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Synthesis of Fluoroalkylated Alkynes via Visible Light Photocatalysis

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Supporting Information

General Considerations

General reagent information

fac-Ir(ppy)$_3$, [Ru(phen)$_3$]Cl$_2$, and acetonitrile (MeCN) were purchased from Sigma-Aldrich chemical company. Commercially available phenylacetylene derivatives were purchased from Sigma-Aldrich, Alfa Aesar, or TCI. Flash column chromatography was performed using ZEOCHEM ZEOprep silica gel 60 (60-200 mesh).

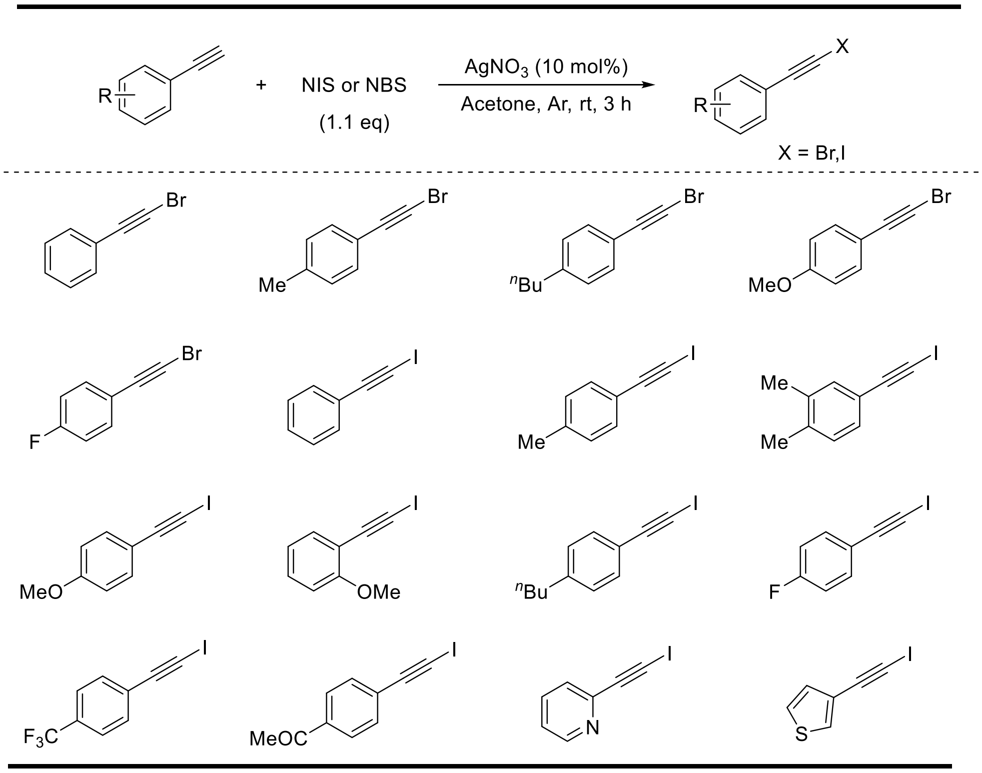
General analytical information

The synthesized fluoroalkylated alkyne compounds were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR) or a Varian 300 MHz instrument (300 MHz for ^{1}H NMR). Copies of ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. ^{19}F NMR spectra are reported in ppm, and all were taken composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 Thermo Scientific FT-IR spectrometer. Reactions were monitored by GC-MS of the crude reaction mixture using 2,2,2-trifluoroacetophenone as internal standard and products were detected by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector

Experimental Procedures

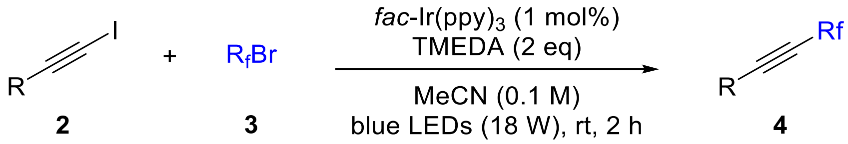
Synthesis of alkynyl halide derivatives

Alkynyl halide derivatives were prepared by following the reported procedures.[1]



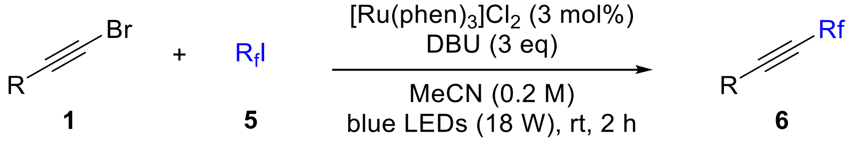
1. Y. Gao, G. Wu, Q. Zhou, and J. Wang, *Angew. Chem. Int. Ed.*, 2018, **57**, 2716 –2720.

Synthesis of difluoroalkylated alkynes (4)



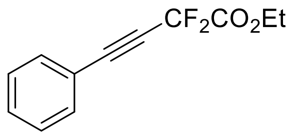
An oven-dried reaction tube, equipped with a magnetic stir bar, was charged with (Iodoethynyl)benzene derivatives **2** (1.5 mmol), and *fac*-Ir(ppy)$_3$ (0.01 mmol) in MeCN (10 mL), followed by the addition of *N*,*N*,*N*,*N*-tetramethylethylenediamine TMEDA (2 mmol). Then, the fluoroalkylating source **3** (1 mmol) was added to the reaction mixture, followed by stirring for 2 h at room temperature under visible-light irradiation. The reaction progress was monitored using TLC. After completion, the mixture was concentrated using a rotary evaporator and purified using silica gel flash column chromatography using a hexane-ethyl acetate mixture as the eluent to give the corresponding fluoroalkylated alkyne product **4**.

Synthesis of perfluoroalkylated alkynes (6)

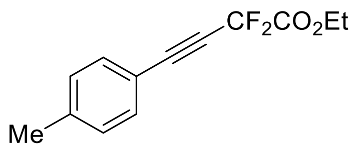


An oven-dried reaction tube, equipped with a magnetic stir bar, was charged with (bromoethynyl)benzene derivatives **1** (1.0 mmol), and $[Ru(phen)_3]Cl_2$ (0.03 mmol) in MeCN (5 mL), followed by the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene DBU (3 mmol). Then, the fluoroalkylating source **5** (2 mmol) was added to the reaction mixture, and it was stirred for 2 h at room temperature under visible-light irradiation, and the reaction progress was monitored using TLC. After completion, the mixture was concentrated using a rotary evaporator and purified using silica gel flash column chromatography using hexane as the eluent to give the corresponding fluoroalkylated alkyne product **6**.

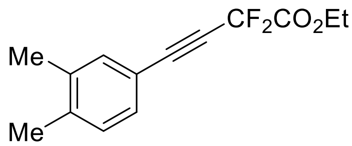
Analytic Data for Fluoroalkylated Alkynes



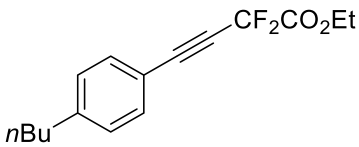
ethyl 2,2-difluoro-4-phenylbut-3-ynoate, **4a**: **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.78 (t, *J* = 34.5 Hz), 132.59, 130.72, 128.77, 119.59, 105.15 (t, *J* = 242.6 Hz), 89.85, 78.61(t, *J* = 37.8 Hz), 64.03, 14.11. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.98. **IR (neat):** ν_{max} = 2988, 2242, 1772, 1272, 1141, 1077, 757, 689 cm^{-1}; $\boldsymbol{R_f}$ = 0.53 (hex/EtOAc 9/1).



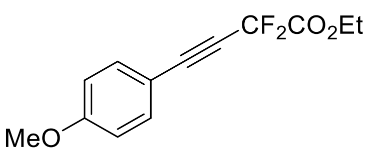
ethyl 2,2-difluoro-4-(*p*-tolyl)but-3-ynoate, **4b**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.85 (t, *J* = 34.7 Hz), 141.27, 132.49, 129.51, 116.47, 105.22 (t, *J* = 242.2 Hz), 90.26, 78.09 (t, *J* = 38.2 Hz), 63.96, 21.84, 14.09. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.69. **IR (neat):** ν_{max} = 2987, 2238, 1771, 1510, 1274, 1137, 1074, 816, 732, 532 cm^{-1}; $\boldsymbol{R_f}$ = 0.55 (hex/EtOAc 9/1).



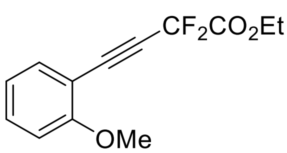
ethyl 4-(3,4-dimethylphenyl)-2,2-difluorobut-3-ynoate, **4c**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.91 (t, *J* = 34.7 Hz), 140.05, 137.27, 133.49, 130.07, 130.03, 116.73, 105.24 (t, *J* = 241.9 Hz), 90.49, 77.85 (t, *J* = 37.9 Hz), 63.94, 20.15, 19.72, 14.12. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.60. **IR (neat):** ν_{max} = 2983, 2231, 1770, 1500, 1272, 1183, 1075, 820, 729, 582 cm^{-1}; ***R_f*** = 0.57 (hex/EtOAc 9/1).



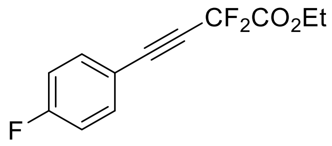
ethyl 4-(4-butylphenyl)-2,2-difluorobut-3-ynoate, **4d**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.59 (tt, *J* = 7.8, 7.4 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.34 (qt, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.85 (t, *J* = 34.7 Hz), 146.21, 132.51, 128.87, 116.64, 105.21 (t, *J* = 242.3 Hz), 90.30, 78.07 (t, *J* = 38.1 Hz), 63.94, 35.89, 33.43, 31.80, 22.46, 14.08. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.72. **IR (neat):** ν_{max} = 2962, 2240, 1774, 1275, 1141, 1077 cm^{-1}; ***R_f*** = 0.63 (hex/EtOAc 9/1).



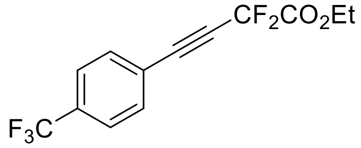
ethyl 2,2-difluoro-4-(4-methoxyphenyl)but-3-ynoate, **4e**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.40 (t, *J* = 7.1, Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.95 (t, *J* = 34.6 Hz), 161.50, 134.30, 114.44, 111.45, 110.24, 105.30 (t, *J* = 242.4 Hz), 90.34, 63.94, 55.61, 14.12. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.43. **IR (neat):** ν_{max} = 2987, 2235, 1770, 1605, 1510, 1252, 1074, 833 cm^{-1}; ***R_f*** = 0.34 (hex/EtOAc 9/1).



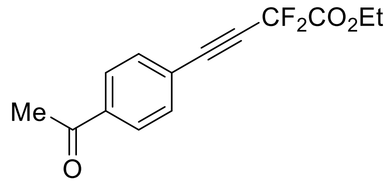
ethyl 2,2-difluoro-4-(2-methoxyphenyl)but-3-ynoate, **4f**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.45 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.38 (td, *J* = 8.4, 1.5 Hz, 1H), 6.91 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.26, 161.62 (t, *J* = 34.74 Hz), 134.42, 132.27, 120.62, 111.07, 108.82, 105.24 (t, *J* = 241.8 Hz), 86.97, 82.22 (t, *J* = 38.0 Hz), 63.83, 55.96, 14.03. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.70. **IR (neat):** ν_{max} = 2983, 2238, 1770, 1598, 1493, 1275, 1072, 752, 517 cm^{-1}; ***R_f*** = 0.34 (hex/EtOAc 9/1).



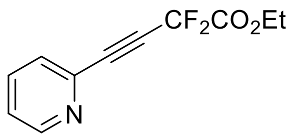
ethyl 2,2-difluoro-4-(4-fluorophenyl)but-3-ynoate, **4g**: colorless liquid; **^{1}H NMR (600 MHz, CDCl3)** δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (151 MHz, CDCl3)** δ 163.18 (t, *J* = 34.4 Hz), 134.85, 132.78, 116.37, 105.08 (t, *J* = 242.8 Hz), 88.79, 78.50 (t, *J* = 37.9 Hz), 64.07, 14.4. **^{19}F NMR (564 MHz, CDCl3)** δ -90.04, 106.78. **IR (neat):** ν_{max} = 2988, 2245, 1773, 1509, 1277, 1144, 1077, 838 cm^{-1}; ***R**$_f$* = 0.54 (hex/EtOAc 9/1).



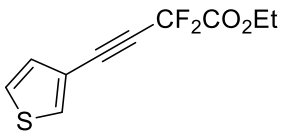
ethyl 2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-ynoate, **4h**: colorless liquid; **^{1}H NMR (600 MHz, CDCl3)** δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, CDCl3)** δ 161.44 (t, *J* = 34.2 Hz), 132.93, 132.48, 125.76, 124.30. 123.32, 104.91 (t, *J* = 243.5 Hz), 87.88, 80.54 (t, *J* = 37.9 Hz), 64.22, 14.09. **^{19}F NMR (564 MHz, CDCl3)** δ -63.24, -90.61. **IR (neat):** ν_{max} = 2988, 2248, 1773, 1321, 1275, 1129, 1060, 843, 741 cm^{-1}; ***R**$_f$* = 0.52 (hex/EtOAc 9/1).



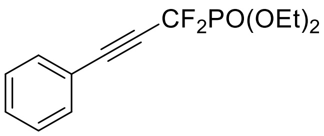
ethyl 4-(4-acetylphenyl)-2,2-difluorobut-3-ynoate, **4i**: White solid; **^{1}H NMR (600 MHz, CDCl3)** δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, CDCl3)** δ 197.17, 161.47 (d, *J* = 68.4 Hz), 138.30, 132.80, 128.50, 124.05, 104.95 (t, *J* = 243.4 Hz), 88.47, 81.04 (t, *J* = 38.6 Hz), 64.19, 26.89, 14.11. **^{19}F NMR (564 MHz, CDCl3)** δ -90.47. **IR (neat):** ν_{max} = 2987, 2244, 1771, 1687, 1260, 1068, 702, 592 cm^{-1}; ***R**$_f$* = 0.46 (hex/EtOAc 9/1).



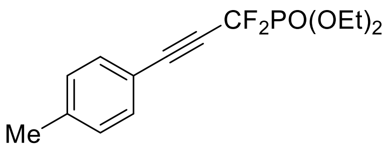
ethyl 2,2-difluoro-4-(pyridin-2-yl)but-3-ynoate, **4j**: colorless liquid; **^{1}H NMR (600 MHz, CDCl3)** δ 8.65 (d, *J* = 4.7 Hz, 1H), 7.73 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 7.7, 4.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, CDCl3)** δ 161.30 (t, *J* = 34.0 Hz), 150.69, 136.61, 128.48, 127.68, 124.96, 104.82 (t, *J* = 243.7 Hz), 87.82, 77.59, 64.22, 14.08.**^{19}F NMR (564 MHz, CDCl3)** δ -90.97. **IR (neat):** ν_{max} = 2988, 2250, 1773, 1463, 1275, 1150, 1082, 780 cm^{-1}; ***R**$_f$* = 0.24 (hex/EtOAc 4/1).



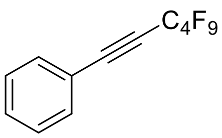
ethyl 2,2-difluoro-4-(thiophen-3-yl)but-3-ynoate, **4k**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 3.0 Hz, 1H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.19 (d, *J* = 5.0, Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 161.73 (t, *J* = 34.5 Hz), 132.86, 129.94, 126.33, 118.69, 105.16 (t, *J* = 242.7 Hz), 85.32, 78.44 (t, *J* = 38.2 Hz), 64.03, 14.09. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -89.83. **IR (neat):** ν_{max} = 2987, 2241, 1770, 1258, 1132, 1073, 787, 700, 625 cm^{-1}; $\boldsymbol{R_f}$ = 0.44 (hex/EtOAc 9/1).



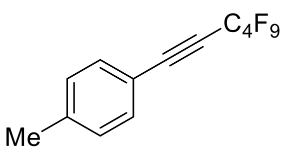
diethyl (1,1-difluoro-3-phenylprop-2-yn-1-yl)phosphonate, **4l**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.5 Hz, 2H), 4.39-4.30 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 132.45, 130.63, 128.72, 119.65, 110.44 (t, *J* = 253.3 Hz), 97.75, 78.61 (t, *J* = 33.4 Hz), 65.63, 16.56 **^{19}F NMR (564 MHz, $CDCl_3$)** δ -96.45. **IR (neat):** ν_{max} = 2987, 2236, 1274, 1116, 1031, 758, 690, 574 cm^{-1}; $\boldsymbol{R_f}$ = 0.51 (hex/EtOAc 3/2).



diethyl (1,1-difluoro-3-(p-tolyl)prop-2-yn-1-yl)phosphonate, **4m**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.41-4.32 (m, 4H), 2.38 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.22, 132.45, 129.53, 116.66, 110.4 (t, *J* = 229.7 Hz), 109.04, 92.22, 65.64, 21.88, 16.62. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -96.02. **IR (neat):** ν_{max} = 2987, 2234, 1510, 1277, 1115, 1036, 817, 574 cm^{-1}; $\boldsymbol{R_f}$ = 0.21 (hex/EtOAc 4/1).

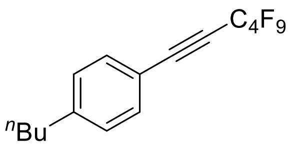


6a: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.8,7.5 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 132.72, 131.32, 128.91, 118.76, 92.59, 74.89. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.15, -97.49, -123.49, -125.51. **IR (neat):** ν_{max} = 2988, 2247, 1352, 1236, 1133, 908, 731, 534 cm^{-1}; $\boldsymbol{R_f}$ = 0.73 (hexane).

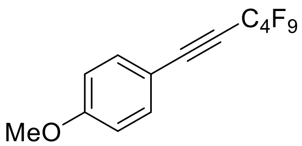


6b: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **13C NMR (151**

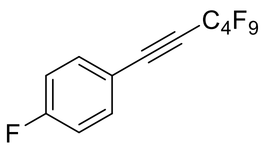
MHz, CDCl$_3$) δ 142.02, 132.65, 129.66, 115.67, 93.02, 74.42, 21.87. (carbon peaks of –C_4F_9– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.15, -97.15, -123.47, -125.50. **IR (neat):** ν_{max} = 2971, 2244, 1511, 1233, 1131, 884, 815, 719, 533 cm^{-1}; ***R$_f$*** = 0.73 (hexane).



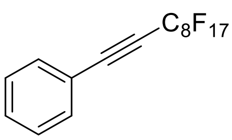
6c: colorless liquid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.62 (tt, *J* = 7.8, 7.4 Hz, 2H), 1.37 (qt, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 146.99, 132.70, 129.04, 115.88, 93.12, 74.43, 36.01, 33.48, 22.52, 14.03. (carbon peaks of –C_4F_9– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.19, -97.18, -123.51, -125.53. **IR (neat):** ν_{max} = 2935, 2244, 1352, 1233, 1132, 884, 742, 537 cm^{-1}; ***R$_f$*** = 0.77 (hexane).



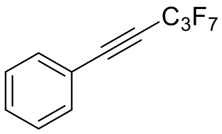
6d: colorless liquid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.50 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 161.99, 134.48, 114.59, 110.55, 93.19, 73.98, 55.62. (carbon peaks of –C_4F_9– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.12, -96.82, -123.43, -125.48. **IR (neat):** ν_{max} = 2970, 2240, 1607, 1512, 1232, 1129, 1031, 884, 831, 735,537 cm^{-1}; ***R$_f$*** = 0.34 (hexane).



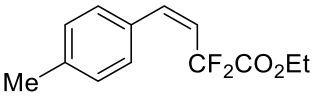
6e: colorless liquid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.57 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 163.39, 134.8, 116.5, 114.81, 91.52, 74.80. (carbon peaks of –C_4F_9– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.04, -97.55, -105.62, -123.41, -125.46. **IR (neat):** ν_{max} = 2971, 2249, 1604, 1509, 1232, 1131, 885, 837, 738, 534 cm^{-1}; ***R$_f$*** = 0.71 (hexane).



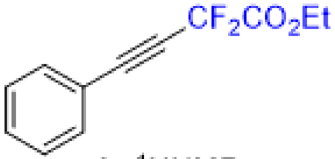
6f: colorless liquid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.5 Hz, 7.7 Hz, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 132.72, 131.30, 128.90, 128.42, 92.50, 74.97. (carbon peaks of –C_8F_{17}– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.87, -97.15, -121.12, -121.86, -121.95, -122.49, -122.77, -126.18. **IR (neat):** ν_{max} = 2987, 2246, 1724, 1407, 1210, 1147, 1066, 756, 659 cm^{-1}; ***R$_f$*** = 0.78 (hexane).



