  $J = 9.0$  Hz, 2H), 6.63-6.61 (m, 1H), 6.13-6.11 (m, 1H), 5.54-5.52 (m, 1H), 5.21 (s, 1H), 4.15-3.98 (m, 2H), 3.40-3.25 (m, 2H), 1.97(br s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 150.4, 147.6, 129.3(2C), 129.1, 123.8(2C), 119.8, 108.2, 105.4, 58.5, 45.7, 43.2; IR(KBr)  $\nu$ : 3431, 2953, 2918, 1635, 1600, 1516, 1343, 1285, 1098, 1075, 717  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_2$  ( $[\text{M}^+]$ ) 243.1002, found 243.1001.



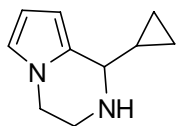
**1-cyclohexyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3l)** 20.4

mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{20} = +50.9$  ( $c = 0.33$ ,  $\text{CHCl}_3$ ); 94% yield, 91% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 98/2, 0.6 mL/min),  $t_{r\text{-major}}$  12.6 min,  $t_{r\text{-minor}}$  14.3 min.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.56-6.54 (m, 1H), 6.16 (t,  $J = 3.0$  Hz, 1H), 5.88 (t,  $J = 1.8$  Hz, 1H), 3.93-3.89 (m, 3H), 3.39-3.32 (m, 1H), 3.16-3.07 (m, 1H), 2.38 (s, 1H), 1.86-1.68 (m, 6H), 1.41-1.03 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 130.5, 118.7, 107.4, 102.6, 58.7, 45.5, 43.1, 42.1, 30.4, 27.2, 26.9, 26.7, 26.6; IR(KBr)  $\nu$ : 3430, 2922, 2852, 1655, 1633, 1458, 1443, 1404, 1383, 1106, 1075, 705, 563  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{20}\text{N}_2$  ( $[\text{M}^+]$ ) 204.1621, found 204.1622.



**1-cyclopentyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3m)**

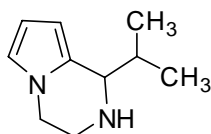
16.0 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{20} = +33.8$  ( $c = 0.23$ ,  $\text{CHCl}_3$ ); 84% yield, 70% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 98/2, 1.0 mL/min),  $t_{r\text{-major}}$  17.2 min,  $t_{r\text{-minor}}$  20.0 min.;  $^1\text{H}$  NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.54-6.53(m, 1H), 6.14(t,  $J = 3.0$  Hz, 1H), 5.95-5.94(m, 1H), 3.95-3.87(m, 3H), 3.36(dt,  $J = 12.6, 3.9$  Hz, 1H), 3.17-3.08(m, 1H), 2.41-2.27(m, 1H), 2.13(br s, 1H), 1.99-1.77(m, 2H), 1.72-1.32(m, 6H);  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6, 118.9, 107.6, 103.5, 58.2, 45.9, 44.8, 43.2, 30.4, 29.2, 26.3, 26.0; IR(KBr)  $\nu$ : 3430, 2949, 2866, 1652, 1605, 1564, 1546, 1453, 1422, 1383, 1295, 1076, 704, 563  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{18}\text{N}_2$  ( $[\text{M}^+]$ ) 190.1465, found 190.1456.



**1-cyclopropyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3n)** 13.5 mg,

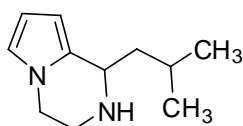
(Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{20} = -23.3$  ( $c = 0.17$ ,  $\text{CHCl}_3$ ); 83% yield, 71% ee; HPLC analysis: Chiralcel OD-H (hexanes/iPrOH = 98/2, 1.0 mL/min),  $t_{r\text{-major}}$  31.5 min,  $t_{r\text{-minor}}$  36.5 min.;  $^1\text{H}$  NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.66(t,  $J = 2.0$  Hz, 1H), 6.17-6.11(m, 2H), 4.02-3.87(m, 2H), 3.36(ddd,  $J = 12.0, 4.5,$

2.7 Hz, 1H), 3.16-3.07(m, 1H), 1.99(br s, 1H), 1.17-1.06(m, 1H), 0.79-0.71(m, 1H), 0.60-0.46(m, 2H), 0.38-0.30(m, 1H);  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6, 119.0, 107.8, 103.2, 60.1, 45.7, 43.7, 16.9, 3.91, 2.48; IR(KBr)  $\nu$ : 3434, 1654, 1637, 1459, 1294, 971, 702, 555  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{14}\text{N}_2$  ( $[\text{M}^+]$ ) 162.1152, found 162.1158.



**1-isopropyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3o)** 14.8

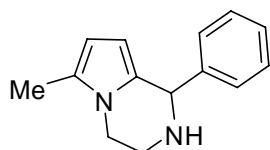
mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_{\text{D}}^{20} = +68.7$  ( $c = 0.21$ ,  $\text{CHCl}_3$ ); 90% yield, 73% ee; HPLC analysis: Chiralcel OD-H (hexanes/*i*PrOH = 98/2, 1.0 mL/min),  $t_{\text{r-major}}$  18.1 min,  $t_{\text{r-minor}}$  20.3 min.  $^1\text{H}$  NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.54(s, 1H), 6.15(t,  $J = 3.0$  Hz, 1H), 5.87-5.86(m, 1H), 3.91-3.89(m, 3H), 3.35(dt,  $J = 12.3, 3.6$  Hz, 1H), 3.17-3.08(m, 1H), 2.29-2.18(m, 1H), 1.68(br s, 1H), 1.11(d,  $J = 6.9$  Hz, 3H), 0.92(d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.0, 118.9, 107.7, 102.9, 54.9, 45.8, 43.5, 32.6, 20.0, 17.0; IR(KBr)  $\nu$ : 3433, 2961, 2926, 1683, 1652, 1641, 1635, 1624, 1583, 1081, 738, 706  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{16}\text{N}_2$  ( $[\text{M}^+]$ ) 164.1308, found 164.1306.



**1-isobutyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3p)**

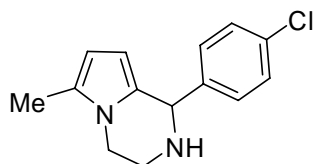
15.0 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_{\text{D}}^{20} = +32.3$  ( $c = 0.25$ ,  $\text{CHCl}_3$ ); 84% yield, 65% ee; HPLC analysis: Chiralcel OD-H (hexanes/*i*PrOH = 98/2, 1.0 mL/min),  $t_{\text{r-major}}$  18.0 min,  $t_{\text{r-minor}}$  17.0 min.  $^1\text{H}$  NMR(300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.54-6.53(m, 1H), 6.14(t,  $J = 3.0$  Hz, 1H), 5.88-5.86(m, 1H), 3.99(dd,  $J = 9.6, 3.9$  Hz, 1H), 3.94-3.90(m, 2H), 3.35(dt,  $J = 12.9, 3.6$  Hz, 1H), 3.19-3.10(m, 1H), 1.96-1.85(m, 1H), 1.77-1.69(m, 1H), 1.63(br s, 1H), 1.61-1.53(m, 1H), 1.01(d,  $J = 6.6$  Hz, 6H);  $^{13}\text{C}$  NMR(75 MHz,  $\text{CDCl}_3$ )  $\delta$  132.4, 119.1, 107.7, 102.4, 51.9, 45.7, 45.3, 43.3, 24.9, 24.2, 22.1; IR(KBr)  $\nu$ : 3429, 2954, 2924, 2868, 1641, 1624, 1605, 1583, 1546, 1462, 1109, 1076, 705, 676, 560  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for

C<sub>11</sub>H<sub>18</sub>N<sub>2</sub> ([M<sup>+</sup>]) 178.1465, found 178.1457.



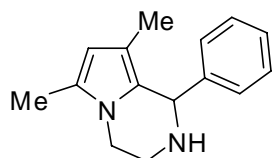
**6-methyl-1-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine(**

**3q**). 19.6 mg, (Flash column chromatography eluent, ethyl acetate), yellow solid: mp 80-82 °C; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +7.8 (c = 0.38, CHCl<sub>3</sub>); 93% yield, 87% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 98/2, 0.6 mL/min), *t*<sub>r-major</sub> 32.6 min, *t*<sub>r-minor</sub> 43.5 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.42-7.33(m, 5H), 5.82(d, *J* = 3.3 Hz, 1H), 5.44(d, *J* = 3.3 Hz, 1H), 5.07(s, 1H), 3.88-3.84(m, 2H), 3.46-3.39(m, 1H), 3.33-3.24(m, 1H), 2.36(br s, 1H), 2.23(s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 143.1, 130.1, 128.5, 127.9, 127.2, 105.6, 104.2, 59.7, 43.1, 30.1, 12.0; IR(KBr)  $\nu$ : 3411, 2917, 1637, 1647, 1421, 1384, 1110, 1061, 700, 558 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub> 212.1308, found 212.1310.



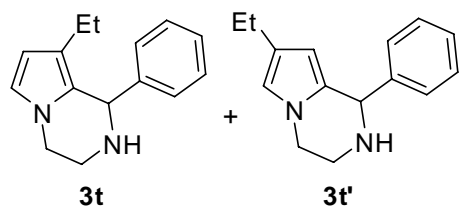
**1-(4-chlorophenyl)-6-methyl-1,2,3,4-tetrahydropyr**

**rolo[1,2-a]pyrazine (3r)**. 23.4 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +4.7 (c = 0.15, CHCl<sub>3</sub>); 95% yield, 83% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 95/5, 0.6 mL/min), *t*<sub>r-major</sub> 17.9 min, *t*<sub>r-minor</sub> 32.3 min. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.36 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.83 (d, *J* = 2.8 Hz, 1H), 5.43 (d, *J* = 3.2 Hz, 1H), 5.04 (s, 1H), 3.87-3.83 (m, 2H), 3.44-3.23 (m, 2H), 2.24 (s, 3H), 1.92 (br s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 141.7, 133.5, 130.0(2C), 129.7, 128.7(2C), 127.4, 105.7, 104.3, 59.0, 43.5, 43.1, 12.0; IR(KBr)  $\nu$ : 3449, 2916, 1655, 1637, 1508, 1459, 1088, 708, 565 cm<sup>-1</sup>; HRMS (EI) *m/z* calcd for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub> 246.0918, found 246.0917.



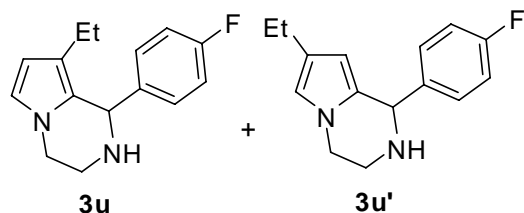
**6,8-dimethyl-1-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine**

**ne (3s).** 20.9 mg, (Flash column chromatography eluent, ethyl acetate), yellow oil;  $[\alpha]_D^{25} = +13.9$  ( $c = 0.36$ ,  $\text{CHCl}_3$ ); 92 % yield, 85% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 95/5, 0.6 mL/min),  $t_{r\text{-major}}$  20.8 min,  $t_{r\text{-minor}}$  30.4 min.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.31-7.26 (m, 5H), 5.73 (s, 1H), 5.13(s, 1H), 3.84-3.76 (m, 2H), 3.24-3.07 (m, 2H), 2.22 (s, 3H), 1.57 (s, 3H), 1.27 (br s, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 143.3, 128.5, 127.5, 126.3, 123.8, 113.3, 107.6, 57.2, 43.2, 41.1, 11.9; IR(KBr)  $\nu$ : 3450, 2916, 1654, 1637, 1509, 1459, 1384, 1114, 698, 564  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2$  198.1152, found 198.1148.

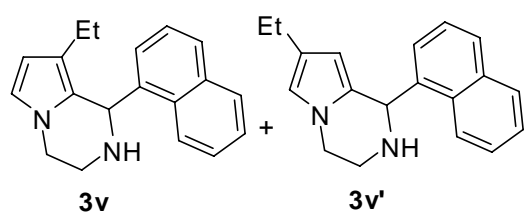


**8-ethyl-1-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3t)** and **7-ethyl-1-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3t')**. (Flash column chromatography eluent, ethyl acetate; mixture of **3t** and **3t'**), yellow solid, 83 % total yield, 94% ee (**3t**), 94% ee (**3t'**); HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 95/5, 0.6 mL/min), **3t**  $t_{r\text{-major}}$  15.0 min,  $t_{r\text{-minor}}$  18.0 min; **3t'**  $t_{r\text{-major}}$  18.9 min,  $t_{r\text{-minor}}$  24.0 min.  $^1\text{H NMR}$ (**3t**) (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.42-7.23(m, 5H), 6.60(d,  $J = 3.0$  Hz, 1H), 6.07(d,  $J = 3.0$  Hz, 1H), 5.18(s, 1H), 4.04-3.88(m, 2H), 3.40-3.05(m, 2H), 2.12(br s, 1H), 2.07-1.88(m, 2H), 0.93(t,  $J = 7.5\text{Hz}$ );  $^1\text{H NMR}$ (**3t'**) (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.42-7.23(m, 5H), 6.39(s, 1H), 5.42(s, 1H), 5.05(s, 1H), 4.04-3.88(m, 2H), 3.40-3.05(m, 2H), 2.44(q,  $J = 7.5$  Hz, 2H), 2.12(br s, 1H), 1.15(t,  $J = 7.5$  Hz);  $^{13}\text{C NMR}$  (mixture of **3t** and **3t'**) (75 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 143.5, 143.1, 133.6, 130.8, 130.2, 128.5, 127.9, 127.6, 126.1, 124.19, 121.1, 118.6, 118.4, 115.9, 107.6, 107.5, 104.9, 103.8, 59.3, 57.2, 57.1, 46.0, 43.2, 41.0, 30.1, 20.5, 19.4, 15.1; IR(KBr)  $\nu$ : 3433,

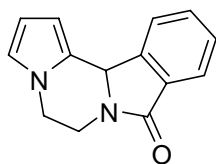
2924, 1654, 1646, 1509, 1420, 1386, 700, 571  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2$  226.1465, found 226.1464.



**8-ethyl-1-(4-fluorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3u)** and **7-ethyl-1-(4-fluorophenyl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3u')**. 20.1 mg (Flash column chromatography eluent, ethyl acetate; mixture of **3u** and **3u'**), yellow solid, 83 % total yield, 92% ee (**3u**), 92% ee (**3u'**); HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 98/2, 0.6 mL/min), **3u**  $t_{r\text{-major}}$  19.7 min,  $t_{r\text{-minor}}$  30.0 min; **3u'**  $t_{r\text{-major}}$  28.3 min,  $t_{r\text{-minor}}$  46.6 min.  $^1\text{H}$  NMR (**3u**) (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.36 (dd,  $J = 8.7, 5.5$  Hz, 1H), 7.19 (dd,  $J = 8.7, 5.4$  Hz, 1H), 6.98 (t,  $J = 9.0$  Hz, 2H), 6.56 (d,  $J = 2.4$  Hz, 1H), 6.04 (d,  $J = 2.7$  Hz, 1H), 5.13 (s, 1H), 4.05-3.85 (m, 2H), 3.32-3.04 (m, 2H), 2.10 (br s, 1H), 2.02-1.87 (m, 2H), 0.91 (t,  $J = 7.5$  Hz, 3H);  $^1\text{H}$  NMR (**3u'**) (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.36 (dd,  $J = 8.7, 5.5$  Hz, 1H), 7.19 (dd,  $J = 8.7, 5.4$  Hz, 1H), 6.98 (t,  $J = 9.0$  Hz, 2H), 6.37 (s, 1H), 5.37 (s, 1H), 5.01 (s, 1H), 4.05-3.85 (m, 2H), 3.32-3.04 (m, 2H), 2.42 (q,  $J = 7.5$  Hz, 2H), 2.10 (br s, 1H), 1.13 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (mixture of **3u** and **3u'**) (75 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 164.1, 163.9, 160.8, 160.6, 139.3, 133.7, 130.7, 130.0, 126.2, 124.0, 121.1, 118.7, 118.5, 115.4, 115.2, 107.7, 107.6, 105.0, 104.2, 103.8, 58.6, 56.5, 56.3, 45.9, 45.5, 43.6, 40.9, 30.1, 20.5, 19.4, 15.0; IR (KBr)  $\nu$ : 3448, 2962, 1655, 1647, 1637, 1629, 1508, 1459, 1093, 735, 562  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{16}\text{FN}_2$  244.1370, found 244.1369.



**8-ethyl-1-(naphthalen-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine(3r)** and **7-ethyl-1-(naphthalen-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3v')**. 26.4 mg (Flash column chromatography eluent, petroleum ether: ethyl acetate=2:1), yellow oil, 92 % total yield; 85% ee (**3v**), 92% ee (**3v'**); HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 95/5, 0.6 mL/min), **3v**  $t_{r\text{-minor}}$  22.6 min,  $t_{r\text{-major}}$  26.3 min; **3v'**  $t_{r\text{-minor}}$  30.2 min,  $t_{r\text{-major}}$  34.8 min.  $^1\text{H NMR}(\mathbf{3v})$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.26-8.20(m, 1H), 7.92-7.77(m, 2H), 7.59-7.31(m, 4H), 6.68(d,  $J = 2.4$  Hz, 1H), 6.13(d,  $J = 2.7$  Hz, 1H), 6.04(s, 1H), 4.16-3.93(m, 2H), 3.48-3.04(m, 2H), 2.23(br s, 1H), 2.07-1.82(m, 2H), 0.90 (t,  $J = 7.5$  Hz, 1H),  $^1\text{H NMR}(\mathbf{3v}')$ (300 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 8.26-8.20(m, 1H), 7.92-7.77(m, 2H), 7.59-7.31(m, 4H), 6.45(s, Hz), 5.86(s, 1H), 5.43(s, 1H), 4.16-3.92(m, 2H), 3.48-3.04(m, 2H), 2.42(q,  $J = 7.5$  Hz, 2H), 2.23(br s, 1H), 1.14(t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C NMR}$  (mixture of **3v** and **3v'**) (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 138.8, 138.6, 138.0, 134.3, 134.1, 133.4, 131.6, 131.3, 130.1, 129.4, 129.1, 128.8, 128.2, 126.6, 126.4, 126.1, 125.6, 125.4, 125.0, 124.2, 124.0, 120.7, 118.5, 115.8, 107.5, 104.9, 104.2, 55.8, 53.2, 46.0, 45.5, 43.4, 40.5, 20.4, 19.1, 15.4, 14.7; IR(KBr)  $\nu$ : 3448, 1655, 1638, 1543, 1509, 1459, 1383, 1110, 671, 559  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_2$  276.1621, found 276.1620.



**1,2,3,4-tetrahydropyrrolo[1,2-a]pyrazine (3w)**. 23.5 mg (Flash column chromatography eluent, dichloromethane: methanol = 30:1), white solid: mp 163-165  $^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}}^{20} = +27.5$  ( $c = 0.04$ ,  $\text{CHCl}_3$ ); 95% yield, 90% ee; HPLC analysis: Chiralcel AD-H (hexanes/iPrOH = 90/10, 0.6 mL/min),  $t_{r\text{-major}}$  29.3 min,  $t_{r\text{-minor}}$  38.9 min;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.84 (d,  $J = 7.5$  Hz, 1H), 7.75 (dd,  $J = 7.6$ , 0.8 Hz, 1H), 7.61 (td,  $J = 7.5$ , 1.8 Hz, 1H), 7.47 (t,  $J = 7.4$  Hz, 1H), 6.09 (t,  $J = 1.8$  Hz, 1H), 6.29-6.27 (m, 1H), 6.20-6.18 (m, 1H), 5.73 (s, 1H), 4.71-4.64 (m, 1H), 4.08-3.93 (m, 2H), 3.65-3.55 (m, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 168.0, 144.5, 132.4, 131.9, 128.7, 125.7, 124.1, 123.2, 120.3, 108.9, 104.4, 56.5, 44.6, 38.0 ; IR (KBr)  $\nu$ :

3416, 2944, 2922, 1684, 1637, 1467, 1442, 1410, 1326, 1075, 720  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}$  266.0372, found 266.0371.

## References:

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### X-ray data of product 3c.

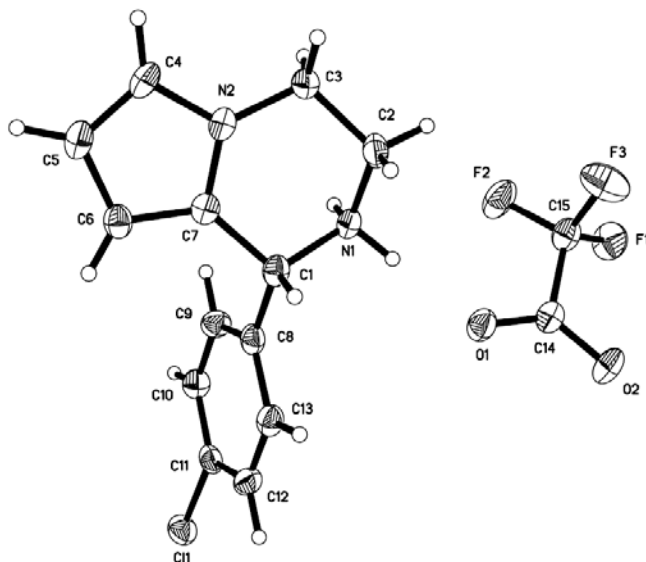


Table 1. Crystal data and structure refinement for 03151m.

Identification code	03151m	
Empirical formula	C <sub>15</sub> H <sub>14</sub> Cl F <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	
Formula weight	346.73	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.0832(4) Å	α = 90°.
	b = 10.0184(7) Å	β = 102.3990(10)°.
	c = 12.8934(9) Å	γ = 90°.
Volume	767.45(9) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.500 Mg/m <sup>3</sup>	
Absorption coefficient	0.291 mm <sup>-1</sup>	
F(000)	356	
Crystal size	0.43 x 0.32 x 0.15 mm <sup>3</sup>	
Theta range for data collection	1.62 to 27.05°.	
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -8 ≤ l ≤ 16	
Reflections collected	3884	

Independent reflections	3065 [R(int) = 0.0155]
Completeness to theta = 27.05°	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9576 and 0.8850
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3065 / 1 / 208
Goodness-of-fit on F <sup>2</sup>	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0749
R indices (all data)	R1 = 0.0345, wR2 = 0.0776
Absolute structure parameter	0.01(5)
Largest diff. peak and hole	0.304 and -0.149 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

for 03151m.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
C(1)	5145(3)	1570(2)	2792(2)	22(1)
C(2)	4292(3)	-184(2)	1417(2)	26(1)
C(3)	6660(3)	-758(2)	1673(2)	24(1)
C(4)	9899(3)	-748(2)	3257(2)	26(1)
C(5)	10643(3)	69(2)	4106(2)	28(1)
C(6)	9044(3)	1111(2)	4061(2)	24(1)
C(7)	7364(3)	882(2)	3179(2)	21(1)
C(8)	5179(3)	3047(2)	3001(2)	22(1)
C(9)	6792(3)	3879(2)	2729(2)	25(1)
C(10)	6803(3)	5241(2)	2965(2)	25(1)
C(11)	5203(3)	5738(2)	3476(2)	23(1)
C(12)	3563(3)	4930(2)	3738(2)	25(1)
C(13)	3558(3)	3585(2)	3490(2)	24(1)
N(1)	4329(3)	1282(2)	1622(1)	22(1)
N(2)	7878(3)	-257(2)	2697(1)	23(1)
Cl(1)	5299(1)	7418(1)	3841(1)	30(1)
C(14)	-1497(3)	1906(2)	295(2)	23(1)
C(15)	-653(3)	1392(2)	-682(2)	27(1)
O(1)	-110(2)	1874(2)	1156(1)	29(1)
O(2)	-3513(2)	2220(2)	112(1)	31(1)
F(1)	-1608(2)	2007(1)	-1580(1)	40(1)
F(2)	1570(2)	1546(2)	-577(1)	42(1)
F(3)	-1065(3)	93(2)	-822(1)	51(1)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for 03151m.

---

C(1)-C(7)	1.502(3)
C(1)-C(8)	1.503(3)
C(1)-N(1)	1.511(2)
C(1)-H(1)	1.0000
C(2)-N(1)	1.491(3)
C(2)-C(3)	1.520(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-N(2)	1.457(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.364(3)
C(4)-N(2)	1.376(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.420(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.376(3)
C(6)-H(6)	0.9500
C(7)-N(2)	1.367(3)
C(8)-C(13)	1.388(3)
C(8)-C(9)	1.389(3)
C(9)-C(10)	1.397(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.380(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.382(3)
C(11)-Cl(1)	1.745(2)
C(12)-C(13)	1.386(3)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
N(1)-H(1A)	0.9200
N(1)-H(1B)	0.9200
C(14)-O(2)	1.239(2)
C(14)-O(1)	1.242(2)
C(14)-C(15)	1.547(3)
C(15)-F(1)	1.331(2)

C(15)-F(3)	1.331(3)
C(15)-F(2)	1.339(2)
C(7)-C(1)-C(8)	114.54(16)
C(7)-C(1)-N(1)	108.84(16)
C(8)-C(1)-N(1)	110.85(16)
C(7)-C(1)-H(1)	107.4
C(8)-C(1)-H(1)	107.4
N(1)-C(1)-H(1)	107.4
N(1)-C(2)-C(3)	110.90(16)
N(1)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2A)	109.5
N(1)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	108.0
N(2)-C(3)-C(2)	109.85(16)
N(2)-C(3)-H(3A)	109.7
C(2)-C(3)-H(3A)	109.7
N(2)-C(3)-H(3B)	109.7
C(2)-C(3)-H(3B)	109.7
H(3A)-C(3)-H(3B)	108.2
C(5)-C(4)-N(2)	108.15(19)
C(5)-C(4)-H(4)	125.9
N(2)-C(4)-H(4)	125.9
C(4)-C(5)-C(6)	107.60(18)
C(4)-C(5)-H(5)	126.2
C(6)-C(5)-H(5)	126.2
C(7)-C(6)-C(5)	106.94(18)
C(7)-C(6)-H(6)	126.5
C(5)-C(6)-H(6)	126.5
N(2)-C(7)-C(6)	108.29(17)
N(2)-C(7)-C(1)	120.59(17)
C(6)-C(7)-C(1)	130.75(18)
C(13)-C(8)-C(9)	119.40(19)
C(13)-C(8)-C(1)	118.65(18)
C(9)-C(8)-C(1)	121.95(19)
C(8)-C(9)-C(10)	120.15(19)
C(8)-C(9)-H(9)	119.9

C(10)-C(9)-H(9)	119.9
C(11)-C(10)-C(9)	119.01(18)
C(11)-C(10)-H(10)	120.5
C(9)-C(10)-H(10)	120.5
C(10)-C(11)-C(12)	121.71(19)
C(10)-C(11)-Cl(1)	119.38(16)
C(12)-C(11)-Cl(1)	118.87(16)
C(11)-C(12)-C(13)	118.66(18)
C(11)-C(12)-H(12)	120.7
C(13)-C(12)-H(12)	120.7
C(12)-C(13)-C(8)	121.03(19)
C(12)-C(13)-H(13)	119.5
C(8)-C(13)-H(13)	119.5
C(2)-N(1)-C(1)	110.73(15)
C(2)-N(1)-H(1A)	109.5
C(1)-N(1)-H(1A)	109.5
C(2)-N(1)-H(1B)	109.5
C(1)-N(1)-H(1B)	109.5
H(1A)-N(1)-H(1B)	108.1
C(7)-N(2)-C(4)	109.00(17)
C(7)-N(2)-C(3)	125.33(16)
C(4)-N(2)-C(3)	125.10(18)
O(2)-C(14)-O(1)	129.19(19)
O(2)-C(14)-C(15)	114.66(16)
O(1)-C(14)-C(15)	116.01(16)
F(1)-C(15)-F(3)	107.46(17)
F(1)-C(15)-F(2)	106.10(17)
F(3)-C(15)-F(2)	106.46(17)
F(1)-C(15)-C(14)	113.30(17)
F(3)-C(15)-C(14)	110.52(17)
F(2)-C(15)-C(14)	112.61(16)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 03151m. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

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$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
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C(1)	19(1)	26(1)	20(1)	3(1)	4(1)	-3(1)
C(2)	23(1)	25(1)	26(1)	-1(1)	-3(1)	-3(1)
C(3)	23(1)	25(1)	23(1)	-2(1)	1(1)	2(1)
C(4)	16(1)	32(1)	30(1)	7(1)	5(1)	3(1)
C(5)	19(1)	38(1)	25(1)	6(1)	2(1)	-1(1)
C(6)	23(1)	29(1)	20(1)	2(1)	4(1)	-3(1)
C(7)	21(1)	22(1)	20(1)	4(1)	5(1)	-2(1)
C(8)	21(1)	28(1)	17(1)	2(1)	0(1)	0(1)
C(9)	25(1)	29(1)	25(1)	0(1)	9(1)	1(1)
C(10)	24(1)	28(1)	24(1)	2(1)	6(1)	-3(1)
C(11)	26(1)	22(1)	18(1)	-1(1)	-3(1)	1(1)
C(12)	21(1)	33(1)	23(1)	-1(1)	6(1)	3(1)
C(13)	20(1)	30(1)	21(1)	2(1)	4(1)	-2(1)
N(1)	16(1)	26(1)	23(1)	1(1)	1(1)	1(1)
N(2)	19(1)	26(1)	24(1)	3(1)	1(1)	0(1)
Cl(1)	34(1)	25(1)	30(1)	-3(1)	2(1)	2(1)
C(14)	21(1)	22(1)	26(1)	6(1)	5(1)	-1(1)
C(15)	23(1)	32(1)	26(1)	5(1)	4(1)	1(1)
O(1)	22(1)	39(1)	23(1)	2(1)	3(1)	4(1)
O(2)	19(1)	39(1)	33(1)	9(1)	4(1)	5(1)
F(1)	40(1)	54(1)	22(1)	8(1)	0(1)	10(1)
F(2)	24(1)	76(1)	30(1)	4(1)	10(1)	6(1)
F(3)	75(1)	32(1)	50(1)	-7(1)	21(1)	-3(1)

---

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for 03151m.

	x	y	z	U(eq)
H(1)	4041	1161	3172	26
H(2A)	3595	-357	662	31
H(2B)	3367	-632	1859	31
H(3A)	6586	-1745	1694	29
H(3B)	7464	-501	1112	29
H(4)	10646	-1522	3083	31
H(5)	11987	-40	4632	33
H(6)	9120	1830	4548	29
H(9)	7890	3522	2382	31
H(10)	7897	5816	2777	30
H(12)	2462	5291	4082	30
H(13)	2427	3021	3657	29
H(1A)	2904	1625	1394	27
H(1B)	5263	1692	1246	27

Table 6. Torsion angles [°] for 03151m.

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N(1)-C(2)-C(3)-N(2)	46.4(2)
N(2)-C(4)-C(5)-C(6)	-0.8(2)
C(4)-C(5)-C(6)-C(7)	0.3(2)
C(5)-C(6)-C(7)-N(2)	0.4(2)
C(5)-C(6)-C(7)-C(1)	173.2(2)
C(8)-C(1)-C(7)-N(2)	-152.70(18)
N(1)-C(1)-C(7)-N(2)	-28.0(2)
C(8)-C(1)-C(7)-C(6)	35.2(3)
N(1)-C(1)-C(7)-C(6)	159.90(19)
C(7)-C(1)-C(8)-C(13)	-129.11(19)
N(1)-C(1)-C(8)-C(13)	107.26(19)
C(7)-C(1)-C(8)-C(9)	50.3(3)
N(1)-C(1)-C(8)-C(9)	-73.4(2)
C(13)-C(8)-C(9)-C(10)	1.2(3)
C(1)-C(8)-C(9)-C(10)	-178.16(18)
C(8)-C(9)-C(10)-C(11)	0.4(3)
C(9)-C(10)-C(11)-C(12)	-1.4(3)
C(9)-C(10)-C(11)-Cl(1)	176.39(15)
C(10)-C(11)-C(12)-C(13)	0.8(3)
Cl(1)-C(11)-C(12)-C(13)	-177.04(15)
C(11)-C(12)-C(13)-C(8)	0.9(3)
C(9)-C(8)-C(13)-C(12)	-1.9(3)
C(1)-C(8)-C(13)-C(12)	177.52(18)
C(3)-C(2)-N(1)-C(1)	-65.4(2)
C(7)-C(1)-N(1)-C(2)	53.3(2)
C(8)-C(1)-N(1)-C(2)	-179.88(16)
C(6)-C(7)-N(2)-C(4)	-0.9(2)
C(1)-C(7)-N(2)-C(4)	-174.64(17)
C(6)-C(7)-N(2)-C(3)	-172.59(17)
C(1)-C(7)-N(2)-C(3)	13.7(3)
C(5)-C(4)-N(2)-C(7)	1.1(2)
C(5)-C(4)-N(2)-C(3)	172.79(18)
C(2)-C(3)-N(2)-C(7)	-21.9(3)
C(2)-C(3)-N(2)-C(4)	167.76(18)
O(2)-C(14)-C(15)-F(1)	35.6(3)
O(1)-C(14)-C(15)-F(1)	-148.30(18)

O(2)-C(14)-C(15)-F(3)	-85.0(2)
O(1)-C(14)-C(15)-F(3)	91.0(2)
O(2)-C(14)-C(15)-F(2)	156.04(18)
O(1)-C(14)-C(15)-F(2)	-27.9(3)

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Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 03151m [ $\text{\AA}$  and  $^\circ$ ].

