Iron-Catalyzed Cross-Coupling Reactions of Alkyl Grignards with Aryl Sulfamates and Tosylates

Toolika Agrawal and Silas P. Cook*

Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, IN 47405-7102

Supporting Information

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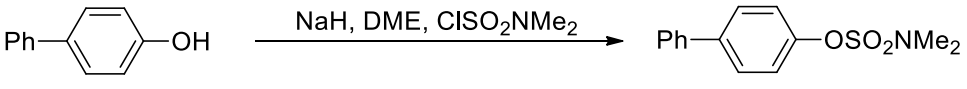
General Methods

All reactions were carried out in oven-dried glassware with rubber septa under a nitrogen atmosphere unless otherwise stated. Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. THF was purified according to the Grubbs procedure.[1] Thin-layer chromatography (TLC) was carried out on Merck 60 F254 precoated, glass silica gel plates which were visualized by ultraviolet light. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Varian I400 (^{1}H-NMR at 400MHz and ^{13}C-NMR at 100MHz) and Varian VXR400 (^{1}H-NMR at 400MHz and ^{13}C-NMR at 100MHz). Chemical shifts are reported in ppm with reference to solvent signals [^{1}H-NMR: $CDCl_3$ (7.26 ppm); ^{13}C-NMR: $CDCl_3$ (77.16 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; quintet; hextet and m, multiplet. Infrared spectra (IR) were obtained on an Avatar 360-FT IR E.S.P. on a NaCl salt plate and recorded in wavenumbers (cm^{-1}). High Resolution Mass (HRMS) analysis was obtained using Electron Impact Ionization (EI) and reported as m/z (relative intensity) for the molecular ion [M], or with Electrospray Ionization (ESI) and reporting the molecular ion $[M+H]^+$ or a suitable fragment ion.

Experimental Procedures

A. General procedure A for the synthesis of aryl sulfamates

A round bottom flask was charged with NaH (8.8 mmol, 1.5 equiv, 60 % dispersion in oil), placed under a N_2 atmosphere and then cooled to 0 °C. A solution of starting alcohol (5.8 mmol, 1 equiv) in DME (40 ml) was added dropwise to NaH. The resulting solution was warmed to 23 °C for 15 min and then cooled to 0 °C. N,N-dimethylsulfamoyl chloride (7.0 mmol, 1.2 equiv) was then added dropwise to the reaction vessel. The reaction was allowed to warm to 23 °C, stirred overnight and quenched with a few drops of water. The solvent was removed under reduced pressure, and the residue dissolved in EtOAc (40 ml) and water (20 ml) and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with 1 M KOH (20 ml) and water (20 ml). The combined aqueous layers were extracted with EtOAc (3 X 20 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure.



SI-1 **1**

4-phenylphenol sulfamate 1. The title compound was synthesized according to general procedure **A**. The crude residue was purified by flash chromatography on silica (6:1 Hex:EtOAc) to yield sulfamate **1** (89% yield) as a white solid.

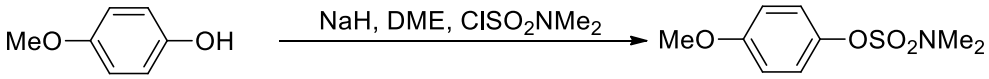
TLC: Rf = 0.40 (hexanes:EtOAc = 4:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 – 7.52 (m, 4H), 7.44 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.39 – 7.31 (m, 3H), 2.99 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.60, 139.86, 128.84, 128.41, 127.58, 127.08, 121.99, 38.77.

HRMS (EI) Calcd. for $C_{14}H_{15}NO_3S$, 277.0773. Found: 277.0758.

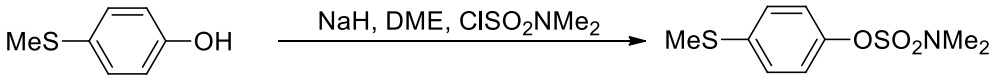
FTIR (NaCl) 3447, 1652, 1484, 1361, 1188, 1150 cm^{-1}.



SI-2 **SI-3**

SI-3 (Table 2, entry 1). The title compound was synthesized according to the general procedure. Purification by flash chromatography on silica (6:1 Hex:EtOAc) yielded sulfamate **SI-3** (77% yield) as a white solid. Spectral data match those previously reported.[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 2.92 (s, 6H).



SI-4 **SI-5**

SI-5 (Table 2, entry 3). Purification by flash chromatography on silica (6:1 Hex:EtOAc) yielded sulfamate **SI-5** (93% yield) as a pale yellow oil.

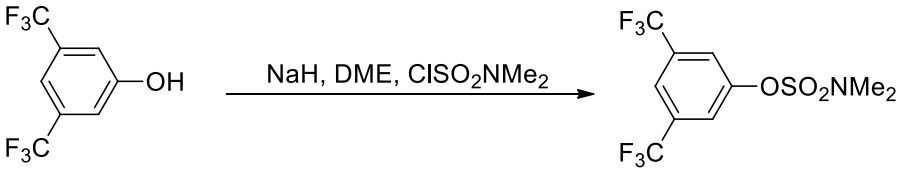
TLC: Rf = 0.40 (hexanes:EtOAc = 4:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (d, 2H), 7.18 (d, 2H), 2.94 (s, 6H), 2.45 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.71, 137.10, 127.78, 122.23, 38.72, 16.15.

HRMS (EI) Calcd. for $C_9H_{13}NO_3S_2$, 247.0337. Found: 247.0336.

FTIR (NaCl) 3442, 1652, 1486, 1363, 1197, 1148 cm^{-1}.



SI-6 **SI-7**

SI-7 (Table 2, entry 5). Purification by flash chromatography on silica (10:1 Hex:EtOAc) yielded sulfamate **SI-7** (73% yield) as a colorless oil.

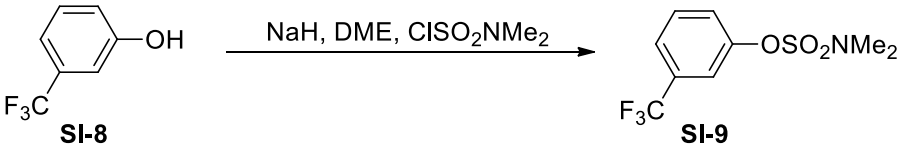
TLC: Rf = 0.25 (hexanes:EtOAc = 10:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (s, 1H), 7.72 (s, 2H), 3.04 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.71, 133.87 (q, *J* = 34.3 Hz), 123.86 (q, *J* = 273.7 Hz), 122.36, 120.39 (quintet, *J* = 4.0 Hz), 38.74.

HRMS (EI) Calcd. for $C_{10}H_9F_6NO_3S$, 337.0207. Found: 337.0202.

FTIR (NaCl) 3532, 2100, 1645, 1457, 1366, 1278, 1131 cm^{-1}.



SI-8 **SI-9**

SI-9 (Table 2, entry 7). Purification by flash chromatography on silica (10:1 Hex:EtOAc) yielded sulfamate **SI-9** (78% yield) as a colorless oil.

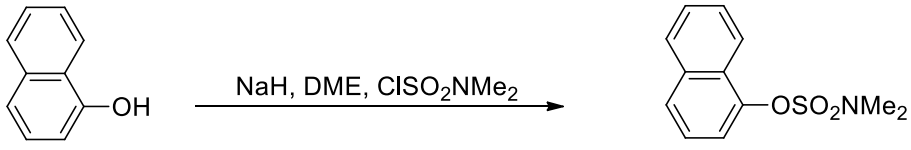
TLC: Rf = 0.20 (hexanes:EtOAc = 10:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 – 7.42 (m, 4H), 2.99 (s, 6H).

^{13}C NMR ($CDCl_3$, 101MHz) δ 150.27, 132.77 (q, J = 33.3 Hz), 127.33 (q, J = 275.7 Hz), 125.19, 123.44 (q, J = 4.0 Hz), 118.97 (q, J = 3.0 Hz), 38.67.

HRMS (EI) Calcd. for $C_9H_{10}F_3NO_3S$, 269.0333. Found: 269.0324.

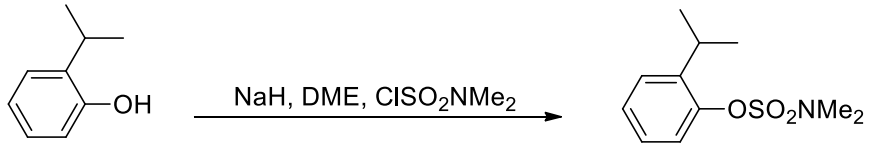
FTIR (NaCl) 3431, 2930, 1652, 1490, 1447, 1374, 1278, 1124 cm^{-1}.



SI-10 **SI-11**

SI-11 (Table 2, entry 9). Purification by flash chromatography on silica (6:1 Hex:EtOAc) yielded sulfamate **SI-11** (91% yield) as a white solid. Spectral data match those previously reported.[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.44 (t, *J* = 7.9 Hz, 1H), 3.04 (s, 6H).



SI-12 **SI-13**

SI-13 (Table 2, entry 11). Purification by flash chromatography on silica (10:1 Hex:EtOAc) yielded sulfamate **SI-13** (80% yield) as a colorless oil.

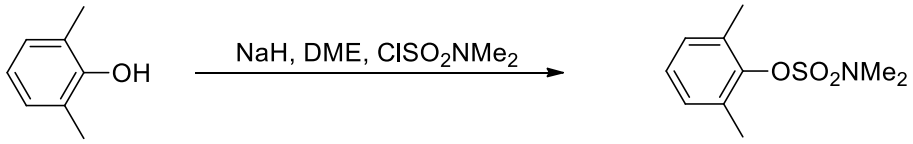
TLC: Rf = 0.30 (hexanes:EtOAC = 10:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (ddd, *J* = 7.1, 5.4, 1.7 Hz, 2H), 7.25 – 7.14 (m, 2H), 3.40 (hept, *J* = 6.9 Hz, 1H), 3.02 (s, 6H), 1.23 (d, *J* = 10.9 Hz, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.45, 141.05, 126.98, 126.79, 126.75, 121.47, 38.70, 26.51, 23.07.

