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Supporting Information to Accompany:

Iridium–Monodentate Phosphoramidite Catalyzed Asymmetic Hydrogenation of Substituted Benzophenone N–H Imines

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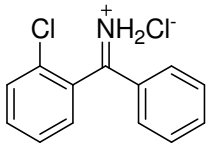
Contents

General: Unless otherwise noted all reactions were run under a nitrogen atmosphere, solvents and reagents were transferred by syringe. All manipulations involving $[Ir(COD)Cl]_2$ and (*S*)-NMe-NBn-Monophos were performed in a N_2-filled glove-box. ^1H NMR spectra (400 or 500 MHz) and ^{13}C NMR spectra (100 or 125 MHz) were recorded in CD_3OD, DMSO-d_6 or $CDCl_3$. Chemical shifts were reported in ppm downfield from internal tetramethysilane.

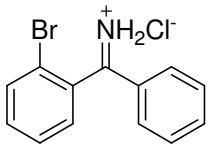
(A) Preparation and Physical Data for N–H Imine Hydrochloride Salts

Representative procedure: A round-bottom flask was charged with nitrile (25.0 mmol) and THF (25 mL). The mixture was cooled to − 78 ºC and PhLi (17.5 mL, 1.8 M in di-*n*-butyl ether) was added dropwise over 0.5 h. After addition, the resulting mixture was stirred for 2 h and quenched with anhydrous MeOH (6 mL). The mixture was then stirred at rt for 2 h. The suspension was filtered on Solka-Floc or Celite and the filtrate was concentrated under vacuum. The residue was dissolved in MTBE (25 mL) and treated with HCl in diethyl ether (25.0 mL, 1 M). The slurry was stirred for 30 min and filtered to obtain the product as free-flowing off-white to yellow solids.

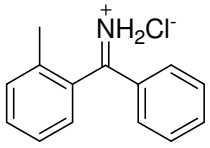


(2-Chlorophenyl)(phenyl)methaniminium chloride (1a): Yield: 95%. ^1H NMR (DMSO-d_6, 400 MHz) δ 13.76 (bs, 2H, NH_2), 7.97 (d, 2H, J = 8.0 Hz, Ar-H), 7.87 (t, 1H, J = 8.0 Hz, Ar-H), 7.79–7.74 (m, 3H, Ar-H), 7.69–7.63 (m, 3H, Ar-H); ^{13}C NMR (CD_3OD, 125 MHz) δ 184.3, 138.6,

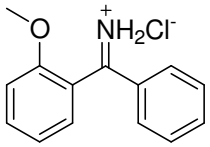
135.9, 133.7, 132.7, 132.24, 132.17, 131.53, 131.3, 129.2; HRMS calcd for $C_{13}H_{11}ClN$: 216.0575, found: 216.0574.



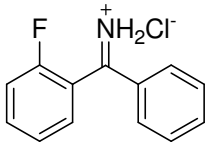
(2-Bromophenyl)(phenyl)methaniminium chloride (1b): Yield: 90%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.90-7.93 (m, 2H), 7.83 (m, 2H), 7.67-7.73 (m, 5H); ^{13}C NMR (CD_3OD, 125 MHz) δ 185.2, 138.6, 135.7, 135.3, 134.4, 132.8, 132.3, 131.4, 131.3, 129.6, 122.0; HRMS calcd for $C_{13}H_{11}BrN$: 260.0070, found: 259.9991.



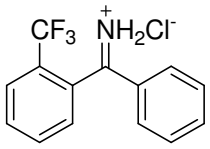
Phenyl(*o*-tolyl)methaniminium chloride (1c): Yield: 85%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.45 (bs, 2H, NH_2), 7.89 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.83 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.65–7.57 (m, 3H, Ar-H), 7.47–7.40 (m, 3H, Ar-H), 2.12 (s, 3H, CH_3). ^{13}C NMR (CD_3OD, 125 MHz) δ 186.8, 138.7, 138.2, 134.5, 133.0, 132.5, 132.3, 131.2, 131.1, 127.8, 20.4; HRMS calcd for $C_{14}H_{14}N$: 196.1126, found: 196.1121.



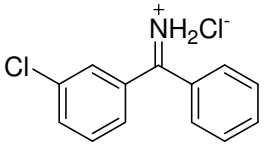
(2-Methoxyphenyl)(phenyl)methaniminium chloride (1d): Yield: 87%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.20 (bs, 2H, NH_2), 7.86 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.79 (t, 1H, *J* = 7.6 Hz, Ar-H), 7.75–7.70 (m, 1H, Ar-H), 7.61 (t, 2H, Ar-H), 7.45–7.42 (m, 1H, Ar-H), 7.31 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.16 (t, 1H, *J* = 7.6 Hz, Ar-H), 3.72 (s, 3H, OCH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 182.9, 161.4, 138.9, 136.5, 135.4, 133.2, 131.9, 130.7, 122.3, 120.0, 114.1, 57.3; HRMS calcd for C14H14NO: 212.1075, found: 212.1070.



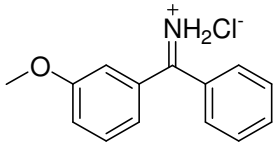
(2-Fluorophenyl)(phenyl)methaniminium chloride (1e): Yield: 78%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.88-7.95 (m, 4H, Ar-H), 7.69-7.74 (m, 3H, Ar-H), 7.48-7.56 (m, 2H, Ar-H); ^{13}C NMR (CD_3OD, 125 MHz) δ 181.7, 163.2, 161.1, 138.9, 138.8, 138.0, 134.2, 132.6, 132.1, 131.0, 126.8, 126.7, 120.8, 120.7, 118.4, 118.3; HRMS calcd for $C_{13}H_{11}FN$: 200.0876, found: 200.0870.



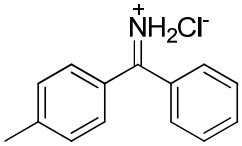
Phenyl(2-(trifluoromethyl)phenyl)methaniminium chloride (1f): Yield: 76%; ^{1}H NMR (CD_3OD, 500 MHz) δ 8.05-8.06 (m, 1H, Ar-H), 7.95-8.00 (m, 2H, Ar-H), 7.90-7.93 (m, 1H, Ar-H), 7.78-7.81 (m, 3H, Ar-H), 7.68-7.71 (m, 2H, Ar-H); ^{13}C NMR (CD_3OD, 125 MHz) δ 185.0, 139.0, 134.4, 132.9, 131.5, 131.2, 130.8, 129.4 (q, *J* = 32 MHz), 128.7 (q, *J* = 4.7 MHz), 124.8 (q, *J* = 273 MHz); HRMS calcd for $C_{14}H_{11}F_3N$: 250.0844, found: 250.0779.



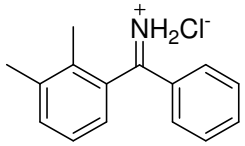
(3-chlorophenyl)(phenyl)methaniminium chloride (1g): Yield: 82%; ^{1}H NMR (500 MHz, CD_3OD) δ 7.86-7.94 (m, 2H), 7.82-7.85 (m, 1H), 7.80-7.82 (m, 2H), 7.68-7.74 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz) δ 184.8, 137.6, 136.7, 136.5, 134.2, 133.2, 132.4, 132.3, 131.9, 131.5, 130.9; HRMS calcd for $C_{13}H_{11}ClN$: 216.0580, found 216.0607.



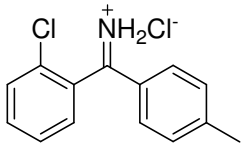
(3-Methoxyphenyl)(phenyl)methaniminium chloride (1h): Yield: 83%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.90-7.93 (m, 1H, Ar-H), 7.85-7.86 (m, 2H, Ar-H), 7.62-7.65 (m, 2H, Ar-H), 7.43-7.47 (m, 2H, Ar-H), 7.32-7.33 (m, 1H, Ar-H), 3.92 (s, 3H, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 185.4, 161.6, 137.2, 133.3, 133.2, 132.1, 131.9, 130.7, 125.8, 123.4, 117.3, 56.7; HRMS calcd for $C_{14}H_{14}NO$: 212.1075, found: 212.1079.



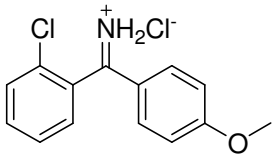
Phenyl(p-tolyl)methaniminium chloride (1i)[1]: Yield: 95%. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.58 (bs, 2H, NH_2), 7.87–7.83 (m, 1H, Ar-H), 7.76–7.74 (m, 2H, Ar-H), 7.70–7.63 (m, 4H, Ar-H), 7.50 (d, 1H, *J* = 8.0 Hz, Ar-H), 2.46 (s, 3H, CH_3).



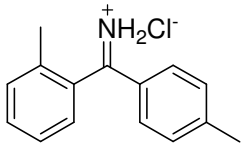
(2,3-Dimethylphenyl)(phenyl)methaniminium chloride (1j): Yield: 80%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.90-7.94 (m, 3H, Ar-H), 7.71-7.74 (m, 2H, Ar-H), 7.59 (d, 1H, *J* = 10 Hz, Ar-H), 7.43 (m, 1H, Ar-H), 7.37 (d, 1H, *J* = 10 Hz, Ar-H), 2.41 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 187.3, 140.5, 138.2, 136.9, 135.7, 133.2, 132.6, 132.4, 131.2, 128.6, 127.6, 20.4, 17.9; HRMS calcd for C15H16N: 210.1277, found: 210.1271.



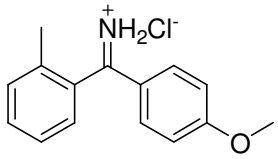
(2-Chlorophenyl)(p-tolyl)methaniminium chloride (1k): Yield: 99%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.72-7.78 (m, 4H), 7.62-7.68 (m, 2H), 7.53 (d, 2H, *J* = 10), 2.52 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 183.5, 151.4, 135.6, 133.6, 132.9, 132.41, 132.37, 132.1, 132.0, 129.1, 128.6, 27.4, 22.3; HRMS calcd for $C_{14}H_{13}ClN$: 230.0737, found: 230.0752.



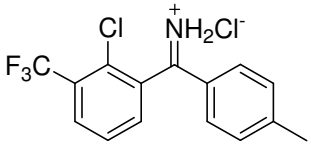
(2-Chlorophenyl)(4-methoxyphenyl)methaniminium chloride (1l): Yield: 99%. ^{1}H NMR (CD_3OD, 500 MHz) δ 7.85-7.87 (m, 2H), 7.73-7.75 (m, 2H), 7.63-7.65 (m, 2H), 7.21-7.23 (m, 2H), 2.98 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 181.5, 169.4, 135.9, 135.3, 133.4, 132.7, 132.1, 132.0, 129.0, 122.9, 117.0, 57.1; HRMS calcd for $C_{14}H_{13}ClNO$: 246.0686, found: 246.0625.



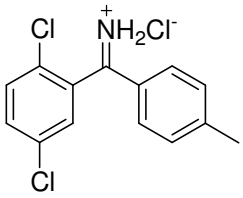
o-Tolyl(p-tolyl)methaniminium chloride (1m): Yield: 87%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.70 (d, 2H, *J* = 10), 7.65 (m, 1H), 7.48-7.52 (m, 5H), 2.52 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 186.2, 150.8, 138.5, 134.3, 133.0, 132.9, 132.8, 132.0, 130.9, 129.3, 127.8, 22.3, 20.3; HRMS calcd for $C_{15}H_{16}N$: 210.1283, found: 210.1287.



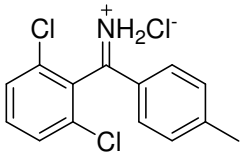
(4-Methoxyphenyl)(o-tolyl)methaniminium chloride (1n): Yield: 86%. ^{1}H NMR (CD_3OD, 500 MHz) δ 7.82 (d, 2H, *J* = 10), 7.64 (m, 1H), 7.46-7.50 (m, 3H), 7.21 (d, 2H, *J* = 10); 3.97 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 184.6, 169.1, 138.2, 135.2, 134.0, 133.4, 132.8, 130.5, 127.7, 123.7, 116.9, 57.1, 20.0; HRMS calcd for $C_{15}H_{16}NO$: 226.1232, found: 226.1241.



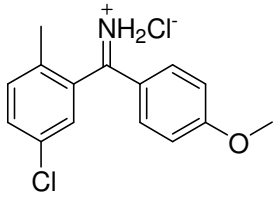
(2-Chloro-3-(trifluoromethyl)phenyl)(p-tolyl)methaniminium chloride (1o): Yield: 98%; ^{1}H NMR (CD_3OD, 500 MHz) δ 8.20 (d, 1H, *J* = 10), 7.98 (m, 1H), 7.86 (m, 1H), 7.79 (m, 2H), 7.55 (d, 2H, *J* = 10), 2.53 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 182.4, 152.1, 135.5, 135.2, 132.9, 132.8 (q, *J* = 5), 132.3, 131.4 (q, *J* = 31), 129.8, 128.1, 125.1 (q, *J* = 271), 22.3; HRMS calcd for $C_{15}H_{12}ClF_3N$: 298.0605, found: 298.0505



(2,5-Dichlorophenyl)(p-tolyl)methaniminium chloride (1p): Yield: 93%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.71-7.81 (m, 5H), 7.54 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 182.1, 151.9, 135.4, 135.1, 133.8, 133.6, 132.9, 132.2, 132.1, 131.9, 128.1, 22.3; HRMS calcd for $C_{14}H_{12}Cl_2N$: 264.0347, found: 264.0285.



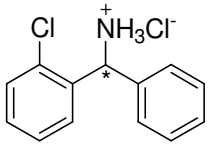
(2,6-Dichlorophenyl)(p-tolyl)methaniminium chloride (1q): Yield: 96%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.93-7.95 (m, 1H), 7.76 (d, 2H, *J* = 10), 7.64 (m, 2H), 7.53 (d, 2H, *J* = 5), 2.52 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 182.5, 151.6, 135.8, 135.7, 134.8, 132.8, 132.1, 131.5, 130.5, 130.2, 128.4, 22.3; HRMS calcd for $C_{14}H_{12}Cl_2N$: 264.0341, found: 264.0255.



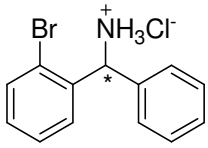
(5-chloro-2-methylphenyl)(4-methoxyphenyl)methaniminium chloride (1r): Yield: 92%; ^{1}H NMR (CD_3OD, 500 MHz) δ 7.83 (d, 2H, *J*= 5), 7.65 (d, 1H, *J* = 10), 7.56 (s, 1H), 7.49 (d, 1H, *J* = 10), 7.23 (d, 2H, *J* = 10), 3.98 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 182.9, 169.4, 136.8, 135.9, 134.9, 134.4, 133.6, 133.5, 129.9, 123.1, 117.1, 57.1, 19.4.

(B) General Procedure for Asymmetric Hydrogenation of N–H imines Hydrochloride salts: A 5.0 mL vial was loaded with $[Ir(COD)Cl]_2$ (2.1 mg, 0.003 mmol) and (*S*)-NMe-NBn-Monophos (5.9 mg, 0.006 mmol). The mixture was dissolved in CH_2Cl_2 (1 mL) and stirred for 20 min at rt in the glovebox. To this solution was added the N–H imine HCl salt in MeOH (2 mL). The vial was then placed into a steel autoclave. The inert atmosphere was replaced by H_2 and the reaction mixture was stirred under 100 atm H_2 (1500 psi) at rt for 36 h. The resulting mixture was concentrated under vacuum and dissolved in saturated aqueous $NaHCO_3$ (5 mL). After stirring for 10 min, the mixture was extracted with CH_2Cl_2 (3×2 mL) and dried over Na_2SO_4. To the resulting solution was added Ac_2O (300 μL) and stirred for 30 min. The resulting solution was then analyzed for conversion directly by GC. After the product was purified by silica gel chromatography using ethyl acetate / hexane (1:2) as eluent. The enantiomeric excess was determined by HPLC or SFC analysis.

(C) Analytical Data for the Hydrogenation Products

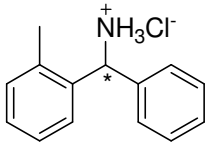


(+)-(2-chlorophenyl)(phenyl)methanaminium chloride (2a)[2] : $[\alpha]_D^{20}$ + 20.2 (*c* 1.0, MeOH), 87% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 10.9 min (major), t_R = 12.4 min (minor). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.20 (bs, 3H, NH_3), 7.85 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.52 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.45–7.35 (m, 6H, Ar-H), 5.83 (s, 1H, CH).

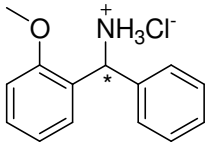


(+)-(2-bromophenyl)(phenyl)methanaminium chloride (2b)[3]: $[\alpha]_D^{20}$ + 20.1 (*c* 1.0, MeOH), 91% ee; SFC condition for corresponding acetamide: Sepapak-4 column, MeOH with

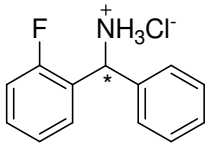
isobutylamine (25 mM): isocratic 25% modifier, hold 2 min, 3 mL/min, 200 bar, 210 nm UV detector, t_R = 8.8 min (major), t_R = 10.3 min (minor). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.20 (bs, 3H, NH_3), 7.82 (d, 1H, J = 8.0 Hz, Ar-H), 7.71 (d, 1H, J = 8.0 Hz, Ar-H), 7.57 (t, 1H, J = 8.0 Hz, Ar-H), 7.42–7.36 (m, 6H, Ar-H), 5.79 (s, 1H, CH).



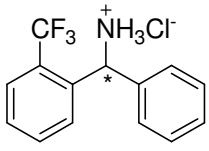
(*R*)-(+)-phenyl(o-tolyl)methanaminium chloride (2c)[4]: $[\alpha]_D^{20}$ + 39.7 (*c* 1.0, MeOH), 82% ee; SFC condition for corresponding acetamide: ChiralCel AD-H, 4% MeOH for 4 min, ramp at 4% / min to 40% MeOH, 2 mL / min, 200 bar, 35 ºC, 215 nm; t_R = 2.8 min (minor), t_R = 3.4 min (major). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.07 (bs, 3H, NH_3), 7.65–7.62 (m, 1H, Ar-H), 7.43–7.37 (m, 4H, Ar-H), 7.35–7.30 (m, 2H, Ar-H), 7.27 (t, 1H, J =7.5 Hz, Ar-H), 7.22 (d, 1H, J =7.5 Hz, Ar-H), 5.69 (s, 1H, CH), 2.24 (s, 3H, CH_3).



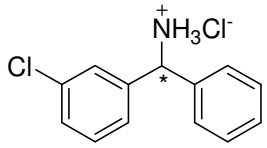
(+)-(2-methoxyphenyl)(phenyl)methanaminium chloride (2d)[5]: $[\alpha]_D^{20}$ + 3.2 (*c* 1.0, MeOH), 76% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 85:15, 1.0 mL/min, 222 nm UV detector, t_R = 7.1 min (minor), t_R = 11.5 min (major). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.03 (bs, 3H, NH_3), 7.56 (d, 1H, J =7.5 Hz, Ar-H), 7.47 (d, 2H, J =7.5 Hz, Ar-H), 7.39–7.30 (m, 4H, Ar-H), 7.07–7.00 (m, 2H, Ar-H), 5.69 (s, 1H, CH), 3.79 (s, 3H, OCH_3).



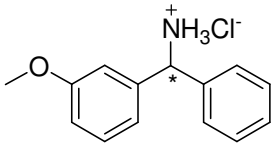
(+)-(2-fluorophenyl)(phenyl)methanaminium chloride (2e)[6]: $[\alpha]_D^{20}$ + 4.4 (*c* 1.0, MeOH), 36% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 8.8 min (major), t_R = 10.8 min (minor). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.30 (bs, 3H, NH_3), 7.80 (s, 1H, Ar-H), 7.42–7.14 (m, 8H, Ar-H), 5.78 (s, 1H, CH).



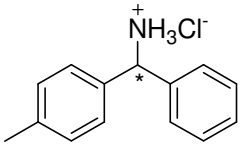
(+)-phenyl(2-(trifluoromethyl)phenyl)methanaminium chloride (2f)[5]: $[\alpha]_D^{20}$ + 3.3 (*c* 1.0, MeOH), 98% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 7.3 min (major), t_R = 10.4 min (minor). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.24 (bs, 3H, NH_3), 7.98 (s, 1H, Ar-H), 7.90–7.85 (m, 2H, Ar-H), 7.69–7.65 (m, 1H, Ar-H), 7.45–7.36 (m, 5H, Ar-H), 5.76 (s, 1H, CH).



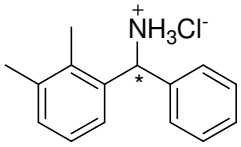
(+)-(3-chlorophenyl)(phenyl)methanaminium chloride (2g)[7]: $[\alpha]_D^{20}$ – 1.9 (*c* 1.0, MeOH), 31% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 10.1 min (minor), t_R = 12.7 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.36 (bs, 3H, NH_3), 7.72 (s, 1H, Ar-H), 7.60–7.54 (m, 3H, Ar-H), 7.49–7.34 (m, 5H, Ar-H), 5.68 (s, 1H, CH).



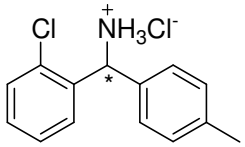
(–)-(3-methoxyphenyl)(phenyl)methanaminium chloride (2h)[5]: $[\alpha]_D^{20}$ – 4.1 (*c* 1.0, MeOH), 46% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 85:15, 1.0 mL/min, 222 nm UV detector, t_R = 8.5 min (major), t_R = 14.5 min (minor). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.20 (bs, 3H, NH_3), 7.55 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.40 (t, 2H, *J* = 7.5 Hz, Ar-H), 7.35–7.28 (m, 2H, Ar-H), 7.23 (s, 1H, Ar-H), 7.05 (d, 1H, *J* = 7.5 Hz, Ar-H), 6.91–6.88 (m, 1H, Ar-H), 5.56 (s, 1H, CH), 3.75 (s, 3H, OCH_3).



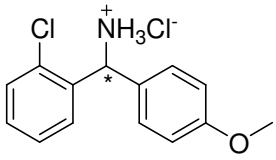
(*S*)-(+)-Phenyl(p-tolyl)methanaminium chloride (2i)[8]: $[\alpha]_D^{20}$ + 1.2 (*c* 1.0, MeOH), 31% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 8.6 min (minor), t_R = 10.2 min (major). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.10 (bs, 3H, NH_2), 7.36 (d, 2H, *J* = 6.4 Hz, Ar-H), 7.27–7.24 (m, 5H, Ar-H), 7.07 (d, 2H, *J* = 7.6 Hz, Ar-H), 5.38 (s, 1H, CH), 2.33 (s, 3H, CH_3).



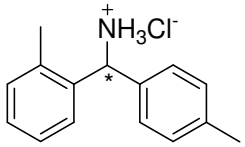
(+)-(2,3-dimethylphenyl)(phenyl)methanaminium chloride (2j): $[\alpha]_D^{20}$ + 16.6 (*c* 1.0, MeOH), 86% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 93:7, 1.0 mL/min, 222 nm UV detector, t_R = 12.7 min (minor), t_R = 14.0 min (major). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.87 (bs, 3H, NH_3), 7.43–7.38 (m, 6H, Ar-H), 7.25–7.21 (m, 2H, Ar-H), 5.81 (s, 1H, CH), 2.25 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 138.1, 137.9, 136.3, 134.6, 130.5, 129.5, 129.3, 128.7, 126.4, 124.0, 54.8, 21.0, 15.4; HRMS calcd $C_{15}H_{17}N$: 212.1439, found: 212.1434.



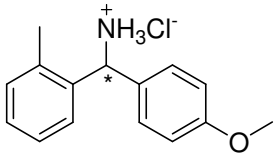
(+)-(2-chlorophenyl)(p-tolyl)methanaminium chloride (2k): $[\alpha]_D^{20}$ + 18.4 (*c* 1.0, MeOH), 92% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 94:6, 1.0 mL/min, 222 nm UV detector, t_R = 16.2 min (minor), t_R = 18.5 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.27 (bs, 3H, NH_3), 7.95 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.54–7.41 (m, 3H, Ar-H), 7.35 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.22 (d, 2H, *J* = 7.6 Hz, Ar-H), 5.78 (s, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 138.2, 135.4, 133.4, 131.9, 130.0, 129.9, 129.2, 128.1, 128.0, 127.7, 53.9, 20.6; HRMS calcd for $C_{14}H_{14}ClN$: 232.0888, found: 232.0889.



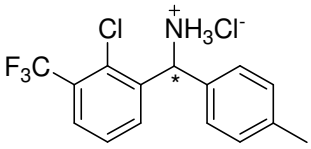
(+)-(2-chlorophenyl)(4-methoxyphenyl)methanaminium chloride (2l): $[\alpha]_D^{20}$ + 30.0 (*c* 1.0, MeOH), 93% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 11.5 min (minor), t_R = 15.1 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.06 (bs, 3H, NH_3), 7.82 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.54–7.48 (m, 2H, Ar-H), 7.45–7.40 (m, 1H, Ar-H), 7.32 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.96 (d, 2H, *J* = 8.8 Hz, Ar-H), 5.77 (s, 1H, CH), 3.73 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 160.1, 135.9, 132.5, 130.8, 130.7, 130.2, 128.6, 128.5, 128.1, 114.8, 55.9, 54.5.



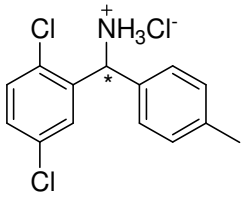
(+)-o-tolyl(p-tolyl)methanaminium chloride (2m): $[\alpha]_D^{20}$ + 55.9 (*c* 1.0, MeOH), 91% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 222 nm UV detector, t_R = 7.6 min (minor), t_R = 9.4 min (major). ^{1}H NMR (CD_3Cl, 400 MHz) δ 9.30 (bs, 3H, NH_3), 7.51 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.26–7.21 (m, 3H, Ar-H), 7.16–7.13 (m, 2H, Ar-H), 7.08 (d, 2H, *J* = 7.6 Hz, Ar-H), 5.58 (s, 1H, CH), 2.35 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 135.4, 134.8, 133.1, 130.9, 129.6, 128.3, 128.0, 126.8, 126.3, 55.3, 21.2, 19.6; HRMS calcd for $C_{15}H_{18}N$: 212.1434, found: 212.1446.



(+)-(4-methoxyphenyl)(o-tolyl)methanaminium chloride (2n): $[\alpha]_D^{20}$ + 43.5 (*c* 1.0, MeOH), 94% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 14.4 min (minor), t_R = 16.9 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.90 (bs, 3H, NH_3), 7.58 (d, 1H, *J* = 7.2 Hz, Ar-H), 7.36–7.21 (m, 5H, Ar-H), 6.95 (d, 2H, *J* = 8.4 Hz, Ar-H), 5.63 (s, 1H, CH), 3.73 (s, 3H, OCH_3), 2.19 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 160.0, 136.7, 136.0, 131.6, 130.2, 129.4, 128.9, 127.0, 126.0, 114.8, 55.9, 54.2, 19.6.

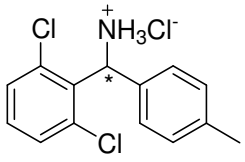


(+)-(2-chloro-3-(trifluoromethyl)phenyl)(p-tolyl)methanaminium chloride (2o): $[\alpha]_D^{20}$ + 12.4 (*c* 1.0, MeOH), 92% ee; HPLC condition for corresponding acetamide: Chiralcel AS column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 9.7 min (minor), t_R = 15.3 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.32 (bs, 3H, NH_3), 8.26 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.91 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.75 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.34 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.22 (d, 2H, *J* = 7.6 Hz, Ar-H), 5.94 (s, 1H, CH), 2.28 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 138.5, 138.1, 132.6, 132.1, 129.7, 129.4, 128.1, 128.0, 127.9, 127.8, 127.5, 124.0, 121.3, 53.8, 20.6; HRMS calcd for $C_{15}H_{14}ClF_3N$: 300.0761, found: 300.0740.

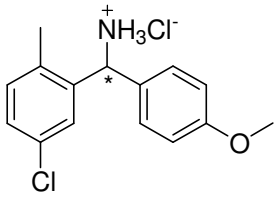


(+)-(2,5-dichlorophenyl)(p-tolyl)methanaminium chloride (2p): $[\alpha]_D^{20}$ + 72.7 (*c* 1.0, MeOH), 72% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 8.9 min (minor), t_R = 13.0 min

(major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.16 (bs, 3H, NH_3), 7.96 (s, 1H, Ar-H), 7.57–7.52 (m, 2H, Ar-H), 7.29 (d, 2H, J = 8.0 Hz, Ar-H), 7.23 (d, 2H, J = 8.0 Hz, Ar-H), 5.77 (s, 1H, CH), 2.28 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 139.4, 137.8, 133.2, 133.1, 132.4, 131.4, 130.7, 130.2, 128.6, 128.3, 54.6, 21.3; HRMS calcd for $C_{14}H_{14}Cl_2N$: 266.0498, found: 266.0523.