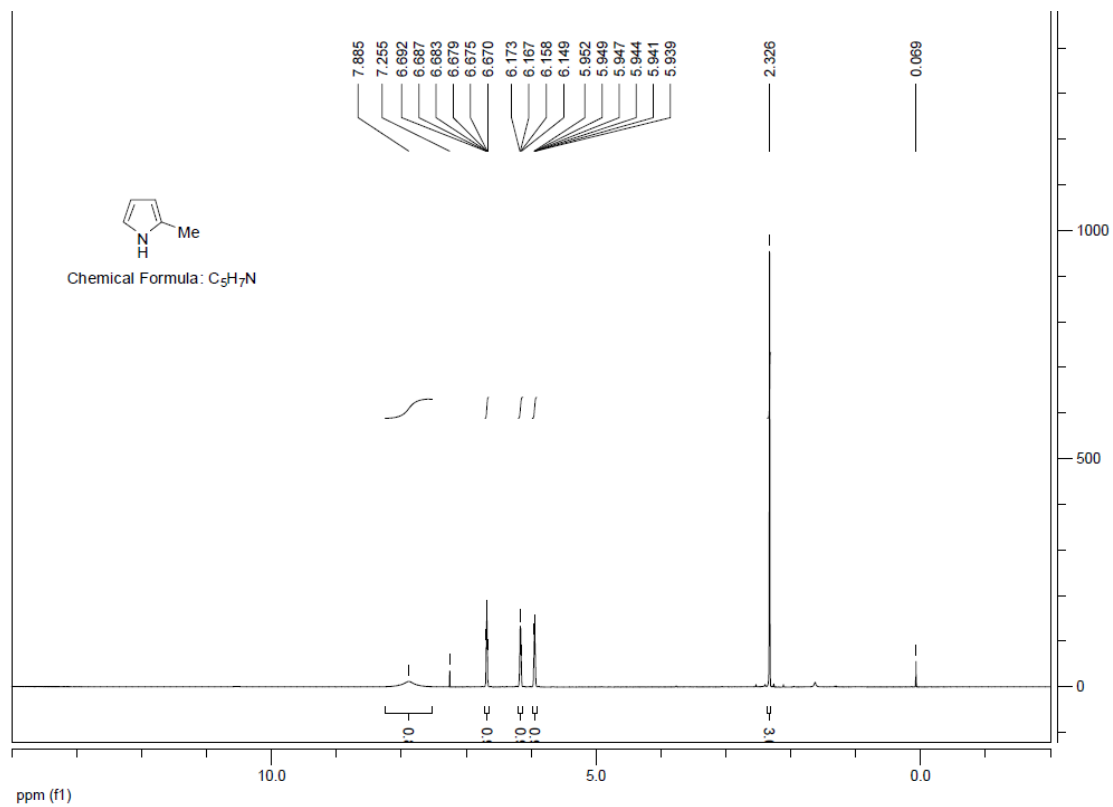
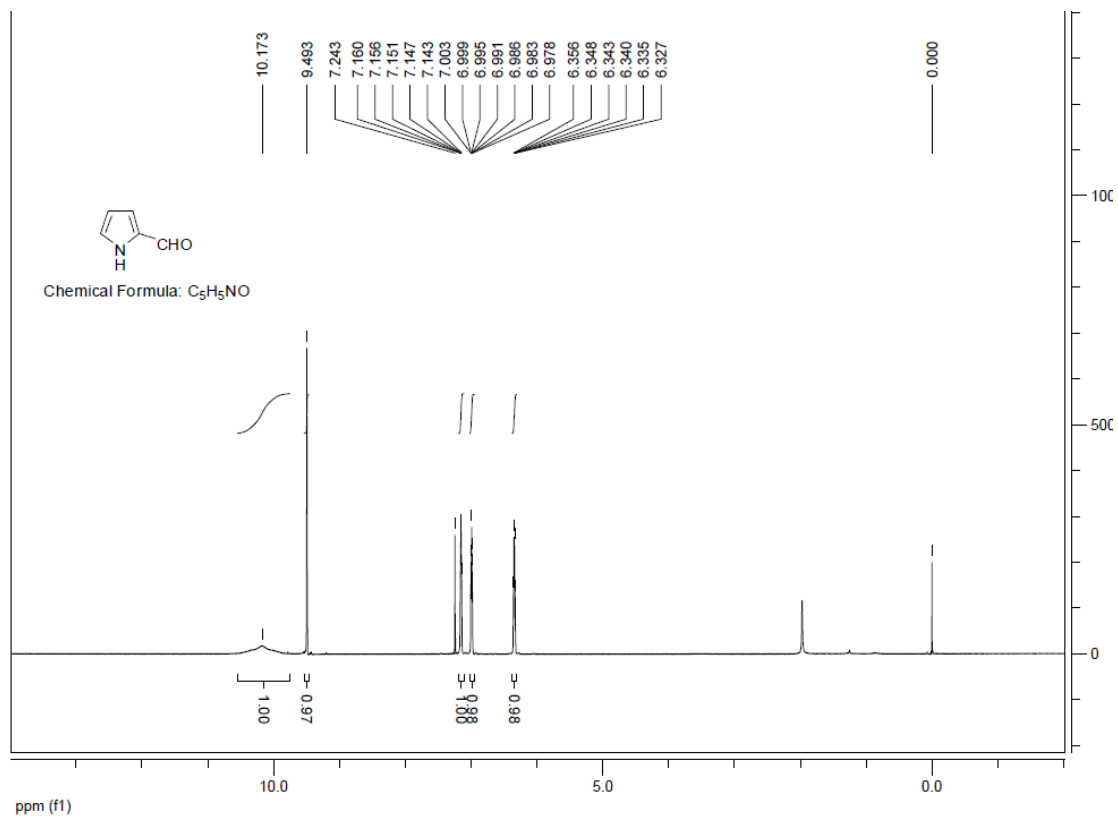
D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1A)...O(1)	0.92	1.81	2.703(2)	162.9
N(1)-H(1B)...O(2)#1	0.92	1.85	2.738(2)	160.3

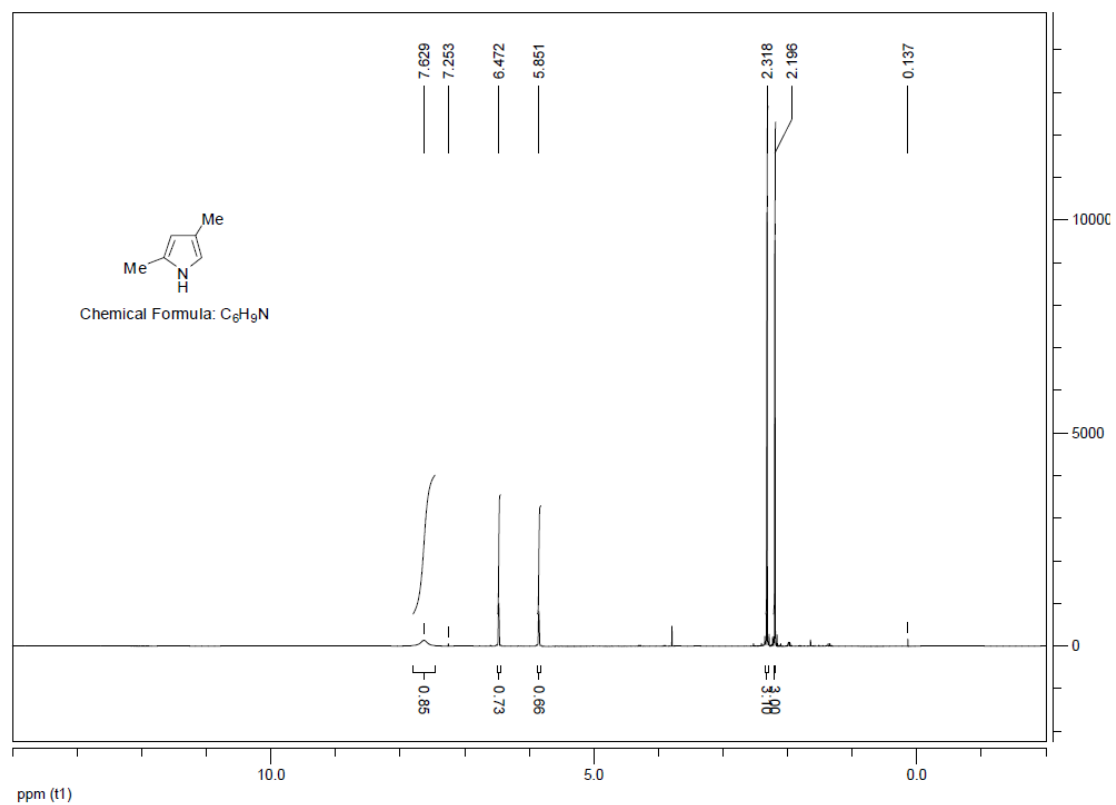
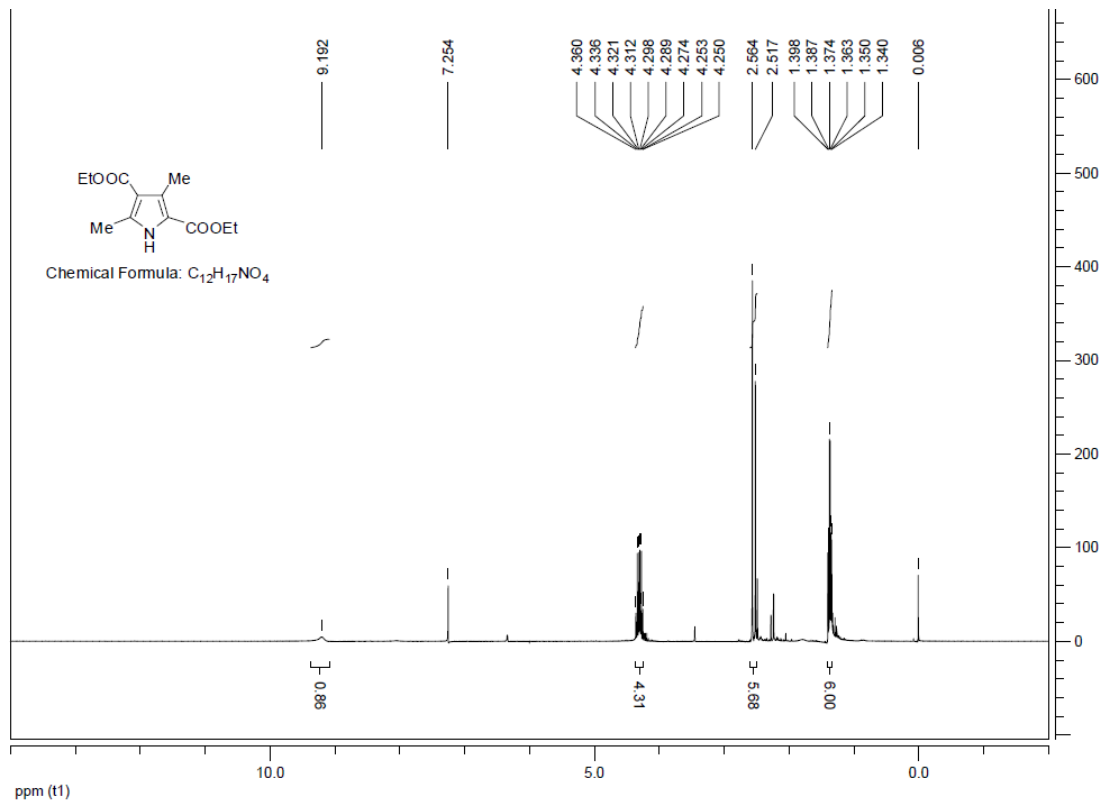
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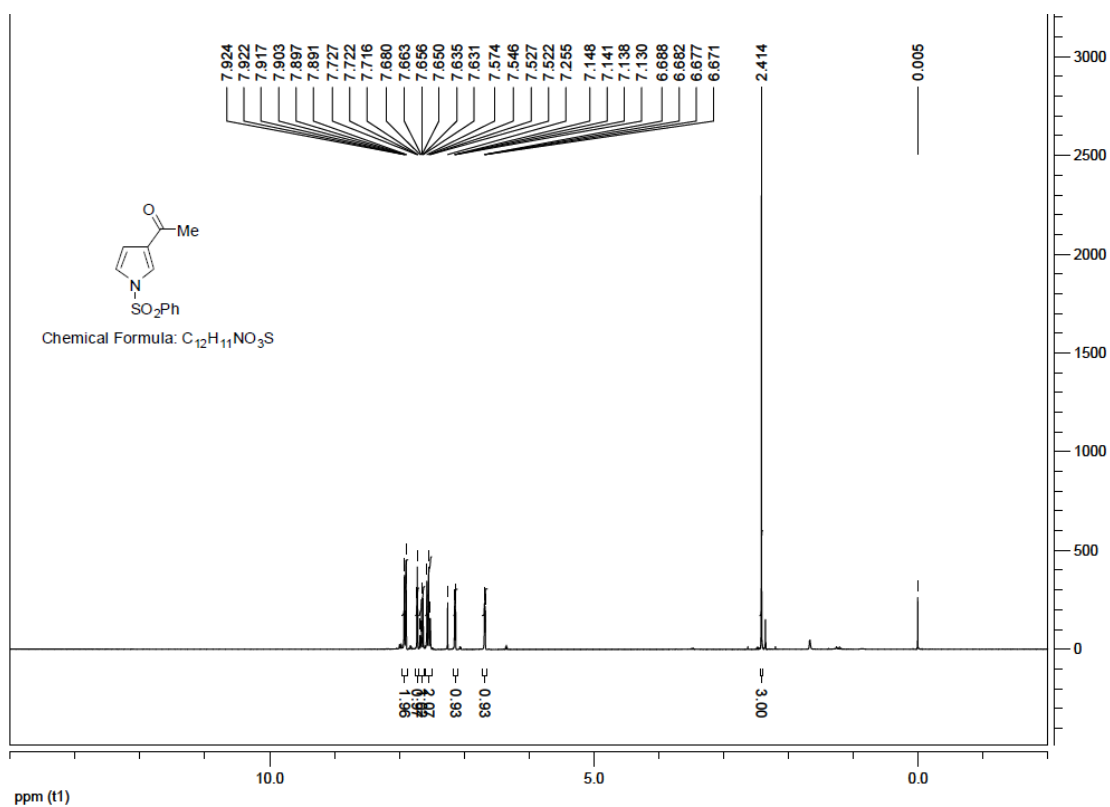
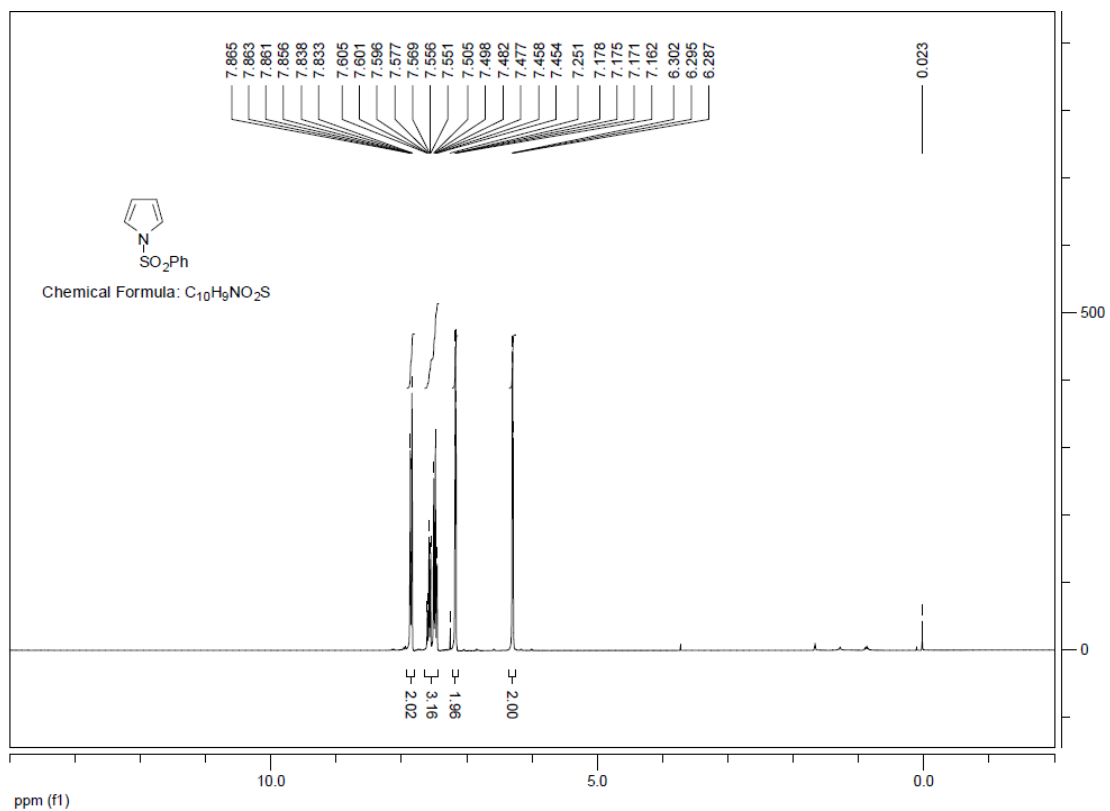
Symmetry transformations used to generate equivalent atoms:

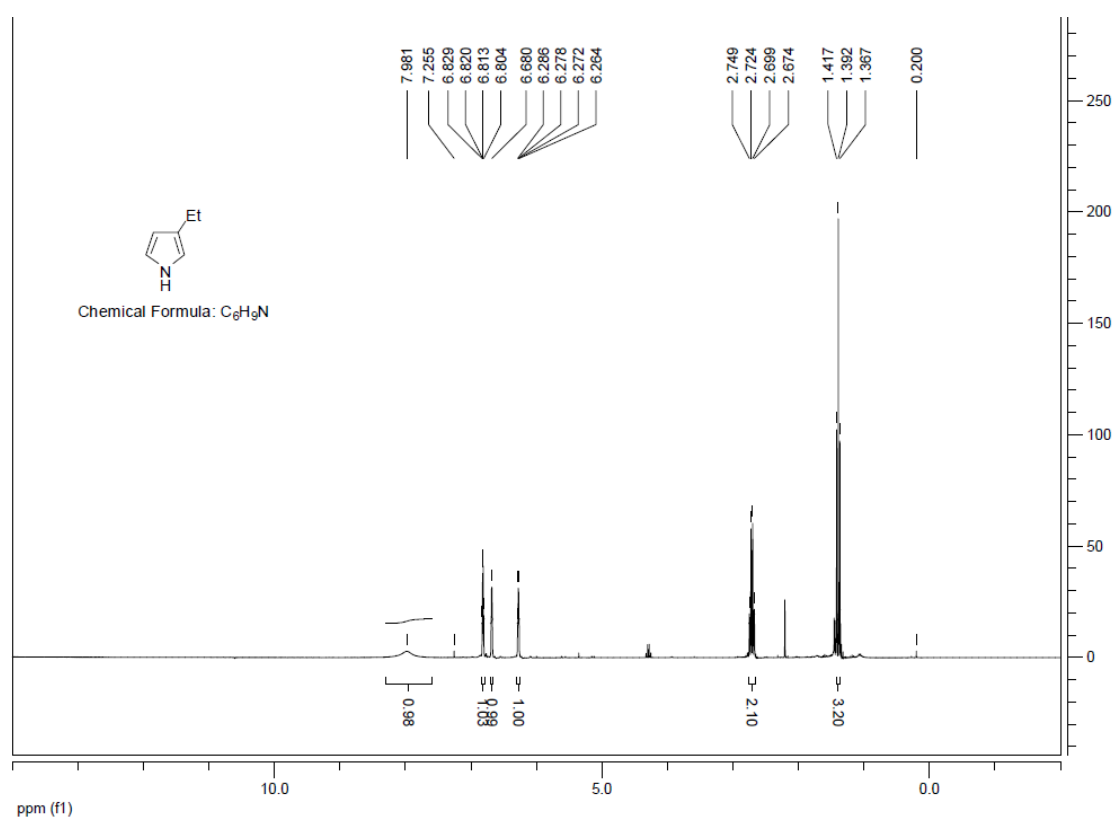
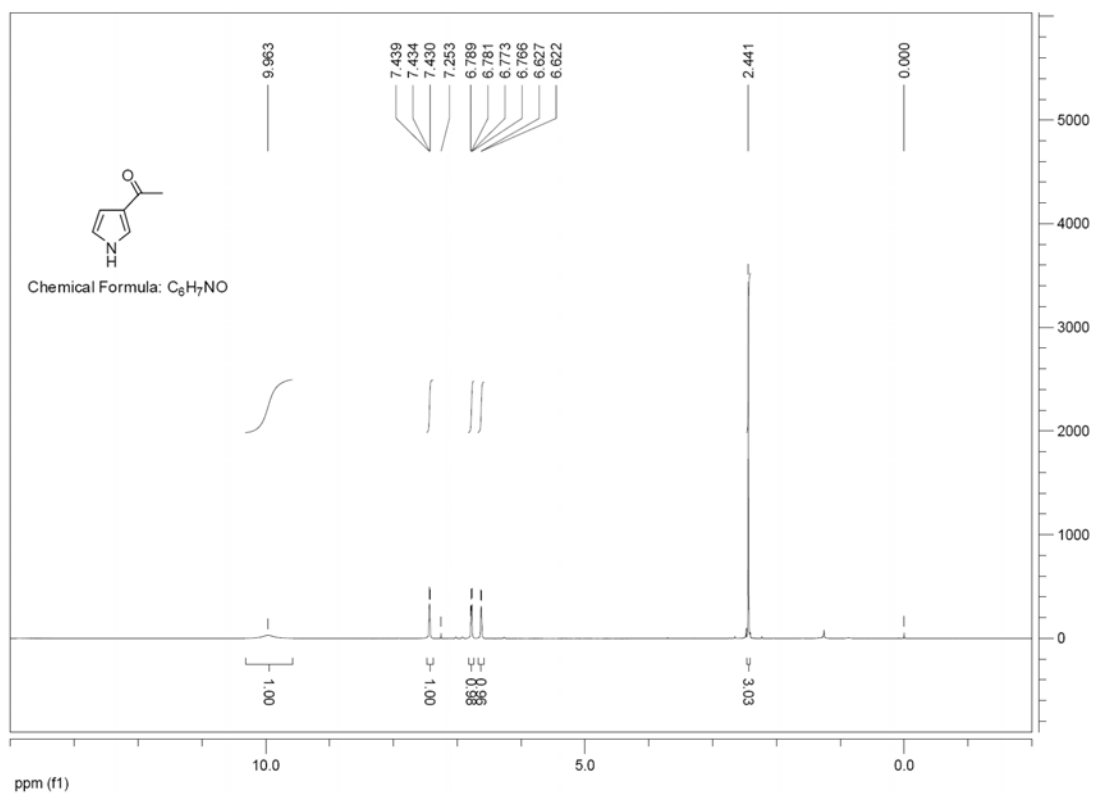
#1 x+1,y,z

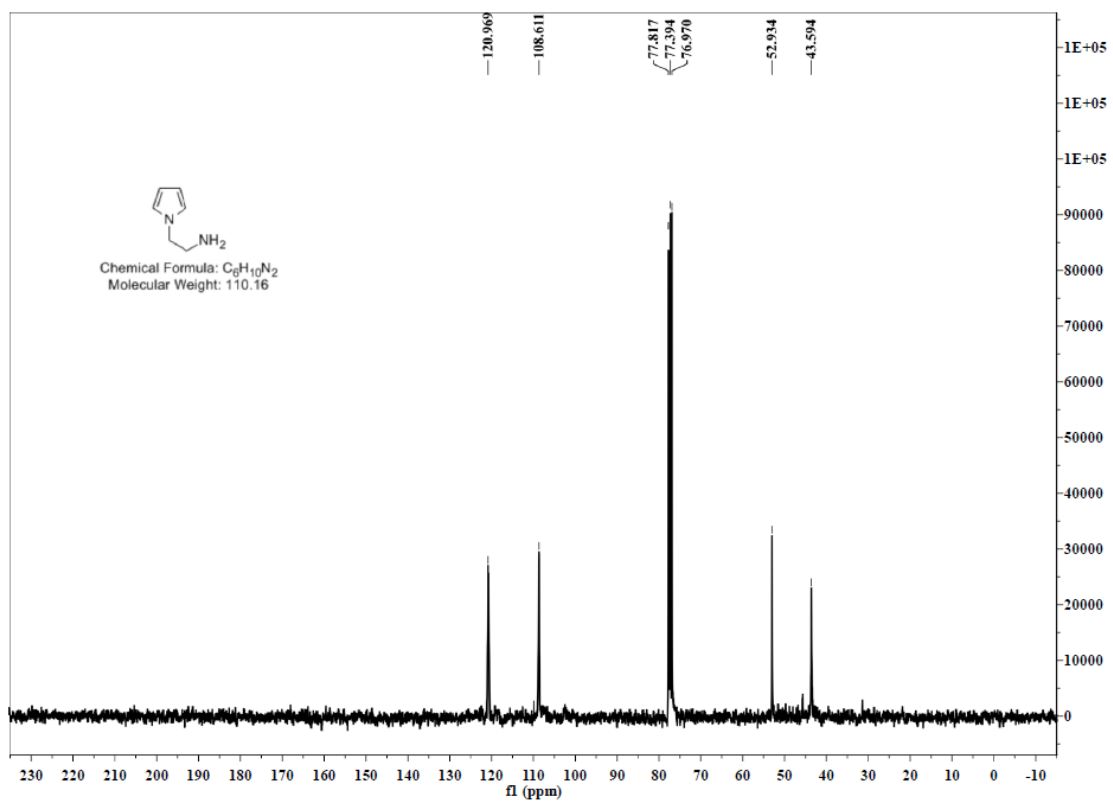
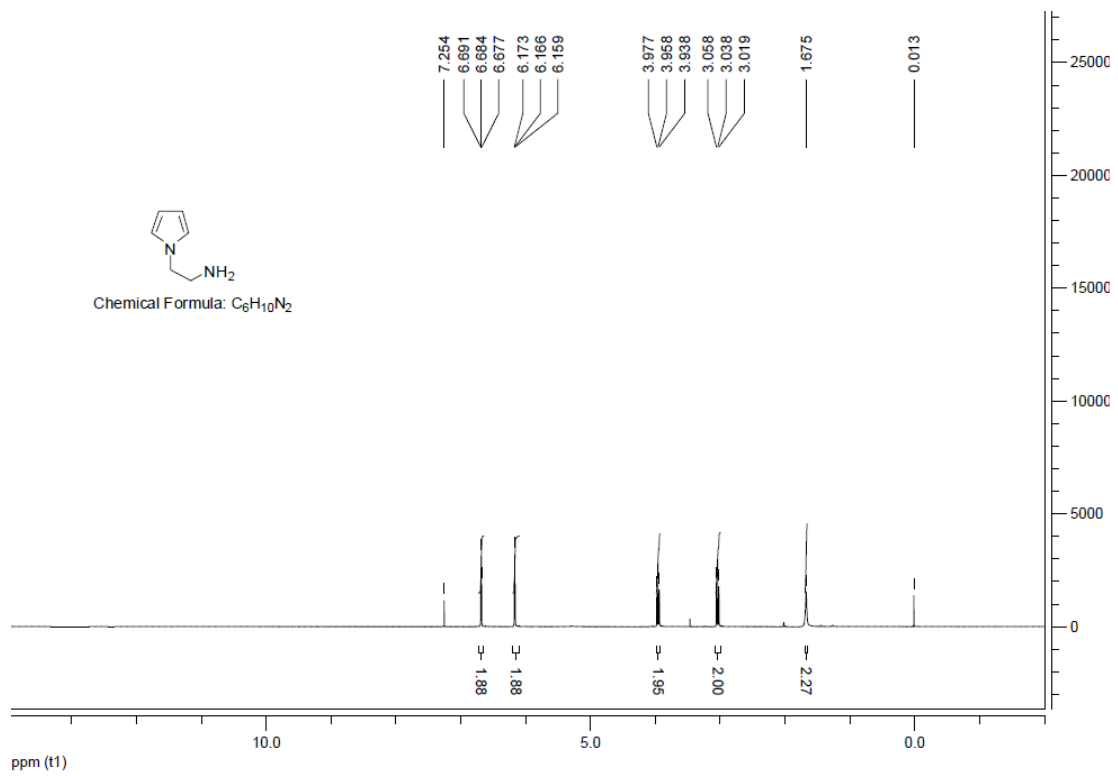
Copies of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and chiral HPLC Spectra for all products

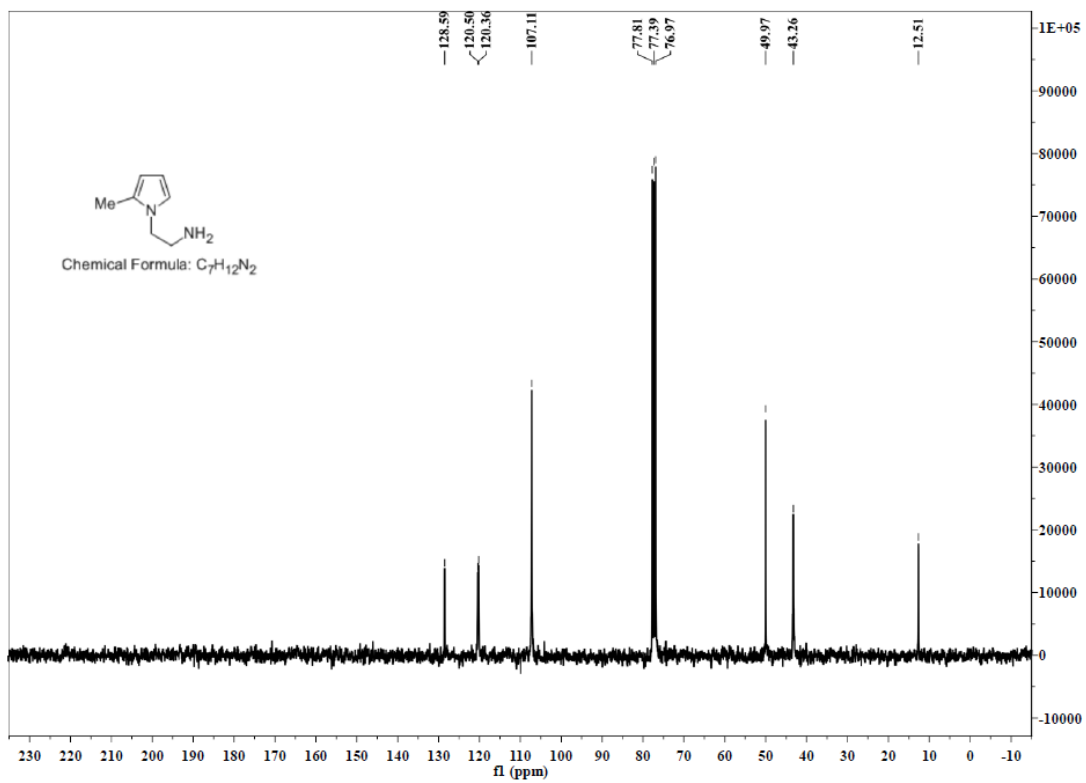
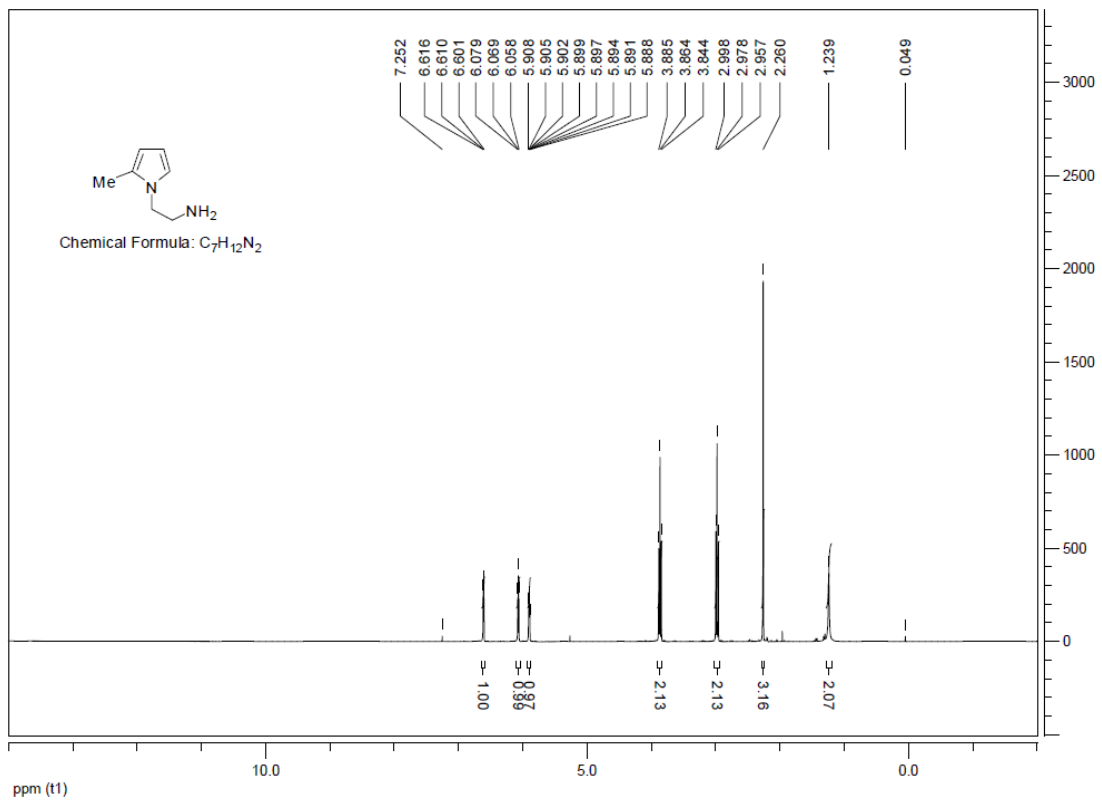


