

**Stereoselective Construction of 5-*aza*-Spiro[2,4]heptane Motif via
Catalytic Asymmetric 1,3-Dipolar Cycloaddition of Azomethine
Ylides and Ethyl Cyclopropylidene Acetate**

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General Remarks.

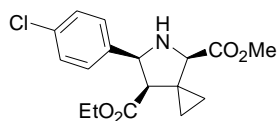
¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d₃. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). ¹³C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in CDCl₃. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude ¹H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralcel AD-H column, a chiralpak AS-H column with hexane and *i*-PrOH as solvents. Ligands **L1** and **L2** were prepared according to the literature procedure reported by us.^[1] Ethyl cyclopropylidene acetate and imino esters were prepared according to the literature procedure.^[1,2] The racemic adducts were attained by using Cu(CH₃CN)₄BF₄/(±)-TF-BiphamPhos as the catalyst. The absolute (4*R*,6*S*,7*R*)-**3aa** achieved by Cu(CH₃CN)₄BF₄/(*S*)-TF-BiphamPhos was determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

General Procedure for racemic 1,3-Dipolar Cycloaddition of Azomethine Ylides with Ethyl Cyclopropylidene Acetate Catalyzed by Cu(CH₃CN)₄BF₄/(±)-TF-BiphamPhos Complex

Under argon atmosphere, (±)-TF-BiphamPhos (4.6 mg, 0.0072 mmol) and Cu(CH₃CN)₄BF₄ (1.9 mg, 0.006 mmol) were dissolved in 2 mL DCM, and stirred at room temperature for about 1h. Then, imine substrate (0.4 mmol), Et₃N (0.03 mmol) and Ethyl cyclopropylidene acetate (0.2 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the cycloaddition product (76-90% yield), which was used as the racemic sample for the chiral HPLC analysis.

General Procedure for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with Ethyl cyclopropylidene acetate Catalyzed by $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4/(\text{S})\text{-TF-BiphamPhos}$ Complex

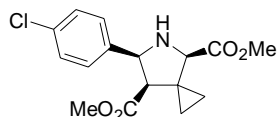
Under argon atmosphere (*S*)-TF-BiphamPhos **1a** (4.6 mg, 0.0072 mmol) and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (1.9 mg, 0.006 mmol) were dissolved in 2 mL DCM, and stirred at room temperature for about 1h. After it was cooled to the indicated temperature, imine substrate (0.4 mmol), Et_3N (0.03 mmol) and Ethyl cyclopropylidene acetate (0.2 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The product purified by column chromatography to give the corresponding cycloaddition product, which was then directly analyzed by chiral HPLC to determine the enantiomeric excess.



(3aa)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-(4-chlorophenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 1)

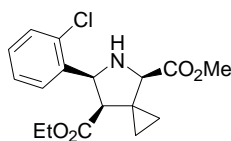
The title compound was prepared according to the general procedure as described above in 90% yield. $[\alpha]_{\text{D}}^{25} = -14.6$ (*c* 0.82, CHCl_3); $^1\text{H NMR}$ (CDCl_3 , TMS, 300 MHz) δ 7.24 (m, 4H), 4.61 (d, *J* = 5.7 Hz, 1H), 3.78-3.71 (m, 6H), 3.41 (br, 1H), 2.76 (d, *J* = 6.0 Hz, 1H), 0.92-0.60 (m, 7H); $^{13}\text{C NMR}$ (CDCl_3 , TMS, 75 MHz) δ 172.01, 171.57, 136.43, 133.07, 128.43, 127.66, 65.49, 64.34, 60.30, 58.47, 52.07, 29.42, 15.52, 13.88, 8.05; IR (KBr) ν 3685, 3624, 3019, 2977, 2400, 1731, 1519, 1426, 1215, 1045, 929, 756 cm^{-1} . HRMS: calcd. for $\text{C}_{17}\text{H}_{20}\text{ClNO}_4$: 337.1076, found. 337.1075. dr > 98:2; 98% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_{r} = 6.69 and 9.80 min.



(3ba)

(4R,6S,7R)-dimethyl 6-(4-chlorophenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 1, entry 9)

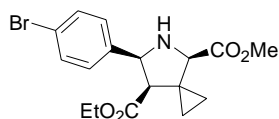
The title compound was prepared according to the general procedure as described above in 87% yield. $[\alpha]_D^{25} = -15.0$ (*c* 0.64, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.23 (m, 4H), 4.61 (d, *J* = 5.7 Hz, 1H), 3.75-3.72 (m, 4H), 3.39 (br, 1H), 3.28 (s, 3H), 2.77 (d, *J* = 5.4 Hz, 1H), 0.92-0.61 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.74, 171.86, 136.58, 133.43, 128.77, 127.86, 65.68, 64.67, 60.56, 58.63, 52.39, 51.53, 15.83, 8.27; IR (KBr) ν 3684, 3626, 3018, 2978, 2401, 1730, 1518, 1427, 1214, 1046, 930, 757 cm⁻¹. *dr* = 86:14; 98% *ee*, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 8.15 and 13.19 min.



(3ab)

(4R,6S,7R)-7-ethyl 4-methyl 6-(2-chlorophenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 2)

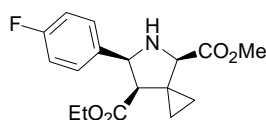
The title compound was prepared according to the general procedure as described above in 97% yield. $[\alpha]_D^{25} = -63.2$ (*c* 0.84, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.43 (d, *J* = 6.6 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.24-7.16 (m, 2H), 4.88 (s, 1H), 3.74 (m, 4H), 3.64 (q, *J* = 6.9 Hz, 7.2 Hz, 2H), 3.09 (s, 1H), 2.92 (br, 1H), 0.95-0.59 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.02, 135.30, 133.26, 129.36, 128.68, 126.87, 126.75, 65.15, 62.46, 60.09, 56.44, 52.10, 29.33, 15.44, 13.85, 8.45; IR (KBr) ν 3683, 3625, 3020, 2976, 2401, 1732, 1520, 1425, 1214, 1047, 926, 754 cm⁻¹. HRMS calcd. for C₁₇H₂₀ClNO₄: 337.1081, found 337.1080. *dr* = 97:3; 97% *ee*, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 5.81 and 11.27 min.



(3ac)

(4R,6S,7R)-7-ethyl 4-methyl 6-(4-bromophenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 3)

The title compound was prepared according to the general procedure as described above in 87% yield. $[\alpha]_D^{25} = -16.5$ (*c* 0.46, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.59 (d, *J* = 5.1 Hz, 1H), 3.78-3.71 (m, 6H), 3.17 (br, 1H), 2.76 (d, *J* = 4.8 Hz, 1H), 0.92-0.60 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 171.99, 171.58, 137.00, 131.32, 127.97, 121.12, 65.44, 64.37, 60.26, 58.39, 52.05, 29.43, 15.48, 13.86, 8.03; IR (KBr) ν 3683, 3622, 3017, 2979, 2402, 1735, 1515, 1423, 1217, 1045, 924, 759 cm⁻¹. HRMS calcd. for C₁₇H₂₀BrNO₄: 381.0576, found 381.0568. *dr* = 95:5; 98% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 7.07 and 11.14 min.

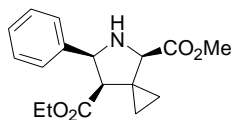


(3ad)

(4R,6S,7R)-7-ethyl 4-methyl 6-(4-fluorophenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 4)

The title compound was prepared according to the general procedure as described above in 85% yield. $[\alpha]_D^{25} = -15.6$ (*c* 0.64, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.27 (d, *J* = 6.6 Hz, 2H), 6.96 (t, *J* = 8.4 Hz, 2H), 4.63 (d, *J* = 5.7 Hz, 1H), 3.77-3.72 (m, 6H), 3.37 (br, 1H), 2.75 (d, *J* = 5.1 Hz, 1H), 0.92-0.60 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.11, 171.63, 163.57, 133.62, 127.93, 115.29, 115.00, 65.52, 60.21, 58.65, 52.05, 29.39, 15.52, 13.86, 8.03; IR (KBr) ν 3681, 3622, 3021, 2980, 2403, 1733, 1516, 1429, 1217, 1049, 924, 751 cm⁻¹. HRMS calcd. for C₁₇H₂₀FNO₄: 321.1376, found 321.1374. *dr* = 97:3; 97% ee, HPLC (Chiralcel AS-H,

i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.58 and 9.39 min.

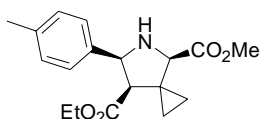


(3ae)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-phenyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate

(Table 2, entry 5)

The title compound was prepared according to the general procedure as described above in 81% yield. $[\alpha]_D^{25} = -20.3$ (*c* 0.54, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.31-7.18 (m, 5H), 4.67 (d, *J* = 5.7 Hz, 1H), 3.75-3.67 (m, 6H), 3.42 (br, 1H), 2.78 (d, *J* = 5.7 Hz, 1H), 0.93-0.60 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.22, 171.68, 137.77, 128.27, 127.29, 126.17, 65.59, 64.97, 60.11, 58.76, 52.02, 29.38, 15.54, 13.78, 8.06; IR (KBr) ν 3681, 3620, 3015, 2972, 2397, 1728, 1523, 1429, 1211, 1040, 926, 759 cm⁻¹. HRMS calcd. for C₁₇H₂₁NO₄: 303.1471, found 303.1478. dr = 95:5; 95% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.06 and 9.36 min.



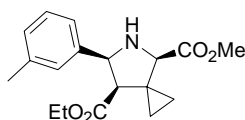
(3af)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-*p*-tolyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate

(Table 2, entry 6)

The title compound was prepared according to the general procedure as described above in 78% yield. $[\alpha]_D^{25} = -14.7$ (*c* 0.64, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.17 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 4.64 (d, *J* = 5.7 Hz, 1H), 3.77-3.70 (m, 6H), 2.75 (d, *J* = 5.7 Hz, 1H), 2.25 (s, 3H), 0.94-0.61 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.31, 171.66, 136.93, 134.57, 128.95, 126.04, 65.56, 64.81, 60.14, 58.79, 52.05, 29.33, 21.03, 15.58, 13.84, 8.02; IR (KBr) ν 3682, 3623, 3016, 2975, 2403, 1727, 1521, 1422, 1214, 1043, 927, 754 cm⁻¹. HRMS calcd.

for C₁₈H₂₃NO₄: 317.1627, found 317.1625. dr = 96:4; 97% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.84 and 9.39 min.

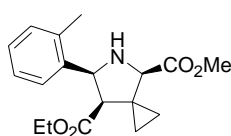


(3ag)

(4R,6S,7R)-7-ethyl 4-methyl 6-*m*-tolyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate

(Table 2, entry 7)

The title compound was prepared according to the general procedure as described above in 90% yield. $[\alpha]_D^{25} = -7.3$ (*c* 0.76, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.20-6.99 (m, 4H), 4.64 (m 1H), 3.78-3.73 (m, 6H), 2.78 (s, 1H), 2.27 (s, 3H), 0.93-0.62 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.32, 171.74, 137.77, 128.11, 127.90, 126.84, 123.18, 65.60, 64.94, 60.01, 58.78, 51.94, 29.44, 21.39, 15.48, 13.77, 8.08; IR (KBr) ν 3685, 3623, 3020, 2974, 2399, 1730, 1518, 1425, 1213, 1043, 932, 754 cm⁻¹. HRMS calcd. for C₁₈H₂₃NO₄: 317.1627, found 317.1631. dr > 98:2; 98% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.57 and 8.72 min.



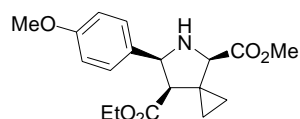
(3ah)

(4R,6S,7R)-7-ethyl 4-methyl 6-*o*-tolyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate

(Table 2, entry 8)

The title compound was prepared according to the general procedure as described above in 87% yield. $[\alpha]_D^{25} = -43.5$ (*c* 0.72, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.32 (d, *J* = 6.6 Hz, 1H), 7.12-7.08 (m, 3H), 4.74 (s, 1H), 3.74 (m, 4H), 3.60 (q, *J* = 7.2 Hz, 2H), 3.37 (br, 1H), 2.83 (d, *J* = 5.1 Hz, 1H), 2.29 (s, 3H), 0.98-0.54 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.07, 135.49, 130.26, 127.36, 125.92, 124.71,

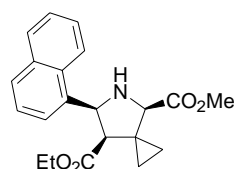
65.29, 62.60, 60.09, 57.20, 52.09, 29.32, 19.75, 15.50, 13.79, 8.60; IR (KBr) ν 3685, 3624, 3020, 2980, 2402, 1732, 1518, 1425, 1214, 1043, 929, 756 cm^{-1} . HRMS calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}_4$: 317.1627; found 317.1626. dr > 98:2; 96% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 5.30 and 10.94 min.



(3ai)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-(4-methoxyphenyl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 9)

The title compound was prepared according to the general procedure as described above in 78% yield. $[\alpha]_D^{25} = -3.2$ (*c* 0.64, CHCl_3); ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 7.22 (d, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 5.1 Hz, 2H), 4.63 (d, *J* = 5.7 Hz, 1H), 3.78-3.72 (m, 9H), 2.74 (d, *J* = 5.7 Hz, 1H), 0.95-0.61 (m, 7H); ^{13}C NMR (CDCl_3 , TMS, 75 MHz) δ 172.77, 172.15, 159.08, 130.24, 127.71, 114.00, 65.98, 64.92, 60.51, 59.27, 55.58, 52.39, 15.92, 14.27, 8.42; IR (KBr) ν 3685, 3624, 3019, 2977, 2400, 1731, 1519, 1426, 1215, 1045, 929, 756 cm^{-1} . HRMS calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}_5$: 333.1576; found 333.1572. dr > 98:2; 98% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); t_r = 9.12 and 12.63 min.

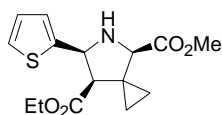


(3aj)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-(naphthalen-1-yl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 10)

The title compound was prepared according to the general procedure as described above in 82% yield. $[\alpha]_D^{25} = -145.7$ (*c* 0.90, CHCl_3); ^1H NMR (CDCl_3 , TMS, 300

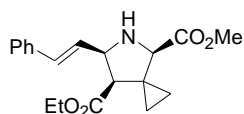
MHz) δ 7.92 (d, $J = 8.7$ Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 8.1$ Hz, 1H), 7.54-7.37 (m, 4H), 5.32 (m 1H), 3.84 (s, 1H), 3.74 (s, 3H), 3.46 (q, $J = 7.2$ Hz, 2H), 3.06 (d, $J = 5.1$ Hz, 1H), 0.99-0.46 (m, 7H), ^{13}C NMR (CDCl_3 , TMS, 75 MHz) δ 171.82, 133.42, 132.92, 131.03, 128.82, 128.07, 126.13, 125.44, 125.08, 122.74, 122.53, 65.14, 61.88, 59.78, 58.64, 51.97, 29.63, 15.40, 13.46, 8.49; IR (KBr) ν 3683, 3622, 3017, 2979, 2403, 1734, 1517, 1426, 1215, 1045, 929, 756 cm^{-1} . HRMS calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_4$: 353.1627, found 353.1628. dr > 98:2; 92% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 11.28$ and 15.66 min.



(3ak)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-(thiophen-2-yl)-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Table 2, entry 11)

The title compound was prepared according to the general procedure as described above in 89% yield. $[\alpha]_D^{25} = -3.0$ (c 0.30, CHCl_3); ^1H NMR (CDCl_3 , TMS, 300 MHz) δ 7.15 (d, $J = 4.8$ Hz, 1H), 6.92-6.84 (m, 2H), 4.74 (m, 1H), 3.87 (q, $J = 7.4$ Hz, 2H), 3.73 (s, 1H), 3.70 (s, 3H), 2.76 (d, $J = 5.4$ Hz, 1H), 0.98-0.62 (m, 7H); ^{13}C NMR (CDCl_3 , TMS, 75 MHz) δ 171.93, 171.17, 140.70, 126.48, 124.01, 123.89, 65.43, 61.33, 60.15, 58.64, 51.77, 29.44, 15.31, 13.71, 7.71; IR (KBr) ν 3684, 3623, 3019, 2977, 2400, 1730, 1519, 1427, 1215, 1045, 929, 756 cm^{-1} . HRMS: calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{S}$: 309.1039, found 309.1041. dr > 98:2; 94% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 9.57$ and 16.36 min.

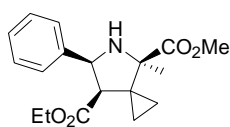


(3al)

(4R,6R,7R)-7-ethyl 4-methyl 6-styryl-5-azaspiro[2.4]heptane-4,7-dicarboxylate

(Table 2, entry 12)

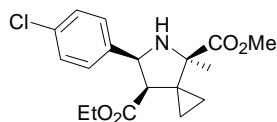
The title compound was prepared according to the general procedure as described above in 87% yield. $[\alpha]_D^{25} = -17.8$ (*c* 0.56, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.37-7.24 (m, 5H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 6.3 Hz, 15.9 Hz, 1H), 4.33-4.28 (m, 1H), 4.13-4.06 (m, 2H), 3.77-3.72 (m, 4H), 2.61 (d, *J* = 5.1 Hz, 1H), 1.18-0.71 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 172.31, 171.57, 136.36, 133.07, 128.53, 127.85, 126.44, 125.05, 65.49, 63.66, 60.45, 57.86, 52.08, 29.64, 15.58, 14.36, 7.76; IR (KBr) ν 3684, 3624, 3019, 2977, 2403, 1731, 1519, 1426, 1216, 1045, 929, 756 cm⁻¹. HRMS calcd. for C₁₉H₂₃NO₄: 329.1627, found 329.1627. *dr* > 98:2; 93% *ee*, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 6.86 and 11.33 min.



(3am)

(4R,6S,7R)-7-ethyl 4-methyl 4-methyl-6-phenyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Figure 2)

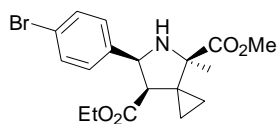
The title compound was prepared according to the general procedure as described above in 89% yield. $[\alpha]_D^{25} = +10.7$ (*c* 0.90, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.31-7.17 (m, 5H), 4.76 (d, *J* = 6.0 Hz, 1H), 3.74 (s, 3H), 3.68 (q, *J* = 7.2 Hz, 2H), 2.82 (d, *J* = 6.6 Hz, 1H), 1.35 (s, 3H), 0.95-0.66 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 175.00, 172.52, 138.43, 132.65, 128.44, 126.54, 67.07, 62.95, 61.02, 60.24, 52.54, 34.37, 24.64, 14.02, 13.00, 9.39; IR (KBr) ν 3688, 3624, 3019, 2981, 2400, 1731, 1523, 1426, 1215, 1050, 929, 756 cm⁻¹. *dr* > 98:2; 98% *ee*, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 7.84 and 8.72 min.



(3an)

(4R,6S,7R)-7-ethyl 4-methyl 6-(4-chlorophenyl)-4-methyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Figure 2)

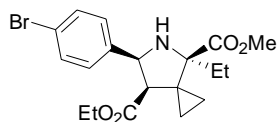
The title compound was prepared according to the general procedure as described above in 87% yield. $[\alpha]_D^{25} = +10.9$ (*c* 0.84, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.24 (m, 4H), 4.75 (d, *J* = 6.3 Hz, 1H), 3.74-3.69 (m, 5H), 2.80 (d, *J* = 6.3 Hz, 1H), 1.36 (s, 3H), 0.93-0.69 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 171.95, 136.60, 133.05, 128.39, 127.79, 66.94, 62.09, 60.23, 52.44, 33.96, 29.67, 24.14, 13.85, 12.76, 9.00; IR (KBr) ν 3685, 3620, 3019, 2977, 2400, 1730, 1519, 1426, 1215, 1045, 931, 756 cm⁻¹. HRMS calcd. for C₁₈H₂₂ClNO₄: 351.1237, found 351.1239. *dr* > 98:2; 97% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 8.94 and 12.17 min.



(3ao)

(4R,6S,7R)-7-ethyl 4-methyl 6-(4-bromophenyl)-4-methyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Figure 2)

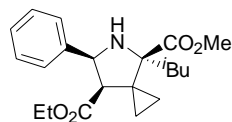
The title compound was prepared according to the general procedure as described above in 88% yield. $[\alpha]_D^{25} = +7.8$ (*c* 0.90, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.65 (d, *J* = 6.0 Hz, 1H), 3.72-3.67 (m, 5H), 2.78 (d, *J* = 6.3 Hz, 1H), 1.31 (s, 3H), 0.88-0.64 (m, 7H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 174.54, 171.92, 137.23, 131.27, 128.12, 121.08, 66.87, 62.10, 60.14, 52.36, 33.99, 29.63, 24.15, 13.82, 12.71, 8.98; IR (KBr) ν 3685, 3625, 3020, 2977, 2399, 1731, 1521, 1426, 1219, 1045, 929, 756 cm⁻¹. *dr* = 95:5; 97% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 9.62 and 12.51 min.



(3ap)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 6-(4-bromophenyl)-4-ethyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Figure 2)

The title compound was prepared according to the general procedure as described above in 74% yield. $[\alpha]_D^{25} = +15.9$ (*c* 0.72, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.61 (d, *J* = 6.0 Hz, 1H), 3.77-3.71 (m, 5H), 2.76 (d, *J* = 6.3 Hz, 1H), 1.58 (m, 2H), 1.01-0.68 (m, 10H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 174.33, 172.11, 137.77, 131.23, 128.25, 120.99, 70.50, 62.26, 60.71, 52.12, 33.60, 29.66, 11.98, 9.63, 8.44; IR (KBr) ν 3685, 3623, 3019, 2977, 2407, 1731, 1519, 1431, 1215, 1045, 929, 756 cm⁻¹. HRMS calcd. for C₁₉H₂₄BrNO₄: 409.0889, found 409.0886. *dr* > 98:2; 97% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 6.44 and 7.72 min.



(3aq)

(4*R*,6*S*,7*R*)-7-ethyl 4-methyl 4-isobutyl-6-phenyl-5-azaspiro[2.4]heptane-4,7-dicarboxylate (Figure 2)

The title compound was prepared according to the general procedure as described above in 81% yield. $[\alpha]_D^{25} = +13.5$ (*c* 0.78, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.32-7.15 (m, 5H), 4.60 (d, *J* = 6.3 Hz, 1H), 3.69-3.61 (m, 5H), 2.84 (d, *J* = 6.3 Hz, 1H), 1.57-1.52 (m, 3H), 0.90-0.53 (m, 13H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 174.38, 172.38, 138.63, 128.13, 127.05, 126.40, 69.54, 62.53, 60.41, 59.90, 51.87, 44.28, 35.35, 29.64, 25.19, 24.47, 22.38, 13.75, 11.74, 9.47; IR (KBr) ν 3686, 3623, 3019, 2979, 2400, 1734, 1519, 1426, 1215, 1045, 926, 756 cm⁻¹. *dr* > 98:2; 97% ee, HPLC (Chiralcel AS-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); *t_r* = 4.69 and 5.41 min.

X-ray Crystal Structures of *endo*-Adducts (**4*R*,6*S*,7*R***)-**3aa** (absolute configuration)

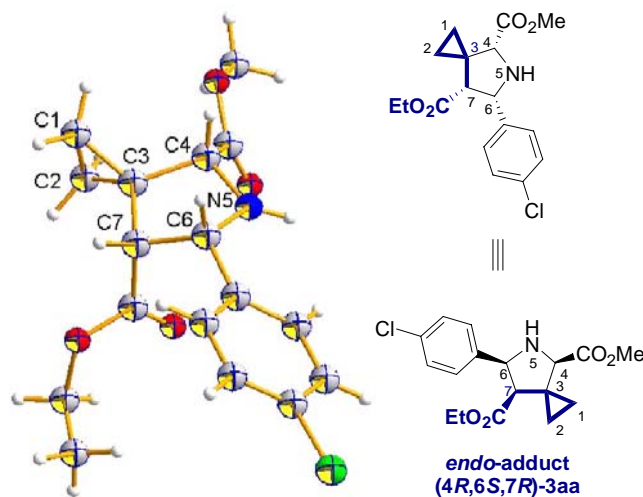


Figure 1. X-ray structure of (**4*R*,6*S*,7*R***)-**3aa**.

Crystal data for (**4*R*,6*S*,7*R***)-**3aa**: $C_{17}H_{20}ClNO_4$, $M_r = 337.79$, $T = 298$ K, Monoclinic, space group $P2(1)$, $a = 9.479(2)$, $b = 27.837(6)$, $c = 13.143(4)$ Å, $V = 3467.8(13)$ Å³, $Z = 8$, 7093 unique reflections, final $R_1 = 0.0514$ and $wR_2 = 0.1506$ for 11687 observed [$I > 2\sigma(I)$] reflections. CCDC 785673 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk)

Proposed transition states of the *endo*-selectivity for asymmetric 1,3-dipolar cycloaddition of imino esters with 2-cyclopropylidene Acetate

Based on the relative and absolute configuration of (**4*R*,6*S*,7*R***)-**3aa** and previous studies,^[1,3] a plausible transition state accounting for the observed *endo*-selectivity of the 1,3-DC addition of imino esters with ethyl 2-cyclopropylidene acetate in the presence of $Cu(CH_3CN)_4BF_4/(S)$ -TF-BiphamPhos (**L1**) is shown in Figure 2. The *in situ*-formed azomethine ylide is coordinated to the metallic center and oriented in

such way because of the steric repulsion between the phenyl group in the ylide and the phenyl ring on the phosphorus atom of the chiral ligand, and the highly steric congestion imposed by the latter effectively blocks the dipolarophile ethyl 2-cyclopropylidene acetate (**1a**) approach from the *Re* (C=N) face of the azomethine ylide and forms the *endo*-(4*R*,6*S*,7*R*)-5-*aza*-spiro[2,4]-heptane through *Si* face attack, which is compatible with the experimental results. The carbonyl group of ethyl 2-cyclopropylidene acetate (**1a**) could coordinate with the Cu(I) center, which can stabilize the negatively charged oxygen atom in the proposed transition states.^[4] It could not rule out the possible hydrogen bond interaction between the carbonyl group of dipolarophile **1a** and the NH₂ group of the chiral (*S*)-TF-BiphamPhos ligand (**L1**), which also facilitates stabilizing the proposed transition states.^[3b,3c] Nevertheless, the real catalytic mechanism still needs further investigation.

