

## SUPPLEMENTARY INFORMATION

### Phenylboronic Acid-Catalysed Tandem Construction of S-S and C-S Bonds: A New Method for the Synthesis of Benzyl Disulfanylsulfone Derivatives from S-Benzyl Thiosulfonates

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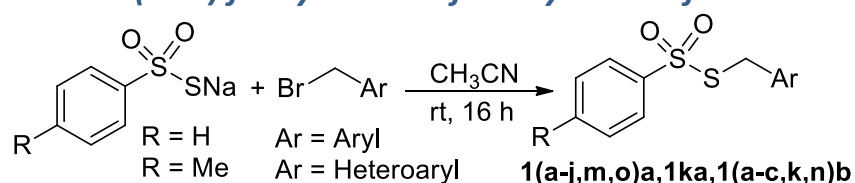
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## General Experimental

All reagents were purchase from Sigma-Aldrich, TCI, Alfa Aesar, SDFine, SRL, Spectrochem and AVRA chemicals used without further purification unless otherwise stated. For all reactions carried out under inert atmosphere, solvents were dried over activated 4 Å molecular sieves. Silicon oil baths on stirrer hotplates were employed with temperature control *via* thermometer. Reaction progress was monitored by Thin Layer Chromatography (TLC) performed using TLC Silica gel 60 F254. TLC plate's visualization was achieved by a combination of ultraviolet light (254 nm), potassium permanganate solution, iodine treatment or *p*-anisaldehyde stains. Flash column chromatography was performed using silica gel (100-200 mesh) as a stationary phase with suitable mobile phase. Generally, all reactions performed in oven-dried glassware under a nitrogen atmosphere unless otherwise stated.

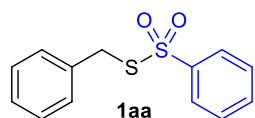
Melting points were measured in open capillaries using DBK digital melting point apparatus and are uncorrected. <sup>1</sup>H- and <sup>13</sup>C NMR's were recorded using Bruker AVIII400 (<sup>1</sup>H = 400 MHz, <sup>13</sup>C = 101 MHz) with the spectrometers at 300 K. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS and coupling constants (*J*) are quoted in Hz to one decimal place. For spectra recorded in chloroform-*d* (CDCl<sub>3</sub>) the  $\delta$  7.26 ppm resonance of residual CHCl<sub>3</sub> for proton spectra and  $\delta$  77.16 ppm resonance of CDCl<sub>3</sub> for carbon spectra were used as internal references. Spectral data for <sup>1</sup>H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons) and the following abbreviations were used for multiplicity in <sup>1</sup>H NMR: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *dd* (doublet of doublets), *dt* (doublet of triplets), *td* (triplet of doublets), *quin* (quintuplet), *bs* (broad singlet), *m* (multiplet), *app.*(apparent). <sup>13</sup>CNMR spectroscopy is reported as chemical shift values. All NMR spectrums are processed using *MestReNova version 6.0.2(v)*. High resolution mass spectroscopy (HRMS) were recorded using ESI with a time of flight analyser (TOF) techniques and was obtained using a lock-mass to adjust the calibrated mass scale.

XRD experiments by measuring X-ray intensity data on a Bruker SMART APEX III single crystal X-ray CCD diffractometer having graphite-monochromatised (Mo-K $\alpha$  = 0.71073 Å) radiation at low temperature (100K). The X-ray generator was operated at 50 Kv and 30 mA. A preliminary sets of cell constant and an orientation matrix were calculated from total 36 frames. The optimized strategy used for data collection consisted different sets of  $\phi$  and  $\omega$  scans with 0.5° steps  $\phi/\omega$ . Data were collected with a time frame of 10 secs for all the components by keeping the sample to detector distance fixed at 40 cm. All the data's were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). SHELX-97 was used for structure solution and full matrix least-squares refinement on F2 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. While the hydrogen atoms associated with oxygen and nitrogen atoms were included in the located positions. The ORTEP diagram was generated by using the X-seed software package version 2.0.

**General Procedure-1 (GP1) for synthesis of benzyl thiosulfonates:**

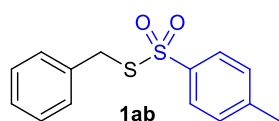
According to known procedure the corresponding sodium thiosulfonates<sup>1</sup> were prepared. A heat gun-dried round bottom flask was charged sodium benzenesulfonothioate or sodium 4-methylbenzenesulfonothioate (2.0 mmol, 1.0 equiv) and benzyl bromide derivatives (3.0 mmol, 1.5 equiv) in CH<sub>3</sub>CN (10 mL). The reaction mixture was stirred at room temperature for 16 h under nitrogen atmosphere and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (30 mL) followed by extraction with EtOAc (3x50 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 5% to 10% ethyl acetate/petether) to afford desired benzyl thiosulfonates.

**S-Benzyl benzenesulfonothioate 1aa:** Following **GP1** using sodium benzenesulfonothioate



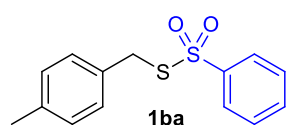
(392.4 mg, 2 mmol) and benzyl bromide (0.36 mL, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1aa** as a white solid (443.6 mg, 84%). **mp:** 40-42 °C [Lit.<sup>2</sup> 40-42 °C]; **IR** (neat):  $\nu$  2372, 2314, 1743, 1705, 1311, 1219, 1138, 1004, 796, 719 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd,  $J$  = 8.5, 1.2 Hz, 2H), 7.58 (tt,  $J$  = 7.8, 1.2 Hz, 1H), 7.48 (t,  $J$  = 7.7 Hz, 2H), 7.24–7.20 (m, 3H), 7.19–7.15 (m, 2H), 4.27 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.9, 133.6(2C), 129.3(2C), 129.2(2C), 128.9(2C), 128.1, 127.0(2C), 40.5; **HRMS** (ESI-TOF) calculated for C<sub>13</sub>H<sub>12</sub>NaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>:  $m/z$  287.0176, found 287.0171. The title compound known in the literature and the data consistent with reported values.<sup>2</sup>

**S-Benzyl 4-methylbenzenesulfonothioate 1ab:** Following **GP1** using sodium 4-methyl-



benzenesulfonothioate (420.5 mg, 2 mmol) and benzyl bromide (0.36 mL, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ab** as pale yellow solid (490.0 mg, 88%). **mp:** 54-56 °C [Lit.<sup>2</sup> 53-54 °C]; **IR** (neat):  $\nu$  2372, 2316, 1745, 1712, 1533, 1417, 1325, 1274, 1211, 1138, 1004, 704 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d,  $J$  = 8.4 Hz, 2H), 7.27 (d,  $J$  = 7.9 Hz, 2H), 7.25–7.20 (m, 3H), 7.20–7.16 (m, 2H), 4.24 (s, 2H), 2.43 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 142.0, 133.7, 129.8(2C), 129.2(2C), 128.8(2C), 128.0, 127.0(2C), 40.3, 21.7; **HRMS** (ESI-TOF) calculated for C<sub>14</sub>H<sub>14</sub>NaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>:  $m/z$  301.0333, found 301.0328. The title compound known in the literature and the data consistent with reported values.<sup>3</sup>

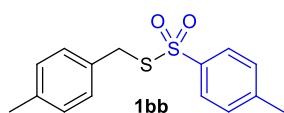
**S-4-Methylbenzyl benzenesulfonothioate 1ba:** Following **GP1** using sodium benzene-



sulfonothioate (392.4 mg, 2 mmol) and 4-methylbenzyl bromide (555.2 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ba** as a colorless solid (395.3 mg, 71%). **mp:** 66-68 °C; **IR** (neat):  $\nu$  3946, 3867, 3604, 3529,

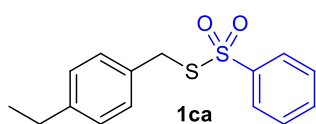
3495, 2372, 2316, 1745, 1712, 1521, 1421, 1369, 1313, 1265, 1211, 1136, 1004, 746, 704  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J = 8.5, 1.2$  Hz, 2H), 7.60 (tt,  $J = 7.4, 1.9$  Hz, 1H), 7.49 (t,  $J = 7.7$  Hz, 2H), 7.08–7.00 (m, 4H), 4.23 (s, 2H), 2.29 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.0, 138.1, 133.6, 130.5, 129.6(2C), 129.3(2C), 129.2(2C), 127.0(2C), 40.3, 21.2; *The title compound known in the literature and the data consistent with reported values.*<sup>4</sup>

**S-4-Methylbenzyl 4-methylbenzenesulfonothioate 1bb:** Following **GP1** using sodium 4-methylbenzenesulfonothioate (420.5 mg, 2 mmol) and 4-methylbenzyl bromide (555.2 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1bb** as a pale yellow solid (450.3 mg, 77%). **mp:** 58–60 °C [Lit.<sup>5</sup>



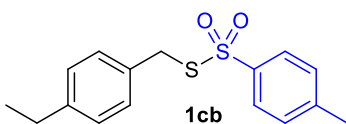
58–59 °C]; **IR** (neat):  $\nu$  2314, 1743, 1533, 1342, 1282, 1213, 1002, 779, 725  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.08–7.01 (m, 4H), 4.21 (s, 2H), 2.44 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 142.1, 137.9, 130.5, 129.8(2C), 129.5(2C), 129.1(2C), 127.1(2C), 40.2, 21.7, 21.2; *The title compound known in the literature and the data consistent with reported values.*<sup>5</sup>

**S-4-Ethylbenzyl benzenesulfonothioate 1ca:** Following **GP1** using sodium benzene sulfonothioate (392.4 mg, 2 mmol) and 4-ethylbenzyl bromide (597.3 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ca** as a pale yellow liquid (427.0 mg, 73%). **IR** (neat):  $\nu$  2314, 1743, 1527, 1311, 1213,



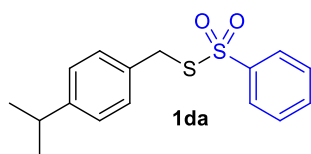
1139, 1002, 785, 754  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.58 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.48 (t,  $J = 7.7$  Hz, 2H), 7.11–7.01 (m, 4H), 4.24 (s, 2H), 2.59 (q,  $J = 7.6$  Hz, 2H), 1.19 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 144.2, 133.5, 130.6, 129.2(2C), 129.1(2C), 128.3(2C), 126.9(2C), 40.2, 28.5, 15.5; **HRMS** (ESI-TOF) calculated for  $\text{C}_{15}\text{H}_{17}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  293.0670, found 293.0668.

**S-4-Ethylbenzyl 4-methylbenzenesulfonothioate 1cb:** Following **GP1** using sodium 4-methylbenzenesulfonothioate (420.5 mg, 2 mmol) and 4-ethylbenzyl bromide (597.3 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1cb** as a pale yellow liquid (422.4 mg, 69%). **IR** (neat):  $\nu$



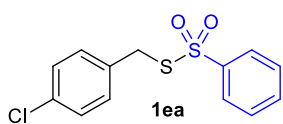
2372, 2314, 1745, 1521, 1421, 1363, 1329, 1274, 1213, 1138, 719  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.9$  Hz, 2H), 7.11–7.04 (m, 4H), 4.22 (s, 2H), 2.59 (q,  $J = 7.6$  Hz, 2H), 2.43 (s, 3H), 1.19 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 144.3, 142.1, 130.7, 129.8(2C), 129.2(2C), 128.3(2C), 127.0(2C), 40.2, 28.6, 21.7, 15.6; **HRMS** (ESI-TOF) calculated for  $\text{C}_{16}\text{H}_{18}\text{NaO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$ :  $m/z$  329.0646, found 329.0642.

**S-4-Isopropylbenzylbenzenesulfonothioate 1da:** Following **GP1** using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 4-isopropylbenzyl bromide (639.3 mg, 3 mmol) and for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1da** as a pale yellow liquid (410.6 mg, 67%). **IR** (neat):  $\nu$  2372, 2316, 1745, 1712, 1521, 1421, 1327, 1274, 1207, 1141, 1006, 717  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,

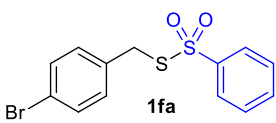


CDCl<sub>3</sub>)  $\delta$  7.83 (dd,  $J$  = 8.5, 1.2 Hz, 2H), 7.58 (tt,  $J$  = 7.4, 1.2 Hz, 1H), 7.47 (t,  $J$  = 7.7 Hz, 2H), 7.11–7.06 (m, 4H), 4.25 (s, 2H), 2.85 (sept,  $J$  = 6.9 Hz, 1H), 1.21 (d,  $J$  = 6.9 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.9, 144.9, 133.5, 130.8, 129.2(2C), 129.1(2C), 126.89(2C), 126.88(2C), 40.3, 33.8, 23.9(2C); HRMS (ESI-TOF) calculated for C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>2</sub> [M+NH<sub>4</sub>]<sup>+</sup>:  $m/z$  324.1092, found 324.1095.

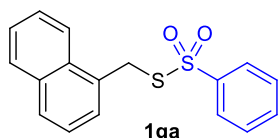
**S-4-Chlorobenzyl benzenesulfonothioate 1ea:** Following GP1 using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 4-chlorobenzyl bromide (616.4 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ea** as a pale yellow liquid (388.4 mg, 65%). IR (neat):  $\nu$  2316, 1743, 1693, 1533, 1351, 1280, 1215, 1136, 1004, 779 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (dd,  $J$  = 8.5, 1.2 Hz, 2H), 7.58 (tt,  $J$  = 7.4, 1.2 Hz, 1H), 7.46 (t,  $J$  = 7.8 Hz, 2H), 7.17–7.07 (m, 4H), 4.22 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 133.6, 133.5, 132.4, 130.3(2C), 129.1(2C), 128.7(2C), 126.7(2C), 39.5; HRMS (ESI-TOF) calculated for C<sub>13</sub>H<sub>15</sub>ClNO<sub>2</sub>S<sub>2</sub> [M+NH<sub>4</sub>]<sup>+</sup>:  $m/z$  316.0233, found 316.0235.



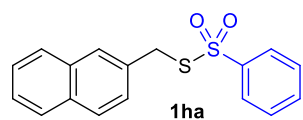
**S-4-Bromobenzyl benzenesulfonothioate 1fa:** Following GP1 using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 4-bromobenzyl bromide (749.8 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1fa** as a pale yellow solid (494.3 mg, 72%). mp: 51–53 °C; IR (neat):  $\nu$  2372, 2316, 1745, 1681, 1521, 1417, 1343, 1274, 1209, 1136, 1002, 705 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (dd,  $J$  = 8.5, 1.2 Hz, 2H), 7.59 (tt,  $J$  = 7.4, 1.2 Hz, 1H), 7.47 (t,  $J$  = 7.8 Hz, 2H), 7.32 (d,  $J$  = 8.4 Hz, 2H), 7.04 (d,  $J$  = 8.5 Hz, 2H), 4.22 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.9, 133.7, 133.0, 131.9(2C), 130.8(2C), 129.3(2C), 126.9(2C), 122.1, 39.8; HRMS (ESI-TOF) calculated for C<sub>13</sub>H<sub>11</sub>BrKO<sub>2</sub>S<sub>2</sub> [M+K]<sup>+</sup>:  $m/z$  380.9021, found 380.9017.



**S-(Naphthalen-1-ylmethyl)benzenesulfonothioate 1ga:** Following GP1 using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 1-(bromomethyl)naphthalene (663.3 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ga** as a pale yellow solid (383.6 mg, 61%). mp: 92–94 °C; IR (neat):  $\nu$  2314, 1710, 1521, 1333, 1274, 1211, 1136, 1004, 719 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.84–7.80 (m, 1H), 7.76 (d,  $J$  = 6.9 Hz, 2H), 7.62 (tt,  $J$  = 7.4, 1.2 Hz, 1H), 7.52 (t,  $J$  = 7.7, 1.2 Hz, 2H), 7.50–7.45 (m, 2H), 7.35–7.28 (m, 2H), 4.70 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 134.0, 133.7, 131.2, 129.6, 129.4(2C), 129.0, 128.8, 128.5, 127.1(2C), 126.9, 126.3, 125.4, 123.2, 38.4; HRMS (ESI-TOF) calculated for C<sub>17</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub> [M-H]<sup>-</sup>:  $m/z$  313.0357, found 313.0351.

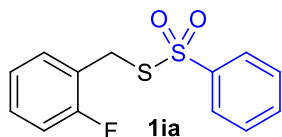


**S-(Naphthalen-2-ylmethyl)benzenesulfonothioate 1ha:** Following GP1 using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 2-(bromomethyl)naphthalene (663.3 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ha** as a yellow solid (371.0 mg, 59%). mp: 60–62 °C; IR (neat):  $\nu$  2316, 1703, 1533, 1323, 1303, 1215, 1002, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (dd,  $J$  = 8.5, 1.2 Hz, 2H), 7.78–7.75 (m, 1H), 7.71–7.68 (m, 1H), 7.67 (d,  $J$  = 8.5 Hz, 1H), 7.61 (s, 1H), 7.50–7.45 (m, 3H), 7.34

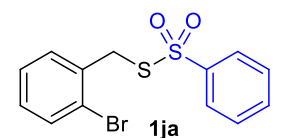


(t,  $J = 7.8$  Hz, 2H), 7.24 (dd,  $J = 8.5, 1.8$  Hz, 1H), 4.44 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 133.5, 133.1, 132.8, 130.9, 129.1(2C), 128.8, 128.3, 127.8, 127.7, 126.9(2C), 126.6, 126.52, 126.48, 40.9; HRMS (ESI-TOF) calculated for  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  315.0513, found 315.0499.

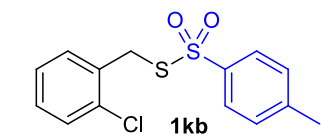
**S-2-Fluorobenzyl benzenesulfonothioate 1ia:** Following **GP1** using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 2-fluorobenzyl bromide (567.1 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ia** as a pale-yellow liquid (344.5 mg, 61%). IR (neat):  $\nu$  2372, 2316, 1745, 1521, 1363, 1316, 1274, 1211, 1138, 1002, 719  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (dd,  $J = 8.5, 1.2$  Hz, 2H), 7.58 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.48 (t,  $J = 7.7$  Hz, 2H), 7.19 (t,  $J = 6.3$  Hz, 2H), 7.02–6.92 (m, 2H), 4.28 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7 (d,  $J = 248.5$  Hz), 144.6, 133.7, 131.1 (d,  $J = 3.2$  Hz), 130.1 (d,  $J = 8.2$  Hz), 129.2(2C), 126.8(2C), 124.3 (d,  $J = 3.7$  Hz), 121.3 (d,  $J = 14.5$  Hz), 115.5 (d,  $J = 21.1$  Hz), 33.6 (d,  $J = 3.4$  Hz); HRMS (ESI-TOF) calculated for  $\text{C}_{13}\text{H}_{11}\text{FNaO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$ :  $m/z$  305.0082, found 305.0083.



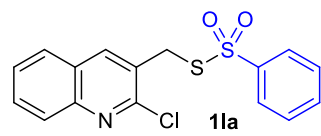
**S-2-Bromobenzyl benzenesulfonothioate 1ja:** Following **GP1** using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 2-bromobenzyl bromide (749.8 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ja** as a pale yellow solid (453.1 mg, 66%). mp: 56–58 °C; IR (neat):  $\nu$  2312, 1743, 1705, 1531, 1335, 1292, 1213, 1138, 1002, 846, 717  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (dd,  $J = 8.5, 1.3$  Hz, 2H), 7.58 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.52–7.46 (m, 3H), 7.24 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.16 (td,  $J = 7.5, 1.4$  Hz, 1H), 7.09 (td,  $J = 7.7, 1.8$  Hz, 1H), 4.35 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 133.7, 133.6, 133.1, 131.3, 129.9, 129.3(2C), 127.8, 127.0(2C), 124.6, 40.8; HRMS (ESI-TOF) calculated for  $\text{C}_{13}\text{H}_{11}\text{BrNaO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$ :  $m/z$  364.9282, found 364.9271.



**S-2-Chlorobenzyl-4-methylbenzenesulfonothioate 1kb:** Following **GP1** using sodium 4-methylbenzenesulfonothioate (420.5 mg, 2 mmol) and 2-chlorobenzyl bromide (616.4 mg 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1kb** as a colorless solid (369.1 mg, 59%). mp: 68–70 °C; IR (neat):  $\nu$  2372, 2314, 1743, 1705, 1527, 1311, 1217, 1138, 1004, 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.4$  Hz, 2H), 7.31–7.27 (m, 3H), 7.24 (d,  $J = 7.5$  Hz, 1H), 7.18 (td,  $J = 7.7, 1.8$  Hz, 1H), 7.12 (td,  $J = 7.4, 1.4$  Hz, 1H), 4.33 (s, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 142.0, 134.4, 132.2, 131.3, 129.9(2C), 129.8, 129.6, 127.2(2C), 127.1, 38.1, 21.8; HRMS (ESI-TOF) calculated for  $\text{C}_{14}\text{H}_{14}\text{ClO}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  313.0124, found 313.0119.

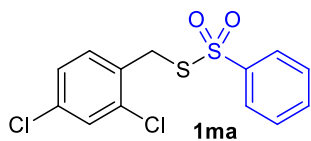


**S-[(2-Chloroquinolin-3-yl)methyl] benzenesulfonothioate 1la:** Following **GP1** using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 3-(bromomethyl)-2-chloroquinoline (769.6 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1la** as a yellow solid (363.8 mg, 52%). mp: 100–102 °C; IR (neat):  $\nu$  2372, 2314, 1743, 1705, 1529, 1315, 1282, 1211, 1138, 1002, 707  $\text{cm}^{-1}$ ; 5% approx. impurity observed in  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00–7.92 (m, 2H), 7.83–7.78 (m, 2H), 7.74–

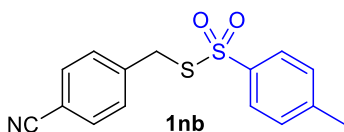


7.66 (m, 2H), 7.57 (t,  $J = 7.0$  Hz, 1H), 7.41 (t,  $J = 7.4$  Hz, 1H), 7.34 (t,  $J = 7.5$  Hz, 2H), 4.49 (d,  $J = 1.8$  Hz, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.6, 144.7, 143.2, 138.6, 133.7, 131.0, 129.2(2C), 128.30, 128.26, 127.7, 127.6, 126.9(2C), 126.8, 40.1; **HRMS** (ESI-TOF) calculated for  $\text{C}_{16}\text{H}_{13}\text{ClNO}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ :  $m/z$  350.0076, found 350.0076.

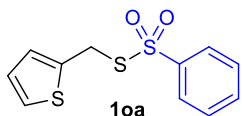
**S-2,4-Dichlorobenzyl benzenesulfonothioate 1ma**: Following **GP1** using sodium benzenesulfonothioate (392.4 mg, 2 mmol) and 2,4-dichlorobenzyl bromide (719.8 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ma** as a colorless solid (293.3 mg, 44%). **mp**: 60-62 °C; **IR** (neat):  $\nu$  2372, 2316, 1795, 1745, 1681, 1521, 1421, 1329, 1274, 1209, 1139, 1004, 717  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J = 8.5, 1.2$  Hz, 2H), 7.60 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.49 (t,  $J = 7.7$  Hz, 2H), 7.28 (d,  $J = 2.1$  Hz, 1H), 7.17 (d,  $J = 8.3$  Hz, 1H), 7.08 (dd,  $J = 8.3, 2.1$  Hz, 1H), 4.30 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 134.9, 134.8, 133.8, 132.0, 130.8, 129.6, 129.3(2C), 127.4, 127.0(2C), 37.6; **HRMS** (ESI-TOF) calculated for  $\text{C}_{13}\text{H}_9\text{Cl}_2\text{O}_2\text{S}_2$   $[\text{M}-\text{H}]^-$ :  $m/z$  330.9421, found 330.9416.



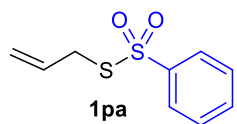
**S-4-Cyanobenzyl-4-methyl benzenesulfonothioate 1nb**: Following **GP1** using sodium 4-methyl benzenesulfonothioate (420.5 mg, 2 mmol) and 4-cyanobenzyl bromide (588.1 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1nb** as a white solid (291.2 mg, 48%). **mp**: 73-75 °C [Lit.<sup>3</sup> 72-72.9 °C]; **IR** (neat):  $\nu$  2372, 2316, 1745, 1691, 1533, 1411, 1328, 1273, 1213, 1138, 1002, 738  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 6.7$  Hz, 2H), 7.49 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 8.5$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 4.27 (s, 2H), 2.43 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.2, 141.9, 139.9, 132.4(2C), 129.9(2C), 129.8(2C), 127.0(2C), 118.4, 111.7, 39.7, 21.7. *The title compound known in the literature and the data consistent with reported values.*<sup>3</sup>



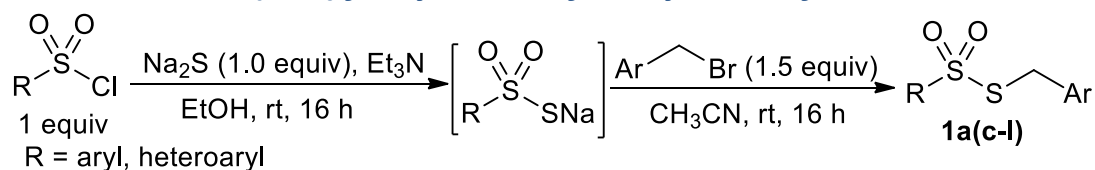
**S-(Thiophen-2-ylmethyl) benzenesulfonothioate 1oa**: Following **GP1** using sodium benzenesulfonothioate (392 mg, 2 mmol) and 2-(bromomethyl) thiophene (527.8 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1oa** as a pale-yellow liquid (281.2 mg, 52%); **IR** (neat):  $\nu$  2372, 2316, 1745, 1712, 1533, 1417, 1315, 1280, 1211, 1138, 1004, 719  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J = 8.5, 1.2$  Hz, 2H), 7.60 (tt,  $J = 7.4, 1.2$  Hz, 1H), 7.50 (t,  $J = 7.7$  Hz, 2H), 7.15 (dd,  $J = 5.1, 1.3$  Hz, 1H), 6.88 (dd,  $J = 3.5, 1.2$  Hz, 1H), 6.83 (dd,  $J = 5.1, 3.5$  Hz, 1H), 4.50 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 136.2, 133.7, 129.3(2C), 127.9, 127.0, 126.9(2C), 126.4, 35.0; **HRMS** (ESI-TOF) calculated for  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{S}_3$   $[\text{M}+\text{H}]^+$ :  $m/z$  270.9921, found 270.9921.



**S-allyl benzenesulfonothioate 1pa**: Following **GP1** using sodium benzenesulfonothioate (392 mg, 2 mmol) and allyl bromide (0.26 mL, 363.0 mg, 3 mmol) for 16 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **1pa** as a colorless liquid (337.1 mg, 74%); *The title compound known in the literature and the data consistent with reported values.*<sup>6</sup>





**General Procedure-2 (GP2) for synthesis of benzyl thiosulfonates:**

This procedure was slightly modified as reported in literature.<sup>7</sup> A heat gun-dried round bottom flask was charged arylsulfonyl chloride (2.0 mmol, 1.0 equiv) and sodium sulfide (Na<sub>2</sub>S, 2.0 mmol, 1.0 equiv) in ethanol (10 mL) at 0 °C under nitrogen atmosphere. To this stirred solution, Et<sub>3</sub>N (2.0 mL) was added drop-wise and the reaction mixture allowed to stir at room temperature for 16 h. The reaction was monitored by TLC the formation of sodium benzenesulfonothioate. The solvent was evaporated under reduced pressure and the crude sodium arylsulfonothioate was dissolved in CH<sub>3</sub>CN (10 mL). The benzyl bromide (3.0 mmol, 1.5 equiv) added and the mixture was stirred at room temperature for 16 h under nitrogen atmosphere and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (30 mL) followed by extraction with EtOAc (3x50 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 5% to 10% ethyl acetate/petether) to afford desired benzyl thiosulfonates.

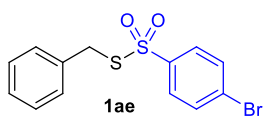
**S-Benzyl 4-fluorobenzenesulfonothioate 1ac:** Following **GP2** using 4-fluorobenzene-1-sulfonyl chloride (389.2 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ac** as a colorless solid (288.0 mg, 51%).

**mp:** 56-58 °C; **IR** (neat):  $\nu$  2372, 2316, 1745, 1521, 1421, 1363, 1280, 1211, 1141, 1006, 704 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, *J* = 5.0 Hz, 1H), 7.78 (d, *J* = 5.0 Hz, 1H), 7.24–7.20 (m, 3H), 7.20–7.15 (m, 2H), 7.10 (t, *J* = 8.3 Hz, 2H), 4.28 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.4 (d, *J* = 256.6 Hz), 141.1 (d, *J* = 3.1 Hz), 133.5, 129.8 (d, *J* = 9.7 Hz), 129.2(2C), 128.9(2C), 128.2(2C), 116.4 (d, *J* = 22.9 Hz), 40.6, *one quaternary aromatic resonance peak could not be identified*; The title compound known in the literature and the data consistent with reported values.<sup>8</sup>

**S-Benzyl 4-chlorobenzenesulfonothioate 1ad:** Following **GP2** using 4-chlorobenzene-1-sulfonyl chloride (422.1 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ad** as a yellow solid (275.0 mg, 46%).

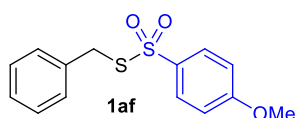
**mp:** 46-48 °C; **IR** (neat):  $\nu$  2314, 1743, 1533, 1325, 1280, 1213, 1136, 1001, 744 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.25–7.20 (m, 3H), 7.20–7.15 (m, 2H), 4.28 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.2, 139.9, 133.3, 129.3(2C), 129.0(2C), 128.7(2C), 128.2(2C), 128.0, 40.5; **HRMS** (ESI-TOF) calculated for C<sub>13</sub>H<sub>11</sub>ClNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: *m/z* 320.9787, found 320.9770. The title compound known in the literature and the data consistent with reported values.<sup>8</sup>

**S-Benzyl 4-bromobenzenesulfonylthioate 1ae:** Following **GP2** using 4-bromobenzene-1-sulfonyl chloride (511.0 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ae** as a colorless solid (329.5 mg, 48%).



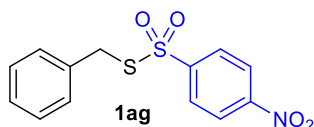
**mp:** 57–59 °C; **IR** (neat):  $\nu$  2372, 2314, 1745, 1710, 1531, 1363, 1273, 1209, 1136, 1004, 738 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66–7.54 (m, 4H), 7.25–7.21 (m, 3H), 7.19–7.41 (m, 2H), 4.28 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.0, 133.4, 132.4(2C), 129.2(2C), 128.9(2C), 128.7, 128.4(2C), 128.2, 40.6; **HRMS** (ESI-TOF) calculated for C<sub>13</sub>H<sub>11</sub>BrNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>:  $m/z$  364.9282, found 364.9278. The title compound known in the literature and the data consistent with reported values.<sup>8</sup>

**S-Benzyl 4-methoxybenzenesulfonylthioate 1af:** Following **GP2** using 4-methoxybenzene-1-sulfonyl chloride (413.3 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 20% EtOAc in petether) yielded title compound **1af** as a colorless solid (376.8 mg, 64%).



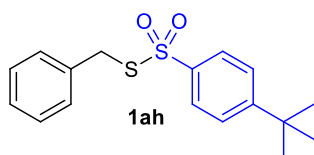
**mp:** 50–52 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1531, 1331, 1220, 1138, 1004, 794, 709 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d,  $J$  = 9.0 Hz, 2H), 7.24–7.22 (m, 3H), 7.21–7.16 (m, 2H), 6.92 (d,  $J$  = 9.0 Hz, 2H), 4.24 (s, 2H), 3.87 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.7, 136.7, 133.8, 129.4(2C), 129.1(2C), 128.9(2C), 128.1, 114.3(2C), 55.9, 40.3; The title compound known in the literature and the data consistent with reported values.<sup>9</sup>

**S-Benzyl 4-nitrobenzenesulfonylthioate 1ag:** Following **GP2** using 4-nitrobenzene-1-sulfonyl chloride (443.2 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 20% EtOAc in petether) yielded title compound **1ag** as a yellow solid (346.5 mg, 56%).



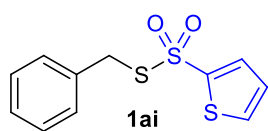
**mp:** 66–68 °C; **IR** (neat):  $\nu$  2372, 2314, 1745, 1710, 1531, 1417, 1328, 1274, 1209, 1138, 1004, 742 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d,  $J$  = 9.0 Hz, 2H), 7.84 (d,  $J$  = 9.1 Hz, 2H), 7.21–7.16 (m, 5H), 4.34 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.15, 150.10, 133.2, 129.2(2C), 128.9(2C), 128.3(2C), 128.1(2C), 124.3, 41.0; **HRMS** (ESI-TOF) calculated for C<sub>13</sub>H<sub>11</sub>NNaO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup>:  $m/z$  332.0027, found 332.0029.

**S-Benzyl 4-(tert-butyl)benzenesulfonylthioate 1ah:** Following **GP2** using 4-(tert-butyl)benzene-1-sulfonyl chloride (465.5 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ah** as a colorless solid (378.1 mg, 59%).



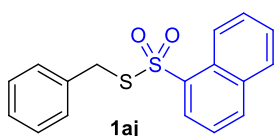
**mp:** 78–80 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1705, 1311, 1280, 1220, 1143, 1002, 742 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d,  $J$  = 8.8 Hz, 2H), 7.46 (d,  $J$  = 8.8 Hz, 2H), 7.21–7.18 (m, 3H), 7.18–7.14 (m, 2H), 4.27 (s, 2H), 1.34 (s, 9H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.5, 142.0, 133.8, 129.1(2C), 128.7(2C), 128.0, 126.8(2C), 126.2(2C), 40.3, 35.3, 31.1(3C); **HRMS** (ESI-TOF) calculated for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>S<sub>2</sub> [M-H]<sup>-</sup>:  $m/z$  319.0827, found 319.0821.

**S-Benzyl thiophene-2-sulfonylthioate 1ai:** Following **GP2** using thiophene-2-sulfonyl chloride



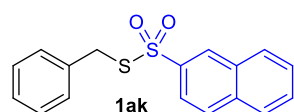
(365.3 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) and followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ai** as a colorless liquid (302.8 mg, 56%). mp: 66–68 °C; **IR** (neat):  $\nu$  2372, 2316, 1745, 1521, 1421, 1332, 1274, 1211, 1138, 1004, 727 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (dd,  $J$  = 5.0, 1.4 Hz, 1H), 7.47 (dd,  $J$  = 3.8, 1.4 Hz, 1H), 7.18–7.14 (m, 3H), 7.14–7.10 (m, 2H), 6.93 (dd,  $J$  = 5.0, 3.8 Hz, 1H), 4.24 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.9, 133.7, 133.3, 133.2, 129.2(2C), 128.9(2C), 128.2, 127.4, 41.0; **HRMS** (ESI-TOF) calculated for C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>:  $m/z$  270.9921, found 270.9921.

**S-Benzyl naphthalene-1-sulfonylthioate 1aj:** Following **GP2** using naphthalene-1-sulfonyl



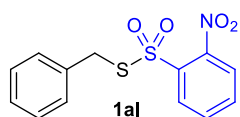
chloride (453.4 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1aj** as a colorless solid (351.7 mg, 56%). mp: 80–82 °C; **IR** (neat):  $\nu$  2314, 1743, 1531, 1329, 1219, 1147, 1002, 736 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.71 (d,  $J$  = 8.7 Hz, 1H), 8.15 (dd,  $J$  = 7.4, 1.2 Hz, 1H), 8.07 (d,  $J$  = 8.2 Hz, 1H), 7.95 (d,  $J$  = 8.1 Hz, 1H), 7.72 (t,  $J$  = 7.1 Hz, 1H), 7.63 (t,  $J$  = 7.5 Hz, 1H), 7.46 (t,  $J$  = 7.9 Hz, 1H), 7.15–7.09 (m, 3H), 7.06–7.02 (m, 2H), 4.22 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.9, 135.5, 134.5, 133.4, 129.6, 129.13, 129.07(2C), 128.7(2C), 128.6, 128.0, 127.6, 127.3, 124.7, 123.9, 40.9; **HRMS** (ESI-TOF) calculated for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>:  $m/z$  315.0513, found 315.0518.

**S-Benzyl naphthalene-2-sulfonylthioate 1ak:** Following **GP2** using naphthalene-2-sulfonyl

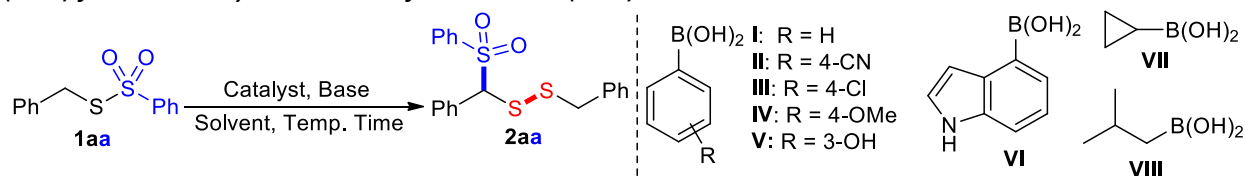


chloride (453.4 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1ak** as a colorless solid (339.6 mg, 54%). mp: 60–62 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1708, 1527, 1363, 1311, 1213, 1004, 742 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d,  $J$  = 1.8 Hz, 1H), 7.95–7.89 (m, 3H), 7.82 (dd,  $J$  = 8.8, 1.9 Hz, 1H), 7.68 (t,  $J$  = 7.5 Hz, 1H), 7.62 (t,  $J$  = 6.9 Hz, 1H), 7.17–7.10 (m, 5H), 4.29 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 135.2, 133.5, 131.8, 129.8, 129.7, 129.5, 129.2(2C), 128.8(2C), 128.6, 128.1, 128.0, 127.9, 122.0, 40.6; **HRMS** (ESI-TOF) calculated for C<sub>17</sub>H<sub>14</sub>NaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>:  $m/z$  337.0333, found 337.0328.

