Supporting Information

Anti-Markovnikov Hydroamination of Alkenes Catalyzed by an Organic Photoredox System

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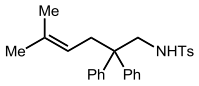
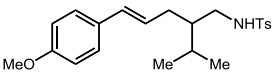
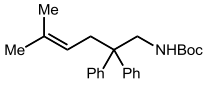
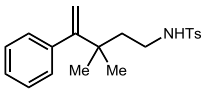
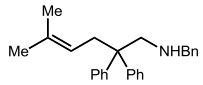
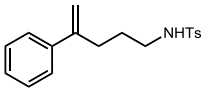
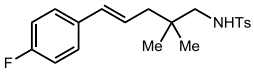
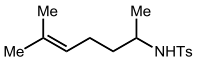
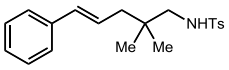
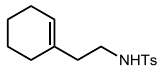
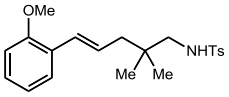
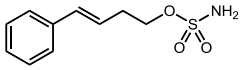
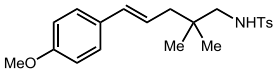
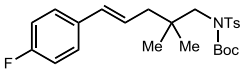
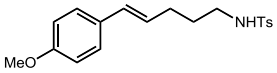
General Methods:

Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer.Proton and carbon magnetic resonance spectra (1H NMR and 13C NMR) were recorded on a Brukermodel DRX 400 (^{1}H NMR at 400 MHz and 600 MHz and ^{13}C NMR at 100 MHz) spectrometer with solvent resonance as the internal standard (1H NMR: $CDCl_3$ at 7.24 ppm; 13C NMR: $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddt = doublet of doublet of triplets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets m = multiplet, brs = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass (now Waters Corporation, 34 Maple Street, Milford, MA 01757) Quattro-II, Triple Quadrupole Mass Spectrometer, with a Z-spray nano-Electrospray source design, in combination with a NanoMate (Advion 19 Brown Road, Ithaca, NY 14850) chip based electrospray sample introduction system and nozzle. Thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm) or cerium ammonium molybdate solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle. Tetrahydrofuran, diethyl ether, dichloromethane, and toluene were dried by passage through a column of neutral alumina under nitrogen prior to use. Irradiation of photochemical reactions was carried out using a 15W PAR38 blue LED floodlamp purchased from EagleLight (Carlsbad, CA). All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. Cyclic voltammograms were obtained with a glassy carbon working electrode, $Ag/AgNO_3$ reference electrode, a platinum wire auxiliary and a BAS CV-27 potentiostat using 1 mM solutions of analyte in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at a scan rate of 0.1V/s. Oxidation potential is reported as the half-wave oxidation potential, taken as the midpoint between the onset of the sloping curve and the minima of the curve.

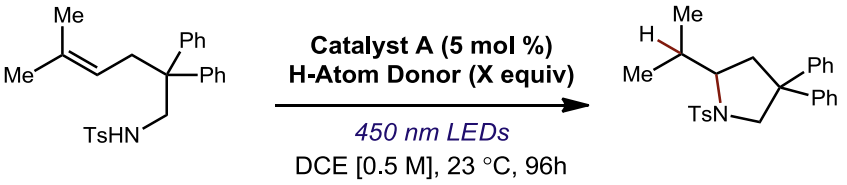
Preparation of Acridinium Photocatalyst (Catalyst A):

The photocatalyst used in this study, *N*-Me-9-mesityl acridinium tetrafluoroborate, was synthesized by the method of Fukuzumi et al.[1] Tetrafluoroboric acid (diethyl ether complex) was substituted for perchloric acid during the hydrolysis. The spectral data matched the values reported in the literature for the perchlorate and hexafluorophosphate salts. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 9.0 Hz, 2H), 8.37 (t, *J* = 9.0 Hz, 2H), 7.84 (s, 4H), 7.23 (s, 2H), 4.81 (s, 3H), 2.46 (s, 3H), 1.68 (s, 6H).

Oxidation Potentials of Substrates vs. $Ag/AgNO_3$:

Substrate	$E_{p/2}$	Substrate	$E_{p/2}$
	1.23 V		0.77 V
	1.31 V		1.44 V
	0.77 V		1.29 V
	1.04 V		1.27 V
	1.03 V		1.38 V
	0.88 V		1.31 V
	0.83 V		1.32 V
	1.02 V		

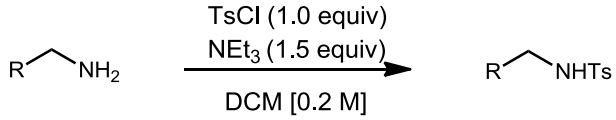
Optimization Studies (Equivalents of thiophenol):



Entry	H-Atom Donor	Yield (by NMR)
1	0.2 equiv PhSH	70%
2	0.5 equiv PhSH	66%
3	0.75 equiv PhSH	54%
4	1.0 equiv PhSH	41%
5	2.0 equiv PhSH	19%

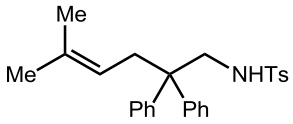
Preparation of Unsaturated Amine Substrates:

General Procedure A: Protection of primary amines with tosylchloride



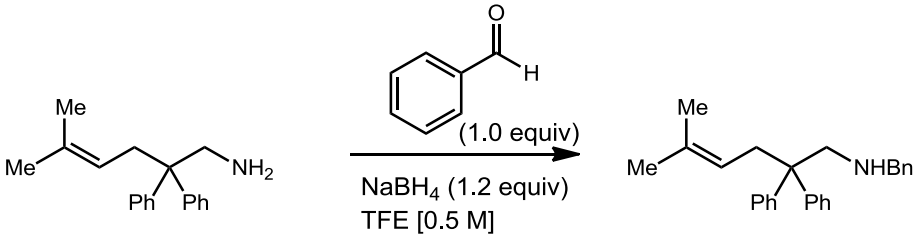
To a clean dry RBF was added a magnetic stir bar and the primary amine (1 equiv) under nitrogen at RT. Dissolved in DCM [0.2 M] and freshly distilled triethylamine (1.5 equiv) then tosylchloride added. Allowed to stir at room temperature overnight, then H_2O added and aqueous layer was extracted 3x with DCM, organic layers washed with brine solution, dried over Na_2SO_2 and concentrated in vacuo. Final substrates were purified by silica gel chromatography using the conditions listed.

4-Methyl-*N*-(5-methyl-2,2-diphenylhex-4-en-1-yl)benzenesulfonamide (9a).



Prepared via general procedure A from 5-methyl-2,2-diphenylhex-4-en-1-amine[2] (prepared from reported literature procedure). Purified in 10% EtOAc/Hex to give a white solid in 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.0 Hz, 2 H), 7.33 - 7.16 (m, 8H), 7.11 - 7.02 (m, 4 H), 4.77 - 4.69 (m, 1 H), 3.87 (t, *J* = 6.1 Hz, 1 H), 3.50 (d, *J* = 6.3 Hz, 2 H), 2.81 (d, *J* = 7.0 Hz, 2 H), 2.42 (s, 3 H), 1.58 - 1.53 (m, 3 H), 1.38 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 143.4, 136.1, 135.5, 129.7, 128.1, 127.2, 126.6, 118.5, 50.2, 49.7, 35.6, 26.0, 21.5, 17.9; **IR** (thin film): 3276, 3058, 2919, 1671, 1598, 1496, 1445, 1406, 1330, 1266 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 420.58; found 420.26

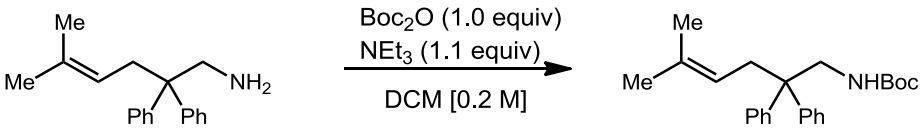
N-Benzyl-5-methyl-2,2-diphenylhex-4-en-1-amine(Table 1, entry 6).



To a clean dry RBF was added a magnetic stir bar, 5-methyl-2,2-diphenylhex-4-en-1-amine[2] (1.0 equiv, prepared from literature procedure) and benzaldehyde (1.0 equiv), dissolved in TFE [0.5 M] under nitrogen. Reaction mixture was heated to 40 °C for ~1 h then sodium borohydride was added. Allowed to stir at 40 °C for ~3 h then heating was discontinued, reaction mixture was filtered through cotton then concentrated in vacuo. Title compound was purified by silica gel chromatography using 10% EtOAc/Hexanes to give a colorless oil in 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 - 7.18 (m, 5 H), 7.18 - 7.12 (m, 5 H), 4.76 - 4.69 (m, 1 H), 3.69 (s, 2 H), 3.15 (s, 2 H), 2.92 (d, *J* = 7.3 Hz, 2 H), 1.53 (s, 3 H), 1.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.3, 140.8, 134.0, 128.3, 127.9,

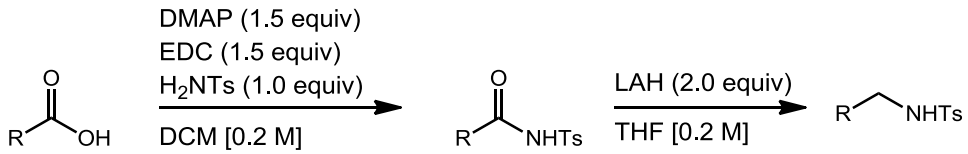
126.7, 125.9, 120.4, 55.7, 54.3, 50.9, 35.8, 26.0, 17.9; **IR** (thin film): 3065, 3058, 3025, 2966, 2912, 2852, 2359, 1943, 1868, 1800, 1749, 1716, 1698, 1683, 1670, 1540, 1495, 1444, 1375, 1361 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 356.52; found 356.19

***tert*-Butyl (5-methyl-2,2-diphenylhex-4-en-1-yl)carbamate (Table 1, entry 7).**



To a clean dry RBF was added a magnetic stir bar and 5-methyl-2,2-diphenylhex-4-en-1-amine[2] (1.0 equiv, prepared from literature procedure) and dissolved in DCM [0.2 M] under nitrogen. Reaction mixture was cooled to -78 °C and freshly distilled triethylamine added then boc anhydride added quickly. Allowed to stir at -78 °C for ~30 min then warmed to 0 °C. After 1 h, saturated ammonium chloride solution was added, the aqueous layer was extracted 3x with DCM, organic layers were combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified via silica gel chromatography with 10% EtOAc/Hexanes to give the desired product as a white solid in 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.30 - 7.24 (m, 4 H), 7.22 - 7.11 (m, 6 H), 4.82 (t, *J* = 6.8 Hz, 1 H), 4.12 (br. s., 1 H), 3.80 (d, *J* = 5.9 Hz, 2 H), 2.77 (d, *J* = 7.1 Hz, 2 H), 1.56 (s, 3 H), 1.39 (s, 3 H), 1.35 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.8, 145.7, 134.8, 128.2, 126.3, 119.3, 50.8, 47.4, 35.9, 28.4, 27.4, 26.0, 17.7; **IR** (thin film): 3442, 2925, 1718, 1498, 1445, 1390, 1365, 1233 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 366.51; found 366.24

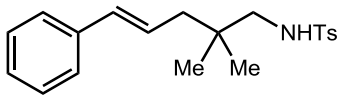
General Procedure B: Preparation of N-tosylamines via amide coupling/reduction sequence



To a clean dry RBF was added a magnetic stir bar, the starting carboxylic acid (1.0 equiv), dimethylaminopyridine (1.5 equiv) and tosylamine (1.0 equiv) under nitrogen at ambient temperature. Dissolved in DCM [0.2 M] then EDC (1.5 equiv) was added. Reaction was stirred at RT overnight. Then 4N HCl was added, phases were separated then aqueous layer extracted three times with DCM. Organic portions were combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Reaction mixtures were then taken onto the reduction step as a crude reaction mixture.

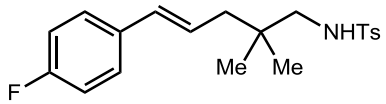
To a clean dry RBF was added a magnetic stir bar, the starting amide (1.0 equiv) and lithium aluminium hydride (2.0 equiv) under nitrogen. Reaction was cooled to 0 °C and slowly dissolved in THF [0.2 M]. Reaction was monitored by TLC and upon complete consumption of starting material, mixture was cooled to 0 °C and a saturated solution of sodium potassium tartrate was added slowly. The reaction was allowed to warm to RT and stirred for ~20 min. Then phases were separated and aqueous layer extracted three times with diethyl ether, and organic layers combined and washed with brine solution. Dried over Na_2SO_4 and concentrated in vacuo. Final substrates were purified by silica gel chromatography using the conditions listed.

***(E)*-*N*-(2,2-Dimethyl-5-phenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (1a).**



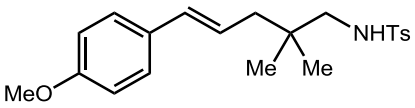
Prepared using general procedure B starting from (*E*)-2,2-dimethyl-5-phenylpent-4-enoic acid[3] (prepared from reported literature procedure). Title compound was purified in 10% EtOAc/Hexanes to give a white solid in 33% yield over two steps. The alkenol was found as a major by-product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2 H), 7.30 - 7.16 (m, 7 H), 6.34 (d, *J* = 15.6 Hz, 1 H), 6.15 - 6.04 (m, 1 H), 5.02 (t, *J* = 6.8 Hz, 1 H), 2.70 (d, *J* = 7.0 Hz, 2 H), 2.37 (s, 3 H), 2.10 (d, *J* = 7.5 Hz, 2 H), 0.90 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.3, 137.5, 137.0, 133.0, 129.7, 128.5, 127.1, 126.1, 52.8, 42.9, 34.8, 25.1, 21.5; **IR** (thin film): 3275, 3025, 2956, 1653, 1597, 1576, 1493, 1457, 1410, 1368, 1321, 1265 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ =344.48; found 344.24

***(E)-N*-(5-(4-Fluorophenyl)-2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide(2a).**



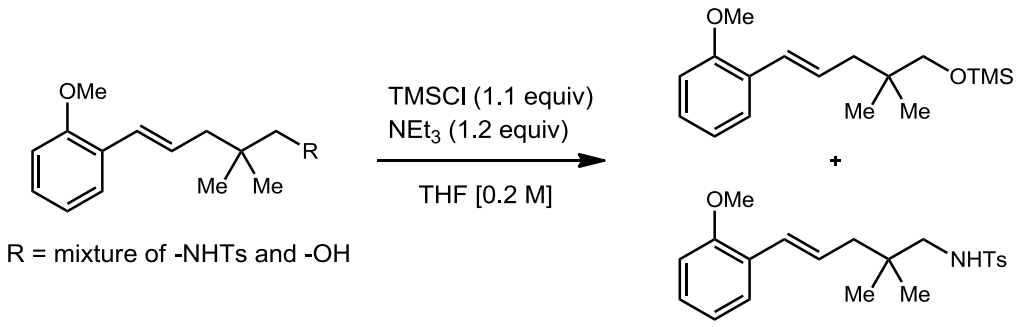
Prepared using general procedure B starting from (*E*)-5-(4-fluorophenyl)-2,2-dimethylpent-4-enoic acid[3] (prepared from reported literature procedure). Title compound was purified in 10% EtOAc/Hexanes to give a white solid in 33% yield over two steps. The alkenol was found as a major by-product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 - 7.68 (dd, 2 H), 7.28 - 7.22 (m, 4 H), 6.96 (dd, *J* = 8.7 Hz, 2 H), 6.30 (d, *J* = 16.1 Hz, 1 H), 6.06 - 5.96 (m, 1 H), 4.34 - 4.27 (m, 1 H), 2.71 (d, *J* = 7.0 Hz, 2 H), 2.39 (s, 3 H), 2.11 - 2.07 (m, 2 H), 0.89 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.2, 160.8, 143.3, 137.0, 133.7, 131.8, 129.7, 127.4, 125.8, 115.4, 115.2, 52.7, 42.8, 34.8, 25.1, 21.5; **IR** (thin film): 3284, 3031, 2961, 1652, 1600, 1508, 1471, 1417, 1325, 1266, 1227 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 362.47; found 362.04

***(E)-N*-(5-(4-Methoxyphenyl)-2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (3a).**



Prepared using general procedure B starting from *(E)*-5-(4-methoxyphenyl)-2,2-dimethylpent-4-enoic acid[3] (prepared from reported literature procedure). Title compound was purified in 10% EtOAc/Hexanes to give a white solid in 25% yield over two steps. The alkenol was found as a major by-product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.32 - 7.27 (m, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.31 (d, *J* = 15.6 Hz, 1 H), 6.04 - 5.92 (m, 1 H), 4.91 (t, *J* = 6.8 Hz, 1 H), 3.82 (s, 3 H), 2.73 (d, *J* = 7.0 Hz, 2 H), 2.42 (s, 3 H), 2.11 (d, *J* = 7.5 Hz, 2 H), 0.92 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.9, 143.3, 136.9, 132.3, 130.3, 129.7, 127.2, 123.7, 113.9, 55.6, 52.8, 42.9, 34.8, 25.1, 21.5, 19.9; **IR** (thin film): 3283, 3030, 2960, 2836, 1770, 1651, 1607, 1576, 1509, 1465, 1419, 1368, 1325, 1247 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 374.51; found 374.22

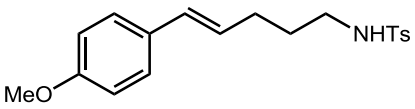
***(E)-N*-(5-(2-Methoxyphenyl)-2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (4a).**



R = mixture of -NHTs and -OH

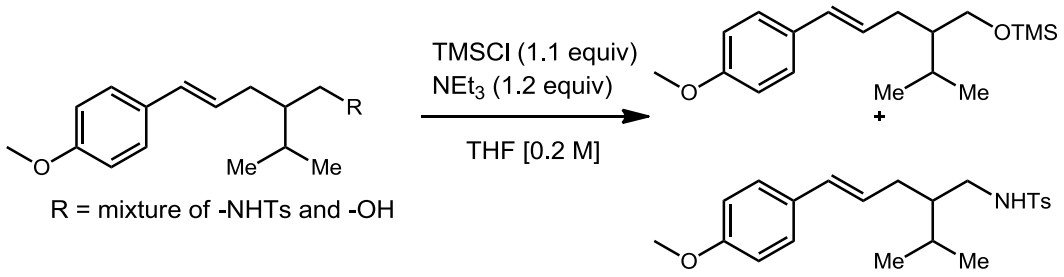
Prepared using general procedure B starting from (*E*)-5-(2-methoxyphenyl)-2,2-dimethylpent-4-enoic acid[3] (prepared from reported literature procedure). Desired product was obtained as an inseparable mixture with the alkenol by-product. To a clean dry RBF was added a magnetic star bar and the amine/alcohol mixture and dissolved in THF [0.2 M] under nitrogen. Then freshly distilled triethylamine (1.2 equiv) and TMSCl (1.1 equiv) added and allowed to stir overnight at room temperature. Then H_2O was added and layers separated. The aqueous layer was extracted 3x with Et_2O, organic layers combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified by silica gel chromatography with 25% EtOAc/Hexanes to give the title compound in 19% yield over three steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.1 Hz, 2 H), 7.30 (dd, *J* = 1.5, 7.6 Hz, 1 H), 7.23 - 7.14 (m, 3 H), 6.91 - 6.81 (m, 2 H), 6.65 (d, *J* = 15.9 Hz, 1 H), 6.13 - 6.03 (m, 1 H), 4.79 (t, *J* = 6.8 Hz, 1 H), 3.81 (s, 3 H), 2.70 (d, *J* = 6.8 Hz, 2 H), 2.38 - 2.35 (m, 3 H), 2.11 (d, *J* = 7.6 Hz, 2 H), 0.90 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 156.4, 143.3, 137.0, 129.7, 128.2, 127.7, 127.1, 126.8, 126.6, 126.5, 120.6, 110.9, 55.5, 52.9, 43.6, 34.8, 25.2, 21.5; **IR** (thin film): 3283, 2960, 1715, 1488, 1463, 1436, 1327, 1242 cm^{-1}; **LRMS** (ESI): Calculated for [M+H$^+$] = 374.51; found 374.16

***(E)-N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide (5a).**



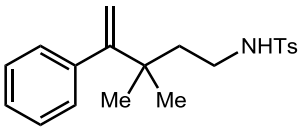
Prepared via general procedure A from (*E*)-5-(4-methoxyphenyl)pent-4-en-1-amine[4] (prepared from reported literature procedure). Purified by silica gel chromatography in 15% EtOAc/Hex to give a colorless oil in 25% yield. **^{1}H NMR (cis)** (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.3 Hz, 2 H), 7.28 - 7.22 (m, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 6.87 - 6.81 (m, 2 H), 6.32 (d, *J* = 11.5 Hz, 1 H), 5.41 (td, *J* = 7.2, 11.6 Hz, 1 H), 4.66 (t, *J* = 6.1 Hz, 1 H), 3.78 (s, 3 H), 2.93 (qd, *J* = 6.7, 13.0 Hz, 2 H), 2.38 (s, *J* = 2.3 Hz, 3 H), 2.27 (dq, *J* = 1.5, 7.4 Hz, 2 H), 1.63 - 1.54 (m, 2 H) **^{1}H NMR (trans)** (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.28 - 7.23 (m, 2 H), 7.19 (d, *J* = 8.8 Hz, 2 H), 6.81 - 6.76 (m, 2 H), 6.23 (d, *J* = 15.8 Hz, 1 H), 5.95 - 5.84 (m, 1 H), 4.77 (t, *J* = 6.1 Hz, 1 H), 3.77 (s, 3 H), 2.98 - 2.92 (m, 2 H), 2.38 (s, 3 H), 2.19 - 2.11 (m, 2 H), 1.67 - 1.57 (m, 2 H); **^{13}C NMR** (**mix of isomers)** (100 MHz, $CDCl_3$) δ = 143.4, 137.0, 130.3, 130.0, 129.7, 129.4, 127.9, 127.0, 113.9, 113.7, 55.3, 42.9, 42.6, 29.8, 29.3, 25.6, 21.5; **IR** (thin film): 3280, 3005, 2933, 1607, 1575, 1509, 1456, 1323 cm^{-1}; **LRMS** (ESI): Calculated for [M+H$^+$] = 346.46; found 346.11

***(E)-N*-(2-Isopropyl-5-(4-methoxyphenyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide (6a).**



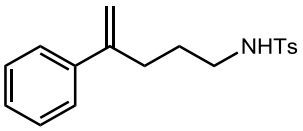
Prepared using general procedure B starting from (*E*)-2-isopropyl-5-(4-methoxyphenyl)pent-4-enoic acid[3] (prepared from reported literature procedure). Desired product was obtained as an inseparable mixture with the alkenol. To a clean dry RBF was added a magnetic star bar and the amine/alcohol mixture and dissolved in THF [0.2 M] under nitrogen. Then freshly distilled triethylamine (1.2 equiv) and TMSCl (1.1 equiv) added and allowed to stir overnight at room temperature. Then H_2O was added and layers separated. The aqueous layer was extracted 3x with Et_2O, organic layers combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified by silica gel chromatography with 20% EtOAc/Hexanes to give the title compound in 18% yield over three steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 2 H), 7.20 (t, *J* = 8.6 Hz, 4 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 6.24 (d, *J* = 16.4 Hz, 1 H), 5.87 (td, *J* = 7.6, 15.5 Hz, 1 H), 4.27 (br. s., 1 H), 3.79 (s, 3 H), 2.98 - 2.81 (m, 2 H), 2.37 (s, 3 H), 2.28 - 2.19 (m, 1 H), 2.07 - 1.98 (m, 1 H), 1.73 (dd, *J* = 6.5, 12.1 Hz, 1 H), 1.48 - 1.37 (m, 1 H), 0.86 (d, *J* = 3.7 Hz, 3 H), 0.84 (d, *J* = 3.7 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.8, 143.2, 136.9, 131.1, 130.3, 129.7, 127.1, 126.4, 113.9, 55.3, 44.4, 44.0, 32.3, 28.2, 21.5, 19.6, 19.2; **IR** (thin film): 3648, 3566, 3283, 3030, 2958, 2933, 2873, 2737, 1918, 1770, 1716, 1652, 1607, 1576, 1510, 1464, 1325, 1440, 1419, 1388, 1368, 1325, 1304, 1289 cm^{-1}; **LRMS** (ESI): Calculated for [M+H$^+$] = 387.54; found 388.13

***N*-(3,3-Dimethyl-4-phenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (7a).**



Prepared using general procedure B starting from 3,3-dimethyl-4-phenylpent-4-enoic acid[3] (prepared from reported literature procedure). Title compound was purified by silica gel chromatography in 25% EtOAc/Hexanes to give a white solid in 45% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.31 - 7.26 (m, 2 H), 7.22 - 7.17 (m, 3 H), 6.96 (dd, *J* = 3.0, 6.5 Hz, 2 H), 5.06 (d, *J* = 1.5 Hz, 1 H), 4.82 (d, *J* = 1.3 Hz, 1 H), 4.67 (t, *J* = 6.0 Hz, 1 H), 3.01 - 2.93 (m, 2 H), 2.41 (s, 3 H), 1.53 - 1.47 (m, 2 H), 1.02 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 156.7, 143.4, 142.6, 137.0, 129.7, 128.7, 127.6, 126.9, 114.2, 40.2, 40.0, 38.4, 27.8, 21.6; **IR** (thin film): 3279, 3080 3053, 2967, 2871, 1810, 1717, 1625, 1598, 1573, 1493, 1439, 1362, 1325, 1267, 1230 cm^{-1}; **LRMS** (ESI): Calculated for [M+H$^+$] = 344.48; found 344.18

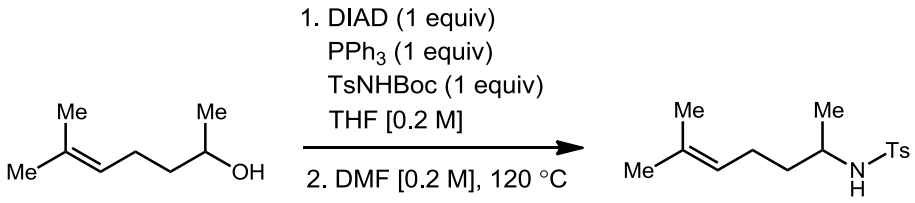
4-Methyl-*N*-(4-phenylpent-4-en-1-yl)benzenesulfonamide (8a).



Prepared using general procedure B starting from 4-phenylpent-4-enoic acid[3] (prepared from reported literature procedure). Title compound was purified by silica gel chromatography in 20% EtOAc/Hexanes to give a white solid in 56% yield over two steps. Spectral data were in agreement with literature values.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 - 7.64 (m, 2 H), 7.31 - 7.15 (m, 5 H),

5.22 - 5.15 (m, 1 H), 4.95 (t, *J* = 6.0 Hz, 1 H), 4.93 (s, 1 H), 2.87 (q, *J* = 6.8 Hz, 2 H), 2.50 - 2.39 (m, 2 H), 2.34 (s, 3 H), 1.59 - 1.47 (m, 2 H)

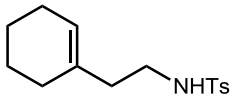
4-Methyl-*N*-(6-methylhept-5-en-2-yl)benzenesulfonamide (10a).



To a clean dry RBF was added a magnetic stir bar, tosylboc amine and triphenylphosphine and solids were dissolved in THF [0.2 M] under nitrogen. Then 6-methylhept-5-en-2-ol (commercially available) was added and reaction was cooled to 0 °C and then DIAD was added and allowed to warm to RT overnight. Then Et_2O was added and aqueous layer was extracted 3x with Et_2O, organic layers were combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified by silica gel chromatography in 10% EtOAc/Hexanes.

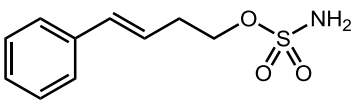
To a clean dry vial was added a magnetic stir bar, tosylboc amine and dissolved in DMF [0.2 M] under nitrogen. The vial was sealed and heated to 120 °C for 48 hours. Heating was discontinued and H_2O was added and then the aqueous layer was extracted 3x with Et_2O, organic layers were combined and washed with brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified by silica gel chromatography in 10% EtOAc/Hexanes to give the title compound as a colorless oil in 27% yield over 2 steps. Spectral data were in agreement with literature values.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 - 7.72 (m, 2 H), 7.25 (d, *J* = 8.3 Hz, 2 H), 4.91 - 4.85 (m, 2 H), 3.31 - 3.19 (m, 1 H), 2.38 (s, 3 H), 1.96 - 1.74 (m, 2 H), 1.59 (s, 3 H), 1.47 (s, 3 H), 1.38 - 1.30 (m, 2 H), 1.00 (d, *J* = 6.5 Hz, 3 H)

***N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfonamide (11a).**



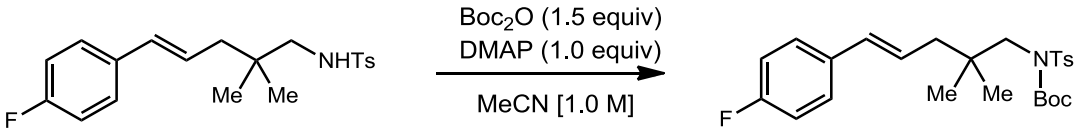
Prepared via general procedure A from commercially available 2-(cyclohex-1-en-1-yl)ethanamine. Purified in 10% EtOAc/Hex to give a white solid in 27% yield. Spectral data were in agreement with literature values.[6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.3 Hz, 2 H), 7.30 - 7.24 (m, 2 H), 5.33 (br. s., 1 H), 4.58 (t, *J* = 5.6 Hz, 1 H), 2.95 (q, *J* = 6.5 Hz, 2 H), 2.39 (s, 3 H), 2.01 (t, *J* = 6.7 Hz, 2 H), 1.94 - 1.86 (m, 2 H), 1.68 (br. s., 2 H), 1.54 - 1.41 (m, 4 H)

***(E)*-4-Phenylbut-3-en-1-yl sulfamate (12a).**



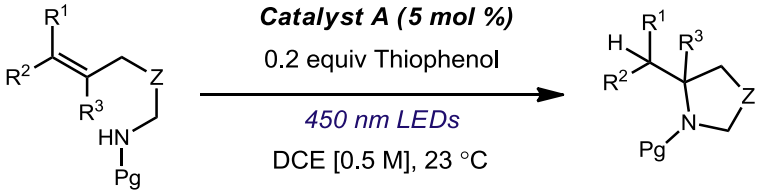
Prepared according to a published procedure;[7] spectral data were in agreement with literature values.[8] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 - 7.28 (m, 4 H), 7.27 - 7.20 (m, 1 H), 6.50 (d, *J* = 15.9 Hz, 1 H), 6.16 (td, *J* = 7.0, 15.8 Hz, 1 H), 5.15 (s, 2 H), 4.28 (t, *J* = 6.6 Hz, 2 H), 2.63 (q, *J* = 6.6 Hz, 2 H)

***(E)*-*tert*-Butyl (5-(4-fluorophenyl)-2,2-dimethylpent-4-en-1-yl)(tosyl)carbamate (13).**



To a clean dry RBF was added a magnetic stir bar and (*E*)-N-(5-(4-fluorophenyl)-2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (1.0 equiv) and DMAP (1.0 equiv) and dissolved in MeCN [1.0 M] under nitrogen. Then boc anhydride was added quickly. Allowed to stir at RT overnight. Water was added, and the aqueous layer extracted 3x with EtOAc, organic layers combined and washed with 1M HCl solution then brine solution, dried over Na_2SO_4 and concentrated in vacuo. Purified via silica gel chromatography with 10% EtOAc/Hexanes to give the desired product as a colorless oil in 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 - 7.68 (m, 2 H), 7.34 - 7.25 (m, 4 H), 6.99 - 6.93 (m, 2 H), 6.40 - 6.32 (m, 1 H), 6.25 - 6.15 (m, 1 H), 3.87 (s, 2 H), 2.41 (s, 3 H), 2.22 (d, *J* = 7.3 Hz, 2 H), 1.22 (s, 9 H), 1.02 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 151.6, 144.0, 137.9, 133.9, 131.5, 129.3, 127.6, 126.6, 115.4, 115.2, 84.1, 56.2, 44.2, 36.7, 27.6, 25.3, 21.6; **IR** (thin film): 3674, 3648, 3028, 3617, 3566, 3437, 3039, 2979, 2932, 2825, 2392, 1808, 1730, 1652, 1636, 1599, 1588, 1508, 1472, 1434, 1395, 1354, 1276, 1225 cm^{-1}; **LRMS** (ESI): Calculated for [M+Na] = 484.59; found 484.15

General Procedure C: Anti-Markovnikov hydroamination reactions



To a clean flame-dried 1 dram vial was added a magnetic stir bar, N-Me-mesityl acridinium catalyst (5.0 mol %) and protected amine substrate (100 mg). Reaction vessel was purged with nitrogen then dichloroethane (sparged for 15 min, [0.5M]) was added, then thiophenol (0.2 equiv). Reaction was sealed with Teflon tape then irradiated with blue LED lamp at room temperature until reaction was complete monitoring by TLC. Reactions were quenched with a solution of TEMPO (~5 mg) in dichloromethane (0.2 mL) and concentrated in vacuo. The final products were purified by silica gel chromatography using the conditions listed.

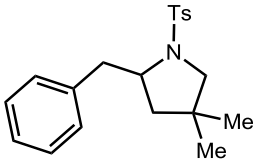
2-Isopropyl-4,4-diphenylpyrrolidine.

Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 3% EtOAc/Hexanes to give a white solid in 65% isolated yield. ^{1}H NMR was very complex, to confirm identity isolated material was submitted to deprotection with TFA.

To a clean dry RBF was added a magnetic stir bar and *tert*-butyl 2-isopropyl-4,4-diphenylpyrrolidine-1-carboxylate and dissolved in DCM:TFA (1:1) under nitrogen at room temperature. After 3 h,

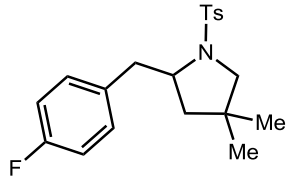
saturated sodium bicarbonate added, aqueous layer extracted 3x with DCM, organic layers combined and washed with brine solution, dried over na2SO4 and concentrated in vacuo. Purified by silica gel chromatography in 50% EtOAc/Hexanes to give the desired 2-isopropyl-4,4-diphenylpyrrolidine. Spectral data were in agreement with literature values.[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.33 - 7.24 (m, 4 H), 7.23 - 7.11 (m, 6 H), 3.73 (dd, *J* = 1.7, 11.2 Hz, 1 H), 3.33 (d, *J* = 11.2 Hz, 1 H), 2.90 - 2.82 (m, 1 H), 2.70 (ddd, *J* = 1.7, 6.5, 12.6 Hz, 1 H), 2.06 (dd, *J* = 9.8, 12.7 Hz, 1 H), 1.71 - 1.60 (m, 1 H), 1.28 (d, *J* = 16.1 Hz, 1 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 0.88 (d, *J* = 6.6 Hz, 3 H)

2-Benzyl-4,4-dimethyl-1-tosylpyrrolidine (1b).



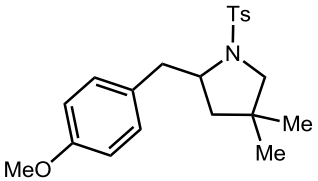
Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 24h then purified in 2% EtOAc/Hexanes to give a white solid in 82% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 7.3 Hz, 2 H), 7.25 - 7.19 (m, 3 H), 3.84 - 3.75 (m, 1 H), 3.58 (dd, *J* = 3.5, 13.1 Hz, 1 H), 3.13 (s, 2 H), 2.78 (dd, *J* = 9.8, 13.1 Hz, 1 H), 2.43 (s, 3 H), 1.54 - 1.42 (m, 2 H), 0.99 (s, 3 H), 0.46 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.3, 138.5, 135.3, 129.6, 129.5, 128.4, 127.6, 126.4, 61.7, 61.6, 45.7, 42.9, 37.2, 26.5, 25.8, 21.6; **IR** (thin film): 3061, 3027, 2960, 1288, 2873, 1599, 1540, 1494, 1245, 1454, 1390, 1347, 1303, 1224 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 344.48; found 344.12

2-(4-Fluorobenzyl)-4,4-dimethyl-1-tosylpyrrolidine (2b).



Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 24h then purified in 2% EtOAc/Hexanes to give a white solid in 89% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.20 - 7.13 (m, 2 H), 7.00 - 6.92 (m, 2 H), 3.78 - 3.69 (m, 1 H), 3.43 (dd, *J* = 3.4, 13.4 Hz, 1 H), 3.07 (q, *J* = 10.5 Hz, 2 H), 2.80 (dd, *J* = 9.5, 13.3 Hz, 1 H), 2.40 (s, 3 H), 1.43 (d, *J* = 8.0 Hz, 2 H), 0.94 (s, 3 H), 0.41 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.4, 135.2, 134.0, 131.1, 131.0, 129.6, 127.5, 115.3, 115.1, 61.6, 61.4, 45.5, 41.7, 37.2, 26.4, 25.8, 21.6; **IR** (thin film): 2962, 1597, 1508, 1465, 1330, 1302, 1218 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 362.47; found 362.10

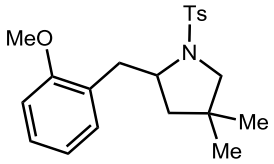
2-(4-Methoxybenzyl)-4,4-dimethyl-1-tosylpyrrolidine (3b).



Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 30h then purified in 5% EtOAc/Hexanes to give a colorless oil in 88% isolated

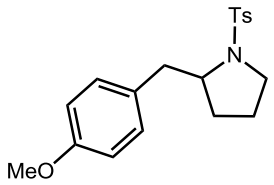
yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.3 Hz, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 3.87 - 3.76 (m, 3 H), 3.75 - 3.68 (m, 1 H), 3.45 (dd, *J* = 3.4, 13.2 Hz, 1 H), 3.13 - 3.04 (m, 2 H), 2.72 (dd, *J* = 9.7, 13.2 Hz, 1 H), 2.40 (s, 3 H), 1.52 - 1.42 (m, 2 H), 1.02 - 0.92 (m, 3 H), 0.42 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.2, 143.3, 135.3, 130.5, 129.6, 127.5, 113.8, 61.7, 55.2, 45.7, 41.8, 37.2, 26.5, 25.8, 21.4; **IR** (thin film): 2958, 2872, 1683, 1612, 1582, 1511, 1464, 1390, 1346, 1302, 1247 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 374.51; found 374.15

2-(2-Methoxybenzyl)-4,4-dimethyl-1-tosylpyrrolidine (4b).



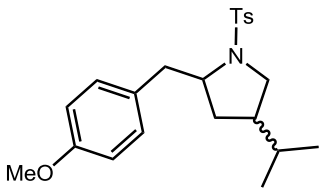
Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 40h then purified in 5% EtOAc/Hexanes to give a white solid in 69% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.20 - 7.12 (m, 2 H), 6.89 - 6.80 (m, 2 H), 3.85 (s, 3 H), 3.83 - 3.76 (m, 1 H), 3.72 (dd, *J* = 3.9, 12.7 Hz, 1 H), 3.22 - 3.16 (m, 1 H), 3.11 - 3.06 (m, 1 H), 2.68 (dd, *J* = 10.3, 12.7 Hz, 1 H), 2.40 (s, 3 H), 1.48 (dd, *J* = 8.2, 12.8 Hz, 1 H), 1.34 (dd, *J* = 7.1, 12.7 Hz, 1 H), 0.99 (s, 3 H), 0.42 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 157.7, 143.1, 135.0, 131.2, 129.4, 127.7, 127.7, 127.2, 120.5, 110.4, 62.1, 60.0, 55.3, 45.8, 37.5, 37.0, 26.7, 26.1, 21.6; **IR** (thin film) 2958, 2872, 1732, 1716, 1698, 1683, 1670, 1652, 1599, 1540, 1507, 1493, 1438, 1396, 1304, 1244 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 374.51; found 374.16

2-(4-Methoxybenzyl)-1-tosylpyrrolidine (5b).



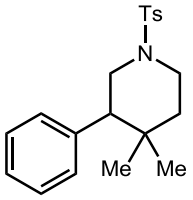
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 48h then purified in 5% EtOAc/Hexanes to give a colorless oil in 79% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.16 - 7.10 (m, 2 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 3.77 (s, 3 H), 3.74 (d, *J* = 3.8 Hz, 1 H), 3.39 - 3.31 (m, 1 H), 3.16 - 3.05 (m, 2 H), 2.69 (dd, *J* = 9.4, 13.4 Hz, 1 H), 2.40 (s, 3 H), 1.65 - 1.54 (m, 2 H), 1.47 - 1.34 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.3, 143.3, 134.8, 130.6, 130.5, 129.7, 127.5, 113.8, 61.7, 55.3, 49.3, 41.7, 29.8, 23.8, 21.5; **IR** (thin film): 2953, 2835, 1612, 1597, 1583, 1511, 1399, 1339, 1247 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 346.46; found 346.12

4-Isopropyl-2-(4-methoxybenzyl)-1-tosylpyrrolidine (6b).



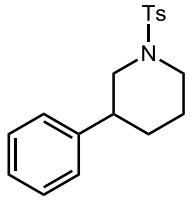
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 39h then purified in 8% EtOAc/Hexanes to give a white solid in 88% isolated yield (average of two trials) in a 1.6:1 dr. **^{1}H NMR (major)** (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 3.2, 8.1 Hz, 2 H), 7.33 - 7.27 (m, 2 H), 7.16 - 7.09 (m, 2 H), 6.85 - 6.78 (m, 2 H), 3.80 (d, *J* = 2.7 Hz, 1 H), 3.76 (s, 3 H), 3.71 - 3.63 (m, 1 H), 3.62 - 3.51 (m, 1 H), 3.30 (dd, *J* = 3.4, 13.4 Hz, 1 H), 2.85 - 2.71 (m, 1 H), 2.41 (s, 3 H), 1.79 (td, *J* = 6.4, 12.8 Hz, 1 H), 1.27 - 1.10 (m, 2 H), 0.70 (t, *J* = 7.3 Hz, 6 H) **^{1}H NMR (minor)** (400 MHz, $CDCl_3$) δ = 7.74 - 7.70 (m, 2 H), 7.30 (d, *J* = 5.1 Hz, 2 H), 7.14 (d, *J* = 6.6 Hz, 2 H), 6.84 - 6.81 (m, 2 H), 3.76 (s, 3 H), 3.72 - 3.63 (m, 1 H), 3.62 - 3.51 (m, 1 H), 3.11 (dd, *J* = 3.4, 13.4 Hz, 1 H), 2.69 - 2.54 (m, 1 H), 2.40 (s, 3 H), 1.73 - 1.65 (m, 1 H), 1.21-1.14 (m, 1H), 1.03 - 0.90 (m, 2 H), 0.78 (d, *J* = 6.6 Hz, 3 H), 0.74 (d, *J* = 6.6 Hz, 3 H) **^{13}C NMR (mix of isomers** (100 MHz, $CDCl_3$) δ = 158.2, 143.3, 135.3, 134.4, 130.7, 130.6, 130.5, 130.3, 129.7, 129.6, 127.5, 127.4, 113.9, 113.8, 62.5, 62.1, 55.3, 55.2, 53.4, 45.4, 44.1, 42.1, 41.9, 36.8, 34.0, 31.8, 31.2, 21.6, 21.5, 21.4, 21.3, 21.1, 21.0 **IR** (thin film): 3060, 3030, 2959, 2871, 2835, 1749, 1716, 1683, 1652, 1613, 1597, 1558, 1540, 1494, 1456, 1386, 1302, 1247 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 388.54; found 388.13

4,4-Dimethyl-3-phenyl-1-tosylpiperidine (7b).



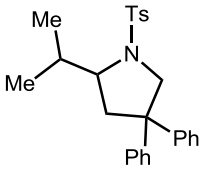
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 48h then purified in 4% EtOAc/Hexanes to give a white solid in 79% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.27 - 7.19 (m, 3 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 3.67 (d, *J* = 12.0 Hz, 1 H), 3.61 (d, *J* = 10.5 Hz, 1 H), 2.80 - 2.67 (m, 2 H), 2.58 (dt, *J* = 2.8, 12.3 Hz, 1 H), 2.44 (s, 3 H), 1.71 (dt, *J* = 4.5, 13.1 Hz, 1 H), 1.52 - 1.45 (m, 1 H), 0.79 (s, 3 H), 0.67 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.5, 139.5, 133.6, 129.7, 129.1, 127.9, 126.9, 51.6, 46.4, 42.8, 39.7, 32.5, 29.9, 21.6, 19.3; **IR** (thin film): 2948, 1597, 1455, 1389, 1340, 1223 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 344.48; found 344.06

3-Phenyl-1-tosylpiperidine (8b).



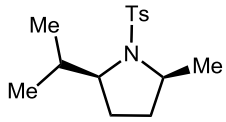
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 5% EtOAc/Hexanes to give a colorless oil in 60% isolated yield (average of two trials). Spectral data were in agreement with literature values.[10] **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2 H), 7.33 - 7.26 (m, 4 H), 7.25 - 7.19 (m, 1 H), 7.16 (d, *J* = 7.0 Hz, 2 H), 3.91 - 3.81 (m, 2 H), 2.92 - 2.81 (m, 1 H), 2.42 (s, 3 H), 2.32 - 2.17 (m, 2 H), 1.93 (d, *J* = 13.3 Hz, 1 H), 1.87 - 1.70 (m, 2 H), 1.48 - 1.35 (m, 1 H)

2-Isopropyl-4,4-diphenyl-1-tosylpyrrolidine (9b).



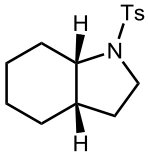
Prepared using general procedure **C** on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 3% EtOAc/Hexanes to give a colorless oil in 70% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 7.3 Hz, 1 H), 7.10 (dd, *J* = 1.9, 10.2 Hz, 4 H), 7.06 - 7.00 (m, 5 H), 4.47 (dd, *J* = 1.8, 11.0 Hz, 1 H), 3.91 (d, *J* = 11.0 Hz, 1 H), 3.74 (s, 1 H), 2.75 - 2.67 (m, 1 H), 2.57 - 2.47 (m, 1 H), 2.33 (s, 3 H), 2.23 (dd, *J* = 10.4, 12.9 Hz, 1 H), 0.88 (d, *J* = 7.0 Hz, 3 H), 0.74 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 146.3, 144.3, 142.5, 136.7, 129.3, 128.6, 128.5, 126.7, 126.7, 126.5, 126.5, 126.1, 64.5, 59.9, 52.4, 36.9, 30.0, 21.5, 19.4, 14.7; **IR** (thin film): 3058, 2962, 1598, 1495, 1447, 1389, 1336, 1304, 1265, 1235 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H^+]$ = 420.58; found 420.15

(2*S*, 5*S*)-2-Isopropyl-5-methyl-1-tosylpyrrolidine (10b).



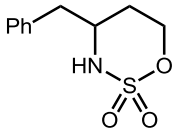
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 3% EtOAc/Hexanes to give a colorless oil in 56% isolated yield (average of two trials) in 3:1 dr. Spectral data were in agreement with literature values.[11] **^{1}H NMR (major)** (400 MHz, $CDCl_3$) δ = 7.71 - 7.67 (m, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 3.71 - 3.63 (m, 1 H), 3.43 - 3.36 (m, 1 H), 2.40 (s, 3 H), 2.11 - 2.00 (m, 1 H), 1.62 (td, *J* = 6.1, 12.1 Hz, 1 H), 1.56 - 1.45 (m, 1 H), 1.44 - 1.34 (m, 1 H), 1.31 - 1.23 (m, 4 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H)

1-Tosyloctahydro-1H-indole (11b).



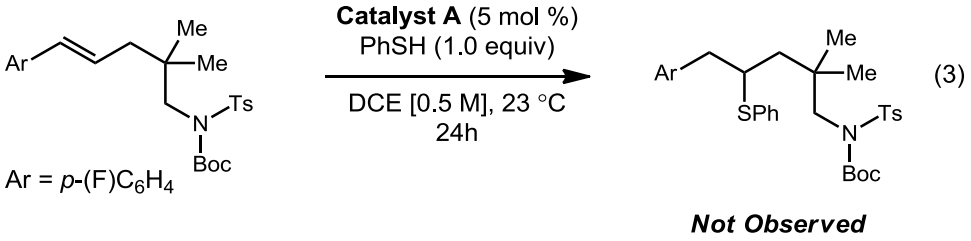
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 5% EtOAc/Hexanes to give a colorless oil in 72% isolated yield (average of two trials) in 12:1 dr. Spectral data were in agreement with literature values.[12] **^{1}H NMR major** (400 MHz, $CDCl_3$) δ = 7.72 - 7.65 (m, 2 H), 7.29 - 7.22 (m, 2 H), 3.56 - 3.42 (m, 2 H), 3.19 - 3.09 (m, 1 H), 2.42 - 2.35 (m, 3 H), 1.91 - 1.69 (m, 3 H), 1.63 - 1.46 (m, 5 H), 1.39 - 1.23 (m, 2 H), 1.23 - 1.11 (m, 1 H)

4-Benzyl-1,2,3-oxathiazinane 2,2-dioxide (12b).



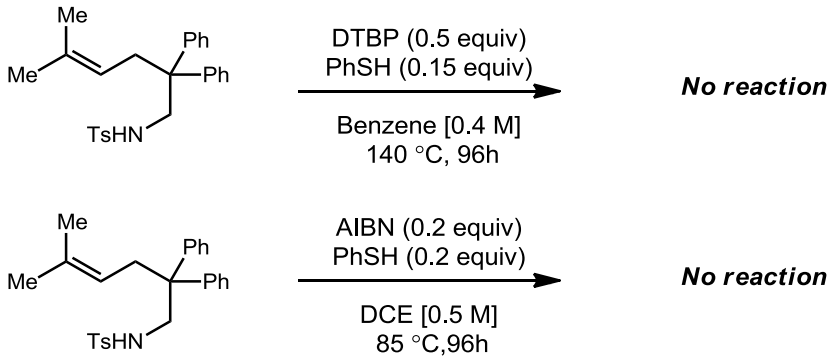
Prepared using general procedure C on a 100 mg scale with 0.2 equiv thiophenol, and dichloroethane [0.5 M]. Irradiated for 96h then purified in 20 % EtOAc/Hexanes to give an off-white solid 54% isolated yield (average of two trials). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36 - 7.29 (m, 2 H), 7.28 - 7.24 (m, 1 H), 7.18 - 7.14 (m, 2 H), 4.66 (dt, *J* = 2.8, 12.0 Hz, 1 H), 4.48 (ddd, *J* = 1.8, 4.9, 11.6 Hz, 1 H), 4.10 (d, *J* = 10.0 Hz, 1 H), 4.03 - 3.90 (m, 1 H), 2.92 (dd, *J* = 5.9, 13.7 Hz, 1 H), 2.77 (dd, *J* = 7.3, 13.7 Hz, 1 H), 1.81 - 1.62 (m, 2 H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 135.4, 129.4, 129.0, 127.4, 72.0, 56.5, 41.1, 29.0 3 **IR** (thin film): 3259, 3086, 3062, 2965, 2925, 2855, 1698, 1683, 1670, 1636, 1602, 1558, 1523, 1497, 1455, 1420, 1360, 1267, 1239, 1220 cm^{-1}; **LRMS** (ESI): Calculated for [$M+H^+$] = 227.28; found 227.99

Procedure for Control Reactions:



(3)

Equation 3: To a clean flame-dried 1 dram vial was added a magnetic stir bar, N-Me-mesityl acridinium catalyst (5.0 mol %), *(E)-tert*-butyl (5-(4-fluorophenyl)-2,2-dimethylpent-4-en-1-yl)(tosyl)carbamate (100 mg). Reaction vessel was purged with nitrogen then dichloroethane (sparged for 15 min, [0.5M]) was added then thiophenol was added (1.0 equiv). Reaction was sealed with teflon tape then irradiated with blue LED lamp at room temperature for 24 hours. Reaction was quenched with a solution of TEMPO (~5 mg) in dichloromethane (0.2 mL) and concentrated in vacuo. Only unchanged starting material was observed by ^{1}H NMR.

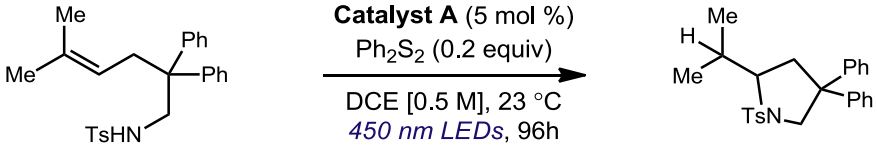


(4)

Equation 4, Conditions A: To a clean dry 20 mL scintillation vial was added a magnetic stir bar, 4-Methyl-*N*-(5-methyl-2,2-diphenylhex-4-en-1-yl)benzenesulfonamide (1 equiv) , benzene [0.4 M], di-*tert*-butyl peroxide (0.5 equiv) and thiophenol (0.15 equiv) under nitrogen. Reaction vessel was sealed and heated to 140 °C for 96 hours, then heating was discontinued and reaction mixture was quenched with TEMPO solution, and concentrated in vacuo. Only unchanged starting material was observed by ^{1}H NMR.

Equation 4, Conditions B: To a clean dry 20 mL scintillation vial was added a magnetic stir bar, 4-Methyl-*N*-(5-methyl-2,2-diphenylhex-4-en-1-yl)benzenesulfonamide (1 equiv) , dichloroethane [0.5

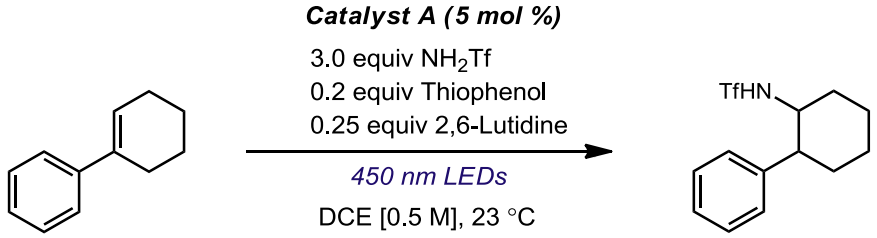
M], azobisisobutyronitrile (0.2 equiv) and thiophenol (0.2 equiv) under nitrogen. Reaction vessel was sealed and heated to 85°C for 96 hours, then heating was discontinued and reaction mixture was quenched with TEMPO solution, and concentrated in vacuo. Only unchanged starting material was observed by ^{1}H NMR.



55%

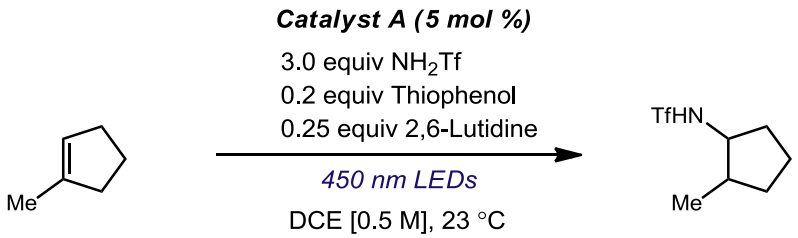
To a clean flame-dried 1 dram vial was added a magnetic stir bar, N-Me-mesityl acridinium catalyst (5.0 mol %), 4-Methyl-*N*-(5-methyl-2,2-diphenylhex-4-en-1-yl)benzenesulfonamide (100 mg) and diphenyldisulfide (0.2 equiv). Reaction vessel was purged with nitrogen then dichloroethane (sparged for 15 min, [0.5M]) was added. Reaction was sealed with teflon tape then irradiated with blue LED lamp at room temperature for 96 hours. Reaction was quenched with a solution of TEMPO (~5 mg) in dichloromethane (0.2 mL) and concentrated in vacuo. Crude ^{1}H NMR with hexamethyldisiloxane indicated a 55% yield of desired product.

1,1,1-trifluoro-N-(2-phenylcyclohexyl)methanesulfonamide (Equation 6).



To a clean dry 2 dram vial was added a magnetic stirbar, catalyst A (5 mol %) and $TfNH_2$ (3.0 equiv). Vial with solids were then brought into the glovebox where 2,6-lutidine (0.25 equiv) and dichloroethane [0.5 M] were added. Reaction vessel was sealed and taken out of the glovebox, then thiophenol (0.2 equiv, freshly sparged) was added. Irradiated for 96h then purified in 5% EtOAc/Hexanes to give a white solid in 55% isolated yield (average of two trials) in 2.6:1 dr. **^{1}H NMR (inseparable mixture of diastereomers)** (400 MHz, $CDCl_3$) δ = 7.36 - 7.29 (m, 4 H), 7.26 (s, 2 H), 7.19 - 7.13 (m, 4 H), 4.67 (br s, 1 H), 4.33 (br s, 1H), 3.95-3.89 (m, 1 H), 3.01 - 2.93 (m, 1 H), 2.43 - 2.31 (m, 1 H), 2.09-1.38 (m, 17 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 141.5, 141.3, 128.8, 128.6, 127.7, 127.6, 127.4, 127.2, 60.0, 57.5, 51.1, 45.8, 35.5, 34.3, 32.6, 25.6, 25.2, 25.0, 19.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -77.68 (minor), -77.79 (major); **IR** (thin film): 3313, 2928, 1421, 1357, 1224 cm^{-1}; **LRMS** (ESI): Calculated for $[M+H_2O]$ = 325.35; found 325.20

1,1,1-trifluoro-N-(2-methylcyclopentyl)methanesulfonamide (Equation 7).



To a clean dry 2 dram vial was added a magnetic stirbar, catalyst A (5 mol %) and $TfNH_2$ (3.0 equiv). Vial with solids were then brought into the glovebox where 2,6-lutidine (0.25 equiv) and dichloroethane [0.5 M] were added. Reaction vessel was sealed and taken out of the glovebox, then thiophenol (0.2 equiv, freshly sparged) was added. Irradiated for 96h then purified in 5% EtOAc/Hexanes to give a colorless oil in 51% isolated yield (average of two trials, obtained an average 63% yield by NMR using hexamethyldisiloxane as an internal standard) in 1.5:1 dr. **^{1}H NMR (inseparable mixture of diastereomers)** (400 MHz, $CDCl_3$) δ = 5.04 (br s, 2 H), 3.86 (m, 2 H), 3.34 (quint, *J* = 7.3 Hz, 2 H), 2.20 – 1.43 (m, 8 H), 1.31 – 1.14 (m, 4 H), 1.05 (d, *J* = 6.4 Hz, 3 H), 0.97 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 121.2, 118.1, 63.4, 60.3, 41.5, 40.5, 37.1, 33.2, 32.4, 31.6, 31.0, 22.9, 21.3, 21.0, 17.2, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -77.54 (major), -77.71 (minor); **IR** (thin film): 3647, 3565, 3303, 2965, 2878, 1622, 1444, 1375, 1269, 1232 cm^{-1}; **LRMS** (ESI): Calculated for [M+H+K] = 271.34; found 271.16