HRMS (EI) Calcd. for $C_{11}H_{17}NO_3S$, 243.0929. Found: 243.0924.

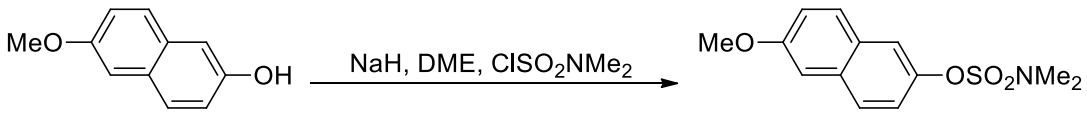
FTIR (NaCl) 3440, 1652, 1367 cm^{-1}.



SI-14 **SI-15**

SI-15 (Table 2, entry 13). Purification by flash chromatography on silica (10:1 Hex:EtOAc) yielded sulafmate **SI-15** (83% yield) as a white solid. Spectral data match those previously reported.[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04 (s, 3H), 3.07 (s, 6H), 2.39 (s, 6H).



SI-16 **SI-17**

SI-17 (Table 2, entry 17). Purification by flash chromatography (5:1 Hex:EtOAc) yielded sulfamate **SI-17** (81% yield) as an off-white solid.

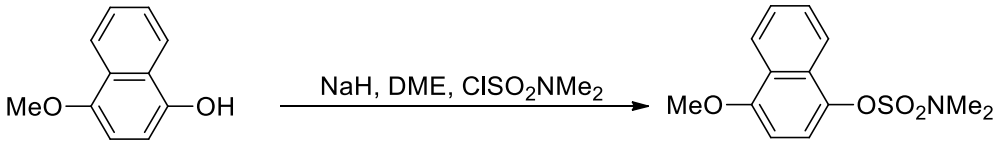
TLC: Rf = 0.30 (hexanes:EtOAc = 4:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (t, *J* = 9.5 Hz, 2H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.17 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.12 (d, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 2.98 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 157.90, 146.08, 133.00, 129.17, 128.87, 128.42, 121.21, 119.83, 119.03, 105.72, 55.32, 38.91.

HRMS (EI) Calcd. for $C_{13}H_{15}NO_4S$, 281.0722. Found: 281.0708.

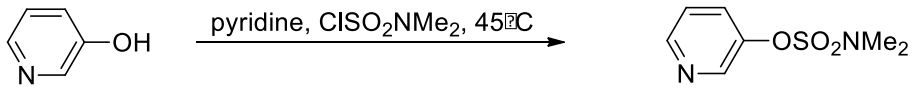
FTIR (NaCl) 3435, 1635, 1506, 1361, 1216, 1173, 1107 cm^{-1}.



SI-18 **SI-19**

SI-19 (Table 2, entry 19). Purification by flash chromatography (5:1 Hex:EtOAc) yielded sulfamate **SI-19** (89% yield) as a light brown coloured solid. Spectral data match those previously reported.[2]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.02 (s, 6H).



SI-20 **SI-21**

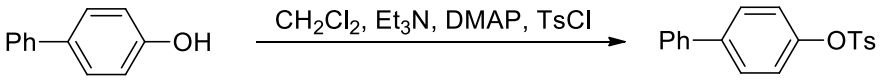
SI-21 (Table 2, entry 15). To a solution of **SI-20** (5.25 mmol, 1.0 equiv) in pyridine (5.3 ml) was added N,N-dimethylsulfamoyl chloride (7.87 mmol, 1.5 equiv). The resulting orange solution was heated to 45 °C and allowed to stir for 24 h. After cooling to 23 °C, the reaction mixture was diluted with Et_2O (10 ml) and 1 M KOH (10 ml). The layers were separated and the aqueous was extracted with Et_2O (2 X 10 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (20:1 DCM:MeOH) to yield sulfamate **SI-21** (50% yield) as a pale yellow oil. Spectral data match those previously reported.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58 – 8.47 (m, 2H), 7.65 (ddd, *J* = 8.4, 2.7, 1.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.99 (s, 6H).

B. General Procedure B for the synthesis of aryl tosylates

To a solution of starting alcohol (2.9 mmol, 1.0 equiv) in CH_2Cl_2 (20 ml) was added Et_3N (4.4 mmol, 1.5 equiv), DMAP (0.29 mmol, 0.1 equiv) and tosyl chloride (3.5 mmol, 1.2 equiv) and the

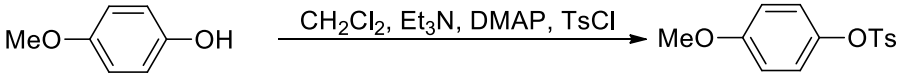
reaction mixture was allowed to stir overnight at 23 °C. The reaction mixture was then diluted with CH_2Cl_2 (15 ml) and extracted with water (3 X 20). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography over silica.



SI-1 **SI-22**

4-phenylphenol tosylate **SI-22**. The title compound was synthesized according to general procedure B. The crude residue was purified by flash chromatography (6:1 Hex:EtOAc) to yield tosylate **SI-22** (96% yield) as a white solid. Spectral data match those previously reported.[4]

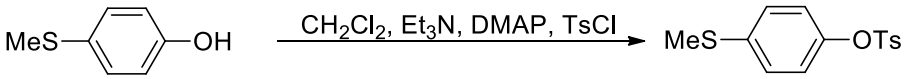
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (dd, *J* = 13.5, 7.7 Hz, 3H), 7.07 – 7.00 (d, *J* = 8.3, 2H), 2.44 (s, 3H).



SI-2 **SI-23**

SI-23 (Table 2, entry 2). Purification by flash chromatography (5:1 Hex:EtOAc) yielded tosylate **SI-23** (91% yield) as a white solid. Spectral data match those previously reported.[5]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 3.74 (s, 3H), 2.43 (s, 3H).



SI-4 **SI-24**

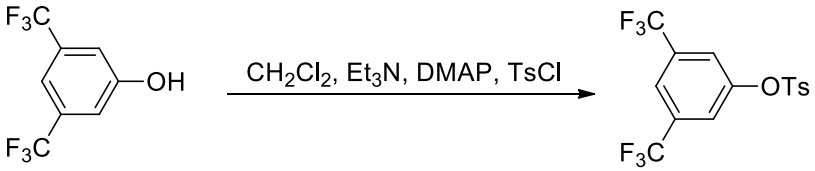
SI-24 (Table 2, entry 4). Purification by flash chromatography (5:1 Hex:EtOAc) yielded tosylate **SI-24** (90% yield) as a white solid.

TLC: Rf = 0.65 (hexanes:EtOAc = 20:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.91 – 6.83 (m, 2H), 2.42 (s, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.03, 145.36, 137.61, 132.25, 129.73, 128.50, 127.30, 122.79, 21.69, 15.89.

HRMS (EI) Calcd. for $C_{14}H_{14}O_3S_2$, 294.0384. Found: 294.0380.



SI-6 **SI-25**

SI-25 (Table 2, entry 6). Purification by flash chromatography (10:1 Hex:EtOAc) yielded tosylate **SI-25** (84% yield) as a white solid.

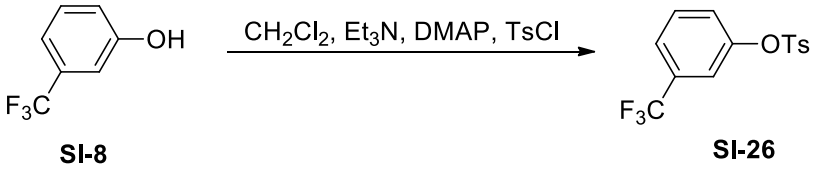
TLC: Rf = 0.40 (hexanes:EtOAc = 10:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.42 (s, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.89, 146.50, 133.70 (q, *J* = 34.3 Hz), 131.32, 130.08, 128.51, 126.40 (q, *J* = 316.1 Hz), 123.27, 120.90 (quintet, *J* = 4.0 Hz), 21.67.

HRMS (EI) Calcd. for $C_{15}H_{10}F_6O_3S$, 384.0255. Found: 384.0233.

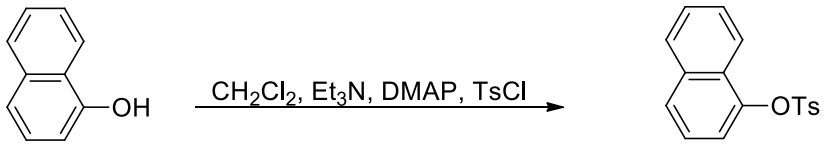
FTIR (NaCl) 3447, 3098, 2928, 1598, 1458, 1389, 1364, 1279, 1138 cm^{-1}.



SI-8 **SI-26**

SI-26 (Table 2, entry 8). Purification by flash chromatography (10:1 Hex:EtOAc) yielded tosylate **SI-26** (89% yield) as a white solid. Spectral data match those previously reported.[6]

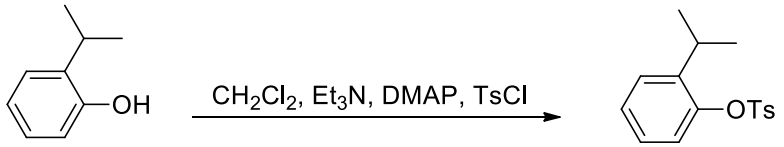
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 2.44 (s, 3H).



SI-10 **SI-27**

SI-27 (Table 2, entry 10). Purification by flash chromatography (10:1 Hex:EtOAc) yielded tosylate **SI-27** (90% yield) as a white solid. Spectral data matched those previously reported.[5]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.70 (m, 4H), 7.43 (dtd, *J* = 16.5, 6.9, 1.2 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0, 1H), 2.40 (s, 3H).



