Asymmetric Synthesis of Tertiary Benzylic Alcohols

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Supporting Information

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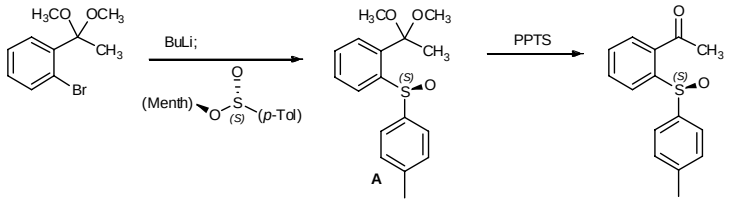
Method and Materials

General. Unless otherwise stated, reactions were performed using freshly purified solvents which were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Gas chromatography (GC) was performed on an HP 6890N autosampling GC with an HP-5 capillary column and equipped with a FID detector. Flash chromatography was performed with indicated solvents using silica gel (particle size 0.032-0.063m) purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova-400 MHz or 500 MHz spectrometer. Chemical shift are reported relative to internal chloroform ($CDCl_3$: 1H, δ = 7.27, 13C, δ = 77.26). Coupling constants are in Hz and are reported as d (doublet), t (triplet), q (quartet). For signals having multiple coupling patterns, the coupling constant are listed in the same order as the pattern (e.g. dt, *J* = 2.0, 4.0; 2.0 is the coupling constant for the doublet and 4.0 is for the coupling constant for the triplet). HPLC analyses were carried out on a Shimadzu LC-2010A system. Optical rotations were measured on a Rudolph Research Analytical Autopol® IV Polarimeter (50/60 Hz). Mass spectra were acquired on a Shimadzu QP5000 GC/MS or Agilent technologies 1200 series LC/MS using indicated ionization methods.

Materials. (*1R ,2S ,5R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate was prepared according to Klunder and Sharpless.[1] Other chemicals were purchased from Aldrich and used without purification.

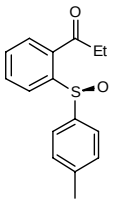
Preparation of (*S*)-Sulfoxide starting materials.

General Procedure 1. Synthesis of substrates from dimethyl acetals.



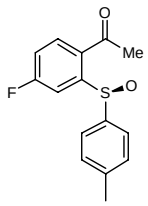
(*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone 1a.[2] To a solution of 1-bromo-2-(1,1-dimethoxyethyl)benzene (9.0 mmol, 2.20 g, 1.1 equiv.) in Et_2O (40 mL) was added *n*- butyllithium (9.0 mmol, 5.6 mL, 1.6 M solution in hexanes, 1.1 equiv) at -78 ^{o}C and the reaction mixture was stirred for 30 min. A solution of (*1R ,2S ,5R*)-(-)-menthyl-(*S*)-*p*-toluenesulfinate (8.0 mmol, 2.36 g, 1.0 equiv) in a mixture of Et_2O/THF (1:1, 20 mL) was then added *via* canula. After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified by flash chromatography (hexane/EtOAc, 70/30) to afford (*S*)-1-(1,1-dimethoxyethyl)-2-(*p*-tolylsulfinyl)benzene (acetal **A**) in 74 % yield (1.80 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.9, 1.1, 1H), 7.50 – 7.59 (m, 1H), 7.39 – 7.49 (m, 4H), 7.17 (d, *J* = 8.0, 2H), 3.12 (s, 3H), 3.04 (s, 3H), 2.32 (s, 3H), 1.36 (s, 3H); MS: EI-MS(*m/z*): 304 $[M]^{+}$.

(*S*)-1-(1,1-dimethoxyethyl)-2-(*p*-tolylsulfinyl)benzene (1.80g, 5.9 mmol) and PTSA (830 mg, 4.3 mmol) were dissolved in a mixture of acetone (130 mL) and water (9 mL). After being stirred for 2 h, the reaction mixture was concentrated under reduce pressure and extracted with EtOAc. The organic layers were dried over $MgSO_4$, filtered, and evaporated to give the product as a white solid in 86 % yield (1.32 g), $[\alpha]_D$ = - 132^{o} (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (dd, *J* = 7.9, 0.8, 1H), 7.91 (d, *J* = 7.7, 1H), 7.86 (t, *J* = 7.7, 1H), 7.52 – 7.66 (m, 3H), 7.15 (d, *J* = 8.1, 2H), 2.55 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 184.2, 148.5, 143.8, 141.2, 134.1, 130.9, 130.5, 129.7, 126.9, 125.4, 27.2, 21.6; MS: EI-MS(*m/z*): 258 $[M]^{+}$.



(*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one 1b. According to General Procedure 1, (*S*)-1-(1,1-dimethoxypropyl)-2-(*p*-tolylsulfinyl)benzene was prepared in 72 % yield (2.06 g). ^{1}H NMR (400 MHz, CDC_3) δ 8.31 (dd, *J* = 8.0, 1.2, 1H), 7.52 – 7.58 (m, 1H), 7.44 – 4.78 (m, 3H), 7.34 – 7.40 (m, 1H), 7.16 (d, *J* = 8.0, 2H), 3.10 (s, 3H), 2.87 (s, 3H), 2.32 (s, 3H), 2.09 (dq, *J* = 14.5, 7.4, 1H), 1.77 (dq, *J* = 15.1, 7.6, 1H), 0.61 (t, *J* = 7.5, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.9, 140.6, 138.8, 130.4, 129.7, 129.2, 128.1, 126.2, 125.7, 106.1, 49.7, 47.5, 30.5, 21.5, 7.9; MS: EI-MS(*m/z*):318 $[M]^{+}$.

The title ketone was prepared as a white solid in 85 % yield (1.38 g), $[\alpha]_D$ = - 167^{o}, c = 1.0 in $CHCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.9, 1H), 7.90 (d, *J* = 7.7, 1H), 7.82 (t, *J* = 7.6, 1H), 7.62 (d, *J* = 8.2, 2H), 7.57 (t, *J* = 7.5, 1H), 7.15 (d, *J* = 8.0, 2H), 2.77 – 3.19 (m, 2H), 2.30 (s, 3H), 1.14 (t, *J* = 7.2, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 140.4, 135.8, 132.9, 125.9, 125.5, 122.3, 121.6, 121.48, 118.6, 117.1, 24.2, 13.4, 13.3; MS: EI-MS(*m/z*): 272 $[M]^{+}$.

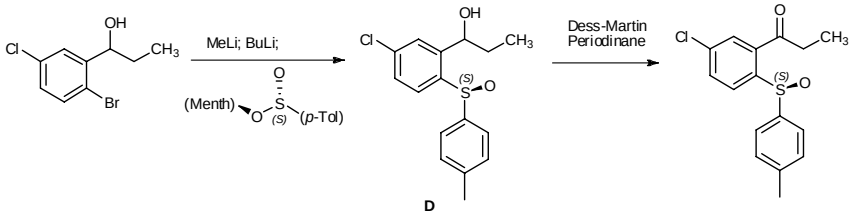


(*S*)-1-(4-fluoro-2-(p-tolylsulfinyl)phenyl)ethanone 1c. According to General Procedure 1 (*S*)-1-(1,1-dimethoxyethyl)-4-fluoro-2-(*p*-tolylsulfinyl)benzene was prepared in 74 % yield (1.81 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 9.2, 2.7, 1H), 7.43 – 7.48 (m, 2H), 7.40 (dd, *J* = 8.6, 5.3, 1H), 7.19 (dd, *J* = 8.5,

0.5, 2H), 7.13 (ddd, *J* = 8.6, 7.4, 2.7, 1H), 3.10 (s, 3H), 3.03 (s, 3H), 2.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (J_{FC} = 252 Hz), 146.9 144.2, 141.3, 136.7 129.9, 129.6, 126.5, 117.8(J_{FC}= 21.75 Hz), 112.9 (J_{FC}= 24.9 Hz), 49.0, 48.4, 25.7, 21.5; MS: EI-MS(*m/z*): 322 $[M]^+$

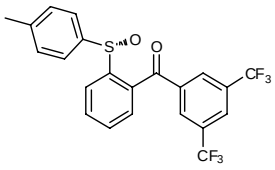
The title ketone was prepared as a white solid in 82 % yield (1.20 g), $[\alpha]_D$ = - 85°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.9 Hz, 2.6 Hz, 1H), 7.93 (dd, *J* = 8.5 Hz, 5.0 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.29 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 166.1 ($^1J_{FC}$ = 209 Hz), 153.1, 143.3, 141.5, 133.7 (J_{FC} = 8.7 Hz), 130.4, (J_{FC} = 3.3 Hz), 129.8, 126.9, 117.4 (J_{FC} = 22 Hz) , 113.1 (J_{FC} = 25 Hz), 27.1, 21.5; MS: EI-MS(*m/z*): 276 $[M]^+$.

General Procedure 2. Synthesis of substrates from secondary alcohols



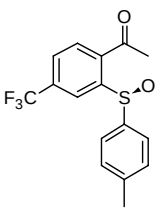
(*S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-one 1d. To a solution of 1-(2-bromo-5-chlorophenyl)propan-1-ol (4.05 mmol, 1.00 g, 1.0 equiv.) in Et_2O (30 mL) was added MeLi (4.85 mmol, 3.0 mL, 1.6 M solution in Et_2O, 1.2 equiv) at -78 °C. After the reaction mixture stirred for 15 min at -78 °C, *tert*-BuLi (8.0 mmol, 4.7 mL, 1.7 M solution in pentane, 2.0 equiv.) was added and stirring was continued for 30 min at this same temperature. A solution of (*1R ,2S ,5R*)-(-)-menthyl-(*S*)-*p*-toluenesulfinate (4.82 mmol, 1.42 g, 1.2 equiv) in a mixture of Et_2O/THF (3:1, 20 mL) was then added *via* canula. After stirring for 3 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give a crude product, which was purified by flash chromatography (hexane/EtOAc, 80/20) to afford (*S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-ol **D** as a mixture of diastereoisomers (1:1) in 72 % yield (900 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.78 (m, 0.5H), 7.55 – 7.63 (m, 0.5H), 7.45 (s, 3H), 7.29 – 7.36 (m, 0.5H), 7.19 (s, 2.5H), 4.85 – 4.96 (m, 1H), 2.33 (s, 3H), 1.60 – 1.71 (m, 1H), 1.38 – 1.55 (m, 0.5H), 0.98 – 1.14 (m, 0.5H), 0.88 – 0.90 (m, 1.5H), 0.77 – 0.87 (s, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 145.7, 142.6, 141.8, 141.5, 141.1, 140.7, 139.2, 137.9, 137.8, 130.3, 130.2, 128.7, 128.6, 127.4, 127.1, 127.0, 126.5, 125.8, 125.6, 70.9, 70.0, 31.5, 31.3, 21.6, 21.6, 10.6, 10.5; MS: EI-MS(*m/z*): 291 $[M - OH]^+$.

To a solution of (*Ss*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-ol (2.60 mmol, 800 mg, 1.0 equiv.) in dichloromethane (35 mL) was added DMP (3.90, 1.65 g, 1.5 equiv.) at 0 °C. After stirring for 1 h at rt, the reaction mixture was successively washed with a 20% aqueous sodium thiosulfate solution, saturated aqueous sodium bicarbonate and then dried over magnesium sulfate, filtered and concentrated under vacuum to give crude product, which was purified by flash chromatography (hexane/EtOAc, 80/20) to afford (*S*)-1-(5-chloro-2-(p-tolylsulfinyl)phenyl)propan in 80 % yield (640 mg),), $[\alpha]_D$ = - 137° (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.5 Hz, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.84-3.02 (m. 2H), 2.31 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 147.5, 143.8, 141.3, 136.8, 135.8, 133.4, 129.7, 129.5, 127.0, 126.6, 32.7, 21.4, 8.0; MS: EI-MS(*m/z*): 306 $[M]^+$.



(*S*)-(3,5-bis(trifluoromethyl)phenyl)(2-(*p*-tolylsulfinyl)phenyl)methanone 1e. According to General Procedure 2, (*S*) (3,5-bis(trifluoromethyl)phenyl)(2-(p-tolylsulfinyl)phenyl)methanol was prepared as a mixture of diaseroisomers (1:1) in 74 % yield 900 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.87 (m, 0.5H), 7.76 (dd, *J* = 7.8 Hz, 1.2 Hz, 0.5H), 7.70 (s, 0.5H), 7.62 (s, 0.5H), 7.42 – 7.51 (m, 3H), 7.35 – 7.42 (m, 2H), 7.32 (dd, *J* = 7.6 Hz, 1.3, 0.5H), 7.30 – 7.19 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.94 – 6.99 (m, 0.5H), 6.34 (s, 0.5H), 6.32 (s, 0.5H), 4.88 (s, 0.5H), 4.46 (s, 0.5H),2.34 (s, 1.5H), 2.3 (s, 1.5H); MS: EI-MS(*m/z*): 458 $[M]^+$.

The title ketone was prepared in 77 % yield (688 mg),), $[\alpha]_D$ = - 68° (c = 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.9 Hz, 1H), 8.07 (s, 1H), 8.03 (s, 2H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.61(m, 3H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.60, 149.5, 142.5, 142.1, 136.7, 134.4, 133.8, 132.4 (q, J_{FC}= 34.1 Hz) 130.4, 130.0, 126.8, 126.5 (sep, J_{CF} = 3.6 Hz), 126.2, 122.9 (q, J_{FC} = 273.1 Hz), 21.4; MS: EI-MS(*m/z*): 456 $[M]^+$.



(*S*)-1-(4'-trifluoromethyl-2'-(*p*-tolylsulfinyl)phenyl)ethanone 1f. To a stirred solution of 4-trifluoromethylbenzylaldehyde (578mg, 3.32mmol) in anhydrous THF (3ml) at 0 °C under N_2 was added MeLi solution (2.75ml, 1.33M in Et_2O). The so formed solution was stirred for another 30 min before a BuLi·TMEDA solution was added. The BuLi·TMEDA solution was made by adding TMEDA (77mg, 0.66mmol) to a BuLi solution (4.3ml, 1.7M in hexanes) at rt and stirring for 30 min. After being stirred at 0 °C for 30 min then rt overnight, the resulting solution was transferred into a solution of (1*R*,2*S*,5*R*)-(−)-

Menthyl (*S*)-*p*-toluenesulfinate in anhydrous THF (40ml) at -78 °C under N_2. The thus formed reaction was stirred overnight. Sat. NH_4Cl aq. was added to quench the reaction. The water layer was extracted by CH_2Cl_2. The combined organic layer was concentrated under reduced pressure and the residue was purified by silica gel chromatography (hexane/ethyl acetate, 3/1-1/1) to afford secondary alcohol.

To a solution of (*Ss*)-1-(4'-trifluoromethyl-2'-(*p*-tolylsulfinyl)phenyl)ethanol (218mg, 0.67mmol) in CH_2Cl_2 (4ml) was added Dess-Martin periodinane (310mg, 0.73mmol). The resulting reaction mixture was stirred at rt for 3h. A 1:1 mixture of 15% $Na_2S_2O_3$ aq. and sat. $NaHCO_3$ aq. was added to quench the reaction. The water layer was extracted by CH_2Cl_2. The combined organic layer was concentrated under reduced pressure and the residue was purified by silica gel chromatography (hexane/ethyl acetate, 3/1) to afford the title compound in 92% yield (200mg). $[\alpha]_D$ +145º (c = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.84 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 2.58 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.2, 150.6, 143.1, 141.8, 136.5, 135.5 (q, *J* = 33.0 Hz), 131.3, 129.9, 127.6, 126.9, 123.4 (q, *J* = 272.0 Hz), 122.6, 27.4, 21.5. EI-MS (*m/z*): 326 $[M]^+$.

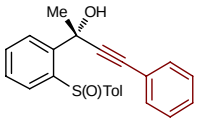
General procedure for the addition of alkynyl-cerium to sulfinyl ketones 1.

A flame-dried, 10 mL, round-bottomed flask was charged with anhydrous cerium chloride (0.91 mmol, 222 mg, 2.20 equiv) in an inert-atmosphere glovebox (cerium chloride was dried in vacuo overnight at 140 °C and stored in the glovebox). The sealed flask was taken out of the glovebox and charged with dry THF (2 mL) under nitrogen atmosphere. After being stirred for 2 h at rt, the resulting suspension was cooled to -78 °C. Separately, the alkynyllithium (0.80 mmol, 1.94 equiv) was prepared by adding *n*-butyllithium (0.80 mmol, 500 µL, 1.6 M solution in hexanes, 1.94 equiv) to a solution of alkyne (0.82 mmol, 2.0 eq) in dry THF (2 mL) at – 78 °C and stirring for 30 min. The alkynyl lithium solution was added via canula to the suspension of $CeCl_3$. The reaction mixture was stirred for 30 min at -78 °C and a solution of (*S*)-sulfoxide (0.41 mmol, 105 mg, 1.0 equiv) in dry THF (2 mL) was added. After 3 h at -78 °C, the reaction mixture was treated with saturated aqueous NH_4Cl, filtered through Celite, and extracted with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified as indicated for individual examples.

General procedure for the addition of aryl-, and alkenylmagnesium bromide to sulfinyl ketones 1.

To a solution of (*S*)-sulfinyl ketone 4 (0.39 mmol, 100 mg, 1.0 equiv) in dry THF (5 mL) at -78 °C was added RMgBr (0.78 mmol, 2.0 equiv). After being stirred for 3 h at – 78 °C, saturated aqueous NH_4Cl was added, followed by extraction with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified as indicated below for individual examples.

Table 2, Entry 1. (*Ss, R*)-4-Phenyl-2-(2-(*p*-tolylsulfinyl)phenyl)but-3-yn-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.41 mmol, 105 mg, 1.0 equiv) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 100 % conversion and d.r. = 50:1. To improve the diastereomeric ratio, the crude product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 95 % yield (140 mg), d.r. > 50:1, $[\alpha]_D$ = -278º, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.07 (m, 1H), 7.64 – 7.70 (m, 1H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.41 – 7.47 (m, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.30 (m, 3 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 3.36 (bs, 1 H), 2.31 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.4, 143.3, 140.9, 131.9, 130.7, 129.6, 128.9, 128.7, 128.4, 126.9, 126.6, 122.7, 93.6, 85.2, 70.7, 32.9, 21.4; MS:LC-APCI-MS (*m/z*): 343 $[M\text{-}OH]^+$.



Single crystals suitable for X-ray crystallography were grown cooling a hot solution in hexane/EtOAc (1:1).

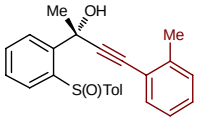


Table 2, Entry 2. (*Ss, R*)-4-(*o*-tolyl)-2-(2-(*p*-tolylsulfinyl)phenyl)but-3-yn-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.41 mmol, 105 mg, 1.0 equiv) and *o*-tolylethynyllithium. ^{1}H NMR analysis of crude product indicated 97 % conversion and d.r. = 50:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 88 % yield (135 mg), d.r. > 50:1, $[\alpha]_D$ = -251º, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.11 (m, 1H), 7.67 – 7.70 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.43 – 7.45 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.07 – 7.21 (m, 5 H), 3.43 (s, 1 H), 2.39 (s, 3 H), 2.30 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.4, 143.3, 141.1, 140.6, 132.3, 130.6, 129.7, 129.6, 128.8, 128.8, 127.0, 126.8, 126.4, 125.8, 122.3, 97.2, 84.3, 71.3, 32.7, 21.5, 21.0; MS:LC-APCI-MS (*m/z*): 357 $[M\text{-}OH]^+$.

Single crystals suitable for X-ray crystallography were grown cooling a hot solution in hexane/EtOAc (1:1).

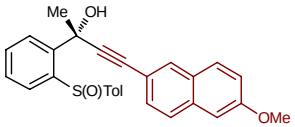


Table 2, Entry 3 (*Ss, R*)-(6-methoxynaphthalen-2-yl)-2-(2-(p -tolylsulfinyl)phenyl) but-3-yn-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.41 mmol, 105 mg, 1.0 equiv) and (6-methoxynaphthalen-2-yl)ethynyllithium. ^{1}H NMR analysis of

crude product indicated 92 % conversion and d.r. = 20:1. Purification by flash chromatography afforded pure product (d.r. = 20:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 81 % yield (146 mg), d.r. > 50:1, $[\alpha]_D$ = -236°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.07 (m, 1 H), 7.77 (s, 1 H), 7.70 – 7.72 (m, 1 H), 7.59 – 7.63 (m, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.44 – 7.46 (m, 2 H), 7.37 (d, *J* = 8.8 Hz, 1 H), 7.11 – 7.31 (m, 3 H), 7.06 (s, 1 H), 3.90 (s, 3 H), 3.41 (s, 1 H), 2.27 (s, 3 H), 1.79 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 144.2, 143.6, 143.4, 140.8, 134.4, 131.8, 130.9, 129.7, 129.6, 129.2, 129.0, 128.5, 126.9, 126.9, 126.8, 126.4, 119.6, 117.4, 105.9, 92.9, 86.1, 70.7, 55.5, 32.6, 21.5; MS:LC-APCI-MS (*m/z*): 423 $[M\text{-}OH]^+$.

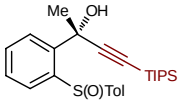


Table 2, Entry 4. (*Ss, R*)-2-(2-(p-tolylsulfinyl)phenyl)-4-(triisopropylsilyl)but-3-yn-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.41 mmol, 105 mg, 1.0 equiv) and ((triisopropylsilyl)ethynyl)lithium. ^{1}H NMR analysis of crude product indicated 100 % conversion and d.r. > 50:1. Purification by flash chromatography afforded pure (S_s, *R*) – isomer (d.r. > 50:1). in 87 % yield (157 mg), $[\alpha]_D$ = -124°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.46 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.23 (bs, 1H), 2.33 (s, 3H), 1.47 (s, 3 H), 1.02 – 1.08 (m, 21 H); ^{13}C NMR (101 MHz, CDCl3) δ 143.8, 143.4, 141.2, 142.8, 130.3, 129.7, 128.6, 127.5, 127.3, 125.5, 111.5, 85.8, 72.0, 33.0, 21.6, 18.8, 11.4; MS: LC-APCI-MS (*m/z*): 423 $[M\text{-}OH]^+$.

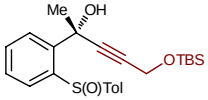


Table 2, Entry 5 (*Ss, R*)-5-((tert-butyldimethylsilyl)oxy)-2-(2-(p-tolylsulfinyl) phenyl)pent-3-yn-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.41 mmol, 105 mg, 1.0 equiv) and (3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)lithium. ^{1}H NMR analysis of crude product indicated 85 % conversion and d.r. = 12:1. Purification by flash chromatography afforded pure product (d.r. = 33:1) in 65 % yield (114 mg), $[\alpha]_D$ = -151°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dm, *J* = 7.4 Hz, 1H), 7.52 (dm, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.36 (td *J* = 7.3 Hz, 1.7 Hz, 1H), 7.33 (td, *J* = 1.7, 7.3 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.25 (d, *J* = 15.6 Hz, 1H), 4.18 (d, *J* = 16 Hz, 1H), 3.25 (s, 1H), 2.25 (s, 3H), 1.51 (s, 3 H), 0.80 (s, 9 H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 148.4, 147.9, 145.9, 135.5, 134.5, 133.7, 131.9, 131.7, 131.1, 93.6, 88.81, 75.7, 56.9, 37.4, 30.9, 26.4, 23.4, 0.0; MS: LC-APCI-MS (*m/z*): 411 $[M\text{-}OH]^+$.

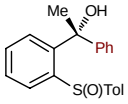


Table 2, Entry 6. (*Ss, R*)-1-phenyl-1-(2-(p-tolylsulfinyl)phenyl)ethanol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 100 mg, 1.0 equiv.) and PhMgBr (0.78 mmol, 0.78 mL, 1.0 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 93% conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 83 % yield (108 mg), $[\alpha]_D$ = -216°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.3 Hz, 1.0, 1H), 7.42 – 7.52 (m, 3H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.36 (m, 5H), 7.11 – 7.15 (m 2H), 2.78 (s, 1H), 2.32 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.2, 144.7, 144.4, 140.6, 130.5, 129.6, 128.7, 128.5, 127.4, 127.0, 126.9, 126.3, 126.0, 77.5, 32.1, 21.5; MS: LC-APCI-MS (*m/z*): 319 $[M\text{-}OH]^+$.

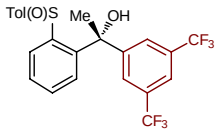


Table 2, Entry 7. (*Ss, R*)-1-(3,5-bis(trifluoromethyl)phenyl)-1-(2-(p-tolylsulfinyl)phenyl)ethanol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 100 mg, 1.0 equiv.) and 3,5- bis(trifluoromethyl)phenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 equiv). ^{1}H NMR analysis of crude product indicated 91 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 82 % yield (150 mg), $[\alpha]_D$ = -92°, (c = 0.5, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.04 (m, 1H), 7.57 -7.62 (m, 6H) , 7.01 – 7.10 (m, 4 H), 4.87 (s, 1H), 2.27 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 150.6, 145.1, 143.6, 142.2, 140.8, 131.4 (q, J_{CF} = 33.7 Hz), 129.7, 129.1, 128.1, 127.2, 126.4, 126.1, 125.7, 123.5 (q, J_{CF} = 272 Hz), 121.7 (sep, J_{CF} = 3.6 Hz), 76.5, 32.4, 21.3, MS: LC-APCI-MS (*m/z*): 455 $[M\text{-}OH]^+$.
Single crystals suitable for X-ray crystallography were grown by cooling a hot solution in hexane/EtOAc (1:1)

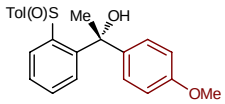


Table 2, Entry 8. (*Ss, R*)-1-(4-methoxyphenyl)-1-(2-(p-tolylsulfinyl)phenyl)ethanol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 100 mg, 1.0 equiv) and 4-Methoxyphenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 94 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 87 % yield (124 mg), $[\alpha]_D$ = -205°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.53 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.7.22 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.78 (m, 2H), 3.76 (s, 3H), 2.74 (bs, 1H), 2.32 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 145.3, 141.6, 140.8, 132.4, 130.9, 130.8, 129.8, 129.0, 128.2, 127.3, 126.3, 124.7, 116.5, 113.9, 77.4, 55.5, 21.6; MS: LC-APCI-MS (*m/z*): 349 $[M\text{-}OH]^+$.

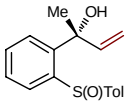


Table 2, Entry 9. (*Ss, R*)-2-(2-(p-tolylsulfinyl)phenyl)but-3-en-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 100 mg, 1.0 equiv) and vinylmagnesium bromide (0.78 mmol, 0.78 mL, 1.0 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 98 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 74 % yield (83 mg), $[\alpha]_D$ = -148°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (td, *J* = 7.4 Hz, 1.2 Hz, 1 H), 7.38 (td, *J* = 7.4 Hz, 1.4 Hz, 1 H), 7.24 – 7.30 (m, 1 H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.22 (dd, *J* = 17 Hz, 10 Hz, 1H), 5.18 (d, *J* = 4.7 Hz, 1H), 5.15 (d, *J* = 1.4 Hz, 1H), 2.70 (bs, 1 H), 2.32 (s, 3 H), 1.53 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8 , 144.5, 144.2, 140.7, 130.4, 129.7, 128.5, 126.7, 126.6, 126.4, 113.9, 76.8, 29.4, 21.5; MS: LC-APCI-MS (*m/z*): 269 $[M\text{-}OH]^+$.

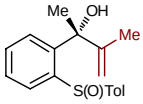


Table 2, Entry 10. (*Ss, R*)-3-methyl-2-(2-(p-tolylsulfinyl)phenyl)but-3-en-2-ol. The title compound was prepared from (*S*)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 100 mg, 1.0 equiv) and isopropenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 eq). ^{1}H NMR analysis of crude product indicated 96 % conversion and d.r. > 33:1. Purification by flash chromatography afforded pure product (d.r. = 33:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 90 % yield (105 mg), d.r. > 50:1, $[\alpha]_D$ = -153°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (td, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.39 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.31 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.97 (t, *J* =1.2 Hz, 1H), 4.94 (s, 1H), 2.42 (s, 1H), 2.33 (s, 3H), 1.73 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 145.0, 144.7, 144.4, 140.6, 130.4, 129.7, 128.5, 126.8, 126.7, 126.5, 112.5, 78.9, 29.3, 21.5, 19.2; MS: EI-MS(*m/z*): 300 $[M]^+$, 283 $[M\text{-}OH]^+$.

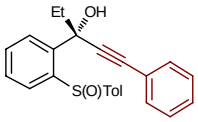


Table 3, Entry 11. (*Ss, R*)-1-phenyl-3-(2-(p-tolylsulfinyl)phenyl)pent-1-yn-3-ol The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.41 mmol, 112 mg, 1.0 equiv) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 90 % conversion and d.r. = 11:1. Purification by flash chromatography afforded pure product (d.r. = 11:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 72% yield (110 mg), d.r. > 50:1, $[\alpha]_D$ = -253°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 8.35 (m, 1H), 7.68 – 7.71 (m, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.43 (m, 2H), 7.35 (m, 2H), 7.23 – 7.27 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.42 (s, 1H), 2.30 (s, 3H), 1.94 (dq, *J* = 14 Hz, 7.3 Hz, 1H), 1.75 (dq, *J* = 14 Hz, 7.3 Hz, 1H), 1.03 (t, *J* = Hz 7.3, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 143.4, 143.3, 140.9, 131.9, 130.6, 129.6, 128.8, 128.7 128.4, 127.3, 126.8, 126.8, 122.6, 92.12, 86.6, 74.7, 37.5, 21.5, 9.0; MS: LC-APCI-MS (*m/z*): 357 $[M\text{-}OH]^+$.
Single crystals suitable for X-ray crystallography were grown by cooling a hot solution in hexane/EtOAc (1:1)

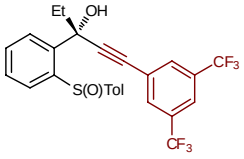


Table 2, Entry 12. (*Ss, R*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(p-tolylsulfinyl) phenyl)pent-1-yn-3-ol. The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.41 mmol, 112 mg, 1.0 equiv) and ((3,5-bis(trifluoromethyl)phenyl)ethynyl)lithium. ^{1}H NMR analysis of crude product indicated 96 % conversion and d.r. = 14:1. Purification by flash chromatography afforded pure product (d.r. = 14:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 81% yield (170 mg), d.r. > 50:1, $[\alpha]_D$ = -153°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 8.00 (m, 1H), 7.76 (s, 1H), 7.66 – 7.73 (m, 3H), 7.39 – 7.51 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.89 (bs, 1H), 2.29 (s, 3H), 2.01 (dq, *J* = 14.0 Hz, 7.2 Hz, 1H), 1.84 (dq, *J* = 14.0 Hz, 7.2 Hz, 1H), 1.04 (t, *J* = 7.2, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.8, 142.5, 141.3, 131.7 (q, J_{CF3} = 35 Hz), 131.7, 130.8, 129.6, 128.9, 127.2, 127.01, 126.5, 125.0, 124.4 (q, J_{CF3} = 274 Hz), 122.0 (sep, J_{CF3} = 3.6 Hz), 95.9, 83.3, 74.6, 37.4, 21.4, 8.9;MS: LC-APCI-MS (*m/z*): 493 $[M\text{-}OH]^+$.

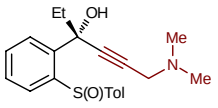


Table 2, Entry 13. (*Ss, R*)-6-(dimethylamino)-3-(2-(p-tolylsulfinyl)phenyl)hex-4-yn-3-ol. The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.41 mmol, 112 mg, 1.0 equiv) and (3-(dimethylamino)prop-1-yn-1-yl)lithium. ^{1}H NMR analysis of crude product indicated 83 % conversion and d.r. = 50:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 71% yield (103 mg), d.r. > 50:1, $[\alpha]_D$ = -184°, c = 0.5,$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 8.08 (m, 1H), 7.54 – 7.68 (m, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.43 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.28 (d, *J* = 16.6 Hz, 1H), 3.20 (d, *J* = 16.6 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 6H), 1.73 – 1.90 (m, 1H), 1.53 – 1.72 (m, 1H), 0.95 (t, *J* = 7.3, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.6, 143.37, 140.9, 130.5, 129.6, 128.7, 127.3, 126.9, 126.5, 89.5, 80.5, 74.0, 48.1, 44.2, 37.4, 21.5, 9.0; MS: LC-APCI-MS (*m/z*): 339 $[M\text{-}OH+H]^+$.

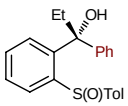


Table 2, entry 14. (*Ss, R*)-1-phenyl-1-(2-(p-tolylsulfinyl)phenyl)propan-1-ol. The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 106 mg, 1.0 equiv) and PhMgBr

(0.78 mmol, 0.78 mL, 1.0 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 96 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 84 % yield (115 mg), $[\alpha]_D$ = -217°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.19 (m, 1H), 7.42 – 7.53 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.36 (m, 2H), 7.23 – 7.30 (m, 3H), 7.17 – 7.23 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 1H), 2.29 (s, 3 H), 2.17 – 2.40 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 150.3, 149.4, 149.1, 148.7, 144.7, 134.61, 133.8, 132.6, 132.5, 131.4, 131.2, 130.9, 130.6, 84.0 , 39.6, 25.7, 12.2; MS: LC-APCI-MS (*m/z*): 333 $[M\text{-}OH]^+$.

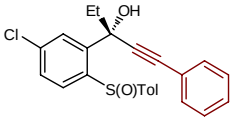


Table 2, Entry 15. (*Ss*, *R*)-(5-chloro-2-(p-tolylsulfinyl)phenyl)-1-phenylpent-1-yn-3-ol. The title compound was prepared from (*S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-one (0.41 mmol, 125 mg, 1.0 equiv.) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 91 % conversion and d.r. = 50:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 78% yield (131 mg), d.r. > 50:1, $[\alpha]_D$ = -167°, (c = 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.68 (m, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.25 - 7.31 (m, 6H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.24 (bs, 1H), 2.31 (s, 3H), 1.77 – 1.90 (m, 1H), 1.52 – 1.69 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 142.7, 141.5, 141.40, 136.8, 131.9, 129.7, 128.9, 128.7, 128.5, 127.8, 127.5, 127.0, 122.4, 91.39, 86.8, 74.8, 37.4, 21.6, 8.9; MS: EI-MS(*m/z*): 390 $[M\text{-}H_2O]^+$,391 $[M\text{-}OH]^+$.

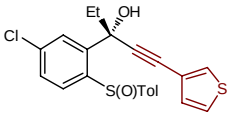


Table 2, Entry 16. (*Ss*, *R*)-3-(5-chloro-2-(p-tolylsulfinyl)phenyl)-1-(thiophen-3-yl)pent-1-yn-3-ol. The title compound was prepared from (*S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 118 mg, 1.0 equiv.) and (thiophen-3-ylethynyl)lithium. ^{1}H NMR analysis of crude product indicated 93 % conversion and d.r. = 33:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 82% yield (140 mg), d.r. > 50:1, $[\alpha]_D$ = -129°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.40 (m, 2H), 7.19 – 7.28 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 6.0 Hz, 1.1 Hz, 1H), 3.69 (bs, 1H), 2.32 (s, 3H), 1.85 (dq, *J* = 14.5 Hz, 7.3 Hz, 1H), 1.64 (dq, *J* = 14.5 Hz, 7.3 Hz, 1H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 142.7, 141.6, 141.4, 136.8, 130.0, 129.7, 129.6, 128.8, 127.9, 127.4, 126.9, 125.6, 121.4, 91.1, 82.1, 74.6, 37.4, 21.6, 8.2; MS: LC-APCI-MS (*m/z*): 397 $[M\text{-}OH]^+$; 399 $[M\text{-}OH]^+$; 398 $[M\text{-}OH]^+$.

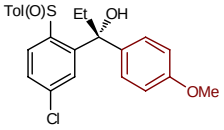


Table 2, Entry 17. (*Ss*, *R*)-1-(5-chloro-2-(p-tolylsulfinyl)phenyl)-1-(4-methoxyphenyl)propan-1-ol. The title compound was prepared from (*S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 118 mg, 1.0 equiv.) and 4-methoxyphenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 eq). ^{1}H NMR analysis of crude product indicated 85 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 79 % yield (127 mg), $[\alpha]_D$ = -129°, (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.38 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.27 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.77 – 6.80 (m, 2H,), 3.75 (s, 3H) 2.57 (bs, 1H), 2.32 (s, 3H), 2.17 – 2.28 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 147.3, 143.9, 143.2, 140.9, 137.6, 136.8, 129.7, 128.7, 128.5, 127.7, 1270, 126.4, 113.9, 79.4, 55.5, 35.0, 21.5, 8.3; MS: LC-APCI-MS (*m/z*): 397 $[M\text{-}OH]^+$; 399 $[M\text{-}OH]^+$; 398 $[M\text{-}OH]^+$.

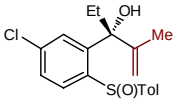


Table 2, Entry 18. (*Ss*, *R*)-3-(5-chloro-2-(p-tolylsulfinyl)phenyl)-2-methylpent-1-en-3-ol. The title compound was prepared from *S*)-1-(5-chloro-2-(*p*-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 118 mg, 1.0 equiv.) and isopropenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 eq). ^{1}H NMR analysis of crude product indicated 89 % conversion and d.r. = 25:1. Purification by flash chromatography afforded pure product (d.r. = 25:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 72% yield (97 mg), d.r. > 50:1, $[\alpha]_D$ = -110°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.3, 2H), 7.41 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 7.25 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 4.99 – 5.08 (m, 1H), 2.33 (s, 3H), 1.89-2.14 (m, 2H), 1.65 (s, 3H), 0.70 (t, *J* = 7.3 Hz, 3H), .^{13}C NMR (101 MHz, $CDCl_3$) δ 147.70, 145.38, 144.45, 144.18, 140.80, 136.50, 129.70, 128.43, 128.24, 126.94, 126.43, 113.38, 81.09, 32.28, 21.53, 19.49, 7.81; LC-APCI-MS (*m/z*): 331 $[M\text{-}OH]^+$; 333 $[M\text{-}OH]^+$; 332 $[M\text{-}OH]^+$.

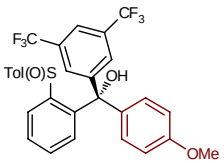


Table 2, Entry 19. (*Ss*, *S*)-(3,5-bis(trifluoromethyl)phenyl)(4-methoxyphenyl)(2-(p-tolylsulfinyl)phenyl)methanol. The title compound was prepared from (*S*)-(3,5-bis(trifluoromethyl)phenyl)(2-(*p*-tolylsulfinyl)phenyl)methanone (0.39 mmol, 177 mg, 1.0 equiv.) and 4-methoxyphenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 87 % conversion and d.r. = 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *S*) – isomer (d.r. > 50:1) in 75 % yield (165

mg), $[\alpha]_D$ = -119°, (c = 0.5,$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.9, 1.3, 1H), . 7.71 (s, 1H), 7.53 (s, 2H), 7.45 – 7.51 (m, 1H), 7.33 (td, *J* = 7.6 Hz, 1.4, 1H), 7.27 – 7.26 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.67- 6.70 (m, 2H), 6.81 (m, 8.9, 2H), 6.69 (dd, *J* = 7.9 Hz, 1.2, 1H), 4.72 (s, 1H), 3.80 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHzCDCl$_3$) δ 159.5, 148.3, 144.4, 144.6, 141.4, 138.4, 131.1 (q, J_{CF3}= 33.4 Hz), 130.8, 130.1, 129.8, 129.2, 129.1, 128.4, 127.0, 123.8, 123.4 (q, J_{CF3}= 272.7 Hz), 121.1 (sep, J_{CF3}= 6.5 Hz), 114.1, 83.1, 55.5, 21.3. MS: LC-APCI-MS (*m/z*): 547 $[M\text{-}OH]^+$.

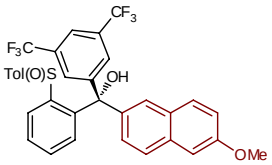


Table 2, Entry 20. (*Ss, S*)-(3,5-bis(trifluoromethyl)phenyl)(6-methoxynaphthalen-2-yl)(2-(p-tolylsulfinyl)phenyl)methanol. The title compound was prepared from (*S*)-(3,5-bis(trifluoromethyl)phenyl)(2-(*p*-tolylsulfinyl)phenyl)methanone (0.39 mmol, 177 mg, 1.0 equiv.) and (6-methoxynaphthalen-2-yl)magnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 85 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *S*) – isomer (d.r. > 50:1) in 79 % yield (189 mg) $[\alpha]_D$ = -130°, (c = 0.5,$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.73 (s, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.58 (s, 2H), 7.46 – 7.55 (m, 2H), 7.29 – 7.45 (m, 2H), 7.10 – 7.19 (m, 5H), 6.85 – 7.00 (m, 2H), 6.73 (dd, *J* = 7.8 Hz, 1.2, 1H), 5.32 (bs, 1H), 3.92 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 148.1, 141.1, 143.9,141.3, 134.2, 131.0, 130.5, 130.1, 130.5 (q, J_{CF3} = 33 Hz), 129.7, 129.1,128.2, 128.1, 127.8, 127.0, 126.7, 126.1, 122.0 (q, J_{CF3} = 273 Hz), 121.2 (sep, J_{CF3} = 3.6 Hz), , 119.5, 105.7, 83.5, 55.6, 21.3; MS: LC-APCI-MS (*m/z*): 596 $[M\text{-}H_2O]^+$.

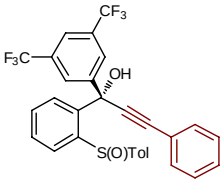


Table 2, entry 21. (*Ss, R*)-1-(3,5-bis(trifluoromethyl)phenyl)-3-phenyl-1-(2-(p-tolylsulfinyl)phenyl)prop-2-yn-1-ol. The title compound was prepared from (*S*)-(3,5-bis(trifluoromethyl)phenyl)(2-(*p*-tolylsulfinyl)phenyl)methanone (0.41 mmol, 187 mg, 1.0 equiv) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 91 % conversion and d.r. = 50:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 77% yield (175 mg), d.r. > 50:1, $[\alpha]_D$ = -151°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 1H), 7.75 (s, 2H), 7.67 (s, 1H), 7.58 – 7.65 (m, 1H), 7.39 – 7.51 (m, 4H), 7.27 – 7.39 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.21 (bs, 1H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.4, 141.5, 141.8, 140.9, 132.0, 131.2 (q, J_{CF3} = 33 Hz), 130.6, 129.9, 129.6, 129.32, 129.1, 128.6, 127.0, 126.7, 122.0 (q, J_{CF3} = 272 Hz), 121.9, 121.5, 90.9, 89.28, 75.1, 21.3; MS: LC-APCI-MS (*m/z*): 541 $[M\text{-}OH]^+$.

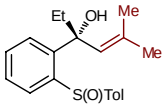


Table 2, Entry 22. (*Ss, R*)-4-methyl-2-(2-(p-tolylsulfinyl)phenyl)pent-3-en-2-ol. The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 106 mg, 1.0 equiv) and 2-methyl-1-propenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 equiv.). ^{1}H NMR analysis of crude product indicated 95 % conversion and d.r. = 25:1. Purification by flash chromatography afforded pure product (d.r. = 50:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 80% yield (103 mg), d.r. > 50:1, $[\alpha]_D$ = -135°, (c = 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 8.07(m, 1 H), 7.55 – 7.70 (m, 1 H), 7.38 – 7.50 (m, 2 H), 7.31 – 7.38 (m, 2 H), 7.13 – 7.21 (m, 2 H), 5.73 – 5.77 (m, 1 H), 2.33 (s, 3 H), 2.10 (bs, 1 H), 1.87 - 193 (m, 2H), 1.44 (d, *J* = 1.2 Hz, 3 H), 1.33 (d, *J* = 1.2 Hz, 3 H), 0.75 (t, *J* = 7.3 Hz, 3 H).); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 140.8, 138.5, 133.0, 130.7, 129.7, 127.9, 127.5, 127.2, 126.6, 76.8, 38.3, 26.6, 21.5, 19.3, 7.9; MS: EI-MS(*m/z*): 311 $[M\text{-}OH]^+$.

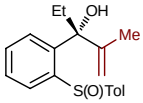


Table 2, Entry 23. (*Ss, R*)-3-methyl-2-(2-(p-tolylsulfinyl)phenyl)but-3-en-2-ol- The title compound was prepared from (*S*)-1-(2-(p-tolylsulfinyl)phenyl)propan-1-one (0.39 mmol, 106 mg, 1.0 equiv) and isopropenylmagnesium bromide (0.78 mmol, 1.56 mL, 0.5 M solution in THF, 2.0 eq). ^{1}H NMR analysis of crude product indicated 96 % conversion and d.r. = 20:1. Purification by flash chromatography afforded pure product (d.r. = 20:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 86% yield (105 mg), d.r. > 50:1, $[\alpha]_D$ = -125°, (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8 Hz, 1.1, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.45 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.39 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 1H), 5.02 (s, 1H), 2.32 (s, 3H), 2.30 (m, 1H), 2.03 (m, 2H), 1.64 (s, 3H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 145.6, 144.8, 143.34, 140.5, 130.2, 129.6, 128.4, 126.9, 126.8, 126.5, 112.8, 81.3, 32.3, 21.5, 19.5, 7.9; MS: EI-MS(*m/z*): 314 $[M]^+$,297 $[M\text{-}OH]^+$.

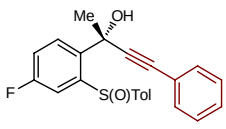


Table 2, Entry 24. (*Ss, R*)-2-(4-fluoro-2-(p-tolylsulfinyl)phenyl)-4-phenylbut-3-yn-2-ol. The title compound was prepared from (*S*)-1-(4-fluoro-2-(p-tolylsulfinyl)phenyl)ethanone (0.40 mmol, 110 mg, 1.0 equiv) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 97 % conversion and d.r. = 14:1. Purification by flash chromatography afforded pure product (d.r. = 14:1). To improve the diastereomeric ratio, the product was suspended in a mixture of hexane/EtOAc (10:1) and filtered to give (S_s, *R*) – isomer in 77% yield (116 mg), d.r. > 50:1, $[\alpha]_D$ = -196°, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 9.0 Hz, 2.7 Hz, 1H), 7.61 (dd, *J* = 8.7 Hz, 5.2 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.46 (m, 2H), 7.26 – 7.37 (m, 3H), 7.16 (d, *J* =

8.1 Hz, 2H), 7.06 (ddd, J = 10.0 Hz, 5.7 Hz, 2.0 Hz, 1H), 3.82 (bs, 1H), 2.32 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, CDC_3) δ 162.5 (d,J_{FC} = 250 Hz), 145.5 (d, J_{FC}= 4.7 Hz), 142.3, 141.6, 140.1 (d, J_{FC}= 3.6 Hz), 132.0, 129.8, 129.2 (d, J_{FC} = 7.3 Hz), 128.7, 128.4, 127.3, 122.6, 117.5 (d, J_{FC}= 21.7 Hz), 112.5 (d, J_{FC} = 25.5 Hz), 93.0, 85.0, 71.4, 32.5, 21.6; MS: EI-MS(*m/z*): 361 $[M\text{-}OH]^+$.

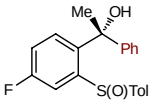


Table 2, Entry 25. **(*Ss, R*)-1-(4-fluoro-2-(*p*-tolylsulfinyl)phenyl)-1-phenylethanol.** The title compound was prepared from (*S*)-1-(4-fluoro-2-(p-tolylsulfinyl)phenyl)ethanone (0.39 mmol, 107 mg, 1.0 equiv) and PhMgBr (0.78 mmol, 0.78 mL, 1.0 M solution in THF, 2.0 eq). ^{1}H NMR analysis of crude product indicated 95 % conversion and d.r. > 50:1. Purification by flash chromatography (hexane/EtOAc, 80/20) afforded pure (S_s, *R*) – isomer (d.r. > 50:1) in 85 % yield (117 mg), $[\alpha]_D$ = -260^o, (c = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.9 Hz, 2.8 Hz, 1H), 7.41 – 7.48 (m, 2H), 7.37 (dd, J = 8.7 Hz, 5.1 Hz, 1H), 7.21 – 7.32 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 7.10 (ddd, J = 8.6 Hz, 7.4 Hz, 2.8 Hz, 1H), 2.49 (s, 1H), 2.34 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, CDC_3) δ 162.6 (d, J_{FC} = 250 Hz), 147.2, 142.0, 141.1, 129.8, 128.8 (d, J_{FC} = 7.11 Hz), 128.6, 127.6, 126.5, 125.9, 117.4 (d, J_{FC} = 21.4 Hz), 113.5 d, J_{FCC} = 25.5 Hz),77.4, 32.0, 21.5.
MS: EI-MS(*m/z*): 337 $[M\text{-}OH]^+$.

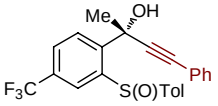


Table 2, Entry 26 (*Ss, R*)-2-(4'-trifluoromethyl-2'-(*p*-tolylsulfinyl)phenyl)-4-phenylbut-3-yn-2-ol. The title compound was prepared from (*S*)-1-(4'-trifluoromethyl-2'-(p-tolylsulfinyl)phenyl)ethanone (200 mg, 0.61mmol) and phenylethynyllithium. ^{1}H NMR analysis of crude product indicated 92% conversion and d.r. = 10:1. Purification by flash chromatography afford pure major product in 79% yield (207mg) and an unseperated mixture of the minor product and substrate 39 mg. $[\alpha]^{25}_D$ – 260.0º (c = 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, J = 1.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.66 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.39 – 7.41 (m, J = 8.0 Hz, 2H), 7.25-7.33 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 3.49 (br, 1H), 2.33 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.2, 143.7, 142.1, 142.0, 132.1, 130.6 (q, J = 33.0 Hz), 129.9, 128.8, 128.5, 128.5, 127.6, 127.4 (q, J = 4.0 Hz), 123.7 (q, J = 271.0 Hz), 121.8 (q, J = 4.0 Hz), 92.3, 85.2, 72.0, 32.3, 21.6. EI-MS (*m/z*): 410 $[M\text{-}H_2O]^+$.

General procedure for the reductive cleavage of sulfoxide. To the solution of sulfoxide in THF (0.1 M) at -78 ^{o}C was added *n*-BuLi (1.6 M solution in hexanes, 4.0 equiv.). After being stirred for 30 min at – 78 ^{o}C, saturated aqueous NH_4Cl was added, followed by extraction with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified by flash chromatography.

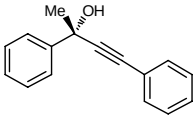


Table 3, Entry 1. (*S*)-2,4-Diphenylbut-3-yn-2-ol.[3] The title compound was prepared from **(***S*s, *R*)-4-(*o*-tolyl)-2-(2-(*p*-tolylsulfinyl)phenyl)but-3-yn-2-ol. (0.17 mmol, 60 mg, 1.0 equiv) and *n*-BuLi (0.68 mmol, 420 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded (*S*)-2,4-diphenylbut-3-yn-2-ol in 96 % (36 mg); ee = 97%. The use of recrystallized **(***S*s, *R*)-4-(*o*-tolyl)-2-(2-(*p*-tolylsulfinyl)phenyl)but-3-yn-2-ol gave product in 97% yield and ee = 99%. $[\alpha]_D$ = +44^o (c = 2.0,Acetone).^{1}H NMR (400 MHz, CDC_3) δ 7.70 – 7.77 (m, 2H), 7.46 – 7.52 (m, 2H), 7.36 – 7.44 (m, 2H), 7.29 – 7.34 (m, 4H), 2.54 (s, 1H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, CDC_3) δ 145.9, 131.9, 128.7, 128.6, 128.5, 128.0, 125.2, 122.8, 92.6, 85.2, 70.6, 33.5; MS: EI-MS(*m/z*): 222 $[M]^+$, 204 $[M\text{-}H_2O]^+$. HPLC condition: Chiracel OD-H column, 1% isopropanol in hexane, 1.0 mL/min, T_R= 24.7 (minor), 36.9 (major).

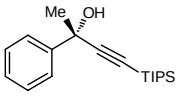


Table 3, Entry 2. (*S*)-2-phenyl-4-(triisopropylsilyl)but-3-yn-2-ol. The title compound was prepared from **(***S*s, *R*)-2-(2-(p-tolylsulfinyl)phenyl)-4-(triisopropylsilyl)but-3-yn-2-ol (0.09 mmol, 40 mg, 1.0 equiv) and *n*-BuLi (0.36 mmol, 220 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded (*S*)-2-phenyl-4-(triisopropylsilyl)but-3-yn-2-ol in 92 % (25 mg); ee = 96%; $[\alpha]_D$ = +14^o, (c = 1.0, Acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.72 (m, 2H), 7.31 – 7.39 (m, 2H), 7.26 – 7.31 (m, 1H), 2.29 (bs, 1H), 1.77 (s, 3H), 1.09 (s, 21H). ^{13}C NMR (101 MHz, CDC_3) δ 145.8, 128.4, 127.8, 125.2, 111.2, 85.9, 70.6, 33.9, 18.9, 11.4.; MS: EI-MS(*m/z*): 302 $[M]^+$. HPLC condition: Chiracel OD-H column, 0.1% isopropanol in hexane, 0.5 mL/min, T_R= 18.9 (minor), 21.1 (major).

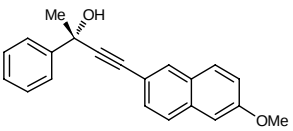


Table 3, Entry 3. (*S*)-4-(6-methoxynaphthalen-2-yl)-2-phenylbut-3-yn-2-ol. The title compound was prepared from **(***S*s, *R*)-4-(6-methoxynaphthalen-2-yl)-2-(2-(p-tolylsulfinyl)phenyl)but-3-yn-2-ol (0.08 mmol, 36 mg, 1.0 equiv) and *n*-BuLi (0.33, 200 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded (*S*)-4-(6-methoxynaphthalen-2-yl)-2-phenylbut-3-yn-2-ol in 94 % (23 mg); ee >99%; $[\alpha]_D$ = -50^o, (c = 0.3 in $CDCl_3$.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.75 – 7.83 (m, 2H), 7.69 (dd, J = 8.6 Hz, 5.7 Hz, 2H), 7.49 (dd, J = 8.5 Hz, 1.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.25 - 7.33 (m, 1H), 7.16 (dd, J = 9.0 Hz, 2.5 Hz,

1H), 7.11 (d, J = 2.4 Hz, 1H), 3.93 (s, 3H), 2.49 (s, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, CDC_3) δ 158.6, 146.0, 134.4, 131.7, 129.5, 129.2, 128.5, 128.0, 127.0, 125.2, 119.7, 117.6, 106.0, 92.2, 85.6, 70.7, 55.7, 33.6; MS: EI-MS(*m/z*): 302 $[M]^+$. HPLC condition: Chiracel OD-H column, 2% isopropanol in hexane, 1.0 mL/min, T_R= 53.9.

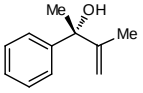


Table 3, Entry 4. (*R*)-3-methyl-2-phenylbut-3-en-2-ol. The title compound was prepared from **(***S*s, *R*)- 3-methyl-2-(2-(*p*-tolylsulfinyl)phenyl)but-3-en-2-ol (0.2 mmol, 60 mg, 1.0 equiv) and *n*-BuLi (0.8 mmol, 500 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded (*R*)-3-methyl-2-phenylbut-3-en-2-ol in 93 % (30 mg); ee = 98%; $[\alpha]_D$ = -8.6^o, (c = 0.86, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.44 (m, 2H), 7.28 – 7.38 (m, 2H), 7.20 – 7.20 (m, 1H), 5.10 – 5.34 (m, 1H), 4.86 – 5.05 (m, 1H), 1.86 (s, 1H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.33, 146.12, 128.36, 127.11, 125.43, 110.88, 77.16, 28.87, 19.32; MS: EI-MS(*m/z*): 145 $[M\text{-}OH]^+$, 163 $[M+H]^+$. HPLC condition: Chiracel OD-H column, 1% isopropanol in hexane, 1.0 mL/min, , T_R= 12.0 (major), 14.6 (minor).

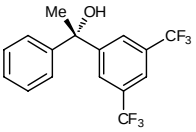


Table 3, Entry 5. (*S*)-1-(3,5-bis(trifluoromethyl)phenyl)-1-phenylethanol. The title compound was prepared from **(***S*s, *R*)- 1-(3,5-bis(trifluoromethyl)phenyl)-1-(2-(*p*-tolylsulfinyl)phenyl)ethanol (0.06 mmol, 30 mg, 1.0 equiv) and *n*-BuLi (0.25 mmol, 160 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded **(***S*)-1-(3,5-bis(trifluoromethyl)phenyl)-1-phenylethanol in 96 % (20 mg); ee >99%; $[\alpha]_D$ = +34^o, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.68 (s, 1H), 7.26 – 7.39 (m, 4H), 7.20 – 7.27 (m, 1H), 2.22 (bs, 1H), 1.93 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 150.9, 146.3, 131.6 (q, J_{FC} = 33.1 Hz), 128.9, 128.1, 126., 125.9, 123.5 (q, J_{FC} = 274 Hz), 121.0, 76.0, 31.0; MS: EI-MS(*m/z*): 334 $[M]^+$. HPLC condition: Chiracel OD-H column, 1% isopropanol in hexane, 1.0 mL/min, T_R= 33.1.

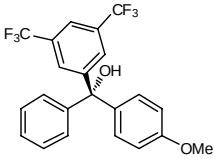


Table 3, Entry 6. (*S*)-(3,5-bis(trifluoromethyl)phenyl)(4-methoxyphenyl)(phenyl) methanol. The title compound was prepared from **(***S*s, *S*)-(3,5-bis(trifluoromethyl)phenyl)(4-methoxyphenyl)(2-(*p*-tolylsulfinyl)phenyl)methanol (0.11 mmol, 62 mg, 1.0 equiv) and *n*-BuLi (0.44 mmol, 270 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded (*S*)-(3,5-bis(trifluoromethyl)phenyl)(4-methoxyphenyl)(phenyl) methanol in 98 % yield (46 mg), ee = 92%. The use of recrystallized (*S*)-(3,5-bis(trifluoromethyl)phenyl)(4-methoxyphenyl)(phenyl)methanol gave product in 99% yield and ee>99%, $[\alpha]_D$ = +4.8^o, (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.72 (s, 1H), 7.23 – 7.32 (m, 3H), 7.14 – 7.20 (m, 2H), 7.02 – 7.07 (m, 2H), 6.77 – 6.83 (m, 2H), 3.74 (s, 3H), 2.73 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.4, 149.8, 145.8, 137.9, 130.7 (q, J_{FC} = 33.2 Hz), 129.4, 128.7, 128.2, 128.0, 127.6, 125.8 (q, J_{FC} = 272.8 Hz), 121.2 , 114.0, 81.5, 55.5; MS: EI-MS(*m/z*): 426 $[M]^+$. HPLC condition: Chiracel OD-H column, 1% isopropanol in hexane, 1.0 mL/min, T_R= 15.9 (major), 21.4 (minor).

