1cPalladium-Catalyzed Intramolecular Acylcyanation of Alkenes Using α-Iminonitriles

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Supporting Information

(125 Pages)

Section A contains general experimental procedures

Section B contains experimental procedures for the preparation of **1b to 1k, 2a to 2l, 3a to 3l, 5a to 5k, and 6b to 6k, 7b to 7j** with tabulated characterization data for these new compounds.

Section C contains copies of NMR spectra for new compounds described in section B.

Section A

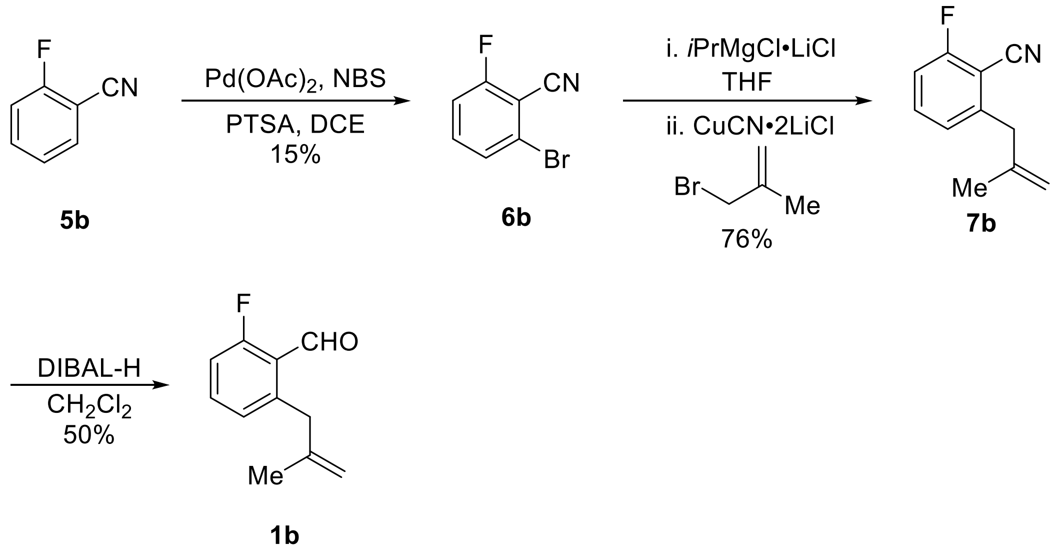
General Details: All reactions were carried out using flame-dried glassware under nitrogen. Acetonitrile, toluene, dichloromethane and THF (tetrahydrofuran) were dried according to published procedures.[1] After drying toluene and dichloromethane were further deoxygenated by bubbling a stream of argon through the liquid for 30 min in a Strauss flask and then stored in a nitrogen-filled glove box. $Pd(PPh_3)_4$ was purchased from Strem Chemicals. All palladium-catalyzed reactions were carried out in a Vacuum Atmospheres Co. nitrogen filled glove box in 1 or 4 dram vials sealed with PTFE lined caps. Heating was applied by aluminum block heaters. All other chemicals were purchased from commercial vendors and used as received.

Analytical thin layer chromatography (TLC) was carried out using 0.25 mm silica plates from Silacycle or 200 μm alumina plates from Sorbent Technologies. Eluted plates are visualized first with UV light and then by staining with potassium permanganate/potassium carbonate solution. Flash chromatography was performed using 230–400 mesh (particle size 0.04–0.063 mm) silica gel purchased from Silacycle or neutral alumina (particle size 50 to 200 μm) purchased from Sorbent Technologies. ^{1}H NMR (300 and 500 MHz), ^{13}C NMR (75 and 126 MHz), and ^{19}F NMR (471 MHz) spectra were obtained on Varian and Bruker FT NMR instruments. NMR spectra were reported as δ values in ppm relative to, chloroform, dichloromethane, hexafluorobenzene, tetramethylsilane or using instrument standard. ^{1}H NMR coupling constants are reported in Hz; multiplicity was indicated as follows; s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); app (apparent); br (broad). Infrared (IR) spectra were obtained on a MIDAC FT-IR spectrometer as a thin-film on NaCl plates (prepared by evaporation from CH_2Cl_2 or $CDCl_3$). Low-resolution mass spectra (LRMS) in EI or CI experiments were performed on a Varian Saturn 2200 GC-MS system or on Bruker BioTOF II using electrospray ionization (ESI) method. The column used for GC-MS was a capillary column of 30 meters in length and 0.4 mm in diameter. The method used begins with initial temperature of 100 °C maintained for two min and increased at the rate of 5 °C per minute until 250 °C which was maintained for 5 min. High-resolution mass spectra (HRMS) with electrospray ionization (ESI) were performed on a Bruker BioTOF II and with chemical ionization (CI) were performed on a Finnigan MAT95 instrument.

Section B

Synthesis of Aldehydes:

2-fluoro-6-(2-methylallyl)benzaldehyde 1b:



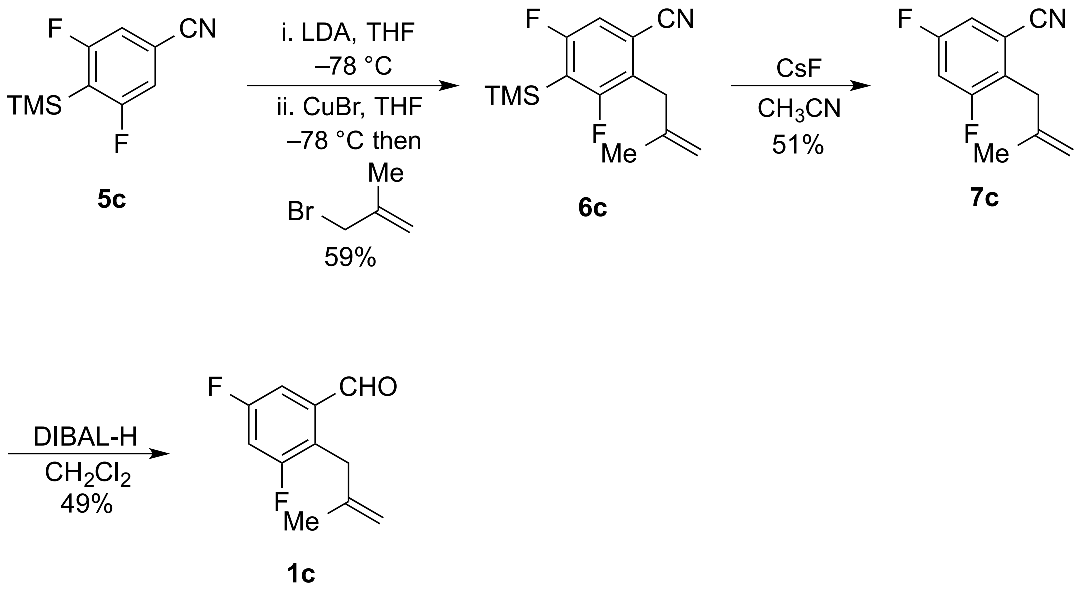
2-(2-methylallyl)benzaldehyde 1b:

2-bromo-6-fluorobenzonitrile **6b** was prepared by slightly modifying the procedure reported by Sun.[2] To the mixture of 2-fluorobenzonitrile **5b** (1.06 g, 8.8 mmol), NBS (3.2 g, 18 mmol) and *p*-toluenesulfonic acid (1.35 g, 7.0 mmol) in 1,2-dichloroethane (30 mL), $Pd(OAc)_2$ (200 mg, 0.9 mmol) was added and the reaction mixture was heated at 80 °C under air for 14 hours. After cooling to room temperature, the reaction mixture was concentrated to remove solvent and other volatiles. The crude material was purified by flash column chromatography on silica (gradient from 20 to 30% EtOAc in hexanes) to give slightly impure 2-bromo-6-fluorobenzonitrile **6b** (0.25 g, 1.32 mmol, 15%). R_f = 0.72 (3:7 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.44 (m, 2H), 7.20 (dt, *J* = 8.2, 1.4 Hz, 1H); ^{13}C NMR (126MHz, $CDCl_3$) δ 163.8 (d, *J* = 263 Hz), 135.2 (app d, *J* = 10 Hz), 128.9, 125.8, 115.1 (d, *J* = 20 Hz), 112.4, 105.6; LRMS (GC-MS, CI, MeOH) *m*/*z* 201 $(M+2+H)^+$ and 199 $(M + H)^+$, t_R = 24.6 min. The material was of suitable purity to undergo next step.

2-bromo-6-fluorobenzonitrile, **6b** (250 mg, 1.26 mmol) was dissolved in THF (0.2 mL) and cooled to 0 °C. *i*PrMgCl•LiCl[3] (1.2 mL of a 1.3 M solution in THF, 1.6 mmol) was added and the reaction mixture was stirred for one hour at 0 °C. CuCN•2LiCl (0.13 mL of 1M solution in THF, 0.13 mmol) and 3-bromo-2-methyl-1-propene (0.2 mL, 2 mmol) were added at 0 °C and the solution was allowed to warm to room temperature and stirred for 14 hours at room temp. The reaction was quenched by addition of aqueous saturated NH_4Cl solution (10 mL) and extracted with diethyl ether (2 × 30 mL). The organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 (15 g) and concentrated. The crude material was purified by flash column chromatography on silica (10% EtOAc in hexanes) to give 2-fluoro-6-(2-methylallyl)benzonitrile, **7b** (167 mg, 1.6 mmol, 76%) R_f = 0.50 (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 8.1, 8.1, 5.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.07 (dt, *J* = 8.6, 1.0 Hz, 1H), 4.92−4.91 (m, 1H), 4.72−4.70 (m, 1H), 3.54 (s, 2H), 1.74 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 177 $(M+H)^+$, t_R = 12.9 min.

DIBAL-H (1.4 mL of 1 M solution in toluene, 1.4 mmol) was added to a solution of 2-fluoro-6-(2-methylallyl)benzonitrile, **7b** (165 mg, 0.93 mmol) in methylene chloride (5 mL) maintained at 0 °C under nitrogen. The reaction was allowed to warm to room temperature and stirred for 14 hours. The reaction mixture was diluted with diethyl ether (7 mL) and cooled to 0 °C. HCl (5 mL, 3N solution) was added. The reaction mixture was heated to reflux for 30 minutes. Diethyl ether (30 mL) was added to the reaction mixture and layers were separated. The aqueous layer was extracted with diethyl ether (30 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated. The crude material was purified by flash column chromatography on silica (5% EtOAc in hexanes) to give **2-(2-methylallyl)benzaldehyde 1b** (84 mg, 1.26 mmol 50%) R_f = 0.70 (1:4 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.49 (ddd, *J* = 8.0, 8.0, 5.8 Hz, 1H), 7.08−7.03 (m, 2H), 4.81−4.79 (m, 1H), 4.43−4.42 (m, 1H), 3.73 (s, 2H), 1.78 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 179 $(M+H)^+$, t_R = 12.7 min.

3,5-difluoro-2-(2-methylallyl)benzaldehyde 1c:



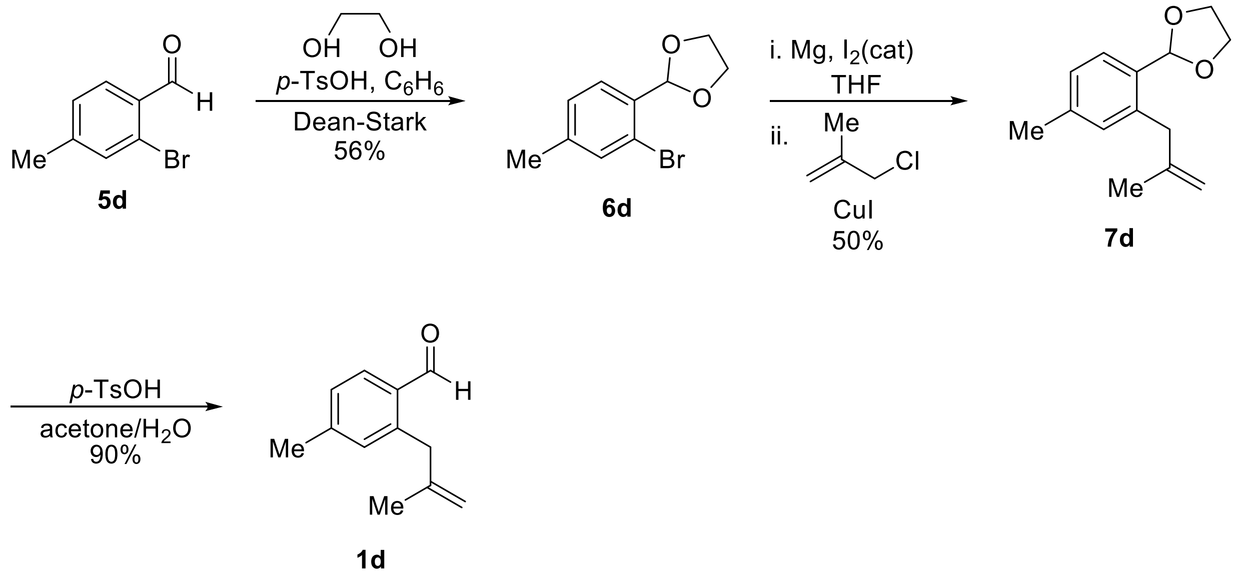
3,5-difluoro-4-(trimethylsilyl)benzonitrile **5c** is prepared using the reported procedure.[4] A solution of diisopropyl amine (1.59 mL, 11.37 mmol) in THF (26 mL) was cooled to –78 °C under nitrogen. A solution of *n*-BuLi in hexanes (1.6 M hexanes, 4.55 mL, 11.37 mmol) was added dropwise and this solution was allowed to stir for 30 minutes. A solution of 3,5-difluoro-4-(trimethylsilyl)benzonitrile **5c** (2.23 g, 10.53 mmol) in THF (4 mL) was added dropwise to the LDA solution and this was allowed to stir at –78 °C for 2 hours. The solution was then transferred *via* cannula cold to a stirred suspension of CuBr (1.5 g, 10.42 mmol) in THF (20 mL) that was cooled at –78 °C. The resulting dark blue solution was allowed to stir for 30 minutes, at which point methallyl bromide (1.06 mL, 10.53 mmol) was added dropwise. The solution was then allowed to warm to room temperature and was stirred for 15 hours. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and the aqueous layer was washed with Et_2O (2 × 40 mL). The organics were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The product was purified by column chromatography (2% EtOAc in hexanes) to yield 3,5-difluoro-2-(2-methylallyl)-4-(trimethylsilyl)benzonitrile **6c** (1.66 g, 6.25 mmol, 59% yield) as an orange oil. $R_f = 0.72$ (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (dd, J = 7.7, 1.2 Hz, 1H), 4.84–4.83 (m, 1H), 4.57 (app s, 1H), 3.49 (s, 2H), 1.79 (s, 3H), 0.39 (t, J = 1.5 Hz, 9H); LRMS (GC-MS, CI, MeOH) *m/z* 266 $(M+H)^+$, t_R = 15.1 min.

To a stirred solution of 3,5-difluoro-2-(2-methylallyl)-4-(trimethylsilyl)benzonitrile **6c** (1.6 g, 6.0 mmol) in distilled acetonitrile (22 mL) at room temperature was added anhydrous CsF (1.098 g, 7.2 mmol). This reaction was allowed to stir at room temperature until no starting material was observed by TLC (~12 hours). The reaction was then diluted with water and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 20 mL) and then the combined organics were washed with brine (40 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography (2% EtOAc in hexanes) to yield 3,5-difluoro-2-(2-methylallyl)benzonitrile **7c** (0.60 g, 3.11 mmol, 51% yield) as an orange oil. $R_f = 0.50$ (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23−7.18 (m, 1H), 7.10 (td, J = 9.2, 2.4 Hz, 1H), 4.85 (m, 1H), 4.59 (m, 1H), 3.53 (s, 2H), 1.79 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 194 $(M+H)^+$, t_R = 8.6 min.

A flame-dried flask under N_2 was charged with 3,5-difluoro-2-(2-methylallyl)benzonitrile **7c** (0.5985 g, 3.1 mmol) and dichloromethane (21 mL). The solution was cooled to 0 °C and a solution of DIBAL-H in toluene (1M, 3.7 mL, 3.7 mmol) was added dropwise. The reaction was allowed to warm to room temperature over 15 h. The reaction mixture was then diluted with Et_2O (18 mL) and HCl (3N, 18 mL) was added. The reaction was headed to reflux for 1 h, after which it was cooled to room temperature and was diluted with more Et_2O (18 mL). The organics were separated and washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL) and then dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash column chromatography

(2% EtOAc in Hexanes) to yield **3,5-difluoro-2-(2-methylallyl)benzaldehyde 1c** (0.2969 g, 1.51 mmol, 49% yield) as a yellow oil. R$_f$ = 0.5 (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.17 (d, *J* = 2.6 Hz, 1H), 7.43 (ddd, *J* = 8.4, 2.6, 1.3 Hz, 1H), 7.07 (ddd, *J* = 9.3, 8.2, 2.7 Hz, 1H), 4.83 (dt, *J* = 2.5, 1.2 Hz, 1H), 4.38 (app s, 1H), 3.70 (s, 2H), 1.83 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 197 (M+H)$^+$, t$_R$ = 9.5 min.

2-(2-methylallyl)benzaldehyde, 1d:

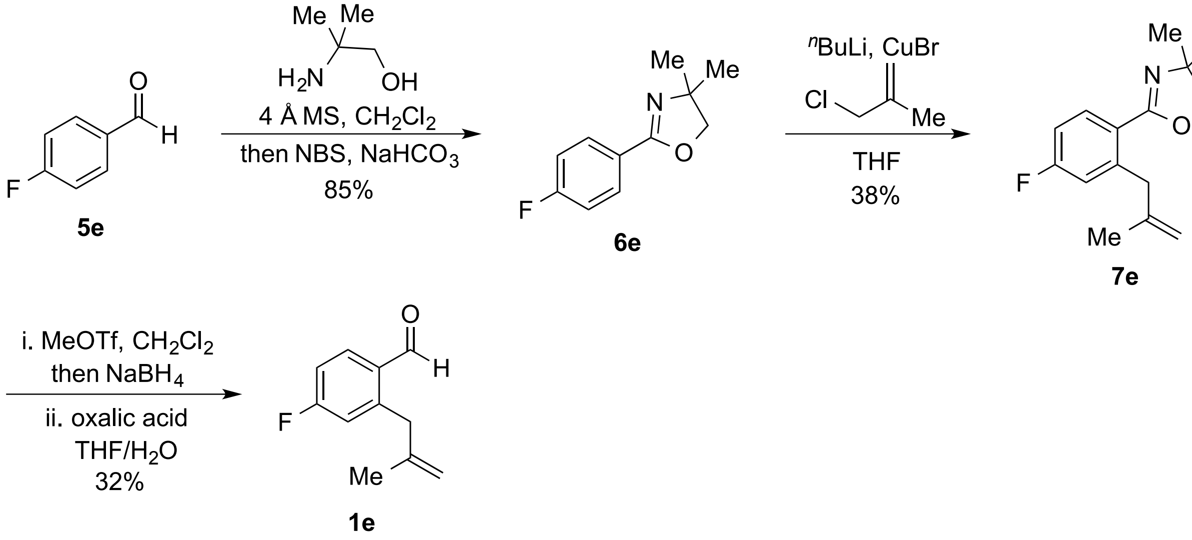


A solution of 2-bromo-4-methylbenzaldehyde, **5d** (1.51 g, 7.6 mmol), ethylene glycol (0.86 mL, 15.2 mmol) benzene (4.2 mL) and *p*-TsOH (29 mg, 0.15 mmol) was heated to reflux for 14 hours with a Dean-Stark trap. The reaction was neutralized with saturated aqueous NaHCO$_3$ solution (20 mL) and extracted twice with diethyl ether (2 × 50 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous Na$_2$SO$_4$ (25 g) and concentrated. The crude material was purified by flash column chromatography on silica (gradient from 5 to 10% EtOAc in hexanes) to give 2-(2-bromo-4-methylphenyl)-1,3-dioxolane, **6d** (1.05 g, 4.32 mmol, 56%) R$_f$ = 0.72 (1:4 EtOAc:Hex); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 0.8 Hz, 1H), 7.14 (app d, *J* = 8.5 Hz, 1H), 6.07 (s, 1H), 4.18−4.03 (m, 4H), 2.33 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 245 (M+2+H)$^+$ and 243 (M+H)$^+$, t$_R$ = 10.0 min.

A round-bottom flask equipped with a reflux condenser and magnetic stir bar under nitrogen was charged with Mg turnings (121 mg, 5.04 mmol) and a small crystal of I_2. The flask was flame-dried under vacuum. A solution of THF (2.5 mL) and 2-(2-bromo-4-methylphenyl)-1,3-dioxolane **6d** (1.02 g, 4.2 mmol) was slowly added. After complete addition the mixture was maintained at reflux for two hours. The resulting solution was allowed to cool to room temperature then added dropwise to a stirred suspension of isobutenyl chloride (0.62 mL, 6.3 mmol) and CuI (80 mg, 0.42 mmol) in THF (3 mL) maintained at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, allowed to warm to room temperature and stirred overnight. CH_2Cl_2 (15 mL) was added and the mixture was washed with a saturated aqueous NH_4Cl (10 mL) solution. The organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica (4% EtOAc in hexanes) to give 2-(4-methyl-2-(2-methylallyl) phenyl)-1,3-dioxolane, **7d** (453 mg, 2.12 mmol, 50%) as colorless oil. R_f = 0.51 (1:9 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.06 (app d, *J* = 8.0 Hz, 1H), 6.99 (app s, 1H), 5.95 (s, 1H), 4.86−4.81 (m, 1H), 4.58−4.53 (m, 1H), 4.16−3.98 (m, 4H), 3.44 (s, 2H), 2.32 (s, 3H), 1.74 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 219 $(M+H)^+$, t_R = 13.5 min.

A solution of 2-(4-methyl-2-(2-methylallyl) phenyl)-1,3-dioxolane, **7d** (450 mg, 2.10 mmol) in water (8 mL), acetone (8 mL) and *p*-TsOH (22 mg, 0.11 mmol) was heated to reflux and maintained for 45 minutes. The reaction mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (40 mL). The organic phase was dried over Na_2SO_4 (10 g) and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography on silica (4% EtOAc in hexanes) to give compound **2-(2-methylallyl)benzaldehyde, 1d** (322 mg, 1.85 mmol, 90%) as a colorless oil R_f = 0.54 (1:9 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.19 (app d, *J* = 7.5 Hz, 1H), 7.08 (app s, 1H), 4.84−4.83 (m, 1H), 4.48−4.44 (m, 1H), 3.70 (s, 2H), 2.40 (s, 3H), 1.78 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 175 $(M+H)^+$, t_R = 9.9 min.

4-fluoro-2-(2-methylallyl)benzaldehyde 1e:



In analogy to the procedure reported by Glorius et al.[5] 2-amino-2-methyl-1-propanol (1.6 mL, 16.6 mmol) and 4-fluorobenzaldehyde, **5e** (2.04 g, 16.4 mmol) were dissolved in CH_2Cl_2 (110 mL) and stirred over 4 Å Molecular Sieves (MS) (24 g) for 14 h. NBS (2.93 g, 16.6 mmol) was added and the solution was stirred for an additional 30 min. The mixture was filtered through Celite and washed with saturated aqueous $NaHCO_3$ (100 mL) and H_2O (50 mL). The organic layer was dried over anhydrous Na_2SO_4 (30 g) and concentrated in vacuo. The resulting residue was purified by flash column chromatography (gradient from 10 to 15% EtOAc in hexanes) to give 4,4-dimethyl-2-(4-fluoro)phenyl-2-oxazoline, **6e** (2.79 g, 14.5 mmol, 85%) R_f = 0.50 (1:4 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.91 (m, 2H), 7.12−7.04 (m, 2H), 4.11 (s, 2H), 1.38 (s, 6H); LRMS (ESI) *m*/*z* 193 $(M+H)^+$.

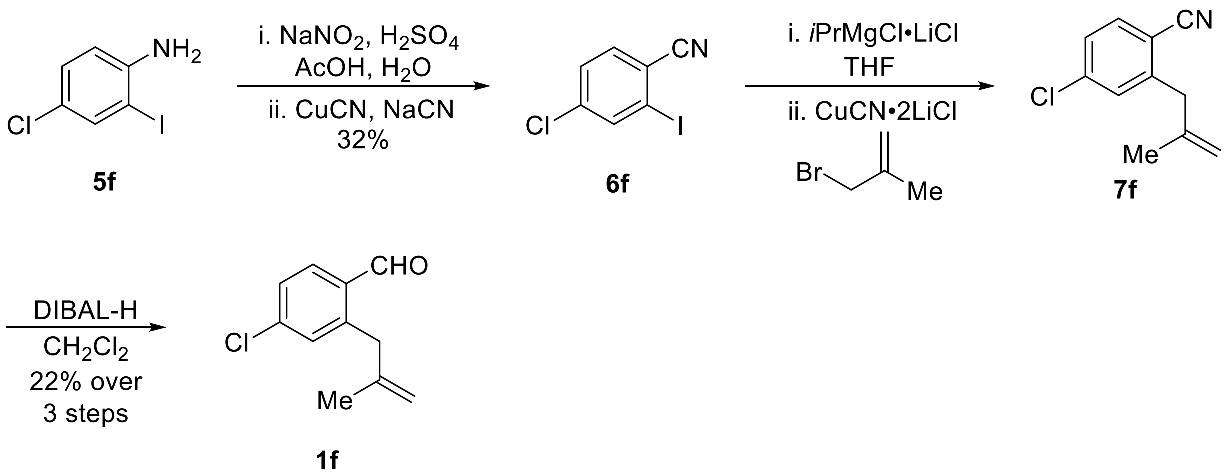
In analogy to the reported procedure[6] *n*-BuLi (2.5 M in hexanes, 3.8 mL, 9.5 mmol) was added dropwise to a solution of 4,4-dimethyl-2-(4-fluoro)phenyl-2-oxazoline **6e** (1.3 g, 6.74 mmol, 1.0 equiv) in THF (19 mL) maintained at 0 °C. The mixture was stirred at 0°C for 3.5 hours and was transferred to a suspension of CuBr (960 mg, 6.1 mmol, 1.1

equiv) in THF (7 mL) *via* cannula. The resulting green mixture was stirred at 0 °C for 1.5 hours and isobutenyl chloride (0.76 mL, 6.1 mmol, 0.9 equiv) was added. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) solution. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 (15 g) and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica (gradient from 5 to 10% EtOAc in hexanes) to give 4,4-dimethyl-2-(4-fluoro-(2-(2-methylallyl))phenyl)-4,5-oxazoline, **7e** (660 g, 2.66 mmol, 38%) as a dark green oil R_f = 0.75 (1:4 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.3, 5.9 Hz, 1H), 6.98−6.90 (m, 2H), 4.81 (app s, 1H), 4.55 (app s, 1H), 4.04 (s, 2H), 3.73 (s, 2H), 1.69 (s, 3H), 1.36 (s, 6H); LRMS (ESI) *m/z* 248 $(M+H)^+$.

To a solution of 4,4-dimethyl-2-(4-fluoro-(2-(2-methylallyl))phenyl)-4,5-oxazoline, **7e** (320 mg, 1.29 mmol) in 2.6 mL of CH_2Cl_2 was added methyl trifluoromethanesulfonate (0.31 mL, 2.7 mmol) in a nitrogen filled glove box and the solution was stirred for 2 hours at ambient temperature inside the nitrogen filled glove box . The solution was taken out of glove box and cooled to 0 °C. A solution of $NaBH_4$ (1.56 g, 4.12 mmol) in THF/MeOH (4:1, 37.5 mL) was added to the mixture. After stirring for 1 h at 0 °C, saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated in vacuo. The resulting residue was dissolved in a solution of THF/H_2O (4:1, 5 mL) and treated with oxalic acid dihydrate (1.05 g, 8.3 mmol). The solution was stirred at room temperature for 18 hours. Diethyl ether (30 mL) was added and the mixture was washed with saturated aqueous $NaHCO_3$ (10 mL) solution, brine (10 mL), dried over anhydrous Na_2SO_4 (15 g) and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica (gradient 5 to 10% EtOAc in hexanes) to give **4-fluoro-2-(2-methylallyl)benzaldehyde**, **1e** (76 mg, 0.43 mmol, 32%) R_f = 0.85 (1:4 EtOAc:Hex); ^{1}H NMR (300MHz, $CDCl_3$) δ 10.17 (s, 1 H), 7.90 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.07 (dt, *J* = 8.2, 2.5 Hz, 1H), 6.99 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.89−4.88 (m, 1H), 4.50

(app s, 1H), 3.73 (s, 2H), 1.78 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 178 $(M+H)^+$, t_R = 13.4 min.

4-chloro-2-(2-methylallyl)benzaldehyde 1f:

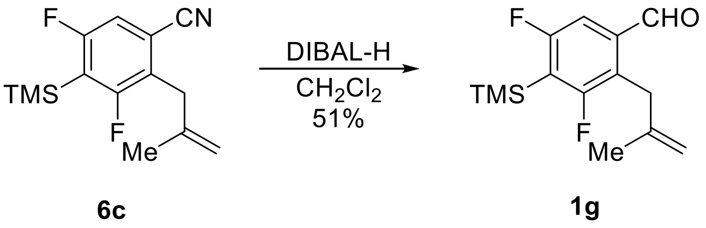


A solution of $NaNO_2$ (330 mg, 5 mmol) in water (1.2 mL) was added dropwise to a solution of 4-chloro-2-iodoaniline, **5f** (1.02 g, 4.1 mmol) in concentrated H_2SO_4 (1 mL), AcOH (4 mL) and water (2 mL) that was maintained at 0 °C. The mixture was stirred for 30 min at 0 °C. The resulting cold diazonium salt mixture was added to the solution of CuCN (390 mg, 4.5 mmol), NaCN (420 mg, 8.3 mmol) and $NaHCO_3$ (2.0 g) in water (4.3 mL) maintained at 0 °C in a very large round bottomed flask (1 L) to prevent the foam formed during the reaction from spilling. The reaction mixture was allowed to warm to room temperature and stirred for one hour. The brown precipitate that was formed was dissolved in dichloromethane (30 mL) and layers were separated. The aqueous layer was extracted again with dichloromethane (20 mL). The combined organic extracts were washed with water (20 mL), saturated $NaHCO_3$ (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4 (20 g) and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography on silica (10% EtOAc in hexanes) to give 4-chloro-2-iodobenzonitrile, **6f** (340 mg, 1.29 mmol, 32%) R_f = 0.75 (1:4 EtOAc:Hex); ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H); LRMS (GC-MS, CI, MeOH) *m/z* 264 $(M+H)^+$, t_R = 15.5 min.

4-chloro-2-iodobenzonitrile, **6f** (316 mg, 1.20 mmol) was dissolved in THF (0.3 mL) and cooled to −10 °C. *i*PrMgCl•LiCl[3] (2 mL of a 0.77 M solution in THF, 1.45 mmol) was added and the reaction mixture was stirred for 30 min at −10 °C. Then CuCN•2LiCl (0.1 mL of 1M solution in THF, 0.2 mmol) and 3-bromo-2-methyl-1-propene (0.18 mL, 1.8 mmol) were added to the reaction at −10 °C. The resulting mixture was slowly allowed to warm to room temperature and stirred for 14 hours. The reaction was quenched with saturated aqueous NH_4Cl solution (15 mL) and extracted using diethyl ether (2 × 30 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated. Attempted purification of the crude product provided mixture of 4-chloro-2-iodobenzonitrile (**7f**) and *p*-chlorobenzonitrile (~15%) which was taken to the next step.

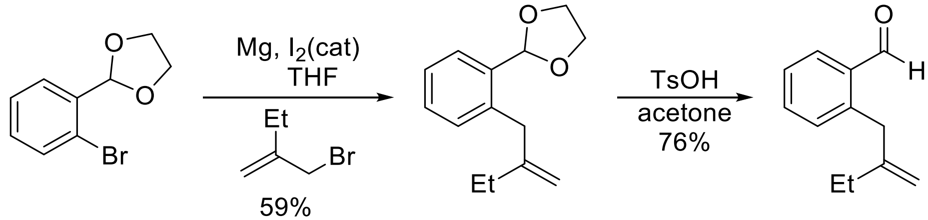
DIBAL-H (1.0 mL of 1 M solution in toluene, 1.5 mmol) was added to a solution of 4-chloro-2-(2-methylallyl)benzonitrile, **7f** (134 mg with ~15 mol % *p*-chlorobenzonitrile) in methylene chloride (2.8 mL) maintained at 0 °C under nitrogen. The reaction was slowly allowed to warm to room temperature and stirred for 14 hours. The reaction mixture was diluted with diethyl ether (5 mL) and cooled to 0 °C. HCl (4 mL of 3N solution) was slowly added at 0 °C and the mixture was refluxed for 30 minutes. Diethyl ether (30 mL) was added to the reaction mixture and layers were separated. The aqueous layer was extracted with diethyl ether (30 mL) and the combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated *in vacuo*. The crude material was purified by flash column chromatography (8% Et_2O in hexanes) on silica to give **4-chloro-2-(2-methylallyl)benzaldehyde, 1f** (50 mg, 0.26 mmol 22%) R_f = 0.80 (1:4 EtOAc:Hex); ^1H NMR (500 MHz , $CDCl_3$) δ 10.19 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 4.89−4.88 (m, 1H), 4.48-4.47 (m, 1H), 3.70 (s, 2H), 1.79 (d, *J* = 0.5 Hz, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 195 $(M + H)^+$, t_R = 14.8 min.

3,5-difluoro-2-(2-methylallyl)-4-(trimethylsilyl)benzaldehyde 1g:



A flame-dried flask under N_2 was charged with 3,5-difluoro-2-(2-methylallyl)-4-(trimethylsilyl)benzonitrile **6c** (1.028 g, 3.87 mmol) and dichloromethane (22 mL). The solution was cooled to 0 °C and a solution of DIBAL-H in toluene (1M, 4.65 mL, 4.65 mmol) was added dropwise. The reaction was allowed to warm slowly to room temperature and was stirred for 15 h. The reaction mixture was then diluted with Et_2O (20 mL) and HCl (3N, 20 mL) was added. The reaction was headed to reflux for 1 h at which time it was cooled back down to room temperature and was diluted with more Et_2O (20 mL). The organics were separated and washed sequentially with H_2O (60 mL), saturated aqueous $NaHCO_3$ (60 mL), brine (60 mL) followed by drying over Na_2SO_4, filtration and concentration. The crude product was purified by column chromatography (2% EtOAc in Hexanes) to yield **3,5-difluoro-2-(2-methylallyl)-4-(trimethylsilyl)benzaldehyde 1g** (0.5325 g, 1.98 mmol, 51% yield) as a yellow oil (Note: The product contains a minor, inseparable impurity observable in the ^1H NMR that we believe is the di-TMS protected product. As this impurity will also undergo the desired key reaction, we have deemed the purity level appropriate to carry on to the key step). R_f = 0.6 (1:9 EtOAc:Hex); ^1H NMR (500 MHz, $CDCl_3$) δ 10.12 (d, J = 2.5 Hz, 1H), 7.30 (dd, J = 8.5, 1.0 Hz, 1H), 4.80 – 4.79 (m, 1H), 4.35 (app s, 1H), 3.64 (s, 2H), 1.80 (s, 3H), 0.37 (t, J = 1.5 Hz, 9H); LRMS (GC-MS, CI, MeOH) *m/z* 269 $(M+H)^+$, t_R = 15.4 min.

2-(2-methylenebutyl)benzaldehyde 1h:

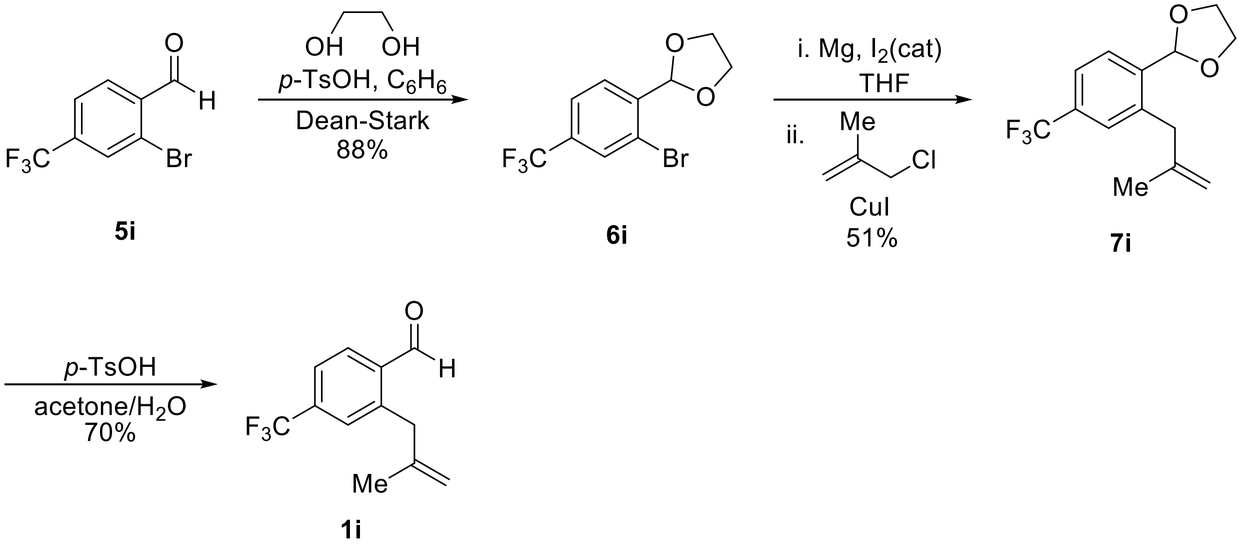


5h **6h** **1h**

A round-bottom flask equipped with a reflux condenser and magnetic stir bar under nitrogen was charged with Mg (72 mg, 3.0 mmol) and a small crystal of I_2. The flask was flame-dried under high vacuum. Solution of 2-(2-bromophenyl)-1,3-dioxolane, **5h** (570 mg, 2.5 mmol)[7] and THF (2.5 mL) was slowly added to Mg at room temperature and the mixture was maintained at reflux for two hours. The resulting solution was allowed to cool to room temperature then added dropwise to a stirring suspension of 2-(bromomethyl) but-1-ene[8](420 mg, 2.82 mmol) and CuI (50 mg, 0.26 mmol) in THF (3 mL) at 0 °C. The reaction mixture was stirred for 2 hours at 0 °C and then allowed to warm to room temperature and stirred overnight. Diethyl ether (30 mL) was added, and the mixture was washed with a saturated aqueous NH_4Cl solution (10 mL). The organic phase was separated, washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica (4% EtOAc in hexanes) to give 2-(2-(2-methylenebutyl) phenyl)-1,3-dioxolane, **6h** (320 mg, 1.47 mmol, 59%) as colorless oil. R_f = 0.75 (1:9 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.30−7.25 (m, 2H), 7.17 (dd, *J* = 7.2, 1.9 Hz, 1H), 5.96 (s, 1H), 4.85−4.84 (m, 1H), 4.52−4.51 (m, 1H), 4.16−4.00 (m, 4H), 3.50 (s, 2H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H) LRMS (GC-MS, CI, MeOH) *m*/*z* 219 $(M+H)^+$, t_R = 16.5 min.

A solution of 2-(2-(2-methylenebutyl)phenyl)-1,3-dioxolane, **6h** (320 mg, 1.47 mmol) in water (5 mL), acetone (5 mL) and *p*-TsOH (10 mg, 0.05 mmol) was heated to reflux for 50 min. The reaction mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (30 mL). The organic phase was separated, washed with brine (10 mL), dried over Na_2SO_4 (10 g) and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (4% EtOAc in hexanes) on silica to give **2-(2-methylenebutyl)benzaldehyde, 1h** (193 mg, 1.11 mmol, 76%) as a colorless oil R$_f$ = 0.80 (1:9 EtOAc:Hex); ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.24 (s, 1H), 7.88 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.39 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.30−7.28 (m, 1H), 4.86−4.85 (m, 1H), 4.42−4.41 (m, 1H), 3.75 (s, 2H), 2.10 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 175 (M+H)$^+$, t$_R$ = 13.5 min.

2-(2-methylallyl)-4-(trifluoromethyl)benzaldehyde 1i:



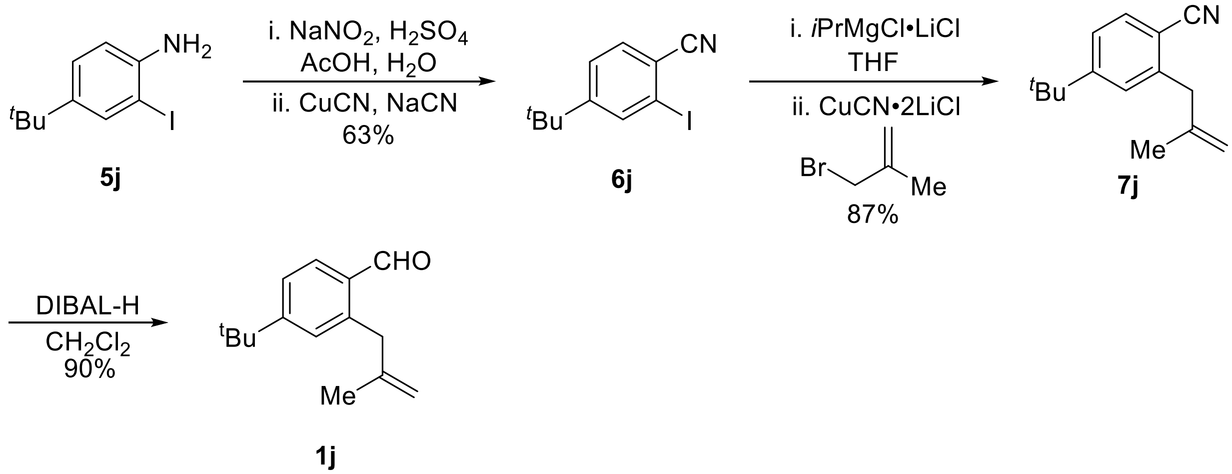
A solution of 2-bromo-4-(trifluoromethyl)benzaldehyde, **5i** (498 mg, 1.97 mmol), ethylene glycol (0.23 mL, 4.0 mmol), *p*-TsOH (8 mg, 0.04 mmol) in benzene (1.3 mL), was heated to reflux with a Dean-Stark trap for 14 hours. The reaction was neutralized with saturated aqueous NaHCO$_3$ solution and extracted with diethyl ether (2 × 30 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$ (10 g) and concentrated. The resulting crude material was purified by flash column chromatography on silica (10% EtOAc in hexanes) to give 2-(2-bromo-4-(trifluoromethyl)phenyl)-1,3-dioxolane, **6i** (496 mg, 1.67 mmol, 88%) as colorless oil R$_f$ =

0.70 (1:4 EtOAc:Hex); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.84 (d, *J* = 0.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.60 (ddd, *J* = 8.1, 1.2, 0.7 Hz, 1H), 6.10 (s, 1 H), 4.17−4.09 (m, 4H); LRMS (GC-MS, CI, MeOH) *m*/*z* 297 $(M + H)^+$ and 299 $(M+H)^+$, t_R = 10.5 min.

A round-bottom flask equipped with a reflux condenser and magnetic stir bar under nitrogen was charged with Mg (40 mg, 1.7 mmol) and a small crystal of I_2. The flask was flame-dried under high vacuum. A solution of THF (2 mL) and 2-(2-bromo-4-(trifluoromethyl)phenyl)-1,3-dioxolane **6i** (390 mg, 1.30 mmol) was slowly added to Mg at room temperature and the mixture was maintained at reflux for two hours. The resulting solution was allowed to cool to room temperature then added dropwise to a suspension of isobutenyl chloride (0.2 mL, 2.1 mmol) and CuI (27 mg, 0.14 mmol) in THF (3 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and then allowed to warm to room temperature overnight. Diethyl ether (30 mL) was added, and the mixture was washed with a saturated aqueous NH_4Cl solution (10 mL). The organic phase was separated, washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated in vacuo. The crude material was purified by flash column chromatography on silica (4% EtOAc in hexanes) to give (2-(2-methylallyl)-4-(trifluoromethyl)phenyl)-1,3-dioxolane, **7i** (140 mg, 0.51 mmol, 40%) as colorless oil. R_f = 0.70 (1:9 EtOAc:Hex); ^{1}H NMR (300MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.51 (app d, *J* = 8.1 Hz, 1H), 7.44 (app s, 1H), 6.00 (s, 1H), 4.90−4.86 (m, 1H), 4.56−4.52 (m, 1H), 4.15−4.03 (m, 4H), 3.53 (s, 2H), 1.75 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 273 $(M+H)^+$, t_R = 9.2 min.

A solution of (2-(2-methylallyl)-4-(trifluoromethyl)phenyl)-1,3-dioxolane, **7i** (140 mg, 0.51 mmol), *p*-TsOH (6 mg, 0.03 mmol), water (2.5 mL) and acetone (2.5 mL) was heated to refluxed for 50 min. The reaction mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 (25 mL). The organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated *in vacuo*. The crude material was purified by flash column chromatograph on silica (4% EtOAc in hexanes) to give **2-(2-methylallyl)-4-(trifluoromethyl)benzaldehyde, 1i** (82 mg, 0.36 mmol, 70%) as a colorless oil R_f = 0.80 (1:9 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.65 (app d, *J* = 8.0 Hz, 1H), 7.54 (app s, 1H), 4.91−4.90 (m, 1H), 4.44 (app s, 1H), 3.77 (s, 2H), 1.81 (s, 3H); LRMS (GC-MS, CI, MeOH) *m/z* 229 $(M+H)^+$, t_R = 9.5 min.

4-(tert-butyl)-2-(2-methylallyl)benzaldehyde 1j:



4-(*tert*-butyl)-2-iodoaniline **5j** was prepared using previously reported procedure.[9] To a solution of 4-(*tert*-butyl)-2-iodoaniline **5j** (2.391g, 8.7 mmol), ice (10g), acetic acid (3.98 mL, 69.6 mmol) and H_2SO_4 (0.97 mL, 17.4 mmol) at 0 °C under N_2 was added a solution of $NaNO_2$ (0.659 g, 9.6 mmol) in H_2O (4 mL). This solution was stirred for 45 minutes at 0 °C. The resulting diazonium salt was then added at 0 °C to a stirred solution of CuCN (0.822 g, 9.14 mmol), NaCN (0.895 g, 18.3 mmol) and $NaHCO_3$ (21.93 g, 261 mmol) in H_2O (15 mL) in a 500 mL Erlenmeyer flask. Slow addition was necessary to control gas evolution and foaming. Deionized water (~50 mL total) was also added to control foaming and ensure the solid remained suspended in solution and not stuck to the side of the flask. After the addition was finished, the flask was allowed to warm to room temperature and was stirred for 1 hr.

Dichloromethane (50 mL) was added to dissolve the resulting brown precipitate and the layers were separated. The aqueous layer was washed again with dichloromethane (50 mL). The organic layers were combined, washed with brine (100 mL), dried over

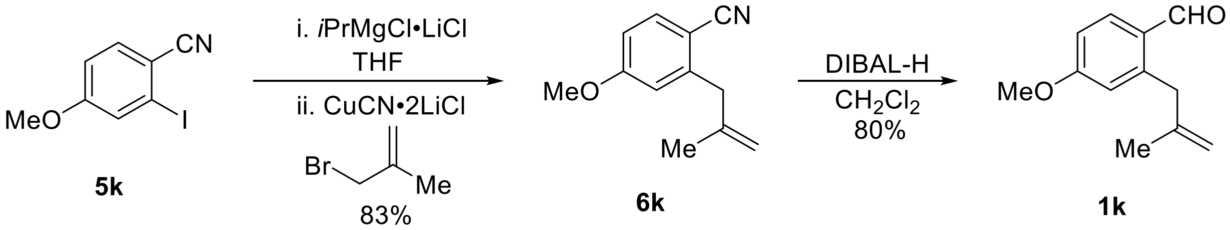
Na_2SO_4 (20 g), filtered and concentrated *in vacuo*. The product was purified by column chromatography (5% EtOAc in Hexanes) to yield 4-(*tert*-butyl)-2-iodobenzonitrile **6j** (1.5644 g, 5.49 mmol, 63% yield) as a yellow oil. R_f = 0.40 (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.7 Hz, 1H), 1.32 (s, 9H);); LRMS (GC-MS, CI, MeOH) *m*/*z* 286 $(M+H)^+$, t_R = 16.3 min.

A flame-dried flask containing a stir bar under N_2 was charged with 4-(*tert*-butyl)-2-iodobenzonitrile **6j** (1.3504 g, 4.47 mmol) and dry THF (2 mL). The solution was cooled to –10 °C. A solution of *i*PrMgCl•LiCl in THF (2.52 mL, 0.76M, 2.3 mmol) was added dropwise and the reaction was allowed to stir for 2 h at –10 °C. CuCN•2LiCl (0.34 mL, 1.12M in THF, 0.038 mmol) and 3-bromo-2-methyl-1-propene (0.29 mL, 2.9 mmol) were added and stirred at –10 °C for 1 h then the reaction was allowed to warm to room temperature and stirred for 15 hours. The reaction was quenched with a saturated aqueous solution of NH_4Cl (20 mL) and extracted with diethyl ether (2 × 20 mL). The organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4 (10 g), filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica (2% EtOAc in hexanes) to give 4-(*tert*-butyl)-2-(2-methylallyl)benzonitrile **7j** (0.874 g, 4.1 mmol, 87%) as a yellow oil. R_f = 0.46 (9:1 Hex:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.32 (m, 2H), 4.87 (app s, 1H), 4.69 (app s, 1H), 3.53 (s, 2H), 1.74 (s, 3H), 1.32 (s, 9H); LRMS (GC-MS, CI, MeOH) *m*/*z* 214 $(M+H)^+$, t_R = 15.6 min.

A flame-dried flask under N_2 was charged with 4-(*tert*-butyl)-2-(2-methylallyl)benzonitrile, **7j** (0.86 g, 4.03 mmol) and dichloromethane (23 mL). The solution was cooled to 0 °C and a solution of DIBAL-H in toluene (1M, 4.84 mL, 4.84 mmol) was added dropwise. The reaction was allowed to warm to room temperature and was stirred for 15 h. The reaction mixture was then diluted with Et_2O (20 mL) and HCl (3N, 20 mL) was added. The reaction was headed at reflux for 1 hour and was allowed to cool to room temperature. The mixture was diluted with more Et_2O (10 mL). The organic portion was separated and washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL) and were dried over Na_2SO_4 (10 g), filtered and concentrated. The product was purified by column chromatography (2% EtOAc in

Hexanes) to yield 4-(*tert*-butyl)-2-(2-methylallyl)benzaldehyde **1j** (0.7878 g, 3.64 mmol, 90% yield) as a yellow oil. R_f = 0.45 (1:9 EtOAc:Hex); ^{1}H NMR (500 MHz , $CDCl_3$) δ 10.19 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.28 (d, *J* = 1.9 Hz, 1H), 4.83 (app s, 1H), 4.46 (app s, 1H), 3.73 (s, 2H), 1.79 (s, 3H), 1.34 (s, 9H); LRMS (GC-MS, CI, MeOH) *m*/*z* 217 $(M+H)^+$, t_R = 15.7 min.

4-methoxy-2-(2-methylallyl)benzaldehyde 1k:

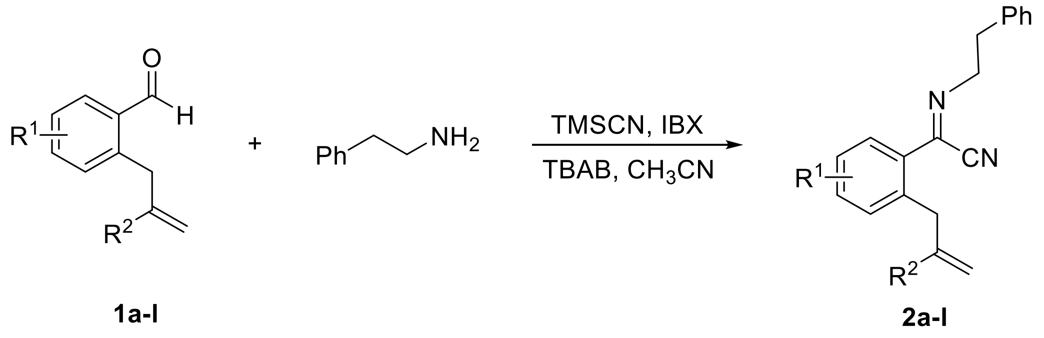


2-iodo-4-methoxybenzonitrile, **5k** (prepared using the procedure reported by Larock et al.[10]) (501 mg, 1.93 mmol) was dissolved in dry THF (0.5 mL) and cooled to −10 °C. *i*PrMgCl•LiCl (3 mL of 0.77 M solution in THF, 2.3 mmol) was added and the reaction mixture was stirred for one hour at −10 °C. CuCN•2LiCl (0.2 mL of 1M solution in THF, 0.2 mmol) and 3-bromo-2-methyl-1-propene (0.3 mL, 2.9 mmol) were added at −10 °C and the reaction mixture was allowed to warm to room temperature and stirred for 14 hours. The reaction was quenched with saturated NH_4Cl solution (15 mL) and extracted with diethyl ether (2 × 30 mL). The organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 (15 g) and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography on silica (6% EtOAc in hexanes) to give 4-methoxy-2-(2-methylallyl)benzonitrile, **6k** (300 mg, 1.6 mmol, 83%) as colorless oil. R_f = 0.75 (1:4 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 6.2, 3.5 Hz, 1H), 6.84−6.80 (m, 2H), 4.92−4.87 (m, 1H), 4.75−4.69 (m, 1H), 3.85 (s, 3H), 3.51 (s, 2H), 1.74 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 188 $(M+H)^+$, t_R = 14.1 min.

DIBAL-H (2.4 mL of 1 M solution in toluene, 2.4 mmol) was added to the solution of 4-methoxy-2-(2-methylallyl)benzonitrile, **6k** (300 mg, 1.6 mmol) in methylene chloride (6.5

mL) maintained at 0 °C under nitrogen. The reaction was allowed to warm to room temperature and stirred for 14 hours. The reaction mixture was diluted with diethyl ether (11 mL) and cooled to 0 °C followed by the addition of HCl (8.5 mL of 3N solution). The reaction mixture was heated to reflux for 30 minutes. The reaction was allowed to cool to room temperature and diethyl ether (30 mL) was added to the reaction mixture and layers were separated. The aqueous layer was extracted again with diethyl ether (30 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (10 g) and concentrated. The crude material was purified by flash column chromatography on silica (5% EtOAc in hexanes) to give **4-methoxy-2-(2-methylallyl)benzaldehyde, 1k** (240 mg, 1.26 mmol 80%) R_f = 0.77 (1:4 EtOAc:Hex); ^1H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 4.85−4.84 (m, 1H), 4.50 (app s, 1H), 3.88 (s, 3H), 3.71 (s, 2H), 1.78 (s, 3H); LRMS (GC-MS, CI, MeOH) *m*/*z* 191 $(M+H)^+$, t_R = 14.3 min.

Synthesis of α-iminonitriles:



General Procedure

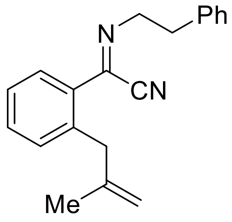
α-Iminonitriles were synthesized by slight modification of procedure reported by Zhu[11] via two procedures.

