

Supporting Information

A New Route to Acyclic Diaminocarbenes via Lithium-Halogen Exchange

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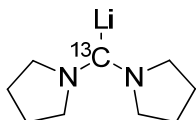
1. General Remarks

All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. THF, CH₂Cl₂, and Et₂O were passed through two packed columns of neutral alumina under positive pressure of dry nitrogen prior to use. Toluene was passed through an alumina column and a copper (II) oxide column under positive pressure of dry nitrogen prior to use. Chloroamidinium salts **1** and **8** were used as received from Aldrich Chemicals, and salts **1'** and Bis(Piperidine)chloroamidinium tetrafluoroborate were prepared according to Fürstner and coworkers.¹ Compound **11** was prepared according to the literature.² All other chemicals were commercially available and were used as received without further purification. NMR spectra were recorded using a FT-NMR

machine, operating at 300 MHz for ^1H NMR and at 75.4 MHz for ^{13}C NMR. All chemical shifts for ^1H and ^{13}C NMR spectroscopy were referenced to residual signals from CDCl_3 (^1H) 7.27 ppm and (^{13}C) 77.23 ppm. High resolution mass spectra were recorded on a GC/MS spectrometer or a TOF-LC/MS spectrometer.

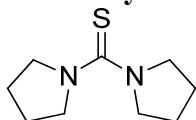
2. Experimental Details

2.1 General Procedure for formation of carbene 3'



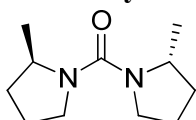
(A) To a Schlenk flask in a glovebox, 100 mg (0.364 mmol) of chloroamidinium **1'** was added, and the flask was connected to a Schlenk line outside the glovebox. THF (2 mL) was added, and the suspension was cooled to $-78\text{ }^\circ\text{C}$ with a dry-ice/acetone bath. After cooling, 2.5M *n*-BuLi in hexanes (0.153mL) was added. After 5 minutes, the suspension turned to a clear and slightly yellowish solution upon formation of carbene. The solution proceeded to stir at $-78\text{ }^\circ\text{C}$ for a total of 1 hour. (B) Alternatively, the chloroamidinium salt can be stored outside of the glovebox in a desiccator, weighed, and then added to a Schlenk flask, successfully yielding the carbene. Typically, the salt is stable under atmospheric air; however certain chloroamidiniums tend to be more hygroscopic than others, with chloride salts being especially hygroscopic when compared to tetrafluoroborate salts. In Florida, this problem is exacerbated by humidity. ^1H NMR (300MHz, THF-d_8) δ = 3.56 (br. s., 8 H), 1.70 (br. s., 8 H). ^{13}C NMR (75MHz, THF-d_8) δ = 233.8.

2.2 Synthesis of bis(pyrrolidine)thiourea 2



Generation of carbene as described in section 2.1 was followed. After formation of carbene, 100 mg (3.125 mmol) of sulfur was added, and the reaction was allowed to slowly warm to room temperature. The resulting suspension stirred for 12 hours, diluted with ether, and filtered over a bed of celite. The filtrate was concentrated and purified by silica-gel chromatography (2:1 hexanes/ethyl acetate). After removal of solvent, 45 mg (0.245 mmol) of a colorless crystal resulted (68% yield). ^1H and ^{13}C NMR matched the values found in literature.³ mp $124.6\text{--}126.2\text{ }^\circ\text{C}$.

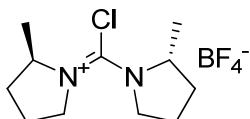
2.3 Synthesis of bis(2S)-Methylpyrrolidine Urea



(2S)-Methylpyrrolidine (8.82 mmol, 0.89 mL), triethyl amine (26.4 mmol, 3.68 mL), and CH_2Cl_2 (17.6 mL) were added to a flame dried Schlenk flask, and the solution was stirred and cooled to $0\text{ }^\circ\text{C}$. Phosgene (4.4 mmol, 2.32 mL) was slowly added in the form of a 20 wt% solution in toluene, and the Schlenk flask was sealed to prevent loss of gaseous phosgene. The reaction was vigorously stirred for 4 hours at which point extra phosgene

(2.2 mmol, 1.16 mL) was added to ensure complete reaction of the amine. Stirring continued for an additional 4 hours, and then the reaction was quenched with water. The aqueous layer was extracted with CH₂Cl₂ (20 mL x 3), dried with MgSO₄, and concentrated. The crude product was purified by silica gel column chromatography (hexanes, ethyl acetate, 1:1) to give the pure urea (0.6152 g, 71%). ¹H NMR (300 MHz, CDCl₃) δ = 3.87 - 4.07 (m, 1 H), 3.18 - 3.40 (m, 2 H), 1.98 - 2.16 (m, 1 H), 1.76 - 1.91 (m, 1 H), 1.59 - 1.76 (m, 1 H), 1.31 - 1.51 (m, 1 H), 1.16 (d, *J*=6 Hz, 3 H). ¹³C NMR (75 MHz, CDCl₃) δ = 161.5, 54.0, 49.7, 34.1, 25.5, 21.0. HRMS Calcd. for C₁₁H₂₀N₂O [M+H]⁺: 197.1648, Found: 197.1643.

2.4 Synthesis of bis((S)-2-Methylpyrrolidine) amidinium chloride tetrafluoroborate

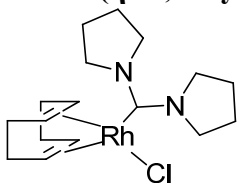


Bis(2S)-Methylpyrrolidine urea (2.09 mmol, 0.400 g) was mixed with toluene (10.45 mL) in a flame dried Schlenk flask. To this solution was added oxalyl chloride (20.1 mmol, 1.70 mL), and the reaction mixture was heated to 50 °C. The reaction was stirred overnight at which point, a brown, oily residue precipitated out of solution. The reaction was cooled to room temperature, and the toluene resting on top of the precipitate was removed with a syringe. The oily residue was washed twice with ether, dissolved in copious amounts of THF, and precipitated with pentanes as a slightly orange solid. CH₂Cl₂ (12 mL) and AgBF₄ (2.09 mmol, 0.407 g) were added to the solid. The reaction was stirred for 1 hour. After this time, the CH₂Cl₂ was removed by filtration and transferred into a dry Schlenk flask under an argon atmosphere, and the solids were washed with CH₂Cl₂, collecting the organics. Volatiles were removed, and the solid was dissolved with generous amounts of THF. The product was precipitated with ether resulting in a white solid (0.4445 g, 70%). ¹H NMR (300 MHz, CDCl₃) δ = 4.20 - 4.56 (m, 2 H), 3.90 - 4.13 (m, 2 H), 3.68 - 3.90 (m, 2 H), 2.25 - 2.56 (m, 2 H), 2.11 (dd, *J*=5, 1 Hz, 4 H), 1.63 - 1.88 (m, 2 H), 1.39 (d, 6 H). ¹³C NMR (75 MHz, CDCl₃) δ = 152.7, 62.4, 55.9, 33.5, 25.4, 20.3. HRMS Calcd. for C₁₁H₂₀N₂Cl [M+H]⁺: 215.1310, Found: 215.1310. mp 85.2-87.8 °C.

2.5 General Procedure for Rhodium and Iridium Complex Formation

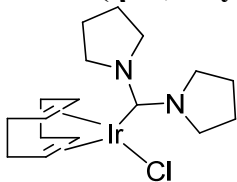
Generation of carbene as described in section 2.1 was followed. After stirring for 1 hour at -78 °C, [M(COD)Cl]₂ (0.5 equiv.) was added, and the reaction slowly warmed to room temperature. Stirring at room temperature proceeded for 12 hours, at which point, solvent was evaporated. To remove any remaining [M(COD)Cl]₂, the product was purified by chromatography on a very short pad of silica-gel. Columns were run starting with a mixture of 2:1 hexanes/ethyl acetate and then transferring to pure ethyl acetate. The complexes showed very slight decomposition on silica gel, so the product was further purified by dissolving the product in ethyl acetate and then precipitating impurities with addition of hexanes. The product is sufficiently soluble in hexanes.

Chloro(η^4 -1,5 -cyclooctadiene)-(bis(pyrrolidinecarbene)rhodium(I) 4



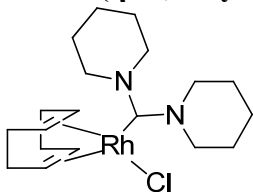
^1H NMR (300MHz, CDCl_3) δ = 4.80 (br. s., 4 H), 4.44 (br. s., 2 H), 3.40 (br. s., 4 H), 3.18 (m, 2 H), 2.52 - 2.17 (m, 4 H), 2.10 - 1.71 (m, 12 H). ^{13}C NMR (75MHz, CDCl_3) δ = 216.8, 216.2, 96.7, 96.6, 68.3, 68.1, 55.7, 51.9, 32.8, 28.9, 26.5, 24.9. HRMS Calcd. for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{Rh}$ $[\text{M}]^+$: 363.1302, Found: 363.1312.

Chloro(η^4 -1,5 -cyclooctadiene)-(bis(pyrrolidinecarbene)iridium(I) 5



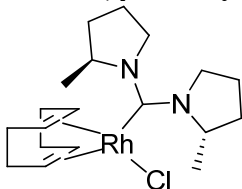
^1H NMR (300MHz, CDCl_3) δ = 4.53 (br. s., 2 H), 4.35 (br. s., 4 H), 4.23 (br. s., 2 H), 3.48 (br. s., 4 H), 3.03 - 2.68 (m, 2 H), 2.40 - 2.00 (m, 4 H), 1.86 (br. s., 8 H), 1.71 - 1.40 (m, 4 H). ^{13}C NMR (75MHz, CDCl_3) δ = 211.7, 81.4, 54.7, 52.0, 33.4, 29.5, 25.7. HRMS Calcd. for $\text{C}_{34}\text{H}_{56}\text{N}_4\text{Ir}_2\text{Cl}$ $[\text{2M}+\text{Cl}]^+$: 941.3436, Found: 941.3376.

Chloro(η^4 -1,5 -cyclooctadiene)-(bis(piperidinecarbene)rhodium(I) 6



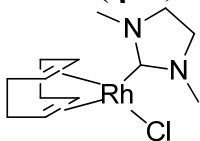
^1H NMR (300MHz, CDCl_3) δ = 4.81 (br. s., 2 H), 3.88-3.82 (m, 8 H), 3.17 (br. s., 2 H), 2.27 (br. s., 4 H), 1.82 (m, 4 H), 1.62 (br. s., 12 H). ^{13}C NMR (75MHz, CDCl_3) δ = 222.3, 221.7, 97.7, 97.6, 68.1, 67.9, 54.0, 32.8, 28.9, 26.7, 24.5.

Chloro(η^4 -1,5 -cyclooctadiene)-bis((S)-2-methylpyrrolidine)rhodium(I) 7



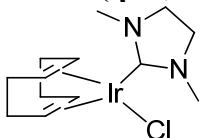
^1H NMR (300MHz, CDCl_3) δ = 6.42 (br. s., 1 H), 5.93 (br. s., 1 H), 5.57 (br. s., 0.4 H), 5.09 - 4.62 (m, 2.3 H), 4.23 - 3.70 (m, 1.4 H), 3.28 (br. s., 5 H), 1.82 (br. s., 22 H). ^{13}C NMR (75MHz, CDCl_3) δ = 97.0, 97.0, 68.6, 68.4, 66.9, 66.7, 63.3, 61.9, 51.2, 50.9, 34.9, 33.2, 33.0, 32.6, 31.6, 31.1, 29.8, 29.3, 28.6, 28.3, 25.0, 23.3, 23.0, 21.0, 20.5, 14.3. HRMS Calcd. for $\text{C}_{19}\text{H}_{32}\text{N}_2\text{Rh}$ $[\text{M}]^+$: 391.1615, Found: 391.1616. $[\alpha]_{\text{D}}^{26}$ -182.6 (c 8.3 mg/mL CHCl_3).

Chloro(η^4 -1,5-cyclooctadiene)-(1,3-dimethylimidazolidin-2-ylidene)iridium(I) 9



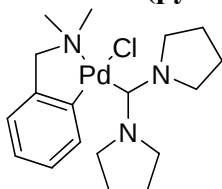
^1H NMR (300MHz, CDCl_3) δ = 4.92 (br. s., 2 H), 4.64 (br. s., 2 H), 3.54 - 3.43 (m, 8 H), 3.33 - 3.18 (m, 2 H), 2.47 - 2.19 (m, 4 H), 2.00 - 1.74 (m, 4 H). ^{13}C NMR (75MHz, CDCl_3) δ = 213.2, 212.6, 99.2, 99.1, 68.3, 68.1, 51.7, 37.4, 33.1, 28.9. HRMS Calcd. for $\text{C}_{13}\text{H}_{22}\text{N}_2\text{Rh}$ $[\text{M}]^+$: 309.0833, Found: 309.0834.

Chloro(η^4 -1,5-cyclooctadiene)-(1,3-dimethylimidazolidin-2-ylidene)iridium(I) 10



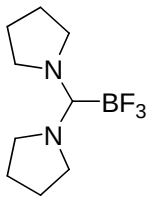
^1H NMR (300MHz, CDCl_3) δ = 4.51 (br. s., 2 H), 3.55 (br. s., 4 H), 3.40 (s, 6 H), 2.98 (br. s., 2 H), 2.16 (br. s., 4 H), 1.78 - 1.54 (m, 4 H). ^{13}C NMR (75MHz, CDCl_3) δ = 207.9, 85.0, 52.0, 52.0, 37.2, 33.6, 29.5. HRMS Calcd. for $\text{C}_{26}\text{H}_{44}\text{N}_4\text{Ir}_2\text{Cl}$ $[\text{2M}+\text{Cl}]^+$: 833.2495, Found: 833.2419.

2.6 Procedure to form Chloro(η^2 -*N,N*-dimethylbenzylamine)-bis(pyrrolidinecarbene)palladium (II) 12



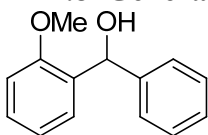
To a Schlenk flask in a glovebox, 0.055 g (0.2 mmol) of chloroamidinium **1** was added, and the flask was connected to a Schlenk line outside the glovebox. THF (2 mL) was added, and the suspension was cooled to -78°C with a dry-ice/acetone bath. After cooling, 1.7M *t*-BuLi in hexanes (0.235 mL) was added. After 5 minutes, the suspension turned to a clear and slightly yellowish solution upon formation of carbene. The solution proceeded to stir at -78°C for a total of 1 hour. After stirring for 1 hour at -78°C , 0.055 g (0.1 mmol) palladium(η^2 -*N,N*-dimethylbenzylamine)chloride dimer was added, and the reaction slowly warmed to room temperature. Stirring at room temperature proceeded for 12 hours, at which point, solvent was evaporated. To remove any remaining metal precursor, the product was purified by chromatography on a short pad of silica-gel. Columns were run starting with ethyl acetate and then transferring to 2.5% MeOH in DCM. ^1H NMR (300MHz, CDCl_3) δ = 6.93 (br. s., 2 H), 6.82 (m, 1 H), 6.64 (d, J = 7.0 Hz, 1 H), 3.74 (br. s., 10 H), 2.66 (s, 6 H), 1.85 (br. s., 8 H). ^{13}C NMR (75MHz, CDCl_3) δ = 204.3, 150.3, 148.6, 135.2, 125.8, 123.6, 122.3, 71.9, 50.0, 25.8. HRMS Calcd. for $\text{C}_{18}\text{H}_{28}\text{N}_3\text{Pd}$ $[\text{M}]^+$: 392.1320, Found: 392.1328.

2.7 Procedure to form *N,N,N',N'*-bis(tetramethylene)-2-formamidinium trifluoroborate 13

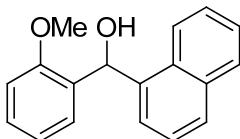


Generation of carbene as described in section 5.1 was followed with 0.50g (1.82 mmol) of chloro-amidinium **1**. After stirring for 30 minutes at -78 °C, 0.23 mL (1.82 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was added, and the reaction slowly warmed to room temperature. Stirring at room temperature proceeded for 12 hours, at which point, solvent was evaporated. The product was purified by silica gel chromatography (1:1 hexanes:ethyl acetate). ^1H NMR (300MHz, CDCl_3) δ = 3.59 (br. s., 8 H), 1.73 (br. s., 8 H). ^{13}C NMR (75MHz, CDCl_3) δ = 180.3, 52.8, 25.4. ^{19}F NMR (282MHz, CDCl_3) δ = 138.95 (q, J = 45 Hz). Anal Calcd for $\text{C}_9\text{H}_{16}\text{N}_2\text{BF}_3$: C, 49.13; H, 7.33; N, 12.73. Found: C, 49.37; H, 7.53; N, 12.59.

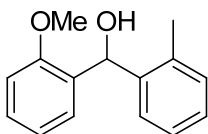
2.8 General Procedure for 1,2-Addition of Aryl Boronic Acids to Aldehydes



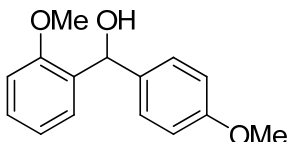
To a flame dried Schlenk flask under argon, 50 mg (0.364 mmol) of *o*-anisaldehyde, 89 mg (0.728 mmol) of phenyl boronic acid, 83 mg (0.728 mmol) of potassium *tert*-butoxide, and 2 mg (0.0052 mmol) of rhodium catalyst **4** were added. 1.22 mL of DME and 0.33 mL of water were added, and the solution was heated to 40 °C. The mixture was stirred for one hour and monitored by TLC (R_f 0.38, 4:1 hexanes/ethyl acetate). The solution was diluted with 10 mL of diethyl ether and 10 mL of water and was then extracted three times. The organic layer was dried and concentrated, and then purified by silica-gel chromatography (8:1 hexanes/ethyl acetate) to isolate the product as a clear oil in 92% yield. Spectroscopic values matched those reported in the literature.⁴ ^1H NMR (300MHz, CDCl_3) δ = 7.49 - 7.11 (m, 8 H), 7.07 - 6.82 (m, 2 H), 6.07 (s, 1 H), 3.78 (s, 3 H), 3.32 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 156.9, 143.5, 132.2, 129.7, 129.0, 128.4, 128.1, 127.4, 126.8, 121.1, 115.6, 111.0, 72.4, 55.7. HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{O}$ $[\text{M}-\text{OH}]^+$: 197.0989, Found: 197.0994.



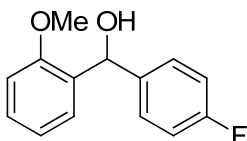
^1H NMR (299MHz, CDCl_3) δ = 8.05 (d, J = 7.4 Hz, 1 H), 7.96 - 7.79 (m, 2 H), 7.71 (d, J = 7.1 Hz, 1 H), 7.60 - 7.39 (m, 3 H), 7.37 - 7.22 (m, 1 H), 7.11 - 6.78 (m, 4 H), 3.91 (s, 3 H), 3.22 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 157.2, 138.4, 134.0, 131.6, 131.3, 129.2, 128.9, 128.7, 128.3, 126.2, 125.7, 124.6, 124.5, 121.1, 110.8, 68.6, 55.8. HRMS Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}$ $[\text{M}-\text{OH}]^+$: 247.1177, Found: 247.1176.



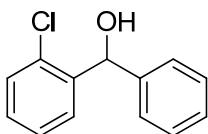
^1H NMR (299MHz, CDCl_3) δ = 7.66 - 7.46 (m, 1 H), 7.43 - 7.13 (m, 4 H), 7.12 - 6.83 (m, 3 H), 6.32 (s, 1 H), 3.88 (s, 3 H), 3.00 (br. s., 1 H), 2.27 (s, 3 H). ^{13}C NMR (75MHz, CDCl_3) δ = 157.3, 140.8, 135.8, 131.5, 130.4, 129.1, 128.1, 127.5, 126.8, 126.2, 121.0, 110.7, 68.5, 55.7, 19.5. HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{O}$ $[\text{M}-\text{OH}]^+$: 211.1176, Found: 211.1185.



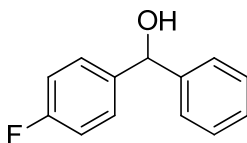
^1H NMR (300MHz, CDCl_3) δ = 7.60 - 7.17 (m, 4 H), 7.11 - 6.73 (m, 4 H), 6.05 (s, 1 H), 3.79 (s, 6 H), 3.30 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 159.0, 156.9, 136.0, 132.6, 128.8, 128.1, 127.8, 121.0, 113.8, 111.0, 71.7, 55.6, 55.5. HRMS Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$ $[\text{M}-\text{OH}]^+$: 226.0994, Found: 226.0987.



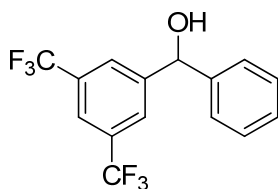
^1H NMR (300MHz, CDCl_3) δ = 7.55 - 7.19 (m, 4 H), 7.13 - 6.79 (m, 4 H), 6.03 (br. s., 1 H), 3.80 (s, 3 H), 3.27 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 163.8, 160.6, 156.8, 139.4, 139.4, 132.1, 129.1, 128.5, 128.4, 127.8, 121.1, 115.3, 115.0, 111.0, 71.7, 55.6. HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_2\text{F}$ $[\text{M}]^+$: 232.0900, Found: 232.0886.



Spectroscopic values matched those reported in the literature.⁴ ^1H NMR (299MHz, CDCl_3) δ = 7.62 (dd, J = 1.4, 7.6 Hz, 1 H), 7.51 - 7.11 (m, 8 H), 6.37 - 6.05 (m, 1 H), 2.88 - 2.58 (m, 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 142.5, 141.3, 132.7, 129.8, 129.0, 128.7, 128.3, 128.0, 127.4, 127.2, 72.9. HRMS Calcd. for $\text{C}_{13}\text{H}_{10}\text{Cl}$ $[\text{M}-\text{OH}]^+$: 201.0446, Found: 201.0472.



Spectroscopic values matched those reported in the literature.⁵ ^1H NMR (300MHz, CDCl_3) δ = 7.45 - 7.18 (m, 7 H), 7.09 - 6.85 (m, 2 H), 5.74 (s, 1 H), 2.63 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 164.0, 160.7, 143.8, 139.8, 139.7, 130.1, 128.8, 128.6, 128.5, 128.4, 127.9, 126.7, 115.6, 115.3, 75.8. HRMS Calcd. for $\text{C}_{13}\text{H}_9\text{F}$ $[\text{M}-\text{OH}]^+$: 185.0761, Found: 185.0772.



^1H NMR (300MHz, CDCl_3) δ = 7.87 (s, 2 H), 7.79 (s, 1 H), 7.55 - 7.19 (m, 5 H), 5.91 (s, 1 H), 2.50 (br. s., 1 H). ^{13}C NMR (75MHz, CDCl_3) δ = 146.3, 142.6, 132.1, 131.7, 129.3, 128.8, 126.9, 126.7, 121.7, 121.6, 75.5. HRMS Calcd. for $\text{C}_{15}\text{H}_{10}\text{F}_6$ $[\text{M}]^+$: 320.0636, Found: 320.0623.

3. References

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4. NMR of Carbene Intermediate

The carbene was generated at $-78\text{ }^\circ\text{C}$, in THF-d_8 , and analyzed by NMR spectroscopy at $-30\text{ }^\circ\text{C}$. First, gHMBC, gHMQC and gDQCOSY experiments were run in about 30 minutes, to quickly characterize the carbene, presumed unstable. The carbene carbon, at 232.9 ppm, displayed couplings in the gHMBC spectrum with two protons, at 3.47 and 3.66 ppm, both triplets. The gDQCOSY spectrum revealed the sequence 3.47–1.89–1.76–3.66. The carbons carrying these protons were detected in the gHMQC spectrum at 48.4, 26.5, 24.5 and 55.8 correspondingly. The non-equivalence of the alpha positions in the tetrahydropyrrole moiety indicates restricted rotation about the carbene carbon – nitrogen bond.

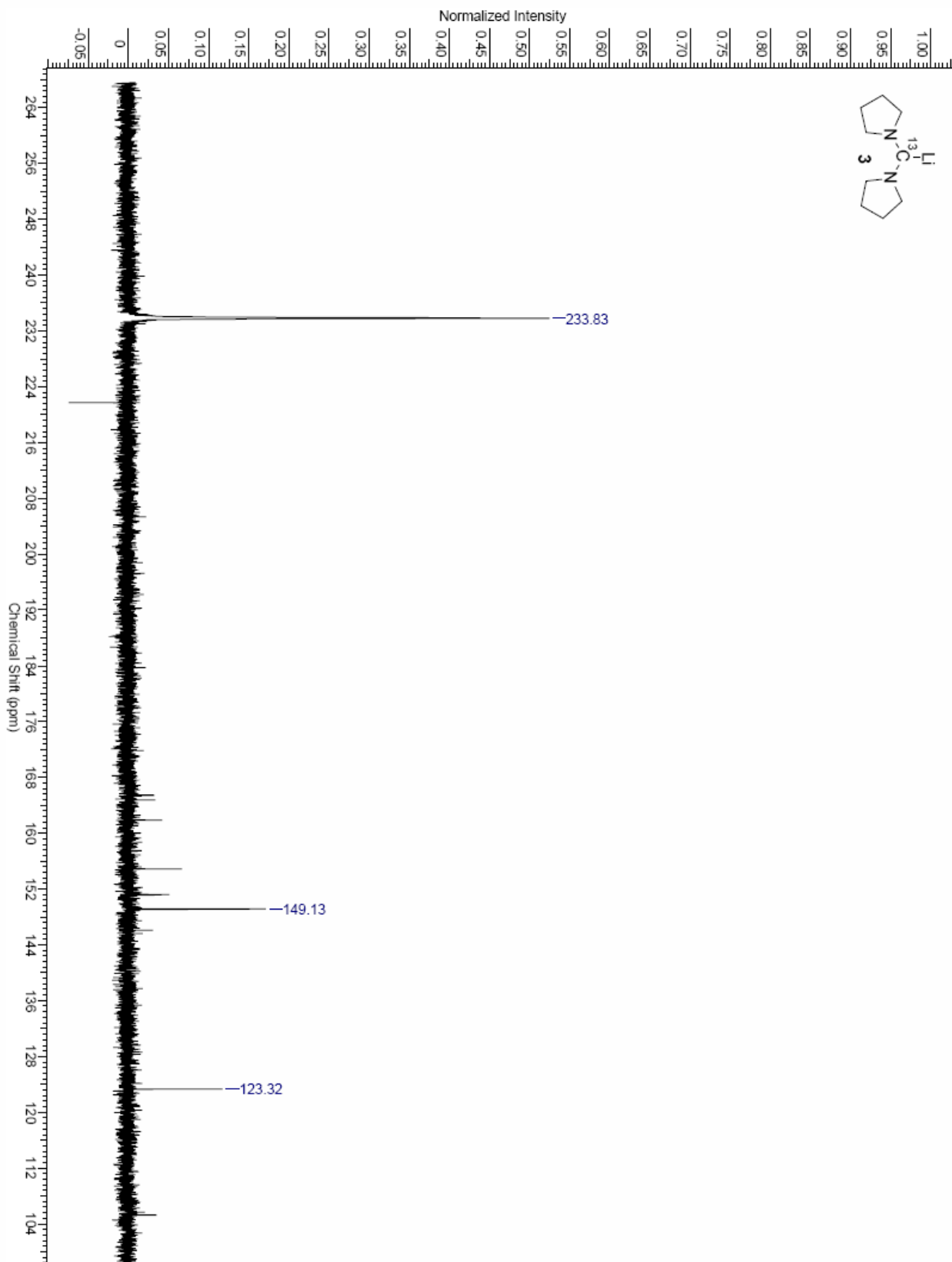
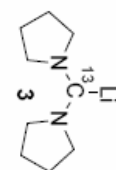
NMR spectra were recorded on a Varian Inova spectrometer, operating at 500 MHz for ^1H and 125 MHz for ^{13}C , and equipped with a 5 mm indirect detection probe, with z-axis gradients. The ^1H and ^{13}C chemical shifts were referenced to internal tetramethylsilane. The solvent was THF-d_8 , and the temperature $-30\text{ }^\circ\text{C}$.