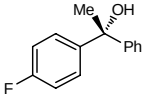
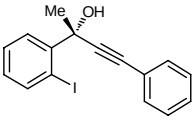
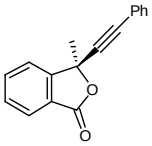


Table 3, Entry 7. (*R*)-1-(4-fluorophenyl)-1-phenylethanol.[4] The title compound was prepared from **(***S*s, *R*)-1-(4-fluoro-2-(p-tolylsulfinyl)phenyl)-1-phenylethanol (0.07 mmol, 26 mg, 1.0 equiv) and *n*-BuLi (0.30 mmol, 180 μL, 1.6 M solution in hexanes, 4.0 equiv.). Purification of the crude product by flash chromatography on silica gel (hexanes/EtOAc 9:1, v/v) yielded **(***R*)-1-(4-fluorophenyl)-1-phenylethanol in 95% (15 mg); ee >99%; $[\alpha]_D$ = -5^o, (c = 0.6, Acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.41 (m, 6H), 7.21 – 7.27 (m, 1H), 6.96 – 7.00 (m, 2H), 2.09 (bs, 1H), 1.93 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.5 (d, J = 245 Hz), 148.0, 144.0 (d, J = 3.2 Hz), 128.5, 127.8 (d, J_{FC} = 8.0 Hz), 127.3, 126.0, 115.1 (t, J_{FC} = 21.0 Hz), 76.1, 31.2. EI-MS(*m/z*): 216 $[M]^+$. HPLC condition: Chiracel OD-H column, 0.4% isopropanol in hexane, 0.4 mL/min, T_R= 53.6.

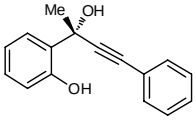
Reactions with electrophile (X = I^+, O_2, CO_2), Scheme 1



(*R*)-2-(2-iodophenyl)-4-phenylbut-3-yn-2-ol 4. To a solution of **2a** (0.14 mmol, 50 mg, 1.0 equiv.) in THF (5 mL) was added MeLi (0.16 mmol, 100 μL, 1.6 M solution in Et_2O, 1.15 equiv) at -78 ^{o}C. After the reaction mixture had been stirred for 10 min at -78 ^{o}C, *tert*-BuLi (0.28 mmol, 165 μL, 1.7 M in pentane, 2.0 equiv.) was added and stirring continued for 15 min at this same temperature. The solution of 1,2-diiodoethane (0.56 mmol, 157 mg, 4.0 equiv) in THF (1 mL) was then added. After stirring for 2 h at -78 ^{o}C, the reaction mixture was warmed up to rt, diluted with EtOAc and successively washed with 20% aqueous sodium thiosulfate solution, brine, dried over magnesium sulfate, filtered and concentrated under vacuum to give crude product, which was purified by flash chromatography (toluene/hexane, 90/10) to afford (*R*)-2-(2-iodophenyl)-4-phenylbut-3-yn-2-ol in 70 % yield (34 mg), $[\alpha]_D$ = 22^o, (c = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.85 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.45 – 7.51 (m, 2H), 7.33 – 7.43 (m, 1H), 7.27 – 7.33 (m, 3H), 6.93 – 7.02 (m, 1H), 3.01 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 142.6, 131.8, 129.5, 128.7, 128.5, 128.5, 126.6, 122.8, 94.7, 91.8, 86.5, 71.2, 30.2; EI-MS(*m/z*): 348 $[M]^+$

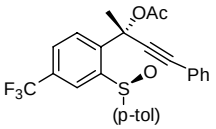


(*R*)-3-methyl-3-(phenylethynyl)isobenzofuran-1(3H)-one 5. To a solution of **2a** (0.14 mmol, 50 mg, 1.0 equiv.) in THF (5 mL) was added MeLi (0.16 mmol, 100 μL, 1.6 M solution in Et_2O, 1.15 equiv) at -78 °C. After the reaction mixture had been stirred for 10 min at -78 °C, *tert*-BuLi (0.28 mmol, 165 μL, 1.7 M in pentane, 2.0 equiv.) was added and stirring continued for 15 min at this same temperature. Dry carbon dioxide was then bubbled through the reaction mixture for 1 h at – 78°C and and 15 min at rt. The reaction was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified by preparative HPLC (2.5% of EtOAC in hexane) to afford (*R*)-3-methyl-3-(phenylethynyl)isobenzofuran-1(3H)-one 71 % yield (26 mg), ee > 99%, $[\alpha]_D = 94.6^o$, (c = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.65 (m, 2H), 7.41 (dd, *J* = 7.8 Hz, 1.6 Hz, 2H), 7.26 – 7.36 (m, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 152.2, 135.0, 132.1, 130.0, 129.3, 128.5, 126.0, 124.9, 121.9, 121.7, 86.8, 86.1, 79.5, 29.1; EI-MS(*m/z*): 219 $[M - CO_2 - H]^+$.HPLC condition: Chiracel OD-H column, 1.0% isopropanol in hexane, 1 mL/min, T_R= 14.7. (Racemic sample prepared analogously from the aryl bromide.)

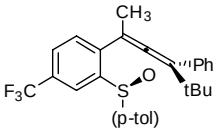


(*R*)-2-(2-hydroxy-4-phenylbut-3-yn-2-yl)phenol 6. To a solution of **2a** (0.14 mmol, 50 mg, 1.0 equiv.) in THF (5 mL) was added MeLi (0.16 mmol, 100 μL, 1.6 M solution in Et_2O, 1.15 equiv) at -78 °C. After the reaction mixture had been stirred for 10 min at -78 °C, *tert*-BuLi (0.28 mmol, 165 μL, 1.7 M in pentane, 2.0 equiv.) was added and stirring continued for 25 min at this same temperature. Oxygen was then bubbled through the reaction mixture for 1 h at – 78°C and and 15 min at rt. The reaction was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc (3X). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated to give crude product, which was purified by flash chromatography (toluene/hexanes, 90:10) to afford (*R*)-2-(2-hydroxy-4-phenylbut-3-yn-2-yl)phenol in 74% yield (24 mg), $[\alpha]_D = -30^o$, (c = 0.8 Acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.55 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.32 – 7.41 (m, 3H), 7.19 – 7.24 (m, 1H), 6.79 – 7.00 (m, 2H), 3.14 (bs, 1H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 156.4, 132.4, 130.4, 129.3, 129.0, 127.6, 123.1, 120.2, 118.7, 91.7, 86.9, 73.5, 31.5; EI-MS(*m/z*): 221 $[M - OH]^+$, 220 $[M - H_2O]^+$.

Synthesis of (*S*$_s$,*S*)-1-(5',5'-dimethyl-4'-phenylhexa-2',3'-dien-2'-yl)- 2-*p*-tolylsulfinyl-4-trifluoromethyl-benzene. Scheme 2.



(*S*$_s$, *R*)-2-(4'-trifluoromethyl-2'-(*p*-tolylsulfinyl)phenyl)-4-phenylbut-3-yn-2-yl acetate. A mixture of (*Ss, R*)-2-(4'-trifluoromethyl-2'-(p-tolylsulfinyl)phenyl)-4-phenylbut-3-yn-2-ol (200mg, 0.47mmol), Ac_2O (305mg, 3.0mmol), Et_3N (223mg, 2.2mmol) and DMAP (3mg, 0.024mmol) in CH_2Cl_2 (2ml) was stirred at rt overnight. The reaction solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 10/1) to afford the title compound in 99% yield (217mg). $[\alpha]^{26}_D$ -140.0º (c=0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.49-7.52 (m, 2H), 7.36-7.38 (m, 2H), 7.19-7.33 (m, 5H), 2.38 (s, 3H), 2.20 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.8, 145.1, 144.1, 142.1, 142.0, 132.1, 130.2, 129.3, 128.5, 128.2 (q, *J* = 4.0 Hz), 127.3, 126.8, 124.6, 123.2 (q, J_{CF3} = 271.0 Hz), 121.7, 88.8, 88.6, 75.9, 31.0, 22.1, 21.6. EI-MS (*m/z*): 470 $[M]^+$.



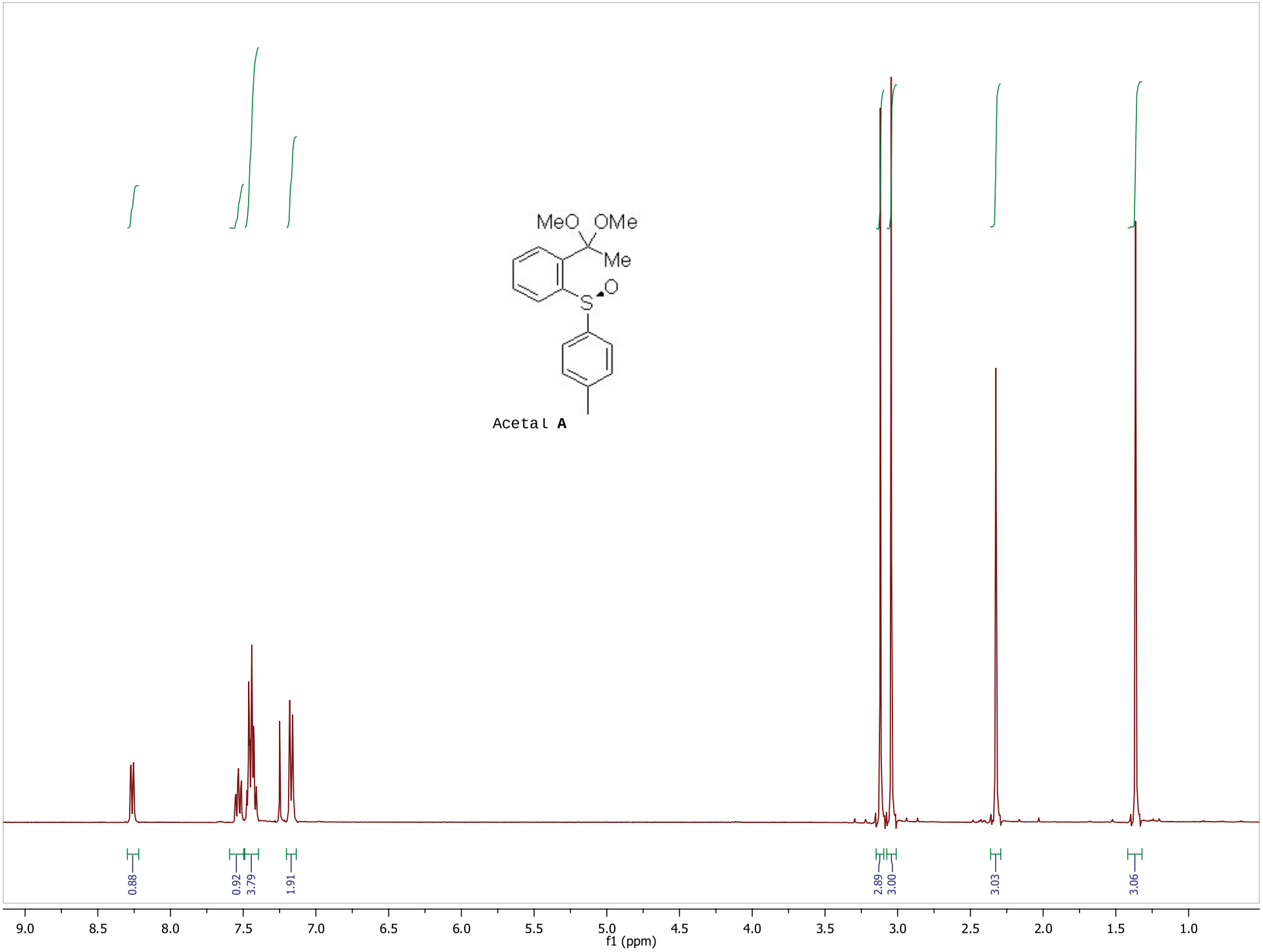
(*S*$_s$,*S*)-1-(5',5'-dimethyl-4'-phenylhexa-2',3'-dien-2'-yl)-2-*p*-tolylsulfinyl-4-trifluoromethyl-benzene 7. To a stirred suspension of CuCN (400mg, 4.5mmol) in anhydrous THF (10ml) at -42 °C (CH_3CN-dry ice) under N_2 was added ^{t}BuLi solution (2.4ml, 1.7M in pentane). The resulting solution was stirred another 10 min before a solution of (*Ss, R*)-2-(4'-trifluoromethyl-2'-(*p*-tolylsulfinyl)phenyl)-4-phenylbut-3-yn-2-yl acetate in anhydrous THF (6ml) was added. The reaction mixture was stirred for 1h under the same conditions. Sat. NH_4Cl aq. was added to quench the reaction. The water layer was extracted by Et_2O. The combined organic layer was concentrated under reduced pressure and the residue was purified by silica gel chromatography (hexane/ethyl acetate, 10/1) to afford the title compound in 97% yield (202mg). $[\alpha]^{26}_D$ -256.0º (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (d, *J* = 1.6 Hz, 1H), 7.65 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.41-7.44 (m, 2H), 7.32-7.36 (m, 2H), 7.27-7.29 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.53 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 200.4, 144.9, 142.2, 141.7, 141.6, 135.1, 130.5, 130.2 (q, *J* = 33.0 Hz), 129.9, 128.6, 128.1, 127.5, 127.3, 127.2 (q, *J* = 4.0 Hz), 124.0 (q, J_{CF3} = 270.2 Hz), 121.8 (q, J_{CF3}= 4.0 Hz), 117.8, 97.3, 35.7, 29.5, 21.6, 20.7. EI-MS (*m/z*): 468 $[M]^+$.

1 Klunder, J. M.; Sharpless, K. B. *J. Org. Chem.* **1987**, *52*, 2598.

2 Novodomska, A.; Dudicova, M.; Leroux, F. R.; Colobert, F. *Tetrahedron: Asymmetry* **2007**, *18*, 1628-1634.

3 (a) Lu, G.; Li, X.; Li, Y.-M.; Kwong, F. Y.; C., A.,S. C. *Adv. Synth Catal.* **2006**, *348*, 1926-1933. (b) Liu, L.; Kang, Y.-F.; Wang, R.; Zhou, Y.; Chen, C.; Ni, M.; Gong, M. *Tetrahedron: Asymmetry* , **2004**, *15*, 3757-3761. (c) Cozzi, P. G.; Alesi, S. *Chem. Commun.* **2004**, 2448-2449. (d) Saito, B.; Katsuki, T. *Synlett* **2004**, 1557-1560. (e) Lu, G.; Li, X.; Jia, X.; Chan, W, L.; Chan, A., S., C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5057-5058.

4 (a) Forrat, V., J.; Prieto, O.; Ramon, D, J.; Yus, M. *Chem. Eur Jl* **2006**, *12*, 4431-4445. (b) Forrat, V, J.; Ramon, D.; Yus, M. *Tetrahedron: Asymmetry* **2008**, *19*, 537-541.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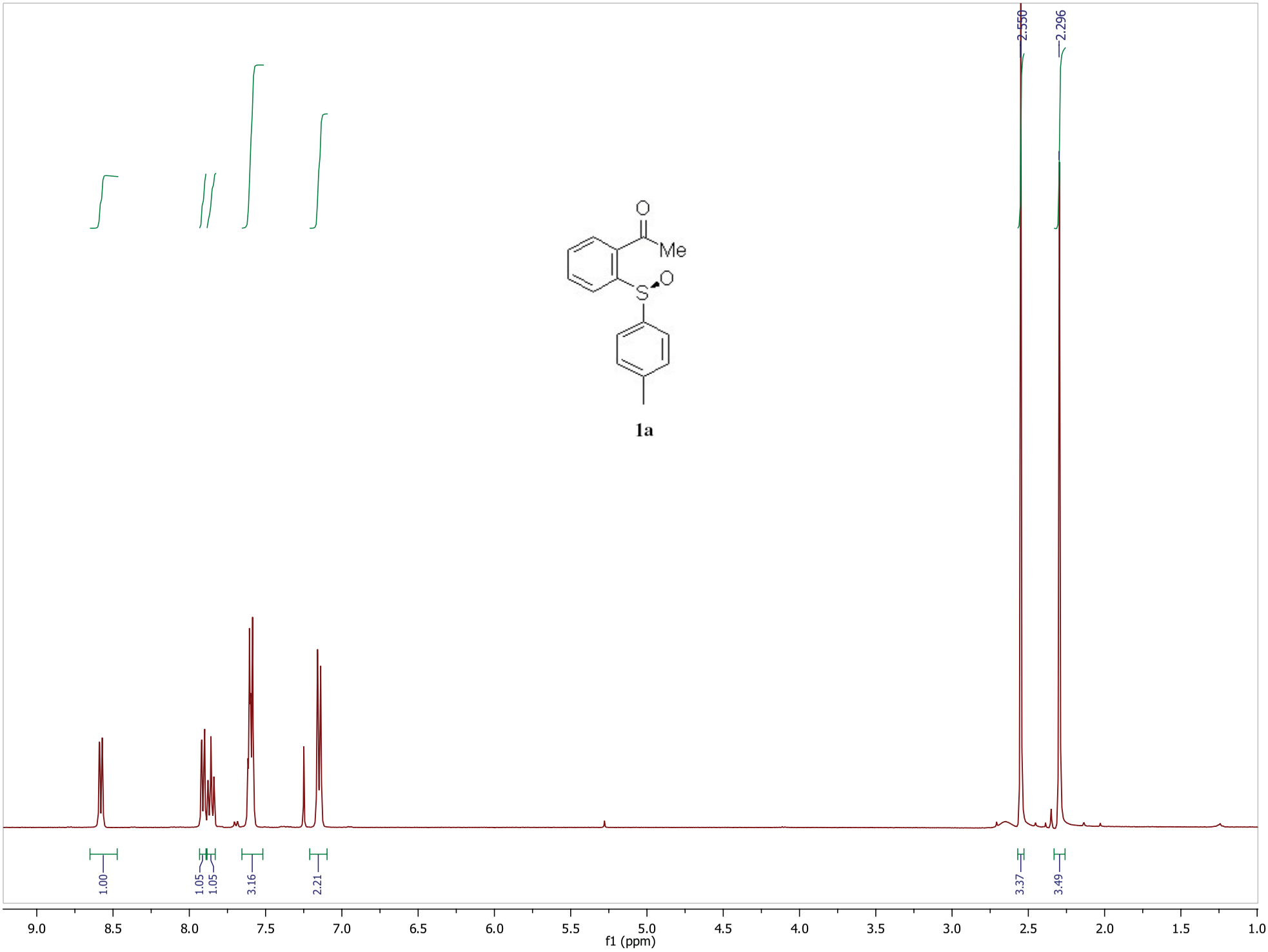
OMe
Me
O
S
Acetal A
0.88
0.92
3.79
1.91
2.89
3.00
3.03
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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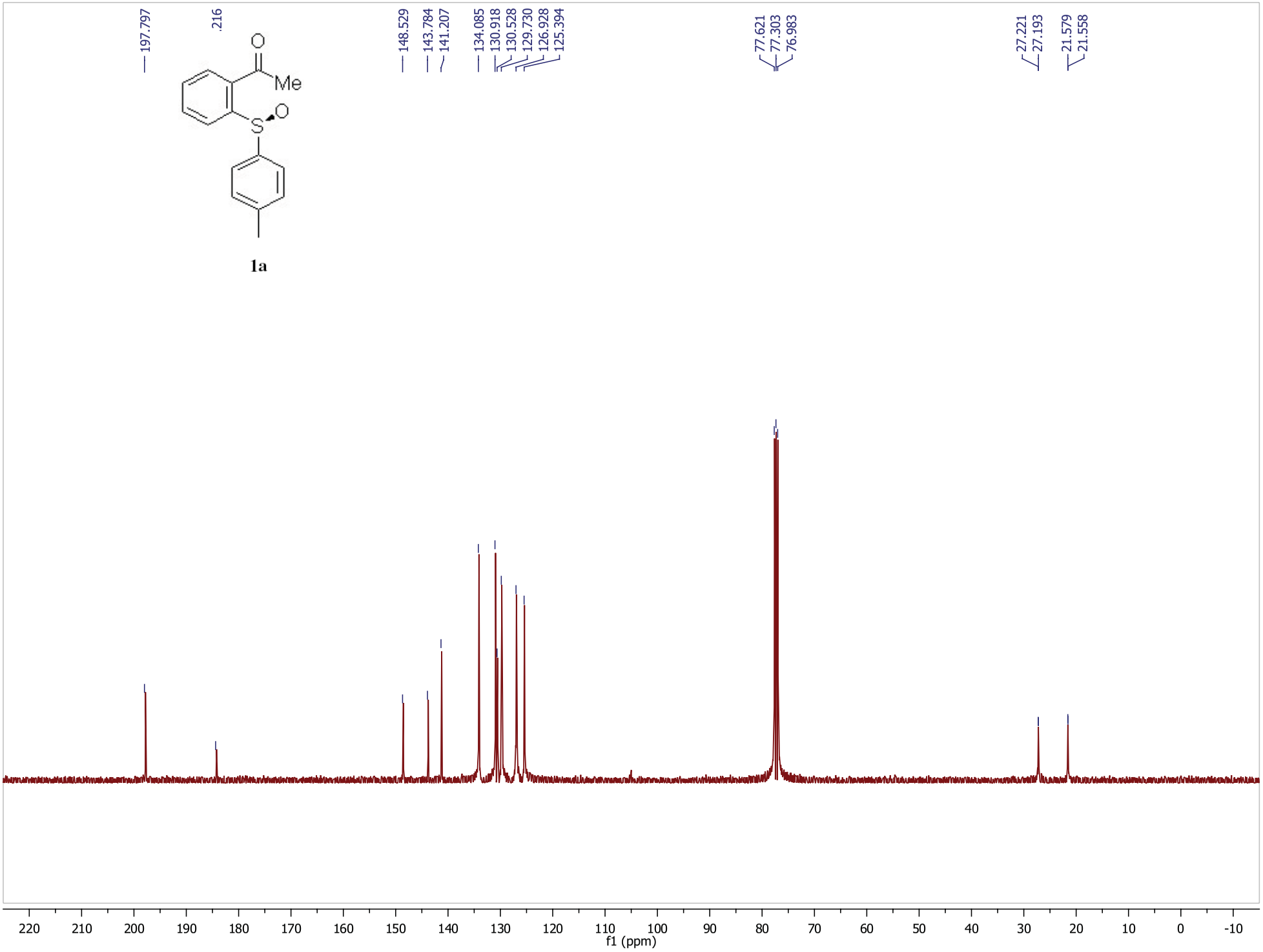
2.296
O
Me
S
O
1.00
1.05
1.05
3.16
2.21
3.37
3.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

1a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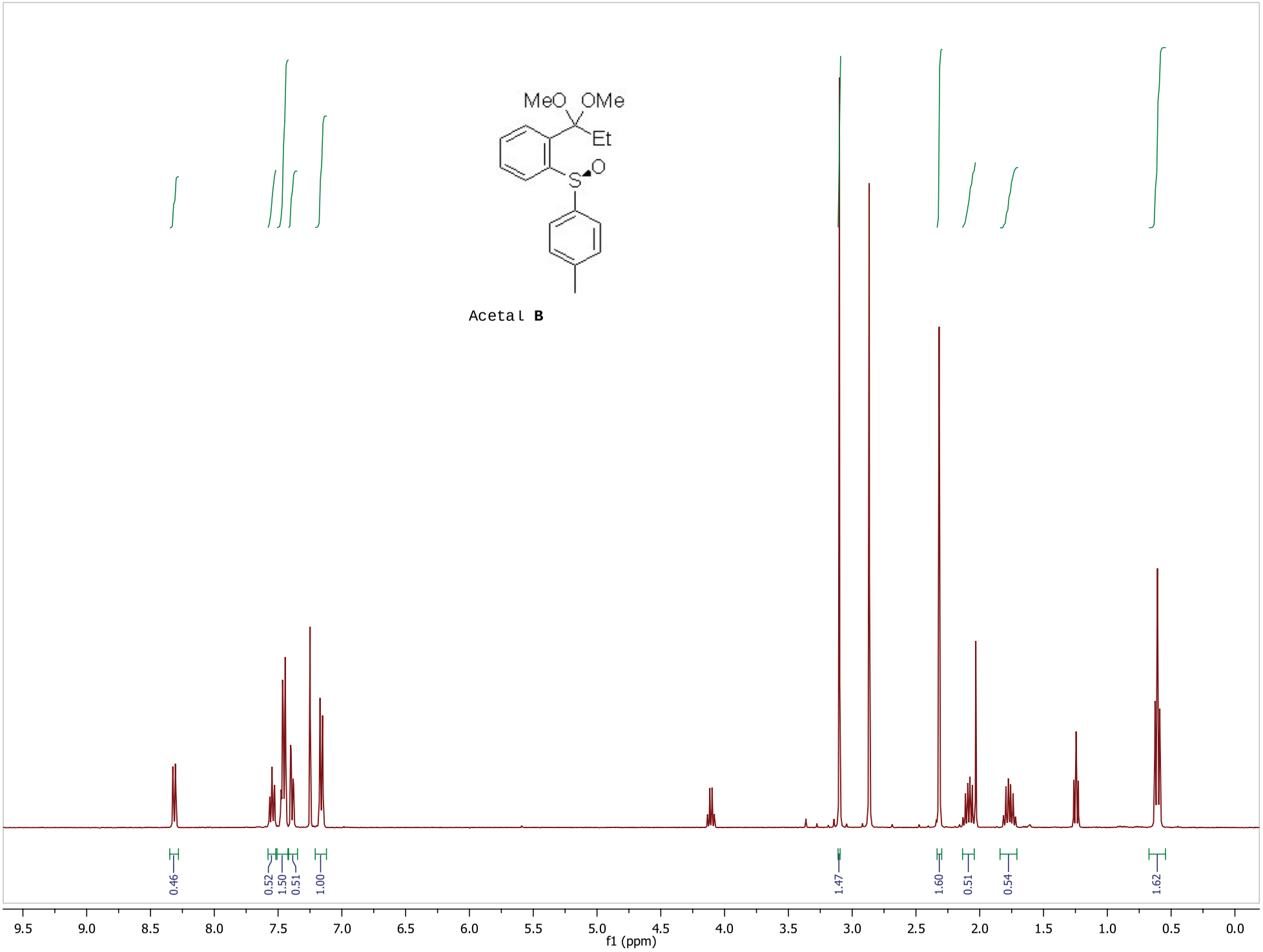
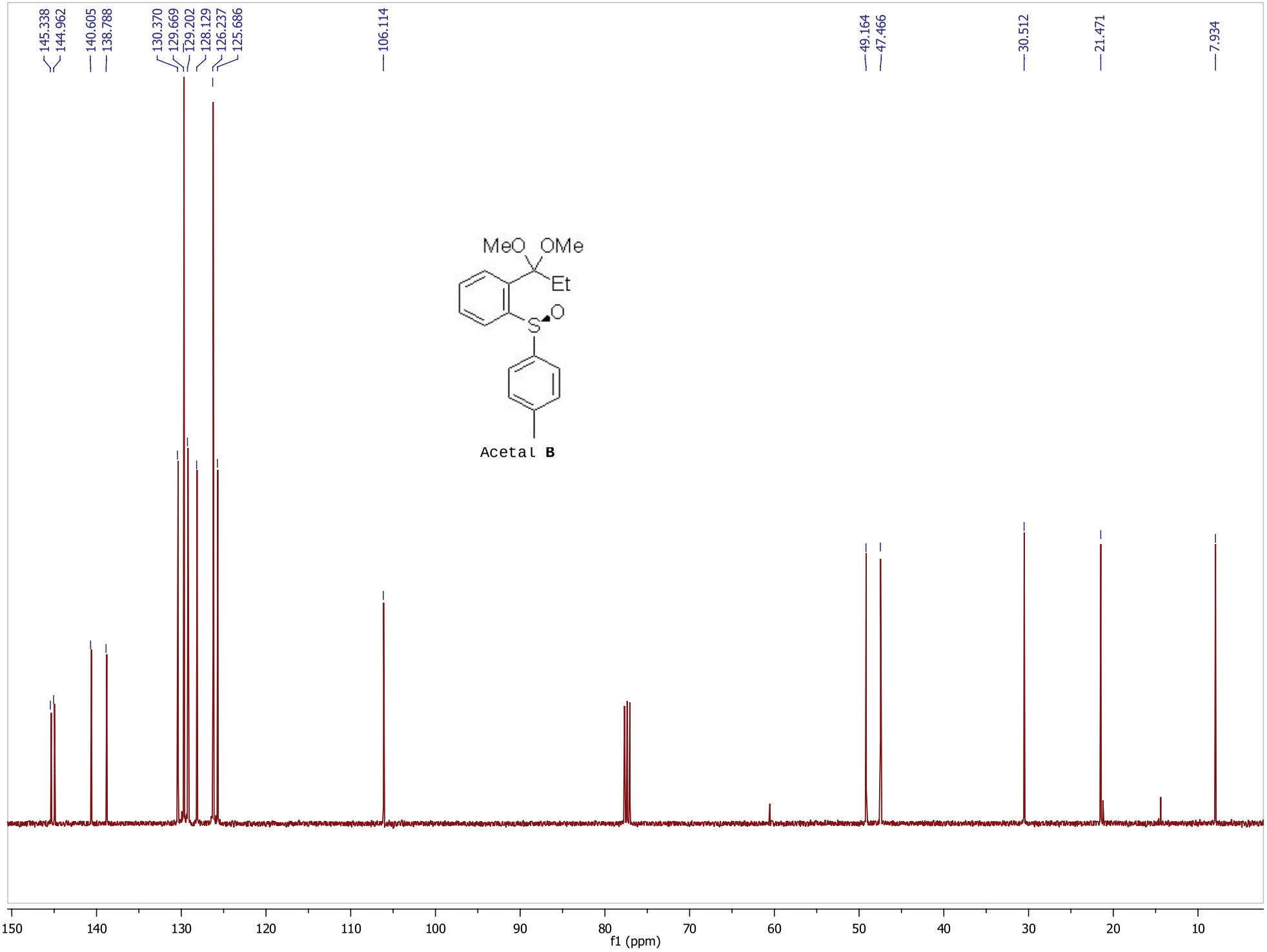
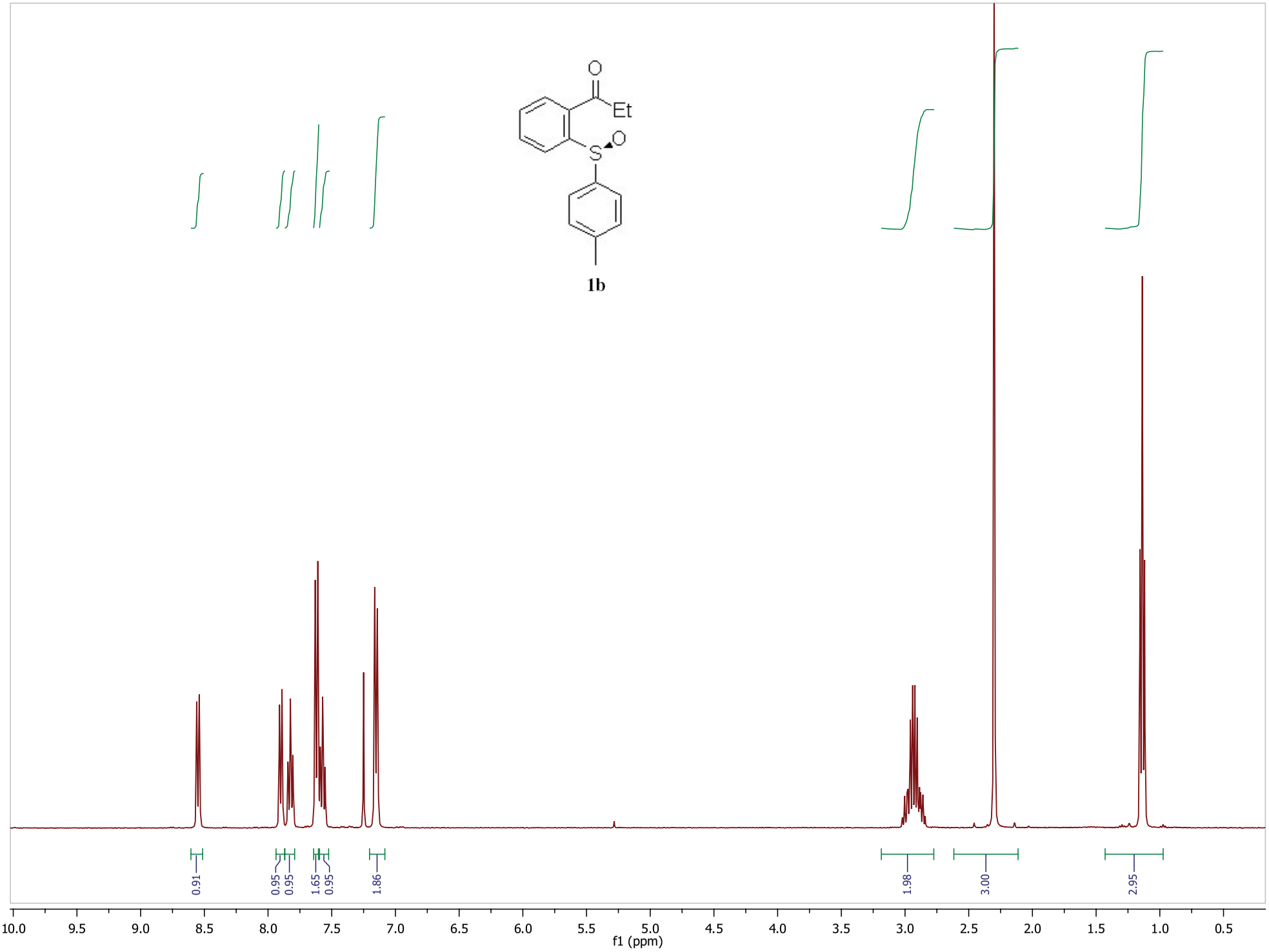
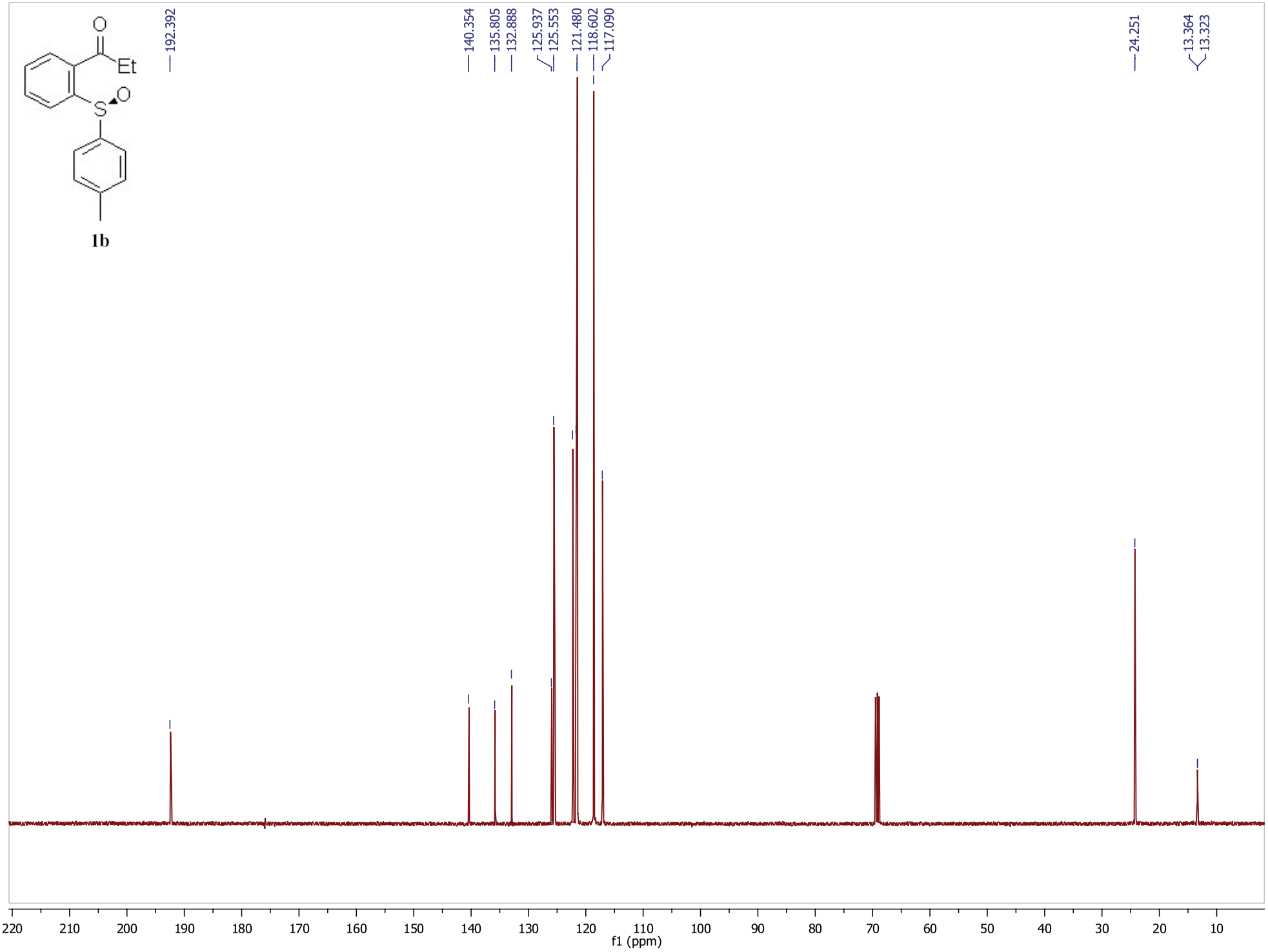
216
148.529
143.784
141.207
134.085
130.918
130.528
129.730
126.928
125.394
77.621
77.303
76.983
27.221
27.193
21.579
21.558
Me
O
S
O
1a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

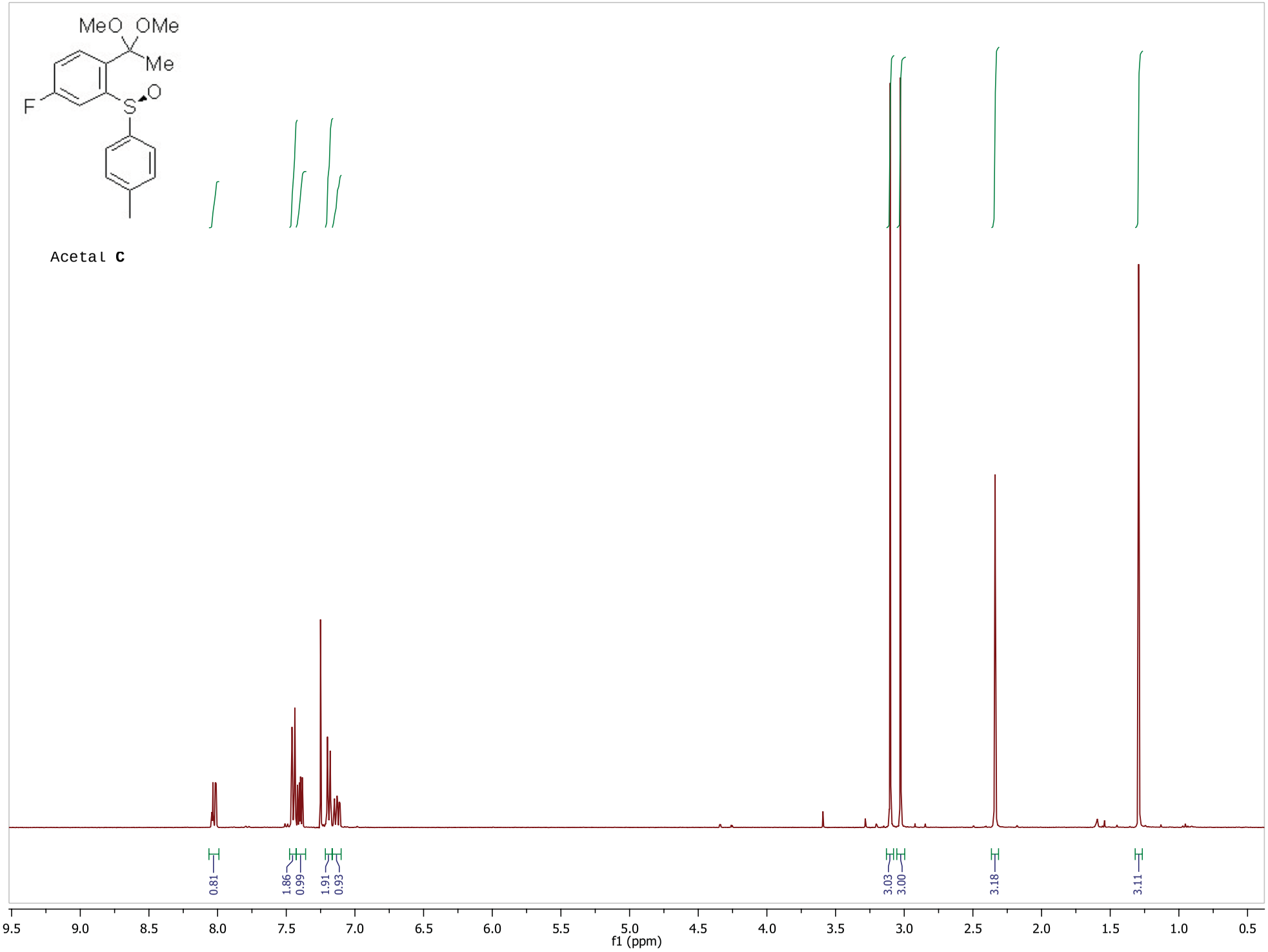

MeO
OMe
Et
O
S
Acetal B
0.46
0.52
1.50
0.51
1.00
1.47
1.60
0.51
0.54
1.62
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.338
144.962
140.605
138.788
130.370
129.669
129.202
128.129
126.237
125.686
106.114
49.164
47.466
30.512
21.471
7.934
MeO
OMe
Et
O
S
Acetal B
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
Et
O
S
0.91
0.95
0.95
1.65
0.95
1.86
1.98
3.00
2.95
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
f1 (ppm)

1b


192.392
140.354
135.805
132.888
125.937
125.553
121.480
118.602
117.090
24.251
13.364
13.323
Et
O
S
O
1b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeO OMe
Me
F
S
O
Acetal C
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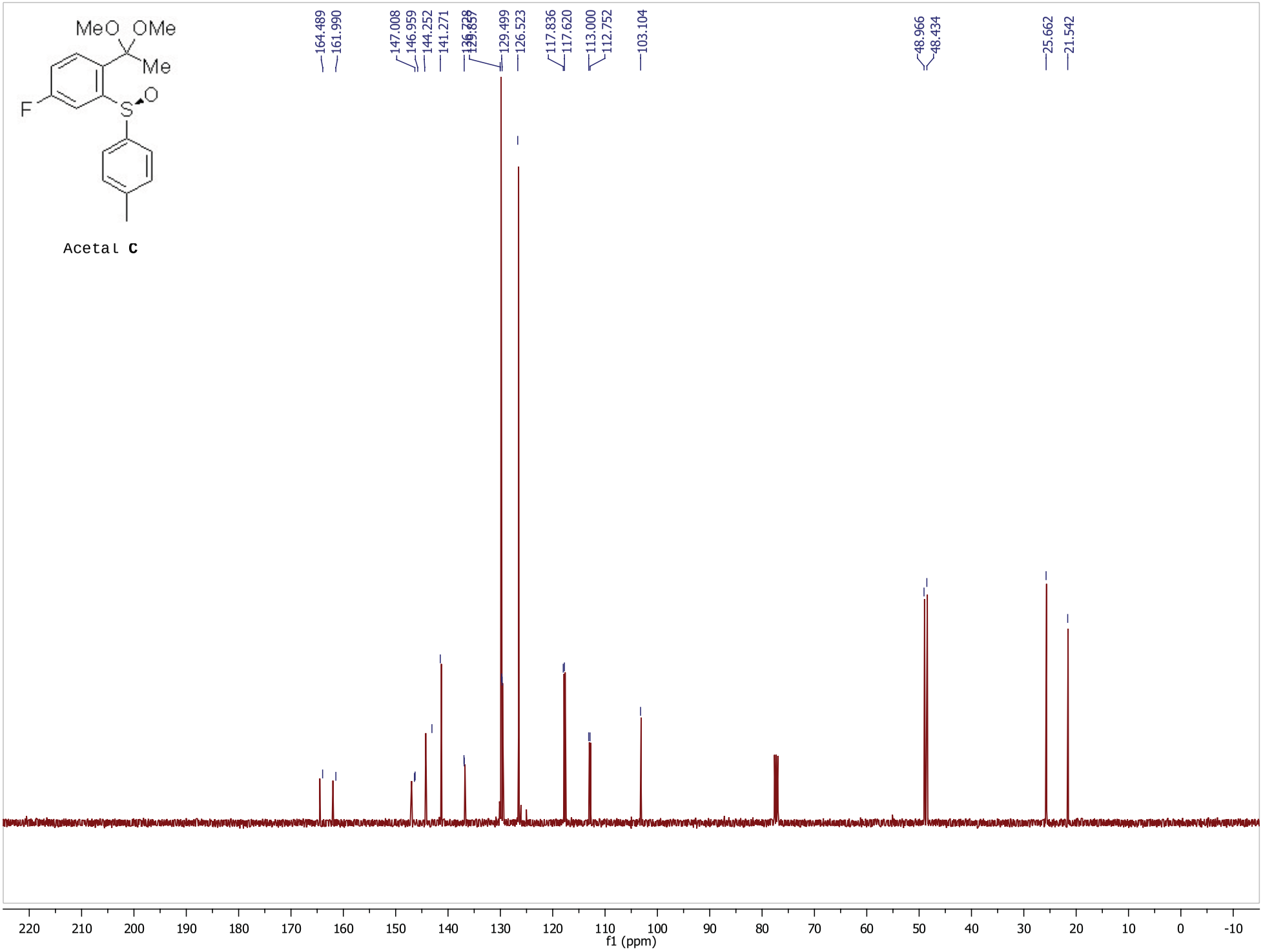
1.86
0.99
1.91
0.93
3.03
3.00
3.18
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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OMe
Me
F
S
O
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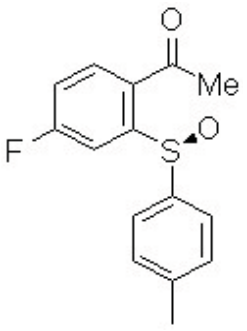
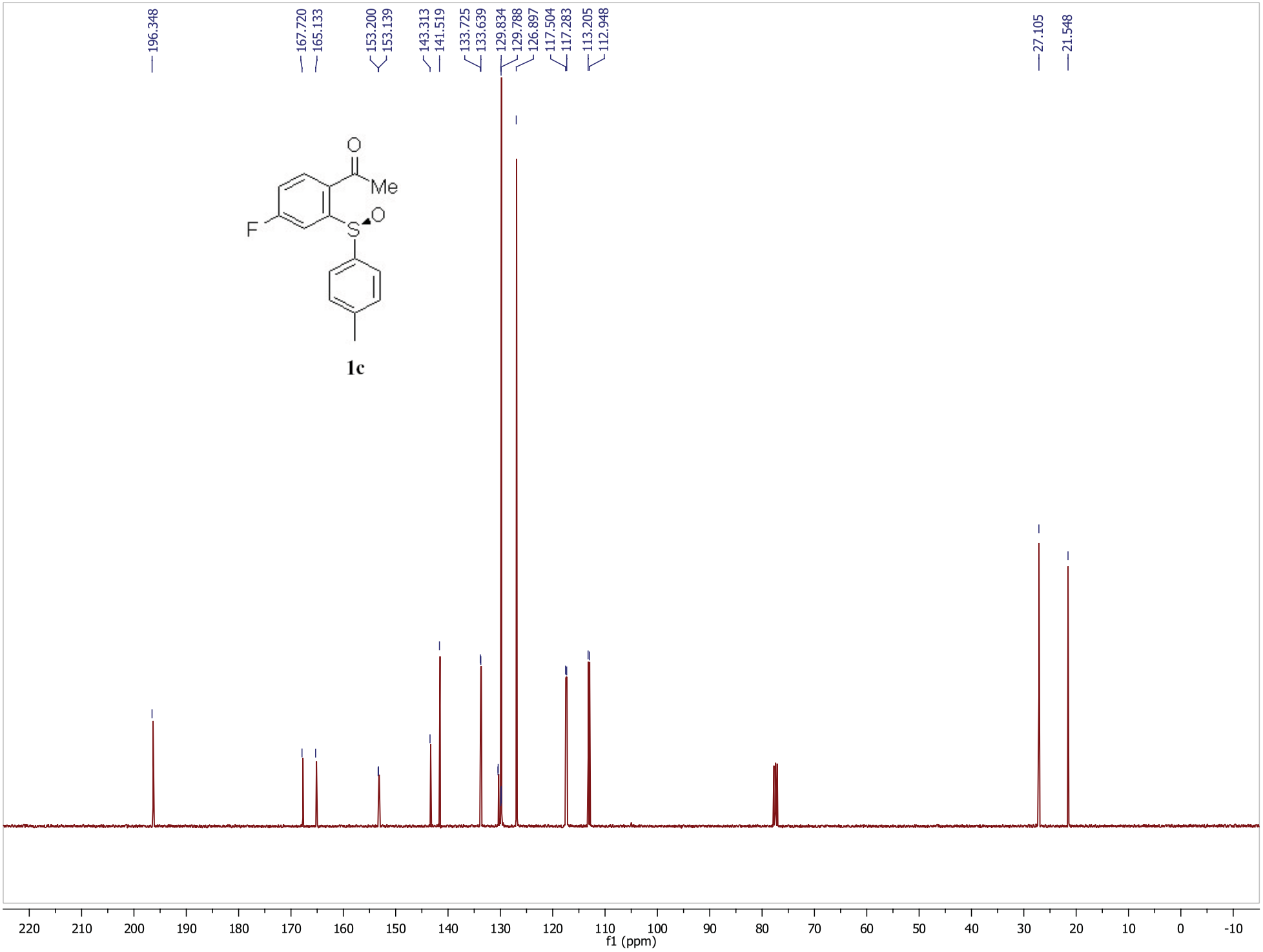
161.990
147.008
146.959
144.252
141.271
136.728
129.857
129.499
126.523
117.836
117.620
113.000
112.752
103.104
48.966
48.434
25.662
21.542
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Acetal **C**