Procedure A: To the stirred solution of aldehyde (0.5 mmol), phenethylamine (0.5 mmol, 1.0 eq) in acetonitrile (0.5 mL, [RCHO] = 1.0 M) at room temperature, TMSCN

(0.55 mmol, 1.1 eq) was added and stirred for 15 minutes. Then finely powdered IBX[12] (0.75 mmol, 1.5 eq) and tetrabutylammonium bromide (0.33 mmol, 1.1 eq) were added. The heterogeneous reaction was stirred at room temperature for two hours. After ensuring complete consumption of starting material by TLC (on alumina plates) the mixture was filtered through Celite and concentrated. The crude product was purified by flash chromatography on neutral alumina (2% EtOAc in hexanes) to afford pure α-iminonitrile. The product appeared to decompose on column and was flushed as quickly as possible.

Procedure B: The aldehyde (0.5 mmol) and phenethylamine (0.5 mmol, 1 eq) were combined in a flask and stirred neat for 1 h at room temperature. At this point, a small (~1 mg) sample was removed to confirm complete conversion to the imine by ^{1}H NMR. The reaction mixture was then diluted with acetonitrile (0.5 mL, [RCHO] = 1.0 M) and TMSCN (0.55 mmol, 1.1 eq) was added dropwise via microsyringe. The reaction was then allowed to stir under nitrogen for 25 min. Finely powdered IBX[12] (0.75 mmol, 1.5 eq) was added portionwise followed by tetrabutylammonium bromide (0.33 mmol, 1.1 eq) also added portionwise. The heterogeneous reaction was stirred at room temperature for 1-2 hours. After ensuring complete consumption of starting material by TLC (on alumina plates), the mixture was filtered through Celite and concentrated. The crude product was purified by flash chromatography on neutral alumina (column diameter: 2 cm, 5 cm alumina height, eluent gradient from 100% hexanes to 2% EtOAc in hexanes) to afford pure α-iminonitrile. The product appeared to decompose on the column and was eluted as quickly as possible.

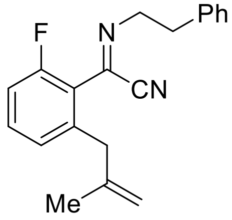
α-iminonitrile 2a:



2a

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde **1a**[13] (302 mg, 1.88 mmol), phenethylamine (229 mg, 1.90 mmol), acetonitrile (2.0 mL), TMSCN (260 µl 2.09 mmol) IBX (800 mg, 2.85 mmol) tetrabutylammonium bromide (673 mg, 2.09 mmol). **iminonitrile 2a** was isolated as a yellow oil (338 mg, 1.17 mmol, 62%) R_f = 0.85 (1:9 EtOAc:Hex on alumina TLC). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.6, 1.3 Hz, 1H), 7.43−7.23 (m, 8H), 4.78 (app s, 1H), 4.43 (app s, 1H), 4.22 (t, J = 7.2 Hz, 2H), 3.58 (s, 2H), 3.11 (t, J = 7.2 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 142.5, 138.9, 138.7, 133.2, 131.5, 130.8, 130.0, 129.0, 128.5, 126.7, 126.5, 112.2, 110.1, 60.4, 41.1, 36.5, 22.6; IR (thin film) 3064, 3027, 2928, 2213, 1604, 1446 cm^{-1}; HRMS (CI, NH_3) calcd for $[C_{20}H_{20}N_2+H]^+$, m/z 289.1700, found 289.1703.

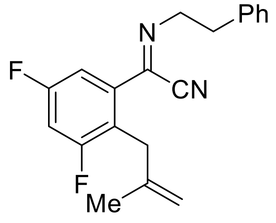
α-iminonitrile 2b:



2b

Prepared using general **procedure B** for α-iminonitrile synthesis using aldehyde **1b** (80 mg, 0.45 mmol), phenethylamine (55 mg, 0.45 mmol), acetonitrile (0.5 mL), TMSCN (85 µl, 0.68 mmol,) IBX (190 mg, 0.68 mmol) tetrabutylammonium bromide (160 mg, 0.49 mmol). Iminonitrile **2b** was isolated as a yellow oil (80 mg, 0.26 mmol, 55%) R_f = 0.75 (1:9 EtOAc:Hex on alumina TLC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.22 (m, 6H), 7.06−7.00 (m, 2H), 4.83 (app s, 1H), 4.48 (app s, 1H), 4.24 (t, J = 7.2 Hz, 2H), 3.31 (s, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (126MHz, CDCl$_3$) δ 160.5 (d, *J* = 250 Hz), 143.2, 140.8, 138.4, 137.2, 131.7 (d, *J* = 9 Hz), 128.9, 128.6, 126.6, 126.3 (d, *J* = 3 Hz), 122.6, (d, *J* = 14 Hz), 114.0, (d, *J* = 21 Hz) 113.2, 109.7, 60.4, 40.4, 36.3, 22.3; ^{19}F NMR (471 MHz, CDCl$_3$) δ -115.5; IR (thin film) 3079, 3029, 2927, 2215, 1623, 1460 cm^{-1}; HRMS (ESI) calcd for [C$_{20}$H$_{19}$FN$_2$+Na]$^+$, *m/z* 329.1424, found 329.1425.

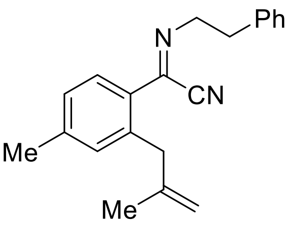
α-iminonitrile 2c:



2c

Prepared using general **procedure B** for α-iminonitrile synthesis using aldehyde **1c** 100 mg, 0.51 mmol), phenethylamine (0.064 mL, 0.51 mmol), acetonitrile (0.51 mL), TMSCN (0.07 mL, 0.56 mmol), IBX (0.214 g, 0.76 mmol), and tetrabutylammonium bromide (0.181 g, 0.56 mmol). Iminonitrile **2c** was isolated (0.043 g, 0.133 mmol, 26% yield) as a yellow oil. R$_f$ = 0.6 (1:9 EtOAc:Hex, alumina TLC); ^{1}H NMR (500 MHz , CDCl$_3$) δ 7.34−7.29 (m, 2H), 7.27−7.21 (m, 3H), 7.18 (ddd, *J* = 8.8, 2.4, 1.6 Hz, 1H), 6.97−6.91 (m, 1H), 4.73−4.69 (m, 1H), 4.26 (app s, 1H), 4.23 (t, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.68 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.5 (dd, *J* = 82.0, 12.5 Hz), 160.5 (dd, *J* = 82.4, 12.5 Hz), 143.2, 140.7 (t, *J* = 3.5 Hz), 138.6, 136.0 (dd, *J* = 8.6, 6.2 Hz), 129.2, 128.8, 126.9, 122.8 (dd, *J* = 17.9, 4.2 Hz), 113.1 (dd, *J* = 23.2, 3.6 Hz), 111.3, 109.6, 106.5 (dd, *J* = 28.0, 24.7 Hz), 60.7, 36.6, 32.1 (d, *J* = 4.4 Hz), 23.0; ^{19}F NMR (471 MHz, CDCl$_3$) δ -110.5 (app t, *J* = 8.6 Hz), -111.2 (app q, *J* = 8.3 Hz); IR (thin film) 3085, 3029, 2928, 2216, 1616,1331 cm^{-1}; HRMS (ESI) calcd for [C$_{20}$H$_{18}$F$_2$N$_2$+Na]$^+$, *m/z* 137.1330, found 137.1320.

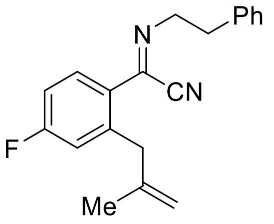
α-iminonitrile 2d:



2d

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde **1d** (101 mg, 0.58 mmol), phenethylamine (70 mg, 0.58 mmol), acetonitrile (0.6 mL), TMSCN (80 µl, 0.64 mmol,) IBX (244 mg, 0.87 mmol) and tetrabutylammonium bromide (206 mg, 0.64 mmol), **iminonitrile 2d** was isolated as a yellow oil (66 mg, 0.22 mmol, 38%) R_f = 0.15 (1:9 EtOAc:Hex on alumina TLC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.34−7.23 (m, overlapped with $CHCl_3$, 5H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.07 (app s, 1H), 4.76 (app s, 1H), 4.41 (app s, 1H), 4.19 (t, *J* = 7.3 Hz, 2H), 3.57 (s, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 142.4, 141.2, 138.9, 138.8, 132.4, 130.4, 130.2, 128.9, 128.4, 127.4, 126.4, 111.9, 110.1, 60.3, 41.1, 36.6, 22.7, 21.3; IR (thin film) 3064, 3027, 2923, 2213, 1649, 1453 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{22}N_2Na]^+$, *m/z* 325.1675, found 325.1670.

α-iminonitrile 2e:

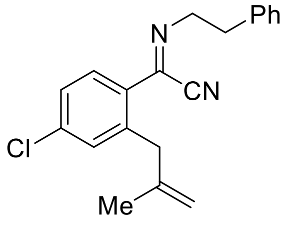


2e

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde **1e** (76 mg, 0.43 mmol), phenethylamine (52 mg, 0.43 mmol), acetonitrile (0.5 mL), TMSCN (60 µl, 0.47 mmol), IBX (181 mg, 0.65 mmol) and tetrabutylammonium bromide (152 mg, 0.47 mmol), **iminonitrile 2e** was isolated as a yellow oil (58 mg, 0.19 mmol, 44%) R_f =

0.82 (1:9 EtOAc:Hex on alumina TLC); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.61 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.32−7.30 (m, 2H), 7.26−7.22 (m, 3H), 7.03−6.98 (m, 2H), 4.82 (app s, 1H), 4.48 (app s, 1H), 4.21 (t, *J* = 7.1 Hz, 2H), 3.56 (s, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 163.8 (d, *J* = 250 Hz), 143.6, 142.3 (d, *J* = 7 Hz), 141.5, 138.6, 132.3 (d, *J* = 10 Hz), 128.9, 128.5, 126.5, 118.2 (d, *J* = 21 Hz), 113.7 (d, *J* = 22 Hz), 112.9, 109.9, 60.4, 41.1, 36.5, 22.5; ^{19}F NMR (282 MHz, CDCl$_3$) δ -105.0; IR IR (thin film) 3064, 3028, 2928, 2215, 1608, 1495, 1100 cm^{-1}; HRMS (CI, NH$_3$) calcd for [C$_{20}$H$_{19}$FN$_2$+H]$^+$, *m/z* 307.1606, found 307.1601.

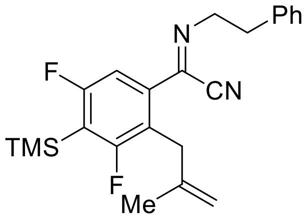
α-iminonitrile 2f:



2f

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde **1f** (49 mg, 0.26 mmol), phenethylamine (32 mg, 0.26 mmol), acetonitrile (0.3 mL), TMSCN (36 μl, 0.29 mmol,) IBX (109 mg, 0.39 mmol), tetrabutylammonium bromide (92 mg, 0.29 mmol), iminonitrile **2f** was isolated as a yellow oil (44 mg, 0.14 mmol, 54%) R$_f$ = 0.85 (1:10 EtOAc:Hex on alumina TLC).^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, *J* = 8.3 Hz, 1H), 7.33−7.30 (m, 3H), 7.27−7.24 (m, overlapped with CHCl$_3$, 4H), 4.82 (app s, 1H), 4.46 (app s, 1H), 4.21 (t, *J* = 7.2 Hz, 2H), 3.55 (s, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (126 MHz, CD$_2$Cl$_2$) δ 144.6, 141.9, 141.8, 139.5, 137.3, 132.4, 132.0, 131.9, 129.5, 129.0, 127.3, 127.0, 113.0, 110.4, 61.1, 41.4, 37.0, 22.9; IR (thin film) 3080, 3028, 2930, 2214, 1604, 1495, 1098 cm^{-1}; HRMS (ESI) calcd for [C$_{20}$H$_{19}$ClN$_2$Na]$^+$, *m/z* 345.1129, found 345.1123.

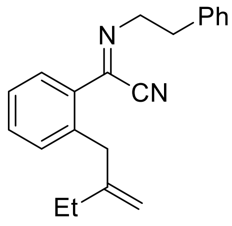
α-iminonitrile 2g:



2g

Prepared using general **procedure B** for α-iminonitrile synthesis using aldehyde **1g** (0.2213 g, 0.82 mmol), phenethylamine (0.1 mL, 0.82 mmol), acetonitrile (0.82 mL), TMSCN (0.07 mL, 0.56 mmol), IBX (0.214 g, 0.76 mmol), and tetrabutylammonium bromide (0.181 g, 0.56 mmol). Iminonitrile **2g** (0.1254 g, 0.316 mmol, 38%) was isolated as a yellow oil. R_f = 0.6 (1:9 EtOAc:Hex, alumina TLC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.28 (m, 2H), 7.25−7.21 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 4.70 (s, 1H), 4.26 (s, 1H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.55 (s, 2H), 3.09 (t, *J* = 7.1 Hz, 2H), 1.68 (s, 3H), 0.38 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (dd, *J* = 49.9, 16.6 Hz), 164.4 (dd, *J* = 50.0, 16.7 Hz), 143.5, 140.8 (t, *J* = 3.8 Hz), 138.7, 136.8 (dd, *J* = 9.5, 6.8 Hz), 129.2, 128.8, 126.8, 121.9 (dd, *J* = 22.7, 4.2 Hz), 117.1 (dd, *J* = 37.9, 33.7 Hz), 112.6 (dd, *J* = 29.3, 3.5 Hz), 110.8, 109.7, 60.7, 36.6, 32.2 (d, *J* = 5.1 Hz), 23.1, 0.2 (t, *J* = 2.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.2, -98.87; IR (thin film) 3083, 3029, 2956, 2215, 1612, 1386, 486 cm^{-1}; HRMS (ESI) calcd for $[C_{23}H_{26}F_2N_2SiNa]^+$, *m/z* 419.1726, found 419.1735.

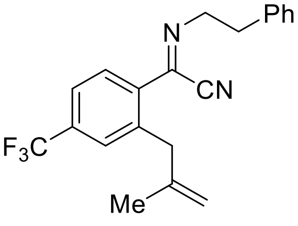
α-iminonitrile 2h:



2h

Prepared using general **procedure B** for α-iminonitrile synthesis using aldehyde **1h** (80 mg, 0.46 mmol), phenethylamine (56 mg, 0.46 mmol), acetonitrile (0.5 mL), TMSCN (63 μl, 0.51 mmol), IBX (193 mg, 0.69 mmol), tetrabutylammonium bromide (164 mg, 0.51 mmol), iminonitrile **2h** was isolated as a yellow oil (61 mg, 0.14 mmol, 44%) R_f = 0.85 (1:10 EtOAc:Hex on alumina TLC). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.39 (dd, *J* = 1.6, 7.4, 1H), 7.35−7.20 (m, overlapped with $CHCl_3$, 7H), 4.80−4.79 (m, 1H), 4.42−4.41 (m, 1H), 4.21 (t, *J* = 7.3 Hz, 2H), 3.62 (s, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 1.94 (q, *J* = 7.7 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 142.6, 139.1, 138.7, 133.4, 131.7, 130.8, 130.0, 129.0, 128.6, 126.7, 126.5, 110.1, 110.0, 60.4, 39.9, 36.5, 28.9, 12.2; IR (thin film) 3063, 3027, 2964, 2932, 2213, 1604, 1453, 1360 cm^{-1}; HRMS (CI, NH_3) calcd for $[C_{21}H_{22}N_2+H]^+$, *m/z* 303.1856, found 303.1878.

α-iminonitrile 2i:

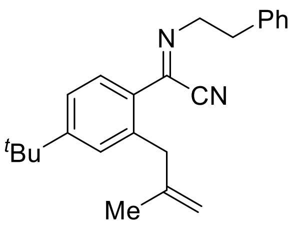


2i

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde **1i** (72 mg, 0.31 mmol), phenethylamine (39 mg, 0.32 mmol), acetonitrile (0.5 mL), TMSCN (43 μl, 0.34 mmol), IBX (132 mg, 0.47 mmol), tetrabutylammonium bromide (110 mg, 0.34

mmol), iminonitrile **2i** was isolated as a yellow oil (66 mg, 0.19 mmol, 59%) R_f = 0.80 (1:10 EtOAc:Hex on alumina TLC). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.53 (app s, 1H), 7.34−7.22 (m, overlapped with $CHCl_3$, 5H), 4.84−4.83 (m, 1H), 4.44−4.43 (m, 1H), 4.25 (t, *J* = 7.1 Hz, 2H), 3.59 (s, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (126 MHz , $CDCl_3$) δ 143.4, 141.4, 140.0, 138.4, 136.4 (app d, *J* = 3 Hz), 132.5 (q, *J* = 33 Hz), 130.4, 129.0, 128.6, 128.2 (q, *J* = 4 Hz), 126.7, 123.6 (q, *J* = 273 Hz), 123.6 (q, *J* = 4 Hz), 113.1, 109.7, 60.6, 41.0, 36.4, 22.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.2; IR (thin film) 3084, 2931, 2929, 2215, 1612, 1454, 1333, 1169, 1086, 837 cm^{-1}; HRMS (CI, NH_3) calcd for $[C_{21}H_{19}F_3N_2+H]^+$, *m/z* 357.1574, found 357.1559.

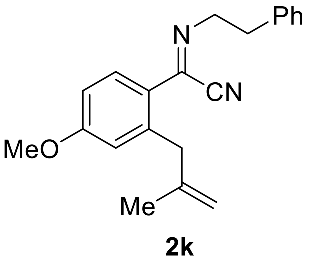
α-iminonitrile 2j:



2j

Prepared using general procedure **B** for α-iminonitrile synthesis using aldehyde **1j** (98 mg, 0.045 mmol), phenethylamine (55 mg, 0.46 mmol), acetonitrile (0.5 mL), TMSCN (85 µl, 0.68 mmol), IBX (190 mg, 0.60 mmol), and tetrabutylammonium bromide (160 mg, 0.49 mmol). **Iminonitrile 2j** was isolated as a yellow oil (92 mg, 0.27 mmol, 59%) R_f = 0.90 (1:9 EtOAc:Hex on alumina TLC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.35−7.29 (m, 3H), 7.27−7.21 (m, overlapped with $CHCl_3$, 5H), 4.76 (app s, 1H), 4.40 (app s, 1H), 4.20 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 1.65 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 144.7, 142.4, 138.8, 138.6, 130.4, 130.1, 128.9, 128.8, 128.5, 126.4, 123.6, 111.9, 110.1, 60.3, 41.5, 36.6, 34.8, 31.0, 22.7; IR (thin film) 3064, 3028, 2964, 2867, 2214, 1604, 1454, 1112 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{28}N_2Na]^+$, *m/z* 367.2145, found 367.2144.

α-iminonitrile 2k:

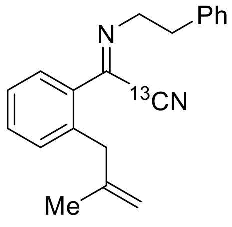


2k

Aldehyde **1k** (76 mg, 0.40 mmol) and phenethylamine (60 mg, 0.50 mmol) were stirred for one hour at room temperature. A small aliquot (~10 µL) was removed and analyzed by NMR to ensure complete formation of imine. Acetonitrile (0.4 mL), TMSCN (60 µL, 0.50 mmol), were added and the mixture was stirred for another 15 min at room temp.

IBX (169 mg, 0.60 mmol) and tetrabutylammonium bromide (144 mg, 0.44 mmol) were added and the mixture was stirred for additional two hours at room temperature. The reaction mixture was diluted with EtOAc (10 mL), filtered through Celite and concentrated. The crude product was purified by flash chromatograph alumina (gradient from 20 to 30% CH_2Cl_2 in hexanes) to afford pure α-iminonitrile **2k** as a yellow oil (55 mg, 0.17 mmol 43%) $R_f = 0.80$ (1:9 EtOAc:Hex on alumina TLC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.7 Hz, 1H), 7.33−7.21 (m, overlapping with $CHCl_3$, 5H), 6.84 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 4.78 (app s, 1H), 4.44 (app s, 1H), 4.18 (t, *J* = 7.3 Hz, 2H), 3.84 (s, 3H), 3.60 (s, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 144.4, 141.9, 141.4, 138.9, 132.3, 128.9, 128.4, 126.4, 125.7, 117.3, 112.0, 111.5, 110.1, 60.2, 55.3, 41.4, 36.7, 22.6; IR (thin film) 3064, 3028, 2936, 2214, 1604, 1497, 1117 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{22}N_2NaO]^+$, *m/z* 341.1624, found 341.1621.

α-iminonitrile 2l:



2l

Prepared using general **procedure A** for α-iminonitrile synthesis using aldehyde 1a (101 mg, 0.63 mmol), phenethylamine (76 mg, 0.63 mmol), acetonitrile (0.7 mL), TMS^{13}CN (88 µl 0.69 mmol), IBX (264 mg, 0.95 mmol) tetrabutylammonium bromide (222 mg, 0.69 mmol). α-iminonitrile **2l** was isolated as a yellow oil (114 mg, 0.39 mmol, 64%) $R_f = 0.85$ (1:9 EtOAc:Hex on alumina TLC).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.2, 7.7 Hz, 1H), 7.41 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.35−7.30 (m, overlapping with $CHCl_3$, 3H), 7.28−7.20 (m, 4H), 4.78 (app s, 1H), 4.43 (d, *J* = 0.8 Hz, 1H), 4.22 (dt, *J* = 1.2, 7.2 Hz, 2H), 3.58 (s, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR[1] (126 MHz, $CDCl_3$) δ 144.4, 142.5 (d, *J* = 65 Hz), 138.9 (d, *J* = 2.5 Hz), 138.7, 133.2 (d, *J* =

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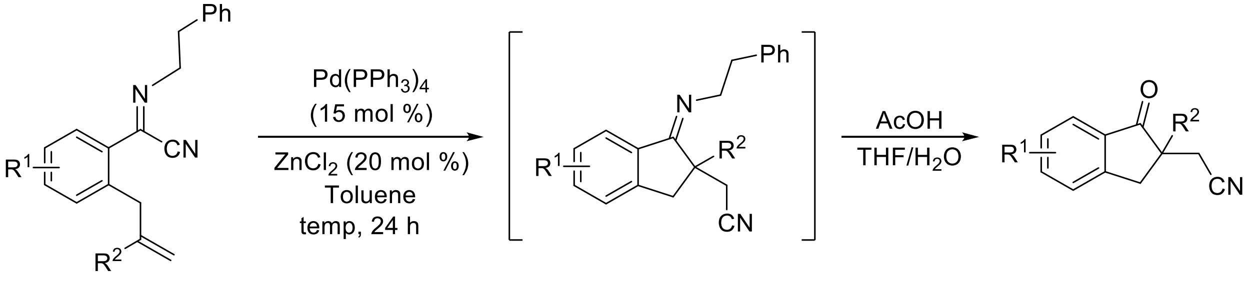
[1] ^{13}C−^{13}C coupling constants are assigned by comparison to ^{13}C NMR of **2a**.

11 Hz), 131.5, 130.8, 130.0, 129.0, 128.5, 126.7, 126.5, 115.8, 112.2, 110.1, 60.4, 41.1, 36.5, 22.6; IR (thin film) 3064, 3028, 2931, 2163, 1604, 1453, 1030 cm^{-1}; HRMS (CI, NH_3) calcd for $[C_{19}{}^{13}CH_{20}N_2Na]^+$, *m/z* 312.1552, found 312.1551.

Cyanoacylation Reaction:



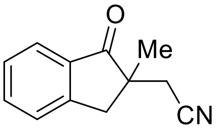
2a-l

3a-l

General Procedure:

In a nitrogen filled glove box, a 1 or 4 dram reaction vial (Chemglass, polytetrafluoroethylene cap) was charged with iminonitrile **2** (0.34 mmol 1 equiv), $Pd(PPh_3)_4$ (0.05 mmol, 0.15 equiv), $ZnCl_2$ (0.07 mmol, 0.20 equiv) and toluene (1.6 mL). The mixture was heated at 120 or 130 °C for 24 h inside a nitrogen filled glove box. The mixture was then taken out of the glove box, filtered through Celite and concentrated. The crude product was dissolved in THF and 30% (v/v) aqueous acetic acid was added dropwise. The reaction was stirred at room temperature for 1.5 to 18 hr. After ensuring complete hydrolysis of imine by silica TLC, the reaction mixture was diluted with diethyl ether (20 mL). The layers were separated and aqueous layer was again extracted with diethyl ether (20 mL). The combined organic extracts were washed with water (50 mL), saturated aqueous $NaHCO_3$ solution (50 mL), brine (50 mL) and were dried over anhydrous Na_2SO_4 (15 g) and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (eluent gradient, EtOAc: Hex) to afford the indanone **3** (acylcyanation product).

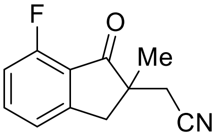
Indanone 3a:



3a

Prepared using the general procedure for cyanoacylation from iminonitrile **2a** (97 mg, 0.34 mmol), Pd(PPh$_3$)$_4$ (59 mg, 0.05 mmol), ZnCl$_2$ (9.2 mg, 0.67 mmol) and toluene (1.6 ml) at 120 °C. Hydrolysis of imine was accomplished with THF (2 ml) and 20% (v/v) aqueous AcOH (3 mL). The crude product was purified by flash column chromatography (10 to 15% EtOAc in hexanes) and indanone **3a** was obtained as a yellow oil (51 mg, 0.28 mmol, 82%) R$_f$ = 0.45 (1:4 EtOAc:Hex) ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80 (app d, *J* = 7.7 Hz, 1H), 7.67 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.54−7.39 (m, 2H), 3.31 (d, *J* = 17.3 Hz, 1H), 3.12 (d, *J* = 17.3 Hz, 1H), 2.71 (d, *J* = 16.7 Hz, 1H), 2.53 (d, *J* = 16.7 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 206.6, 151.3, 135.8, 134.1, 128.1, 126.7, 124.8, 117.4, 46.6, 40.0, 25.9, 23.7; IR (thin film) 2967, 2929, 2249, 1714, 1615, 1459, 1394, 1251, cm^{-1}; HRMS (ESI) calcd for [C$_{12}$H$_{11}$NNaO]$^+$, *m/z* 208.0738, found 208.0735.

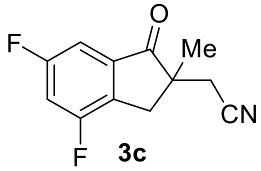
Indanone 3b:



3b

Prepared using the general procedure for cyanoacylation from iminonitrile **2b** (31 mg, 0.10 mmol), Pd(PPh$_3$)$_4$ (18 mg, 0.015 mmol), ZnCl$_2$ (3 mg, 0.02 mmol) and toluene (0.45 mL) at 130 °C. Hydrolysis of imine was accomplished by stirring with THF (0.4 mL) and 30% (v/v) aqueous AcOH (9 mL) for two hours. The crude product was purified by flash column chromatography (20% EtOAc in hexanes) and indanone **3b** was isolated as a yellow oil (15.0 mg, 0.076 mmol, 73%) R$_f$ = 0.40 (1:3 EtOAc:Hex) (The sample could not be separated from 1% triphenylphosphine oxide and the yield was corrected accordingly); ^{1}H NMR[2] (500 MHz, $CDCl_3$) δ 7.65 (dt, J = 7.9, 5.0 Hz, 1H), 7.28−7.27 (d, J = 6.7 Hz, overlapping with $CHCl_3$, 1H), 7.05 (app t, J = 8.6 Hz, 1H), 3.32 (d, J = 17.5 Hz, 1H), 3.13 (d, J = 17.5 Hz, 1H), 2.71 (d, J = 16.8 Hz, 1H), 2.56 (d, J = 16.8 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 159.5 (d, J = 265 Hz), 153.1, 137.8 (d, J = 10 Hz), 122.6, 122.2, 117.3, 115.0 (d, J = 19 Hz), 47.3, 39.9, 25.9, 23.8; ^{19}F NMR (471 MHz , $CDCl_3$) δ -113.9; IR (thin film) 3082, 2968, 2929, 2248, 1714, 1615, 1475, 1198 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_{10}FNNaO]^+$, *m/z* 226.0639, found 226.0633.

Indanone 3c:



3c

Prepared using the general procedure for cyanoacylation from iminonitrile **2c** (36 mg, 0.116 mmol), $Pd(PPh_3)_4$ (12.7 mg, 0.011 mmol), $ZnCl_2$ (3 mg, 0.022 mmol) and toluene (0.53 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with (0.5 mL), water (1.11 mL) and AcOH (0.184 mL) for one hour. The crude product was purified by flash column chromatography (15% DCM in hexanes) and indanone **3c** was isolated as an orange oil. (15.6 mg, 0.071 mmol, 64%) R_f = 0.6 (1:4 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, J = 6.7, 2.1 Hz, 1H), 7.13 (dt, J = 8.5, 2.1 Hz, 1H), 3.25 (d, J = 17.4 Hz, 1H), 3.11 (d, J = 17.4 Hz, 1H), 2.70 (d, J = 16.8 Hz, 1H), 2.58 (d, J = 16.8 Hz, 1 H), 1.39 (s, 3H);^{13}C NMR (126 MHz, $CDCl_3$) δ 204.7, 163.3 (dd, J = 252.4, 9.2 Hz), 160.1 (dd, J = 254.9, 11.5 Hz), 137.8 (dd, J = 8.6, 5.9 Hz), 133.4 (dd, J = 19.9, 2.7 Hz), 129.2 (d, J = 167.2 Hz), 117.1, 111.0 (dd, J = 27.3, 23.7 Hz), 107.2 (dd, J = 22.2, 4.4 Hz), 47.5, 35.6, 26.1, 24.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.3 (app q, J = 8.2, 1.7 Hz), -113.3 (app t, J = 7.9 Hz); IR (thin film) 3061, 2972, 2917, 2251, 1724, 1490, 1327 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_9F_2N_2{+}Na]^+$, *m/z* 244.0539, found 244.0545.

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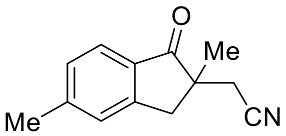
[2] No attempt was made to distinguish ^{19}F−^{1}H coupling from ^{1}H−^{1}H coupling.

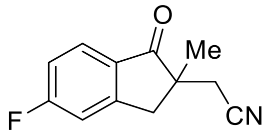
Indanone 3d:



3d

Prepared using the general procedure for cyanoacylation from iminonitrile **2d** (30 mg, 0.10 mmol), Pd(PPh$_3$)$_4$ (17 mg, 0.015 mmol), ZnCl$_2$ (2.7 mg, 0.02 mmol) and toluene (0.5 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with THF (0.4 mL) and 20% (v/v) aqueous AcOH (0.8 mL) for six hours. The crude product was purified by flash column chromatography (gradient from 10 to 15% EtOAc in hexanes) and indanone **3d** was isolated as a yellow oil (16.1 mg, 0.081 mmol, 81%) R$_f$ = 0.45 (1:4 EtOAc:Hex). ^{1}H NMR (300 MHz ,CDCl$_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.28−7.22 (m, overlapping with CHCl$_3$, 2H), 3.24 (d, *J* = 17.4 Hz, 1H), 3.06 (d, *J* = 17.3 Hz, 1H), 2.69 (d, *J* = 16.7 Hz, 1H), 2.54−2.46 (m, 4H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 206.1, 151.9, 147.3, 131.9, 129.4, 127.1, 124.7, 117.6, 46.8, 39.9, 26.1, 23.7, 22.2; IR (thin film) 2966, 2927, 2248, 1709, 1709, 1609, 1456, 1331, 1282, 987 cm^{-1}; HRMS (ESI) calcd for [C$_{13}$H$_{13}$NNaO]$^+$, *m/z* 222.0895, found 222.0883.

Indanone 3e:

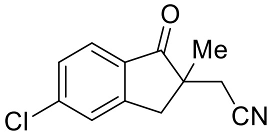


3e

Prepared using the general procedure for cyanoacylation from iminonitrile **2e** (53 mg, 0.174 mmol), Pd(PPh$_3$)$_4$ (30 mg, 0.026 mmol), ZnCl$_2$ (4.8 mg, 0.035 mmol) and toluene (0.8 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with THF (0.7 mL) and 30% aqueous AcOH (0.8 mL) for 1.5 hours. The crude product was purified by flash column chromatography (gradient from 10 to 15% EtOAc in hexanes) and indanone **3e** was isolated as a yellow oil (30.0 mg, 0.148 mmol, 85%) R$_f$ = 0.40 (1:4 EtOAc:Hex). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.17−7.12 (m, 2H), 3.29 (d, *J* =

17.5 Hz, 1H), 3.11 (d, *J* = 17.5 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.54 (d, *J* = 16.8 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (126 MHz ,CDCl$_3$) δ 204.7, 167.8 (d, *J* = 258 Hz), 154.3 (d, *J* = 10 Hz), 130.6, 127.3 (d, *J* = 10 Hz), 117.3, 116.6 (d, *J* = 24 Hz), 113.5 (d, *J* = 23 Hz), 47.0, 39.9, 26.0, 23.8; ^{19}F NMR (282 MHz , CDCl$_3$) δ -101.7; IR (thin film) 2968, 2930, 2250, 1715, 1615, 1594, 1456, 1251, 1086, 988, cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{10}FNNaO]^+$, *m/z* 226.0639, found 226.0644.

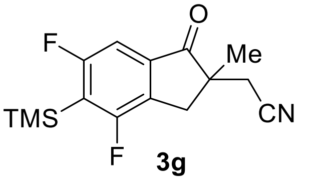
Indanone 3f:



3f

Prepared using the general procedure for cyanoacylation from iminonitrile **2f** (30 mg, 0.09 mmol), Pd(PPh$_3$)$_4$ (16 mg, 0.014 mmol), ZnCl$_2$ (2.5 mg, 0.02 mmol) and toluene (0.4 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with THF (0.4 mL) and 30% (v/v) aqueous AcOH (0.7 mL) for 2 hours. The crude product was purified by flash column chromatography (15% EtOAc in hexanes) and indanone **3f** was isolated as a yellow oil (16.1 mg, 0.073 mmol, 79%) R$_f$ = 0.40 (1:4 EtOAc:Hex). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 0.9 Hz, 1H), 7.42 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.28 (d, *J* = 17.5 Hz, 1H), 3.10 (d, *J* = 17.5 Hz, 1H), 2.70 (d, *J* = 16.8 Hz, 1H), 2.54 (d, *J* = 16.8 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (126 MHz , CDCl$_3$) δ 205.2, 152.8, 142.5, 132.6, 129.1, 127.0, 126.0, 117.2, 47.0, 39.7, 25.9, 23.8; IR (thin film) 3061, 2968, 2930, 2248, 1715, 1600, 1578, 1327, 1310, 1071, 897, cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{10}ClNNaO]^+$, *m/z* 242.0343, found 242.0347.

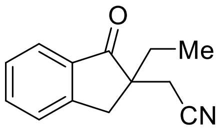
Indanone 3g:



3g

Prepared using the general procedure for cyanoacylation from iminonitrile **2g** (56.6 mg, 0.142 mmol), $Pd(PPh_3)_4$ (16.5 mg, 0.014 mmol), $ZnCl_2$ (3.9 mg, 0.029 mmol) and toluene (0.68 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with THF (0.59 mL), water (1.43 mL) and AcOH (0.24 mL) for one hour. The crude product was purified by column chromatography (gradient from pure hexanes to 15% DCM in hexanes with steps of a column volume of hexanes, 2 column volumes of 5% DCM, 1 column volume of 10% DCM and 1 column volume of 15% DCM) and indanone **3g** was isolated as an orange oil (0.0263 g, 0.09 mmol 63%). R_f = 0.6 (1:4 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 6.9 Hz, 1H), 3.21 (d, J = 17.5 Hz, 1H), 3.06 (d, J = 17.4 Hz, 1H), 2.68 (d, J = 16.8 Hz, 1H), 2.56 (d, J = 16.8 Hz, 1H), 1.38 (s, 3H), 0.42 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.0 (t, J = 3.2 Hz), 167.2 (app dd, J = 246.6, 13.1 Hz), 163.9 (app dd, J = 248.8, 15.4 Hz), 138.6 (dd, J = 9.6, 6.7 Hz), 132.8 (dd, J = 25.2, 2.8 Hz), 129.0 (d, J = 18.2 Hz), 122.90 (app dd, J = 36.5, 32.6 Hz), 117.28, 106.8 (dd, J = 28.3, 4.5 Hz), 47.6, 35.8, 26.2, 24.0, 0.17 (t, J = 3.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -96.1, -101.3; IR (thin film) 2962, 2930, 2359, 2250, 1723, 1411, 1012, 848 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{17}F_2NNaO]^+$, m/z 316.0940, found 316.0934.

Indanone 3h:

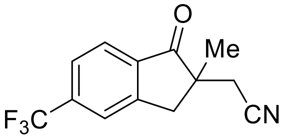


3h

Prepared using the general procedure for cyanoacylation from iminonitrile **2h** (21 mg, 0.070 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), $ZnCl_2$ (2.0 mg, 0.014 mmol) and toluene (0.35 mL) at 130 °C. Hydrolysis of imine was accomplished by stirring with THF (0.5

mL) and 30% (v/v) aqueous AcOH (0.7 mL) for 12 hours. The crude product was purified by flash column chromatography (10% EtOAc in hexanes) and indanone **3h** was isolated as a yellow oil (10.5 mg, 0.079 mmol, 76%) R_f = 0.45 (1:4 EtOAc:Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.66 (app dt, *J* = 1.1, 7.4 Hz, 1 H), 7.50 (app d, *J* = 7.8 Hz, 1H), 7.42 (app t, *J* = 7.5 Hz, 1H), 3.21 (s, 2H), 2.71 (d, *J* = 16.7 Hz, 1H), 2.55 (d, *J* = 16.7 Hz, 1H), 1.92 - 1.70 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.7, 152.0, 135.7, 135.5, 128.1, 126.6, 124.5, 117.4, 50.3, 37.4, 30.2, 24.9, 8.5; IR (thin film) 2967, 2924, 2880, 2248, 1711, 1608, 1465, 1298, 1187, 927, cm^{-1}. HRMS (ESI) calcd for $[C_{13}H_{13}NNaO]^+$, *m/z* 222.0895, found 222.0900.

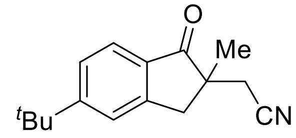
Indanone 3i:



3i

Prepared using the general procedure for cyanoacylation from iminonitrile **2i** (31 mg, 0.087 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), $ZnCl_2$ (2.5 mg, 0.018 mmol) and toluene (0.4 mL) at 120 °C. Hydrolysis of imine was accomplished by stirring with THF (0.4 mL) and 30% aqueous AcOH (0.8 mL) for 1.5 hours. The crude product was purified by flash column chromatography (15% EtOAc in hexanes) and indanone **3i** was isolated as a yellow oil (20 mg, 0.079 mmol, 90%) R_f = 0.38 (1:4 EtOAc:Hex) ^{1}H NMR (300 MHz ,$CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 3.37 (d, *J* = 17.5 Hz, 1H), 3.19 (d, *J* = 17.6 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 2.58 (d, *J* = 17.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.7, 151.5, 137.1 (q, *J* = 26 Hz), 136.9, 125.5, 125.3 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 3.5 Hz), 123.4 (q, *J* = 274 Hz), 117.0, 47.2, 39.9, 25.8, 23.8; ^{19}F NMR (282 MHz , $CDCl_3$) δ -64.2; IR (thin film) 2971, 2932, 2248, 1723, 1622, 1456, 1206, 1170, 930, cm^{-1}. HRMS (ESI) calcd for $[C_{13}H_{10}F_3NNaO]^+$ *m/z* 276.0607, found 276.0612.

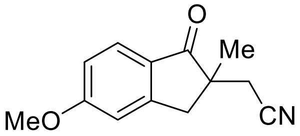
Indanone 3j:



3j

Prepared using the general procedure for cyanoacylation from iminonitrile **2j** (37 mg, 0.11 mmol), $Pd(PPh_3)_4$ (25 mg, 0.021 mmol), $ZnCl_2$ (2.9 mg, 0.02 mmol) and toluene (0.5 mL) at 130 °C. Hydrolysis of imine was accomplished by stirring with THF (0.4 mL) and 30% (v/v) aqueous AcOH (0.9 mL) for 18 hours. The crude product was purified by flash column chromatography (gradient from 10 to 15% EtOAc in hexanes) and indanone **3j** was isolated as a light yellow oil (20.2 mg, 0.084 mmol, 77%) R_f = 0.40 (1:4 EtOAc:Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (app dd, *J* = 7.2, 1.5 Hz, 1H), 7.49−7.46 (m, 2H), 3.27 (d, *J* = 17.2 Hz, 1H), 3.09 (d, *J* = 17.2 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.51 (d, *J* = 16.8 Hz, 1H), 1.42−1.37 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.2, 160.3, 151.7, 131.8, 126.0, 124.5, 123.3, 117.6, 46.8, 40.1, 35.6, 31.1, 26.0, 23.7; IR (thin film) 2965, 2870, 2248, 1711, 1608, 1438, 1225, 987, cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{19}NNaO]^+$; *m/z* 264.1359, found 264.1364.

Indanone 3k:

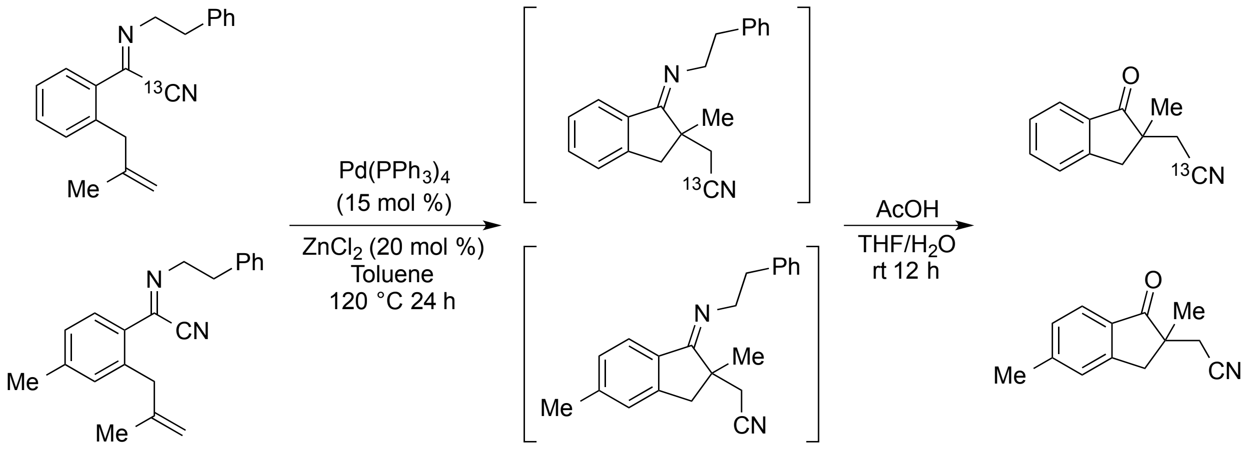


3k

Prepared using the general procedure for cyanoacylation from iminonitrile **2k** (51 mg, 0.16 mmol), $Pd(PPh_3)_4$ (37 mg, 0.032 mmol), $ZnCl_2$ (4.4 mg, 0.032 mmol) and toluene (0.7 mL) at 130 °C. Hydrolysis of imine was accomplished by stirring with THF (0.5 mL) and 30% (v/v) aqueous AcOH (0.7 mL) for 14 hours. The crude product was purified by flash column chromatography (20% EtOAc in hexanes) and indanone **3k** was isolated as a colorless oil (21 mg, 0.097 mmol, 60%) R_f = 0.40 (3:7 EtOAc:Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.90 (app d, *J* =

1.9 Hz, 1H), 3.91 (s, 3H), 3.24 (d, *J* = 17.3 Hz, 1H), 3.06 (d, *J* = 17.3 Hz, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.50 (d, *J* = 16.8 Hz, 1H), 1.37 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 166.2, 154.4, 127.2, 126.6, 117.7, 116.3, 109.7, 55.8, 46.8, 40.1, 26.2, 23.8; IR (thin film) 2967, 2930, 2248, 1702, 1599, 1490, 1340, 1295, 1104, 986, cm^{-1}; HRMS (ESI) calcd for $[C_{13}H_{13}NNaO_2]^+$; *m/z* 238.0844, found 238.0843.

Crossover Experiment: In a nitrogen filled glove box, a 1 dram reaction vial was charged with iminonitrile **1b** (38 mg 0.125 mmol), and **1l** (36 mg 0.125 mmol) $Pd(PPh_3)_4$ (43 mg, 0.038 mmol), $ZnCl_2$ (7.0 mg, 0.05 mmol) and toluene (1.0 mL). The mixture was heated at 120 °C for 24 h inside a nitrogen filled glove box. The mixture was then removed from the glove box, filtered through Celite and concentrated. The crude product was dissolved in THF (1.5 mL) and then 30% aqueous acetic acid (2.5 mL) was added. The reaction was stirred at room temperature for 12 h. After ensuring complete hydrolysis of imine by silica TLC, the reaction was diluted with diethyl ether (20 mL). The layers were separated and aqueous layer was again extracted with diethyl ether (20 mL). The combined organic layers were washed with water (50 mL), sat $NaHCO_3$ (50 mL), brine (50 mL), were dried over anhydrous Na_2SO_4 (15 g) and concentrated *in vacuo*. The crude purified by flash column chromatography on silica gel (15% EtOAc in Hex) to afford the mixture of indanones **2b** and **2l** (39 mg). No crossover of labeled ^{13}CN was observed by ^{13}C NMR (Please find the attached spectra for more details).



Not observed

Notes and references

1. W. L. F. Argamengo and C. L. L. Chai, *Purification of Laboratory Chemicals*, Elsevier, 2003.
2. B. Du, X. Jiang and P. Sun, *J. Org. Chem.*, 2013, **78**, 2786-2791.
3. A. Krasovskiy and P. Knochel, *Angew. Chem., Int. Ed.*, 2004, **43**, 3333-3336.
4. I. Kinoyama, T. Miyazaki, Y. Koganemaru, N. Shiraishi, Y. Kawamoto and T. Washio, Astellas Pharma Inc., Japan, Aug 8, 2011.
5. K. Schwekendiek and F. Glorius, *Synthesis*, 2006, 2996-3002.
6. S. Nicolai, S. Erard, D. F. Gonzalez and J. Waser, *Org. Lett.*, 2010, **12**, 384-387.
7. I. Bonnaventure and A. B. Charette, *J. Org. Chem.*, 2008, **73**, 6330-6340.
8. B. Cheng, J. D. Sunderhaus and S. F. Martin, *Org. Lett.*, 2010, **12**, 3622-3625.
9. L. D. Shirtcliff, T. J. R. Weakley, M. M. Haley, F. Köhler and R. Herges, *J. Org. Chem.*, 2004, **69**, 6979-6985.
10. A. A. Pletnev, Q. Tian and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 9276-9287.
11. P. Fontaine, A. Chiaroni, G. Masson and J. Zhu, *Org. Lett.*, 2008, **10**, 1509-1512.
12. M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537-4538.
13. E. V. Beletskiy, C. Sudheer and C. J. Douglas, *J. Org. Chem.*, 2012, **77**, 5884-5893.

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9/26/2013 4:33:18 PM

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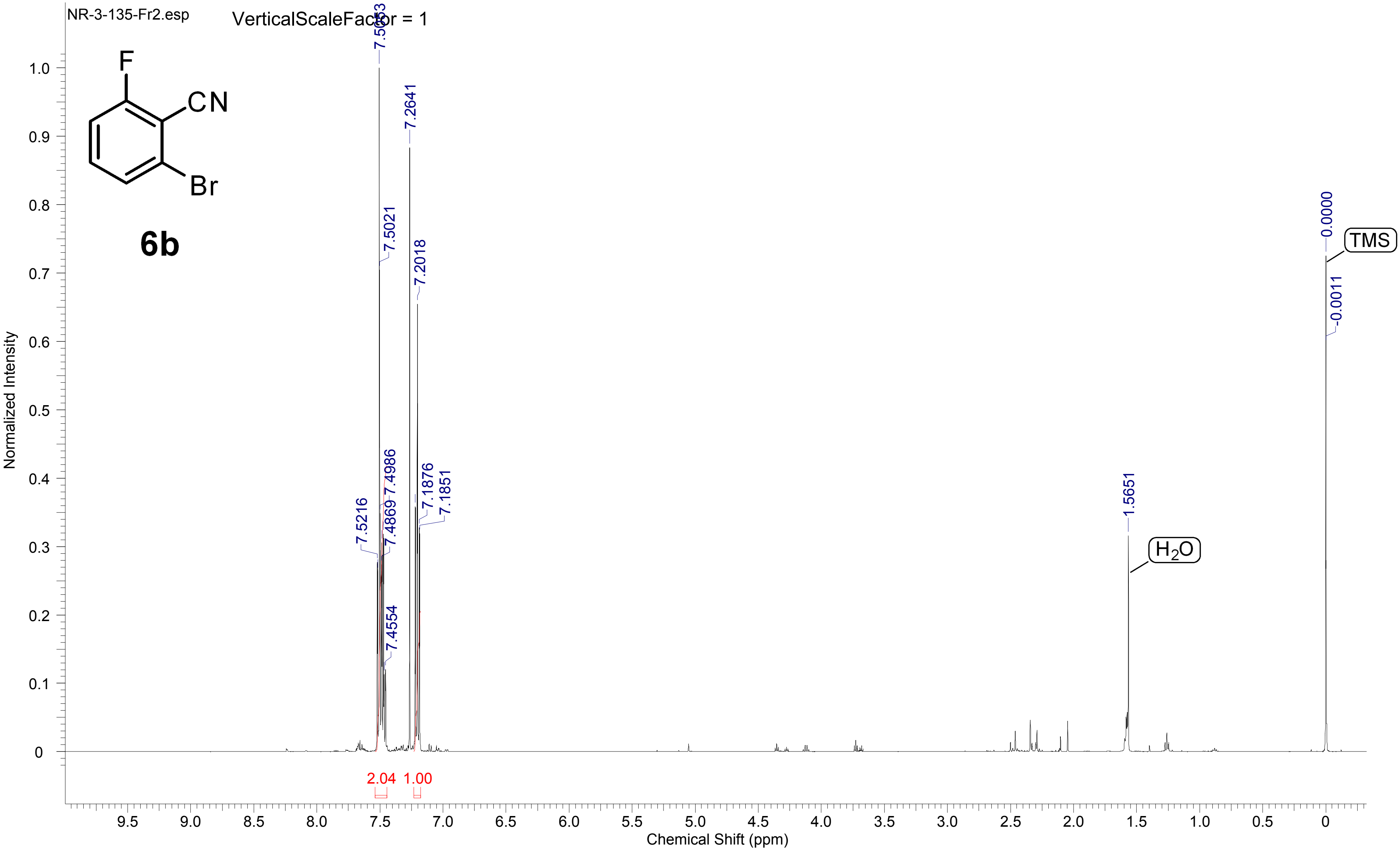

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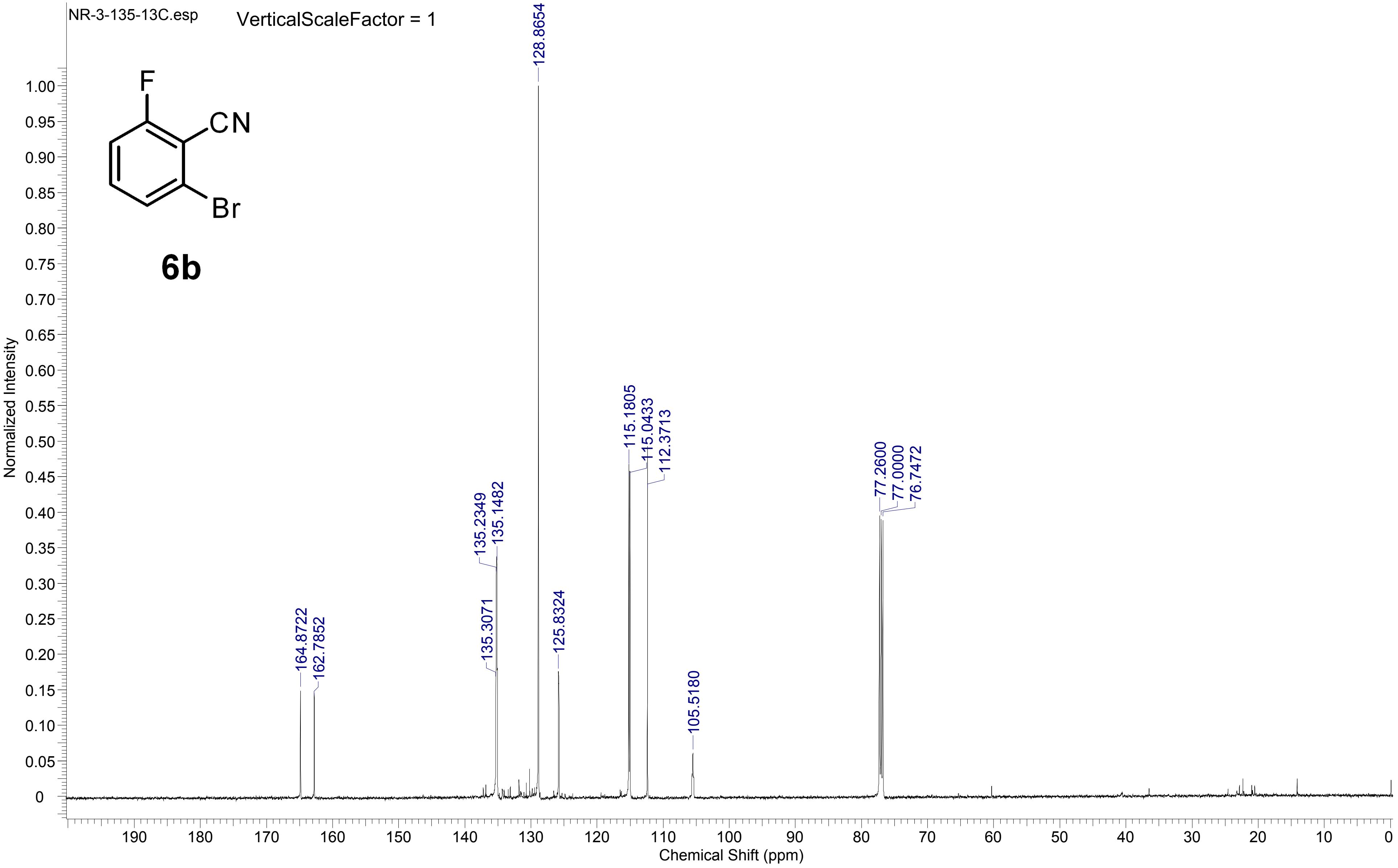

