

Supporting information

Cinchona Alkaloid Squaramide Catalyzed Asymmetric Pictet-Spengler Reaction and Related Theoretical Studies

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I. General Information and Procedure

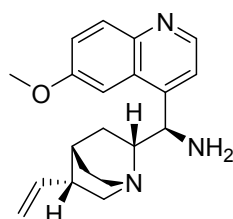
1. 1 General information

All reactions were carried out in oven-dried glassware with magnetic stirring under air unless otherwise mentioned. All other reagents were used without purification as commercially available. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. Solvents were purified and dried according to standard methods prior to use. Powdered 4Å molecular sieves were activated at 200 °C for 2 h. Catalysts C1-C8 were prepared according to the methods reported in the literature^[1-2]. C9 were purchased from Energy Chemistry.

¹H NMR spectra were recorded on 500 MHz or 600 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in CDCl₃. The following abbreviations may be used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. ¹³C NMR spectra were recorded on 125 MHz or 150 MHz spectrometer, referred to the internal solvent signals (77.0 for CDCl₃). Analytical HPLC was recorded on a HPLC machine equipped with Agilent 1100 series quaternary pump with a UV diode array detector. The chiral stationary phase was Daicel Chiralcel AD-H and OD-H column. Optical rotations were determined using a Rudolph Autopol V polarimeter at 25 °C.

1.2 General procedure for the preparation of catalysts

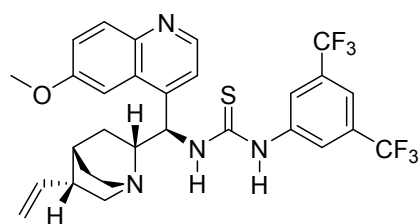
9-Amino-(9-deoxy)-epi-quinine (S1)^[3]



Quinine (2.0 g, 6.33 mmol) and Ph₃P (2.2 g, 8.43 mmol) was placed under vacuum and purged with N₂ three times, anhydrous THF (30 mL) was added and the solution was cooled to 0 °C. Diisopropyl azodicarboxylate (1.55 mL, 7.87 mmol) was added followed by the dropwise addition of a solution of diphenyl phosphoryl azide (1.65 mL, 7.66 mmol) in anhydrous THF (13 mL).

The mixture was then allowed to warm to room temperature and stir for 16 h, at which point the mixture was heated at 50 °C for 2 h. Ph₃P (2.4 g, 8.96 mmol) was then added and mixture was stirred for a further 2 h at 50 °C. The solution was allowed to cool to room temperature before H₂O (0.7 mL) was added and then stirred for a further 3 h. The mixture was then concentrated in vacuo and the crude residue was dissolved in CH₂Cl₂ (30 mL) and diluted with 2 M HCl (30 mL) and the aqueous phase was washed with CH₂Cl₂ (2 x 30 mL). Excess concentrated aqueous ammonia was added to the aqueous phase followed by extraction with CH₂Cl₂ (3 x 30 mL), the combined organic phases were dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by column chromatography afforded amine **S1** as a white solid (1.9 g, 93%). ¹H NMR (600 MHz, CDCl₃) δ: 8.76 (d, J=6Hz, 1H), 8.02-8.05(m, 1H), 7.28-7.67 (m, 5H), 5.86-5.92(m, 1H), 5.07-5.10(m, 2H), 4.70(br, 1H), 3.97 (s, 3H), 2.96-3.01(m, 4H), 2.29-2.32(m, 1H), 1.55-1.63(m, 3H), 1.13-1.17(m, 1H), 0.95-0.99(m, 1H), 0.88-0.90(m, 1H).

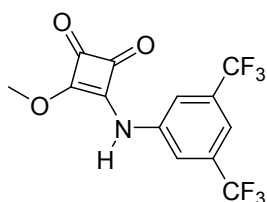
N-[3,5-Bis(trifluoromethyl)phenyl]-N'-[(8a,9S)-6'-methoxy-9-cinchonanyl]thiourea (S2)^[4]



Amine **S1** (1.9 g, 5.89 mmol) was placed under vacuum and purged with N₂ three times, dissolved in anhydrous THF (20 mL). Solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1.2 mL, 6.60 mmol) in anhydrous THF (10 mL) was added dropwise at room temperature and the resulting mixture was stirred for 16 h. The reaction mixture was concentrated in vacuo and purified by column chromatography to afford thiourea **S2** as an off white solid (3.2 g, 91%). ¹H NMR (600 MHz, CDCl₃) δ: 8.67 (d, J=4.7 Hz, 1H), 8.09 (s, 2H), 8.07 (br 1H), 7.93 (d, J=9.3 Hz, 1H), 7.59 (1H, br s), 7.56 (1H, d, J=4.8

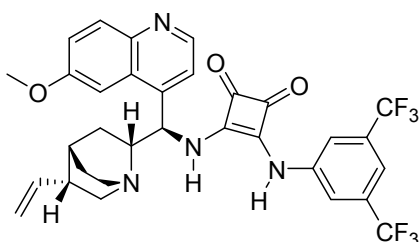
Hz), 7.43 (d, $J=9.3$, 1H), 6.38 (br, 1H), 5.84-5.87 (m, 1H), 5.07-4.96 (m, 2H), 4.01 (s, 3H), 3.73-3.57 (m, 1H), 3.54-3.40 (m, 1H), 3.36-3.25 (m, 1H), 2.93-2.77 (m, 2H), 2.45-2.31 (m, 1H), 1.79-1.56 (m, 3H), 1.54-1.40 (m, 1H), 0.94-0.80 (m, 1H). Proton NMR were consistent with literature data.

3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-methoxycyclobut-3-ene-1,2-dione (S3) ^[5]



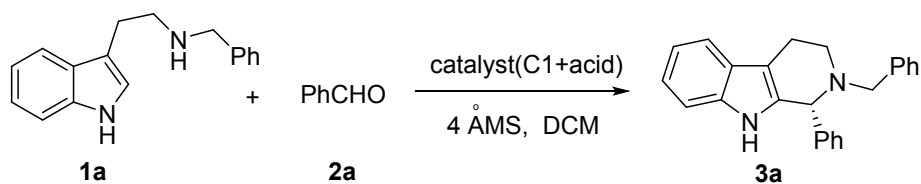
To a solution of 3,4-dimethoxy-3-cyclobutane-1,2-dione (2.00g, 14.1mmol) in MeOH (20ml) was added 3,5-bis(trifluoromethyl)aniline (2.40ml, 15.5mmol, 1.1equiv) at rt. The mixture was stirred at rt for 3 days. The reaction mixture was filtrate and washed with MeOH. Obtained yellow solid was dried in vacuo to give desired product 2a (4.59, 13.5mmol, 96%). ¹H NMR (600 MHz, DMSO) δ : 4.22(s, 3H), 7.78(s, 1H), 8.05(s, 2H), 11.19(s, 1H). Proton NMR were consistent with literature data.

3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-(((R)-(6-methoxy-quinolin-4-yl)((1S,2S,4S,5R)-5-vinylquinuclidin-2-yl)methyl)amino)-cyclobut-3-ene-1,2-dione. (S4) ^[6]



To a solution of 9-Amino-(9-deoxy)-epi-quinidine (1.0 mmol) in 5 mL CH₂Cl₂ was added S3 (1.0 mmol). The reaction mixture was stirred for 48 h at room temperature. The desired product was obtained through filtration or by silica gel column chromatography. Yellow solid, 84% yield. ¹H NMR (600

MHz, CDCl₃): δ = 8.56 (s, 1H), 7.95 (d, J =12Hz, 1H), 7.70 (s, 1H), 7.41 (s, 1H), 7.31-7.35(m, 2H), 6.22 (br, 1H), 5.82-5.88 (m, 1H), 5.19 (d, J =18Hz, 1H), 5.12 (d, J =12Hz, 1H), 3.97 (s, 3H), 3.42 (br, 1H), 3.21 (br, 1H), 2.82-3.01 (m, 3H), 2.28 (br, 1H), 1.69 (s, 1H), 1.56 (br, 2H), 1.07-1.28 (m, 3H). Proton NMR were consistent with literature data.

Table 1. Screening of the asymmetric organic salts^a

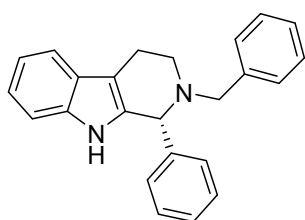
Entry	Acid	Temp (°C)	Time (h)	Yield ^b (%)	ee ^c (%)
1	PhCO ₂ H	rt	36	86	49
2	AcOH	rt	36	79	61
3	TfOH	rt	28	92	32
4	diphenyl phosphate	rt	36	96	72
5	diphenyl phosphate	10	72	77	52

^a Reactions were performed with 0.05mmol of **1a**, 0.06mmol of **2a**, 20 mol% of catalyst **C1** and 20 mol % acid in 0.5 mL DCM. ^b Yield of the isolated product. ^c Determined by HPLC analysis on Daicel Chiralcel AD-H column.

2. General procedure for the enantioselective Pictet-Spengler reaction

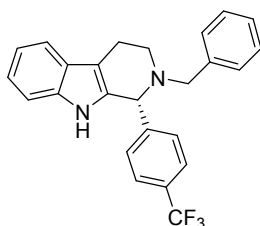
A mixture of *N*-protected tryptamine **1** (0.05 mmol), aldehyde **2** (0.06 mmol), catalyst **C2**(20% mol), 4 Å molecular sieves (0.1-0.2g, powdered) in 0.5 mL toluene and DCM was stirred at room temperature. The reaction was monitored with TLC. After the reaction was completed, the reaction mixture was directly purified by flash column chromatography (ethyl acetate / petroleum ether = 1/15 to 1/10, with 2% TEA) to give the desired product **3**.

(*R*)-2-benzyl-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3a)



This product was obtained in 93% yield as a white solid after chromatography and 89% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 90:10, 0.8mL/min, λ =254nm, t (major)=10.87min, t (minor)=12.25min]. $[\alpha]_D^{25} = -63.1$ (c =0.97, CH_2Cl_2); **HRMS** (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ [$\text{M}+\text{H}$] $^+$:339.1856; Found: 339.1862. **^1H NMR** (500 MHz, CDCl_3) δ 2.65-2.70(m, 1H), 2.79-2.83(m, 1H), 2.90-2.96(m, 1H), 3.23-3.27(m, 1H), 3.37(d, J =13.5Hz, 1H), 3.90(d, J =13.5Hz, 1H), 4.65(s, 1H), 7.10-7.14(m, 2H), 7.18-7.19(m, 1H), 7.25-7.28(m, 1H), 7.32-7.35(m, 3H), 7.36-7.39(m, 4H), 7.47(m, 2H), 7.53-7.54(m, 1H). **^{13}C NMR** (125 MHz, CDCl_3) δ 141.46, 139.57, 136.29, 134.86, 129.02, 128.76, 128.70, 128.23, 128.08, 127.21, 126.92, 121.49, 119.35, 118.30, 110.78, 108.95, 64.60, 58.33, 48.35, 21.18.

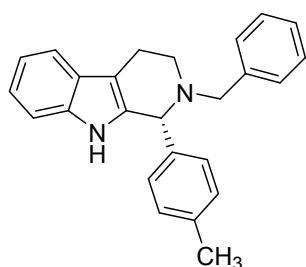
(*R*)-2-benzyl-1-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3b)



This product was obtained in 95% yield as a white solid after chromatography and 80% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 90:10,

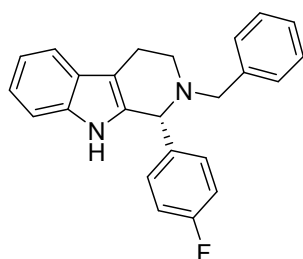
0.8mL/min, λ =225nm, t (major)=8.6 min, t (minor)=10.6 min]. $[\alpha]_D^{25} = -42.3$ (c=1.4, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₅H₂₂F₃N₂ [M+H]⁺: 407.1730; Found: 407.1742. **¹H NMR** (600 MHz, CDCl₃) δ 2.69-2.73(m, 1H), 2.82-2.85(m, 1H), 2.89-2.94(m, 1H), 3.21-3.32(m, 1H), 3.43(d, J =13.8Hz, 1H), 3.84(d, J =13.8Hz, 1H), 4.73(s, 1H), 7.11-7.16(m, 2H), 7.21(d, J =7.2Hz, 1H), 7.25-7.35(m, 1H), 7.54(s, 1H), 7.56-7.64(m, 4H). **¹³C NMR** (150 MHz, CDCl₃) 145.85, 139.12, 136.39, 133.60, 130.43, 130.21, 129.33, 128.69, 128.38, 127.18, 127.07, 125.75, 125.73, 125.01, 123.21, 121.90, 119.61, 118.47, 110.91, 109.48, 63.78, 58.38, 48.01, 20.91.

(*R*)-2-benzyl-1-(*p*-tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3c)



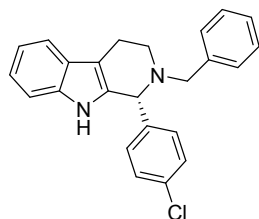
This product was obtained in 76% yield as a white solid after chromatography and 74% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 95:5, 0.8mL/min, λ =254nm, t (major)=13.1 min, t (minor) =17.9 min]. $[\alpha]_D^{25} = -57.3$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₄H₂₅N₂[M+H]⁺:353.1956; Found: 353.1962. **¹H NMR** (600 MHz, CDCl₃) δ 2.42(s, 3H), 2.73-2.77(m, 1H), 2.83-2.87(m, 1H), 2.94-2.99(m, 1H), 3.30-3.33(m, 1H), 3.55(d, J =13.8Hz, 1H), 4.09(d, J =13.8Hz, 1H), 4.71(s, 1H), 7.13-7.18(m, 2H), 7.21-7.23(m, 1H), 7.24(d, J =7.8Hz, 1H), 7.32(s, 1H), 7.40(d, J =7.8Hz, 2H), 7.49-7.54(m, 2H), 7.56-7.58(m, 2H), 7.82(s, 1H), 7.85-7.89(m, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 138.34, 137.88, 137.33, 136.32, 135.08, 133.39, 132.82, 129.52, 129.06, 127.92, 127.73, 127.29, 127.28, 127.21, 125.97, 125.54, 121.50, 119.38, 118.34, 110.85, 108.96, 64.39, 58.48, 48.36, 21.25, 21.22.

(*R*)-2-benzyl-1-(4-fluorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3d)



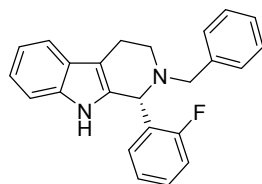
This product was obtained in 89% yield as a white solid after chromatography and 84% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 90:10, 0.8mL/min, λ =254nm, *t* (major)=10.8 min, *t* (minor)=13.8 min]. $[\alpha]_D^{25}$ = -43.3(*c*=0.9, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₄H₂₂FN₂[M+H]⁺:357.1756; Found: 353.1760. **¹H NMR** (500 MHz, CDCl₃) δ 2.68-2.73(m, 1H), 2.81-2.86(m, 1H), 2.90-2.96(m, 1H), 3.22-3.27(m, 1H), 3.39(d, *J*= 8.5Hz, 1H), 3.89(d, *J*=8.5Hz, 1H), 4.67(s, 1H), 7.04-7.08(m, 2H), 7.10-7.15(m, 2H), 7.20-7.23(m, 1H), 7.26-7.28(m, 1H), 7.32-7.36(m, 4H), 7.39-7.43(m, 2H), 7.53(d, *J*=6.0Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 163.50, 161.54, 139.39, 137.24, 136.31, 134.47, 130.59, 130.53, 128.68, 128.29, 127.16, 127.02, 121.67, 119.47, 118.37, 115.70, 115.53, 110.82, 109.18, 63.61, 58.18, 48.16, 21.03. IR: 705.58, 747.30, 896.02, 1265.33, 1421.86, 2305.65, 2685.53, 2986.91, 3054.20, 3943.98.

(*R*)-2-benzyl-1-(4-chlorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3e)



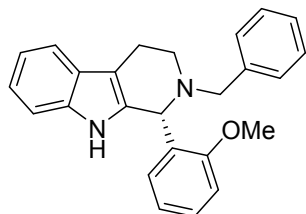
This product was obtained in 83% yield as a white solid after chromatography and 72% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 90:10, 0.8mL/min, λ =225nm, *t* (major)=11.3 min, *t* (minor)=13.4 min]. $[\alpha]_D^{25}$ = -35.8(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₄H₂₂ClN₂ [M+H]⁺: 373.1466; Found: 373.1475. **¹H NMR** (500 MHz, CDCl₃) δ 2.68-2.70(m, 1H), 2.80-2.84(m, 1H), 2.89-2.91(m, 1H), 3.21-3.25(m, 1H), 3.39(d, *J*=8.5Hz, 1H), 3.86(d, *J*=8.5Hz, 1H), 4.64(s, 1H), 7.12-7.16(m, 2H), 7.20-7.23(m, 1H), 7.27-7.30(m, 1H), 7.34-7.36(m, 6H), 7.38-7.40(m, 2H), 7.54(d, *J*=7.5Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 140.08, 139.24, 136.32, 134.11, 133.78, 130.32, 128.92, 128.66, 128.30, 127.10, 127.05, 121.72, 119.49, 118.37, 110.83, 109.24, 63.64, 58.23, 48.09, 20.99.

(*R*)-2-benzyl-1-(2-fluorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3f)



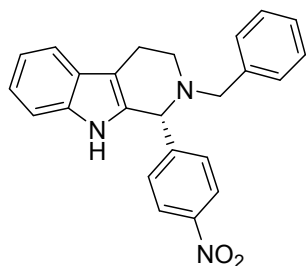
This product was obtained in 82% yield as a white solid after chromatography and 32% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, λ =225nm, *t* (major)=6.9 min, *t* (minor)=8.0 min]. $[\alpha]_D^{25}$ = -29.4(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₄H₂₂FN₂[M+H]⁺:357.1757; Found: 353.1763. **¹H NMR** (500 MHz, CDCl₃) δ 2.72-2.73(m, 1H), 2.83-2.86(m, 1H), 2.92-2.94(m, 1H), 3.24-3.27(m, 1H), 3.51(d, *J*=8.5Hz, 1H), 3.90(d, *J*=8.5Hz, 1H), 5.22(s, 1H), 7.12-7.20(m, 4H), 7.24-7.25(m, 1H), 7.28-7.32(m, 2H), 7.34-7.41(m, 4H), 7.48(s, 1H), 7.50-7.53(m, 1H), 7.55(d, *J*=6.0Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 162.38, 160.43, 136.29, 130.59, 129.41, 128.70, 128.25, 126.98, 124.74, 124.71, 121.67, 119.42, 118.29, 115.51, 115.34, 110.82, 109.64, 58.45, 56.28, 47.80, 20.94.

(*R*)-2-benzyl-1-(2-methoxyphenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3g)



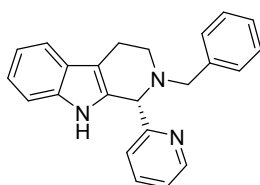
This product was obtained in 77% yield as a white solid after chromatography and 58% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 98:2, 0.8mL/min, λ =254nm, *t* (major) = 26.1 min, *t* (minor) =29 min]. $[\alpha]_D^{25}$ = -32.1(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₅H₂₅ON₂[M+H]⁺:369.1957; Found: 353.1761. **¹H NMR** (500 MHz, CDCl₃) δ 2.64-2.69(m, 1H), 2.76-2.79(m, 1H), 2.86-2.89(m, 1H), 3.24-3.26(m, 1H), 3.40(d, *J*=13.5Hz, 1H), 3.88(d, *J*=13.5Hz, 1H), 3.95(s, 3H), 5.26(s, 1H), 6.91-6.94(m,1H), 6.98-7.00(m, 1H), 7.04-7.10(m, 2H), 7.18-7.20(m, 1H), 7.23-7.27(m, 2H), 7.30-7.33(m, 2H), 7.36(d, *J*=6.0Hz, 2H), 7.48-7.50(m, 1H), 7.57-7.59(m, 1H), 7.67(b, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 157.50, 138.43, 136.29, 133.59, 131.41, 128.70, 128.41, 128.23, 127.25, 127.19, 121.98, 120.74, 119.71, 118.67, 112.42, 111.29, 111.14, 105.51, 58.85, 56.40, 55.70, 48.29, 21.07.

(*R*)-2-benzyl-1-(4-nitrophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3h)



This product was obtained in 91% yield as a light yellow solid after chromatography and 50% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, λ =225nm, t (major)=7.2 min, t (minor)=8.1 min]. $[\alpha]_D^{25} = -12.9$ (c=1.2, CH₂Cl₂); HRMS (ESI-TOF) calcd for C₂₄H₂₂ON₃[M+H]⁺:384.1667; Found: 384.1669. ¹H NMR (500 MHz, CDCl₃) δ 2.73-2.78(m, 1H), 2.87-2.91(m, 2H), 3.18-3.23(m, 1H), 3.50(d, J=13.5Hz, 1H), 3.81(d, J=13.5Hz, 1H), 4.79(s,1H), 7.13-7.18(m, 2H), 7.23-7.25(m, 1H), 7.29-7.30(m, 1H), 7.35-7.39(m, 5H), 7.56(d, J=7.5Hz 1H), 7.58(d, J=7.5Hz, 2H), 8.18(d, J=9.0Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 149.47, 147.62, 138.79, 136.44, 132.67, 129.72, 128.65, 128.40, 127.27, 126.95, 123.86, 122.06, 119.67, 118.49, 110.93, 109.71, 63.06, 58.38, 47.61, 20.59. IR: 705.29, 739.04, 896.01, 1265.35, 1349.48, 1421.74, 1524.46, 1635.76, 2305.46, 2987.06, 3054.44, 3451.23.

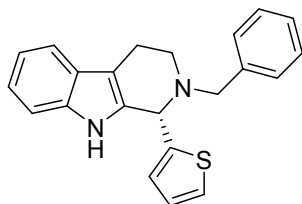
(S)-2-benzyl-1-(pyridin-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3i)



This product was obtained in 76% yield as a yellow solid after chromatography and 83% ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, λ =225nm, t (minor)=8.9 min, t (major)=28.8 min]. $[\alpha]_D^{25} = -63.2$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₃H₂₂N₃ [M+H]⁺: 340.1808; Found: 340.1798. ¹H NMR (600 MHz, CDCl₃) δ 2.76-2.80(m, 1H), 2.89-2.91(m, 1H), 3.00-3.05(m, 1H), 3.32-3.36(m, 1H), 3.58(d, J=14.4Hz, 1H), 4.02(d, J=14.4Hz, 1H), 5.11(s, 1H), 7.15-7.20(m, 2H), 7.22-7.24(m, 1H), 7.32-7.35(m, 2H), 7.39(t, J=7.2, 7.8Hz, 2H), 7.48(d, J=13.2Hz, 2H), 7.60(d, J= 7.2Hz, 1H), 7.75-7.78(m, 1H), 7.91(d,

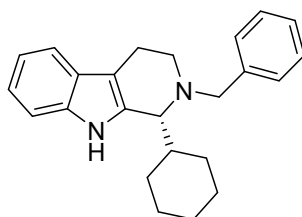
$J=7.8\text{Hz}$, 1H), 8.39(d, $J=4.8\text{Hz}$, 1H), 9.63(s, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 162.55, 148.39, 139.23, 137.57, 136.85, 134.03, 128.59, 128.43, 127.11, 126.98, 122.76, 122.37, 121.46, 119.13, 118.34, 111.01, 108.37, 65.77, 59.10, 48.42, 21.31. IR: 705.37, 739.22, 896.07, 1141.22, 1200.29, 1265.36, 1421.84, 1681.12, 2305.57, 2987.00, 3051.31, 3445.91.

(S)-2-benzyl-1-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3j)



This product was obtained in 79% yield as a white solid after chromatography and 65% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, $\lambda=225\text{nm}$, t (major)=7.8 min, t (minor)=11.2 min]. $[\alpha]_{\text{D}}^{25} = -16.7$ ($c=1.0$, CH_2Cl_2); **HRMS** (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 345.1308; Found: 345.1302. ^1H NMR (500 MHz, CDCl_3) δ 2.72-2.77(m, 1H), 2.82-2.91(m, 2H), 3.26-3.31(m, 1H), 3.50(d, $J=14.0\text{Hz}$, 1H), 4.02(d, $J=14.0\text{Hz}$, 1H), 5.50(s, 1H), 7.02-7.03(m, 1H), 7.12-7.19(m, 3H), 7.25(d, $J=7.5\text{Hz}$, 1H), 7.30-7.34(m, 2H), 7.36(t, $J=7.5\text{Hz}$, 2H), 7.46(d, $J=6.0\text{Hz}$, 3H), 7.53(d, $J=7.5\text{Hz}$). ^{13}C NMR (125 MHz, CDCl_3) δ 145.97, 139.24, 136.21, 133.94, 128.72, 128.28, 127.23, 127.03, 126.26, 126.24, 126.19, 121.71, 119.41, 118.47, 110.88, 108.58, 59.17, 58.20, 47.86, 20.81.

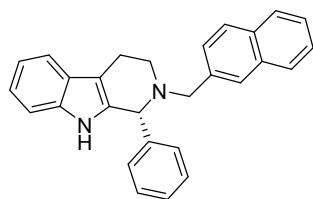
(R)-2-benzyl-1-cyclohexyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3k)



This product was obtained in 82% yield as a white solid after chromatography and 78% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 90:10, 0.8mL/min, $\lambda=225\text{nm}$, t (minor)=5.9 min, t (major)=6.4 min]. $[\alpha]_{\text{D}}^{25} = +21.89$ ($c=1.0$, CH_2Cl_2); **HRMS** (ESI-TOF) calcd for $\text{C}_{24}\text{H}_{29}\text{N}_2$ $[\text{M}+\text{H}]^+$: 345.2318; Found: 345.2322. ^1H NMR (600 MHz, CDCl_3) δ 0.88-0.95(m, 1H), 1.05-1.10(m, 2H), 1.14-1.30(m, 5H), 1.68-1.87(m, 7H), 2.30(d, $J=13.2\text{Hz}$, 1H), 2.53-2.57(m, 1H), 2.98-3.05(m, 2H),

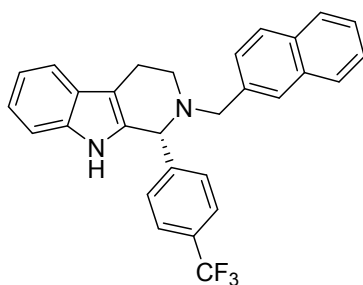
3.23(d, $J=9.0\text{Hz}$, 1H), 3.31-3.34(m, 1H), 3.610(d, $J=13.2\text{Hz}$, 1H), 3.76(d, $J=13.2\text{Hz}$, 1H), 7.14-7.18(m, 1H), 7.18-7.21(m, 1H), 7.27(t, $J=7.2\text{Hz}$, 1H), 7.32-7.38(m, 5H), 7.56(d, $J=7.8\text{Hz}$, 1H), 7.67(s, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 140.13, 135.57, 134.56, 129.14, 128.14, 127.33, 126.92, 121.40, 119.21, 118.14, 110.59, 107.70, 104.38, 62.15, 57.59, 43.79, 42.72, 41.93, 31.17, 31.00, 27.12, 26.60, 26.54, 26.45, 26.41, 25.73, 17.15.

(*R*)-2-(naphthalen-2-ylmethyl)-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3l)



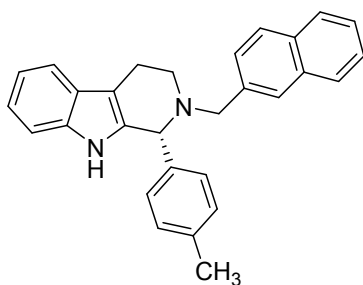
This product was obtained in 90% yield as a white solid after chromatography and 99% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, $\lambda=225\text{nm}$, t (major)=7.6 min, t (minor)=13.2 min]. $[\alpha]_{\text{D}}^{25} = -61.89$ ($c=1.0$, CH_2Cl_2); **HRMS** (ESI-TOF) calcd for $\text{C}_{28}\text{H}_{25}\text{N}_2$ $[\text{M}+\text{H}]^+$: 389.2012; Found: 389.2018. ^1H NMR (600 MHz, CDCl_3) δ 2.75-2.76(m, 1H), 2.86-2.91(m, 2H), 3.26-3.29(m, 1H), 3.87(d, $J=13.2\text{Hz}$, 1H), 4.34(d, $J=13.8\text{Hz}$, 1H), 4.76(s, 1H), 7.13-7.19(m, 2H), 7.23(d, $J=7.2\text{Hz}$, 1H), 7.35(s, 1H), 7.37-7.38(m, 1H), 7.39-7.45(m, 3H), 7.47-7.49(m, 3H), 7.49-7.51(m, 1H), 7.57(d, $J=7.2\text{Hz}$, 1H), 7.61(d, $J=7.2\text{Hz}$, 1H), 7.81(d, $J=8.4\text{Hz}$, 1H), 7.87(d, $J=7.8\text{Hz}$, 1H), 8.08(d, $J=8.4\text{Hz}$, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 141.34, 136.31, 135.00, 134.71, 133.82, 132.40, 129.42, 128.63, 128.39, 128.18, 127.77, 127.22, 127.19, 125.55, 125.28, 124.69, 121.58, 119.40, 118.35, 110.85, 109.39, 65.22, 56.59, 48.19, 20.92. IR: 705.33, 746.45, 896.01, 1142.43, 1205.67, 1265.28, 1421.71, 1683.23, 2305.52, 2987.12, 3054.40, 3446.79.

(*R*)-2-(naphthalen-2-ylmethyl)-1-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3m)



This product was obtained in 92% yield as a white solid after chromatography and 69% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 80:20, 0.8mL/min, λ =225nm, *t* (major)=6.6 min, *t* (minor)=12.5 min]. $[\alpha]_D^{25}$ = -51.89(*c*=1.2, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₉H₂₄N₂F₃ [M+H]⁺: 457.1852; Found: 457.1858. **¹H NMR** (600 MHz, CDCl₃) δ 2.72-2.76(m, 1H), 2.85-2.88(m, 1H), 2.92-2.95(m, 1H), 3.24-3.27(m, 1H), 3.46(d, *J*=13.8Hz, 1H), 3.87(d, *J*=13.8Hz, 1H), 4.76(s, 1H), 7.14-7.19(m, 2H), 7.24(d, *J*=7.2Hz, 1H), 7.30-7.32(m, 1H), 7.36-7.38(m, 4H), 7.57(s, 1H), 7.59(d, *J*=8.4Hz, 2H), 7.65(d, *J*=7.8Hz, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 145.85, 139.12, 136.39, 133.60, 130.43, 130.21, 129.33, 128.69, 128.38, 127.18, 127.07, 125.75, 125.73, 125.01, 123.21, 121.90, 119.61, 118.47, 110.91, 109.48, 63.78, 58.38, 48.01, 20.91.

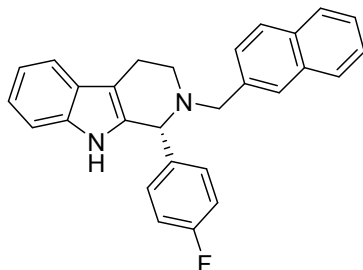
(*R*)-2-(naphthalen-2-ylmethyl)-1-(*p*-tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3n)



This product was obtained in 81% yield as a white solid after chromatography and 76% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 95:5, 0.8mL/min, λ =254nm, *t* (major)=12.8 min, *t* (minor) =21.3 min]. $[\alpha]_D^{25}$ = -39.1(*c*=1.1, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₉H₂₇N₂ [M+H]⁺: 403.2152; Found: 403.2159. **¹H NMR** (600 MHz, CDCl₃) δ 2.39(s, 3H), 2.65-2.70(m, 1H), 2.80-2.83(m, 1H), 2.92-2.94(m, 1H), 3.24-3.27(m, 1H), 3.69(d, *J*=7.8Hz, 1H), 3.92(d, *J*=7.8Hz, 1H), 4.64(s, 1H), 7.12-7.15(m, 2H), 7.20(d, 7.2Hz, 3H), 7.26-7.29(m, 2H), 7.33-7.39(m, 7H), 7.54(d, *J*=7.2Hz, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 139.68, 138.34, 137.80, 136.28, 135.17, 129.46, 128.97, 128.72, 128.23, 127.26, 126.89, 121.44, 119.32,

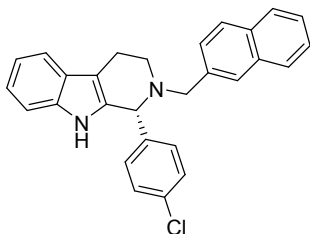
118.29, 110.79, 108.87, 64.42, 58.28, 48.46, 21.28, 21.21.

(R)-1-(4-fluorophenyl)-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3o)



This product was obtained in 93% yield as a white solid after chromatography and 87% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 70:30, 0.8mL/min, λ =225nm, *t* (major)=7.3 min, *t* (minor)=12.2 min]. $[\alpha]_D^{25}$ = -59.3(*c*=1.2, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₈H₂₄FN₂[M+H]⁺:407.1847; Found: 407.1843. **¹H NMR** (600 MHz, CDCl₃) δ 2.76-2.80(m, 1H), 2.85-2.89(m, 1H), 2.92-2.97(m, 1H), 3.28-3.32(m, 1H), 3.59(d, *J*=13.2Hz, 1H), 4.05(d, *J*=13.2Hz, 1H), 4.73(s, 1H), 7.10-7.13(m, 2H), 7.15-7.21(m, 2H), 7.25(d, *J*=7.2Hz, 1H), 7.30(s, 1H), 7.45-7.47(m, 2H), 7.51-7.55(m, 3H), 7.59(d, *J*=7.8Hz, 1H), 7.81(s, 1H), 7.86-7.90(m, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 163.39, 161.75, 137.28, 137.26, 137.04, 136.35, 134.39, 133.39, 132.86, 130.68, 130.63, 128.05, 127.76, 127.72, 127.32, 127.21, 127.08, 126.07, 125.66, 121.75, 119.53, 118.44, 115.75, 115.60, 110.89, 109.27, 63.51, 58.38, 48.05, 20.96.

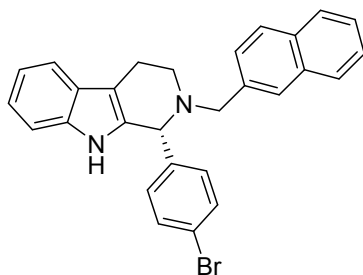
(R)-1-(4-chlorophenyl)-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3p)



This product was obtained in 84% yield as a white solid after chromatography and 31% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 70:30, 0.8mL/min, λ =225nm, *t* (major) =7.5 min, *t* (minor)=12.1 min]. $[\alpha]_D^{25}$ = -35.8(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₈H₂₄ClN₂ [M+H]⁺: 423.1623; Found: 423.1620. **¹H NMR** (500 MHz, CDCl₃) δ 2.77-2.18(m, 1H), 2.86-2.88(m, 1H), 3.28-

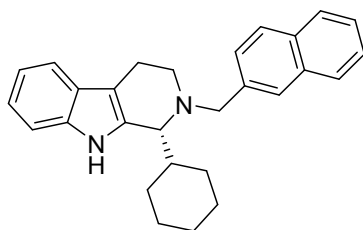
3.32(m, 1H), 3.60(d, $J=13.5\text{Hz}$, 1H), 4.04(d, $J=13.5\text{Hz}$, 1H), 4.71(s, 1H), 7.17-7.23(m, 2H), 7.24-7.26(m, 1H), 7.31(s, 1H), 7.40-7.44(m, 4H), 7.51-7.57(m, 3H), 7.60-7.62(m, 1H), 7.82(s, 1H), 7.88(t, $J=8.5, 10.0\text{Hz}$, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 140.07, 136.86, 136.32, 133.97, 133.76, 133.33, 132.81, 130.34, 128.89, 127.99, 127.69, 127.65, 127.26, 127.12, 126.99, 126.01, 125.60, 121.73, 119.49, 118.37, 110.84, 109.27, 63.45, 58.36, 47.89, 20.85.

(*R*)-1-(4-bromophenyl)-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3q)



This product was obtained in 87% yield as a white solid after chromatography and 23% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 90:10, 0.8mL/min, $\lambda=225\text{nm}$, t (major)=13.9 min, t (minor)=29.1 min]. $[\alpha]_{\text{D}}^{25} = -31.4$ ($c=1.2$, CH_2Cl_2); **HRMS** (ESI-TOF) calcd for $\text{C}_{28}\text{H}_{24}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 467.1023; Found: 467.1020. ^1H NMR (600 MHz, CDCl_3) δ 2.53-2.56(m, 1H), 2.63-2.69(m, 2H), 3.02-3.05(m, 1H), 3.37-3.41(m, 1H), 3.75-3.79(m, 1H), 4.56(s, 1H), 6.90-6.96(m, 2H), 6.98-7.05(m, 2H), 7.25-7.28(m, 3H), 7.34-7.36(m, 3H), 7.40-7.43(m, 2H), 7.53(d, $J=10.2\text{Hz}$, 1H), 7.60-7.64(m, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.82, 136.73, 136.42, 133.46, 133.37, 132.89, 129.37, 128.12, 127.76, 127.71, 127.36, 127.11, 126.98, 126.12, 125.73, 121.94, 119.64, 118.49, 110.93, 109.56, 63.63, 58.56, 47.86, 20.79.

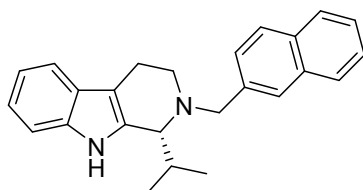
(*R*)-1-cyclohexyl-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-*b*]indole(3r)



This product was obtained in 91% yield as a white solid after chromatography and 92%

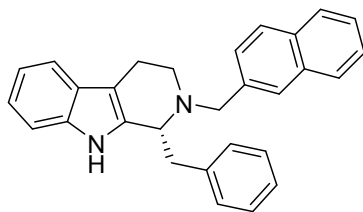
ee as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol=98:2, 0.8mL/min, λ =225nm, *t* (major)=16.1 min, *t* (minor)=17.7 min]. $[\alpha]_D^{25} = +51.4$ (c=1.1, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₈H₃₁N₂ [M+H]⁺: 395.2433; Found: 395.2428. **¹H NMR** (600 MHz, CDCl₃) δ 0.81-0.87(m, 2H), 0.95-0.99(m, 1H), 1.06-1.25(m, 4H), 1.60-1.75(m, 6H), 2.29(d, *J*=13.2Hz, 1H), 2.51-2.54(m, 1H), 2.95-3.06(m, 2H), 3.19(m, 1H), 3.31-3.36(m, 1H), 3.71(d, *J*=13.2Hz, 1H), 3.86(d, *J*=13.2Hz, 1H), 7.10-7.12(m, 1H), 7.15-7.17(m, 1H), 7.30(d, *J*=7.8Hz, 1H), 7.41-7.45(m, 2H), 7.53(d, *J*=8.4Hz, 1H), 7.58-7.63(m, 3H), 7.74-7.76(m, 1H), 7.79-7.82(m, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 137.71, 135.60, 134.52, 133.32, 132.86, 127.79, 127.73, 127.70, 127.43, 127.36, 125.90, 125.52, 121.43, 119.24, 118.17, 110.61, 107.67, 61.96, 57.71, 44.02, 42.72, 31.18, 31.01, 29.78, 26.57, 26.46, 26.40, 17.21. IR: 705.42, 738.60, 895.95, 1265.30, 1421.81, 1636.01, 2305.42, 2986.89, 3054.32, 3455.35.

(*R*)-1-isopropyl-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3s)



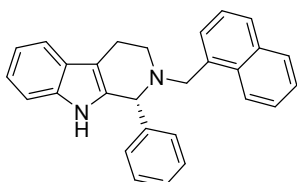
This product was obtained in 88% yield as a white solid after chromatography and 85% *ee* as determined by HPLC [Daicel Chiralpak OD-H, n-hexane/i-propanol= 80:20, 0.8mL/min, λ =225nm, *t* (major)=7.1 min, *t* (minor)=8.1 min]. $[\alpha]_D^{25} = +38.8$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₅H₂₇N₂ [M+H]⁺: 355.2123; Found: 355.2129. **¹H NMR** (600 MHz, CDCl₃) δ 0.88-1.10(m, 6H), 1.20-1.25(m, 1H), 2.00(d, *J*=6.6Hz, 1H), 2.52(d, *J*=15.6Hz, 1H), 2.97-3.32(m, 3H), 3.68-3.89(m, 2H), 7.11-7.18(m, 2H), 7.32(d, *J*=7.8Hz, 1H), 7.43-7.45(m, 2H), 7.54(d, *J*=7.2Hz, 1H), 7.59-7.65(m, 2H), 7.75-7.81(m, 2H). **¹³C NMR** (150 MHz, CDCl₃) δ 137.67, 135.63, 134.66, 133.30, 132.83, 127.70, 127.66, 127.41, 125.89, 125.51, 121.44, 119.24, 118.16, 110.62, 107.95, 63.03, 57.85, 44.13, 33.11, 21.04, 20.45, 17.32.

(*R*)-1-benzyl-2-(naphthalen-2-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3t)



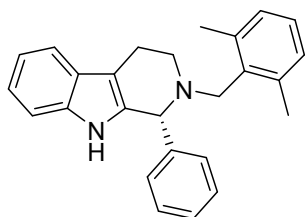
This product was obtained in 89% yield as a white solid after chromatography and 87% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 70:30, 0.8mL/min, λ =225nm, *t* (major)=7.3 min, *t* (minor)=8.0 min]. $[\alpha]_D^{25} = +42.3$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₉H₂₇N₂ [M+H]⁺: 403.2143; Found: 403.2147. **¹H NMR** (600 MHz, CDCl₃) δ 2.53-2.57(m, 1H), 2.86-2.93(m, 2H), 3.01-3.04(m, 1H), 3.18-3.21(m, 1H), 3.30-3.35(m, 1H), 3.85-3.91(m, 3H), 6.85(s, 1H), 6.98-7.04(m, 6H), 7.11(s, 1H), 7.15-7.18(m, 3H), 7.31(d, *J*=7.8Hz, 1H), 7.33-7.37(m, 2H), 7.43-7.45(m, 1H), 7.54(s, 1H), 7.62-7.65(m, 2H), 7.71-7.73(m, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 139.21, 135.62, 133.40, 132.86, 129.71, 128.54, 127.98, 127.84, 127.72, 127.11, 127.08, 127.06, 126.59, 125.94, 125.58, 121.54, 119.32, 118.20, 110.75, 107.89, 58.35, 57.57, 44.64, 41.22, 18.14.

(*R*)-2-(naphthalen-1-ylmethyl)-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3u)



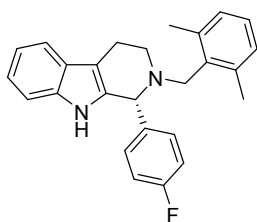
This product was obtained in 94% yield as a white solid after chromatography and 74% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 90:10, 0.8mL/min, λ =225nm, *t* (major)=10.4 min, *t* (minor)=12.5 min]. $[\alpha]_D^{25} = -62.6$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₈H₂₅N₂ [M+H]⁺: 389.2012; Found: 389.2007. **¹H NMR** (600 MHz, CDCl₃) δ 2.69-2.74(m, 1H), 2.80-2.91(m, 2H), 3.22-3.26(m, 1H), 3.83(d, *J*=16.2Hz, 1H), 4.30(d, *J*=15.6Hz, 1H), 4.73(s, 1H), 7.10-7.16(m, 2H), 7.21-7.22(m, 1H), 7.32-7.35(m, 2H), 7.36-7.37(m, 1H), 7.38-7.41(m, 1H), 7.42-7.48(m, 4H), 7.53-7.55(m, 1H), 7.58(d, *J*=8.4Hz, 1H), 7.77-7.79(d, *J*=10.2Hz, 1H), 7.84-7.85(d, *J*=9.6Hz, 1H), 8.04-8.06(d, *J*=10.2Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 141.32, 136.31, 134.97, 134.68, 133.80, 132.38, 129.39, 128.60, 128.36, 128.16, 127.74, 127.20, 127.18, 125.52, 125.25, 124.66, 121.55, 119.38, 118.31, 110.82, 109.36, 77.29, 77.03, 76.78, 65.19, 56.55, 48.15, 20.88.