O
Me
F
S
O

1c

0.82
0.93
1.76
1.18
1.83
2.99
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
f1 (ppm)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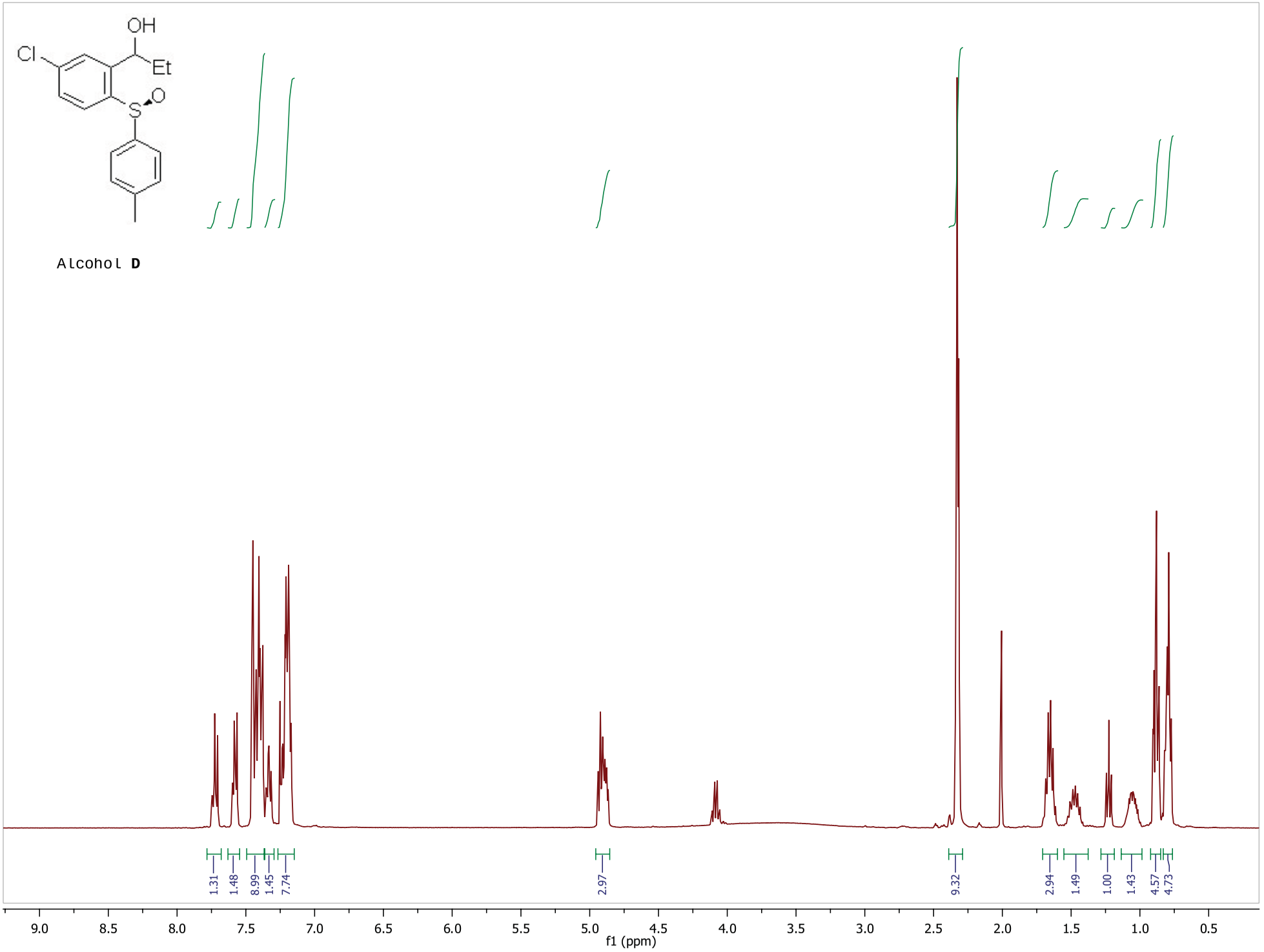
167.720
165.133
153.200
153.139
143.313
141.519
133.725
133.639
129.834
129.788
126.897
117.504
117.283
113.205
112.948
27.105
21.548
O
Me
F
S
O
1c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Cl
Et
O
S
Alcohol D
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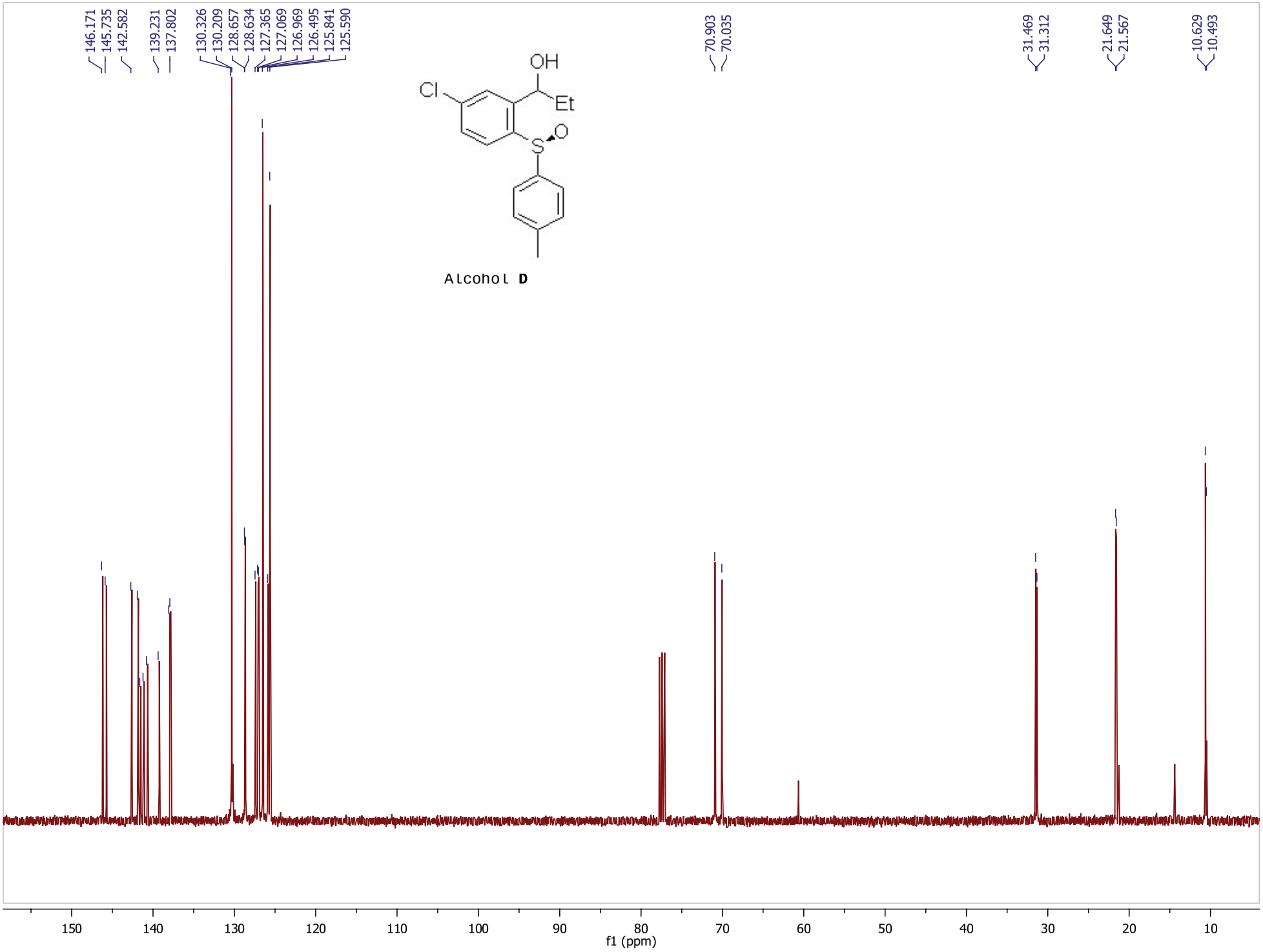
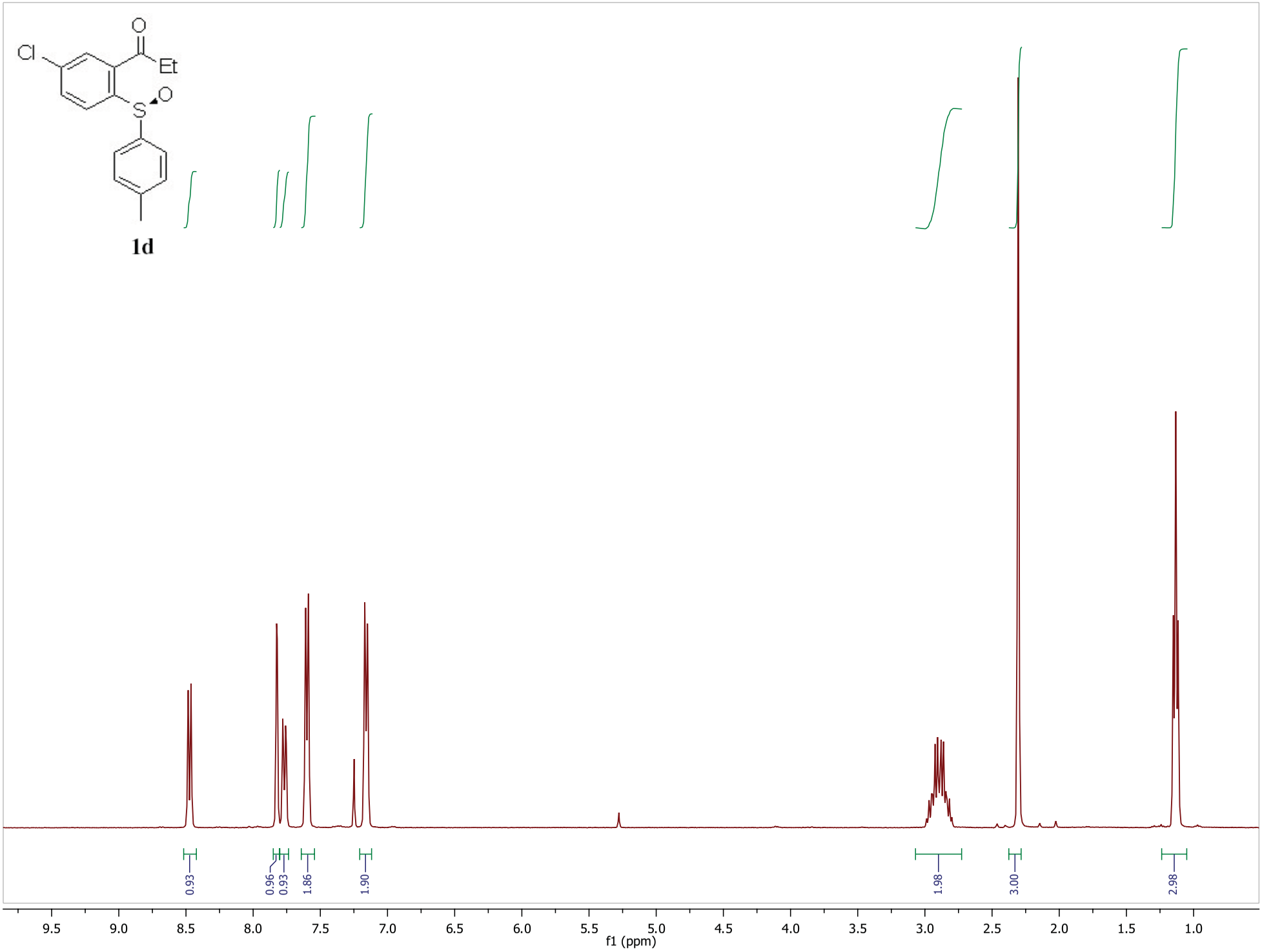
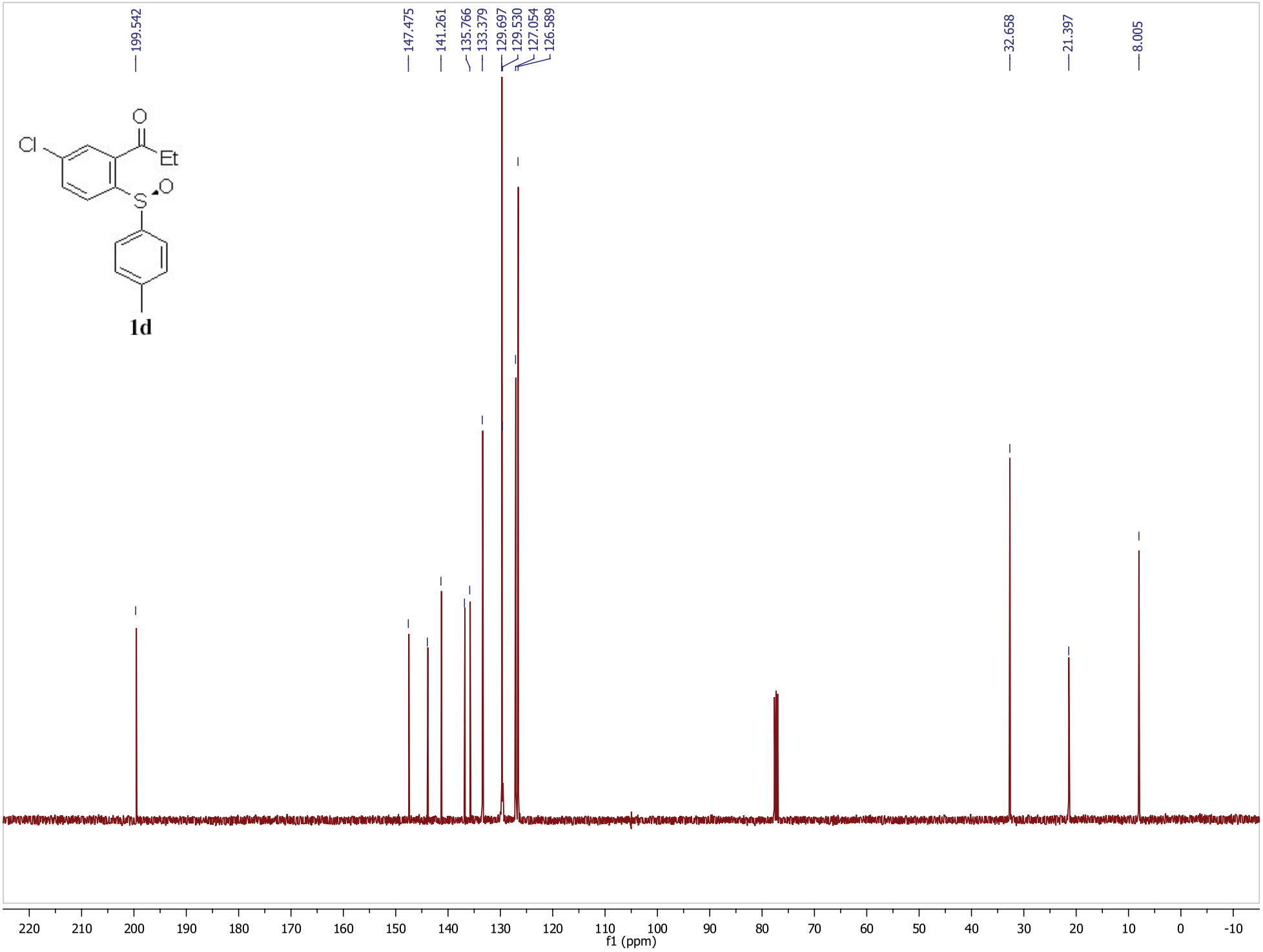
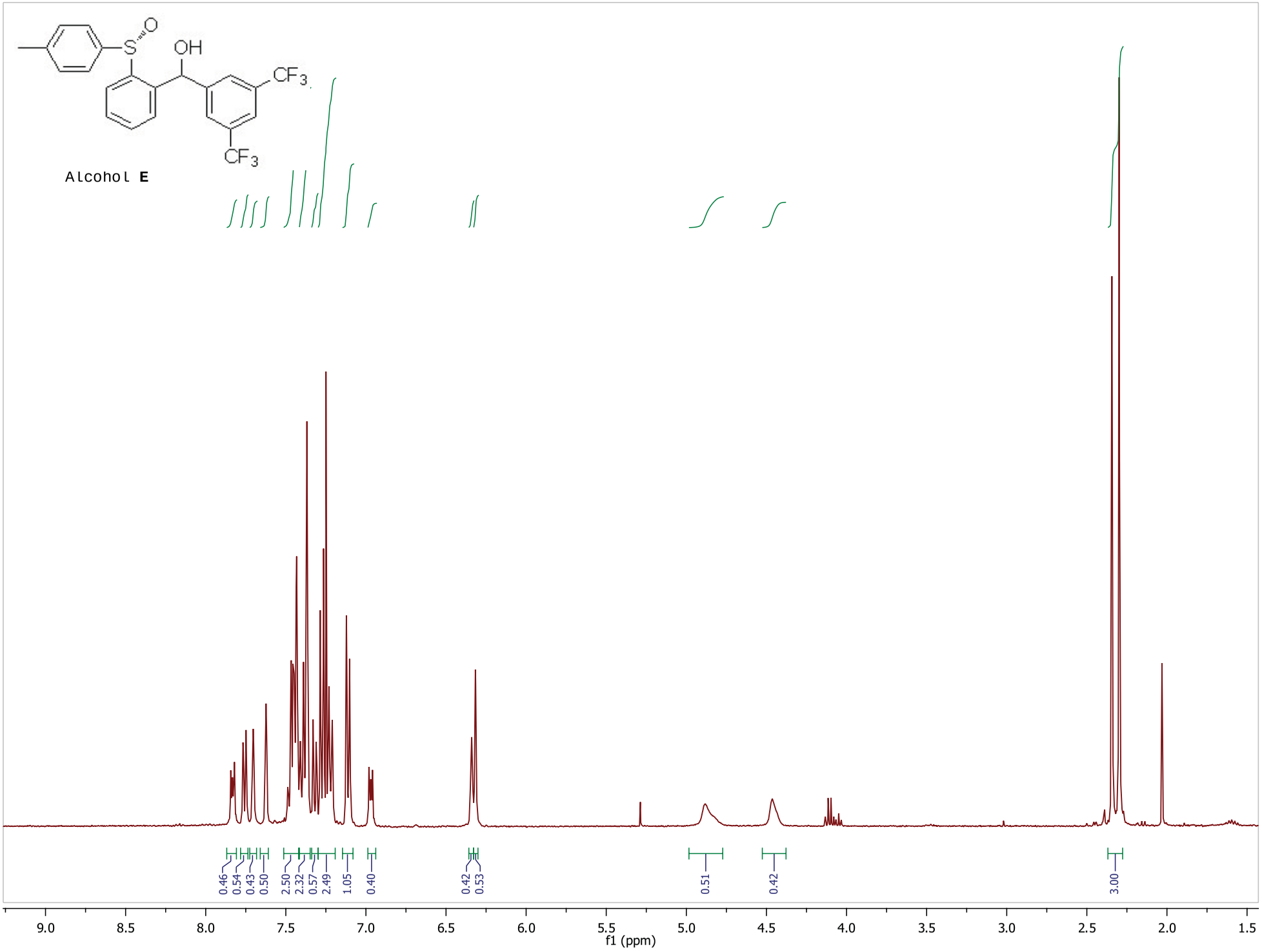
1.48
8.99
1.45
7.74
2.97
9.32
2.94
1.49
1.00
1.43
4.57
4.73
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


146.171
145.735
142.582
139.231
137.802
130.326
130.209
128.657
128.634
127.365
127.069
126.969
126.495
125.841
125.590
70.903
70.035
31.469
31.312
21.649
21.567
10.629
10.493
OH
Cl
Et
S
O
Alcohol D
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
O
Et
S
O
1d
0.93
0.96
0.93
1.86
1.90
1.98
3.00
2.98
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
f1 (ppm)


199.542
147.475
141.261
135.766
133.379
129.697
129.530
127.054
126.589
32.658
21.397
8.005
Cl
O
Et
S
O
1d
220
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)


O
S
OH
CF3
CF3
Alcohol E
0.46
0.54
0.43
0.50
2.50
2.32
0.57
2.49
1.05
0.40
0.42
0.53
0.51
0.42
3.00
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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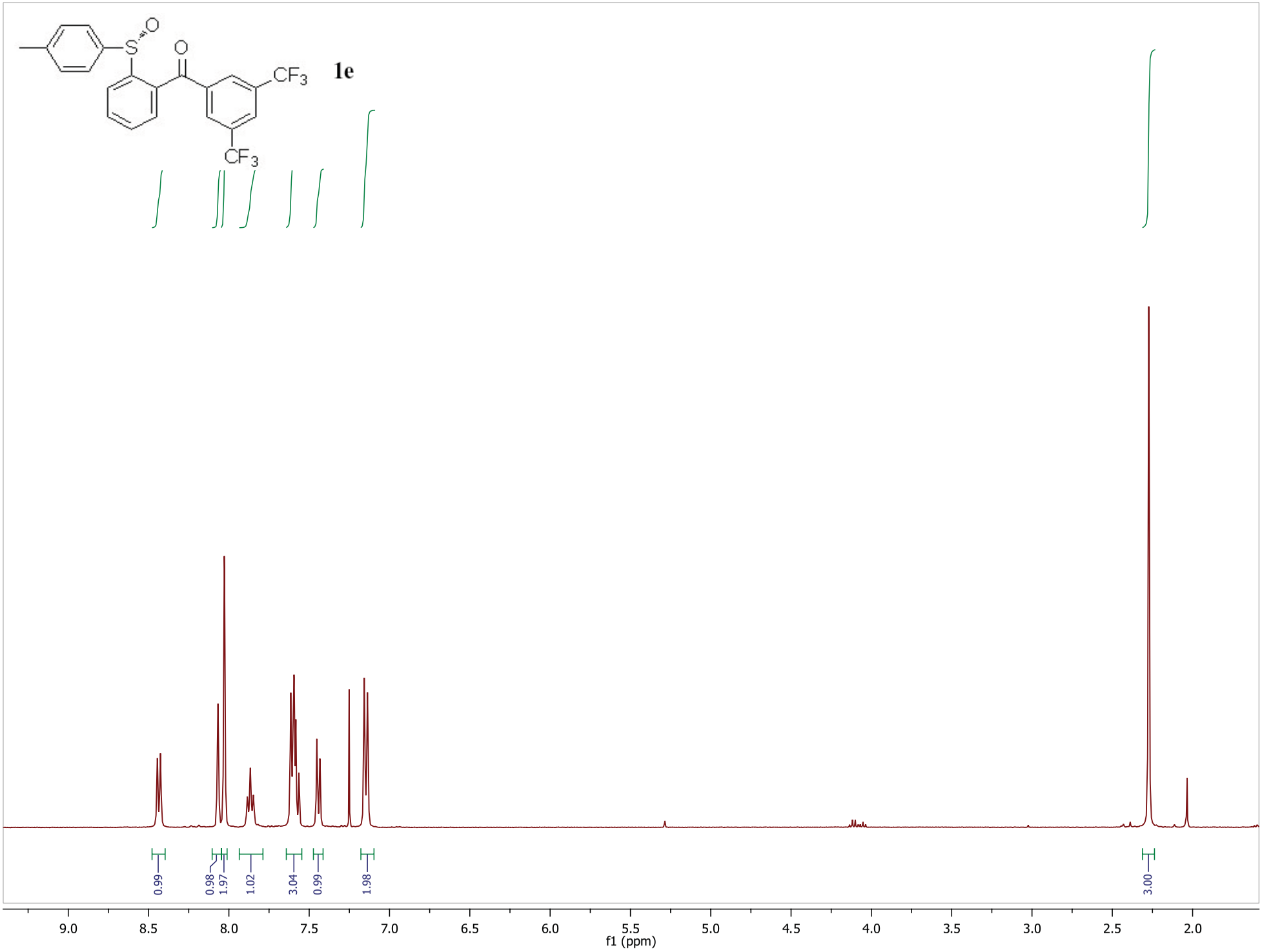
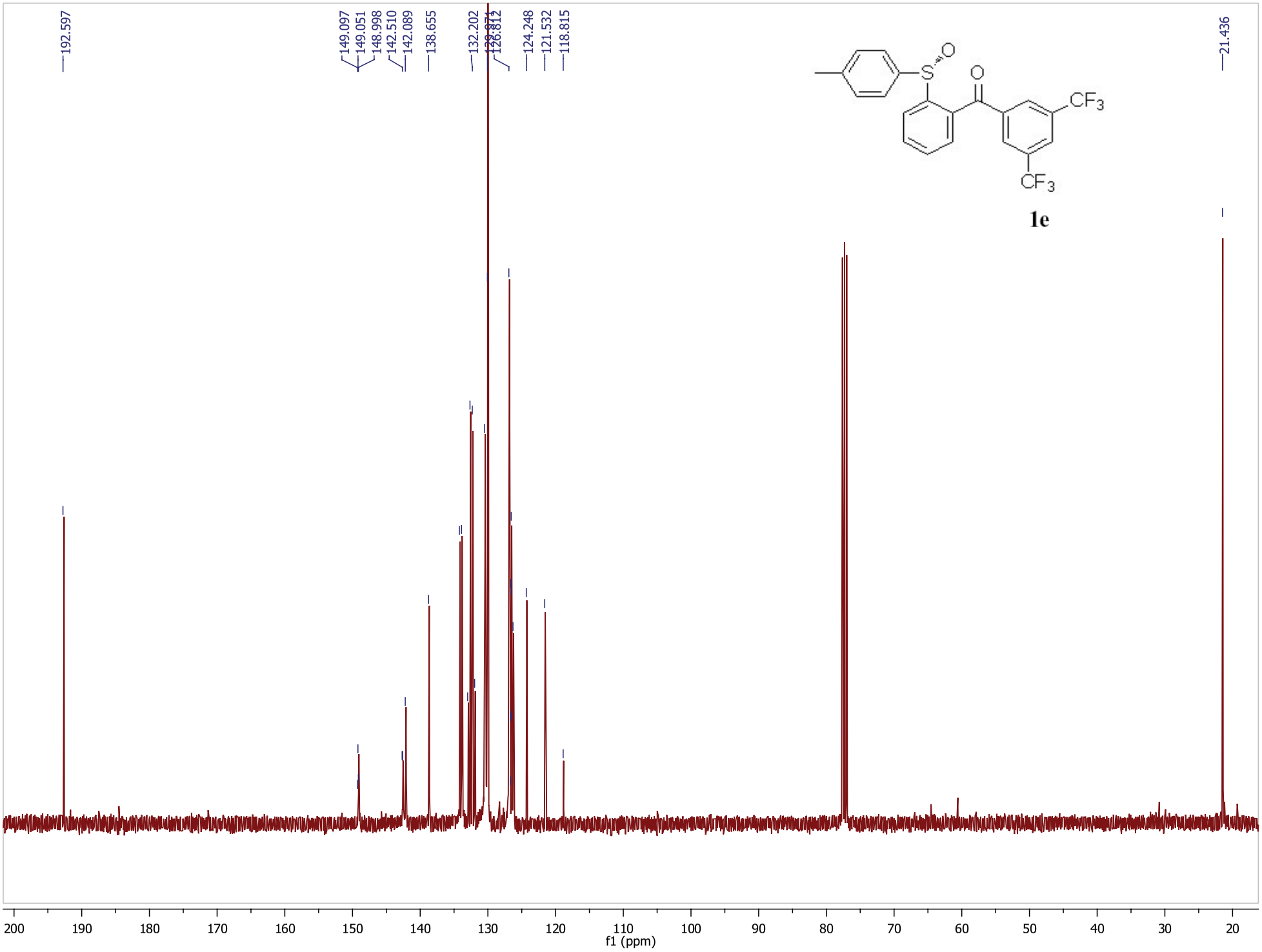
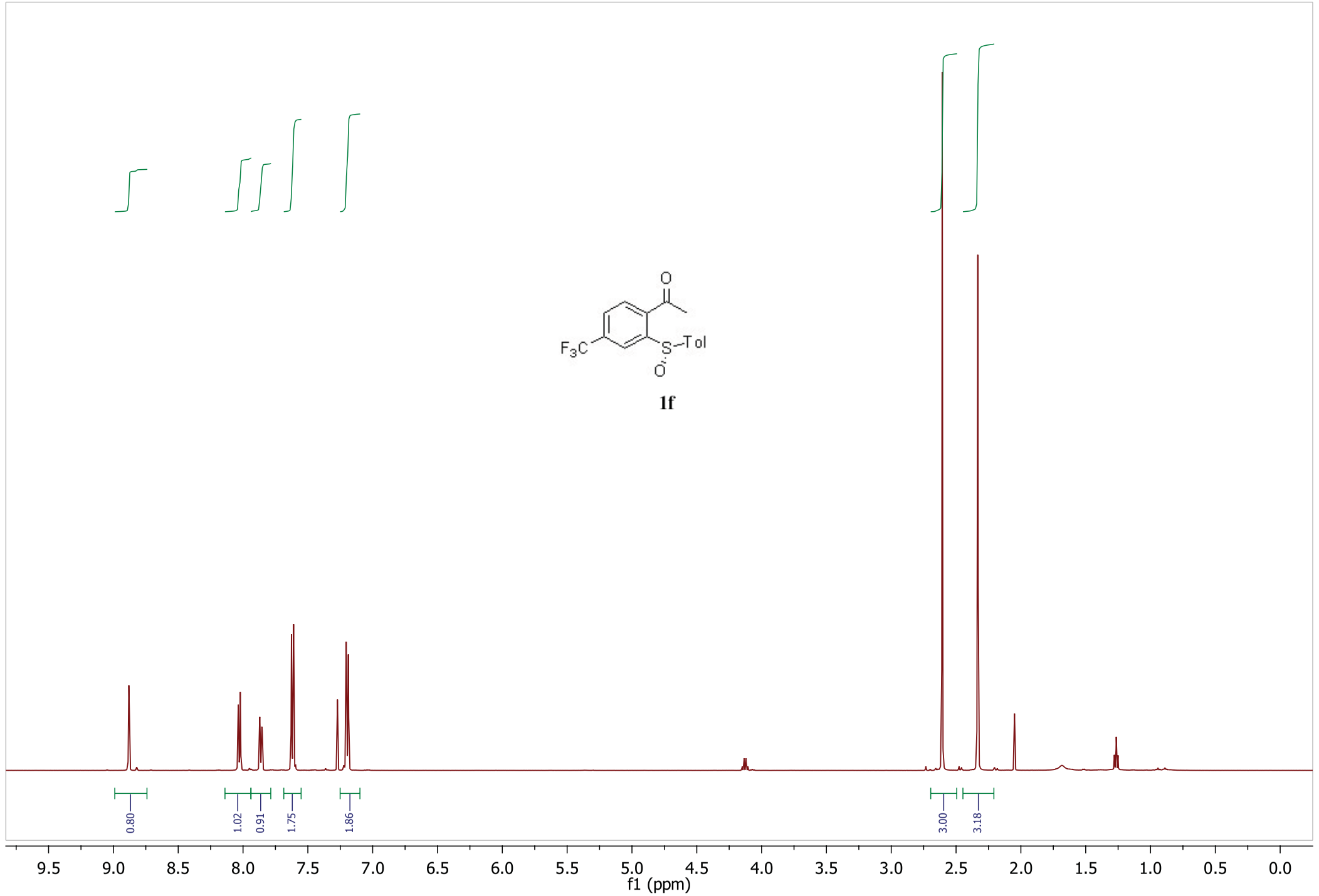
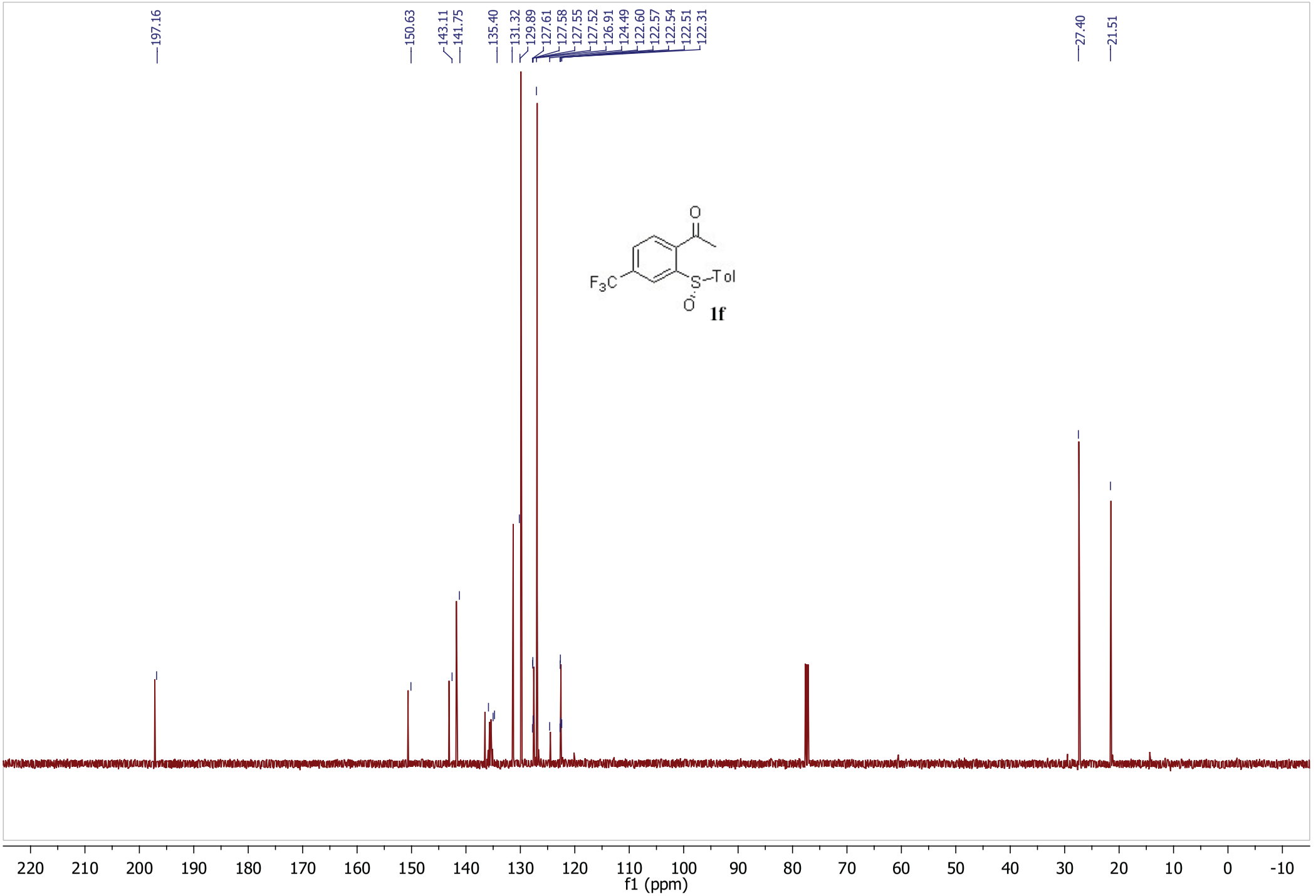
3.0
2.5
2.0
1.5
f1 (ppm)


O
S
O
CF3
CF3
1e
0.99
0.98
1.97
1.02
3.04
0.99
1.98
3.00
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
f1 (ppm)


192.597
149.097
149.051
148.998
142.510
142.089
138.655
132.202
124.248
121.532
118.815
21.436
O
S
O
CF3
CF3
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


O
F3C
S
Tol
O
1f
0.80
1.02
0.91
1.75
1.86
3.00
3.18
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)


197.16
150.63
143.11
141.75
135.40
131.32
129.89
127.61
127.58
127.55
127.52
126.91
124.49
122.60
122.57
122.54
122.51
122.31
27.40
21.51
O
F3C
S
Tol
O
1f
220
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)

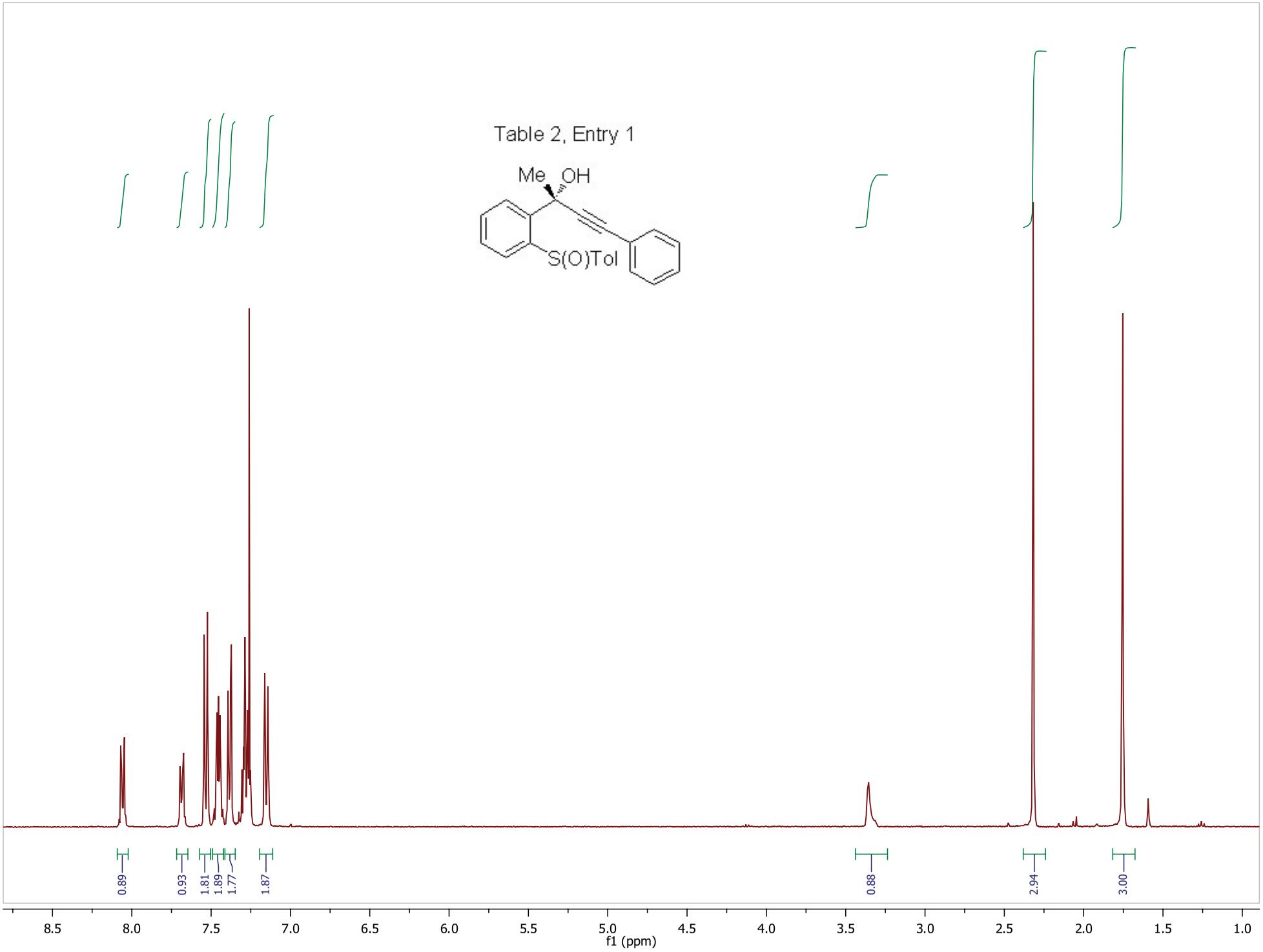
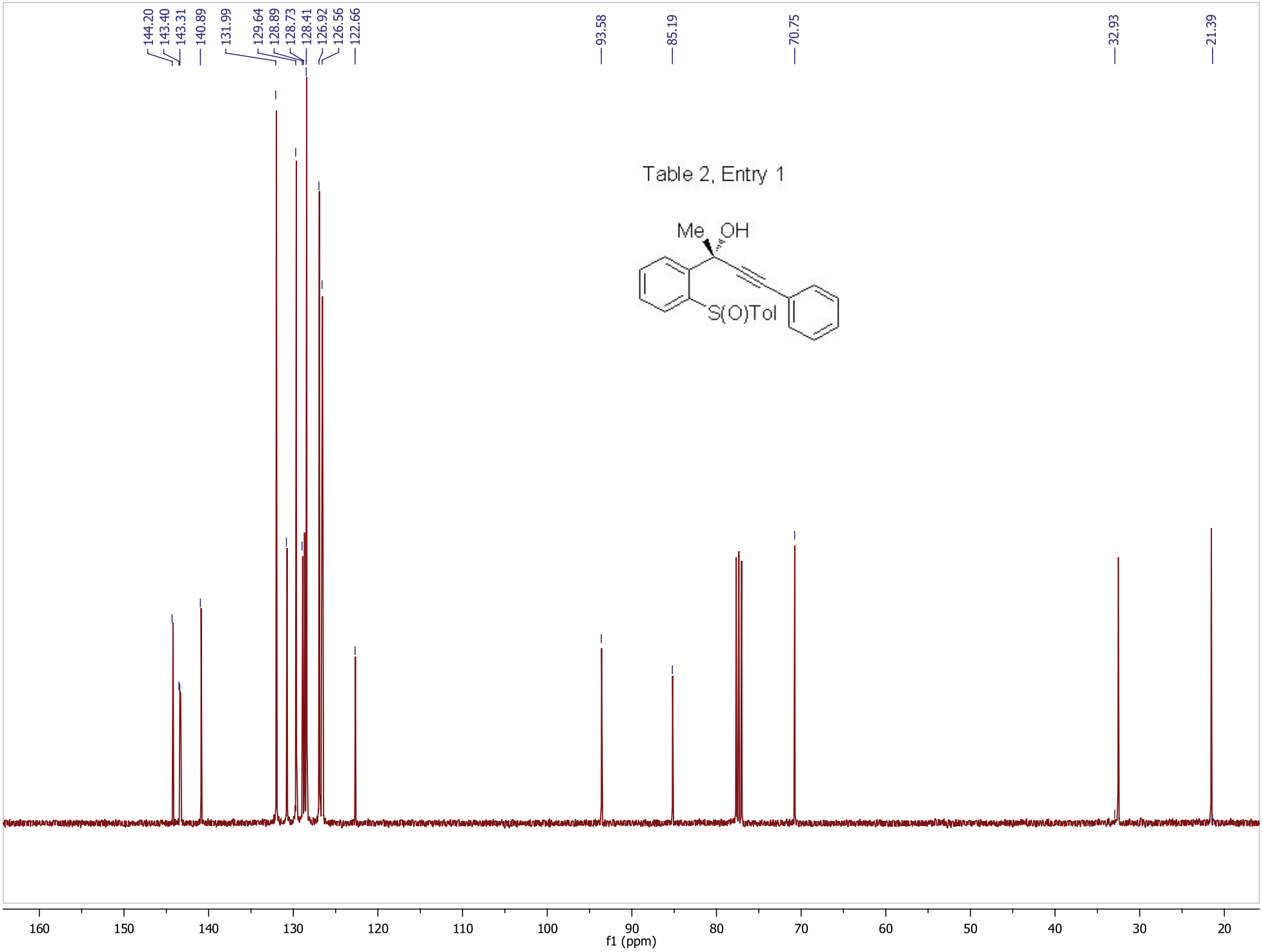
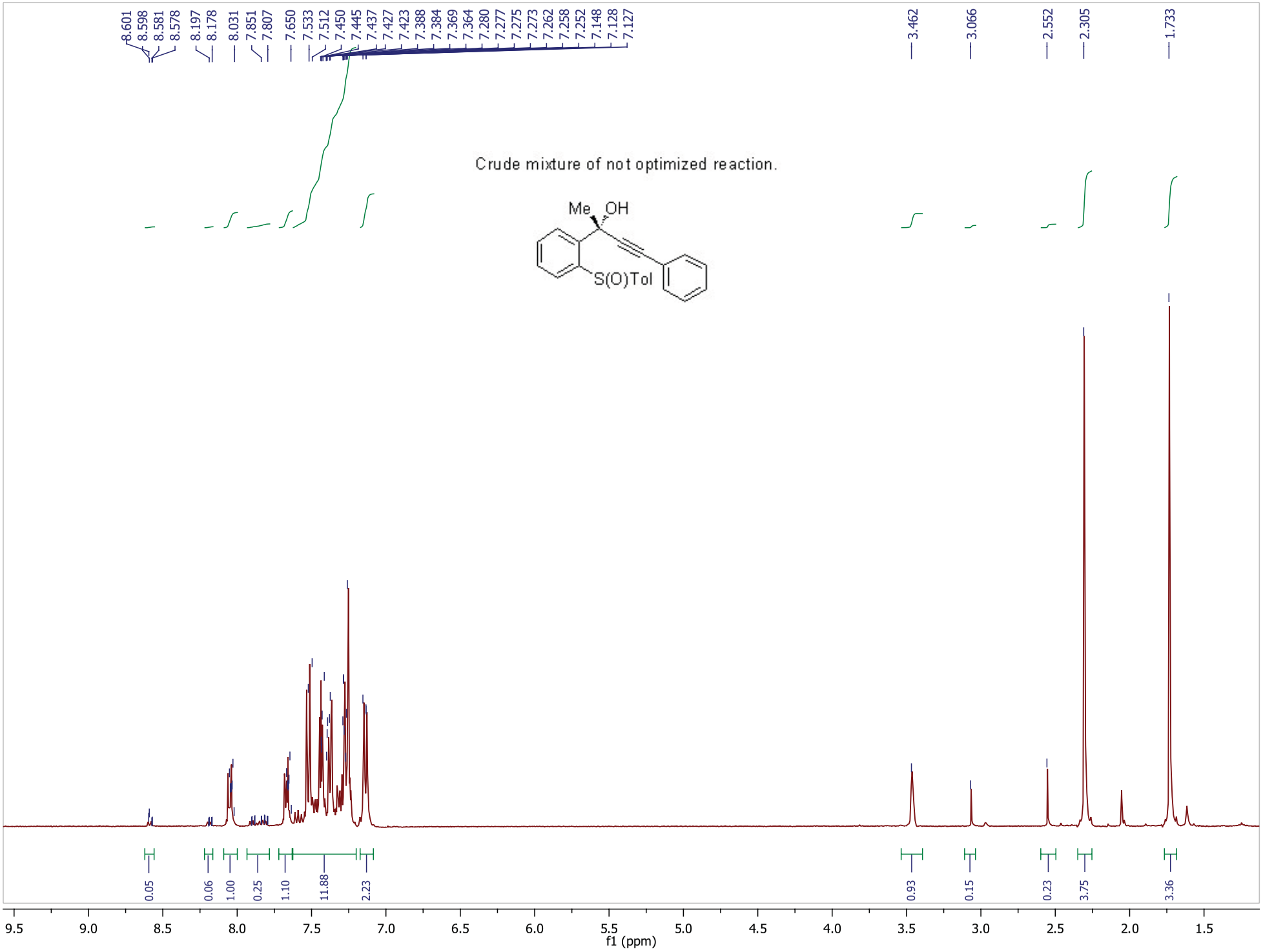
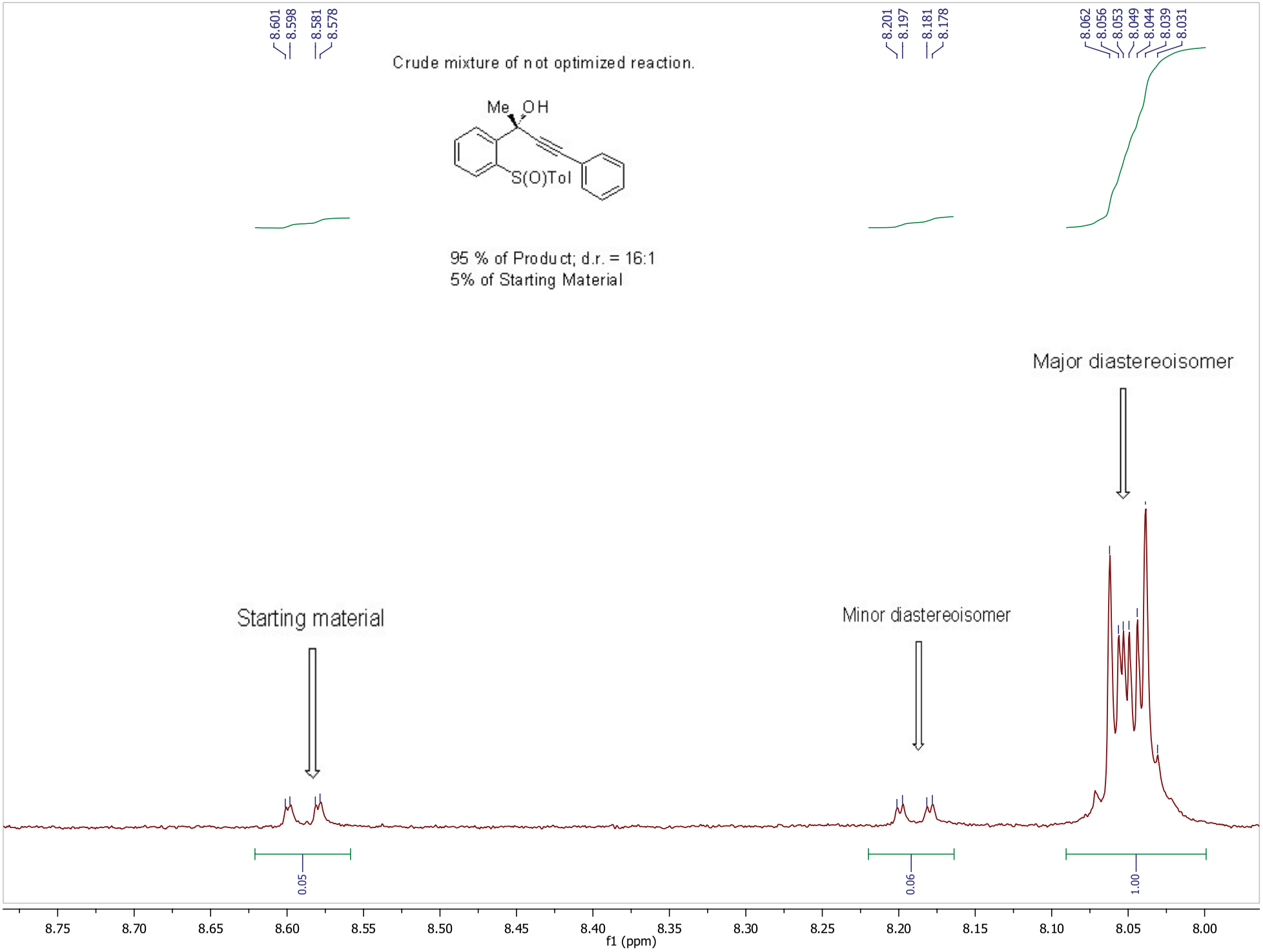


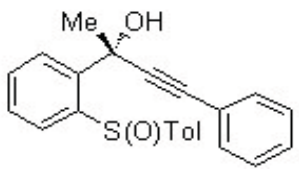
Table 2, Entry 1
Me
OH
S(O)Tol
0.89
0.93
1.81
1.89
1.77
1.87
0.88
2.94
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


144.20
143.40
143.31
140.89
131.99
129.64
128.89
128.73
128.41
126.92
126.56
122.66
93.58
85.19
70.75
32.93
21.39
Table 2, Entry 1
Me
OH
S(O)Tol
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.601
8.598
8.581
8.578
8.197
8.178
8.031
7.851
7.807
7.650
7.533
7.512
7.450
7.445
7.437
7.427
7.423
7.388
7.384
7.369
7.364
7.280
7.277
7.275
7.273
7.262
7.258
7.252
7.148
7.128
7.127
3.462
3.066
2.552
2.305
1.733
Crude mixture of not optimized reaction.
Me
OH
S(O)Tol
0.05
0.06
1.00
0.25
1.10
11.88
2.23
0.93
0.15
0.23
3.75
3.36
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
f1 (ppm)


8.601
8.598
8.581
8.578
8.201
8.197
8.181
8.178
8.062
8.056
8.053
8.049
8.044
8.039
8.031
Crude mixture of not optimized reaction.
Me
OH
S(O)Tol
95 % of Product; d.r. = 16:1
5% of Starting Material
Major diastereoisomer
Starting material
Minor diastereoisomer
0.05
0.06
1.00
8.75
8.70
8.65
8.60
8.55
8.50
8.45
8.40
8.35
8.30
8.25
8.20
8.15
8.10
8.05
8.00
f1 (ppm)

Crude mixture of optimized reaction.



Major diastereoisomer

Minor diastereoisomer

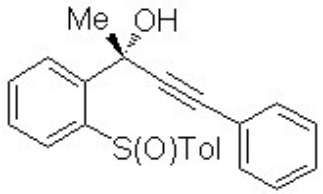
1.00

89.82

8.42 8.40 8.38 8.36 8.34 8.32 8.30 8.28 8.26 8.24 8.22 8.20 8.18 8.16 8.14 8.12 8.10 8.08 8.06 8.04 8.02 8.00 7.98

f1 (ppm)

Table 2, Entry 1



Purifired major diastereomer

Major diastereoisomer

Major diastereoisomer

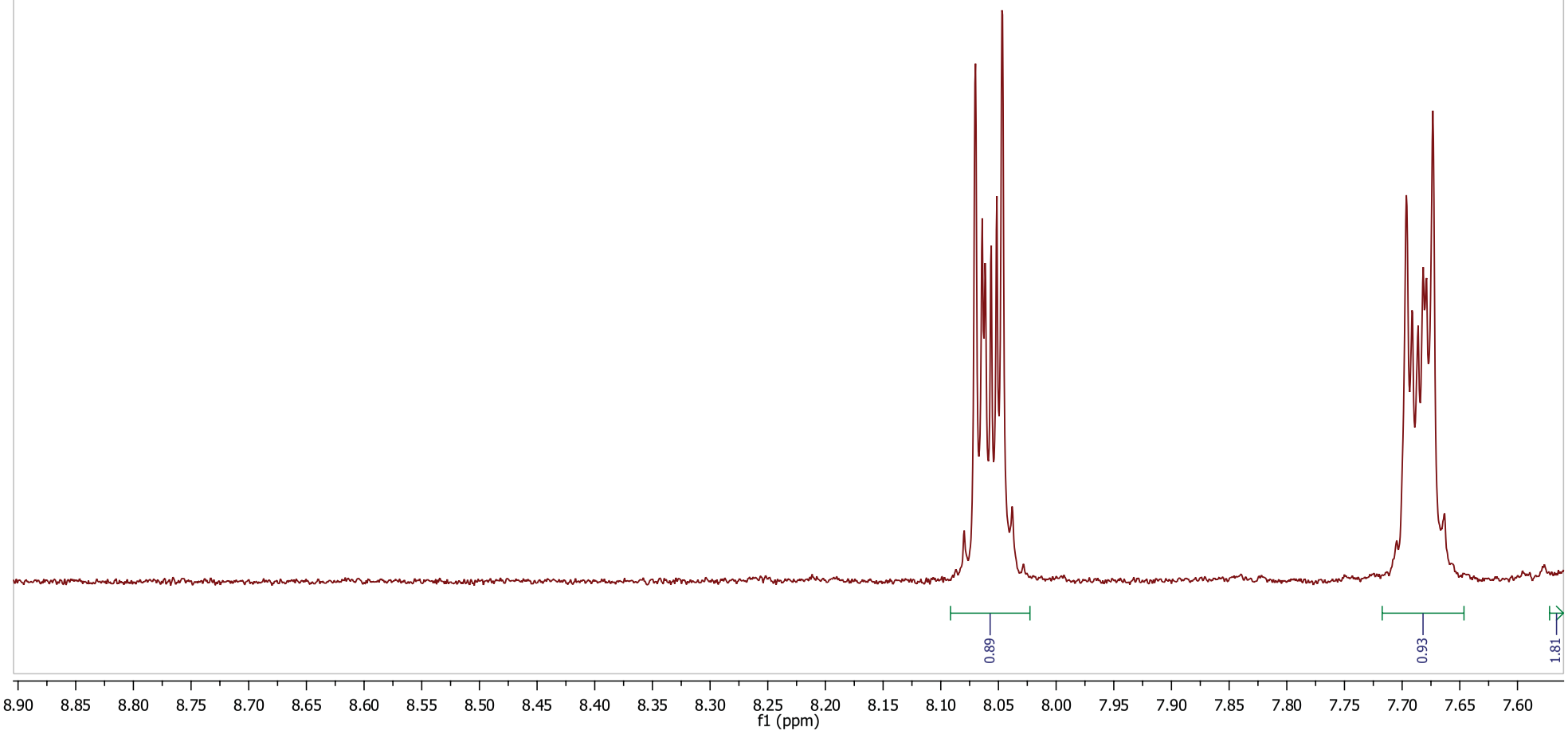
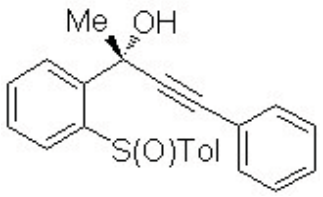
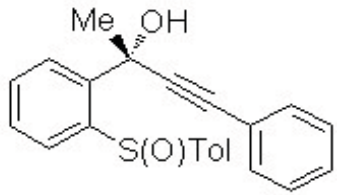


Table 2, Entry 1

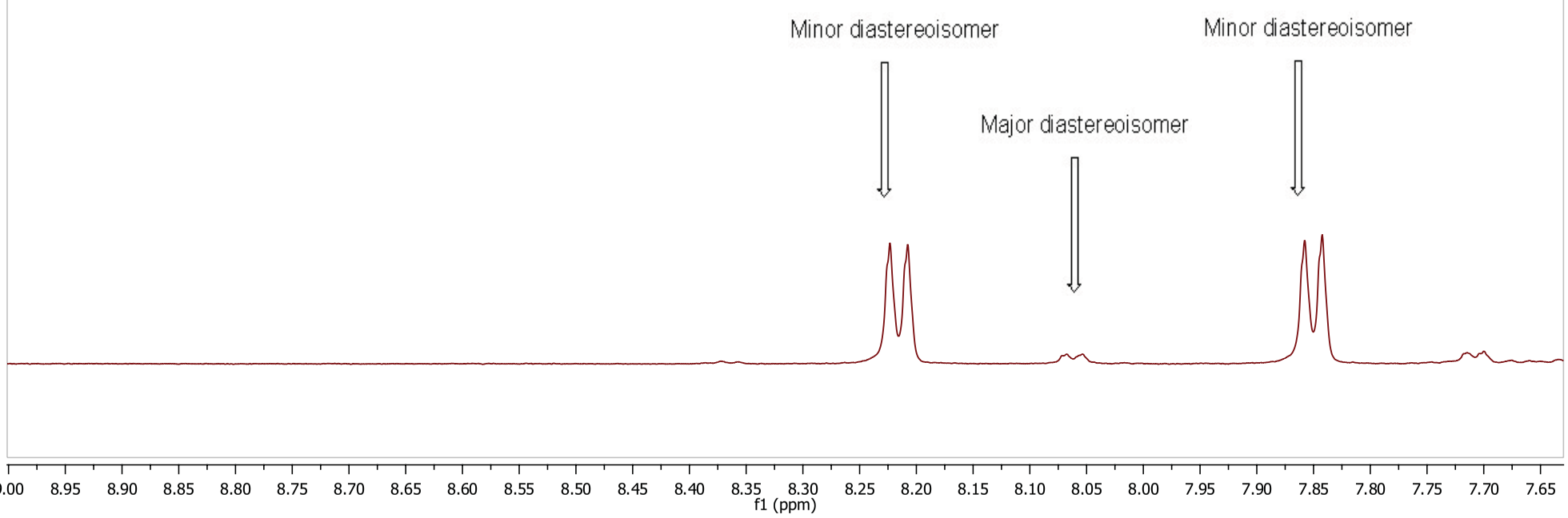


Purifired major diastereomer

Table 2, Entry 1



Purifired minor diastereomer



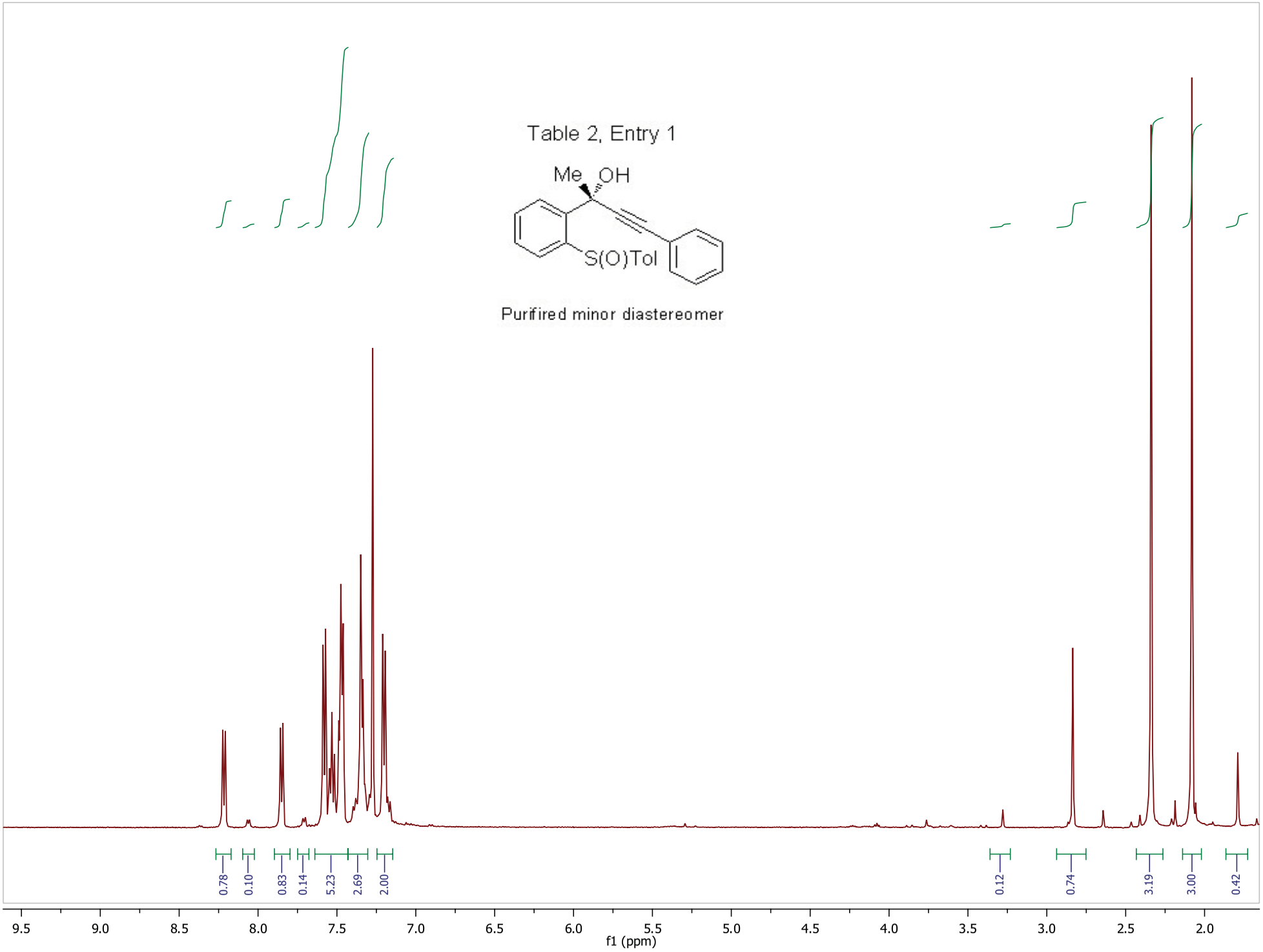


Table 2, Entry 1
Me
OH
S(O)Tol
Purifired minor diastereomer
0.78
0.10
0.83
0.14
5.23
2.69
2.00
0.12
0.74
3.19
3.00
0.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