6b

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Date Stamp	Sep 17 2013	***File Name***	C:\Users\Naveen\Desktop\NR-3-136-P.fid\fid			***Frequency (MHz)***	499.87
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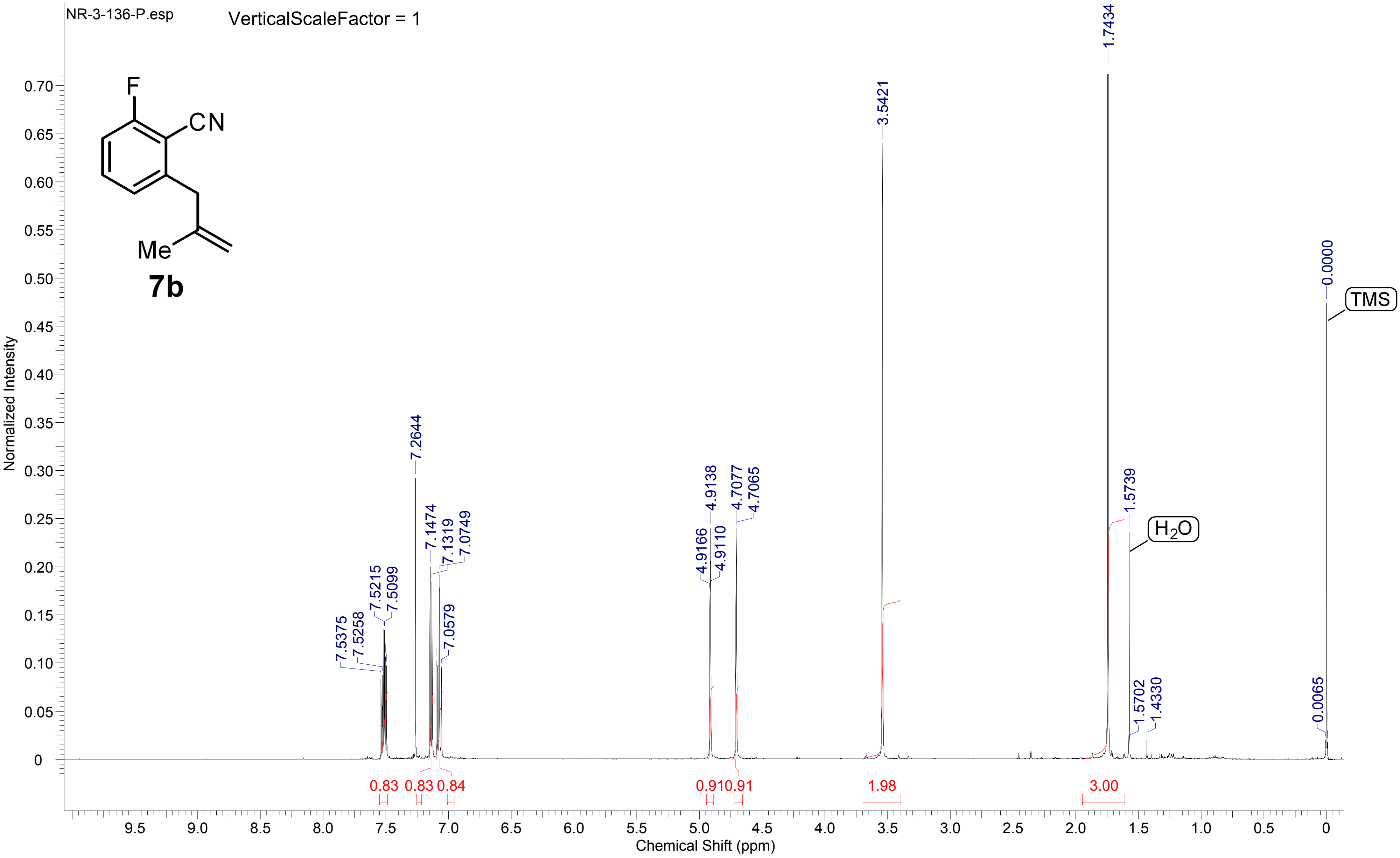
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2498.4626	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE


7b

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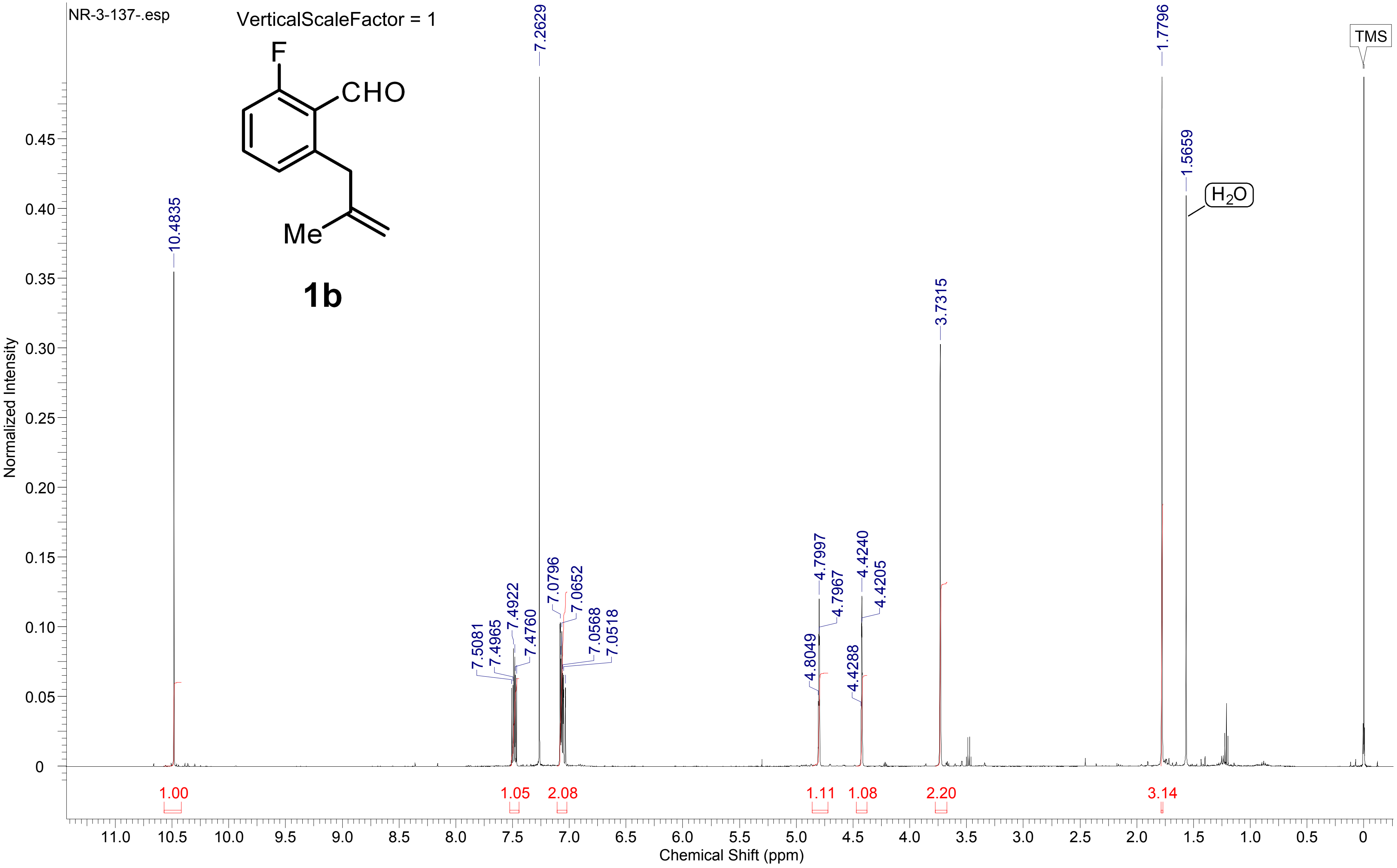
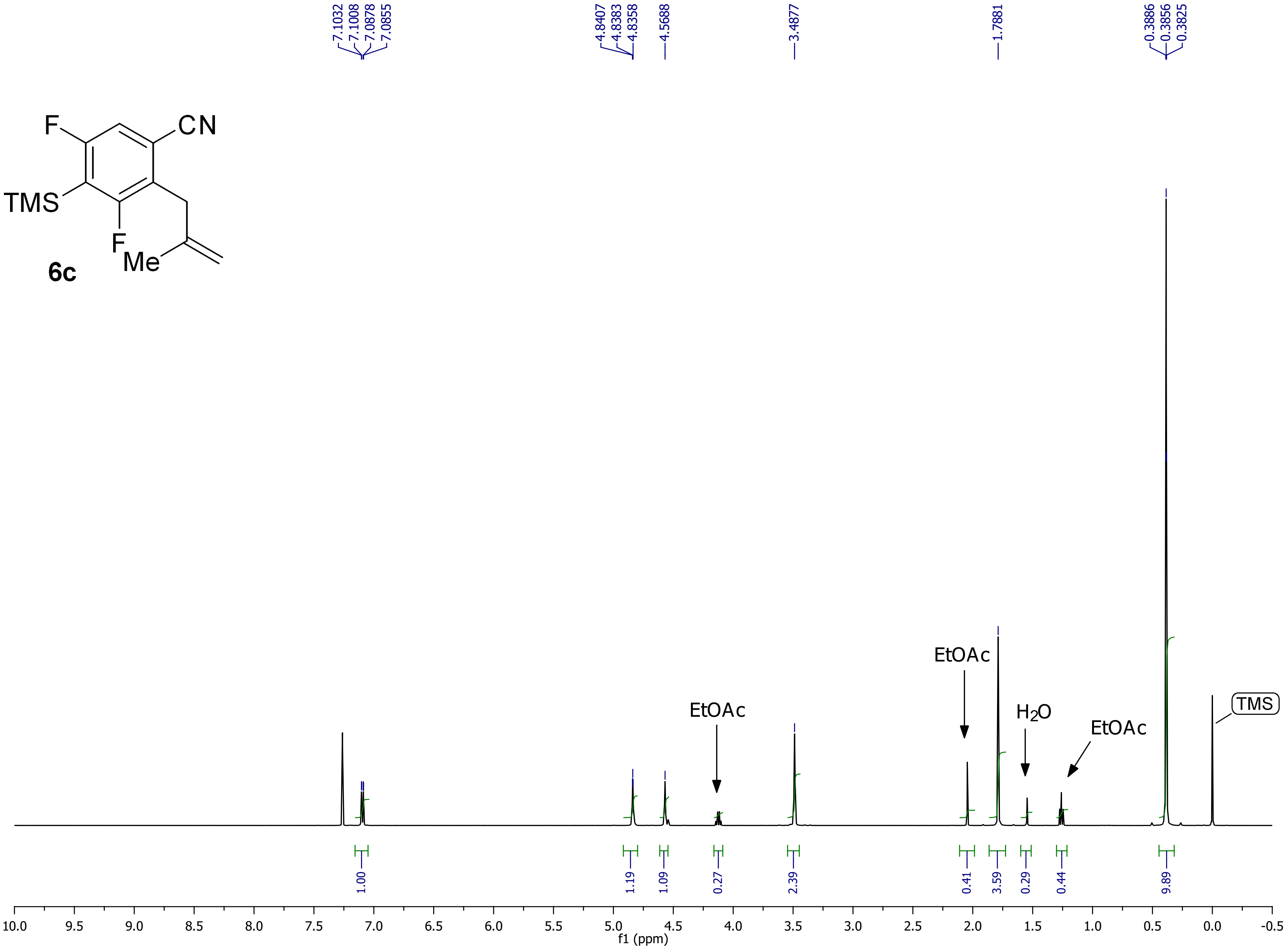
9/26/2013 4:53:01 PM

Acquisition Time (sec)	3.2768	***Date***	18 Sep 2013 21:03:44			***Date Stamp***	18 Sep 2013 21:03:44
File Name	C:\Users\Naveen\Desktop\NR-3-137-P\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	105.23	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3077.2781	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	21.000				





6c

F
CN
TMS
F
Me
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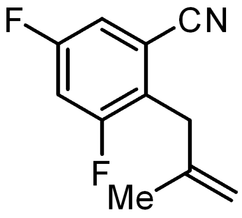
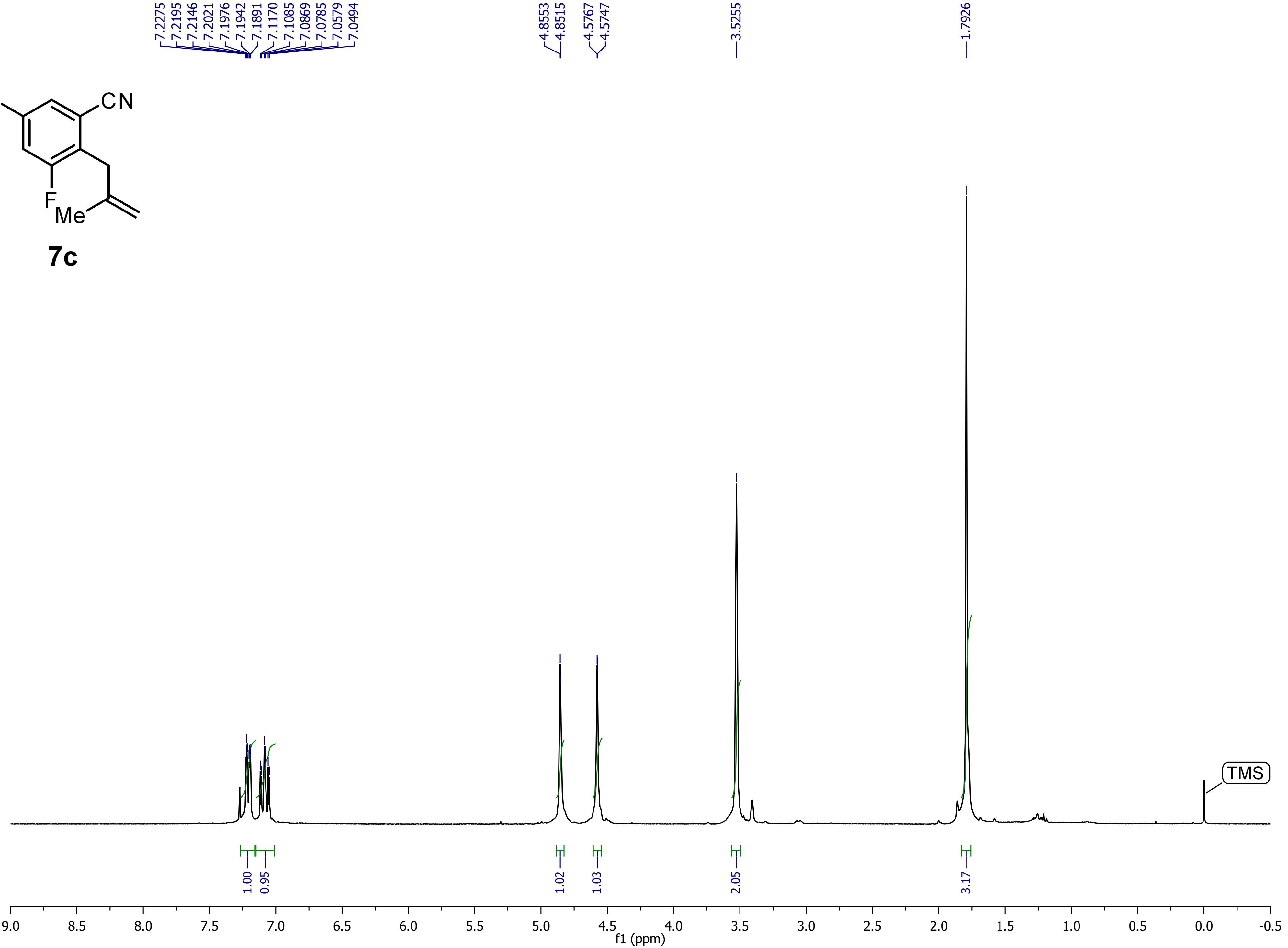
7.1008
7.0878
7.0855
4.8407
4.8383
4.8358
4.5688
3.4877
1.7881
0.3886
0.3856
0.3825
EtOAc
EtOAc
H2O
EtOAc
TMS
1.00
1.19
1.09
0.27
2.39
0.41
3.59
0.29
0.44
9.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


F
CN
F
Me

7c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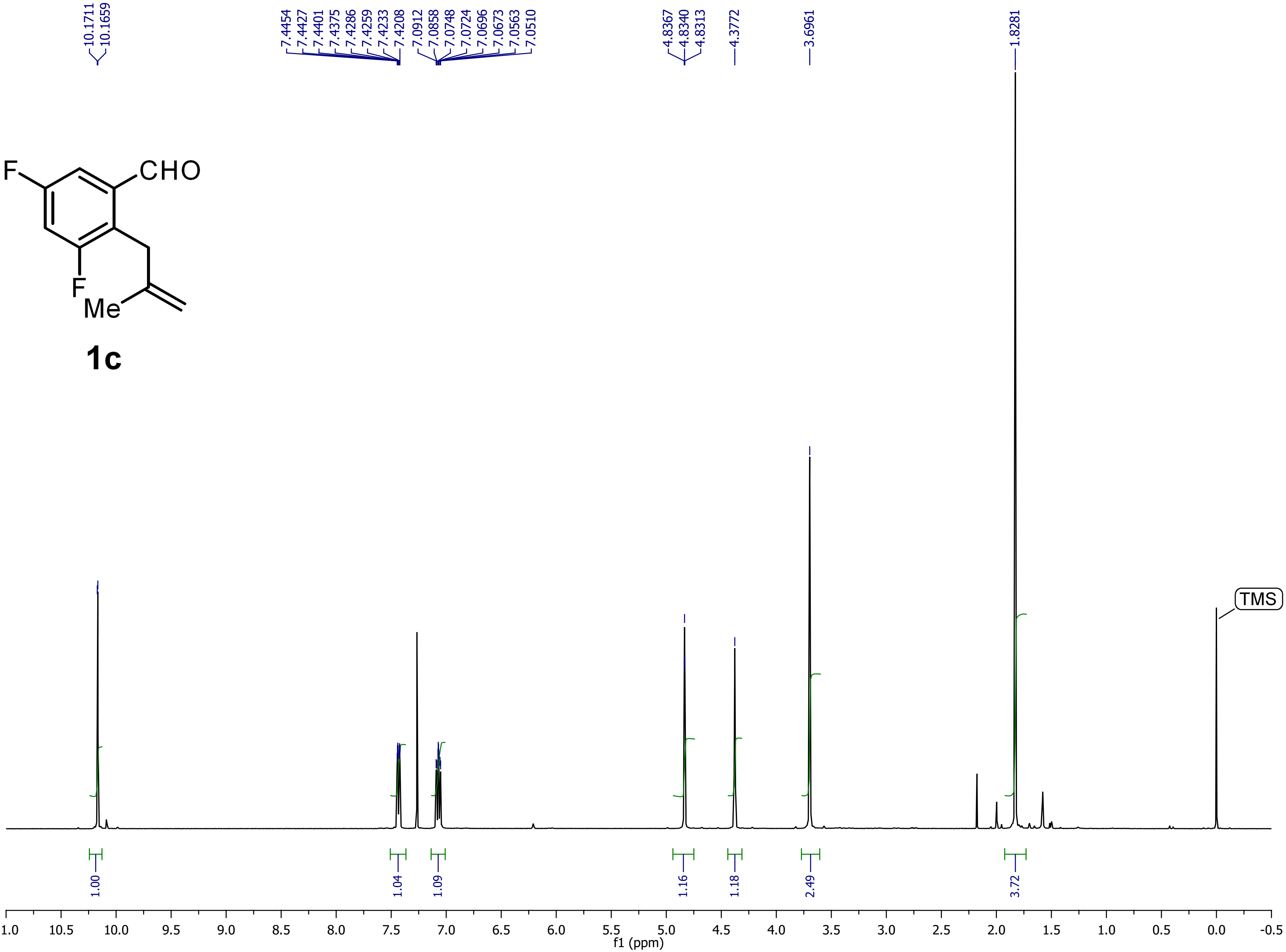
7.2195
7.2146
7.2021
7.1976
7.1942
7.1891
7.1170
7.1085
7.0869
7.0785
7.0579
7.0494
4.8553
4.8515
4.5767
4.5747
3.5255
1.7926
TMS
1.00
0.95
1.02
1.03
2.05
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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10.1659
7.4454
7.4427
7.4401
7.4375
7.4286
7.4259
7.4233
7.4208
7.0912
7.0858
7.0748
7.0724
7.0696
7.0673
7.0563
7.0510
4.8367
4.8340
4.8313
4.3772
3.6961
1.8281
F
CHO
F
Me
TMS
1.00
1.04
1.09
1.16
1.18
2.49
3.72
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1c

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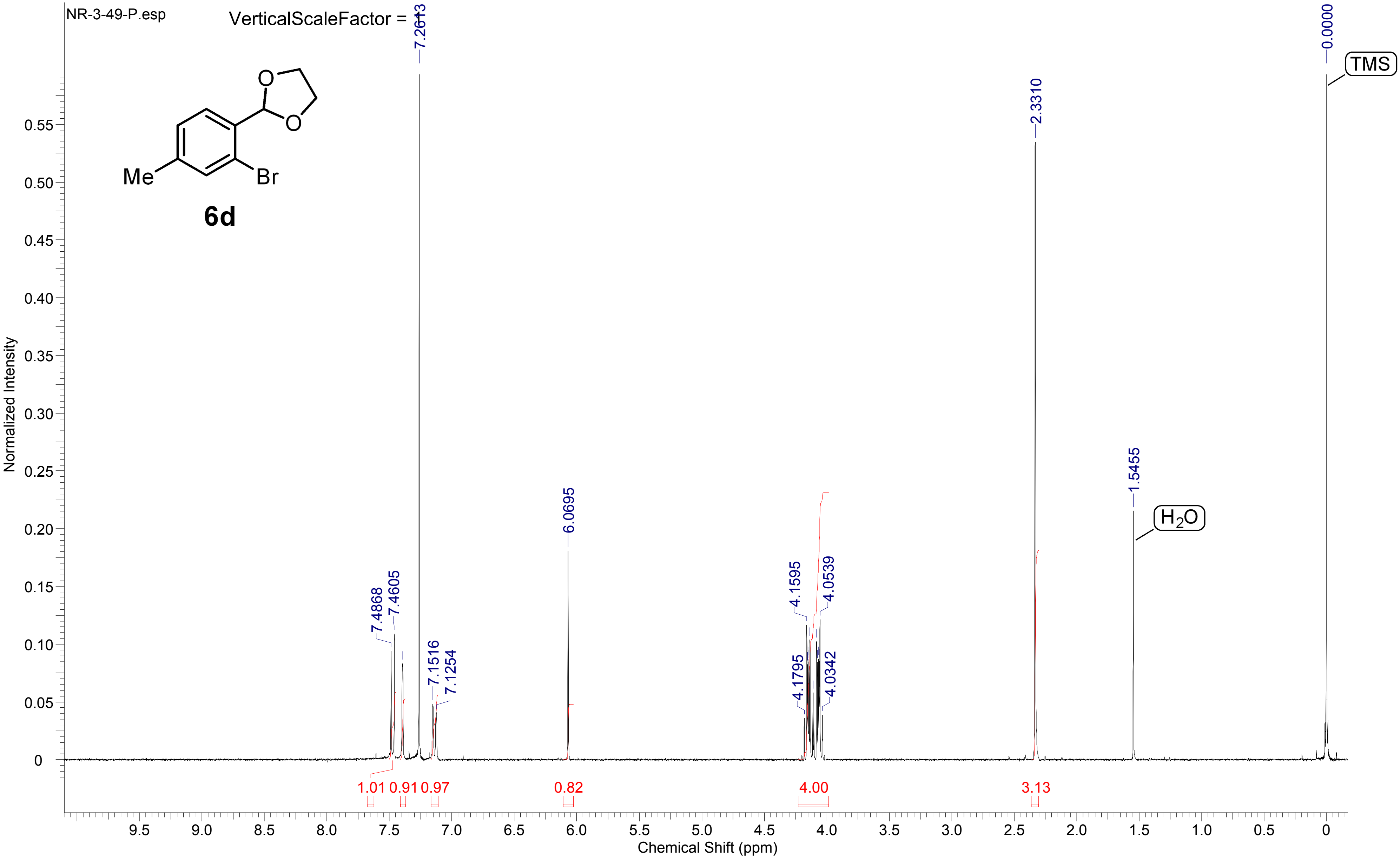
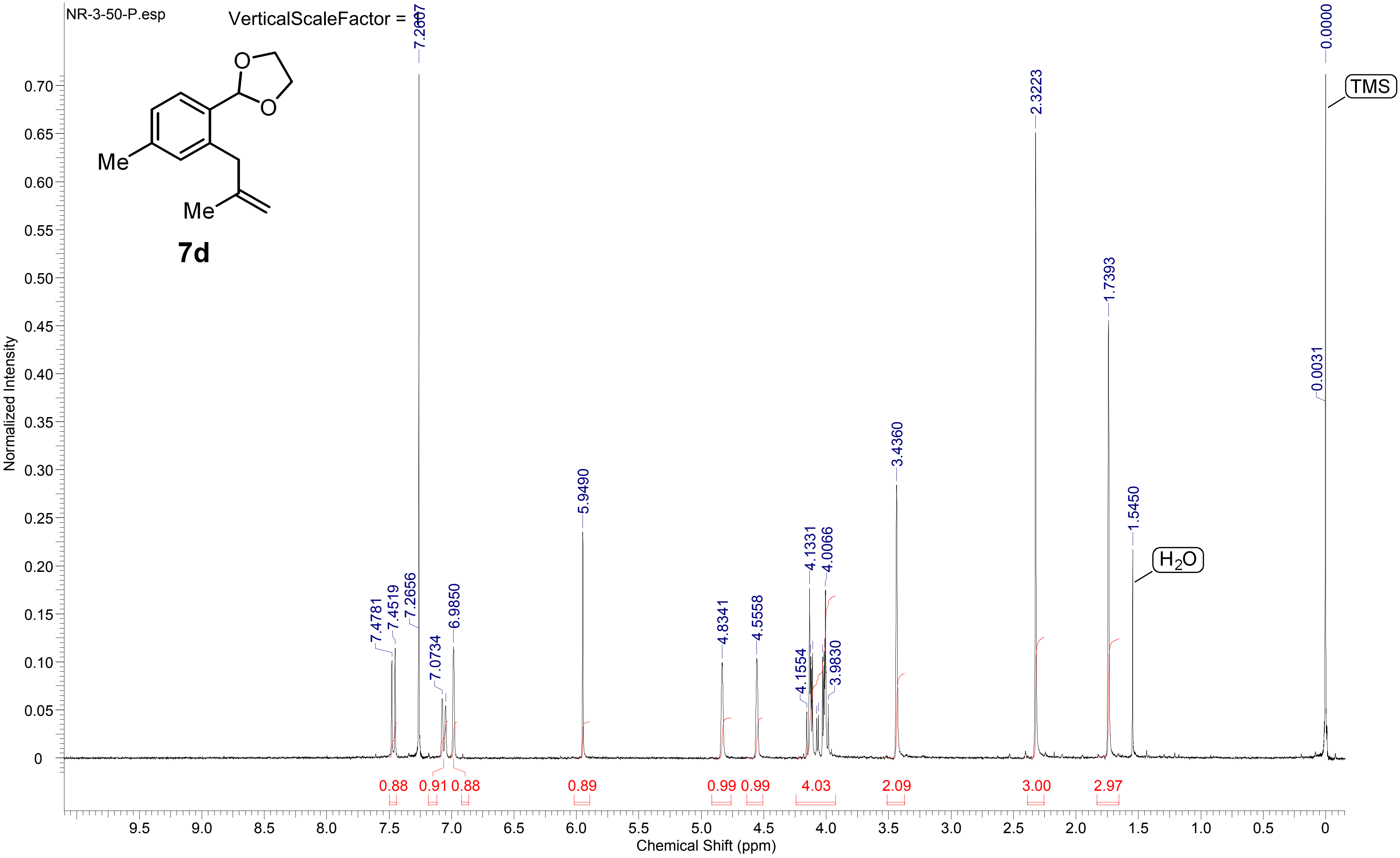
9/26/2013 5:00:03 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-49-P University of Minnesota Department of Chemistry VAC-300				
Date	May 1 2013	***Date Stamp***	May 1 2013	***File Name***	C:\Users\Naveen\Desktop\130501v3_4102.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.4790	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



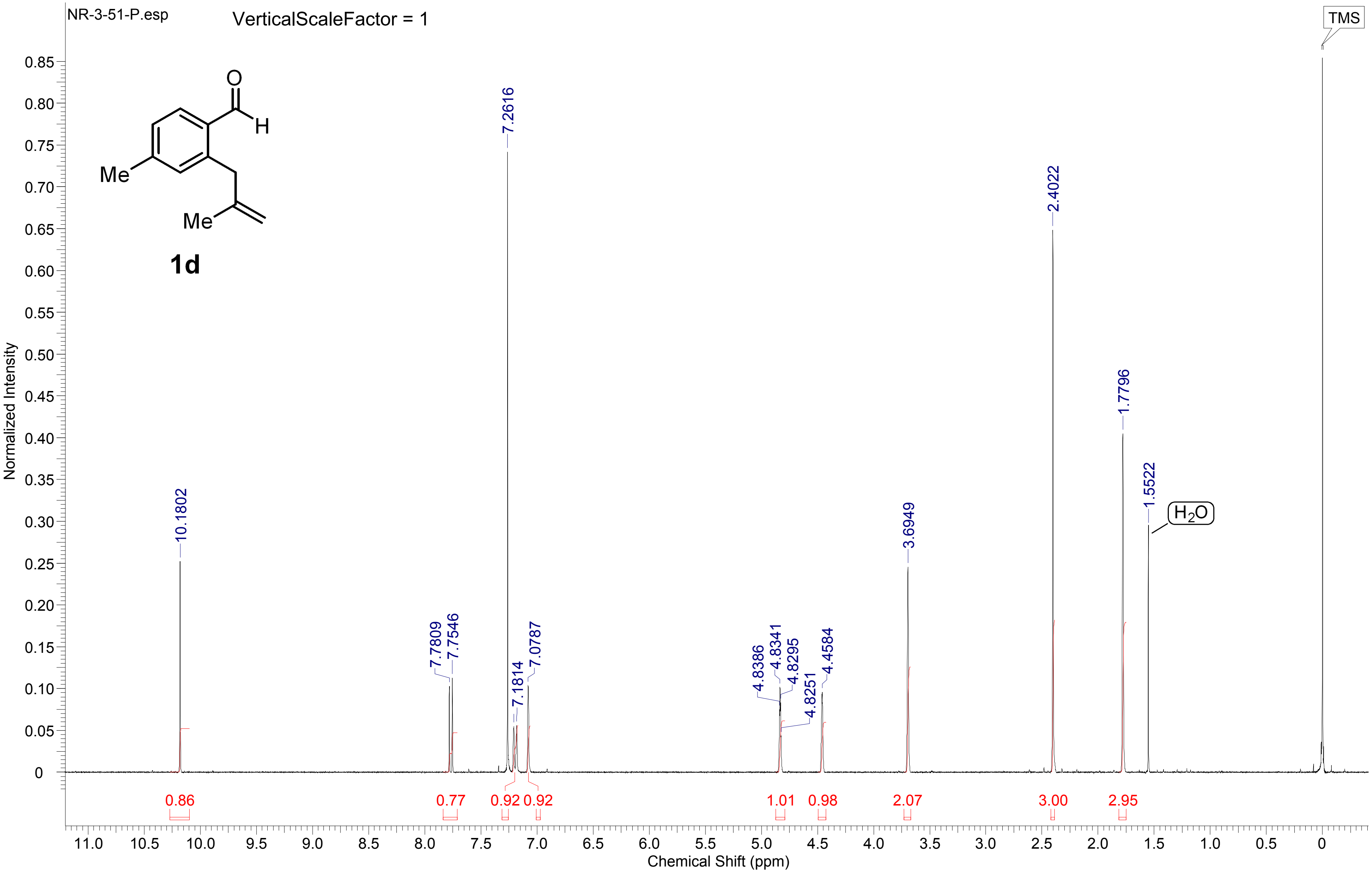
9/26/2013 5:07:44 PM

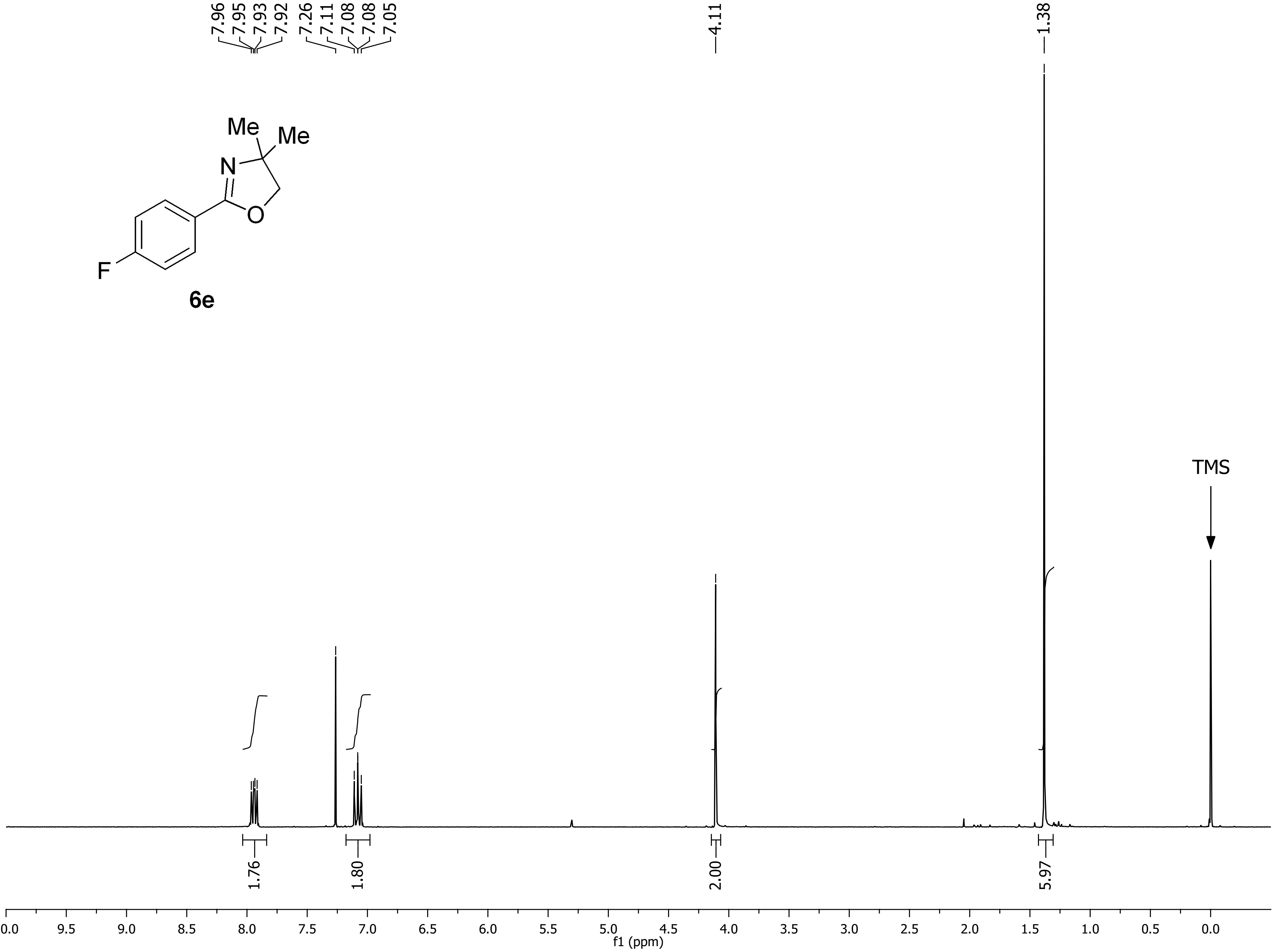
Acquisition Time (sec)	2.0001	***Comment***	NR-3-50-P University of Minnesota Department of Chemistry VAC-300				
Date	May 3 2013	***Date Stamp***	May 3 2013	***File Name***	C:\Users\Naveen\Desktop\130503v3_0802.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.4331	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



9/26/2013 5:14:56 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-51-P University of Minnesota Department of Chemistry VAC-300				
Date	May 4 2013	***Date Stamp***	May 4 2013	***File Name***	C:\Users\Naveen\Desktop\130504v3_0502.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5706	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE

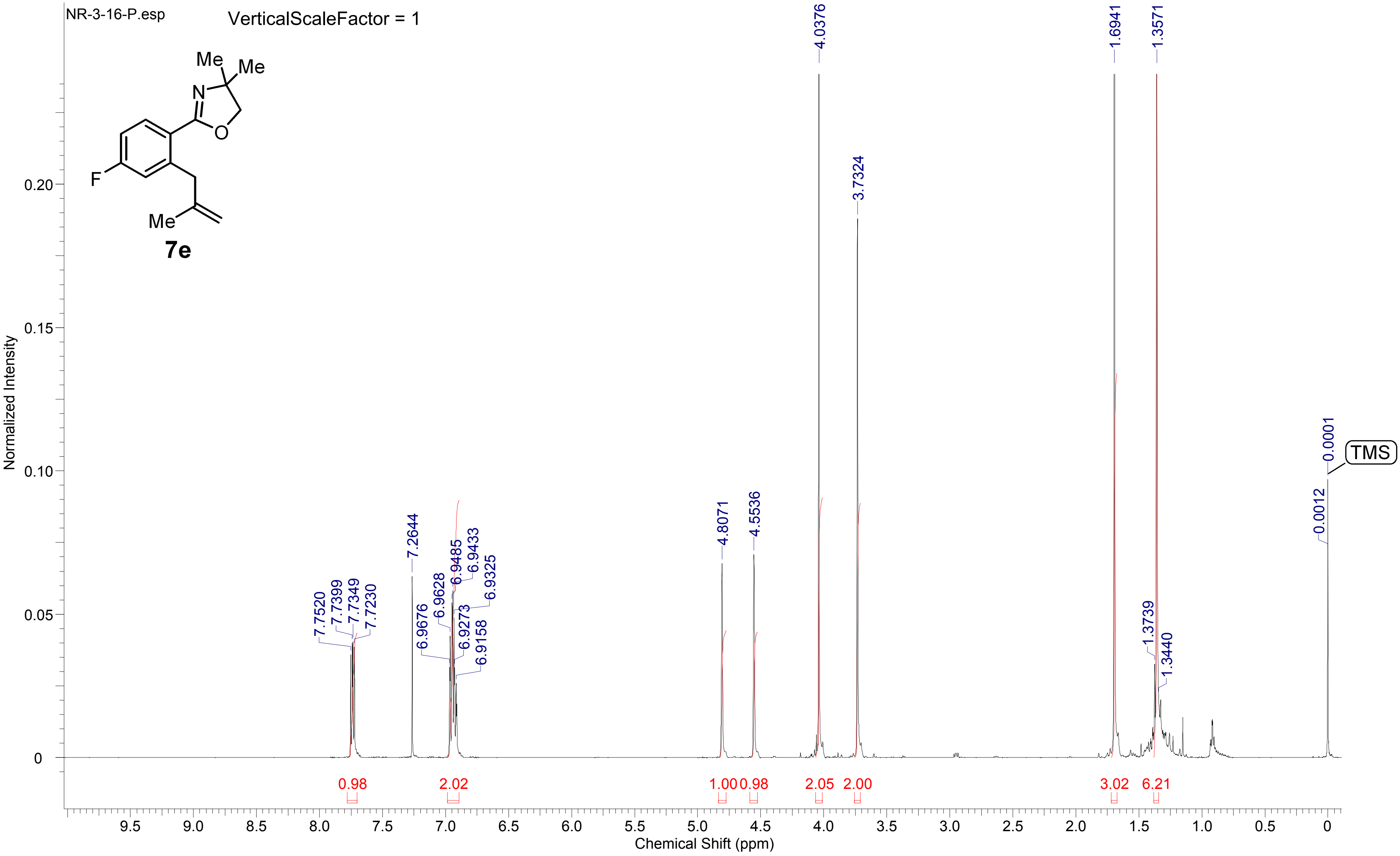



7.96
7.95
7.93
7.92
7.26
7.11
7.08
7.08
7.05
4.11
1.38
Me
Me
N
O
F
TMS
1.76
1.80
2.00
5.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

6e

9/27/2013 10:31:34 AM

Acquisition Time (sec)	1.8920	***Comment***	Univ of Minnesota, VI-500			***Date***	Jan 8 2013
Date Stamp	Jan 8 2013	***File Name***	C:\Users\Naveen\Desktop\NR-3-16-P.fid\fid			***Frequency (MHz)***	499.87
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	15136	***Points Count***	131072
Pulse Sequence	s2pul	***Receiver Gain***	54.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2498.9509	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE



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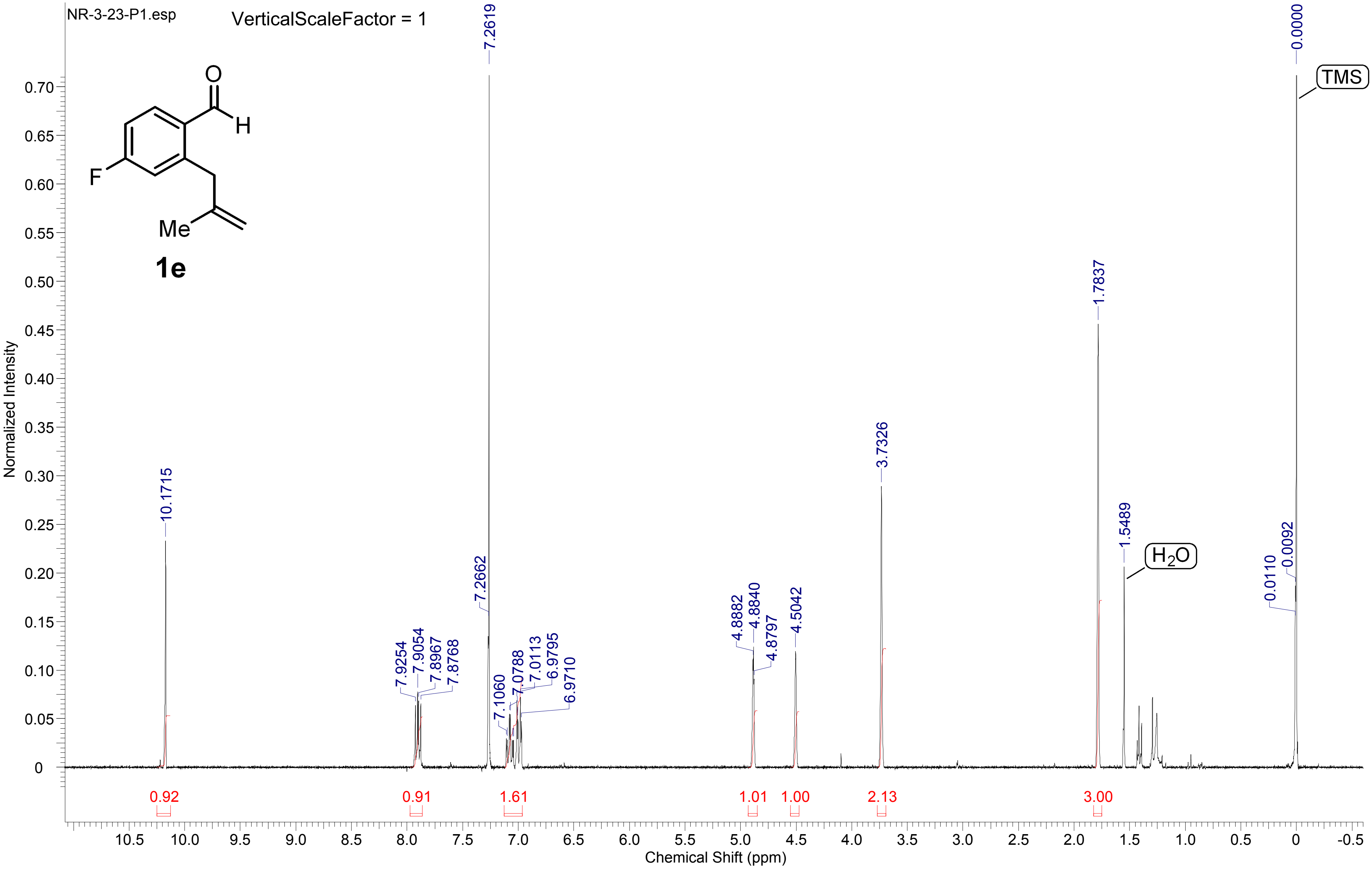
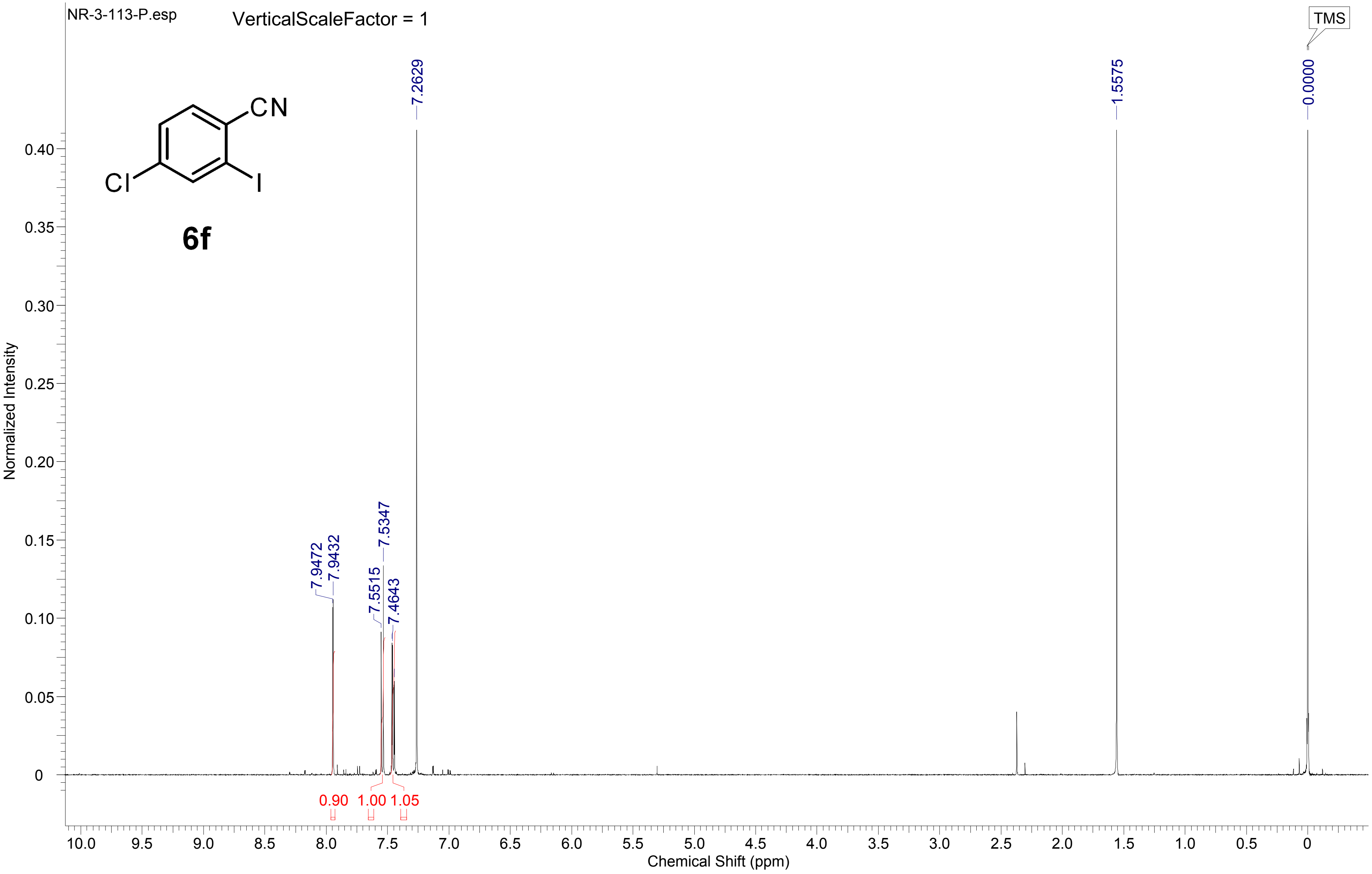
9/27/2013 10:41:21 AM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-23-P1 University of Minnesota Department of Chemistry VAC-300				
Date	Mar 15 2013	***Date Stamp***	Mar 15 2013	***File Name***	C:\Users\Naveen\Desktop\130315v3_1402.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7993	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



9/27/2013 11:37:13 AM

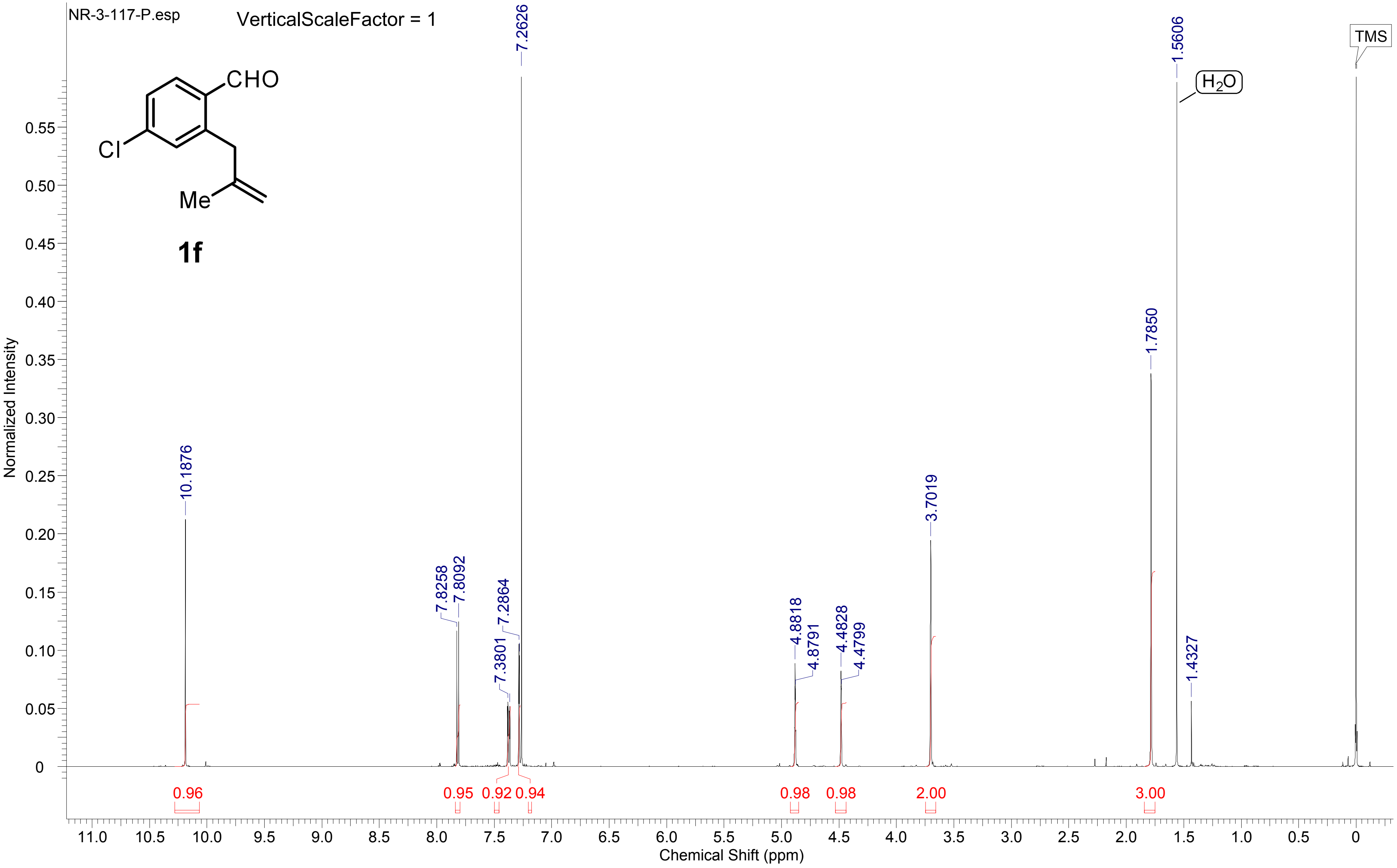
Acquisition Time (sec)	1.8920	***Comment***	Univ of Minnesota, VI-500			***Date***	Jul 18 2013
Date Stamp	Jul 18 2013	***File Name***	C:\Users\Naveen\Desktop\Cyanoacylation NMRs\NR-3-112-P.fid\fid				
Frequency (MHz)	499.87	***Nucleus***	1H	***Number of Transients***	8	***Original Points Count***	15136
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2497.6692	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE

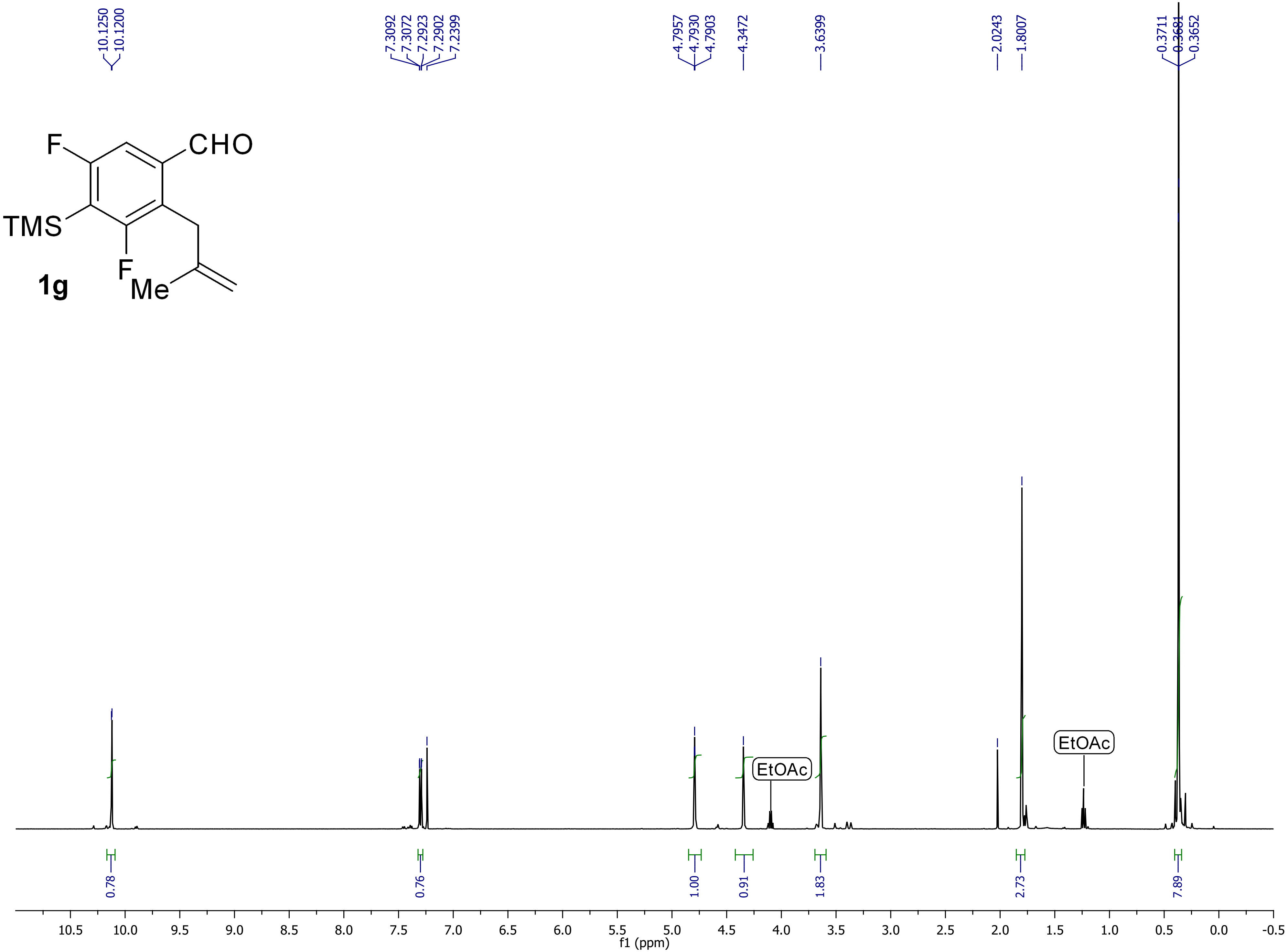


6f

9/27/2013 11:43:42 AM

Acquisition Time (sec)	3.2768	***Date***	20 Jul 2013 16:56:16			***Date Stamp***	20 Jul 2013 16:56:16
File Name	C:\Users\Naveen\Desktop\NR-3-117-P\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	127.25	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3077.3545	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	20.998				




