

Supporting Information

A One-Pot “Back-to-Front” Approach for the Synthesis of Benzene Ring Substituted Indoles Using Allylboronic Acids

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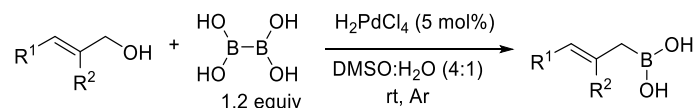
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Experimental Section:

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen atmosphere. THF was obtained from Merck India, and was freshly distilled over Na-benzophenone under nitrogen. All other solvents were also obtained from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light and dipping into KMnO₄ solution. Silica gel (particle size 100-200 mesh) was purchased from SRL India for performing column chromatography by using mixture of hexane and ethylacetate eluent. NaH (60% dispersion in mineral oil), indole-2-carboxylic acid and indole-3-carboxaldehyde were received from Spectrochem Pvt. Ltd and used as received. Pyrrole was received from Sigma Aldrich. The ¹H NMR spectroscopic data were recorded with a Bruker 400, 500 or 600 MHz instruments. ¹³C NMR spectra were similarly recorded at 101, 126, 151 MHz NMR Machines, using a broadband decoupled mode. Proton and carbon signals are reported relative to the residual signal present in CDCl₃ (δ= 7.26, 77.16) and DMSO-*d*₆ (δ= 2.50, 39.52). Coupling constant (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets, m: multiplet. Infrared (IR) spectra were recorded by Perkin Elmer ATIR spectrometer, and reported in terms of wave number (cm⁻¹). High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method.

Synthesis of allylic alcohols: All the allylic alcohols were synthesized according to known literature procedure.¹

General Procedure (GP I): The Synthesis of Allylboronic Acids:^{2,3}



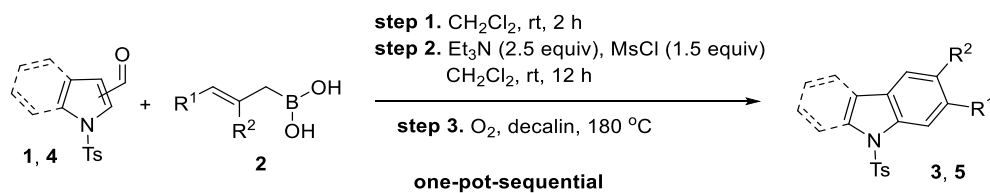
A 10 mL two neck round bottom flask was charged with allyl alcohol (2.0 mmol) and the flask was then backfilled with nitrogen thrice. Then DMSO (1.6 mL) and H₂O (0.4 mL) were added to it and the resulting reaction mixture was stirred for 2 minutes. Next, freshly prepared catalyst H₂PdCl₄ (0.3 M, 0.34 mL, 0.05 mmol) and diboronic acid (216 mg, 2.4 mmol, 1.2 equiv) were added sequentially, and the reaction mixture was stirred at room temperature for another 2 to 24 hours. Upon complete consumption of allyl alcohol as evidenced by TLC (*p*-anisaldehyde stain), reaction mixture was allowed to settle down over 2 to 3 hours for the complete sedimentation of Pd. Then the crude mixture was transferred via syringe to a 25 mL round bottom flask under nitrogen (*Note: For some boronic acids which are unstable under air, the reaction mixture was filtered through HPLC Teflon filter immediately after the completion of reaction*). Then the filtered crude allyl-boronic acid was washed by using 8 mL of degassed chloroform followed by 8 mL of degassed 16% aq. NaCl solution (repeated four times). The mixture was stirred under argon for 1 min. After separation of the two layers, the organic layer was taken into a 25 mL syringe and the aqueous layer was discarded. The organic layer was syringed back into the round bottom flask, and was similarly washed twice more with 16% aq. NaCl. Finally, the organic layer was taken off and transferred into another 25 mL round bottom flask containing Na₂SO₄ under nitrogen with occasional shaking. The resulting crude allylboronic acid solution was used immediately for allylation of desired aldehyde.

(Note: [a] all the solvents were degassed for 3 hours with 99.999% Ar under sonication

[b] If in some cases, all allyl alcohols are not consumed even after prolonged reaction time, then additional 1-2 mol% H₂PdCl₄ was added along with 0.2-0.4 equiv of B₂(OH)₄. The stirring was continued further until all allyl alcohol get completely consumed.)

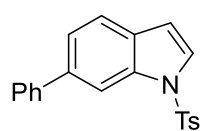
Synthesis of pyrrole and indole derivatives: All the protected pyrrole and indole derivatives were synthesized according to known literature procedures.⁴

General Procedure II (GP II): One-Pot Synthesis of Indoles and Carbazoles:



A 10 mL screw cap seal reaction tube was charge with pyrrole **1** or indole derivatives **4** (0.2 mmol, 1.0 equiv). Then allyl boronic acid **2** solution in CH₂Cl₂ (2 mL, 0.3 mmol, 1.5 equiv) was added to it and the resulting mixture was stirred at room temperature under inert atmosphere. After completion of first allylation step, Et₃N (70 µL, 0.5 mmol, 2.5 equiv) and methanesulfonyl chloride (23.2 µL, 0.3 mmol, 1.5 equiv) were added and the resulting mixture was stirred at room temperature for 12 h. After completion of elimination step, 2 mL of decalin was added to the reaction mixture, the seal tube is flushed with oxygen gas and stirring was continued at 180 °C under O₂ for 24-36 h. After complete consumption of starting material as indicated by TLC, the reaction was cool down to room temperature. Then, the crude residue was diluted with ethylacetate and carefully transferred to a round bottom flask. After evaporating the ethylacetate in *vacuo*, the crude product was purified by silica gel column chromatography by using ethylacetate/hexane as eluent to obtain the pure desired indoles **3** or carbazoles **5**.

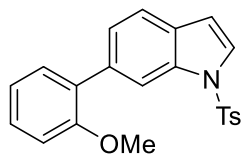
6-Phenyl-1-tosyl-1*H*-indole (**3a**):⁵



The titled compound **3a** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), cinnamyl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 µL, 0.3 mmol, 1.5 equiv), Et₃N (70 µL, 0.5 mmol, 2.5 equiv). The indole **3a** (53 mg, 0.15 mmol, 76%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.25 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.60 (m, 2H), 7.52 – 7.49 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.70 (d, *J* = 3.6 Hz, 1H), 2.36 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 145.12, 141.57, 138.30, 135.65, 135.54, 130.10, 130.07, 128.98, 127.66, 127.39, 126.98, 123.14, 121.64, 112.19, 108.98, 21.69.

6-(2-Methoxyphenyl)-1-tosyl-1*H*-indole (**3b**):⁶

The titled compound **3b** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(2-methoxyphenyl) allyl) boronic acid (0.3



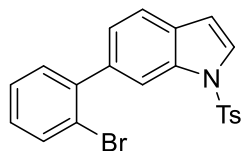
mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3b** (47 mg, 0.12 mmol, 62%) was isolated as white sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 8.24 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 3.6 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 9.0 Hz, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.67 (d, J = 3.5 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 156.66, 144.96, 135.65, 135.25, 135.04, 131.38, 130.96, 129.96, 129.78, 128.77, 127.06, 126.72, 125.32, 121.09, 120.77, 114.77, 111.52, 109.03, 55.76, 21.66.

6-(3-Methoxyphenyl)-1-tosyl-1H-indole (3c):

The titled compound **3c** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(3-methoxyphenyl) allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3c** (51.3 mg, 0.14 mmol, 68%) was isolated as white sticky solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.21 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.56 (s, 1H), 7.47 (dd, J = 8.2, 1.5 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.18 – 7.17 (m, 1H), 6.93 (dd, J = 7.8, 2.1 Hz, 1H), 6.67 (d, J = 3.6 Hz, 1H), 3.90 (s, 3H), 2.33 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) 160.12, 145.12, 143.10, 138.13, 135.54, 135.47, 130.21, 130.06, 129.95, 127.03, 126.97, 123.15, 121.60, 120.19, 113.57, 112.61, 112.22, 108.96, 55.48, 21.68. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2925, 1369, 1169, 674, 577, 540. **HRMS (ESI)**: calculated for C₂₂H₂₀NO₃S ([M+H]⁺): 378.1156; found 378.1162.

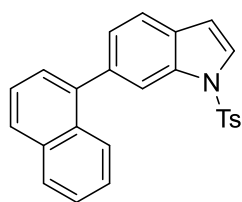
6-(2-Bromophenyl)-1-tosyl-1H-indole (3d):

The titled compound **3d** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(2-bromophenyl) allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3d** (57 mg, 0.13 mmol, 67%) was isolated as white sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.06 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H),



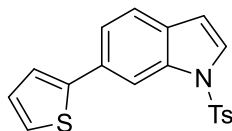
7.60 (dd, $J = 3.6, 1.1$ Hz, 1H), 7.56 (d, $J = 8.8$ Hz, 1H), 7.41 – 7.35 (m, 2H), 7.26 – 7.25 (m, 1H), 7.25 – 7.21 (m, 3H), 6.68 (d, $J = 3.6$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 145.15, 142.84, 137.84, 135.54, 134.68, 133.26, 131.82, 130.27, 130.04, 128.93, 127.56, 127.21, 127.20, 125.01, 123.06, 120.97, 114.84, 109.00, 21.69. **FTIR**: ν_{max} (neat)/ $\text{cm}^{-1} = 2924, 1371, 1171, 1127, 676, 581$. **HRMS (ESI)**: calculated for $\text{C}_{21}\text{H}_{17}\text{BrNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 426.0158; found 426.0159.

6-(Naphthalen-1-yl)-1-tosyl-1H-indole (3e):



The titled compound **3e** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(naphthalen-1-yl) allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3e** (52.5 mg, 0.13 mmol, 66%) was isolated as white solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.12 (s, 1H), 7.94 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.81 – 7.75 (m, 3H), 7.65 – 7.62 (m, 2H), 7.58 – 7.50 (m, 2H), 7.46 (d, $J = 6.9$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 1H), 7.26 – 7.23 (m, 2H), 6.74 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 145.13, 140.38, 137.45, 135.44, 134.95, 133.99, 131.95, 130.05, 128.50, 127.86, 127.51, 127.17, 126.96, 126.18, 126.11, 125.92, 125.84, 125.55, 121.17, 115.13, 108.94, 21.75. **FTIR**: ν_{max} (neat)/ $\text{cm}^{-1} = 2923, 1372, 1174, 779, 674, 591$. **HRMS (ESI)**: calculated for $\text{C}_{25}\text{H}_{20}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 398.1209; found 398.1210.

6-(Thiophen-2-yl)-1-tosyl-1H-indole (3f):



The titled compound **3f** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(thiophen-2-yl) allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3f** (38.2 mg, 0.10 mmol, 54%) was isolated as yellowish sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.23 (s, 1H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 3.6$ Hz, 1H), 7.50 (s, 2H), 7.37 – 7.36 (m, 1H), 7.31 – 7.30 (m, 1H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.12 – 7.10 (m, 1H), 6.64 (d, $J = 3.5$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 145.21, 144.91, 135.48, 135.34, 131.37, 130.26, 130.10, 128.26, 127.09, 127.00, 124.97, 123.40, 122.13,

121.79, 110.92, 109.10, 21.72. **FTIR:** ν_{max} (neat)/ cm^{-1} = 1361, 1163, 1119, 811, 668, 579. **HRMS (ESI):** calculated for $\text{C}_{19}\text{H}_{16}\text{NO}_2\text{S}_2$ ($[\text{M}+\text{H}]^+$): 354.0617; found 354.0620.

6-Methyl-1-tosyl-1*H*-indole (**3g**):⁷

The titled compound **3g** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-but-2-en-1-yl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3g** (35.4 mg, 0.12 mmol, 62%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl_3): δ (ppm) 7.79 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 3.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 7.9 Hz, 1H), 6.59 (d, J = 3.7 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H). **¹³C NMR** (101 MHz, CDCl_3): δ (ppm) 144.93, 135.64, 135.41, 134.83, 129.99, 128.58, 126.90, 125.85, 124.97, 121.02, 113.77, 109.06, 22.09, 21.69.

6-Propyl-1-tosyl-1*H*-indole (**3h**):

The titled compound **3h** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-hex-2-en-1-yl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3h** (35.7 mg, 0.11 mmol, 57%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl_3): δ (ppm) 7.80 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 3.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.05 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 3.6 Hz, 1H), 2.70 (t, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.71 – 1.63 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl_3): δ (ppm) 144.90, 139.80, 135.46, 129.93, 128.90, 127.00, 126.96, 125.99, 124.46, 121.05, 113.41, 109.15, 38.58, 25.14, 21.66, 13.85. **FTIR:** ν_{max} (neat)/ cm^{-1} = 2930, 1220, 1174, 773, 674. **HRMS (ESI):** calculated for $\text{C}_{18}\text{H}_{20}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 314.1209; found 314.1214.

6-Benzyl-1-tosyl-1*H*-indole (**3i**):

The titled compound **3i** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(4-phenylbut-2-en-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3i** (40.5 mg, 0.11 mmol, 56%) was isolated as gummy liquid after column chromatography on silica gel

by using 5% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.80 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.18 – 7.14 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 4.09 (s, 2H), 2.33 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) 144.93, 141.53, 138.17, 135.27, 135.22, 129.91, 129.18, 129.04, 128.60, 126.99, 126.24, 124.75, 121.34, 114.00, 109.06, 42.34, 21.70. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 1369, 1171, 1117, 674, 584, 538. **HRMS (ESI)**: calculated for C₂₂H₂₀NO₂S ([M+H]⁺): 362.1209; found 362.1212.

6-Isopropyl-1-tosyl-1*H*-indole (3j):

The titled compound **3j** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(4-methylpent-2-en-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The indole **3j** (38.2 mg, 0.12 mmol, 61%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.85 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.33 (s, 3H), 1.30 (d, *J* = 6.9 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) 146.12, 144.94, 135.49, 135.37, 129.91, 128.98, 126.95, 126.04, 122.46, 121.12, 111.28, 109.07, 34.64, 24.51, 21.66. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2960, 2869, 1370, 1171, 998, 669, 580. **HRMS (ESI)**: calculated for C₁₈H₂₀NO₂S ([M+H]⁺): 314.1209; found 314.1212.

6-Cyclohexyl-1-tosyl-1*H*-indole (3k):

The titled compound **3k** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-cyclohexyl allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The indole **3k** (39 mg, 0.11 mmol, 55%) was isolated as gummy liquid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.84 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 3.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 2.65 – 2.59 (m, 1H), 2.33 (s, 3H), 1.91 – 1.87 (m, 4H), 1.79 – 1.76 (m, 1H), 1.49 – 1.40 (m, 4H), 1.34 – 1.27 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) 145.36, 144.92, 135.50, 135.39, 129.92, 128.98, 126.93, 126.01, 122.90, 121.05, 111.69, 109.12, 45.09, 35.00, 27.10, 26.29, 21.67. **FTIR**: ν_{max}

(neat)/ cm^{-1} = 2924, 2852, 1372, 1177, 1119, 813, 679, 881. **HRMS (ESI)**: calculated for $\text{C}_{21}\text{H}_{24}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 354.1522; found 354.1524.

6-(2,6-Dimethylhept-5-en-1-yl)-1-tosyl-1*H*-indole (**3l**):

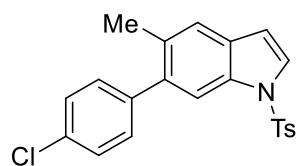
The titled compound **3l** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(5,9-dimethyldeca-2,8-dien-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3l** (33.6 mg, 0.09 mmol, 44%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 7.78 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 3.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.01 (dd, J = 8.0, 1.3 Hz, 1H), 6.59 (d, J = 4.3 Hz, 1H), 5.10 – 5.07 (m, 1H), 2.78 – 2.75 (m, 1H), 2.51 – 2.47 (m, 1H), 2.40 – 2.38 (m, 1H), 2.33 (s, 3H), 2.12 – 2.04 (m, 1H), 2.01 – 1.94 (m, 1H), 1.79 – 1.73 (m, 1H), 1.70 (s, 3H), 1.62 (s, 3H), 1.42 – 1.37 (m, 1H), 0.84 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 144.88, 138.64, 135.61, 135.39, 131.35, 129.90, 128.93, 126.96, 126.01, 125.13, 124.94, 120.90, 114.19, 109.23, 44.14, 36.89, 35.20, 29.85, 25.85, 21.65, 19.44, 17.84. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3306, 1600, 1372, 1217, 1119, 775, 677, 540. **HRMS (ESI)**: calculated for $\text{C}_{24}\text{H}_{30}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 396.1992; found 396.1996.

5-Methyl-6-phenyl-1-tosyl-1*H*-indole (**3m**):

The titled compound **3m** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(2-methyl-3-phenylallyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The indole **3m** (31.8 mg, 0.09 mmol, 44%) was isolated as gummy liquid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 7.85 (s, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 3.6 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.39 (s, 1H), 7.37 (d, J = 7.0 Hz, 1H), 7.33 (d, J = 7.1 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 3.6 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 144.95, 142.34, 139.36, 135.56, 133.62, 131.05, 130.22, 129.97, 129.64, 128.23, 127.01, 126.98, 126.84, 122.37, 114.59, 108.76, 21.68, 20.84. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2928, 1217, 1174, 772, 671, 596. **HRMS (ESI)**: calculated for $\text{C}_{22}\text{H}_{20}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 362.1209; found 362.1212.

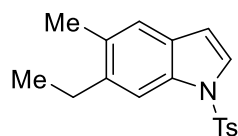
6-(4-Chlorophenyl)-5-methyl-1-tosyl-1H-indole(3n):

The titled compound **3n** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(4-chlorophenyl)-2-methylallyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3n** (35.4 mg, 0.12 mmol, 62%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.83 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 3.5 Hz, 1H), 7.43 (s, 1H), 7.42 – 7.41 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 145.04, 140.74, 138.01, 135.53, 133.59, 133.14, 130.94, 130.87, 130.46, 130.00, 128.46, 127.03, 126.96, 122.55, 114.47, 108.71, 21.68, 20.77. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2930, 1600, 1370, 1123, 809, 766, 674. **HRMS (ESI)**: calculated for C₂₂H₁₉ClNO₂S ([M+H]⁺): 396.0820; found 396.0819.



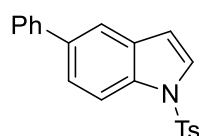
6-Ethyl-5-methyl-1-tosyl-1H-indole (3o):

The titled compound **3o** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-2-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-but-2-en-1-yl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3o** (28.2 mg, 0.09 mmol, 45%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.78 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 3.7 Hz, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 3.6 Hz, 1H), 2.72 (q, *J* = 7.5 Hz, 2H), 2.335 (s, 3H), 2.325 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 144.80, 139.86, 135.63, 134.11, 131.55, 129.89, 128.97, 126.91, 125.88, 122.09, 112.66, 108.90, 26.93, 21.65, 19.50, 14.93. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 1217, 772, 738, 669, 422. **HRMS (ESI)**: calculated for C₁₈H₂₀NO₂S ([M+H]⁺): 314.1209; found 314.1213.



5-Phenyl-1-tosyl-1H-indole (3p):⁸

The titled compound **3p** was synthesized according to **GP II** by using 1-tosyl-1H-pyrrole-3-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), cinnamyl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3p** (42.4 mg, 0.12 mmol, 61%)



was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (600 MHz, CDCl₃): δ (ppm) 8.04 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.72 (s, 1H), 7.59 – 7.58 (m, 3H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 3.4 Hz, 1H), 2.35 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃): δ (ppm) 145.14, 141.40, 136.94, 135.44, 134.36, 131.44, 130.06, 128.91, 127.48, 127.17, 127.06, 126.99, 124.33, 119.94, 113.86, 109.41, 21.72.

5-Isopropyl-1-tosyl-1*H*-indole (3q):

The titled compound **3q** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-3-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(4-methylpent-2-en-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The indole **3q** (39.5 mg, 0.13 mmol, 63%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.89 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 3.5 Hz, 1H), 7.36 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.59 (d, *J* = 3.4 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.34 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 144.71, 144.07, 135.63, 133.32, 130.90, 129.81, 126.83, 126.32, 123.67, 118.45, 113.28, 108.95, 33.97, 24.28, 21.49. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2965, 1373, 1220, 772, 674. **HRMS (ESI)**: Calculated for C₁₈H₂₀NO₂S ([M+H]⁺): 314.1209; found 314.1216.

5-(4-Chlorophenyl)-6-methyl-1-tosyl-1*H*-indole(3r):

The titled compound **3r** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-3-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(4-chlorophenyl)-2-methylallyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The indole **3r** (50.7 mg, 0.13 mmol, 64%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (600 MHz, CDCl₃): δ (ppm) 7.89 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.33 (s, 1H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃): δ (ppm) 145.07, 140.56, 136.84, 135.60, 134.65, 132.95, 132.52, 130.86, 130.08, 128.96, 128.39, 126.98, 126.40, 122.20, 114.68, 108.94, 21.74, 21.51. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2925, 1220,

1165, 772, 671. **HRMS (ESI)**: Calculated for C₂₂H₁₉ClNO₂S ([M+H]⁺): 396.0820; found 396.0826.

5-Ethyl-6-methyl-1-tosyl-1*H*-indole (3s):

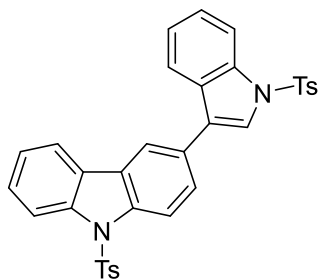
The titled compound **3s** was synthesized according to **GP II** by using 1-tosyl-1*H*-pyrrole-3-carbaldehyde (50 mg, 0.2 mmol, 1.0 equiv), (*E*)-(2-methylpent-2-en-1-yl)boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The indole **3s** (40 mg, 0.13 mmol, 64%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 7.76 (*J* = 2.7 Hz, 2H), 7.74 (s, 1H), 7.44 (d, *J* = 3.5 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.56 (d, *J* = 3.5 Hz, 1H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 144.77, 138.15, 135.88, 133.75, 133.29, 129.96, 129.26, 126.92, 125.73, 119.98, 114.52, 109.00, 26.29, 21.66, 20.23, 14.62. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 1217, 1171, 772, 669, 422. **HRMS (ESI)**: Calculated for C₁₈H₂₀NO₂S ([M+H]⁺): 314.1209; found 314.1213.

3-Phenyl-9-tosyl-9*H*-carbazole (5a):⁹

The titled compound **5a** was synthesized according to **GP II** by using 1-tosyl-1*H*-indole-3-carbaldehyde (59.9 mg, 0.2 mmol, 1.0 equiv), cinnamyl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The carbazole **5a** (58.8 mg, 0.15 mmol, 74%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (600 MHz, CDCl₃): δ (ppm) 8.38 (d, *J* = 8.6 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.09 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.71 (m, 3H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.39 – 7.34 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃): δ (ppm) 145.05, 141.05, 138.99, 137.93, 137.46, 135.18, 129.85, 129.02, 127.69, 127.44, 127.41, 127.07, 126.87, 126.68, 126.57, 124.11, 120.18, 118.53, 115.51, 115.38, 21.64.

9-Tosyl-3-(1-tosyl-1*H*-indol-3-yl)-9*H*-carbazole (5b):

The titled compound **5b** was synthesized according to **GP II** by using 1-tosyl-1*H*-indole-3-carbaldehyde (59.9 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(1-tosyl-1*H*-indol-3-yl)allyl)boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μ L, 0.3 mmol, 1.5 equiv), Et₃N (70 μ L, 0.5 mmol, 2.5 equiv). The carbazole **5b** (76.8 mg, 0.13 mmol, 65%) was isolated as white solid

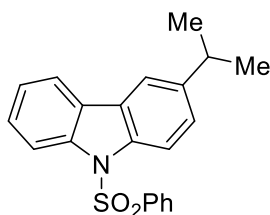


after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.40 (d, *J* = 8.6 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.11 – 8.06 (m, 2H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.81 (m, 3H), 7.75 – 7.70 (m, 4H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H),

2.28 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃): δ (ppm) 145.25, 145.15, 138.90, 137.86, 135.66, 135.35, 135.10, 130.12, 129.90, 129.50, 129.08, 127.87, 127.45, 127.12, 127.06, 126.68, 126.27, 125.17, 124.17, 123.80, 123.79, 123.15, 120.46, 120.26, 119.29, 115.66, 115.36, 114.07, 21.74, 21.69. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 1373, 1175, 755, 584. **HRMS (ESI)**: calculated for C₃₄H₂₇N₂O₄S₂ ([M+H]⁺): 591.1407; found 591.1411.

3-Isopropyl-9-(phenylsulfonyl)-9H-carbazole (5c):

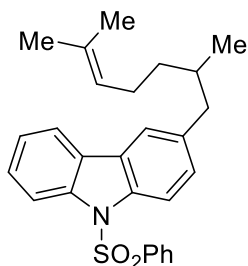
The titled compound **5c** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-(4-methylpent-2-en-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5c** (41.2 mg, 0.12 mmol, 59%) was isolated as white solid after column chromatography on silica gel by



using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 8.33 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.75 (s, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 3.09 – 3.04 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 145.00, 138.71, 138.11, 136.77, 133.78, 129.11, 127.31, 126.70, 126.58, 126.53, 126.43, 123.97, 120.03, 117.46, 115.20, 115.01, 34.11, 24.42. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2960, 1362, 1164, 982, 820, 744, 556. **HRMS (ESI)**: calculated for C₂₁H₂₀NO₂S ([M+H]⁺): 350.1209; found 350.1208.

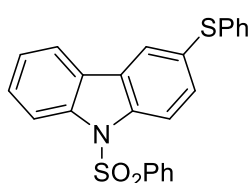
3-(2,6-Dimethylhept-5-en-1-yl)-9-(phenylsulfonyl)-9H-carbazole (5d):

The titled compound **5d** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1H-indole-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-(5,9-dimethyldeca-2,8-dien-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5d** (42.3 mg, 0.99 mmol, 49%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane



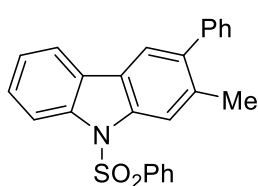
as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 8.30 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.24 (m, 3H), 5.08 (t, *J* = 7.0 Hz, 1H), 2.77 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.48 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.93 (m, 1H), 1.83 – 1.76 (m, 1H), 1.68 (s, 3H), 1.59 (s, 3H), 1.43 – 1.37 (m, 1H), 1.26 – 1.17 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 138.78, 138.14, 137.71, 136.86, 133.78, 131.37, 129.09, 128.90, 127.35, 126.72, 126.61, 126.57, 124.85, 124.02, 120.35, 120.06, 115.34, 114.89, 43.56, 36.91, 35.03, 25.85, 25.78, 19.51, 17.80. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 3070, 2922, 2951, 1601, 1445, 1370, 1172, 977, 724, 685. **HRMS (ESI)**: calculated for C₂₇H₃₀NO₂S ([M+H]⁺): 432.1992; found 432.1998.

9-(Phenylsulfonyl)-3-(phenylthio)-9H-carbazole (5e):



The titled compound **5e** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1*H*-indole-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(phenylthio) allyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5e** (51.5 mg, 0.12 mmol, 62%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (500 MHz, CDCl₃): δ (ppm) 8.32 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.7 Hz, 1H), 7.95 (s, 1H), 7.84 – 7.82 (m, 3H), 7.54 – 7.46 (m, 3H), 7.36 – 7.33 (m, 3H), 7.30 – 7.27 (m, 4H), 7.24 – 7.21 (m, 1H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 138.87, 138.02, 137.90, 136.95, 134.08, 131.62, 130.46, 130.14, 129.35, 129.28, 128.06, 127.62, 126.91, 126.66, 125.79, 124.31, 124.02, 120.37, 116.03, 115.31. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 1584, 1437, 1370, 1173, 975, 683, 553, 474. **HRMS (ESI)**: calculated for C₂₄H₁₈NO₂S₂ ([M+H]⁺): 416.0774; found 416.0776.

2-Methyl-3-phenyl-9-(phenylsulfonyl)-9H-carbazole (5f):

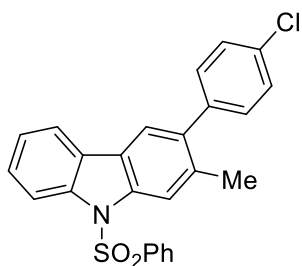


The titled compound **5f** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1*H*-indole-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-(2-methyl-3-phenylallyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5f** (43.7 mg, 0.11 mmol, 55%) was isolated as

white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.32 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.49 – 7.43 (m, 4H), 7.39 – 7.34 (m, 6H), 2.46 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 141.88, 138.67, 138.62, 138.32, 137.99, 135.68, 133.90, 129.55, 129.24, 128.32, 127.19, 127.11, 126.67, 126.65, 124.48, 124.12, 121.09, 119.92, 116.27, 115.24, 21.80. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2933, 2852, 1446, 1174, 1086, 724, 570, 422. **HRMS (ESI)**: calculated for C₂₅H₂₃NO₂S ([M+NH₄]⁺): 415.1474; found 415.1499.

3-(4-Chlorophenyl)-2-methyl-9-(phenylsulfonyl)-9H-carbazole (5g):

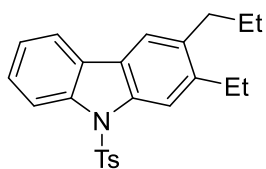
The titled compound **5g** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1*H*-indole-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-(3-(4-chlorophenyl)-2-methylallyl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5g** (56.7 mg, 0.13 mmol, 65%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent.



¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.32 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.50 – 7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃): δ (ppm) 140.28, 138.69, 138.29, 138.16, 137.30, 135.50, 133.93, 133.22, 130.88, 129.25, 128.52, 127.33, 126.65, 126.46, 124.57, 124.17, 121.00, 119.93, 116.39, 115.25, 21.73. **FTIR**: ν_{max} (neat)/ cm⁻¹ = 2928, 1447, 1368, 1090, 831, 746, 596. **HRMS (ESI)**: calculated for C₂₅H₂₂ClN₂O₂S ([M+NH₄]⁺): 449.1085; found 449.1080.

2-Ethyl-3-propyl-9-tosyl-9H-carbazole (5h):

The titled compound **5h** was synthesized according to **GP II** by using 1-tosyl-1*H*-indole-3-carbaldehyde (59.9 mg, 0.2 mmol, 1.0 equiv), (*E*)-(2-ethylhex-2-en-1-yl) boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The carbazole **5h** (40 mg, 0.10 mmol, 51%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **¹H NMR** (600 MHz, DMSO-*d*₆): δ (ppm) 8.21 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.83 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.9 Hz,



2H), 2.77 (q, $J = 7.5$ Hz, 2H), 2.63 (t, $J = 8.0$ Hz, 2H), 2.16 (s, 3H), 1.62 – 1.56 (m, 2H), 1.25 (t, $J = 7.5$ Hz, 3H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6): δ (ppm) 145.48, 142.05, 137.72, 136.51, 136.35, 133.84, 130.05, 127.23, 126.18, 126.10, 124.26, 123.82, 120.51, 120.34, 114.67, 113.88, 34.04, 25.80, 23.95, 20.92, 15.62, 14.05. **FTIR**: ν_{max} (neat)/ $\text{cm}^{-1} = 2960, 2871, 1454, 1367, 1168, 810, 747, 541$. **HRMS (ESI)**: calculated for $\text{C}_{24}\text{H}_{26}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 392.1679; found 392.1681.

6-Phenyl-9-(phenylsulfonyl)-9H-pyrido[2,3-b]indole (5i):

The titled compound **5i** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), cinnamyl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The carbazole **5i** (43.8 mg, 0.11 mmol, 57%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.59 (dd, $J = 4.9, 1.6$ Hz, 1H), 8.55 (d, $J = 8.7$ Hz, 1H), 8.24 (dd, $J = 7.7, 1.6$ Hz, 1H), 8.19 – 8.17 (m, 2H), 8.12 (s, 1H), 7.81 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.68 – 7.64 (m, 2H), 7.54 – 7.47 (m, 3H), 7.44 – 7.37 (m, 3H), 7.31 (dd, $J = 7.7, 4.9$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 151.37, 147.36, 140.78, 138.88, 137.52, 137.13, 134.08, 129.09, 128.55, 127.89, 127.69, 127.58, 127.44, 123.53, 119.38, 119.16, 118.98, 115.44. **FTIR**: ν_{max} (neat)/ $\text{cm}^{-1} = 2917, 2852, 1469, 1379, 1182, 974, 752, 591$. **HRMS (ESI)**: calculated for $\text{C}_{23}\text{H}_{16}\text{N}_2\text{O}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 407.0824; found 407.0833.

2-Phenyl-9-(phenylsulfonyl)-9H-carbazole (5j):

The titled compound **5j** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1H-indole-2-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), cinnamyl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The carbazole **5j** (51.4 mg, 0.13 mmol, 67%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.59 (s, 1H), 8.35 (d, $J = 8.4$ Hz, 1H), 7.96 – 7.91 (m, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.1$ Hz, 2H), 7.63 – 7.61 (m, 1H), 7.54 – 7.49 (m, 3H), 7.48 – 7.38 (m, 3H), 7.36 – 7.31 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 141.30, 141.03, 139.22, 138.97, 138.17, 133.96, 129.24, 129.08, 127.74, 127.71, 127.57, 126.65, 126.37, 125.72, 124.26, 123.62, 120.36,

120.20, 115.37, 113.80. **FTIR**: ν_{\max} (neat)/ cm^{-1} = 1372, 1173, 979, 755, 690, 594. **HRMS (ESI)**: calculated for $\text{C}_{24}\text{H}_{18}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 384.1053; found 384.1053.

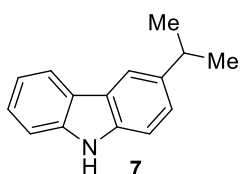
9-(Phenylsulfonyl)-2-propyl-9H-carbazole (5k):

The titled compound **5k** was synthesized according to **GP II** by using 1-(phenylsulfonyl)-1H-indole-2-carbaldehyde (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-hex-2-en-1-ylboronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL , 0.3 mmol, 1.5 equiv), Et_3N (70 μL , 0.5 mmol, 2.5 equiv). The carbazole **5k** (35.6 mg, 0.10 mmol, 51%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 8.31 (d, J = 8.4 Hz, 1H), 8.14 (s, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.80 – 7.78 (m, 3H), 7.47 – 7.42 (m, 2H), 7.35 – 7.29 (m, 3H), 7.19 (d, J = 7.9 Hz, 1H), 2.79 (t, J = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 142.90, 138.94, 138.67, 138.20, 133.82, 129.12, 127.04, 126.81, 126.63, 124.96, 124.54, 124.11, 119.84, 119.79, 115.41, 115.15, 38.83, 25.14, 13.85. **FTIR**: ν_{\max} (neat)/ cm^{-1} = 2959, 2930, 1460, 1370, 1091, 723. **HRMS (ESI)**: calculated for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 350.1209; found 350.1210.