SI-12 **SI-28**

SI-28 (Table 2, entry 12). Purification by flash chromatography (20:1 Hex:EtOAc) yielded tosylate **SI-28** (90% yield) as a colourless oil.

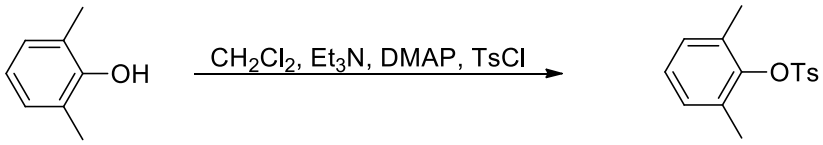
TLC: Rf = 0.35 (hexanes:EtOAc = 10:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 2H), 7.12 – 7.06 (m, 1H), 7.02 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.09 (hept, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.01, 145.22, 141.72, 133.17, 129.73, 128.37, 127.23, 127.06, 126.57, 122.00, 26.62, 23.04, 21.64.

HRMS (EI) Calcd. for $C_{16}H_{18}O_3S$, 290.0977. Found: 290.0964.

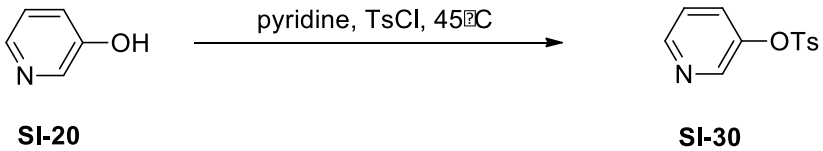
FTIR (NaCl) 3422, 2966, 1652, 1597, 1486, 1448, 1373, 1192 cm^{-1}.



SI-14 **SI-29**

SI-29 (Table 2, entry 14). Purification by flash chromatography (10:1 Hex:EtOAc) yielded tosylate **SI-29** (96% yield) as a colourless oil. Spectral data match those previously reported.[7]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.02 (m, 3H), 2.45 (s, 3H), 2.12 (s, 6H).



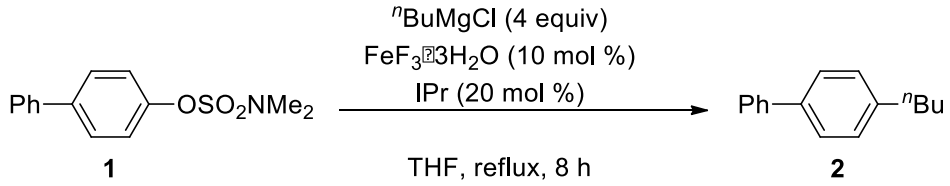
SI-20 **SI-30**

SI-30 (Table 2, entry 16). To a solution of **SI-20** (5.25 mmol, 1.0 equiv) in pyridine (5 ml) was added tosyl chloride (6.3 mmol, 1.2 equiv). This orange coloured solution was heated to 45 °C and allowed to stir for 24 h. After cooling the reaction mixture to 23 °C, it was diluted with water (10 ml) and allowed to stir for 3 h. To this was added benzene (60 ml) and the layers were separated. The organic layer was extracted with 10% NaOH solution (2 X 30 ml), washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was

purified by flash chromatography (2:1 Hex:EtOAc) to yield tosylate **SI-30** (92% yield) as a yellow solid. Spectral data match those previously reported.[5]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (dd, *J* = 4.7, 1.2 Hz, 1H), 8.12 (d, *J* = 2.6 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.43 (ddd, *J* = 8.4, 2.7, 1.4 Hz, 1H), 7.34 – 7.22 (m, 3H), 2.41 (s, 3H).

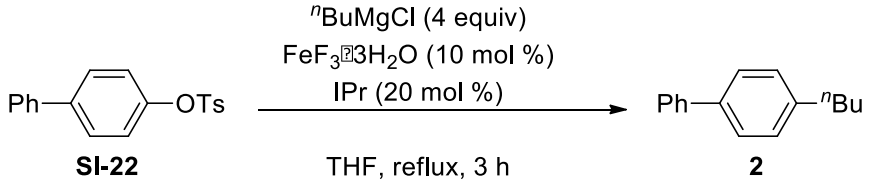
C. Cross-coupling of aryl sulfamates and tosylates



1 **2**

Representative example (coupling of 4-phenylphenol sulfamate 61 is used as an example)
An oven-dried 25 ml 2-neck round bottom flask was charged with sulfamate **1** (0.721 mmol, 1.0 equiv), $FeF_3.3H_2O$ (0.072 mmol, 0.1 equiv) and IPr (0.144 mmol, 0.2 equiv). The flask was evacuated and back filled with N_2, THF (0.1 M) was added and the reaction mixture was heated to reflux. Next, a solution of *n*-butyl magnesium chloride in Et_2O (2 M in Et_2O, 2.88 mmol, 4 equiv) was added slowly to the refluxing solution. The reaction mixture was refluxed for 8 h. After cooling the round bottom flask to 23 °C, the reaction was quenched with 1 M HCl (3 ml). The layers were separated and the aqueous layer was extracted with diethylether (2 X 5 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (50:1 Pentane:EtOAc) to yield **SI-31** (90% yield) as a colourless oil. Spectral data match those previously reported.[8]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 1.73 (quintet, *J* = 8.0 Hz, 2H), 1.49 (hextet, *J* = 8.0 Hz, 2H), 0.98 (t, *J* = 8.0 Hz, 3H).

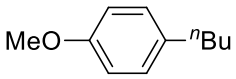


SI-22 **2**

Representative example (coupling of 4-phenylphenol tosylate SI-22 is used as an example)
An oven-dried 25 ml 2-neck round bottom flask was charged with tosylate **SI-22** (0.616 mmol, 1.0 equiv), $FeF_3.3H_2O$ (0.061 mmol, 0.1 equiv) and IPr (0.123 mmol, 0.2 equiv). The flask was evacuated and back filled with N_2, THF (0.1 M) was added and the reaction mixture was heated to reflux. Next, a solution of *n*-butyl magnesium chloride in Et_2O (2 M in Et_2O, 2.46 mmol, 4 equiv) was added slowly to the refluxing solution. The reaction mixture was refluxed for 3 h. After cooling the round bottom flask to 23 °C, the reaction was quenched with 1 M HCl (3 ml).

The layers were separated and the aqueous layer was extracted with diethylether (2 X 5 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (50:1 Pentane:EtOAc) to yield **SI-31** (74% yield) as a colourless oil. Spectral data match those previously reported.[8]

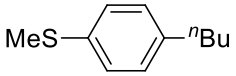
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 1.73 (quintet, *J* = 8.0 Hz, 2H), 1.49 (hextet, *J* = 8.0 Hz, 2H), 0.98 (t, *J* = 8.0 Hz, 3H).



SI-32

SI-32 (Table 2, entries 1 & 2). Purification by flash chromatography (75:1 pentane:EtOAc) yielded **SI-32** as a colorless oil. Spectral data match those previously reported.[9]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.57 (quintet, *J* = 8.0 Hz, 2H), 1.35 (hextet, *J* = 8.0 Hz, 2H), 0.92 (t, *J* = 8.0 Hz, 3H).



SI-33

SI-33 (Table 2, entries 3 & 4). Purification by flash chromatography (75:1 pentane:EtOAc) yielded **SI-33** as a colorless oil.

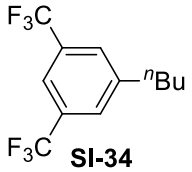
TLC: Rf = 0.40 (hexanes:EtOAc = 4:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 3.20 (t, *J* = 7.5 Hz, 2H), 3.07 (s, 3H), 2.31 (quintet, *J* = 7.3 Hz, 2H), 1.97 (hextet, *J* = 7.3 Hz, 2H), 1.56 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.62, 135.58, 129.55, 127.77, 35.71, 34.23, 22.92, 16.98, 14.55.

HRMS (EI) Calcd. for $C_{11}H_{16}S$, 180.0973. Found: 180.0968.

FTIR (NaCl) 2956, 2925, 2856, 1494 cm^{-1}.



SI-34

SI-34 (Table 2, entries 5 & 6). Purification by flash chromatography (100% pentane) yielded **SI-34** as a colorless oil.

TLC: Rf = 0.9 (100% pentane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (s, 1H), 7.60 (s, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.63 (quintet, *J* = 8.0 Hz, 2H), 1.36 (hextet, *J* = 8.0 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.13, 131.88 (q, *J* = 33.3 Hz), 128.45, 127.50 (q, *J* = 273.7 Hz), 119.78 (quintet, *J* = 4.0 Hz), 35.32, 33.13, 22.20, 13.76.

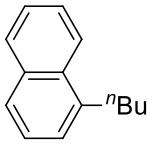
HRMS (EI) Calcd. for $C_{12}H_{12}F_6$, 270.0843. Found: 270.0836.

FTIR (NaCl) 3429, 1652 cm^{-1}.

SI-35

SI-35 (Table 2, entries 7 & 8). Purification by flash chromatography (100% pentane) yielded **SI-35** as a colorless oil. Spectral data match those previously reported.[10]

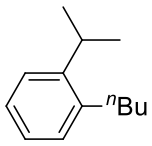
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (s, 2H), 7.41 – 7.33 (m, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.69 (quintet, *J* = 8.0 Hz, 2H), 1.43 (hextet, *J* = 8.0 Hz, 2H), 0.94 (t, *J* = 8.0 Hz, 3H).



SI-36

SI-36 (Table 2, entries 9 & 10). Purification by flash chromatography (100:1 pentane:EtOAc) yielded **SI-36** as a colorless oil. Spectral data match those previously reported.[11]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 3.15 (t, *J* = 8.0 Hz, 2H), 1.84 (quintet, *J* = 8.0 Hz, 2H), 1.56 (hextet, *J* = 8.0 Hz, 2H), 1.01 (t, *J* = 8.0 Hz, 3H).