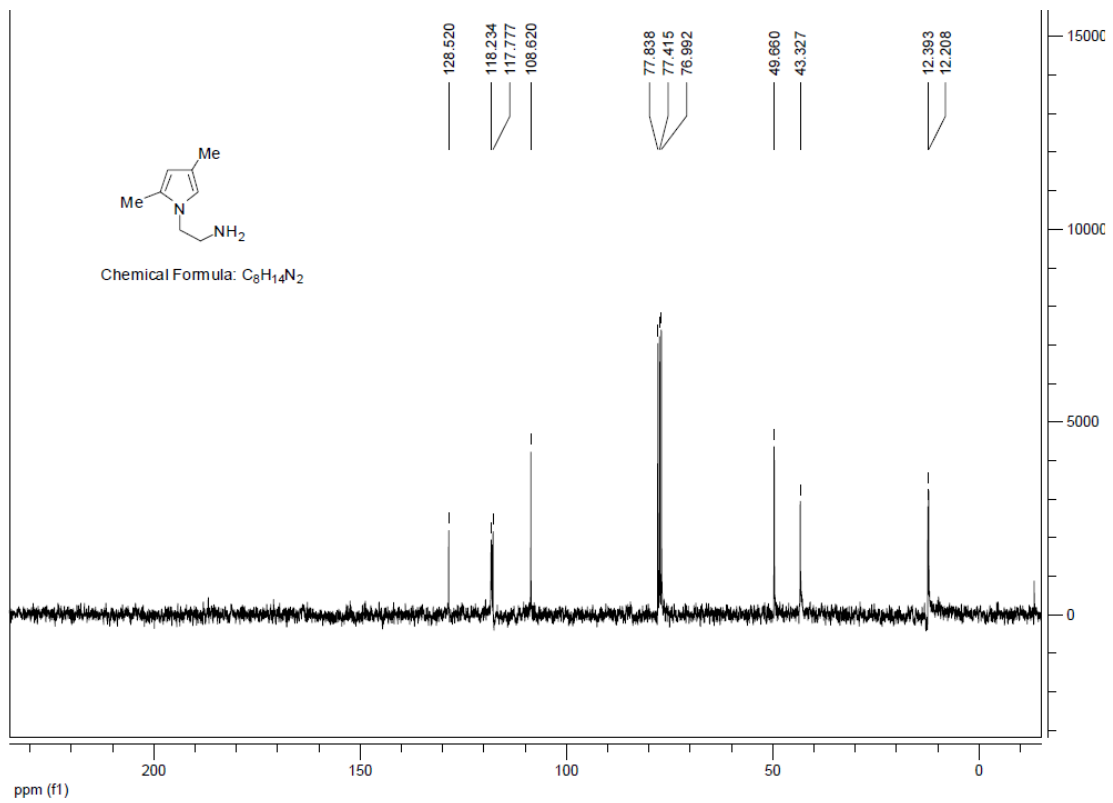
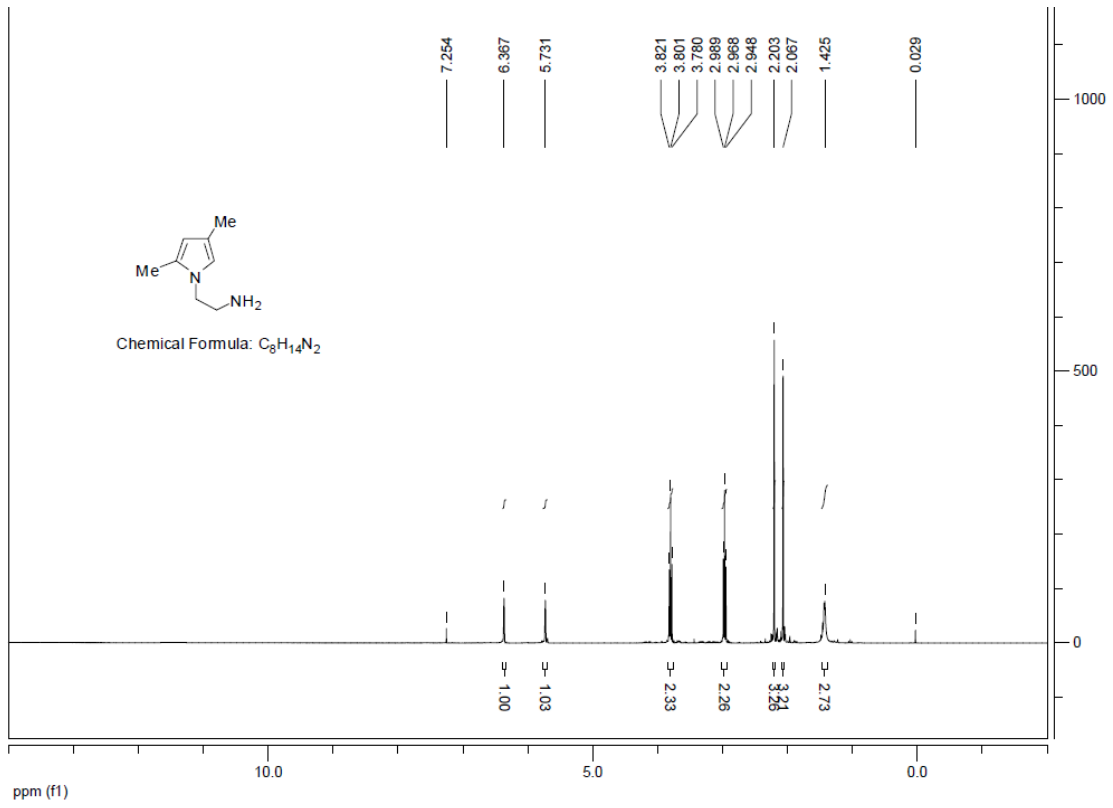






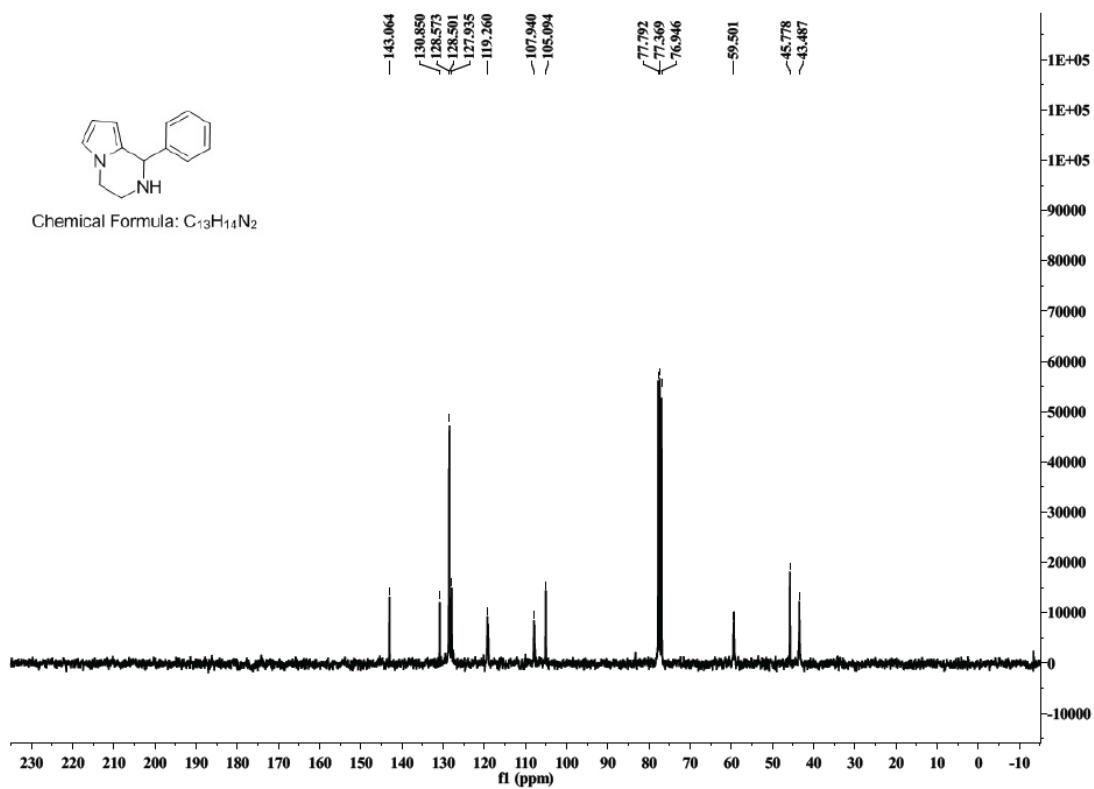
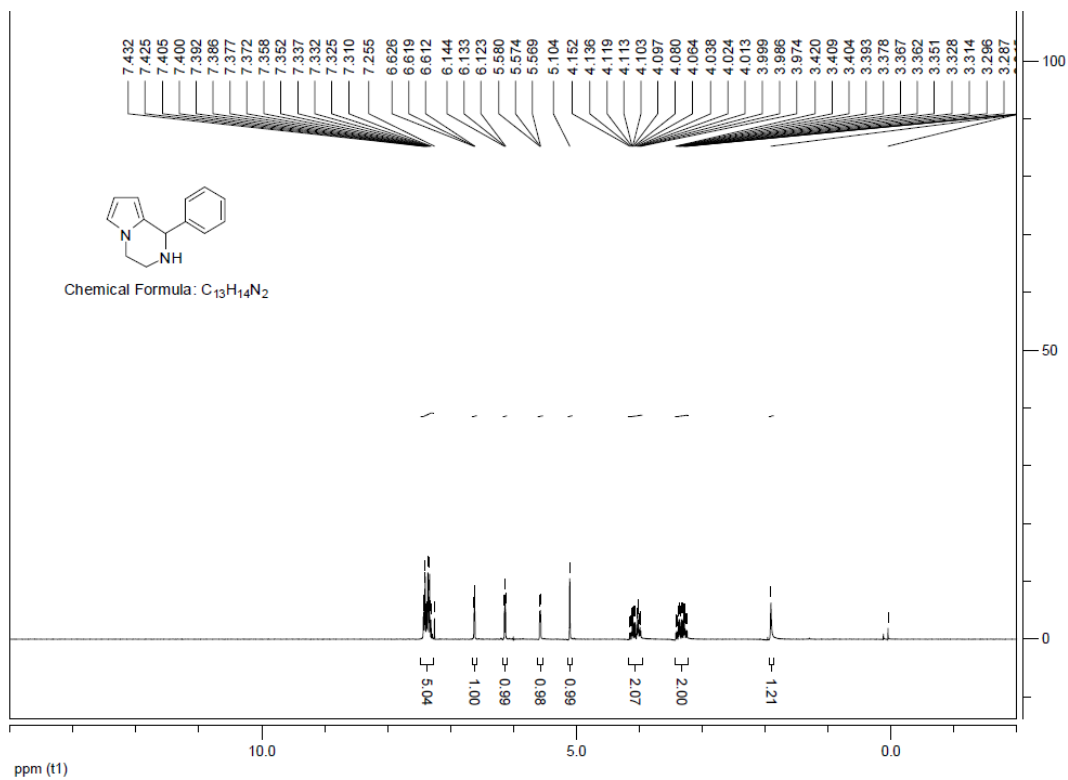




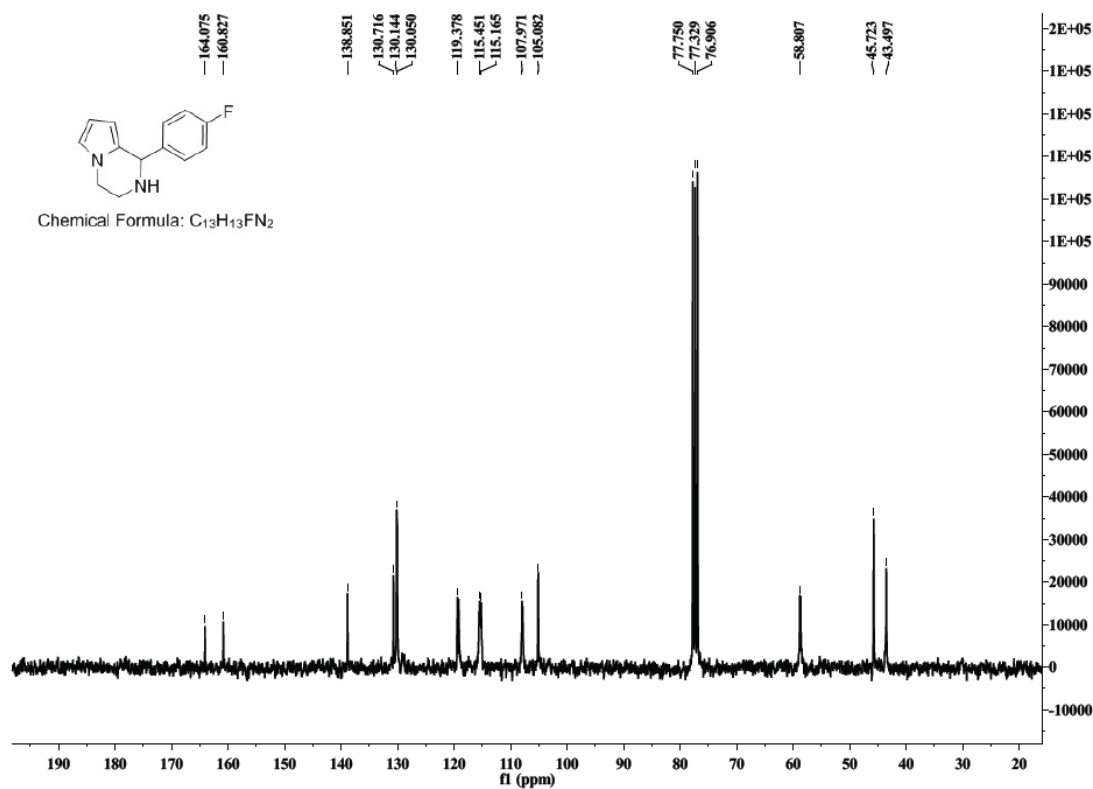
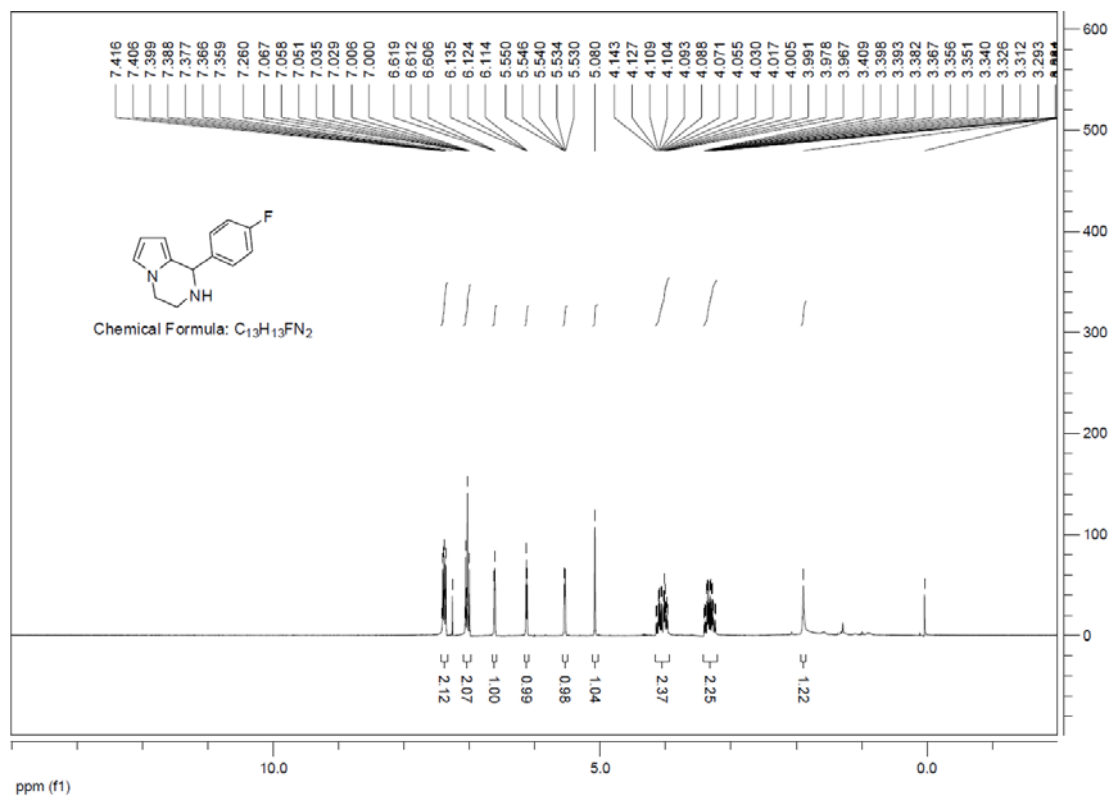




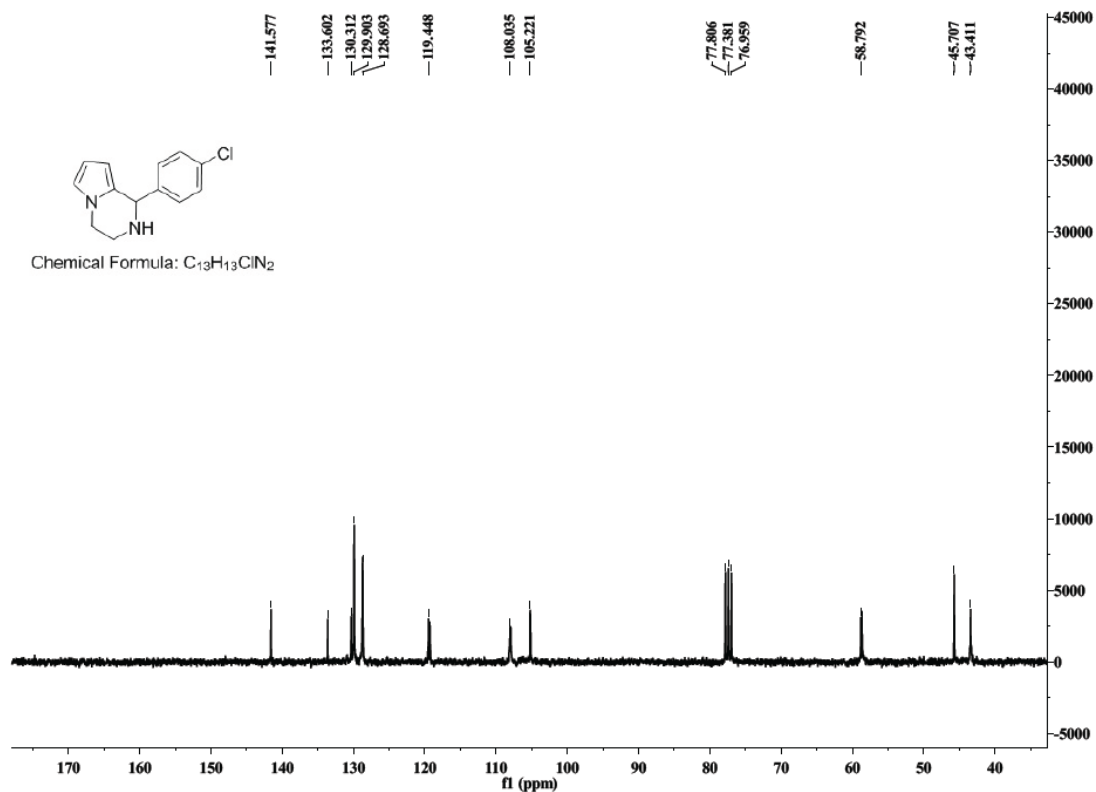
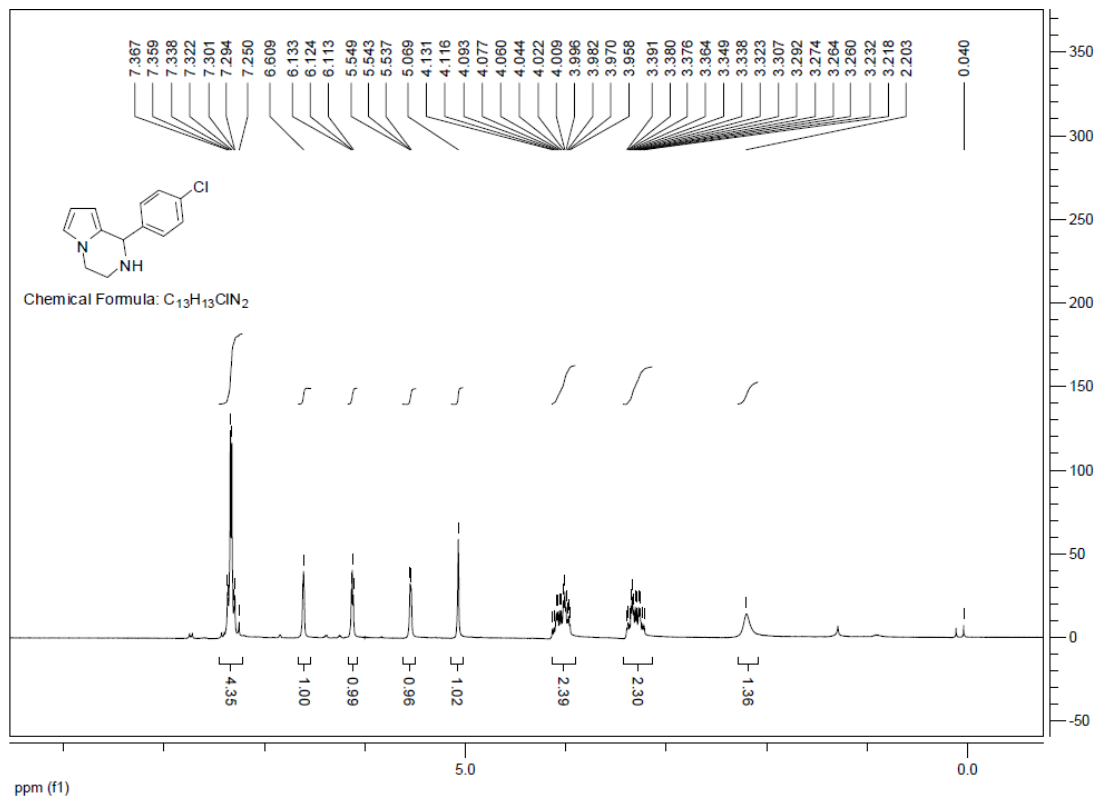
Product 3a



Product 3b



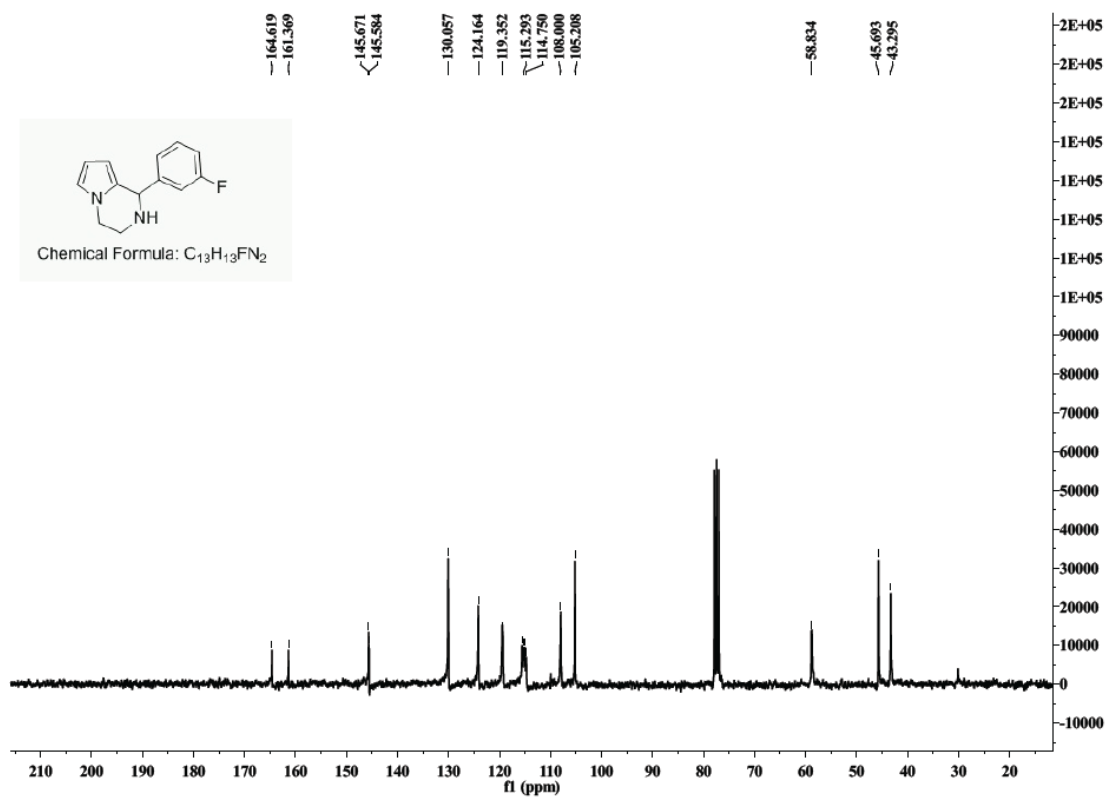
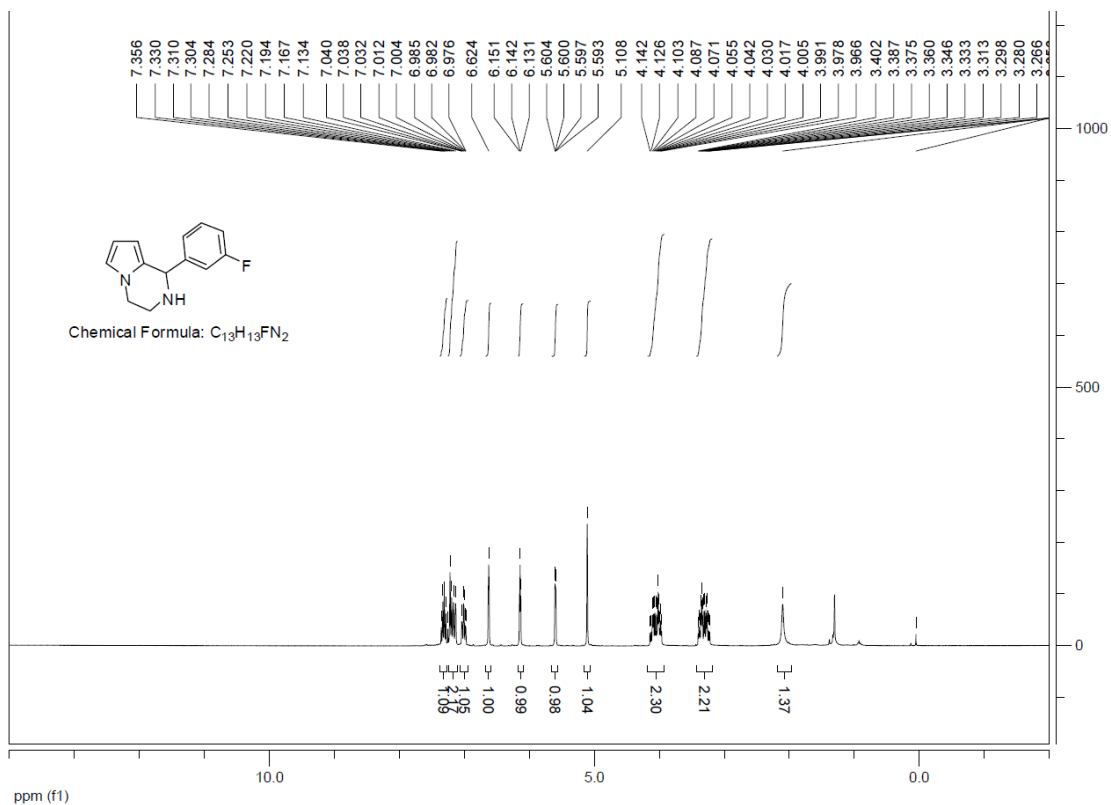
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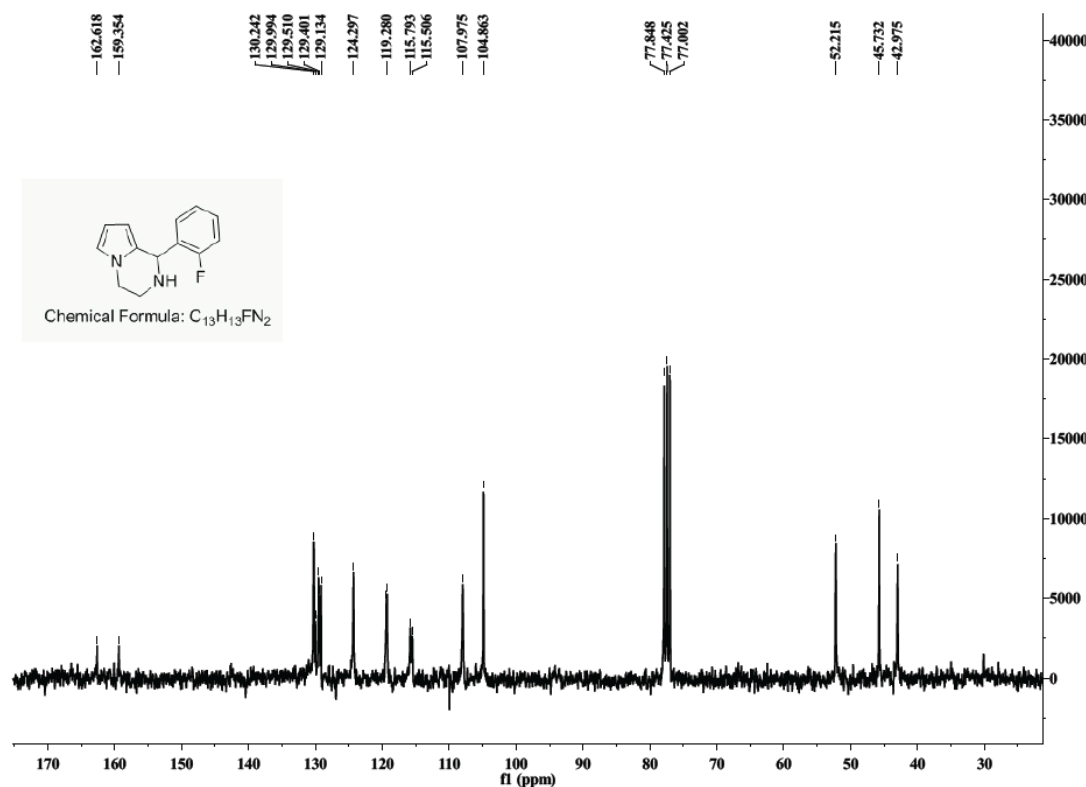
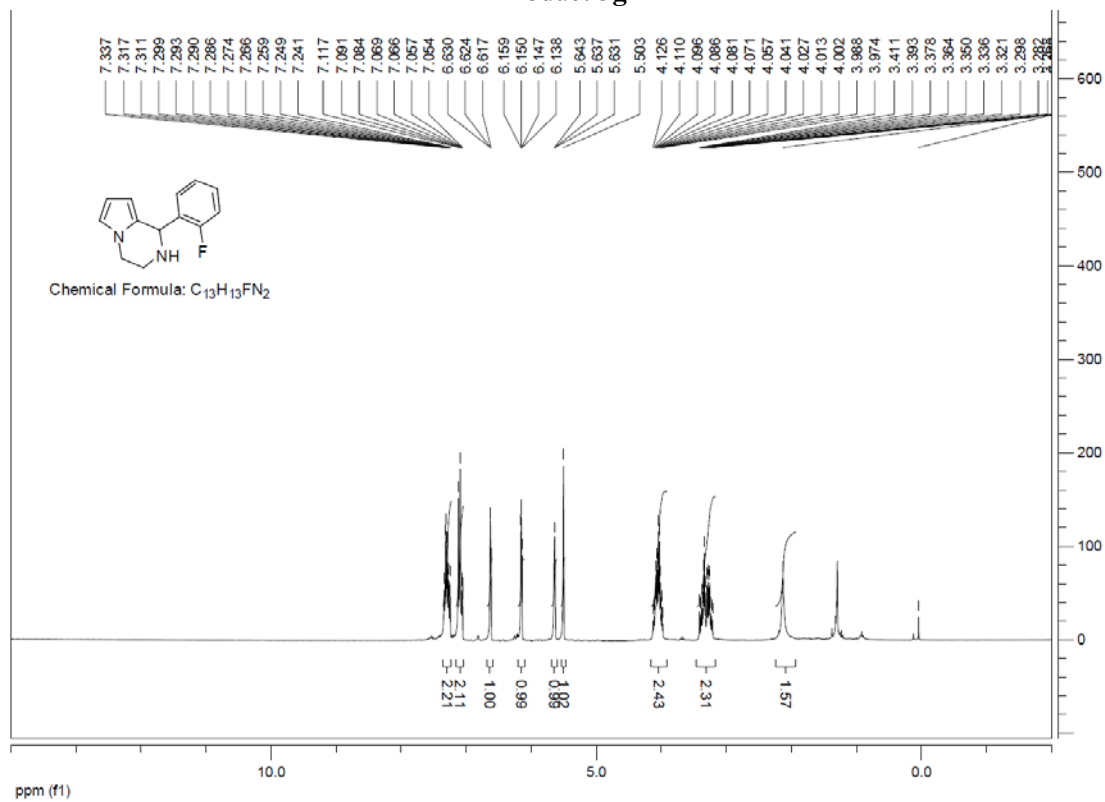