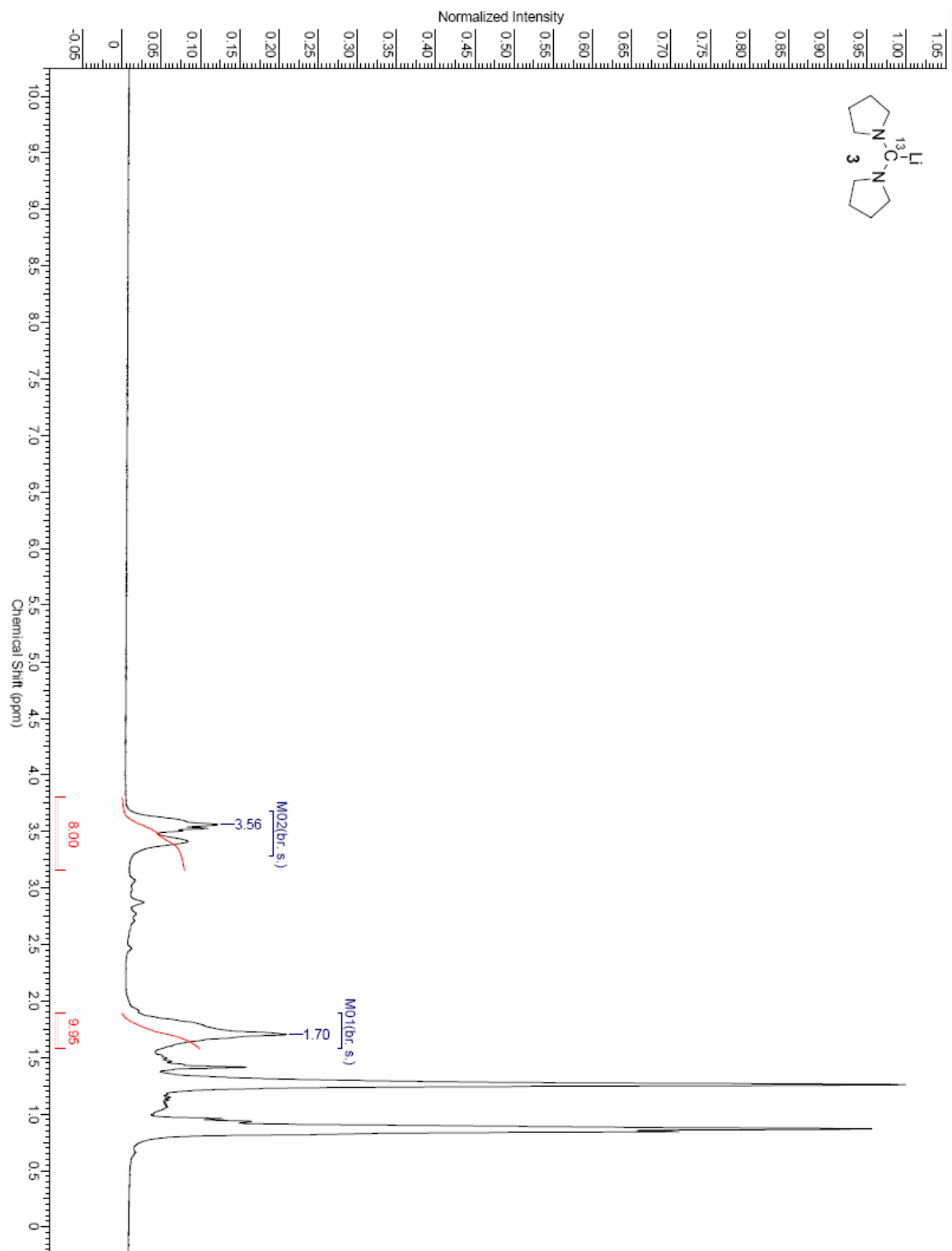
The gHMBC experiment was run with the standard vnmr pulse sequence. 2048 points were acquired in f2, on a spectral window from 0.1 to 4.3 ppm. The acquisition time was 0.49 s, with a relaxation delay of 0.5 s. 512 increments were acquired in f1, for a spectral window from 0 to 300 ppm, in 1 transient per increment. The total experiment time was 9 minutes.

The gHMQC experiment was run with the standard vnmr pulse sequence. 1024 points were acquired in f2, on a spectral window from 0.5 to 4.0 ppm. The acquisition time was 0.29 s, with a relaxation delay of 1 s. 256 increments were acquired in f1, for a spectral

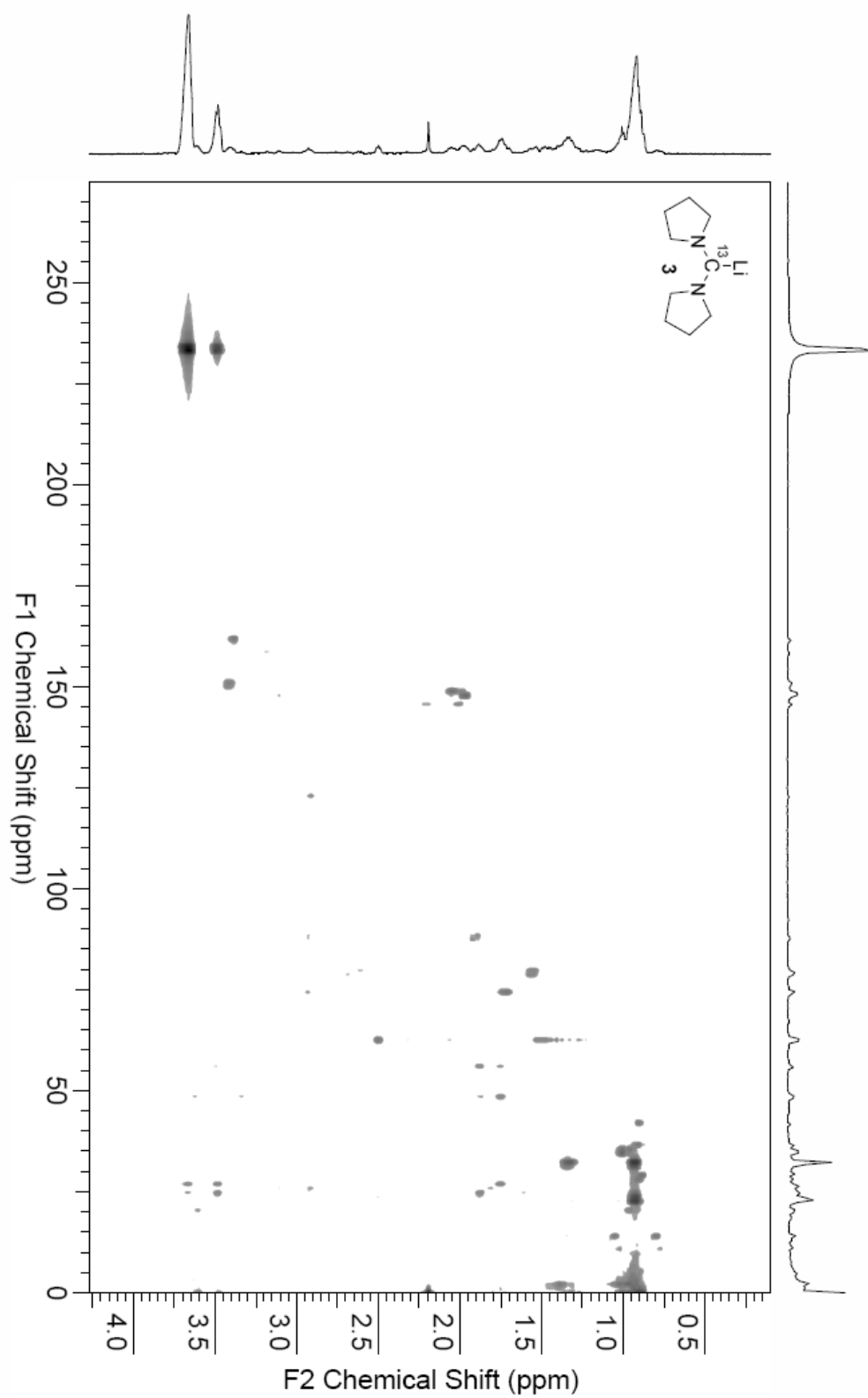
window from 10 to 80 ppm, in 1 transient per increment. The total experiment time was 6 minutes.

The gDQCOSY experiment was run with the standard vnmr pulse sequence. 2048 points were acquired in f2, on a spectral window from 0.64 to 3.64 ppm. The acquisition time was 0.64 s, with a relaxation delay of 1 s. 512 increments were acquired in f1, in 1 transient per increment. The total experiment time was 16 minutes.