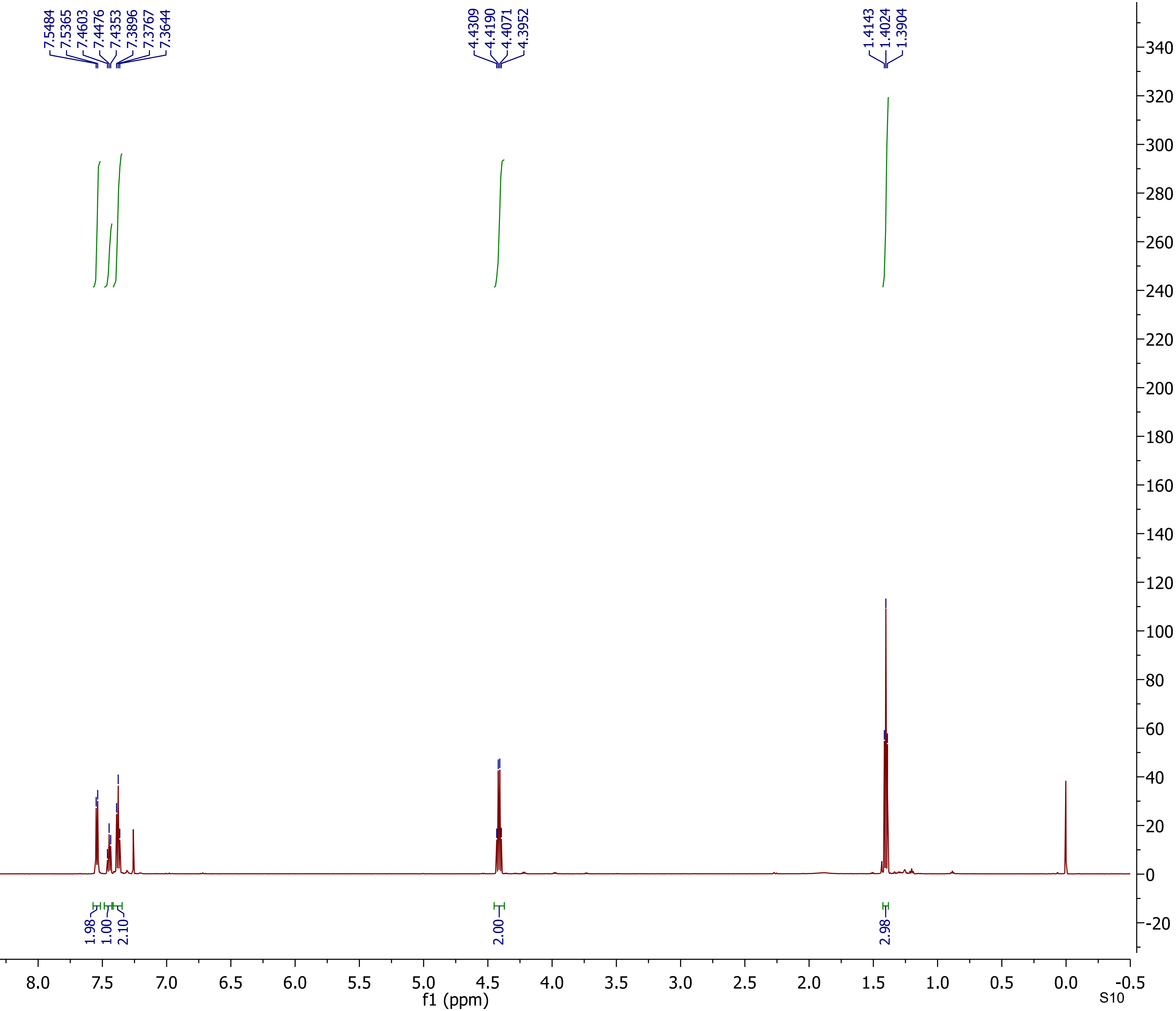
6g: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.5, 7.7 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 132.73, 131.31, 128.91, 118.74, 92.50, 74.75. (carbon peaks of –C_3F_7– are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.19, -98.24, -126.92. **IR (neat):** ν_{max} = 2987, 2242, 1228, 1066, 906, 651 cm^{-1}; ***R_f*** = 0.79 (hexane).



ethyl (Z)-2,2-difluoro-4-(p-tolyl)but-3-enoate**, 4bb**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 12.6 Hz, 1H), 5.81 (d, *J* = 12.6 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.32, 163.72 (t, *J* = 33.9 Hz), 138.95, 131.62, 129.22, 129.12, 121.27 (t, *J* = 27.9 Hz), 112.60 (t, *J* = 245.9 Hz), 63.08, 22.88, 14.32. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -94.11. **IR (neat):** ν_{max} = 2987, 1767, 1647, 1514, 1307, 1151, 1069, 789 cm^{-1}; ***R_f***= 0.45 (hex/EtOAc 9/1).