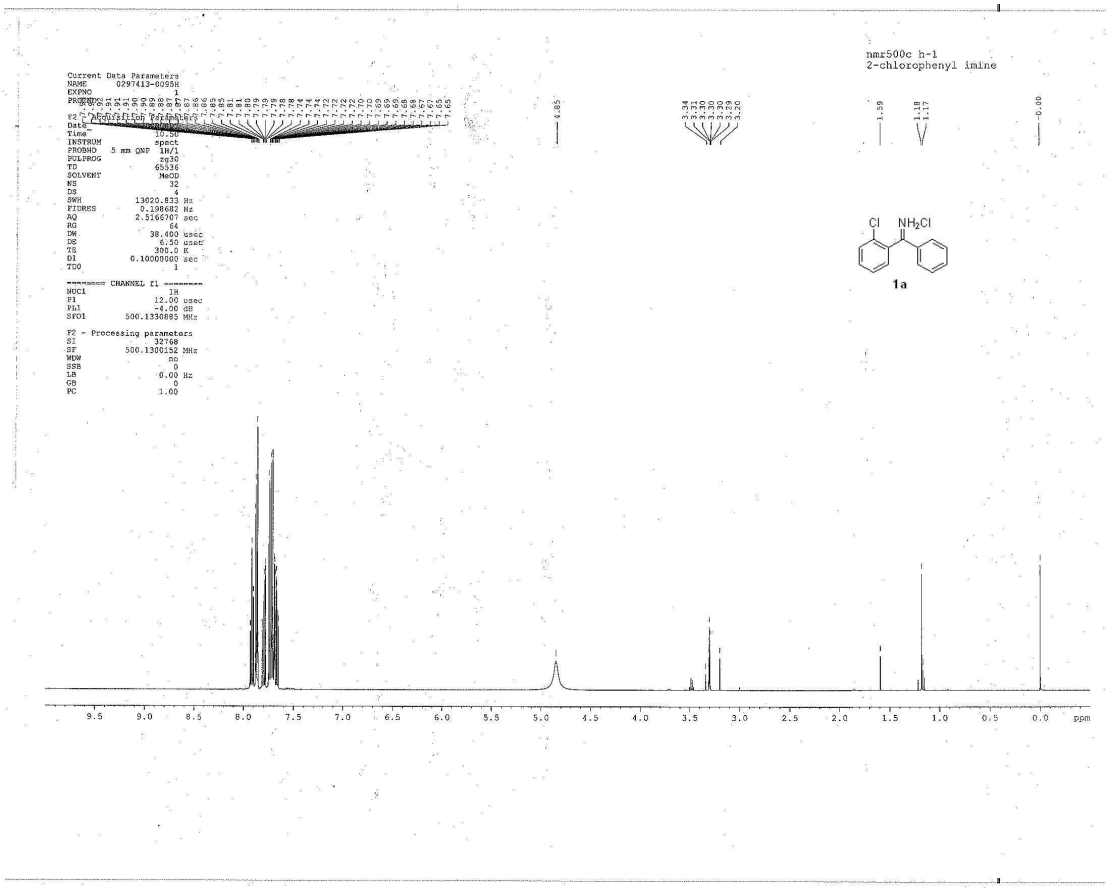


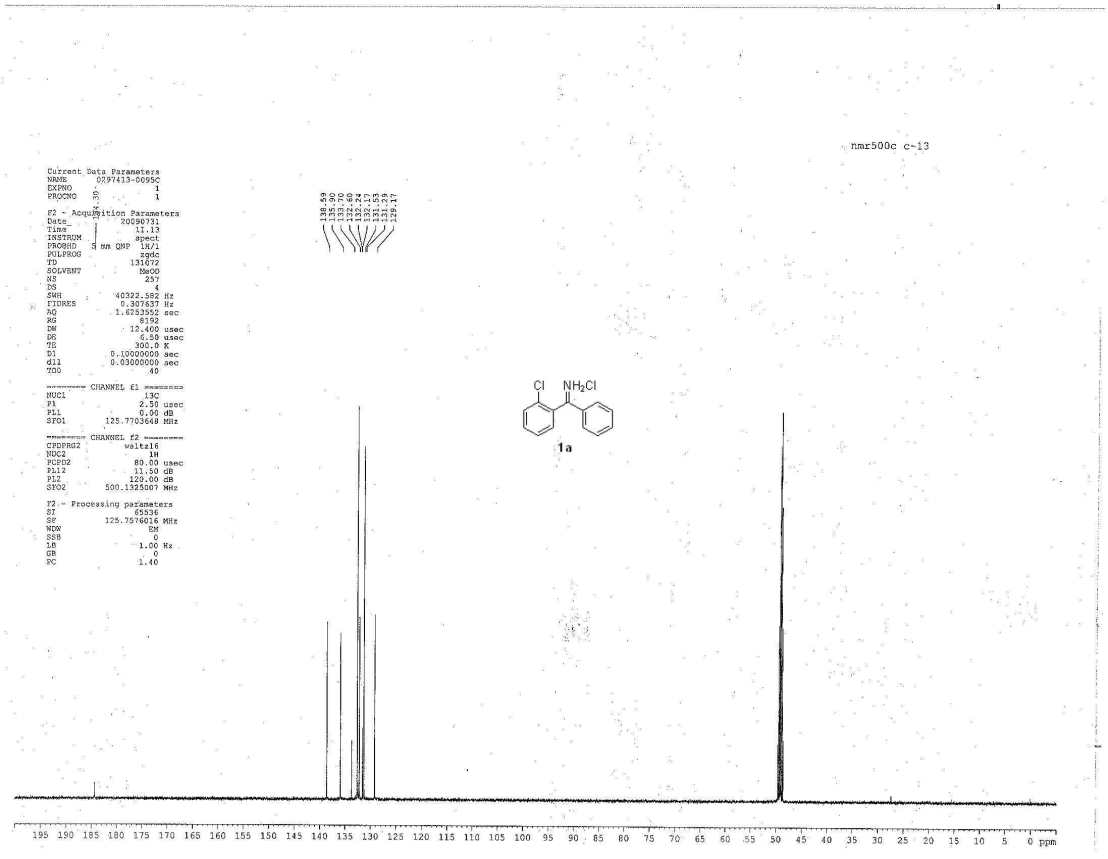
(–)-(2,6-dichlorophenyl)(p-tolyl)methanaminium chloride (2q): $[\alpha]_D^{20}$ – 8.2 (*c* 1.0, MeOH), 81% ee; HPLC condition for corresponding acetamide: Chiralcel AS column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 13.5 min (major), t_R = 21.9 min (minor). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.20 (bs, 3H, NH_3), 7.82 (d, 1H, J = 7.6 Hz, Ar-H), 7.69 (d, 1H, J = 7.6 Hz, Ar-H), 7.55 (t, 1H, J = 7.6 Hz, Ar-H), 7.29 (d, 2H, J = 8.0 Hz, Ar-H), 7.21 (d, 2H, J = 8.0 Hz, Ar-H), 5.83 (s, 1H, CH), 2.27 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 139.3, 138.4, 133.3, 133.2, 131.2, 130.7, 130.1, 129.4, 128.7, 127.0, 55.3, 21.3; HRMS calcd for $C_{14}H_{14}Cl_2N$: 266.0498, found: 266.0516.

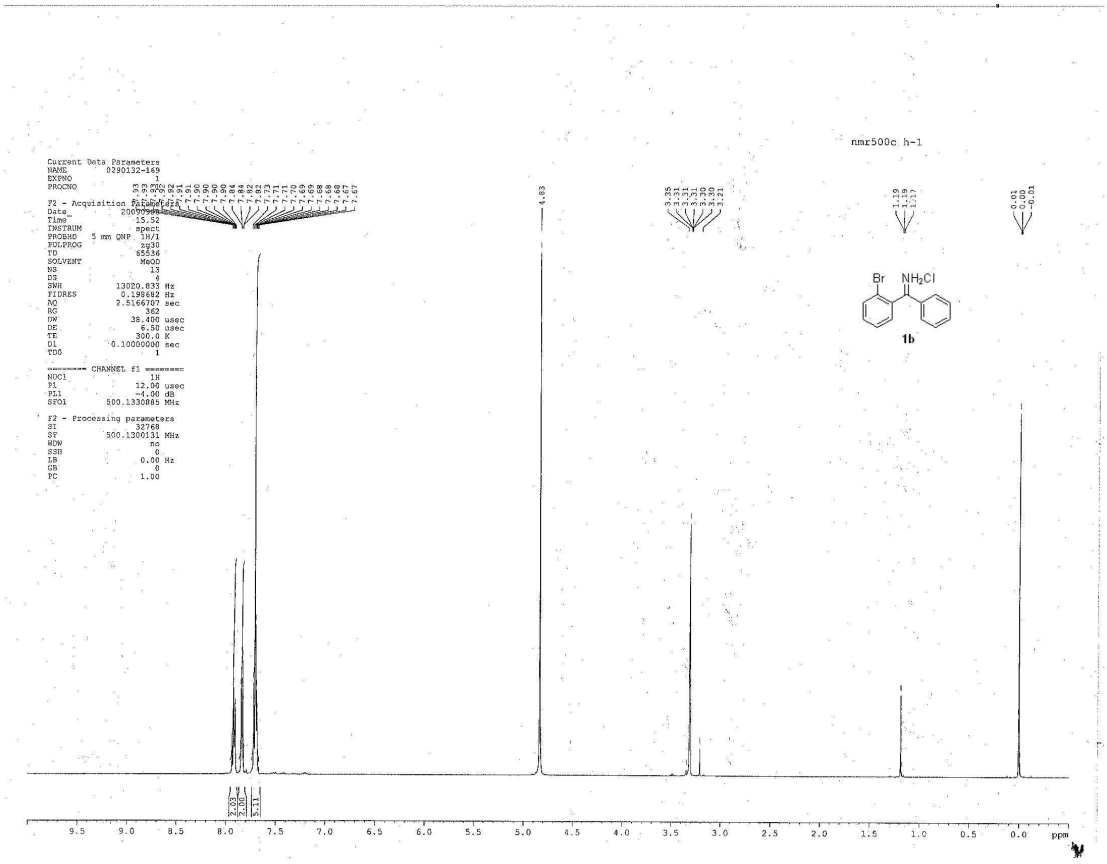


(+)-(5-chloro-2-methylphenyl)(4-methoxyphenyl)methanaminium chloride (2r): $[\alpha]_D^{20}$ + 123.8 (*c* 1.0, MeOH), 74% ee; HPLC condition for corresponding acetamide: Chiralcel OD-H column, *n*-hexane/2-propanol = 90:10, 1.0 mL/min, 230 nm UV detector, t_R = 10.5 min (minor), t_R = 18.4 min (major). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.89 (bs, 3H, NH_3), 7.66–7.64 (m, 1H, Ar-H), 7.37–7.34 (m, 1H, Ar-H), 7.30–7.25 (m, 3H, Ar-H), 6.97 (d, 2H, J = 8.8 Hz, Ar-H), 5.65 (s, 1H, CH), 3.74 (s, 3H, OCH_3), 2.15 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 159.4, 138.1, 134.5, 132.7, 130.8, 129.5, 128.0, 125.3, 114.2, 55.2, 53.3, 18.4; HRMS calcd for $C_{15}H_{17}ClNO$: 262.0993, found: 262.1021.

(D) NMR Spectra of New Products



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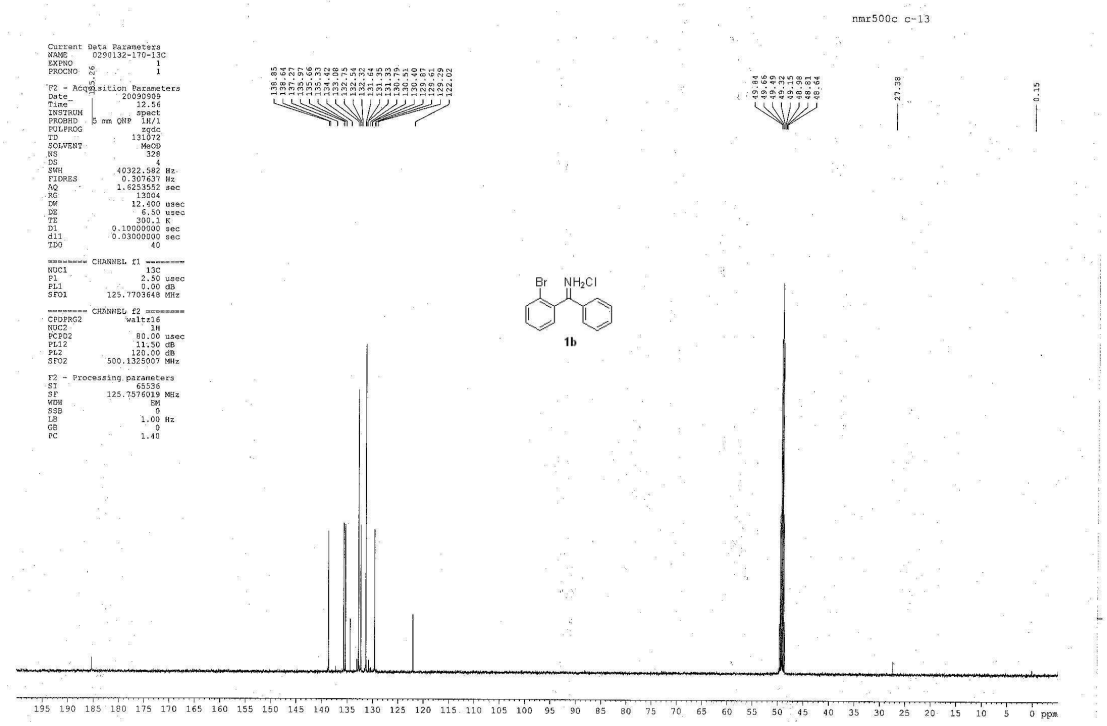
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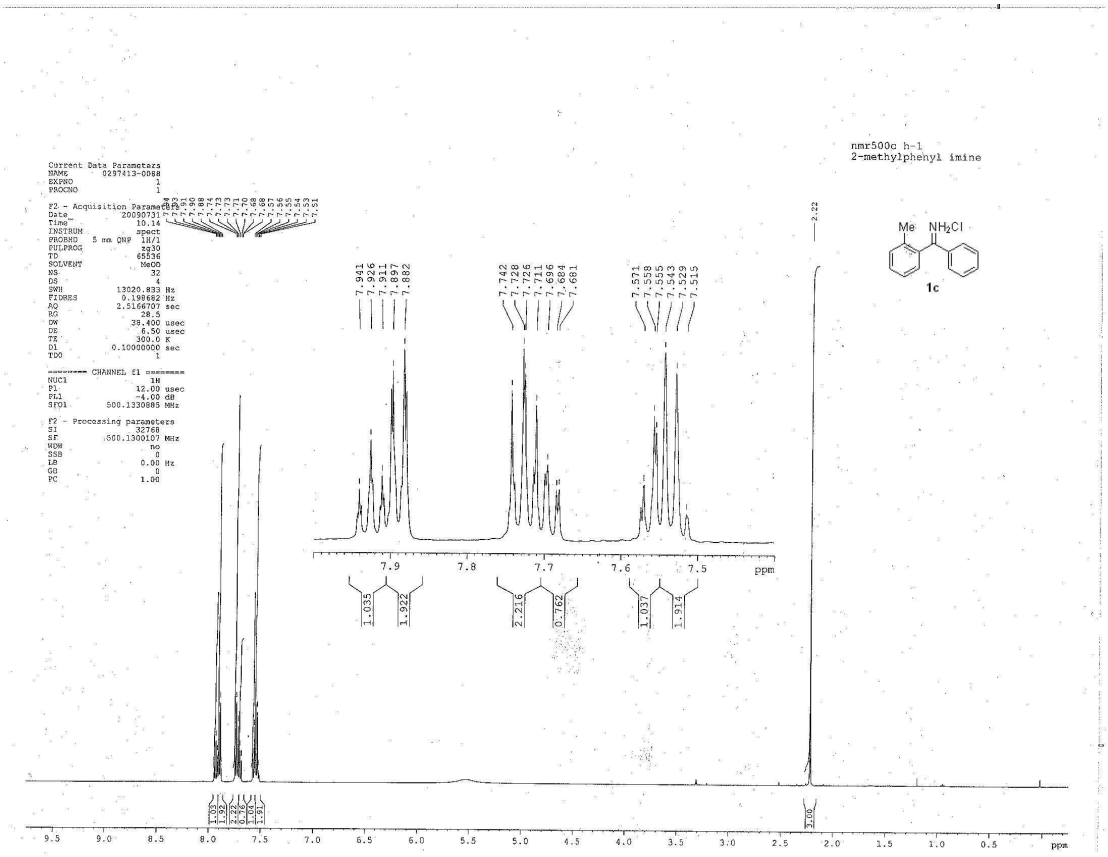
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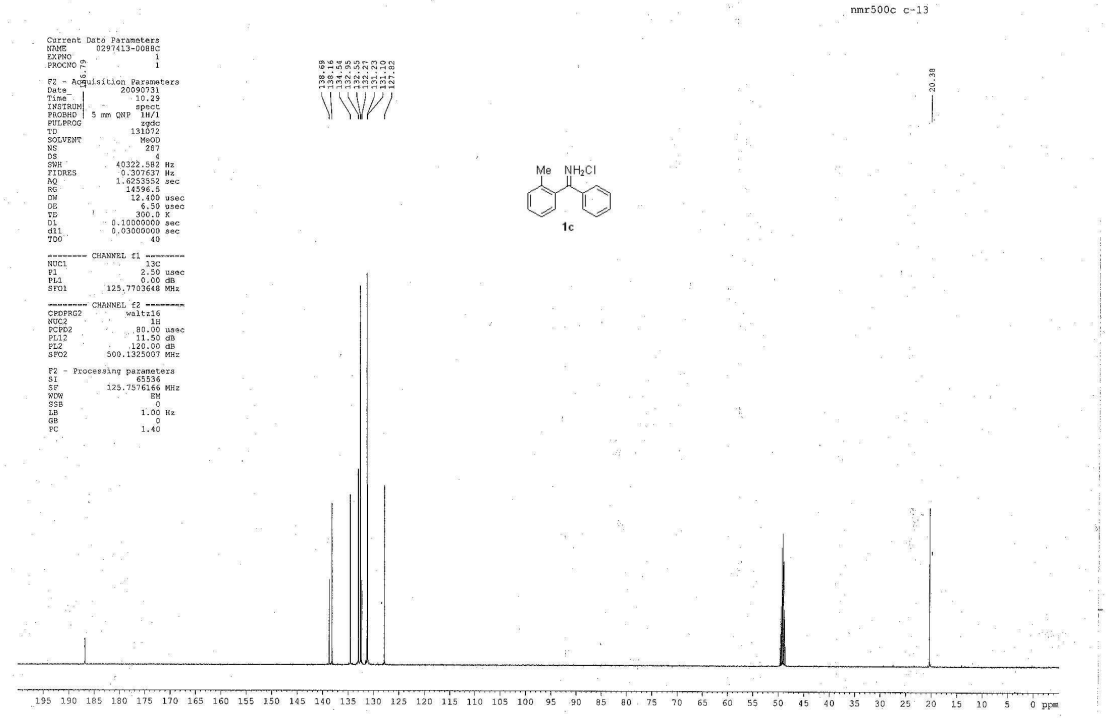
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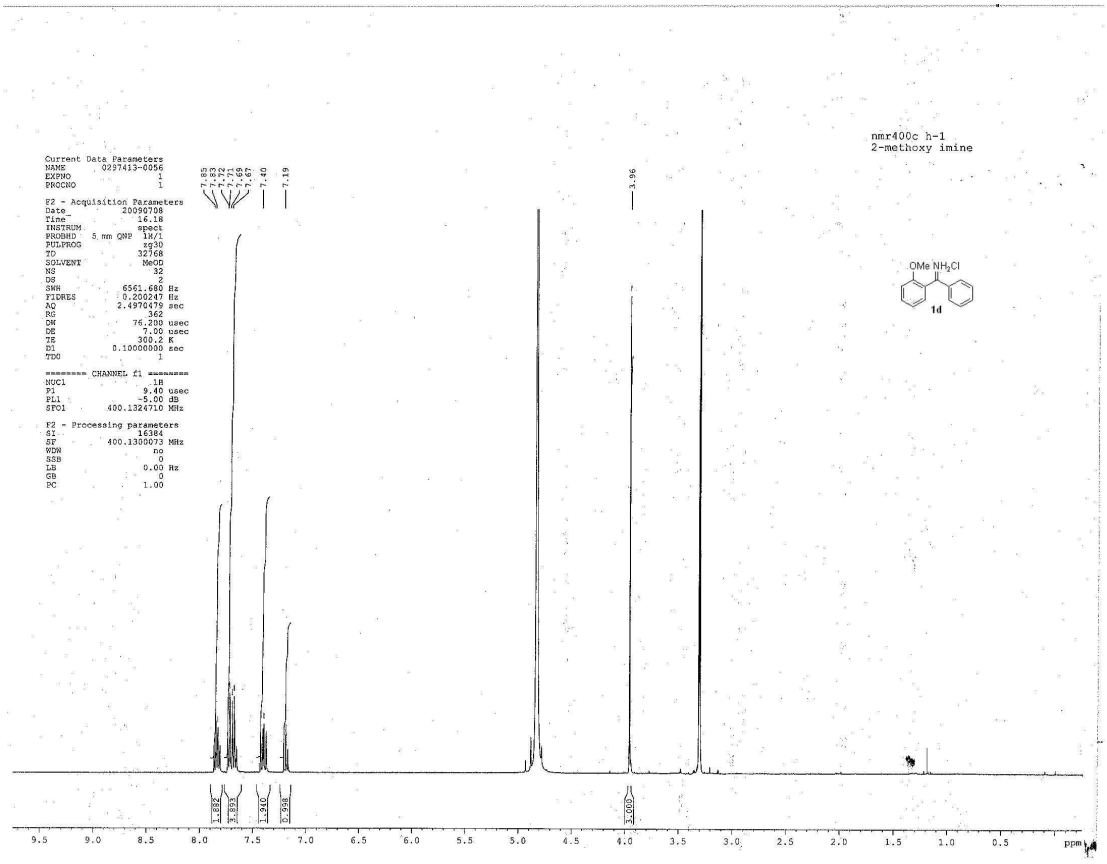
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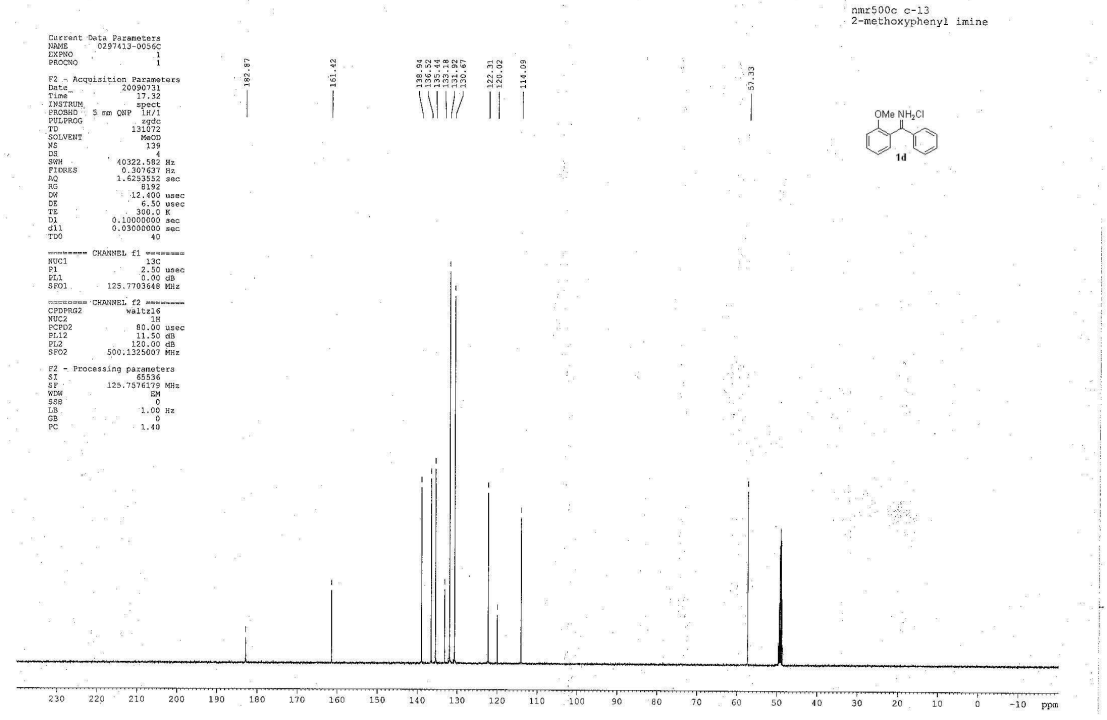
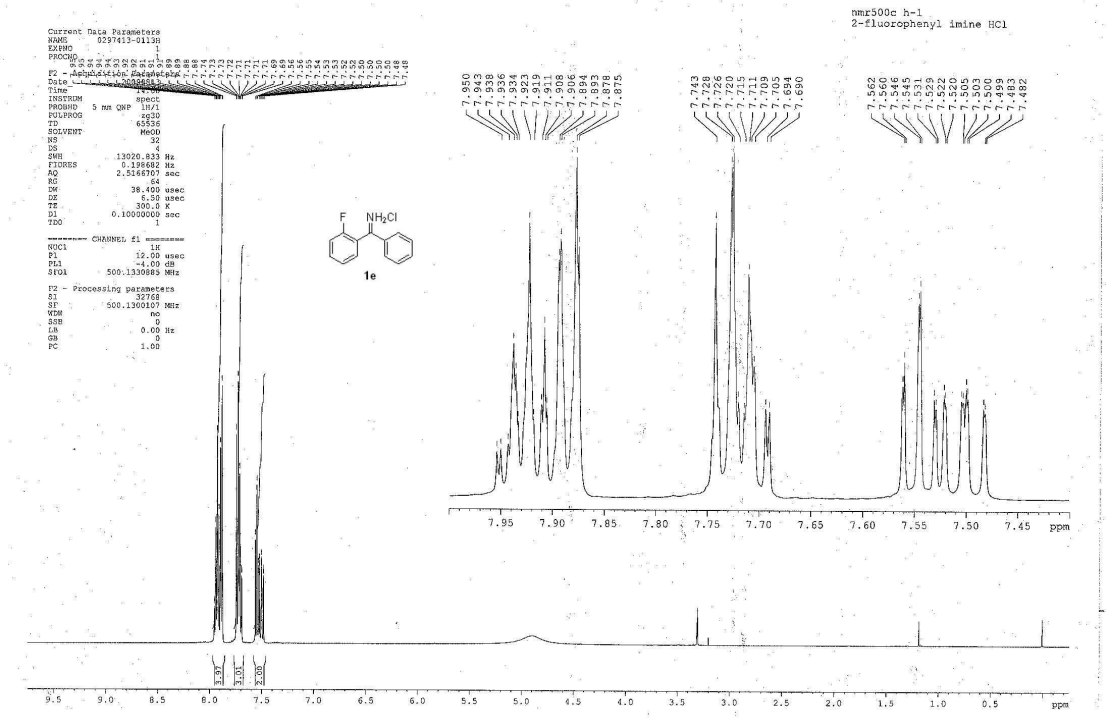
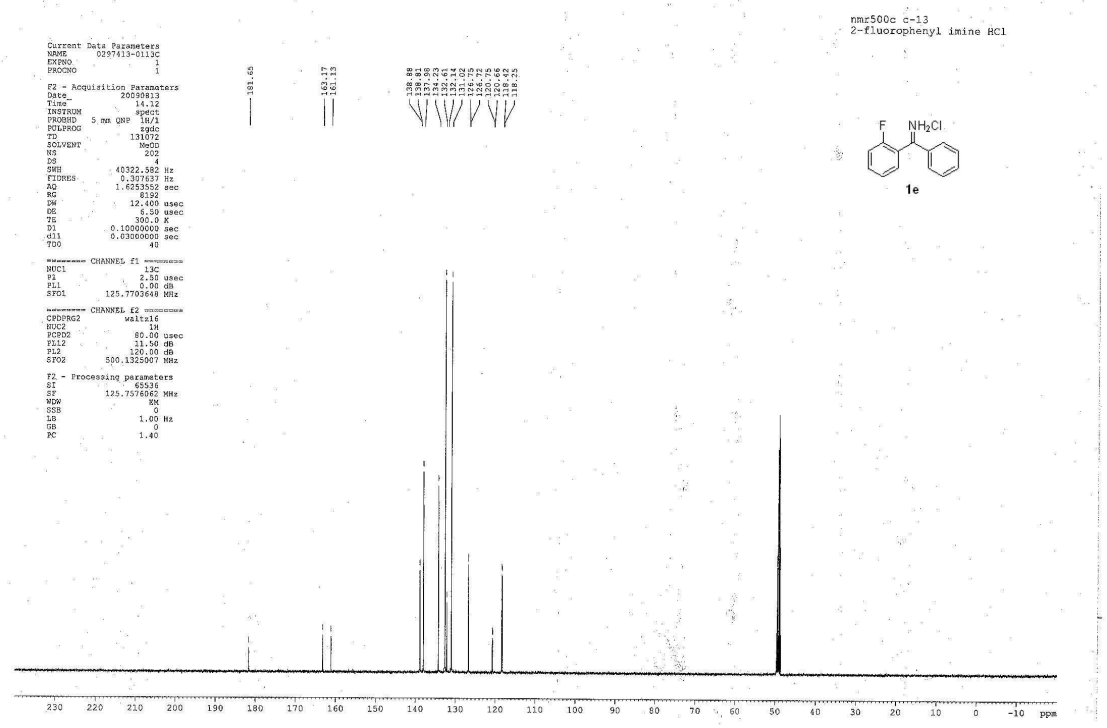
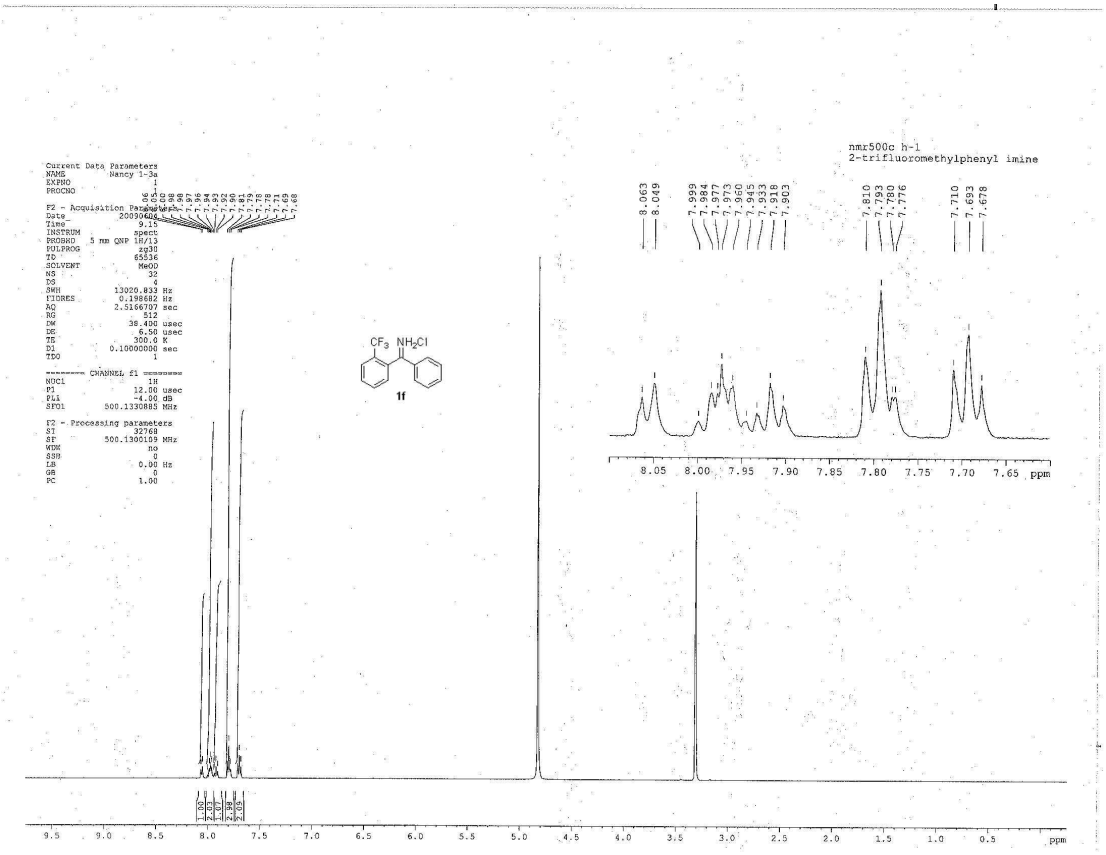
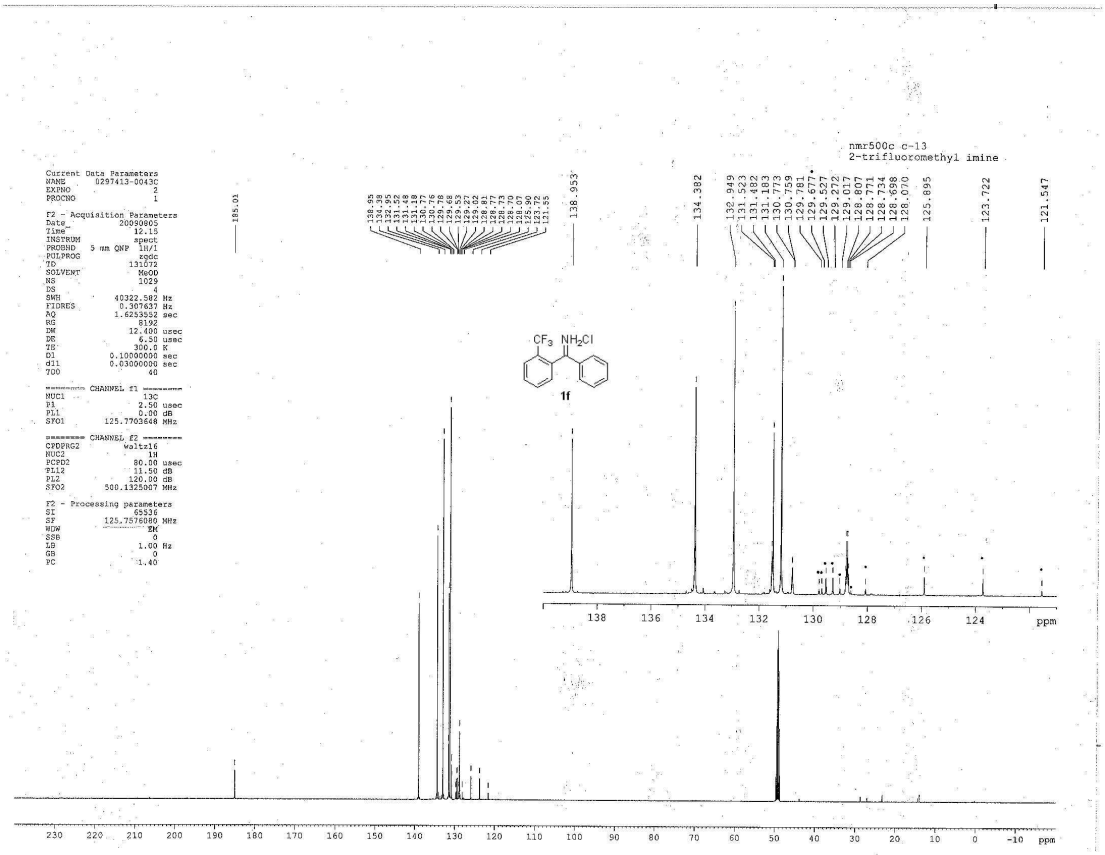
3.000
ppm