(R)-2-(2,6-dimethylbenzyl)-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3v)



This product was obtained in 82% yield as a white solid after chromatography and 82% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 90:10, 0.8mL/min, λ =225nm, *t* (major)=8.3 min, *t* (minor)=7.6 min]. $[\alpha]_D^{25}$ = -42.7(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₈H₂₅N₂ [M+H]⁺: 367.2142; Found: 367.2147. **¹H NMR** (500 MHz, CDCl₃) δ 2.98(m, 2H), 3.04-3.08(m, 1H), 3.35-3.39(m, 1H), 3.78(s, 3H), 3.82(s, 3H), 3.90-3.98(m, 2H), 5.54(s, 1H), 6.41-6.43(m, 1H), 6.53(m, 1H), 7.12-7.17(m, 2H), 7.21-7.27(m, 2H), 7.31-7.38(m, 3H), 7.44(m, 5H), 7.55-7.59(m, 3H), 7.91(b, 1H), 8.10(d, *J*=9.0Hz, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 160.71, 158.67, 136.27, 132.92, 130.94, 130.02, 129.69, 128.23, 127.43, 126.83, 121.57, 119.28, 118.14, 110.88, 108.42, 104.84, 98.43, 57.22, 55.44, 55.30, 54.94, 46.77, 19.83.

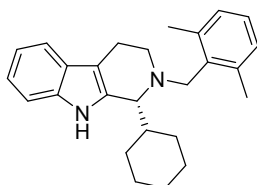
(R)-2-(2,6-dimethylbenzyl)-1-(4-fluorophenyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole(3w)



This product was obtained in 93% yield as a white solid after chromatography and 81% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/*i*-propanol= 95:5, 0.8mL/min, λ =225nm, *t* (major)=12.3 min, *t* (minor)=13.1 min]. $[\alpha]_D^{25}$ = -49.7(*c*=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₆H₂₆FN₂ [M+H]⁺: 385.2075; Found: 385.2067. **¹H NMR** (600 MHz, CDCl₃) δ 2.27(s, 6H), 2.69-2.73(m, 1H), 2.79-2.82(m, 2H), 3.07-3.11(m, 1H), 3.52(d, *J*=12.6Hz, 1H), 3.79(d, *J*=12.6Hz, 1H), 4.56(s, 1H), 7.01(d, *J*=7.8Hz, 1H), 7.08-7.15(m, 3H), 7.20(d, *J*=7.2Hz, 1H), 7.29-7.31(m, 3H), 7.31-7.34(m, 3H), 7.54(d, *J*=7.2Hz, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 141.26,

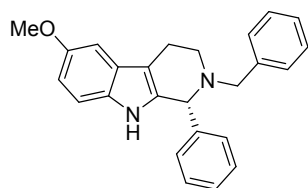
138.61, 136.25, 135.28, 134.67, 129.69, 128.27, 128.22, 128.01, 127.18, 126.97, 121.53, 119.37, 118.32, 110.87, 109.75, 64.87, 52.16, 46.98, 20.88, 20.53.

(R)-1-cyclohexyl-2-(2,6-dimethylbenzyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3x)



This product was obtained in 82% yield as a white solid after chromatography and 99% *ee* as determined by HPLC [Daicel Chiralpak OJ-H, n-hexane/i-propanol= 98:1.2, 0.8mL/min, λ =225nm, *t* (major)=18.4 min, *t* (minor)=31.1 min]. $[\alpha]_D^{25} = +42.7$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₆H₃₃N₂ [M+H]⁺: 373.2638; Found: 373.2644. **¹H NMR** (600 MHz, CDCl₃) δ 0.52-0.54(m, 1H), 0.97-1.06(m, 1H), 1.08-1.14(m, 3H), 1.25-1.31(m, 1H), 1.60-1.67(m, 5H), 1.98-2.00(m, 1H), 2.27(s, 6H), 2.60-2.64(m, 1H), 3.04-3.16(m, 3H), 3.39-3.43(m, 1H), 3.52-3.55(m, 1H), 3.85-3.88(m, 1H), 7.02-7.03(m, 2H), 7.09-7.10(m, 1H), 7.15-7.17(m, 1H), 7.19-7.25(m, 1H), 7.35-7.37(m, 1H), 7.59-7.60(m, 1H), 7.70(s, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 138.40, 135.80, 135.62, 134.81, 128.02, 127.46, 126.79, 121.33, 119.18, 118.17, 110.61, 107.88, 104.39, 77.32, 77.11, 76.89, 59.48, 50.14, 45.02, 42.25, 41.94, 31.00, 30.49, 27.13, 26.55, 26.46, 26.29, 26.20, 26.03, 25.74, 20.12, 17.49.

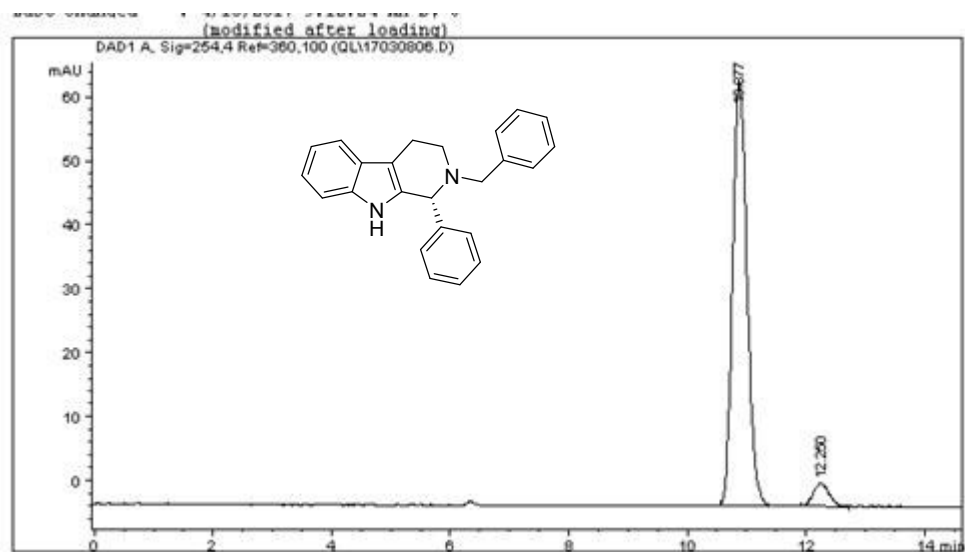
(S)-2-benzyl-6-methoxy-1-phenyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3y)



This product was obtained in 93% yield as a white solid after chromatography and 20% *ee* as determined by HPLC [Daicel Chiralpak AD-H, n-hexane/i-propanol= 90:10, 0.8mL/min, λ =225nm, *t* (major)=15.1 min, *t* (minor)=21.7 min]. $[\alpha]_D^{25} = -22.7$ (c=1.0, CH₂Cl₂); **HRMS** (ESI-TOF) calcd for C₂₅H₂₅N₂O [M+H]⁺: 369.1961; Found: 369.1963. **¹H NMR** (600 MHz, CDCl₃) δ 2.68-2.72(m, 1H), 2.79-2.82(m, 1H), 2.90-2.96(m, 1H), 3.25-3.29(m, 1H), 3.40(d, J=13.8Hz, 1H), 3.89(s, 3H), 3.92(d, J=13.8Hz,

1H), 4.68(s, 1H), 6.80-6.82(m, 1H), 7.02-7.03(m, 1H), 7.09(d, J=9.0Hz, 1H), 7.19(b, 1H), 7.28-7.30(m, 1H), 7.35-7.37(m, 3H), 7.39-7.41(m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 154.04, 141.38, 139.47, 135.77, 131.43, 129.03, 128.77, 128.25, 128.09, 127.59, 126.96, 64.65, 58.31, 56.01, 48.33, 21.21. IR: 705.25, 738.68, 895.96, 1265.31, 1421.76, 1634.69, 2305.33, 2987.16, 3054.50, 3449.53.

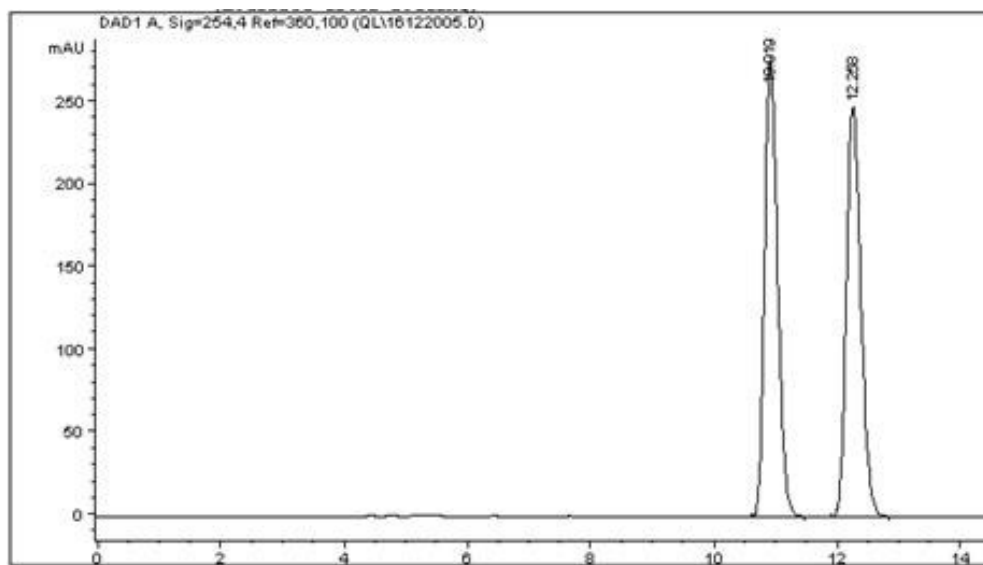
II. HPLC Spectra



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

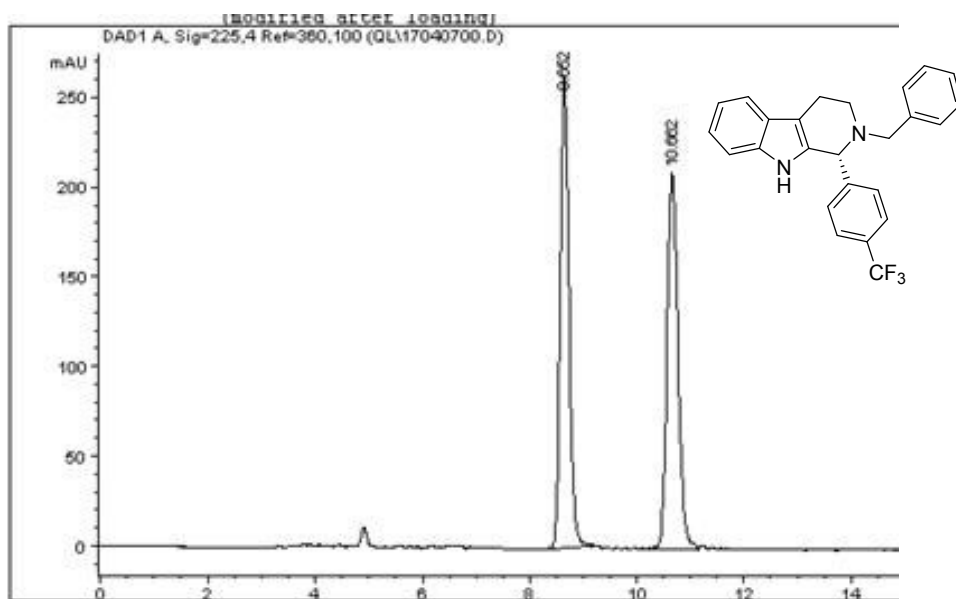
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.877	BB	0.2629	1118.40259	66.26492	94.4330
2	12.250	PB	0.2482	65.93214	3.59083	5.5670

Totals : 1184.33472 69.85575



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.919	BB	0.2270	4043.51904	275.86627	49.9974
2	12.258	BB	0.2546	4043.94165	247.51805	50.0026

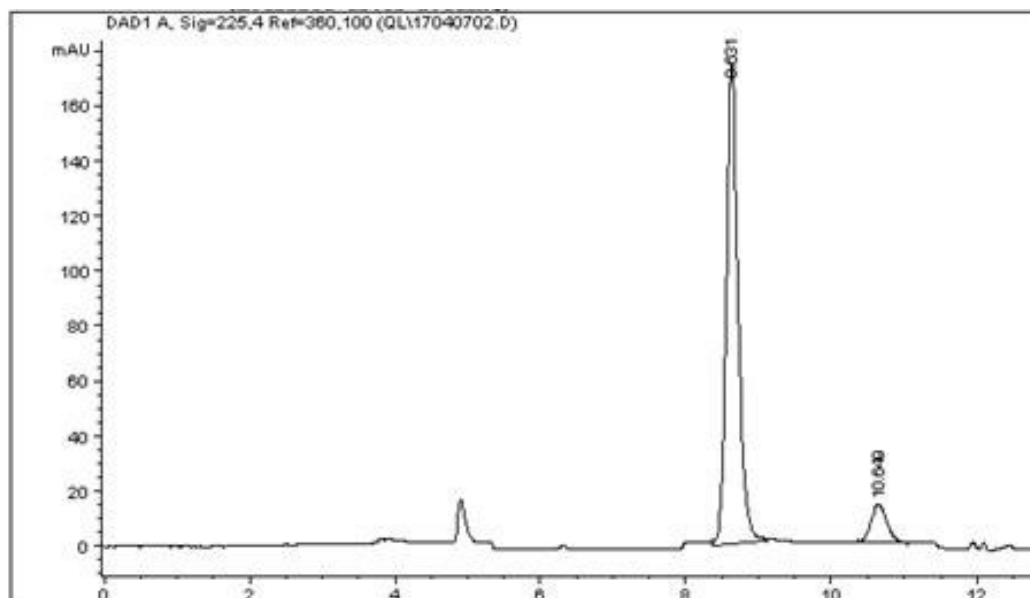
Totals : 8087.46069 523.38432



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.652	PB	0.1718	2934.78931	263.78473	49.4902
2	10.662	VV	0.2202	2995.24731	210.22977	50.5098

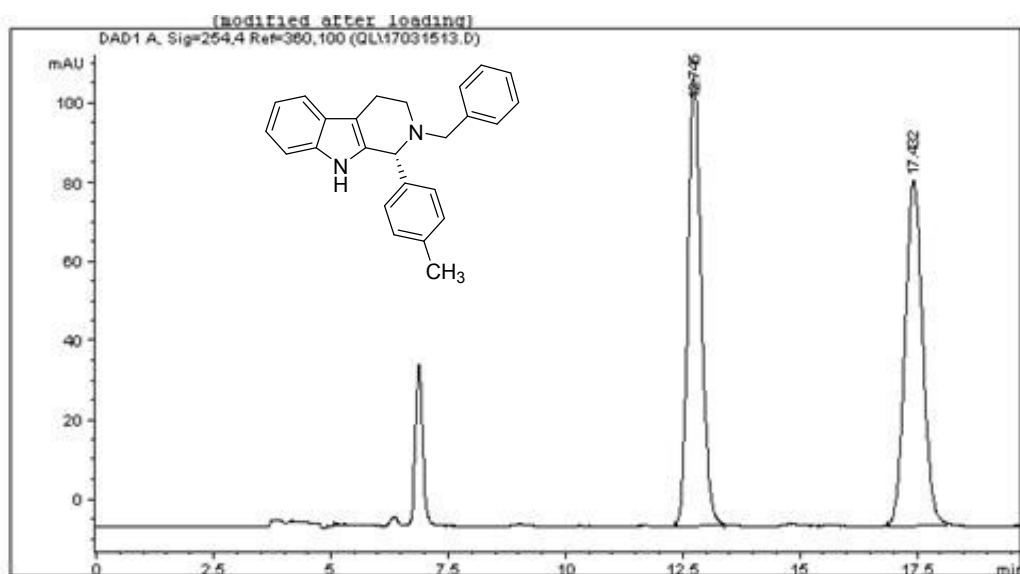
Totals : 5930.03662 474.01450



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.631	BB	0.1701	1979.02527	174.79721	90.5281
2	10.649	BB	0.2277	207.06453	14.06584	9.4719

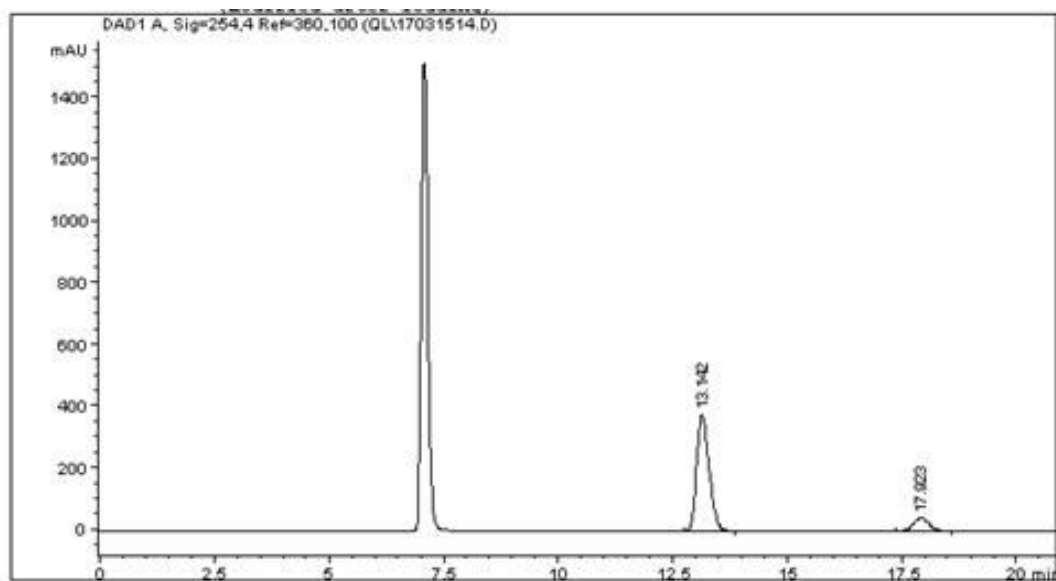
Totals : 2186.08980 188.86305



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.745	BB	0.3065	2261.14722	113.44754	49.9697
2	17.432	BB	0.4038	2263.88770	86.92844	50.0303

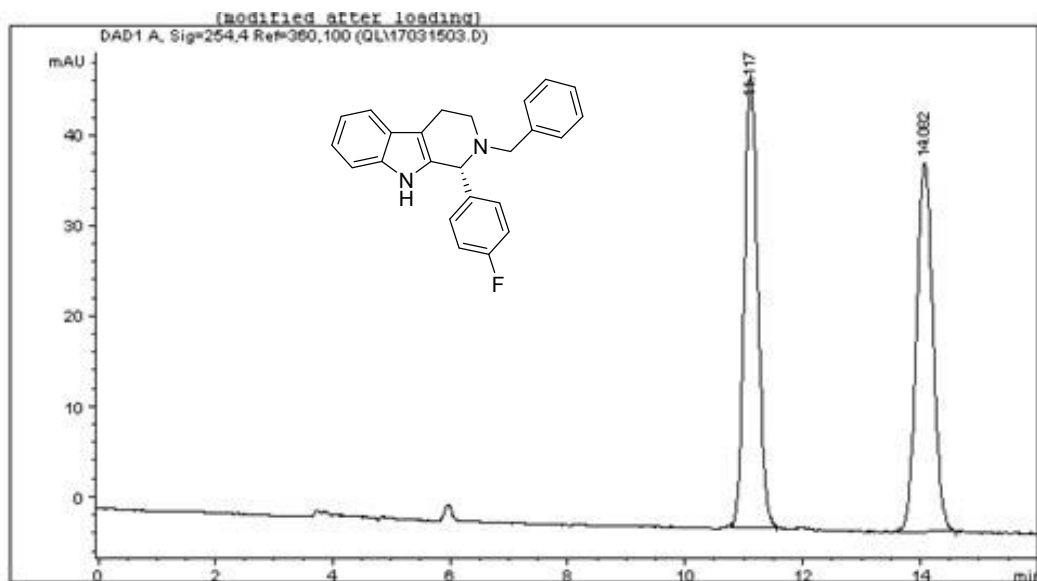
Totals : 4525.03491 200.37598



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.142	BB	0.2957	7152.24951	376.36246	87.0969
2	17.923	BB	0.3820	1059.57642	42.63131	12.9031

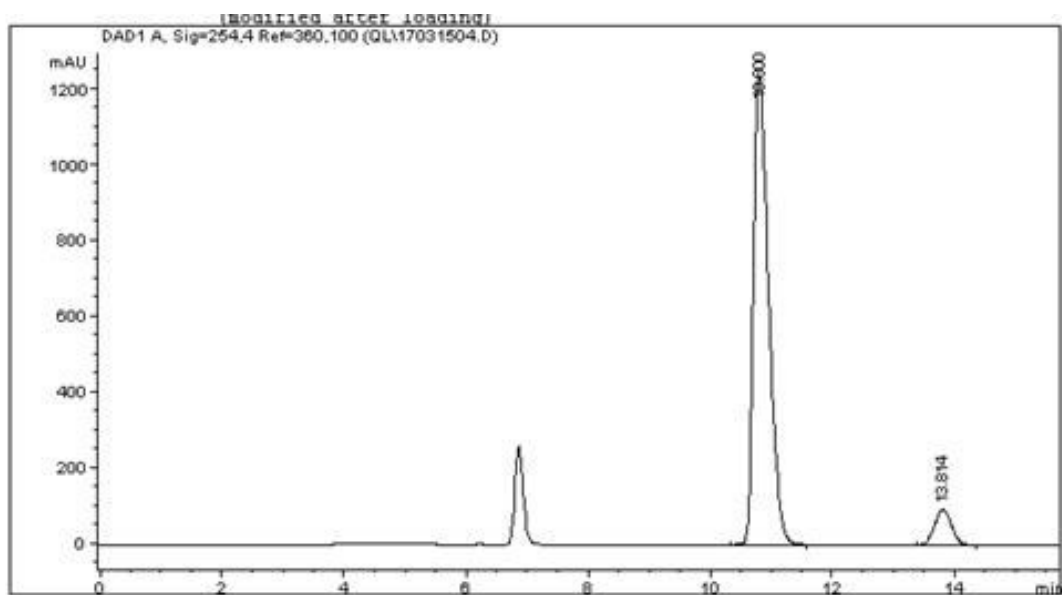
Totals : 8211.82593 418.99377



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.117	BB	0.2473	798.06152	50.24357	50.0647
2	14.082	BP	0.2954	795.99927	40.83504	49.9353

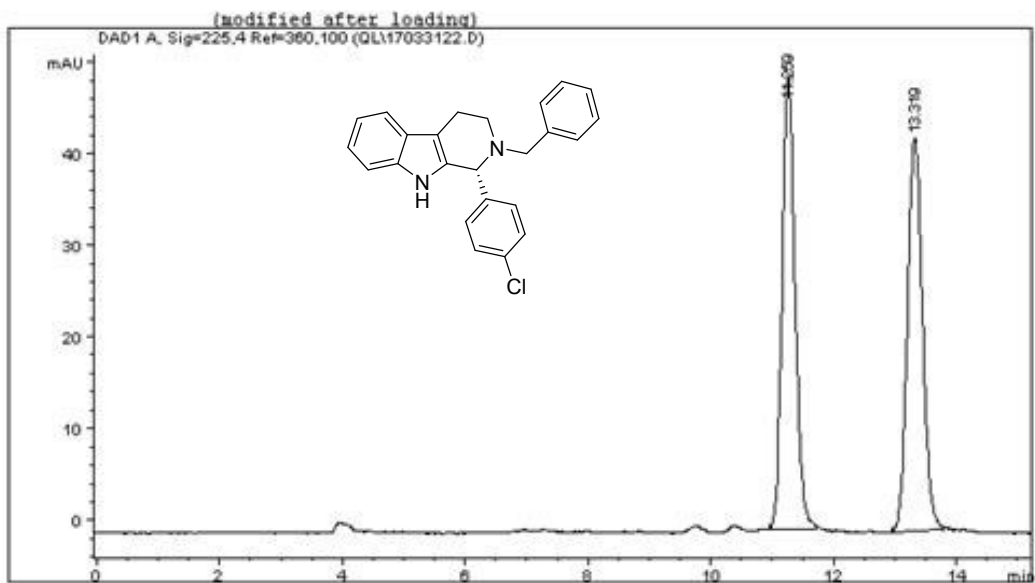
Totals : 1594.06079 91.07861



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.800	BB	0.2720	2.14711e4	1240.24365	92.1137
2	13.814	BB	0.3007	1838.24927	94.58796	7.8863

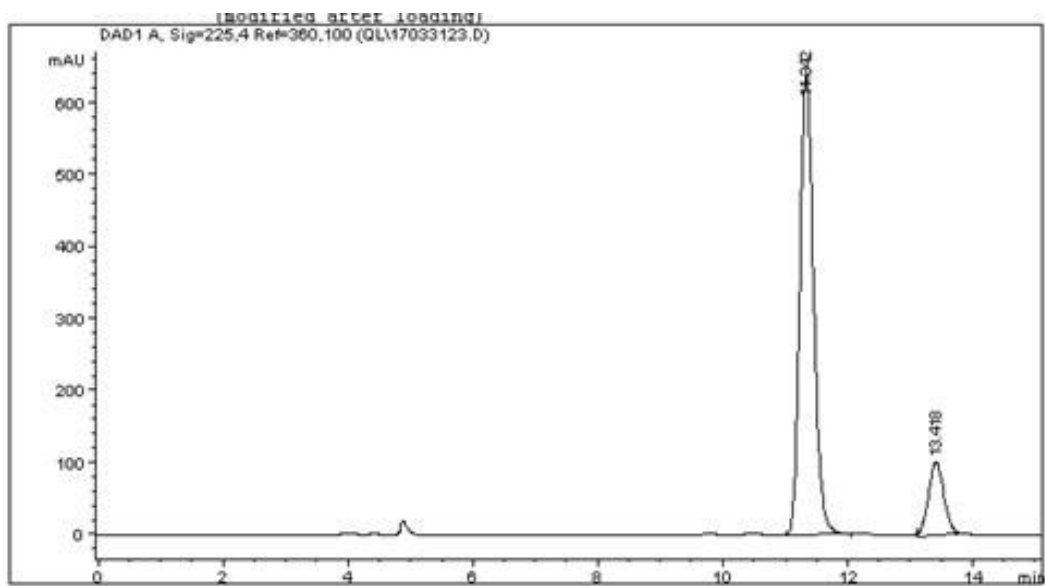
Totals : 2.33094e4 1334.83161



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.259	BB	0.2253	726.30432	49.47593	50.0113
2	13.319	BB	0.2624	725.97693	42.69013	49.9887

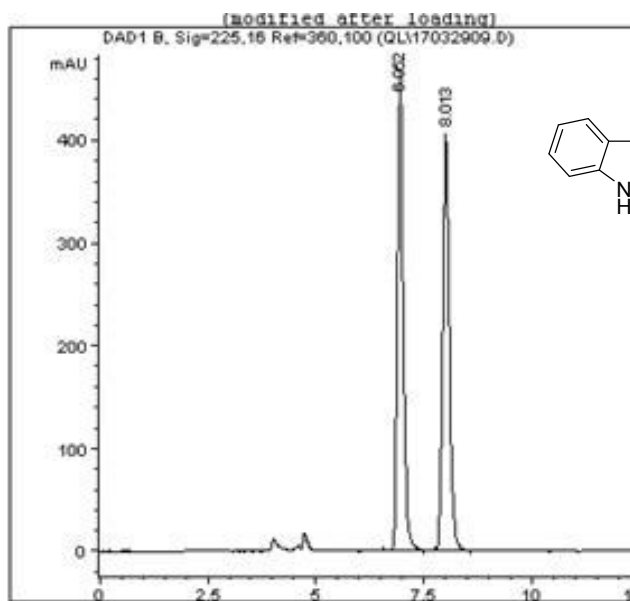
Totals : 1452.28125 92.16607



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.342	BB	0.2355	9752.93652	641.21844	84.9540
2	13.418	MM R	0.2836	1727.31873	101.50385	15.0460

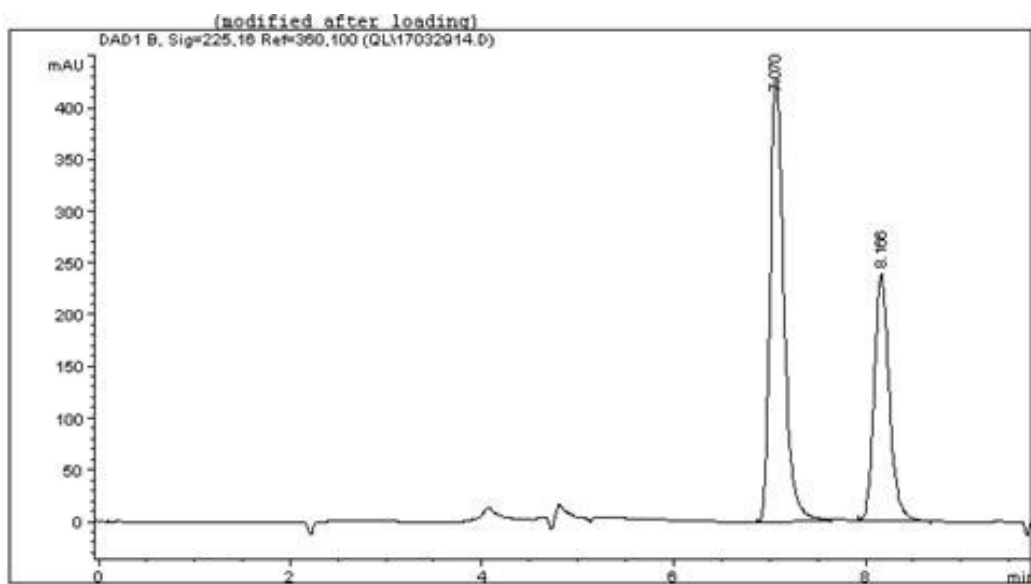
Totals : 1.14803e4 742.72230



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.952	PB	0.1445	4376.30957	461.91544	50.1342
2	8.013	PB	0.1649	4352.88867	406.72025	49.8658

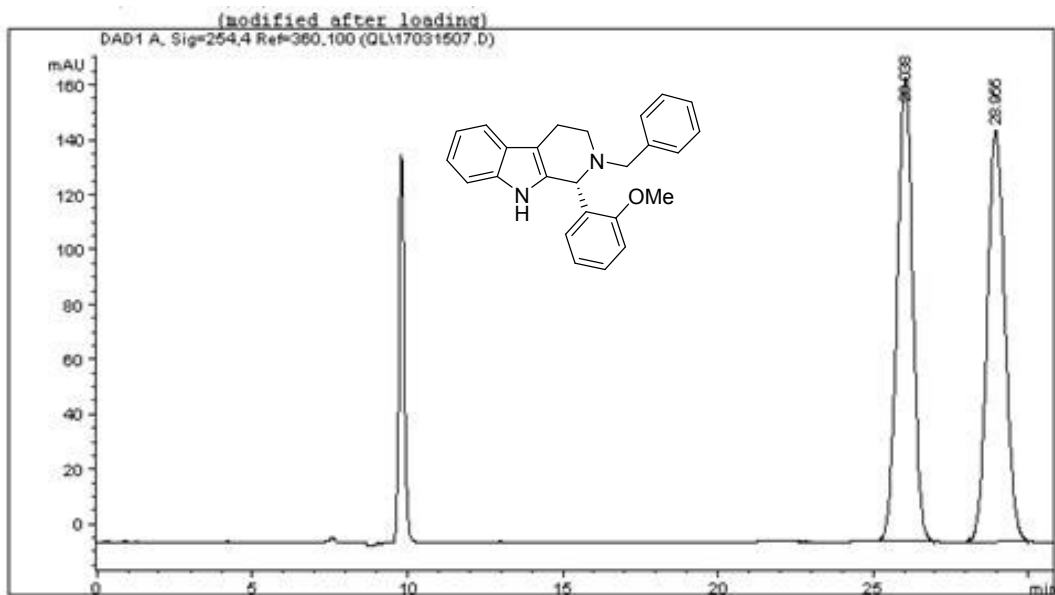
Totals : 8729.19824 868.63568



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.070	PB	0.1518	4270.34229	430.05682	62.1369
2	8.166	PB	0.1671	2602.13306	238.88309	37.8631

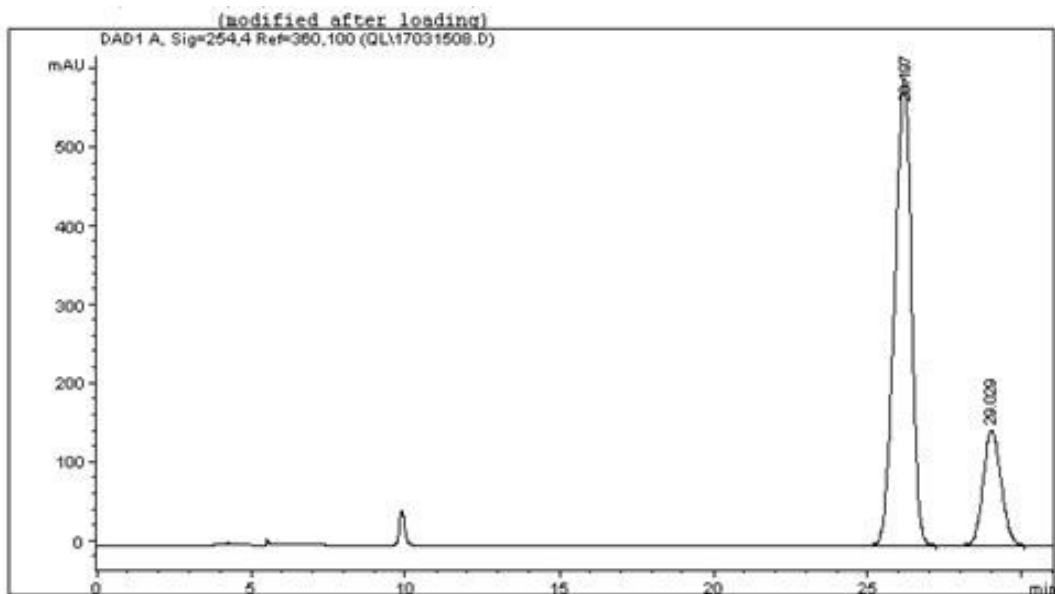
Totals : 6872.47534 668.93991



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.038	BB	0.5408	5917.55176	168.89098	49.9814
2	28.955	BB	0.6042	5921.95703	149.49207	50.0186

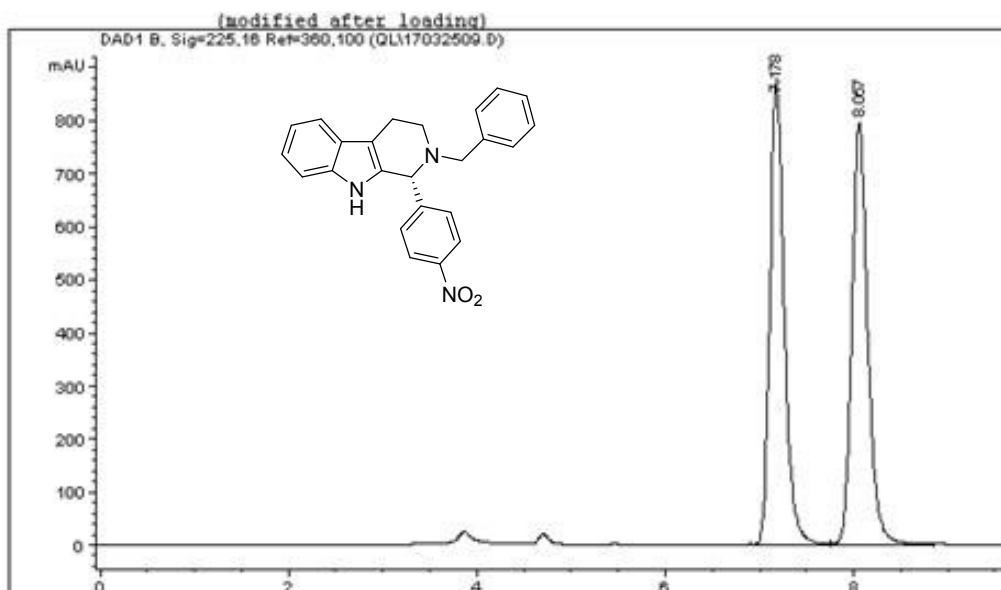
Totals : 1.18395e4 318.38304



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.197	BB	0.5916	2.24761e4	593.81097	79.0369
2	29.029	BB	0.6285	5961.35352	146.58566	20.9631

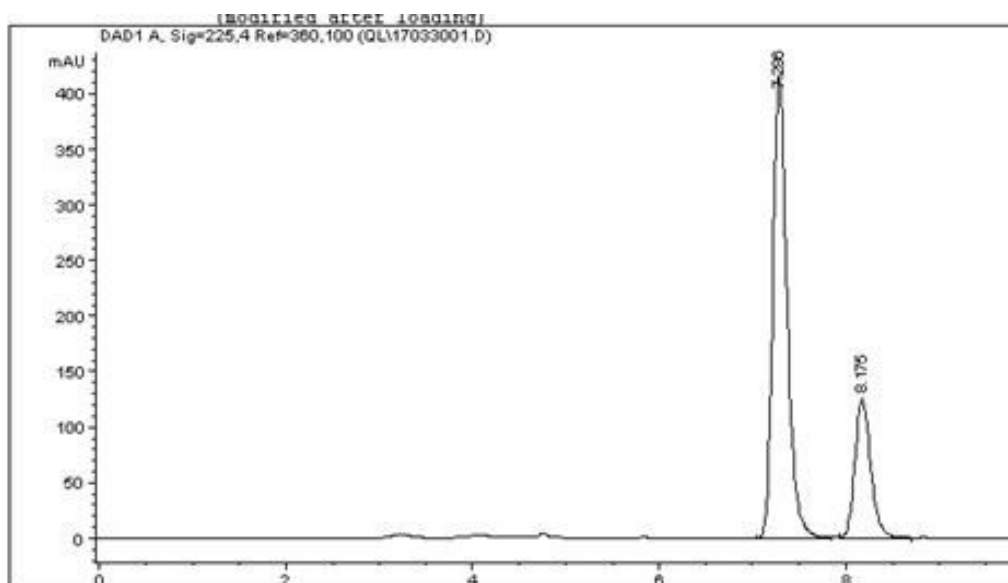
Totals : 2.84374e4 740.39664



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.178	BV	0.1607	9252.60156	879.50702	49.7971
2	8.057	VB	0.1787	9327.99219	796.01758	50.2029

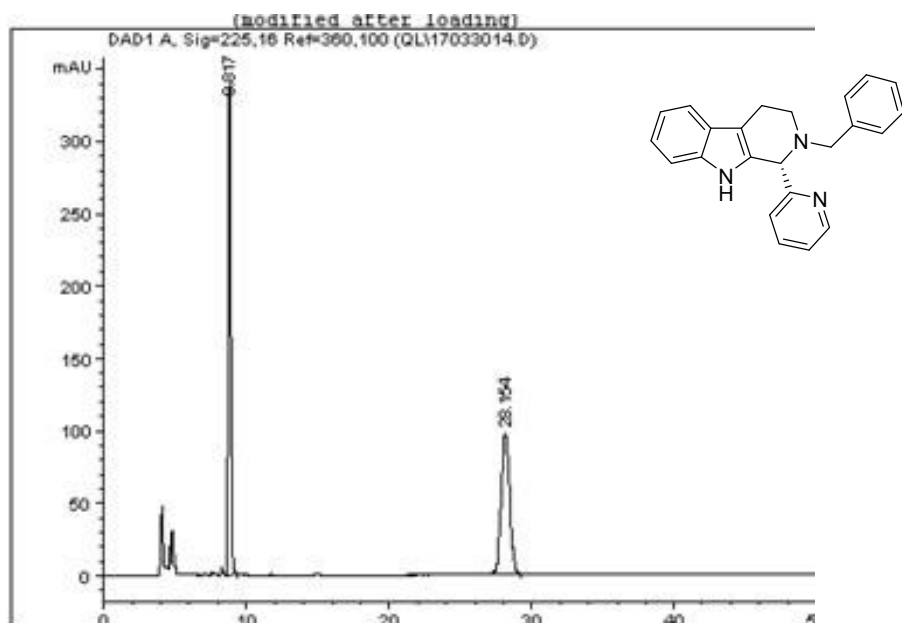
Totals : 1.85806e4 1675.52460



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.286	BB	0.1621	4446.21045	417.85513	74.9852
2	8.175	BB	0.1821	1483.23938	125.28889	25.0148

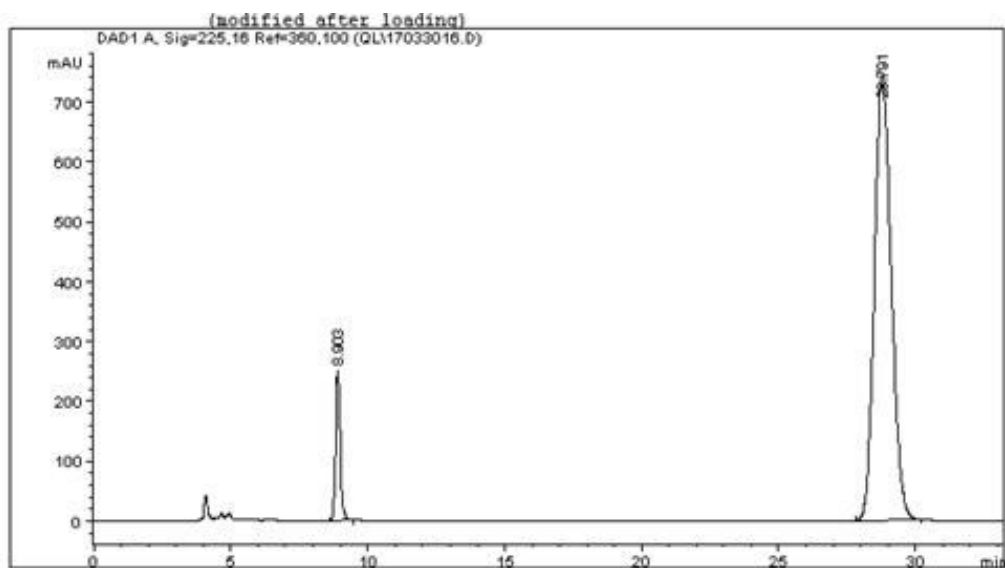
Totals : 5929.44983 543.14403



Signal 1: DAD1 A, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.817	BB	0.1775	3966.41357	341.48544	49.8341
2	28.154	BB	0.6309	3992.82861	97.67559	50.1659

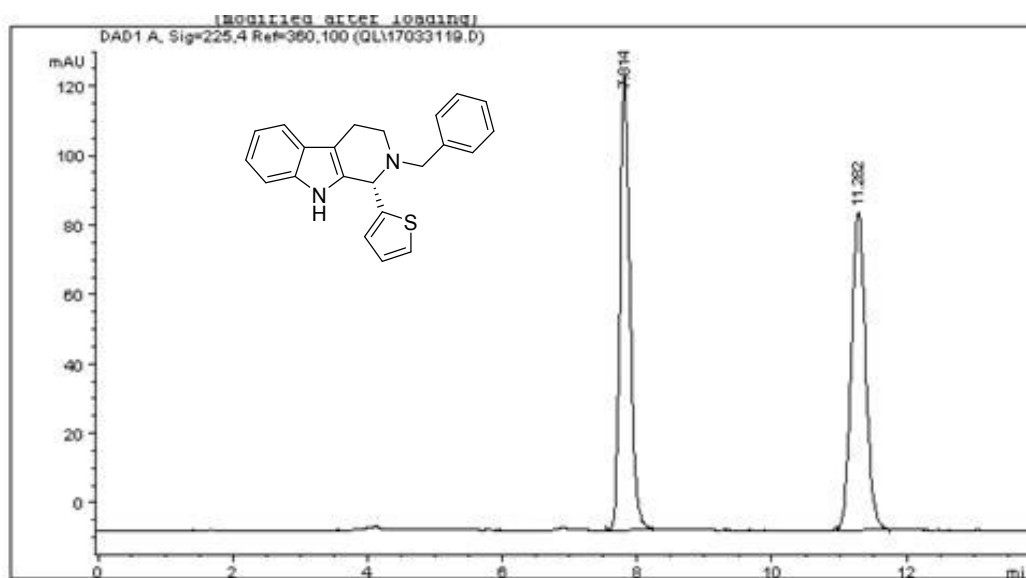
Totals : 7959.24219 439.16103



Signal 1: DAD1 A, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.903	PB	0.1837	2999.71313	250.47339	8.5989
2	28.791	BB	0.6684	3.18850e4	743.40369	91.4011