**S-Benzyl 2-nitrobenzenesulfonylthioate 1al:** Following **GP2** using 2-nitrobenzene-1-sulfonyl



chloride (443.2 mg, 2 mmol), sodium sulfide (156.1 mg, 2 mmol), Et<sub>3</sub>N (2 mL) followed by treatment of benzyl bromide (0.36 mL, 3 mmol) in CH<sub>3</sub>CN. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **1al** as a yellow solid (296.8 mg, 48%), mp: 120–122 °C; **IR** (neat):  $\nu$  2314, 1743, 1529, 1311, 1215, 1139, 1006, 854, 702 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.71 (td,  $J$  = 7.3, 1.6 Hz, 1H), 7.58 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.51 (td,  $J$  = 7.3, 1.6 Hz, 1H), 7.33–7.27 (m, 5H), 4.81 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 134.9, 132.9, 132.1, 131.7, 131.1(2C), 129.2, 128.9(2C), 127.4, 124.7, 62.8; **HRMS** (ESI-TOF) calculated for C<sub>13</sub>H<sub>12</sub>NO<sub>4</sub>S<sub>2</sub> [M+H]<sup>+</sup>:  $m/z$  310.0208, found 310.0211.

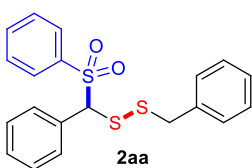
**Table-S1:** Optimization for the synthesis of 1-benzyl-2-[phenyl(phenylsulfonyl)methyl]disulfane (**2aa**) from *S*-benzyl benzenesulfonothioate (**1aa**).<sup>a</sup>

Entry	ArB(OH) <sub>2</sub>	Catalyst	Base (equiv)	Solvent	Temp (°C)	Time	Yield
1	I (1.5 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	90 °C	3 h	69%
2	I (1.5 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	rt	3 h	39%
3	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	90 °C	3 h	79%
4	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	DCE	80 °C	3 h	67%
5	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	DMF	80 °C	6 h	NR
6	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	Toluene	80 °C	6 h	62%
7	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	DMSO	80 °C	6 h	NR
8	I (1.0 equiv)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	1,4-Dioxane	80 °C	6 h	53%
9	I (20 mol%)	CuI (20mol%)	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	90 °C	3 h	58%
10	I (10 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	90 °C	4 h	87%
11	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (2.0 eq)	PhCl	90 °C	3 h	94%
12	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	3 h	97%
13	II (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	71%
14	III (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	6 h	86%
15	IV (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	8 h	80%
16	V (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	NR
17	VI (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	24 h	65%
18	VII (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	4 h	78%
19	VIII (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	4 h	73%
20	B(OH) <sub>3</sub> (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	NR
21	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (0.5 eq)	PhCl	90 °C	3 h	72%
22	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl (2 mL)	90 °C	3 h	89%
23	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	50 °C	16 h	71%
24	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	110 °C	3 h	85%
25	I (20 mol%)	-----	-----	PhCl	90 °C	16h	NR
26	-----	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	NR
27	I (20 mol%)	-----	Cs <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	10%
28	I (20 mol%)	-----	Na <sub>2</sub> CO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	traces
29	I (20 mol%)	-----	NaHCO <sub>3</sub> (1.0 eq)	PhCl	90 °C	16 h	NR
30	I (20 mol%)	-----	DABCO(1.0 eq)	PhCl	90 °C	16 h	NR
31	I (20 mol%)	-----	DBU (1.0 eq)	PhCl	90 °C	3 h	mix
32	I (20 mol%)	-----	LiHMDS (1.0 eq)	PhCl	90 °C	1 h	Decom.
33	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	DCM	50 °C	16 h	53%
34	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	DCE	80 °C	3 h	77%
35	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	Toluene	80 °C	3 h	62%
36	I (20 mol%)	-----	K <sub>2</sub> CO <sub>3</sub> (1.0 eq)	1,4-Dioxane	80 °C	3 h	59%

**Reaction conditions:** <sup>a</sup> All reactions performed on a 0.2 mmol scale of **1aa** (1.0 equiv), boronic acid (0.1 to 1.0 equiv), K<sub>2</sub>CO<sub>3</sub> (0.5 to 2.0 equiv) in 1.0 mL of solvent. <sup>b</sup> Isolated yields; NR: No Reaction

**General Procedure-3 (GP3) for synthesis of benzyl dithiosulfones:**

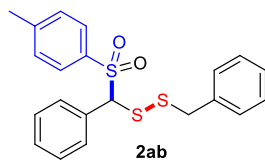
A heat gun-dried Schlenk tube was charged benzyl thiosulfonates **1(a-j,m,o)a**, **1(a-c,k,n)b** and **1a(a-l)** (0.5 mmol, 1.0 equiv), phenylboronic acid (0.1 mmol, 0.2 equiv, 20 mol%) and K<sub>2</sub>CO<sub>3</sub> (0.5 mmol, 1 equiv) in chlorobenzene (2.5 mL). The reaction mixture was stirred at 90 °C for 3 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (20 mL) followed by extraction with EtOAc (3x30 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 10% to 15% ethyl acetate/petether) to afford desired benzyl sulfonodisulfane **2** derivatives.

**1-Benzyl-2-(phenyl(phenylsulfonyl)methyl)disulfane 2aa:**

Following **GP3** using *S*-benzyl benzenesulfonothioate **1aa** (132.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2aa** as a colorless solid (92.7 mg, 96%). **mp**: 104-106 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1517, 1363, 1280, 1211, 1138, 1004, 717 cm<sup>-1</sup>;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33-7.29 (m, 4H), 7.25-7.22 (m, 4H), 7.02 (d, *J* = 7.1 Hz, 2H), 4.57 (s, 1H), 3.92 (ABq, *J* = 12.8, 3.4 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.1, 137.0, 134.0, 131.6, 129.9(2C), 129.7(2C), 129.6(2C), 129.5, 128.8(4C), 128.5(2C), 127.8, 79.4, 44.0; **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>19</sub>O<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>: *m/z* 387.0547, found 387.0551.

**Gram-Scale Reaction:** Following **GP3** using *S*-benzyl benzenesulfonothioate **1aa** (1.32 g, 5 mmol), phenylboronic acid (121.0 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (691.0 g, 0.5 mmol) in chlorobenzene (20 mL) for 5 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2aa** as a colorless solid (0.90 g, 93%).

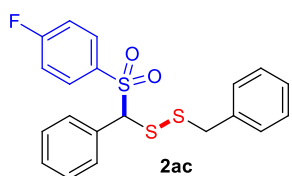
**1-Benzyl-2-(phenyl(tosyl)methyl)disulfane 2ab:**

Following **GP3** using *S*-benzyl 4-methylbenzenesulfonothioate **1ab** (139.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ab** as a colorless solid (98.1 mg, 98%). **mp**: 138-140 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1517, 1423, 1363, 1280, 1213, 1139, 1002, 704

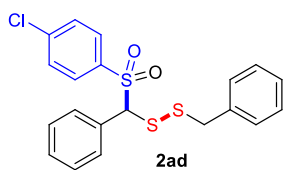
cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 8.3 Hz, 2H), 7.31-7.29 (m, 4H), 7.25-7.20 (m, 6H), 7.04 (d, *J* = 7.1 Hz, 2H), 4.57 (s, 1H), 3.91 (ABq, *J* = 12.8, 4.4 Hz, 2H), 2.41 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 137.1, 135.8, 134.0, 132.8, 131.8, 129.9(2C), 129.7, 129.6(2C), 129.5, 129.4, 128.8(2C), 128.5, 128.1, 127.8, 79.4, 44.0, 21.8; **HRMS** (ESI-TOF) calculated for C<sub>21</sub>H<sub>20</sub>NaO<sub>2</sub>S<sub>3</sub> [M+Na]<sup>+</sup>: *m/z* 423.0523, found 423.0529.

**Gram-Scale Reaction:** Following **GP3** using *S*-benzyl 4-methyl benzenesulfonothioate **1ab** (1.39 g, 5 mmol), phenylboronic acid (121.0 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (691.0 g, 5 mmol) in chlorobenzene (20 mL) for 5 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ab** as a colorless solid (0.95 g, 95%).

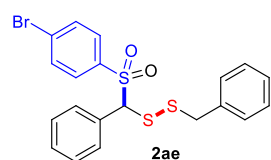
**1-Benzyl-2-[[[(4-fluorophenyl)sulfonyl](phenyl)methyl]disulfane 2ac:** Following **GP3** using *S*-phenyl 4-fluorobenzenesulfonothioate **1ac** (141.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ac** as a colorless solid (92.0 mg, 91%). **mp:** 120-122 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1521, 1421, 1342, 1274, 1217, 1139, 1002, 719 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63–7.57 (m, 2H), 7.31–7.27 (m, 4H), 7.25–7.21 (m, 4H), 7.08 (t, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.53 (s, 1H), 3.92 (ABq, *J* = 12.8, 4.6 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.03 (d, *J* = 257.0 Hz), 137.0, 132.9 (d, *J* = 3.1 Hz), 132.5 (d, *J* = 9.7 Hz), 131.3, 129.8(2C), 129.6, 129.5(3C), 128.83(2C), 128.75, 128.6(2C), 127.8, 116.2 (d, *J* = 22.6 Hz), 79.3, 44.0; **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>16</sub>FO<sub>2</sub>S<sub>3</sub> [M-H]<sup>-</sup>: *m/z* 403.0297, found 403.0291.



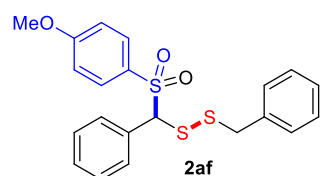
**1-Benzyl-2-[[[(4-chlorophenyl)sulfonyl](phenyl)methyl]disulfane 2ad:** Following **GP3** using *S*-benzyl 4-chlorobenzenesulfonothioate **1ad** (149.4 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ad** as a colorless liquid (94.7 mg, 90%). **IR** (neat):  $\nu$  2372, 2316, 1743, 1521, 1421, 1346, 1273, 1220, 1143, 1004, 717 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.31–7.27 (m, 4H), 7.25–7.21 (m, 4H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.50 (s, 1H), 3.92 (ABq, *J* = 12.8, 5.5 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.9, 137.0, 135.5, 131.2, 131.1(2C), 129.8(2C), 129.7, 129.6(2C), 129.2(2C), 128.9(2C), 128.6(2C), 127.8, 79.3, 44.0; **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>18</sub>ClO<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>: *m/z* 421.0157, found 421.0152.



**1-Benzyl-2-[[[(4-bromophenyl)sulfonyl](phenyl)methyl]disulfane 2ae:** Following **GP3** using *S*-phenyl 4-bromobenzenesulfonothioate **1ae** (171.6 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2ae** as a colorless solid (102.4 mg, 88%). **mp:** 91-93 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1519, 1343, 1280, 1215, 1138, 1004, 704 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.24–7.20 (m, 4H), 7.19–7.16 (m, 4H), 6.93 (d, *J* = 7.1 Hz, 2H), 4.44 (s, 1H), 3.93 (ABq, *J* = 12.8, 5.9 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.0, 136.0, 132.1(2C), 131.2, 131.1(2C), 129.8(2C), 129.7, 129.52(2C), 129.48, 128.8(2C), 128.6(2C), 127.8, 79.2, 44.0; **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>18</sub>BrO<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>: *m/z* 464.9652, found 464.9648.

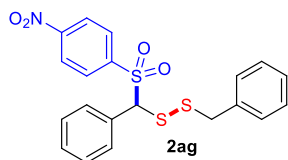


**1-Benzyl-2-[[[(4-methoxyphenyl)sulfonyl](phenyl)methyl]disulfane 2af:** Following **GP3** using *S*-benzyl 4-methoxybenzenesulfonothioate **1af** (147.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2af** as a colorless solid (97.9 mg, 94%). **mp:** 110-112 °C; **IR** (neat):  $\nu$  2370, 2316, 1743, 1517, 1423, 1366, 1282, 1138, 1004, 704 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (d, *J* = 9.0 Hz, 2H), 7.32–



7.28 (m, 4H), 7.27–7.22 (m, 4H), 7.03 (d,  $J = 7.1$  Hz, 2H), 6.87 (d,  $J = 9.0$  Hz, 2H), 4.56 (s, 1H), 3.92 (ABq,  $J = 12.8, 5.2$  Hz, 2H), 3.85 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 137.0, 131.8(2C), 129.8(2C), 129.5(2C), 129.4, 128.8(2C), 128.4(2C), 128.3, 127.7, 114.0(2C), 79.4, 55.7, 43.9, *one quaternary aromatic resonance peak could not be identified*; **HRMS** (ESI-TOF) calculated for  $\text{C}_{21}\text{H}_{20}\text{NaO}_3\text{S}_3$   $[\text{M}+\text{Na}]^+$ :  $m/z$  439.0472, found 439.0469.

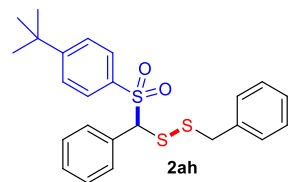
**1-Benzyl-2-[(4-nitrophenyl)sulfonyl](phenyl)methyl]disulfane 2ag**: Following **GP3** using S-benzyl



4-nitrobenzenesulfonothioate **1ag** (154.7 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (69 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2ag** as a colorless solid (93.8 mg, 87%). **mp**: 96–98°C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1521, 1421, 1363, 1274, 1213, 1138,

1004, 729  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 8.9$  Hz, 2H), 7.78 (d,  $J = 8.9$  Hz, 2H), 7.35–7.29 (m, 4H), 7.29–7.23 (m, 4H), 6.99 (d,  $J = 7.2$  Hz, 2H), 4.51 (s, 1H), 3.94 (ABq,  $J = 12.9, 5.2$  Hz, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 142.9, 136.9, 131.1(2C), 130.5, 130.0, 129.8(2C), 129.6(2C), 129.0(2C), 128.8(2C), 128.0, 123.9(2C), 79.3, 44.1; **HRMS** (ESI-TOF) calculated for  $\text{C}_{20}\text{H}_{18}\text{NO}_4\text{S}_3$   $[\text{M}+\text{H}]^+$ :  $m/z$  432.0398, found 432.0398.

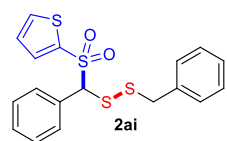
**1-Benzyl-2-[(4-(tert-butyl)phenyl)sulfonyl](phenyl)methyl]disulfane 2ah**: Following **GP3** using S-



benzyl 4-(*tert*-butyl)benzenesulfonothioate **1ah** (160.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (69 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2ah** as a colorless liquid (98.5 mg, 89%). **IR** (neat):  $\nu$  2372, 2316, 1743, 1521, 1421, 1353, 1280, 1211, 1141,

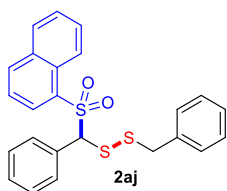
1006, 738  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.6$  Hz, 2H), 7.42 (d,  $J = 8.7$  Hz, 2H), 7.31–7.26 (m, 4H), 7.25–7.20 (m, 4H), 7.05 (d,  $J = 7.2$  Hz, 2H), 4.60 (s, 1H), 3.87 (ABq,  $J = 12.8, 2.0$  Hz, 2H), 1.30 (d,  $J = 1.7$  Hz, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 137.0, 133.9, 131.7, 129.8(2C), 129.50(2C), 129.49(2C), 129.4, 128.8(2C), 128.4(2C), 127.7, 125.8(2C), 79.4, 43.9, 35.3, 31.1(3C); **HRMS** (ESI-TOF) calculated for  $\text{C}_{24}\text{H}_{26}\text{O}_2\text{S}_3$   $[\text{M}-\text{H}]^-$ :  $m/z$  441.1017, found 441.1011

**2-[[[(Benzyl)disulfanyl](phenyl)methyl]sulfonyl]thiophene 2ai**: Following **GP3** using S-benzyl

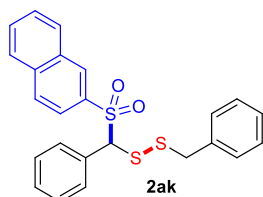


thiophene-2-sulfonothioate **1ai** (135.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ai** as a colorless liquid (84.4 mg, 86%). **IR** (neat):  $\nu$  2372, 2316,

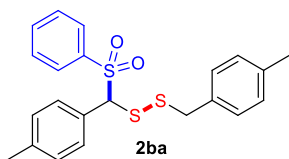
1743, 1531, 1348, 1274, 1213, 1138, 1004, 738  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J = 5.0, 1.3$  Hz, 1H), 7.38 (dd,  $J = 3.8, 1.4$  Hz, 1H), 7.34–7.30 (m, 4H), 7.28–7.27 (m, 4H), 7.07 (d,  $J = 7.1$  Hz, 2H), 7.04 (dd,  $J = 4.9, 3.8$  Hz, 1H), 4.66 (s, 1H), 3.96 (ABq,  $J = 12.8, 1.6$  Hz, 2H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 137.0, 136.1, 135.3, 131.6, 129.64(2C), 129.57(2C), 129.4, 128.9(2C), 128.6(2C), 127.8, 127.7, 80.4, 44.03; **HRMS** (ESI-TOF) calculated for  $\text{C}_{18}\text{H}_{16}\text{NaO}_2\text{S}_4$   $[\text{M}+\text{Na}]^+$ :  $m/z$  414.9931, found 414.9932.

**1-Benzyl-2-[(naphthalen-1-ylsulfonyl)(phenyl)methyl]disulfane 2aj:**

Following **GP3** using S-benzyl naphthalene-1-sulfonothioate **1aj** (157.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2aj** as a colorless solid (85.1 mg, 78%). **mp**: 104-106 °C; **IR** (neat):  $\nu$  2372, 2314, 1745, 1712, 1521, 1421, 1359, 1265, 1211, 1004, 731  $cm^{-1}$ ;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.64 (d,  $J$  = 8.7 Hz, 1H), 8.07 (d,  $J$  = 8.2 Hz, 1H), 8.03 (dd,  $J$  = 7.4, 1.2 Hz, 1H), 7.96 (d,  $J$  = 7.4 Hz, 1H), 7.71 (td,  $J$  = 7.4, 1.4 Hz, 1H), 7.66 (t,  $J$  = 7.5, 1.5 Hz, 1H), 7.47-7.42 (m, 1H), 7.24-7.14 (m, 6H), 7.04 (dd,  $J$  = 7.9, 1.5 Hz, 2H), 6.95 (d,  $J$  = 7.1 Hz, 2H), 4.81 (s, 1H), 3.76 (s, 2H);  **$^{13}C$  NMR** (101 MHz  $CDCl_3$ ),  $\delta$  137.0, 135.6, 134.1, 132.7, 132.3, 131.2, 129.7(2C), 129.6, 129.5, 129.4(3C), 128.83, 128.81(2C), 128.4(2C), 127.6, 126.9, 124.4, 124.3, 78.6, 43.9; **HRMS** (ESI-TOF) calculated for  $C_{24}H_{20}NaO_2S_3$   $[M+Na]^+$ :  $m/z$  459.0523, found 459.0518.

**1-Benzyl-2-[(naphthalen-2-ylsulfonyl)(phenyl)methyl]disulfane 2ak:**

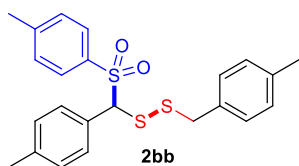
Following **GP3** using S-benzyl naphthalene-2-sulfonothioate **1ak** (157.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ak** as a colorless solid (89.5 mg, 82%). **mp**: 120-122°C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1519, 1421, 1355, 1274, 1211, 1141, 1006, 729  $cm^{-1}$ ;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.22 (s, 1H), 7.90 (d,  $J$  = 9.1 Hz, 2H), 7.85 (d,  $J$  = 8.7 Hz, 1H), 7.67 (td,  $J$  = 7.0, 1.2 Hz, 1H), 7.6 (td,  $J$  = 6.9, 1.4 Hz, 1H), 7.55 (dd,  $J$  = 8.6, 1.8 Hz, 1H), 7.33-7.27 (m, 4H), 7.24-7.20 (m, 4H), 7.05 (d,  $J$  = 7.2 Hz, 2H), 4.65 (s, 1H), 3.91 (ABq,  $J$  = 13.0, 1.0 Hz, 2H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  137.1, 135.5, 134.1, 132.0, 131.8, 131.6, 130.0(2C), 129.57, 129.55(2C), 129.5, 128.9, 128.8(2C), 128.5(2C), 128.1, 127.8, 127.7, 124.2, 79.3, 44.0, *one quaternary aromatic resonance peak could not be identified*; **HRMS** (ESI-TOF) calculated for  $C_{24}H_{20}NaO_2S_3$   $[M+Na]^+$ :  $m/z$  459.0523, found 459.0529.

**1-(4-Methylbenzyl)-2-[(phenylsulfonyl)(p-tolyl)methyl]disulfane 2ba:**

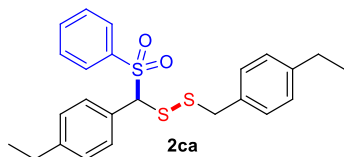
Following **GP3** using S-4-methylbenzyl benzenesulfonothioate **1ba** (139.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ba** as a colorless liquid (93.1 mg, 90%); **IR** (neat):  $\nu$  2372, 2316, 1743, 1517, 1339, 1274, 1215, 1138, 1004, 719  $cm^{-1}$ ;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.65 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.59 (t,  $J$  = 7.5 Hz, 1H), 7.44 (t,  $J$  = 7.8 Hz, 2H), 7.13-7.08 (m, 4H), 7.05 (d,  $J$  = 7.9 Hz, 2H), 6.92 (d,  $J$  = 8.1 Hz, 2H), 4.53 (s, 1H), 3.86 (ABq,  $J$  = 12.7, 5.9 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  139.6, 137.5, 137.2, 134.0, 133.9, 129.75(2C), 129.65, 129.54(2C), 129.47(2C), 129.45, 129.2(2C), 128.8(2C), 128.4, 79.1, 43.7, 21.4, 21.3; **HRMS** (ESI-TOF) calculated for  $C_{22}H_{22}O_2S_3Na$   $[M+Na]^+$ :  $m/z$  437.0680, found 437.0650.



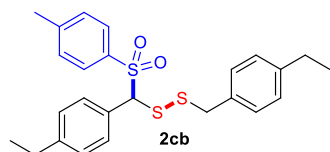
**1-(4-Methylbenzyl)-2-(p-tolyl(tosyl)methyl)disulfane 2bb:** Following **GP3** using S-4-methylbenzyl 4-methylbenzenesulfonothioate **1bb** (146.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2bb** as a colorless liquid (98.6 mg, 92%). **IR** (neat): 2372, 2316, 1743, 1519, 1421, 1363, 1280, 1211, 1139, 1002, 717 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13-7.09 (m, 4H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 4.54 (s, 1H), 3.87 (ABq, *J* = 12.7, 4.1 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.0, 139.5, 137.4, 134.2, 133.9, 129.9, 129.76(2C), 129.75(2C), 129.50(2C), 129.45(2C), 129.2(2C), 128.64, 128.61, 79.1, 43.7, 21.8, 21.4, 21.3; **HRMS** (ESI-TOF) calculated for C<sub>23</sub>H<sub>25</sub>O<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>: *m/z* 429.1017, found 429.1011.



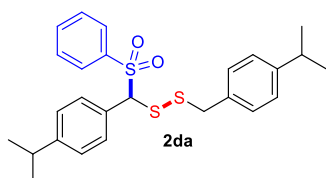
**1-(4-Ethylbenzyl)-2-[(4-ethylphenyl)(phenylsulfonyl)methyl]disulfane 2ca:** Following **GP3** using S-4-ethylbenzyl benzenesulfonothioate **1ca** (146.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ca** as a yellow color liquid (97.4 mg, 88%); **IR** (neat): ν 2372, 2316, 1743, 1519, 1423, 1346, 1280, 1211, 1138, 1004, 717 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.16-7.11 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 4.53 (s, 1H), 3.87 (ABq, *J* = 12.8, 5.1 Hz, 2H), 2.68-2.59 (m, 4H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.8, 143.8, 137.1, 134.1, 133.9, 129.7(2C), 129.6(2C), 129.5(2C), 128.7(2C), 128.5, 128.3(2C), 127.9(2C), 79.0, 43.7, 28.64, 28.62, 15.6, 15.4; **HRMS** (ESI-TOF) calculated for C<sub>24</sub>H<sub>27</sub>O<sub>2</sub>S<sub>3</sub> [M+H]<sup>+</sup>: *m/z* 443.1173, found 443.1169.



**1-(4-Ethylbenzyl)-2-[(4-ethylphenyl)(tosyl)methyl]disulfane 2cb:** Following **GP3** using S-4-methylbenzyl 4-methylbenzenesulfonothioate **1cb** (153.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2cb** as a yellow color liquid (101.6 mg, 89%); **IR** (neat): ν 2372, 2314, 1745, 1521, 1421, 1341, 1331, 1274, 1211, 1004, 719 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16-7.10 (m, 4H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.55 (s, 1H), 3.87 (ABq, *J* = 12.7, 5.6 Hz, 2H), 2.68-2.59 (m, 4H), 2.42 (s, 3H), 1.27-1.19 (m, 6H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.7, 144.9, 143.8, 134.19, 134.17, 129.8(2C), 129.7(2C), 129.5(2C), 129.4(2C), 128.8, 128.3(2C), 128.0(2C), 79.1, 43.7, 28.69, 28.66, 21.8, 15.6, 15.5; **HRMS** (ESI-TOF) calculated for C<sub>25</sub>H<sub>28</sub>NaO<sub>2</sub>S<sub>3</sub> [M+Na]<sup>+</sup>: *m/z* 479.1149, found 479.1149.

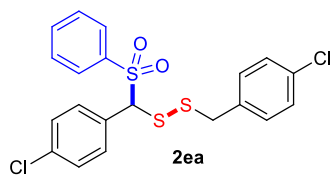


**1-(4-Isopropylbenzyl)-2-[(4-isopropylphenyl)(phenylsulfonyl)methyl]disulfane 2da:** Following **GP3** using S-4-isopropylbenzyl benzenesulfonothioate **1da** (153.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2da** as a colorless



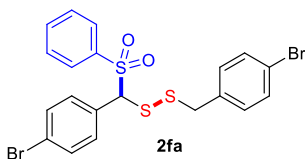
solid (102.4 mg, 87%). **mp**: 99-101 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1517, 1423, 1338, 1274, 1211, 1138, 1002, 704  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.58 (t,  $J = 7.5$  Hz, 1H), 7.42 (t,  $J = 7.8$  Hz, 2H), 7.17–7.13 (m, 4H), 7.09 (d,  $J = 8.2$  Hz, 2H), 6.94 (d,  $J = 8.2$  Hz, 2H), 4.55 (s, 1H), 3.87 (ABq,  $J = 12.7, 6.9$  Hz, 2H), 2.95–2.84 (m, 2H), 1.26 (d,  $J = 6.9$  Hz, 6H), 1.21 (d,  $J = 6.9$  Hz, 6H);  **$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 148.5, 137.2, 134.4, 133.9, 129.8(2C), 129.7(2C), 129.5(2C), 128.74(2C), 128.67, 126.9(2C), 126.6(2C), 79.0, 43.9, 34.0, 33.9, 24.14, 24.07, 24.0, 23.9; **HRMS** (ESI-TOF) calculated for  $\text{C}_{26}\text{H}_{34}\text{NO}_2\text{S}_3$   $[\text{M}+\text{NH}_4]^+$ :  $m/z$  488.1752, found 488.1752.

**1-(4-Chlorobenzyl)-2-[(4-chlorophenyl)(phenylsulfonyl)methyl]disulfane 2ea**: Following **GP3** using *S*-4-chlorobenzyl benzenesulfonothioate **1ea** (149.4 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2ea** as a colorless solid (96.8 mg, 85%). **mp**: 138-140 °C; **IR** (neat):  $\nu$  2372, 2316, 1743,



1519, 1421, 1340, 1280, 1211, 1138, 1004, 717  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.6 5–7.60 (m, 3H), 7.45 (t,  $J = 8.0$  Hz, 2H), 7.25–7.21 (m, 4H), 7.18 (d,  $J = 8.4$  Hz, 2H), 6.94 (d,  $J = 8.5$  Hz, 2H), 4.49 (s, 1H), 3.91 (s, 2H);  **$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.7, 135.8, 135.4, 134.3, 133.8, 130.98(2C), 130.95(2C), 130.1, 129.6(2C), 129.1(2C), 129.0(2C), 128.8(2C), 79.1, 43.0; **HRMS** (ESI-TOF) calculated for  $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{NaO}_2\text{S}_3$   $[\text{M}+\text{Na}]^+$ :  $m/z$  476.9587, found 476.9580.

**1-(4-Bromobenzyl)-2-[(4-bromophenyl)(phenylsulfonyl)methyl]disulfane 2fa**: Following **GP3** using *S*-4-bromobenzyl benzenesulfonothioate **1fa** (171.6 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2fa** as a colorless solid (112.9 mg, 83%). **mp**: 117-119 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1517,



1423, 1327, 1274, 1211, 1138, 1004, 717  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66–7.58 (m, 3H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.42–7.35 (m, 4H), 7.11 (d,  $J = 8.3$  Hz, 2H), 6.86 (d,  $J = 8.5$  Hz, 2H), 4.45 (s, 1H), 3.89 (s, 2H);  **$^{13}\text{C NMR}$**  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 135.9, 134.3, 132.0(2C), 131.8(2C), 131.3(2C), 131.2(2C), 130.5, 129.6(2C), 129.1(2C), 124.0, 121.9, 79.1, 43.1; **HRMS** (ESI-TOF) calculated for  $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{NO}_2\text{S}_3$   $[\text{M}+\text{NH}_4]^+$ :  $m/z$  559.9023, found 559.9025.

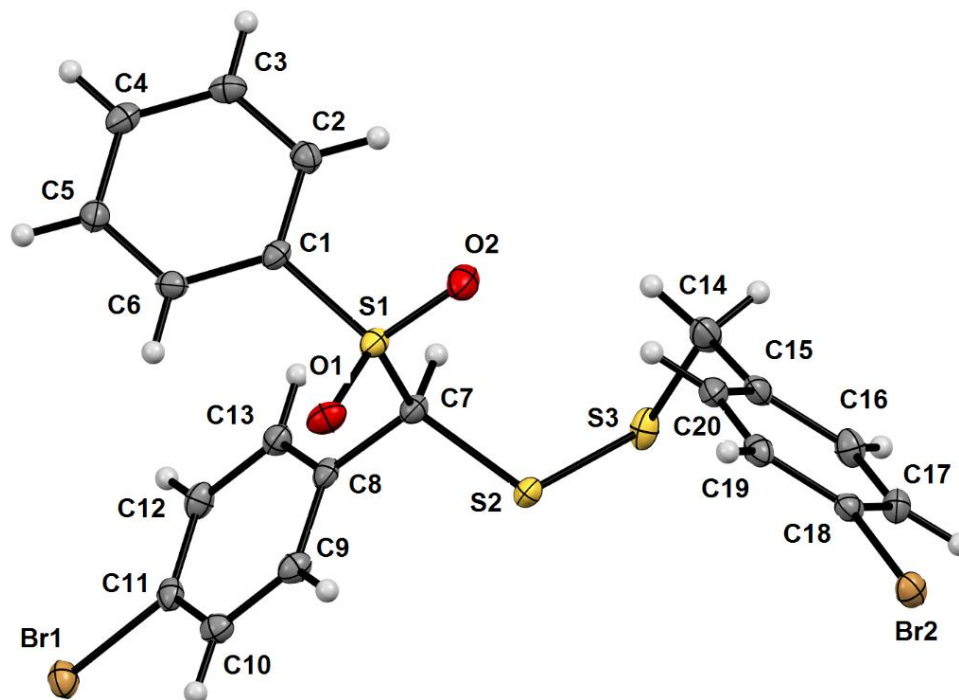
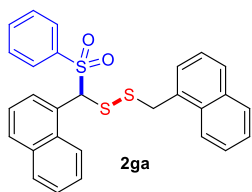


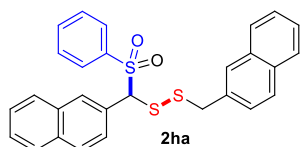
Figure 1: ORTEP diagram of **2fa** (CCDC Deposition Number 1987266).

**1-[Naphthalen-1-yl(phenylsulfonyl)methyl]-2-(naphthalen-1-ylmethyl)disulfane **2ga**:** Following



**GP3** using *S*-benzyl naphthalene-1-sulfonothioate **1ga** (157.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ga** as a colorless liquid (102.2 mg, 84%); IR (neat):  $\nu$  2372, 2316, 1743, 1710, 1521, 1329, 1273, 1211, 1141, 1004, 744  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.83 (d,  $J$  = 9.4 Hz, 1H), 7.72–7.67 (m, 2H), 7.63 (d,  $J$  = 7.5 Hz, 2H), 7.53 (d,  $J$  = 8.2 Hz, 1H), 7.46 (d,  $J$  = 7.3 Hz, 2H), 7.39–7.33 (m, 3H), 7.27 (t,  $J$  = 7.5 Hz, 2H), 7.16–7.09 (m, 4H), 7.06–7.00 (m, 2H), 5.53 (s, 1H), 4.30 (ABq,  $J$  = 12.7, 5.9 Hz, 2H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  137.0, 134.0, 133.8, 133.3, 131.9, 131.1, 131.0, 130.1, 129.5(2C), 128.93, 128.85, 128.8, 128.7(2C), 128.61, 128.58, 127.8, 126.9, 126.4, 126.0, 125.8, 125.3, 125.0, 123.9, 122.0, 74.4, 42.1; HRMS (ESI-TOF) calculated for  $C_{28}H_{21}O_2S_3$  [M-H] $^-$ :  $m/z$  485.0704, found 485.0698.

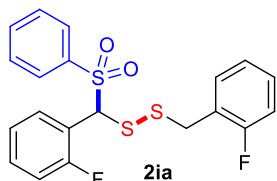
**1-(Naphthalen-2-yl(phenylsulfonyl)methyl)-2-(naphthalen-2-methyl)disulfane **2ha**:** Following



**GP3** using *S*-benzyl naphthalene-1-sulfonothioate **1ha** (157.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ha** as a colorless solid (105.8 mg, 87%). mp: 120–122 °C; IR (neat):  $\nu$  2372, 2316, 1743, 1519, 1421, 1351, 1274, 1209, 1138, 1004, 717  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.86 (d,  $J$  = 7.9 Hz, 1H), 7.83 (d,  $J$  = 8.5 Hz, 1H), 7.75 (d,  $J$  = 7.8 Hz, 1H), 7.61 (d,  $J$  = 8.0 Hz, 1H), 7.58 (s, 1H), 7.57–7.52 (m, 5H), 7.51–7.47 (m, 2H), 7.47–7.43 (m, 2H), 7.40 (dd,  $J$  = 8.4, 1.7 Hz, 1H), 7.37–7.32 (m, 2H), 7.06 (s, 1H), 6.89 (dd,  $J$  = 8.5, 1.8 Hz, 1H), 4.45 (s, 1H), 4.03 (ABq,  $J$  = 13.0, 7.3 Hz, 2H);  $^{13}C$  NMR

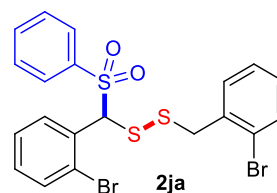
(101 MHz, CDCl<sub>3</sub>)  $\delta$  136.9, 134.3, 134.0, 133.38, 133.37, 132.8, 132.6, 129.8, 129.6(2C), 128.8(2C), 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.2, 127.1, 126.6, 126.5, 126.4, 126.2, 79.1, 44.3, one quaternary aromatic resonance peak could not be identified; **HRMS** (ESI-TOF) calculated for C<sub>28</sub>H<sub>22</sub>O<sub>3</sub>S<sub>3</sub>Na [M+Na]<sup>+</sup>:  $m/z$  509.0680, found 509.0666.

**1-(2-Fluorobenzyl)-2-[(2-fluorophenyl)(phenylsulfonyl)methyl]disulfane 2ia**: Following **GP3**



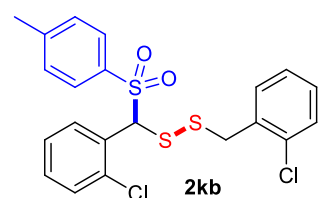
using S-2-fluorobenzyl benzenesulfonothioate **1ia** (141.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 10% EtOAc in petether) yielded title compound **2ia** as a colorless solid (86.6 mg, 82%). **mp**: 98-100 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1531, 1343, 1265, 1219, 1139, 1004, 736 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.60 (t,  $J$  = 7.5 Hz, 1H), 7.55 (t,  $J$  = 7.4 Hz, 1H), 7.44 (t,  $J$  = 7.9 Hz, 2H), 7.34–7.27 (m, 2H), 7.27–7.21 (m, 1H), 7.17 (t,  $J$  = 7.6 Hz, 1H), 7.06 (d,  $J$  = 8.6 Hz, 1H), 7.00 (d,  $J$  = 8.5 Hz, 1H), 6.87 (t,  $J$  = 9.0 Hz, 1H), 5.30 (s, 1H), 4.04 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.9 (d,  $J$  = 248.3 Hz), 159.9 (d,  $J$  = 249.8 Hz), 137.0, 134.2, 131.7 (d,  $J$  = 3.7 Hz), 131.4 (d,  $J$  = 8.5 Hz), 130.7 (d,  $J$  = 1.6 Hz), 129.8 (d,  $J$  = 8.1 Hz), 129.5(2C), 129.0(2C), 124.6 (d,  $J$  = 3.7 Hz), 124.3 (d,  $J$  = 3.7 Hz), 123.9 (d,  $J$  = 14.8 Hz), 119.5 (d,  $J$  = 14.0 Hz), 115.7 (d,  $J$  = 21.3 Hz), 115.3 (d,  $J$  = 22.2 Hz), 72.1, 37.2 (d,  $J$  = 2.3 Hz); **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>16</sub>F<sub>2</sub>NaO<sub>2</sub>S<sub>3</sub> [M+Na]<sup>+</sup>:  $m/z$  445.0178, found 445.0184.

**1-(2-Bromobenzyl)-2-[(2-bromophenyl)(phenylsulfonyl)methyl]disulfane 2ja**: Following **GP3**



using S-2-bromobenzyl benzenesulfonothioate **1ja** (171.6 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2ja** as a colorless solid (107.5 mg, 79%). **mp**: 110-112 °C; **IR** (neat):  $\nu$  2372, 2316, 1745, 1712, 1531, 1349, 1274, 1211, 1004, 744 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 7.71 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.60 (tt,  $J$  = 7.2, 1.4 Hz, 1H), 7.53 (dd,  $J$  = 7.9, 1.2 Hz, 1H), 7.46–7.40 (m, 3H), 7.38 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 7.31 (dd,  $J$  = 7.6, 1.7 Hz, 1H), 7.24–7.16 (m, 2H), 7.12 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 5.77 (s, 1H), 4.13 (ABq,  $J$  = 12.7 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.3, 136.0, 134.3, 133.2, 132.8, 132.0, 131.9, 131.3, 130.9, 129.6(2C), 129.5, 129.0(2C), 128.0, 127.6, 125.6, 124.8, 77.9, 44.6; **HRMS** (ESI-TOF) calculated for C<sub>20</sub>H<sub>16</sub>Br<sub>2</sub>NaO<sub>2</sub>S<sub>3</sub> [M+Na]<sup>+</sup>:  $m/z$  564.8577, found 564.8581.