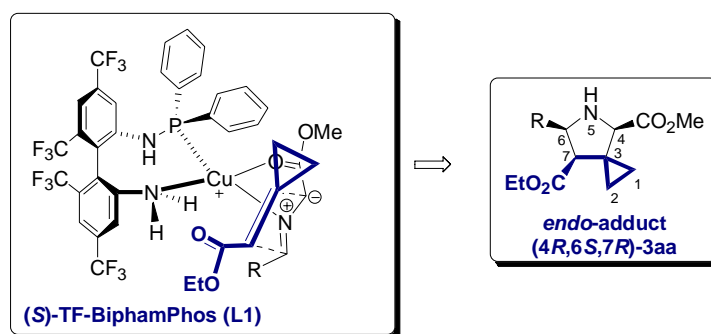
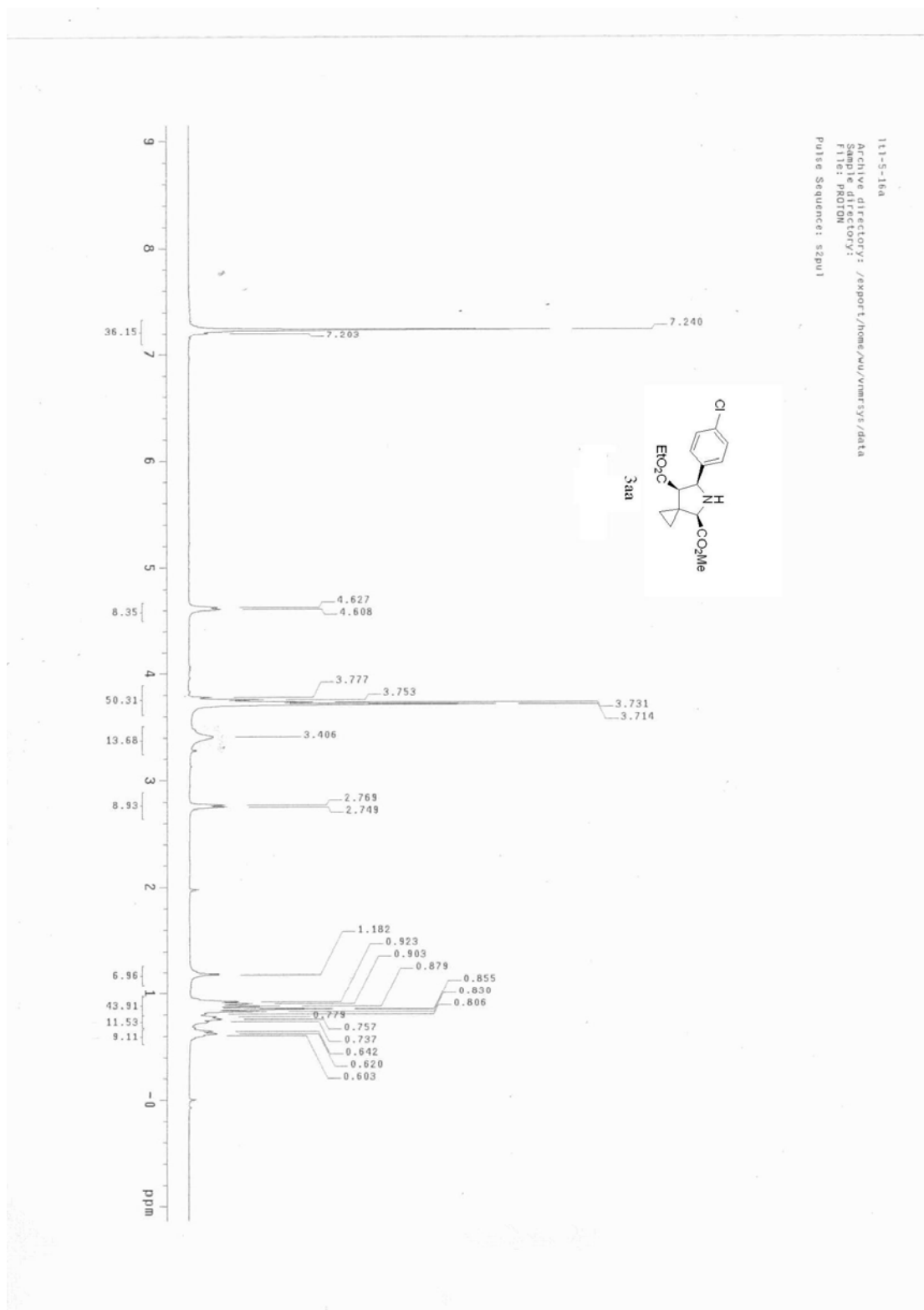
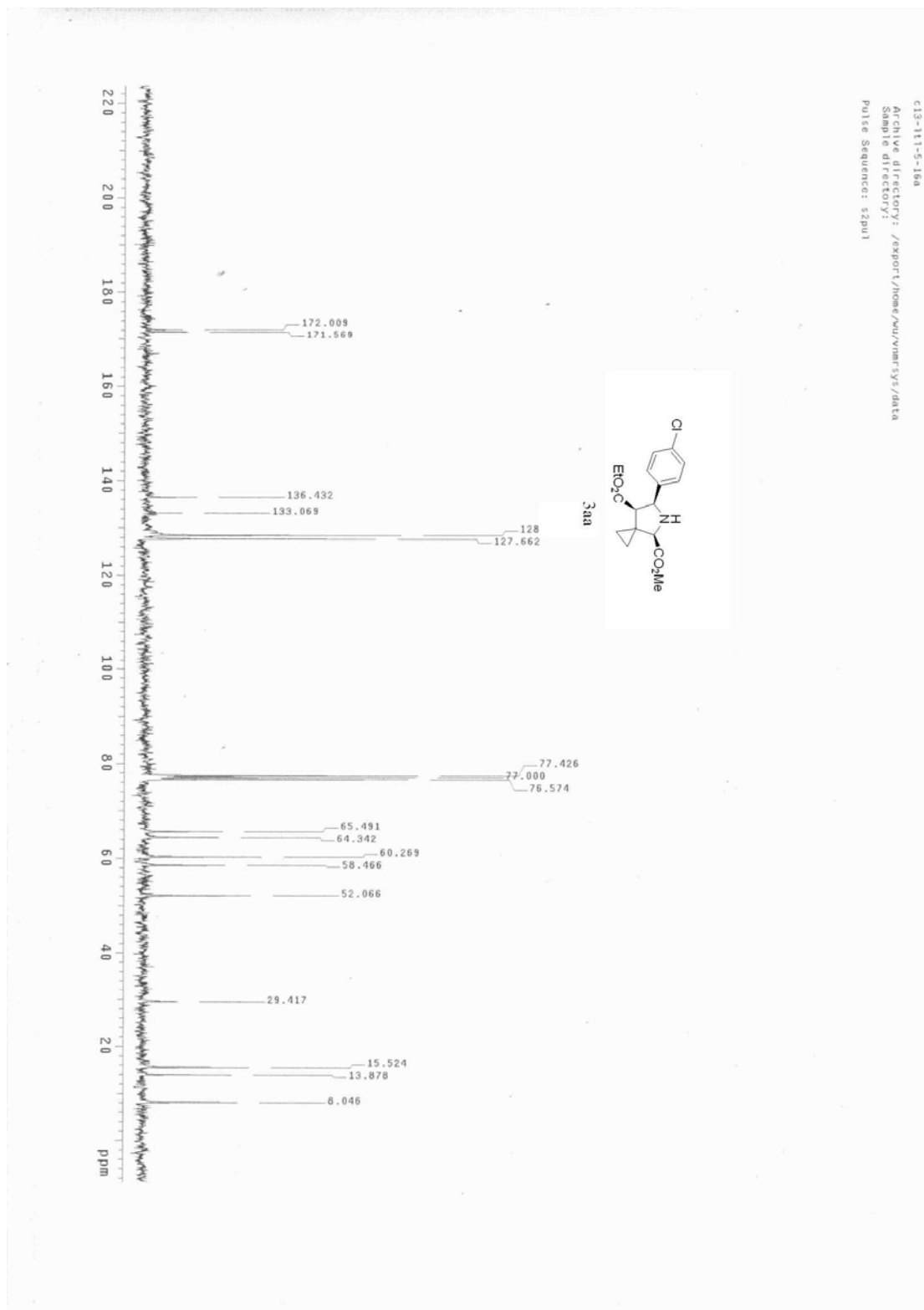


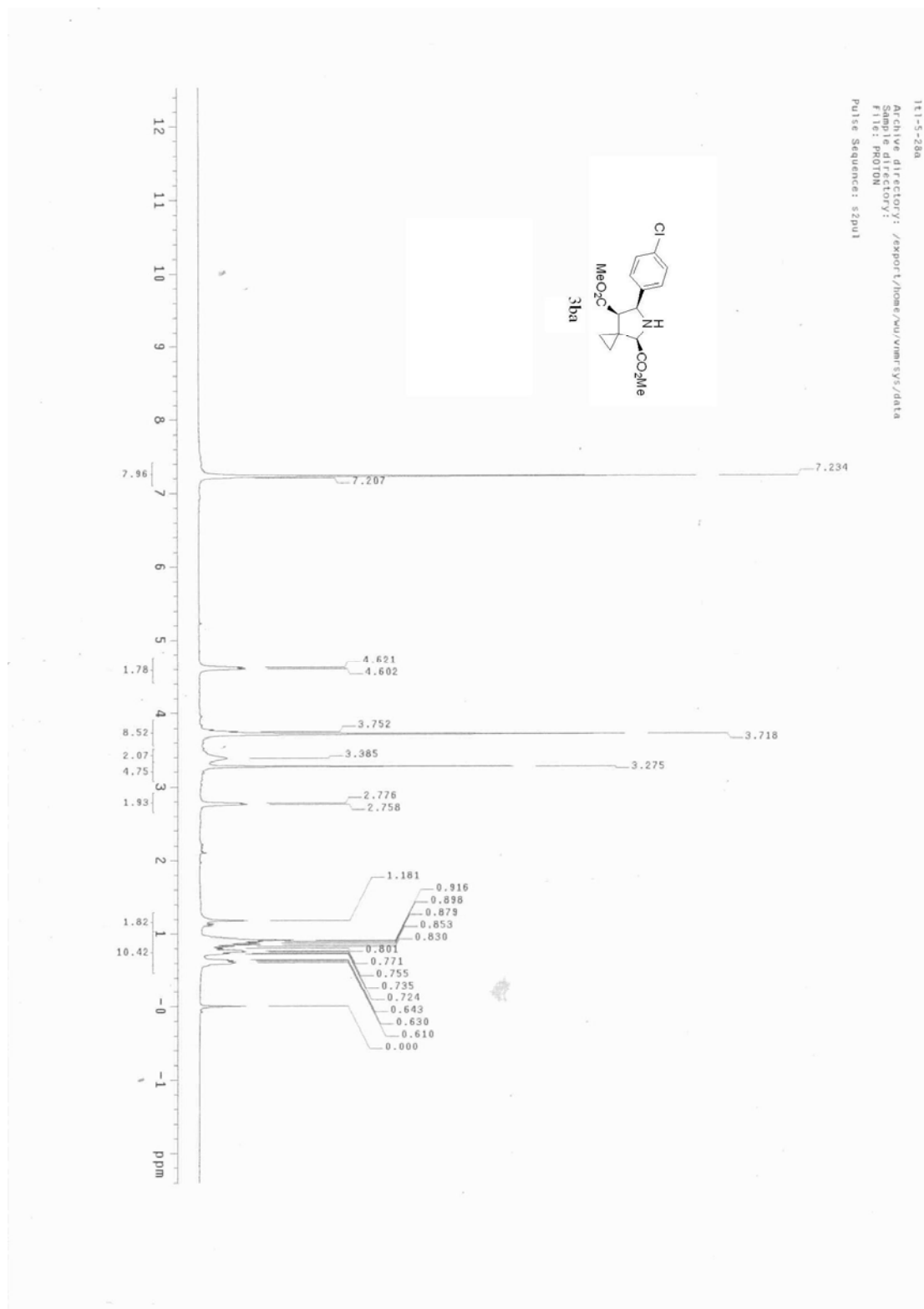
Figure 2. Proposed transition states leading to (4*R*,6*S*,7*R*)-5-*aza*-spiro[2,4]-heptanes.

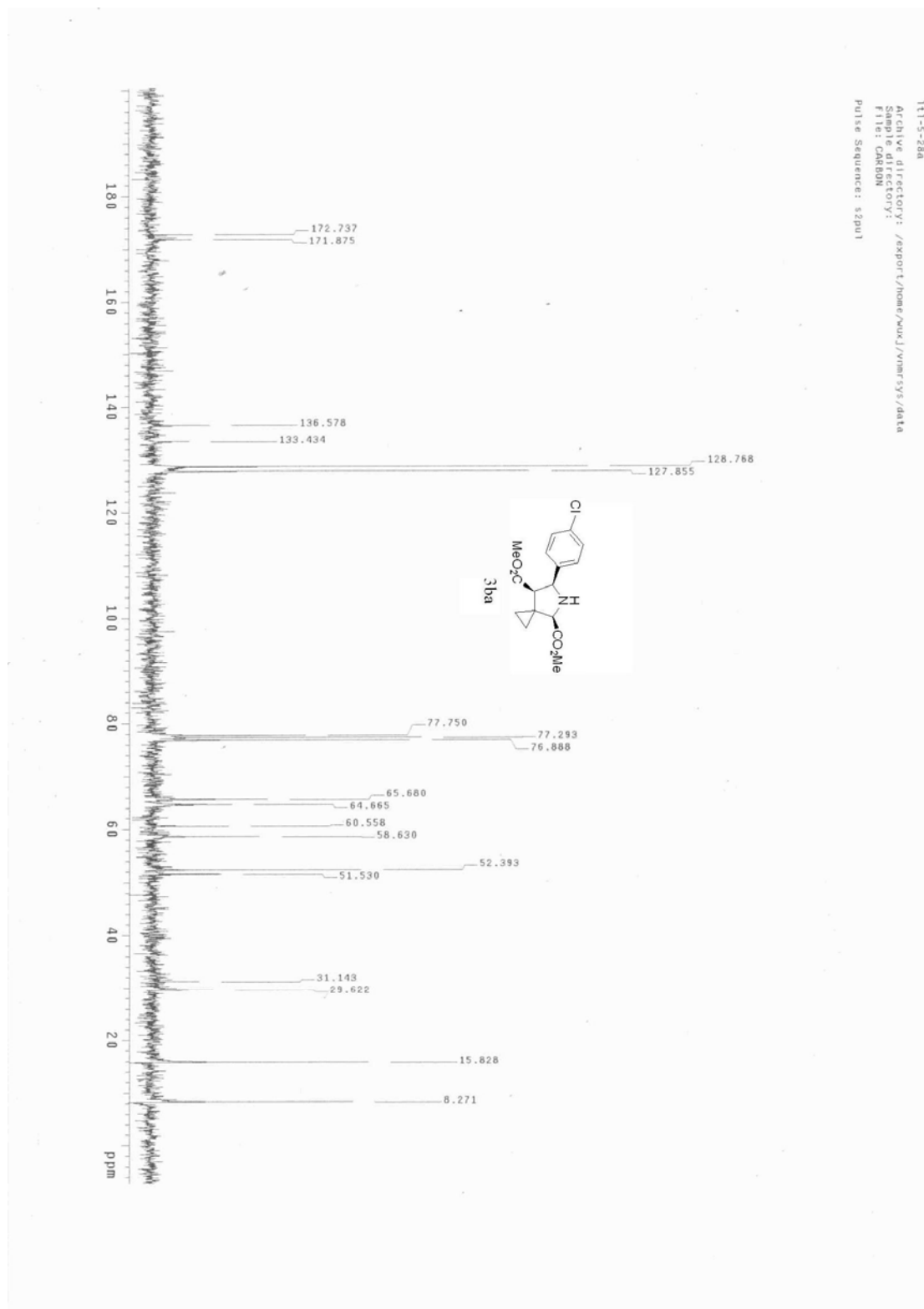
References

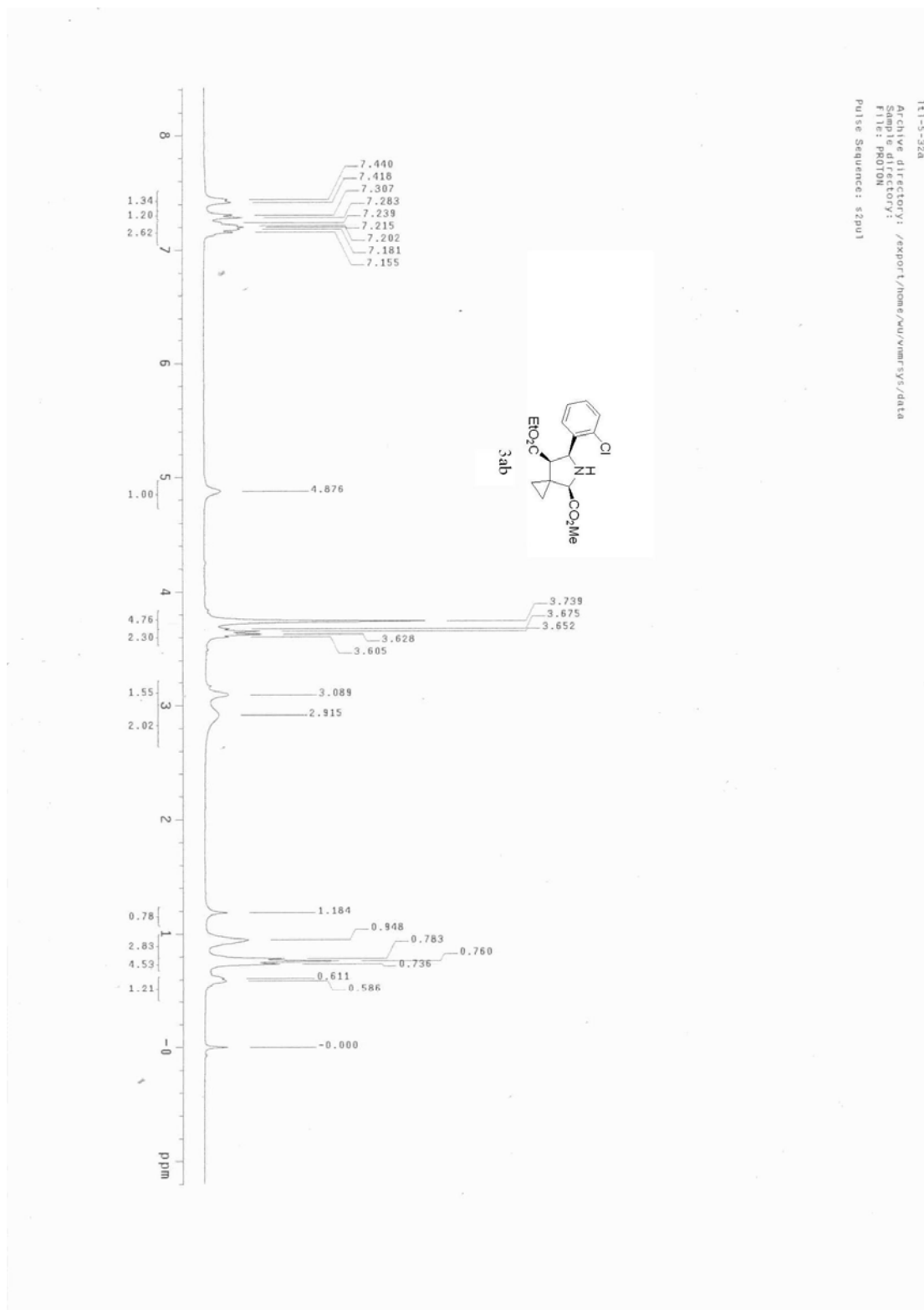
1. a) C.-J. Wang, G. Liang, Z.-Y. Xue, F. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 17250; b) C.-J. Wang, Z.-Y. Xue, G. Liang, Z. Lu, *Chem. Commun.* **2009**, 2905; c) G. Liang, M.-C. Tong, C.-J. Wang, *Adv. Synth. Catal.* **2009**, *351*, 3101; d) Z.-Y. Xue, T.-L. Liu, Z. Lu.; H. Huang, H.-Y. Tao, C.-J. Wang, *Chem. Commun.* **2010**, *46*, 1727.
- 2 a) J.; Salaun, J. Marguerite, *Org. Synth. Coll. Vol.* *7*, 131; *Vol.* *63*, 147; b) J. R. Henderson, M. Parvez, B. A. Keay, *Org. Lett.* **2007**, *9*, 5167.
- 3 a) S. Cabrera, R. G. Arrayás, B. Martín-Matute, F. P. Cossío, J. C. Carretero, *Tetrahedron* **2007**, *63*, 6587; b) W. Zeng, G.-Y. Chen, Y.-G. Zhou, Y.-X. Li, *J. Am. Chem. Soc.* **2007**, *129*, 750; c) H. Y. Kim, H.-J. Shih, W. E. Knabe, K. Oh, *Angew. Chem., Int. Ed.* **2009**, *48*, 7420; d) J. M. Longmire, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2002**, *124*, 13400; e) W. Gao, X. Zhang, M. Raghunath, *Org. Lett.* **2005**, *7*, 4241.
- 4 X.-X. Yan, Q. Peng, Y. Zhang, K. Zhang, W. Hong, X.-L. Hou, Y.-D. Wu, *Angew. Chem., Int. Ed.* **2006**, *45*, 1979.



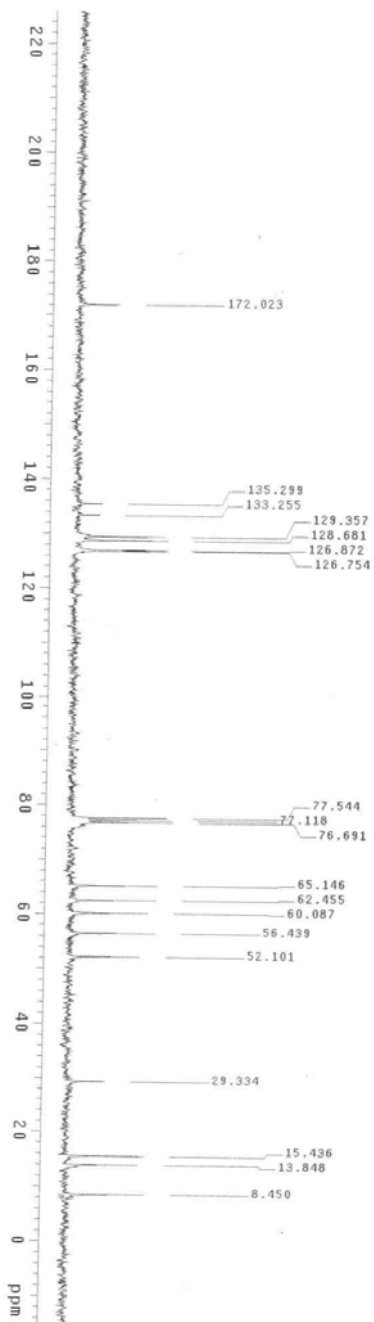
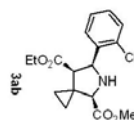