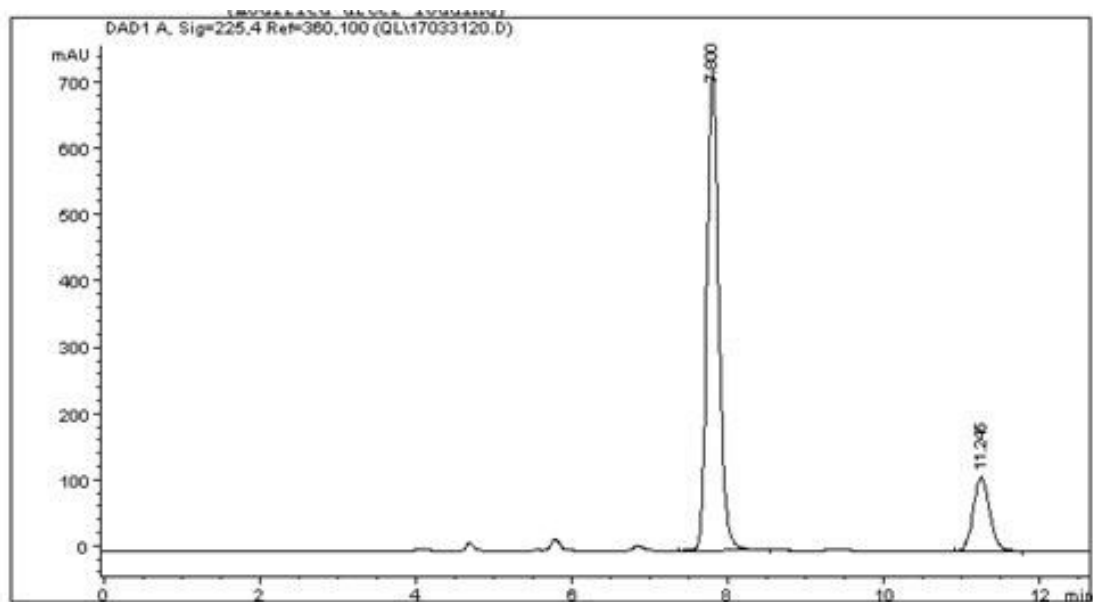
Totals : 3.48848e4 993.87708



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.814	BB	0.1579	1350.05078	131.34187	49.9797
2	11.282	BB	0.2281	1351.14758	91.60321	50.0203

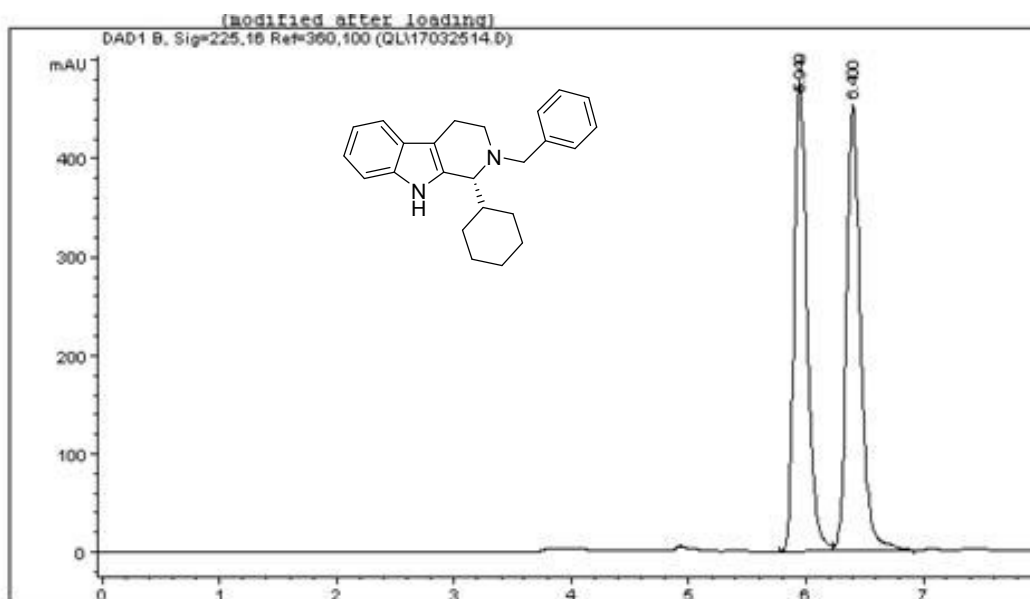
Totals : 2701.19836 222.94508



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.800	PB	0.1613	7701.92139	728.76111	82.5256
2	11.246	BB	0.2279	1630.84009	110.65745	17.4744

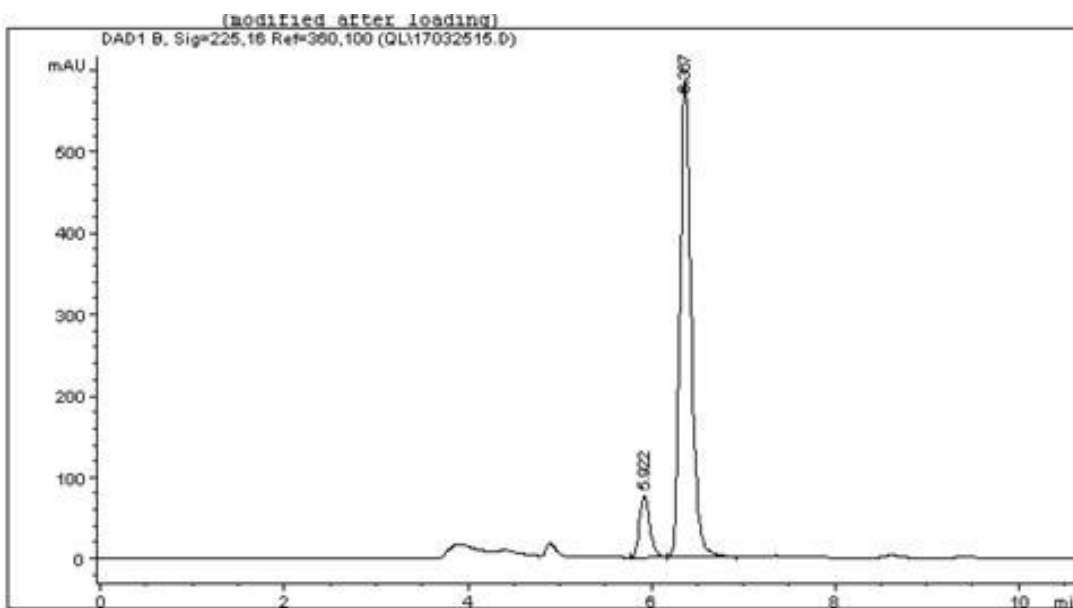
Totals : 9332.76147 839.41856



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.949	PV	0.1152	3685.00122	482.04904	49.2573
2	6.400	VB	0.1276	3796.12183	453.95169	50.7427

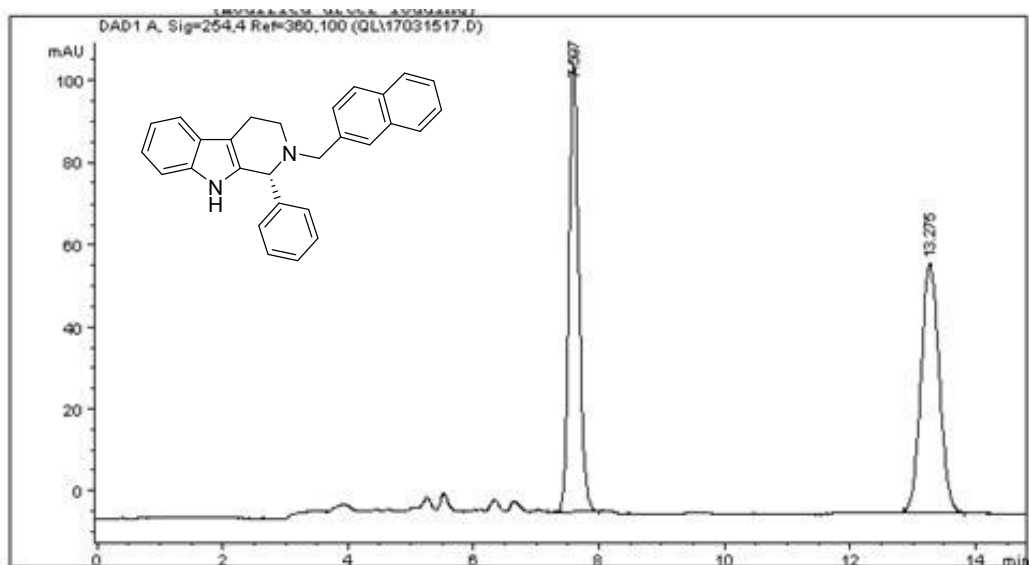
Totals : 7481.12305 936.00073



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.922	PV	0.1200	604.49060	76.68356	10.8082
2	6.367	VB	0.1289	4988.38135	588.58972	89.1918

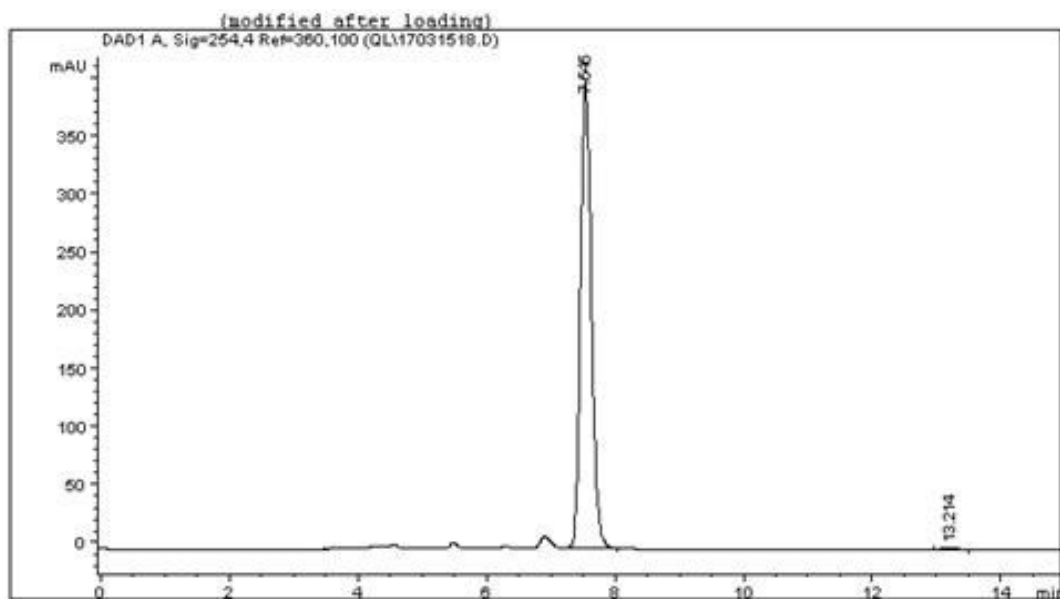
Totals : 5592.87195 665.27328



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.597	VB	0.1747	1224.05469	109.26099	50.0102
2	13.275	BB	0.3127	1223.55298	60.83273	49.9898

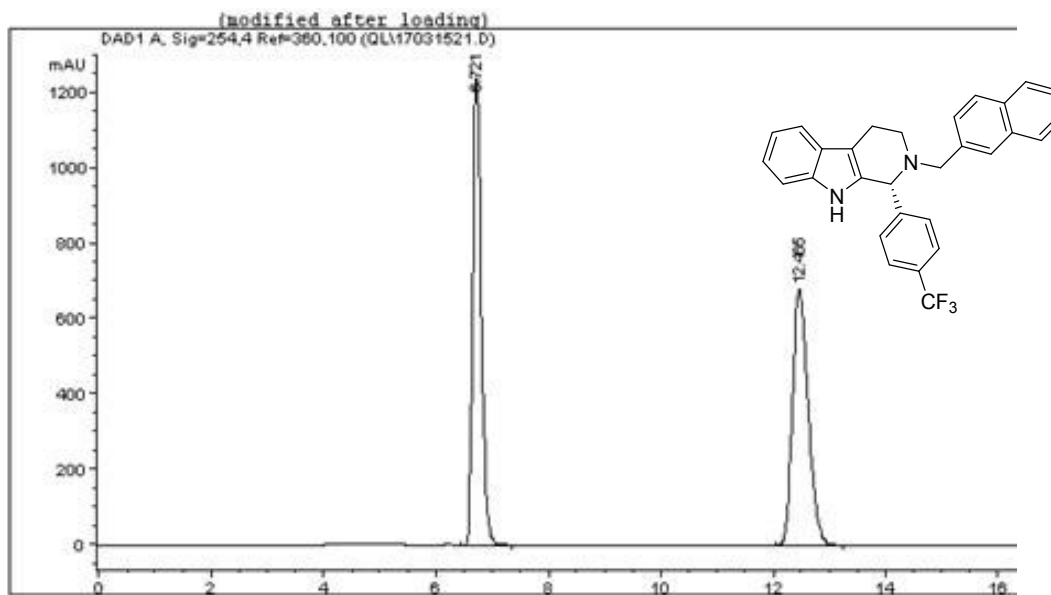
Totals : 2447.60767 170.09372



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.545	PB	0.1772	4687.60352	404.35477	99.5399
2	13.214	MM R	0.3371	21.66702	1.07120	0.4601

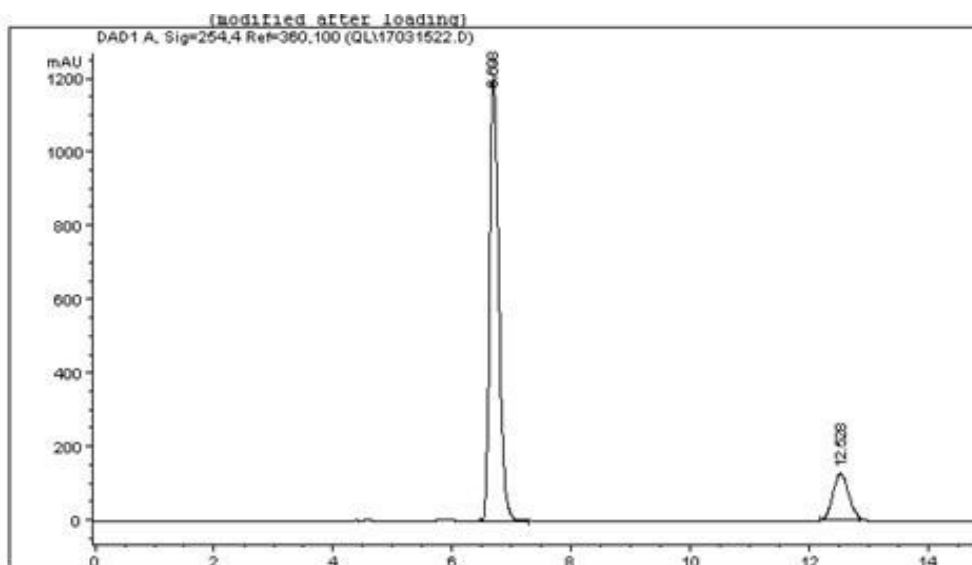
Totals : 4709.27054 405.42597



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.721	VB	0.1617	1.29375e4	1240.41443	49.3829
2	12.465	BB	0.3033	1.32608e4	680.69025	50.6171

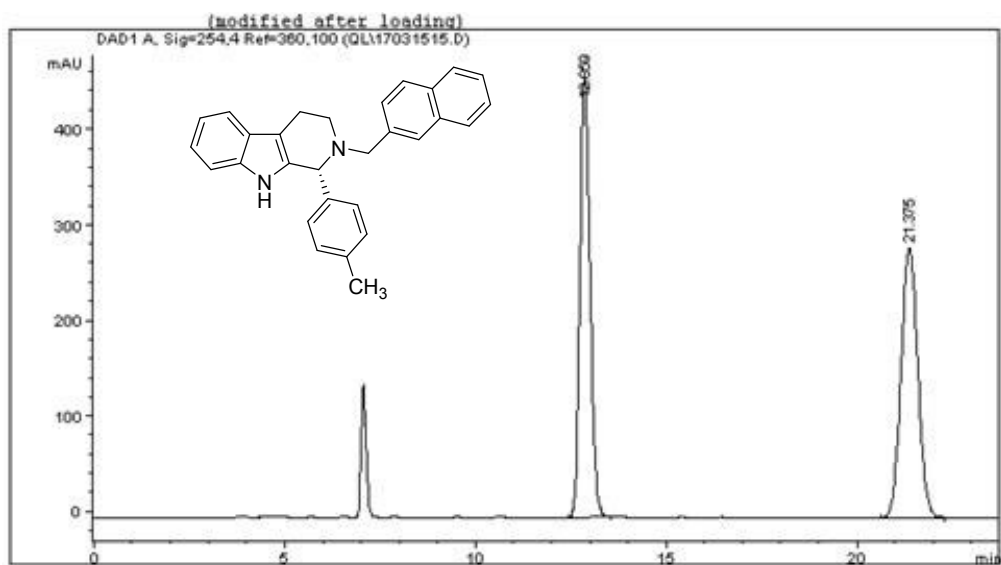
Totals : 2.61982e4 1921.10468



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.698	PB	0.1639	1.28936e4	1214.29700	84.9497
2	12.528	MM R	0.3032	2284.33179	125.56242	15.0503

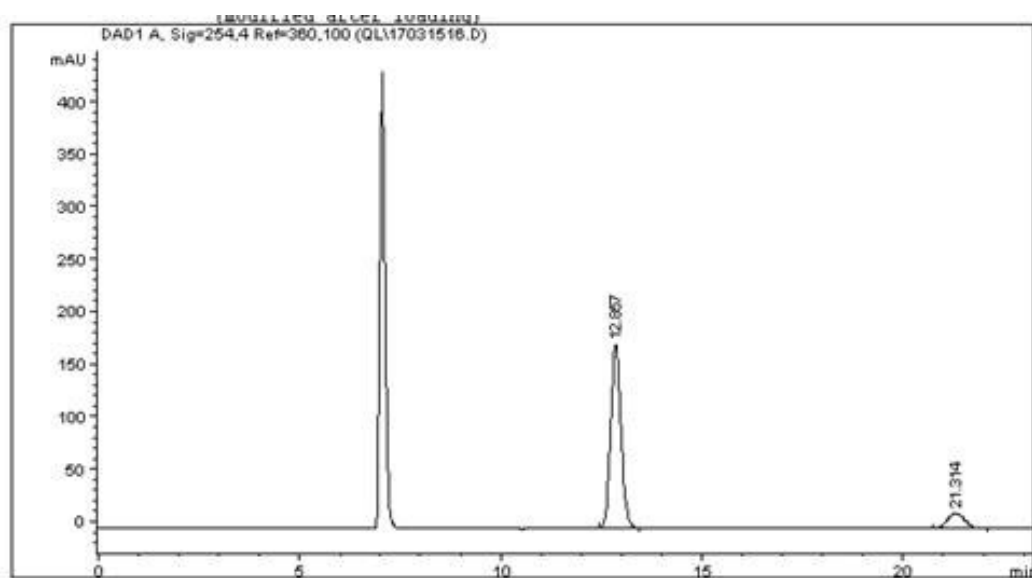
Totals : 1.51780e4 1339.85942



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.859	BB	0.2857	8547.62207	462.37381	49.8238
2	21.375	BB	0.4802	8608.07520	281.91815	50.1762

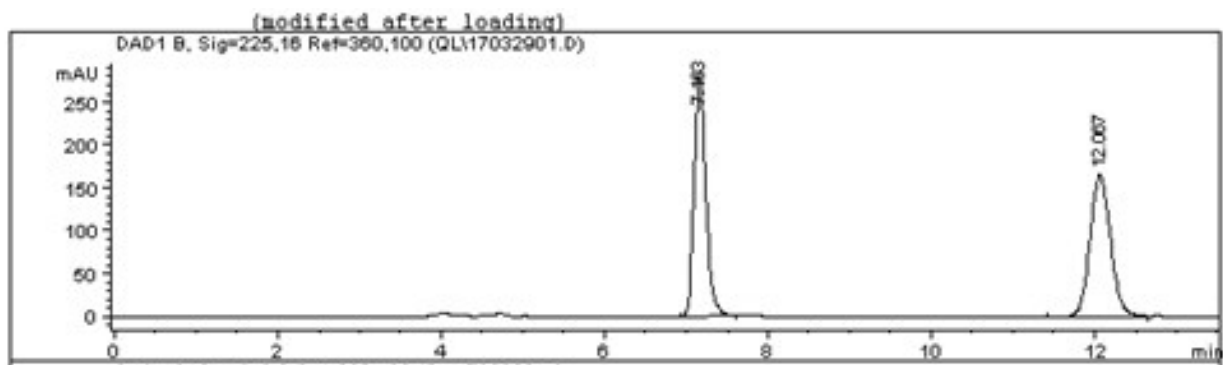
Totals : 1.71557e4 744.29196



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.857	BB	0.2806	3137.13721	173.79868	88.0497
2	21.314	BB	0.4183	425.77960	14.26348	11.9503

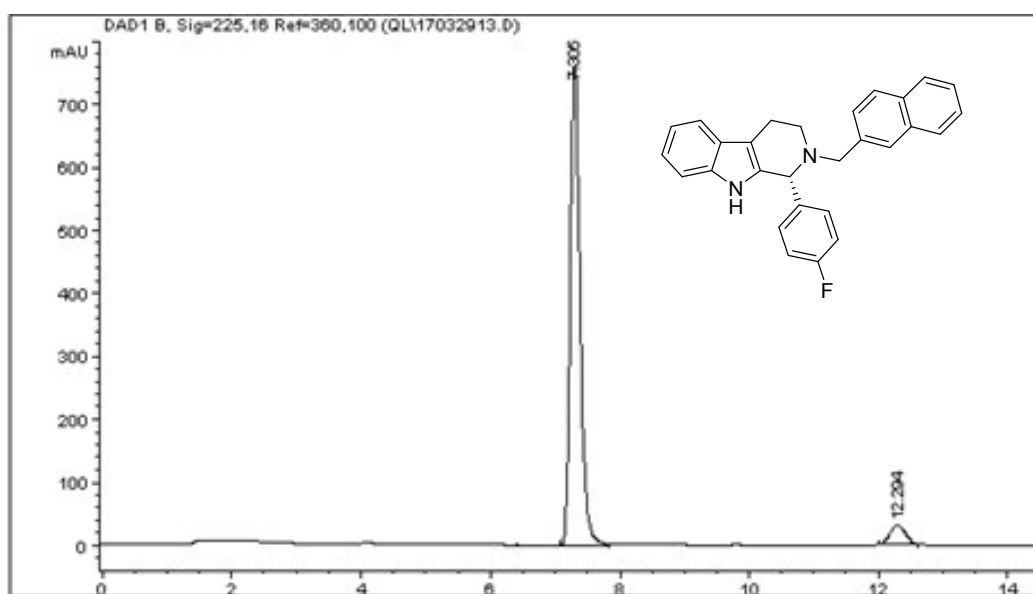
Totals : 3562.91681 188.06216



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.163	PB	0.1525	2821.78833	282.64340	49.5102
2	12.067	VB	0.2682	2877.62500	164.41800	50.4898

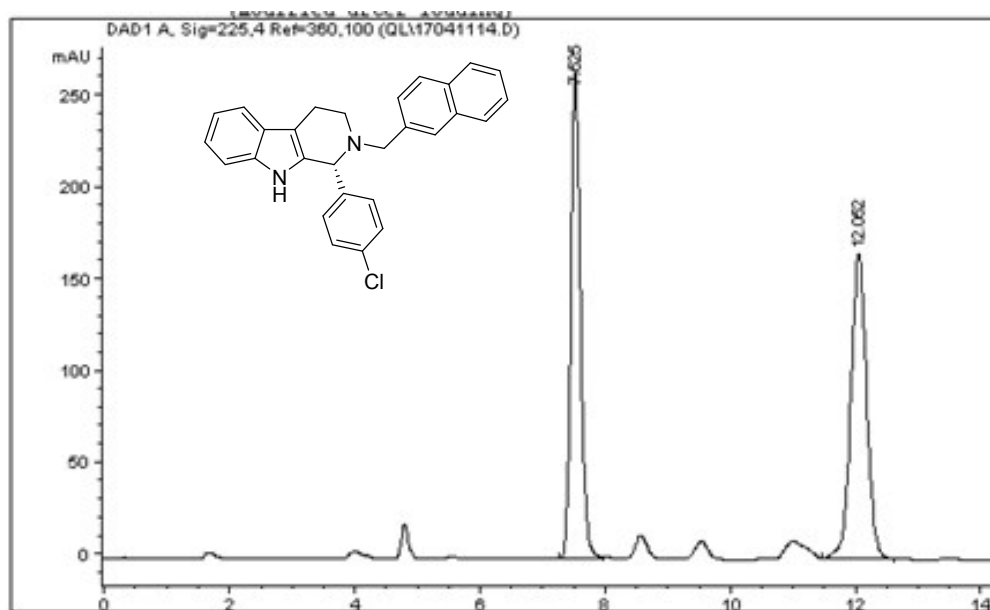
Totals : 5699.41333 447.06140



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.305	BV	0.1594	7930.84912	762.28625	93.9994
2	12.294	HM R	0.2750	506.28104	30.68754	6.0006

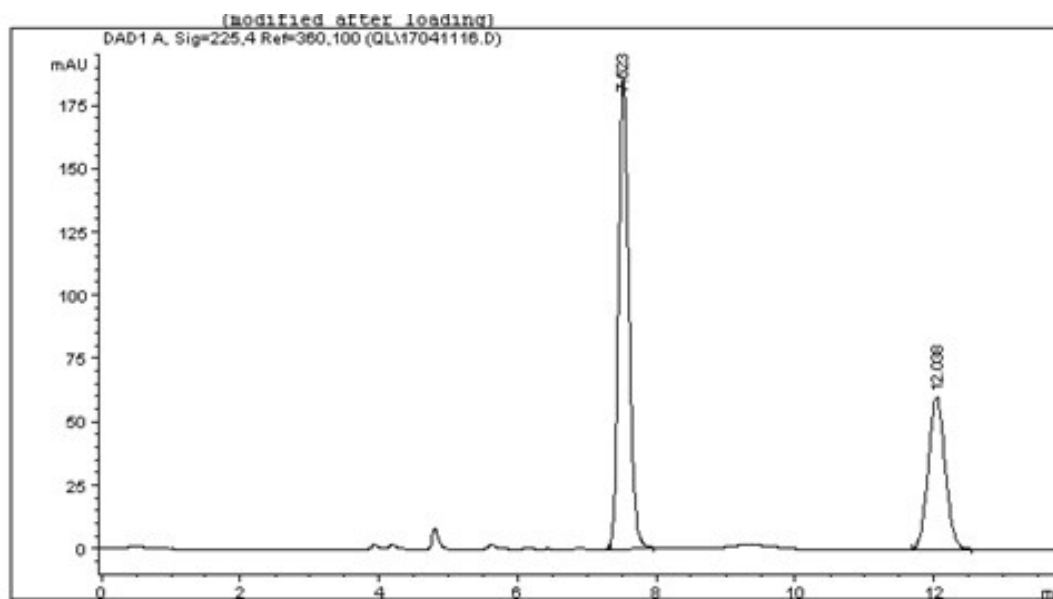
Totals : 8437.13016 792.97379



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.525	BB	0.1635	2816.07471	265.99380	49.0871
2	12.052	VB	0.2695	2920.82300	165.84569	50.9129

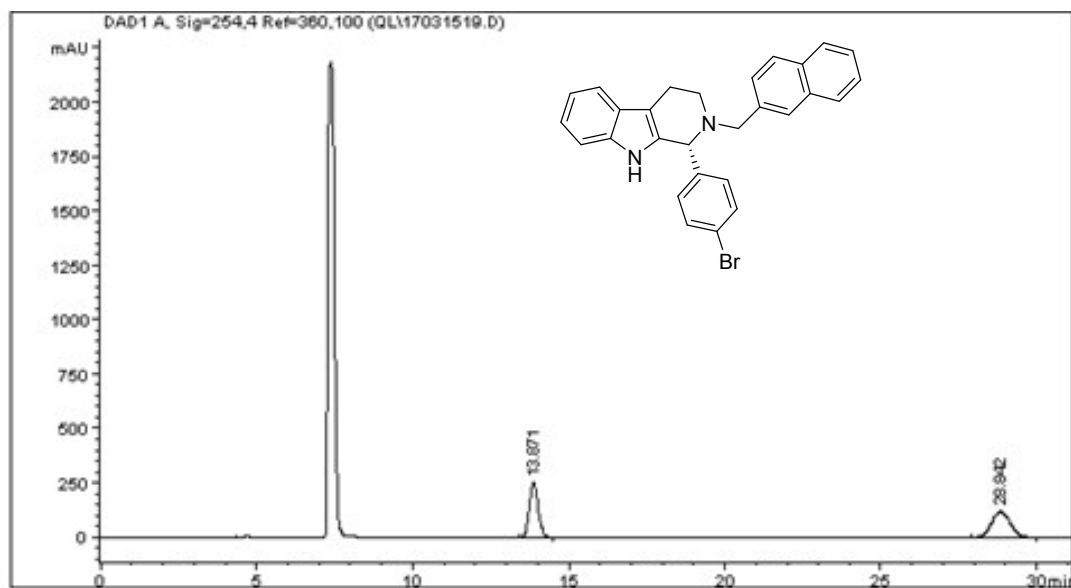
Totals : 5736.89771 431.83949



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.523	BB	0.1600	1916.24243	186.33054	65.2509
2	12.038	BB	0.2636	1020.48541	60.25605	34.7491

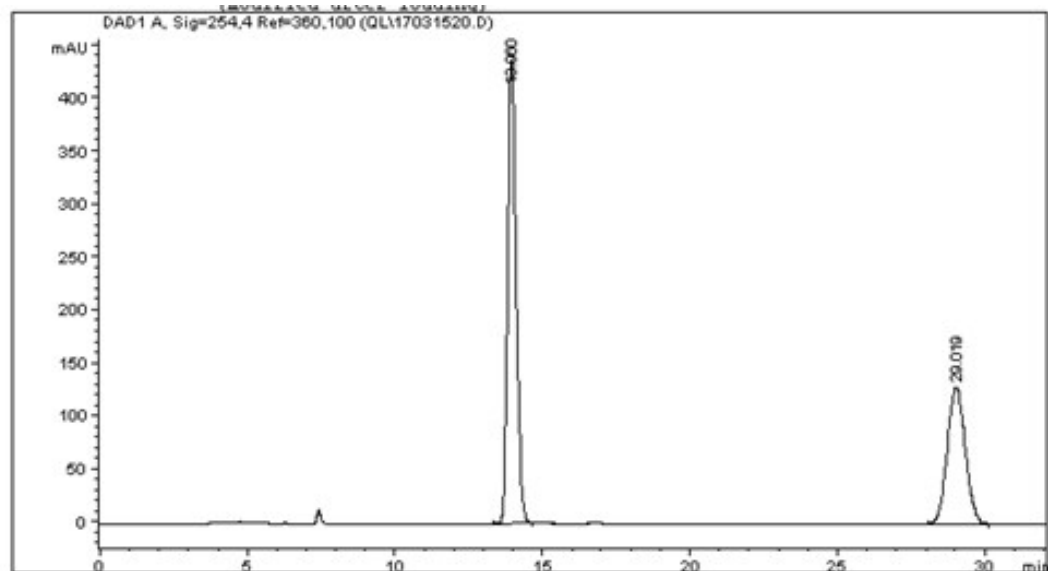
Totals : 2936.72784 246.58658



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.871	BB	0.3117	5051.85889	254.32344	49.8223
2	28.842	BB	0.6402	5087.89404	120.11194	50.1777

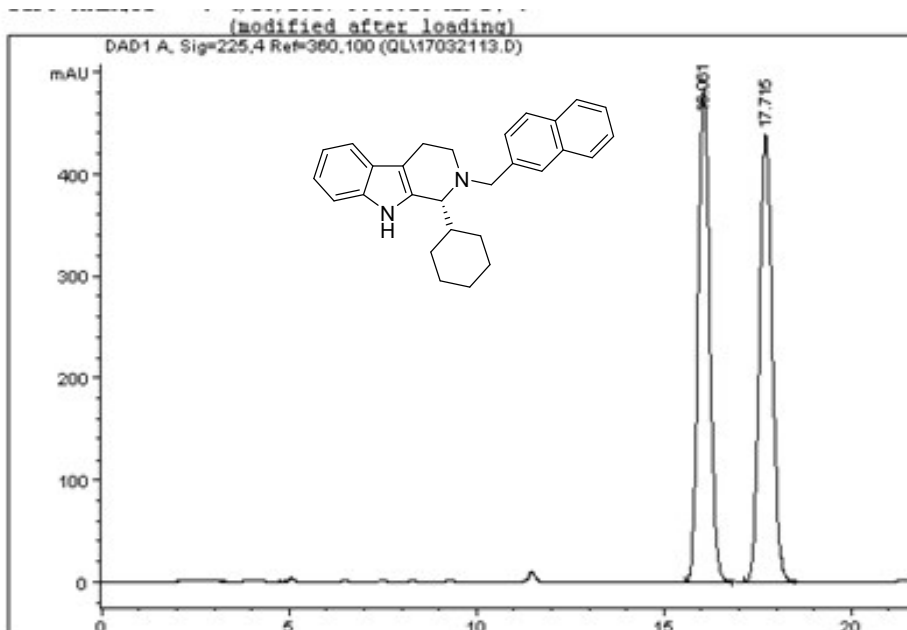
Totals : 1.01398e4 374.43538



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.960	PB	0.3129	8808.35156	437.42719	61.5846
2	29.019	BB	0.6547	5494.50342	129.58992	38.4154

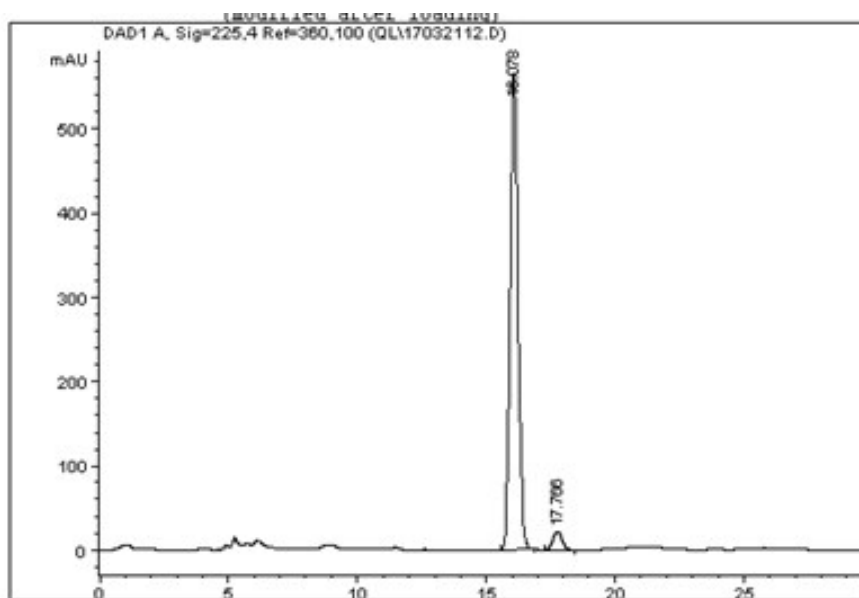
Totals : 1.43029e4 567.01711



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.061	BB	0.3345	1.04161e4	485.09653	50.0009
2	17.715	BB	0.3687	1.04157e4	439.22363	49.9991

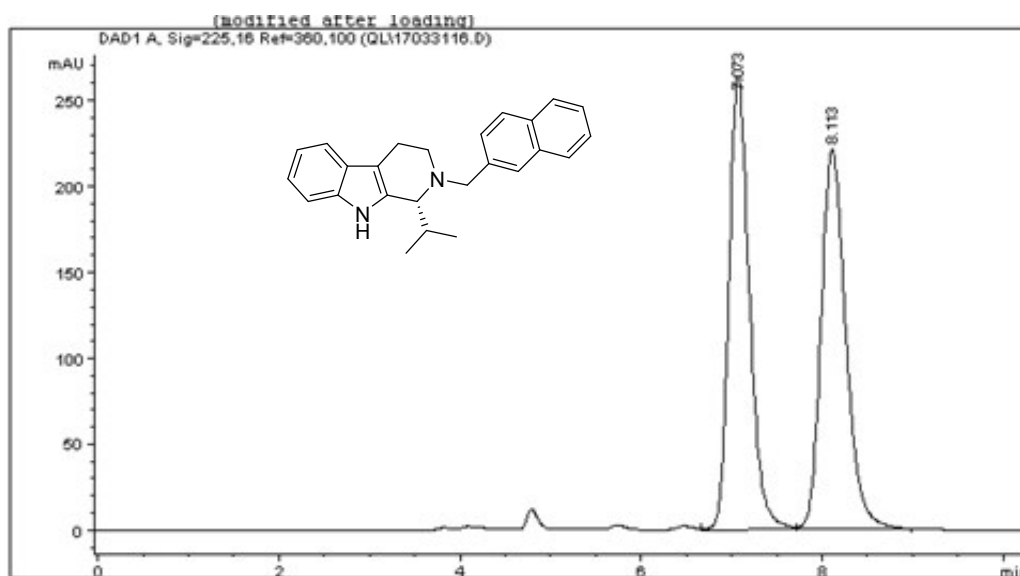
Totals : 2.08317e4 924.32016



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.078	BB	0.3339	1.21345e4	566.40436	95.7611
2	17.766	BB	0.3625	537.14093	22.66155	4.2389

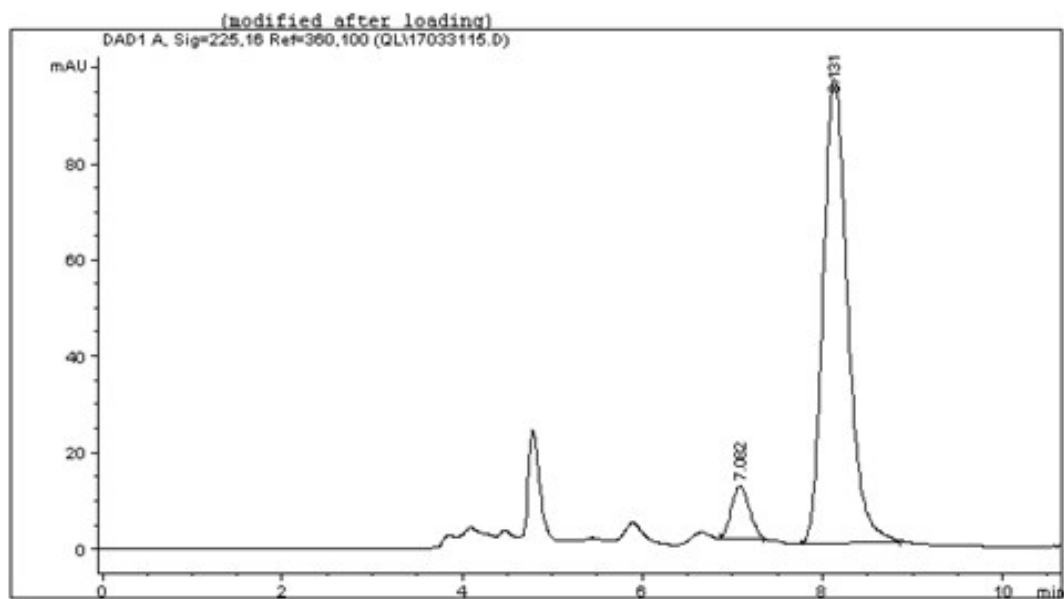
Totals : 1.26716e4 589.06591



Signal 1: DAD1 A, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.073	VV	0.2424	4175.00098	264.14563	49.7718
2	8.113	VB	0.2944	4213.29004	221.03796	50.2282

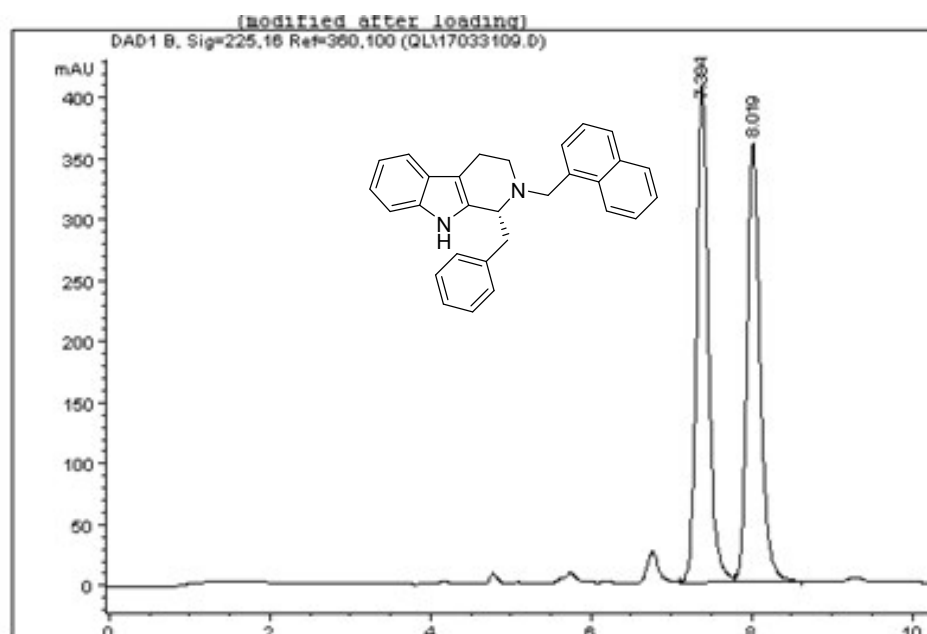
Totals : 8388.29102 485.18359



Signal 1: DAD1 A, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.082	MM R	0.2303	150.36864	10.88231	7.6002
2	8.131	BB	0.2907	1828.11157	96.63808	92.3998

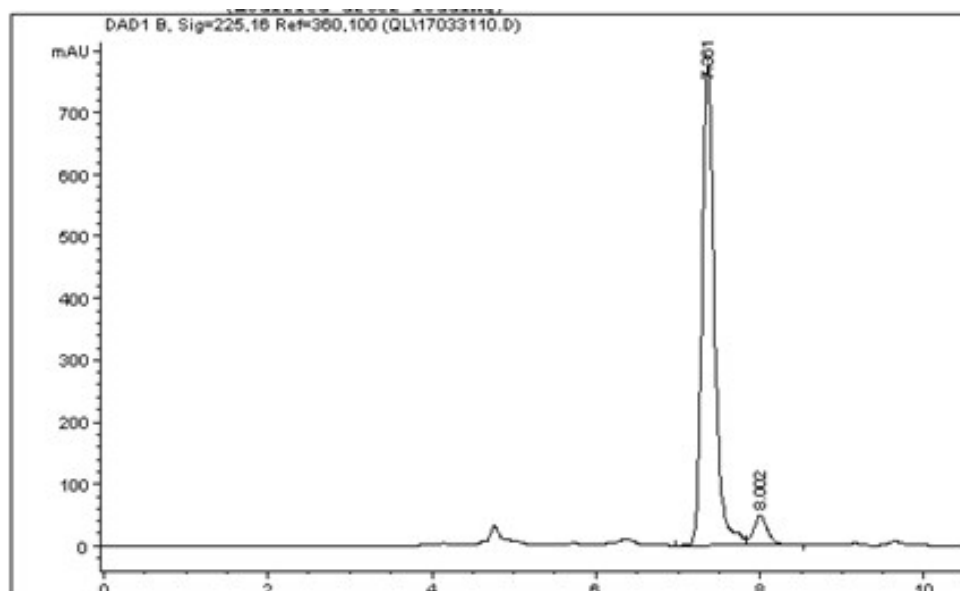
Totals : 1978.48021 107.52039



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.384	BV	0.1575	4272.72656	410.44431	50.8547
2	8.019	VB	0.1736	4129.10791	360.50876	49.1453

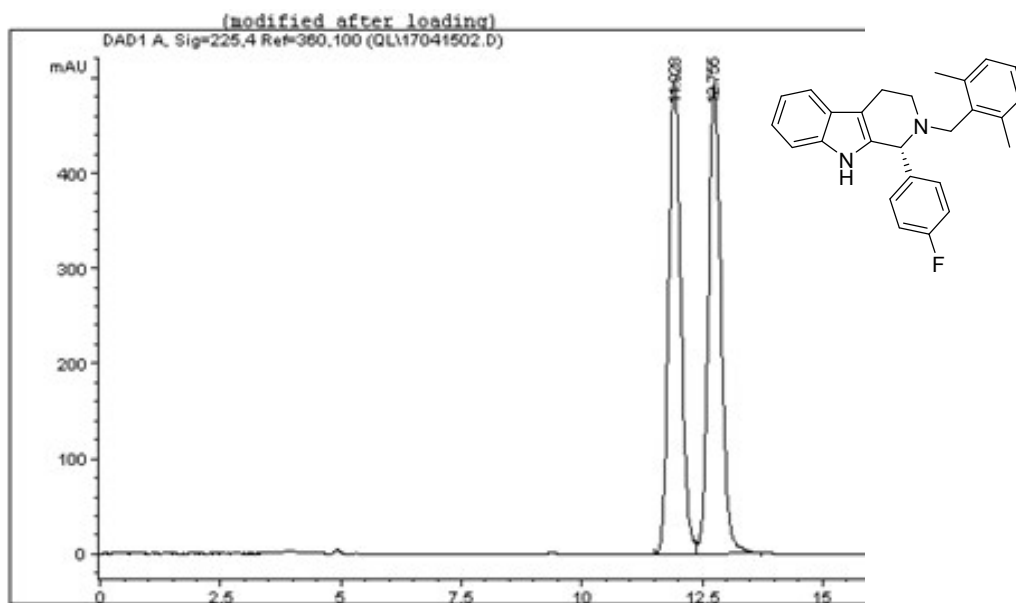
Totals : 8401.83447 770.95306



Signal 1: DAD1 B, Sig=225,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.361	VV	0.1611	8206.56055	777.46655	93.3753
2	8.002	VB	0.1814	582.22766	48.04111	6.6247