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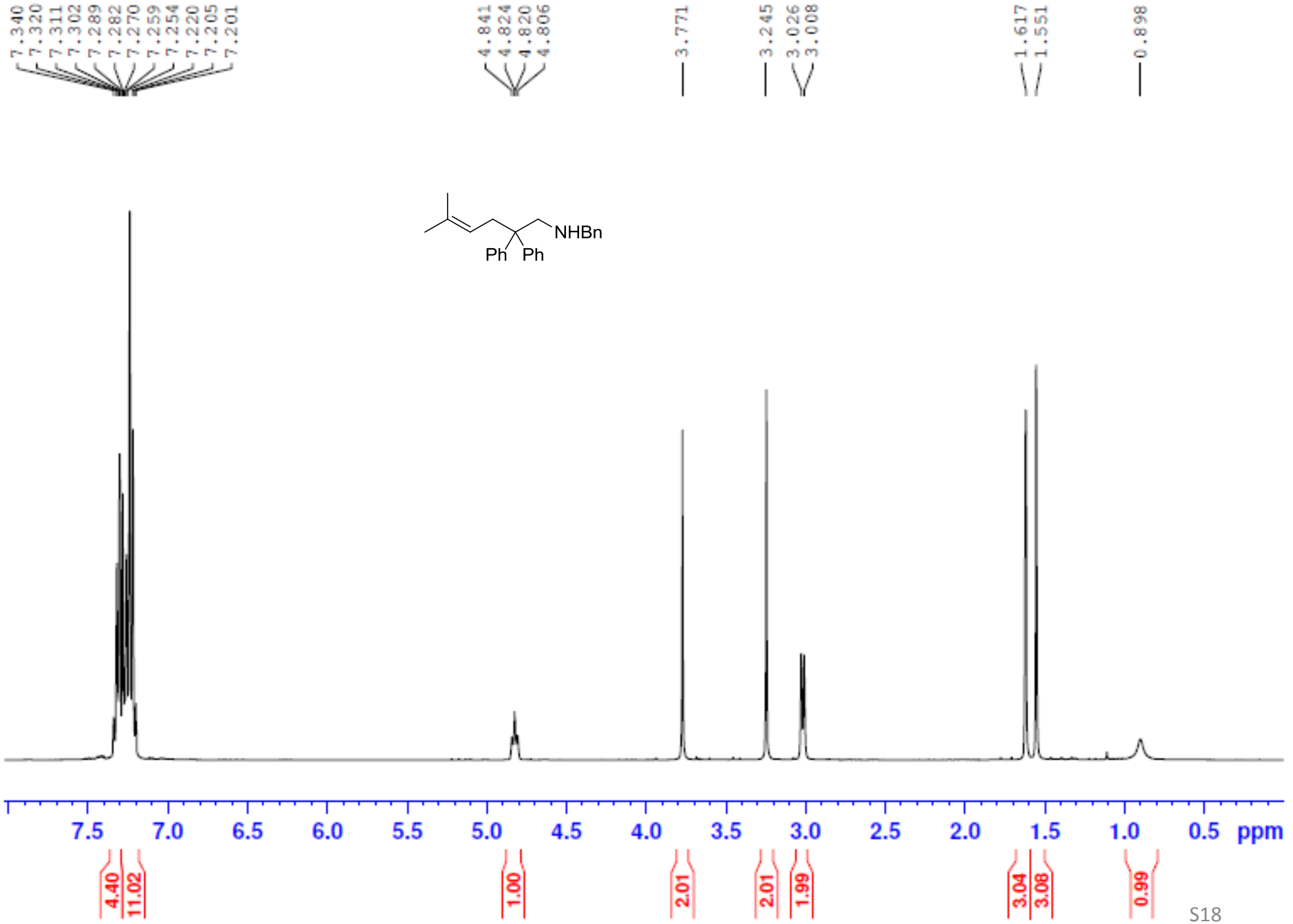
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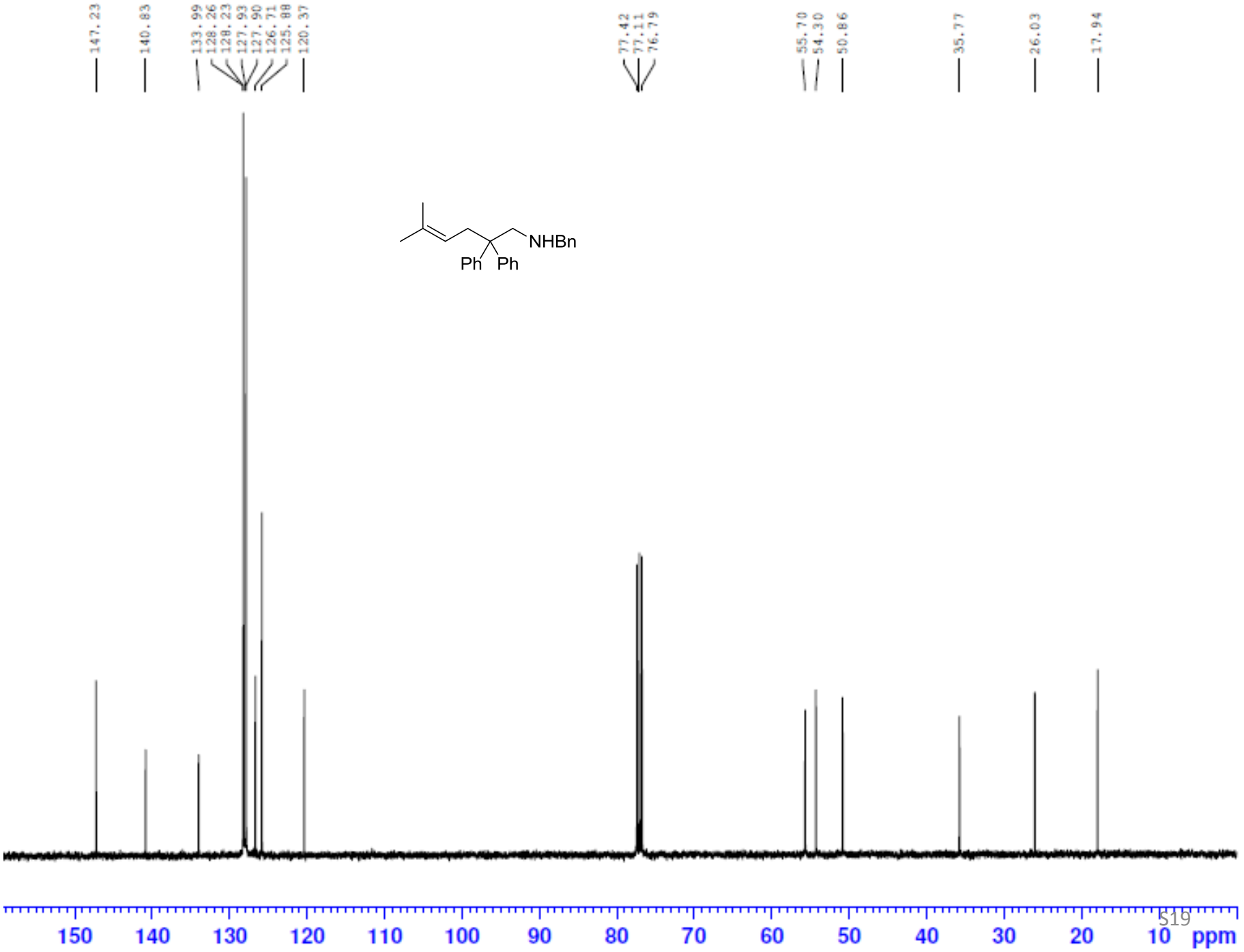
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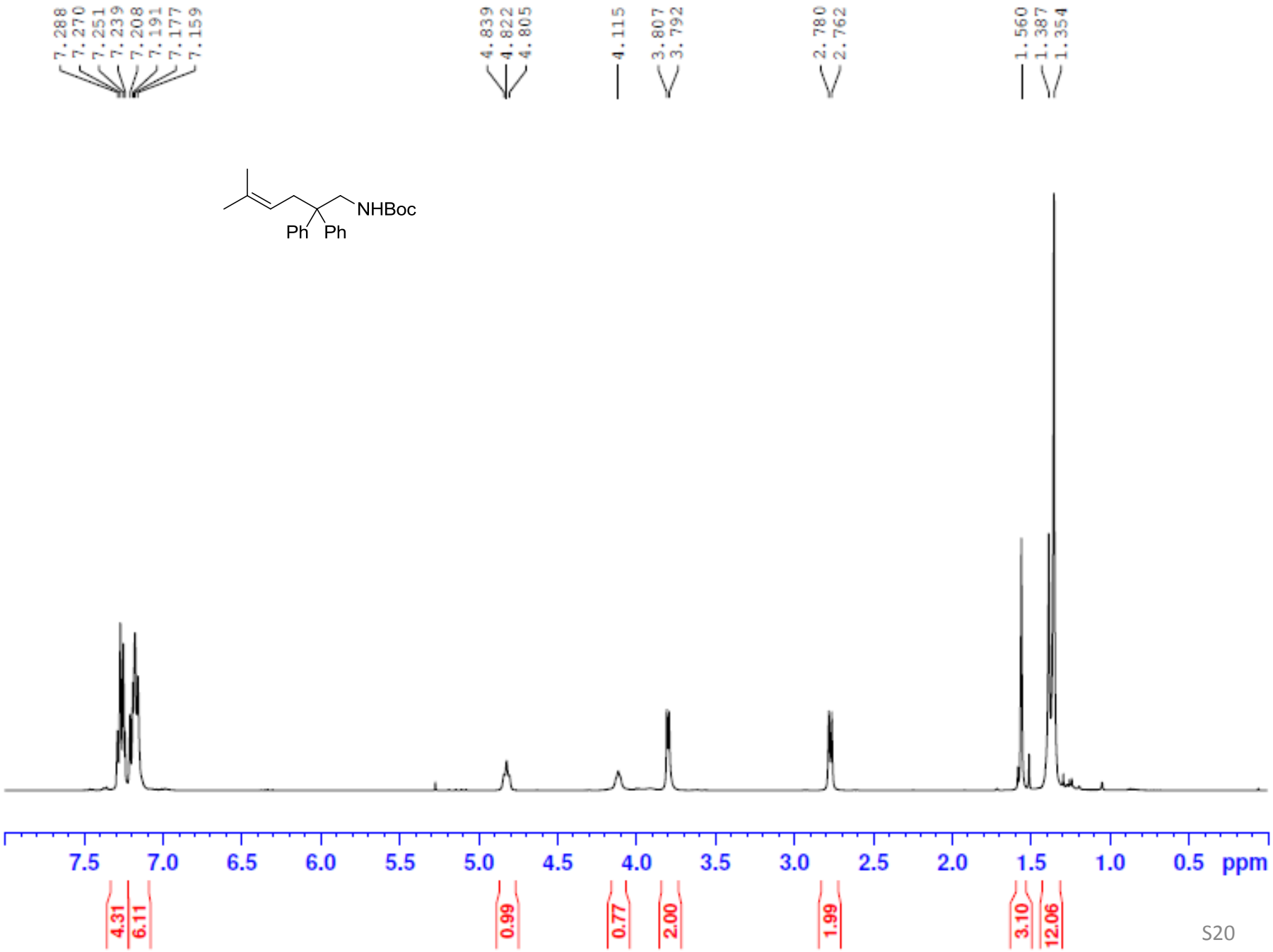
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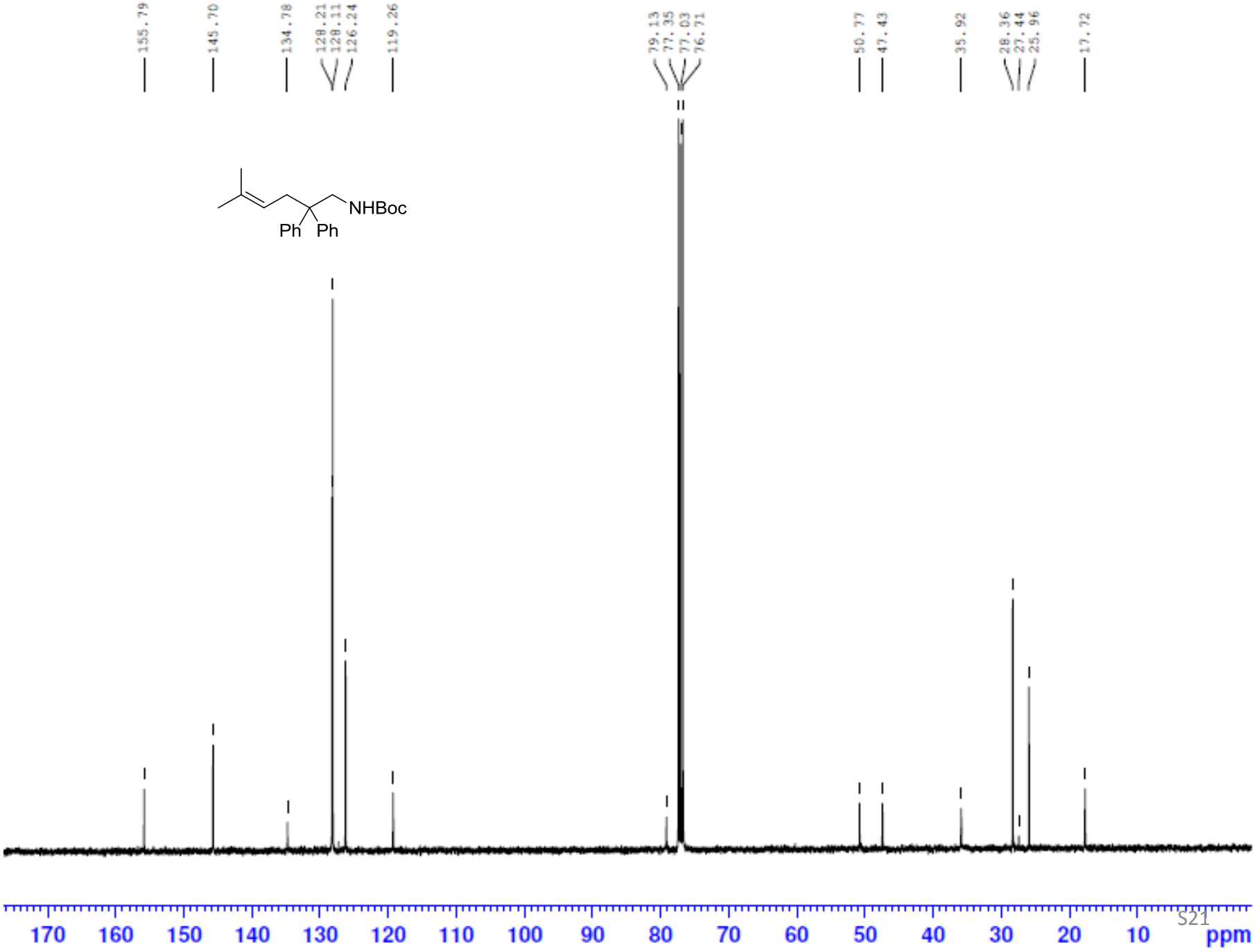
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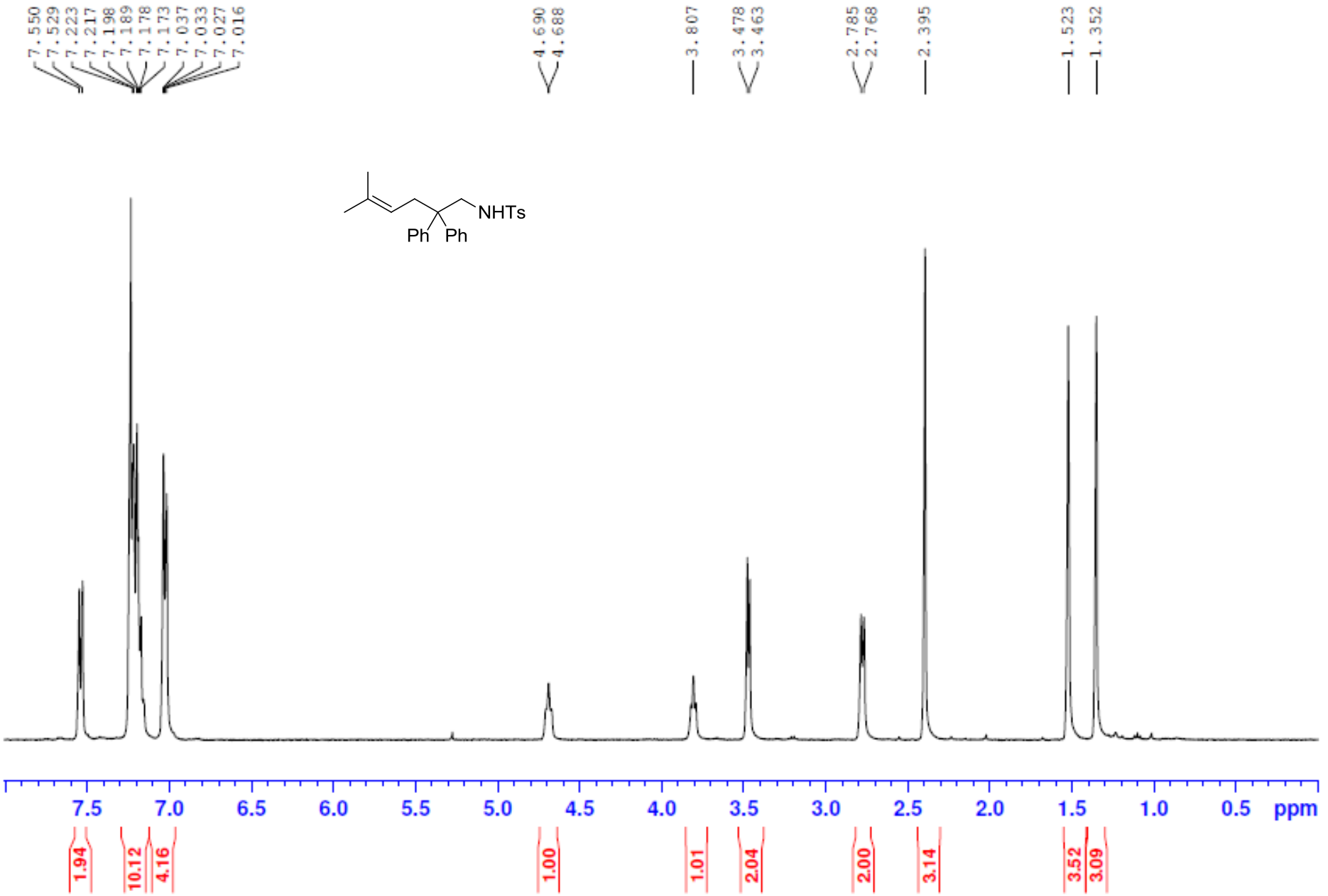
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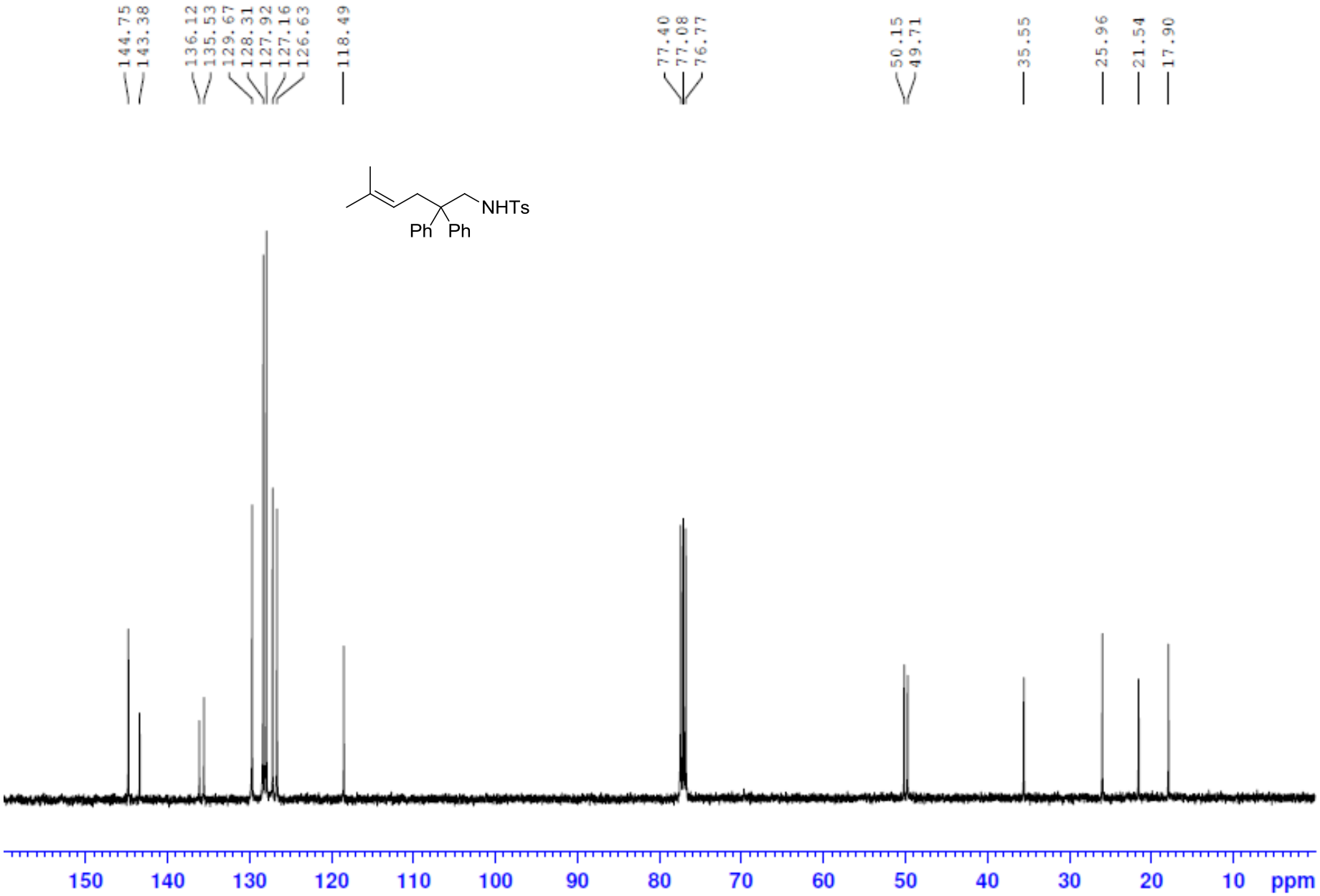
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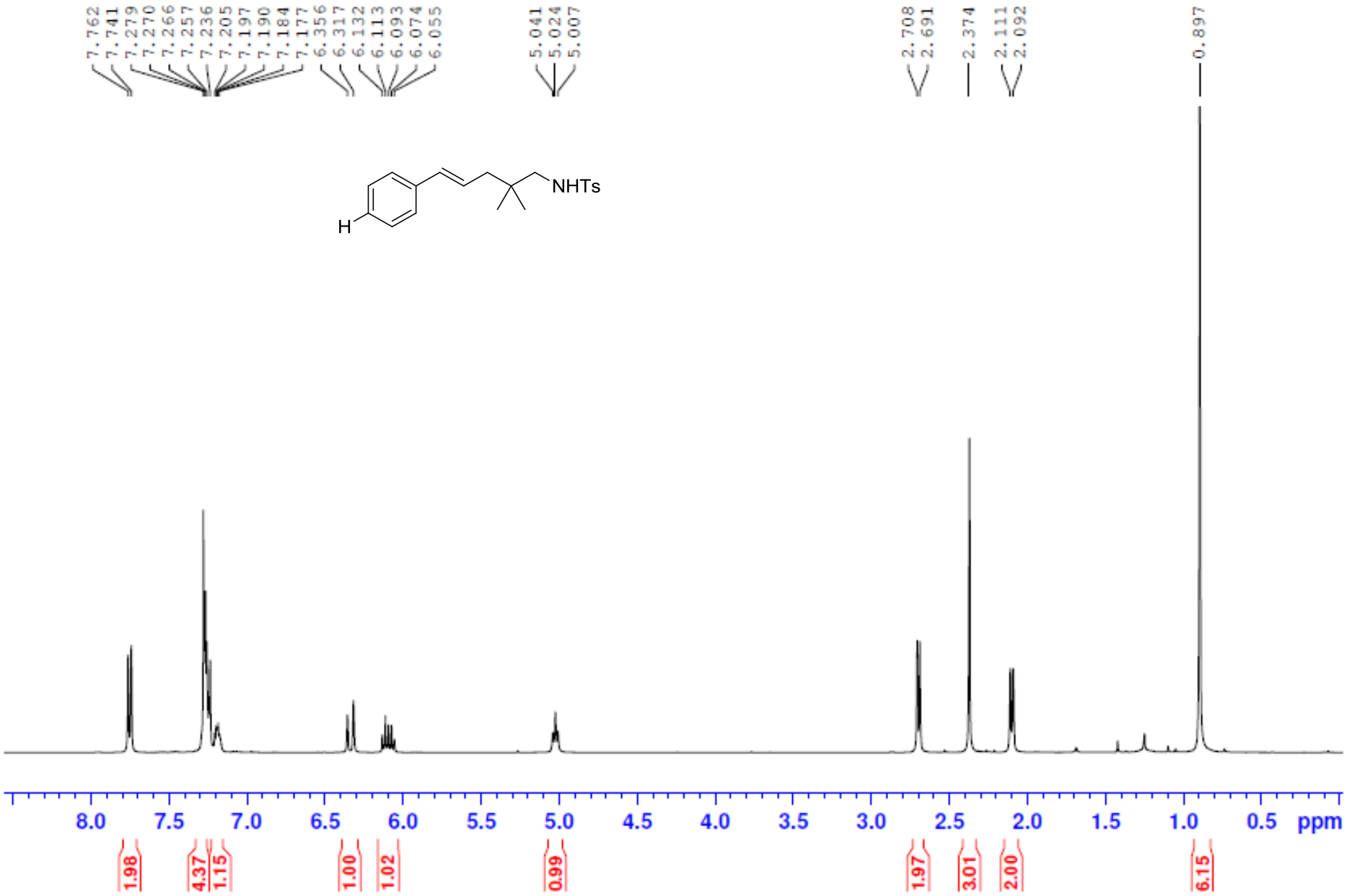
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6.317
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H
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3.0
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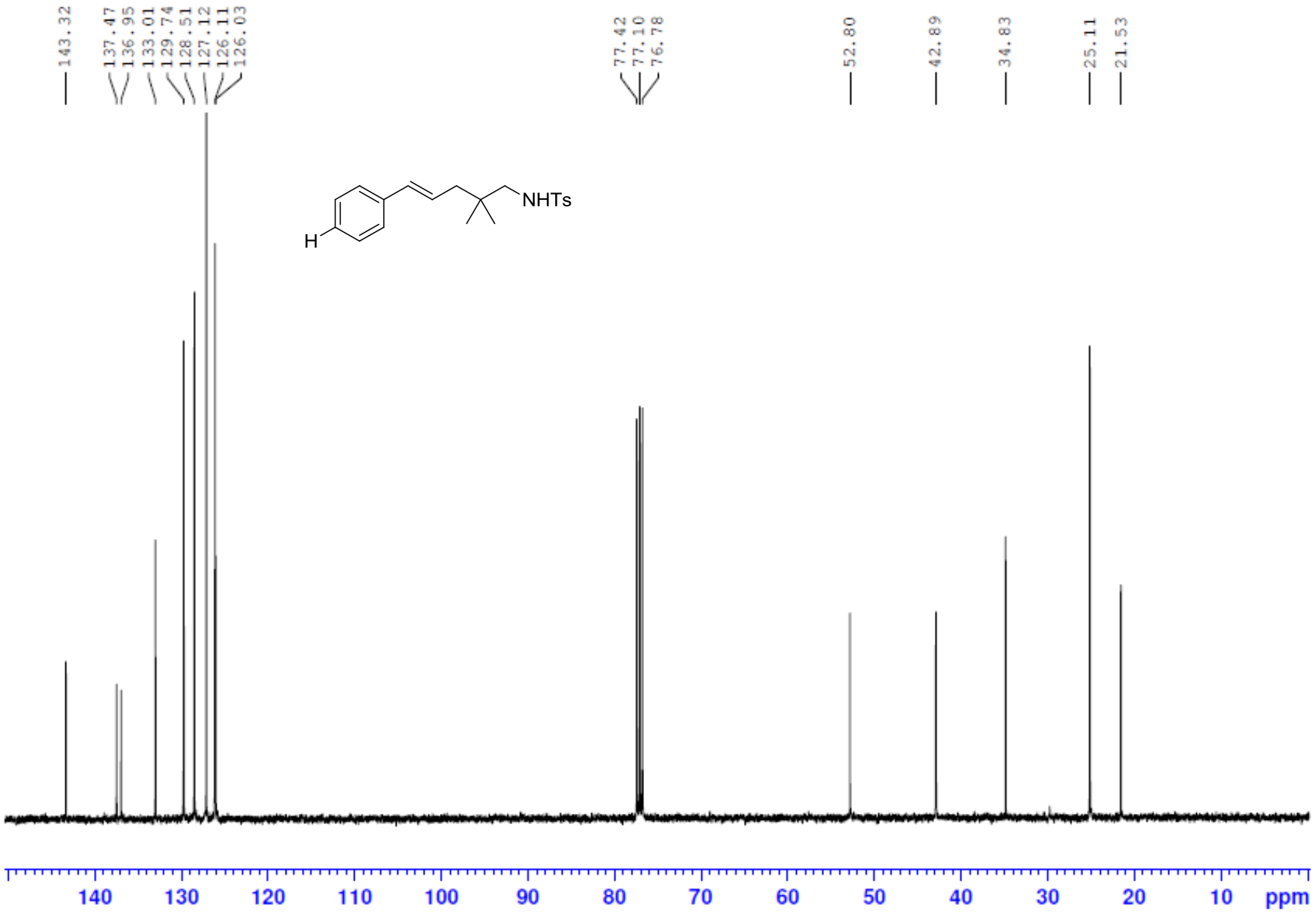
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H
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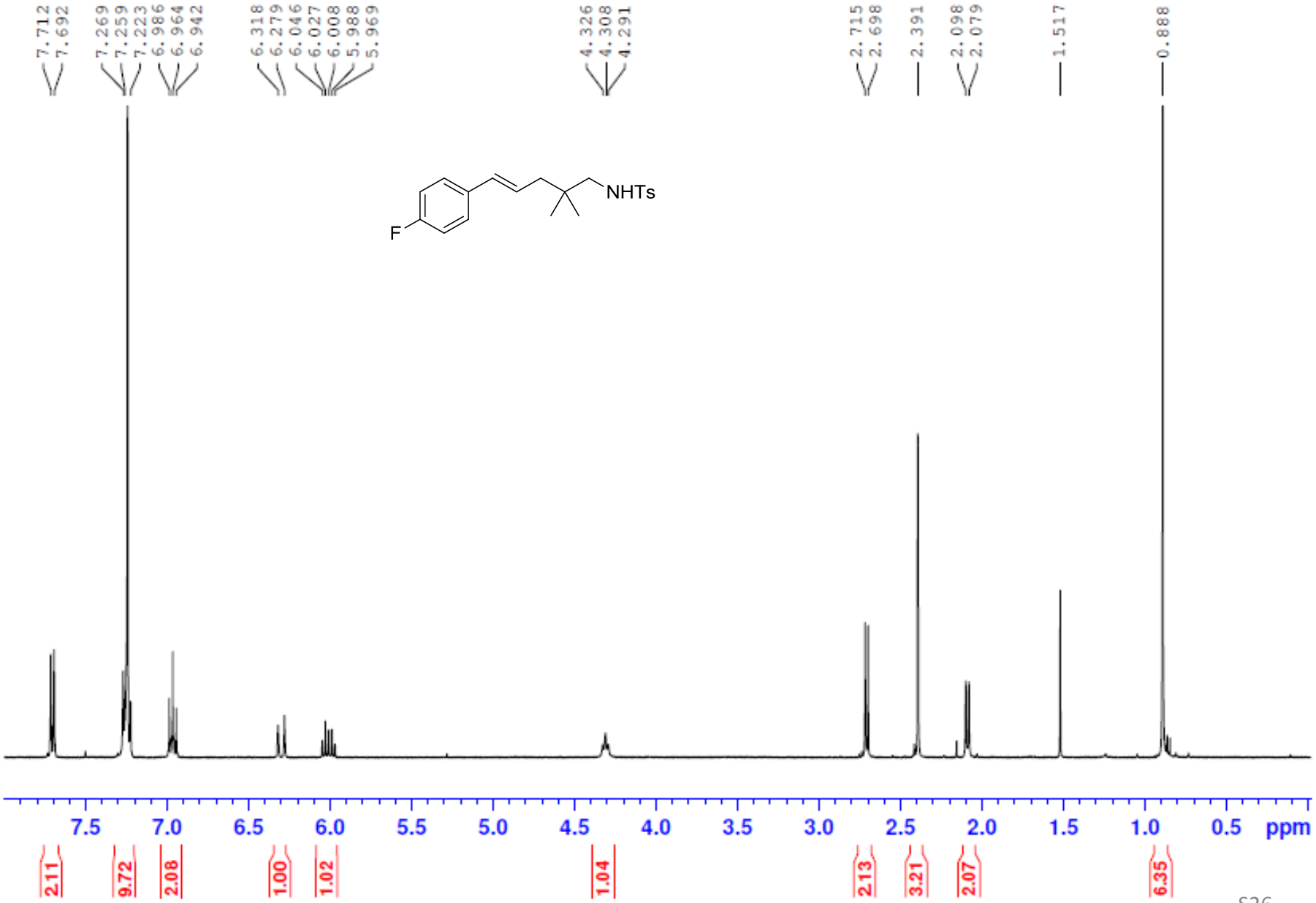
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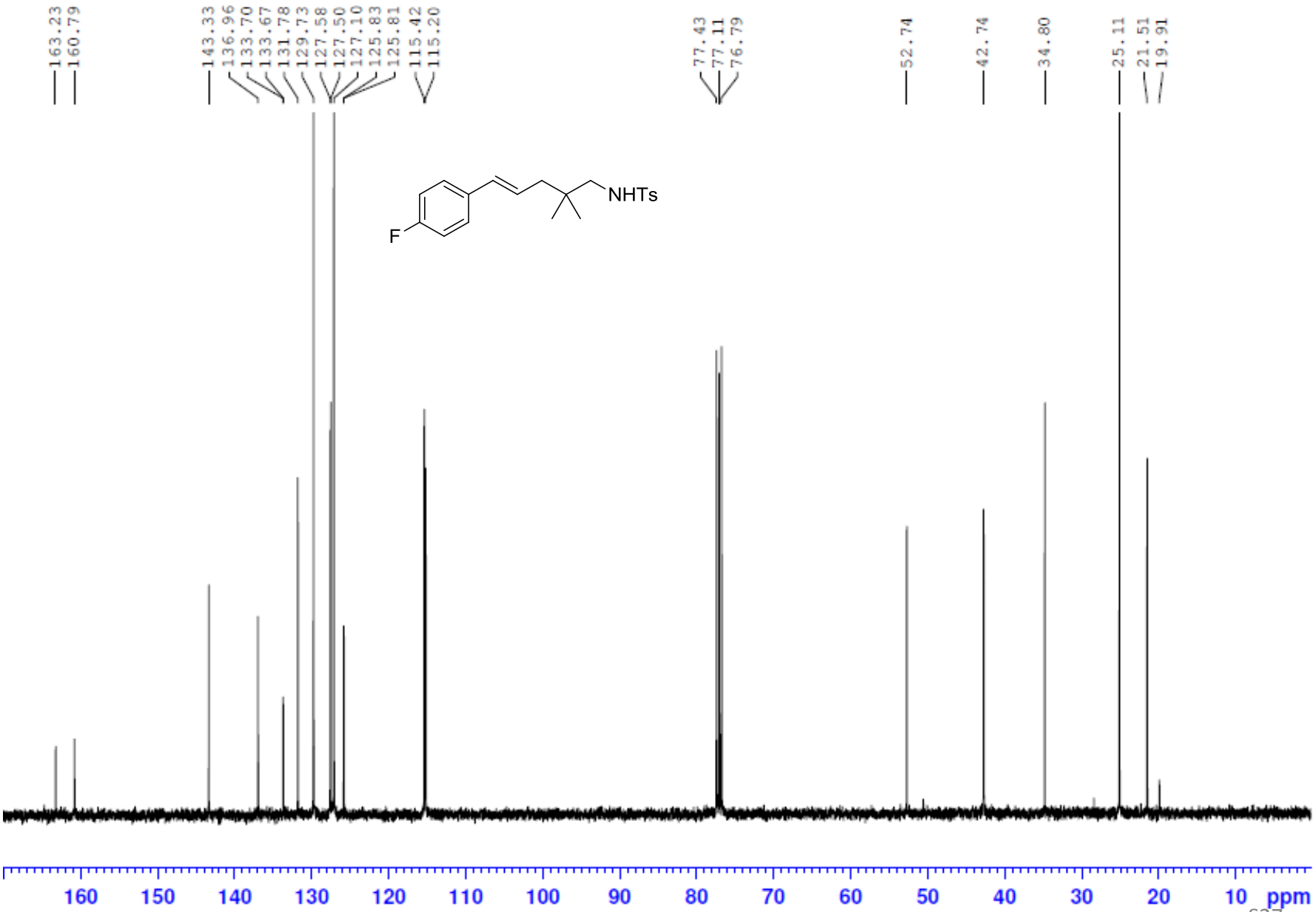
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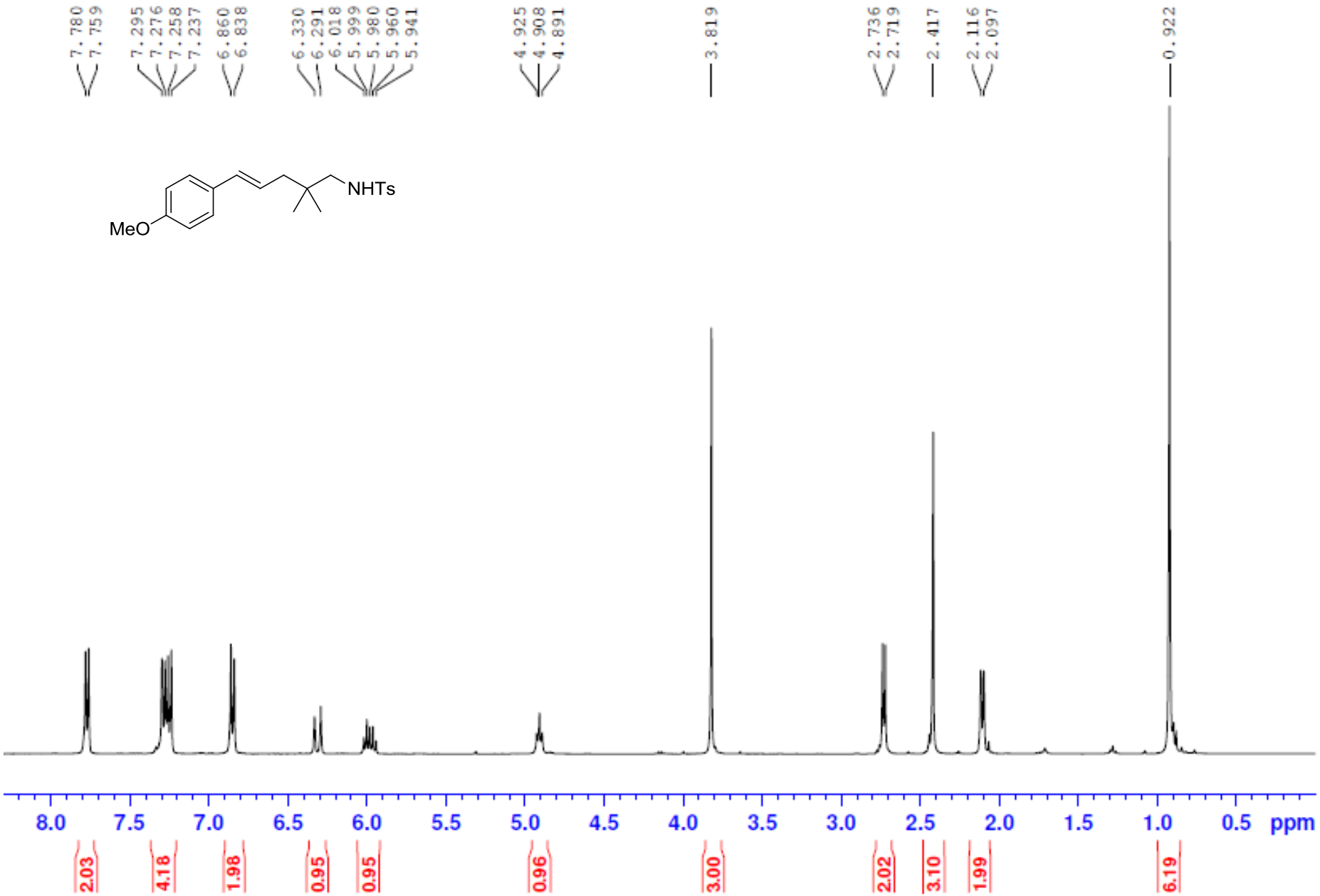
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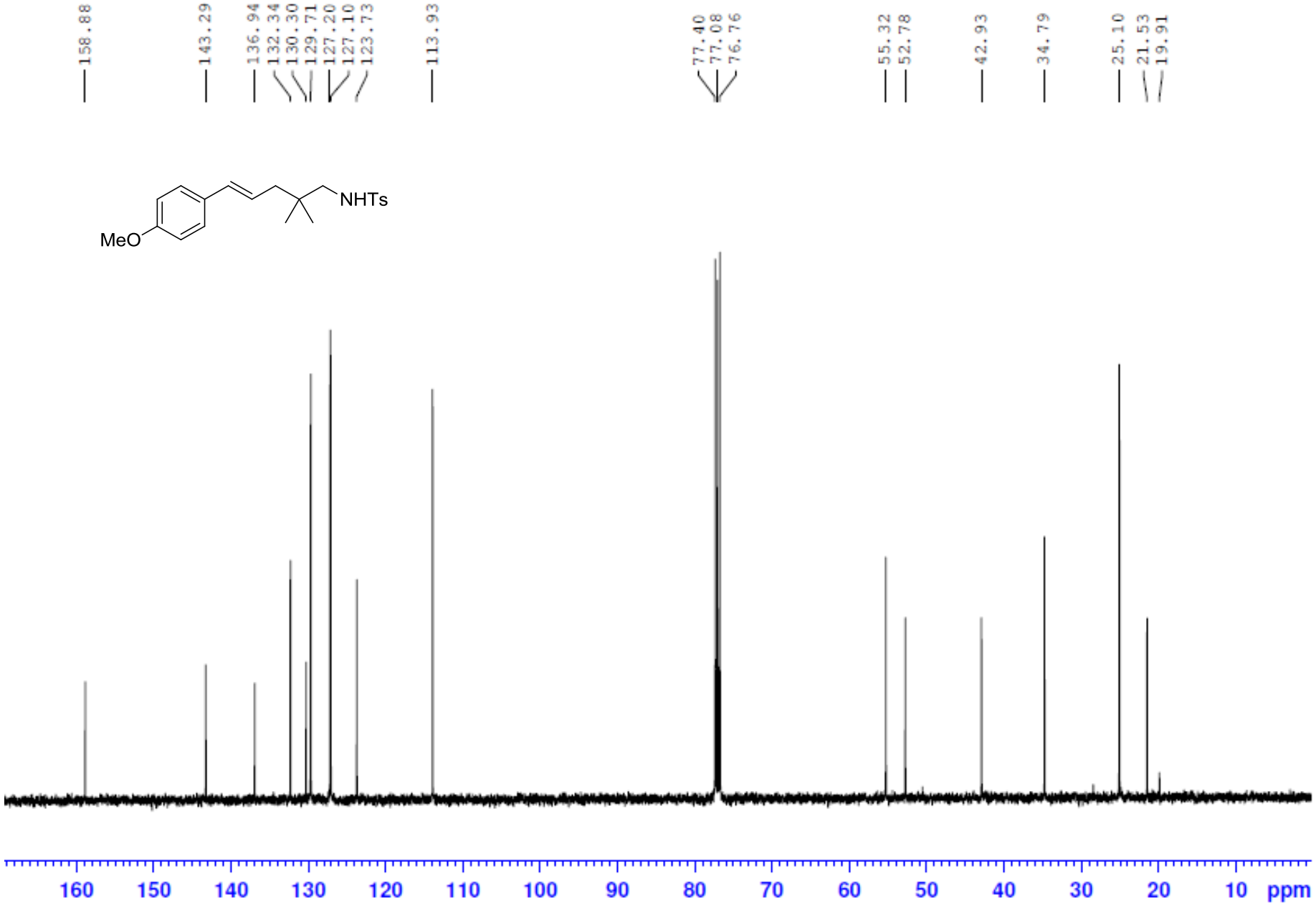
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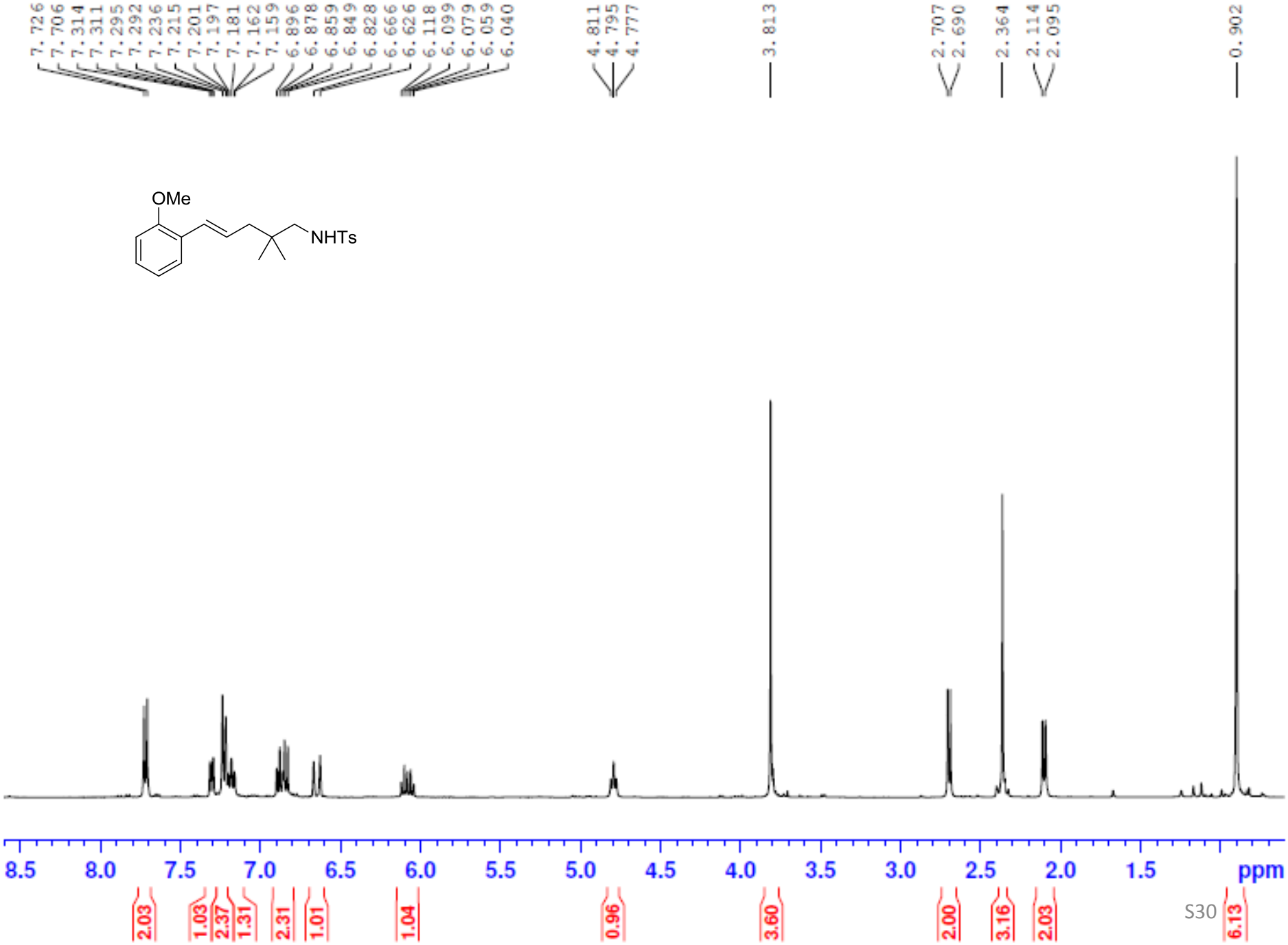
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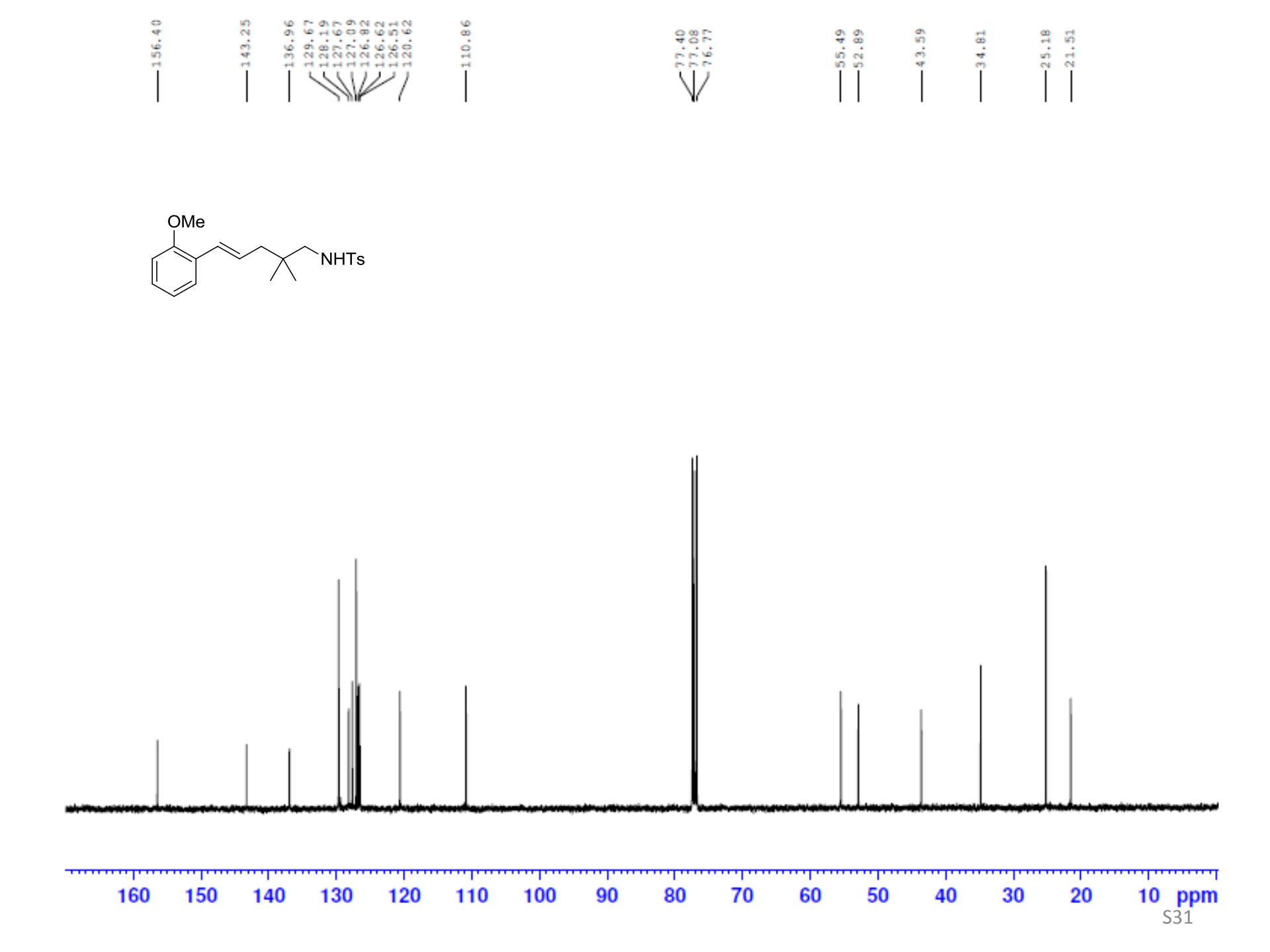
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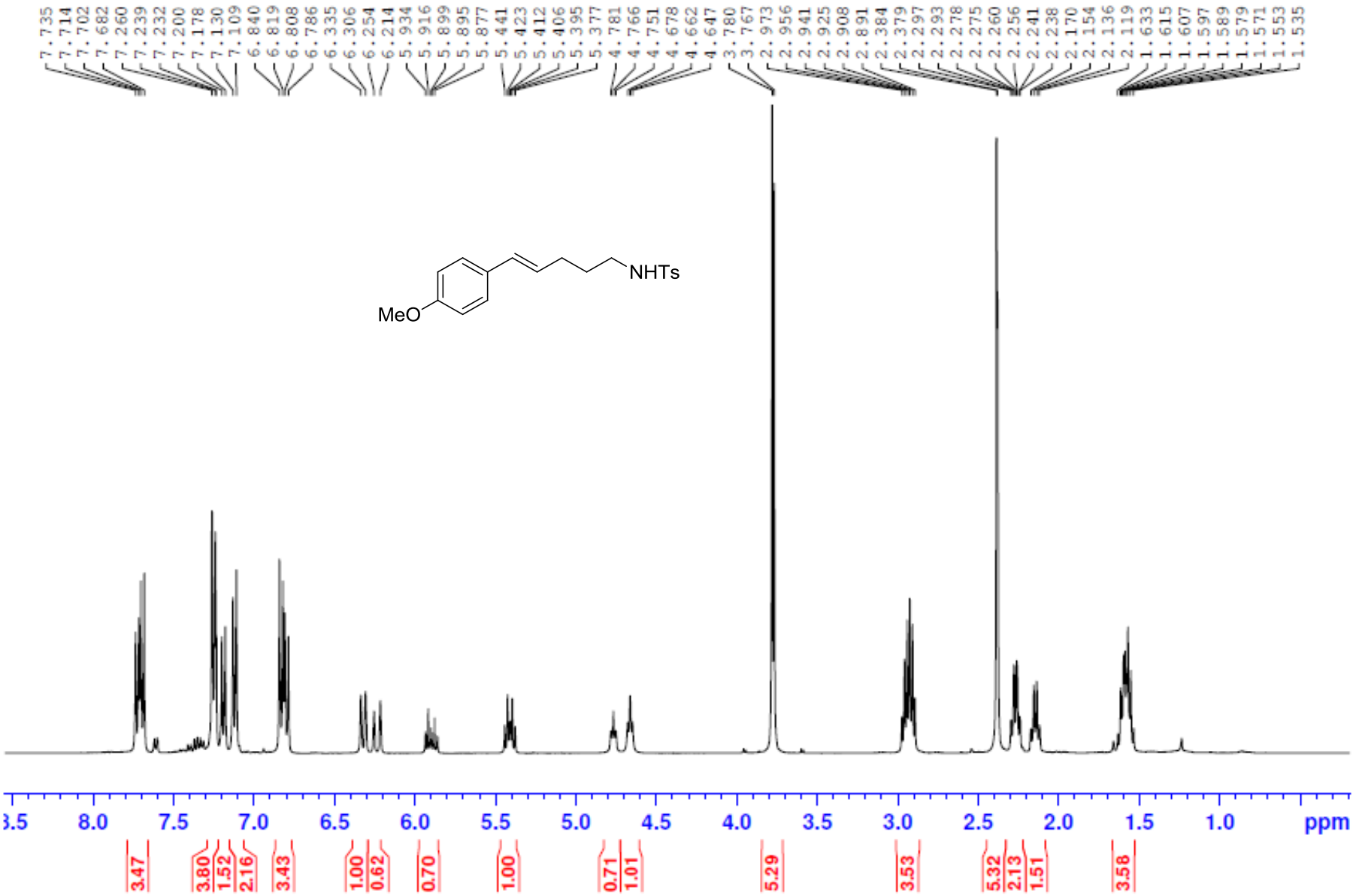
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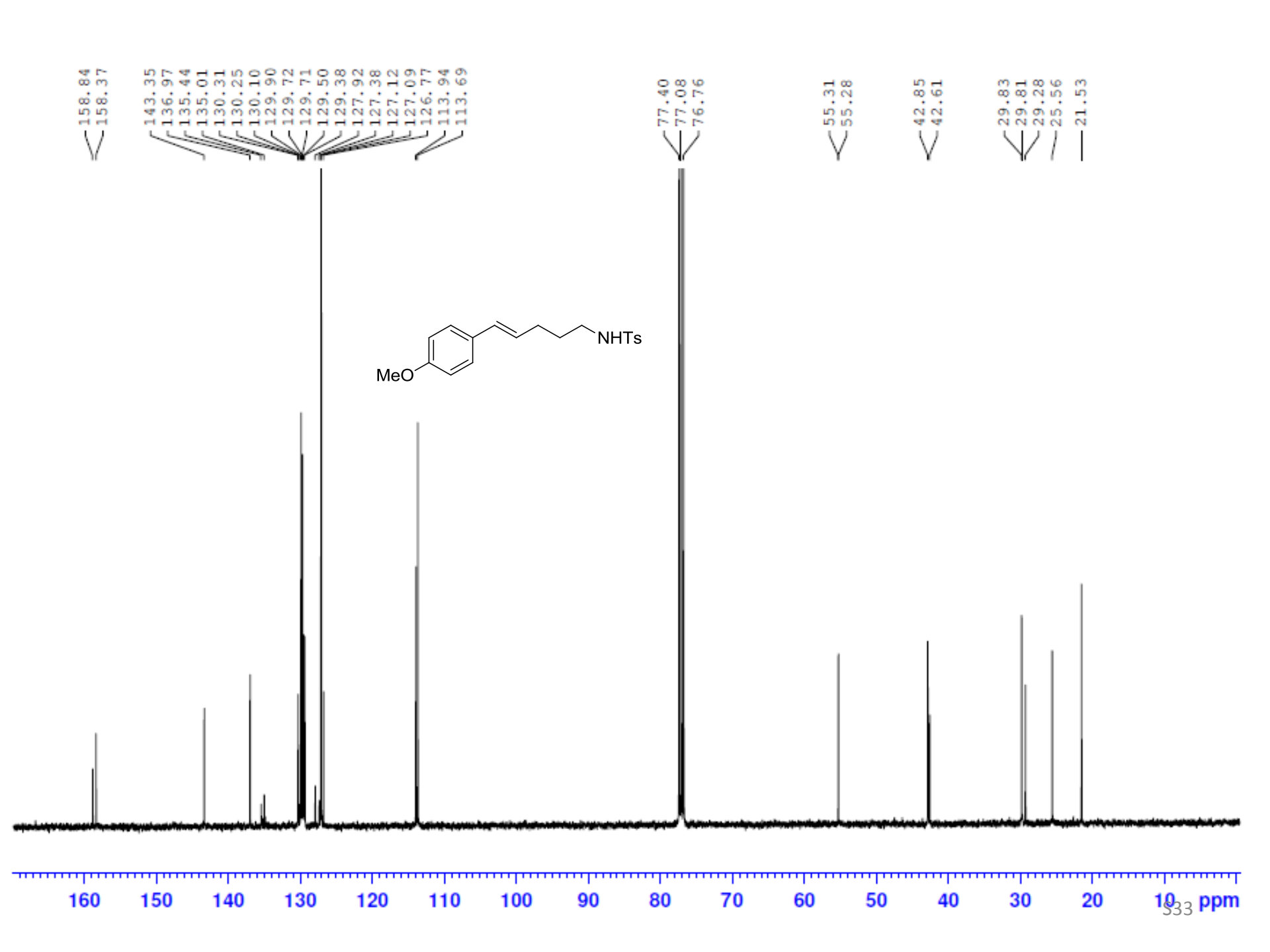
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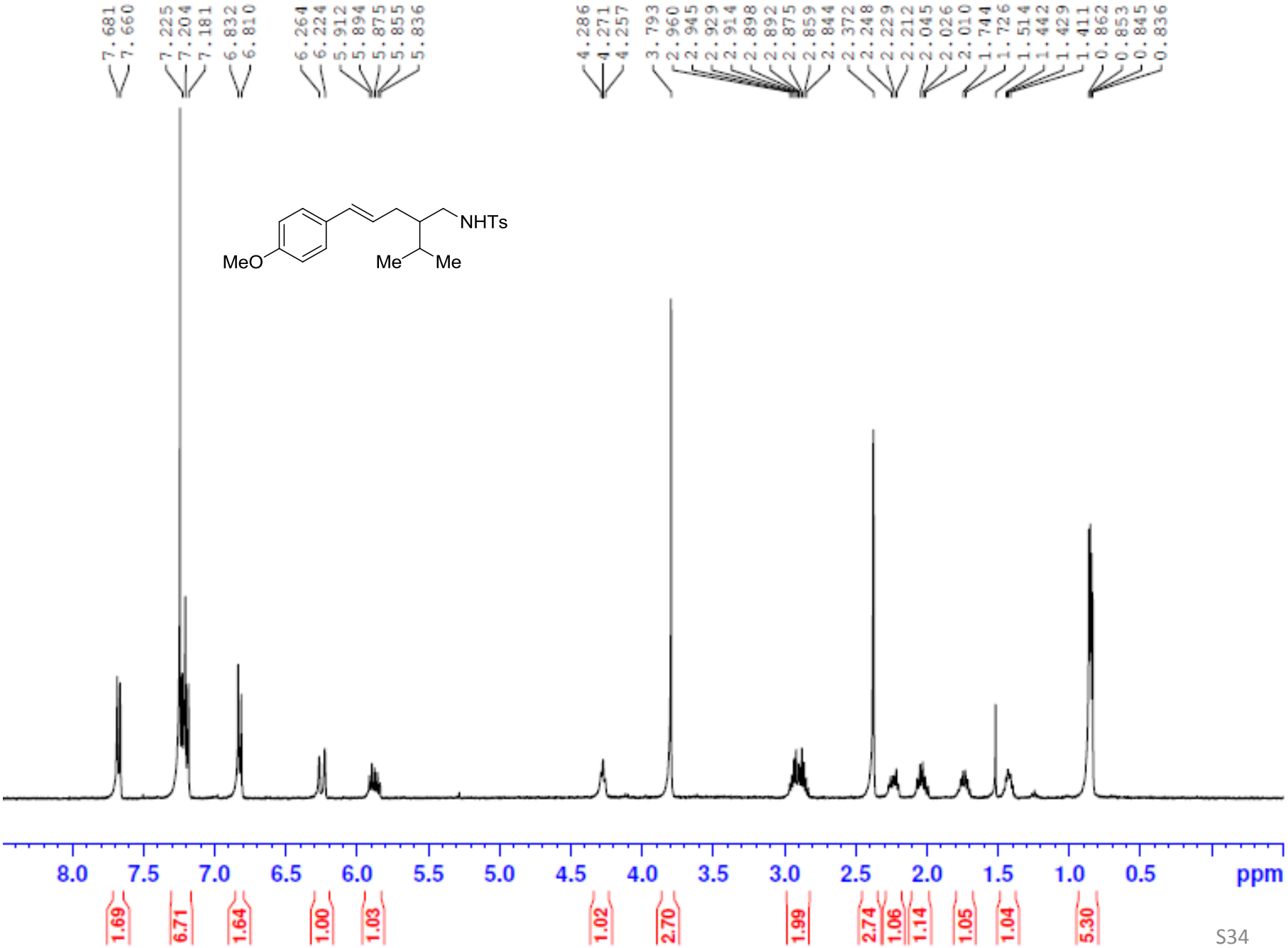
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Me
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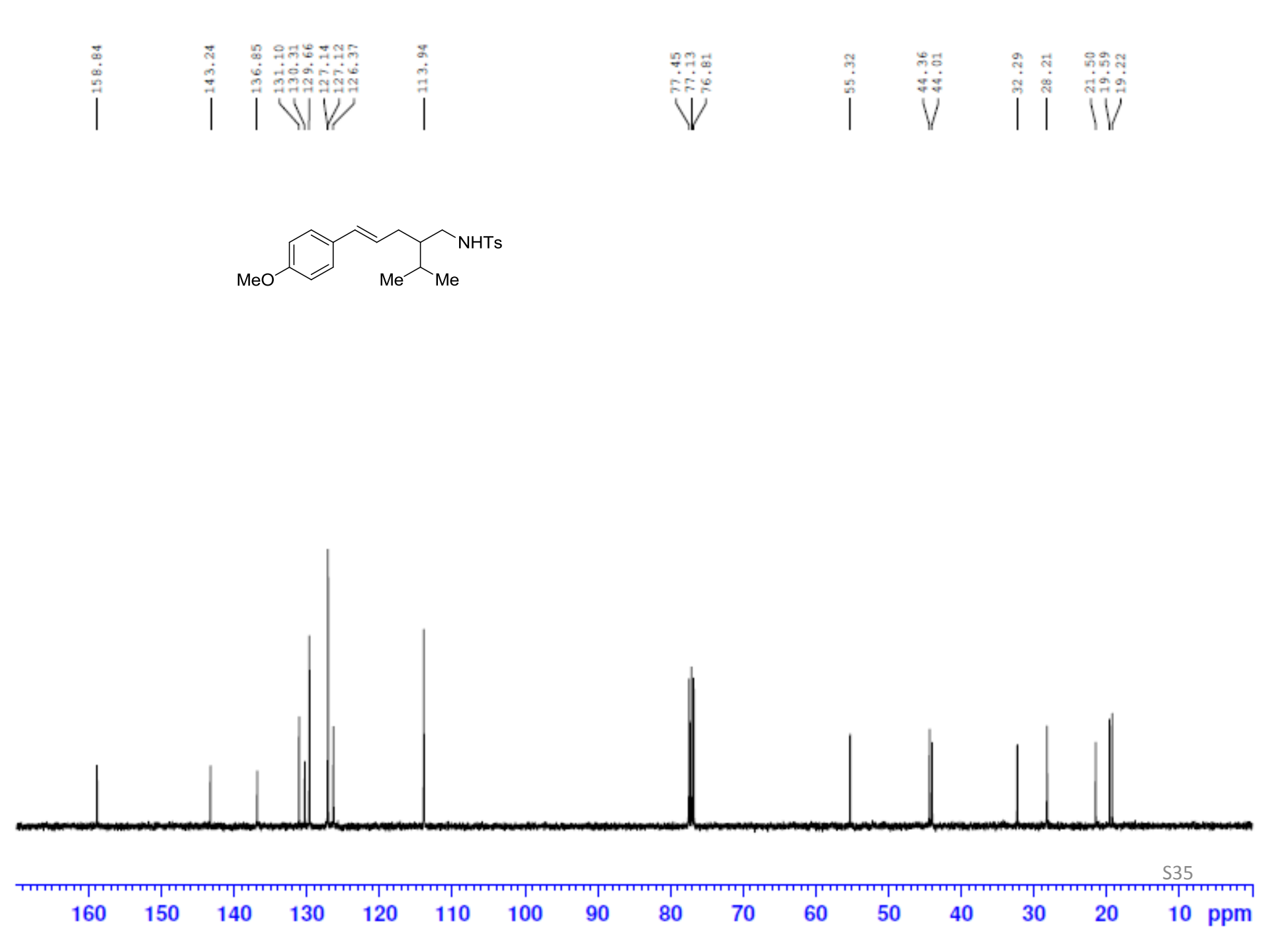
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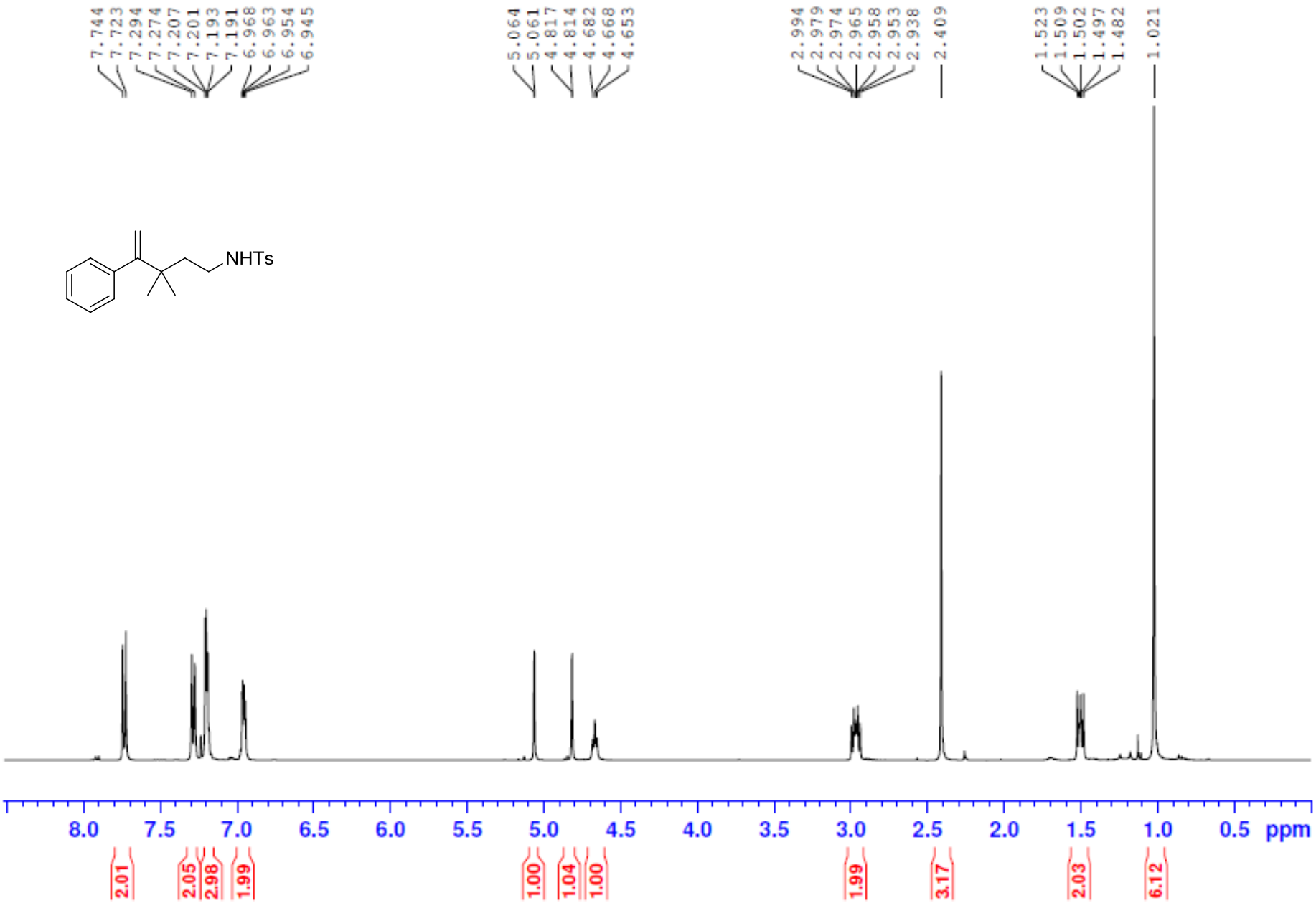
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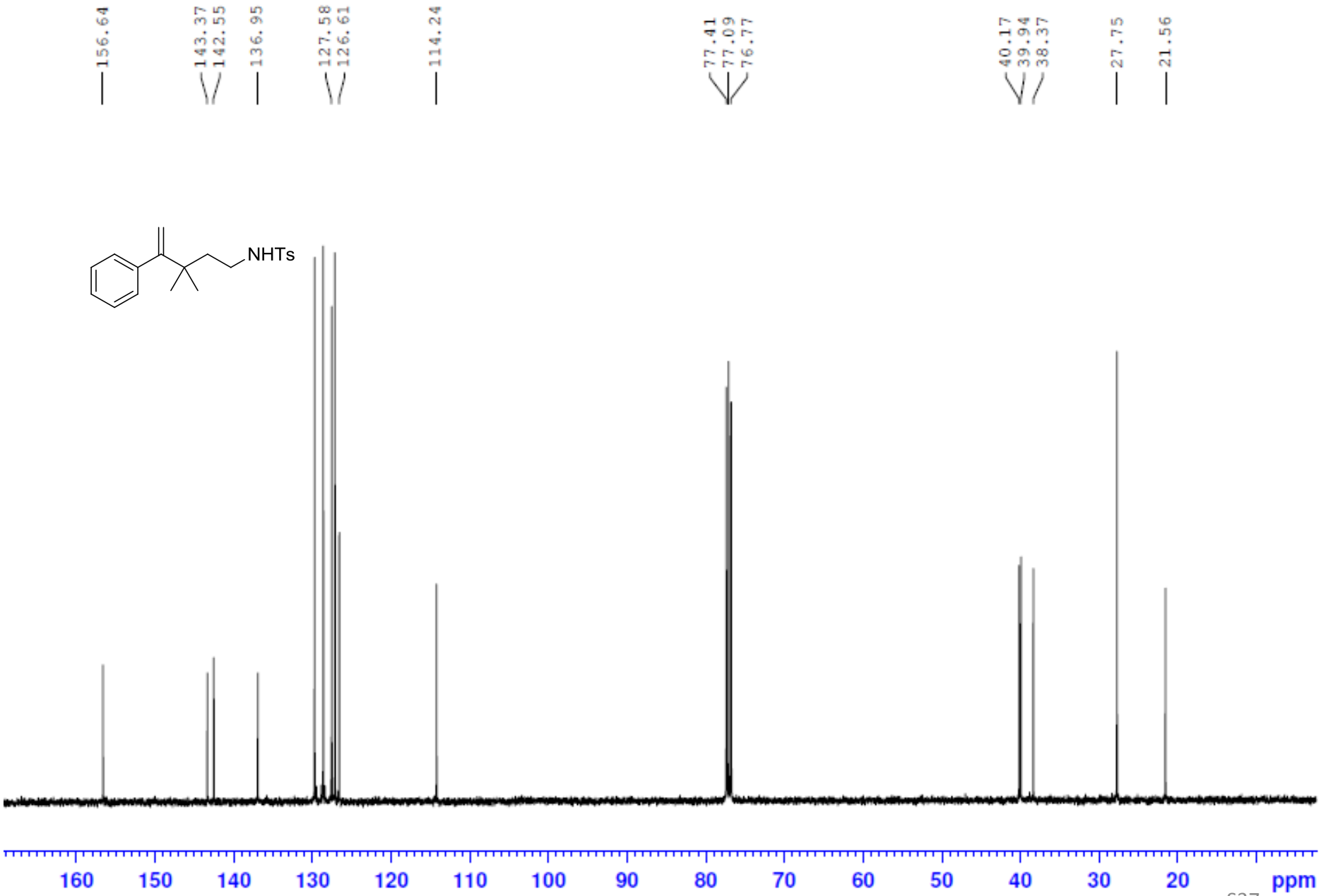
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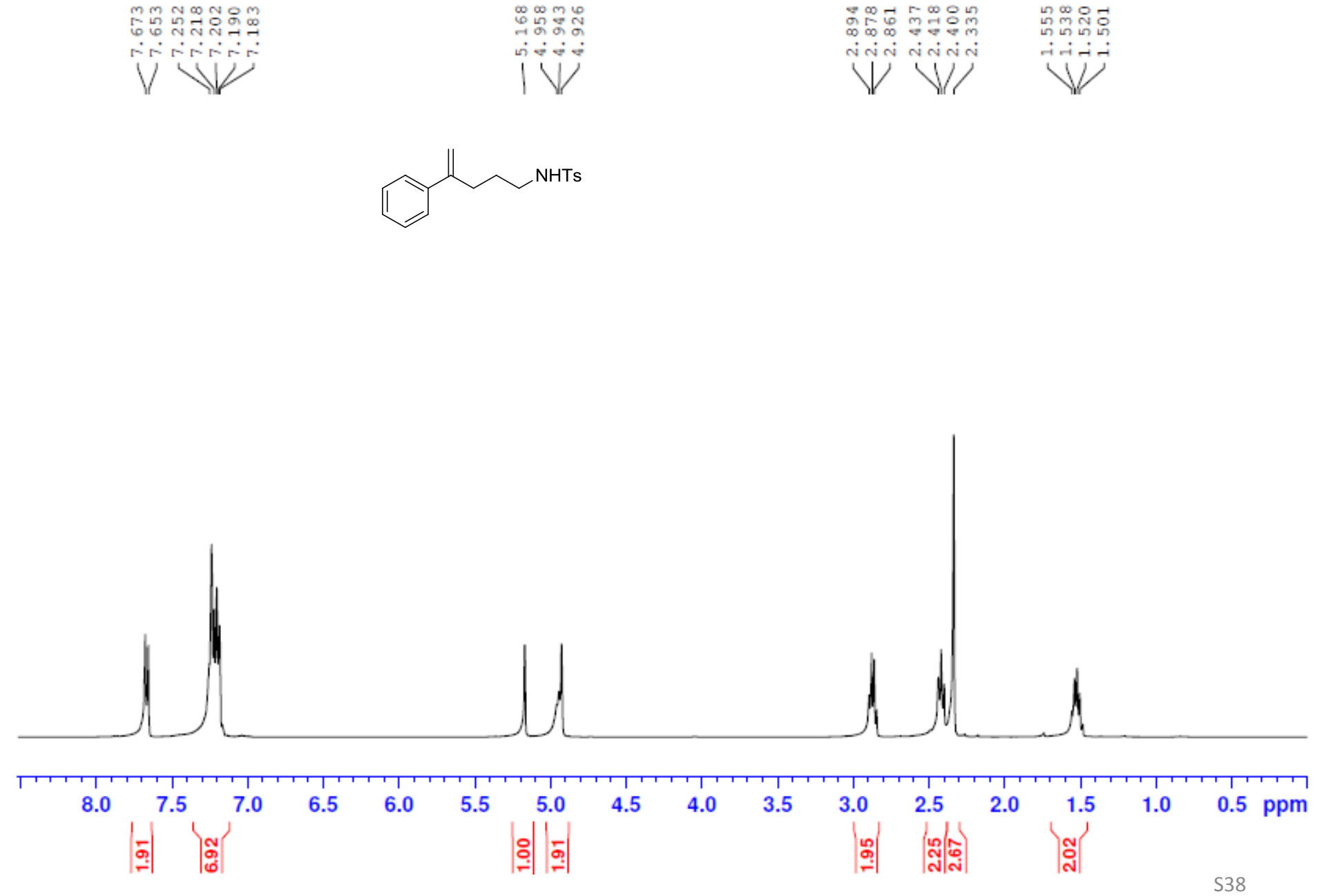
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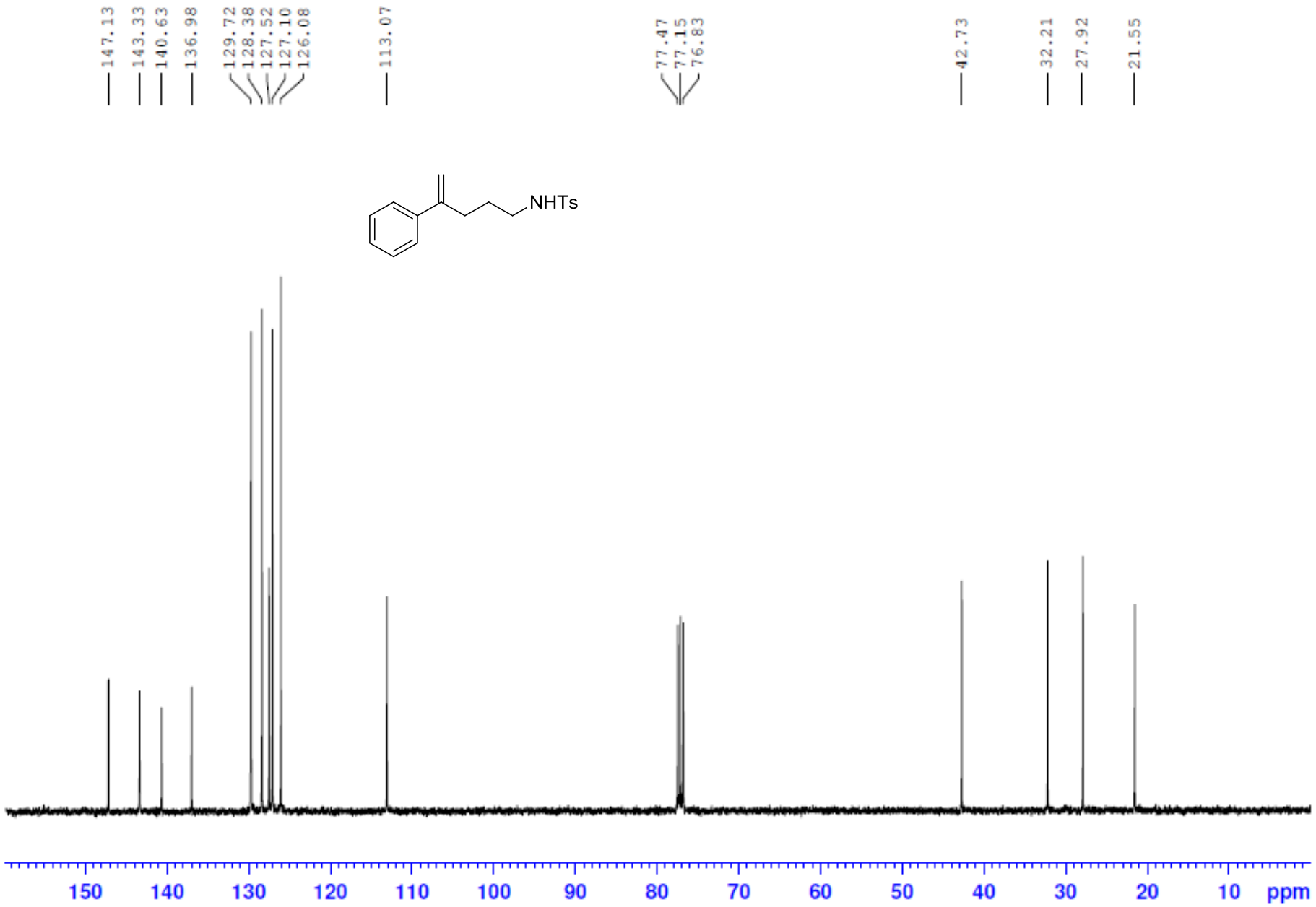
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NHTs
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110
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90
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50
40
30
20
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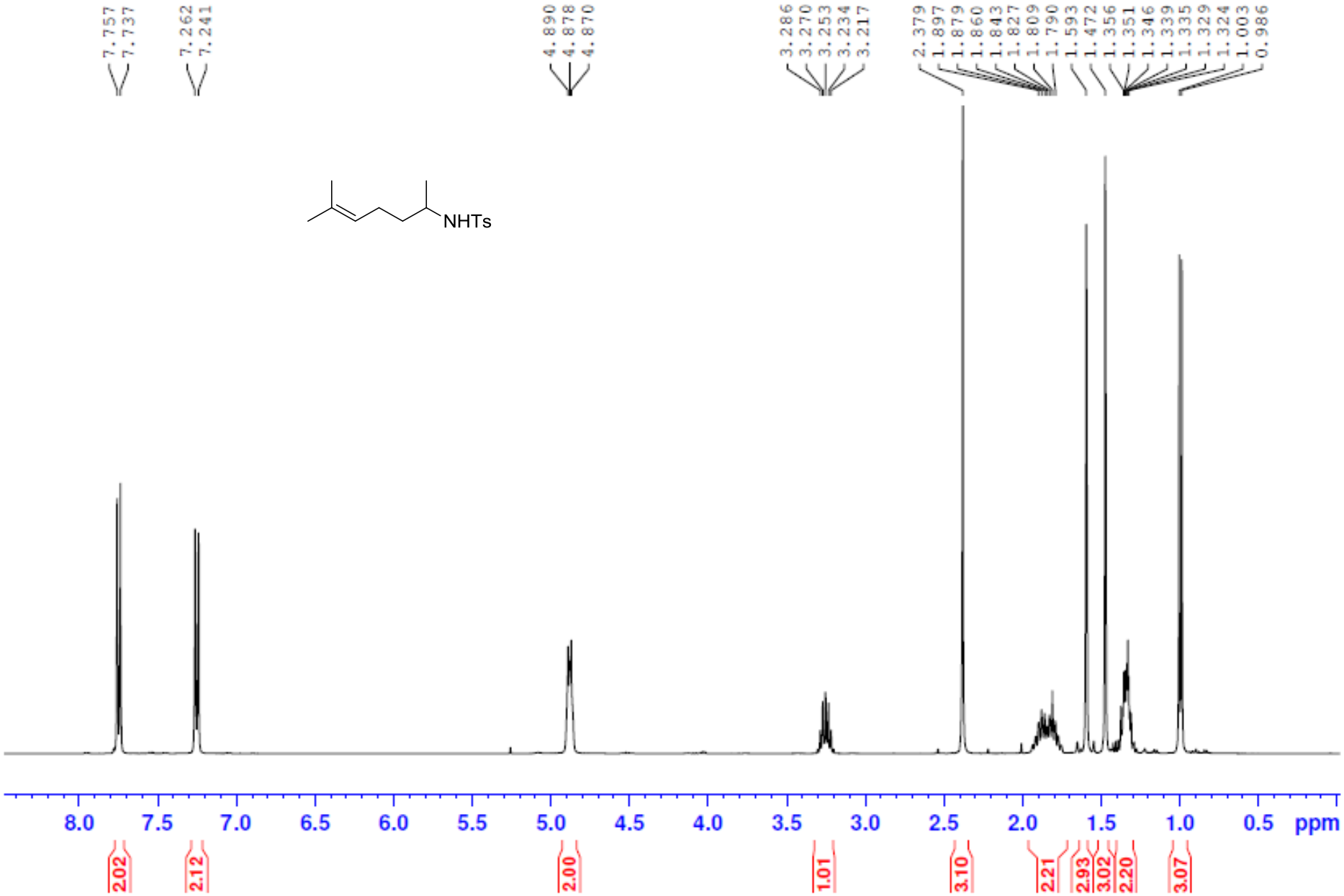
ppm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1.335
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NHTs
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3.5
3.0
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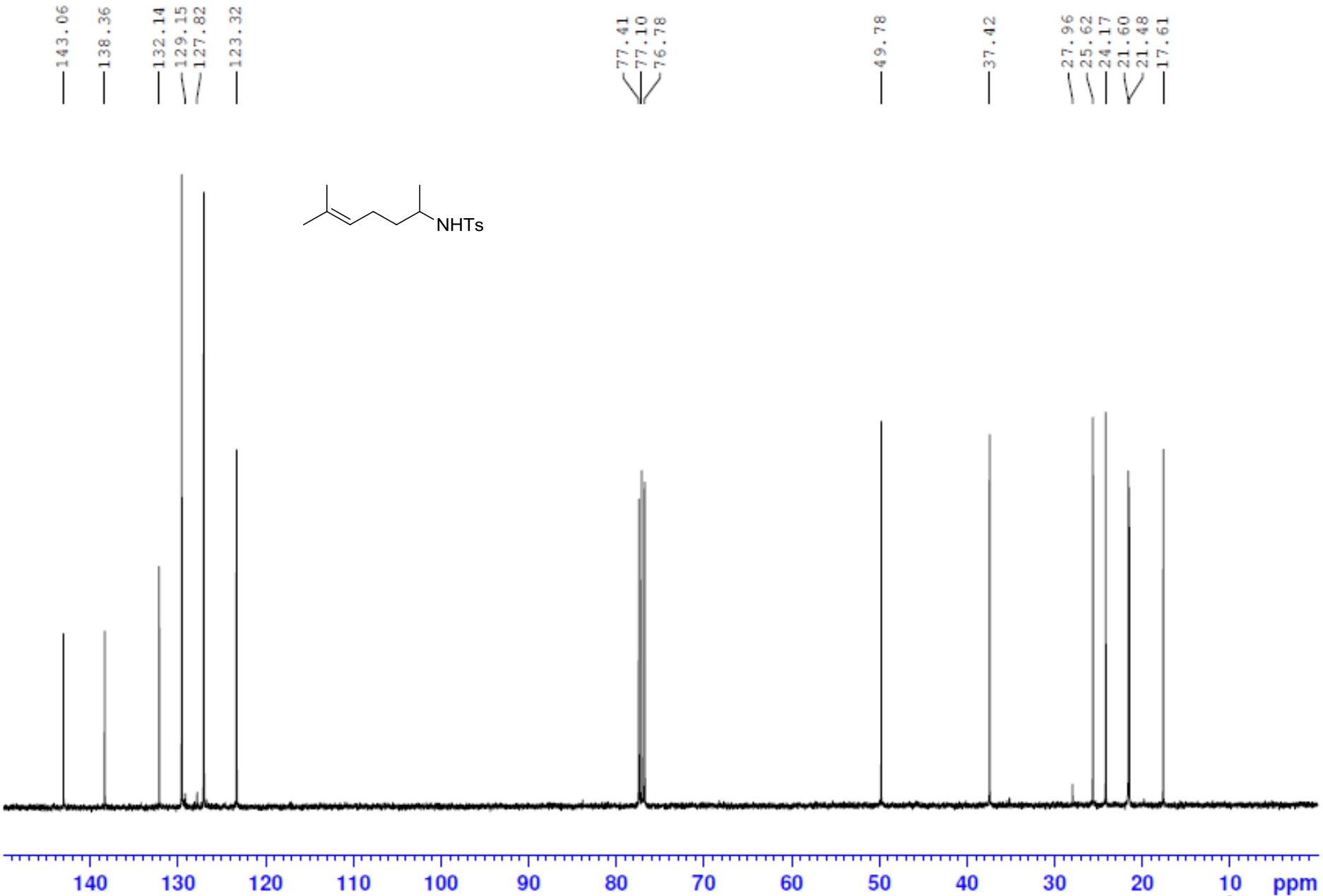
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24.17
21.60
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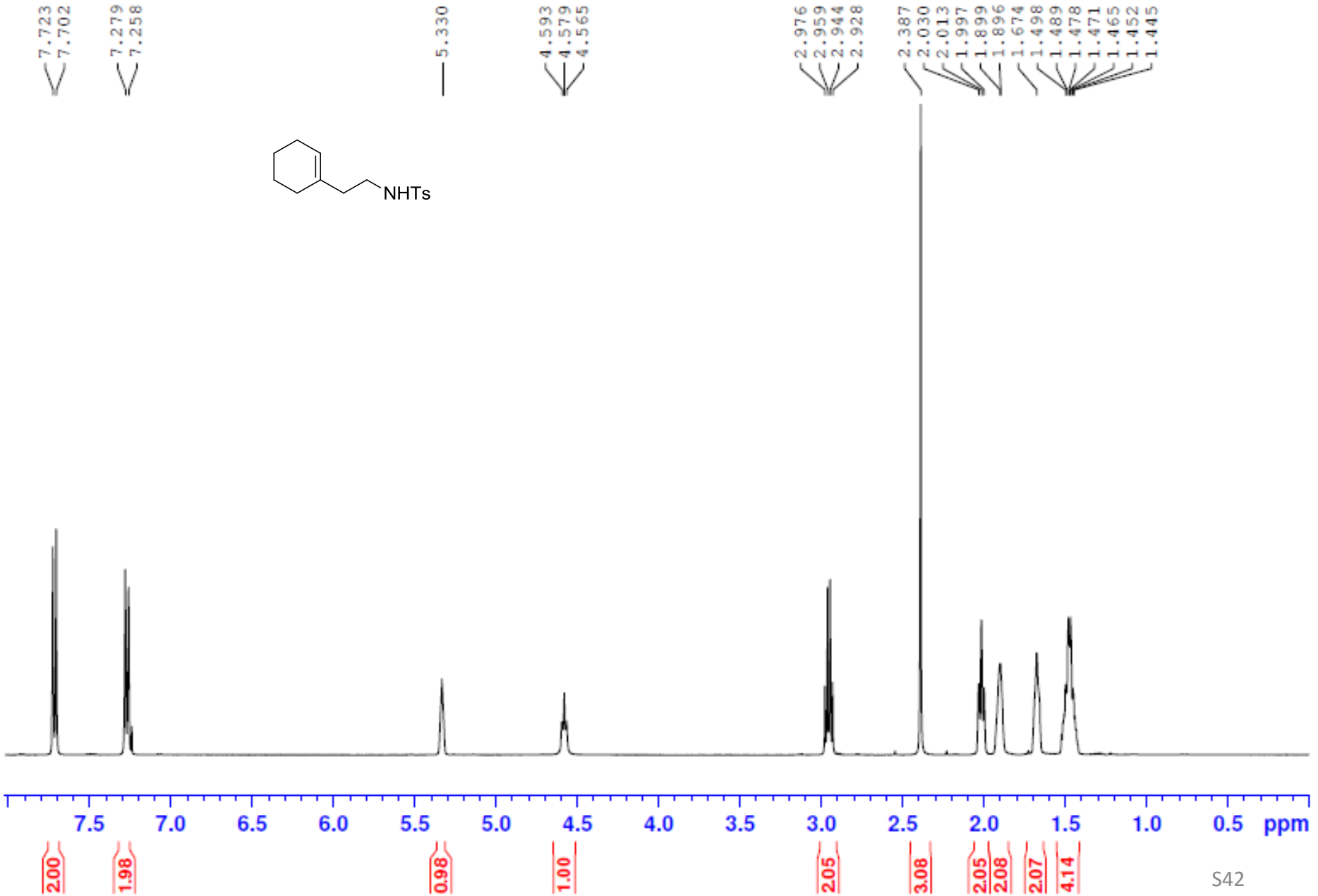
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1.498