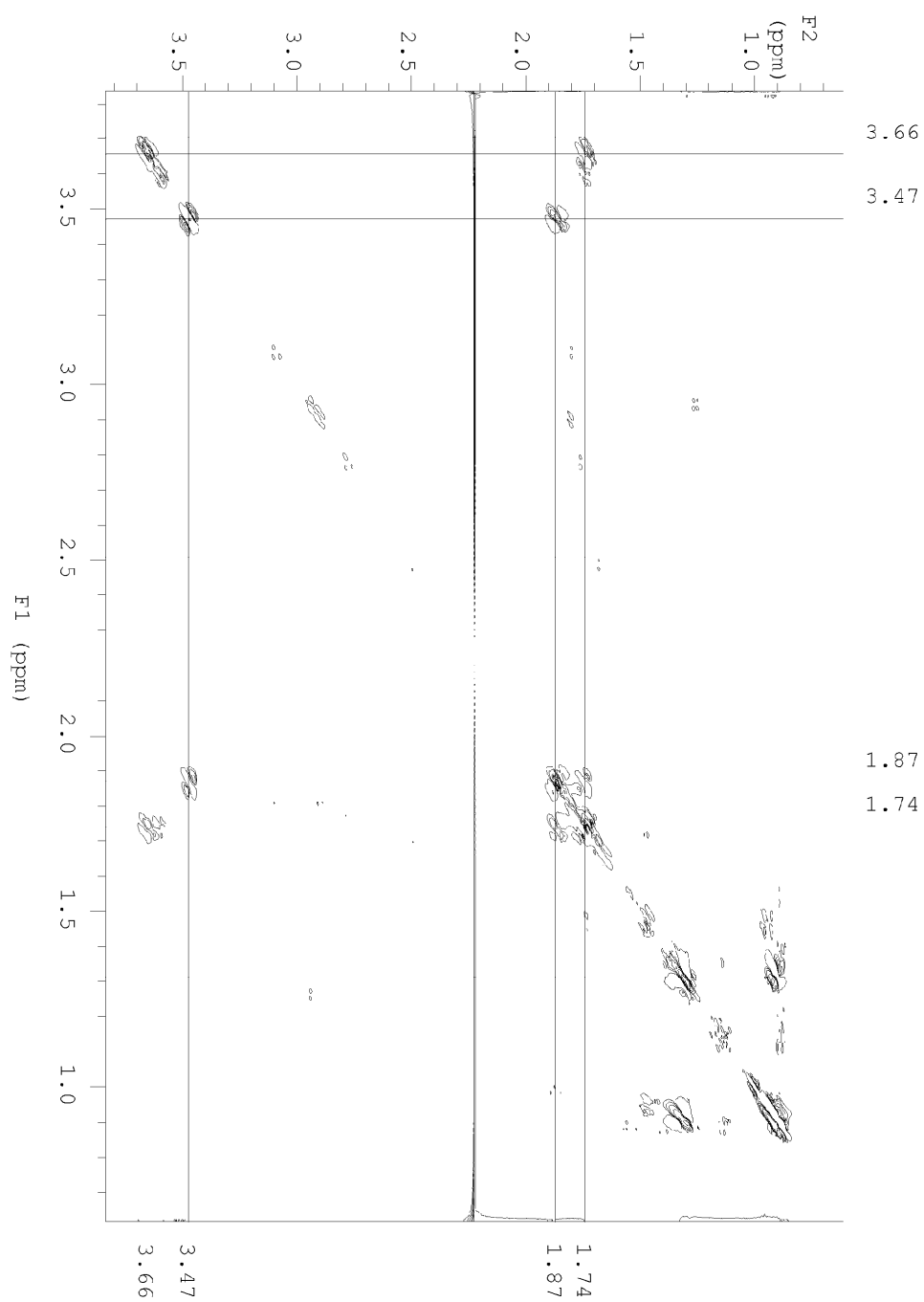




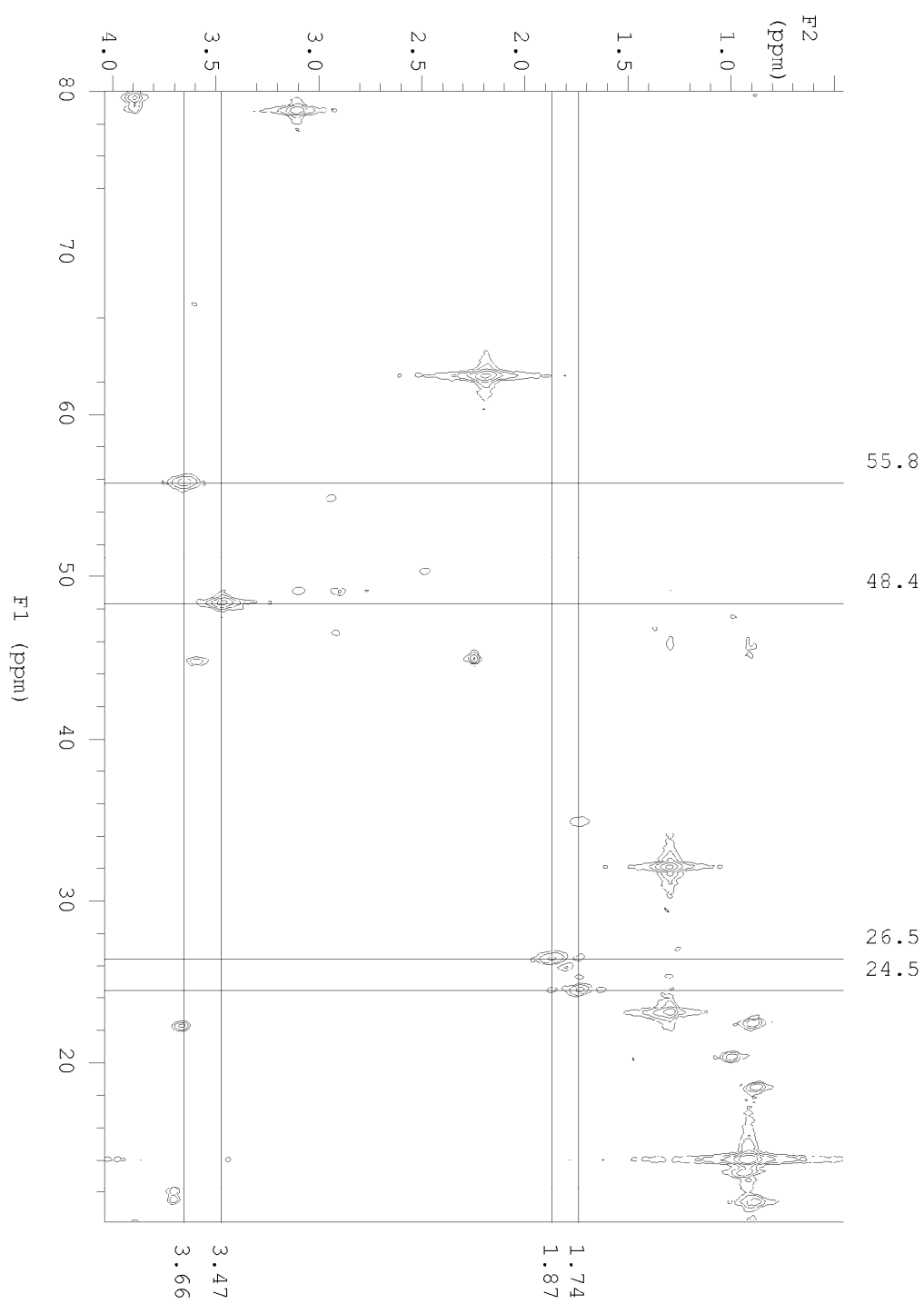
4.1 gHMBC



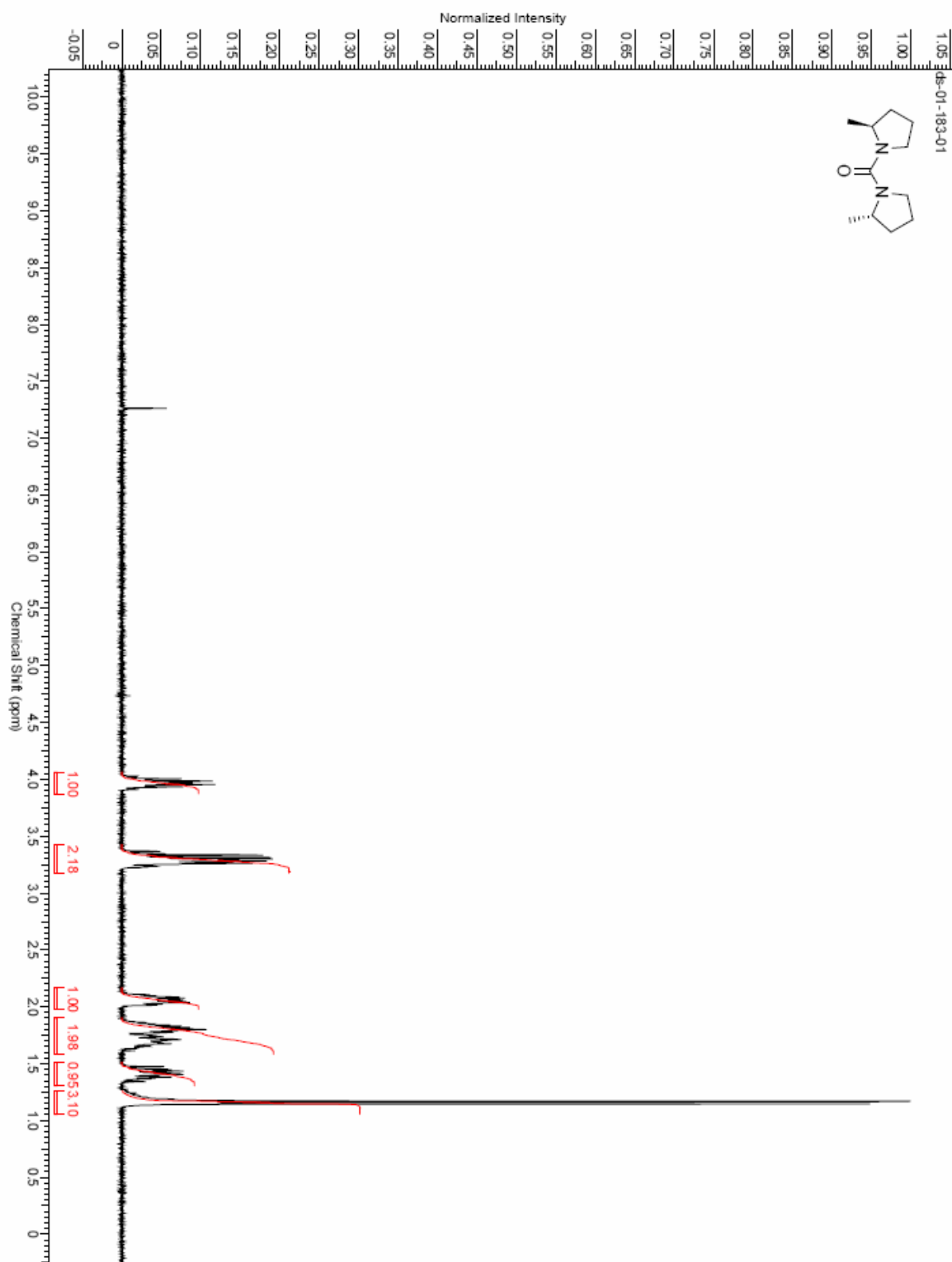
4.2 gDQCOSY

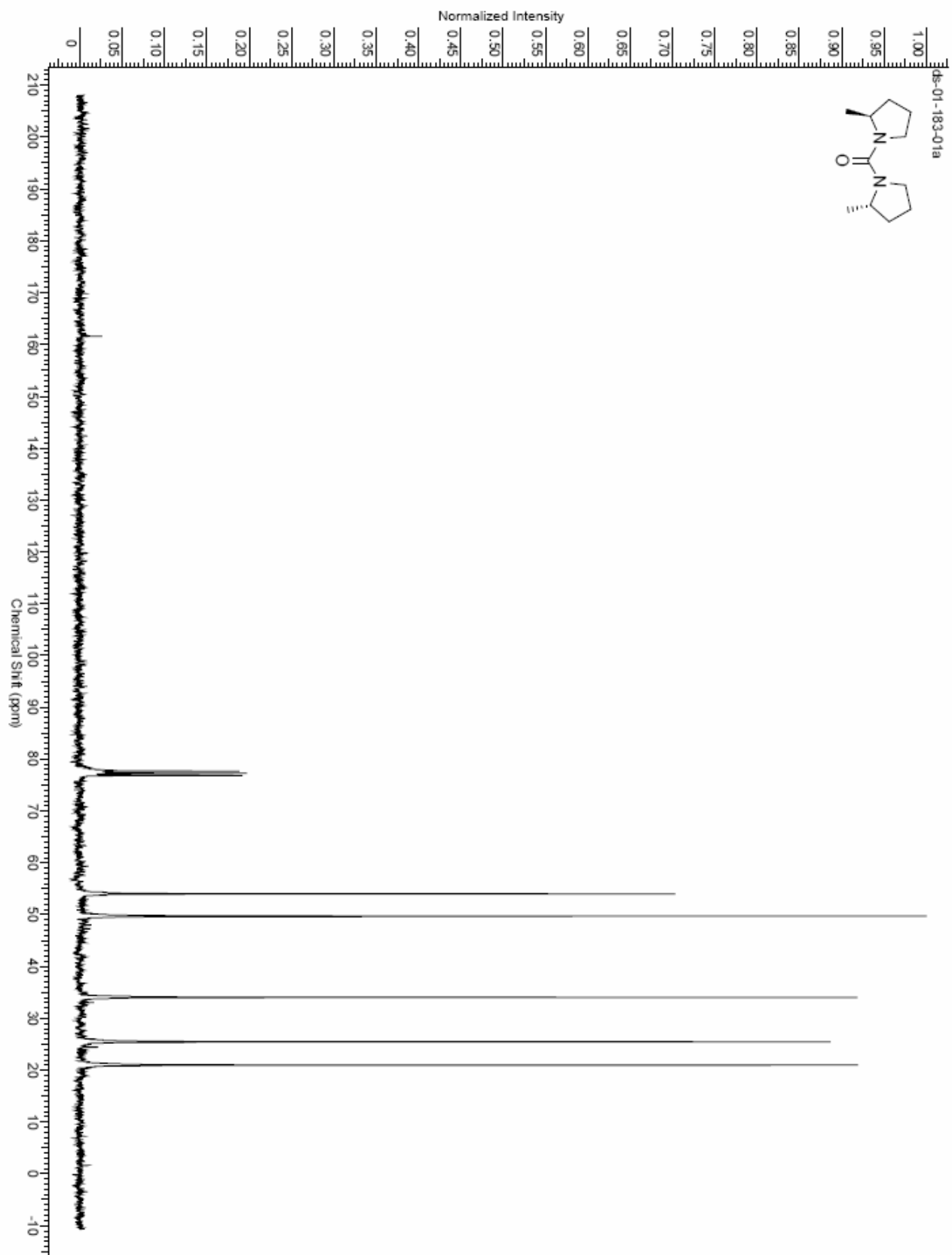


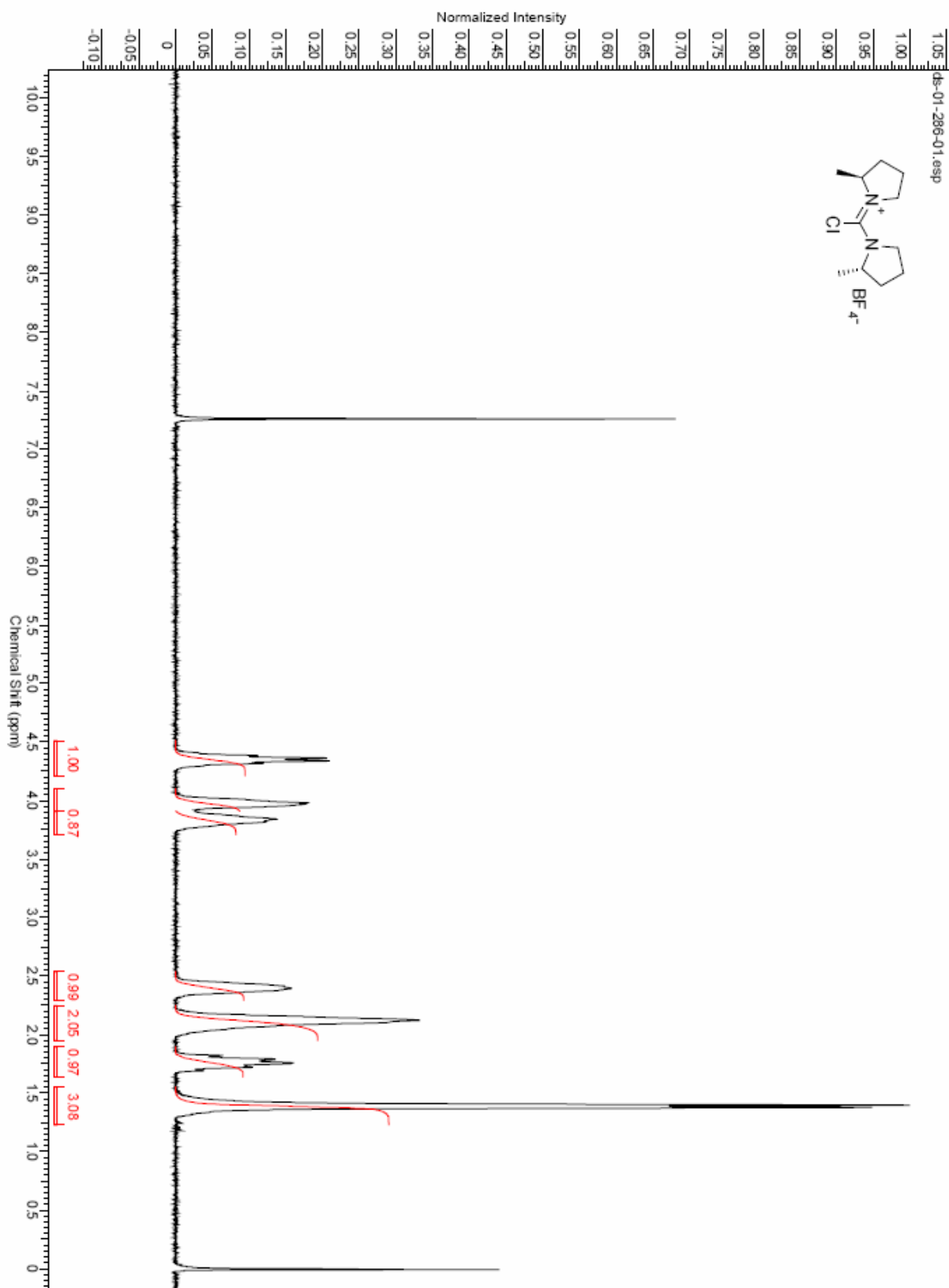
4.3 gHMQC

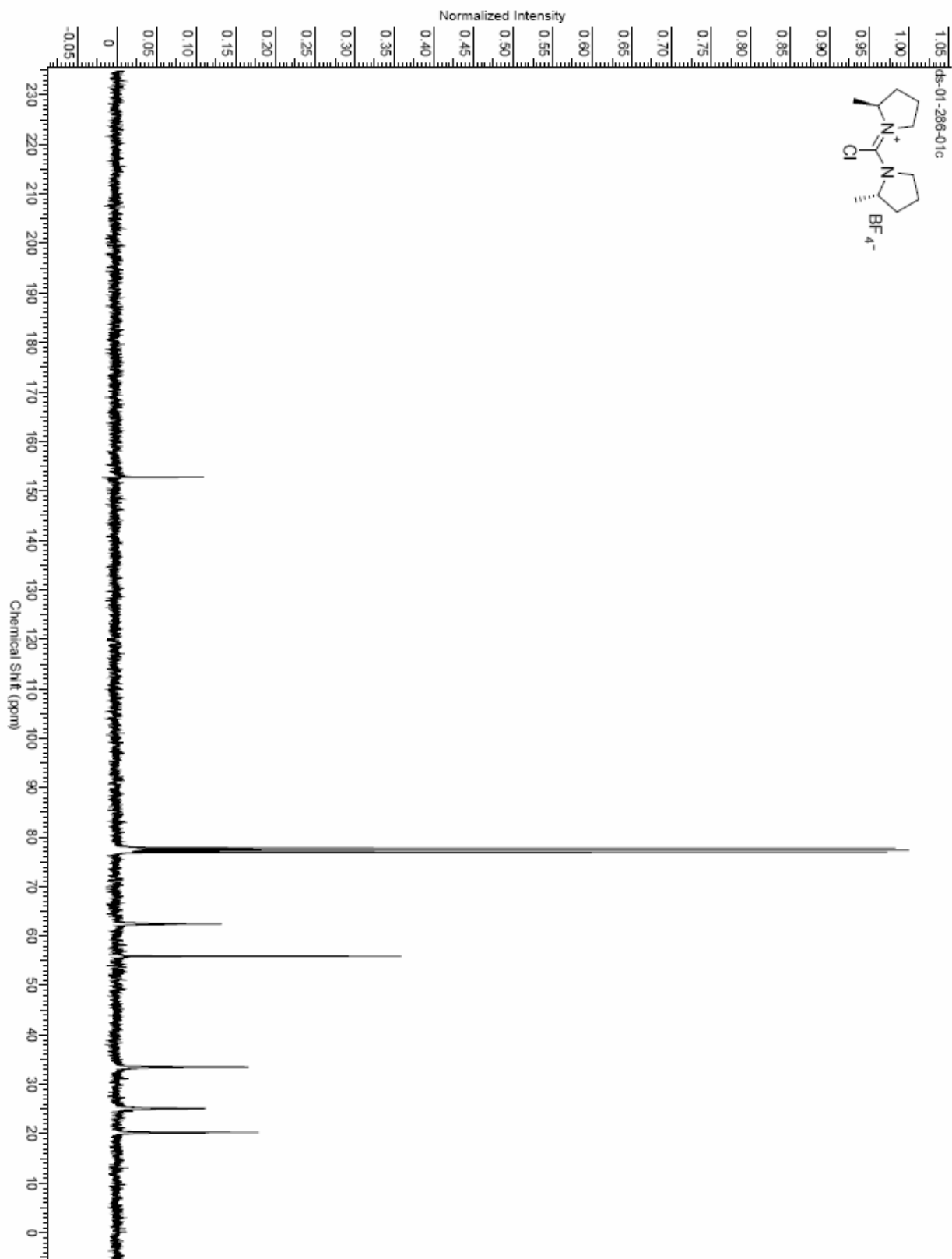


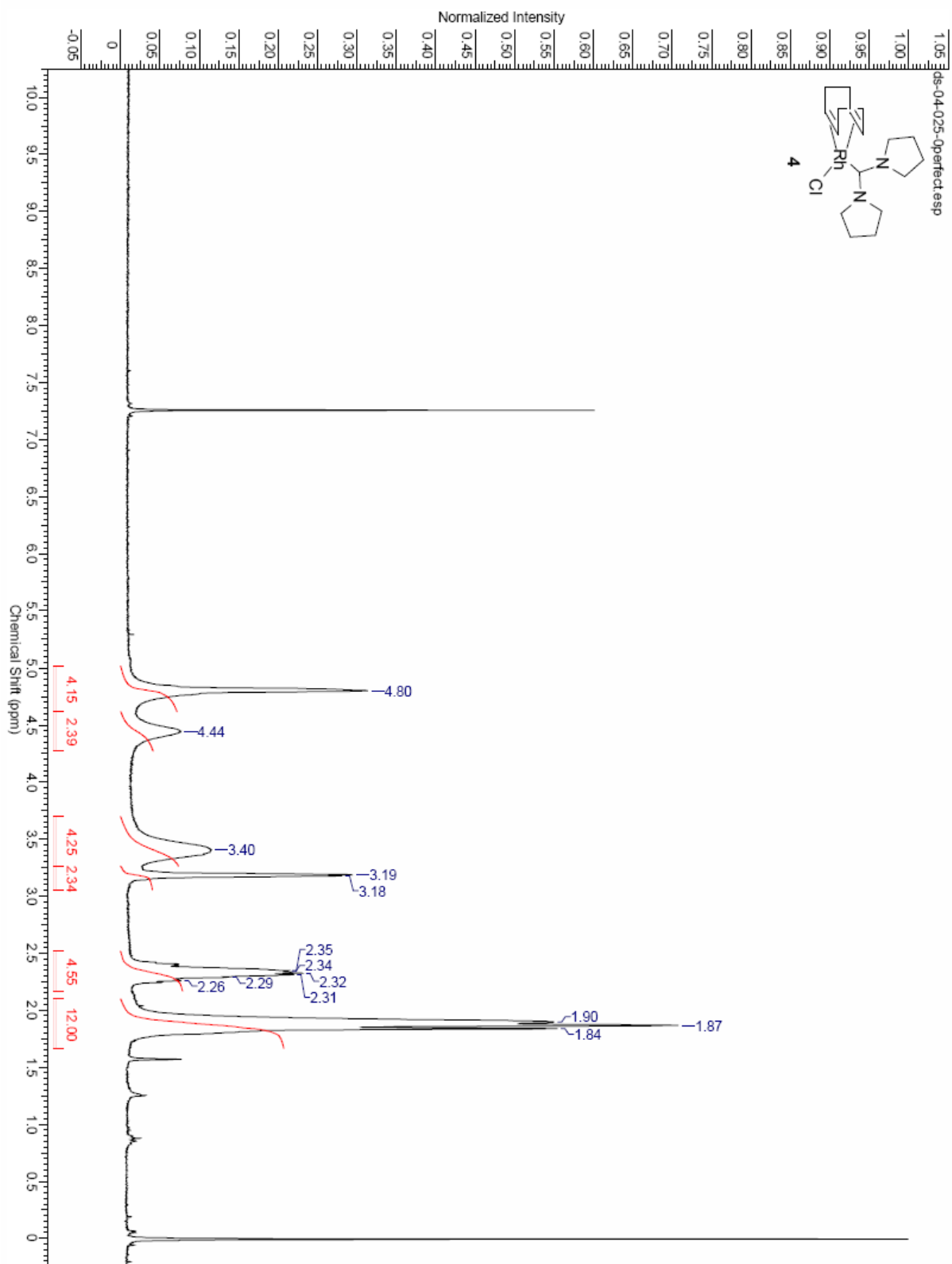
5. NMR of New Compounds and Catalytic Results

