Gold(I)-Catalyzed Rearrangement of Aryl Alkynylaziridines to Spiro[isochroman-4,2'-pyrrolines]

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Supporting Information

Preparation and characterization of compounds	S2
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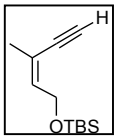
General Information:

Proton (^{1}H NMR) and Carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on the following 300 or 400 MHz instruments. The chemical shifts are given in part per million (ppm) on the delta scale. The solvent peak was used as reference values. For ^{1}H NMR: $CDCl_3$ = 7.26 ppm. For ^{13}C NMR: $CDCl_3$= 77.23 ppm. Data are presented as follow; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), integration and coupling constants (J/Hz). Assignments were determined either on the basis of unambiguous chemical shifts or coupling patterns, COSY, HMQC, HMBC, ROESY experiments to fully interpreted spectra for related compounds. Infrared spectra were recorded in $CHCl_3$ or neat. Wavelengths of maximum absorbance (ν_{max}) are quoted in wave numbers (cm^{-1}). High Resolution Mass spectra were recorded using ElectroSpray Ionization method (ESI). The parent ions $[M+H]^+$, $[M+Na]^+$ or $[M+K]^+$ are quoted. Analytical Thin Layer Chromatography (TLC) was carried out on silica gel 60 F_{254} plates with visualization by ultra violet, potassium permanganate dip. Flash column chromatography was carried out using silica gel 60 (40-63 µm) and the procedure includes the subsequent evaporation of solvents *in vacuo*. Reagents and solvents were purified using standard means. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under an argon atmosphere; THF was distilled from sodium metal/benzophenone and stored under an argon atmosphere. All other chemicals were used as received. All other extractive procedures were performed using non-distilled solvents and all aqueous solution used were saturated.

(*Z*)-1-*tert*-Butyldimethylsilyloxy-3-methylpent-2-en-4-yne (I): *tert*-Butyldimethylsilyl chloride

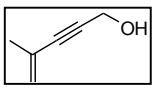


(1.56 g, 11 mmol) was added to a solution of distillated (*Z*)-3-methylpent-2-en-4-yn-1-ol (1 g, 10 mmol) and imidazole (817 mg, 12 mmol) in dry CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 16h. The reaction was quenched by addition of water (10 mL). The aqueous phase was extracted twice with CH_2Cl_2 (10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4. After filtration and evaporation, the crude mixture was filtered through a pad of silica gel with cyclohexane to afford 1.8 g of the title compound (85%, 8.5 mmol) as a colorless oil. R*f* = 0.75 (Cyclohexane/EtOAc 15%); IR (neat) ν_{max} 2954, 2929, 2857, 1471, 1463, 1361, 1253, 1104, 1058, 1004, 938, 832, 776 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6 H), 0.90 (s, 9 H), 1.87 (s, 3 H), 3.13 (s, 1 H), 4.36 (d, 2 H, *J* = 6.3 Hz), 5.85 (t, 1 H, *J* = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1, 18.3, 22.8, 26.0, 62.1, 81.8, 82.0, 117.7, 138.6.

General Procedure 1 for Preparation of Enynyl Alcohol:

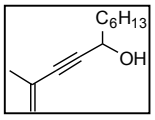
To a solution of *n*-BuLi (1.6 M in hexanes, 10.5 mmol) in THF (20 mL) was added the corresponding enyne (10 mmol) at -78°C under argon. The resulting reaction mixture was stirred at the same temperature for 30 min and was then allowed to warm at -20°C over 5 min. Ketone or aldehyde (11 mmol) was then added at -78°C. The reaction mixture was stirred for 30 min at -78°C, was then allowed to reach room temperature and was stirred further until completion of reaction as monitored by TLC. The mixture was quenched with satd NH_4Cl solution (20 mL) and extracted twice with Et_2O (20 mL). The combined organic extracts were dried over Na_2SO_4. After filtration and evaporation, the crude product was purified by flash chromatography (Cyclohexane/EtOAc) to afford the title compound.

4-Methylpent-4-en-2-yn-1-ol (Ia): Prepared following the *general procedure 1* in 85% yield (1.63 g)

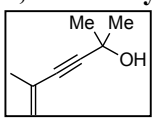


from 1.32 g of 2-methylbut-1-en-3-yne and 696 mg of *p*-formaldehyde. Pale yellow oil; R*f* = 0.23 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3300, 2925, 2210, 1613, 1435, 1289, 1070, 999, 896; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (t, 1 H, *J* = 5.7 Hz, -OH), 1.88 (dd, 3 H, *J* = 1.3 Hz, 1.3 Hz), 4.38 (d, 2 H, *J* = 5.2 Hz), 5.23 (quint, 1 H, *J* = 1.7 Hz,), 5.30 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 51.4, 86.3, 86.8, 122.3, 126.2.

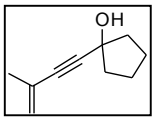
2-Methylundec-1-en-3-yn-5-ol (Ic): Prepared following the *general procedure 1* in 73% yield (1.29 g) from 0.661 g of 2-methylbut-1-en-3-yne and 1.232 g of heptanal. Pale yellow oil; R*f* = 0.21 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3334, 3097, 2954, 2924, 2857, 2223, 1614, 1455, 1434, 1373, 1337, 1335, 1286, 1182, 1041, 1009, 893, 725; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (m, 3 H), 1.40 (m, 10 H), 1.74 (m, 2 H), 1.90 (s, 3 H), 4.50 (t, 1 H, *J* = 6.4 Hz), 5.24 (s, 1 H), 5.30 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 23.4, 25.1, 28.9, 31.7, 37.8, 62.8, 85.9, 89.3, 122.0, 126.3.



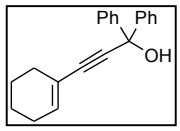
2,5-Dimethylhex-5-en-3-yn-2-ol (Id): Prepared following the *general procedure 1* in 85% yield (1.63 g) from 1.32 g of 2-methylbut-1-en-3-yne and 696 mg of *p*-formaldehyde. Pale yellow oil; R*f* = 0.25 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3305, 2925, 2210, 1611, 1440, 1289, 1073, 1001; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 6 H), 1.85 (s, 3 H), 2.32 (broad, 1 H, -OH), 5.18 (m, 1 H), 5.24 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 31.4, 65.3, 83.1, 92.8, 121.7, 126.3.



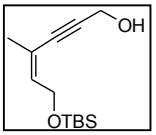
1-(3-Methylbut-3-en-1-ynyl)cyclopentanol (Ie): Prepared following the *general procedure 1* in 56% yield (586 mg) from 462 mg of 2-methylbut-1-en-3-yne and 647 mg of cyclopentanone. Pale yellow oil; R*f* = 0.34 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3340, 2961, 2214, 1614, 1205, 994, 892; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (m, 4 H), 1.87 (m, 4 H), 1.95 (m, 4 H), 5.20 (quint, 1 H, *J* = 1.7 Hz), 5.26 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 23.6, 42.5, 74.8, 84.3, 91.9, 121.7, 126.5.



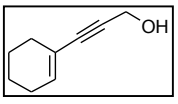
3-Cyclohexenyl-1,1-diphenylprop-2-yn-1-ol (If): Prepared following the *general procedure 1* in 83% yield (2.4 g) from 1.05 g of 1-ethynylcyclohexene and 2 g of benzophenone. Pale yellow oil; R*f* = 0.54 (Cyclohexane/EtOAc 25%); IR (neat) ν_{max} 3421, 3061, 3025, 2929, 2270, 2215, 1668, 1488, 1448, 1362, 1289, 1161, 1029, 985, 915, 830, 748; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61-1.70 (m, 4 H), 2.15 (m, 2 H), 2.21 (m, 2 H), 2.79 (broad, 1 H, -OH), 6.23 (qt, 1 H, *J* = 1.8 Hz), 7.24-7.37 (m, 6 H), 7.61 (d, 4 H, *J* = 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22.2, 25.6, 29.1, 74.7, 89.0, 89.1, 120.0, 126.0, 127.7, 128.5, 135.8, 145.3.



(*Z*)-6-(*tert*-Butyldimethylsilyloxy)-4-methylhex-4-en-2-yn-1-ol (Ig): Prepared following the *general procedure 1* in 63% yield (1.25 g) from 1.75 g of (*Z*)-*tert*-butyldimethyl(3-methylpent-2-en-4-ynyloxy)silane and 262 mg of *p*-formaldehyde. Pale yellow oil; R*f* = 0.44 (Cyclohexane/EtOAc 25%); IR (neat) ν_{max} 3343, 2953, 2856, 1471, 1462, 1379, 1360, 1253, 1198, 1110, 1065, 1034, 1002, 938, 832, 812, 774; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 6 H), 0.90 (s, 9 H), 1.78 (broad, 1 H, -OH), 1.85 (s, 3 H), 4.34 (dd, 2 H, *J* = 6.4, 1.2 Hz), 4.41 (d, 2 H, *J* = 4.7 Hz), 5.79 (dt, 1 H, *J* = 6.4, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1, 18.3, 23.0, 26.0, 51.5, 62.1, 84.0, 91.9, 118.2, 137.2.



3-(Cyclohex-1-enyl)prop-2-yn-1-ol (Ih): Prepared following the *general procedure 1* in 72% yield (2.03 g) from 2.1 g of 1-ethynylcyclohexene and 732 mg of *p*-formaldehyde. Pale yellow oil; R*f* = 0.20 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3317, 3026, 2926, 2857, 2834, 2218, 1631, 1434, 1346, 1270, 1206, 1135, 1017, 975, 918, 844, 799; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (m, 4 H), 1.74 (s, 1 H), 2.09 (m, 4 H), 4.37 (s, 2 H), 6.10 (quint, 1 H, *J* = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 22.2, 25.5, 29.0, 51.5, 84.5, 87.4, 120.0, 135.4.

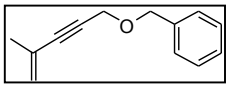


General Procedure 2 for Preparation of Enynyl Benzyl Ethers

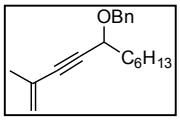
To a solution of the propargylic alcohol (8 mmol) in THF (20 mL) were added *N*-tetrabutylammonium iodide (0.8 mmol) and sodium hydride by portions (8.8 mmol) at 0°C. The solution was stirred under argon for 20 min. Benzyl (or 2-Me-naphtyl) bromide (8.8 mmol) was then added at 0°C. The mixture was then warmed to room temperature and was stirred further until completion of the reaction as monitored by TLC. The mixture was quenched with satd NH_4Cl (10 mL). THF was removed under

vacuo and the aqueous layer was extracted twice with Et_2O (20 mL). The combined organic extracts were dried over Na_2SO_4. After filtration and evaporation, the crude product was purified by flash chromatography (Pentane/Et_2O) to afford the title compound.

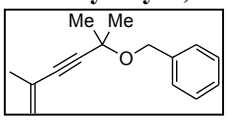
5-Benzyloxy-2-methylpent-1-en-3-yne (IIa): Prepared following the *general procedure 2* in 94% yield (1.65 g) from 900 mg of **Ia**. Colorless liquid; R*f* = 0.57 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2962, 1724, 1454, 1259, 1070, 1010, 795, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (dd, 3 H, J = 1.3 Hz, 1.3 Hz), 4.29 (s, 2 H), 4.61 (s, 2 H), 5.26 (s, 1 H), 5.33 (s, 1 H), 7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 57.8, 71.6, 76.6, 122.0, 127.9, 128.1, 128.4, 128.8, 129.0, 137.5.



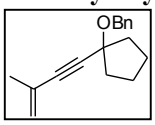
5-Benzyloxy-2-methylundec-1-en-3-yne (IIc): Prepared following the *general procedure 2* in 99% yield (1.93 g) from 1.29 g of **Ic**. Colorless liquid; R*f* = 0.63 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2923, 2856, 1454, 1065, 895, 733, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3 H, J = 6.6 Hz), 1.30 (m, 6 H), 1.47 (m, 2 H), 1.77 (m, 2 H), 1.93 (dd, 3 H, J = 1.3 Hz, 1.3 Hz), 4.21 (t, 1 H, J = 6.5 Hz), 4.33 (d, 1 H, J_{AB} = 11.6 Hz), 4.66 (d, 1 H, J_{AB} = 11.6 Hz), 5.23 (quint, 1 H, J = 1.4 Hz), 5.32 (s, 1 H), 7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 23.6, 25.4, 29.0, 31.8, 35.8, 69.1, 70.5, 87.1, 87.5, 121.9, 126.5, 127.6, 128.0, 128.3, 138.2.



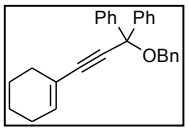
5-Benzyloxy-2,2-dimethylpent-1-en-3-yne (IId): Prepared following the *general procedure 2* in 88% yield (1.52 g) from 1 g of **Id**. Colorless liquid; R*f* = 0.55 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2984, 2924, 2851, 1590, 1453, 1377, 1292, 1150, 832, 732, 695; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 6 H), 1.89 (dd, 3 H, J = 1.3 Hz, 1.3 Hz), 4.63 (s, 2 H), 5.22 (m, 1 H), 5.27 (m, 1 H), 7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.6, 29.0, 66.6, 71.0, 72.2, 85.7, 90.6, 121.8, 127.4, 127.8, 128.4, 139.3.



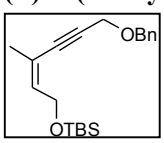
1-Benzyloxy-1-(3-methylbut-3-en-1-ynyl)-cyclopentane (IIe): Prepared following the *general procedure 2* in 91% yield (830 mg) from 571 mg of **Ie**. Colorless liquid; R*f* = 0.64 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2955, 2870, 1613, 1495, 1453, 1372, 1291, 1201, 1084, 1051, 1027, 894, 731, 694; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71-1.85 (m, 4 H), 1.90 (s, 3 H), 1.97 (m, 2 H), 2.12 (m, 2 H), 4.60 (s, 2 H), 5.22 (quint, 1 H, J = 1.7 Hz), 5.28 (m, 1 H), 7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 23.6, 39.7, 67.0, 80.9, 86.3, 90.0, 121.5, 126.8, 127.3, 127.7, 129.3, 139.2.



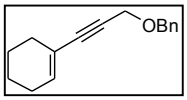
[1-(3-Benzyloxy-3,3-diphenyl)prop-1-ynyl]cyclohex-1-ene (IIf): Prepared following the *general procedure 2* in a quantitative yield (780 mg) from 560 mg of **If**. Yellow oil; R*f* = 0.68 (Cyclohexane/EtOAc 25%); IR (neat) ν_{max} 3060, 3028, 2926, 2857, 2212, 1677, 1567, 1489, 1447, 1377, 1270, 1166, 1084, 1050, 1001, 915, 841, 746; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48-1.75 (m, 4 H), 2.17 (m, 2 H), 2.27 (m, 2 H), 4.62 (s, 2 H), 6.27 (quint, 1 H, J = 2.0 Hz), 7.25-7.47 (m, 11 H), 7.61 (d, 4 H, J = 4.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.3, 25.7, 27.0, 29.3, 66.7, 80.8, 86.1, 91.7, 120.2, 126.7, 127.3, 127.5, 127.6, 128.2, 135.6, 139.0, 144.1.



(*Z*)-6-(Benzyloxy)-1-(*tert*-butyl)dimethylsilyloxy-3-methylhex-2-en-4-yne (IIg): Prepared following the *general procedure 2* in 99% yield (1.5 mg) from 1.1 g of **Ig**. Colorless oil; R*f* = 0.70 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2952, 2928, 2884, 2855, 1471, 1452, 1352, 1253, 1084, 1066, 1028, 1004, 938, 833, 775; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.91 (s, 9 H), 1.89 (s, 3 H), 4.34 (s, 2 H), 4.39 (d, 2 H, J = 6.5 Hz), 4.63 (s, 2 H), 5.82 (t, 1 H, J = 6.4 Hz), 7.30-7.37 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.0, 18.4, 23.0, 26.0, 57.8, 62.3, 71.5, 84.9, 89.8, 118.2, 127.9, 128.1, 128.4, 137.3, 137.5.

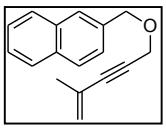


[1-(3-Benzyloxy)prop-1-ynyl]cyclohex-1-ene (IIh): Prepared following the *general procedure 2* in

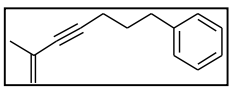


77% yield (1.69 g) from 1.32 g of **Ih**. Colorless liquid; R*f* = 0.53 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2927, 2853, 1453, 1348, 1205, 1070, 918, 734, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (m, 4 H), 2.12 (m, 4 H), 4.30 (s, 2 H), 4.62 (s, 2 H), 6.15 (quint, 1 H, J = 2.0 Hz), 7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.3, 25.6, 29.2, 58.0, 71.4, 82.5, 88.6, 120.5, 127.8, 128.1, 128.4, 135.4, 138.0.

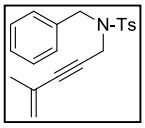
5-(Naphth-2-yl)methyloxy-2-methylpent-1-en-3-yne (IIl): Prepared following the *general procedure 2* in 99% yield (1060 mg) from 439 mg of **Ia**. Colorless liquid; R*f* = 0.56 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3040, 2929, 2856, 1083, 894, 814, 749, 474; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (dd, 3 H, J = 1.3 Hz, 1.3 Hz), 4.35 (s, 2 H), 4.80 (s, 2 H), 5.28 (quint, 1 H, J = 1.3 Hz), 5.36 (s, 1 H), 7.49 (d, 1 H, J_{ab} = 9.5 Hz), 7.50 (m, 2 H), 7.84 (s, 1 H), 7.84 (m, 2 H), 7.85 (d, 1 H, J_{ab} = 9.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 34.1, 57.9, 77.7, 84.1, 87.8, 122.4, 126.0, 126.1, 127.0, 127.3, 127.9, 128.4, 128.8, 133.1, 133.3, 135.0.



7-Phenyl-2-methylhept-1-en-3-yne (IIj): To a solution of commercially available 5-phenyl-1-pentyne (800 mg, 5.5 mmol) in dry THF (5 mL) were added copper(I) iodide (50 mg, 0.26 mmol) and $Pd(PPh_3)_2Cl_2$ (91 mg, 0.13 mmol) while stirring under argon. Triethylamine (1.1 g, 10.8 mmol) and 2-bromopropene (1050 mg, 8.6 mmol) were then added. The solution was stirred at room temperature under argon for 24 h. Volatile compounds were then removed in vacuo, and the residue was dissolved in Et_2O (15 mL) and washed with 1N HCl (20 mL), satd $NaHCO_3$ (20 mL), water (2 x 20 mL) and brine (20 mL). The organic layer was then dried over Na_2SO_4. After filtration and evaporation, the crude product was purified on a pad of silica gel (cyclohexane/EtOAc) to afford **IIj** as an orange oil (4.88 mmol, 88%); IR (neat) ν_{max} 2940, 1604, 1495, 1453, 890, 742, 697; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.20 (m, 3H), 5.23 (s, 1H), 5.16 (s, 1H), 2.74 (t, 2H, J = 7.5 Hz), 2.32 (t, 2H, J = 7.1 Hz), 1.86 (m, 2H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 127.3, 125.9, 120.5, 88.9, 82.4, 34.8, 30.3, 23.9, 18.7.



***N*-Benzyl-*N*-tosyl-4-methylpent-4-en-2-yn-1-amine (IIk):** To a solution of *N*-benzyl-*N*-tosylprop-2-



yn-1-amine[1] (913 mg, 3.05 mmol) in dry and degassed THF (10 mL) were added successfully 2-bromopropene (553 mg, 410 µL), $Pd(PPh_3)_2Cl_2$ (64 mg, 3 mol%) and CuI (35 mg, 6 mol%). The solution was stirred under argon for 5 minutes. Dry diisopropylamine (1.75 mL) was then added, the resulted dark solution was heated at 50°C for 2h30. The reaction was monitoring by TLC until complete consumption of the starting alkyne. Volatile materials were then removed under reduced pressure. The resulting dark solid was dissolved in EtOAc (20 mL) and this organic layer was washed with satd NH_4Cl (2 x 30 mL), water (2 x 20 mL), brine (20 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (Cyclohexane/EtOAc 5%) to afford (**IIk**) as an orange solid in 76% yield (783 mg, 2.31 mmol). IR (neat) ν_{max} 3010-2870, 1590, 1385, 1325, 1164, 1120, 1091, 895, 815, 769, 730, 699, 654, 571; R*f* = 0.52 (Cyclohexane/EtOAc 30%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (dd, 3H, J = 1.3 Hz, 1.3 Hz), 2.41 (s, 3H), 4.03 (s, 2H), 4.32 (s, 2H), 4.95 (m, 1H), 5.10 (m, 1H, J = 1.6 Hz), 7.30 (d, 2H, J_{AB} = 8.3 Hz), 7.32 (m, 5H), 7.78 (d, 2H, J_{AB} = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 23.5, 27.4, 36.8, 50.4, 81.0, 87.6, 122.5, 128.3, 128.5, 129.1, 129.2, 129.9, 135.5, 136.4, 143.9.

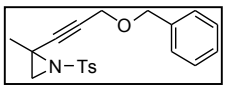
General Procedure 3 for Aziridination of Enyne[2]

To a solution of enyne ether (2 mmol) in acetonitrile (10 mL) were added $[Cu(MeCN)_4]ClO_4$ (0.1 mmol) and 4Å molecular sieves (500 mg). The nitrogen transfer reagent (TsN=IPh or NsN=IPh, 2.2

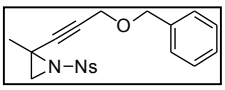
[1] *J. Org. Chem*. **2008**, *73*, 1586-1589
[2] Södergren, M. J.; Alonso, D. A.; Bedekar, A. V.; Andersson, P. G. *Tetrahedron Lett.* **1997**, *38*, 6897–6900.

mmol)[3] was added by portions under argon over 3 h, the reaction was then monitored by thin-layer chromatography (SiO_2) and stopped before total conversion of the starting material (circa 2 hours for TsN=IPh, 5 hours for NsN=IPh) to avoid degradation. The solution was filtrated, concentrated in vacuo and the crude residue was purified by flash chromatography (Cyclohexane/EtOAc) to afford the title compound. Starting material could also be recovered.

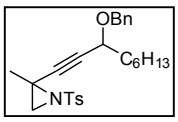
2-(3-(Benzyloxy)prop-1-ynyl)-2-methyl-1-tosylaziridine (1a): Prepared following the *general procedure 3* in 48% yield (455 mg) from 500 mg of **IIa**. Pale yellow oil; R*f* = 0.24 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3040-2860, 2240, 1598, 1450, 1325, 1159, 1087, 1068, 868, 694, 571; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3 H), 2.43 (s, 3 H), 2.45 (s, 1 H), 2.92 (s, 1 H), 4.20 (s, 2 H), 4.63 (s, 2 H), 7.32 (m, 7 H), 7.86 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 23.7, 38.0, 41.8, 57.2, 71.6, 80.8, 83.2, 127.8, 128.3, 128.4, 129.6, 131.3, 136.7, 137.4, 144.3; HR-MS 378.109 ($C_{20}H_{21}NO_3S$+Na calcd 378.113).



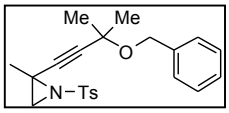
2-(3-(Benzyloxy)prop-1-ynyl)-2-methyl-1-(4-nitrophenylsulfonyl)aziridine (1b): Prepared following the *general procedure 3* in 36 % yield (260 mg) from 366 mg of **IIa**. Pale yellow oil; R*f* = 0.22 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2925, 2851, 1530, 1346, 1165, 1087, 1010, 854, 791, 740, 686; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (s, 3 H), 2.53 (s, 1 H), 3.00 (s, 1 H), 4.20 (s, 2 H), 4.62 (s, 2 H), 7.33 (m, 5 H), 8.17 (d, 2 H, *J* = 8.6 Hz), 8.35 (d, 2 H, *J* = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.8, 30.9, 42.6, 57.1, 71.7, 81.6, 82.4, 124.2, 128.0, 128.3, 128.5, 129.2, 137.2, 145.1, 150.5; HR-MS 409.080 ($C_{19}H_{18}N_2O_5S$+Na calcd 409.083).



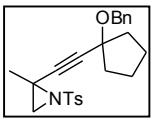
2-(3-(Benzyloxy)non-1-ynyl)-2-methyl-1-tosylaziridine (1c): Prepared following the *general procedure 3* in 48 % yield (311 mg, *dr* 1:1) from 400 mg of **IIc**. Mixture of diastereoisomers: pale yellow oil; R*f* = 0.34 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2959, 2927, 2855, 1465, 1328, 1160, 1088, 814, 732, 693, 549; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3 H, *J* = 6.4 Hz), 1.27 (m, 6 H), 1.43 (m, 2 H), 1.63 (s, 3 H), 1.73 (m, 2 H), 2.43 (s, 3 H), 2.44 (s, 1 H), 2.93 (s, 1 H), 4.10 (t, 1 H, *J* = 6.6 Hz), 4.53 (d, 1 H, J_{ab} = 11.6 Hz), 4.79 (dd, 1 H, J_{ab} = 11.6 Hz, 6.4 Hz), 7.31 (d, 2 H, *J* = 11.6 Hz), 7.33 (m, 5 H), 7.87 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.6, 22.6, 24.0, 25.2, 29.0, 31.7, 35.5, 38.1, 41.8, 68.6, 70.6, 82.4, 84.3, 127.6, 127.8, 128.1, 128.4, 129.6, 136.8, 138.1, 144.3; HR-MS 462.204 ($C_{26}H_{33}NO_3S$+Na calcd 462.207).



2-(3-(Benzyloxy)-3-methylbut-1-ynyl)-2-methyl-1-tosylaziridine (1d): Prepared following the *general procedure 3* in 44% yield (552 mg) from 647 mg of **IId**. Pale yellow oil; R*f* = 0.27 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2983, 2930, 2861, 1724, 1453, 1328, 1158, 1087, 1059, 814, 664, 550; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 6 H), 1.61 (s, 3 H), 2.42 (s, 3 H), 2.43 (s, 1 H), 2.91 (s, 1 H), 4.64 (s, 2 H), 7.34 (m, 7 H), 7.86 (d, 2 H, *J* = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 24.0, 28.7, 38.1, 41.9, 66.7, 70.6, 81.2, 87.0, 127.3, 127.8, 127.9, 128.3, 129.6, 137.0, 139.2, 144.3; HR-MS 390.176 ($C_{22}H_{25}NO_3S$+Li calcd 390.171).