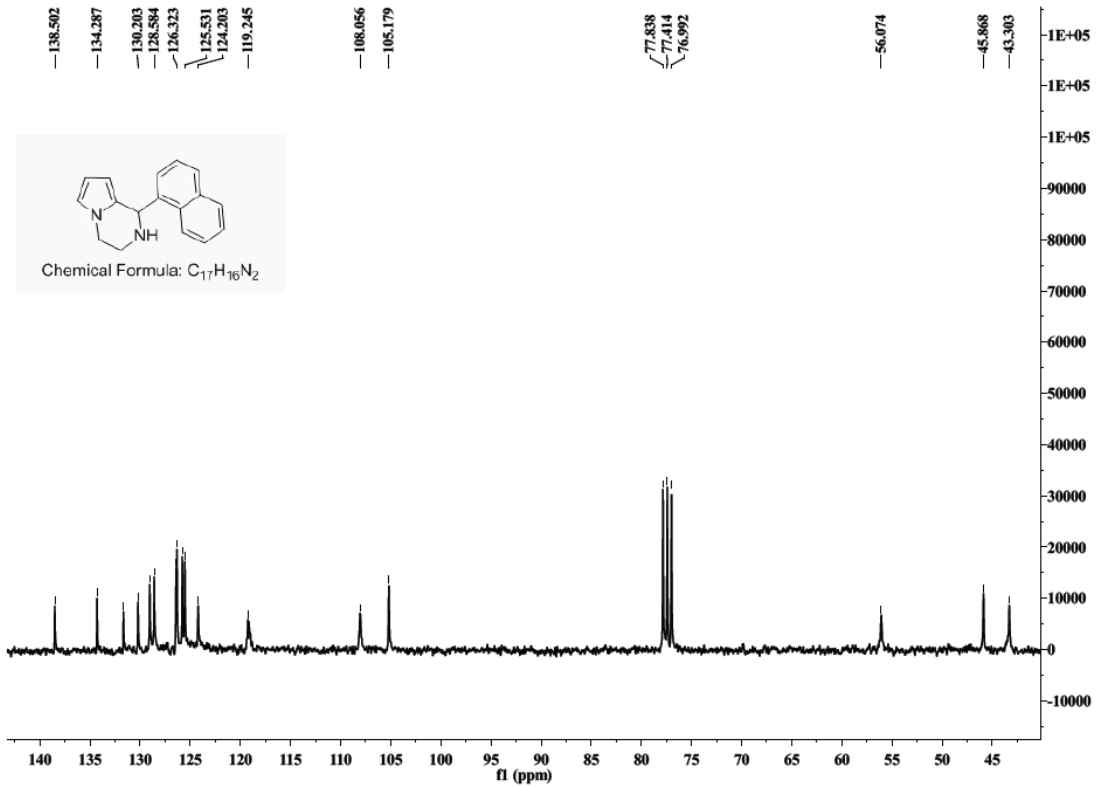
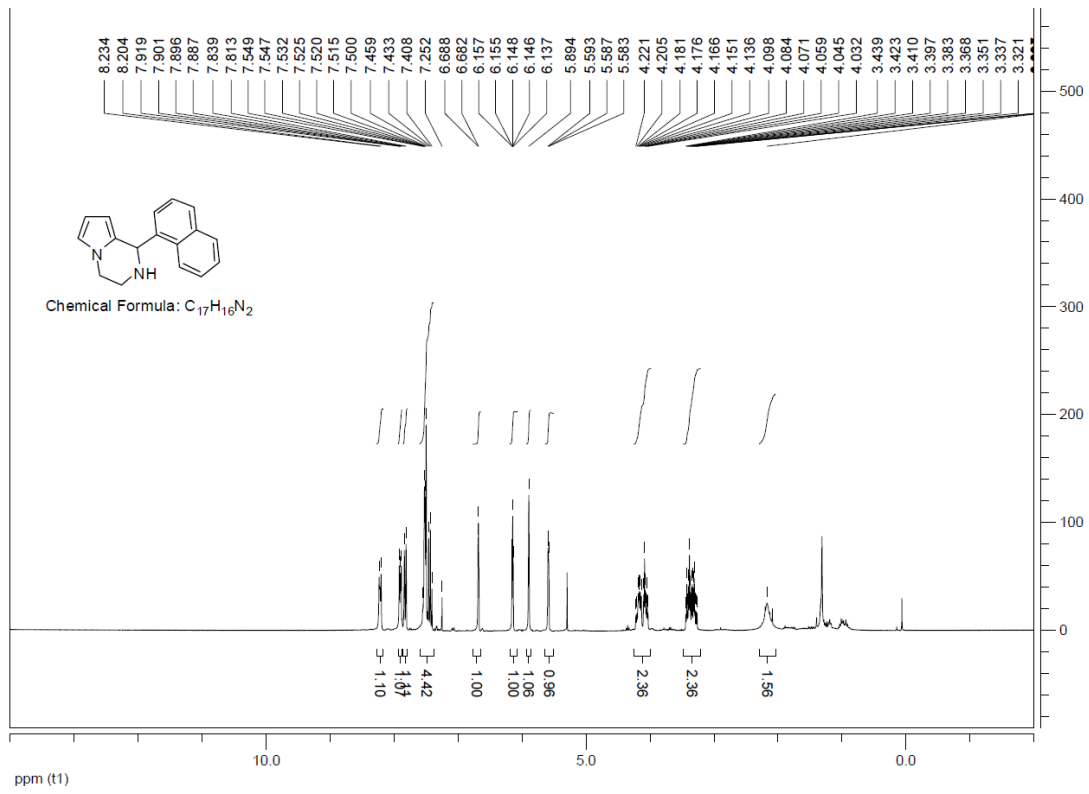
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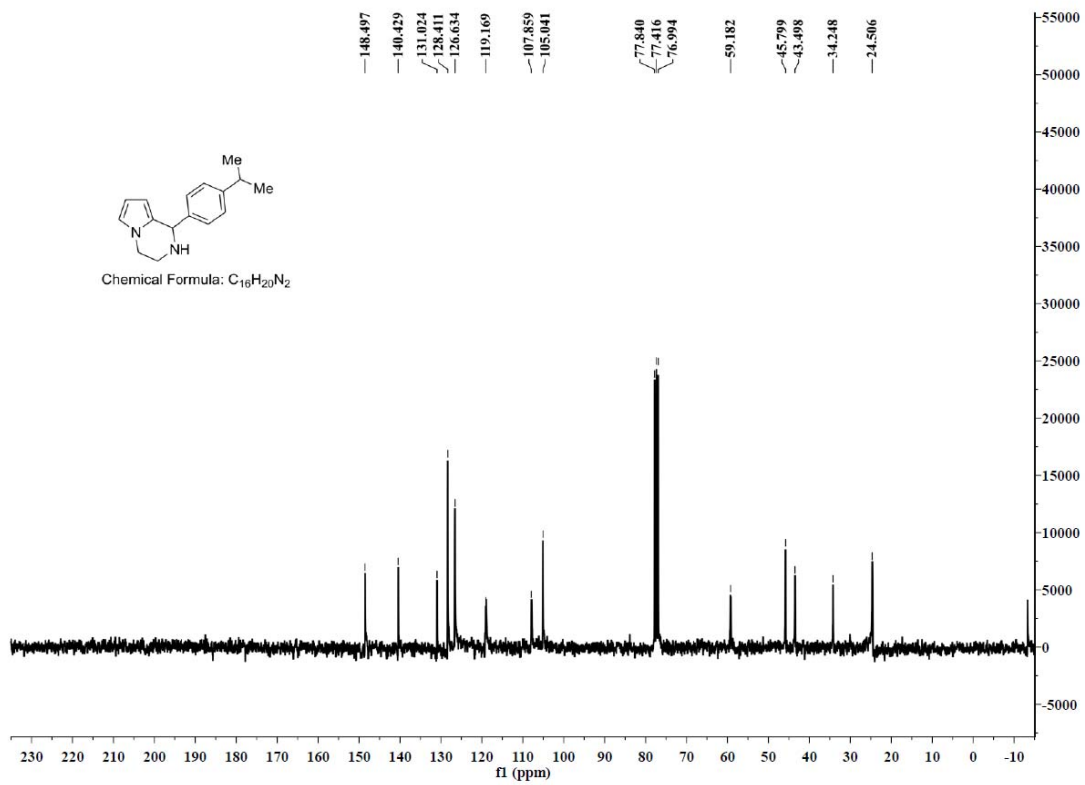
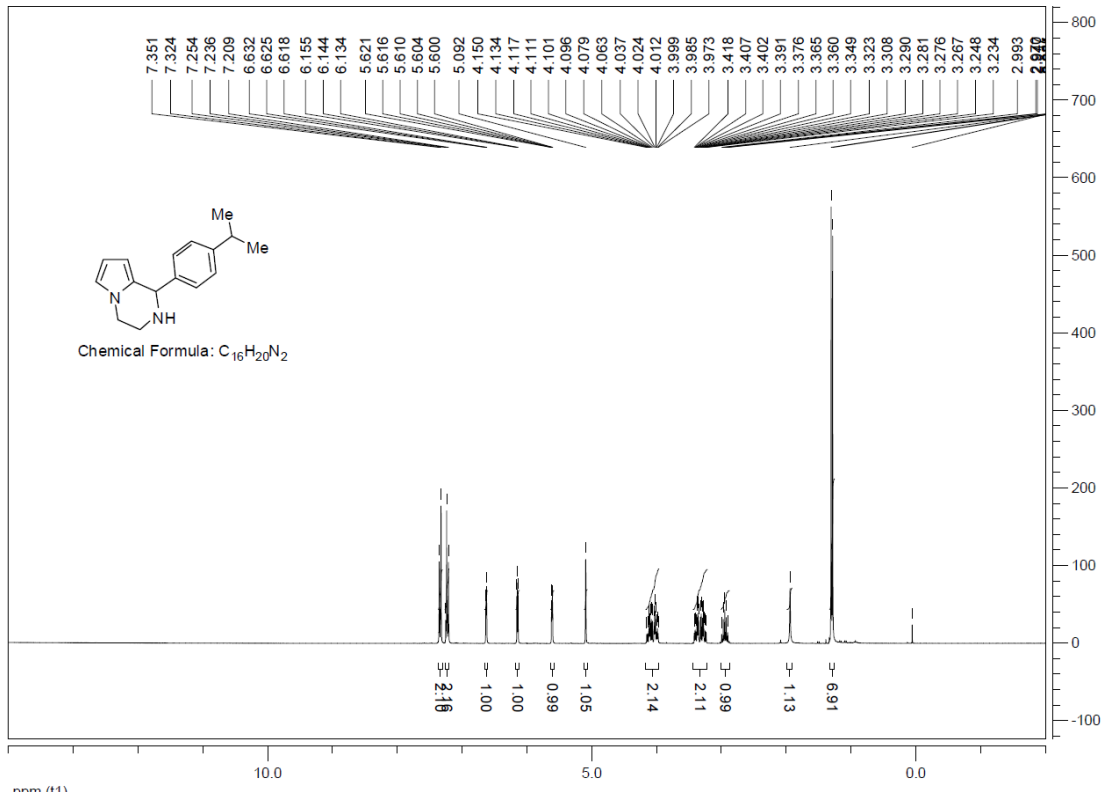
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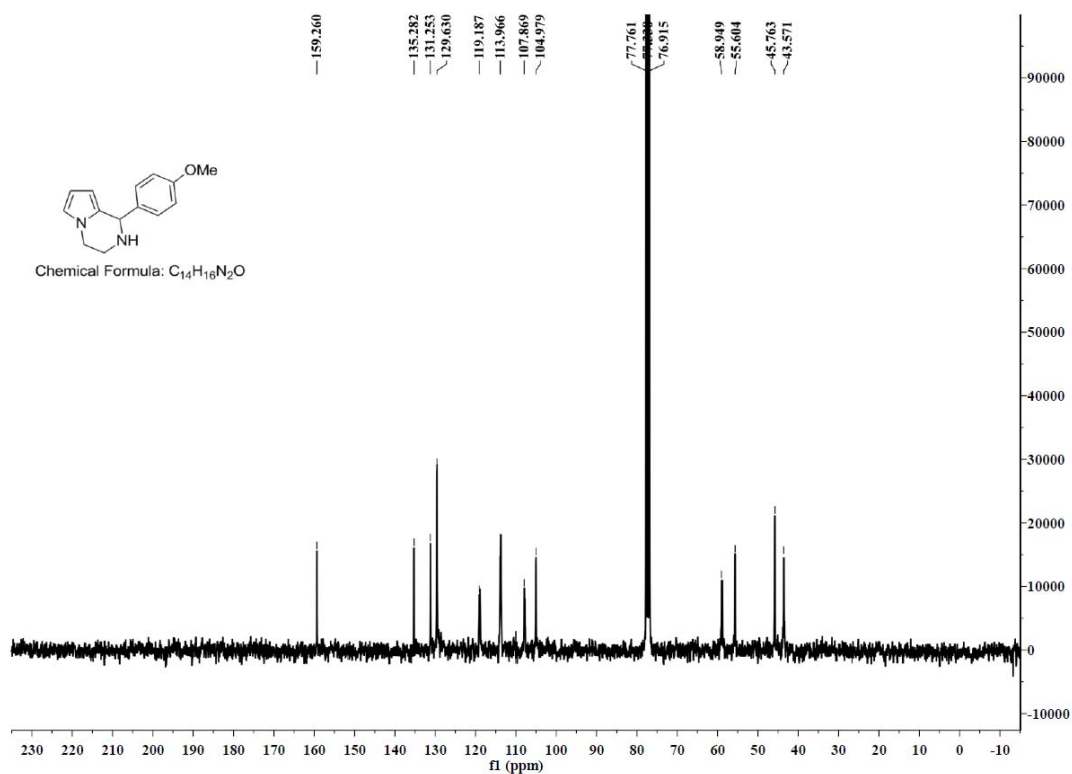
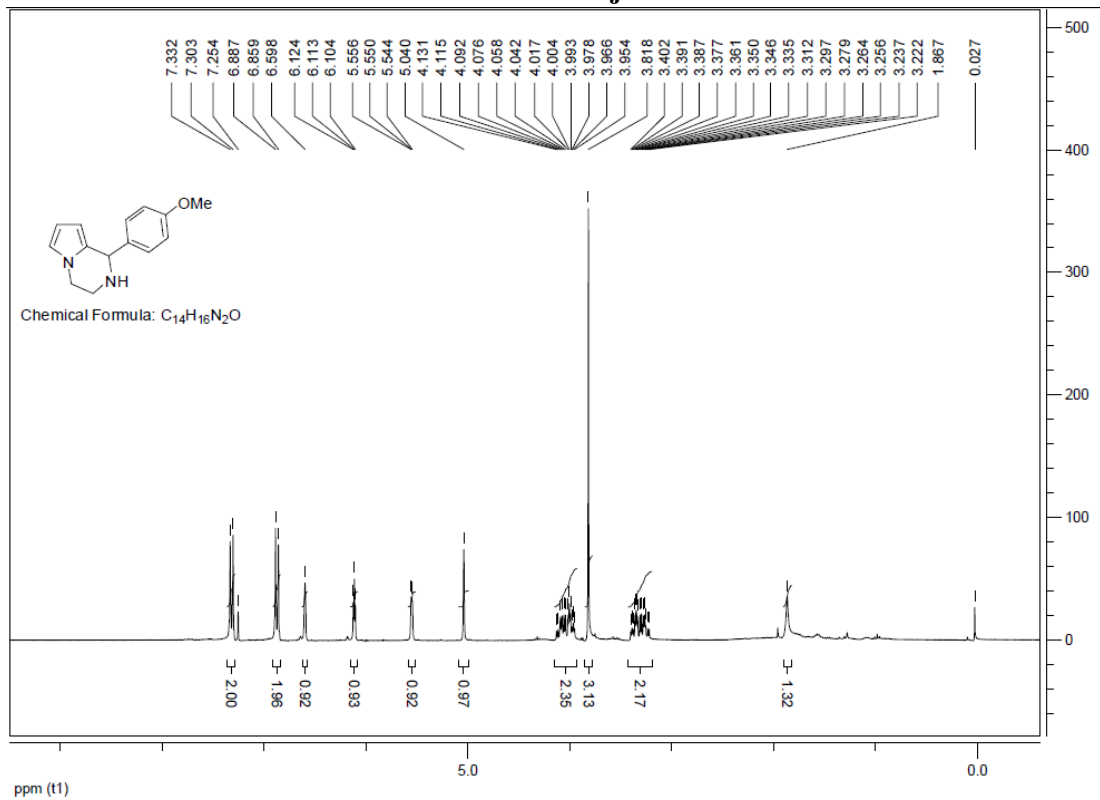
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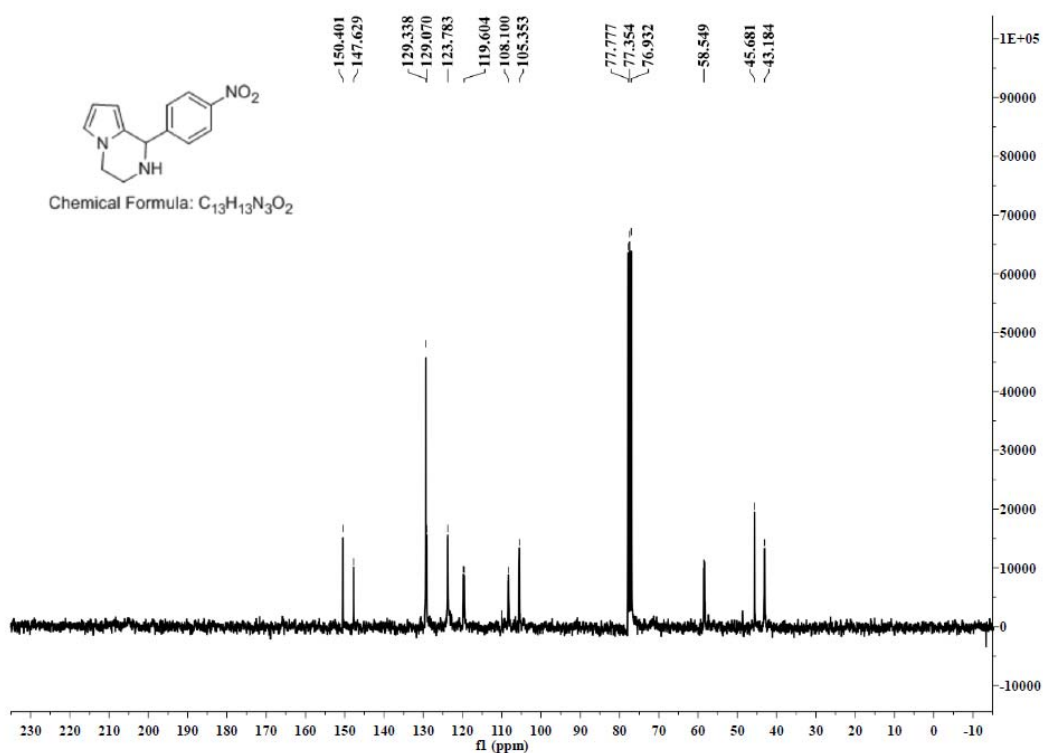
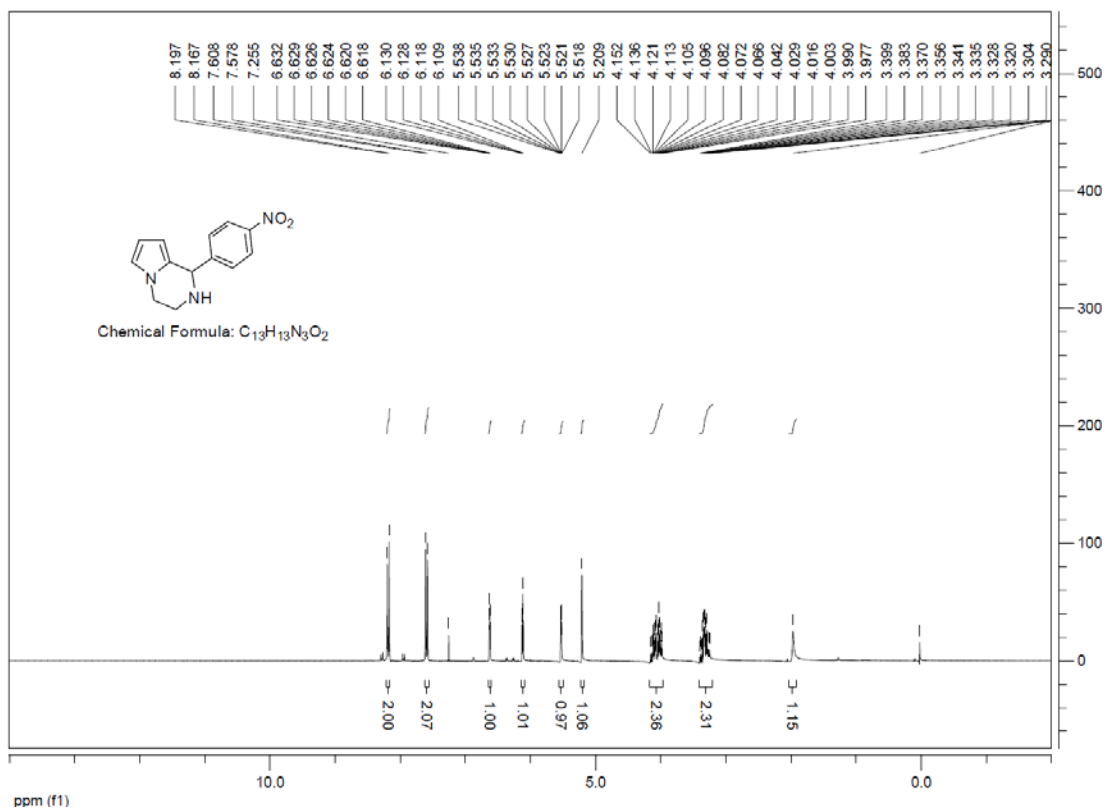
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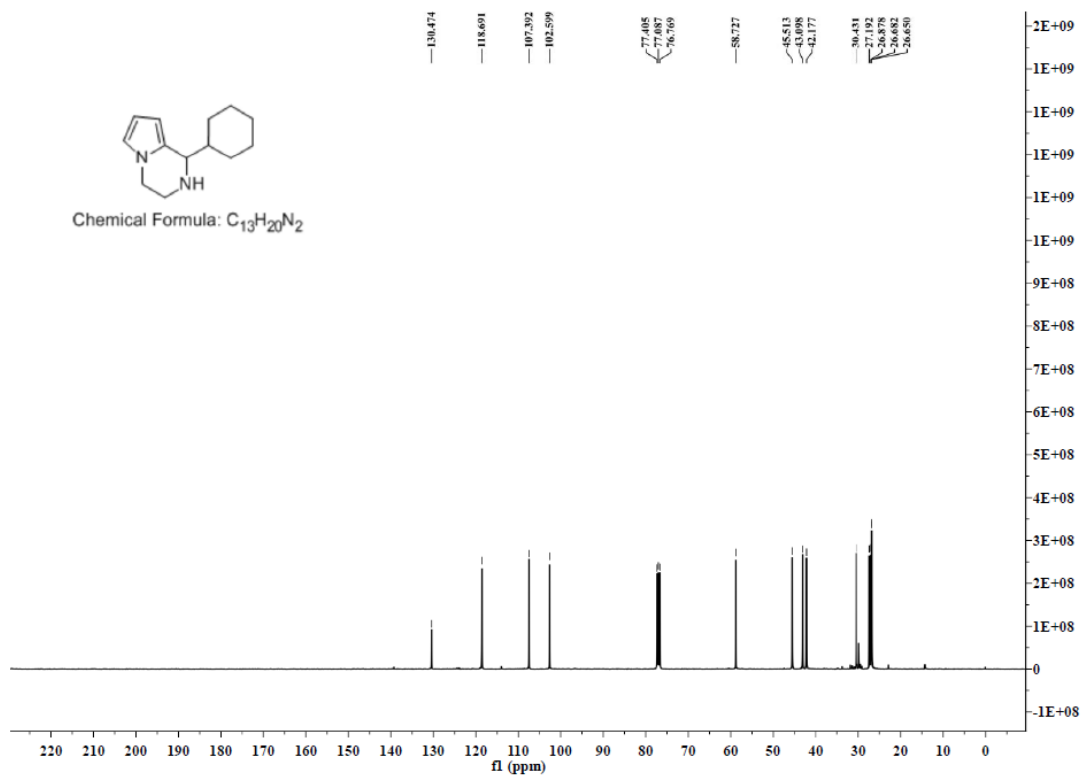
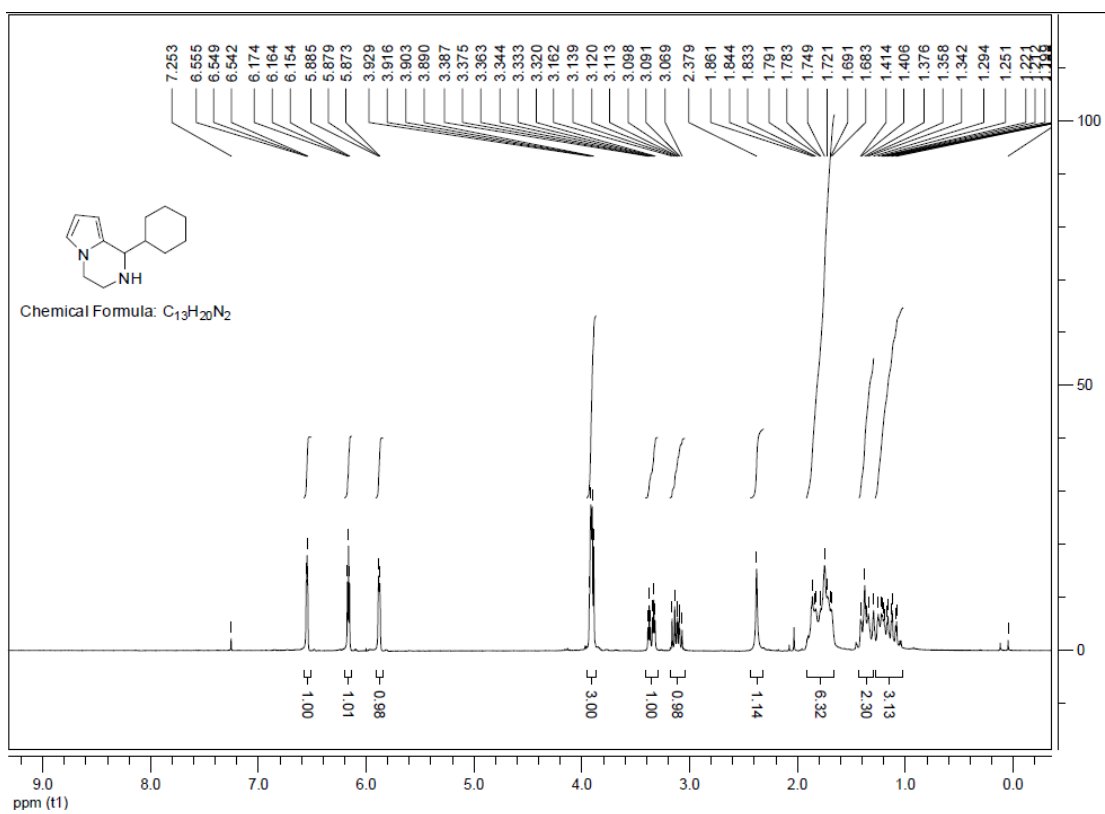
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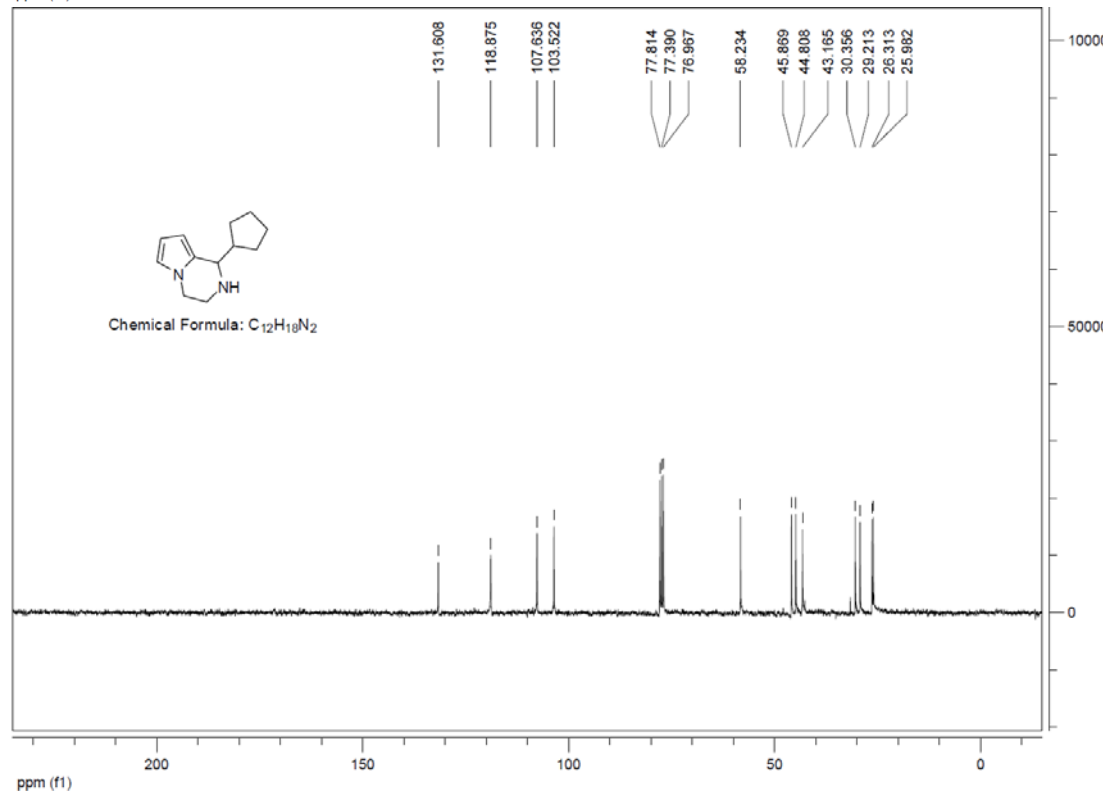
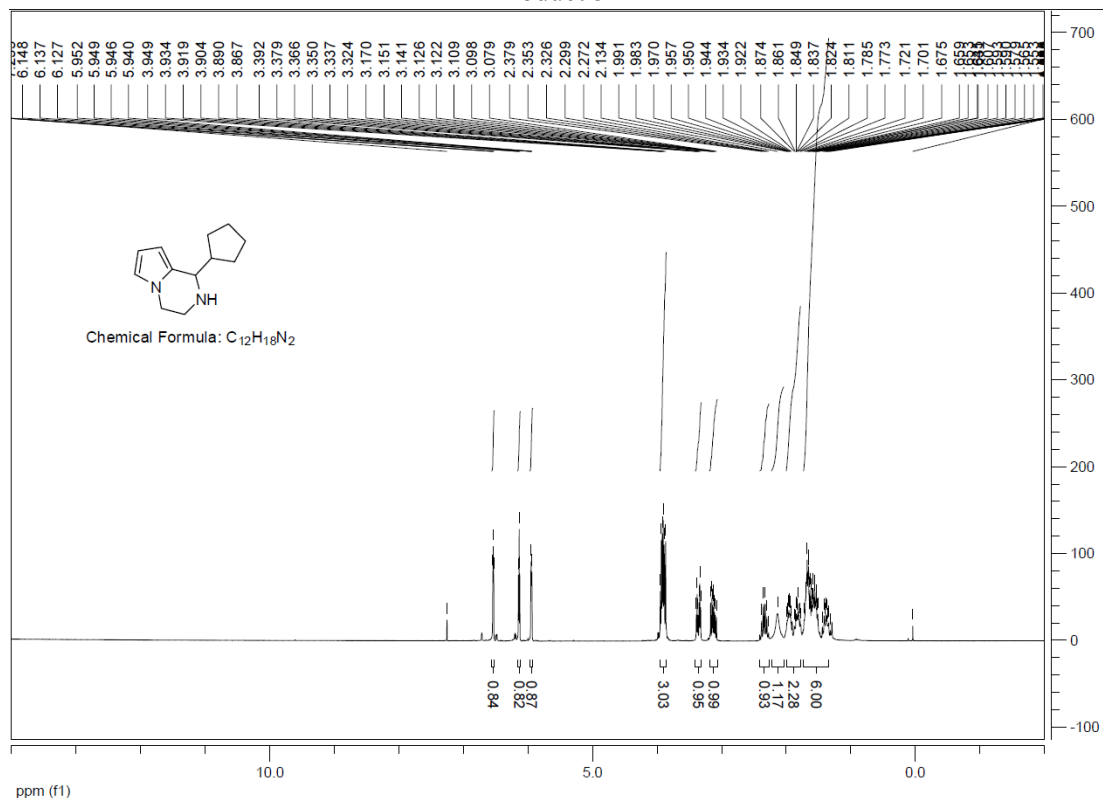
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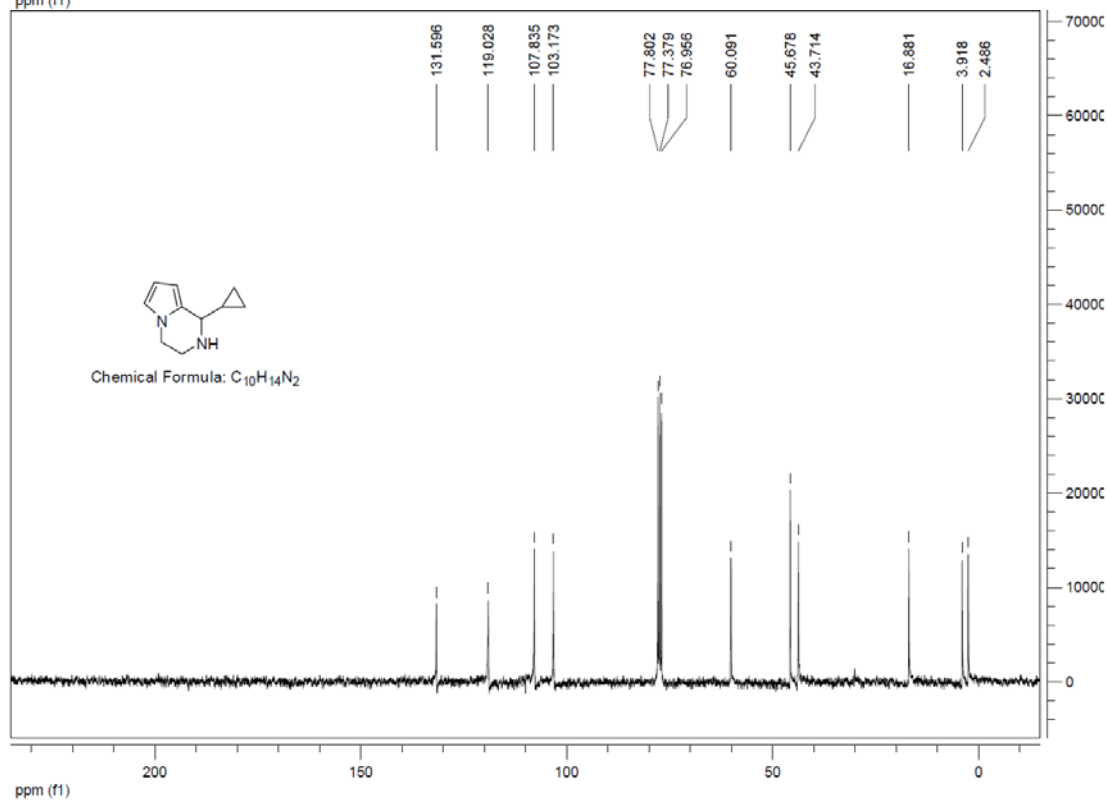
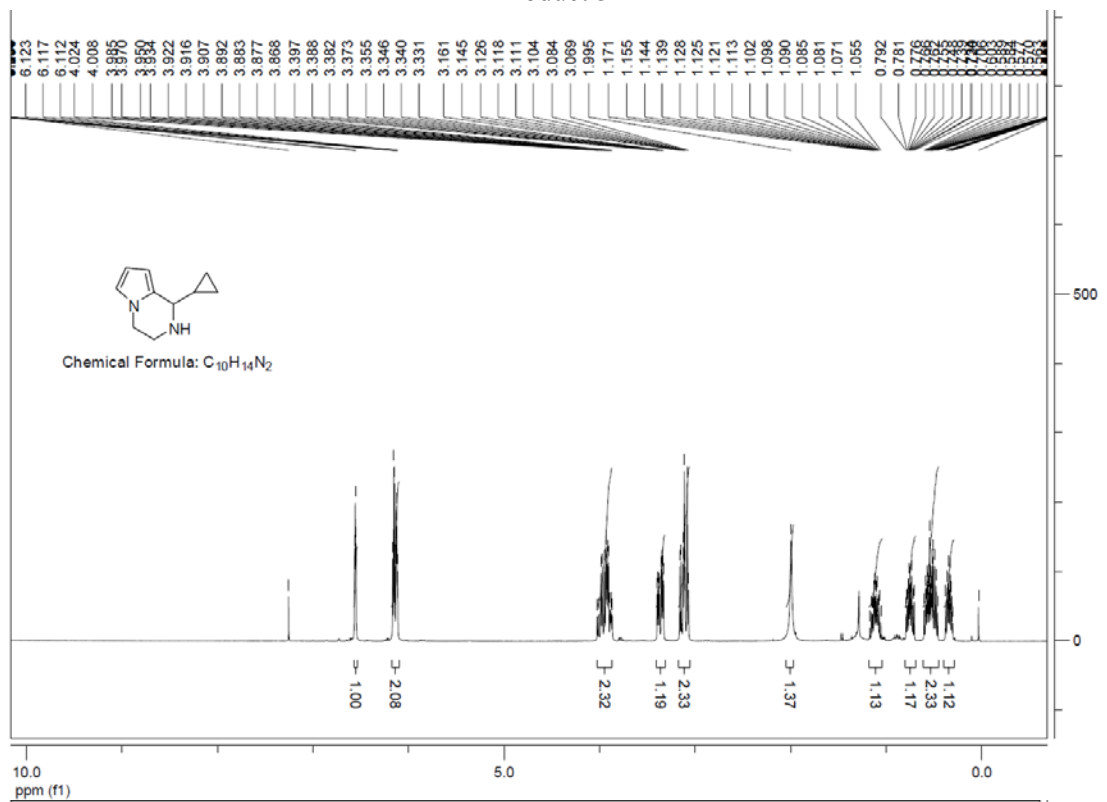
Product 31