SI-37

SI-37 (Table 2, entries 11 & 12). Purification by flash chromatography (100% pentane) yielded **SI-37** (35% yield) as a colorless oil.

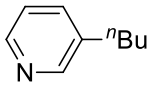
TLC: Rf = 0.70 (100% pentane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 – 7.07 (m, 4H), 3.18 (hept, *J* = 7.0 Hz, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.55 (quintet, *J* = 8.0 Hz, 2H), 1.41 (hextet, *J* = 4 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 146.44, 139.56, 129.30, 126.04, 125.41, 125.13, 33.97, 32.59, 28.50, 24.03, 22.80, 13.99.

HRMS (EI) Calcd. for $C_{13}H_{20}$, 176.1565. Found: 176.1564.

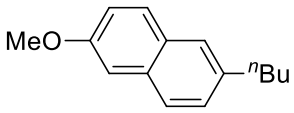
FTIR (NaCl) 3446, 2960, 2926, 1652, 1457 cm^{-1}.



SI-38

SI-38 (Table 2, entries 15 & 16). Purification by flash chromatography yielded **SI-38** as a colorless oil. Spectral data match those previously reported.[12]

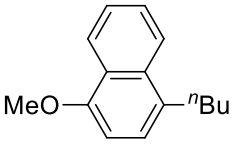
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.41 (s, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.16 (dd, *J* = 7.7, 4.8 Hz, 1H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.65 (quintet, *J* = 7.3 Hz, 2H), 1.40 (hextet, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).



SI-39

SI-39 (Table 2, entry 17). Purification by flash chromatography (75:1 Hex:EtOAc) yielded **SI-39** as a colorless oil and 2-methoxy naphthalene as an inseparable mixture (81% yield, 8.6:1 ratio by NMR). Spectral data match those previously reported.[13]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (dd, *J* = 9.0, 3.8 Hz, 2H), 7.52 (s, 1H), 7.28 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.11 (dd, *J* = 7.9, 5.4 Hz, 2H), 3.90 (s, 3H), 2.78 (t, *J* = 8.0 Hz, 2H), 1.73 (quintet, *J* = 8.0 Hz, 2H), 1.44 (hextet, *J* = 8.0 Hz, 2H), 0.93 (t, *J* = 8.0 Hz, 3H).



SI-40

SI-40 (Table 2, entry 19). Purification by flash chromatography (20:1 Hex:DCM) yielded **SI-40** as a colorless oil and 1-methoxy naphthalene as an inseparable mixture(58% yield, 10.6:1 ratio by NMR).

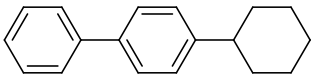
TLC: Rf = 0.5 (hexanes:DCM = 10:1)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.54 (dddd, *J* = 20.2, 8.0, 6.8, 1.3 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.02 (s, 1H), 4.00 (s, 3H), 3.03 (t, *J* = 8 Hz, 2H), 1.75 (quintet, *J* = 8 Hz, 2H), 1.49 (hextet, *J* = 8 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 153.97, 132.70, 130.85, 127.45, 126.39, 126.14, 125.96, 125.86, 125.47, 125.17, 124.70, 123.77, 122.57, 120.23, 103.77, 103.40, 55.43, 33.13, 32.37, 22.87, 14.06.

HRMS (EI) Calcd. for $C_{15}H_{18}O$, 214.1358. Found: 214.1355.

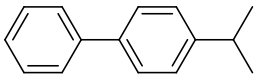
FTIR (NaCl) 3449, 2928, 1635, 1586, 1463, 1390, 1270, 1244, 1157 cm^{-1}.



SI-41

SI-41 (Table 3, entries 2 & 5). Purification by flash chromatography (100:1 pentane:EtOAc) yielded **SI-41** as a white solid. Spectral data match those previously reported.[14]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 – 7.54 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 16.1, 7.7 Hz, 3H), 2.60 – 2.47 (m, 1H), 1.98 – 1.80 (m, 4H), 1.76 (d, *J* = 12.5 Hz, 1H), 1.56 – 1.33 (m, 4H), 1.33 – 1.20 (m, 1H).



SI-42

SI-42 (Table 3, entry 3 & 6). Purification by flash chromatography (100:1 pentane:EtOAc) yielded **SI-42** as a colorless liquid (65% yield, 6.5:1 branched:linear ratio by NMR). Spectral data match those previously reported.[15]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 3H), 3.00 (hept, *J* = 6.9 Hz, 1H), 2.68 (t, *J* = 7.3 Hz 0.3H), 1.73 (hextet, *J* = 7.3 Hz 0.3H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.03 (t, *J* = 7.3 Hz, 0.5H).