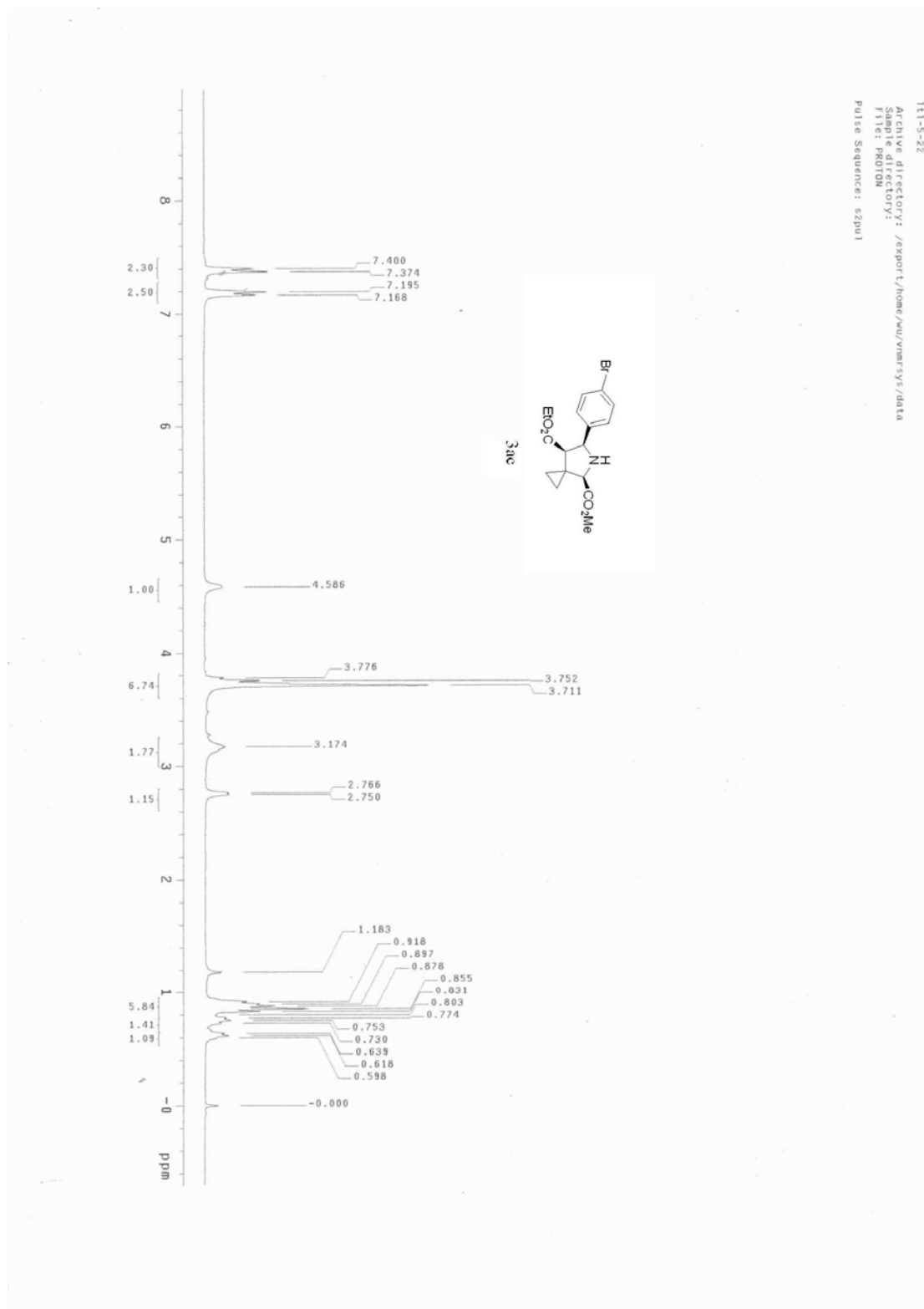


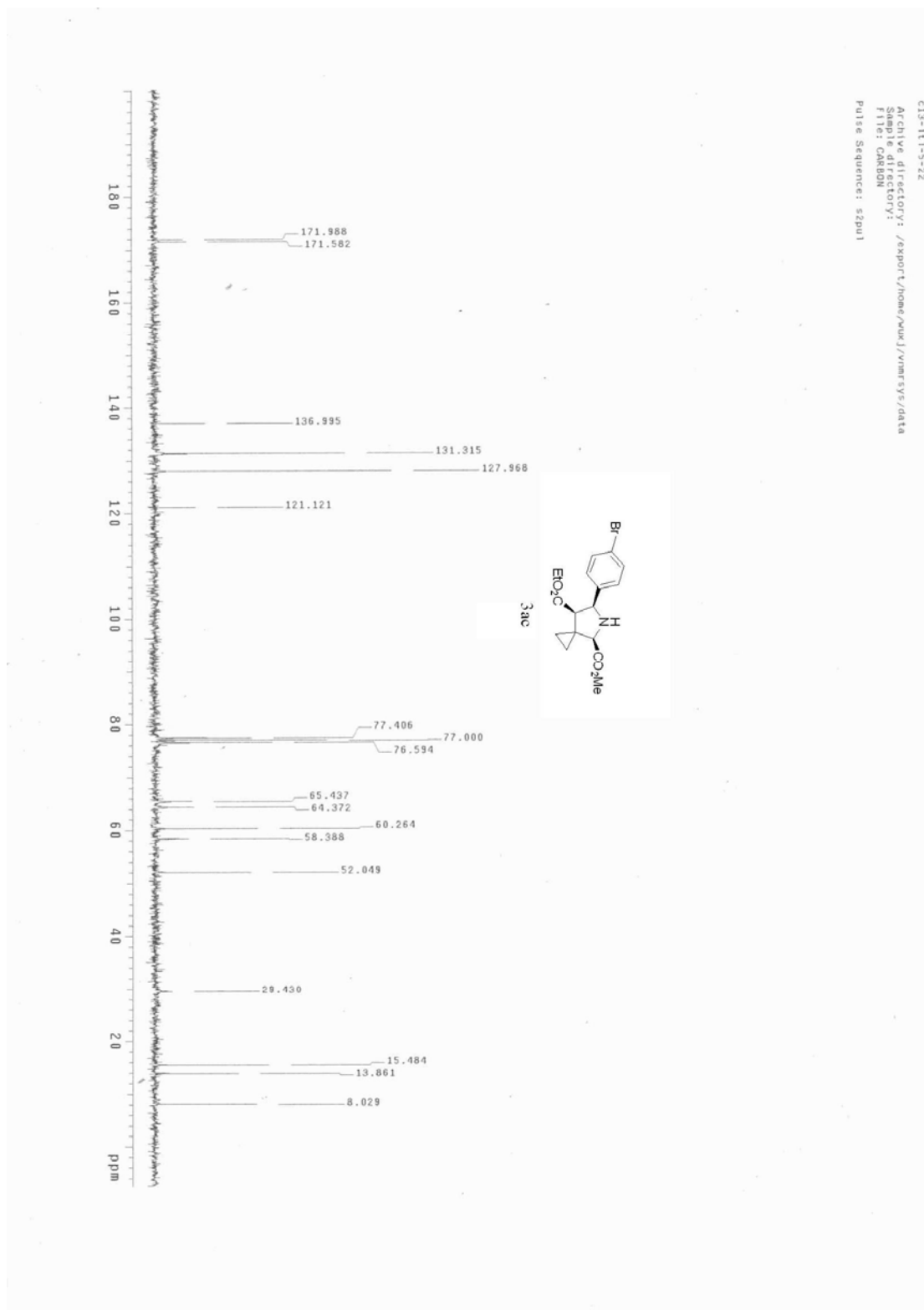


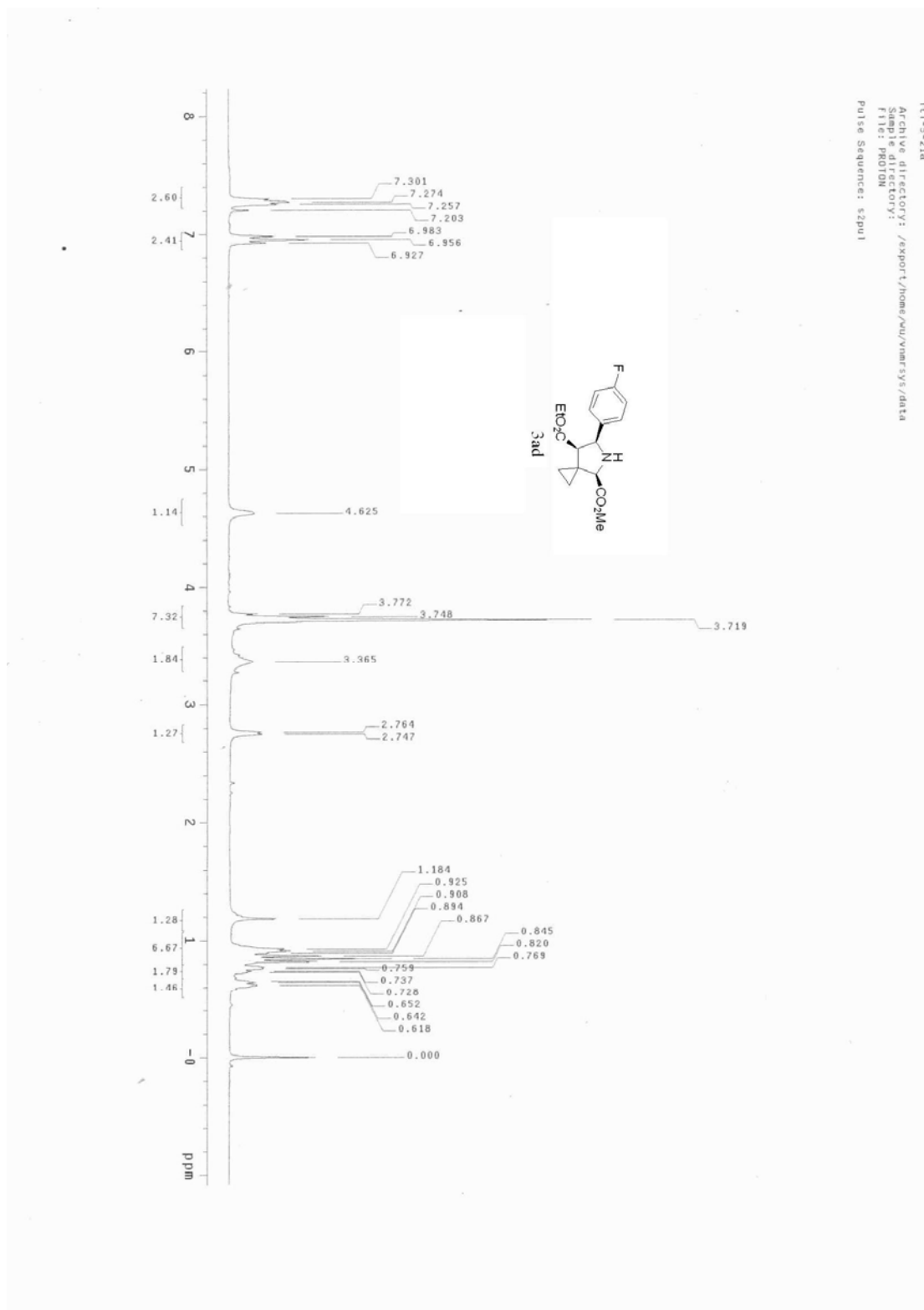


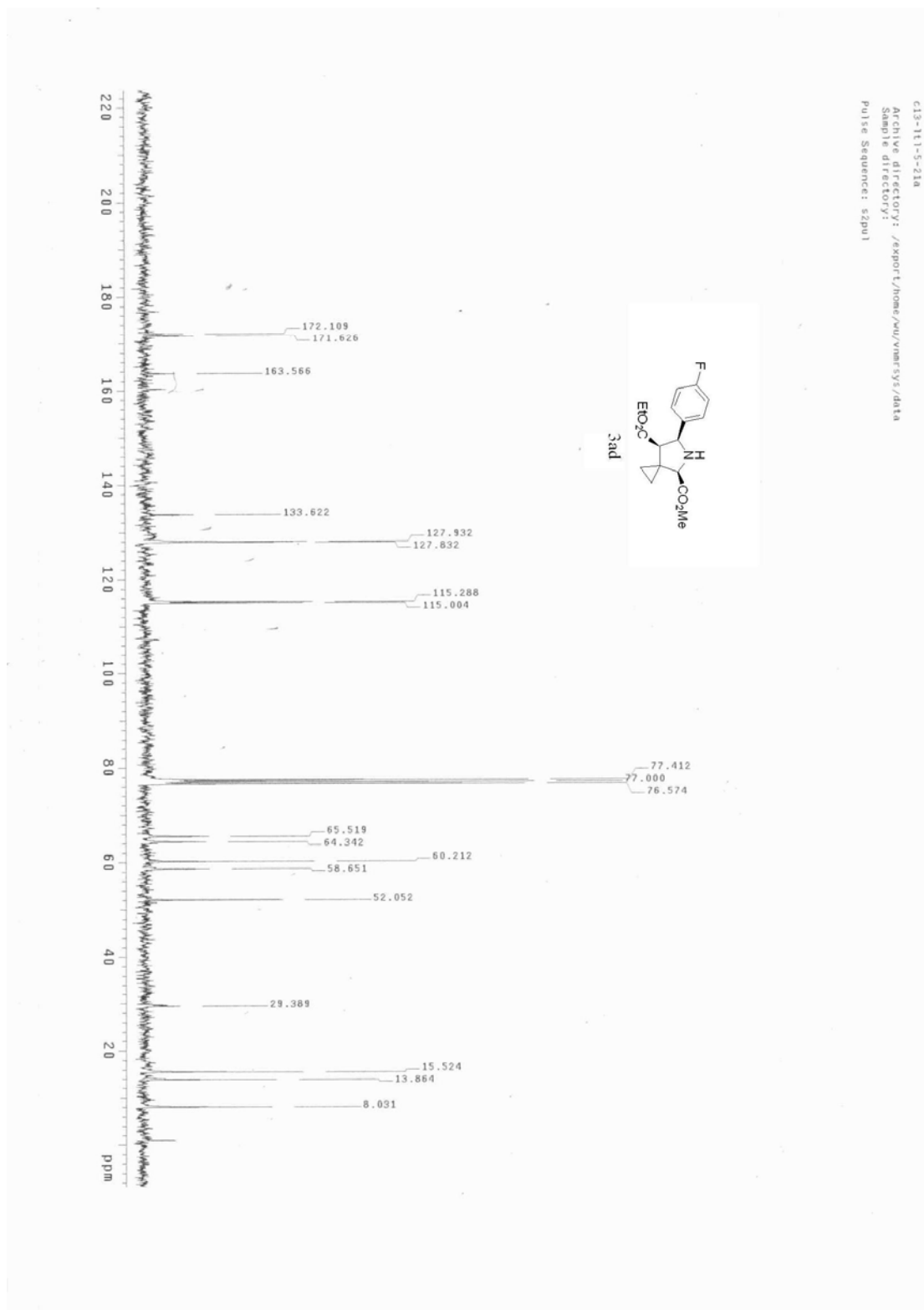
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SFO 125.130 MHz
AQ 0.10000000
DECOUPLE H1, 300.0821962 MHz
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continuously on
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DATA ACQUISITION
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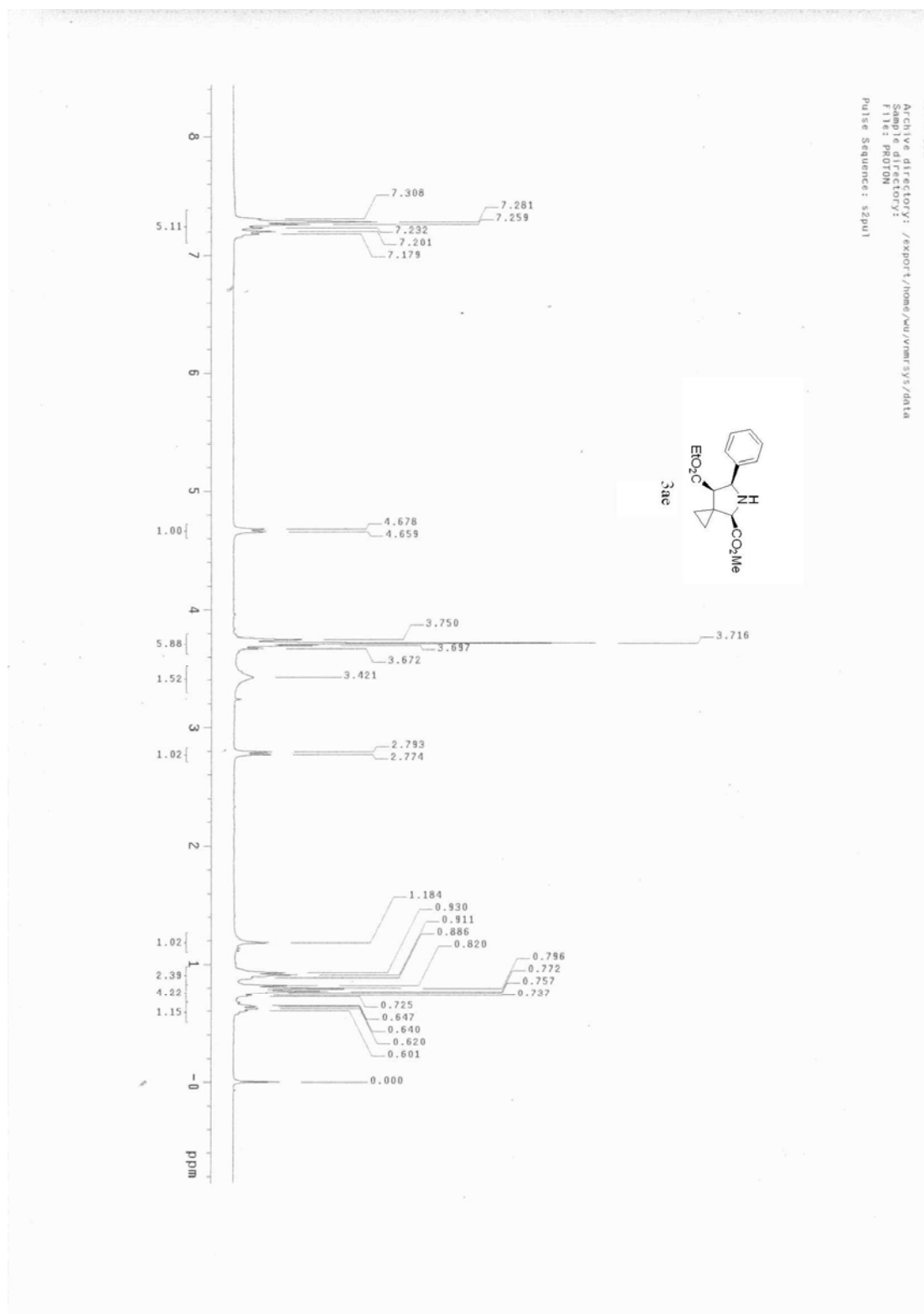


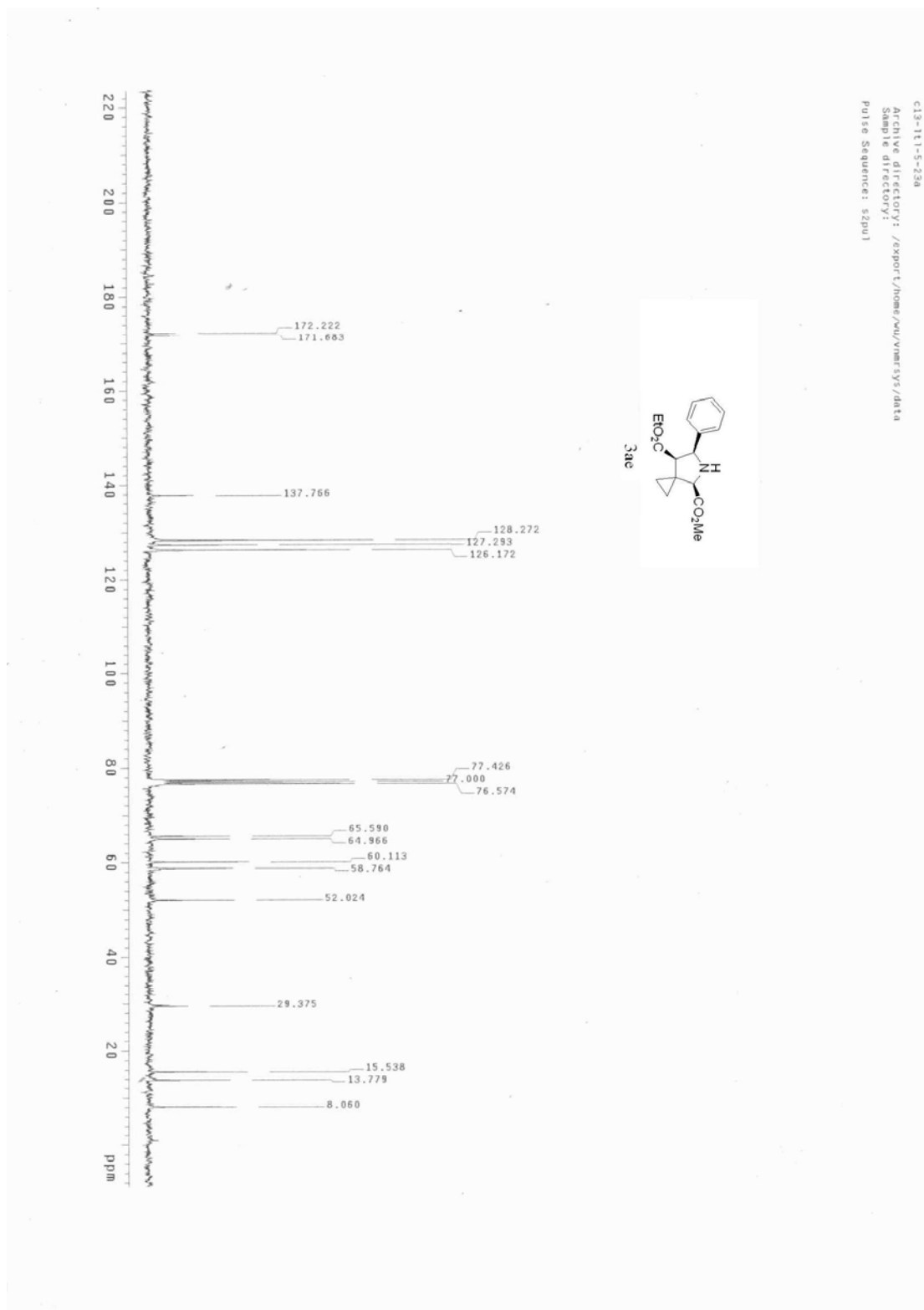


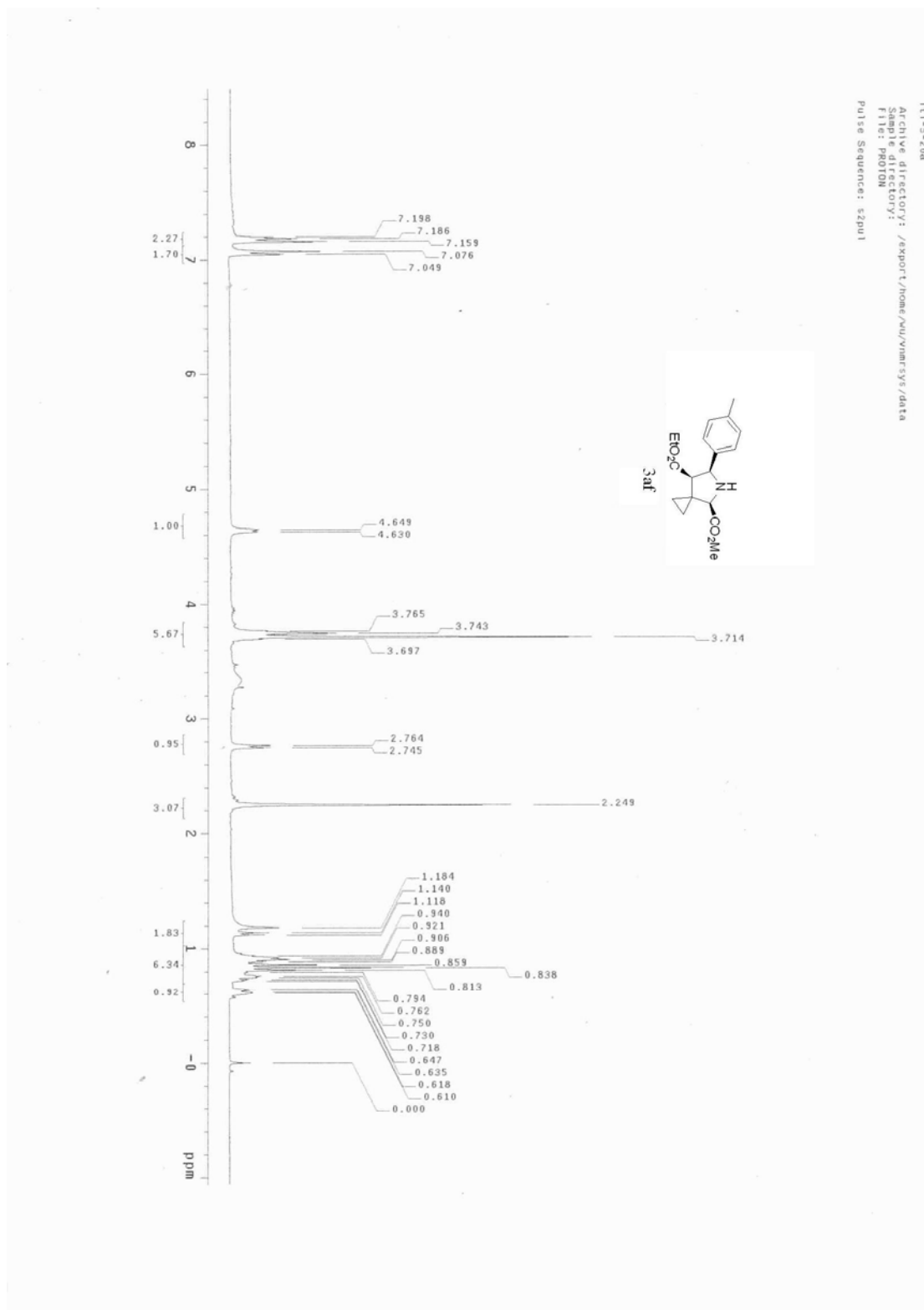


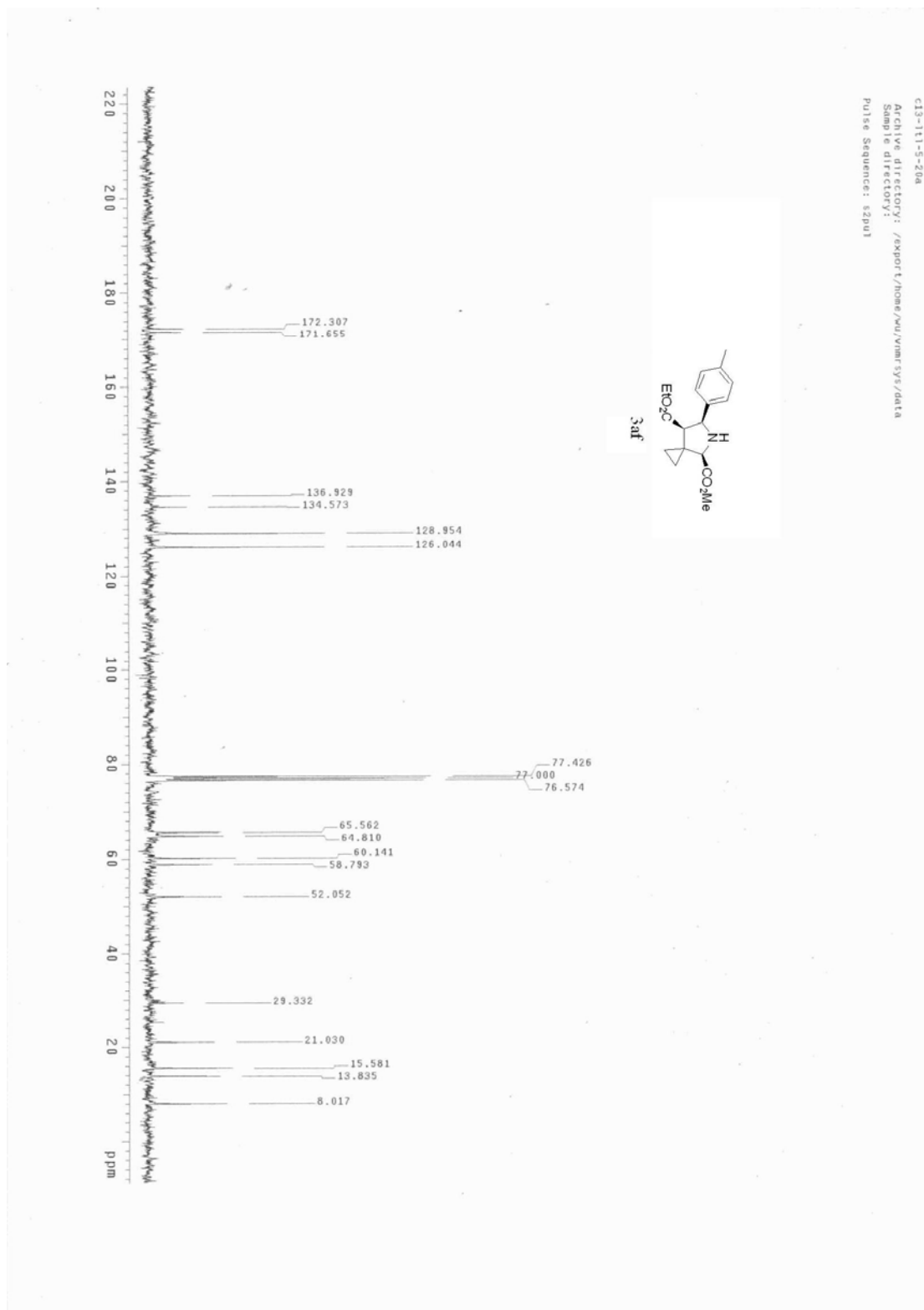


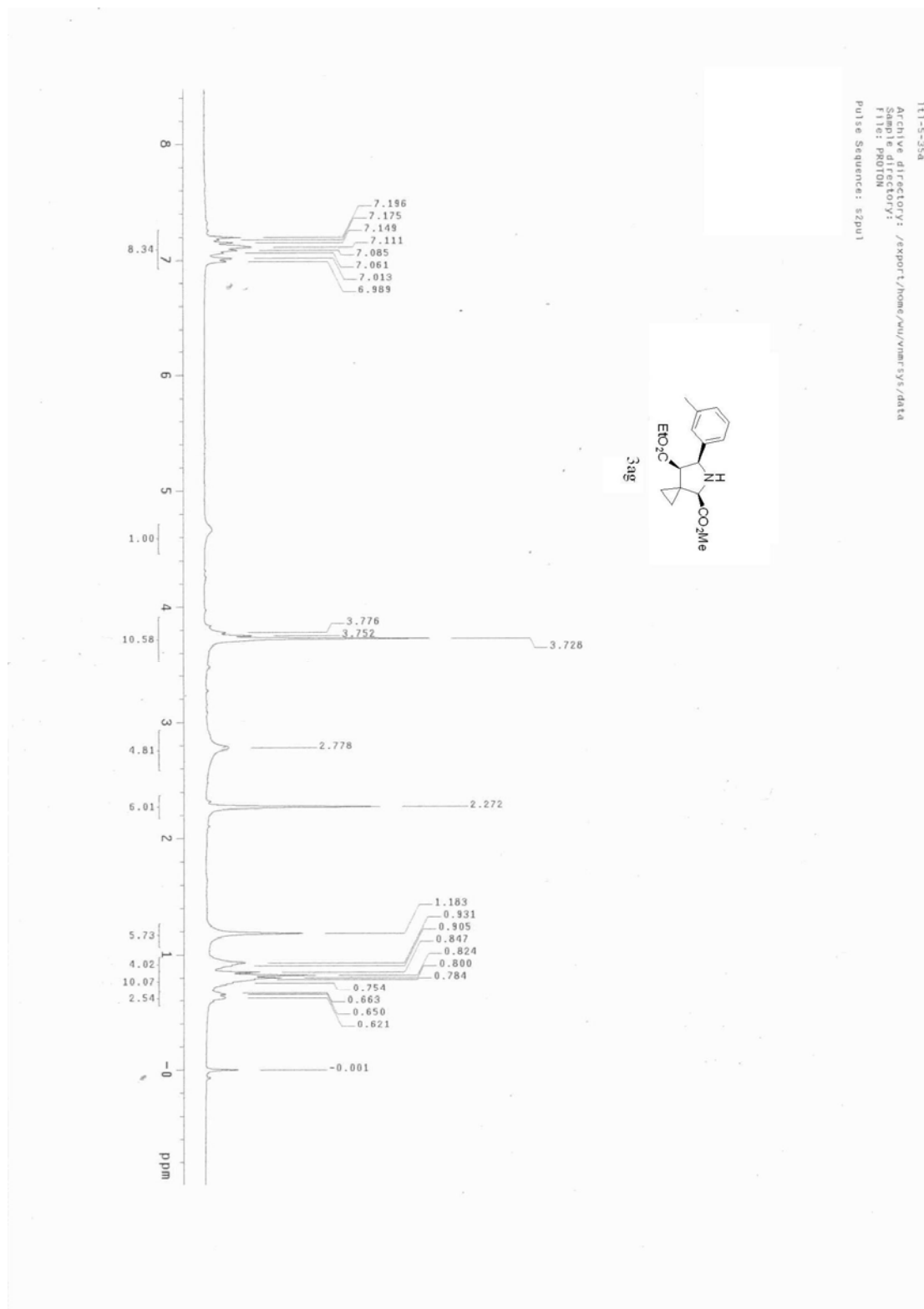


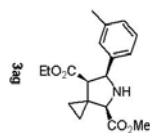
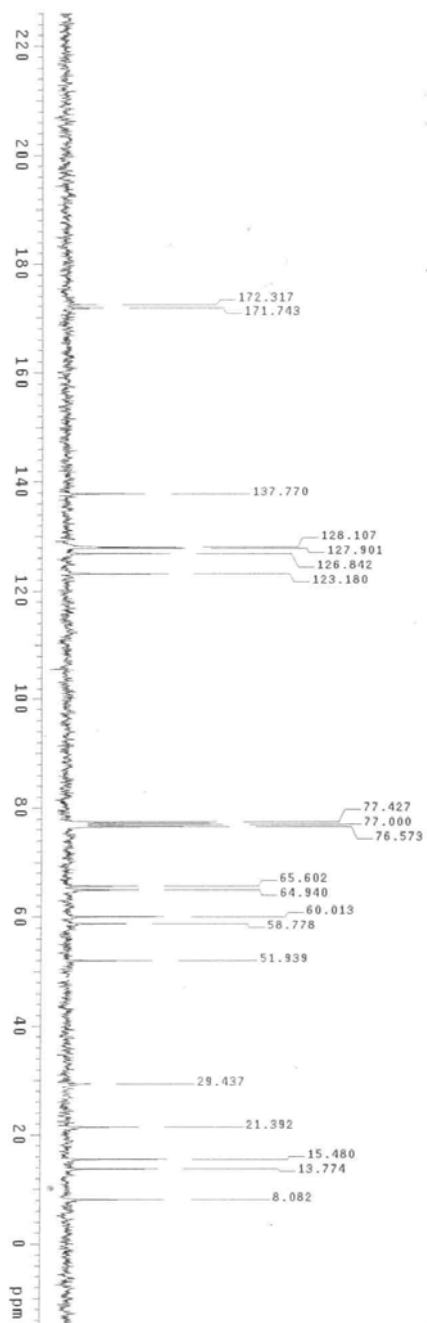