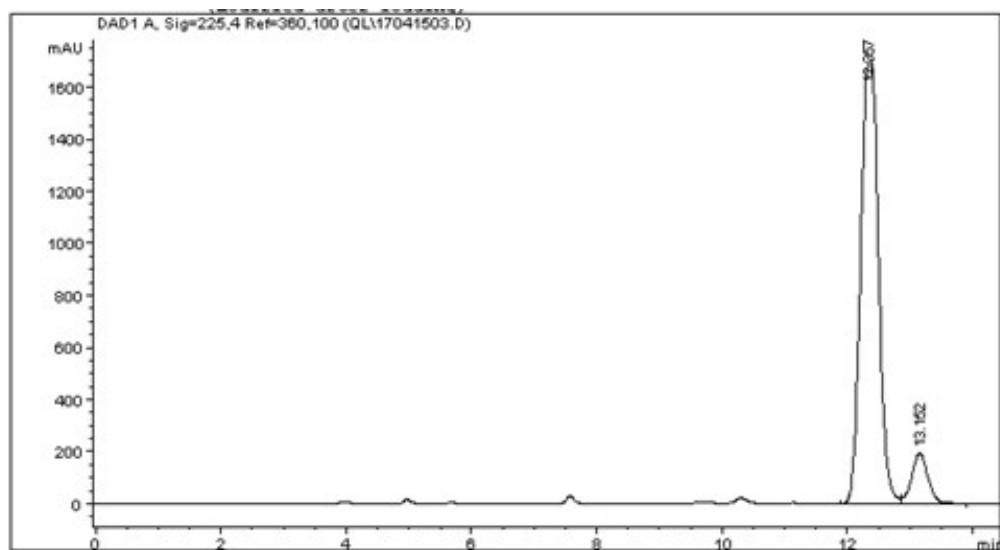
Totals : 8788.78821 825.50766



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.928	BV	0.2750	8841.19727	498.39099	49.3927
2	12.755	VB	0.2833	9058.59961	495.44147	50.6073

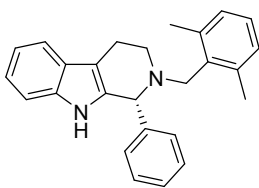
Totals : 1.78998e4 993.83246



Signal 1: DAD1 A, Sig=225,4 Ref=360,100

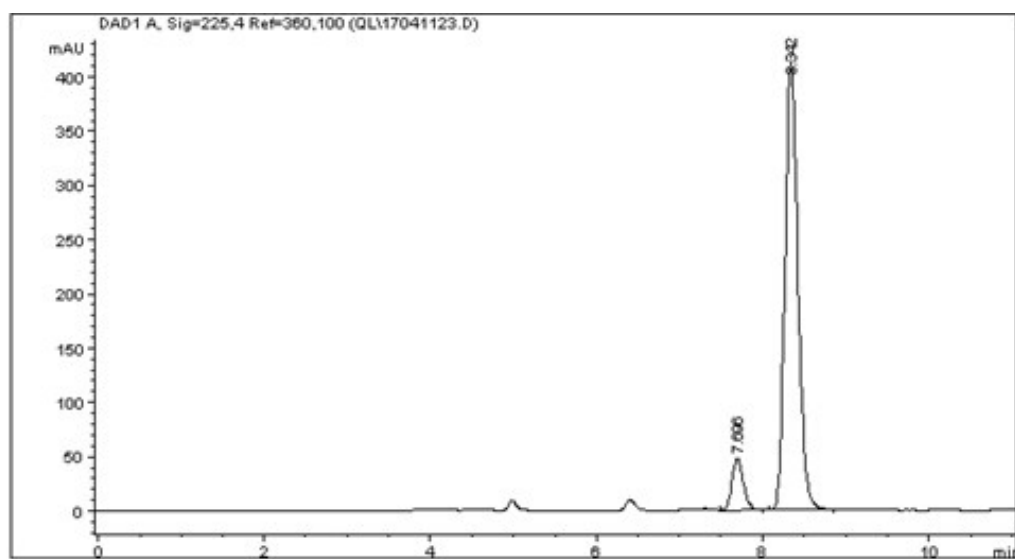
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.357	VV	0.3165	3.36437e4	1703.19690	90.4740
2	13.152	VB	0.2806	3542.34058	194.36292	9.5260

Totals : 3.71860e4 1897.55981



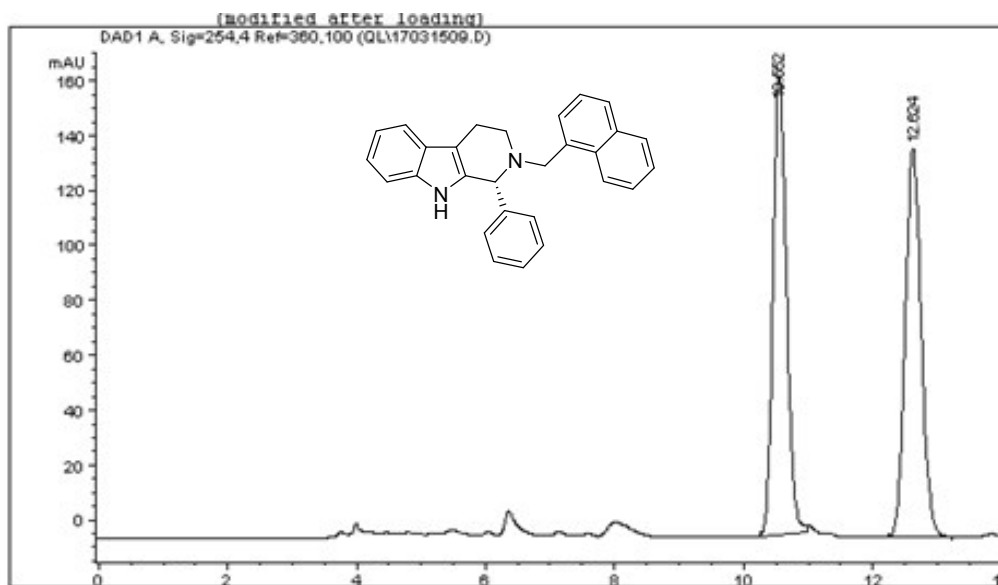
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.569	VV	0.1761	2663.64331	235.16385	49.4739
2	8.216	VB	0.1862	2720.28857	223.13480	50.5261

Totals :	5383.93188	458.29865
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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.696	VB	0.1499	457.43643	47.69006	9.3293
2	8.342	BB	0.1674	4445.79980	413.51263	90.6707

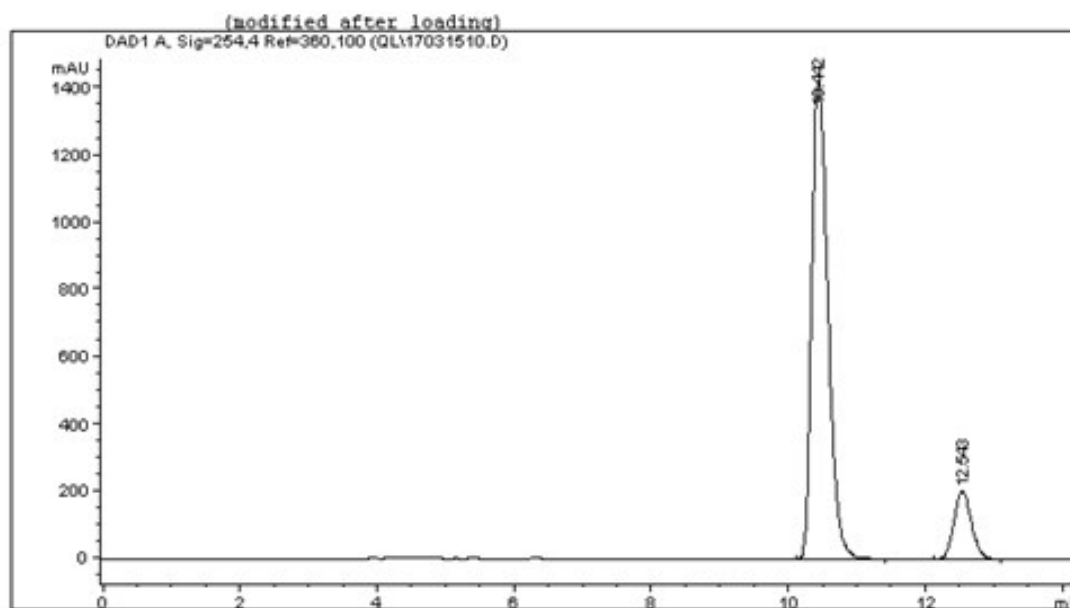
Totals : 4903.23624 461.20269



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.552	PB	0.2250	2424.86206	167.39313	49.7489
2	12.624	BB	0.2694	2449.34106	141.90109	50.2511

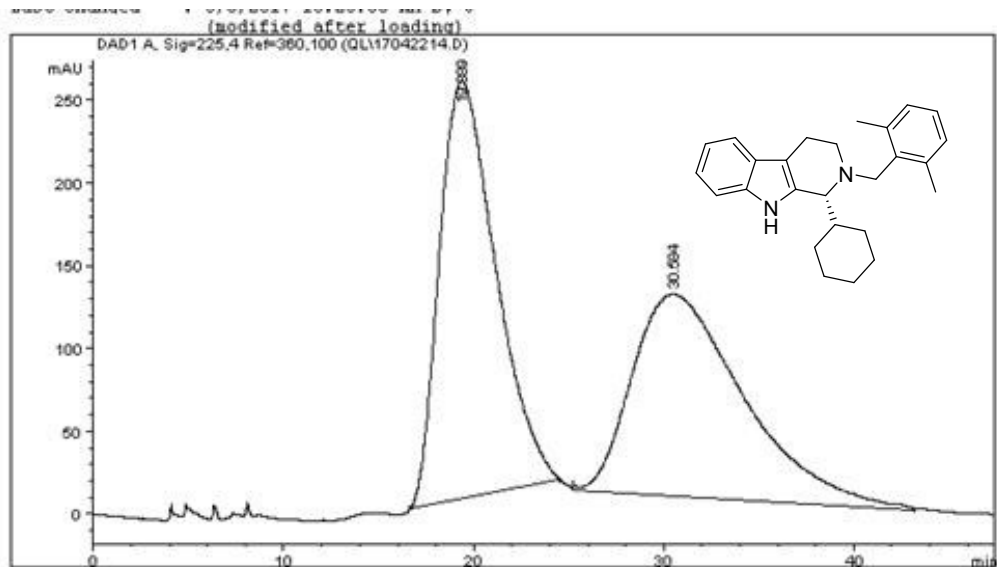
Totals : 4874.20312 309.29422



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

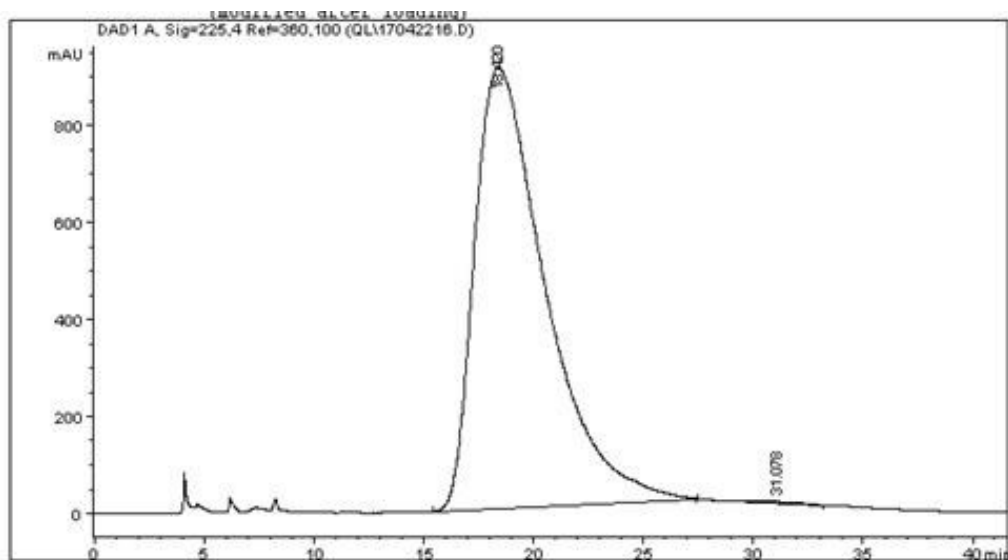
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.442	BB	0.2576	2.34095e4	1425.29712	86.7778
2	12.543	BB	0.2748	3566.87158	201.25774	13.2222

Totals : 2.69764e4 1626.55486



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.389	MM R	3.4166	5.16347e4	251.88289	51.0405
2	30.584	MM R	6.7834	4.95294e4	121.69187	48.9595

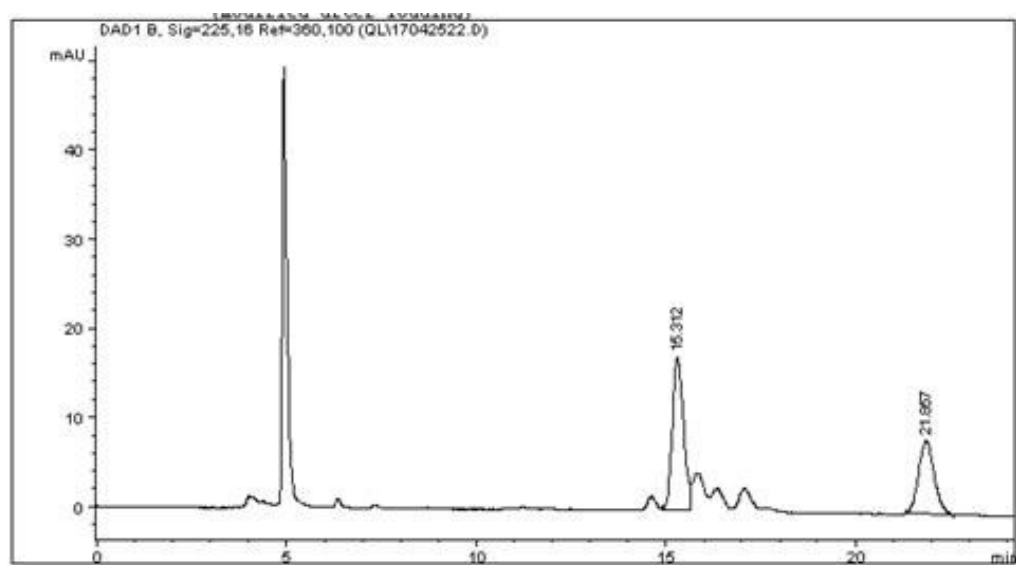
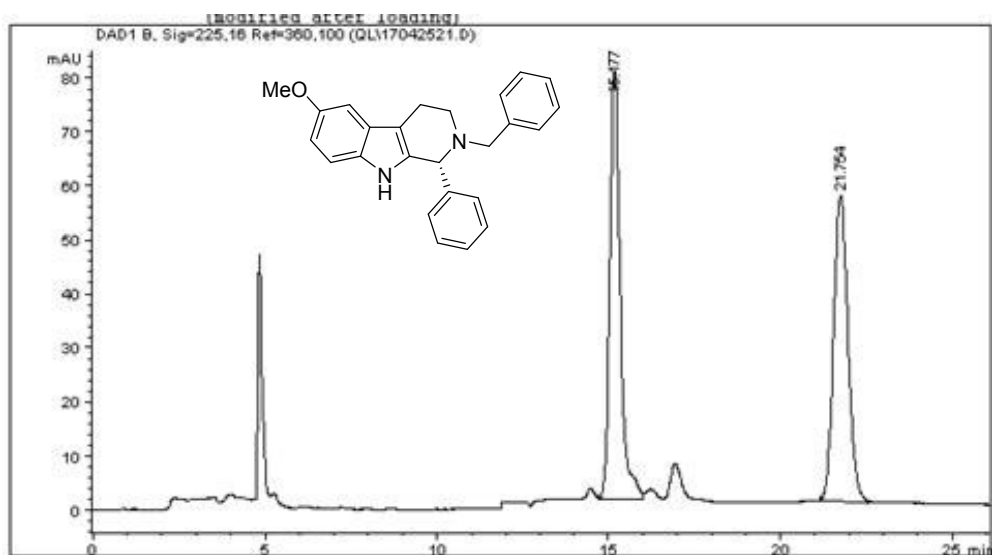
Totals : 1.01164e5 373.57476



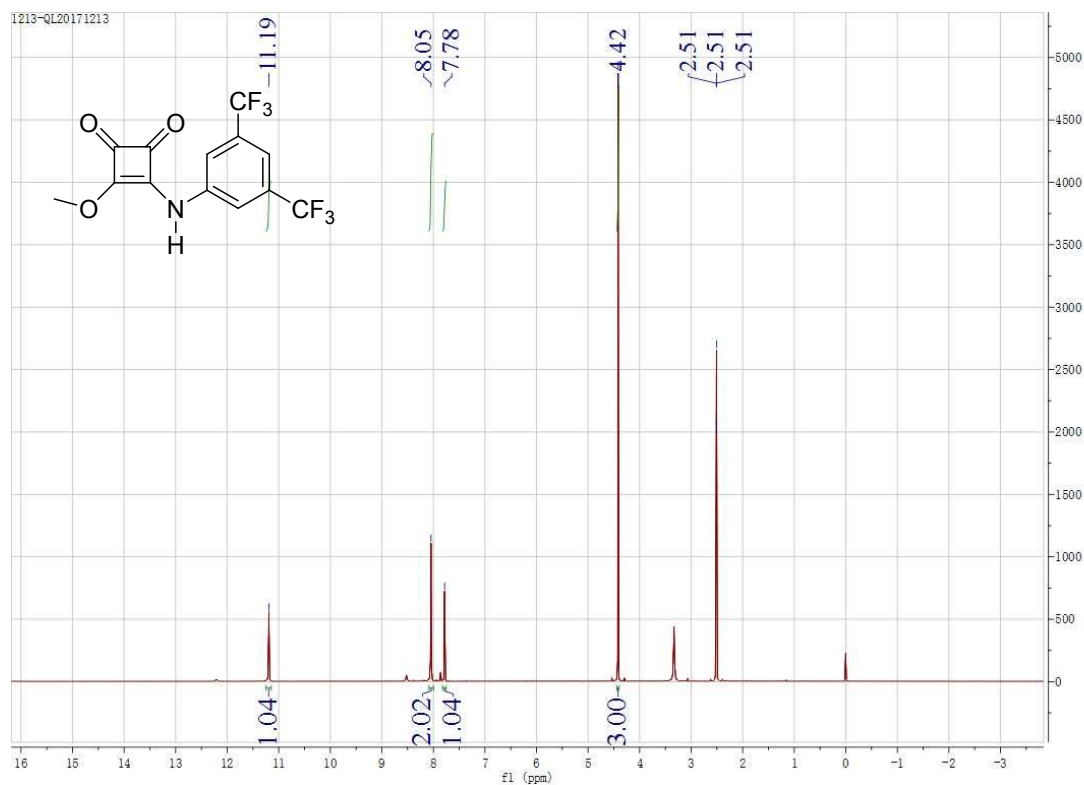
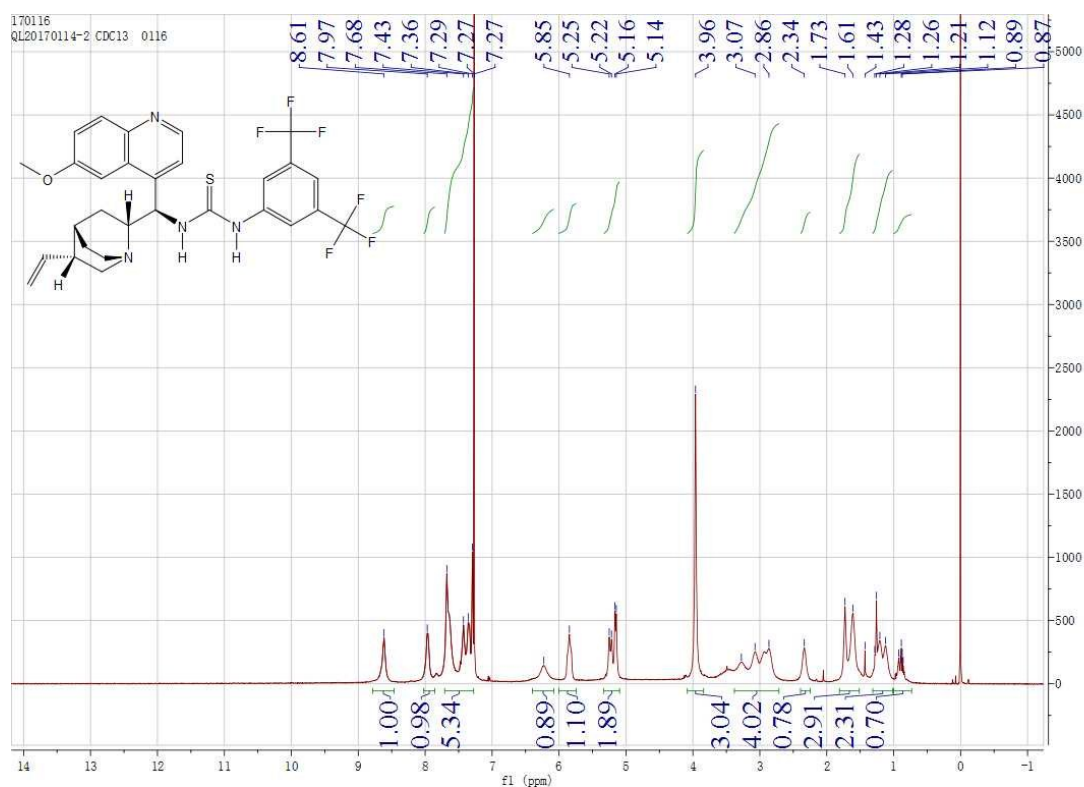
Signal 1: DAD1 A, Sig=225,4 Ref=360,100

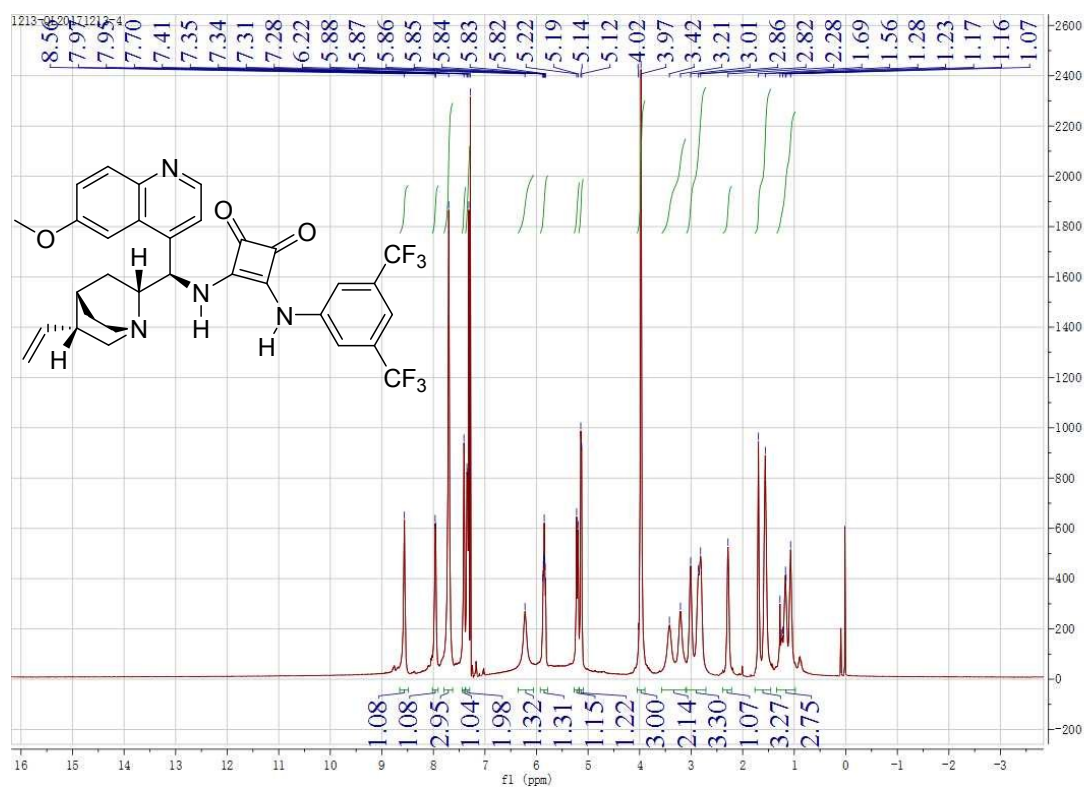
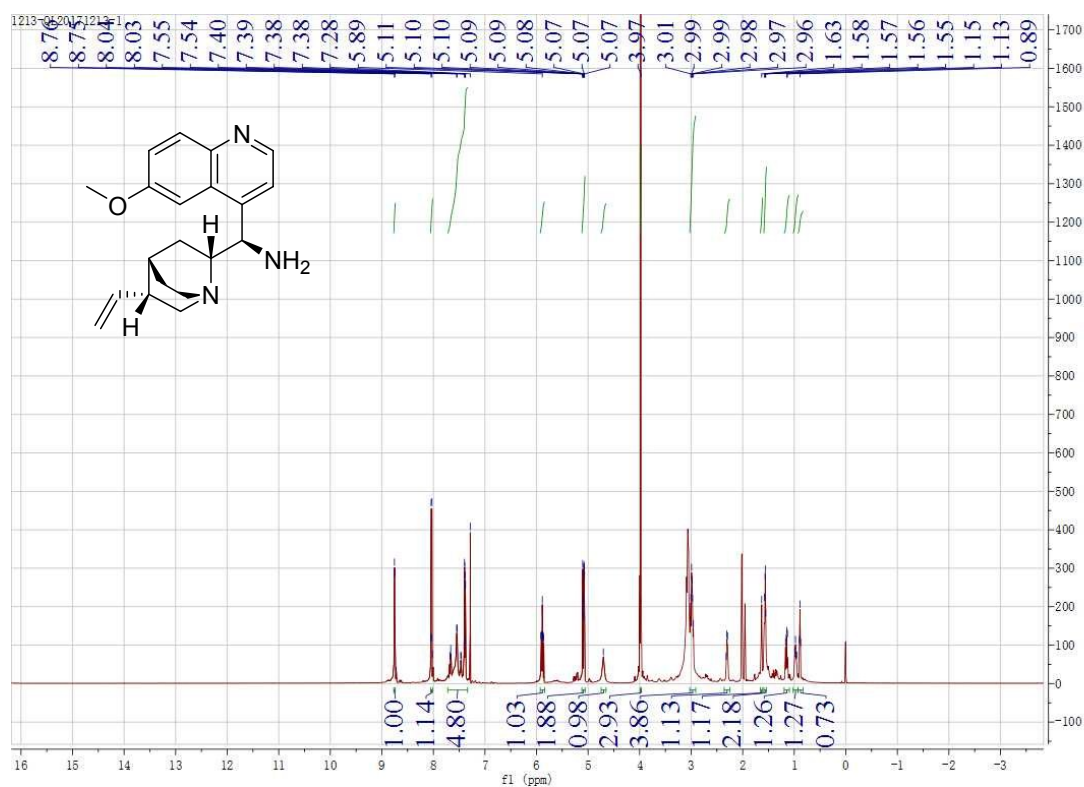
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.420	PB	2.6277	2.03965e5	910.41663	99.6904
2	31.078	MM R	3.3917	633.51562	3.11310	0.3096

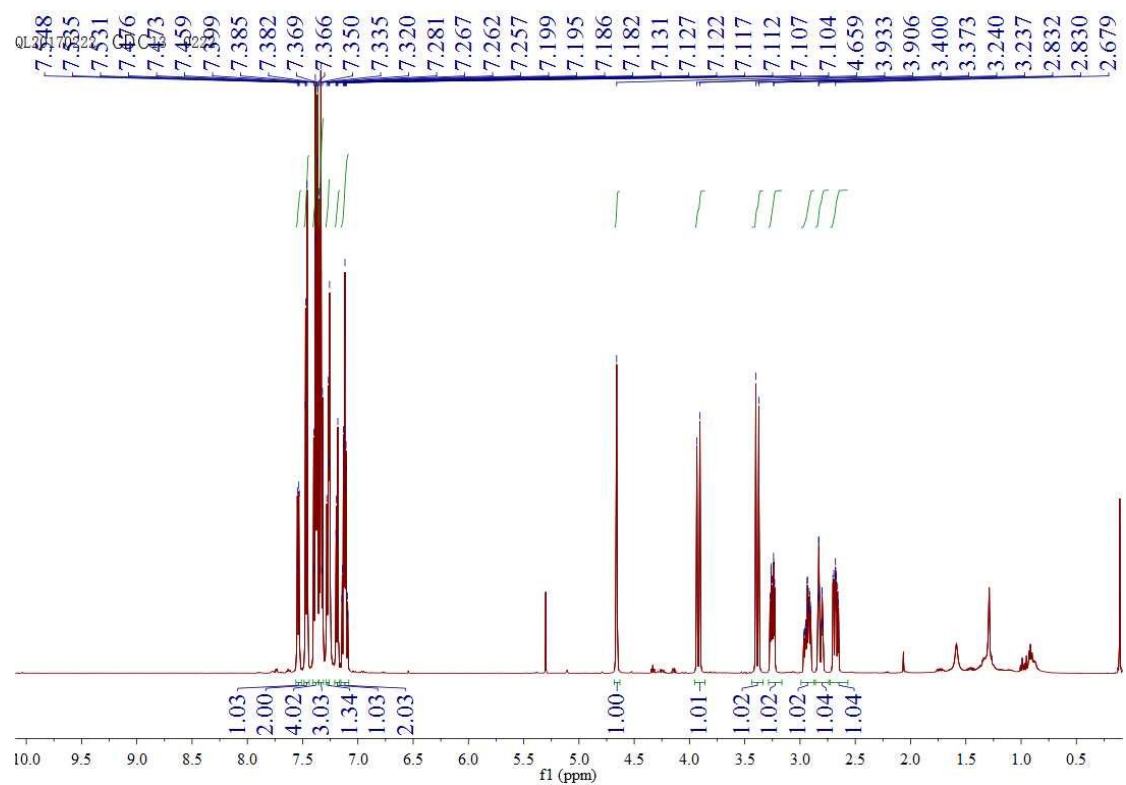
Totals : 2.04599e5 913.52972



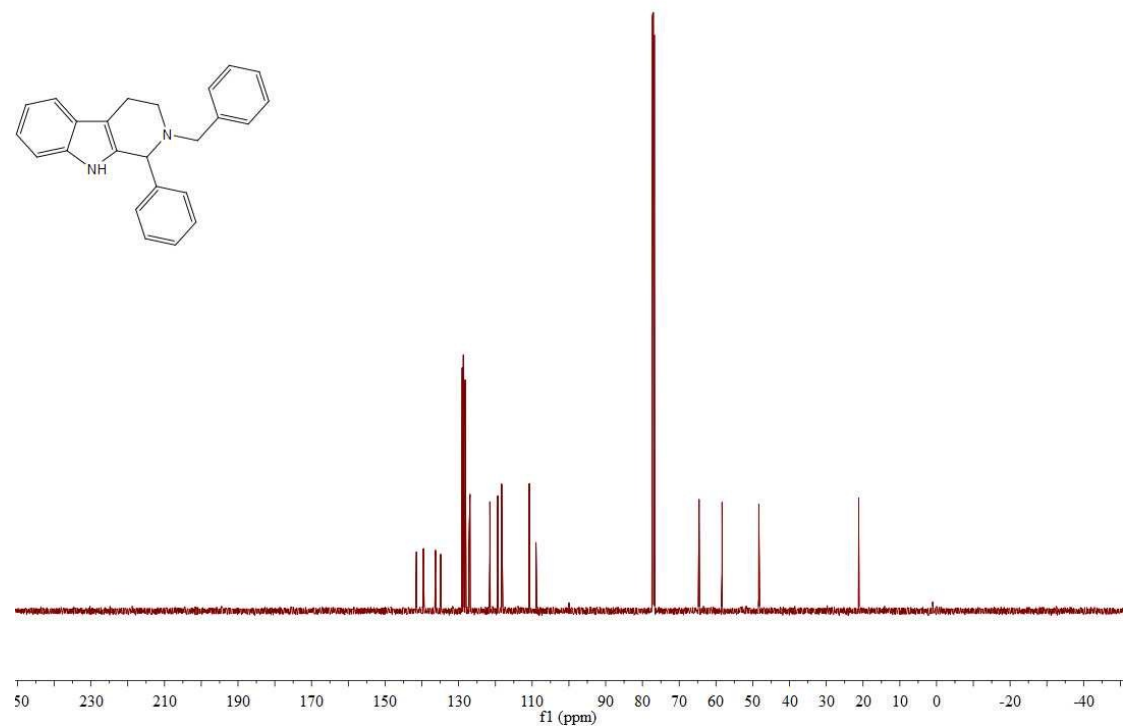
III. Copies of ^1H and ^{13}C NMR Spectra

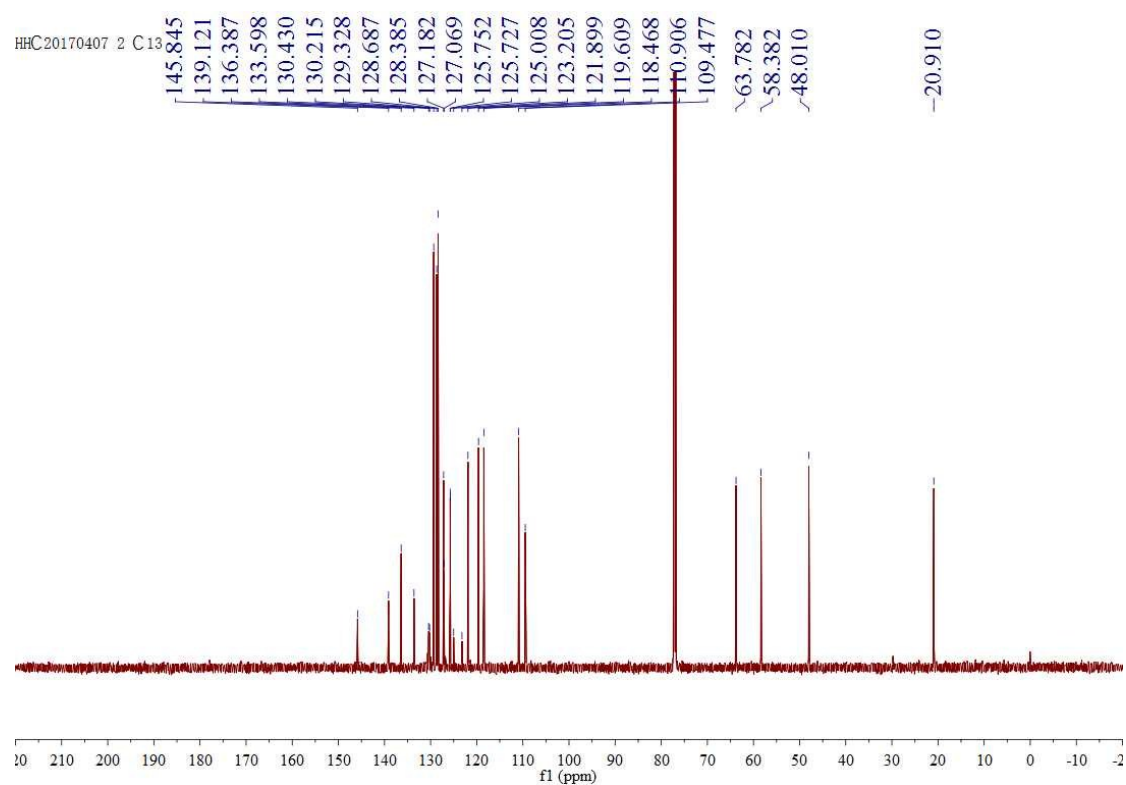
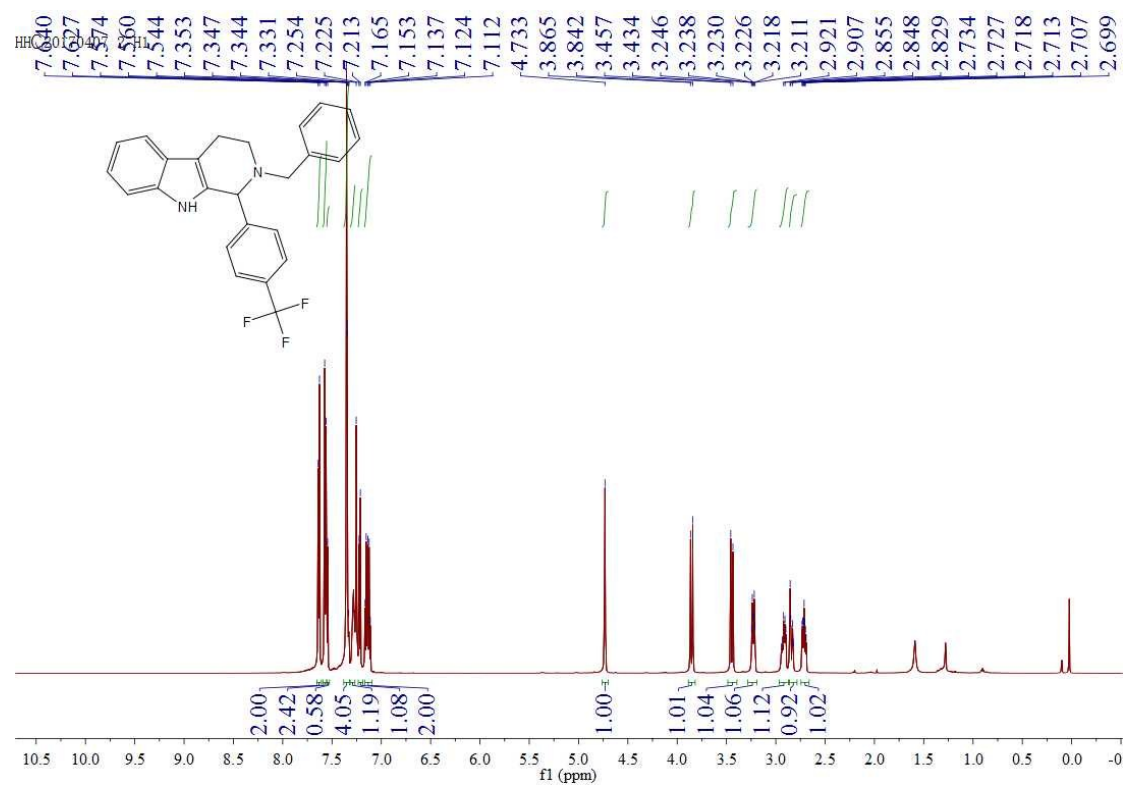


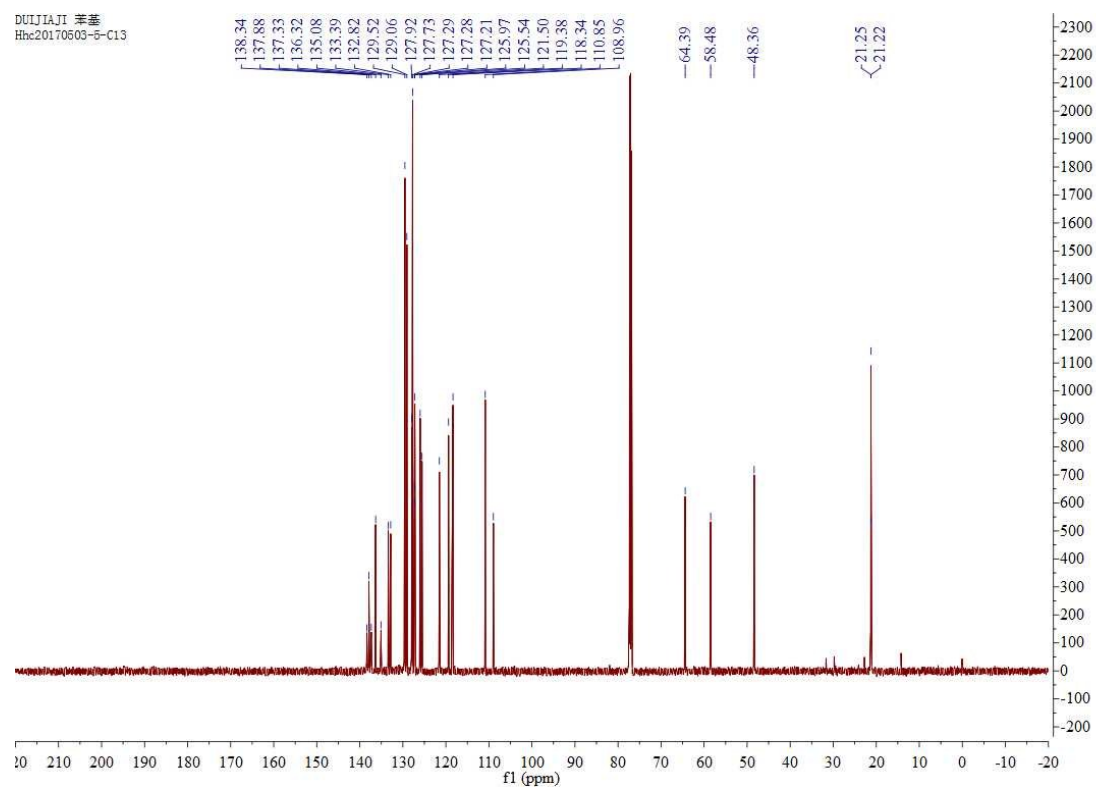
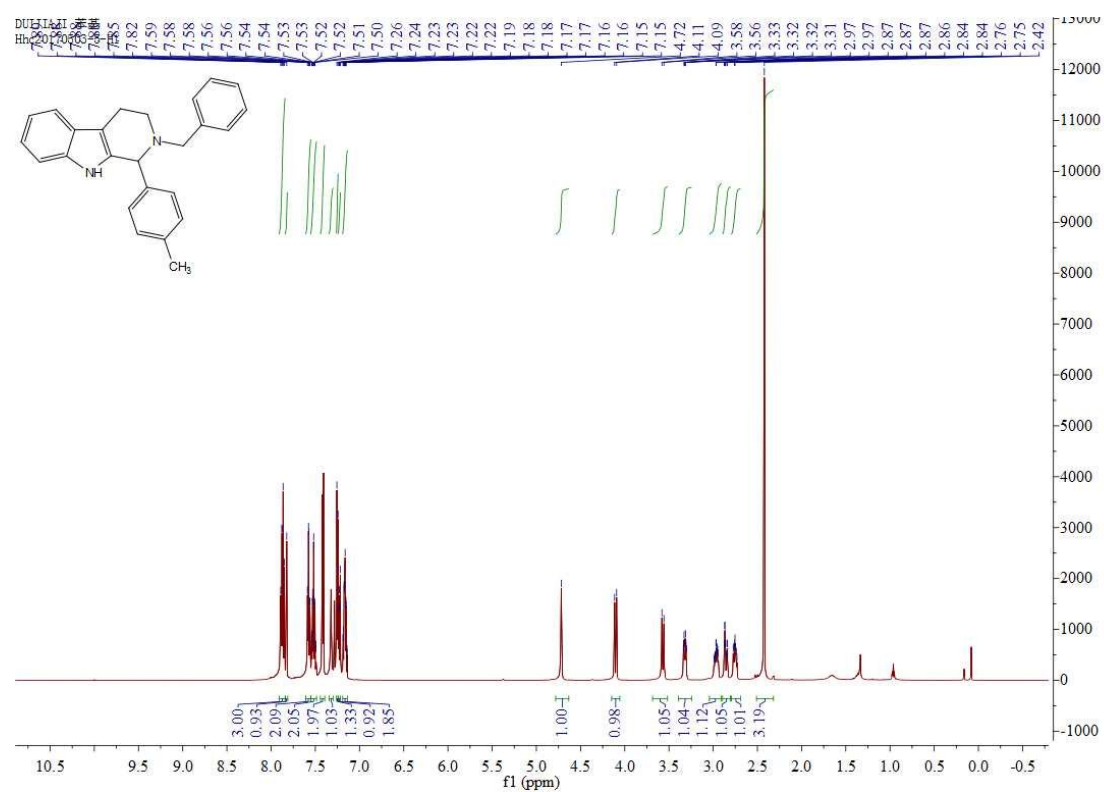