4a [1]HNMR



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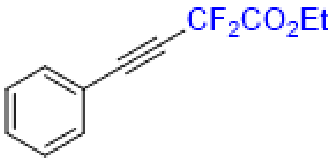
2.98
f1 (ppm)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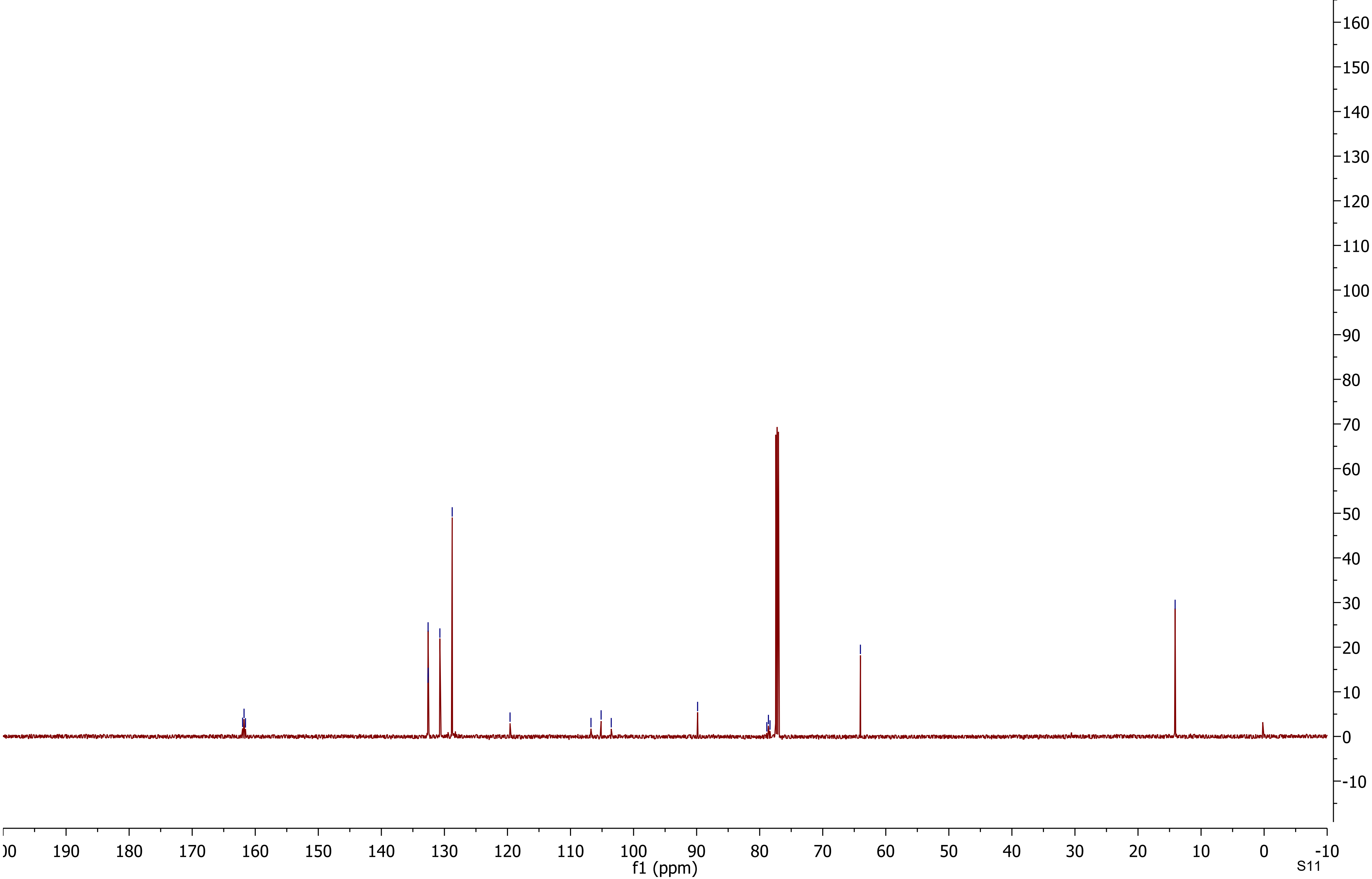
4a ^{13}CNMR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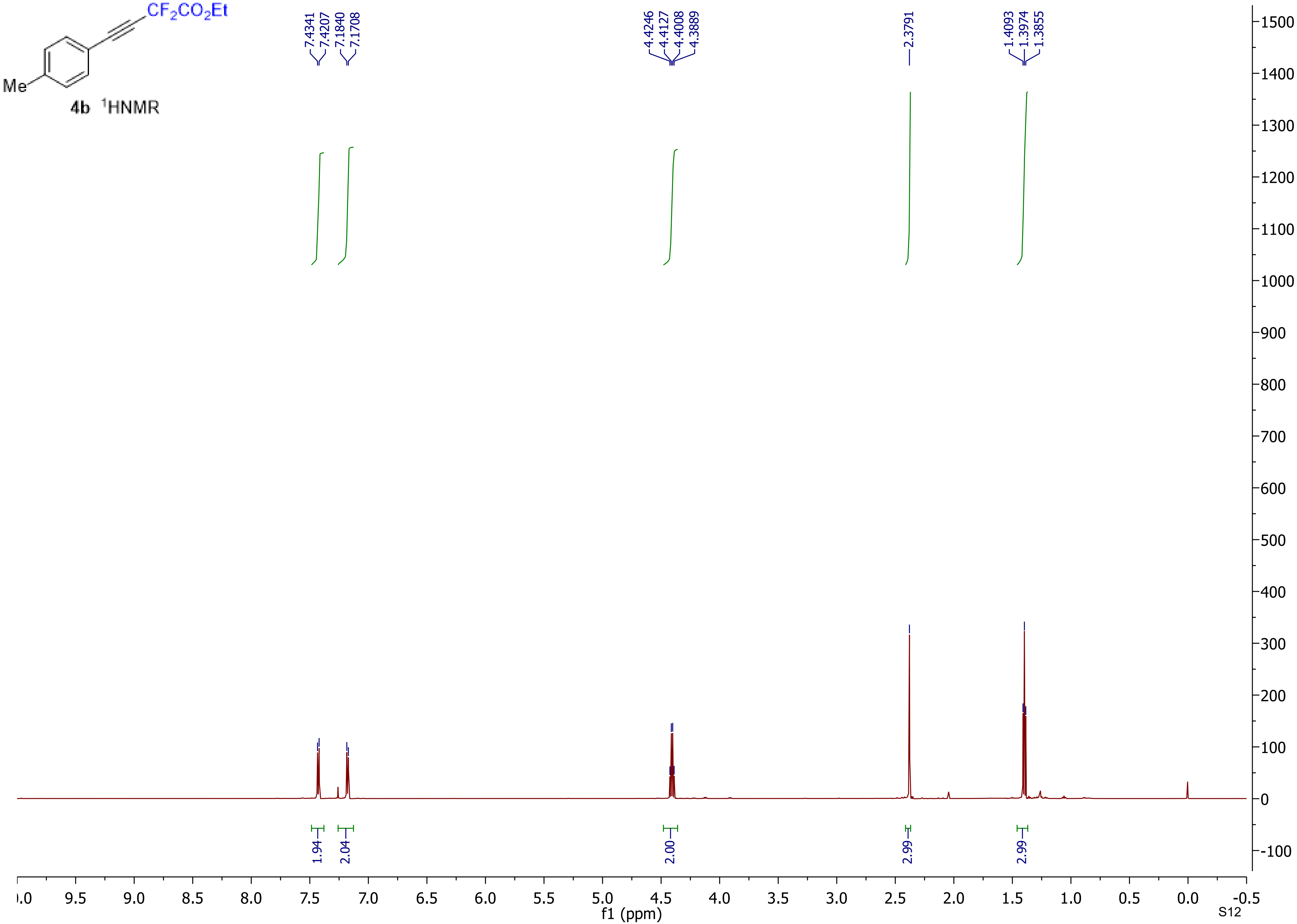
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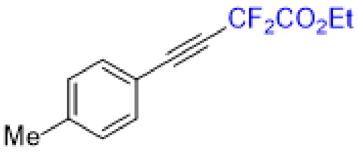
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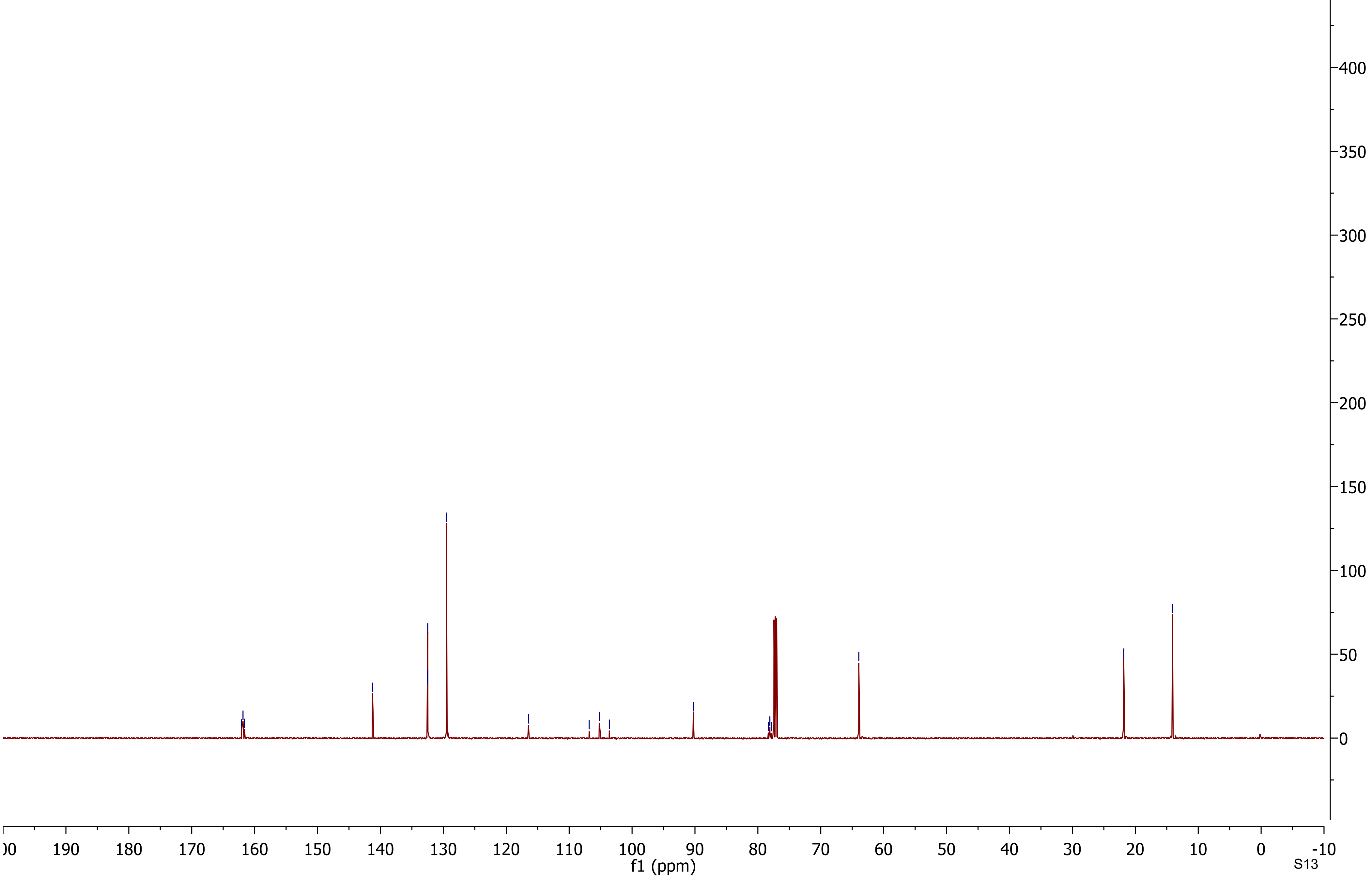
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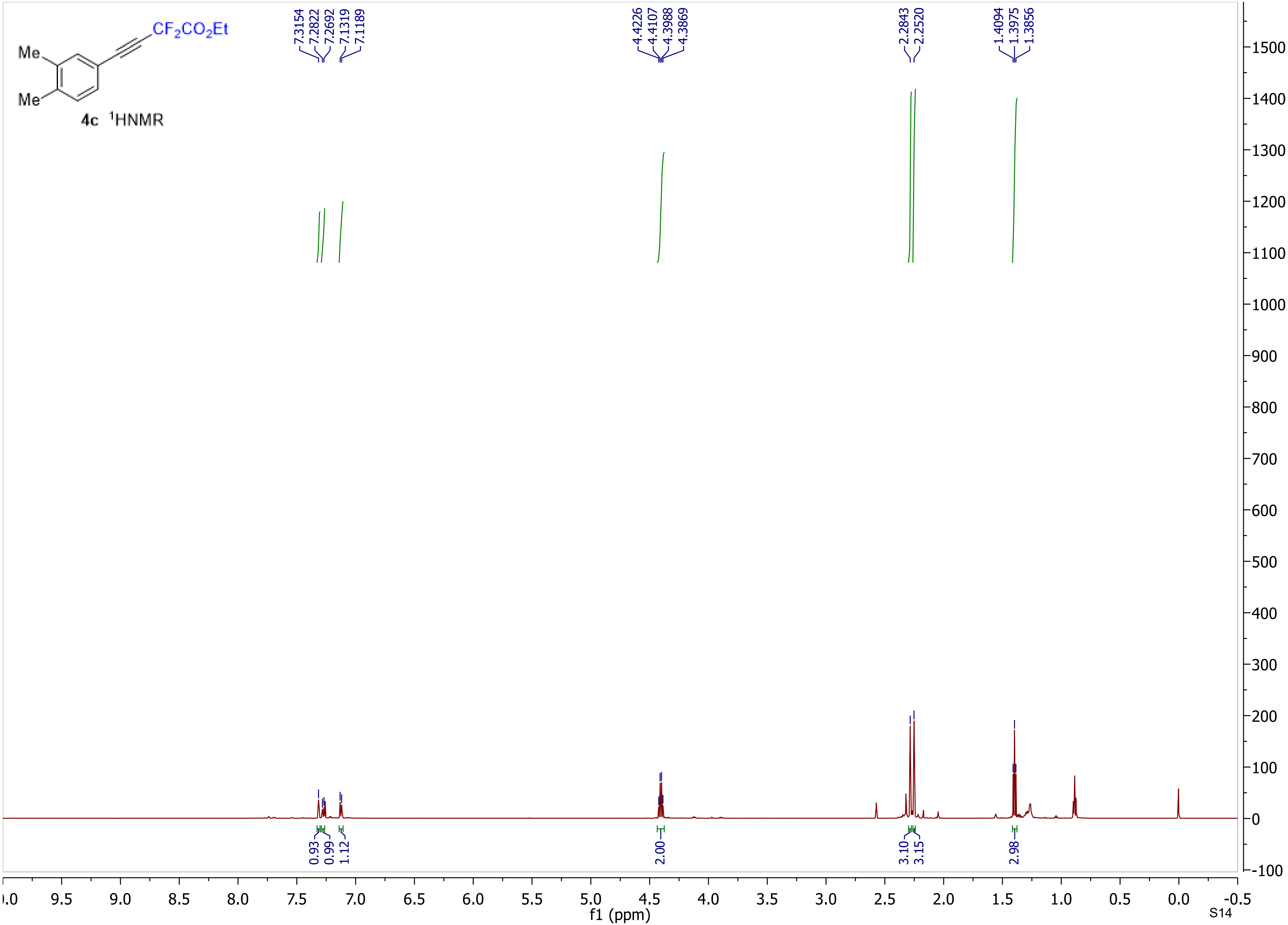
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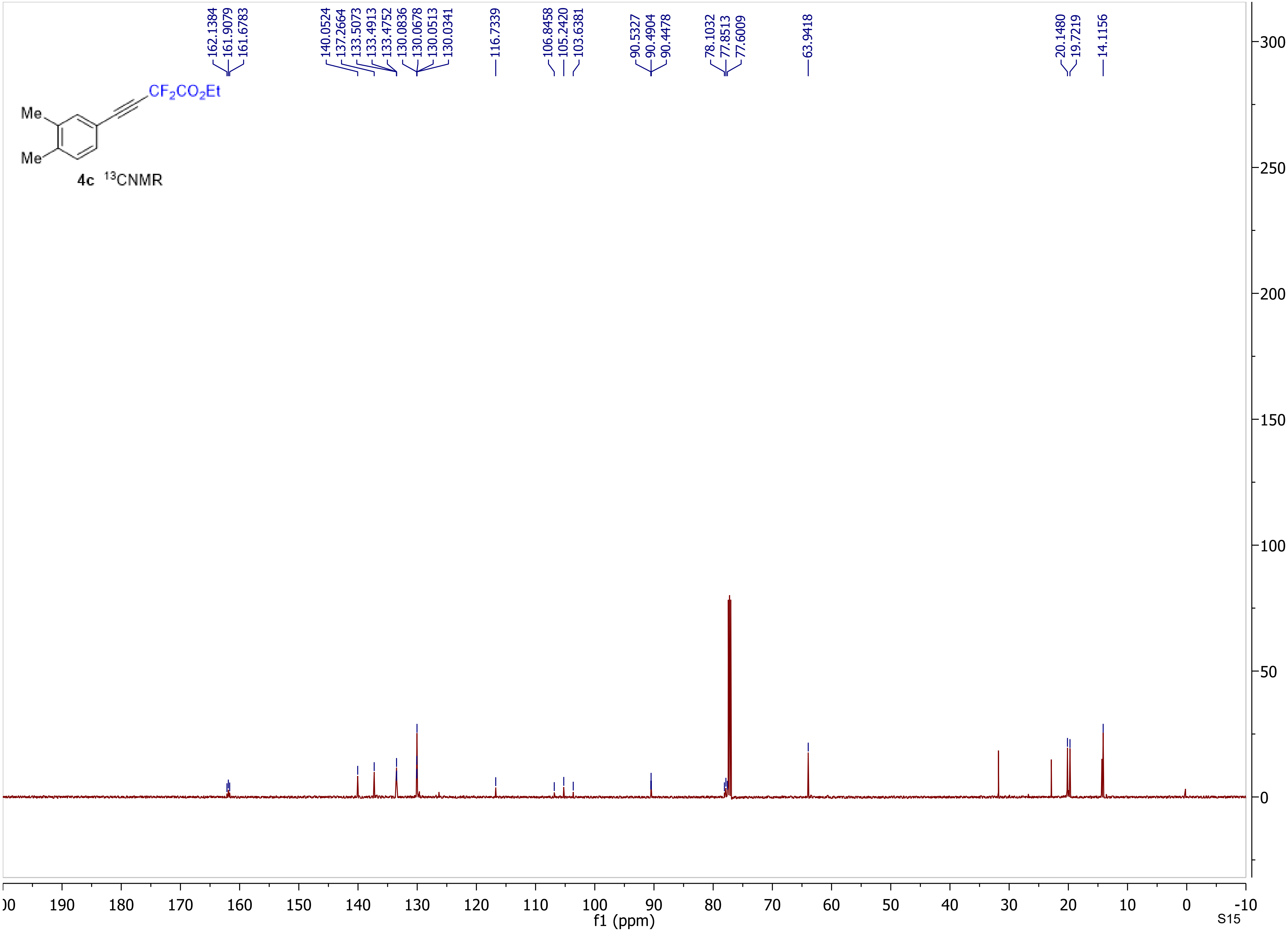
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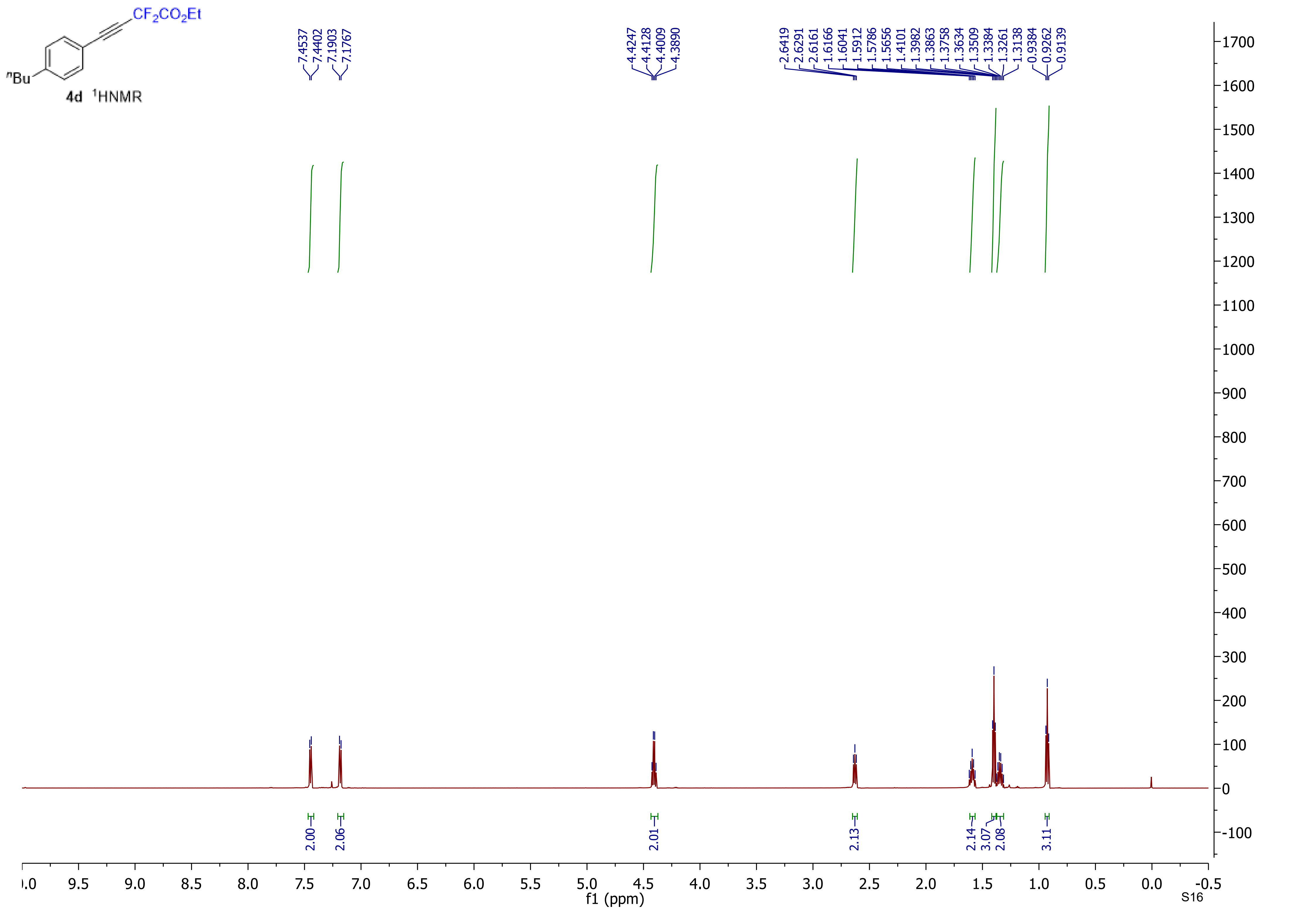
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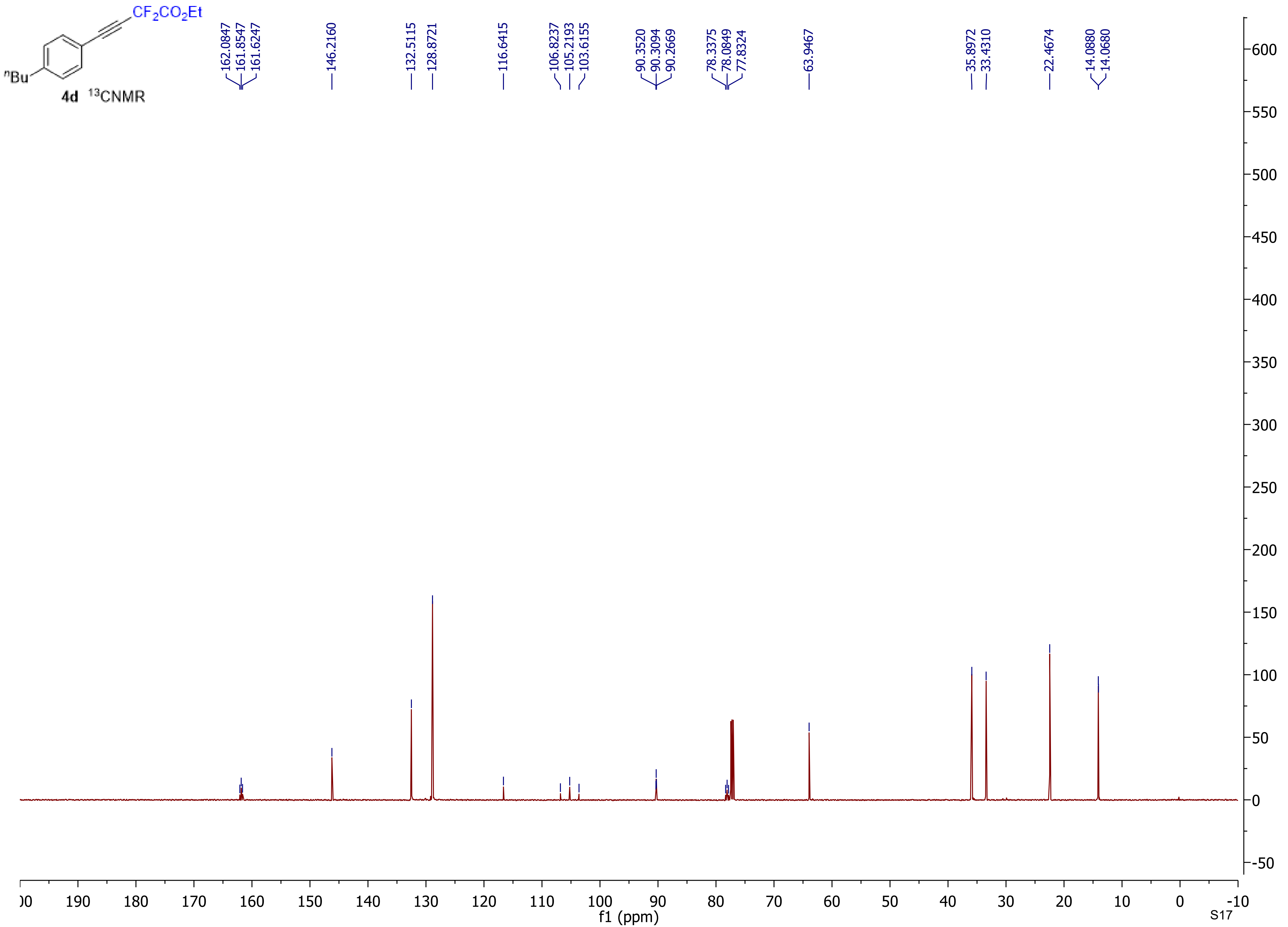
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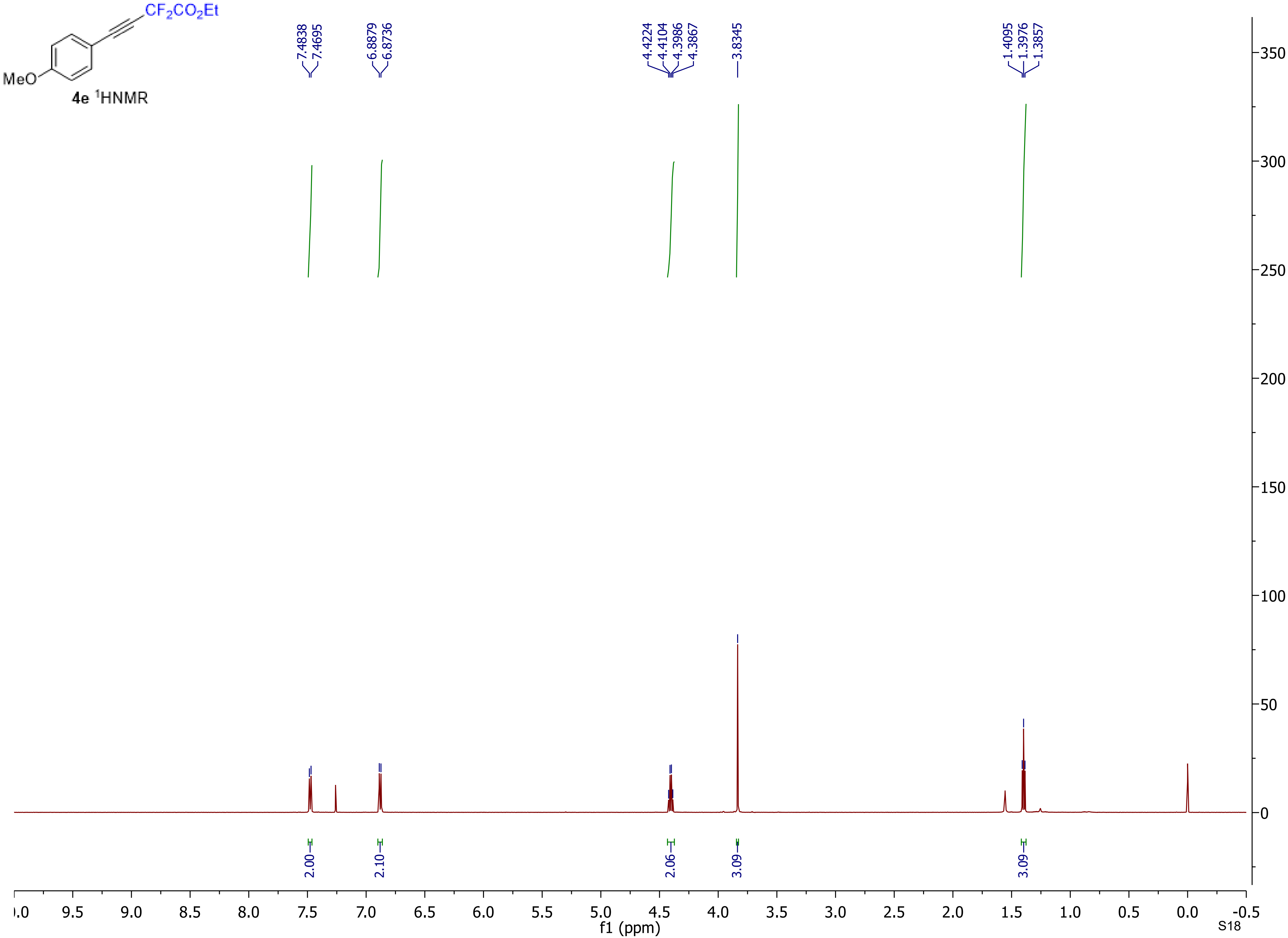
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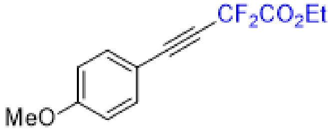
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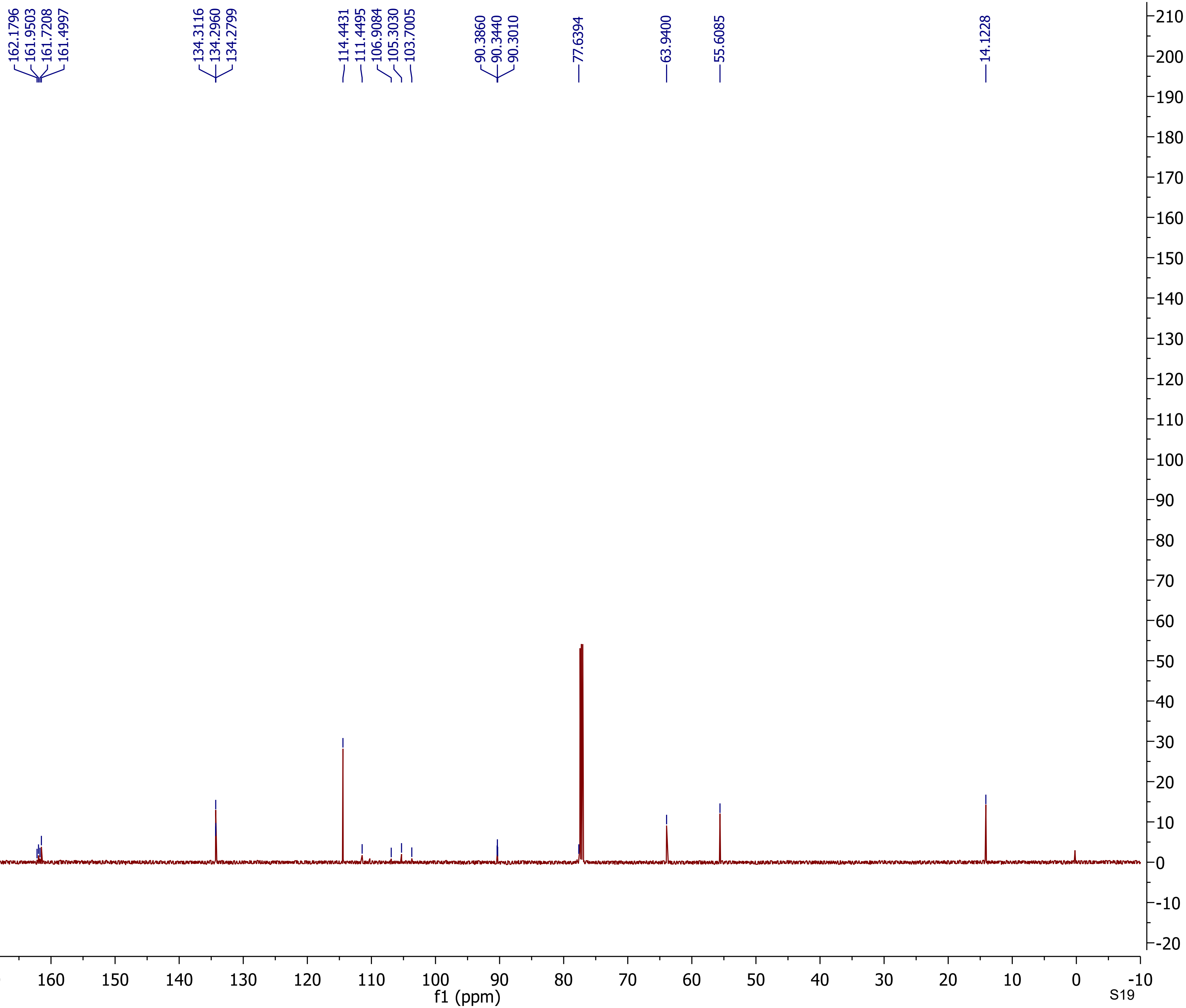
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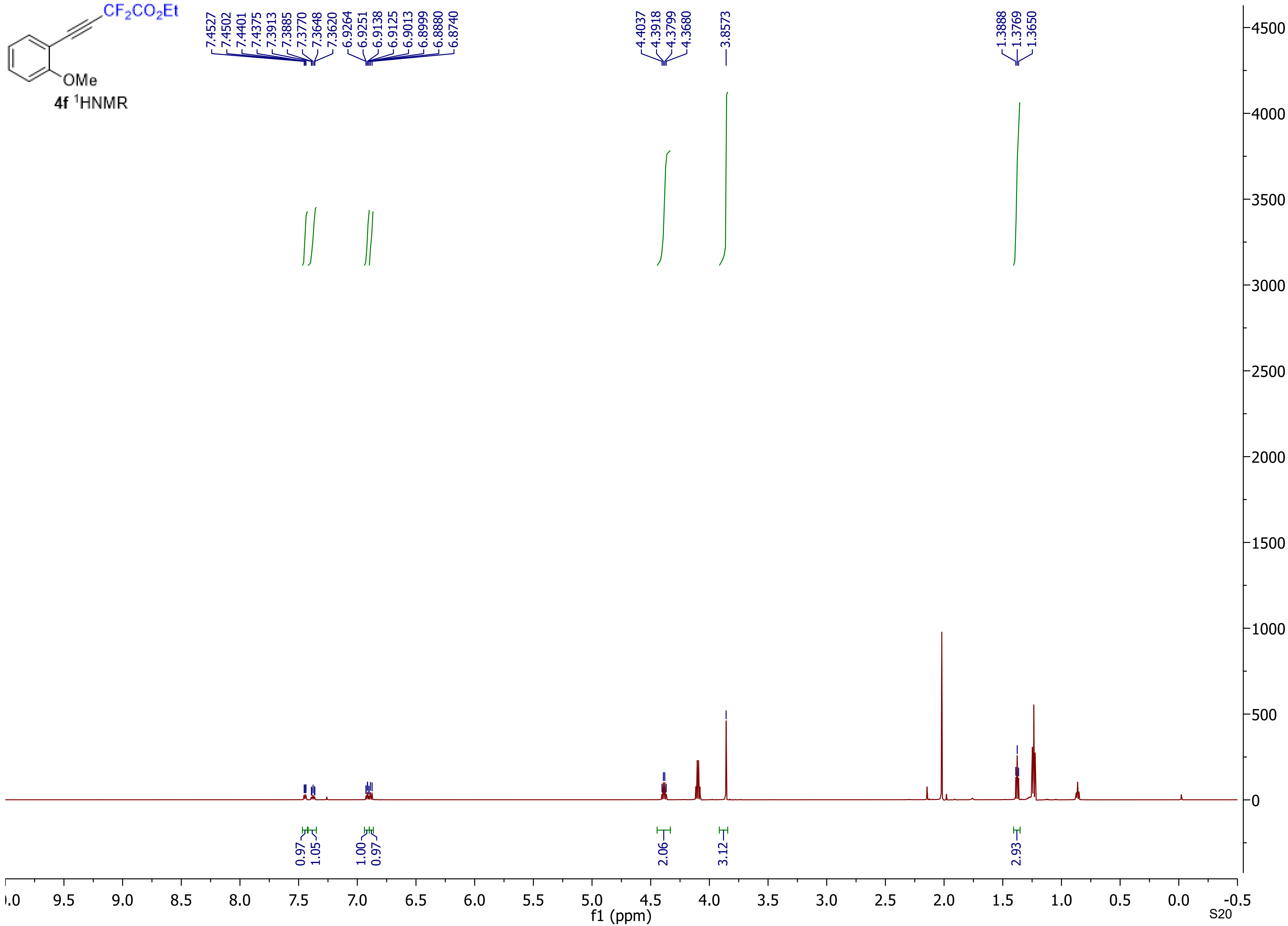
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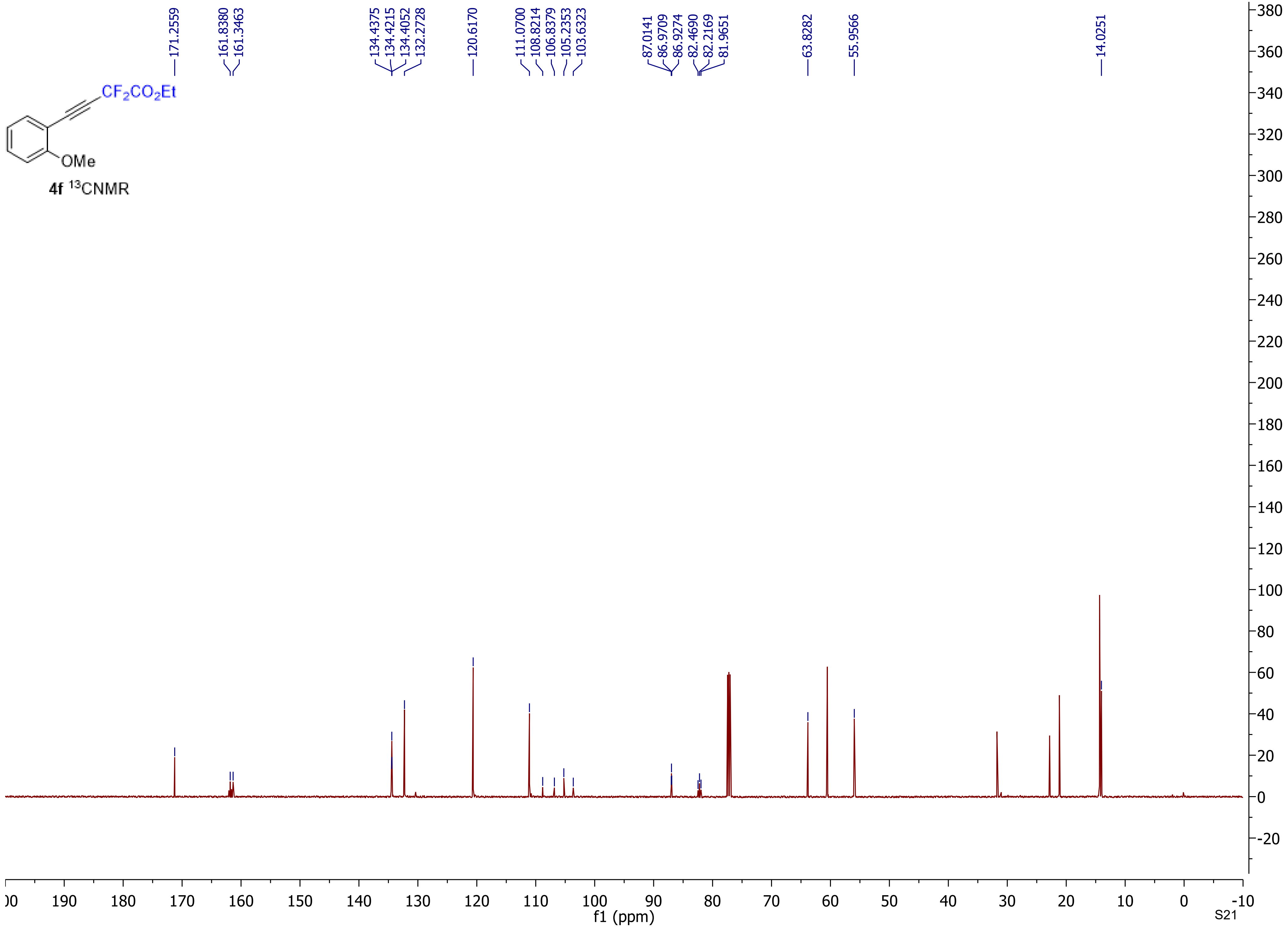
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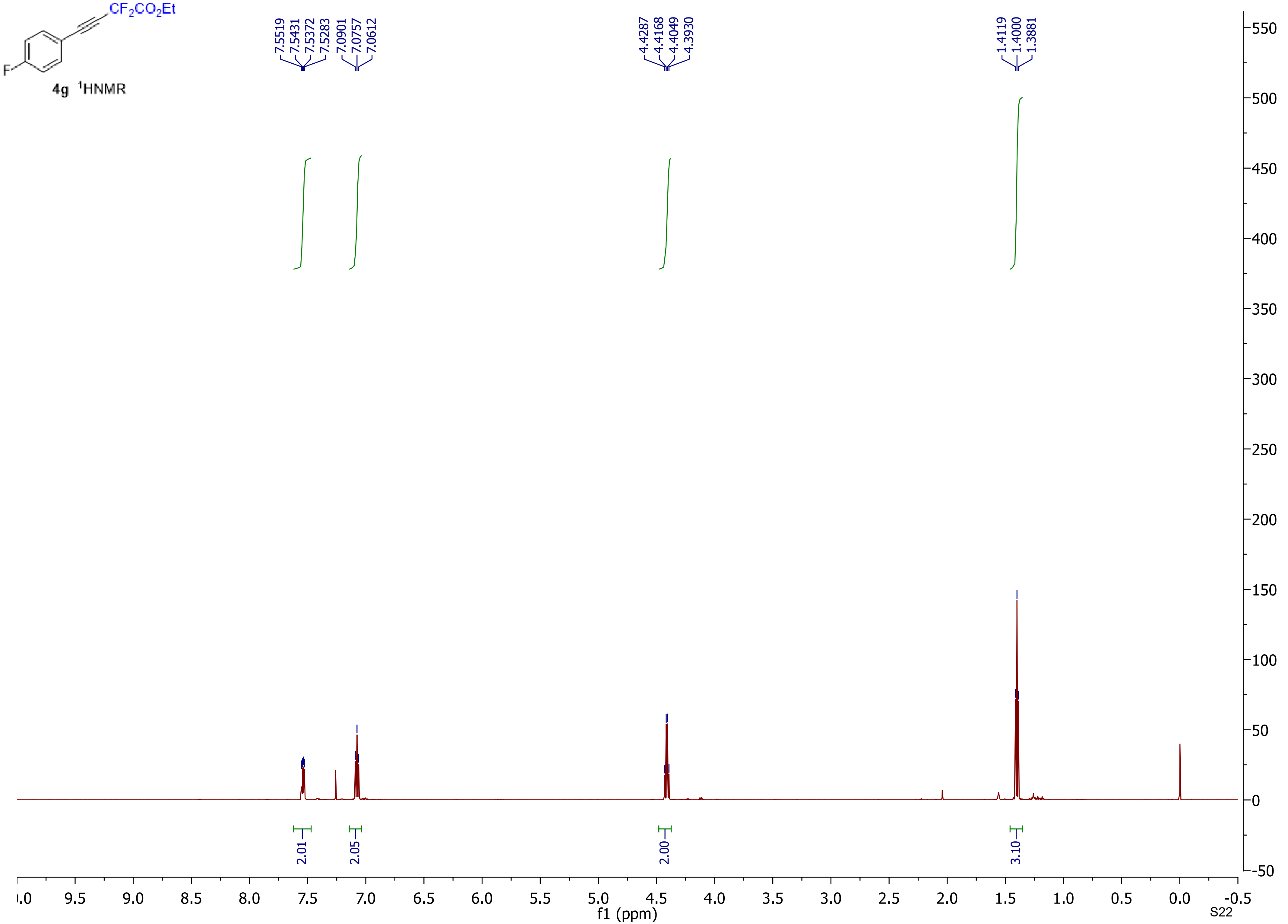
f1 (ppm)