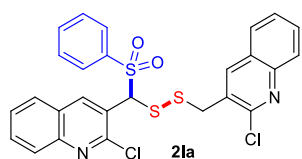
**1-(2-Chlorobenzyl)-2-[(2-chlorophenyl)(tosyl)methyl]disulfane 2kb**: Following **GP3** using S-2-



chlorobenzyl 4-methylbenzenesulfonothioate **1kb** (156.4 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 15% EtOAc in petether) yielded title compound **2kb** as a colorless solid (95.0 mg, 81%). **mp**: 88-90 °C; **IR** (neat):  $\nu$  2372, 2316, 1743, 1519, 1423, 1326, 1274, 1213, 1138, 1004, 717 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d,  $J$  = 7.9 Hz, 1H), 7.57 (d,  $J$  = 8.3 Hz, 2H), 7.34 (dd,  $J$  = 7.7, 1.5 Hz, 1H), 7.31 (dd,  $J$  = 7.0, 1.3 Hz, 2H), 7.25–7.22 (m, 3H), 7.21–7.15 (m, 3H), 5.69 (s, 1H), 4.12 (d,  $J$  = 2.3 Hz, 2H), 2.41 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.3, 134.5, 134.25, 134.20, 131.7, 131.0, 130.6, 130.2,

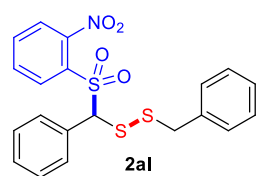
129.8, 129.6(2C), 129.4(2C), 129.3, 129.2, 127.3, 127.1, 126.9, 75.1, 41.8, 21.8; **HRMS** (ESI-TOF) calculated for  $C_{21}H_{18}Cl_2KO_2S_3$   $[M+K]^+$ :  $m/z$  506.9483, found 506.9478.

### 2-Chloro-3-[(2-chloroquinolin-3-yl)(phenylsulfonyl)methyl]disulfanyl)methyl]quinoline **2la**:



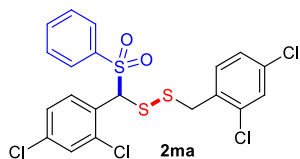
Following **GP3** using S-[(2-chloroquinolin-3-yl)methyl]benzenesulfonothioate **1la** (174.9 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 3 h. Purified by flash column chromatography (silica gel, 20% EtOAc in petether) yielded title compound **2la** as a colorless solid (100.3 mg, 72%). **mp**: 148-150 °C; **IR** (neat):  $\nu$  2372, 2314, 1743, 1519, 1423, 1337, 1274, 1211, 1143, 1004, 717  $cm^{-1}$ ;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.55 (s, 1H), 8.13 (s, 1H), 7.99 (d,  $J = 8.2$  Hz, 1H), 7.91 (d,  $J = 8.9$  Hz, 2H), 7.78–7.72 (m, 3H), 7.65–7.61 (m, 3H), 7.60–7.54 (m, 2H), 7.40 (t,  $J = 7.9$  Hz, 2H), 5.78 (s, 1H), 4.34-4.20 (m, 2H);  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  147.9, 147.7, 144.0, 143.0, 139.7, 139.0, 136.9, 135.7, 134.7, 132.0, 130.7, 130.0, 129.39(2C), 129.38(2C), 128.5, 128.4, 128.1, 127.9, 127.6, 127.1, 126.6, 126.1, 76.1, 43.6; **HRMS** (ESI-TOF) calculated for  $C_{26}H_{19}Cl_2N_2O_2S_3$   $[M+H]^+$ :  $m/z$  556.9986, found 556.9981.

## Unsuccessful Attempts



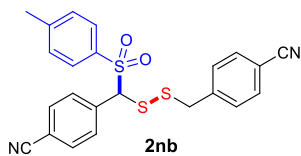
### 1-Benzyl-2-[[[(2-nitrophenyl)sulfonyl](phenyl)methyl]disulfane] **2al**:

Following **GP3** using S-benzyl 2-nitrobenzenesulfonothioate **1al** (154.7 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 6 h and monitored by TLC. The desired product was not observed and starting material remained under optimal reaction conditions.



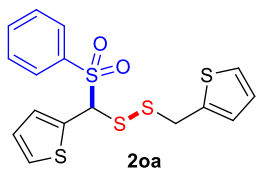
### 1-(2,4-Dichlorobenzyl)-2-[[[(2,4-dichlorophenyl)(phenylsulfonyl)methyl]disulfane] **2ma**:

Following **GP3** using S-2,4-dichloro-benzyl benzenesulfonothioate **1ma** (166.6 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 6 h and monitored by TLC. The desired product was not observed and starting material remained under optimal reaction conditions.



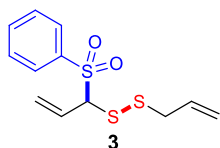
### 4-[[[(4-Cyanobenzyl)disulfanyl](tosyl)methyl]benzonitrile] **2nb**:

Following **GP3** using S-4-cyanobenzyl 4-methylbenzenesulfonothioate **1nb** (151.7 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 6 h and monitored by TLC. The desired product was not observed and starting material remained under optimal reaction conditions.



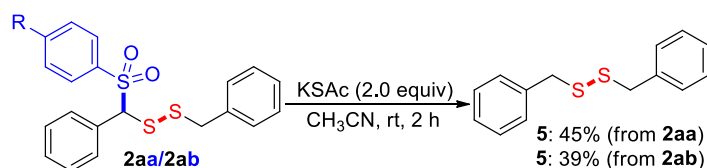
### 2-[[[(Phenylsulfonyl)((thiophen-2-yl)methyl)disulfanyl)methyl]thiophene] **2oa**:

Following **GP3** using S-(thiophen-2-yl)methyl benzenesulfonothioate **1oa** (135.2 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 24 h and monitored by TLC. The isolated product **2oa** was not pure as confirmed by  $^1H$  NMR analysis.



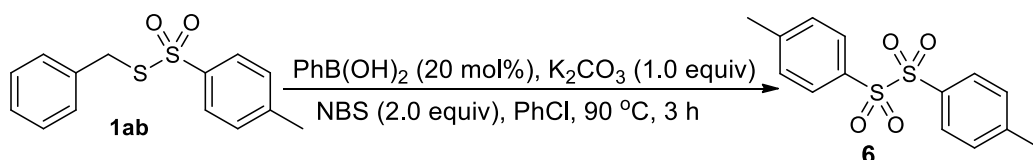
**1-Allyl-2-(1-tosylallyl)disulfane 2pa:** Following **GP3** using *S*-allyl benzenesulfonothioate **1pa** (107.1 mg, 0.5 mmol), phenylboronic acid (12.1 mg, 0.1 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) for 24 h and monitored by TLC. The isolated product **3** was not pure as confirmed by  $^1H$  NMR analysis.

### Synthesis of dibenzyl disulfane (5):



A heat gun-dried round bottom flask was charged with (*S*)-1-benzyl-2-[phenyl(phenylsulfonyl)methyl]disulfane **2aa** (193.0 mg, 0.5 mmol, 1.0 equiv) *or* 1-benzyl-2-[phenyl(tosyl)methyl]disulfane **2ab** (200.3 mg, 0.5 mmol, 1.0 equiv) and potassium thioacetate (KSAc, 114.0 mg, 1.0 mmol, 2 equiv) in acetonitrile solvent (2.5 mL). The reaction mixture was stirred at room temperature for 2 h and monitored by TLC. The mixture was quenched by addition of water (20 mL) followed by extraction with EtOAc (3x30 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous  $Na_2SO_4$  and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with Hexane) to afford dibenzyl disulfane **5** as a brown colour solid (55.1 mg, 45%; 48.0 mg, 39%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35–7.21 (m, 5H), 3.59 (s, 2H). *The title compound known in the literature and the  $^1H$ -NMR data matched those reported.*<sup>10</sup>

### Synthesis of bis(4-methylphenyl)disulfone (6):



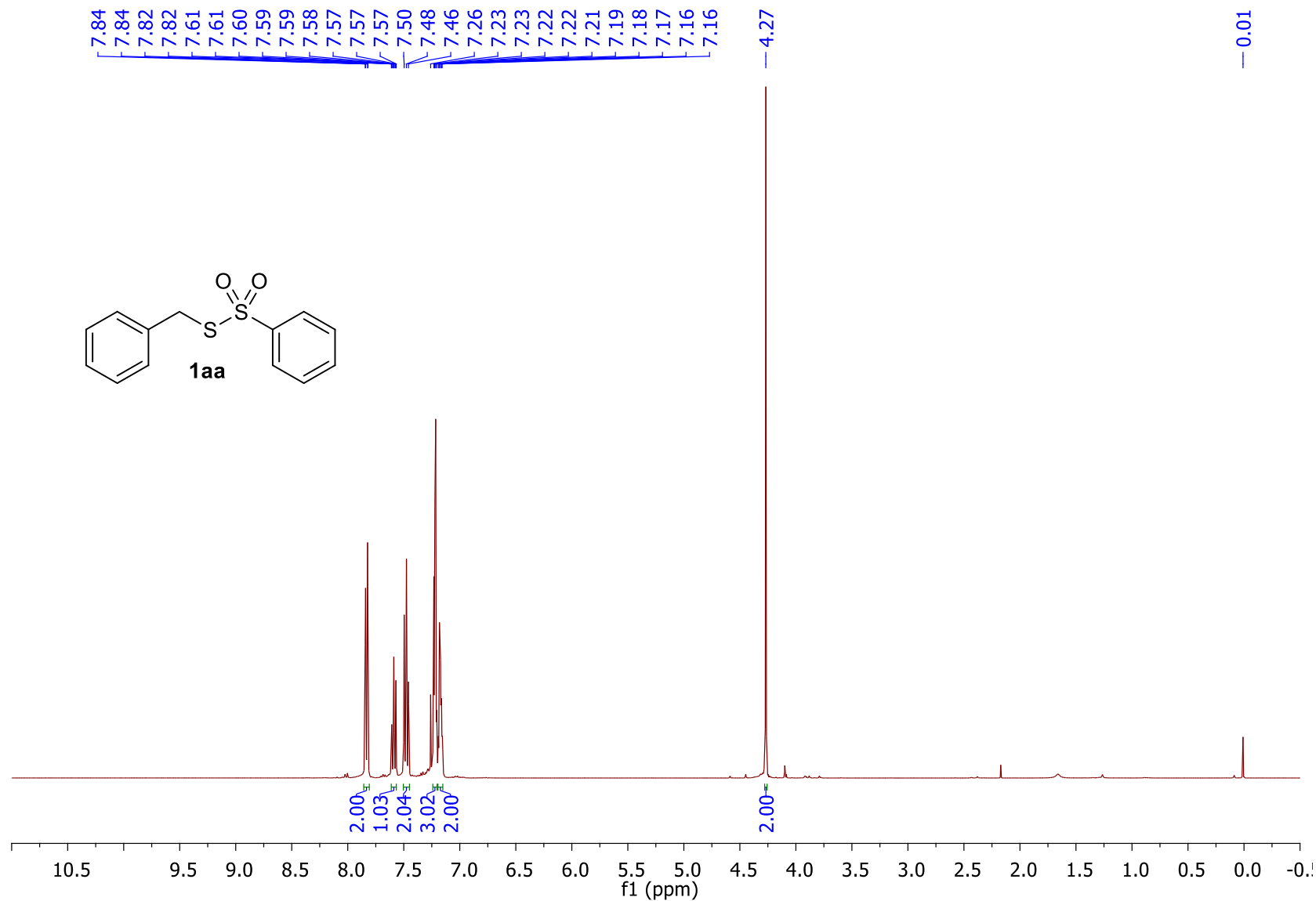
A heat gun-dried round bottom flask was charged *S*-benzyl 4-methylbenzenesulfonothioate **1ab** (139.2 mg, 0.5 mmol, 1.0 equiv), phenylboronic acid (12.1 mg, 0.1 mmol, 20 mol%, 0.2 equiv), NBS (71.2 mg, 1 mmol, 2 equiv) and  $K_2CO_3$  (69.1 mg, 0.5 mmol, 1 equiv) in chlorobenzene (2.5 mL). The reaction mixture was stirred at 90 °C for 3 h and monitored by TLC. The mixture was quenched by addition of water (20 mL) followed by extraction with EtOAc (3x30 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous  $Na_2SO_4$  and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 20% ethyl acetate/petether) to afford title product **6** as a white solid (60.5 mg, 78%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.89 (d,  $J$  = 8.5 Hz, 4H), 7.40 (d,  $J$  = 8.1 Hz, 4H), 2.49 (s, 6H). *The title compound known in the literature and the  $^1H$ -NMR data matched those reported.*<sup>11</sup>

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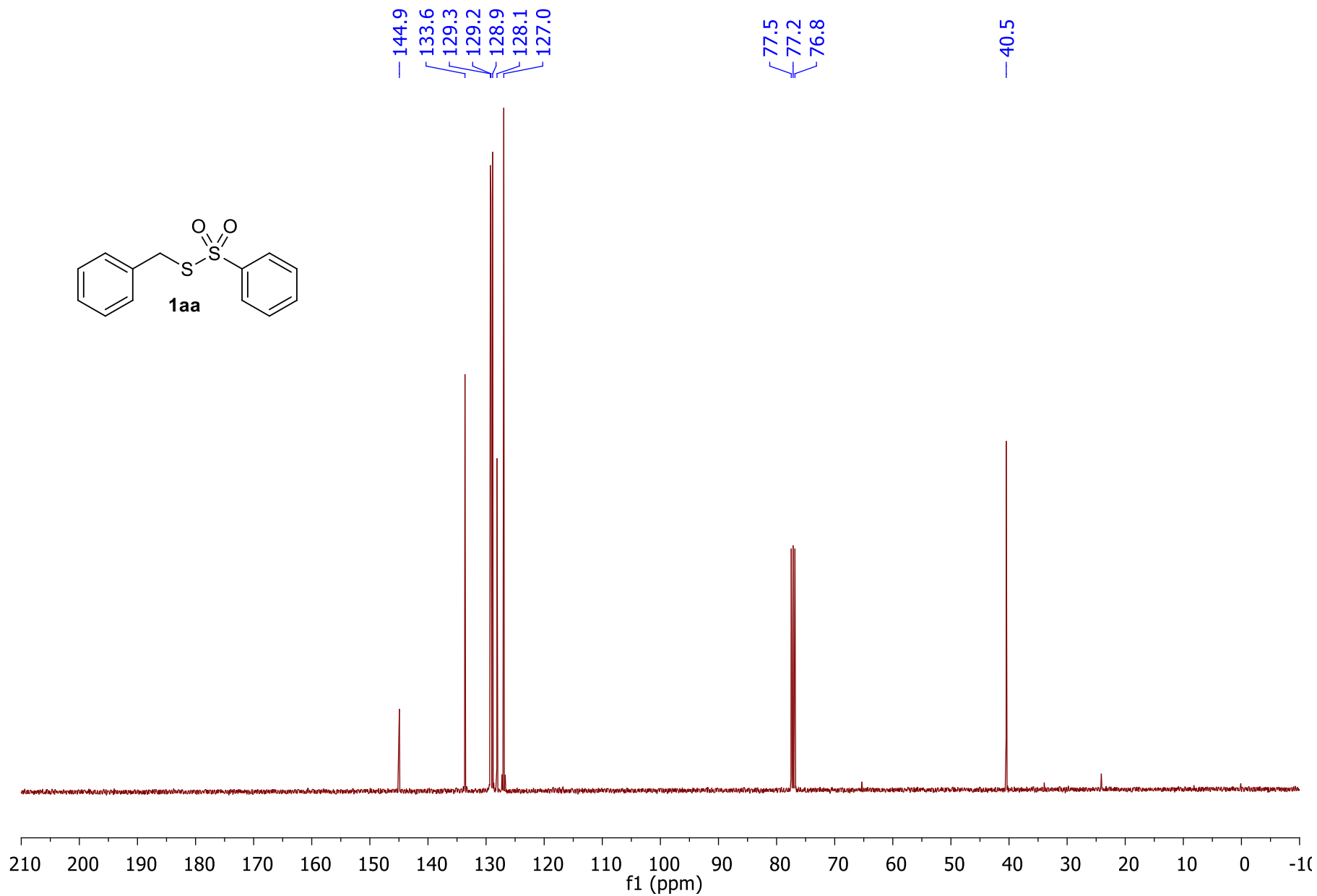
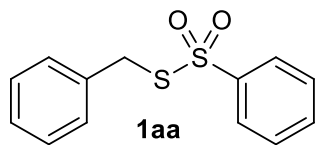
## $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Starting Materials

(Note: Common laboratory solvents as trace impurities, peaks at  $\delta$  1.25 & 1.58 refers to grease and moisture respectively in a  $^1\text{H}$  NMR in  $\text{CDCl}_3$ . For  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ , a peak at  $\delta$  29.7 represents to grease; Ref. H. E. Gottlie, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, **1997**, 62, 7512).

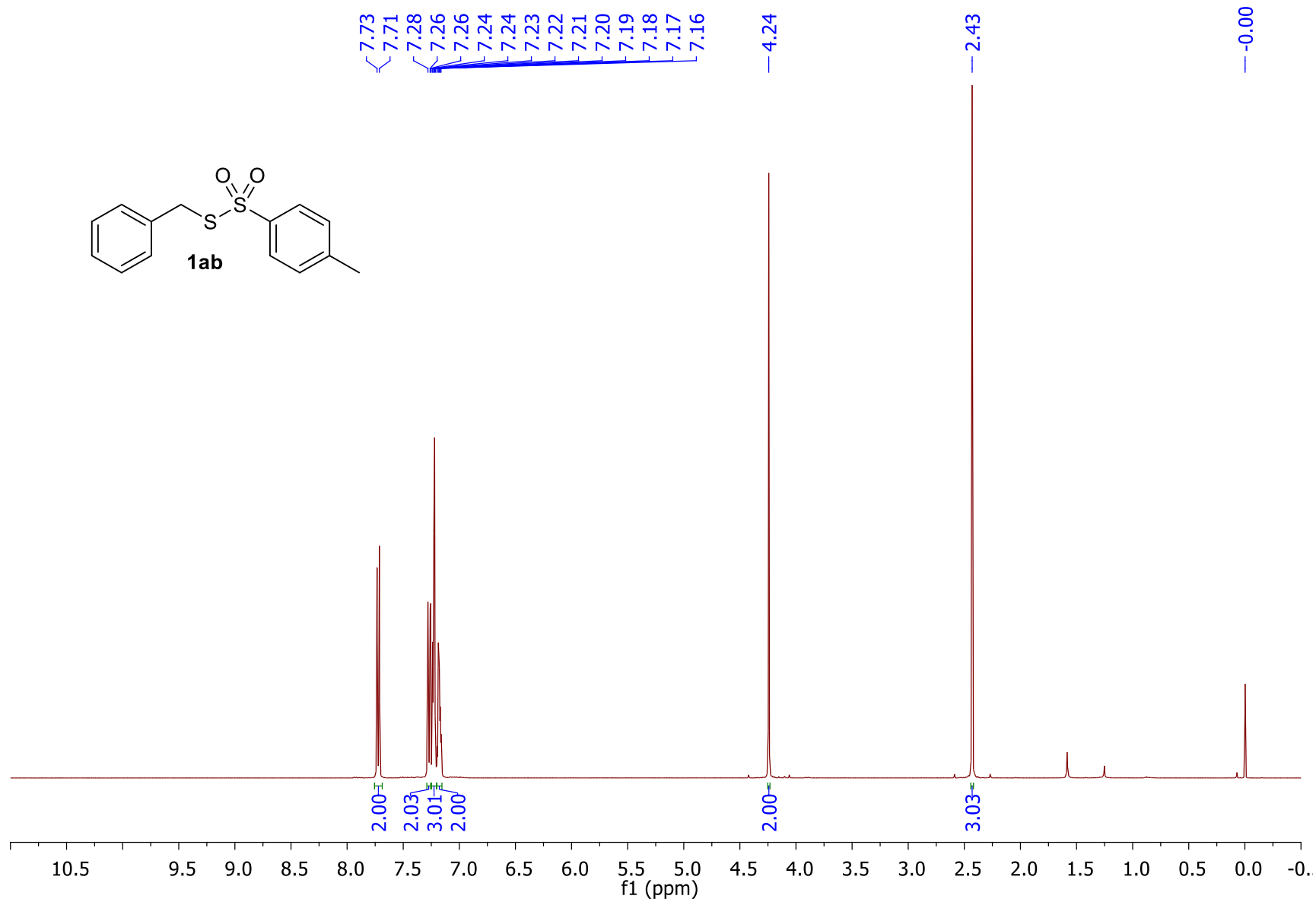




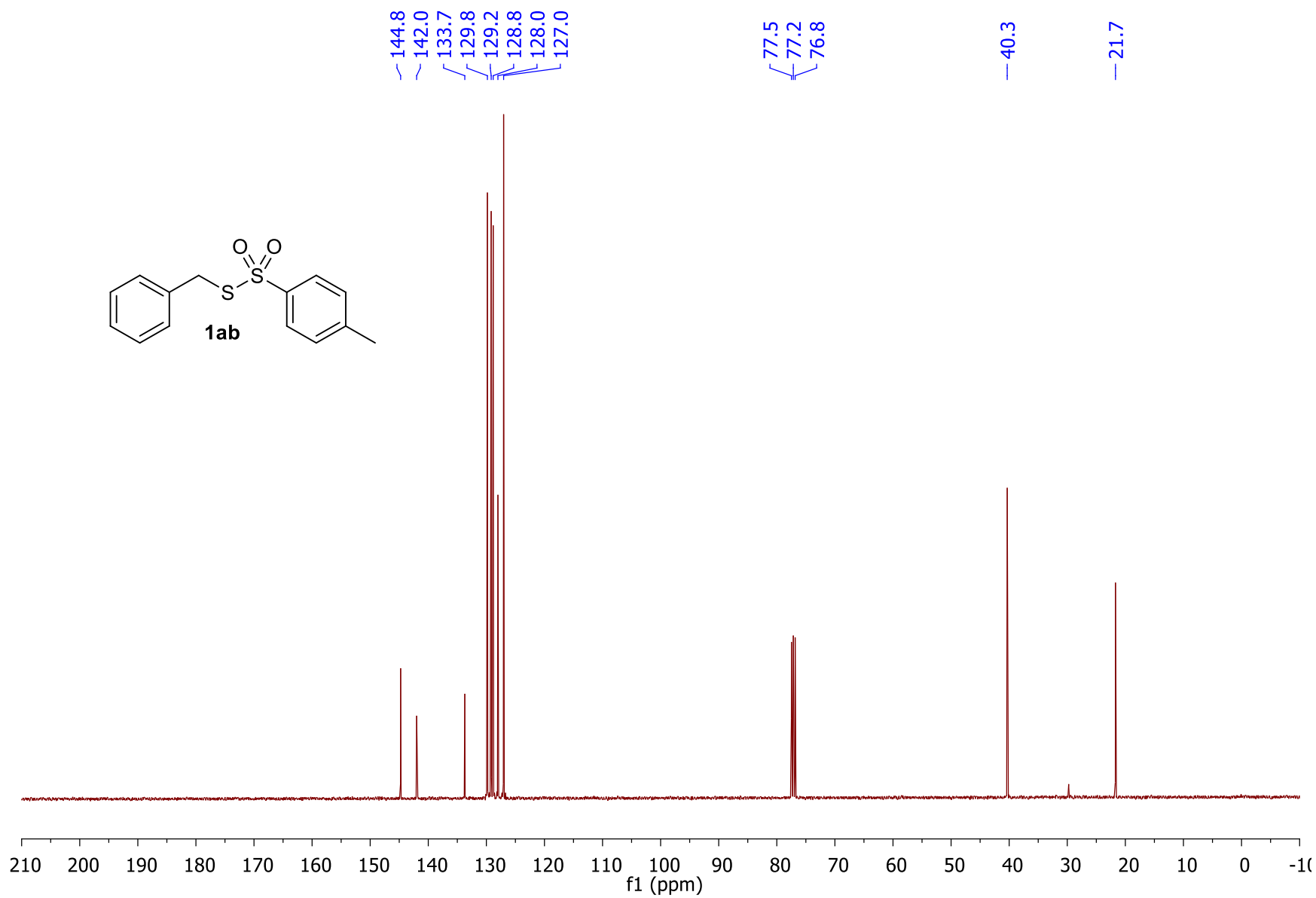
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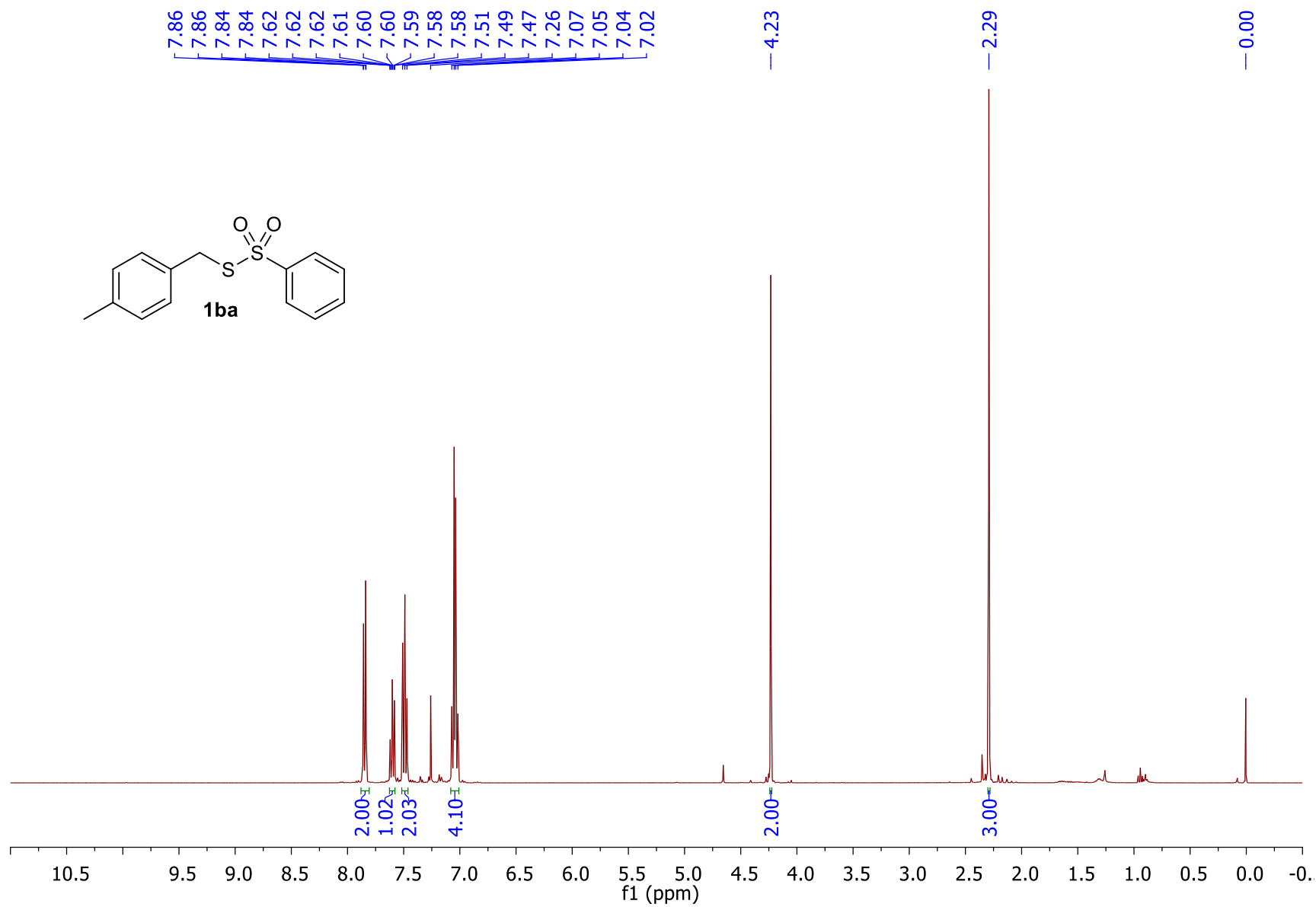
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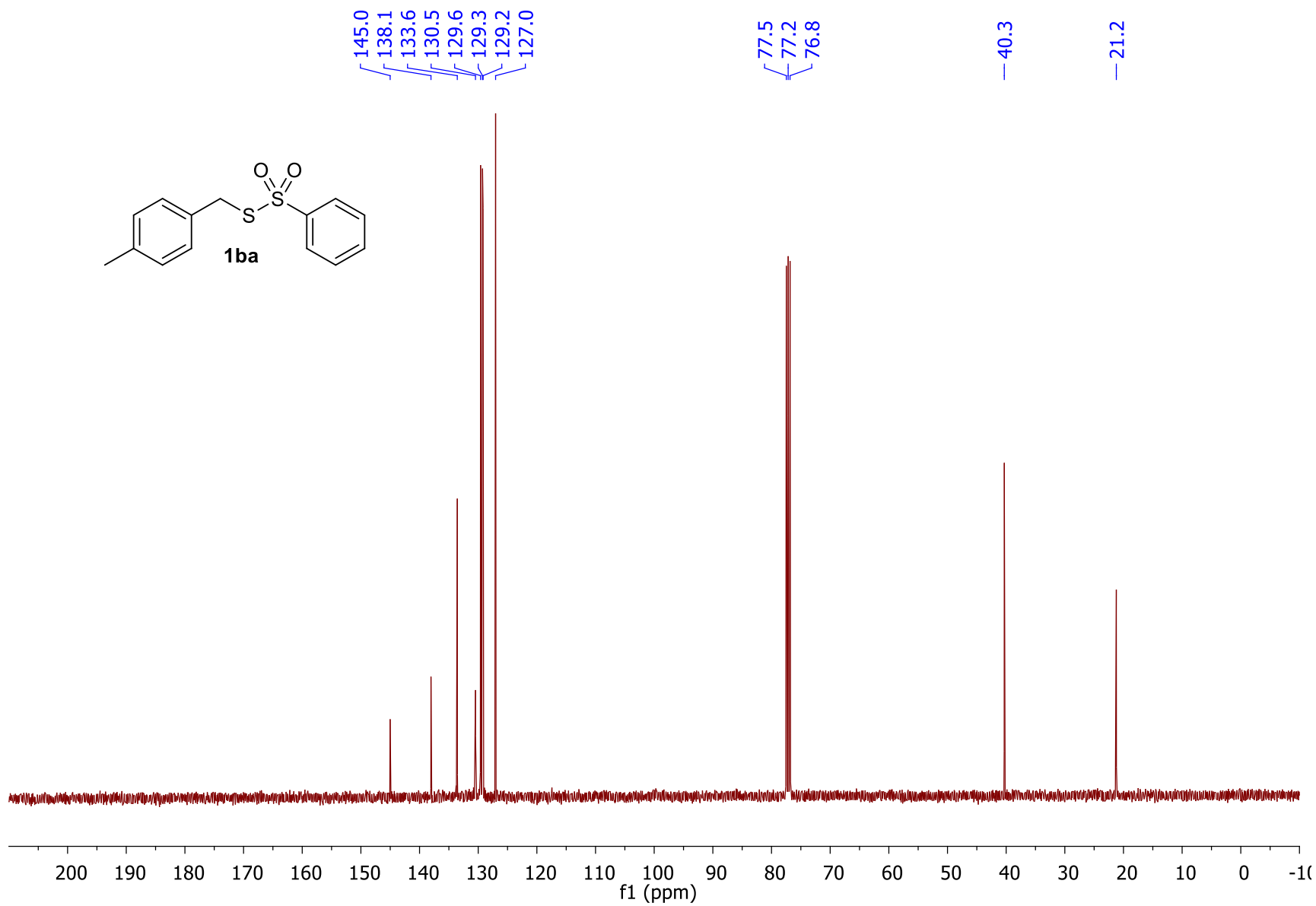
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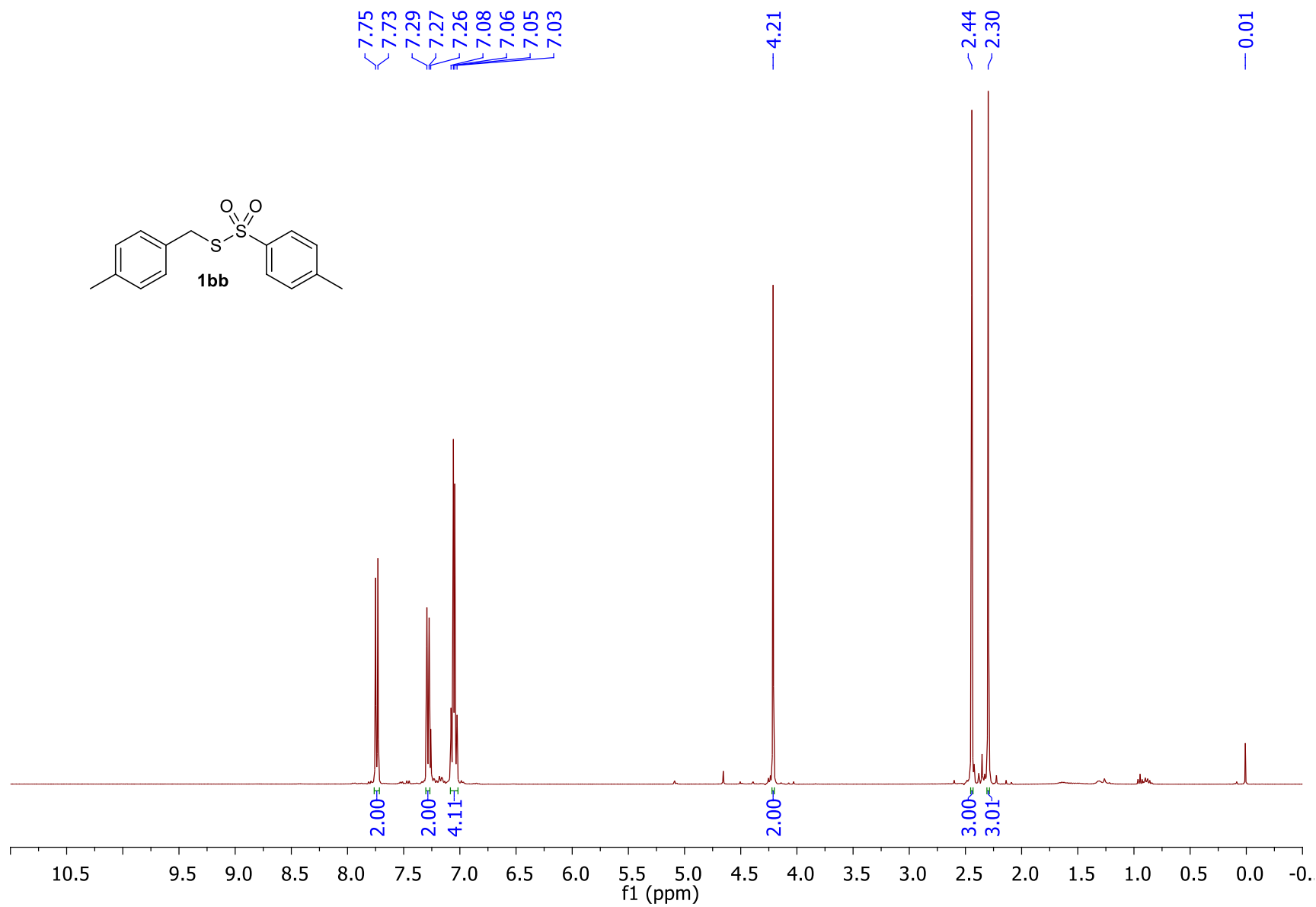
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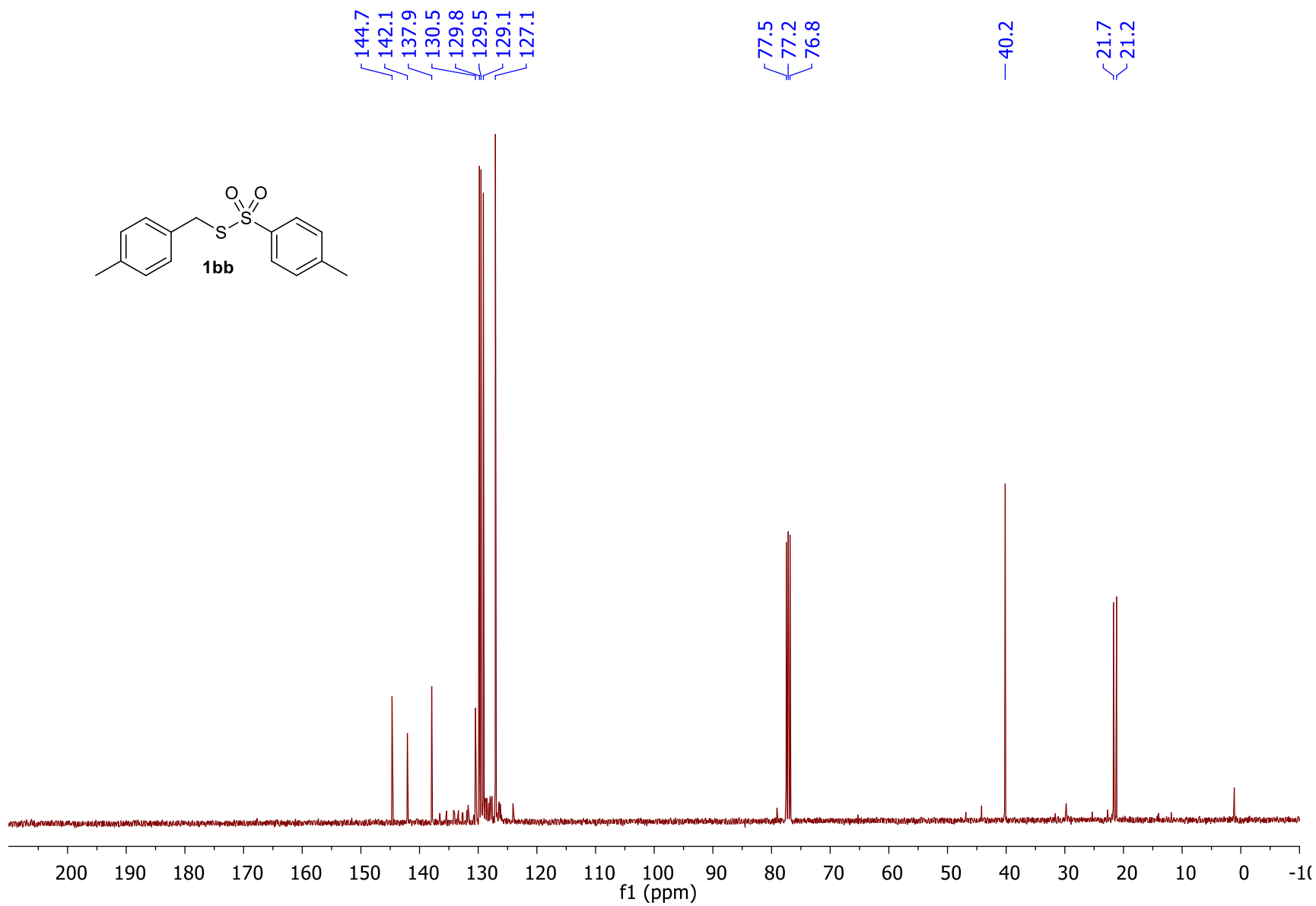
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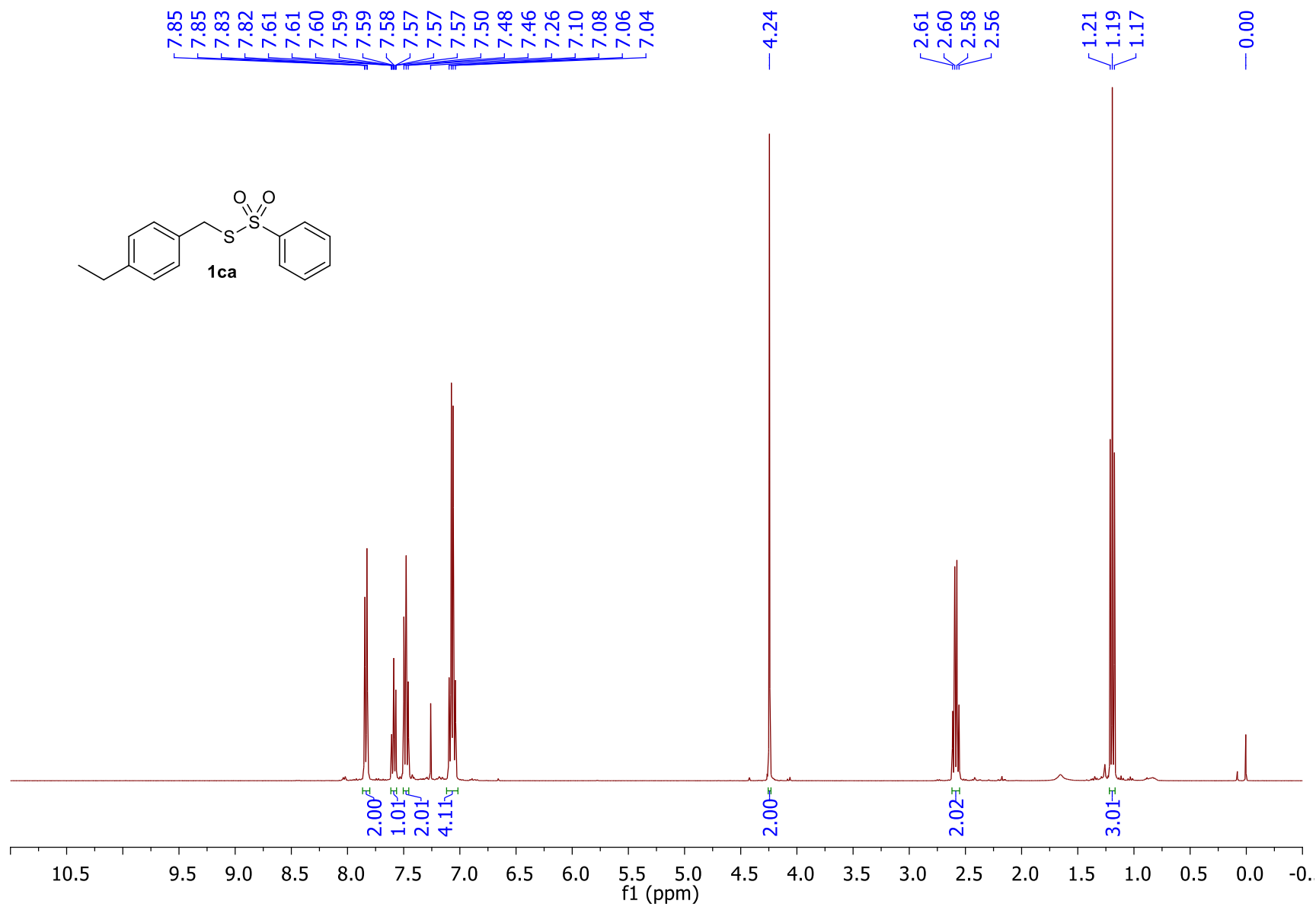
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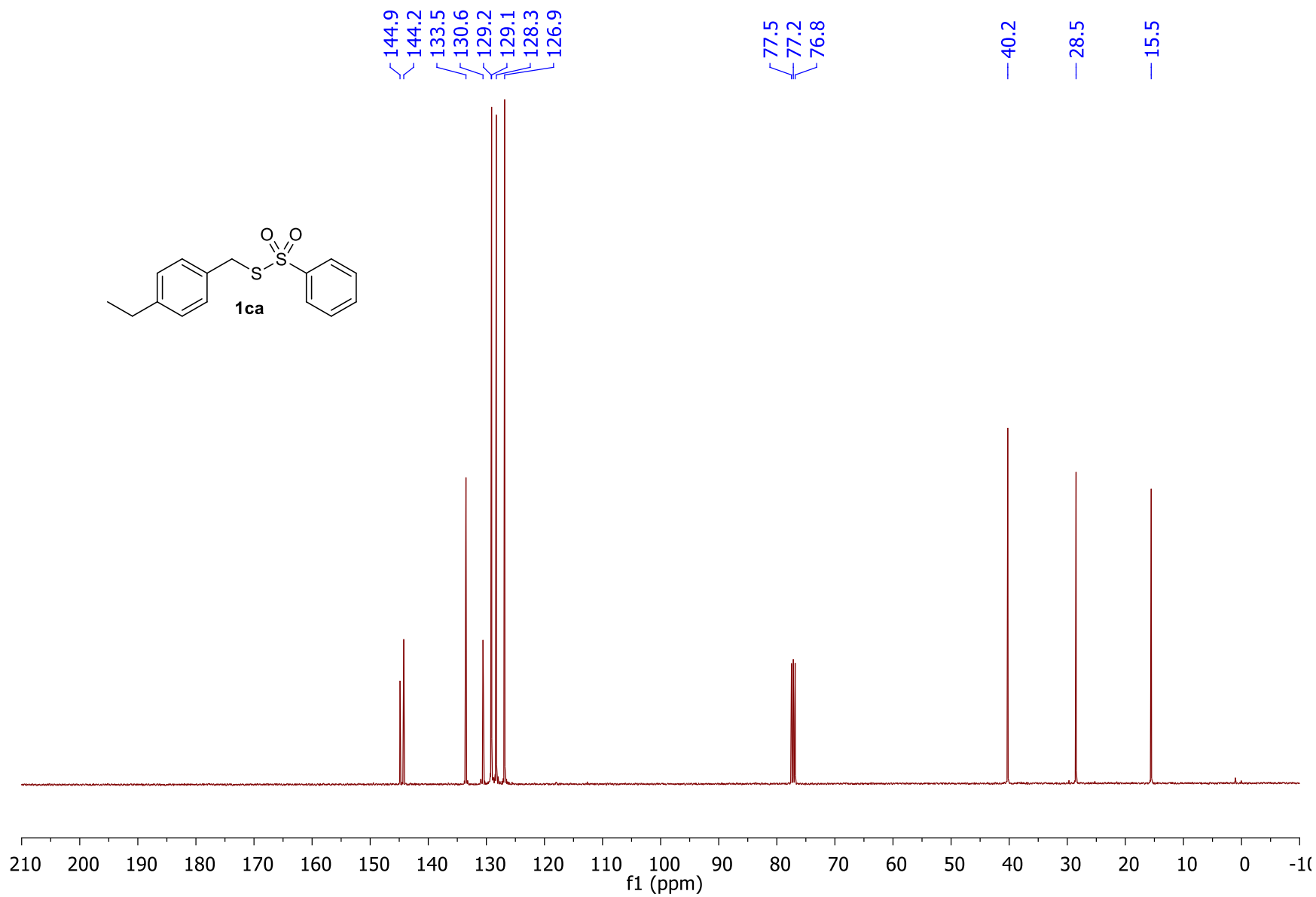