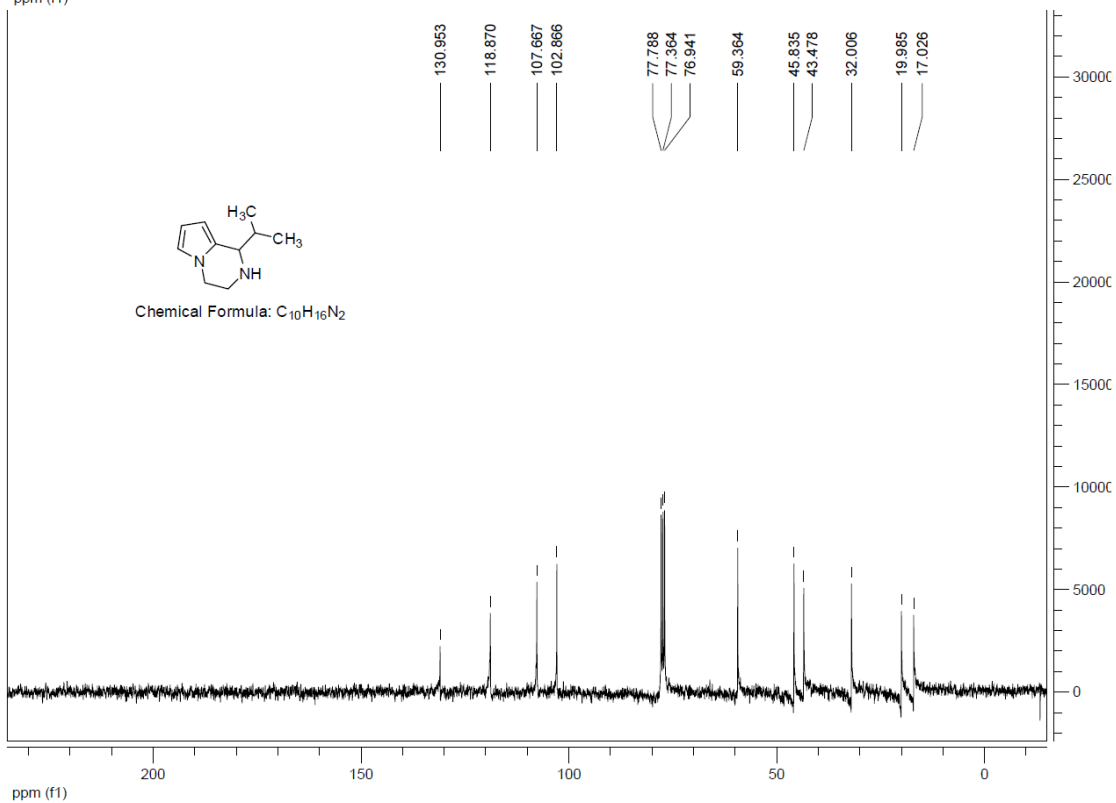
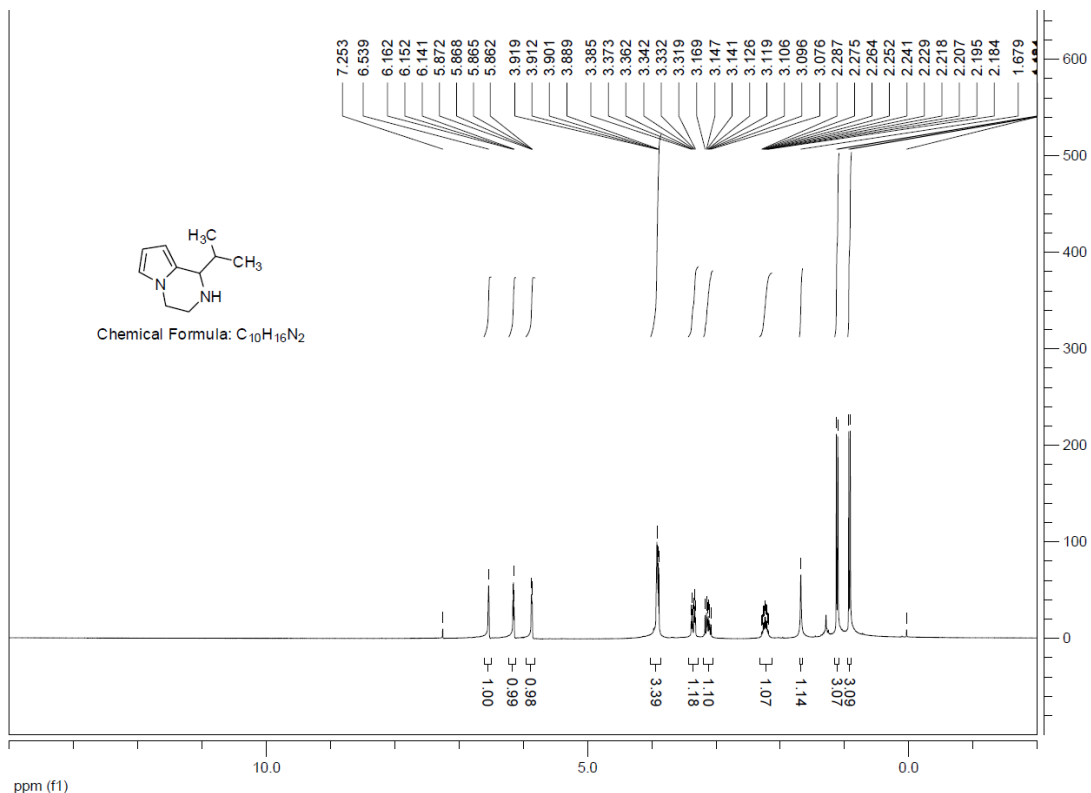
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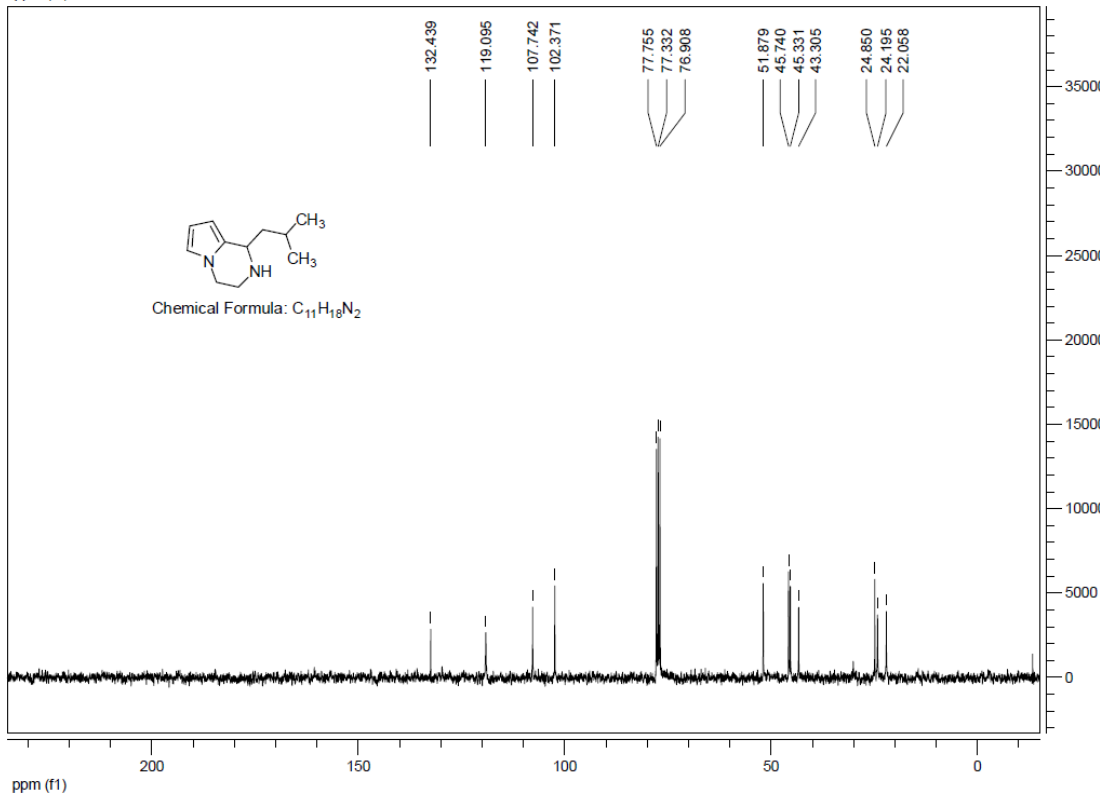
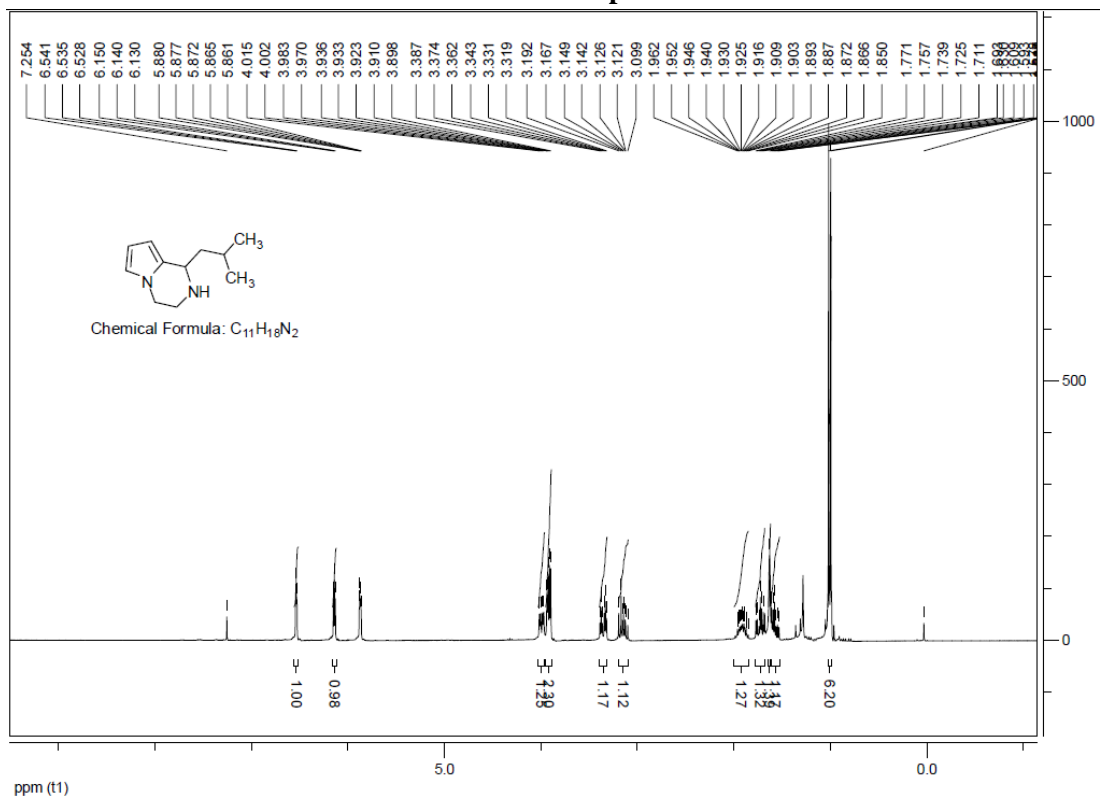
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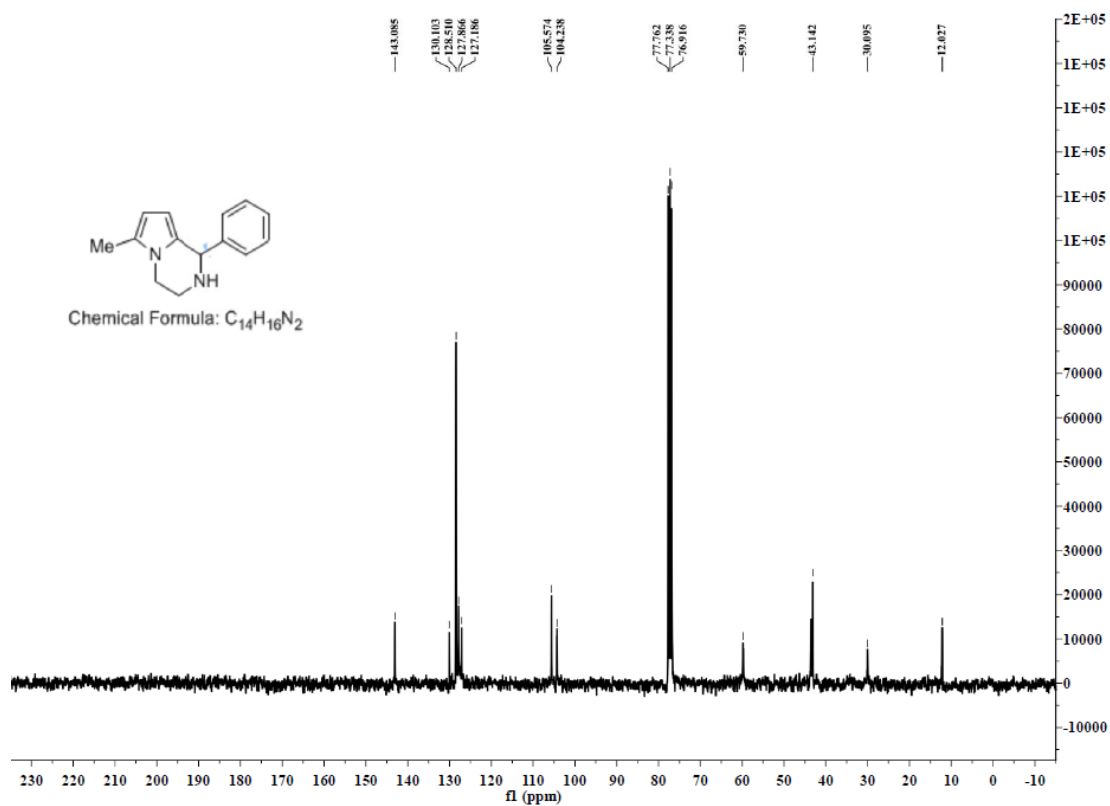
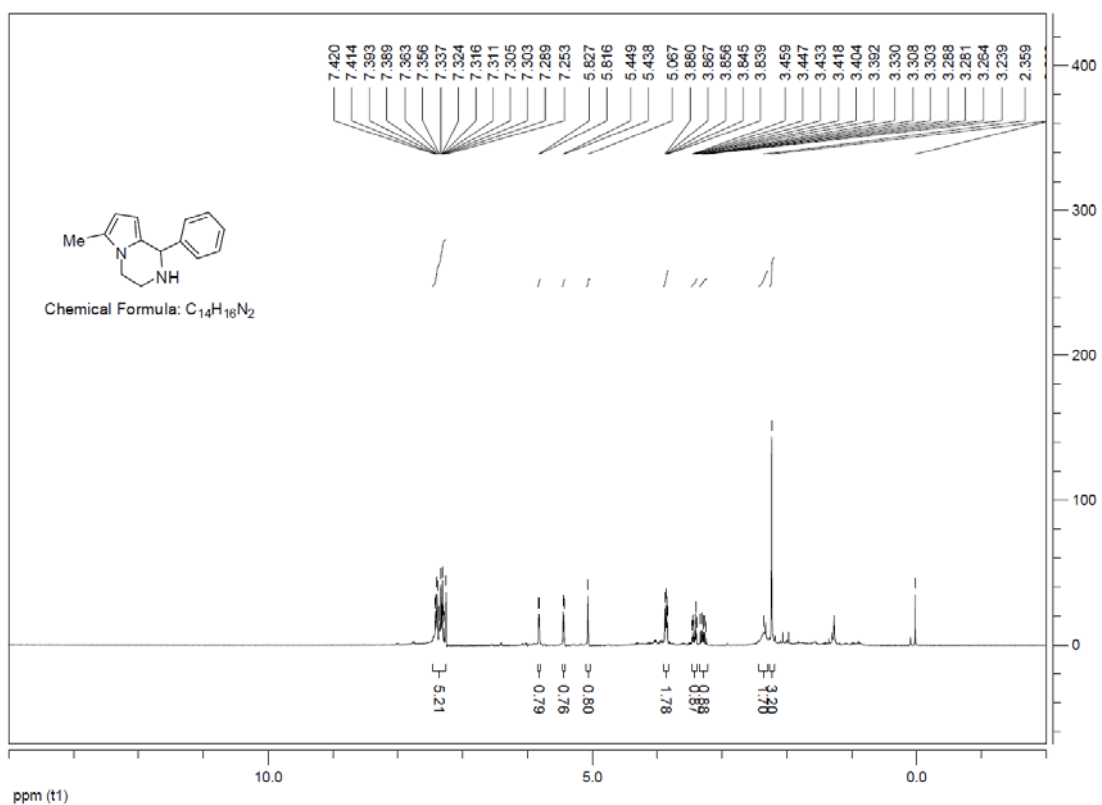
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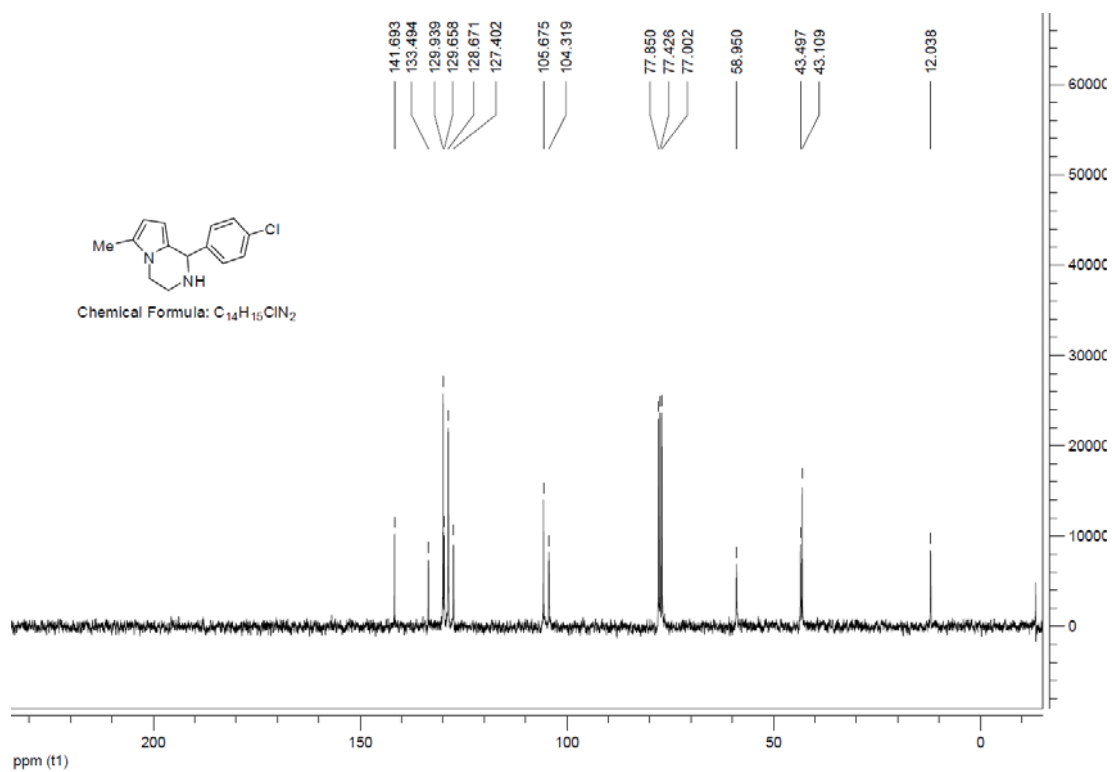
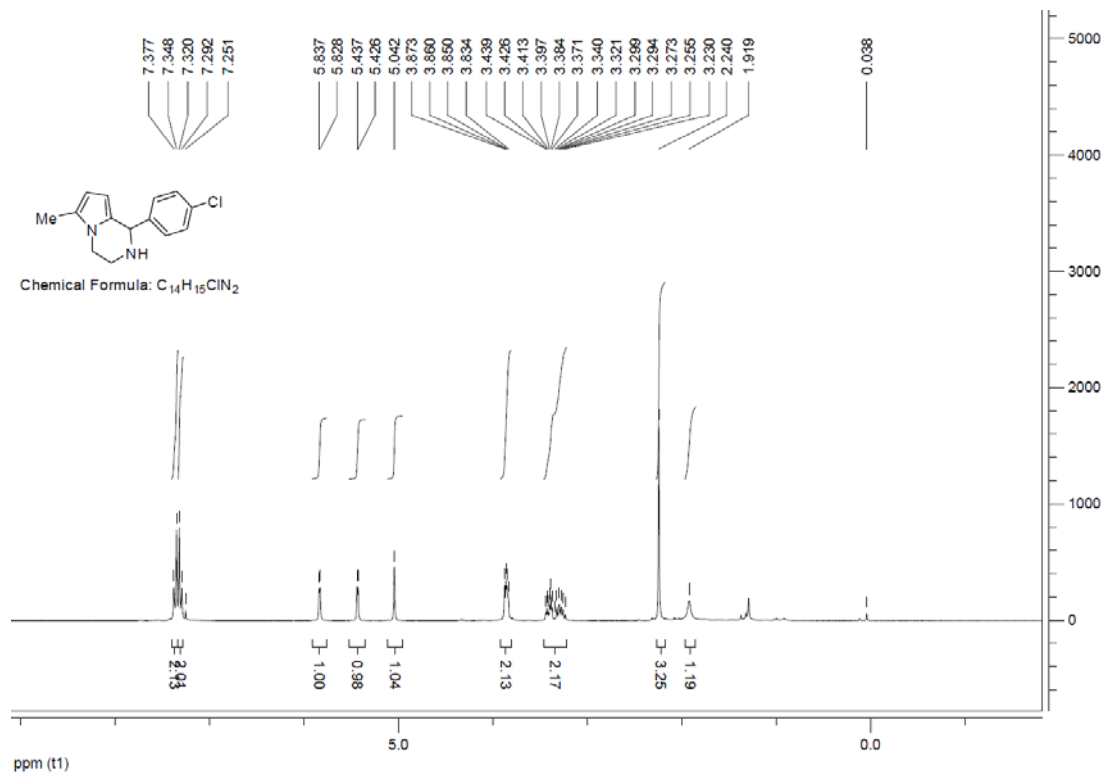
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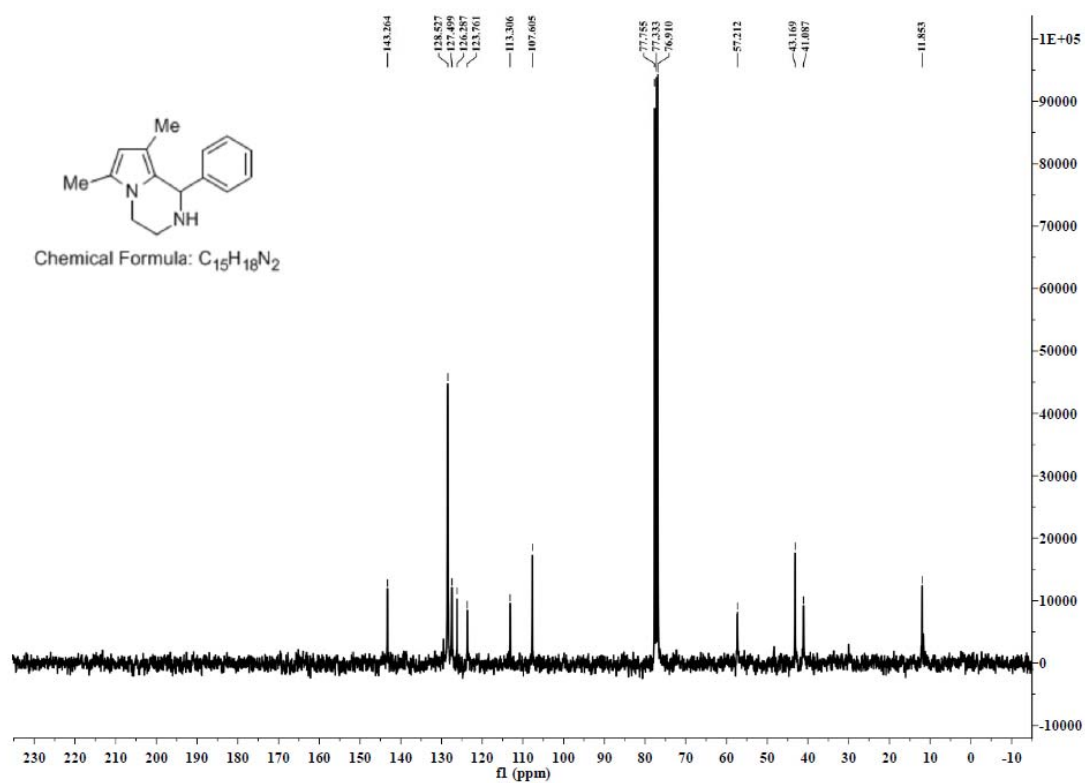
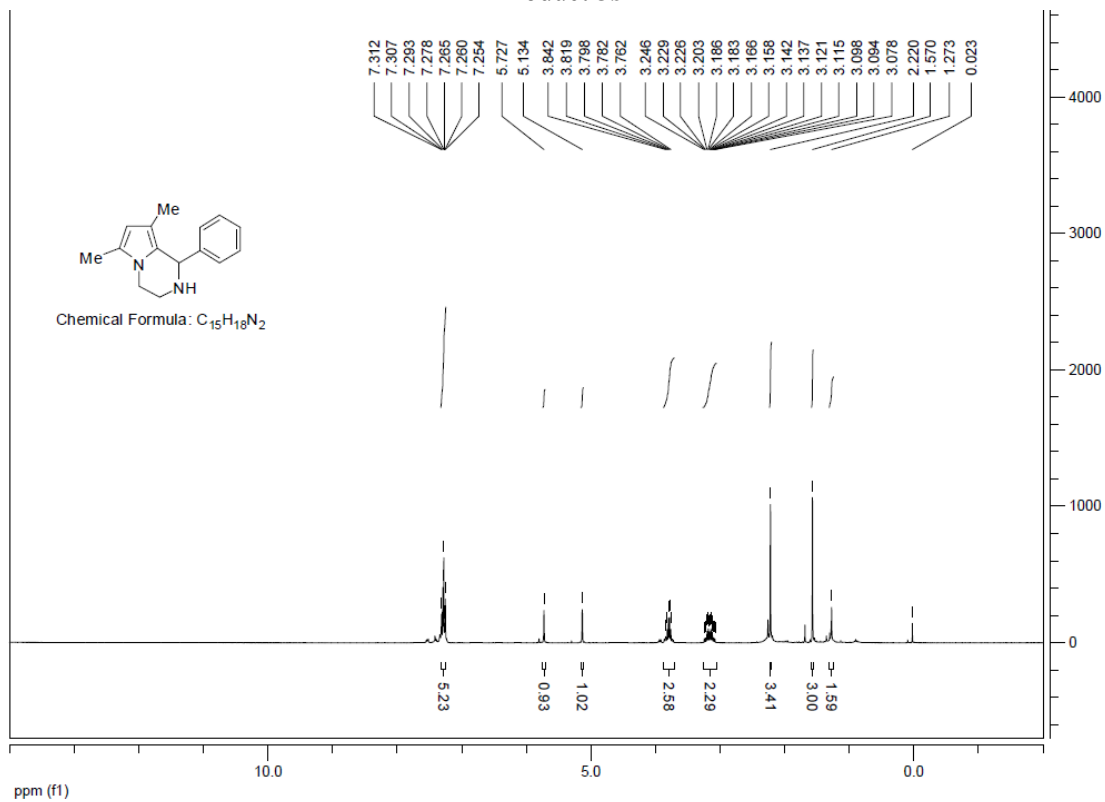
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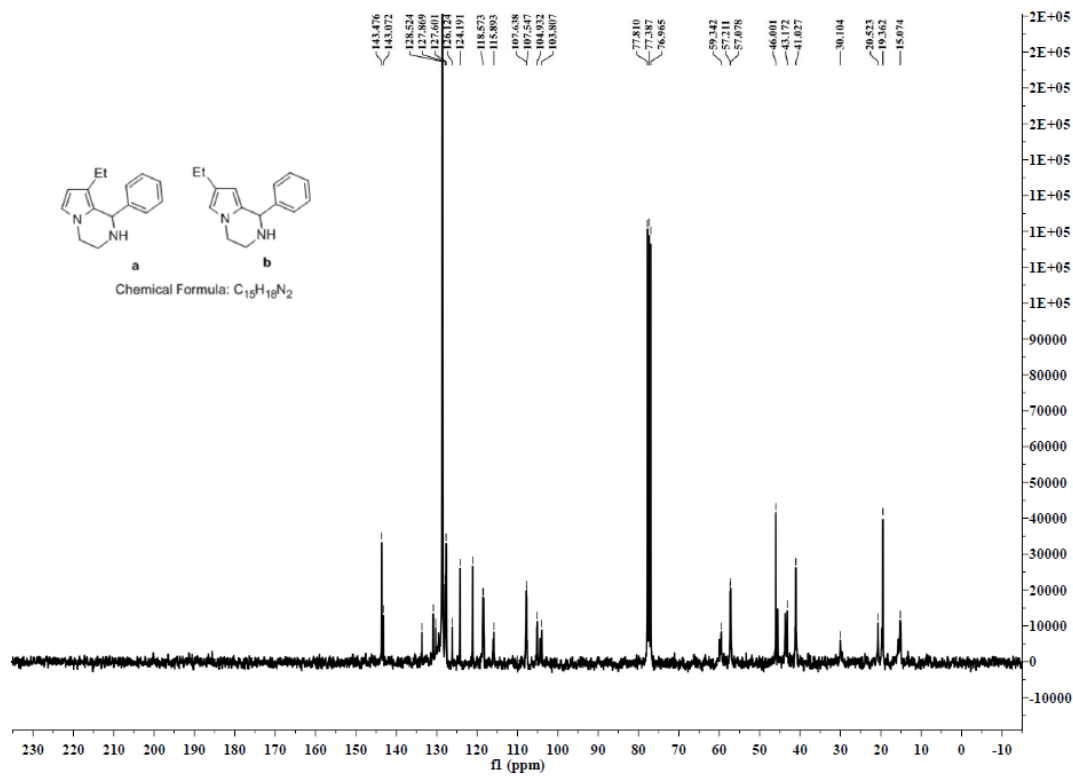
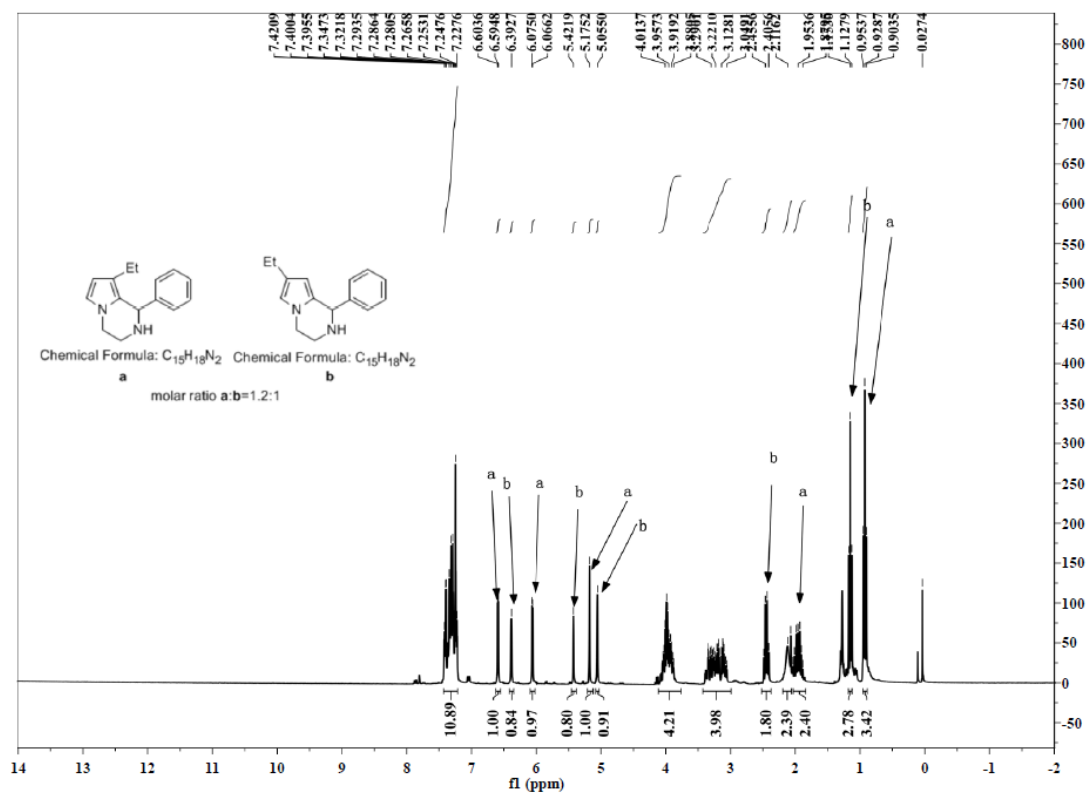
Product 3r