6-Phenyl-1H-indole (6):¹⁰

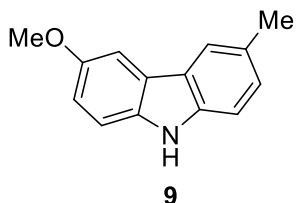
To a stirred solution of **3a** (34.7 mg, 0.1 mmol, 1 equiv) in MeOH (2 mL) was added 2 mL of KOH (4N) dropwise, and the resulting reaction mixture was refluxed at 80 $^{\circ}\text{C}$ for 48 h. On complete consumption of all the starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH_4Cl solution. The aqueous layer was extracted with ethylacetate (2 \times 2 mL), the combined organic layers were dried over Na_2SO_4 , and evaporated under reduced pressure. The indole **6** (14.6 mg, 0.08 mmol, 76%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^1H NMR** (500 MHz, CDCl_3): δ (ppm) 8.21 (s, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.61 (s, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.40 (dd, J = 8.2, 1.4 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 2.7 Hz, 1H), 6.59 – 6.58 (m, 1H). **^{13}C NMR** (126 MHz, CDCl_3): δ (ppm) 142.49, 136.56, 135.80, 128.83, 127.54, 127.39, 126.74, 124.92, 121.06, 119.98, 109.68, 102.75.

3-Isopropyl-9H-carbazole (**7**):¹¹



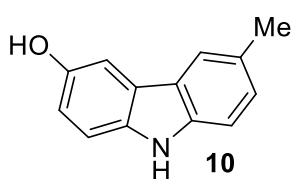
To a stirred solution of **5c** (34.9 mg, 0.1 mmol, 1 equiv) in dry THF (2 mL) was added TBAF (0.4 mmol, 1 M in THF, 4 equiv) dropwise, and the resulting reaction mixture was refluxed at 75 °C for 3 h. On complete consumption of all the starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH₄Cl solution. The aqueous layer was extracted with ethylacetate (2×2 mL), the combined layers were dried over Na₂SO₄, and evaporated under reduced pressure. The carbazole **7** (20.3 mg, 0.09 mmol, 97%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.08 (d, *J* = 7.8 Hz, 1H), 7.94 (s, 2H), 7.41 – 7.39 (m, 2H), 7.34 – 7.31 (m, 2H), 7.25 – 7.21 (m, 1H), 3.17 – 3.06 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 140.38, 140.01, 138.11, 125.73, 124.97, 123.55, 123.51, 120.34, 119.34, 117.61, 110.68, 110.46, 34.34, 24.85.

3-Methoxy-6-methyl-9H-carbazole (Glycozoline) (**9**):¹¹



To synthesize compound **9**, at first the corresponding *N*-tosyl-protected carbazole was synthesized according to **GP II** by using 5-methoxy-1-(phenylsulfonyl)-1*H*-indole-3-carbaldehyde **8** (57.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-but-2-en-1-yl boronic acid (0.3 mmol, 1.5 equiv), methanesulfonyl chloride (23.2 μL, 0.3 mmol, 1.5 equiv), Et₃N (70 μL, 0.5 mmol, 2.5 equiv). The corresponding *N*-tosyl-protected carbazole (33 mg, 0.09 mmol, 47%) was isolated as white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. Then to a stirred solution of *N*-tosyl-protected carbazole (33 mg, 0.09 mmol, 1 equiv) in dry THF (2 mL) was added TBAF (0.4 mmol, 4 equiv) dropwise, and the resulting reaction mixture was refluxed at 75 °C for 3 h. On complete consumption of all the starting material as indicated by TLC, the reaction mixture was quenched by adding saturated aq. NH₄Cl solution. The aqueous layer was extracted with ethylacetate (2×2 mL), the combined layers were dried over Na₂SO₄, and evaporated under reduced pressure. The carbazole **9** (20.2 mg, 0.08 mmol, 96%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.84 (s, 2H), 7.57 – 7.48 (m, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.06 – 7.01 (m, 1H), 3.93 (s, 3H), 2.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 153.87, 138.68, 134.88, 128.47, 127.32, 123.78, 123.66, 120.27, 115.01, 111.40, 110.55, 103.21, 56.20, 21.56.

6-Methyl-9H-carbazol-3-ol (Glycozolinol) (10**):**¹¹

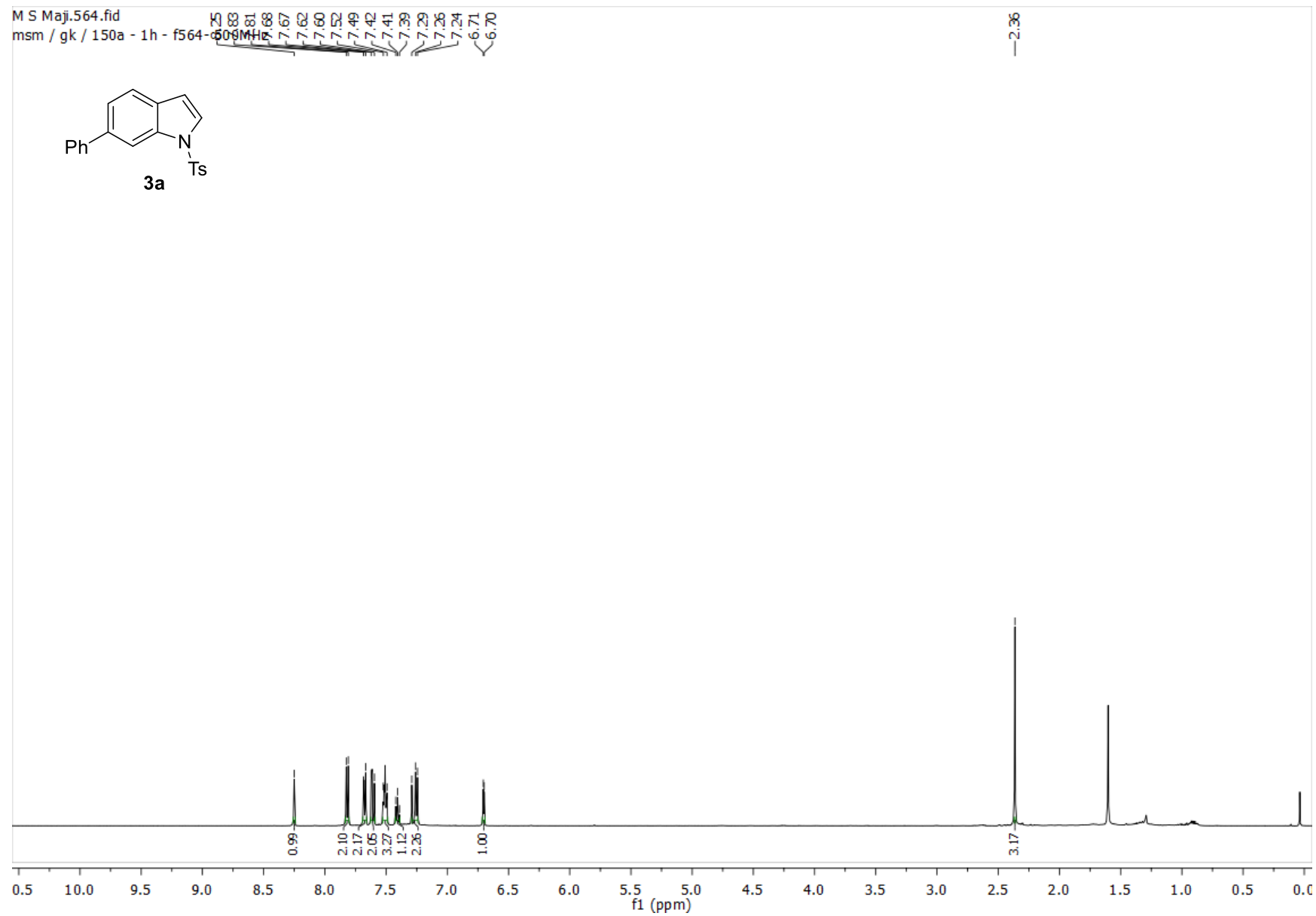


To a stirred solution of **9** (20.2 mg, 0.08 mmol, 1 equiv) in dry CH₂Cl₂ (2 mL) was added BBr₃ (0.16 mmol, 2 equiv) dropwise, and the resulting reaction mixture was refluxed at 75 °C for 3 h. On complete consumption of all the starting material as indicated by TLC, the

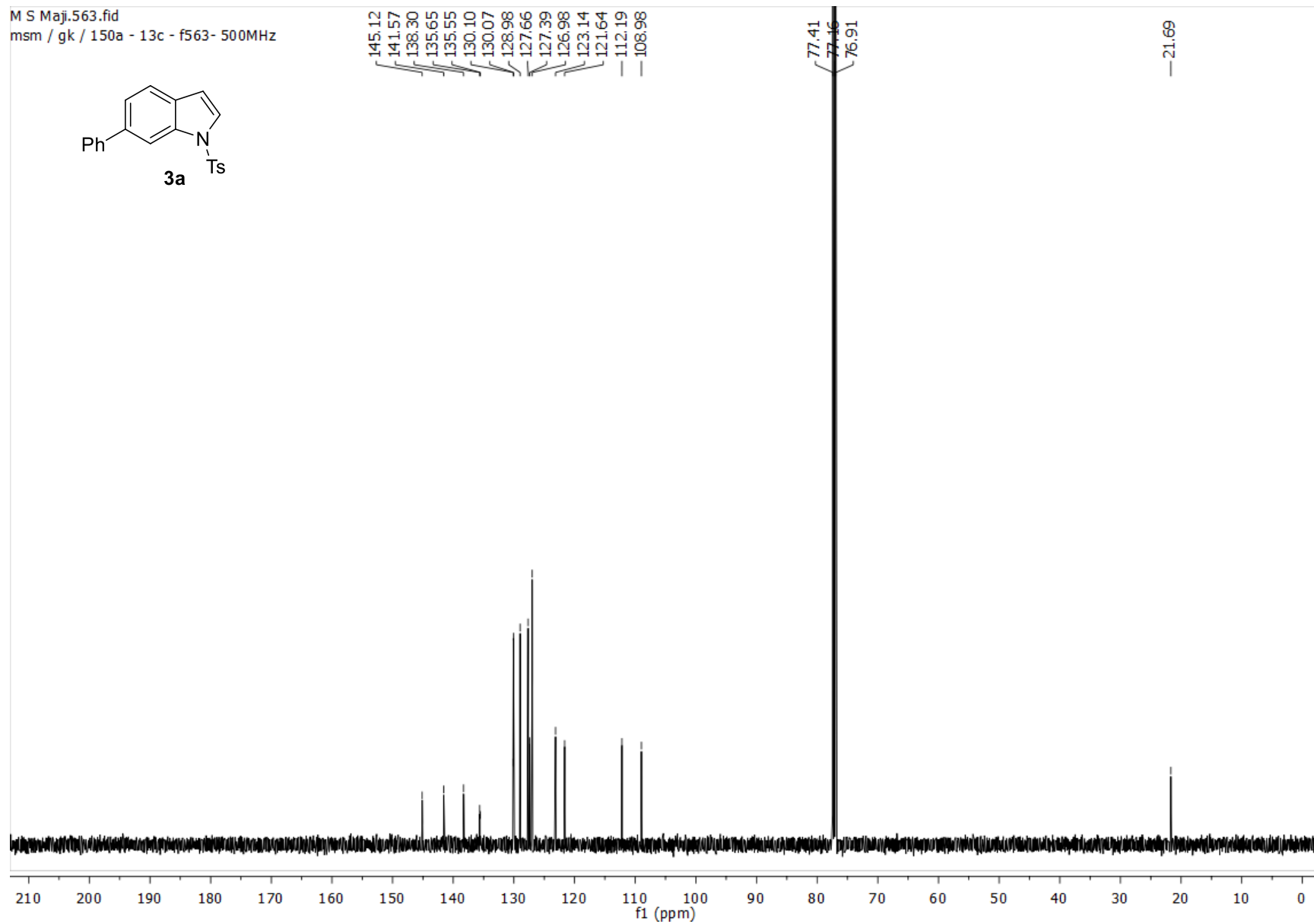
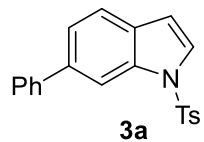
reaction mixture was quenched by adding saturated aq. NH₄Cl solution. The aqueous layer was extracted with ethylacetate (2×2 mL), the combined layers were dried over Na₂SO₄, and evaporated under reduced pressure. The carbazole **10** (14.5 mg, 0.07 mmol, 92%) was isolated as gummy liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 10.70 (s, 1H), 8.86 (s, 1H), 7.75 (s, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.4 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 150.15, 138.68, 134.07, 126.50, 126.21, 122.82, 122.41, 119.73, 114.78, 111.16, 110.50, 104.69, 21.01.

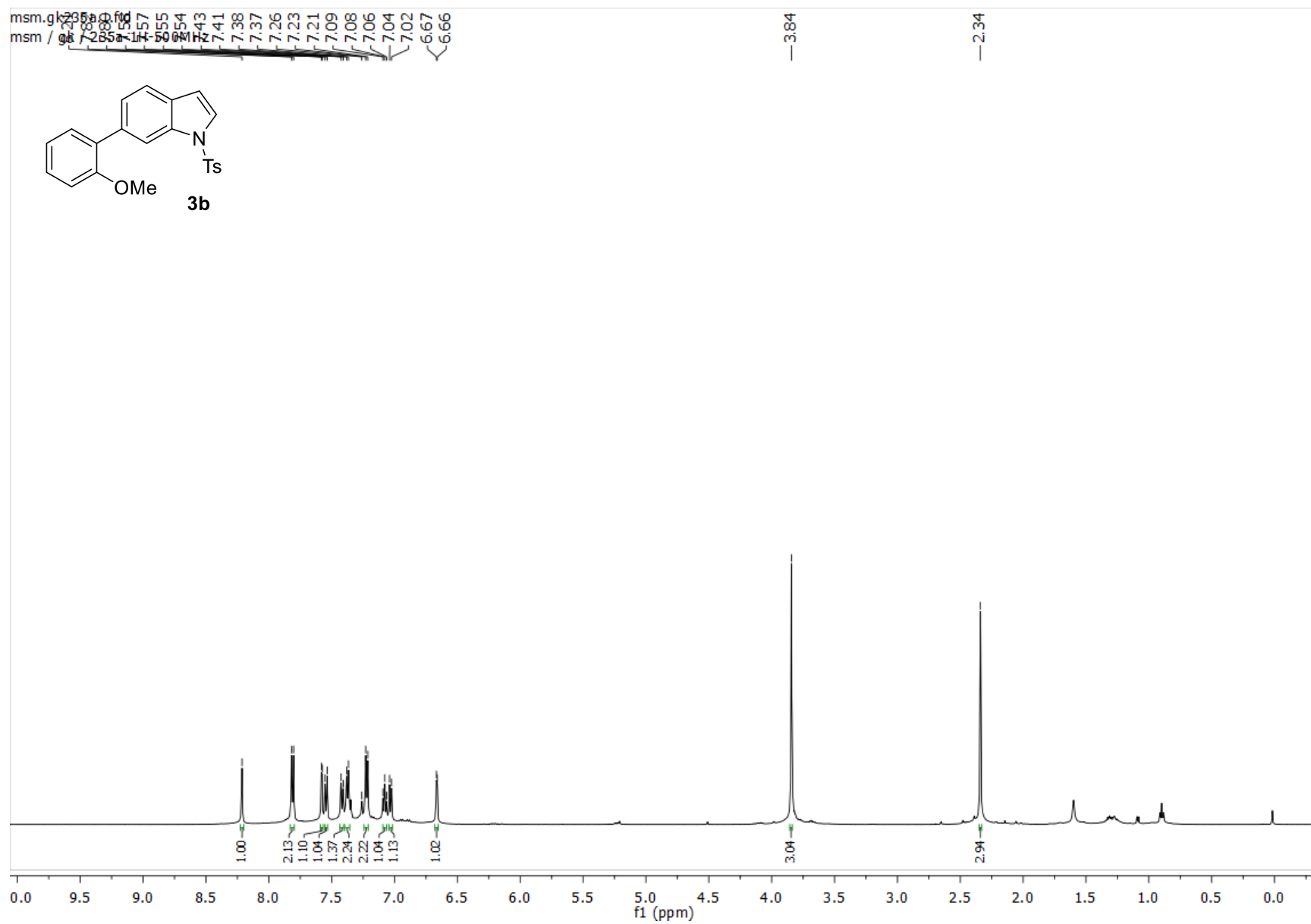
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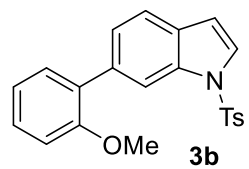
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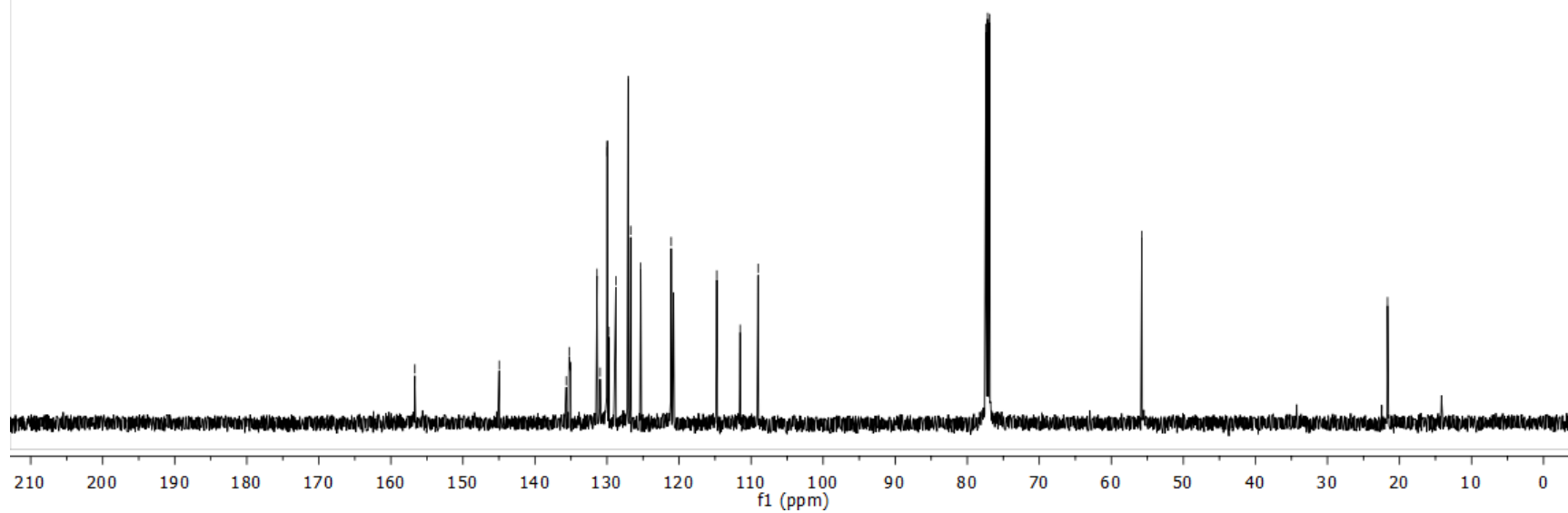


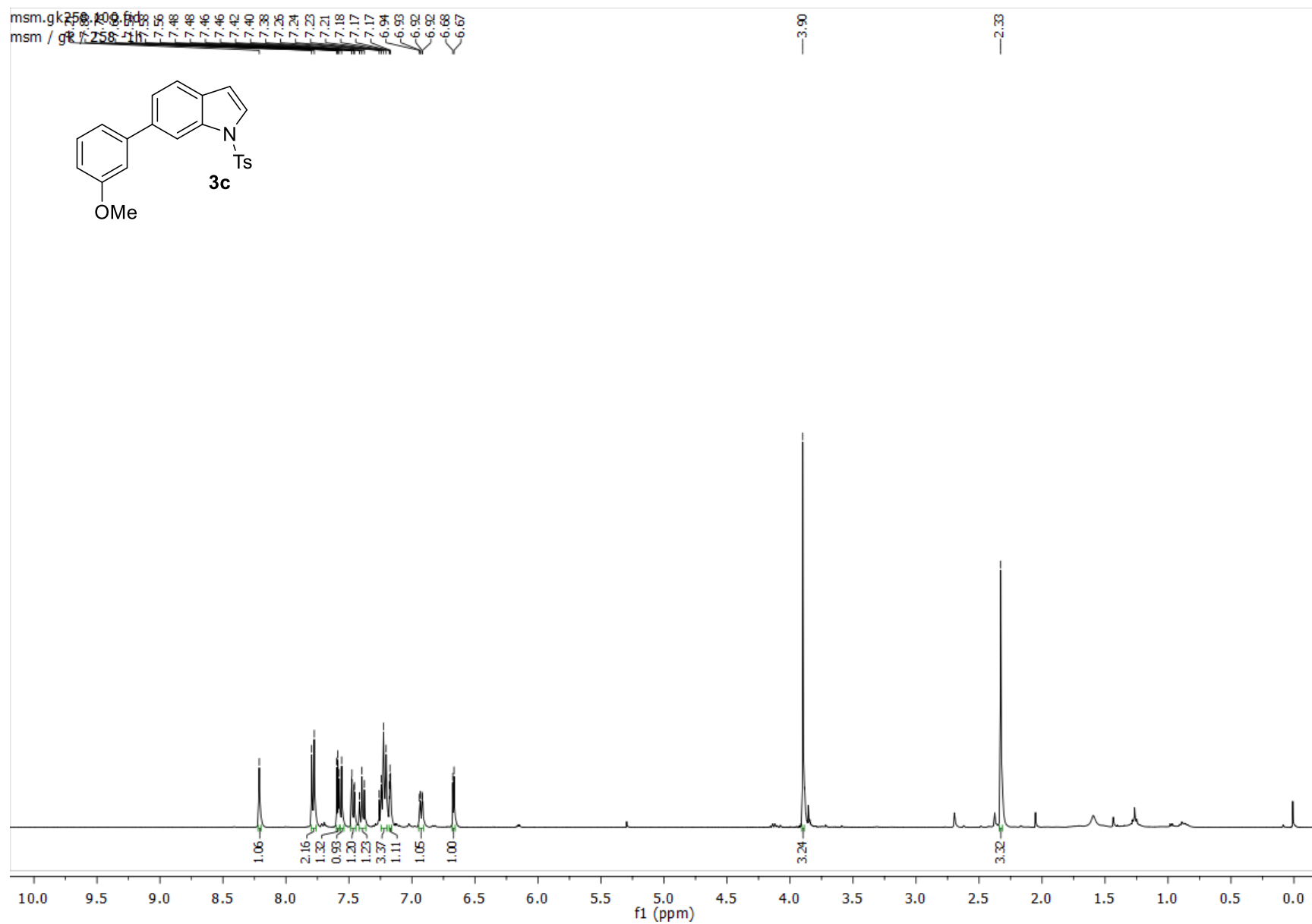
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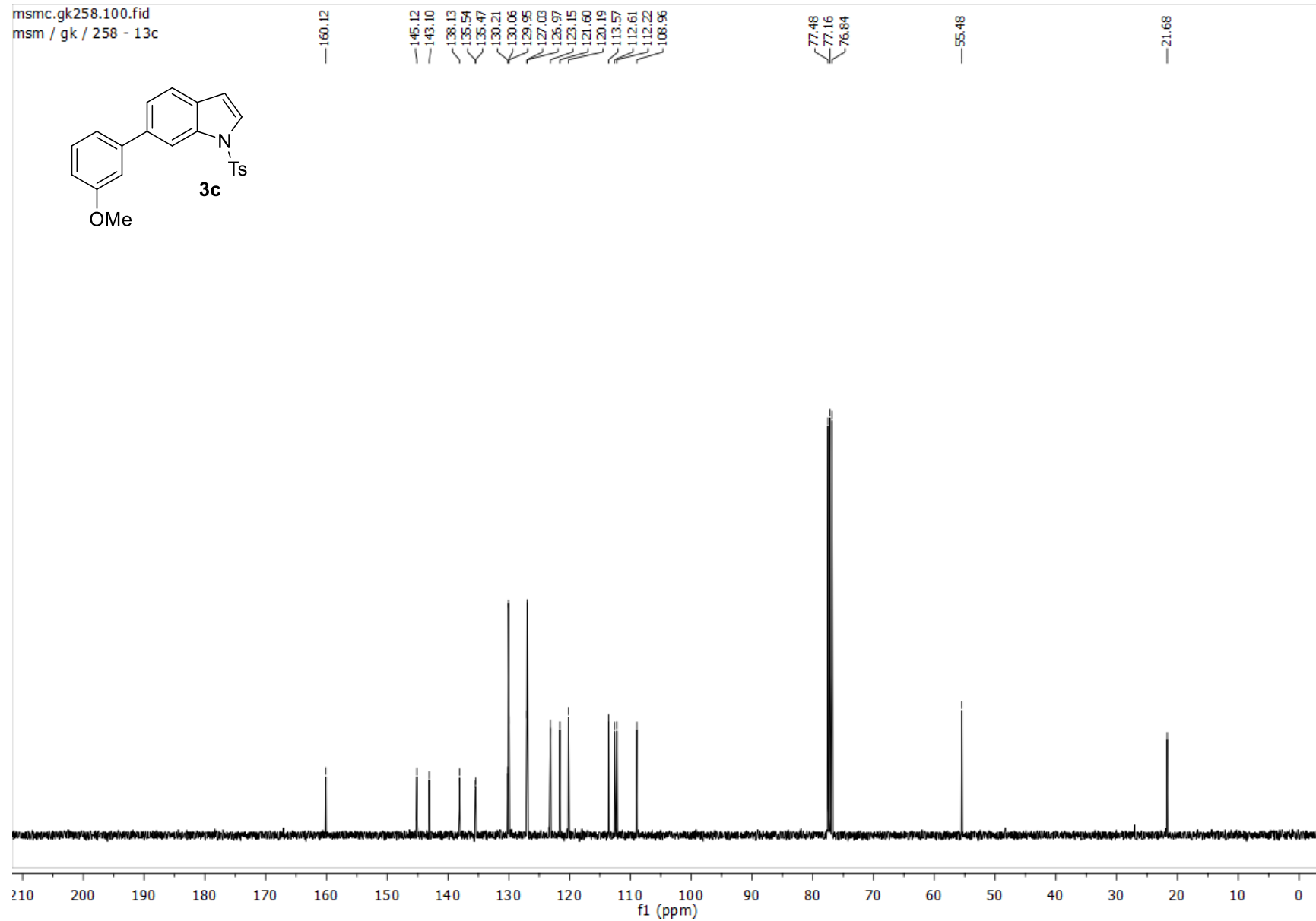
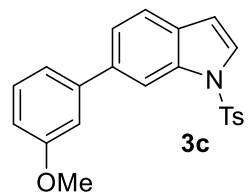


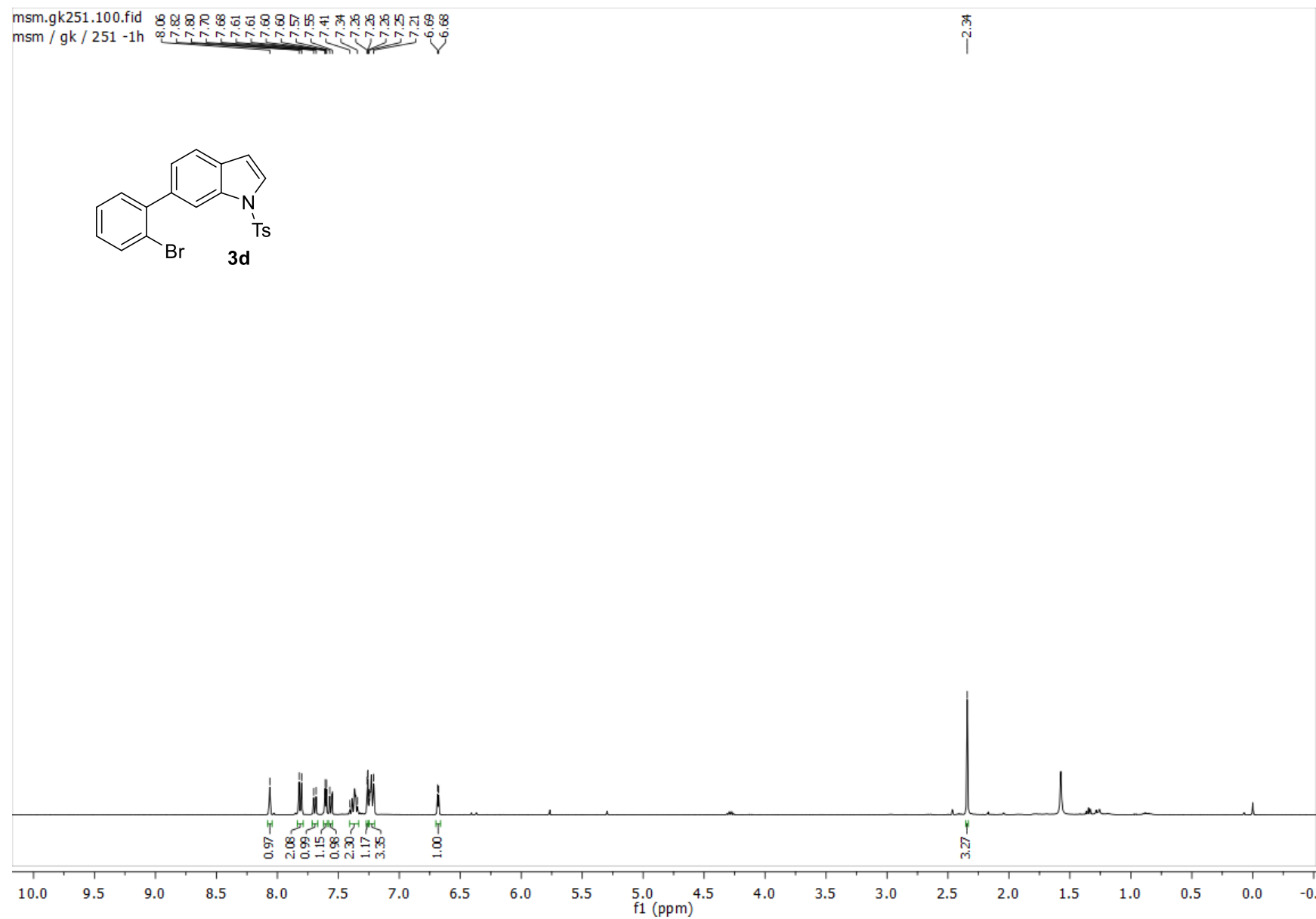
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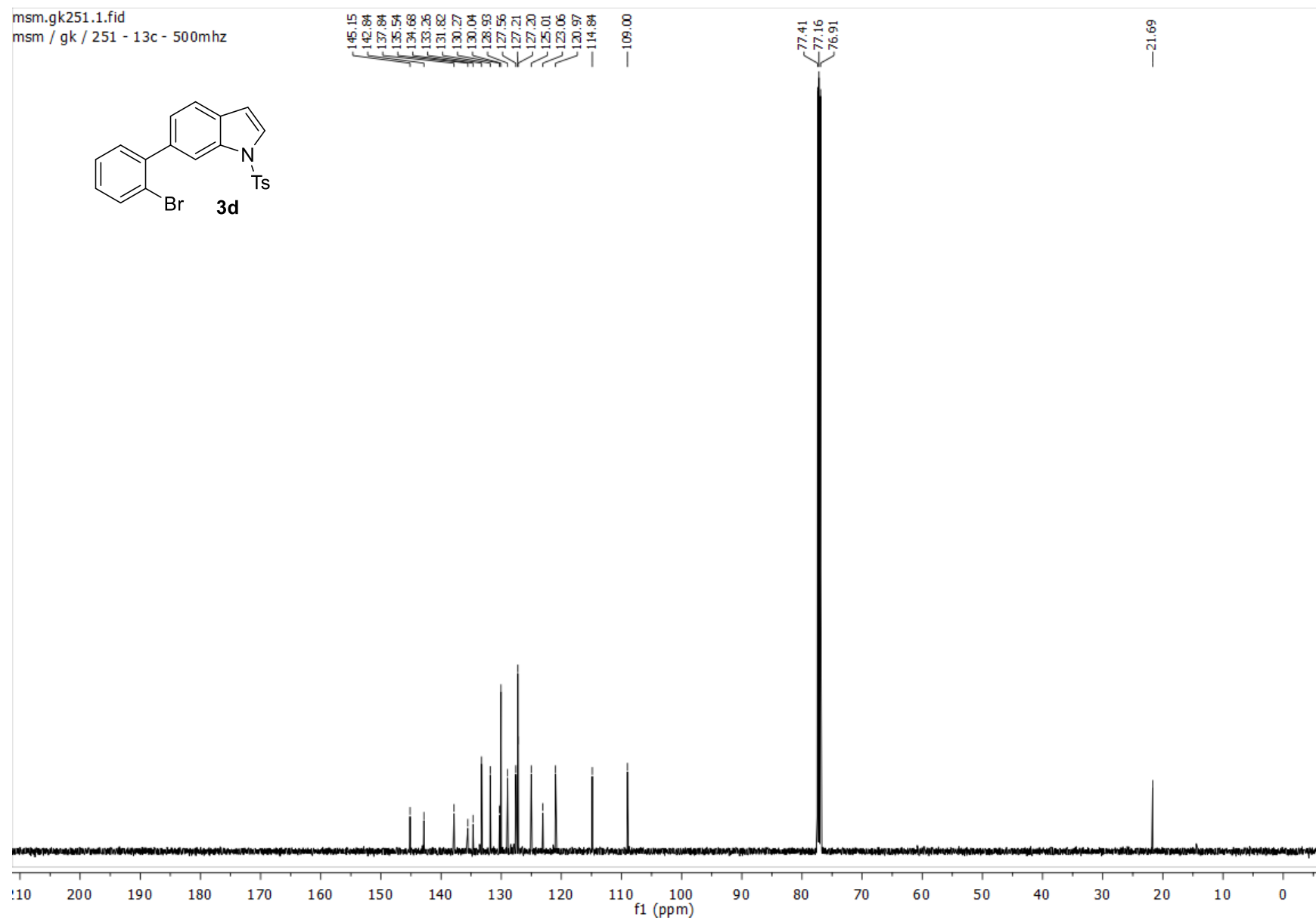