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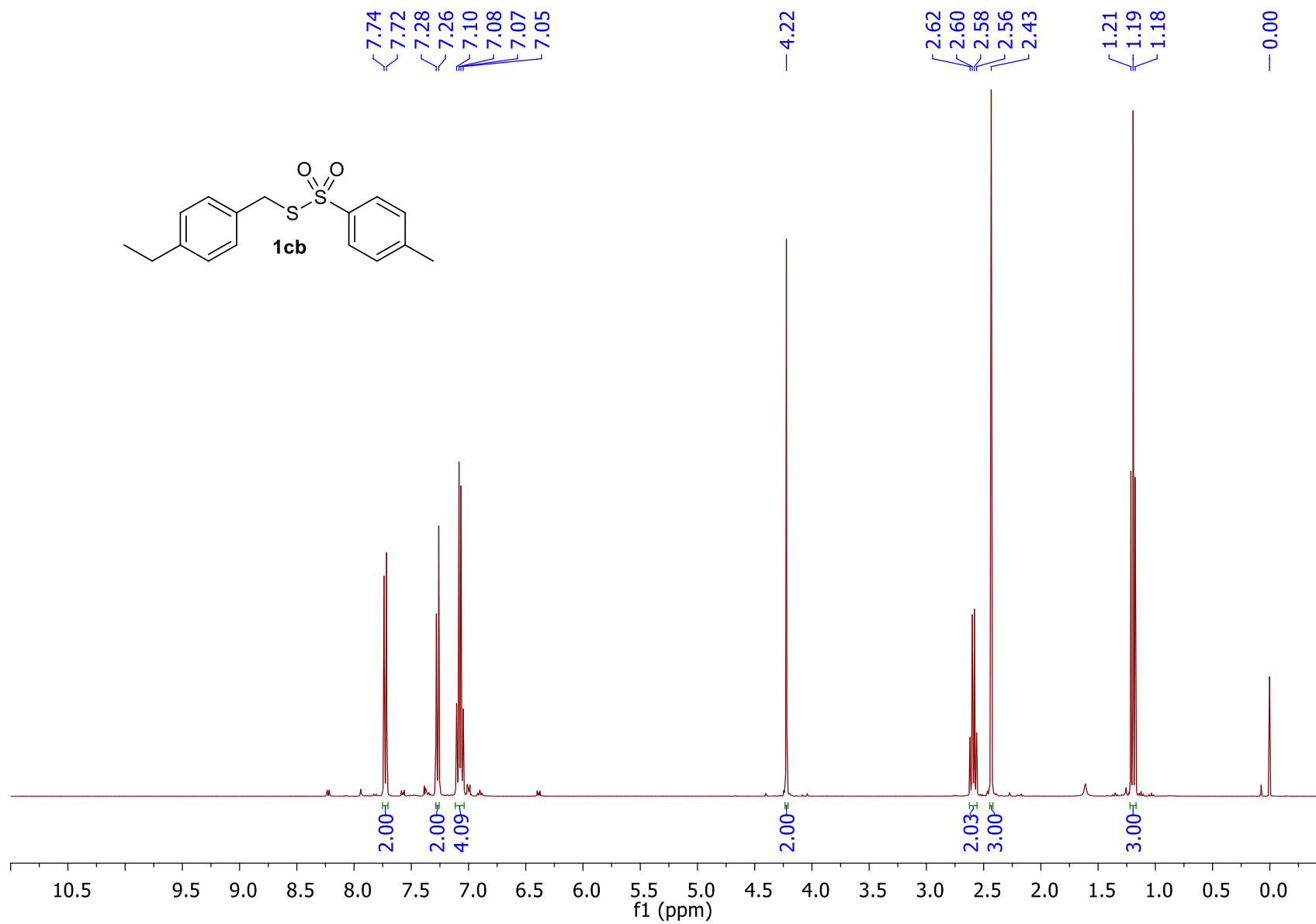




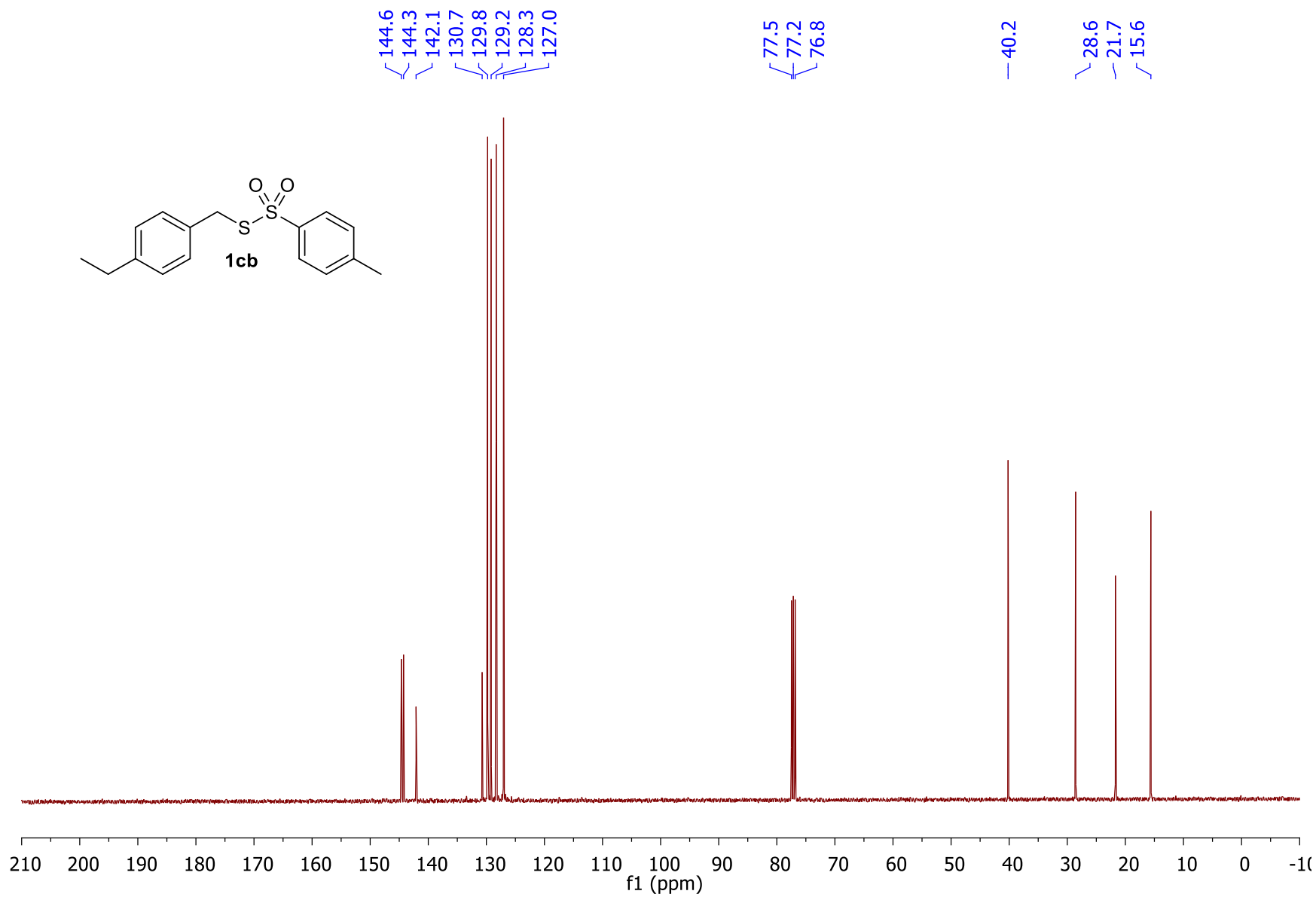
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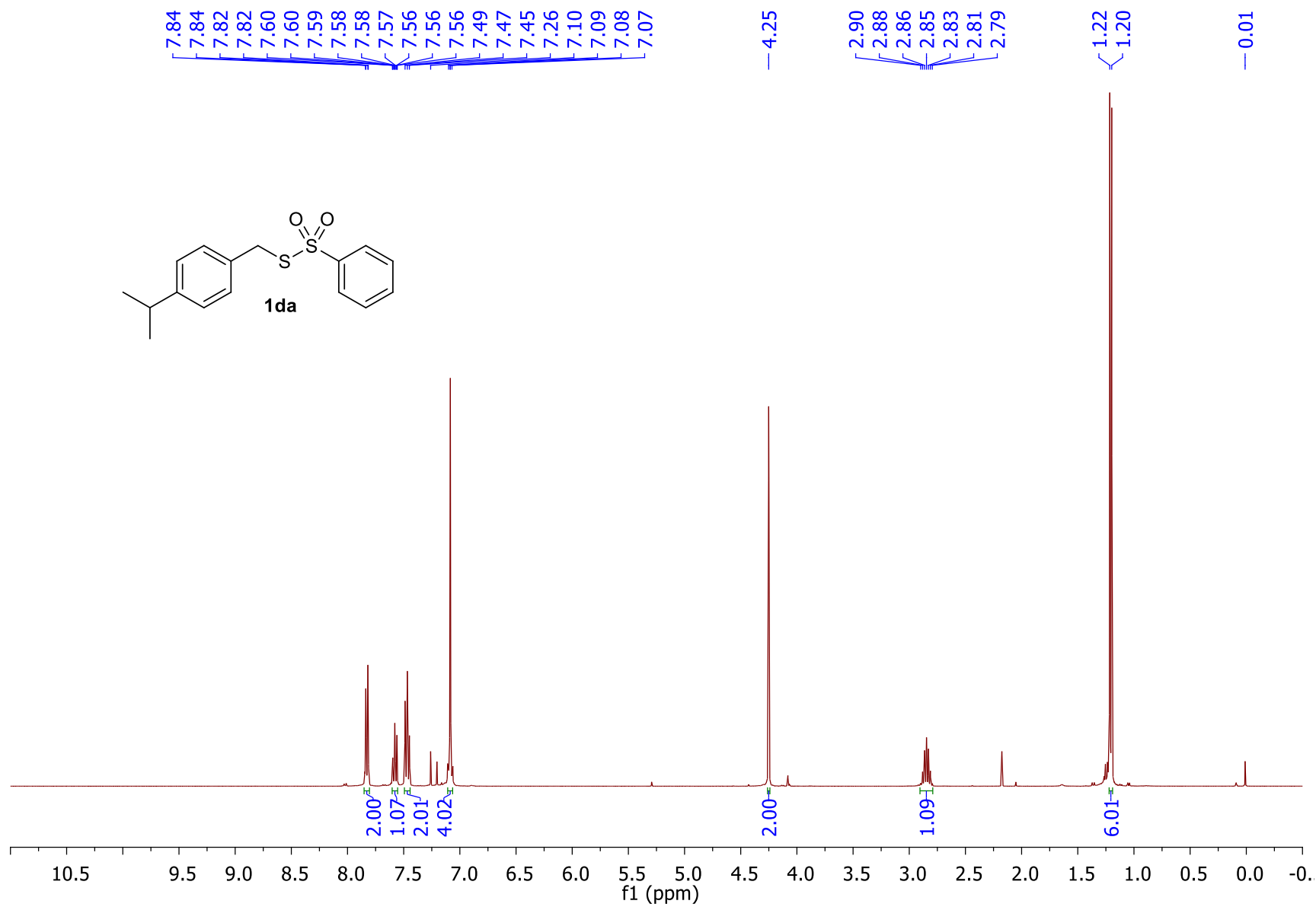
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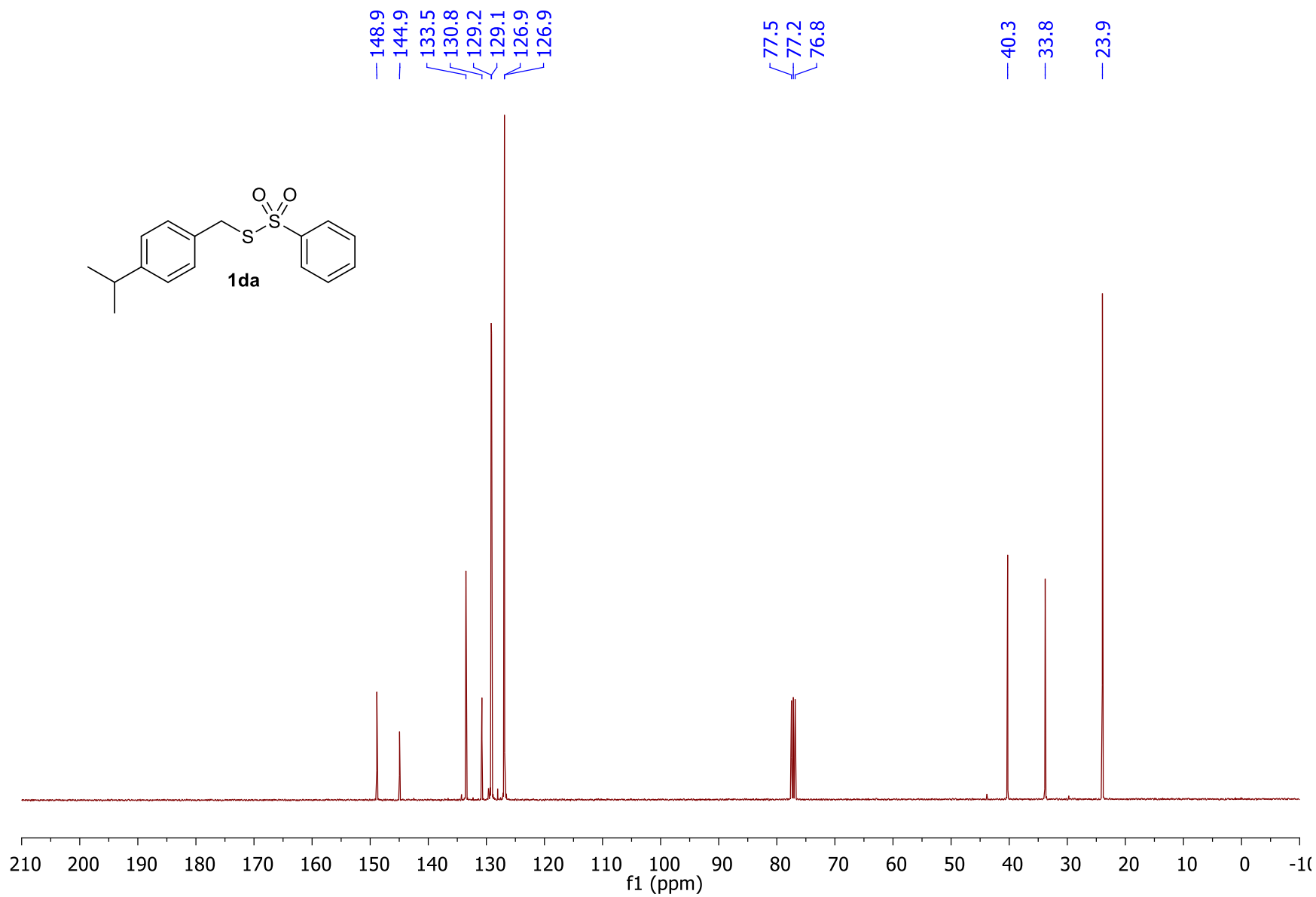
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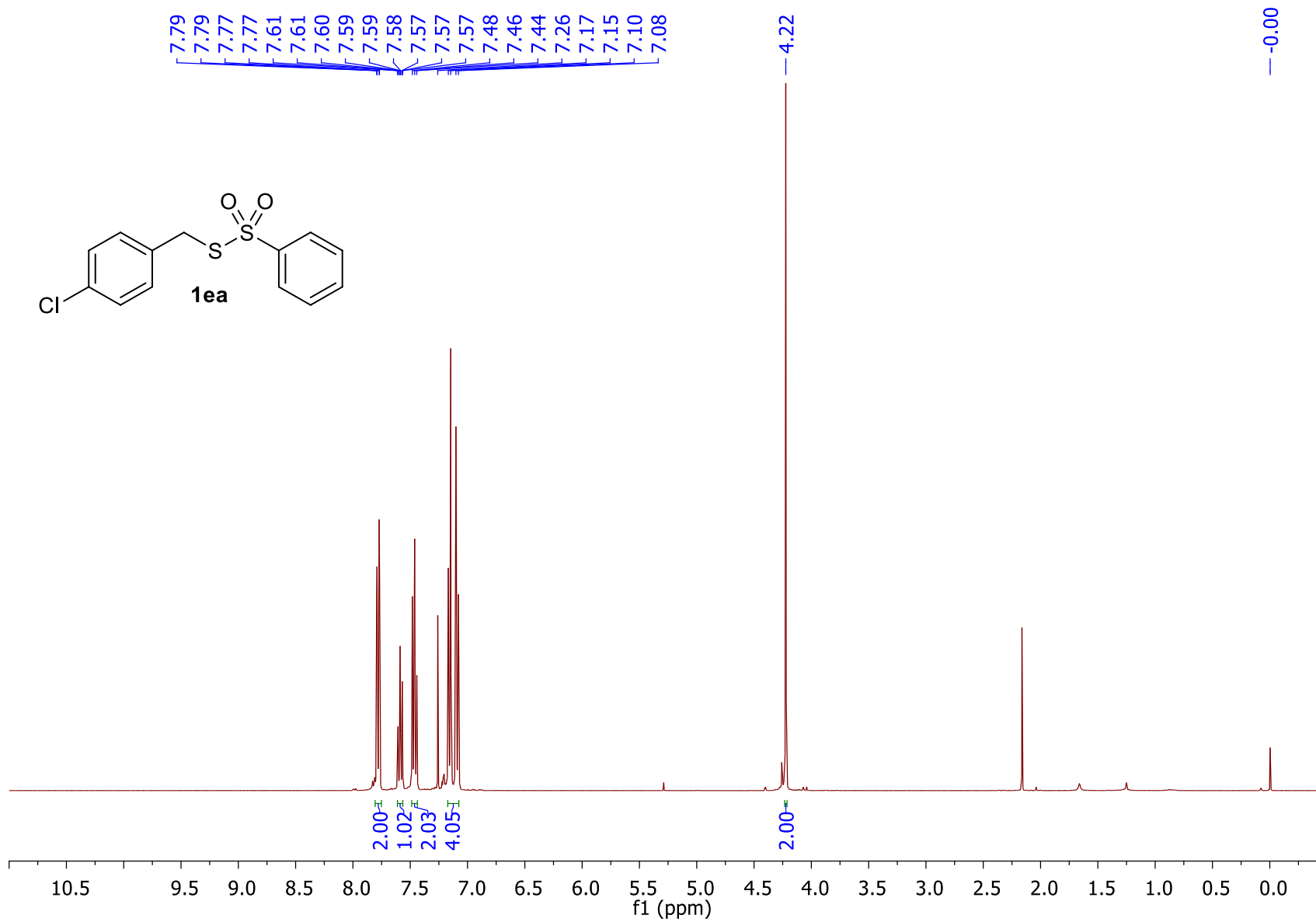
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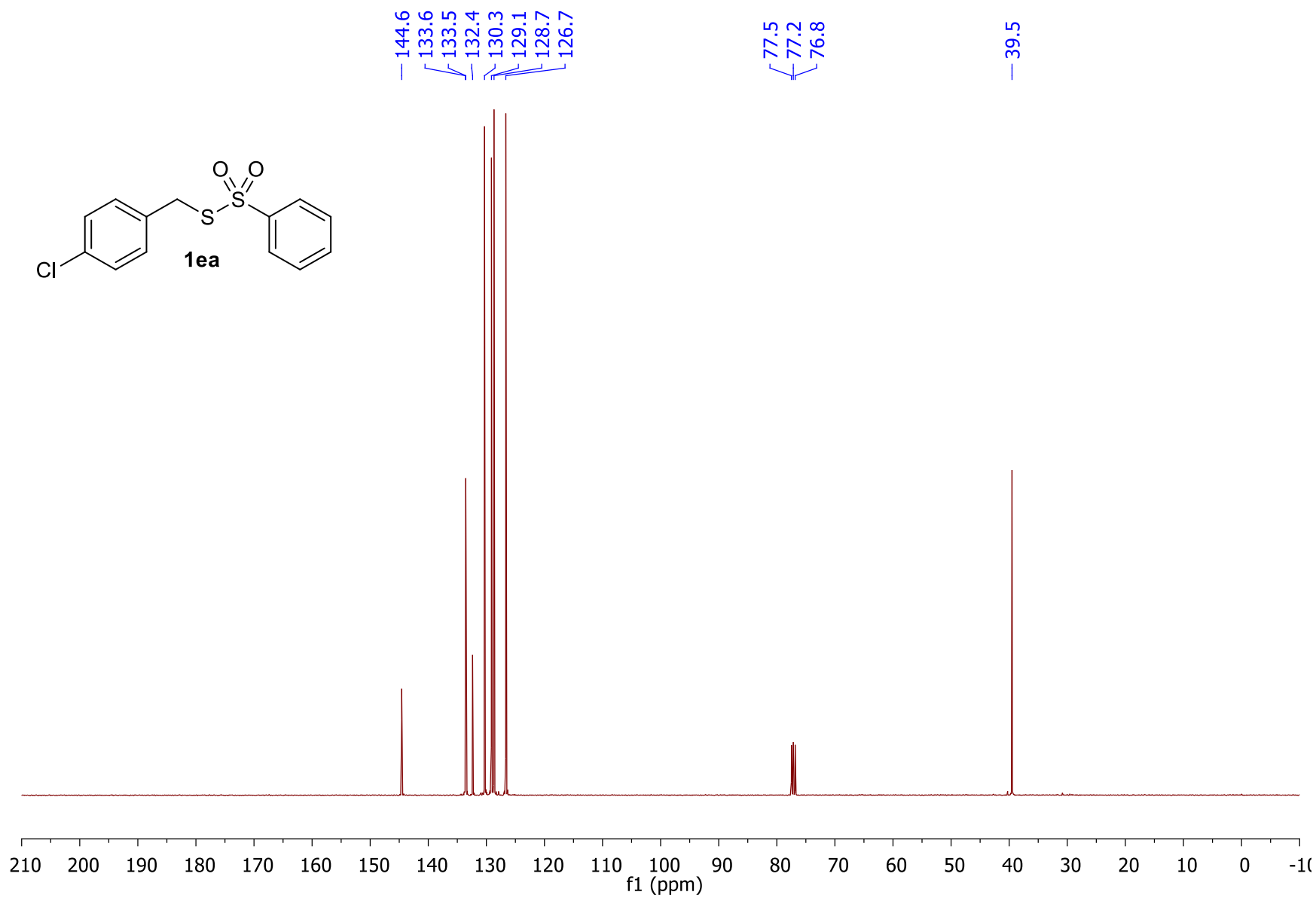
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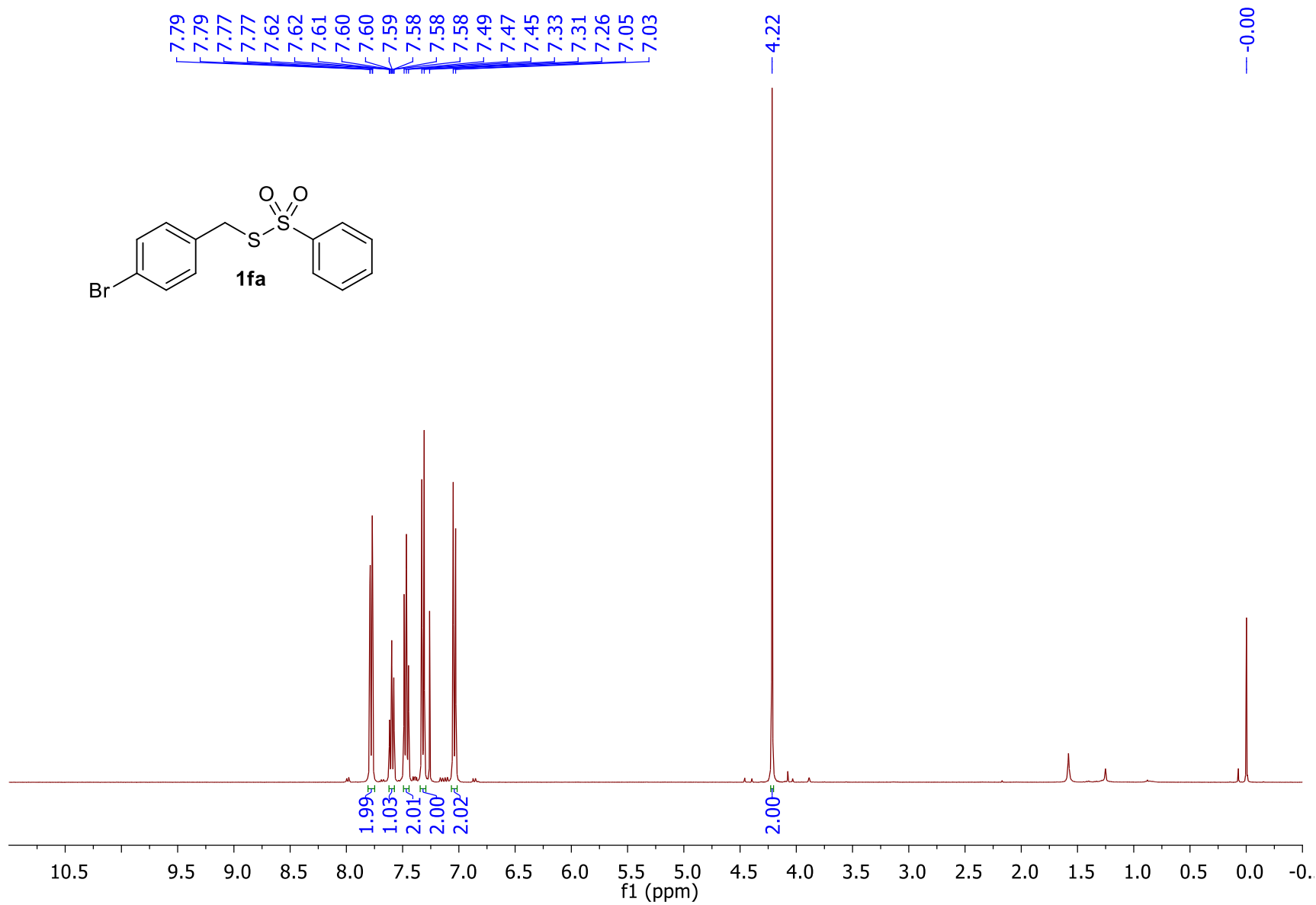
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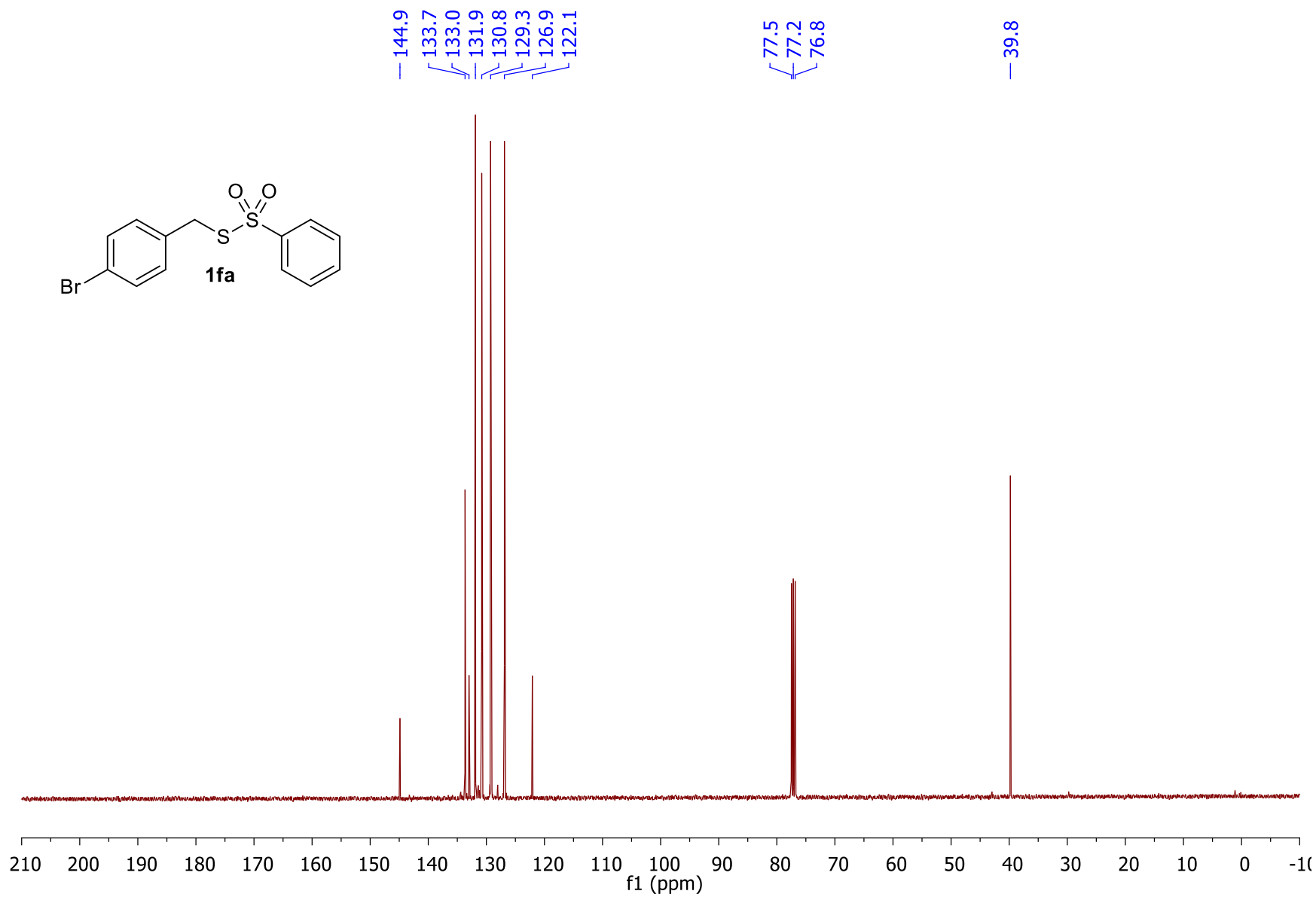