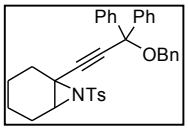


2-((1-(Benzyloxy)cyclopentyl)ethynyl)-2-methyl-1-tosylaziridine (1e): Prepared following the *general procedure 3* in 45 % yield (311 mg) from 400 mg of **IIe**. Pale yellow oil; R*f* = 0.37 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2976, 2947, 2848, 1595, 1446, 1381, 1324, 1085, 1061, 1022, 923, 902, 817, 732, 693; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3 H), 1.77 (m, 4 H), 2.03 (m, 4 H), 2.42 (s, 1 H), 2.42 (s, 3 H), 2.93 (s, 1 H), 4.61 (s, 2 H), 7.31 (m, 5 H), 7.31 (d, 2 H, *J* = 8.3 Hz), 7.86 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 23.4, 24.1, 36.2, 39.4, 41.9, 67.2, 80.6, 81.6, 86.6, 127.3, 127.8, 126.2, 129.6, 136.9, 139.1, 144.2; HR-MS 432.163 ($C_{24}H_{27}NO_3S$+Na, calcd 432.160).

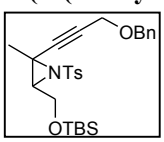


[3] Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361–362.

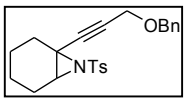
1-(3-(Benzyloxy)-3,3-diphenylprop-1-ynyl)-7-tosyl-7-azabicyclo[4.1.0]heptane (1f): Prepared following the *general procedure 3* in 31 % yield (325 mg) from 730 mg of **IIf**. White powder; mp = 48°C; R*f* = 0.42 (Cyclohexane/EtOAc 25%). IR (neat) ν_{max} 3060, 3030, 2938, 2863, 1596, 1490, 1448, 1383, 1325, 1263, 1170, 1119, 1089, 1052, 1026, 1001, 967, 917; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21-1.47 (m, 4 H), 1.62-1.76 (m, 1 H), 1.90-1.99 (m, 2 H), 2.22-2.31 (m, 1 H), 2.43 (s, 3 H), 3.50 (d, 1 H, *J* = 5.2 Hz), 4.67 (s, 2 H), 7.24-7.49 (m, 13 H), 7.74 (d, 4 H, *J* = 8.2 Hz), 7.87 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 19.2, 21.6, 22.5, 27.0, 31.5, 40.5, 46.7, 66.9, 80.5, 85.7, 86.2, 126.8, 127.3, 127.5, 127.6, 127.7, 128.2, 129.5, 137.3, 139,0, 143.4, 143.9; HR-MS 570.206 ($C_{35}H_{33}NO_3S$+Na, calcd 570.207).



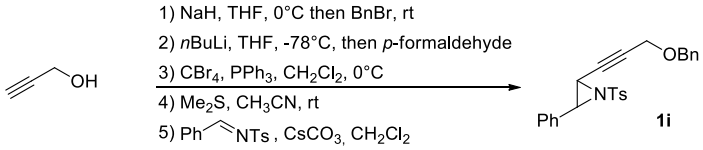
2-(3-(Benzyloxy)prop-1-ynyl)-3-((*tert*-butyldimethylsilyloxy)methyl)-2-methyl-1-tosylaziridine (1g): Prepared following the *general procedure 3*, in 17 % yield (250 mg) from 700 mg of **IIg**. Colorless oil. R*f* = 0.5 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 2952, 2928, 2883, 2856, 1680, 1455, 1357, 1328, 1303, 1253, 1224, 1159, 1087, 1026, 1006, 966, 897, 833, 777; ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.04 (s, 3 H), -0.01 (s, 3 H), 0.83 (s, 9 H), 1.99 (s, 3 H), 2.42 (s, 3 H), 3.17 (dd, 1 H, *J* = 6.3, 5.3 Hz), 3.59 (dd, 1 H, *J* = 11.2, 6.5 Hz), 3.81 (dd, 1 H, *J* = 11.2, 5.3 Hz), 4.17 (s, 2 H), 4.55 (s, 2 H), 7.30-7.37 (m, 7 H), 7.86 (d, 2 H, *J* = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.61, 18.1, 20.3, 21.5, 43.8, 52.4, 57.2, 62.3, 71.6, 79.4, 83.5, 127.5, 127.9, 128.0, 128.4, 129.4, 137.1, 137.5, 144.0; HR-MS 522.210 ($C_{27}H_{37}NO_4SSi$+Na calcd 522.209).



1-(3-(Benzyloxy)prop-1-ynyl)-7-tosyl-7-azabicyclo[4.1.0]heptane (1h): Prepared following the *general procedure 3* in 57 % yield (498 mg) from 500 mg of **IIh**. Pale yellow oil; R*f* = 0.34 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2937, 2855, 1325, 1154, 1089, 958, 916, 810, 696, 672, 527; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (m, 4 H), 1.64 (m, 1 H), 1.90 (m, 2 H), 2.16 (m, 1 H), 2.42 (s, 3 H), 3.36 (dd, 1 H, *J* = 5.2 Hz, 1.1 Hz), 4.22 (s, 2 H); 4.64 (s, 2 H), 7.33 (m, 7 H), 4.65 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 19.2, 21.6, 22.6, 31.3, 40.4, 46.8, 57.3, 71.5, 81.7, 83.4, 127.7, 127.8, 128.0, 128.4, 129.5, 137.2, 137.5, 143.9; HR-MS 418.141 ($C_{23}H_{25}NO_3S$+Na calcd 418.145).



The compound **1i** was prepared in 5 steps from propargylic alcohol:



1-Benzyloxyprop-2-yne[4] (Ii): To a solution of propargylic alcohol (5.6 g, 100 mmol) in THF (125 mL) were added N-tetrabutylammonium iodide (5 mmol) and sodium hydride by portions (55% array, 4.8 g, 110 mmol) at 0°C. The solution was stirred under argon for 20 min. Benzyl bromide (13.1 mL, 110 mmol) was then added at 0°C. The mixture was then warmed to room temperature and was stirred further until completion of the reaction as monitored by TLC. The mixture was quenched with saturated NH_4Cl aqueous solution (50 mL). THF was removed under vacuo and the aqueous layer was extracted twice with Et_2O (50 mL). The combined organic extracts were dried over Na_2SO_4. After filtration and evaporation, the crude product was purified by flash chromatography (Pentane/Et_2O 97:3) to afford the title compound in 86% yield (12.63 g) as a colorless liquid.

4-(Benzyloxy)but-2-yn-1-ol (IIi): To a solution of **Ii** (2631mg, 18 mmol) in THF (25 mL) was added *n*-BuLi (1.6 M in hexanes, 21.6 mmol) at -78°C under argon. The solution was stirred at -78°C for 10 min, then *p*-formaldehyde (95%, 681mg, 21.6 mmol) was added solid. The reaction mixture was then warmed to room temperature and stirred for 2 h before quenching with satd NH_4Cl (10 mL). THF was removed in vacuo and the aqueous layer was extracted with EtOAc (2x 10 mL). The organic layer was then washed with clear water (2x 10 mL), brine (2x 10 mL) then dried over Na_2SO_4. After filtration

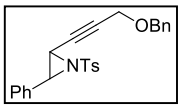
[4] Li, H.-J.; Guillot, R.; Gandon, R. *J. Org. Chem.* **2010**, *75*, 8435–8449.

and evaporation, the crude product was purified on a short silica column (Cyclohexane/EtOAc 7:3) to afford the title compound in 82% yield (2.6 g) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (t, 1 H, J = 1.8 Hz), 4.22 (t, 2 H, J = 1.8 Hz), 4.32 (dt, 2 H, J = 6.0 Hz, 1.8 Hz), 4.60 (s, 2 H), 7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.2, 57.4, 71.8, 81.8, 84.8, 127.9, 128.1, 128.5, 137.3.

1-(Benzyloxy)-4-bromo-but-2-yne (IIIi): To a solution of **IIi** (1.4 g, 7.94 mmol) in DCM (25 mL) were added triphenylphosphine (2.5 g, 9.53 mmol) and carbon tetrabromide (3.16 g, 9.53 mmol) at 0°C. Solution was stirred for 30 min at 0°C, followed by 2 h at room temperature. DCM was then removed in vacuo, and the crude mixture was directly purified by flash chromatography (Pentane/Et_2O 95:5) to afford the title compound in 88% yield (1.66 g) as a colorless oil. Rf = 0.11 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.97 (d, 2 H, J = 2.0 Hz), 4.23 (t, 2 H, J = 2.0 Hz), 4.60 (s, 2 H), 7.33 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.4, 71.8, 81.5, 83.1, 128.0, 128.2, 128.5, 137.2.

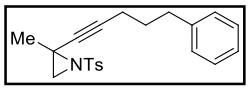
(4-(Benzyloxy)but-2-ynyl)dimethylsulfonium bromide (IVi): To a solution of **IIIi** (1.6 g, 6.72 mmol) in acetonitrile (3 mL) was added dimethyl sulfide (417 mg, 6.72 mmol). Solution was stirred for 20 h at room temperature. Volatile components were then removed in vacuo, the resulting solid was washed three times with Et_2O then dried under vacuum to afford the title compound in 88% yield (1.77 g) as a white powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (s, 6 H), 4.27 (t, 2 H, J = 1.8 Hz), 4.57 (s, 2 H), 5.11 (t, 2 H, J = 1.8 Hz), 7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.7, 33.2, 57.2, 72.0, 72.3, 87.7, 128.0, 128.2, 128.6, 136.8.

2-(3-(Benzyloxy)prop-1-ynyl)-3-phenyl-1-tosylaziridine (1i): To a solution of *N*-benzylidene-4-



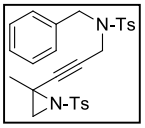
methylbenzenesulfonamide[5] (250 mg, 0.965 mmol) and IV (347 mg, 1.158 mmol) in DCM (5 mL) was added Cs_2CO_3 (211 mg, 1.158 mmol) and the mixture was stirred under argon at room temperature for 4 h. The solution was then filtered to remove inorganic salts and concentrated in vacuo. The oily residue was then purified by flash chromatography (Cyclohexane/EtOAc 10%) to afford the title compound in 69% yield (277 mg) as an orange oil. Rf = 0.32 (Cyclohexane/EtOAc 20%); IR (neat) ν_{max} 3029, 2866, 1596, 1496, 1454, 1329, 1159, 1089, 1018, 878, 784 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 3.70 (dt, 1 H, J = 6.9 Hz, 1.6 Hz), 3.99 (t, 2 H, J = 1.6 Hz), 4.04 (d, 1 H, J = 6.8 Hz), 4.20 (s, 2 H), 7.32 (m, 10 H), 7.91 (d, 2 H, J_{AB} = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 35.7, 46.1, 56.9, 71.0, 78.9, 81.4, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 129.9, 132.0, 134.5, 137.1, 145.1; HR-MS 440.130 ($C_{25}H_{23}NO_3S$+Na calcd 440.129).

2-Methyl-2-(5-phenylpent-1-ynyl)-1-tosylaziridine (1j): Prepared following the general procedure 3



in 44 % yield (337 mg) from 400 mg of **IIj**. Pale yellow oil; Rf = 0.30 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2928, 1598, 1325, 1559, 1089, 909, 814, 730, 730; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 2H, J_{ab} = 8.3 Hz), 7.31 (d, 2H, J_{ab} = 8.3 Hz), 7.22 (m, 5H), 2.87 (s, 1H); 2.74 (dd, 2H, J = 7.0 Hz); 2.44 (s, 1H), 2.43 (s, 3H), 2.22 (t, 2H, J = 7.0 Hz), 1.85 (m, 2H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 141.6, 137.0, 129.5, 128.6, 128.4, 127.8, 125.9, 85.3, 77.3, 42.0, 35.0, 34.7, 30.0, 24.2, 21.6, 18.3; HR-MS 376.132 ($C_{21}H_{23}NO_2S$+Na calcd 376.134).

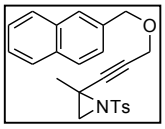
2-(*N*-Benzyl-*N*-tosyl-3-aminoprop-1-ynyl)-2-methyl-1-tosylaziridine (1k): Prepared following the



general procedure 3 in 52% yield (390 mg) from 500 mg of (**IIk**). White solid: mp = 103-104°C; Rf = 0.42 (Cyclohexane/EtOAc 30%); IR (neat) ν_{max} 3080-2925, 1605, 1457, 1325, 1156, 1094, 899, 815, 766, 693, 665, 535; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 3H), 2.24 (s, 1H), 2.42 (s + s, 3H + 3H), 2.50 (s, 1H), 3.91 (d, 1H, J_{AB} = 18.7 Hz), 4.03 (d, 1H, J_{AB} = 18.7 Hz), 4.37 (d, 1H, J_{AB} = 13.7 Hz), 4.46 (d, 1H, J_{AB} = 13.7 Hz), 7.25-7.37 (m, 7H), 7.41 (m, 1H), 7.44 (m, 1H), 7.79 (d, 2H, J_{AB} = 8.3 Hz), 7.81 (d, 2H, J_{AB} = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 23.4, 35.8, 37.4, 41.6, 49.9, 77.7, 82.5, 127.6, 127.8, 127.9, 128.6, 129.0, 129.5, 129.5, 135.1, 136.3, 136.7, 143.3, 144.4; HR-MS 531.137 ($C_{27}H_{28}N_2O_2S$+Na calcd 531.139).

[5] Solladié-Cavallo, A.; Roje, M.; Welter, R.; Šunjić V. *J. Org. Chem.* **2004**, *69*, 1409–1412.

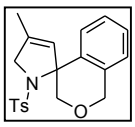
2-Methyl-2-(3-naphthalen-2-ylmethoxy)prop-1-ynyl)-1-tosylaziridine (1l): Prepared following the *general procedure 3* in 51 % yield (444 mg) from 500 mg of **III**. Pale yellow oil; R*f* = 0.32 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3075, 2993, 2941, 2853, 2232, 1585, 1325, 1160, 1086, 909, 868, 813, 728, 691; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 3 H), 2.42 (s, 3 H), 2.46 (s, 1 H), 2.93 (s, 1 H), 4.25 (s, 2 H), 4.80 (s, 2 H), 7.31 (d, 2 H, *J* = 8.3 Hz), 7.49 (m, 3 H), 7.86 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 23.7, 38.1, 41.8, 57.2, 71.6, 80.7, 83.3, 126.0, 126.1, 126.2, 127.3, 127.6, 127.8, 128.0, 128.2, 129.6, 133.1, 133.3, 134.9, 136.7, 144.4; HR-MS 428.124 ($C_{24}H_{27}NO_3S$+Na, calcd 428.129).



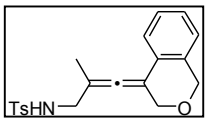
General Procedure 4 for Preparation of Spiro[isochroma-4,2'pyrrolines

To a solution of alkynylaziridine (0.1 mmol) in CH_2Cl_2 (1 mL) was added $Ph_3PAuNTf_2$ (0.005 mmol) at 0°C. The reaction was allowed to warm at room temperature and maintained at that temperature until complete conversion of the starting material as monitored by thin-layer chromatography (SiO_2). Solvent was removed in vacuo, and the crude residue was purified by flash chromatography (Cyclohexane/EtOAc).

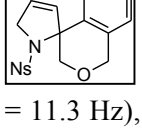
4'-Methyl-1'-tosyl-1',5'-dihydrospiro[isochroman-4,2'-pyrrole] (2a): Prepared following the *general procedure 4* in 70 % yield (35 mg) from 50 mg of **1a**. Colorless oil; R*f* = 0.18 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2924, 2849, 1448, 1337, 1157, 1092, 814, 760, 710, 698, 577, 543; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (dd, 3 H, *J* = 1.4 Hz), 2.40 (s, 3 H), 3.91 (d, 1 H, J_{ab} = 10.8 Hz), 4.14 (d, J_{ab} = 13.1 Hz), 4.25 (d, J_{ab} = 13.0 Hz), 4.61 (d, 1 H, J_{ab} = 10.8 Hz), 4.72 (d, 1 H, J_{ab} = 14.4 Hz), 4.91 (d, 1 H, J_{ab} = 14.4 Hz), 5.56 (m, 1 H), 6.99 (m, 3 H), 7.15 (dd, 1 H, *J* = 7.2, 1.5 Hz), 7.19 (d, 2 H, *J* = 8.3 Hz), 7.49 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.5, 58.8, 68.7, 72.9, 73.4, 123.9, 126.8, 127.1, 127.4, 127.6, 129.2, 129.7, 131.4, 134.6, 136.6, 137.3, 143.0; HR-MS 362.144 ($C_{20}H_{21}NO_3S$+Li, calcd 362.140).



***N*-(3-(Isochroman-4-ylidene)-2-methylallyl)-4-methylbenzenesulfonamide (3a)**: Isolated as trace following the *general procedure 4* in 5 % yield (5 mg) from 100 mg of **1a**. Colorless oil; R*f* = 0.22 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3254, 2911, 2837, 1329, 1158, 1088, 811, 762; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3 H), 2.41 (s, 3 H), 3.60 (d, 2 H, *J* = 6.0 Hz), 4.40 (d, 2 H, *J* = 1.9 Hz), 4.57 (m, 1 H), 4.76 (s, 2 H), 7.02 (m, 1 H), 7.17 (m, 2 H), 7.30 (m, 3 H), 7.72 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 21.6, 45.8, 67.7, 88.7, 101.1, 102.8, 124.7, 126.3, 127.0, 127.1, 127.3, 128.5, 129.8, 133.9, 136.7, 143.5, 195; HR-MS 378.111 ($C_{20}H_{21}NO_3S$+Na, calcd 378.113).

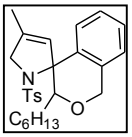


4'-Methyl-1'-(4nitrophenylsulfonyl)-1',5'-dihydrospiro[isochroman-4,2'-pyrrole] (2b): Prepared following the *general procedure 4* in 60 % yield (30 mg) from 50 mg of **1b**. Pale yellow solid; mp = 164-165°C; R*f* = 0.24 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3103, 2918, 2851, 1529, 1347, 1158, 1090, 948, 852, 738, 688, 608, 554, 459; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (m, 3 H), 3.91 (d, 1 H, J_{ab} = 11.3 Hz), 4.29 (s, 2 H), 4.51 (d, 1 H, J_{ab} = 11.3 Hz), 4.71 (d, 1 H, J_{ab} = 14.7 Hz), 4.92 (d, 1 H, J_{ab} = 14.7 Hz), 5.49 (m, 1 H), 6.74 (d, 1 H, *J* = 7.4 Hz), 6.92 (t, 1 H, *J* = 7.4 Hz), 7.02 (d, 1 H, *J* = 7.4 Hz), 7.18 (dt, 1 H, *J* =1.0 Hz, 7.4 Hz), 7.69 (d, 2 H, *J* = 8.8 Hz), 8.18 (d, 2 H, *J* = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 59.2, 68.6, 72.8, 73.4, 123.8, 124.2, 126.6, 126.8, 127.7, 129.0, 132.1, 135.1, 135.3, 145.6, 149.7; HR-MS 409.080 ($C_{19}H_{18}N_2O_5S$+Na, calcd 409.083).



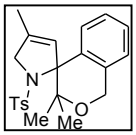
3-Hexyl-4'-methyl-1'-tosyl-1',5'-dihydrospiro[isochroman-4,2'-pyrrole] (2c): Prepared following the *general procedure 4* in 77 % yield (77 mg, *dr* 1:1) from 100 mg of **1c**. Mixture of diastereoisomers: IR (neat) ν_{max} 2959, 2848, 1447, 1335, 1156, 1094, 763, 720, 669, 579, 545; HR-MS 462.204 ($C_{26}H_{33}NO_3S$+Na calcd 462.208).

Diastereoisomer 1: Colorless oil; R*f* = 0.48 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.9 Hz), 1.25 (m, 8 H), 1.56 (s, 2 H), 1.76 (d, 3 H, *J* = 1.3 Hz), 2.41 (s, 3 H), 4.11 (d, 1 H, J_{ab} = 13.0 Hz), 4.30 (d, 1 H, J_{ab} = 13.0 Hz), 4.39 (dd, 1 H, *J* = 8.9 Hz, 2.5 Hz), 4.77 (d, 1 H, J_{ab} = 14.4 Hz), 4.94 (d, 1 H, J_{ab} = 14.4 Hz), 5.39 (q, 1 H, *J* = 1.5 Hz), 6.99-7.03 (m, 3 H),



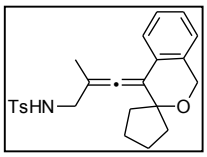
7.12-7.20 (m, 1 H), 7.22 (d, 2 H, J = 8.3 Hz), 7.52 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 14.1, 21.5, 22.7, 26.4, 29.6, 30.5, 31.2, 59.2, 69.2, 80.5, 123.6, 126.7, 126.9, 127.2, 127.6, 127.7, 129.3, 131.2, 134.5, 137.6, 138.4, 143.0.
Diastereoisomer 2: Colorless oil; Rf = 0.45 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3 H, J = 6.8 Hz), 1.25 (m, 8 H), 1.56 (s, 2 H), 1.84 (d, 3 H, J = 1.3 Hz), 2.35 (s, 3 H), 3.43 (dd, 1 H, J = 9.5 Hz, 2.2 Hz), 4.13 (d, 1 H, J_{ab} = 13.4 Hz), 4.28 (d, 1 H, J_{ab} = 13.4 Hz), 4.73 (d, 1 H, J_{ab} = 15.4 Hz), 5.03 (m, 1 H), 5.05 (d, 1 H, J_{ab} = 15.4 Hz), 6.84 (d, 1 H, J = 7.3 Hz), 6.95 (t, 1 H, J = 7.1 Hz), 7.17 (m, 1 H), 7.21 (t, 2 H, J = 6.2 Hz), 7.26 (d, 2 H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 14.1, 21.4, 22.7, 26.4, 29.2, 29.4, 31.9, 60.2, 88.1, 74.5, 81.5, 123.7, 126.2, 127.1, 127.6, 128.7, 128.9, 134.2, 135.6, 135.9, 137.8, 142.2.

3,3,4'-Trimethyl-1'-tosyl-1',5'-dihydrospiro[isochroman-4,2'-pyrrole] (2d): Prepared following

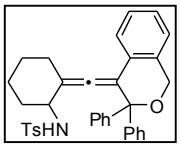


the *general procedure 4* in 70 % yield (35 mg) from 50 mg of **1d** using $Ph_3PAuSbF_6$ instead of $Ph_3PAuNTf_2$. Colorless oil; Rf = 0.21 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2983, 2921, 2844, 1447, 1343, 1156, 1093, 1039, 907, 814, 726, 686, 532, 543; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 3 H), 1.21 (s, 3 H), 1.65 (s, 3 H), 2.35 (s, 3 H), 4.07 (d, 1 H, J_{ab} = 13.8 Hz), 4.21 (d, 1 H, J_{AB} = 13.8 Hz), 4.86 (d, 1 H, J_{ab} = 15.6 Hz), 5.04 (d, 1 H, J_{ab} = 15.6 Hz), 5.14 (q, 1 H, J = 1.6 Hz), 7.11 (m, 4 H), 7.06 (d, 2 H, J = 8.3 Hz), 7.16 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 21.4, 21.7, 24.0, 30.2, 30.9, 59.8, 62.9, 123.2, 126.0, 126.2, 127.6, 127.7, 128.7, 129.1, 132.5, 136.3, 136.4, 137.7, 142.2; HR-MS 406.143 ($C_{22}H_{25}NO_3S$+Na, calcd 406.145).

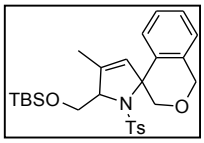
4-Methyl-*N*-(2-methyl-3-(spiro[cyclopentane-1,3'-isochroman]-4'-ylidene)allyl)benzenesulfonamide (3e): Prepared following either the *general procedure 4* or the *general procedure 5* in 74 % yield (37 mg) from 50 mg of **1e**. Orange crystalline powder; mp = 136-137°C; Rf = 0.27 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3288, 2955, 2859, 1326, 1156, 1079, 812, 762, 726, 661, 546; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 (m, 6 H), 1.82 (s, 3 H), 2.00 (m, 2 H), 2.41 (s, 3 H), 3.60 (dd, 2 H, J = 5.9 Hz, 2.0 Hz), 4.57 (t, 1 H, J = 5.9 Hz), 4.77 (s, 2 H), 7.03 (m, 1 H), 7.15 (m, 2 H), 7.25 (m, 1 H), 7.26 (d, 2 H, J = 8.3 Hz), 7.72 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 21.5, 23.6, 37.2, 37.6, 45.9, 63.1, 83.8, 102.9, 108.7, 124.4, 126.8, 127.0, 127.1, 129.8, 133.4, 136.6, 143.5, 195.5; HR-MS 432.157 ($C_{24}H_{27}NO_3S$+Na, calcd 432.160).



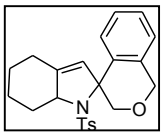
***N*-(2-((3,3-Diphenylisochroman-4-ylidene)methylene)cyclohexyl)-4- methylbenzenesulfonamide (3f):** Prepared following the *general procedure 4* in 52% yield (52 mg, *dr* 2:1) from 100 mg of **1f**.



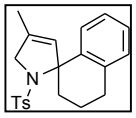
Mixture of diastereoisomers: IR (neat) ν_{max} 3357, 2930, 2840, 1953, 1598, 1488, 1444, 1325, 1155, 1090, 1067, 1030, 925, 810, 775; HR-MS 570.206 ($C_{35}H_{33}NO_3S$+Na calcd 570.207).
Major diastereoisomer: Yellow solid; mp = 185°C; Rf = 0.34 (Cyclohexane/EtOAc 25%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.51 (dq, 1 H, J = 12.6, 3.1 Hz), 0.76-0.92 (m, 1 H), 1.14-1.27 (m, 1 H), 1.56-1.62 (m, 2 H), 1.80-1.85 (m, 1 H), 2.00 (dt, 1 H, J = 13.5, 3.8 Hz), 2.32 (s, 3 H), 3.54 (ddd, 1 H, J = 11.7, 9.2, 4.8 Hz), 3.77 (d, 1 H, J = 9.1 Hz), 4.60 (d, 1 H, J_{ab} = 15.5 Hz), 4.81 (d, 1 H, J_{ab} = 15.5 Hz), 6.93-6.99 (m, 3 H), 7.08-7.19 (m, 3 H), 7.28-7.40 (m, 10 H), 7.57 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 24.8, 25.4, 31.0, 35.6, 52.3, 63.4, 83.2, 109.3, 110.9, 124.0, 126.7, 126.8, 127.7, 127.8, 128.0, 128.1, 128.8, 129.1, 129.4, 133.2, 138.0, 141.9, 142.5, 145.6, 195.9.
Minor diastereoisomer: Yellow oil; Rf = 0.26 (Cyclohexane/EtOAc 25%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18-1.67 (m, 6 H), 1.71-1.79 (m, 1 H), 1.95-2.03 (m, 1 H), 2.35 (s, 3 H), 3.29 (ddd, 1 H, J = 8.8, 4.4, 4.4 Hz), 4.48 (d, 1 H, J = 4.9 Hz), 4.56 (d, 1 H, J_{ab} = 15.6 Hz), 4.71 (d, 1 H, J_{ab} = 15.4 Hz), 6.93 (dd, 1 H, J = 7.3, 0.7 Hz), 7.02-7.36 (m, 14 H), 7.42 (dd, 1 H, J = 7.9, 1.3 Hz), 7.56 (d, 2 H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 21.4, 27.6, 28.4, 31.9, 53.1, 63.4, 83.3, 108.6, 110.2, 120.2, 124.1, 125.2, 126.5, 127.0, 127.1, 127.3, 127.8, 128.1, 128.6, 129.0, 129.5, 137.7, 142.7, 143.4, 147.0, 195.8.