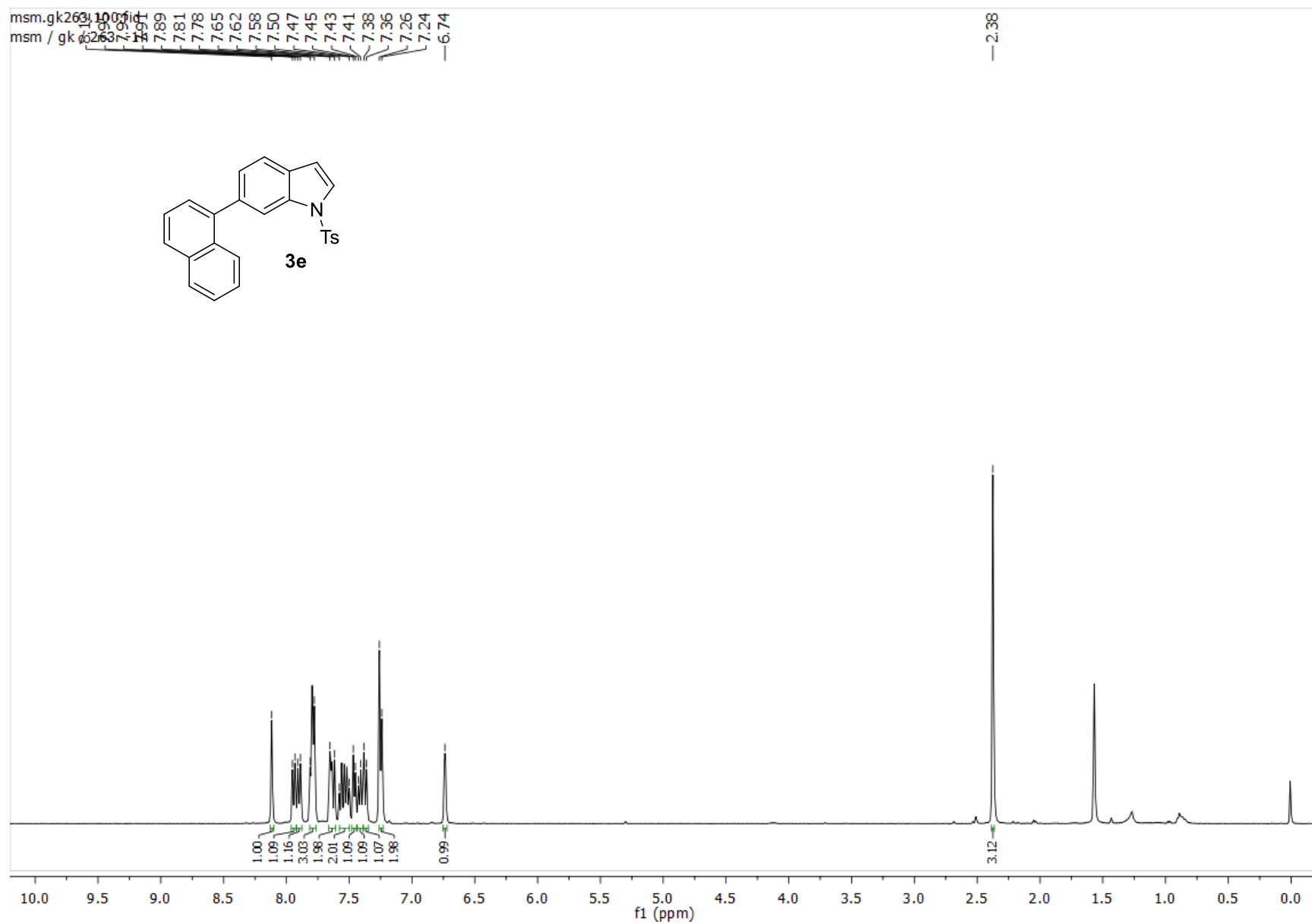


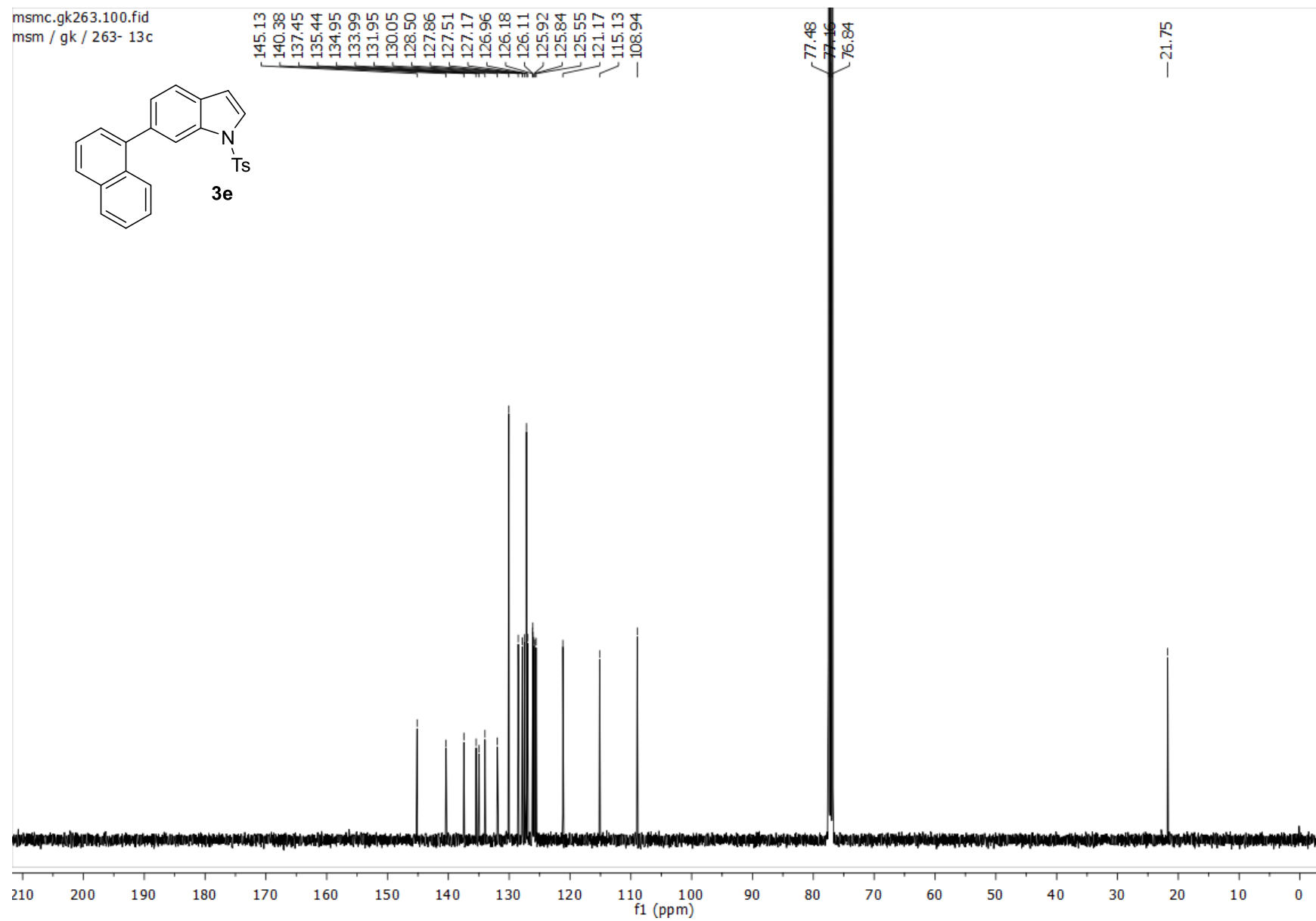
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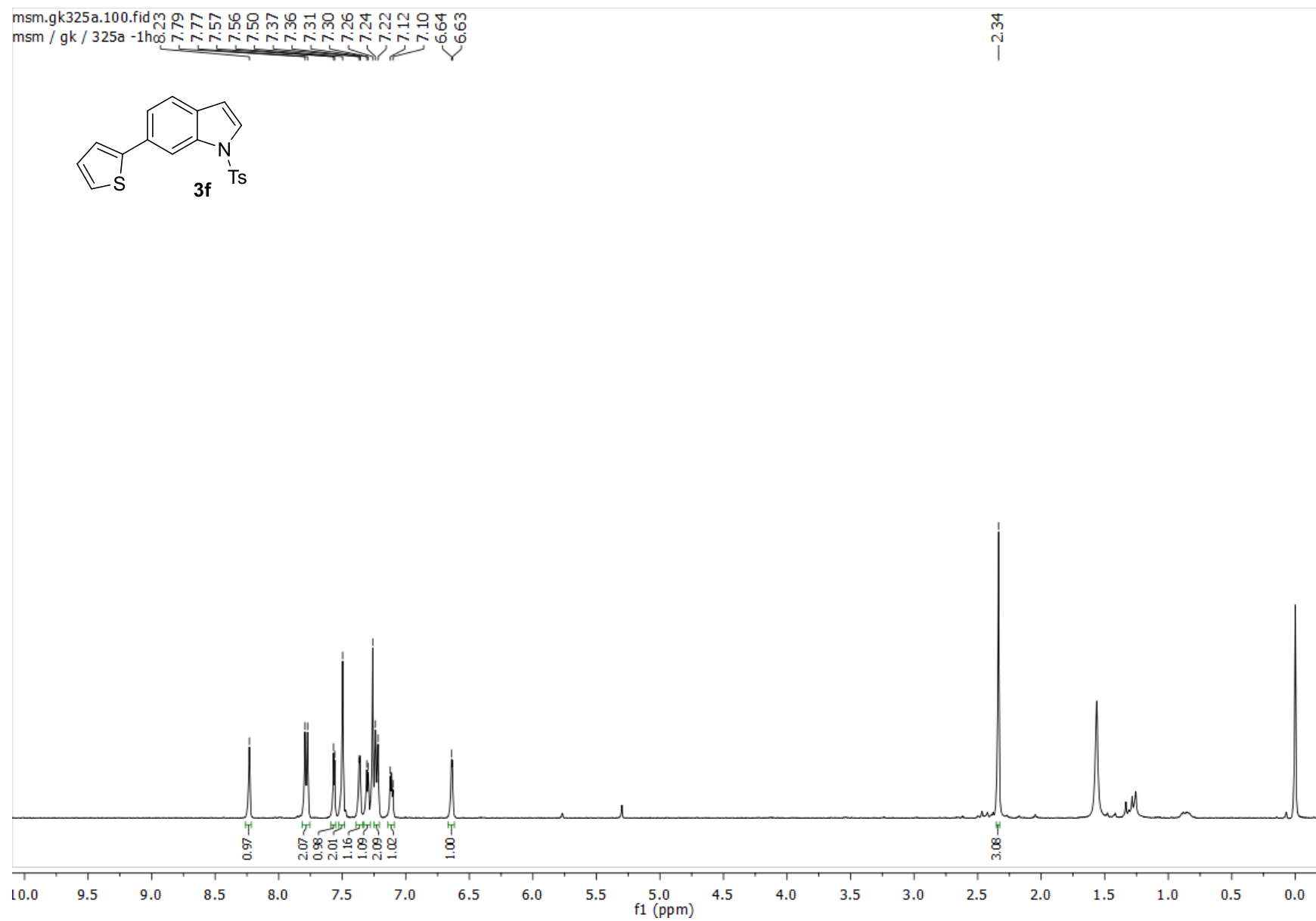




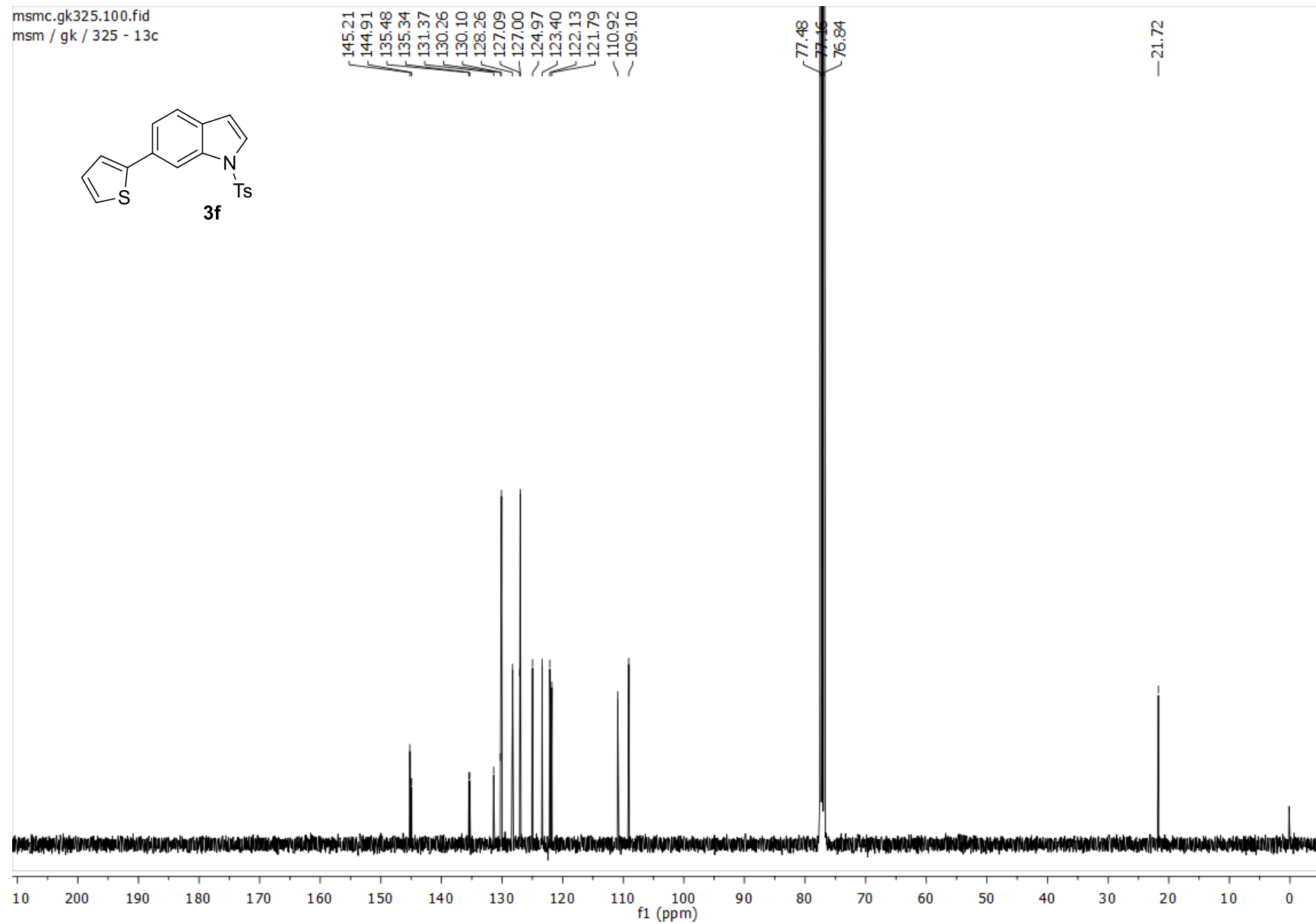
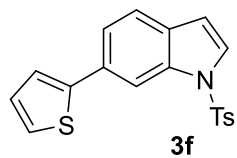




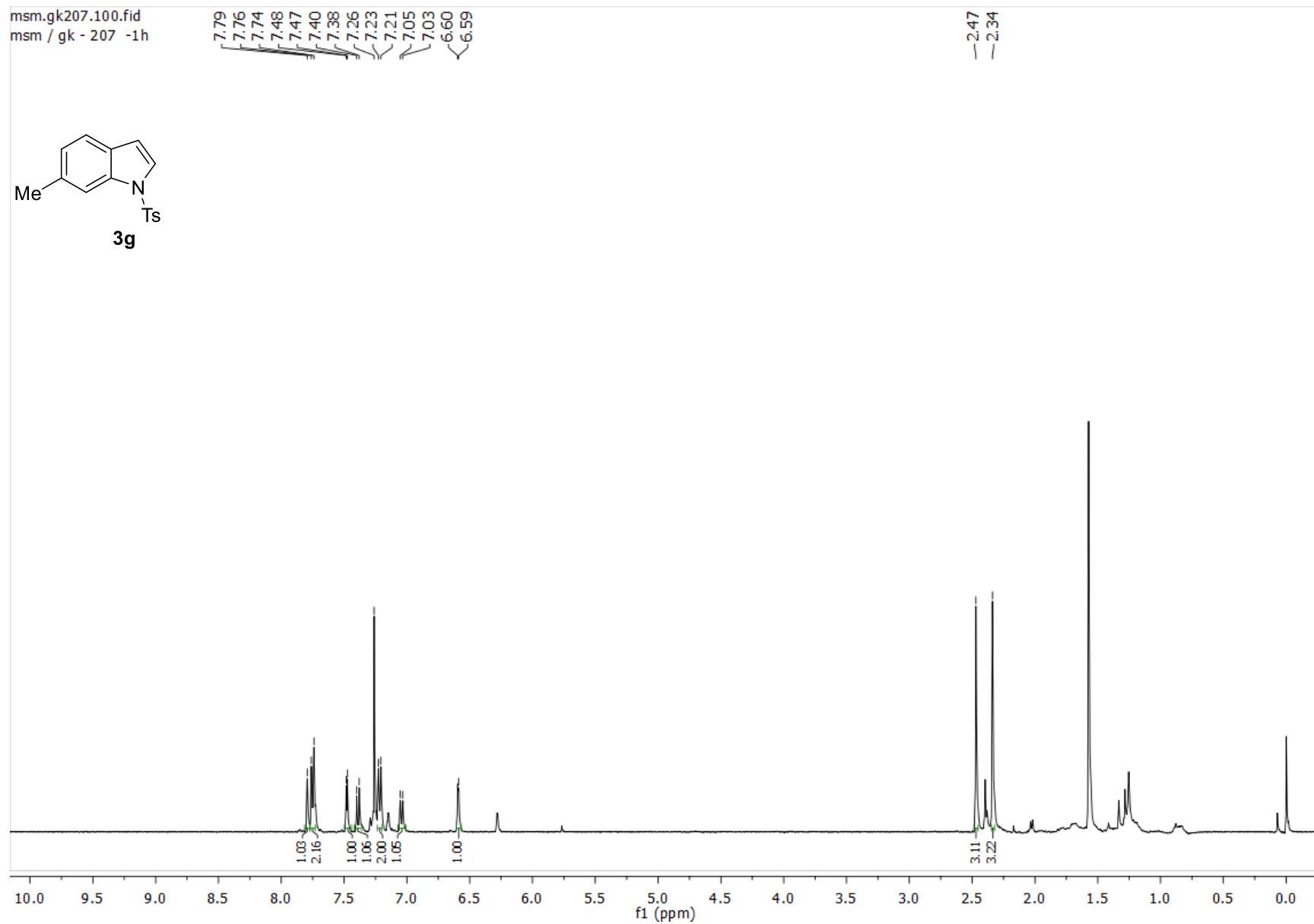
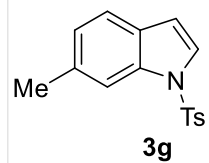




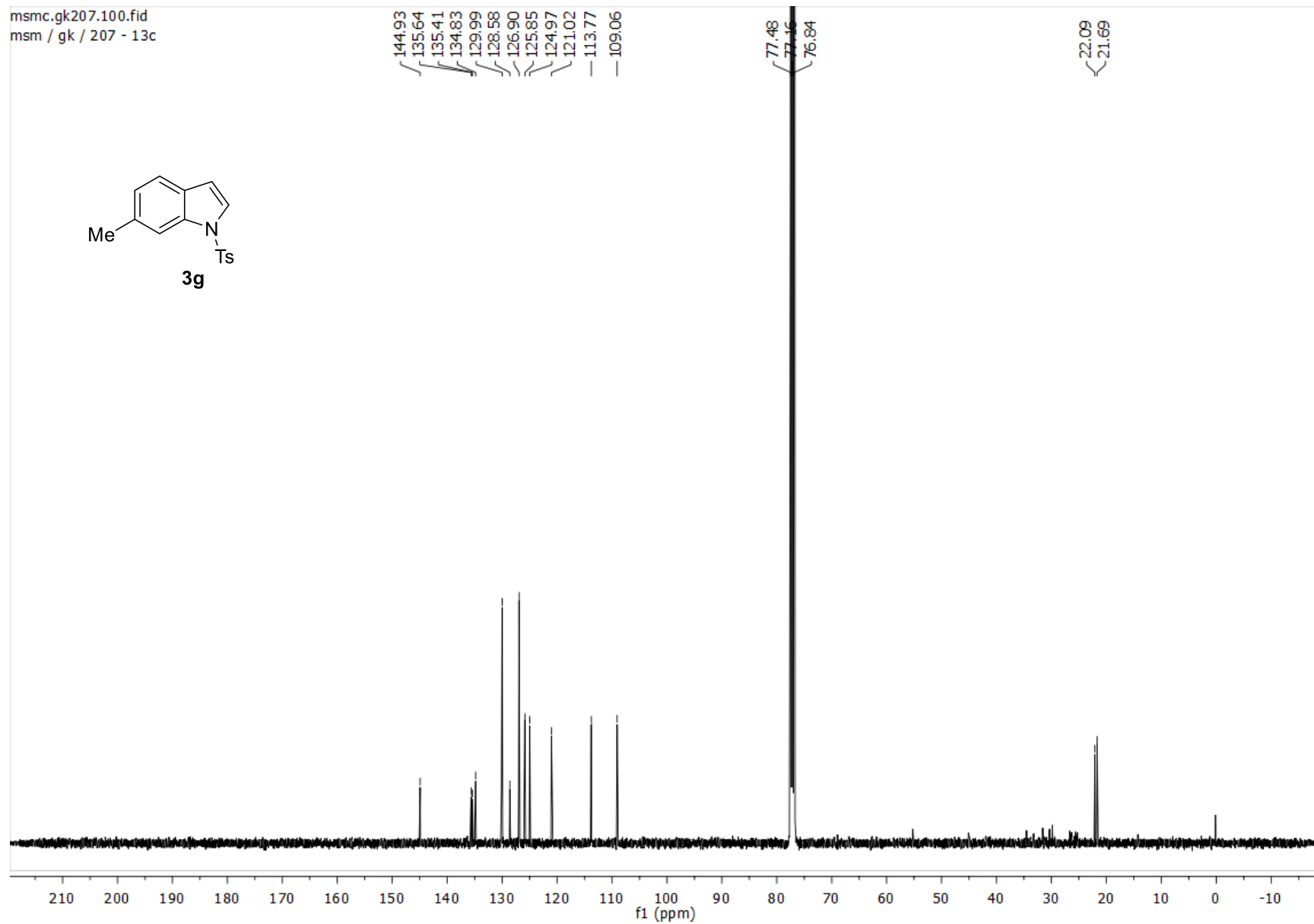
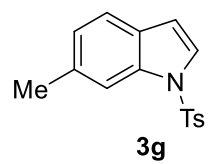
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msm / gk / 325 - 13c

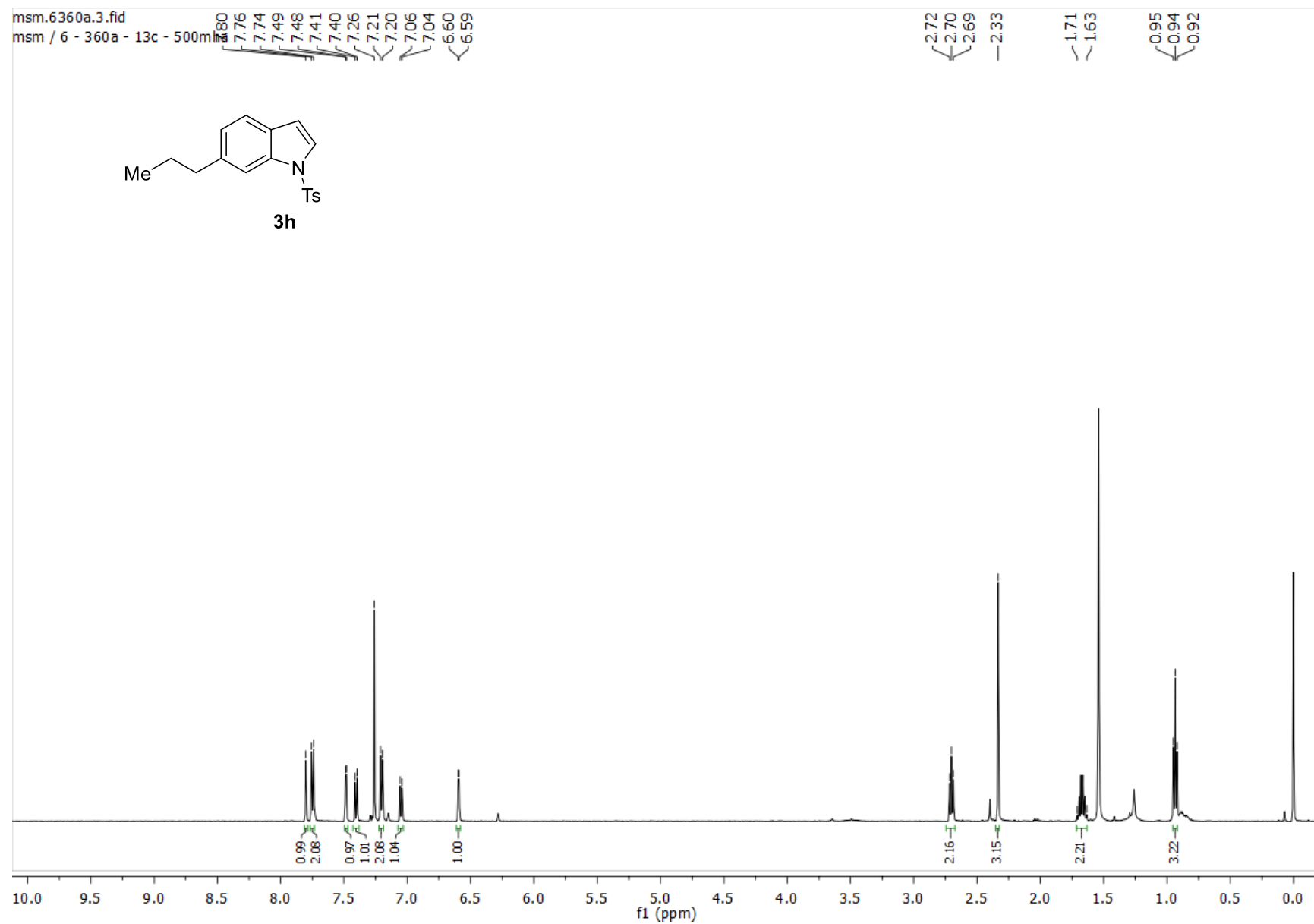


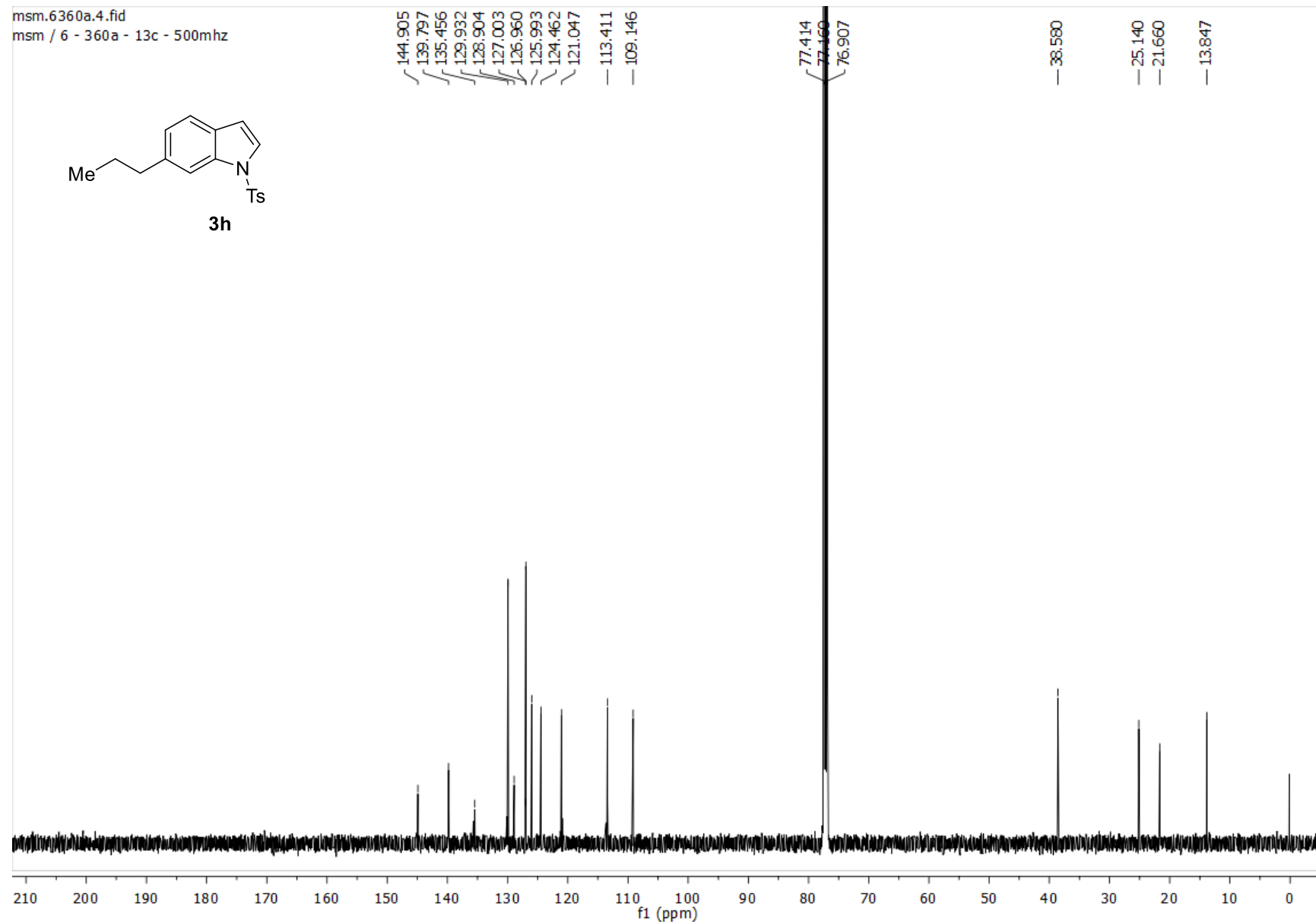
msm.gk207.100.fid
msm / gk - 207 -1h



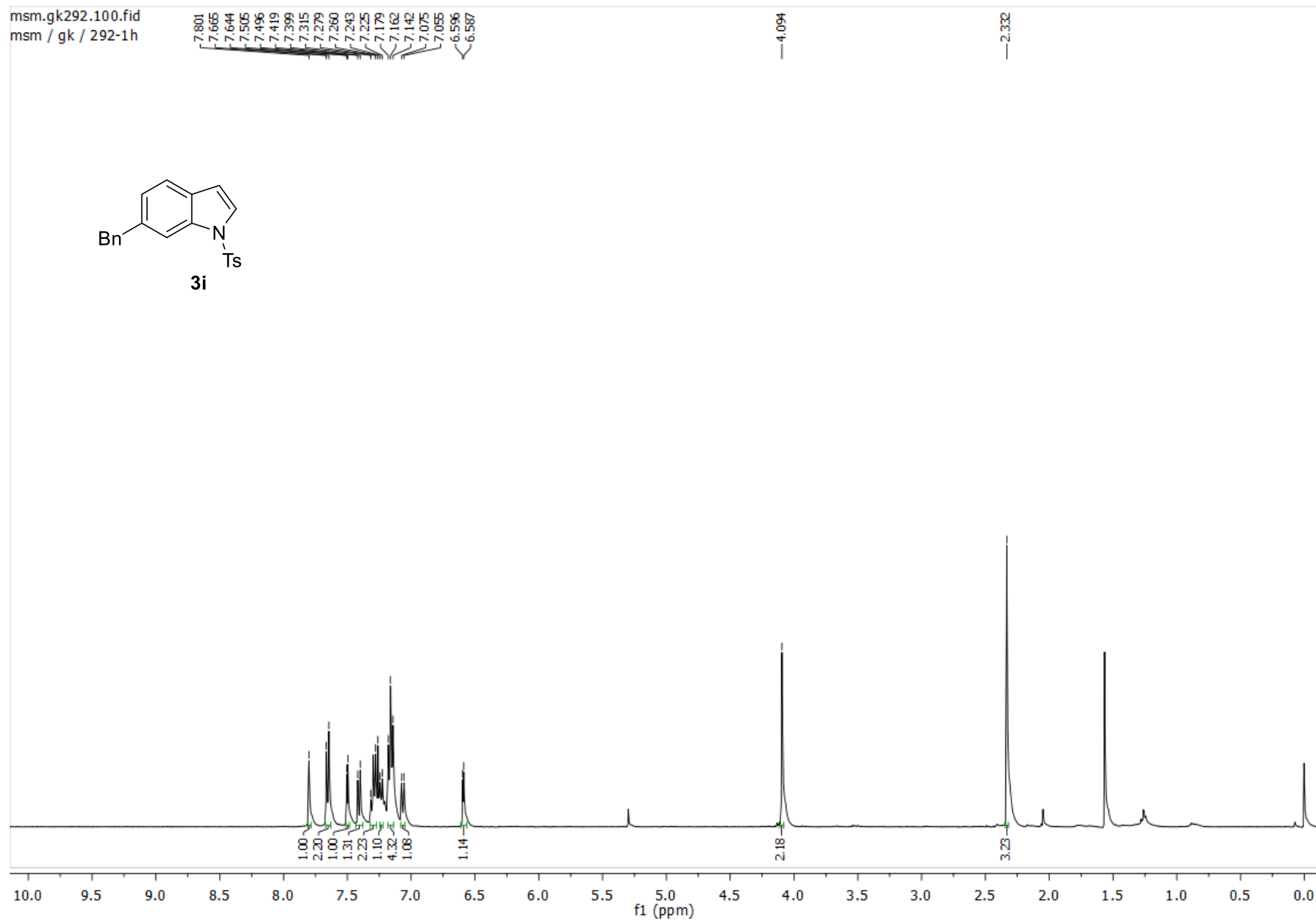
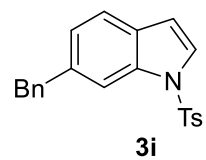
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msm / gk / 207 - 13c