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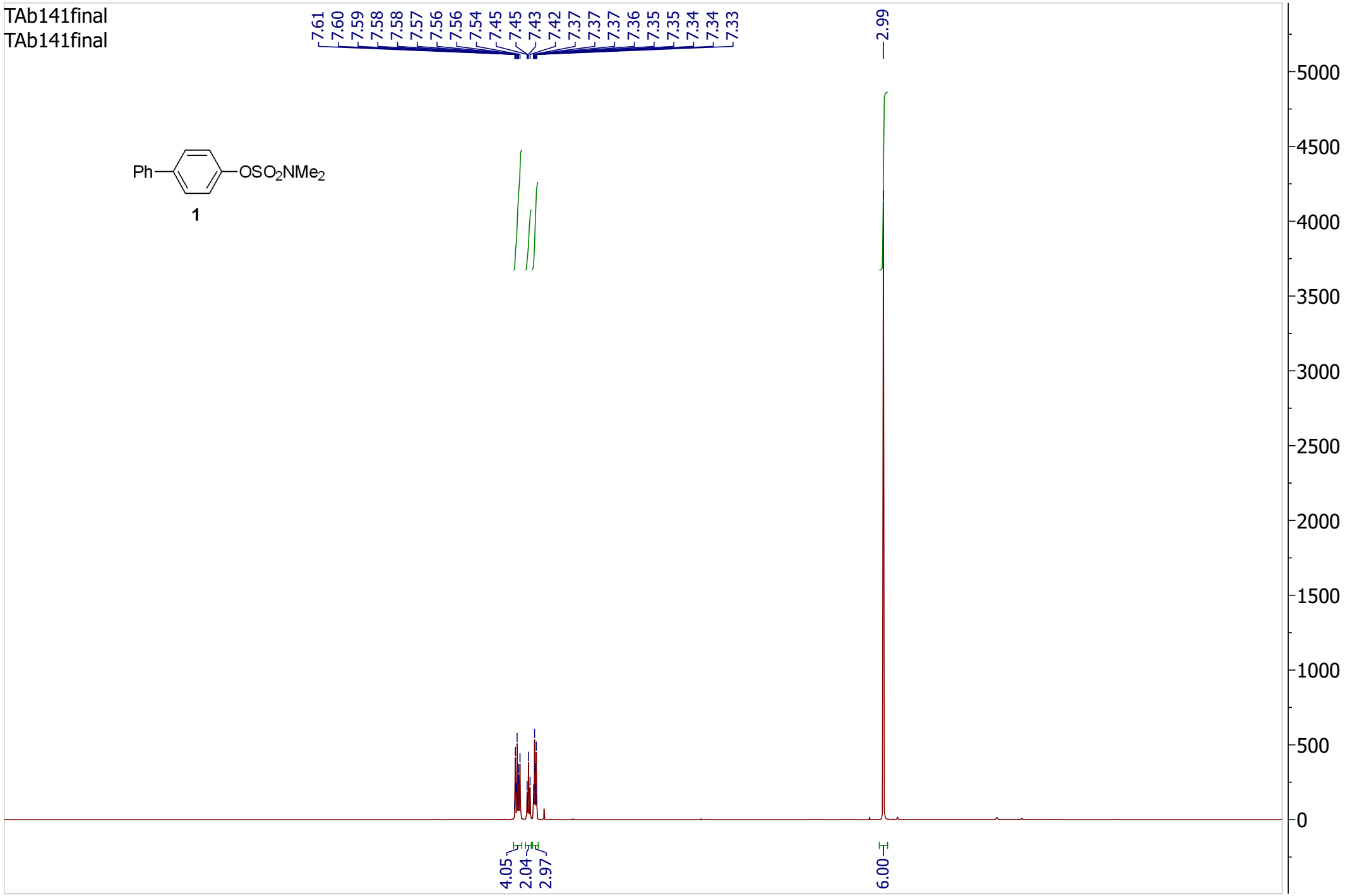
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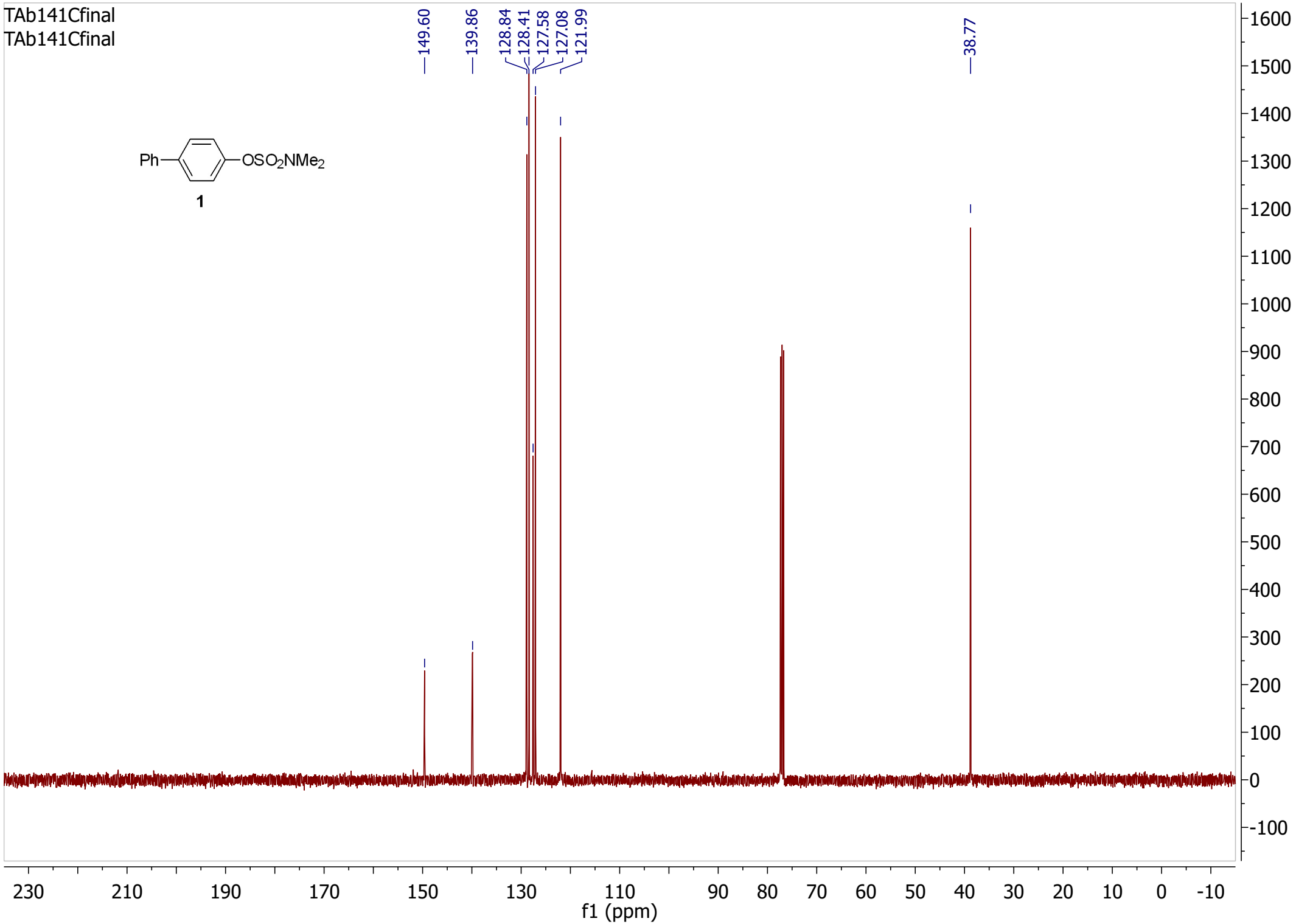
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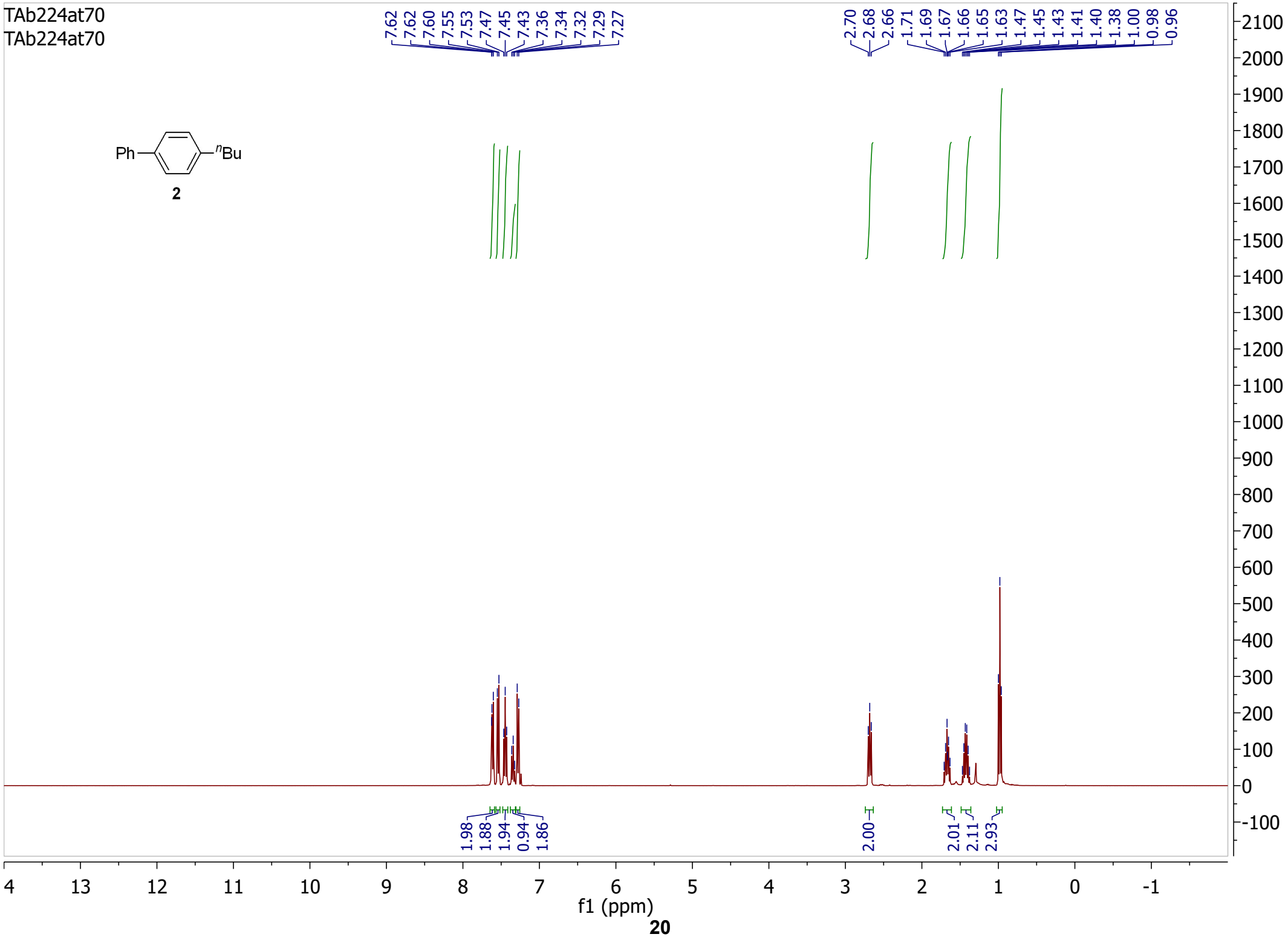
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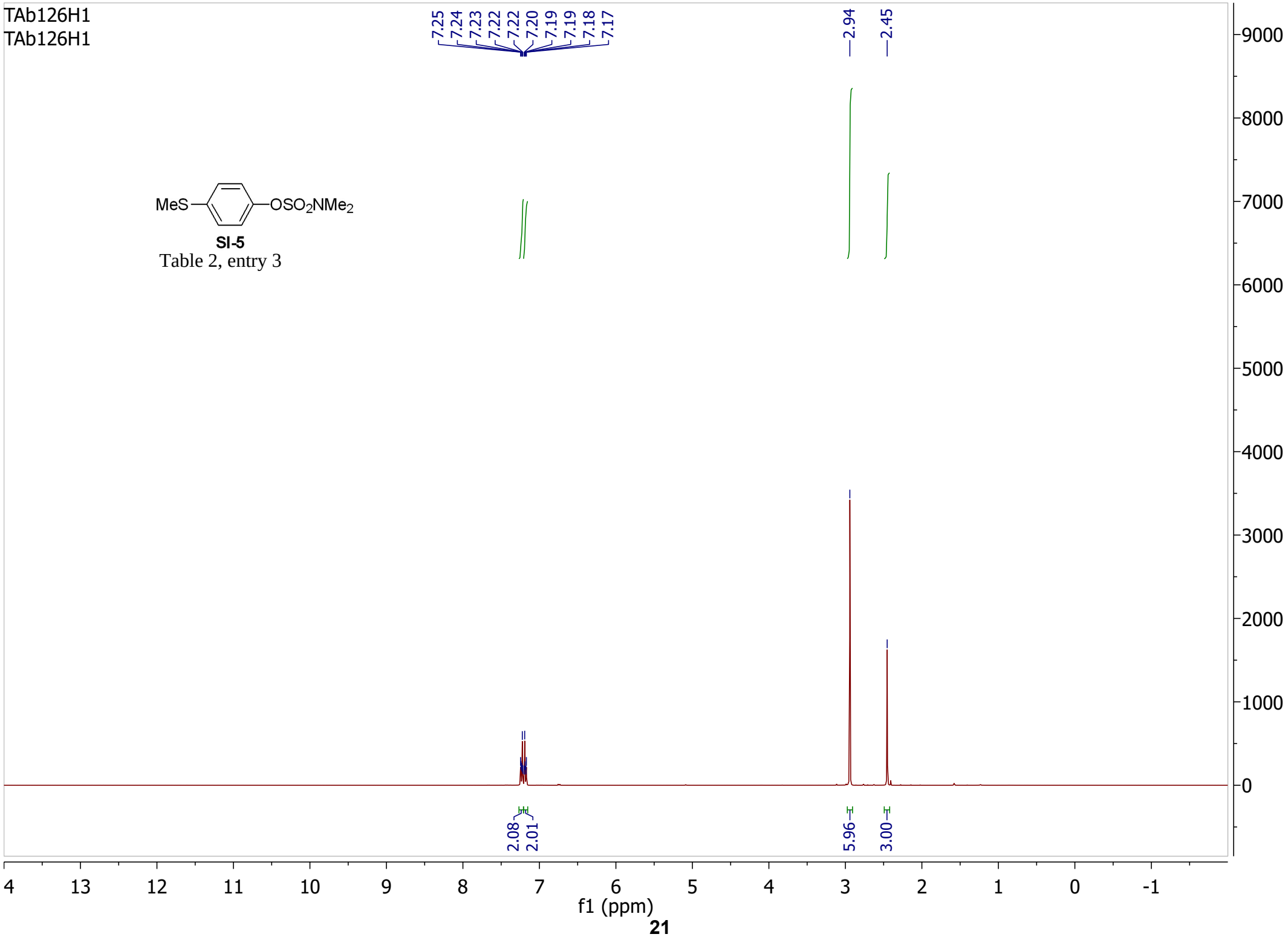
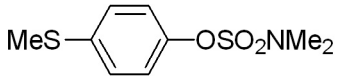
7.47
7.45
7.43
7.36
7.34
7.32
7.29
7.27
2.70
2.68
2.66
1.71
1.69
1.67
1.66
1.65
1.63
1.47
1.45
1.43
1.41
1.40
1.38
1.00
0.98
0.96
Ph
nBu
2
1.98
1.88
1.94
0.94
1.86
2.00
2.01
2.11
2.93
f1 (ppm)