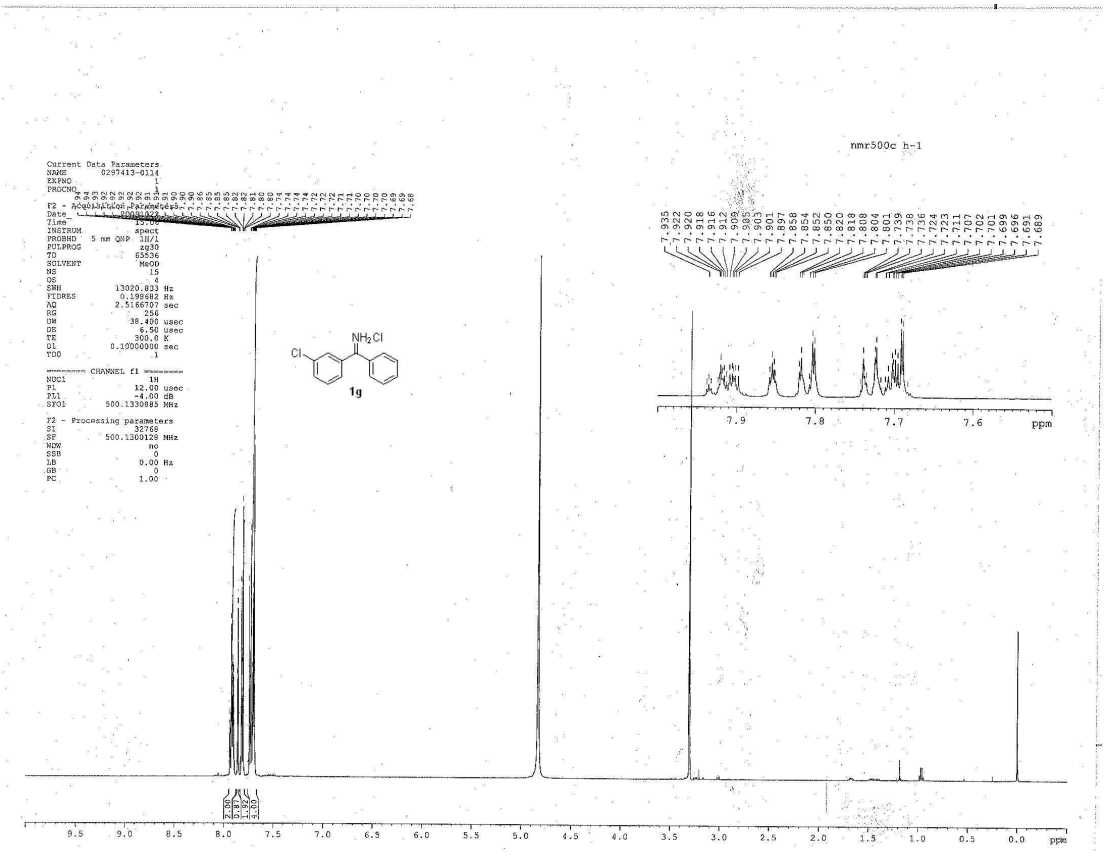

nmr500c c-13
2-methoxyphenyl imine
OMe NH2Cl
1d
182.87
161.42
138.54
136.92
135.44
133.38
131.64
130.67
122.31
120.02
114.09
51.33
ppm

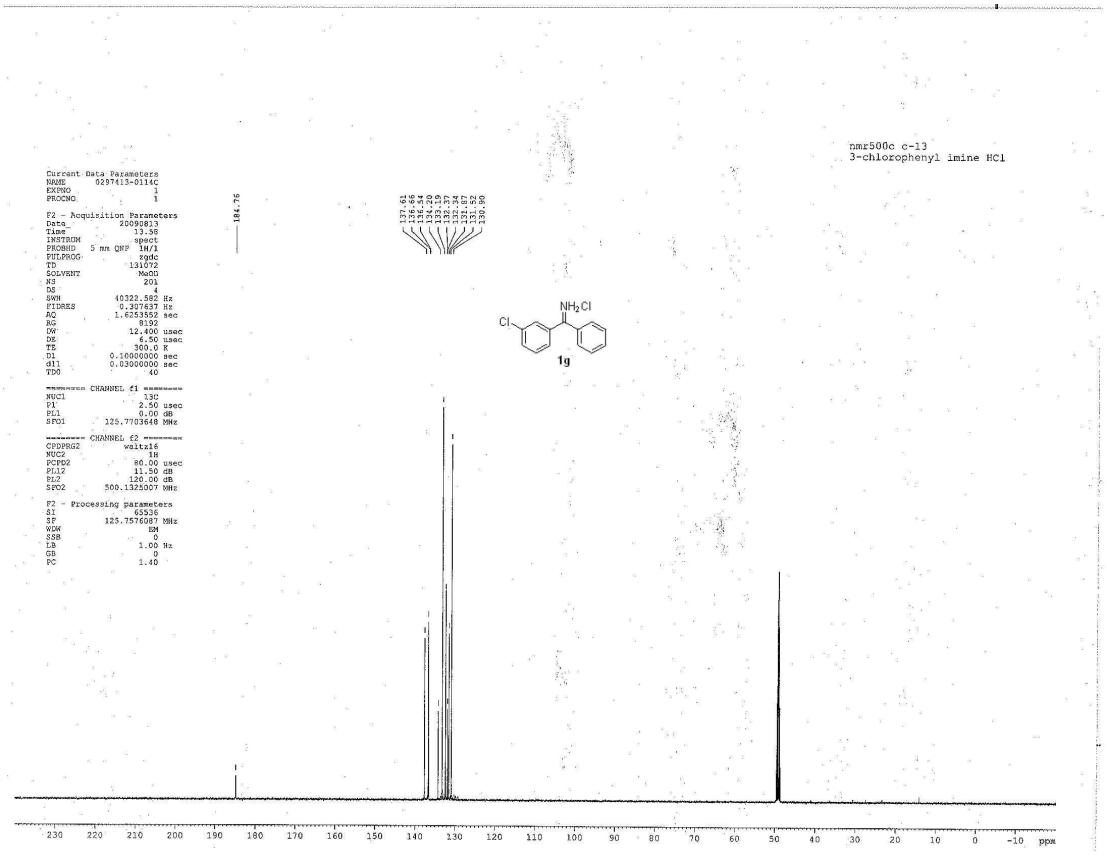

nmr500c h-1
2-fluorophenyl imine HCl
1e

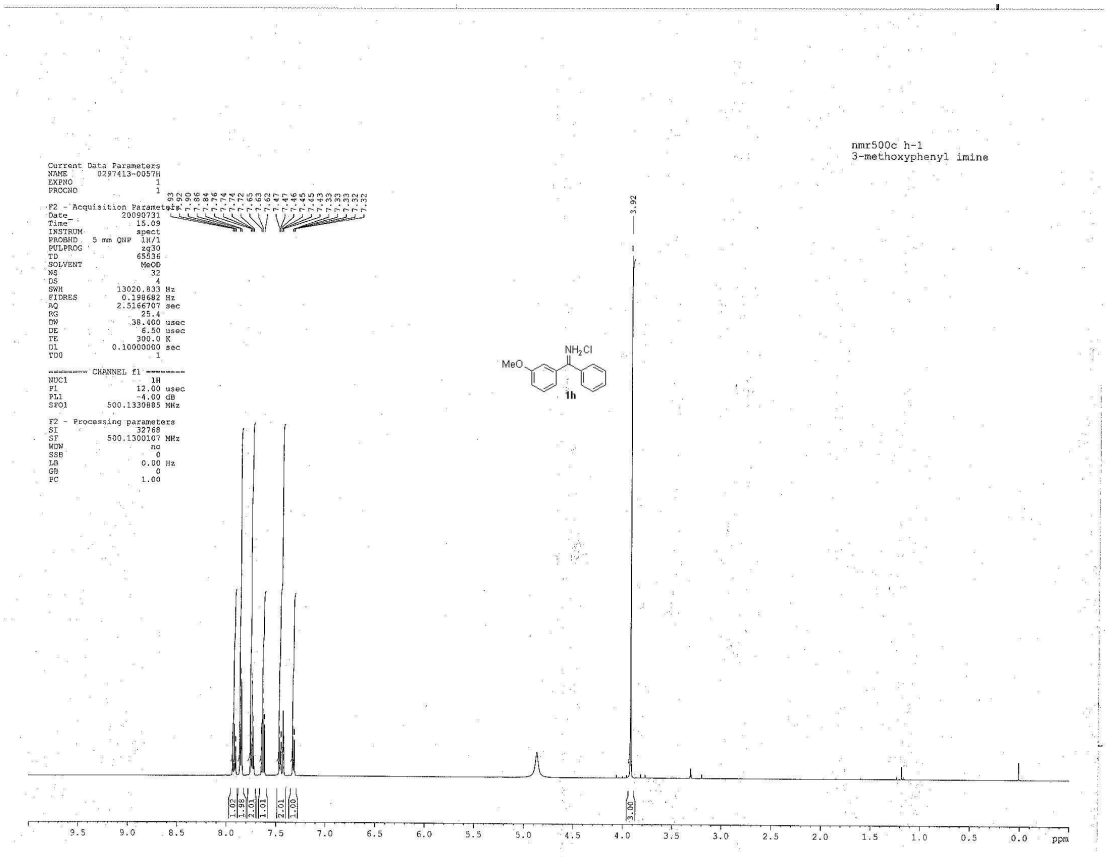

nmr500c c-13
2-fluorophenyl imine HCl
1e

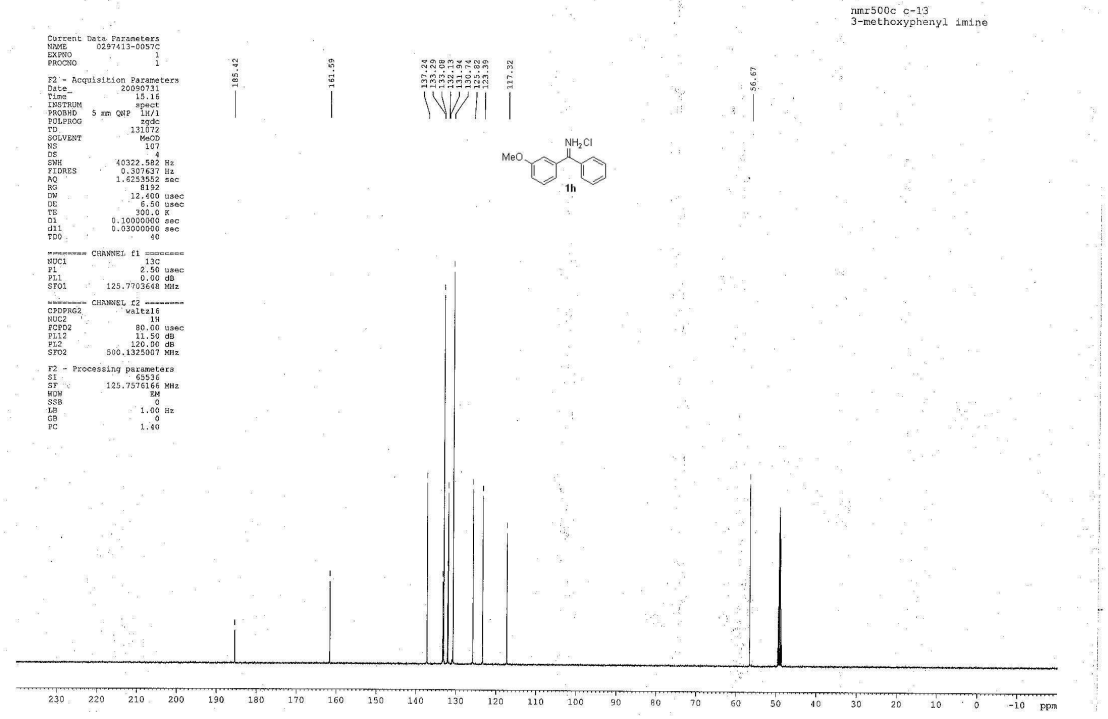

nmr500c h-1
2-trifluoromethylphenyl imine
1f

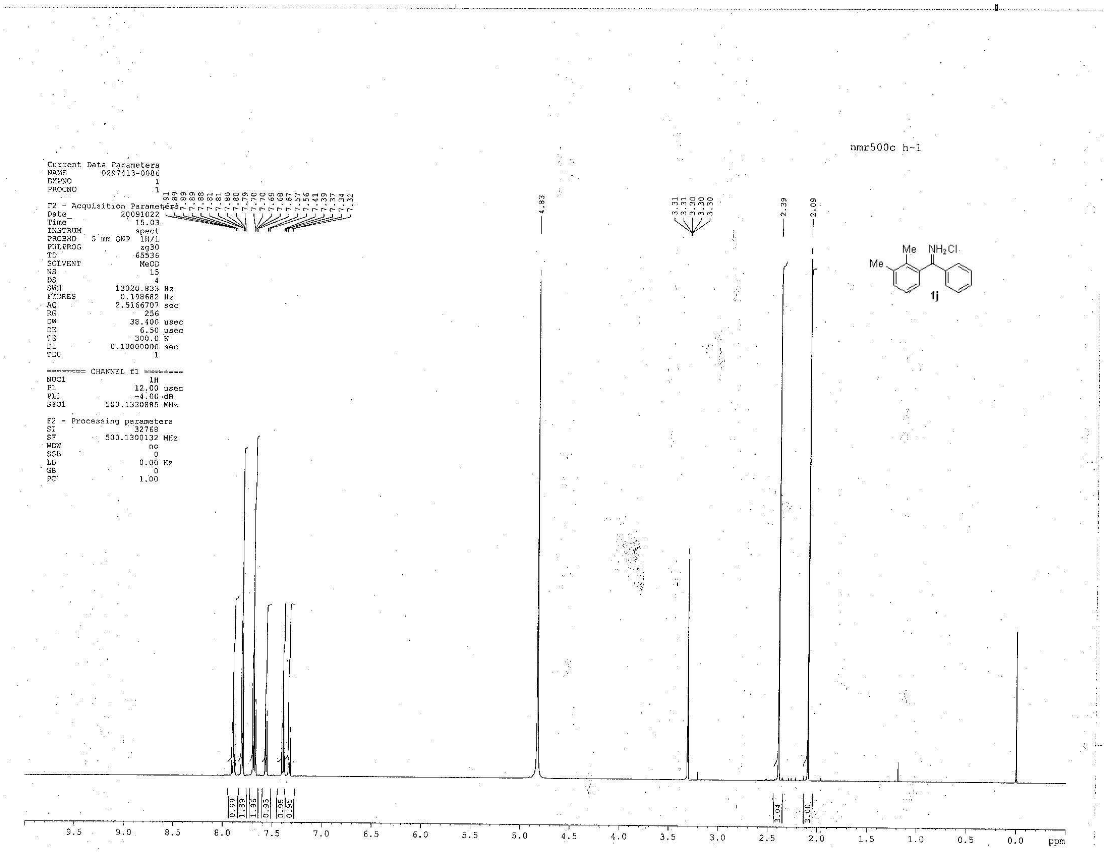

nmr500c c-13
2-trifluoromethyl imine
1f

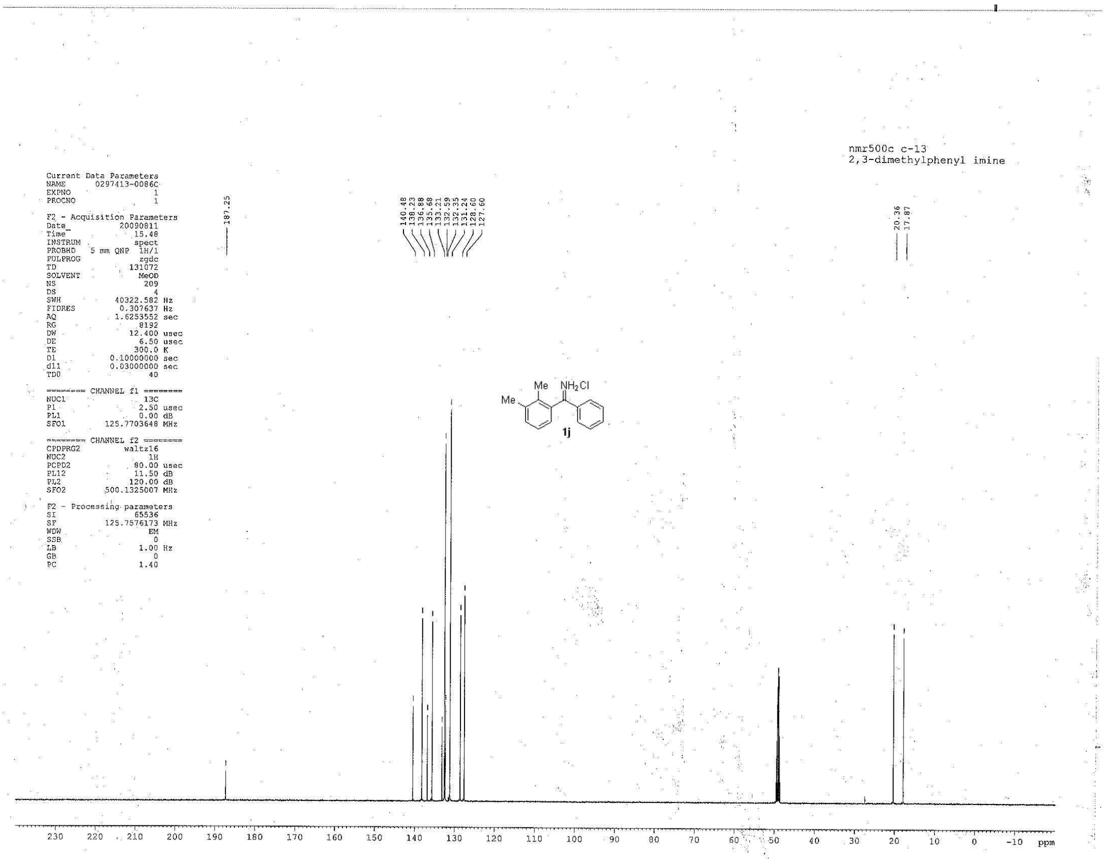

nmr500c h-1
Current Data Parameters
NAME 0297413-0114
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090822
Time 12.56
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 256
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330083 MHz
F2 - Processing parameters
SI 32768
SF 500.1300128 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
NH2Cl
Cl
1g
ppm

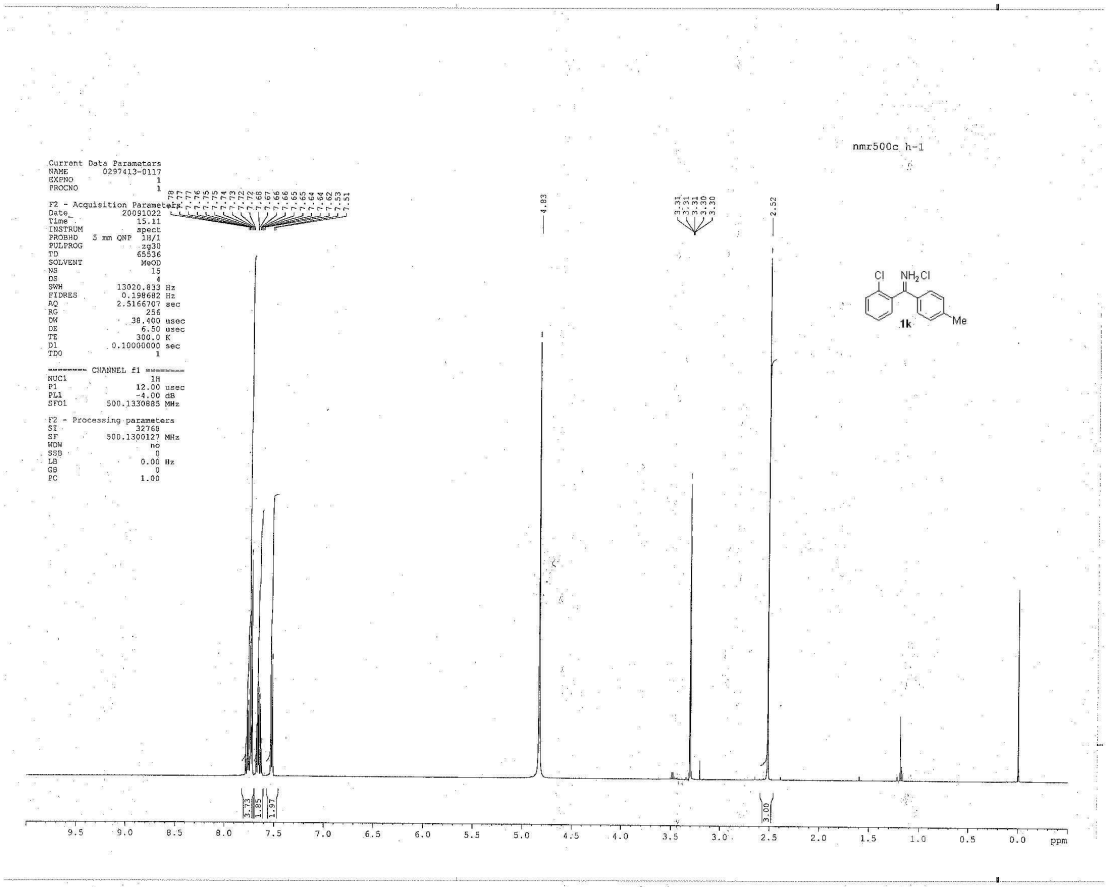

nmr500c c-13
3-chlorophenyl imine HCl
Current Data Parameters
NAME 0297413-0114C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090813
Time 13.58
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 201
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 8192
DW 12.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7576087 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NH2Cl
Cl
1g
ppm

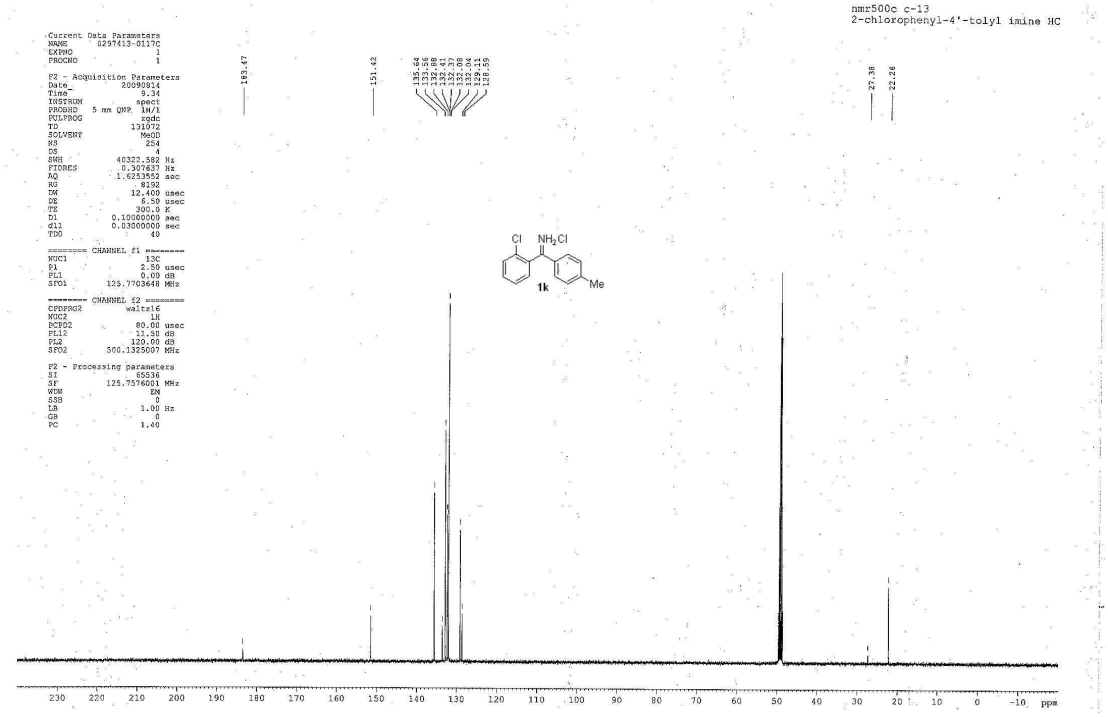

nmr500c h-1
3-methoxyphenyl imine
Current Data Parameters
NAME 0297413-0057H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090731
Time 15.09
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 32
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 25.4
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300107 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.93
7.92
7.86
7.84
7.76
7.74
7.72
7.63
7.62
7.47
7.46
7.45
7.33
7.33
7.33
7.32
3.92
MeO
NH2Cl
1h
1.07
1.98
2.05
1.00
2.01
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

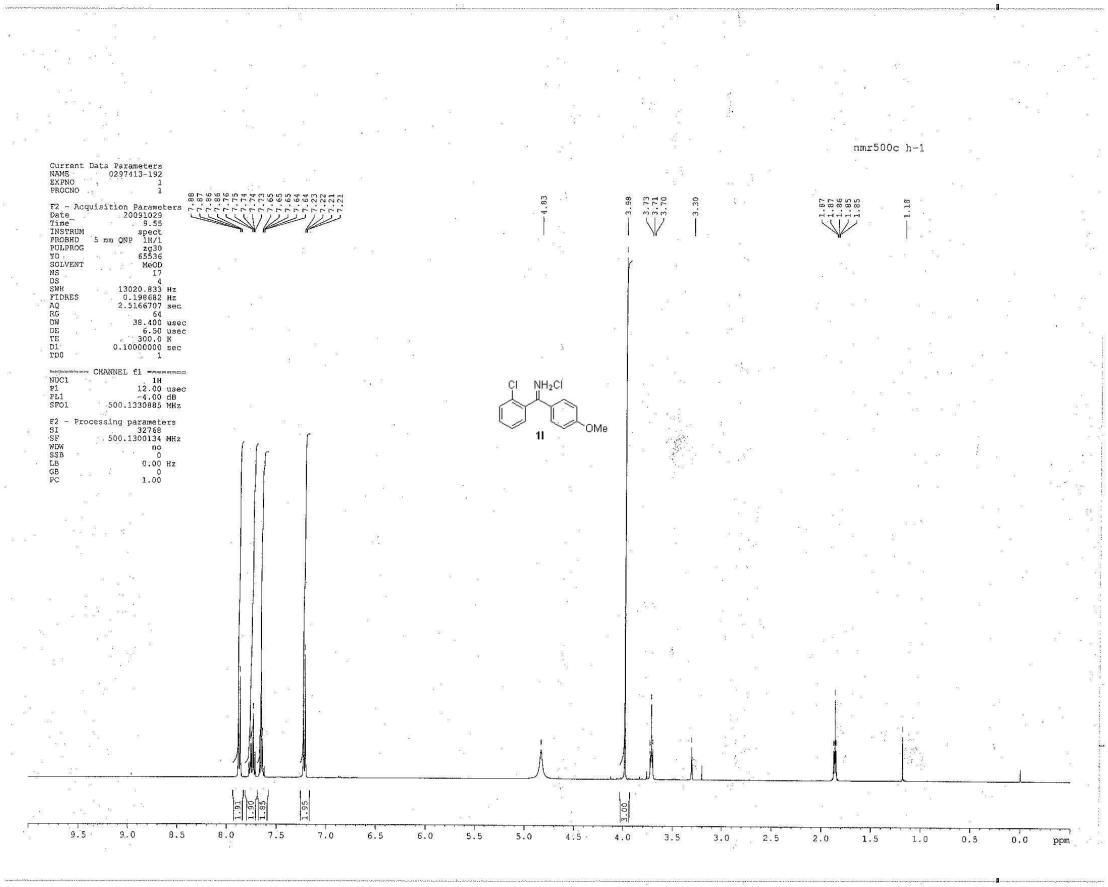

nmr500c c-13
3-methoxyphenyl imine
Current Data Parameters
NAME 0297413-0057C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090731
Time 15.16
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 107
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 8192
DW 12.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7576166 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
185.42
161.59
137.24
133.29
131.38
132.13
131.74
125.82
123.99
117.32
56.67
MeO
NH2Cl
1h
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