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1.471
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1.452
1.445
NHTs
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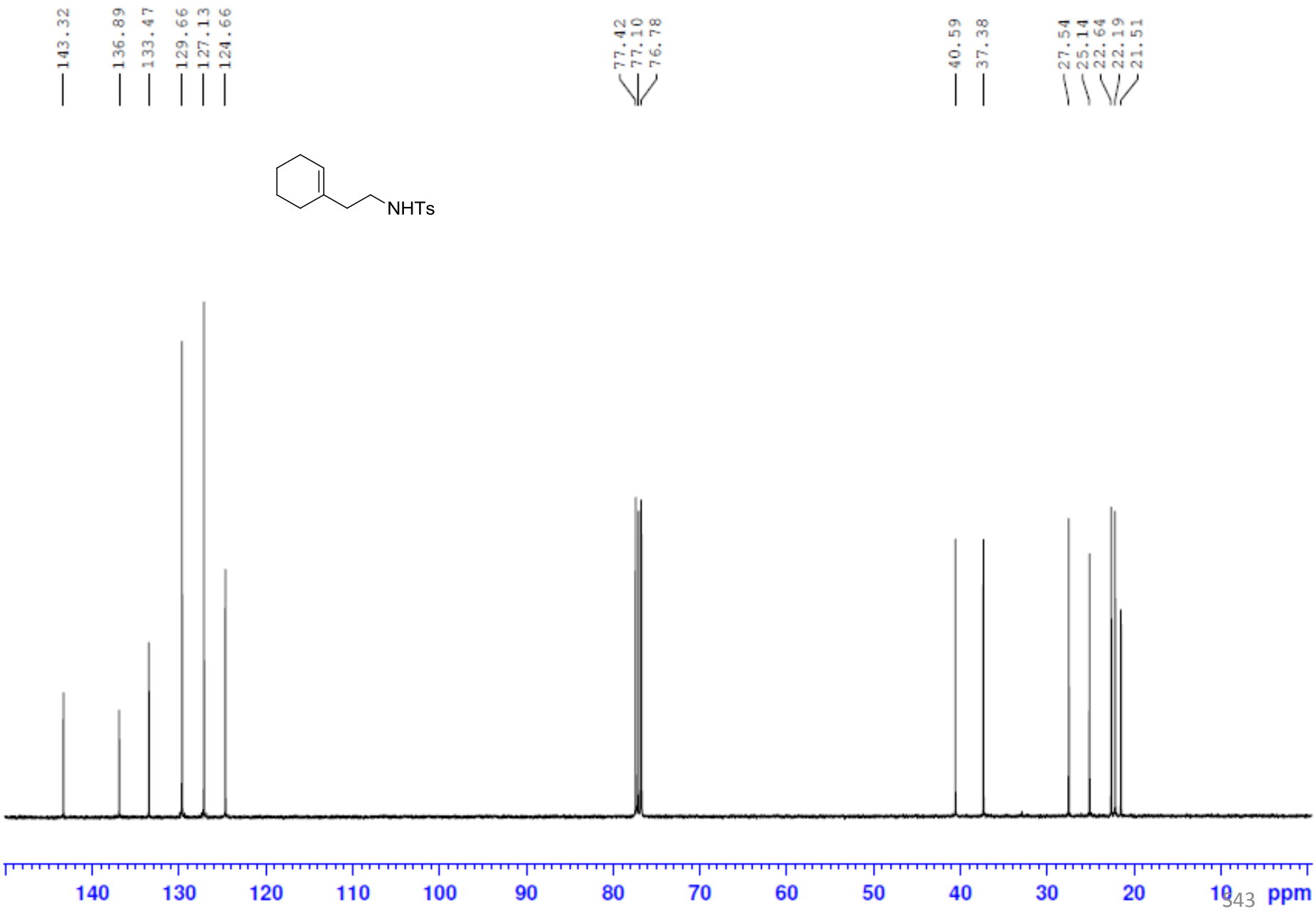
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22.64
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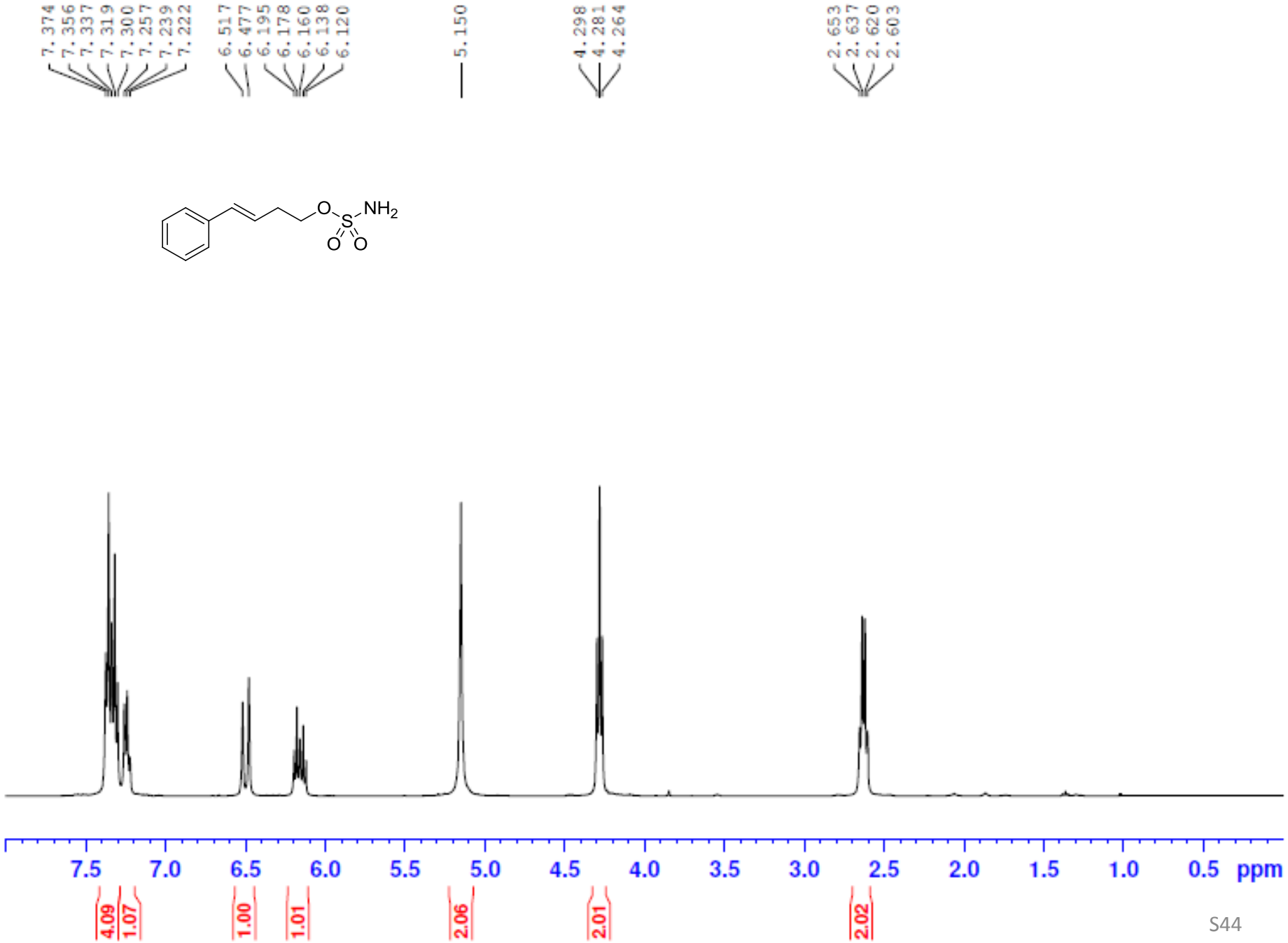
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7.222
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6.160
6.138
6.120
5.150
4.298
4.281
4.264
2.653
2.637
2.620
2.603
O
S
NH2
O
O
7.5
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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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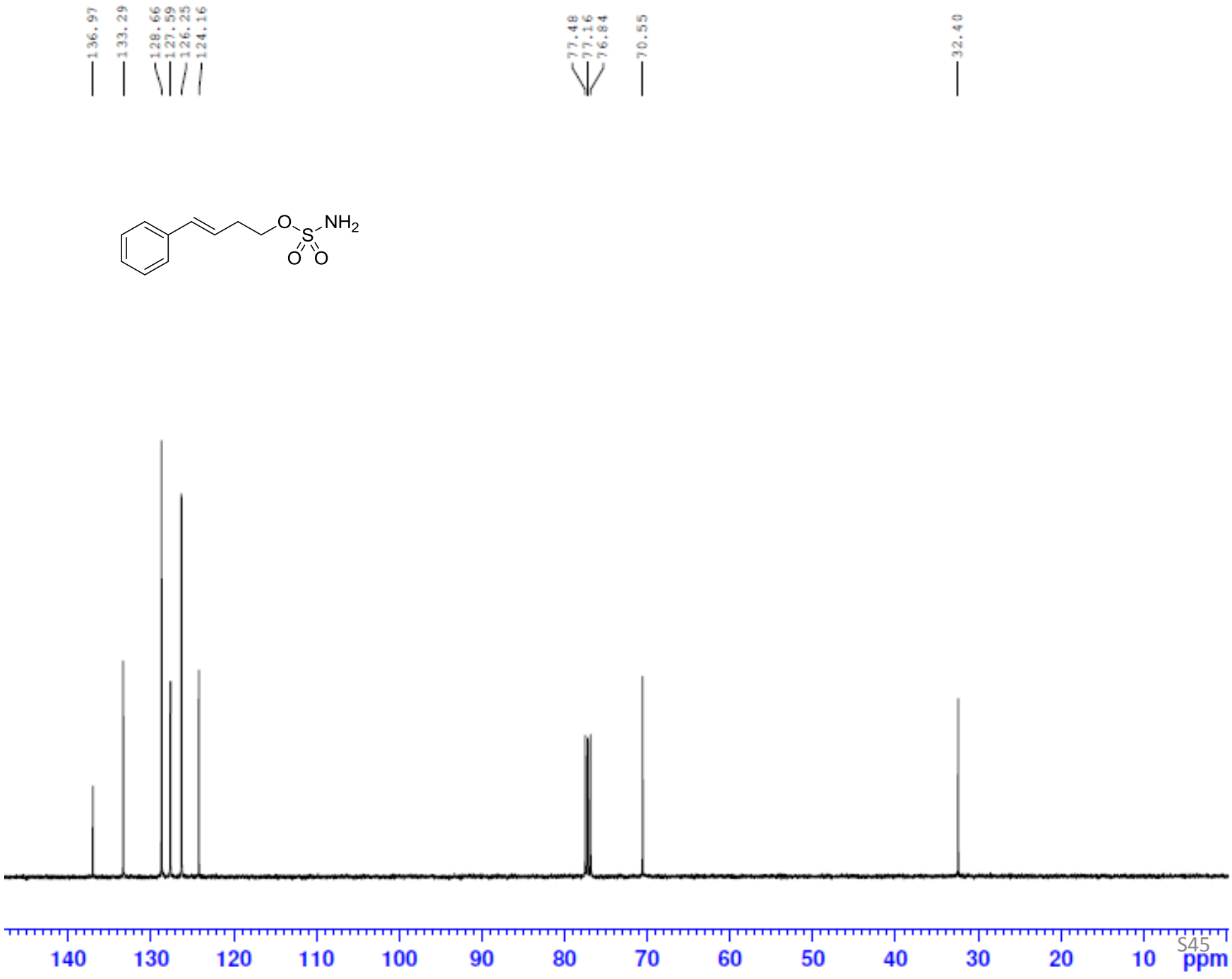
2.02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O
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NH2
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O
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20
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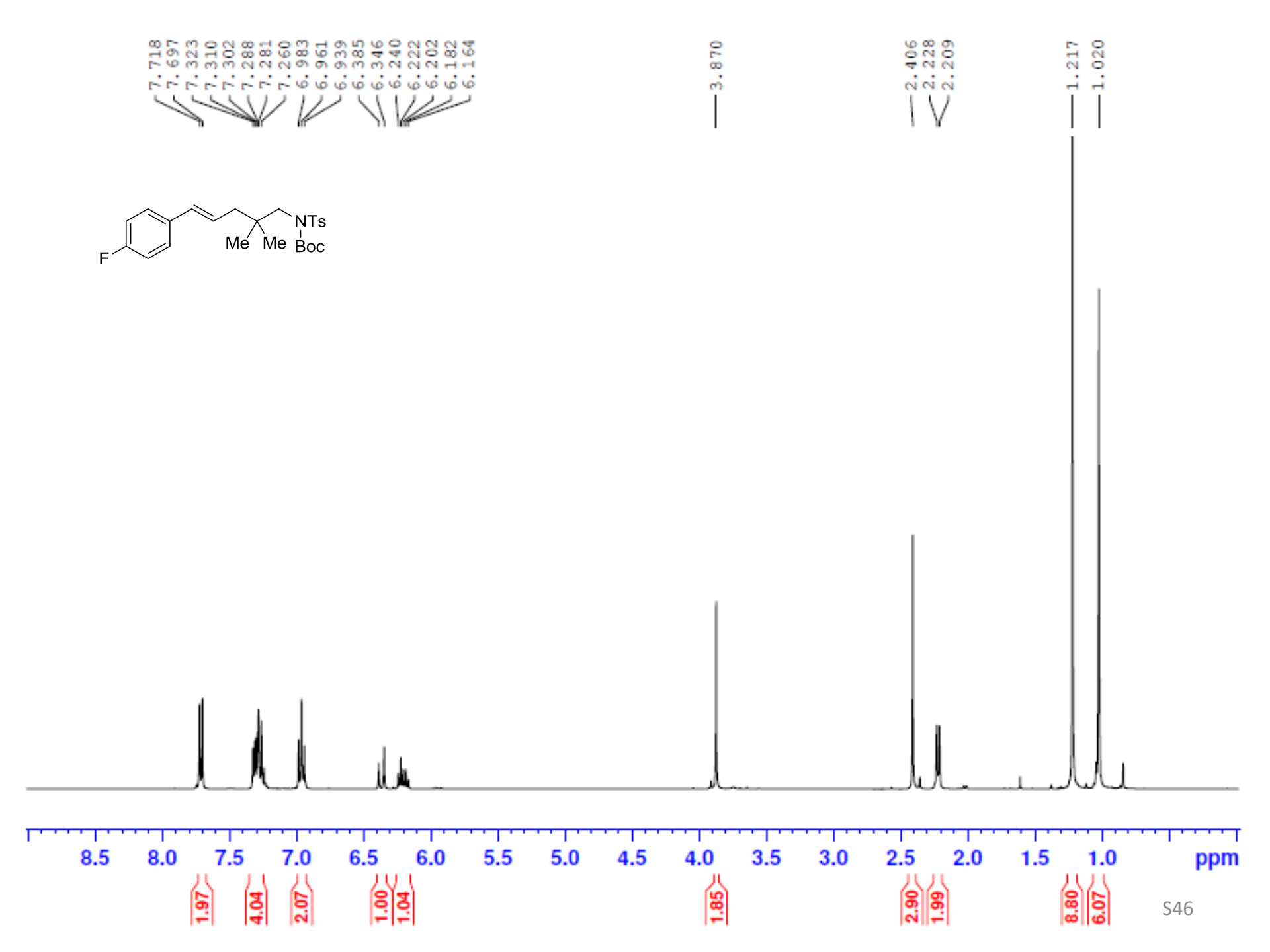
ppm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6.240
6.222
6.202
6.182
6.164
3.870
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2.228
2.209
1.217
1.020
NTs
Me
Me
Boc
F
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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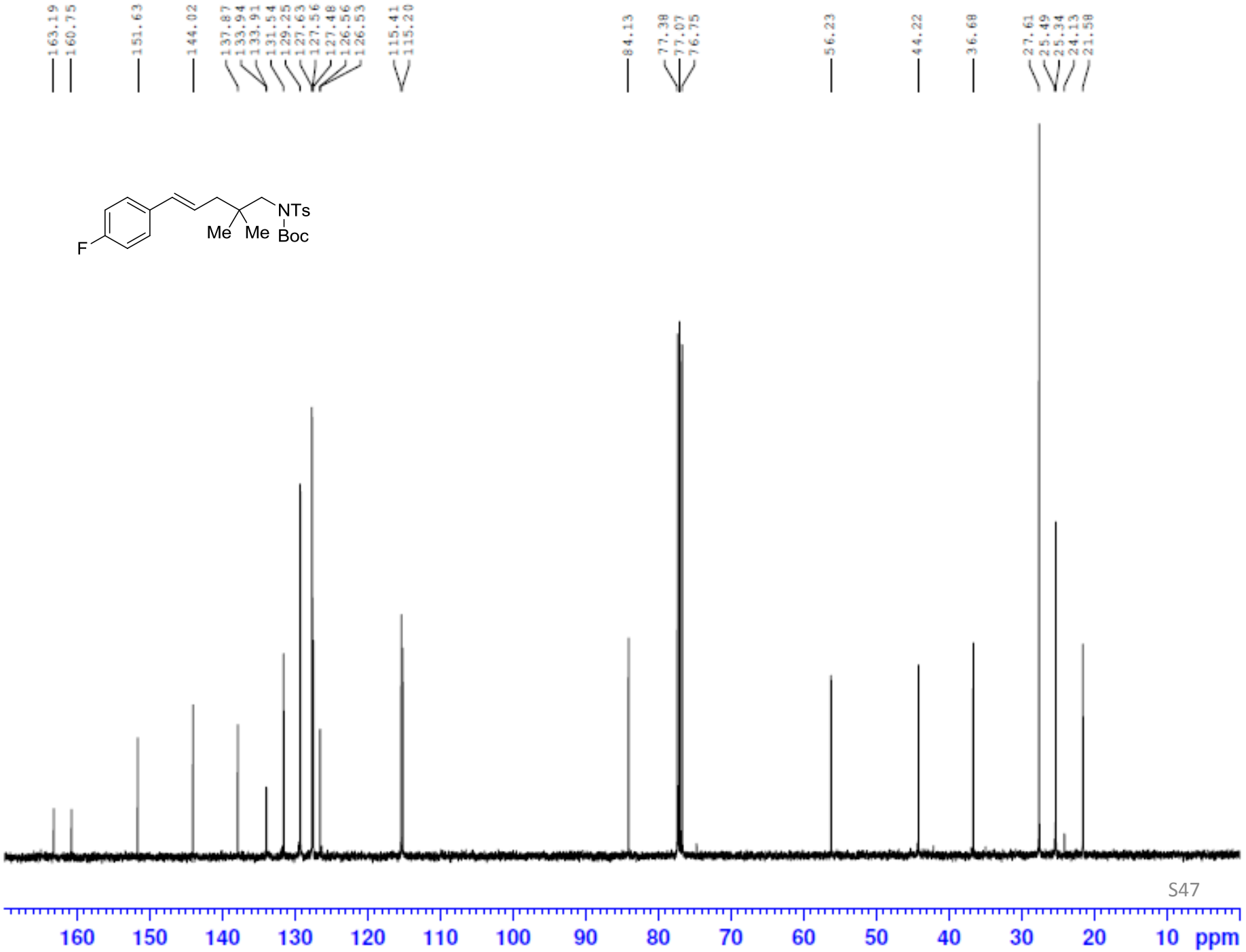
8.80
6.07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127.56
127.48
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126.53
115.41
115.20
84.13
77.38
77.07
76.75
56.23
44.22
36.68
27.61
25.49
25.34
24.13
21.58
F
Me
Me
NTs
Boc
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150
140
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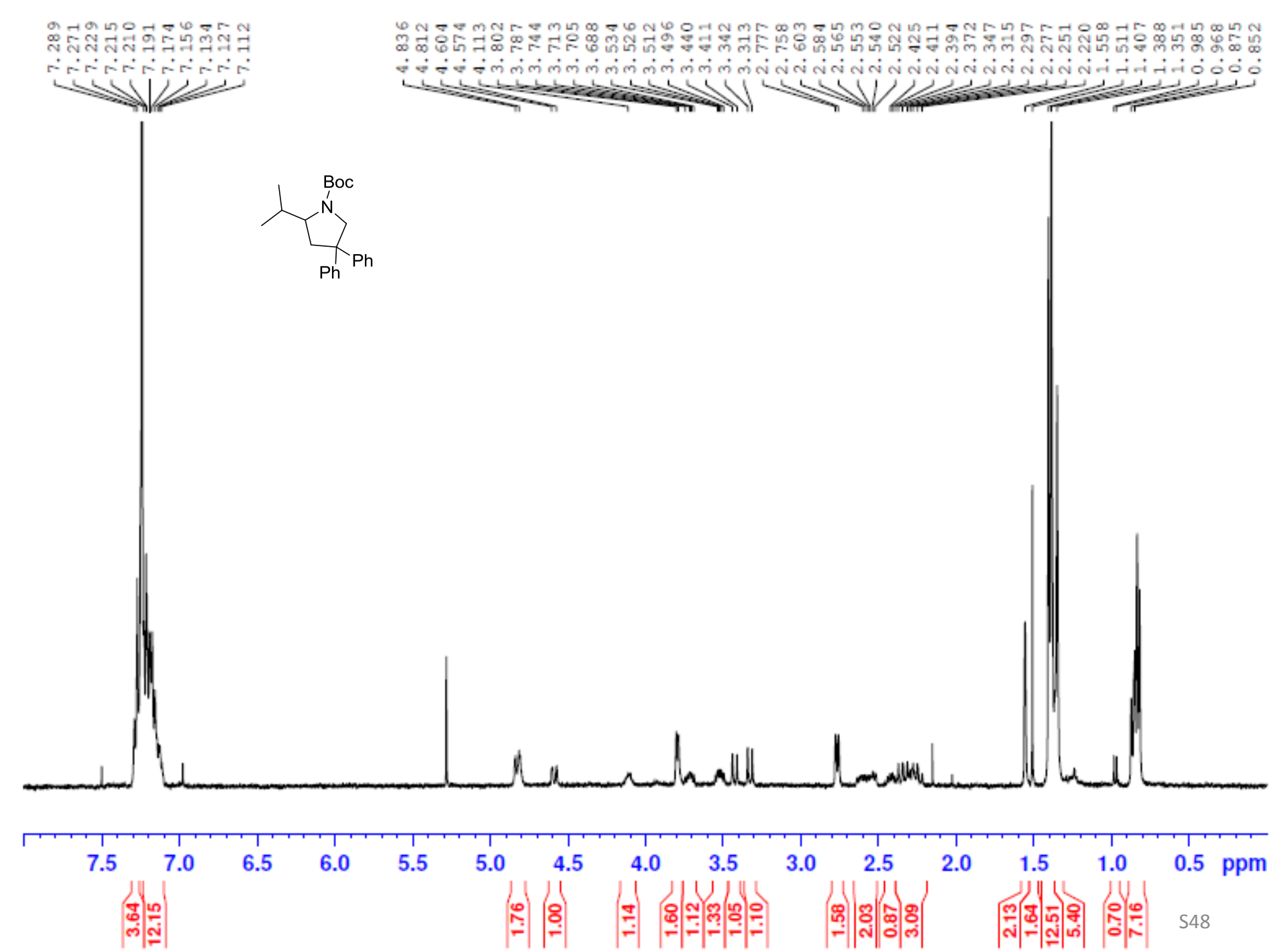
ppm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4.574
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3.744
3.713
3.705
3.688
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3.526
3.512
3.496
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3.342
3.313
2.777
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2.565
2.553
2.540
2.522
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2.315
2.297
2.277
2.251
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1.388
1.351
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0.968
0.875
0.852
Boc
N
Ph
Ph
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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
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1.00
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1.60
1.12
1.33
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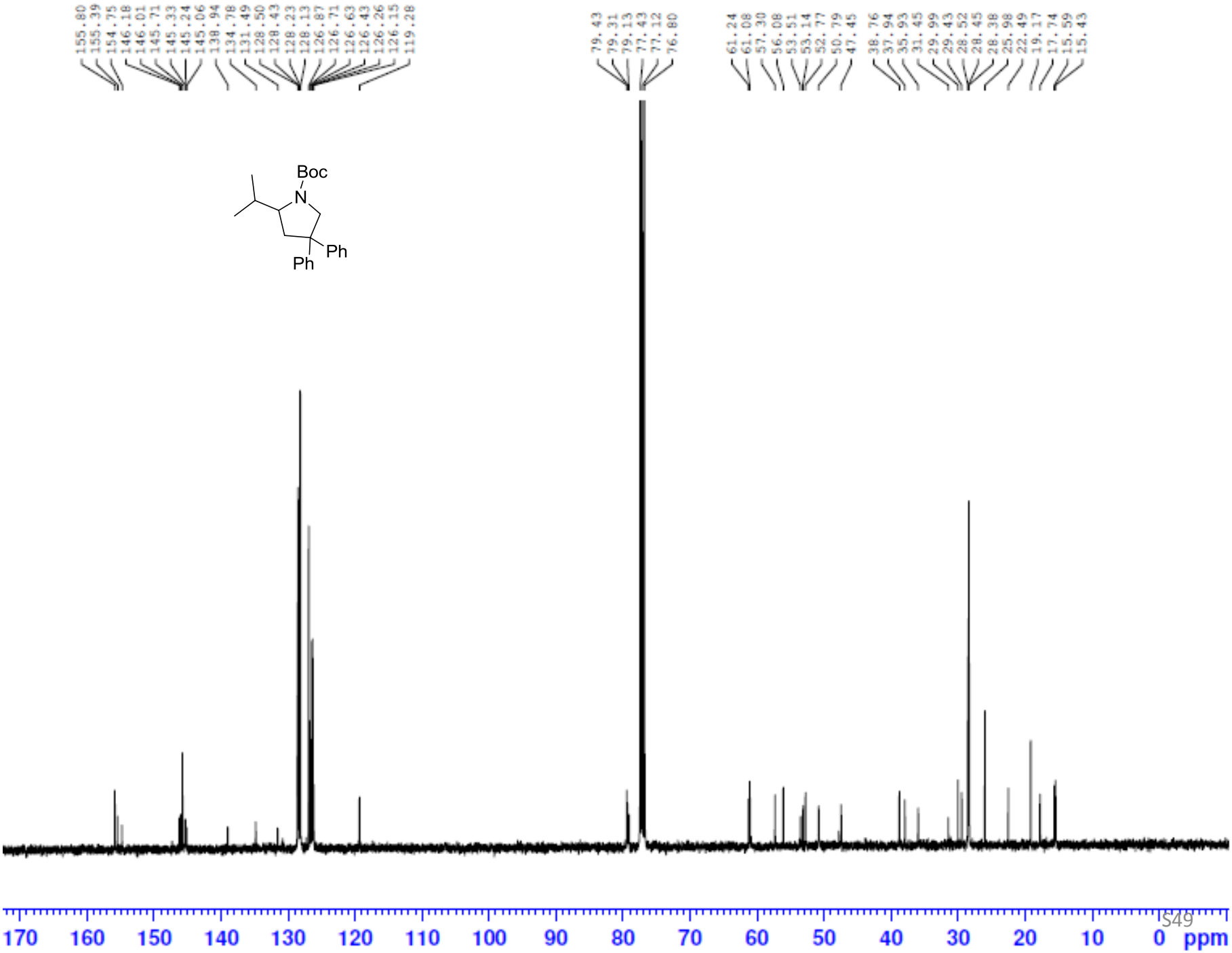
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128.23
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126.87
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126.63
126.43
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126.15
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79.43
79.31
79.13
77.43
77.12
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61.08
57.30
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50.79
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38.76