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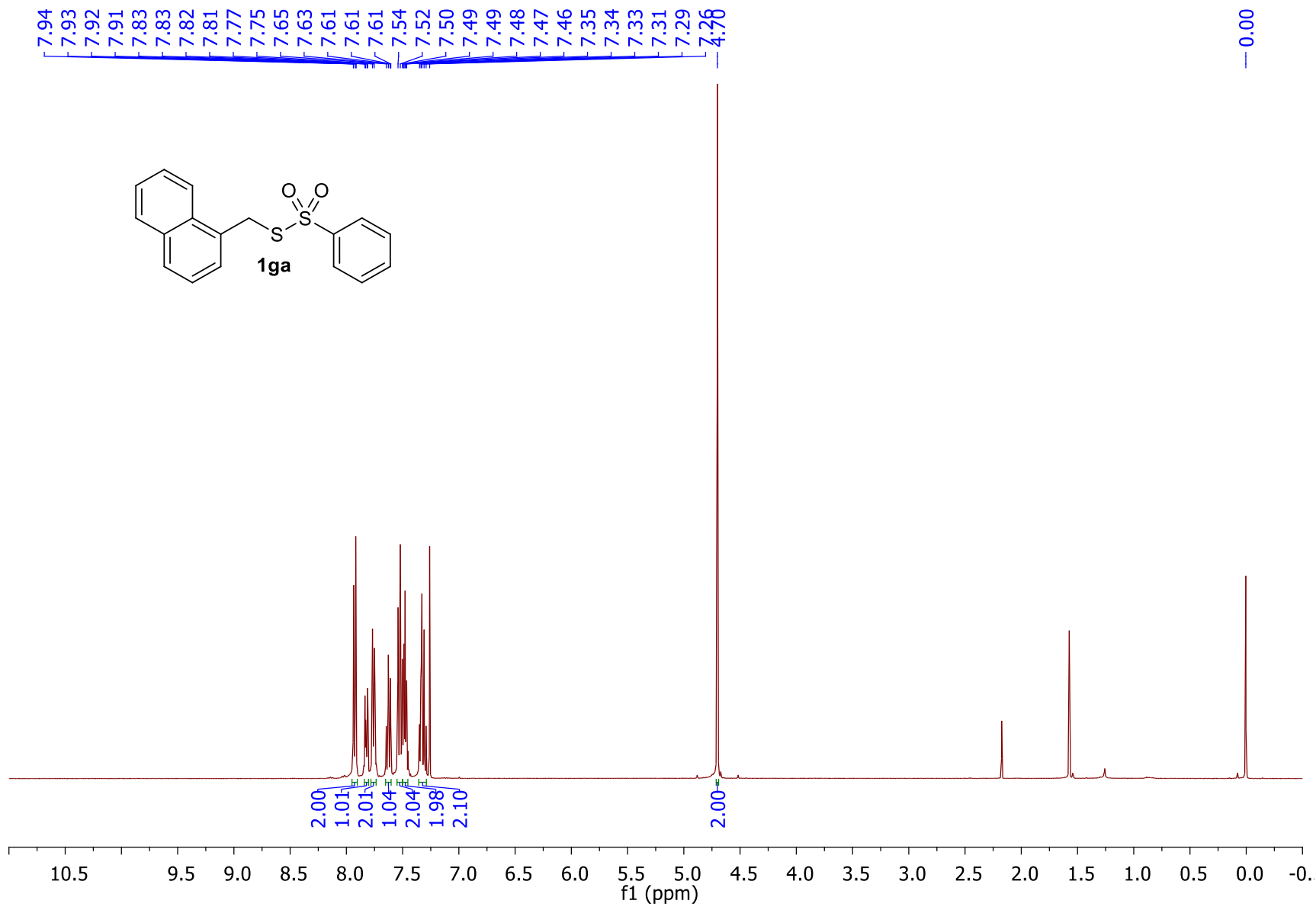




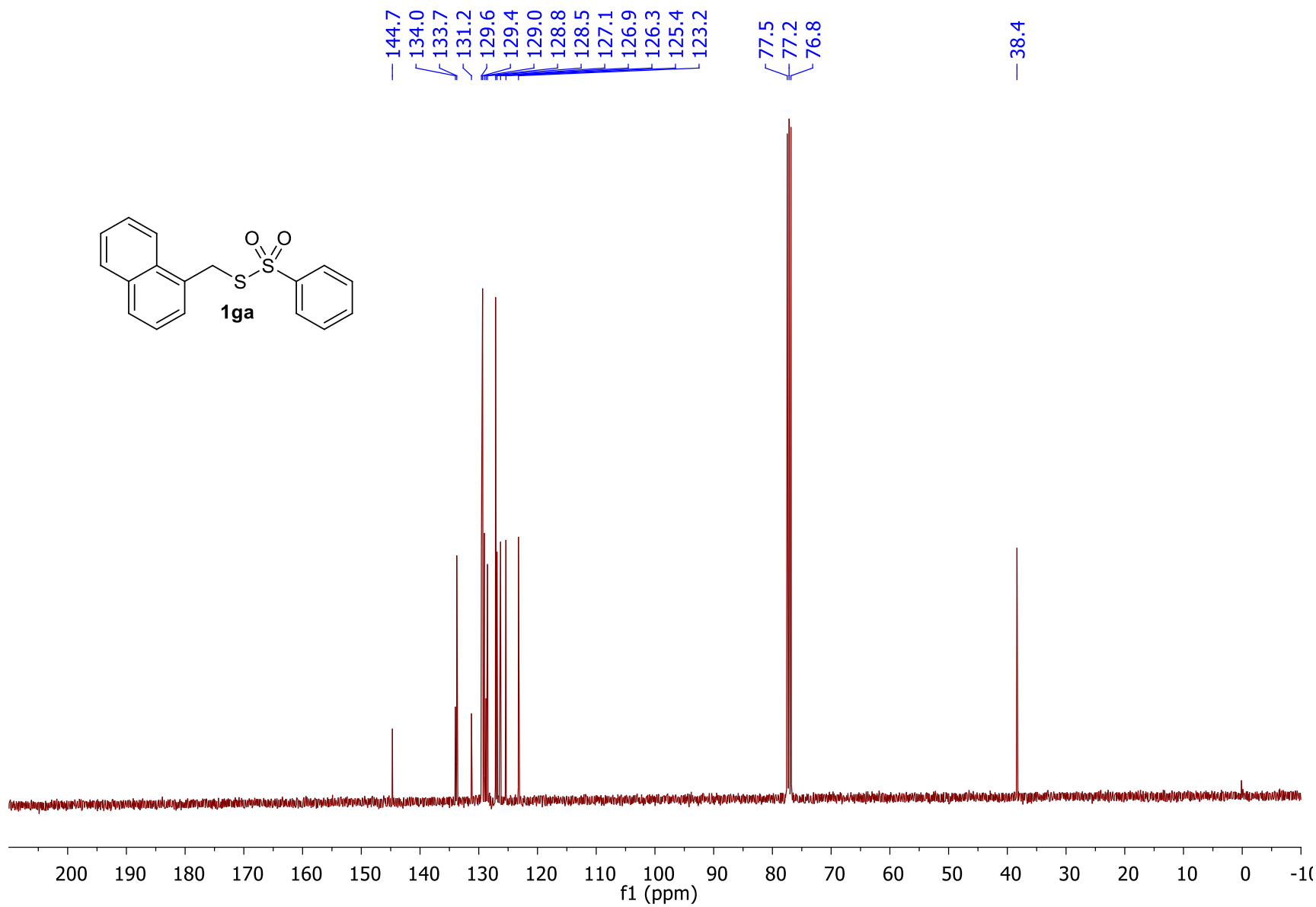
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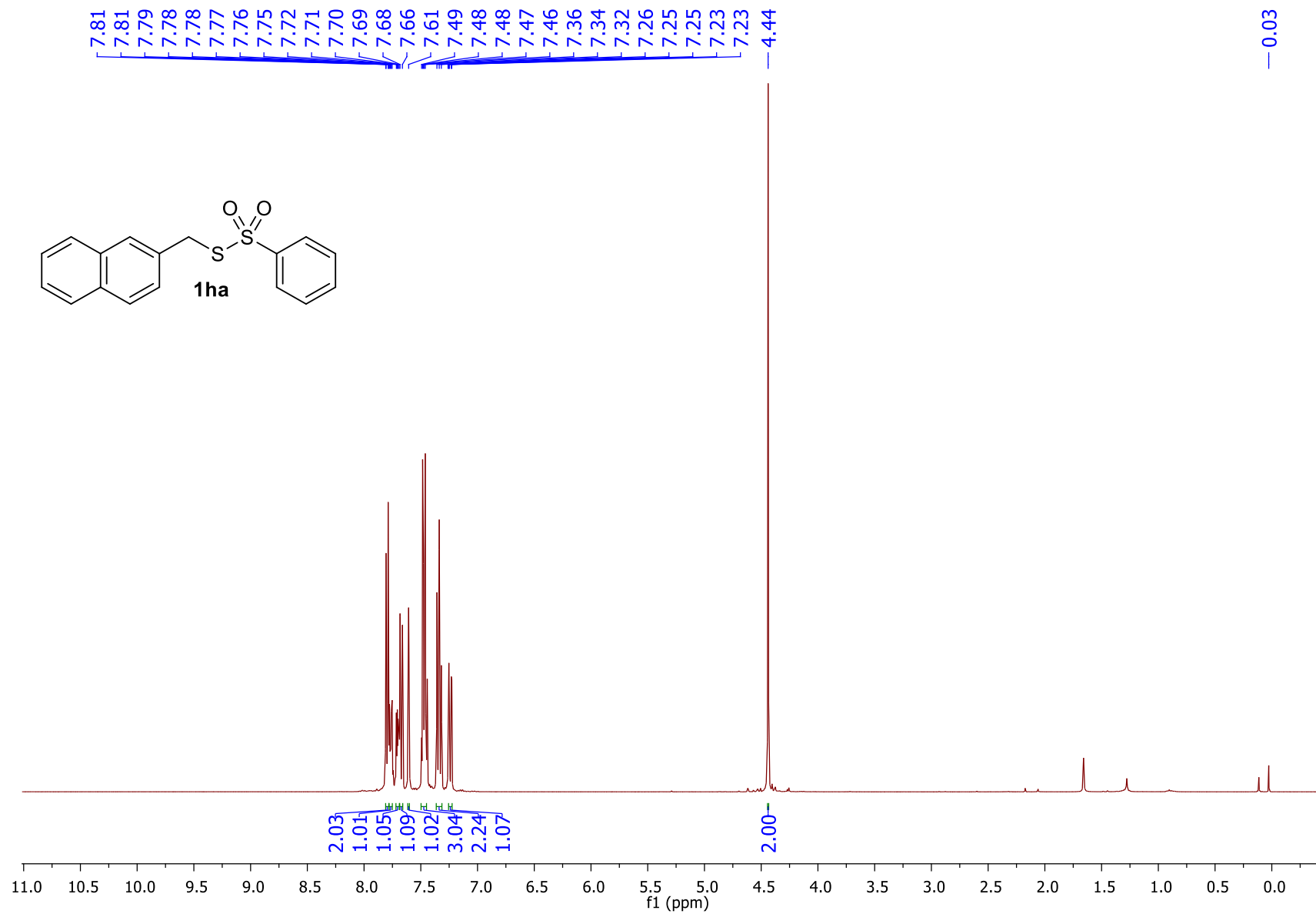
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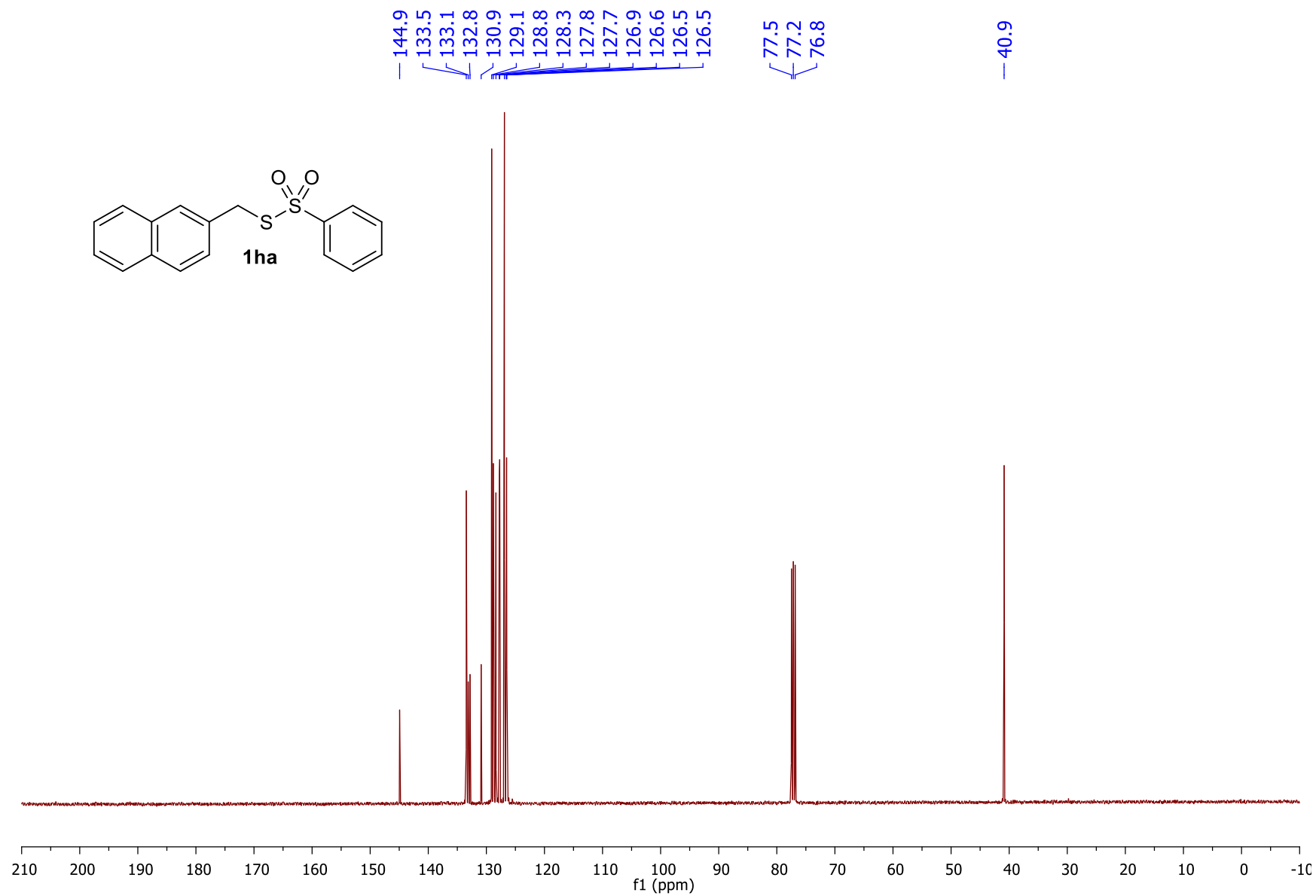
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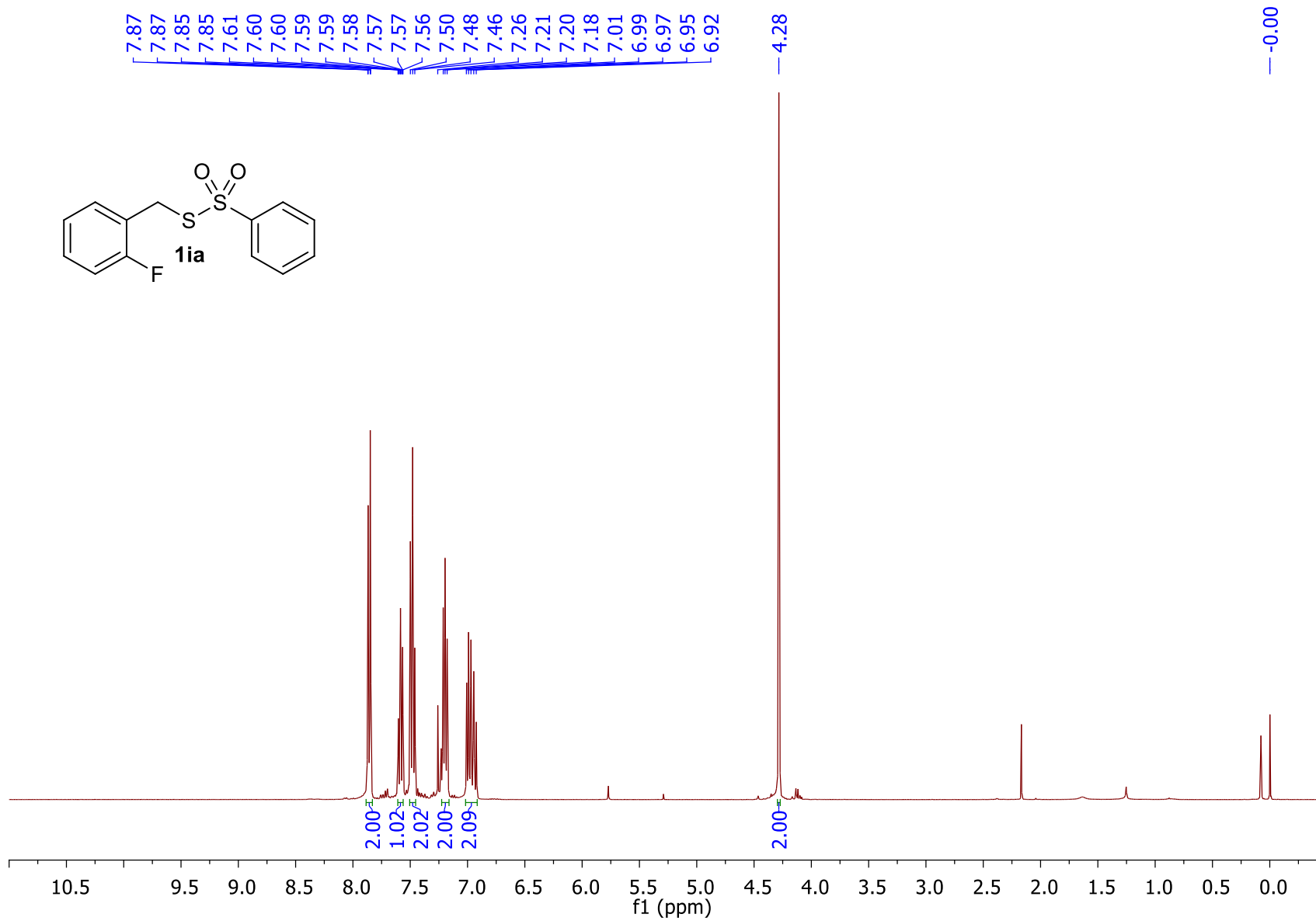
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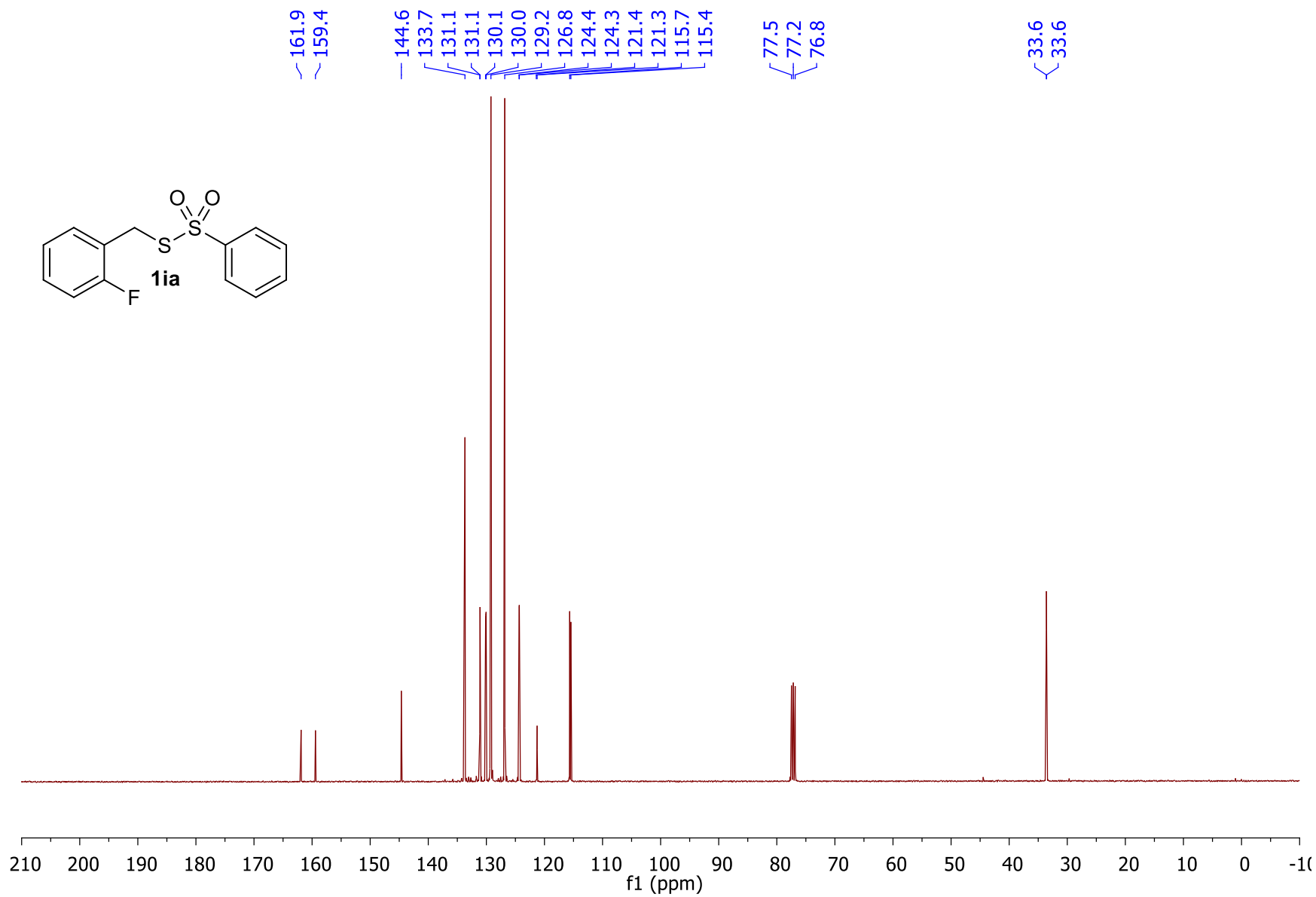
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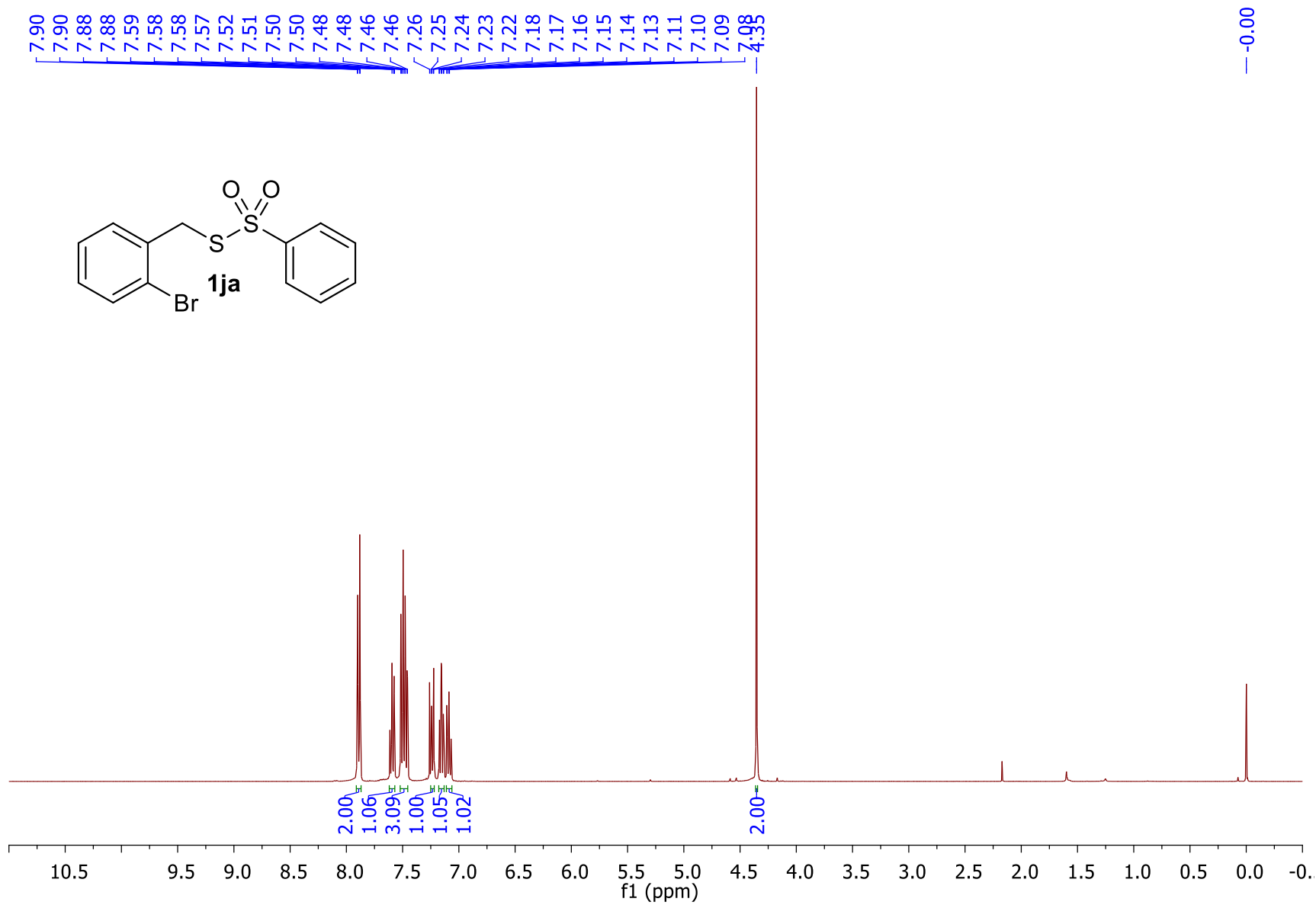
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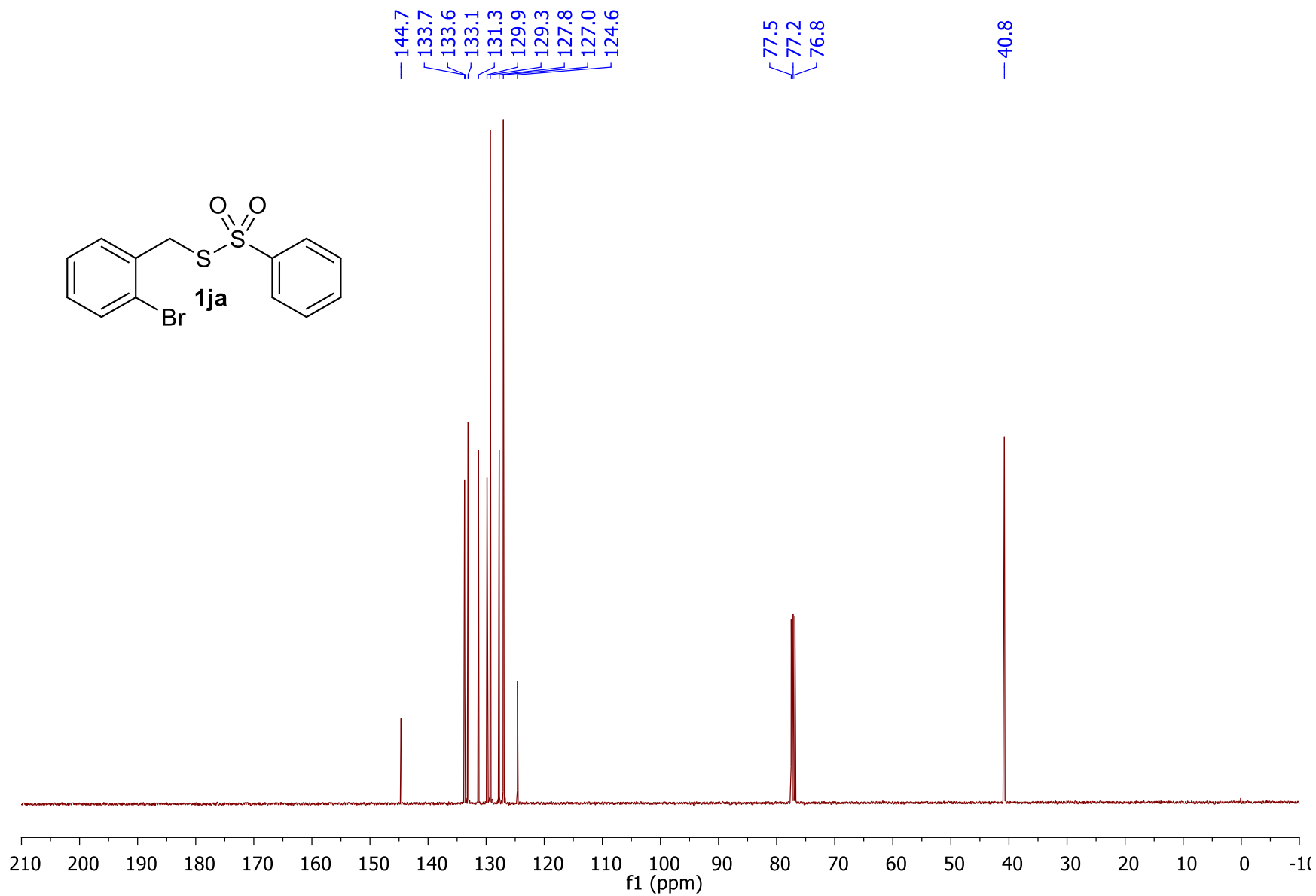
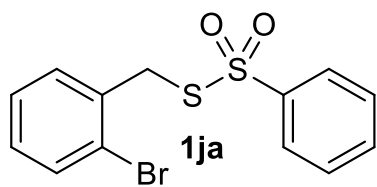


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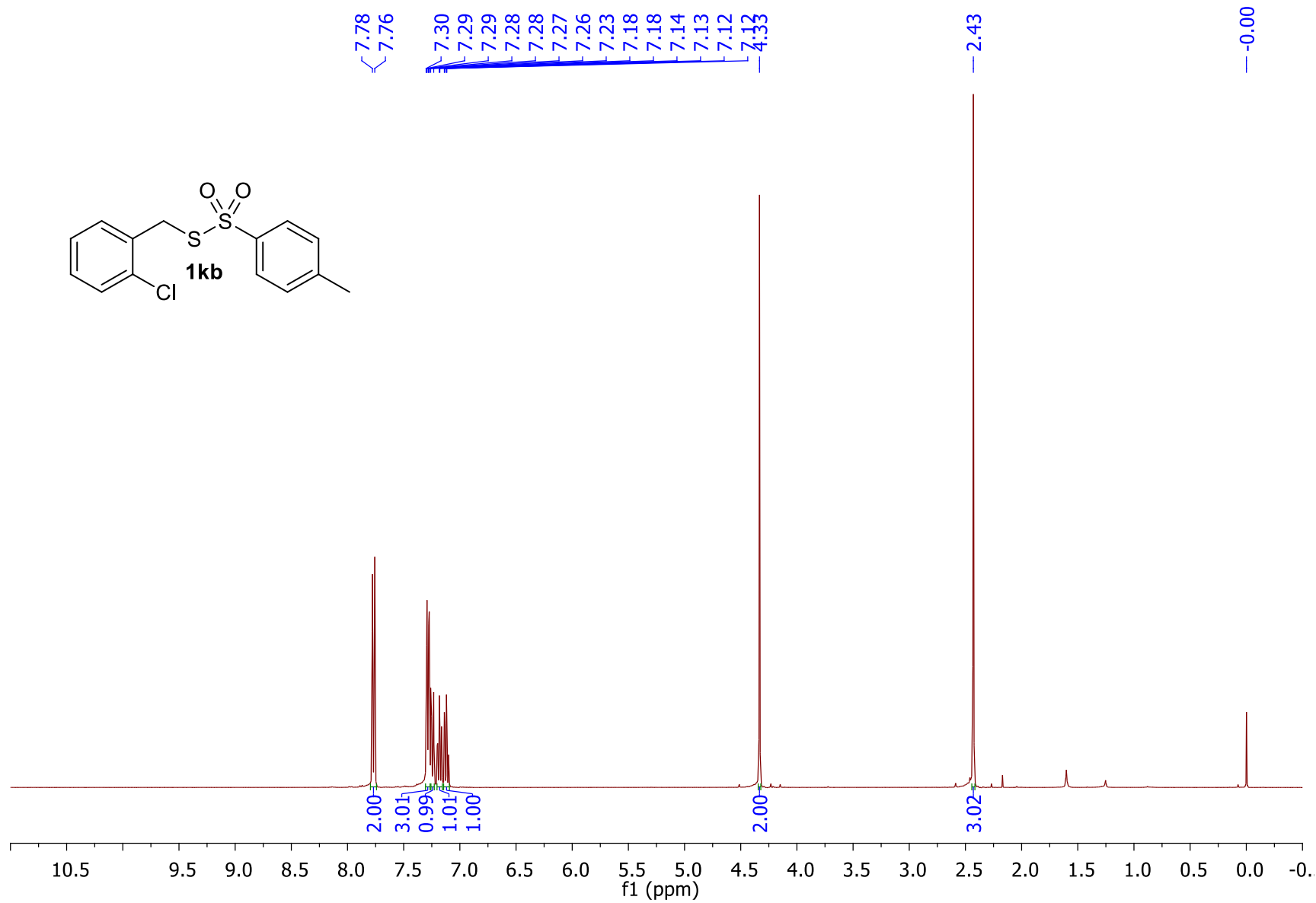