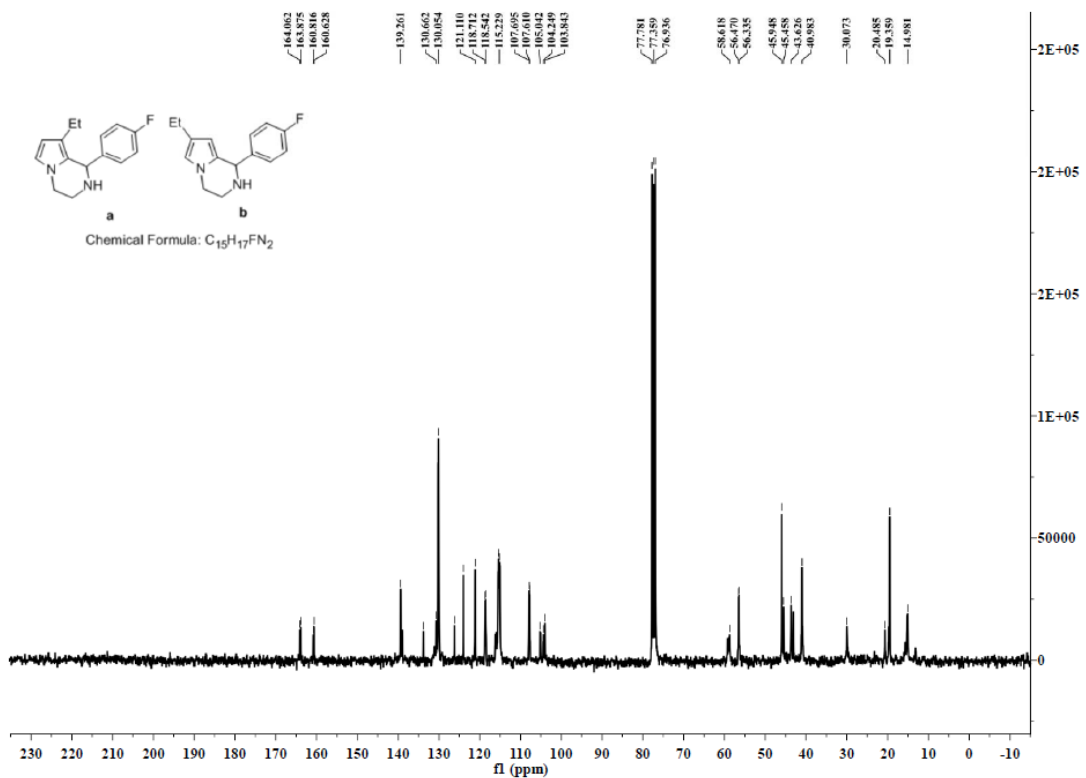
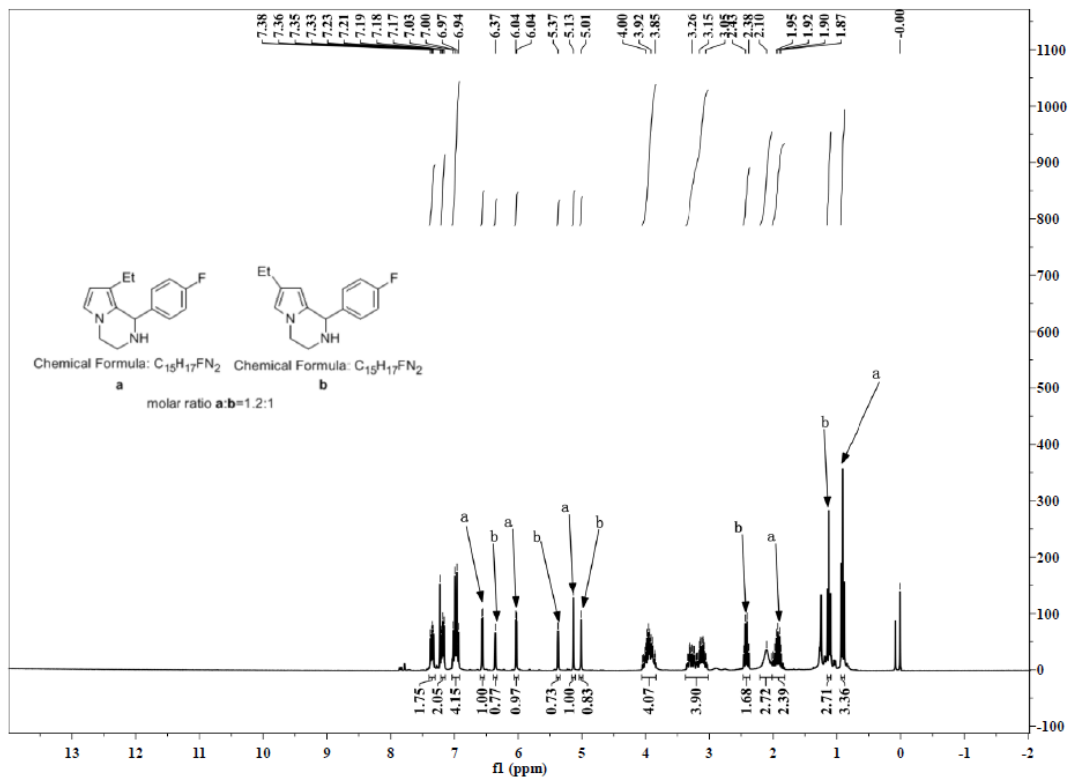
### Product 3s



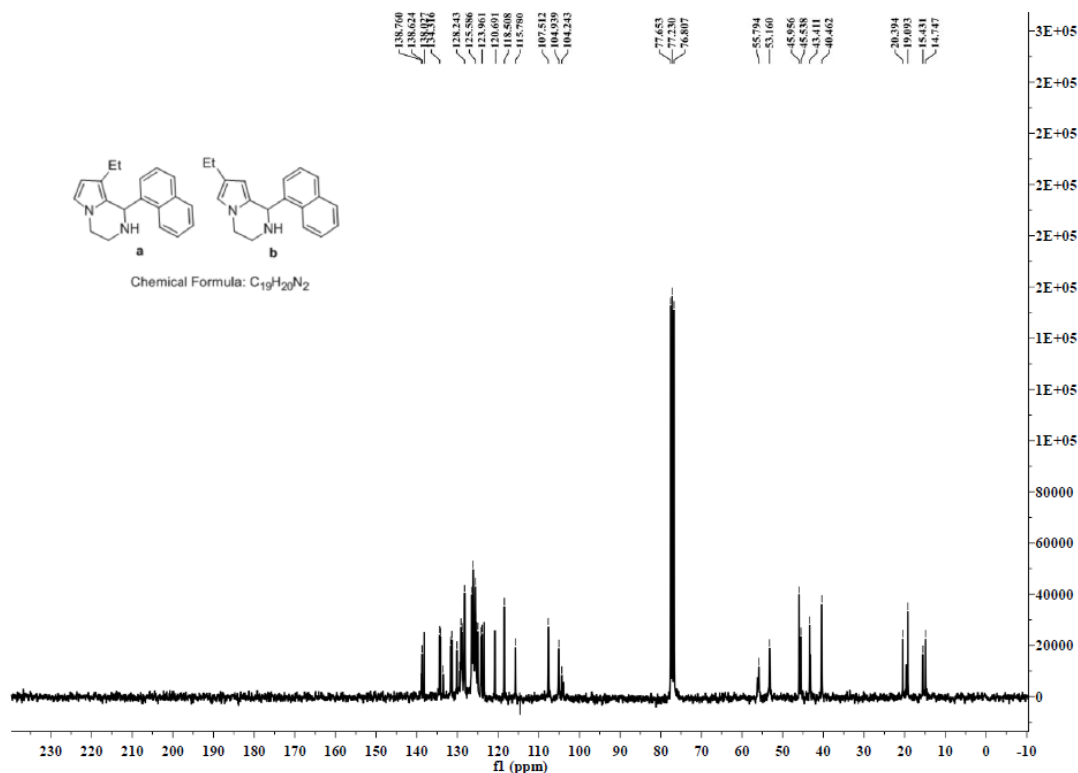
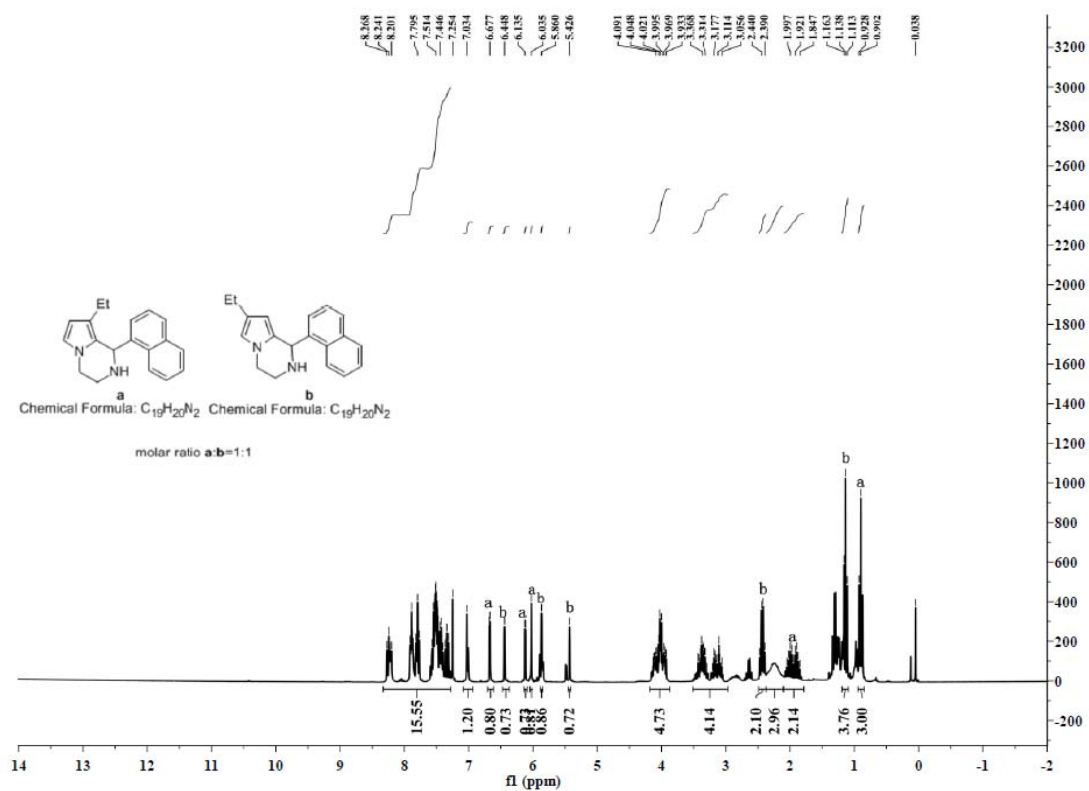
Product 3t



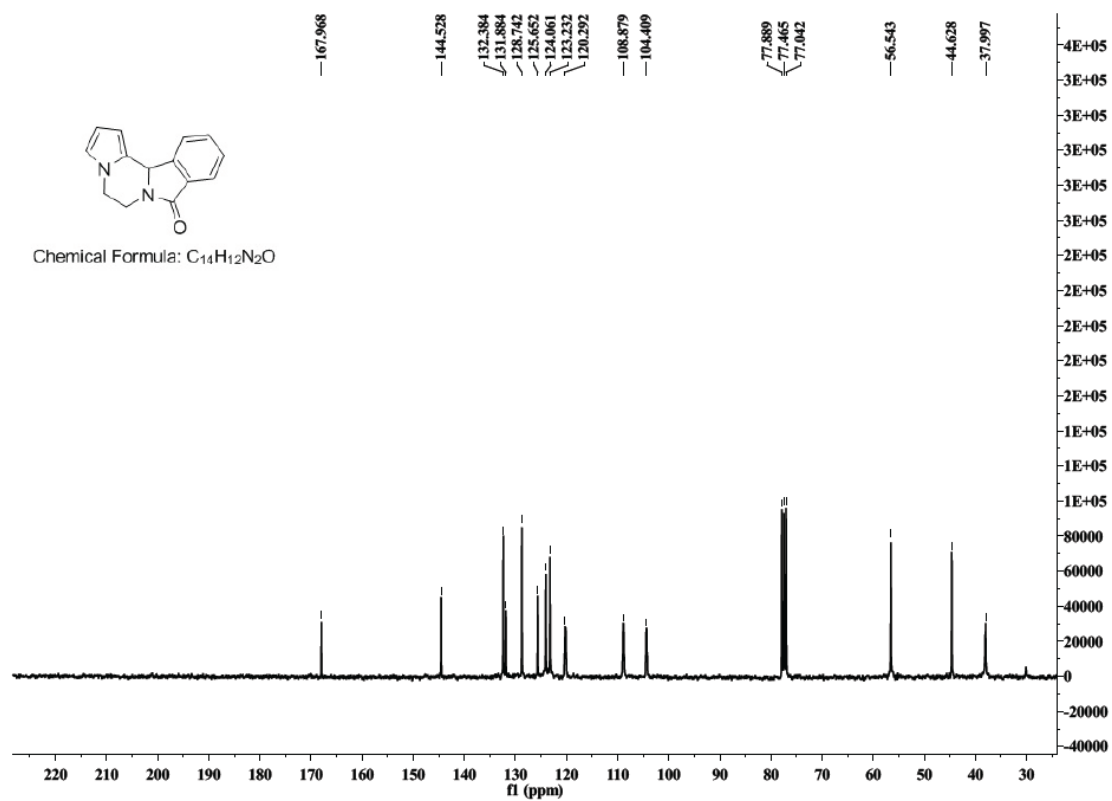
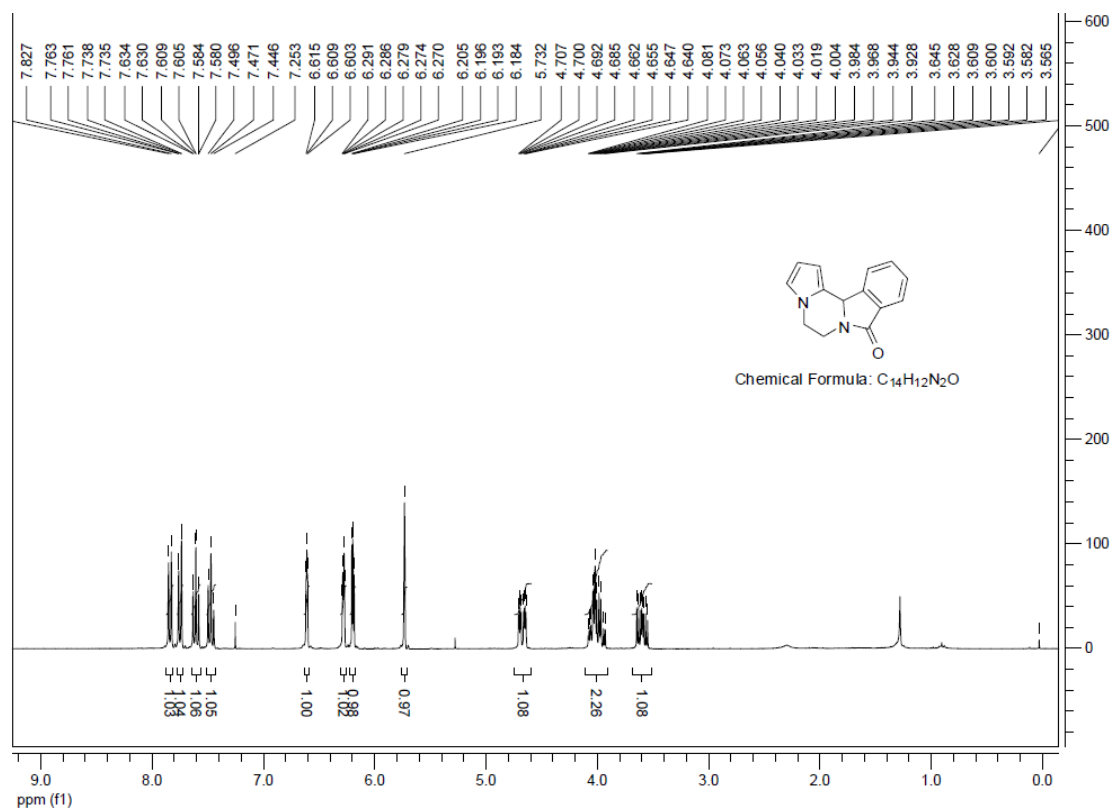
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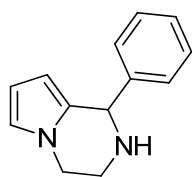


### Product 3v



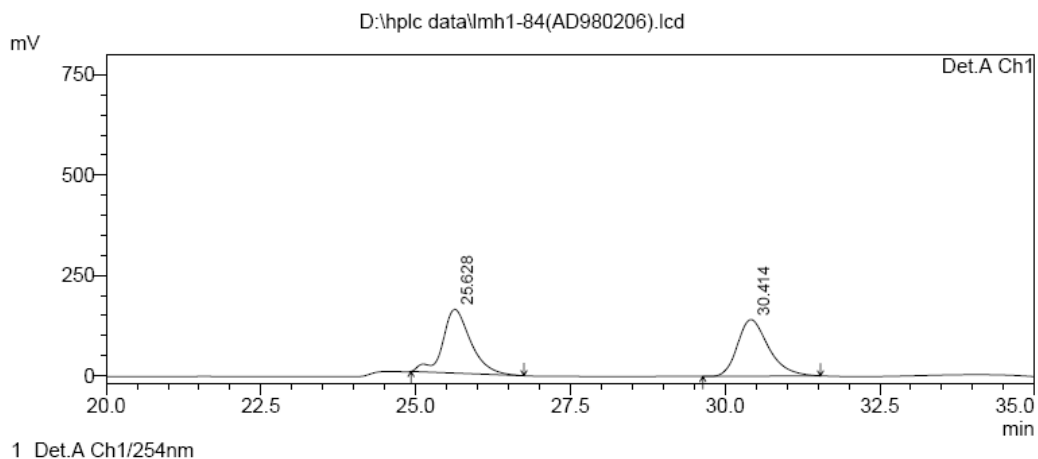
Product 3w





**3a** (the top one is racemic and bottom one is chiral)

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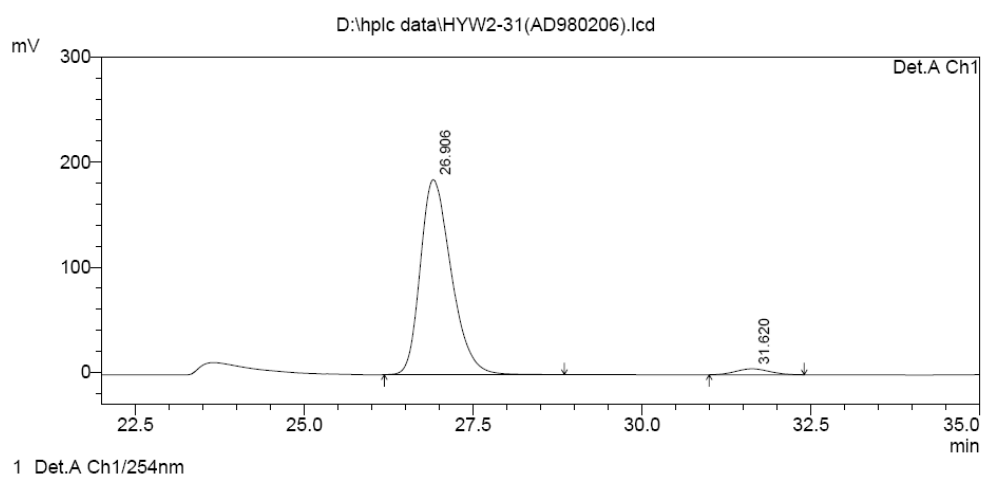


PeakTable

Detector A Ch1 254nm

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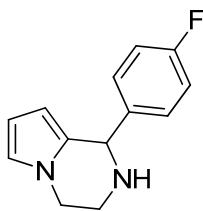
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PeakTable

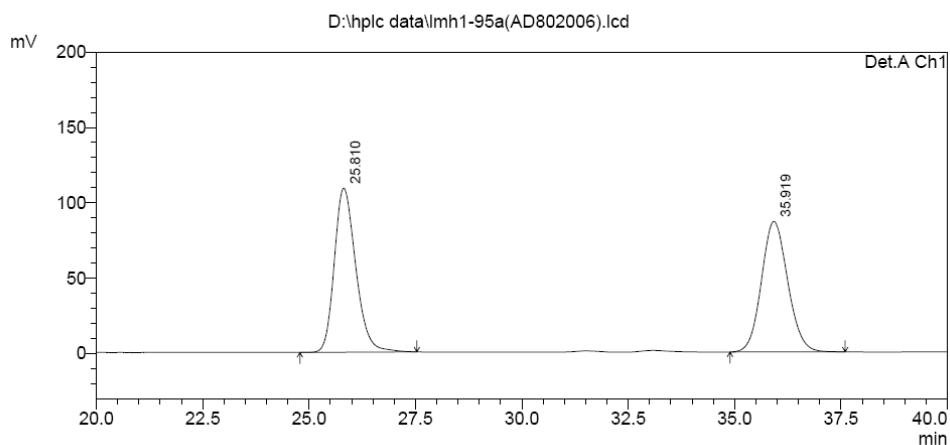
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.906	5915490	185540	96.822	97.060
2	31.620	194188	5620	3.178	2.940
Total		6109678	191161	100.000	100.000



**3b** (the top one is racemic and bottom one is chiral)

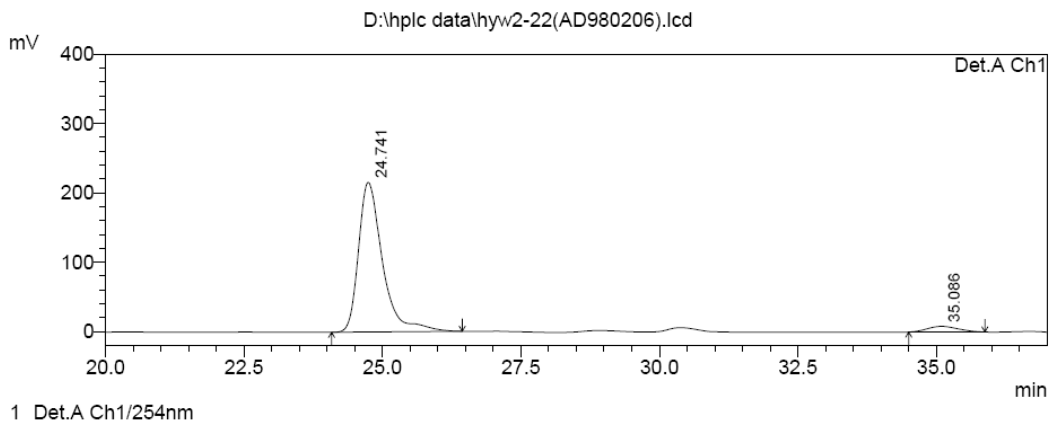
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PeakTable

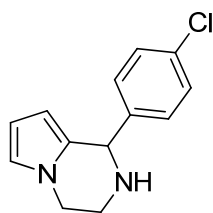
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.810	3822790	108972	50.681	55.714
2	35.919	3720030	86620	49.319	44.286
Total		7542821	195592	100.000	100.000

<Chromatogram>



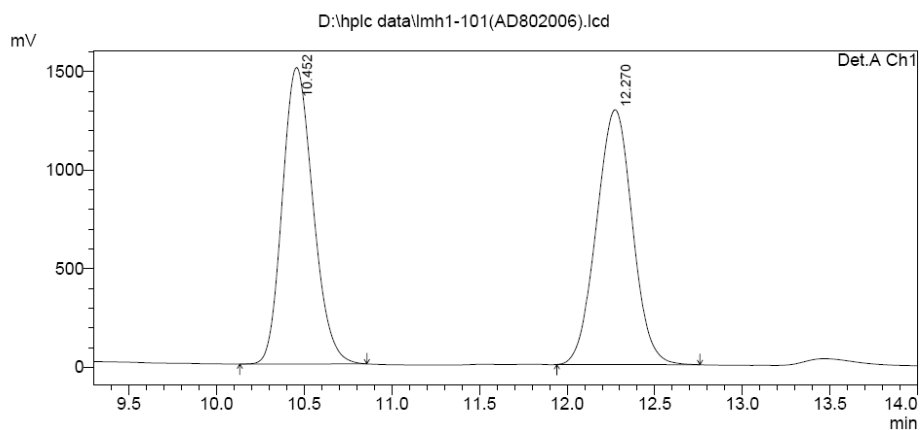
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.741	6512855	215903	95.445	96.377
2	35.086	310828	8115	4.555	3.623
Total		6823683	224018	100.000	100.000



3c (the top one is racemic and bottom one is chiral)

<Chromatogram>

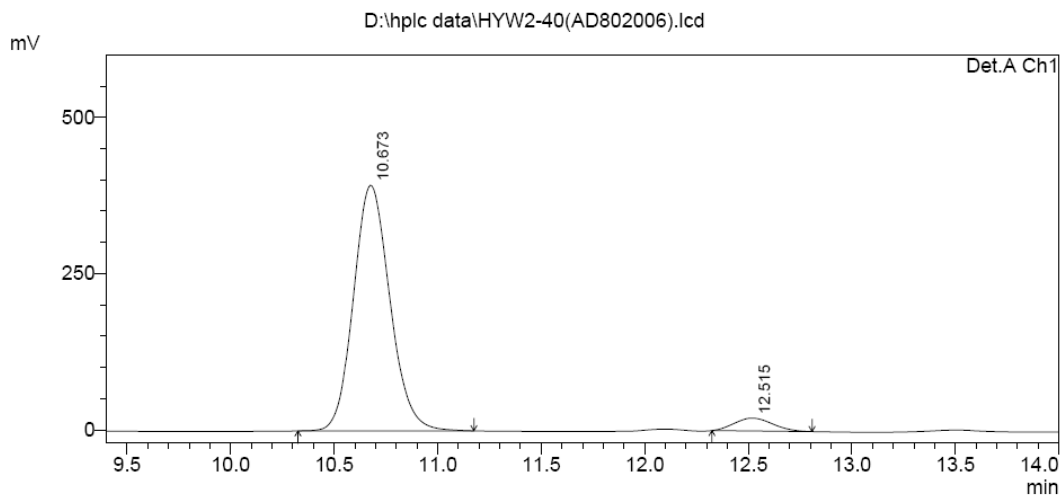


1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.452	18327387	1503685	49.796	53.778
2	12.270	18477560	1292391	50.204	46.222
Total		36804947	2796077	100.000	100.000

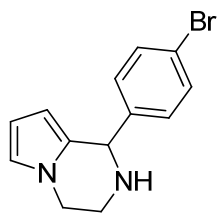
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1 Det.A Ch1/254nm

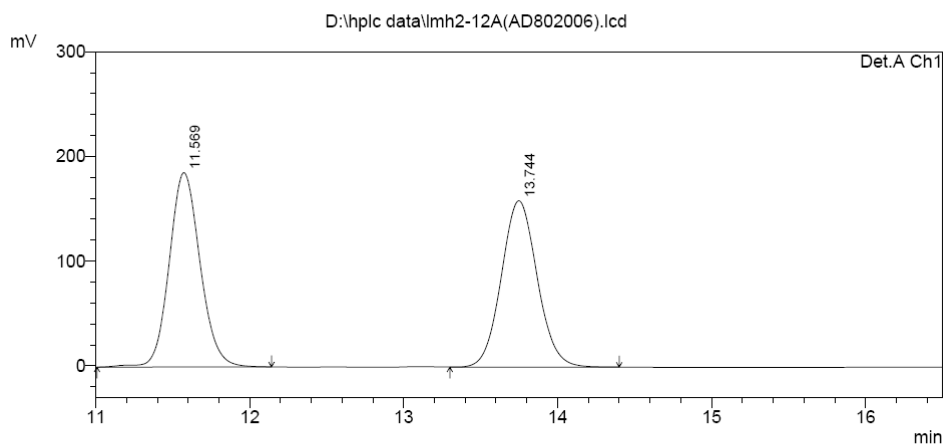
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.673	4809777	392928	94.803	95.041
2	12.515	263661	20501	5.197	4.959
Total		5073438	413430	100.000	100.000



**3d** (The top one is racemic and bottom one is chiral)

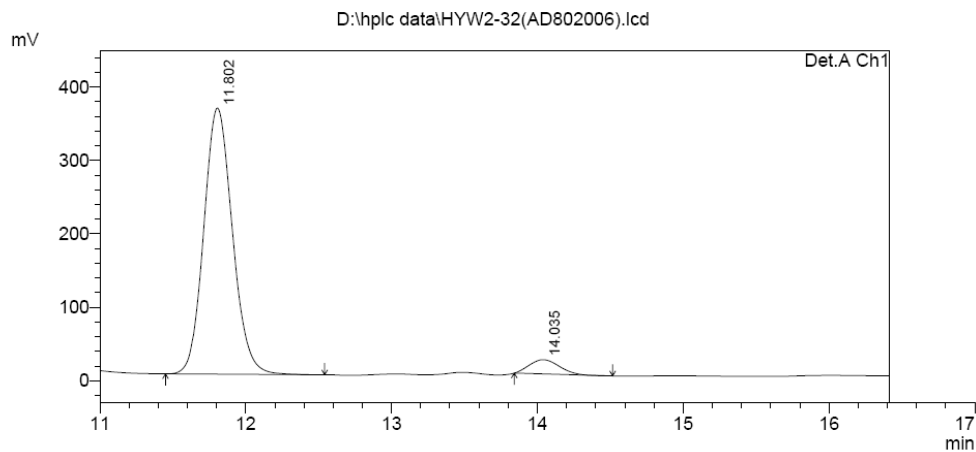
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PeakTable

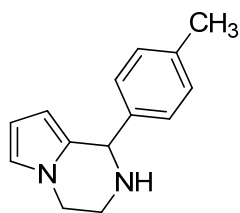
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.569	2597251	185695	50.243	53.898
2	13.744	2572081	158835	49.757	46.102
Total		5169332	344530	100.000	100.000

<Chromatogram>



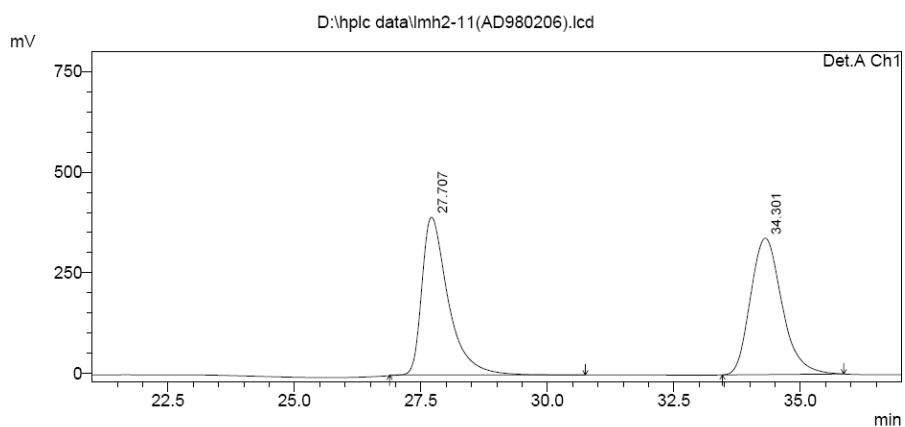
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.802	4943756	362365	94.757	94.935
2	14.035	273560	19332	5.243	5.065
Total		5217316	381698	100.000	100.000



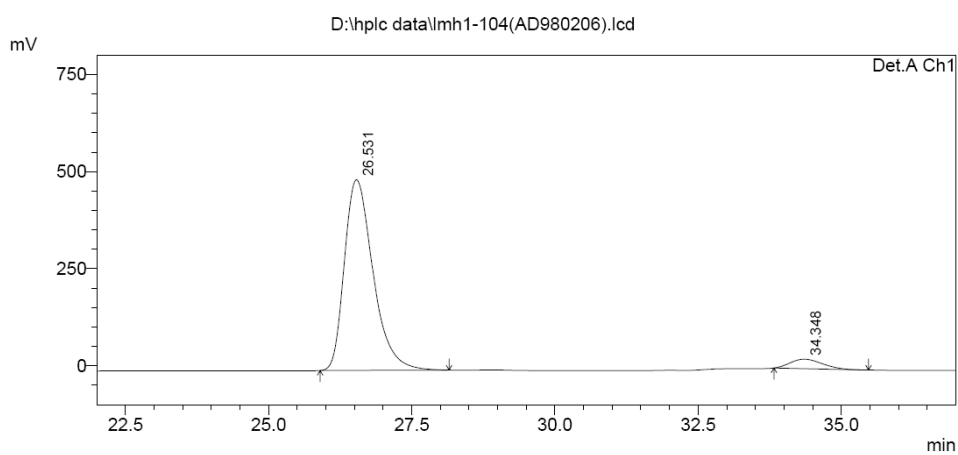
**3e** (The top one is racemic and bottom one is chiral)

<Chromatogram>



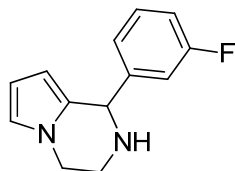
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.707	14215071	392202	49.263	53.638
2	34.301	14640460	338993	50.737	46.362
Total		28855532	731195	100.000	100.000



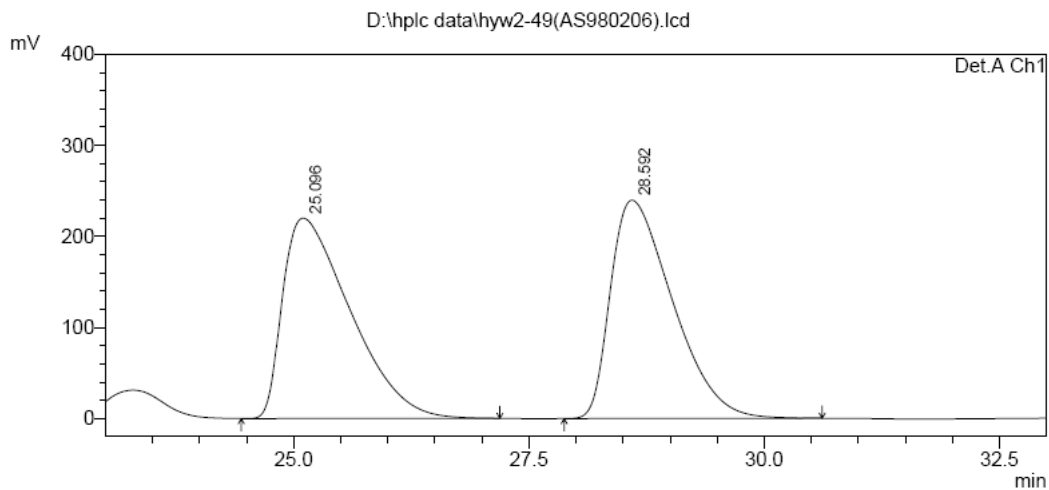
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.531	17103436	490865	94.737	95.273
2	34.348	950225	24354	5.263	4.727
Total		18053661	515219	100.000	100.000