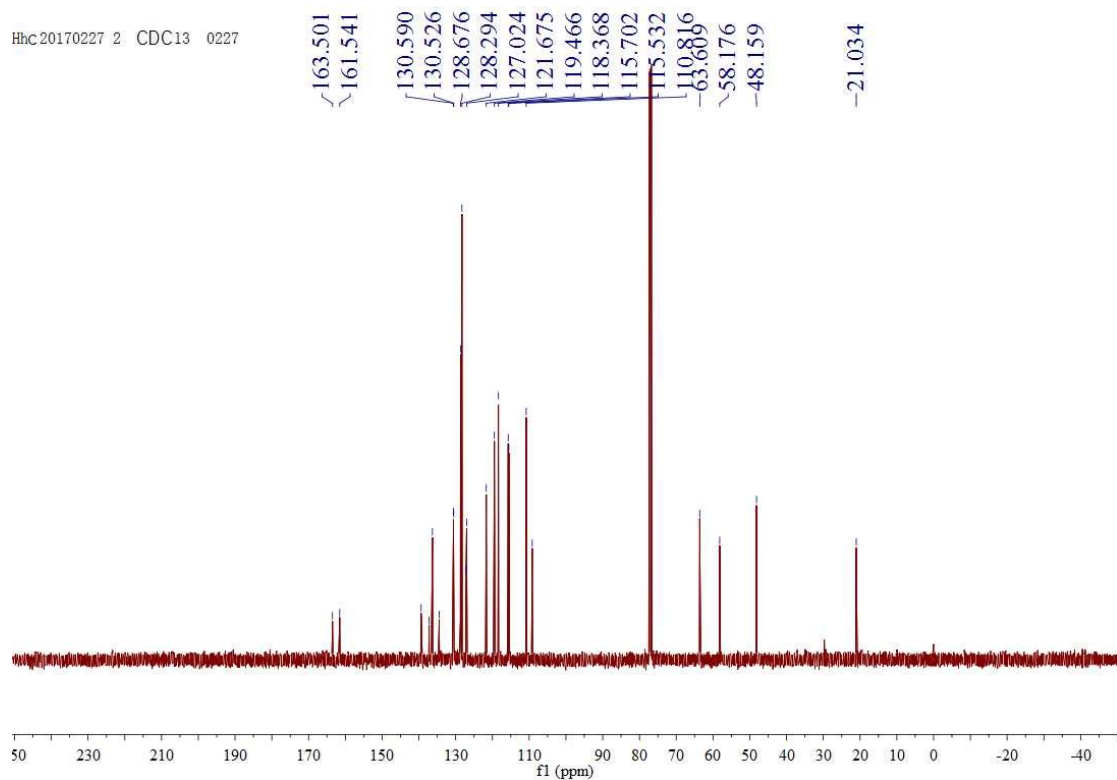
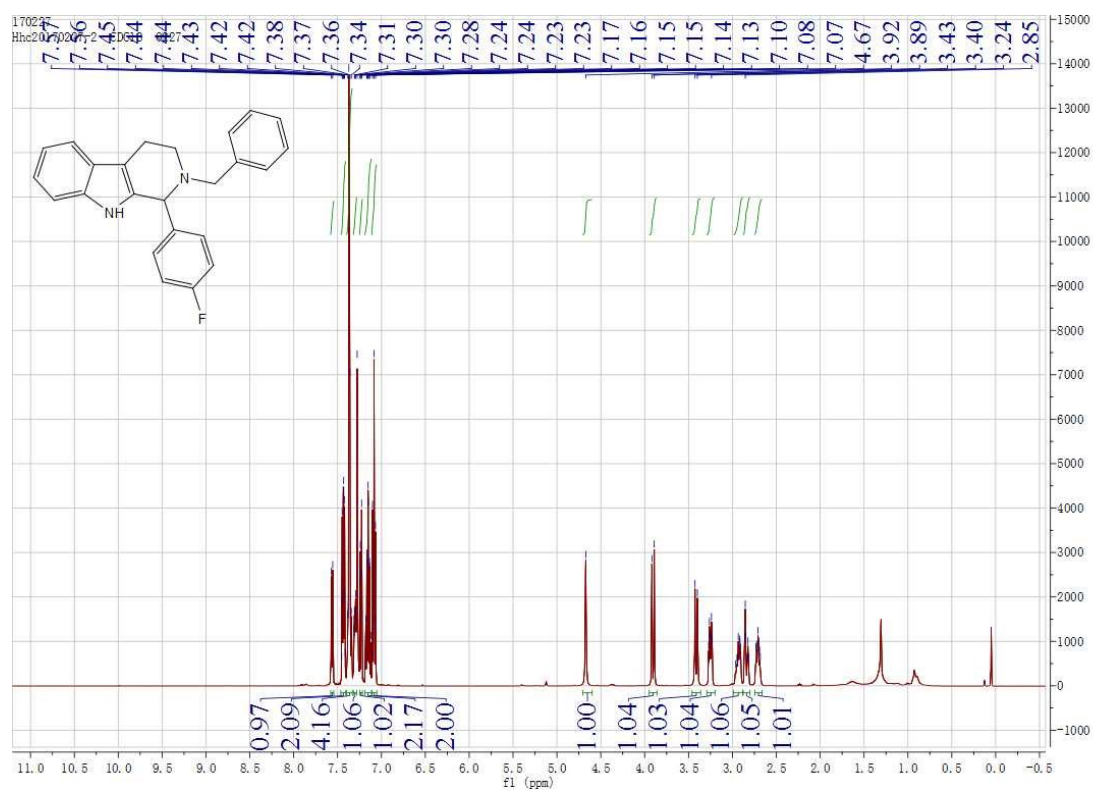


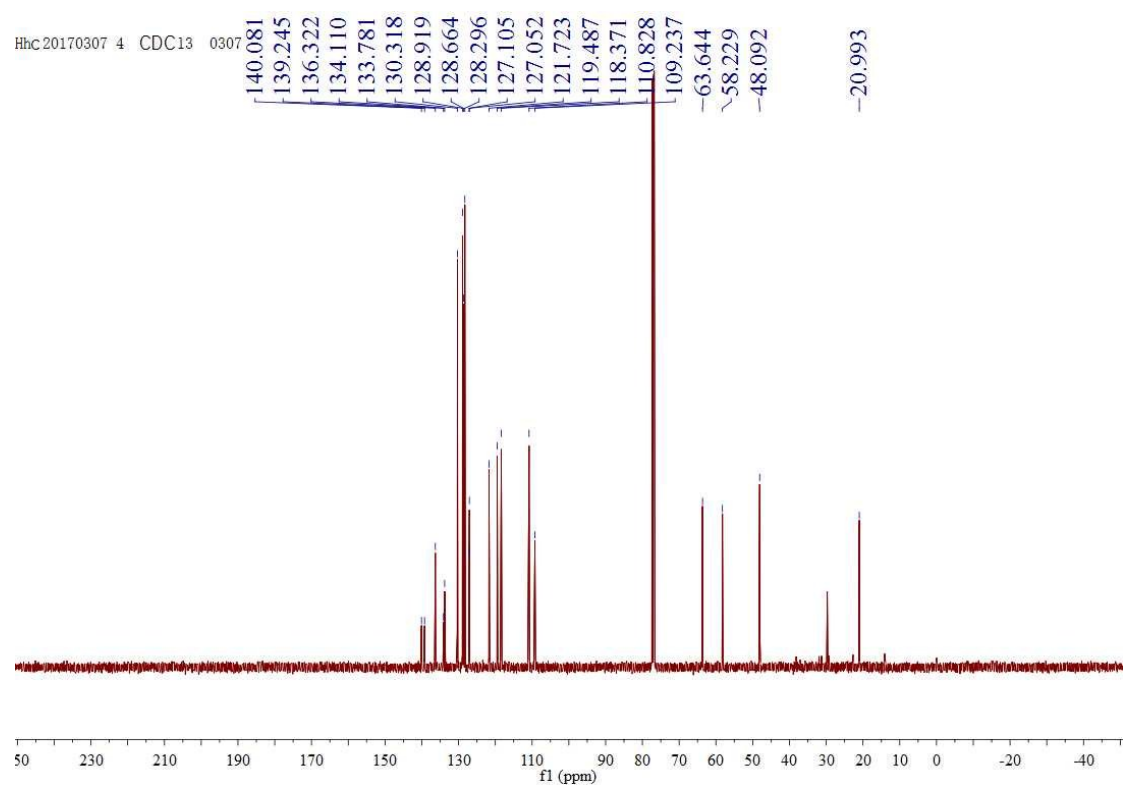
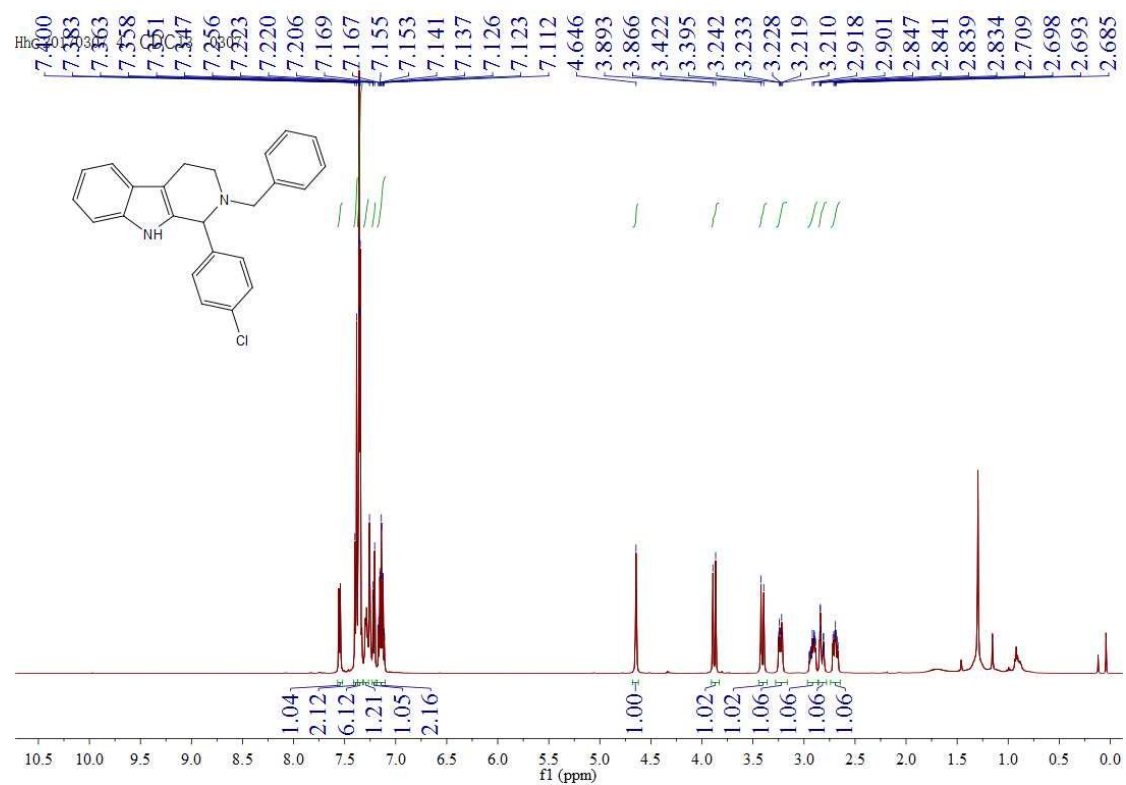
QL20170222 CDC13 0222

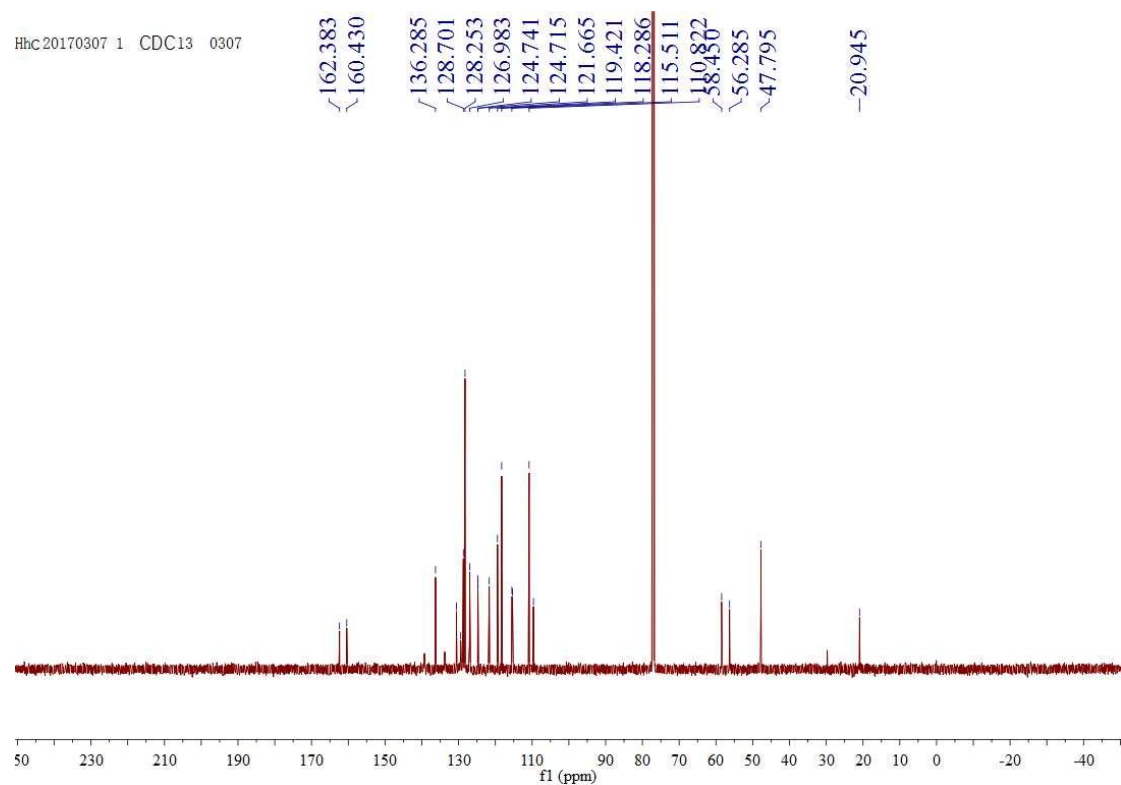
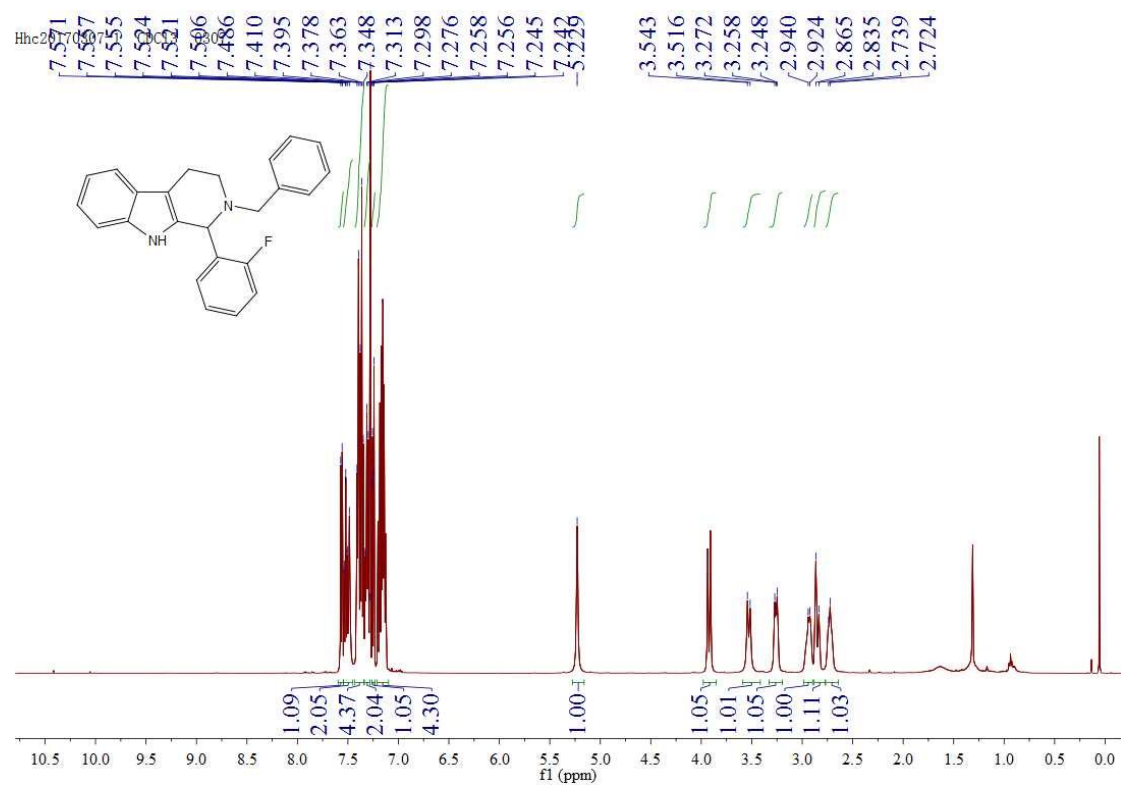


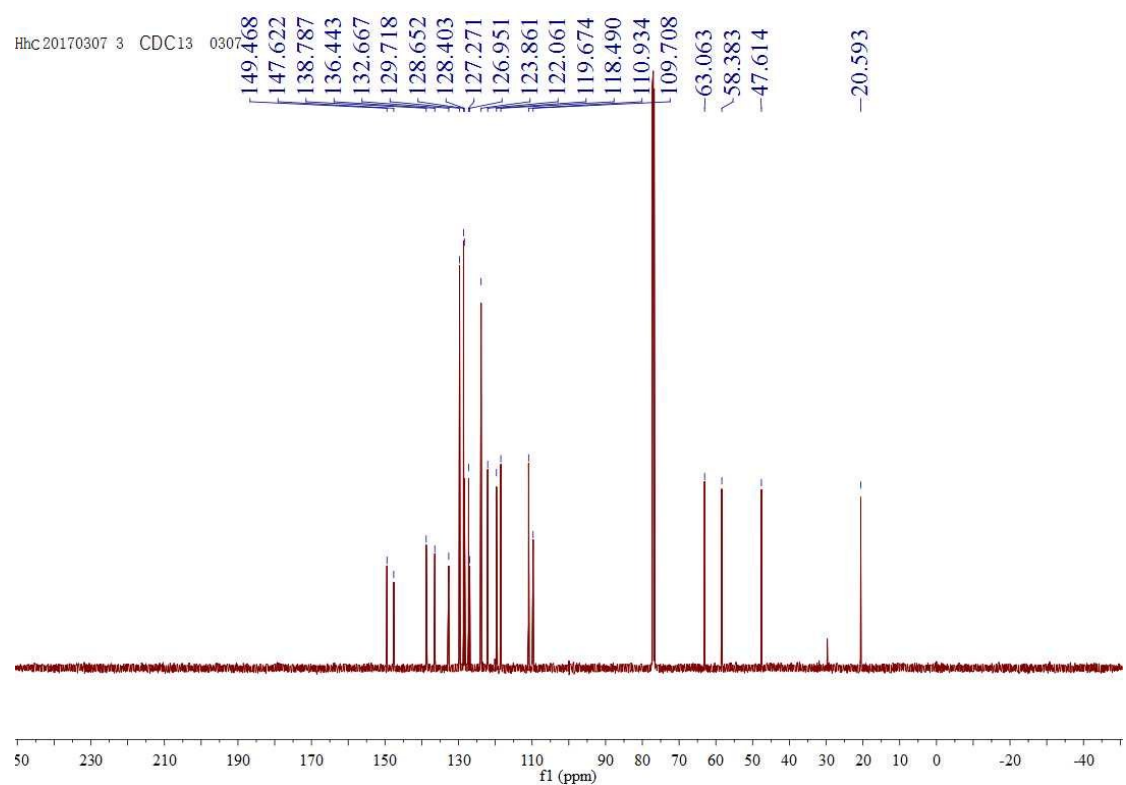
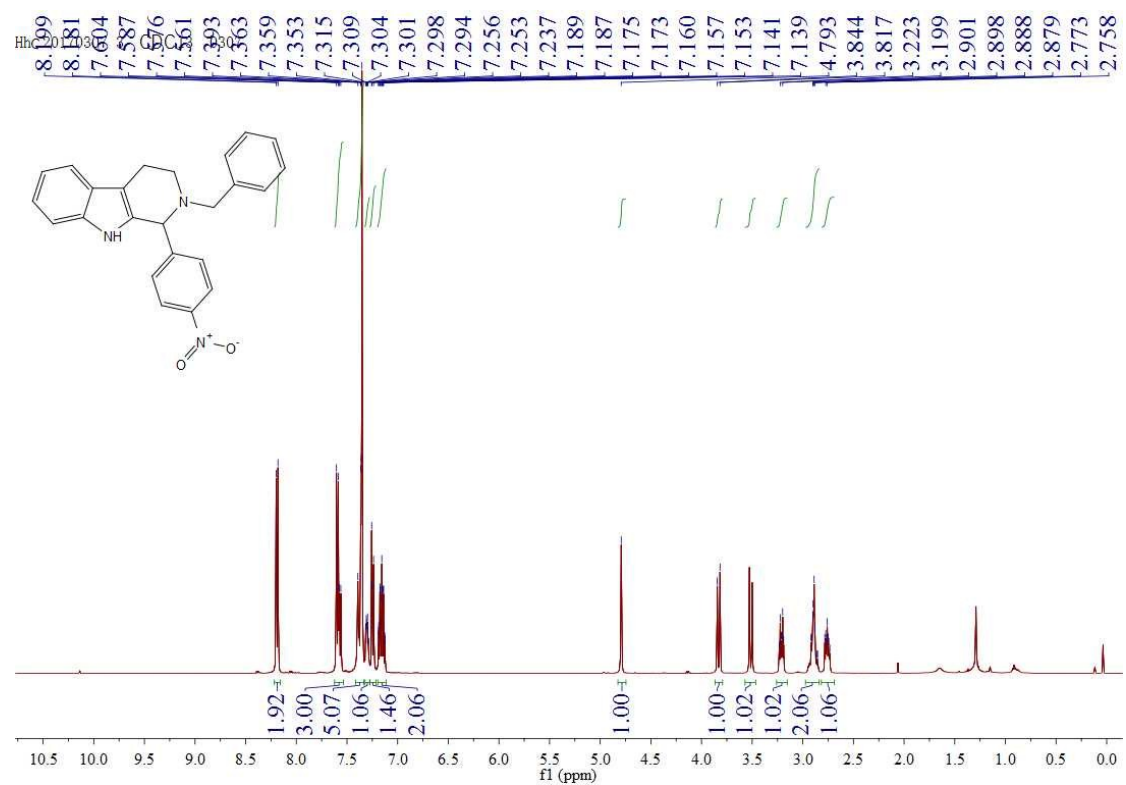


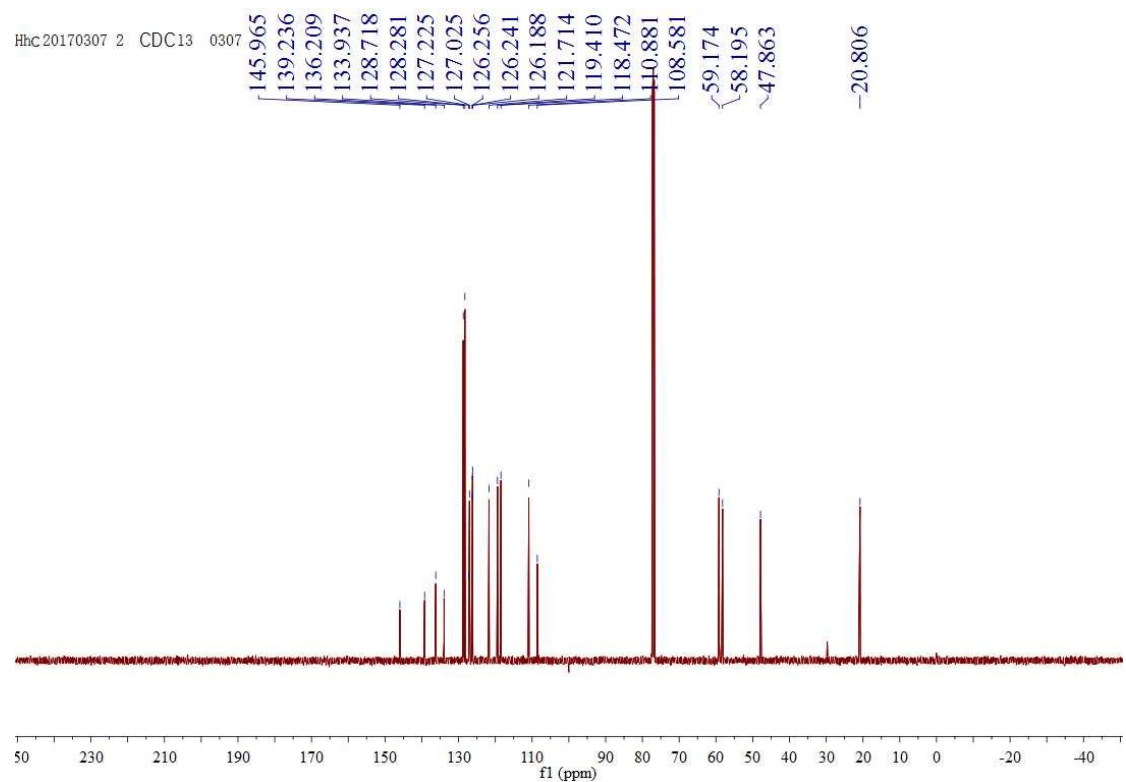
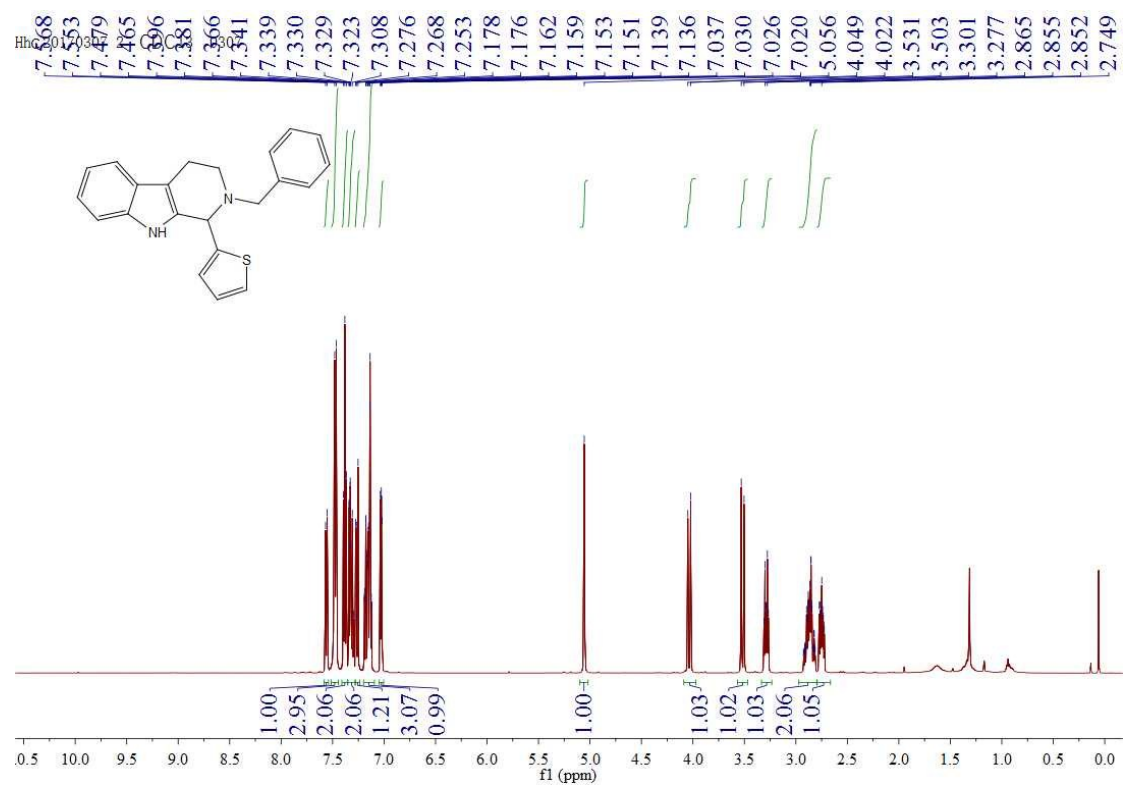


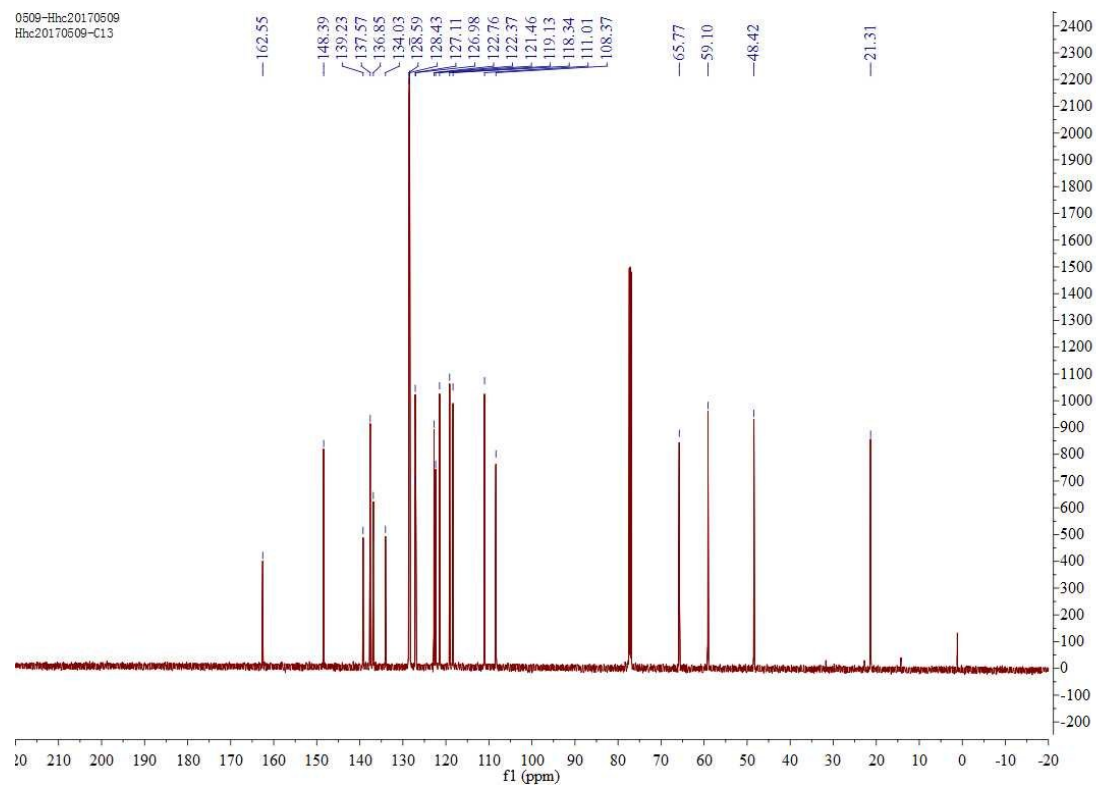
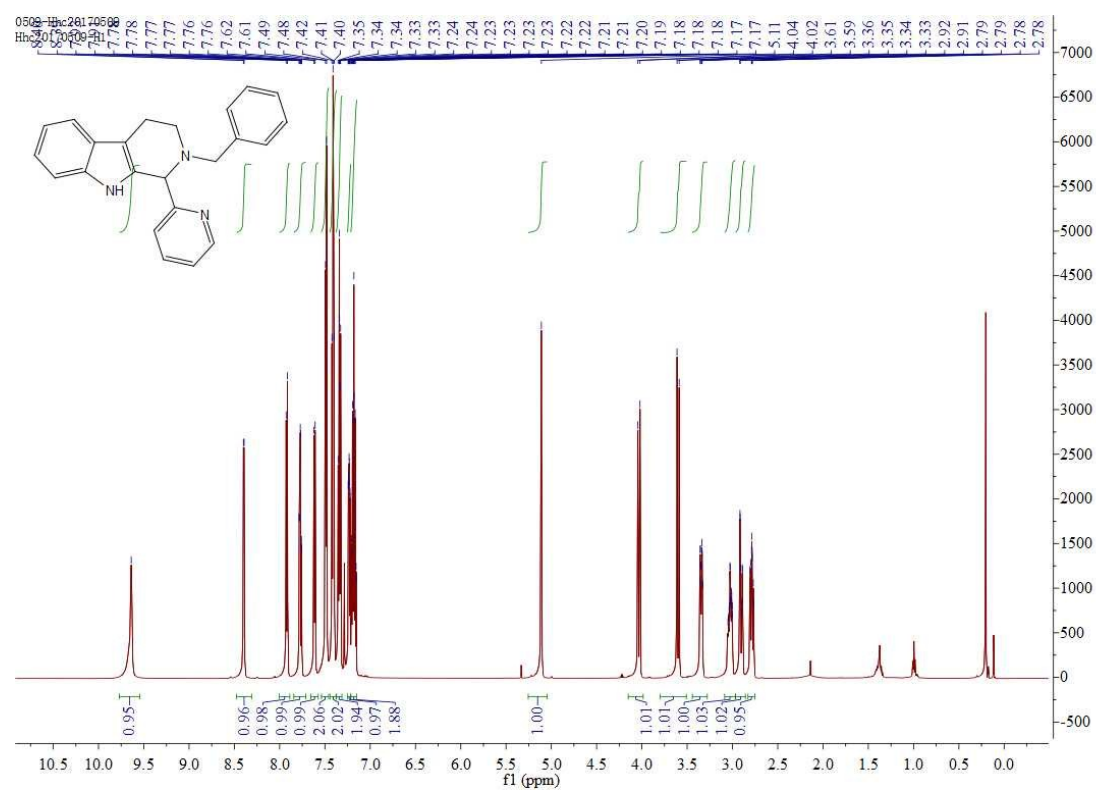


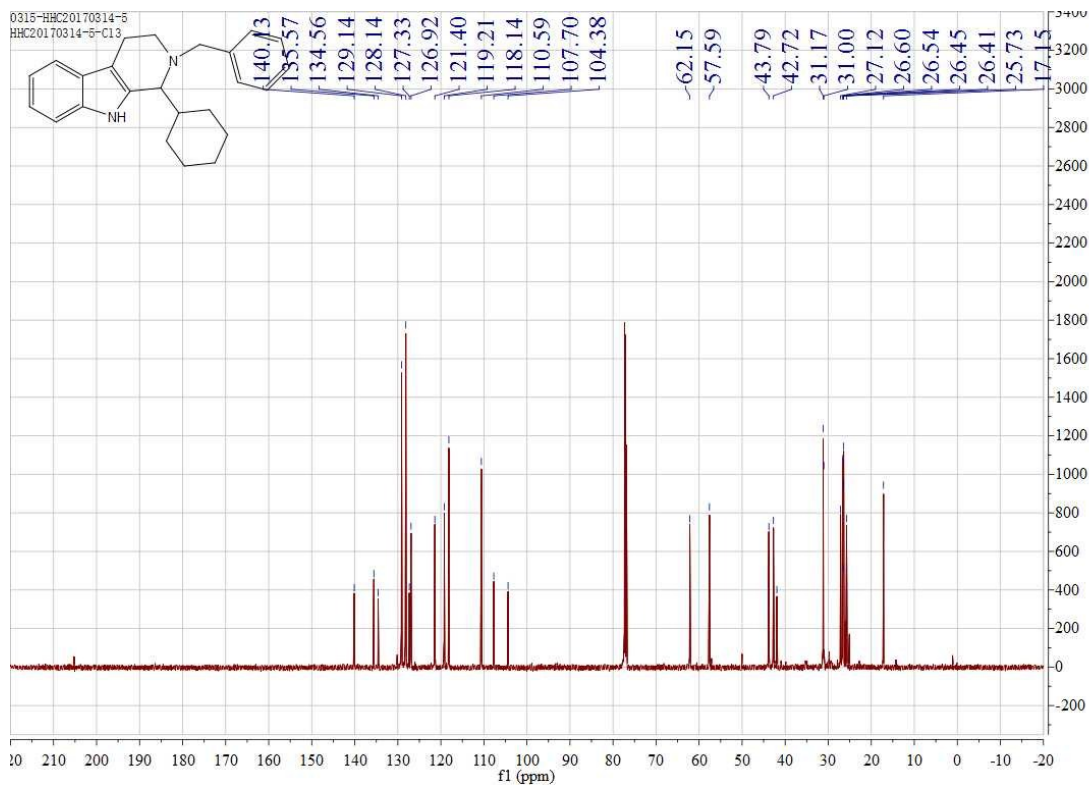
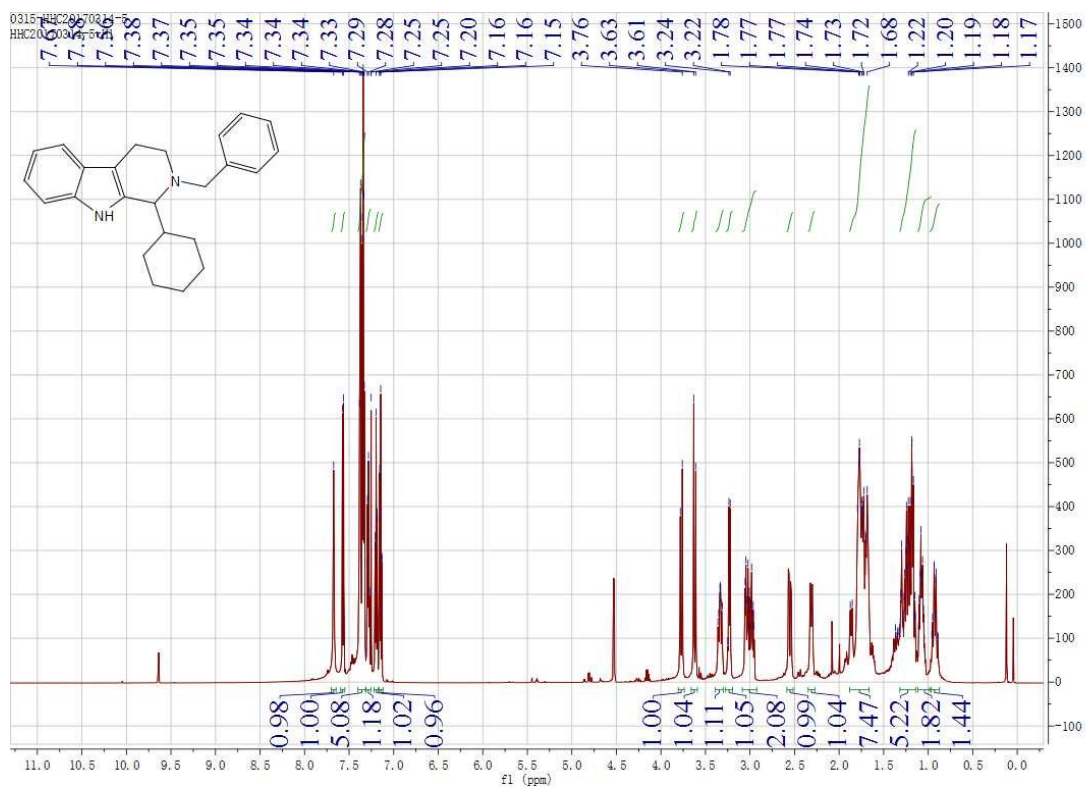