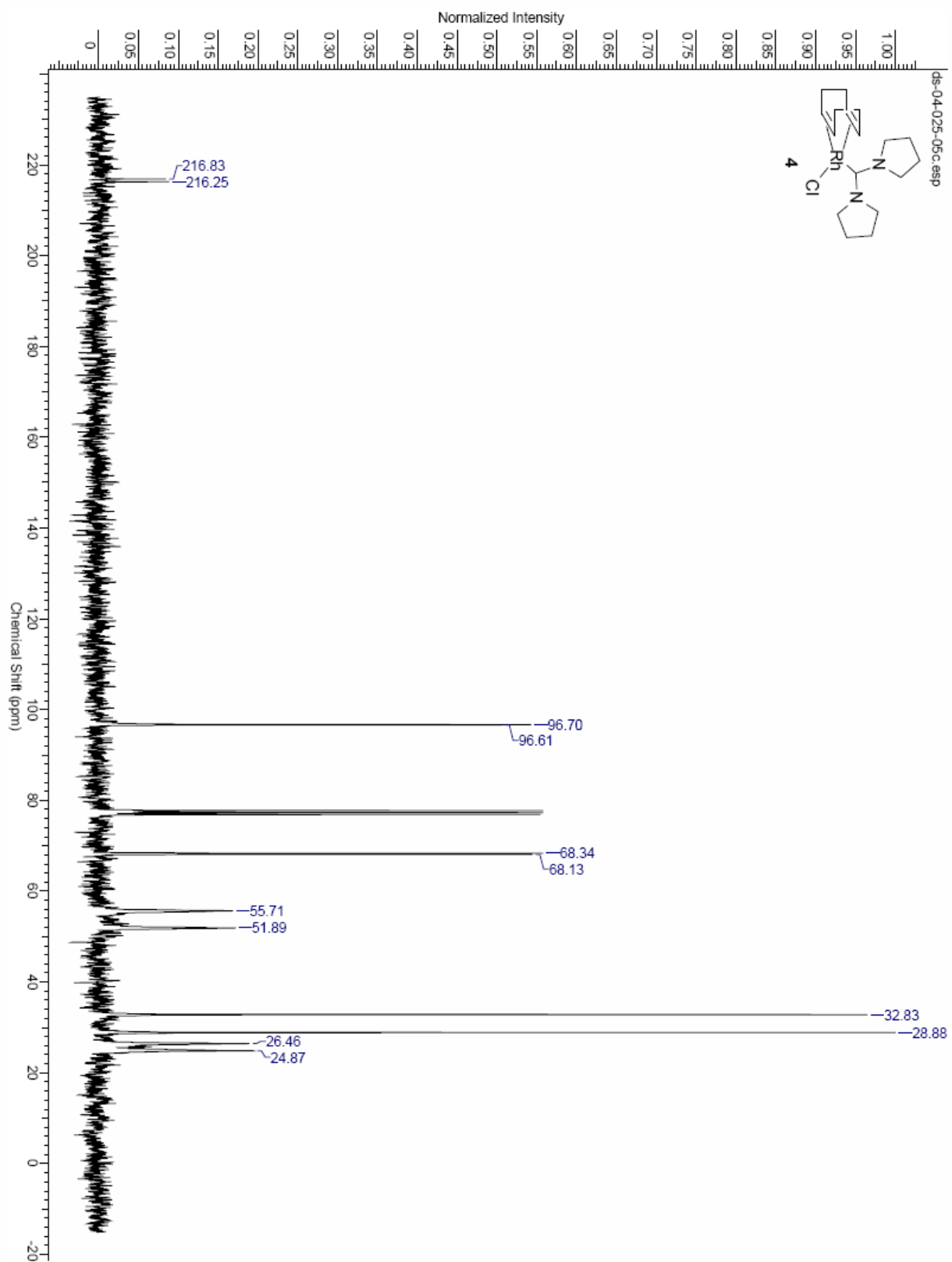


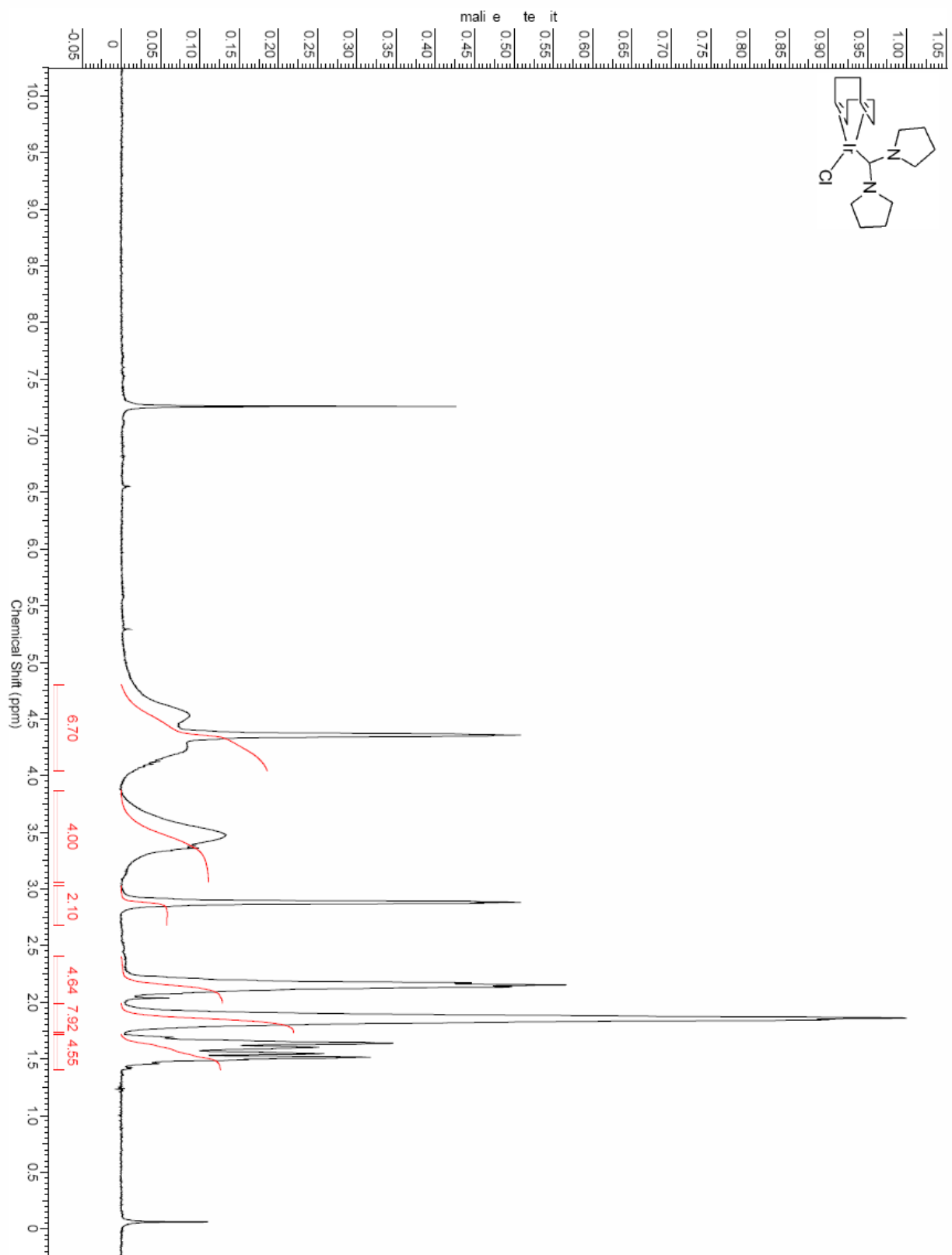


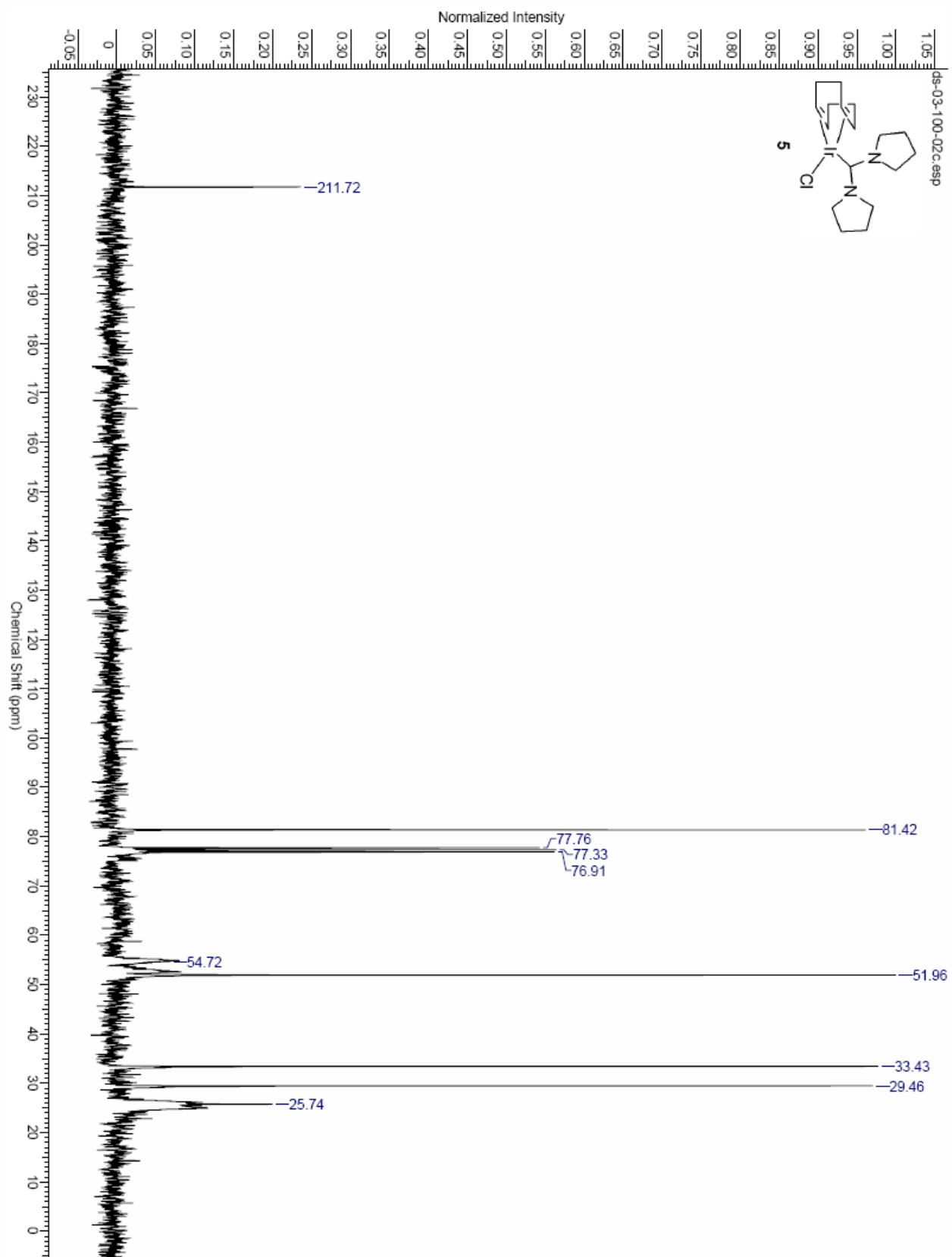


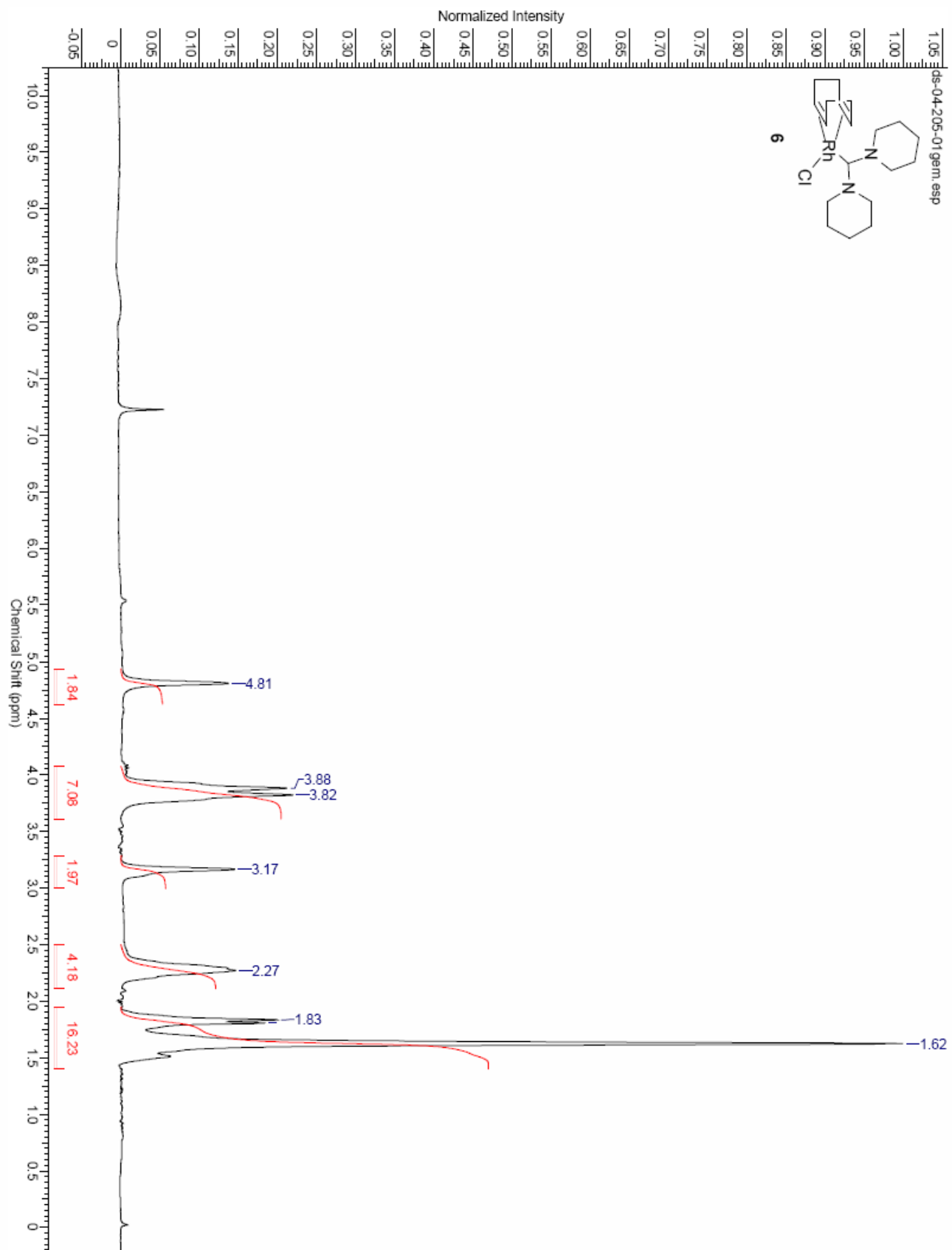


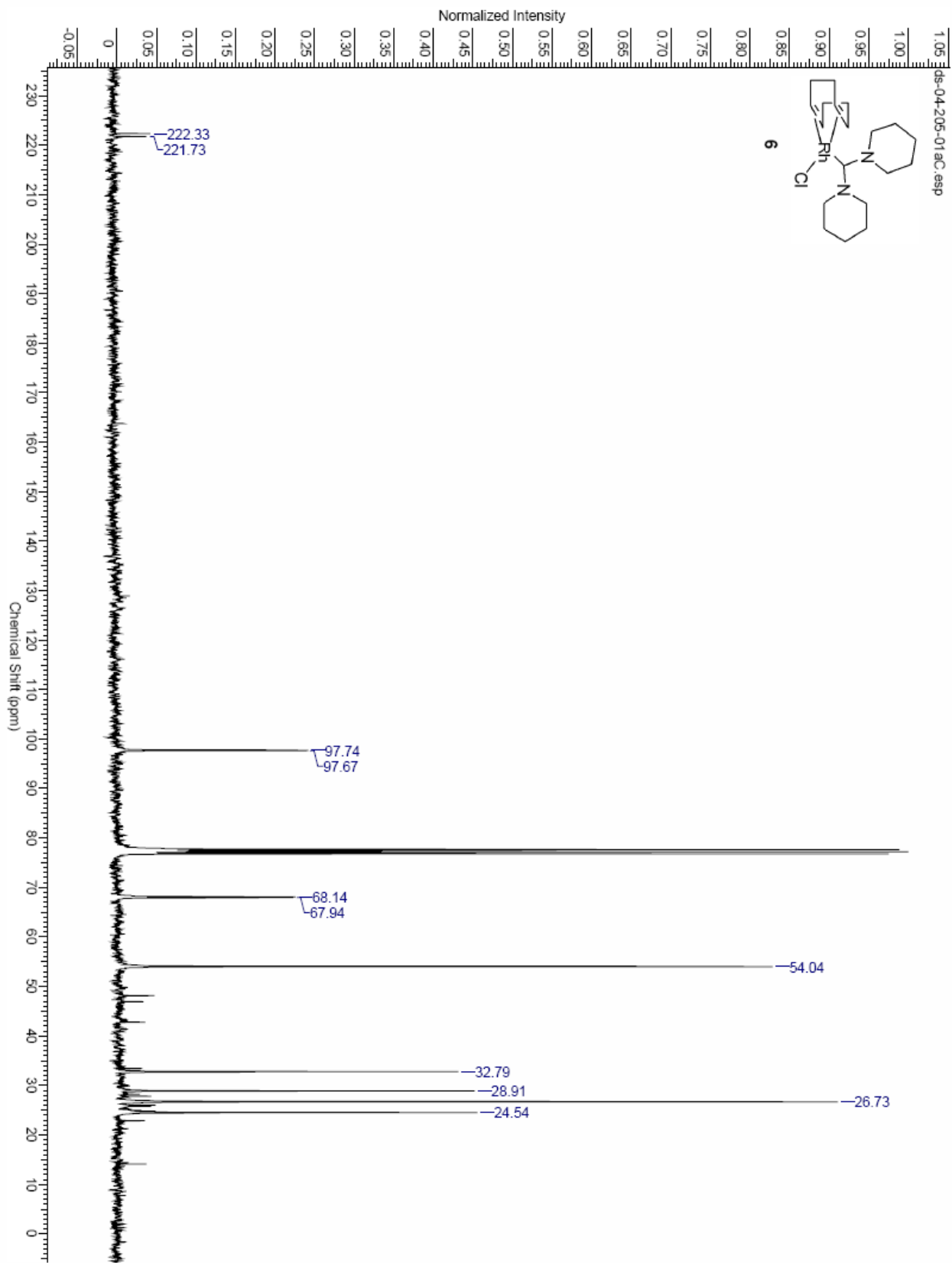


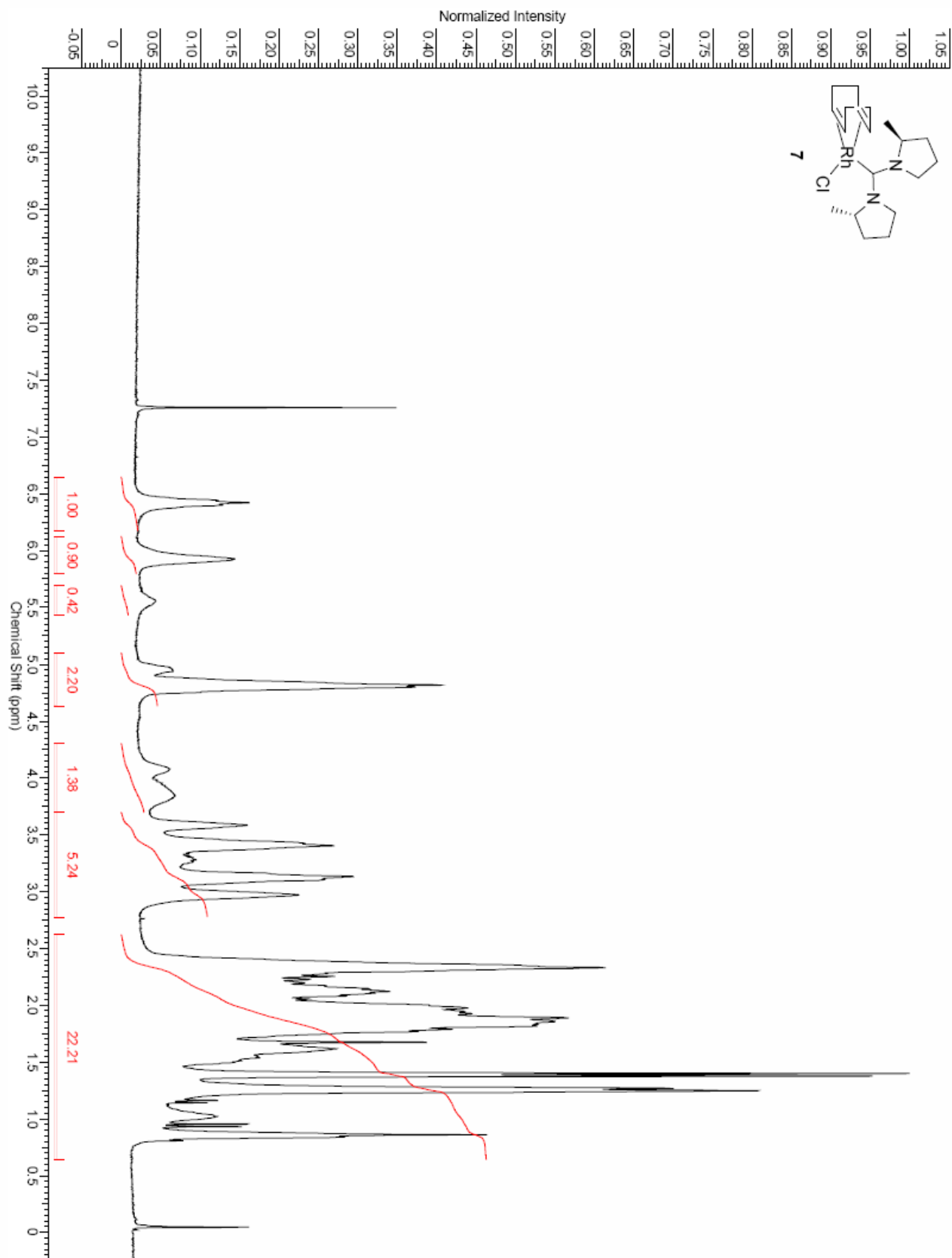


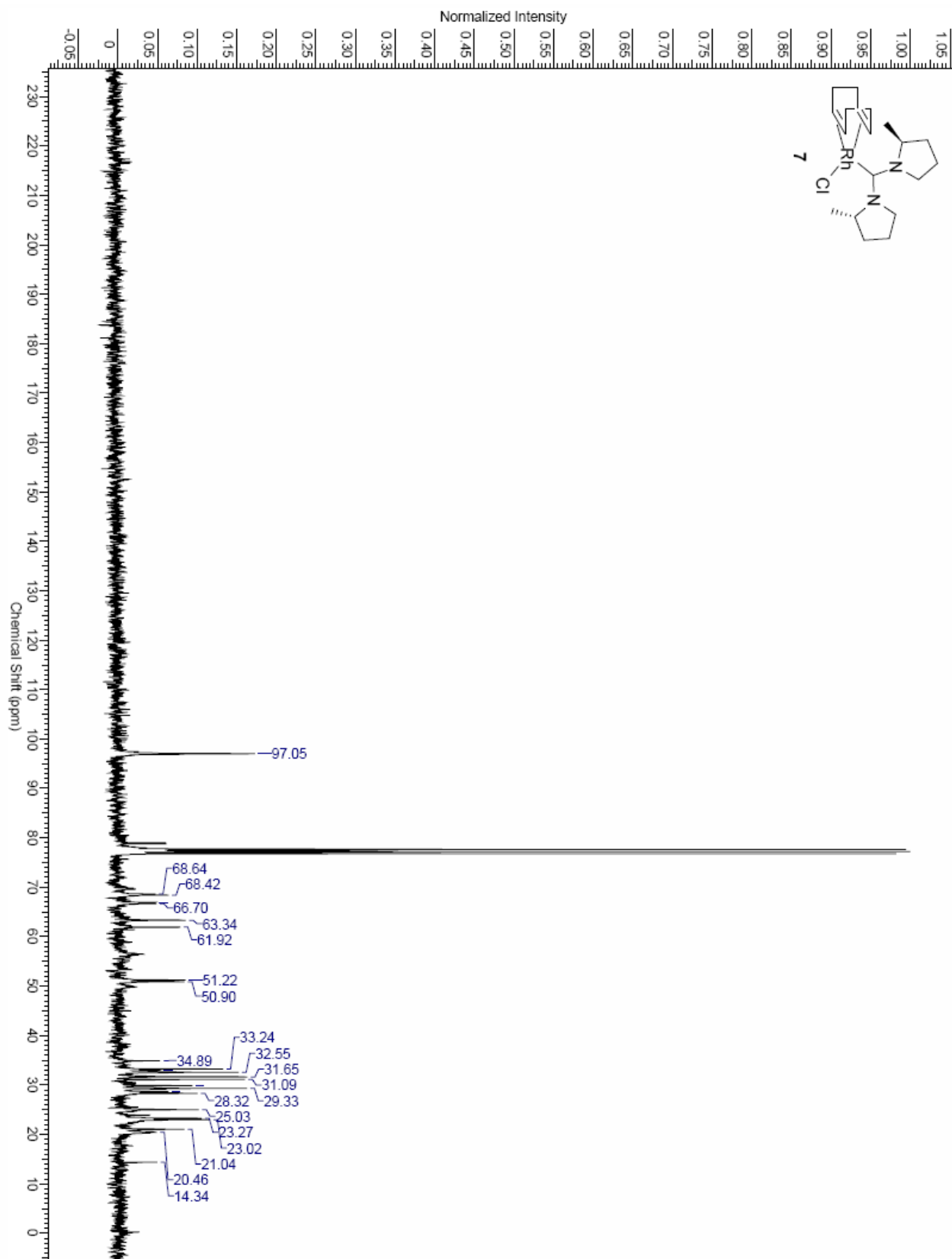


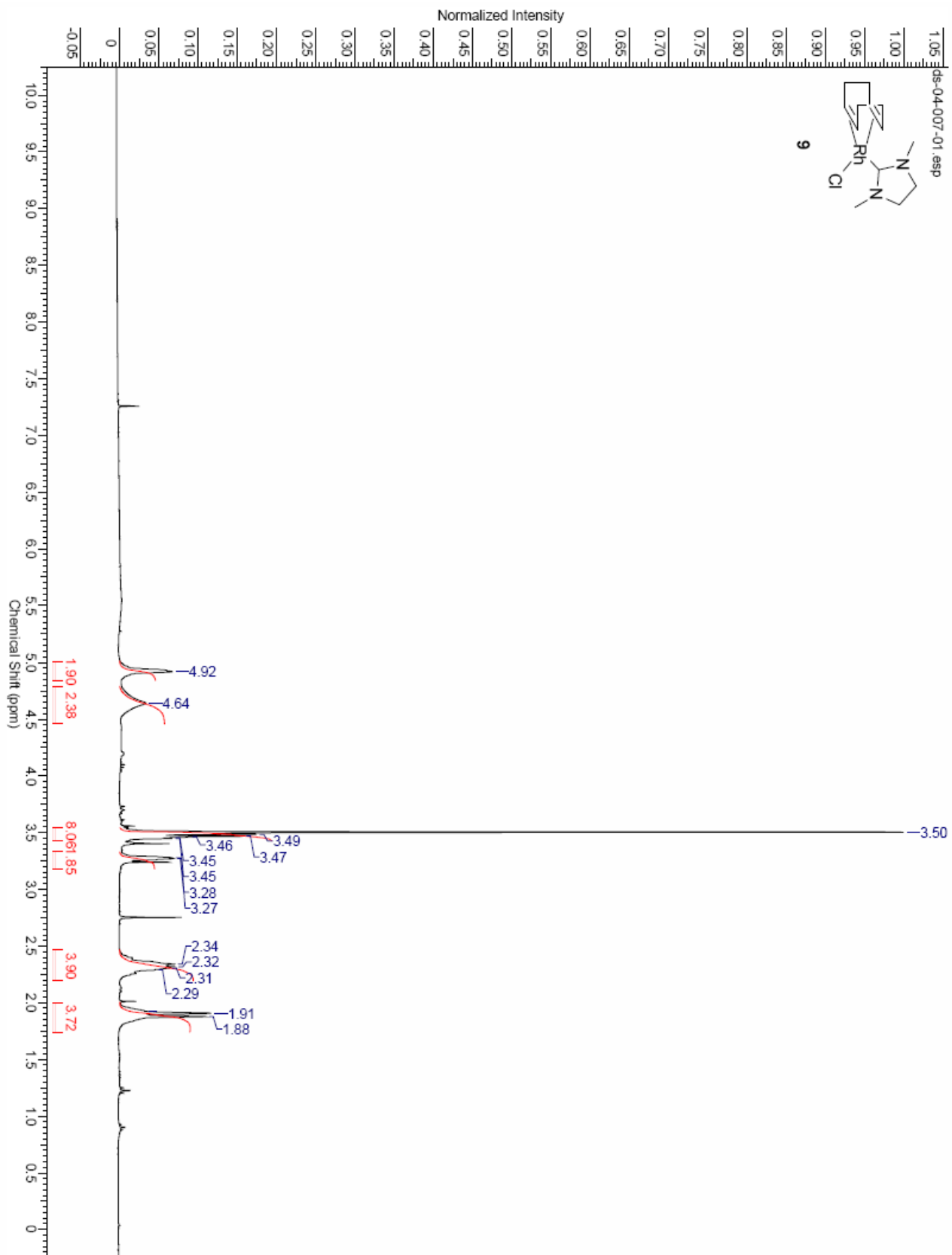


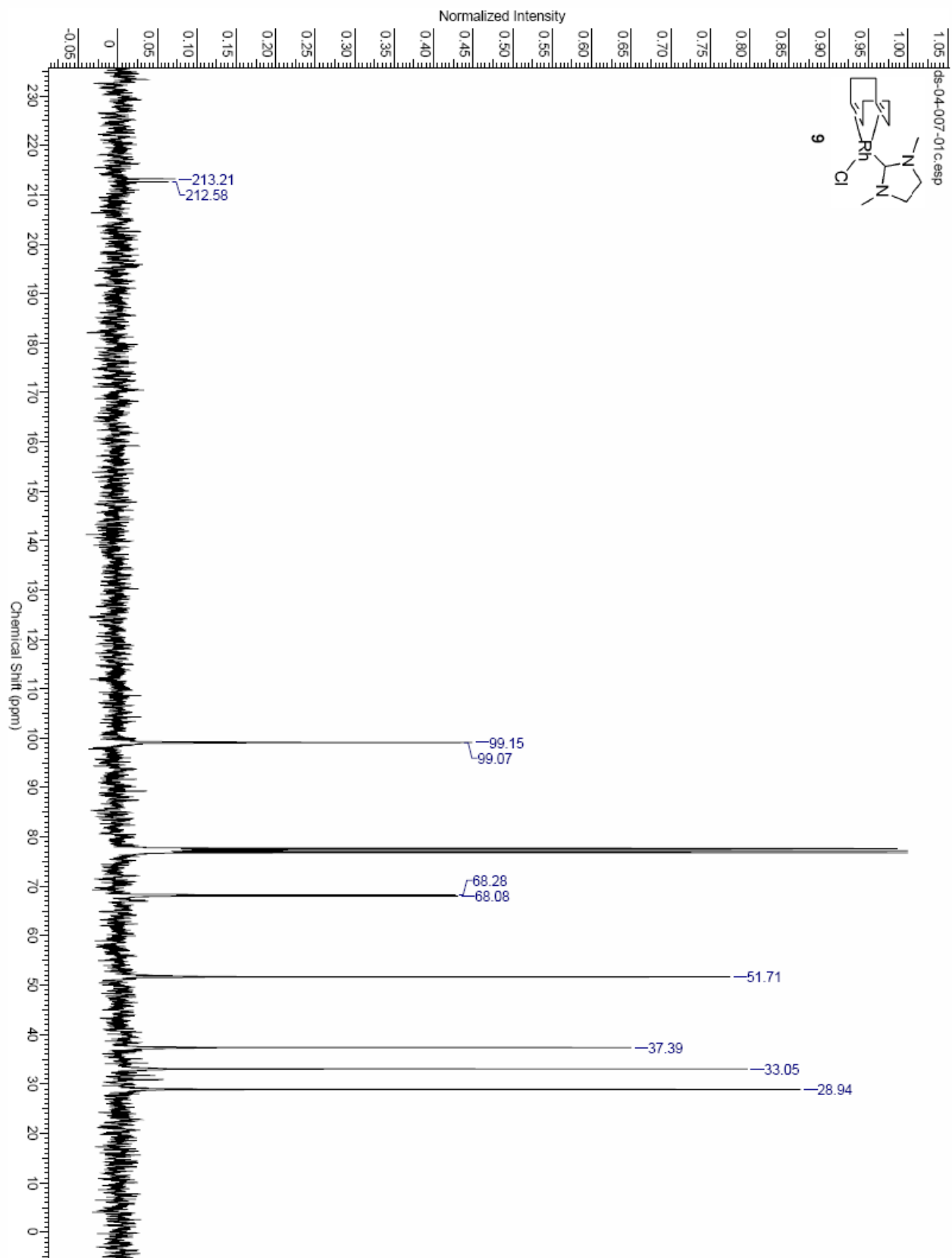


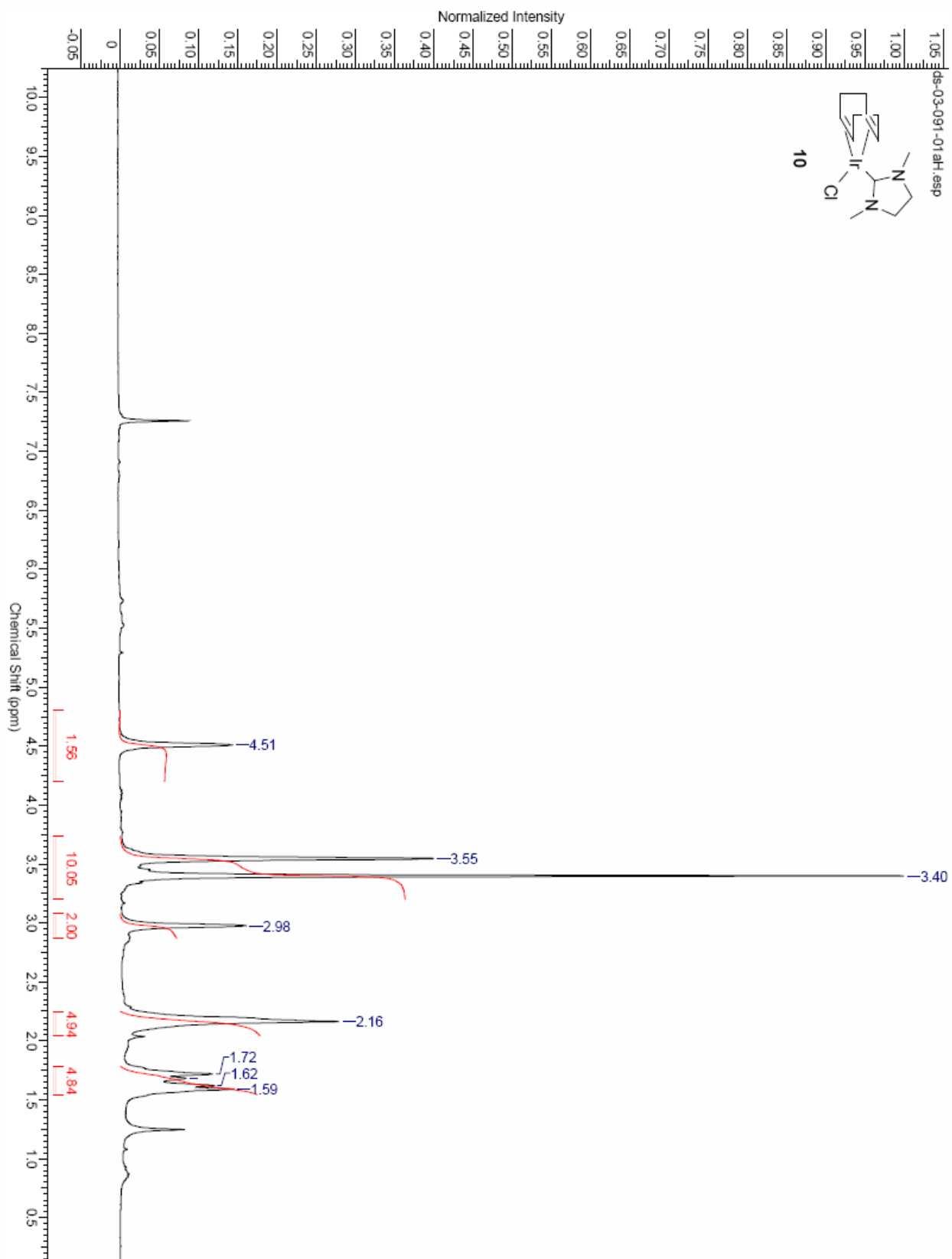


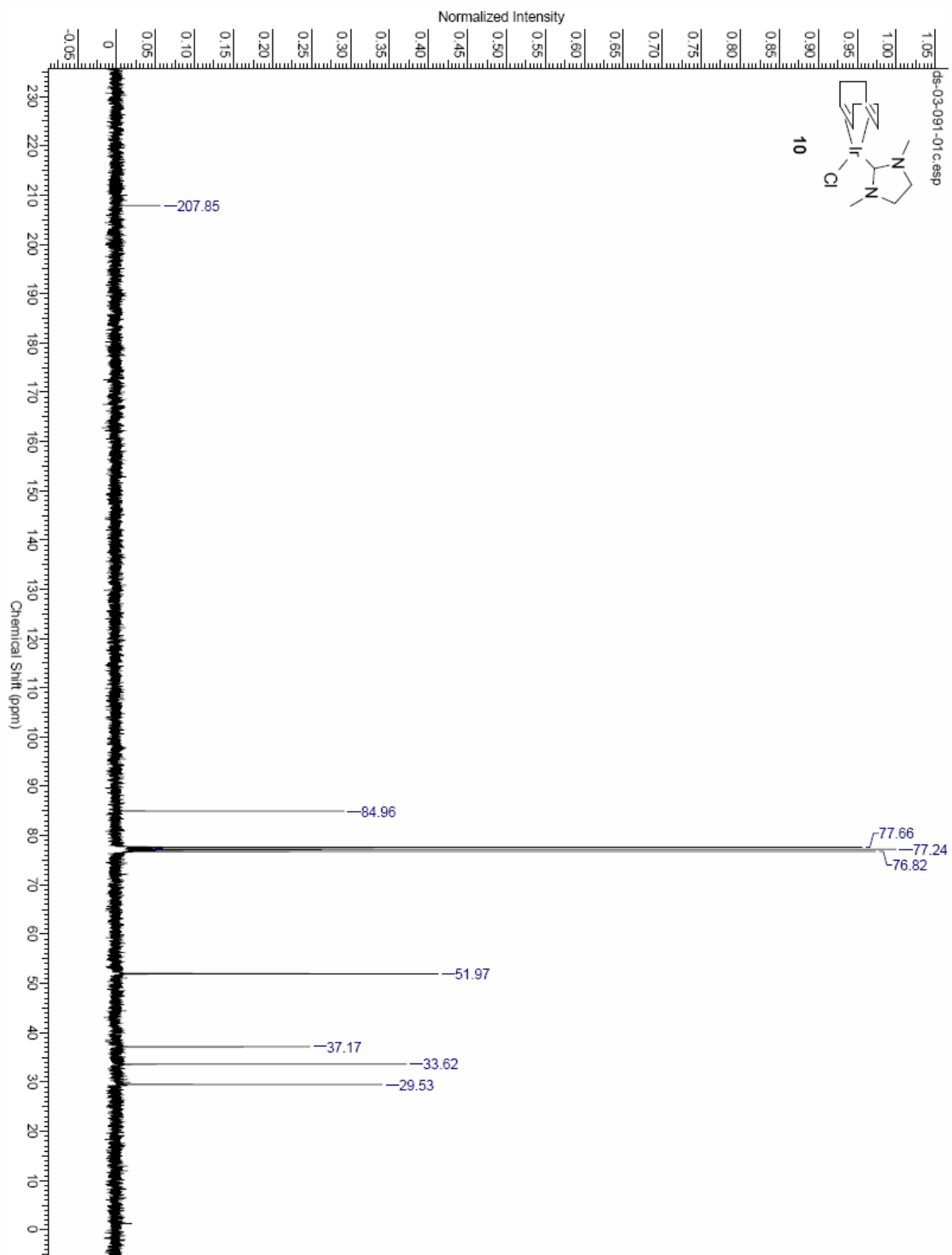


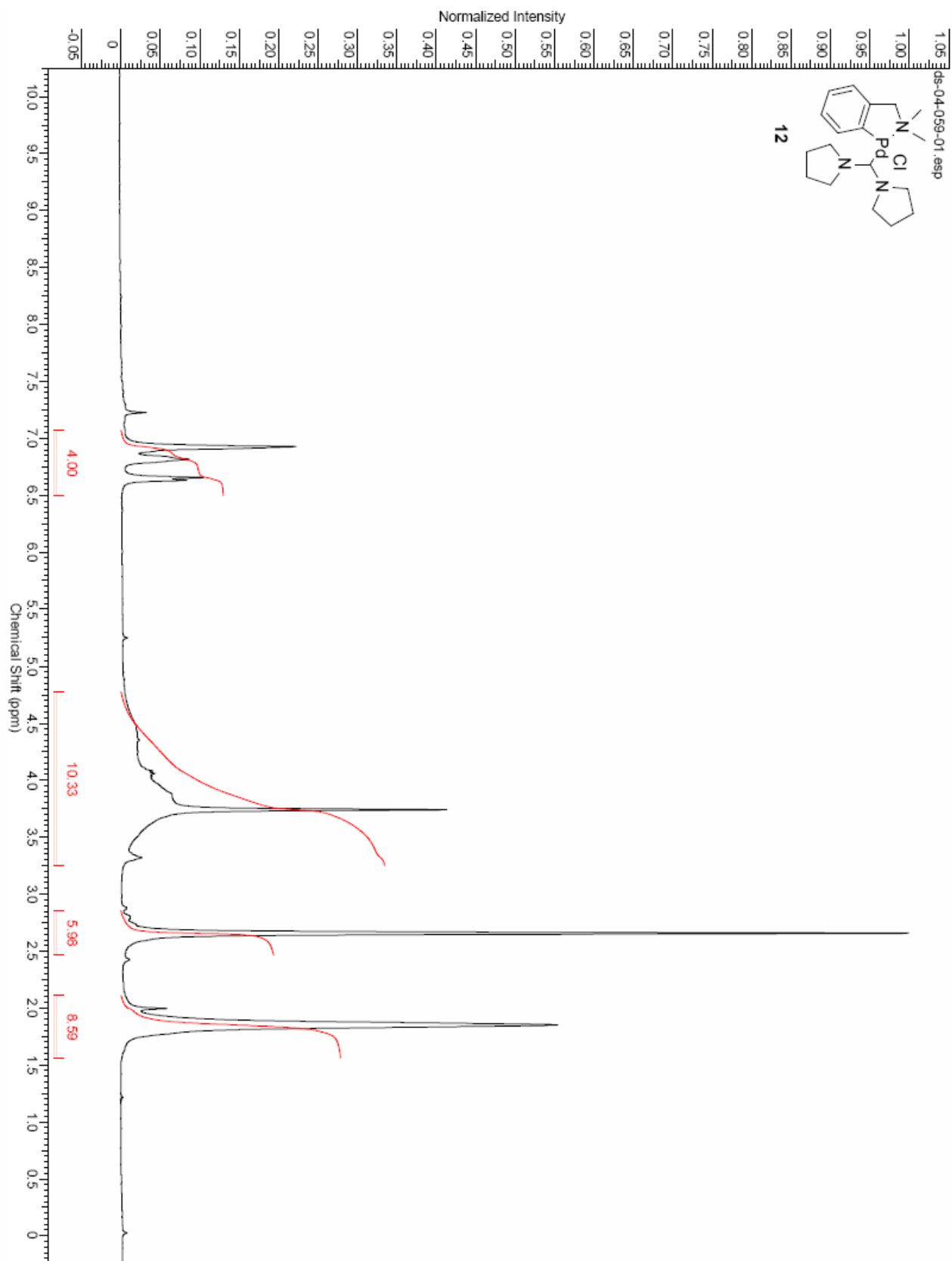


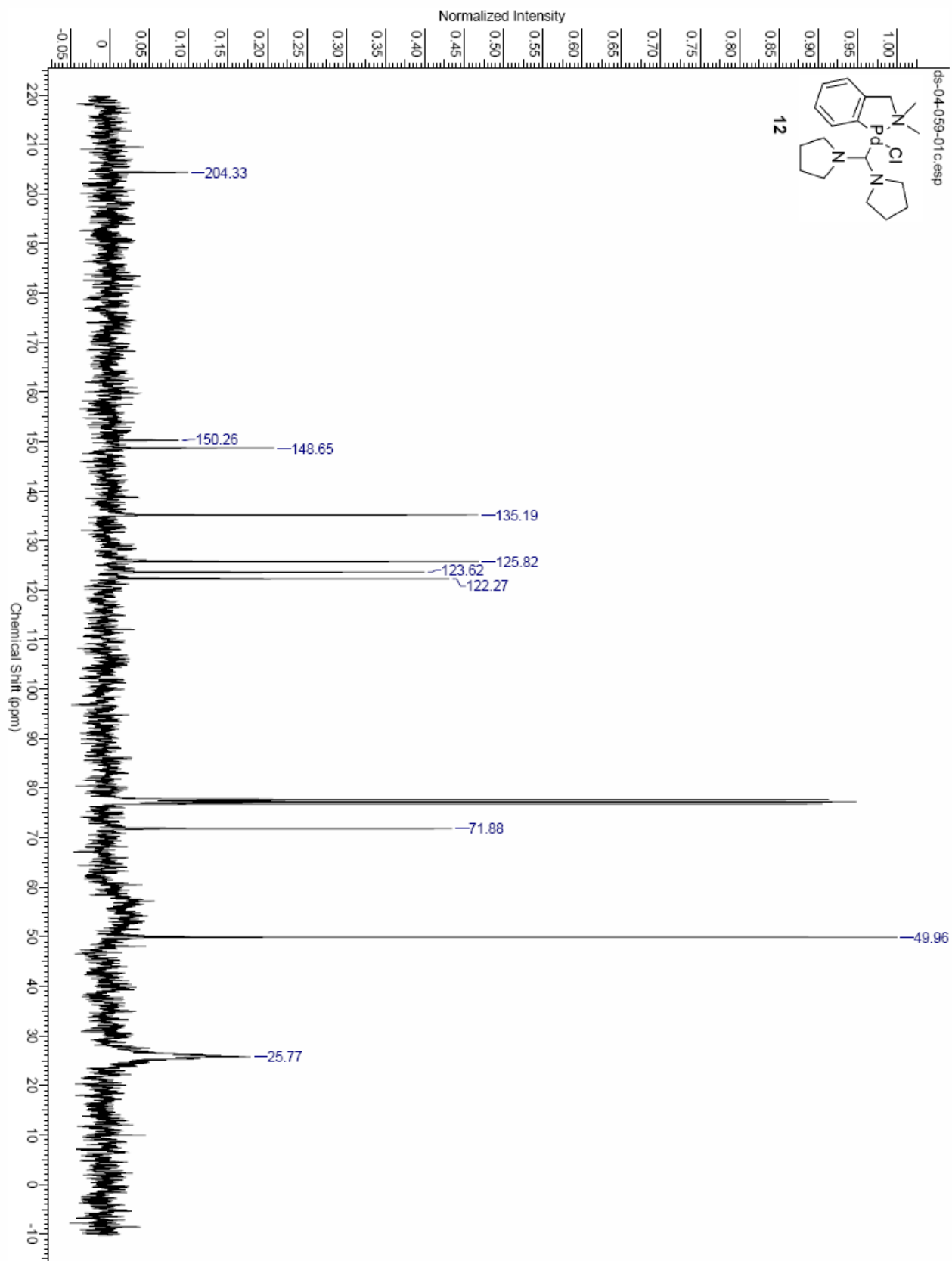


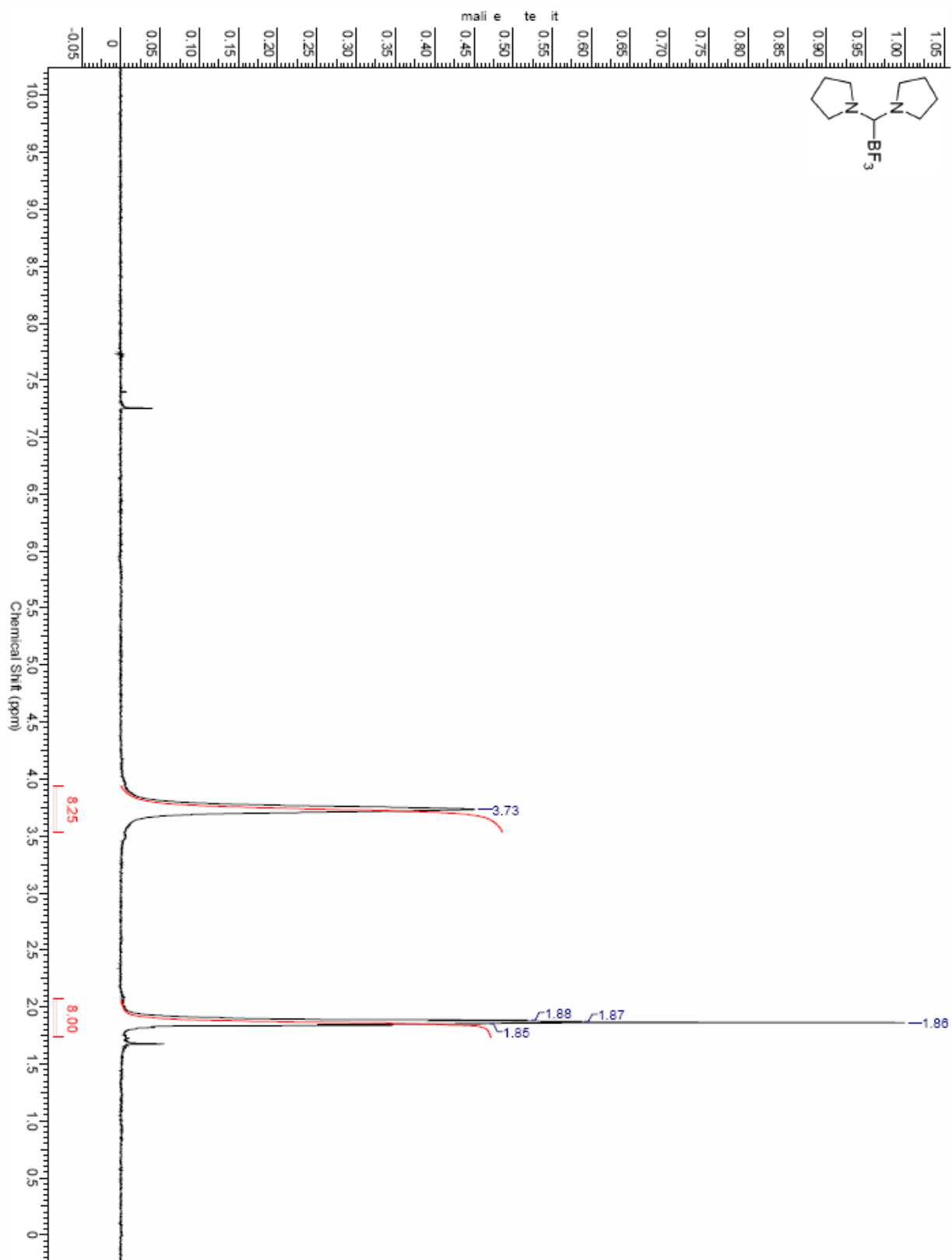


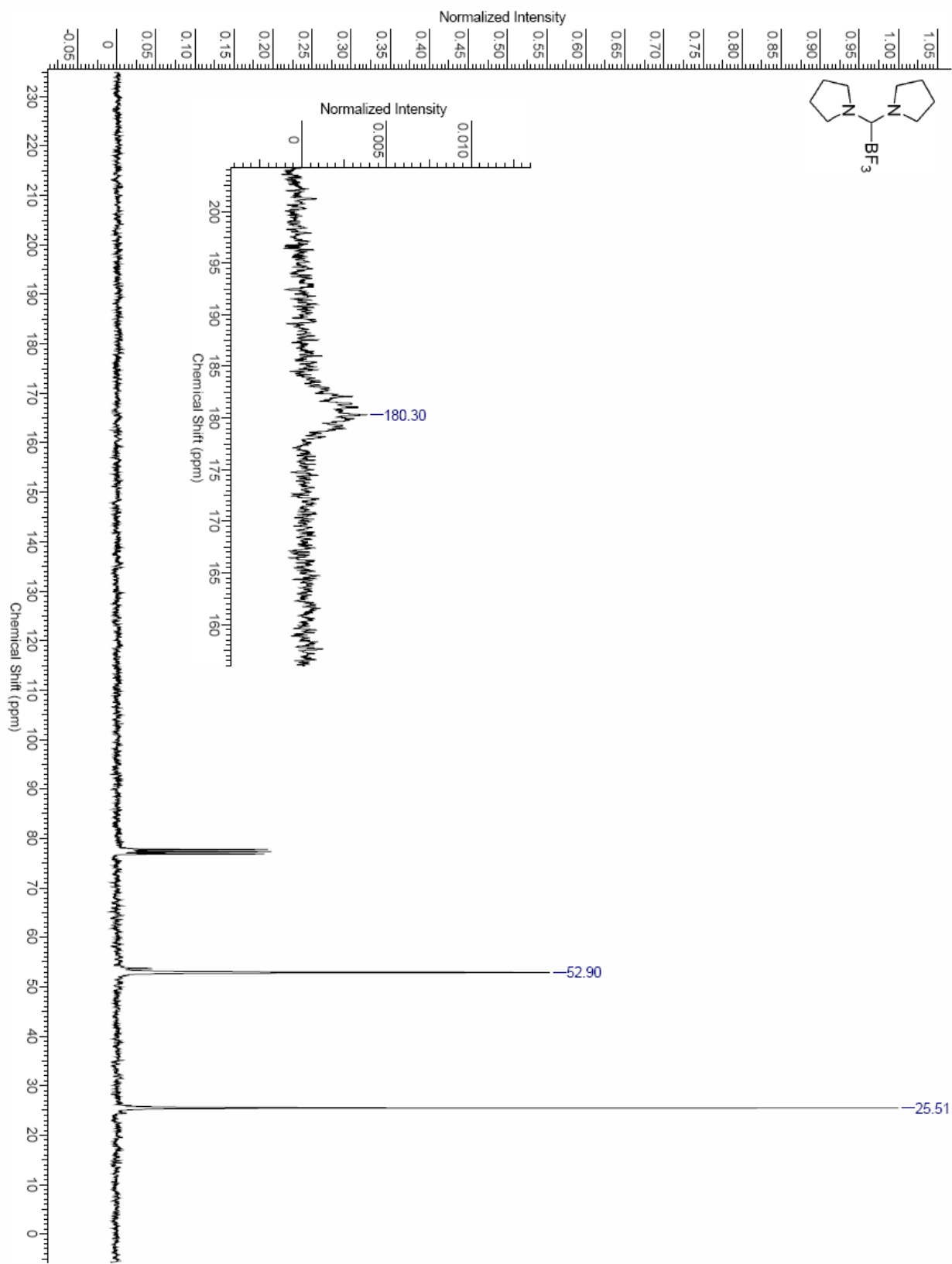


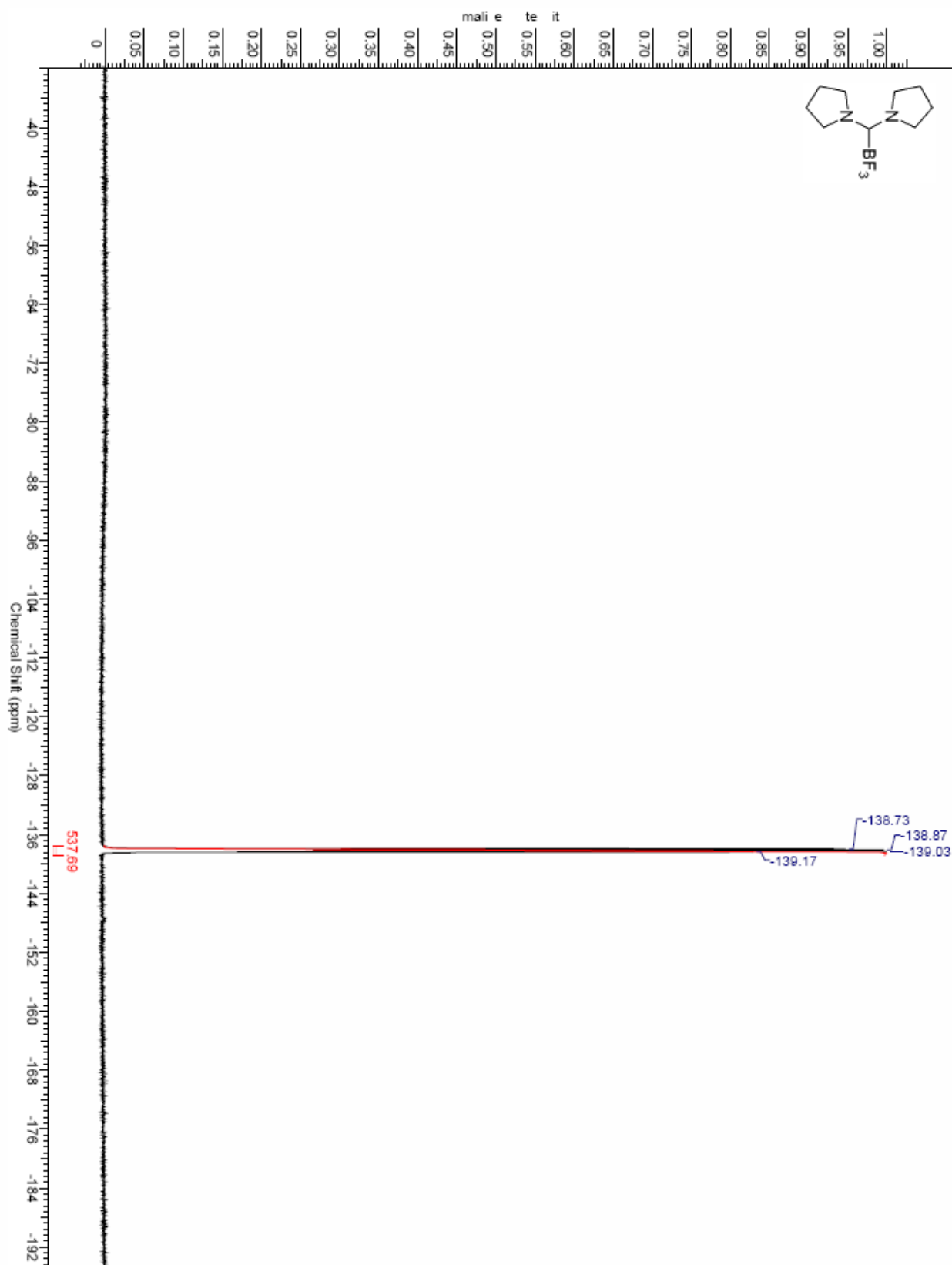


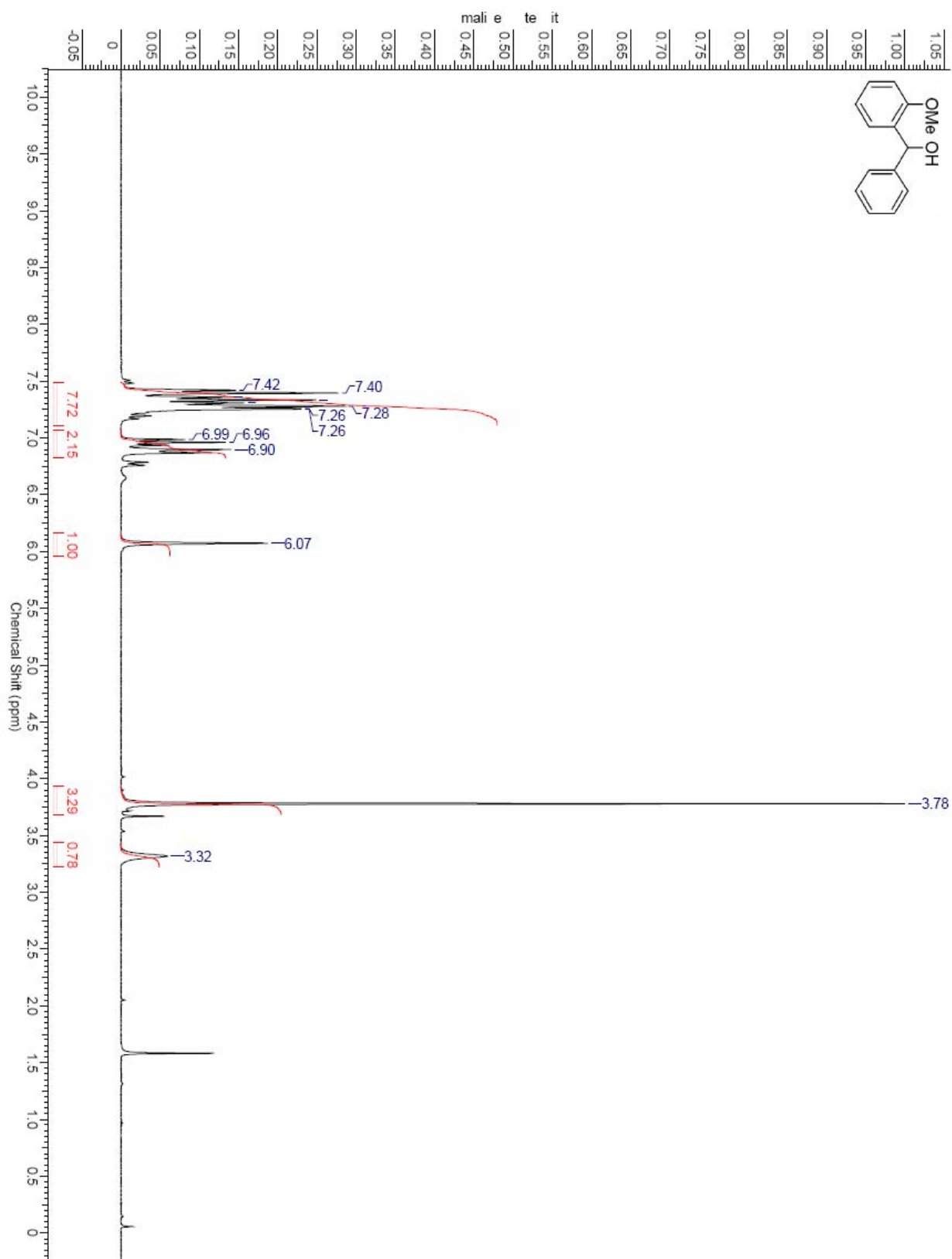


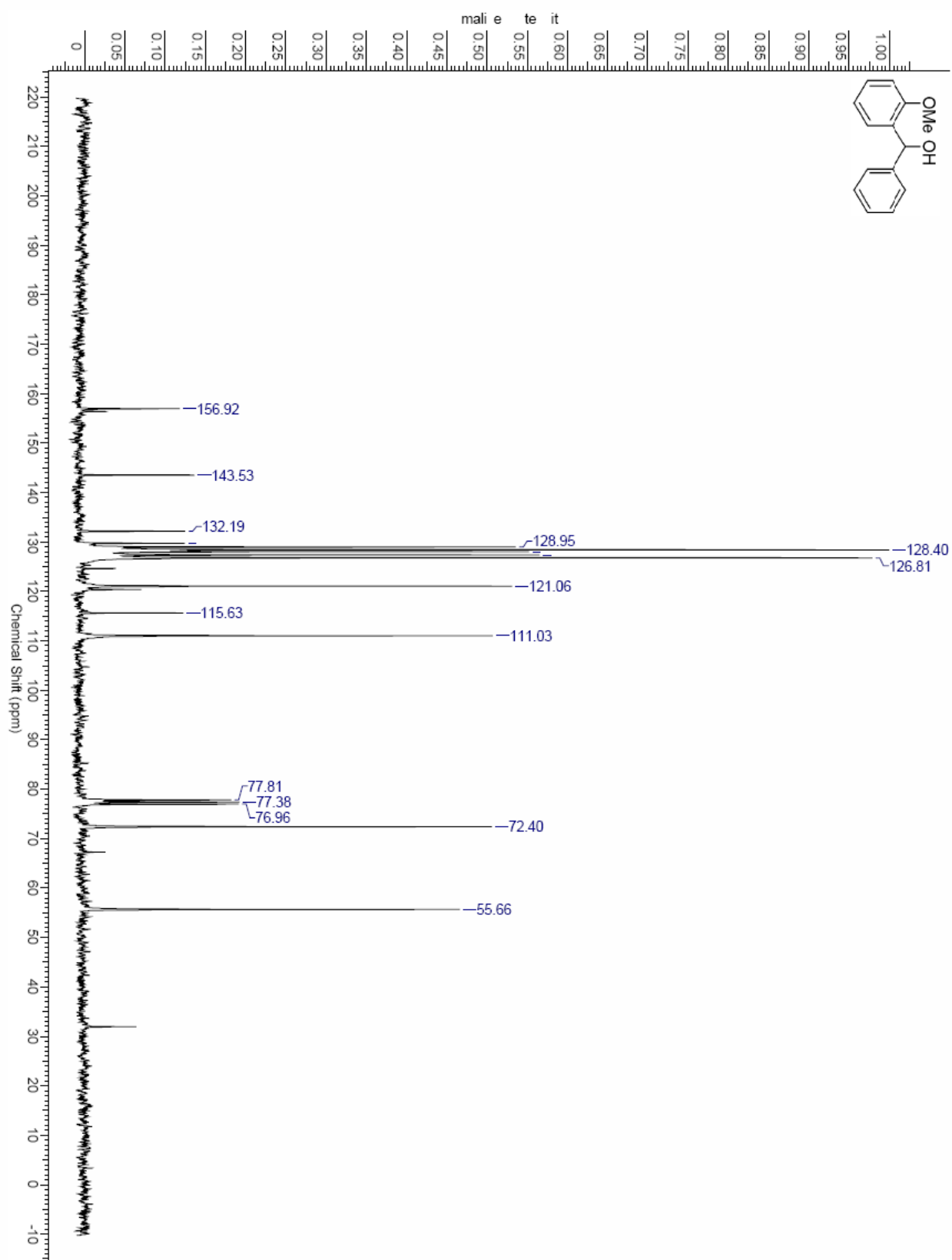


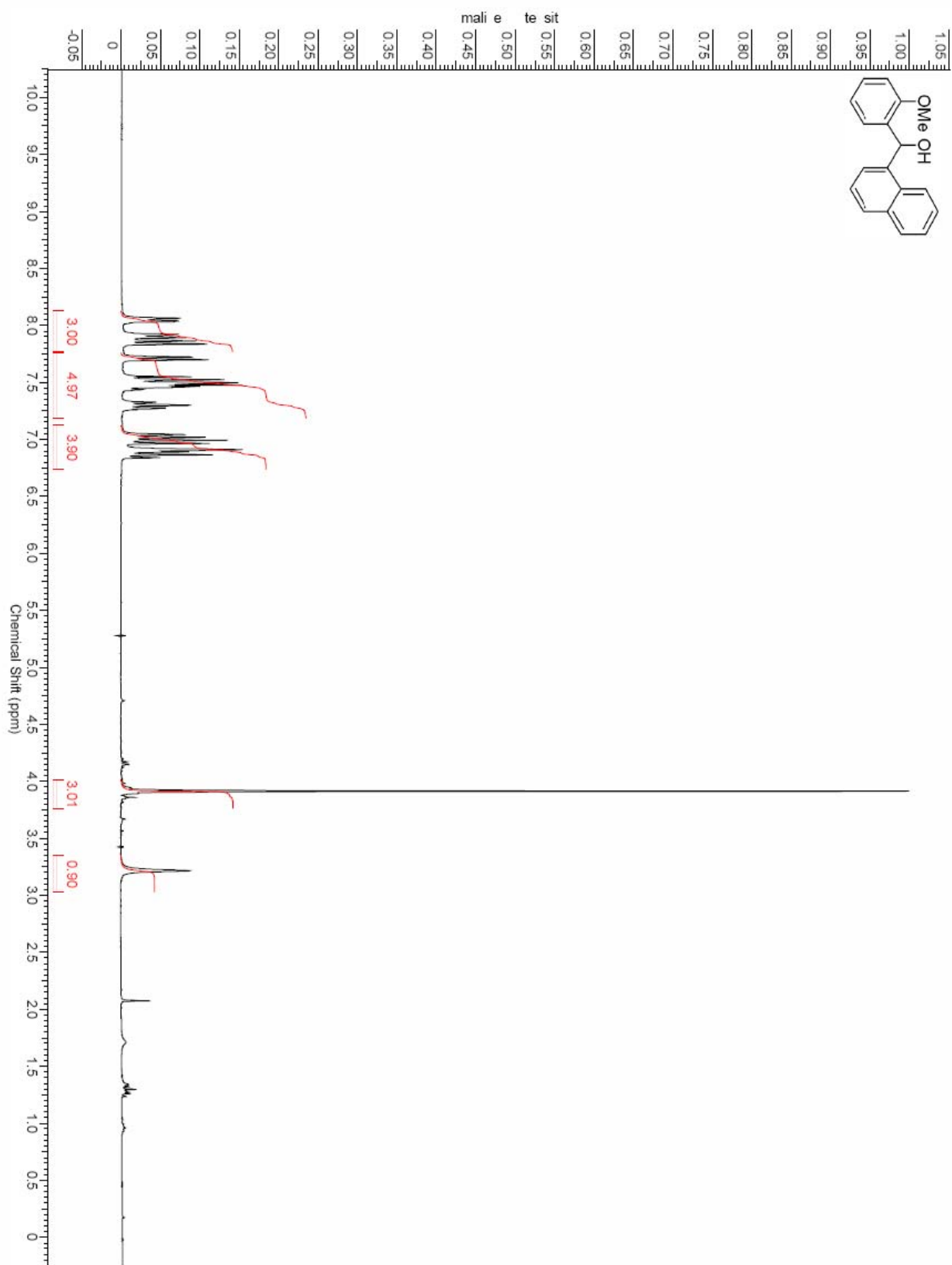


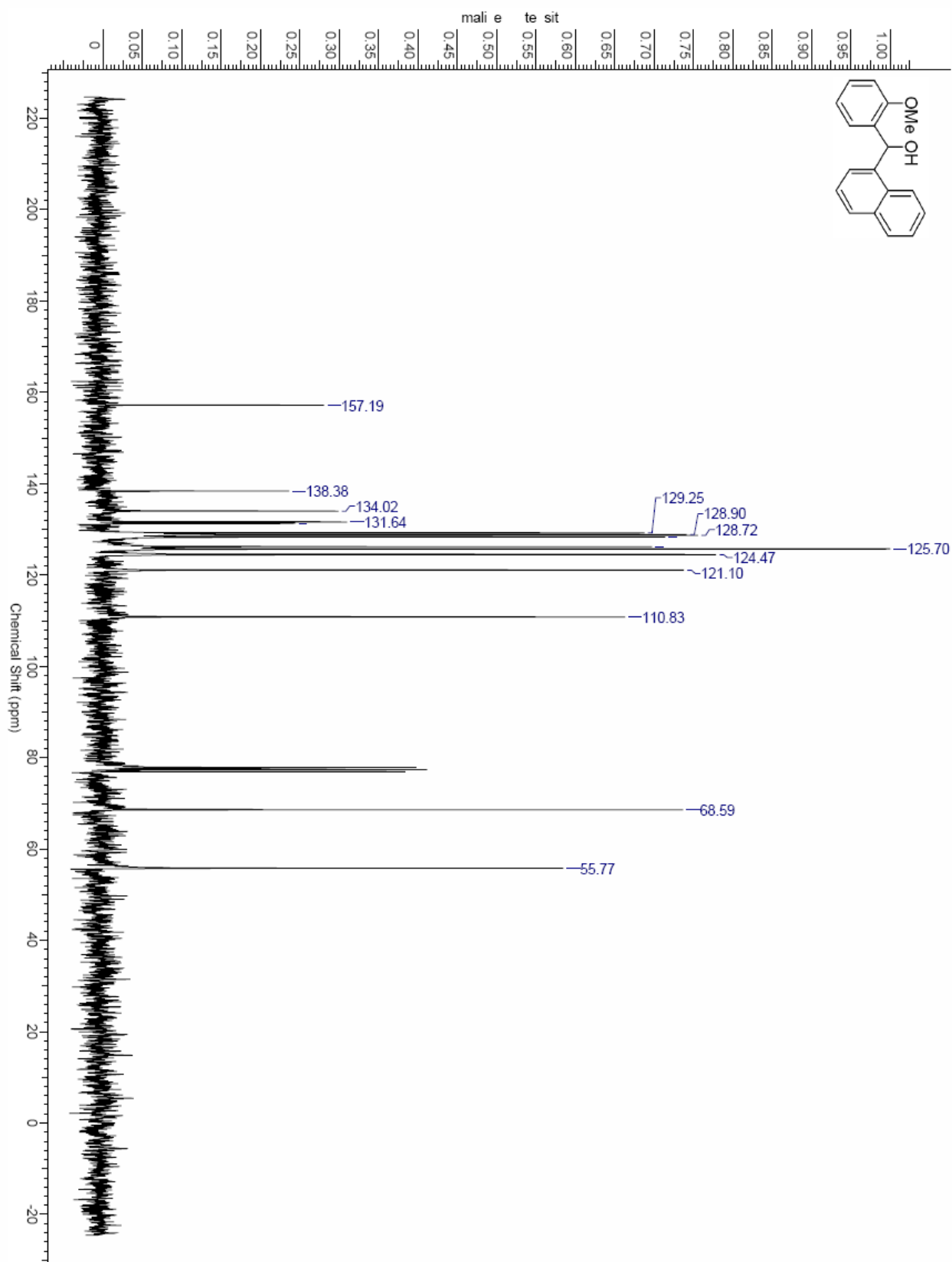


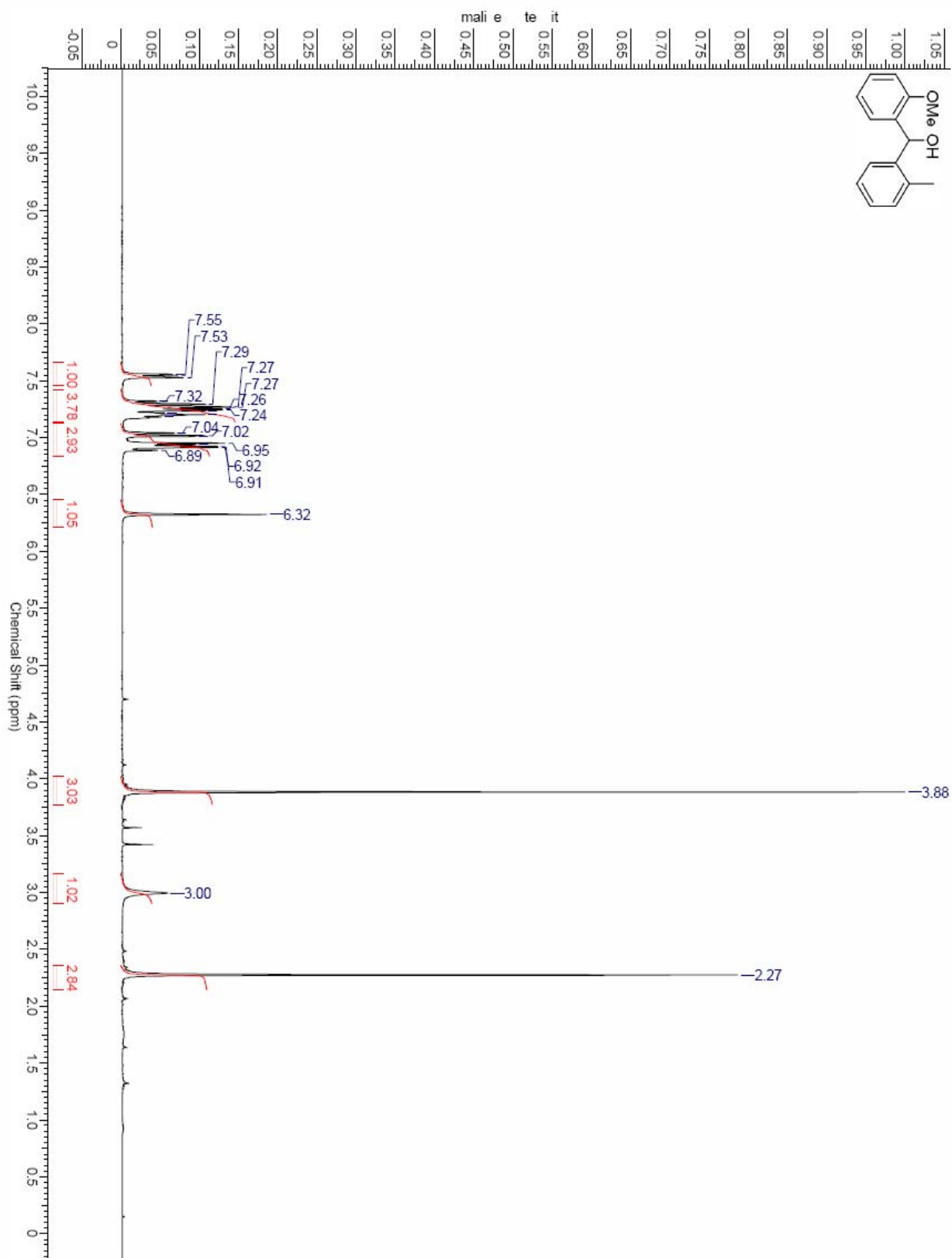


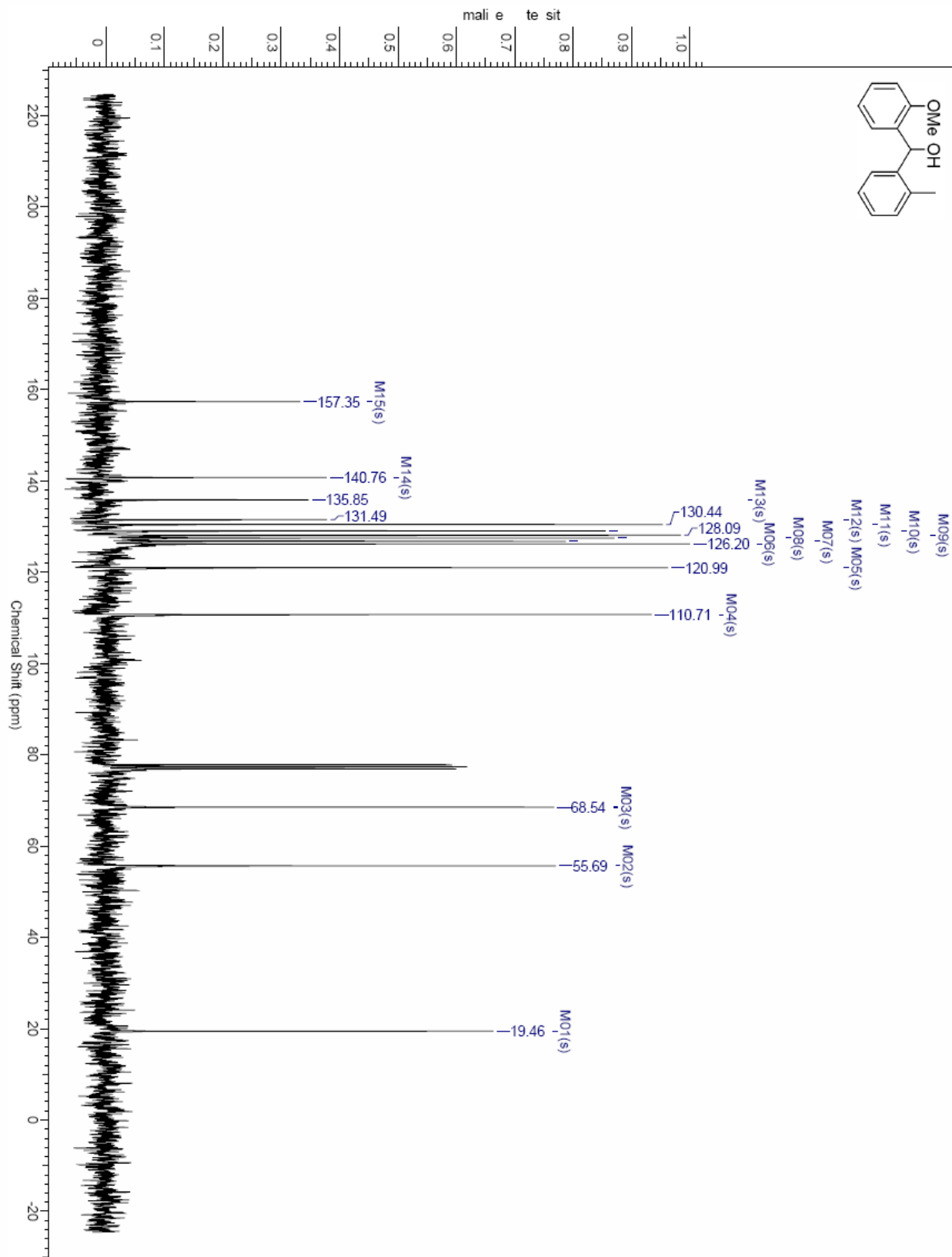


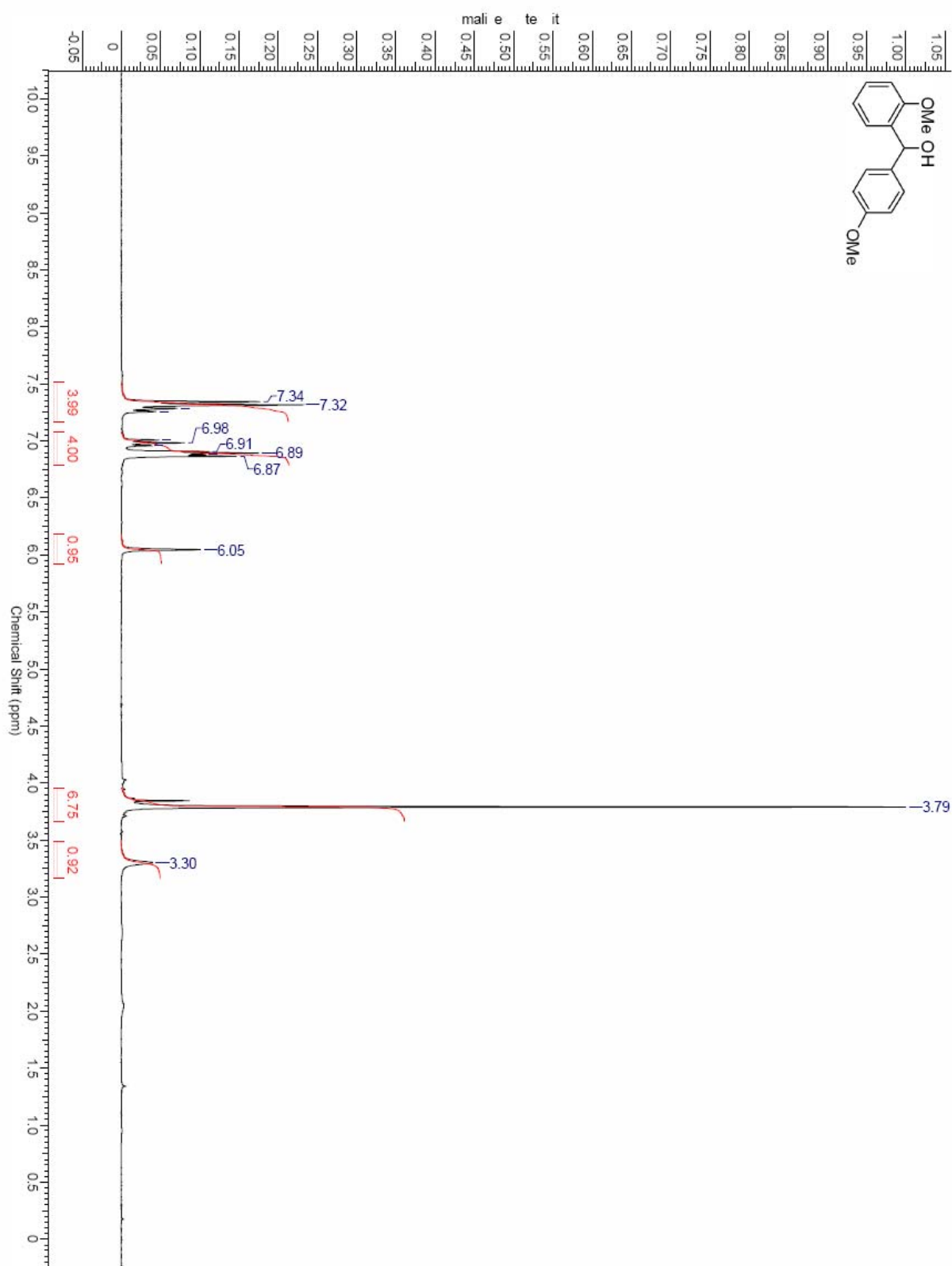


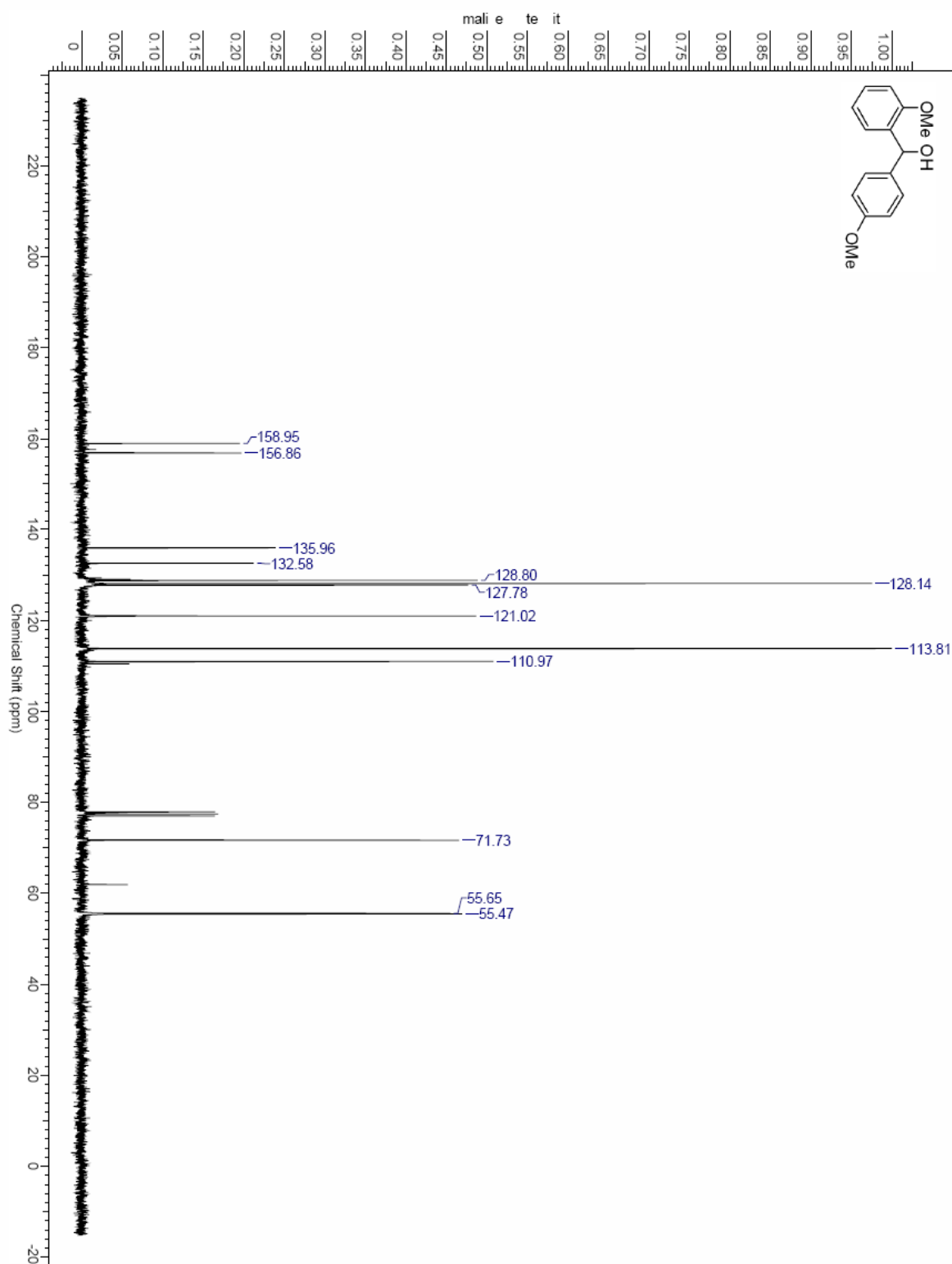


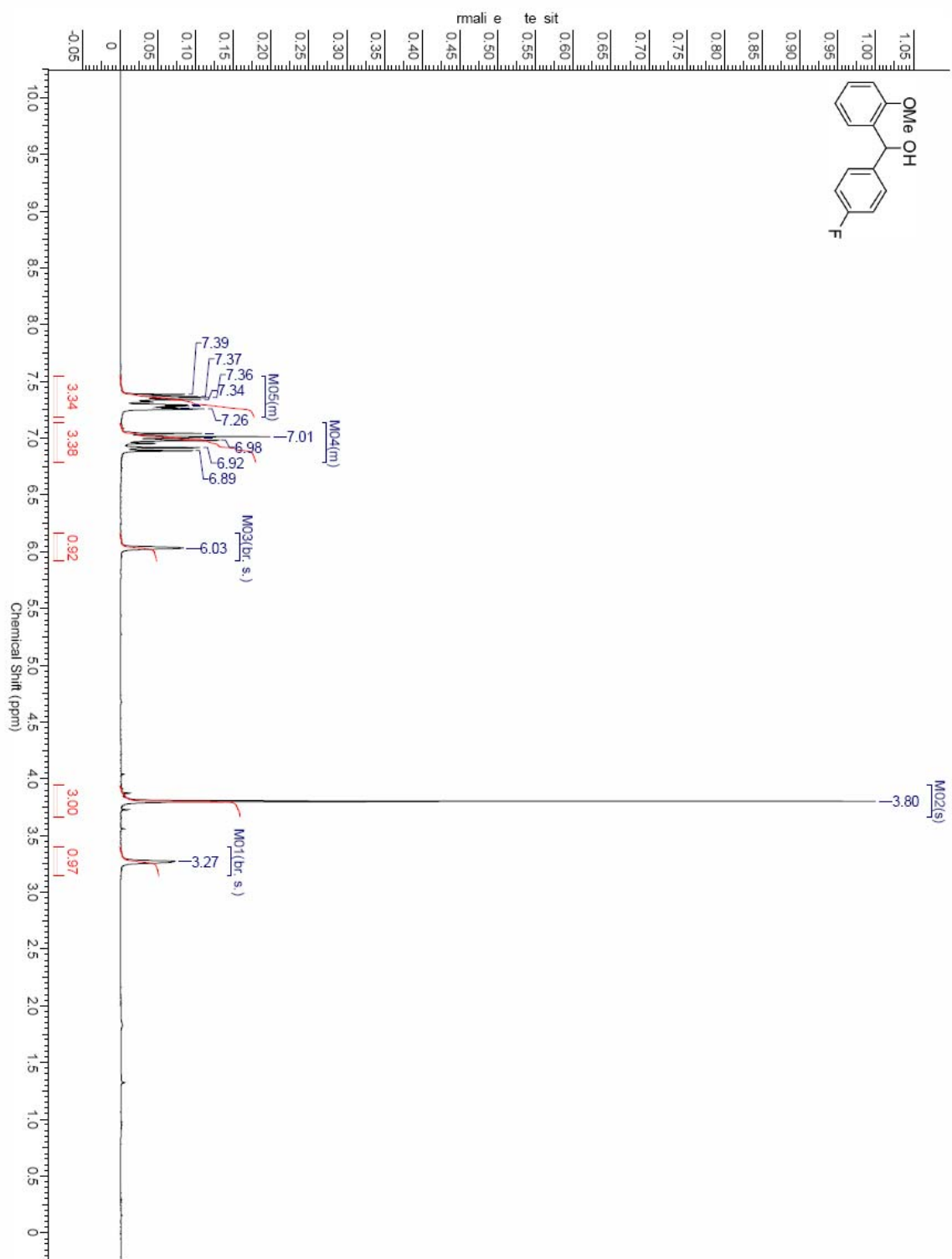


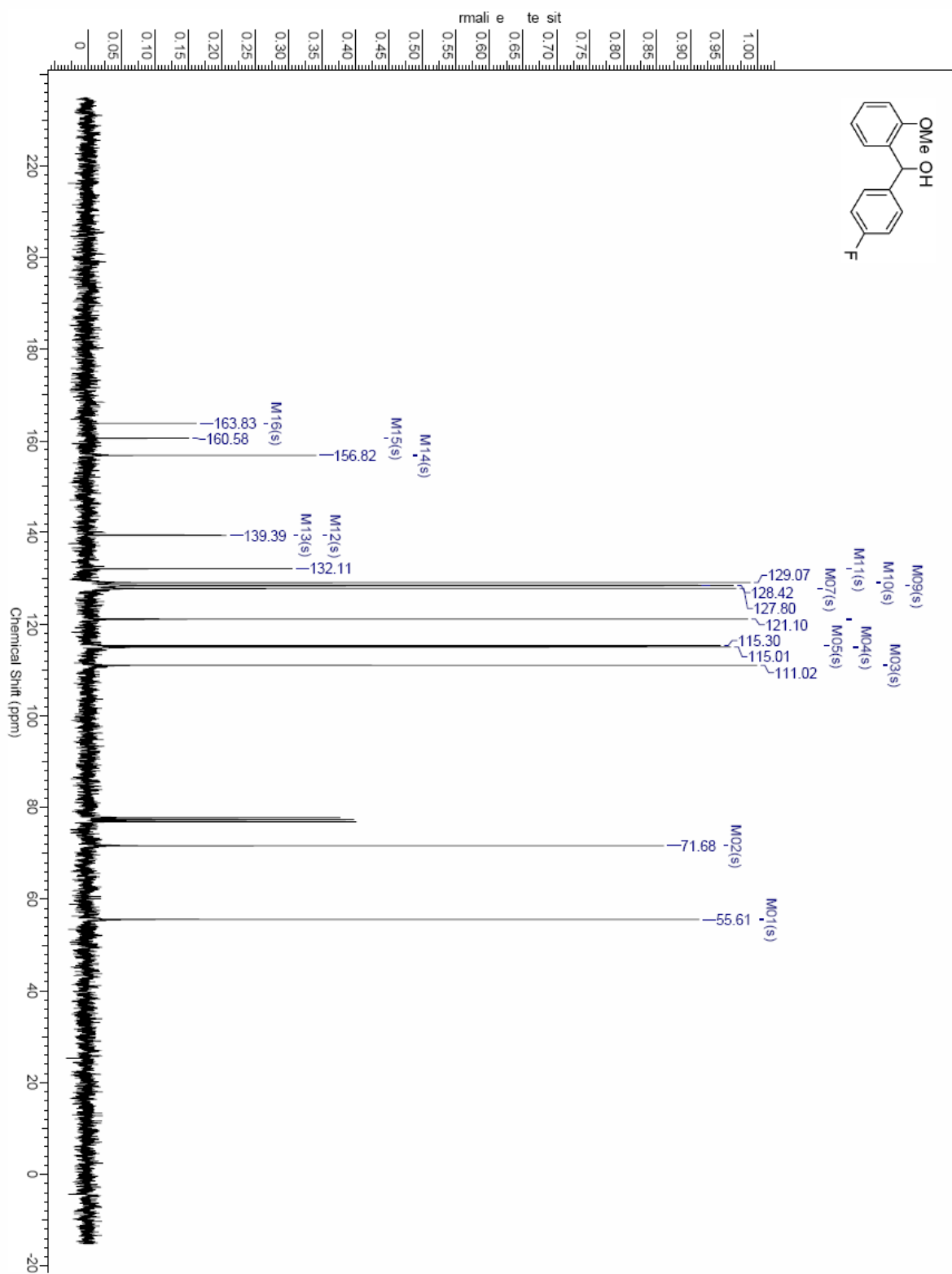


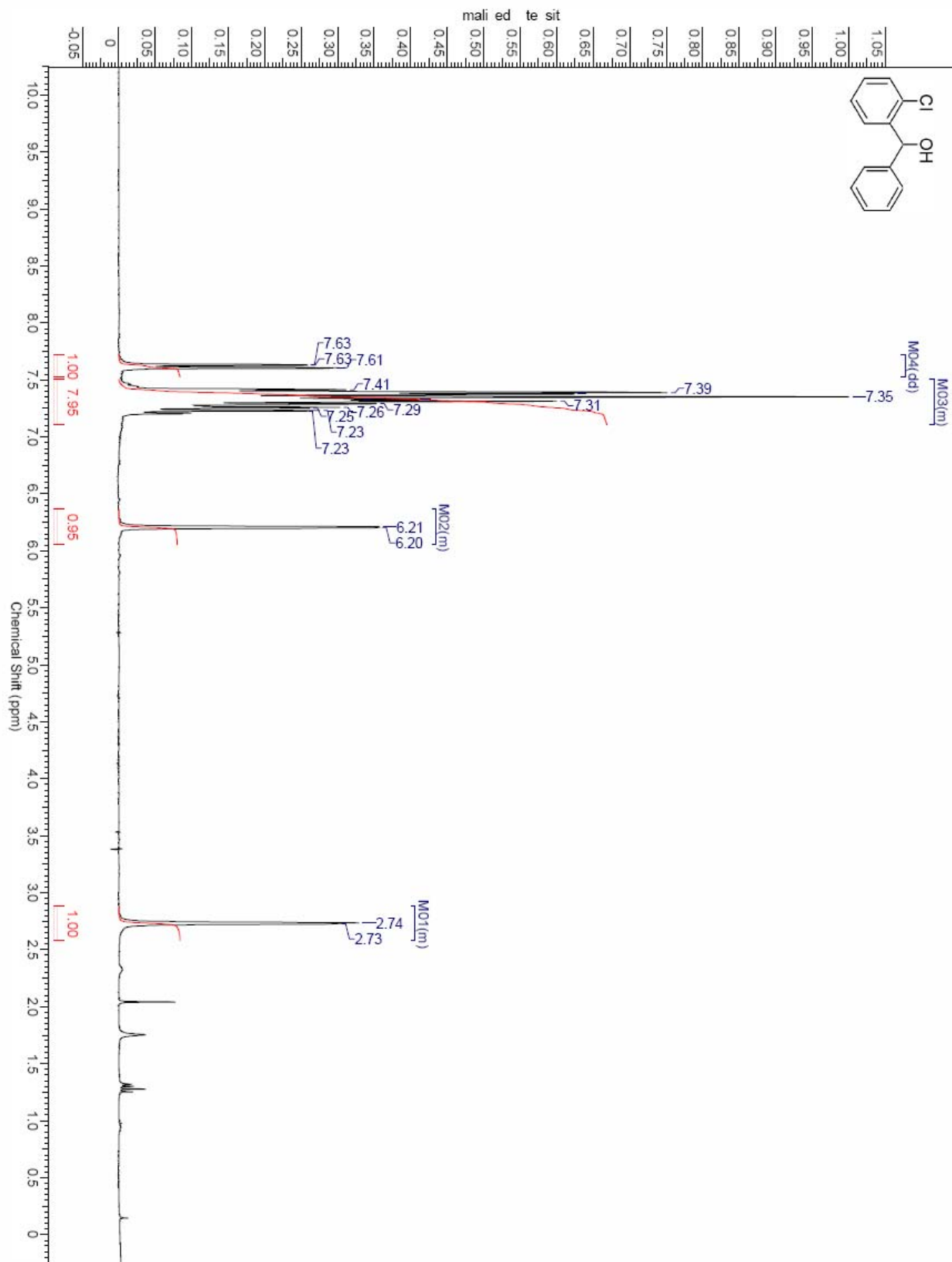


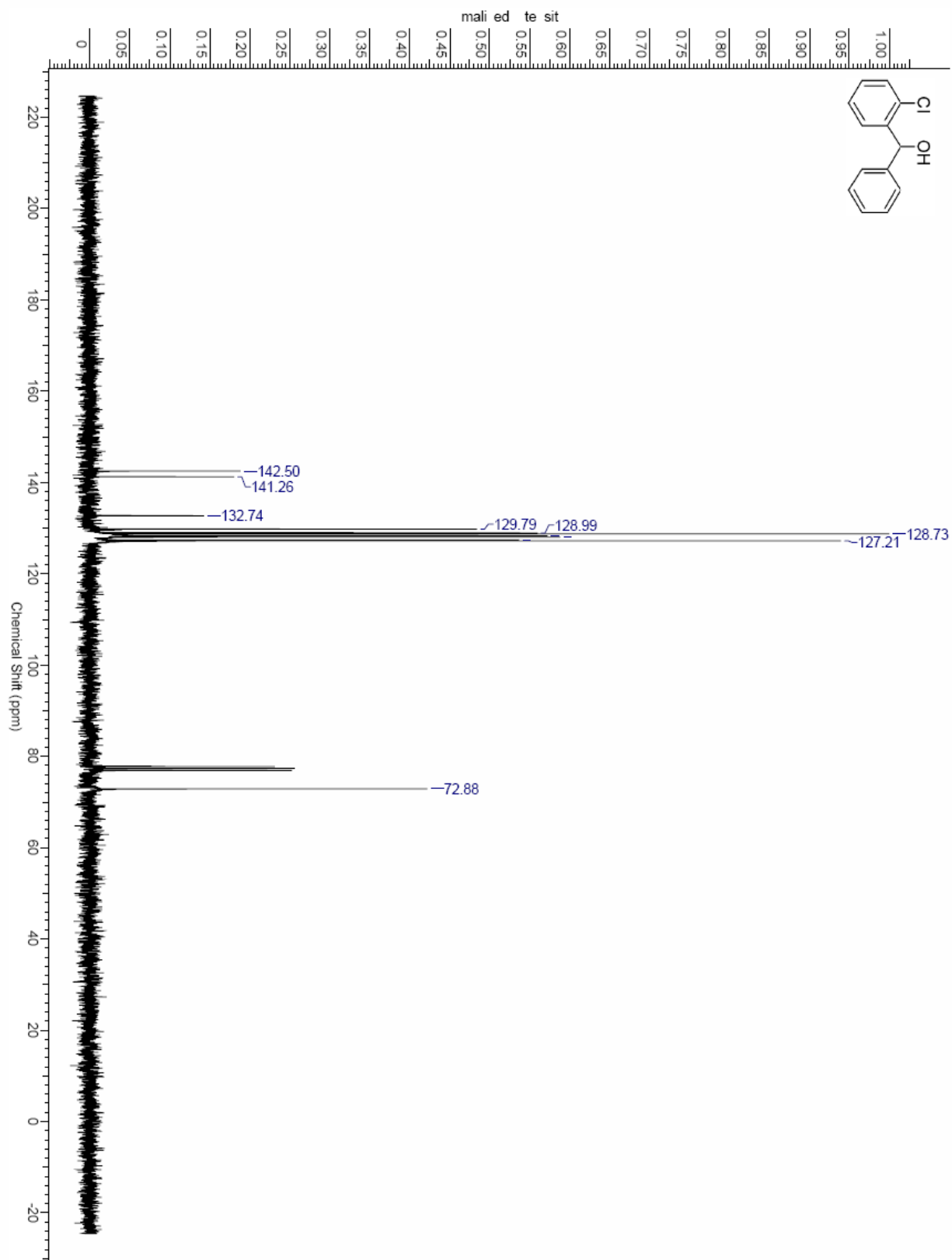


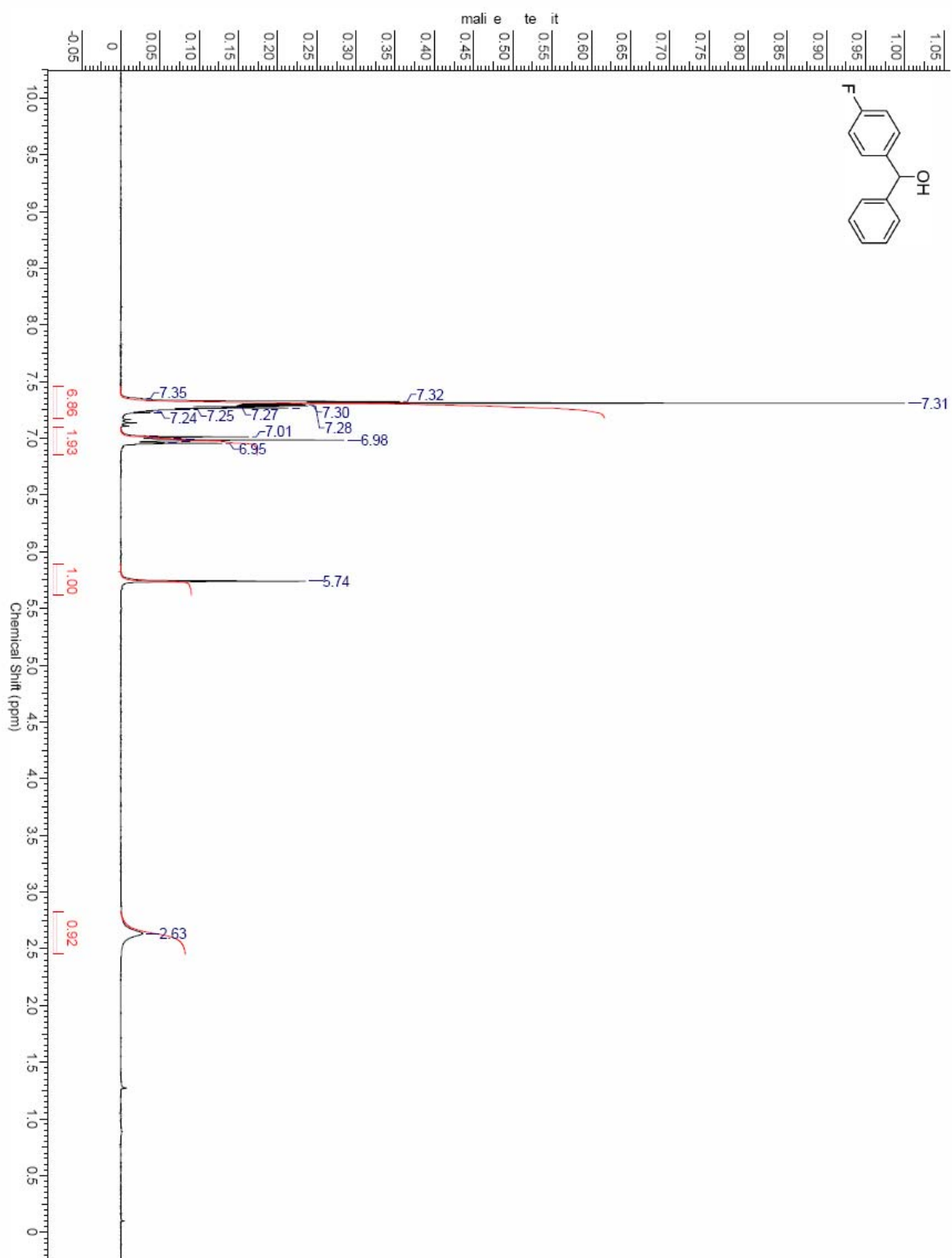


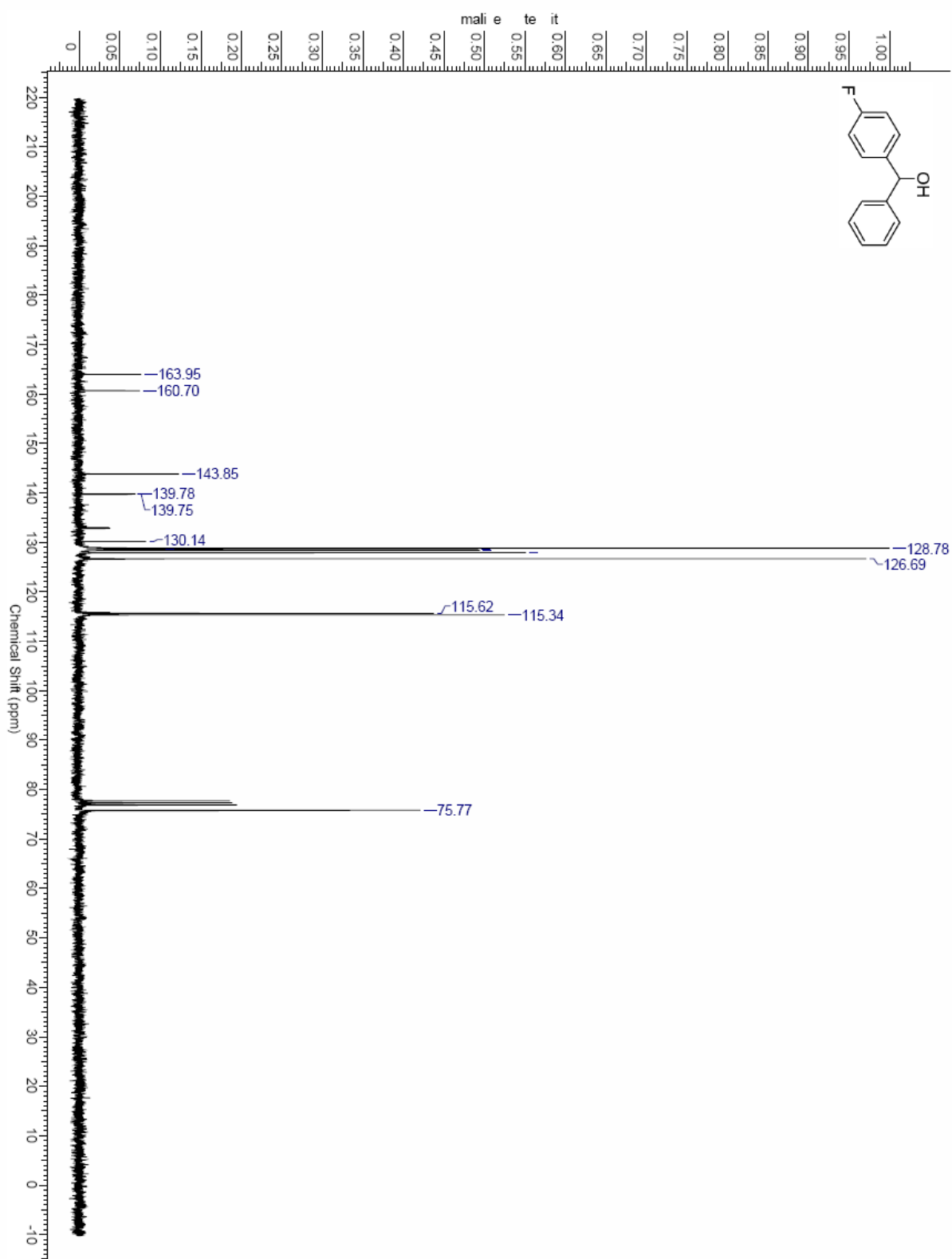


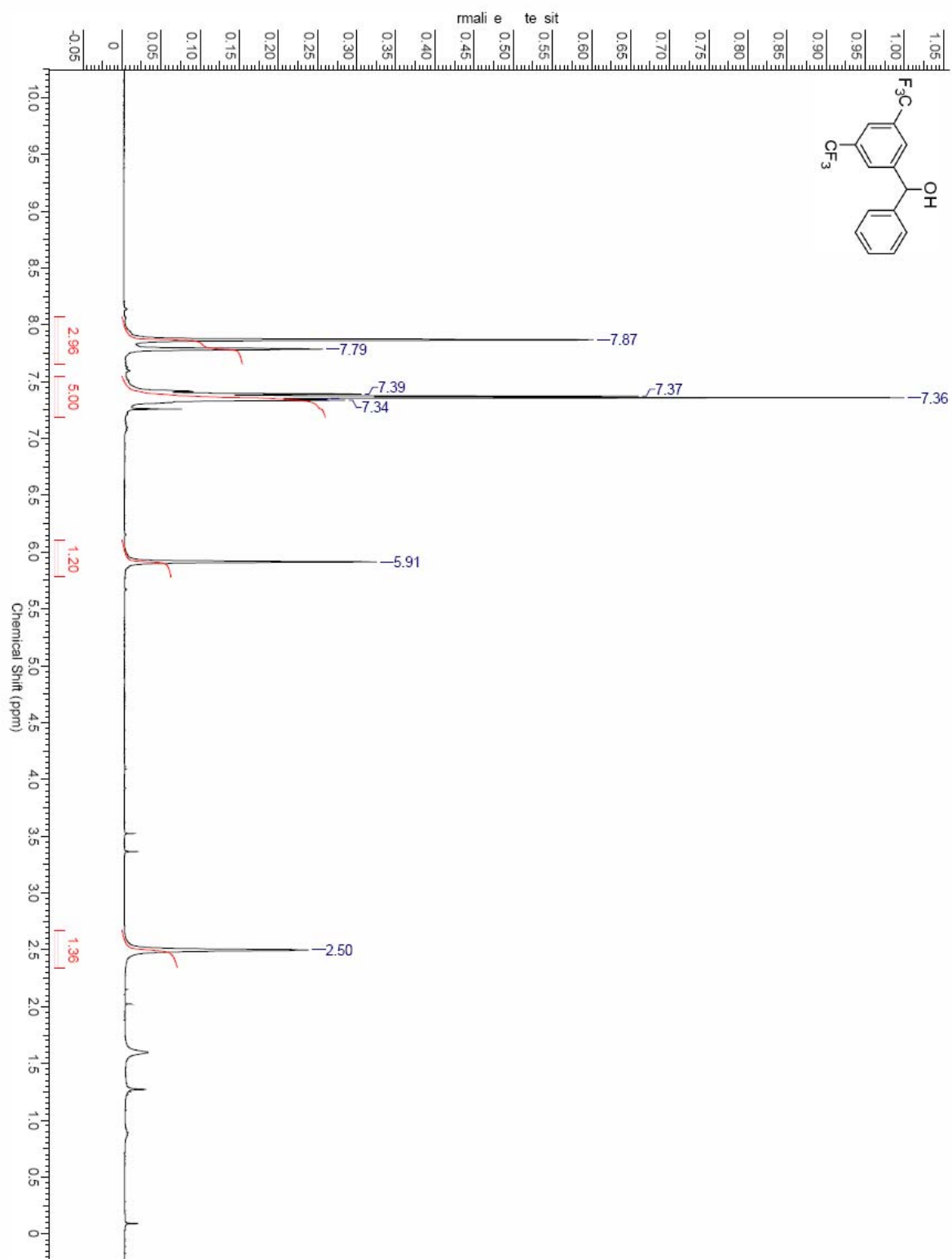


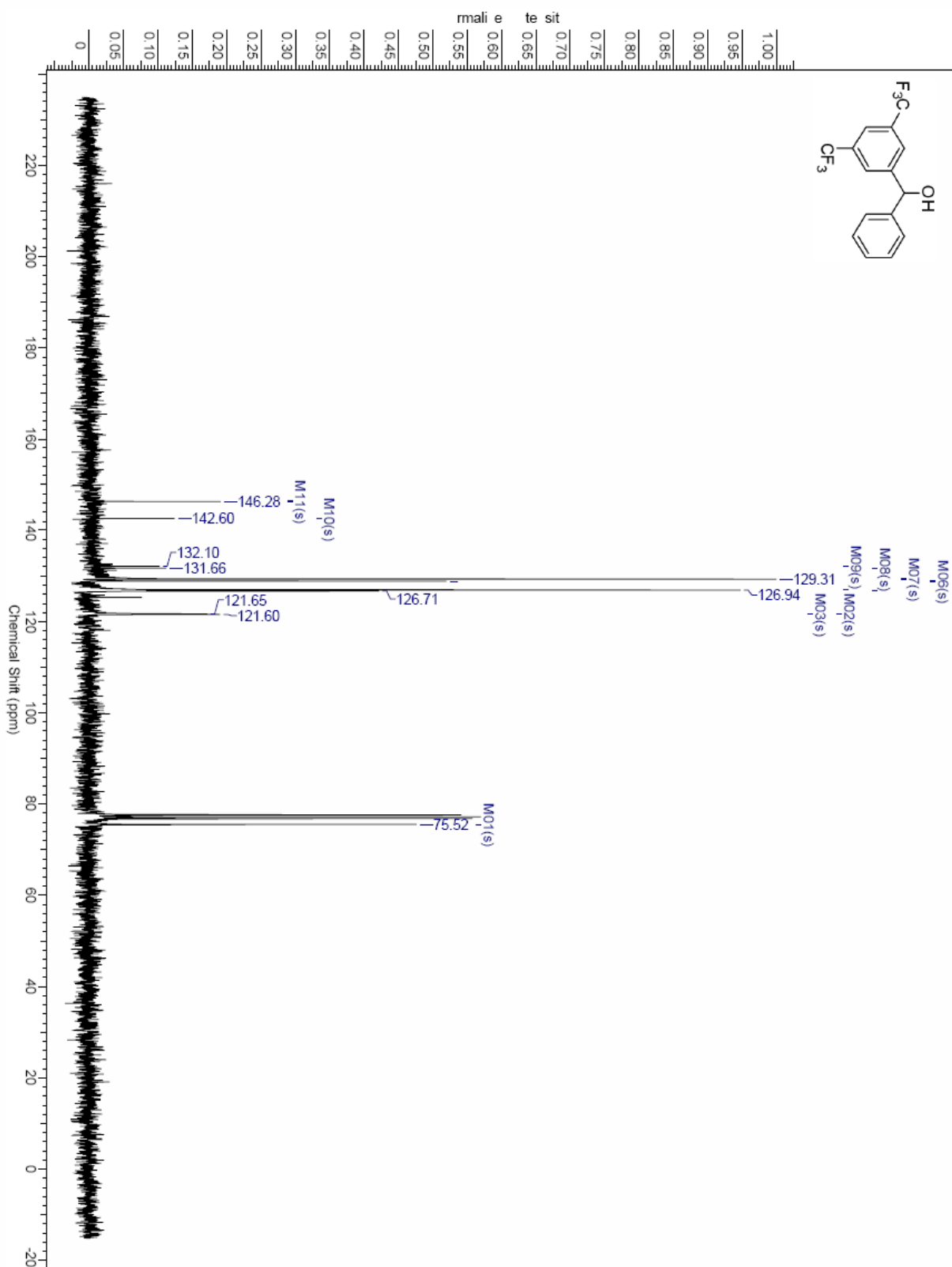












6. X-Ray Analysis for Compound 4.

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 190 parameters were refined in the final cycle of refinement using 3490 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.13% and 7.99%, respectively. Refinement was done using F^2 .

Table 1. Crystal data and structure refinement for 4.

Identification code	4	
Empirical formula	C17 H28 Cl N2 Rh	
Formula weight	398.77	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 6.5715(6)$ Å	$\alpha = 90^\circ$.
	$b = 18.7963(18)$ Å	$\beta = 94.439(2)^\circ$.
	$c = 13.7990(13)$ Å	$\gamma = 90^\circ$.
Volume	$1699.3(3)$ Å ³	
Z	4	
Density (calculated)	1.559 Mg/m ³	
Absorption coefficient	1.158 mm ⁻¹	
F(000)	824	
Crystal size	0.26 x 0.13 x 0.07 mm ³	
Theta range for data collection	1.83 to 27.50°.	
Index ranges	$-8 \leq h \leq 8$, $-21 \leq k \leq 24$, $-16 \leq l \leq 17$	
Reflections collected	11259	
Independent reflections	3899 [$R(\text{int}) = 0.0697$]	
Completeness to $\theta = 27.50^\circ$	99.7 %	
Absorption correction	Integration	

Max. and min. transmission	0.9233 and 0.7528
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3899 / 0 / 190
Goodness-of-fit on F ²	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0799 [3490]
R indices (all data)	R1 = 0.0351, wR2 = 0.0820
Largest diff. peak and hole	1.031 and -0.952 e.Å ⁻³