**3f** (The top one is racemic and bottom one is chiral)

<Chromatogram>

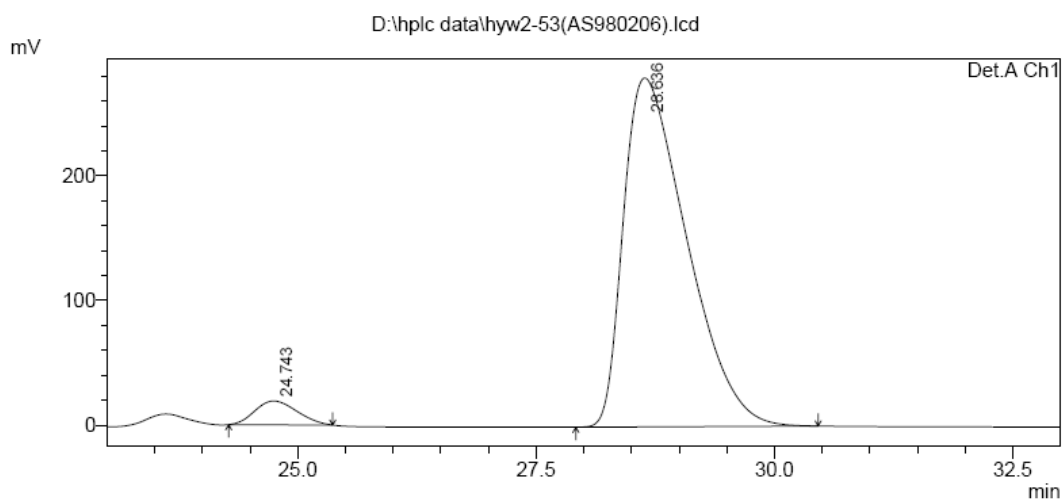


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.096	11002866	220040	50.005	47.855
2	28.592	11000661	239762	49.995	52.145
Total		22003527	459802	100.000	100.000

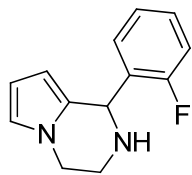
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PeakTable

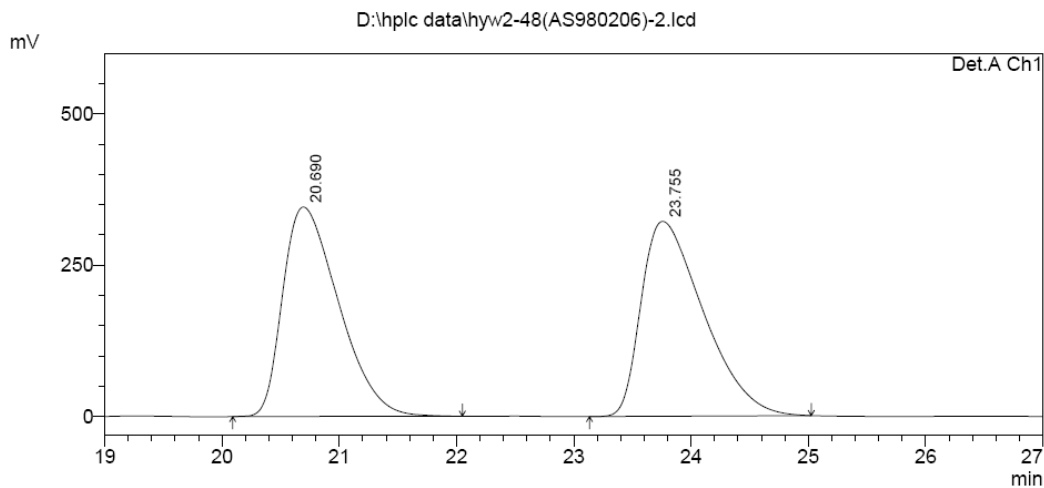
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.743	587599	19133	4.350	6.401
2	28.636	12921797	279787	95.650	93.599
Total		13509396	298920	100.000	100.000



**3g** (The top one is racemic and bottom one is chiral)

<Chromatogram>

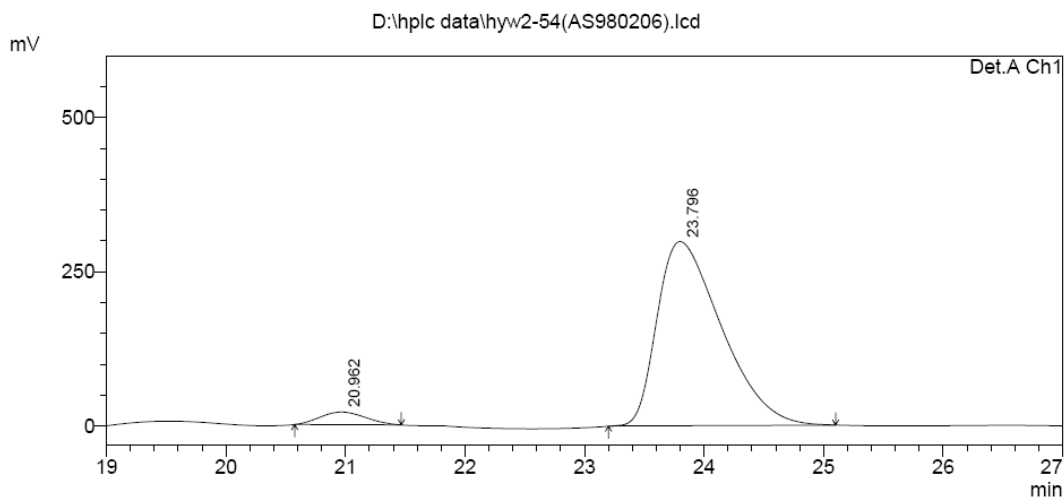


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.690	11464896	345988	49.123	51.792
2	23.755	11874432	322039	50.877	48.208
Total		23339328	668026	100.000	100.000

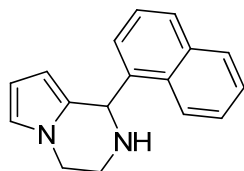
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PeakTable

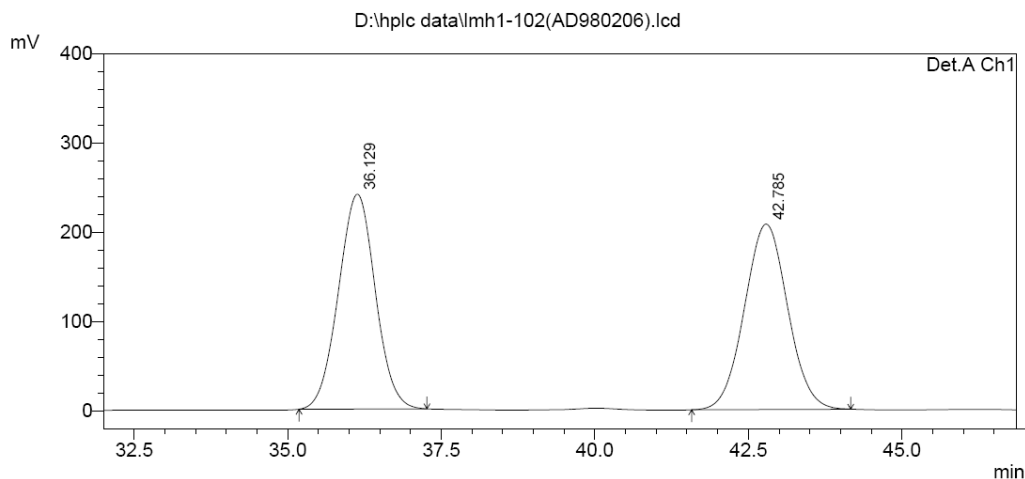
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.962	542074	20499	4.627	6.429
2	23.796	11172459	298371	95.373	93.571
Total		11714533	318870	100.000	100.000



**3h** (The top one is racemic and bottom one is chiral)

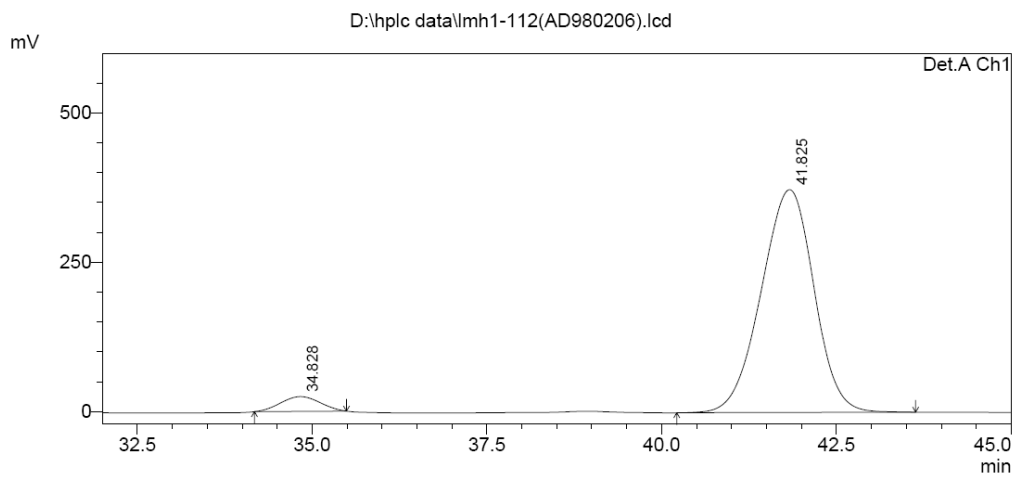
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PeakTable

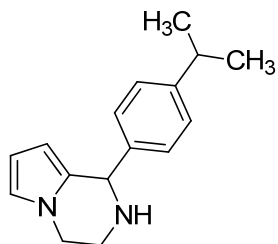
Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.129	10060227	240535	49.719	53.662
2	42.785	10174134	207707	50.281	46.338
Total		20234361	448243	100.000	100.000

<Chromatogram>



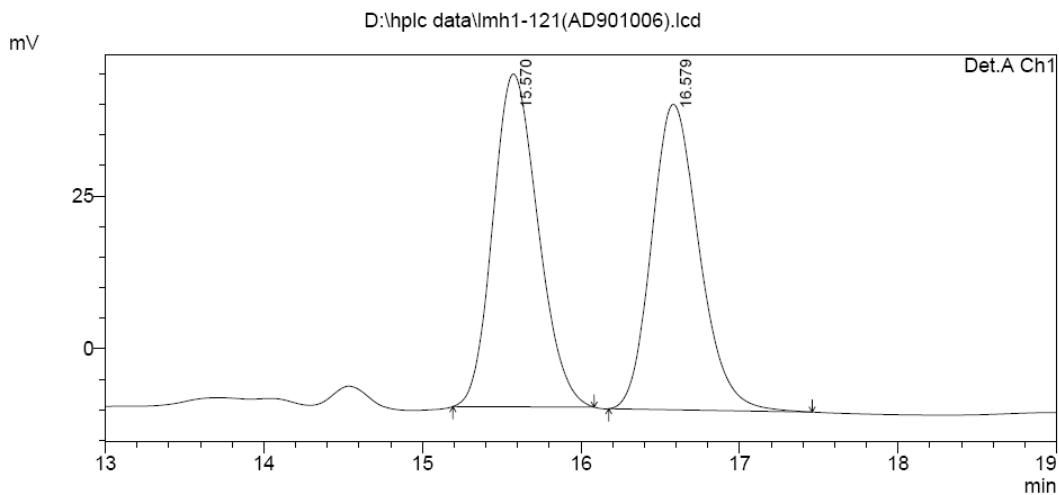
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.828	971368	24790	4.721	6.230
2	41.825	19603991	373094	95.279	93.770
Total		20575359	397884	100.000	100.000



3i (The top one is racemic and bottom one is chiral)

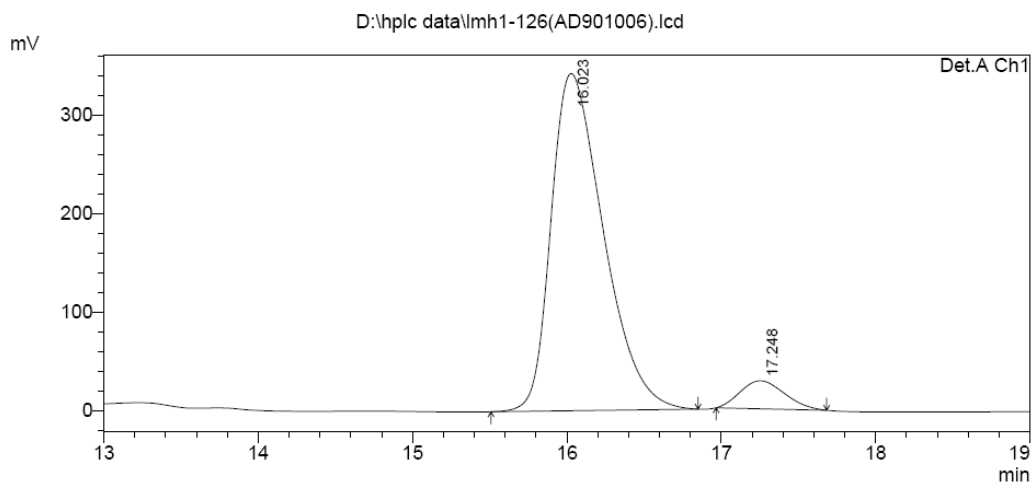
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PeakTable

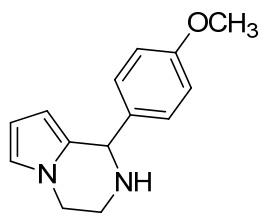
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.570	1079257	54513	50.780	52.149
2	16.579	1046095	50021	49.220	47.851
Total		2125352	104535	100.000	100.000

<Chromatogram>



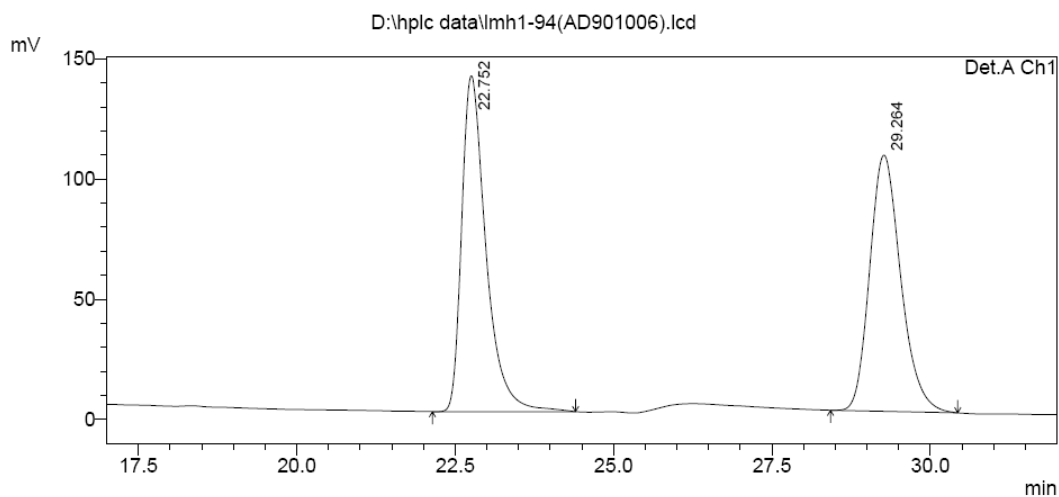
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.023	8072575	342381	93.441	92.349
2	17.248	566661	28366	6.559	7.651
Total		8639236	370747	100.000	100.000



3j (The top one is racemic and bottom one is chiral)

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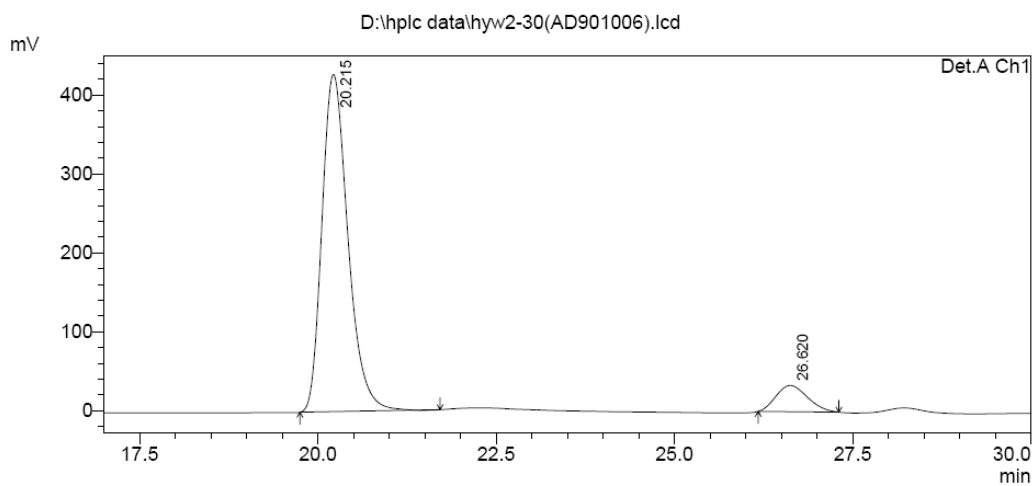


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.752	3715903	139548	50.549	56.717
2	29.264	3635209	106495	49.451	43.283
Total		7351112	246043	100.000	100.000

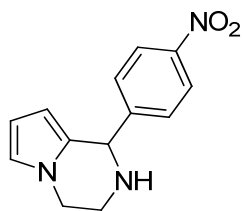
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PeakTable

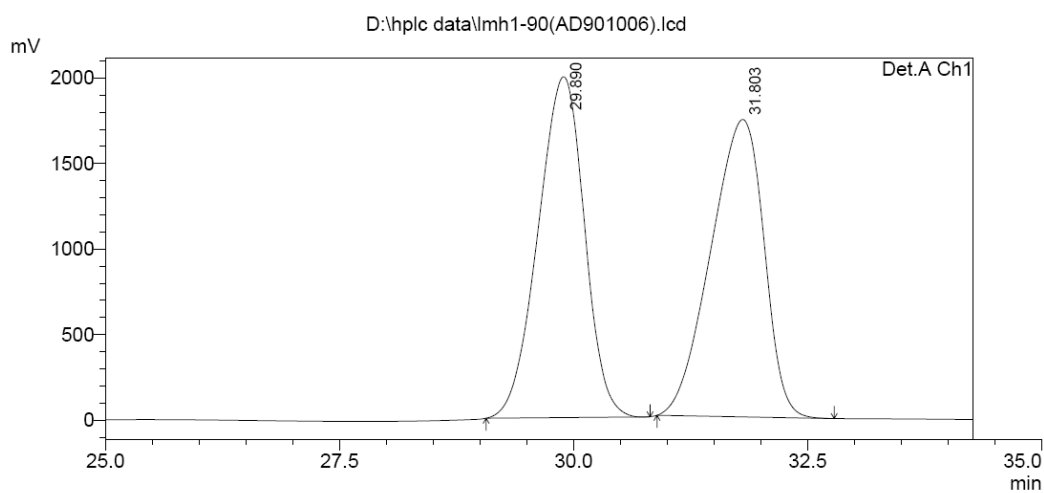
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.215	10811648	427380	91.365	92.788
2	26.620	1021797	33218	8.635	7.212
Total		11833444	460598	100.000	100.000



3k (The top one is racemic and bottom one is chiral)

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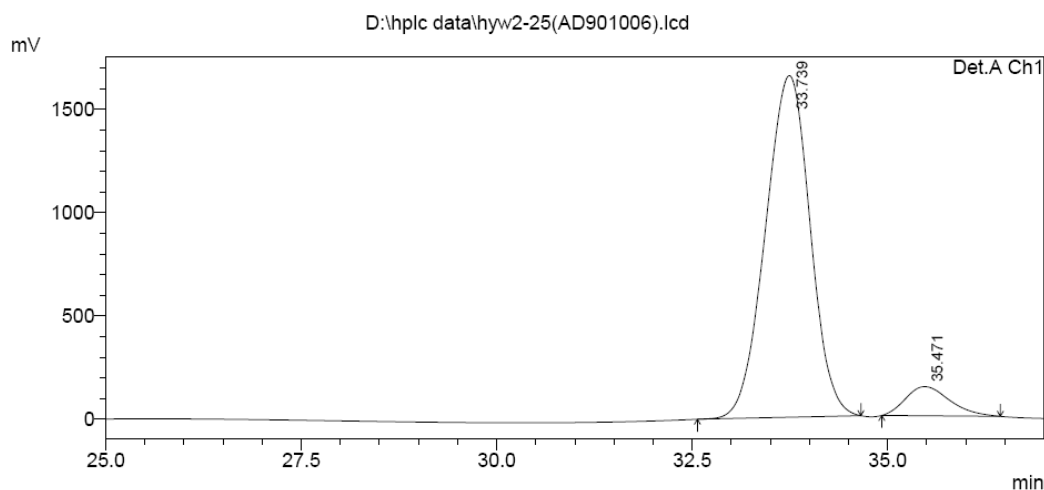


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.890	68681010	1992245	49.999	53.401
2	31.803	68683916	1738501	50.001	46.599
Total		137364926	3730746	100.000	100.000

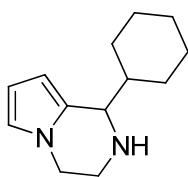
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PeakTable

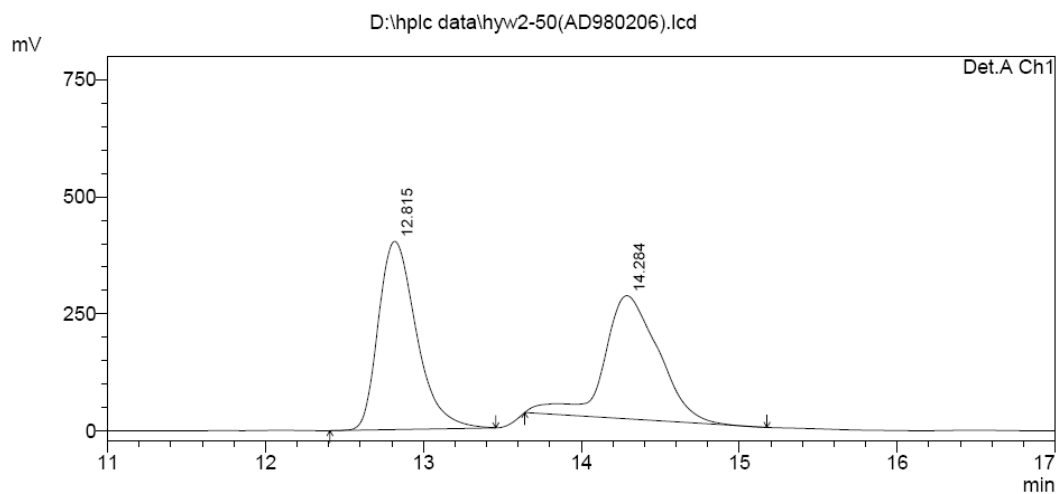
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.739	65688311	1653603	92.199	92.111
2	35.471	5557781	141617	7.801	7.889
Total		71246091	1795219	100.000	100.000



**31** (The top one is racemic and bottom one is chiral)

<Chromatogram>

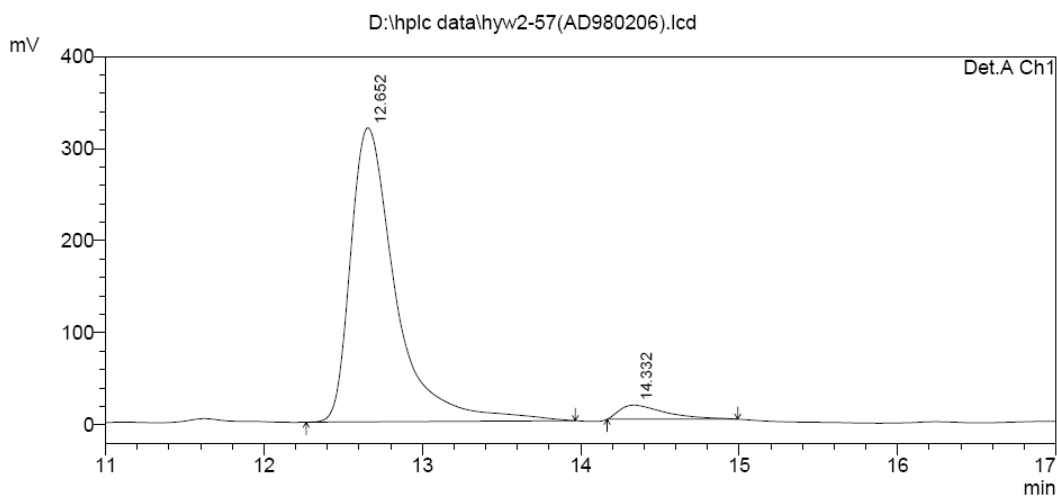


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.815	6733392	401394	51.420	60.471
2	14.284	6361479	262389	48.580	39.529
Total		13094871	663783	100.000	100.000

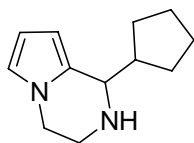
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PeakTable

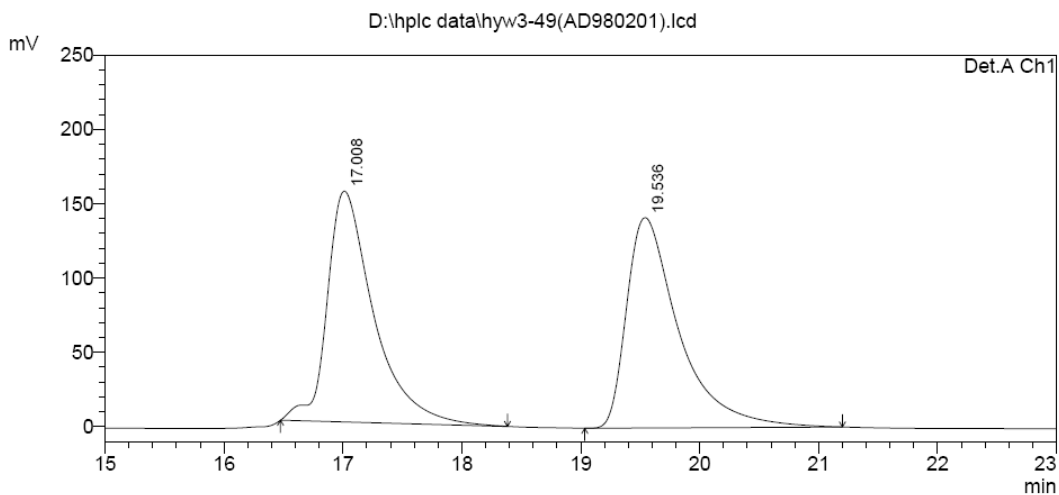
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.652	6335820	319517	95.337	95.420
2	14.332	309887	15336	4.663	4.580
Total		6645707	334854	100.000	100.000



**3m** (The top one is racemic and bottom one is chiral)

<Chromatogram>

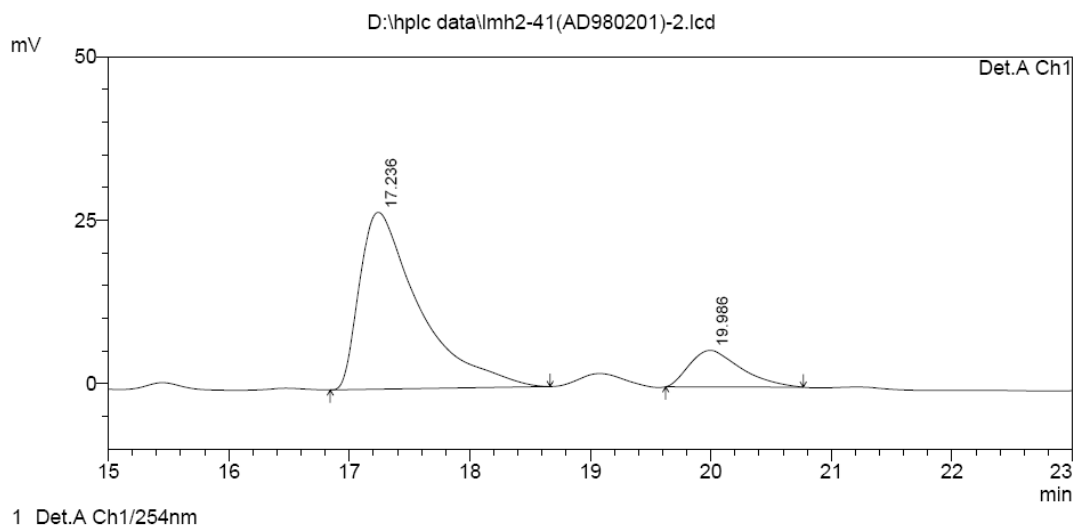


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.008	4233595	155267	49.444	52.318
2	19.536	4328846	141508	50.556	47.682
Total		8562440	296776	100.000	100.000

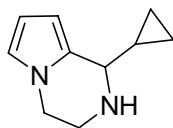
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PeakTable

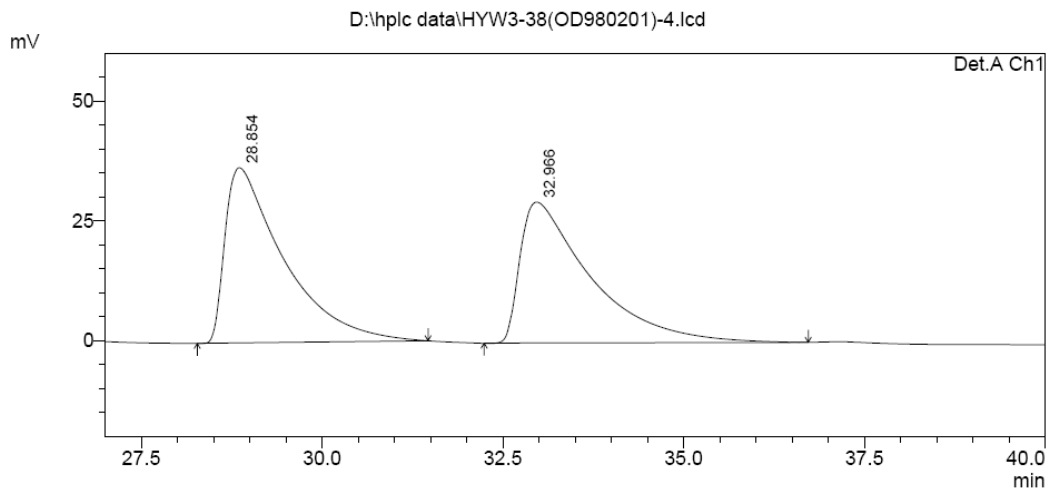
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.236	933688	27056	84.913	82.883
2	19.986	165899	5588	15.087	17.117
Total		1099587	32644	100.000	100.000



**3n** (The top one is racemic and bottom one is chiral)

<Chromatogram>

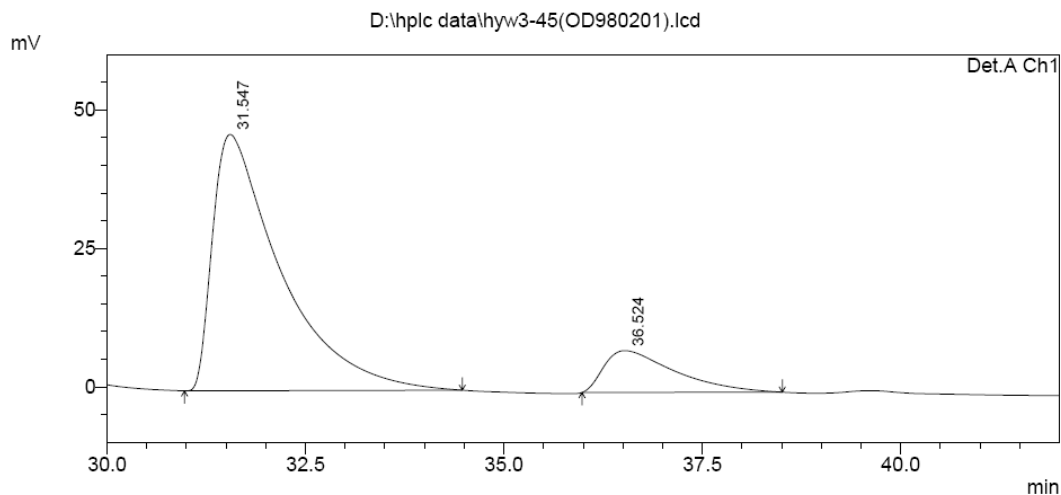


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.854	2062386	36584	50.941	55.431
2	32.966	1986206	29414	49.059	44.569
Total		4048591	65998	100.000	100.000

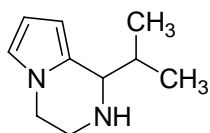
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PeakTable

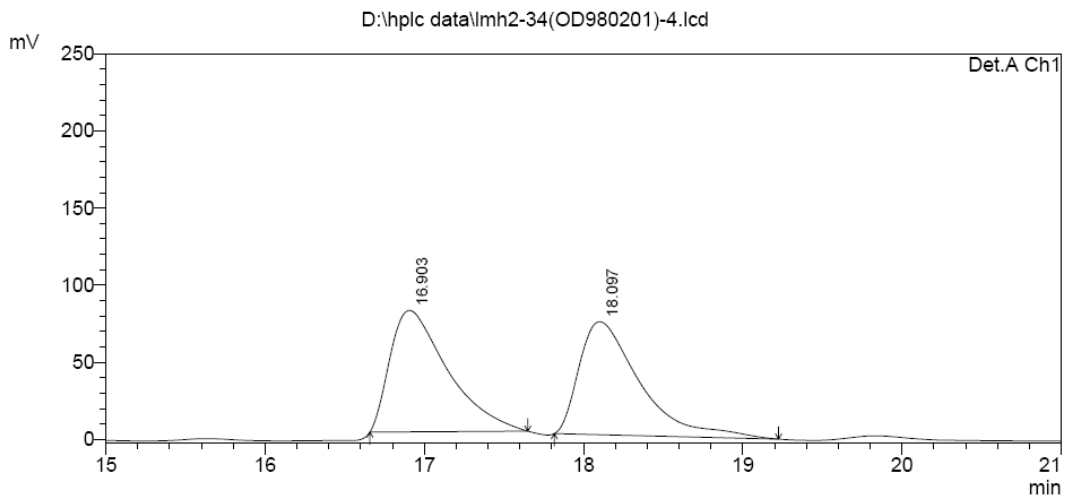
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.547	2765024	46286	85.552	85.988
2	36.524	466968	7543	14.448	14.012
Total		3231993	53829	100.000	100.000