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35.93
31.45
29.99
29.43
28.52
28.45
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25.98
22.49
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Boc
N
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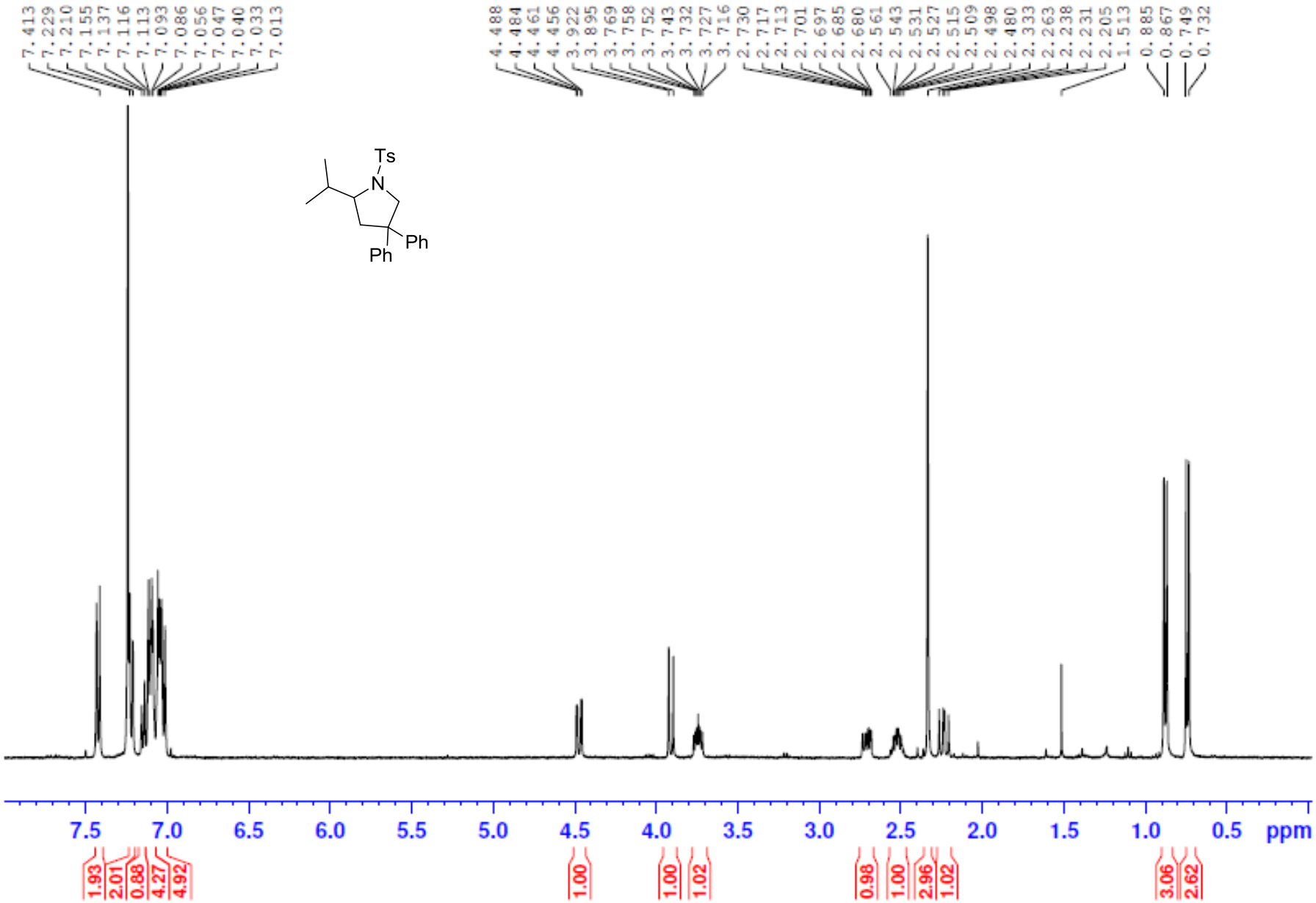
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7.033
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4.461
4.456
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3.895
3.769
3.758
3.752
3.743
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3.727
3.716
2.730
2.717
2.713
2.701
2.697
2.685
2.680
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2.543
2.531
2.527
2.515
2.509
2.498
2.480
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2.263
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2.231
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0.867
0.749
0.732
Ts
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Ph
Ph
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3.5
3.0
2.5
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1.0
0.5
ppm
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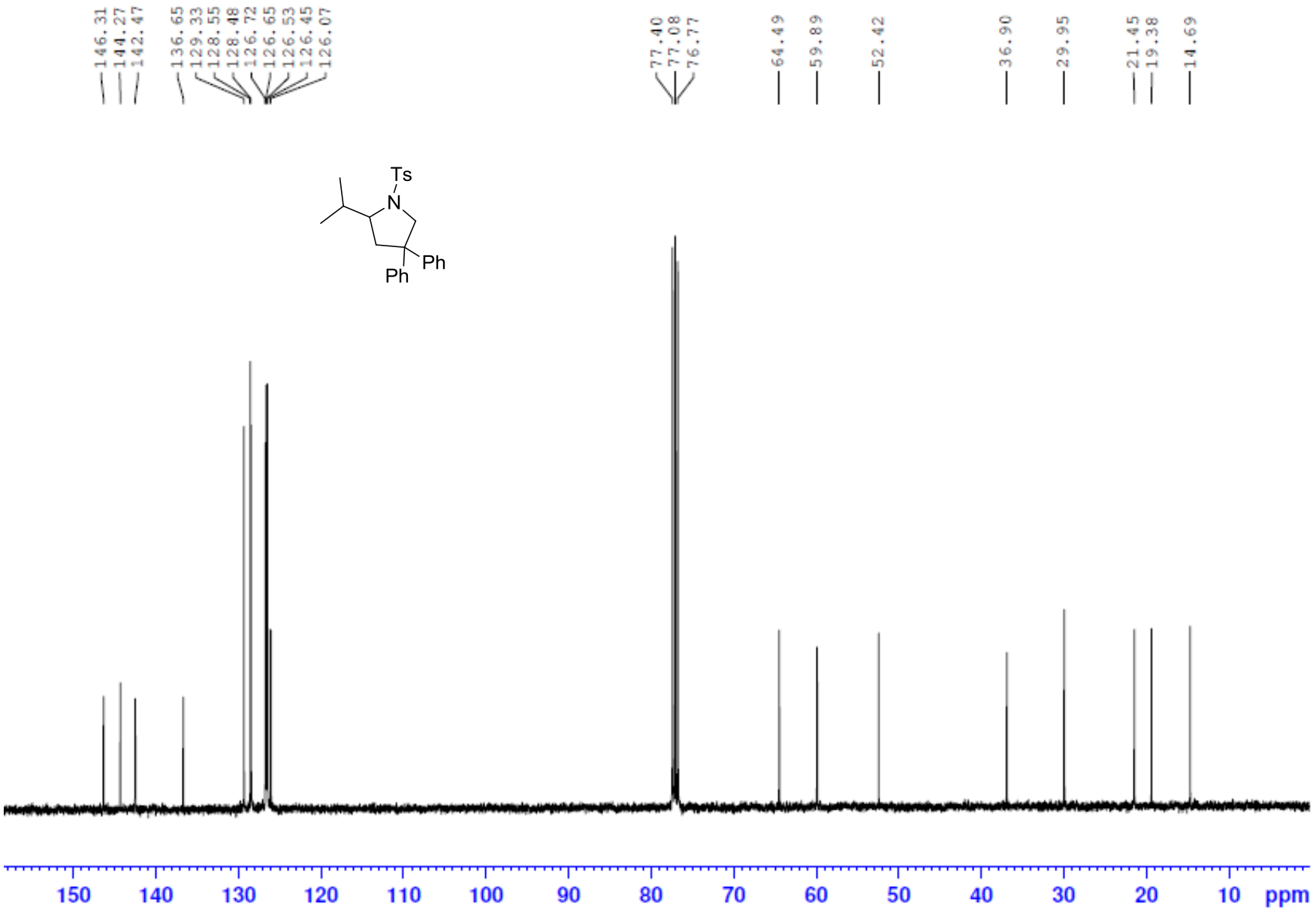
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77.08
76.77
64.49
59.89
52.42
36.90
29.95
21.45
19.38
14.69
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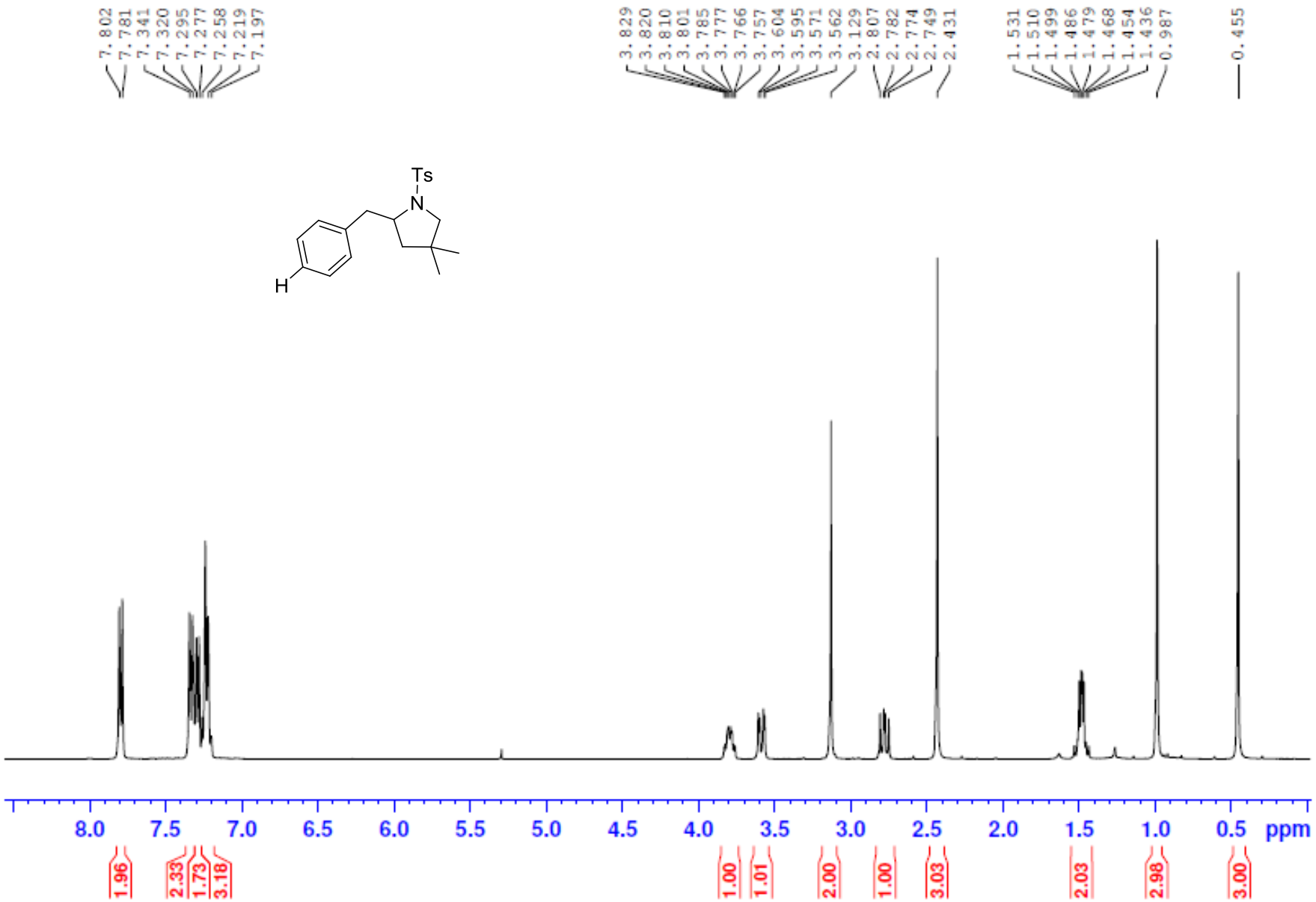
ppm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1.479
1.468
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1.436
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0.455
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H
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5.5
5.0
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3.0
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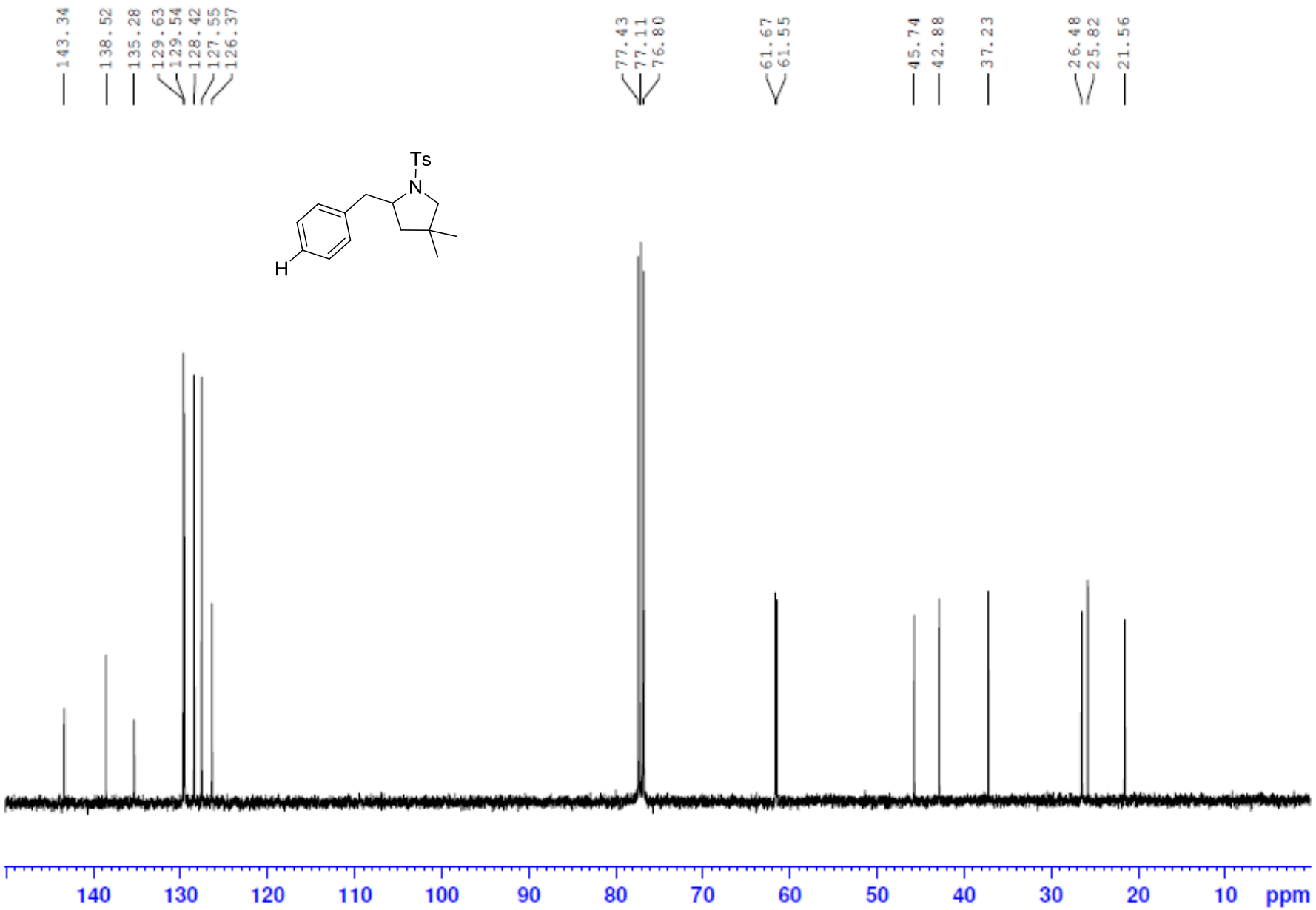
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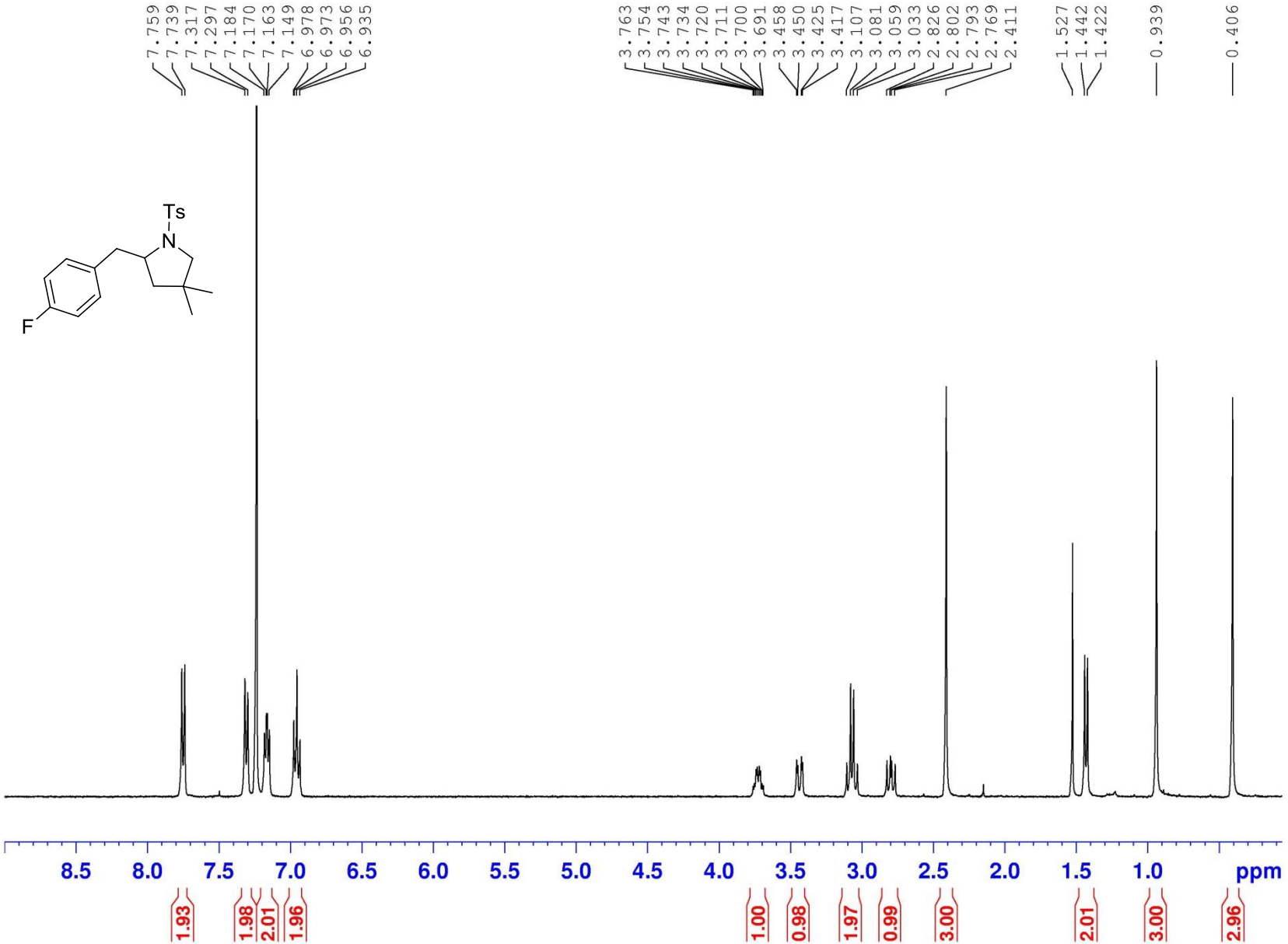
ppm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3.711
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0.406
Ts
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F
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4.0
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1.0
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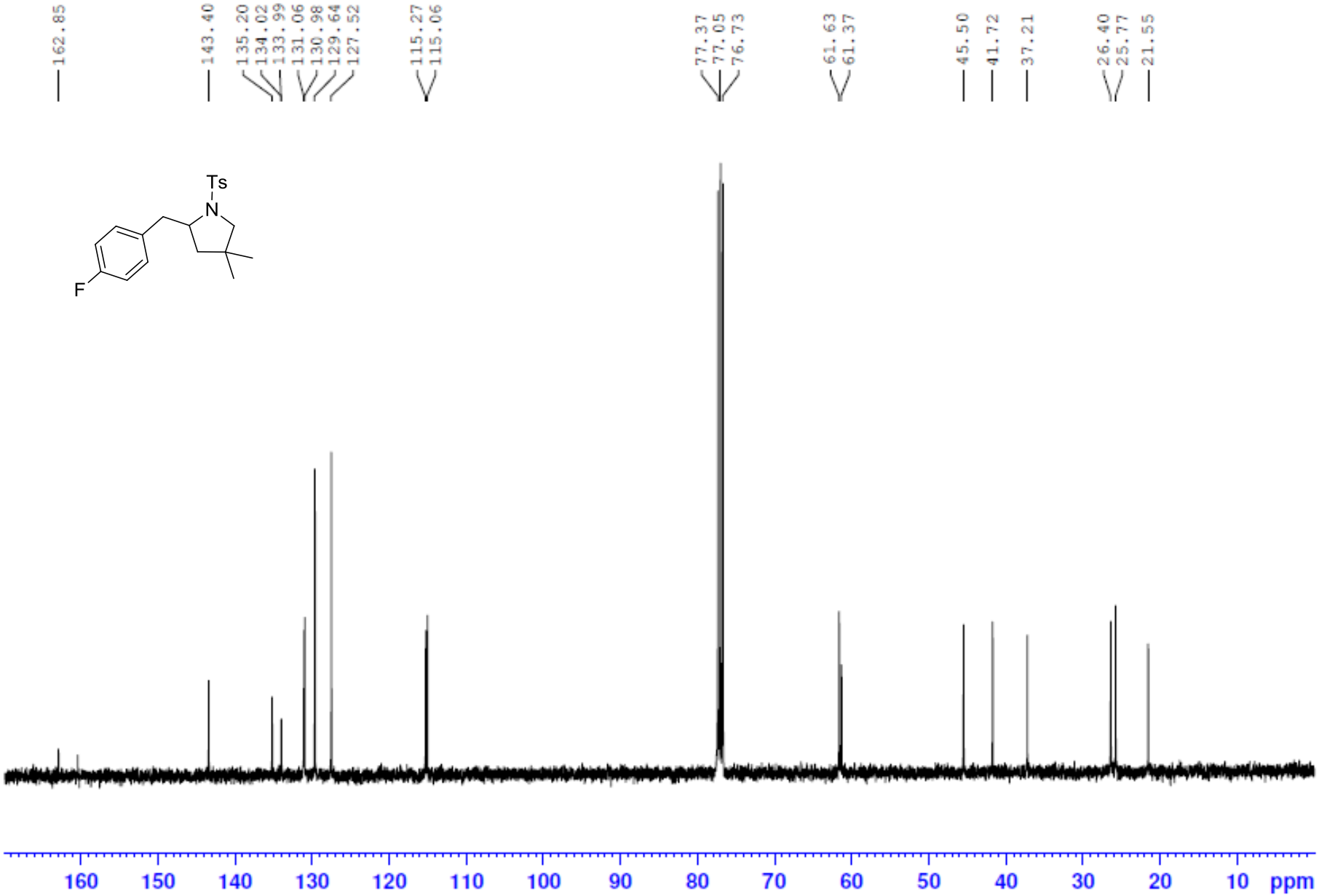
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61.37
45.50
41.72
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26.40
25.77
21.55
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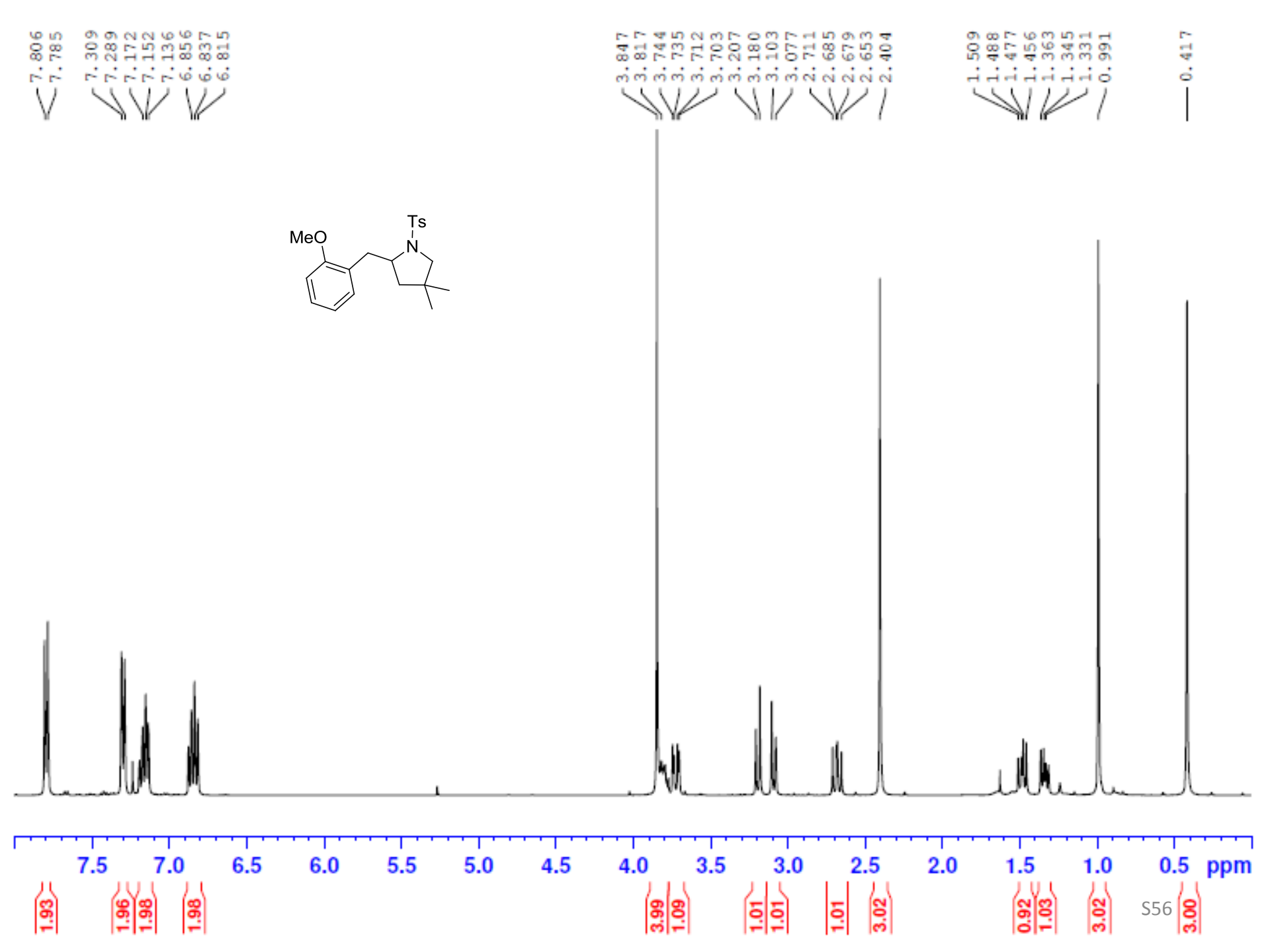
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1.477
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MeO
Ts
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4.0
3.5
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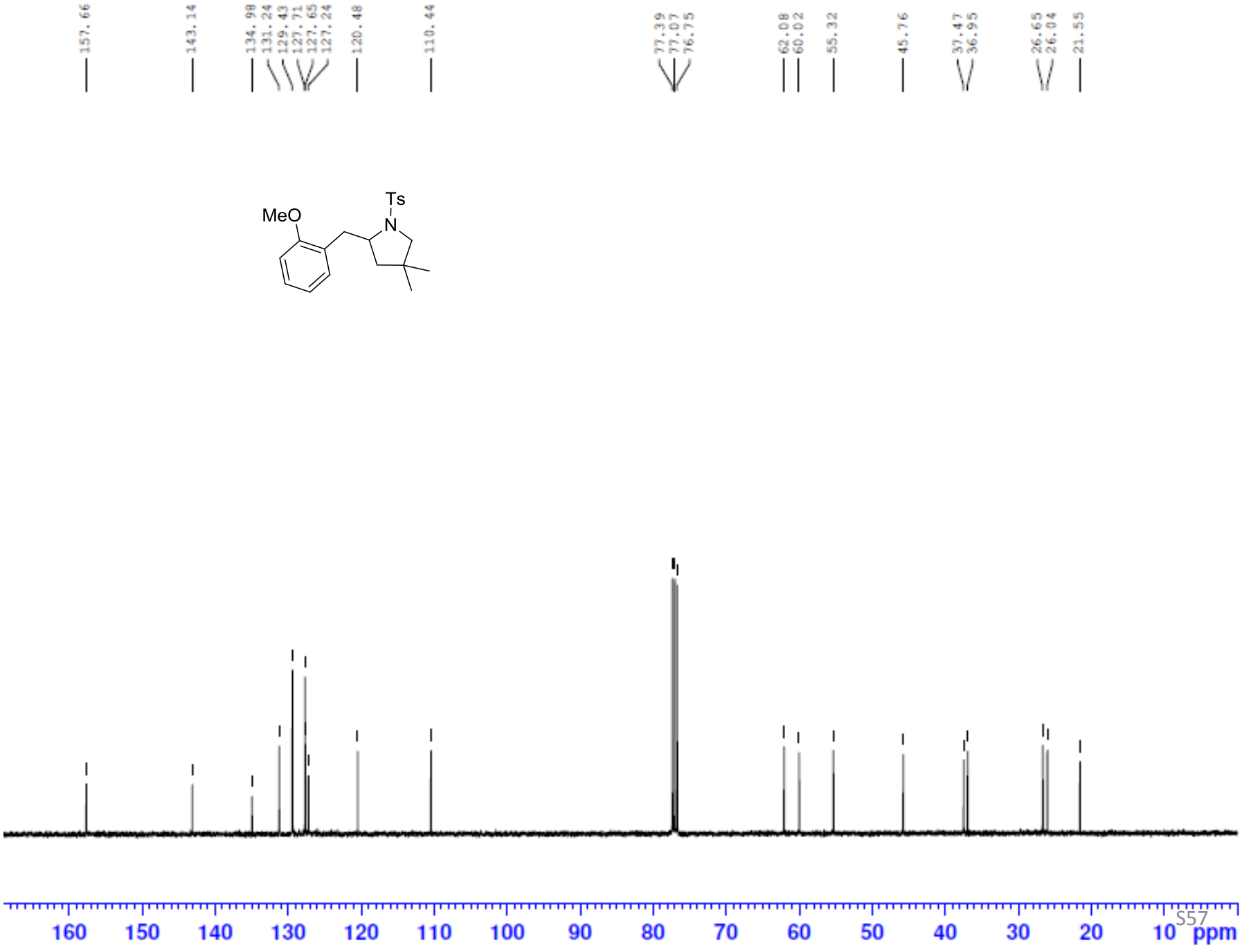
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37.47
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26.04
21.55
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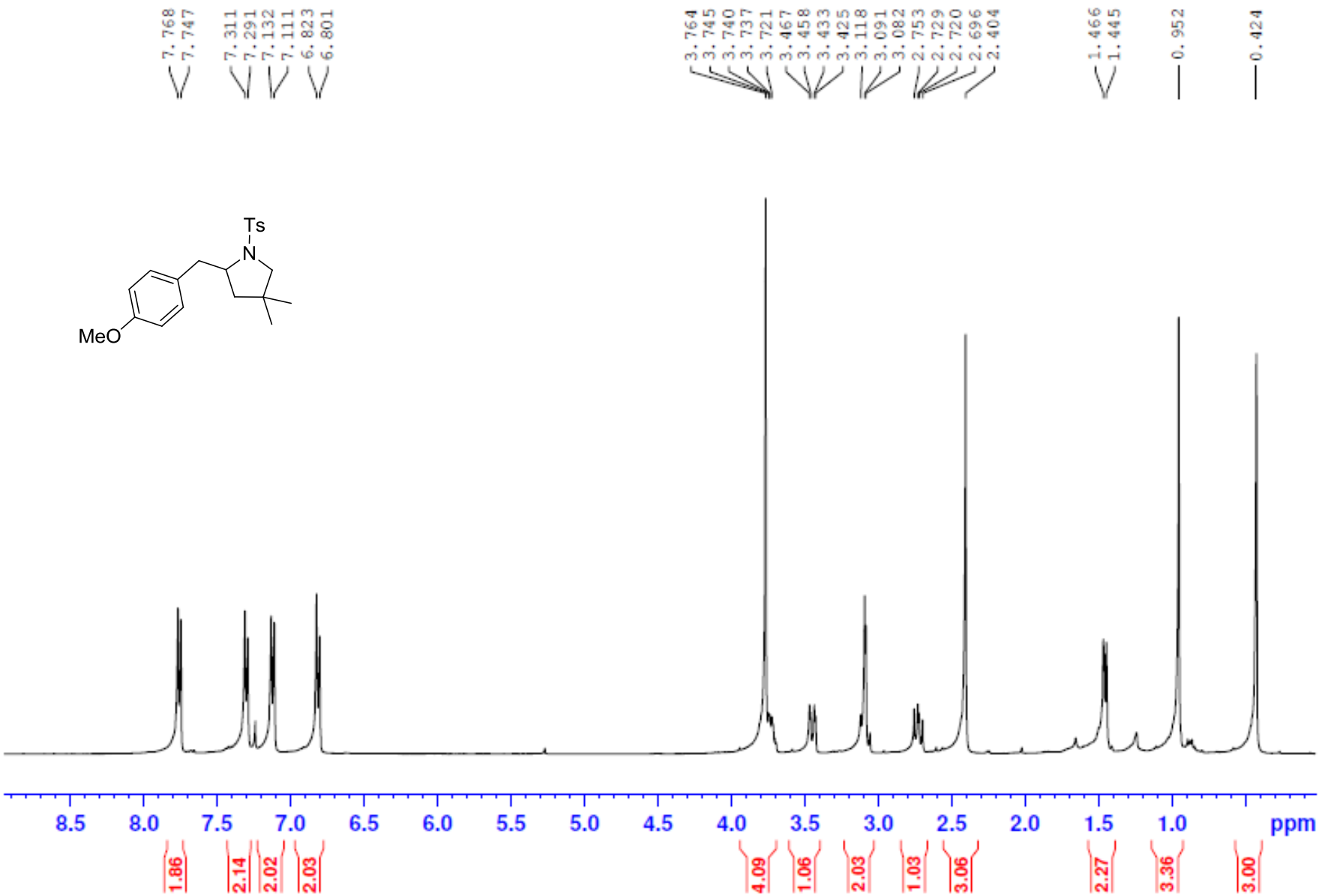
10
ppm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3.458
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2.729