$R1 = \sum(F_o - F_c) / \sum F_o \quad wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ $S = [\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2} \quad w = 1/[\sigma^2(F_o^2) + (m^*p)^2 + n^*p], p = [\max(F_o^2, 0) + 2 * F_c^2]/3, m \text{ \& } n \text{ are constants.}$	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for 4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh1	-9011(1)	1198(1)	7500(1)	20(1)
Cl1	-7103(1)	2143(1)	6852(1)	35(1)
C9	-8831(3)	1741(1)	8767(2)	22(1)
C8	-12906(4)	326(1)	7093(2)	31(1)
C2	-9521(4)	220(1)	8182(2)	26(1)
C1	-11410(4)	553(1)	7931(2)	26(1)
C6	-10340(4)	912(1)	6041(2)	27(1)
C3	-8598(4)	-386(1)	7644(2)	30(1)
C7	-12543(4)	711(1)	6137(2)	32(1)
C4	-8841(4)	-300(1)	6535(2)	32(1)
C13	-5585(4)	1185(1)	9318(2)	31(1)
C17	-11857(4)	2400(1)	8124(2)	29(1)
N1	-7363(3)	1630(1)	9486(1)	24(1)
C11	-5951(6)	1238(2)	11011(2)	49(1)
C14	-9854(4)	2894(1)	9516(2)	28(1)
N2	-10203(3)	2253(1)	8893(1)	23(1)
C5	-8684(4)	471(1)	6234(2)	27(1)
C12	-4340(6)	1171(2)	10271(2)	51(1)
C10	-7422(4)	1785(1)	10537(2)	35(1)

C16	-12965(4)	3027(1)	8525(2)	38(1)
C15	-11233(4)	3458(1)	9017(2)	38(1)

Table 3. Bond lengths [Å] and angles [°] for 4.

Rh1-C9	2.022(2)
Rh1-C2	2.104(2)
Rh1-C1	2.110(2)
Rh1-C6	2.197(2)
Rh1-C5	2.241(2)
Rh1-Cl1	2.3885(6)
C9-N2	1.339(3)
C9-N1	1.345(3)
C8-C1	1.521(3)
C8-C7	1.538(3)
C8-H8B	0.9900
C8-H8A	0.9900
C2-C1	1.410(3)
C2-C3	1.513(3)
C2-H2A	1.0000
C1-H1A	1.0000
C6-C5	1.379(3)
C6-C7	1.512(3)
C6-H6A	1.0000
C3-C4	1.535(3)
C3-H3B	0.9900
C3-H3A	0.9900
C7-H7B	0.9900
C7-H7A	0.9900
C4-C5	1.513(3)
C4-H4B	0.9900
C4-H4A	0.9900
C13-N1	1.470(3)
C13-C12	1.495(4)
C13-H13B	0.9900
C13-H13A	0.9900
C17-N2	1.485(3)
C17-C16	1.512(3)
C17-H17B	0.9900

C17-H17A	0.9900
N1-C10	1.483(3)
C11-C10	1.524(4)
C11-C12	1.531(5)
C11-H11B	0.9900
C11-H11A	0.9900
C14-N2	1.488(3)
C14-C15	1.523(3)
C14-H14B	0.9900
C14-H14A	0.9900
C5-H5A	1.0000
C12-H12B	0.9900
C12-H12A	0.9900
C10-H10B	0.9900
C10-H10A	0.9900
C16-C15	1.514(4)
C16-H16B	0.9900
C16-H16A	0.9900
C15-H15B	0.9900
C15-H15A	0.9900
C9-Rh1-C2	93.14(8)
C9-Rh1-C1	92.33(8)
C2-Rh1-C1	39.08(9)
C9-Rh1-C6	155.28(9)
C2-Rh1-C6	97.54(8)
C1-Rh1-C6	82.30(9)
C9-Rh1-C5	168.51(8)
C2-Rh1-C5	81.06(8)
C1-Rh1-C5	89.38(9)
C6-Rh1-C5	36.18(8)
C9-Rh1-Cl1	87.16(6)
C2-Rh1-Cl1	157.54(7)
C1-Rh1-Cl1	163.37(6)
C6-Rh1-Cl1	91.24(6)
C5-Rh1-Cl1	94.43(6)

N2-C9-N1	117.90(18)
N2-C9-Rh1	118.71(15)
N1-C9-Rh1	123.36(15)
C1-C8-C7	112.73(19)
C1-C8-H8B	109.0
C7-C8-H8B	109.0
C1-C8-H8A	109.0
C7-C8-H8A	109.0
H8B-C8-H8A	107.8
C1-C2-C3	126.4(2)
C1-C2-Rh1	70.68(12)
C3-C2-Rh1	110.75(15)
C1-C2-H2A	113.6
C3-C2-H2A	113.6
Rh1-C2-H2A	113.6
C2-C1-C8	124.5(2)
C2-C1-Rh1	70.23(13)
C8-C1-Rh1	113.54(15)
C2-C1-H1A	113.7
C8-C1-H1A	113.7
Rh1-C1-H1A	113.7
C5-C6-C7	125.4(2)
C5-C6-Rh1	73.62(12)
C7-C6-Rh1	107.23(15)
C5-C6-H6A	114.2
C7-C6-H6A	114.2
Rh1-C6-H6A	114.2
C2-C3-C4	113.28(18)
C2-C3-H3B	108.9
C4-C3-H3B	108.9
C2-C3-H3A	108.9
C4-C3-H3A	108.9
H3B-C3-H3A	107.7