3o (The top one is racemic and bottom one is chiral)

<Chromatogram>

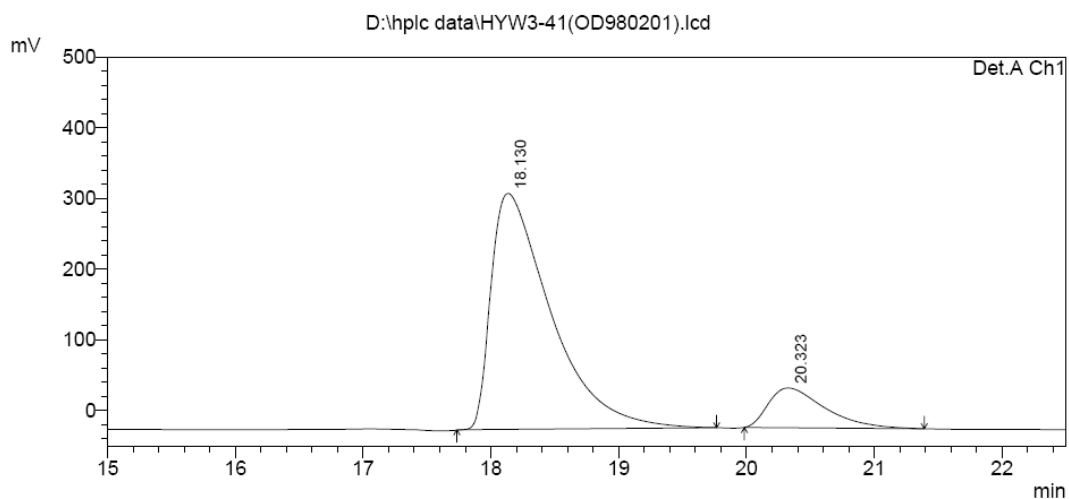


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.903	1977611	78655	50.518	51.781
2	18.097	1937050	73246	49.482	48.219
Total		3914661	151901	100.000	100.000

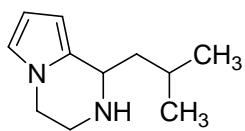
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PeakTable

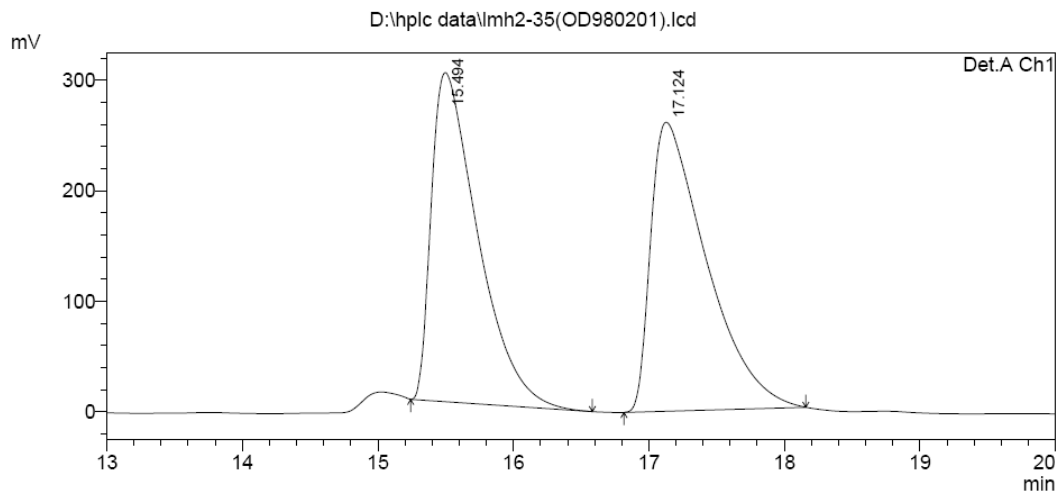
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.130	10855013	333825	86.349	85.587
2	20.323	1716025	56218	13.651	14.413
Total		12571038	390043	100.000	100.000



**3p** (The top one is racemic and bottom one is chiral)

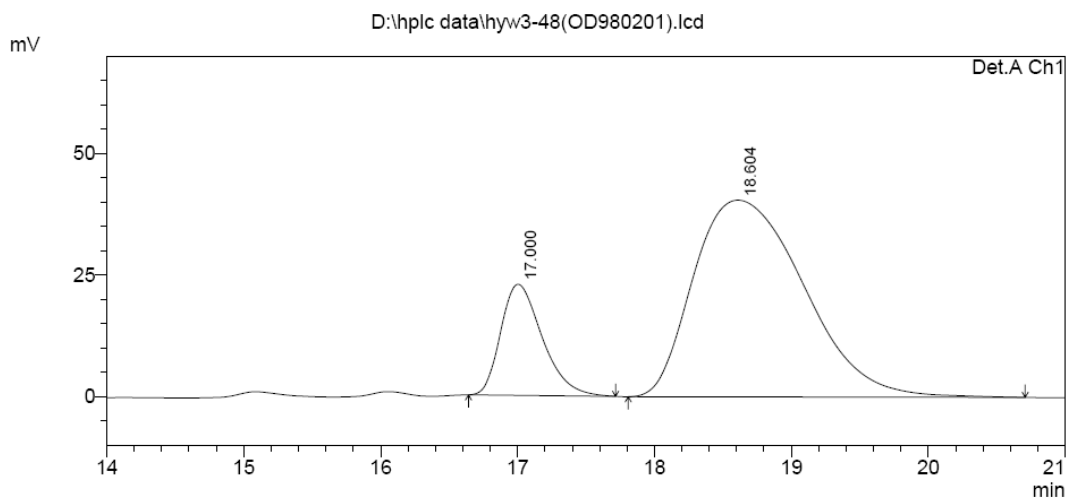
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PeakTable

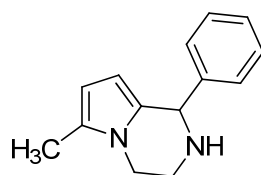
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.494	7091080	297605	48.633	53.248
2	17.124	7489638	261298	51.367	46.752
Total		14580718	558903	100.000	100.000

<Chromatogram>



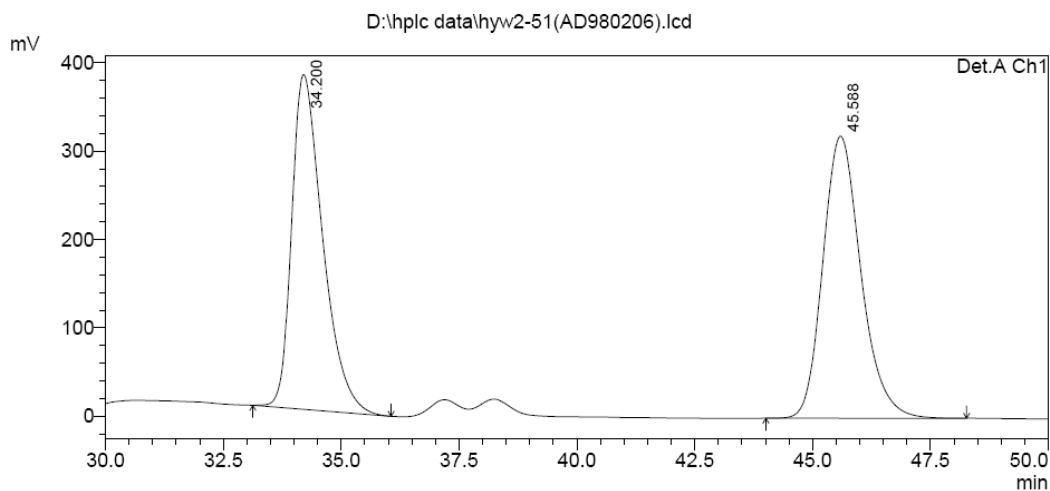
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.000	482976	22847	17.531	36.076
2	18.604	2272068	40485	82.469	63.924
Total		2755044	63332	100.000	100.000



**3q** (The top one is racemic and bottom one is chiral)

<Chromatogram>

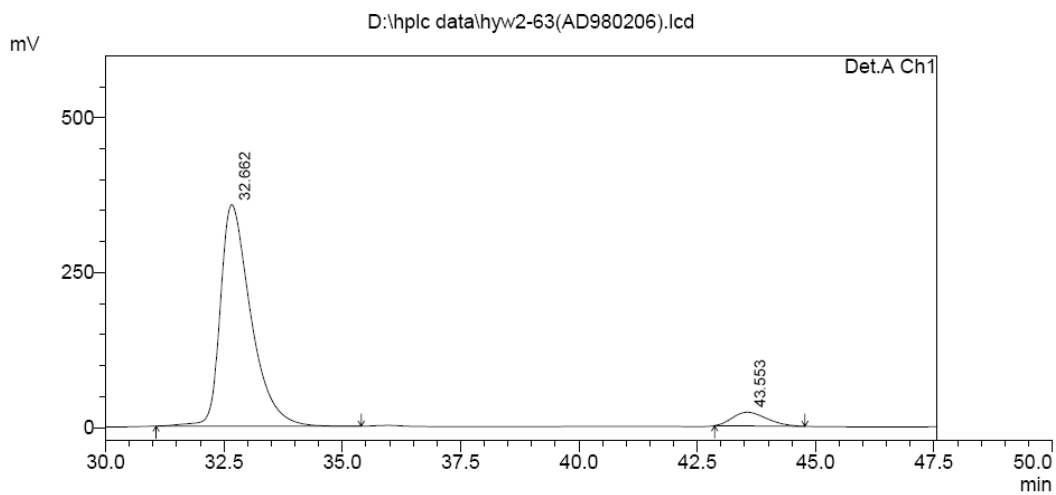


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.200	17326428	378615	49.108	54.268
2	45.588	17955729	319066	50.892	45.732
Total		35282157	697682	100.000	100.000

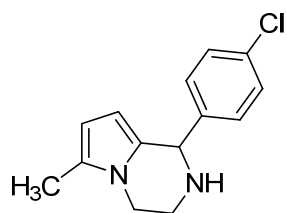
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PeakTable

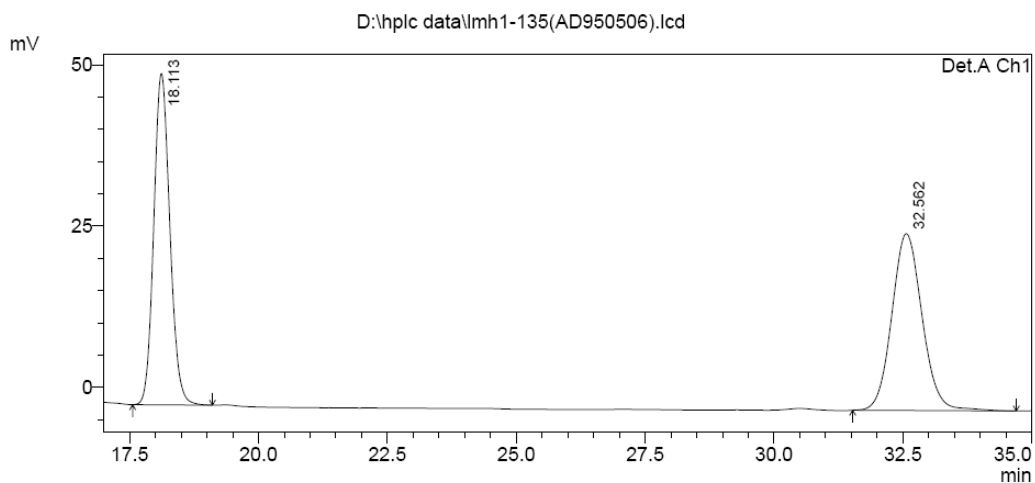
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.662	16023248	357262	93.533	94.201
2	43.553	1107790	21995	6.467	5.799
Total		17131038	379256	100.000	100.000



**3r** (The top one is racemic and bottom one is chiral)

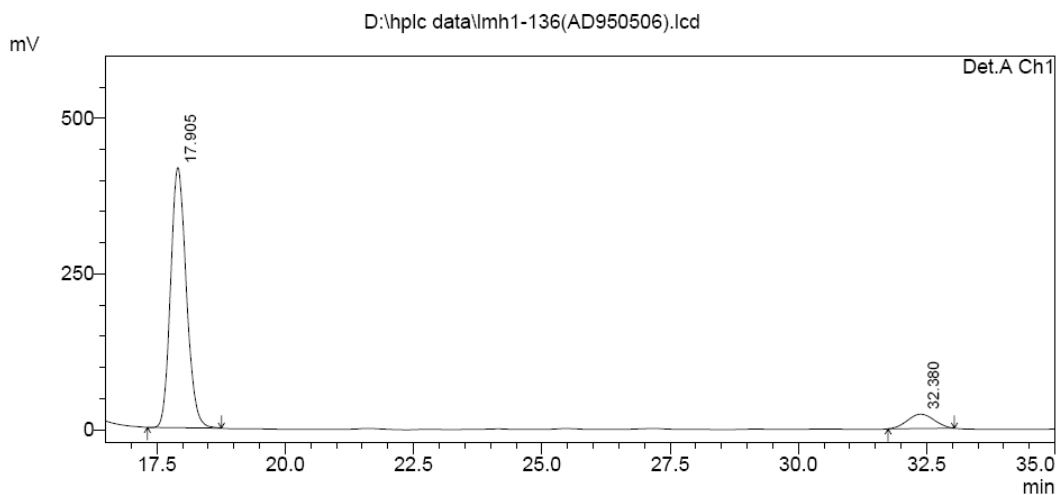
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PeakTable

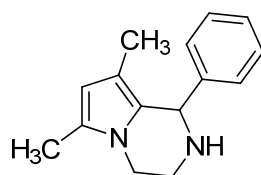
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.113	1115609	51399	49.906	65.208
2	32.562	1119829	27424	50.094	34.792
Total		2235438	78822	100.000	100.000

<Chromatogram>



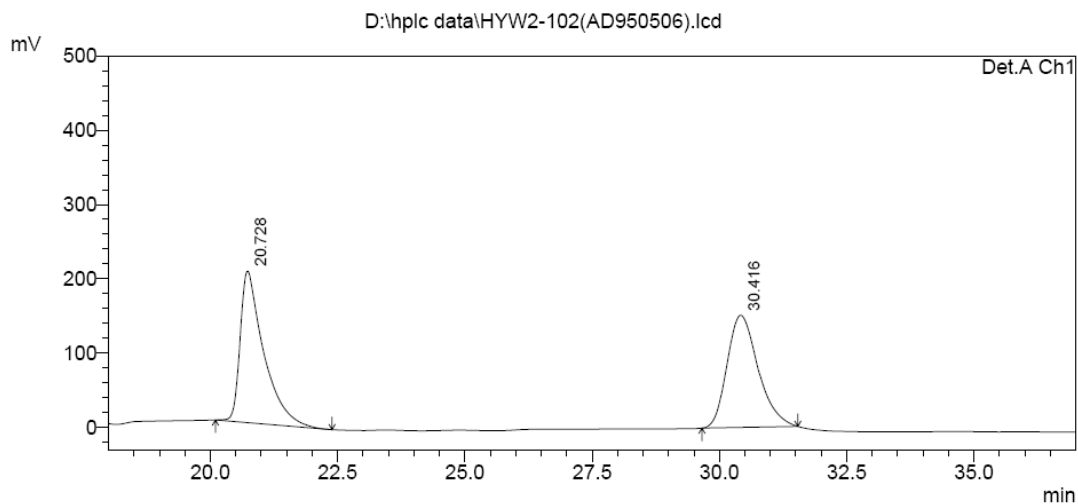
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.905	8921107	417493	91.427	94.770
2	32.380	836572	23039	8.573	5.230
Total		9757680	440532	100.000	100.000



**3s** (The top one is racemic and bottom one is chiral)

<Chromatogram>

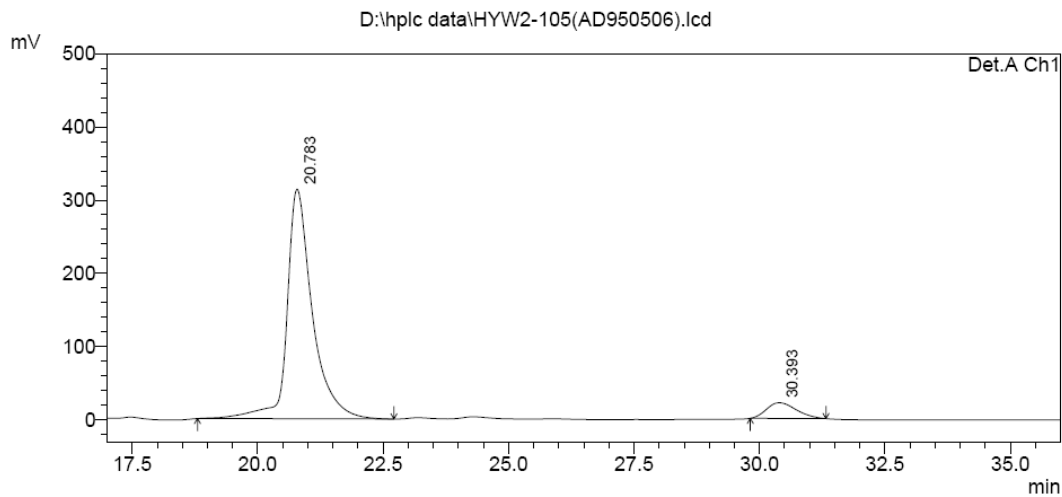


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.728	6545545	203927	50.491	57.457
2	30.416	6418134	150992	49.509	42.543
Total		12963679	354919	100.000	100.000

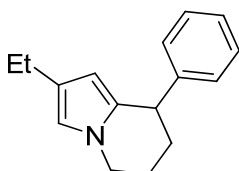
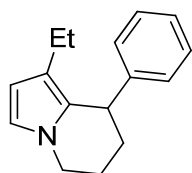
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PeakTable

Detector A Ch1 254nm

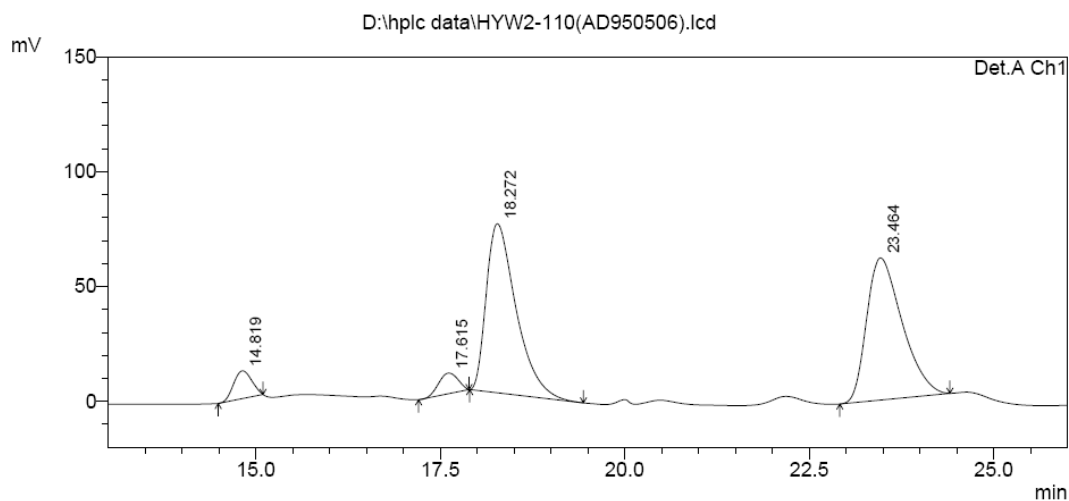
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.783	11027140	313488	92.559	93.573
2	30.393	886555	21532	7.441	6.427
Total		11913695	335020	100.000	100.000



**3t** and **3t'** (The top one is racemic and bottom one

is chiral)

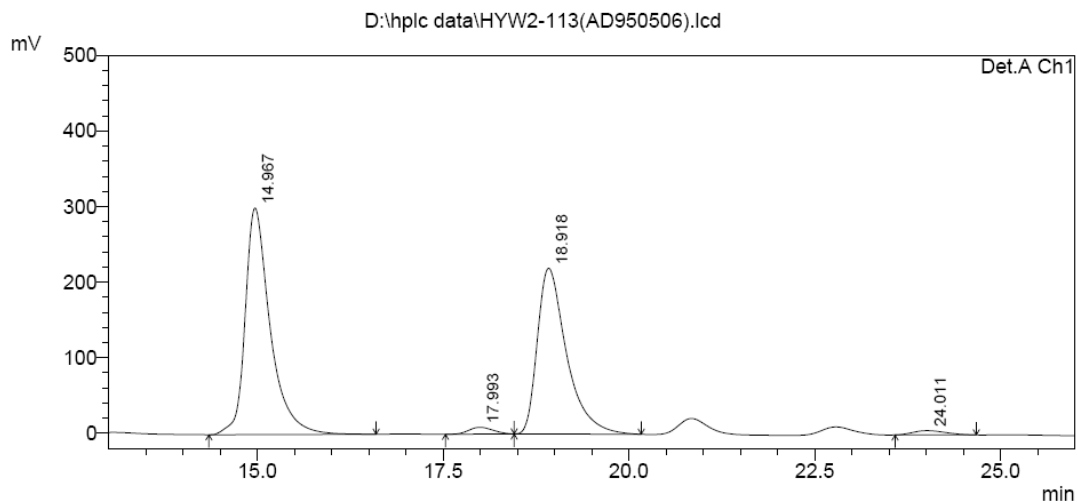
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PeakTable

Detector A Ch1 254nm

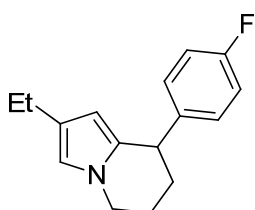
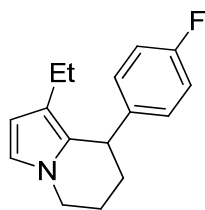
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.819	206864	12109	4.581	7.734
2	17.615	163337	8970	3.617	5.729
3	18.272	2071996	73571	45.883	46.990
4	23.464	2073630	61917	45.919	39.547
Total		4515827	156566	100.000	100.000



PeakTable

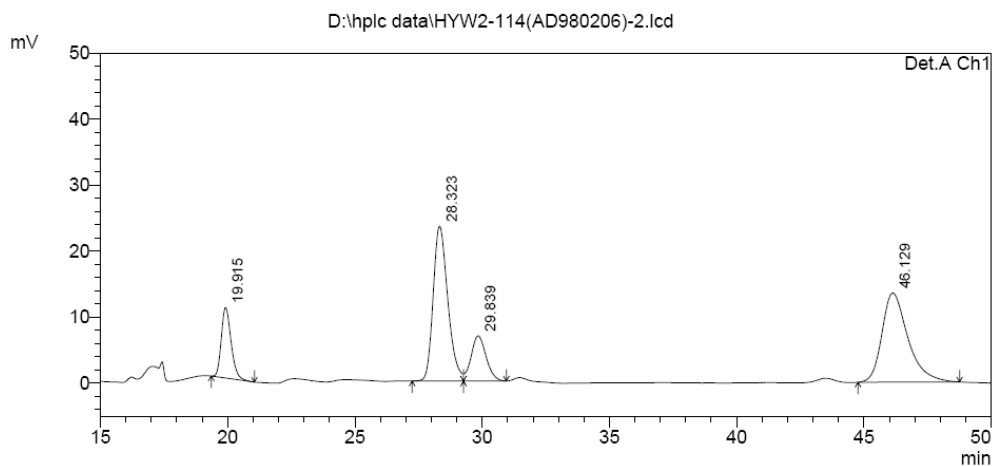
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.967	7033795	299734	52.414	56.162
2	17.993	203427	8998	1.516	1.686
3	18.918	6008142	219280	44.771	41.087
4	24.011	174241	5686	1.298	1.065
Total		13419605	533698	100.000	100.000



**3u** and **3u'** (The top one is racemic and bottom one is chiral)

<Chromatogram>



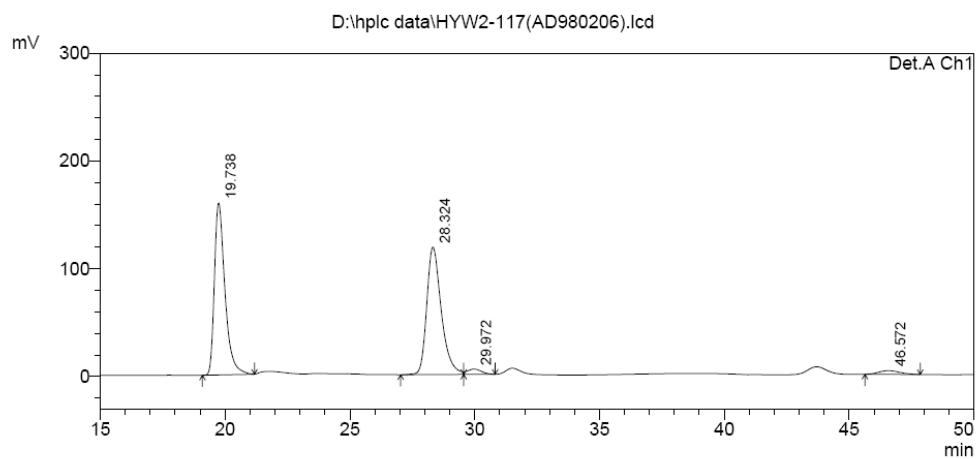
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.915	286132	10682	11.629	19.602
2	28.323	936302	23462	38.053	43.053
3	29.839	280699	6851	11.408	12.571
4	46.129	957407	13501	38.910	24.775
Total		2460540	54496	100.000	100.000

<Chromatogram>

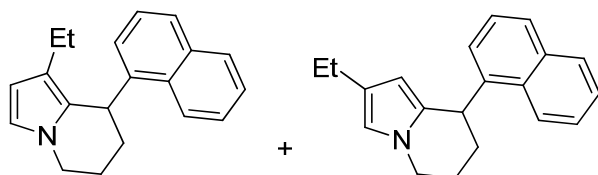


1 Det.A Ch1/254nm

PeakTable

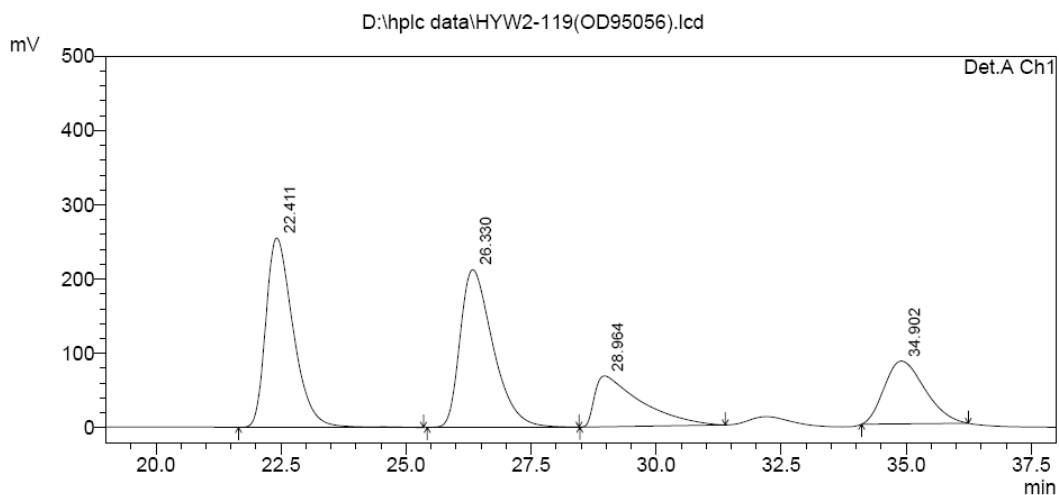
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.738	4685958	159620	47.484	55.742
2	28.324	4785622	118346	48.493	41.328
3	29.972	195038	4954	1.976	1.730
4	46.572	201968	3436	2.047	1.200
Total		9868586	286356	100.000	100.000



**3v** and **3v'** (The top one is racemic and bottom one is chiral)

<Chromatogram>



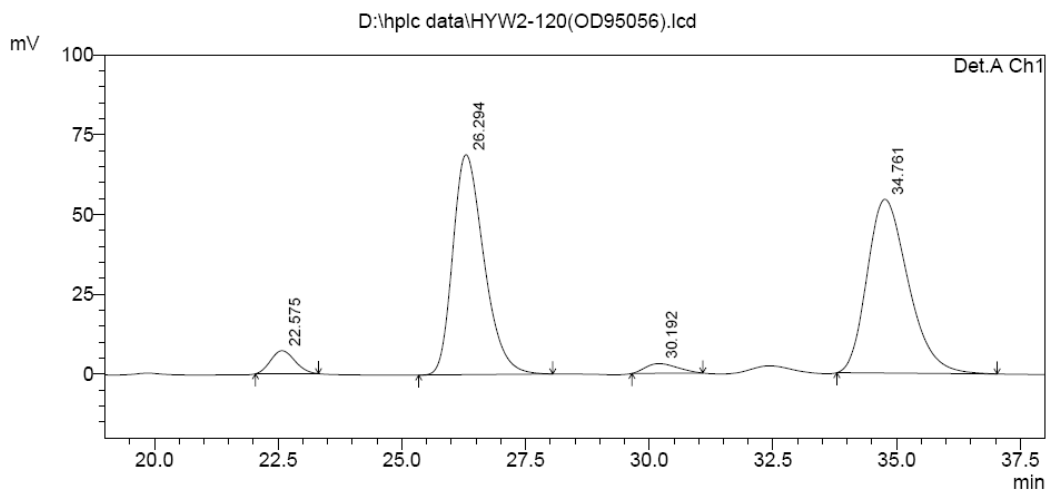
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.411	9698348	254756	34.008	41.109
2	26.330	9689931	211989	33.978	34.208
3	28.964	4343433	68384	15.230	11.035
4	34.902	4786498	84582	16.784	13.649
Total		28518210	619711	100.000	100.000

<Chromatogram>

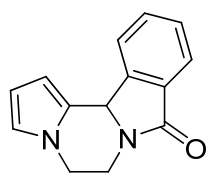


1 Det.A Ch1/254nm

PeakTable

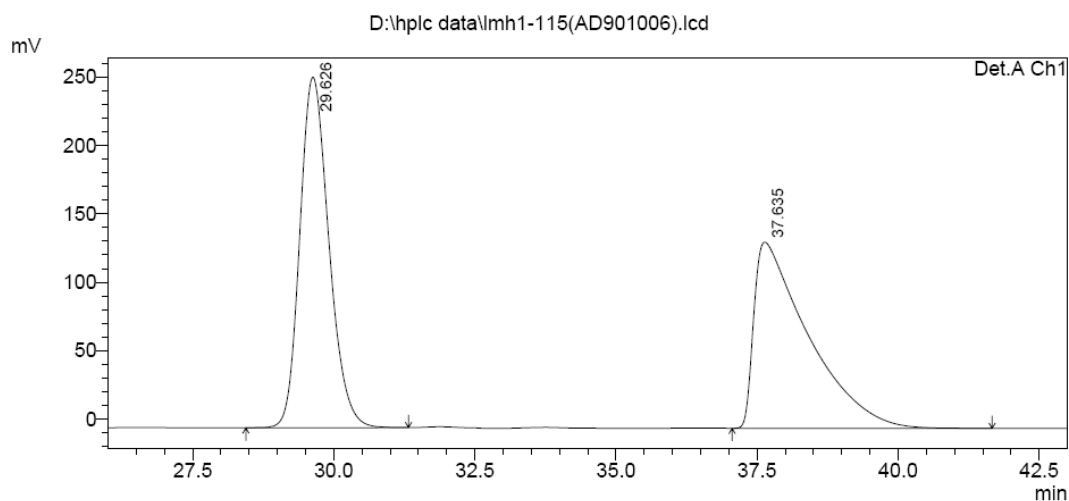
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.575	245908	7222	3.750	5.403
2	26.294	3021719	68957	46.084	51.592
3	30.192	136044	3038	2.075	2.273
4	34.761	3153324	54441	48.091	40.732
Total		6556994	133658	100.000	100.000



3w (The top one is racemic and bottom one is chiral)

<Chromatogram>

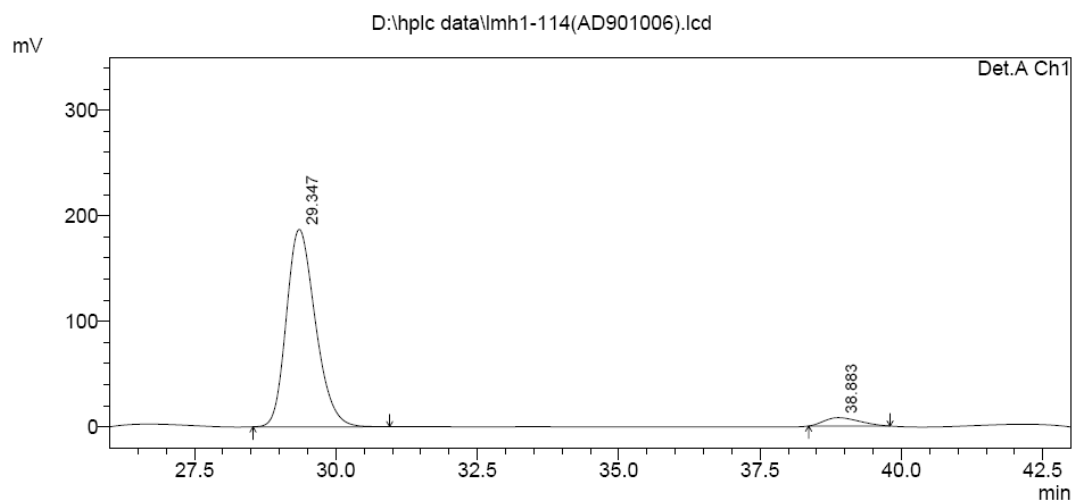


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.626	9183555	256317	50.211	65.322
2	37.635	9106549	136076	49.789	34.678
Total		18290104	392393	100.000	100.000

<Chromatogram>



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.347	6690747	187143	95.130	95.944
2	38.883	342525	7911	4.870	4.056
Total		7033272	195053	100.000	100.000