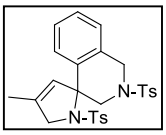
5'-((*tert*-Butyldimethylsilyloxy)methyl)-4'-methyl-1'-tosyl-1',5'-dihydrospiro[isochroman-4,2'-pyrrole] (2g). 

Prepared following the *general procedure 4* in 74 % yield (74 mg, *dr* 2:1) from 100 mg of alkynyl aziridine **1g**. Mixture of diastereoisomers: colorless oil; IR (neat) ν_{max} 2959, 2929, 2851, 1686, 1592, 1328, 1303, 1253, 1224, 1159, 1087, 1026, 1006, 966; HR-MS 522.210 ($C_{27}H_{37}NO_4SSi$+Na calcd 522.210).
Major diastereoisomer (2'S,5'S*):* Colorless oil; R*f* = 0.40 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3 H), 0.06 (s, 3 H), 0.89 (s, 9 H), 1.75 (s, 3 H), 2.38 (s, 3 H), 3.83 (dd, 1 H, J_{ab} = 10.7, 1.9 Hz), 4.00 (dd, 1 H, J_{ab} = 11.0, 2.0 Hz), 4.01 (d, 1 H, J = 11.2 Hz), 4.51 (m, 1 H), 4.52 (d, 1 H, J = 11.2 Hz), 4.69 (d, 1 H, J_{ab} = 14.5 Hz), 4.91 (d, 1 H, J_{ab} = 10.5 Hz), 5.48 (s, 1 H), 6.75 (d, 1 H, J = 7.9 Hz), 6.90 (t, 1 H, J = 7.4 Hz), 7.00 (d, 1 H, J = 7.6 Hz), 7.11 (d, 2 H, J = 7.9 Hz), 7.14 (t, 1 H, J = 7.4 Hz), 7.33 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.71, -5.38, 13.7, 18.3, 21.4, 25.9, 62.2, 68.6, 71.5, 71.9, 74.6, 124.0, 126.3, 127.0, 127.6, 128.5, 128.9, 129.5, 133.8, 135.1, 135.9, 138.7, 142.6.
Minor diastereoisomer (2'S,5'R*):* Colorless oil; R*f* = 0.32 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.92 (s, 9 H), 1.73 (s, 3 H), 2.36 (s, 3 H), 3.73 (d, 1 H, J = 10.5 Hz), 4.00 (dd, 1 H, J = 11.1, 2.0 Hz), 4.35 (dd, 1 H, J = 11.0, 3.3 Hz), 4.44 (m, 1 H), 4.70 (d, 1 H, J_{ab} = 14.7 Hz), 4.76 (d, 1 H, J = 10.7 Hz), 4.83 (d, 1 H, J_{ab} = 14.5 Hz), 5.60 (s, 1 H), 6.87 (dd, 1 H, J = 7.2, 0.7 Hz), 7.06-7.14 (m, 4 H), 7.56 (d, 2 H, J = 8.4 Hz), 7.86 (dd, 1 H, J = 8.8, 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.52, -5.35, 13.8, 18.4, 21.5, 25.9, 62.6, 68.7, 70.9, 72.0, 73.2, 123.3, 126.7, 127.0, 127.8, 128.6, 129.1, 130.0, 133.2, 133.8, 137.5, 138.1, 142.9.

1-Tosyl-1,4,5,6,7,7a-hexahydrospiro[indole-2,4'-isochroman] (2h): Prepared following the *general procedure 4* in 68 % yield (34 mg, *dr* 3/1) from 50 mg of **1h**. Mixture of diastereoisomers: colorless oil; IR (neat) ν_{max} 2855, 2840, 1337, 1096, 1029, 949, 757, 666, 578, 544; HR-MS 418.145 ($C_{23}H_{25}NO_3S$+Na calcd 418.145).


Major diastereoisomer (2S,7aR*):* R*f* = 0.38 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.38 (m, 3 H), 1.79-1.82 (m, 2H), 1.96-2.07 (m, 1 H), 2.39 (s, 3 H), 2.39-2.46 (m, 1 H), 2.53-2.57 (m, 1 H), 3.99 (dd, 1 H, J = 10.8, 1.0 Hz), 4.30 (m, 1 H), 4.64 (d, 1 H, J = 10.8 Hz), 4.70 (d, 1 H, J_{ab} = 14.4 Hz), 4.92 (d, 1 H, J_{ab} = 14.4 Hz), 5.49 (m, 1 H), 6.71 (dd, 1 H, J = 7.4, 1.0 Hz), 6.91 (dt, 1 H, J = 1.0 Hz, 7.4 Hz), 6.99 (d, 1 H, J = 7.4 Hz), 7.11-7.14 (m, 3 H), 7.34 (d, 2 H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 23.9, 26.6, 28.3, 37.6, 67.3, 68.8, 72.7, 75.4, 124.0, 124.9, 126.5, 127.0, 127.6, 128.2, 129.0, 135.3, 135.7, 138.4, 138.5, 142.8.
Minor diastereoisomer (2S,7aS*):* R*f* = 0.38 (Cyclohexane/EtOAc 20%); ^{1}H NMR (300 MHz, C_6D_6) δ 0.71-1.96 (m, 7 H), 1.83 (s, 3 H), 2.78-2.87 (m, 1 H), 3.90 (d, 1 H, J = 10.4 Hz), 4.16 (dd, 1 H, J = 11.0, 4.7 Hz), 4.56 (d, 1 H, J_{ab} = 14.8 Hz), 4.76 (d, 1 H, J_{ab} = 14.8 Hz), 5.03 (d, 1 H, J = 10.4 Hz), 5.34 (m, 1 H), 6.59-6.68 (m, 3 H), 6.77 (d, 1 H, J = 7.9 Hz), 6.92 (dt, 1 H, J = 3.8, 1.5 Hz), 7.02 (t, 1 H, J = 7.1 Hz), 7.66 (d, 2 H, J = 8.4 Hz); ^{13}C NMR (75 MHz, C C_6D_6) δ 21.3, 24.1, 26.6, 27.4, 38.6, 67.0, 69.2, 73.7, 76.0, 124.2, 126.3, 127.2, 127.3, 128.3, 128.5129.5, 135.1, 138.0, 138.5, 140.0, 142.6.

4'-Methyl-1'-tosyl-1',3,4,5'-tetrahydro-2H-spiro[naphthalene-1,2'-pyrrole] (2j): Prepared following the *general procedure 4* in 72 % yield (36 mg) from 50 mg of **1j**. Colorless oil; R*f* = 0.40 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 3158, 2923, 1330, 1151, 1093, 1046, 765, 688, 659, 582, 540; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, 2H, J_{ab} = 8.3 Hz), 7.15 (d, 2H, J_{ab} = 8.3 Hz), 7.06 (m, 2H), 6.88 (m, 2H), 5.47 (q, 1H, J = 1.7 Hz), 4.16 (m, 2H), 2.93 (m, 2H), 2.70 (m, 1H), 2.38 (s, 3H), 1.72 (s, 1H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 139.3, 137.8, 137.3, 131.5, 129.6, 129.1, 128.7, 128.5, 128.3, 127.4, 126.8, 125.9, 76.3, 58.5, 36.6, 30.2, 29.7, 22.1, 21.5, 14.0; HR-MS 376.132 ($C_{21}H_{23}NO_2S$+Na calcd 376.134).


4'-Methyl-1',2-ditosyl-1',2,3,5'-tetrahydro-1H-spiro[isoquinoline-4,2'-pyrrole] (2k): Prepared following the *general procedure 4* in 68 % yield (34 mg) from 50 mg of **1k**. White solid: mp = 115°C (d.); R*f* = 0.43 (Cyclohexane/EtOAc 30%); IR (neat) ν_{max} 3040-2880, 1597, 1460, 1332, 1155, 1094, 1056, 899, 811, 765, 730, 701, 543; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (m, 3H), 2.43 (s, 3H), 2.46 (s, 3H), 3.61 (d, 1H, J = 10.6 Hz), 3.82 (d, 1H, J = 14.6 Hz), 3.89 (dd, 1H, J = 10.6 Hz, 1.8 Hz), 4.17 (d, 1H, J_{AB} = 13.1 Hz), 4.25 (d, 1H, J_{AB} = 13.1 Hz), 4.64 (dd, 1H, J =14.3 Hz, 1.9 Hz), 5.70 (q, 1H, J= 1.8 Hz), 6.91 (m, 1H), 7.03


(m, 2H), 7.15 (ddd, 1H, *J* =7.2 Hz, 8.3 Hz, 1.0 Hz), 7.21 (d, 2H, J_{AB} =8.3 Hz), 7.37 (d, 2H, J_{AB} = 8.3 Hz), 7.39 (d, 2H, J_{AB} = 8.3 Hz), 7.70 (d, 2H, J_{AB} = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.6, 21.6, 48.6, 53.2, 58.8, 74.7, 126.0, 127.2, 127.4, 127.4, 127.6, 127.7, 129.3, 129.8, 129.9, 131.1, 131.3, 132.8, 137.1, 137.3, 143.3, 144.1; HR-MS 531.137 ($C_{27}H_{28}N_2O_2S$+Na calcd 531.139).

4'-Methyl-1'-tosyl-1',2,4,5'-tetrahydrospiro[benzo[f]isochromene-1,2'-pyrrole] (2l): Prepared following the *general procedure 4* in 78 % yield (39 mg) from 50 mg of **1l**. Colorless oil; R*f* = 0.32 (Cyclohexane/EtOAc 20%). IR (neat) ν_{max} 2926, 2844, 1529, 1344, 1156, 1093, 808, 730, 706, 688, 666, 582, 544; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (m, 3 H), 2.27 (s, 3 H), 3.93 (d, 1 H, J_{ab} = 11.3 Hz), 4.27 (d, 1 H, J_{ab} = 13.8 Hz), 4.47 (d, 1 H, J_{ab} = 13.8 Hz), 4.60 (d, 1 H, J_{ab} = 11.3 Hz), 4.85 (d, 1 H, J_{ab} = 15.2 Hz), 5.11 (d, 1 H, J_{ab} = 15.2 Hz), 5.63 (q, 1 H, *J* = 1.7 Hz), 6.82 (d, 2 H, *J* = 8.2 Hz), 6.97 (ddd, 1 H, *J* =7.1 Hz, 8.3 Hz, 1.5 Hz), 7.10 (m, 3H), 7.27 (ddd, 1 H, 7.1 Hz, 8.3 Hz, 1.5 Hz), 7.39 (d, 1 H, *J* = 8.7 Hz), 7.72 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 21.5, 60.0, 69.8, 72.4, 75.7, 122.5, 124.2, 124.5, 125.6, 127.0, 128.5, 128.6, 128.7, 128.8, 129.6, 131.7, 132.8, 133.1, 134.7, 136.3, 142.5; HR-MS 428.126 ($C_{24}H_{23}NO_3S$+Na, calcd 428.129).

***N*-(2-(Isochroman-4-ylidenemethylene)cyclohexyl)-4-methylbenzenesulfonamide (3h)**: Prepared in 20 % yield (20 mg, *dr* 3:1) from 100 mg of **1g** following the *general procedure 4* at 0°C by quenching the reaction after 10 min.

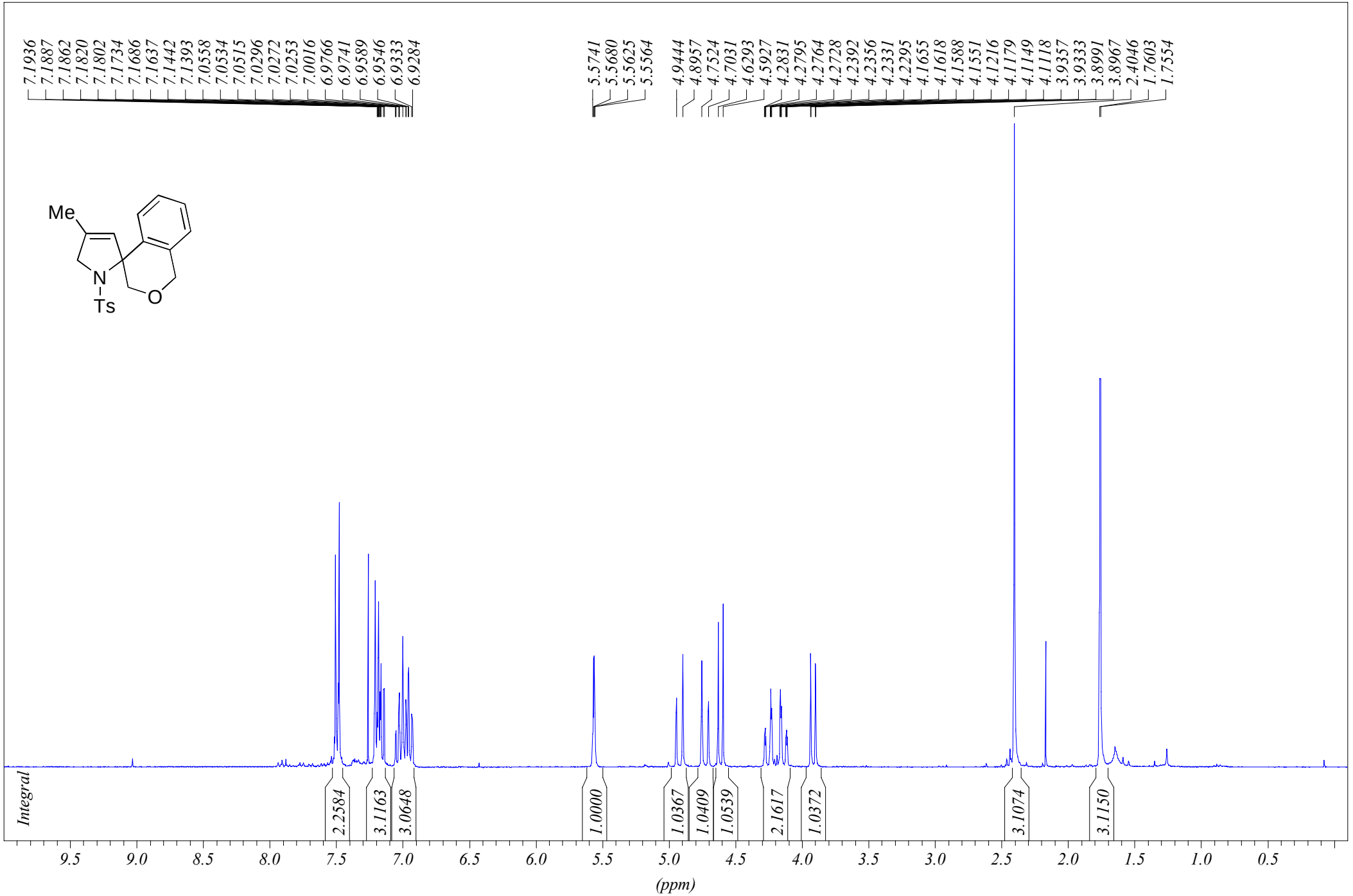
Mixture of diastereoisomers: IR (neat) ν_{max} 3158, 2925, 2851, 1444, 1314, 1152, 1097, 926, 810, 758, 734, 656, 545; HR-MS 418.141 ($C_{23}H_{25}NO_3S$+Na, calcd 418.145).

Major diastereoisomer **3h-maj** *(2S*,R*)*: colorless crystalline powder, mp = 153°C; R*f* = 0.19 (Cyclohexane/EtOAc 20%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (m, 2 H), 1.78 (m, 2 H), 2.06 (m, 1 H), 2.26 (m, 1 H), 2.38 (m, 1 H), 2.40 (s, 3 H), 3.66 (m, 1 H), 4.46 (d, 2 H, *J* = 2.1 Hz), 4.79 (m, 1 H), 4.79 (s, 2 H), 6.95 (d, 1 H, *J* = 7.4 Hz), 7.02 (d, 1 H, *J* = 7.6 Hz), 7.08 (d, 1 H, *J* = 7.6 Hz), 7.14 (d, 2 H, *J* = 8.3 Hz), 7.19 (d, 1 H, *J* = 7.4 Hz), 7.63 (d, 2 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 24.4, 26.8, 31.1, 36.8, 53.0, 68.2, 68.7, 102.4, 110.7, 124.6, 126.4, 126.8, 126.9, 127.3, 128.6, 129.6, 133.9, 137.6, 143.0, 190.5.

Minor diastereoisomer **3h-min** *(2R*,R*)*: white crystalline powder; mp = 114 °C; R*f* = 0.24 (Cyclohexane/EtOAc 20%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14-1.97 (m, 6 H), 2.25-2.37 (m, 2 H), 2.43 (s, 3 H), 3.68 (m, 1 H), 4.13 (d, 1 H, J_{ab} = 12.7 Hz), 4.25 (d, 1 H, J_{ab} = 12.7 Hz), 4.63 (d, 1 H, *J* = 7.6 Hz), 4.78 (d, 2 H, *J* = 3.0 Hz), 7.05 (m, 1 H), 7.20 (m, 2 H), 7.33 (m, 1 H), 7.30 (d, 2 H, *J* = 8.1 Hz), 7.73 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 25.0, 27.2, 31.6, 37.6, 53.3, 67.5, 68.7, 102.7, 111.3, 124.9, 125.7, 127.0, 127.3, 127.5, 128.6, 129.7, 134.0, 137.9, 143.3, 190.1.