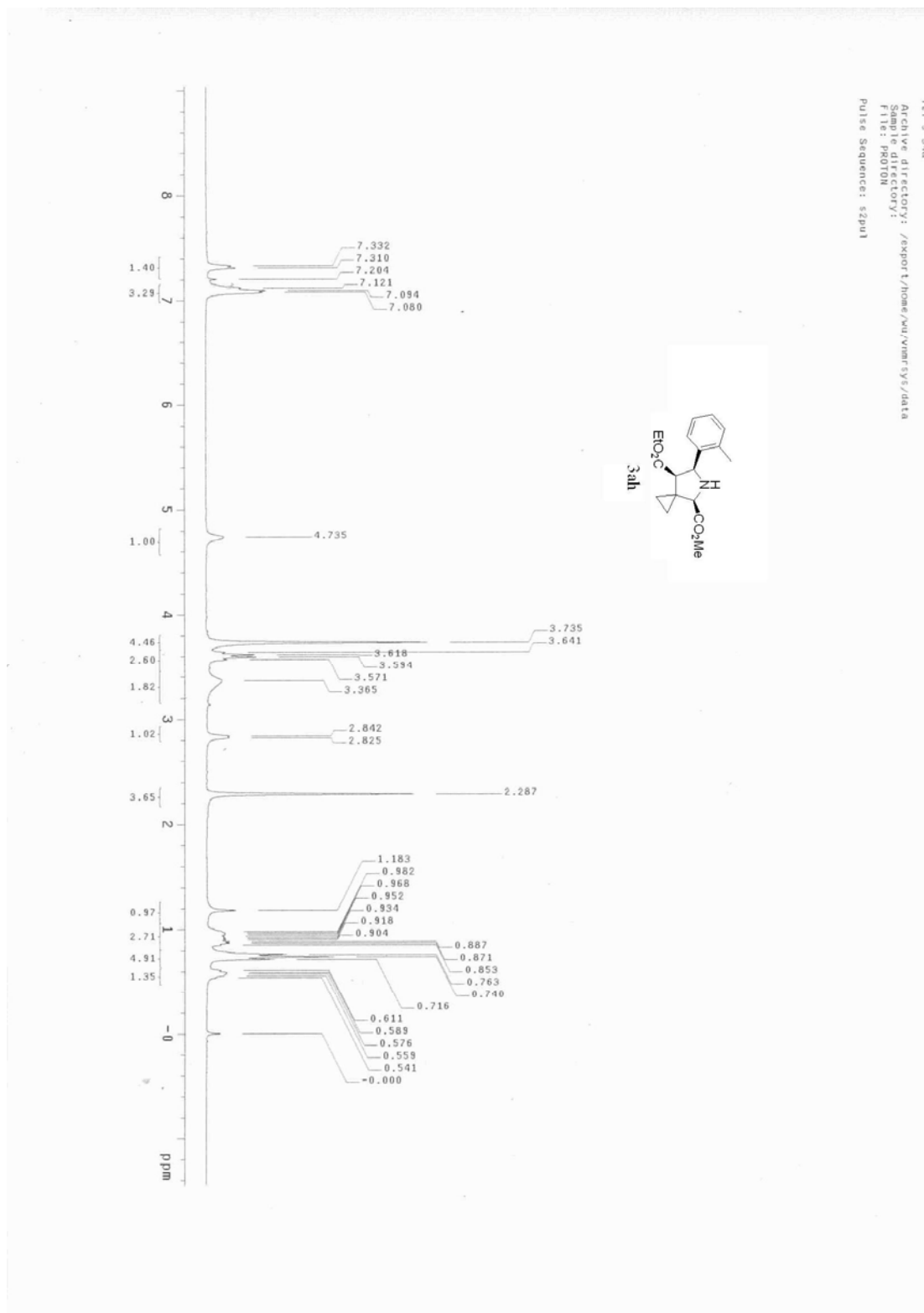


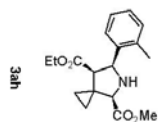
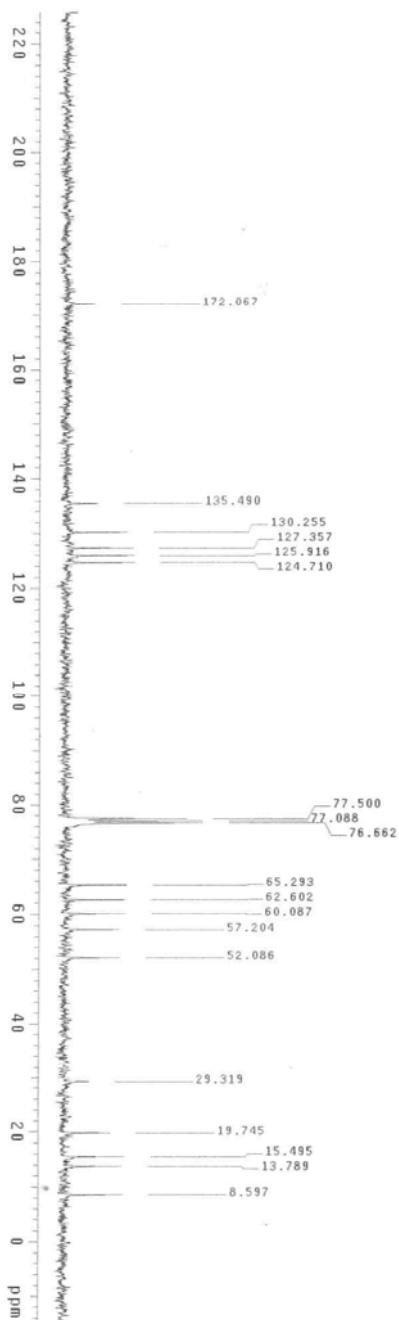




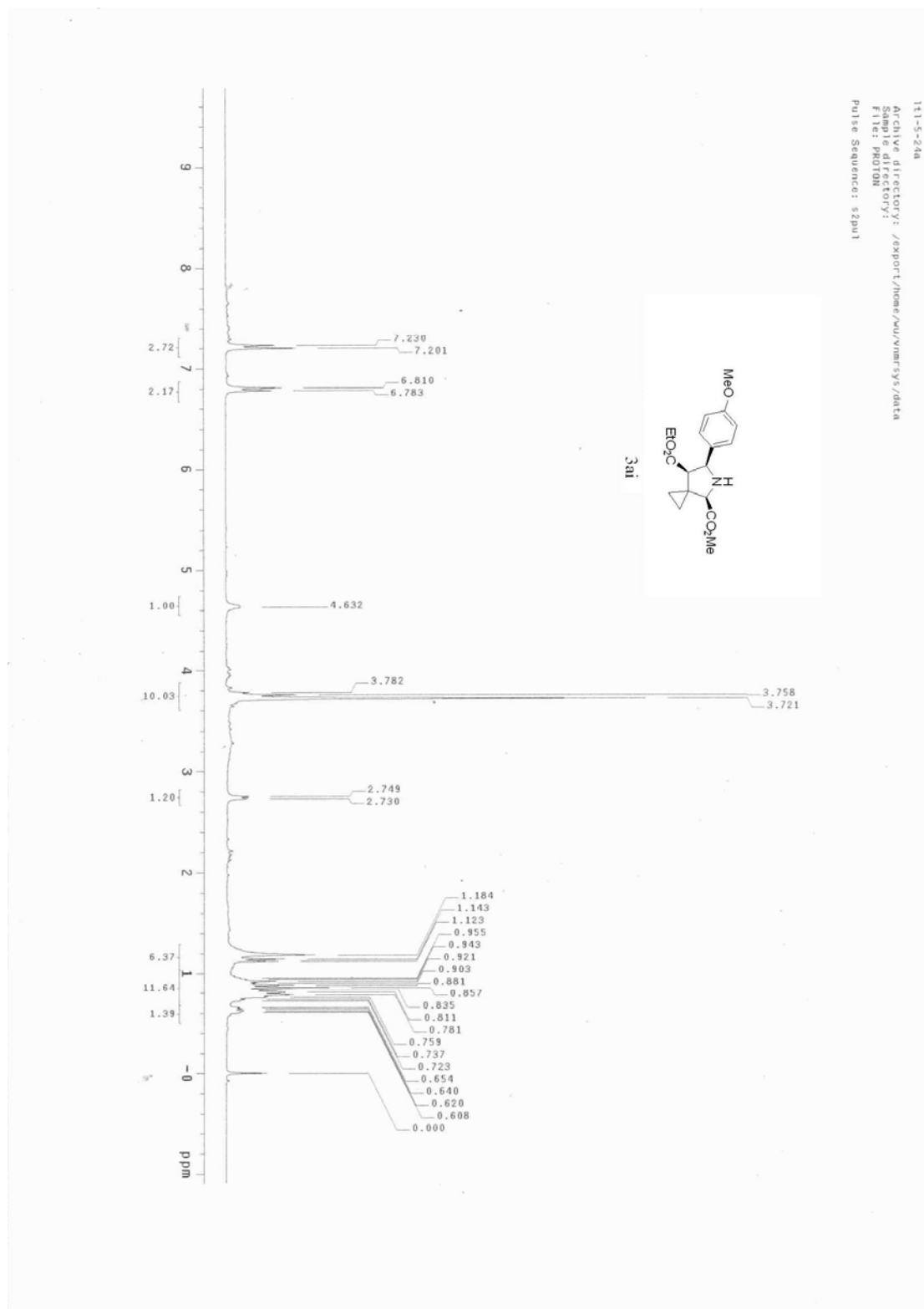


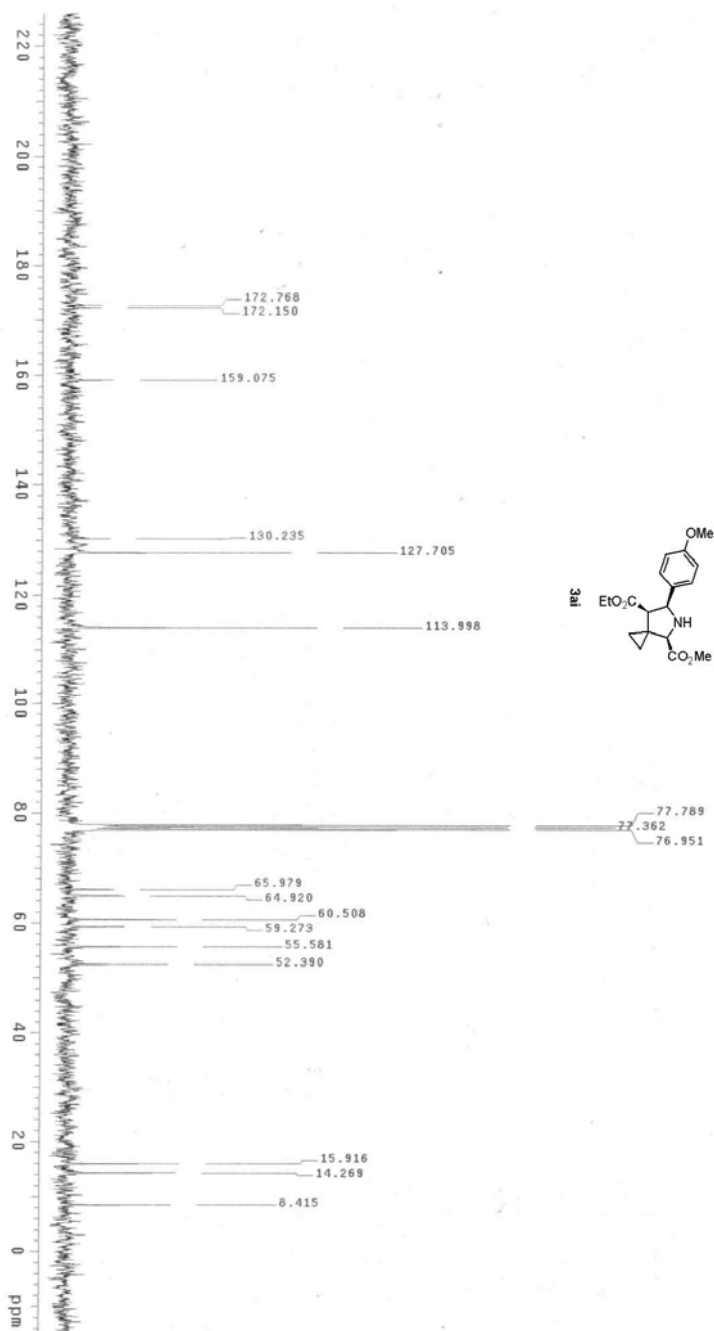
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120 repetitions
OBSERVE C13, 75.4552461 MHz
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DATA PROCESSING
Line broadening 4.0 HZ
Gamma 2.00000000
Total time 1 hr, 27 min, 30 sec



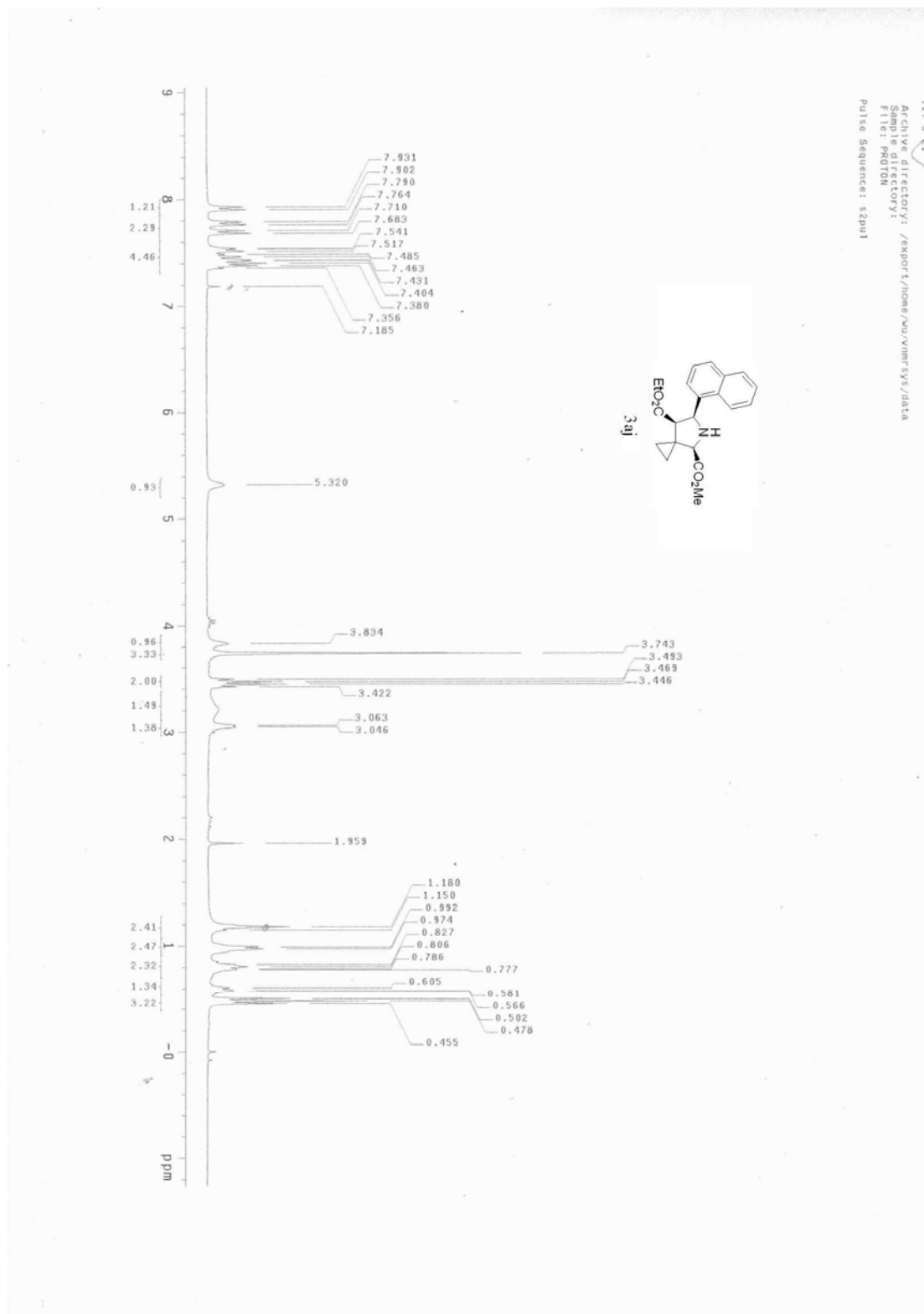


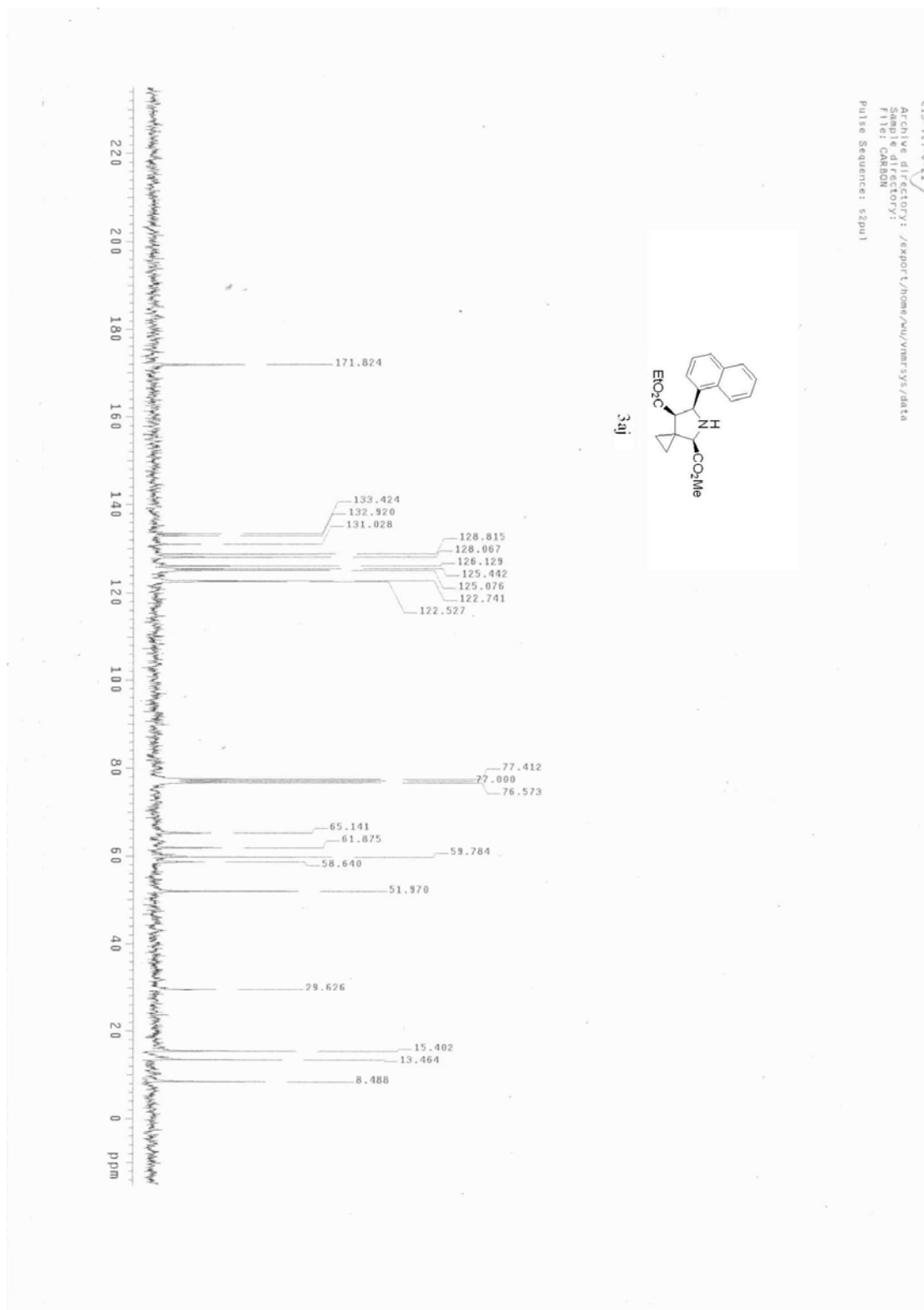
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OBSERVE CH3 75.4552472 MHz
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Power 40 db
continuously on
WALTZ-16 modulated
DATA PROCESSING
F2 size 32768
Total time 1 hr, 27 min, 39 sec