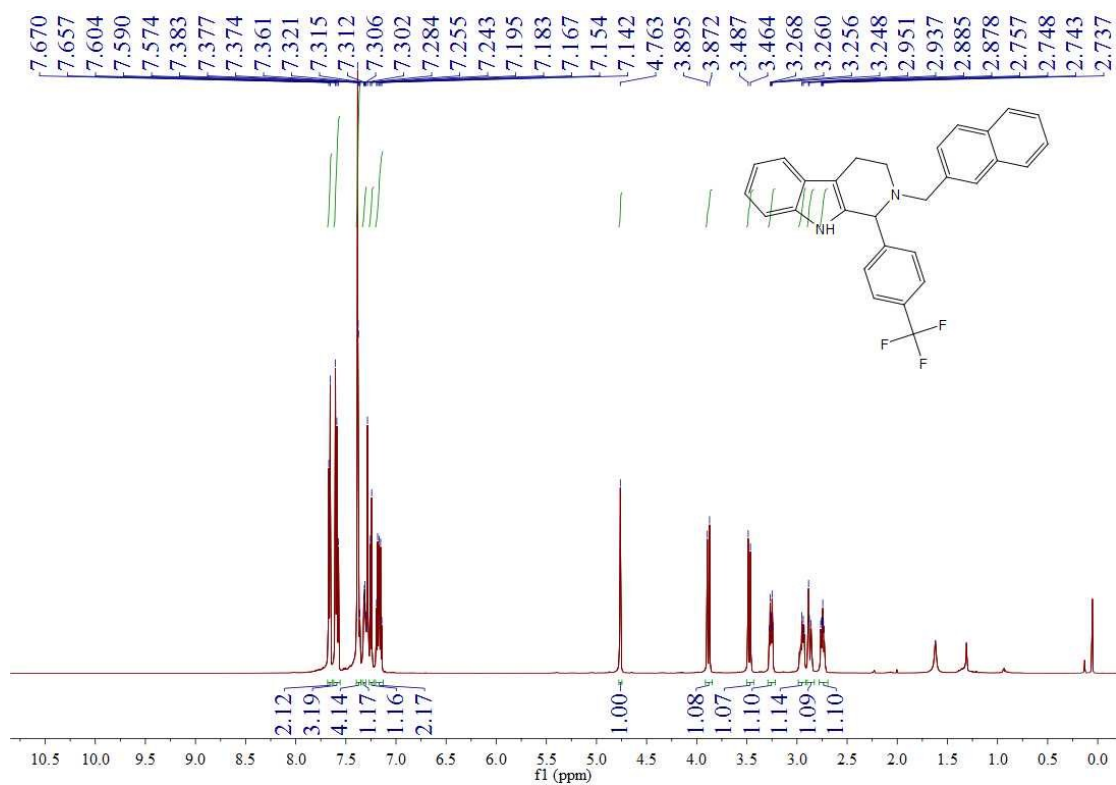


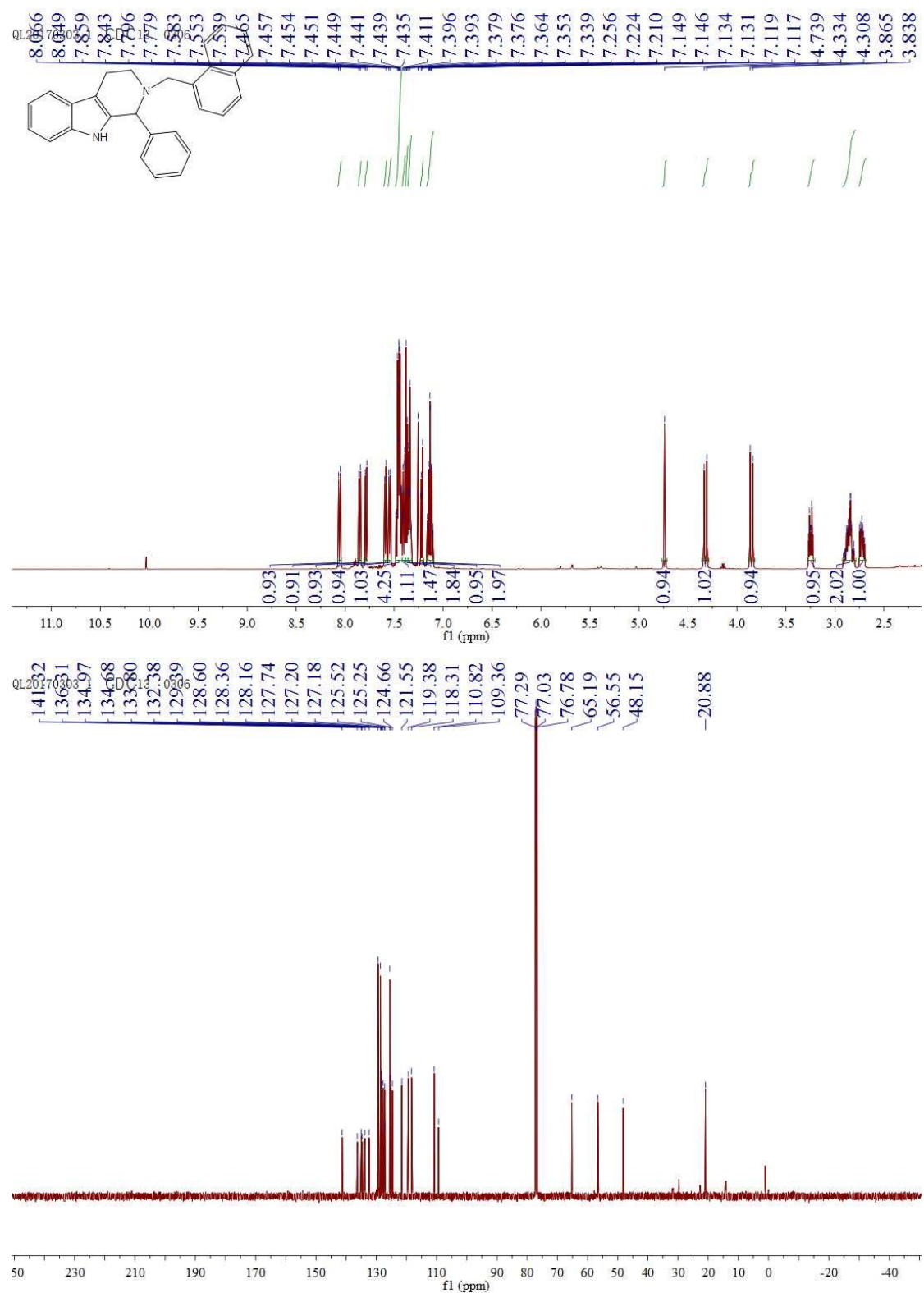


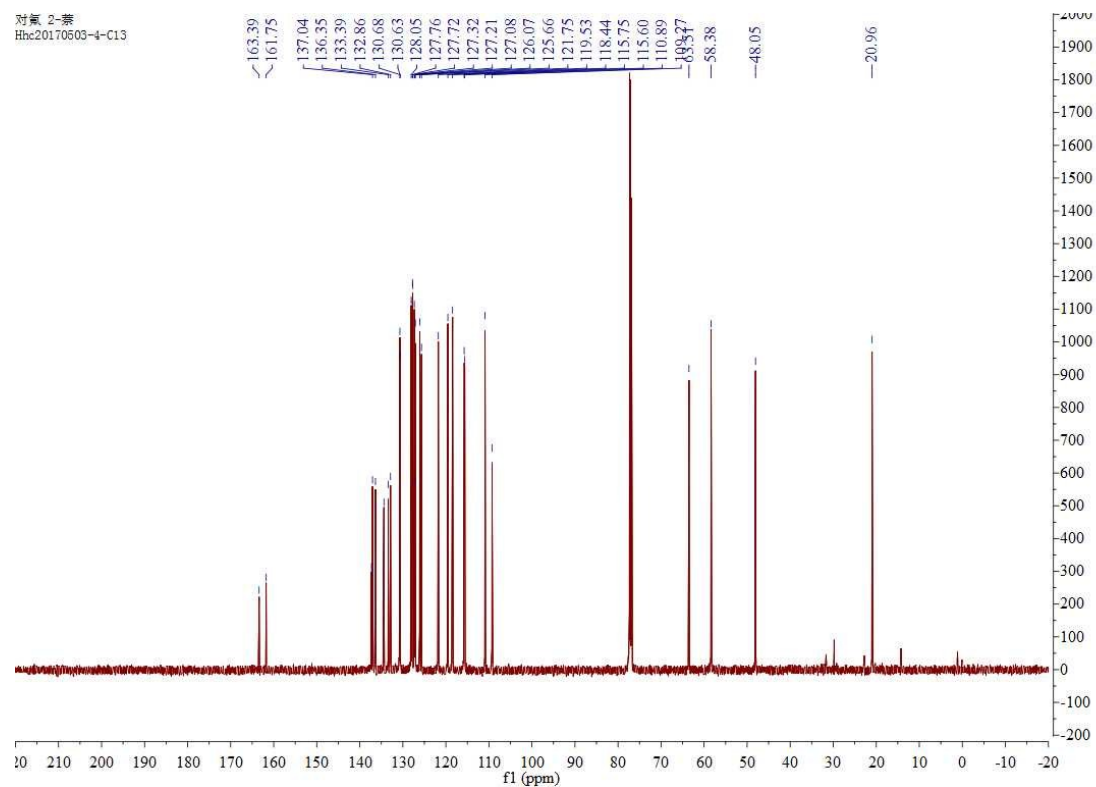
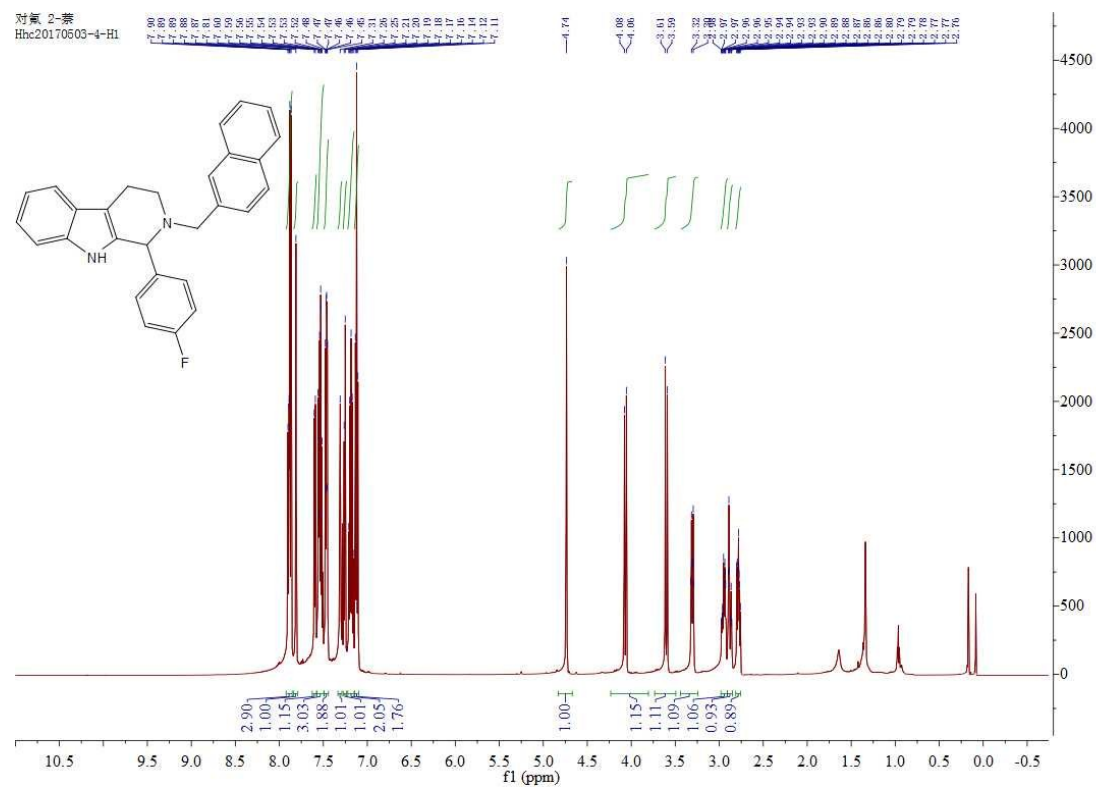


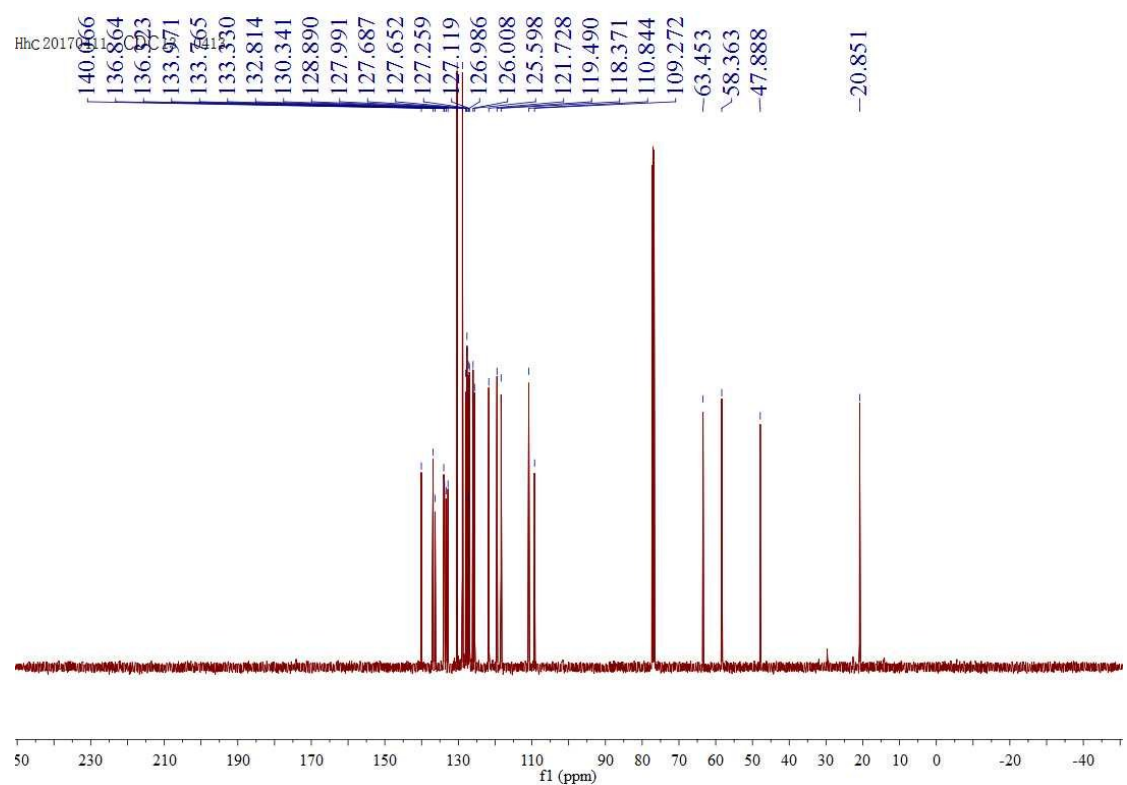
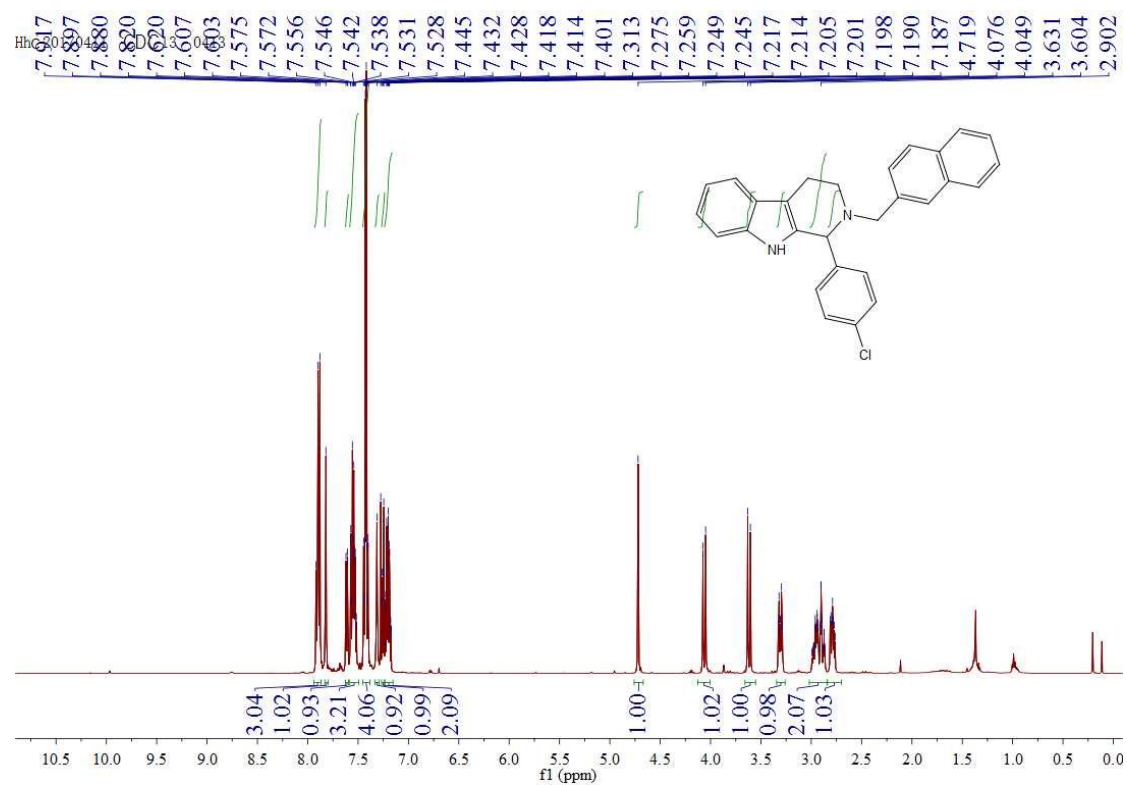


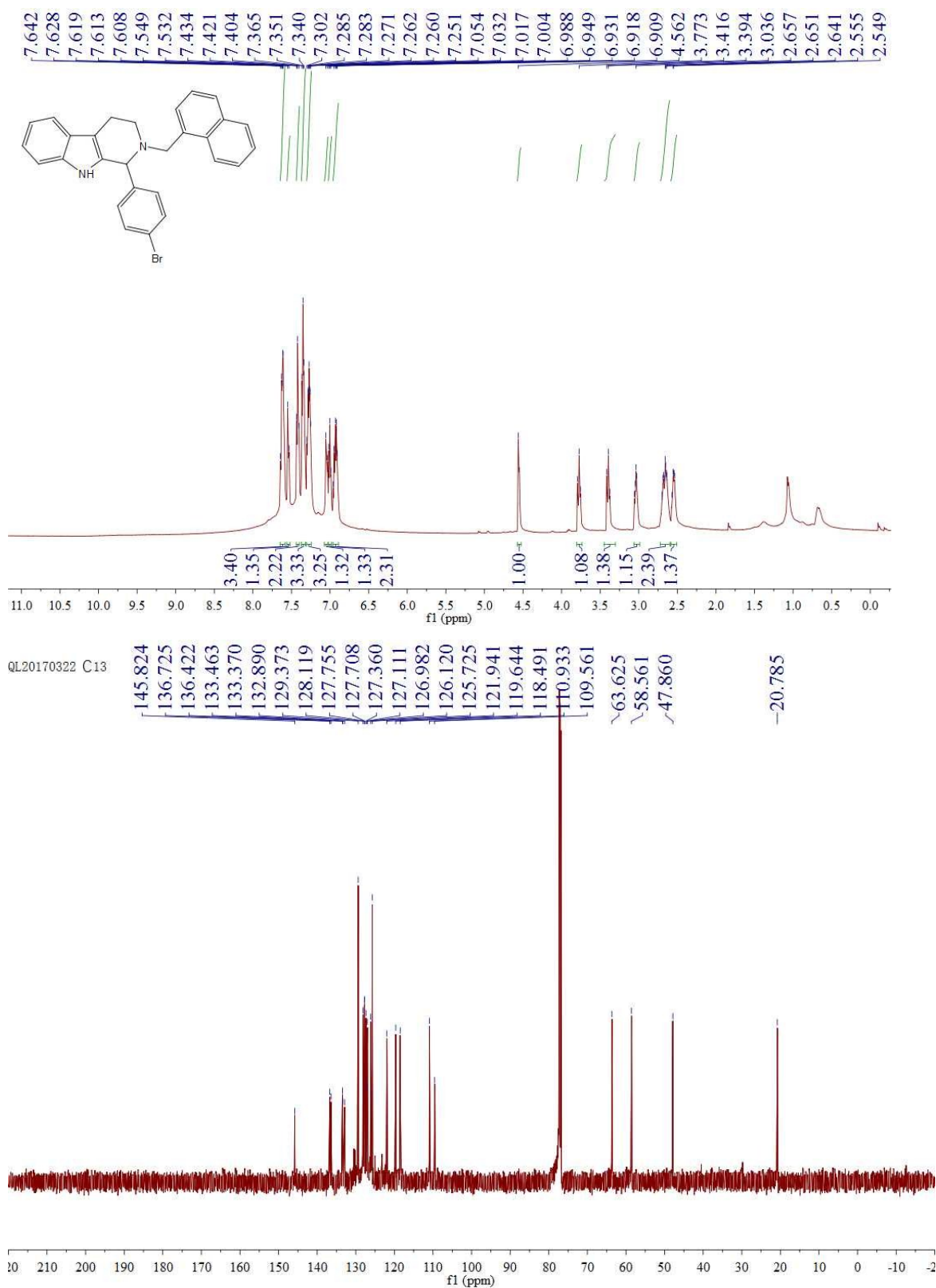


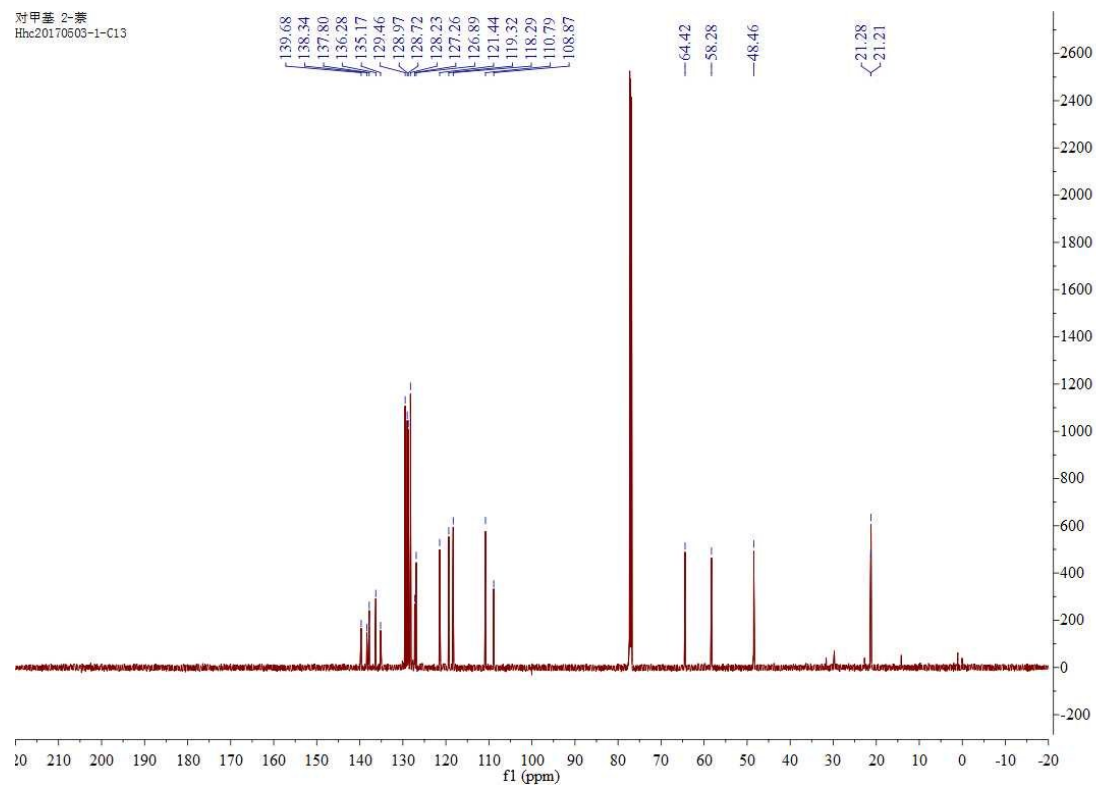
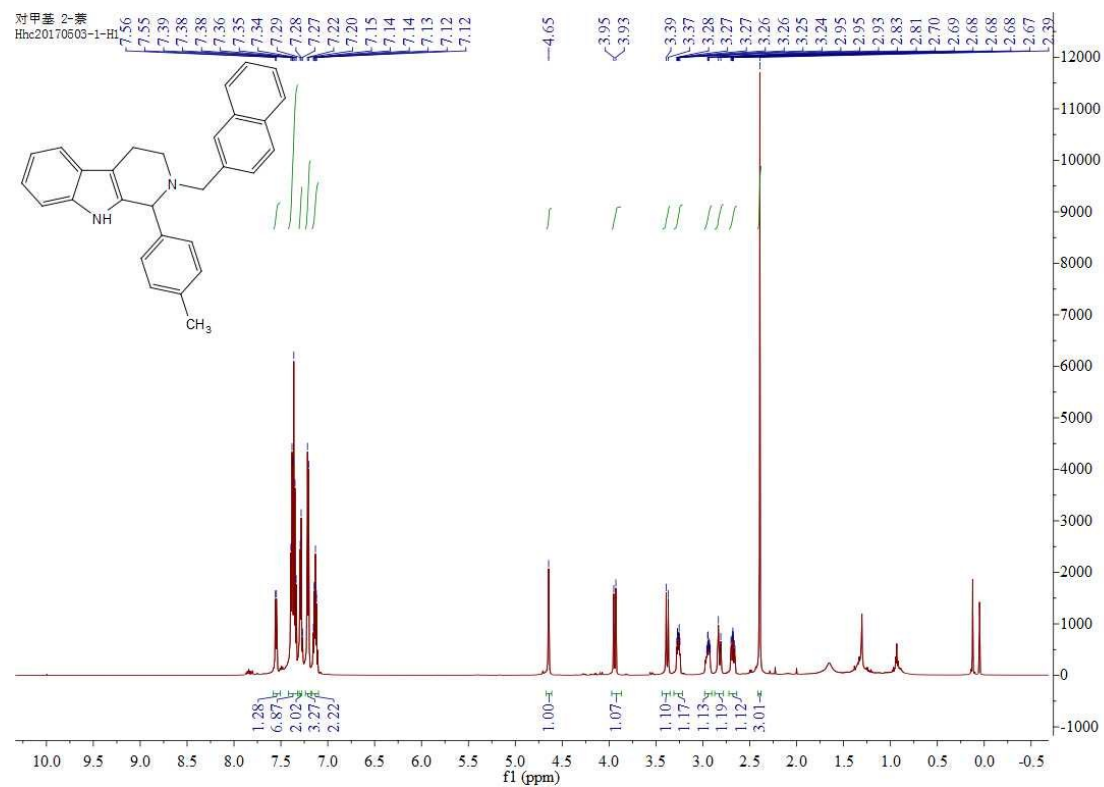


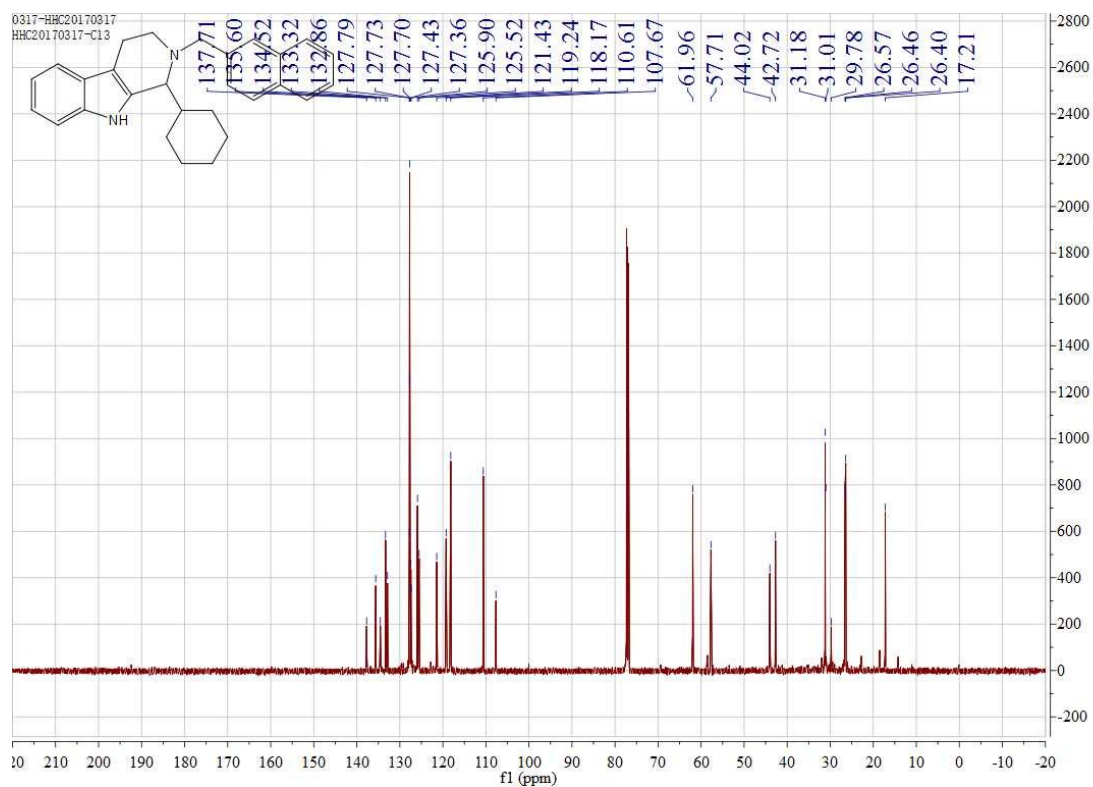
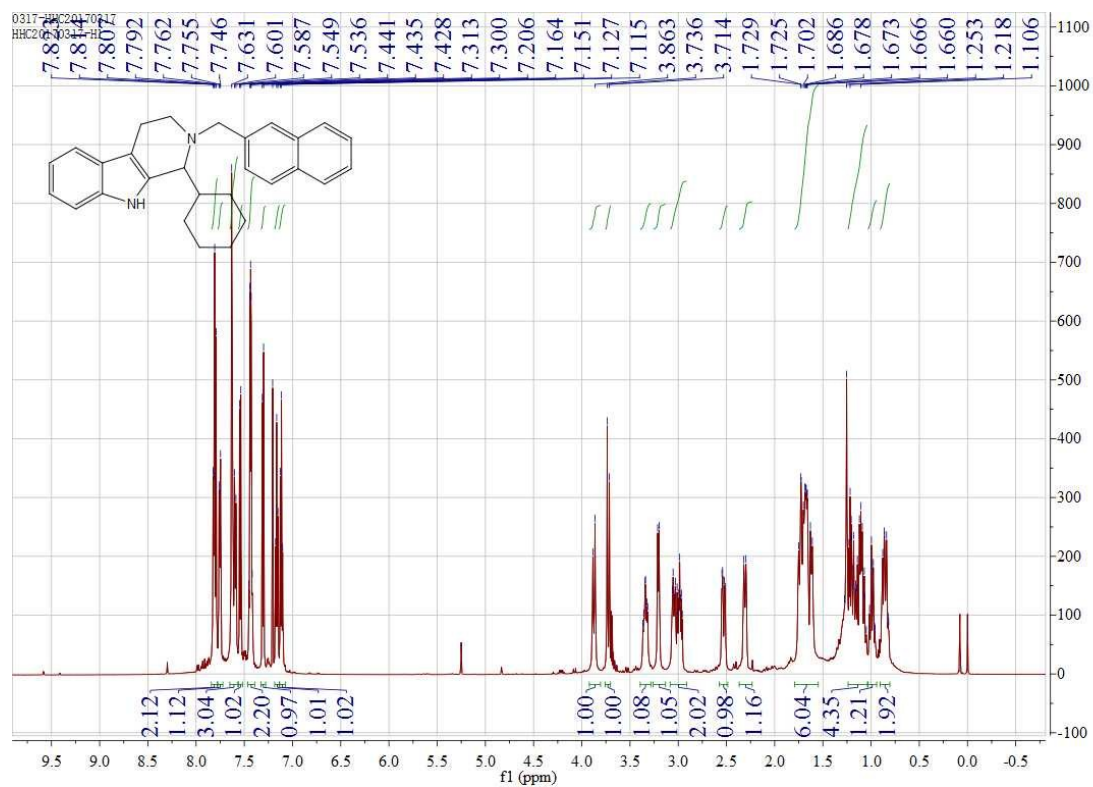


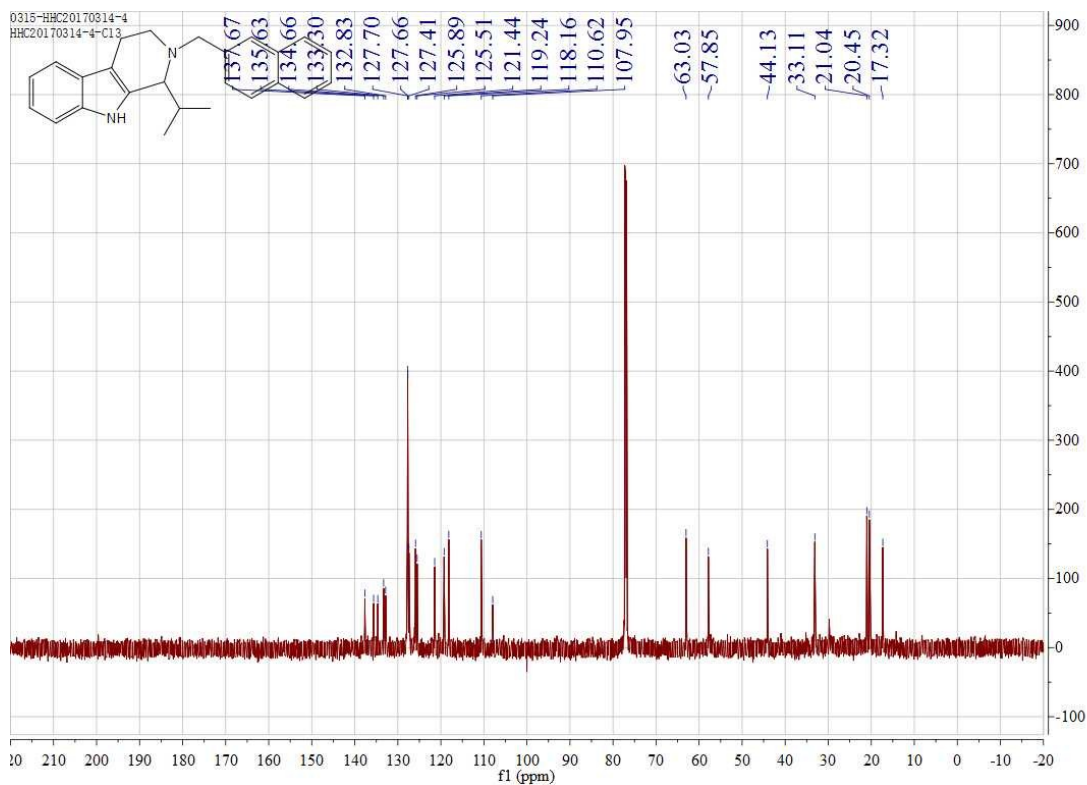
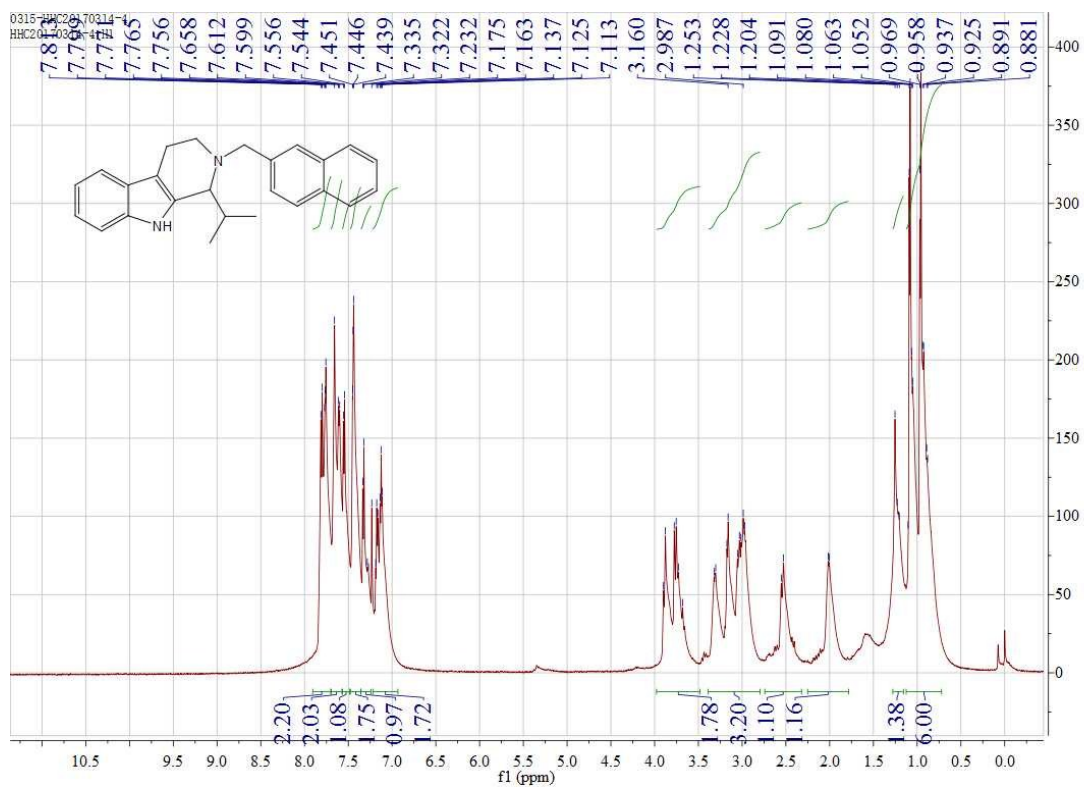


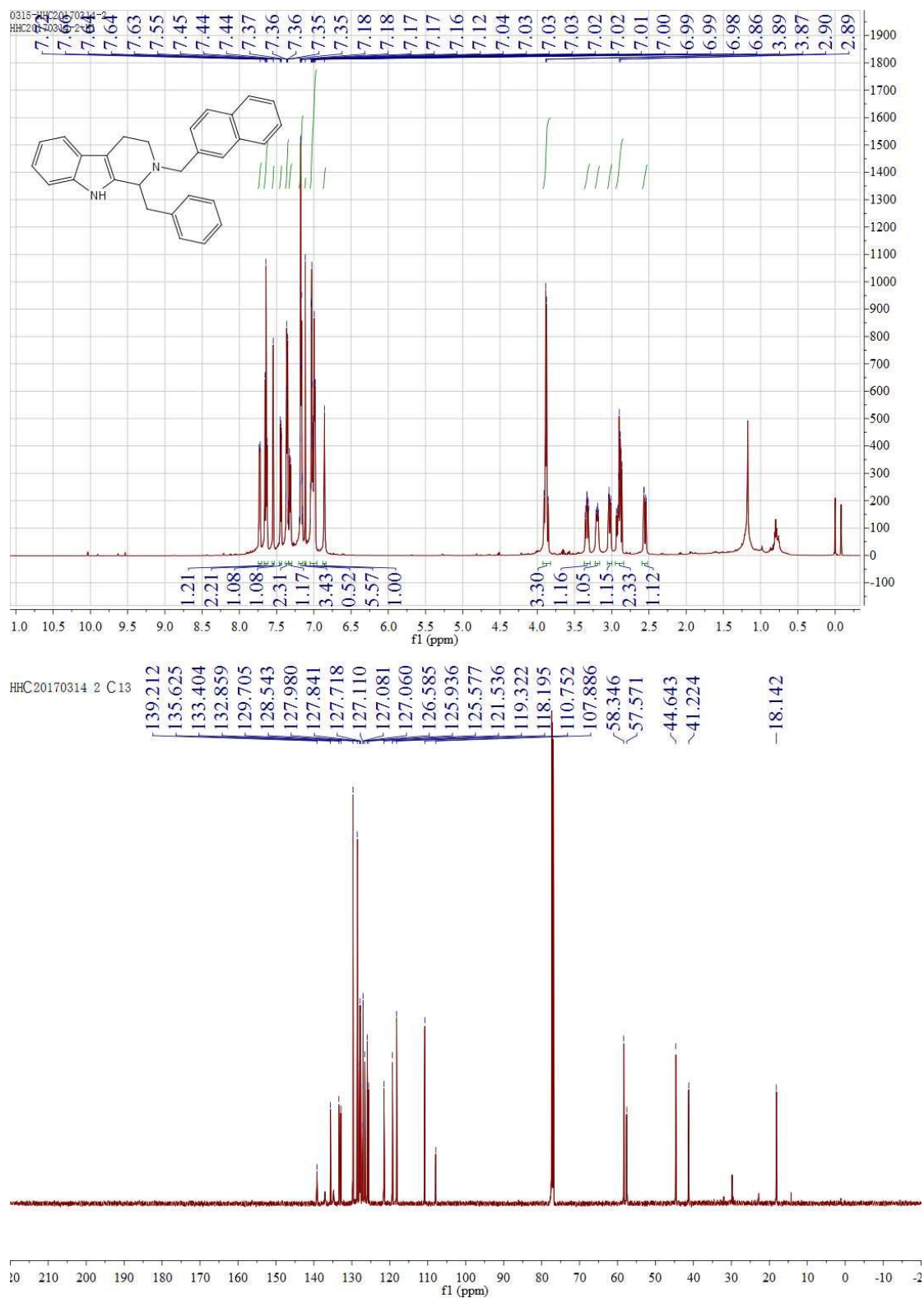


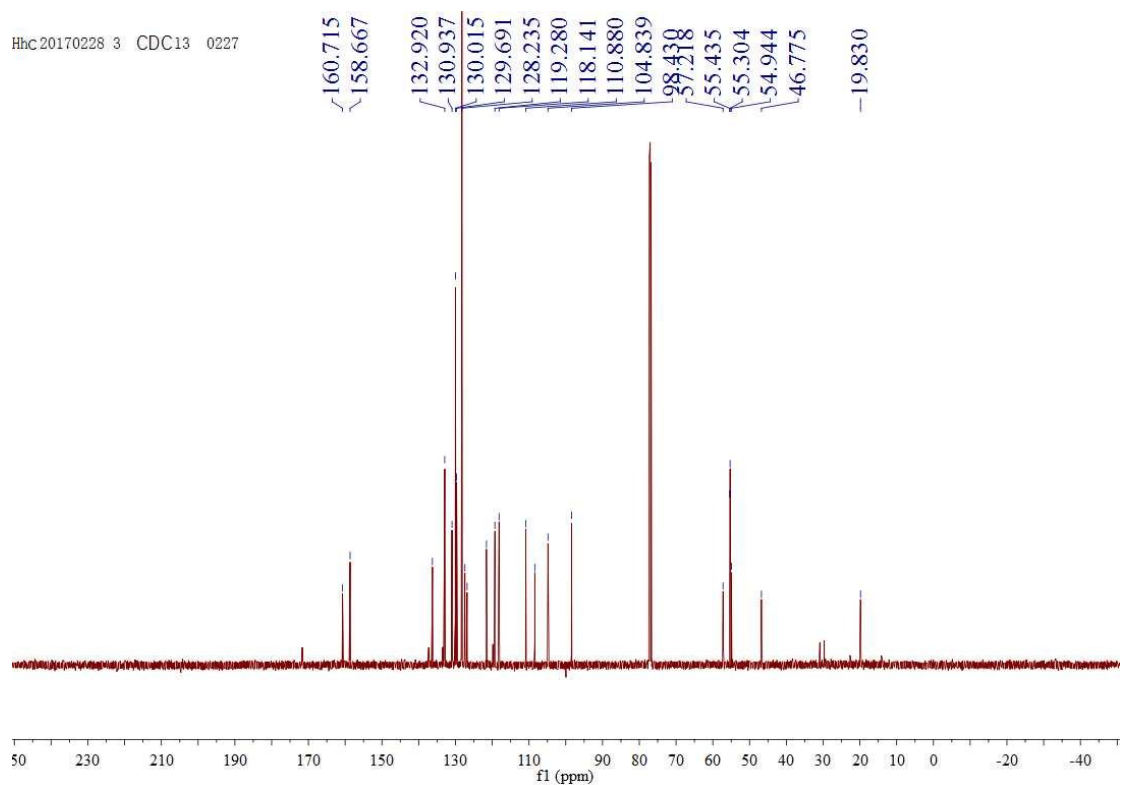
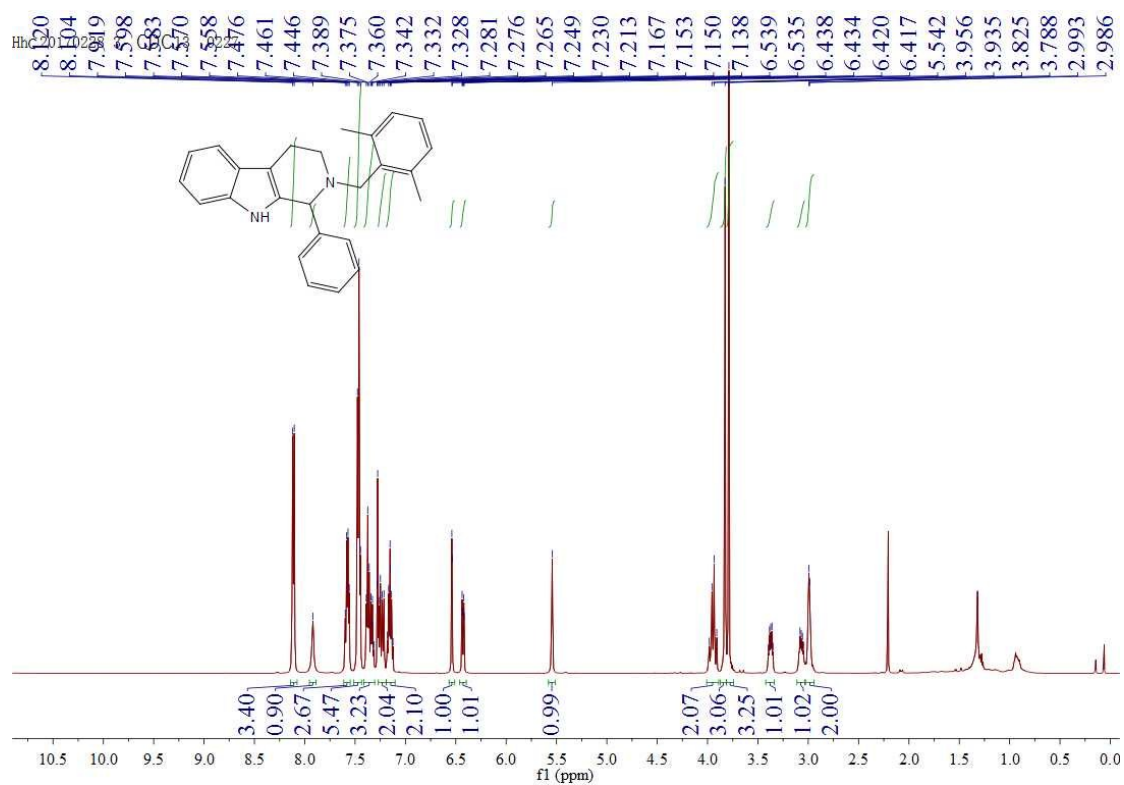