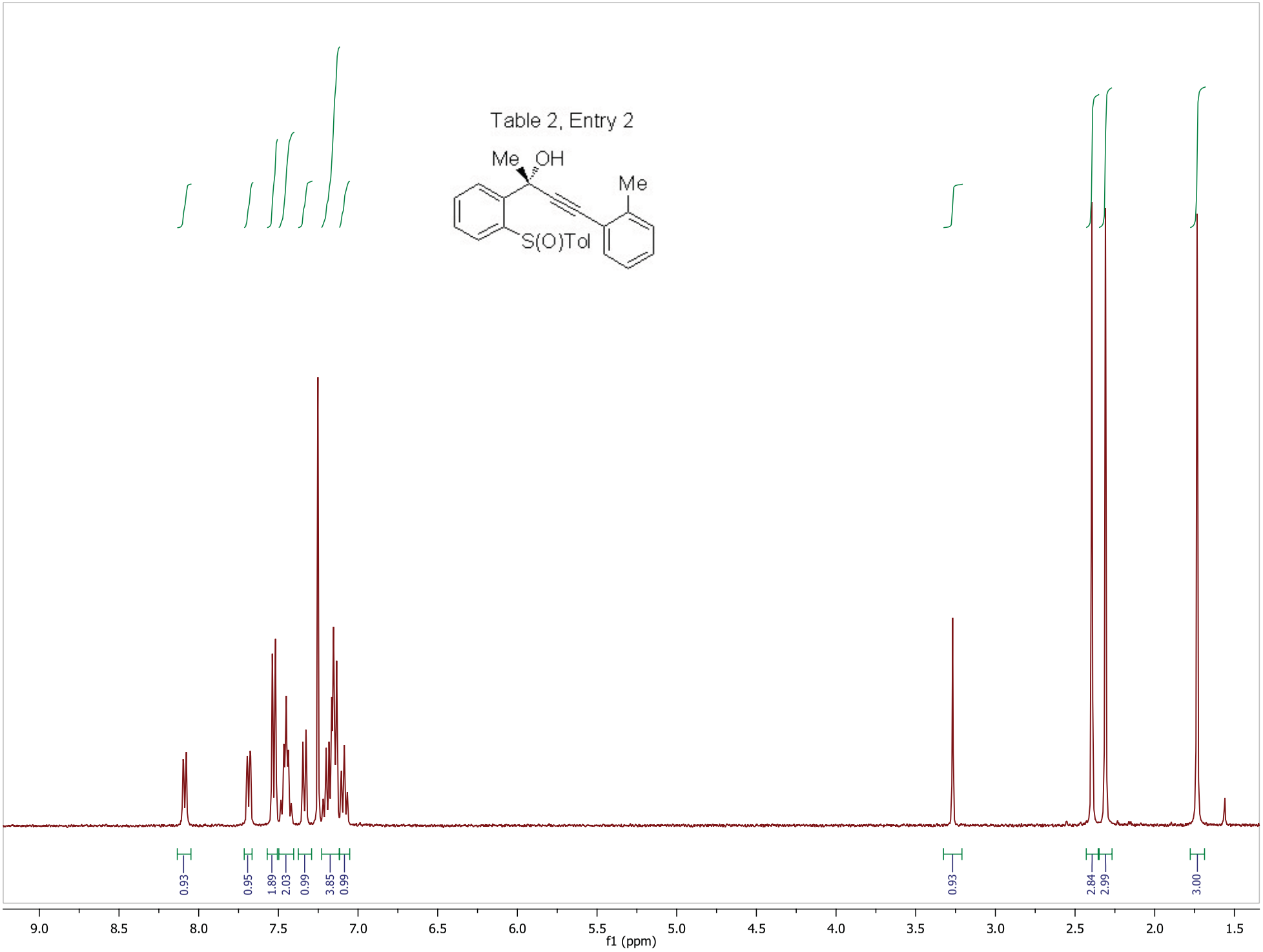
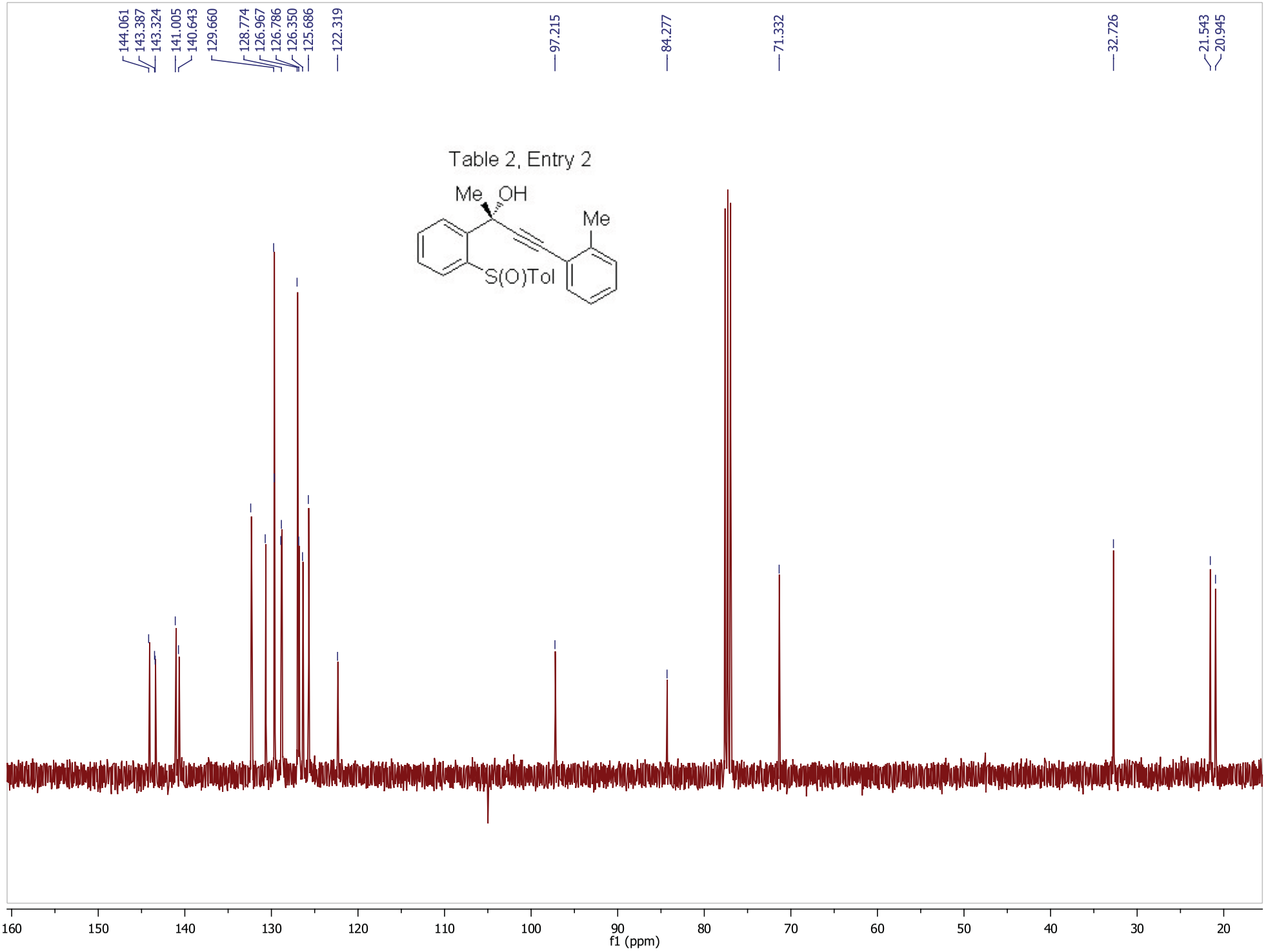


Table 2, Entry 2
Me
OH
Me
S(O)Tol
0.93
0.95
1.89
2.03
0.99
3.85
0.99
0.93
2.84
2.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


144.061
143.387
143.324
141.005
140.643
129.660
128.774
126.967
126.786
126.350
125.686
122.319
97.215
84.277
71.332
32.726
21.543
20.945
Table 2, Entry 2
Me
OH
Me
S(O)Tol
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

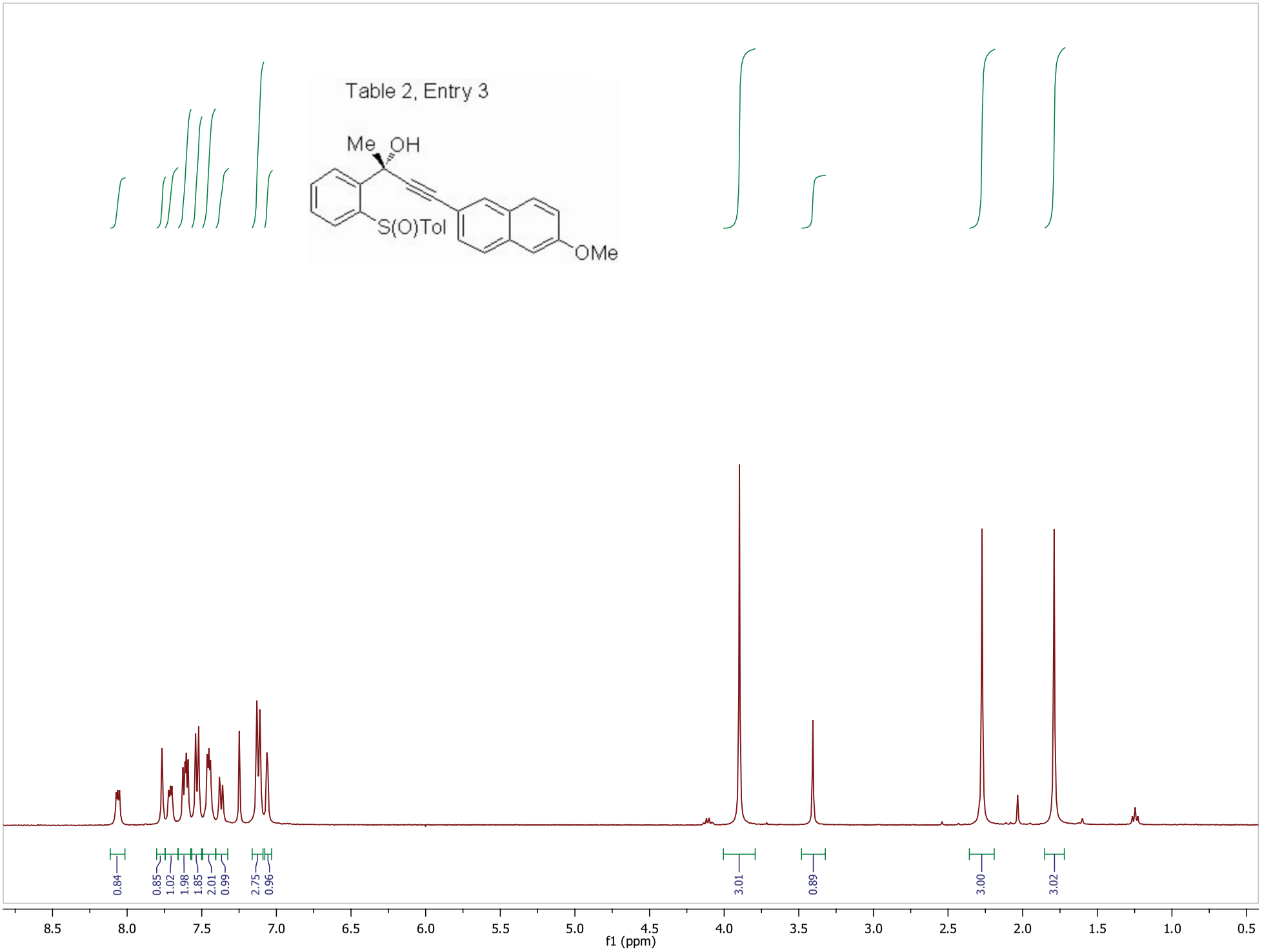


Table 2, Entry 3
Me
OH
S(O)Tol
OMe
0.84
0.85
1.02
1.98
1.85
2.01
0.99
2.75
0.96
3.01
0.89
3.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

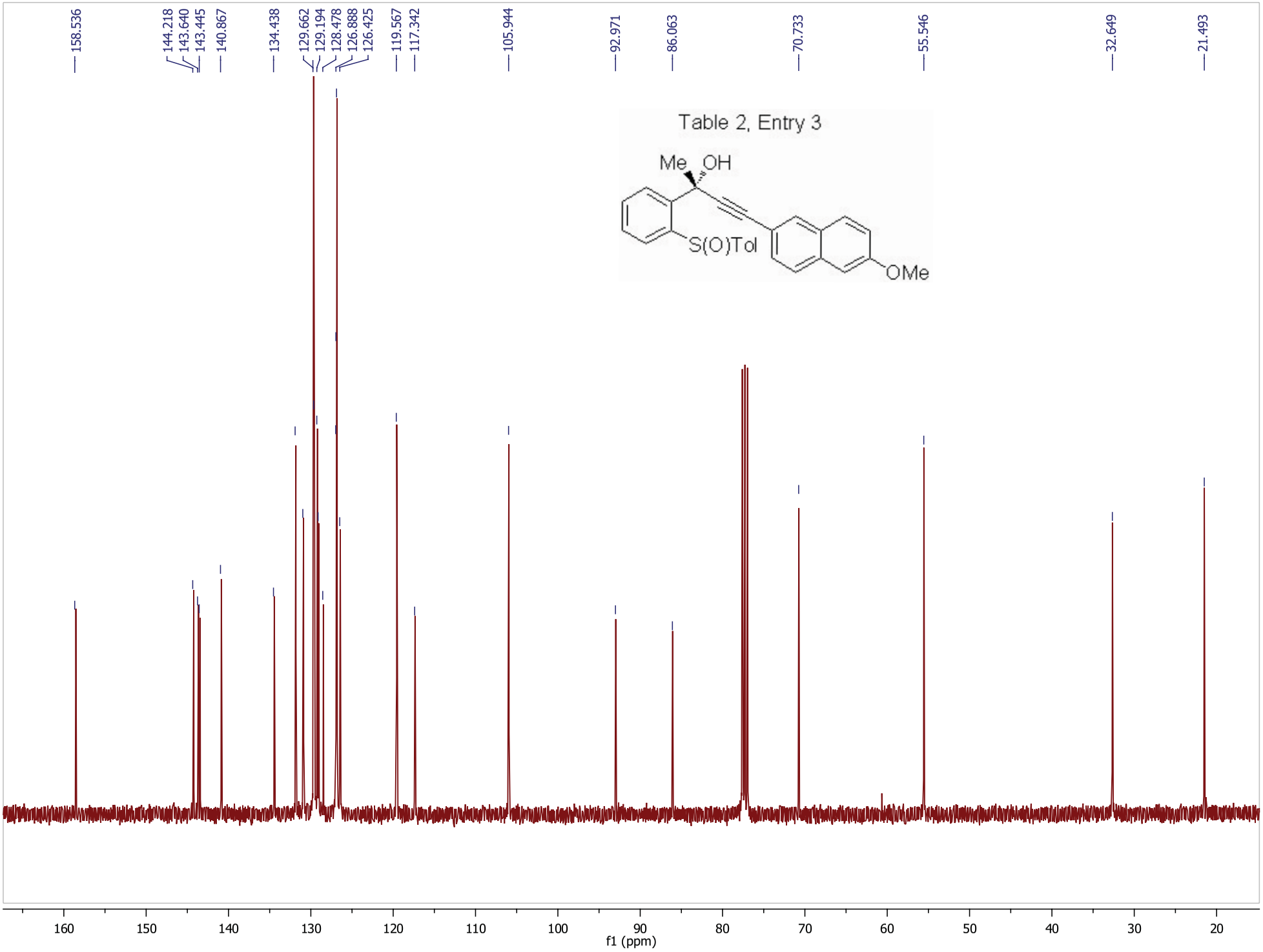
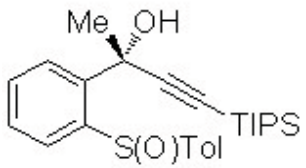

158.536
144.218
143.640
143.445
140.867
134.438
129.662
129.194
128.478
126.888
126.425
119.567
117.342
105.944
92.971
86.063
70.733
55.546
32.649
21.493
Table 2, Entry 3
Me
OH
S(O)Tol
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Table 2, Entry 4



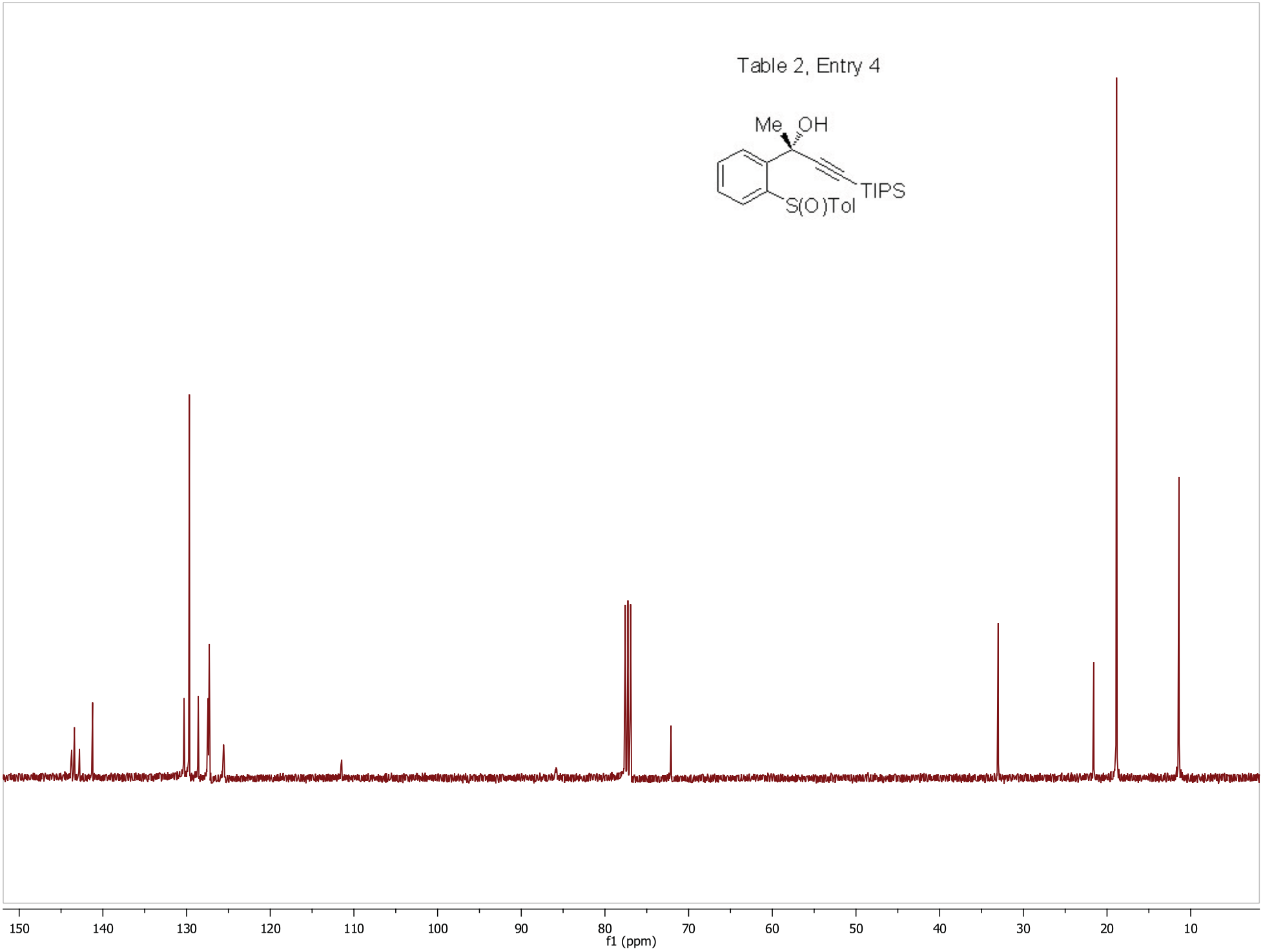


Table 2, Entry 4
Me
OH
TIPS
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

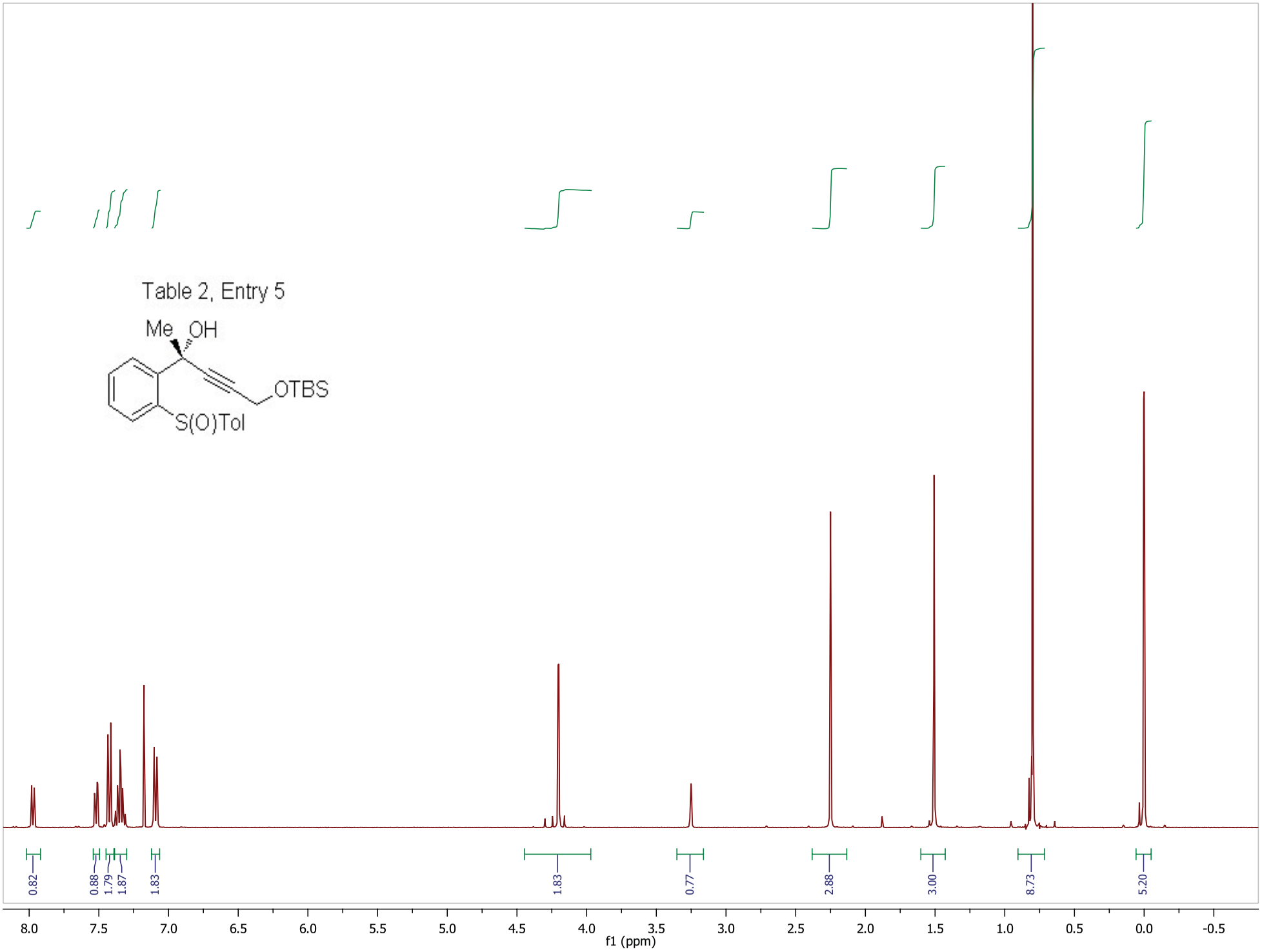
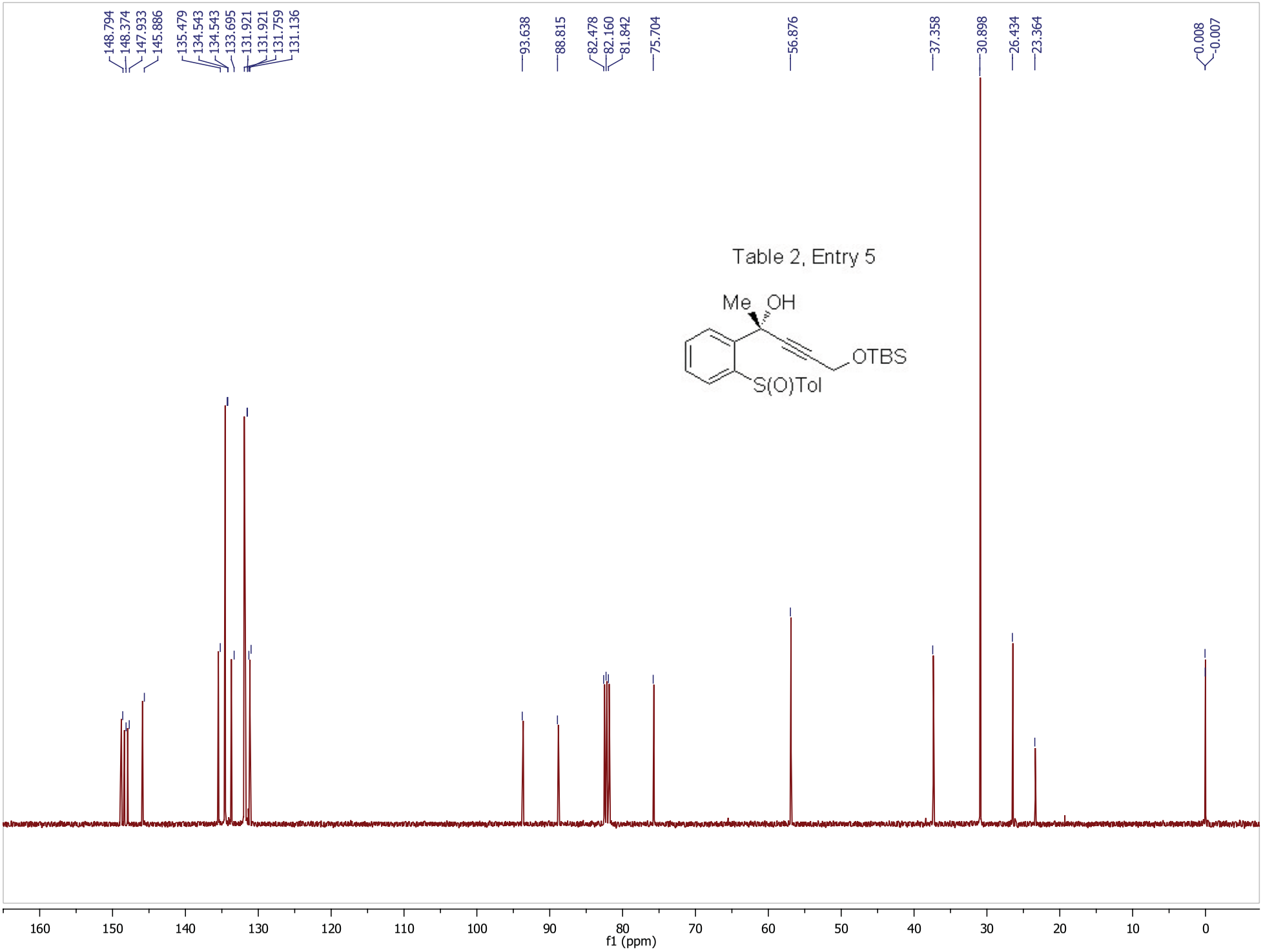


Table 2, Entry 5
Me
OH
OTBS
S(O)Tol
0.82
0.88
1.79
1.87
1.83
1.83
0.77
2.88
3.00
8.73
5.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


148.794
148.374
147.933
145.886
135.479
134.543
134.543
133.695
131.921
131.921
131.759
131.136
93.638
88.815
82.478
82.160
81.842
75.704
56.876
37.358
30.898
26.434
23.364
0.008
-0.007
Table 2, Entry 5
Me
OH
OTBS
S(O)Tol
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

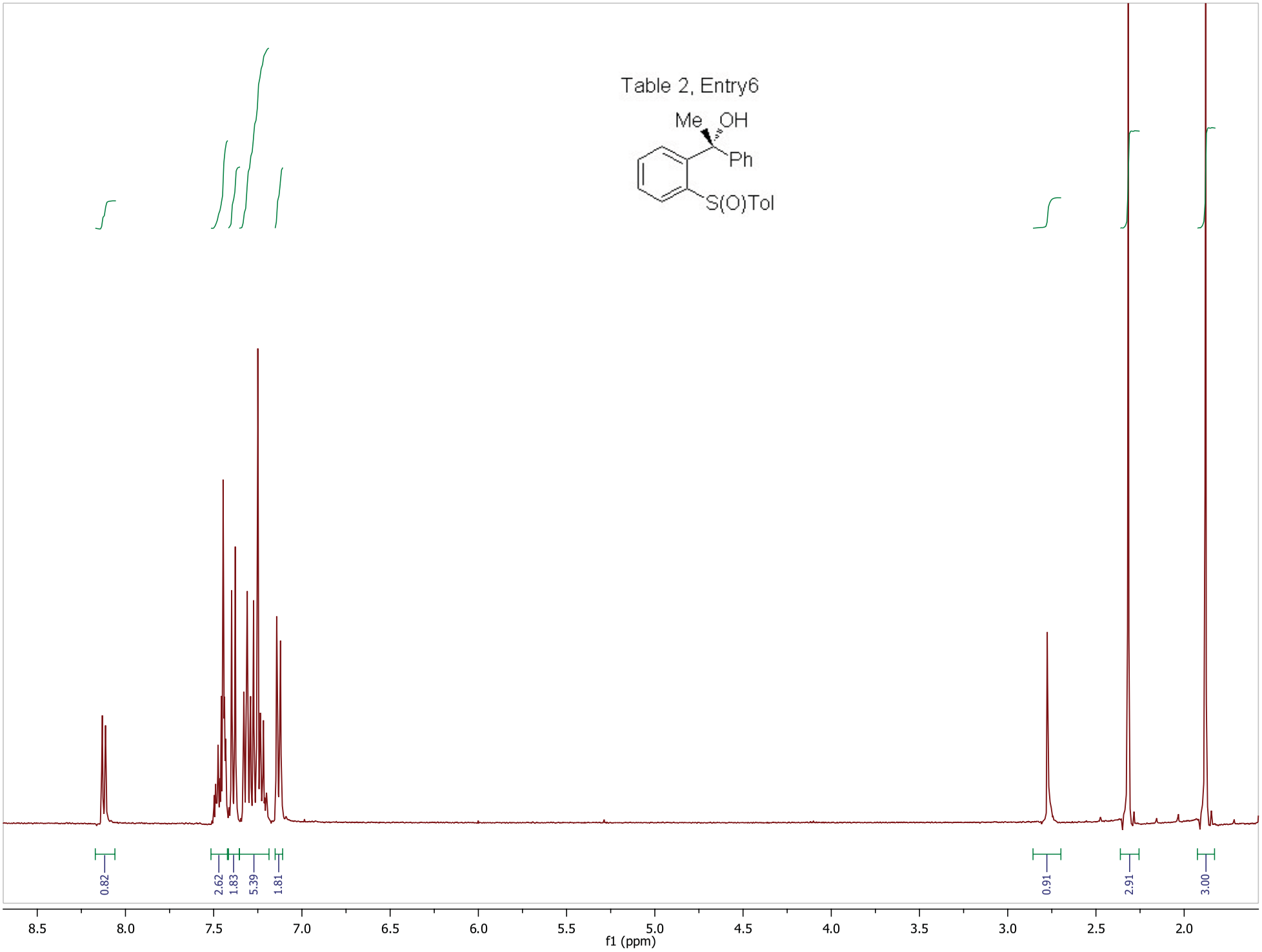
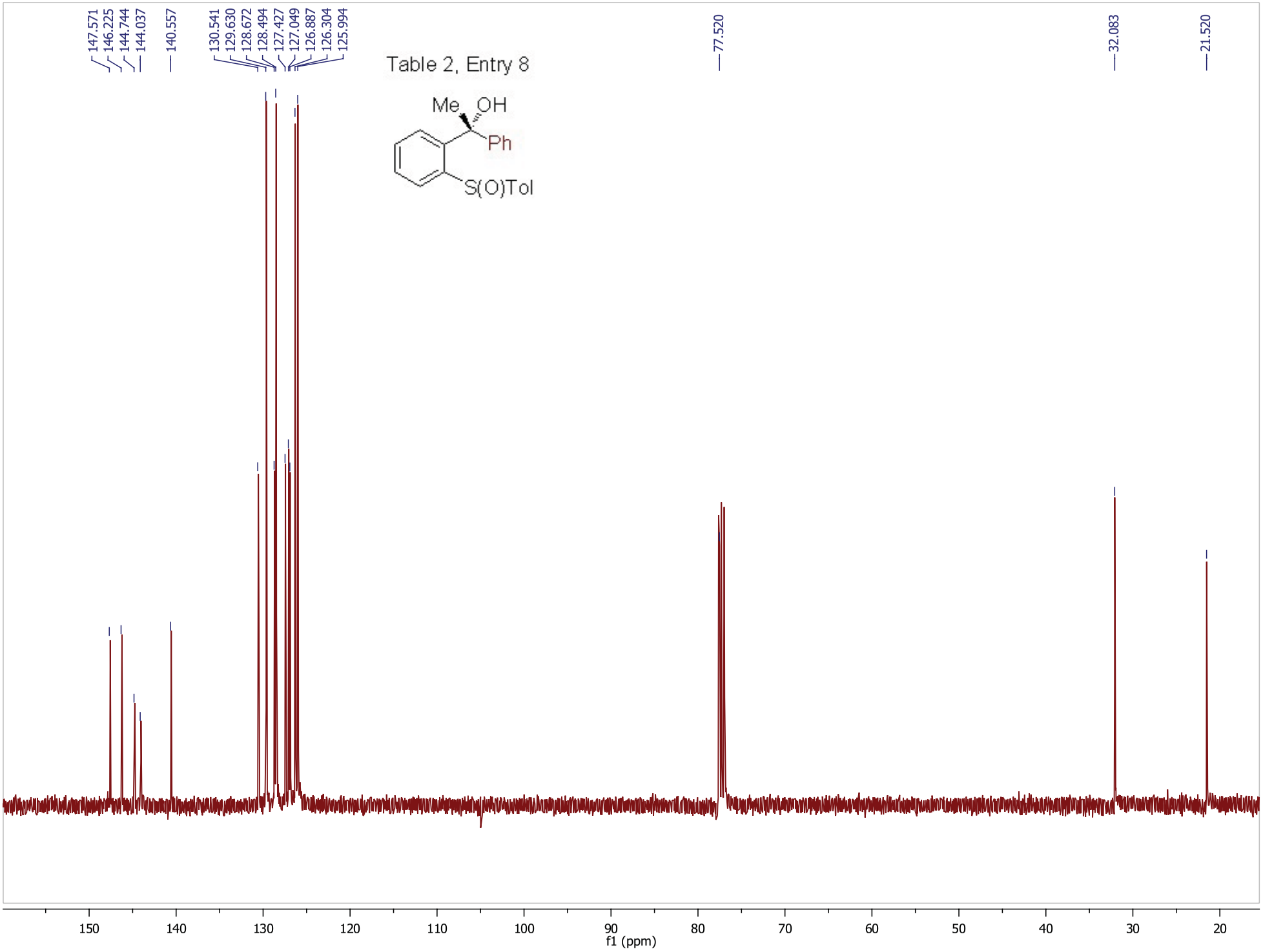


Table 2, Entry6
Me
OH
Ph
S(O)Tol
0.82
2.62
1.83
5.39
1.81
0.91
2.91
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


147.571
146.225
144.744
144.037
140.557
130.541
129.630
128.672
128.494
127.427
127.049
126.887
126.304
125.994
77.520
32.083
21.520
Table 2, Entry 8
Me
OH
Ph
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

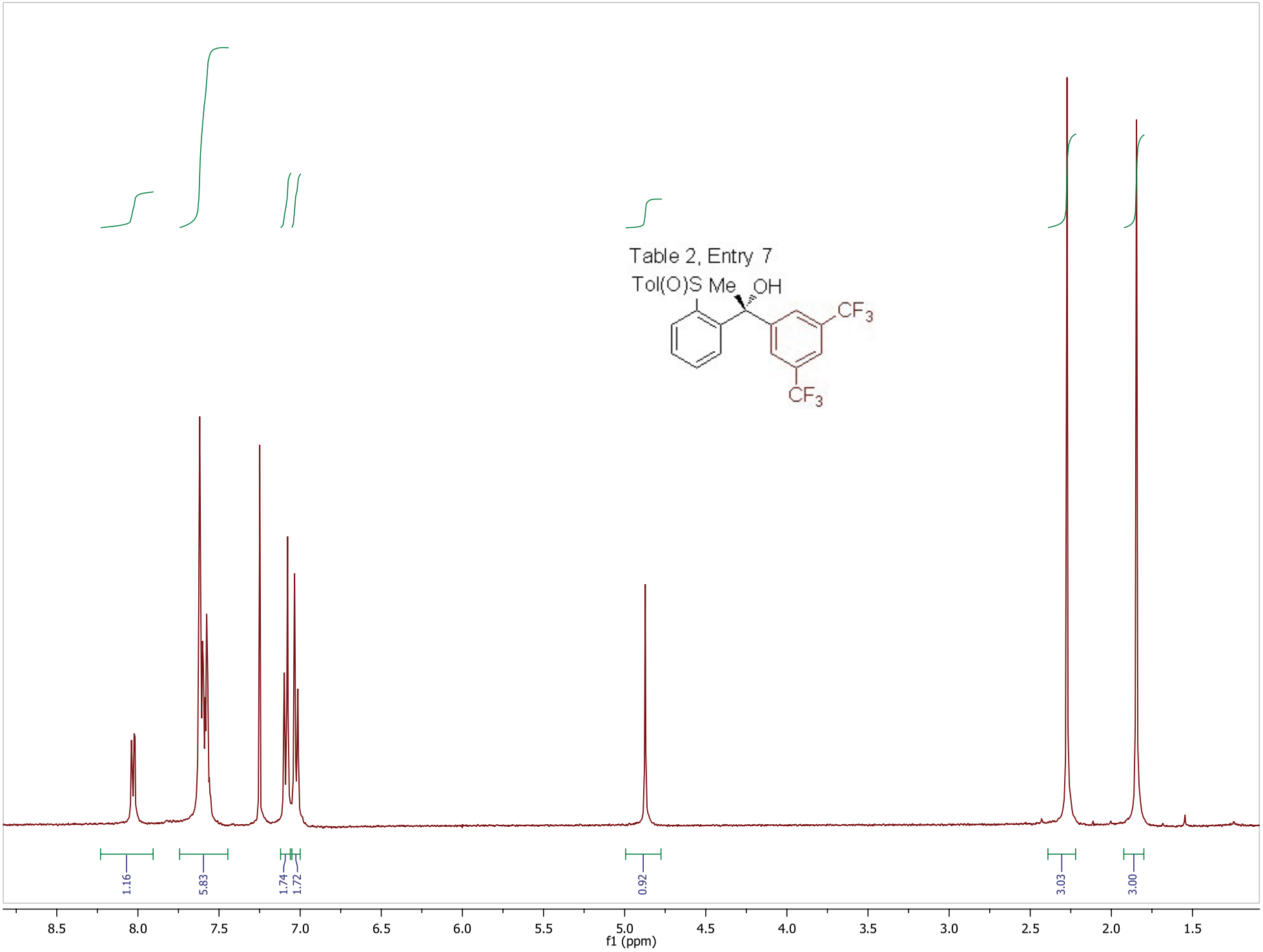
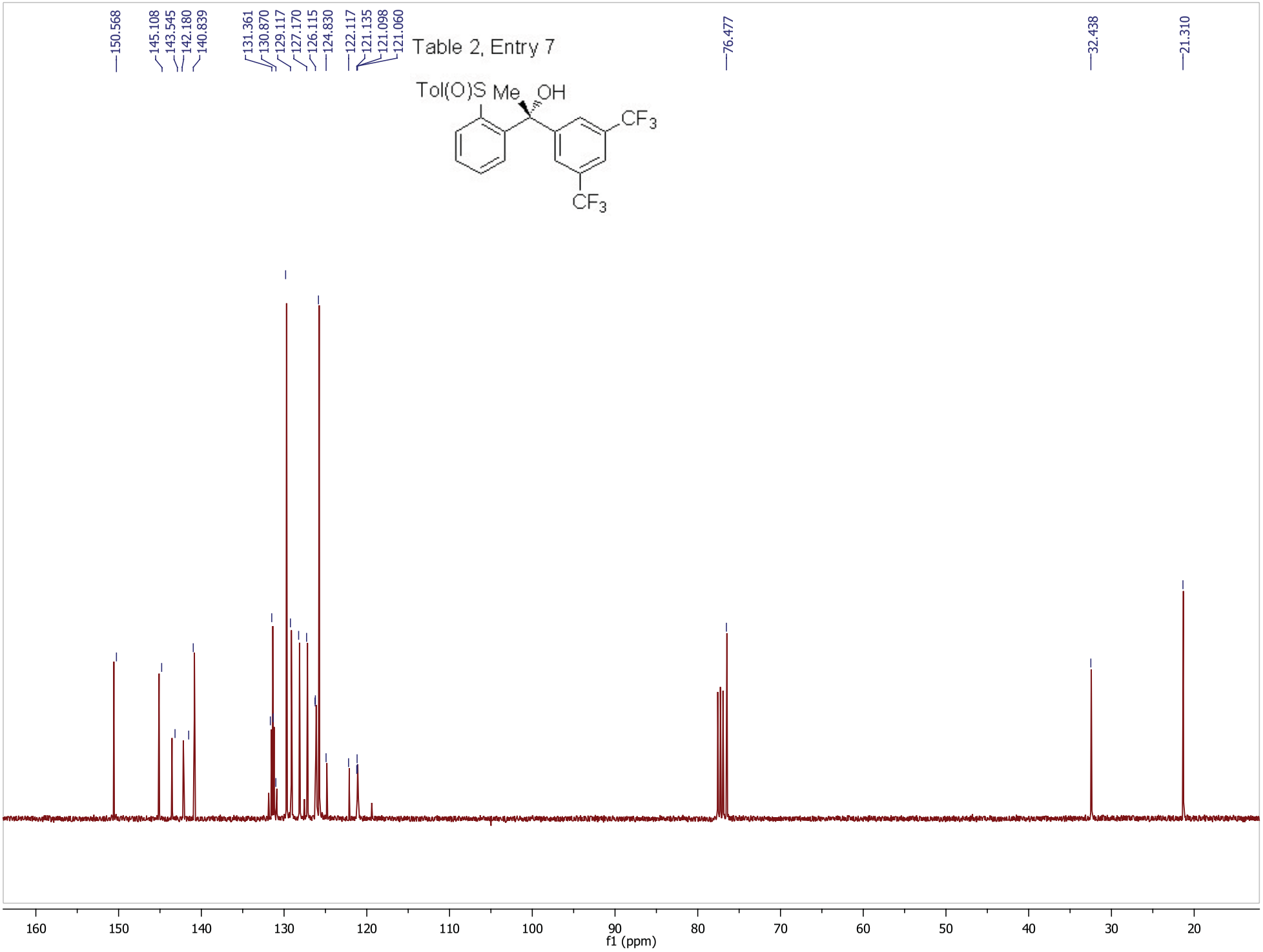


Table 2, Entry 7
Tol(O)S Me OH
CF3
CF3
1.16
5.83
1.74
1.72
0.92
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


150.568
145.108
143.545
142.180
140.839
131.361
130.870
129.117
127.170
126.115
124.830
122.117
121.135
121.098
121.060
76.477
32.438
21.310
Table 2, Entry 7
Tol(O)S
Me
OH
CF3
CF3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

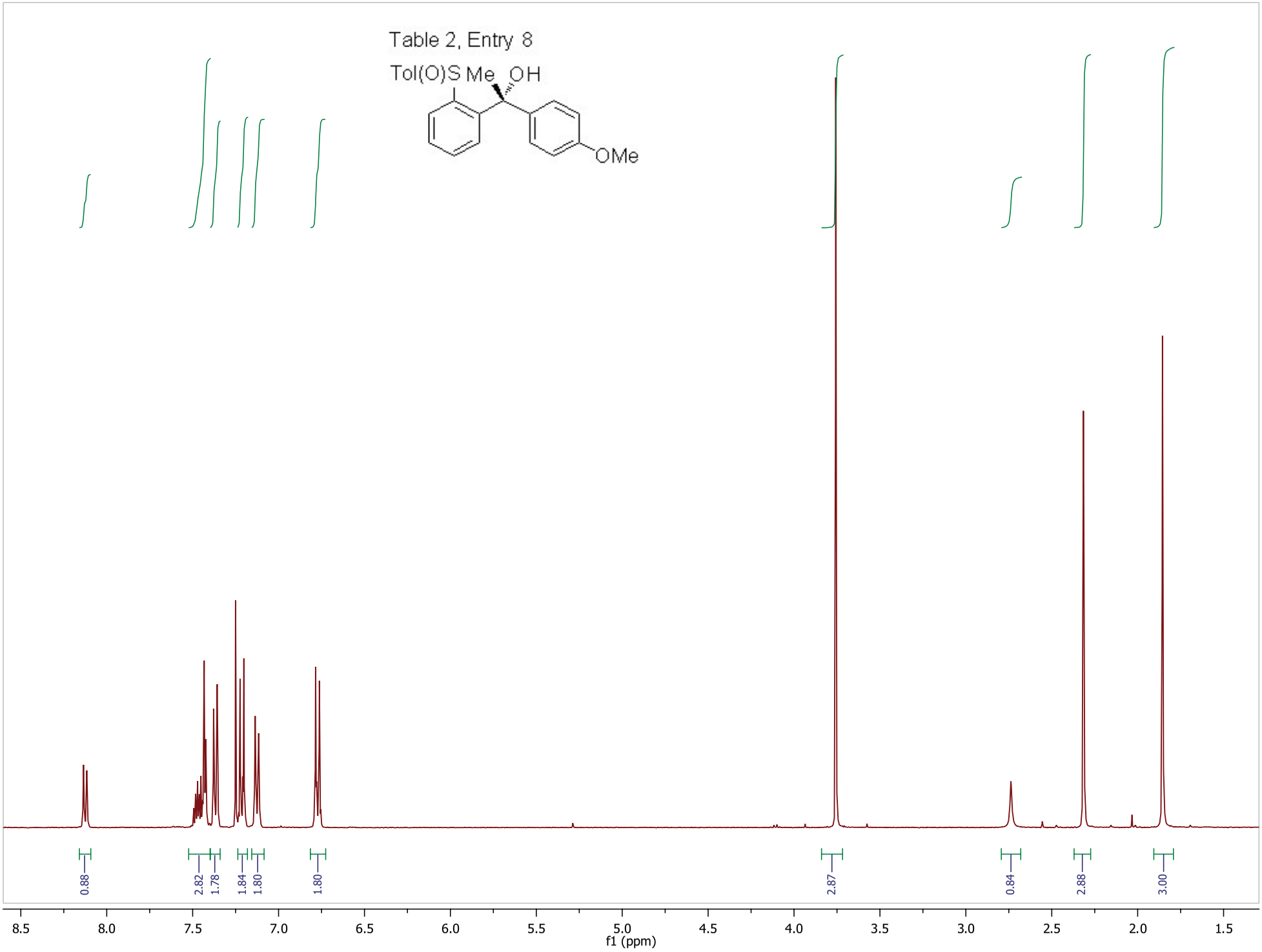
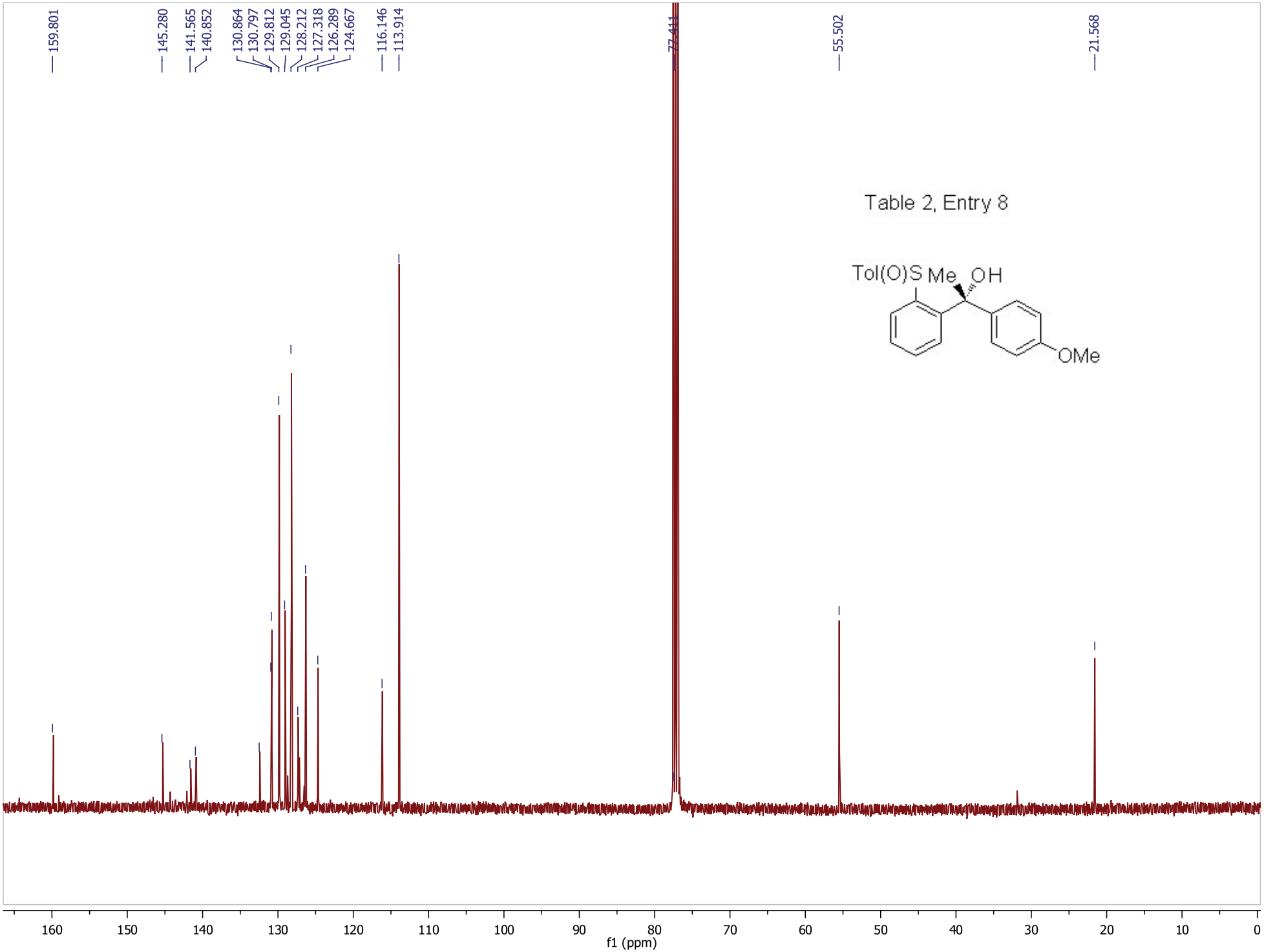


Table 2, Entry 8
Tol(O)S Me OH
OMe
0.88
2.82
1.78
1.84
1.80
1.80
2.87
0.84
2.88
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


159.801
145.280
141.565
140.852
130.864
130.797
129.812
129.045
128.212
127.318
126.289
124.667
116.146
113.914
77.411
55.502
21.568
Table 2, Entry 8
Tol(O)S
Me
OH
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

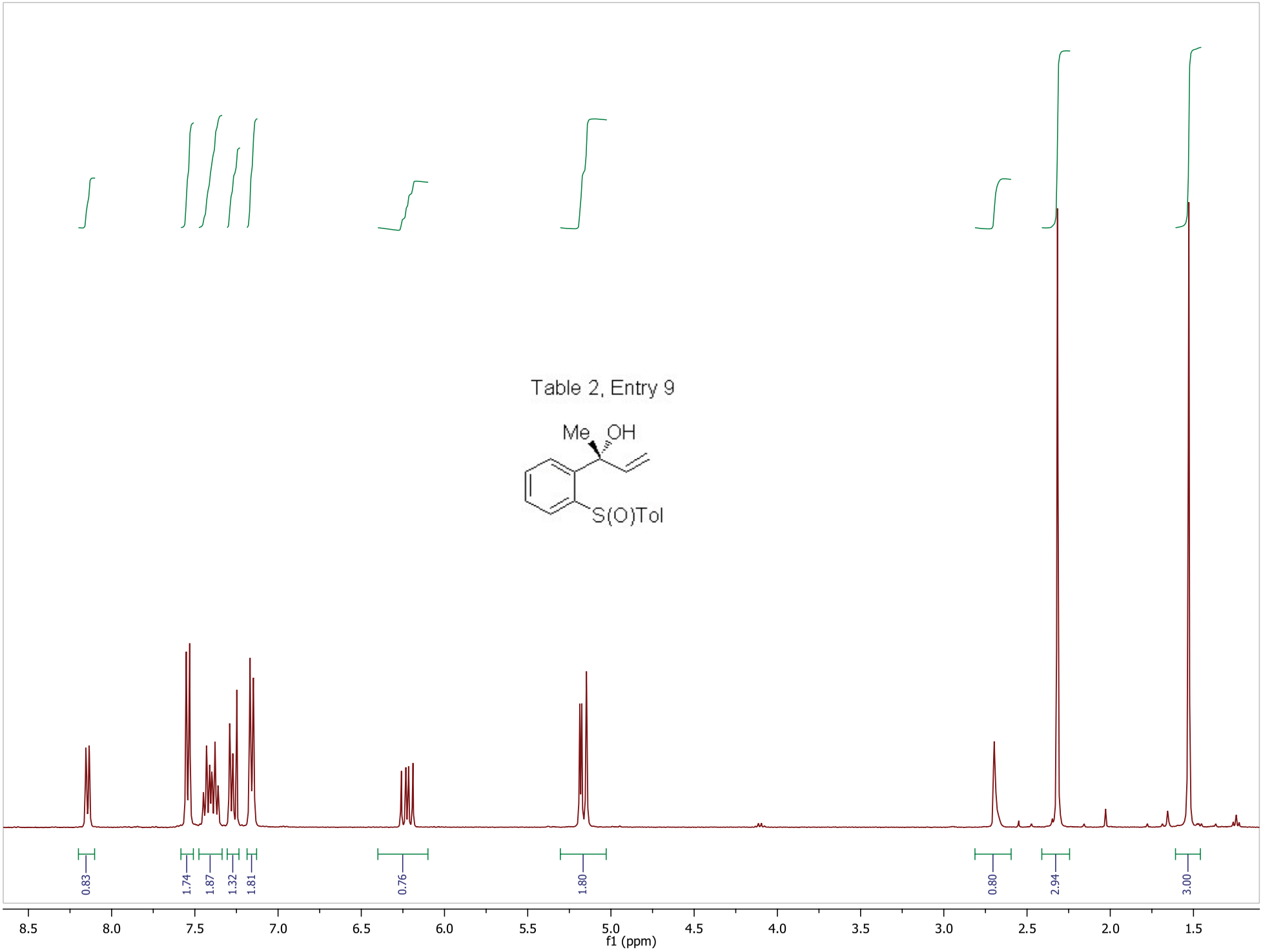
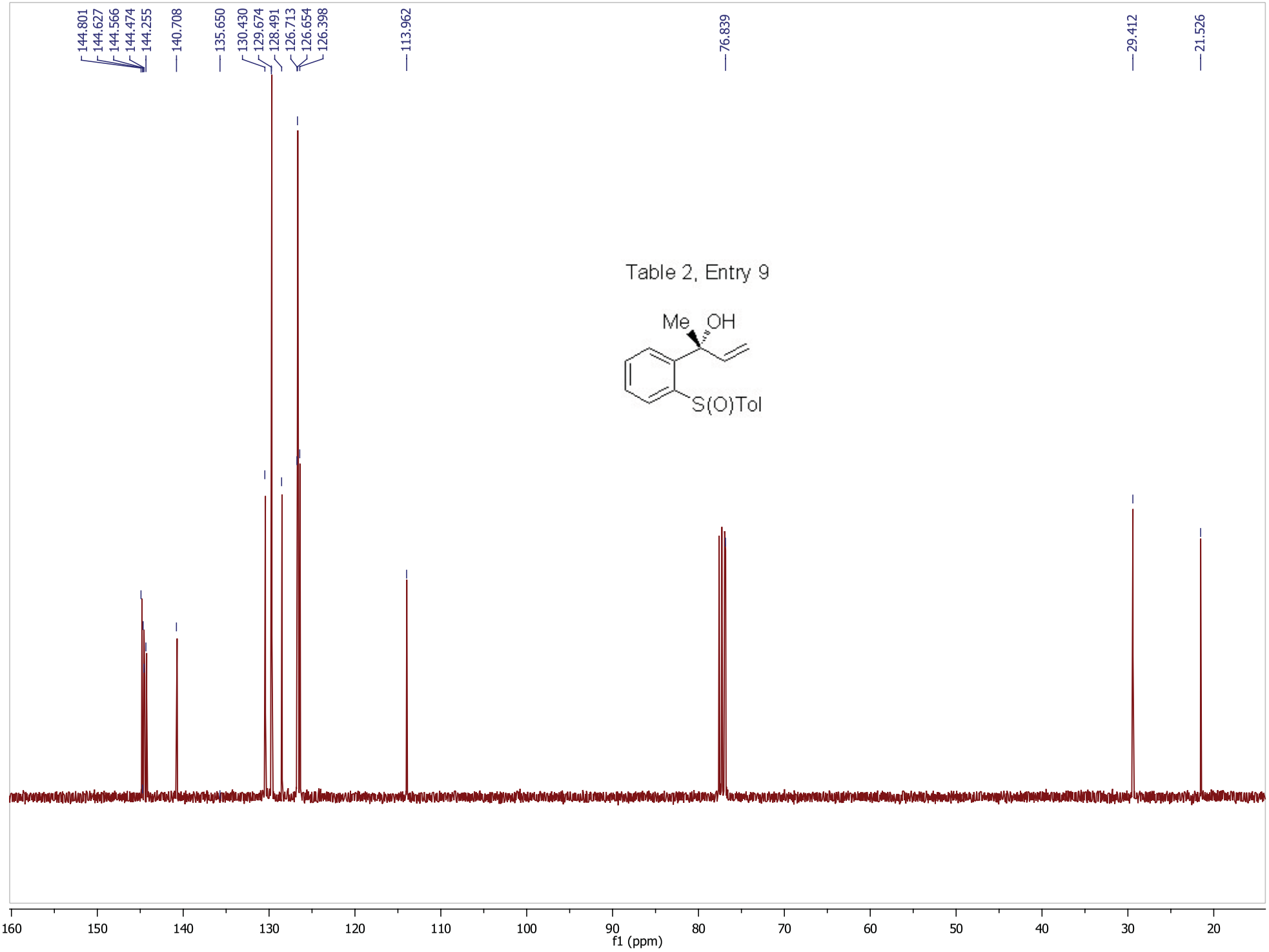


Table 2, Entry 9
Me
OH
S(O)Tol
0.83
1.74
1.87
1.32
1.81
0.76
1.80
0.80
2.94
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


144.801
144.627
144.566
144.474
144.255
140.708
135.650
130.430
129.674
128.491
126.713
126.654
126.398
113.962
76.839
29.412
21.526
Table 2, Entry 9
Me
OH
S(O)Tol
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

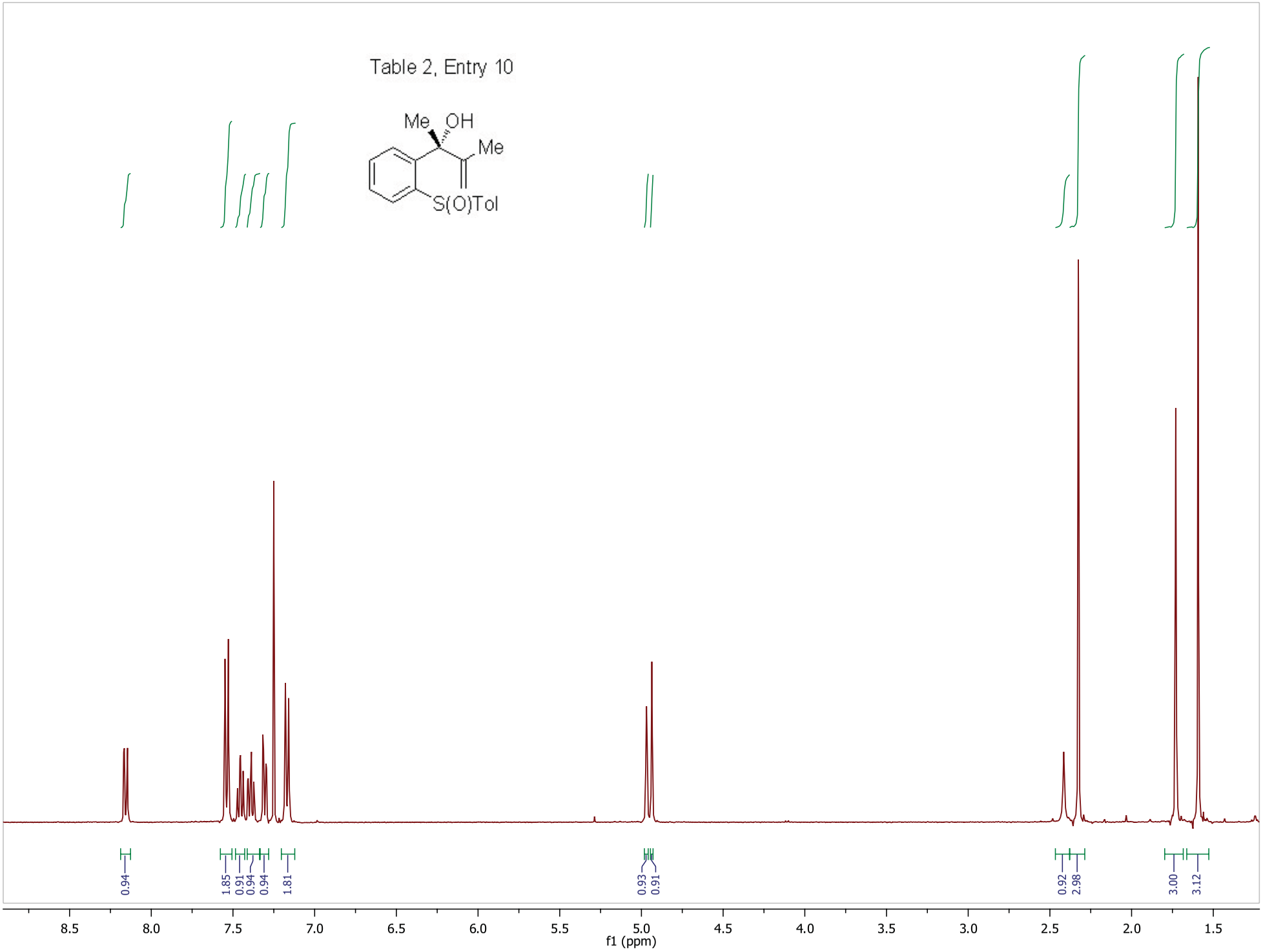


Table 2, Entry 10
Me
OH
Me
S(O)Tol
0.94
1.85
0.91
0.94
0.94
1.81
0.93
0.91
0.92
2.98
3.00
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