1g
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10.1200
7.3092
7.3072
7.2923
7.2902
7.2399
4.7957
4.7930
4.7903
4.3472
3.6399
2.0243
1.8007
0.3711
0.3681
0.3652
F
CHO
TMS
F
Me
EtOAc
EtOAc
0.78
0.76
1.00
0.91
1.83
2.73
7.89
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

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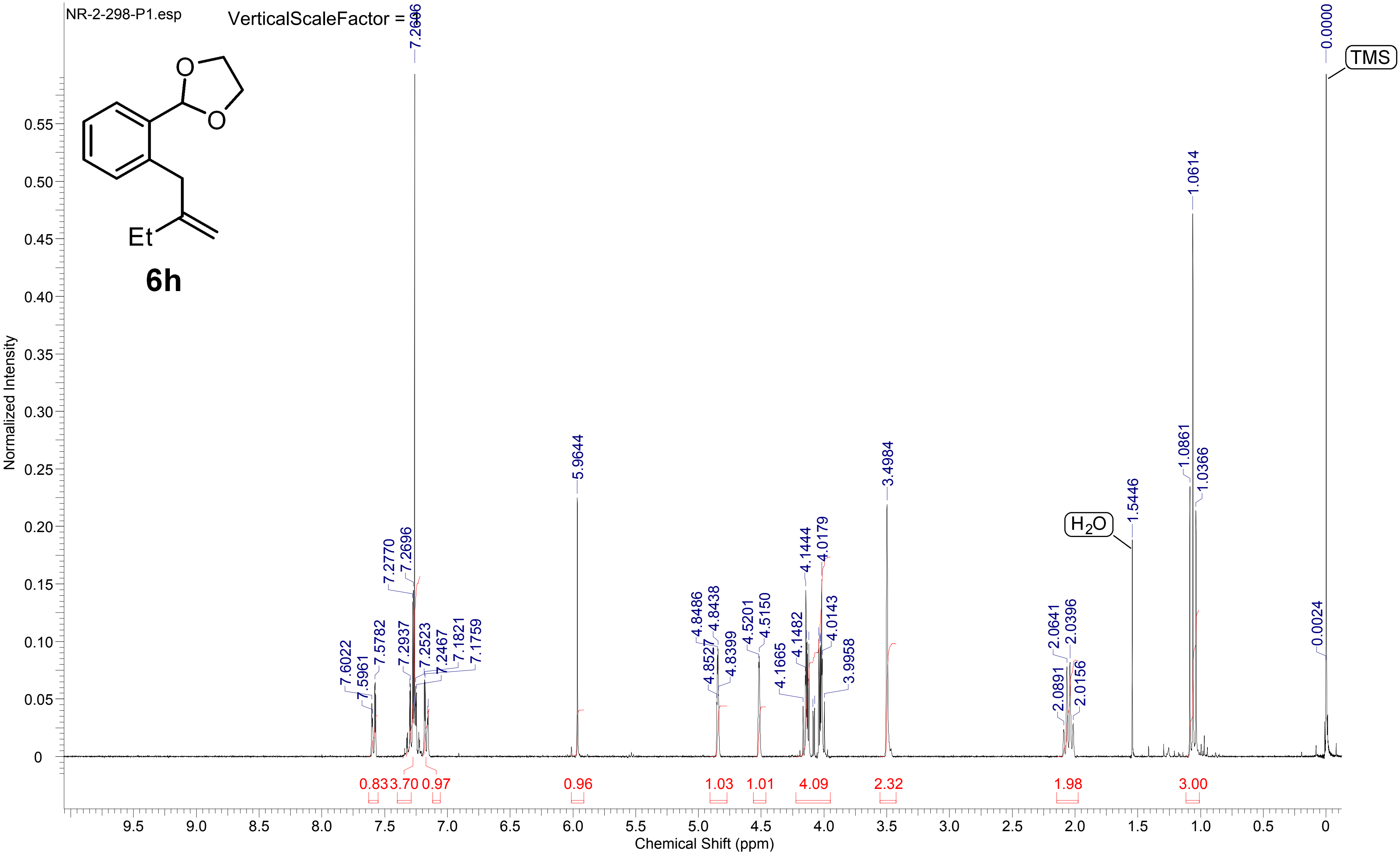
9/27/2013 11:54:24 AM

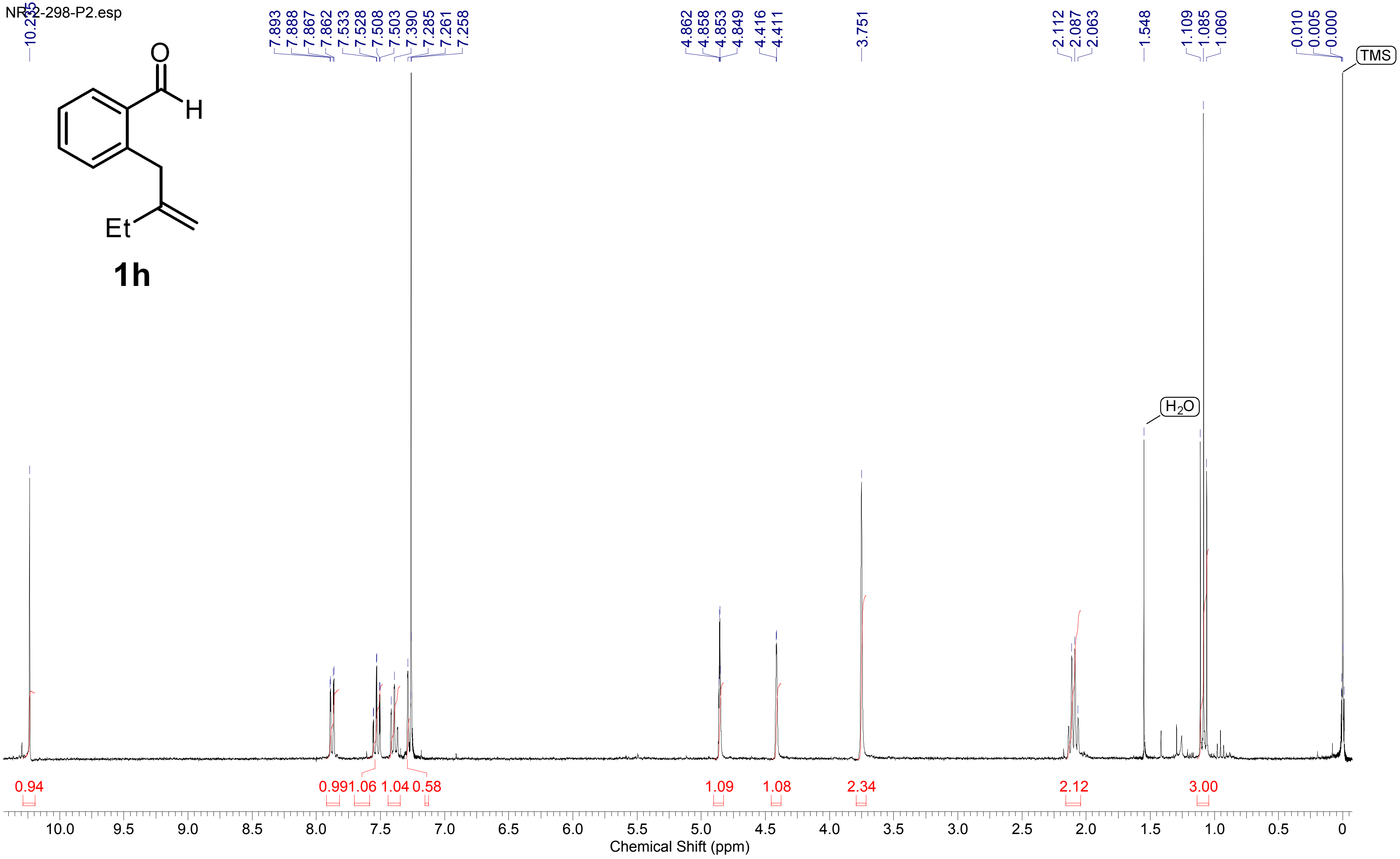
Acquisition Time (sec)	2.0001	***Comment***	NR-2-298-P1 University of Minnesota Department of Chemistry VAC-300				
Date	Dec 13 2012	***Date Stamp***	Dec 13 2012	***File Name***	C:\Users\Naveen\Desktop\121213v3_2302.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.1584	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

1/8/2014 1:13:04 PM

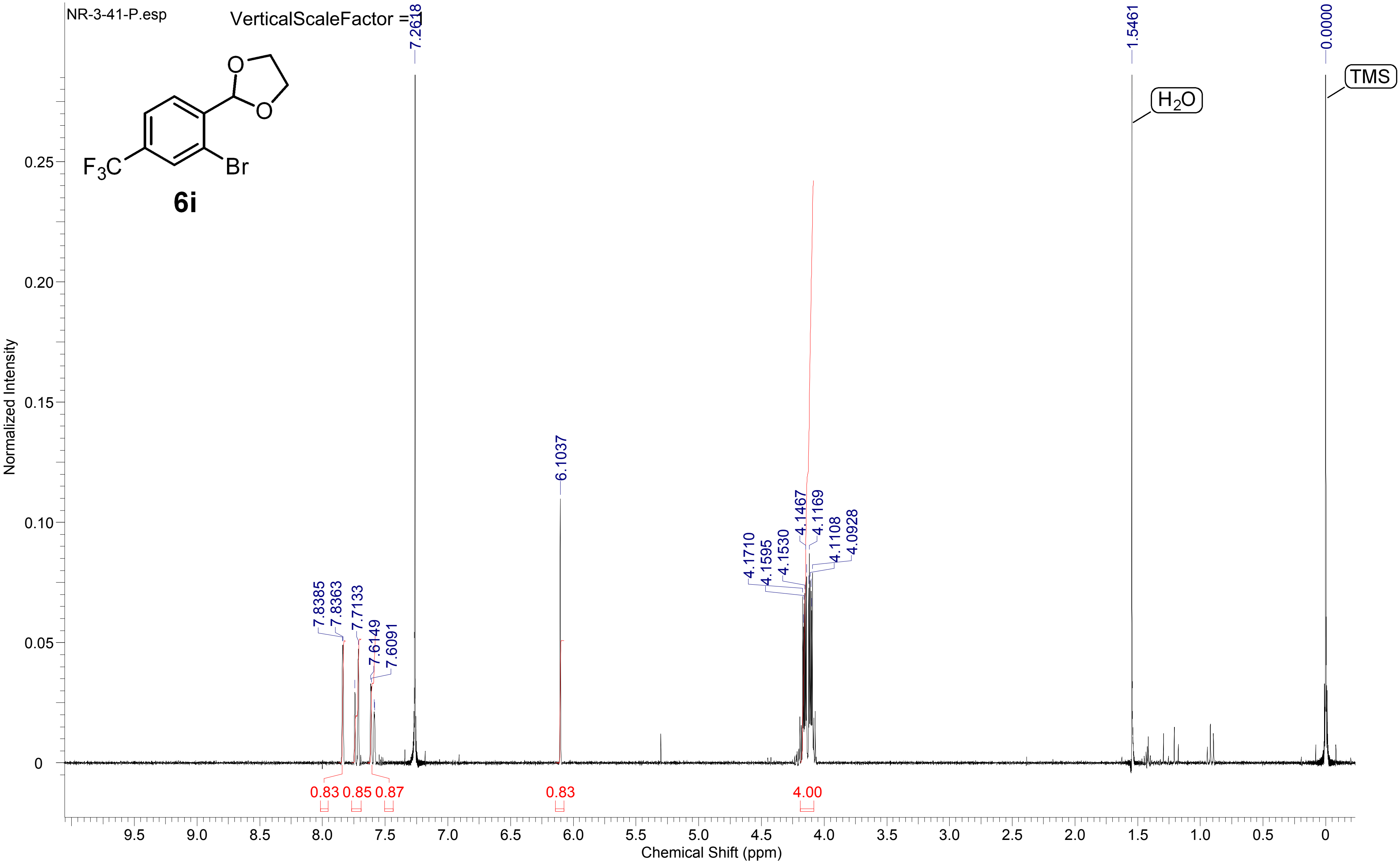
Acquisition Time (sec)	2.0001	***Comment***	NR-2-298-P2 University of Minnesota Department of Chemistry VAC-300				
Date	Dec 14 2012	***Date Stamp***	Dec 14 2012	***File Name***	C:\Users\Naveen\Desktop\121214v3_1302.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5706	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



1h

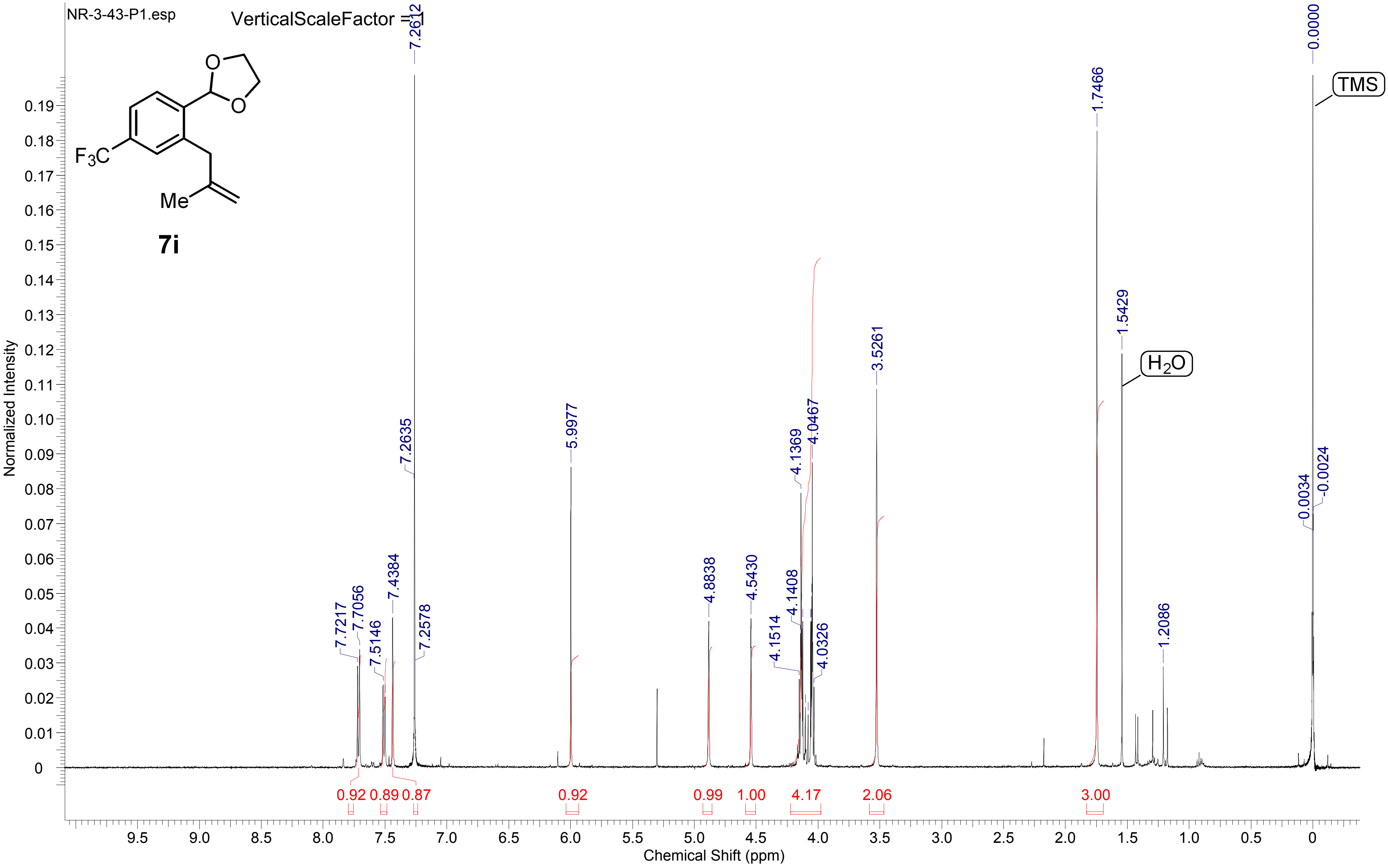
9/27/2013 12:06:27 PM

Acquisition Time (sec)	2.0001	**Comment**	NR-3-41-P University of Minnesota Department of Chemistry VAC-300				
Date	Apr 18 2013	**Date Stamp**	Apr 18 2013	**File Name**	C:\Users\Naveen\Desktop\130418v3_4302.fid\fid		
Frequency (MHz)	299.96	**Nucleus**	1H	**Number of Transients**	16	**Original Points Count**	11998
Points Count	131072	**Pulse Sequence**	s2pul	**Receiver Gain**	38.00	**Solvent**	CHLOROFORM-d
Spectrum Offset (Hz)	2399.5706	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	5998.80	**Temperature (degree C)**	AMBIENT TEMPERATURE



9/27/2013 12:13:30 PM

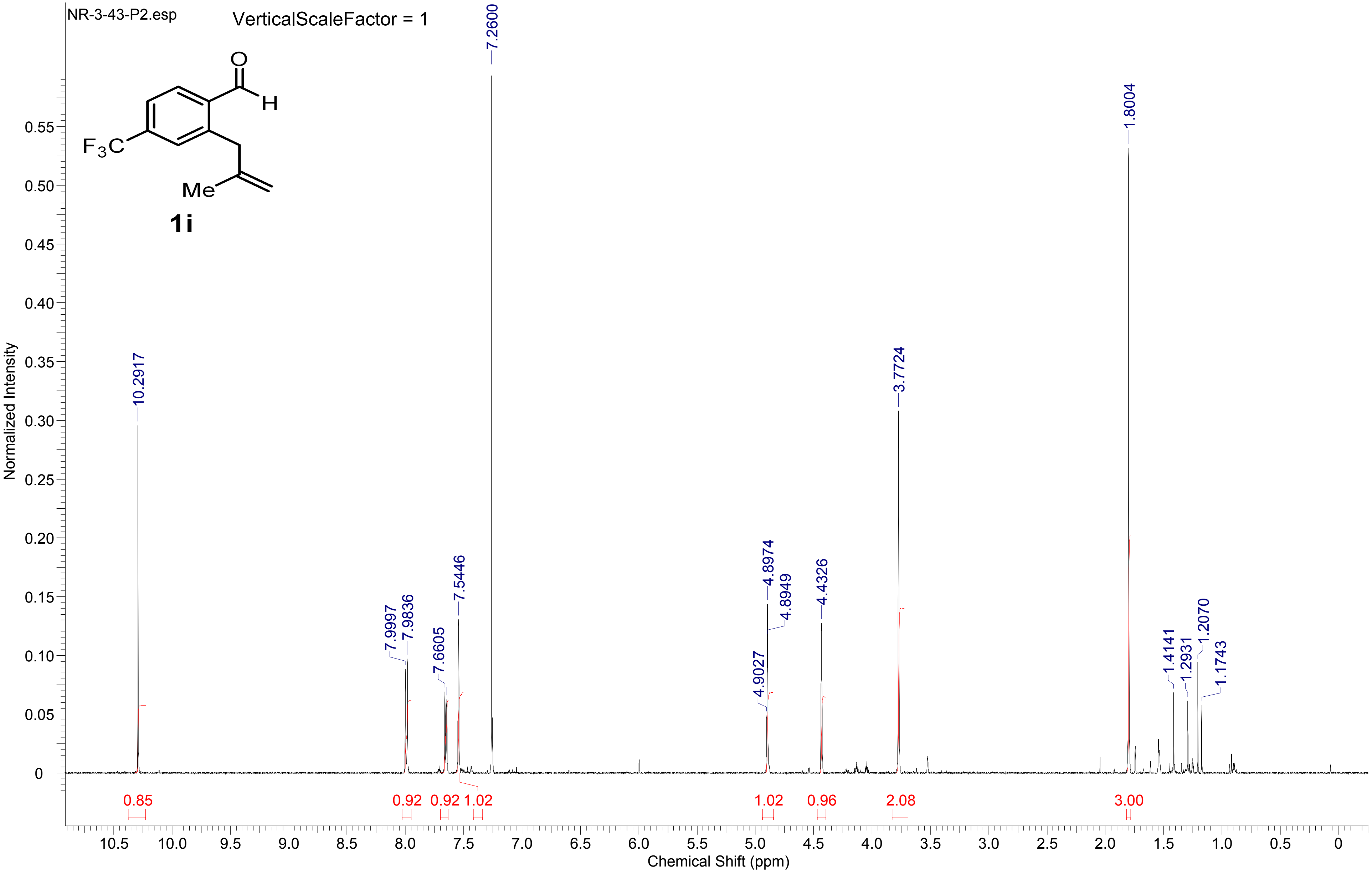
Acquisition Time (sec)	1.8920	***Comment***	Univ of Minnesota, VI-500			***Date***	Apr 25 2013
Date Stamp	Apr 25 2013	***File Name***	C:\Users\Naveen\Desktop\NR-3-43-P1.fid\fid			***Frequency (MHz)***	499.87
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	15136	***Points Count***	131072
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2497.0588	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE



7i

9/27/2013 12:16:07 PM

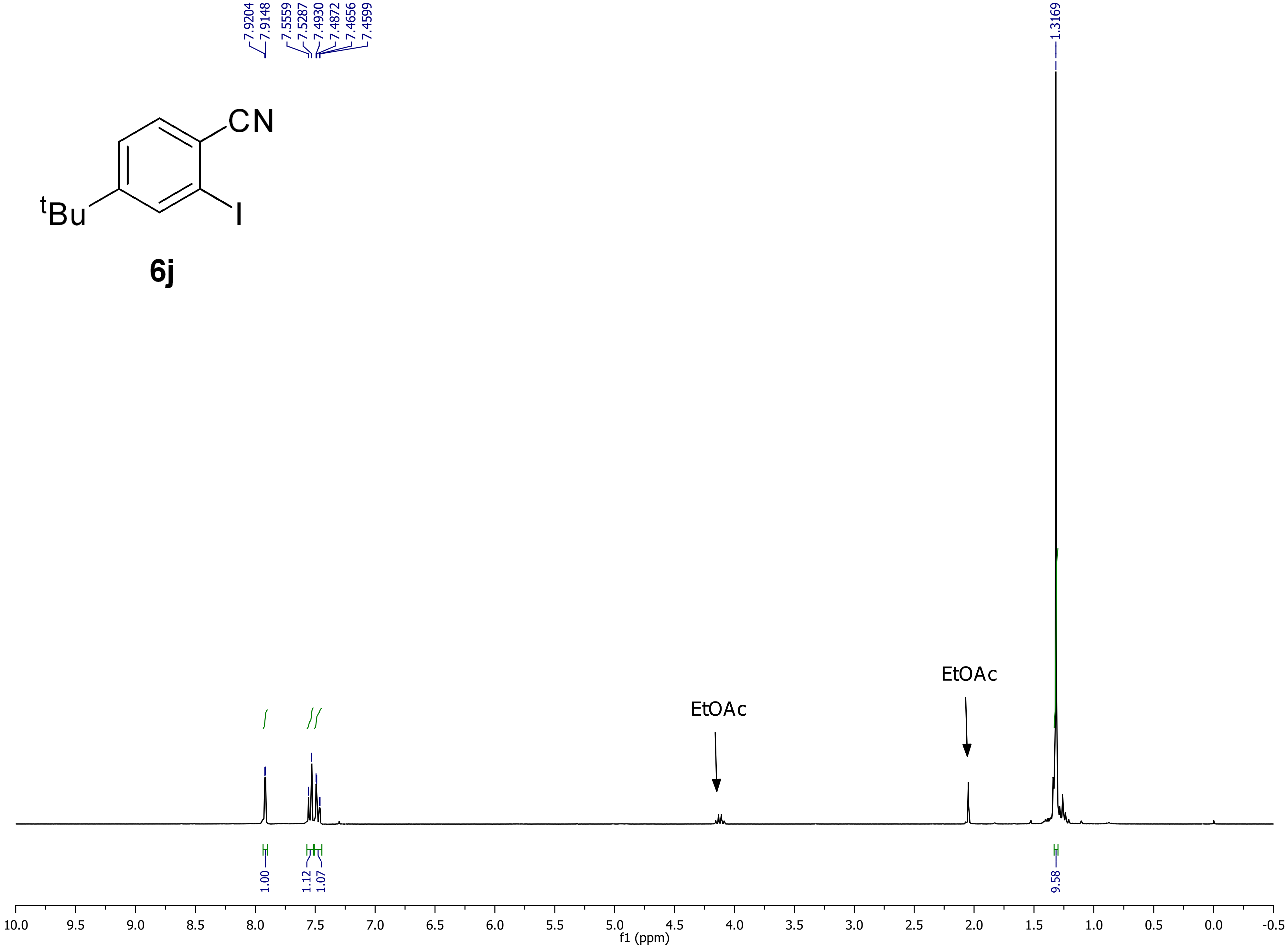
Acquisition Time (sec)	1.8920	***Comment***	Univ of Minnesota, VI-500			***Date***	Apr 25 2013
Date Stamp	Apr 25 2013	***File Name***	C:\Users\Naveen\Desktop\NR-3-43-P2.fid\fid			***Frequency (MHz)***	499.87
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	15136	***Points Count***	131072
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2496.1409	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE



1i

CN
I
tBu

6j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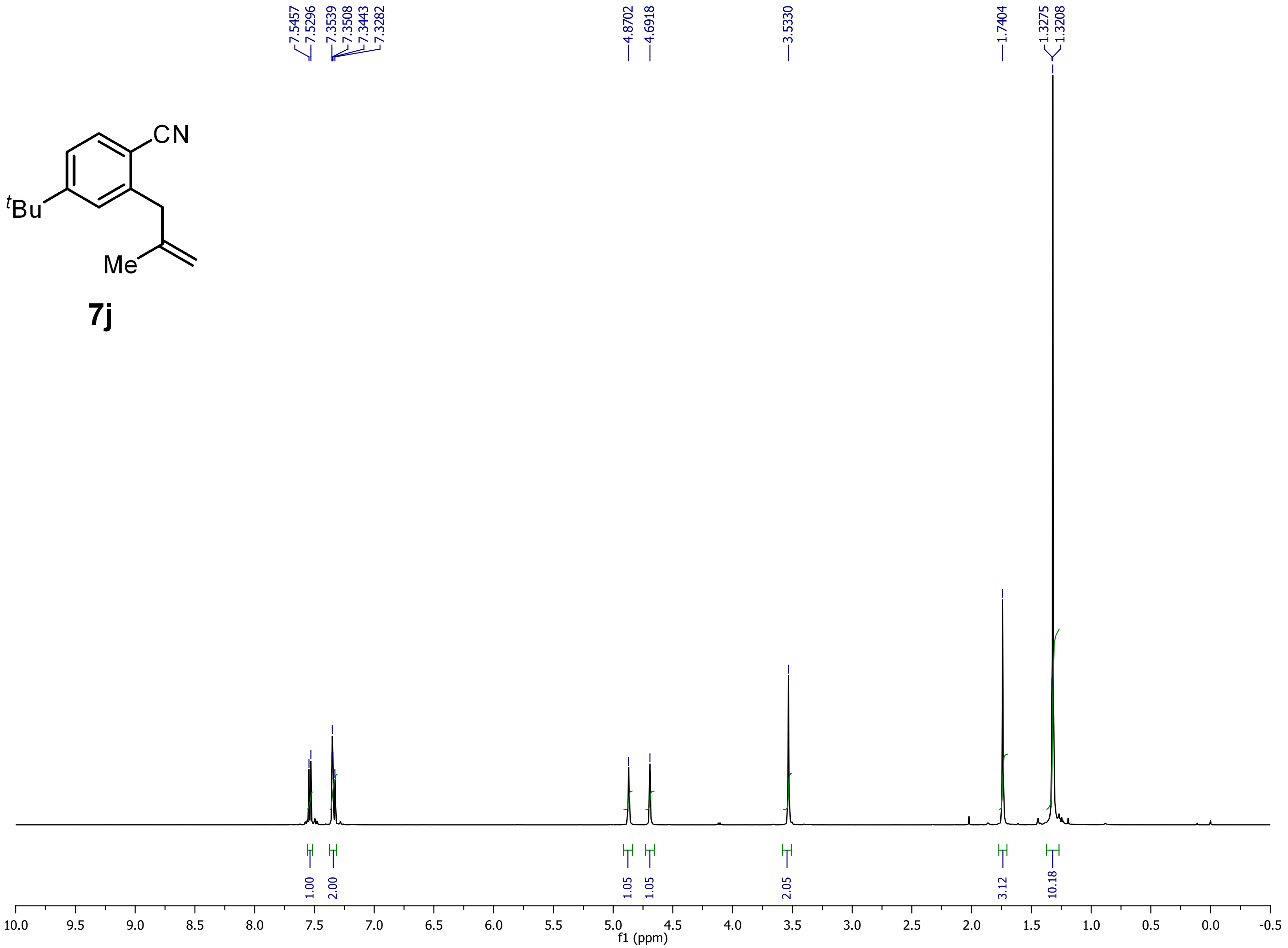
7.4930
7.4872
7.4656
7.4599
1.3169
EtOAc
EtOAc
1.00
1.12
1.07
9.58
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


CN
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Me
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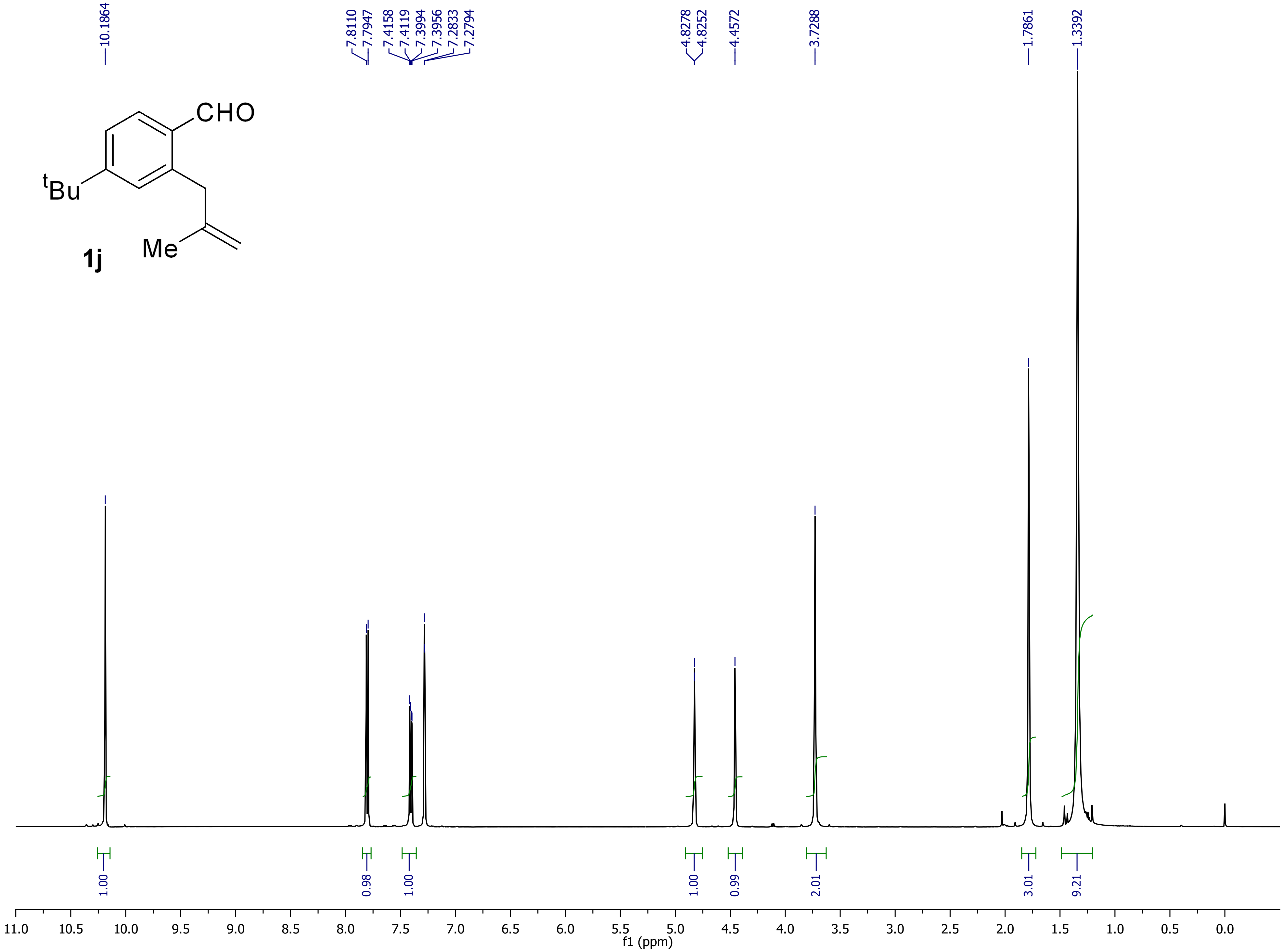
7.5296
7.3539
7.3508
7.3443
7.3282
4.8702
4.6918
3.5330
1.7404
1.3275
1.3208
1.00
2.00
1.05
1.05
2.05
3.12
10.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

7j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7.4158
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4.4572
3.7288
1.7861
1.3392
CHO
tBu
Me
1j
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0.98
1.00
1.00
0.99
2.01
3.01
9.21
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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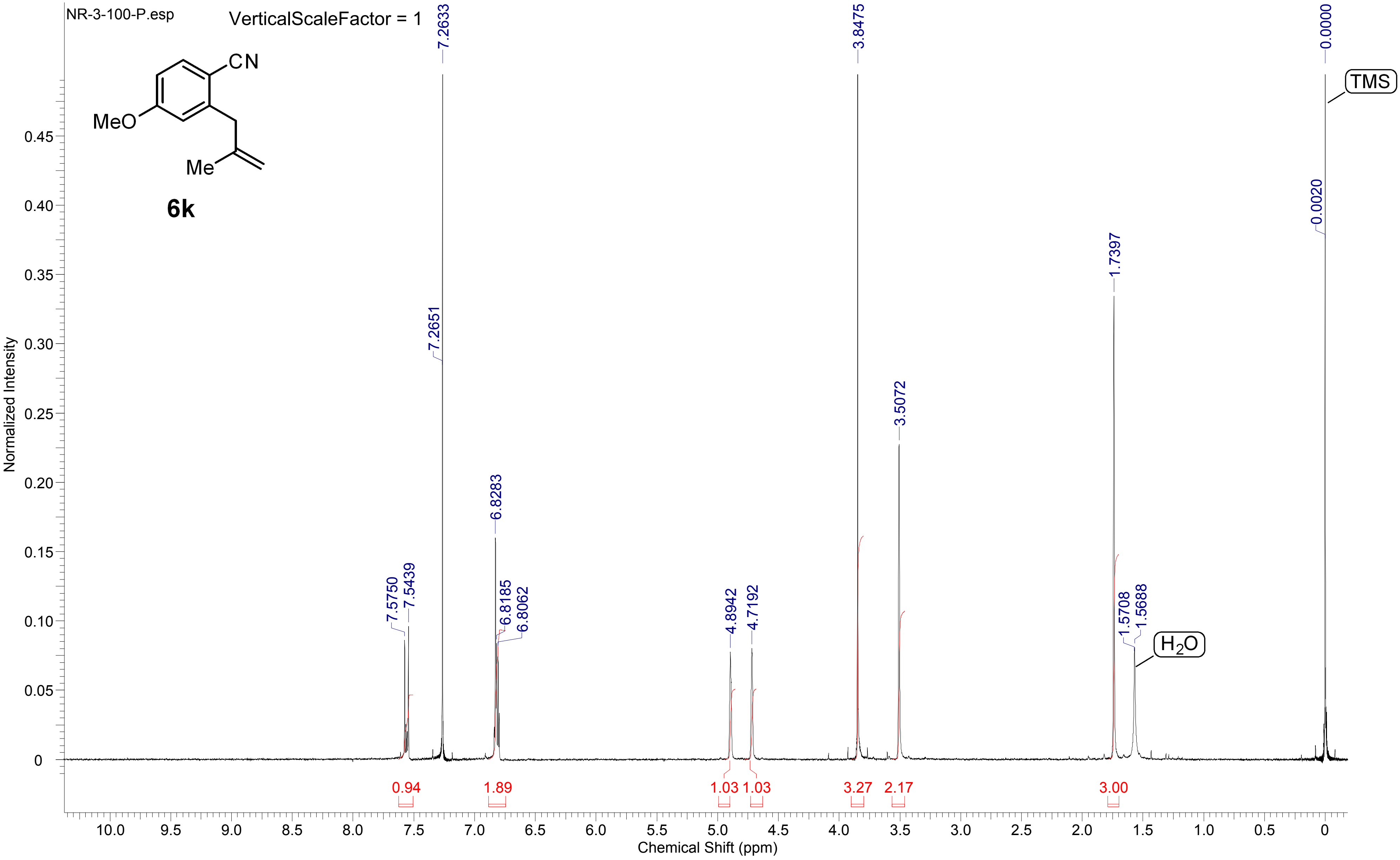
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

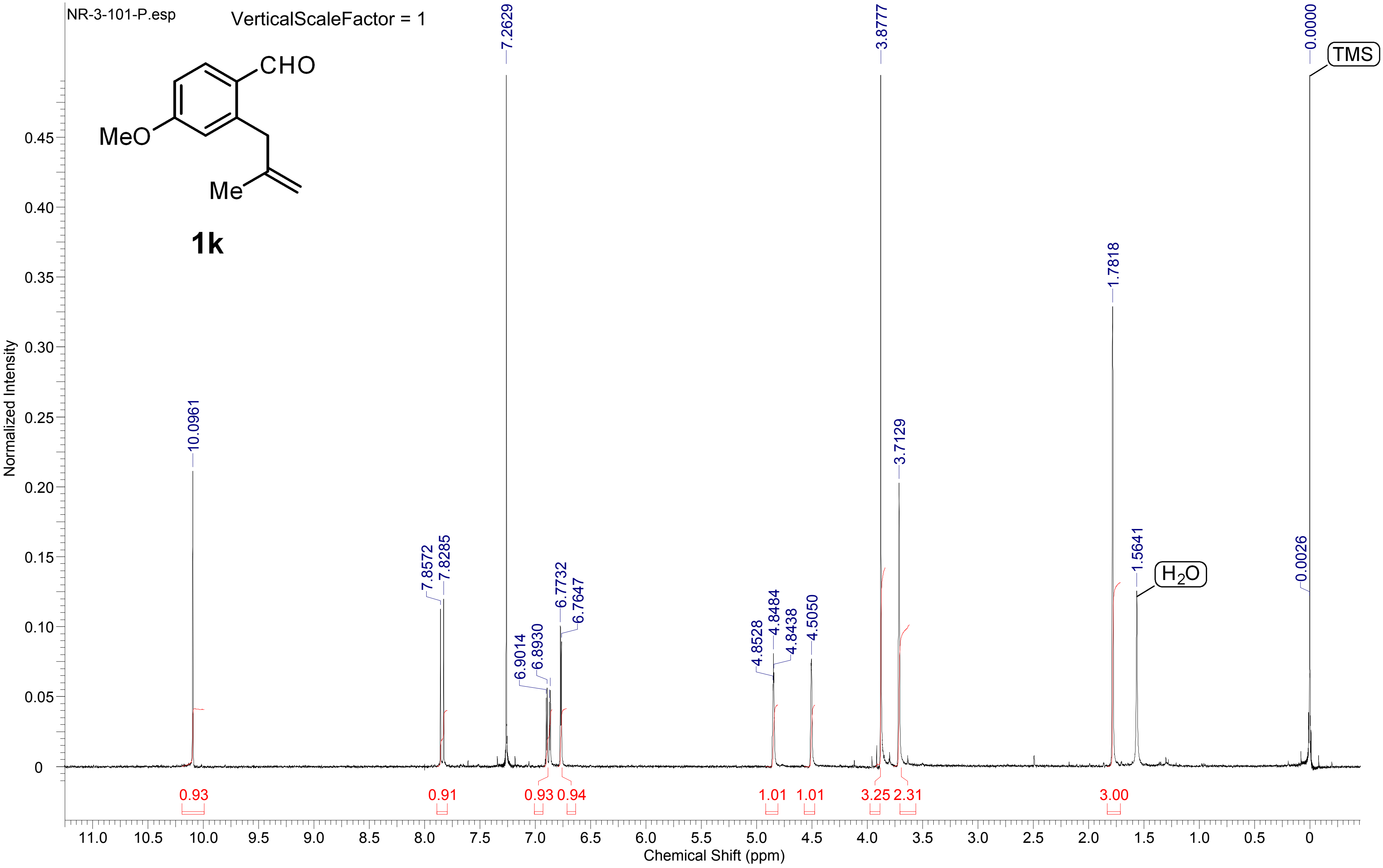
9/27/2013 12:27:10 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-100-P University of Minnesota Department of Chemistry VAC-300				
Date	Jun 26 2013	***Date Stamp***	Jun 26 2013	***File Name***	C:\Users\Naveen\Desktop\130626v3_2402.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2400.0740	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



9/27/2013 12:30:25 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-101-P University of Minnesota Department of Chemistry VAC-300				
Date	Jun 27 2013	***Date Stamp***	Jun 27 2013	***File Name***	C:\Users\Naveen\Desktop\130627v3_6702.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7993	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



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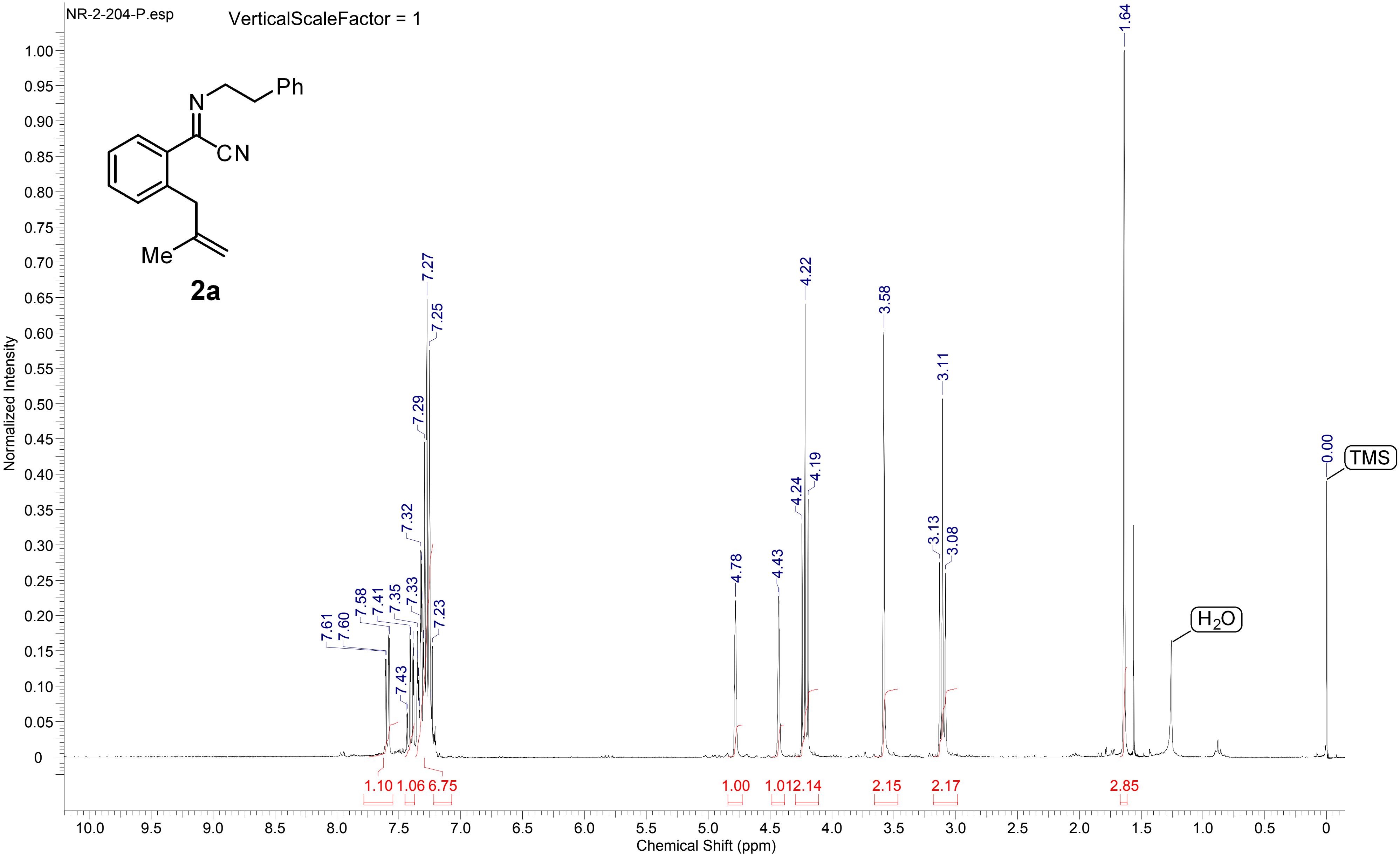
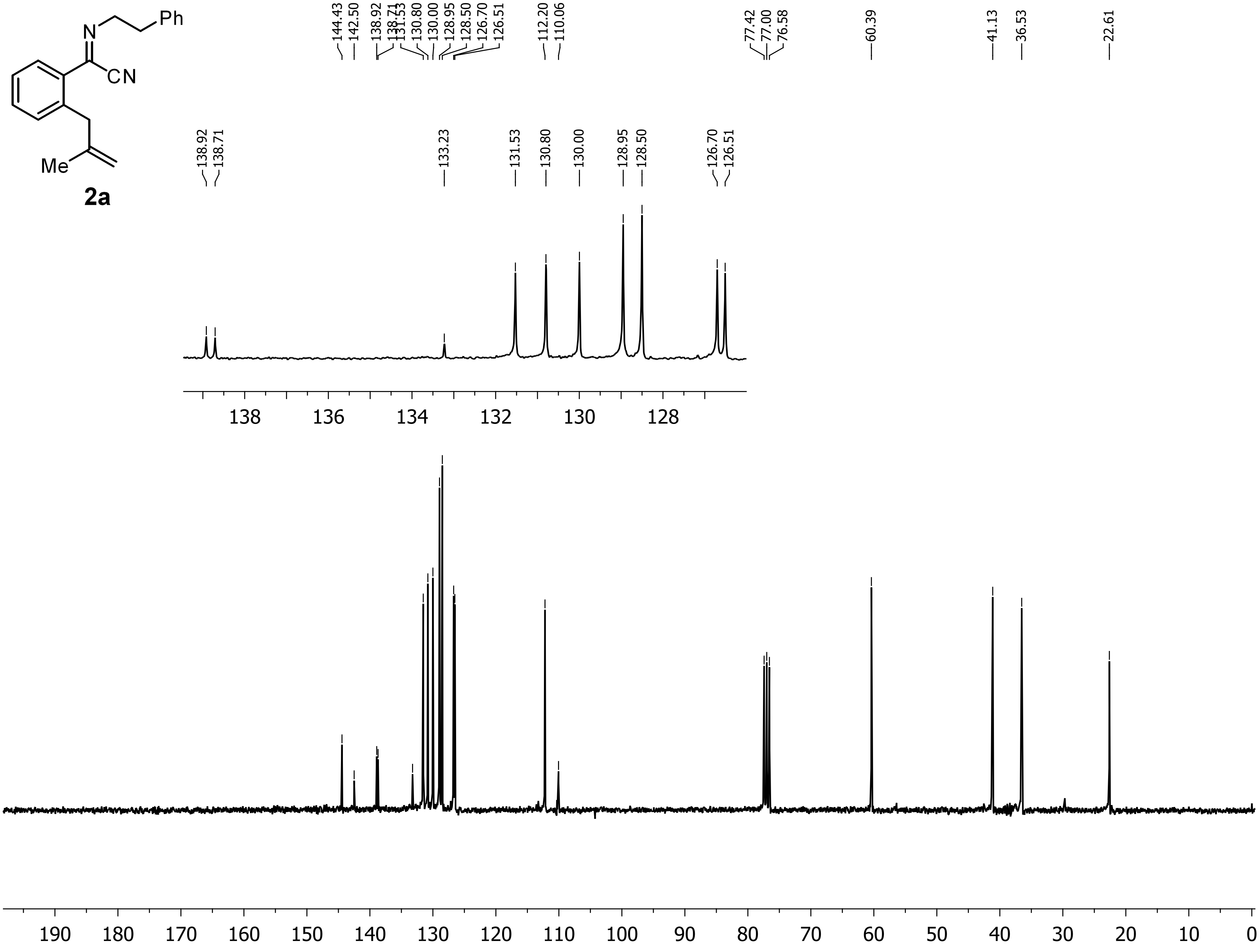
8/22/2013 5:37:35 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-2-204-P University of Minnesota Department of Chemistry VAC-300				
Date	Aug 20 2012	***Date Stamp***	Aug 20 2012	***File Name***	C:\Users\Naveen\Desktop\120820v3_2202.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2396.8245	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE




2a
N
Ph
CN
Me
144.43
142.50
138.92
138.71
131.53
130.80
130.00
128.95
128.50
126.70
126.51
112.20
110.06
77.42
77.00
76.58
60.39
41.13
36.53
22.61
138.92
138.71
133.23
131.53
130.80
130.00
128.95
128.50
126.70
126.51
138
136
134
132
130
128
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

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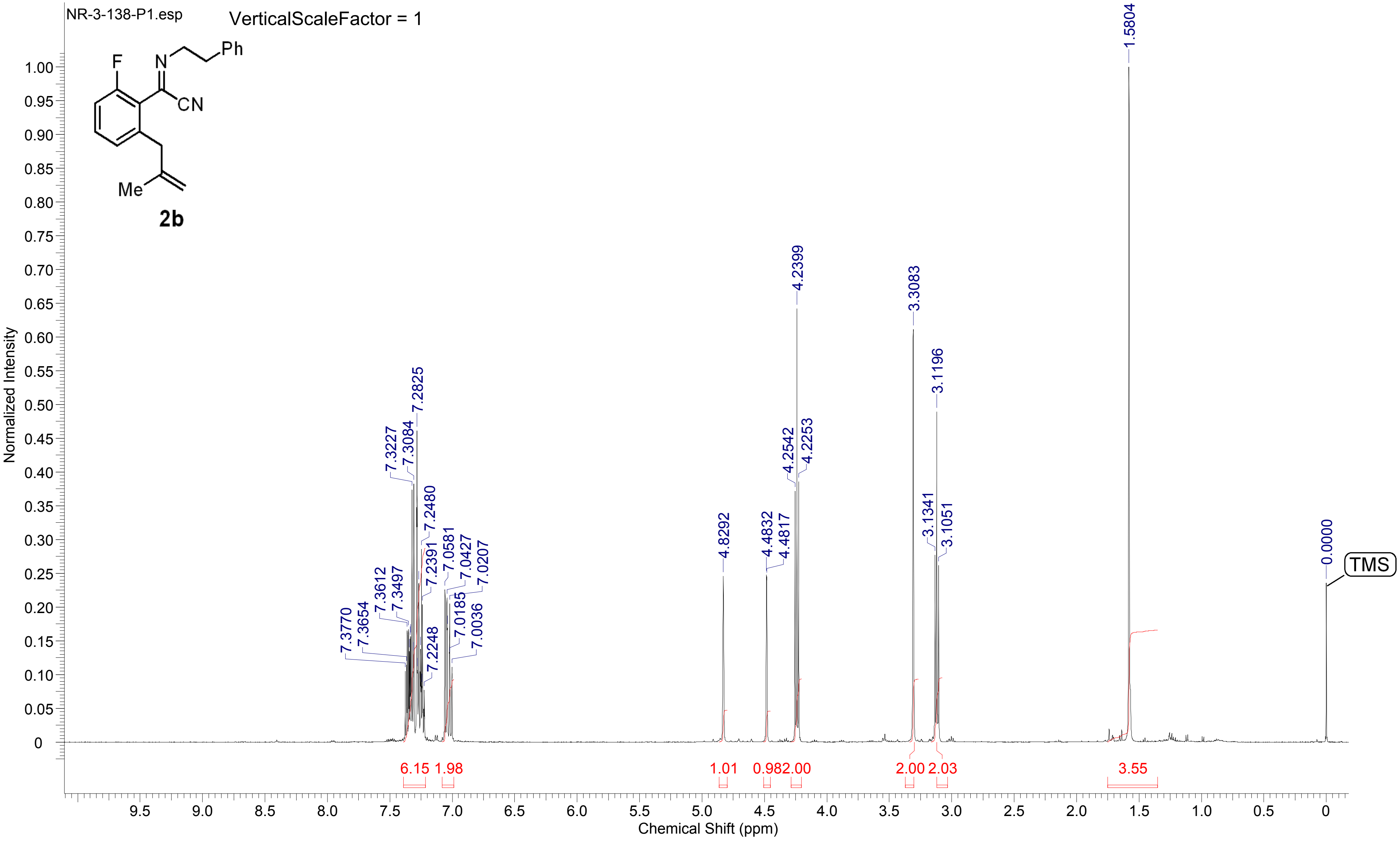
9/24/2013 1:31:52 PM

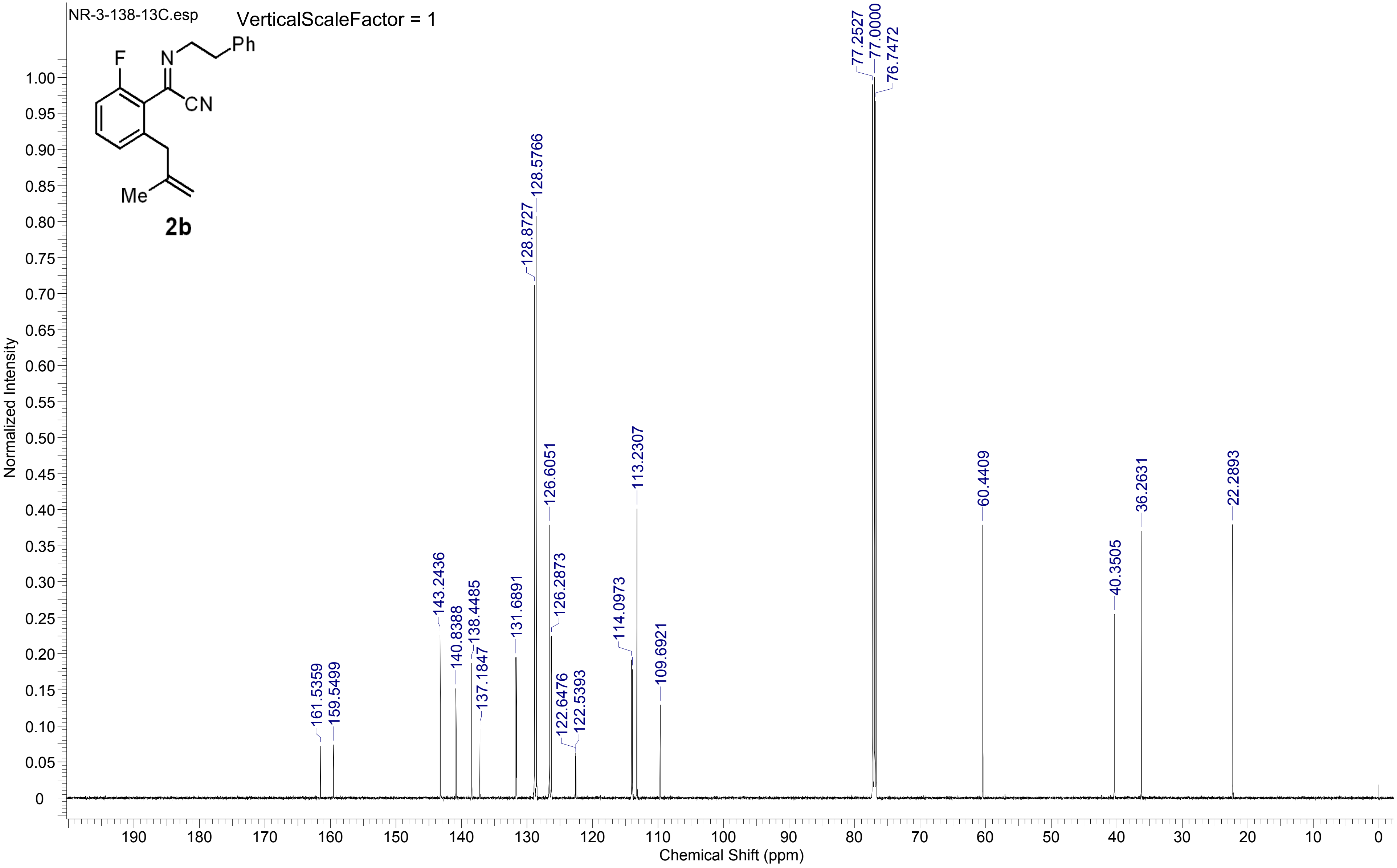
Acquisition Time (sec)	3.2768	***Date***	21 Sep 2013 17:02:40			***Date Stamp***	21 Sep 2013 17:02:40
File Name	C:\Users\Naveen\Desktop\NR-3-138-P1\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	29.25	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3069.8013	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	21.000				