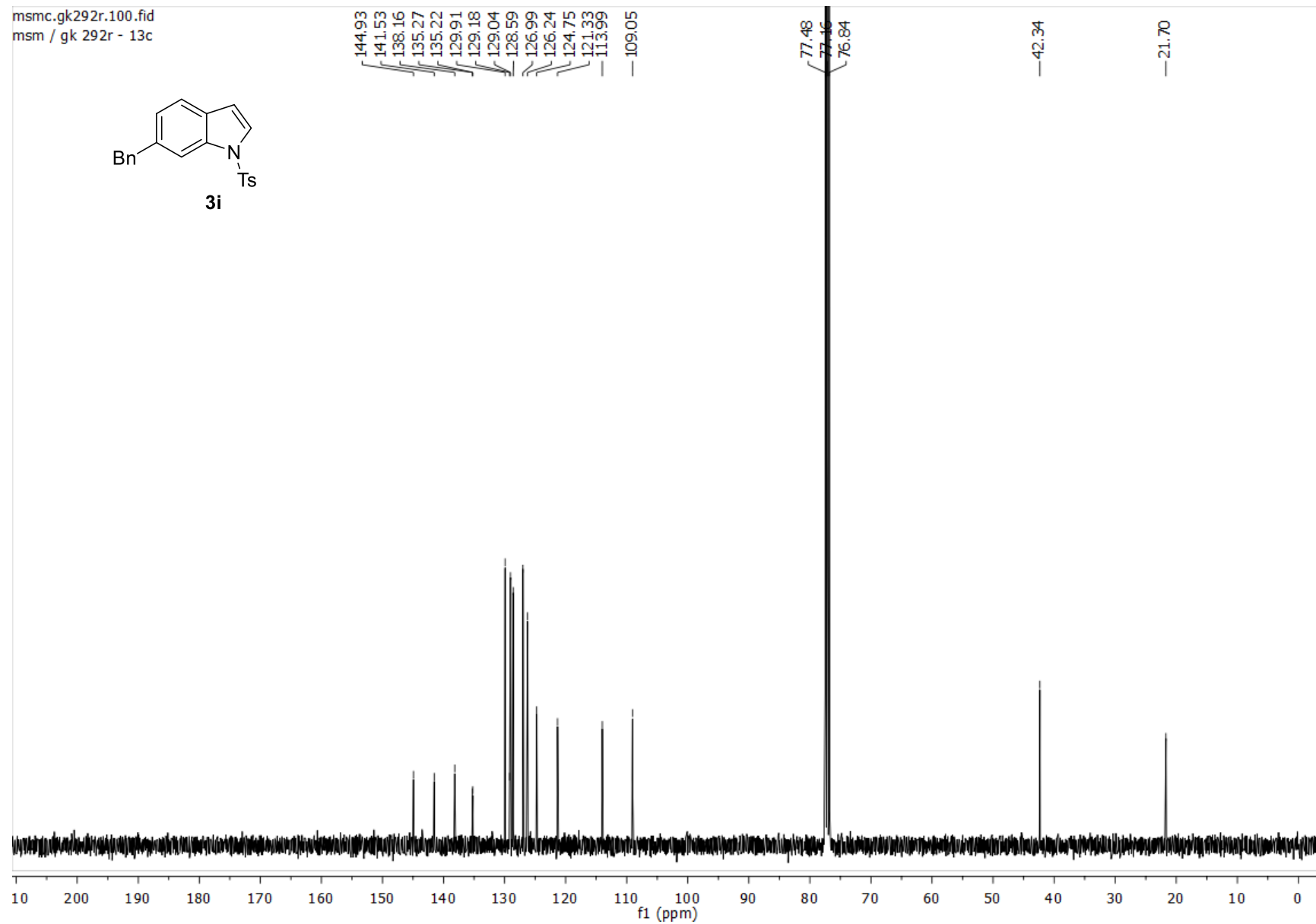
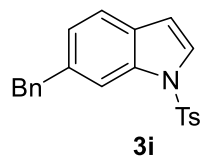




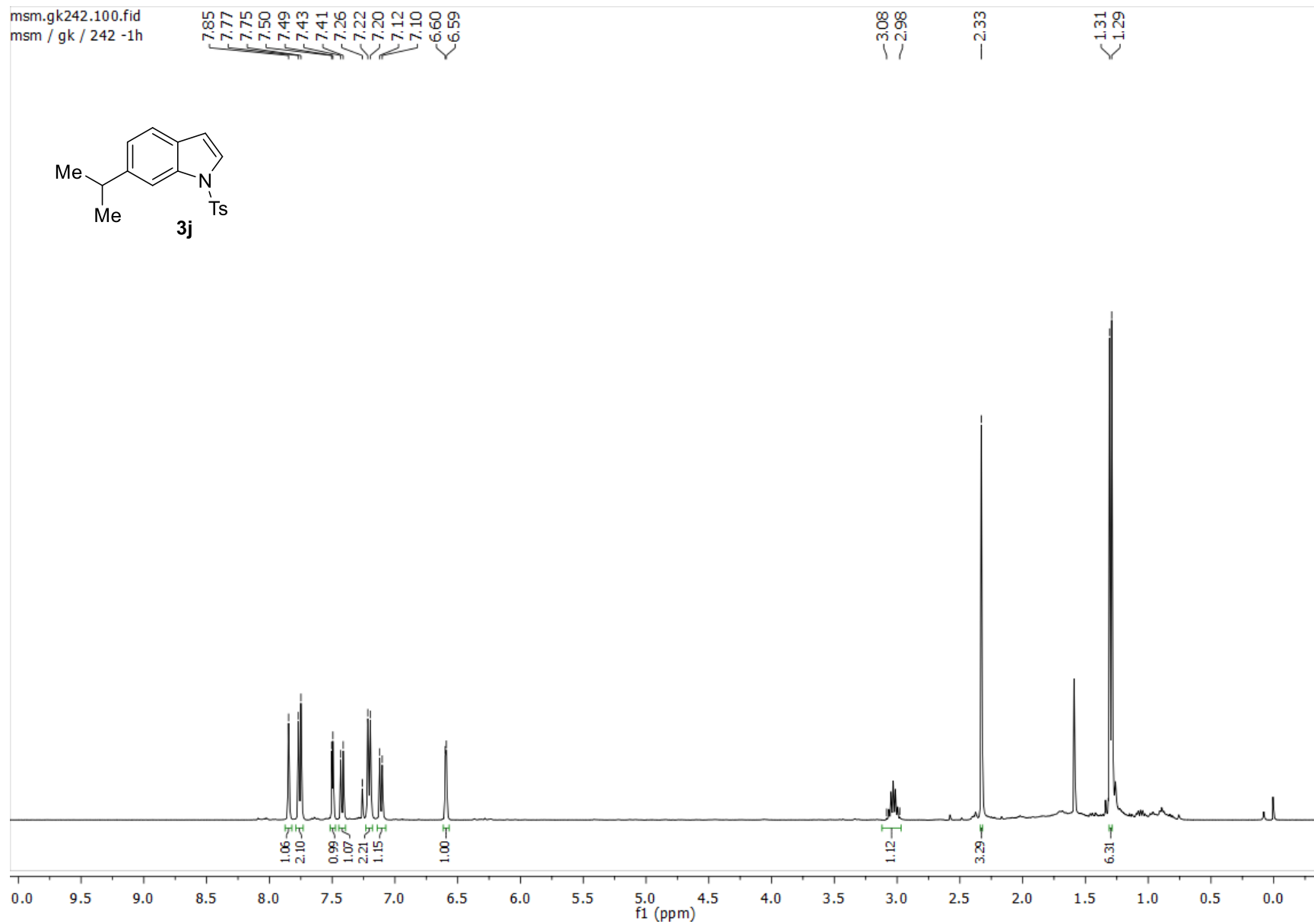
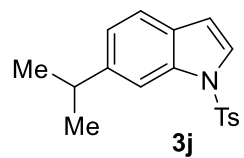
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msm / gk / 292-1h



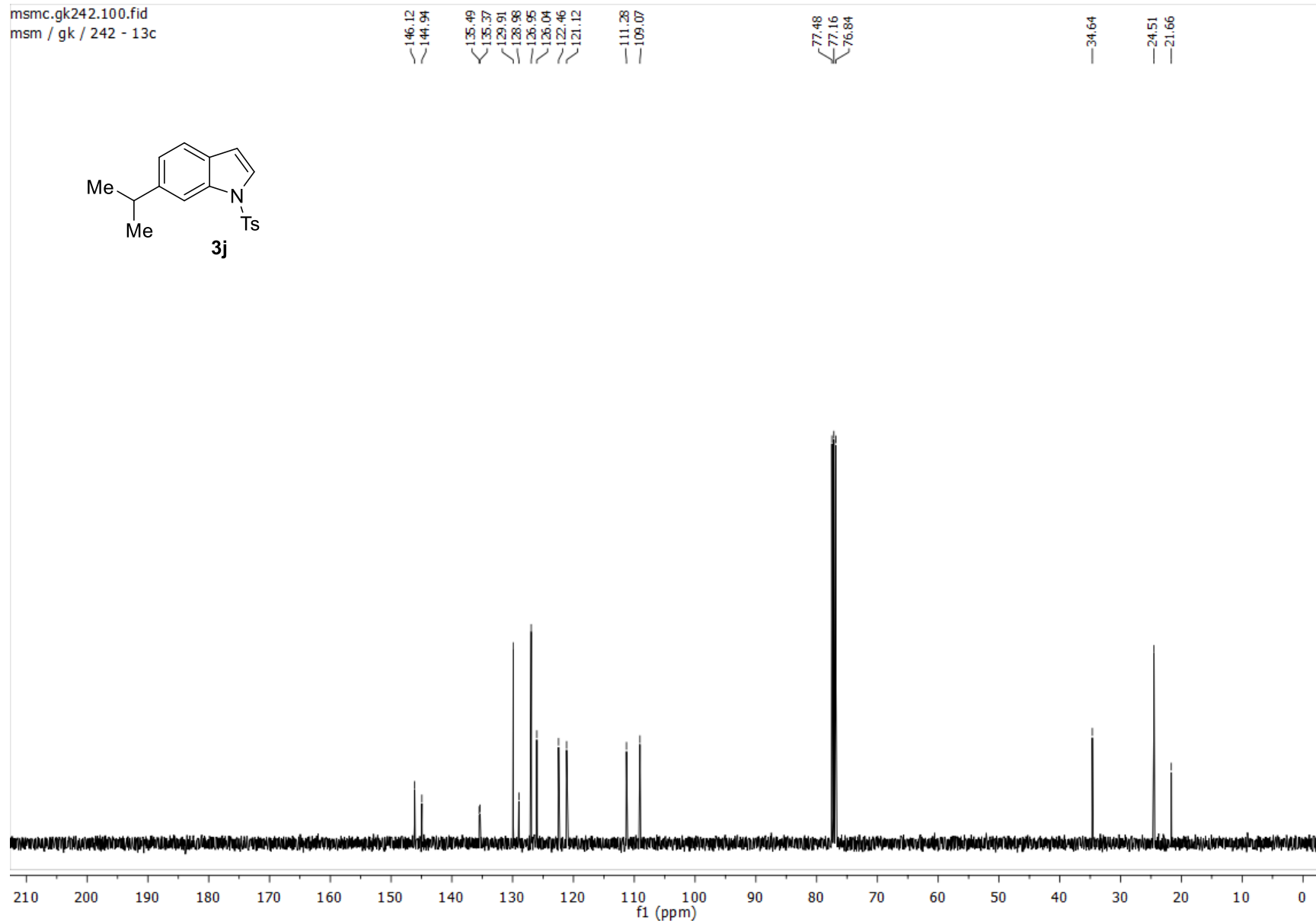
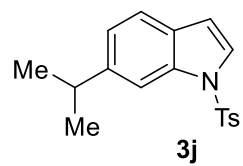
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msm / gk 292r - 13c



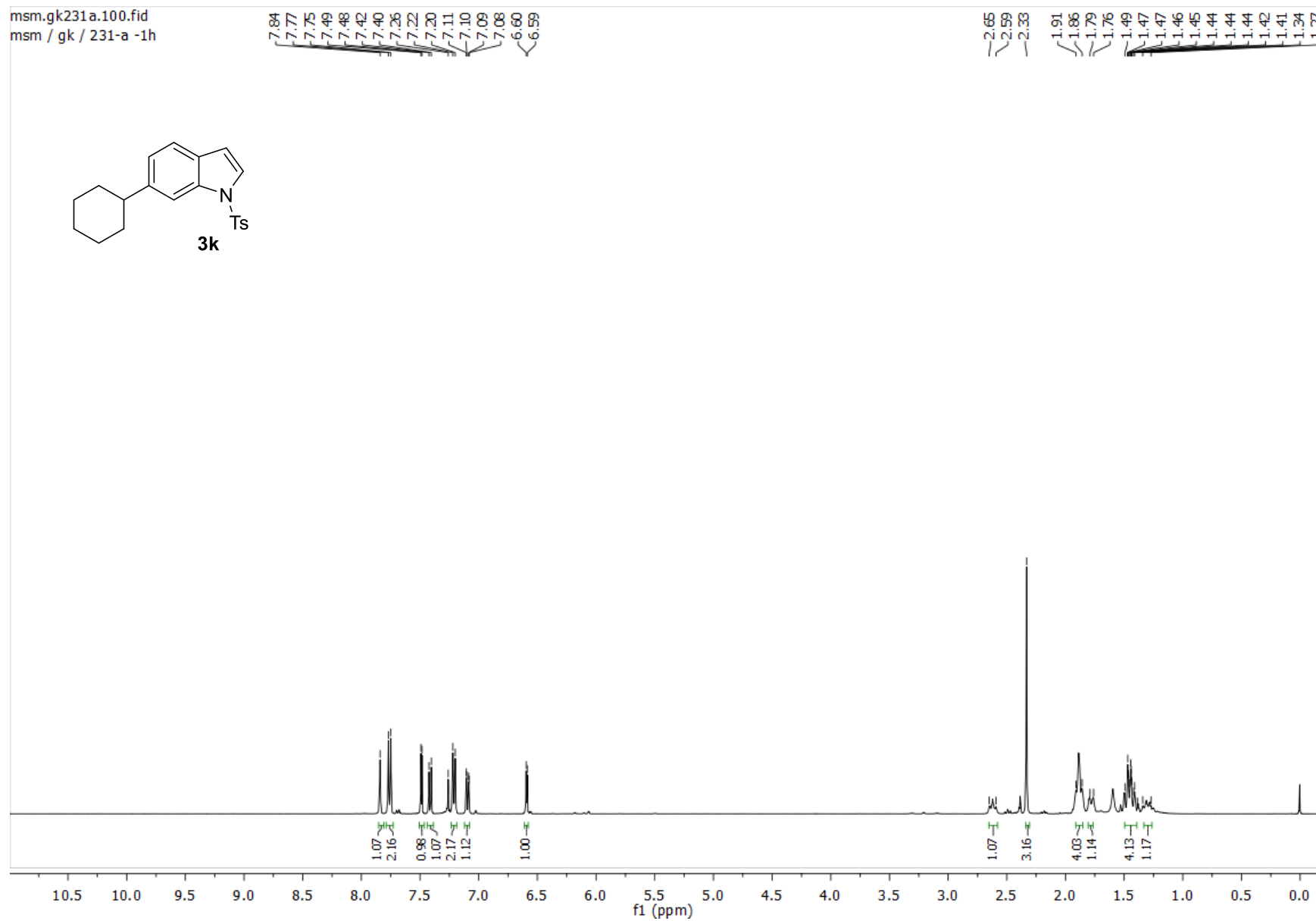
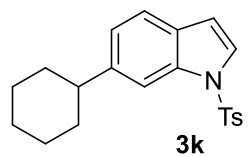
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msm / gk / 242 -1h



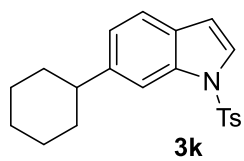
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msm / gk / 242 - 13c



msm.gk231a.100.fid
msm / gk / 231-a -1h



msmc.gk231a.100.fid
msm / gk / 231-a - 13c



145.36
144.92

135.50
135.39

129.92
128.98

126.93
126.01

122.90
121.05

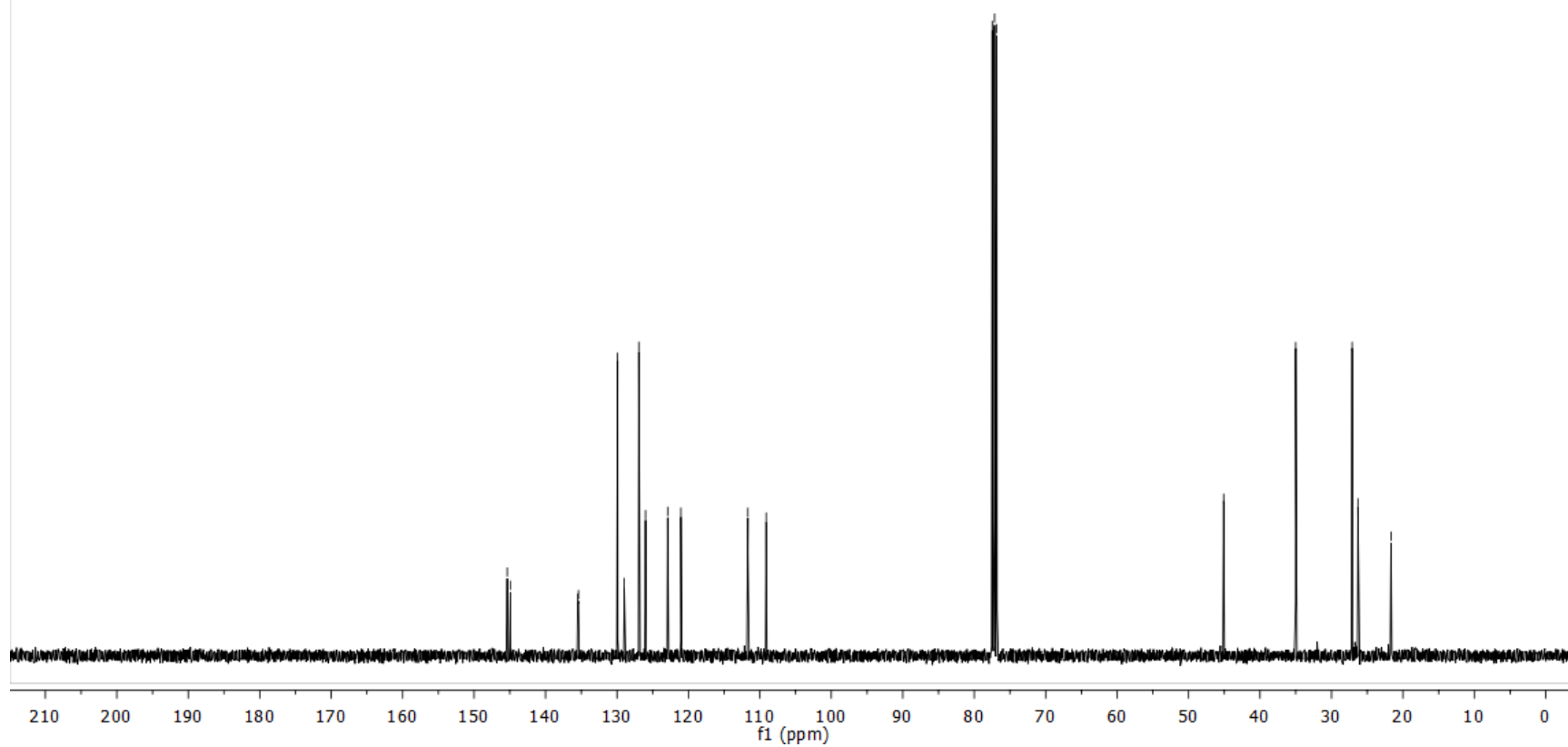
111.69
109.12

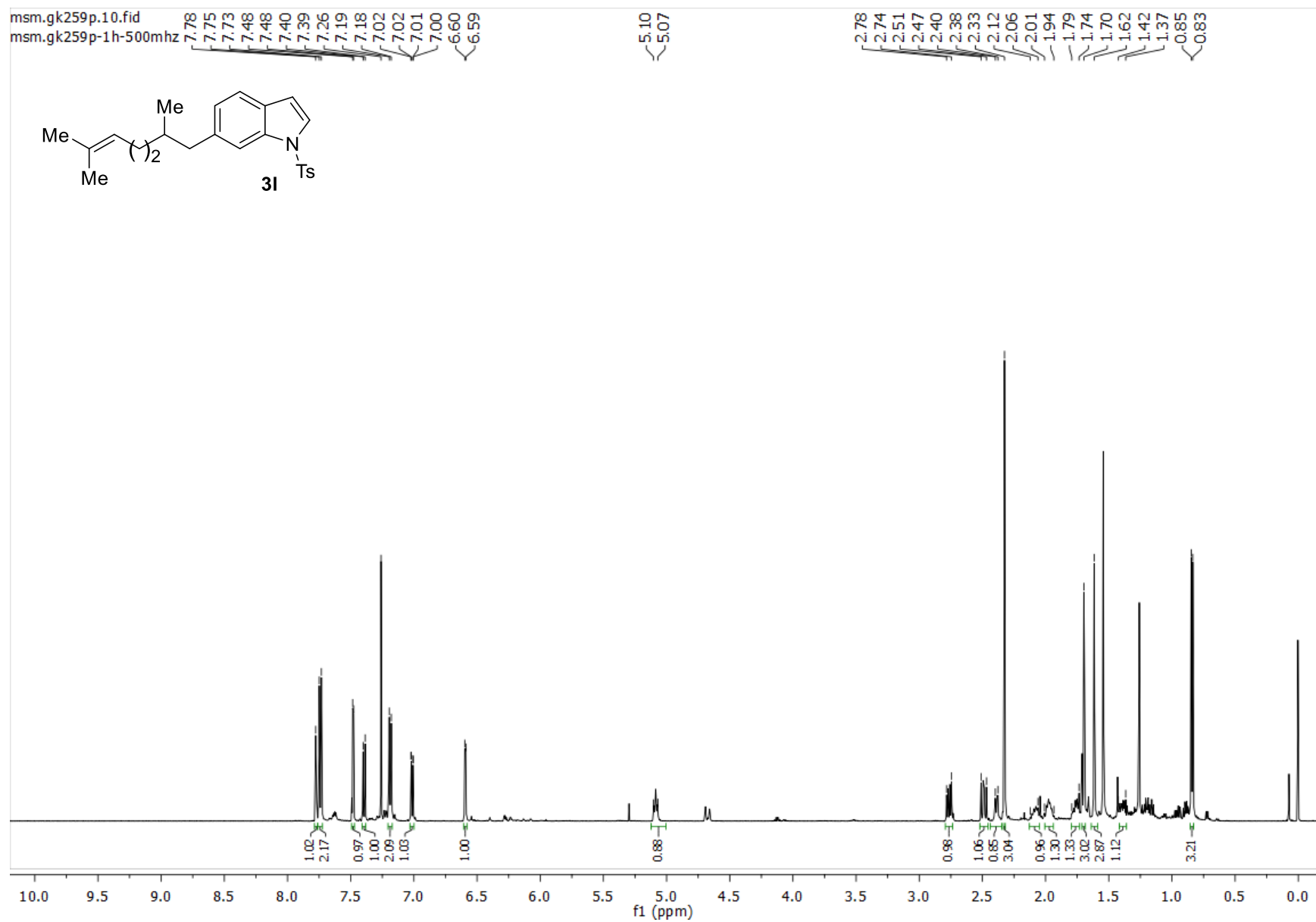
77.48
77.16
76.84

45.09

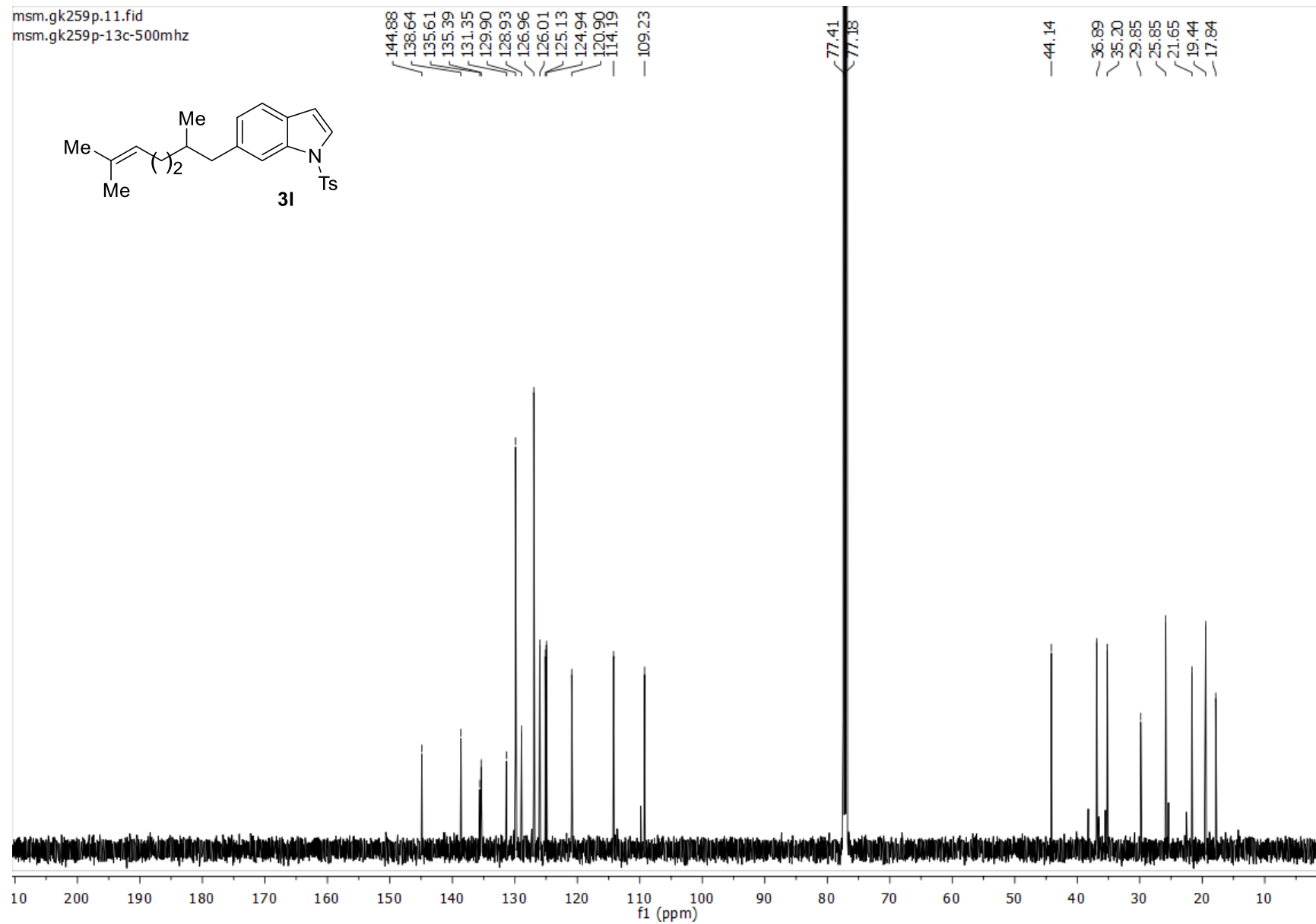
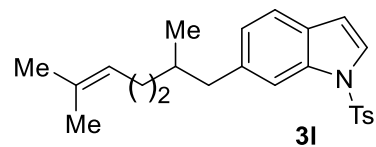
35.00