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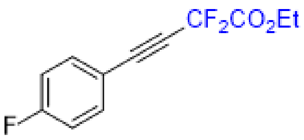
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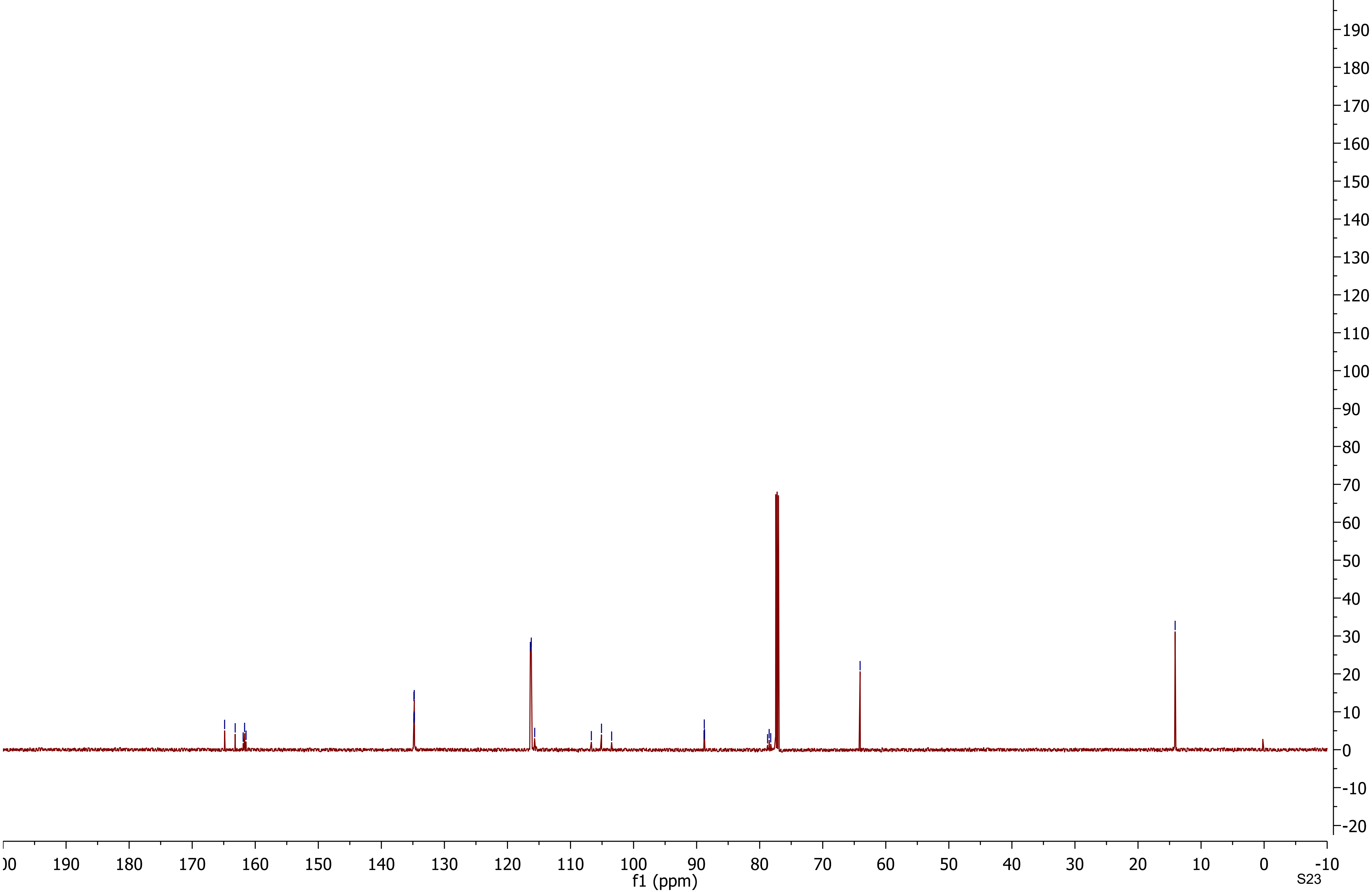
4g ^{13}CNMR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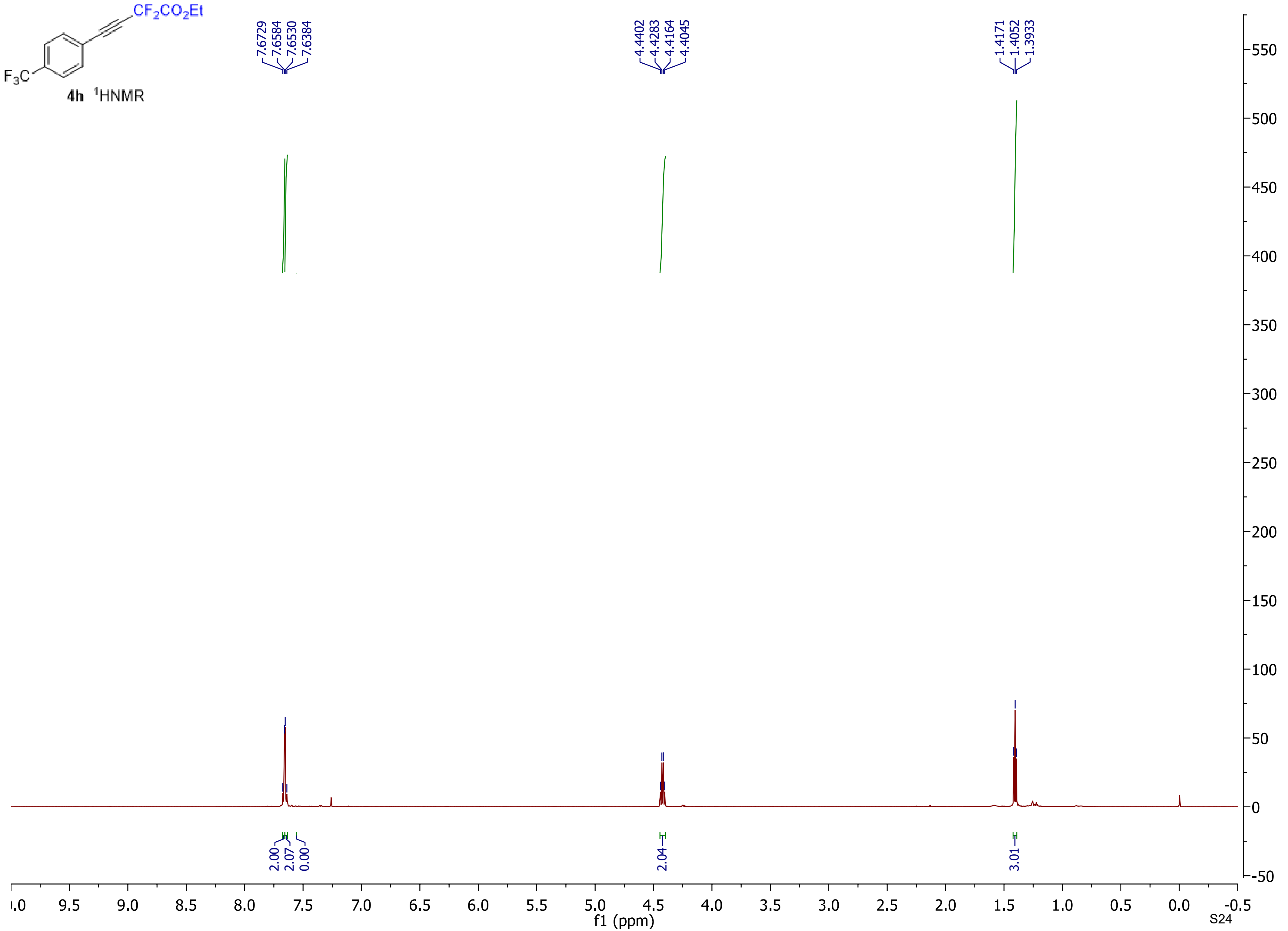