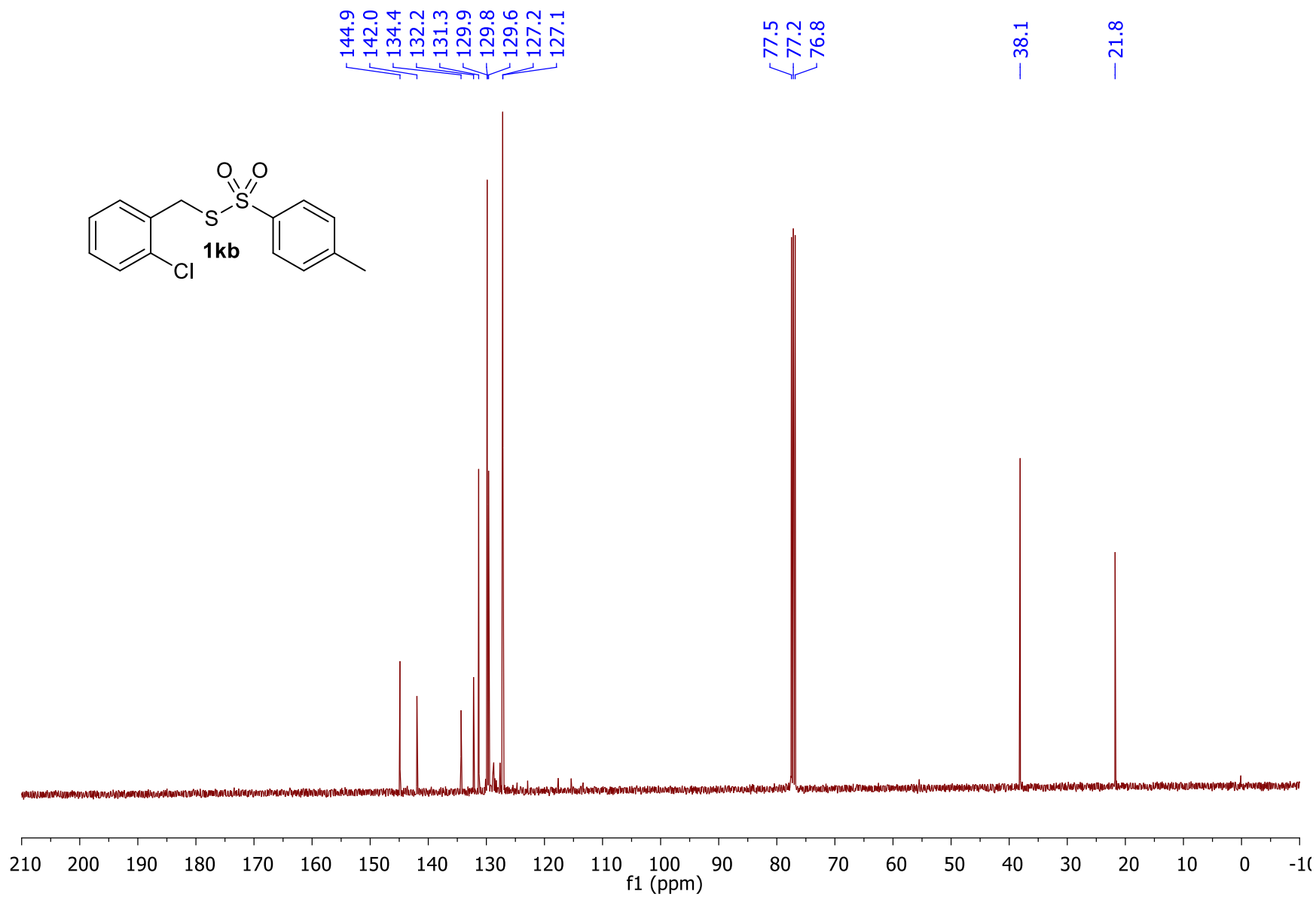
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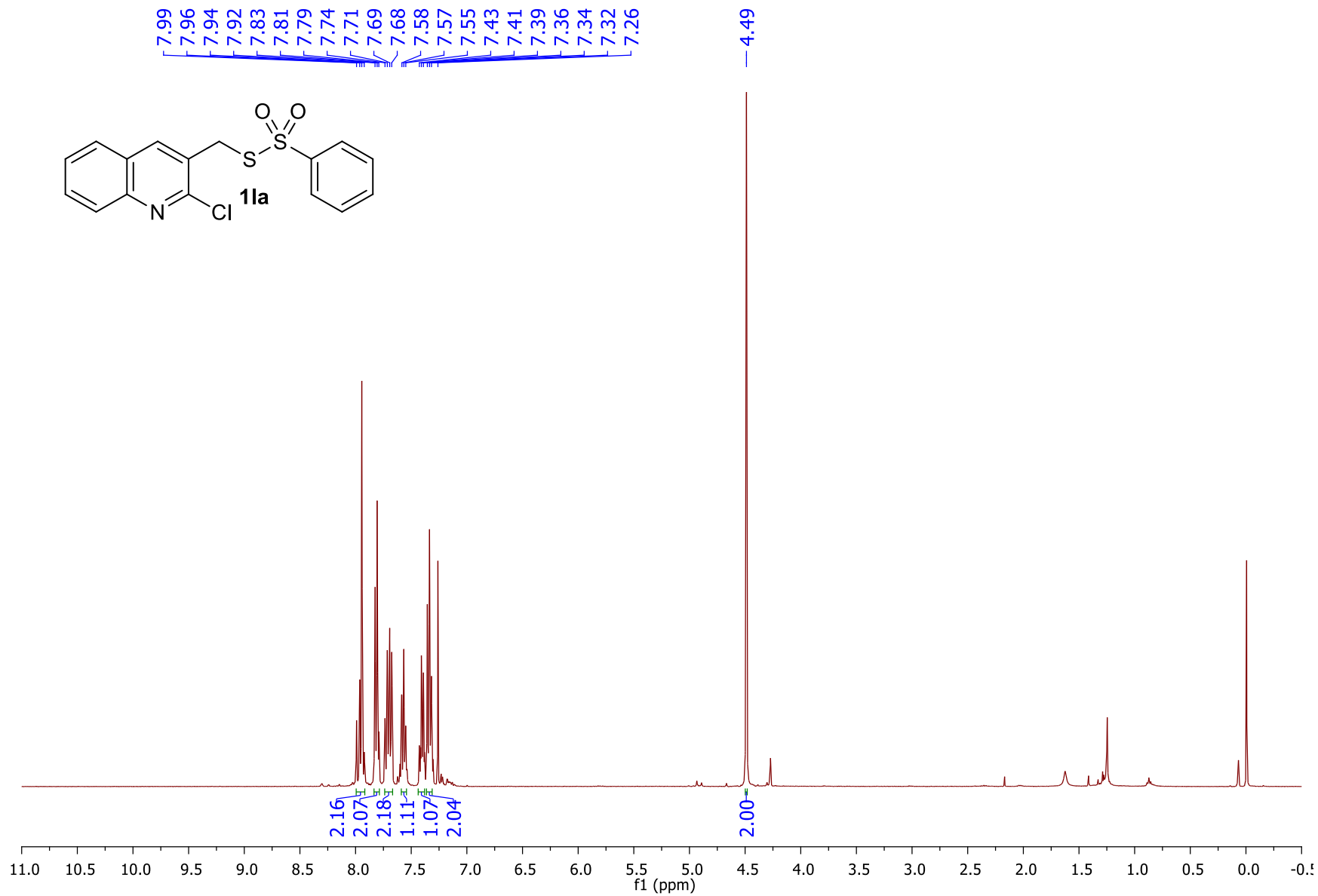
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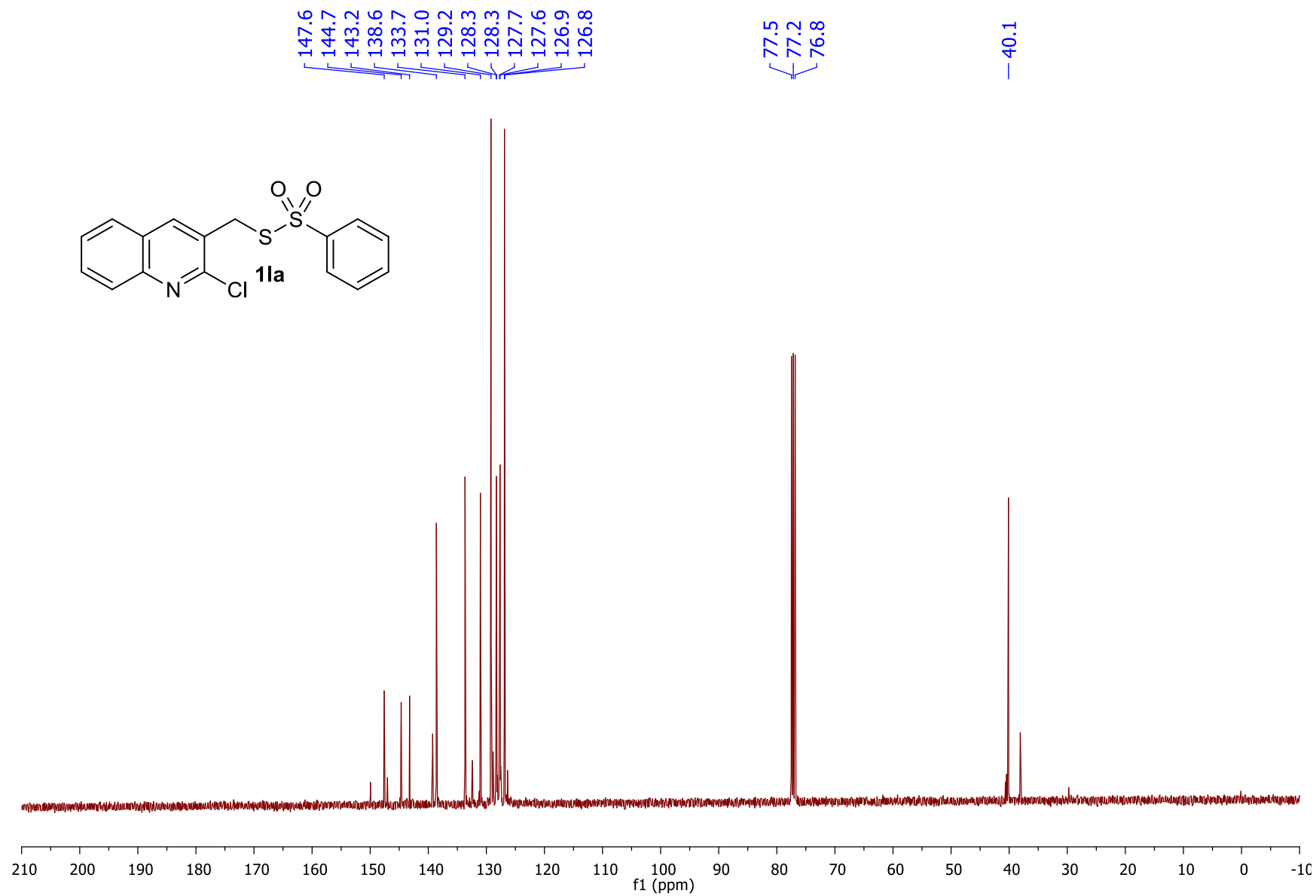
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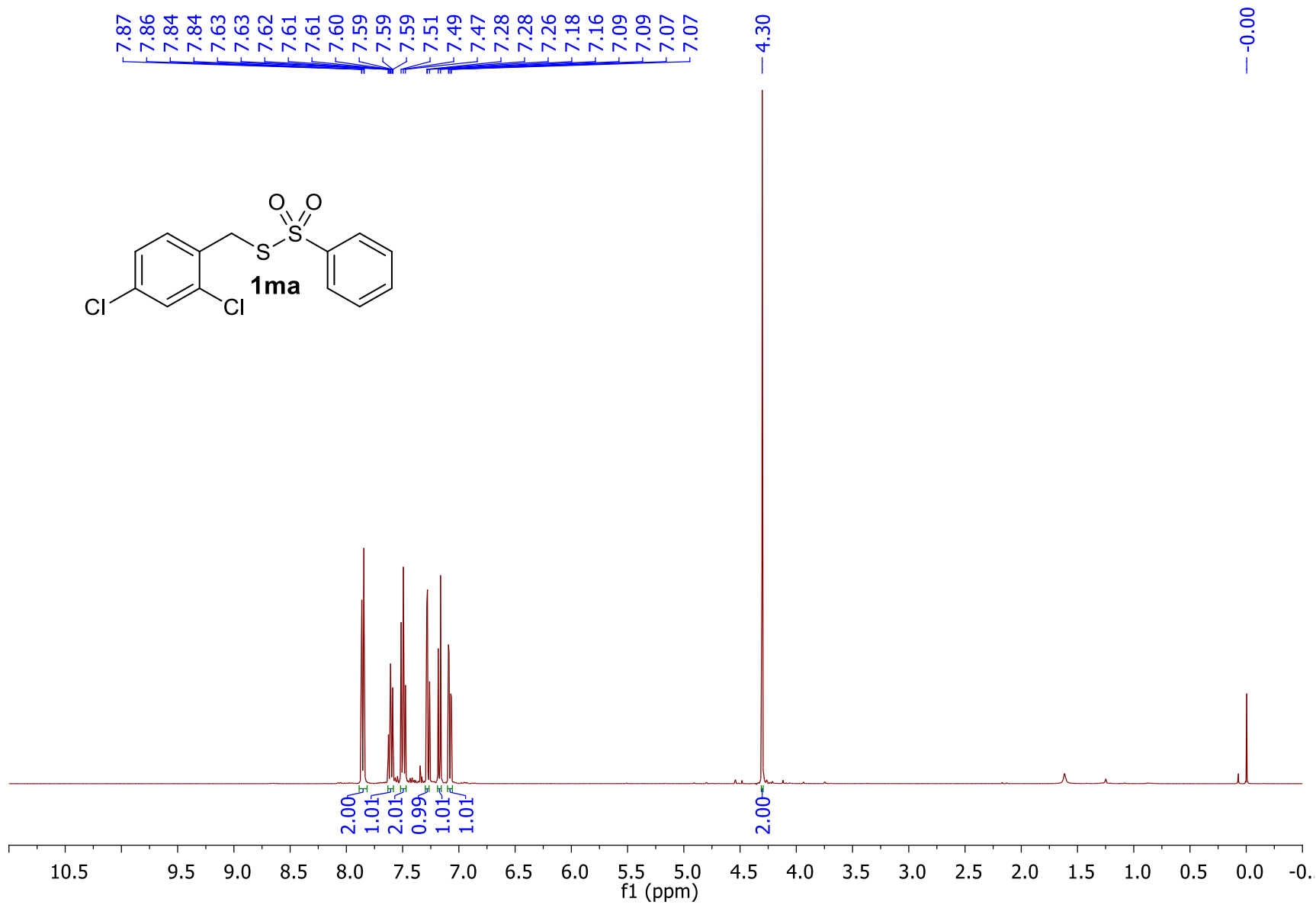
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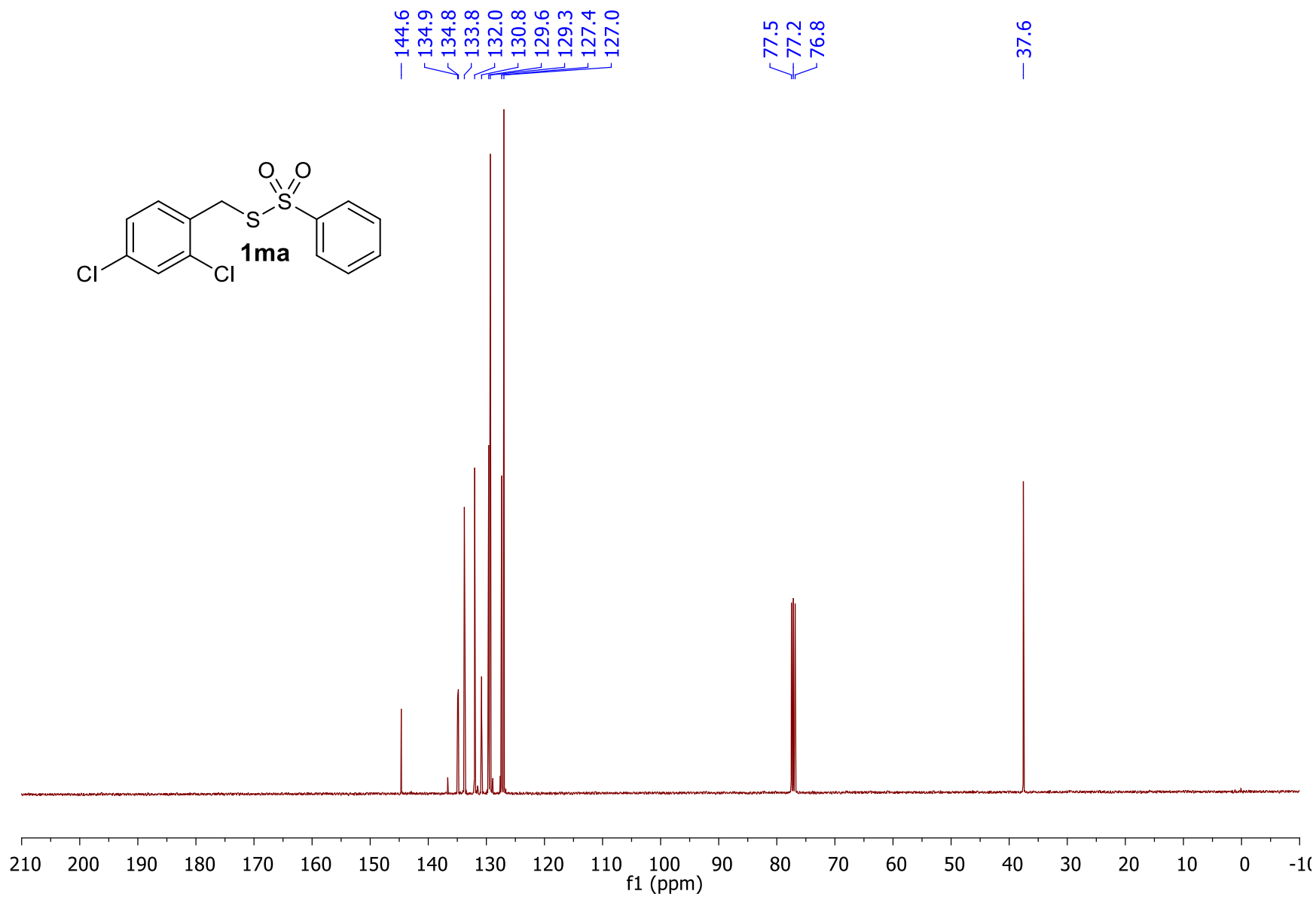
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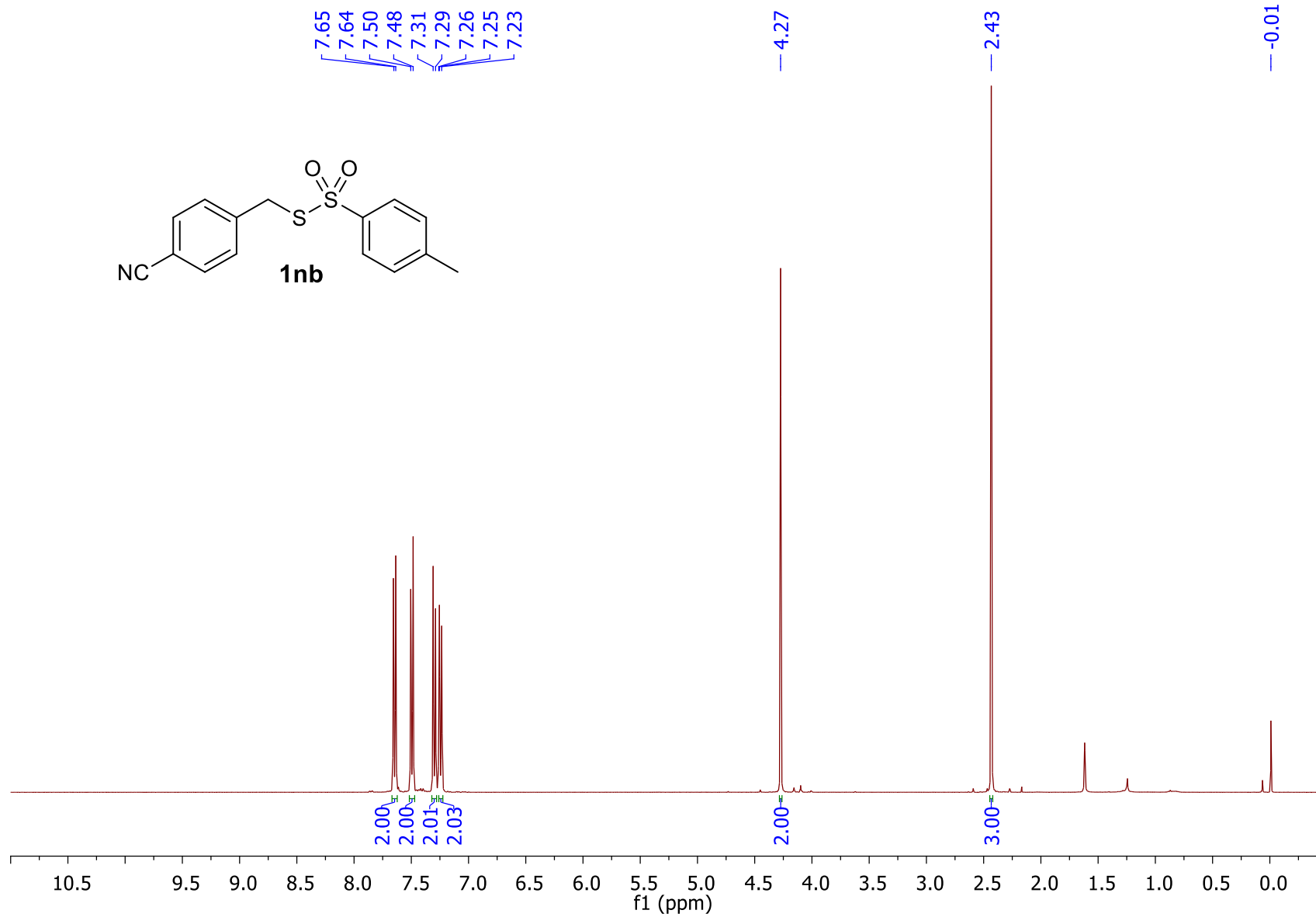
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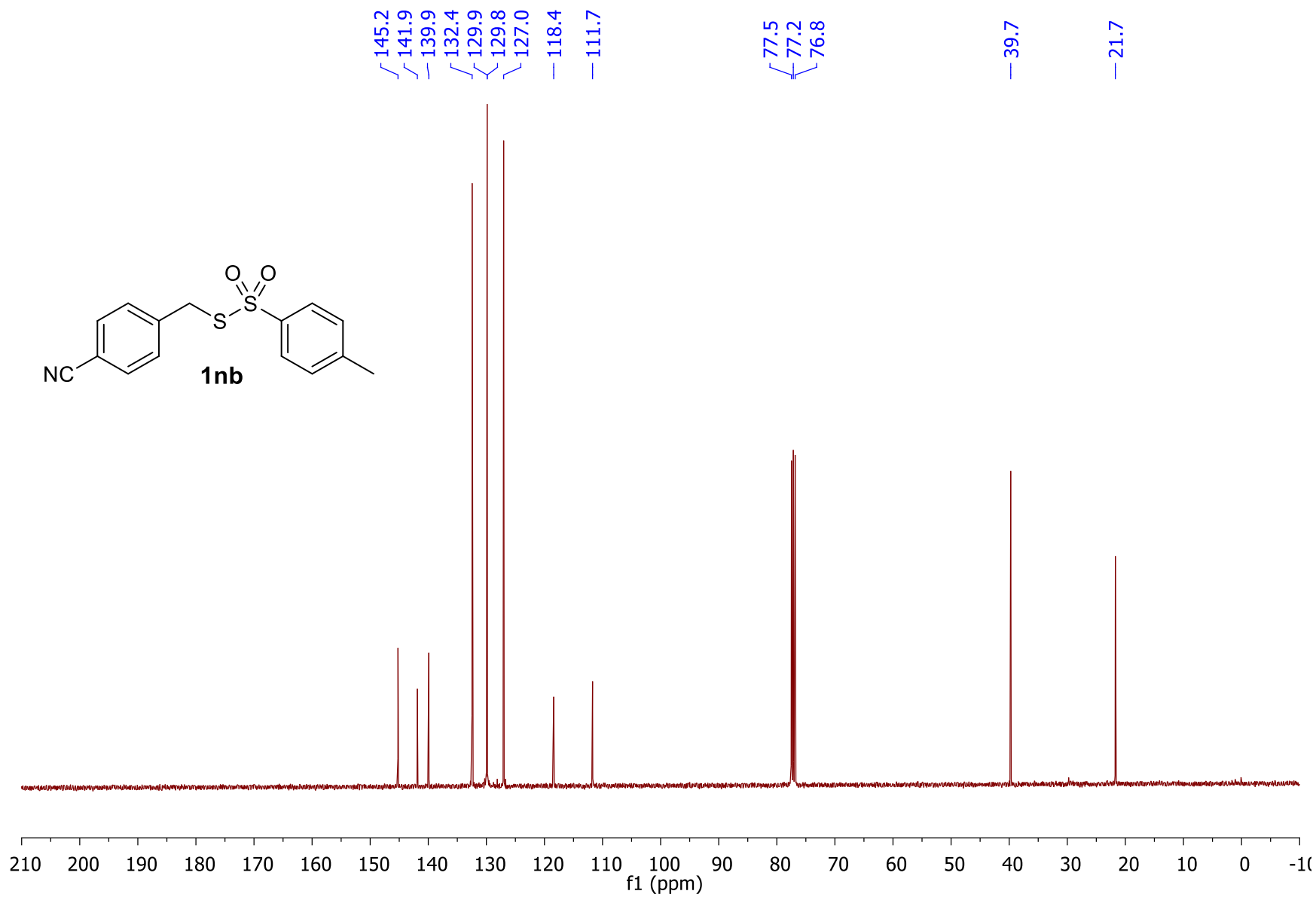


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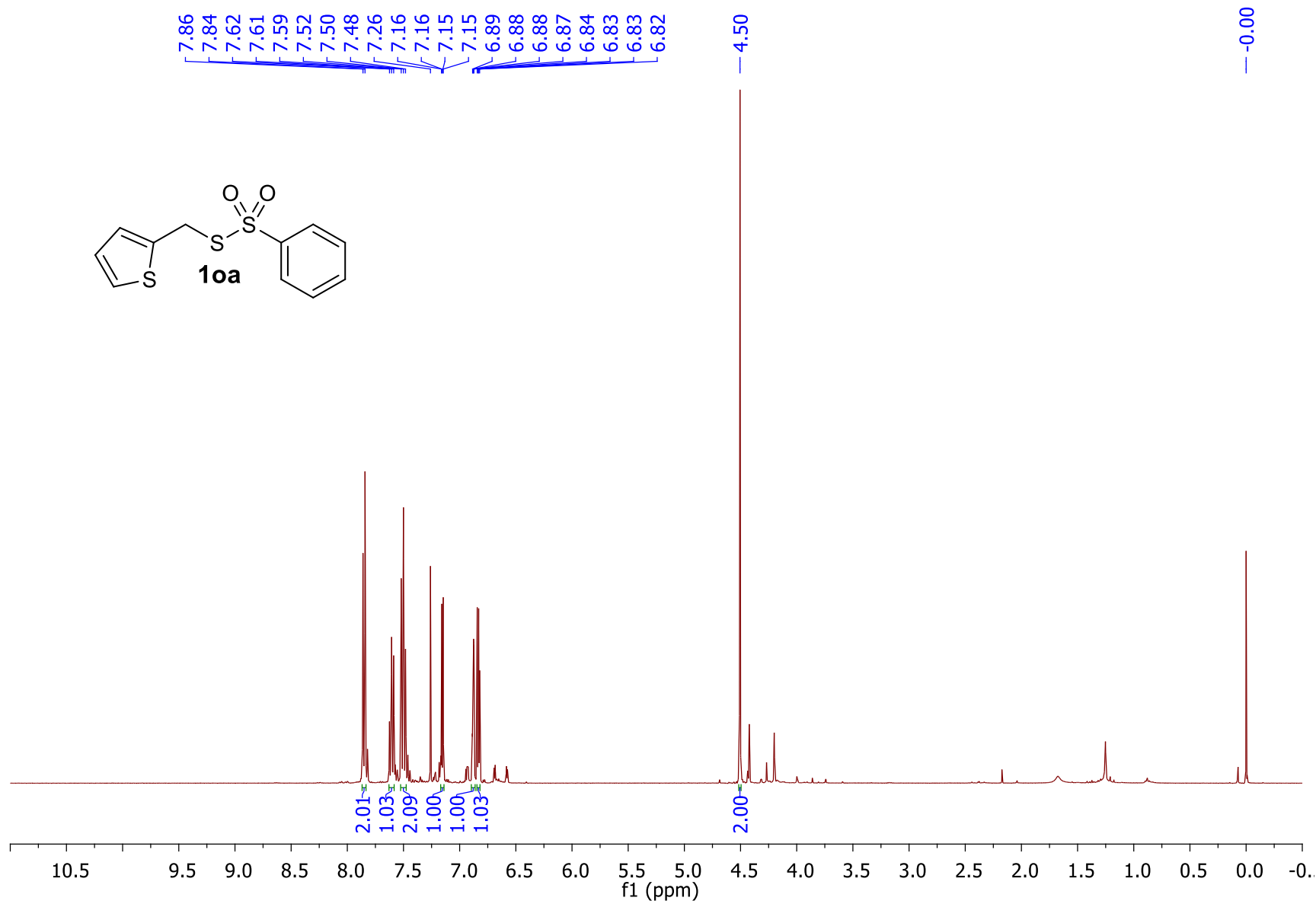




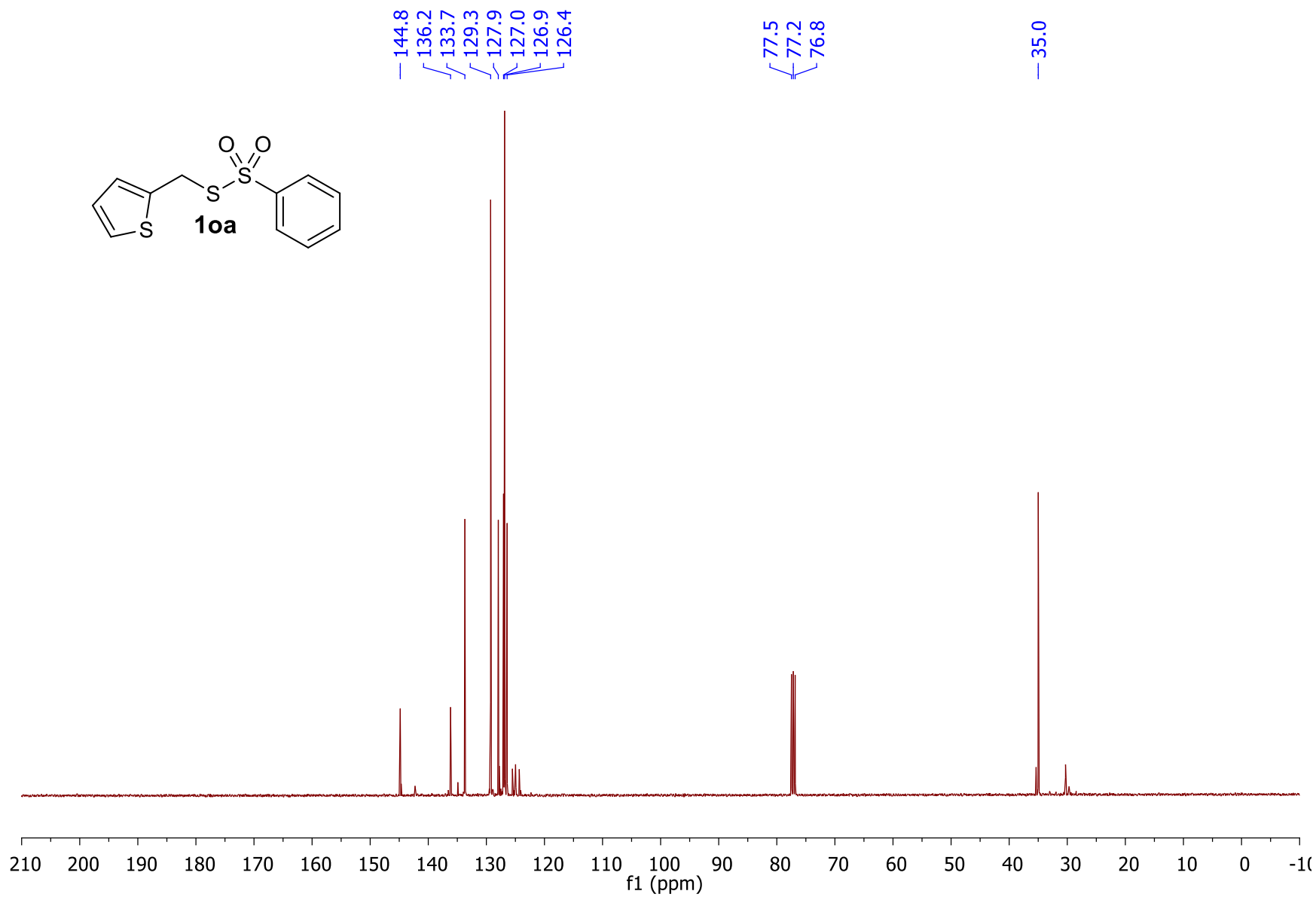
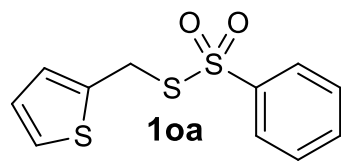
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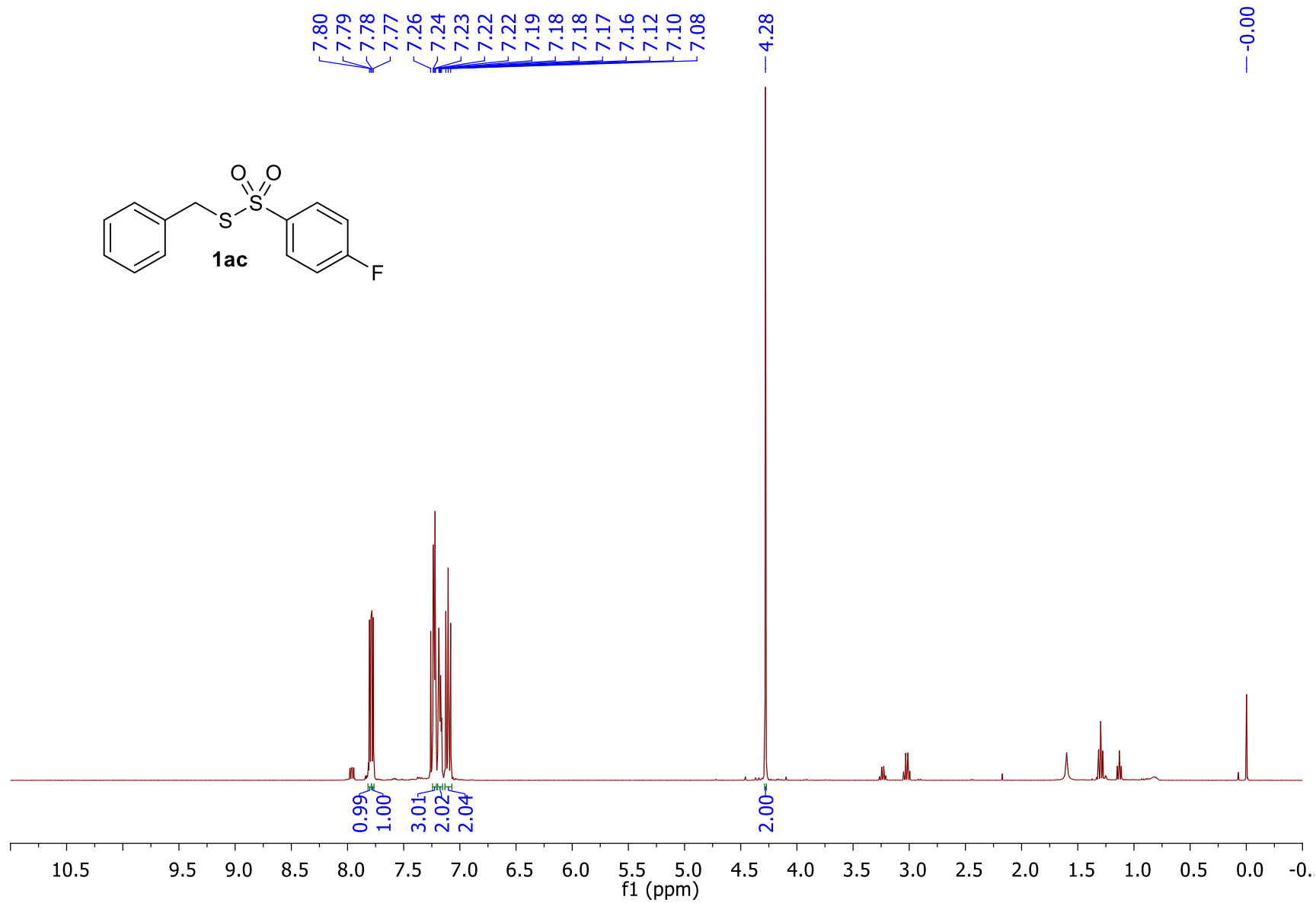
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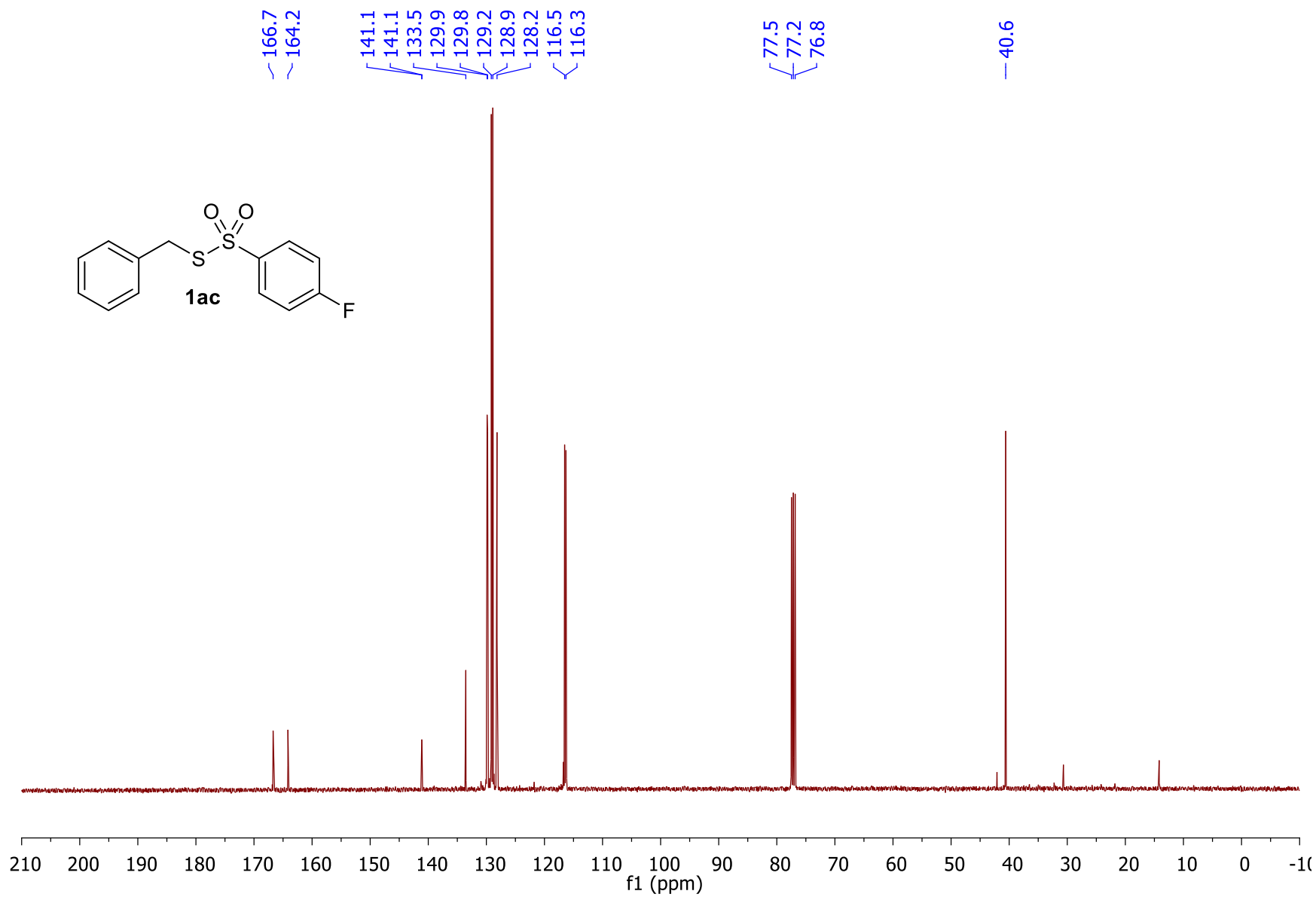
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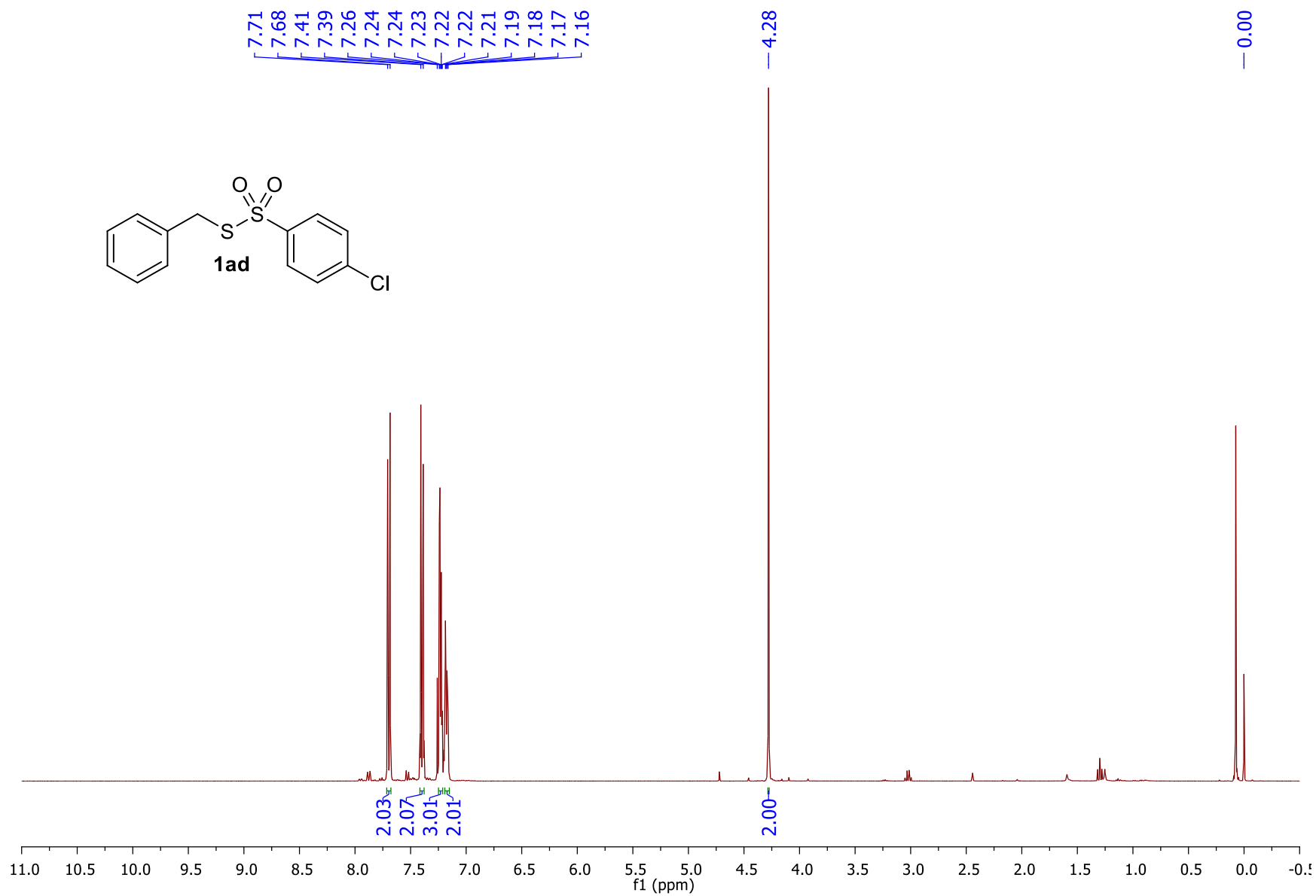
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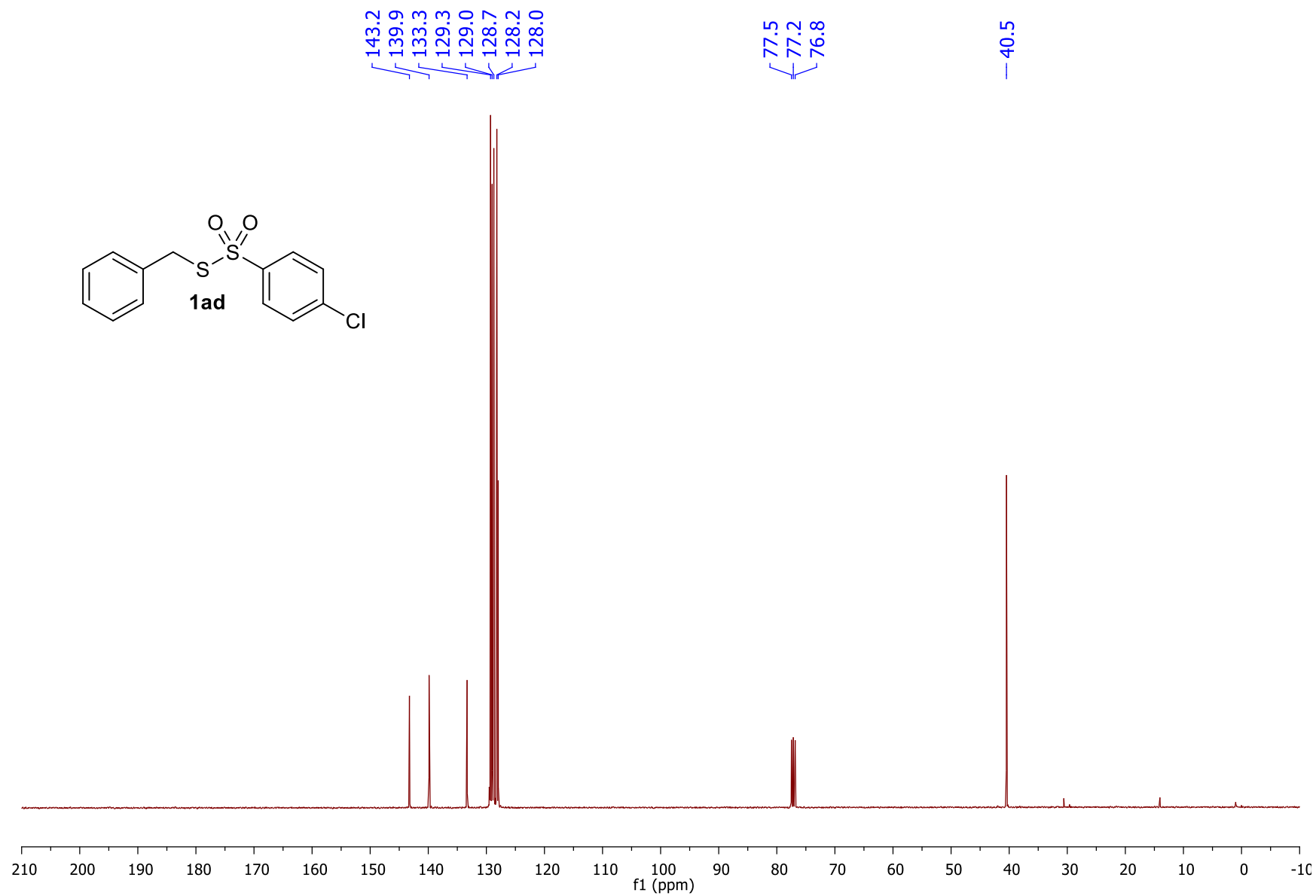
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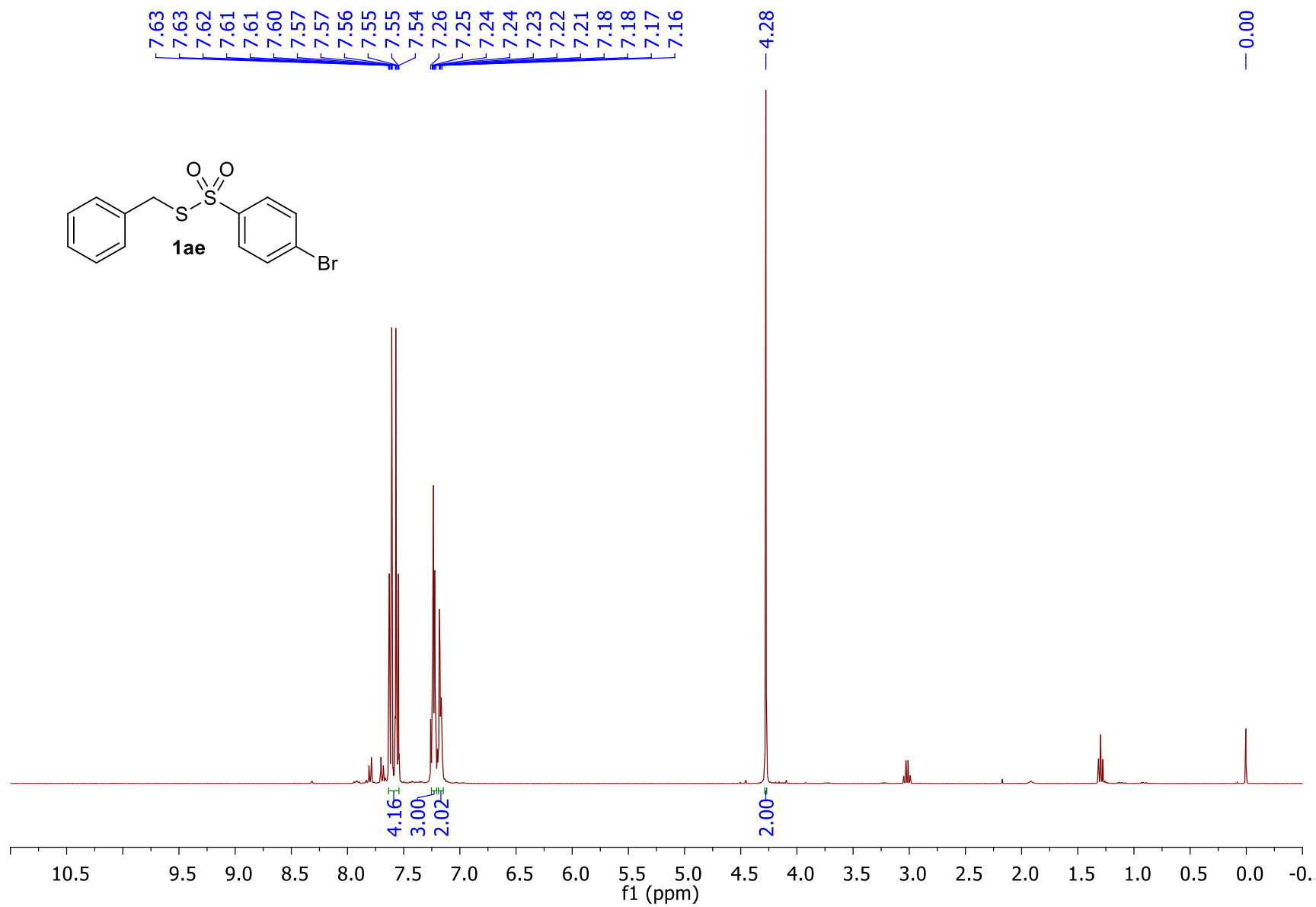
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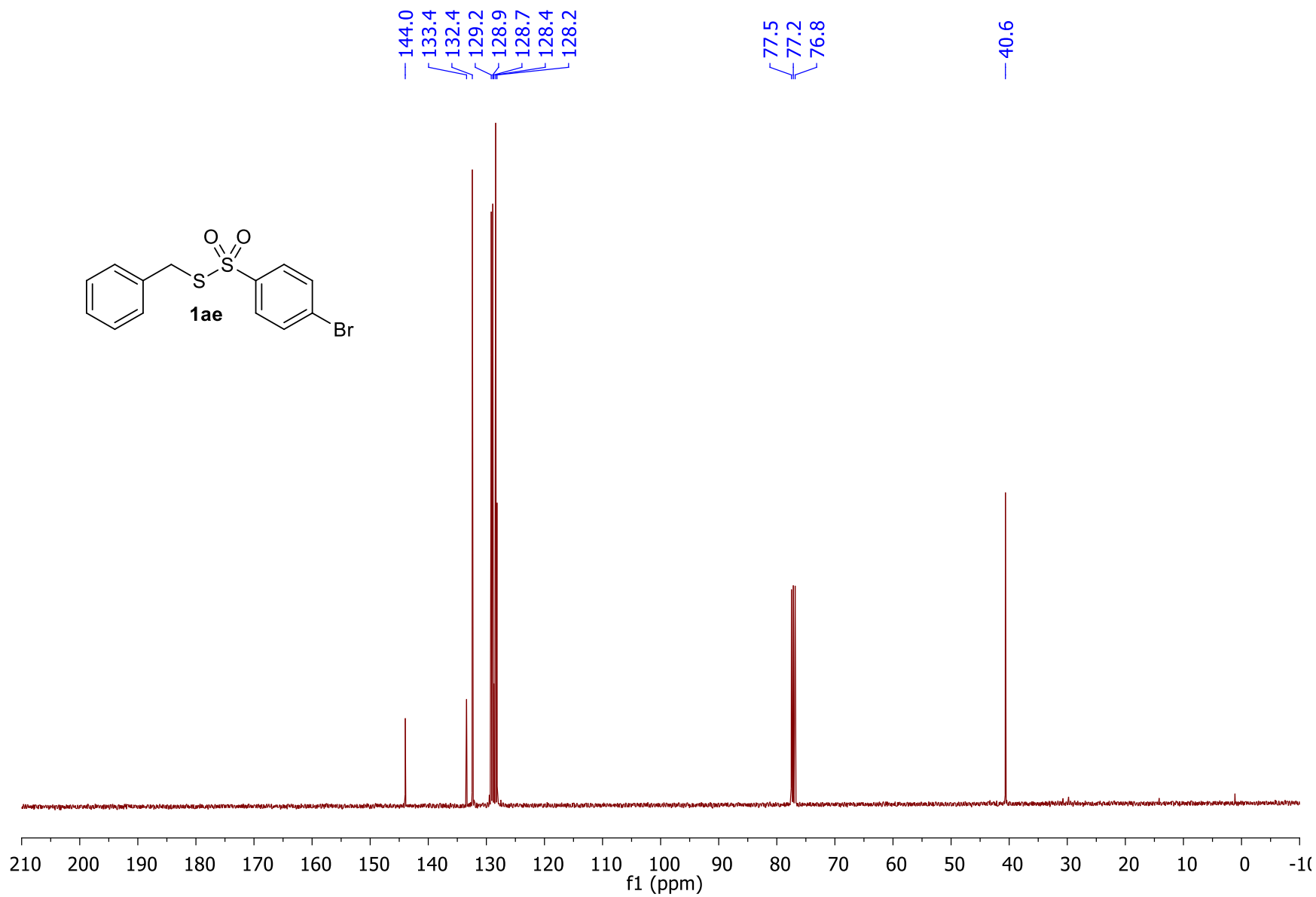