C6-C7-C8	113.96(18)
C6-C7-H7B	108.8
C8-C7-H7B	108.8

C6-C7-H7A	108.8
C8-C7-H7A	108.8
H7B-C7-H7A	107.7
C5-C4-C3	111.76(18)
C5-C4-H4B	109.3
C3-C4-H4B	109.3
C5-C4-H4A	109.3
C3-C4-H4A	109.3
H4B-C4-H4A	107.9
N1-C13-C12	105.0(2)
N1-C13-H13B	110.7
C12-C13-H13B	110.7
N1-C13-H13A	110.7
C12-C13-H13A	110.7
H13B-C13-H13A	108.8
N2-C17-C16	103.34(18)
N2-C17-H17B	111.1
C16-C17-H17B	111.1
N2-C17-H17A	111.1
C16-C17-H17A	111.1
H17B-C17-H17A	109.1
C9-N1-C13	120.38(18)
C9-N1-C10	128.26(19)
C13-N1-C10	110.28(18)
C10-C11-C12	102.6(2)
C10-C11-H11B	111.3
C12-C11-H11B	111.3
C10-C11-H11A	111.3
C12-C11-H11A	111.3
H11B-C11-H11A	109.2
N2-C14-C15	103.98(18)
N2-C14-H14B	111.0
C15-C14-H14B	111.0
N2-C14-H14A	111.0
C15-C14-H14A	111.0
H14B-C14-H14A	109.0

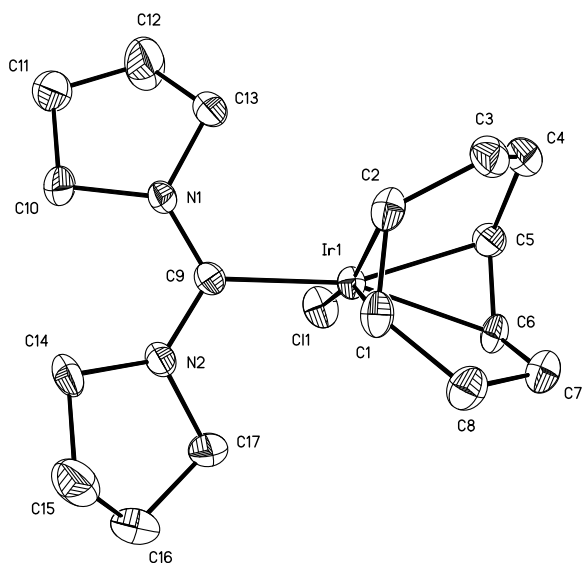
C9-N2-C17	120.29(17)
C9-N2-C14	125.54(18)
C17-N2-C14	109.51(17)
C6-C5-C4	124.1(2)
C6-C5-Rh1	70.20(12)
C4-C5-Rh1	110.95(15)
C6-C5-H5A	114.5
C4-C5-H5A	114.5
Rh1-C5-H5A	114.5
C13-C12-C11	103.1(3)
C13-C12-H12B	111.2
C11-C12-H12B	111.2
C13-C12-H12A	111.2
C11-C12-H12A	111.2
H12B-C12-H12A	109.1
N1-C10-C11	102.9(2)
N1-C10-H10B	111.2
C11-C10-H10B	111.2
N1-C10-H10A	111.2
C11-C10-H10A	111.2
H10B-C10-H10A	109.1
C17-C16-C15	102.3(2)
C17-C16-H16B	111.3
C15-C16-H16B	111.3
C17-C16-H16A	111.3
C15-C16-H16A	111.3
H16B-C16-H16A	109.2
C16-C15-C14	103.41(19)
C16-C15-H15B	111.1
C14-C15-H15B	111.1
C16-C15-H15A	111.1
C14-C15-H15A	111.1
H15B-C15-H15A	109.0

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh1	23(1)	21(1)	16(1)	0(1)	2(1)	1(1)
Cl1	39(1)	37(1)	31(1)	3(1)	9(1)	-9(1)
C9	24(1)	22(1)	20(1)	2(1)	5(1)	-1(1)
C8	28(1)	33(1)	33(1)	-2(1)	1(1)	-3(1)
C2	34(1)	23(1)	20(1)	2(1)	1(1)	1(1)
C1	29(1)	25(1)	24(1)	1(1)	5(1)	-1(1)
C6	33(1)	30(1)	17(1)	-1(1)	-2(1)	1(1)
C3	36(1)	25(1)	29(1)	1(1)	-1(1)	4(1)
C7	30(1)	36(1)	29(1)	-1(1)	-5(1)	1(1)
C4	39(1)	29(1)	28(1)	-7(1)	1(1)	8(1)
C13	26(1)	40(1)	28(1)	0(1)	2(1)	7(1)
C17	28(1)	28(1)	31(1)	-1(1)	-3(1)	5(1)
N1	26(1)	30(1)	17(1)	-1(1)	1(1)	4(1)
C11	73(2)	49(2)	24(1)	4(1)	-3(1)	24(1)
C14	37(1)	24(1)	25(1)	-6(1)	2(1)	4(1)
N2	26(1)	22(1)	22(1)	-1(1)	1(1)	3(1)
C5	30(1)	32(1)	19(1)	-4(1)	2(1)	2(1)
C12	51(2)	60(2)	41(2)	-2(1)	-11(1)	17(1)
C10	49(2)	39(1)	18(1)	0(1)	-2(1)	11(1)
C16	35(1)	31(1)	47(2)	-4(1)	-3(1)	11(1)
C15	49(2)	26(1)	38(1)	-6(1)	-6(1)	11(1)

7. X-Ray Analysis for Compound 5



Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of two chemically equivalent but crystallographically independent complexes. A total of 379 parameters were refined in the final cycle of refinement using 7041 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 3.23% and 7.47%, respectively. Refinement was done using F^2 .

Table 1. Crystal data and structure refinement for 5.

Identification code	5	
Empirical formula	C ₁₇ H ₂₈ Cl Ir N ₂	
Formula weight	488.06	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 9.8235(9)$ Å	$\alpha = 90^\circ$.