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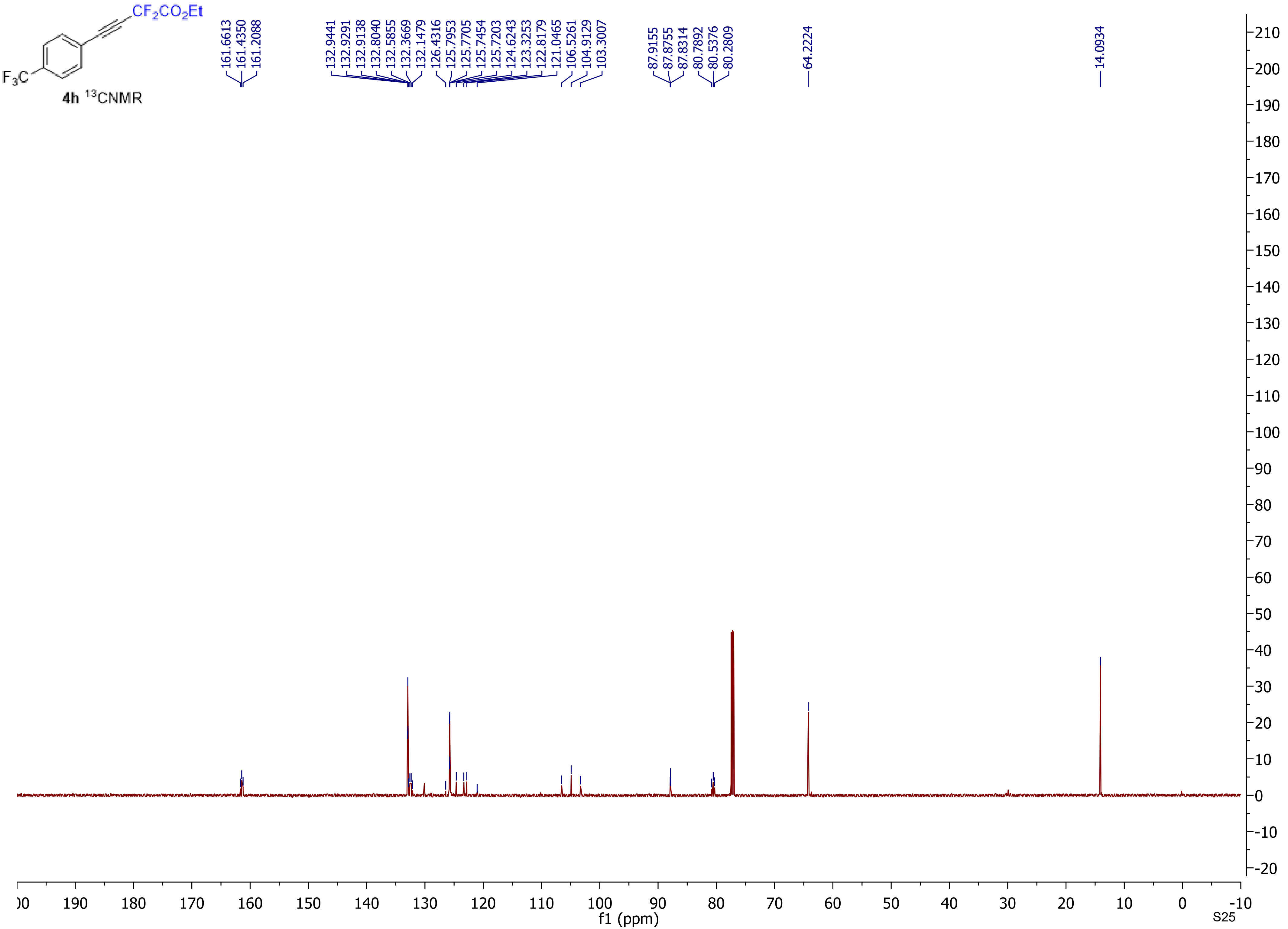
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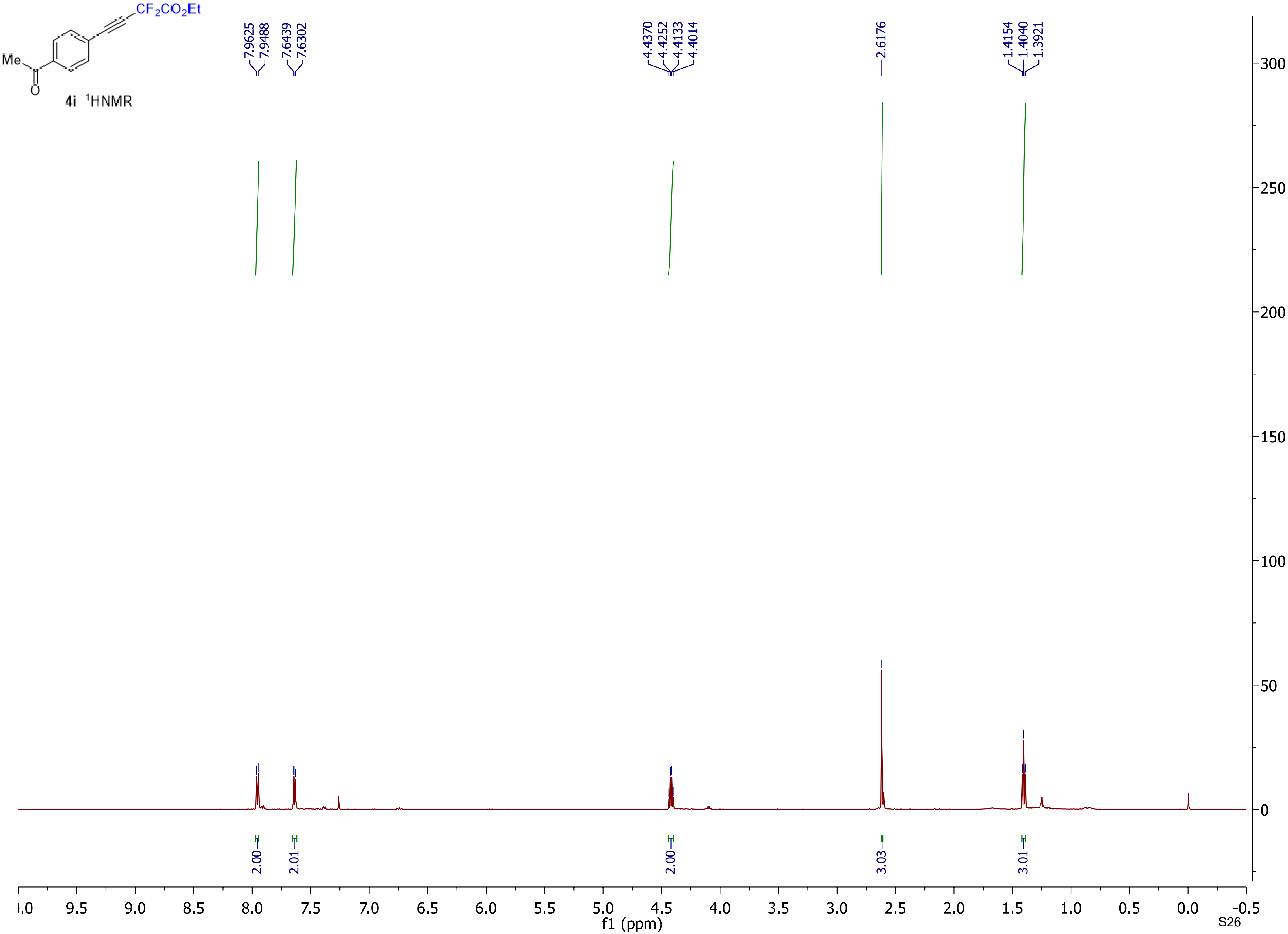
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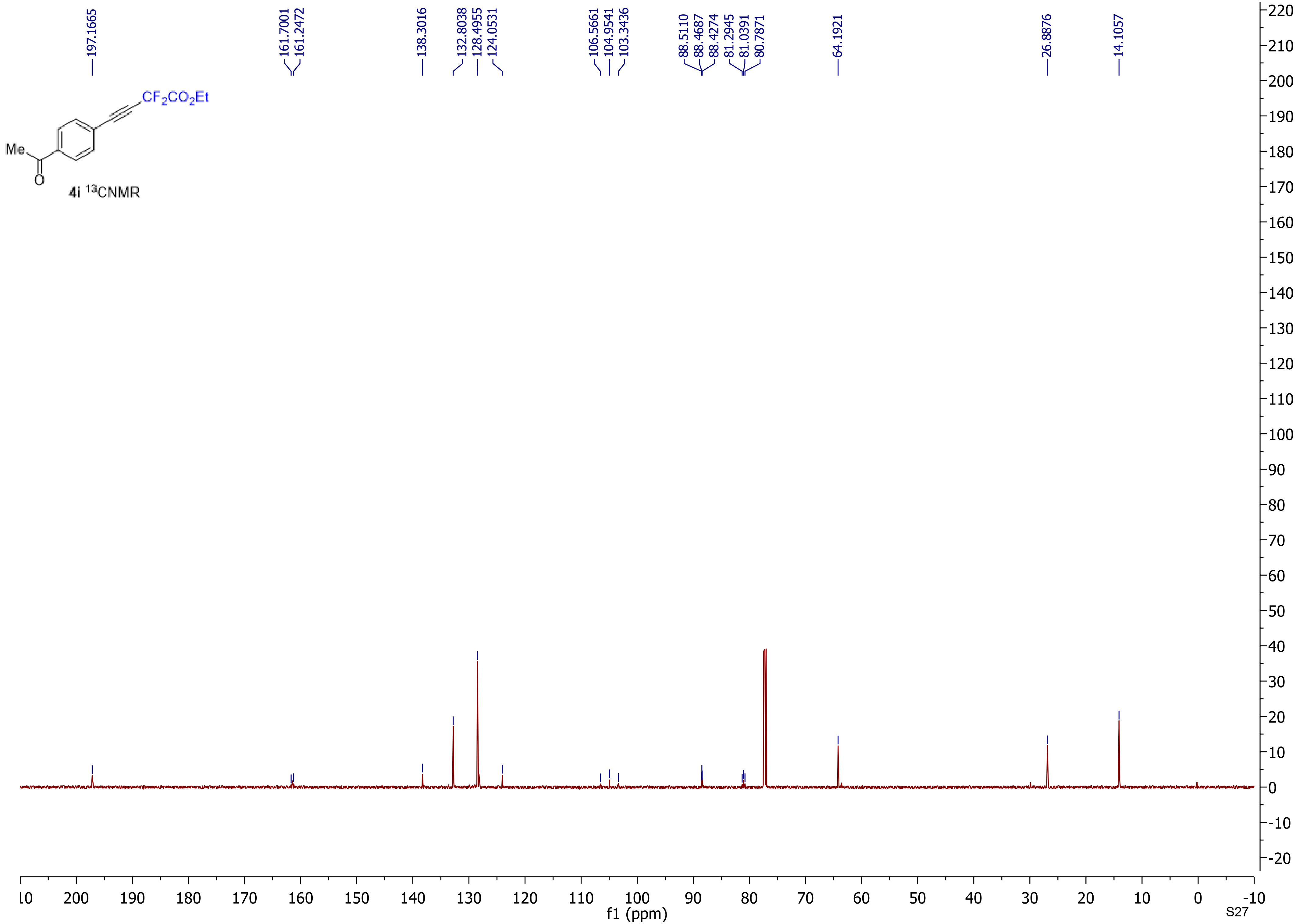
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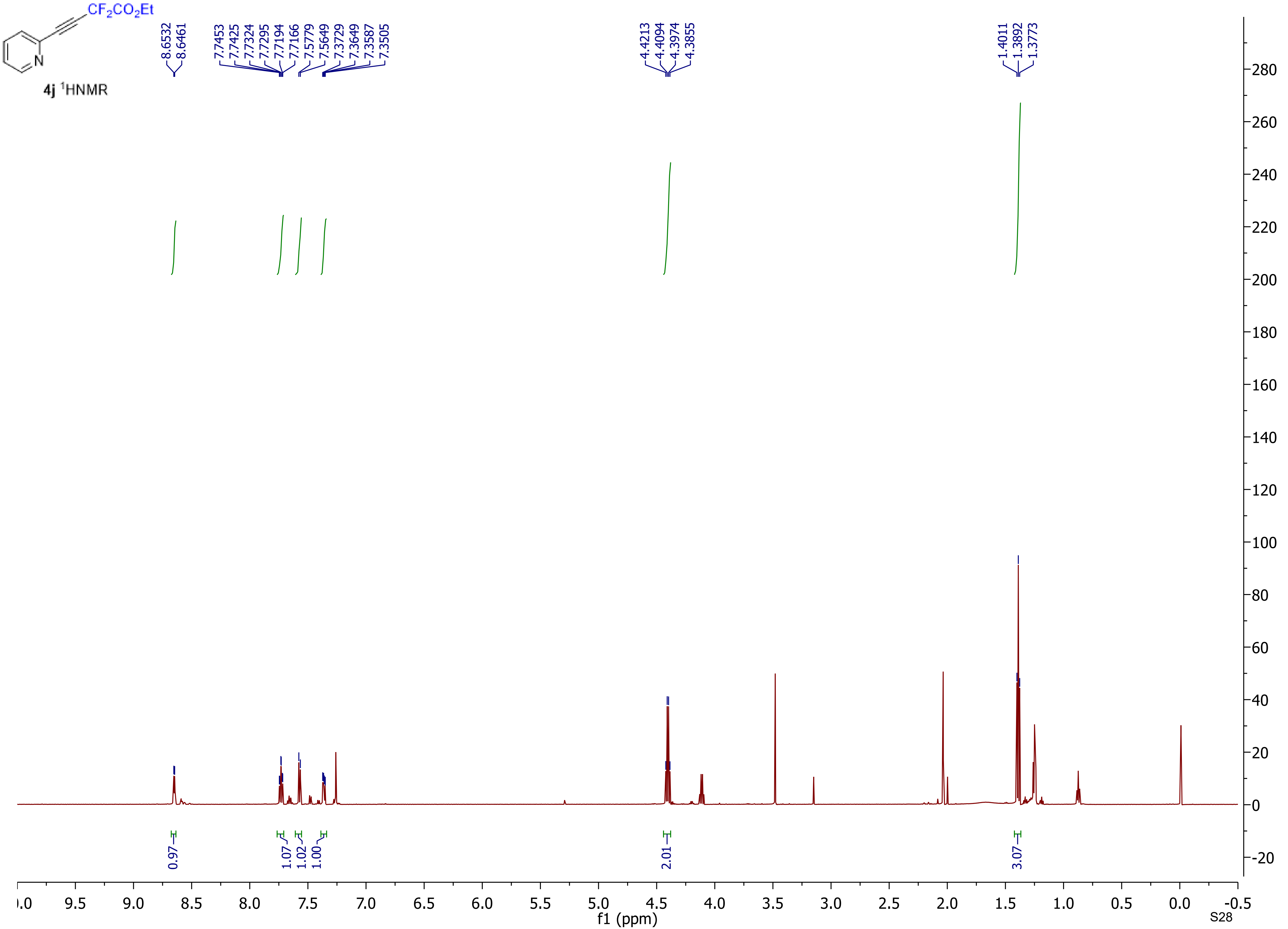
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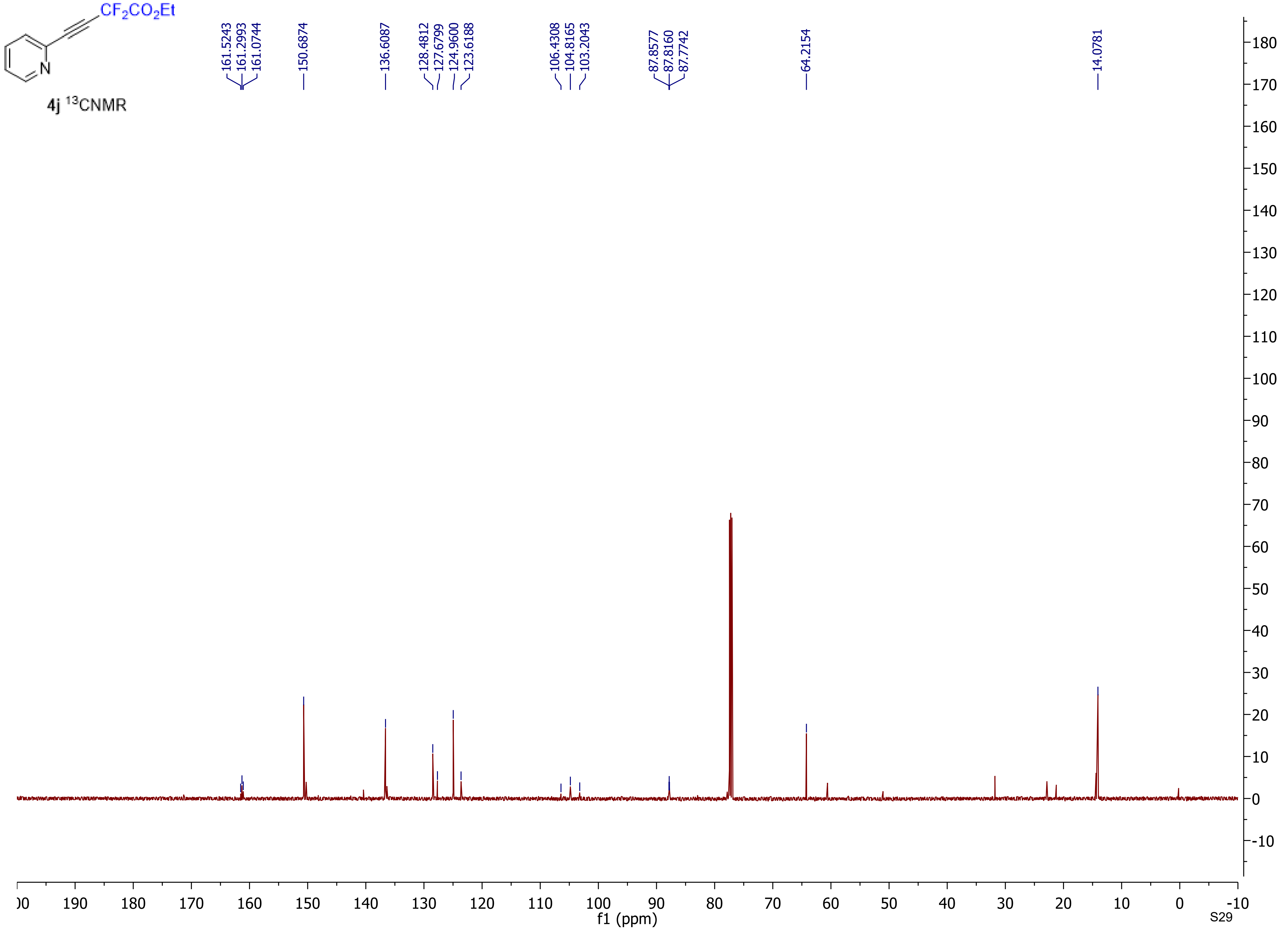
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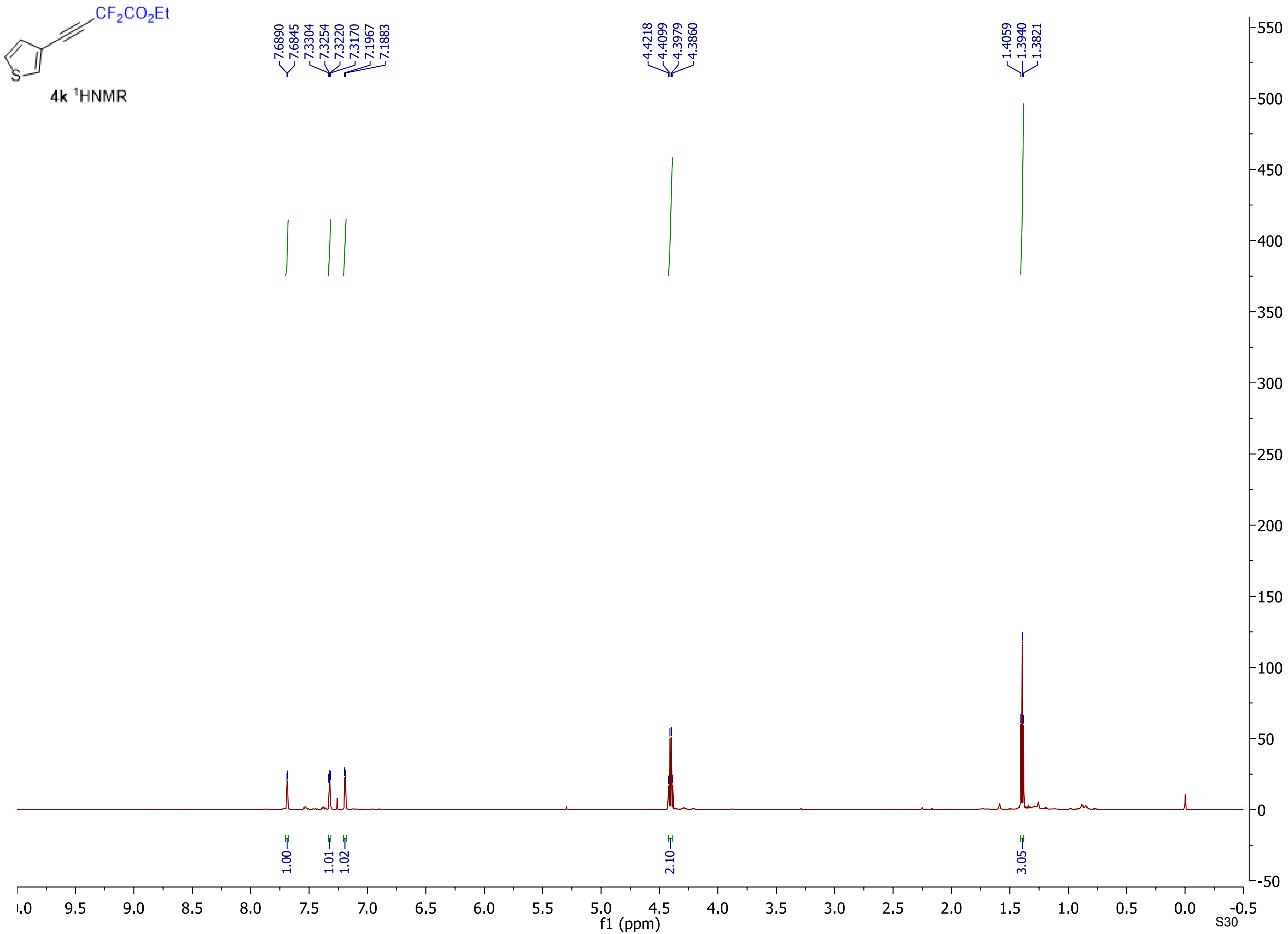
4j ^{13}CNMR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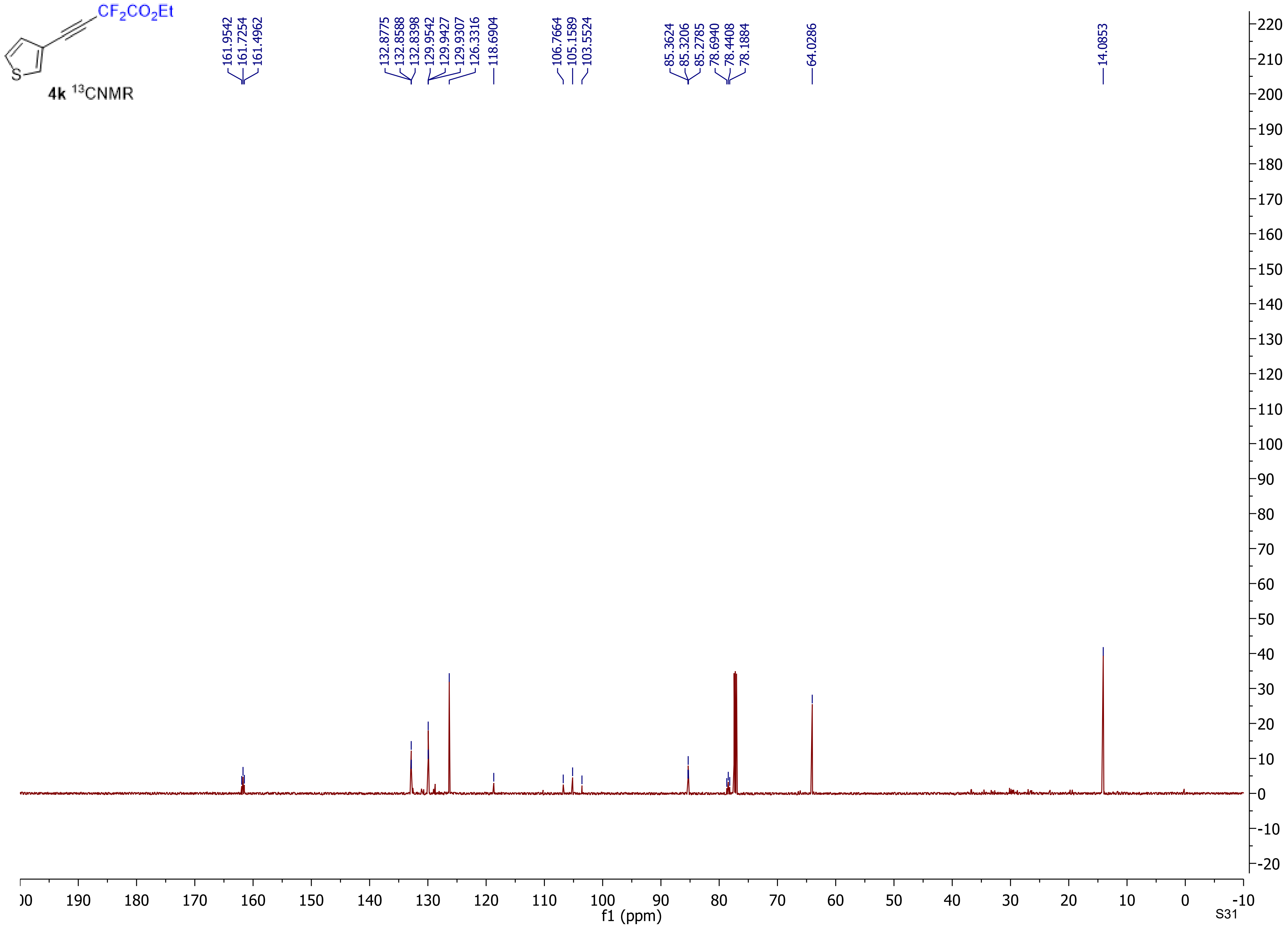
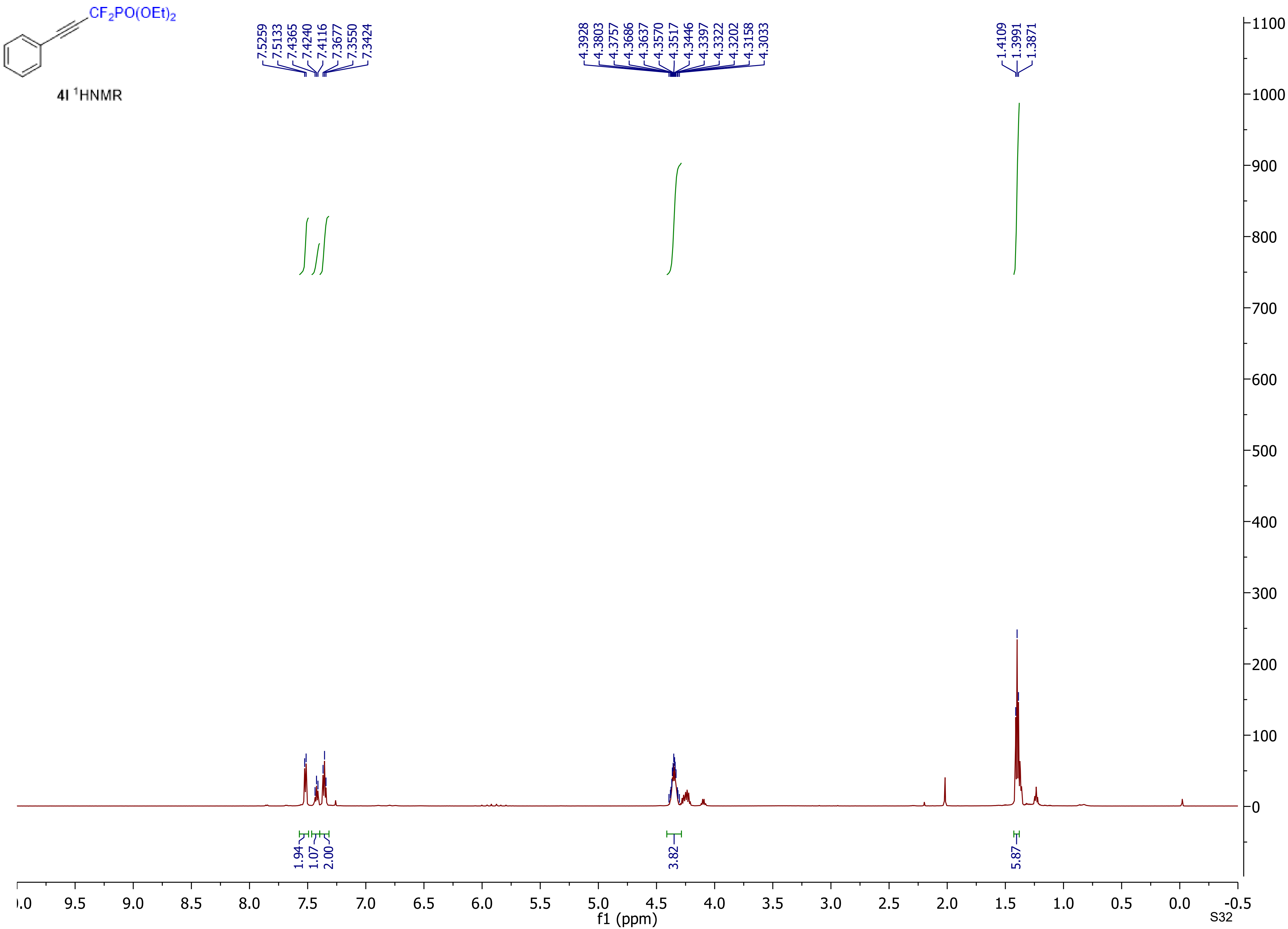
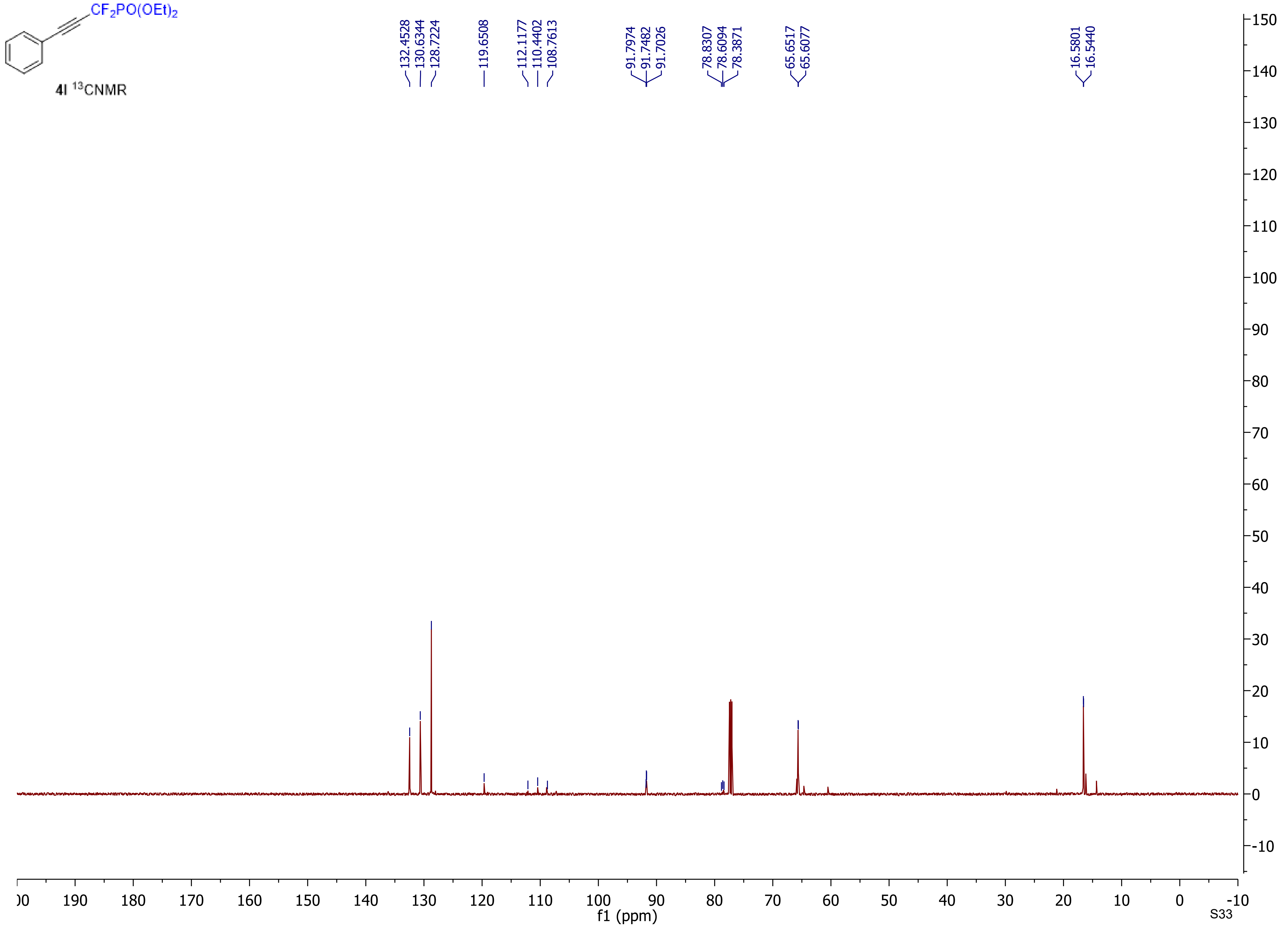
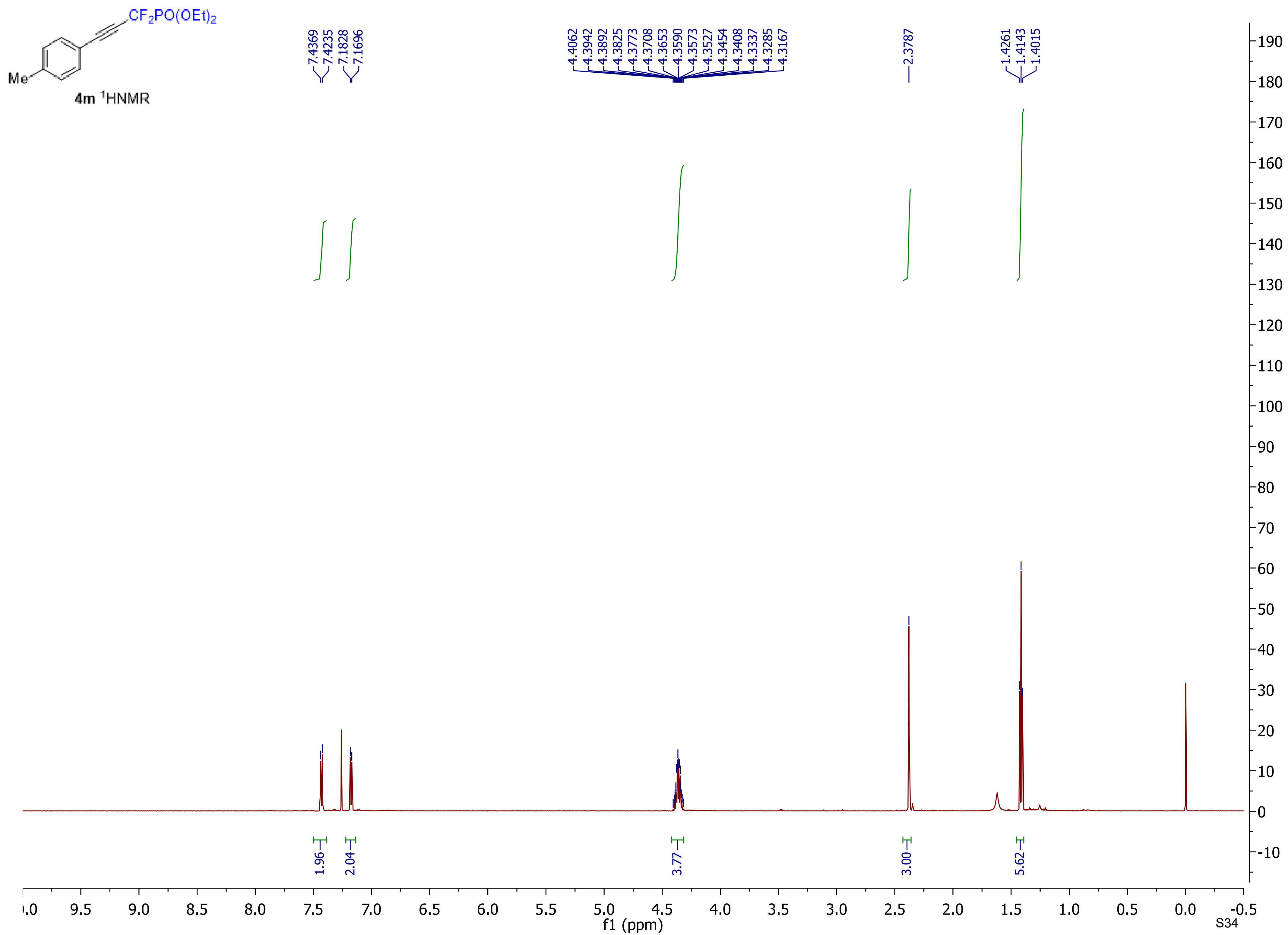
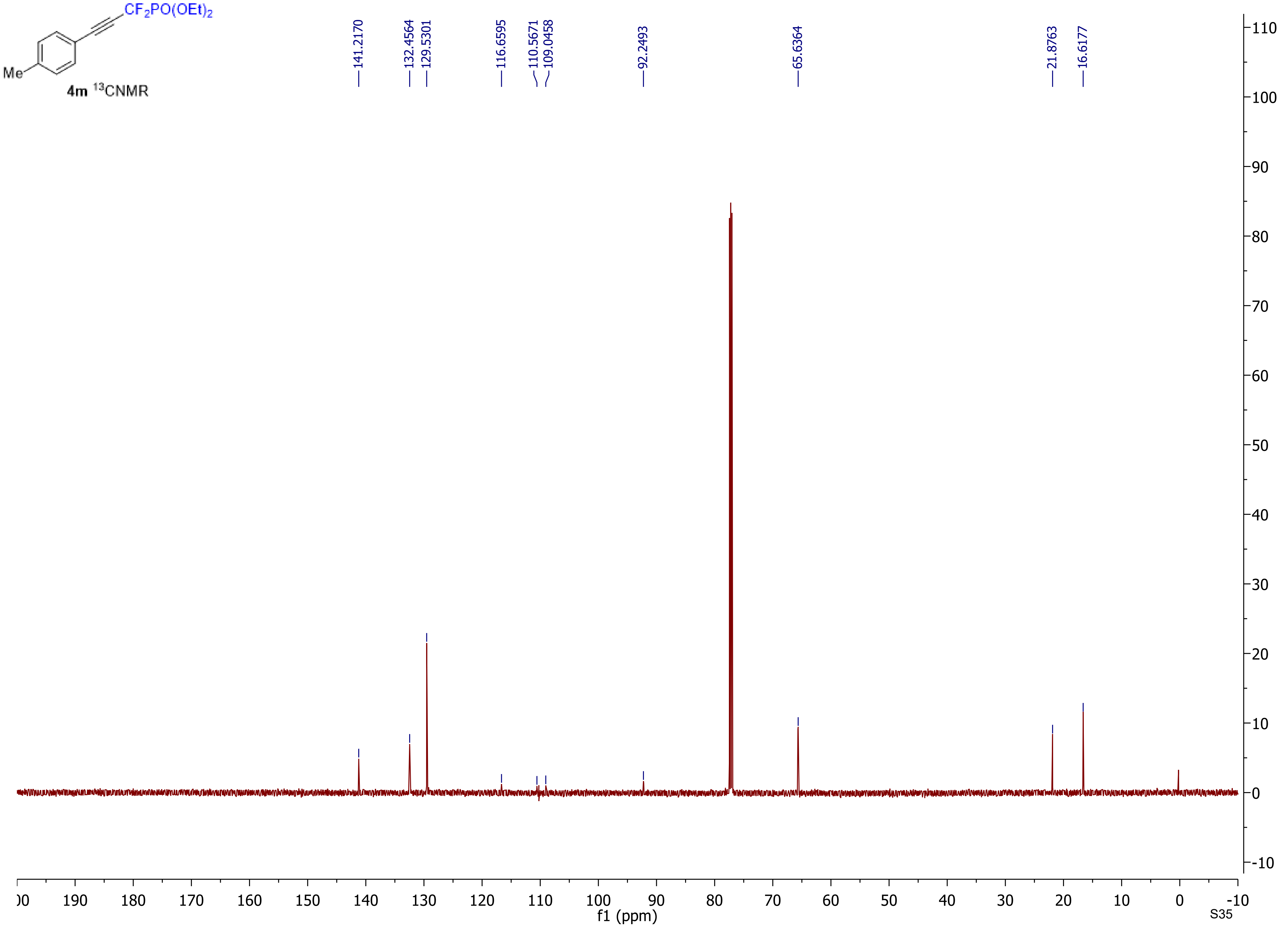
2.10
3.05
f1 (ppm)