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

9/24/2013 1:55:31 PM

Acquisition Time (sec)	1.1010	***Date***	21 Sep 2013 17:58:08			***Date Stamp***	21 Sep 2013 17:58:08
File Name	C:\Users\Naveen\Desktop\NR-3-138-13C1\10\fid			***Frequency (MHz)***	125.77	***Nucleus***	13C
Number of Transients	1000	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	182.64	***SW(cyclical) (Hz)***	29761.90
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	12566.6855	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.00	***Temperature (degree C)***	20.999				



9/27/2013 1:28:56 PM

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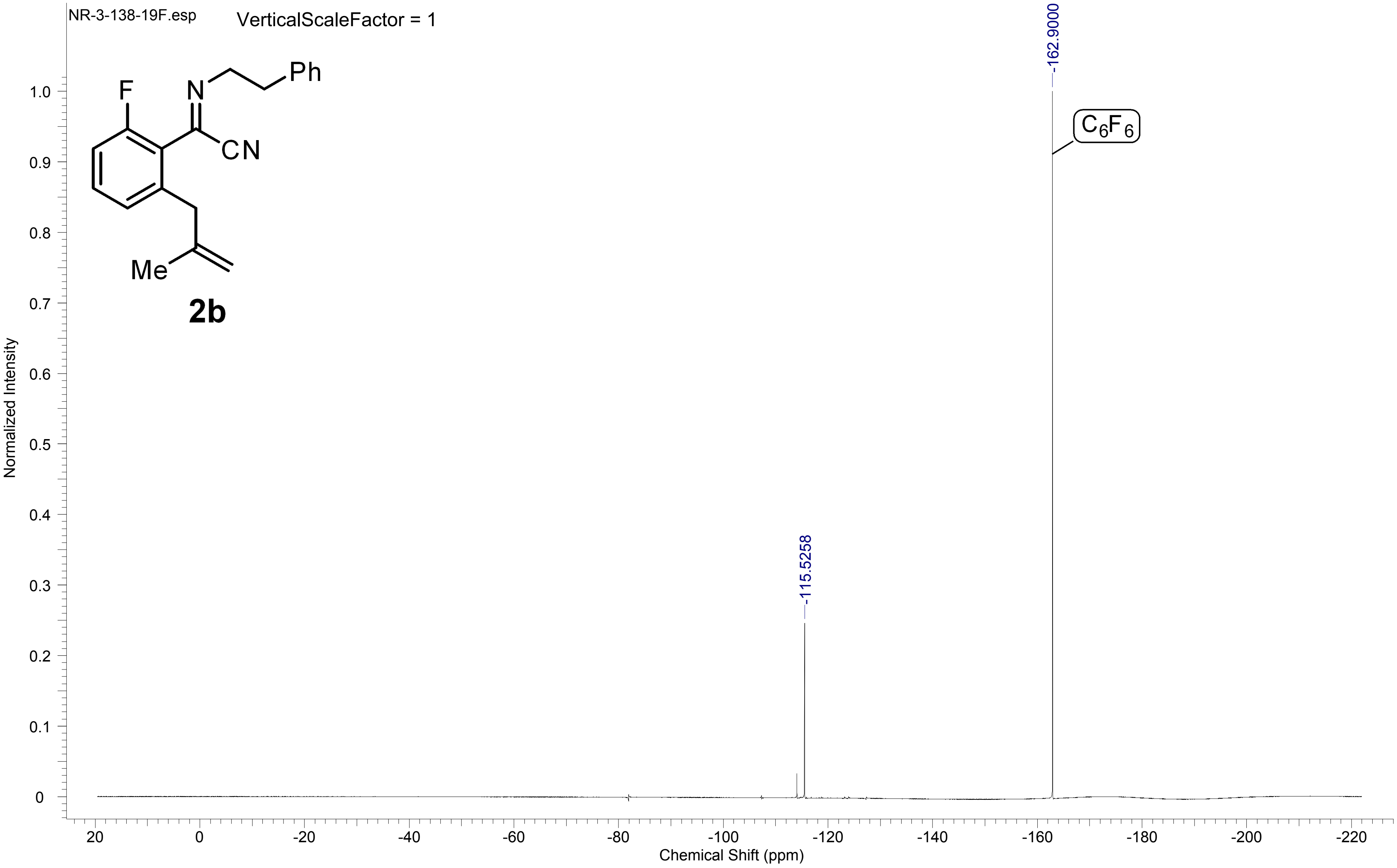
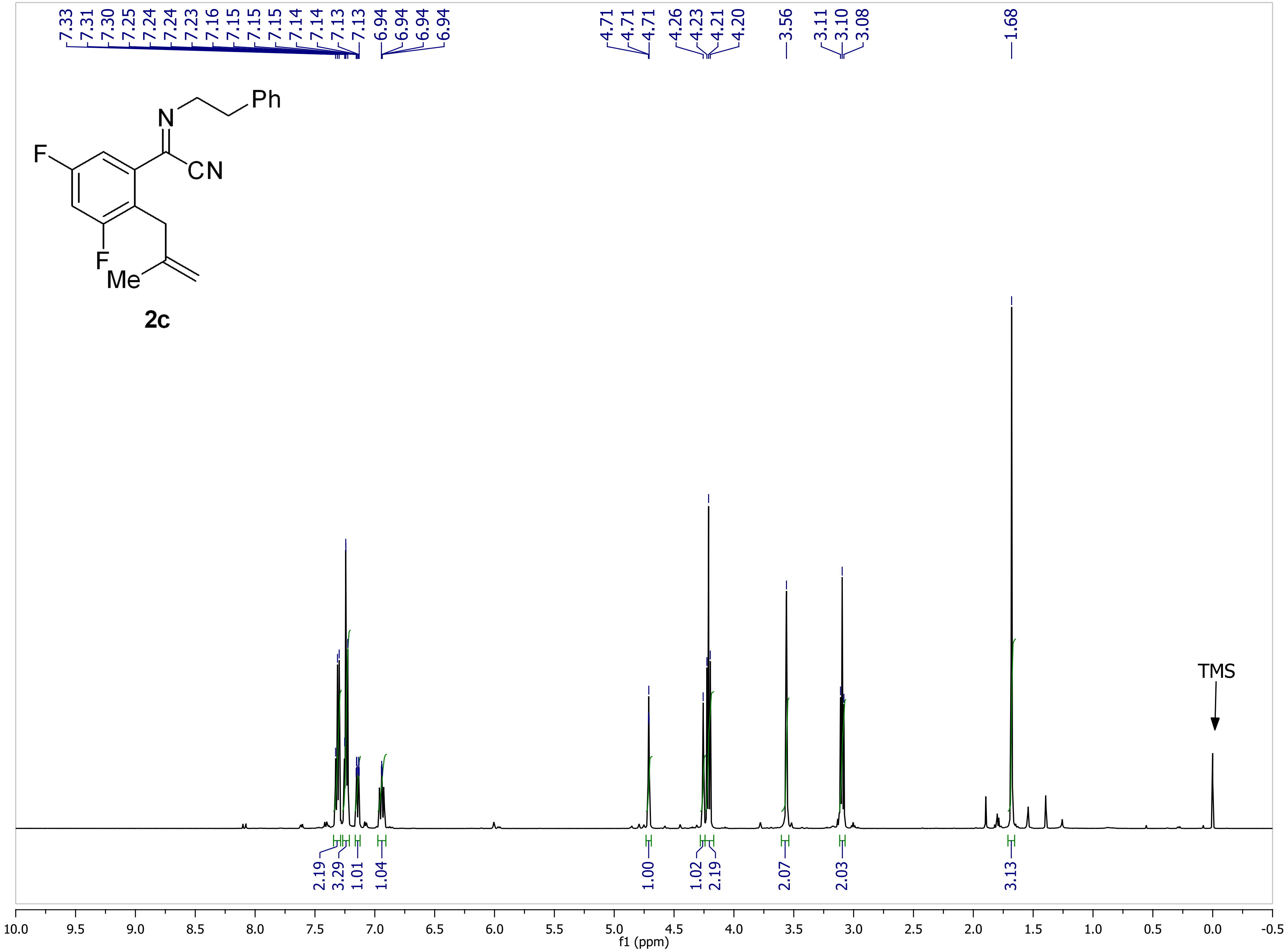
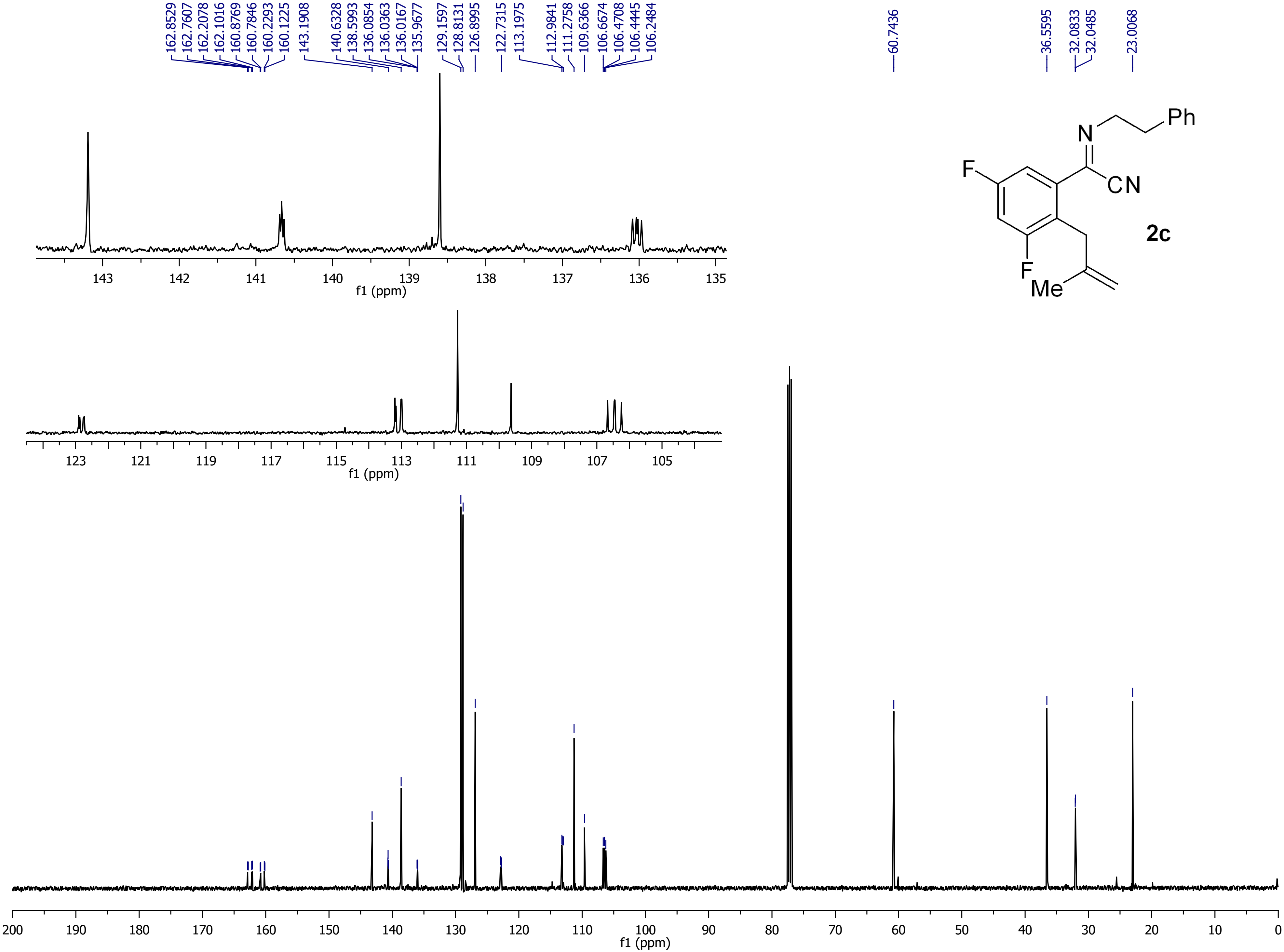
File Name	C:\Users\Naveen\Desktop\NR-3-138-19F\10\fid			***Frequency (MHz)***	470.55	***Nucleus***	19F
Number of Transients	16	***Origin***	spect	***Original Points Count***	65536	***Owner***	auto
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	182.64	***SW(cyclical) (Hz)***	113636.37
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-47628.0508	***Spectrum Type***	STANDARD
Sweep Width (Hz)	113634.63	***Temperature (degree C)***	21.000				

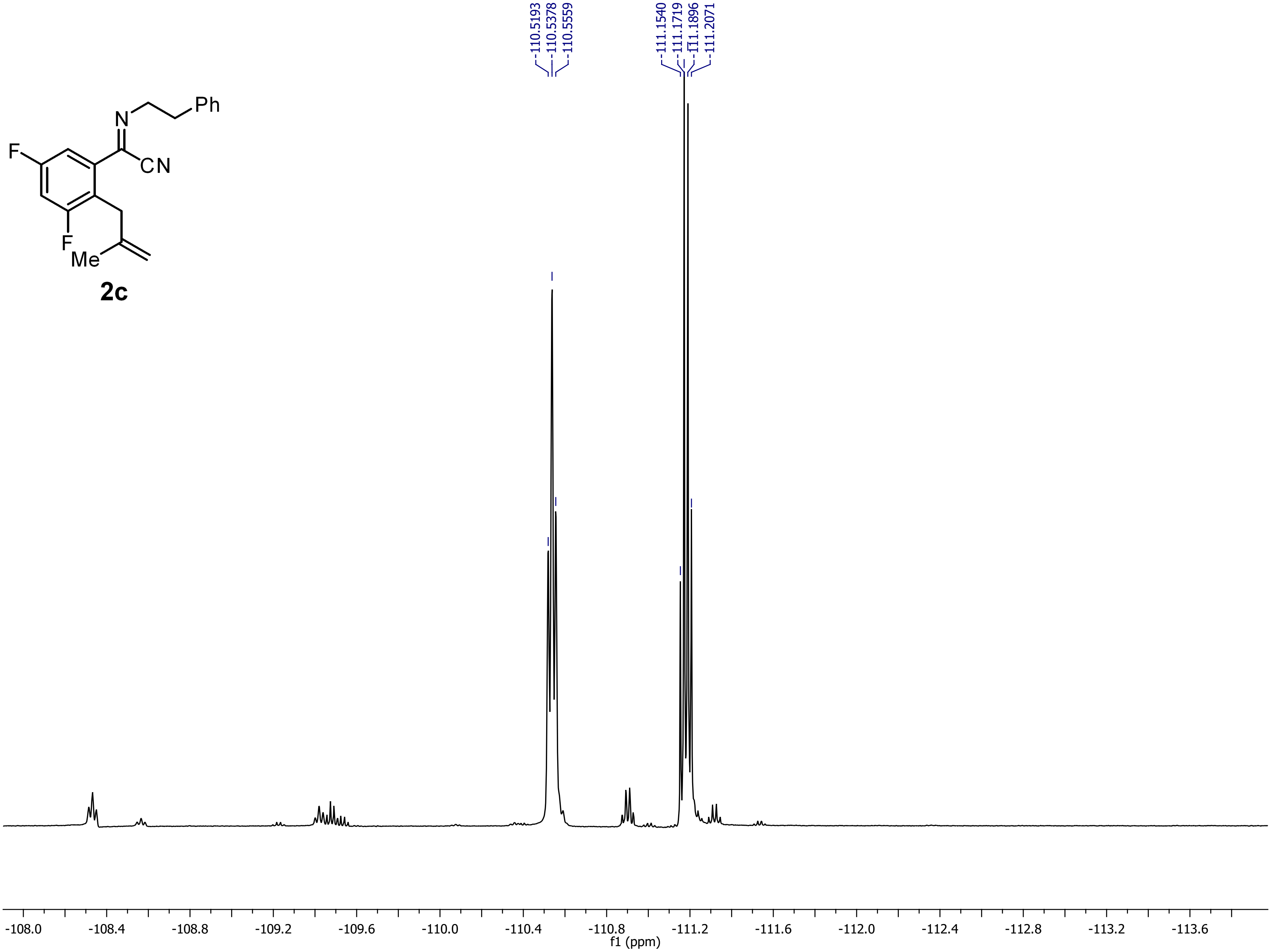


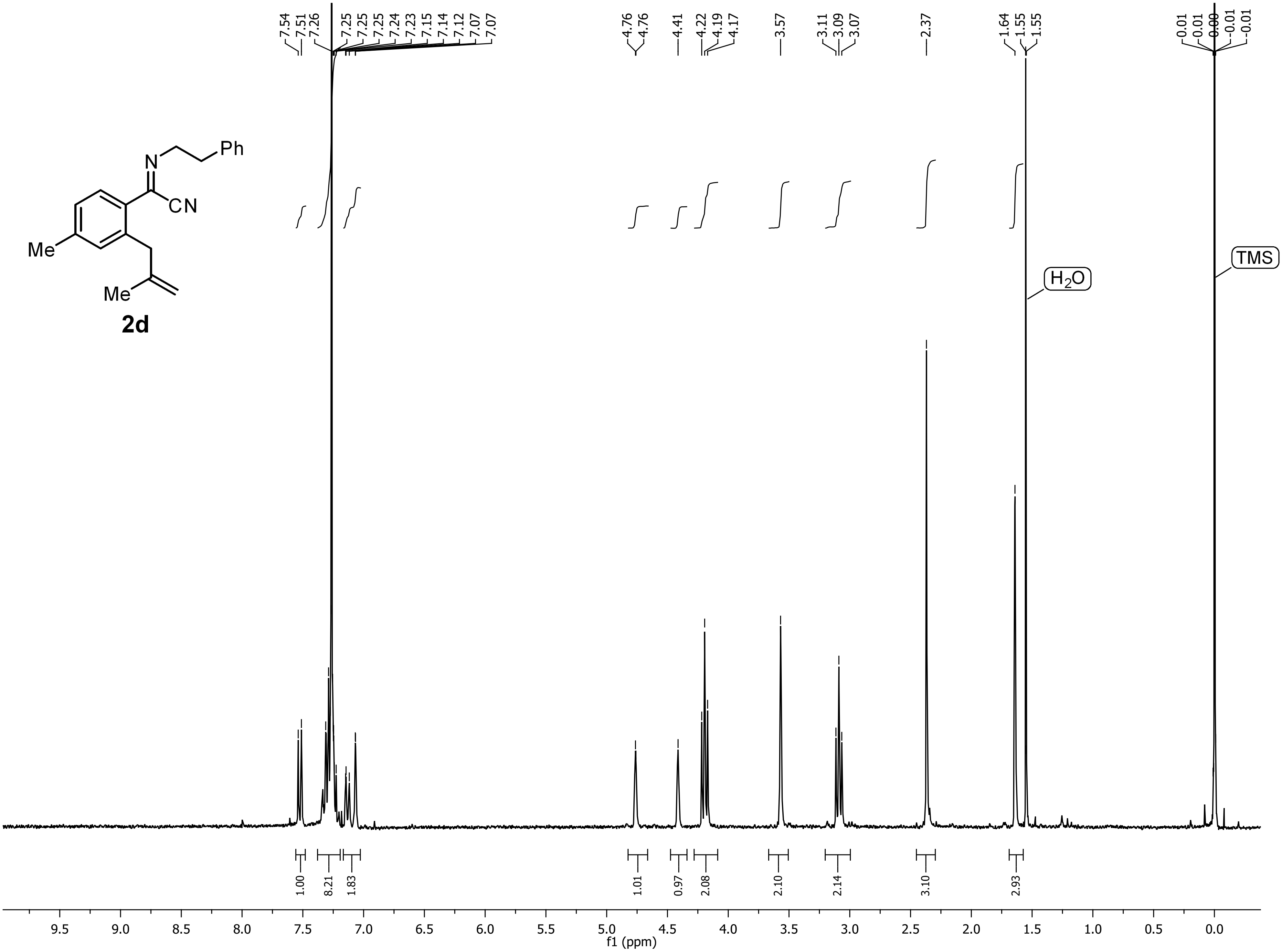

7.33
7.31
7.30
7.25
7.24
7.24
7.23
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.13
6.94
6.94
6.94
6.94
4.71
4.71
4.71
4.26
4.23
4.21
4.20
3.56
3.11
3.10
3.08
1.68
Ph
N
F
CN
F
Me
2c
TMS
2.19
3.29
1.01
1.04
1.00
1.02
2.19
2.07
2.03
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

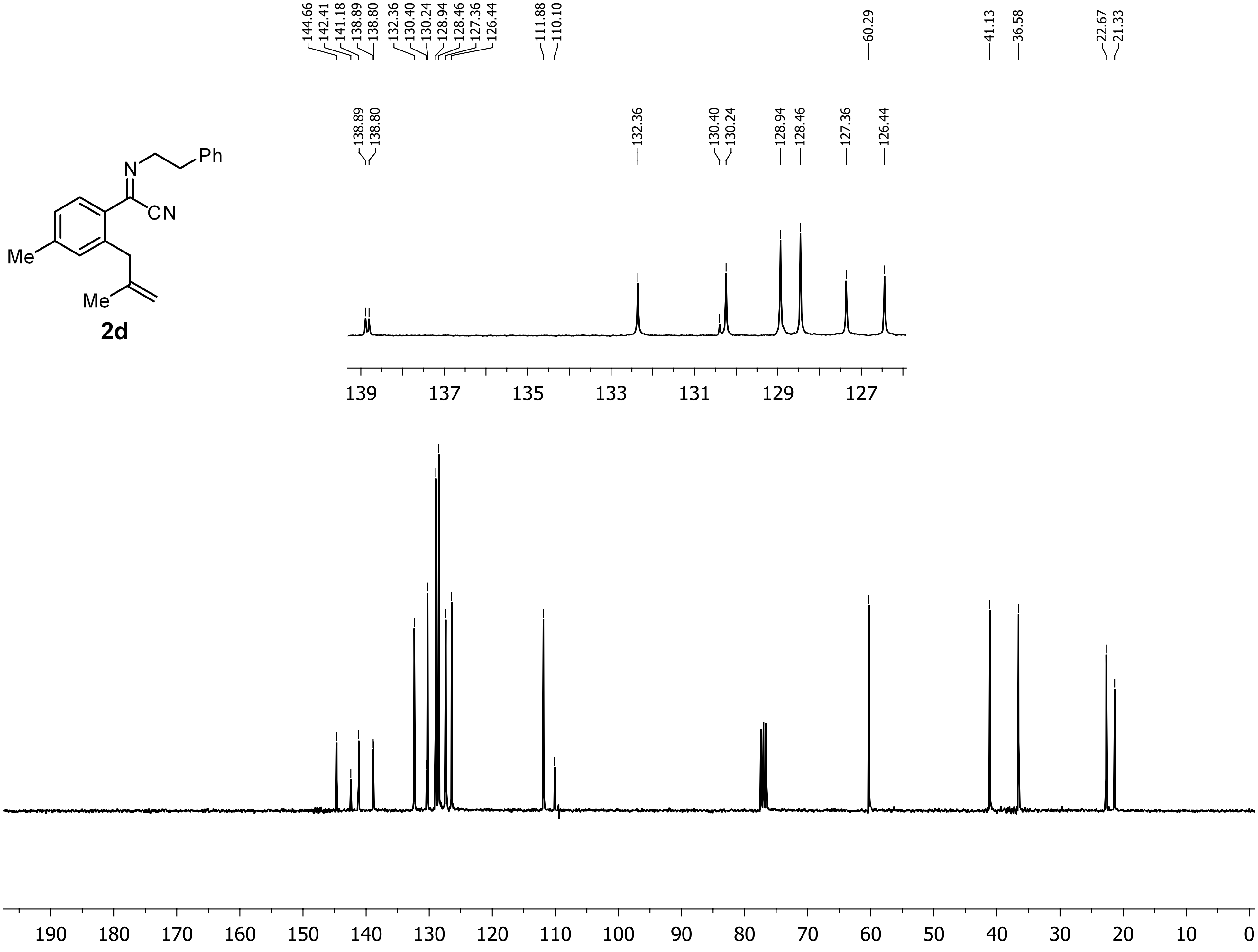

162.8529
162.7607
162.2078
162.1016
160.8769
160.7846
160.2293
160.1225
143.1908
140.6328
138.5993
136.0854
136.0363
136.0167
135.9677
129.1597
128.8131
126.8995
122.7315
113.1975
112.9841
111.2758
109.6366
106.6674
106.4708
106.4445
106.2484
60.7436
36.5595
32.0833
32.0485
23.0068
F
N
Ph
CN
F
Me
2c
143
142
141
140
139
138
137
136
135
f1 (ppm)
123
121
119
117
115
113
111
109
107
105
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Ph
N
F
CN
F
Me

2c


-110.5193
-110.5378
-110.5559
-111.1540
-111.1719
-111.1896
-111.2071
-108.0
-108.4
-108.8
-109.2
-109.6
-110.0
-110.4
-110.8
-111.2
-111.6
-112.0
-112.4
-112.8
-113.2
-113.6
f1 (ppm)


7.54
7.51
7.26
7.25
7.25
7.25
7.24
7.23
7.15
7.14
7.12
7.07
7.07
4.76
4.76
4.41
4.22
4.19
4.17
3.57
3.11
3.09
3.07
2.37
1.64
1.55
1.55
0.01
0.01
0.00
-0.01
-0.01
N
Ph
CN
Me
Me
2d
H2O
TMS
1.00
8.21
1.83
1.01
0.97
2.08
2.10
2.14
3.10
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.66
142.41
141.18
138.89
138.80
132.36
130.40
130.24
128.94
128.46
127.36
126.44
111.88
110.10
60.29
41.13
36.58
22.67
21.33
N
Ph
CN
Me
Me
138.89
138.80
132.36
130.40
130.24
128.94
128.46
127.36
126.44
139
137
135
133
131
129
127
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2d

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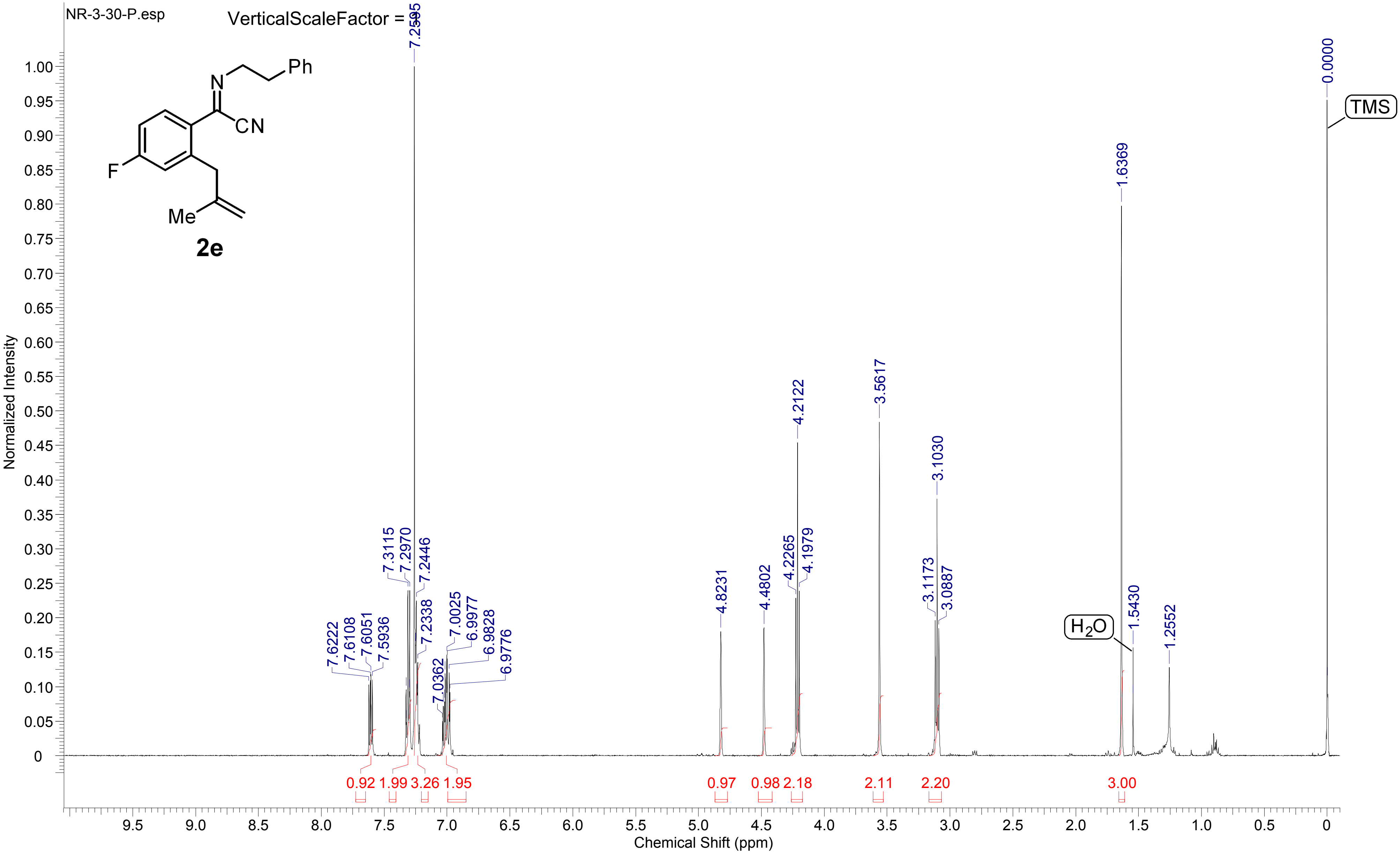
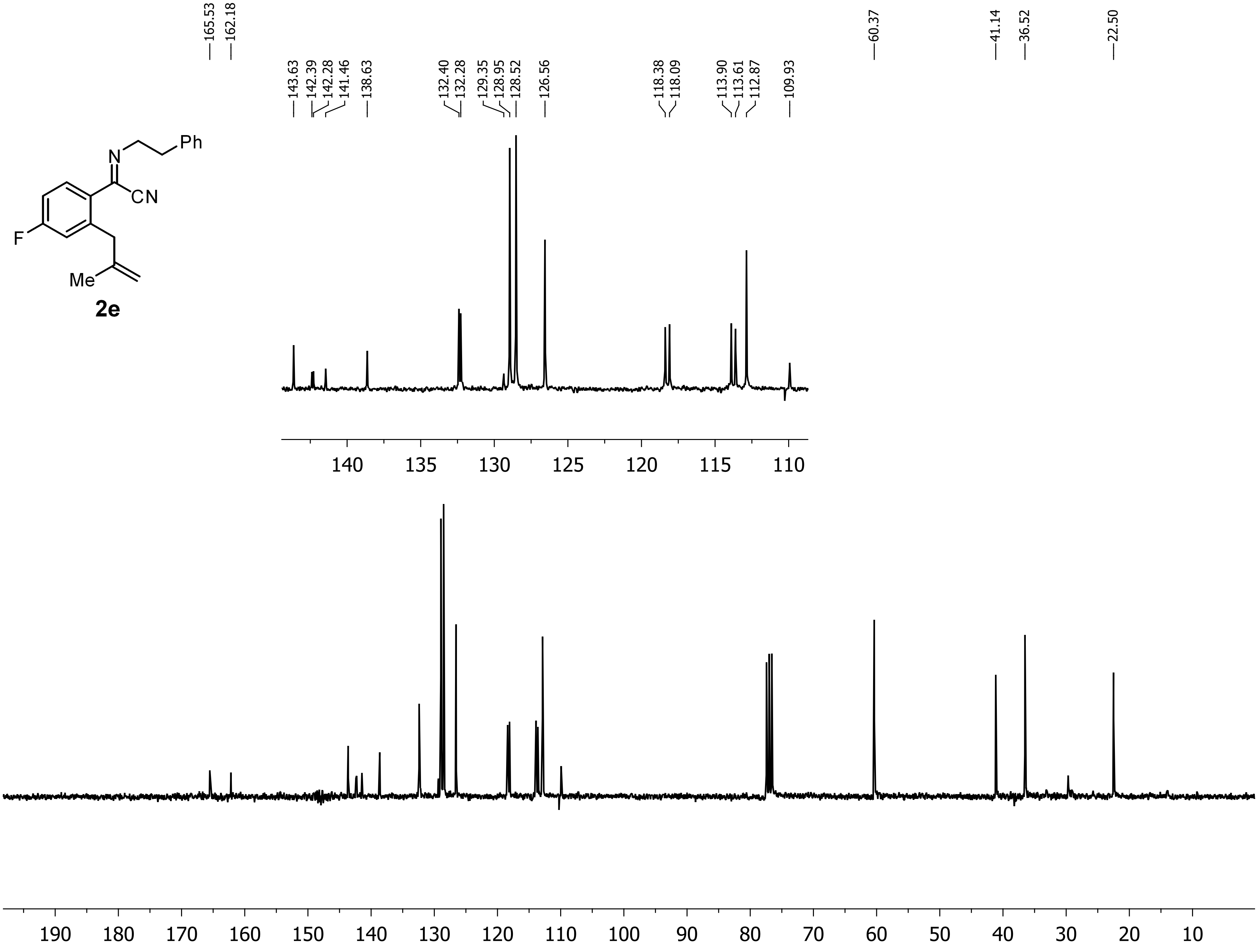
8/22/2013 6:11:14 PM

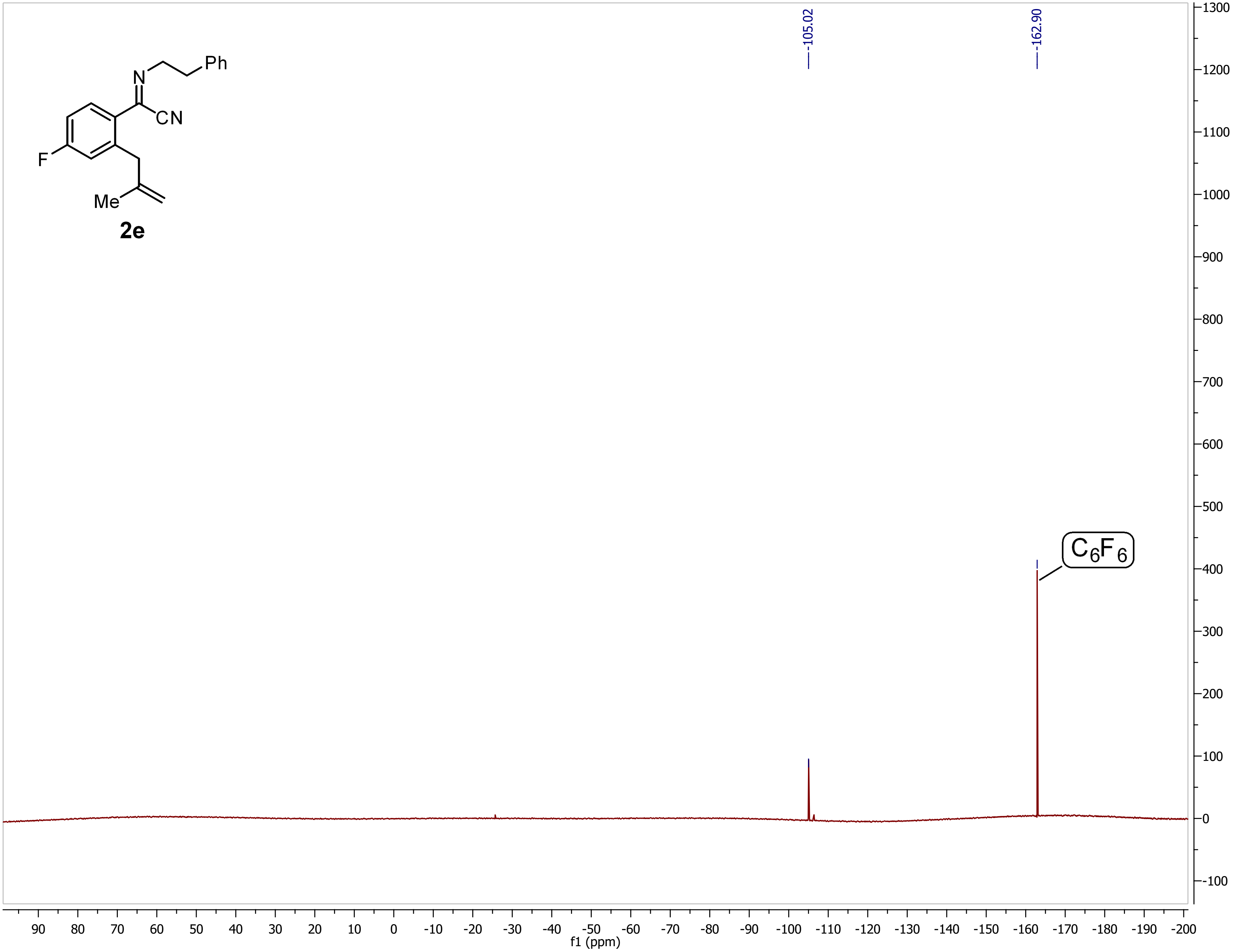
Acquisition Time (sec)	1.8920	***Comment***	Univ of Minnesota, VI-500			***Date***	Mar 27 2013
Date Stamp	Mar 27 2013	***File Name***	C:\Users\Naveen\Desktop\NR-3-30-P.fid\fid			***Frequency (MHz)***	499.87
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	15136	***Points Count***	131072
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2496.1433	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	8000.00	***Temperature (degree C)***	AMBIENT TEMPERATURE

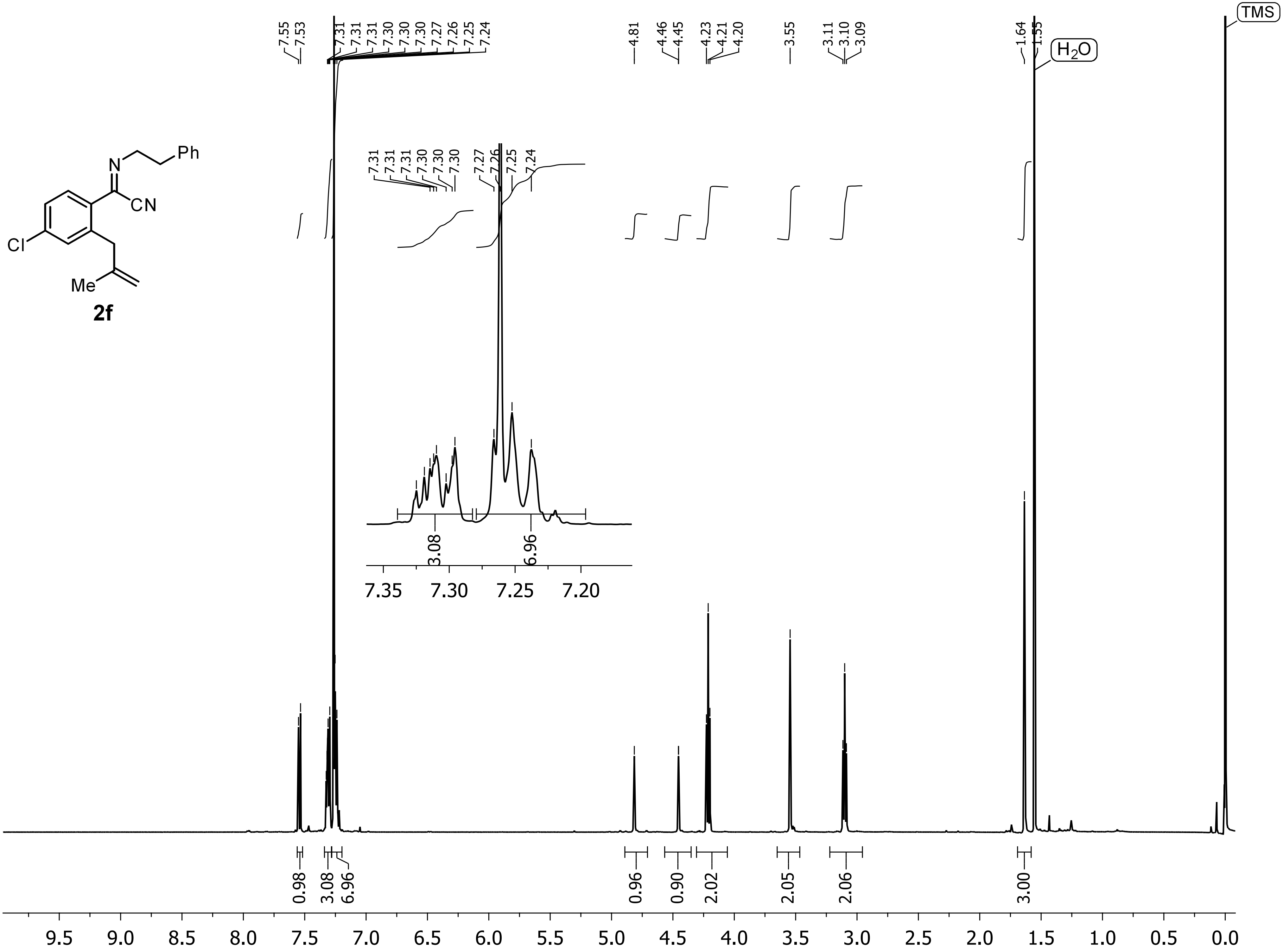




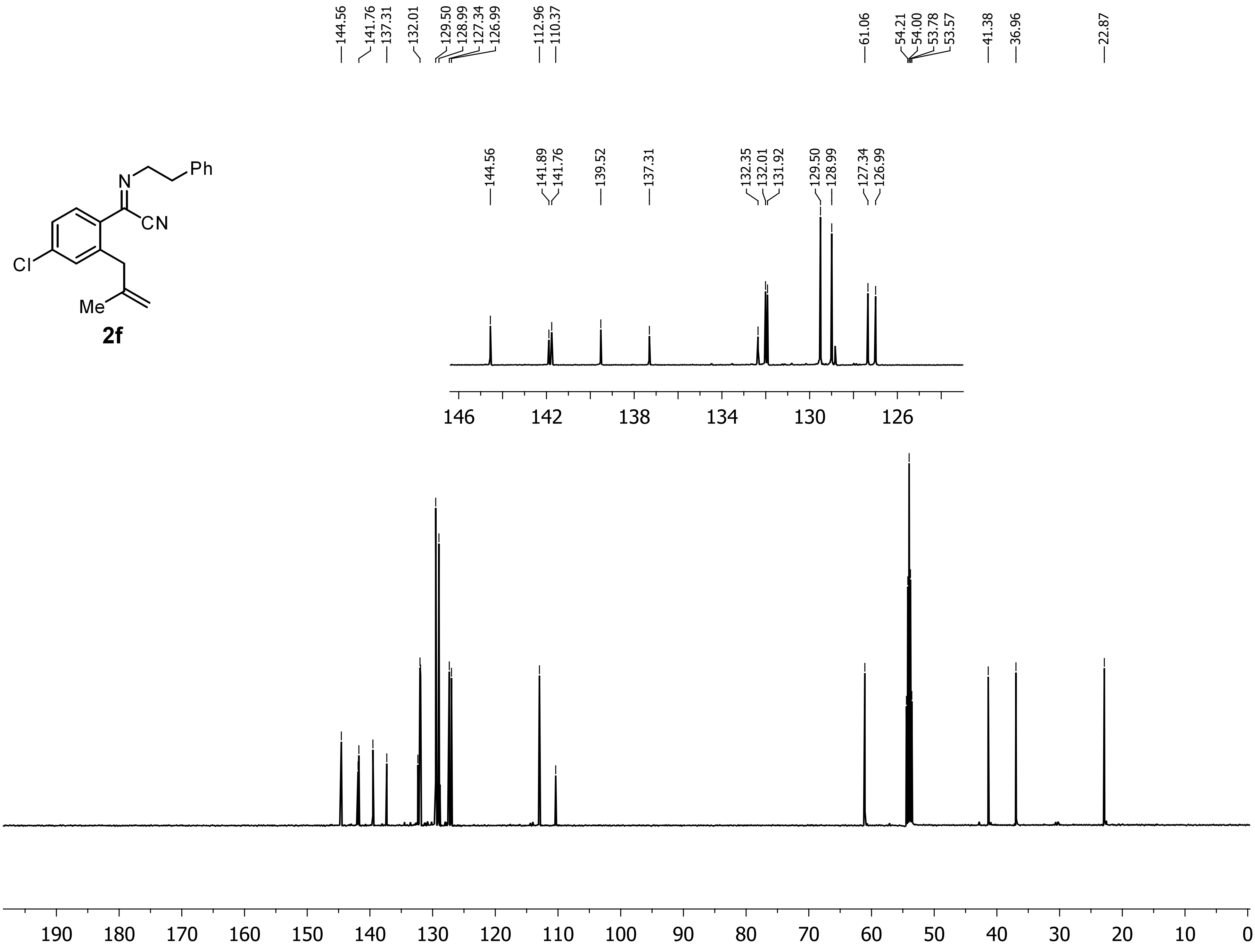
2e

N
Ph
CN
F
Me
165.53
162.18
143.63
142.39
142.28
141.46
138.63
132.40
132.28
129.35
128.95
128.52
126.56
118.38
118.09
113.90
113.61
112.87
109.93
60.37
41.14
36.52
22.50
140
135
130
125
120
115
110
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


-105.02
-162.90
Ph
N
CN
F
Me
2e
C6F6
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

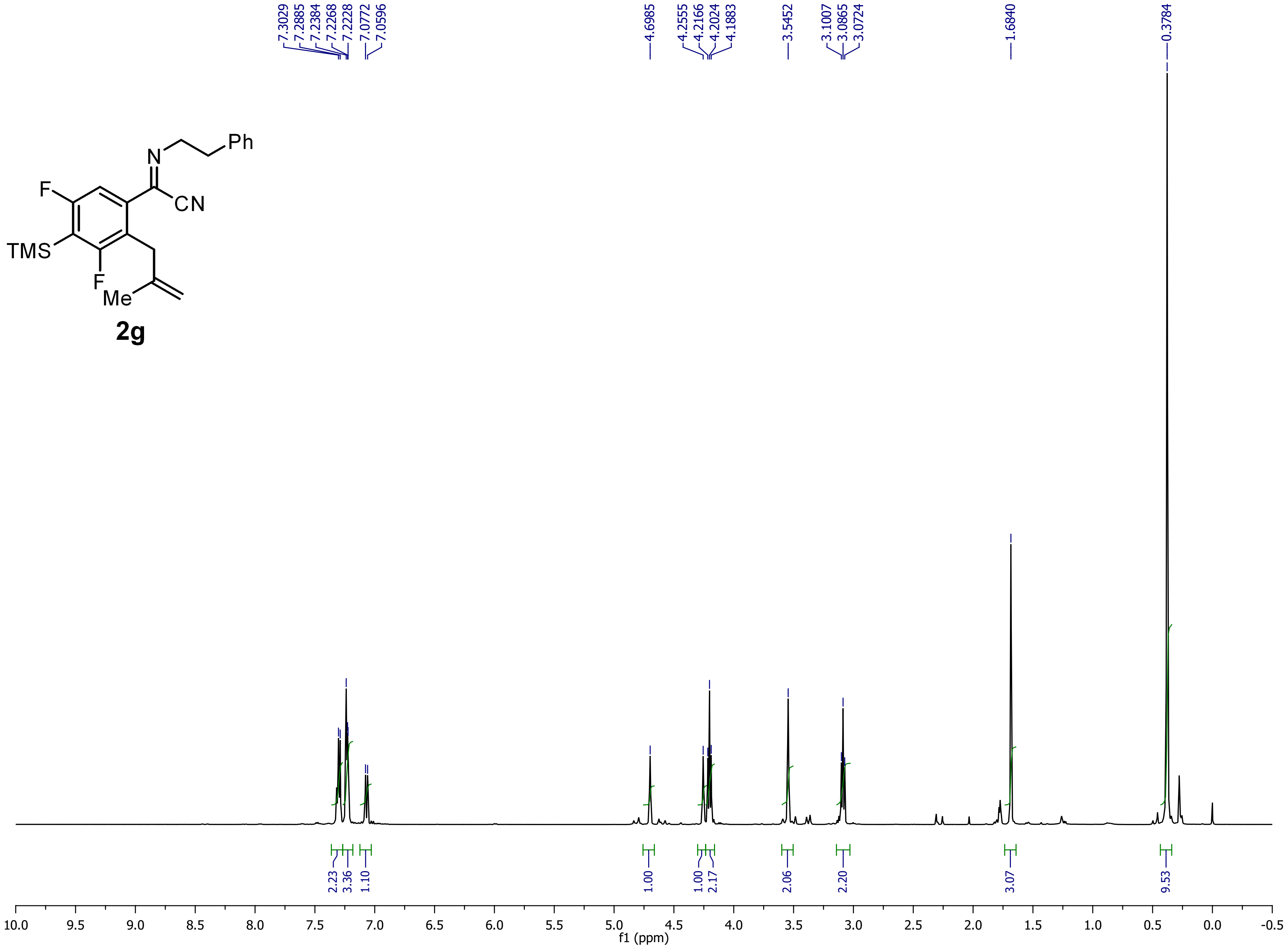

7.55
7.53
7.31
7.31
7.31
7.30
7.30
7.30
7.27
7.26
7.25
7.24
4.81
4.46
4.45
4.23
4.21
4.20
3.55
3.11
3.10
3.09
1.64
1.55
H2O
TMS
N
Ph
CN
Cl
Me
3.08
6.96
7.35
7.30
7.25
7.20
0.98
3.08
6.96
0.96
0.90
2.02
2.05
2.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

2f

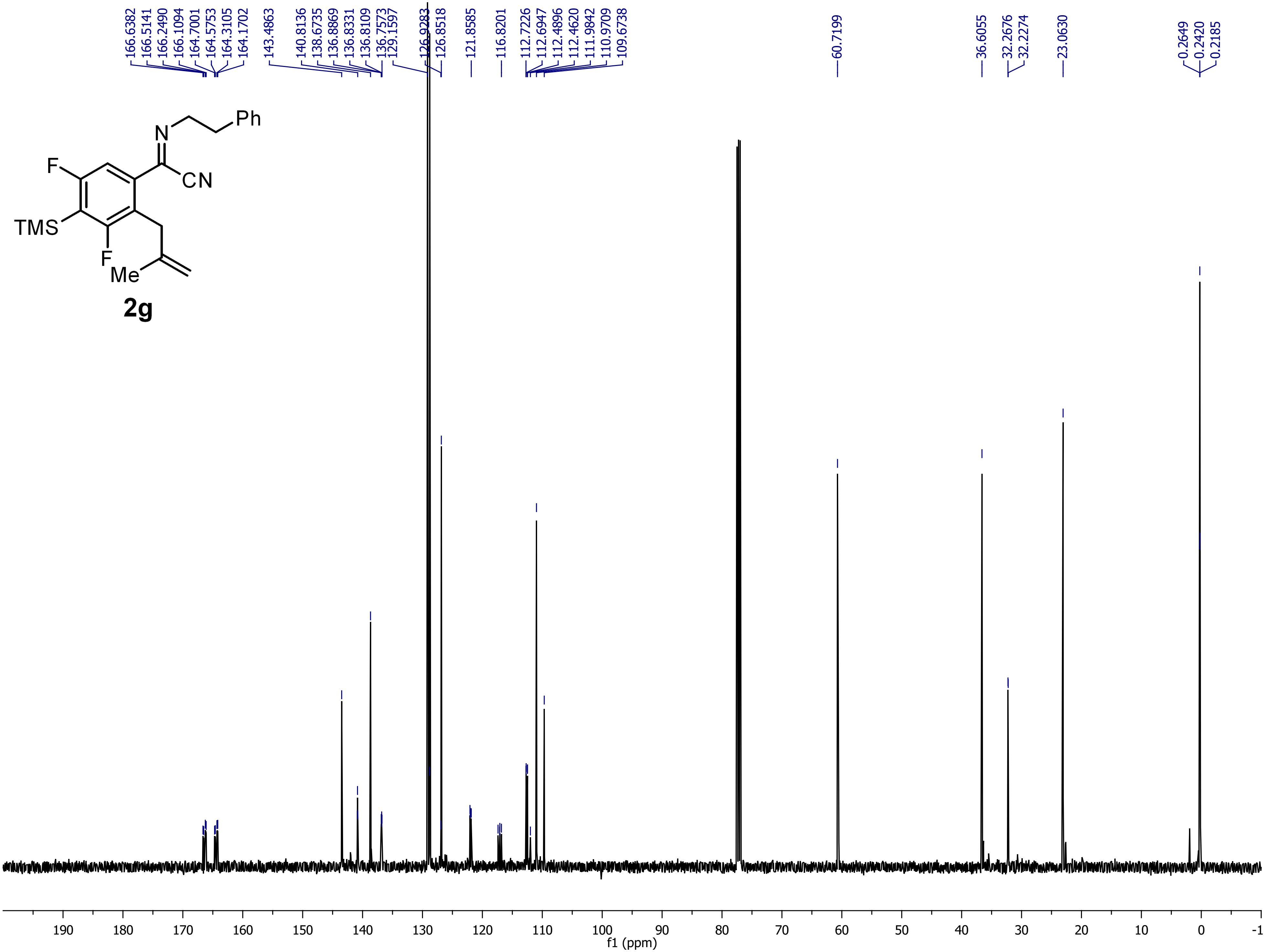

144.56
141.76
137.31
132.01
129.50
128.99
127.34
126.99
112.96
110.37
61.06
54.21
54.00
53.78
53.57
41.38
36.96
22.87
144.56
141.89
141.76
139.52
137.31
132.35
132.01
131.92
129.50
128.99
127.34
126.99
146
142
138
134
130
126
N
Ph
CN
Cl
Me
2f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Ph
N
F
CN
TMS
F
Me