2.720
2.696
2.404
1.466
1.445
0.952
0.424
Ts
N
MeO
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1.5
1.0
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1.03
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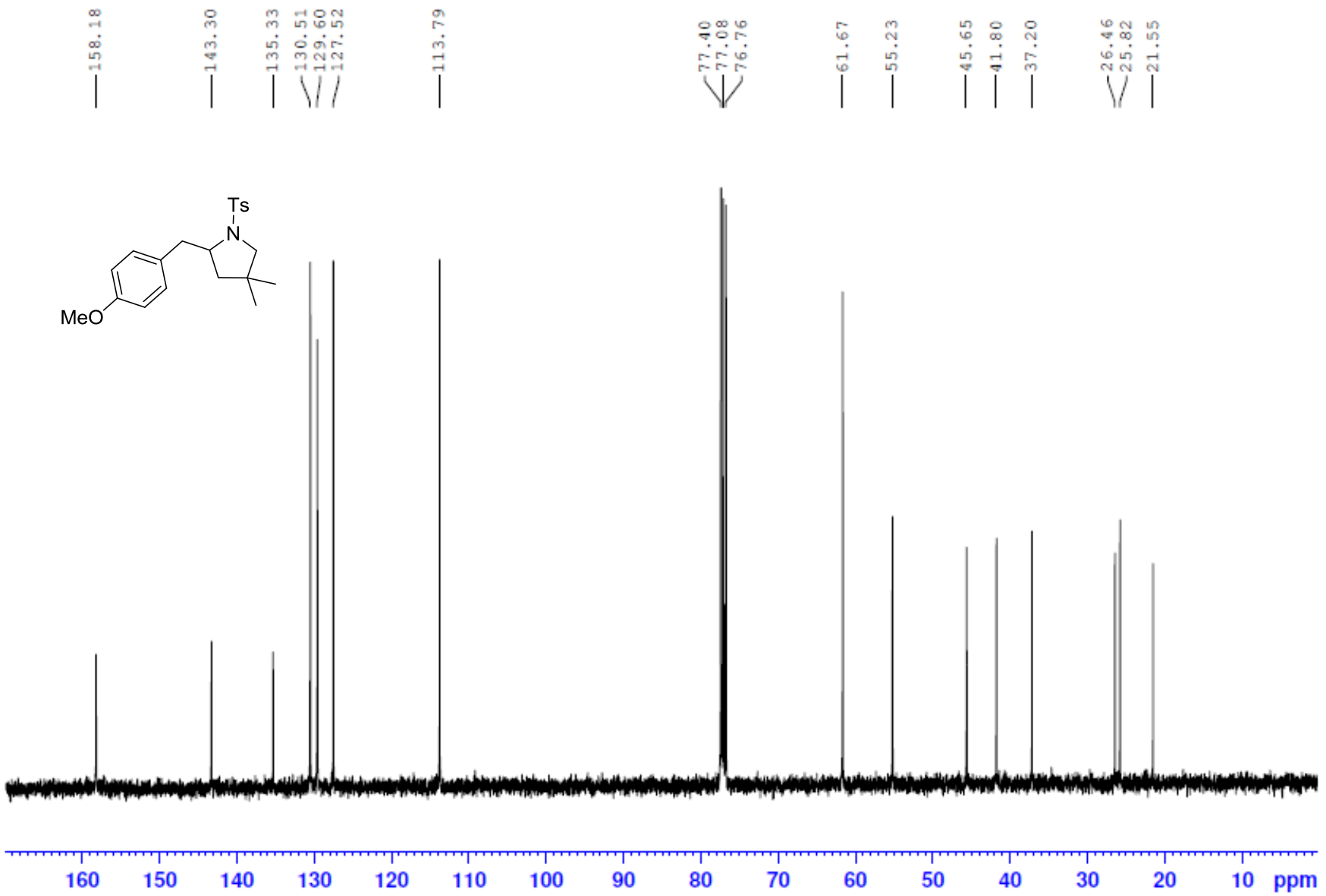
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41.80
37.20
26.46
25.82
21.55
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MeO
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130
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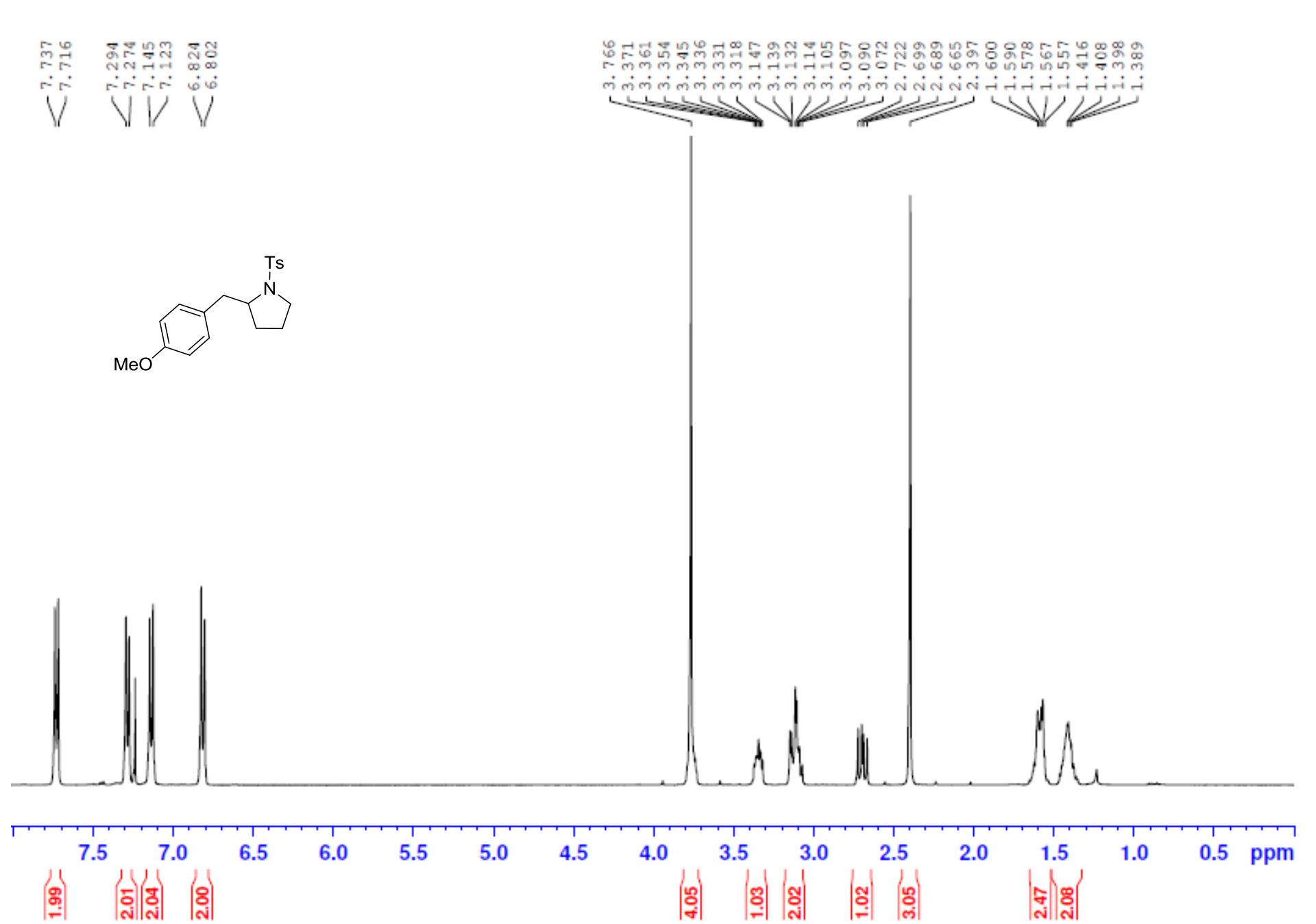
ppm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MeO
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1.02
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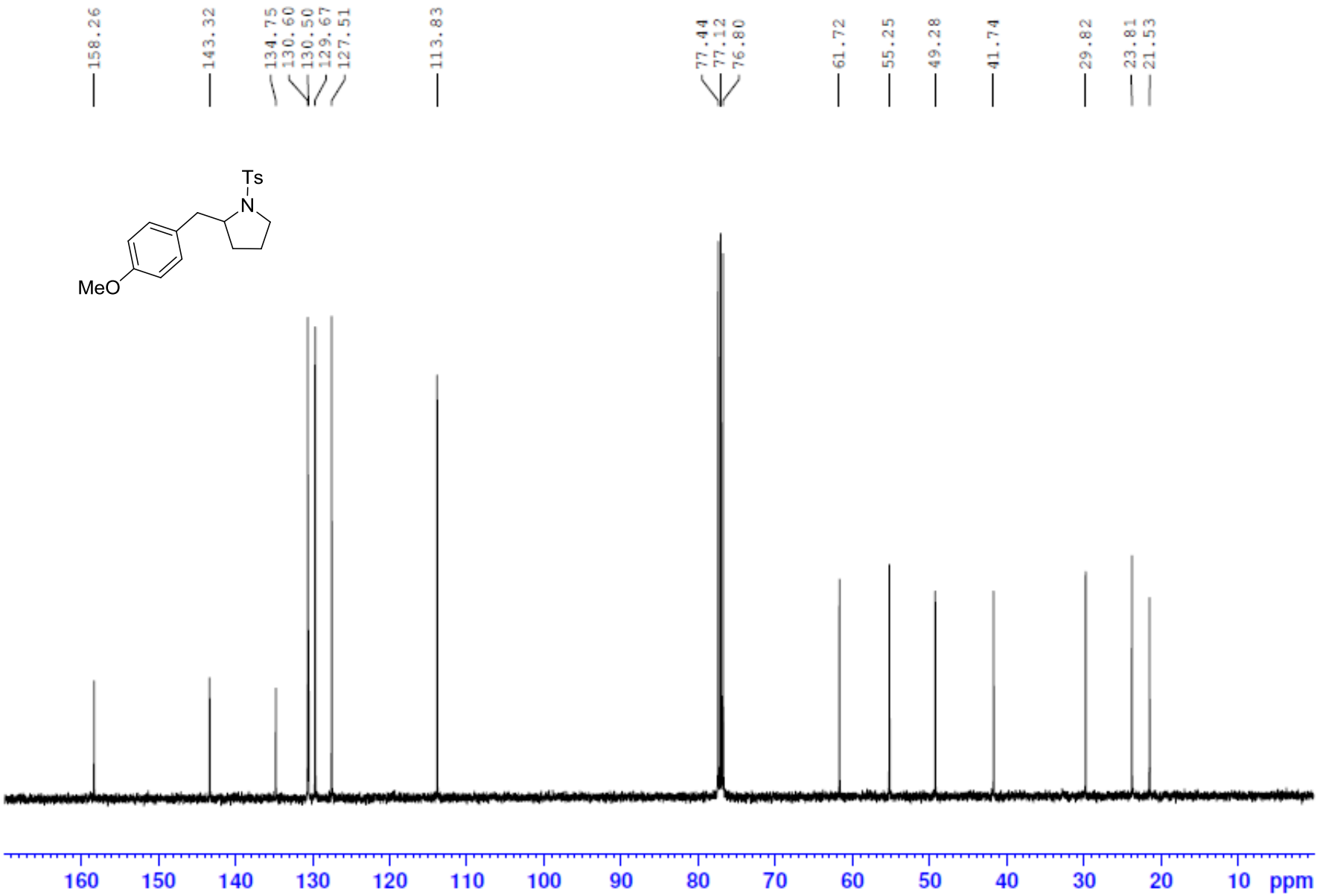
2.08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49.28
41.74
29.82
23.81
21.53
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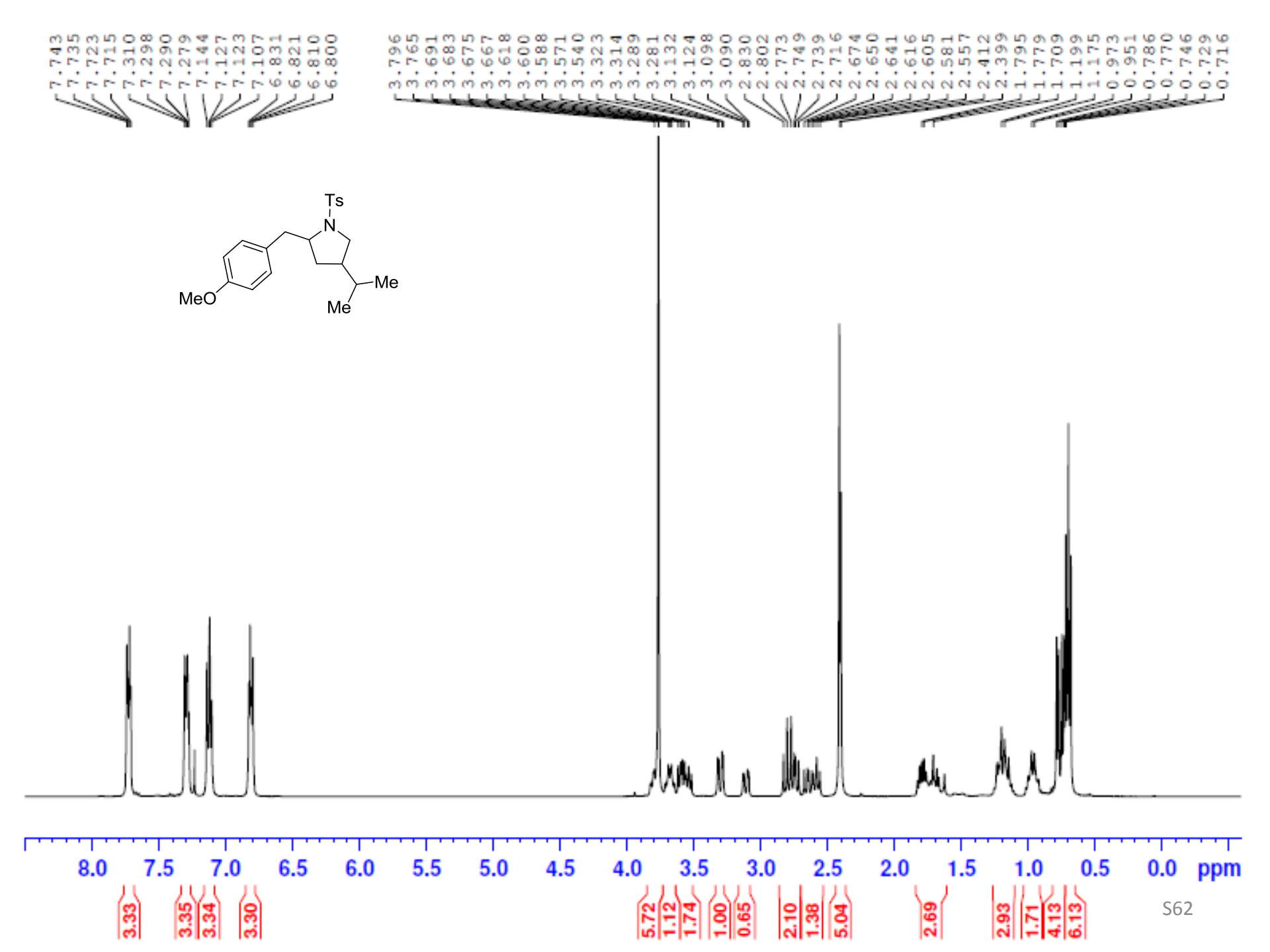
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6.821
6.810
6.800
3.796
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3.683
3.675
3.667
3.618
3.600
3.588
3.571
3.540
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3.289
3.281
3.132
3.124
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3.090
2.830
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2.773
2.749
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2.716
2.674
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2.641
2.616
2.605
2.581
2.557
2.412
2.399
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1.709
1.199
1.175
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0.951
0.786
0.770
0.746
0.729
0.716
Ts
N
MeO
Me
Me
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7.0
6.5
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5.0
4.5
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3.0
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0.0
ppm
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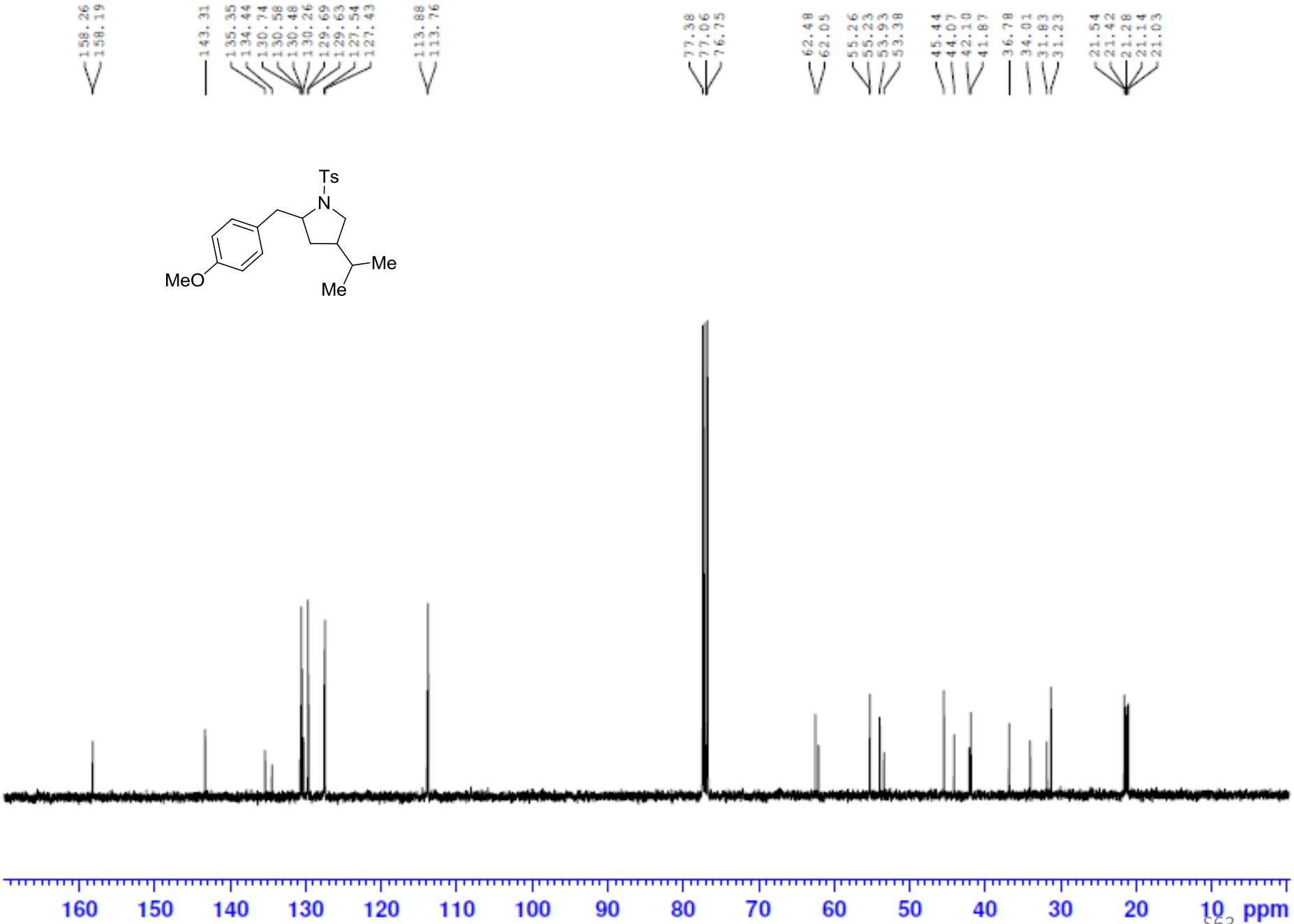
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113.76
77.38
77.06
76.75
62.48
62.05
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55.23
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53.38
45.44
44.07
42.10
41.87
36.78
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31.83
31.23
21.54
21.42
21.28
21.14
21.03
Ts
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MeO
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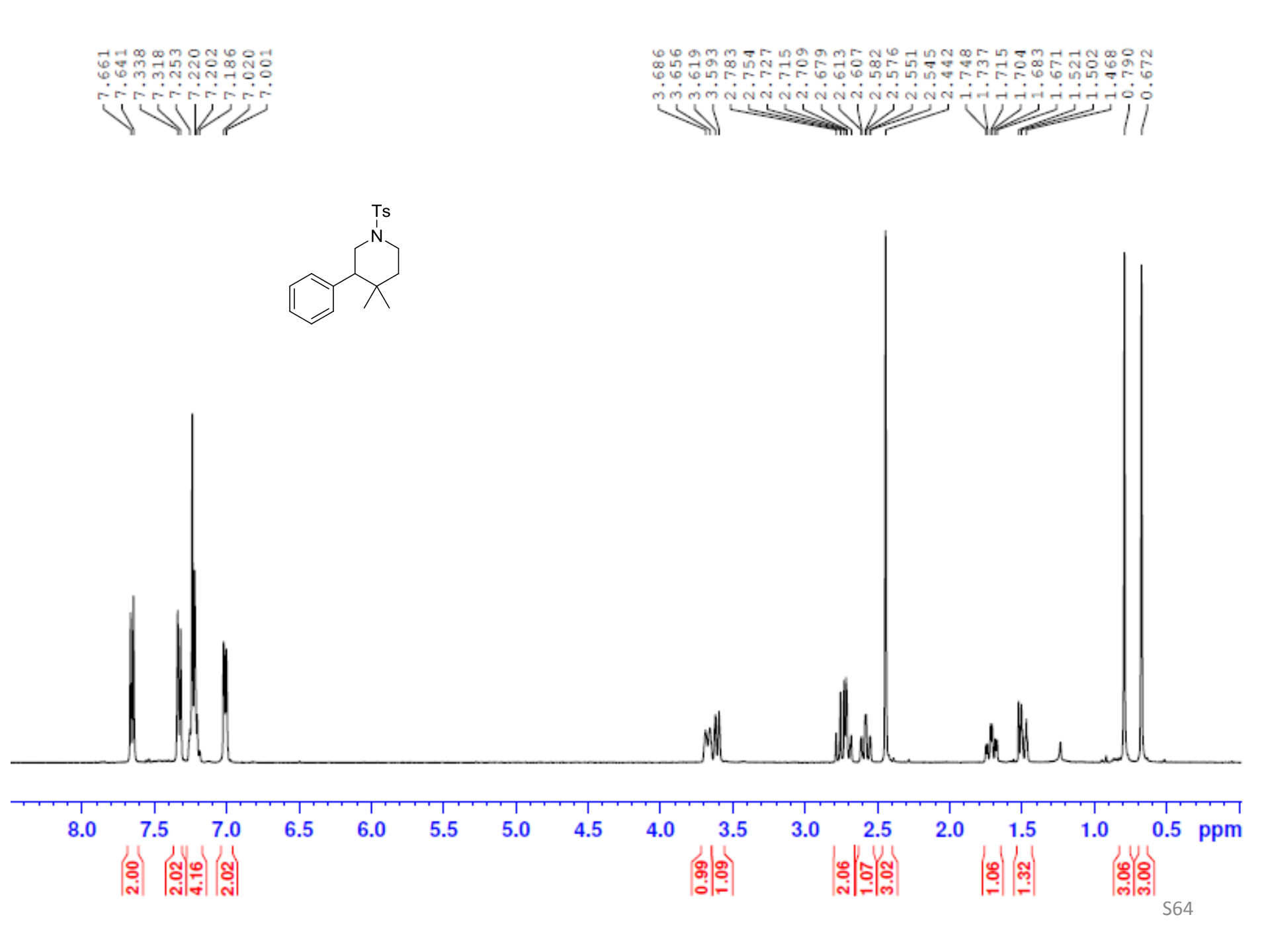
ppm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3.656
3.619
3.593
2.783
2.754
2.727
2.715
2.709
2.679
2.613
2.607
2.582
2.576
2.551
2.545
2.442
1.748
1.737
1.715
1.704
1.683
1.671
1.521
1.502
1.468
0.790
0.672
Ts
N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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3.02
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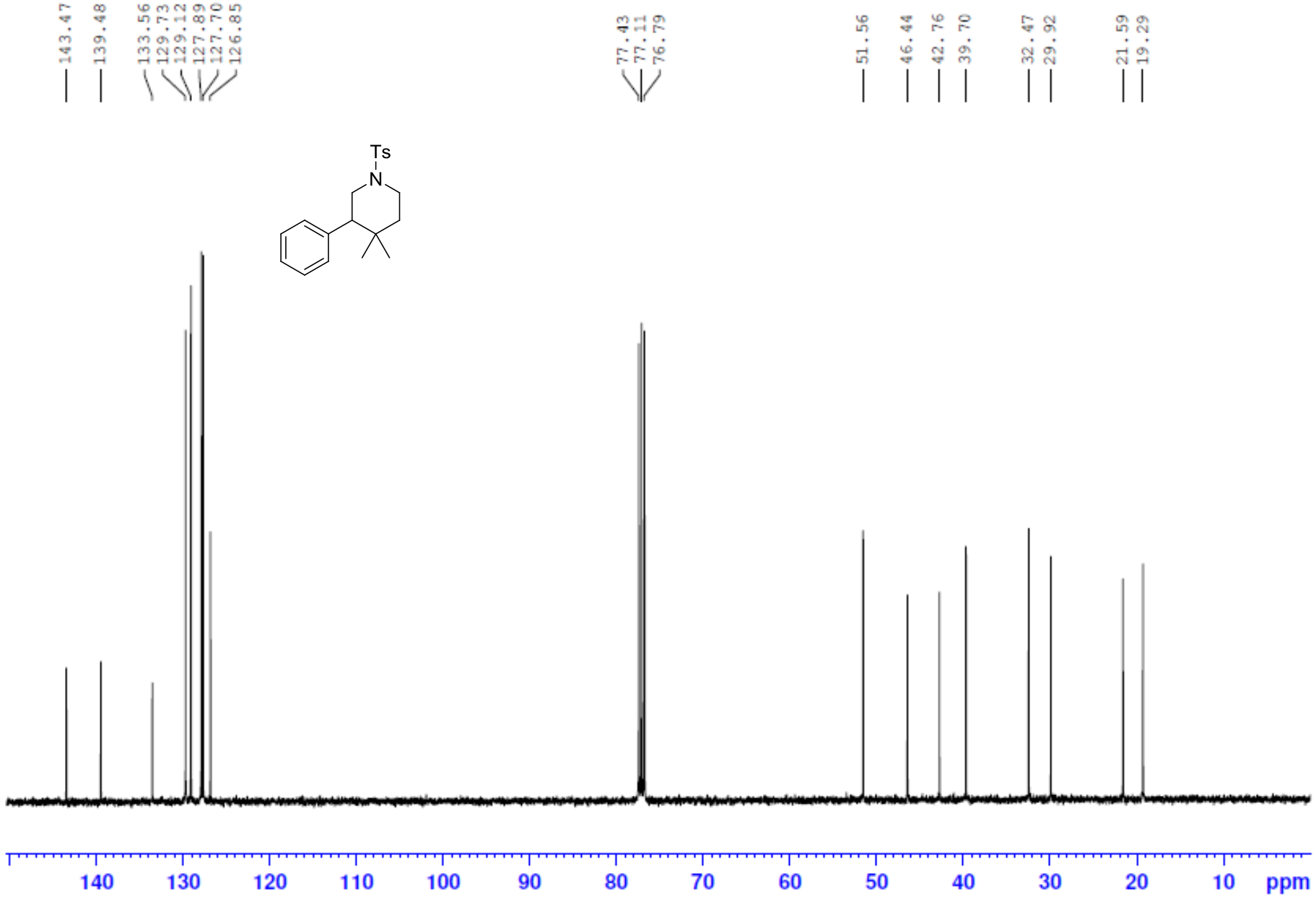
1.32
3.06
3.00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42.76
39.70
32.47
29.92
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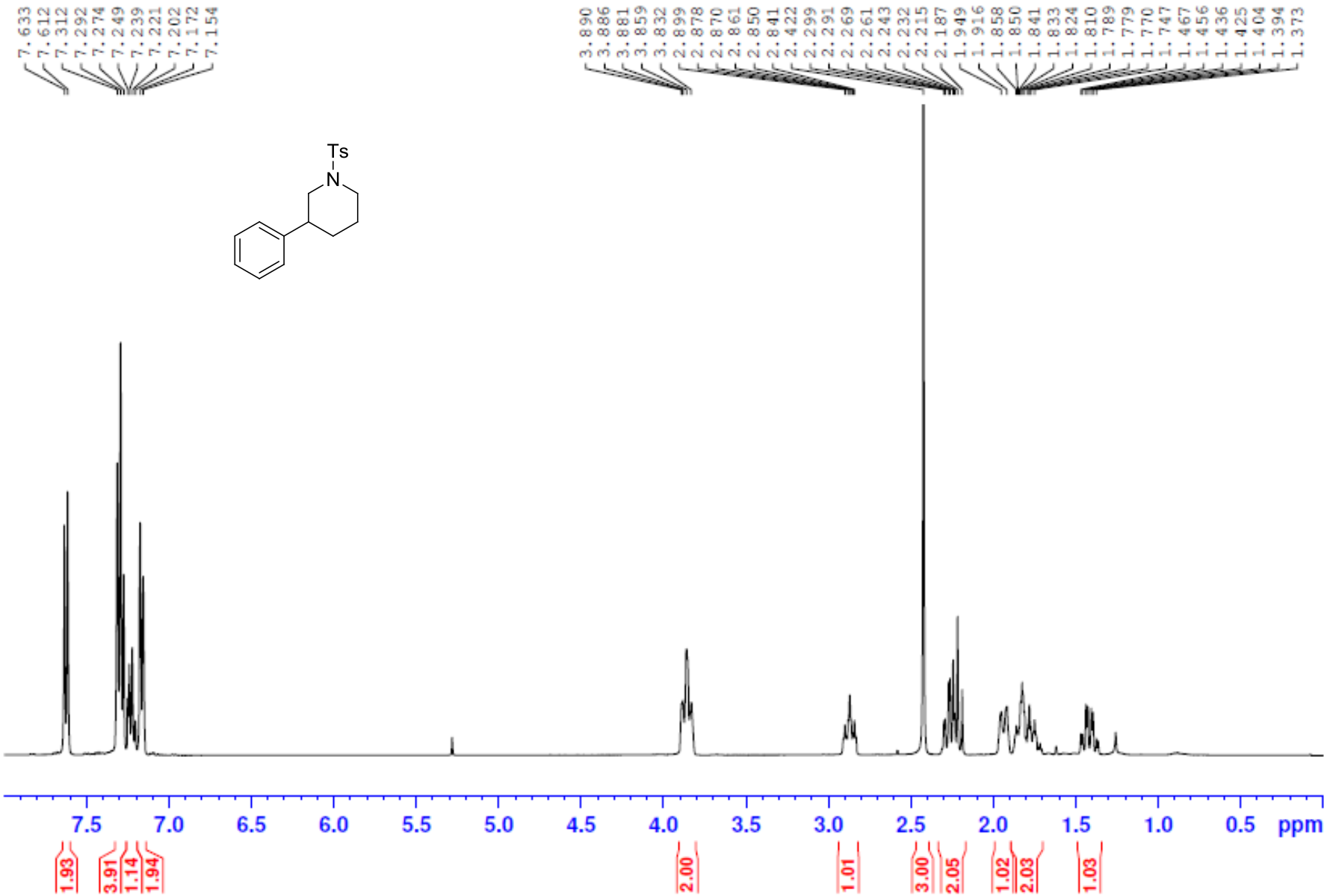
20
10
ppm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7.221