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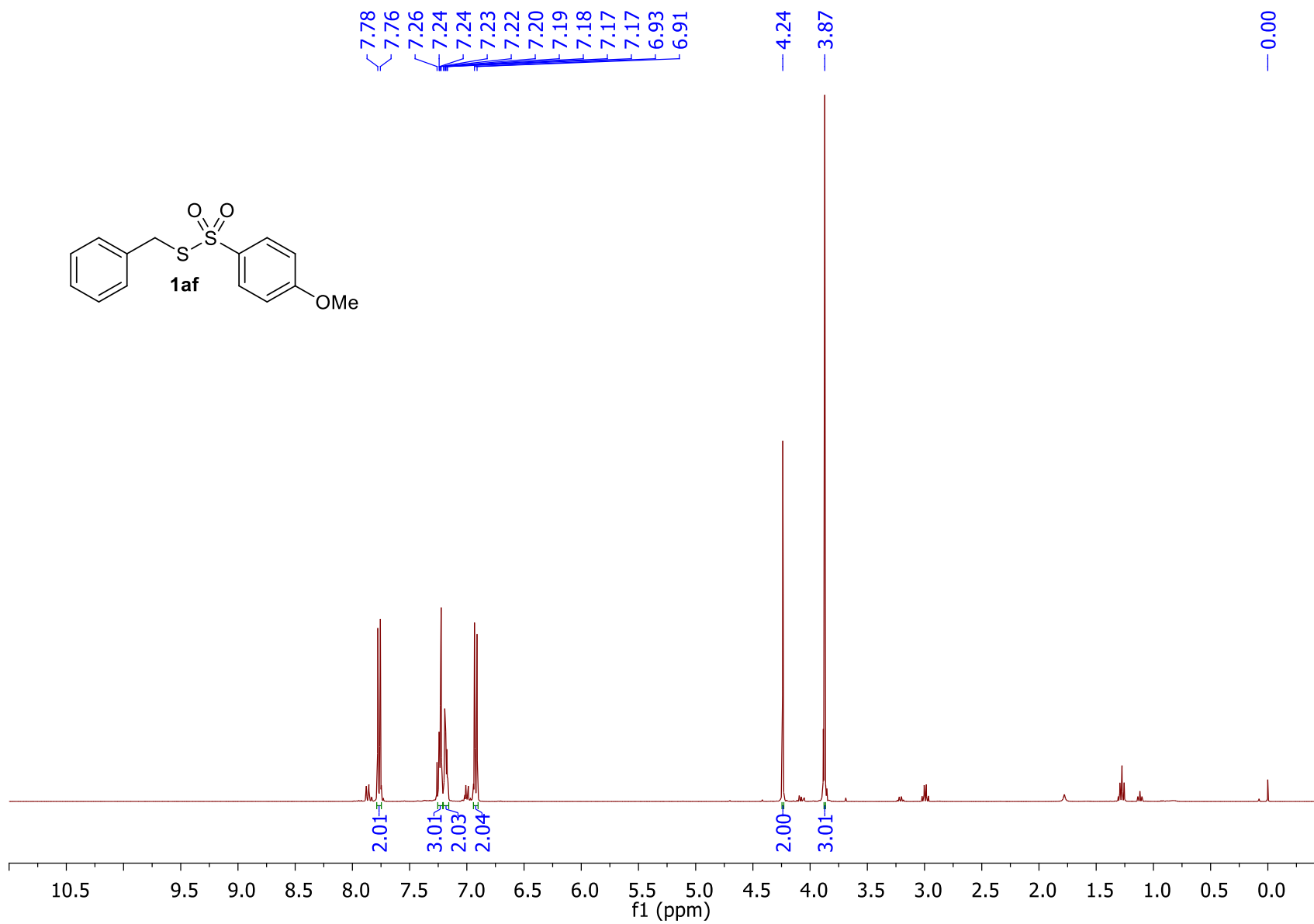




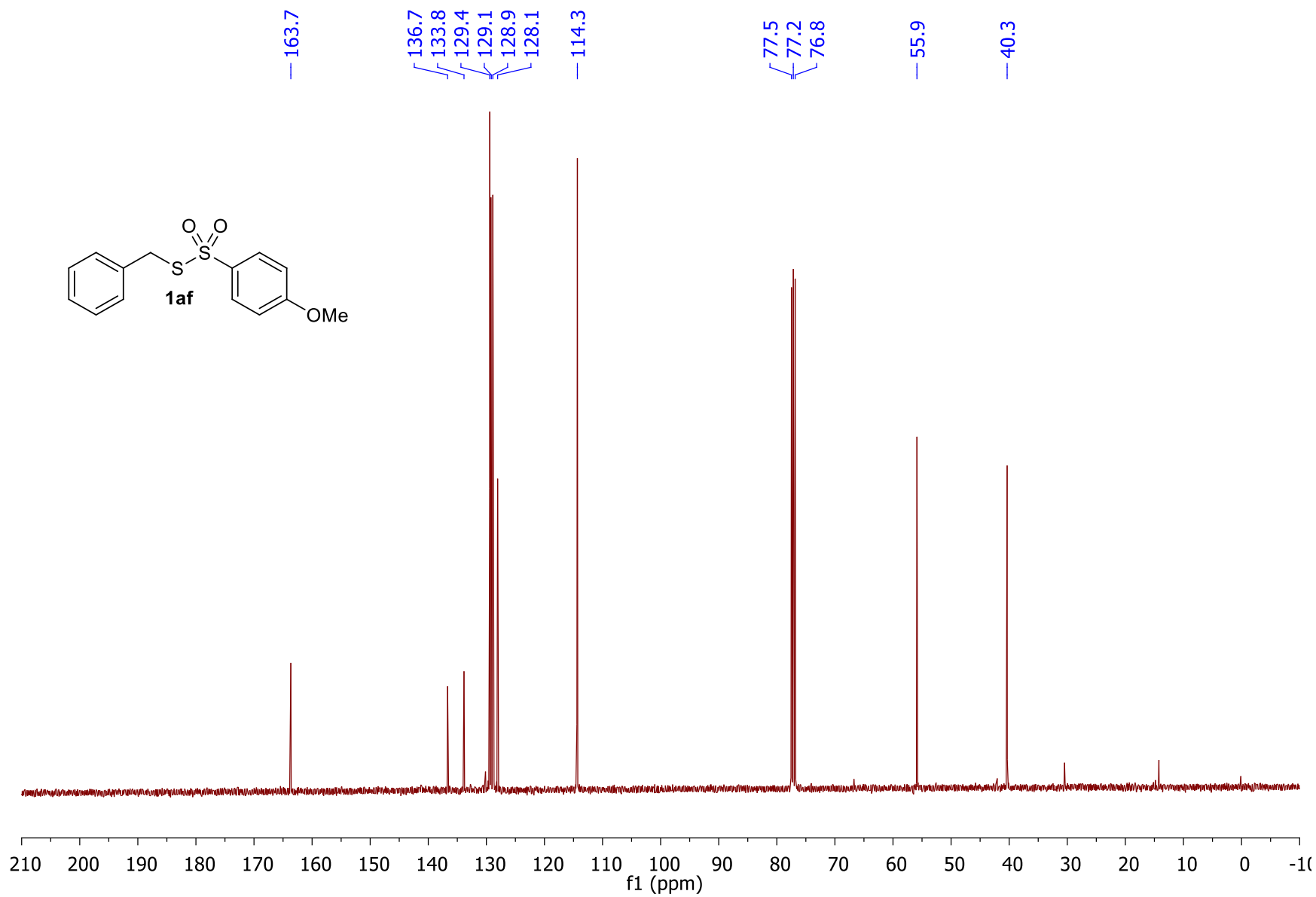
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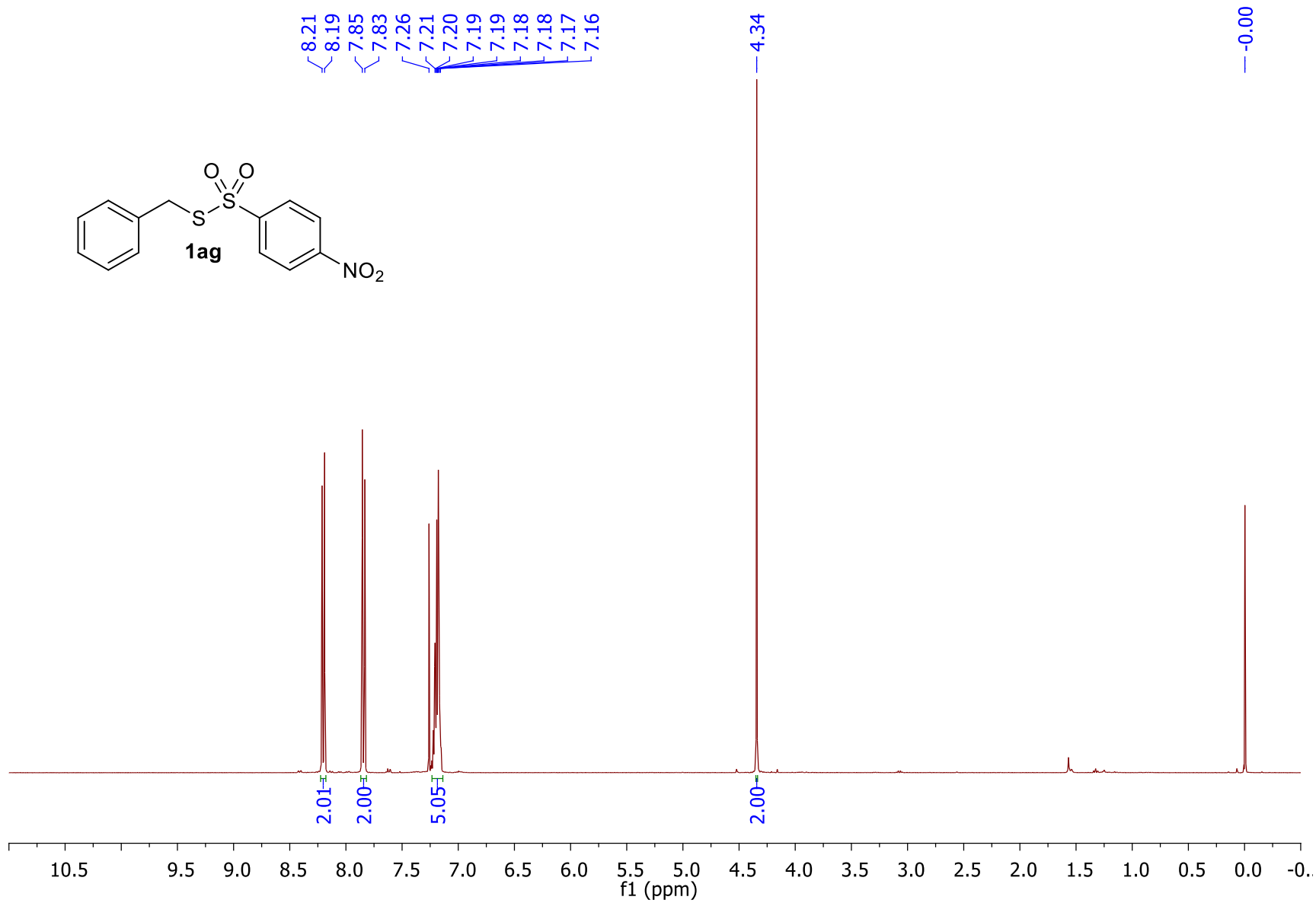
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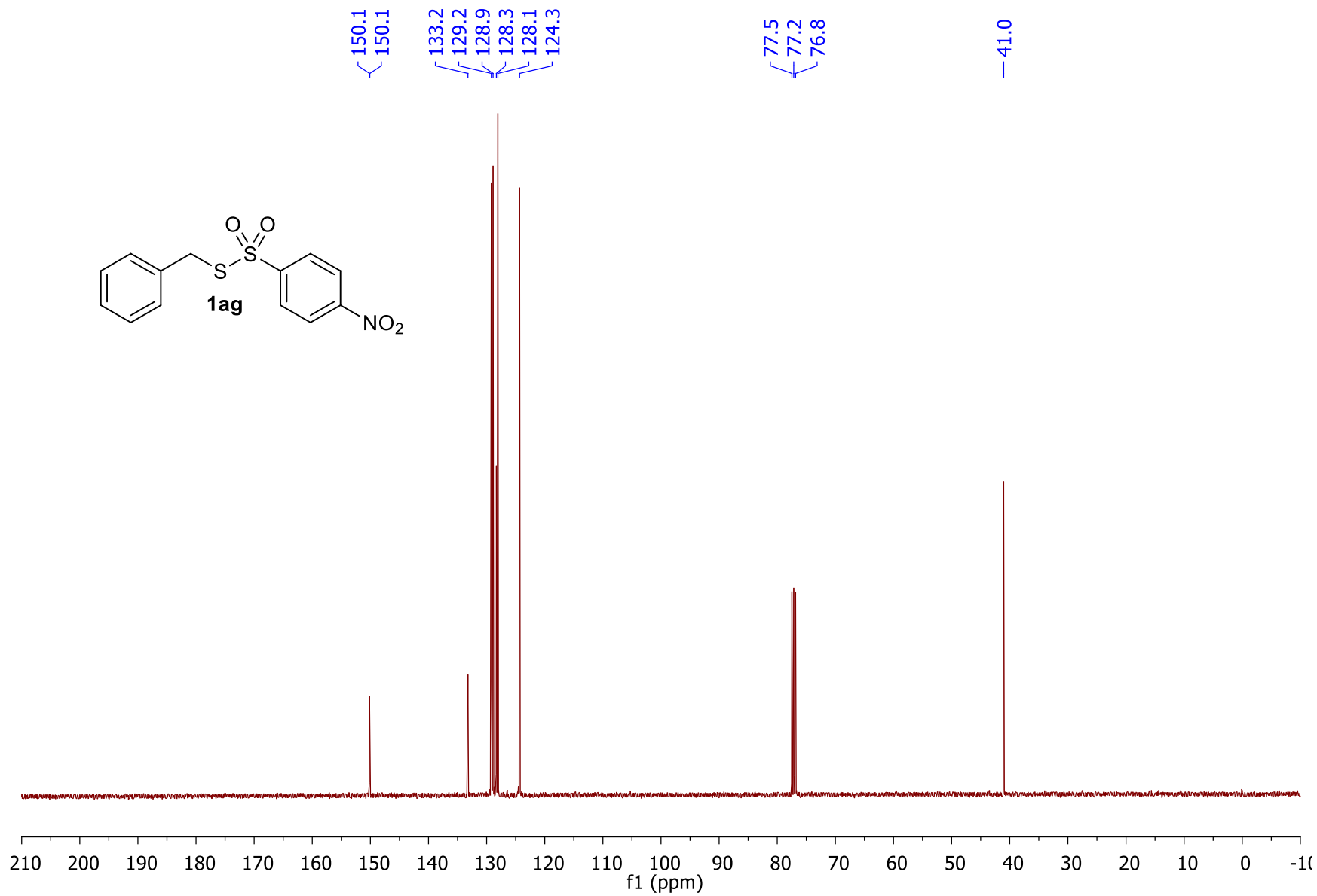
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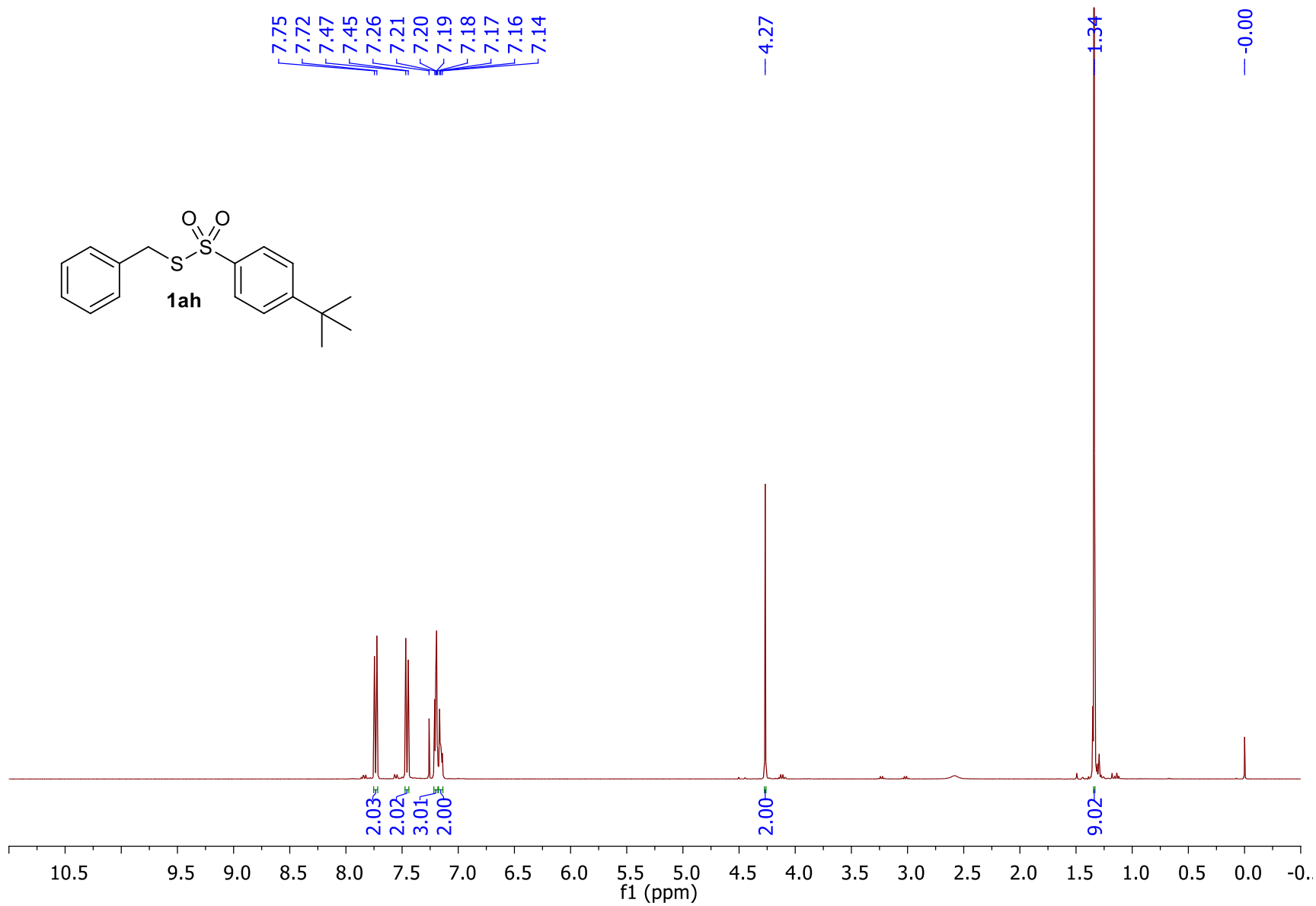
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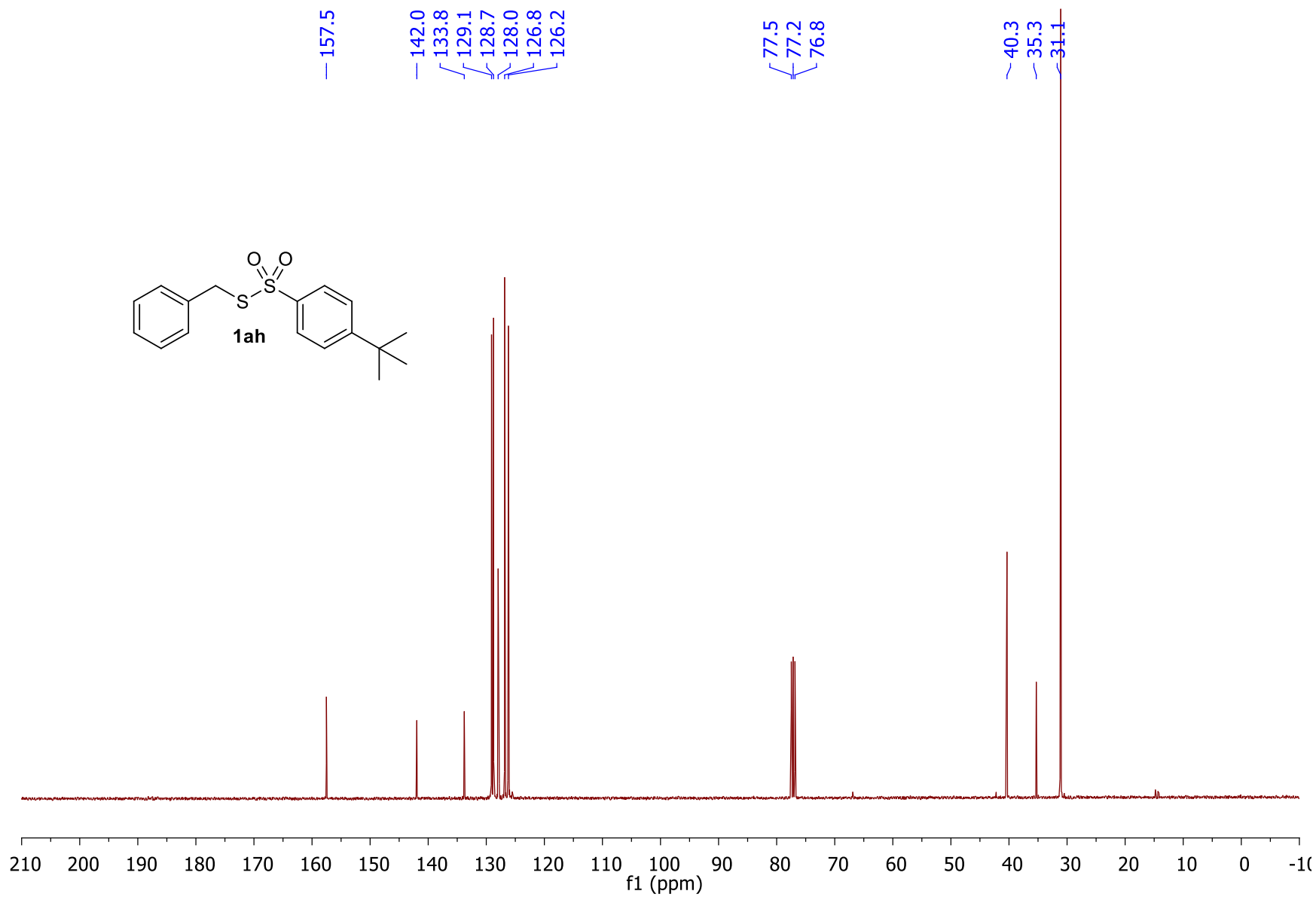
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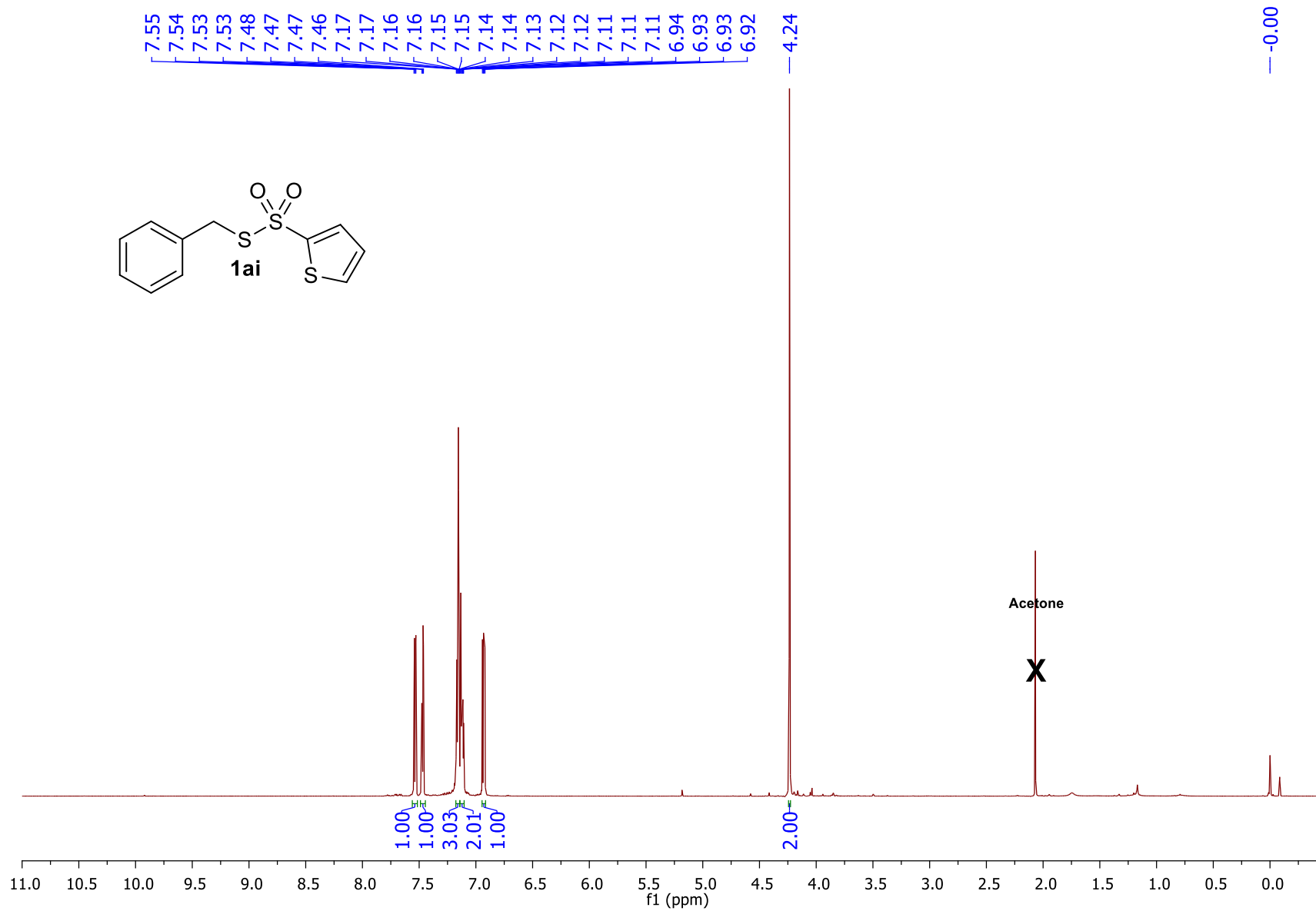
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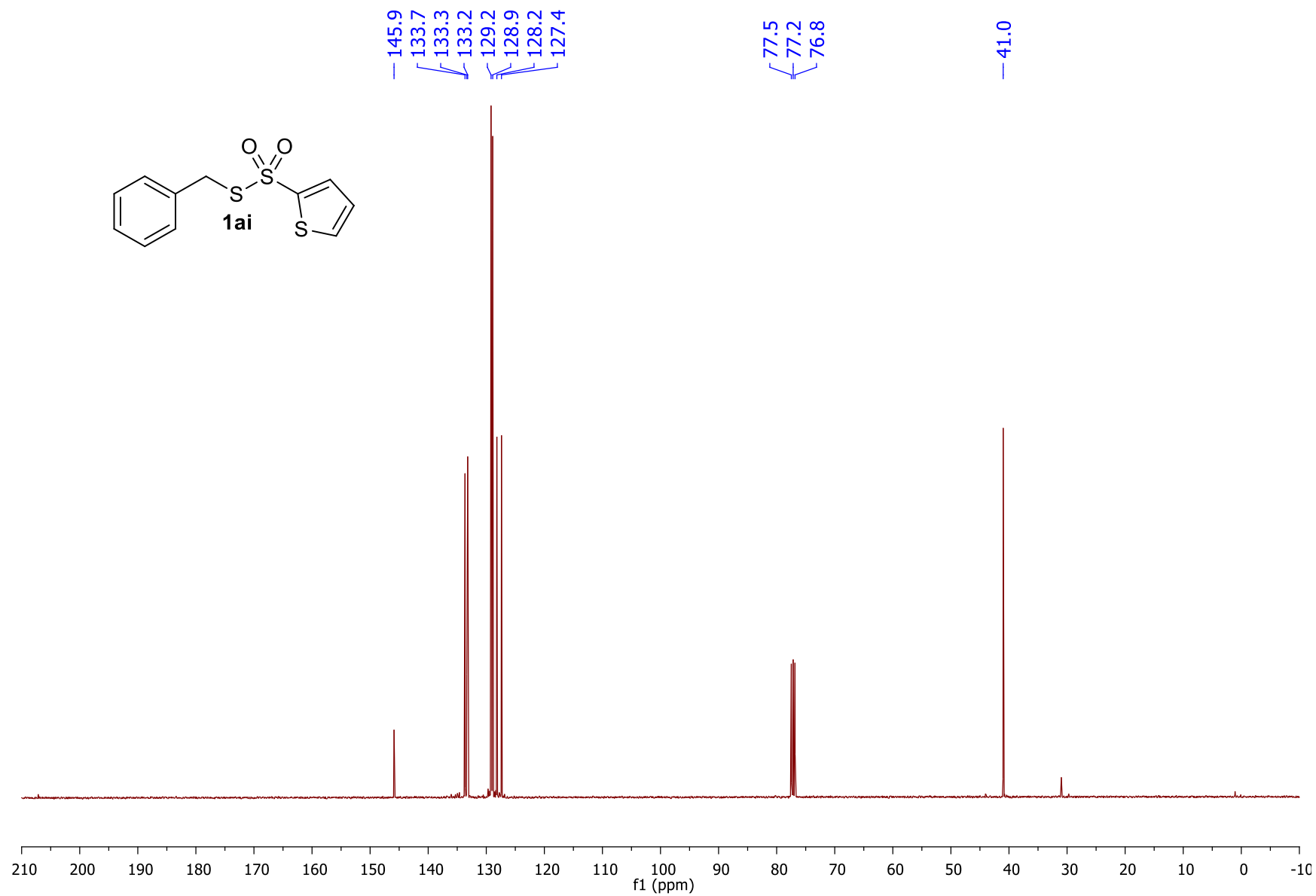