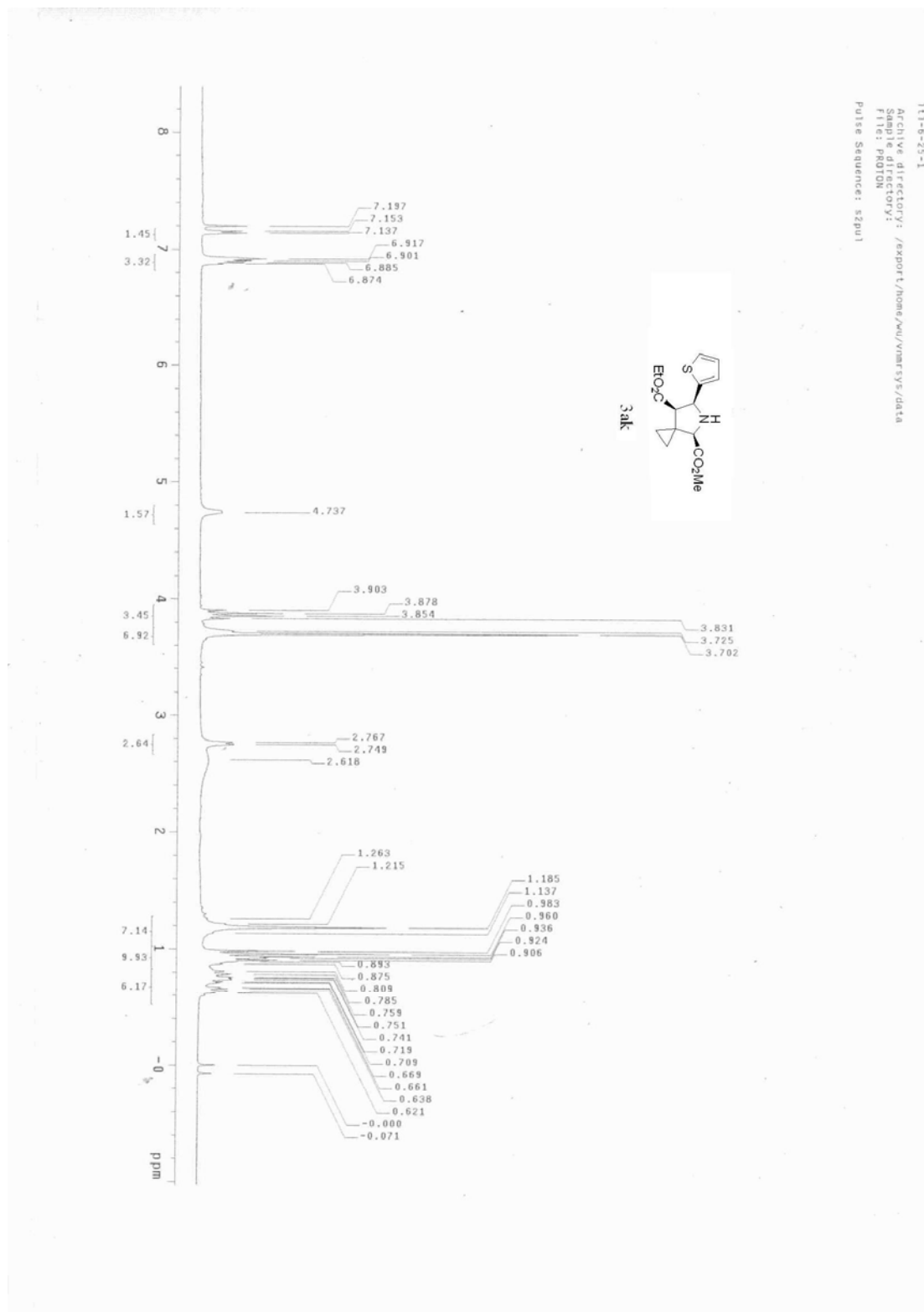


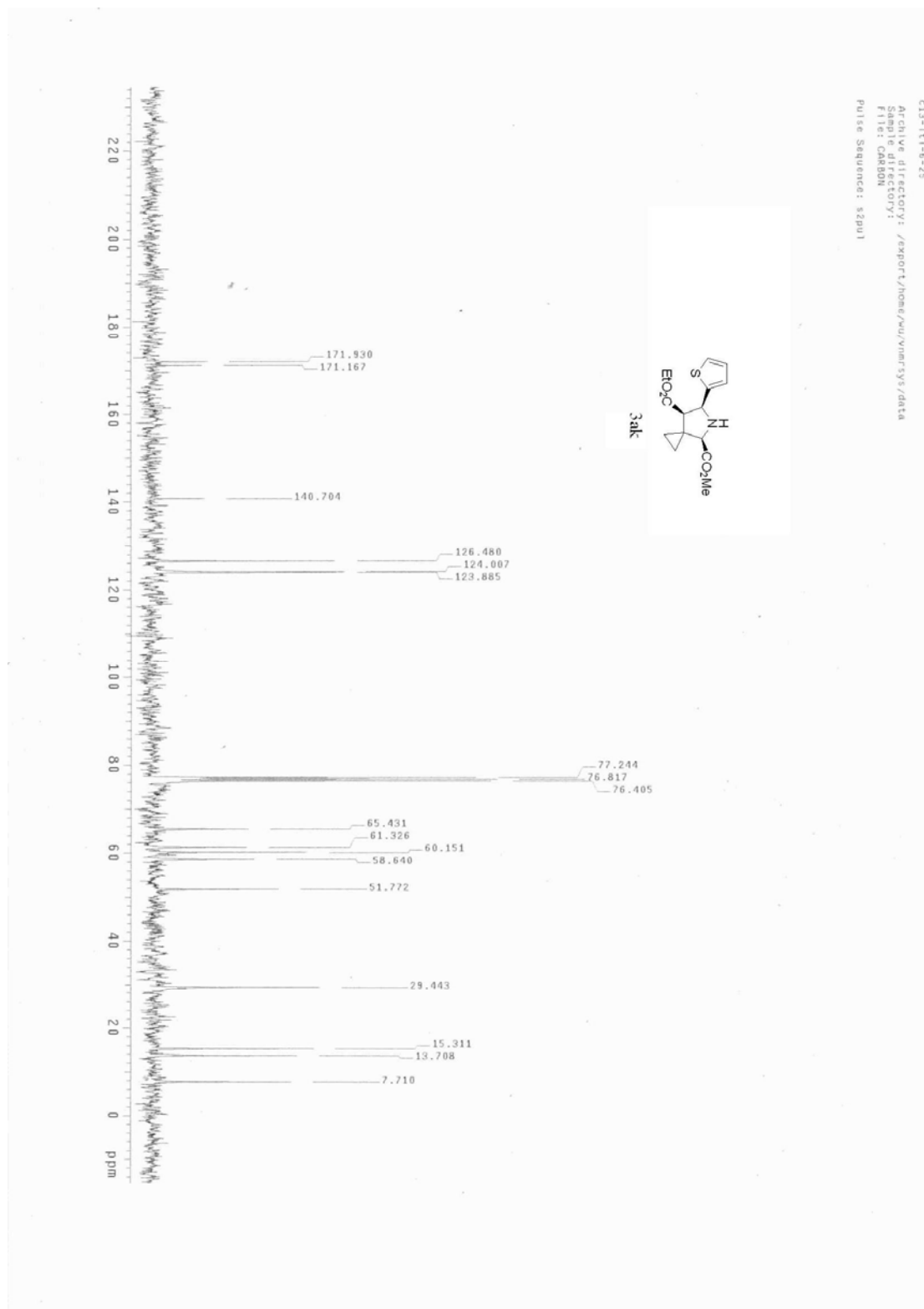


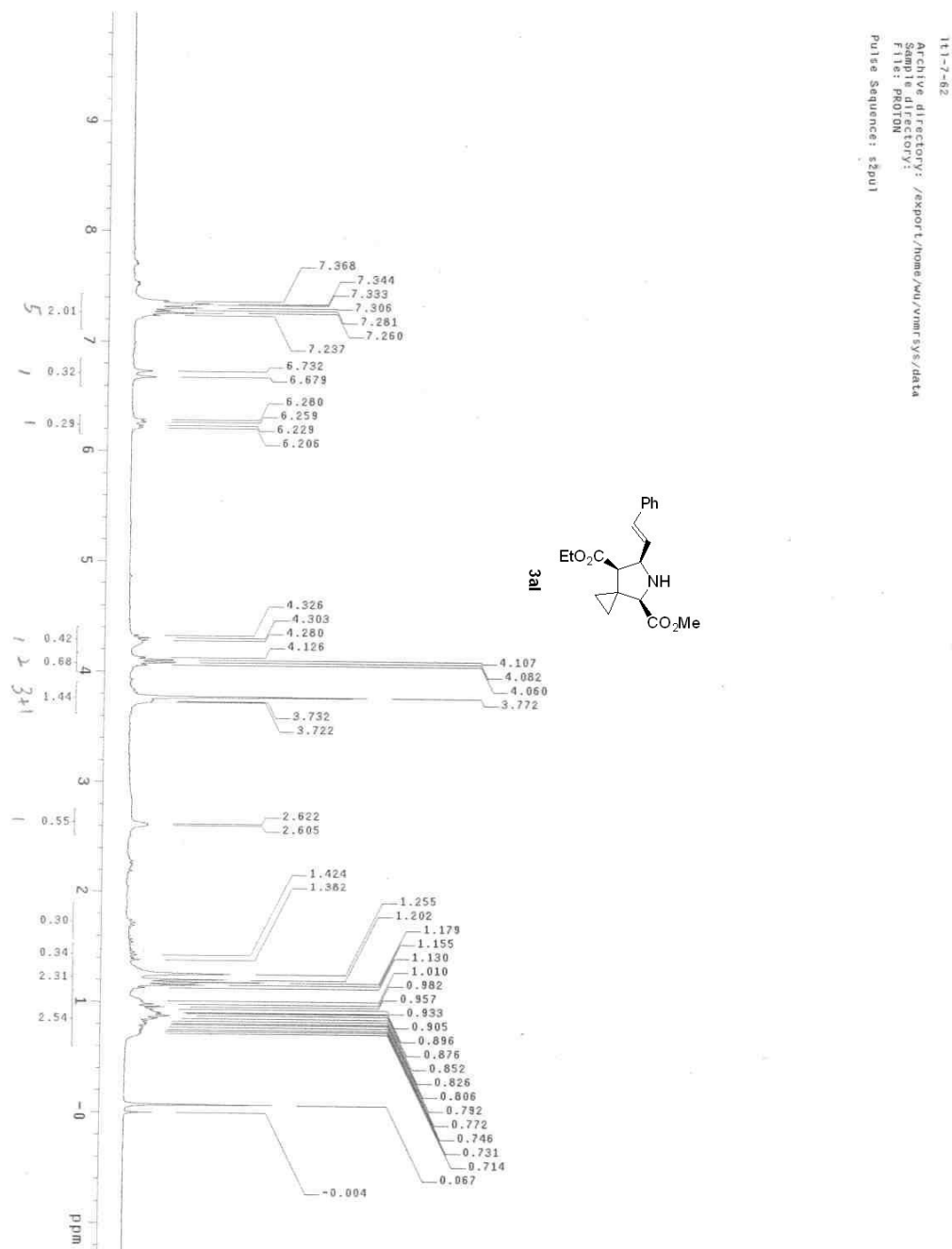
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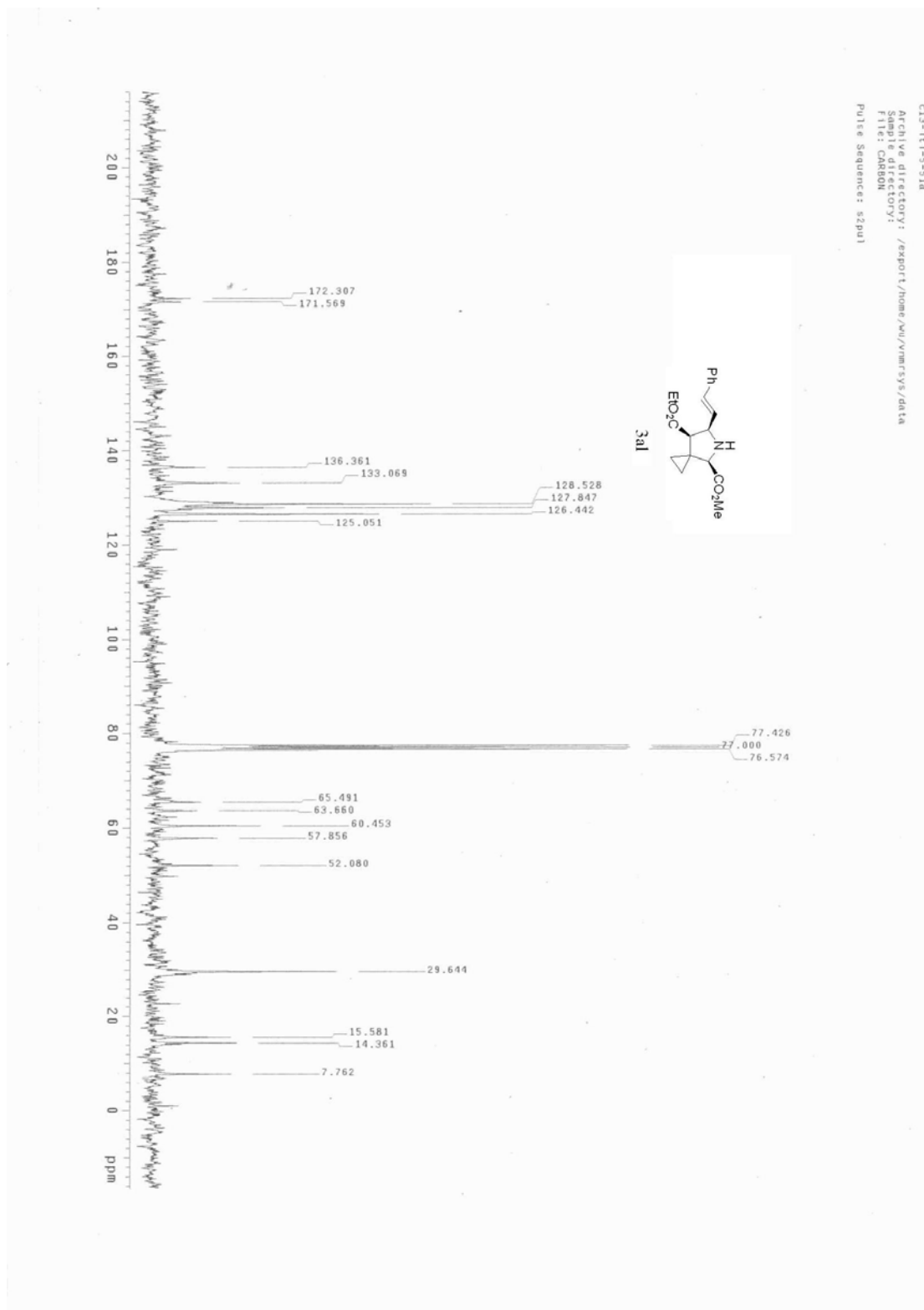