CF2CO2Et
S
4k 13CNMR
161.9542
161.7254
161.4962
132.8775
132.8588
132.8398
129.9542
129.9427
129.9307
126.3316
118.6904
106.7664
105.1589
103.5524
85.3624
85.3206
85.2785
78.6940
78.4408
78.1884
64.0286
14.0853
f1 (ppm)

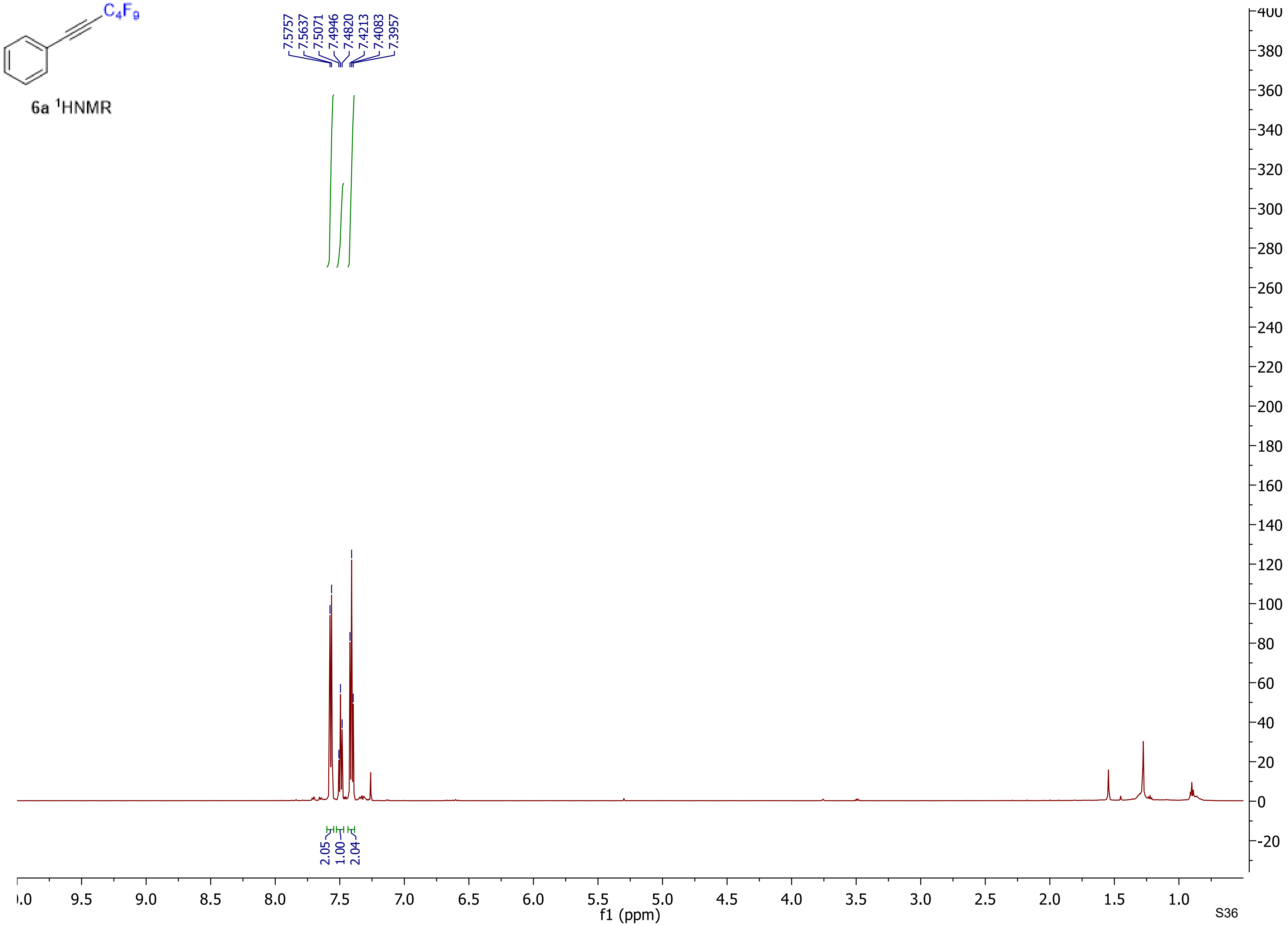

CF2PO(OEt)2
4l 1HNMR
7.5259
7.5133
7.4365
7.4240
7.4116
7.3677
7.3550
7.3424
4.3928
4.3803
4.3757
4.3686
4.3637
4.3570
4.3517
4.3446
4.3397
4.3322
4.3202
4.3158
4.3033
1.4109
1.3991
1.3871
1.94
1.07
2.00
3.82
5.87
f1 (ppm)

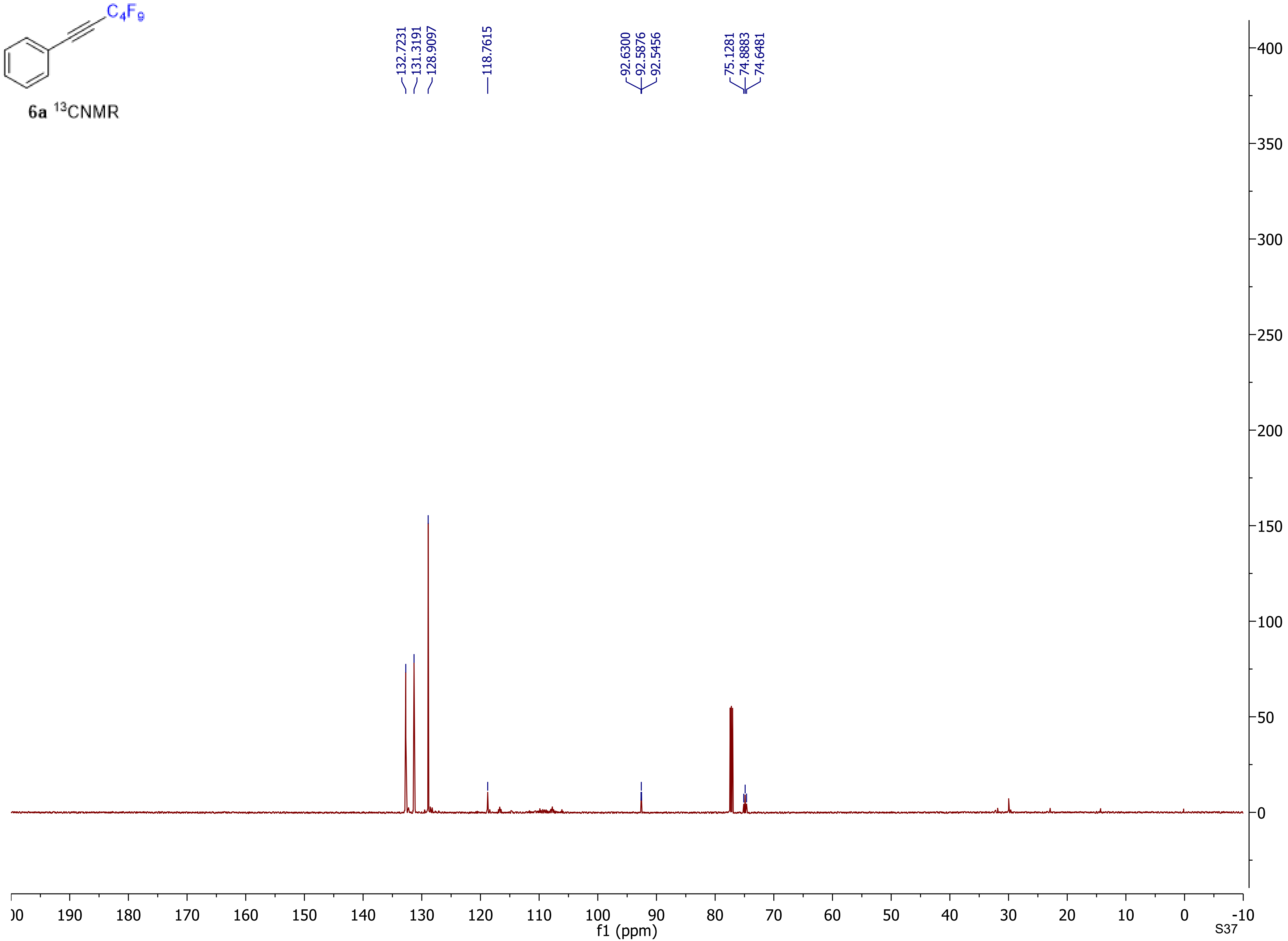

CF2PO(OEt)2
4l 13CNMR
132.4528
130.6344
128.7224
119.6508
112.1177
110.4402
108.7613
91.7974
91.7482
91.7026
78.8307
78.6094
78.3871
65.6517
65.6077
16.5801
16.5440
f1 (ppm)

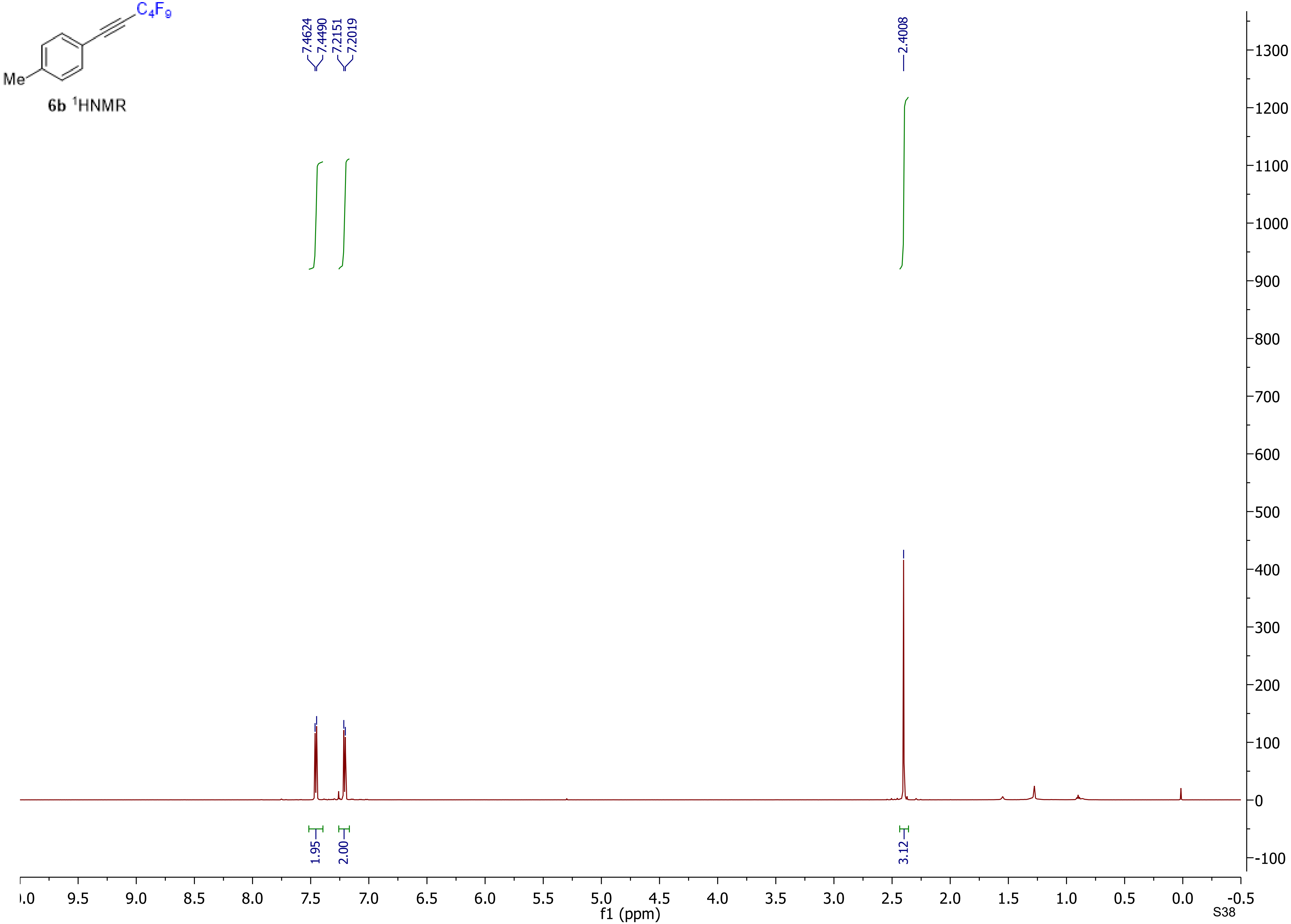

CF2PO(OEt)2
Me
4m 1HNMR
7.4369
7.4235
7.1828
7.1696
4.4062
4.3942
4.3892
4.3825
4.3773
4.3708
4.3653
4.3590
4.3573
4.3527
4.3454
4.3408
4.3337
4.3285
4.3167
2.3787
1.4261
1.4143
1.4015
1.96
2.04
3.77
3.00
5.62
f1 (ppm)