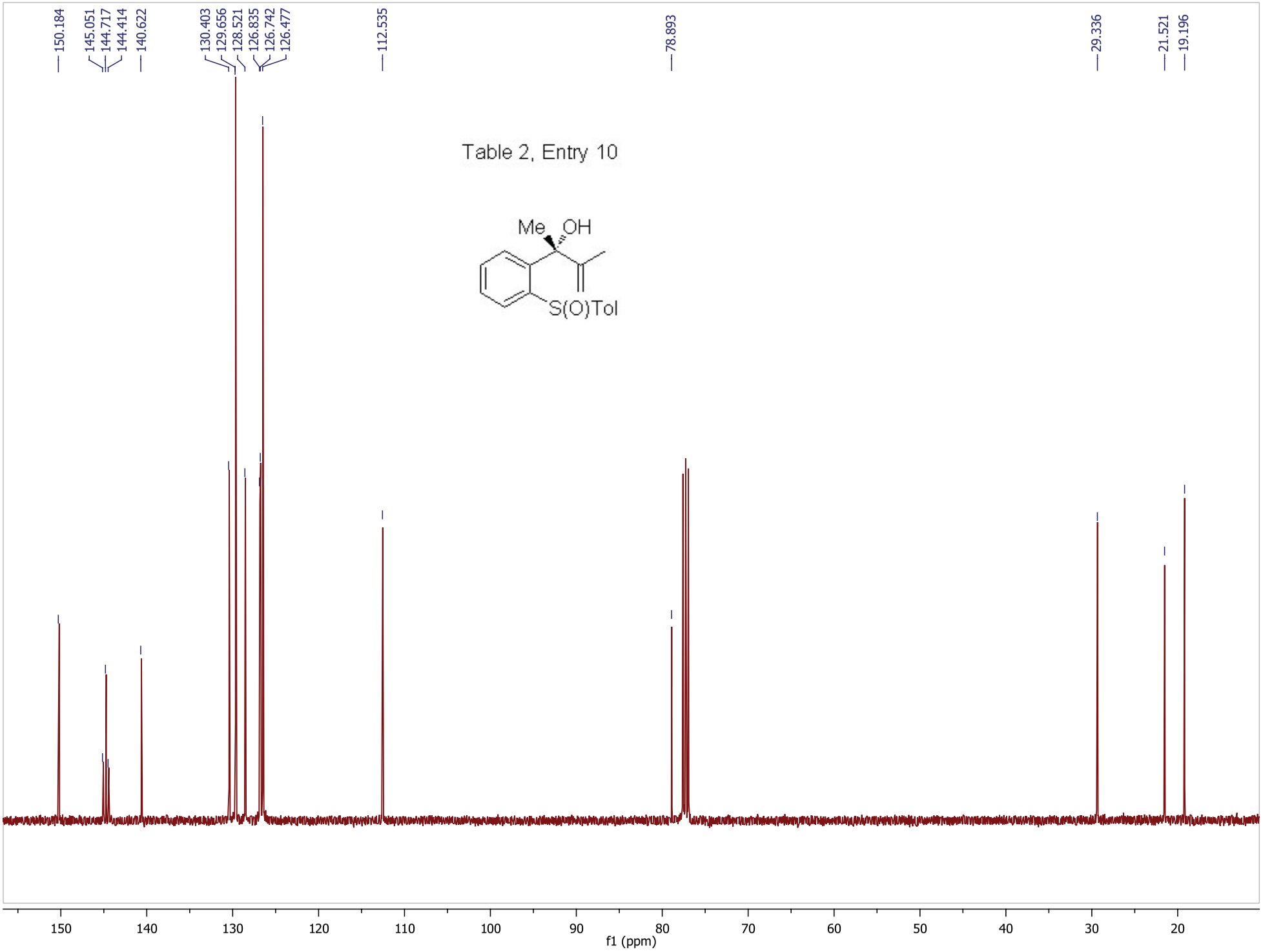
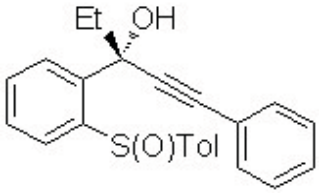
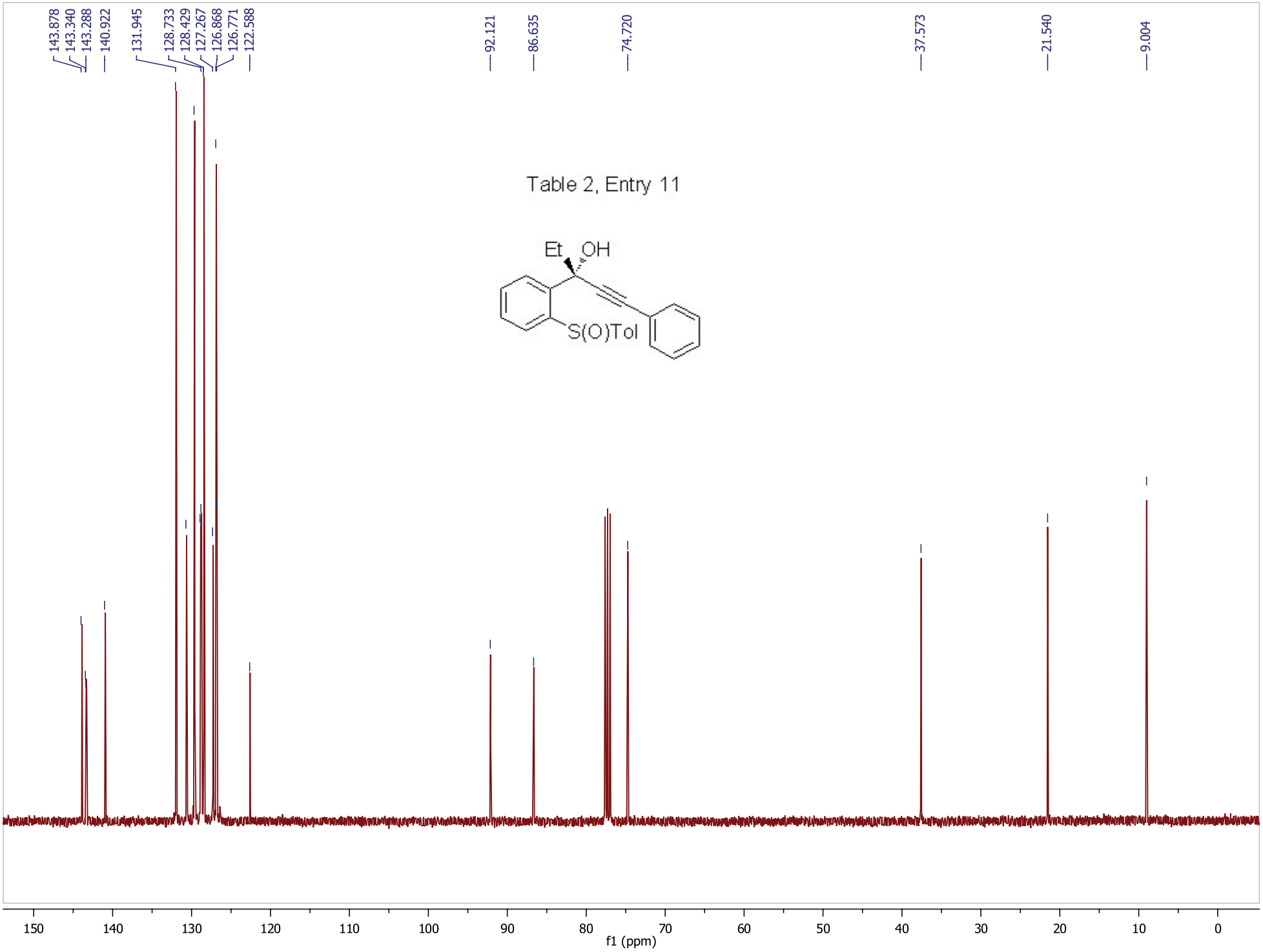

150.184
145.051
144.717
144.414
140.622
130.403
129.656
128.521
126.835
126.742
126.477
112.535
78.893
29.336
21.521
19.196
Table 2, Entry 10
Me
OH
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Table 2, Entry 11




143.878
143.340
143.288
140.922
131.945
128.733
128.429
127.267
126.868
126.771
122.588
92.121
86.635
74.720
37.573
21.540
9.004
Table 2, Entry 11
Et
OH
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

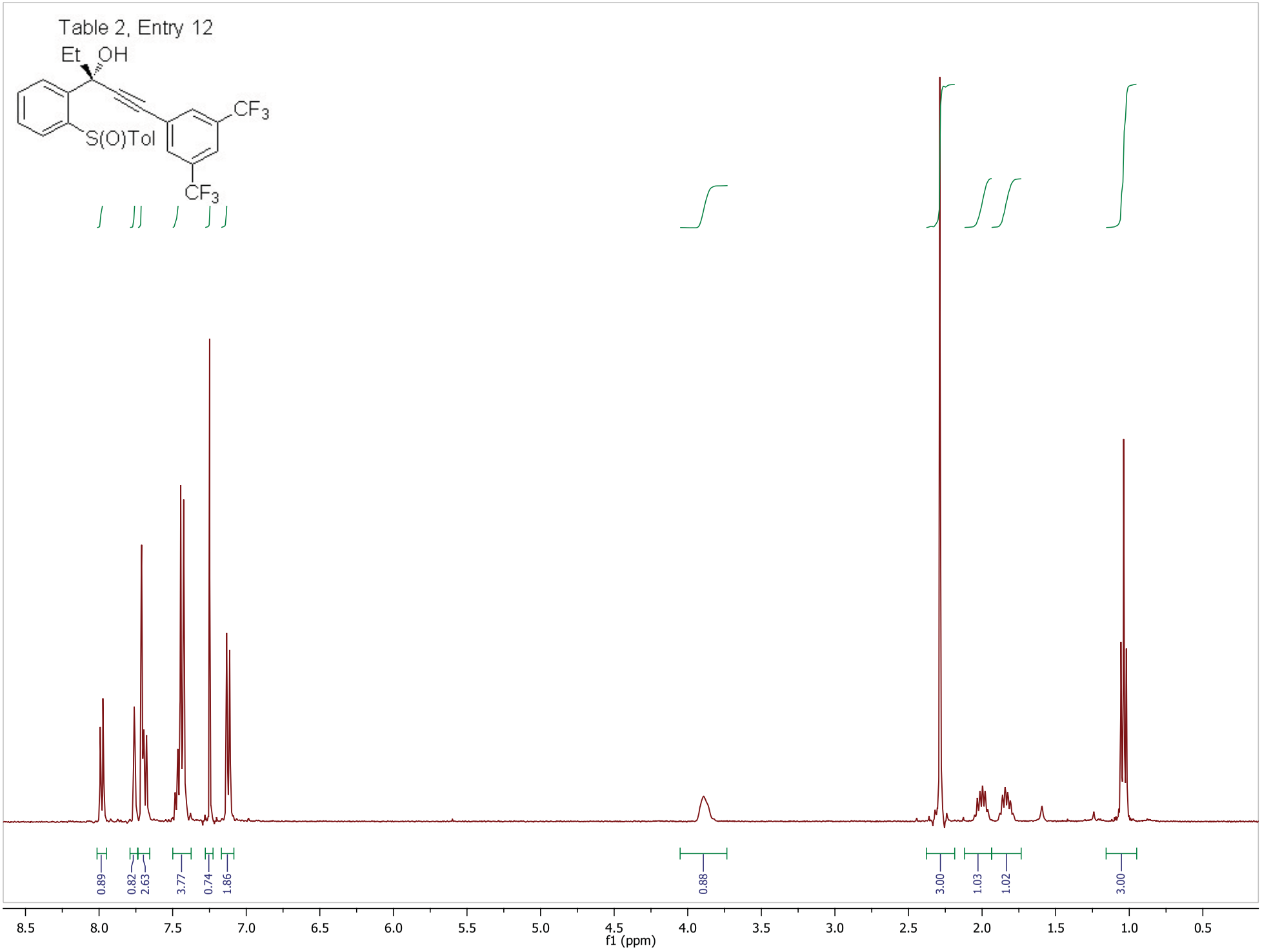


Table 2, Entry 12
Et
OH
CF3
S(O)Tol
CF3
0.89
0.82
2.63
3.77
0.74
1.86
0.88
3.00
1.03
1.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

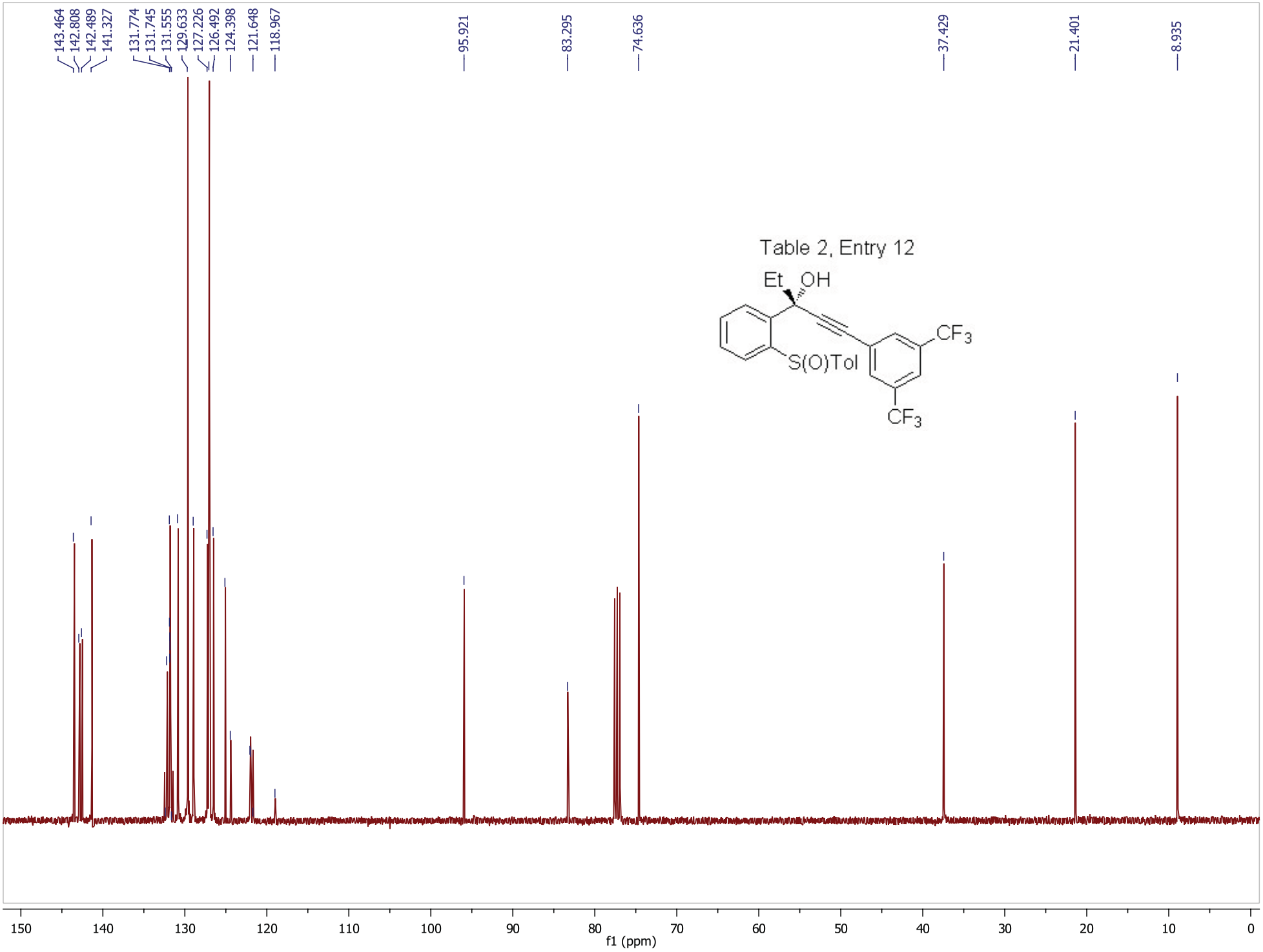
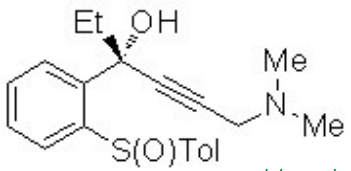

143.464
142.808
142.489
141.327
131.774
131.745
131.555
129.633
127.226
126.492
124.398
121.648
118.967
95.921
83.295
74.636
37.429
21.401
8.935
Table 2, Entry 12
Et
OH
S(O)Tol
CF3
CF3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Table 2, Entry 13



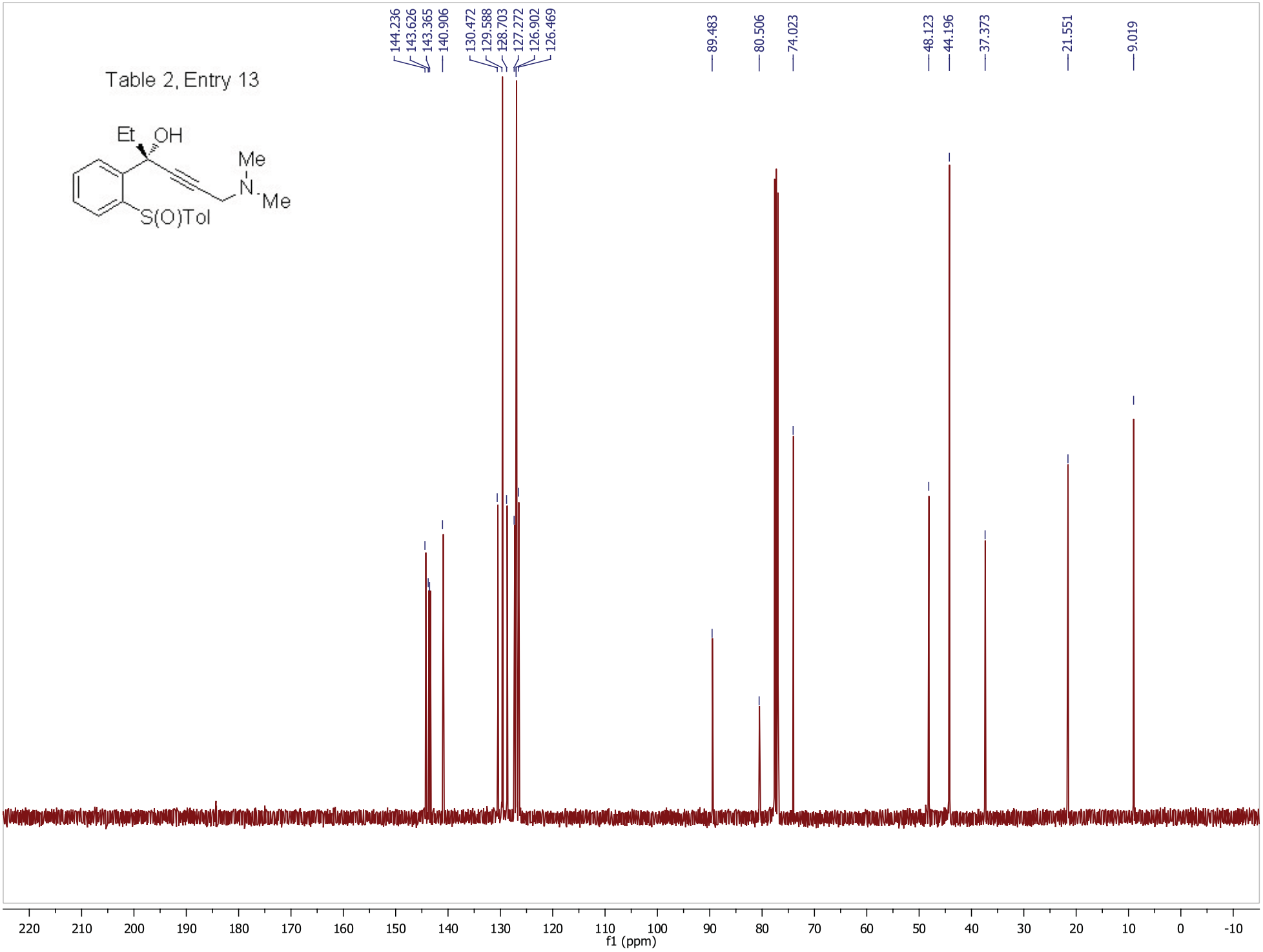
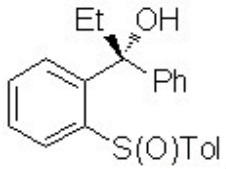
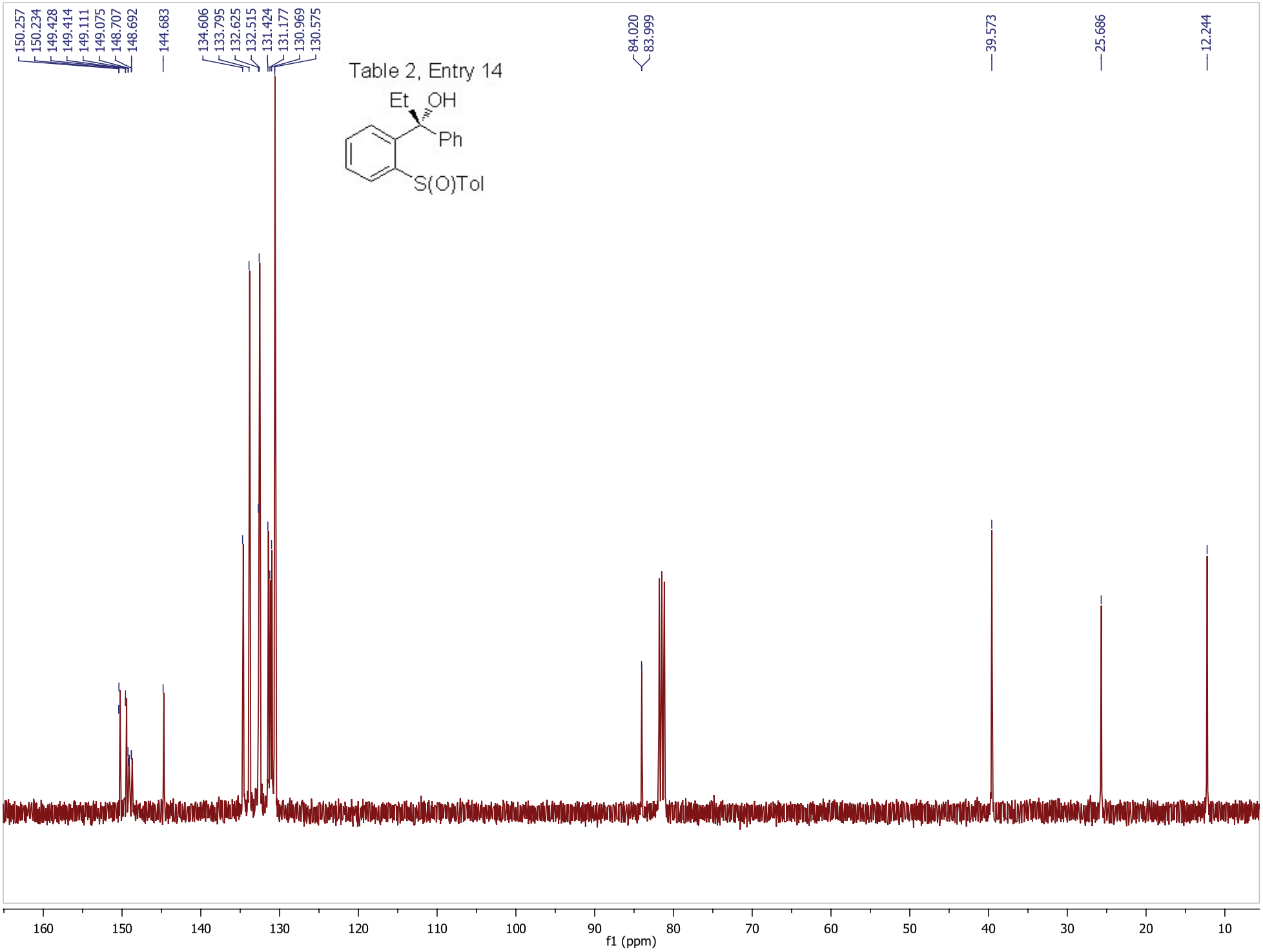


Table 2, Entry 13
Et
OH
Me
N
Me
S(O)Tol
144.236
143.626
143.365
140.906
130.472
129.588
128.703
127.272
126.902
126.469
89.483
80.506
74.023
48.123
44.196
37.373
21.551
9.019
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Table 2, Entry 14




150.257
150.234
149.428
149.414
149.111
149.075
148.707
148.692
144.683
134.606
133.795
132.625
132.515
131.424
131.177
130.969
130.575
84.020
83.999
39.573
25.686
12.244
Table 2, Entry 14
Et
OH
Ph
S(O)Tol
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

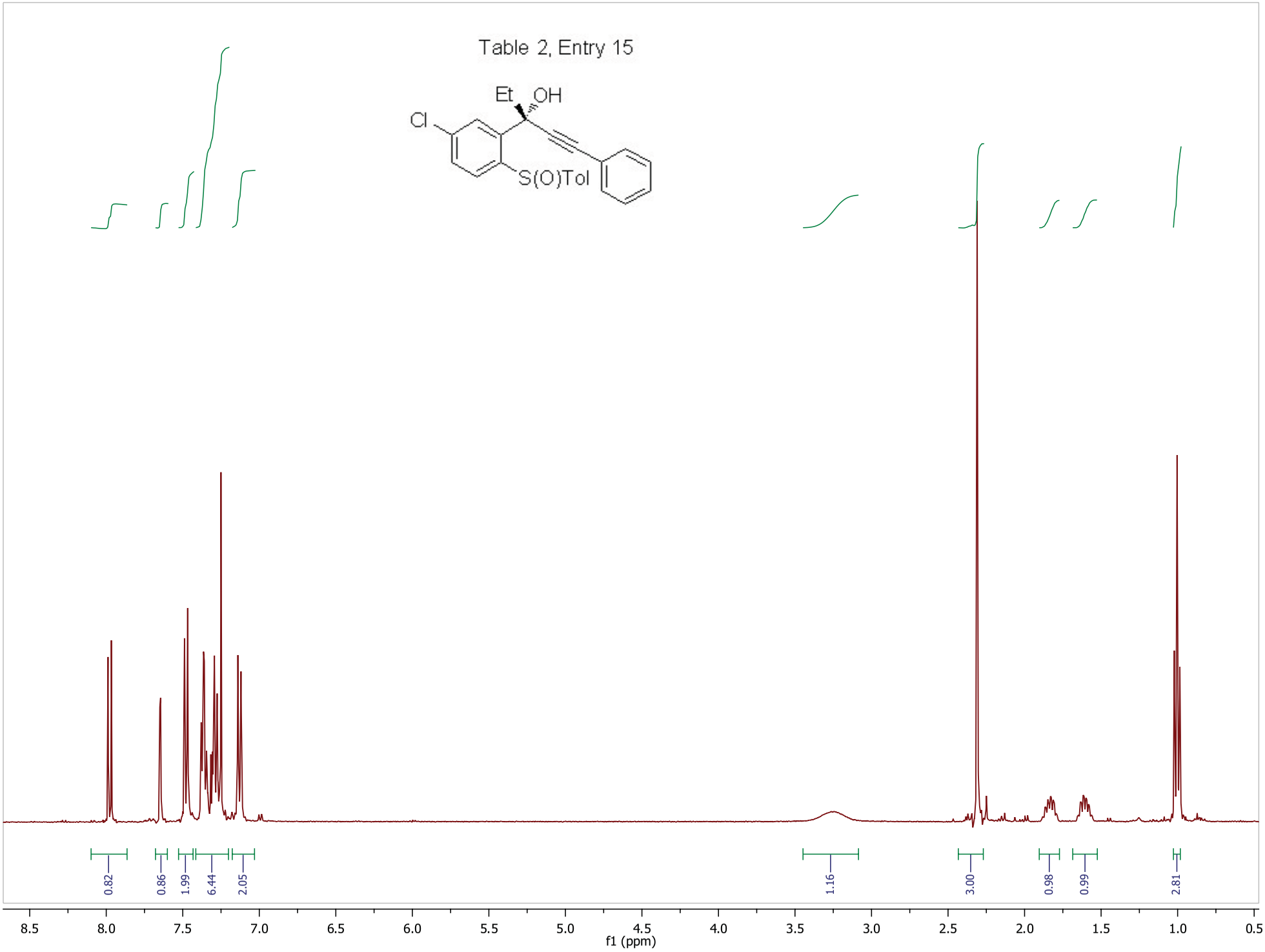


Table 2, Entry 15
Et
OH
Cl
S(O)Tol
0.82
0.86
1.99
6.44
2.05
1.16
3.00
0.98
0.99
2.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

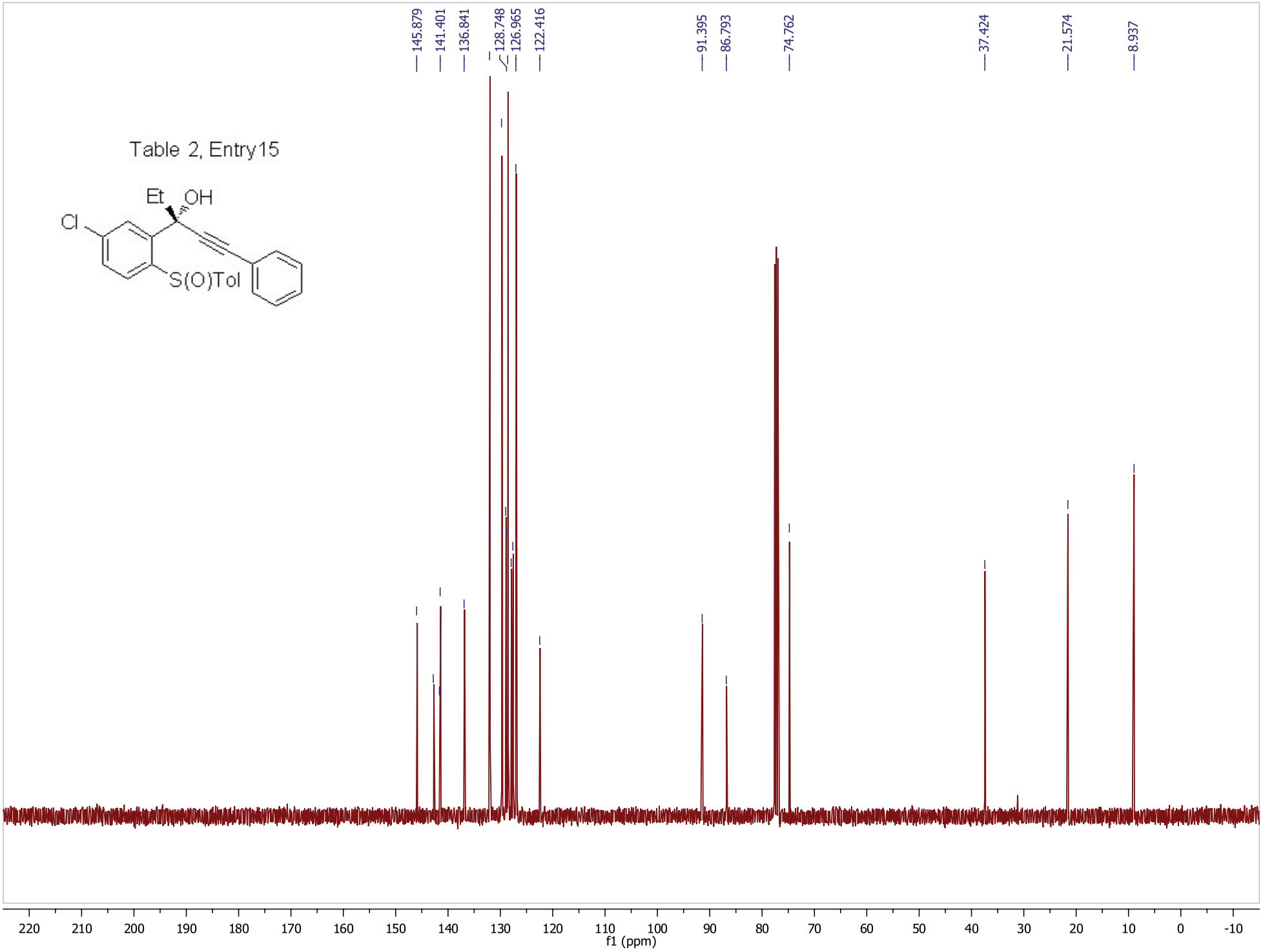
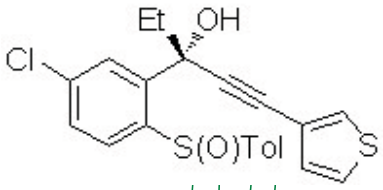

145.879
141.401
136.841
128.748
126.965
122.416
91.395
86.793
74.762
37.424
21.574
8.937
Table 2, Entry15
Et
OH
Cl
S(O)Tol
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Table 2, Entry 16



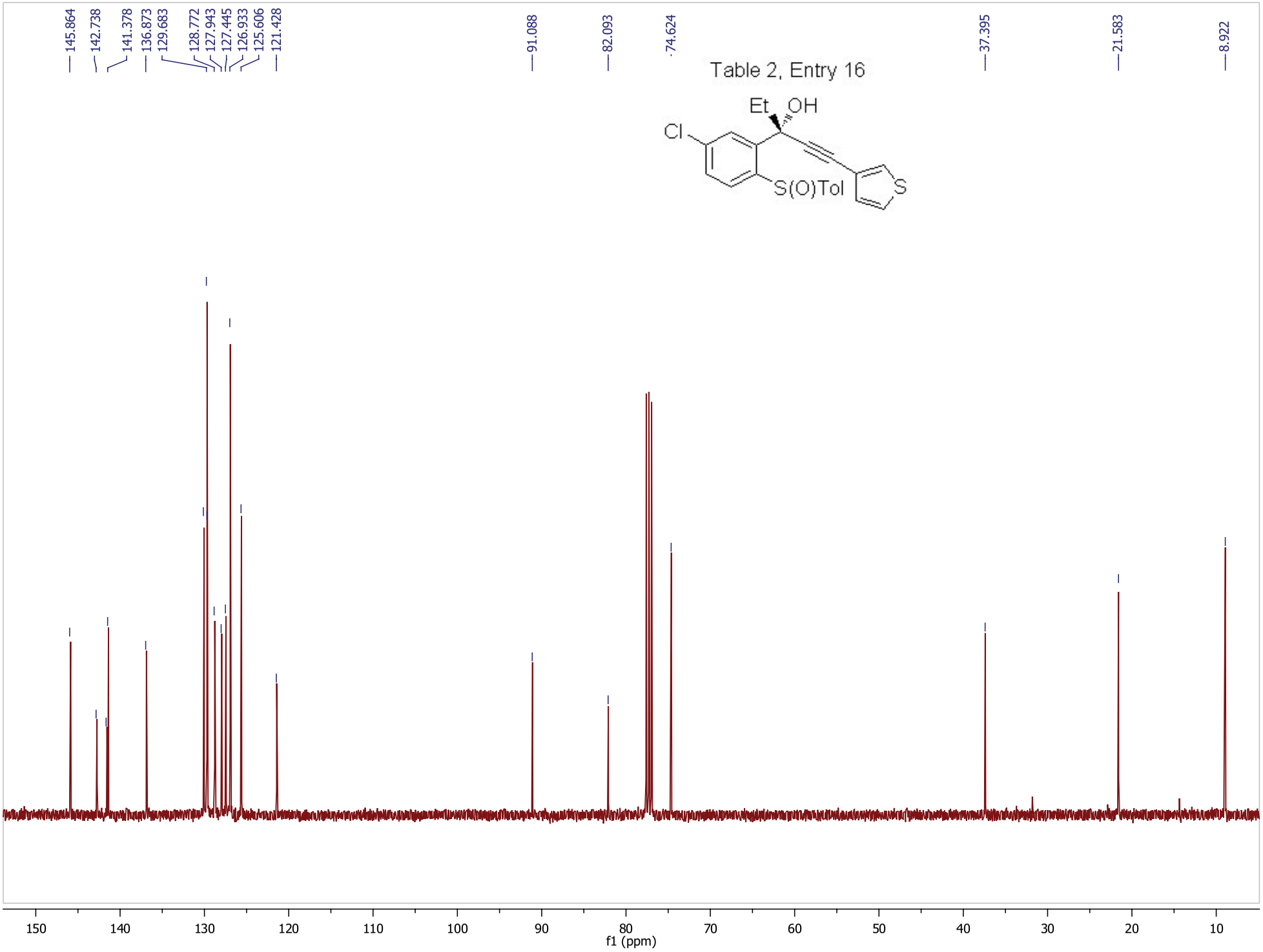
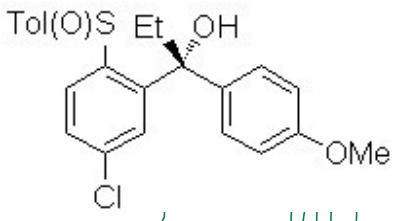
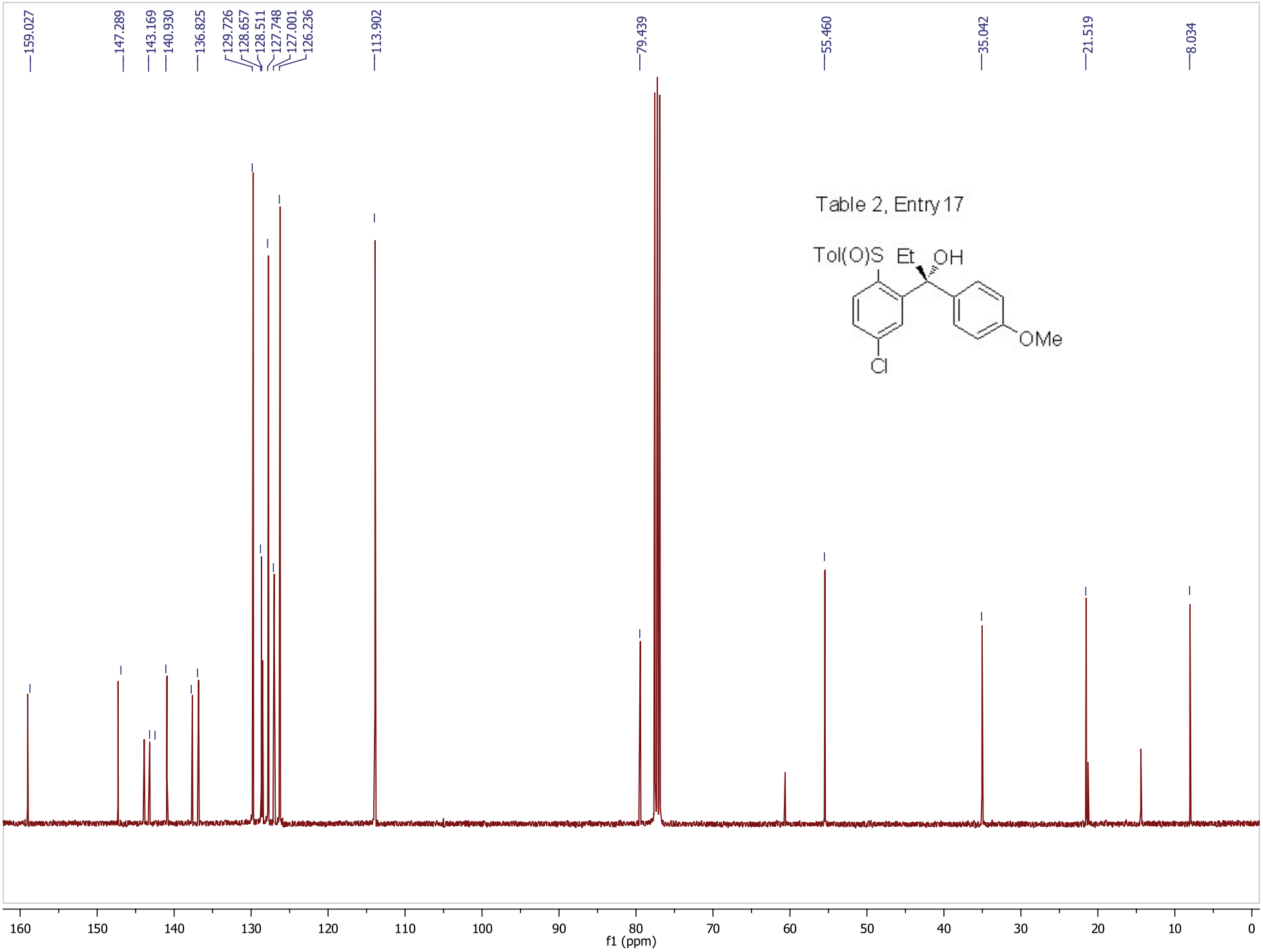

145.864
142.738
141.378
136.873
129.683
128.772
127.943
127.445
126.933
125.606
121.428
91.088
82.093
74.624
37.395
21.583
8.922
Table 2, Entry 16
Et
OH
Cl
S(O)Tol
S
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Table 2, Entry 17




159.027
147.289
143.169
140.930
136.825
129.726
128.657
128.511
127.748
127.001
126.236
113.902
79.439
55.460
35.042
21.519
8.034
Table 2, Entry 17
Tol(O)S
Et
OH
OMe
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

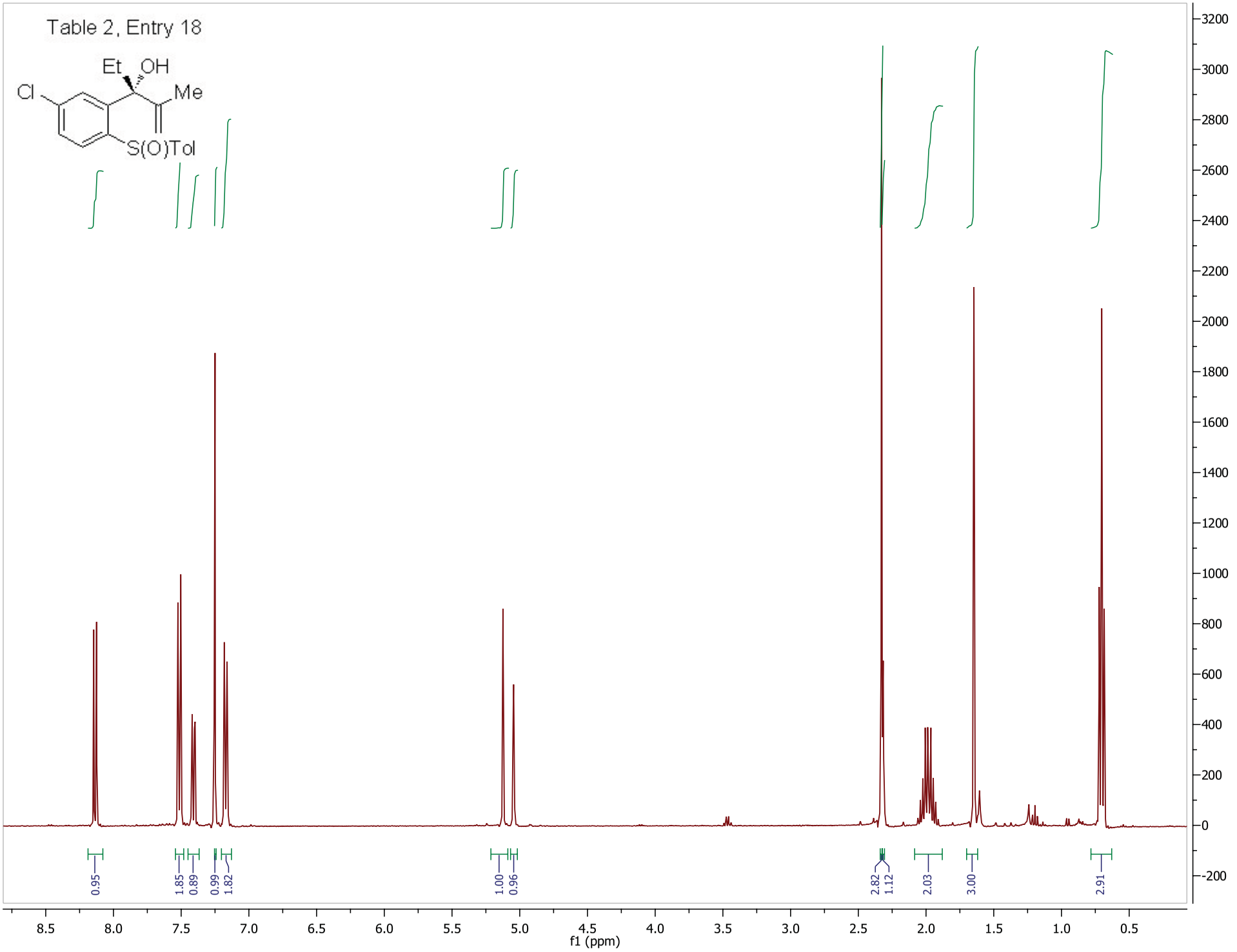
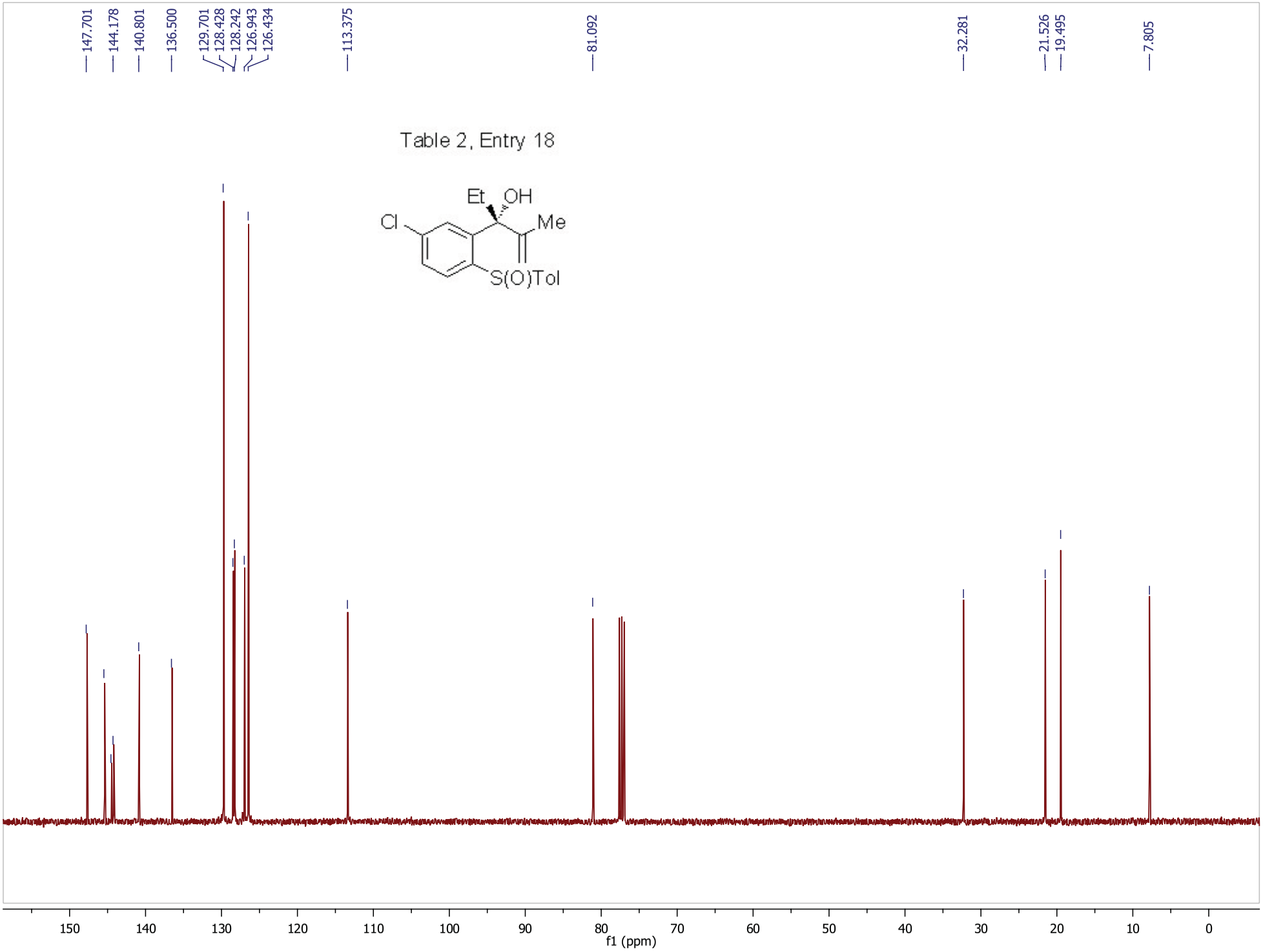


Table 2, Entry 18
Et
OH
Cl
Me
S(O)Tol
0.95
1.85
0.89
0.99
1.82
1.00
0.96
2.82
1.12
2.03
3.00
2.91
f1 (ppm)


147.701
144.178
140.801
136.500
129.701
128.428
128.242
126.943
126.434
113.375
81.092
32.281
21.526
19.495
7.805
Table 2, Entry 18
Et
OH
Cl
Me
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

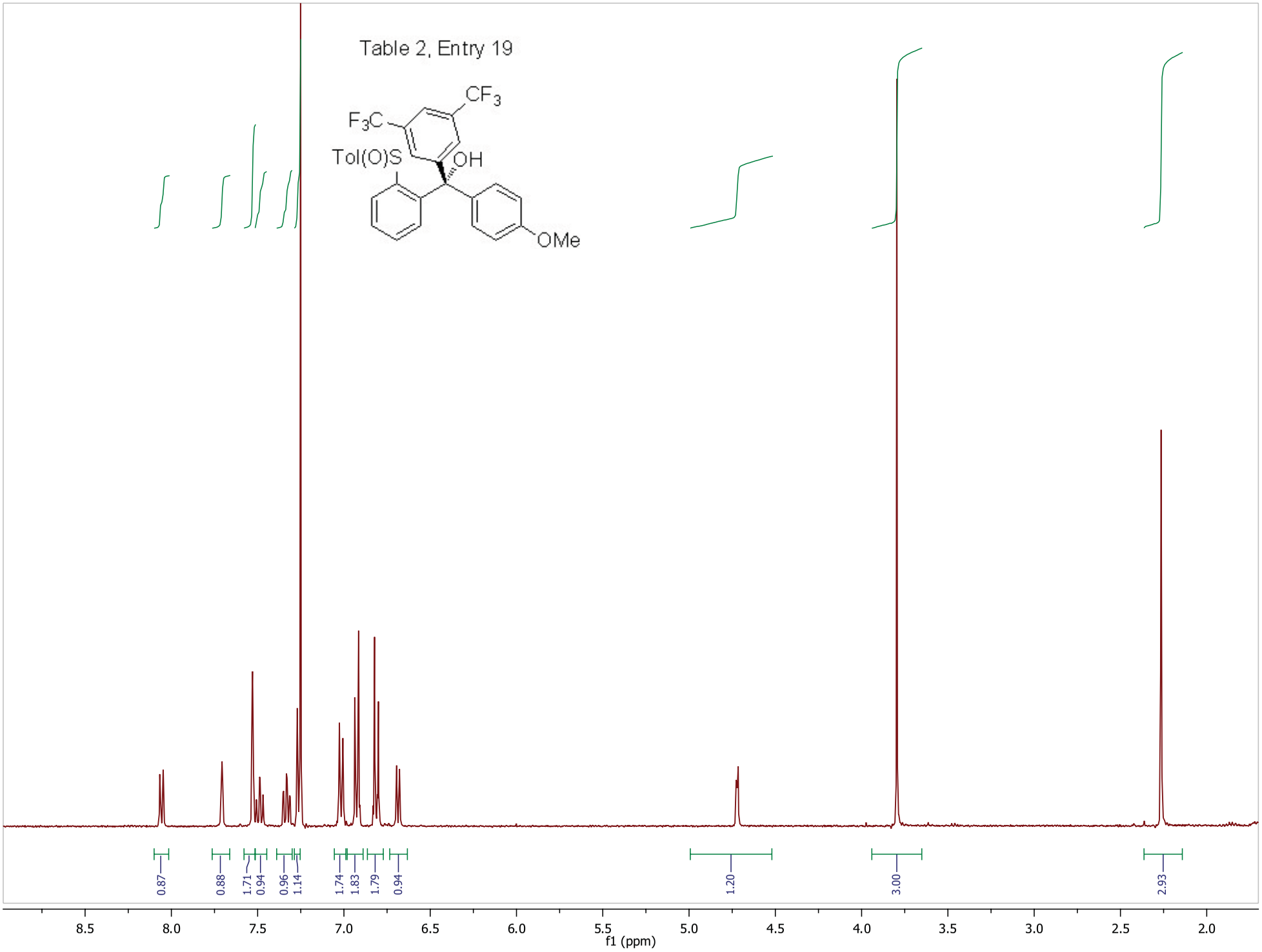
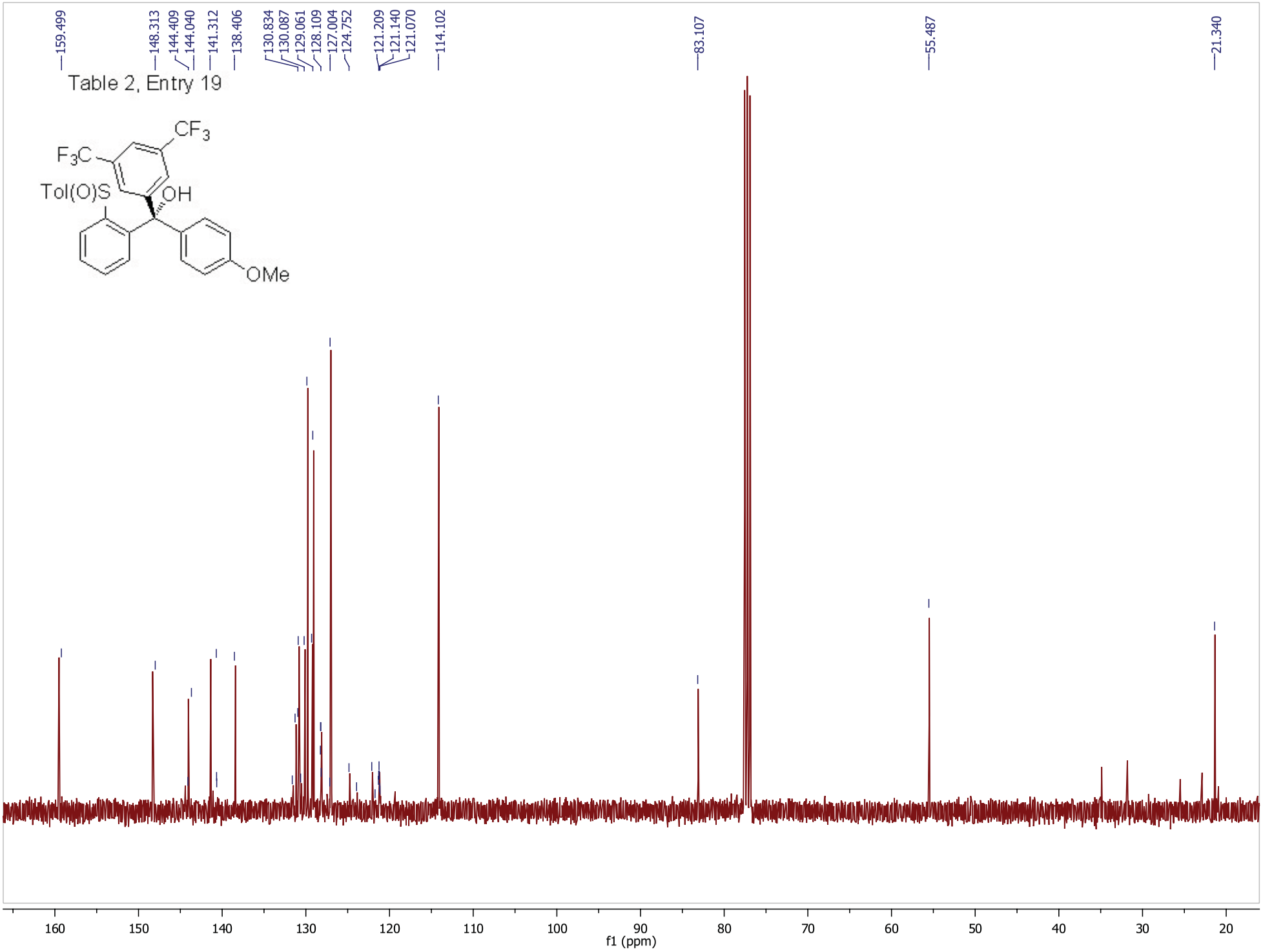


Table 2, Entry 19
CF3
F3C
Tol(O)S
OH
OMe
0.87
0.88
1.71
0.94
0.96
1.14
1.74
1.83
1.79
0.94
1.20
3.00
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