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7.172
7.154
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3.886
3.881
3.859
3.832
2.899
2.878
2.870
2.861
2.850
2.841
2.422
2.299
2.291
2.269
2.261
2.243
2.232
2.215
2.187
1.949
1.916
1.858
1.850
1.841
1.833
1.824
1.810
1.789
1.779
1.770
1.747
1.467
1.456
1.436
1.425
1.404
1.394
1.373
Ts
N
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.94
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1.01
3.00
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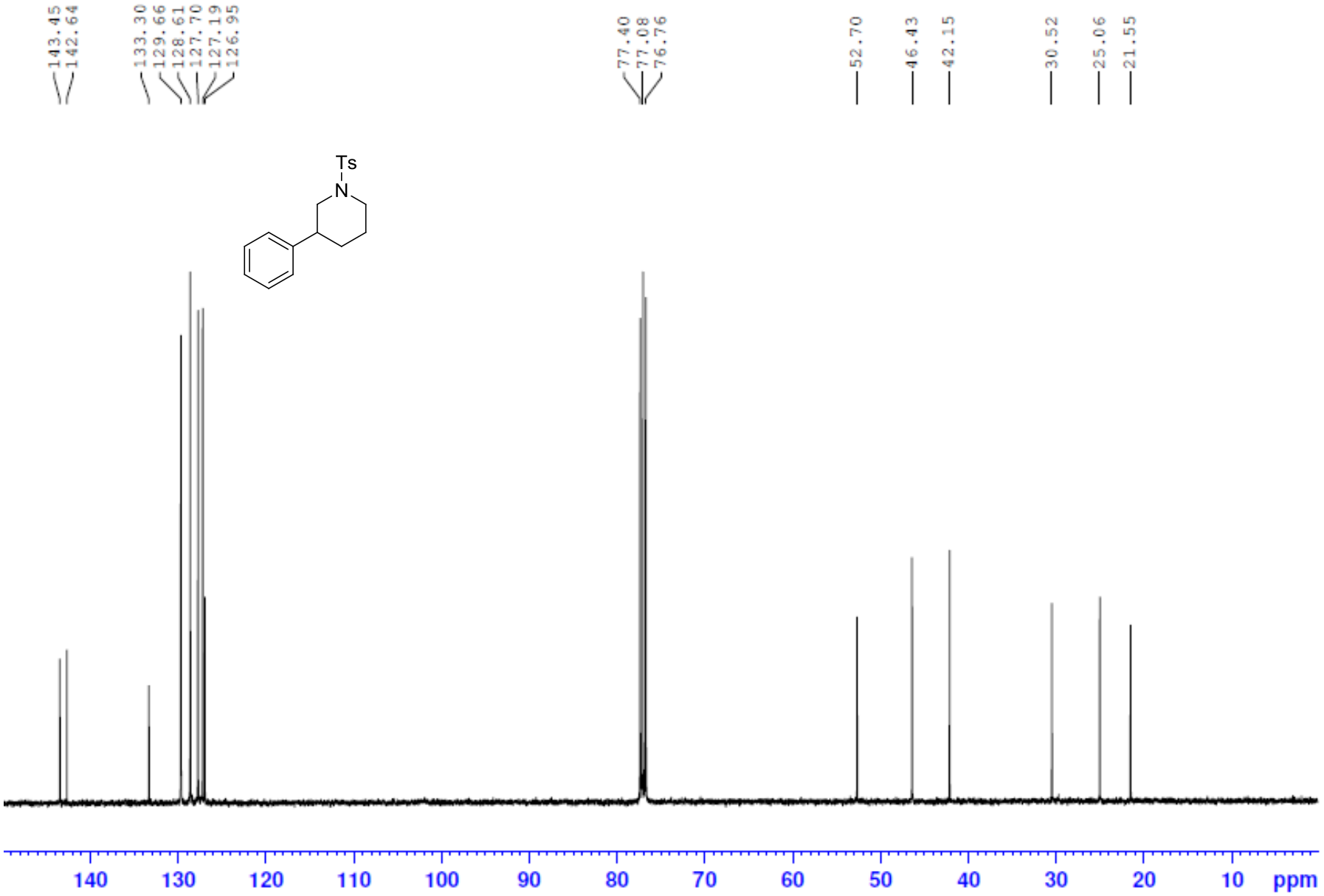
1.02
2.03
1.03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76.76
52.70
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42.15
30.52
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N
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130
120
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70
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50
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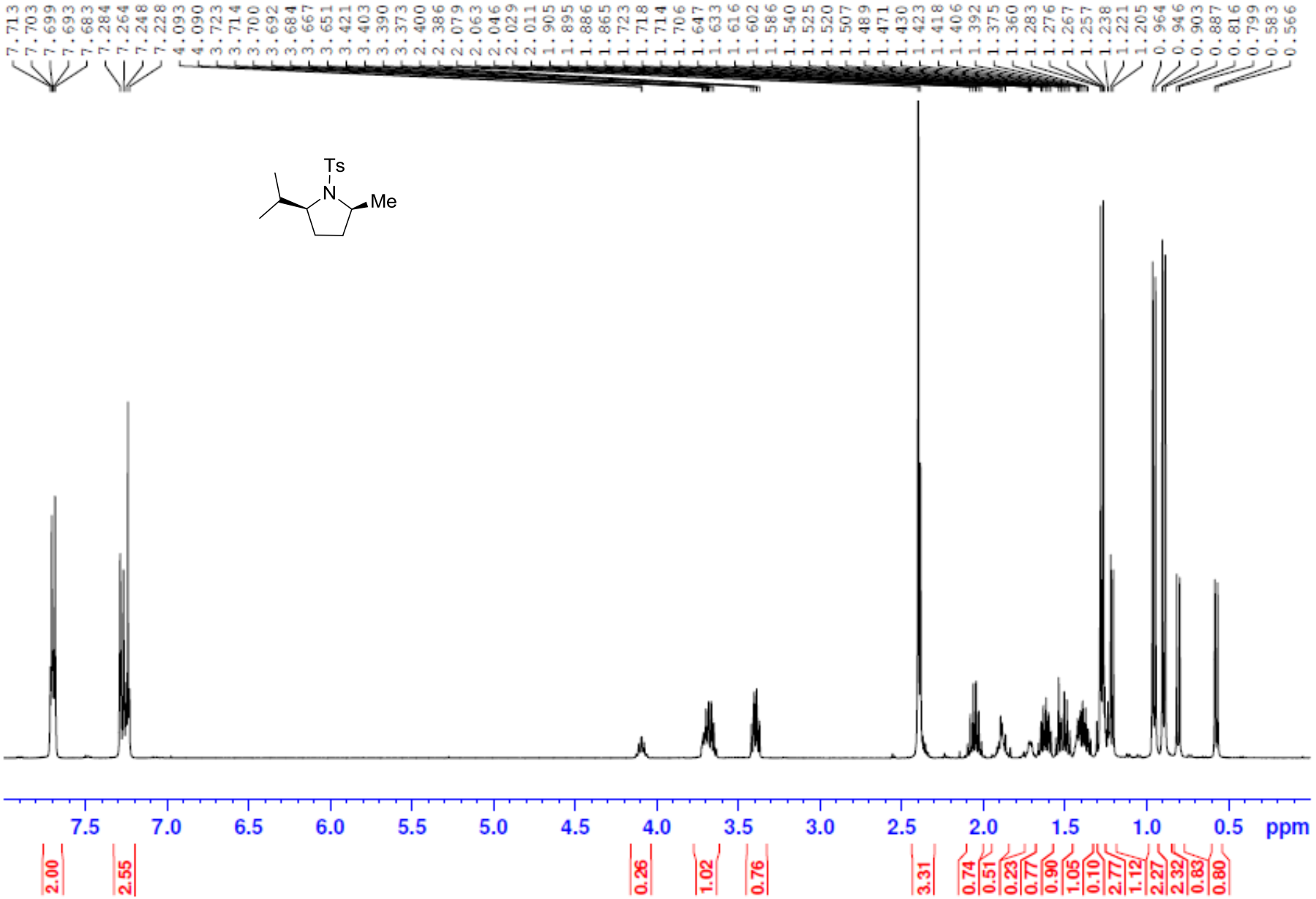
30
20
10
ppm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Ts
N
Me
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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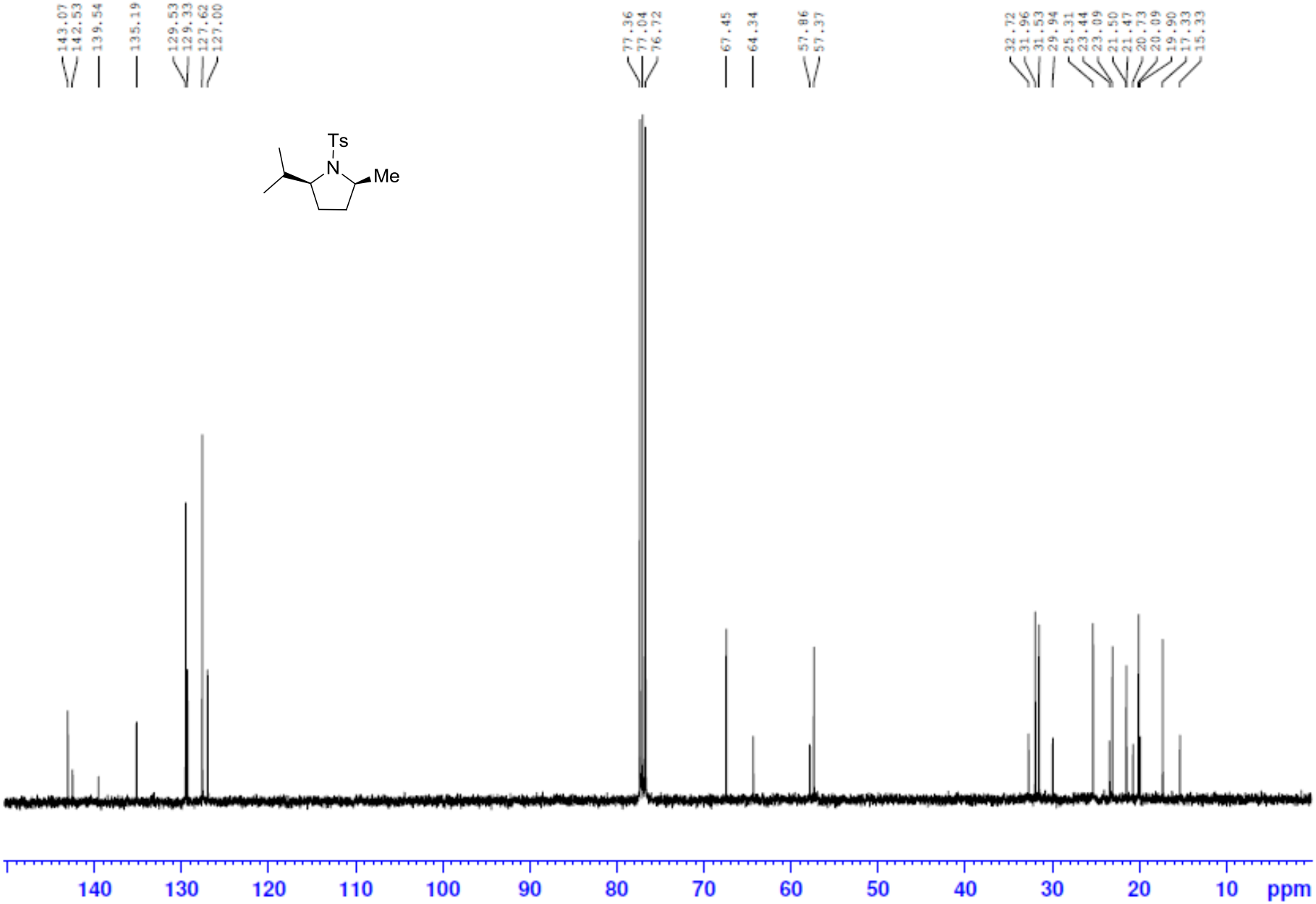
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57.37
32.72
31.96
31.53
29.94
25.31
23.44
23.09
21.50
21.47
20.73
20.09
19.90
17.33
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Me
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130
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70
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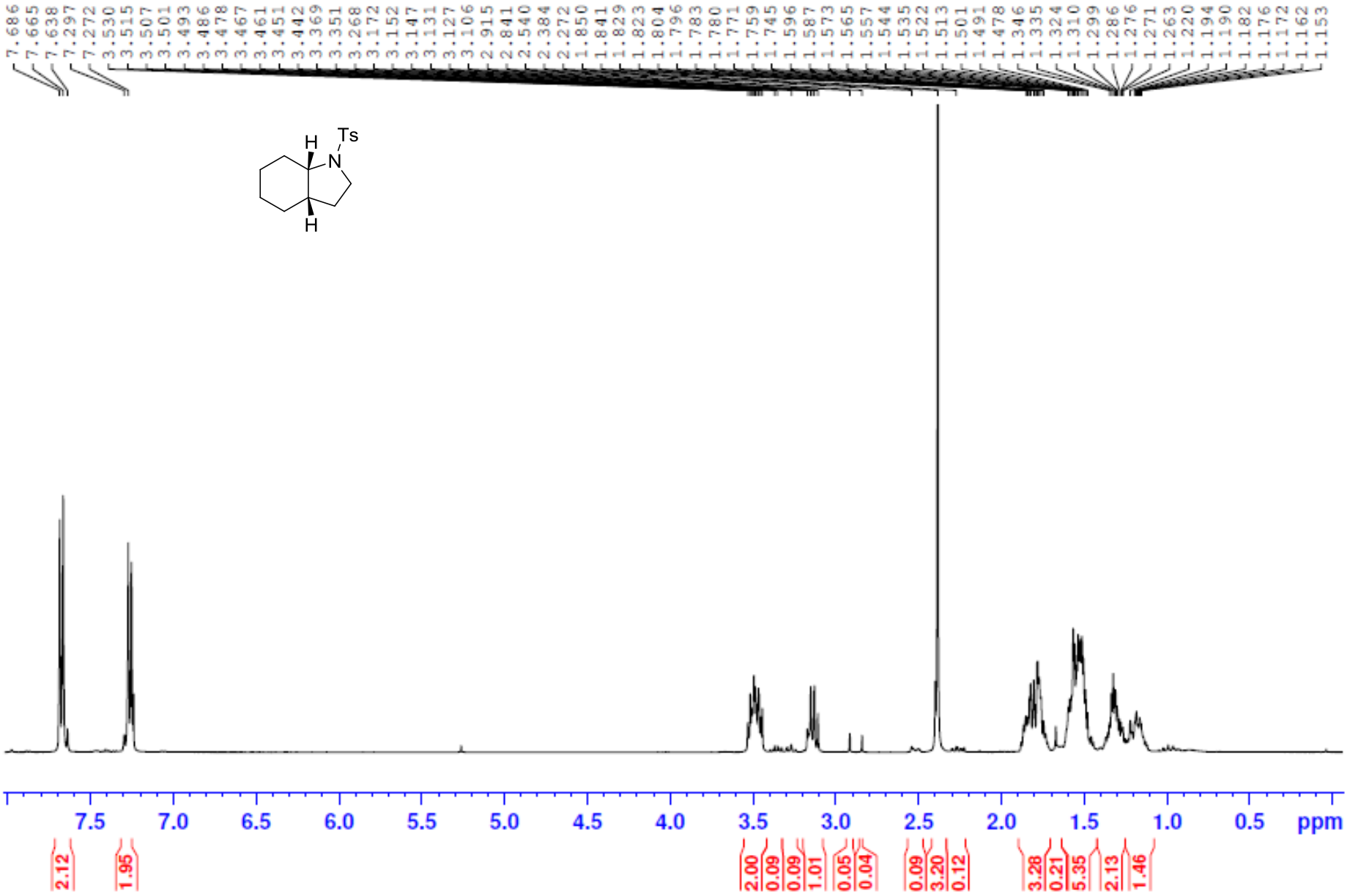
10
ppm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3.461
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3.442
3.369
3.351
3.268
3.172
3.152
3.147
3.131
3.127
3.106
2.915
2.841
2.540
2.384
2.272
1.850
1.841
1.829
1.823
1.804
1.796
1.783
1.780
1.771
1.759
1.745
1.596
1.587
1.573
1.565
1.557
1.544
1.535
1.522
1.513
1.501
1.491
1.478
1.346
1.335
1.324
1.310
1.299
1.286
1.276
1.271
1.263
1.220
1.194
1.190
1.182
1.176
1.172
1.162
1.153
H
Ts
N
H
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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
ppm
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2.00
0.09
0.09
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0.04
0.09
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3.28
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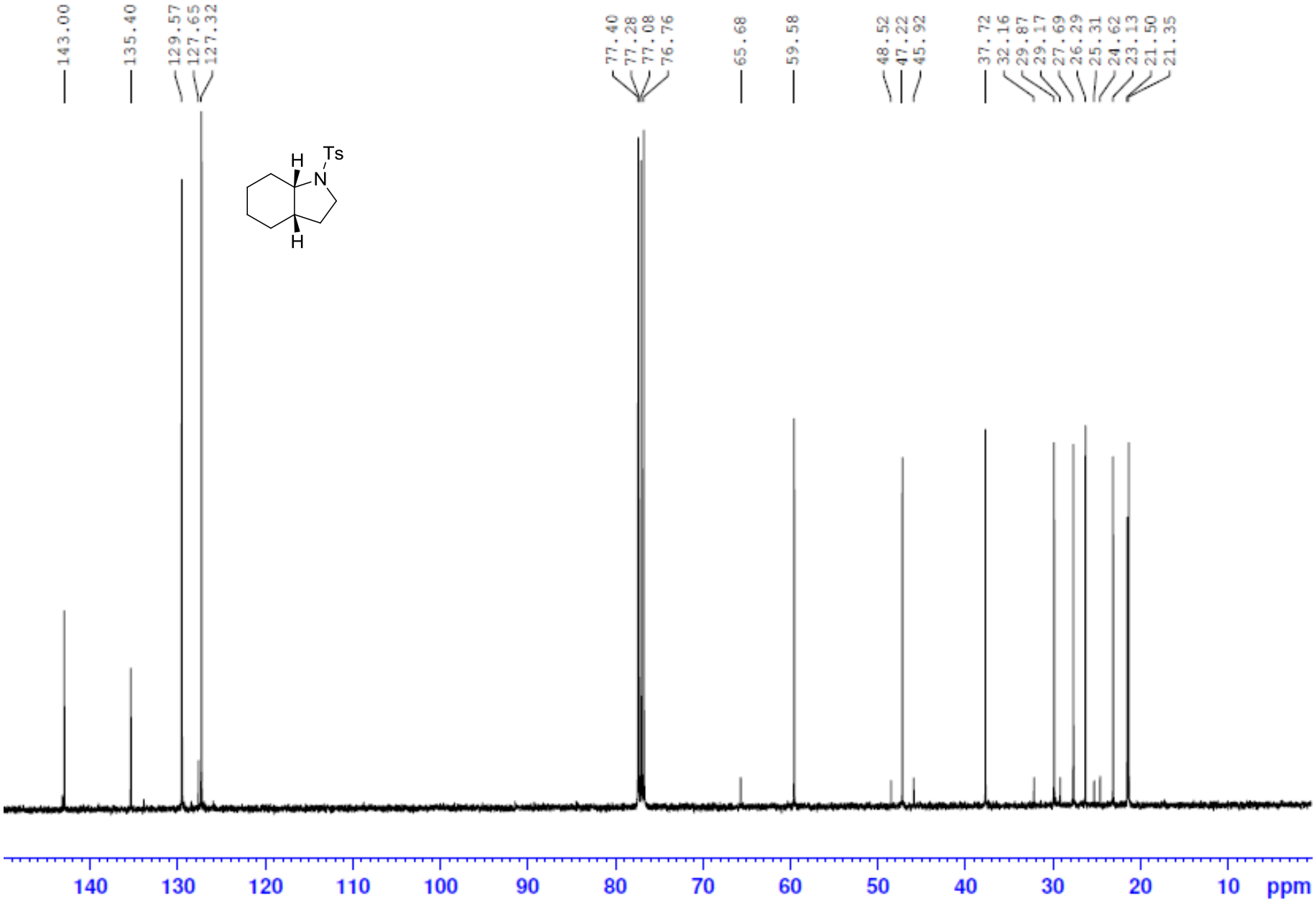
1.46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47.22
45.92
37.72
32.16
29.87
29.17
27.69
26.29
25.31
24.62
23.13
21.50
21.35
H
Ts
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H
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130
120
110
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70
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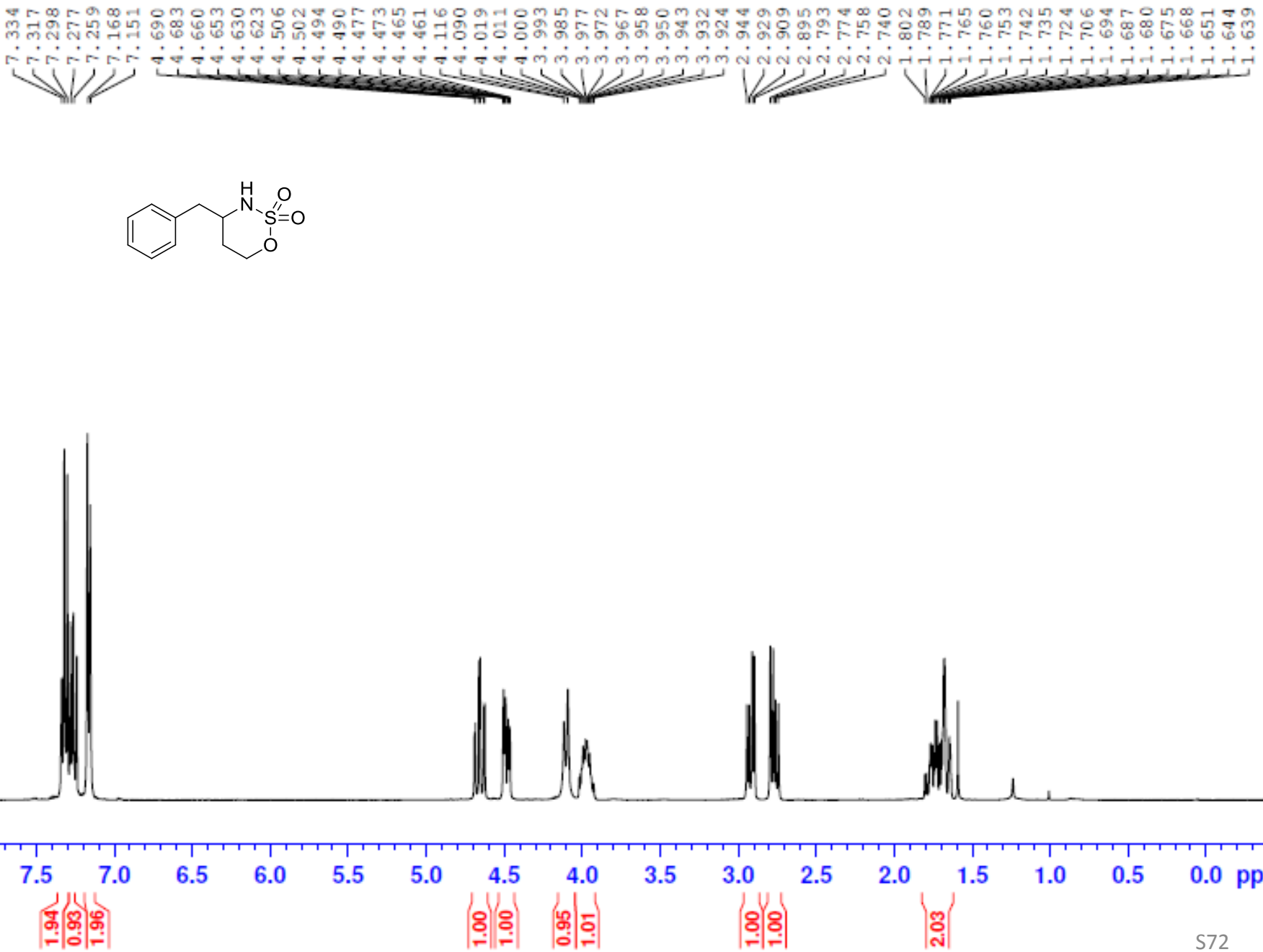
40
30
20
10
ppm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4.506
4.502
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4.490
4.477
4.473
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4.011
4.000
3.993
3.985
3.977
3.972
3.967
3.958
3.950
3.943
3.932
3.924
2.944
2.929
2.909