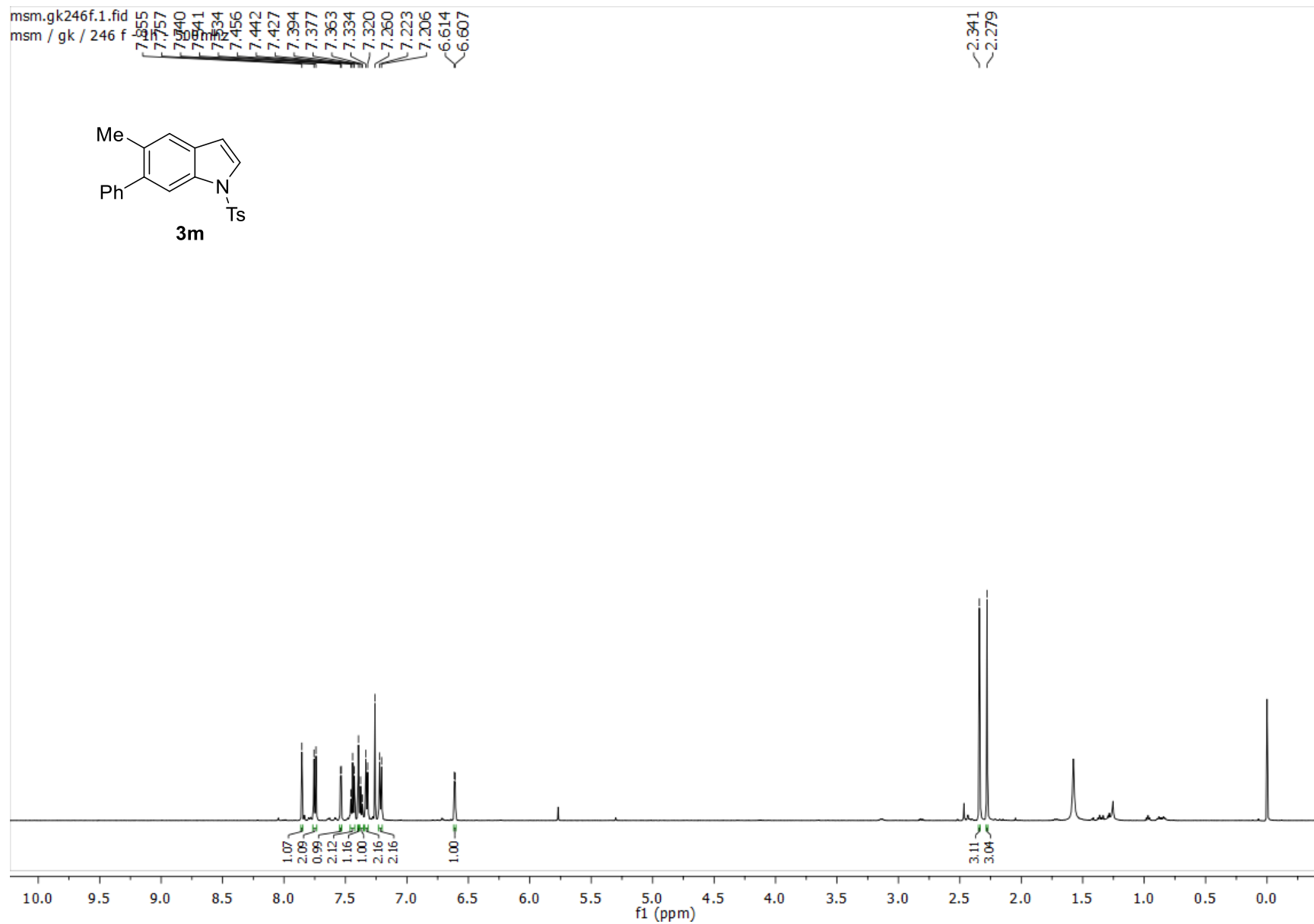
27.10
26.29
21.67

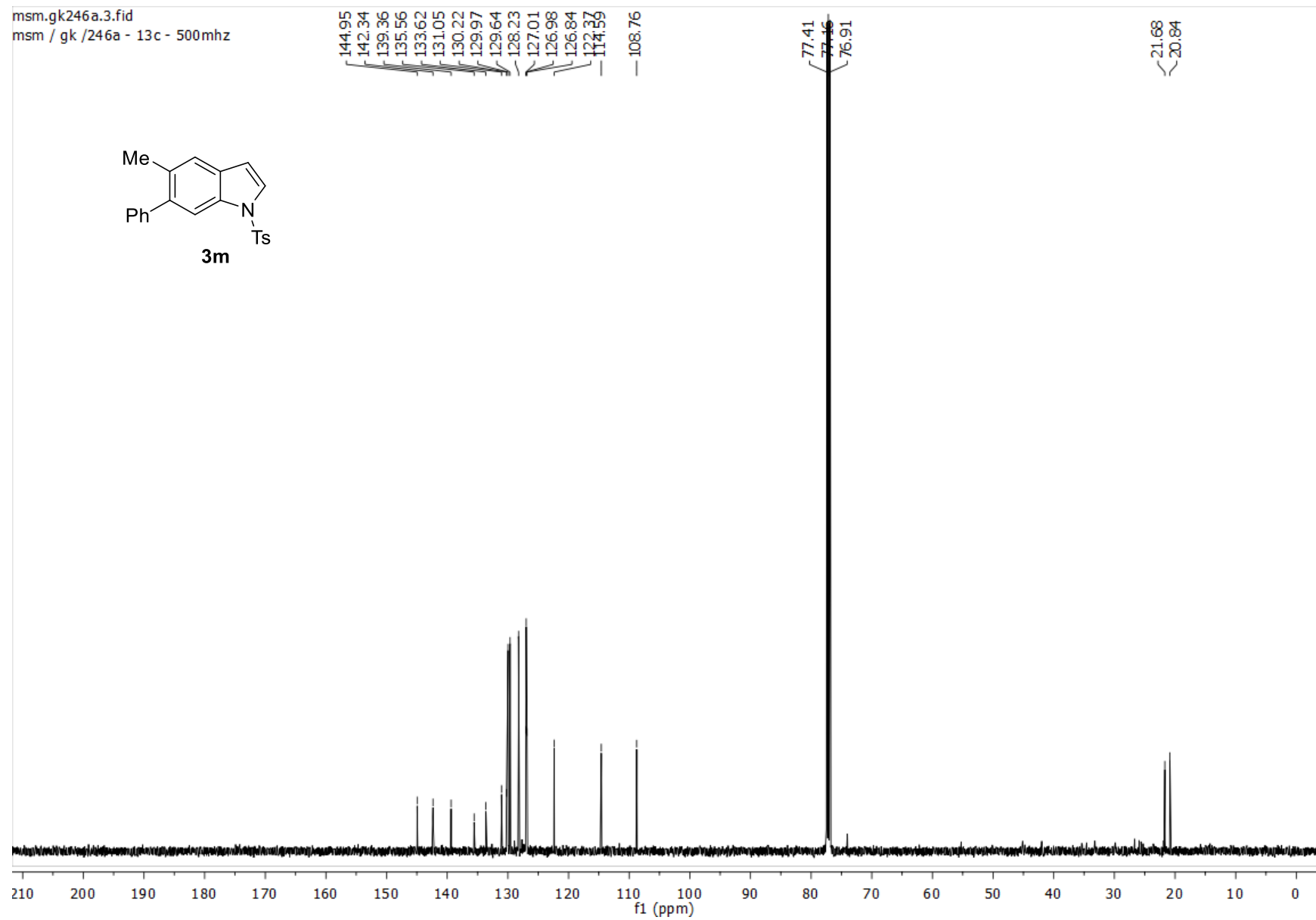


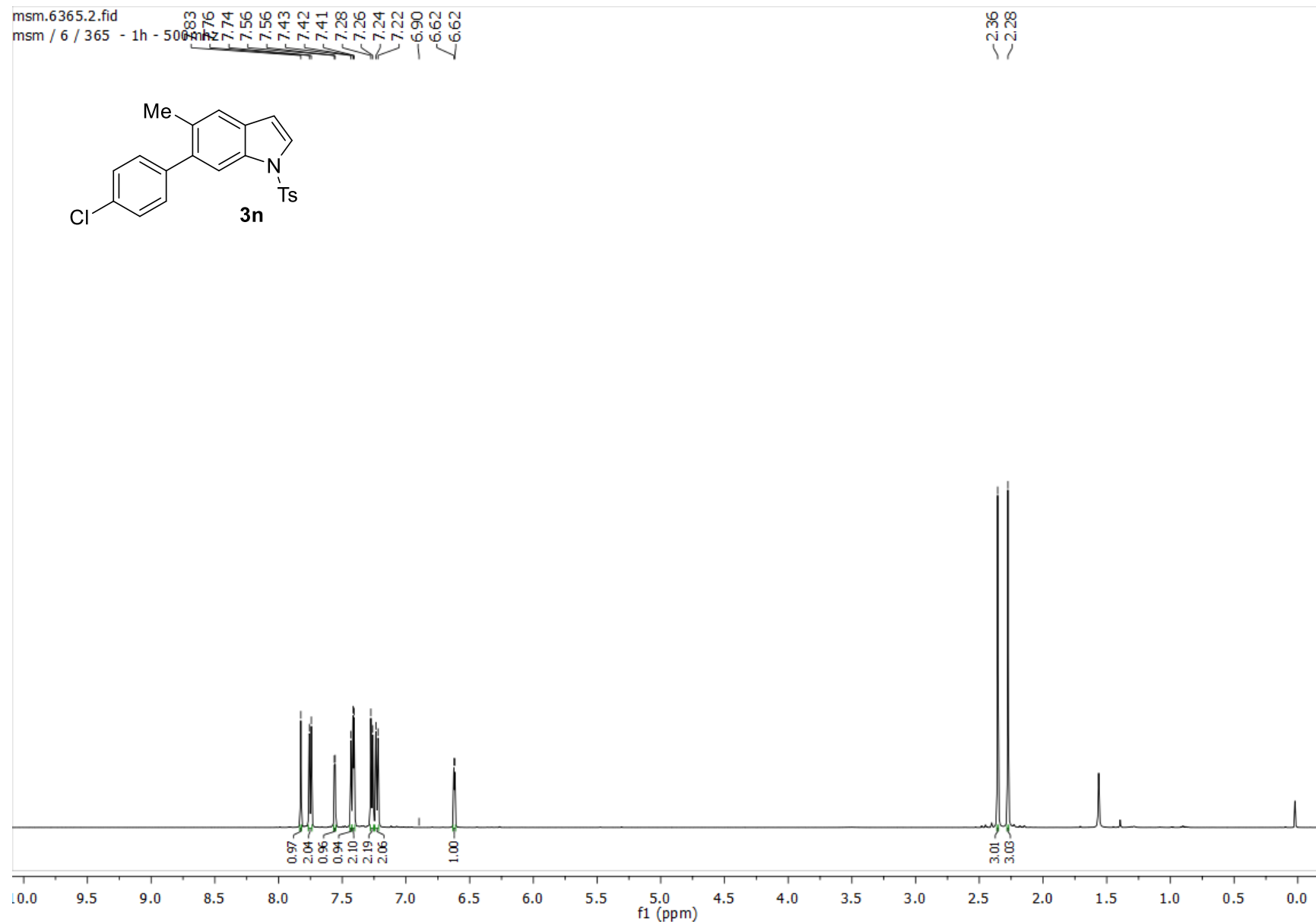


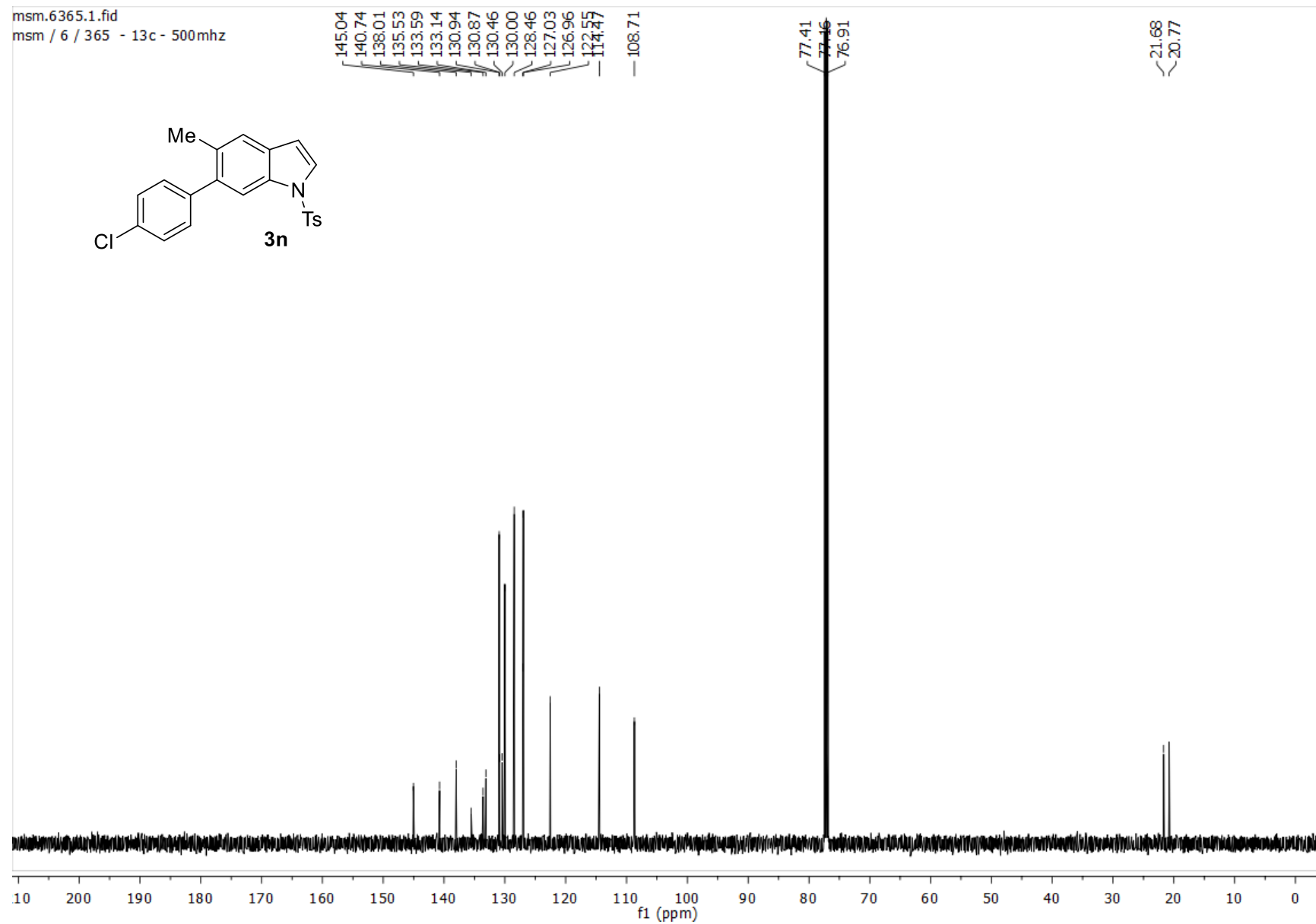
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msm.gk259p-13c-500mhz

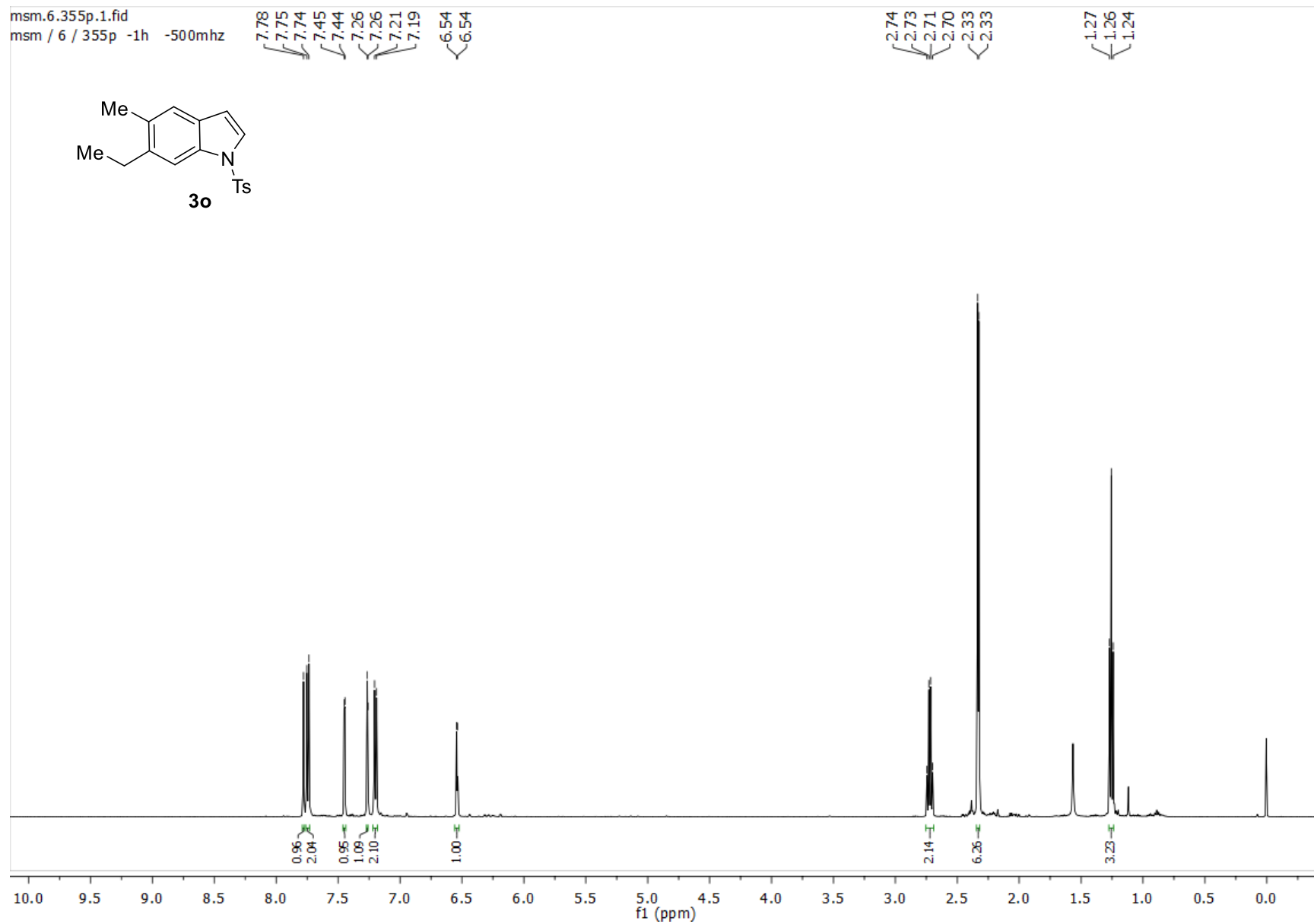


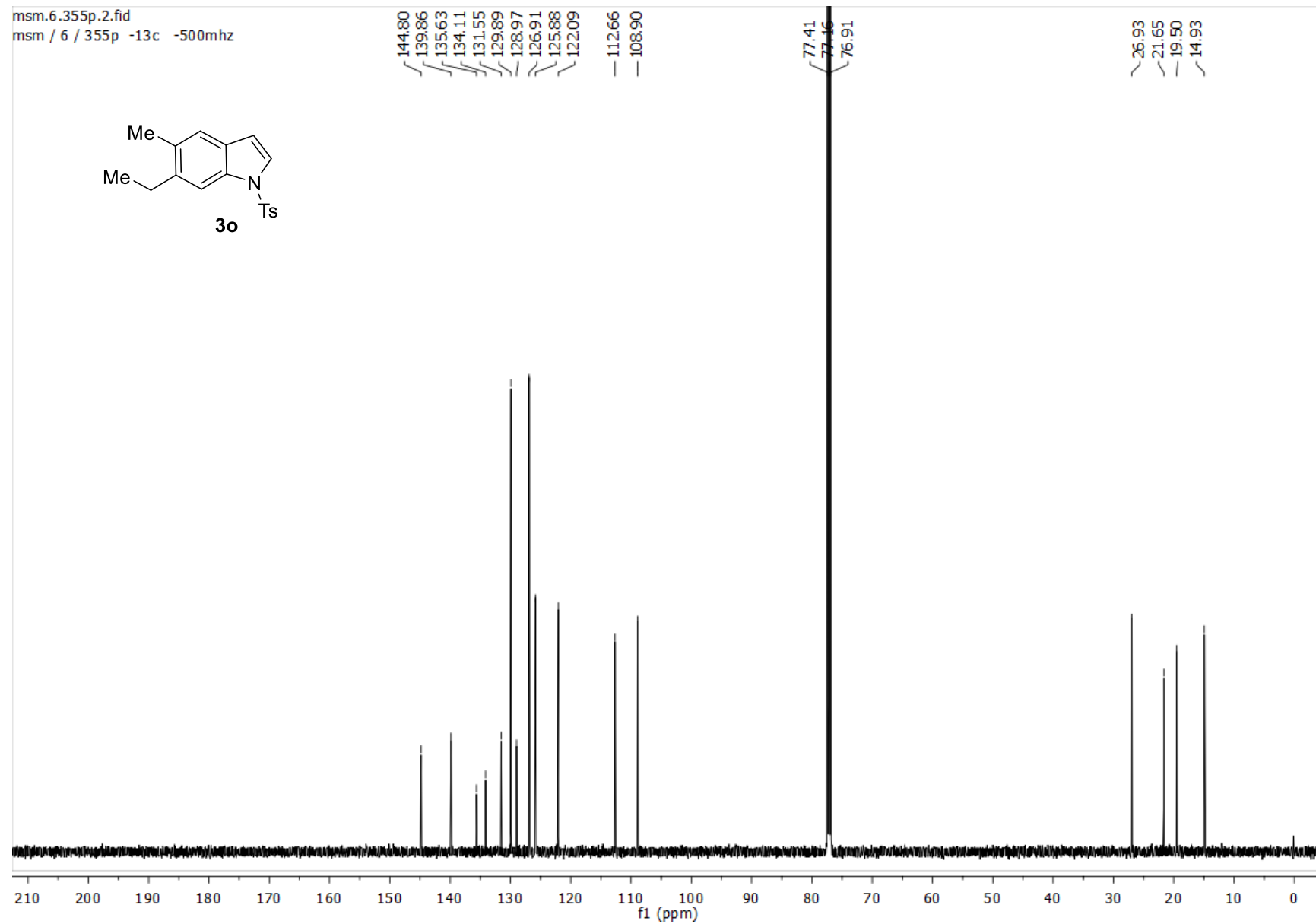


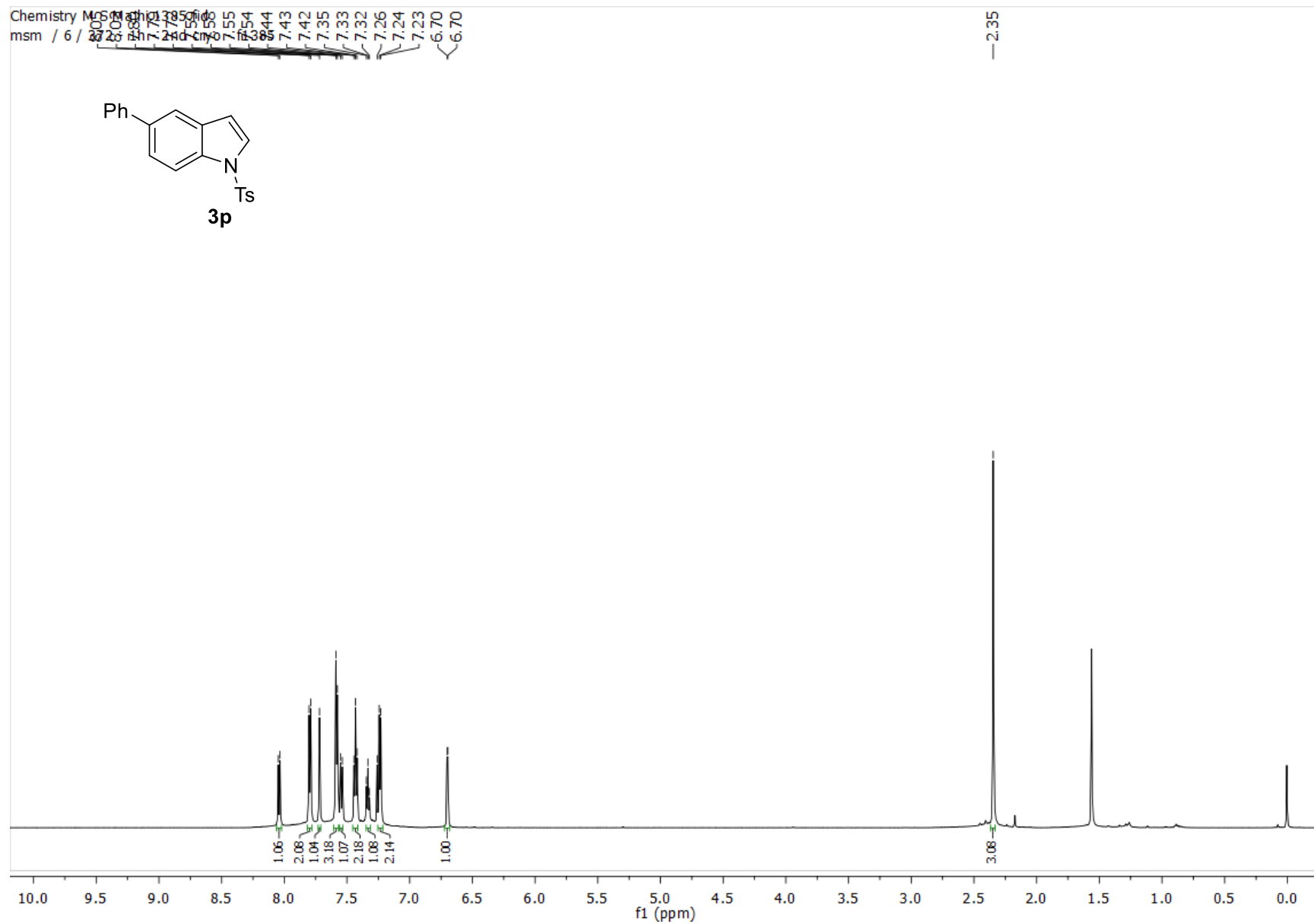




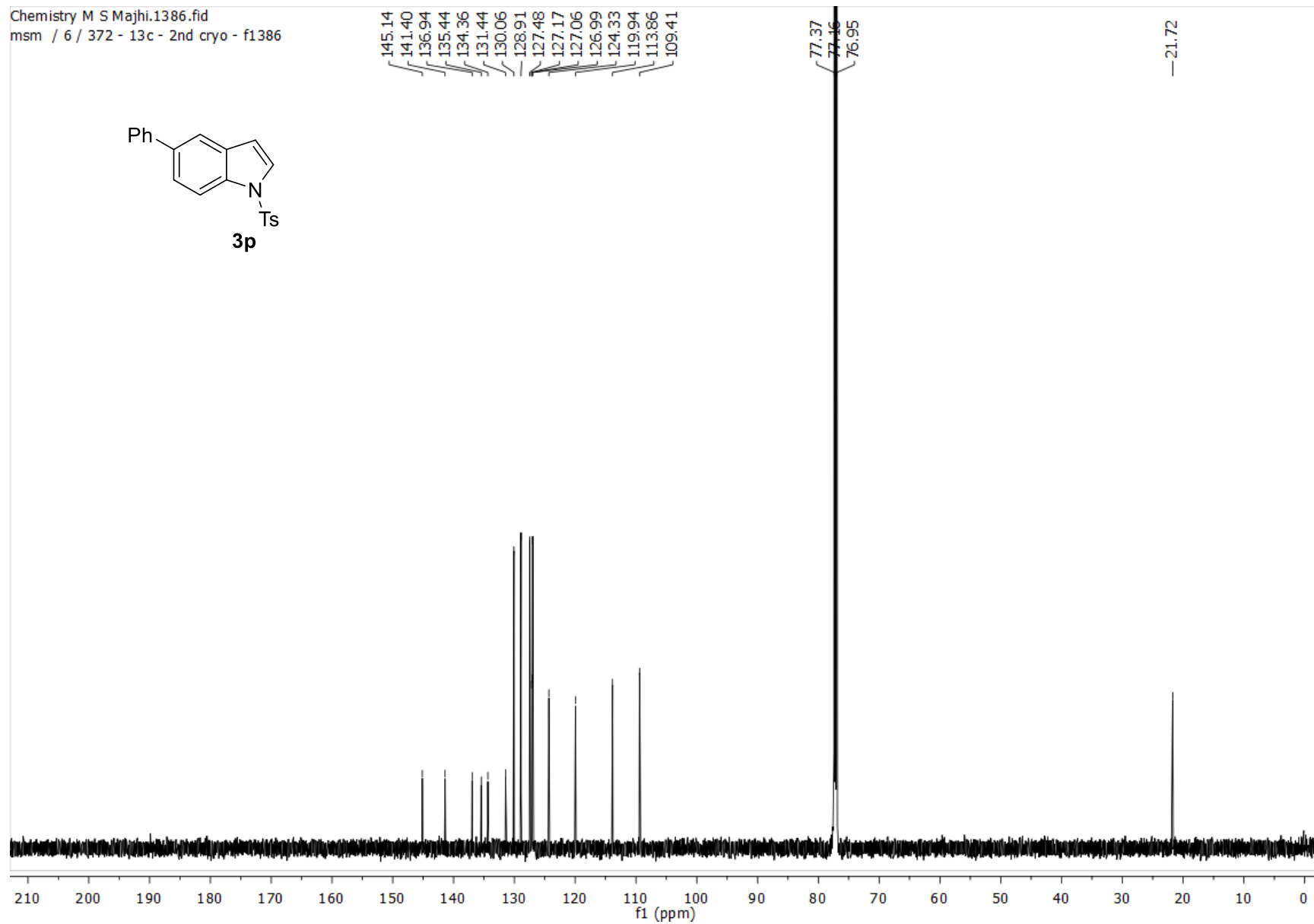
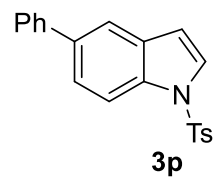