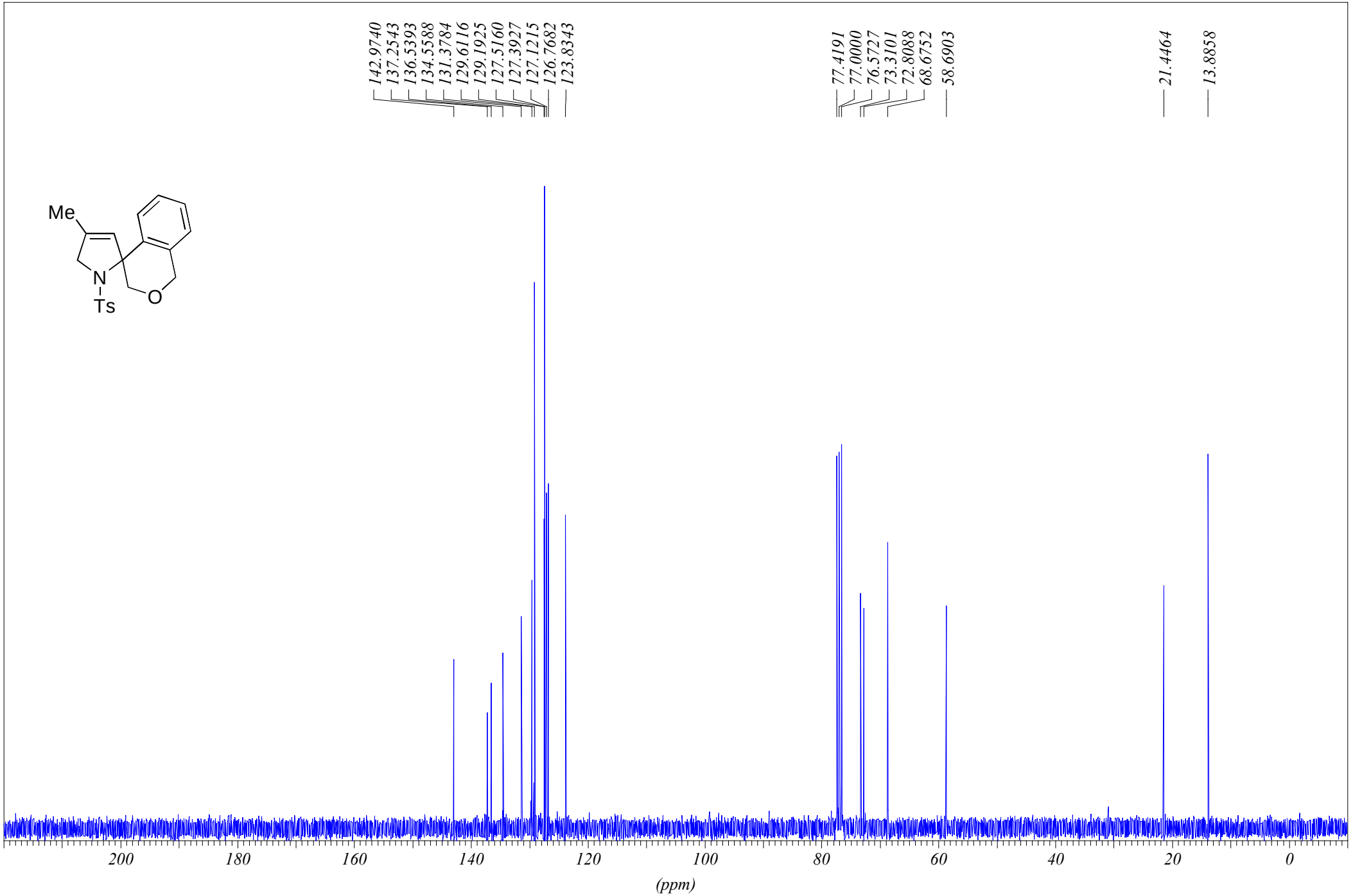
Proton CDCl3 300 MHz

2a



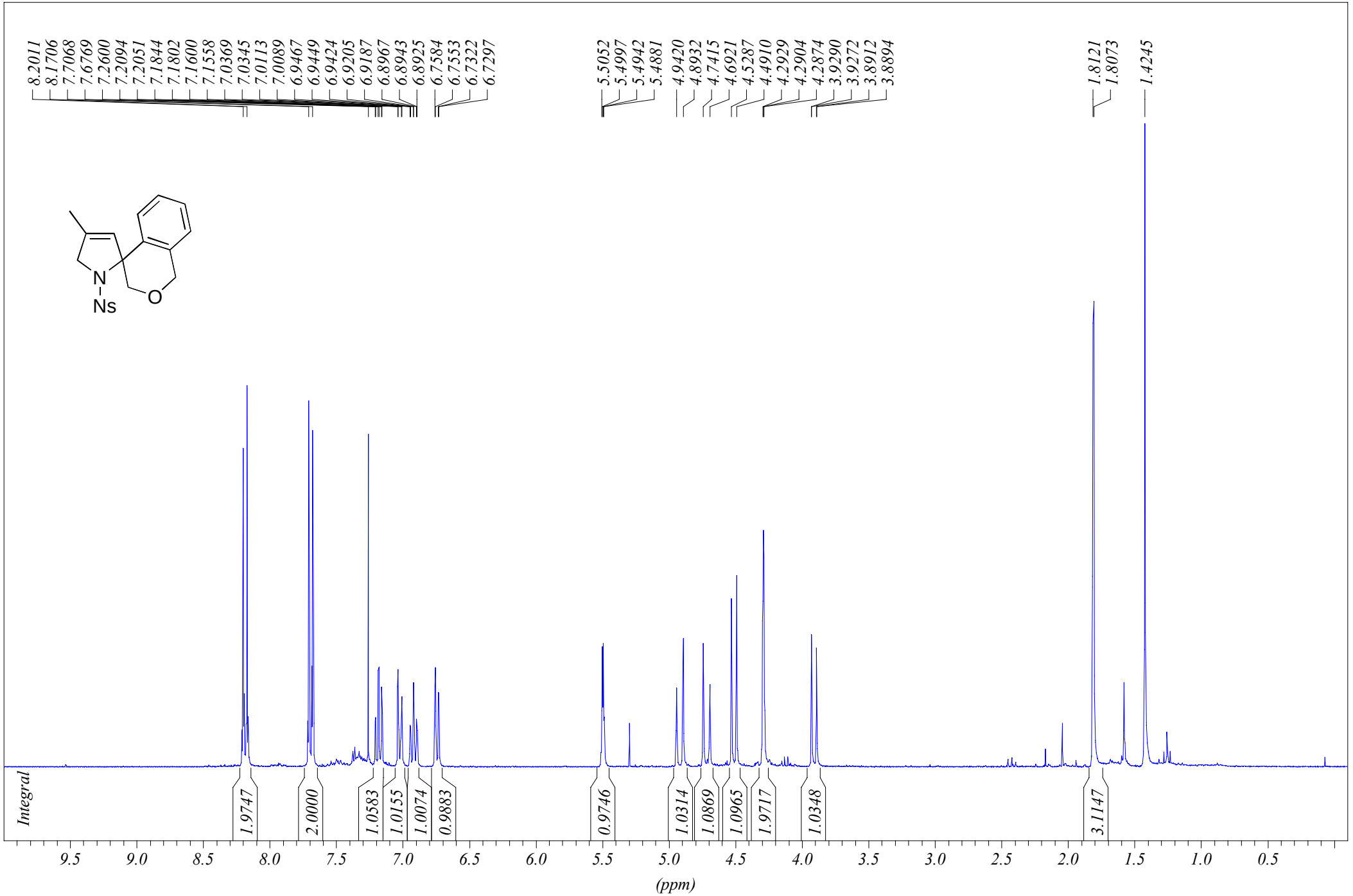
Carbon CDCl3 75 MHz

2a



Proton CDCl3 300 MHz

2b



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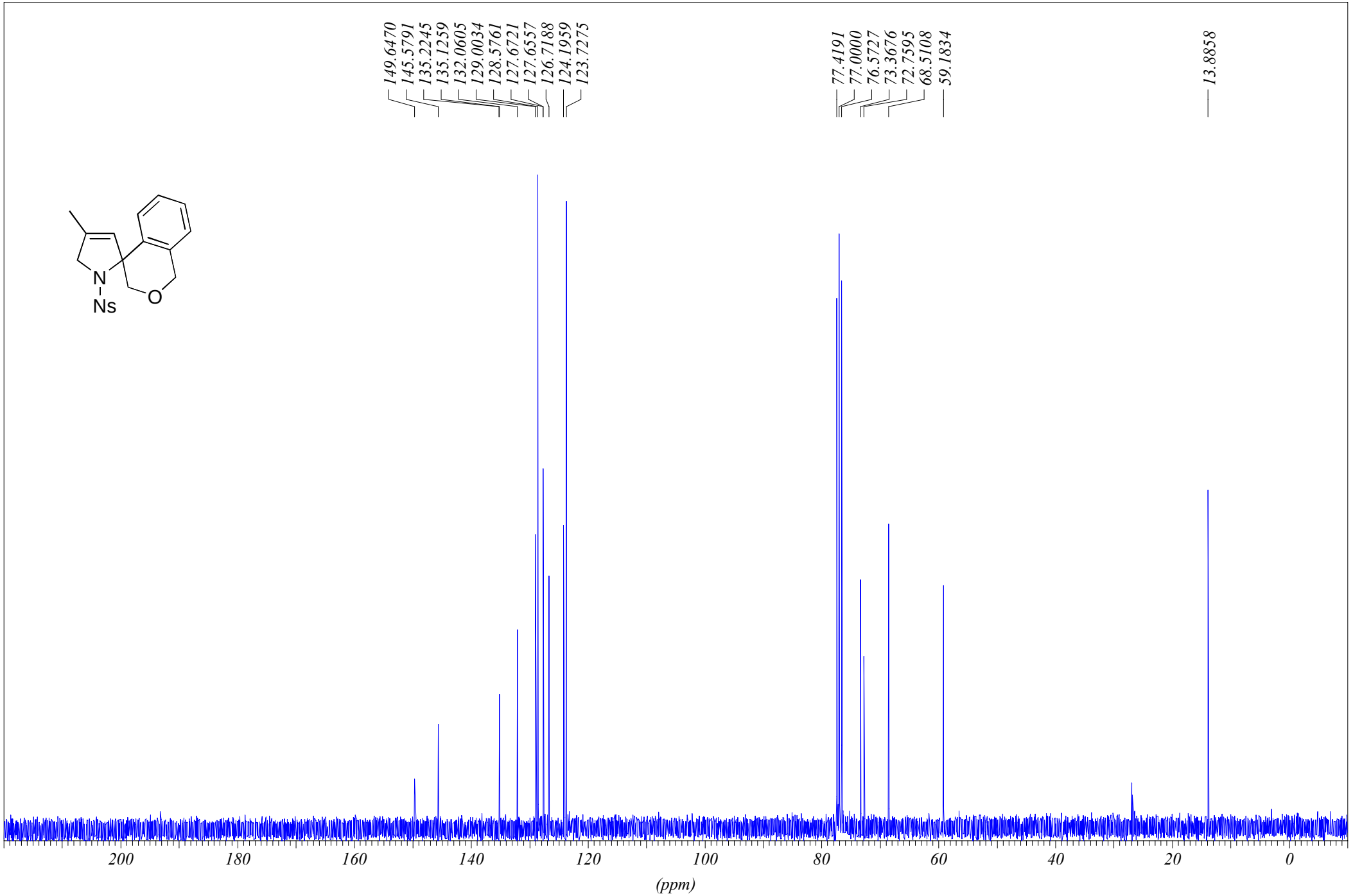
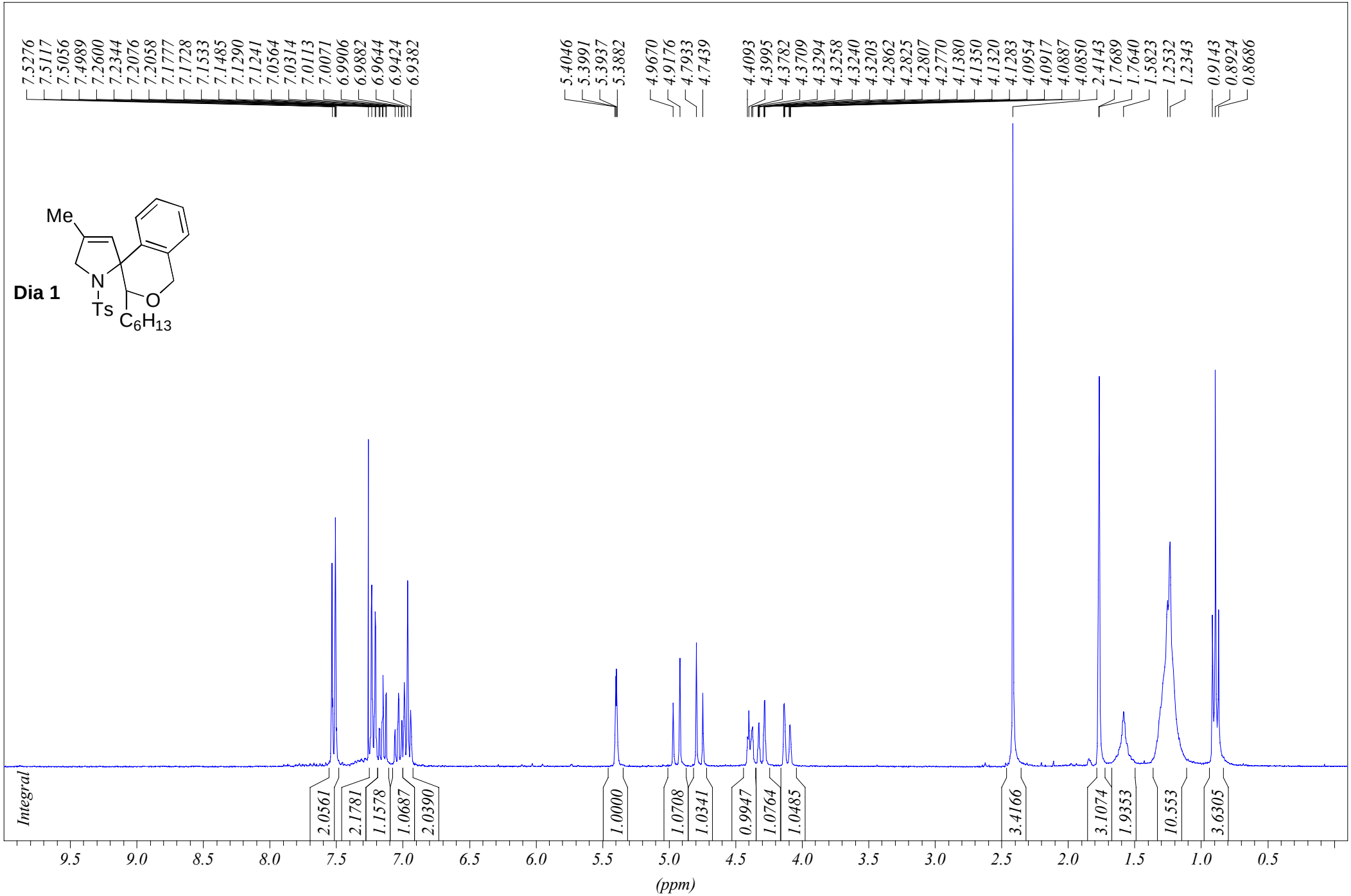
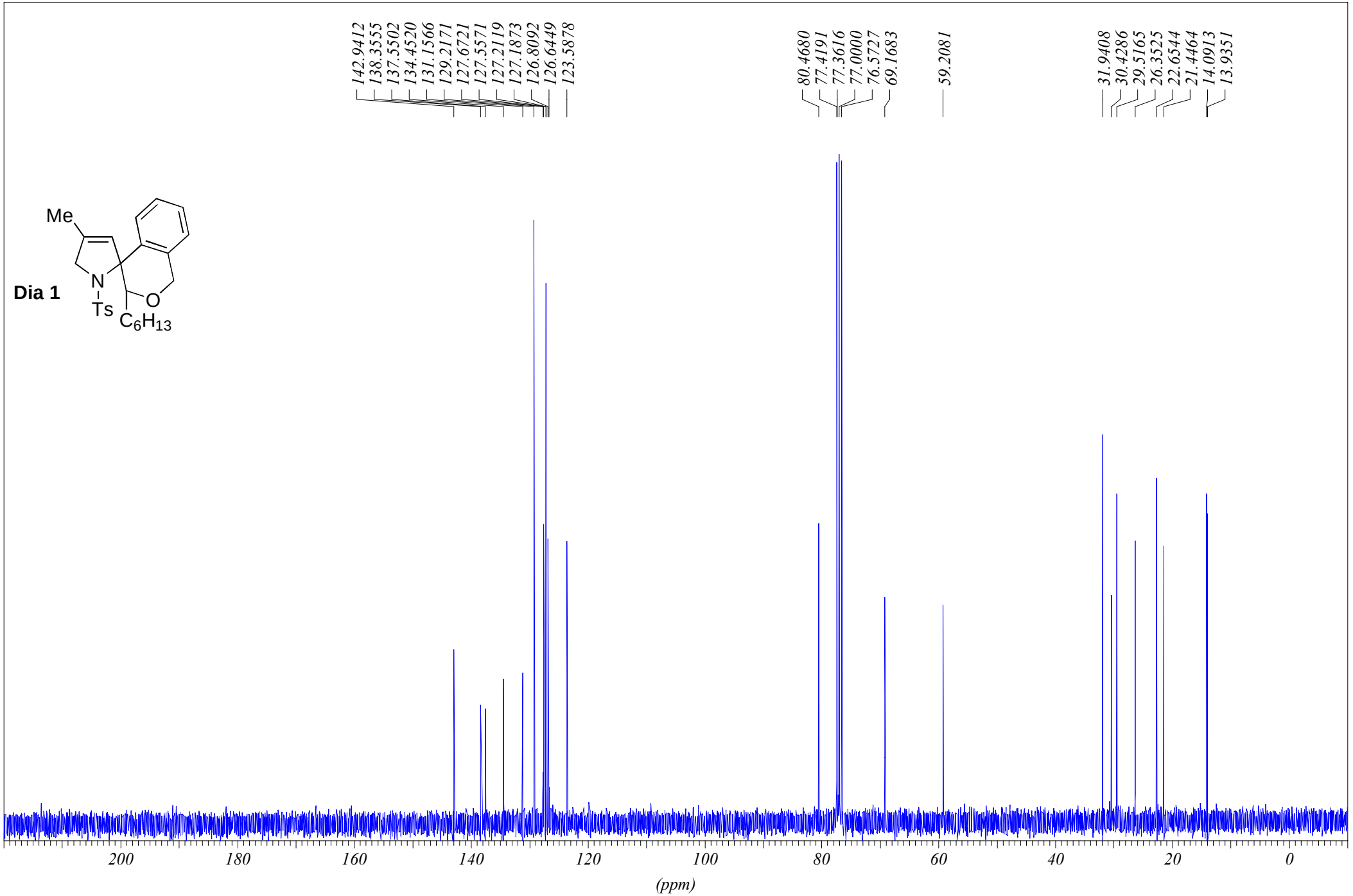
2b

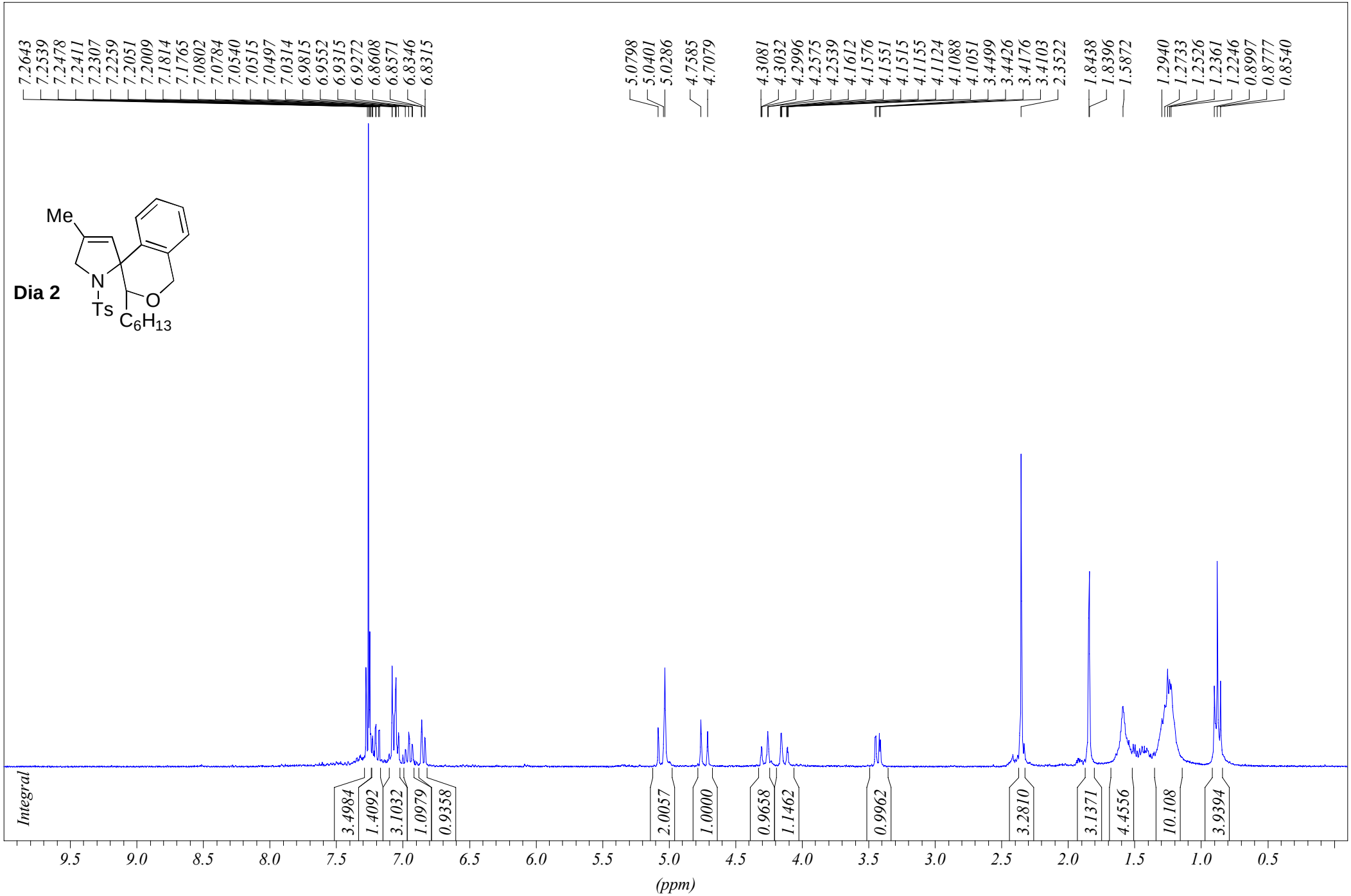




Carbon CDCl3 75 MHz

2c





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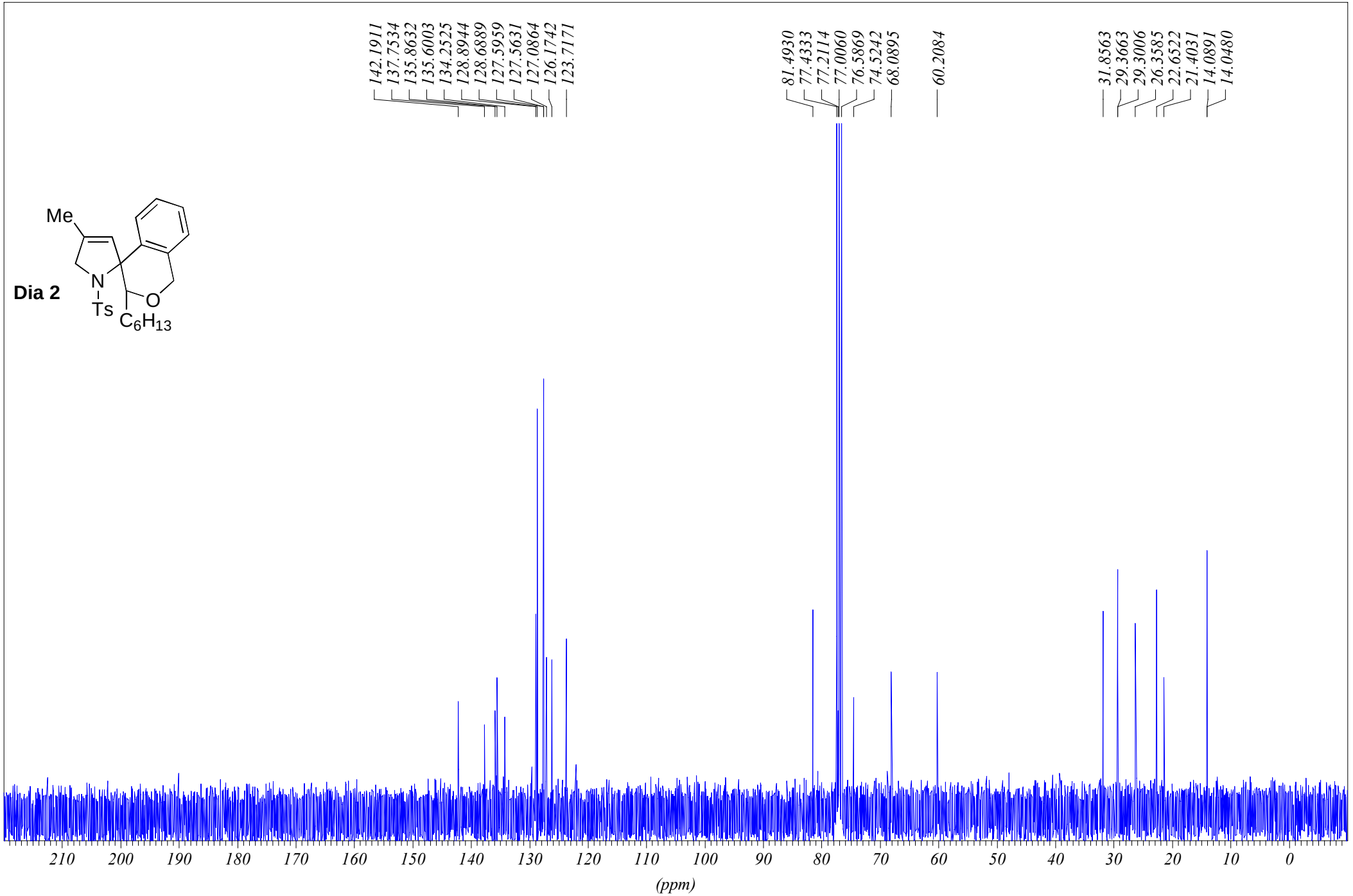
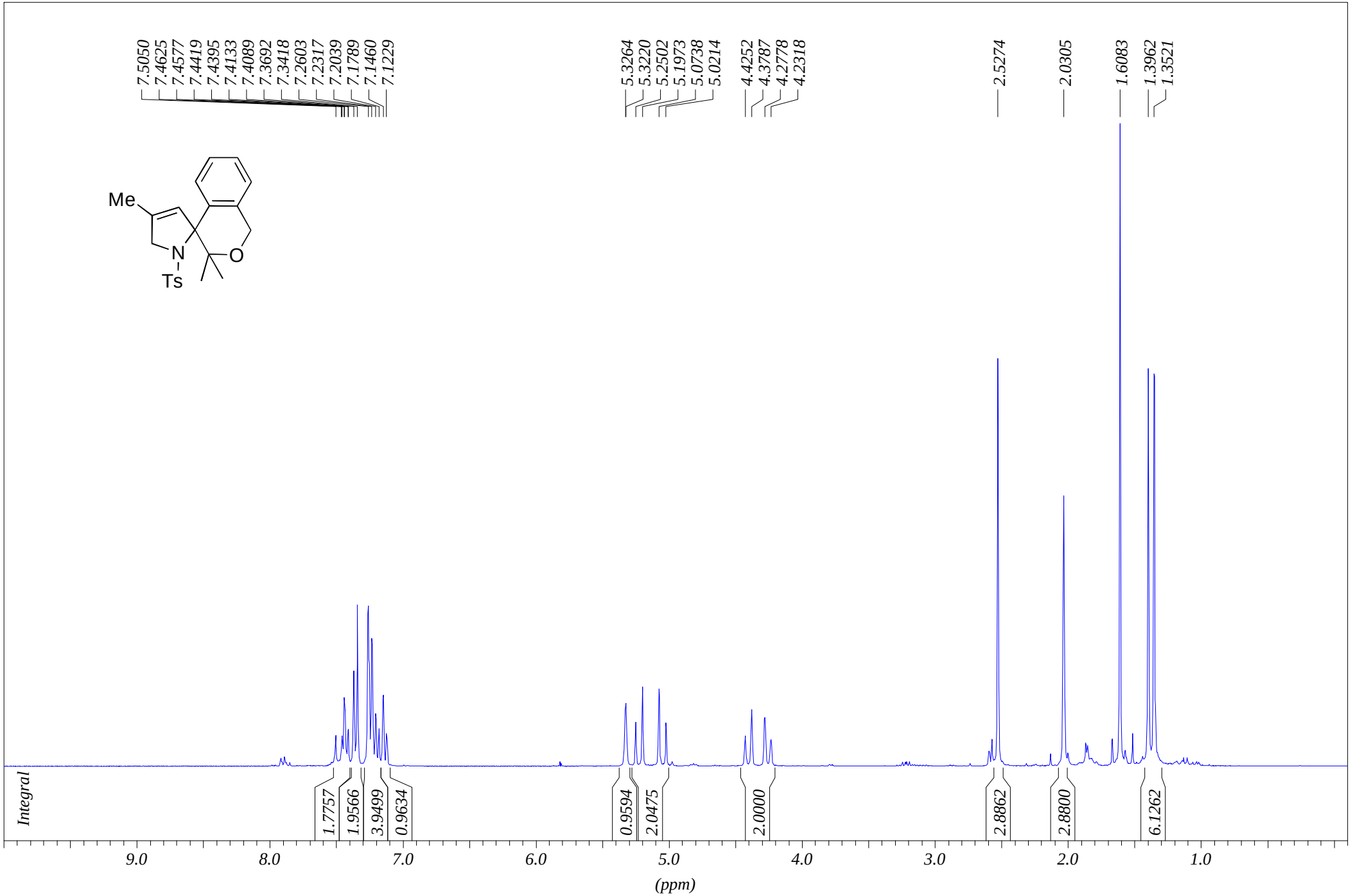
2c