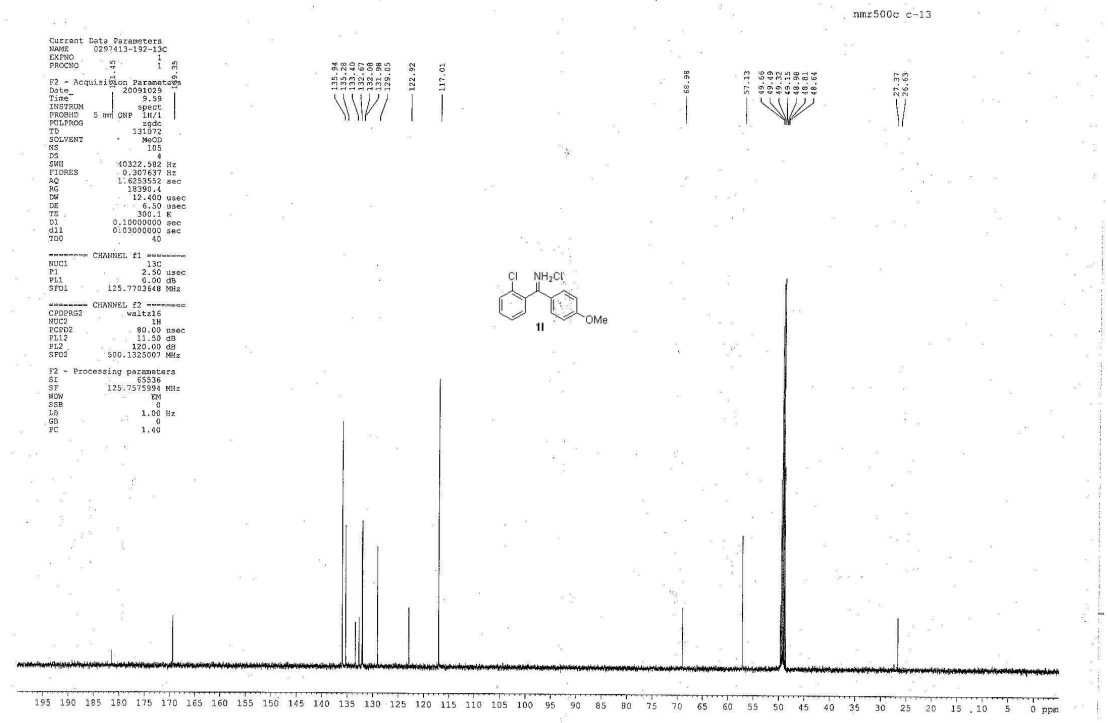

nmr500c h-1
1j

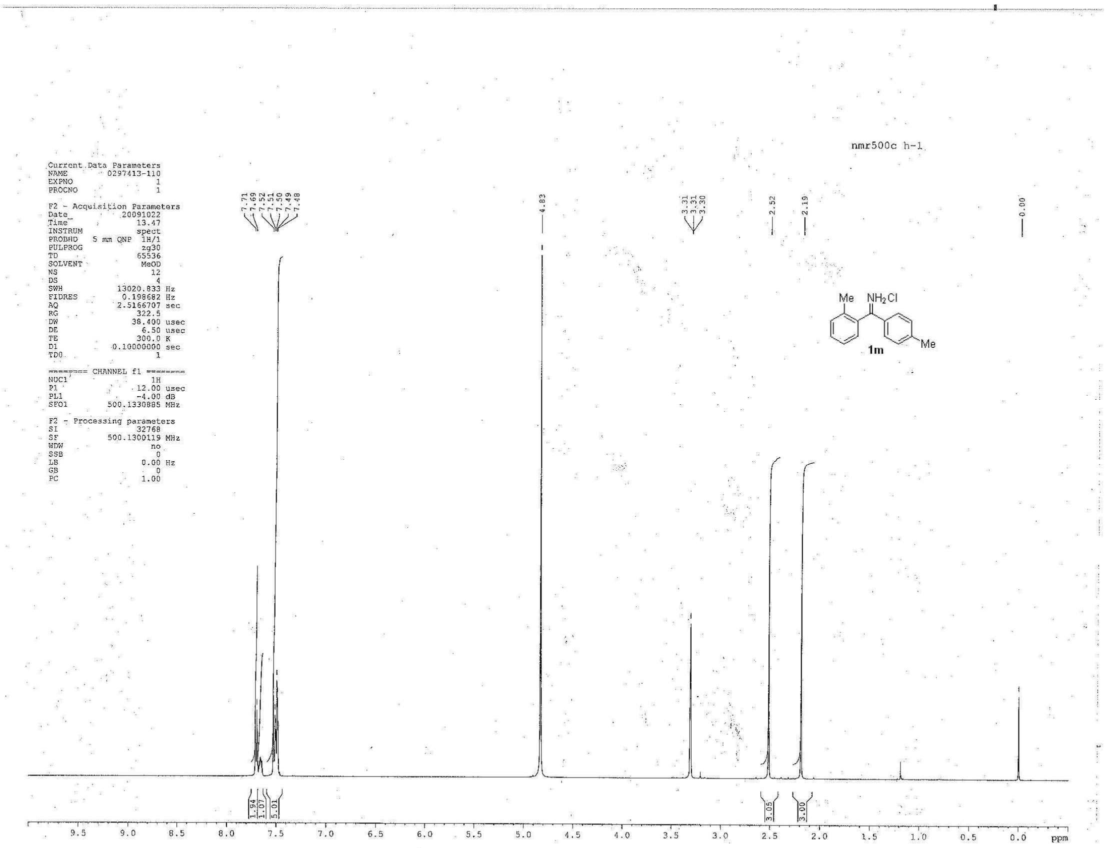

nmr500c c-13
2,3-dimethylphenyl imine
1j

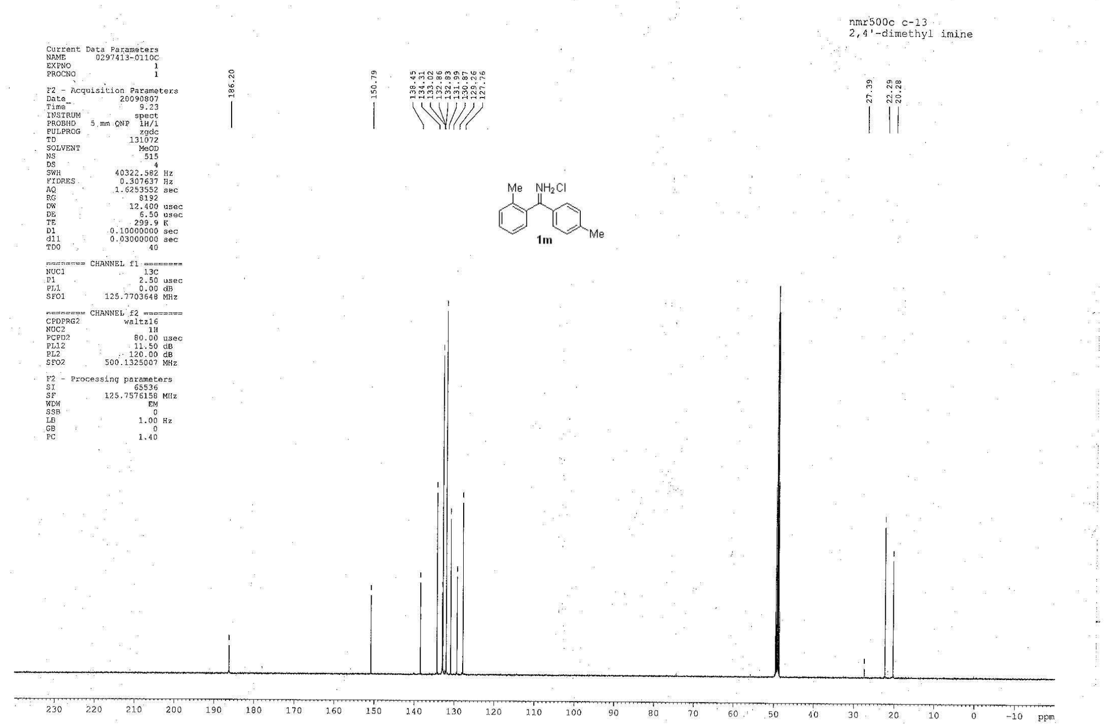

nmr500c h-1
Current Data Parameters
NAME 0297413-0117
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091022
Time 15.11
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 256
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300127 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.79
7.77
7.76
7.75
7.74
7.72
7.67
7.66
7.65
7.64
7.62
7.53
7.51
4.83
3.31
3.31
3.31
3.30
3.30
2.52
Cl
NH2Cl
Me
1k
3.03
1.85
1.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

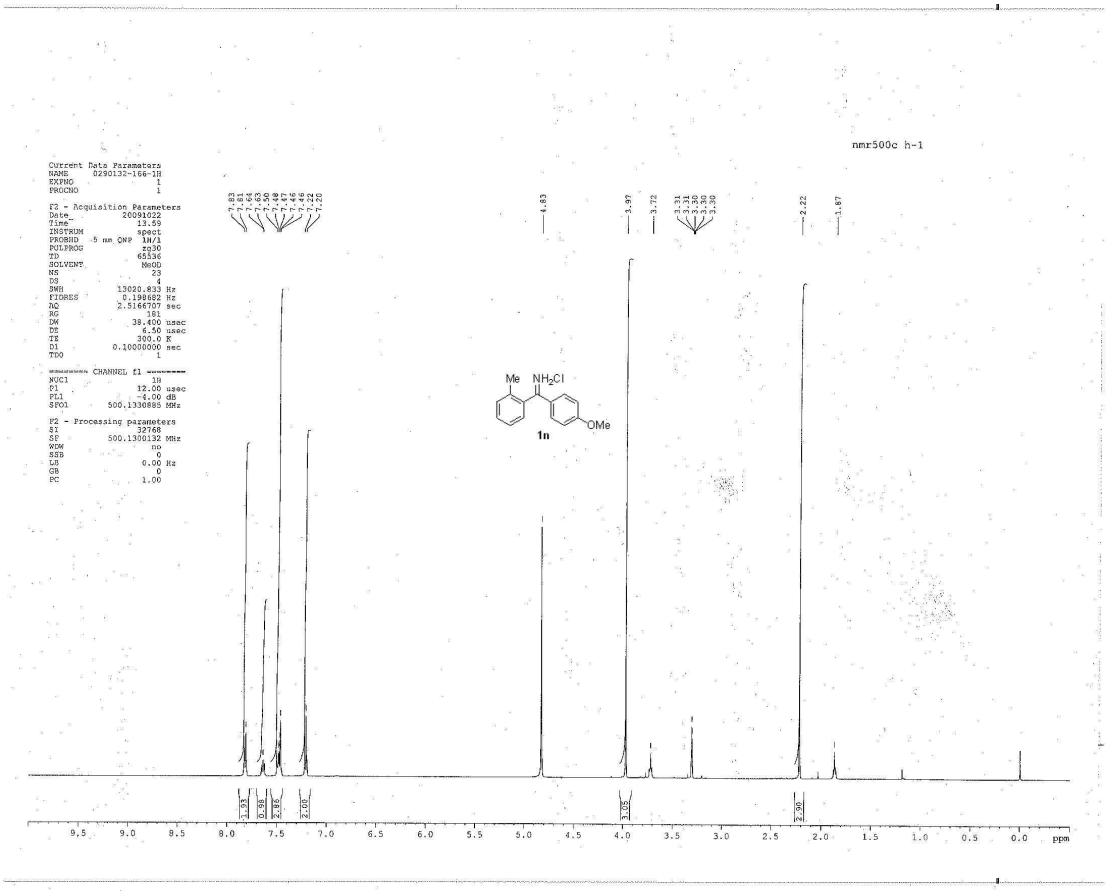

nmr500c c-13
2-chlorophenyl-4'-tolyl imine HC
Current Data Parameters
NAME 0297413-0117C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090914
Time 9.34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 254
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 8192
DW 12.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7576001 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
183.47
151.42
135.64
133.56
132.88
132.41
132.37
132.04
131.74
129.11
128.59
27.38
22.26
Cl
NH2Cl
Me
1k
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

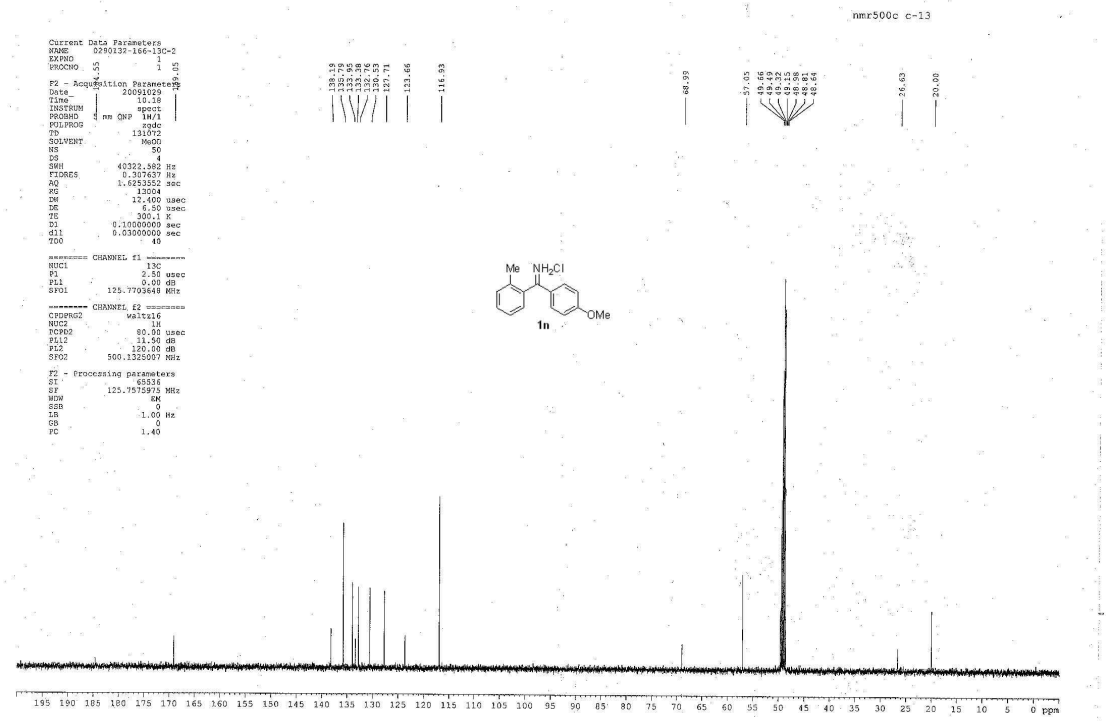

nmr500c h-1
Current Data Parameters
NAME 0297413-192
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091029
Time 8.55
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 17
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 64
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300134 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.88
7.87
7.86
7.86
7.76
7.75
7.74
7.73
7.65
7.65
7.64
7.64
7.22
7.21
4.03
3.58
3.73
3.71
3.70
3.39
1.87
1.87
1.86
1.85
1.85
1.18
Cl
NH2Cl
OMe
1l
1.01
1.00
1.05
1.55
3.05
ppm

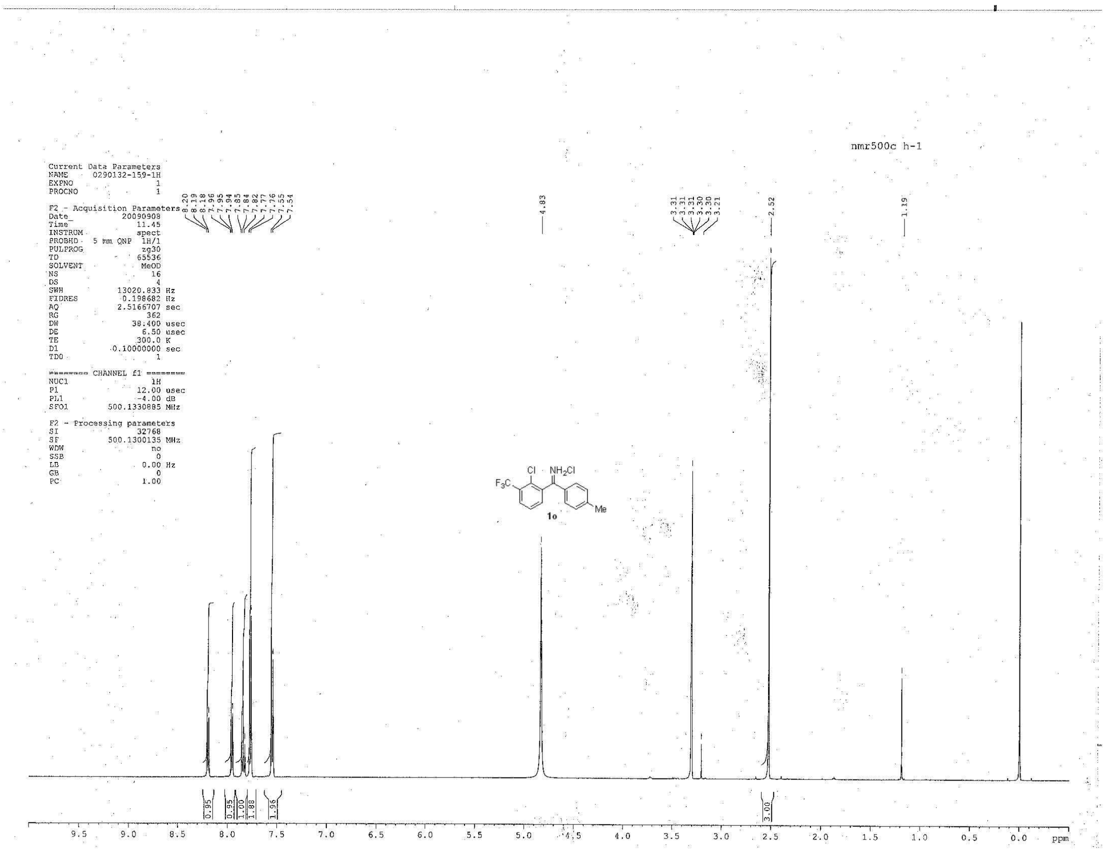

nmr500c c-13
Current Data Parameters
NAME 0297413-192-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091029
Time 9.59
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 105
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 18390.4
DW 12.400 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7575994 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
135.84
135.26
133.45
132.67
132.09
131.98
129.65
122.92
117.01
68.98
57.13
49.66
49.49
49.32
49.15
48.98
48.81
48.64
25.37
25.03
Cl
NH2Cl
OMe
1l
ppm

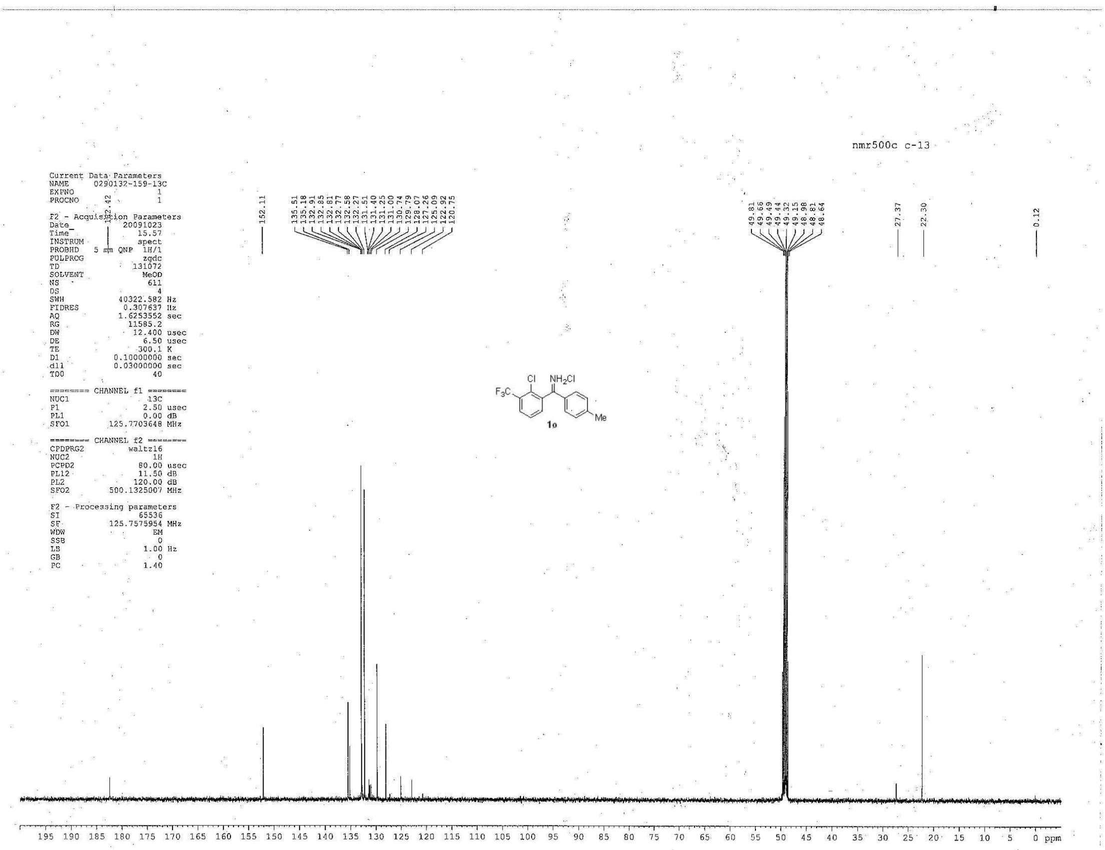

nmr500c h-1
Current Data Parameters
NAME 0297413-110
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091022
Time 13.47
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 12
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 322.5
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300119 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.71
7.69
7.52
7.51
7.50
7.49
7.48
4.83
3.31
3.31
3.30
2.52
2.19
0.00
Me
NH2Cl
Me
1m
1.94
1.07
5.01
3.05
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

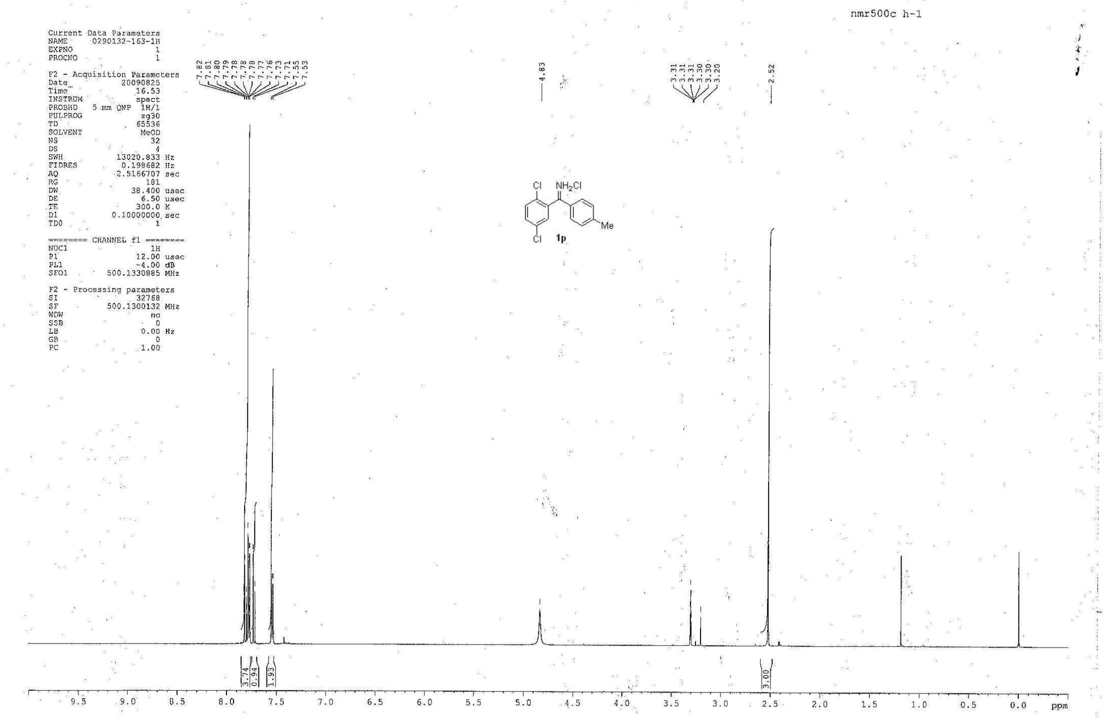

nmr500c c-13
2,4'-dimethyl imine
Current Data Parameters
NAME 0297413-0110C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090807
Time 9.23
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 515
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 8192
DW 12.400 usec
DE 6.50 usec
TE 299.9 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7576158 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
186.20
150.79
138.45
134.31
133.02
132.86
132.83
131.99
130.87
129.26
127.76
27.39
22.29
20.28
Me
NH2Cl
Me
1m
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

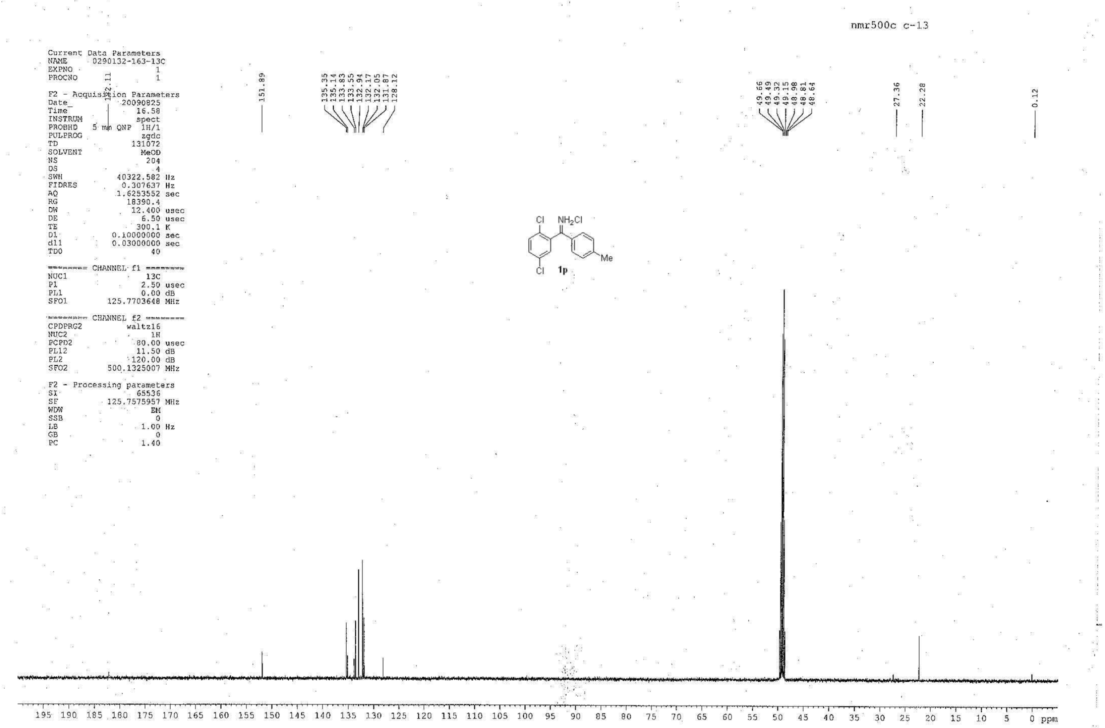

nmr500c h-1
Current Data Parameters
NAME 0290132-166-1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091022
Time 13.59
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 23
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 181
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300132 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.83
7.81
7.64
7.63
7.50
7.49
7.47
7.46
7.23
7.20
4.83
3.97
3.72
3.31
3.30
3.30
3.30
2.22
1.87
Me
NH2Cl
OMe
1n
1.93
0.86
0.86
2.00
3.05
2.90
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

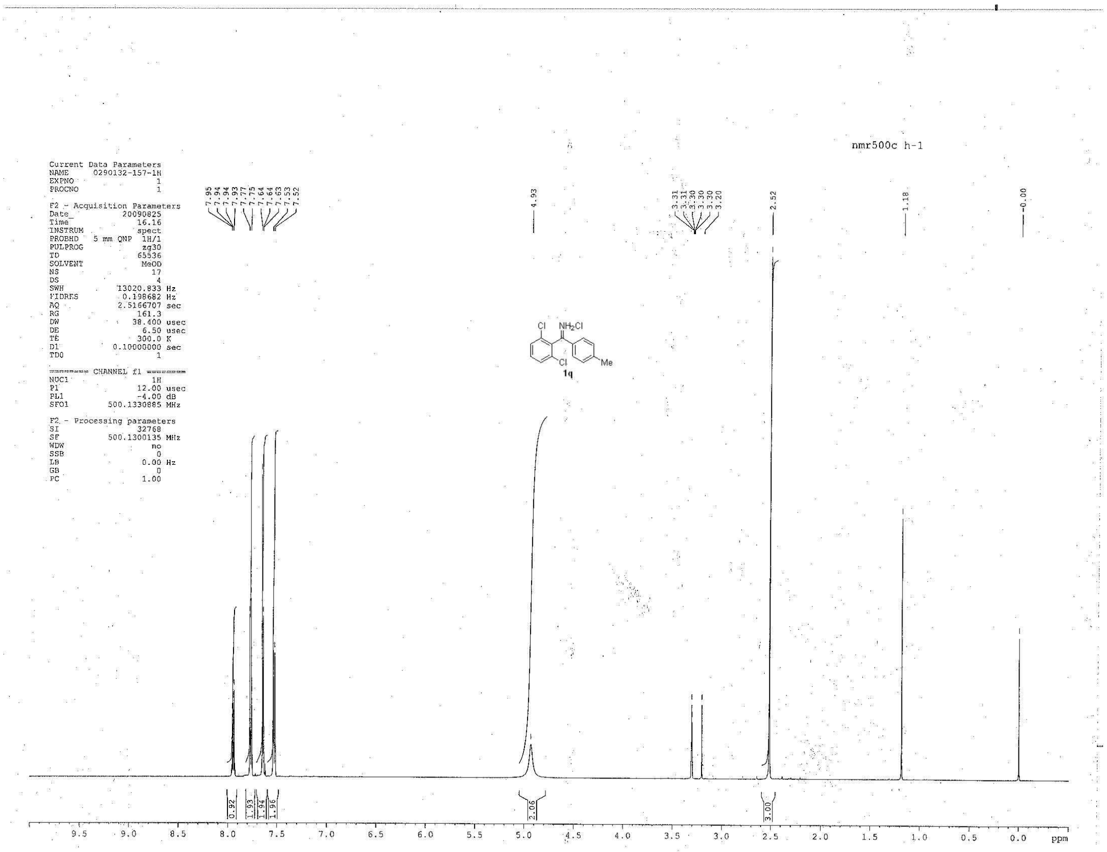

nmr500c c-13
Current Data Parameters
NAME 0290132-166-13C-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091029
Time 10.18
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 50
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 13004
DW 12.400 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 48
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7575975 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
194.55
139.05
138.59
135.79
133.95
133.38
132.76
130.53
127.71
123.66
116.93
68.99
57.05
49.66
49.49
49.32
49.15
48.98
48.81
48.64
26.63
20.00
Me
NH2Cl
OMe
1n
195
190
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0 ppm