TAb126H1
TAb126H1
7.25
7.24
7.23
7.22
7.22
7.20
7.19
7.19
7.18
7.17
2.94
2.45
MeS
OSO2NMe2
SI-5
Table 2, entry 3
2.08
2.01
5.96
3.00
f1 (ppm)

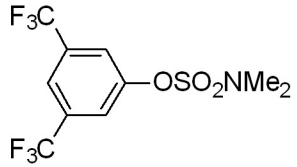
TAb126C13
TAb126C1



SI-5

Table 2, entry 3

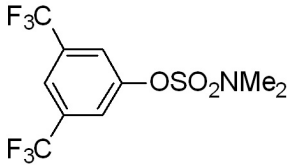
TAb273H1
TAb273H1



SI-7

Table 2, entry 5

TAb273C13
TAb273C13



SI-7

Table 2, entry 5

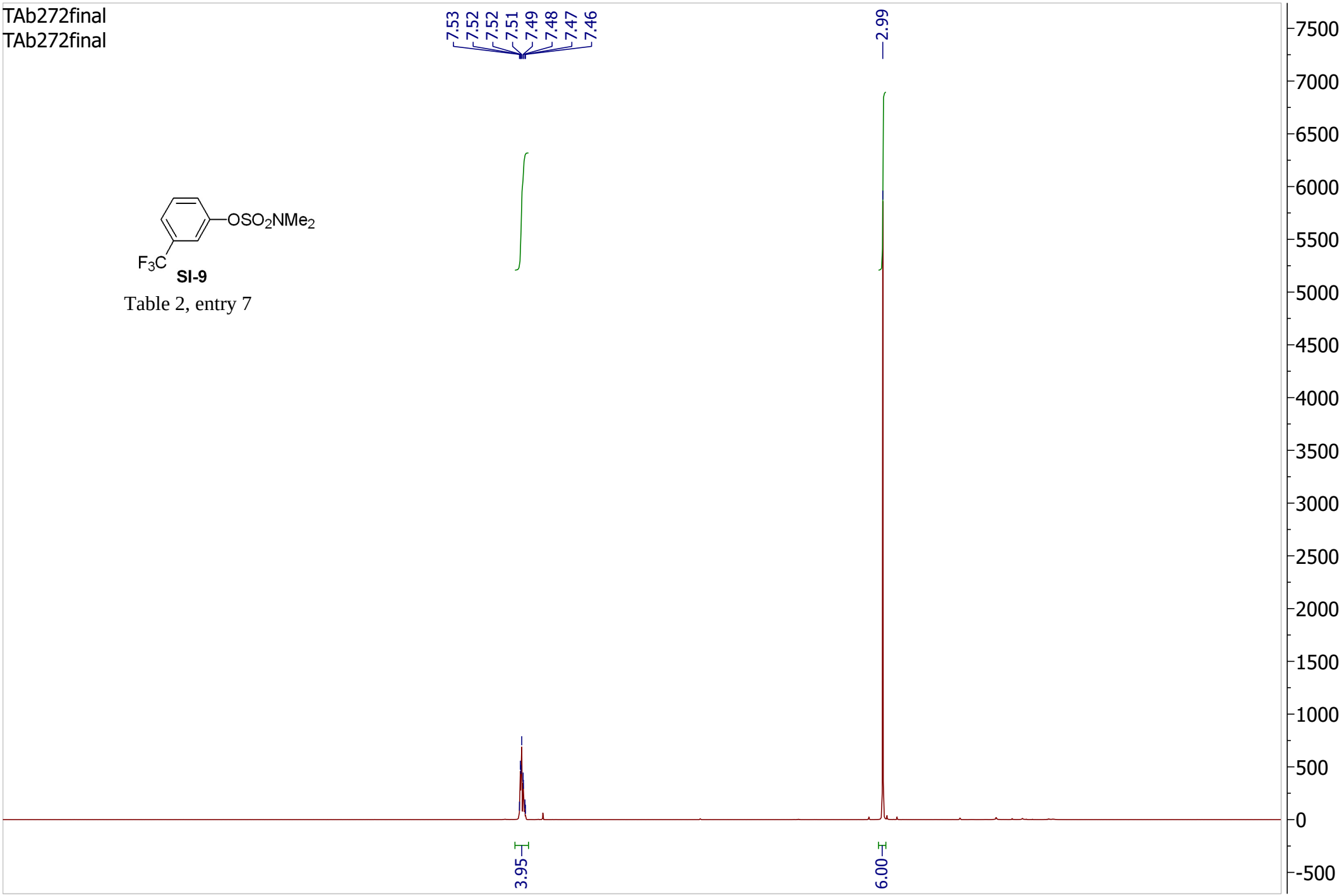


Table 2, entry 7

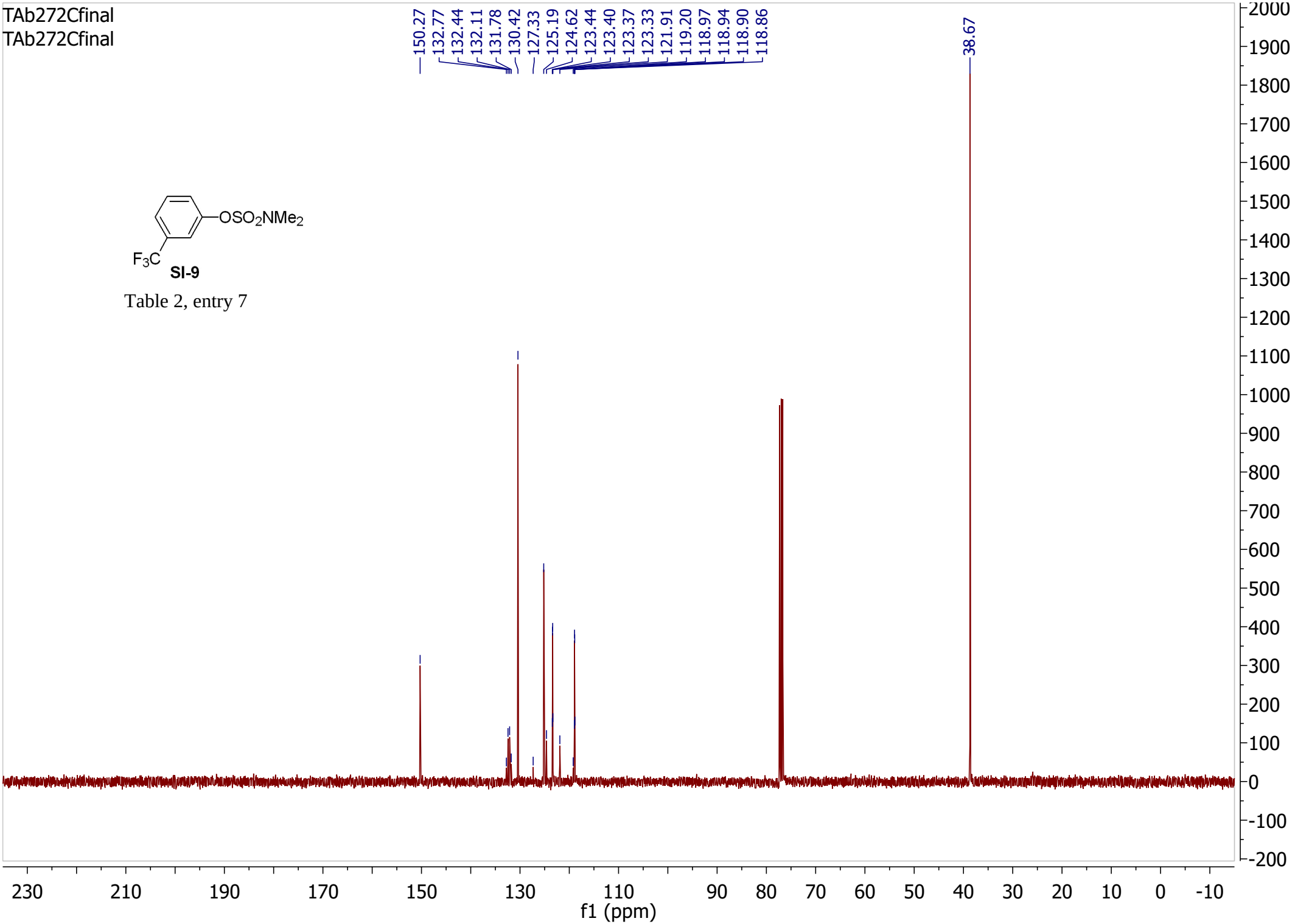
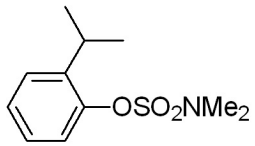