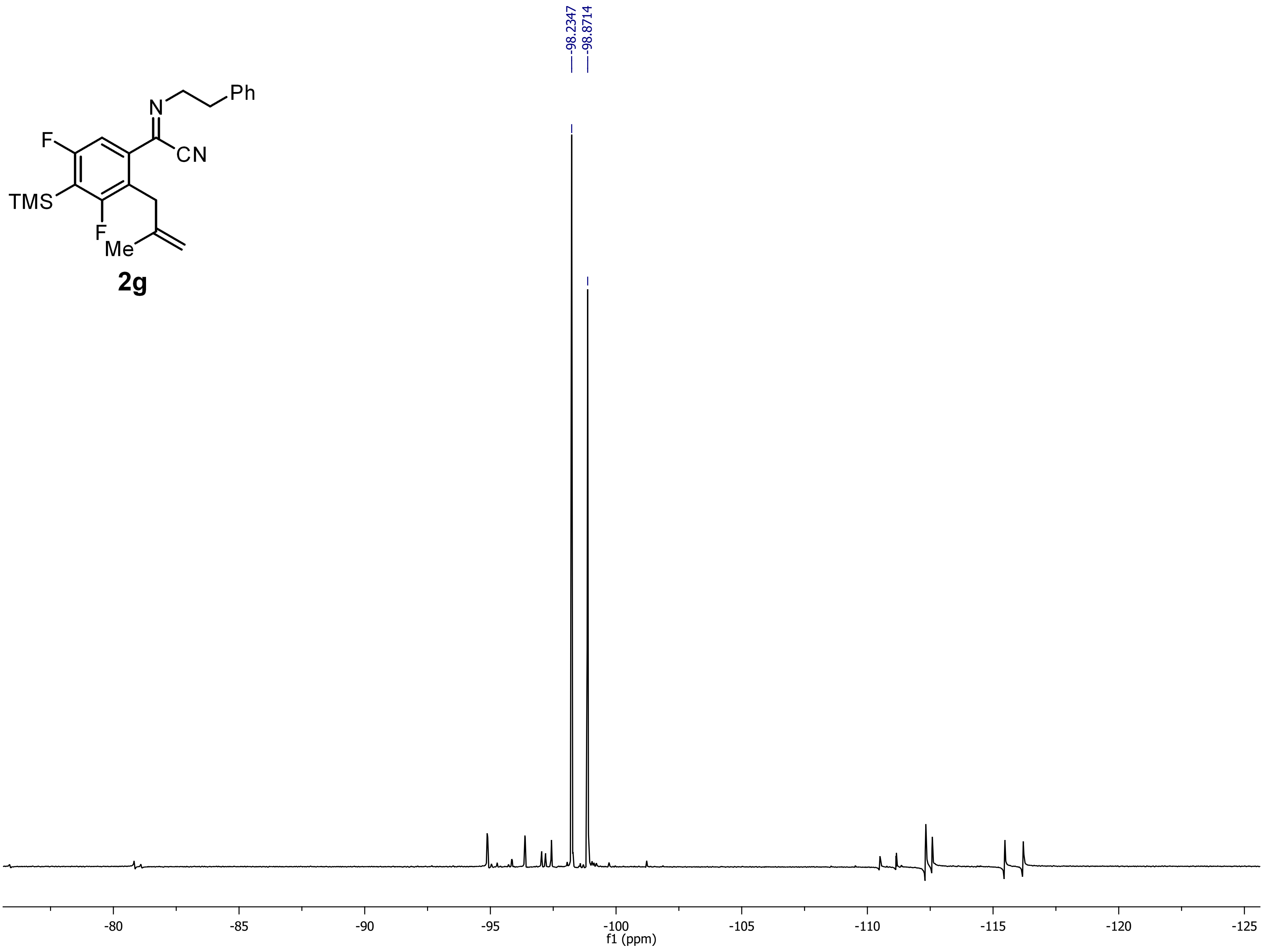
2g



7.3029
7.2885
7.2384
7.2268
7.2228
7.0772
7.0596
4.6985
4.2555
4.2166
4.2024
4.1883
3.5452
3.1007
3.0865
3.0724
1.6840
0.3784
2.23
3.36
1.10
1.00
1.00
2.17
2.06
2.20
3.07
9.53
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.6382
166.5141
166.2490
166.1094
164.7001
164.5753
164.3105
164.1702
143.4863
140.8136
138.6735
136.8869
136.8331
136.8109
136.7573
129.1597
126.9283
126.8518
121.8585
116.8201
112.7226
112.6947
112.4896
112.4620
111.9842
110.9709
109.6738
60.7199
36.6055
32.2676
32.2274
23.0630
0.2649
0.2420
0.2185
F
TMS
F
Me
N
Ph
CN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

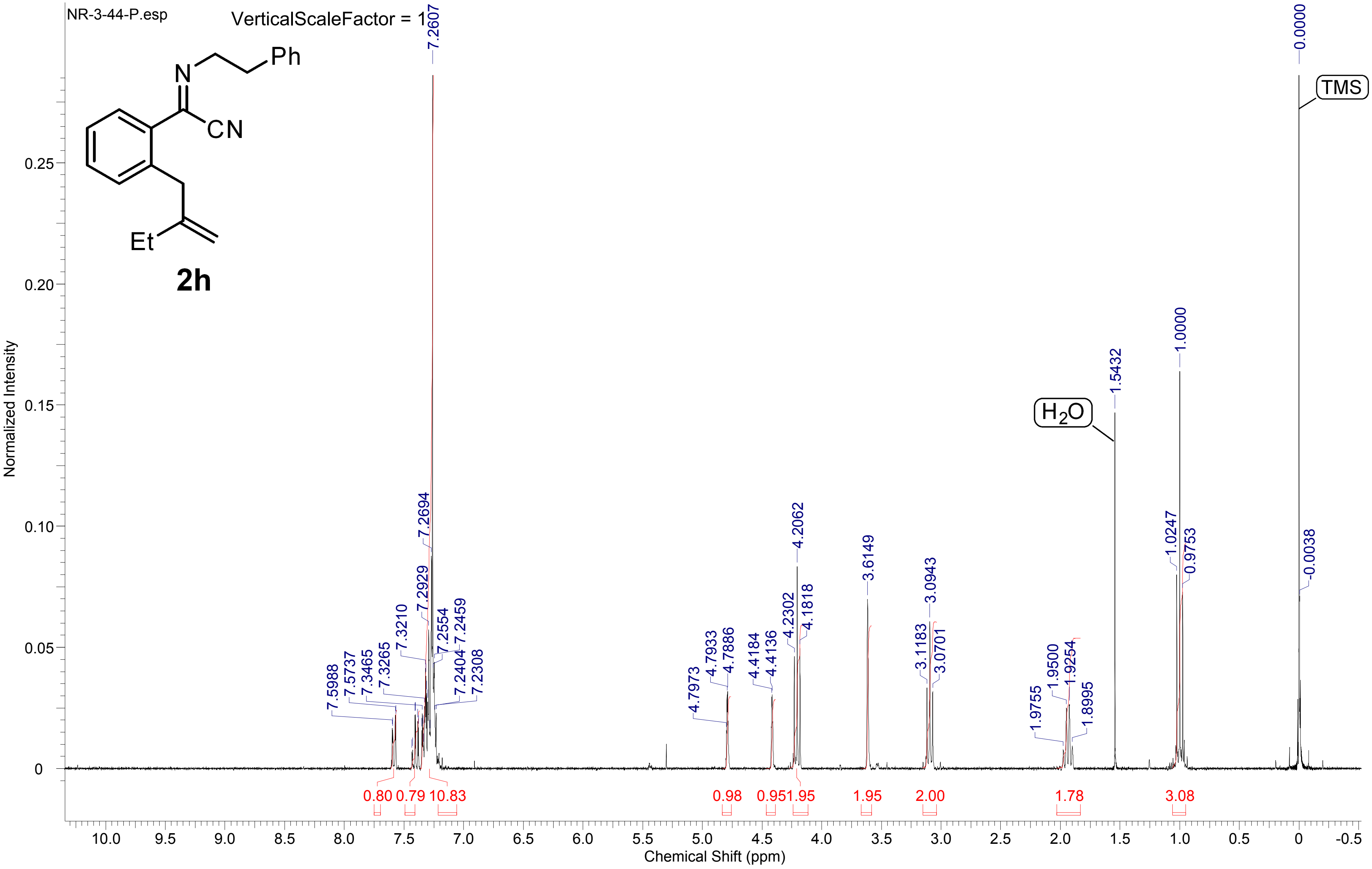
2g

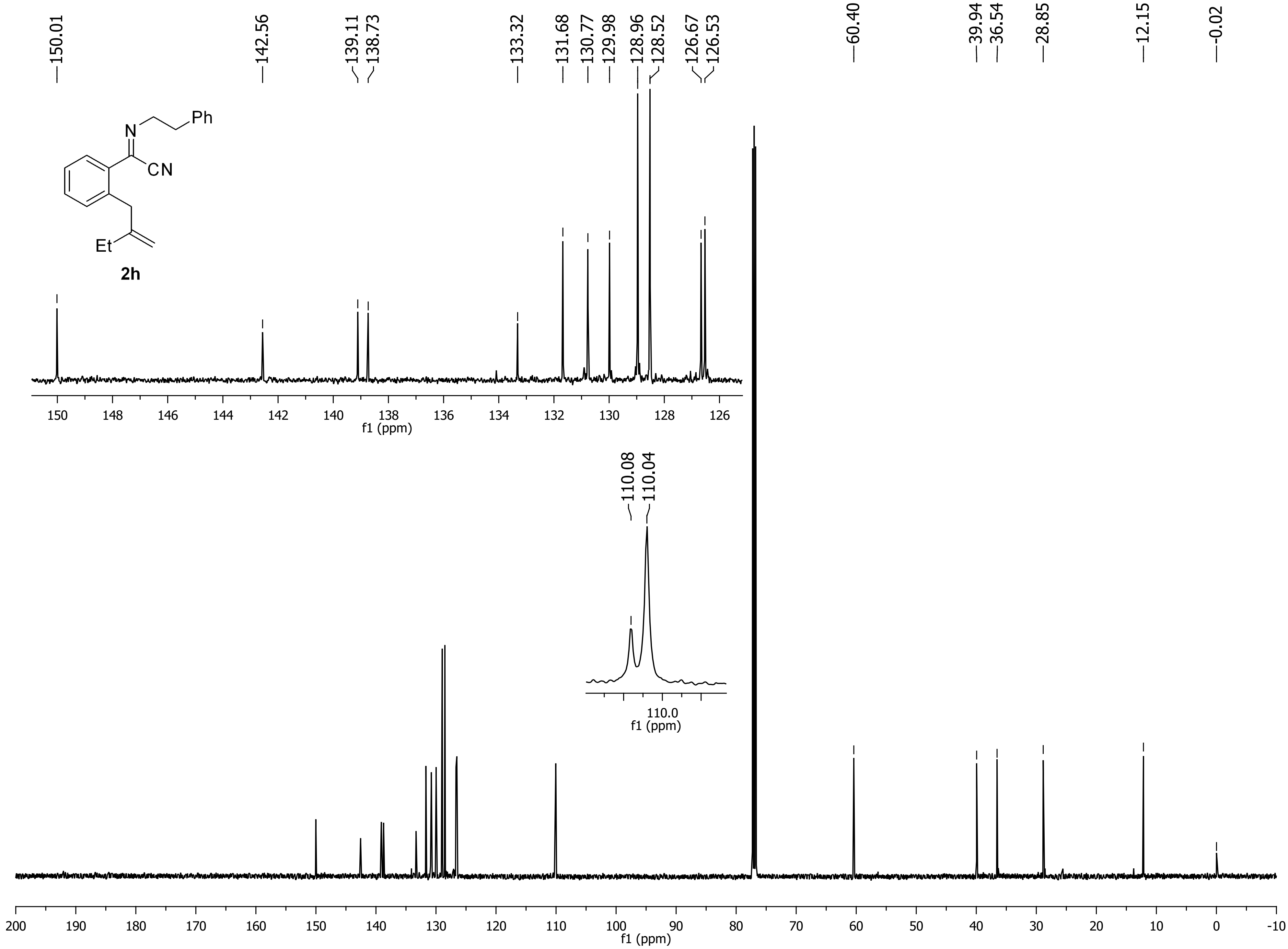

-98.2347
-98.8714
F
F
TMS
N
Ph
CN
Me
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

2g

9/26/2013 2:52:47 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-44-P University of Minnesota Department of Chemistry VAC-300				
Date	Apr 23 2013	***Date Stamp***	Apr 23 2013	***File Name***	C:\Users\Naveen\Desktop\130423v3_3702.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.2959	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE




2h

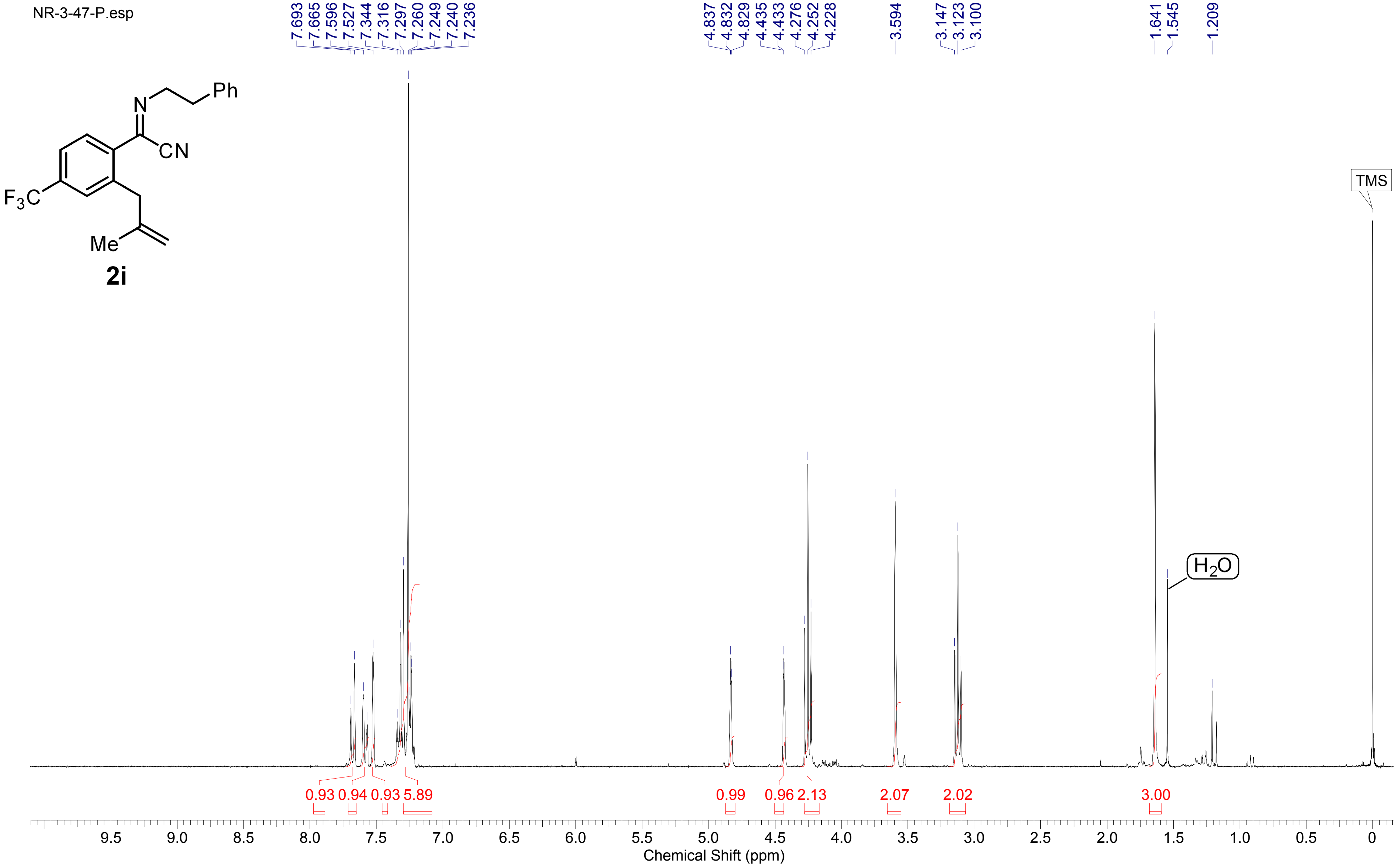
150.01
142.56
139.11
138.73
133.32
131.68
130.77
129.98
128.96
128.52
126.67
126.53
60.40
39.94
36.54
28.85
12.15
-0.02
N
Ph
CN
Et
150
148
146
144
142
140
138
136
134
132
130
128
126
f1 (ppm)
110.08
110.04
110.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

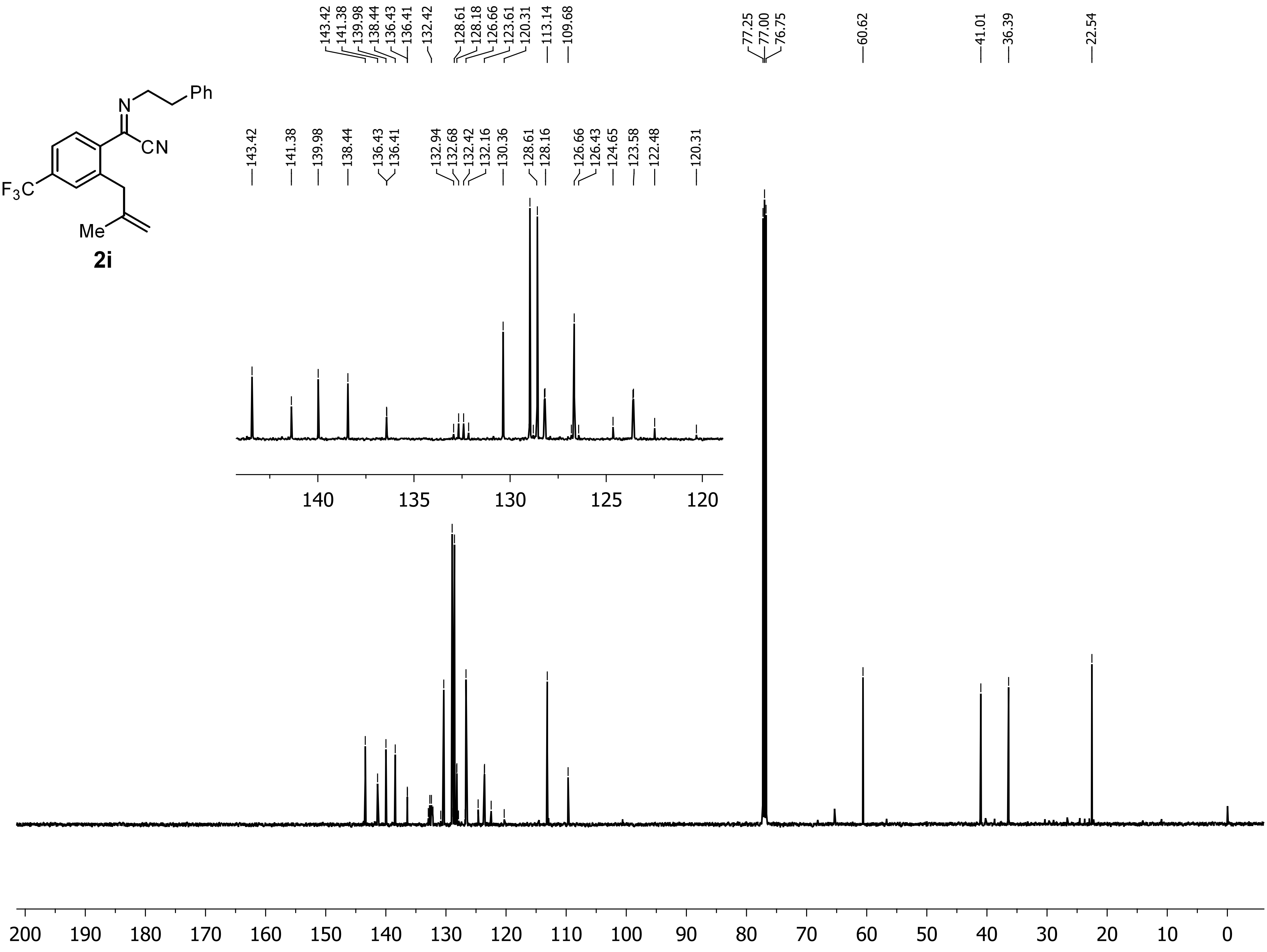
1/9/2014 12:42:56 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-47-P University of Minnesota Department of Chemistry VAC-300				
Date	Apr 27 2013	***Date Stamp***	Apr 27 2013	***File Name***	C:\Users\Naveen\Desktop\130427v3_0102.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.0212	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE

NR-3-47-P.esp

2i




143.42
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77.25
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76.75
60.62
41.01
36.39
22.54
N
Ph
CN
F3C
Me
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141.38
139.98
138.44
136.43
136.41
132.94
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132.42
132.16
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125
120
200
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180
170
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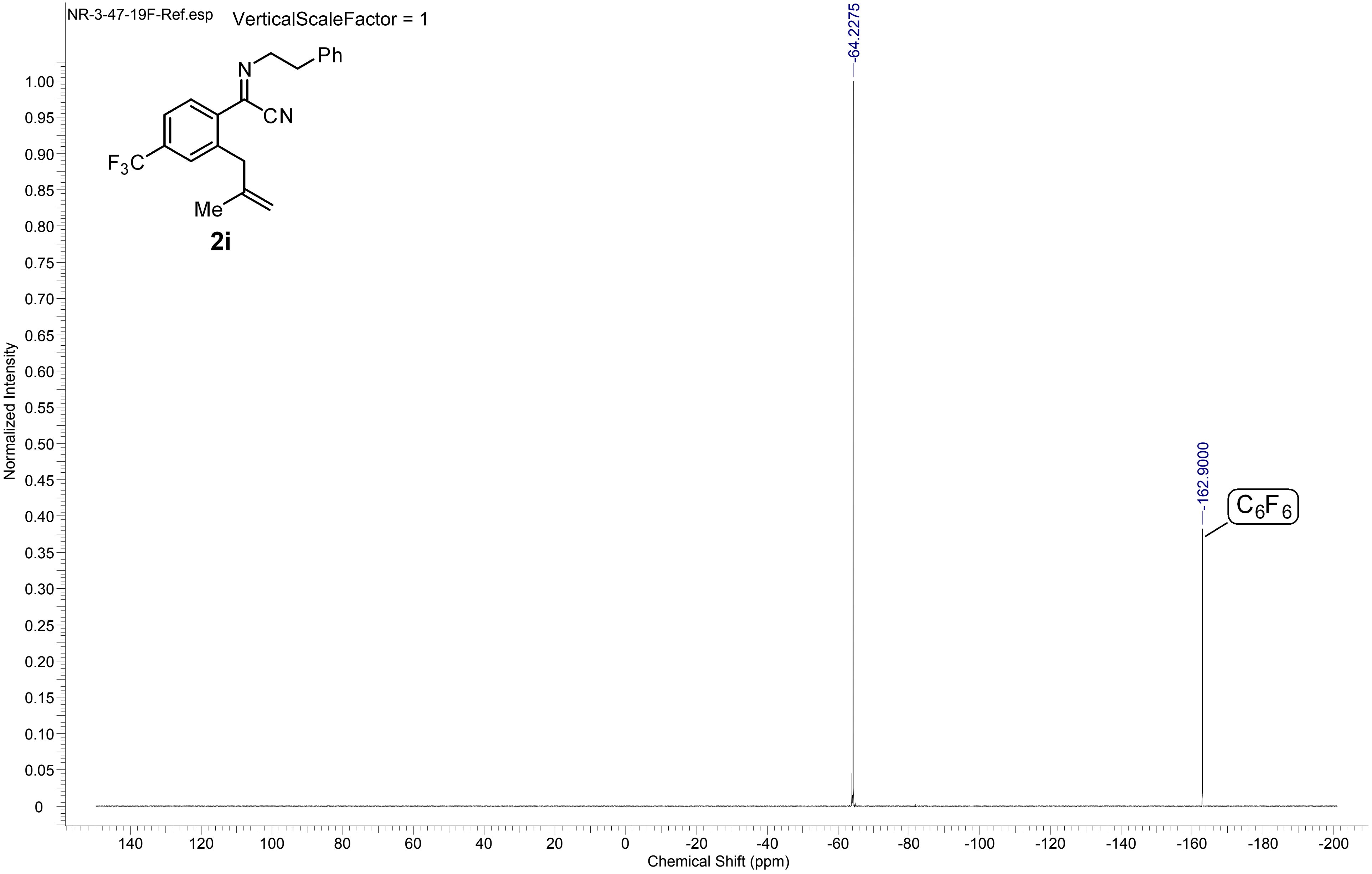
2i

9/26/2013 3:12:04 PM

Acquisition Time (sec)	0.6464	***Comment***	NR-3-47-19F-Ref University of Minnesota Department of Chemistry VAC-300				
Date	May 9 2013	***Date Stamp***	May 9 2013	***File Name***	C:\Users\Naveen\Desktop\130509v3_1102.fid\fid		
Frequency (MHz)	282.23	***Nucleus***	19F	***Number of Transients***	32	***Original Points Count***	64000
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	12.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	-7242.4761	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	99009.90	***Temperature (degree C)***	AMBIENT TEMPERATURE



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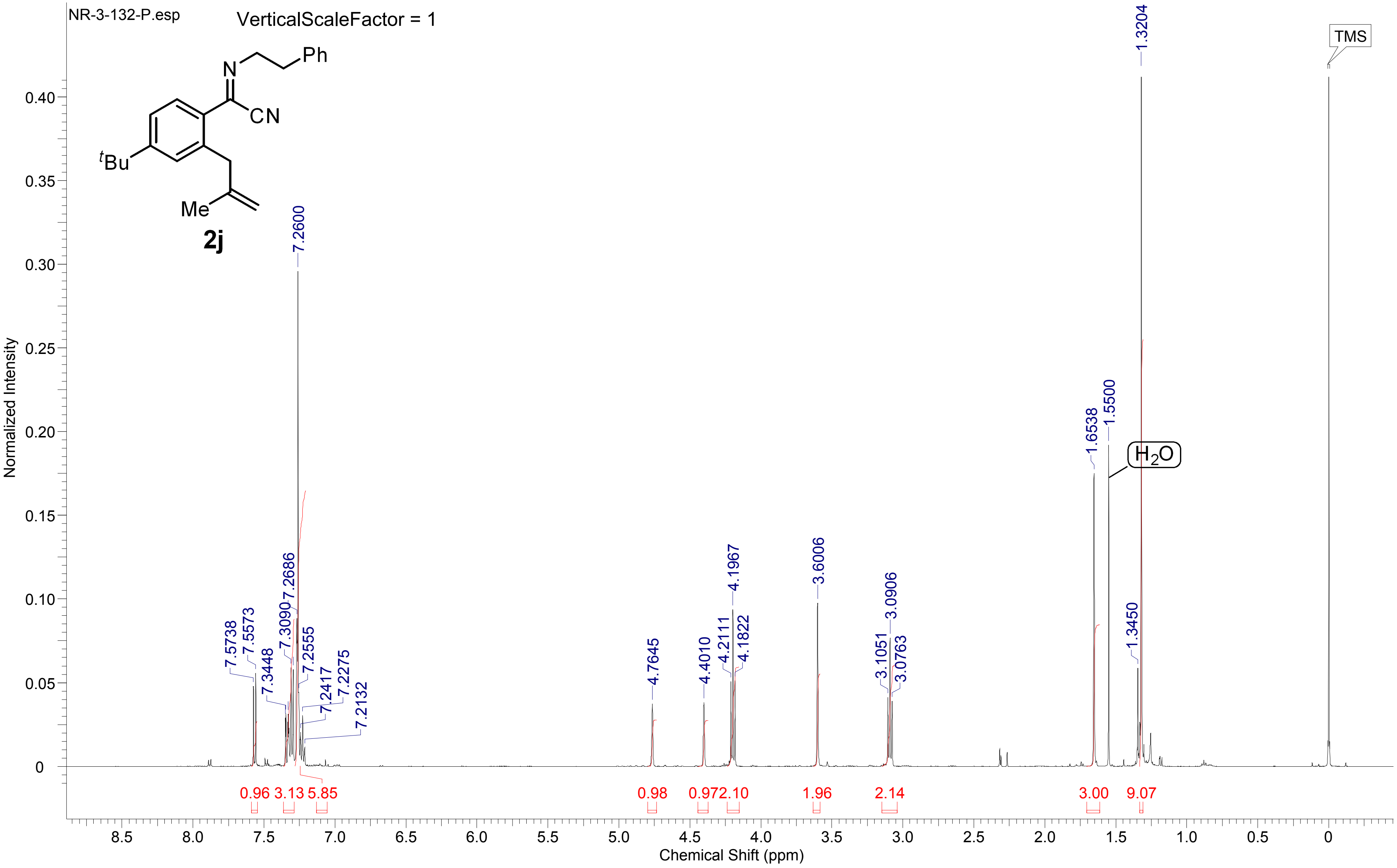
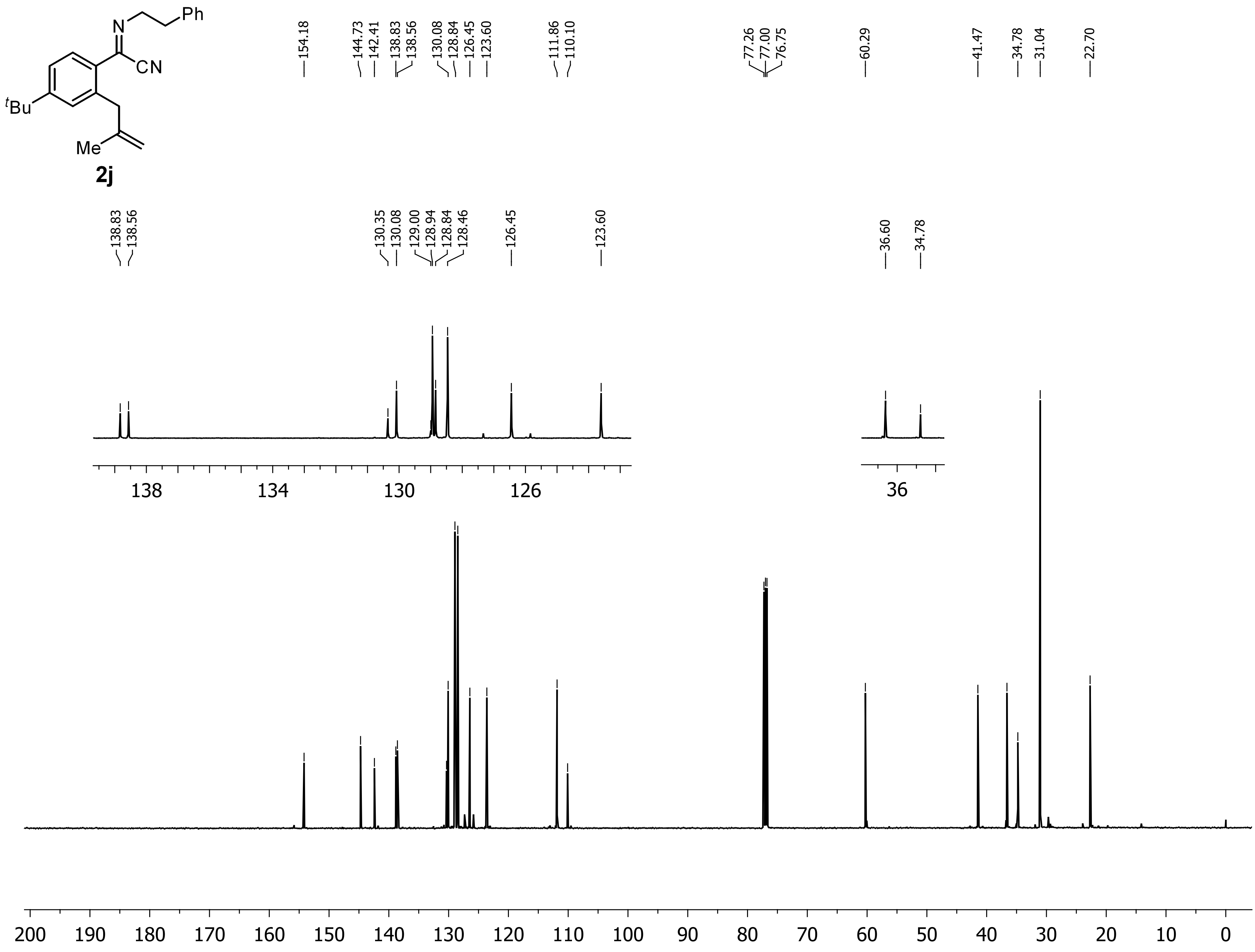
8/28/2013 6:37:07 PM

Acquisition Time (sec)	3.2768	***Date***	26 Aug 2013 15:48:00			***Date Stamp***	26 Aug 2013 15:48:00
File Name	C:\Users\Naveen\Desktop\NR-3-132-P\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	92.58	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3075.7522	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	21.000				




2j

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111.86
110.10
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77.00
76.75
60.29
41.47
34.78
31.04
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130.35
130.08
129.00
128.94
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123.60
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134
130
126
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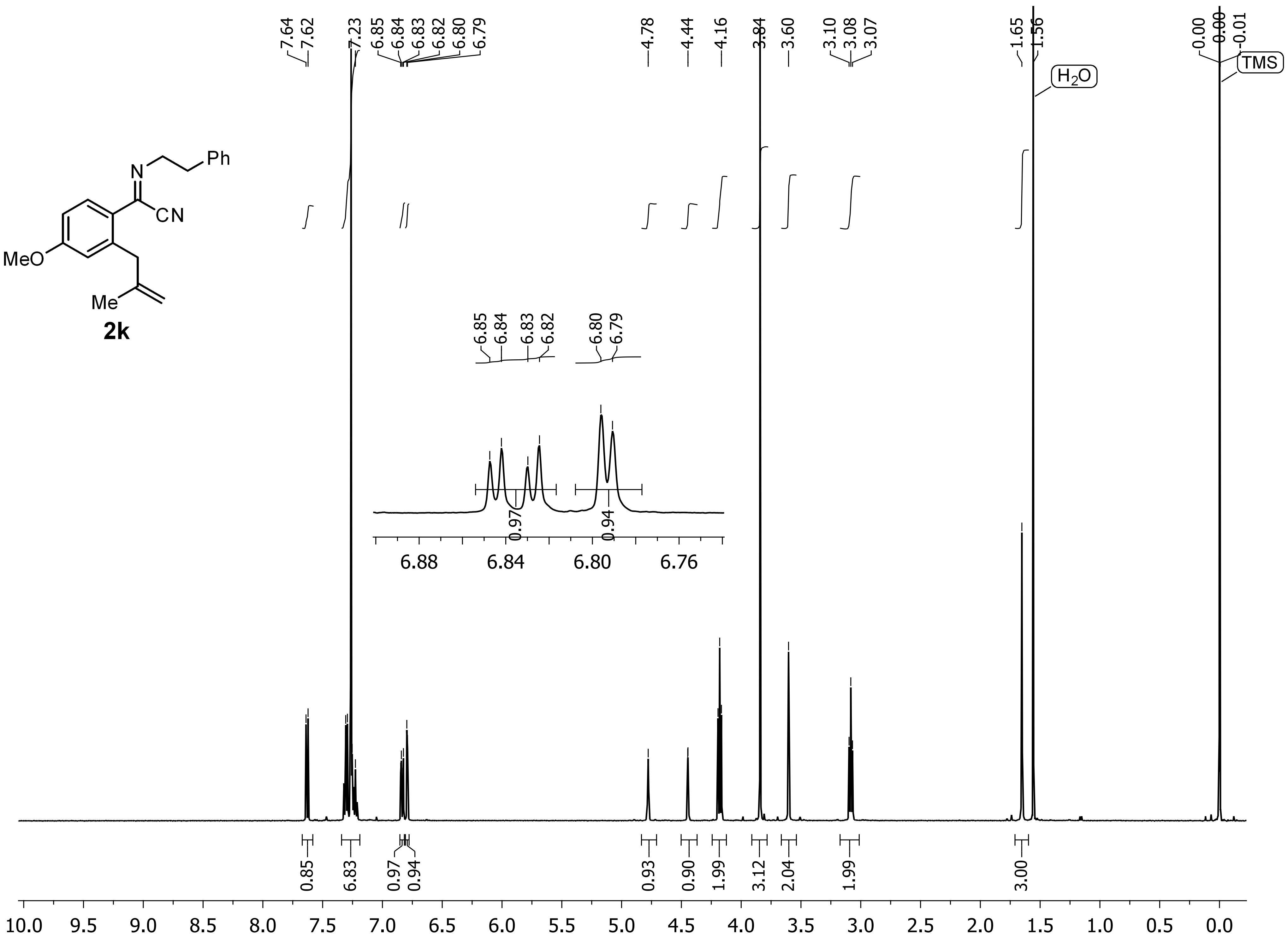
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3.10
3.08
3.07
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1.56
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0.00
-0.01
H2O
TMS
N
Ph
CN
MeO
Me
2k
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6.84
6.83
6.82
6.80
6.79
0.97
0.94
6.88
6.84
6.80
6.76
0.85
6.83
0.97
0.94
0.93
0.90
1.99
3.12
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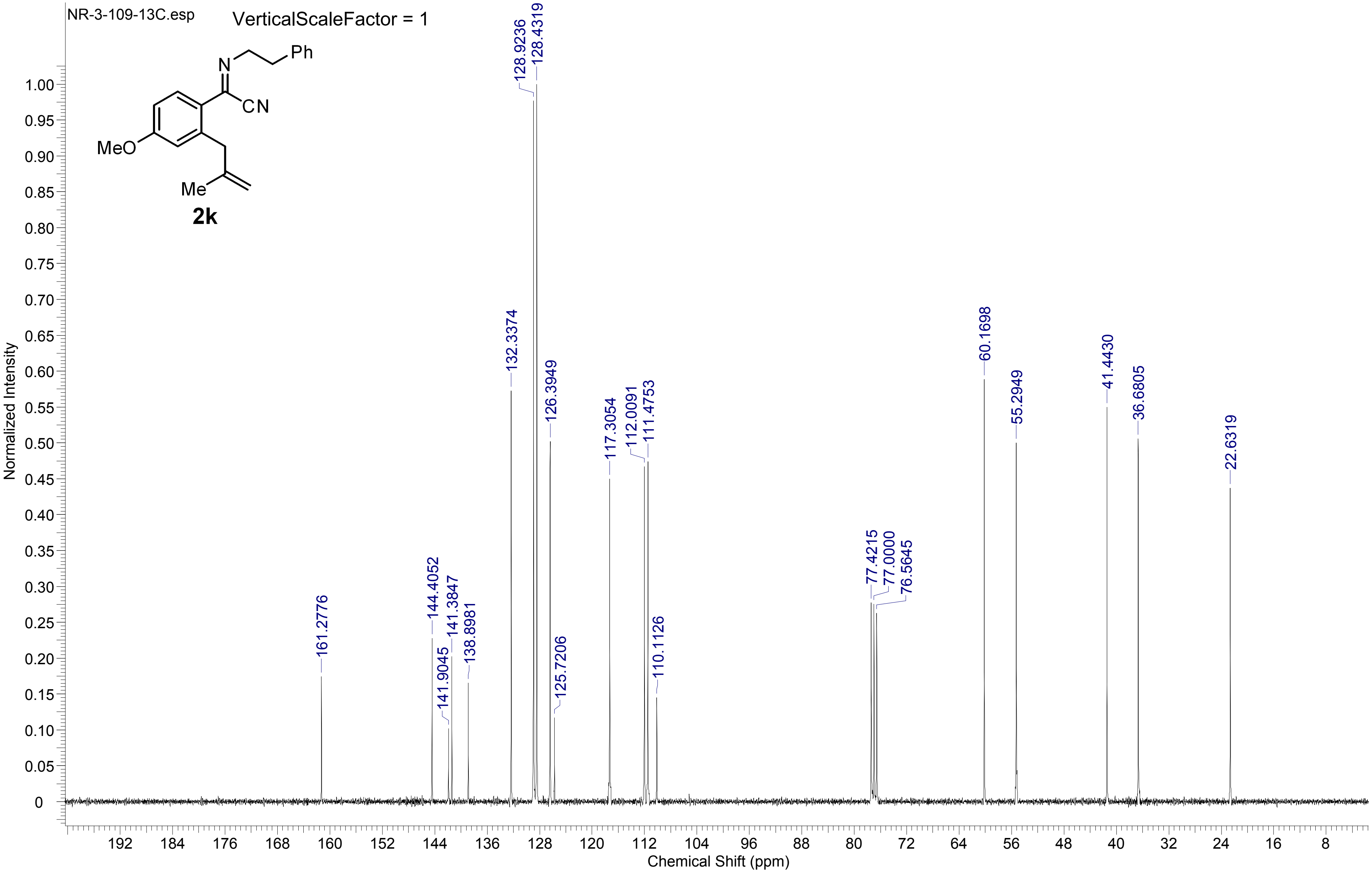
9/26/2013 3:10:36 PM

Acquisition Time (sec)	0.8000	***Comment***	NR-3-109-13C University of Minnesota Department of Chemistry VAC-300				
Date	Jul 8 2013	***Date Stamp***	Jul 8 2013	***File Name***	C:\Users\Naveen\Desktop\130708v3_3203.fid\fid		
Frequency (MHz)	75.43	***Nucleus***	13C	***Number of Transients***	1024	***Original Points Count***	13889
Points Count	16384	***Pulse Sequence***	s2pul	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	7860.3169	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	17361.11	***Temperature (degree C)***	AMBIENT TEMPERATURE



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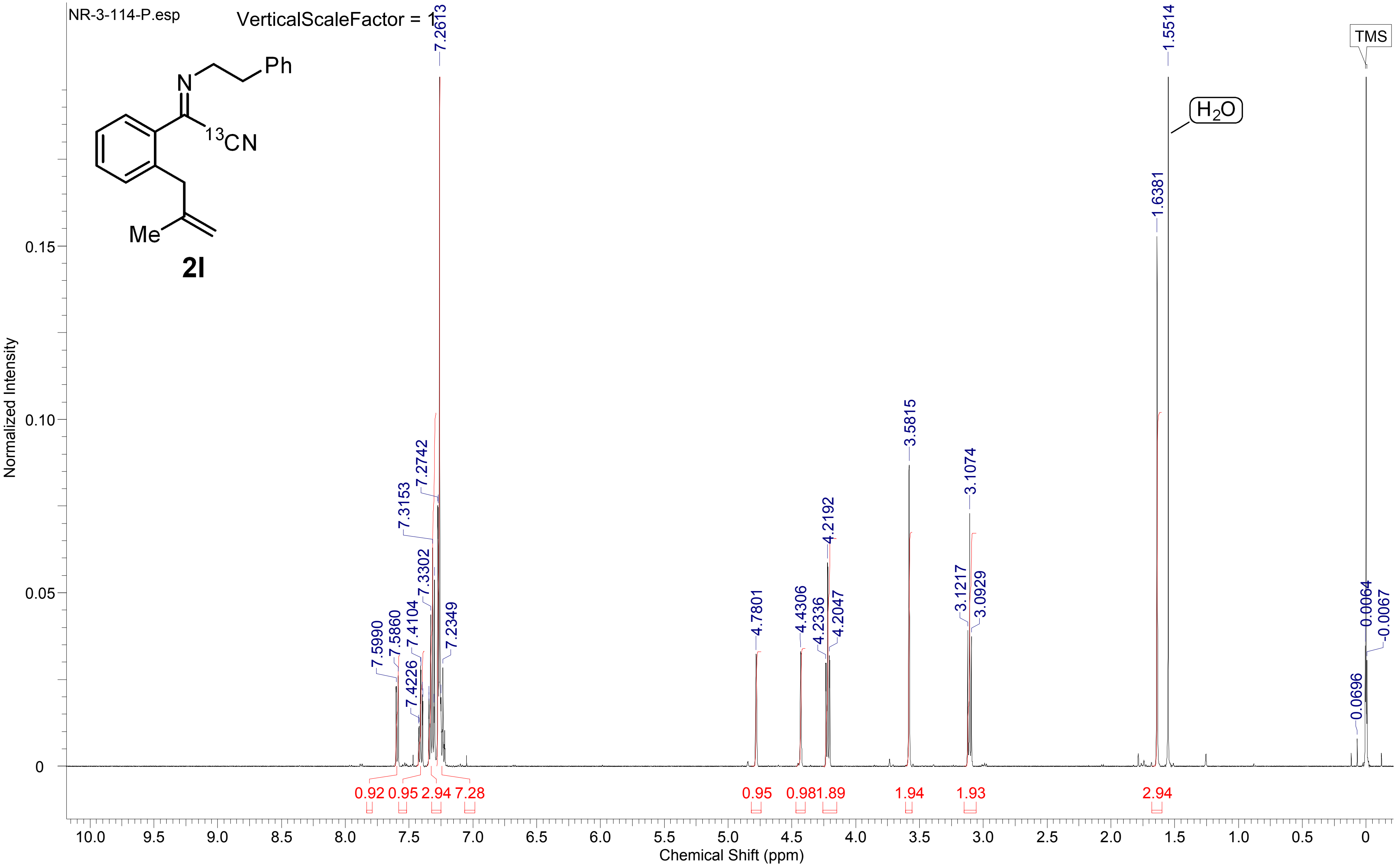
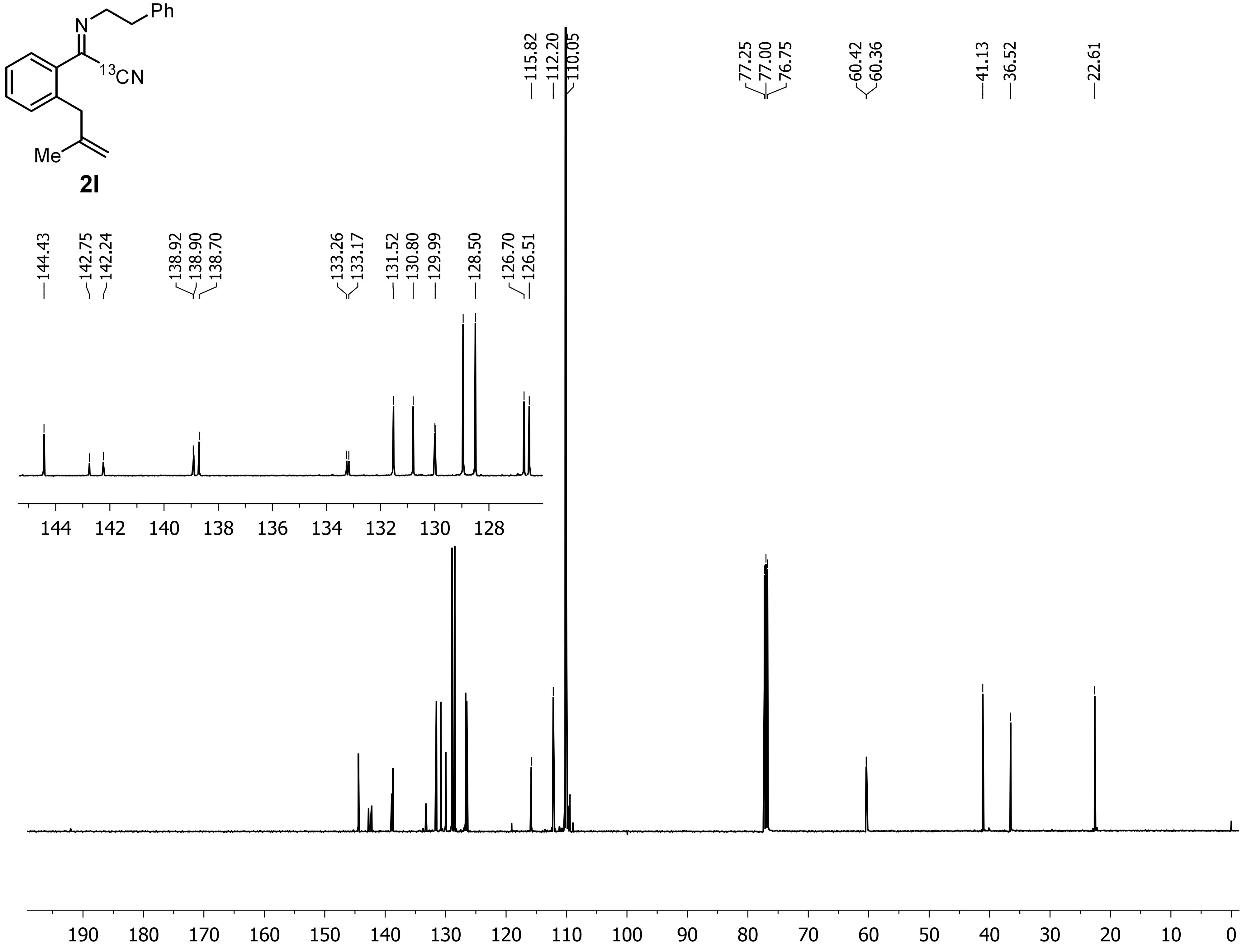
8/20/2013 4:00:28 PM

Acquisition Time (sec)	3.2768	**Date**	15 Jul 2013 15:24:32			**Date Stamp**	15 Jul 2013 15:24:32
File Name	C:\Users\Naveen\Desktop\NR-3-114-P\10\fid			**Frequency (MHz)**	500.13	**Nucleus**	1H
Number of Transients	16	**Origin**	spect	**Original Points Count**	32768	**Owner**	auto
Points Count	131072	**Pulse Sequence**	zg30	**Receiver Gain**	127.25	**SW(cyclical) (Hz)**	10000.00
Solvent	CHLOROFORM-d			**Spectrum Offset (Hz)**	3076.6677	**Spectrum Type**	STANDARD
Sweep Width (Hz)	9999.92	**Temperature (degree C)**	20.999				




N
Ph
13CN
Me
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60.36
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36.52
22.61
144.43
142.75
142.24
138.92
138.90
138.70
133.26
133.17
131.52
130.80
129.99
128.50
126.70
126.51
144
142
140
138
136
134
132
130
128
190
180
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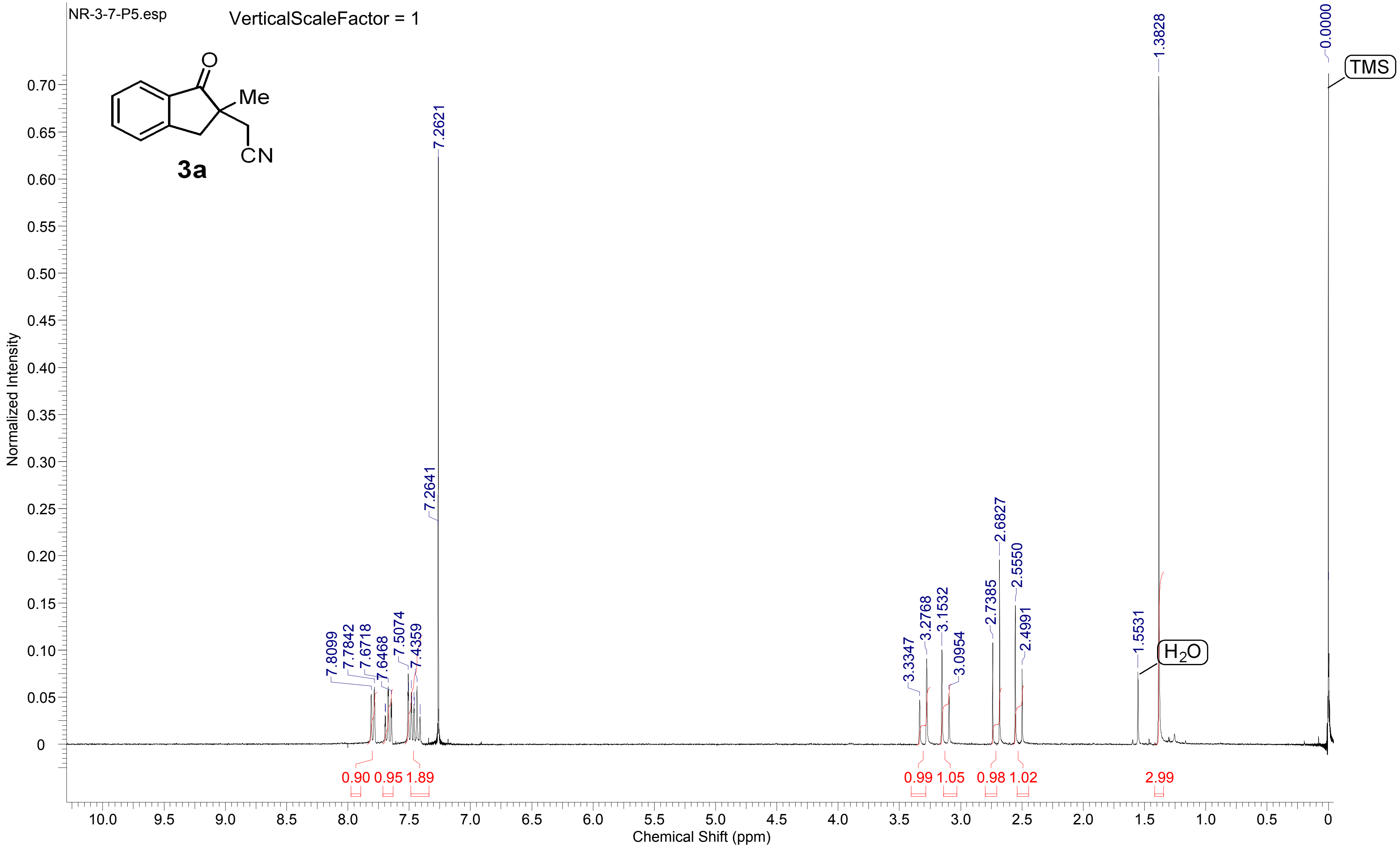
2l

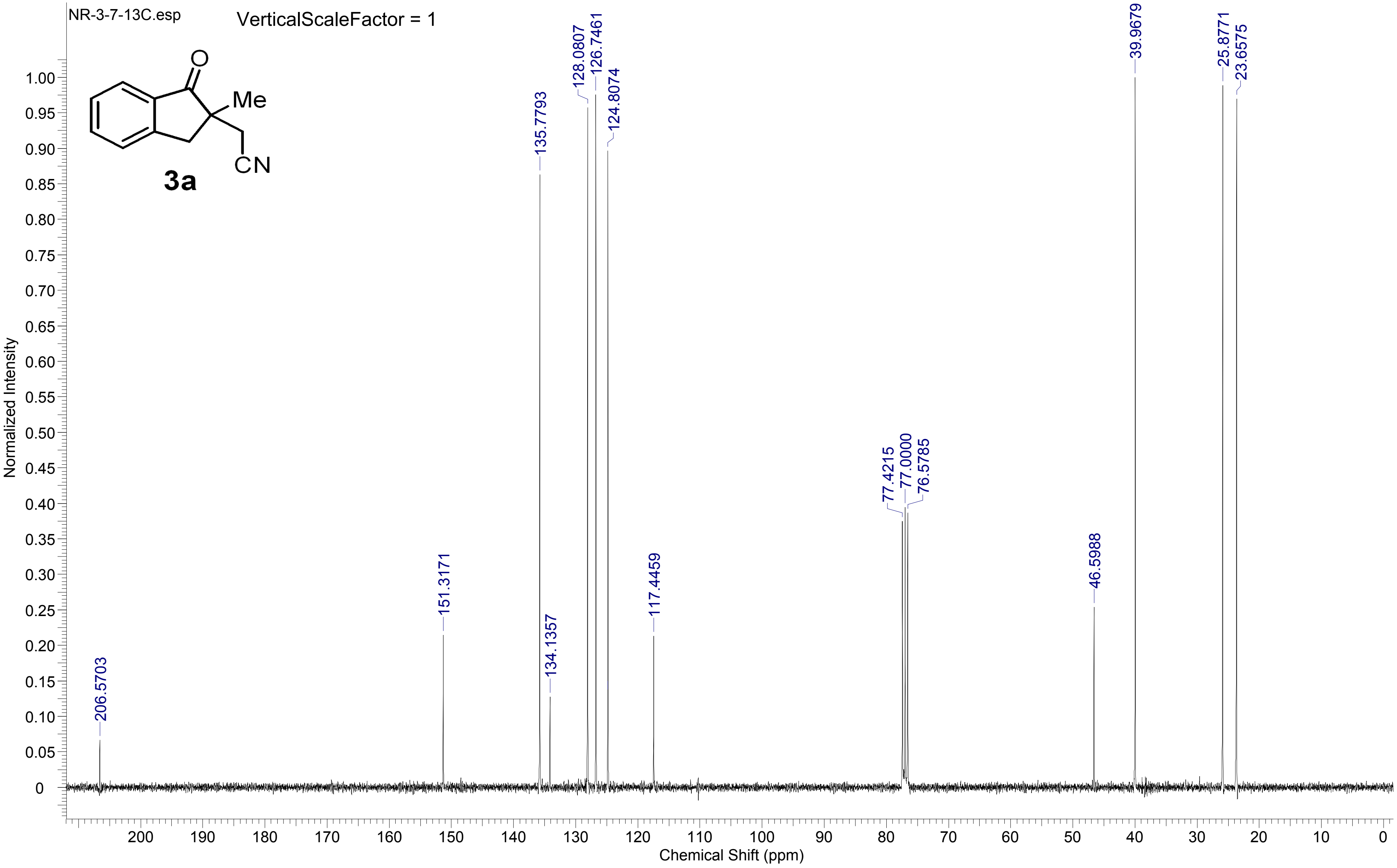
8/20/2013 6:19:53 PM

Acquisition Time (sec)	2.0001	**Comment**	NR-3-7-P5 University of Minnesota Department of Chemistry VAC-300				
Date	Dec 20 2012	**Date Stamp**	Dec 20 2012	**File Name**	C:\Users\Naveen\Desktop\121220v3_1302.fid\fid		
Frequency (MHz)	299.96	**Nucleus**	1H	**Number of Transients**	16	**Original Points Count**	11998
Points Count	131072	**Pulse Sequence**	s2pul	**Receiver Gain**	38.00	**Solvent**	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7993	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	5998.80	**Temperature (degree C)**	AMBIENT TEMPERATURE