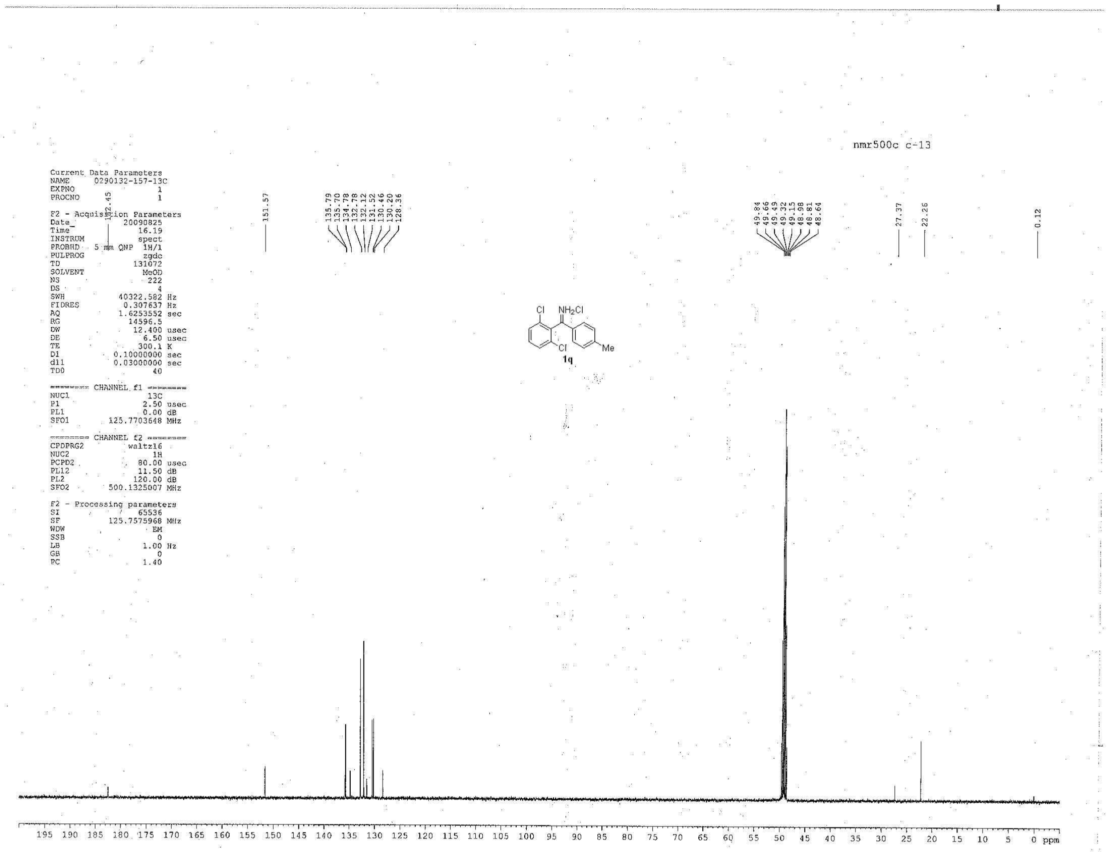


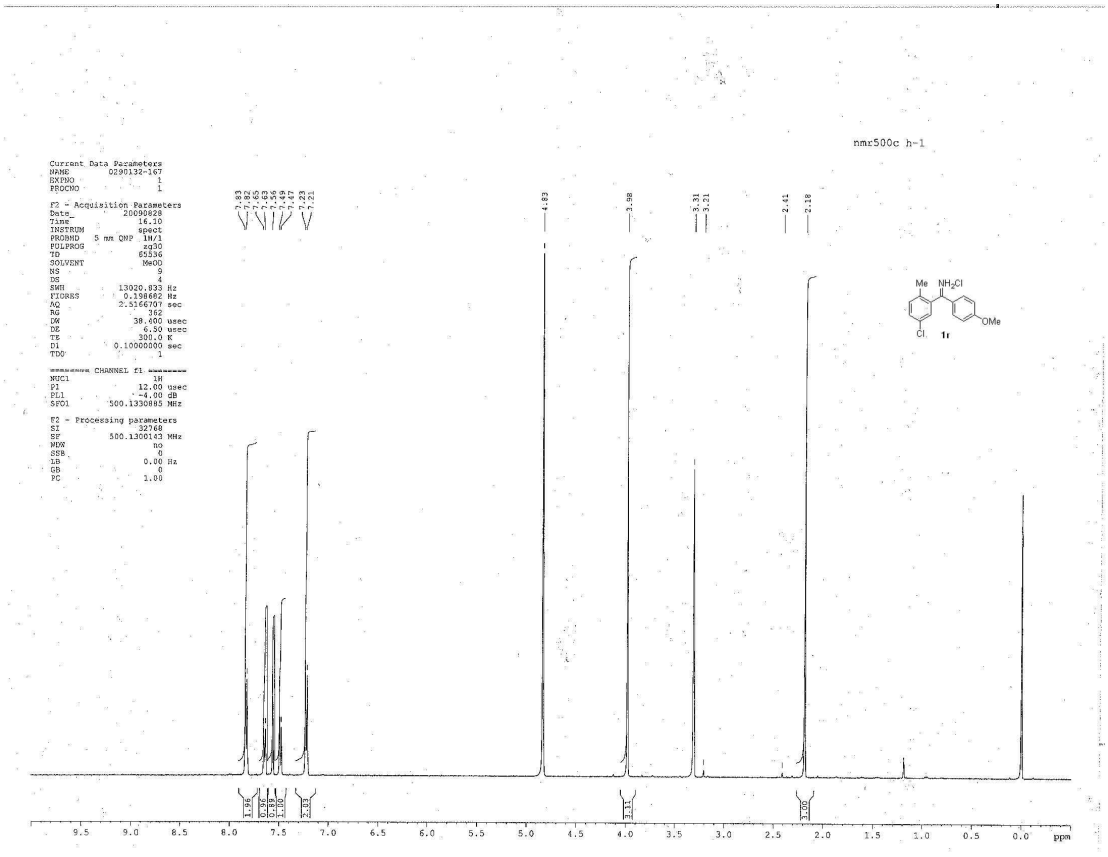


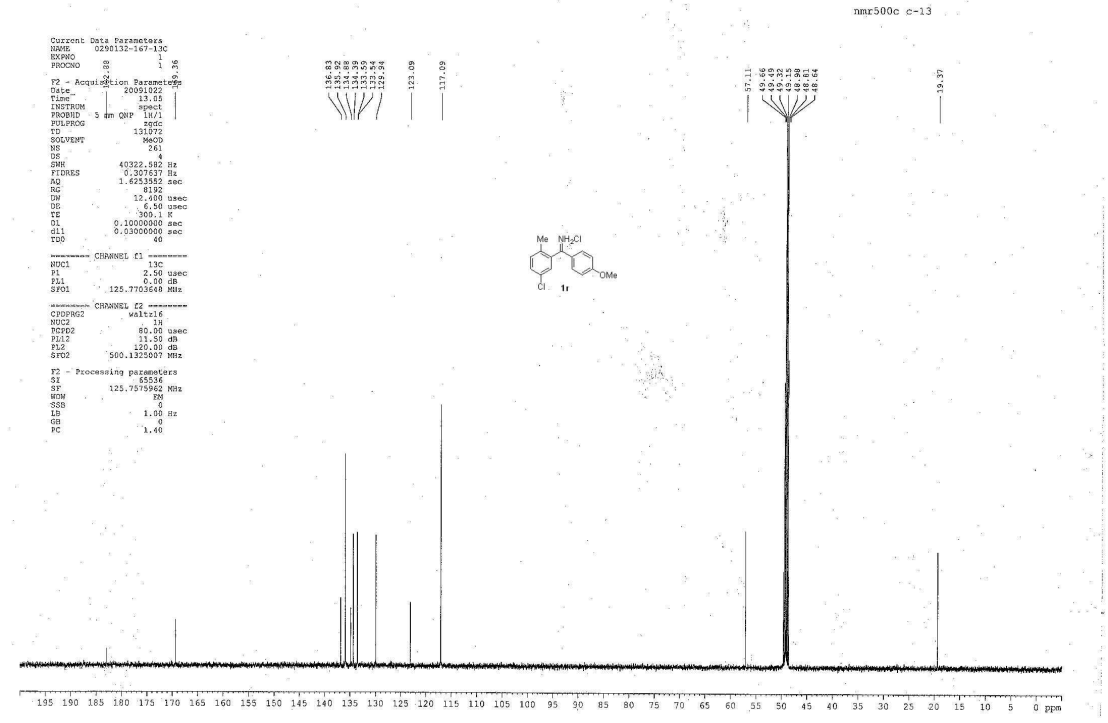

nmr500c h-1
Current Data Parameters
NAME 0290132-163-1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090825
Time 16.53
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 32
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 181
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300132 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.82 7.81 7.80 7.79 7.78 7.78 7.77 7.77 7.76 7.73 7.71 7.55 7.53
4.83
3.31 3.31 3.31 3.30 3.30 3.20
2.52
Cl
NH2Cl
Me
Cl
1p
3.74 0.94 1.93
3.00
ppm


nmr500c c-13
Current Data Parameters
NAME 0290132-163-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090825
Time 16.58
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 204
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 18390.4
DW 12.400 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7575957 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
182.11
151.89
135.35 135.14 133.83 133.55 132.94 132.17 132.05 131.87 128.12
49.66 49.49 49.32 49.15 48.98 48.81 48.64
27.36
22.28
0.12
Cl
NH2Cl
Me
Cl
1p
ppm

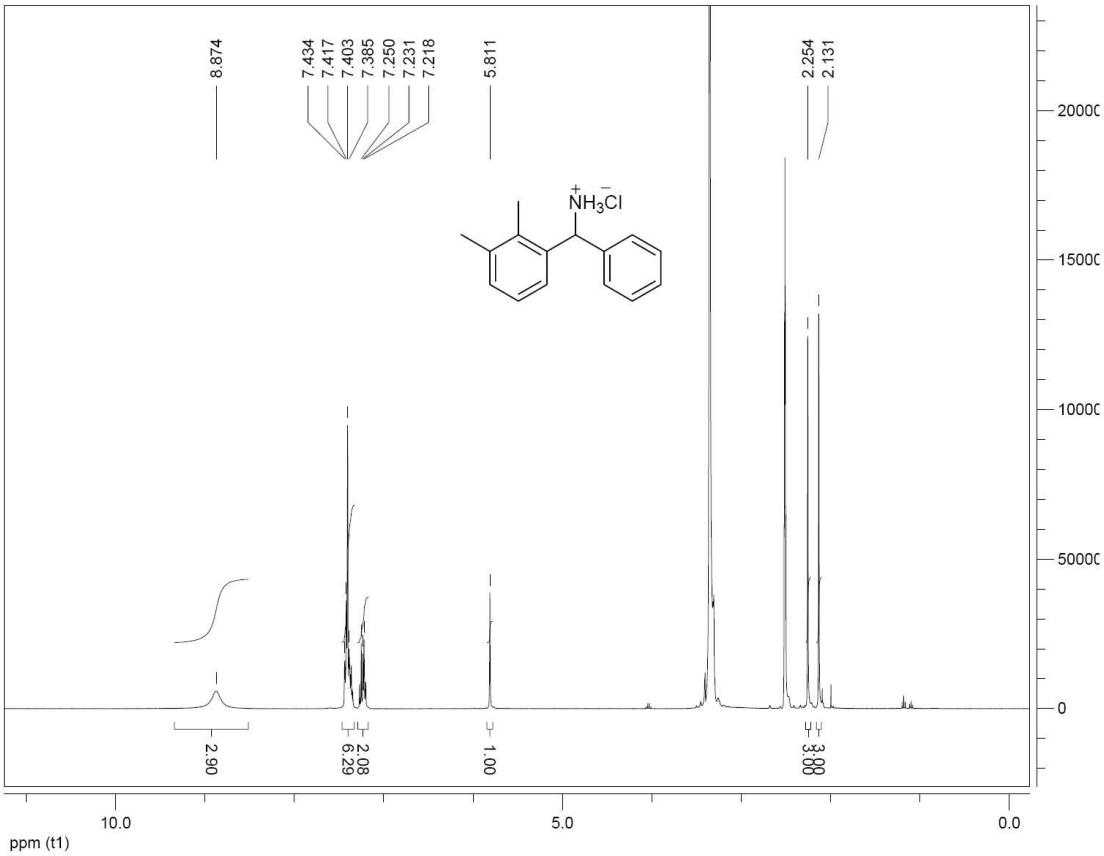

nmr500c h-1
Current Data Parameters
NAME 0290132-157-1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090825
Time 16.16
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 17
DS 4
SWH 13020.833 Hz
FIDRES 0.198682 Hz
AQ 2.5166707 sec
RG 161.3
DW 38.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 12.00 usec
PL1 -4.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300135 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.95 7.94 7.93 7.77 7.75 7.64 7.64 7.63 7.53 7.52
4.93
3.31 3.31 3.30 3.30 3.30 3.20
2.52
1.18
-0.00
Cl NH2Cl Cl Me
1q
0.92 1.93 1.94 1.96
2.06
3.00
ppm

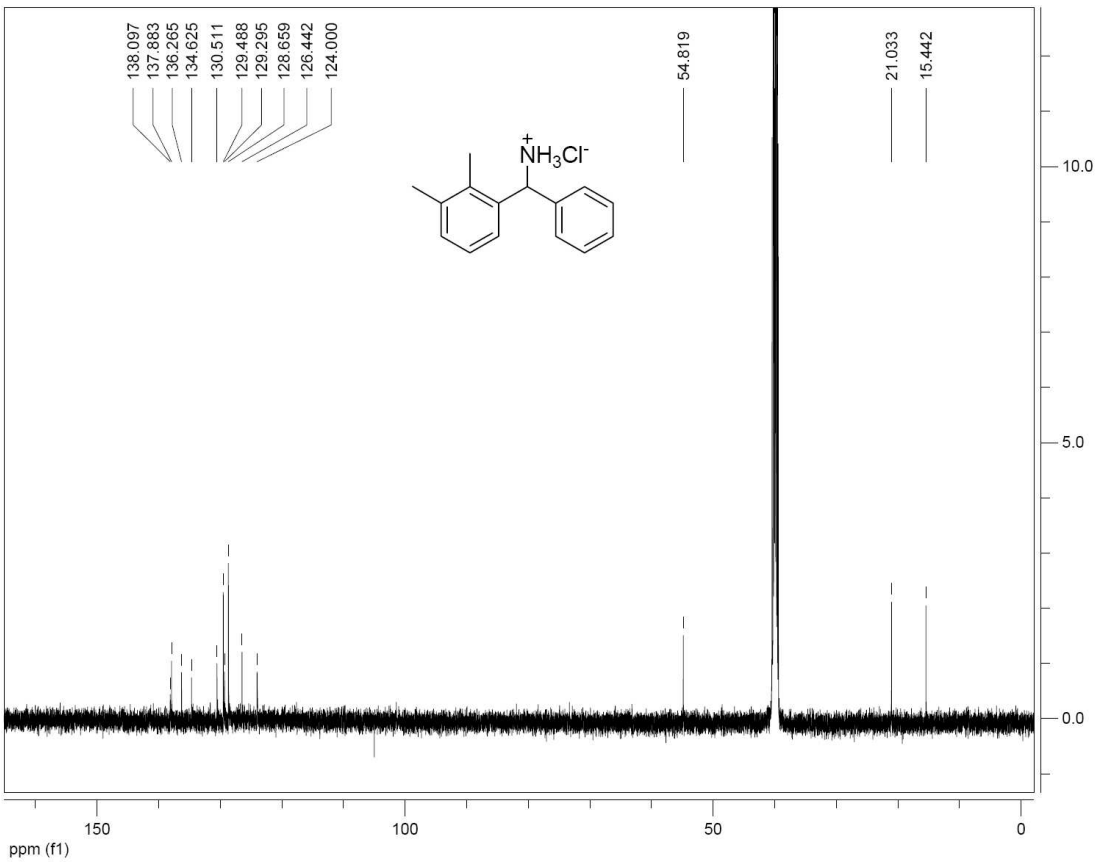

nmr500c c-13
Current Data Parameters
NAME 0290132-157-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090825
Time 16.19
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgdc
TD 131072
SOLVENT MeOD
NS 222
DS 4
SWH 40322.582 Hz
FIDRES 0.307637 Hz
AQ 1.6253552 sec
RG 14596.5
DW 12.400 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
d11 0.03000000 sec
TD0 40
CHANNEL f1
NUC1 13C
P1 2.50 usec
PL1 0.00 dB
SFO1 125.7703648 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 11.50 dB
PL2 120.00 dB
SFO2 500.1325007 MHz
F2 - Processing parameters
SI 65536
SF 125.7575968 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
182.45
151.57
135.79 135.70 134.78 132.78 132.12 131.52 130.46 130.20 128.36
49.84 49.66 49.49 49.32 49.15 48.98 48.81 48.64
27.37
22.26
0.12
Cl NH2Cl Cl Me
1q
ppm



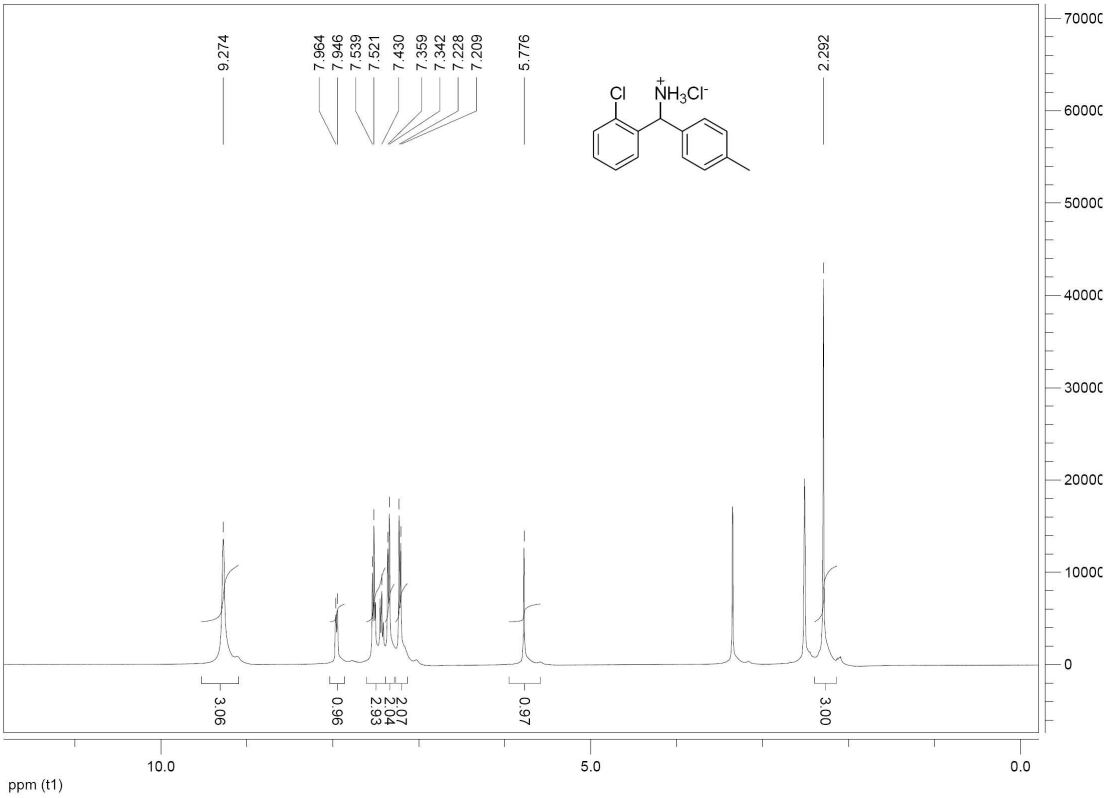


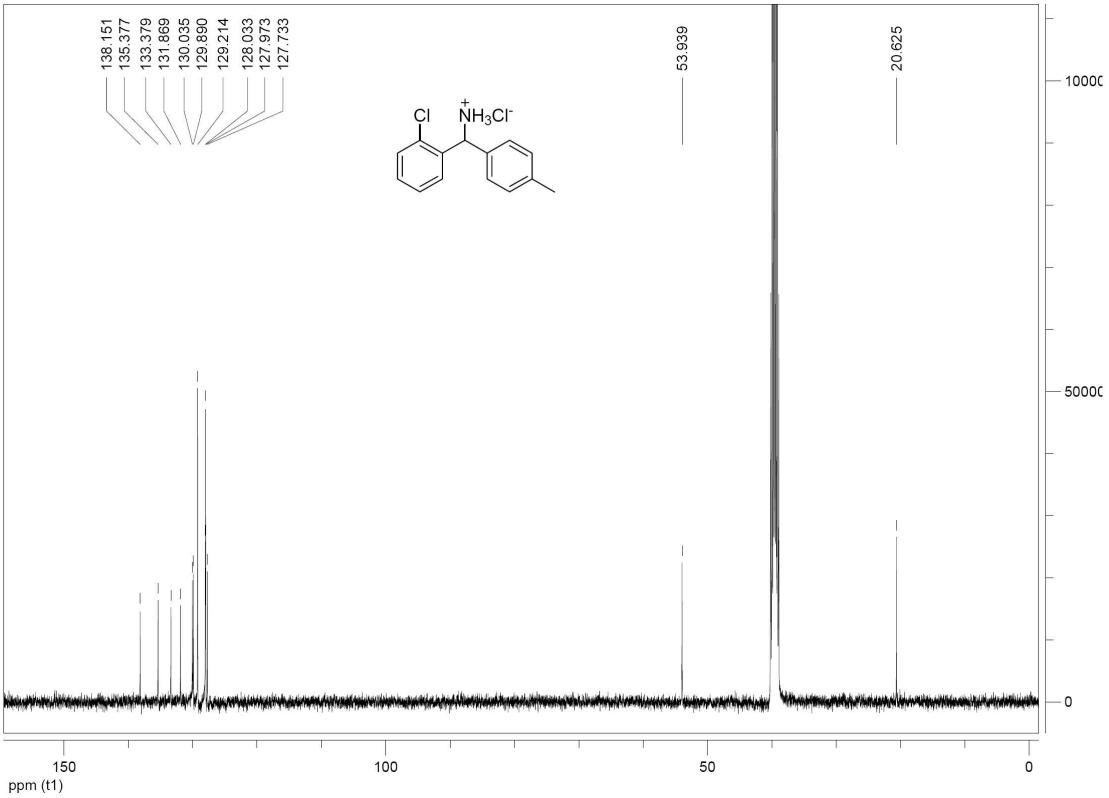
(2,3-dimethylphenyl)(phenyl)methanaminium chloride (2j)


8.874
7.434
7.417
7.403
7.385
7.250
7.231
7.218
5.811
2.254
2.131
NH3Cl
2.90
6.29
2.08
1.00
3.00
3.00
20000
15000
10000
50000
0
10.0
5.0
0.0
ppm (t1)

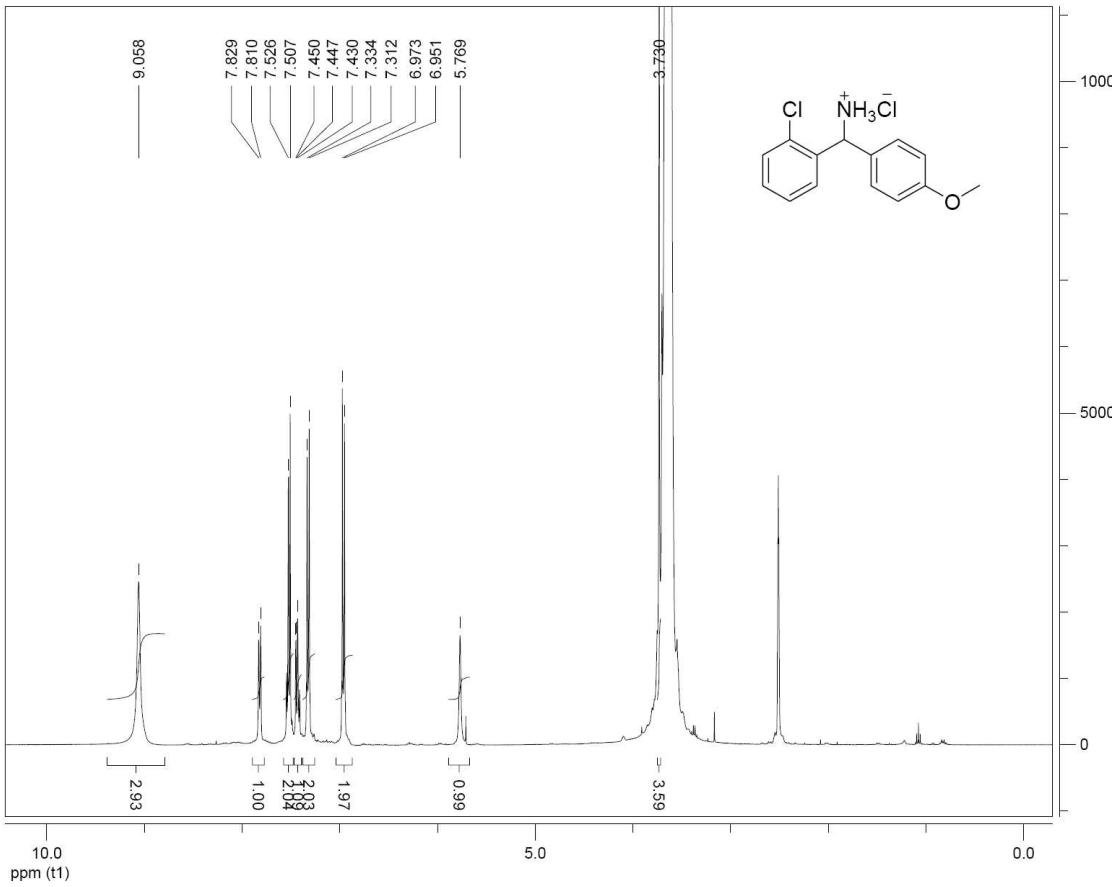

138.097
137.883
136.265
134.625
130.511
129.488
129.295
128.659
126.442
124.000
54.819
21.033
15.442
NH3Cl
10.0
5.0
0.0
150
100
50
0
ppm (f1)

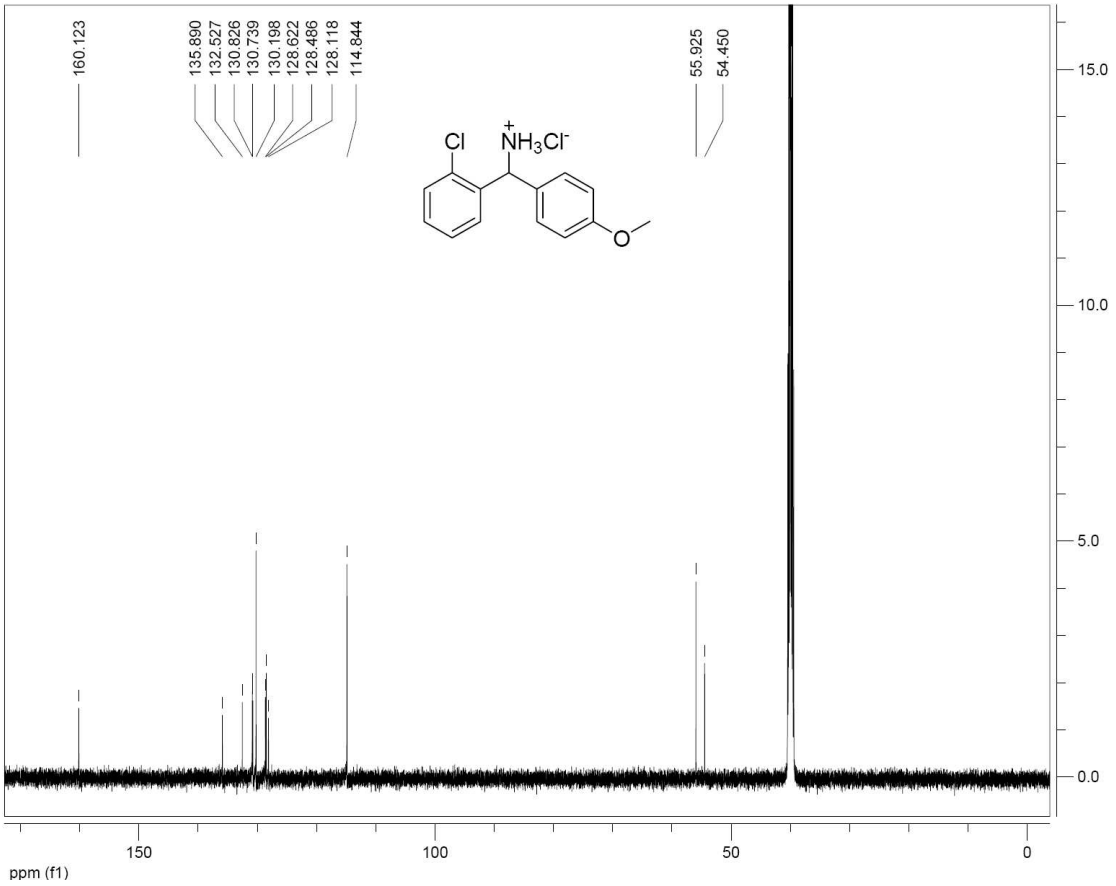
(2-chlorophenyl)(p-tolyl)methanaminium chloride (2k)