	$b = 14.9332(14) \text{ \AA}$	$\beta = 91.616(2)^\circ$.
	$c = 23.221(2) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$3405.0(5) \text{ \AA}^3$	
Z	8	
Density (calculated)	1.904 Mg/m^3	
Absorption coefficient	7.995 mm^{-1}	
F(000)	1904	
Crystal size	$0.34 \times 0.23 \times 0.17 \text{ mm}^3$	
Theta range for data collection	$1.62 \text{ to } 27.50^\circ$.	
Index ranges	$-12 \leq h \leq 9, -12 \leq k \leq 19, -30 \leq l \leq 29$	
Reflections collected	21406	
Independent reflections	7805 [$R(\text{int}) = 0.0360$]	
Completeness to $\theta = 27.50^\circ$	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.3435 and 0.1719	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7805 / 0 / 379	
Goodness-of-fit on F^2	1.224	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0323, wR2 = 0.0747 [7041]$	
R indices (all data)	$R1 = 0.0370, wR2 = 0.0766$	
Largest diff. peak and hole	$0.933 \text{ and } -1.257 \text{ e.\AA}^{-3}$	
$R1 = \sum(F_o - F_c) / \sum F_o $	$wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$	
$S = [\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	$w = 1/[\sigma^2(F_o^2) + (m^*p)^2 + n^*p], p = [\max(F_o^2, 0) + 2 * F_c^2] / 3, m \text{ \& } n \text{ are constants.}$	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ir1A	274(1)	2396(1)	1735(1)	20(1)
Cl1A	145(1)	2023(1)	743(1)	33(1)
N1A	3139(4)	1760(2)	1826(2)	22(1)
N2A	2952(4)	3235(2)	1538(2)	24(1)
C1A	394(5)	3190(3)	2482(2)	26(1)
C2A	337(5)	2269(3)	2638(2)	26(1)
C3A	-918(5)	1830(3)	2883(2)	33(1)
C4A	-1833(5)	1398(3)	2420(2)	33(1)
C5A	-1766(5)	1871(3)	1844(2)	26(1)
C6A	-1862(4)	2807(3)	1768(2)	26(1)
C7A	-2132(5)	3454(3)	2250(2)	31(1)
C8A	-808(5)	3836(3)	2518(2)	31(1)
C9A	2348(5)	2463(2)	1694(2)	21(1)
C10A	4592(5)	1643(3)	1683(2)	32(1)
C11A	4805(6)	630(4)	1688(3)	49(2)
C12A	3470(7)	237(4)	1727(4)	74(2)
C13A	2557(5)	888(3)	1981(2)	33(1)
C14A	4291(5)	3579(3)	1724(2)	29(1)
C15A	4089(6)	4584(3)	1728(3)	44(1)
C16A	3093(6)	4733(3)	1234(2)	44(1)
C17A	2112(5)	3960(3)	1283(2)	34(1)
Ir1B	4760(1)	2562(1)	4213(1)	21(1)
Cl1B	4758(2)	2652(1)	3195(1)	47(1)
N1B	1917(4)	3236(2)	4291(2)	24(1)
N2B	2046(4)	1719(2)	4127(2)	23(1)
C1B	4787(5)	1960(3)	5029(2)	26(1)
C2B	4830(5)	2907(3)	5090(2)	28(1)
C3B	6112(5)	3429(3)	5283(2)	33(1)
C4B	6934(5)	3733(3)	4764(2)	32(1)
C5B	6794(4)	3119(3)	4254(2)	24(1)

C6B	6920(5)	2181(3)	4279(2)	30(1)
C7B	7273(5)	1674(3)	4823(2)	29(1)
C8B	5999(5)	1342(3)	5121(2)	33(1)
C9B	2677(5)	2511(3)	4200(2)	22(1)
C10B	450(5)	3330(3)	4174(2)	26(1)
C11B	207(5)	4348(3)	4170(2)	34(1)
C12B	1579(6)	4736(3)	4022(2)	40(1)
C13B	2552(5)	4132(3)	4359(3)	39(1)
C14B	762(5)	1417(3)	4394(2)	26(1)
C15B	899(6)	409(3)	4405(2)	41(1)
C16B	1757(6)	205(3)	3885(2)	37(1)
C17B	2808(5)	941(3)	3915(2)	34(1)

Table 3. Bond lengths [Å] and angles [°] for 5.