159.499
148.313
144.409
144.040
141.312
138.406
130.834
130.087
129.061
128.109
127.004
124.752
121.209
121.140
121.070
114.102
83.107
55.487
21.340
Table 2, Entry 19
CF3
F3C
Tol(O)S
OH
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

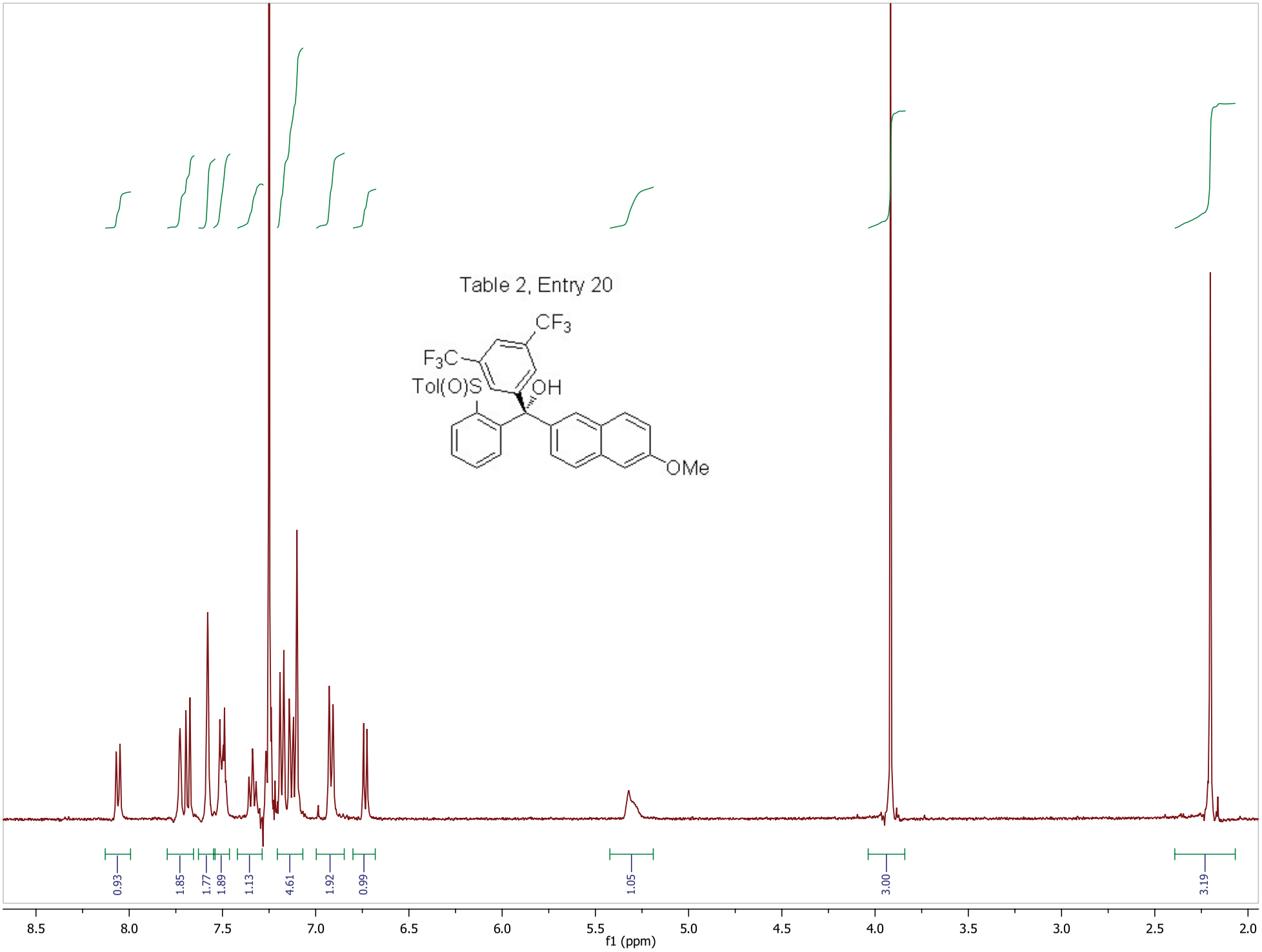
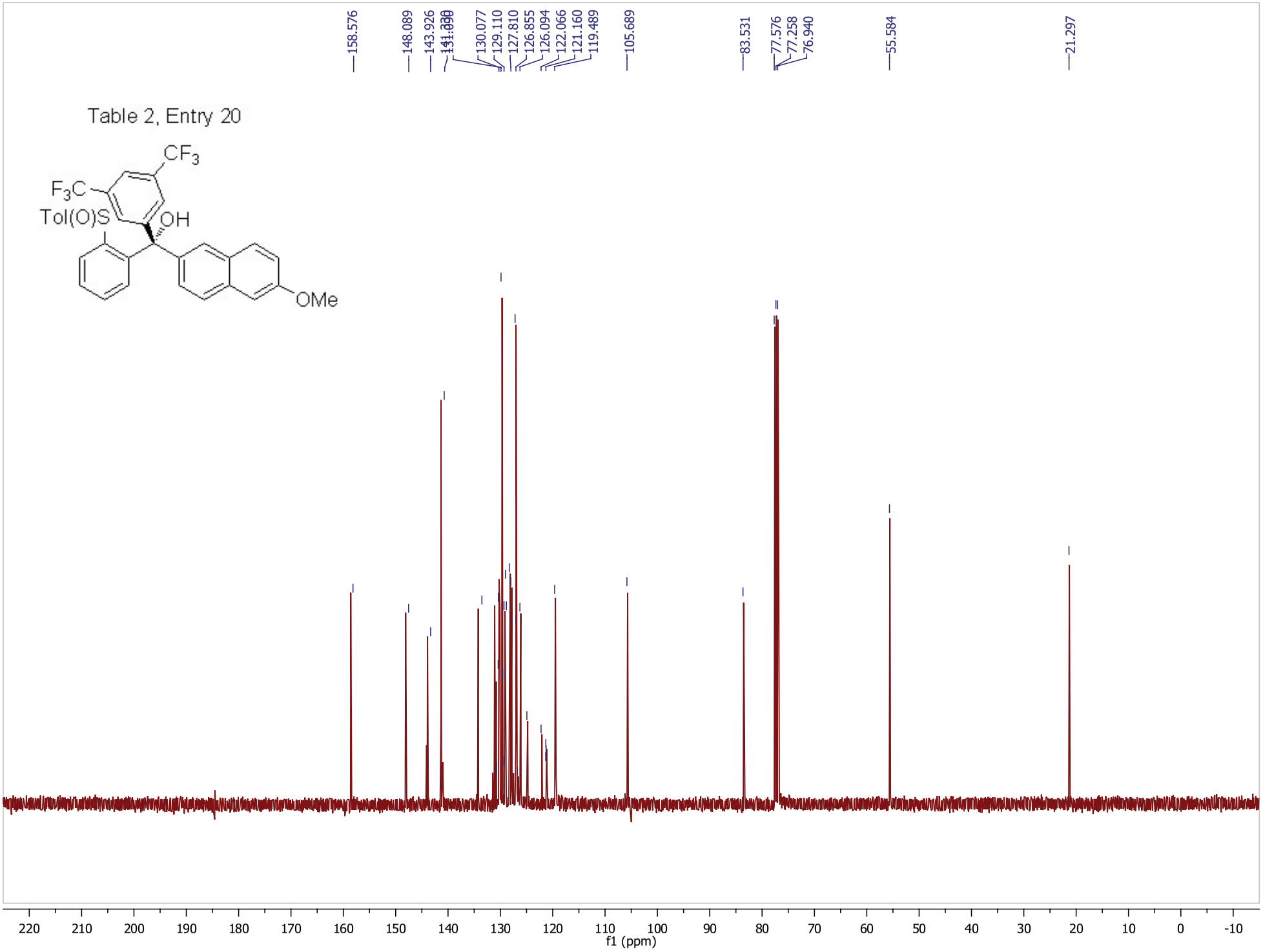


Table 2, Entry 20
CF3
F3C
Tol(O)S
OH
OMe
0.93
1.85
1.77
1.89
1.13
4.61
1.92
0.99
1.05
3.00
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


158.576
148.089
143.926
130.077
129.110
127.810
126.855
126.094
122.066
121.160
119.489
105.689
83.531
77.576
77.258
76.940
55.584
21.297
Table 2, Entry 20
CF3
F3C
Tol(O)S
OH
OMe
220
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)

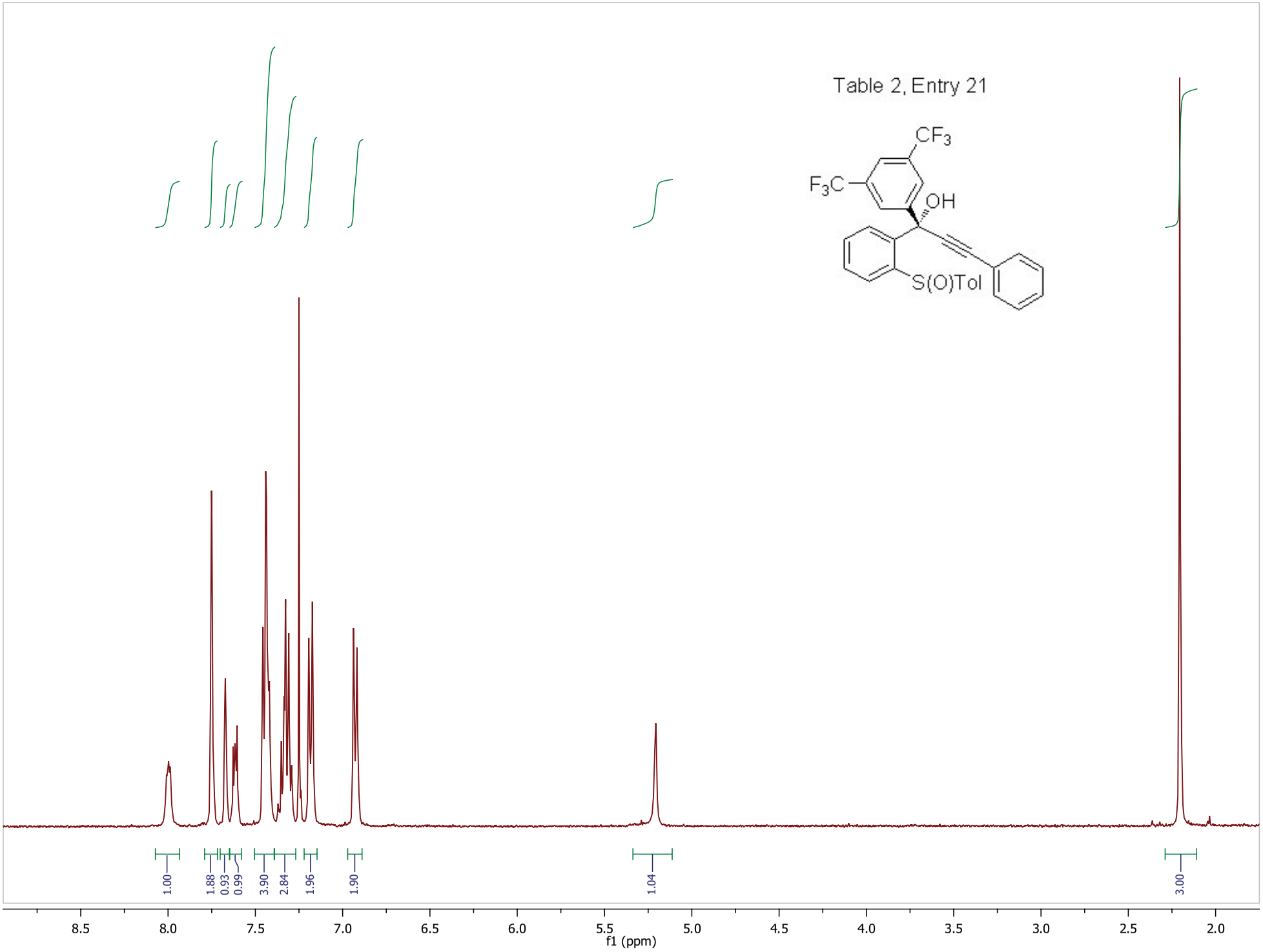


Table 2, Entry 21
CF3
F3C
OH
S(O)Tol
1.00
1.88
0.93
0.99
3.90
2.84
1.96
1.90
1.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

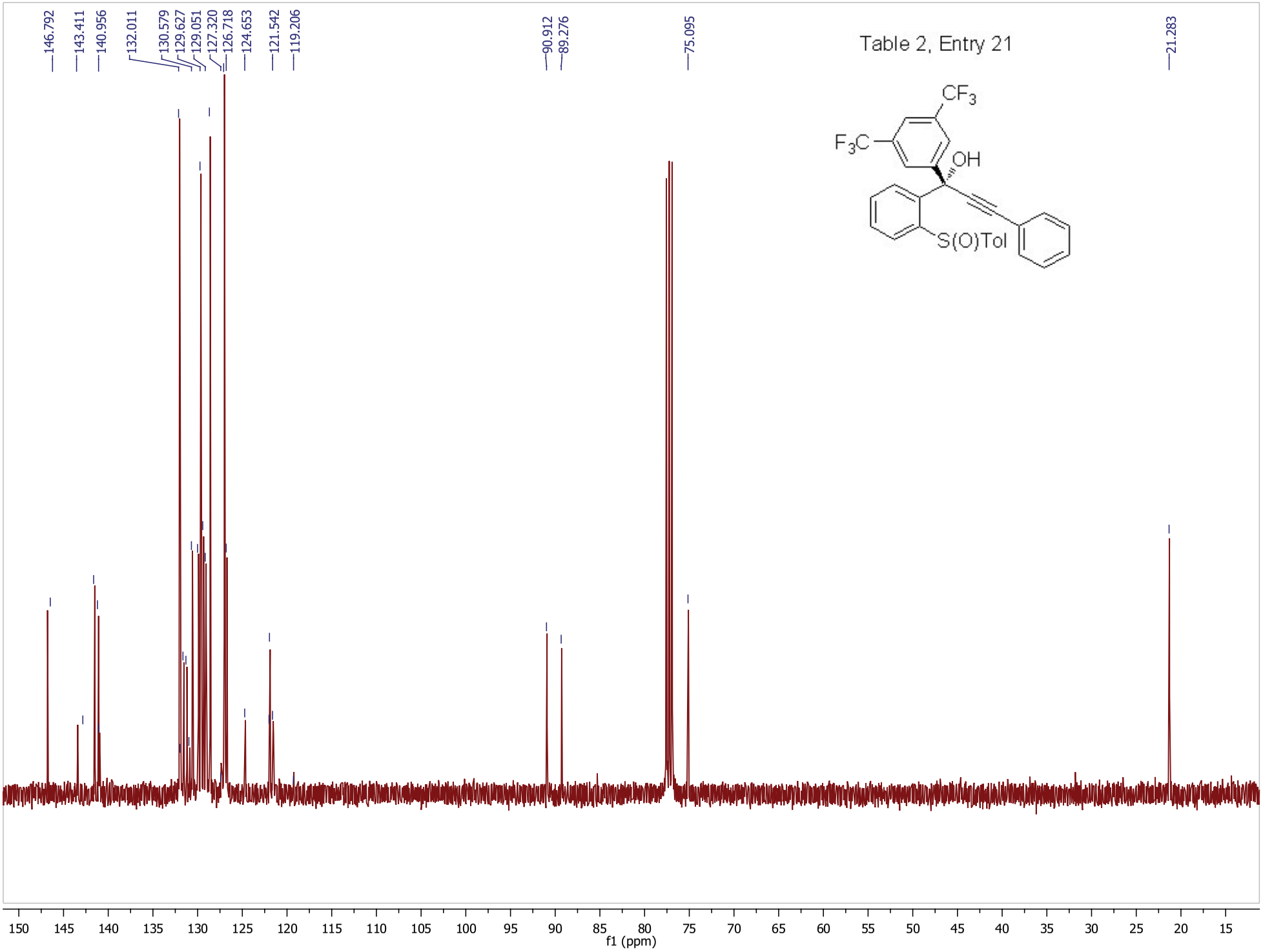
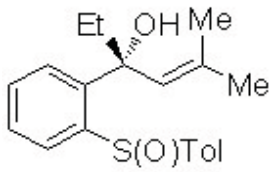
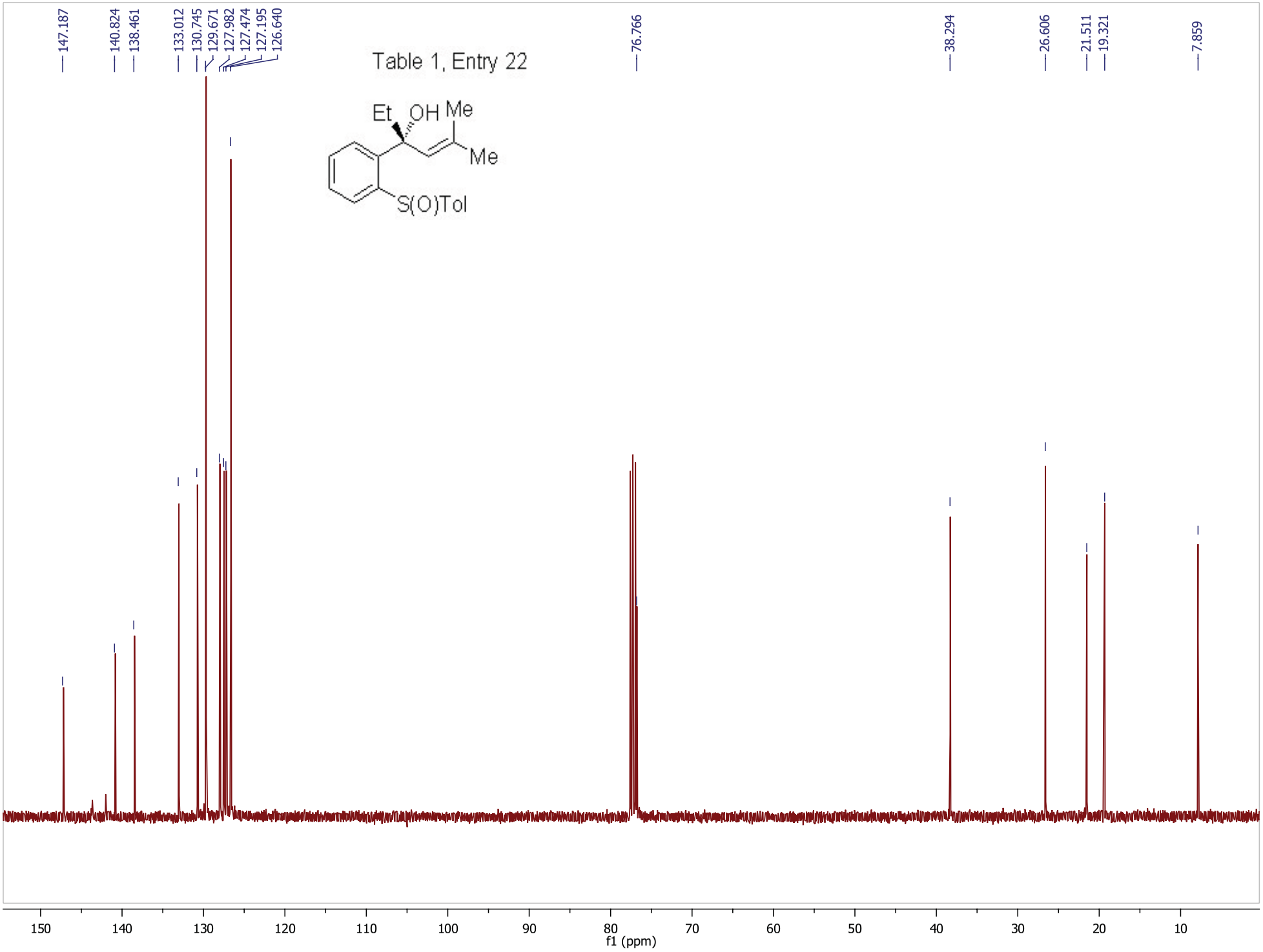

146.792
143.411
140.956
132.011
130.579
129.627
129.051
127.320
126.718
124.653
121.542
119.206
90.912
89.276
75.095
21.283
Table 2, Entry 21
CF3
F3C
OH
S(O)Tol
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

Table 1, Entry 22




147.187
140.824
138.461
133.012
130.745
129.671
127.982
127.474
127.195
126.640
76.766
38.294
26.606
21.511
19.321
7.859
Table 1, Entry 22
Et
OH
Me
Me
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

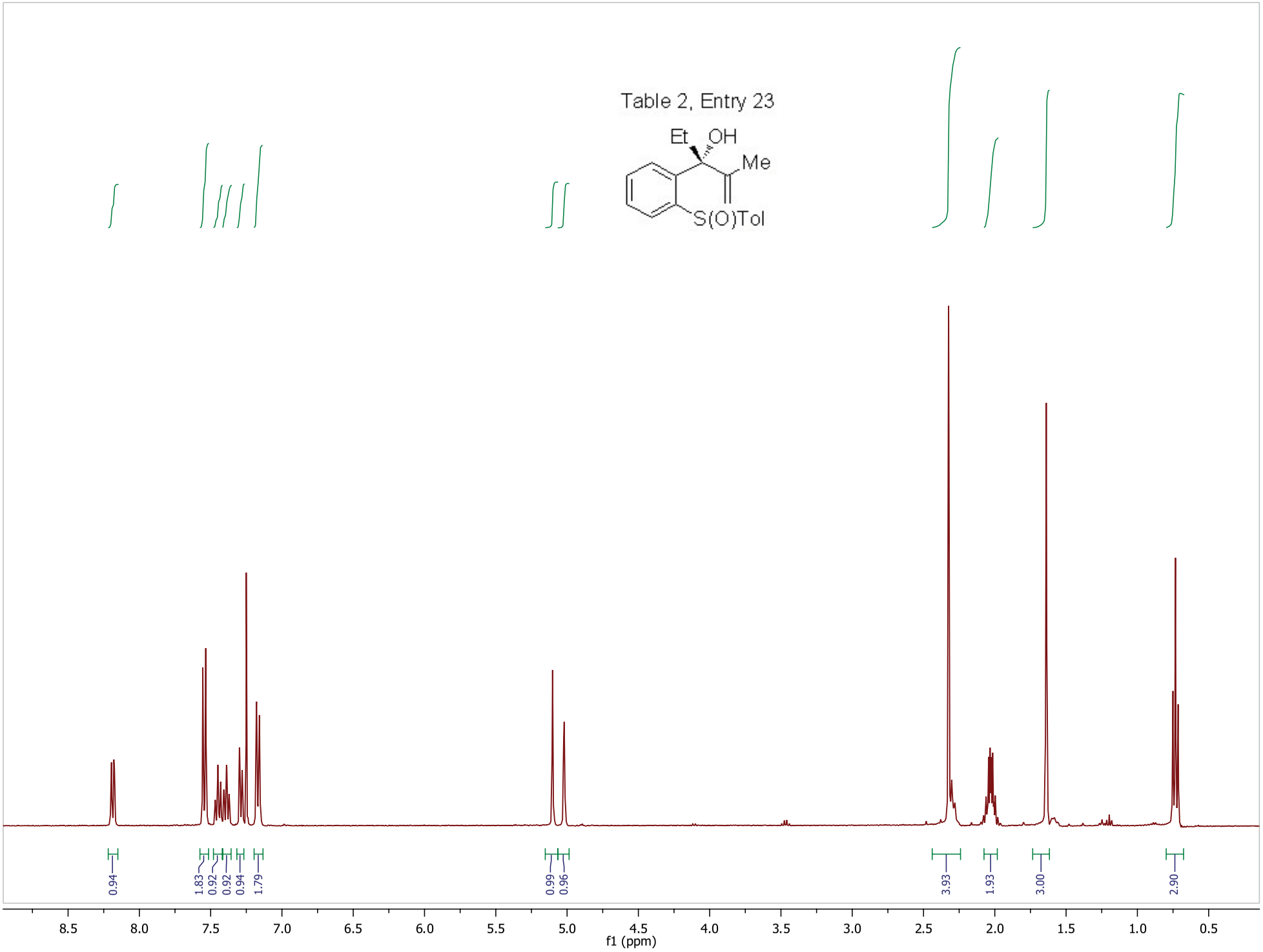
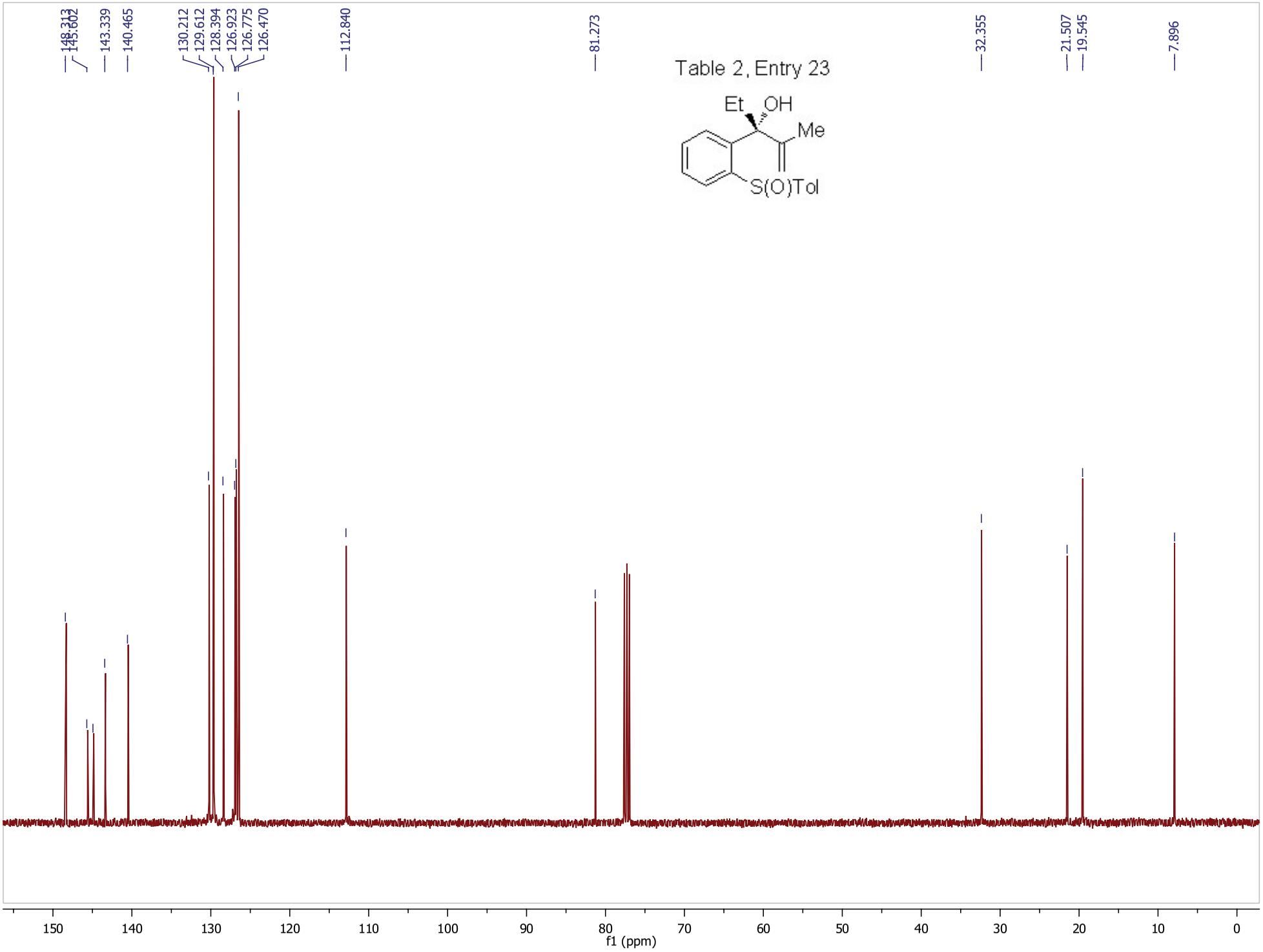


Table 2, Entry 23
Et
OH
Me
S(O)Tol
0.94
1.83
0.92
0.92
0.94
1.79
0.99
0.96
3.93
1.93
3.00
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


148.313
145.602
143.339
140.465
130.212
129.612
128.394
126.923
126.775
126.470
112.840
81.273
32.355
21.507
19.545
7.896
Table 2, Entry 23
Et
OH
Me
S(O)Tol
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

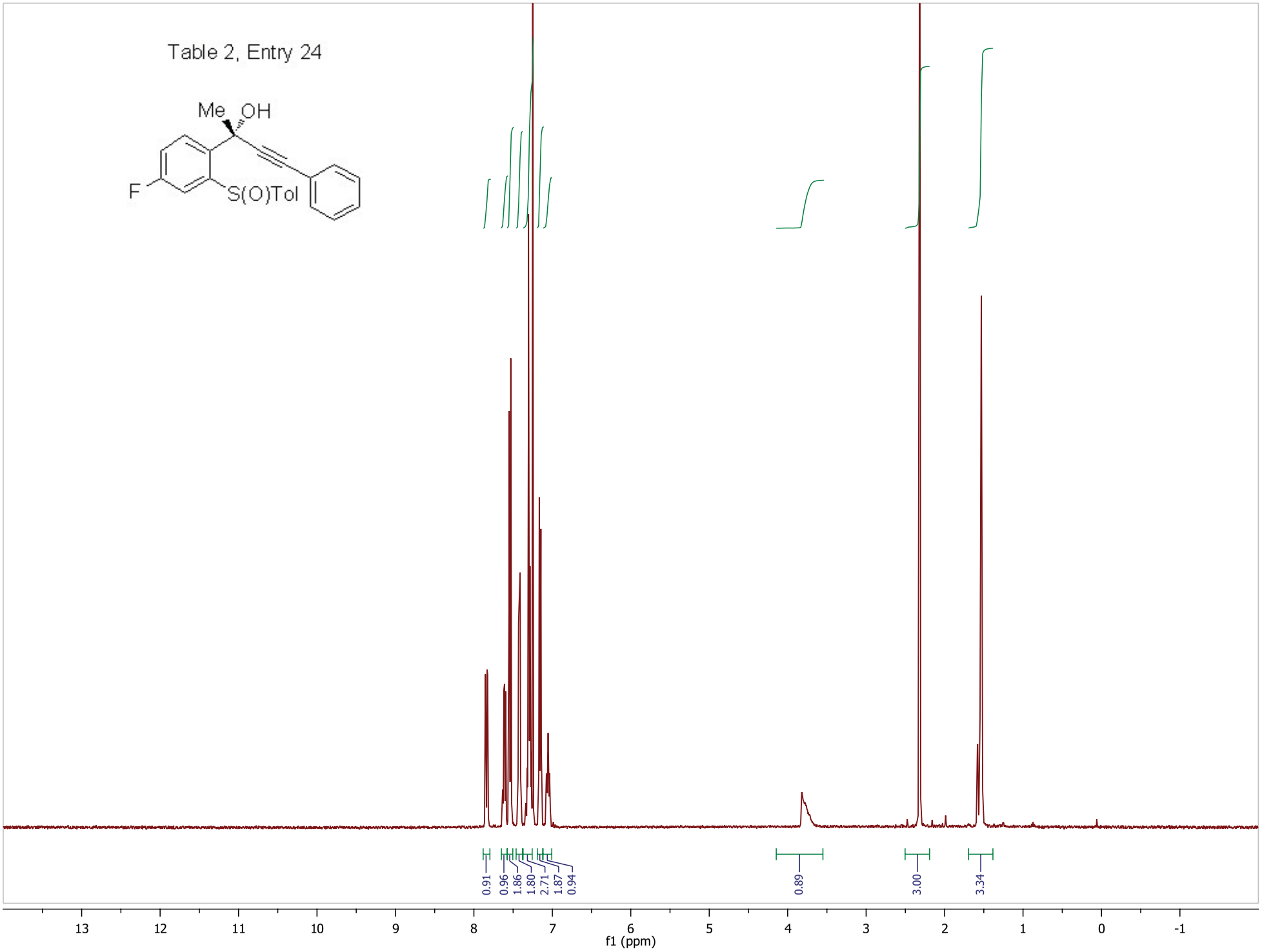
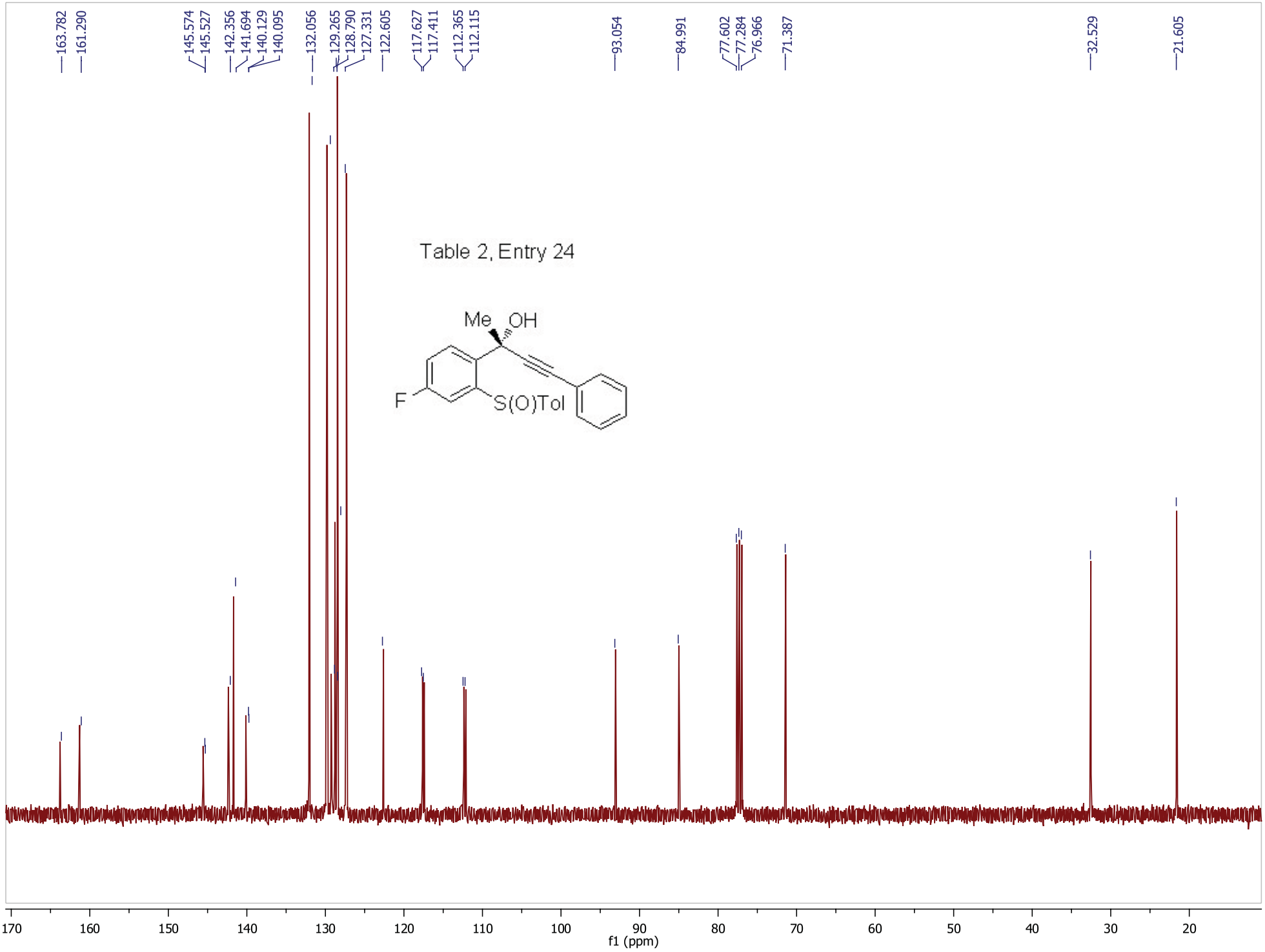


Table 2, Entry 24
Me
OH
F
S(O)Tol
0.91
0.96
1.86
1.80
2.71
1.87
0.94
0.89
3.00
3.34
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


163.782
161.290
145.574
145.527
142.356
141.694
140.129
140.095
132.056
129.265
128.790
127.331
122.605
117.627
117.411
112.365
112.115
93.054
84.991
77.602
77.284
76.966
71.387
32.529
21.605
Table 2, Entry 24
Me
OH
F
S(O)Tol
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

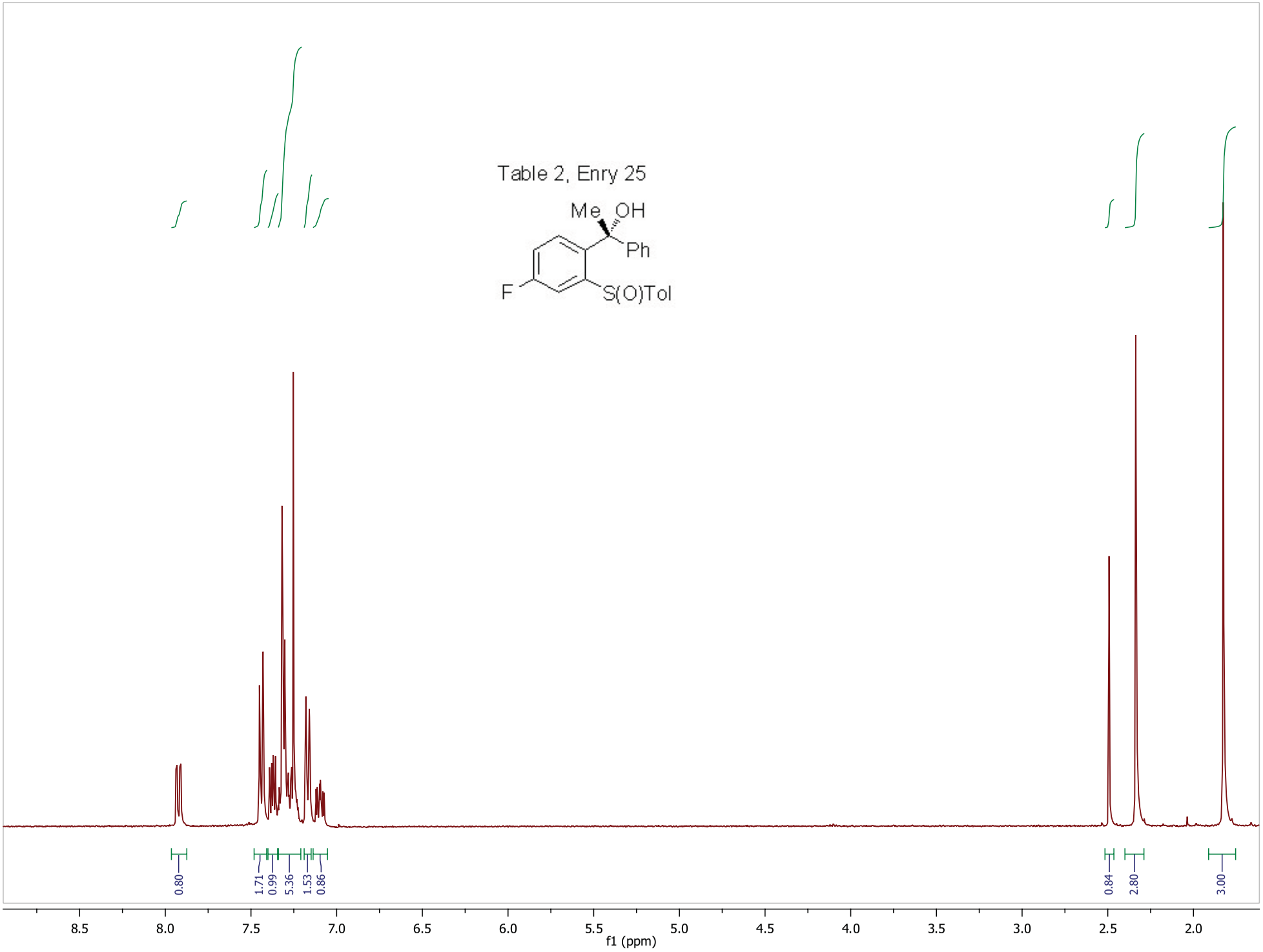


Table 2, Enry 25
Me
OH
Ph
F
S(O)Tol
0.80
1.71
0.99
5.36
1.53
0.86
0.84
2.80
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

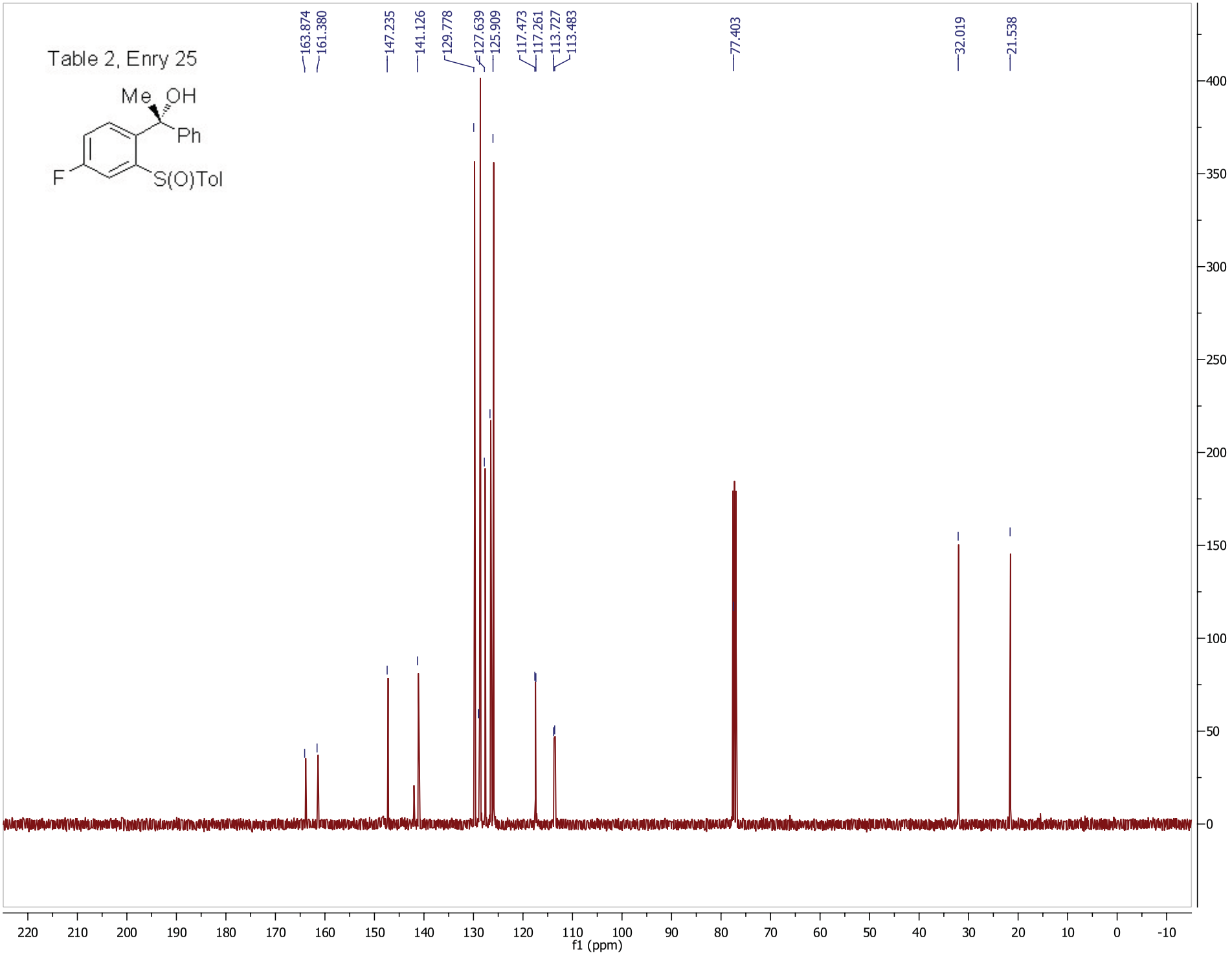


Table 2, Enry 25
Me
OH
Ph
F
S(O)Tol
163.874
161.380
147.235
141.126
129.778
127.639
125.909
117.473
117.261
113.727
113.483
77.403
32.019
21.538
400
350
300
250
200
150
100
50
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

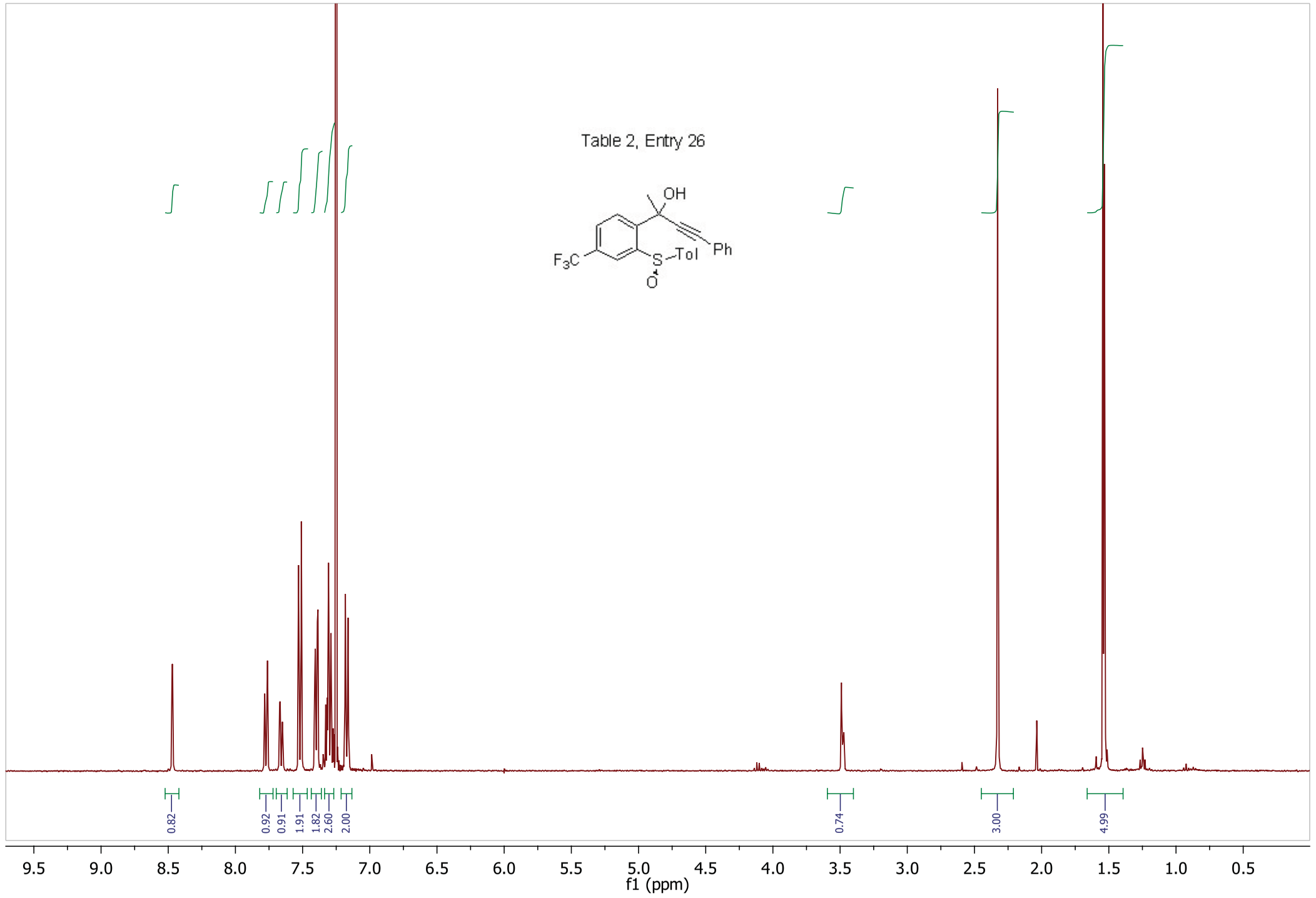
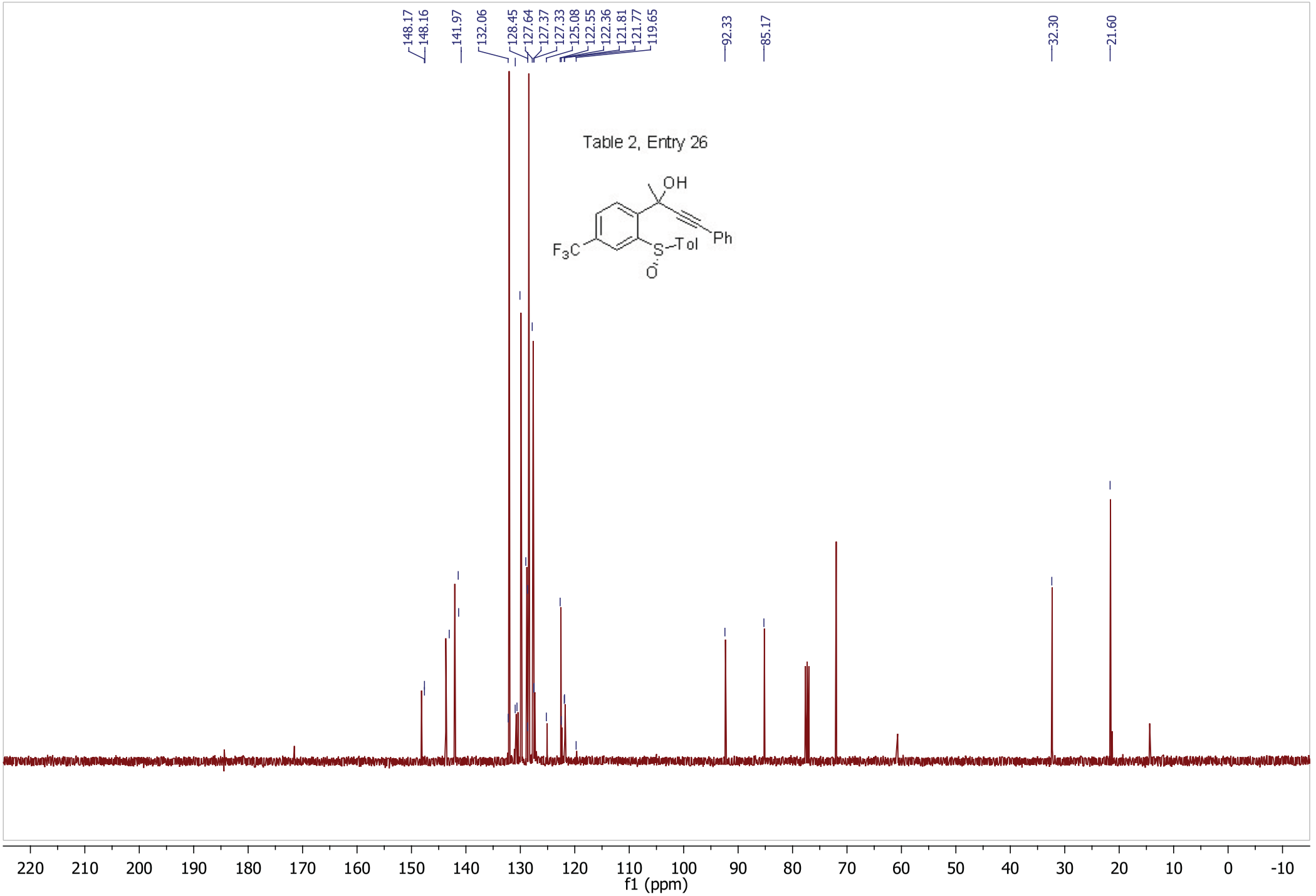


Table 2, Entry 26
OH
Ph
Tol
S
O
F3C
0.82
0.92
0.91
1.91
1.82
2.60
2.00
0.74
3.00
4.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


148.17
148.16
141.97
132.06
128.45
127.64
127.37
127.33
125.08
122.55
122.36
121.81
121.77
119.65
92.33
85.17
32.30
21.60
Table 2, Entry 26
OH
Ph
F3C
S
Tol
O
220
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)

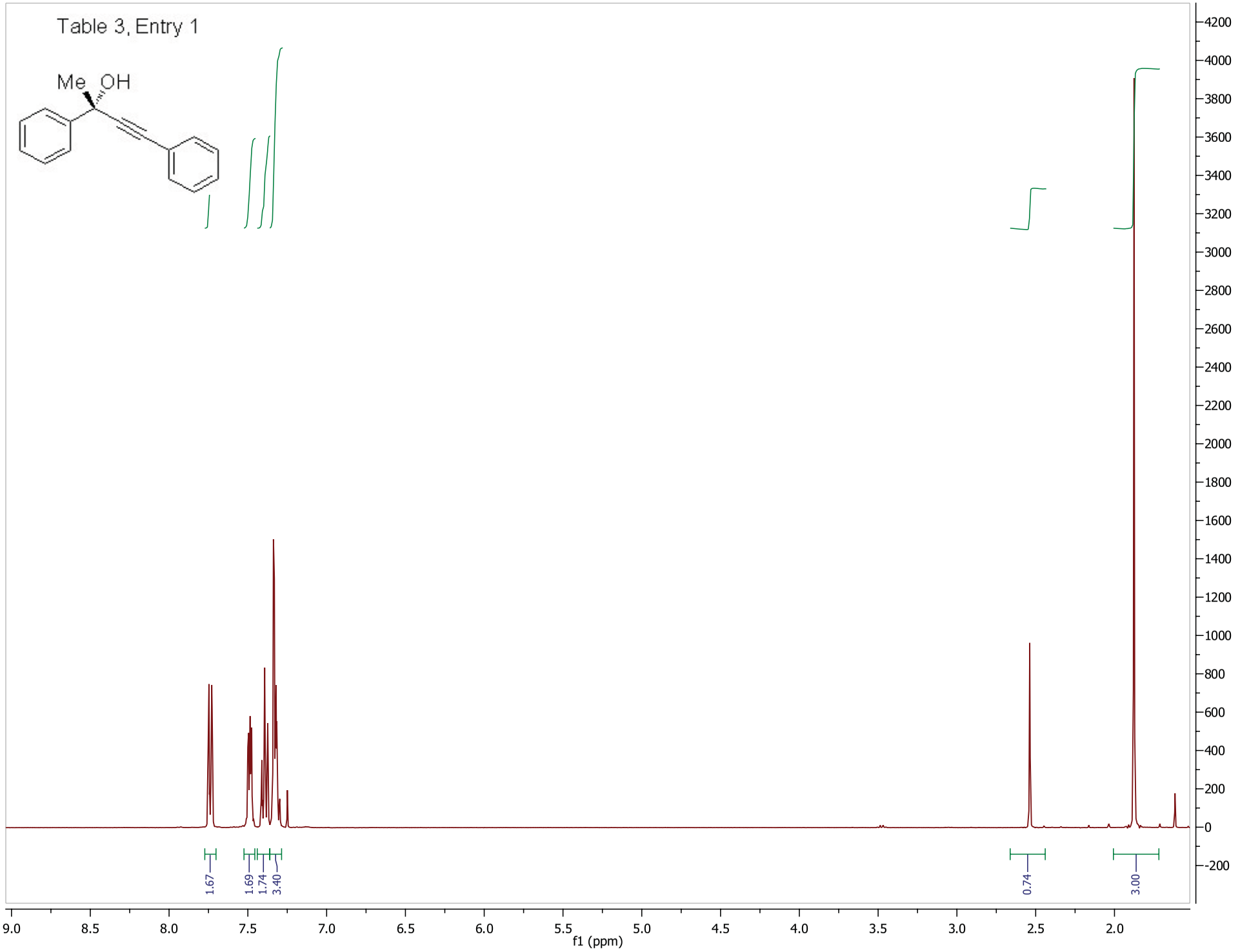
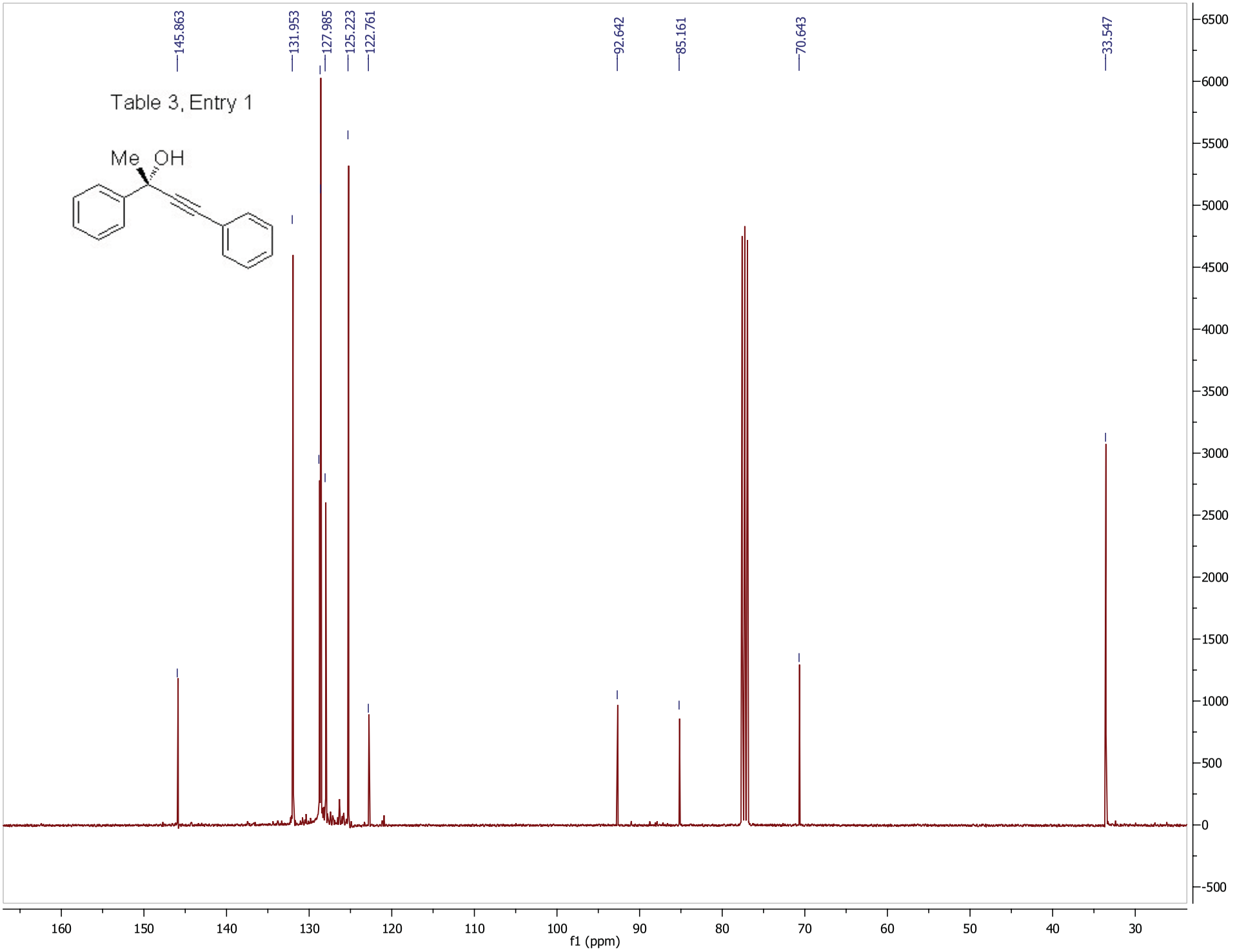