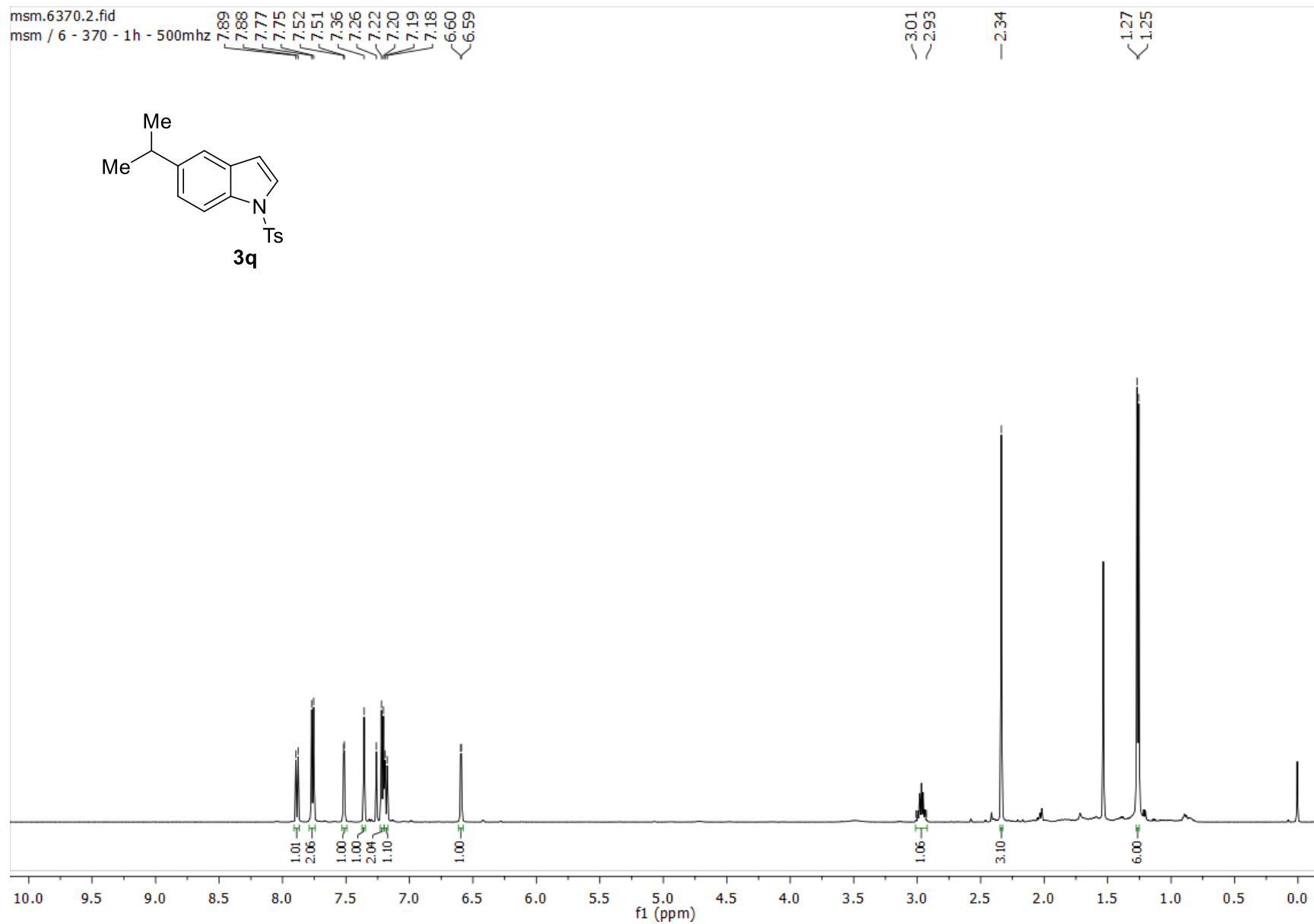


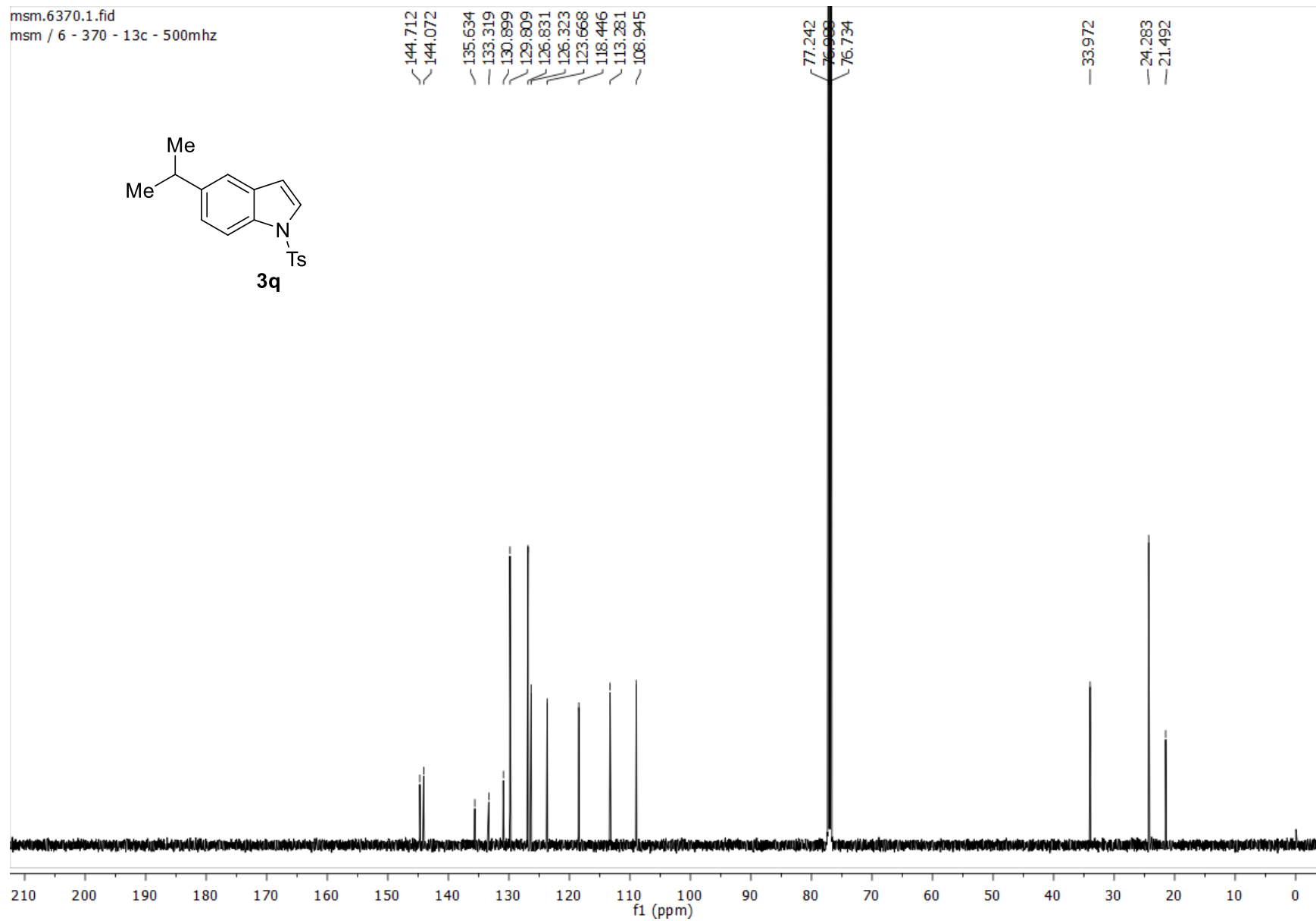


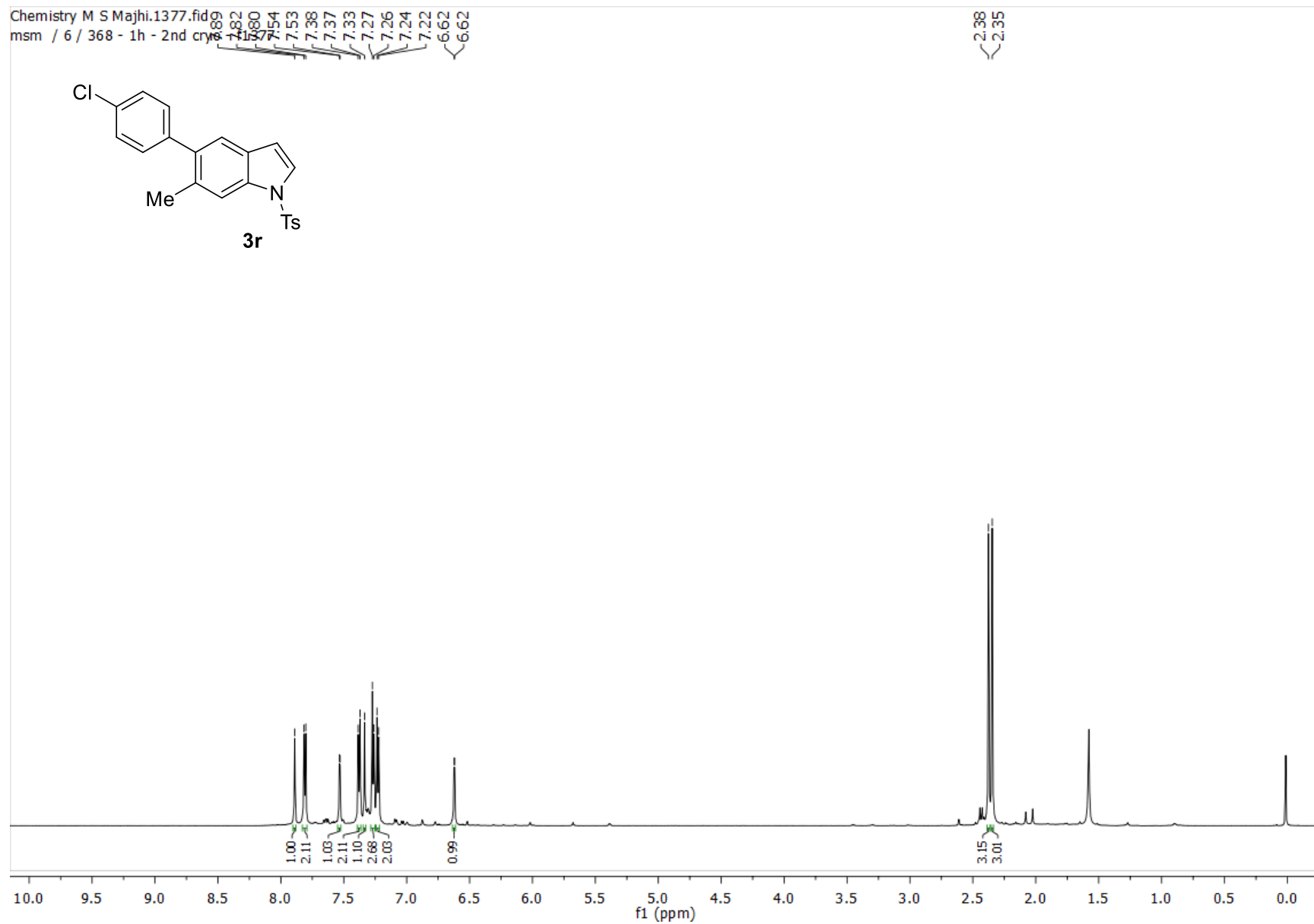


Chemistry M S Majhi.1386.fid
msm / 6 / 372 - 13c - 2nd cryo - f1386

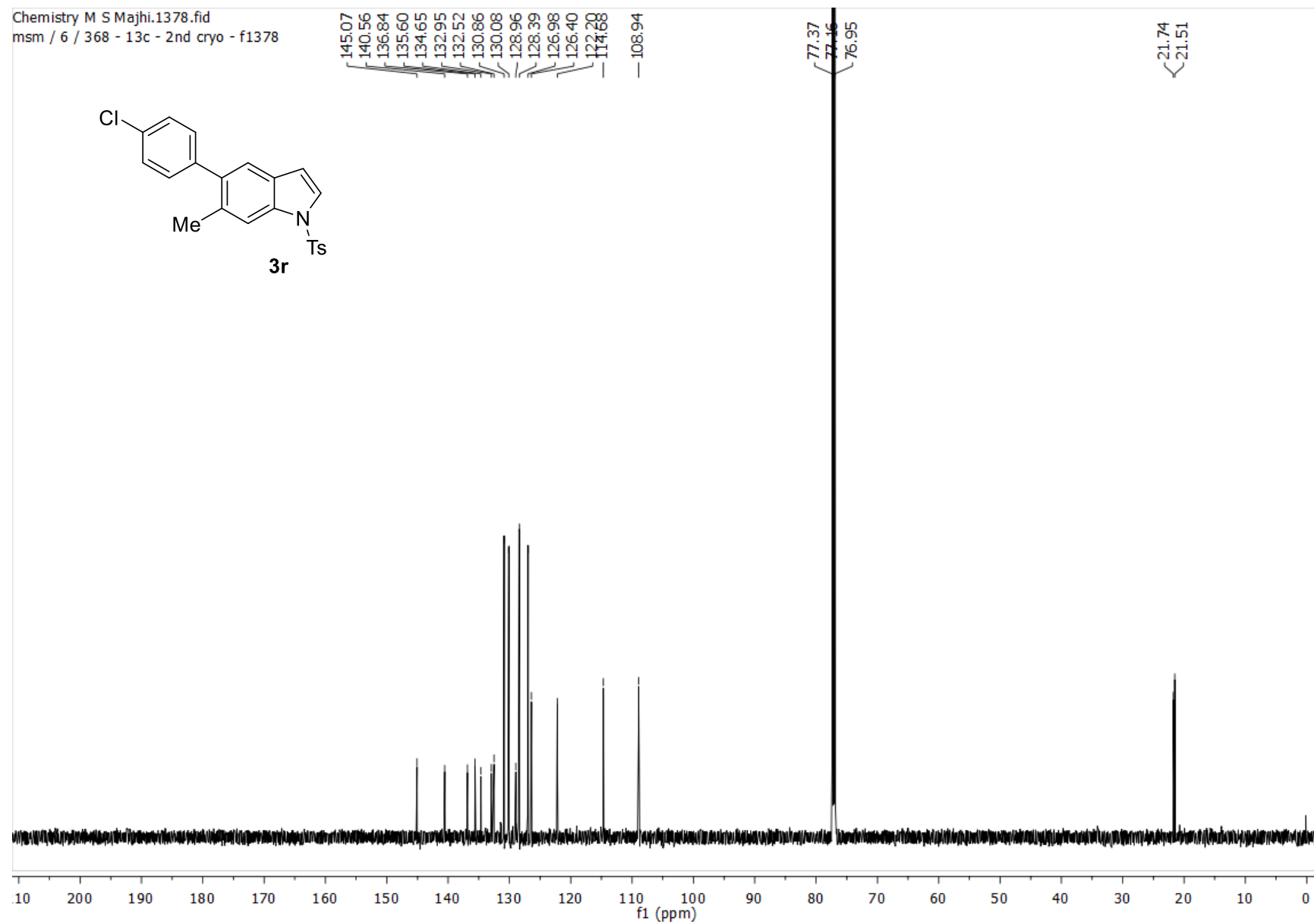


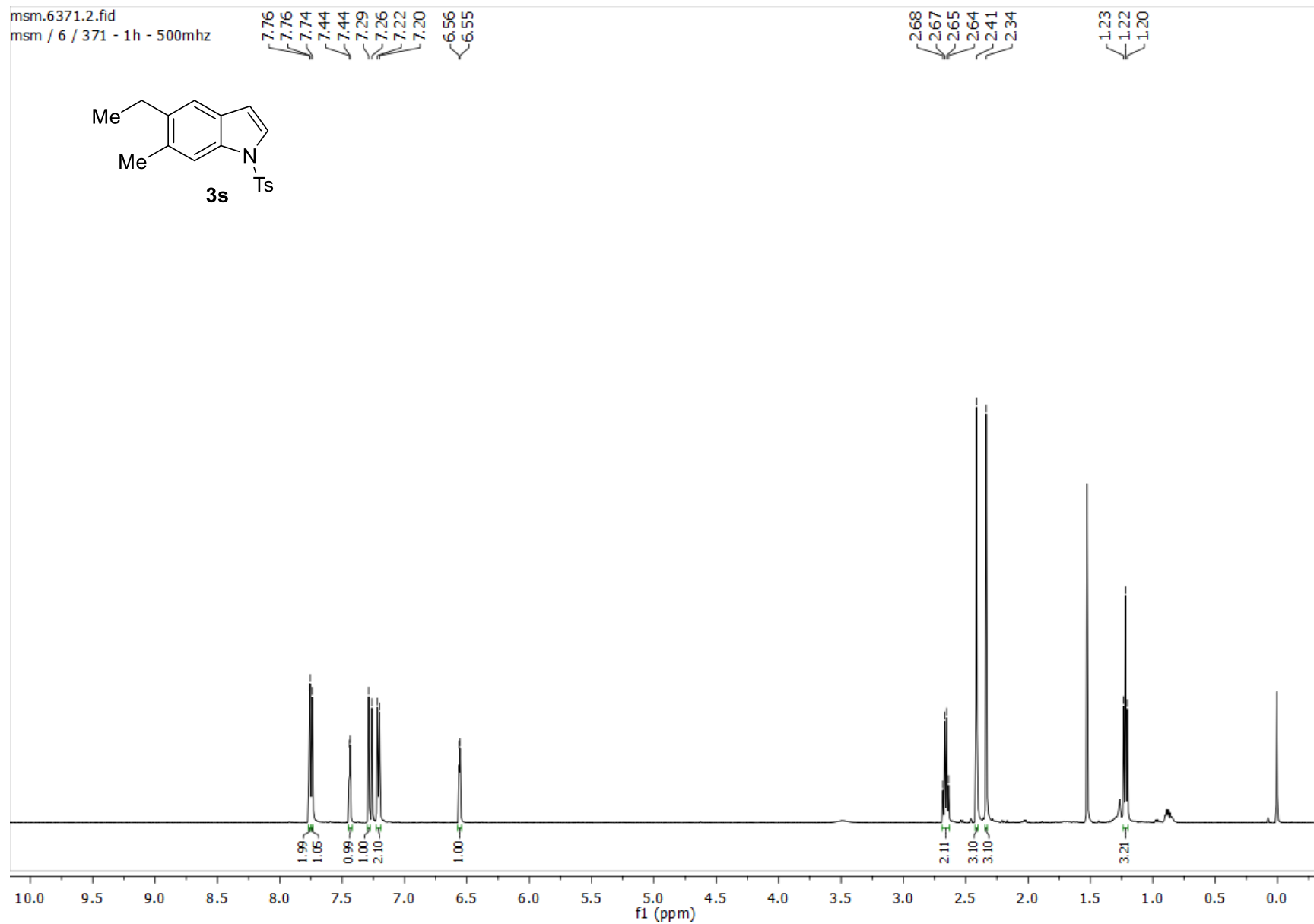


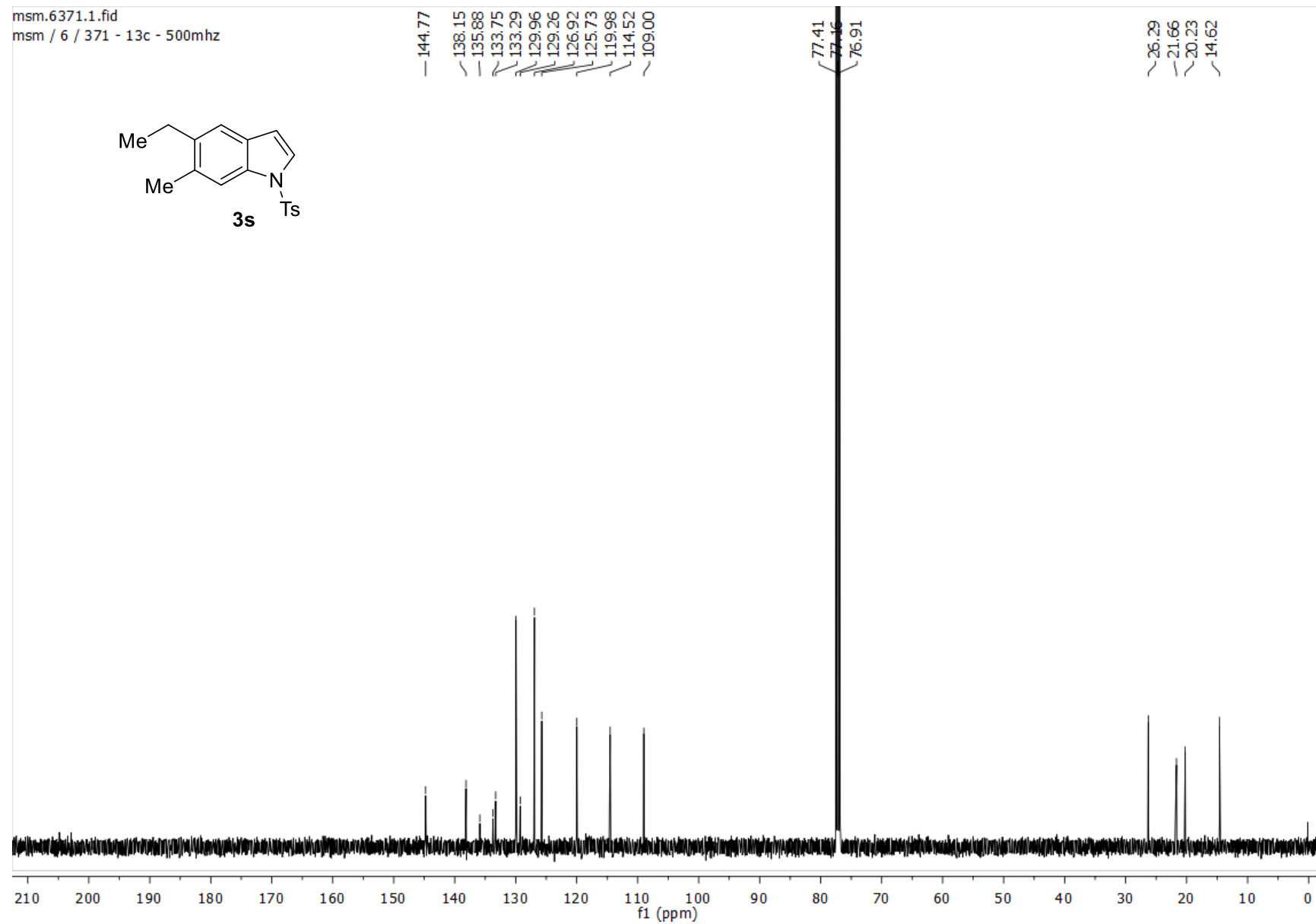


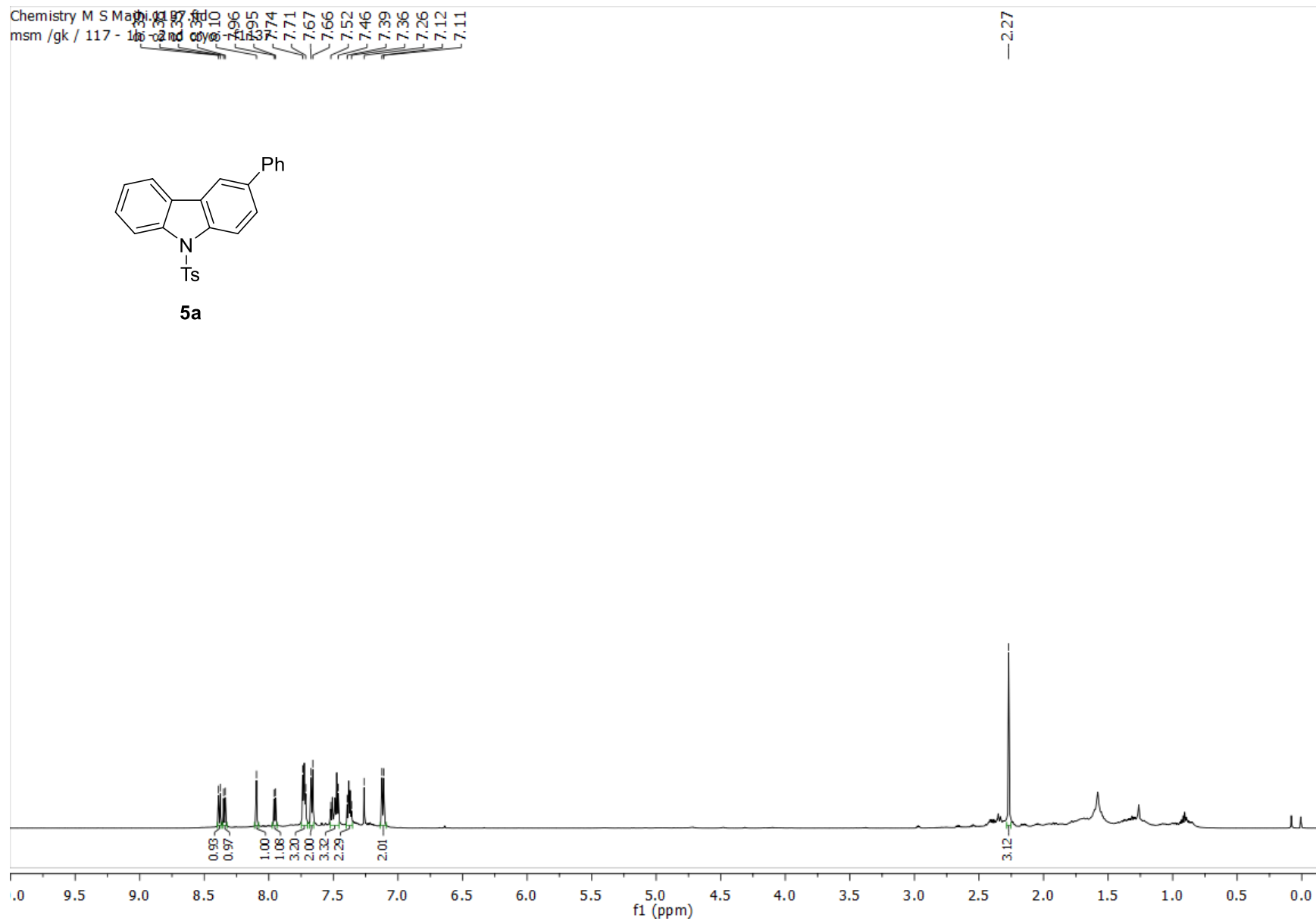


Chemistry M S Majhi.1378.fid
msm / 6 / 368 - 13c - 2nd cryo - f1378

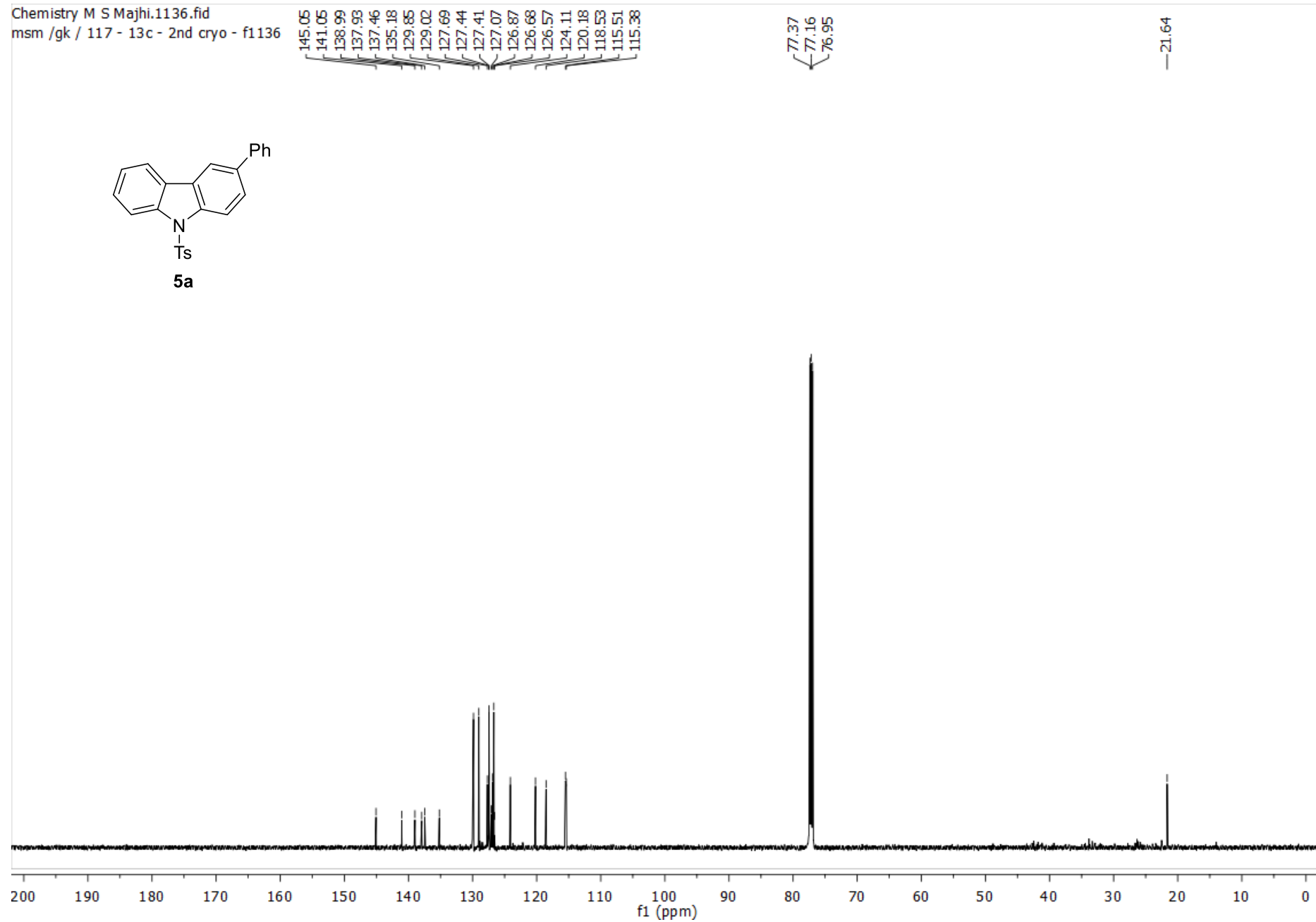
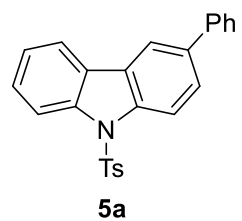


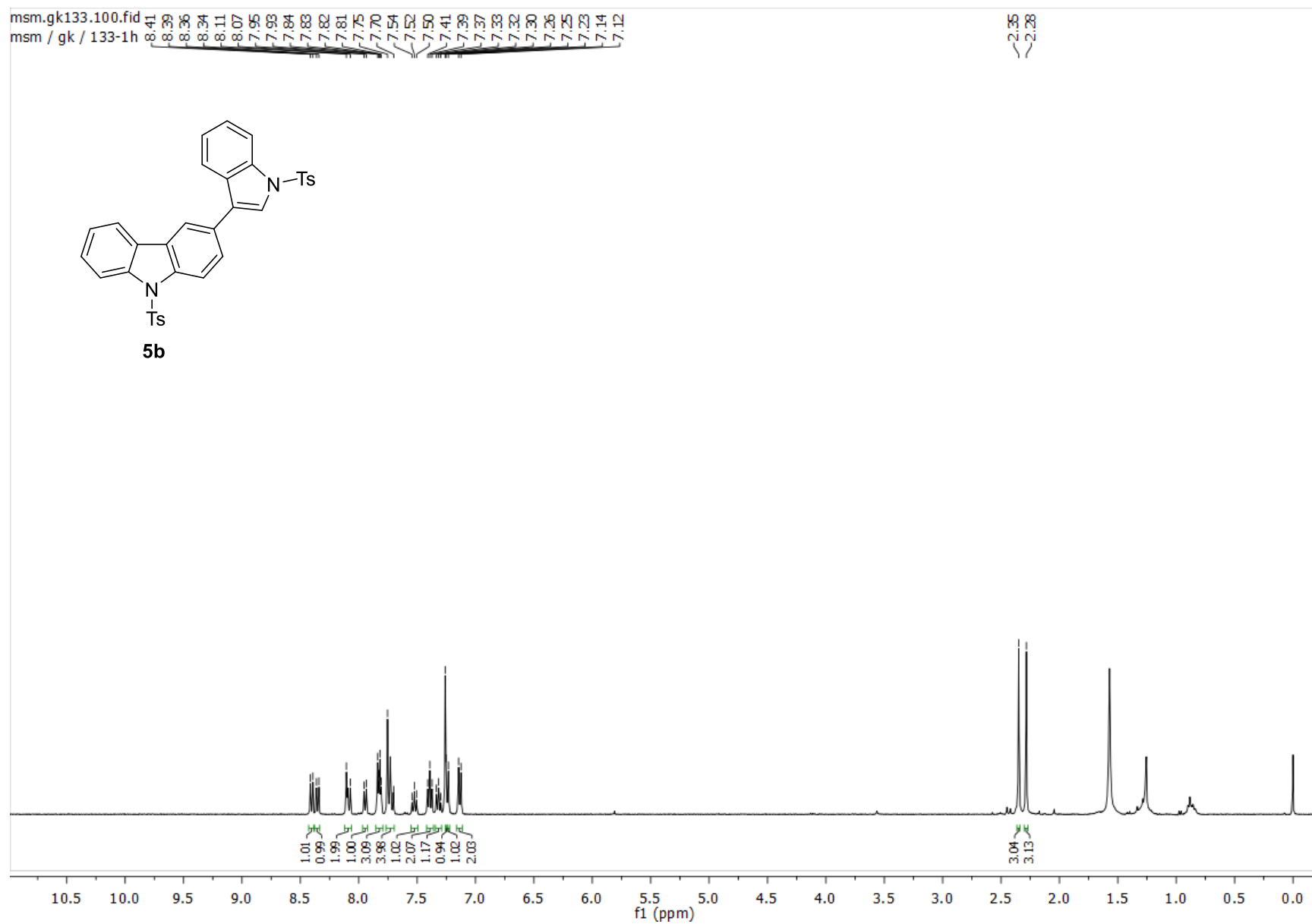


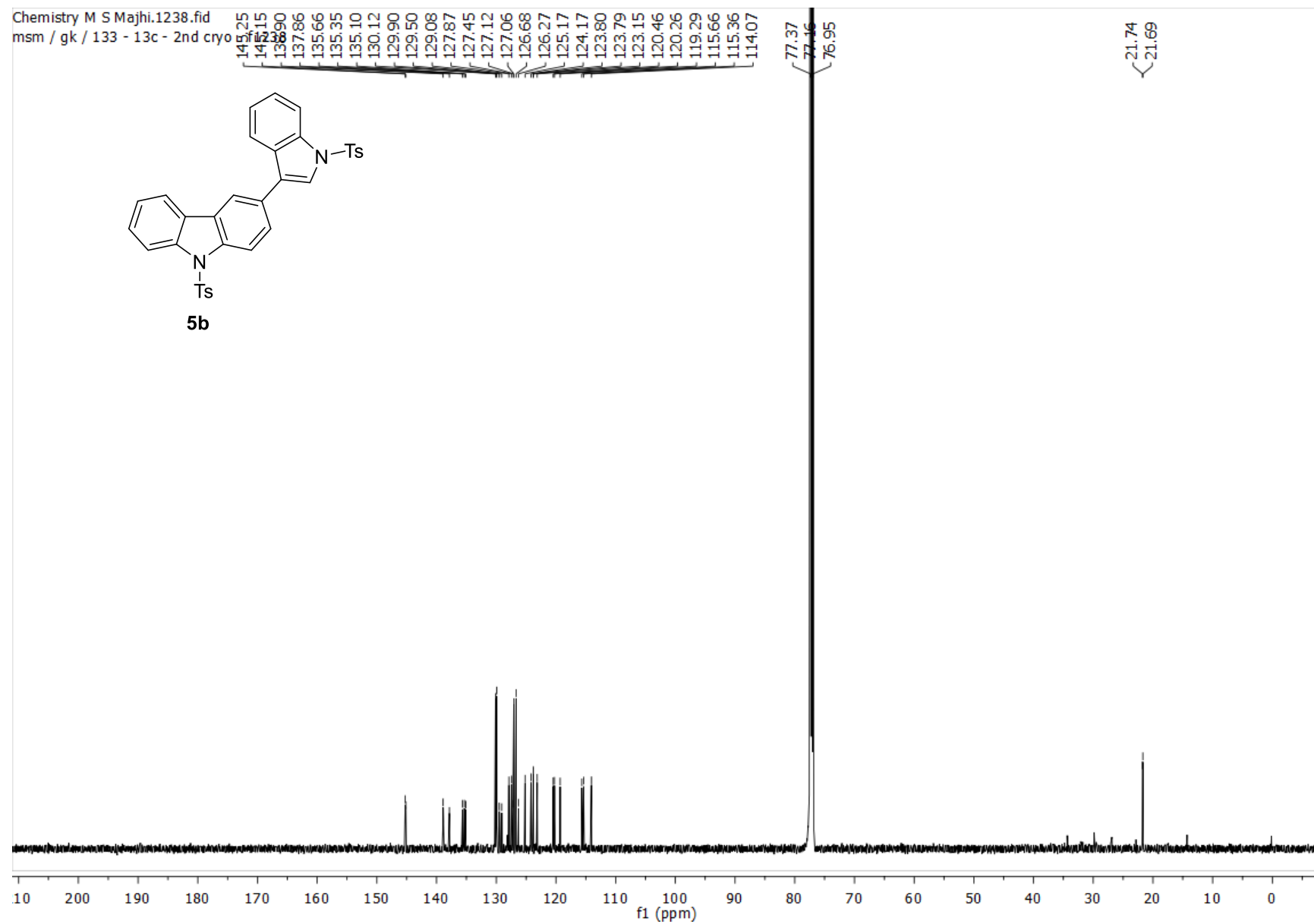


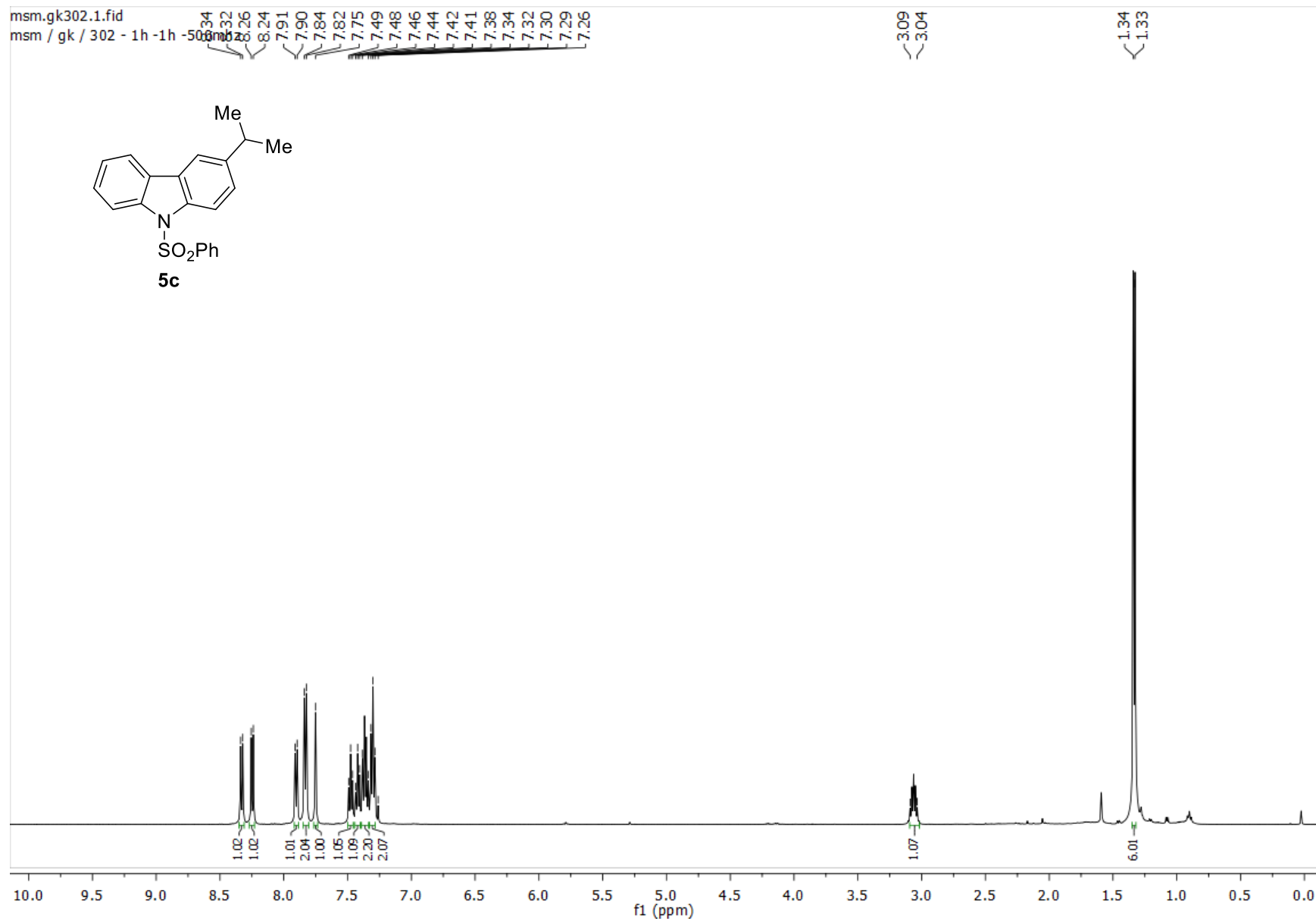


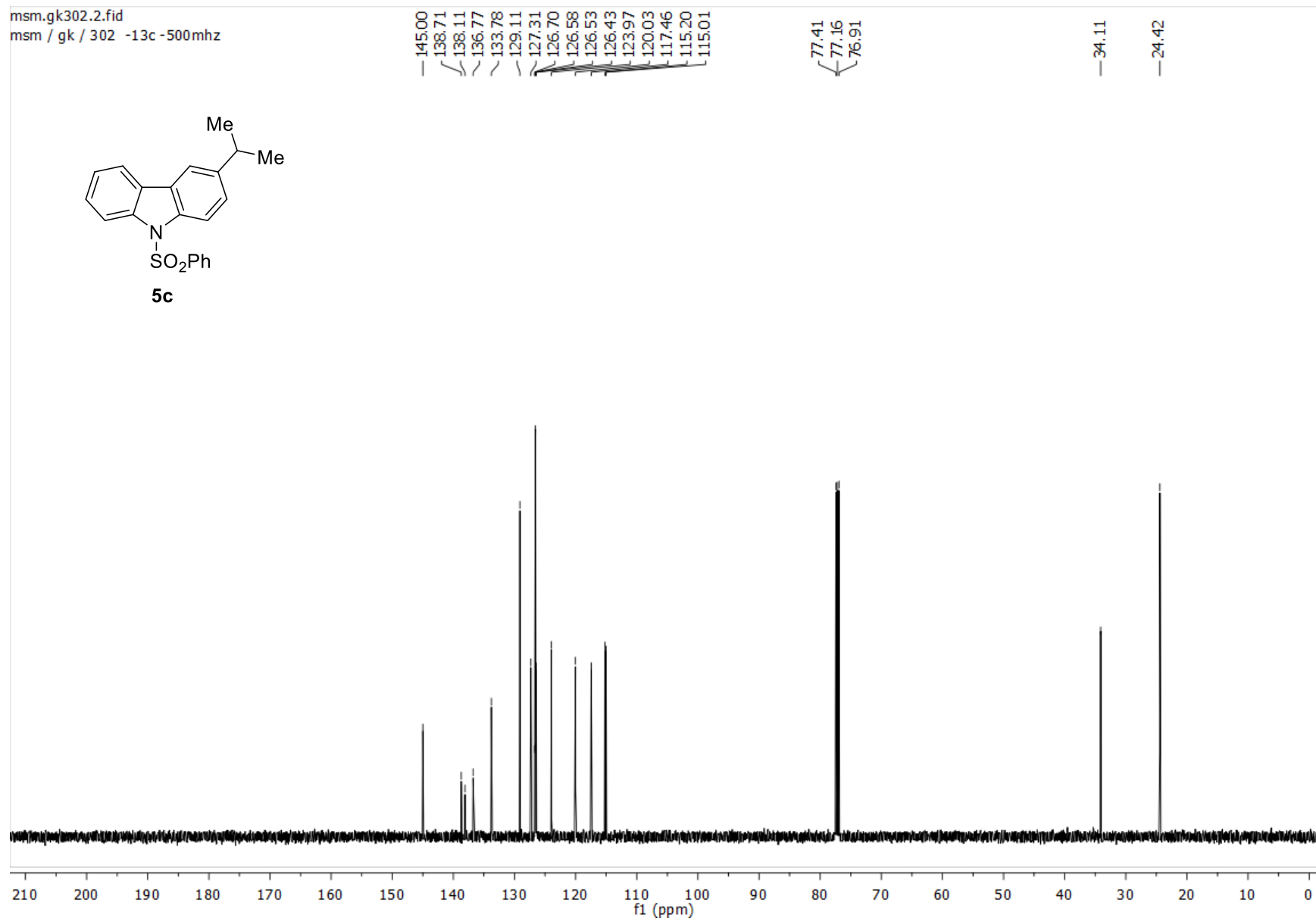
Chemistry M S Majhi.1136.fid
msm /gk / 117 - 13c - 2nd cryo - f1136