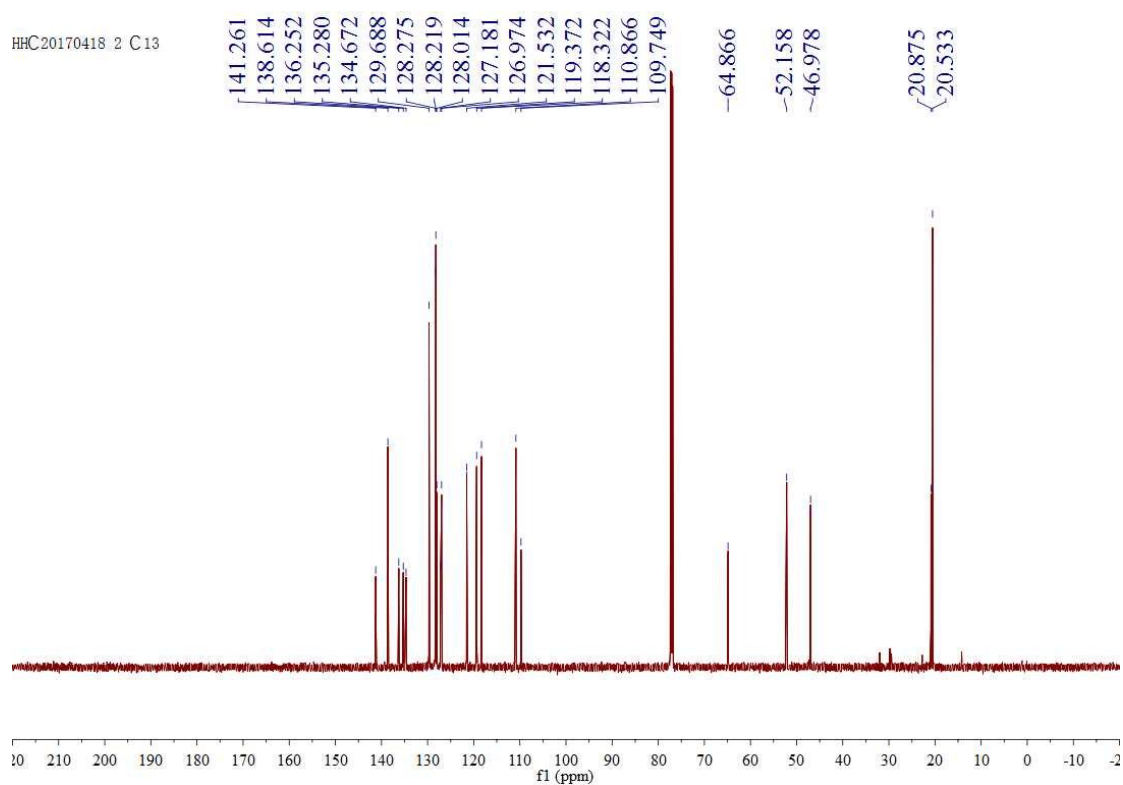
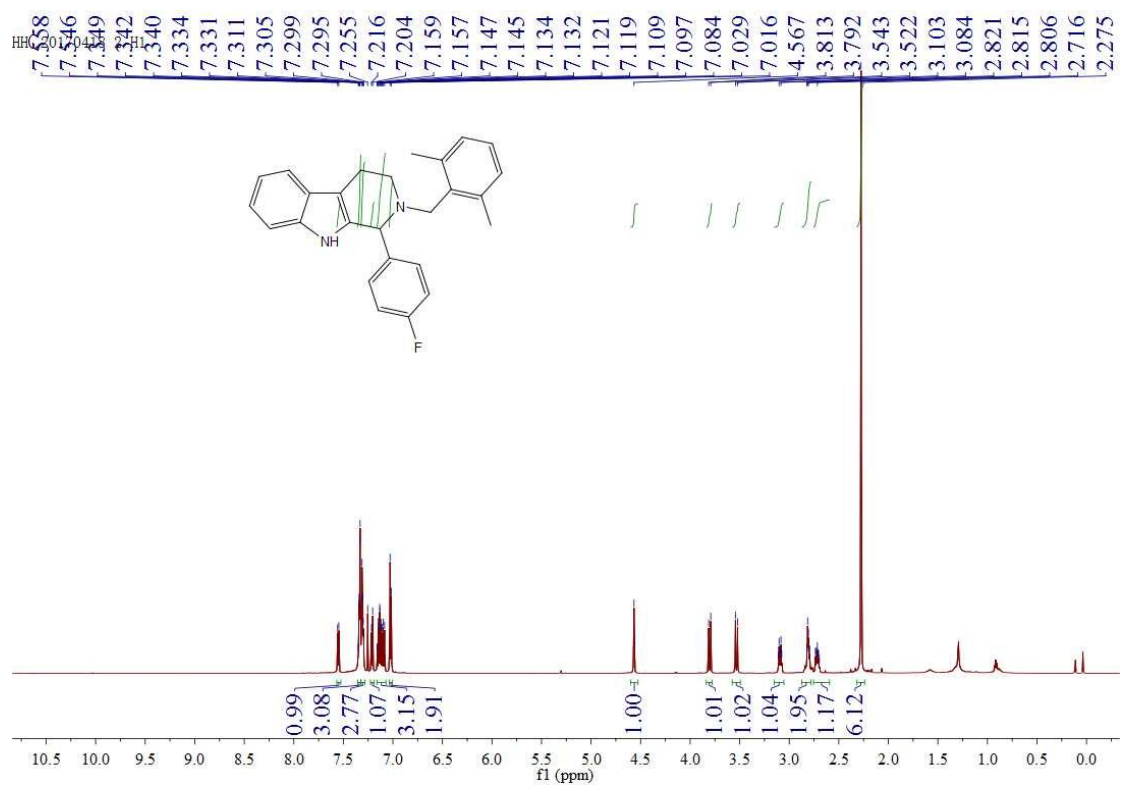


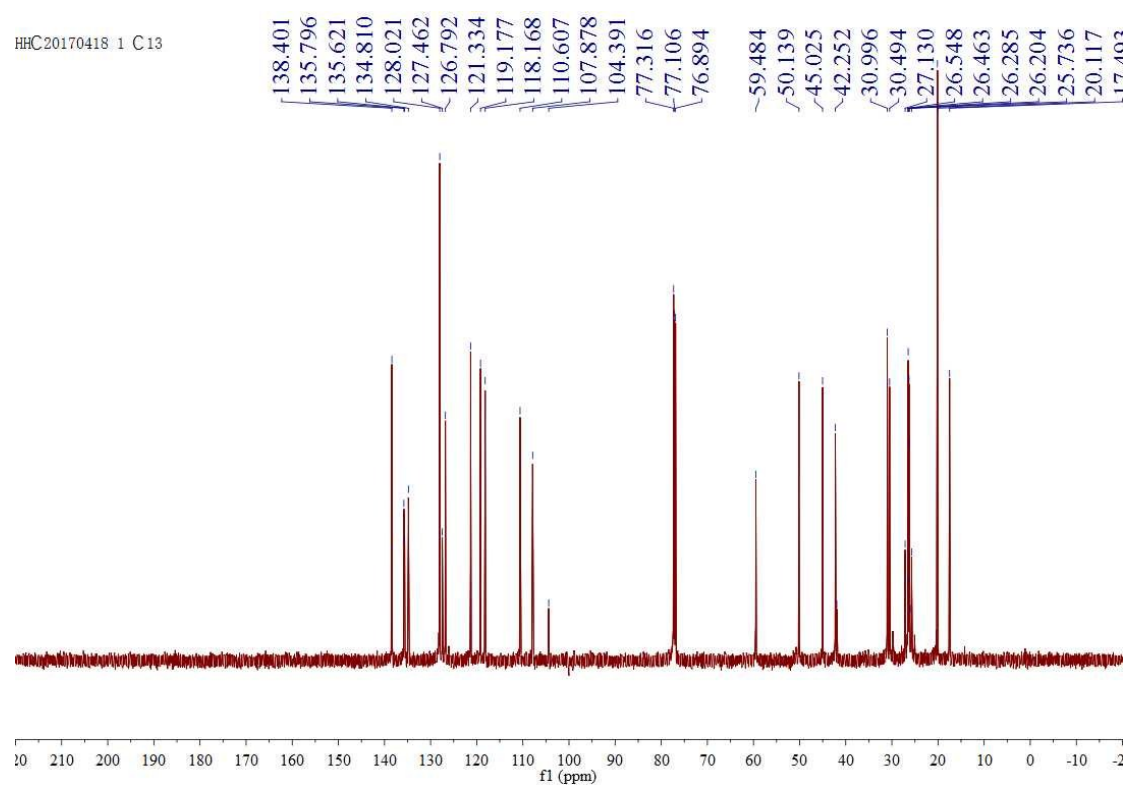
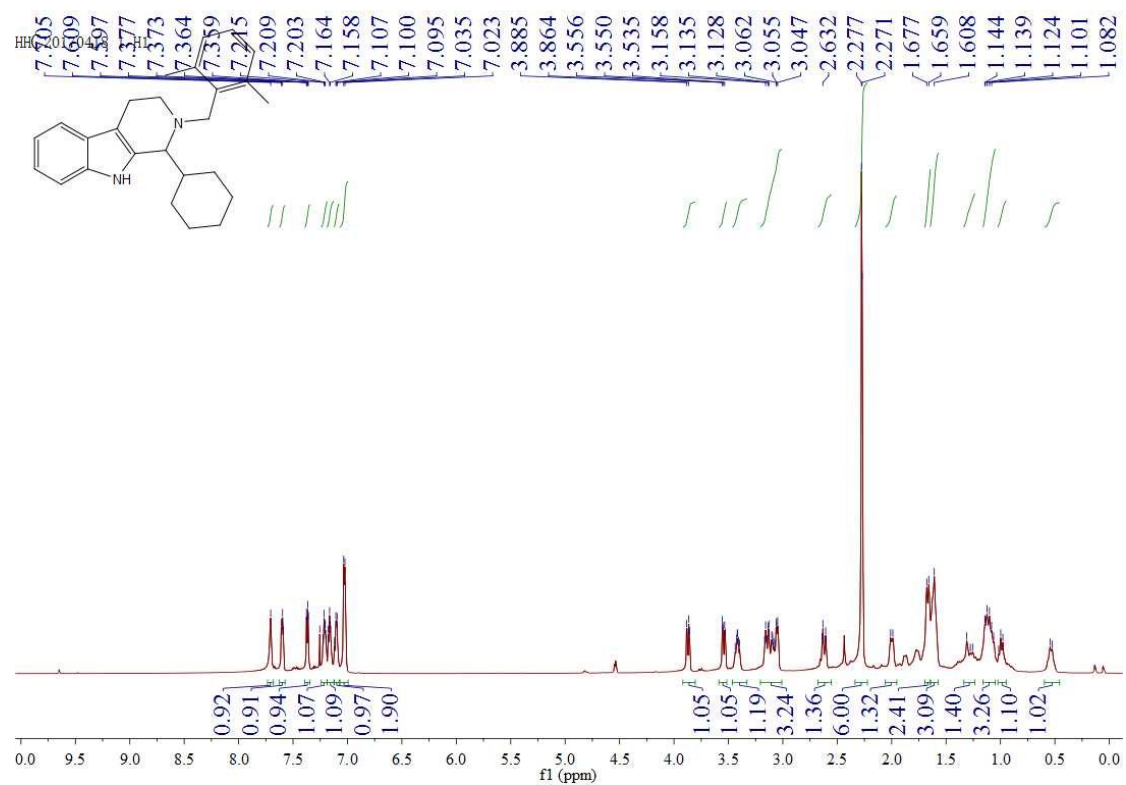


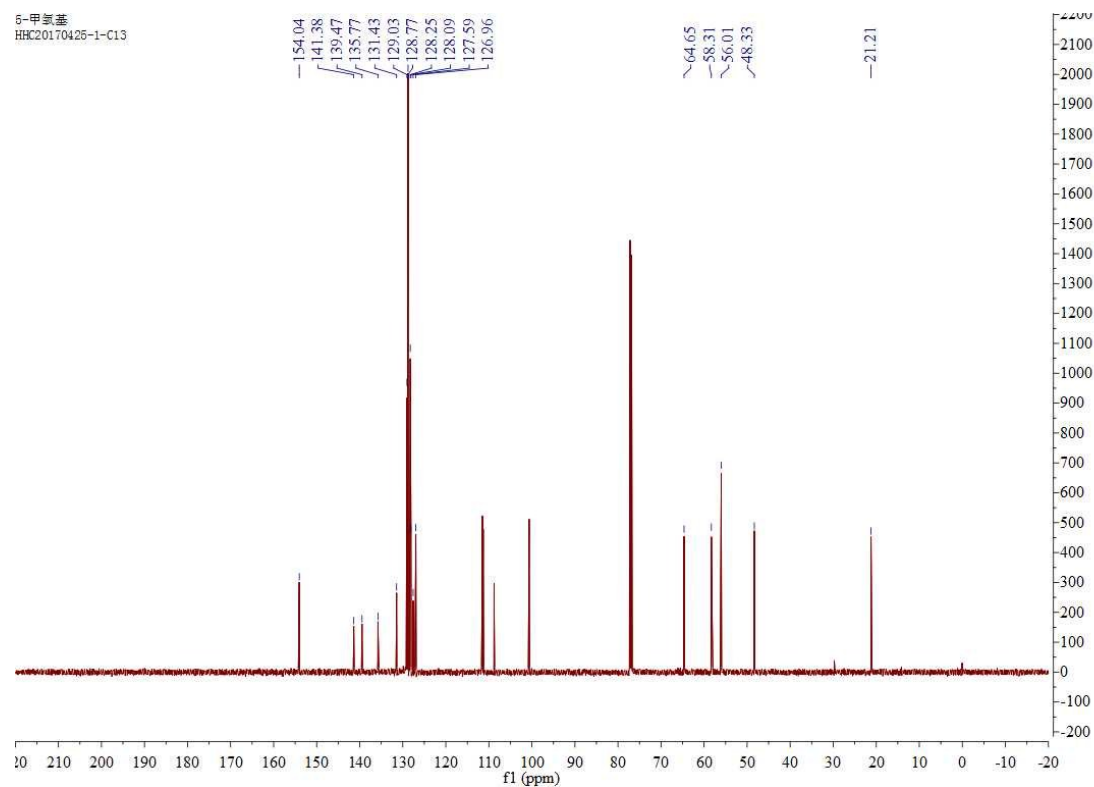
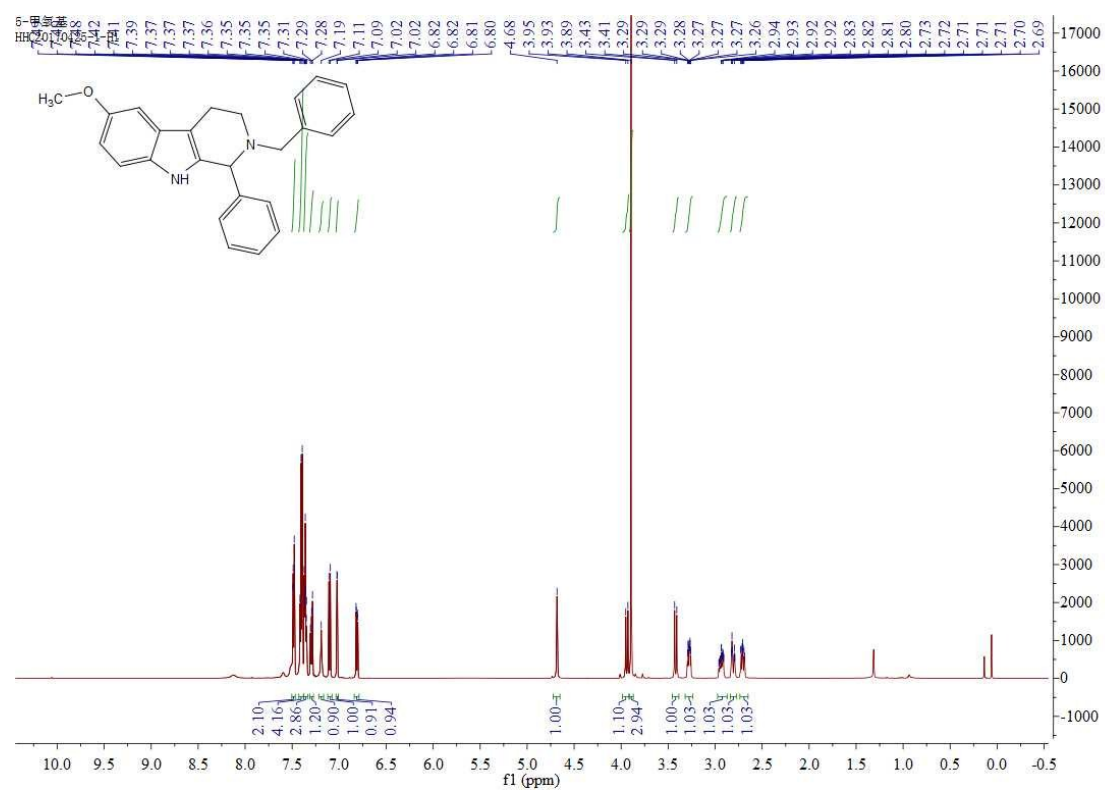












IV. Cartesian coordinates for all of the calculated structures

73				H	-3.927979	-1.953536	-0.749819
1				H	-7.651398	0.041633	0.082139
C	-1.450584	-0.748750	-0.461504	C	-6.560118	-2.321244	-0.761457
C	-0.065435	-0.632592	-0.524741	C	-6.566633	2.441830	0.861060
C	0.101372	-2.031065	-0.977469	F	-6.232121	-3.329940	0.051207
C	-1.422065	-2.171416	-0.897455	F	-6.229062	-2.691122	-2.001746
O	-2.228271	-3.045465	-1.111214	F	-7.889352	-2.185042	-0.721196
O	1.047914	-2.712964	-1.287355	F	-6.216492	2.754202	2.115907
N	-2.373474	0.188134	-0.106302	F	-7.893273	2.315485	0.831124
H	-2.005065	1.090457	0.166251	F	-6.240044	3.495042	0.099684
N	0.827431	0.336426	-0.316633	N	3.603422	-2.021446	3.221426
H	0.594219	1.272934	0.009601	C	4.524344	3.199113	1.119280
C	-3.767303	0.098020	-0.068764	C	4.821645	2.974016	-0.363034
C	-4.476904	1.227118	0.345144	C	3.075516	2.732164	1.376909
C	-4.462536	-1.057935	-0.428799	H	5.229144	2.627990	1.736273
C	-5.862756	1.201424	0.398853	H	4.657729	4.255124	1.387667
H	-3.945959	2.136235	0.626708	H	3.060759	1.786118	1.926242
C	-5.850651	-1.056606	-0.368041	H	2.518785	3.459296	1.981116
C	-6.568389	0.060093	0.042603	C	4.441889	1.524319	-0.692224
C	2.263240	0.077764	-0.351749	H	4.840220	1.214805	-1.667544
H	2.444739	-0.588493	-1.206253	H	4.883047	0.855389	0.059189
C	2.745731	-0.654645	0.886483	C	2.907956	1.441277	-0.690776
C	3.860728	-1.546455	0.823606	H	2.549214	1.636500	-1.713466
C	2.098970	-0.527305	2.091774	H	5.881240	3.154921	-0.580809
C	4.578004	-1.834158	-0.355563	C	2.493719	3.773748	-0.680851
C	4.242560	-2.200968	2.035380	H	1.775323	3.767131	-1.510732
C	2.568235	-1.218894	3.229549	H	2.230858	4.624576	-0.035799
H	1.220332	0.109197	2.178289	C	3.946962	3.923327	-1.210783
C	5.632969	-2.722251	-0.347146	H	3.991423	3.575379	-2.255787
H	4.315163	-1.388094	-1.310769	N	2.336511	2.545911	0.112671
C	5.333836	-3.097968	2.011219	C	4.407646	5.344114	-1.189047
H	2.051714	-1.091518	4.182504	H	4.384322	5.846534	-0.217493
C	6.021047	-3.359838	0.854615	C	4.823182	6.020759	-2.255262
H	5.599149	-3.578332	2.949357	H	4.852775	5.559510	-3.241788
H	6.851797	-4.059157	0.865244	H	5.149329	7.055205	-2.190110
O	6.249289	-2.927897	-1.535158				
C	7.287908	-3.876220	-1.594620	77			
H	6.943089	-4.876671	-1.299146	2			
H	7.615832	-3.908046	-2.635137	C	-0.951775	-1.686405	-0.942371
H	8.140100	-3.589946	-0.962187	C	0.413716	-1.424141	-0.940397

C	0.758175	-2.848539	-1.131327	F	-7.531831	1.141222	-0.485787
C	-0.749542	-3.145610	-1.112019	F	-5.726110	2.329104	-0.442860
O	-1.456355	-4.123761	-1.195666	N	3.499943	-1.549473	3.474013
O	1.794352	-3.457245	-1.262286	C	4.793822	2.973515	0.353420
N	-1.973714	-0.799699	-0.830632	C	5.068236	2.524971	-1.082198
H	-1.687892	0.161711	-0.664713	C	3.370246	2.501680	0.716039
N	1.159371	-0.318780	-0.848996	H	5.531283	2.531558	1.034997
H	0.723358	0.566492	-0.586292	H	4.894526	4.062753	0.448484
C	-3.334704	-1.023500	-0.670004	H	3.404390	1.648134	1.397554
C	-4.134417	0.114309	-0.509041	H	2.804876	3.291132	1.230939
C	-3.923625	-2.287768	-0.643763	C	4.721219	1.032538	-1.167952
C	-5.491766	-0.010182	-0.277921	H	5.115121	0.577538	-2.086749
H	-3.678606	1.100135	-0.574839	H	5.184744	0.501081	-0.324925
C	-5.296746	-2.385125	-0.430401	C	3.189882	0.916189	-1.136129
C	-6.093503	-1.265172	-0.233674	H	2.824571	0.962588	-2.173282
C	2.597519	-0.412235	-0.631775	H	6.117034	2.697595	-1.352832
H	2.962751	-1.202357	-1.302479	C	2.711484	3.208983	-1.452413
C	2.928103	-0.829952	0.789314	H	1.968186	3.068435	-2.248563
C	4.075082	-1.628333	1.085422	H	2.450722	4.144248	-0.931869
C	2.106562	-0.479277	1.834306	C	4.145894	3.307152	-2.043694
C	4.963630	-2.130205	0.111869	H	4.170678	2.800479	-3.022153
C	4.310090	-1.948880	2.458522	N	2.601801	2.109723	-0.482365
C	2.437037	-0.852412	3.154286	C	4.567322	4.723927	-2.257819
H	1.202878	0.100015	1.650239	H	4.584032	5.363361	-1.369940
C	6.049845	-2.900348	0.470423	C	4.904326	5.245116	-3.433608
H	4.814678	-1.948836	-0.948795	H	4.894752	4.644557	-4.342450
C	5.436585	-2.733494	2.791866	H	5.204330	6.284305	-3.538180
H	1.782625	-0.550784	3.974104	C	-1.644483	3.751265	0.966956
C	6.294189	-3.201755	1.830667	C	-1.323390	5.095609	1.173185
H	5.589188	-2.956788	3.844610	C	-2.294799	5.979201	1.621578
H	7.148311	-3.807498	2.117994	C	-3.586127	5.517439	1.864796
O	6.839993	-3.327239	-0.543864	C	-3.911479	4.174682	1.670961
C	7.912872	-4.185677	-0.240183	C	-2.941842	3.291525	1.228240
H	7.568691	-5.116222	0.232265	H	-0.309270	5.439182	0.971203
H	8.391611	-4.427652	-1.190803	H	-2.051431	7.026180	1.780845
H	8.651289	-3.703715	0.416215	H	-4.347832	6.210492	2.213761
H	-3.316990	-3.183846	-0.790022	H	-4.919810	3.817690	1.862210
H	-7.159399	-1.362778	-0.056166	H	-3.167305	2.235202	1.100024
C	-5.889945	-3.764993	-0.395783	C	-0.616731	2.848228	0.456356
C	-6.301522	1.211563	0.024904	H	0.408186	3.270487	0.358831
F	-5.349993	-4.492421	0.586944	O	-0.816063	1.687908	0.129327
F	-5.662562	-4.417833	-1.538725				
F	-7.213010	-3.742297	-0.199996	124			
F	-6.436286	1.380235	1.351835	TS23			

C	-0.229158	-2.877730	1.229406	F	5.291665	-6.323931	0.585701
C	-1.515364	-2.341139	1.236670	F	5.392356	-0.615113	-0.374740
C	-2.173506	-3.677465	1.294721	F	6.871793	-1.741379	0.805226
C	-0.734611	-4.292409	1.320362	F	5.542886	-0.270311	1.766048
O	-0.239691	-5.406672	1.390051	N	-3.360633	-0.890881	-3.673245
O	-3.336572	-4.052882	1.296630	C	-5.055565	2.728766	0.068369
N	0.954046	-2.239666	1.112399	C	-5.847566	1.978244	1.151940
H	0.932127	-1.262424	0.707895	C	-3.598372	2.204314	0.098659
N	-2.055101	-1.119553	1.200297	H	-5.503487	2.532947	-0.914983
H	-1.500524	-0.266054	1.240684	H	-5.091566	3.813315	0.242992
C	2.226498	-2.789382	1.186123	H	-3.419968	1.497298	-0.715804
C	3.288165	-1.884745	1.179690	H	-2.870235	3.018853	0.003324
C	2.525111	-4.160086	1.220377	C	-5.563921	0.475044	0.975957
C	4.595619	-2.307934	1.048503	H	-6.256381	-0.126345	1.581426
H	3.062668	-0.830077	1.263433	H	-5.709603	0.204106	-0.077219
C	3.851687	-4.560997	1.165064	C	-4.103527	0.194676	1.416495
C	4.902889	-3.657509	1.034771	H	-4.095073	-0.101619	2.475860
C	-3.424964	-0.985613	0.687440	H	-6.921638	2.180230	1.060691
H	-3.946729	-1.900903	1.003109	C	-3.804490	2.307268	2.528166
C	-3.408749	-0.966974	-0.838647	H	-3.420794	1.871587	3.458938
C	-4.518048	-1.481940	-1.586309	H	-3.369434	3.309448	2.419185
C	-2.300231	-0.533310	-1.534928	C	-5.356216	2.405542	2.554250
C	-5.641116	-2.105418	-1.003012	H	-5.761845	1.690439	3.288273
C	-4.447892	-1.389285	-3.011999	N	-3.314809	1.473856	1.378230
C	-2.323414	-0.511812	-2.948351	C	-5.805884	3.786132	2.932097
H	-1.384744	-0.231169	-1.024800	H	-5.417705	4.598704	2.311695
C	-6.680612	-2.578023	-1.777792	C	-6.619689	4.061111	3.945977
H	-5.717460	-2.267756	0.066663	H	-7.014547	3.273918	4.587713
C	-5.535496	-1.865492	-3.777208	H	-6.925023	5.077944	4.181309
H	-1.439367	-0.176180	-3.487711	C	2.136332	0.373490	-2.484011
C	-6.627918	-2.439988	-3.185714	C	3.228999	0.082584	-3.303834
H	-5.452739	-1.771575	-4.855032	C	3.152647	0.317903	-4.672054
H	-7.441421	-2.804655	-3.803662	C	1.985505	0.844457	-5.223289
O	-7.718990	-3.165257	-1.111771	C	0.891972	1.132918	-4.406792
C	-8.792382	-3.743274	-1.880658	C	0.966003	0.895461	-3.039486
H	-8.430355	-4.535278	-2.551987	H	4.129500	-0.339769	-2.859051
H	-9.472990	-4.175169	-1.143756	H	3.999829	0.089172	-5.311917
H	-9.326634	-2.985509	-2.472202	H	1.926132	1.026538	-6.292711
H	1.727720	-4.902244	1.264787	H	-0.016454	1.542591	-4.841354
H	5.924918	-4.000487	0.923971	H	0.130367	1.114206	-2.379009
C	4.172487	-6.007597	1.293282	C	2.238328	0.195316	-1.030459
C	5.613670	-1.256664	0.830979	H	3.114647	-0.371943	-0.702963
F	3.154313	-6.789373	0.863741	O	1.084151	0.159096	-0.262887
F	4.421984	-6.348280	2.585433	C	0.763568	4.420369	1.527750

C	-0.624235	4.092861	1.493058	O	2.516032	4.231742	-0.489281
C	-1.575305	5.063142	1.155641	N	-1.504182	1.928690	-0.543439
C	-1.134777	6.338598	0.841421	H	-1.349665	0.915761	-0.500456
C	0.233448	6.666764	0.865076	N	1.555171	1.087214	-0.459597
C	1.182634	5.719910	1.210889	H	0.994006	0.270161	-0.694112
C	1.475363	3.227161	1.902926	C	-2.840028	2.327343	-0.627537
C	0.524565	2.251176	2.085161	C	-3.786378	1.307532	-0.774095
H	-2.639687	4.838794	1.145715	C	-3.266478	3.652277	-0.562377
H	-1.861109	7.103221	0.579322	C	-5.135244	1.601975	-0.815333
H	0.541032	7.680225	0.621824	H	-3.456658	0.275778	-0.856440
H	2.238293	5.981919	1.253860	C	-4.631767	3.925887	-0.626153
H	0.658900	1.205984	2.335291	C	-5.578728	2.919641	-0.741158
N	-0.743217	2.757858	1.830210	C	3.012352	0.999211	-0.657184
H	-1.592774	2.170539	1.745876	H	3.271346	1.654870	-1.501985
C	2.962119	3.043113	1.845416	C	3.407824	-0.415118	-0.995543
H	3.431199	3.955940	1.452668	C	4.453507	-0.694857	-1.932077
H	3.399420	2.850052	2.835504	C	2.810267	-1.481573	-0.368224
C	3.322011	1.855635	0.925607	C	5.117176	0.281425	-2.704813
H	4.394557	1.823397	0.704734	C	4.834297	-2.064065	-2.090133
H	3.053559	0.930119	1.447537	C	3.276661	-2.794563	-0.596411
N	2.498031	1.878349	-0.307651	H	2.011578	-1.334673	0.354755
H	1.397721	1.348586	-0.040878	C	6.115951	-0.067360	-3.591590
C	2.655630	3.067971	-1.175229	H	4.862882	1.336053	-2.641089
H	2.022803	3.862426	-0.753160	C	5.866037	-2.385247	-2.999248
H	2.242981	2.795353	-2.157911	H	2.810357	-3.616558	-0.050588
C	4.072258	3.567542	-1.327108	C	6.499810	-1.420298	-3.738450
C	5.133222	2.690456	-1.568781	H	6.132218	-3.435007	-3.090577
C	4.329564	4.937989	-1.246439	H	7.286329	-1.702287	-4.431479
C	6.426019	3.179021	-1.729162	O	6.678749	0.950213	-4.285026
H	4.951472	1.618967	-1.604680	C	7.694270	0.649662	-5.212787
C	5.621306	5.428696	-1.418774	H	7.333497	-0.013364	-6.011408
H	3.504465	5.623454	-1.054189	H	7.999954	1.600575	-5.652629
C	6.672945	4.549024	-1.659794	H	8.564985	0.185432	-4.728991
H	7.245522	2.488085	-1.908206	H	-2.546949	4.467393	-0.472376
H	5.807115	6.497846	-1.358770	H	-6.638636	3.152806	-0.779148
H	7.683627	4.927212	-1.787356	C	-5.048264	5.366949	-0.564718
124				C	-6.142684	0.497824	-0.912974
3				F	-4.525207	6.062330	-1.578829
C	-0.388519	2.691332	-0.522570	F	-4.626373	5.943144	0.565519
C	0.948281	2.288319	-0.489062	F	-6.376421	5.509990	-0.618671
C	1.432393	3.688497	-0.504326	F	-5.564955	-0.690089	-1.111463
C	-0.025181	4.131895	-0.533714	F	-7.001638	0.707315	-1.916973
O	-0.606794	5.191651	-0.558316	F	-6.869514	0.411668	0.208768
				N	4.258314	-3.091844	-1.409793

C	6.226112	0.722919	1.987130	C	-0.839575	-1.156165	3.030444
C	5.910985	2.168414	1.600640	C	0.018000	-0.127731	2.713554
C	4.914202	-0.082049	1.885212	H	3.394014	-2.523971	2.705805
H	6.983078	0.309031	1.309333	H	2.876115	-4.907311	3.178096
H	6.648869	0.670657	2.998873	H	0.560388	-5.630148	3.658039
H	4.919128	-0.740715	1.009619	H	-1.302504	-4.005058	3.658482
H	4.770432	-0.724410	2.765504	H	-0.203077	0.914840	2.501295
C	5.160589	2.128196	0.264746	N	1.319693	-0.580191	2.667352
H	5.084183	3.119588	-0.201322	H	2.140780	-0.047337	2.336872
H	5.700471	1.471392	-0.432737	C	-2.334738	-1.126841	3.045482
C	3.743518	1.614393	0.557481	H	-2.713295	-1.988774	3.614168
H	3.143453	2.499644	0.790361	H	-2.714834	-0.233845	3.559218
H	6.831211	2.759148	1.516175	C	-2.907972	-1.151651	1.620172
C	3.840675	1.777176	2.910844	H	-4.010976	-1.167212	1.633260
H	2.876277	2.290342	3.030994	H	-2.626041	-0.212513	1.132932
H	4.015326	1.204404	3.834007	N	-2.369422	-2.271405	0.854561
C	4.985995	2.796333	2.667156	H	-0.487498	-1.022371	0.688894
H	4.562602	3.719978	2.240319	C	-3.140290	-3.506189	0.994510
N	3.738085	0.810969	1.798143	H	-3.211535	-3.715865	2.072386
C	5.689699	3.157002	3.934404	H	-2.561594	-4.329078	0.560736
H	6.160596	2.333215	4.479489	C	-4.529211	-3.482728	0.405157
C	5.764615	4.387513	4.431926	C	-4.733384	-3.722378	-0.955595
H	5.300260	5.231736	3.923777	C	-5.637150	-3.219799	1.211747
H	6.287531	4.602348	5.360043	C	-6.013190	-3.687035	-1.495353
C	-1.058070	-3.138107	-1.037689	H	-3.877408	-3.956113	-1.589653
C	-1.252899	-3.456790	-2.377987	C	-6.920362	-3.187578	0.676060
C	-0.549979	-4.506681	-2.963371	H	-5.488408	-3.054289	2.279822
C	0.349700	-5.246229	-2.205743	C	-7.109950	-3.421853	-0.680745
C	0.546810	-4.931544	-0.862850	H	-6.158679	-3.879018	-2.556017
C	-0.142421	-3.875244	-0.282702	H	-7.772371	-2.981853	1.319554
H	-1.958876	-2.873358	-2.969375	H	-8.110930	-3.398676	-1.104691
H	-0.708011	-4.746086	-4.012126				
H	0.897418	-6.068717	-2.658875	124			
H	1.242934	-5.513460	-0.261066	TS34			
H	0.005755	-3.631944	0.770463	C	-1.159291	2.413237	1.234303
C	-1.773027	-1.960427	-0.422178	C	0.226179	2.551363	1.074535
H	-2.496417	-1.555404	-1.163394	C	0.116800	3.775461	0.285419
O	-0.830760	-0.894417	-0.217741	C	-1.396923	3.657294	0.430759
C	-0.017040	-2.324337	3.176896	O	-2.355380	4.281872	0.028826
C	1.319103	-1.927693	2.929396	O	0.904078	4.515391	-0.278437
C	2.375300	-2.843452	2.920458	N	-1.790021	1.377139	1.800887
C	2.076716	-4.169963	3.178835	H	-1.165352	0.240338	1.537751
C	0.757858	-4.581337	3.449770	N	1.288101	1.830005	1.488939
C	-0.285849	-3.673579	3.451745	H	1.144579	1.014202	2.073594

C	-3.157530	1.200443	1.821073	H	4.546193	-0.434797	0.930326
C	-3.612275	-0.037316	2.302365	H	4.845885	-1.177000	2.498250
C	-4.117532	2.106745	1.330146	C	5.059588	2.440813	1.341324
C	-4.950794	-0.396201	2.217572	H	5.067085	3.538644	1.324328
H	-2.887118	-0.740369	2.711967	H	5.254475	2.103500	0.310892
C	-5.453488	1.737228	1.284186	C	3.701109	1.934460	1.844664
C	-5.895283	0.482778	1.706768	H	3.334848	2.649610	2.595895
C	2.573127	1.971002	0.809474	H	7.083639	2.402956	2.163682
H	2.574189	3.000803	0.430973	C	4.425890	1.049629	3.901196
C	2.652265	1.024741	-0.375833	H	3.638533	1.508543	4.511967
C	2.840561	1.491488	-1.712301	H	4.739627	0.130975	4.419041
C	2.465094	-0.327725	-0.194847	C	5.634466	2.018371	3.742411
C	3.020710	2.848188	-2.059162	H	5.288615	3.055543	3.879757
C	2.822782	0.507976	-2.756084	N	3.870728	0.665609	2.592449
C	2.503095	-1.214060	-1.292478	C	6.694204	1.761340	4.763085
H	2.315836	-0.733725	0.805205	H	7.126631	0.756345	4.772787
C	3.177879	3.224853	-3.377499	C	7.123148	2.655165	5.648945
H	2.985835	3.643270	-1.319759	H	6.712130	3.663612	5.679450
C	2.981124	0.932829	-4.094512	H	7.896331	2.421169	6.375768
H	2.404571	-2.288502	-1.113035	C	-1.938106	-0.128810	-1.165074
C	3.157741	2.254949	-4.408852	C	-3.183624	0.489049	-1.318446
H	2.960645	0.164449	-4.862902	C	-3.292459	1.685273	-2.016296
H	3.278584	2.550136	-5.446826	C	-2.156485	2.284662	-2.548697
O	3.350884	4.546421	-3.603781	C	-0.910869	1.679312	-2.396177
C	3.443540	4.996189	-4.933721	C	-0.800190	0.479988	-1.706773
H	2.542696	4.748043	-5.512313	H	-4.068881	0.041109	-0.866751
H	3.542484	6.081786	-4.883758	H	-4.260557	2.172517	-2.095999
H	4.323450	4.581836	-5.446079	H	-2.235936	3.244902	-3.050615
H	-3.805391	3.074645	0.935765	H	-0.014203	2.157861	-2.786963
H	-6.941352	0.204563	1.632665	H	0.183910	0.040971	-1.550376
C	-6.432906	2.640686	0.599592	C	-1.901570	-1.352911	-0.346843
C	-5.306560	-1.793554	2.610072	H	-2.707734	-1.423862	0.385371
F	-7.660398	2.545497	1.124192	O	-0.731993	-0.775841	1.160756
F	-6.545919	2.300451	-0.701234	C	2.055140	-4.446432	0.339114
F	-6.070614	3.920788	0.638750	C	2.988688	-3.719483	1.116079
F	-4.684364	-2.681078	1.798799	C	4.362279	-3.793898	0.887683
F	-6.613265	-2.042761	2.530278	C	4.796574	-4.606362	-0.146355
F	-4.909541	-2.086126	3.853115	C	3.888276	-5.338757	-0.928908
N	2.658833	-0.823846	-2.536852	C	2.526735	-5.273151	-0.690551
C	6.282819	0.389832	1.961146	C	0.741599	-4.099780	0.808486
C	6.130274	1.874428	2.285131	C	0.919828	-3.204021	1.828218
C	4.866065	-0.220491	1.953813	H	5.068389	-3.232463	1.495885
H	6.761596	0.261739	0.982075	H	5.860871	-4.679861	-0.355171
H	6.932353	-0.105354	2.694753	H	4.265568	-5.969844	-1.729666

H	1.832134	-5.858071	-1.292861	C	-5.348654	-2.294075	-1.053018
H	0.185207	-2.659778	2.407198	C	-5.918843	-1.160966	-1.632669
N	2.267012	-2.978729	2.026285	C	2.671166	-1.690240	-0.596153
H	2.651591	-2.306935	2.674385	H	2.779180	-2.725857	-0.251511
C	-0.536412	-4.661605	0.273315	C	2.656602	-0.776722	0.617704
H	-0.345171	-5.133485	-0.700414	C	2.924051	-1.253455	1.938870
H	-0.903230	-5.478150	0.912190	C	2.327214	0.553426	0.475230
C	-1.695878	-3.685461	0.135761	C	3.269512	-2.586991	2.245800
H	-2.571121	-4.221849	-0.257105	C	2.814952	-0.307199	3.010531
H	-1.969129	-3.282080	1.117699	C	2.308095	1.409597	1.597765
N	-1.423127	-2.527661	-0.736041	H	2.123807	0.967045	-0.511514
H	0.107519	-0.605474	0.708364	C	3.489213	-2.978741	3.550485
C	-0.655556	-2.754324	-1.961549	H	3.314535	-3.359934	1.484635
H	0.355132	-3.098811	-1.703940	C	3.037505	-0.746728	4.334622
H	-0.537637	-1.792670	-2.470148	H	2.116872	2.476298	1.451281
C	-1.329192	-3.738453	-2.881171	C	3.368672	-2.048271	4.609942
C	-2.688626	-3.623558	-3.173687	H	2.943439	-0.005039	5.123635
C	-0.586644	-4.751060	-3.485800	H	3.538861	-2.354980	5.637587
C	-3.295357	-4.513302	-4.051322	O	3.822104	-4.276670	3.735325
H	-3.271540	-2.827719	-2.708976	C	3.962407	-4.754220	5.050848
C	-1.191203	-5.638360	-4.370079	H	3.038881	-4.623566	5.632262
H	0.477760	-4.835213	-3.264057	H	4.179694	-5.820583	4.968994
C	-2.547735	-5.522921	-4.651035	H	4.790707	-4.262087	5.580622
H	-4.355848	-4.417055	-4.270995	H	-3.573432	-3.411809	-0.574804
H	-0.601672	-6.423902	-4.836352	H	-6.983629	-0.967920	-1.558247
H	-3.023665	-6.218910	-5.337259	C	-6.208595	-3.179645	-0.205871
124				C	-5.562600	1.007975	-2.864592
4				F	-5.801276	-4.446564	-0.200606
C	-1.005048	-2.521155	-1.041328	F	-7.489765	-3.164153	-0.588577
C	0.395282	-2.481228	-0.852716	F	-6.187977	-2.756884	1.078812
C	0.411680	-3.669217	-0.003177	F	-4.974856	2.045946	-2.223149
C	-1.098851	-3.716885	-0.135579	F	-6.880548	1.166333	-2.736917
O	-1.981422	-4.402620	0.342846	F	-5.257696	1.149721	-4.157848
O	1.273988	-4.311652	0.575500	N	2.517222	1.006966	2.829634
N	-1.747410	-1.655671	-1.726898	C	6.473603	-0.110703	-1.340818
H	-0.900244	-0.322808	-2.248393	C	6.259377	-1.486147	-1.966272
N	1.379019	-1.666172	-1.278693	C	5.091713	0.564962	-1.245645
H	1.133594	-0.864739	-1.861112	H	6.921604	-0.212281	-0.344397
C	-3.114703	-1.635034	-1.737544	H	7.171630	0.488567	-1.939983
C	-3.708797	-0.530578	-2.382122	H	4.732837	0.585759	-0.212903
C	-3.983216	-2.541049	-1.087584	H	5.148214	1.612300	-1.576121
C	-5.071148	-0.285540	-2.300891	C	5.124268	-2.161893	-1.188998
H	-3.060161	0.164333	-2.916382	H	5.071483	-3.239628	-1.392057
				H	5.292488	-2.048799	-0.105760

C	3.807414	-1.490932	-1.610307	H	-0.971591	4.841818	-0.158195
H	3.428988	-2.022226	-2.495487	H	-1.225384	4.761896	-1.878609
H	7.178000	-2.084243	-1.927956	C	-1.817038	3.003147	-0.906232
C	4.666823	-0.255909	-3.428246	H	-2.849222	3.369212	-0.828623
H	3.882051	-0.531870	-4.143289	H	-1.740467	2.363224	-1.793387
H	5.050950	0.728913	-3.737138	N	-1.578241	2.096327	0.260469
C	5.813396	-1.307177	-3.435384	H	-0.110754	0.718485	-1.420245
H	5.416005	-2.273231	-3.786059	C	-0.949833	2.656903	1.467674
N	4.075756	-0.107440	-2.085922	H	0.006580	3.108827	1.184242
C	6.924134	-0.916652	-4.354464	H	-0.722660	1.835177	2.150960
H	7.408626	0.043364	-4.151698	C	-1.848588	3.662952	2.142351
C	7.341769	-1.642931	-5.386742	C	-3.232690	3.501920	2.184738
H	6.880351	-2.599652	-5.628650	C	-1.267371	4.745851	2.803449
H	8.155577	-1.316851	-6.028824	C	-4.025072	4.416501	2.869162
C	-2.085445	-0.141849	1.202048	H	-3.703904	2.654975	1.685767
C	-3.250097	-0.902011	1.426441	C	-2.059096	5.654936	3.494411
C	-3.211638	-1.996973	2.272481	H	-0.184017	4.862838	2.781247
C	-2.007494	-2.382780	2.857066	C	-3.440464	5.494708	3.524453
C	-0.840742	-1.657144	2.618604	H	-5.103606	4.283338	2.891622
C	-0.875383	-0.536781	1.804764	H	-1.594761	6.493317	4.007524
H	-4.183370	-0.622733	0.939831	H	-4.061316	6.209372	4.058468
H	-4.112978	-2.583259	2.427367				
H	-1.970779	-3.277294	3.472177	121			
H	0.108659	-1.983548	3.040255	5			
H	0.048696	-0.008967	1.574475	C	-0.807969	-1.730544	-1.643489
C	-2.171785	0.929643	0.244426	C	0.590503	-1.703918	-1.476462
H	-2.857788	0.773450	-0.599666	C	0.718953	-3.133243	-1.264226
O	-0.323962	0.500610	-2.336181	C	-0.780470	-3.238288	-1.501107
C	1.682224	4.373911	-0.438493	O	-1.580442	-4.151810	-1.522084
C	2.870216	3.762540	-0.908900	O	1.634623	-3.886186	-0.962982
C	4.115070	4.042943	-0.345501	N	-1.601910	-0.675404	-1.770723
C	4.160687	4.948681	0.701173	N	1.492215	-0.708242	-1.473575
C	2.996932	5.580911	1.169146	H	1.208531	0.228927	-1.726045
C	1.763146	5.310121	0.602985	C	-2.962543	-0.784950	-1.920205
C	0.591511	3.828575	-1.199685	C	-3.667902	0.419222	-2.130094
C	1.149819	2.957794	-2.099530	C	-3.736725	-1.960573	-1.791242
H	5.022521	3.571435	-0.715773	C	-5.053312	0.465803	-2.118906
H	5.116705	5.181355	1.163122	H	-3.086816	1.330923	-2.272451
H	3.072652	6.302084	1.979231	C	-5.125763	-1.890791	-1.787112
H	0.869422	5.826221	0.953328	C	-5.811188	-0.688437	-1.936491
H	0.670514	2.322143	-2.833427	C	2.858621	-0.945070	-1.047610
N	2.518279	2.921543	-1.943745	H	3.087063	-1.978743	-1.345753
H	3.087976	2.159800	-2.302670	C	2.994445	-0.875683	0.465025
C	-0.855431	4.176914	-1.024546	C	3.860579	-1.756120	1.184266