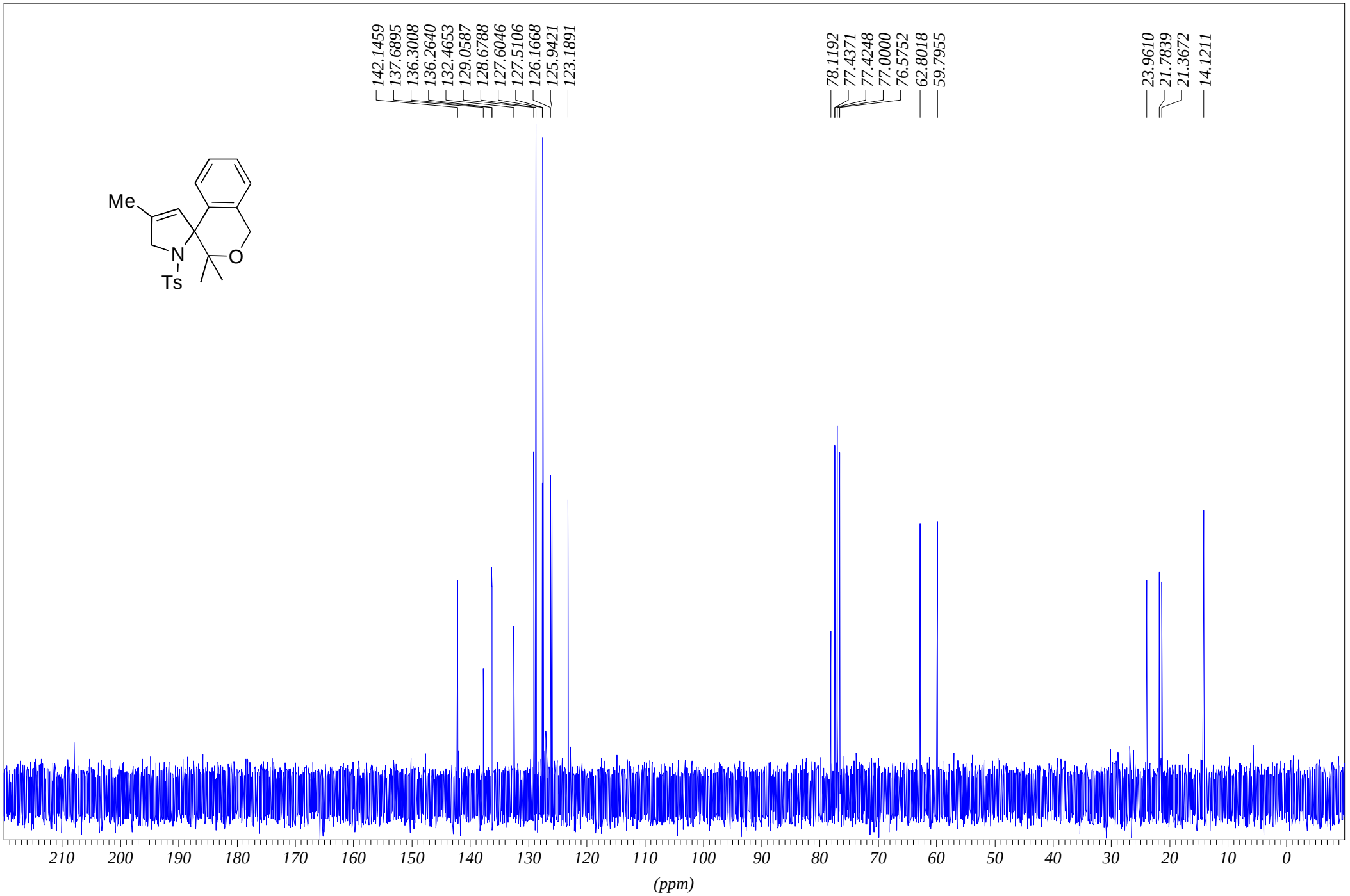
Proton CDCl3 300 MHz

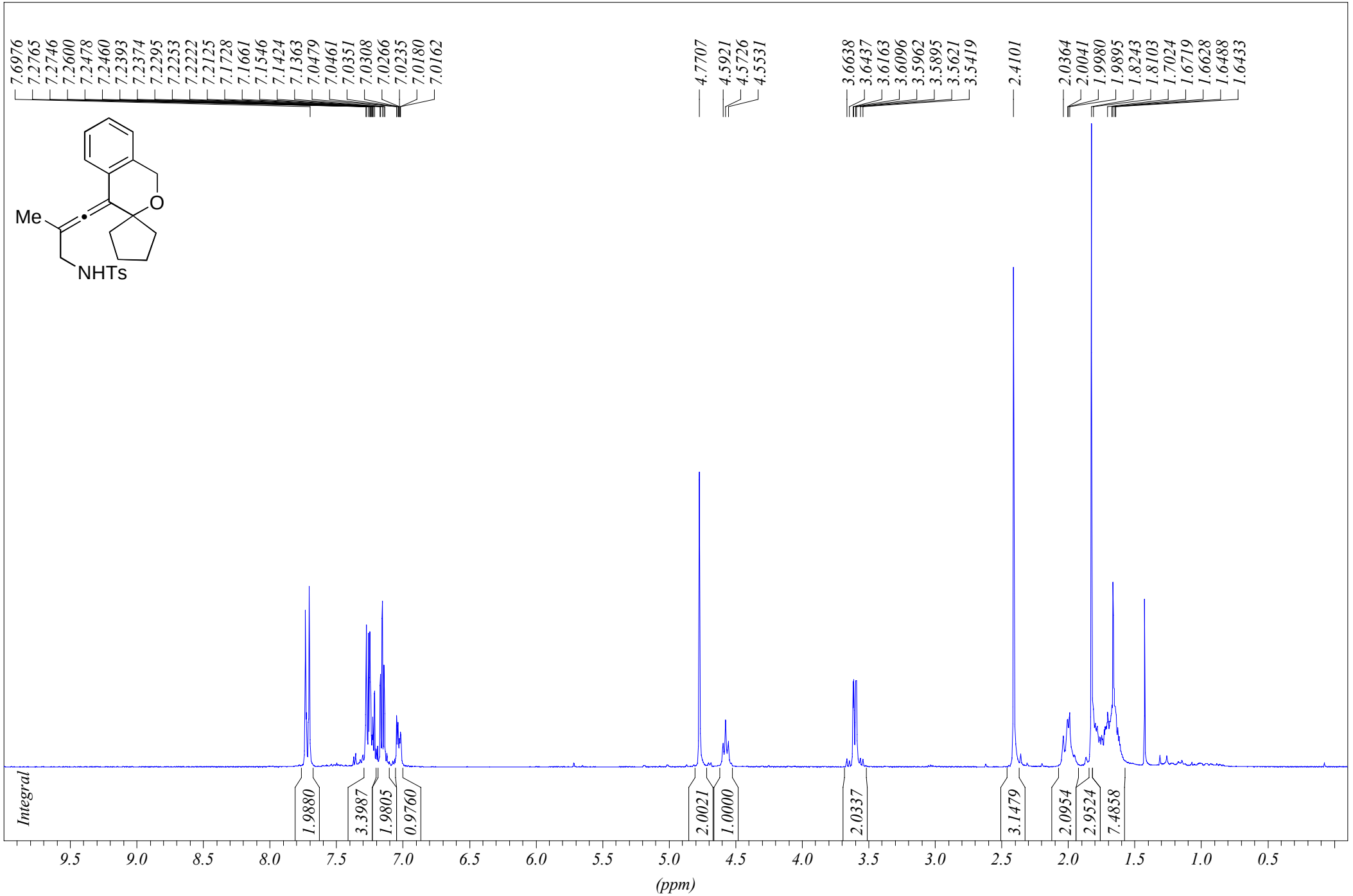
2d



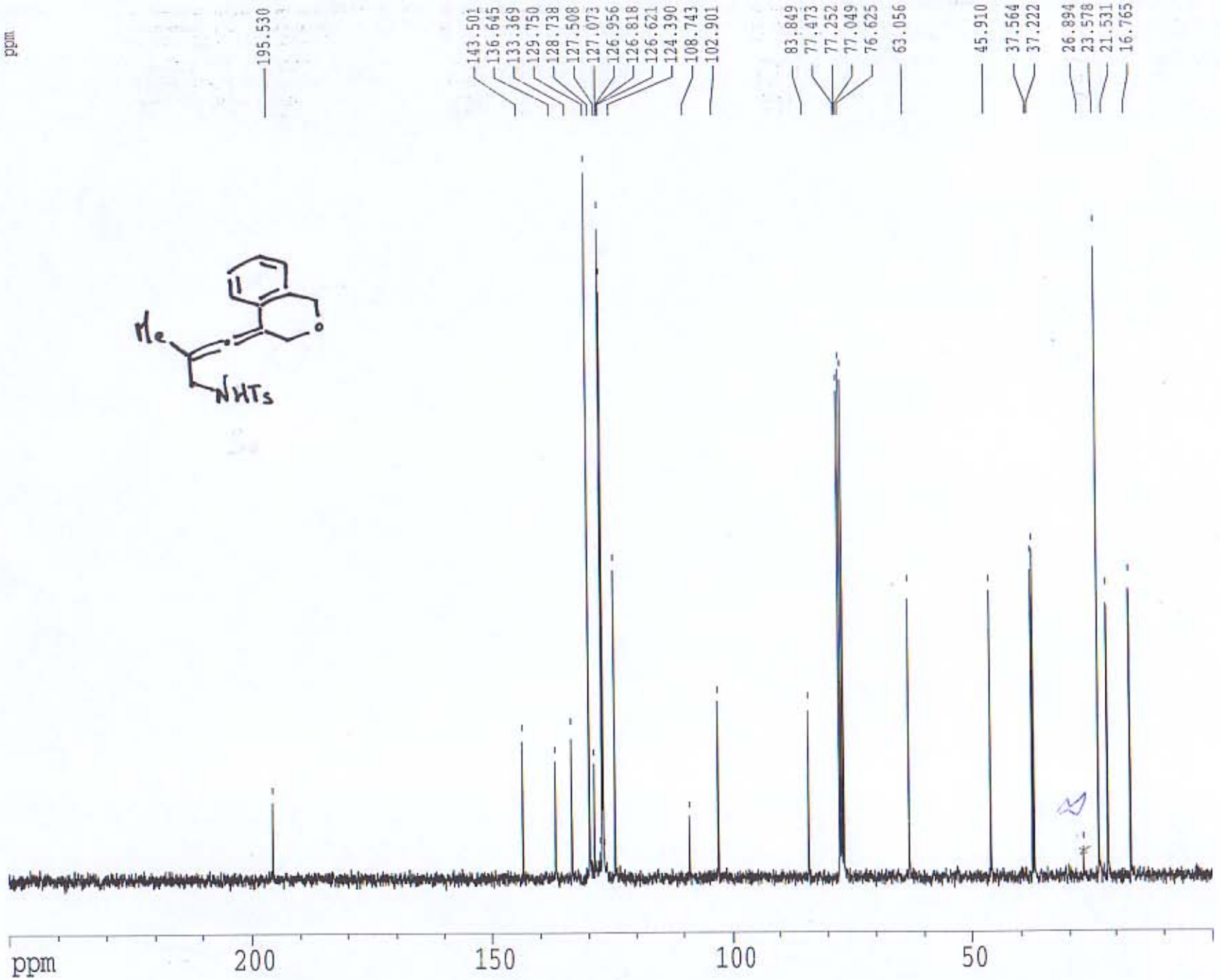
Carbon CDCl3 75 MHz

2d





3e

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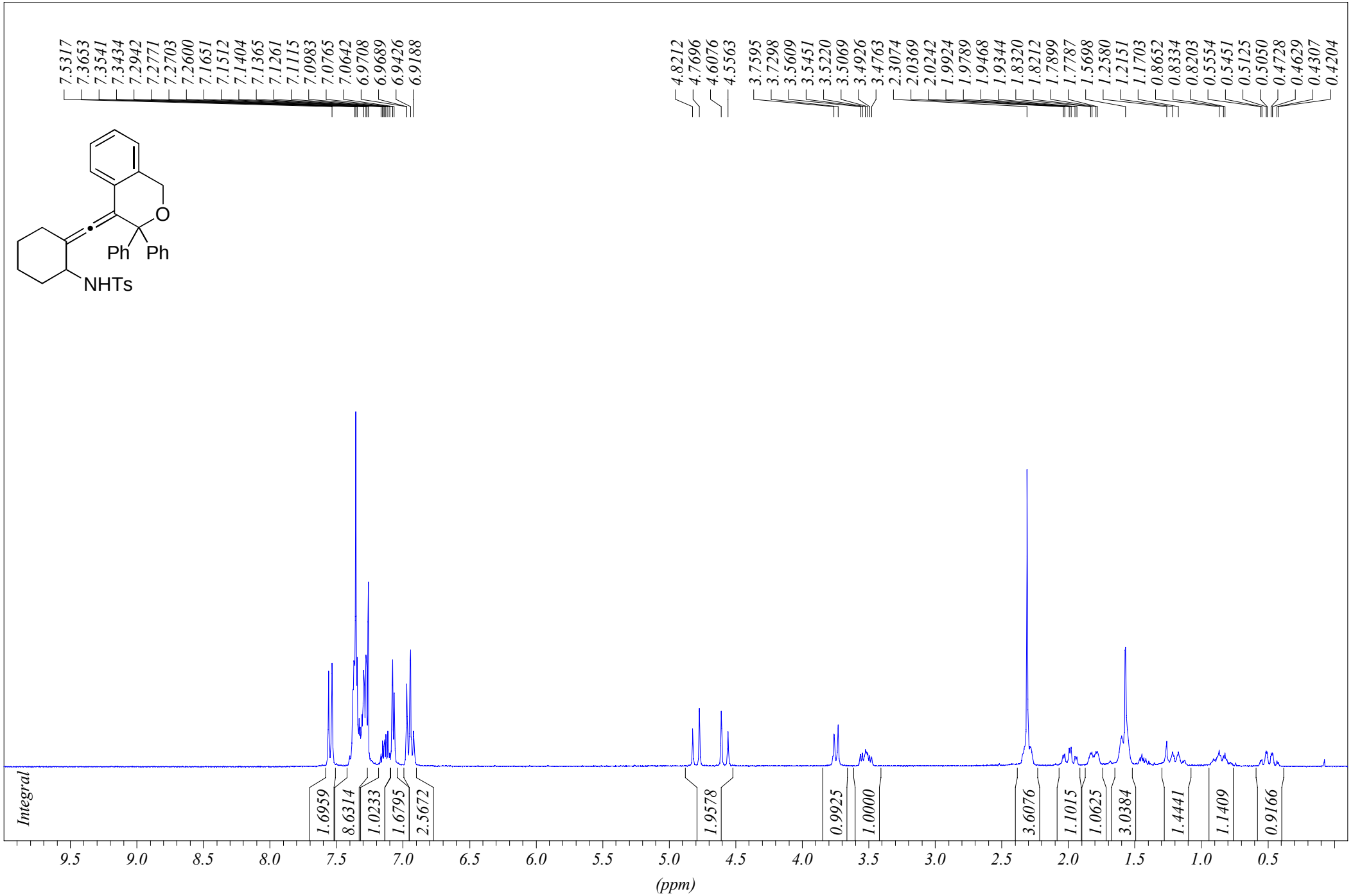
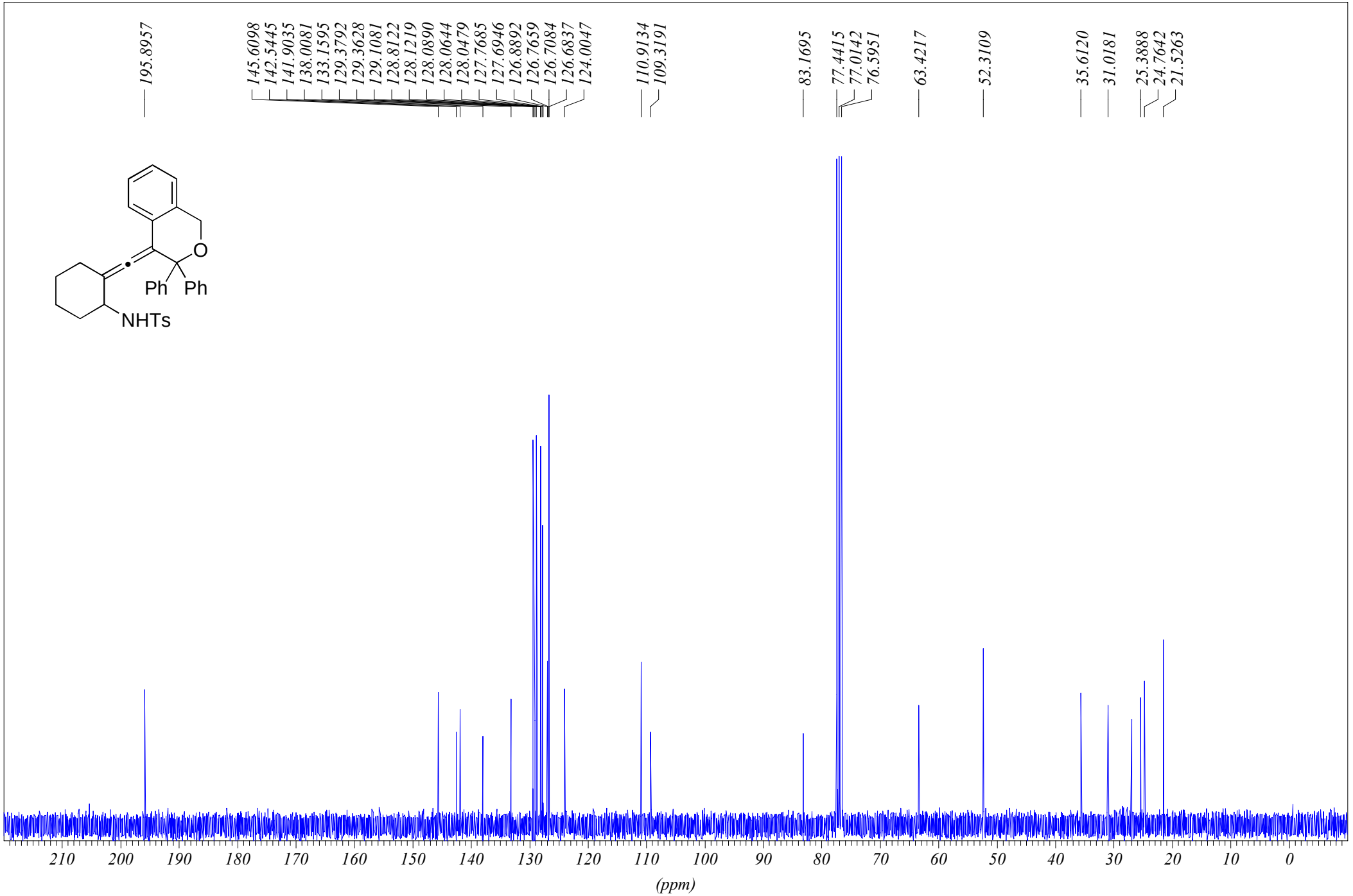
Proton CDCl3 300 MHz

3f-maj



Carbon CDCl3 75 MHz

3f-maj



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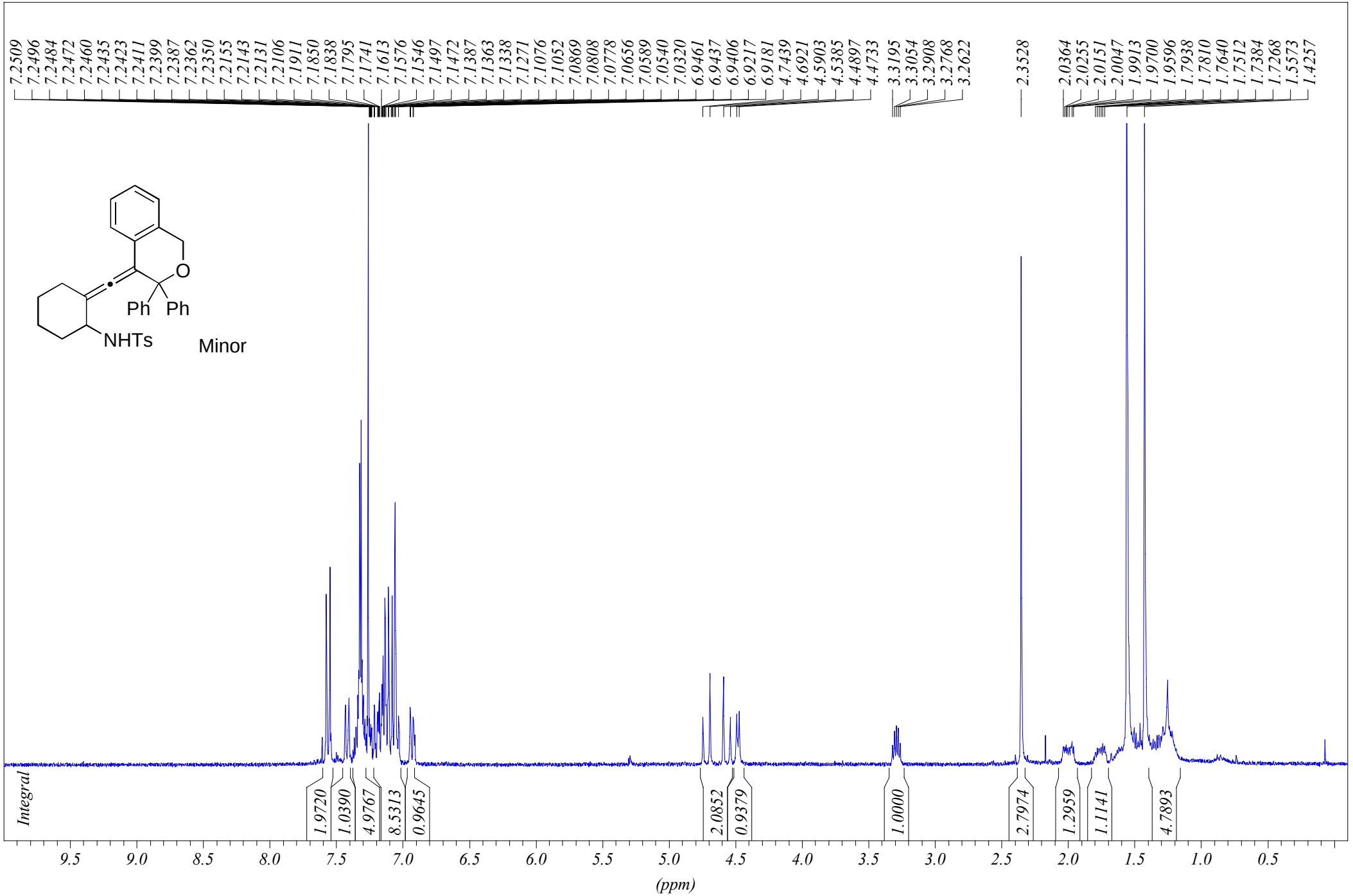
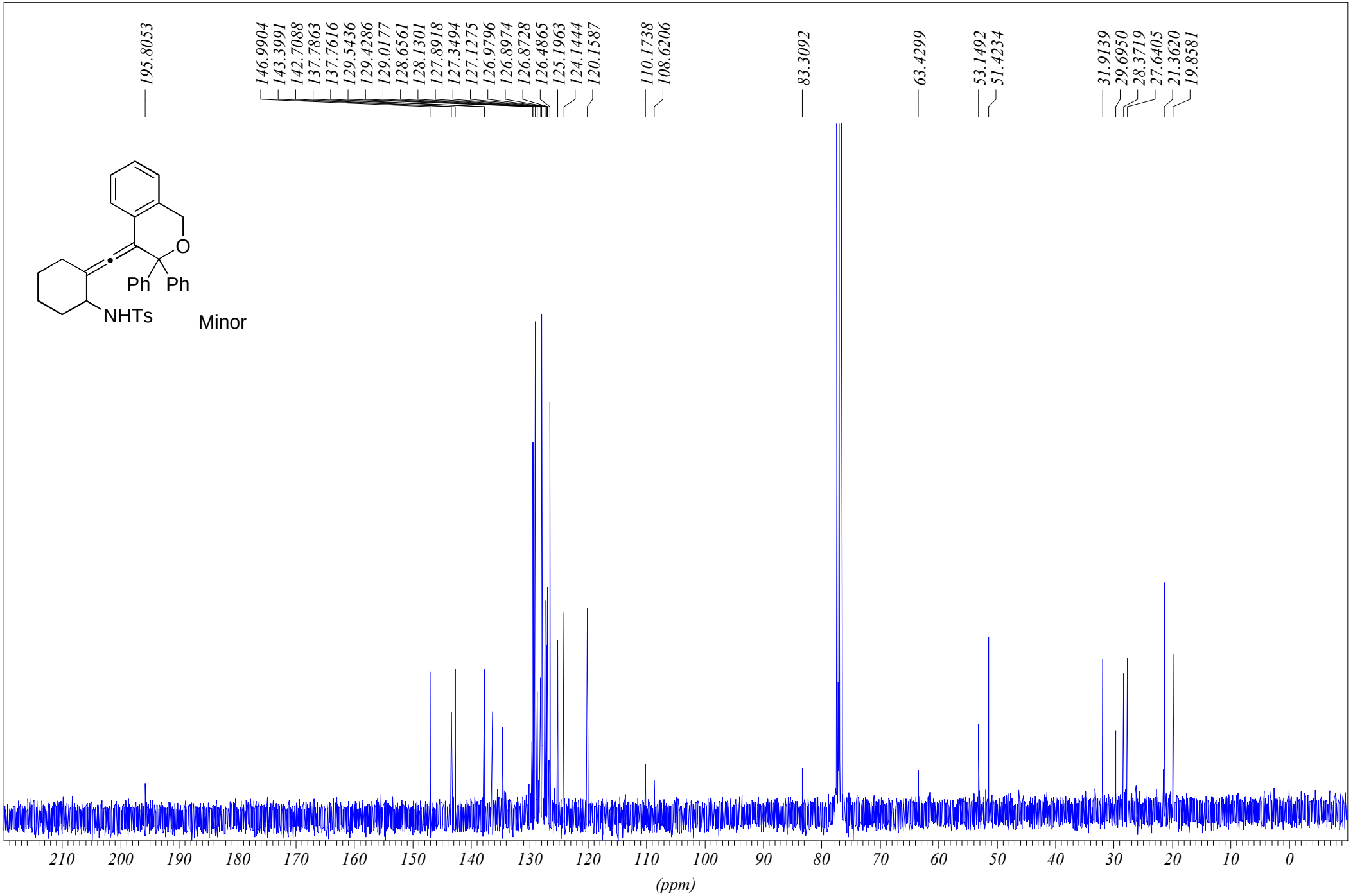