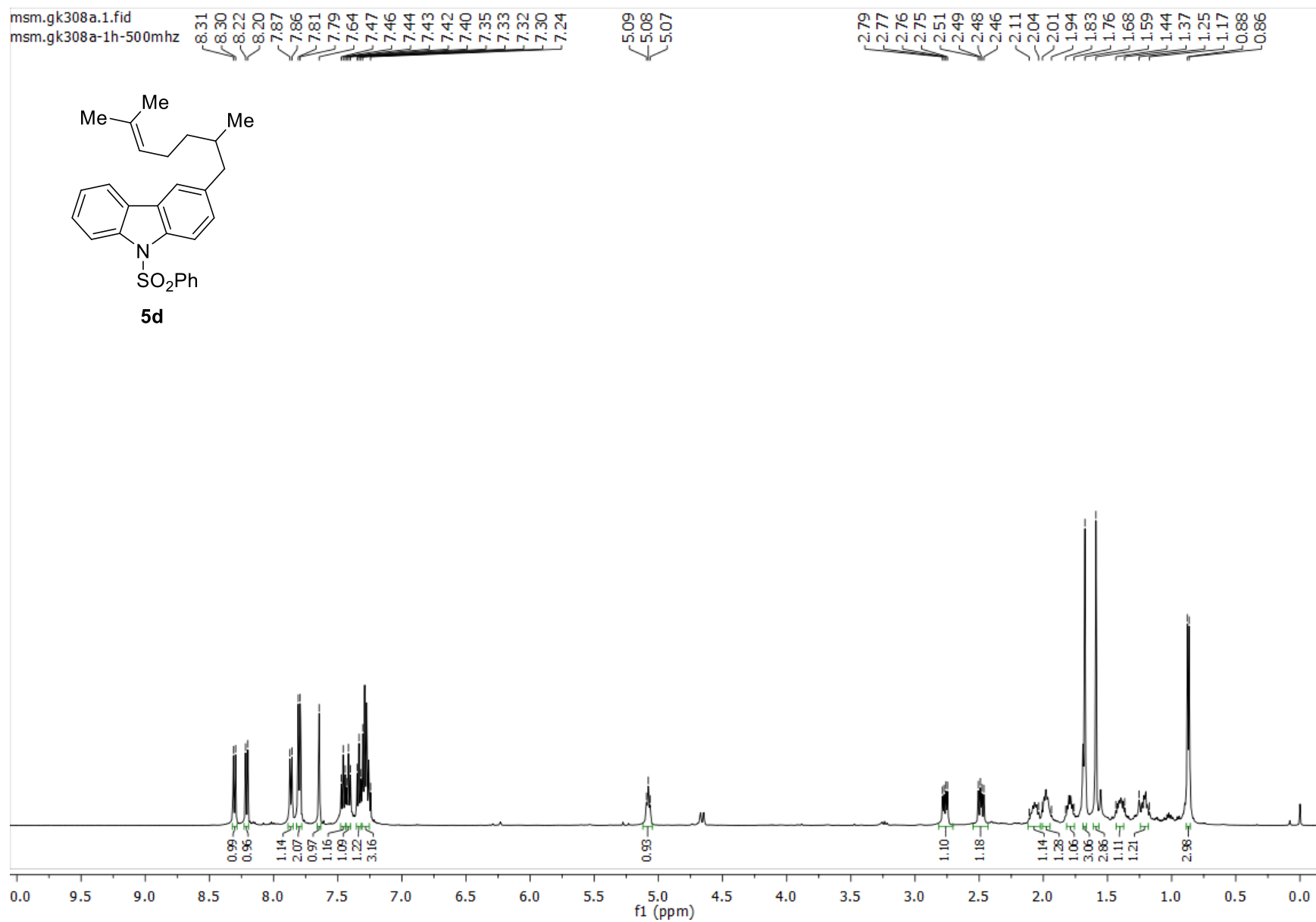




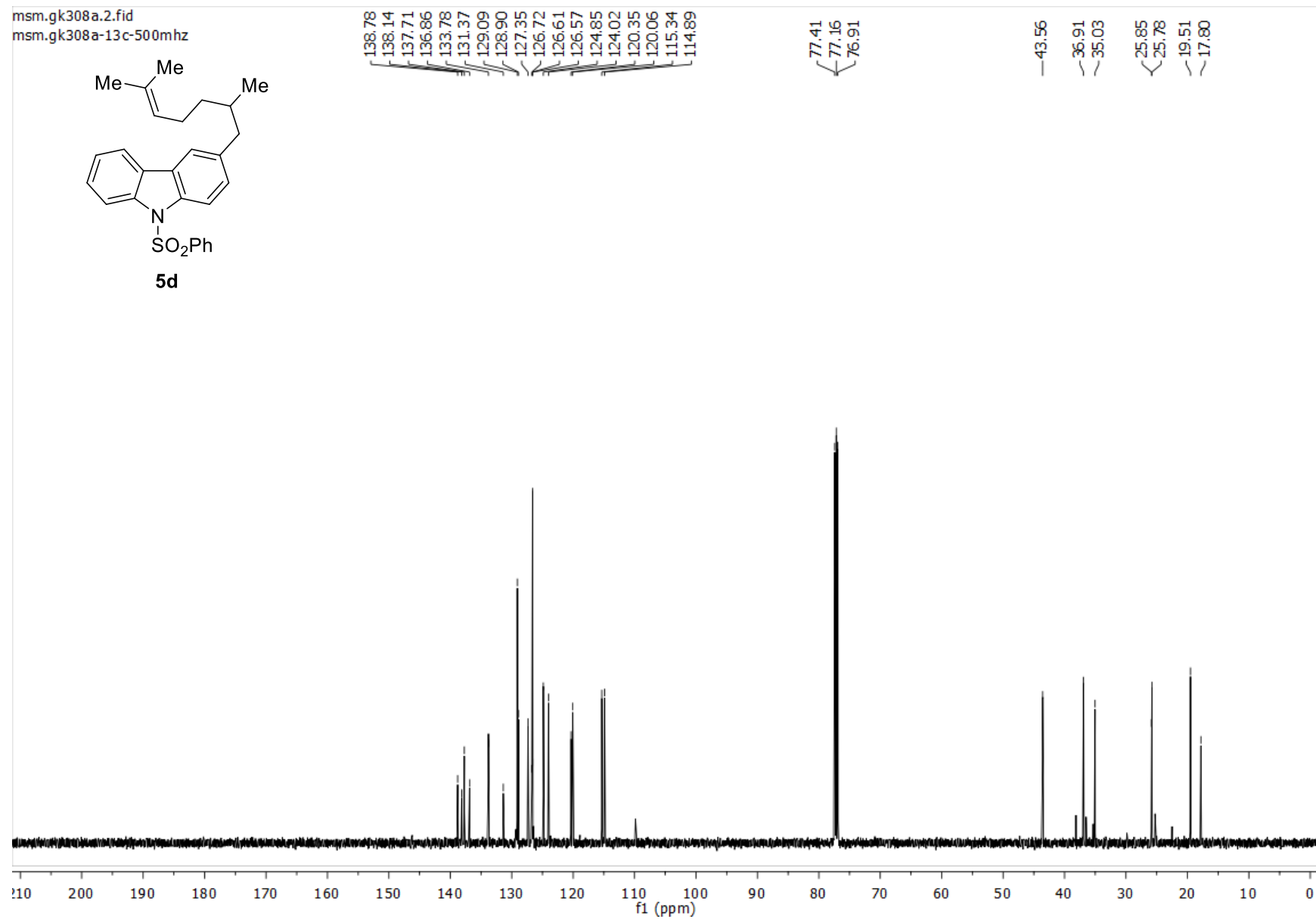
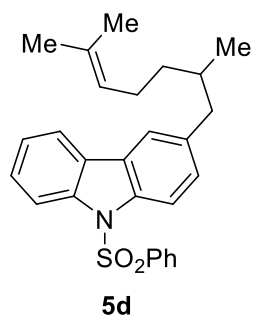


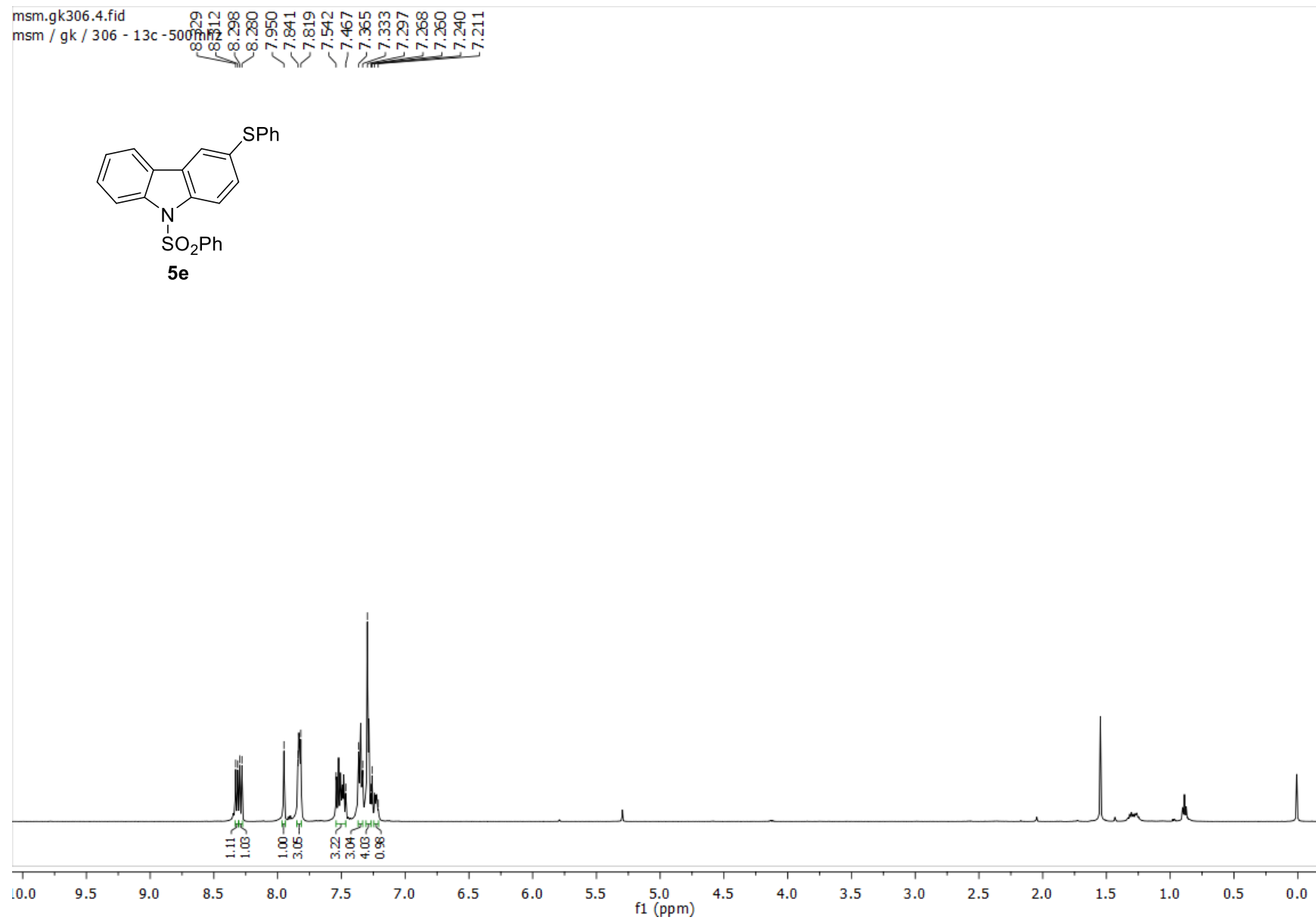


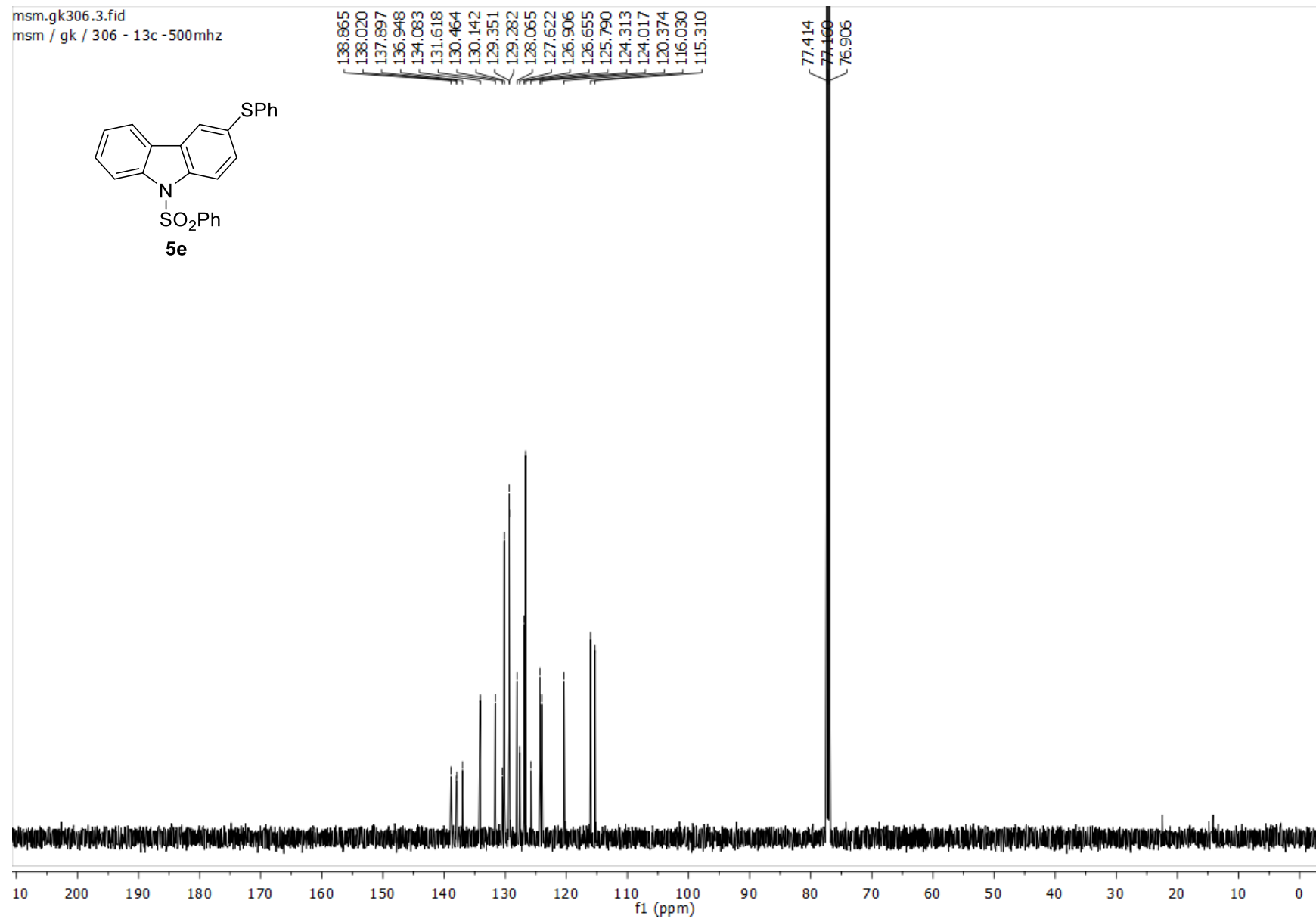


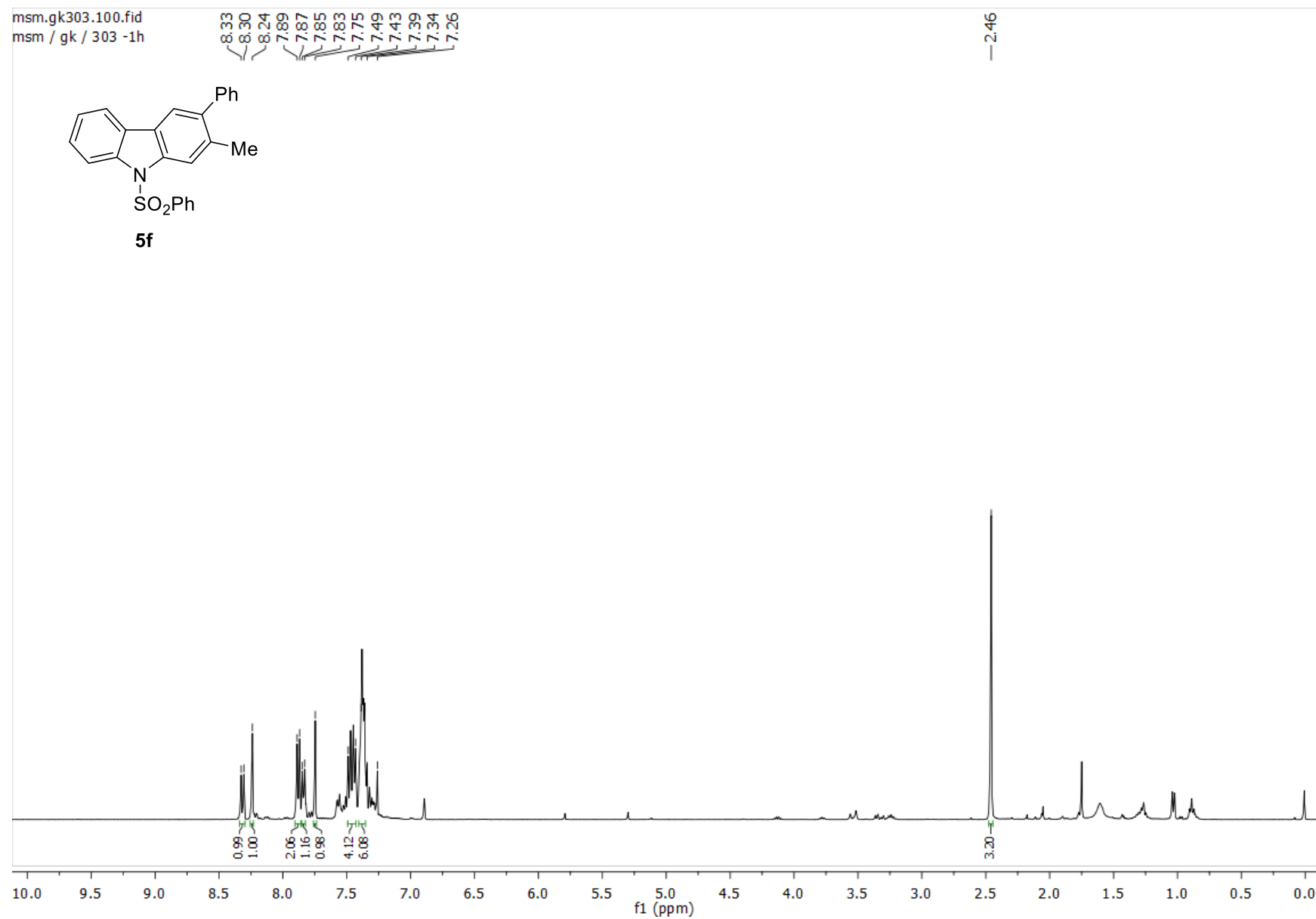


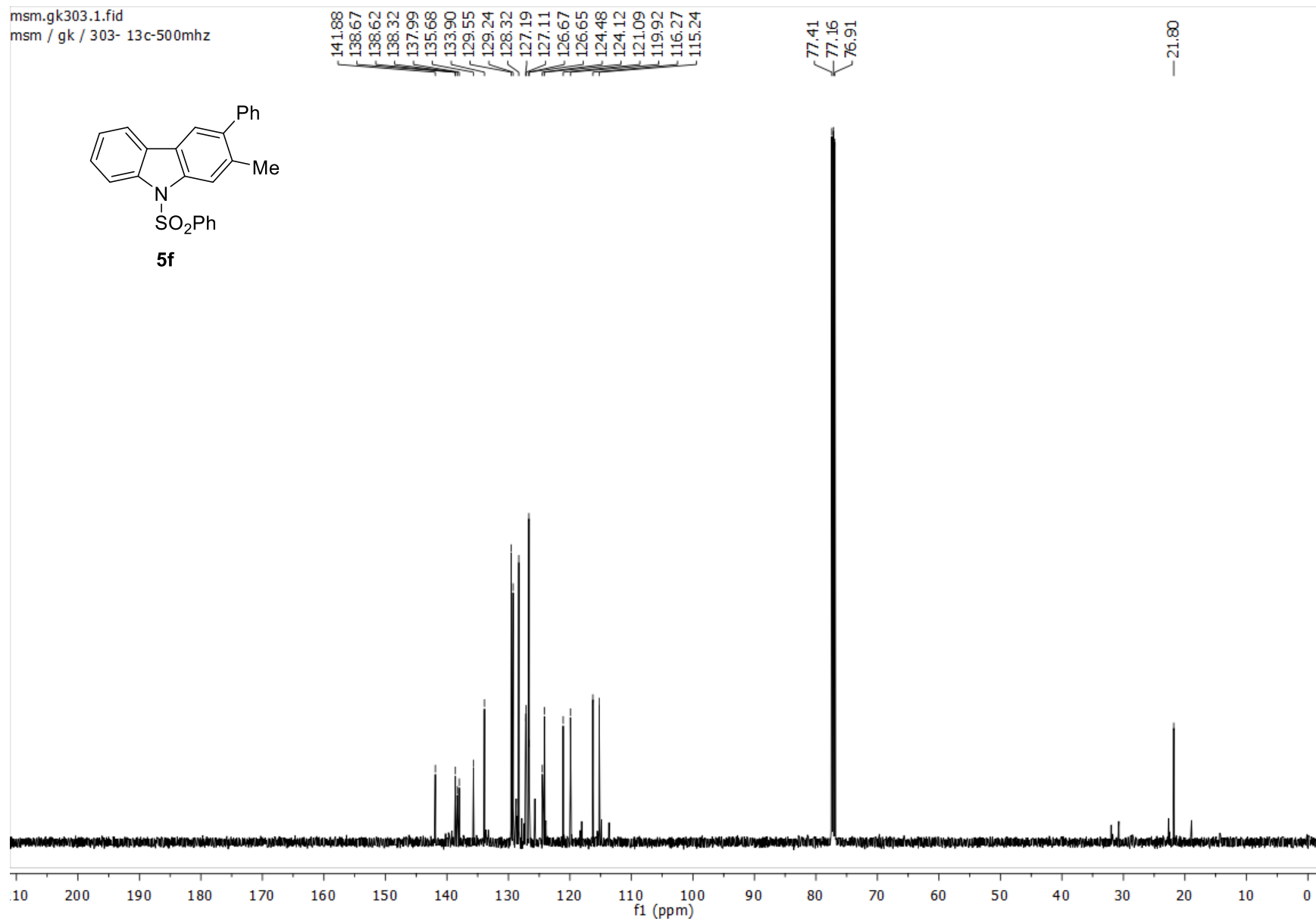
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msm.gk308a-13c-500mhz

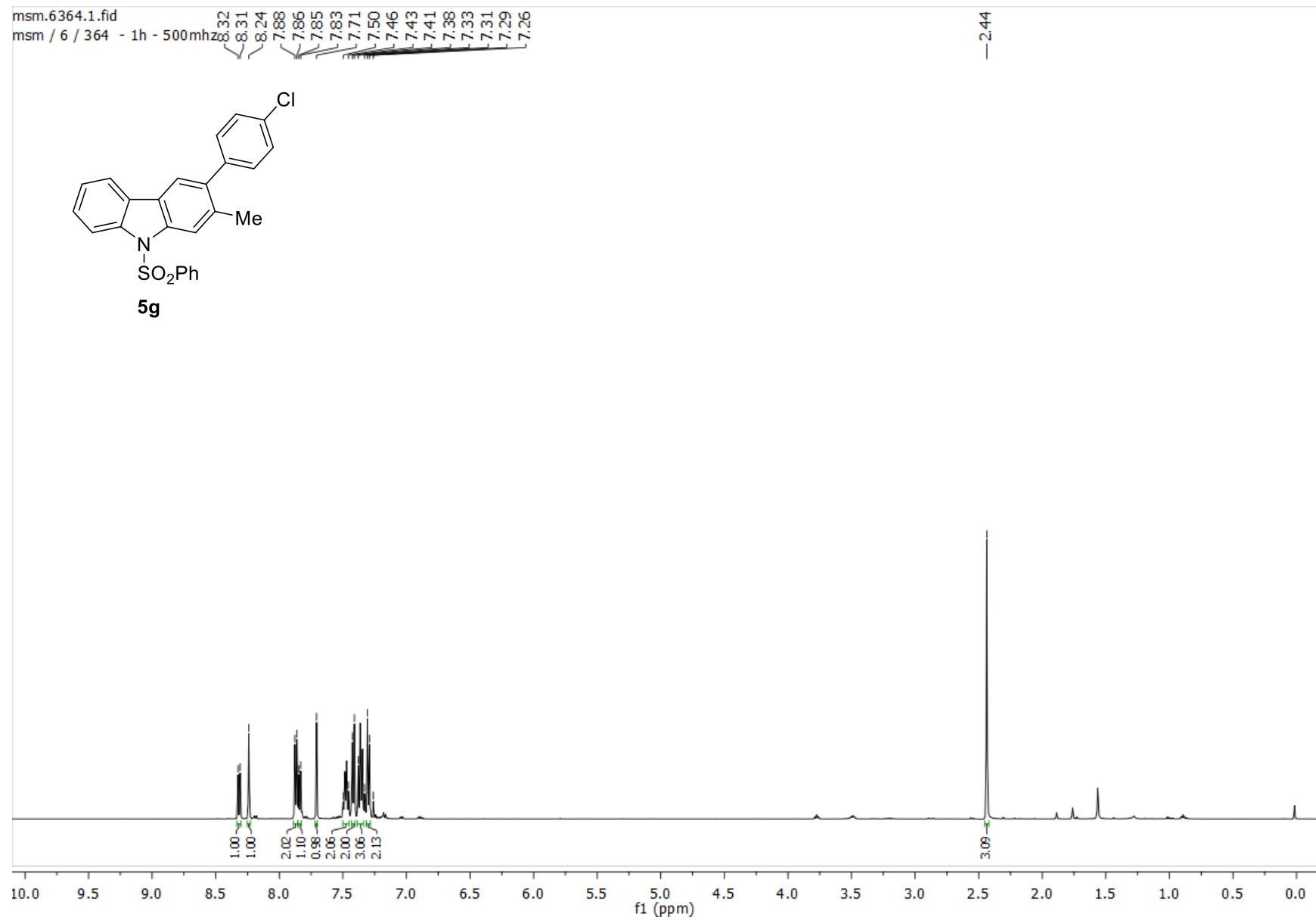


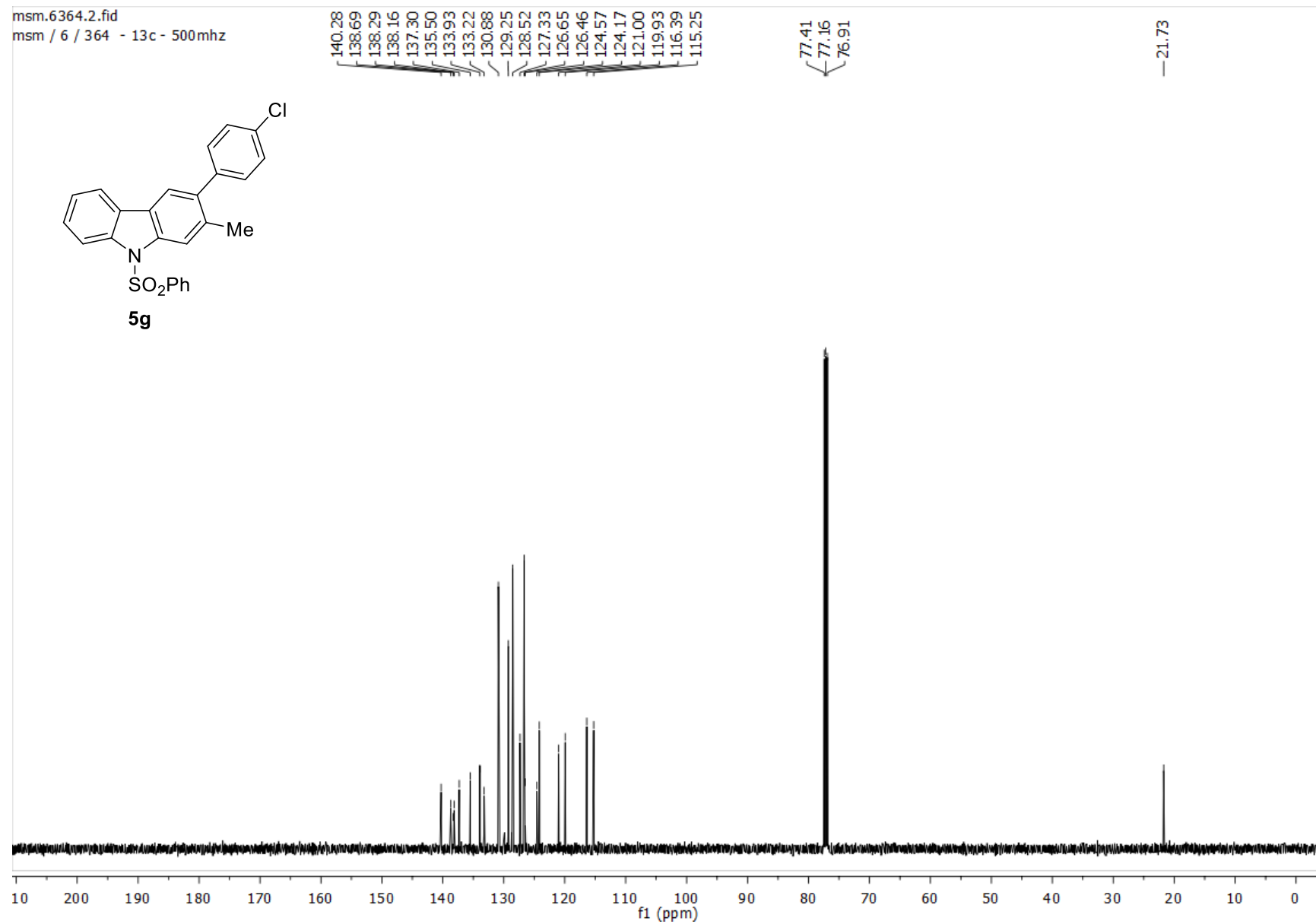


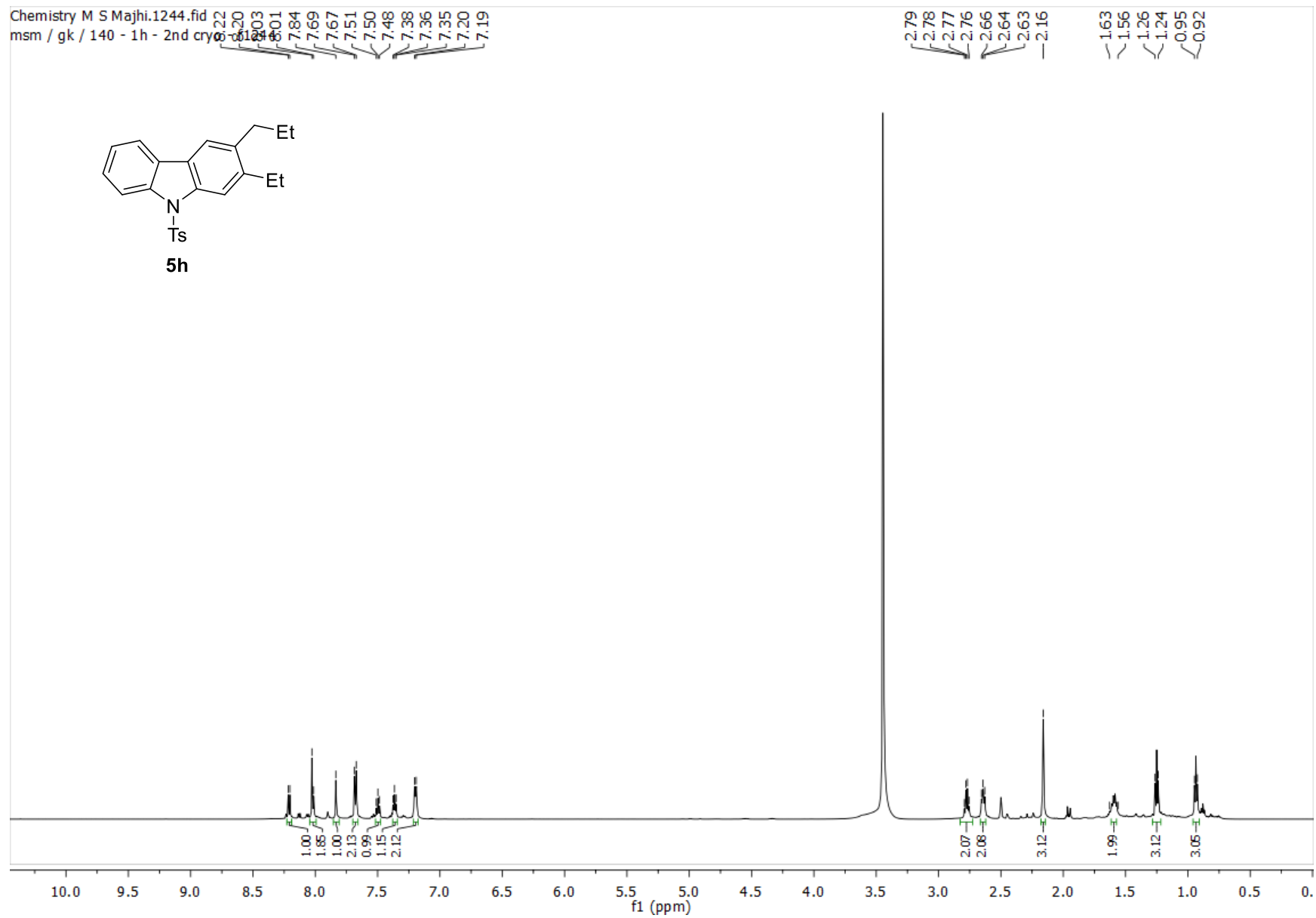




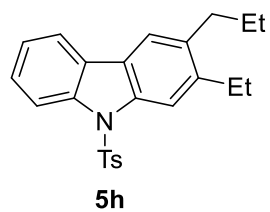






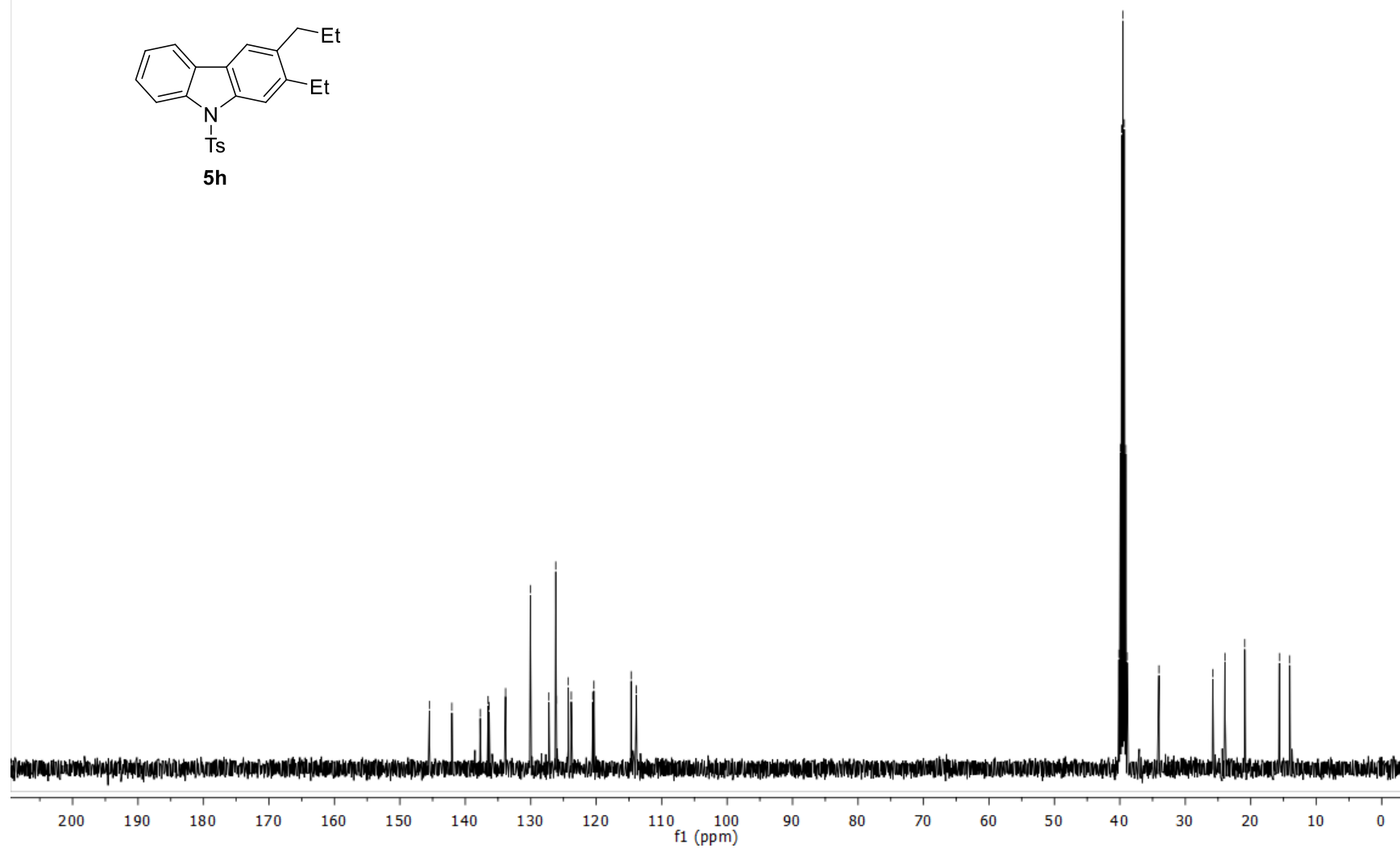


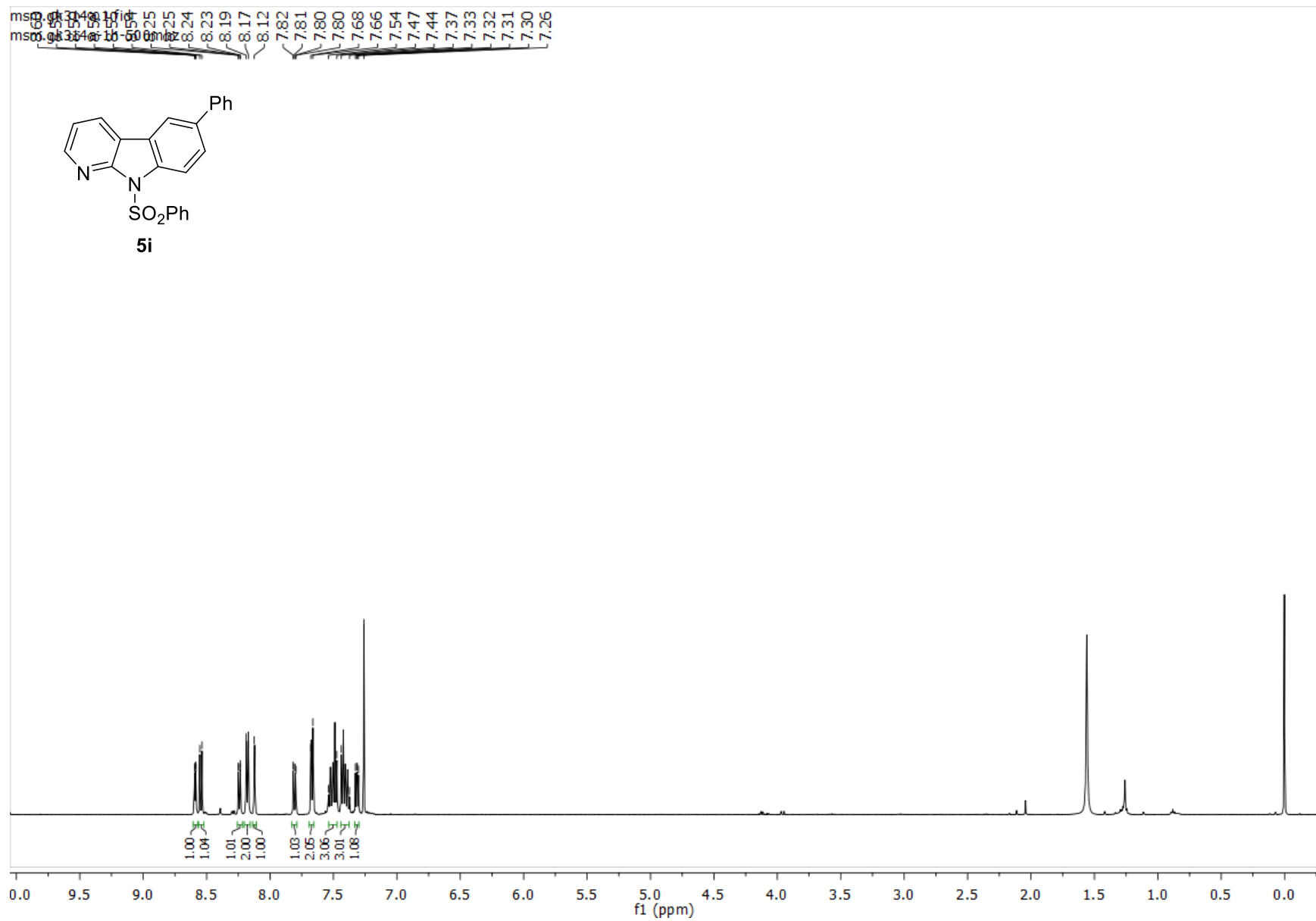
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msm / gk / 140 - 13c