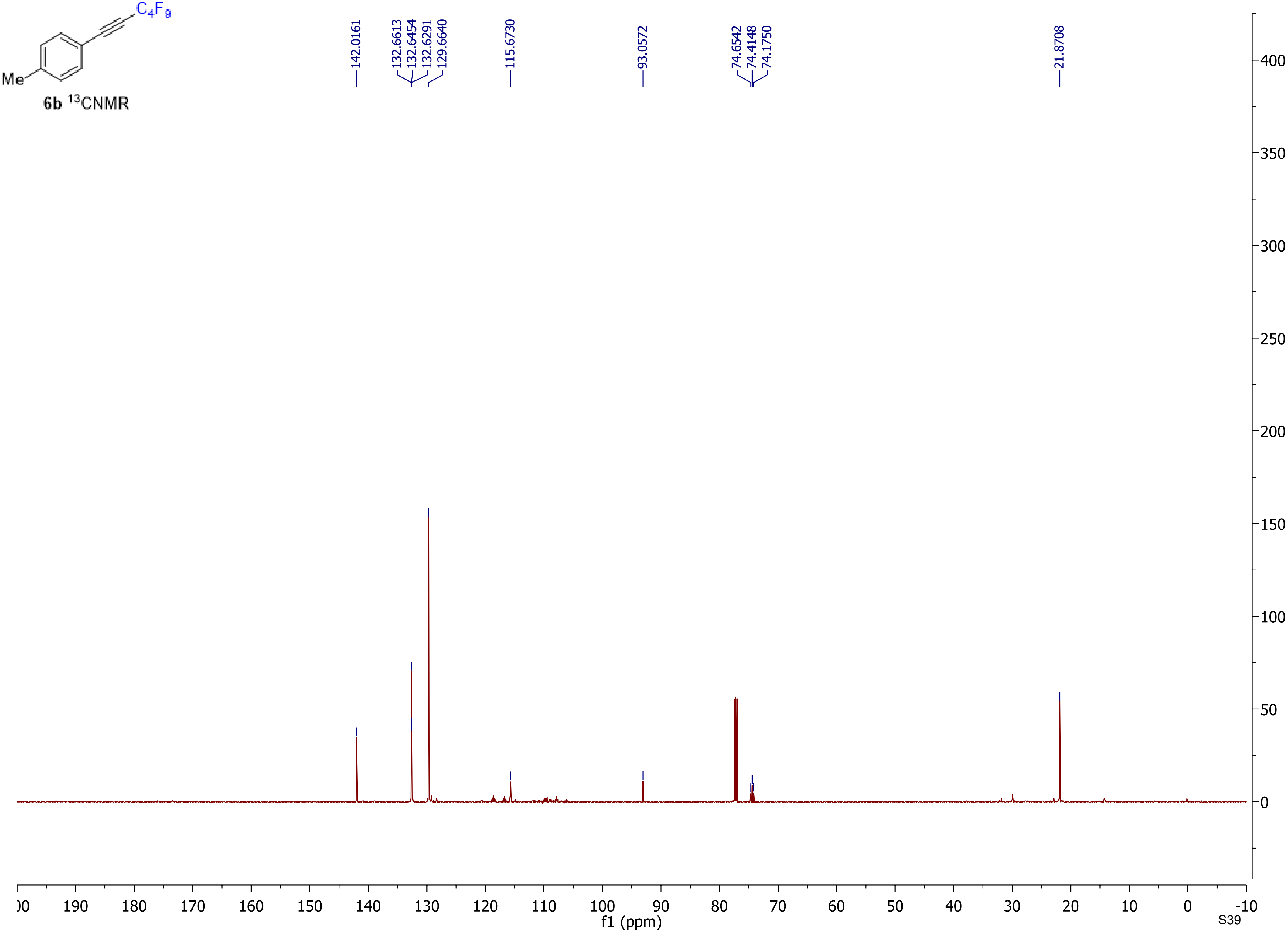


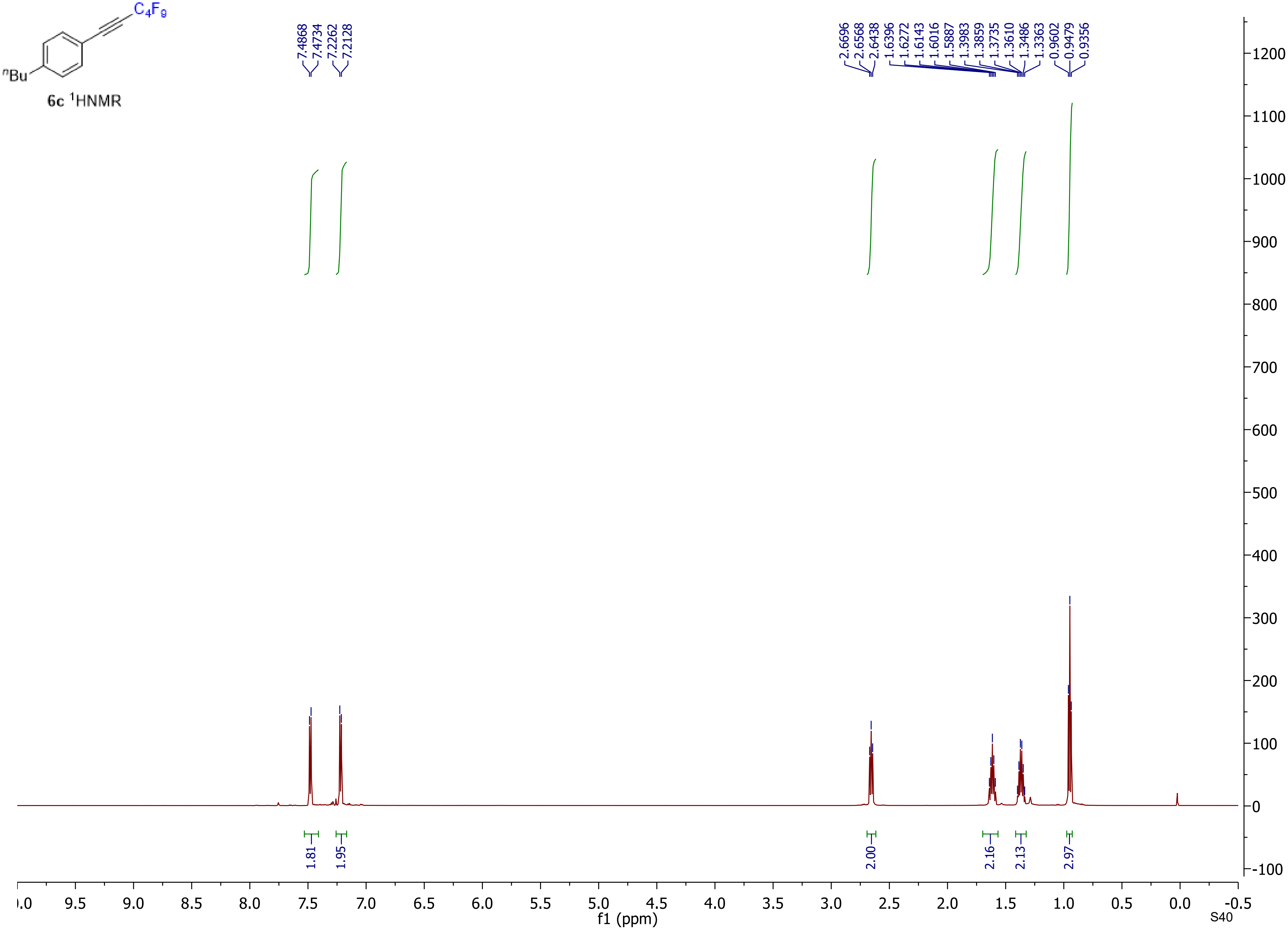
CF2PO(OEt)2
Me
4m 13CNMR
141.2170
132.4564
129.5301
116.6595
110.5671
109.0458
92.2493
65.6364
21.8763
16.6177
f1 (ppm)


C4F9
6a 1HNMR
7.5757
7.5637
7.5071
7.4946
7.4820
7.4213
7.4083
7.3957
2.05
1.00
2.04
f1 (ppm)

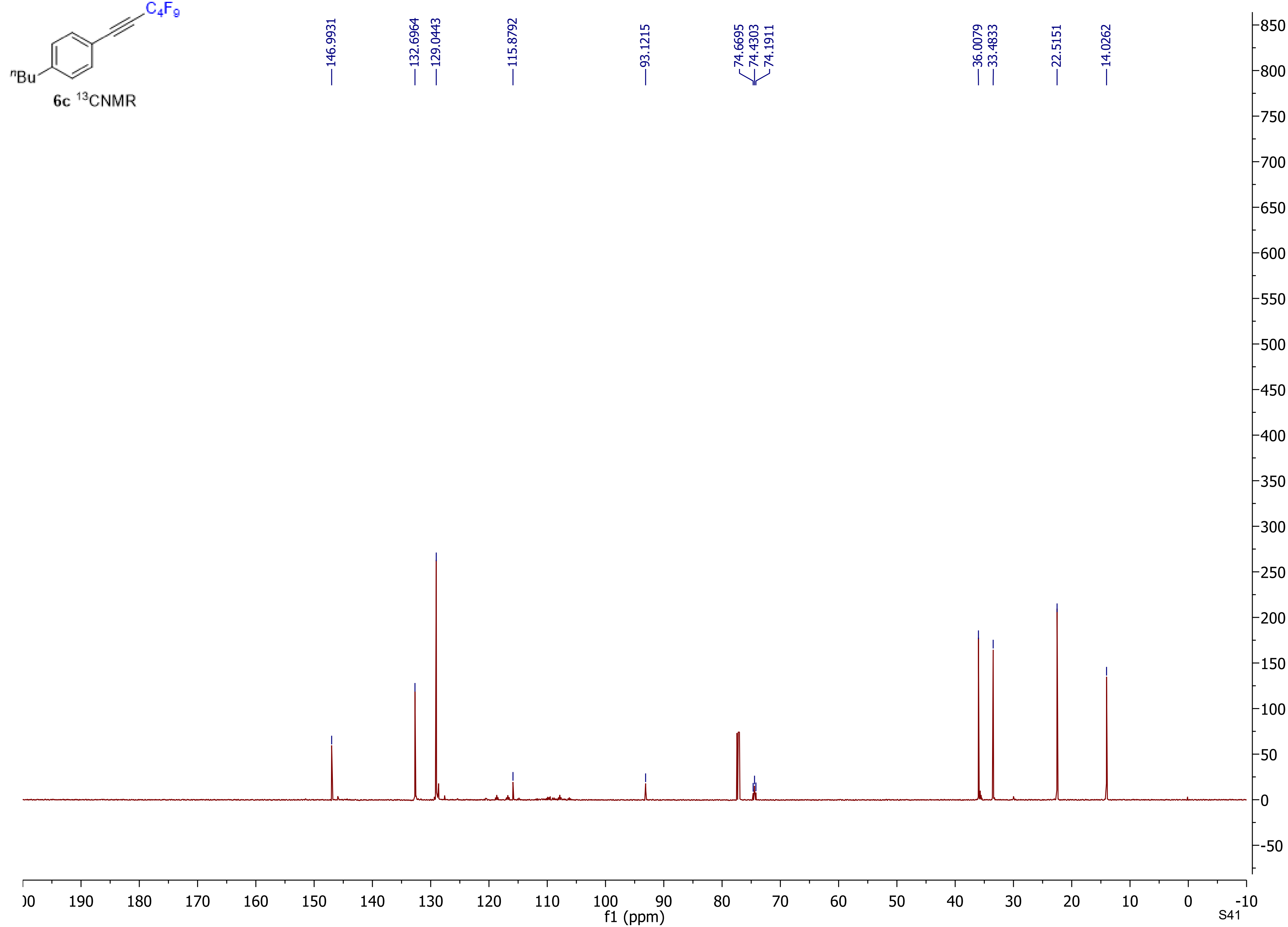

C4F9
6a 13CNMR
132.7231
131.3191
128.9097
118.7615
92.6300
92.5876
92.5456
75.1281
74.8883
74.6481
f1 (ppm)

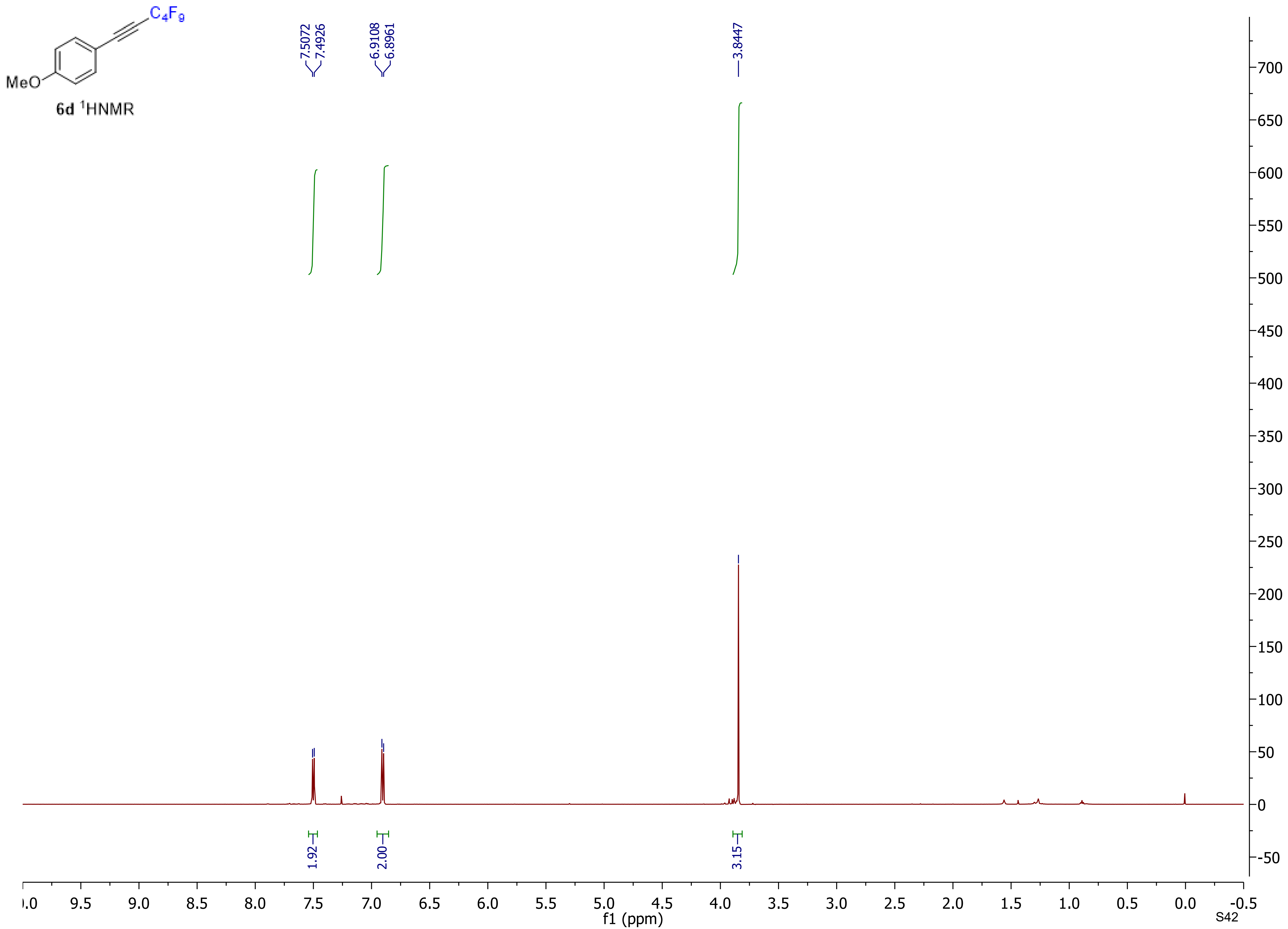

C4F9
Me
6b 1HNMR
7.4624
7.4490
7.2151
7.2019
2.4008
1.95
2.00
3.12
f1 (ppm)


C4F9
Me
6b 13CNMR
142.0161
132.6613
132.6454
132.6291
129.6640
115.6730
93.0572
74.6542
74.4148
74.1750
21.8708
f1 (ppm)

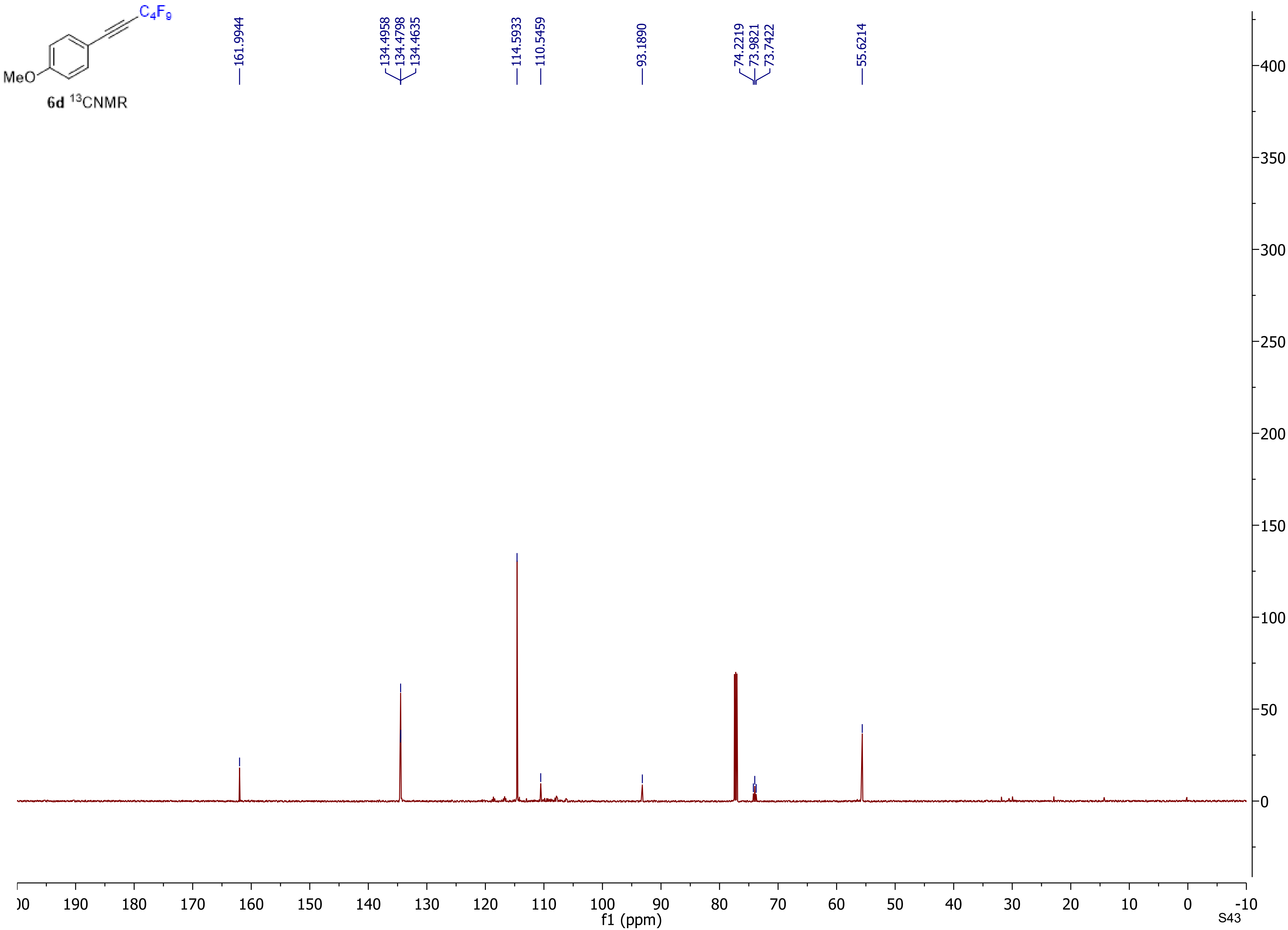


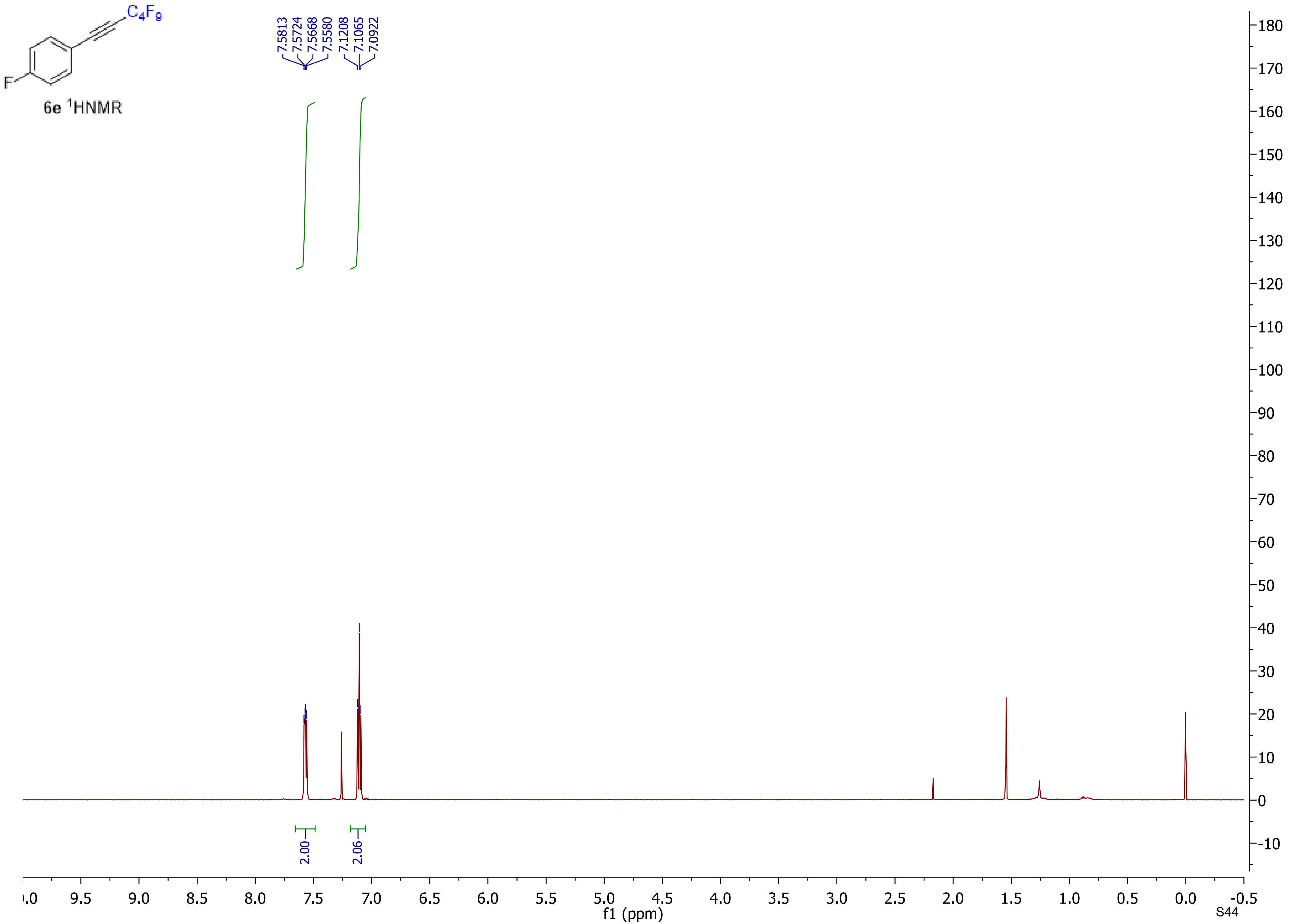
C4F9
nBu
6c 1HNMR
7.4868
7.4734
7.2262
7.2128
2.6696
2.6568
2.6438
1.6396
1.6272
1.6143
1.6016
1.5887
1.3983
1.3859
1.3735
1.3610
1.3486
1.3363
0.9602
0.9479
0.9356
1.81
1.95
2.00
2.16
2.13
2.97
f1 (ppm)