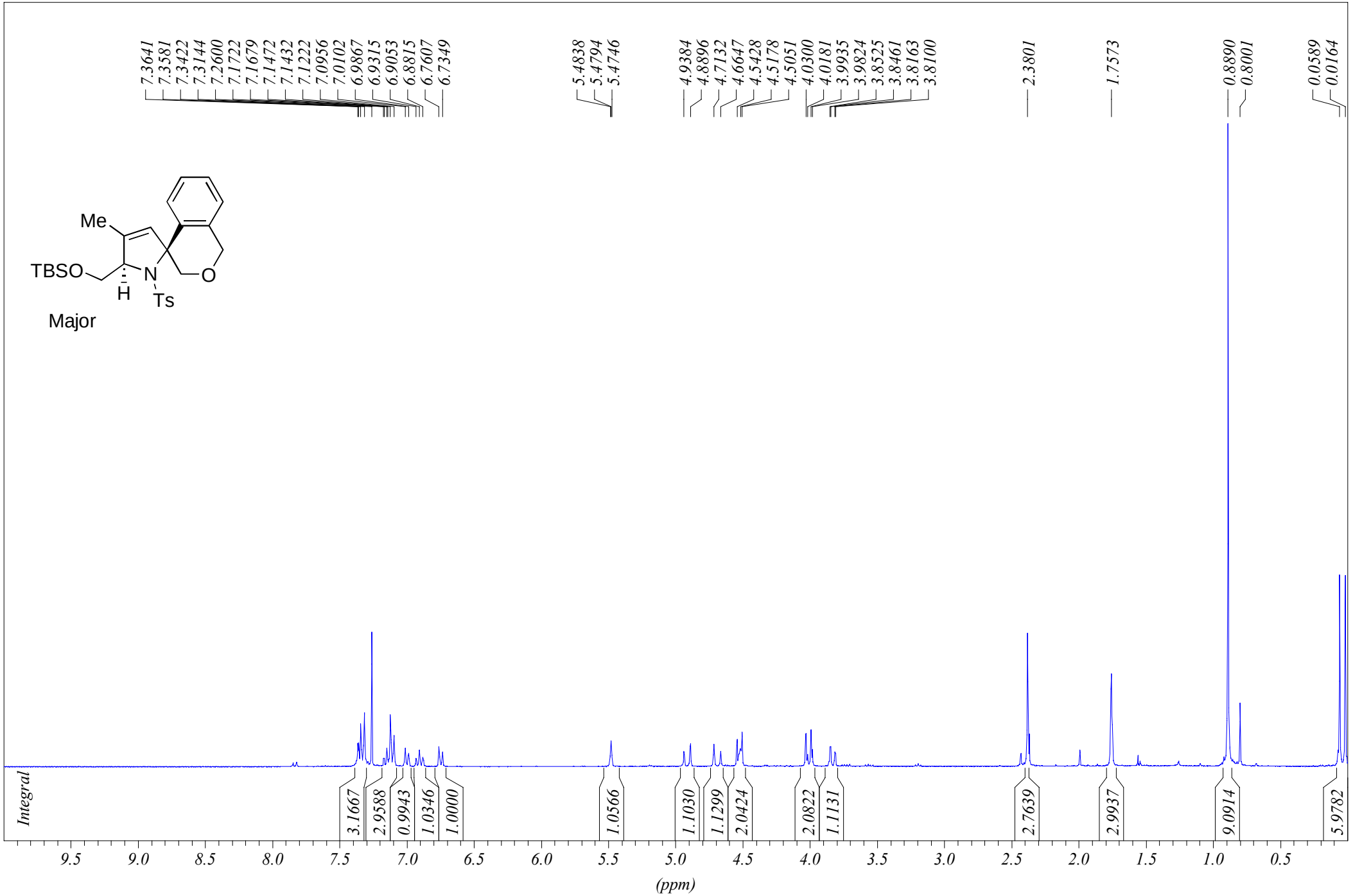
Carbon CDCl3 75 MHz

3f-minor



Proton CDCl3 300 MHz

2g-major



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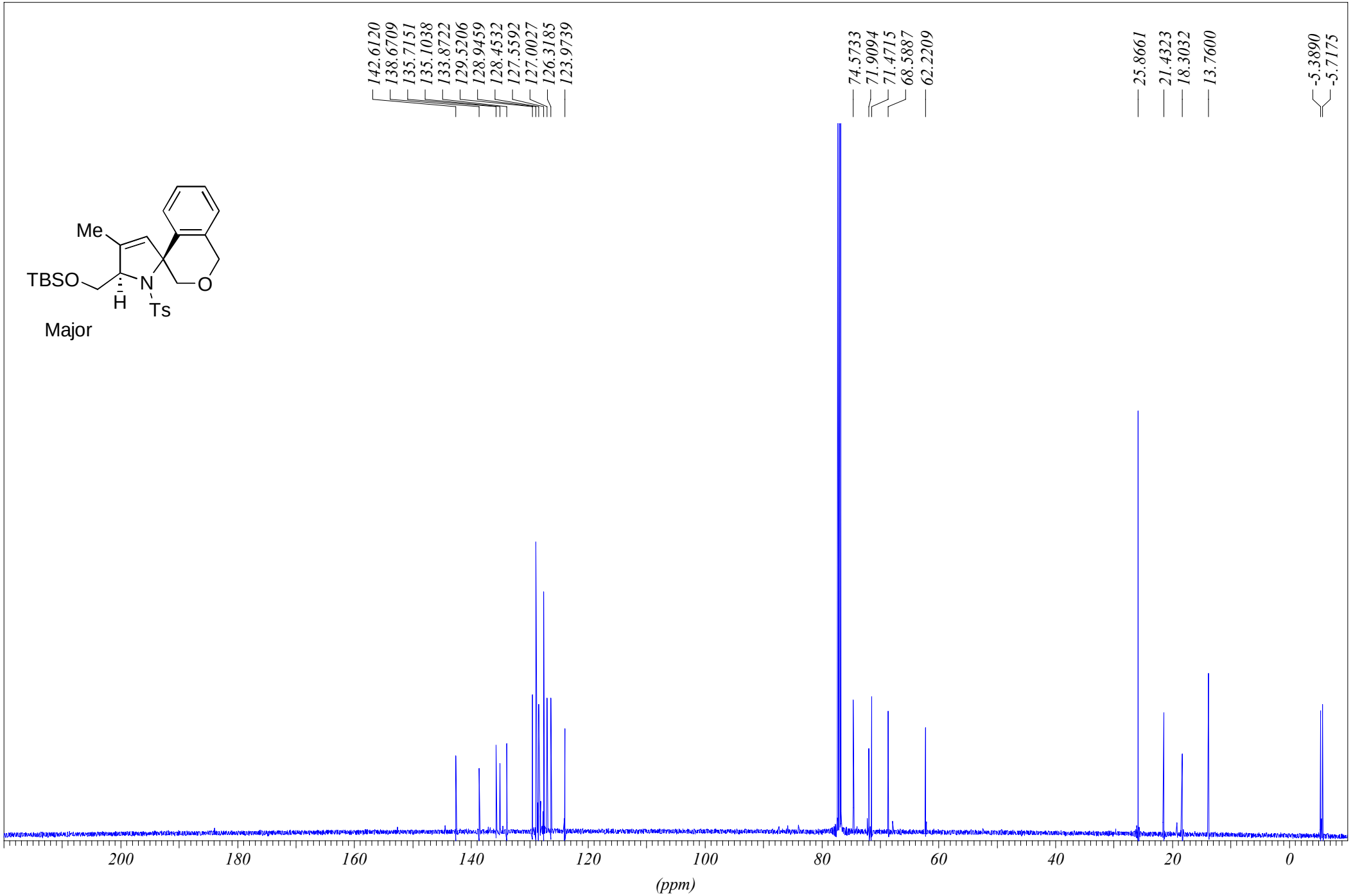
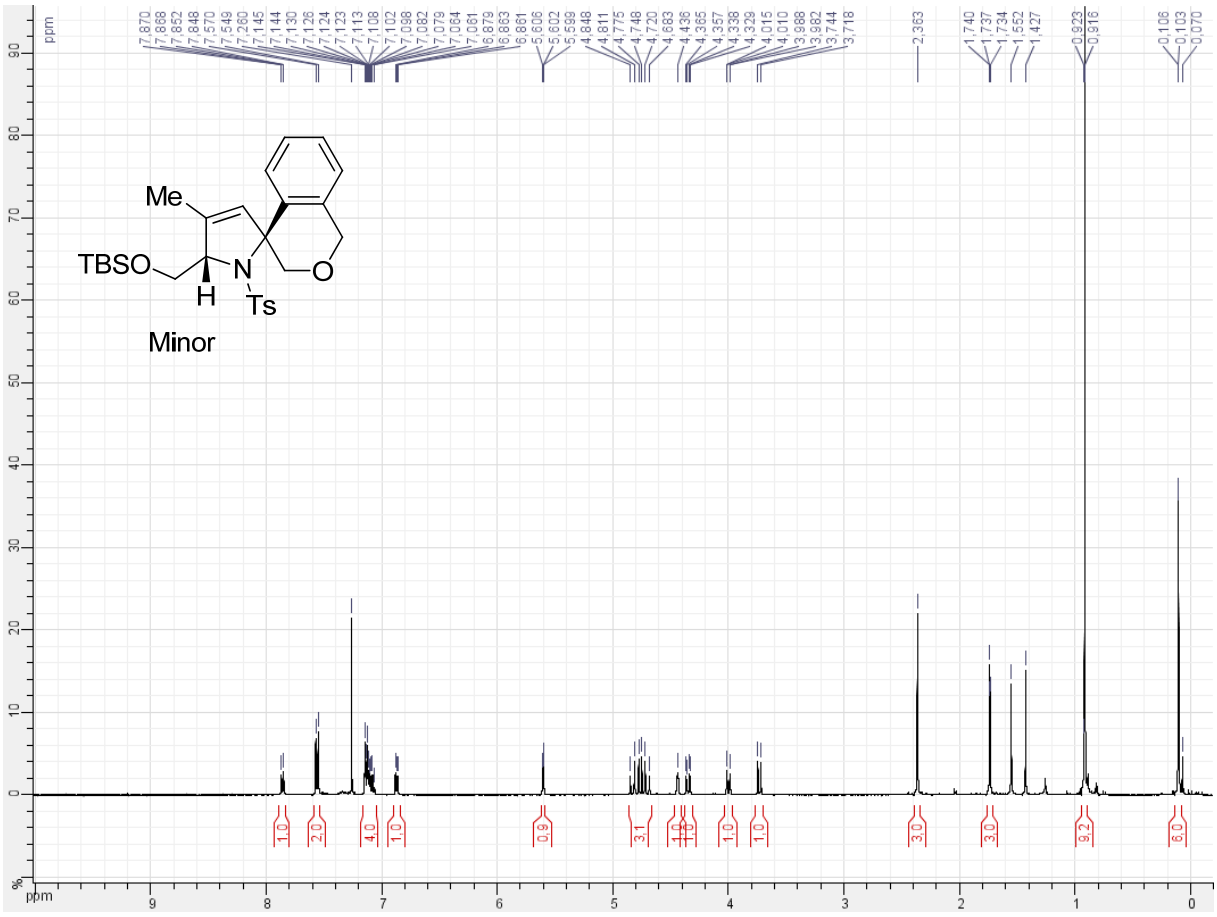
2g-major




Me
TBSO
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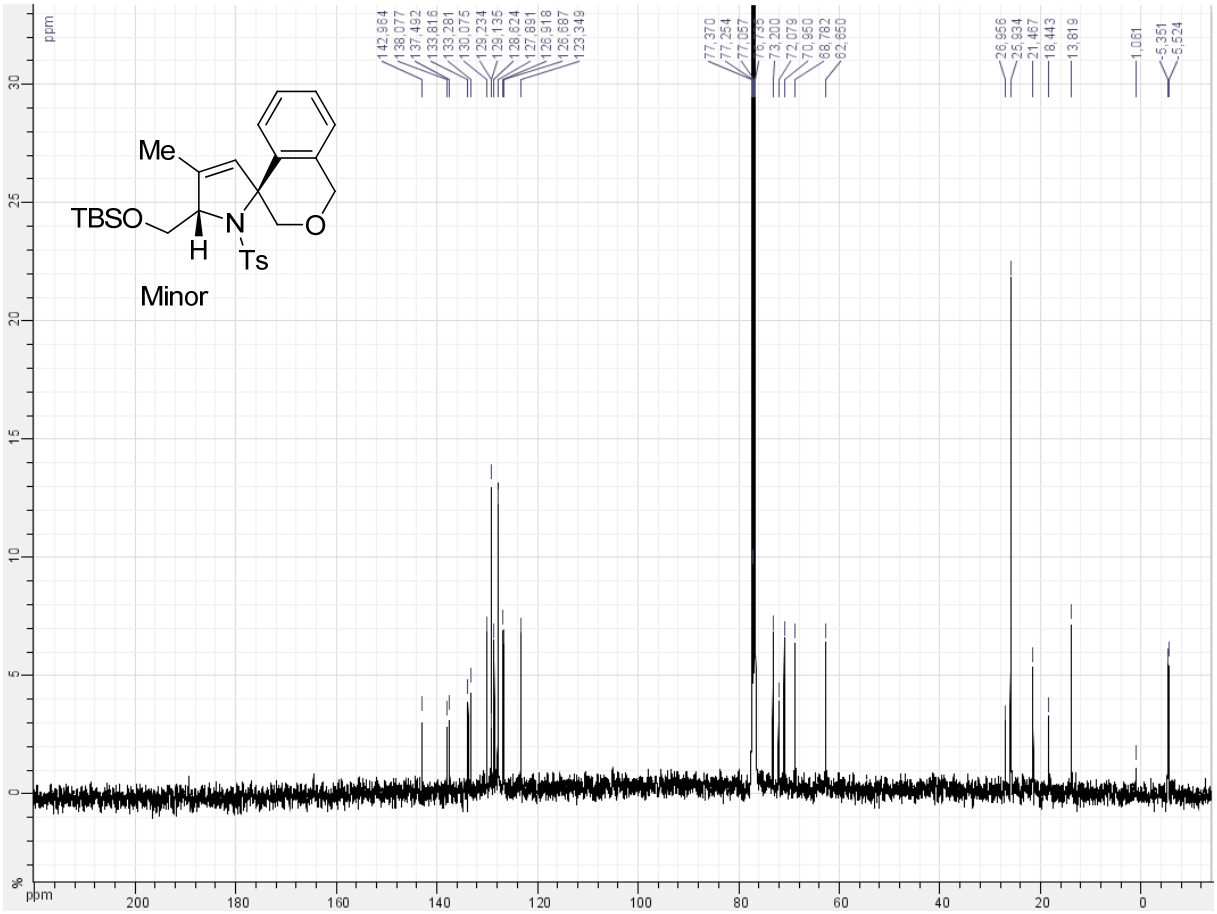
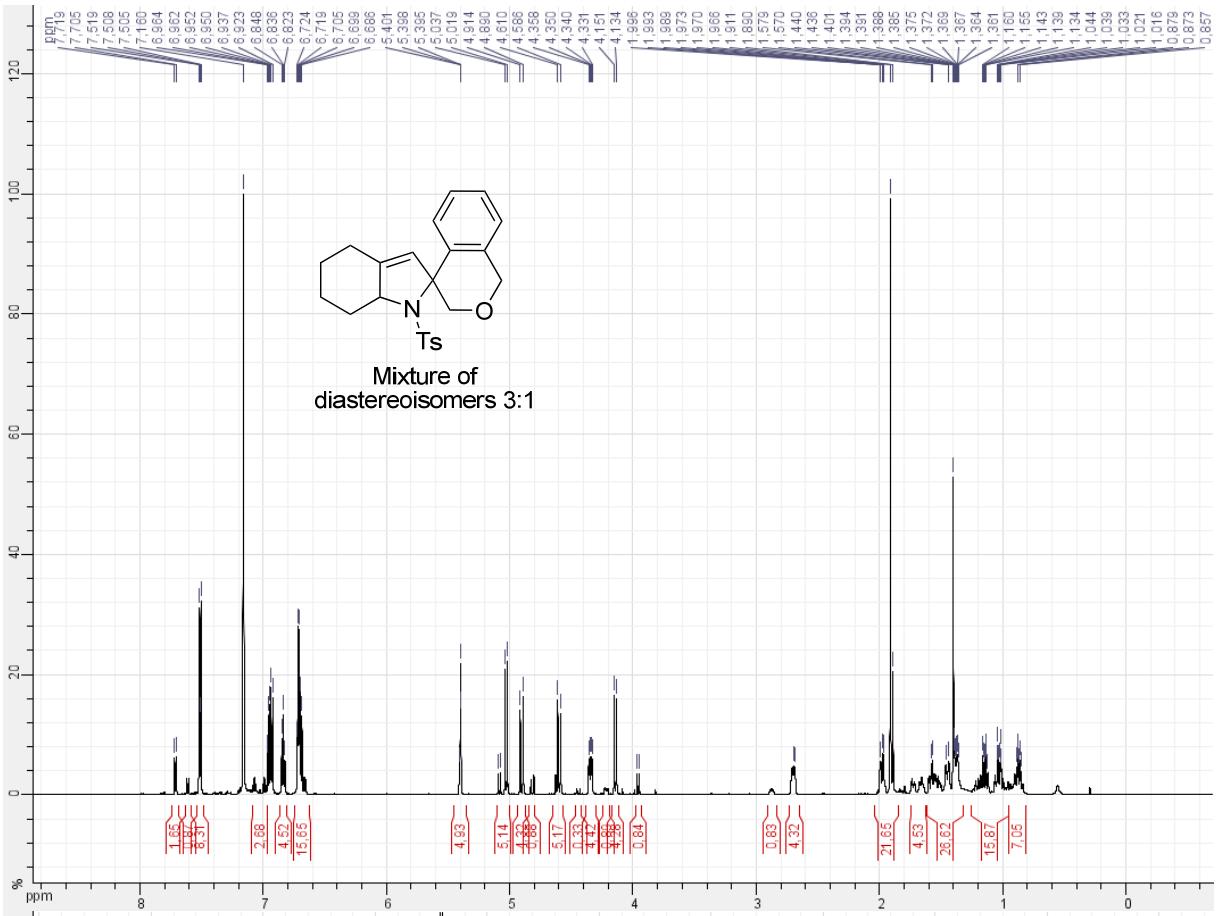
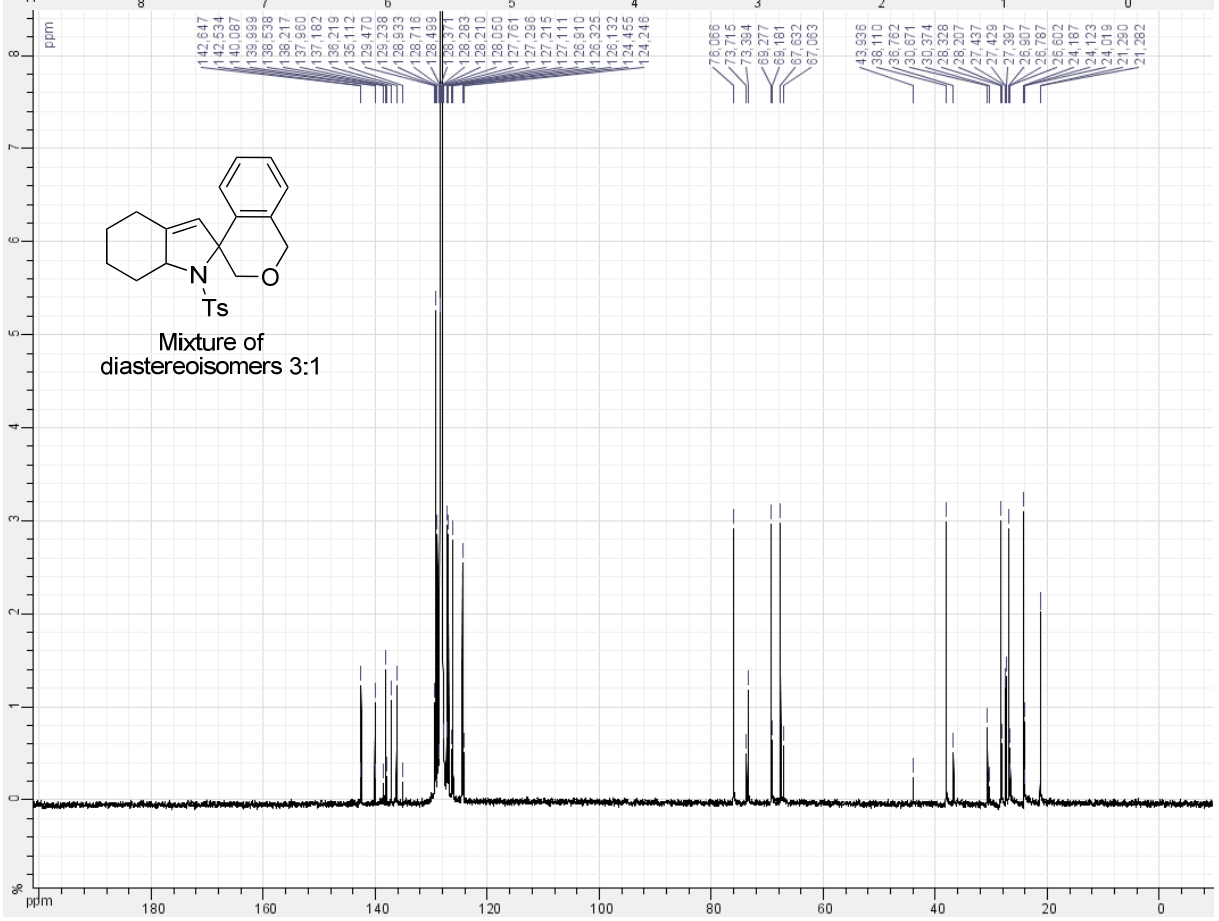
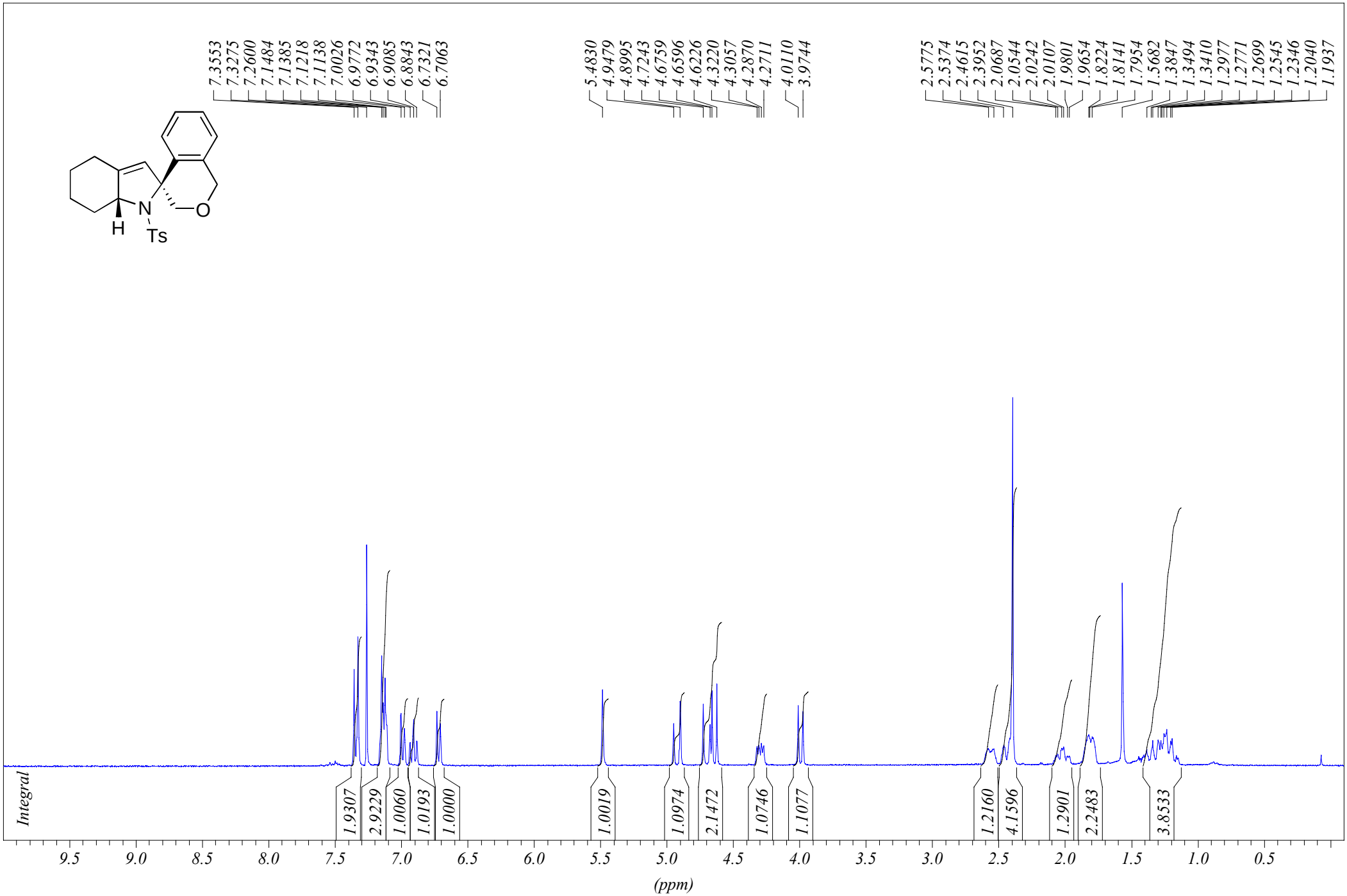
O
H
Ts
Minor