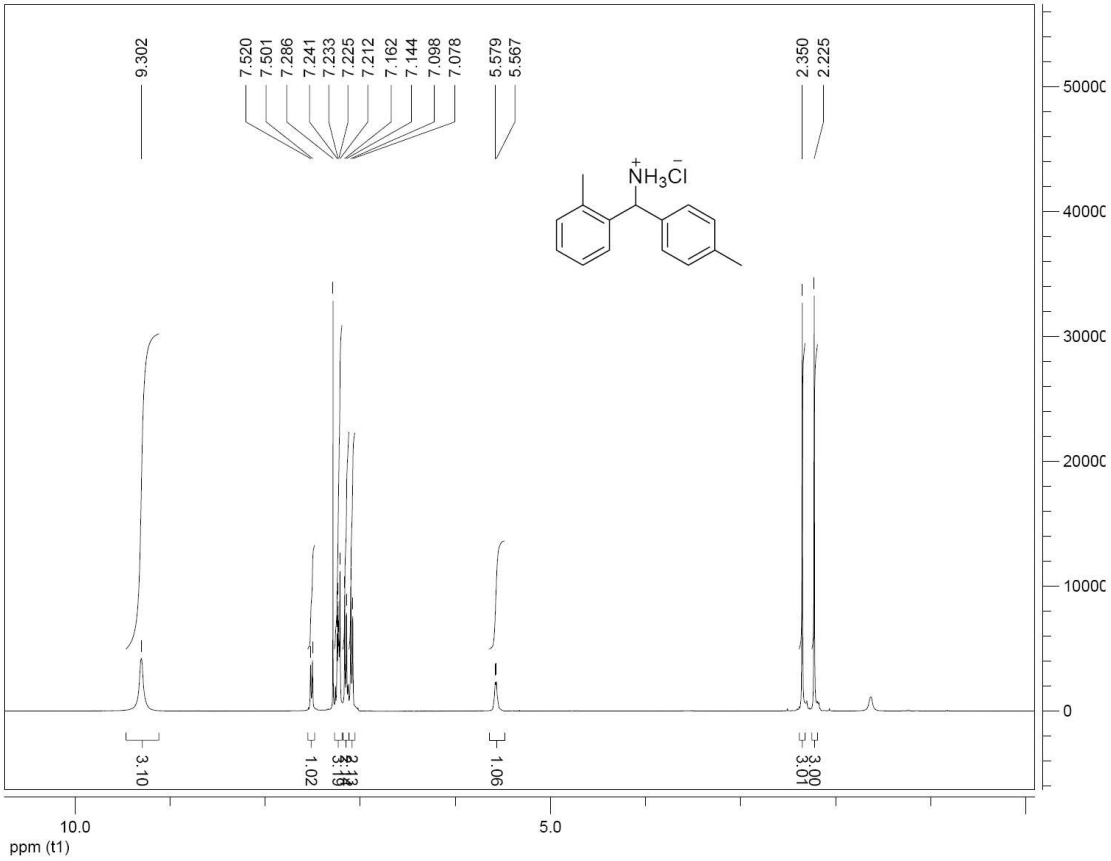


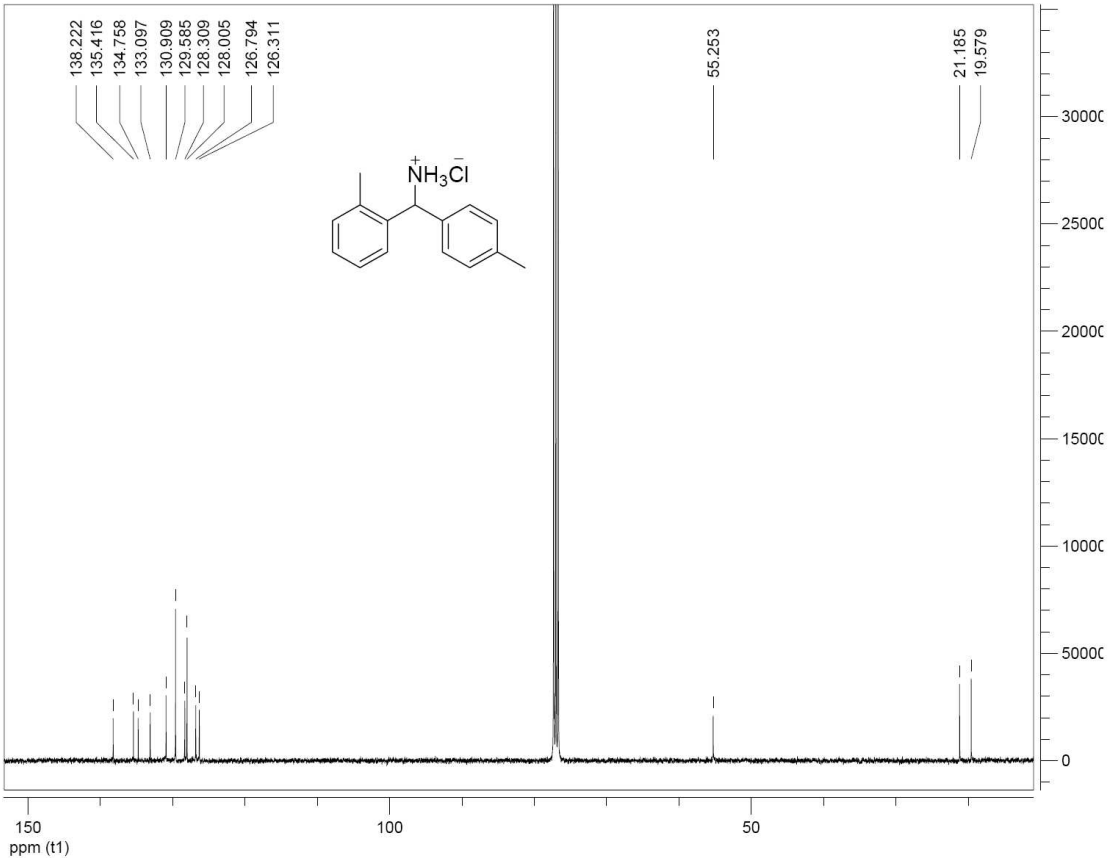
(2-chlorophenyl)(4-methoxyphenyl)methanaminium chloride (2l)



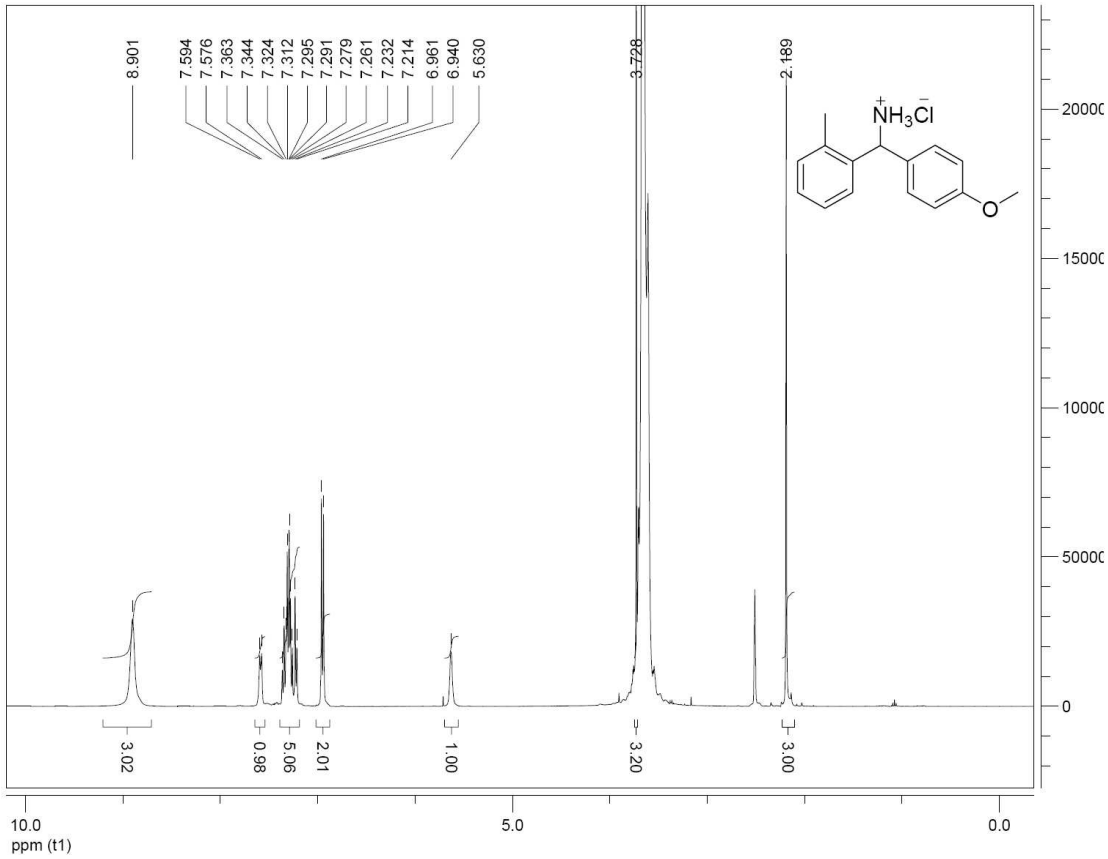


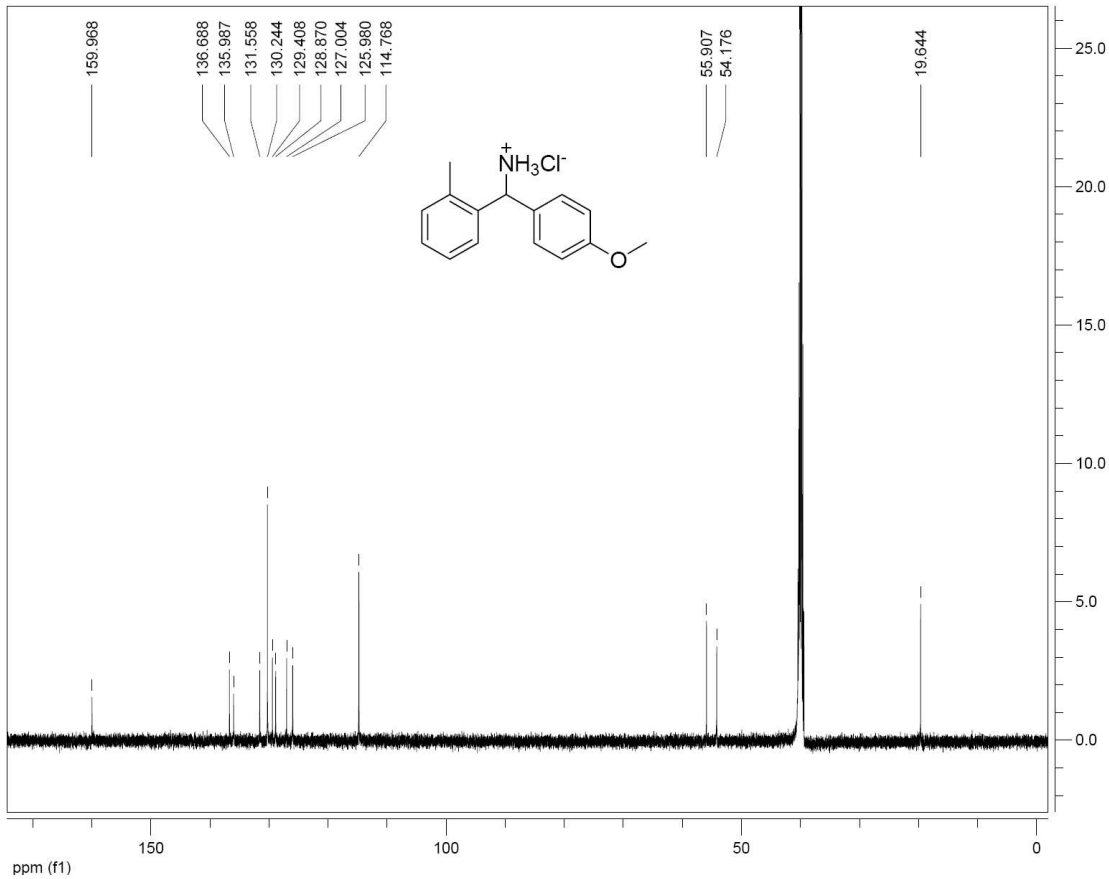
o-tolyl(p-tolyl)methanaminium chloride (2m)



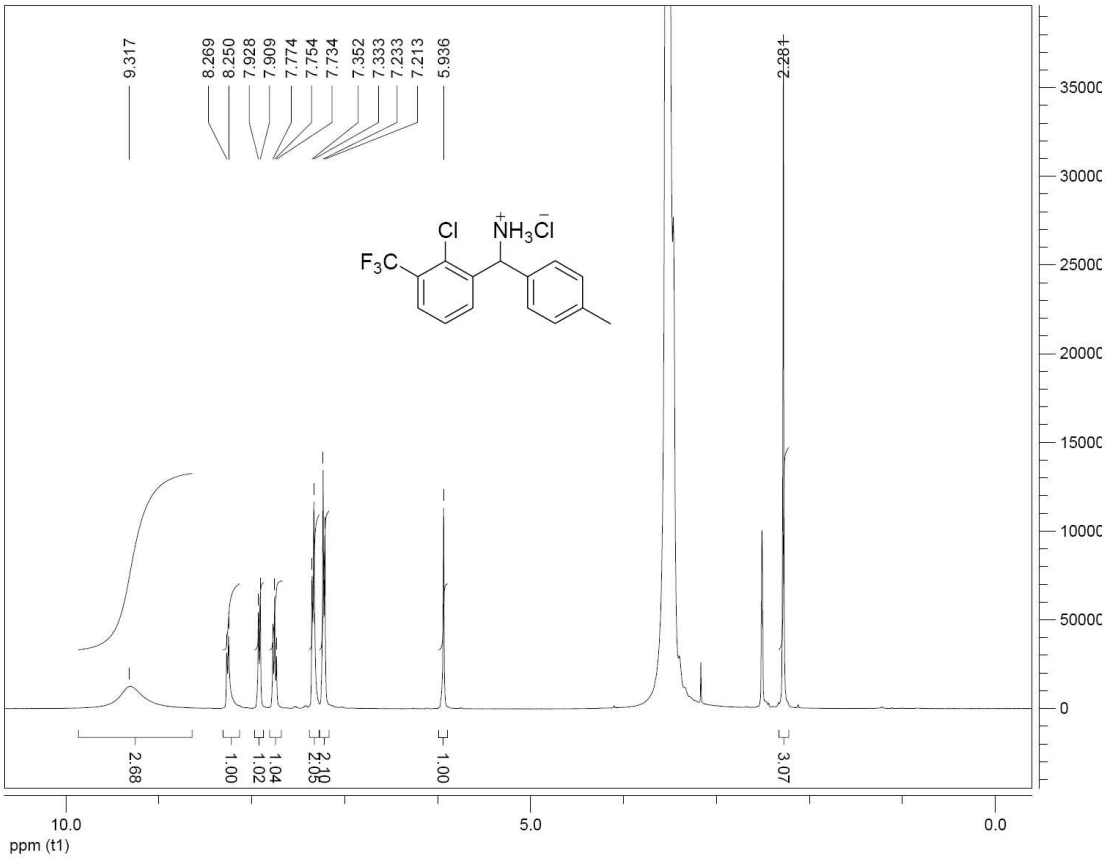


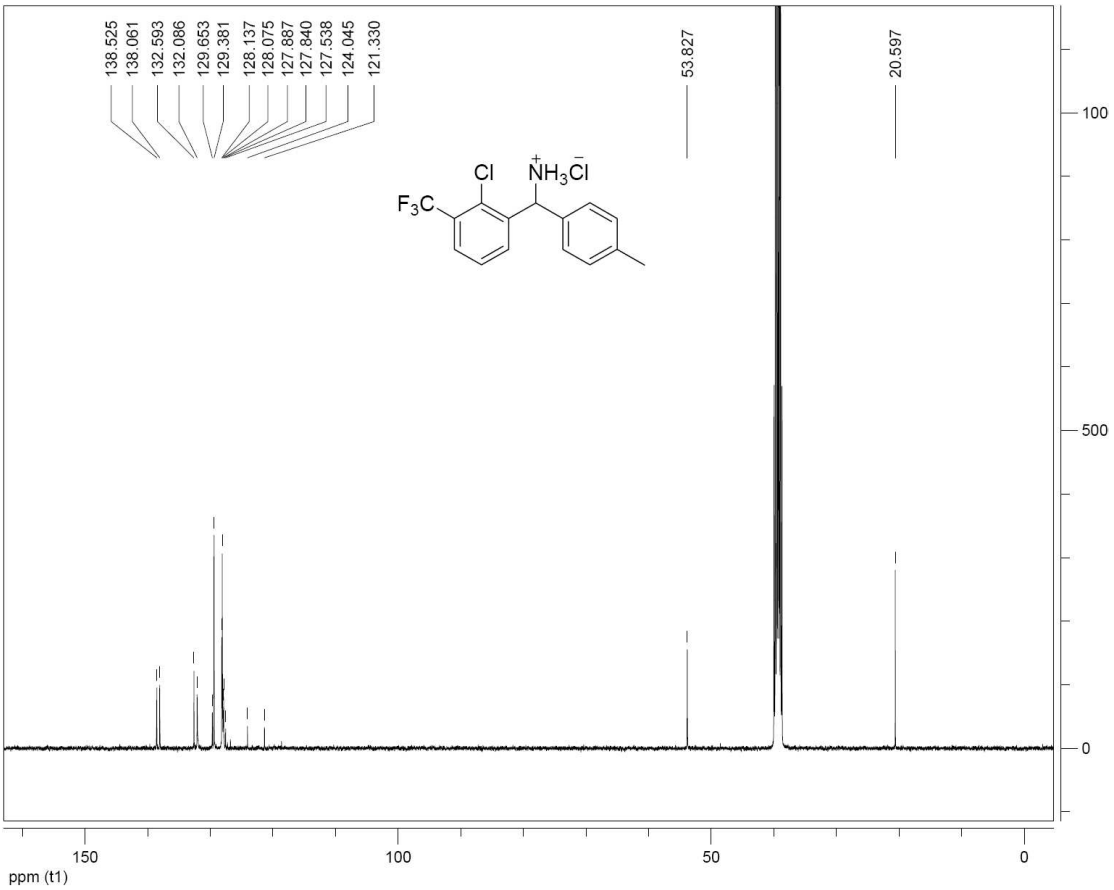
(4-methoxyphenyl)(o-tolyl)methanaminium chloride (2n)



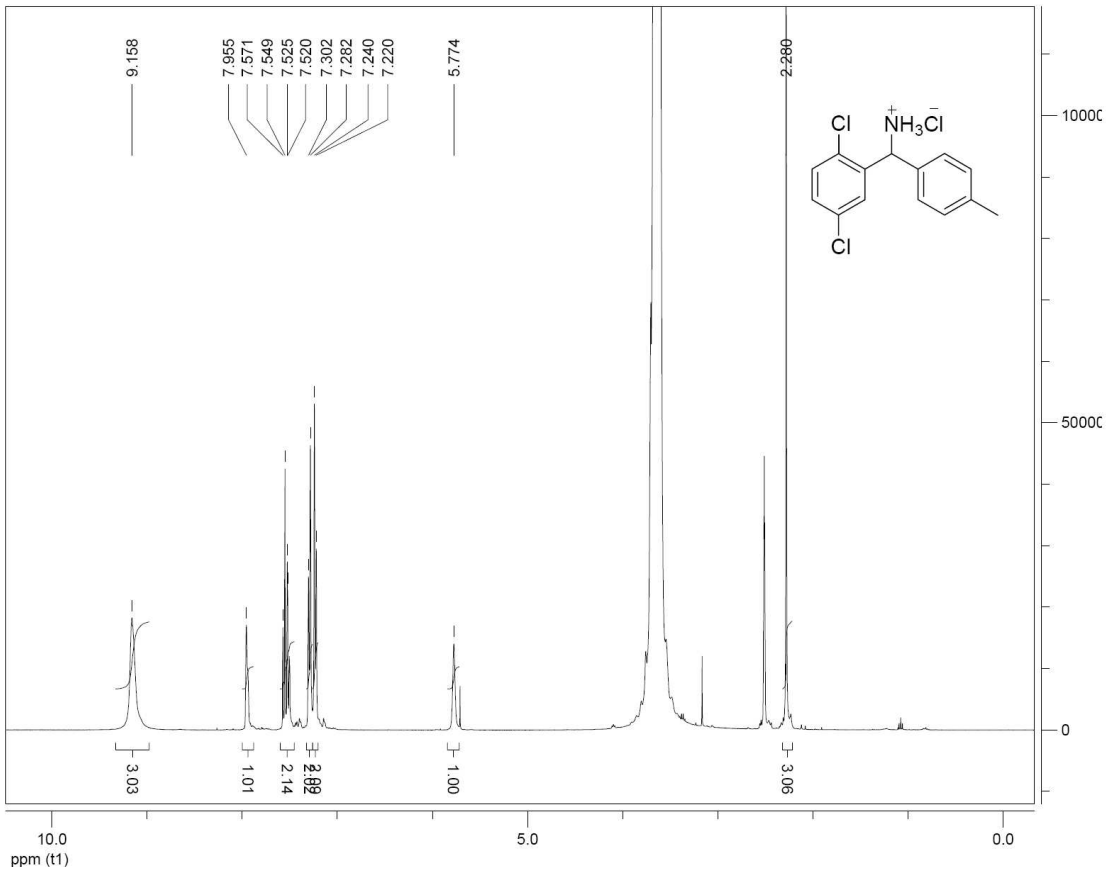


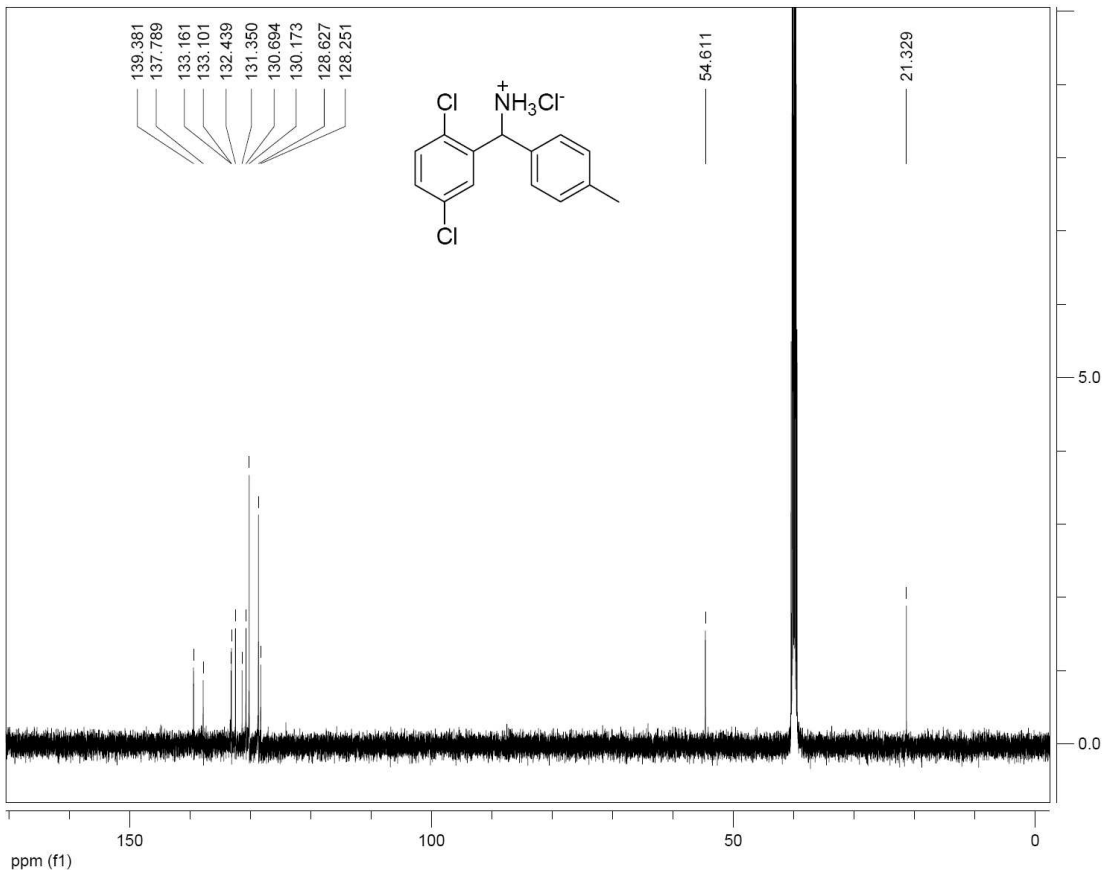
(2-chloro-3-(trifluoromethyl)phenyl)(p-tolyl)methanaminium chloride (2o)



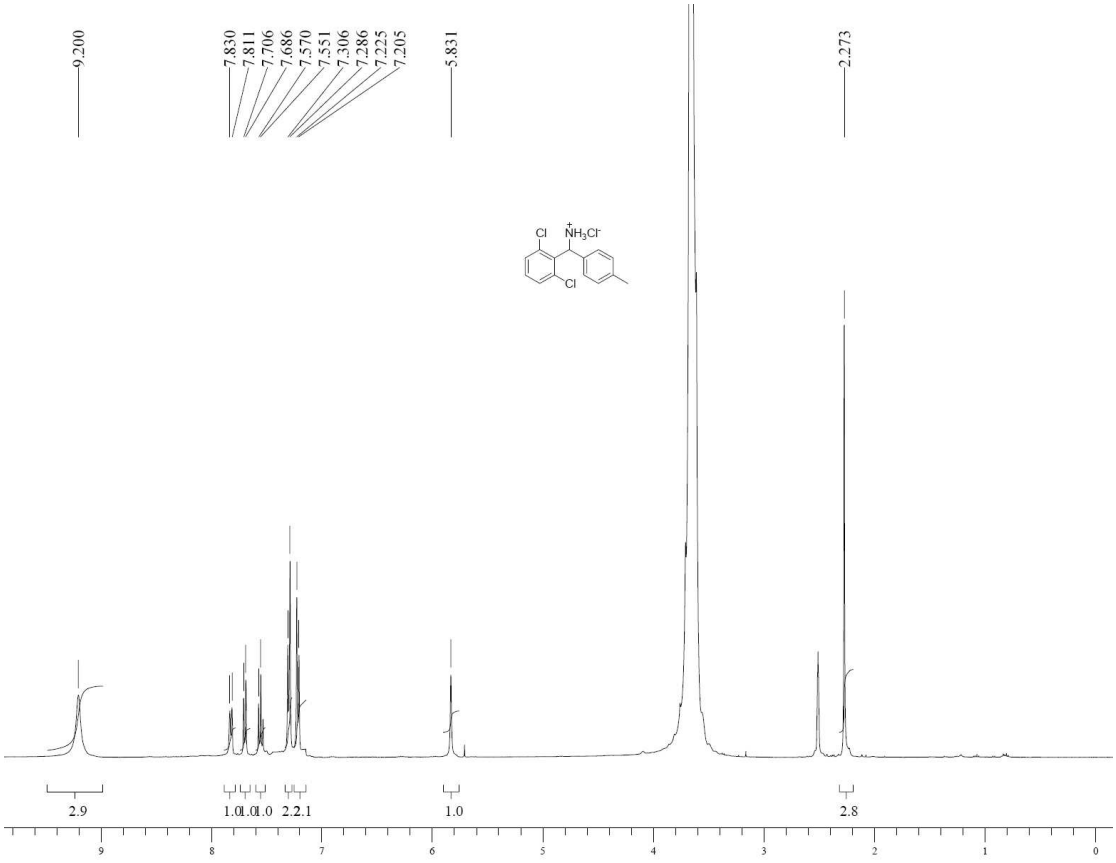


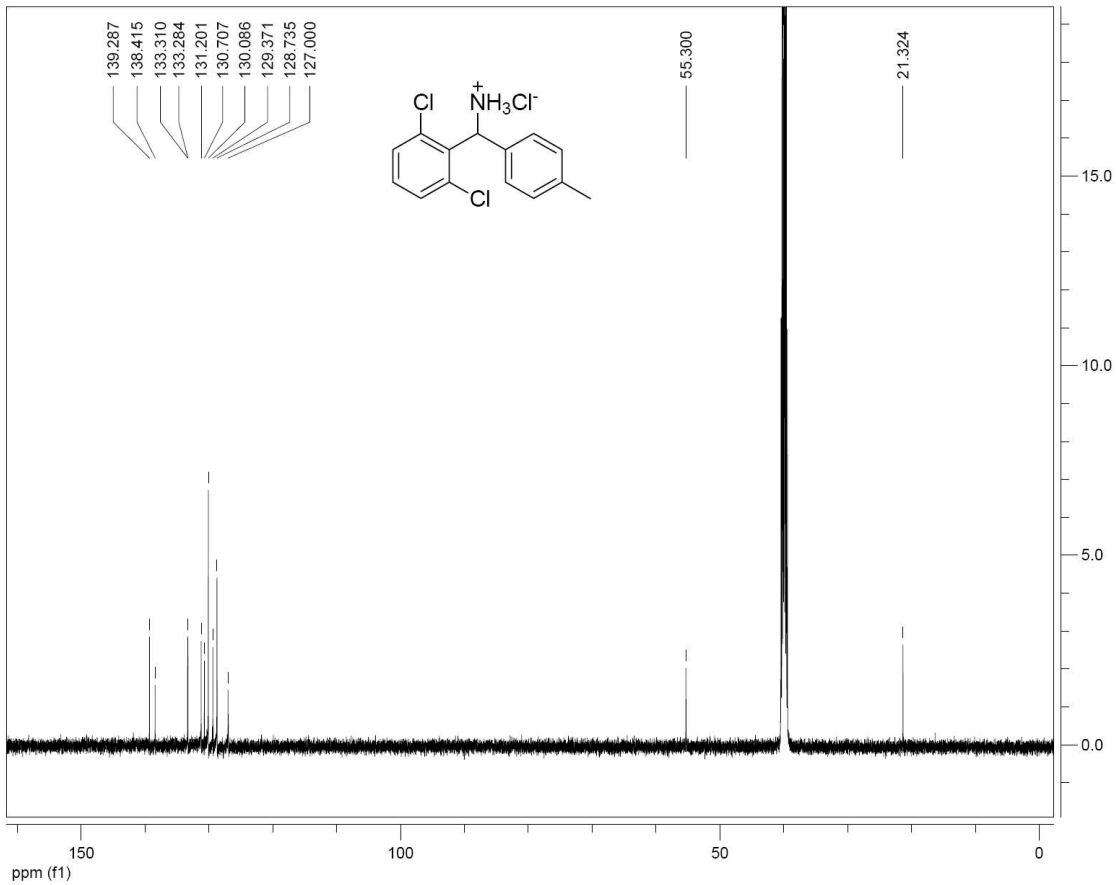
(2,5-dichlorophenyl)(p-tolyl)methanaminium chloride (2p)