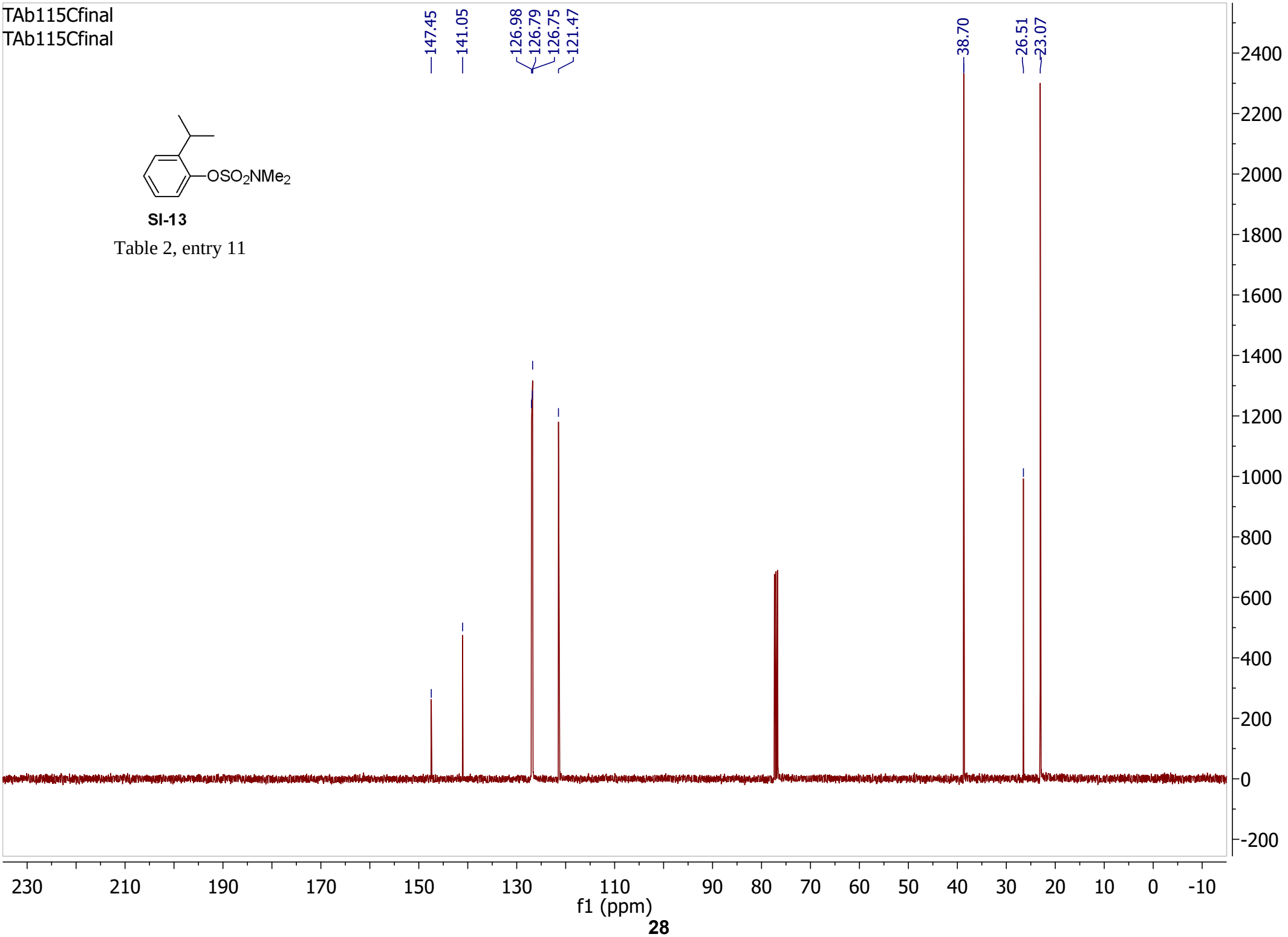
Table 2, entry 7

TAb115final
TAb115final

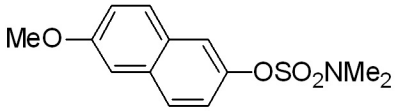


SI-13

Table 2, entry 11


TAb115Cfinal
TAb115Cfinal
147.45
141.05
126.98
126.79
126.75
121.47
38.70
26.51
23.07
OSO2NMe2
SI-13
Table 2, entry 11
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

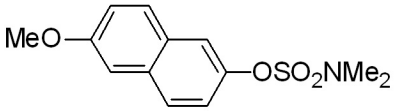
TAb110a
TAb110a



SI-17

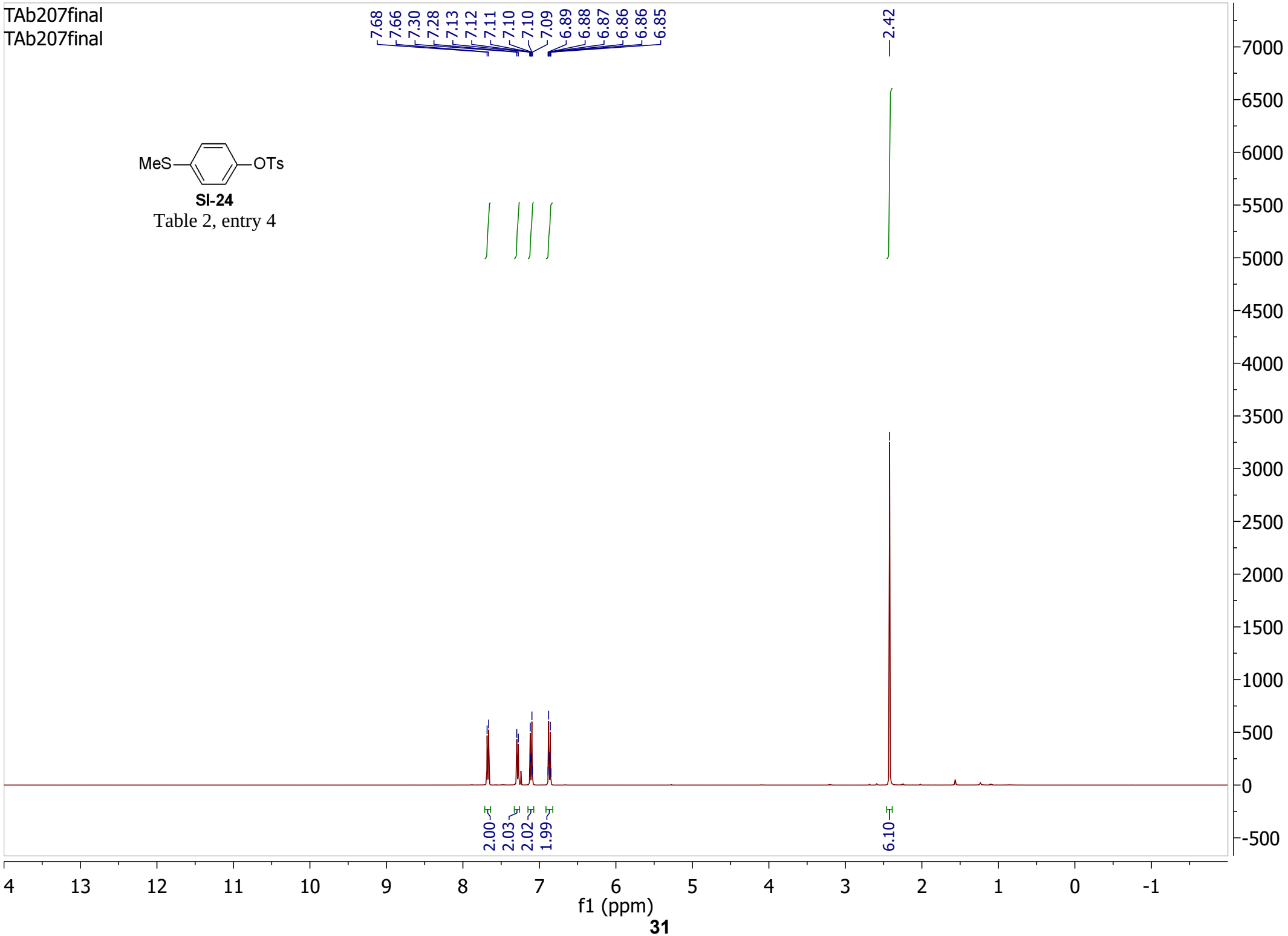
Table 2, entry 17

TAb110Cfinal
TAb110C13final



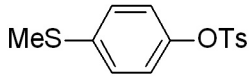
SI-17

Table 2, entry 17


TAb207final
TAb207final
7.68
7.66
7.30
7.28
7.13
7.12
7.11
7.10
7.10
7.09
6.89
6.88
6.87
6.86
6.86
6.85
2.42
MeS
OTs
SI-24
Table 2, entry 4
2.00
2.03
2.02
1.99
6.10
f1 (ppm)