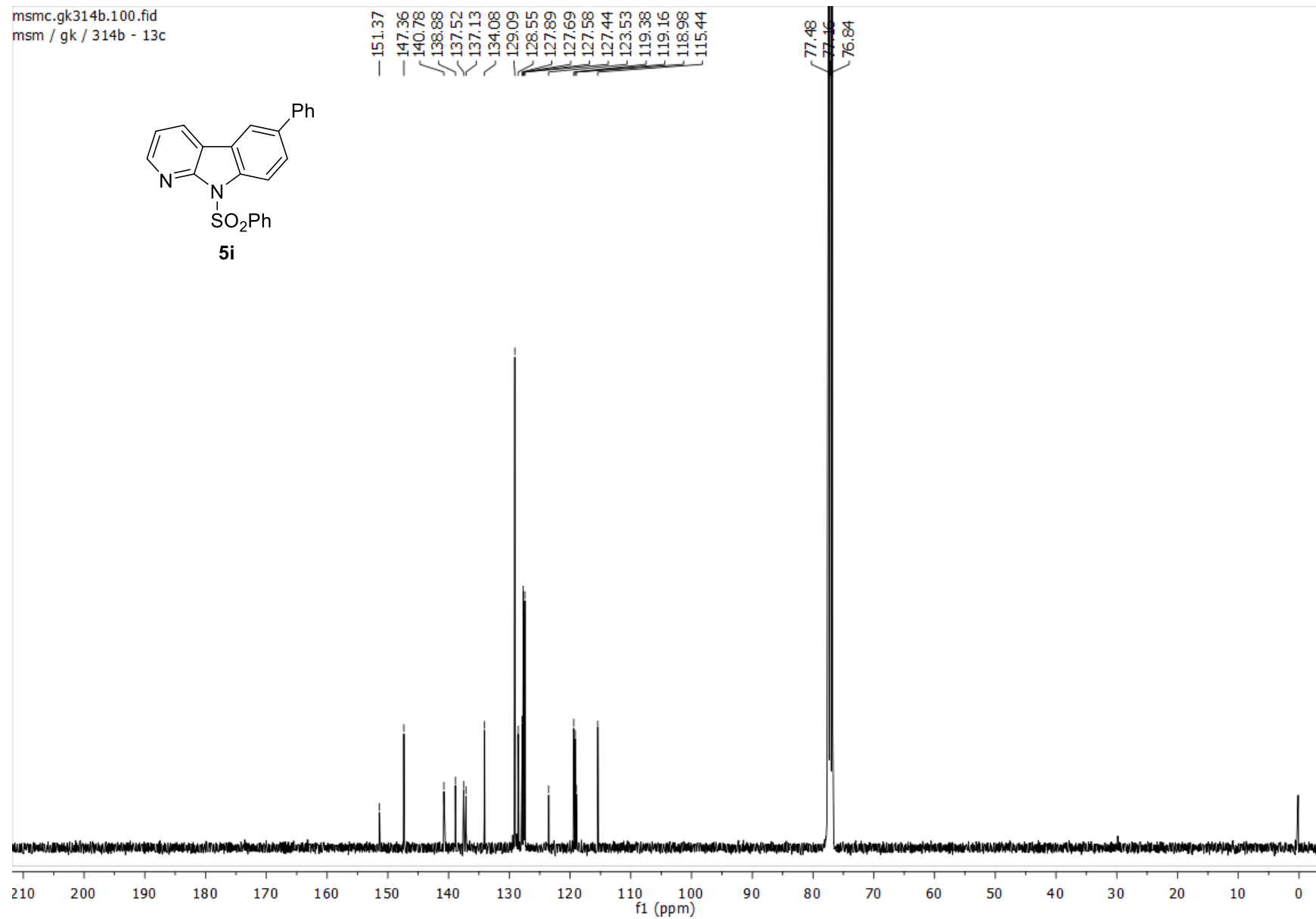
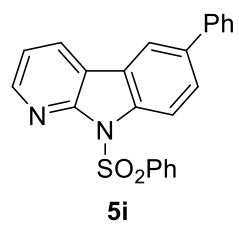
145.48
142.05
137.72
136.51
136.35
133.84
130.05
127.23
126.18
126.10
124.26
123.82
120.51
120.34
114.67
113.88

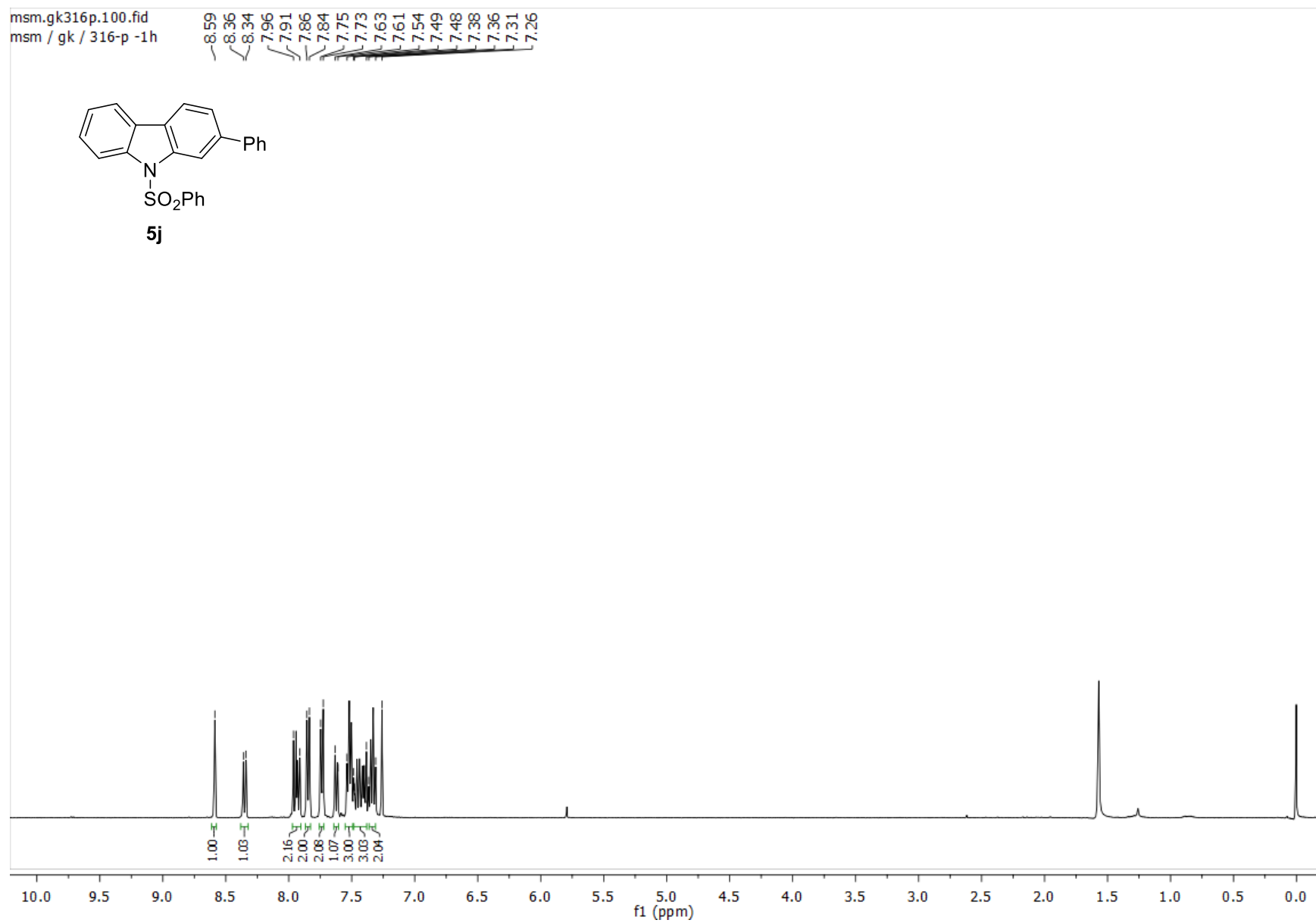
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.04
25.80
23.95
20.92
15.62
14.05

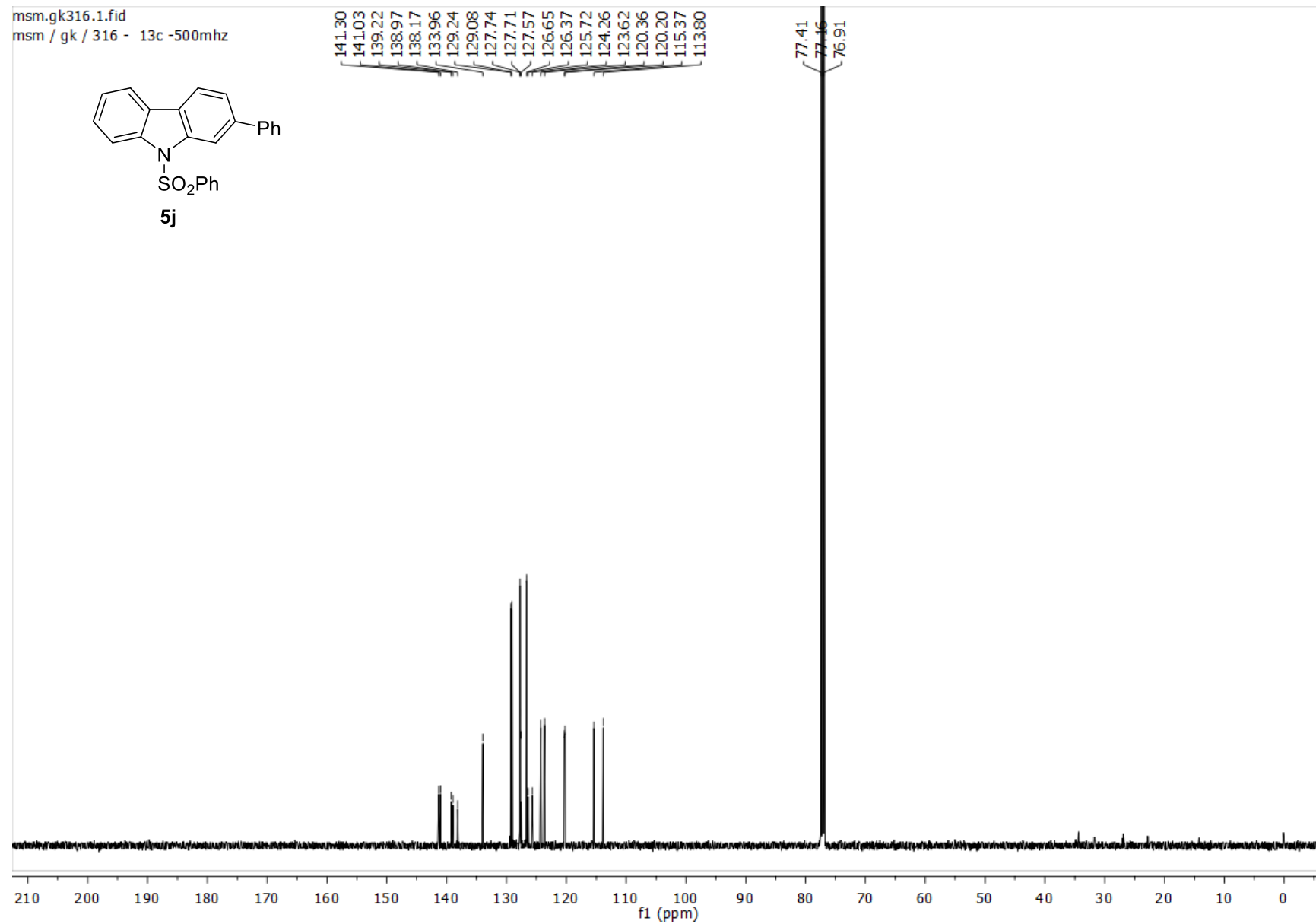


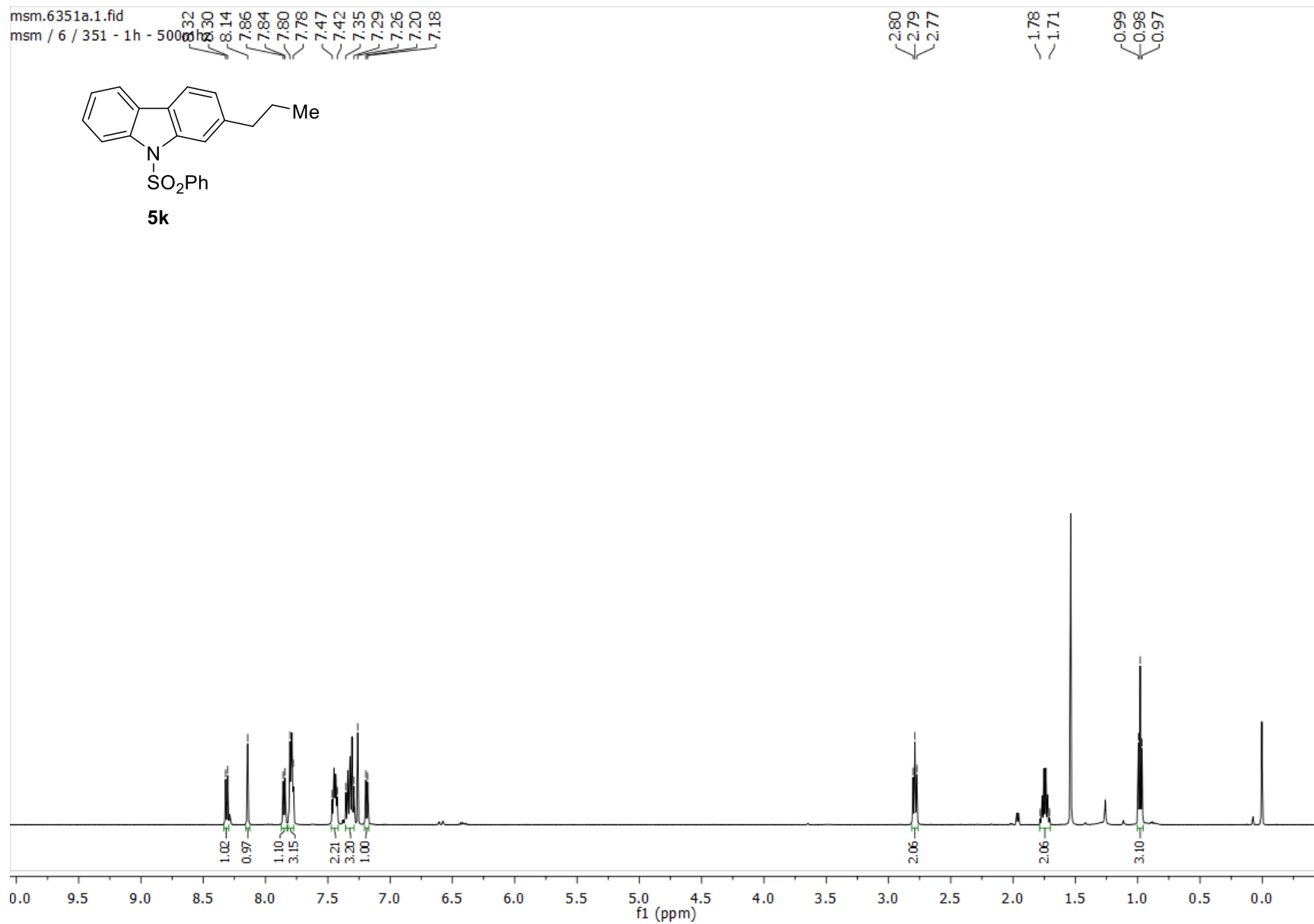


msmc.gk314b.100.fid
msm / gk / 314b - 13c

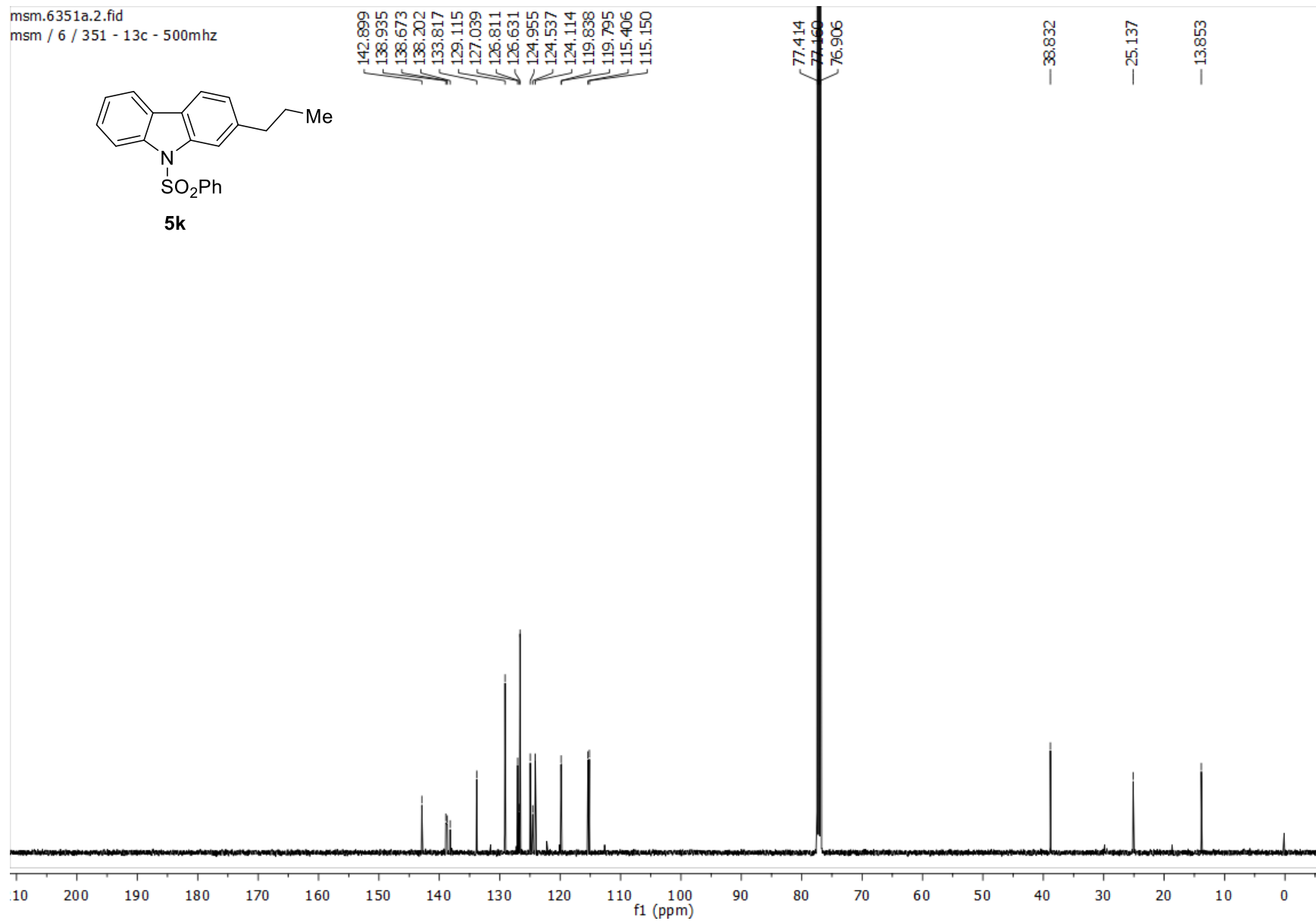
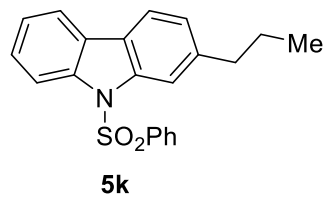


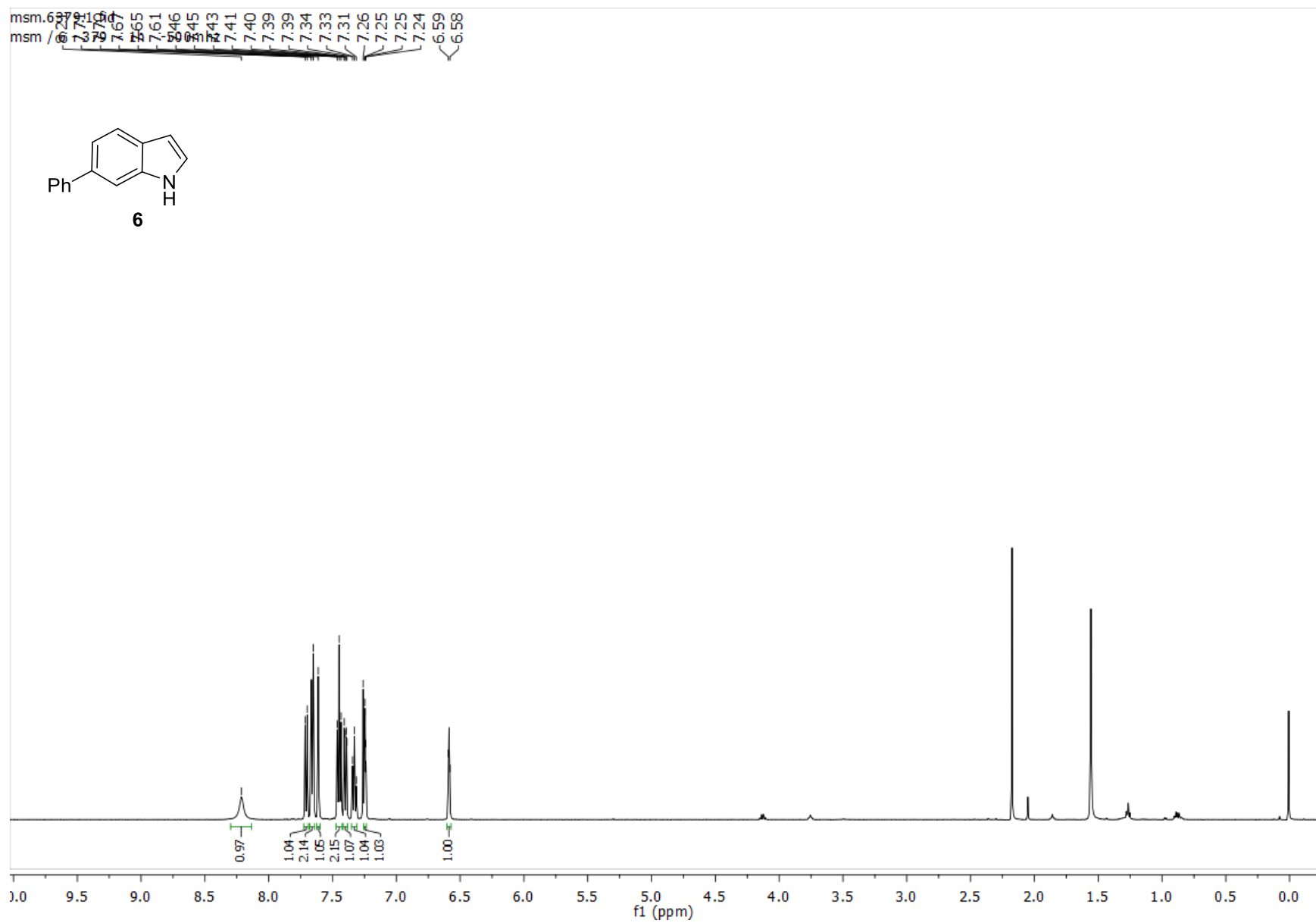






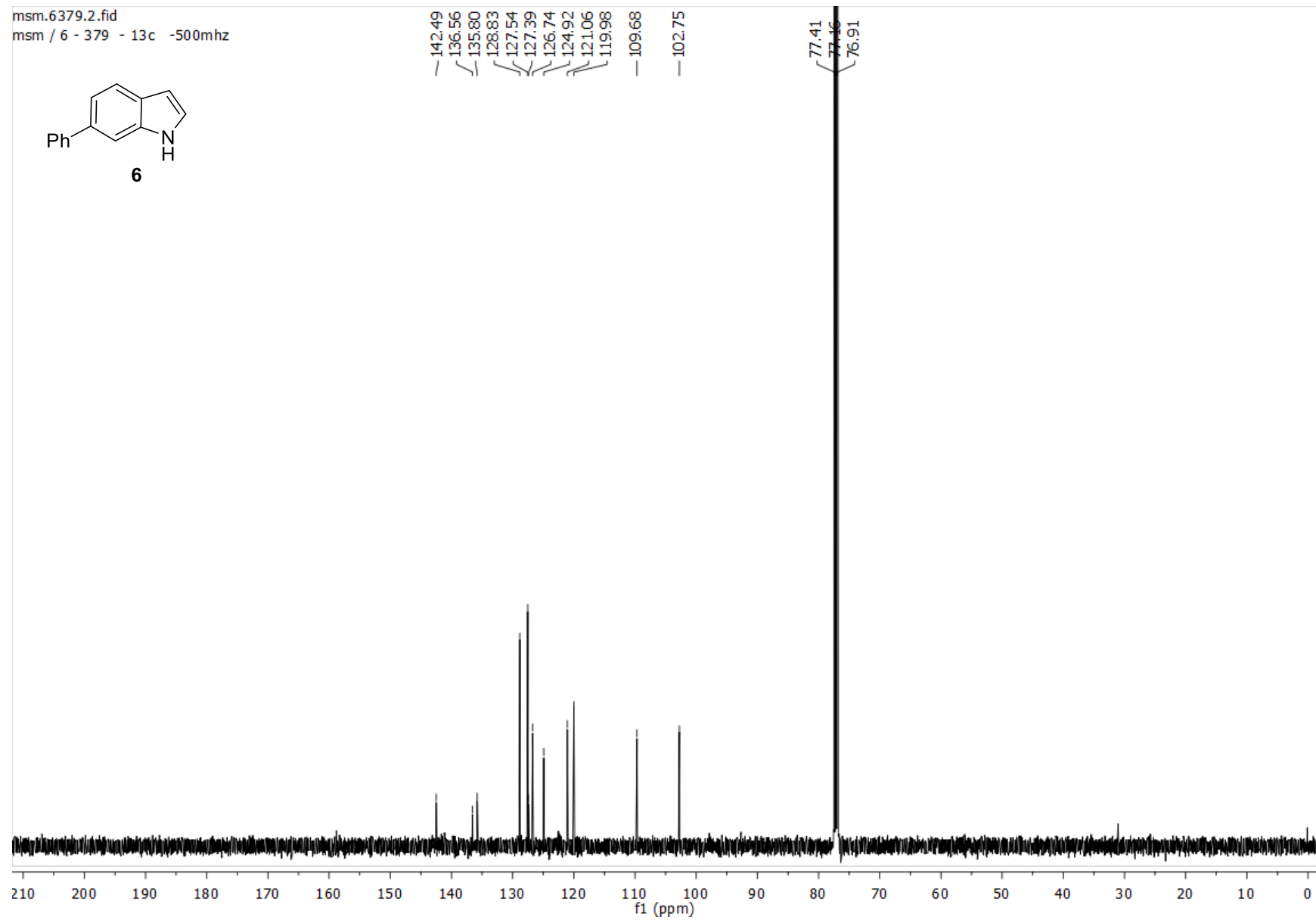
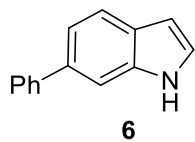
msm.6351a.2.fid
msm / 6 / 351 - 13c - 500mhz

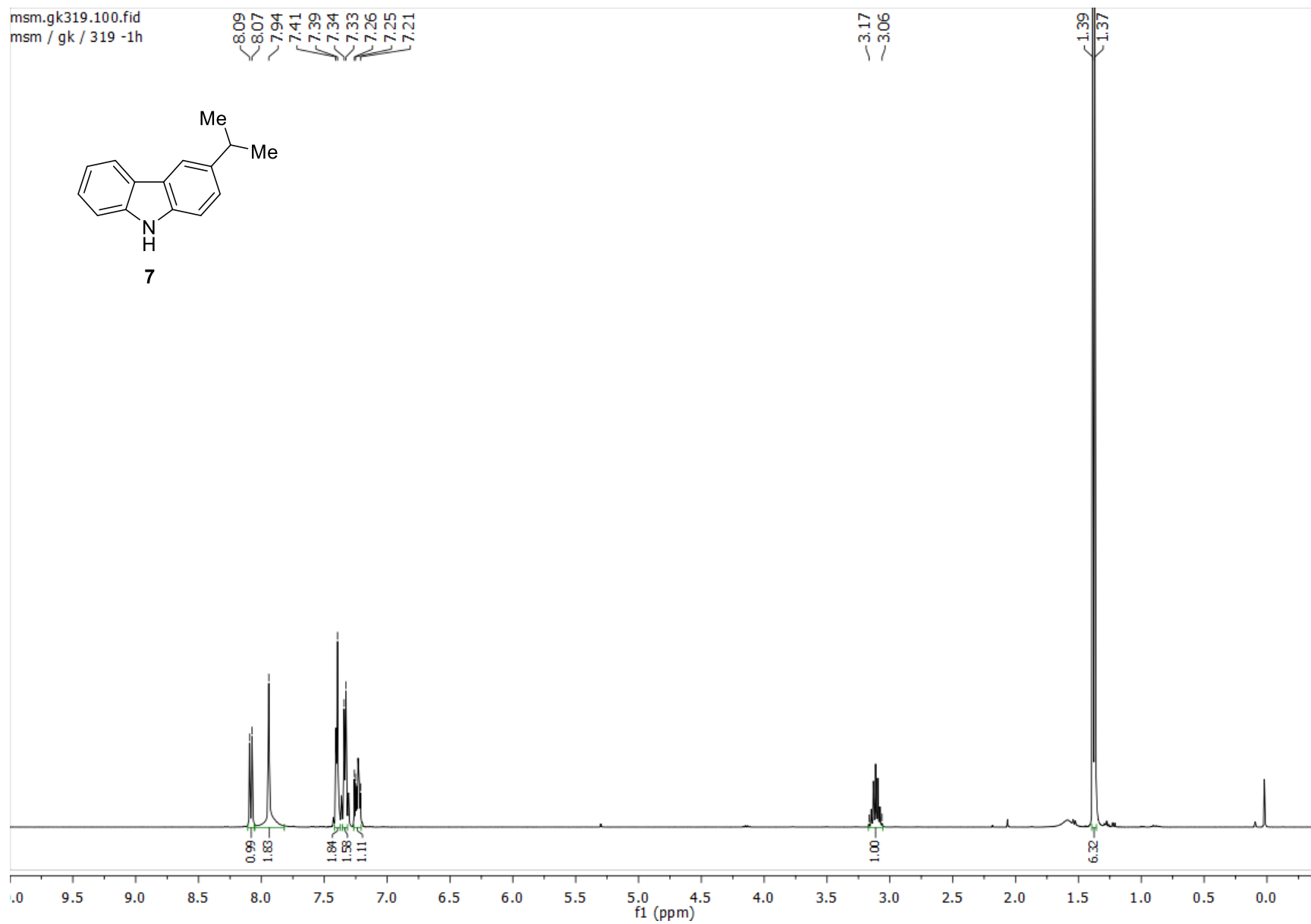




msm.6379.2.fid

msm / 6 - 379 - 13c -500mhz





msmc.gk319.100.fid
msm / gk / 319 - 13c