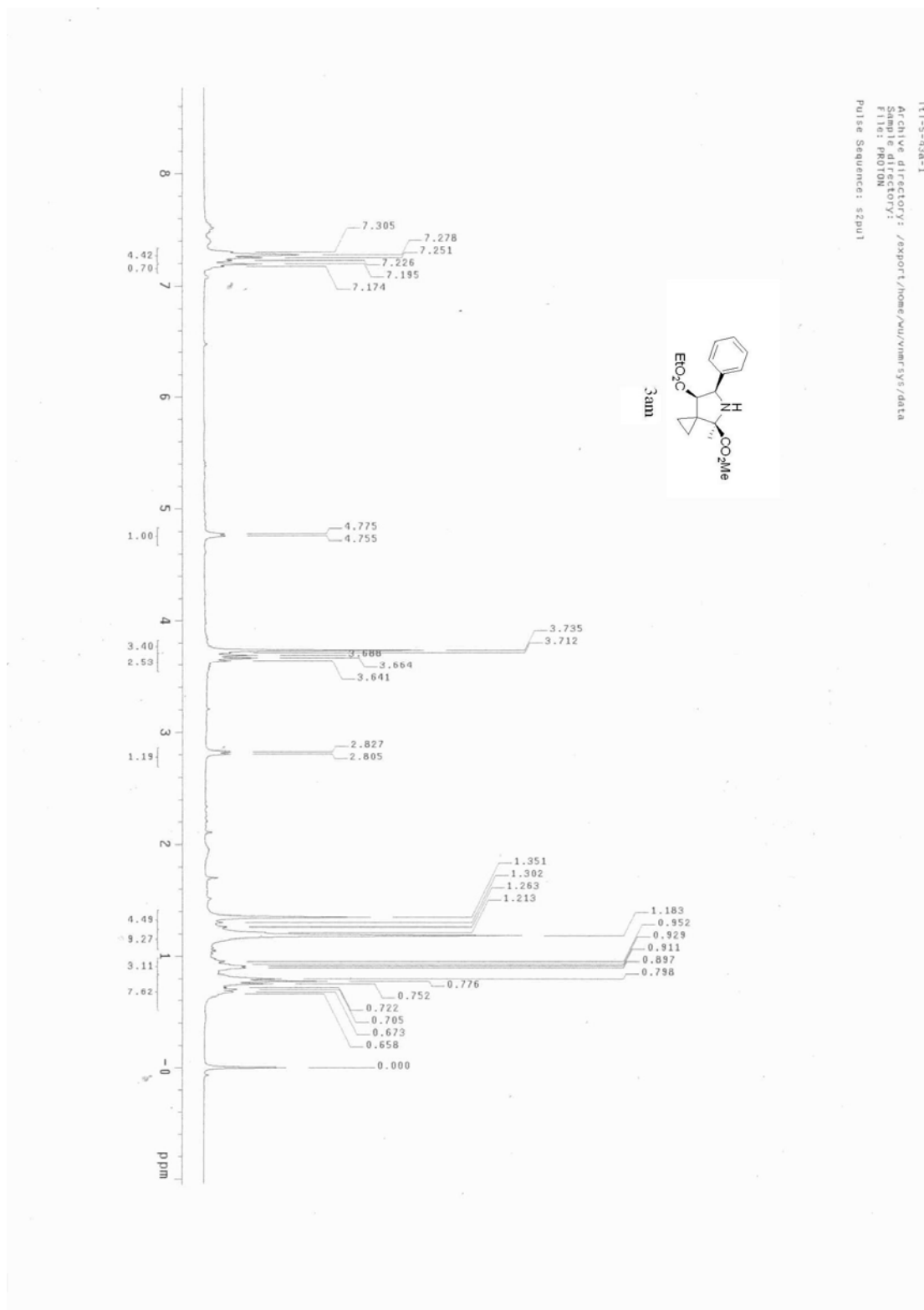


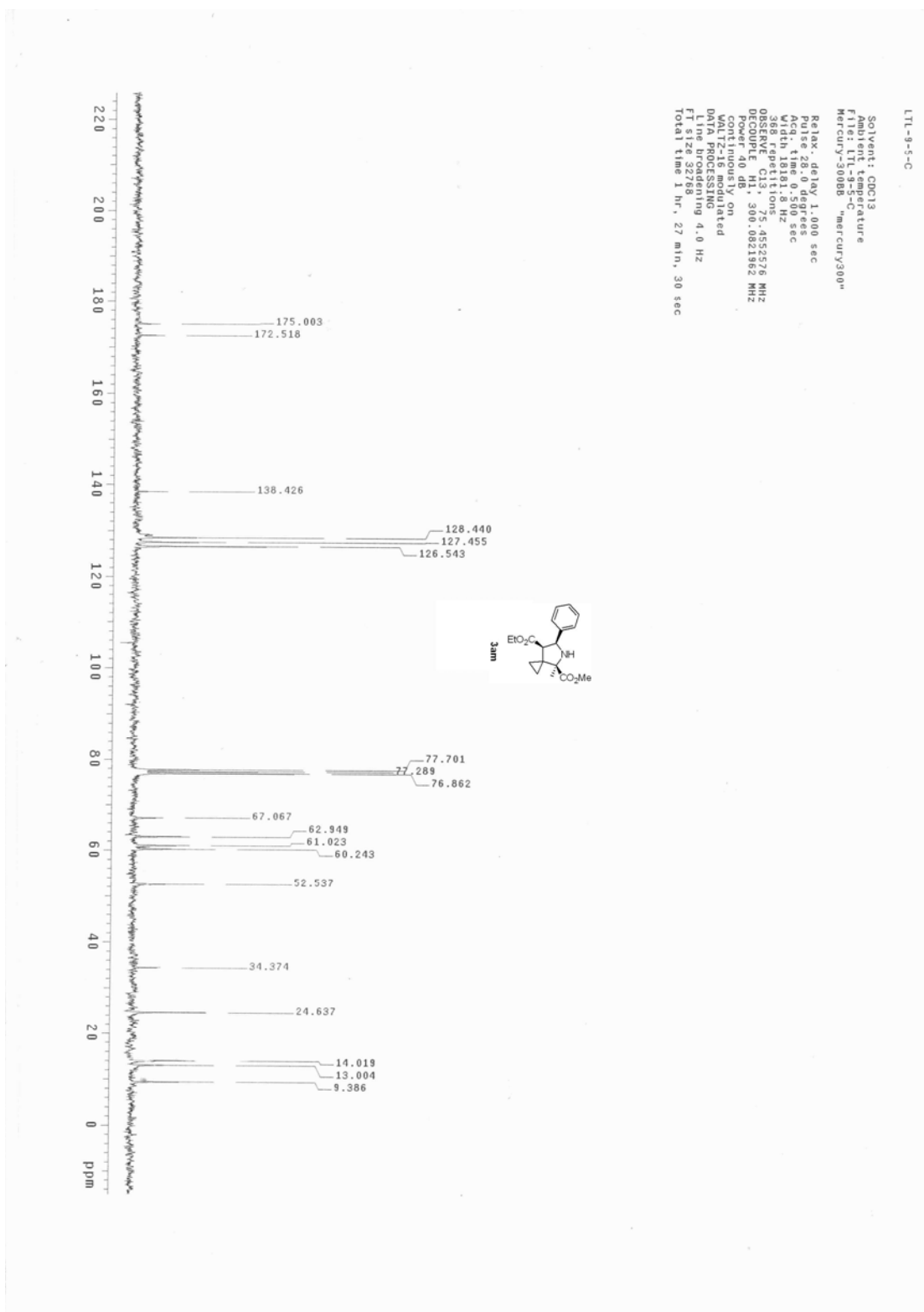


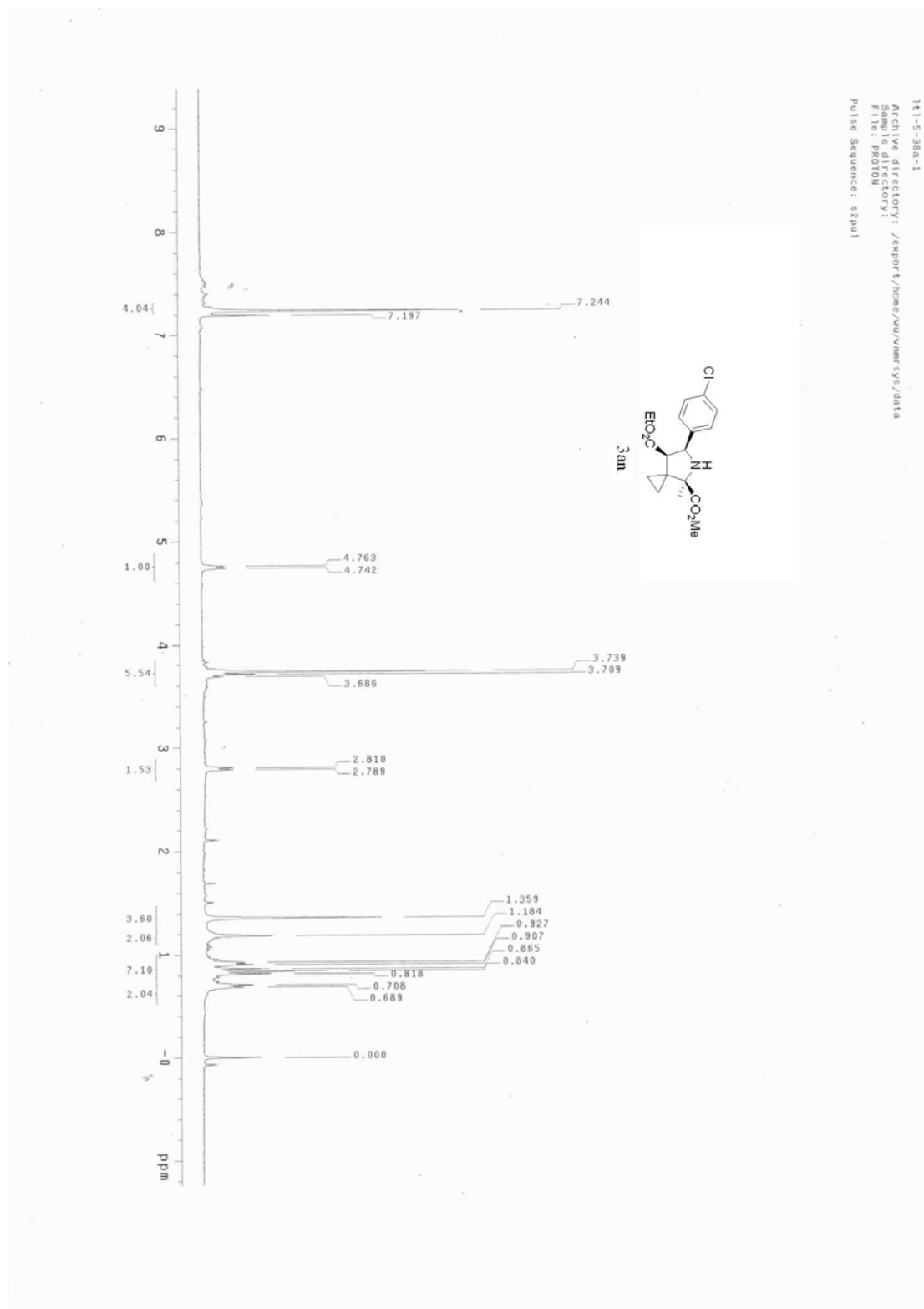


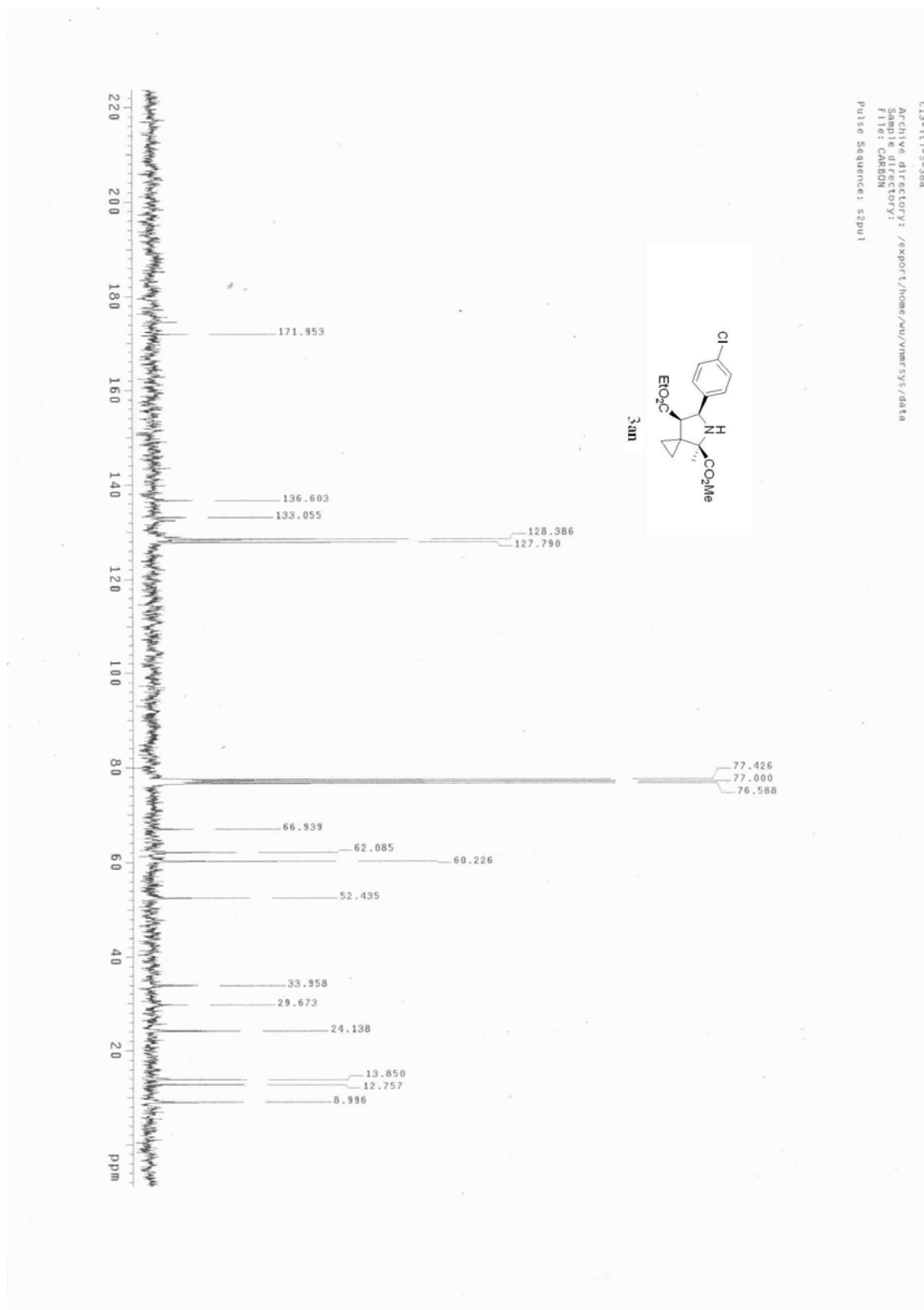


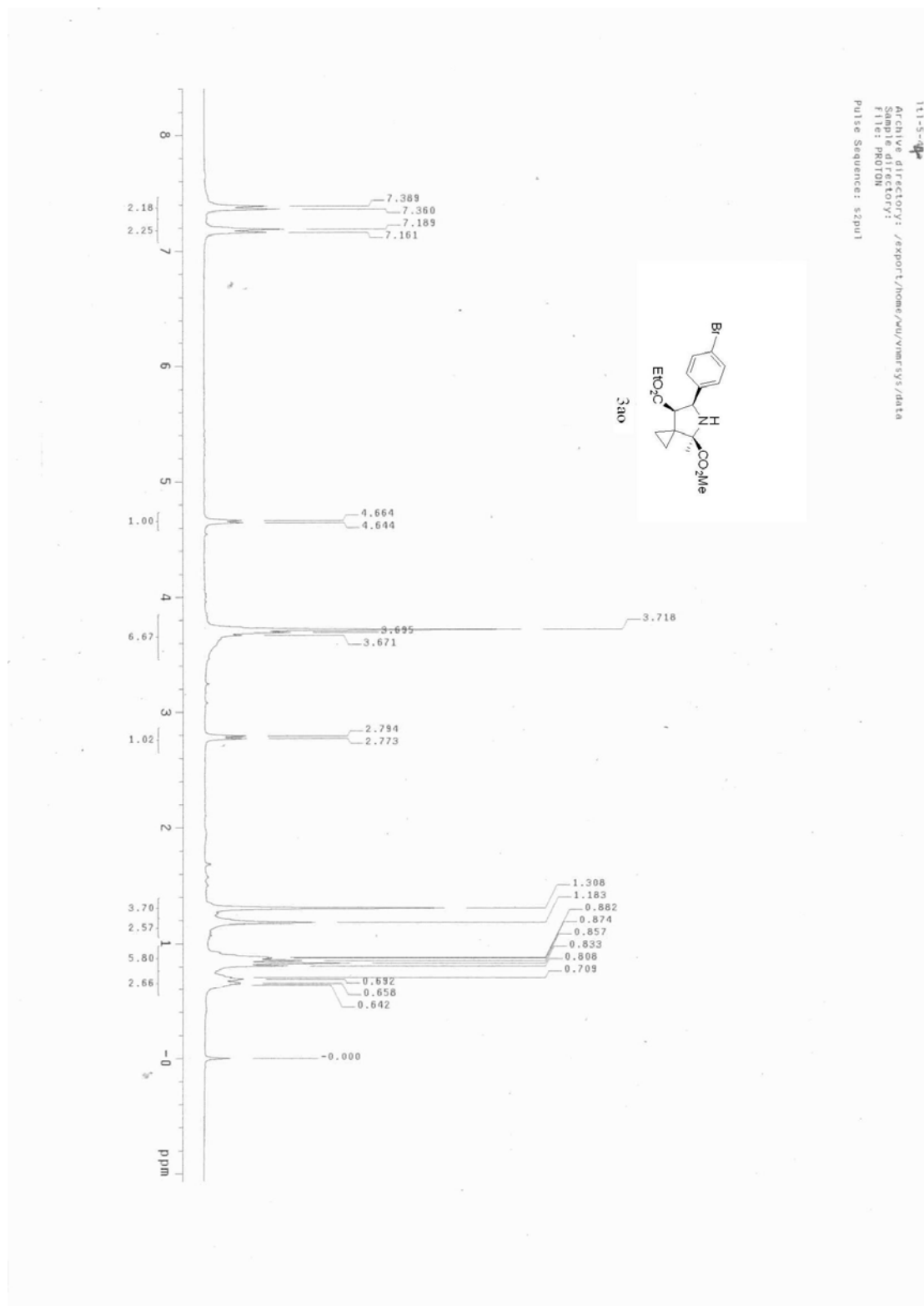


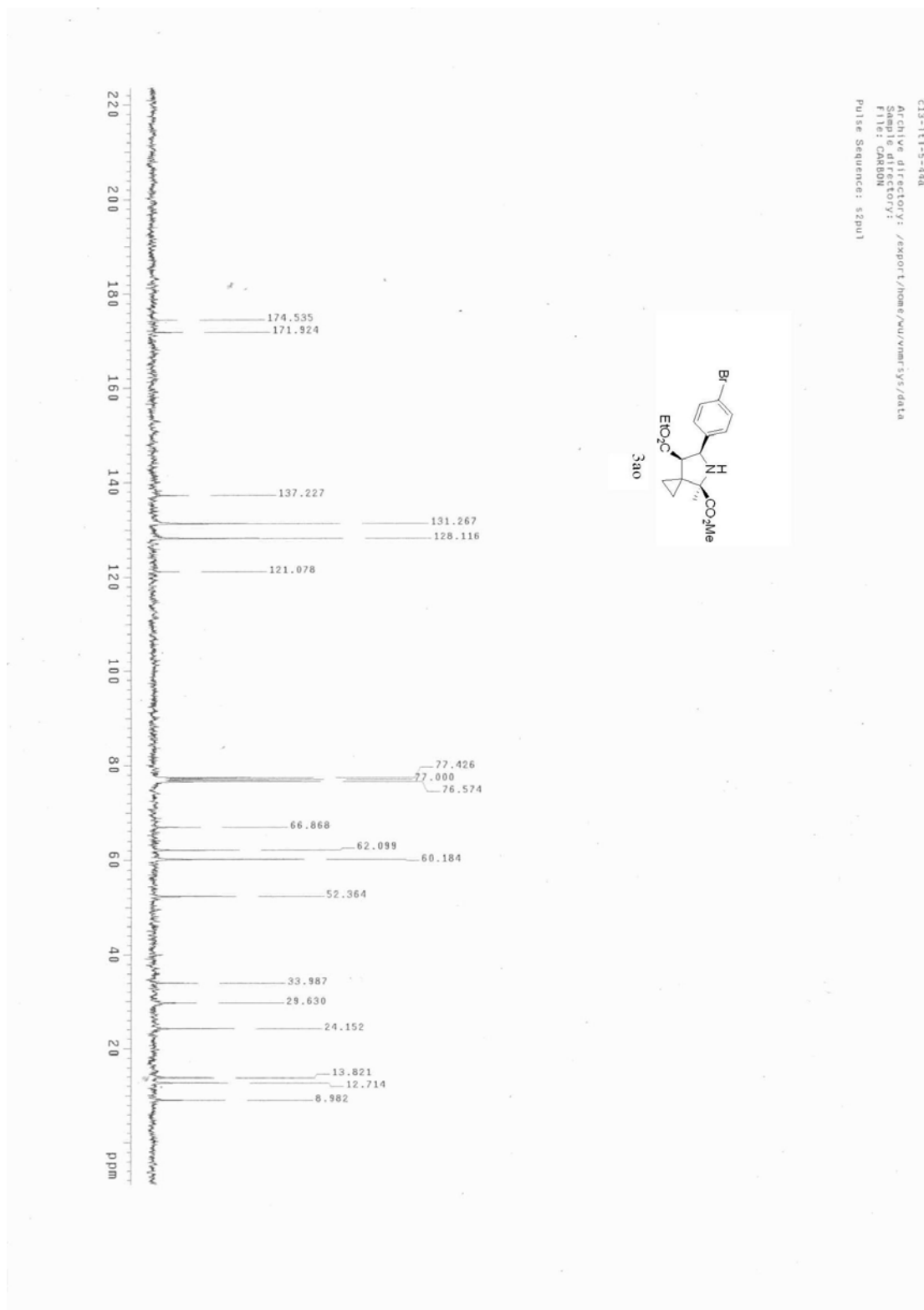


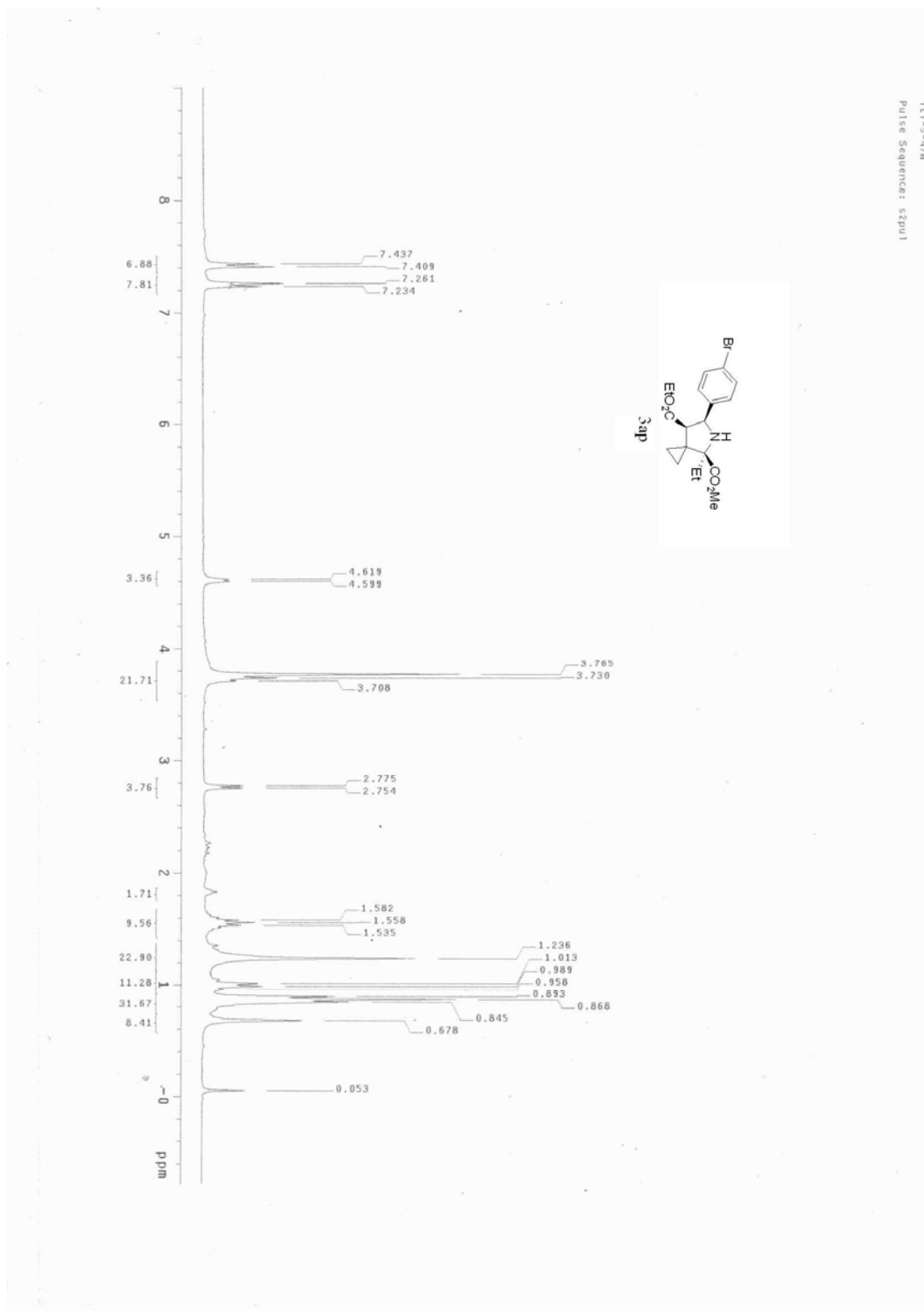


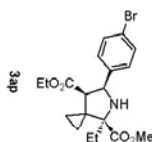
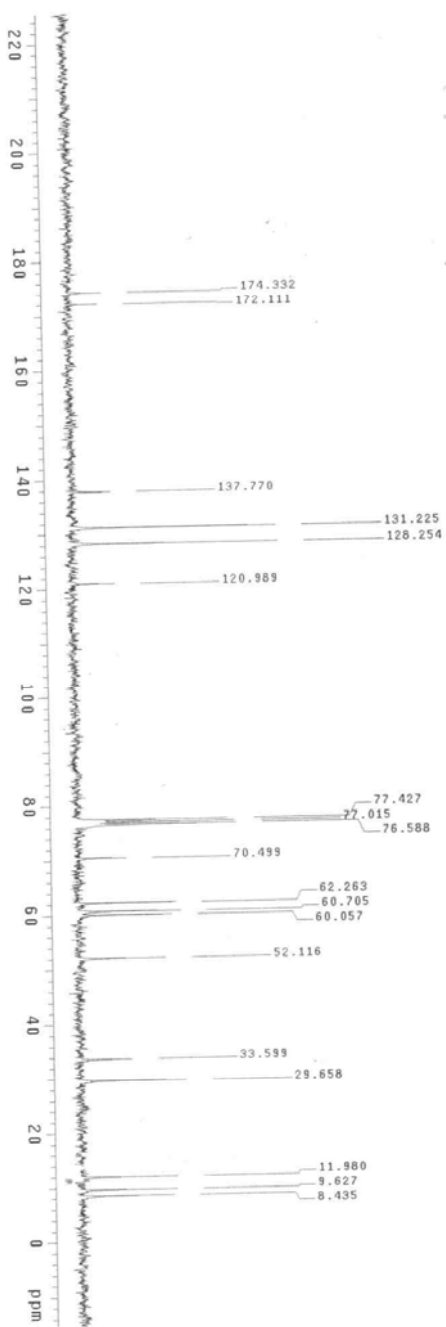




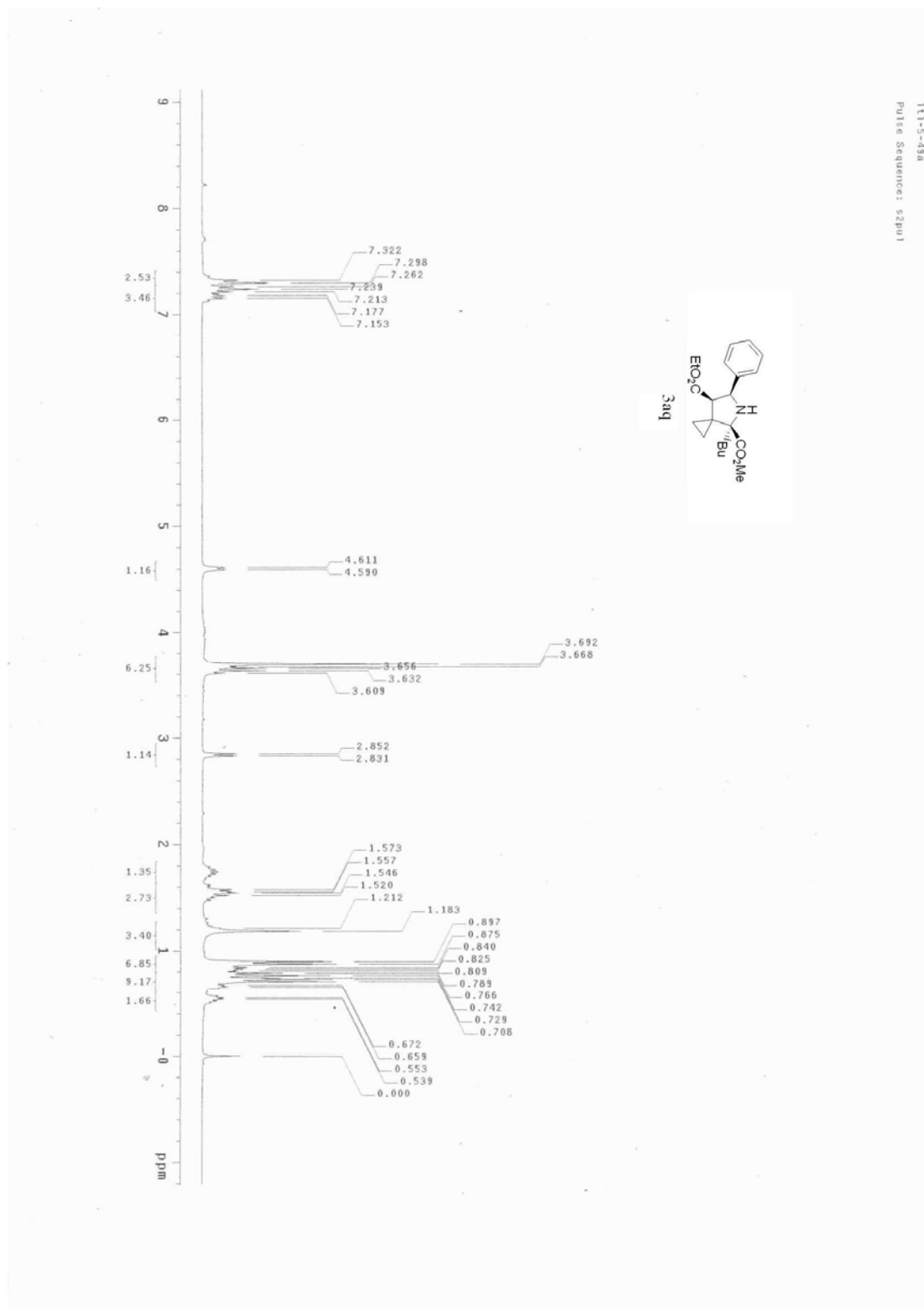


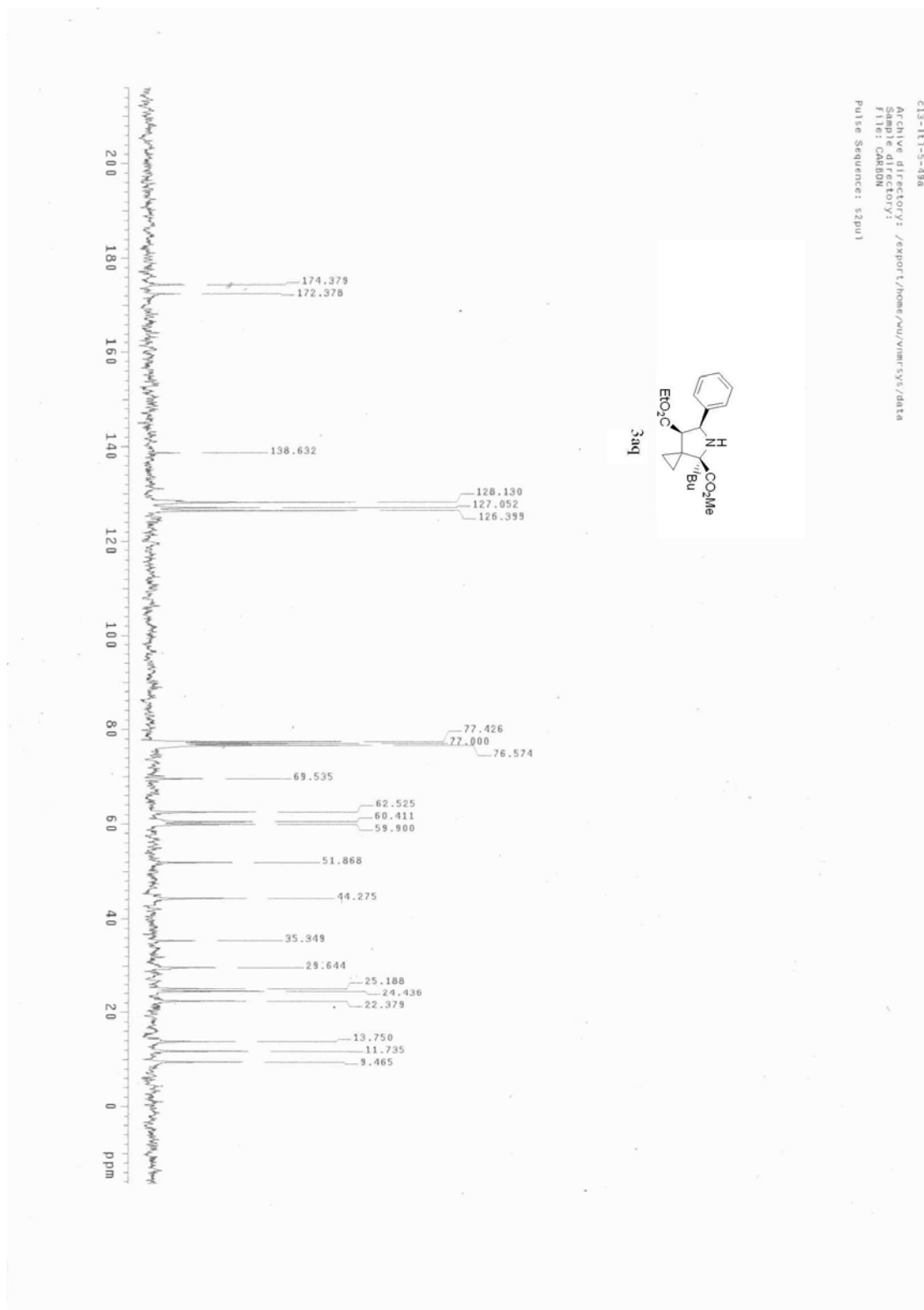






C13-1t1-9-5b
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Pulse delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.500 sec
Width 18181.8 Hz
Observed frequency 50.625450 MHz
Observed chemical shift 5.4552794 MHz
Decouple H1 300.0821962 MHz
Power 40 dB
Continuously on
Pulse program
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 27 min, 30 sec

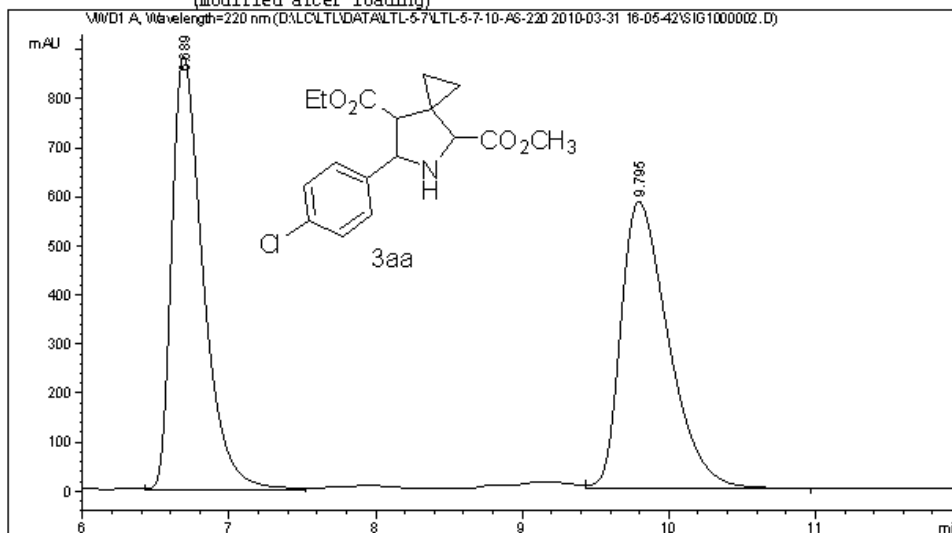




Data File D:\LC\LTL\DATA\LTL-5-7\LTL-5-7-10-AS-220 2010-03-31 16-05-42\SIG1000002.D
 Sample Name: LTL-5-7-1.0-AS-220

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 32
Injection Date  : 3/31/2010 4:18:05 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-7\LTL-5-7-10-AS-220 2010-03-31 16-05-42\ASH-10-90-
10ML-220NM-60MIN.M
Last changed    : 11/15/2009 6:41:50 PM by DXQ
Analysis Method : D:\LC\LTL\DATA\LTL-5-7\LTL-5-7-10-AS-220 2010-03-31 16-05-42\SIG1000002.D\
D.M (ASH-10-90-10ML-220NM-60MIN.M)
Last changed    : 4/3/2010 9:49:57 AM by THL
(modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

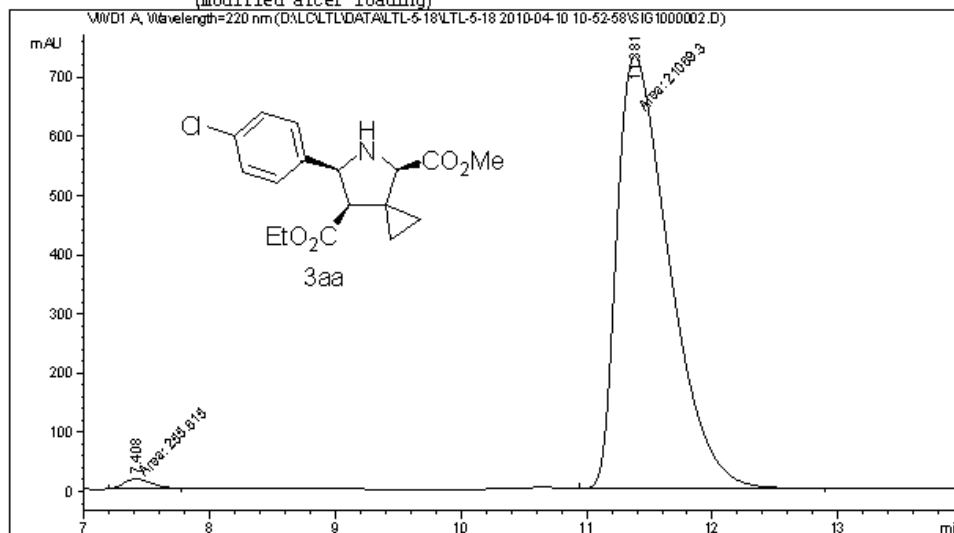
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.689	WV	0.2253	1.30994e4	883.82678	49.8755
2	9.795	WB	0.3455	1.31648e4	585.05493	50.1245

Totals : 2.62643e4 1468.88171

Data File D:\LC\LTL\DATA\LTL-5-18\LTL-5-18 2010-04-10 10-52-58\SIG1000002.D
 Sample Name: LTL-5-18

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 25
Injection Date  : 4/10/2010 11:05:26 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-18\LTL-5-18 2010-04-10 10-52-58\ASH-10-90-10ML-220NM-
14MIN.M
Last changed    : 4/3/2010 9:58:28 AM by THL
Analysis Method : D:\LC\LTL\DATA\LTL-5-18\LTL-5-18 2010-04-10 10-52-58\SIG1000002.D\DA.M (
ASH-10-90-10ML-220NM-14MIN.M)
Last changed    : 4/10/2010 11:22:17 AM by tmc
(modified after loading)
    
```



Area Percent Report

```

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.408	MM	0.2554	255.61493	16.67875	1.1987
2	11.381	MM	0.4807	2.10693e4	730.46185	98.8013
Totals :				2.13250e4	747.14061	

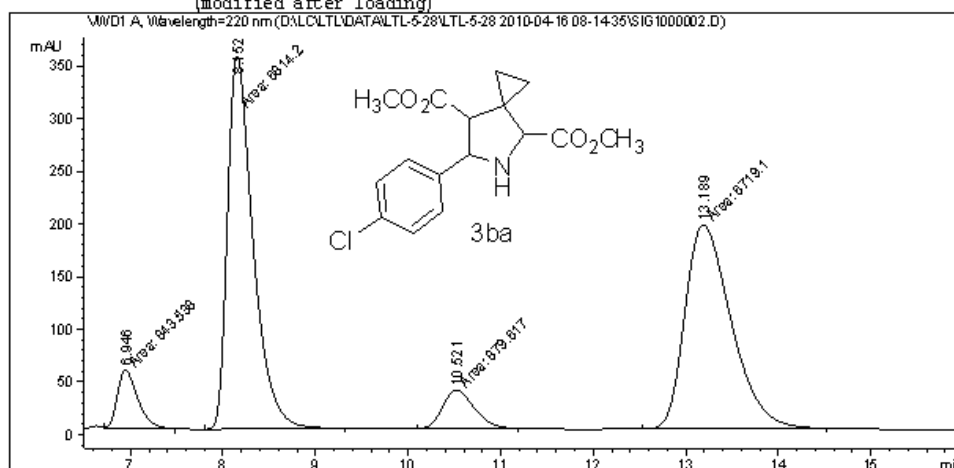
Instrument 1 4/10/2010 11:22:23 AM tmc

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\SIG1000002.D
 Sample Name: LTL-5-28A

```

=====
Acq. Operator   : LTL                      Seq. Line :    2
Acq. Instrument : Instrument 1              Location  : Vial 24
Injection Date  : 4/16/2010 8:27:09 AM     Inj       :    1
                                                Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\ASH-10-90-10ML-220NM-
20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\SIG1000002.D\DA.M (
ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/16/2010 9:38:00 AM by TMC
(modified after loading)
    
```



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

```

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.946	MM	0.2547	843.53784	55.20173	5.5291
2	8.152	MM	0.3208	6814.19873	354.07333	44.6644
3	10.521	MM	0.3992	879.61652	36.72753	5.7655
4	13.189	MM	0.5782	6719.09766	193.67729	44.0410

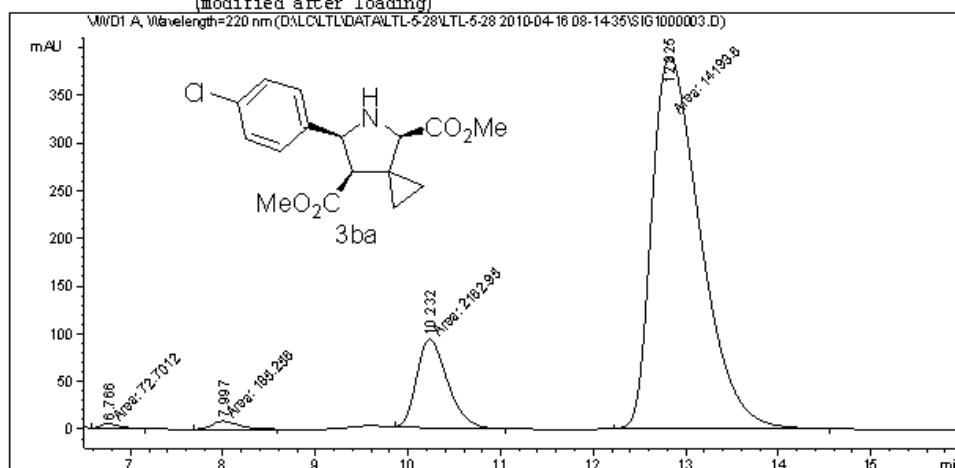
Totals : 1.52565e4 639.67988

=====
 *** End of Report ***

Data File D:\LC\LTL\DATA\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\SIG1000003.D
 Sample Name: LTL-5-28B

```

=====
Acq. Operator   : LTL                      Seq. Line :    3
Acq. Instrument : Instrument 1              Location  : Vial 25
Injection Date  : 4/16/2010 8:48:29 AM     Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\ASH-10-90-10ML-220NM-
20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-28\LTL-5-28 2010-04-16 08-14-35\SIG1000003.D\DA.M (
ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/16/2010 9:36:37 AM by TMC
(modified after loading)
    
```



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

```

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.766	MM	0.2508	72.70116	4.83173	0.4376
2	7.997	MM	0.3480	185.25603	8.87340	1.1150
3	10.232	MM	0.3886	2162.94849	92.77558	13.0184
4	12.825	MM	0.6055	1.41936e4	390.71750	85.4290

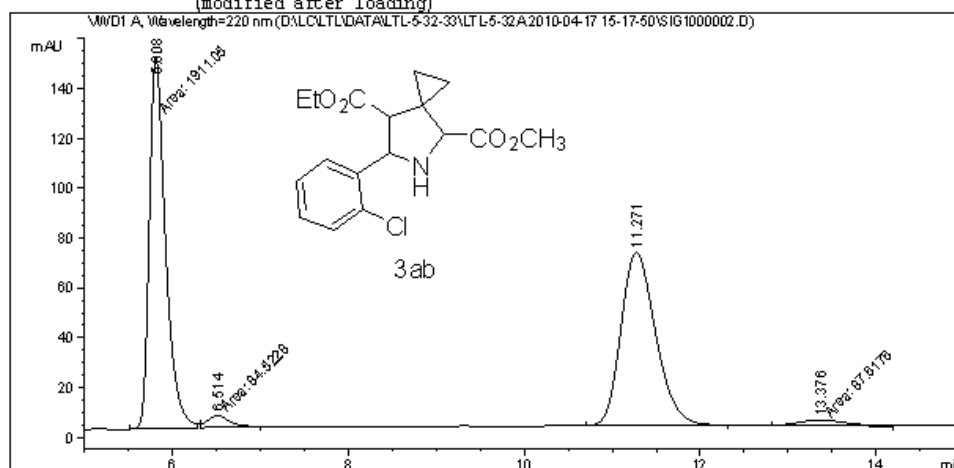
Totals : 1.66145e4 497.19820

=====
 *** End of Report ***

Data File D:\LC\LTL\DATA\LTL-5-32-33\LTL-5-32A 2010-04-17 15-17-50\SIG1000002.D
 Sample Name: LTL-5-32A

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 61
Injection Date  : 4/17/2010 3:30:13 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-32-33\LTL-5-32A 2010-04-17 15-17-50\ASH-10-90-10ML-
                220NM-60MIN.M
Last changed    : 11/15/2009 6:41:50 PM by DXQ
Analysis Method : D:\LC\LTL\DATA\LTL-5-32-33\LTL-5-32A 2010-04-17 15-17-50\SIG1000002.D\DA.M
                (ASH-10-90-10ML-220NM-60MIN.M)
Last changed    : 4/17/2010 5:36:32 PM by LTL
                (modified after loading)
    
```



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

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

Signal 1: WWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	5.808	MF	0.2130	1911.05139	47.8540	149.55931
2	6.514	MM	0.2842	84.52280	2.1165	4.95612
3	11.271	BF	0.4253	1910.31030	47.8355	69.54221
4	13.376	MM	0.6479	87.61762	2.1940	2.25378

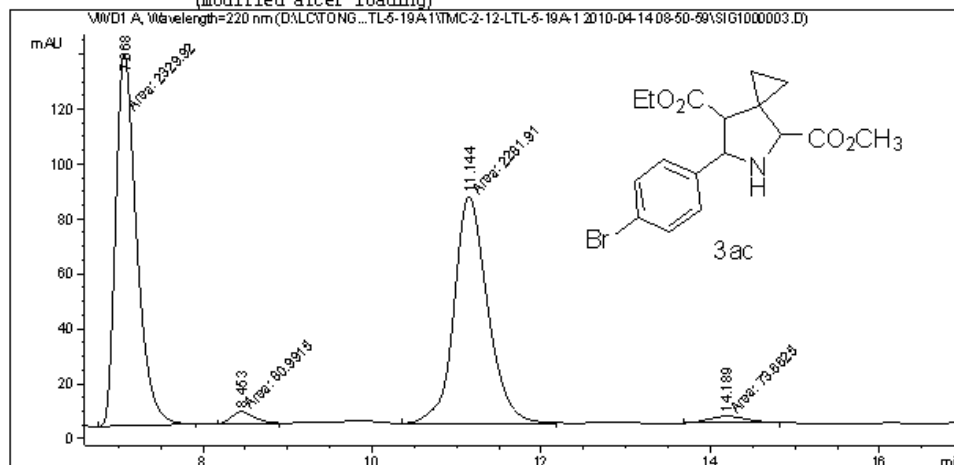
Totals : 3993.50212 226.31142

=====
 *** End of Report ***

Data File D:\LC\TONG...2-LTL-5-19A-1\TMC-2-12-LTL-5-19A-1 2010-04-14 08-50-59\SIG1000003.D
 Sample Name: LTL-5-19A-1

```

=====
Acq. Operator   : TMC                      Seq. Line :    3
Acq. Instrument : Instrument 1              Location  : Vial 16
Injection Date  : 4/14/2010 10:05:05 AM    Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\Tong\Data\TMC-2-12-LTL-5-19A-1\TMC-2-12-LTL-5-19A-1 2010-04-14 08-
50-59\ASH-10-90-10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\TONG\DATA\TMC-2-12-LTL-5-19A-1\TMC-2-12-LTL-5-19A-1 2010-04-14 08-
50-59\SIG1000003.D\DA.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/17/2010 3:20:08 PM by LTL
                  (modified after loading)
    
```



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

```

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

Signal 1: VWD1 A, Wavelength=220 nm

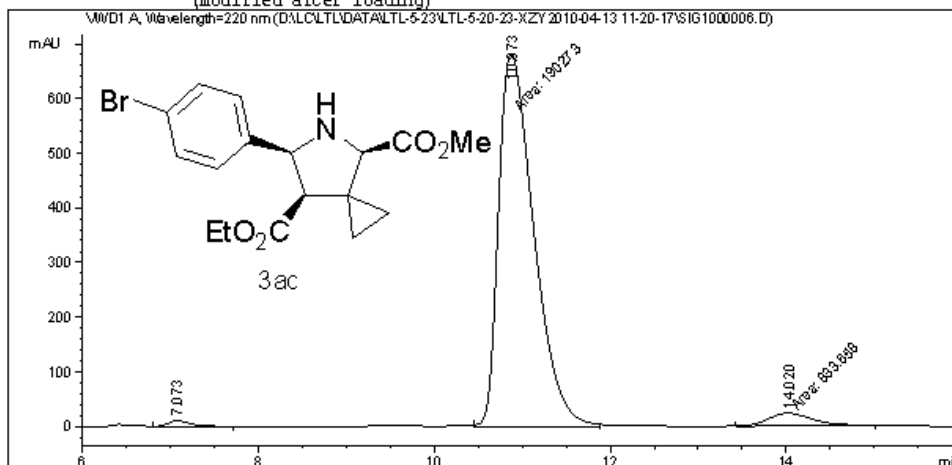
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.068	MM	0.2862	2329.92407	135.66257	48.8813
2	8.453	MM	0.3132	80.99151	4.31001	1.6992
3	11.144	MM	0.4609	2281.91309	82.51217	47.8741
4	14.189	MM	0.5210	73.66246	2.35661	1.5454