TAb207Cfinal

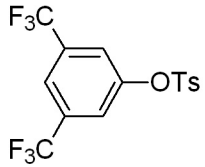
TAb207Cfinal



SI-24

Table 2, entry 4

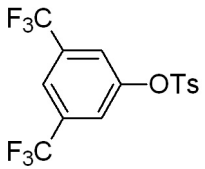
TAb279final
TAb279final



SI-25

Table 2, entry 6

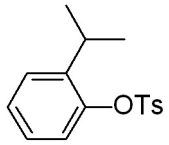
TAb279Cfinal
TAb279Cfinal



SI-25

Table 2, entry 6

TAb206final
TAb206final

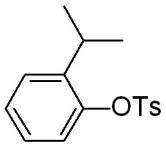


SI-28

Table 2, entry 12

TAb206Cfinal

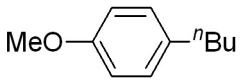
TAb206Cfinal



SI-28

Table 2, entry 12

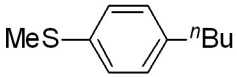
TAb252
TAb252



SI-32

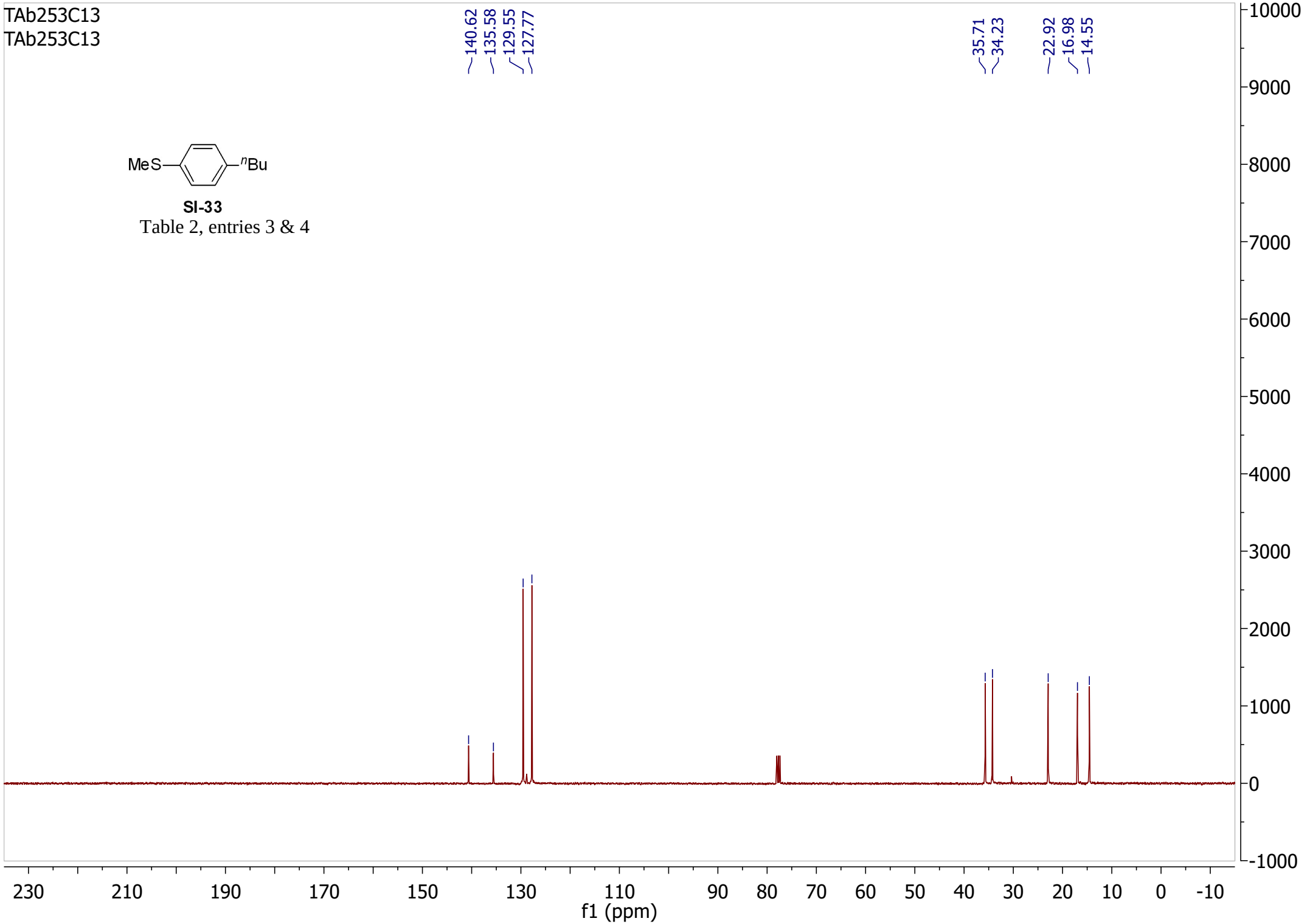
Table 2, entries 1 & 2

TAb253H1
TAb253H1



SI-33

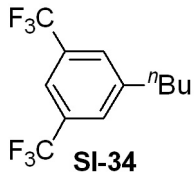
Table 2, entries 3 & 4



SI-33

Table 2, entries 3 & 4

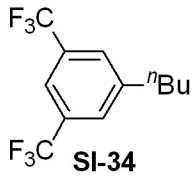
TAb283H1
TAb283H1



SI-34

Table 2, entries 5 & 6

TAb283C13
TAb283C13



SI-34

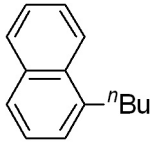
Table 2, entries 5 & 6

TAb276
TAb276

SI-35

Table 2, entries 7 & 8

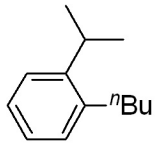
TAb259
TAb259



SI-36

Table 2, entries 9 & 10

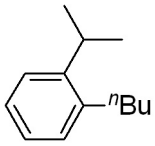
TAb255H1
TAb255H1



SI-37

Table 2, entries 11 & 12

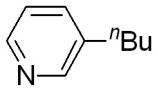
TAb255C13
TAb255C13



SI-37

Table 2, entries 11 & 12

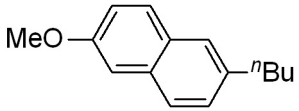
TAb277a
TAb277



SI-38

Table 2, entries 15 & 16

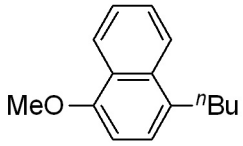
TAb268
TAb268



SI-39

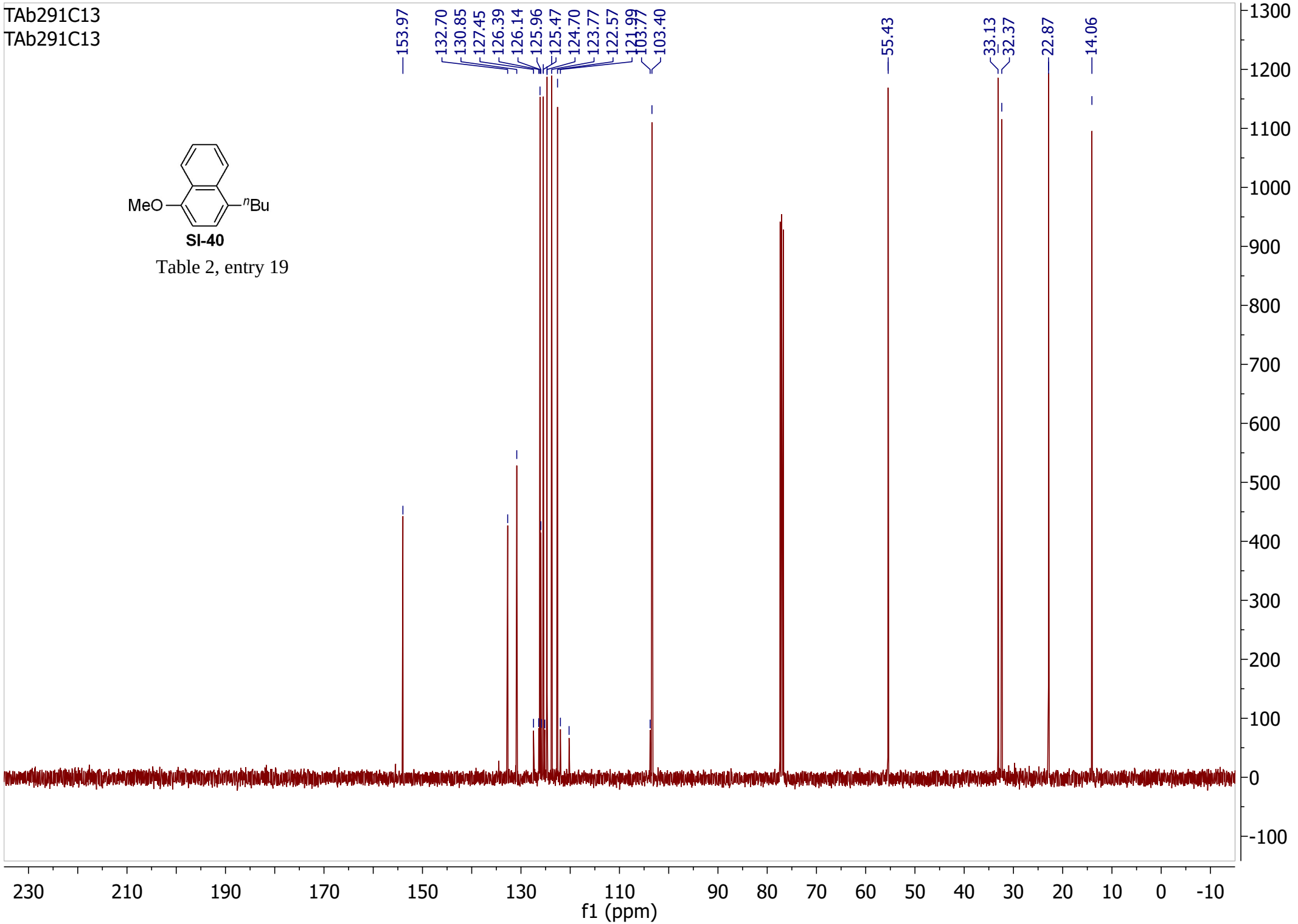
Table 2, entry 17

TAb291H1
TAb291H1

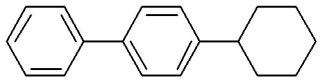


SI-40

Table 2, entry 19


TAb291C13
TAb291C13
153.97
132.70
130.85
127.45
126.39
126.14
125.96
125.47
124.70
123.77
122.57
121.99
103.77
103.40
55.43
33.13
32.37
22.87
14.06
MeO
nBu
SI-40
Table 2, entry 19
f1 (ppm)

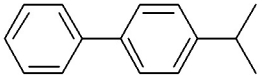
TAb232a
TAb232a



SI-41

Table 3, entries 2 & 5

TAb238
TAb238



SI-42

Table 4, entry 8