8/20/2013 6:24:57 PM

Acquisition Time (sec)	0.8000	***Comment***	NR-3-7-13C University of Minnesota Department of Chemistry VAC-300				
Date	Dec 21 2012	***Date Stamp***	Dec 21 2012				
File Name	C:\Data\Study\Chris\Cyanoacylation\NMRs Cyanoacylation\121221v3_2403.fid\fid					***Frequency (MHz)***	75.43
Nucleus	13C	***Number of Transients***	1024	***Original Points Count***	13889	***Points Count***	16384
Pulse Sequence	s2pul	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	7860.3169
Spectrum Type	STANDARD	***Sweep Width (Hz)***	17361.11	***Temperature (degree C)***	AMBIENT TEMPERATURE		



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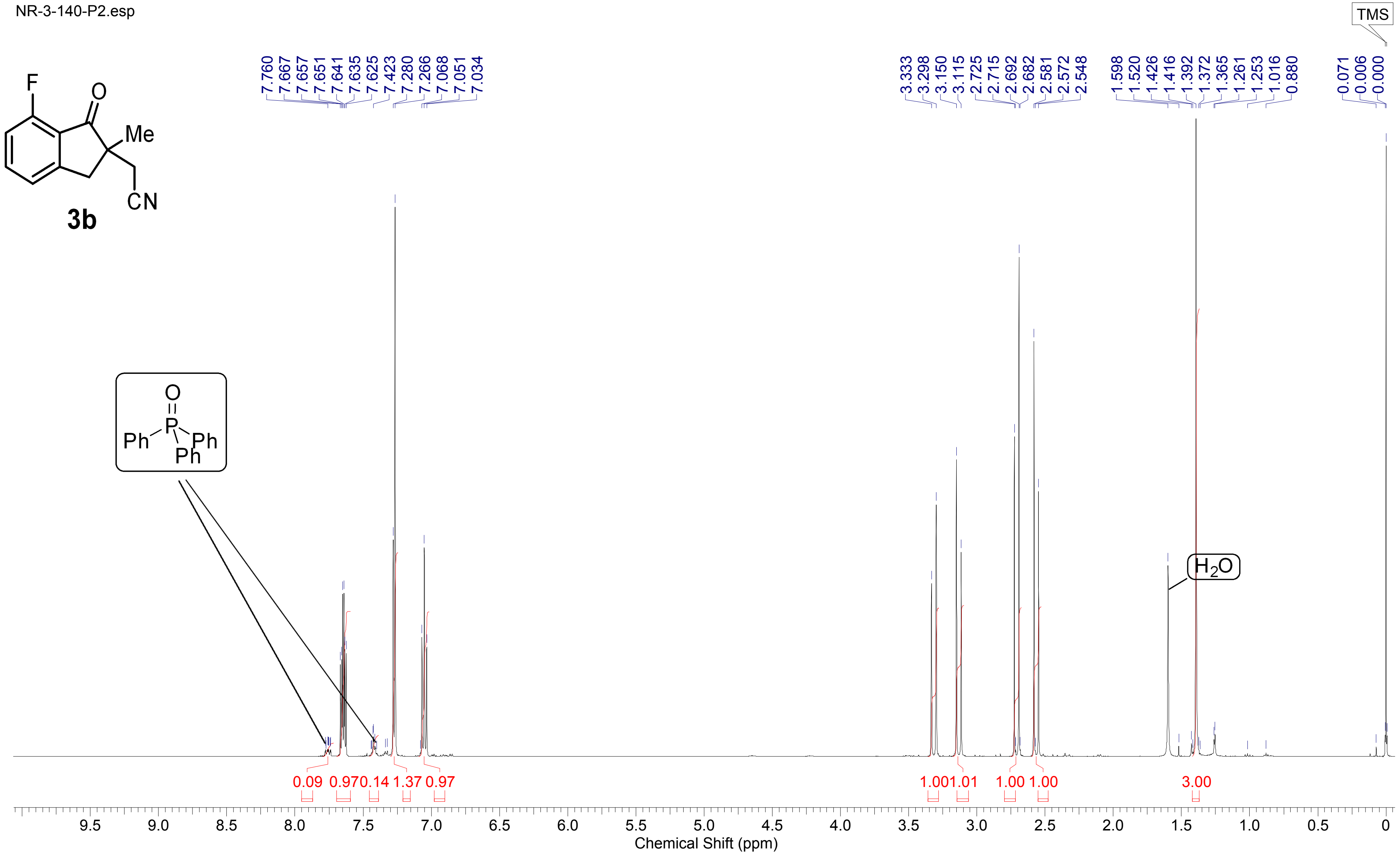
1/10/2014 11:10:14 AM

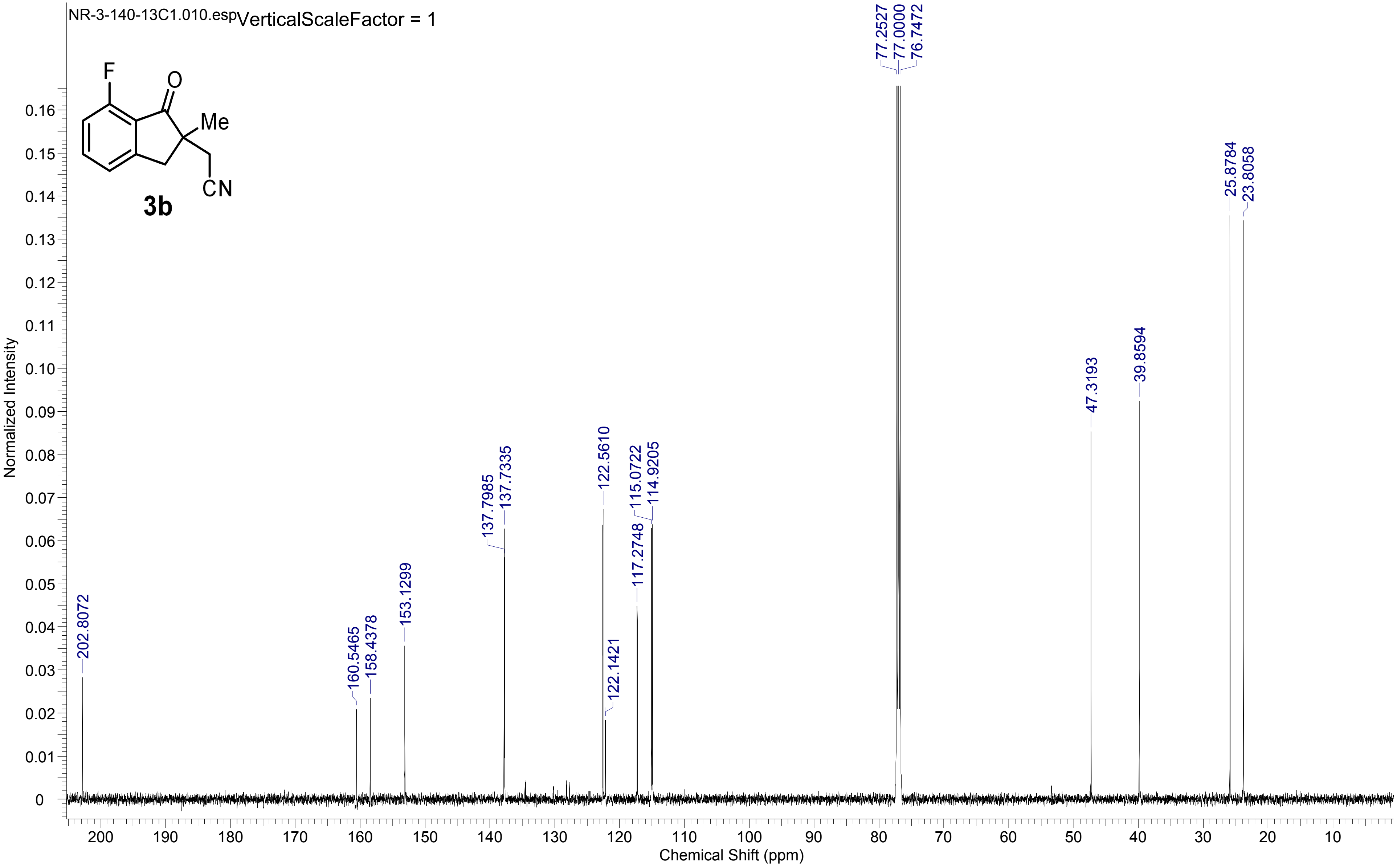
Acquisition Time (sec)	3.2768	***Date***	25 Sep 2013 14:26:56			***Date Stamp***	25 Sep 2013 14:26:56
File Name	C:\Users\Naveen\Desktop\NR-3-140-P2\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	73.82	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3078.9565	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	21.000				

NR-3-140-P2.esp



9/26/2013 12:09:49 PM

Acquisition Time (sec)	1.1010	***Date***	25 Sep 2013 21:29:20			***Date Stamp***	25 Sep 2013 21:29:20
File Name	C:\Users\Naveen\Desktop\NR-3-140-13C1\10\fid			***Frequency (MHz)***	125.77	***Nucleus***	13C
Number of Transients	1000	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	182.64	***SW(cyclical) (Hz)***	29761.90
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	12569.4092	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.00	***Temperature (degree C)***	21.000				



9/26/2013 1:53:49 PM

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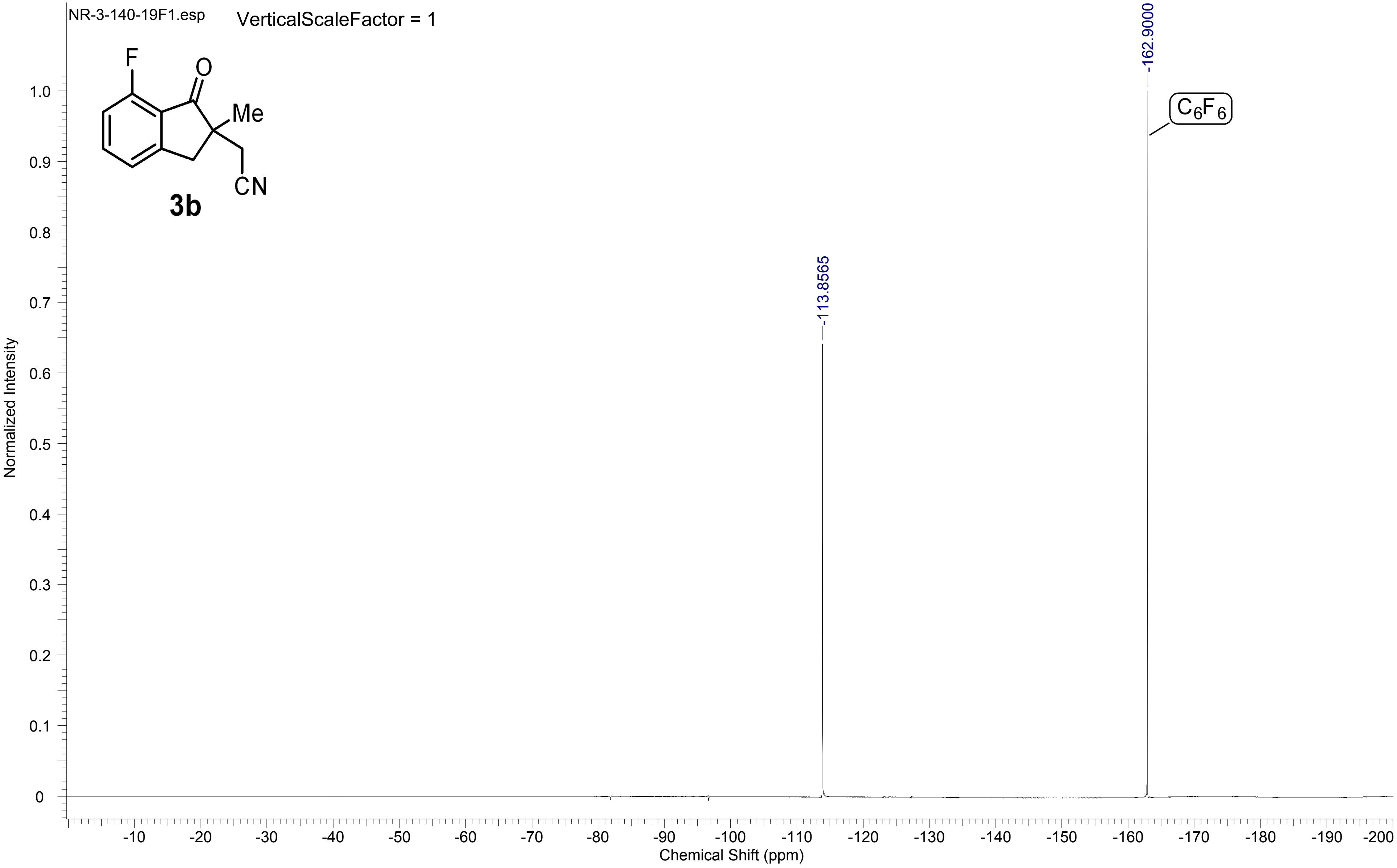
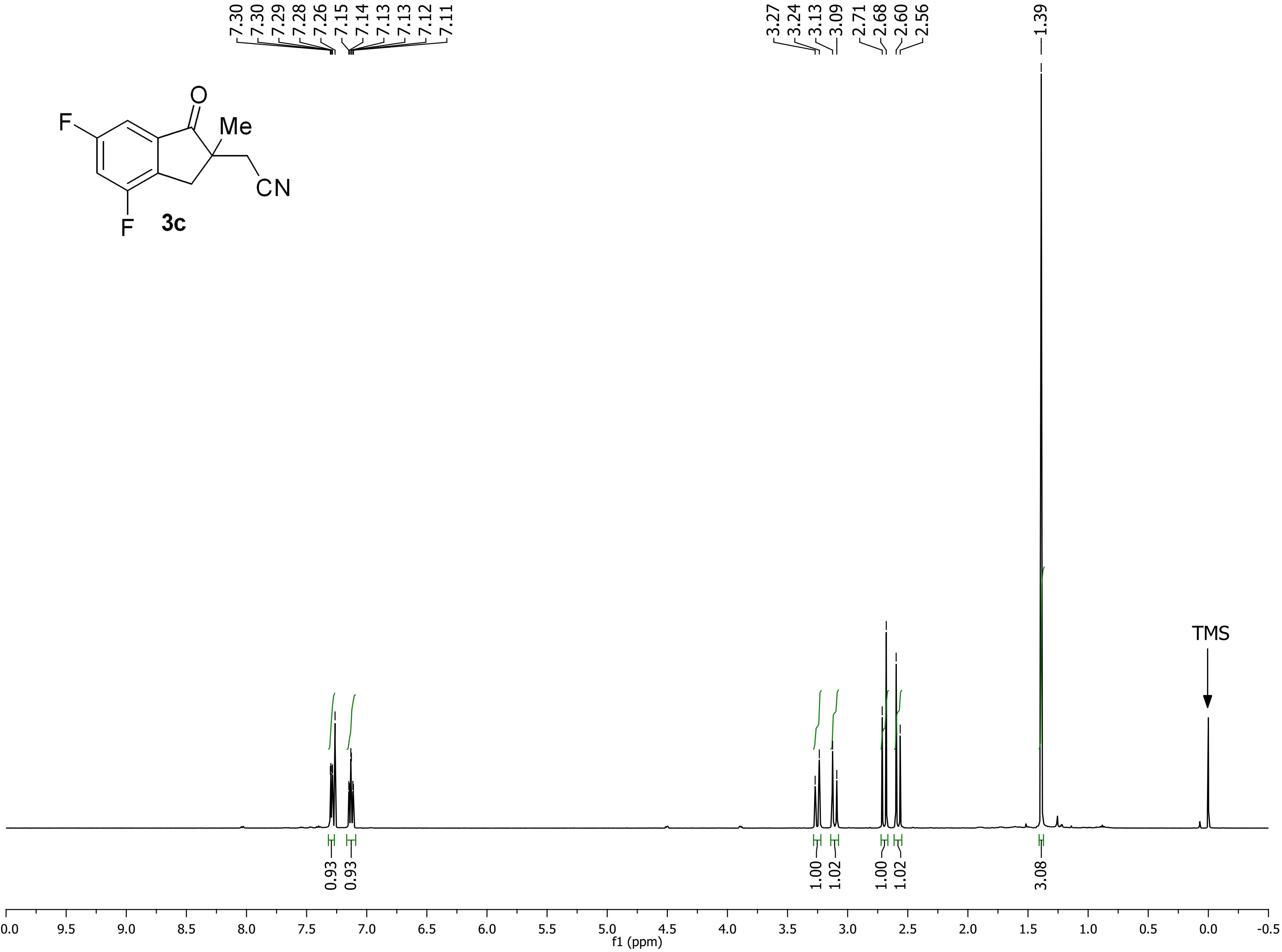
File Name	C:\Users\Naveen\Desktop\NR-3-140-19F1\10\fid			***Frequency (MHz)***	470.55	***Nucleus***	19F
Number of Transients	16	***Origin***	spect	***Original Points Count***	65536	***Owner***	auto
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	182.64	***SW(cyclical) (Hz)***	113636.37
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-47624.5820	***Spectrum Type***	STANDARD
Sweep Width (Hz)	113634.63	***Temperature (degree C)***	21.000				





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3.13
3.09
2.71
2.68
2.60
2.56
1.39
F
O
Me
CN
F
3c
TMS
0.93
0.93
1.00
1.02
1.00
1.02
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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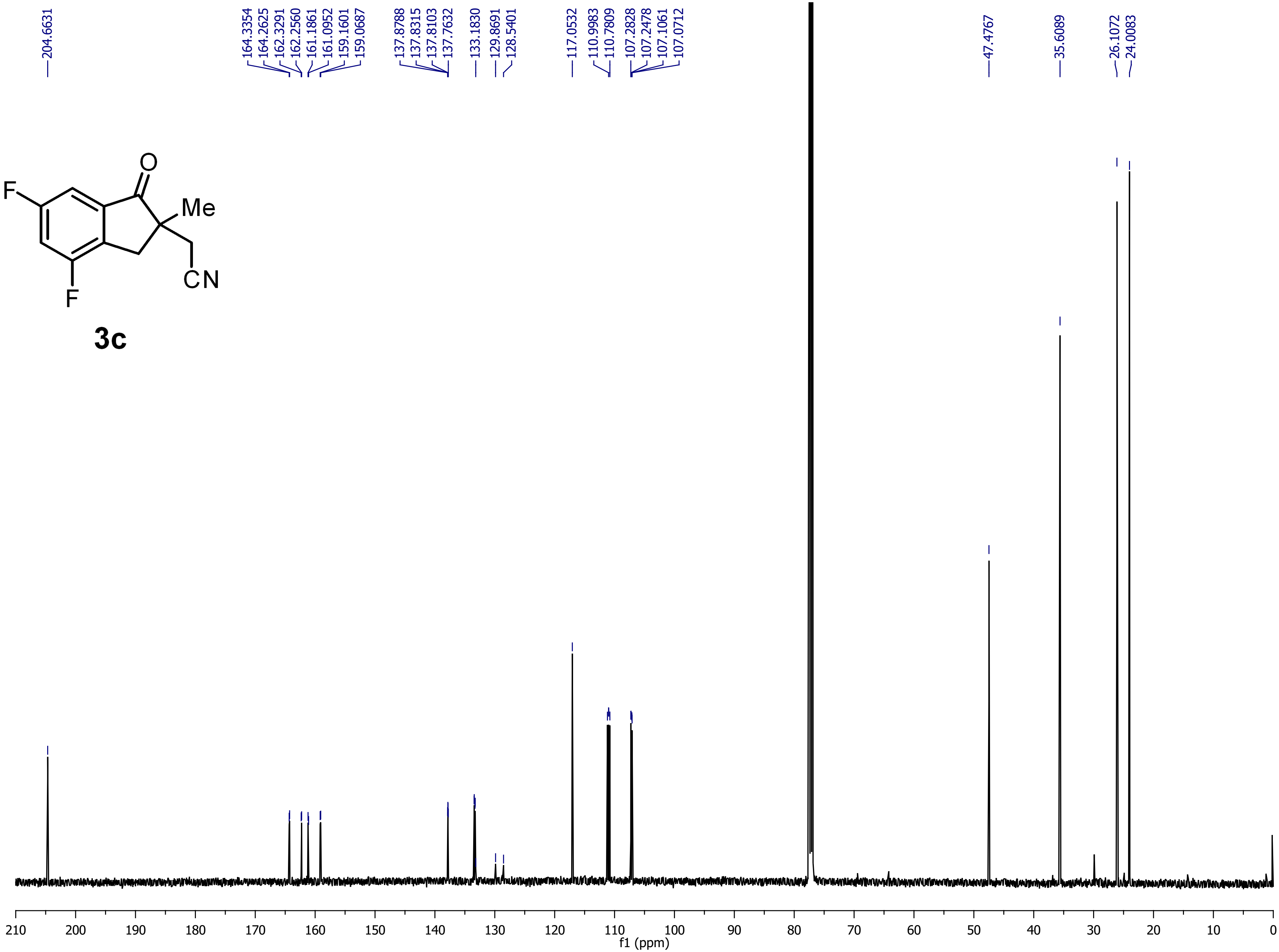
f1 (ppm)



3c

F
F
O
Me
CN
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159.1601
159.0687
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137.8315
137.8103
137.7632
133.1830
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128.5401
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110.7809
107.2828
107.2478
107.1061
107.0712
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35.6089
26.1072
24.0083
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180
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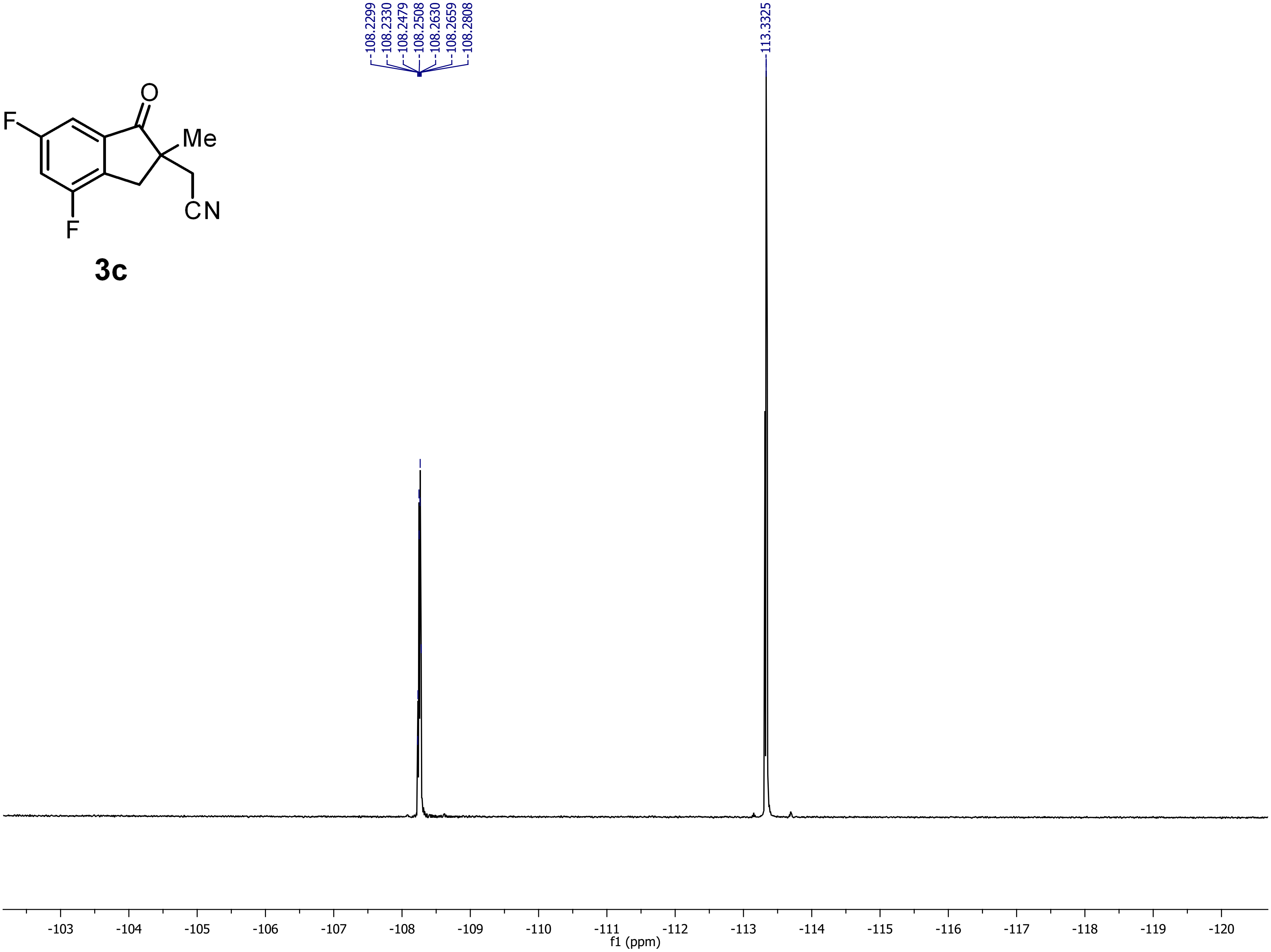
f1 (ppm)



F
O
Me
F
CN

3c

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113.3325
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-104
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-114
-115
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-117
-118
-119
-120
f1 (ppm)

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8/20/2013 6:27:24 PM

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Date	May 9 2013	***Date Stamp***	May 9 2013	***File Name***	C:\Users\Naveen\Desktop\130509v3_0702.fid\fid		
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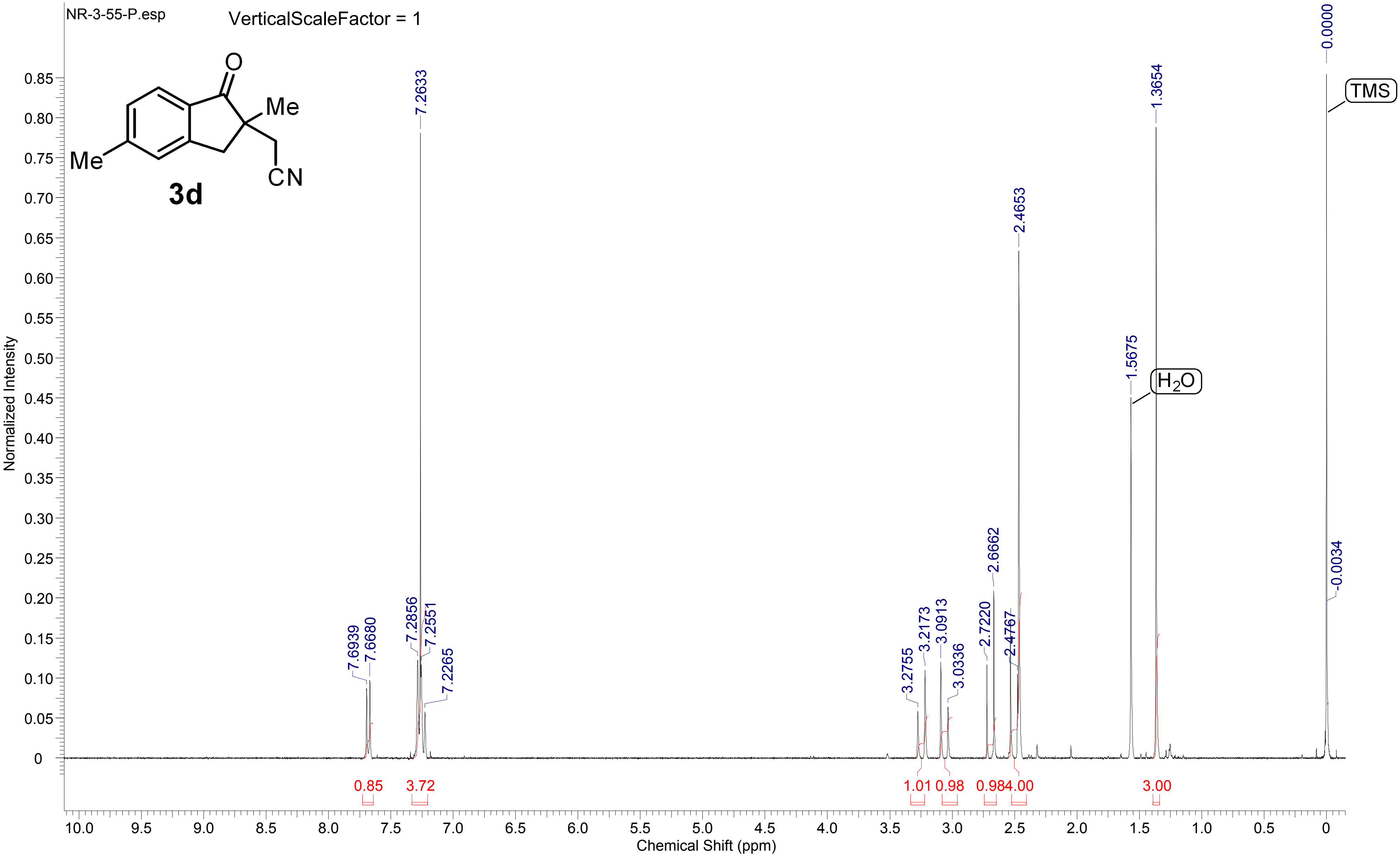
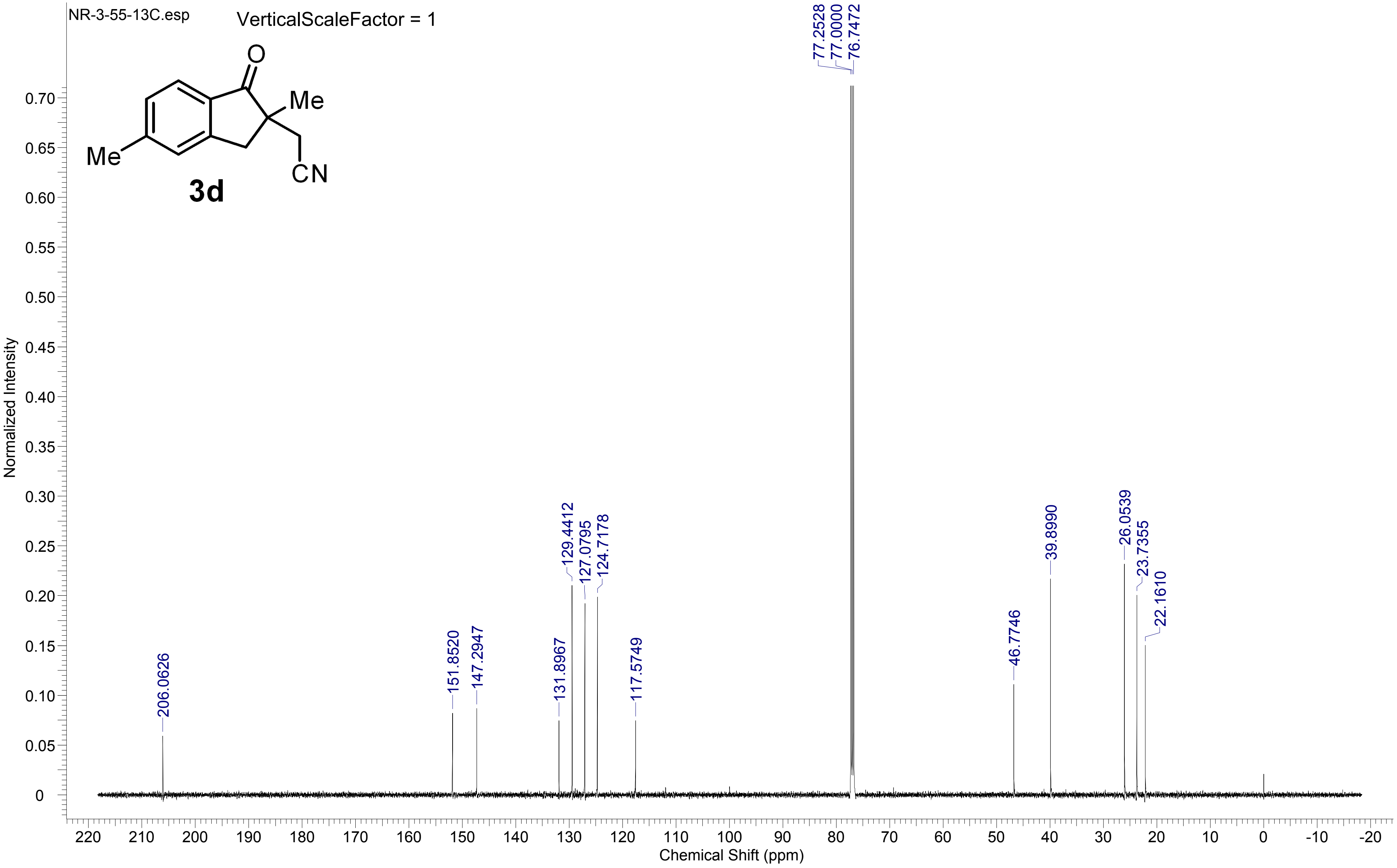
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2400.1196	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



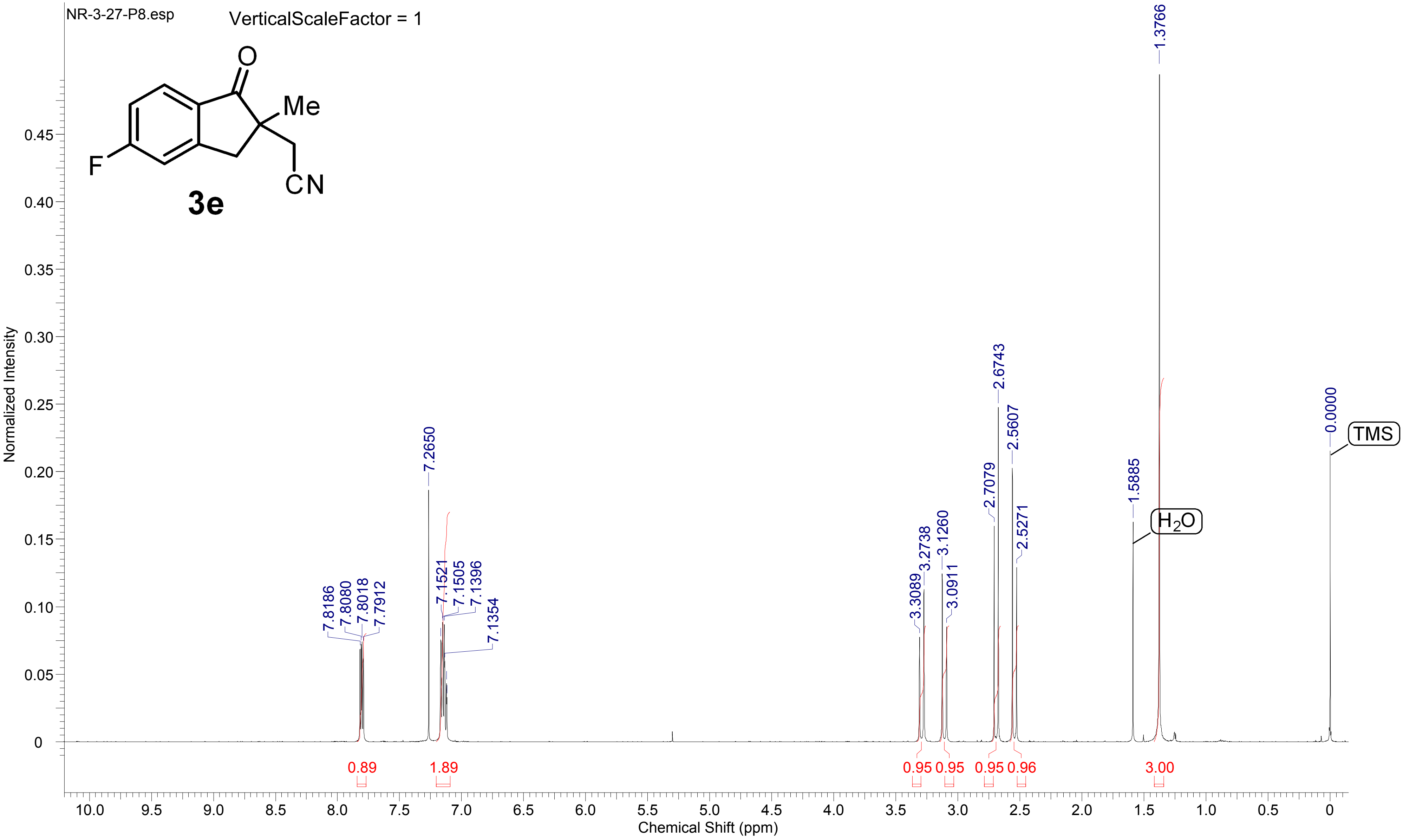
8/20/2013 6:30:20 PM

Acquisition Time (sec)	1.1010	***Comment***	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0030			***Date***	09 May 2013 18:13:04
Date Stamp	09 May 2013 18:13:04			***File Name***	C:\Users\Naveen\Desktop\NR-3-55-13C\1\fid		
Frequency (MHz)	125.76	***Nucleus***	13C	***Number of Transients***	868	***Origin***	spect
Original Points Count	32768	***Owner***	cdonrr	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	194.68	***SW(cyclical) (Hz)***	29761.90	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	12569.3496	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	25.025



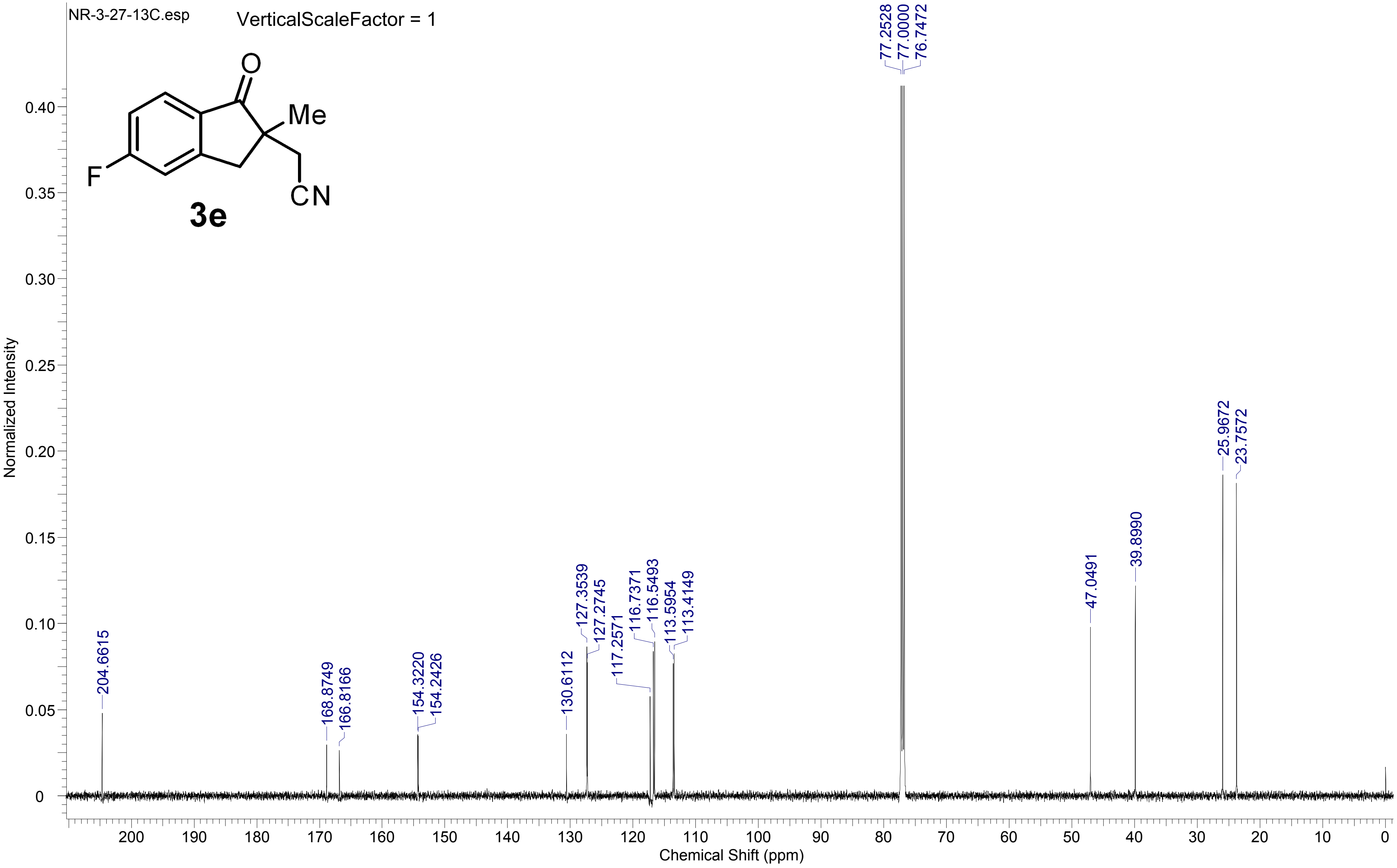
8/20/2013 6:33:00 PM

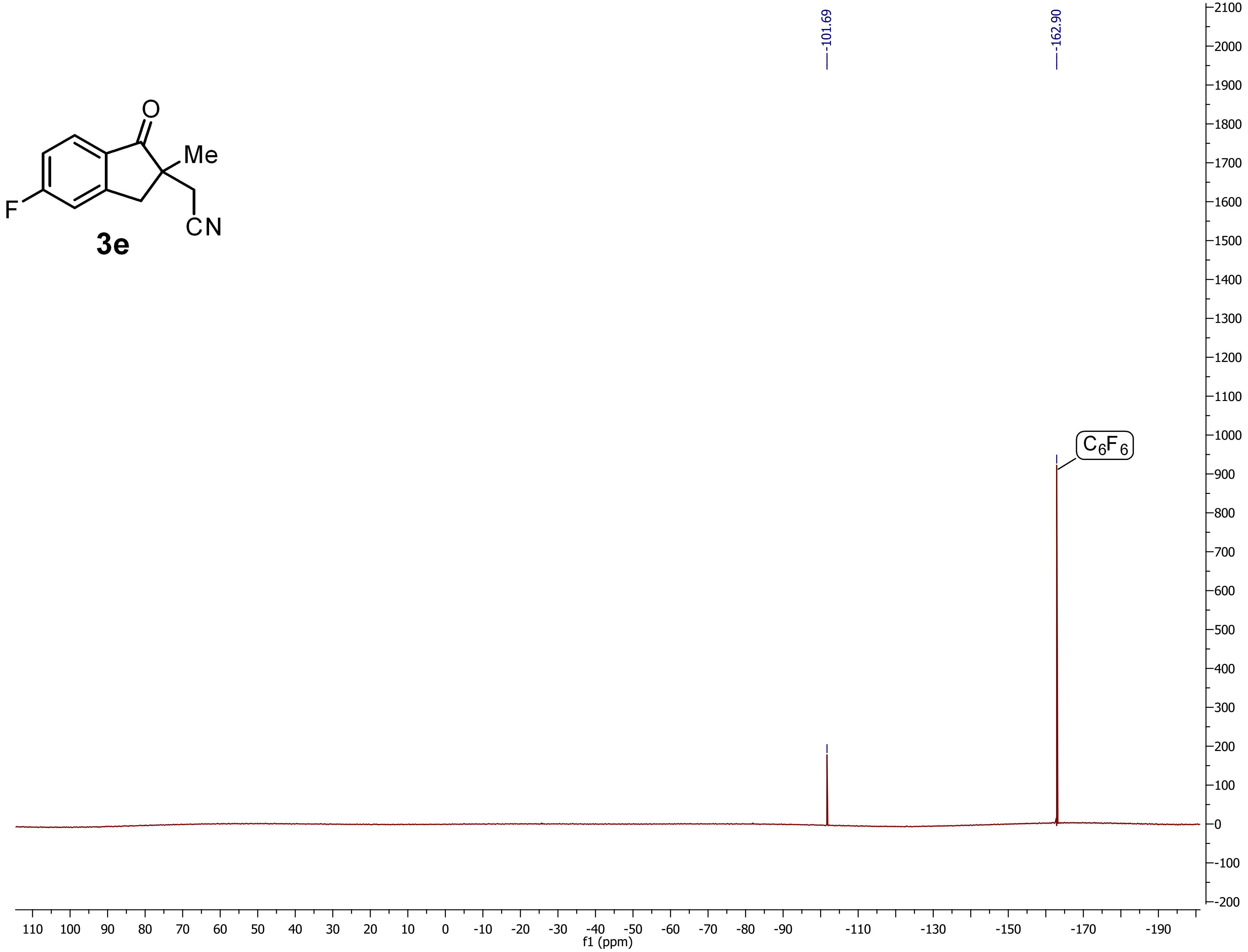
Acquisition Time (sec)	3.2768	***Comment***	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0030			***Date***	15 May 2013 20:16:48
Date Stamp	15 May 2013 20:16:48			***File Name***	C:\Users\Naveen\Desktop\NR-3-27-P8\1\fid		
Frequency (MHz)	500.13	***Nucleus***	1H	***Number of Transients***	16	***Origin***	spect
Original Points Count	32768	***Owner***	cdonrr	***Points Count***	131072	***Pulse Sequence***	zg30
Receiver Gain	127.25	***SW(cyclical) (Hz)***	10000.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	3077.2781	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	9999.92	***Temperature (degree C)***	25.001



8/20/2013 6:35:17 PM

Acquisition Time (sec)	1.1010	***Comment***	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0030			***Date***	15 May 2013 19:19:12
Date Stamp	15 May 2013 19:19:12			***File Name***	C:\Users\Naveen\Desktop\NR-3-27-13C\1\fid		
Frequency (MHz)	125.76	***Nucleus***	13C	***Number of Transients***	981	***Origin***	spect
Original Points Count	32768	***Owner***	cdonrr	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	194.68	***SW(cyclical) (Hz)***	29761.90	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	12570.2578	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	25.036





3e

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f1 (ppm)
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90
80
70
60
50
40
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20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
2100
2000
1900
1800
1700
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900
800
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400
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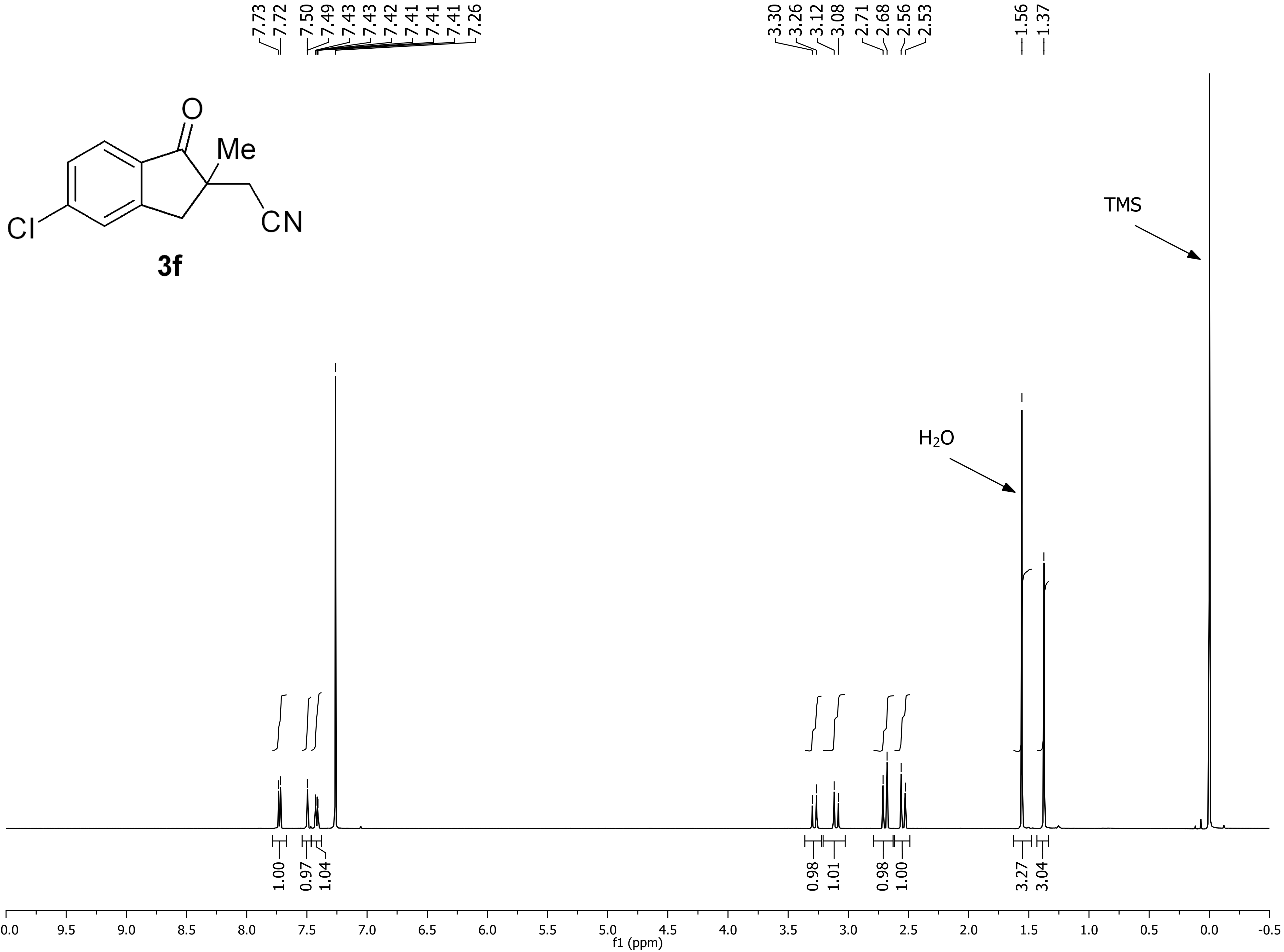
-200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2.56
2.53
1.56
1.37
O
Me
Cl
CN
3f
TMS
H2O
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1.04
0.98
1.01
0.98
1.00
3.27
3.04
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7.5
7.0
6.5
6.0
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5.0
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2.0
1.5
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0.0
-0.5
f1 (ppm)

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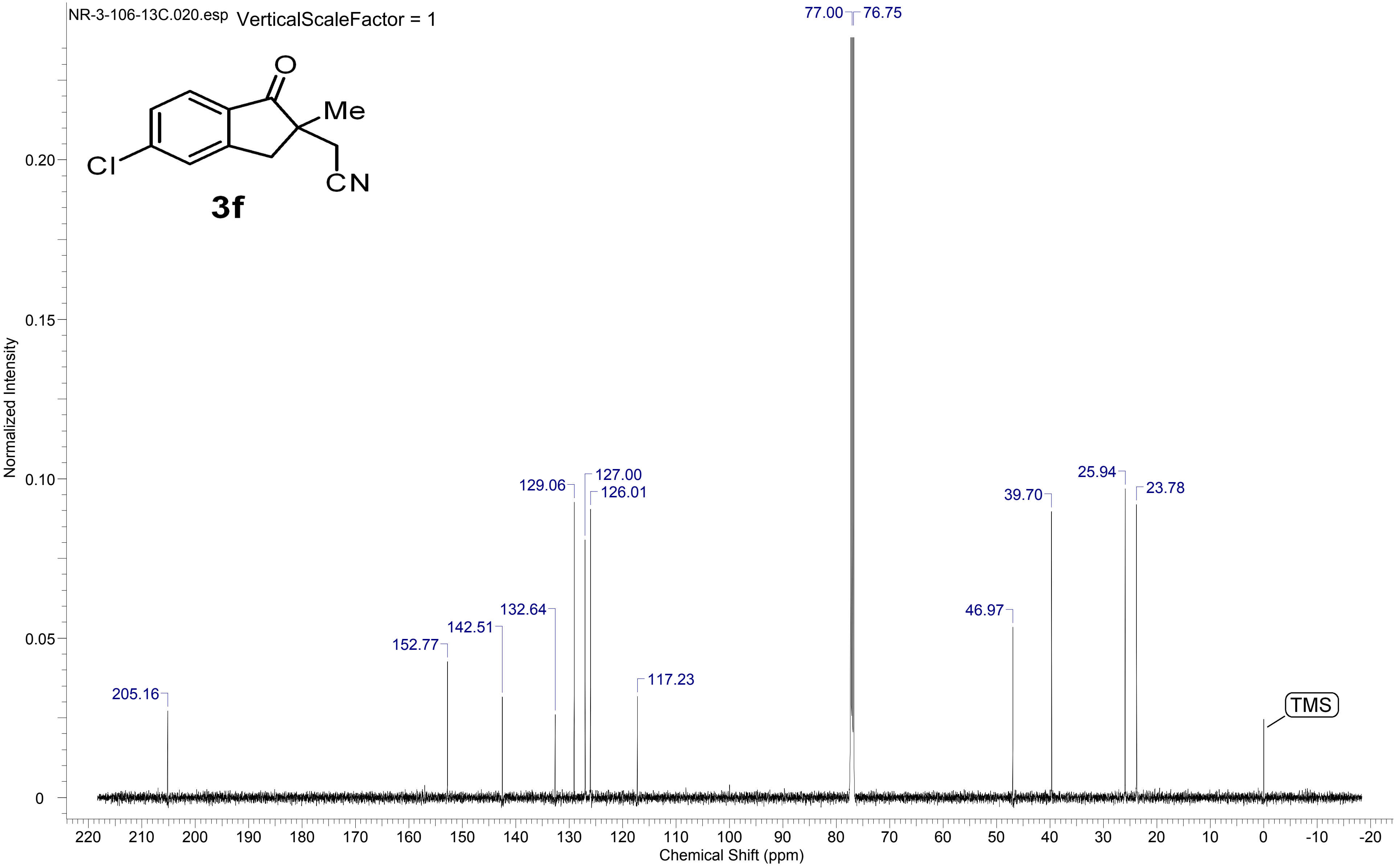
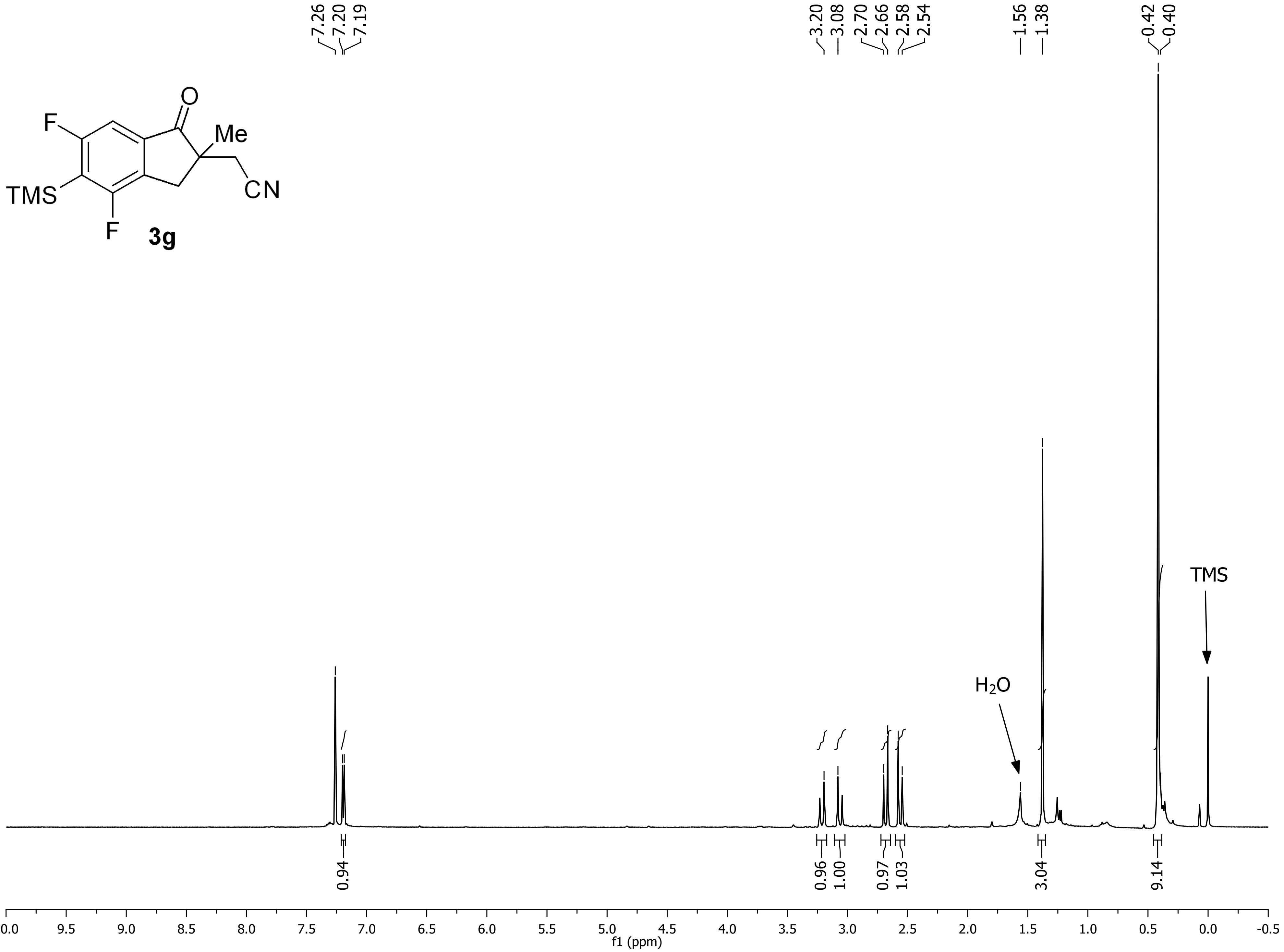
10/1/2013 9:37:08 PM