Totals : 4766.49113 224.84135

=====
 *** End of Report ***

Data File D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000006.D
Sample Name: LTL-5-22

```
=====
Acq. Operator   : LTL                      Seq. Line :    6
Acq. Instrument : Instrument 1              Location  : Vial 6
Injection Date  : 4/13/2010 1:09:13 PM     Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\ASH-10-90-
10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000006.D\
D.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/24/2010 9:15:05 AM by LTL
                 (modified after loading)
=====
```



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

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

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.073	VE	0.2572	180.70602	10.51890	0.9017
2	10.873	MM	0.4636	1.90273e4	683.97577	94.9387
3	14.020	MM	0.5959	833.65845	23.31755	4.1596

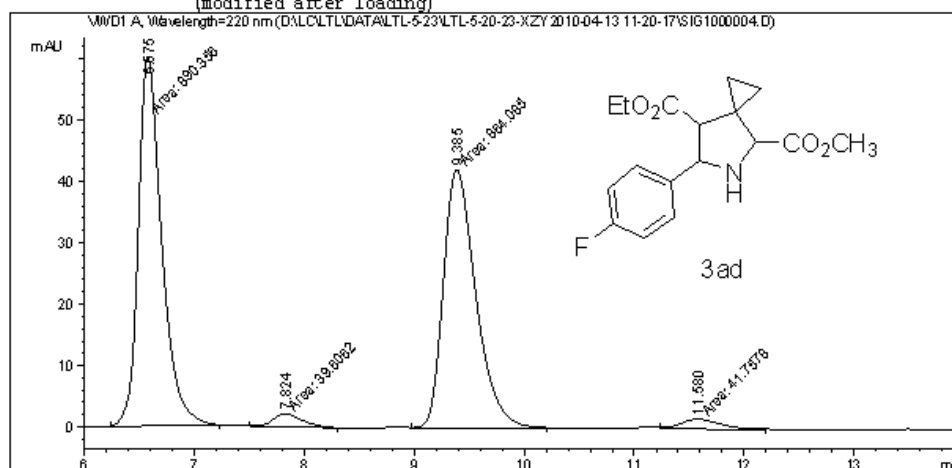
Totals : 2.00417e4 717.81222

=====
*** End of Report ***
=====

Data File D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000004.D
 Sample Name: LTL-5-21A

```

=====
Acq. Operator   : LTL                               Seq. Line :    4
Acq. Instrument : Instrument 1                       Location  : Vial 4
Injection Date  : 4/13/2010 12:26:01 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\ASH-10-90-
                10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000004.D\
                DA.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/13/2010 9:08:43 PM by LTL
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.575	MM	0.2465	890.35608	60.20549	48.4995
2	7.824	MM	0.3099	39.60619	2.13029	2.1574
3	9.385	MM	0.3421	864.08478	42.09634	47.0684
4	11.580	MM	0.4273	41.75775	1.62868	2.2746

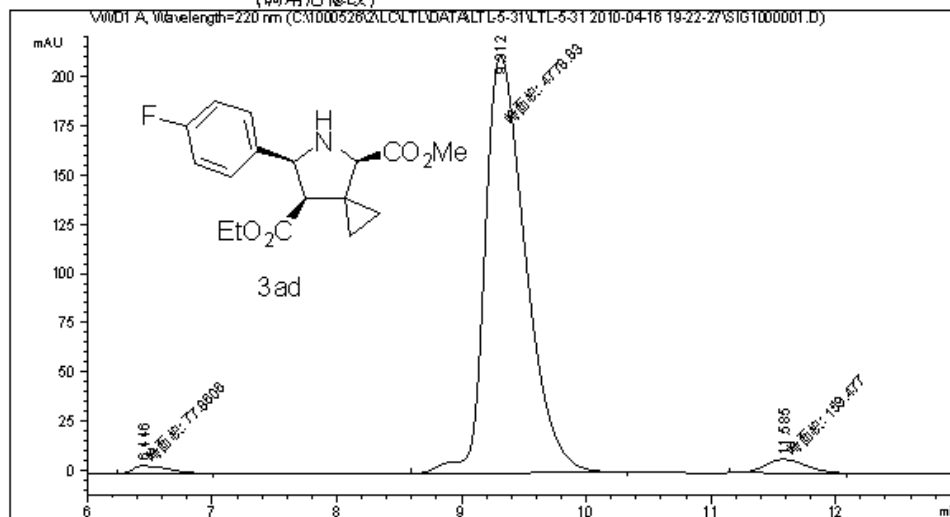
Totals : 1835.80480 106.06081

*** End of Report ***

数据文件: C:\1000526\2\LC\LTL\DATA\LTL-5-31\LTL-5-31 2010-04-16 19-22-27\SIG1000001.D
样品名称: LTL-5-31A

```

=====
操作者       : LTL                      序列行 : 1
仪器         : Instrument 1              位置   : 样品瓶 43
进样日期     : 2010-4-17 10:24:00 上午  进样次数: 1
                                           进样量 : 5 µl
采集方法     : D:\LC\LTL\data\LTL-5-31\LTL-5-31 2010-04-16 19-22-27\ASH-10-90-10ML-
                                           220NM-20MIN.M
最后修改     : 2010-4-1 8:54:37 上午 : LTL
分析方法     : C:\1000526\2\LC\LTL\DATA\LTL-5-31\LTL-5-31 2010-04-16 19-22-27\
                                           SIG1000001.D\DA.M (ASH-10-90-10ML-220NM-20MIN.M)
最后修改     : 2010-7-24 10:28:32 上午
                                           (调用后修改)
=====
    
```



面积百分比报告

```

=====
排序       : 信号
乘积因子   : 1.0000
稀释因子   : 1.0000
内标使用乘积因子和稀释因子
    
```

信号 1: WVD1 A, Wavelength=220 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	6.446	MM	0.3187	77.86063	4.07179	1.5522
2	9.312	MM	0.3757	4778.83447	211.98970	95.2686
3	11.585	MM	0.3825	159.47664	6.94917	3.1792

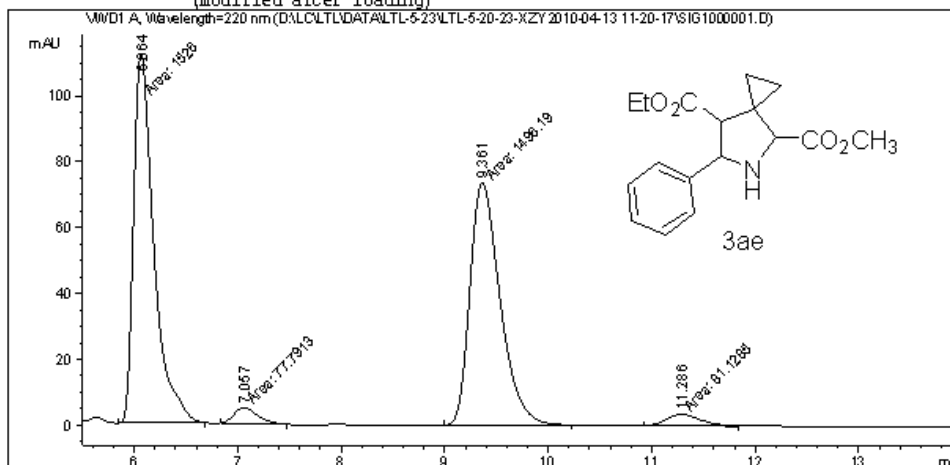
总量 : 5016.17175 223.01067

*** 报告结束 ***

Data File D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000001.D
 Sample Name: LTL-5-23A

```

=====
Acq. Operator   : LTL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 1
Injection Date  : 4/13/2010 11:21:32 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\ASH-10-90-
                10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000001.D\
                DA.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/13/2010 9:01:15 PM by LTL
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	6.064	MM	0.2265	1525.99890	47.9707	112.28498
2	7.057	MM	0.2611	77.79130	2.4454	4.96639
3	9.361	MM	0.3387	1496.19031	47.0336	73.62195
4	11.286	MM	0.3822	81.12847	2.5503	3.53753

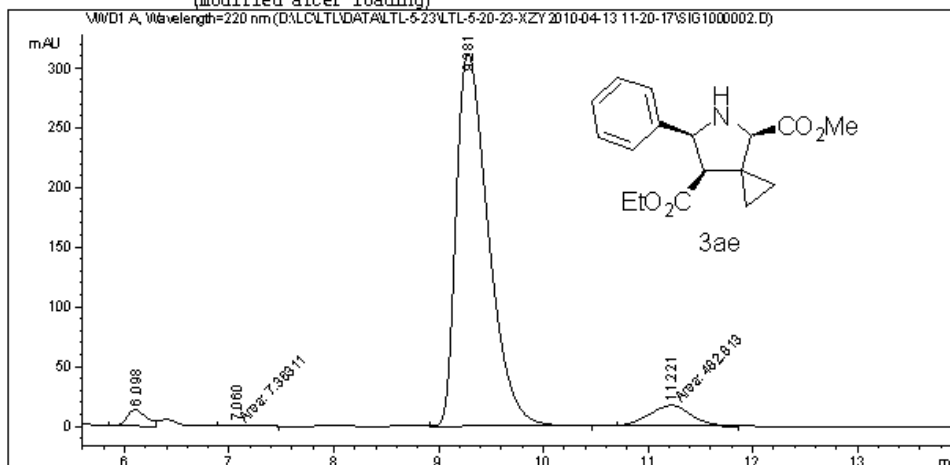
Totals : 3181.10898 194.41085

*** End of Report ***

Data File D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000002.D
Sample Name: LTL-5-23B

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 2
Injection Date  : 4/13/2010 11:43:10 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\ASH-10-90-
                10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-23\LTL-5-20-23-XZY 2010-04-13 11-20-17\SIG1000002.D\
                D\M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/13/2010 9:03:22 PM by LTL
                (modified after loading)
    
```



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

```

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

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	6.098	VV	0.1954	174.70584	13.69851	2.3876	
2	7.060	MM	0.2400	7.36311	5.11364e-1	0.1006	
3	9.281	VE	0.3286	6652.47070	312.32367	90.9136	
4	11.221	MM	0.4672	482.81299	17.22181	6.5982	

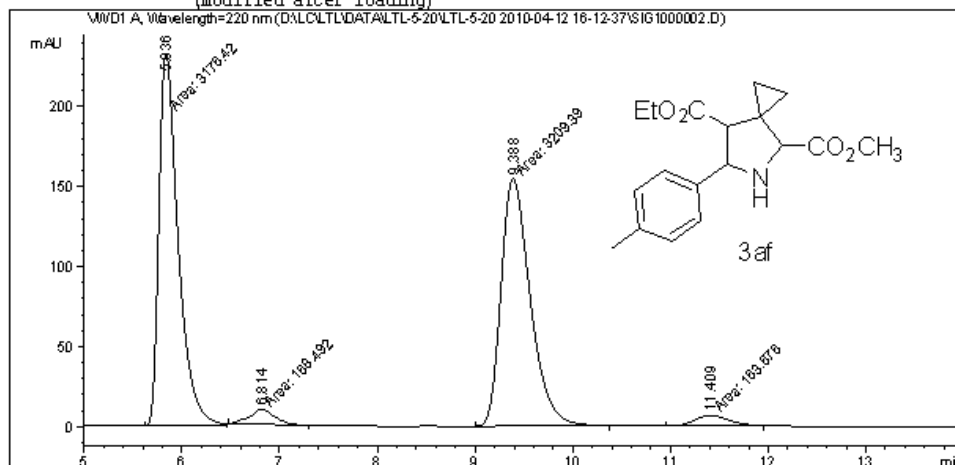
Totals : 7317.35264 343.75536

=====
*** End of Report ***

Data File D:\LC\LTL\DATA\LTL-5-20\LTL-5-20 2010-04-12 16-12-37\SIG1000002.D
 Sample Name: LTL-5-20A

```

=====
Acq. Operator   : LTL                      Seq. Line :    2
Acq. Instrument : Instrument 1              Location  : Vial 51
Injection Date  : 4/12/2010 4:25:00 PM     Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-20\LTL-5-20 2010-04-12 16-12-37\ASH-10-90-10ML-220NM-
20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-20\LTL-5-20 2010-04-12 16-12-37\SIG1000002.D\DA.M (
ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/13/2010 9:04:58 PM by LTL
(modified after loading)
    
```



Area Percent Report

```

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	5.836	MM	0.2274	3176.42310	47.2824	232.76852
2	6.814	MM	0.3047	168.49199	2.5081	9.21537
3	9.388	MM	0.3463	3209.38770	47.7731	154.45337
4	11.409	MM	0.4078	163.67644	2.4364	6.68915

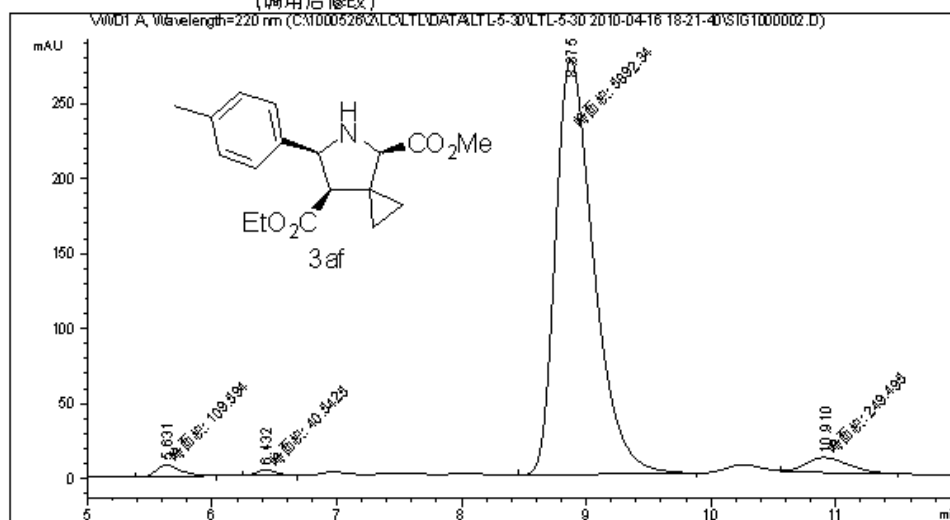
Totals : 6717.97922 403.12641

*** End of Report ***

数据文件: C:\1000526\2\LC\LTL\DATA\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\SIG1000002.D
样品名称: LTL-5-30A

```

=====
操作者       : LTL                      序列行 : 2
仪器        : Instrument 1              位置   : 样品瓶 41
进样日期    : 2010-4-17 9:34:01 上午   进样次数 : 1
                                           进样量 : 5 µl
采集方法    : D:\LC\LTL\data\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\ASH-10-90-10ML-
                                           220NM-20MIN.M
最后修改    : 2010-4-1 8:54:37 上午 : LTL
分析方法    : C:\1000526\2\LC\LTL\DATA\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\
                                           SIG1000002.D\DA.M (ASH-10-90-10ML-220NM-20MIN.M)
最后修改    : 2010-7-24 10:22:17 上午
                                           (调用后修改)
=====
    
```



面积百分比报告

```

=====
排序       : 信号
乘积因子   : 1.0000
稀释因子   : 1.0000
内标使用乘积因子和稀释因子
    
```

信号 1: WVD1 A, Wavelength=220 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	5.631	MM	0.2327	109.59352	7.84948	1.7418
2	6.432	MM	0.1748	40.54253	3.86616	0.6444
3	8.875	MM	0.3549	5892.34473	276.70813	93.6486
4	10.910	MM	0.4124	249.49547	10.08218	3.9653

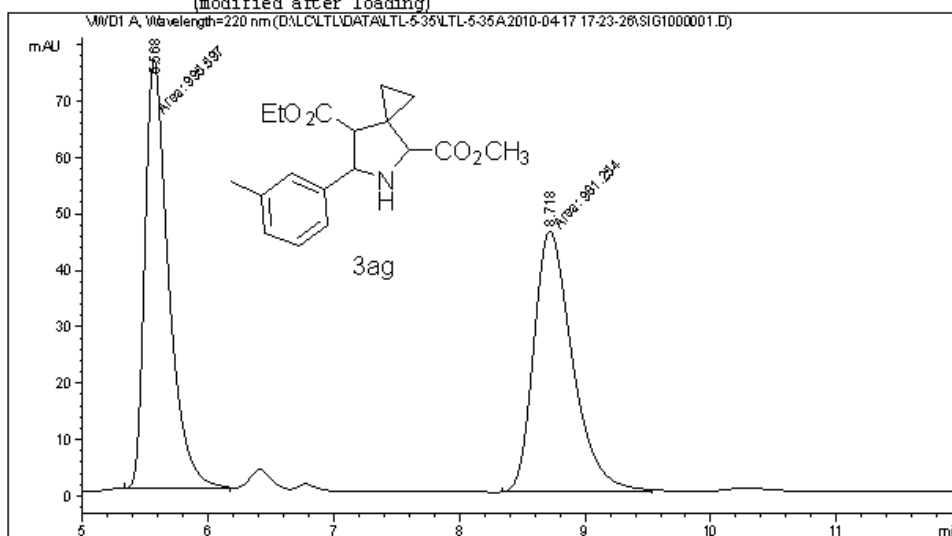
总量 : 6291.97625 298.50595

*** 报告结束 ***

Data File D:\LC\LTL\DATA\LTL-5-35\LTL-5-35A 2010-04-17 17-23-26\SIG1000001.D
 Sample Name: LTL-5-35A

```

=====
Acq. Operator   : LTL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 66
Injection Date  : 4/17/2010 5:24:58 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method    : D:\LC\LTL\data\LTL-5-35\LTL-5-35A 2010-04-17 17-23-26\ASH-10-90-10ML-
                220NM-60MIN.M
Last changed   : 11/15/2009 6:41:50 PM by DXQ
Analysis Method : D:\LC\LTL\DATA\LTL-5-35\LTL-5-35A 2010-04-17 17-23-26\SIG1000001.D\DA.M (
                ASH-10-90-10ML-220NM-60MIN.M)
Last changed   : 4/17/2010 5:49:12 PM by LTL
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

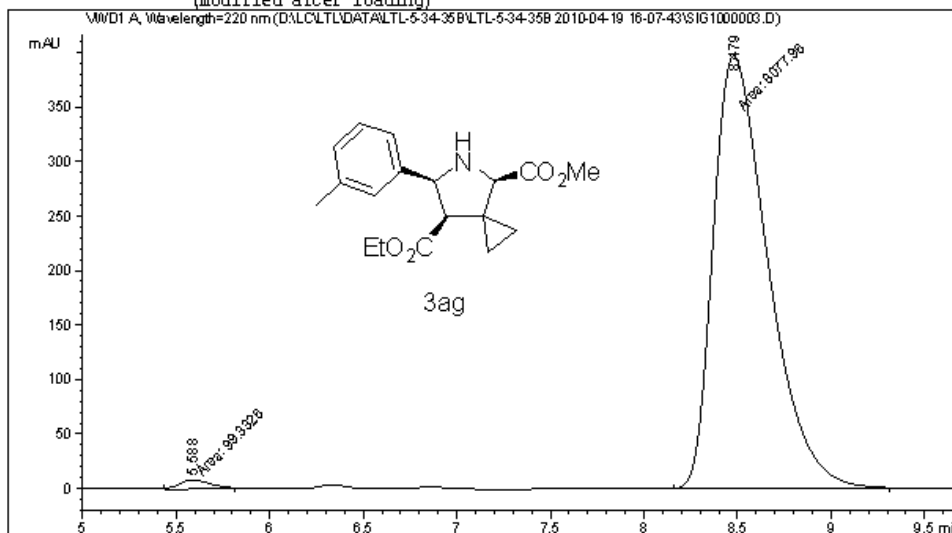
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	5.568	MM	0.2181	995.59680	76.07470	50.3628
2	8.718	MM	0.3545	981.25439	46.13061	49.6372

Totals : 1976.85120 122.20531

Data File D:\LC\LTL\DATA\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\SIG1000003.D
 Sample Name: LTL-5-35B

```

=====
Acq. Operator   : LTL                               Seq. Line :    3
Acq. Instrument : Instrument 1                       Location  : Vial 72
Injection Date  : 4/19/2010 4:41:29 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\ASH-10-90-
10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\SIG1000003.D\
D.A.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/19/2010 5:19:06 PM by LTL
(modified after loading)
    
```



Area Percent Report

```

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

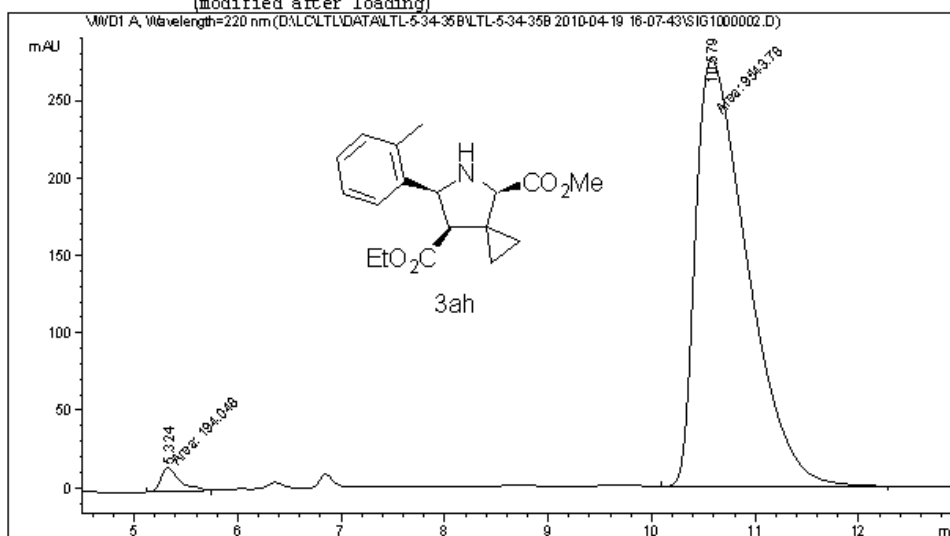
Signal 1: WMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	5.588	MM	0.1947	99.33256	8.50452	1.2147
2	8.479	MM	0.3395	8077.96289	396.52243	98.7853

Totals : 8177.29545 405.02695

Data File D:\LC\LTL\DATA\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\SIG1000002.D
Sample Name: LTL-5-34B

```
=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 71
Injection Date  : 4/19/2010 4:20:03 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\ASH-10-90-
                10ML-220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-34-35B\LTL-5-34-35B 2010-04-19 16-07-43\SIG1000002.D\
                DA.M (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 4/19/2010 5:15:53 PM by LTL
                (modified after loading)
=====
```



Area Percent Report

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

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.324	MM	0.2137	194.04799	15.13305	1.9927
2	10.579	MM	0.5770	9543.77930	275.69281	98.0073

Totals : 9737.82729 290.82586

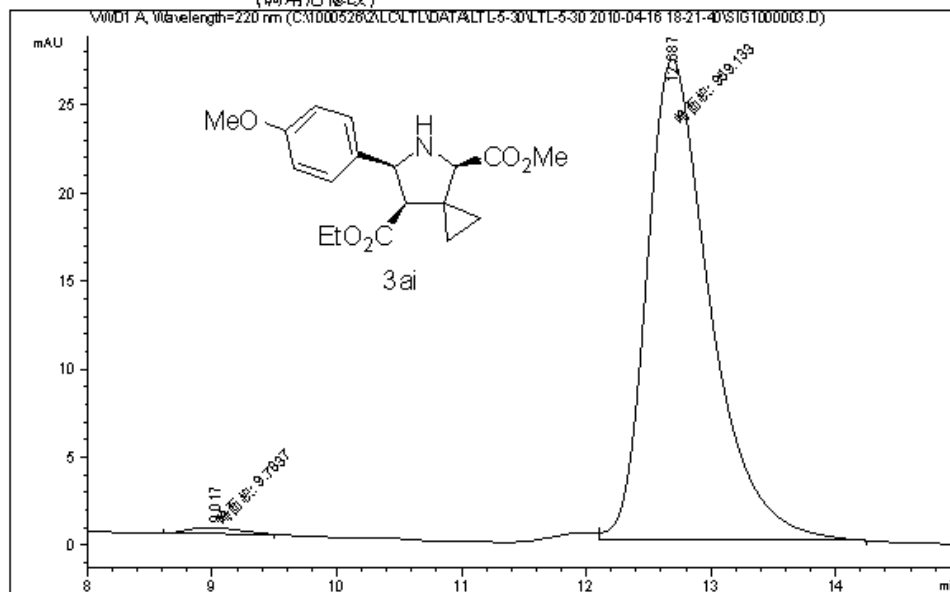
Instrument 1 4/19/2010 5:15:57 PM LTL

Page 1 of 1

数据文件: C:\1000526\2\LC\LTL\DATA\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\SIG1000003.D
样品名称: LTL-5-30B

```

=====
操作者       : LTL                      序列行 : 3
仪器         : Instrument 1              位置   : 样品瓶 42
进样日期     : 2010-4-17 9:55:36 上午   进样次数 : 1
                                           进样量 : 5 µl
采集方法     : D:\LC\LTL\data\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\ASH-10-90-10ML-
                                           220NM-20MIN.M
最后修改     : 2010-4-1 8:54:37 上午 : LTL
分析方法     : C:\1000526\2\LC\LTL\DATA\LTL-5-30\LTL-5-30 2010-04-16 18-21-40\
                                           SIG1000003.D\DA.M (ASH-10-90-10ML-220NM-20MIN.M)
最后修改     : 2010-7-24 10:25:46 上午
                                           (调用后修改)
=====
    
```



=====
面积百分比报告
=====

```

排序       : 信号
乘积因子   : 1.0000
稀释因子   : 1.0000
内标使用乘积因子和稀释因子
    
```

信号 1: WVD1 A, Wavelength=220 nm

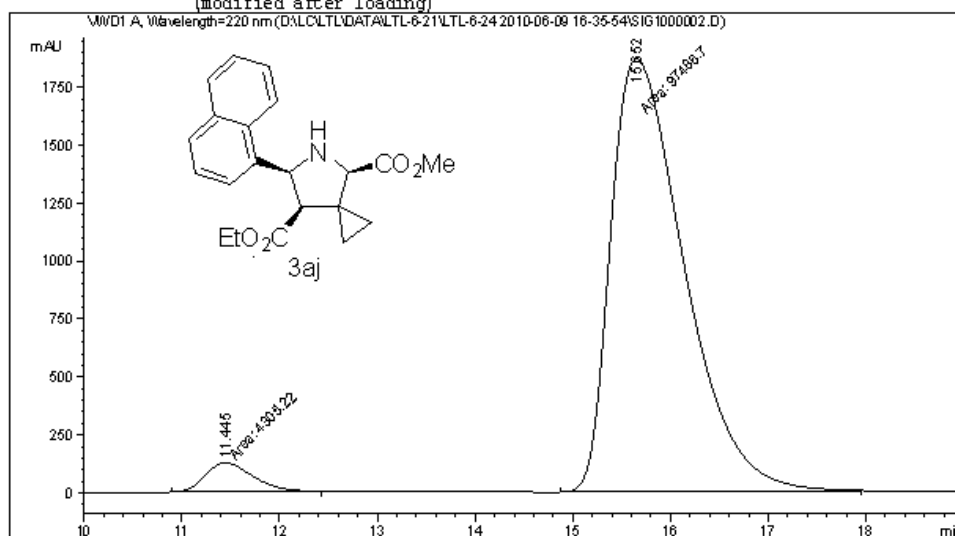
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.017	MM	0.5045	9.78370	3.23239e-1	1.0098
2	12.687	MM	0.5857	959.13269	27.29437	98.9902

总量 : 968.91639 27.61761

=====
*** 报告结束 ***

Data File D:\LC\LTL\DATA\LTL-6-21\LTL-6-24 2010-06-09 16-35-54\SIG1000002.D
Sample Name: LTL-6-24