C	2.257664	0.028323	1.196342	C	5.344581	1.608645	-3.396708
C	4.636720	-2.768760	0.582427	H	5.294797	0.790959	-4.133795
C	3.913991	-1.605791	2.606698	N	3.463907	1.409107	-1.757661
C	2.398228	0.094981	2.598751	C	6.117196	2.727220	-4.016497
H	1.562585	0.702454	0.693222	H	6.231254	3.631519	-3.411369
C	5.442864	-3.591308	1.341183	C	6.651308	2.693566	-5.233362
H	4.606055	-2.955114	-0.486854	H	6.552279	1.815698	-5.870635
C	4.755869	-2.460825	3.352612	H	7.205303	3.534072	-5.642436
H	1.824359	0.837724	3.160979	C	-1.977004	-1.728723	1.385075
C	5.509246	-3.431346	2.745475	C	-2.883460	-2.805836	1.334634
H	4.777281	-2.317502	4.429759	C	-2.439071	-4.097426	1.548981
H	6.144913	-4.075513	3.345659	C	-1.085417	-4.338838	1.777895
O	6.141648	-4.531527	0.663327	C	-0.171369	-3.287087	1.785528
C	6.922846	-5.444910	1.395151	C	-0.609914	-1.988584	1.582353
H	6.316859	-6.017958	2.110529	H	-3.932186	-2.616823	1.115948
H	7.352950	-6.134233	0.666293	H	-3.142931	-4.922507	1.488687
H	7.739023	-4.945267	1.936171	H	-0.731633	-5.358017	1.905549
H	-3.244100	-2.927671	-1.669167	H	0.893797	-3.481367	1.885212
H	-6.894359	-0.651541	-1.916627	H	0.118447	-1.185819	1.492920
C	-5.872842	-3.170408	-1.561093	C	-2.522945	-0.433747	1.092260
C	-5.701516	1.808690	-2.242368	H	-3.409591	-0.437379	0.452133
F	-5.557818	-3.708984	-0.363531	C	-0.089964	4.419653	0.369403
F	-5.577945	-4.091539	-2.479463	C	1.044651	4.131292	-0.421861
F	-7.199017	-2.999825	-1.569978	C	2.084918	5.050496	-0.572353
F	-5.400865	2.588639	-1.178673	C	1.984445	6.255022	0.103683
F	-7.032587	1.737979	-2.305024	C	0.870569	6.551053	0.906754
F	-5.277367	2.473016	-3.321859	C	-0.169688	5.647782	1.039213
N	3.191996	-0.682101	3.294683	C	-0.965484	3.285694	0.280767
C	5.751830	2.026920	-0.963014	C	-0.343469	2.369055	-0.529490
C	5.988425	1.046887	-2.110922	H	2.936487	4.840584	-1.217122
C	4.242710	2.018845	-0.654064	H	2.778605	6.990753	0.001744
H	6.325265	1.721800	-0.078903	H	0.823103	7.509093	1.418780
H	6.101201	3.032787	-1.230101	H	-1.039833	5.893708	1.646744
H	4.035015	1.456277	0.259059	H	-0.687801	1.386991	-0.865526
H	3.856351	3.031859	-0.485171	N	0.867691	2.879336	-0.963229
C	5.285194	-0.266144	-1.741369	H	1.612211	2.345295	-1.419155
H	5.601001	-1.093256	-2.391047	C	-2.284738	3.233705	0.975523
H	5.553791	-0.548864	-0.713182	H	-2.166034	3.637671	1.990977
C	3.772316	-0.037708	-1.884665	H	-3.001680	3.911391	0.484918
H	3.484775	-0.292958	-2.915956	C	-2.998878	1.899472	1.044746
H	7.060632	0.883654	-2.274156	H	-3.870674	1.994972	1.705660
C	3.903308	2.042184	-3.015269	H	-3.360269	1.611746	0.053640
H	3.194648	1.791838	-3.814761	N	-2.189020	0.751504	1.534680
H	3.855028	3.133118	-2.875775	C	-1.187012	0.990971	2.586499

H	-0.380020	1.592997	2.149385
H	-0.770603	0.020726	2.870694
C	-1.768777	1.667650	3.796994
C	-2.840598	1.091657	4.479561
C	-1.203214	2.848260	4.277065
C	-3.345314	1.693859	5.625011
H	-3.274543	0.160554	4.112680
C	-1.702495	3.446131	5.429141
H	-0.373180	3.303857	3.734527
C	-2.775026	2.871075	6.101788
H	-4.181105	1.240164	6.151618
H	-1.255923	4.365783	5.798476
H	-3.168216	3.339493	7.000512

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C	-0.271192	2.554106	0.062724
C	1.076674	2.113569	0.073643
C	1.528421	3.095345	1.063162
C	0.078566	3.655015	1.068165
O	-0.520083	4.565828	1.623943
O	2.596043	3.309069	1.647907
N	-1.310653	2.039358	-0.577192
N	1.742331	1.107494	-0.548268
H	1.355642	0.701111	-1.401168
C	-2.615553	2.473127	-0.460331
C	-3.591004	1.706003	-1.132443
C	-3.077865	3.570405	0.301887
C	-4.938987	1.991241	-1.018332
H	-3.271999	0.874373	-1.755214
C	-4.432683	3.849919	0.372973
C	-5.387624	3.069335	-0.268006
C	3.188745	0.966584	-0.285054
H	3.623512	1.975232	-0.266130
C	3.854981	0.120627	-1.339707
C	5.180438	0.418434	-1.799514
C	3.238403	-1.012426	-1.816726
C	5.899802	1.577650	-1.445071
C	5.795354	-0.530228	-2.676457
C	3.930062	-1.876558	-2.694493
H	2.234937	-1.286474	-1.500194
C	7.181212	1.796710	-1.910889
H	5.472987	2.347751	-0.811536
C	7.108935	-0.282395	-3.130863

H	3.433061	-2.777679	-3.049516
C	7.792821	0.844845	-2.761028
H	7.546289	-1.025115	-3.790617
H	8.799930	1.005572	-3.130456
O	7.784022	2.953074	-1.508012
C	9.109372	3.249243	-1.992022
H	9.131209	3.337829	-3.087717
H	9.369617	4.210378	-1.543498
H	9.838248	2.488852	-1.676453
H	-2.366623	4.199446	0.838531
H	-6.441606	3.310217	-0.196487
C	-4.887242	4.961450	1.247710
C	-5.911333	1.033420	-1.584003
F	-3.997651	5.982303	1.267466
F	-5.048860	4.556542	2.538469
F	-6.092087	5.448943	0.840763
F	-5.429250	0.394363	-2.694039
F	-7.095357	1.603671	-1.904223
F	-6.192434	0.029440	-0.685072
N	5.168180	-1.669758	-3.101854
C	5.495550	-1.555432	2.112940
C	5.136243	-0.241586	2.826438
C	4.367868	-1.868770	1.095284
H	6.450091	-1.435938	1.583235
H	5.612558	-2.371238	2.838802
H	4.689308	-1.664250	0.072712
H	4.054682	-2.920484	1.154189
C	4.794225	0.793774	1.739274
H	4.725487	1.814698	2.137211
H	5.573009	0.765167	0.963902
C	3.412882	0.428733	1.155717
H	2.663573	0.955516	1.759688
H	5.969418	0.104164	3.450172
C	2.827557	-1.190833	2.828352
H	1.821365	-0.791648	3.012848
H	2.817001	-2.269984	3.043713
C	3.883718	-0.464528	3.712456
H	3.496410	0.523207	4.007001
N	3.147887	-1.034925	1.366852
C	4.185085	-1.253999	4.952007
H	4.559822	-2.268375	4.790492
C	4.020903	-0.800233	6.190300
H	3.642362	0.203152	6.382559
H	4.255131	-1.406440	7.062351

C	-0.630586	-1.278076	-1.849869	H	-6.438781	-5.752581	0.296615
C	-0.428825	-0.240414	-2.774816	H	-8.019445	-4.306094	-0.955729
C	0.276353	-0.476907	-3.952877	C	-3.466477	-1.158574	0.673364
C	0.777803	-1.746441	-4.224092	H	-4.063785	-1.999870	1.037340
C	0.606985	-2.772324	-3.295218	H	-4.149521	-0.386661	0.300016
C	-0.075069	-2.539096	-2.105264				
H	-0.825256	0.748785	-2.538174	121			
H	0.424252	0.331971	-4.662900	6_R			
H	1.319949	-1.934030	-5.147012	C	-0.313440	2.310976	0.725805
H	1.014791	-3.759734	-3.497227	C	1.023888	1.855951	0.686880
H	-0.163007	-3.334543	-1.370615	C	1.420160	2.493399	1.924758
C	-1.493179	-0.949117	-0.678251	C	0.009354	3.068603	2.005425
H	-1.627812	0.145819	-0.612607	O	-0.575651	3.804078	2.767711
C	-1.083393	-2.611390	2.165836	O	2.424000	2.520015	2.627124
C	0.173634	-2.971381	1.573410	N	-1.289359	1.993562	-0.101131
C	0.683719	-4.271126	1.716221	N	1.641673	1.008828	-0.202877
C	-0.077567	-5.191737	2.405473	H	1.266022	1.070625	-1.147584
C	-1.335798	-4.853980	2.969586	C	-2.582365	2.462842	0.039871
C	-1.838454	-3.577032	2.862133	C	-3.552138	1.872247	-0.794131
C	-1.317659	-1.253047	1.849473	C	-3.025163	3.454700	0.937283
C	-0.306589	-0.879036	0.909004	C	-4.889821	2.226693	-0.716801
H	1.639953	-4.541583	1.276215	H	-3.233072	1.107318	-1.501455
H	0.288449	-6.208783	2.519384	C	-4.367424	3.812429	0.982914
H	-1.897416	-5.618720	3.497925	C	-5.320530	3.206570	0.172570
H	-2.799017	-3.312884	3.299432	C	3.108441	0.911686	-0.117711
H	0.057628	0.133374	0.761745	H	3.494260	1.915928	0.113644
N	0.656706	-1.911749	0.864724	C	3.699781	0.448901	-1.422320
H	1.702388	-1.647980	0.768949	C	4.906535	1.020205	-1.939530
C	-2.609035	-0.552790	1.864625	C	3.114664	-0.567459	-2.140295
H	-3.171541	-0.712636	2.791708	C	5.591679	2.104427	-1.351018
H	-2.477780	0.524308	1.700683	C	5.433860	0.451802	-3.141197
N	-2.601395	-1.657206	-0.401286	C	3.730406	-1.050583	-3.315184
C	-2.780109	-3.072374	-0.809391	H	2.191242	-1.032759	-1.798882
H	-2.255763	-3.752694	-0.118676	C	6.745593	2.609798	-1.914685
H	-2.337337	-3.175873	-1.807850	H	5.233506	2.587371	-0.445569
C	-4.244675	-3.426806	-0.863591	C	6.623332	0.985107	-3.684814
C	-5.137911	-2.611179	-1.562260	H	3.258533	-1.872470	-3.857171
C	-4.719519	-4.549577	-0.186149	C	7.272994	2.038669	-3.095832
C	-6.491087	-2.925918	-1.588157	H	6.997817	0.527527	-4.596891
H	-4.789489	-1.704204	-2.048824	H	8.183030	2.429874	-3.541187
C	-6.073964	-4.874416	-0.229525	O	7.311806	3.658035	-1.272089
H	-4.023251	-5.163179	0.384598	C	8.471369	4.235643	-1.821402
C	-6.960889	-4.062740	-0.931765	H	8.294133	4.623207	-2.834405
H	-7.180342	-2.268084	-2.110086	H	8.739392	5.067660	-1.167729

H	9.308559	3.524267	-1.851591	H	1.043070	-1.563630	-5.507866
H	-2.318341	3.934890	1.614113	H	1.069160	-3.537974	-4.006719
H	-6.365581	3.491501	0.227352	H	0.127338	-3.379606	-1.728675
C	-4.786747	4.839821	1.992482	C	-1.175279	-1.164735	-0.615271
C	-5.894985	1.452778	-1.506630	H	-1.291080	-0.081494	-0.441694
F	-3.964857	5.892664	2.001130	C	-0.849214	-2.915934	2.280748
F	-4.781960	4.329914	3.232152	C	0.282890	-3.440294	1.582813
F	-6.024166	5.299738	1.762178	C	0.882699	-4.645020	1.986143
F	-5.415512	1.032744	-2.688020	C	0.312606	-5.308755	3.047856
F	-7.005071	2.153187	-1.752633	C	-0.837747	-4.821817	3.726137
F	-6.272985	0.344013	-0.838972	C	-1.422230	-3.640463	3.355001
N	4.850968	-0.581828	-3.804992	C	-1.151397	-1.685095	1.697327
C	5.653639	-1.984278	1.515384	C	-0.256744	-1.482105	0.569039
C	5.337863	-0.844704	2.485246	H	1.754191	-5.035014	1.465612
C	4.466635	-2.104708	0.538692	H	0.752344	-6.245607	3.381707
H	6.579038	-1.767914	0.967113	H	-1.245255	-5.399117	4.550798
H	5.822595	-2.924521	2.057464	H	-2.295871	-3.252982	3.873775
H	4.722277	-1.697478	-0.444502	H	0.366197	-0.566944	0.571558
H	4.184304	-3.156061	0.377067	N	0.609312	-2.628659	0.548703
C	4.907103	0.363231	1.648629	H	1.597725	-2.439617	0.320372
H	4.868380	1.287689	2.239710	C	-2.360230	-0.869838	1.788097
H	5.630545	0.516435	0.834077	H	-2.910729	-1.016554	2.721870
C	3.496213	0.073924	1.116280	H	-2.116335	0.195440	1.680825
H	2.803500	0.436775	1.884458	N	-2.552703	-1.715990	-0.601674
H	6.210318	-0.605532	3.105405	C	-2.788518	-3.097963	-0.987329
C	3.064080	-1.824009	2.438035	H	-2.474029	-3.807291	-0.195054
H	2.062588	-1.513608	2.770823	H	-2.169469	-3.312320	-1.866400
H	3.083907	-2.925788	2.460394	C	-4.234625	-3.337884	-1.338397
C	4.151653	-1.250905	3.384585	C	-4.963910	-2.362215	-2.018308
H	3.766716	-0.336724	3.864018	C	-4.856154	-4.539428	-1.005423
N	3.268900	-1.393361	1.039807	C	-6.292156	-2.583134	-2.356662
C	4.514821	-2.219832	4.461757	H	-4.484653	-1.415294	-2.260108
H	4.912771	-3.184997	4.132420	C	-6.182694	-4.769294	-1.357095
C	4.380184	-1.987801	5.763935	H	-4.295632	-5.301542	-0.463708
H	3.983935	-1.041931	6.130931	C	-6.904395	-3.789945	-2.031029
H	4.662107	-2.724063	6.512077	H	-6.847471	-1.796731	-2.863485
C	-0.495322	-1.325906	-1.945317	H	-6.657285	-5.711265	-1.091839
C	-0.482382	-0.211364	-2.791740	H	-7.945383	-3.963241	-2.292975
C	0.068839	-0.295984	-4.065822	C	-3.284790	-1.285419	0.575539
C	0.614638	-1.494673	-4.510773	H	-3.940882	-2.104894	0.891229
C	0.629773	-2.602134	-3.668285	H	-3.923633	-0.420228	0.350864
C	0.088746	-2.516388	-2.389924				
H	-0.899040	0.729029	-2.428928	121			
H	0.070256	0.578373	-4.711584	TS67_R			

C	0.277571	-1.951275	-0.947537	F	6.323724	0.118005	0.073286
C	-1.053781	-1.482705	-0.926785	F	7.323361	-1.781315	0.525512
C	-1.614925	-2.675270	-1.592127	F	5.804701	-0.955766	1.895039
C	-0.166584	-3.215375	-1.708430	N	-4.708706	3.488519	0.446443
O	0.379989	-4.168821	-2.231740	C	-5.602563	-1.657324	2.950344
O	-2.740212	-3.059732	-1.887018	C	-5.245213	-2.821425	2.013540
N	1.433497	-1.501729	-0.456474	C	-4.467200	-0.605879	2.838591
N	-1.714344	-0.369462	-0.454540	H	-6.559063	-1.213488	2.642488
H	-1.415534	0.539622	-0.836145	H	-5.715253	-2.013215	3.983327
C	2.713082	-2.025054	-0.682944	H	-4.784446	0.243007	2.228391
C	3.754601	-1.502208	0.091829	H	-4.174489	-0.223022	3.826012
C	3.030406	-2.989220	-1.651415	C	-4.879096	-2.213171	0.642722
C	5.069056	-1.857883	-0.154084	H	-4.835003	-2.971332	-0.149809
H	3.521557	-0.815836	0.897517	H	-5.631429	-1.456607	0.365149
C	4.352427	-3.352560	-1.853849	C	-3.482013	-1.575516	0.790235
C	5.392675	-2.779481	-1.135185	H	-2.748995	-2.367135	0.587210
C	-3.197173	-0.511058	-0.288112	H	-6.081419	-3.525022	1.921576
H	-3.604043	-0.940843	-1.212033	C	-2.944645	-2.463075	2.933926
C	-3.778430	0.855730	-0.030296	H	-1.931879	-2.797838	2.676295
C	-4.789871	1.411761	-0.874887	H	-2.971536	-2.243737	4.011687
C	-3.288692	1.625294	1.000313	C	-4.002153	-3.560945	2.580045
C	-5.361999	0.738236	-1.972478	H	-3.602519	-4.215296	1.789086
C	-5.207645	2.752629	-0.593515	N	-3.235667	-1.186884	2.210512
C	-3.791729	2.925290	1.216910	C	-4.326718	-4.404447	3.776217
H	-2.531620	1.219299	1.664208	H	-4.742119	-3.871045	4.635410
C	-6.301275	1.351049	-2.777568	C	-4.130078	-5.717159	3.847109
H	-5.089260	-0.279756	-2.228293	H	-3.711847	-6.275546	3.010119
C	-6.168532	3.352919	-1.436856	H	-4.375264	-6.290937	4.737998
H	-3.408772	3.517497	2.046431	C	0.365181	1.910839	-1.324439
C	-6.703893	2.680602	-2.502856	C	0.154352	1.436921	-2.625006
H	-6.461420	4.370649	-1.198702	C	-1.000782	1.770927	-3.328947
H	-7.439226	3.172474	-3.130622	C	-1.954702	2.601995	-2.746938
O	-6.786736	0.609478	-3.814949	C	-1.751557	3.086738	-1.456685
C	-7.761830	1.200235	-4.697660	C	-0.613158	2.726661	-0.739704
H	-7.363084	2.087979	-5.209791	H	0.901051	0.791607	-3.082868
H	-7.986117	0.426147	-5.434655	H	-1.156357	1.376151	-4.328997
H	-8.682954	1.473894	-4.163069	H	-2.868518	2.853514	-3.280200
H	2.249994	-3.483681	-2.222312	H	-2.503945	3.715348	-0.989205
H	6.423986	-3.047193	-1.331400	H	-0.503194	3.049631	0.292763
C	4.657859	-4.425160	-2.838509	C	1.631589	1.502748	-0.604167
C	6.135107	-1.139036	0.581041	H	2.117393	0.744824	-1.239214
F	3.748743	-4.448775	-3.843860	C	1.729288	0.705077	3.042330
F	4.651887	-5.658320	-2.268172	C	0.366090	0.408007	2.766254
F	5.893956	-4.248774	-3.379914	C	-0.523933	0.025941	3.779752

C	-0.036955	-0.009794	5.070463	N	1.886415	1.095902	0.790204
C	1.310038	0.312325	5.367099	H	1.342193	0.439861	1.353758
C	2.195014	0.665031	4.369258	C	-2.337922	2.357743	1.226618
C	2.345405	1.008371	1.795389	C	-3.203212	1.521064	1.958674
C	1.384517	0.845581	0.782947	C	-2.926004	3.470261	0.575419
H	-1.550468	-0.228478	3.518313	C	-4.574051	1.661369	1.897719
H	-0.700149	-0.292920	5.883976	H	-2.753125	0.736333	2.555694
H	1.645745	0.269994	6.399415	C	-4.305041	3.616524	0.570416
H	3.233376	0.897141	4.593529	C	-5.157271	2.702660	1.186639
H	1.461188	-0.464550	0.240658	C	3.342721	0.928940	0.759851
N	0.147029	0.550791	1.424292	H	3.805390	1.674644	1.428630
H	-0.695416	0.187512	0.937337	C	3.892357	1.120436	-0.642893
C	3.707501	1.591081	1.575633	C	5.238265	1.559644	-0.857534
H	3.820924	2.455019	2.251109	C	3.128958	0.806599	-1.741391
H	4.510232	0.885180	1.830777	C	6.096031	2.018805	0.162866
N	2.640003	2.576734	-0.491006	C	5.723994	1.536006	-2.203021
C	2.183421	3.809696	0.177475	C	3.696115	0.838207	-3.033326
H	1.858054	3.630697	1.221726	H	2.095892	0.502776	-1.620719
H	1.318412	4.184156	-0.384747	C	7.389320	2.414379	-0.110852
C	3.266053	4.861501	0.157799	H	5.764018	2.116438	1.190770
C	3.877262	5.199402	-1.053397	C	7.056452	1.932930	-2.449443
C	3.663673	5.506927	1.327333	H	3.081424	0.569024	-3.890500
C	4.862671	6.178644	-1.091771	C	7.876318	2.357640	-1.438220
H	3.577336	4.668579	-1.953874	H	7.391690	1.899615	-3.481225
C	4.649578	6.492365	1.289307	H	8.891887	2.664277	-1.664538
H	3.194842	5.238682	2.273167	O	8.130404	2.850154	0.953061
C	5.249249	6.830283	0.080213	C	9.453548	3.362981	0.703727
H	5.333813	6.437010	-2.036747	H	9.434511	4.218556	0.013456
H	4.951347	6.992365	2.206072	H	9.824331	3.689402	1.678026
H	6.019090	7.596523	0.049108	H	10.122912	2.589281	0.299378
C	3.881621	2.035397	0.101577	H	-2.287255	4.211425	0.091476
H	4.655837	2.806851	0.036934	H	-6.232872	2.828633	1.149636
H	4.207814	1.180378	-0.504062	C	-4.906550	4.717779	-0.225995
				C	-5.395815	0.577507	2.466537
121				F	-5.048094	4.367578	-1.537060
TS56_s				F	-4.149958	5.839636	-0.201771
				F	-6.153136	5.029737	0.224115
C	-0.039855	2.663725	0.630997	F	-5.527189	-0.471440	1.569395
C	1.301462	2.277205	0.494085	F	-6.648825	0.961358	2.789010
C	1.766860	3.568242	-0.051061	F	-4.815527	0.009584	3.565890
C	0.262653	4.026859	0.026898	N	4.955093	1.159457	-3.270194
O	-0.388613	5.015995	-0.278803	C	5.398193	-2.660729	0.213927
O	2.844950	4.039493	-0.388527	C	5.324719	-2.276329	1.700569
N	-1.033640	1.932988	1.135685	C	4.177787	-2.019464	-0.492974

H	6.326638	-2.269839	-0.223007	H	-0.851433	-4.764542	-4.762121
H	5.404134	-3.752474	0.095630	H	-2.156848	-2.732369	-4.191787
H	4.469189	-1.134277	-1.059369	H	-0.253134	0.399320	-0.585086
H	3.696811	-2.719079	-1.188902	N	0.652158	-1.507773	-0.975431
C	5.103590	-0.748359	1.766327	H	1.523727	-1.417836	-0.398075
H	5.284705	-0.365347	2.780236	C	-2.557489	-0.247426	-2.326778
H	5.804399	-0.253902	1.080943	H	-2.377545	0.727364	-2.801423
C	3.640095	-0.468085	1.358356	H	-3.189467	-0.856042	-2.984066
H	3.026769	-0.512651	2.273879	C	-3.331375	0.063136	-0.984223
H	6.247155	-2.556185	2.223452	H	-2.969455	1.006141	-0.565163
C	2.891919	-2.755151	1.418179	H	-4.404234	0.135540	-1.170961
H	1.979611	-2.569135	1.999023	N	-3.043659	-0.989482	-0.024646
H	2.719456	-3.638304	0.782345	C	-3.787577	-2.290591	-0.092232
C	4.115056	-2.993614	2.355808	H	-4.325018	-2.393735	0.857193
H	3.923673	-2.521139	3.332618	H	-3.043357	-3.094045	-0.162723
N	3.138714	-1.596996	0.507086	C	-4.752560	-2.387439	-1.245273
C	4.344671	-4.459465	2.572931	C	-4.421525	-3.151903	-2.364984
H	4.559020	-5.045356	1.675299	C	-5.990480	-1.737793	-1.200543
C	4.286914	-5.064178	3.755263	C	-5.300003	-3.245434	-3.441646
H	4.071891	-4.509883	4.668412	H	-3.465218	-3.672299	-2.392618
H	4.455449	-6.133035	3.864711	C	-6.865672	-1.827169	-2.278771
C	-1.501451	-2.055169	1.494235	H	-6.253990	-1.163787	-0.316728
C	-0.582264	-3.084633	1.294509	C	-6.521043	-2.576513	-3.402017
C	-0.384343	-4.053056	2.279411	H	-5.034589	-3.846229	-4.307825
C	-1.106766	-4.011717	3.465379	H	-7.823500	-1.315595	-2.240085
C	-2.048338	-3.002858	3.660176	H	-7.208121	-2.646168	-4.240901
C	-2.250995	-2.034531	2.685282				
H	-0.029536	-3.143825	0.367497	121			
H	0.341637	-4.845095	2.110562	6_S			
H	-0.947939	-4.766366	4.230269	C	-0.314176	2.449956	-0.903692
H	-2.633497	-2.969545	4.574873	C	-1.643203	2.015593	-0.826052
H	-3.016710	-1.278231	2.842992	C	-2.178611	3.330272	-0.459854
C	-1.808786	-0.947153	0.528887	C	-0.727982	3.838653	-0.499385
H	-1.467260	0.057794	0.860615	O	-0.169719	4.888876	-0.273575
C	-0.800317	-2.155439	-2.596484	O	-3.276055	3.794413	-0.228755
C	0.423831	-2.465616	-1.923794	N	0.728486	1.708179	-1.282527
C	1.143904	-3.624689	-2.243777	N	-2.096388	0.761240	-1.028613
C	0.662801	-4.430702	-3.256013	H	-1.422501	0.146107	-1.475321
C	-0.523809	-4.111700	-3.958178	C	2.002278	2.241825	-1.325844
C	-1.254420	-2.986837	-3.640277	C	2.935602	1.597486	-2.164222
C	-1.282053	-0.938869	-2.044668	C	2.468807	3.300889	-0.526416
C	-0.426778	-0.606224	-0.962979	C	4.266617	1.975872	-2.178919
H	2.061471	-3.874528	-1.716957	H	2.584040	0.777166	-2.785704
H	1.210590	-5.328313	-3.529631	C	3.812802	3.659639	-0.548960

C	4.729833	3.006640	-1.362219	H	-2.906268	-1.291844	-2.208467
C	-3.485723	0.343721	-1.049692	H	-5.465785	-3.971643	-1.373449
H	-3.985280	0.753570	-1.945444	C	-2.151611	-3.130230	-0.951179
C	-4.239576	0.851999	0.160639	H	-1.376849	-2.848524	-1.676131
C	-5.626288	1.186586	0.092117	H	-1.658397	-3.765160	-0.199660
C	-3.597984	1.046663	1.357435	C	-3.308755	-3.890586	-1.652835
C	-6.411007	1.099097	-1.076686	H	-3.317204	-3.634281	-2.724811
C	-6.243268	1.657754	1.292254	N	-2.634765	-1.918722	-0.270222
C	-4.307898	1.515073	2.481448	C	-3.137918	-5.371143	-1.546503
H	-2.530692	0.861322	1.440141	H	-3.074852	-5.779970	-0.533523
C	-7.743952	1.453975	-1.071725	C	-3.037185	-6.197716	-2.583273
H	-5.995309	0.767554	-2.024230	H	-3.083001	-5.829221	-3.607461
C	-7.612904	2.001926	1.265530	H	-2.910135	-7.269363	-2.455206
H	-3.774952	1.650066	3.425581	C	1.411188	-2.847007	0.025640
C	-8.357590	1.906995	0.118688	C	1.236533	-3.502725	1.247222
H	-8.048833	2.356632	2.195858	C	0.793900	-4.818247	1.284073
H	-9.406262	2.187590	0.131625	C	0.540061	-5.506040	0.097392
O	-8.396844	1.335420	-2.253950	C	0.736531	-4.871379	-1.122431
C	-9.742928	1.741394	-2.316930	C	1.166422	-3.546666	-1.153402
H	-9.862165	2.801151	-2.052238	H	1.464243	-2.976799	2.174162
H	10.060079	1.597478	-3.351471	H	0.656519	-5.315067	2.241700
H	10.384527	1.135352	-1.661501	H	0.196737	-6.537507	0.126098
H	1.770902	3.856758	0.098083	H	0.543413	-5.401212	-2.052230
H	5.779604	3.284453	-1.359366	H	1.320726	-3.045752	-2.109789
C	4.276058	4.698300	0.427235	C	1.936313	-1.431514	-0.030604
C	5.276812	1.203528	-2.962983	H	1.872157	-1.084619	-1.084505
F	4.291406	4.190991	1.677293	C	0.812553	0.082482	3.056029
F	3.474944	5.761347	0.454342	C	-0.402881	-0.467473	2.532910
F	5.515819	5.127148	0.168020	C	-1.538364	-0.585044	3.361157
F	6.091874	0.521427	-2.129318	C	-1.419209	-0.167563	4.665242
F	6.063865	1.994475	-3.696358	C	-0.215674	0.371905	5.197320
F	4.725250	0.301929	-3.782289	C	0.894403	0.497706	4.409269
N	-5.585638	1.802421	2.472755	C	1.739906	0.068978	2.027589
C	-4.505318	-3.394782	0.490286	C	1.092234	-0.422116	0.812545
C	-4.620323	-3.361835	-1.032740	H	-2.470658	-0.992249	2.982269
C	-3.435232	-2.359490	0.891765	H	-2.283685	-0.252950	5.320052
H	-5.471006	-3.146169	0.947317	H	-0.192142	0.685912	6.236526
H	-4.240447	-4.400047	0.842071	H	1.823169	0.911477	4.795168
H	-3.896005	-1.473623	1.342218	H	0.955346	0.475708	0.098914
H	-2.729938	-2.777412	1.626157	N	-0.231161	-0.810760	1.245592
C	-4.809615	-1.893678	-1.442696	H	-1.001809	-1.097251	0.617496
H	-5.145580	-1.804731	-2.484376	C	3.178967	0.401372	2.053068
H	-5.589250	-1.438364	-0.816396	H	3.336194	1.480275	2.203757
C	-3.459976	-1.183891	-1.260691	H	3.634690	-0.104171	2.918186

C	3.824641	-0.073252	0.767635
H	3.625701	0.638411	-0.049102
H	4.912101	-0.131670	0.885250
N	3.329027	-1.409665	0.438661
C	4.226281	-2.067146	-0.508391
H	4.415824	-1.428485	-1.395286
H	3.724613	-2.972026	-0.877196
C	5.526609	-2.463869	0.137020
C	5.518698	-3.103102	1.379241
C	6.744202	-2.232012	-0.498976
C	6.707791	-3.510470	1.968774
H	4.562926	-3.268105	1.875379
C	7.936328	-2.645266	0.089279
H	6.755681	-1.717128	-1.457893
C	7.921140	-3.284626	1.323193
H	6.690645	-4.008769	2.935689
H	8.880960	-2.458071	-0.416117
H	8.852864	-3.603657	1.784537

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TS67_s

C	0.238744	-2.395476	-0.998692
C	1.575946	-2.010310	-1.102690
C	2.095632	-3.409899	-0.932702
C	0.590529	-3.835219	-0.753692
O	-0.024129	-4.860042	-0.501006
O	3.191896	-3.937374	-0.933879
N	-0.865141	-1.618147	-1.130206
N	2.085405	-0.793676	-1.302462
H	1.419080	-0.045352	-1.494073
C	-2.144344	-2.184081	-1.308449
C	-3.037334	-1.506953	-2.149294
C	-2.613783	-3.281751	-0.578921
C	-4.368766	-1.879088	-2.207413
H	-2.677087	-0.666913	-2.732787
C	-3.961549	-3.612980	-0.625727
C	-4.855313	-2.913635	-1.420376
C	3.497557	-0.404047	-1.262478
H	3.976770	-0.656740	-2.222517
C	4.259993	-1.090535	-0.146035
C	5.673267	-1.303024	-0.244234
C	3.620269	-1.501007	0.997160
C	6.446538	-1.010219	-1.387095
C	6.327876	-1.861179	0.899448

C	4.354705	-2.065707	2.061781
H	2.546005	-1.395089	1.095212
C	7.808748	-1.228614	-1.408709
H	6.003209	-0.619917	-2.296846
C	7.725104	-2.060636	0.851564
H	3.826770	-2.387671	2.958050
C	8.455627	-1.752705	-0.264398
H	8.187618	-2.482088	1.738641
H	9.526664	-1.924560	-0.269194
O	8.458188	-0.913122	-2.569730
C	9.870583	-1.186435	-2.661254
H	10.087166	-2.255367	-2.521789
H	10.156921	-0.886710	-3.671766
H	10.448506	-0.602780	-1.929914
H	-1.920815	-3.888817	0.000009
H	-5.909614	-3.169583	-1.425320
C	-4.467307	-4.581786	0.376057
C	-5.345992	-1.049390	-2.945826
F	-4.513175	-3.985340	1.611576
F	-3.664985	-5.662079	0.503520
F	-5.724609	-5.001153	0.091150
F	-6.166054	-0.390779	-2.061114
F	-6.163281	-1.783428	-3.737342
F	-4.746658	-0.095461	-3.704158
N	5.665254	-2.225798	2.038208
C	4.669904	2.892606	0.990716
C	4.700571	3.212483	-0.511361
C	3.587019	1.805777	1.221314
H	5.652416	2.514134	1.303225
H	4.456045	3.796927	1.575099
H	4.042432	0.835391	1.431057
H	2.927940	2.075585	2.056846
C	4.835698	1.868352	-1.258479
H	5.103887	2.025267	-2.312703
H	5.629586	1.273764	-0.787863
C	3.475817	1.144320	-1.166398
H	2.873522	1.458248	-2.036607
H	5.541985	3.873369	-0.752026
C	2.218168	3.015057	-0.344027
H	1.400771	2.918653	-1.063398
H	1.796156	3.466401	0.565030
C	3.368314	3.893389	-0.921320
H	3.313685	3.900012	-2.022326
N	2.704954	1.648972	0.017751

C	3.271704	5.309274	-0.435003
H	3.244801	5.436613	0.650238
C	3.212987	6.375139	-1.227241
H	3.228525	6.278818	-2.312562
H	3.152419	7.386631	-0.831389
C	-1.272019	2.677107	-0.107458
C	-1.164984	3.323639	1.126269
C	-0.712123	4.635986	1.189954
C	-0.382511	5.322628	0.018344
C	-0.509768	4.691251	-1.214051
C	-0.954445	3.368841	-1.275065
H	-1.461041	2.785346	2.024053
H	-0.630777	5.135712	2.151844
H	-0.042717	6.352874	0.068468
H	-0.264495	5.226602	-2.128045
H	-1.072710	2.873710	-2.238868
C	-1.891305	1.295688	-0.169511
H	-1.852945	0.950488	-1.225599
C	-0.905128	-0.716189	2.758492
C	0.346349	-0.149210	2.373408
C	1.456729	-0.257142	3.228423
C	1.296833	-0.923080	4.427089
C	0.059845	-1.495244	4.807762
C	-1.039696	-1.392824	3.985367
C	-1.838948	-0.378969	1.754295
C	-1.148896	0.272015	0.705744
H	2.412487	0.184329	2.968576
H	2.144333	-1.003873	5.103344
H	-0.013275	-2.015040	5.758383
H	-1.997133	-1.824640	4.266996
H	-0.972293	-0.745797	-0.258330
N	0.201283	0.466701	1.163740
H	0.997543	0.921708	0.660649
C	-3.315361	-0.551389	1.818846
H	-3.605037	-1.613825	1.803772
H	-3.647962	-0.125625	2.778311
C	-4.002986	0.186471	0.667869
H	-4.108000	-0.469609	-0.203847
H	-5.012934	0.486291	0.973762
N	-3.291883	1.436964	0.314554
C	-4.110725	2.191345	-0.662113
H	-4.397786	1.555854	-1.524016
H	-3.499432	3.022651	-1.038353
C	-5.340571	2.754904	0.007578

C	-5.181219	3.567778	1.132795
C	-6.621649	2.477708	-0.466687
C	-6.291675	4.120014	1.759686
H	-4.174994	3.749482	1.504827
C	-7.735497	3.032065	0.163065
H	-6.741342	1.802326	-1.309467
C	-7.572665	3.856347	1.272458
H	-6.163623	4.756940	2.631264
H	-8.732592	2.811019	-0.209306
H	-8.441254	4.287664	1.763624

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Product_R

C	0.241113	2.197928	-0.349479
C	1.125285	3.039112	-1.027866
C	1.508997	4.255894	-0.481347
C	1.010014	4.650953	0.757355
C	0.140108	3.815399	1.447466
C	-0.238302	2.592440	0.899633
H	1.517407	2.716687	-1.991967
H	2.196157	4.901425	-1.023315
H	1.304206	5.606459	1.184890
H	-0.242169	4.111249	2.421717
H	-0.898222	1.927947	1.455564
C	-0.106832	0.871906	-0.986496
H	-0.211197	1.073068	-2.069760
C	-2.957894	-1.320528	-0.097969
C	-3.553553	-0.038693	-0.005545
C	-4.897466	0.132516	0.319022
C	-5.651981	-1.008182	0.544616
C	-5.083658	-2.288974	0.450514
C	-3.746144	-2.454177	0.132827
C	-1.581773	-1.117299	-0.443488
C	-1.385488	0.233850	-0.529649
H	-5.339737	1.124151	0.390579
H	-6.705019	-0.909004	0.797418
H	-5.706379	-3.161538	0.633276
H	-3.310036	-3.449587	0.063554
N	-2.576231	0.892997	-0.284948
H	-2.689368	1.894090	-0.259381
C	-0.500908	-2.096570	-0.756176
H	-0.116917	-2.579928	0.157003
H	-0.881964	-2.914148	-1.384600
C	0.627980	-1.368540	-1.495181

H	1.523354	-1.998454	-1.559661
H	0.306298	-1.154230	-2.524555
N	1.005431	-0.090694	-0.887147
C	1.554434	-0.254375	0.457003
H	0.846579	-0.728002	1.164761
H	1.757436	0.747955	0.856348
C	2.843519	-1.027947	0.432452
C	3.894446	-0.596307	-0.380206
C	3.022538	-2.162524	1.219357
C	5.099977	-1.283837	-0.398520
H	3.740856	0.283902	-1.003332
C	4.231902	-2.852893	1.206280
H	2.203123	-2.505611	1.851099
C	5.272684	-2.414911	0.396973
H	5.912269	-0.937453	-1.033878
H	4.357329	-3.737353	1.826743
H	6.217599	-2.953198	0.382718

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Product_S

C	-0.064894	1.904289	-0.338248
C	-0.184109	2.019858	1.048740
C	-0.304086	3.269690	1.638811
C	-0.297412	4.419900	0.851187
C	-0.170276	4.312796	-0.527845
C	-0.056082	3.056051	-1.119631
H	-0.179264	1.110819	1.648360
H	-0.399871	3.352103	2.718988
H	-0.392595	5.398715	1.315369
H	-0.167916	5.206229	-1.147934
H	0.028615	2.964725	-2.202804
C	0.100247	0.533968	-0.962109
H	0.069285	0.658691	-2.071462
C	3.043321	-1.432705	0.128598
C	3.623074	-0.181013	-0.198513
C	4.986229	0.064378	-0.054318
C	5.776730	-0.969647	0.423146
C	5.224431	-2.219558	0.746038
C	3.868035	-2.459422	0.601982
C	1.637609	-1.319225	-0.130112
C	1.420380	-0.052804	-0.583833
H	5.415098	1.032107	-0.306111
H	6.844994	-0.809496	0.548892
H	5.875121	-3.008470	1.116036

H	3.445219	-3.430054	0.856586
N	2.611158	0.641556	-0.648590
H	2.688739	1.631225	-0.826407
C	0.515657	-2.288772	0.000593
H	0.806009	-3.288086	-0.353207
H	0.209271	-2.403733	1.051183
C	-0.660503	-1.779231	-0.819785
H	-0.444679	-1.907420	-1.902339
H	-1.563647	-2.361264	-0.599590
N	-0.958172	-0.378154	-0.523281
C	-2.240153	0.010474	-1.094182
H	-2.289807	-0.236785	-2.176709
H	-2.316058	1.105556	-1.024103
C	-3.405853	-0.608557	-0.374055
C	-3.486717	-0.523358	1.017504
C	-4.427861	-1.247964	-1.071269
C	-4.574350	-1.058610	1.693965
H	-2.677232	-0.034589	1.557356
C	-5.521501	-1.782813	-0.396035
H	-4.363378	-1.326579	-2.156335
C	-5.596944	-1.688470	0.988355
H	-4.627932	-0.984689	2.777899
H	-6.312276	-2.280002	-0.953271
H	-6.448442	-2.108358	1.518800

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H2O

O	0.000000	0.000000	0.118010
H	0.000000	0.757695	-0.472039
H	0.000000	-0.757695	-0.472039

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Aldehyde

C	1.318976	-1.327973	0.000000
C	2.204355	-0.249879	0.000255
C	1.727162	1.057514	0.000144
C	0.357811	1.288119	-0.000121
C	-0.530408	0.213284	-0.000330
C	-0.046923	-1.097967	-0.000304
H	1.702675	-2.345486	0.000050
H	3.276902	-0.432070	0.000429
H	2.422977	1.893012	0.000291
H	-0.036487	2.304704	-0.000210
H	-0.766905	-1.914074	-0.000492

C	-1.981552	0.467661	-0.000610	H	-0.231648	0.028888	-1.371129
H	-2.251436	1.553537	0.001076	H	0.203120	-1.324359	-2.387998
O	-2.830532	-0.395523	0.000581	C	-0.833217	-1.897276	-0.596160
37				H	-1.813636	-1.818688	-1.086449
Amine				H	-0.523685	-2.947144	-0.698679
C	2.291973	0.191494	-0.396230	N	-1.006964	-1.638215	0.825119
C	3.516860	-0.243119	0.162433	H	-0.155453	-1.899144	1.314365
C	4.496040	0.650382	0.596911	C	-1.329313	-0.259725	1.162962
C	4.229972	2.002482	0.463671	H	-0.558092	0.470540	0.849367
C	3.019809	2.457701	-0.088358	H	-1.366124	-0.199908	2.260762
C	2.053514	1.566940	-0.519648	C	-2.658415	0.171527	0.601927
C	1.526844	-0.977980	-0.729570	C	-3.773602	-0.664485	0.694945
C	2.294522	-2.051005	-0.364330	C	-2.803034	1.418559	-0.002516
H	5.433164	0.298270	1.023194	C	-5.005818	-0.254386	0.202850
H	4.971349	2.726669	0.792981	H	-3.650725	-1.646163	1.149483
H	2.846556	3.527434	-0.178043	C	-4.037644	1.835186	-0.491628
H	1.120743	1.926960	-0.952790	H	-1.933823	2.071816	-0.086624
H	2.085797	-3.110957	-0.451044	C	-5.142566	0.998489	-0.390197
N	3.494154	-1.617684	0.167555	H	-5.866592	-0.915165	0.280498
H	4.225904	-2.213324	0.517757	H	-4.133988	2.812817	-0.958877
C	0.161525	-0.997500	-1.338763	H	-6.107900	1.319042	-0.775277

V. References

- [1]. Sandra, M.; Harper, M.; Balmond, E.; Miranda, S.; Galan, M. C. *Org. Lett.*, **2016**, *18*, 4222-4225.
- [2]. Valderas, C.; Casarrubios, L.; María, C.; Sierra, M. A. *Tetrahedron Lett.*, **2017**, *58*, 326-328.
- [3]. M. Sandra, M. Harper, E. Balmond, S. Miranda, M. C. Galan, *Org. Lett.*, **2016**, *18*, 4222.
- [4]. B. Vakulya, S. Varga, A. Csampai, T. Soós, *Org. Lett.* **2005**, *7*, 1967.
- [5]. Y. Qian, G. Y. Ma, J. Zhao, V. H. Rawal, *Chem. Commun.* **2010**, *46*, 3004.
- [6]. W. Yang, D. M. Du, *Org. Lett.* **2010**, *12*, 5450.