Table 3, Entry 1
Me
OH
1.67
1.69
1.74
3.40
0.74
3.00
f1 (ppm)


145.863
131.953
127.985
125.223
122.761
92.642
85.161
70.643
33.547
Table 3, Entry 1
Me
OH
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

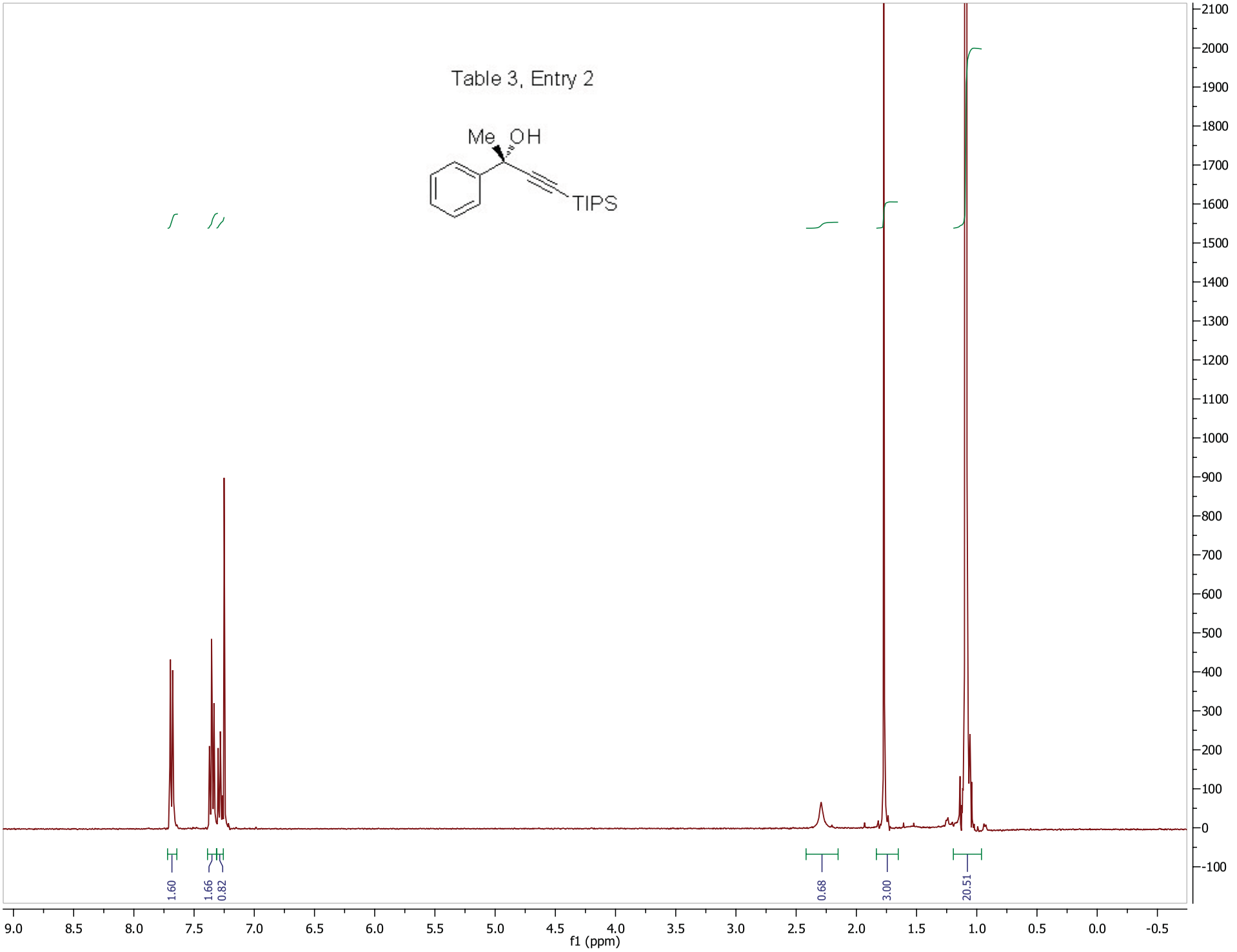
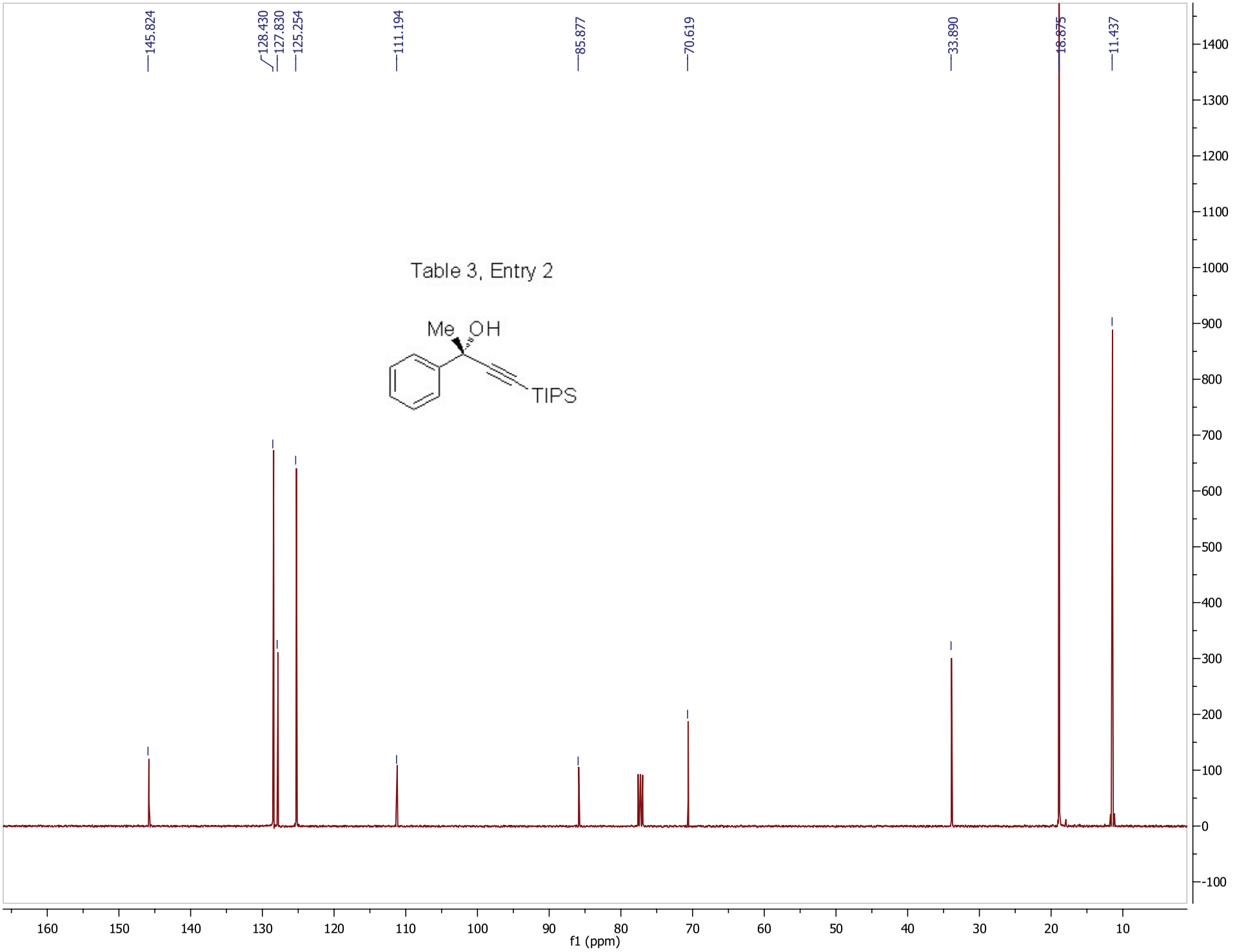


Table 3, Entry 2
Me
OH
TIPS
1.60
1.66
0.82
0.68
3.00
20.51
f1 (ppm)


145.824
128.430
127.830
125.254
111.194
85.877
70.619
33.890
18.875
11.437
Table 3, Entry 2
Me
OH
TIPS
f1 (ppm)

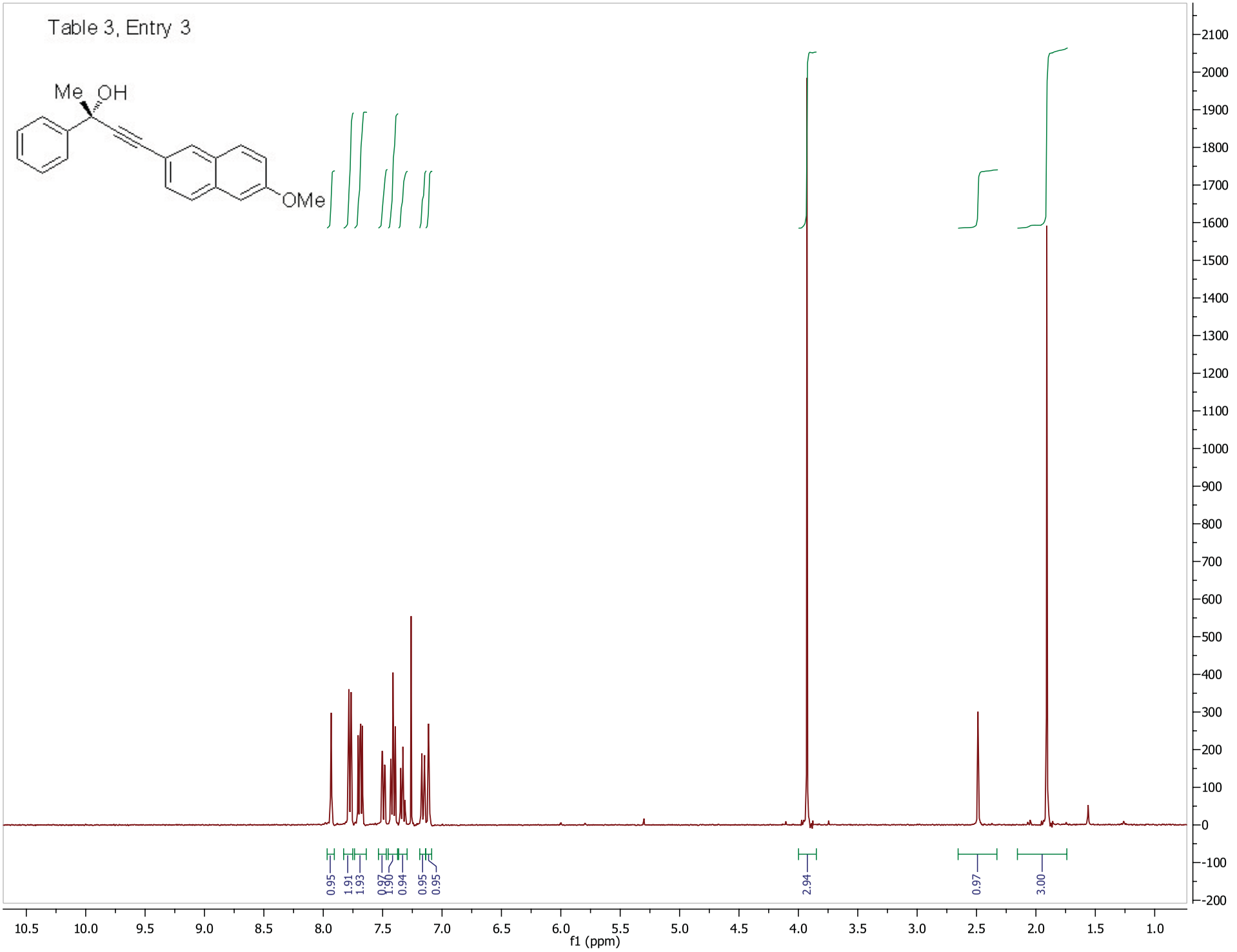
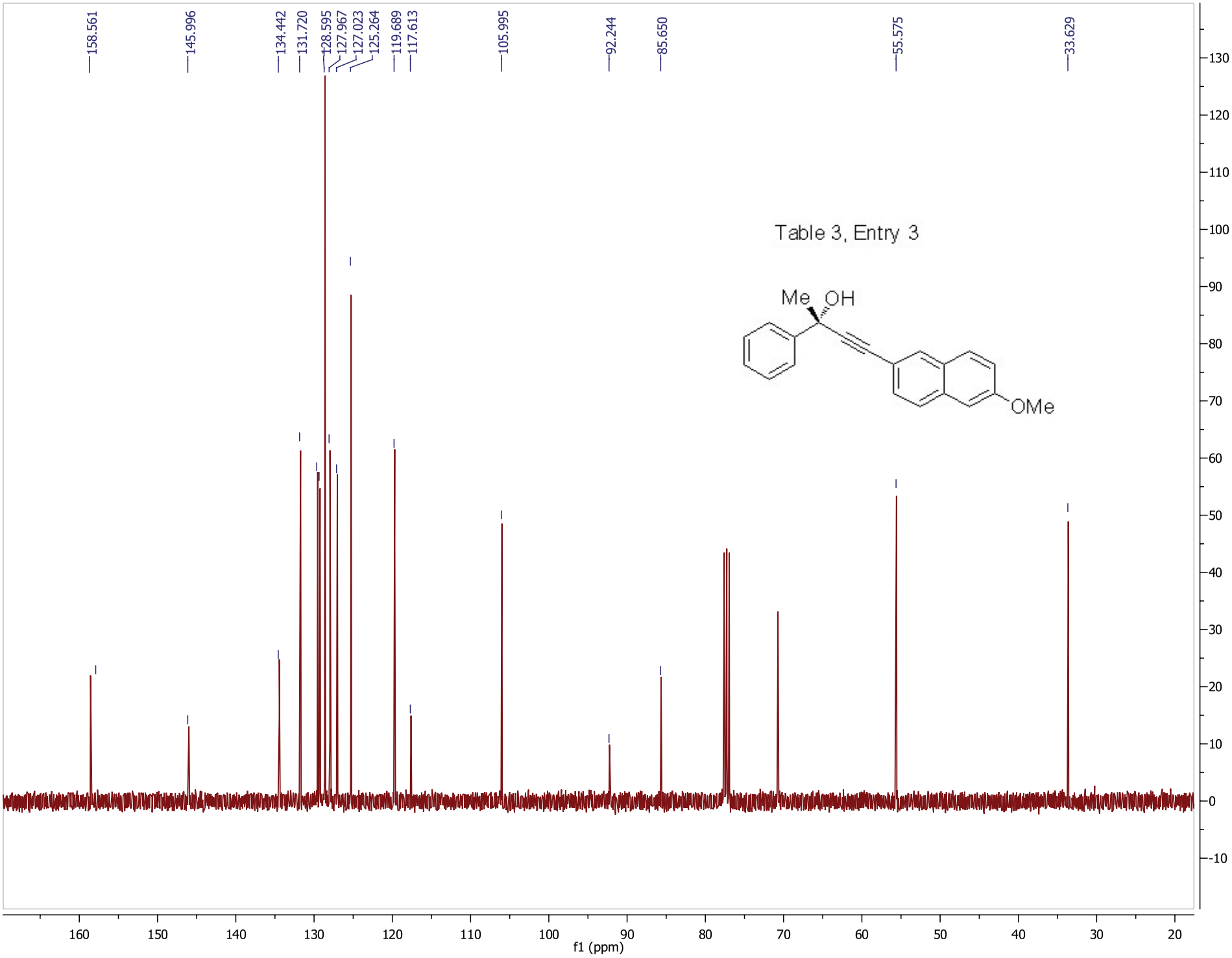
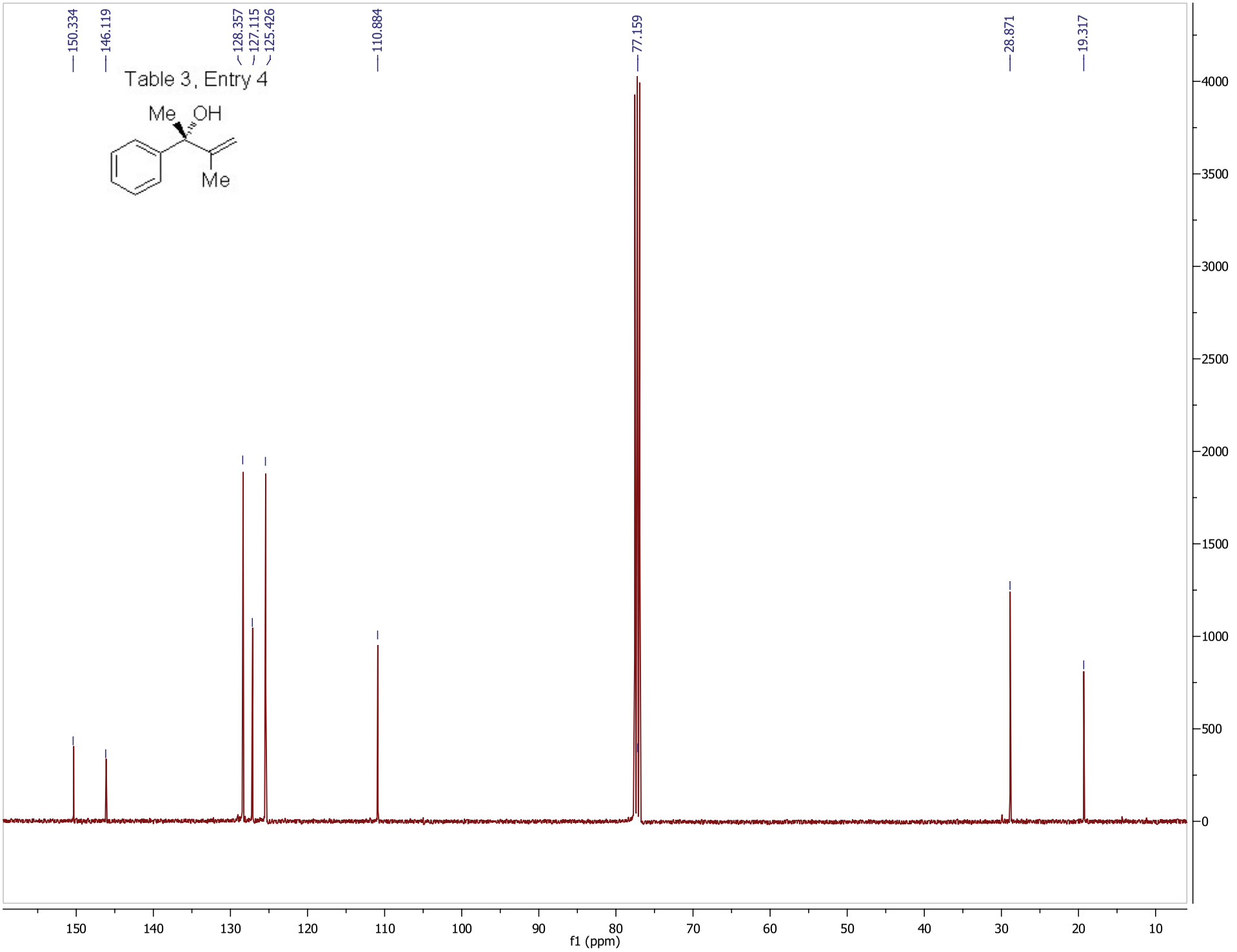


Table 3, Entry 3
Me
OH
OMe
0.95
1.91
1.93
0.97
1.96
0.94
0.95
0.95
2.94
0.97
3.00
f1 (ppm)


158.561
145.996
134.442
131.720
128.595
127.967
127.023
125.264
119.689
117.613
105.995
92.244
85.650
55.575
33.629
Table 3, Entry 3
Me
OH
OMe
f1 (ppm)


150.334
146.119
128.357
127.115
125.426
110.884
77.159
28.871
19.317
Table 3, Entry 4
Me
OH
Me
4000
3500
3000
2500
2000
1500
1000
500
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

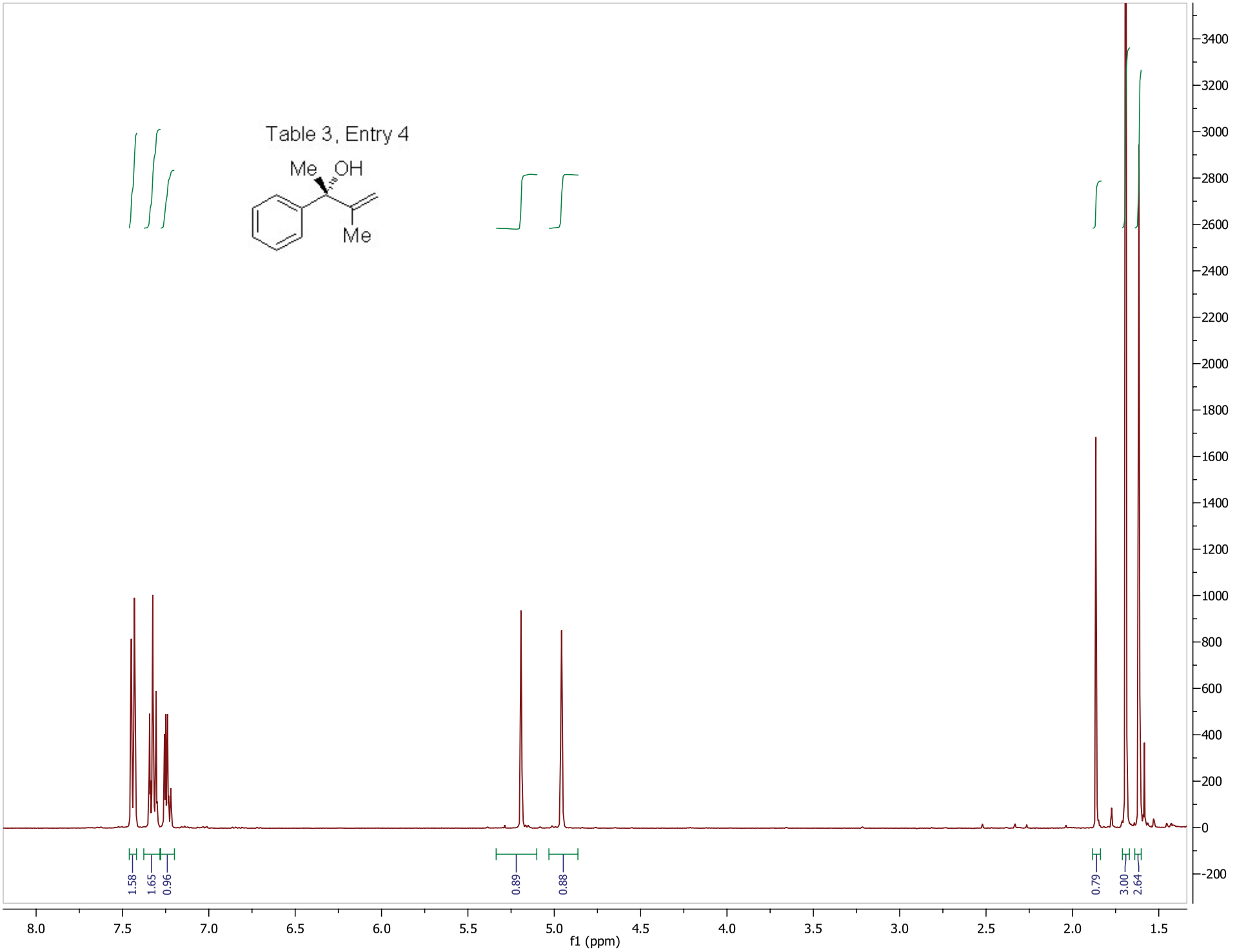


Table 3, Entry 4
Me
OH
Me
1.58
1.65
0.96
0.89
0.88
0.79
3.00
2.64
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

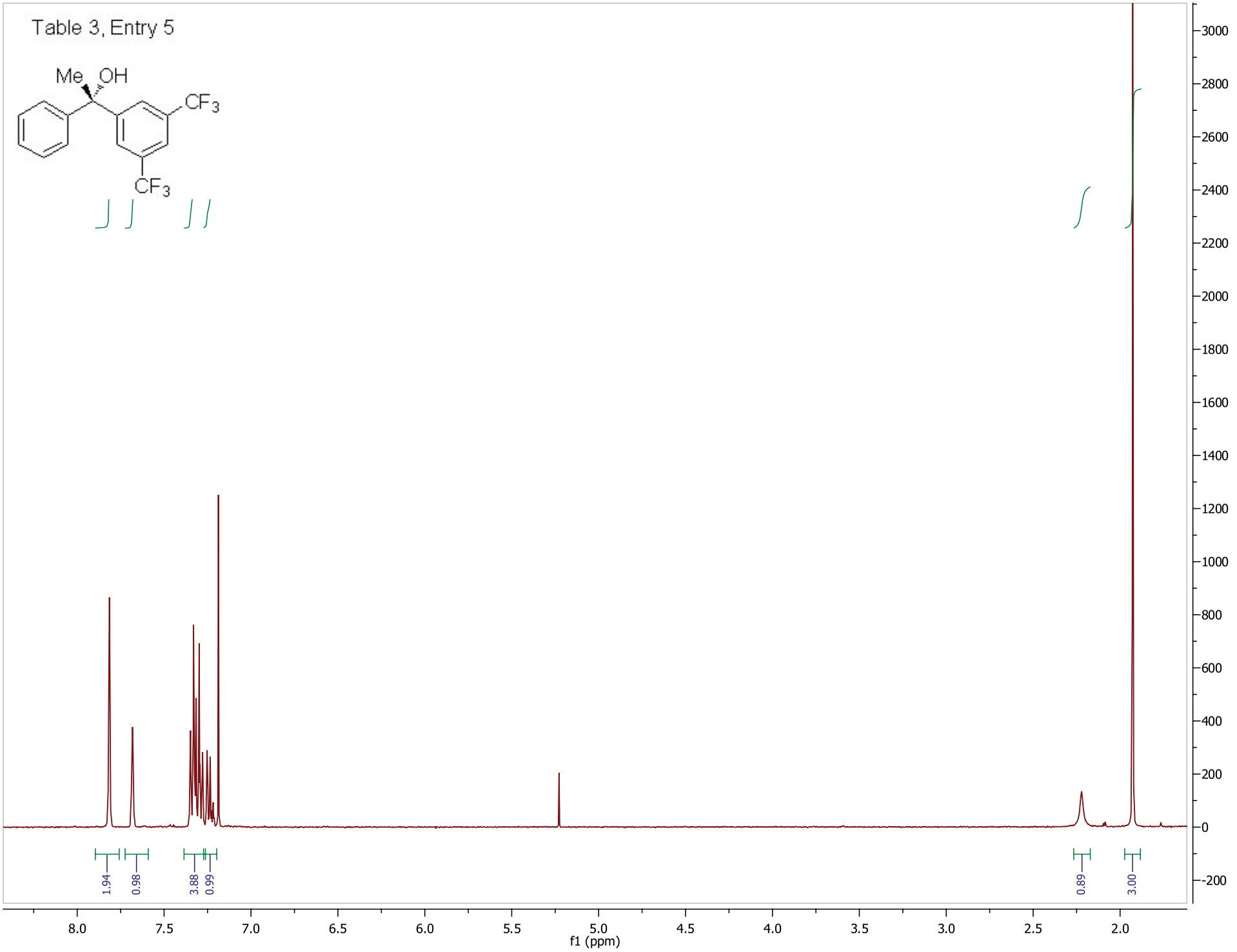
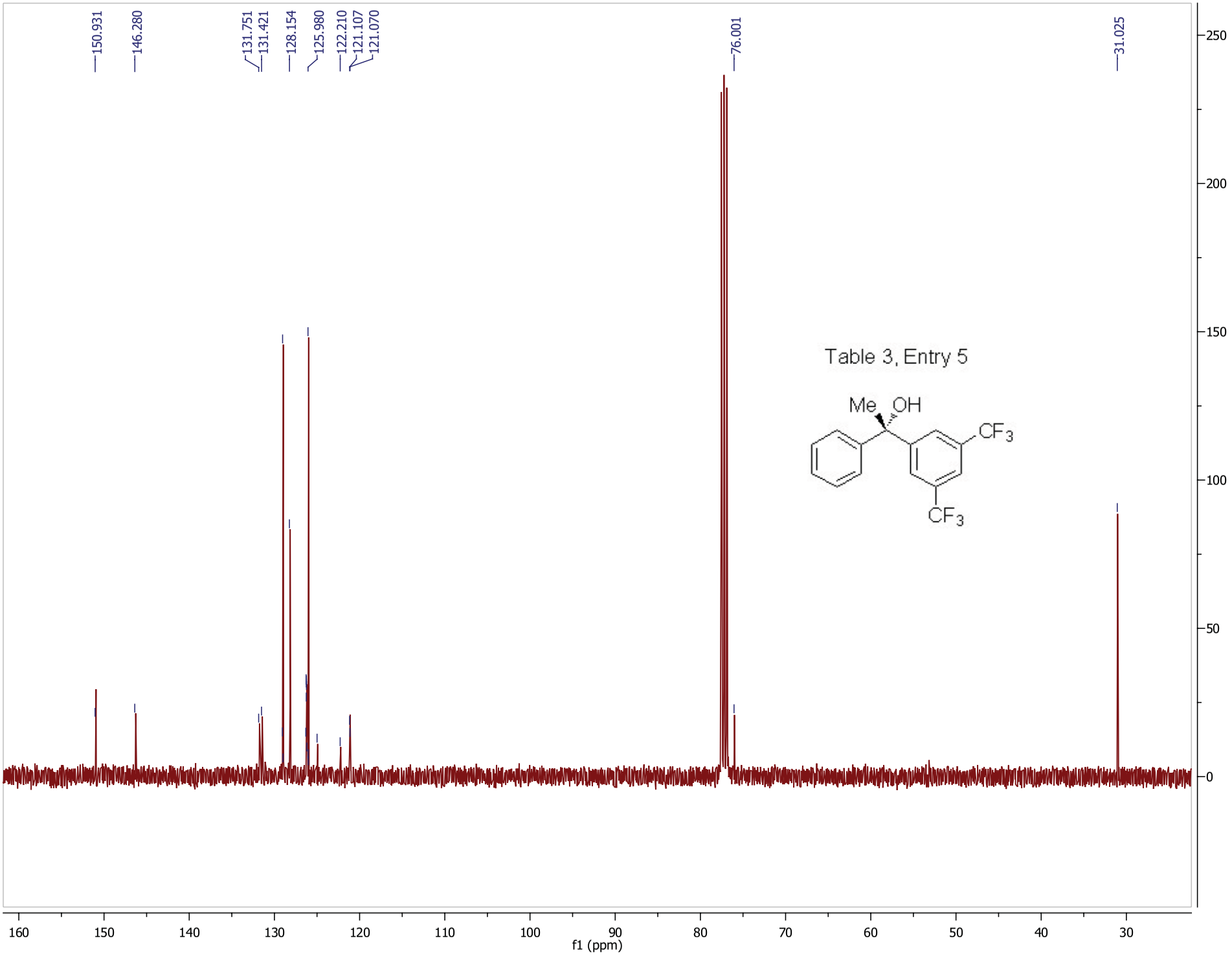


Table 3, Entry 5
Me
OH
CF3
CF3
1.94
0.98
3.88
0.99
0.89
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


150.931
146.280
131.751
131.421
128.154
125.980
122.210
121.107
121.070
76.001
31.025
Table 3, Entry 5
Me
OH
CF3
CF3
250
200
150
100
50
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

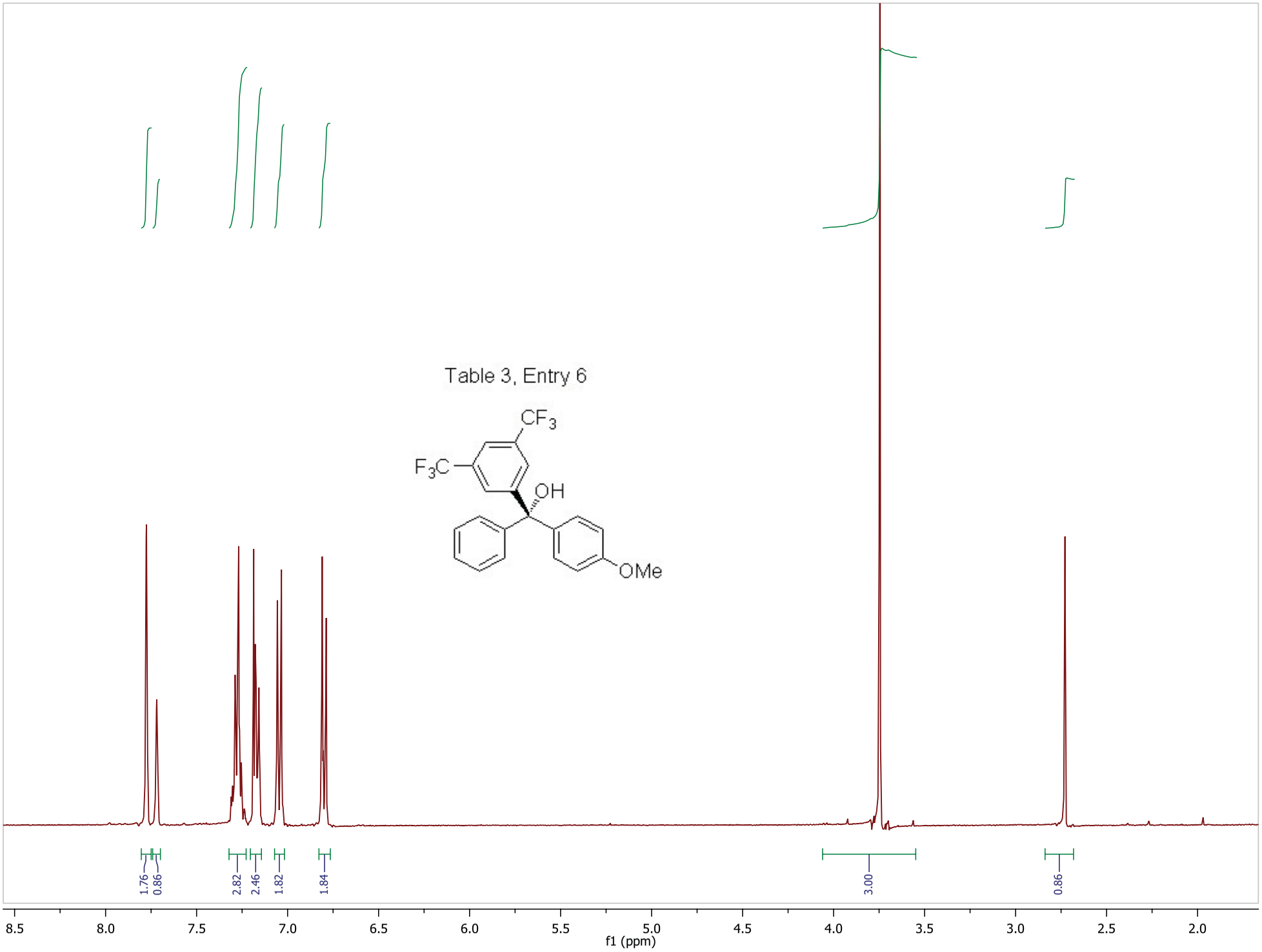


Table 3, Entry 6
CF3
F3C
OH
OMe
1.76
0.86
2.82
2.46
1.82
1.84
3.00
0.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

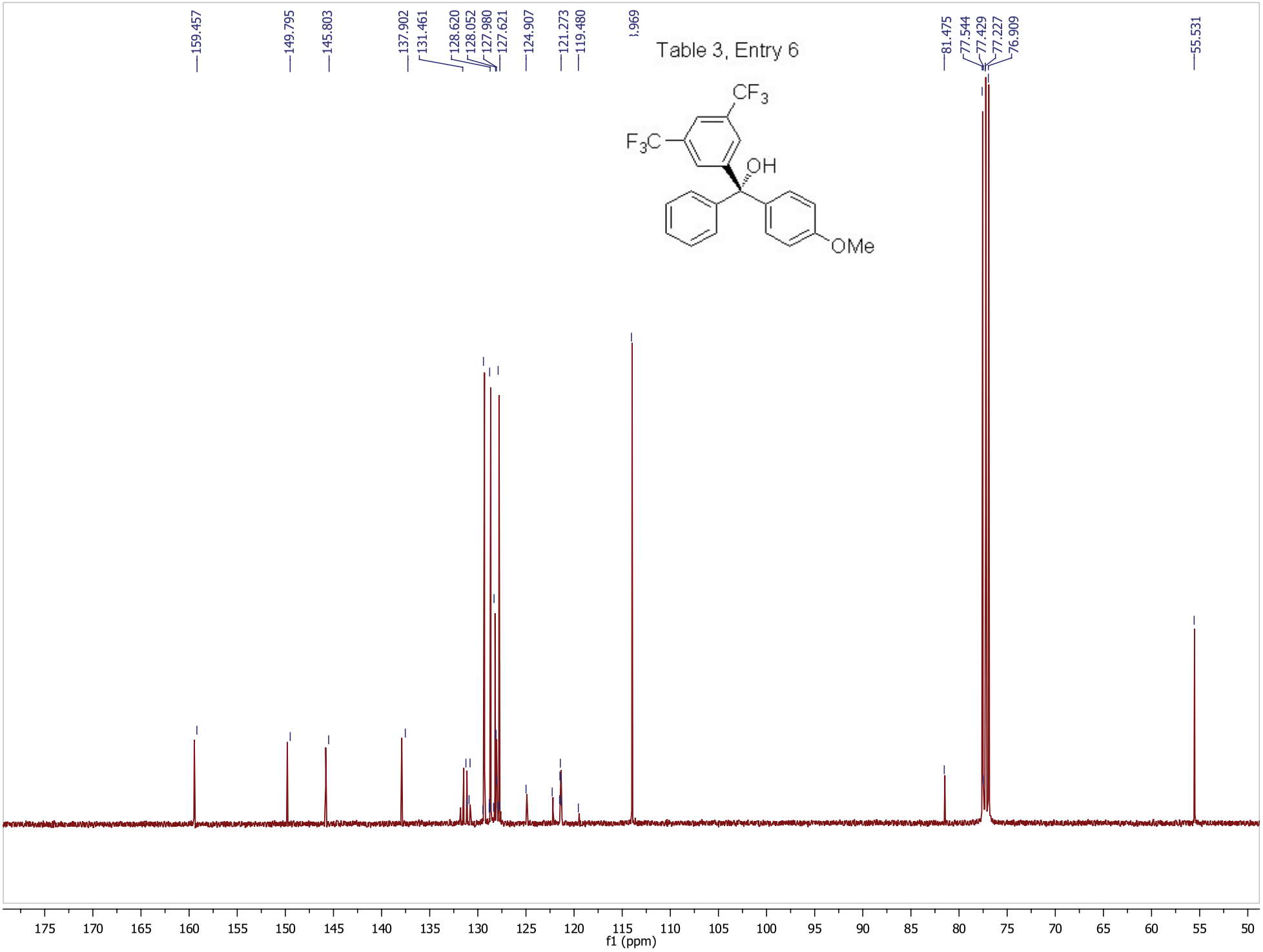
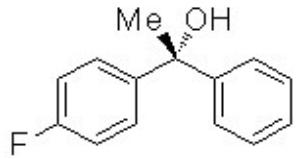
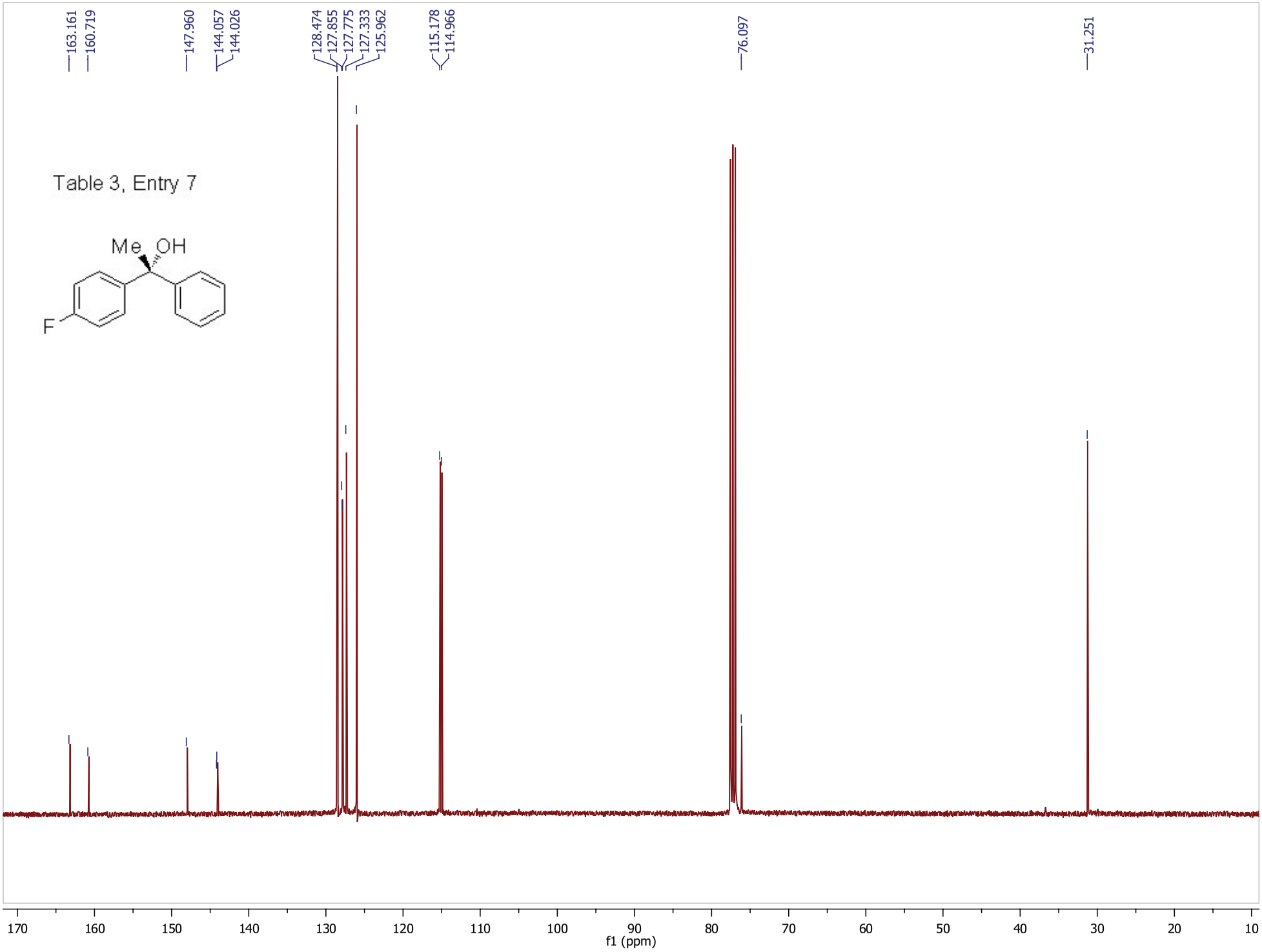
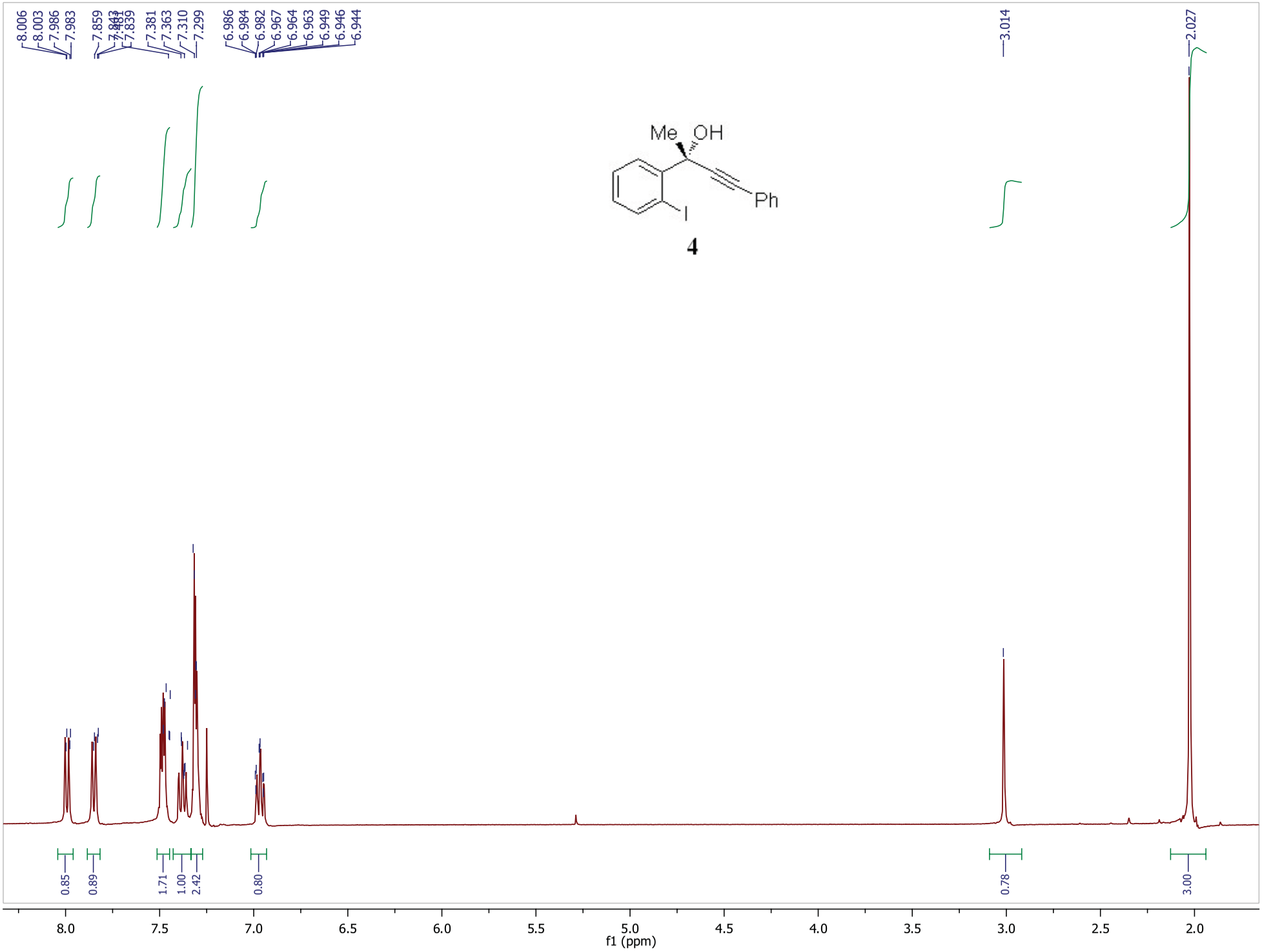
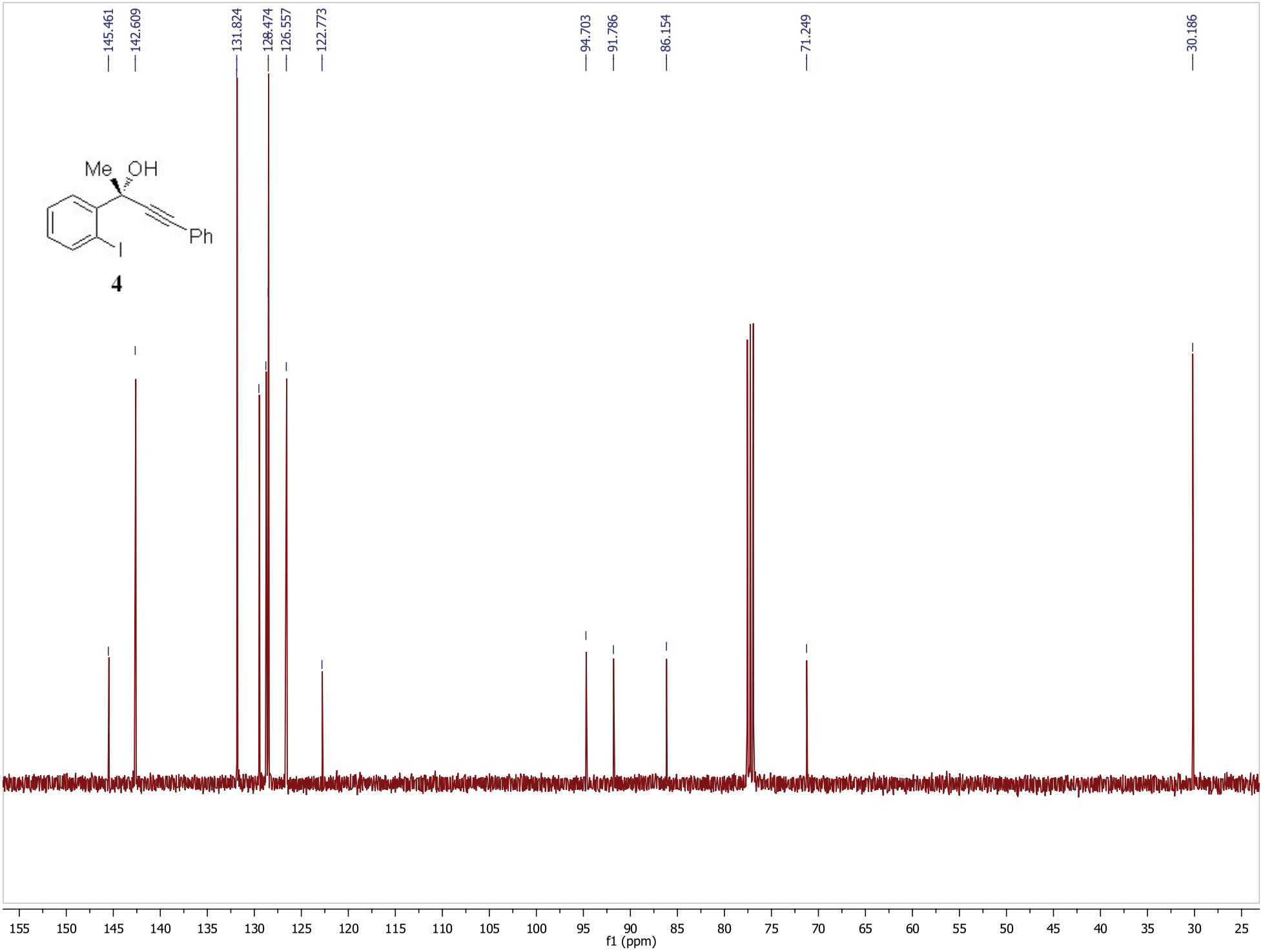

159.457
149.795
145.803
137.902
131.461
128.620
128.052
127.980
127.621
124.907
121.273
119.480
81.475
77.544
77.429
77.227
76.909
55.531
Table 3, Entry 6
CF3
F3C
OH
OMe
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

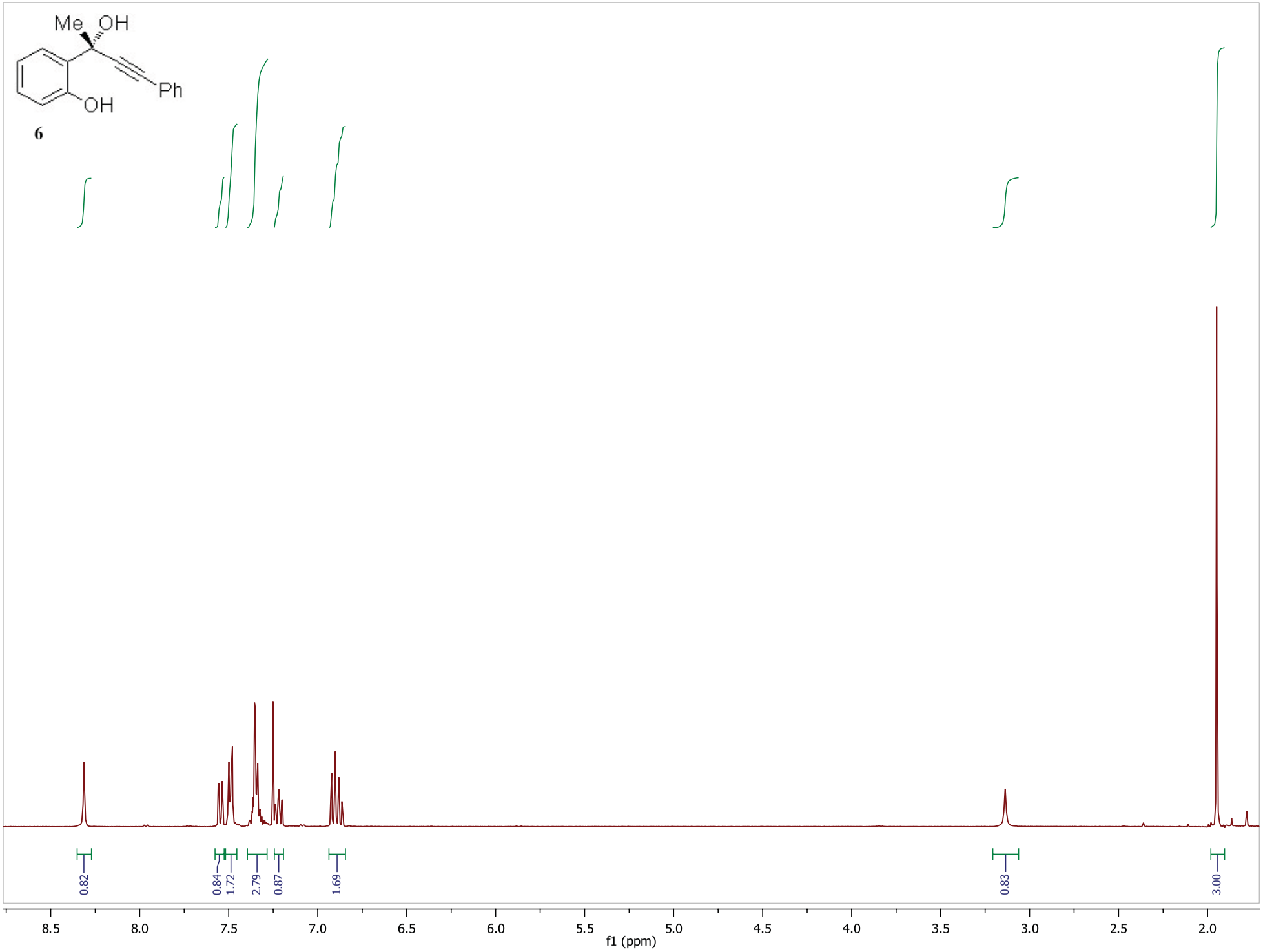
Table 3, Entry 7

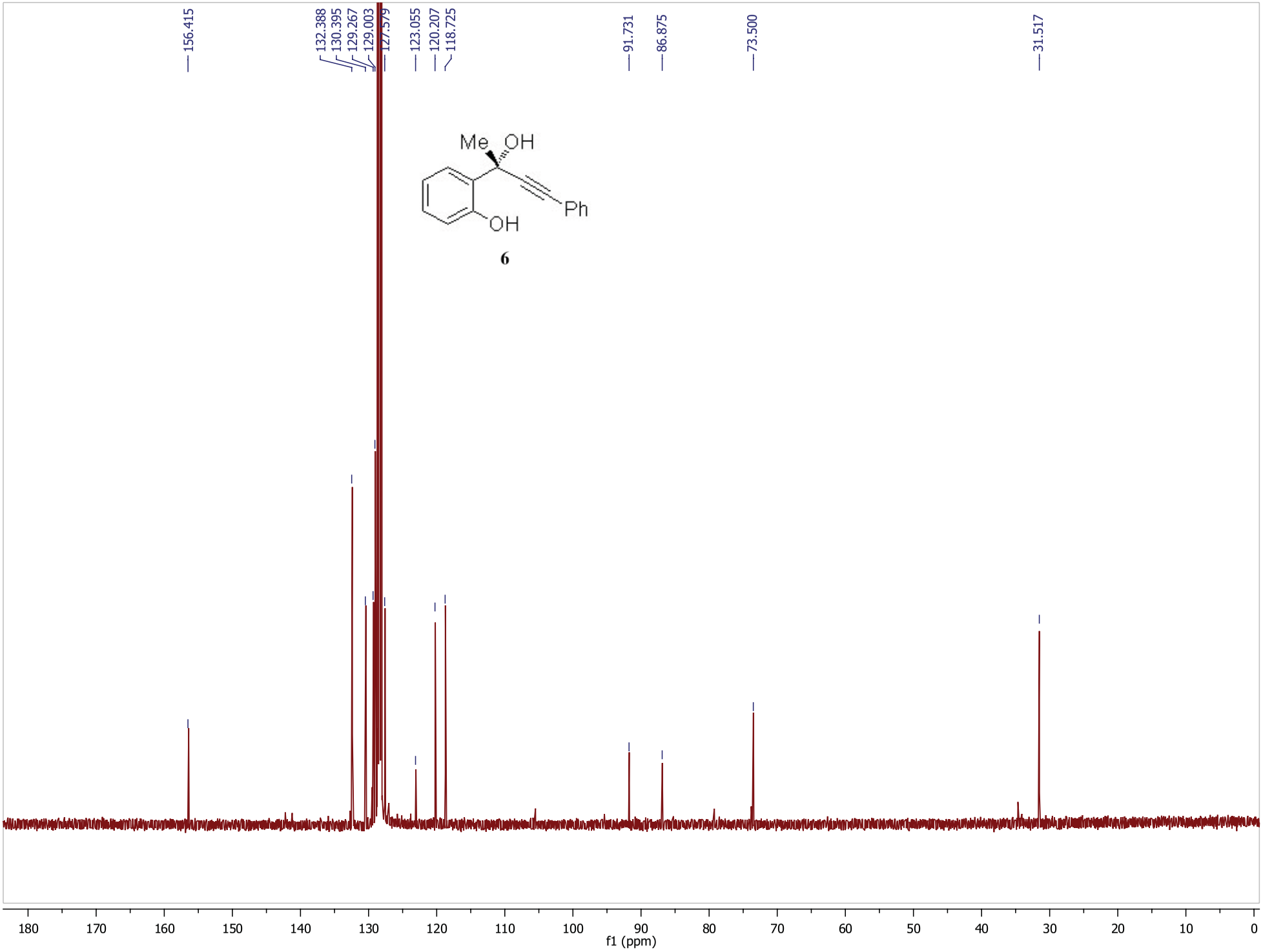


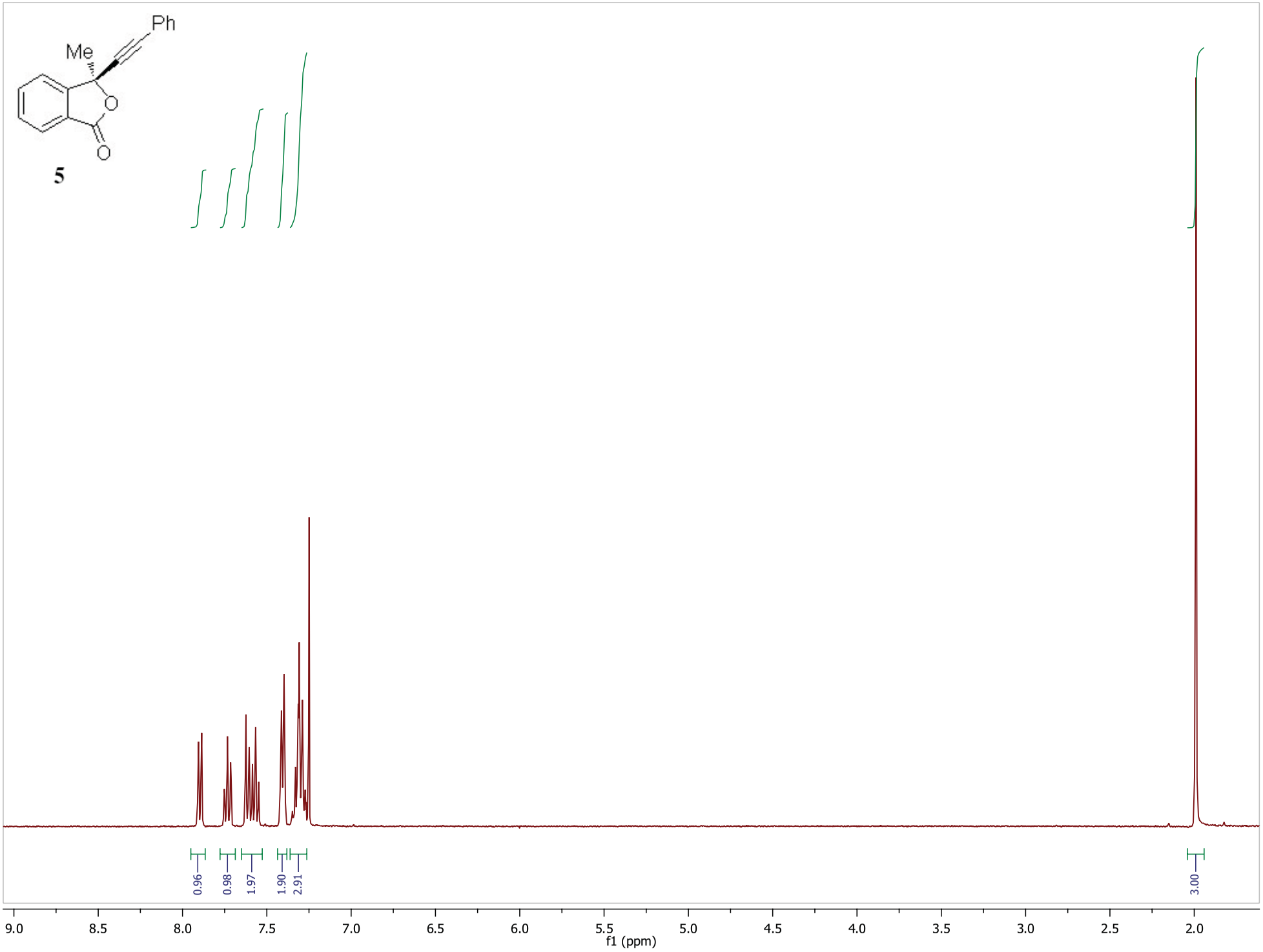

163.161
160.719
147.960
144.057
144.026
128.474
127.855
127.775
127.333
125.962
115.178
114.966
76.097
31.251
Table 3, Entry 7
Me
OH
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