```
=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 43
Injection Date  : 6/9/2010 4:48:19 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-6-21\LTL-6-24 2010-06-09 16-35-54\ASH-10-90-10ML-220NM-
20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-6-21\LTL-6-24 2010-06-09 16-35-54\SIG1000002.D\DA.M (
ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 6/9/2010 5:09:46 PM by LTL
(modified after loading)
=====
```



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

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	11.445	MM	0.5668	4305.21631	126.59375	4.2294	
2	15.652	MM	0.8702	9.74867e4	1867.12585	95.7706	

Totals : 1.01792e5 1993.71960

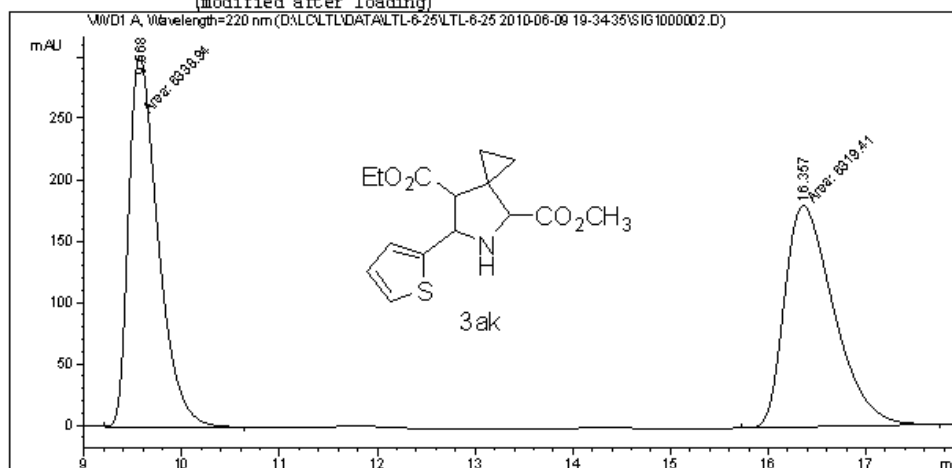
Instrument 1 6/9/2010 5:09:50 PM LTL

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-6-25\LTL-6-25 2010-06-09 19-34-35\SIG1000002.D
 Sample Name: LTL-6-25

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 44
Injection Date  : 6/9/2010 7:47:00 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-6-25\LTL-6-25 2010-06-09 19-34-35\ASH-5-95-10ML-220NM-
60MIN.M
Last changed    : 6/9/2010 8:05:19 PM by LTL
(modified after loading)
Analysis Method : D:\LC\LTL\DATA\LTL-6-25\LTL-6-25 2010-06-09 19-34-35\SIG1000002.D\DA.M (
ASH-5-95-10ML-220NM-60MIN.M)
Last changed    : 6/9/2010 8:08:42 PM by LTL
(modified after loading)
    
```



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

```

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

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	9.568	MM	0.3494	6338.94092	302.37076	50.0772
2	16.357	MM	0.5855	6319.40674	179.87982	49.9228

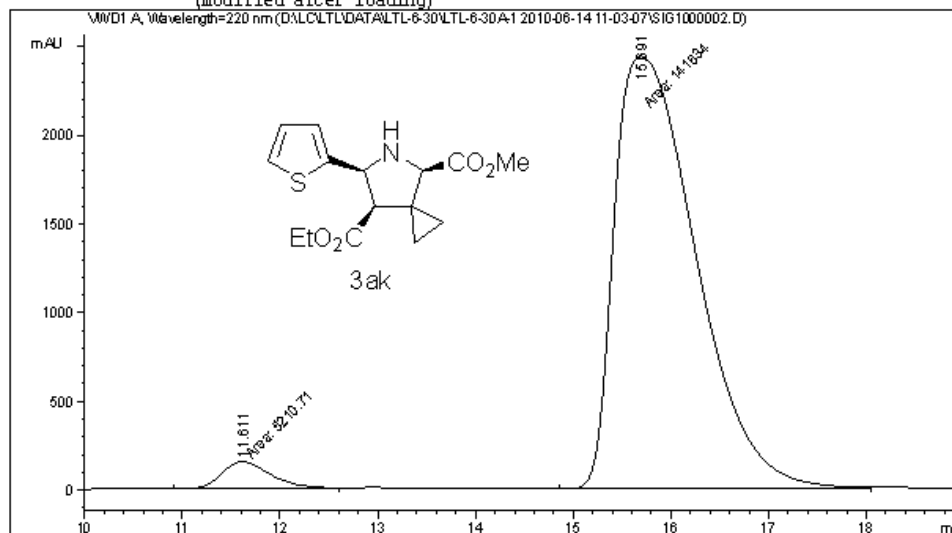
Totals : 1.26583e4 482.25058

=====
 *** End of Report ***

Data File D:\LC\LTL\DATA\LTL-6-30\LTL-6-30A-1 2010-06-14 11-03-07\SIG1000002.D
 Sample Name: LTL-6-30A-1

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 64
Injection Date  : 6/14/2010 11:15:35 AM            Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-6-30\LTL-6-30A-1 2010-06-14 11-03-07\ASH-10-90-10ML-
                220NM-20MIN.M
Last changed    : 3/31/2010 4:54:37 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-6-30\LTL-6-30A-1 2010-06-14 11-03-07\SIG1000002.D\DA.M
                (ASH-10-90-10ML-220NM-20MIN.M)
Last changed    : 6/14/2010 11:37:14 AM by LTL
                (modified after loading)
    
```



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

```

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

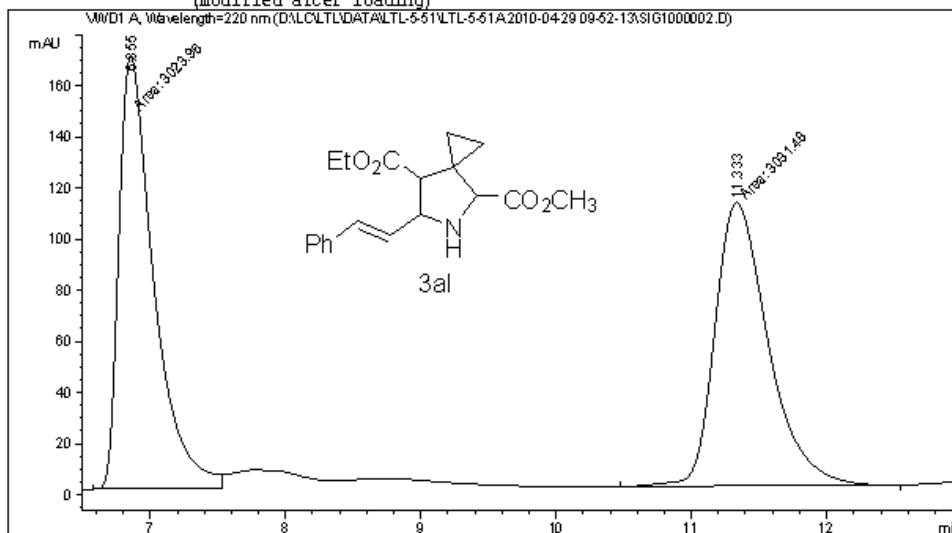
Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	11.611	MM	0.5741	5210.70508	151.27429	3.5484
2	15.691	MF	0.9677	1.41634e5	2439.41235	96.4516

Totals : 1.46845e5 2590.68665

Data File D:\LC\LTL\DATA\LTL-5-51\LTL-5-51A 2010-04-29 09-52-13\SIG1000002.D
Sample Name: LTL-5-51A

```
=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 84
Injection Date  : 4/29/2010 10:04:35 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-51\LTL-5-51A 2010-04-29 09-52-13\ASH-10-90-10ML-
                220NM-60MIN.M
Last changed    : 11/15/2009 6:41:50 PM by DXQ
Analysis Method : D:\LC\LTL\DATA\LTL-5-51\LTL-5-51A 2010-04-29 09-52-13\SIG1000002.D\A.M (
                ASH-10-90-10ML-220NM-60MIN.M)
Last changed    : 5/25/2010 8:09:43 PM by thl
                (modified after loading)
=====
```



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

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

Signal 1: WMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.855	MF	0.2975	3023.96216	169.41603	49.9379
2	11.333	NM	0.4558	3031.48486	110.84300	50.0621

Totals : 6055.44702 280.25903

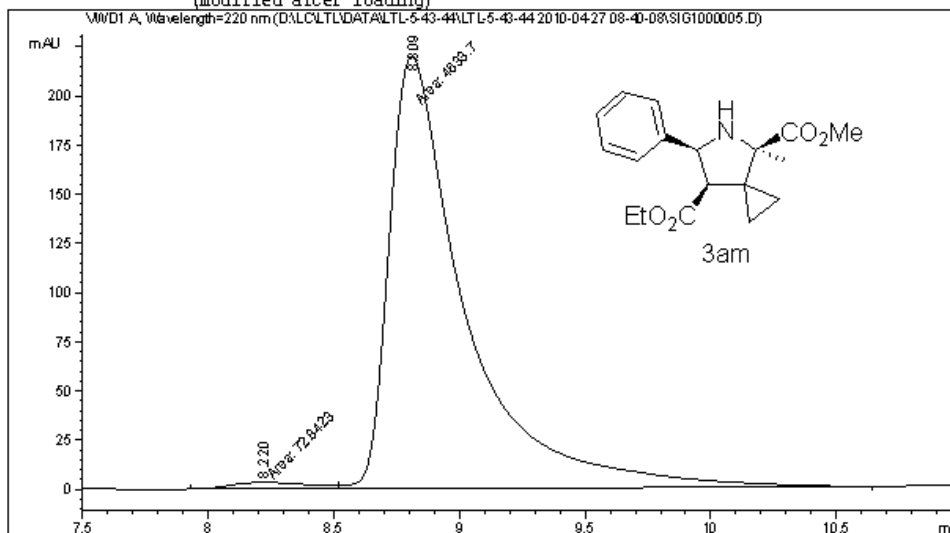
Instrument 1 5/25/2010 8:09:47 PM thl

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000005.D
 Sample Name: LTL-5-44B

```

=====
Acq. Operator   : LTL                               Seq. Line :    5
Acq. Instrument : Instrument 1                       Location  : Vial 97
Injection Date  : 4/27/2010 9:57:04 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\ADH-5-95-10ML-
                220NM-20MIN.M
Last changed    : 4/27/2010 8:37:49 AM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000005.D\
                DA.M (ADH-5-95-10ML-220NM-20MIN.M)
Last changed    : 5/4/2010 8:43:45 PM by TMC
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	8.220	MF	0.3677	72.84235	3.30209	1.5477
2	8.809	FM	0.3513	4633.69922	219.85823	98.4523

Totals : 4706.54156 223.16032

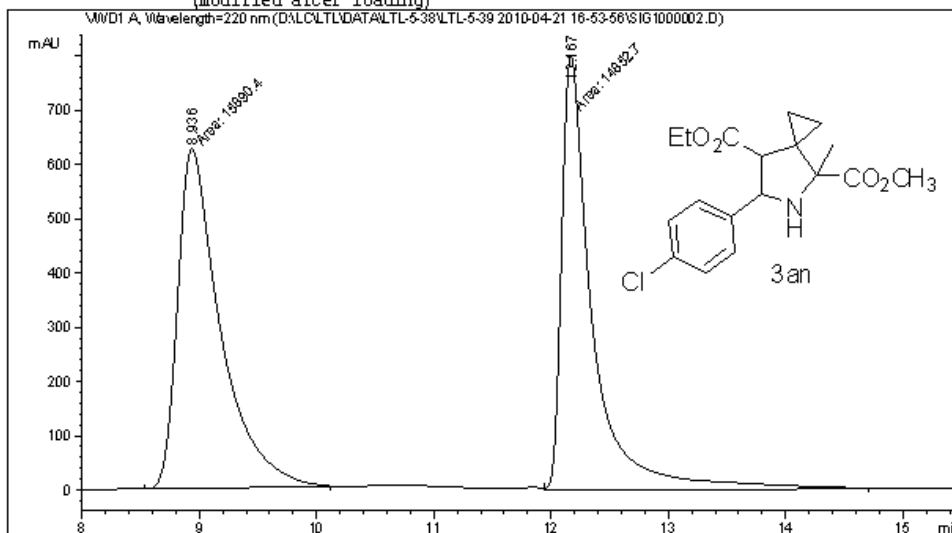
Instrument 1 5/4/2010 8:43:59 PM TMC

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\SIG1000002.D
Sample Name: LTL-5-38A

```

=====
Acq. Operator   : LTL                               Seq. Line :    2
Acq. Instrument : Instrument 1                       Location  : Vial 67
Injection Date  : 4/21/2010 5:06:40 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\ADH-5-95-10ML-220NM-
30MIN.M
Last changed    : 4/21/2010 4:53:23 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\SIG1000002.D\DA.M (
ADH-5-95-10ML-220NM-30MIN.M)
Last changed    : 4/21/2010 6:58:01 PM by LTL
(modified after loading)
    
```



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

```

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	8.936	MM	0.4228	1.58904e4	626.41632	51.6876	
2	12.167	MM	0.3089	1.48527e4	801.25385	48.3124	

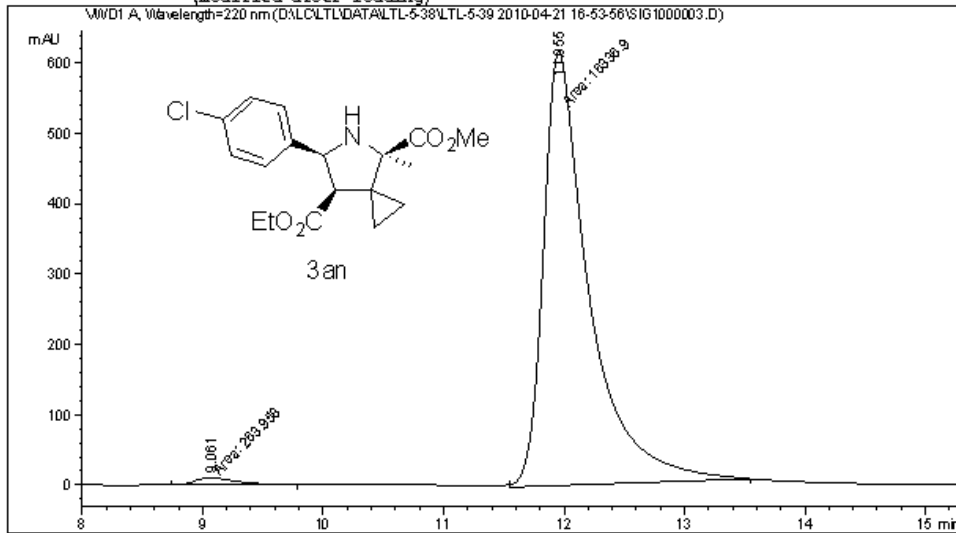
Totals : 3.07431e4 1427.67017

Instrument 1 4/21/2010 6:58:06 PM LTL

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\SIG1000003.D
Sample Name: LTL-5-39

```
=====
Acq. Operator   : LTL                               Seq. Line :    3
Acq. Instrument : Instrument 1                       Location  : Vial 69
Injection Date  : 4/21/2010 5:38:00 PM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\ADH-5-95-10ML-220NM-
30MIN.M
Last changed    : 4/21/2010 4:53:23 PM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-38\LTL-5-39 2010-04-21 16-53-56\SIG1000003.D\DA.M (
ADH-5-95-10ML-220NM-30MIN.M)
Last changed    : 4/21/2010 6:55:47 PM by LTL
(modified after loading)
=====
```



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

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

Signal 1: VMD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	9.061	MM	0.4165	263.95801	10.56129	1.5900
2	11.955	MM	0.4414	1.63369e4	616.88617	98.4100
Totals :				1.66008e4	627.44746	

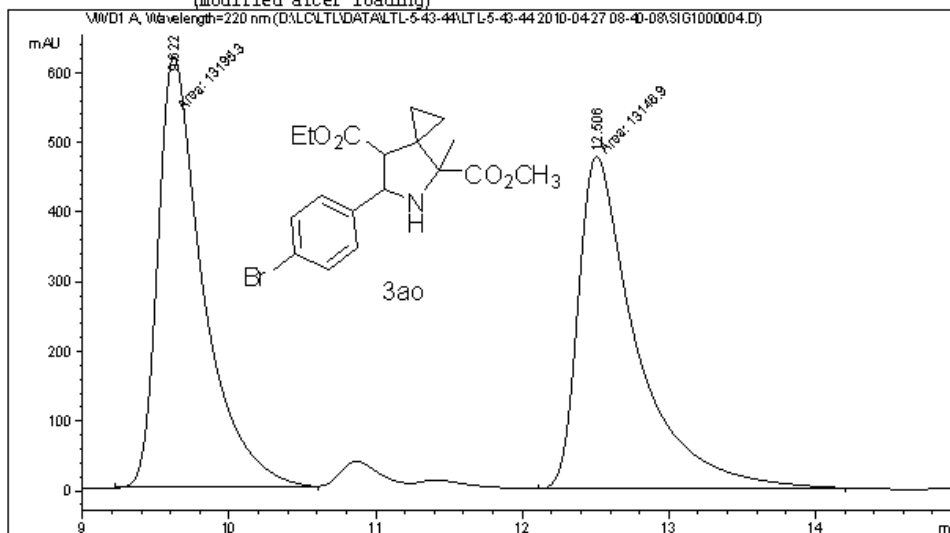
Instrument 1 4/21/2010 6:56:07 PM LTL

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000004.D
 Sample Name: LTL-5-44A

```

=====
Acq. Operator   : LTL                      Seq. Line :    4
Acq. Instrument : Instrument 1              Location  : Vial 95
Injection Date  : 4/27/2010 9:35:39 AM     Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method    : D:\LC\LTL\data\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\ADH-5-95-10ML-
                220NM-20MIN.M
Last changed   : 4/27/2010 8:37:49 AM by LTL
Analysis Method: D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000004.D\
                DA.M (ADH-5-95-10ML-220NM-20MIN.M)
Last changed   : 5/4/2010 8:45:11 PM by TMC
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.622	MM	0.3556	1.31952e4	618.37079	50.0918
2	12.506	MM	0.4594	1.31469e4	476.90692	49.9082

Totals : 2.63421e4 1095.27771

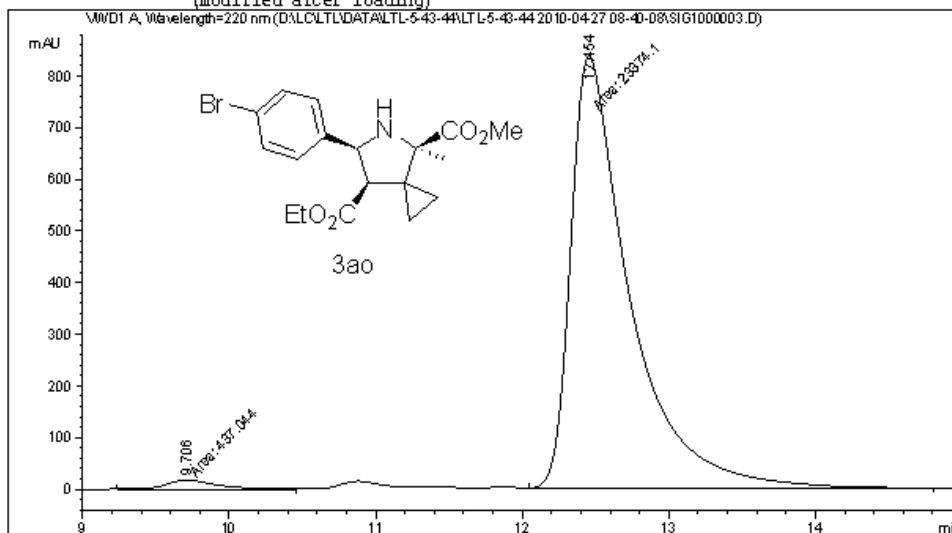
Instrument 1 5/4/2010 8:45:14 PM TMC

Page 1 of 1

Data File D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000003.D
 Sample Name: LTL-5-43B

```

=====
Acq. Operator   : LTL                               Seq. Line :    3
Acq. Instrument : Instrument 1                       Location  : Vial 96
Injection Date  : 4/27/2010 9:14:16 AM             Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method    : D:\LC\LTL\data\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\ADH-5-95-10ML-
                220NM-20MIN.M
Last changed   : 4/27/2010 8:37:49 AM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-43-44\LTL-5-43-44 2010-04-27 08-40-08\SIG1000003.D\
                DA.M (ADH-5-95-10ML-220NM-20MIN.M)
Last changed   : 5/4/2010 8:46:35 PM by TMC
                (modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

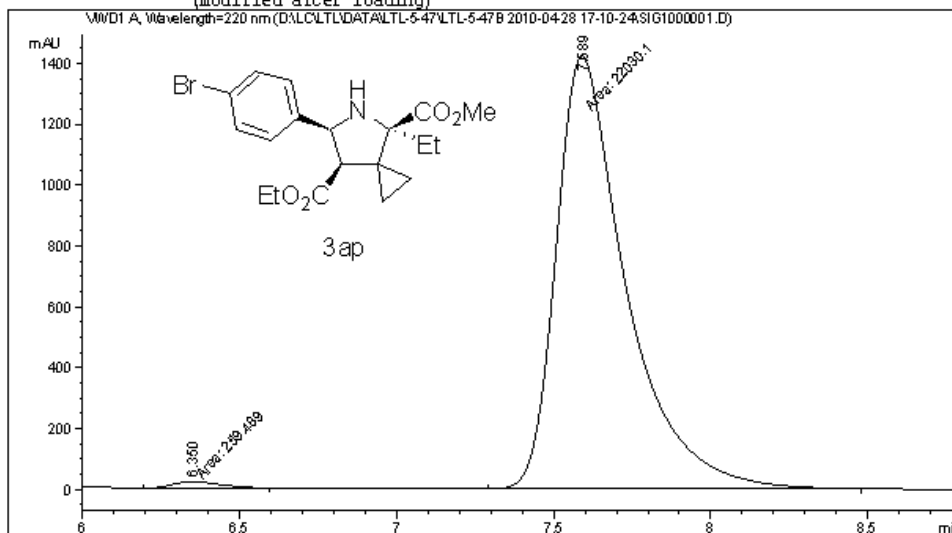
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	9.706	MM	0.4029	437.04388	18.08111	1.8355
2	12.454	MM	0.4661	2.33741e4	835.77728	98.1645

Totals : 2.38111e4 853.85840

Data File D:\LC\LTL\DATA\LTL-5-47\LTL-5-47B 2010-04-28 17-10-24\SIG1000001.D
 Sample Name: LTL-5-47B

```

=====
Acq. Operator   : LTL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 8
Injection Date  : 4/28/2010 5:12:02 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-47\LTL-5-47B 2010-04-28 17-10-24\ADH-5-95-10ML-210MM-20MIN.M
Last changed    : 4/26/2010 9:35:52 PM by DXQ
Analysis Method : D:\LC\LTL\DATA\LTL-5-47\LTL-5-47B 2010-04-28 17-10-24\SIG1000001.D\DA.M (
                ADH-5-95-10ML-210MM-20MIN.M)
Last changed    : 4/28/2010 6:13:55 PM by LTL
                (modified after loading)
    
```



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

```

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

Signal 1: WVD1 A, Wavelength=220 nm

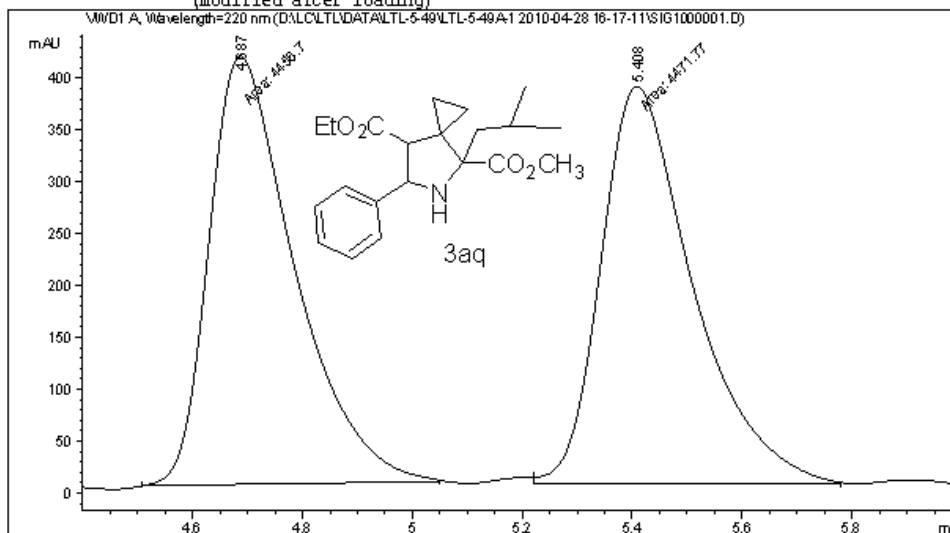
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	6.350	MM	0.1928	259.48907	22.43086	1.1642
2	7.589	MM	0.2579	2.20301e4	1423.69861	98.8358

Totals : 2.22896e4 1446.12947

Data File D:\LC\LTL\DATA\LTL-5-49\LTL-5-49A-1 2010-04-28 16-17-11\SIG1000001.D
 Sample Name: LTL-5-49A

```

=====
Acq. Operator   : LTL                               Seq. Line :    1
Acq. Instrument : Instrument 1                       Location  : Vial 6
Injection Date  : 4/28/2010 4:18:50 PM              Inj       :    1
                                                    Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-49\LTL-5-49A-1 2010-04-28 16-17-11\ADH-5-95-10ML-
220NM-20MIN.M
Last changed    : 4/27/2010 8:37:49 AM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-49\LTL-5-49A-1 2010-04-28 16-17-11\SIG1000001.D\DA.M
(ADH-5-95-10ML-220NM-20MIN.M)
Last changed    : 4/28/2010 8:33:25 PM by LTL
(modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

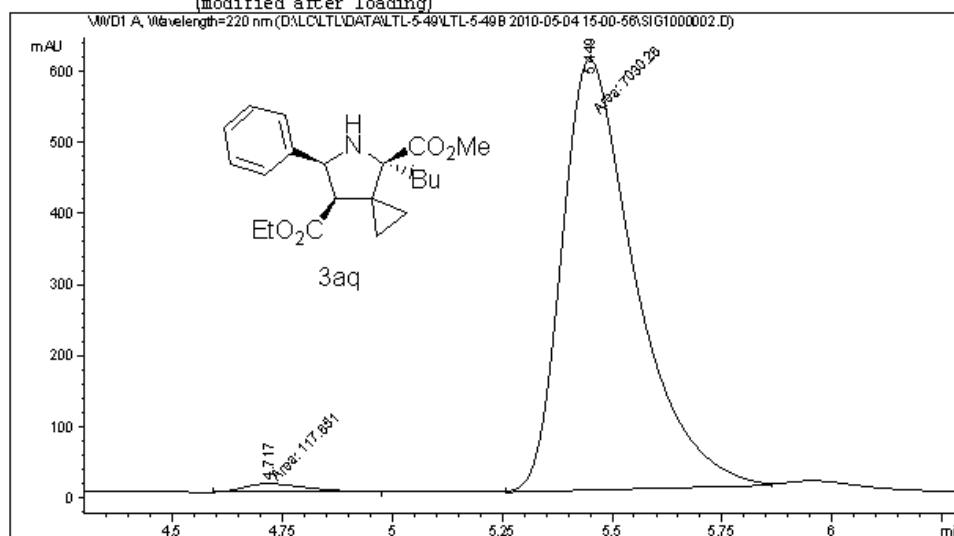
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	4.687	MM	0.1797	4456.70459	413.35596	49.9156
2	5.408	MM	0.1941	4471.77148	383.97849	50.0844

Totals : 8928.47607 797.33444

Data File D:\LC\LTL\DATA\LTL-5-49\LTL-5-49B 2010-05-04 15-00-56\SIG1000002.D
 Sample Name: LTL-5-49B

```

=====
Acq. Operator   : LTL                      Seq. Line :    2
Acq. Instrument : Instrument 1              Location  : Vial 12
Injection Date  : 5/4/2010 3:13:34 PM      Inj       :    1
                                           Inj Volume: 5 µl
Acq. Method     : D:\LC\LTL\data\LTL-5-49\LTL-5-49B 2010-05-04 15-00-56\ADH-5-95-10ML-220NM-
20MIN.M
Last changed    : 4/27/2010 8:37:49 AM by LTL
Analysis Method : D:\LC\LTL\DATA\LTL-5-49\LTL-5-49B 2010-05-04 15-00-56\SIG1000002.D\DA.M (
ADH-5-95-10ML-220NM-20MIN.M)
Last changed    : 5/4/2010 3:52:19 PM by TMC
(modified after loading)
    
```



Area Percent Report

```

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

Signal 1: WVD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	4.717	MM	0.1646	117.65134	11.91053	1.6460
2	5.449	MM	0.1930	7030.26367	607.06598	98.3540

Totals : 7147.91502 618.97650