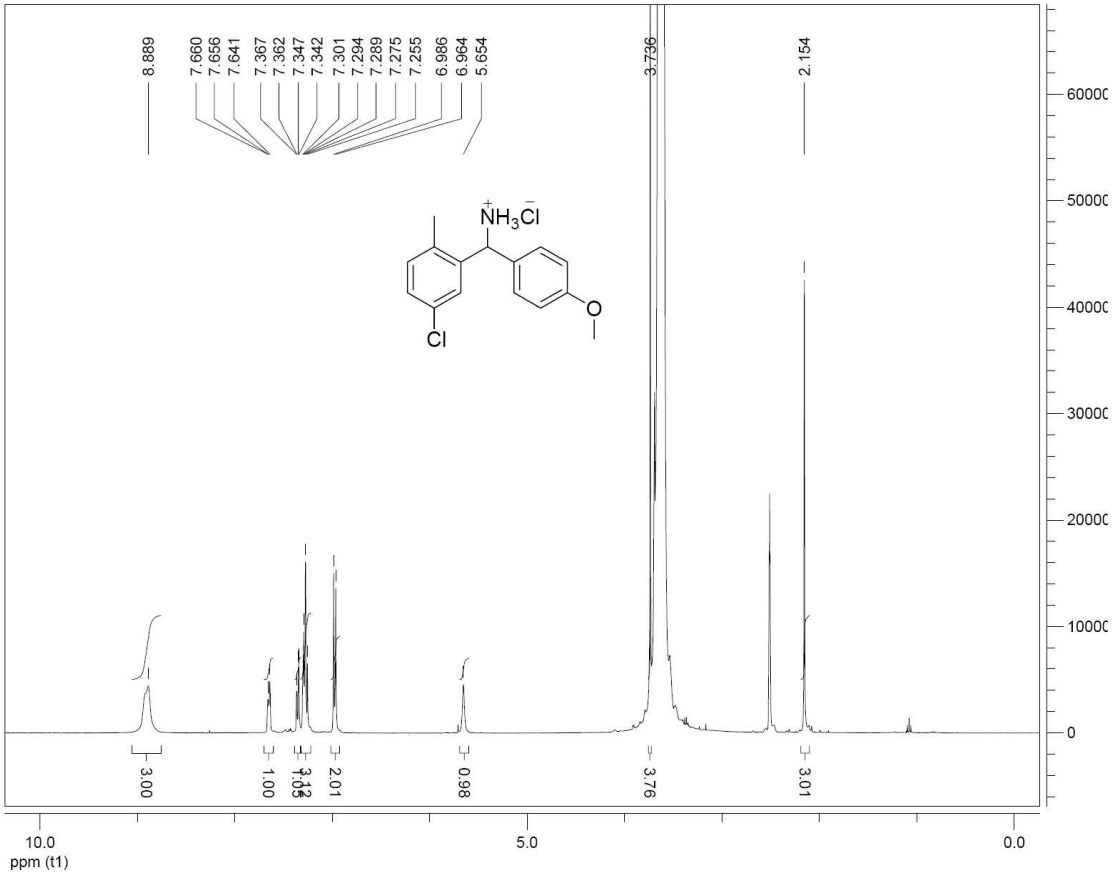


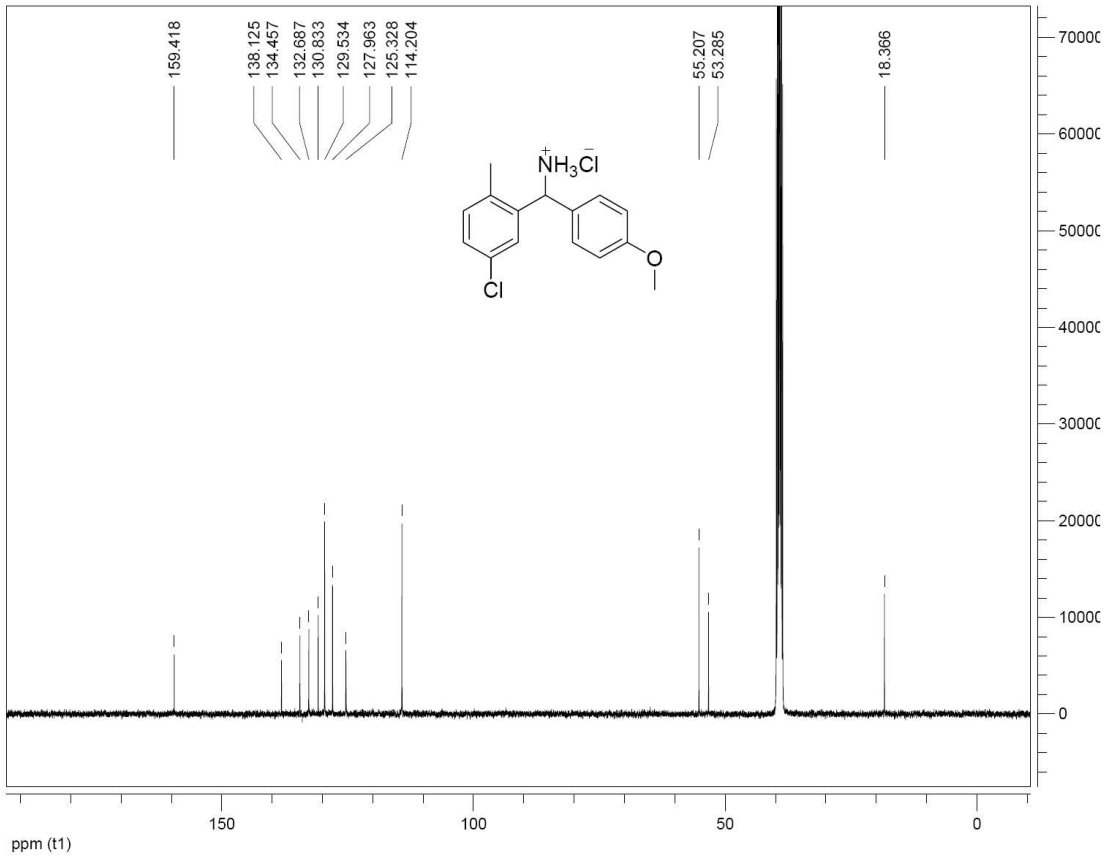
(2,6-dichlorophenyl)(p-tolyl)methanaminium chloride (2q)



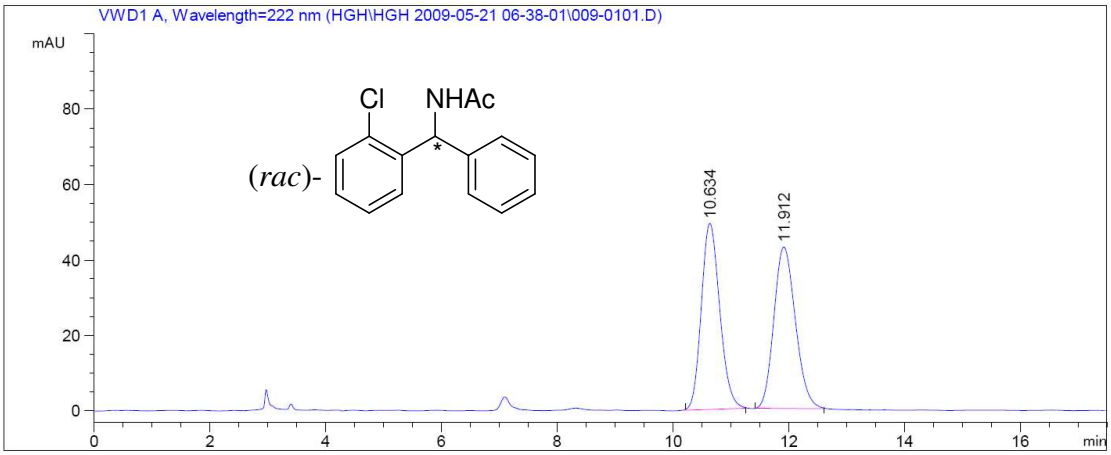


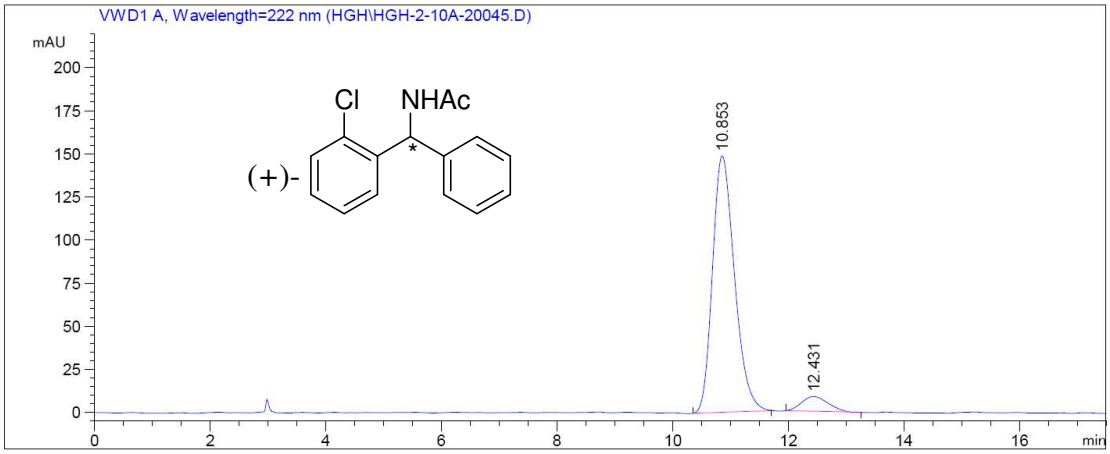
(5-chloro-2-methylphenyl)(4-methoxyphenyl)methanaminium chloride (2r)



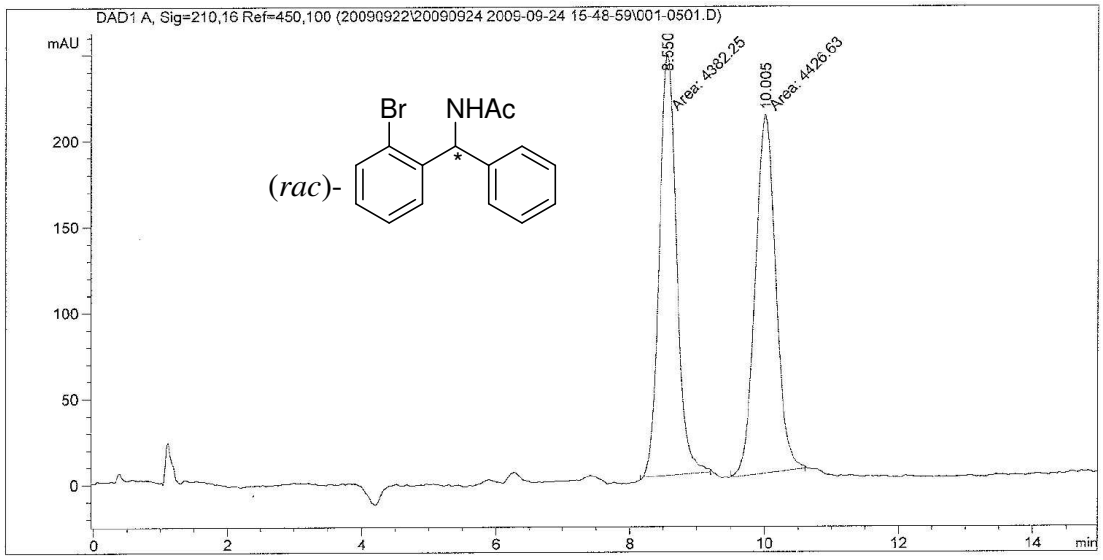


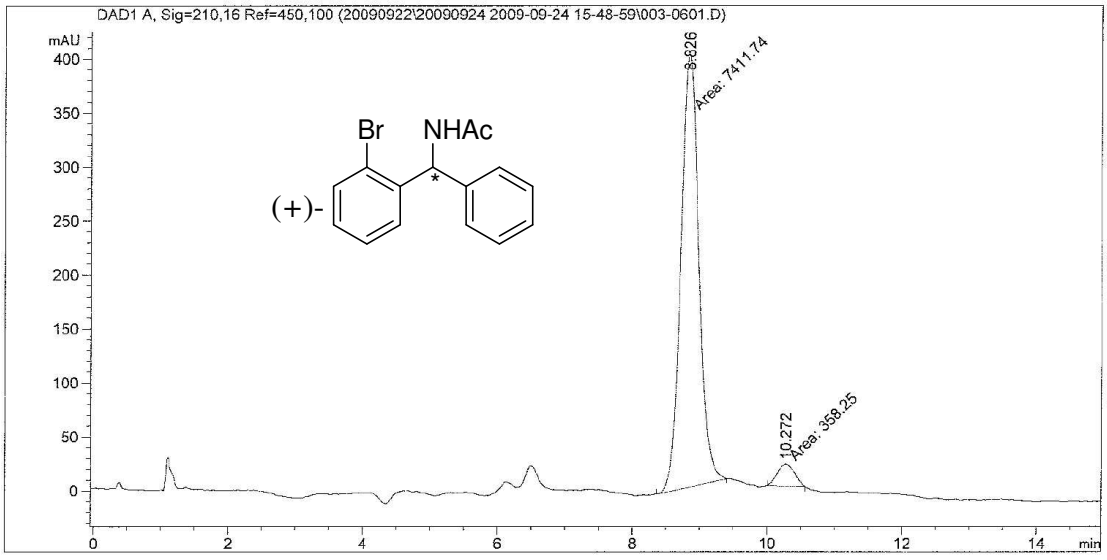
(E) GC / SFC Chromatograms for Hydrogenation Products





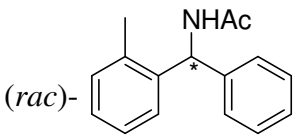
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.853	BB	0.4082	3947.02441	148.91452	93.4167
2	12.431	BB	0.4957	278.15778	8.65831	6.5833
Totals :				4225.18219	157.57283	





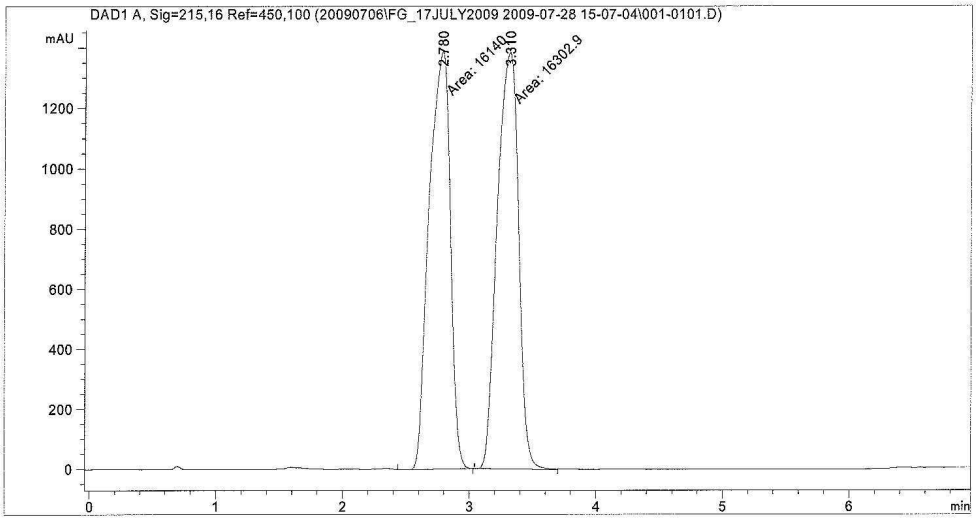
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.826	MM	0.3077	7411.74219	401.46710	95.3893
2	10.272	MM	0.2944	358.25040	20.28088	4.6107
Totals :				7769.99258	421.74798	

(*rac*)-



Data File C:\HPCHEM\1\DATA\20090706\FG_17JULY2009 2009-07-28 15-07-04\001-0101.D
Sample Name: 2-methylphenyl acetamide

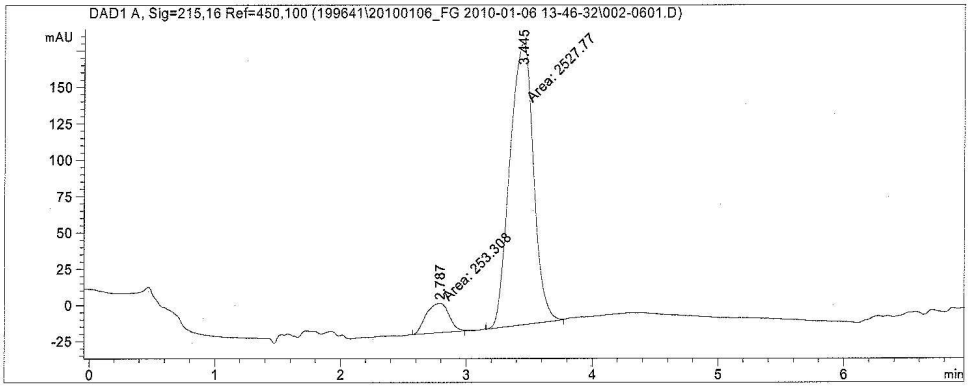
```
==========================================================================
Acq. Operator   :                                  Seq. Line :   1
Acq. Instrument : Instrument 1                      Location : Vial 1
Injection Date  : 7/28/2009 3:13:07 PM                  Inj :   1
                                                  Inj Volume : 20 µl
Acq. Method     : C:\HPCHEM\1\DATA\20090706\FG_17JULY2009 2009-07-28 15-07-04\NANCY.M
Last changed    : 7/21/2009 12:04:10 PM
Analysis Method : C:\HPCHEM\1\DATA\20090706\FG_17JULY2009 2009-08-19 15-08-39\_ADH_
                  MEOH_GRAD.M
Last changed    : 9/11/2008 10:41:25 AM by Belyk
Method Info     : AD-H_MeOH_grad:  4% MeOH/CO2 for 4 min, then ramp at 4%/min to 40%
                  MeOH. hold 2 min, 2 mL/min, 200 bar, 35C, 215 nm, 15 min total run
                  time.
```




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

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


Signal 1: DAD1 A, Sig=215,16 Ref=450,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   2.780 MM    0.1938 1.61400e4  1387.90063  49.7490
   2   3.310 MM    0.1964 1.63029e4  1383.54932  50.2510