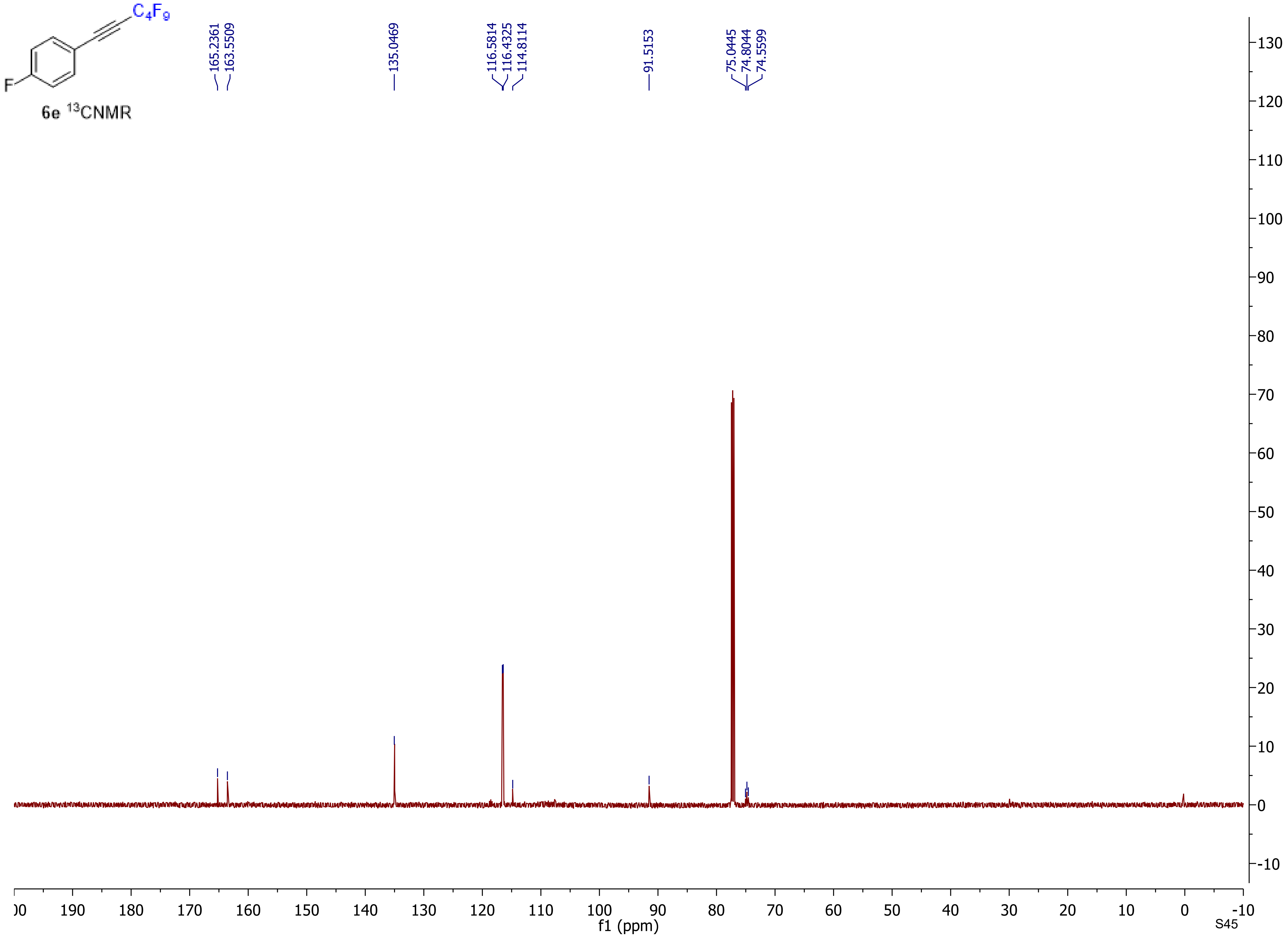

C4F9
nBu
6c 13CNMR
146.9931
132.6964
129.0443
115.8792
93.1215
74.6695
74.4303
74.1911
36.0079
33.4833
22.5151
14.0262
f1 (ppm)



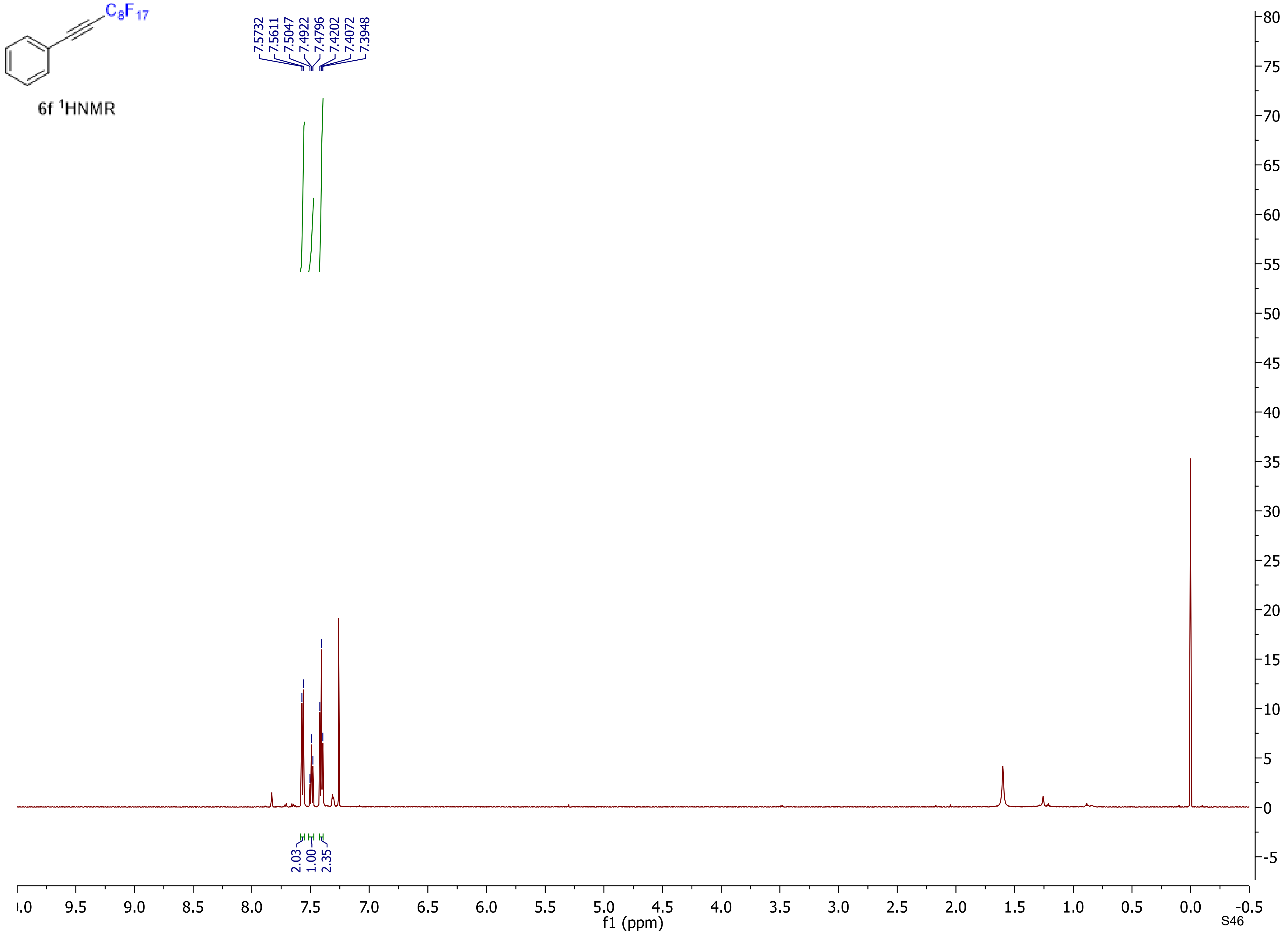
C4F9
MeO
6d 1HNMR
7.5072
7.4926
6.9108
6.8961
3.8447
1.92
2.00
3.15
f1 (ppm)


C4F9
MeO
6d 13CNMR
161.9944
134.4958
134.4798
134.4635
114.5933
110.5459
93.1890
74.2219
73.9821
73.7422
55.6214
f1 (ppm)

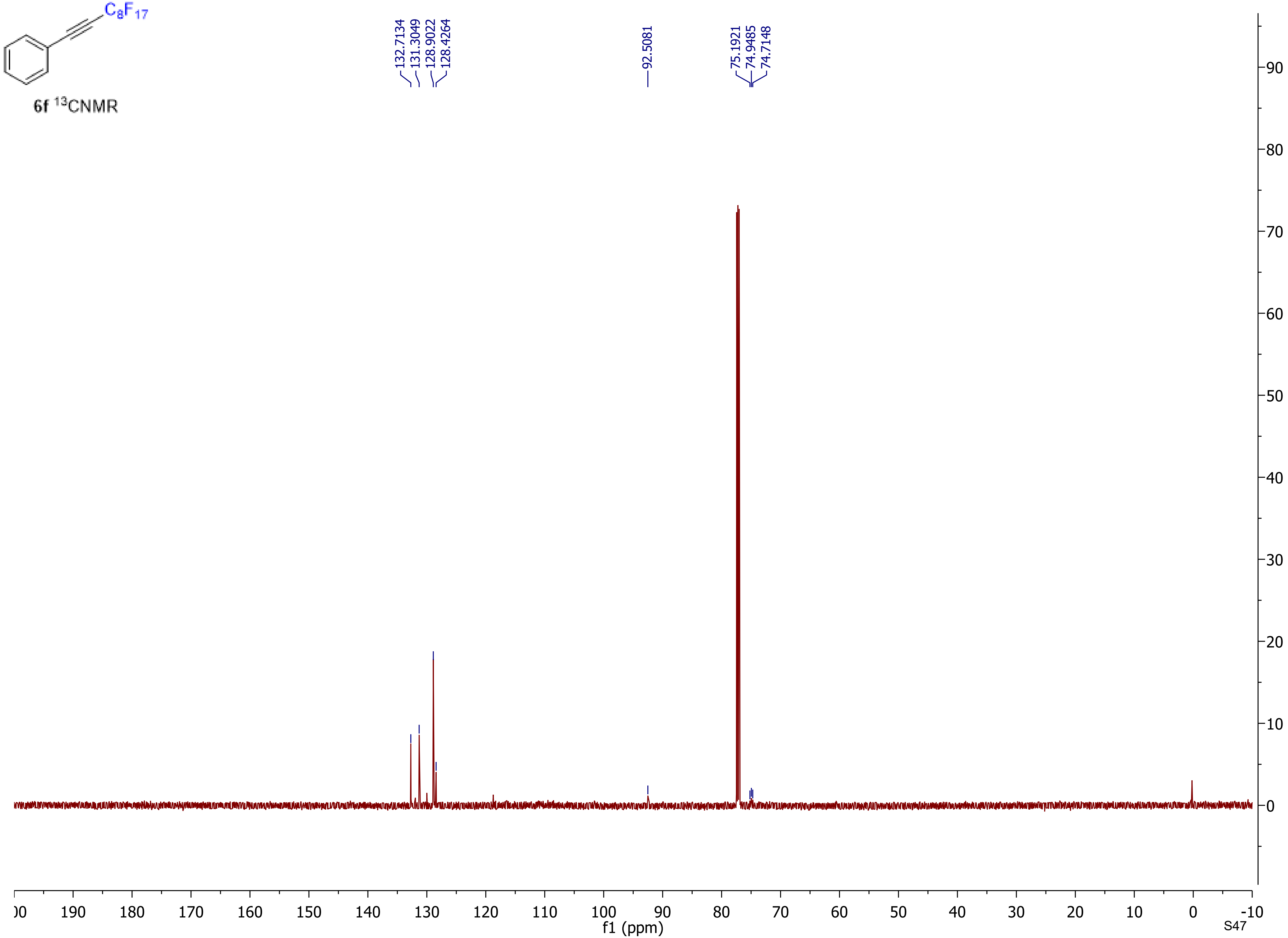

C4F9
F
6e 1HNMR
7.5813
7.5724
7.5668
7.5580
7.1208
7.1065
7.0922
2.00
2.06
f1 (ppm)



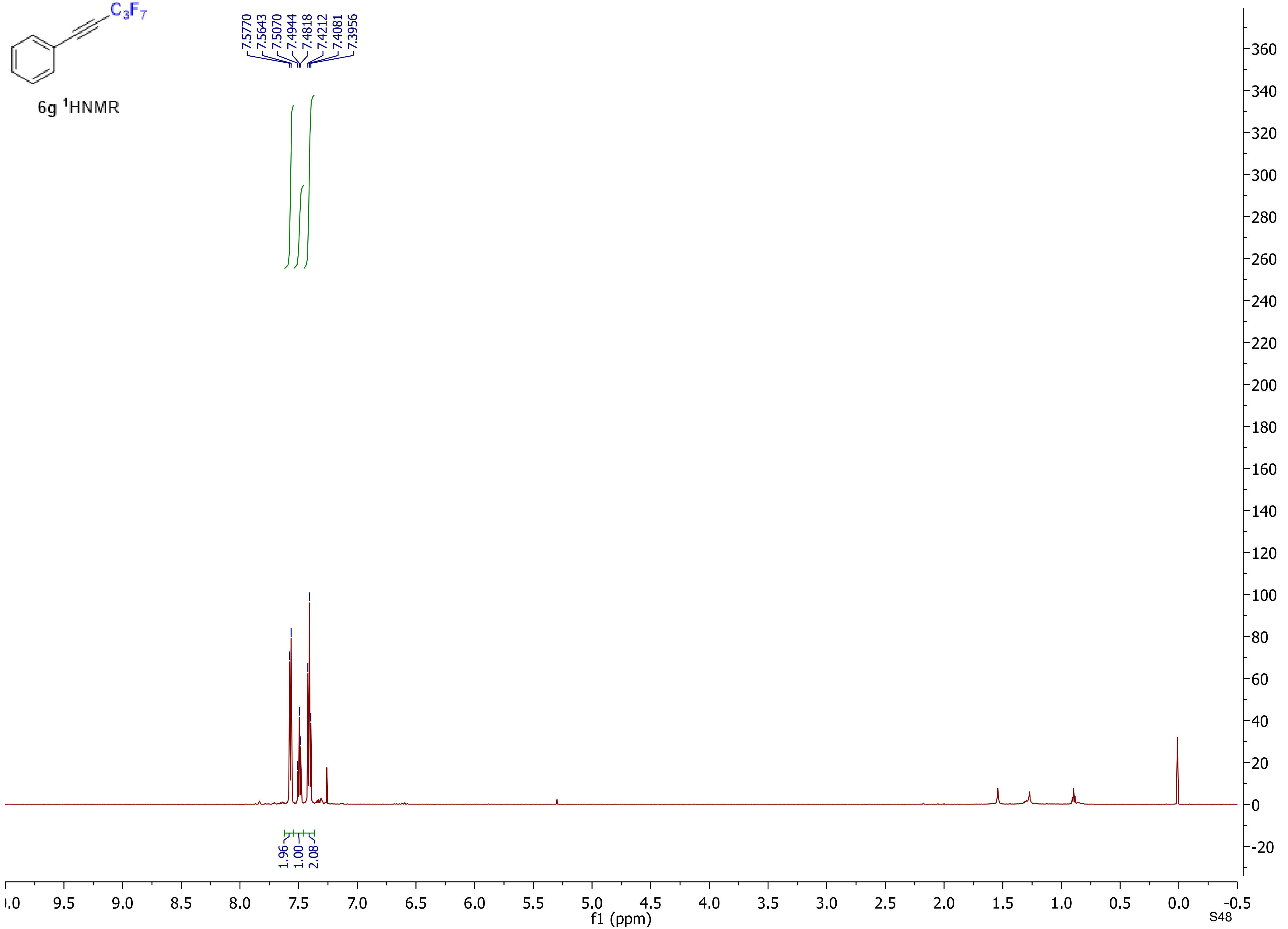
C4F9
F
6e 13CNMR
165.2361
163.5509
135.0469
116.5814
116.4325
114.8114
91.5153
75.0445
74.8044
74.5599
f1 (ppm)



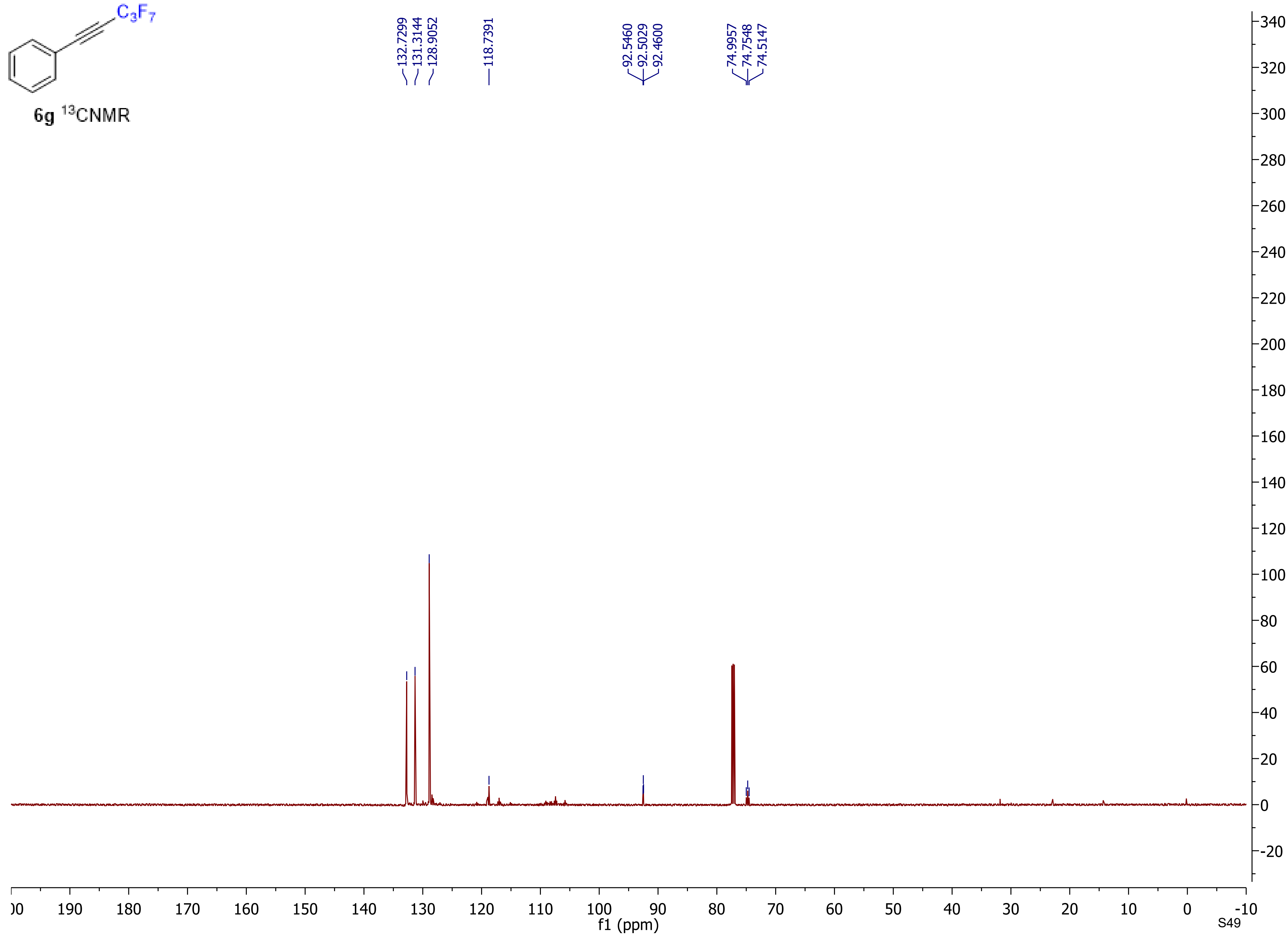
C8F17
6f 1HNMR
7.5732
7.5611
7.5047
7.4922
7.4796
7.4202
7.4072
7.3948
2.03
1.00
2.35
f1 (ppm)



C_8F_{17}
6f ^{13}CNMR
132.7134
131.3049
128.9022
128.4264
92.5081
75.1921
74.9485
74.7148
f1 (ppm)



C_3F_7
6g [1]HNMR
7.5770
7.5643
7.5070
7.4944
7.4818
7.4212
7.4081
7.3956
1.96
1.00
2.08
f1 (ppm)


C3F7
6g 13CNMR
132.7299
131.3144
128.9052
118.7391
92.5460
92.5029
92.4600
74.9957
74.7548
74.5147
f1 (ppm)