Me
TBSO
N
O
H
Ts
Minor

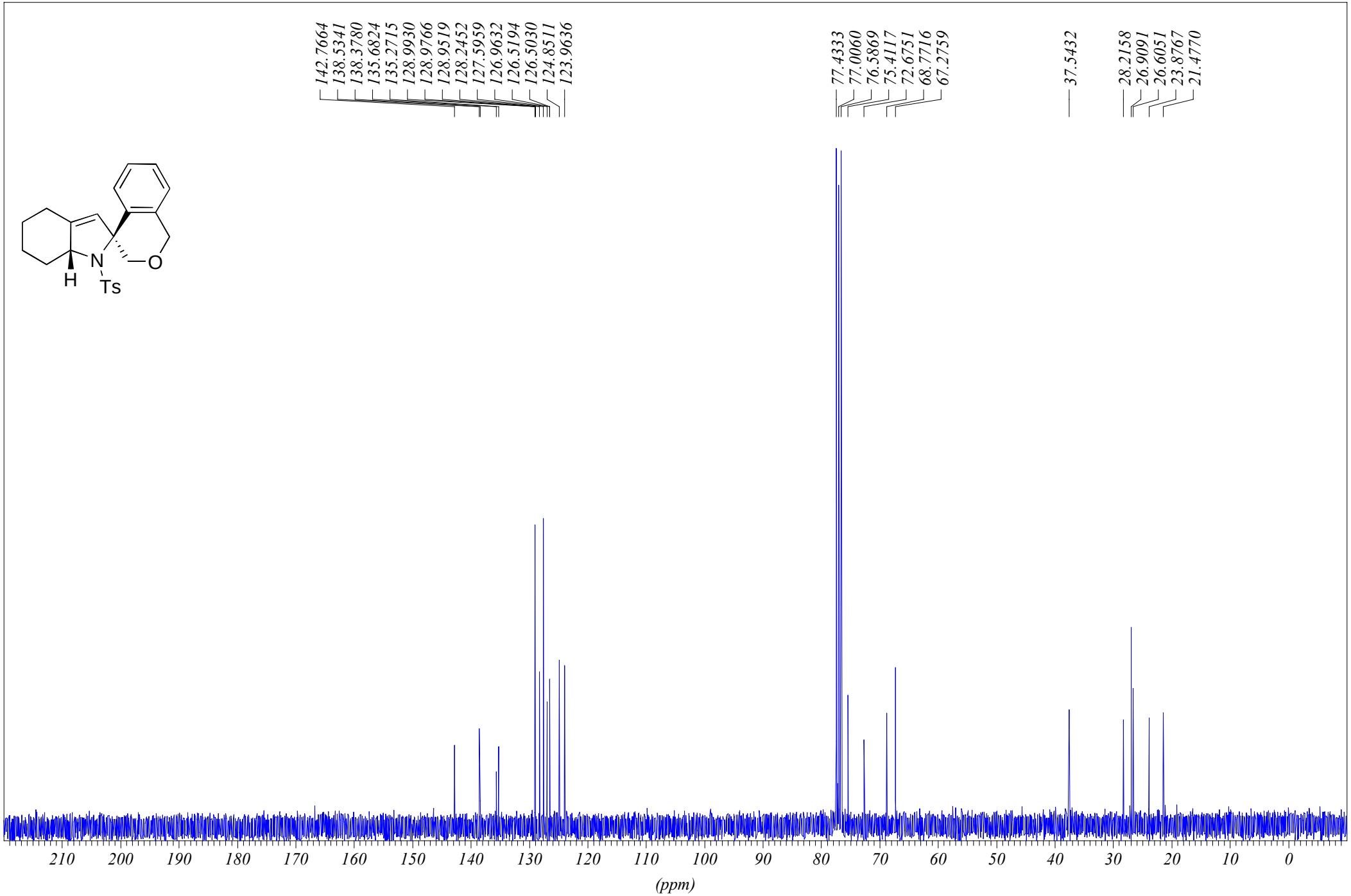

Ts
Mixture of
diastereoisomers 3:1

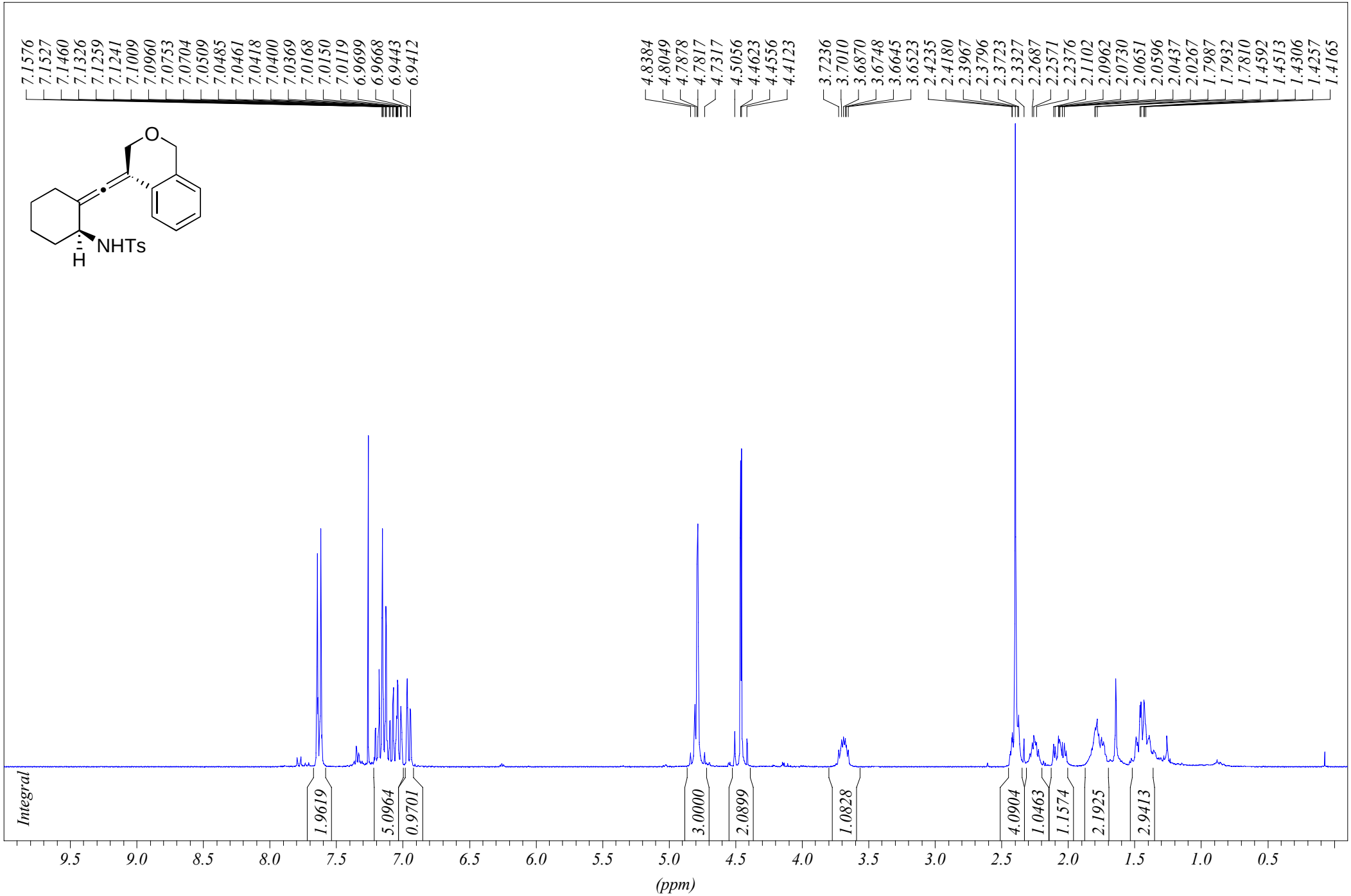

Ts
Mixture of
diastereoisomers 3:1



Carbon CDCl3 75 MHz

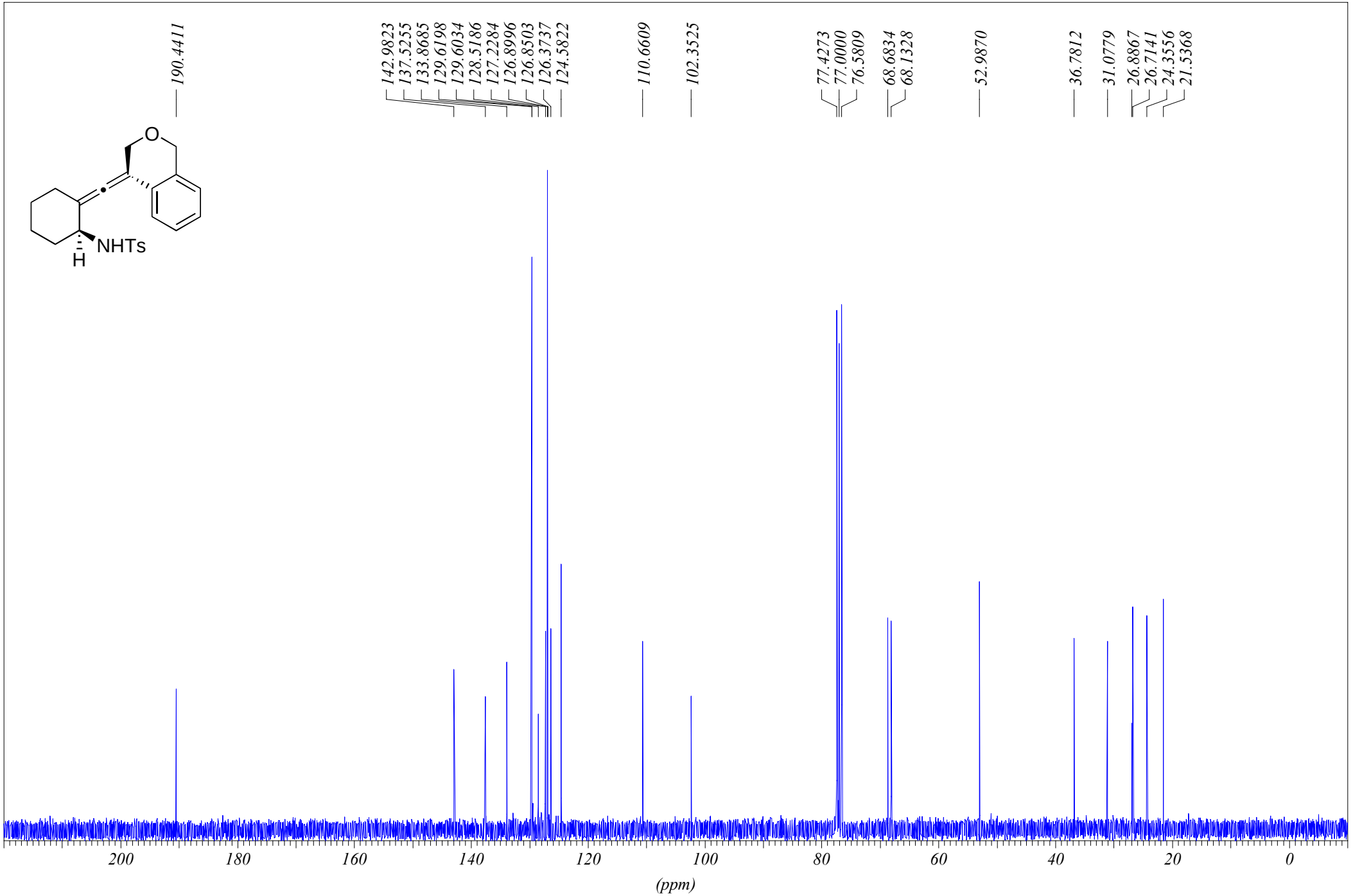
2h-major





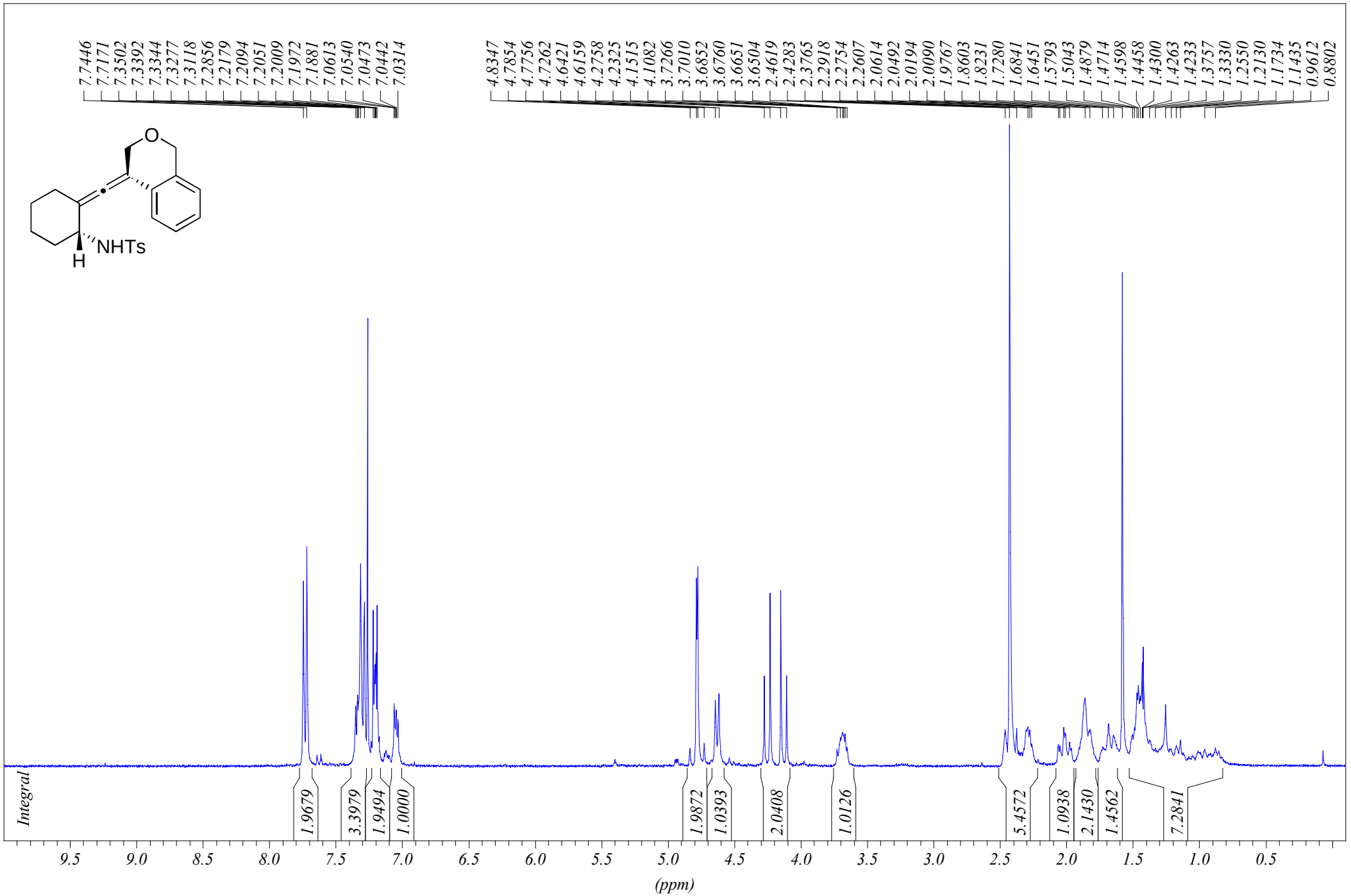
Carbon CDCl3 75 MHz

3h-major



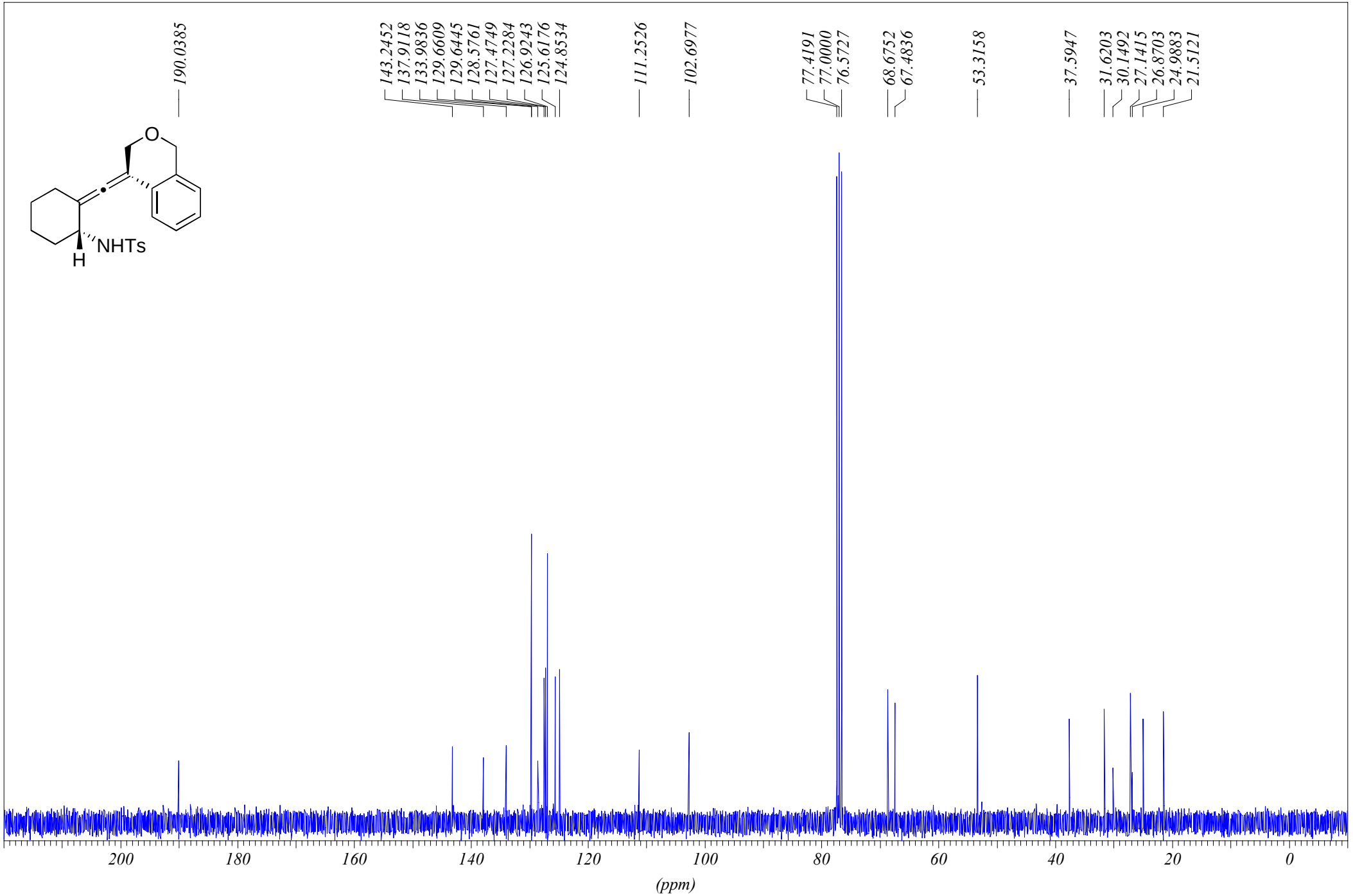
Proton CDCl3 300 MHz

3h-minor



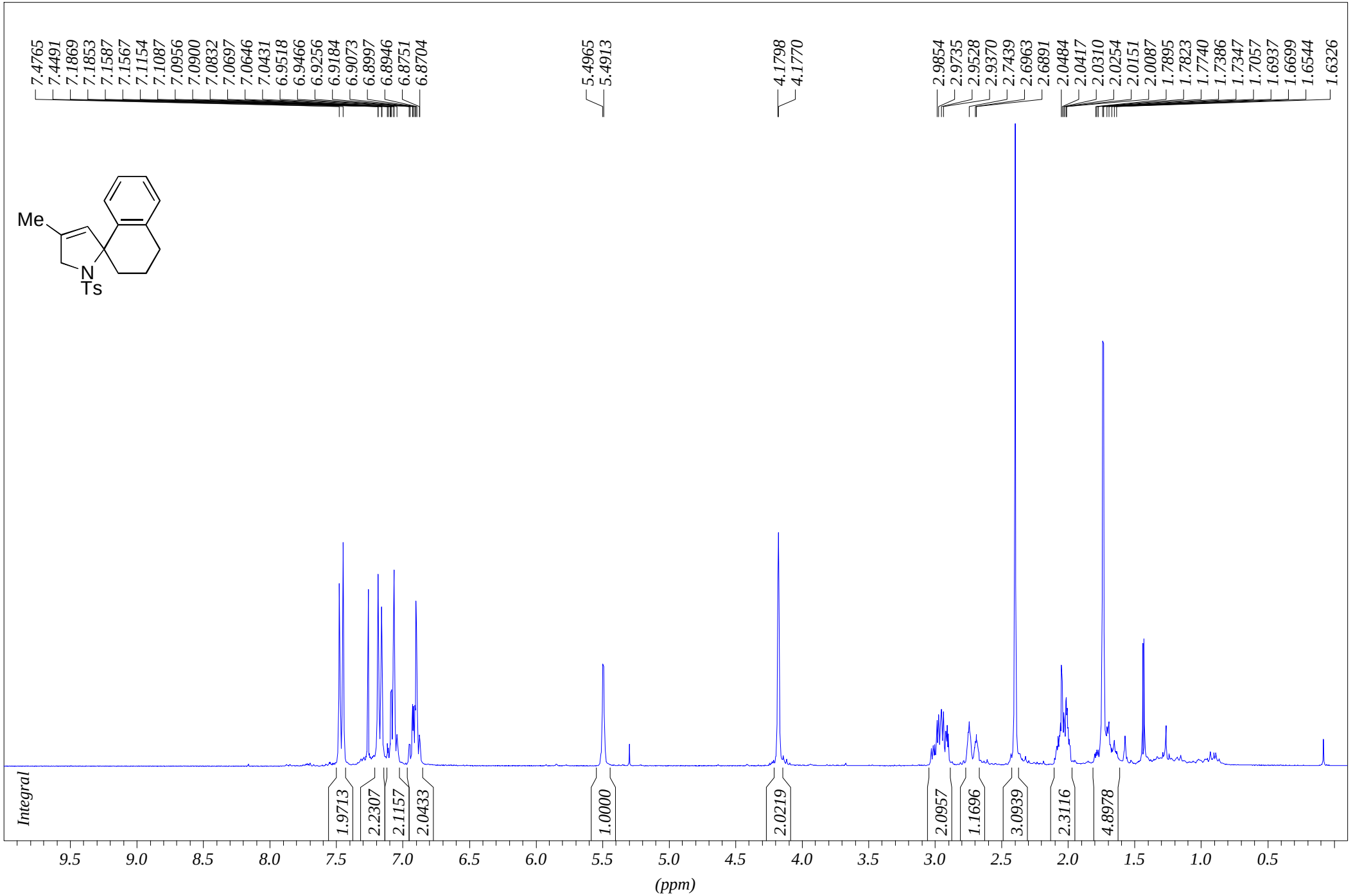
Carbon CDCl3 75 MHz

3h-minor



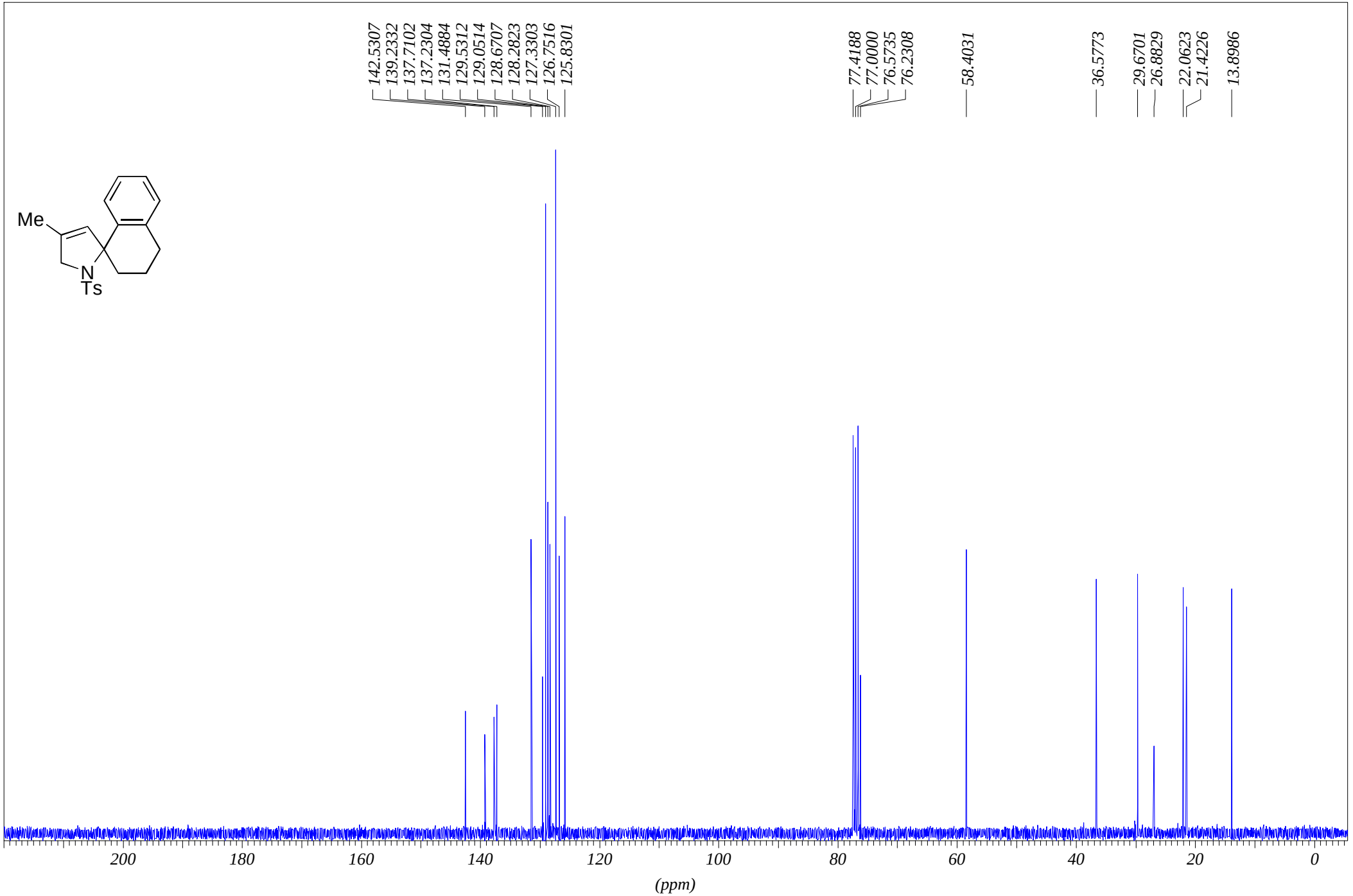
Proton CDCl3 300 MHz

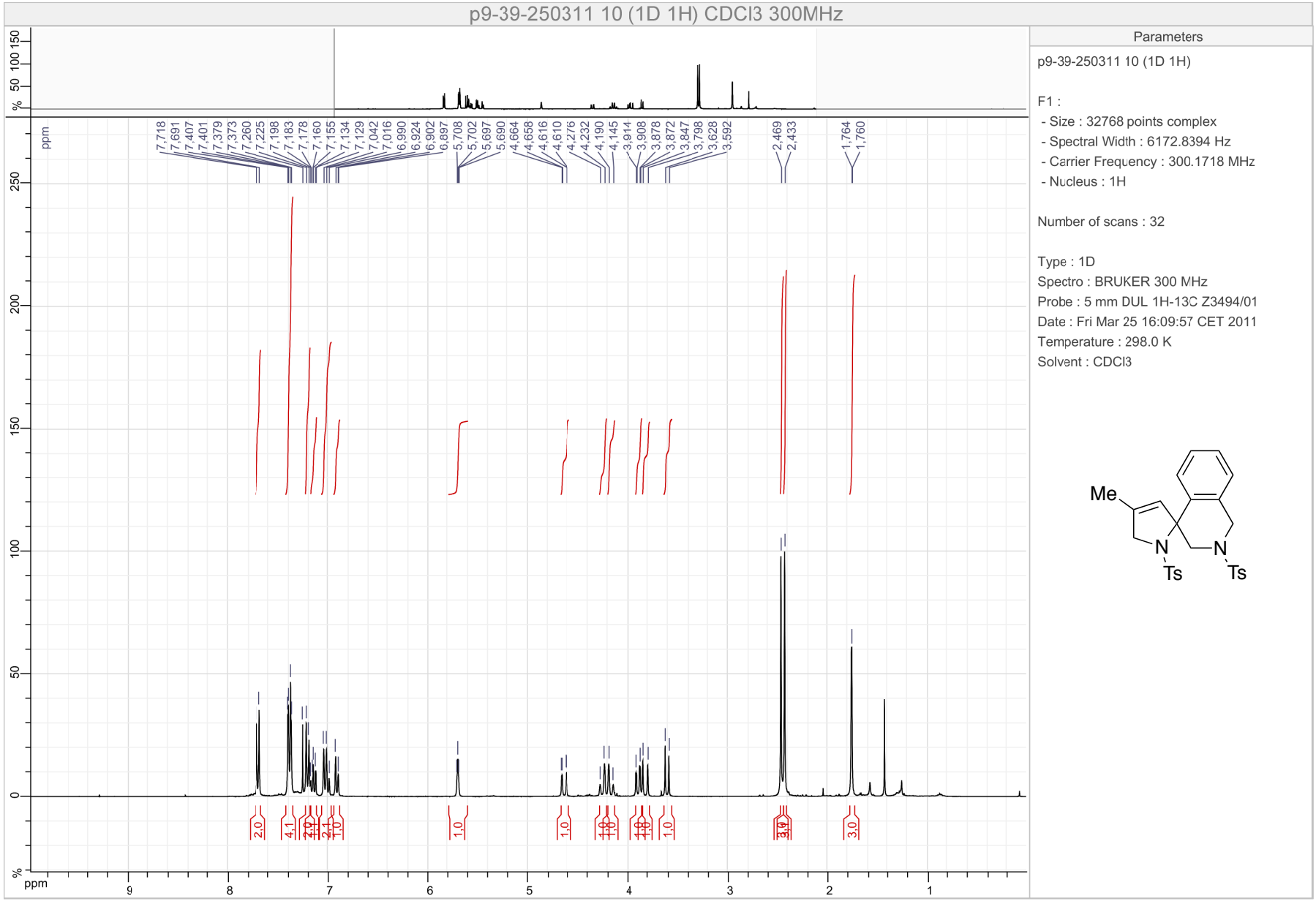
2j



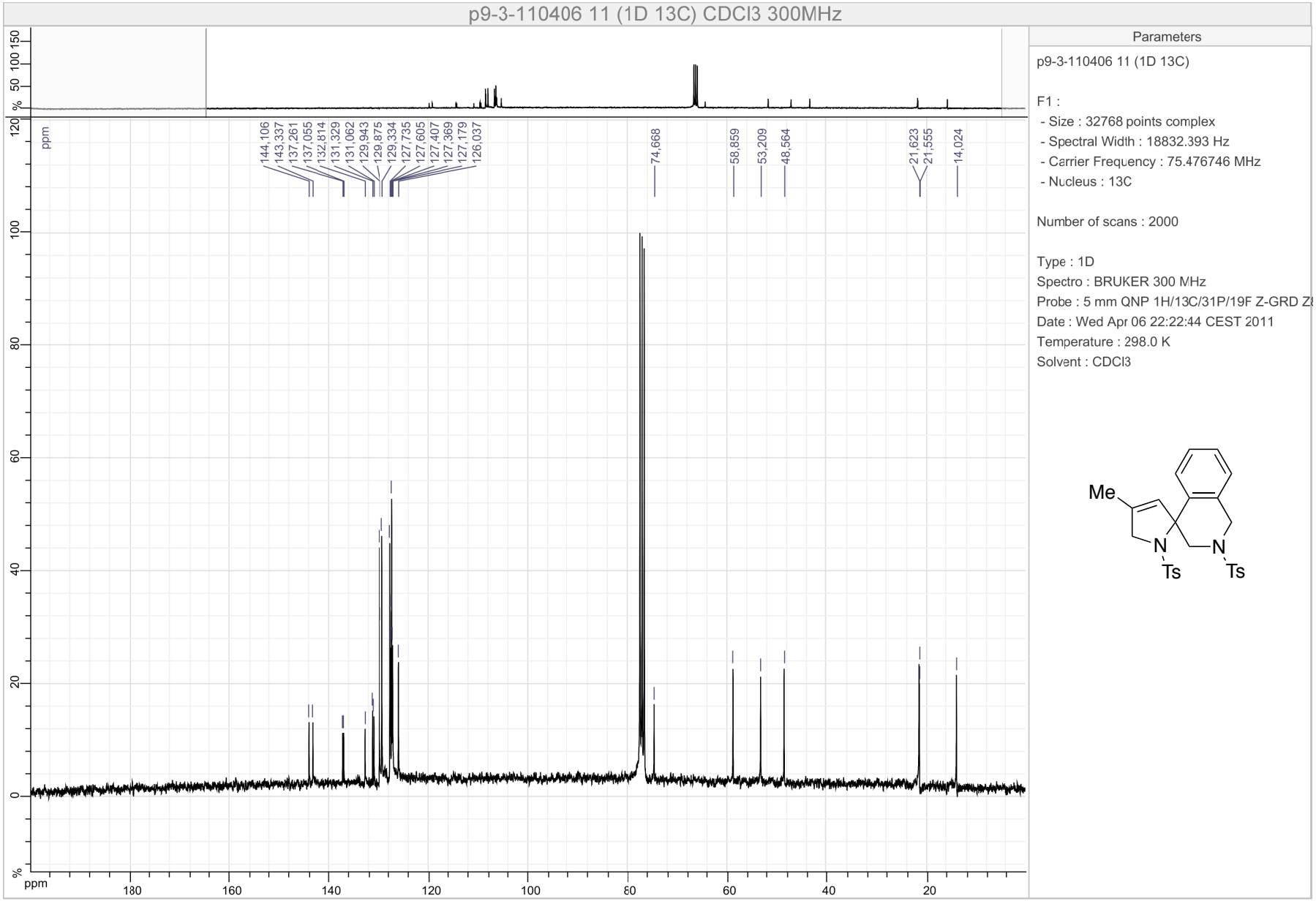
Carbon CDCl3 75 MHz

2j



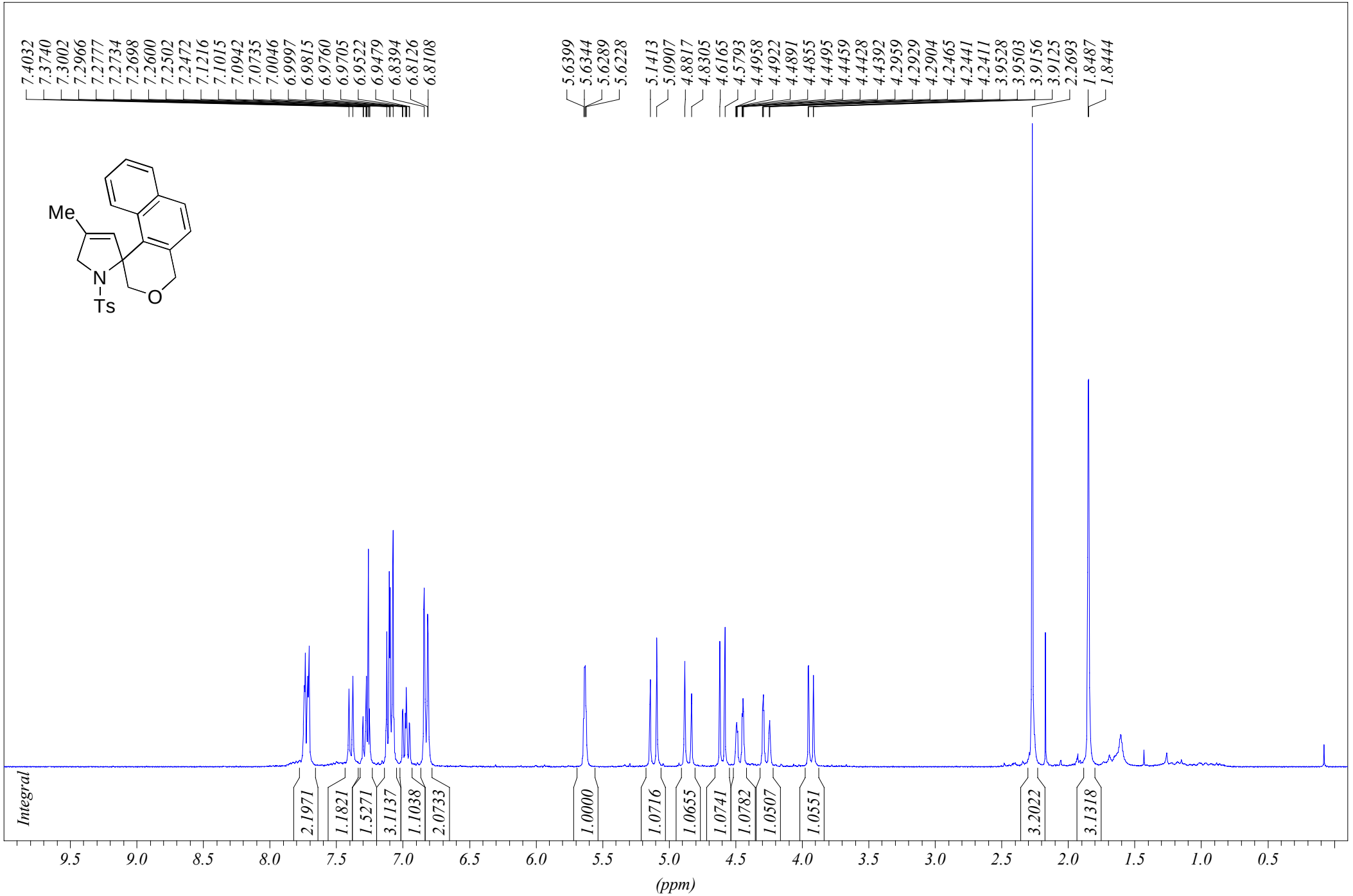


2k **S42**


p9-3-110406 11 (1D 13C) CDCl3 300MHz
Parameters
p9-3-110406 11 (1D 13C)
F1 :
- Size : 32768 points complex
- Spectral Width : 18832.393 Hz
- Carrier Frequency : 75.476746 MHz
- Nucleus : 13C
Number of scans : 2000
Type : 1D
Spectro : BRUKER 300 MHz
Probe : 5 mm QNP 1H/13C/31P/19F Z-GRD Z
Date : Wed Apr 06 22:22:44 CEST 2011
Temperature : 298.0 K
Solvent : CDCl3
144,106
143,337
137,261
137,055
132,814
131,329
131,062
129,943
129,875
129,334
127,735
127,605
127,407
127,369
127,179
126,037
74,668
58,859
53,209