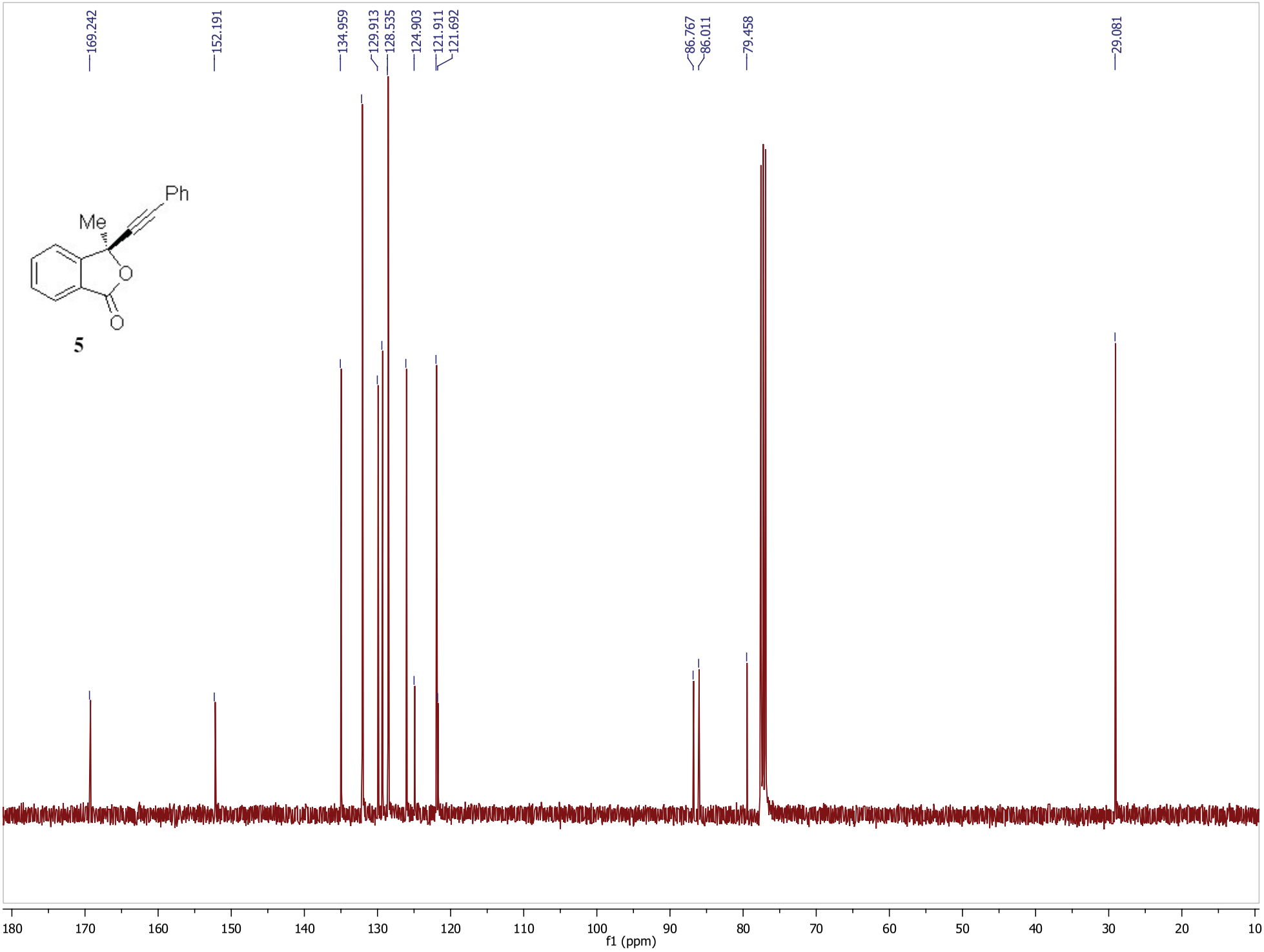

8.006
8.003
7.986
7.983
7.859
7.843
7.839
7.381
7.363
7.310
7.299
6.986
6.984
6.982
6.967
6.964
6.963
6.949
6.946
6.944
3.014
2.027
Me
OH
Ph
I
4
0.85
0.89
1.71
1.00
2.42
0.80
0.78
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

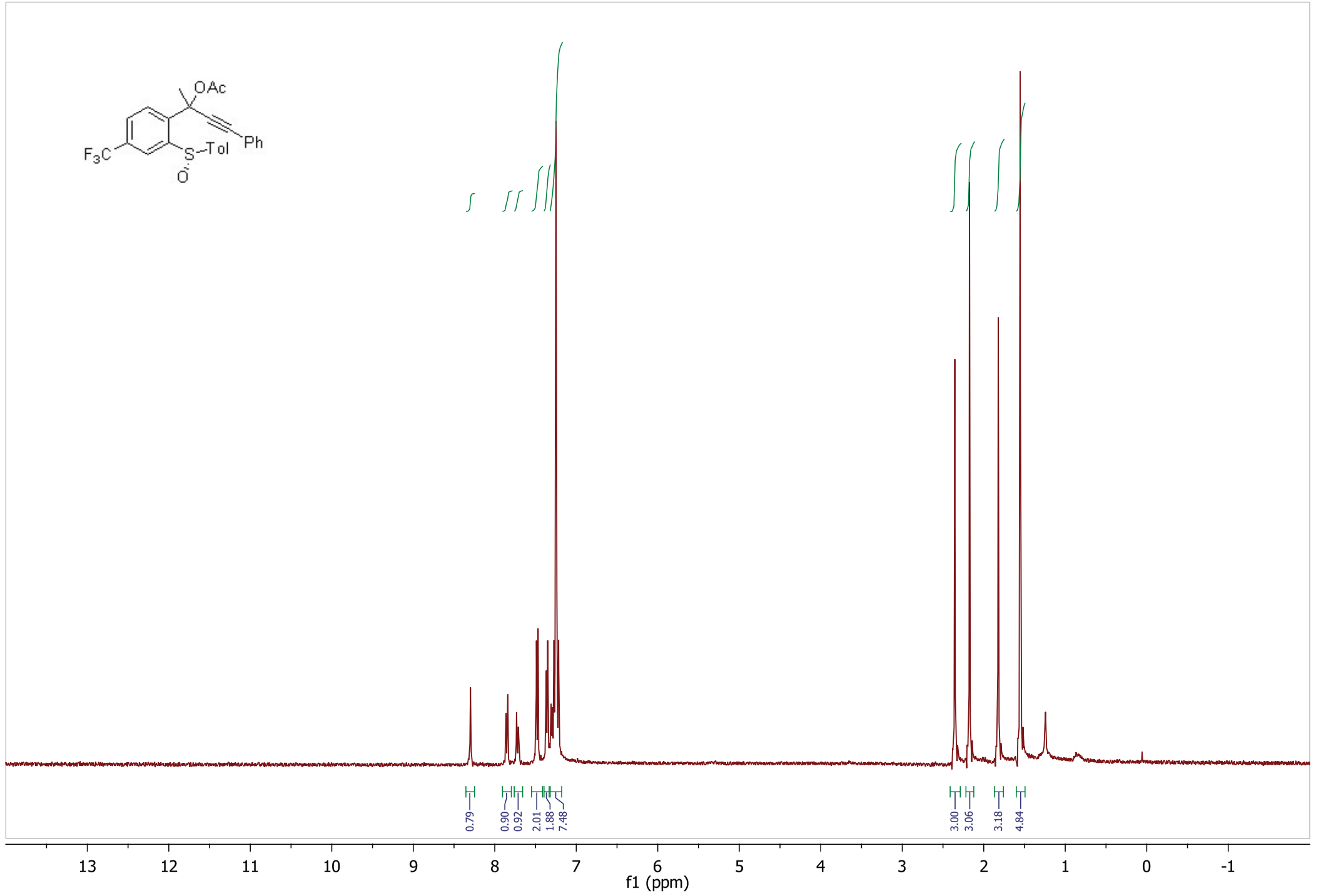

145.461
142.609
131.824
128.474
126.557
122.773
94.703
91.786
86.154
71.249
30.186
Me
OH
Ph
I
4
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

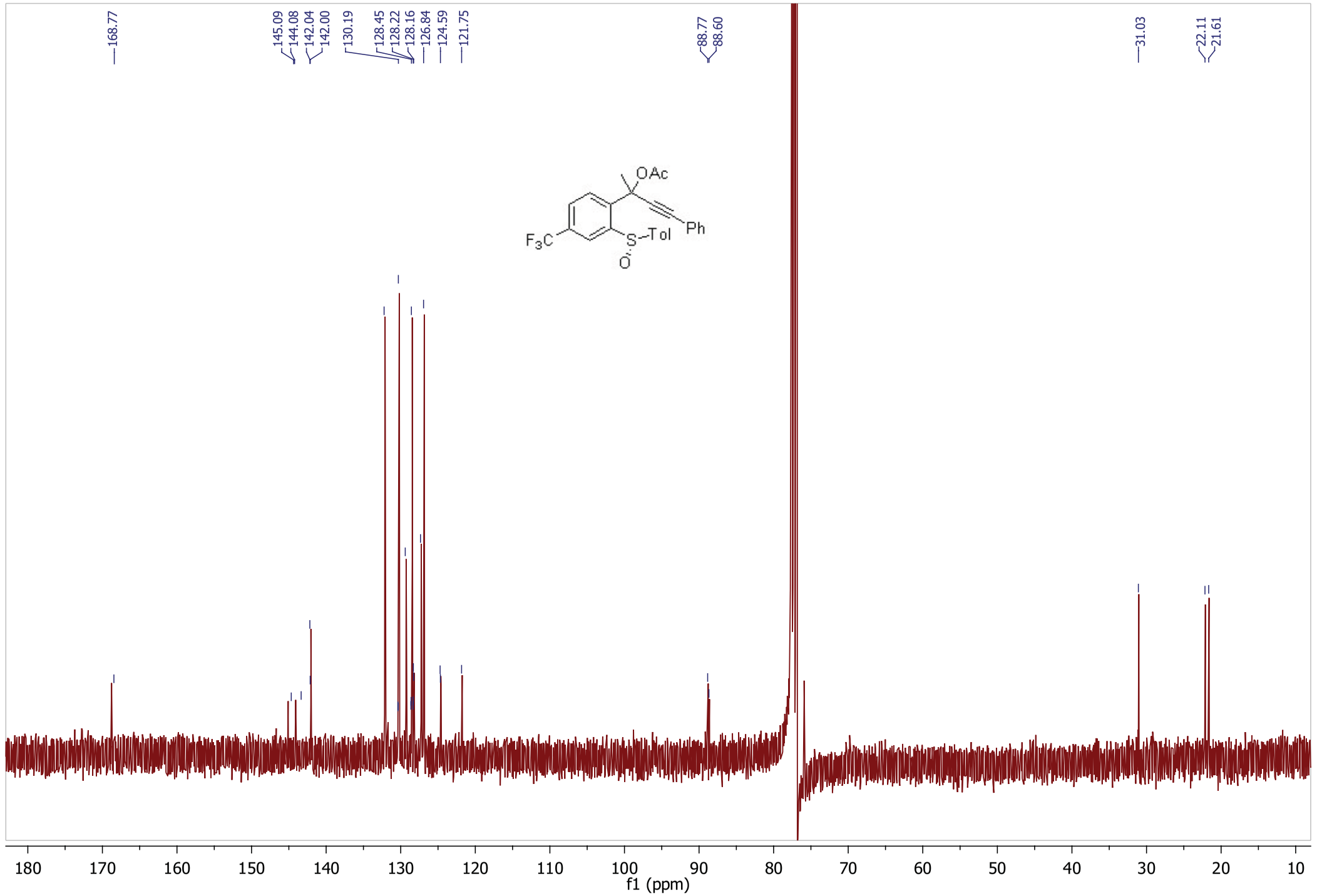

Me
OH
Ph
OH
6
0.82
0.84
1.72
2.79
0.87
1.69
0.83
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

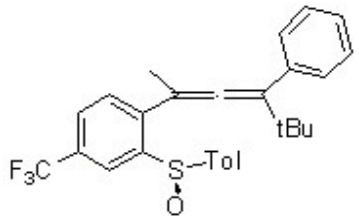

156.415
132.388
130.395
129.267
129.003
127.579
123.055
120.207
118.725
91.731
86.875
73.500
31.517
Me
OH
Ph
OH
6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Me
O
O
5
0.96
0.98
1.97
1.90
2.91
3.00
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
f1 (ppm)


169.242
152.191
134.959
129.913
128.535
124.903
121.911
121.692
86.767
86.011
79.458
29.081
Ph
Me
O
O
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

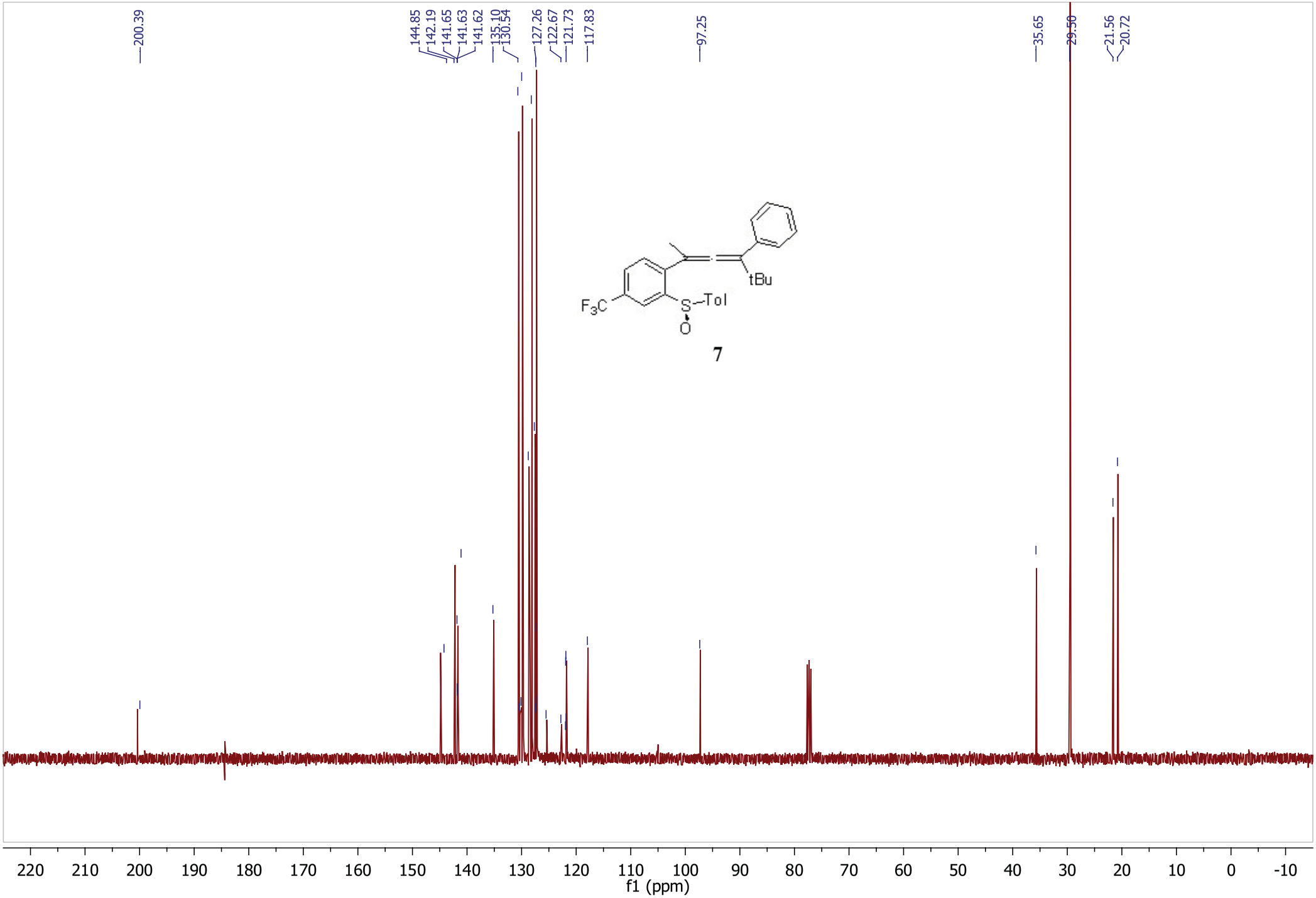

OAc
Ph
F3C
S
Tol
O
0.79
0.90
0.92
2.01
1.88
7.48
3.00
3.06
3.18
4.84
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


168.77
145.09
144.08
142.04
142.00
130.19
128.45
128.22
128.16
126.84
124.59
121.75
88.77
88.60
31.03
22.11
21.61
OAc
Ph
F3C
S
Tol
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


tBu
F3C
S
Tol
O

7

0.86
0.94
1.99
2.00
1.97
1.97
1.92
2.96
3.00
9.68
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)


200.39
144.85
142.19
141.65
141.63
141.62
135.10
130.54
127.26
122.67
121.73
117.83
97.25
35.65
29.50
21.56
20.72
tBu
F3C
S
Tol
O
7
220
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)

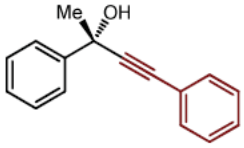
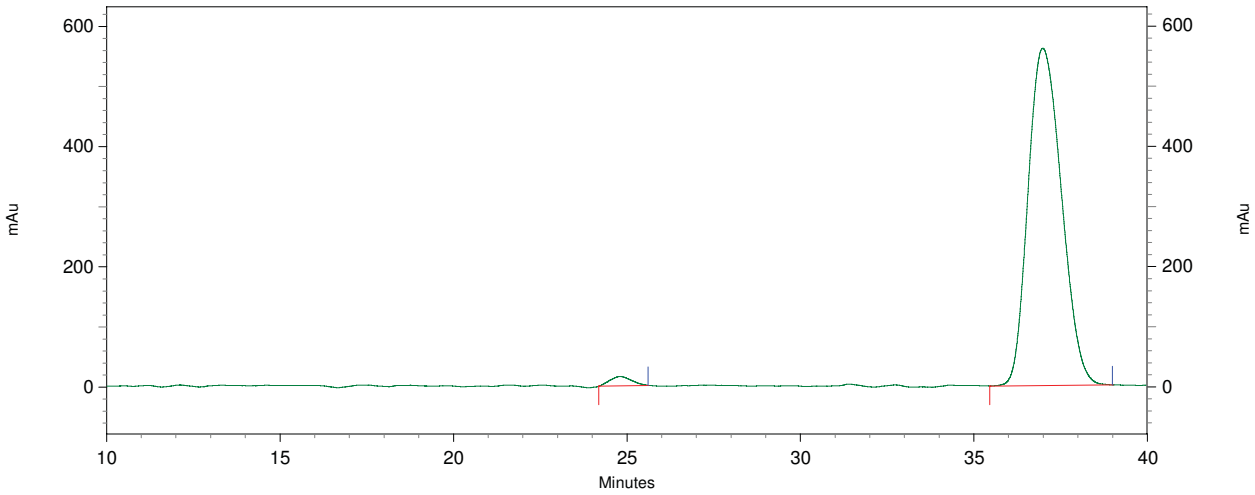
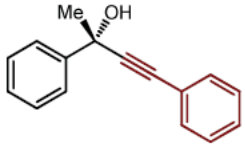


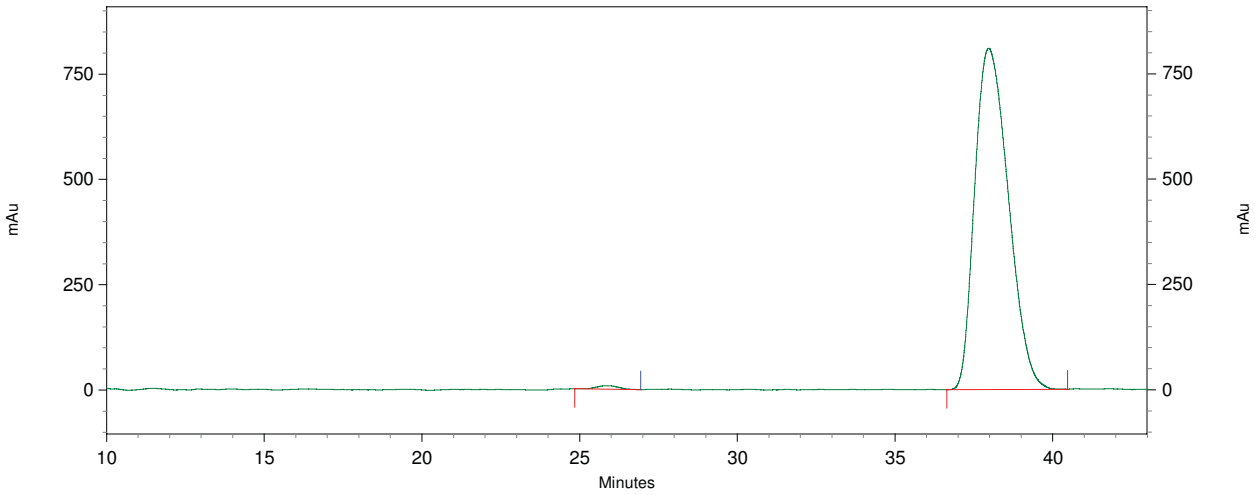
Table 3, Entry 1.



Retention Time	Height	Height Percent	Area	Area Percent
24.795	15667	2.716	677784	1.772
36.965	561103	97.284	37562276	98.228
Totals	576770	100.000	38240060	100.000

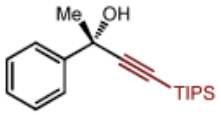
Table 3, Entry 1.

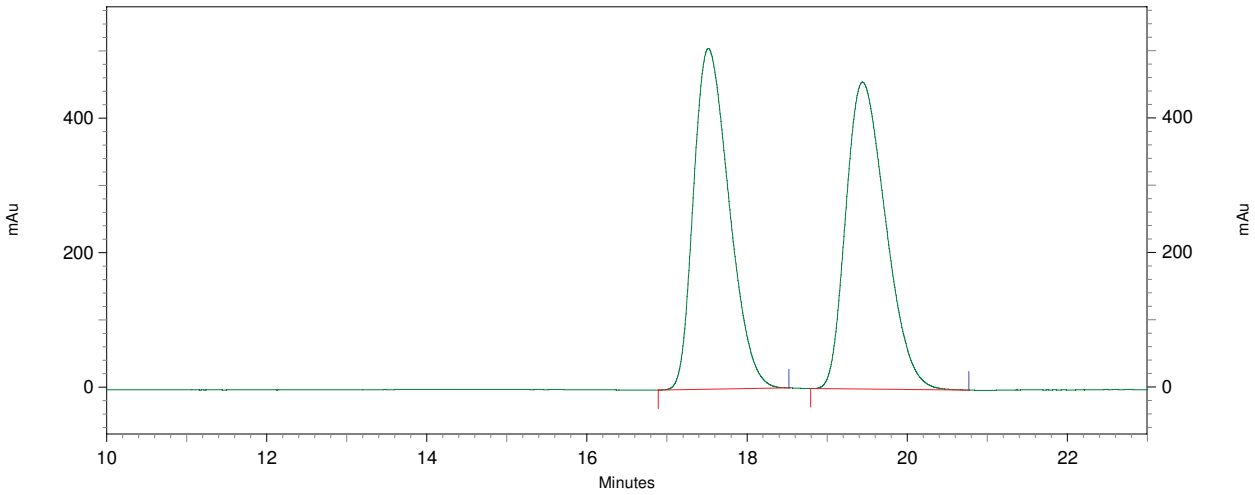




Retention Time	Height	Height Percent	Area	Area Percent
25.840	8021	0.980	398625	0.659
37.947	810362	99.020	60104042	99.341
Totals	818383	100.000	60502667	100.000

Table 3, Entry 2. Racemic.





Retention Time	Height	Height Percent	Area	Area Percent
17.509	506967	52.608	15597985	49.722
19.440	456695	47.392	15772101	50.278

Totals	963662	100.000	31370086	100.000

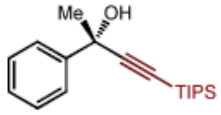
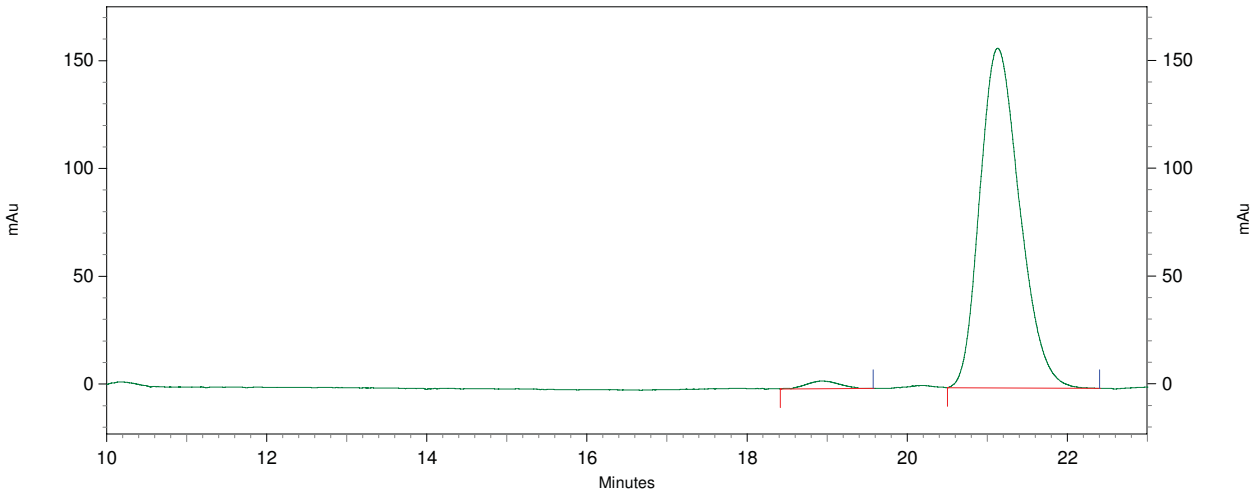
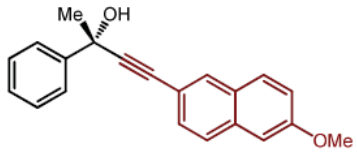


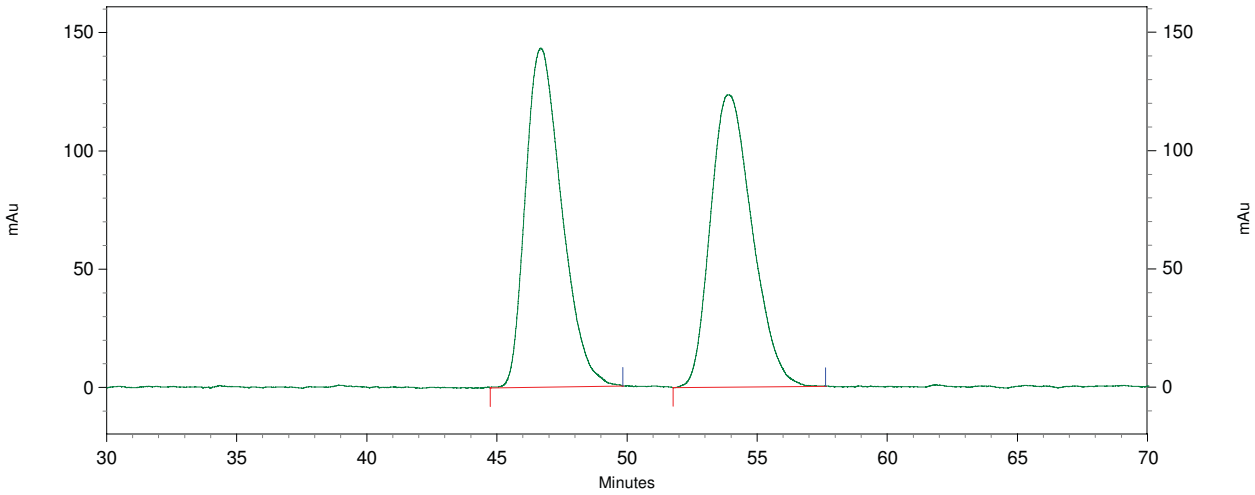
Table 3, Entry 2.



Retention Time	Height	Height Percent	Area	Area Percent
18.928	3614	2.242	104957	1.892
21.125	157595	97.758	5443252	98.108
Totals	161209	100.000	5548209	100.000

Table 3, Entry 3. Racemic.





Retention Time	Height	Height Percent	Area	Area Percent
46.667	143342	53.695	13857605	50.087
53.861	123612	46.305	13809663	49.913

Totals	266954	100.000	27667268	100.000

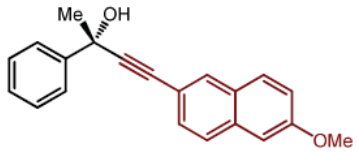
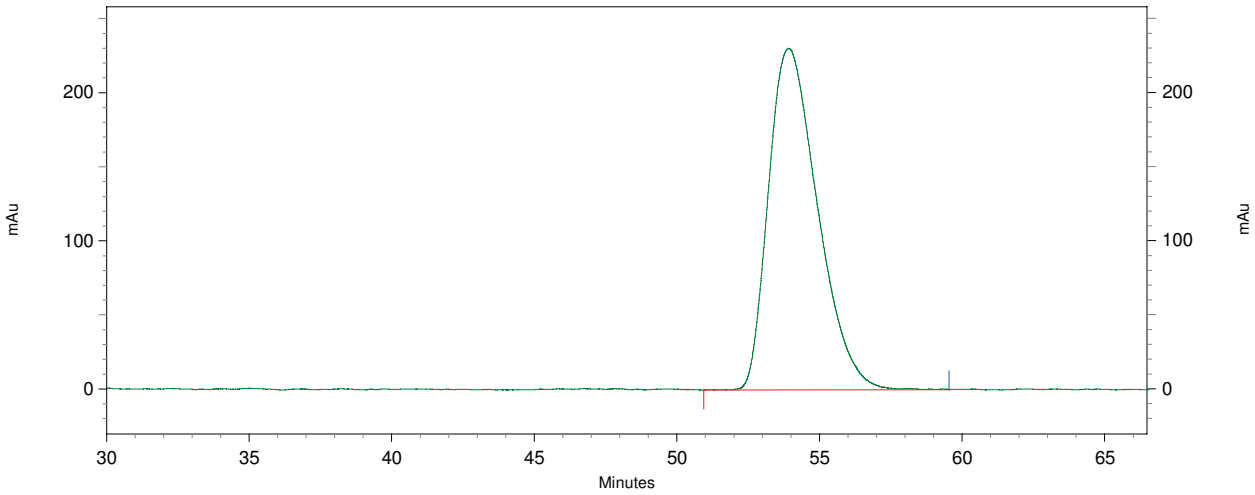


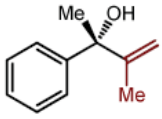
Table 3. Entry 3.

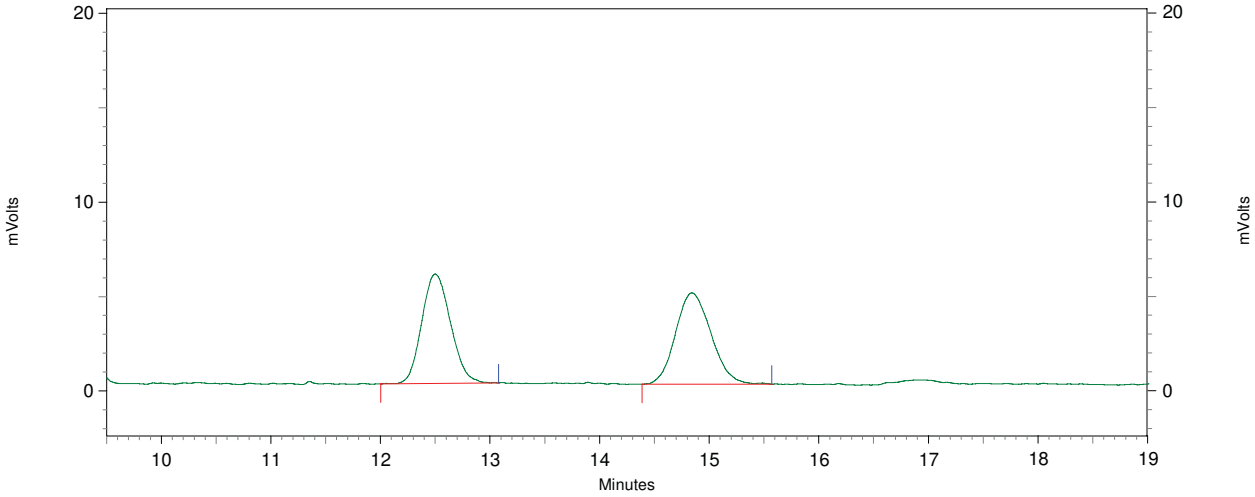


Retention Time	Height	Height Percent	Area	Area Percent
53.909	230608	100.000	27630078	100.000

Totals	230608	100.000	27630078	100.000

Table 3, Entry 4. Racemic.

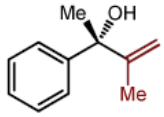


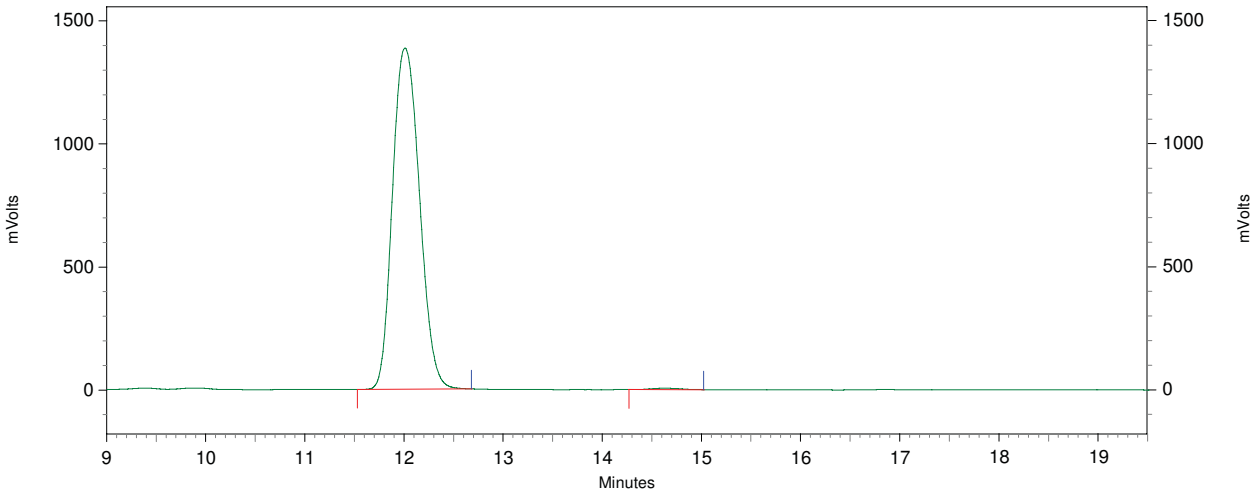


Retention Time	Height	Height Percent	Area	Area Percent
12.500	5789	54.500	105897	49.291
14.833	4833	45.500	108944	50.709

Totals	10622	100.000	214841	100.000

Table 3, Entry 4.





Retention Time	Height	Height Percent	Area	Area Percent
12.008	1386757	99.601	26258557	99.550
14.625	5551	0.399	118692	0.450

Totals				
	1392308	100.000	26377249	100.000

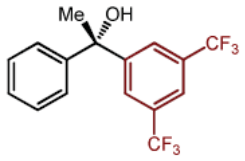
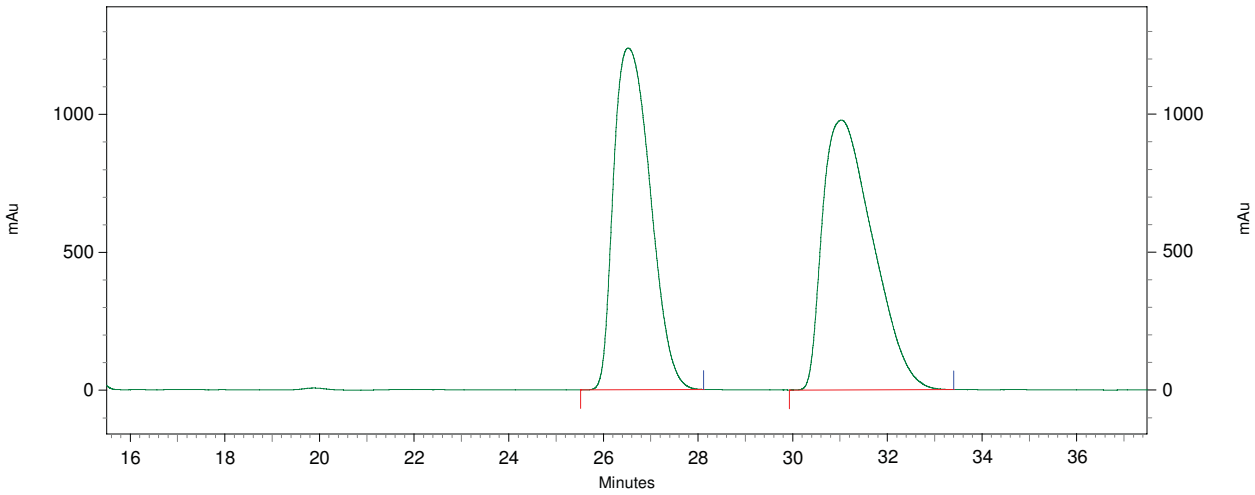


Table 3, Entry 5. Racemic.



Retention Time	Height	Height Percent	Area	Area Percent
26.523	1238669	55.875	66886811	48.121
31.019	978181	44.125	72110229	51.879
Totals	2216850	100.000	138997040	100.000

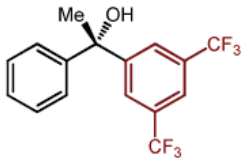
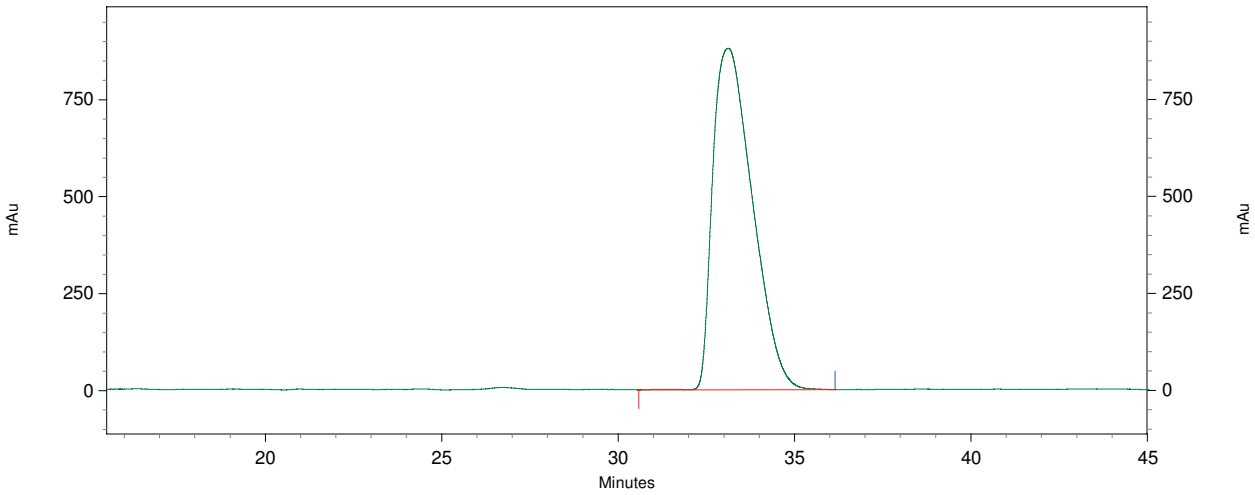


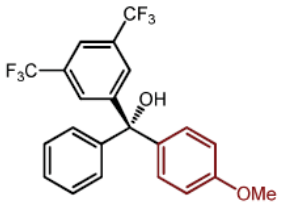
Table 3, Entry 5.

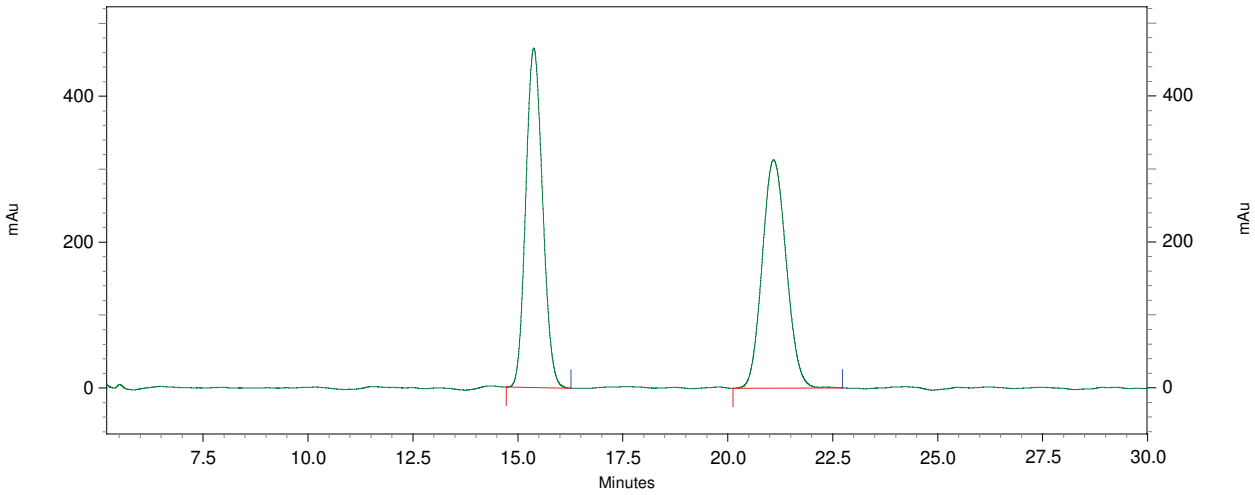


Retention Time	Height	Height Percent	Area	Area Percent
33.115	881008	100.000	68907435	100.000

Totals	881008	100.000	68907435	100.000

Table 3, Entry 6. Racemic.





Retention Time	Height	Height Percent	Area	Area Percent
15.371	465379	59.779	12982613	50.973
21.077	313123	40.221	12487019	49.027
Totals	778502	100.000	25469632	100.000

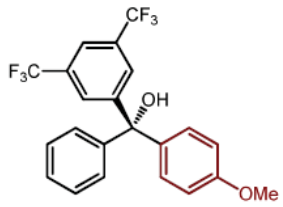
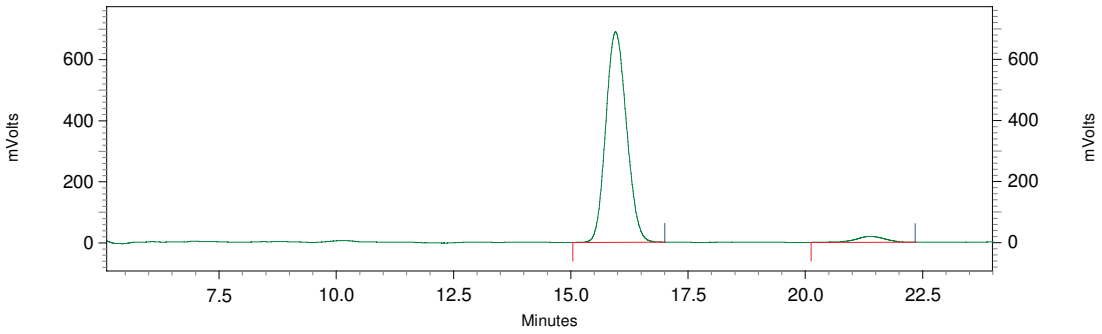


Table 3, Entry 6.



Retention Time	Area	Area %	Height	Height %
15.942	21157585	96.04	689110	97.25
21.367	871816	3.96	19522	2.75
Totals	22029401	100.00	708632	100.00

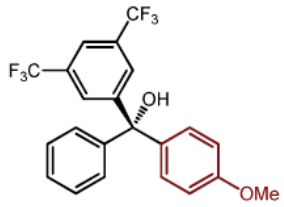
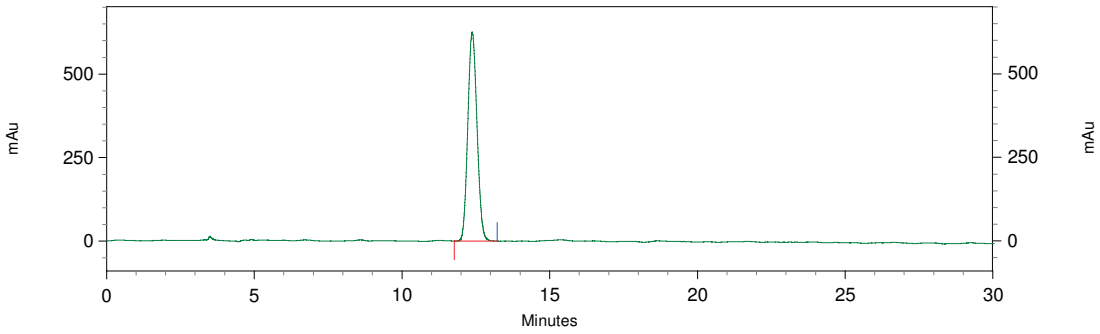


Table 3, Entry 6.



Retention Time	Area	Area %	Height	Height %
12.368	888152	100.00	41113	100.00

Totals	888152	100.00	41113	100.00

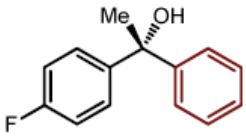
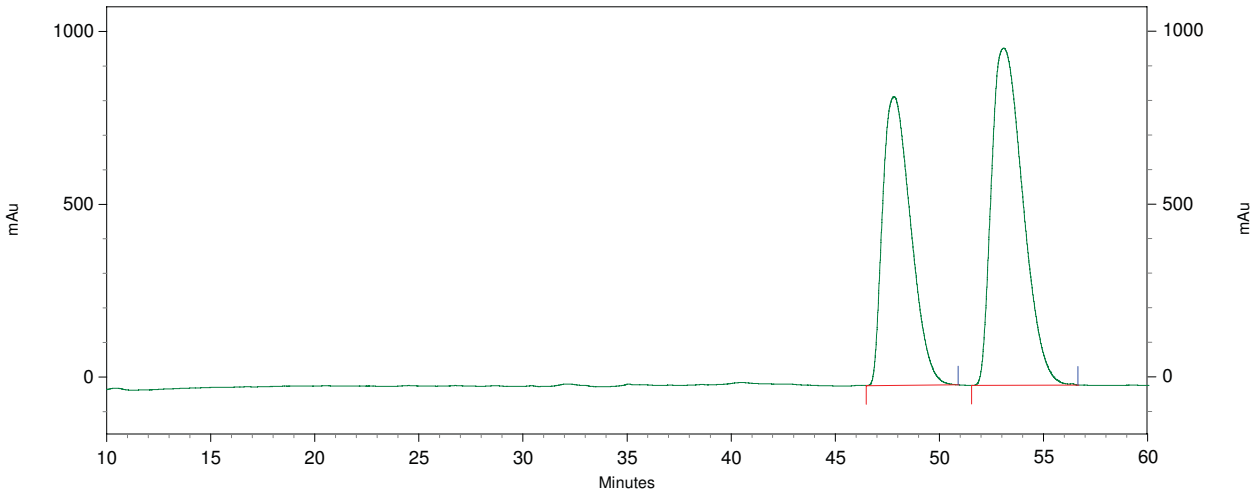


Table 3, Entry 7. Racemic.



Retention Time	Height	Height Percent	Area	Area Percent
47.797	835964	46.134	78423687	43.394
53.061	976081	53.866	102302670	56.606
Totals	1812045	100.000	180726357	100.000

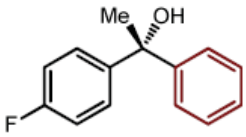
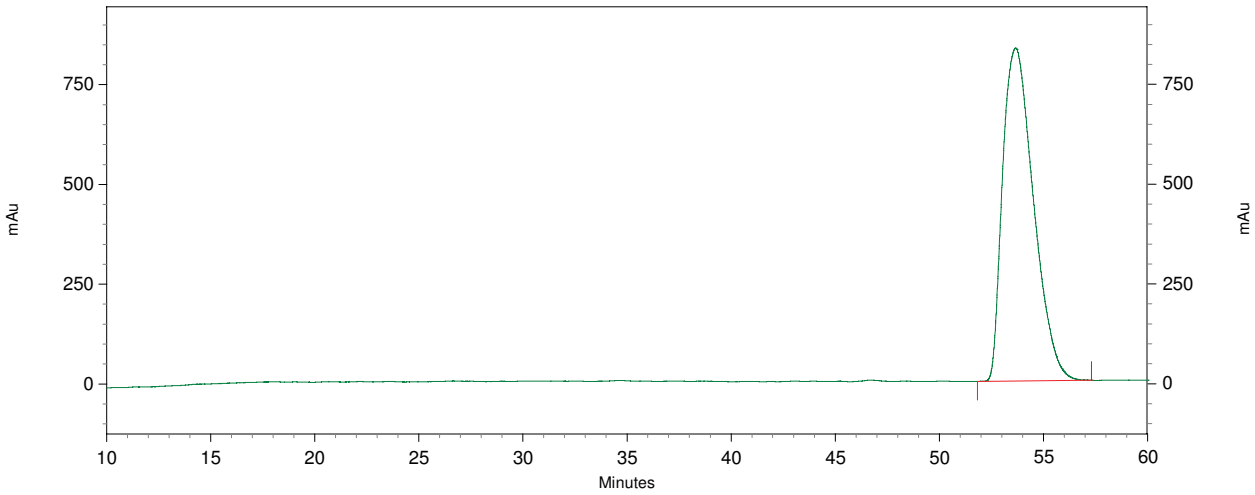


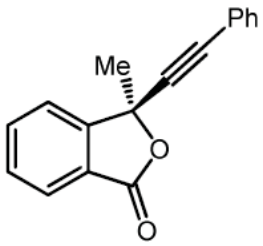
Table 3, Entry 7.

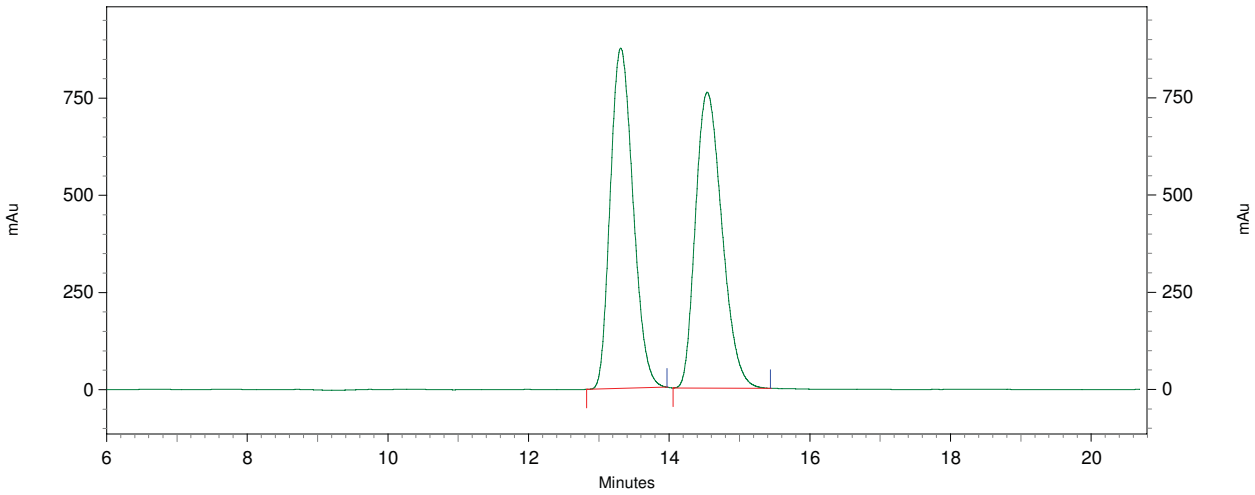


Retention Time	Height	Height Percent	Area	Area Percent
53.637	834651	100.000	86116497	100.000

Totals	834651	100.000	86116497	100.000

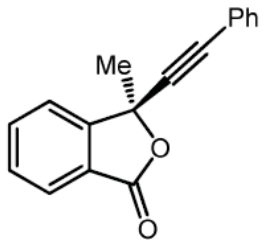
Scheme 1. Compound 5. Racemic.



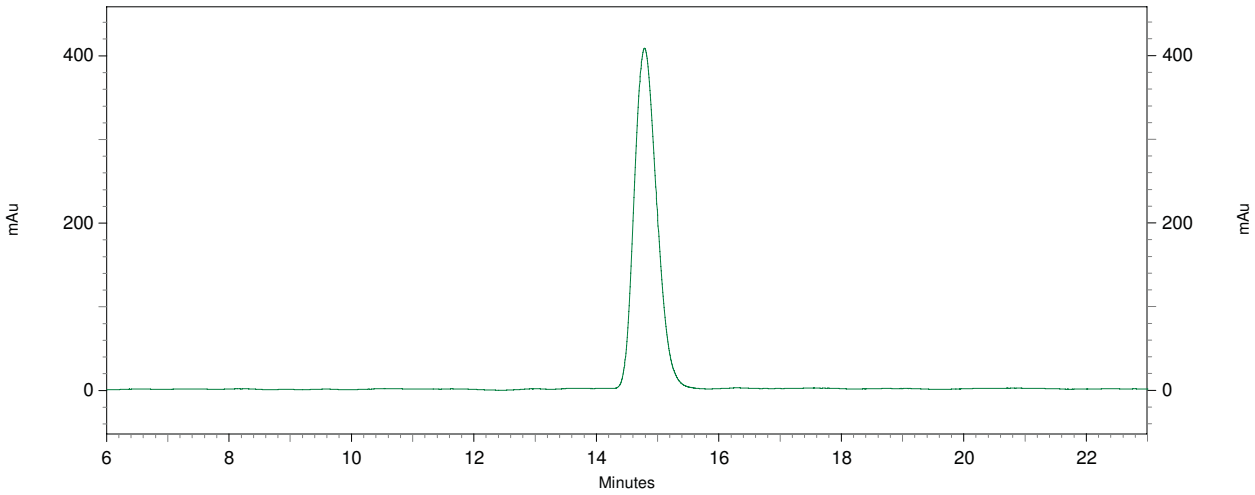


Retention Time	Height	Height Percent	Area	Area Percent
13.307	875834	53.496	19711809	49.729
14.533	761355	46.504	19926333	50.271

Totals	1637189	100.000	39638142	100.000



Scheme 1. Compound 5.



Retention Time	Height	Height Percent	Area	Area Percent
14.779	286503	100.000	7257075	100.000

Totals	286503	100.000	7257075	100.000