Totals :                  3.24428e4  2771.44995
```

Data File C:\HPCHEM\1\DATA\199641\20100106_FG 2010-01-06 13-46-32\002-0601.D
Sample Name: 0297413-0099 chiral

Acq. Operator	:	Seq. Line	: 6
Acq. Instrument	: Instrument 1	Location	: Vial 2
Injection Date	: 1/6/2010 2:33:23 PM	Inj	: 1
		Inj Volume	: 20 µl
Acq. Method	: C:\HPCHEM\1\DATA\199641\20100106_FG 2010-01-06 13-46-32\NANCY.M		
Last changed	: 7/21/2009 12:04:10 PM		
Analysis Method	: C:\HPCHEM\1\METHODS\NANCY.M		
Last changed	: 1/6/2010 4:05:26 PM (modified after loading)		
Method Info	: AD-H_MeOH_grad: 4% MeOH/CO2 for 4 min, then ramp at 4%/min to 40% MeOH. hold 2 min, 2 mL/min, 200 bar, 35C, 215 nm, 15 min total run time.		



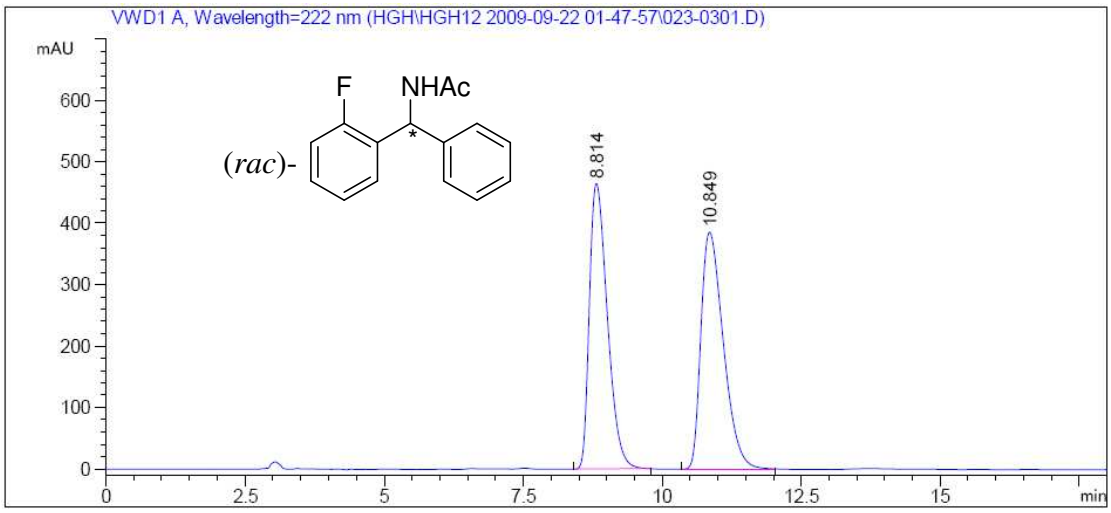
Area Percent Report

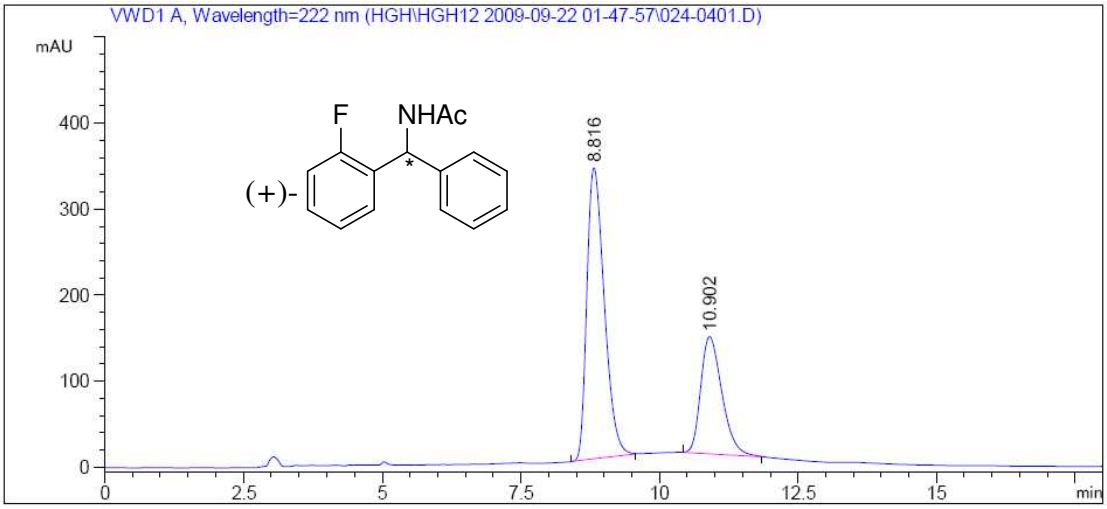
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=215,16 Ref=450,100

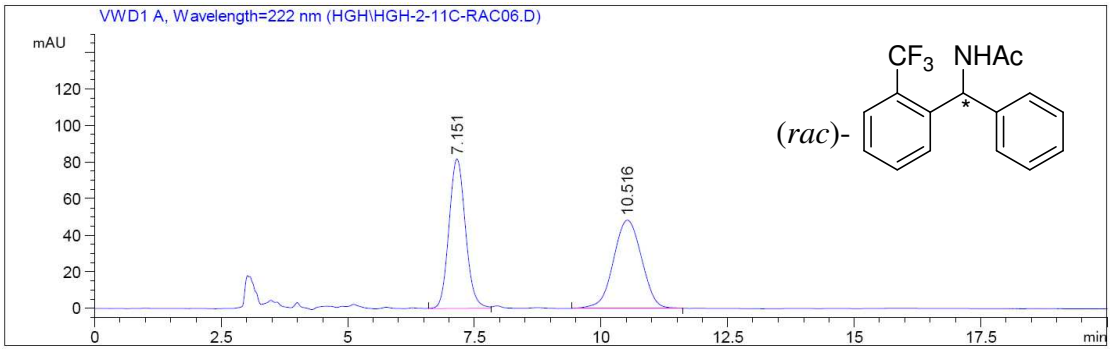
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.787	MM	0.2102	253.30818	20.08652	9.1083
2	3.445	MM	0.2179	2527.76831	193.34416	90.8917
Totals :				2781.07649	213.43069	

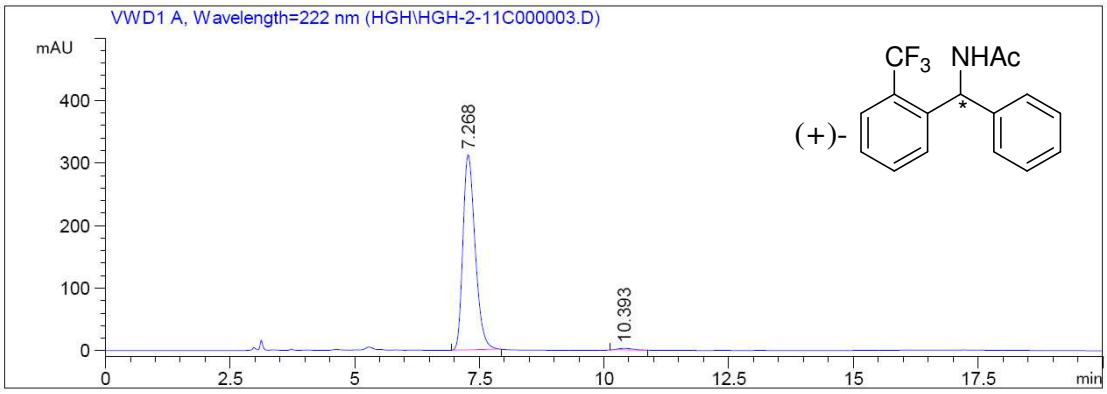
*** End of Report ***



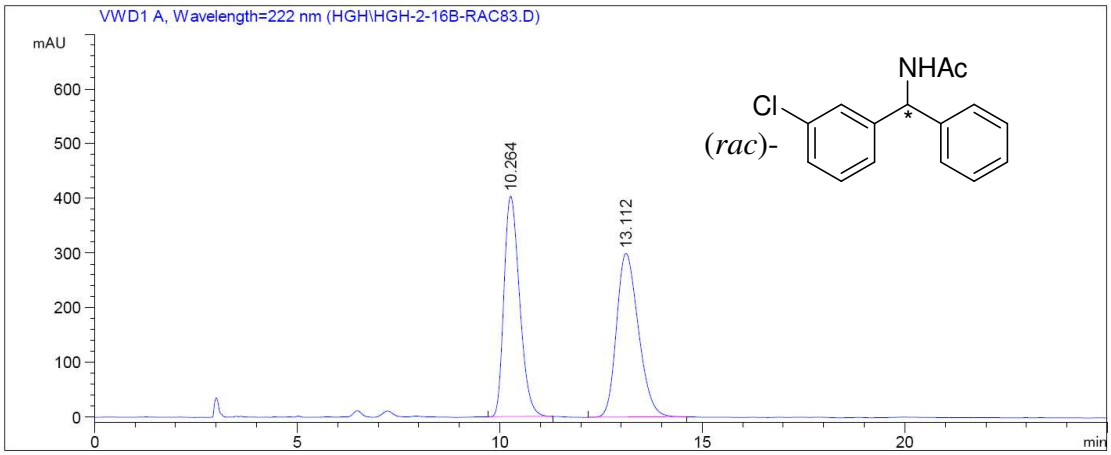


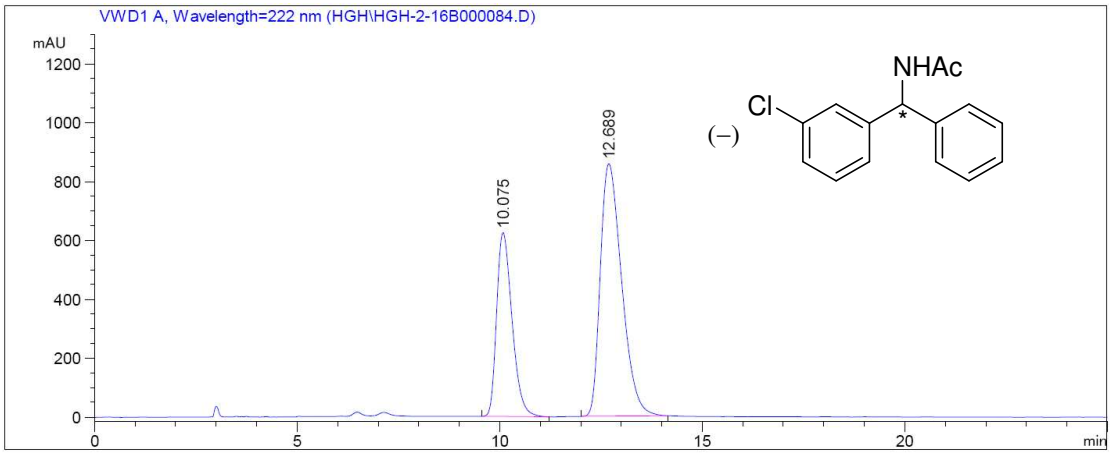
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.816	BB	0.3395	7395.63135	338.24771	67.0702
2	10.902	BB	0.4124	3631.06909	136.12071	32.9298
Totals :				1.10267e4	474.36842	



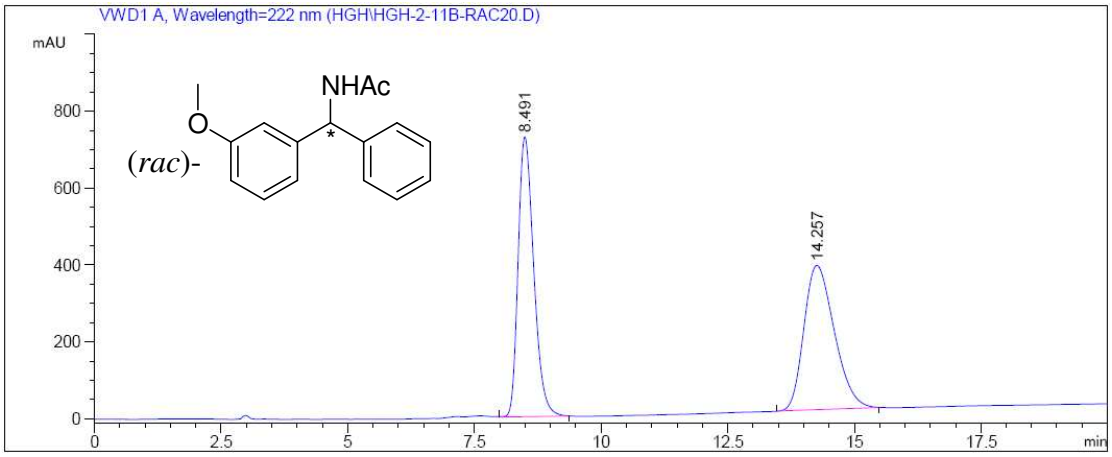


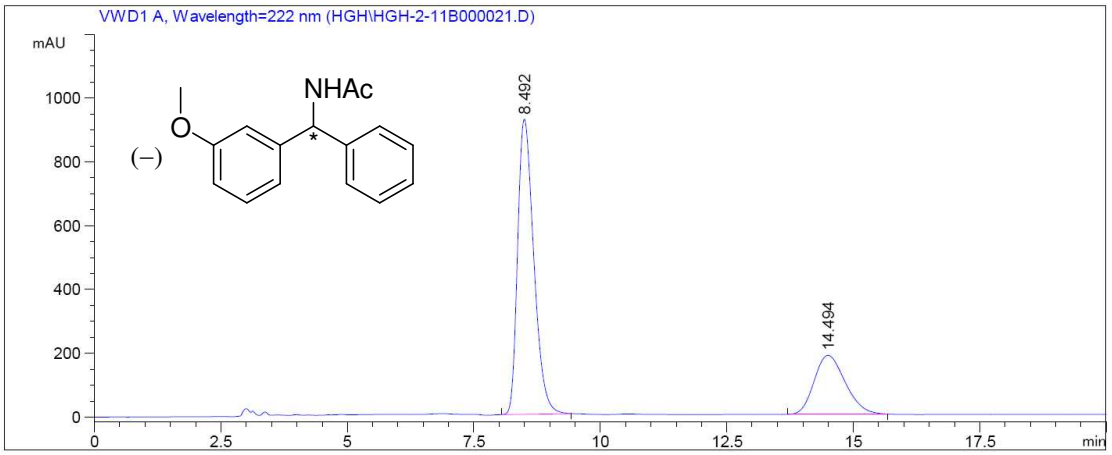
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.268	BB	0.2644	5330.98779	312.17780	98.8497
2	10.393	BB	0.2665	62.03613	2.74605	1.1503
Totals :				5393.02393	314.92385	



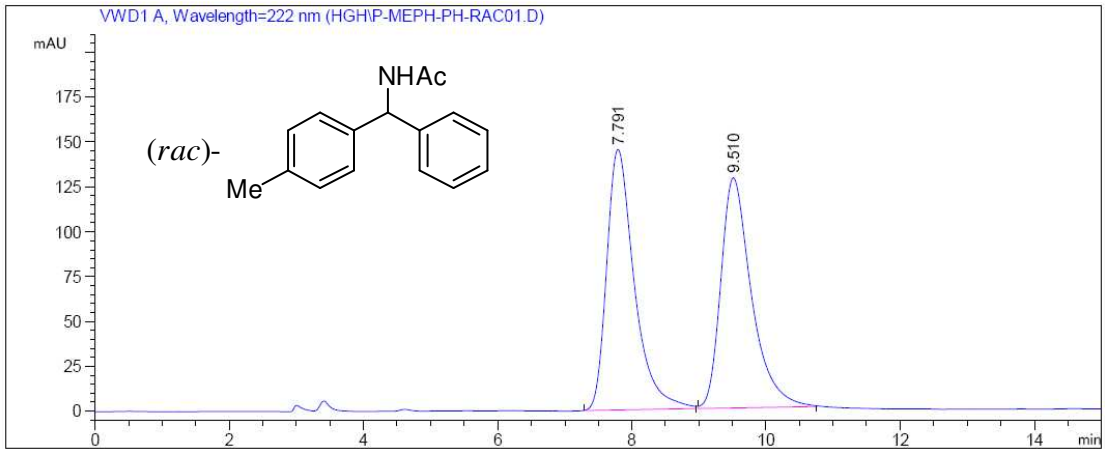


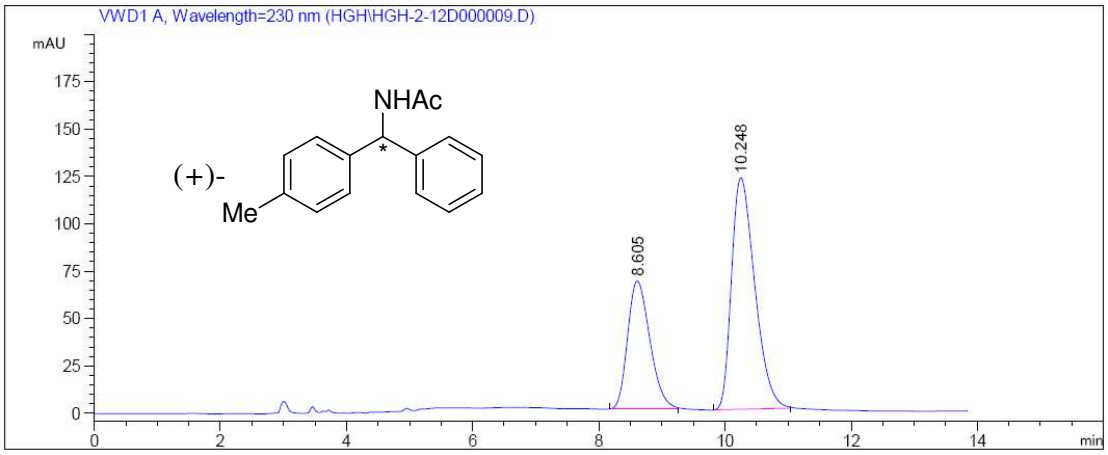
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.492	BB	0.3399	2.01932e4	922.22784	72.9223
2	14.494	BB	0.6420	7498.18652	180.46710	27.0777
Totals :				2.76914e4	1102.69495	



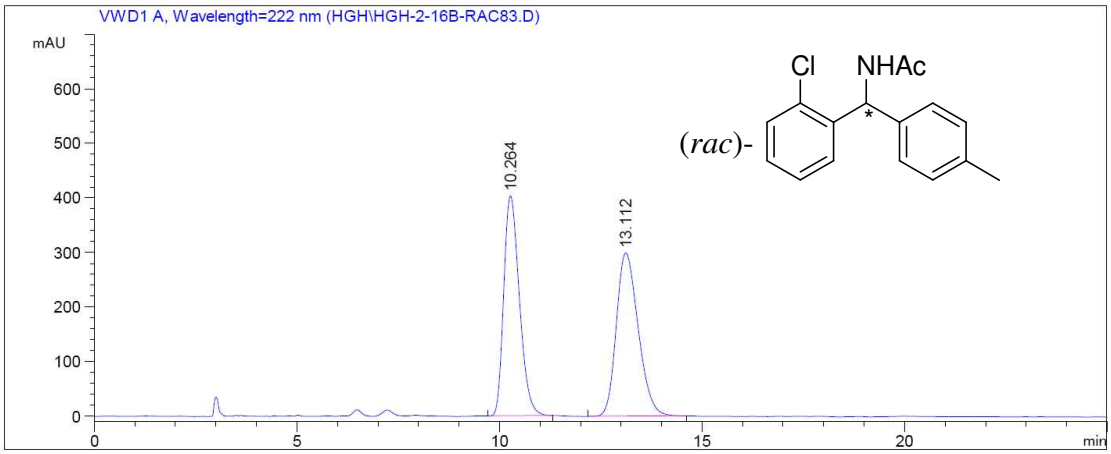


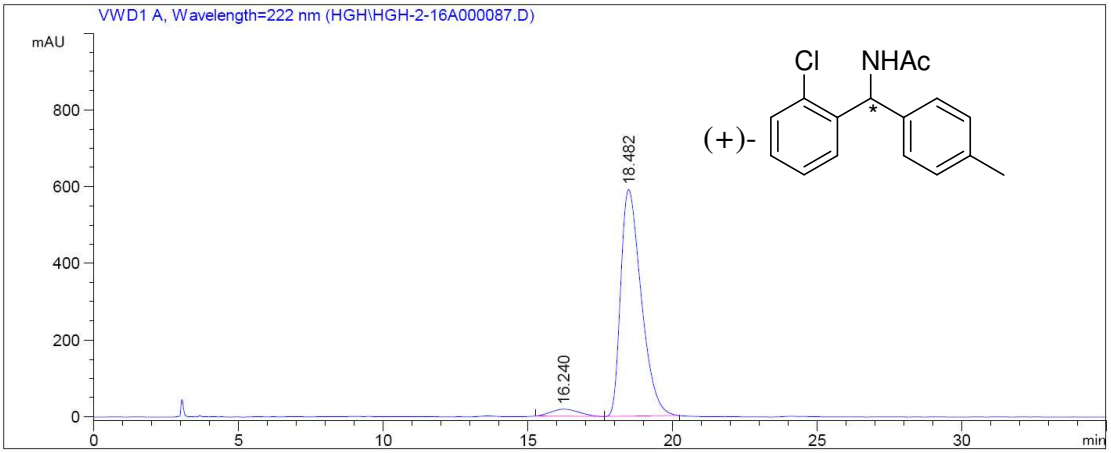
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.492	BB	0.3399	2.01932e4	922.22784	72.9223
2	14.494	BB	0.6420	7498.18652	180.46710	27.0777
Totals :				2.76914e4	1102.69495	



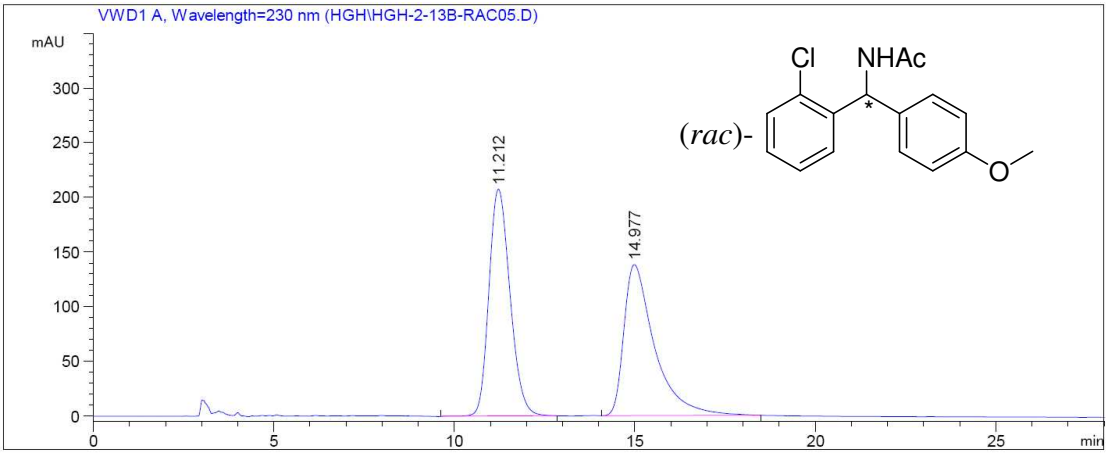


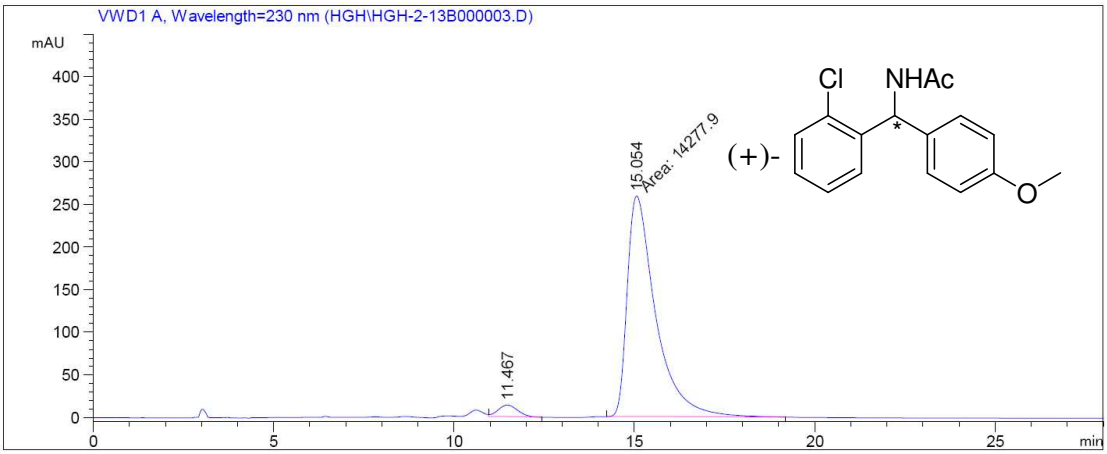
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.605	BB	0.3838	1654.67761	67.44470	34.5804
2	10.248	BB	0.3996	3130.33569	122.09138	65.4196
Totals :				4785.01331	189.53609	



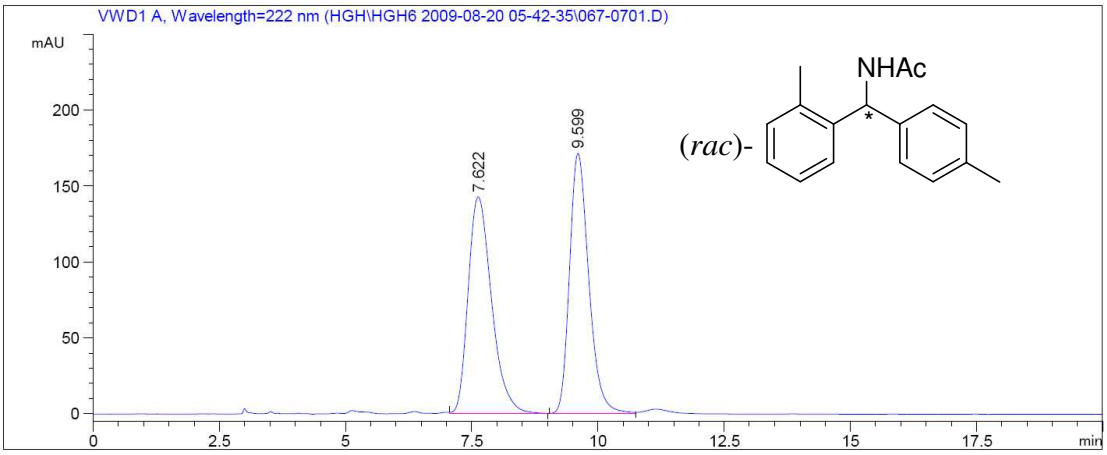


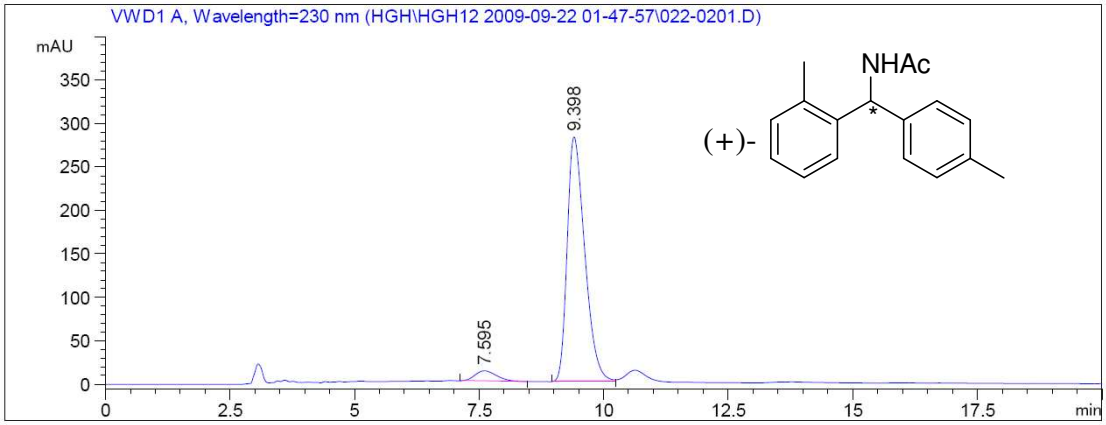
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.240	BV	0.8119	1272.54065	18.65311	4.1679
2	18.482	VB	0.7530	2.92591e4	591.09137	95.8321
Totals :				3.05317e4	609.74448	



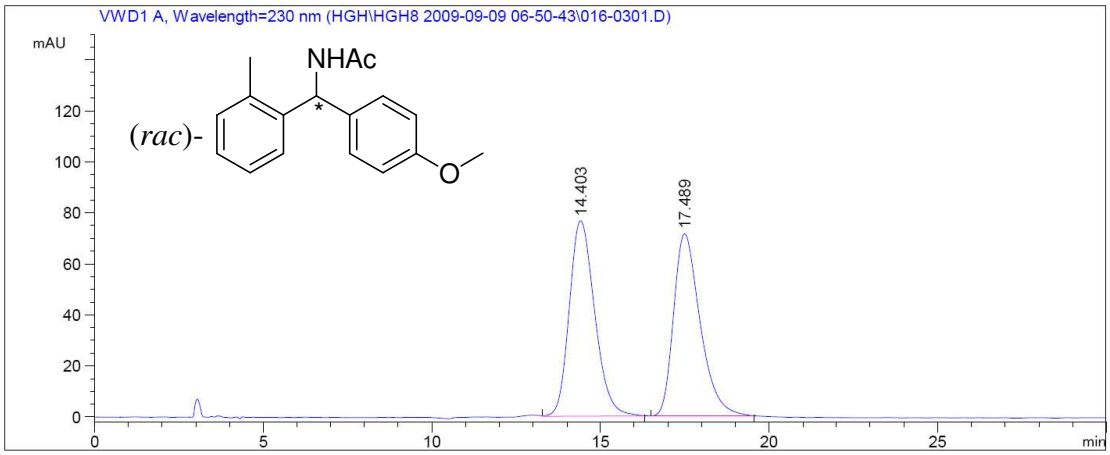


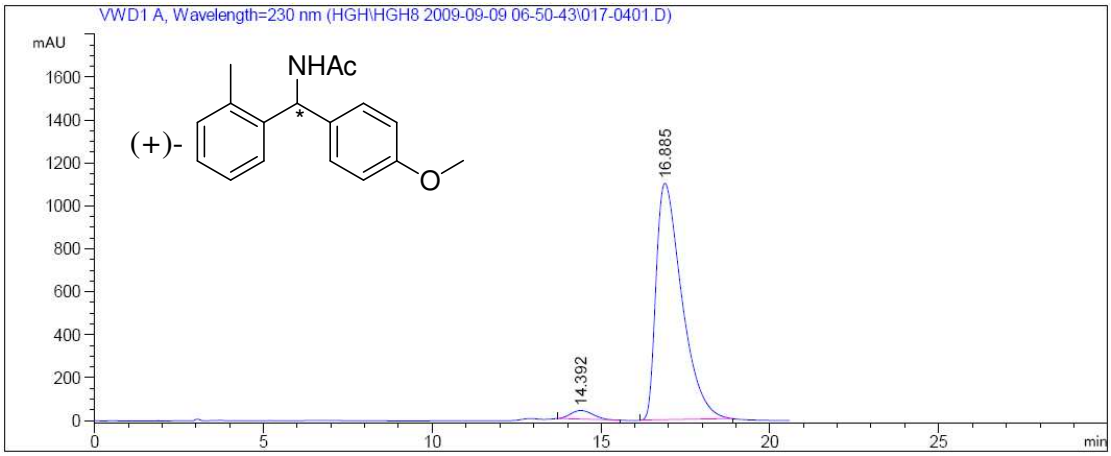
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.467	VB	0.5892	526.34552	13.79613	3.5554
2	15.054	MM	0.9186	1.42779e4	259.04318	96.4446
Totals :				1.48042e4	272.83931	



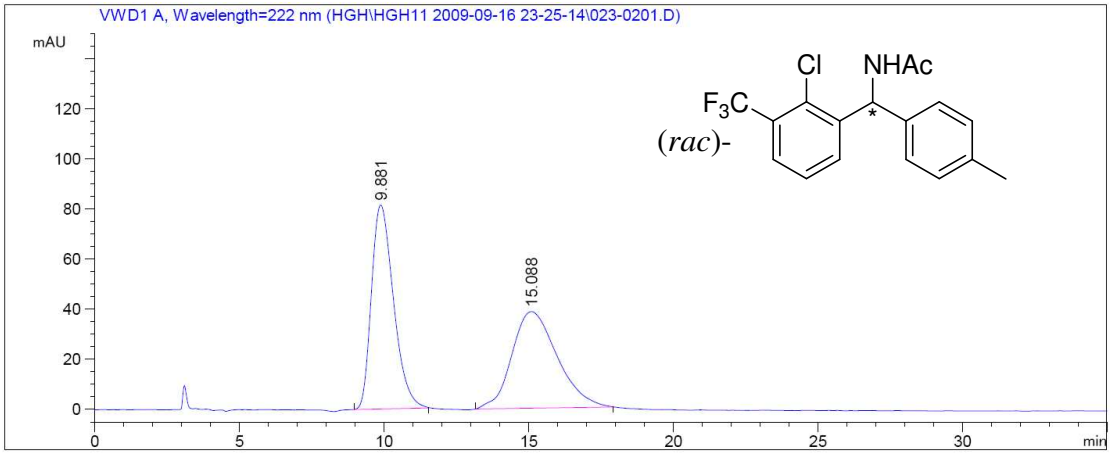


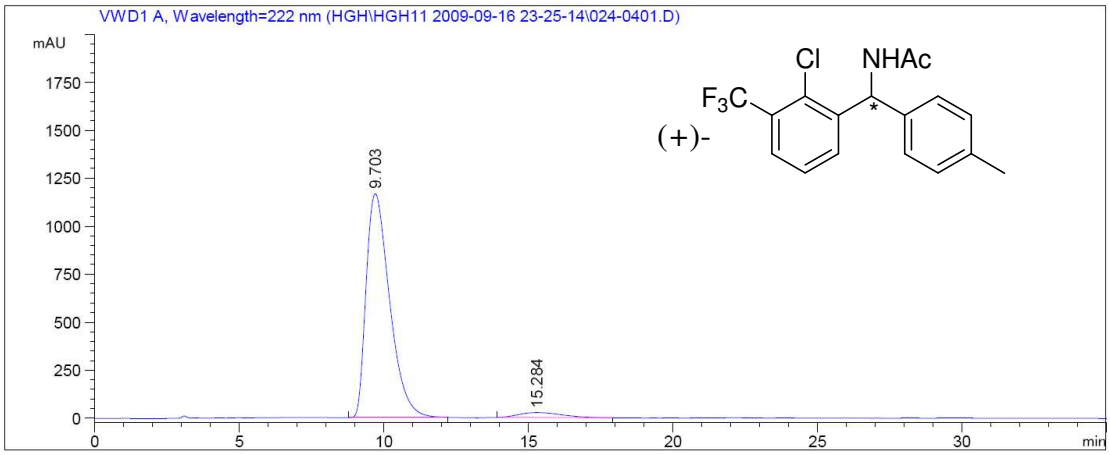
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.566	VB	0.4419	1409.70557	49.86446	4.4225
2	9.352	BB	0.3811	3.04659e4	1243.84448	95.5775
Totals :				3.18756e4	1293.70895	



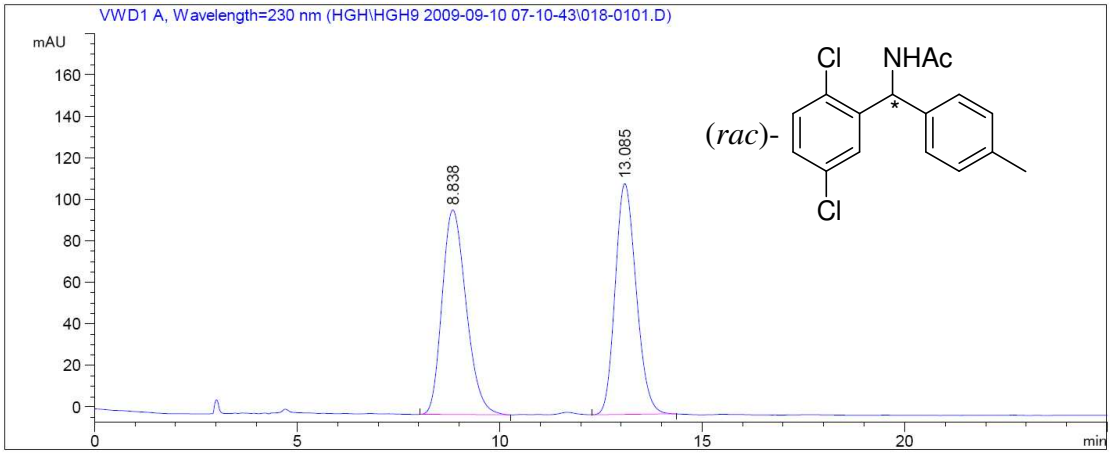


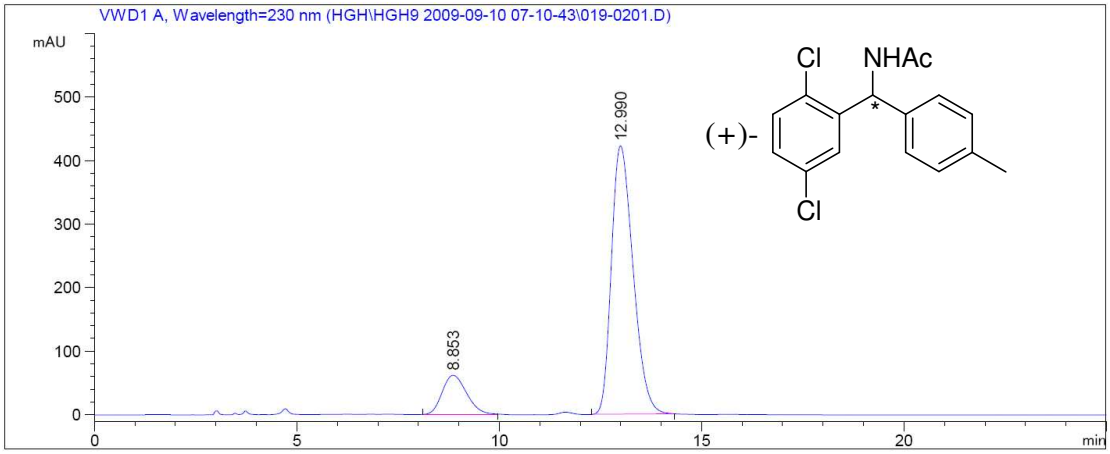
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.392	BB	0.5483	1862.33044	40.37658	3.0838
2	16.885	BB	0.7744	5.85280e4	1101.83801	96.9162
Totals :				6.03904e4	1142.21459	



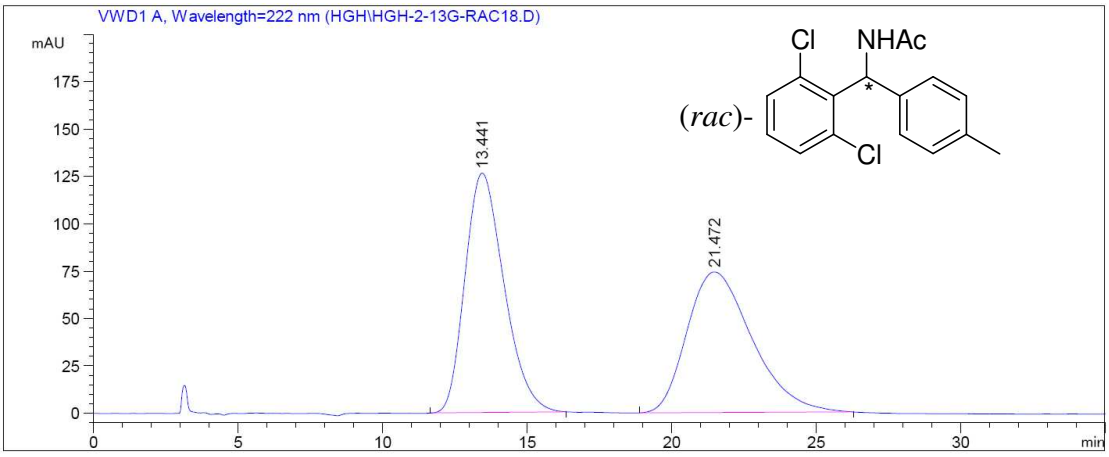


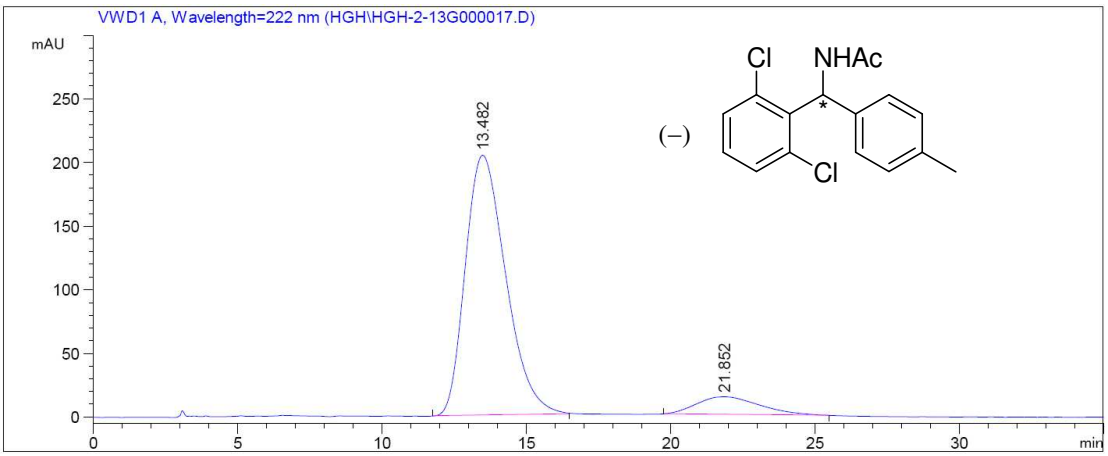
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.703	BB	0.8701	6.59456e4	1166.19067	95.9622
2	15.284	BB	1.2313	2774.82373	26.52598	4.0378
Totals :				6.87204e4	1192.71665	



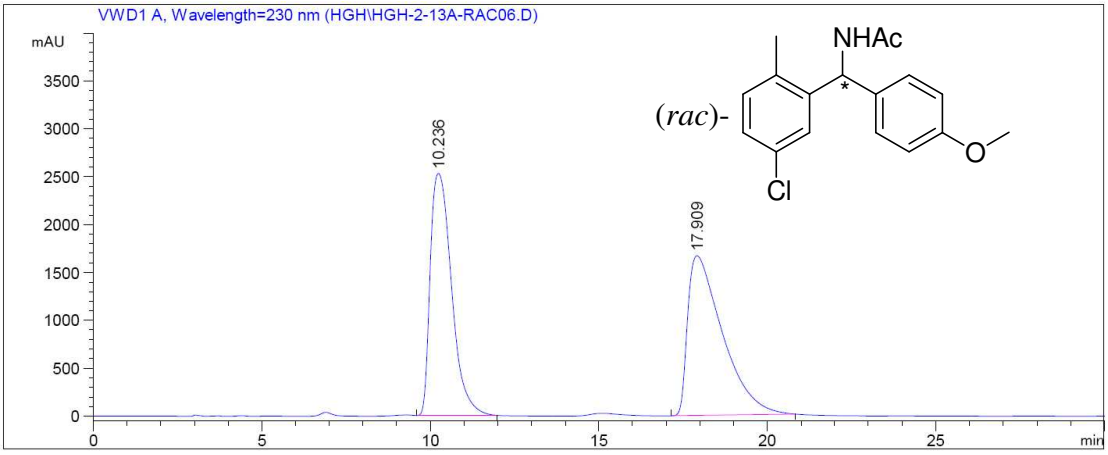


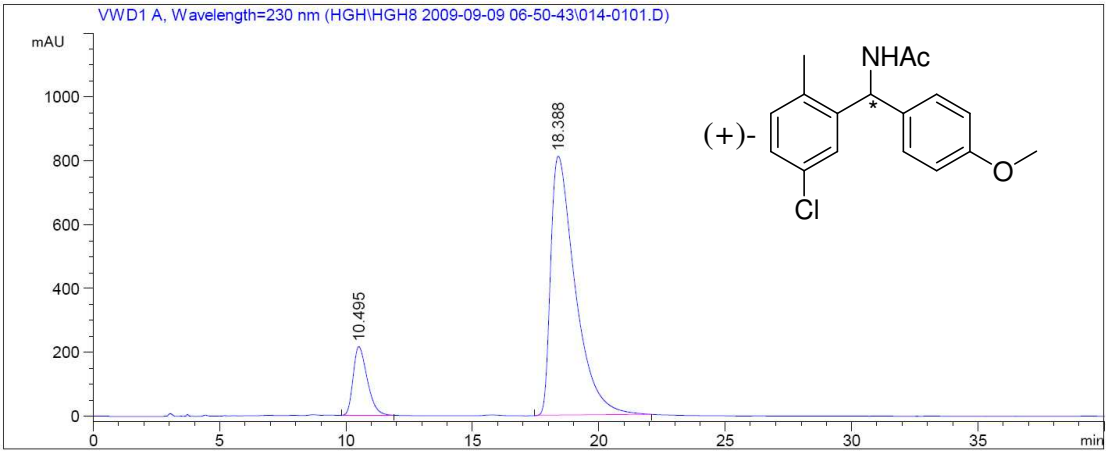
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.853	BB	0.6414	2575.97021	61.51865	14.0480
2	12.990	BB	0.5786	1.57609e4	422.53748	85.9520
Totals :				1.83369e4	484.05613	





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.482	BB	1.4843	1.99202e4	204.26927	90.2857
2	21.852	BB	1.7954	2143.32959	13.99550	9.7143
Totals :				2.20636e4	218.26477	





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.495	BB	0.5867	8353.27344	215.58632	13.1888
2	18.388	BB	0.9892	5.49828e4	812.21735	86.8112
Totals :				6.33360e4	1027.80367	

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