Ir1A-C9A	2.045(5)
Ir1A-C1A	2.101(4)
Ir1A-C2A	2.104(4)
Ir1A-C5A	2.173(5)
Ir1A-C6A	2.189(4)
Ir1A-Cl1A	2.3713(11)
N1A-C9A	1.338(5)
N1A-C13A	1.470(5)
N1A-C10A	1.484(6)
N2A-C9A	1.351(5)
N2A-C14A	1.466(6)
N2A-C17A	1.474(6)
C1A-C2A	1.425(6)
C1A-C8A	1.529(6)
C1A-H1AA	1.0000
C2A-C3A	1.521(6)
C2A-H2AA	1.0000
C3A-C4A	1.526(7)
C3A-H3AA	0.9900
C3A-H3AB	0.9900
C4A-C5A	1.516(6)
C4A-H4AA	0.9900
C4A-H4AB	0.9900
C5A-C6A	1.411(6)
C5A-H5AA	1.0000
C6A-C7A	1.508(6)
C6A-H6AA	1.0000
C7A-C8A	1.536(7)
C7A-H7AA	0.9900
C7A-H7AB	0.9900
C8A-H8AA	0.9900
C8A-H8AB	0.9900
C10A-C11A	1.527(7)
C10A-H10A	0.9900

C10A-H10B	0.9900
C11A-C12A	1.442(8)
C11A-H11A	0.9900
C11A-H11B	0.9900
C12A-C13A	1.458(7)
C12A-H12C	0.9900
C12A-H12D	0.9900
C13A-H13A	0.9900
C13A-H13B	0.9900
C14A-C15A	1.514(7)
C14A-H14A	0.9900
C14A-H14B	0.9900
C15A-C16A	1.502(8)
C15A-H15C	0.9900
C15A-H15D	0.9900
C16A-C17A	1.511(7)
C16A-H16C	0.9900
C16A-H16D	0.9900
C17A-H17A	0.9900
C17A-H17B	0.9900
Ir1B-C9B	2.047(5)
Ir1B-C1B	2.096(4)
Ir1B-C2B	2.099(4)
Ir1B-C5B	2.163(4)
Ir1B-C6B	2.197(5)
Ir1B-C11B	2.3671(13)
N1B-C9B	1.336(5)
N1B-C10B	1.466(6)
N1B-C13B	1.482(5)
N2B-C9B	1.344(5)
N2B-C17B	1.474(5)
N2B-C14B	1.491(5)
C1B-C2B	1.421(7)
C1B-C8B	1.517(6)
C1B-H1BA	1.0000
C2B-C3B	1.537(7)

C2B-H2BA	1.0000
C3B-C4B	1.537(7)
C3B-H3BA	0.9900
C3B-H3BB	0.9900
C4B-C5B	1.502(6)
C4B-H4BA	0.9900
C4B-H4BB	0.9900
C5B-C6B	1.406(6)
C5B-H5BA	1.0000
C6B-C7B	1.506(6)
C6B-H6BA	1.0000
C7B-C8B	1.530(6)
C7B-H7BA	0.9900
C7B-H7BB	0.9900
C8B-H8BA	0.9900
C8B-H8BB	0.9900
C10B-C11B	1.539(6)
C10B-H10C	0.9900
C10B-H10D	0.9900
C11B-C12B	1.516(7)
C11B-H11C	0.9900
C11B-H11D	0.9900
C12B-C13B	1.515(7)
C12B-H12A	0.9900
C12B-H12B	0.9900
C13B-H13C	0.9900
C13B-H13D	0.9900
C14B-C15B	1.512(6)
C14B-H14C	0.9900
C14B-H14D	0.9900
C15B-C16B	1.522(7)
C15B-H15A	0.9900
C15B-H15B	0.9900
C16B-C17B	1.508(7)
C16B-H16A	0.9900
C16B-H16B	0.9900

C17B-H17C	0.9900
C17B-H17D	0.9900
C9A-Ir1A-C1A	88.76(17)
C9A-Ir1A-C2A	92.85(18)
C1A-Ir1A-C2A	39.62(17)
C9A-Ir1A-C5A	161.13(15)
C1A-Ir1A-C5A	97.99(17)
C2A-Ir1A-C5A	81.58(18)
C9A-Ir1A-C6A	160.94(16)
C1A-Ir1A-C6A	81.09(17)
C2A-Ir1A-C6A	89.56(18)
C5A-Ir1A-C6A	37.75(16)
C9A-Ir1A-Cl1A	89.51(13)
C1A-Ir1A-Cl1A	159.21(13)
C2A-Ir1A-Cl1A	161.16(13)
C5A-Ir1A-Cl1A	90.21(12)
C6A-Ir1A-Cl1A	94.29(12)
C9A-N1A-C13A	121.6(4)
C9A-N1A-C10A	126.6(4)
C13A-N1A-C10A	109.5(3)
C9A-N2A-C14A	128.1(4)
C9A-N2A-C17A	119.3(4)
C14A-N2A-C17A	110.4(3)
C2A-C1A-C8A	124.0(4)
C2A-C1A-Ir1A	70.3(2)
C8A-C1A-Ir1A	112.1(3)
C2A-C1A-H1AA	114.2
C8A-C1A-H1AA	114.2
Ir1A-C1A-H1AA	114.2
C1A-C2A-C3A	123.3(4)
C1A-C2A-Ir1A	70.1(2)
C3A-C2A-Ir1A	114.2(3)
C1A-C2A-H2AA	113.9
C3A-C2A-H2AA	113.9
Ir1A-C2A-H2AA	113.9

C2A-C3A-C4A	112.7(4)
C2A-C3A-H3AA	109.1
C4A-C3A-H3AA	109.1
C2A-C3A-H3AB	109.1
C4A-C3A-H3AB	109.1
H3AA-C3A-H3AB	107.8
C5A-C4A-C3A	112.6(4)
C5A-C4A-H4AA	109.1
C3A-C4A-H4AA	109.1
C5A-C4A-H4AB	109.1
C3A-C4A-H4AB	109.1
H4AA-C4A-H4AB	107.8
C6A-C5A-C4A	124.5(4)
C6A-C5A-Ir1A	71.8(2)
C4A-C5A-Ir1A	109.5(3)
C6A-C5A-H5AA	114.3
C4A-C5A-H5AA	114.3
Ir1A-C5A-H5AA	114.3
C5A-C6A-C7A	123.7(4)
C5A-C6A-Ir1A	70.5(2)
C7A-C6A-Ir1A	113.2(3)
C5A-C6A-H6AA	114.0
C7A-C6A-H6AA	114.0
Ir1A-C6A-H6AA	114.0
C6A-C7A-C8A	112.0(4)
C6A-C7A-H7AA	109.2
C8A-C7A-H7AA	109.2
C6A-C7A-H7AB	109.2
C8A-C7A-H7AB	109.2
H7AA-C7A-H7AB	107.9
C1A-C8A-C7A	113.0(4)
C1A-C8A-H8AA	109.0
C7A-C8A-H8AA	109.0
C1A-C8A-H8AB	109.0
C7A-C8A-H8AB	109.0
H8AA-C8A-H8AB	107.8

N1A-C9A-N2A	118.4(4)
N1A-C9A-Ir1A	121.6(3)
N2A-C9A-Ir1A	120.0(3)
N1A-C10A-C11A	104.3(4)
N1A-C10A-H10A	110.9
C11A-C10A-H10A	110.9
N1A-C10A-H10B	110.9
C11A-C10A-H10B	110.9
H10A-C10A-H10B	108.9
C12A-C11A-C10A	106.2(4)
C12A-C11A-H11A	110.5
C10A-C11A-H11A	110.5
C12A-C11A-H11B	110.5
C10A-C11A-H11B	110.5
H11A-C11A-H11B	108.7
C11A-C12A-C13A	109.0(5)
C11A-C12A-H12C	109.9
C13A-C12A-H12C	109.9
C11A-C12A-H12D	109.9
C13A-C12A-H12D	109.9
H12C-C12A-H12D	108.3
C12A-C13A-N1A	104.0(4)
C12A-C13A-H13A	110.9
N1A-C13A-H13A	110.9
C12A-C13A-H13B	110.9
N1A-C13A-H13B	110.9
H13A-C13A-H13B	109.0
N2A-C14A-C15A	103.4(4)
N2A-C14A-H14A	111.1
C15A-C14A-H14A	111.1
N2A-C14A-H14B	111.1
C15A-C14A-H14B	111.1
H14A-C14A-H14B	109.0
C16A-C15A-C14A	103.0(4)
C16A-C15A-H15C	111.2
C14A-C15A-H15C	111.2

C16A-C15A-H15D	111.2
C14A-C15A-H15D	111.2
H15C-C15A-H15D	109.1
C15A-C16A-C17A	103.4(4)
C15A-C16A-H16C	111.1
C17A-C16A-H16C	111.1
C15A-C16A-H16D	111.1
C17A-C16A-H16D	111.1
H16C-C16A-H16D	109.0
N2A-C17A-C16A	103.9(4)
N2A-C17A-H17A	111.0
C16A-C17A-H17A	111.0
N2A-C17A-H17B	111.0
C16A-C17A-H17B	111.0
H17A-C17A-H17B	109.0
C9B-Ir1B-C1B	89.12(17)
C9B-Ir1B-C2B	91.67(18)
C1B-Ir1B-C2B	39.61(18)
C9B-Ir1B-C5B	159.46(16)
C1B-Ir1B-C5B	97.92(17)
C2B-Ir1B-C5B	81.89(17)
C9B-Ir1B-C6B	162.56(16)
C1B-Ir1B-C6B	80.73(17)
C2B-Ir1B-C6B	89.48(18)
C5B-Ir1B-C6B	37.62(16)
C9B-Ir1B-C11B	90.80(13)
C1B-Ir1B-C11B	157.85(13)
C2B-Ir1B-C11B	162.44(14)
C5B-Ir1B-C11B	89.80(12)
C6B-Ir1B-C11B	93.33(13)
C9B-N1B-C10B	126.8(4)
C9B-N1B-C13B	120.9(4)
C10B-N1B-C13B	110.0(3)
C9B-N2B-C17B	119.9(4)
C9B-N2B-C14B	127.4(4)
C17B-N2B-C14B	110.2(3)

C2B-C1B-C8B	124.8(4)
C2B-C1B-Ir1B	70.3(2)
C8B-C1B-Ir1B	112.3(3)
C2B-C1B-H1BA	113.9
C8B-C1B-H1BA	113.9
Ir1B-C1B-H1BA	113.9
C1B-C2B-C3B	123.7(4)
C1B-C2B-Ir1B	70.1(2)
C3B-C2B-Ir1B	114.3(3)
C1B-C2B-H2BA	113.8
C3B-C2B-H2BA	113.8
Ir1B-C2B-H2BA	113.8
C2B-C3B-C4B	111.4(4)
C2B-C3B-H3BA	109.3
C4B-C3B-H3BA	109.3
C2B-C3B-H3BB	109.3
C4B-C3B-H3BB	109.3
H3BA-C3B-H3BB	108.0
C5B-C4B-C3B	113.5(4)
C5B-C4B-H4BA	108.9
C3B-C4B-H4BA	108.9
C5B-C4B-H4BB	108.9
C3B-C4B-H4BB	108.9
H4BA-C4B-H4BB	107.7
C6B-C5B-C4B	124.7(4)
C6B-C5B-Ir1B	72.5(3)
C4B-C5B-Ir1B	109.4(3)
C6B-C5B-H5BA	114.2
C4B-C5B-H5BA	114.2
Ir1B-C5B-H5BA	114.2
C5B-C6B-C7B	123.7(4)
C5B-C6B-Ir1B	69.9(2)
C7B-C6B-Ir1B	112.8(3)
C5B-C6B-H6BA	114.2
C7B-C6B-H6BA	114.2
Ir1B-C6B-H6BA	114.2

C6B-C7B-C8B	111.7(4)
C6B-C7B-H7BA	109.3
C8B-C7B-H7BA	109.3
C6B-C7B-H7BB	109.3
C8B-C7B-H7BB	109.3
H7BA-C7B-H7BB	107.9
C1B-C8B-C7B	112.8(4)
C1B-C8B-H8BA	109.0
C7B-C8B-H8BA	109.0
C1B-C8B-H8BB	109.0
C7B-C8B-H8BB	109.0
H8BA-C8B-H8BB	107.8
N1B-C9B-N2B	118.4(4)
N1B-C9B-Ir1B	122.0(3)
N2B-C9B-Ir1B	119.5(3)
N1B-C10B-C11B	104.3(4)
N1B-C10B-H10C	110.9
C11B-C10B-H10C	110.9
N1B-C10B-H10D	110.9
C11B-C10B-H10D	110.9
H10C-C10B-H10D	108.9
C12B-C11B-C10B	104.0(4)
C12B-C11B-H11C	111.0
C10B-C11B-H11C	111.0
C12B-C11B-H11D	111.0
C10B-C11B-H11D	111.0
H11C-C11B-H11D	109.0
C13B-C12B-C11B	101.9(4)
C13B-C12B-H12A	111.4
C11B-C12B-H12A	111.4
C13B-C12B-H12B	111.4
C11B-C12B-H12B	111.4
H12A-C12B-H12B	109.2
N1B-C13B-C12B	103.0(4)
N1B-C13B-H13C	111.2
C12B-C13B-H13C	111.2

N1B-C13B-H13D	111.2
C12B-C13B-H13D	111.2
H13C-C13B-H13D	109.1
N2B-C14B-C15B	103.4(4)
N2B-C14B-H14C	111.1
C15B-C14B-H14C	111.1
N2B-C14B-H14D	111.1
C15B-C14B-H14D	111.1
H14C-C14B-H14D	109.0
C14B-C15B-C16B	103.7(4)
C14B-C15B-H15A	111.0
C16B-C15B-H15A	111.0
C14B-C15B-H15B	111.0
C16B-C15B-H15B	111.0
H15A-C15B-H15B	109.0
C17B-C16B-C15B	102.3(4)
C17B-C16B-H16A	111.3
C15B-C16B-H16A	111.3
C17B-C16B-H16B	111.3
C15B-C16B-H16B	111.3
H16A-C16B-H16B	109.2
N2B-C17B-C16B	103.6(4)
N2B-C17B-H17C	111.0
C16B-C17B-H17C	111.0
N2B-C17B-H17D	111.0
C16B-C17B-H17D	111.0
H17C-C17B-H17D	109.0

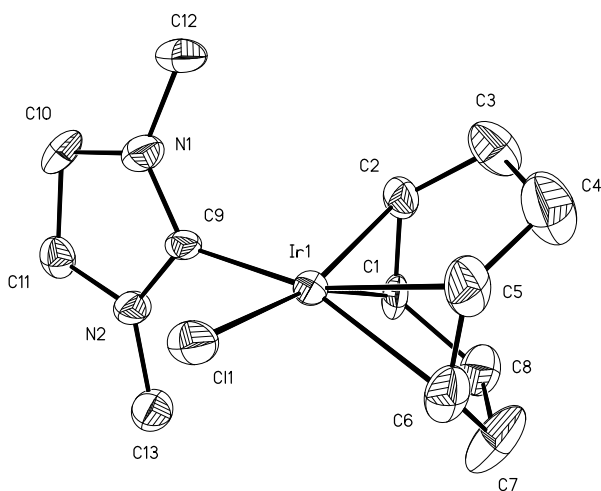
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir1A	17(1)	23(1)	18(1)	-1(1)	1(1)	-1(1)
Cl1A	33(1)	44(1)	20(1)	-4(1)	1(1)	-6(1)
N1A	19(2)	26(2)	23(2)	4(1)	5(2)	-1(1)
N2A	21(2)	26(2)	25(2)	3(1)	2(2)	-4(1)
C1A	20(2)	36(2)	23(2)	-7(2)	1(2)	-1(2)
C2A	21(2)	41(2)	17(2)	-1(2)	-1(2)	5(2)
C3A	32(3)	41(3)	25(2)	8(2)	5(2)	0(2)
C4A	31(3)	36(3)	32(3)	6(2)	6(2)	-1(2)
C5A	22(2)	30(2)	26(2)	5(2)	-4(2)	-2(2)
C6A	14(2)	32(2)	30(2)	-3(2)	-1(2)	3(2)
C7A	26(3)	35(2)	32(3)	-3(2)	4(2)	6(2)
C8A	31(3)	31(2)	31(3)	-7(2)	1(2)	4(2)
C9A	22(2)	23(2)	19(2)	0(2)	3(2)	-2(2)
C10A	22(2)	37(3)	37(3)	5(2)	9(2)	4(2)
C11A	38(3)	39(3)	73(4)	12(3)	25(3)	11(2)
C12A	45(4)	31(3)	149(8)	-4(4)	37(4)	6(3)
C13A	29(3)	26(2)	45(3)	7(2)	12(2)	0(2)
C14A	21(2)	36(2)	31(3)	4(2)	0(2)	-11(2)
C15A	46(4)	35(3)	52(3)	-6(2)	6(3)	-13(2)
C16A	50(4)	29(2)	54(3)	10(2)	3(3)	-3(2)
C17A	32(3)	29(2)	40(3)	11(2)	-1(2)	2(2)
Ir1B	19(1)	26(1)	18(1)	1(1)	2(1)	-1(1)
Cl1B	43(1)	77(1)	20(1)	6(1)	3(1)	-10(1)
N1B	20(2)	22(2)	29(2)	-2(1)	-1(2)	-1(1)
N2B	17(2)	27(2)	25(2)	-3(1)	5(2)	1(1)
C1B	18(2)	39(2)	21(2)	3(2)	2(2)	-4(2)
C2B	23(2)	42(3)	21(2)	-2(2)	3(2)	3(2)
C3B	29(3)	42(3)	29(3)	-12(2)	3(2)	-7(2)
C4B	26(3)	33(2)	38(3)	-4(2)	4(2)	-7(2)
C5B	17(2)	29(2)	27(2)	1(2)	11(2)	-9(2)

C6B	29(3)	28(2)	32(3)	1(2)	8(2)	3(2)
C7B	19(2)	36(2)	33(3)	3(2)	0(2)	3(2)
C8B	30(3)	39(3)	29(3)	11(2)	1(2)	2(2)
C9B	25(2)	24(2)	16(2)	3(1)	2(2)	1(2)
C10B	24(2)	26(2)	28(2)	-3(2)	1(2)	4(2)
C11B	32(3)	29(2)	41(3)	-2(2)	-2(2)	7(2)
C12B	43(3)	25(2)	50(3)	4(2)	6(3)	1(2)
C13B	28(3)	22(2)	66(4)	-1(2)	-4(3)	-4(2)
C14B	22(2)	29(2)	26(2)	3(2)	0(2)	-2(2)
C15B	43(3)	29(2)	49(3)	7(2)	0(3)	-4(2)
C16B	42(3)	24(2)	46(3)	-5(2)	-6(2)	2(2)
C17B	31(3)	29(2)	40(3)	-9(2)	4(2)	5(2)

8. X-Ray Analysis for Compound 10.



Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective

carbon atoms. A total of 154 parameters were refined in the final cycle of refinement using 3128 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.96% and 6.52%, respectively. Refinement was done using F^2 .

Table 1. Crystal data and structure refinement for 10.

Identification code	10	
Empirical formula	C13 H22 Cl Ir N2	
Formula weight	433.98	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.2770(15) Å	$\alpha = 90^\circ$.
	b = 12.449(3) Å	$\beta = 90^\circ$.
	c = 15.738(3) Å	$\gamma = 90^\circ$.
Volume	1425.7(5) Å ³	
Z	4	
Density (calculated)	2.022 Mg/m ³	
Absorption coefficient	9.534 mm ⁻¹	
F(000)	832	
Crystal size	0.20 x 0.02 x 0.01 mm ³	
Theta range for data collection	2.09 to 27.50°.	
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -20 ≤ l ≤ 12	
Reflections collected	9737	
Independent reflections	3271 [R(int) = 0.0628]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.9107 and 0.2515	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3271 / 0 / 154	
Goodness-of-fit on F^2	1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0296, wR2 = 0.0652 [3128]	
R indices (all data)	R1 = 0.0320, wR2 = 0.0659	
Absolute structure parameter	-0.021(13)	
Largest diff. peak and hole	1.197 and -0.918 e.Å ⁻³	

$$R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

$$w = 1/[\sigma^2(F_o^2) + (m^*p)^2 + n^*p], p = [\max(F_o^2, 0) + 2^* F_c^2]/3, m \text{ \& } n \text{ are constants.}$$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 10. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ir1	1971(1)	4848(1)	5732(1)	21(1)
Cl1	3452(2)	5953(2)	6737(1)	32(1)
N1	-769(8)	4116(5)	7047(4)	31(1)
N2	1670(8)	3125(4)	7054(4)	28(1)
C1	1485(10)	3619(6)	4833(4)	29(2)
C2	-54(10)	4304(6)	4887(4)	31(2)
C3	-560(11)	5136(6)	4252(5)	46(2)
C4	945(15)	5910(9)	4025(7)	67(3)
C5	2396(12)	6027(7)	4711(5)	42(2)
C6	3922(12)	5367(7)	4756(5)	40(2)
C7	4354(15)	4421(8)	4173(6)	63(3)
C8	2825(12)	3612(6)	4102(5)	39(2)
C9	845(9)	3968(5)	6683(4)	22(1)
C10	-1206(10)	3325(6)	7710(5)	33(2)
C11	496(10)	2605(5)	7704(5)	31(2)
C12	-2135(8)	4899(6)	6792(4)	35(2)
C13	3442(10)	2682(6)	6839(5)	37(2)

Table 3. Bond lengths [Å] and angles [°] for 10.

Ir1-C9	2.028(7)
Ir1-C2	2.097(7)
Ir1-C1	2.113(7)
Ir1-C6	2.189(7)
Ir1-C5	2.197(7)
Ir1-Cl1	2.3570(17)
N1-C9	1.320(9)
N1-C12	1.449(8)
N1-C10	1.470(9)
N2-C9	1.343(9)
N2-C13	1.443(9)
N2-C11	1.482(9)
C1-C2	1.410(11)
C1-C8	1.508(10)
C1-H1A	1.0000
C2-C3	1.486(10)
C2-H2A	1.0000
C3-C4	1.502(12)
C3-H3A	0.9900
C3-H3B	0.9900
C4-C5	1.517(13)
C4-H4A	0.9900
C4-H4B	0.9900
C5-C6	1.383(12)
C5-H5A	1.0000
C6-C7	1.526(12)
C6-H6A	1.0000
C7-C8	1.506(12)
C7-H7A	0.9900
C7-H7B	0.9900
C8-H8A	0.9900
C8-H8B	0.9900
C10-C11	1.529(10)
C10-H10A	0.9900

C10-H10B	0.9900
C11-H11A	0.9900
C11-H11B	0.9900
C12-H12A	0.9800
C12-H12B	0.9800
C12-H12C	0.9800
C13-H13A	0.9800
C13-H13B	0.9800
C13-H13C	0.9800

C9-Ir1-C2	90.5(3)
C9-Ir1-C1	92.0(3)
C2-Ir1-C1	39.1(3)
C9-Ir1-C6	160.0(3)
C2-Ir1-C6	96.1(3)
C1-Ir1-C6	81.5(3)
C9-Ir1-C5	163.2(3)
C2-Ir1-C5	81.4(3)
C1-Ir1-C5	91.0(3)
C6-Ir1-C5	36.8(3)
C9-Ir1-Cl1	90.25(19)
C2-Ir1-Cl1	159.2(2)
C1-Ir1-Cl1	161.5(2)
C6-Ir1-Cl1	90.1(2)
C5-Ir1-Cl1	92.1(2)
C9-N1-C12	125.8(6)
C9-N1-C10	114.0(6)
C12-N1-C10	119.9(6)
C9-N2-C13	126.6(6)
C9-N2-C11	112.6(6)
C13-N2-C11	120.7(5)
C2-C1-C8	124.3(7)
C2-C1-Ir1	69.8(4)
C8-C1-Ir1	114.0(5)
C2-C1-H1A	113.7
C8-C1-H1A	113.7

Ir1-C1-H1A	113.7
C1-C2-C3	125.3(7)
C1-C2-Ir1	71.0(4)
C3-C2-Ir1	112.1(5)
C1-C2-H2A	113.6
C3-C2-H2A	113.6
Ir1-C2-H2A	113.6
C2-C3-C4	115.2(7)
C2-C3-H3A	108.5
C4-C3-H3A	108.5
C2-C3-H3B	108.5
C4-C3-H3B	108.5
H3A-C3-H3B	107.5
C3-C4-C5	113.5(7)
C3-C4-H4A	108.9
C5-C4-H4A	108.9
C3-C4-H4B	108.9
C5-C4-H4B	108.9
H4A-C4-H4B	107.7
C6-C5-C4	122.6(9)
C6-C5-Ir1	71.3(4)
C4-C5-Ir1	111.0(5)
C6-C5-H5A	114.7
C4-C5-H5A	114.7
Ir1-C5-H5A	114.7
C5-C6-C7	126.4(8)
C5-C6-Ir1	72.0(5)
C7-C6-Ir1	109.1(5)
C5-C6-H6A	113.8
C7-C6-H6A	113.8
Ir1-C6-H6A	113.8
C8-C7-C6	114.1(7)
C8-C7-H7A	108.7
C6-C7-H7A	108.7
C8-C7-H7B	108.7
C6-C7-H7B	108.7

H7A-C7-H7B	107.6
C7-C8-C1	114.6(6)
C7-C8-H8A	108.6
C1-C8-H8A	108.6
C7-C8-H8B	108.6
C1-C8-H8B	108.6
H8A-C8-H8B	107.6
N1-C9-N2	108.6(6)
N1-C9-Ir1	127.2(5)
N2-C9-Ir1	124.2(5)
N1-C10-C11	102.3(6)
N1-C10-H10A	111.3
C11-C10-H10A	111.3
N1-C10-H10B	111.3
C11-C10-H10B	111.3
H10A-C10-H10B	109.2
N2-C11-C10	102.4(5)
N2-C11-H11A	111.3
C10-C11-H11A	111.3
N2-C11-H11B	111.3
C10-C11-H11B	111.3
H11A-C11-H11B	109.2
N1-C12-H12A	109.5
N1-C12-H12B	109.5
H12A-C12-H12B	109.5
N1-C12-H12C	109.5
H12A-C12-H12C	109.5
H12B-C12-H12C	109.5
N2-C13-H13A	109.5
N2-C13-H13B	109.5
H13A-C13-H13B	109.5
N2-C13-H13C	109.5
H13A-C13-H13C	109.5
H13B-C13-H13C	109.5

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir1	19(1)	24(1)	20(1)	0(1)	0(1)	0(1)
Cl1	25(1)	36(1)	33(1)	-13(1)	-4(1)	0(1)
N1	24(3)	36(3)	33(3)	2(3)	6(3)	1(2)
N2	24(3)	31(3)	28(3)	9(2)	5(2)	7(2)
C1	37(5)	38(4)	12(3)	0(3)	2(3)	-6(3)
C2	28(4)	43(4)	22(3)	1(3)	-5(3)	-5(3)
C3	45(4)	40(4)	51(5)	6(5)	-20(4)	-6(3)
C4	62(7)	77(7)	61(7)	29(5)	-20(5)	-25(5)
C5	46(6)	40(4)	39(5)	17(4)	-1(4)	-16(3)
C6	40(4)	48(5)	32(4)	3(4)	2(3)	-22(4)
C7	69(7)	71(6)	50(6)	-24(5)	34(5)	-26(5)
C8	51(5)	34(4)	31(4)	-2(3)	5(4)	0(3)
C9	15(3)	29(4)	23(3)	-8(3)	-2(3)	1(3)
C10	34(4)	35(4)	31(4)	-7(3)	17(3)	-8(3)
C11	31(4)	34(4)	26(4)	0(3)	-4(3)	-9(3)
C12	24(3)	34(4)	45(4)	-5(3)	0(3)	9(4)
C13	38(4)	37(4)	34(4)	5(3)	5(3)	9(3)