48,564
21,623
21,555
14,024
Me
N
Ts
N
Ts
ppm

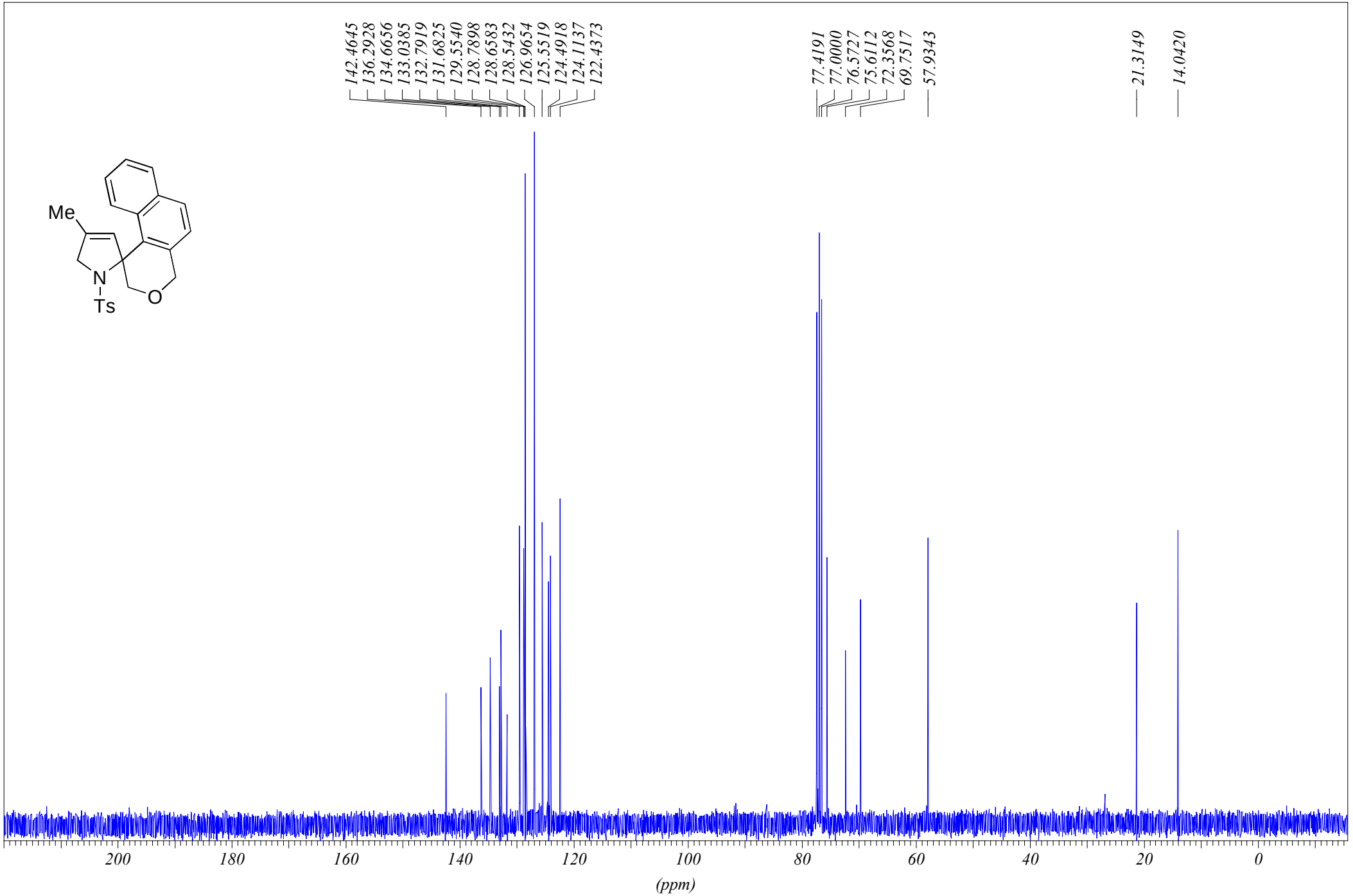
Proton CDCl3 300 MHz

2l



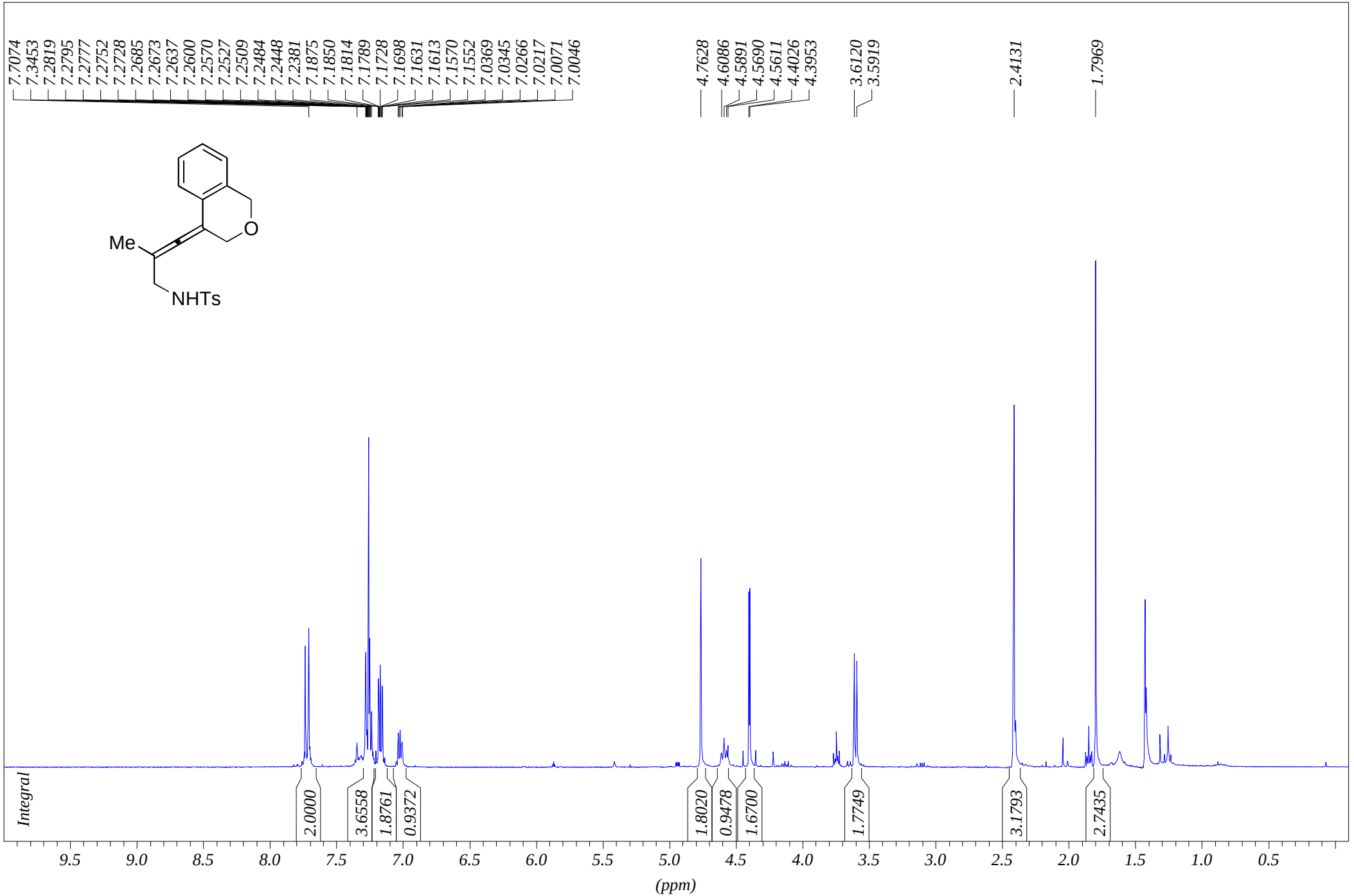
Carbon CDCl3 75 MHz

2l



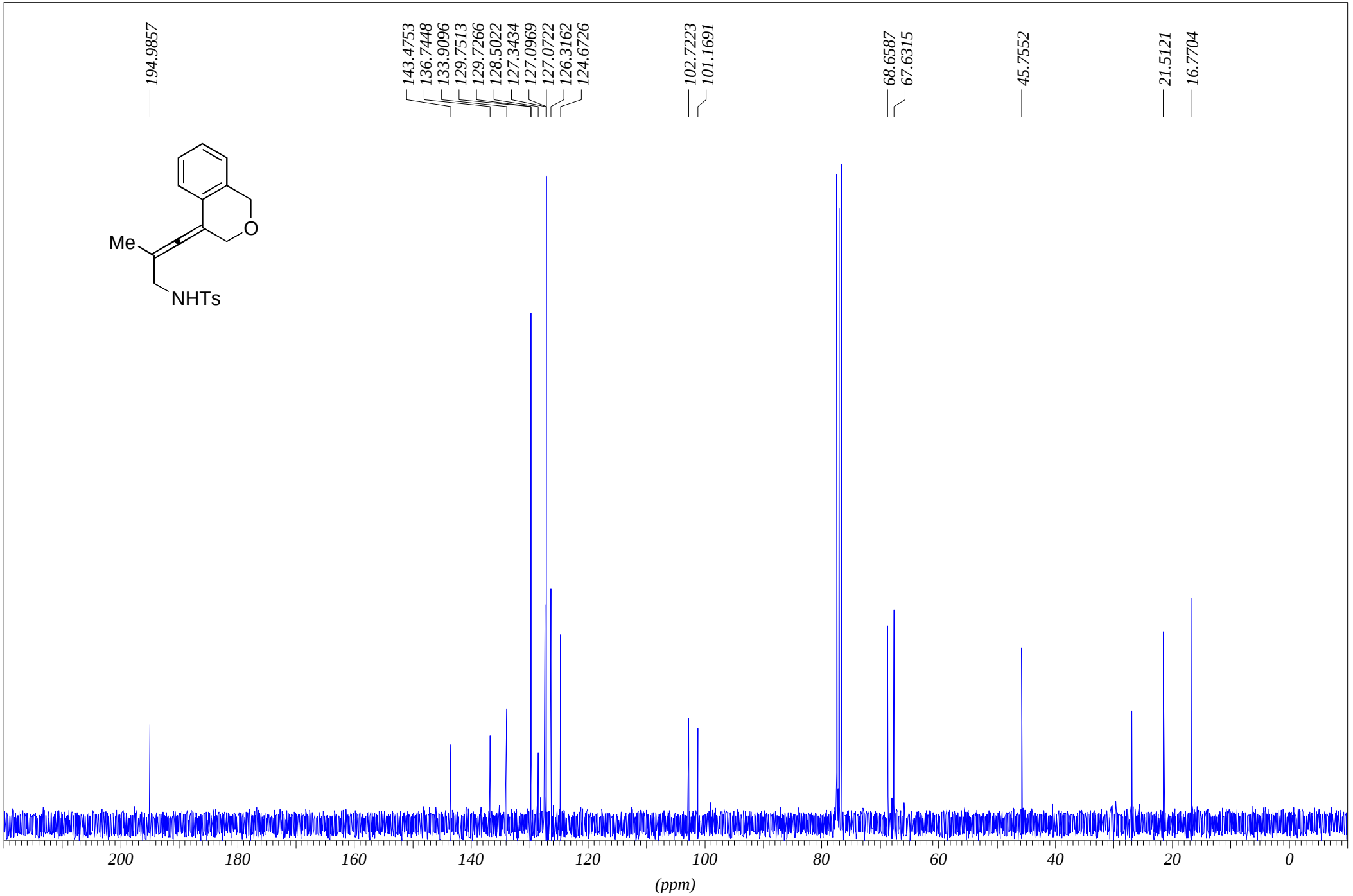
Proton CDCl3 300 MHz

3a



Carbon CDCl3 75 MHz

3a



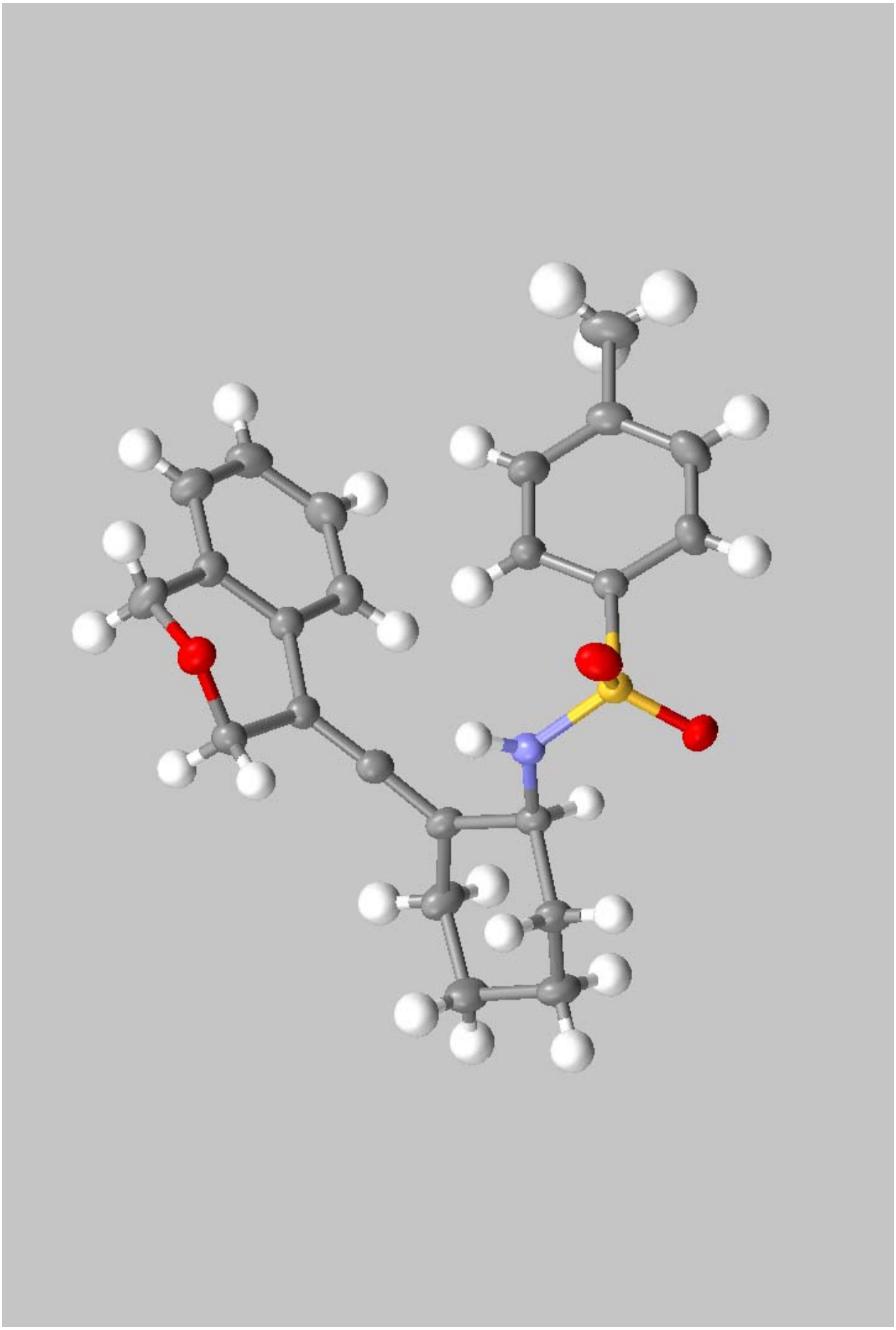
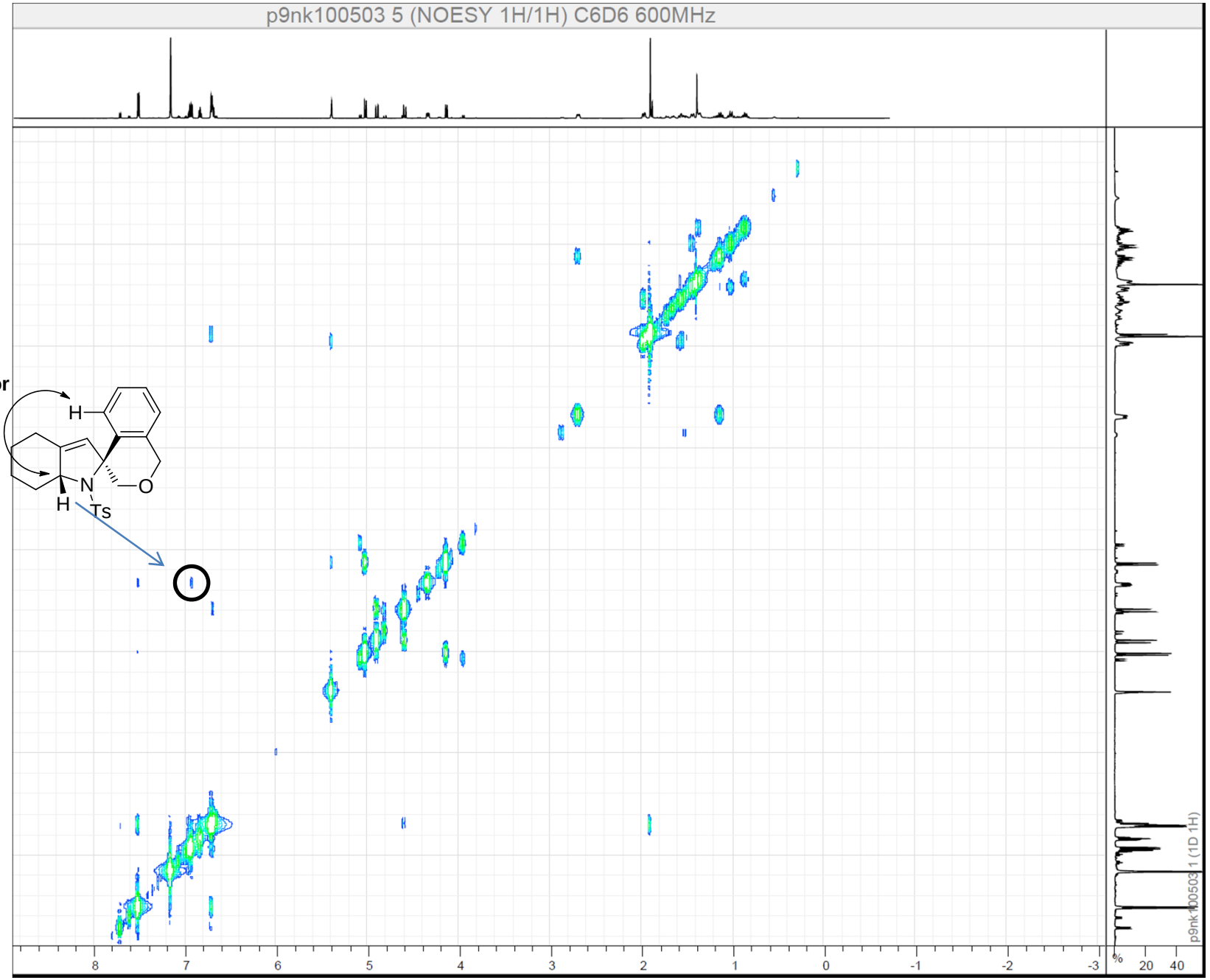


Table of crystal data and refinement details for **3h-maj**:

Formula	$C_{23}H_{25}NO_3S$
Formula weight	395.50
Crystal system	triclinic
Space group	P -1
a (Å)	8.9140(4)
b (Å)	9.2060(5)
c (Å)	13.1630(5)
α (°)	78.806(3)
β (°)	78.180(3)
γ (°)	73.5490(19)
V ($Å^3$)	1003.28(8)
Z	2
Density (g cm^{-3})	1.309
mu (MoKα) (mm^{-1})	0.185
F(000)	420
Data collection	
Temperature (K)	173(2)
Radiation (Å)	MoKα - 0.71073
Theta min - max	1.60 - 30.06
Dataset[h, k, l]	-12/12, -12/12, -18/18
Tot., Uniq. Data, R(int)	8282, 5843, 0.0235
Observed data (>2σ(I))	4234
Refinement	
Nreflections, Nparameters	5843, 253
R2, R1, wR2, wR1, Goof	0.0810, 0.0509, 0.1801, 0.1440, 1.082
Max. and Av. Shift/Error	0.000, 0.000
Min, Max. Resd Dens. (e-/$Å^3$)	-0.614, 0.440


p9nk100503 5 (NOESY 1H/1H) C6D6 600MHz
NOE
2h-major
H
N
O
H
Ts
8
7
6
5
4
3
2
1
0
-1
-2
-3
%
20
40
p9nk100503 1 (1D 1H)