2.895
2.793
2.774
2.758
2.740
1.802
1.789
1.771
1.765
1.760
1.753
1.742
1.735
1.724
1.706
1.694
1.687
1.680
1.675
1.668
1.651
1.644
1.639
H
N
S
O
O
O
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6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.95
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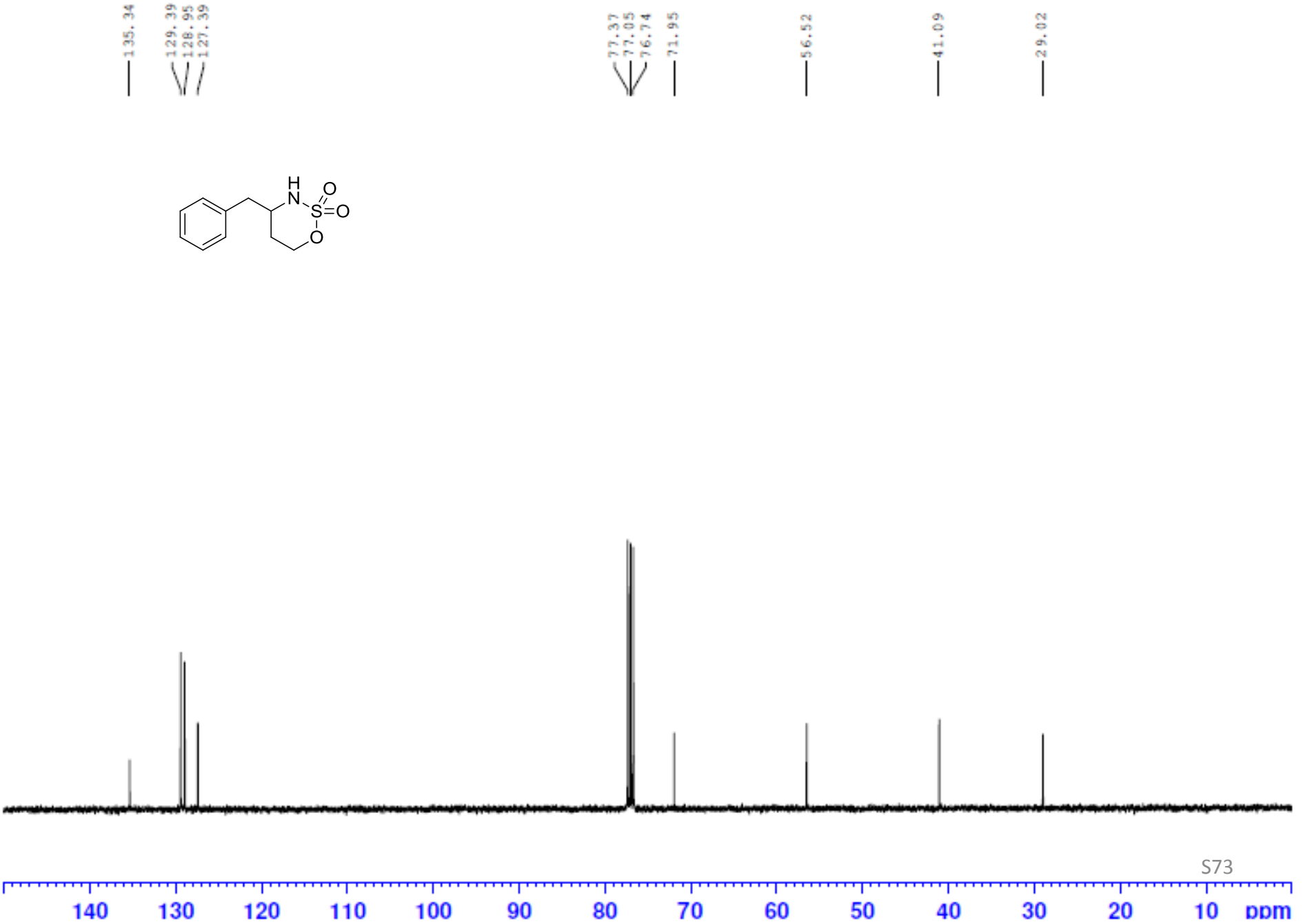
1.00
1.00
2.03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O
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30
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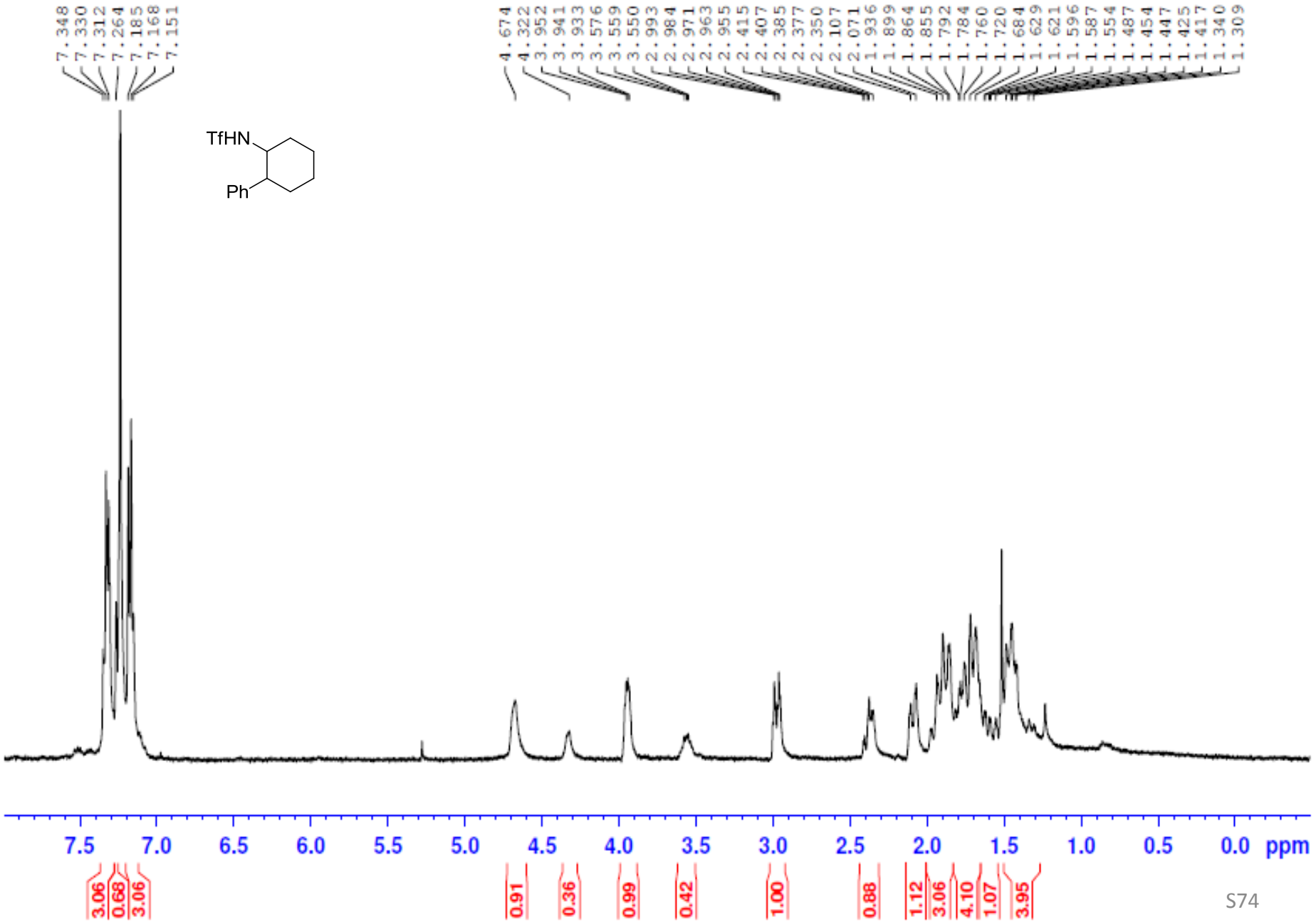
10
ppm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3.559
3.550
2.993
2.984
2.971
2.963
2.955
2.415
2.407
2.385
2.377
2.350
2.107
2.071
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1.899
1.864
1.855
1.792
1.784
1.760
1.720
1.684
1.629
1.621
1.596
1.587
1.554
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1.447
1.425
1.417
1.340
1.309
TfHN
Ph
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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0.0
ppm
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1.00
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1.12
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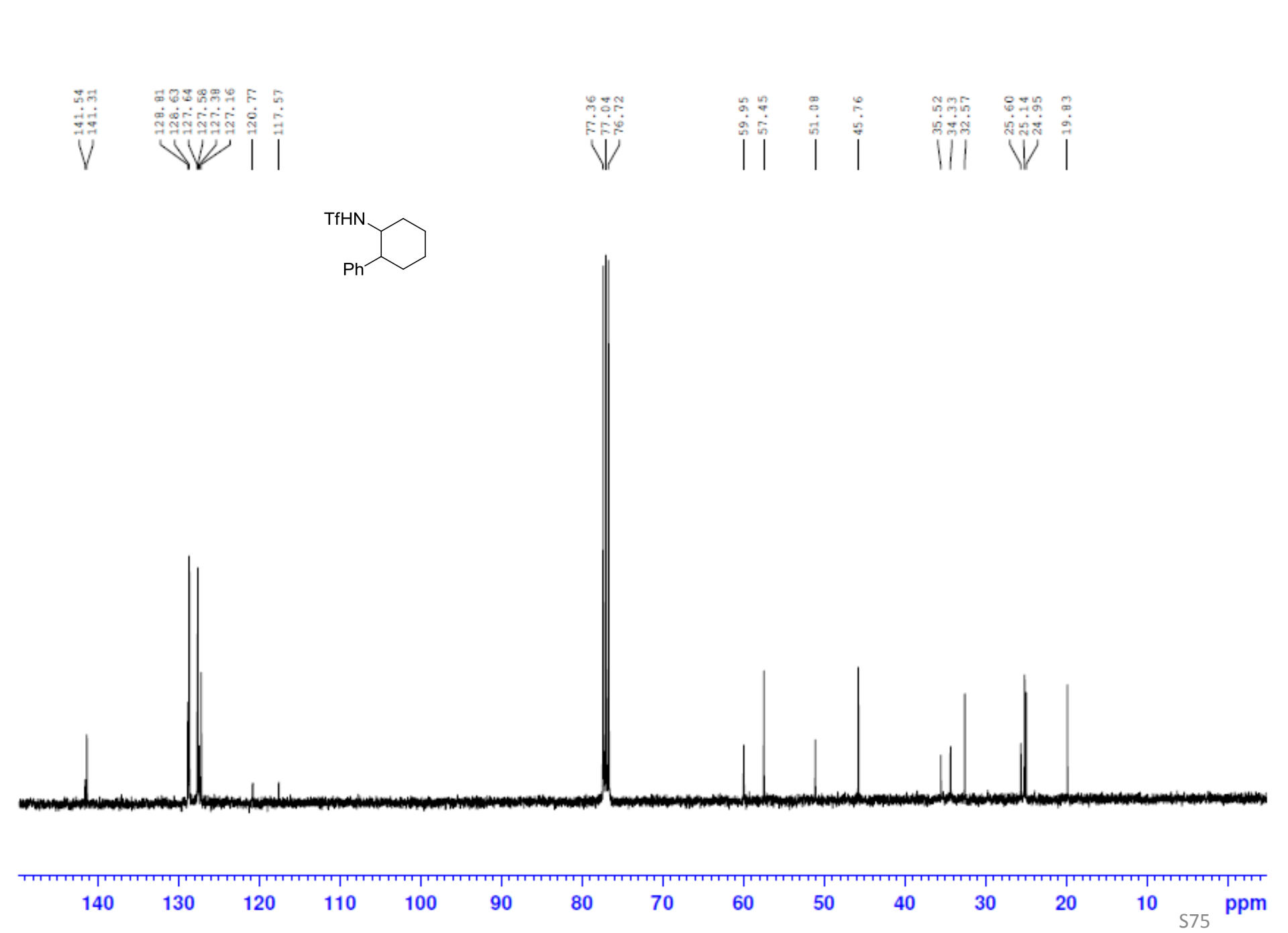
4.10
1.07
3.95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120.77
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77.36
77.04
76.72
59.95
57.45
51.08
45.76
35.52
34.33
32.57
25.60
25.14
24.95
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TfHN
Ph
140
130
120
110
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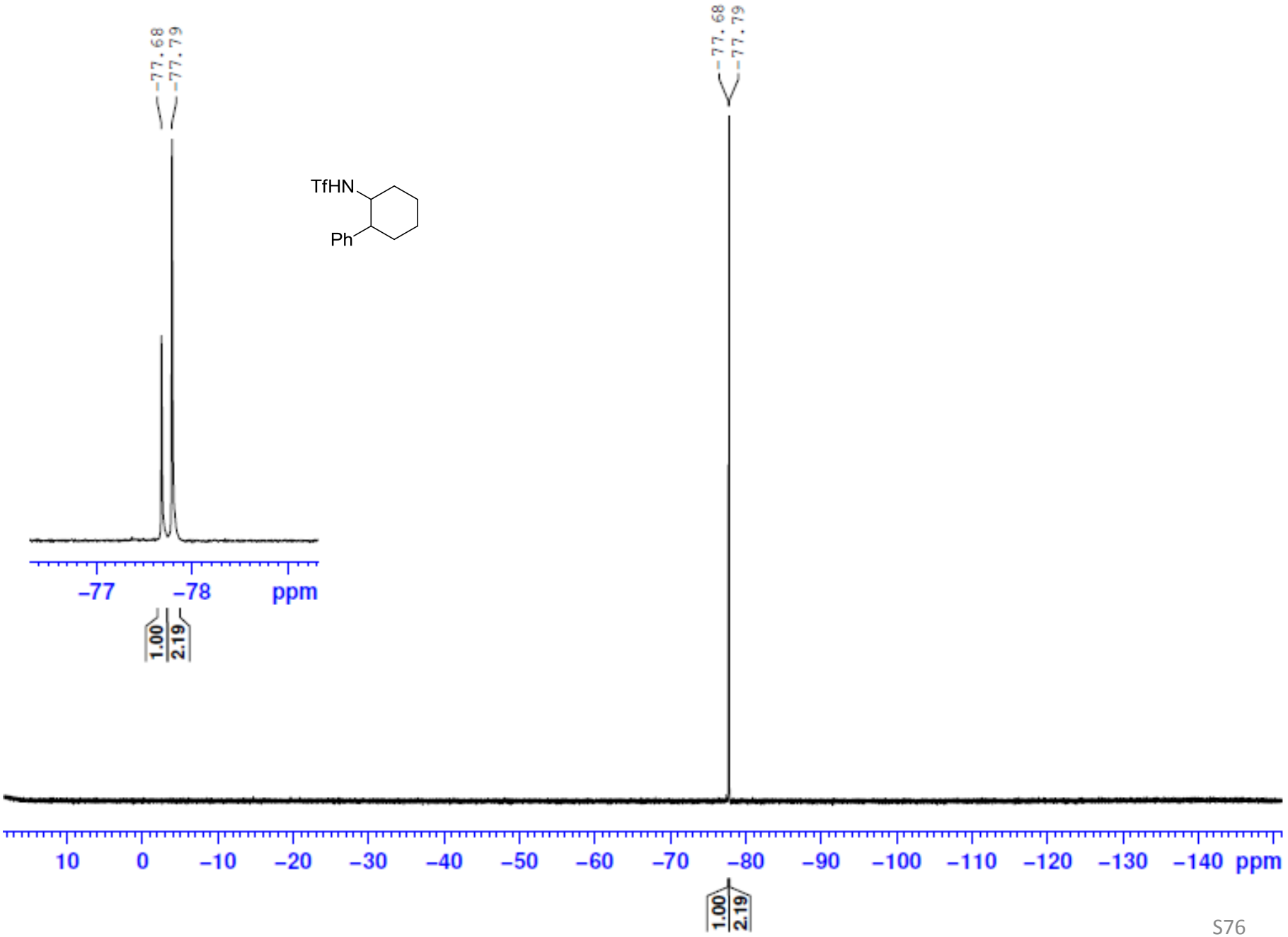
70
60
50
40
30
20
10
ppm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-77.79
TfHN
Ph
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-78
ppm
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2.19
-77.68
-77.79
10
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-10
-20
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-70
-80
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-120
-130
-140
ppm
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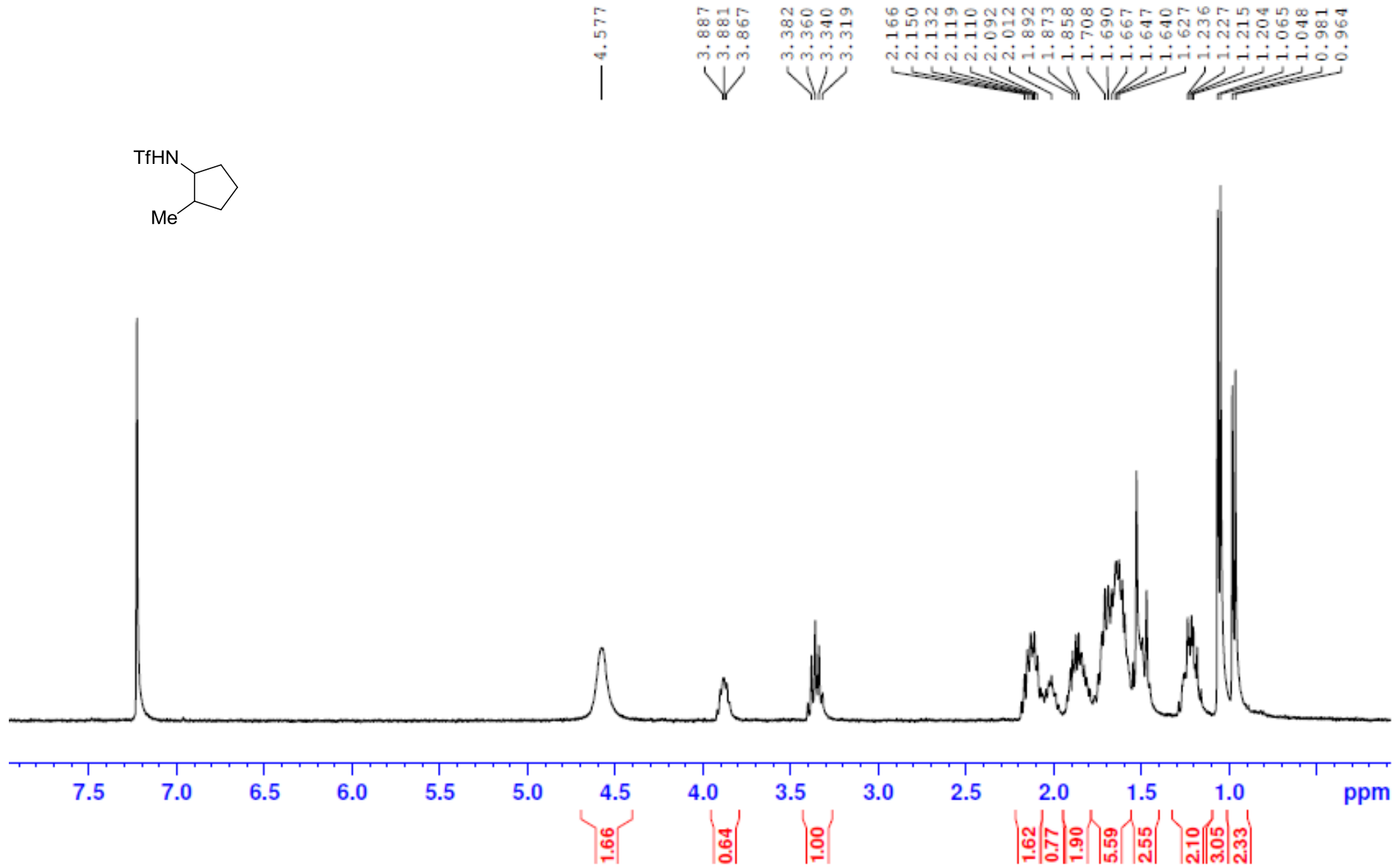
2.19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2.119
2.110
2.092
2.012
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1.873
1.858
1.708
1.690
1.667
1.647
1.640
1.627
1.236
1.227
1.215
1.204
1.065
1.048
0.981
0.964
TfHN
Me
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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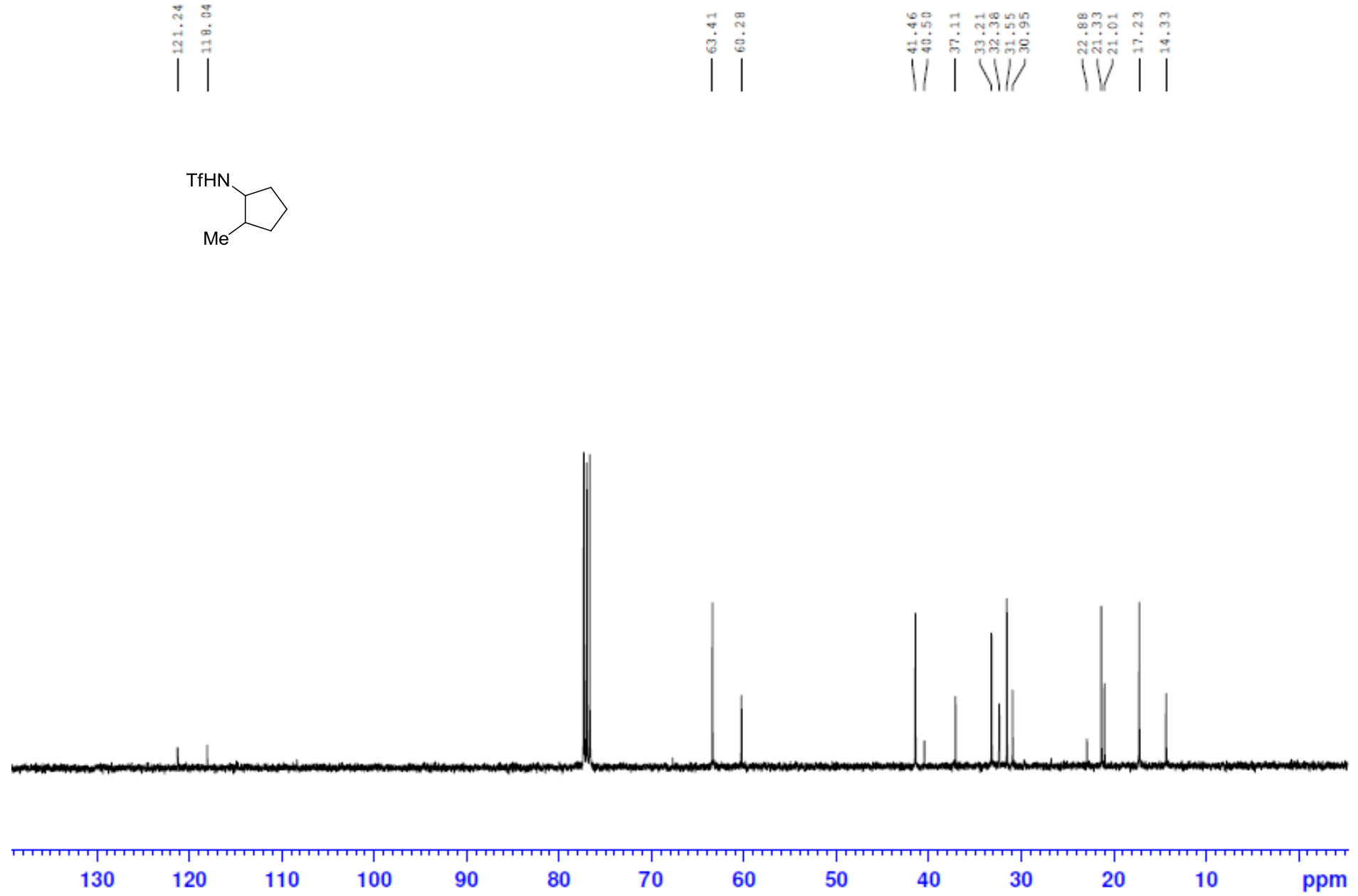
2.33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40.50
37.11
33.21
32.38
31.55
30.95
22.88
21.33
21.01
17.23
14.33
TfHN
Me
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110
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70
60
50
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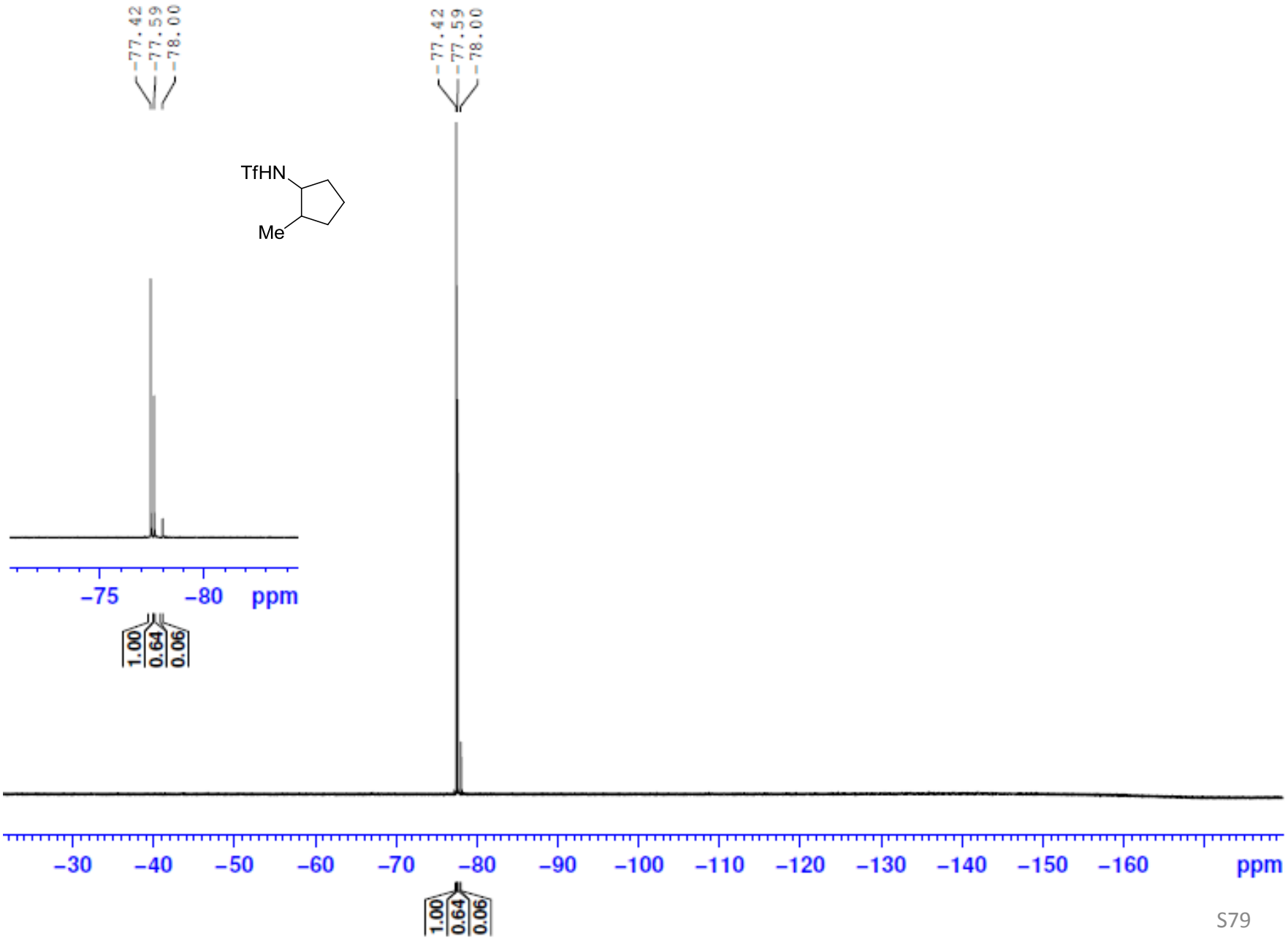
30
20
10
ppm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Me
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-80
ppm
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-77.59
-78.00
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm
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0.64
0.06