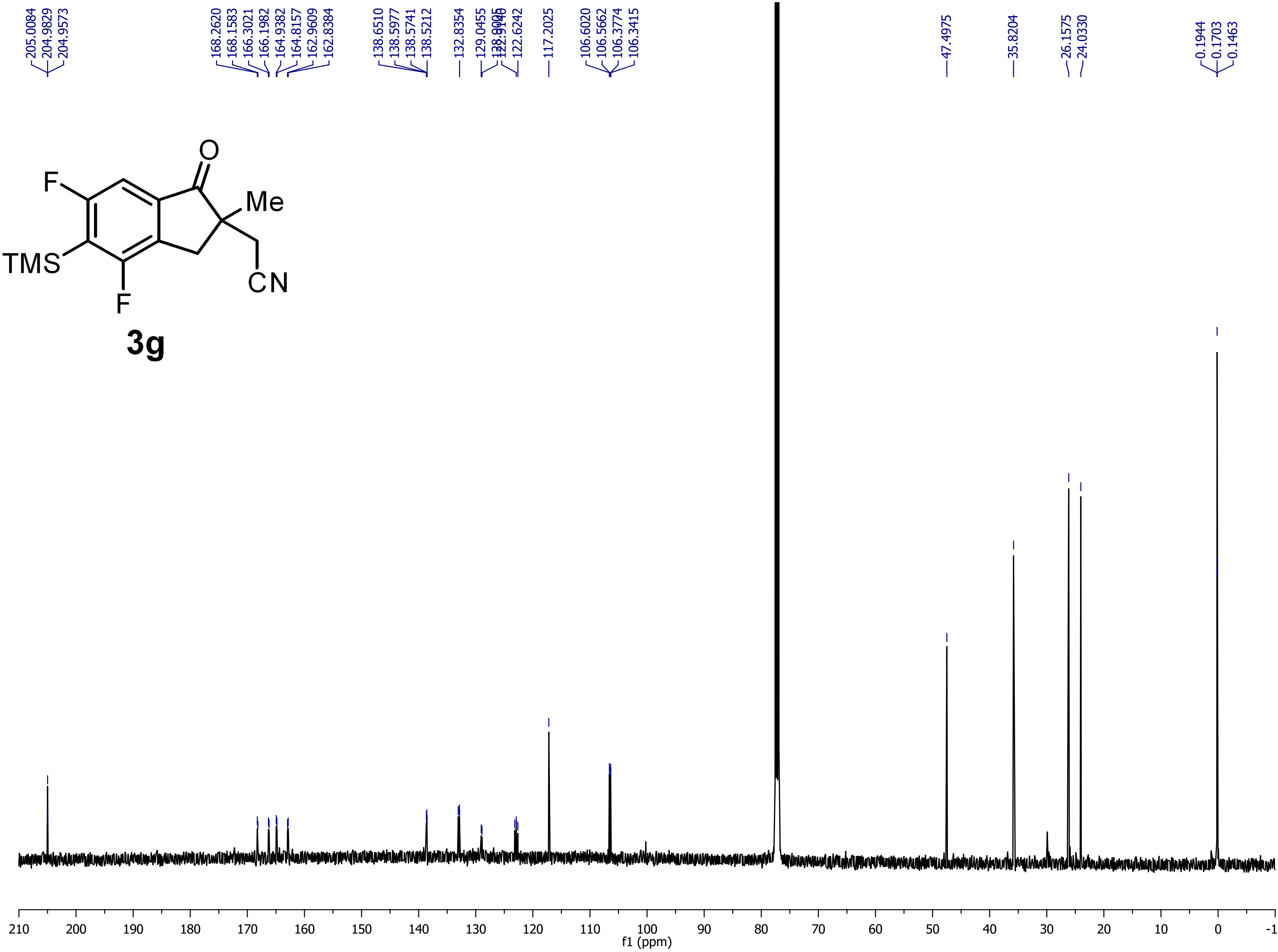
Acquisition Time (sec)	1.1010	***Date***	12 Jul 2013 17:24:00			***Date Stamp***	12 Jul 2013 17:24:00
File Name	C:\Users\Naveen\Desktop\Cyanoacylation NMRs\NR-3-106-13C\20\fid					***Frequency (MHz)***	125.77
Nucleus	13C	***Number of Transients***	1024	***Origin***	spect	***Original Points Count***	32768
Owner	auto	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	194.68
SW(cyclical) (Hz)	29761.90	***Solvent***	CHLOROFORM-d			***Spectrum Offset (Hz)***	12570.3184
Spectrum Type	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	20.999		



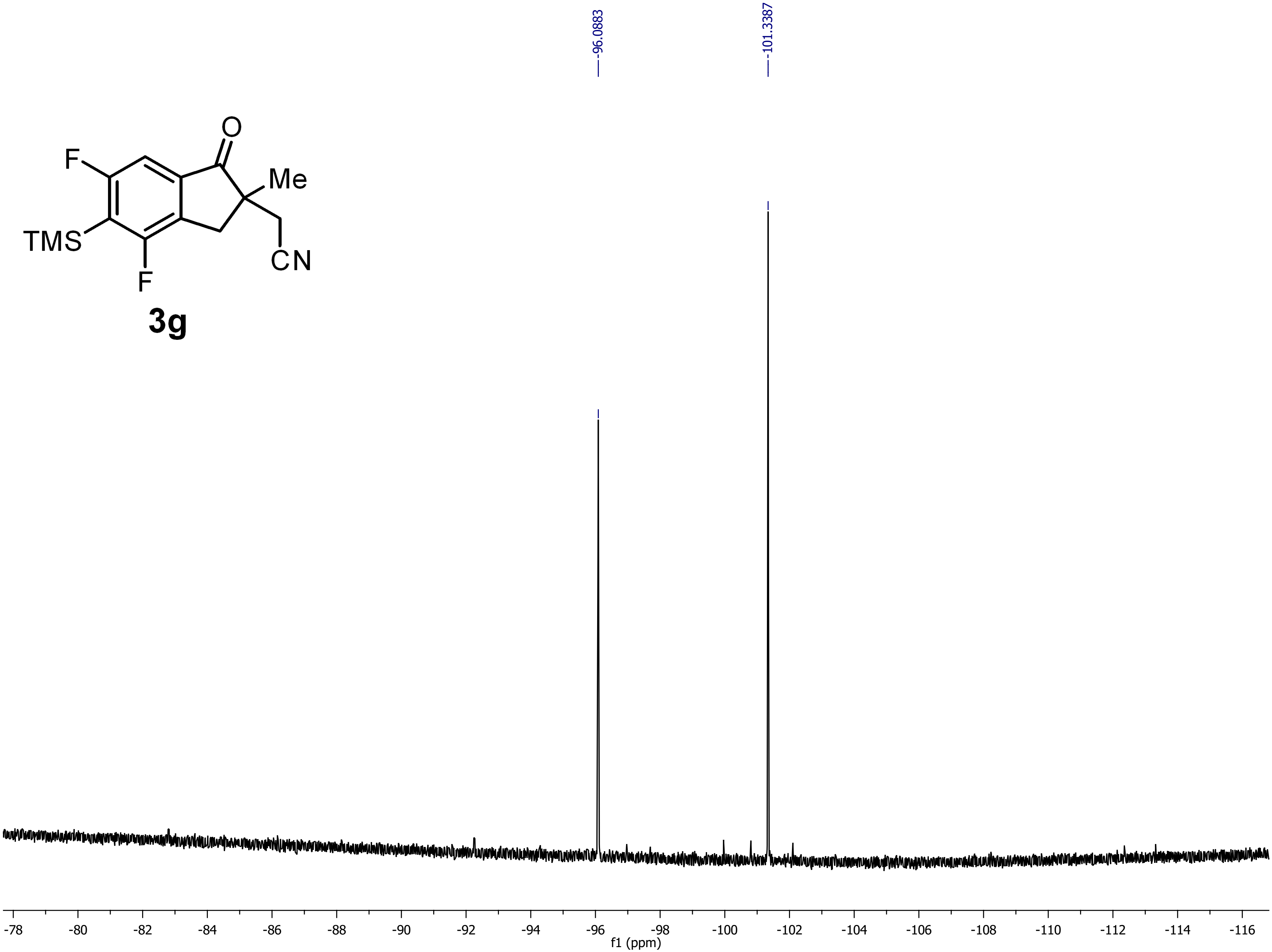


3g

7.26
7.20
7.19
3.20
3.08
2.70
2.66
2.58
2.54
1.56
1.38
0.42
0.40
O
Me
F
TMS
CN
F
TMS
H_2O
0.94
0.96
1.00
0.97
1.03
3.04
9.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

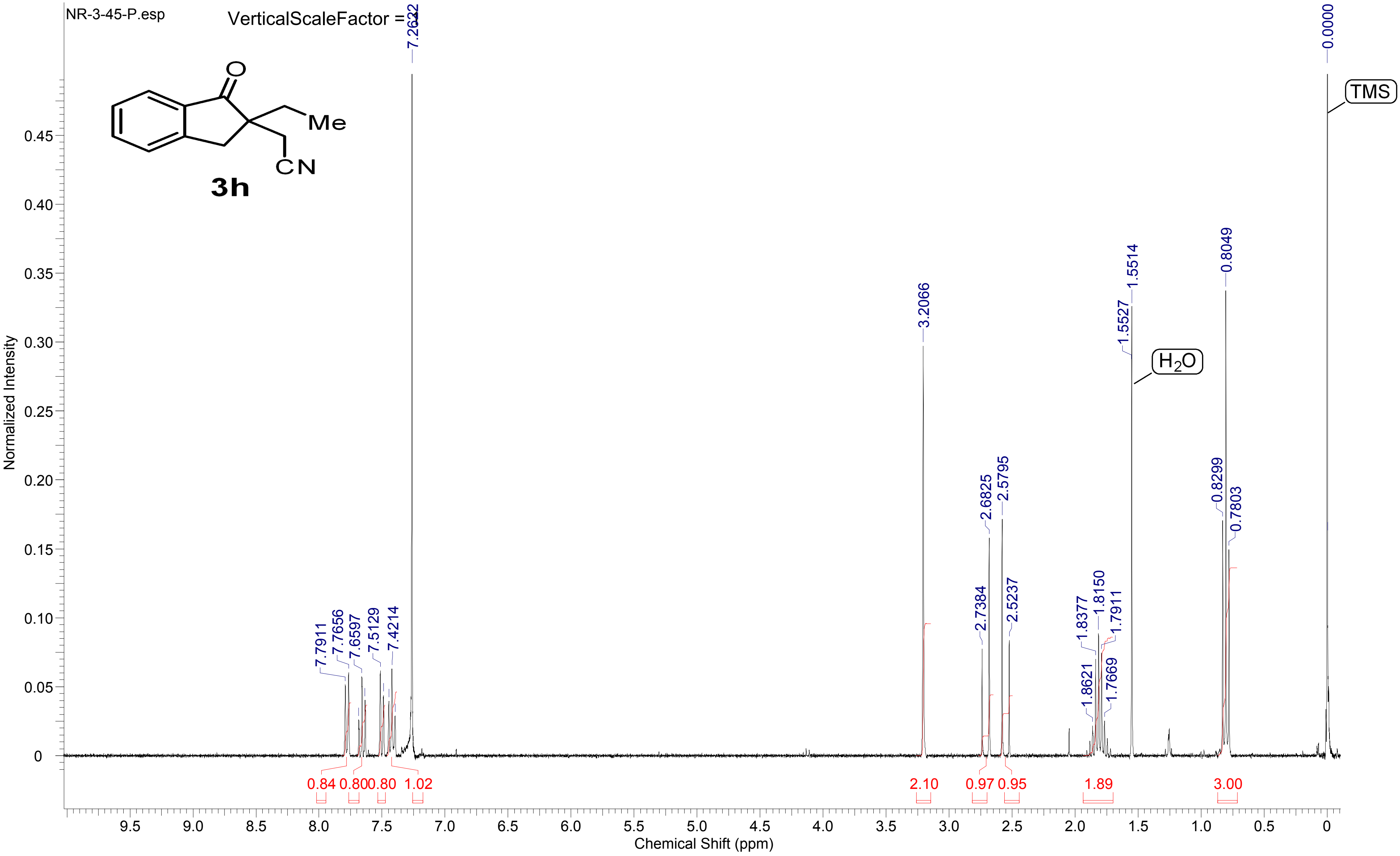
205.0084
204.9829
204.9573
168.2620
168.1583
166.3021
166.1982
164.9382
164.8157
162.9609
162.8384
138.6510
138.5977
138.5741
138.5212
132.8354
129.0455
128.9905
122.9140
122.6242
117.2025
106.6020
106.5662
106.3774
106.3415
47.4975
35.8204
26.1575
24.0330
0.1944
0.1703
0.1463
O
F
Me
TMS
CN
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3g


-96.0883
-101.3387
F
F
TMS
O
Me
CN
3g
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
f1 (ppm)

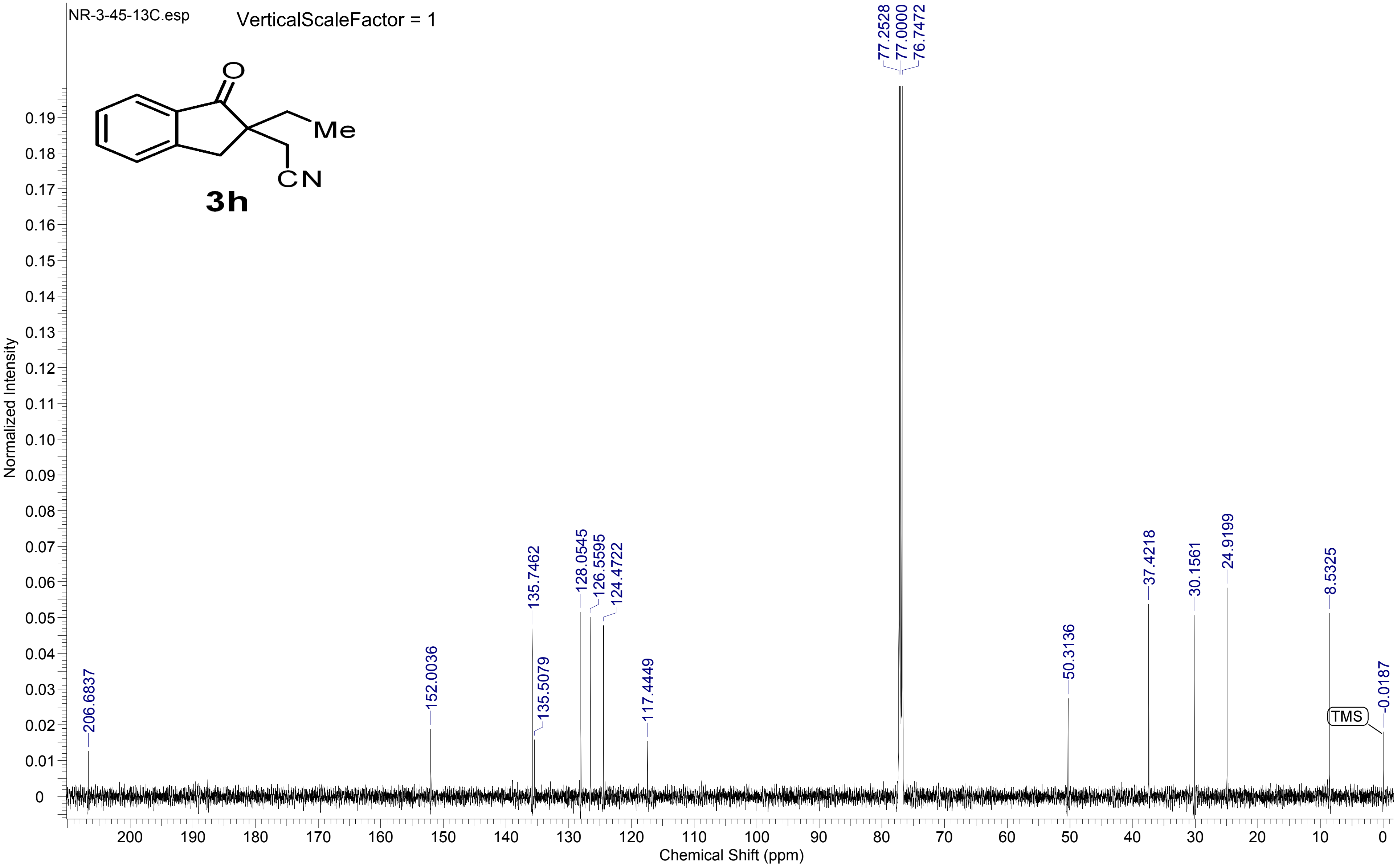
8/20/2013 5:35:40 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-45-P University of Minnesota Department of Chemistry VAC-300				
Date	Apr 26 2013	***Date Stamp***	Apr 26 2013	***File Name***	C:\Users\Naveen\Desktop\130426v3_2302.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7534	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



8/20/2013 6:15:29 PM

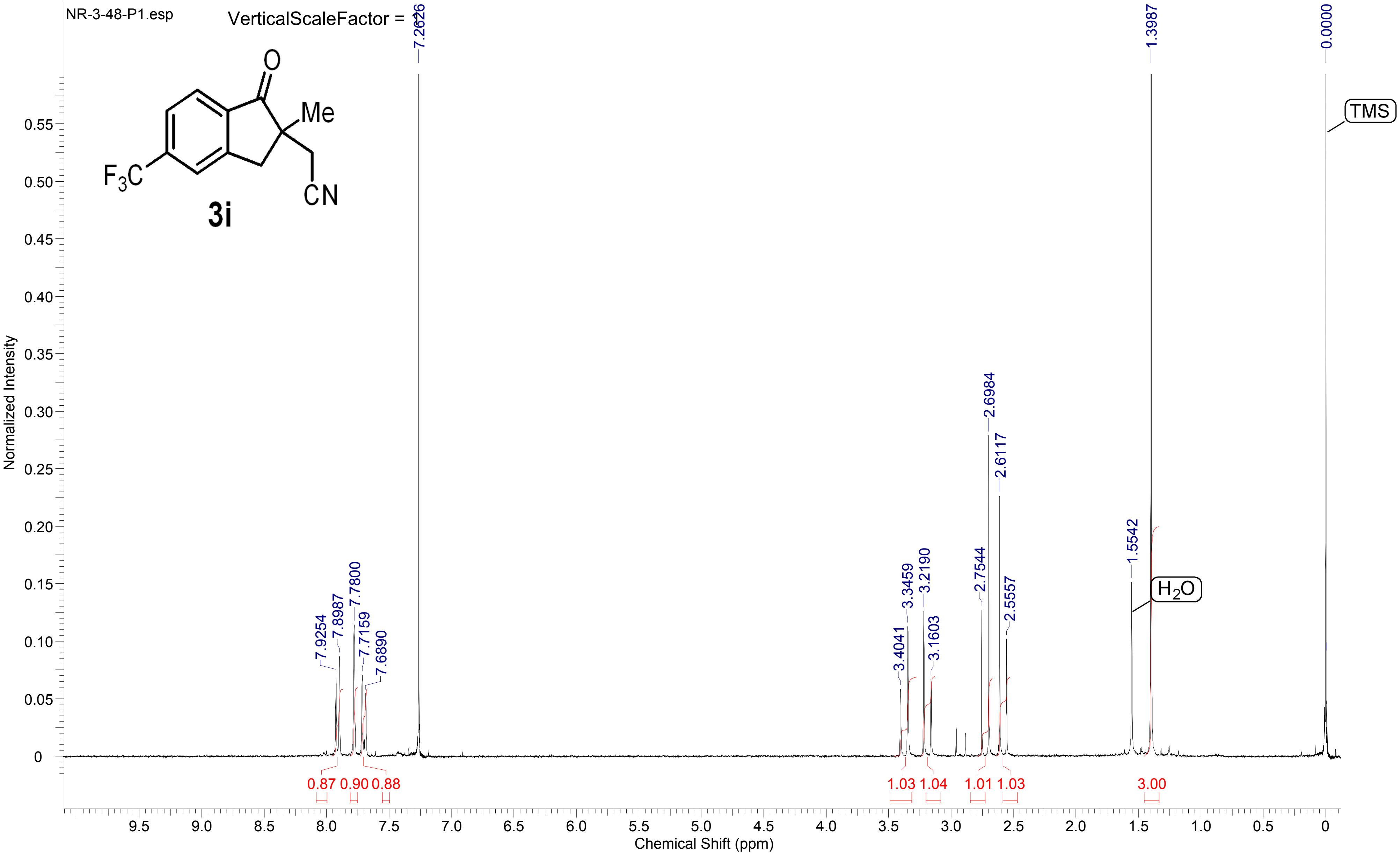
Acquisition Time (sec)	1.1010	***Comment***	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0030			***Date***	27 Apr 2013 12:44:32
Date Stamp	27 Apr 2013 12:44:32			***File Name***	C:\Users\Naveen\Desktop\NR-3-45-13C\1\fid		
Frequency (MHz)	125.76	***Nucleus***	13C	***Number of Transients***	1024	***Origin***	spect
Original Points Count	32768	***Owner***	cdonrr	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	194.68	***SW(cyclical) (Hz)***	29761.90	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	12571.1660	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	24.999



This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

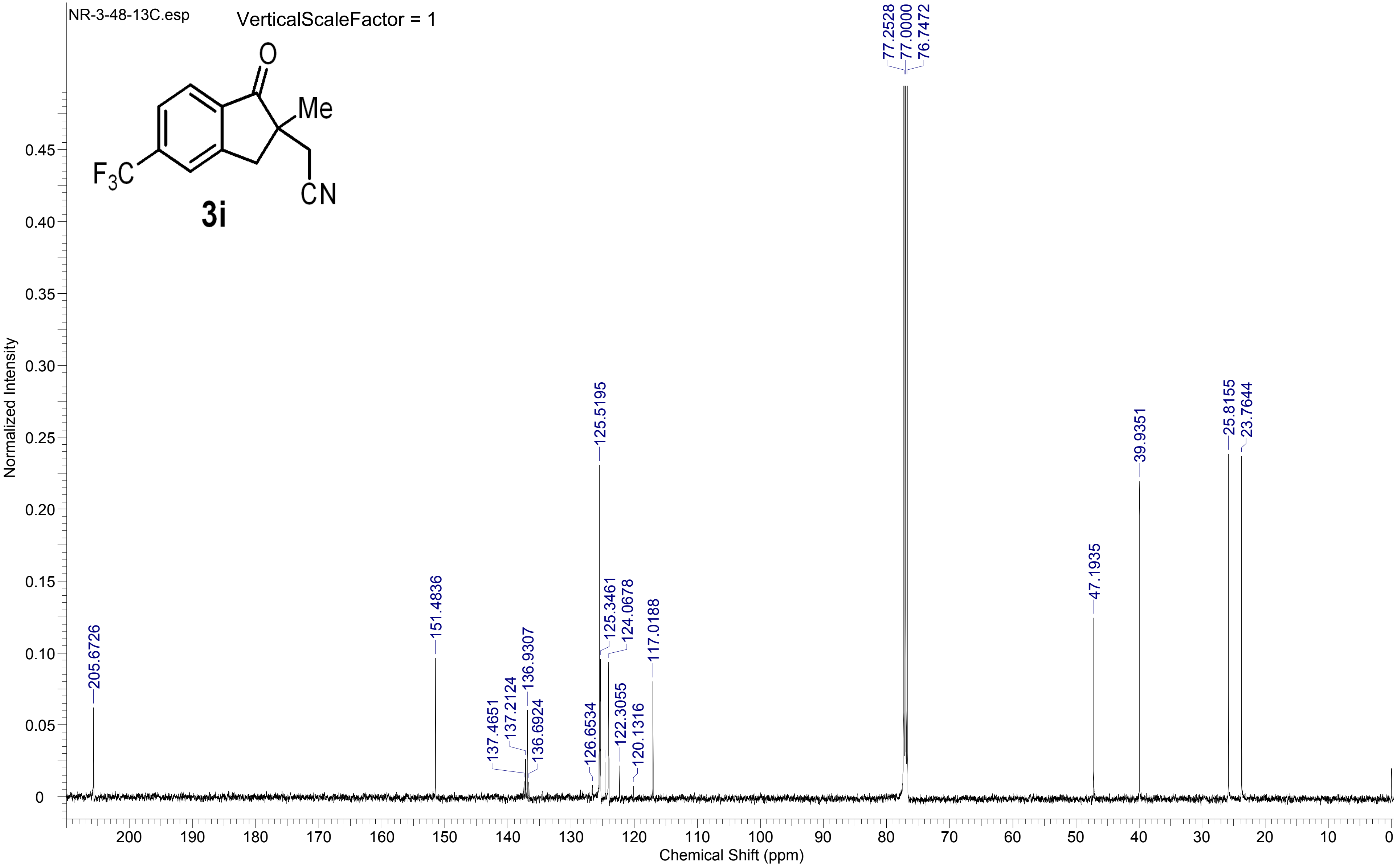
8/20/2013 6:43:15 PM

Acquisition Time (sec)	2.0001	***Comment***	NR-3-48-P1 University of Minnesota Department of Chemistry VAC-300				
Date	Apr 30 2013	***Date Stamp***	Apr 30 2013	***File Name***	C:\Users\Naveen\Desktop\130430v3_6902.fid\fid		
Frequency (MHz)	299.96	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	11998
Points Count	131072	***Pulse Sequence***	s2pul	***Receiver Gain***	38.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2399.7534	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	5998.80	***Temperature (degree C)***	AMBIENT TEMPERATURE



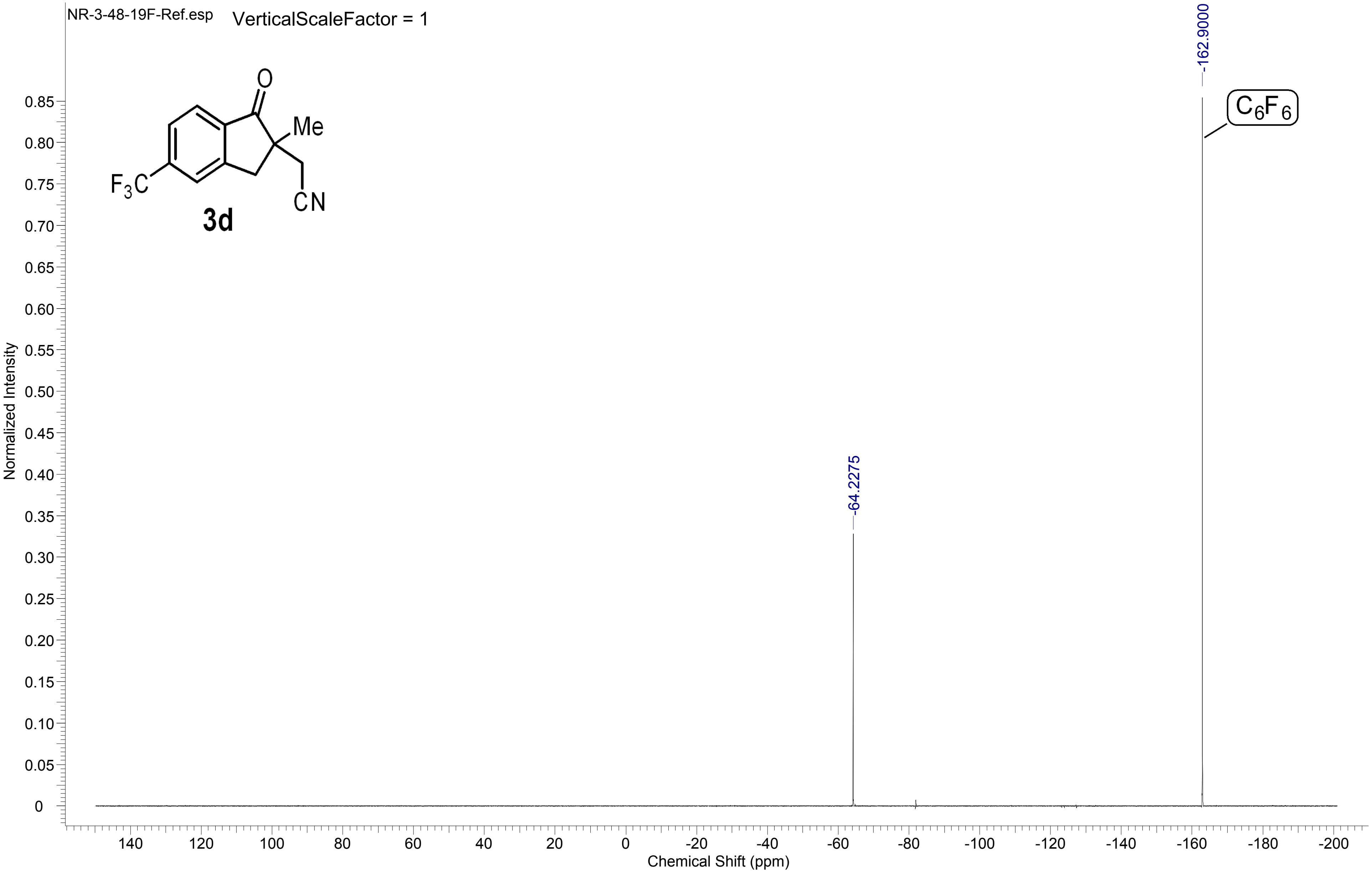
8/20/2013 6:45:54 PM

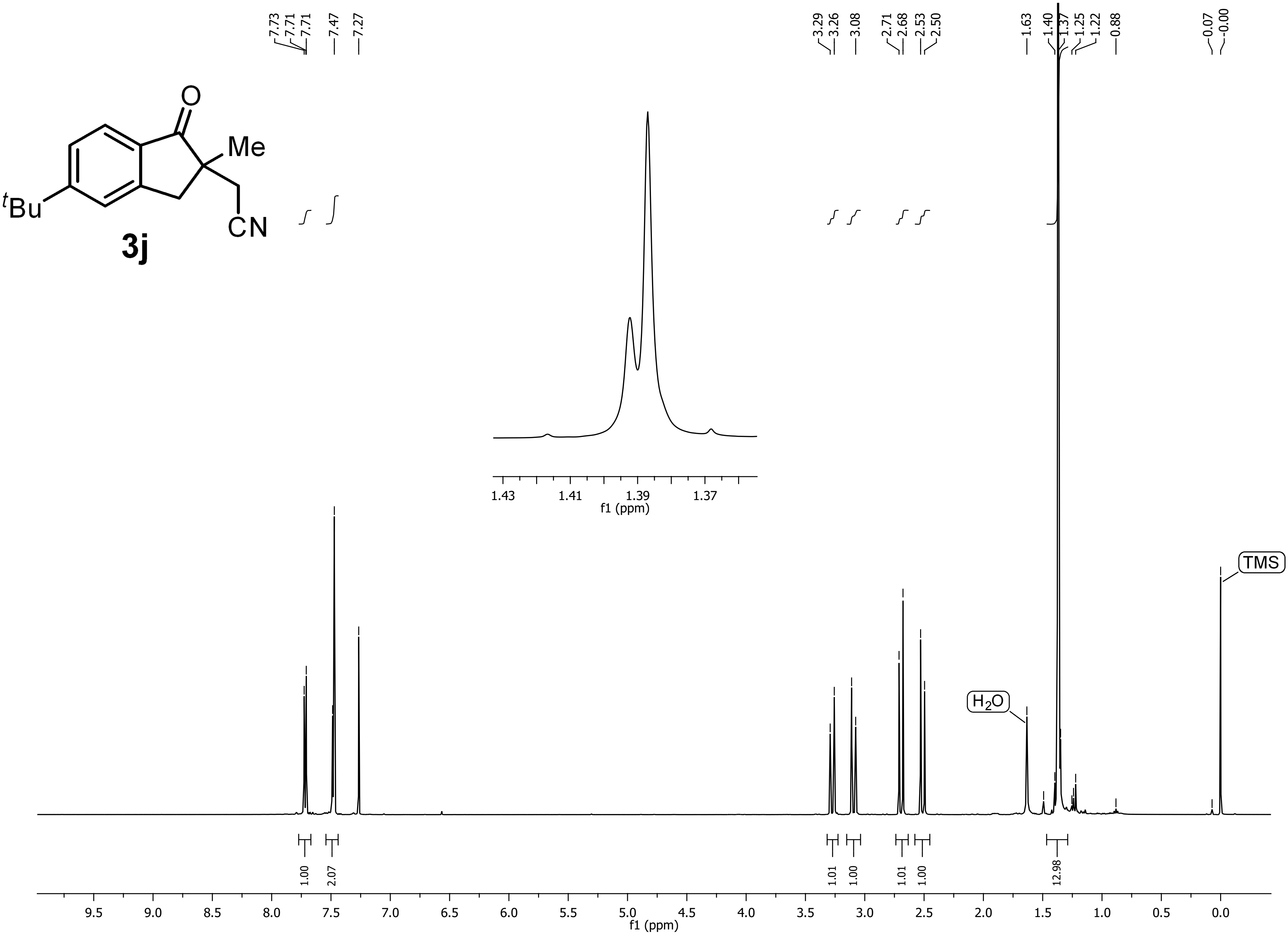
Acquisition Time (sec)	1.1010	***Comment***	5 mm PABBO BB/19F-1H/D Z-GRD Z119470/0030			***Date***	01 May 2013 17:04:48
Date Stamp	01 May 2013 17:04:48			***File Name***	C:\Users\Naveen\Desktop\NR-3-48-13C\1\fid		
Frequency (MHz)	125.76	***Nucleus***	13C	***Number of Transients***	1024	***Origin***	spect
Original Points Count	32768	***Owner***	cdonrr	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	194.68	***SW(cyclical) (Hz)***	29761.90	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	12570.2578	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	29761.00	***Temperature (degree C)***	25.159



9/26/2013 12:21:26 PM

Acquisition Time (sec)	0.6464	***Comment***	NR-3-48-19F University of Minnesota Department of Chemistry VAC-300				
Date	May 7 2013	***Date Stamp***	May 7 2013	***File Name***	C:\Users\Naveen\Desktop\130507v3_6902.fid\fid		
Frequency (MHz)	282.23	***Nucleus***	19F	***Number of Transients***	32	***Original Points Count***	64000
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	12.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	-7240.9688	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	99009.90	***Temperature (degree C)***	AMBIENT TEMPERATURE





7.73
7.71
7.71
7.47
7.27
3.29
3.26
3.08
2.71
2.68
2.53
2.50
1.63
1.40
1.37
1.25
1.22
0.88
0.07
-0.00
O
Me
ᵗBu
CN
H2O
TMS
1.43
1.41
1.39
1.37
f1 (ppm)
1.00
2.07
1.01
1.00
1.01
1.00
12.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3j

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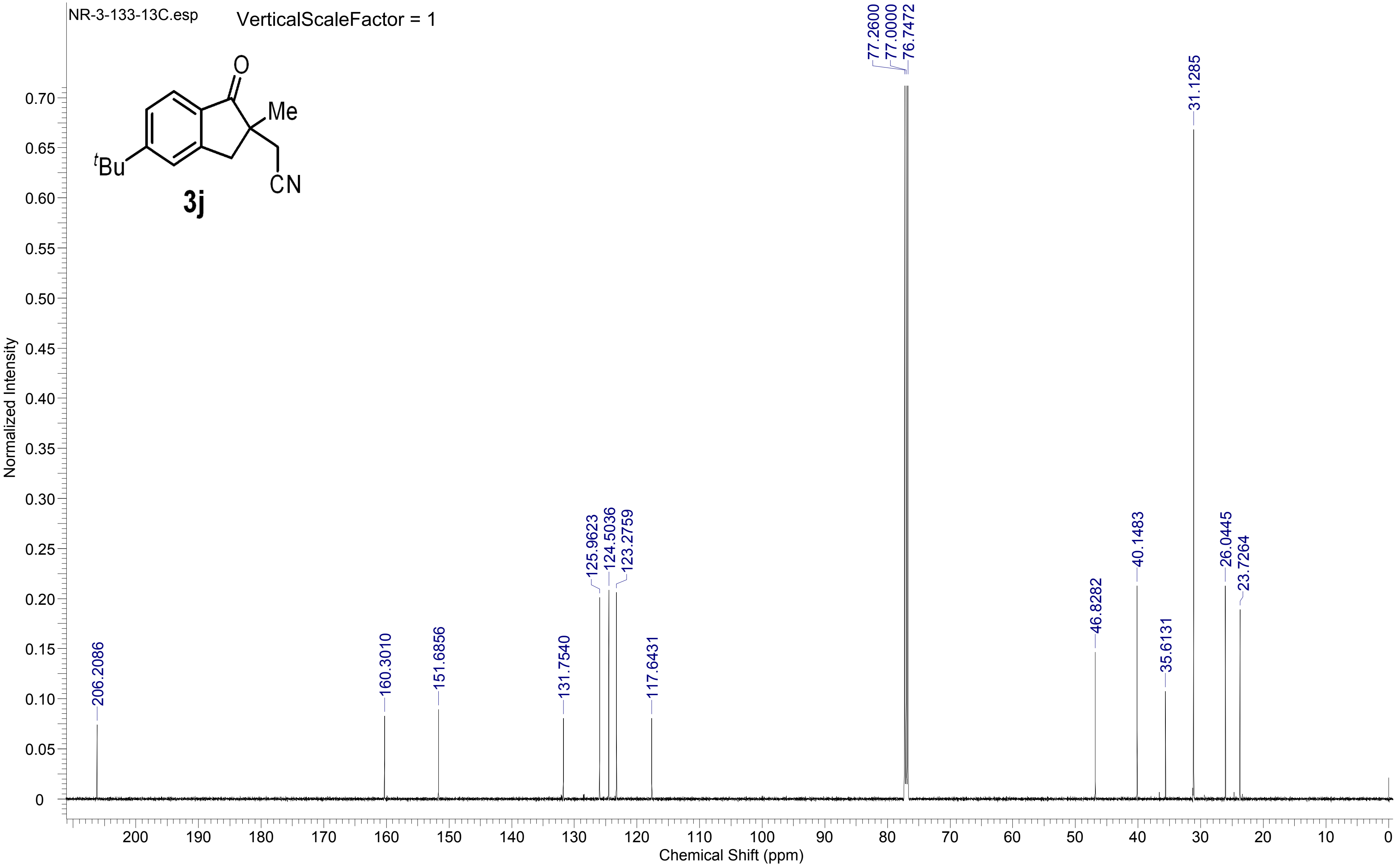
8/29/2013 11:39:11 AM

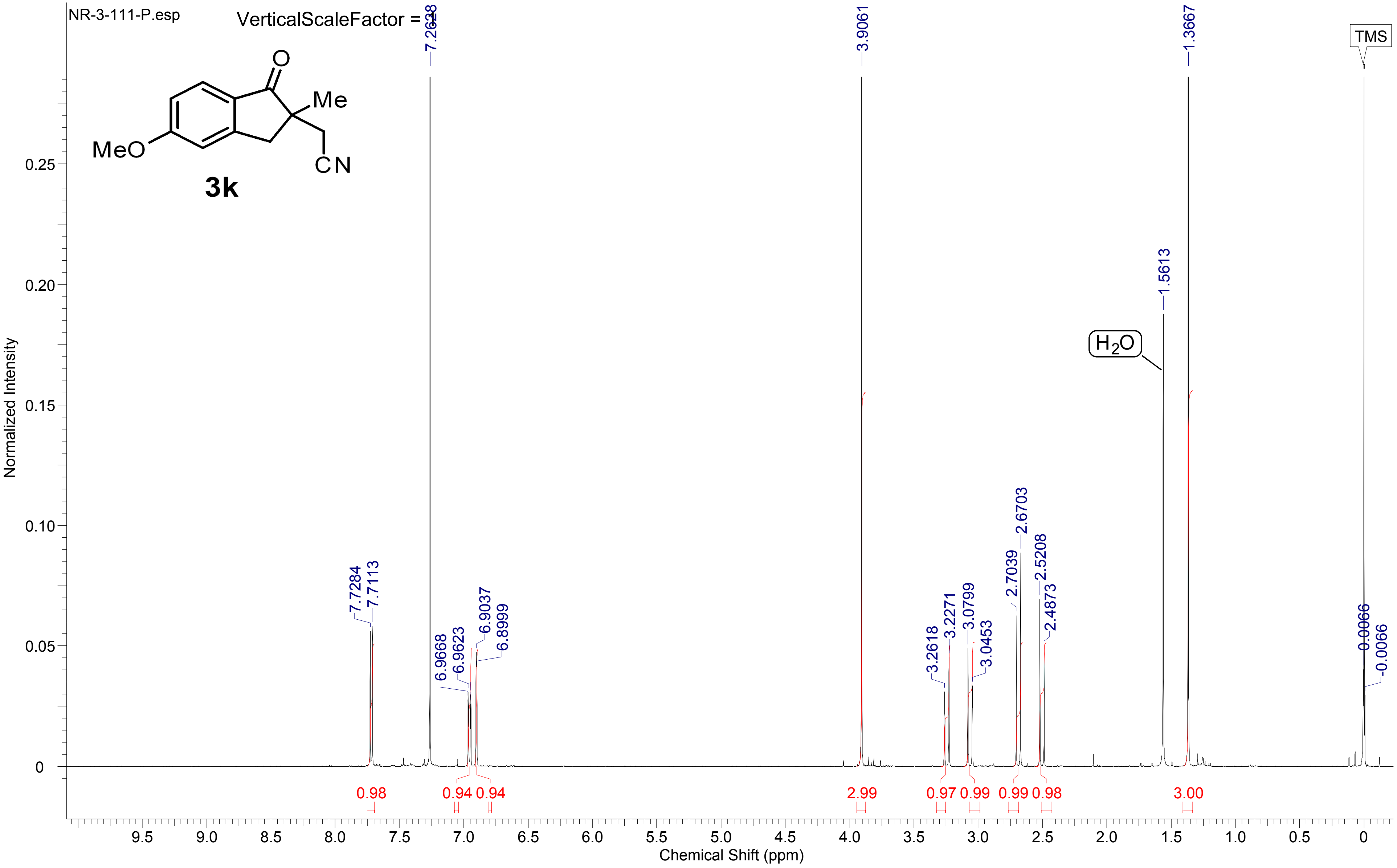
Acquisition Time (sec)	1.1010	***Date***	28 Aug 2013 19:10:40			***Date Stamp***	28 Aug 2013 19:10:40
File Name	C:\Users\Naveen\Desktop\NR-3-133-13C\10\fid			***Frequency (MHz)***	125.77	***Nucleus***	13C
Number of Transients	1024	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	182.64	***SW(cyclical) (Hz)***	29761.90
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	12569.4092	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.00	***Temperature (degree C)***	21.000				



3j

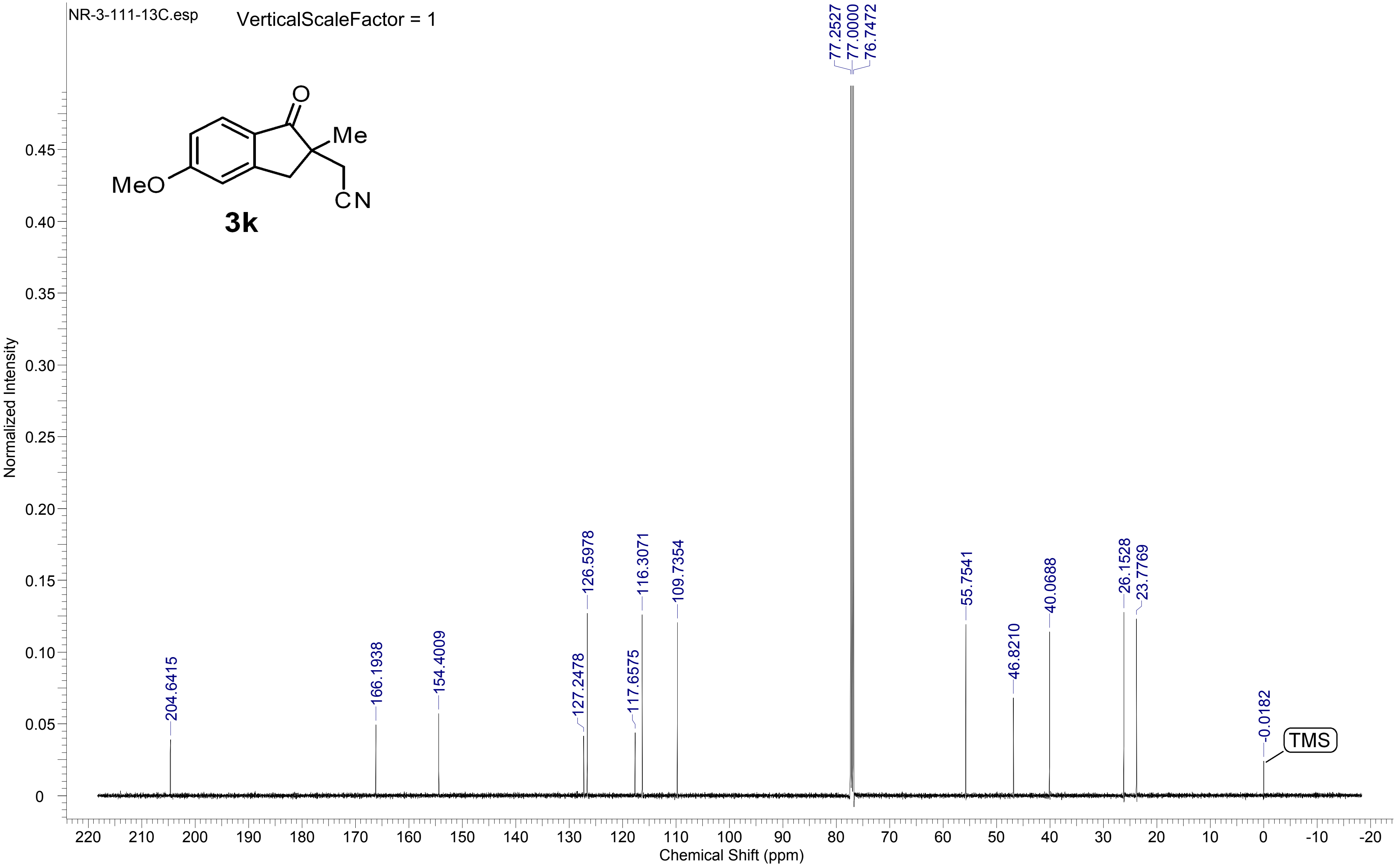
9/26/2013 3:59:25 AM

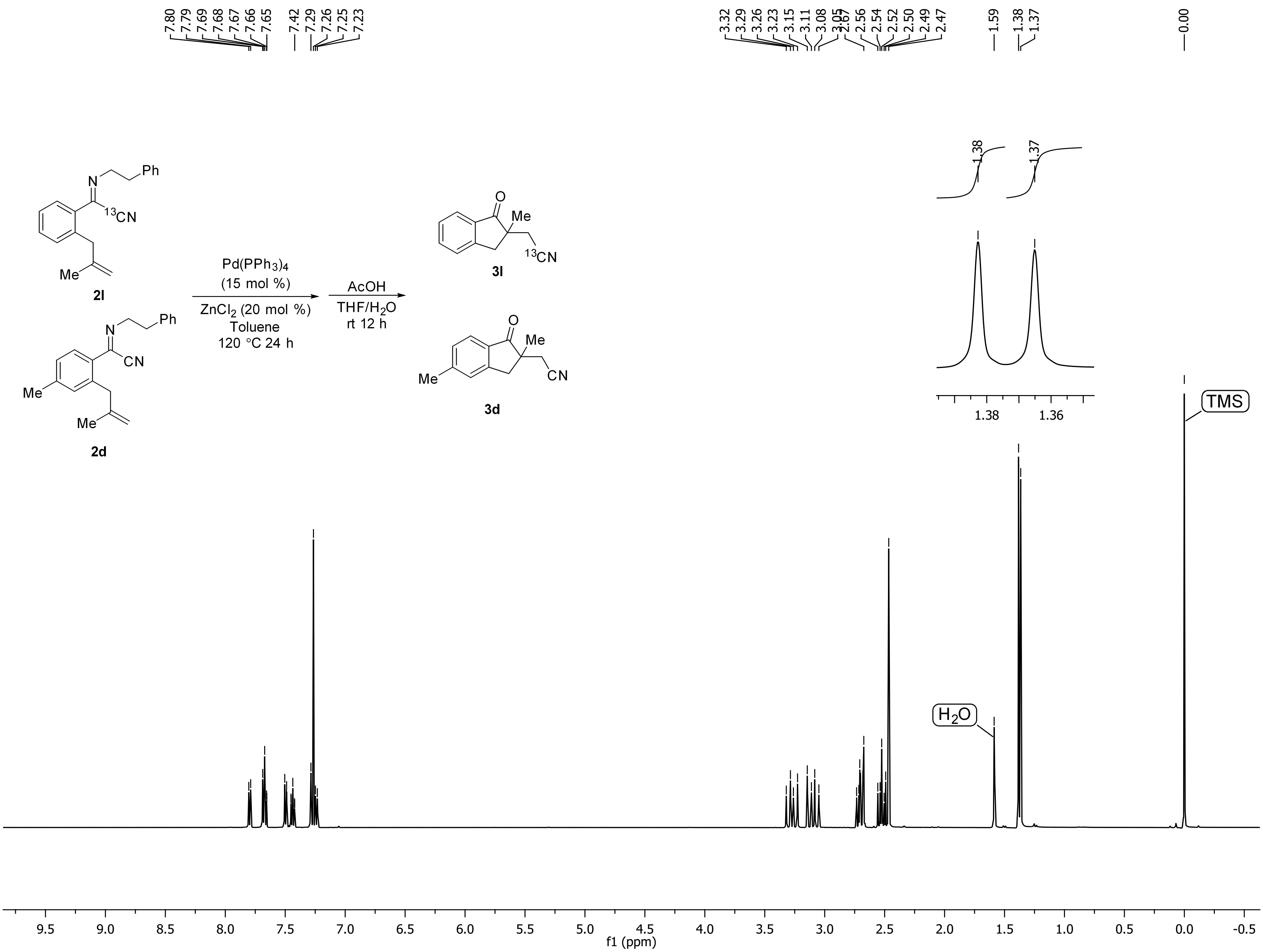
Acquisition Time (sec)	3.2768	***Date***	11 Jul 2013 15:33:04			***Date Stamp***	11 Jul 2013 15:33:04
File Name	C:\Users\Naveen\Desktop\NR-3-111-P\10\fid			***Frequency (MHz)***	500.13	***Nucleus***	1H
Number of Transients	16	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	131072	***Pulse Sequence***	zg30	***Receiver Gain***	127.25	***SW(cyclical) (Hz)***	10000.00
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	3077.3545	***Spectrum Type***	STANDARD
Sweep Width (Hz)	9999.92	***Temperature (degree C)***	21.001				



12/8/2013 7:42:24 PM

Acquisition Time (sec)	1.1010	***Date***	11 Jul 2013 19:06:24			***Date Stamp***	11 Jul 2013 19:06:24
File Name	C:\Users\Naveen\Desktop\NR-3-111-13C\10\fid			***Frequency (MHz)***	125.77	***Nucleus***	13C
Number of Transients	1024	***Origin***	spect	***Original Points Count***	32768	***Owner***	auto
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	194.68	***SW(cyclical) (Hz)***	29761.90
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	12569.4092	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.00	***Temperature (degree C)***	21.001				




7.80
7.79
7.69
7.68
7.67
7.66
7.65
7.42
7.29
7.26
7.25
7.23
3.32
3.29
3.26
3.23
3.15
3.11
3.08
3.05
2.67
2.56
2.54
2.52
2.50
2.49
2.47
1.59
1.38
1.37
0.00
Ph
N
^{13}CN
Me
2l
Ph
N
CN
Me
Me
2d
Pd(PPh$_3$)$_4$
(15 mol %)
ZnCl$_2$ (20 mol %)
Toluene
120 °C 24 h
AcOH
THF/H$_2$O
rt 12 h
O
Me
^{13}CN
3l
O
Me
Me
CN
3d
1.38
1.37
1.38
1.36
H$_2$O
TMS
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

9/28/2013 6:34:11 PM

Acquisition Time (sec)	1.1010	**Date**	17 Jul 2013 15:56:32			**Date Stamp**	17 Jul 2013 15:56:32
File Name	C:\Users\Naveen\Desktop\NR-3-115-13C\10\fid			**Frequency (MHz)**	125.77	**Nucleus**	13C
Number of Transients	800	**Origin**	spect	**Original Points Count**	32768	**Owner**	auto
Points Count	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	194.68	**SW(cyclical) (Hz)**	29761.90
Solvent	CHLOROFORM-d			**Spectrum Offset (Hz)**	12564.8691	**Spectrum Type**	STANDARD
Sweep Width (Hz)	29761.00	**Temperature (degree C)**	21.001