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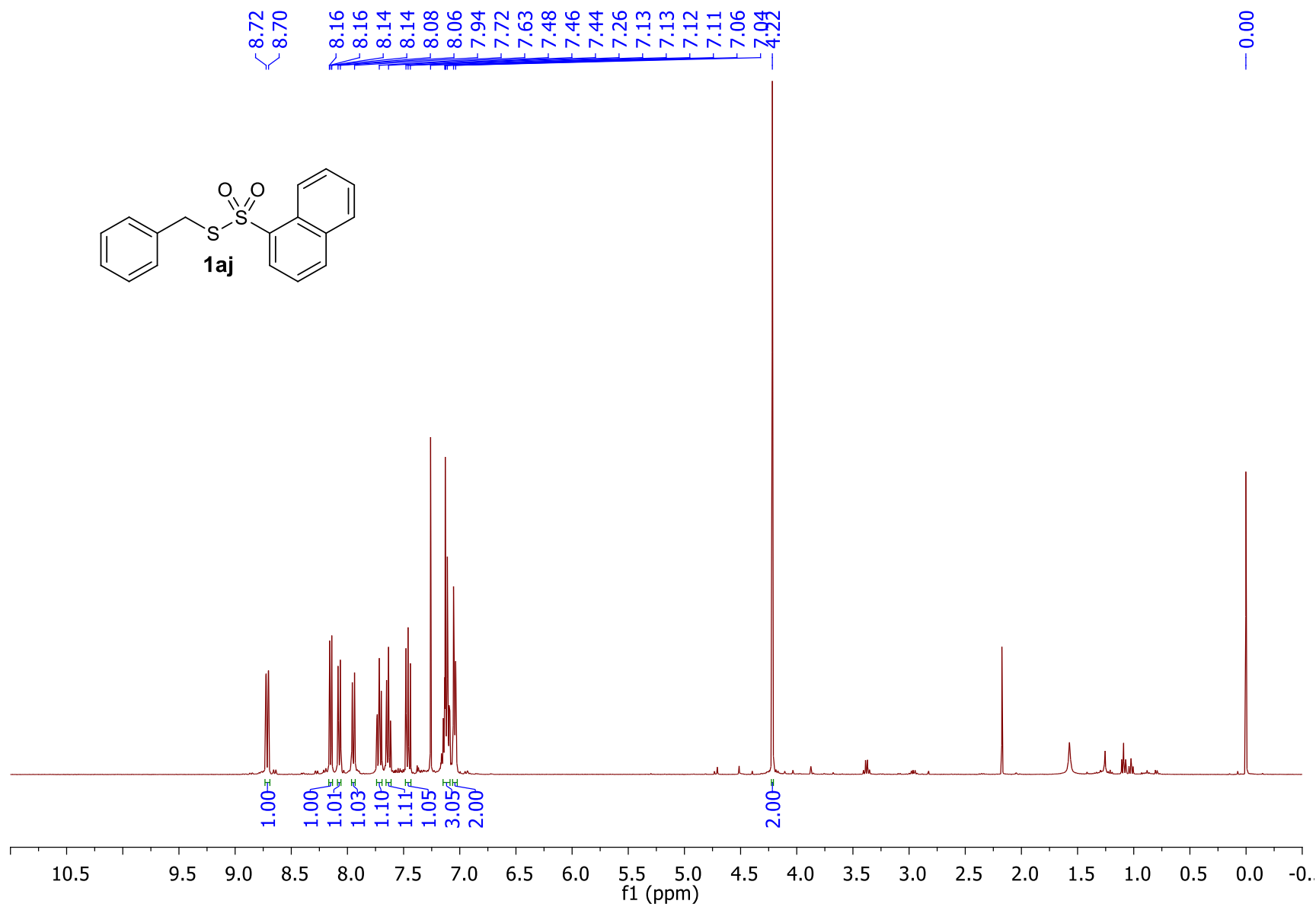




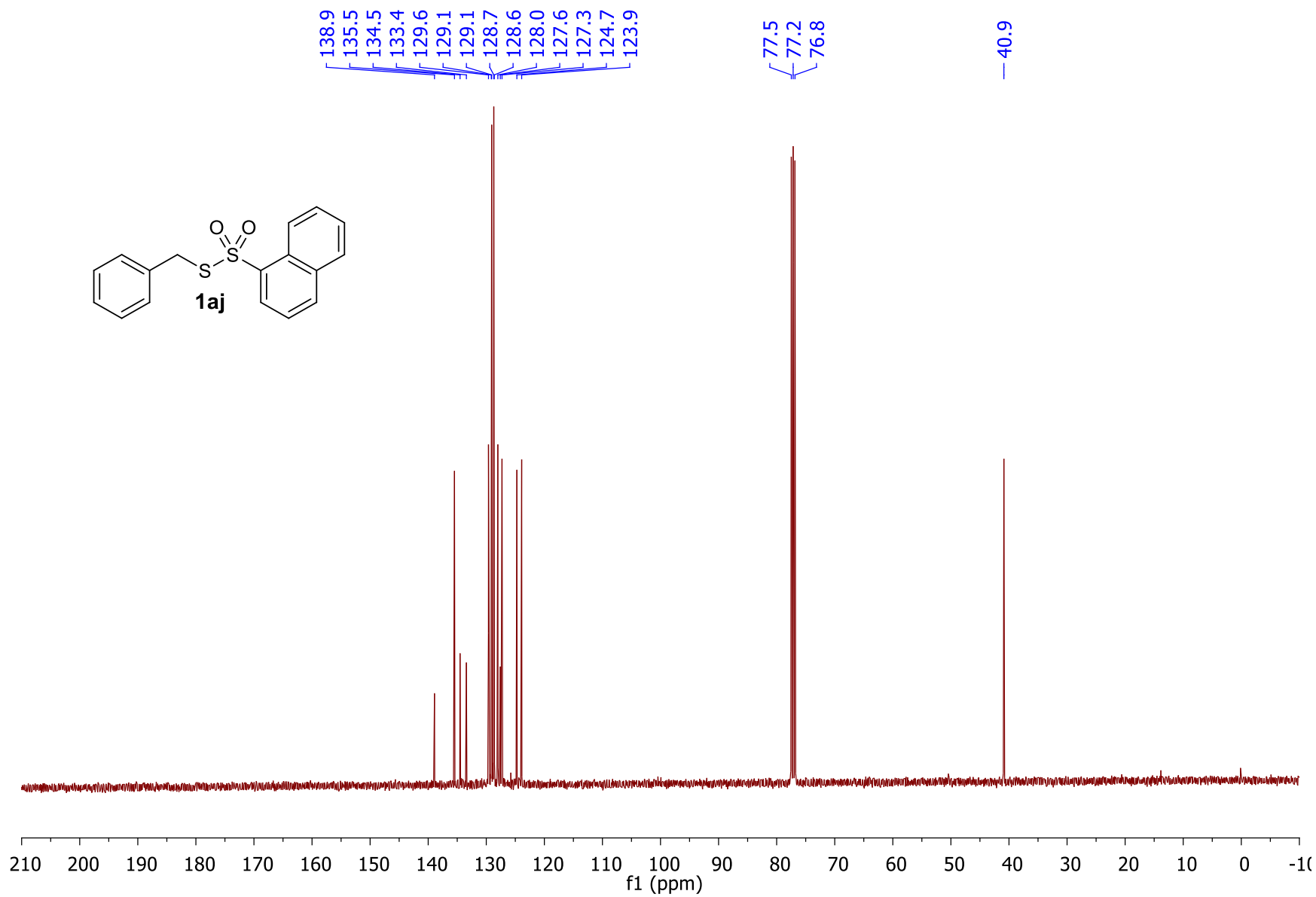
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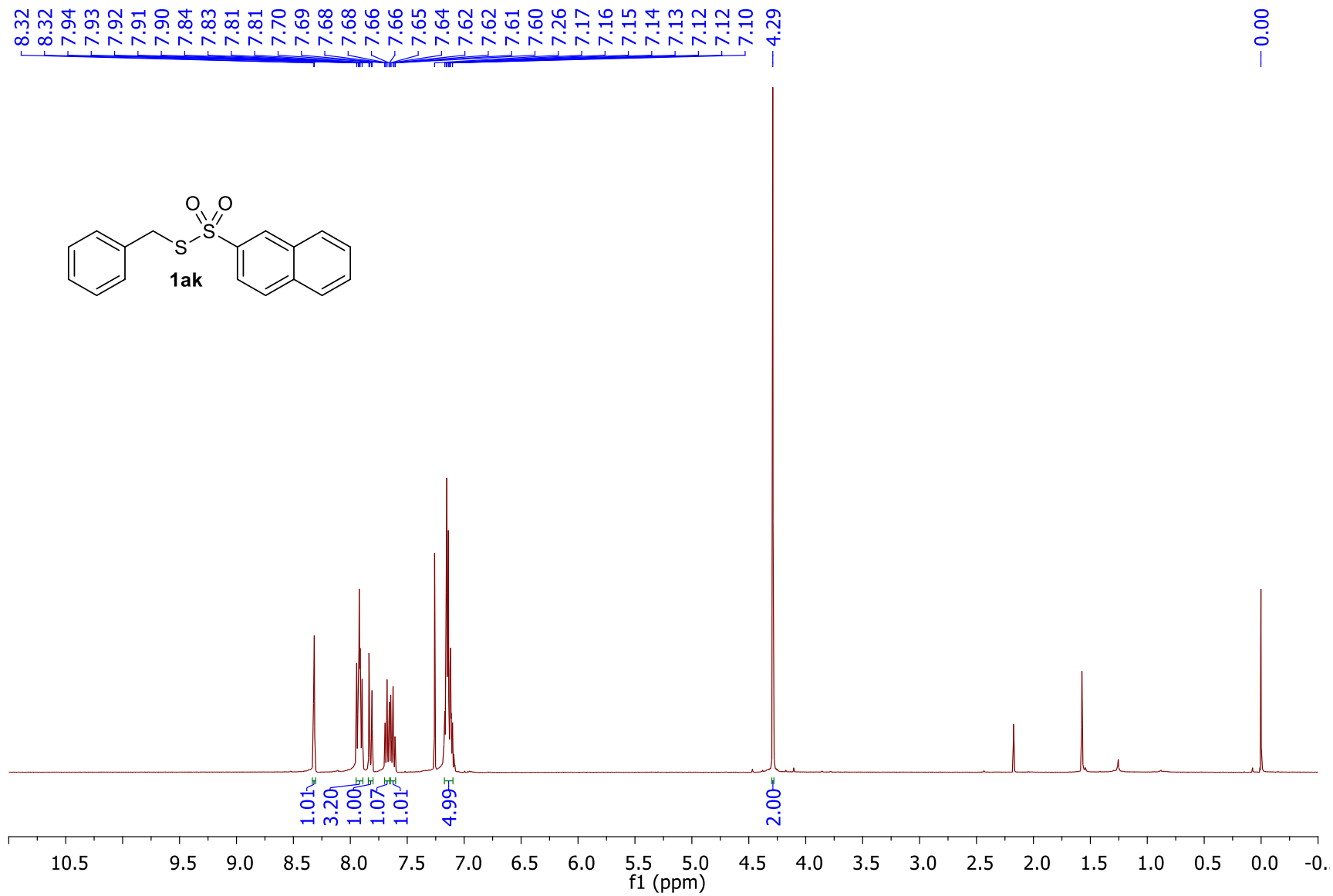
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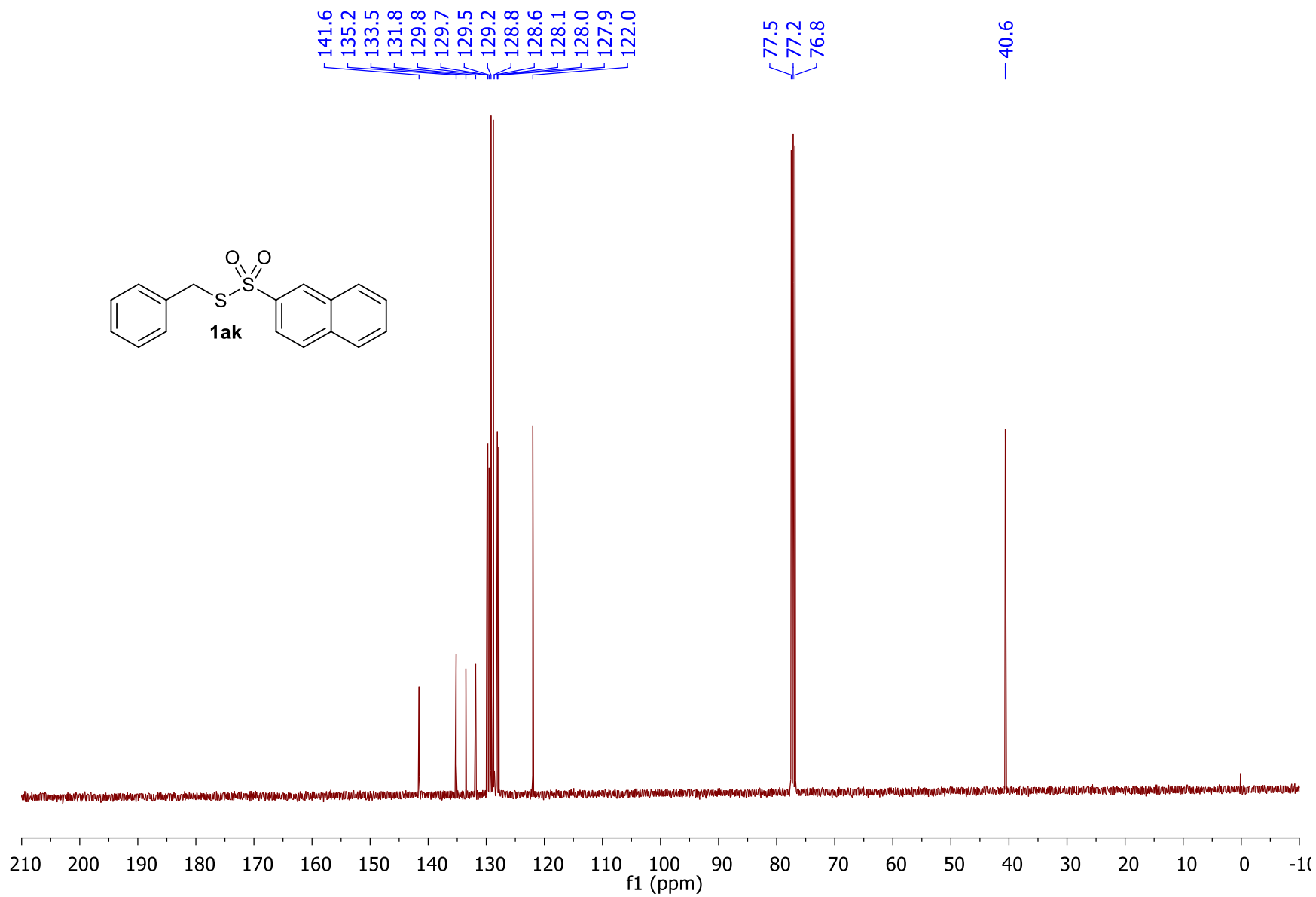
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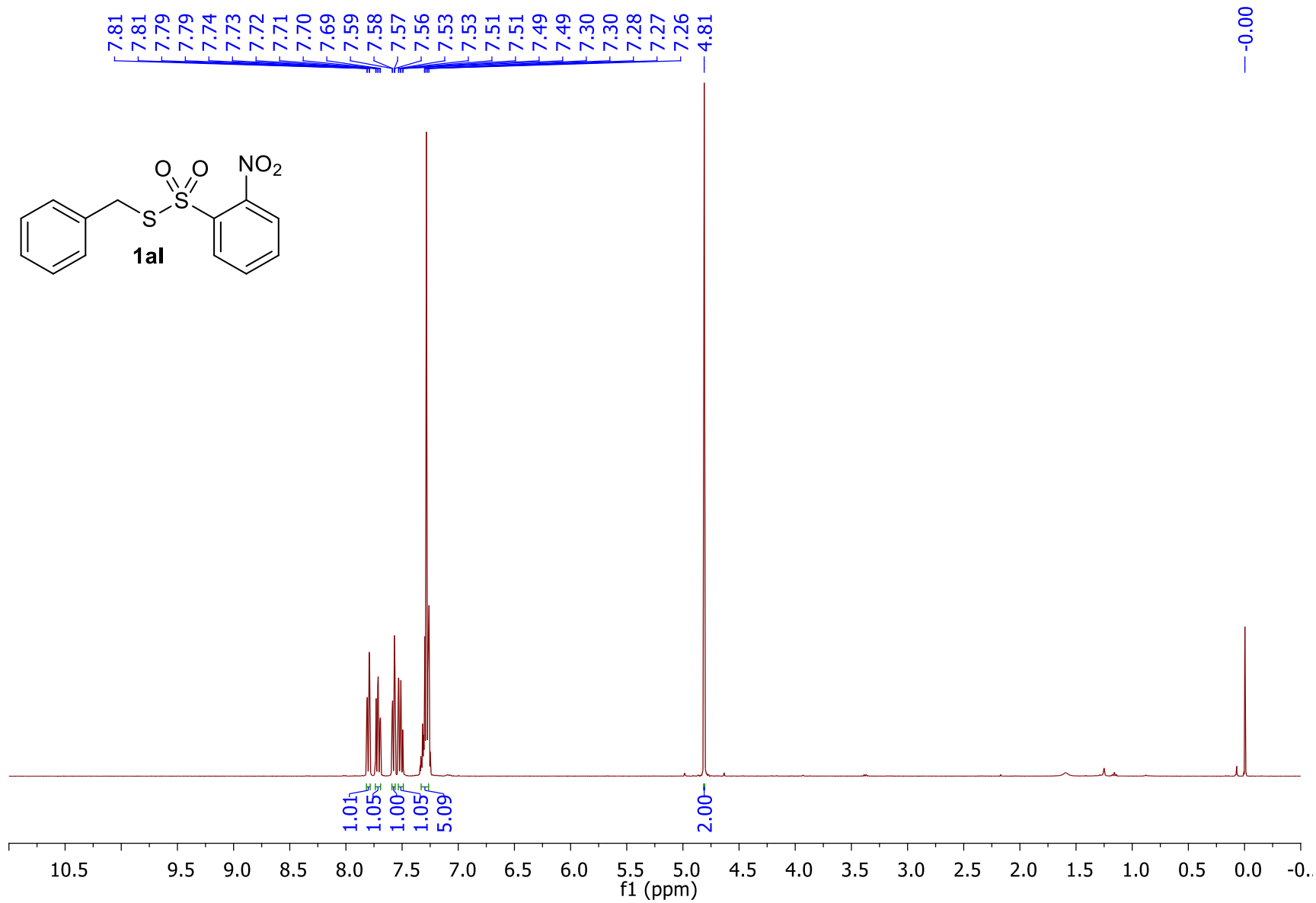
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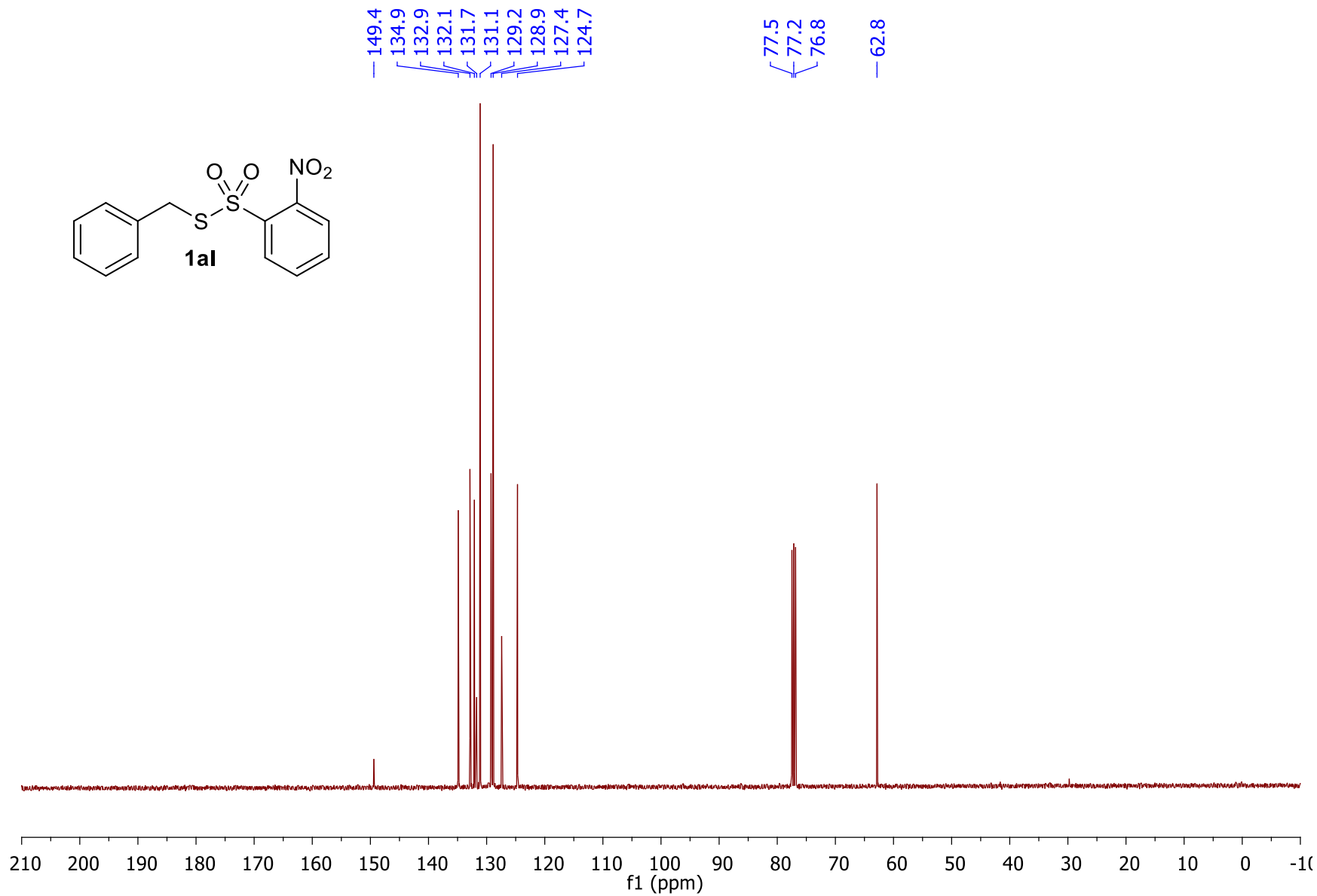
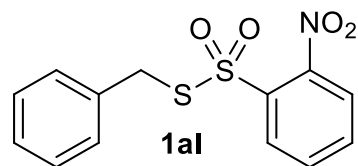
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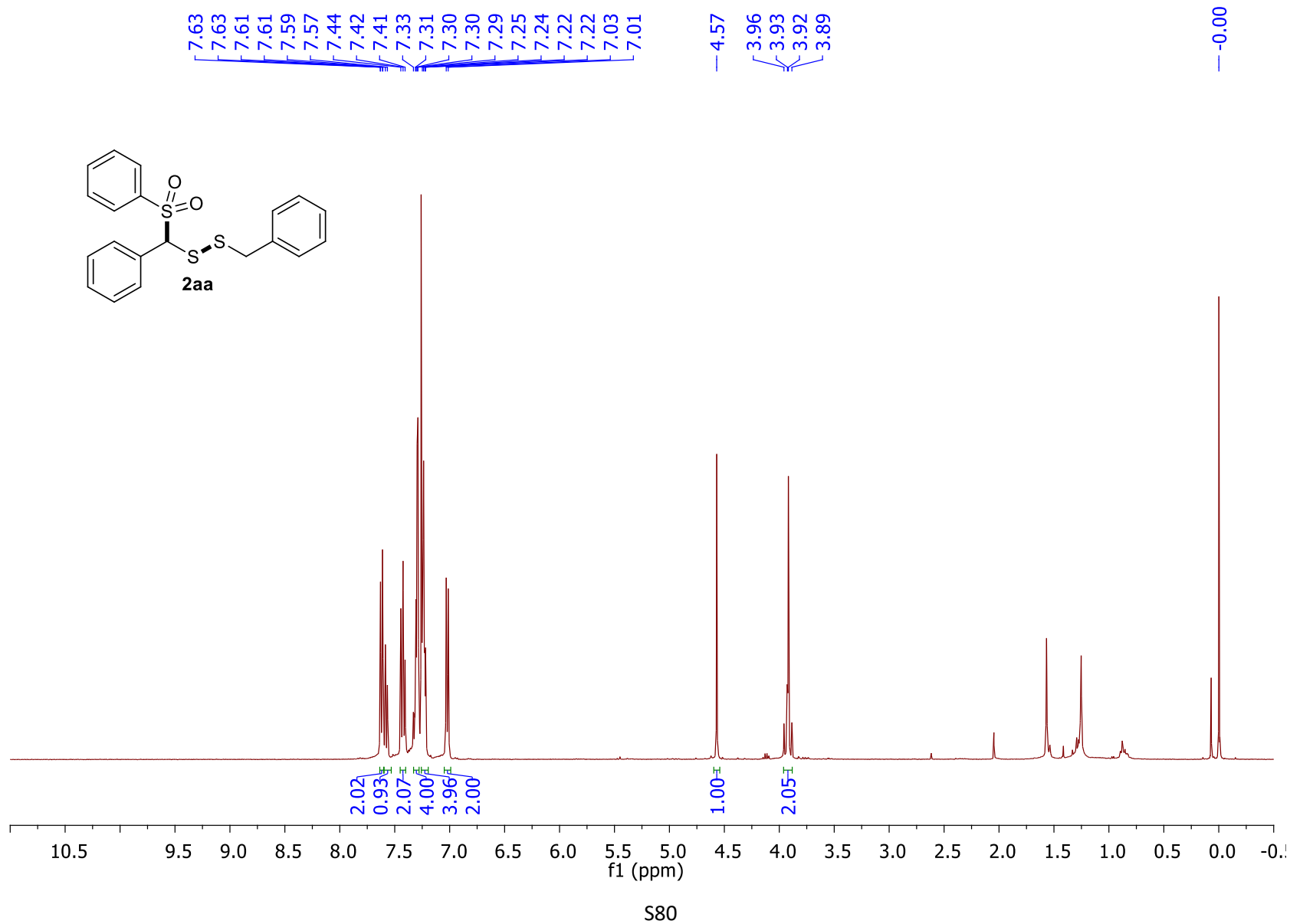


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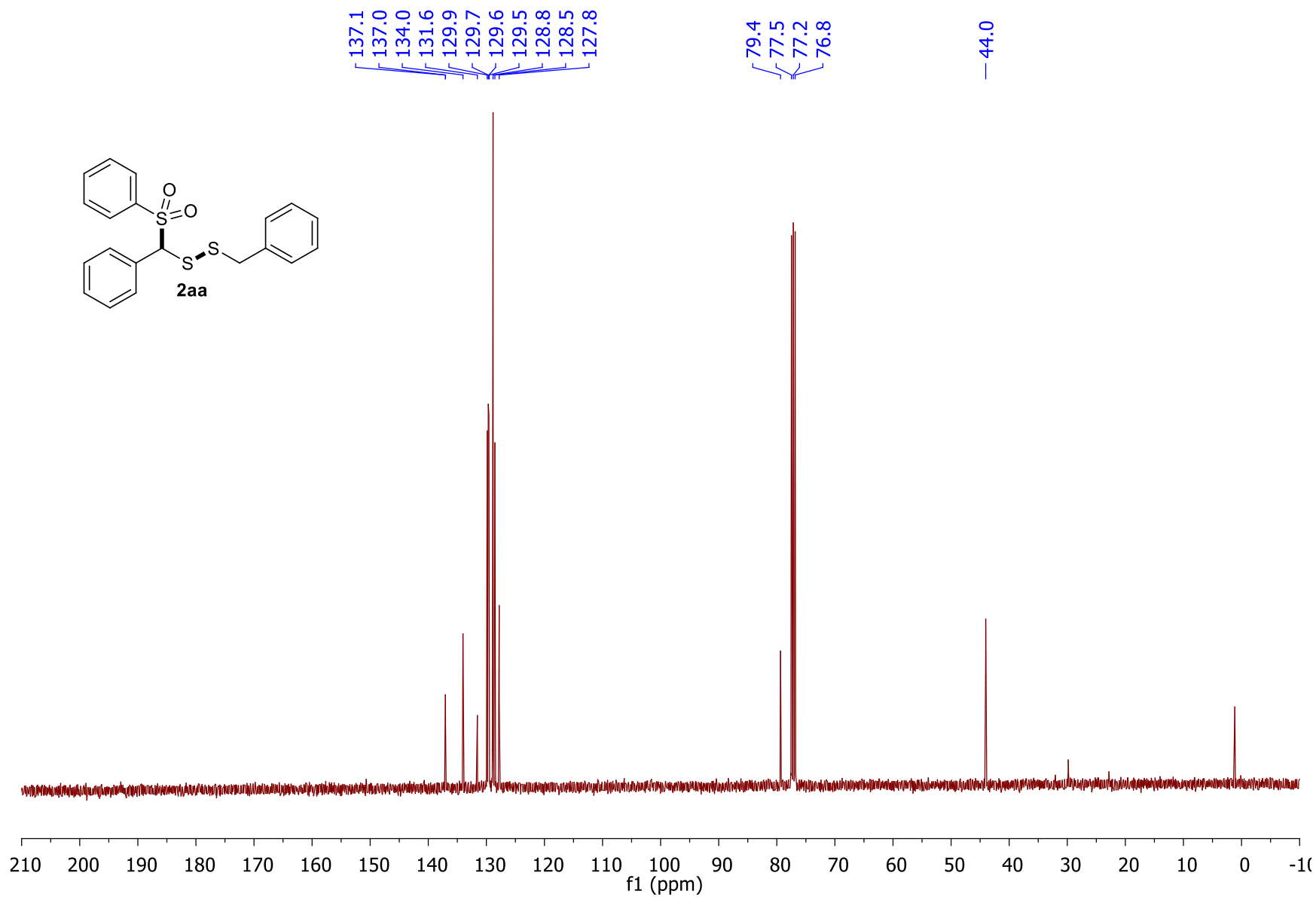
## <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Final Products

(**Note:** Common laboratory solvents as trace impurities, peaks at  $\delta$  1.25 & 1.58 refers to grease and moisture respectively in a <sup>1</sup>H NMR in CDCl<sub>3</sub>. For <sup>13</sup>C NMR in CDCl<sub>3</sub>, a peak at  $\delta$  29.7 represents to grease; Ref. H. E. Gottlie, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, **1997**, 62, 7512).

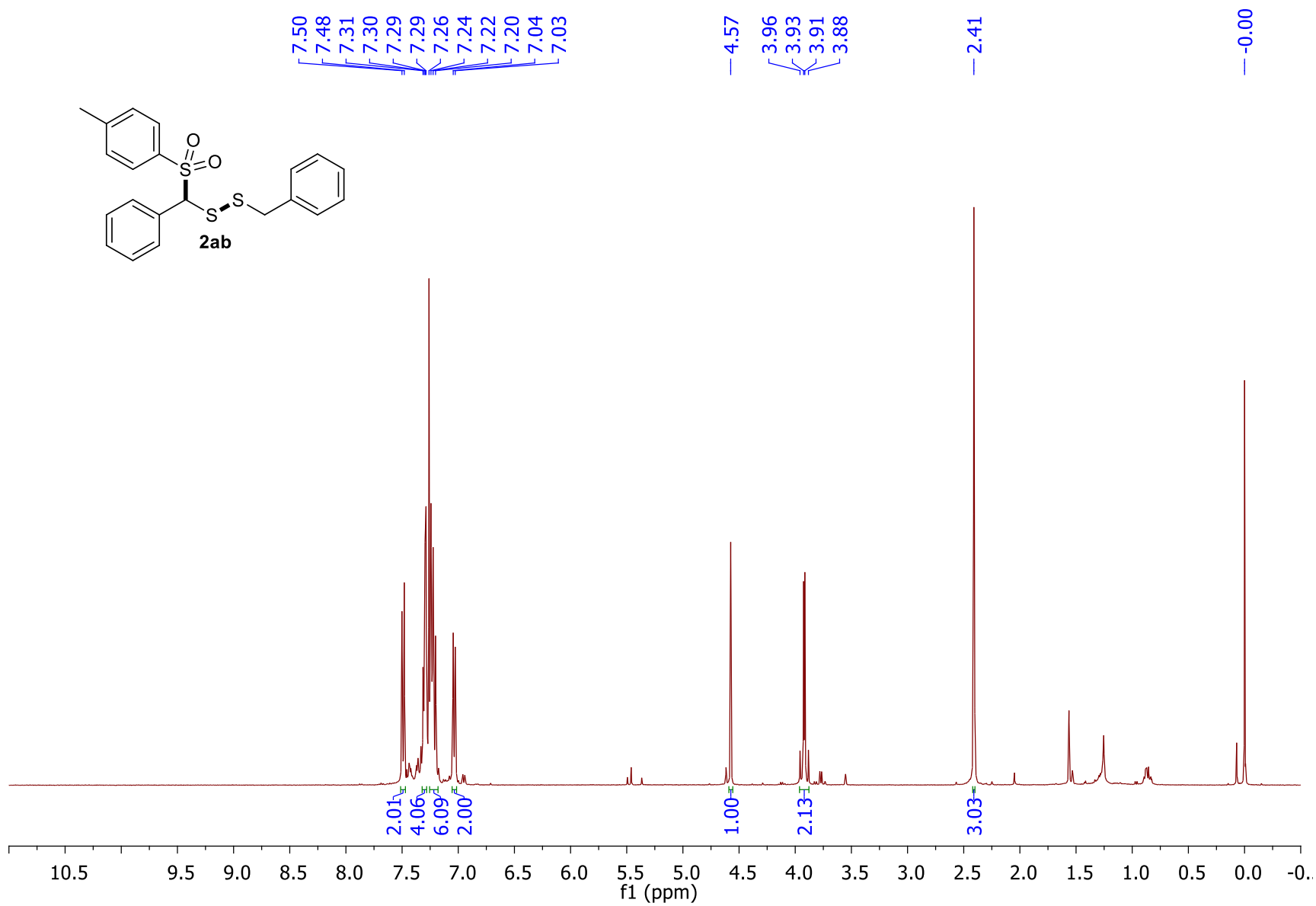




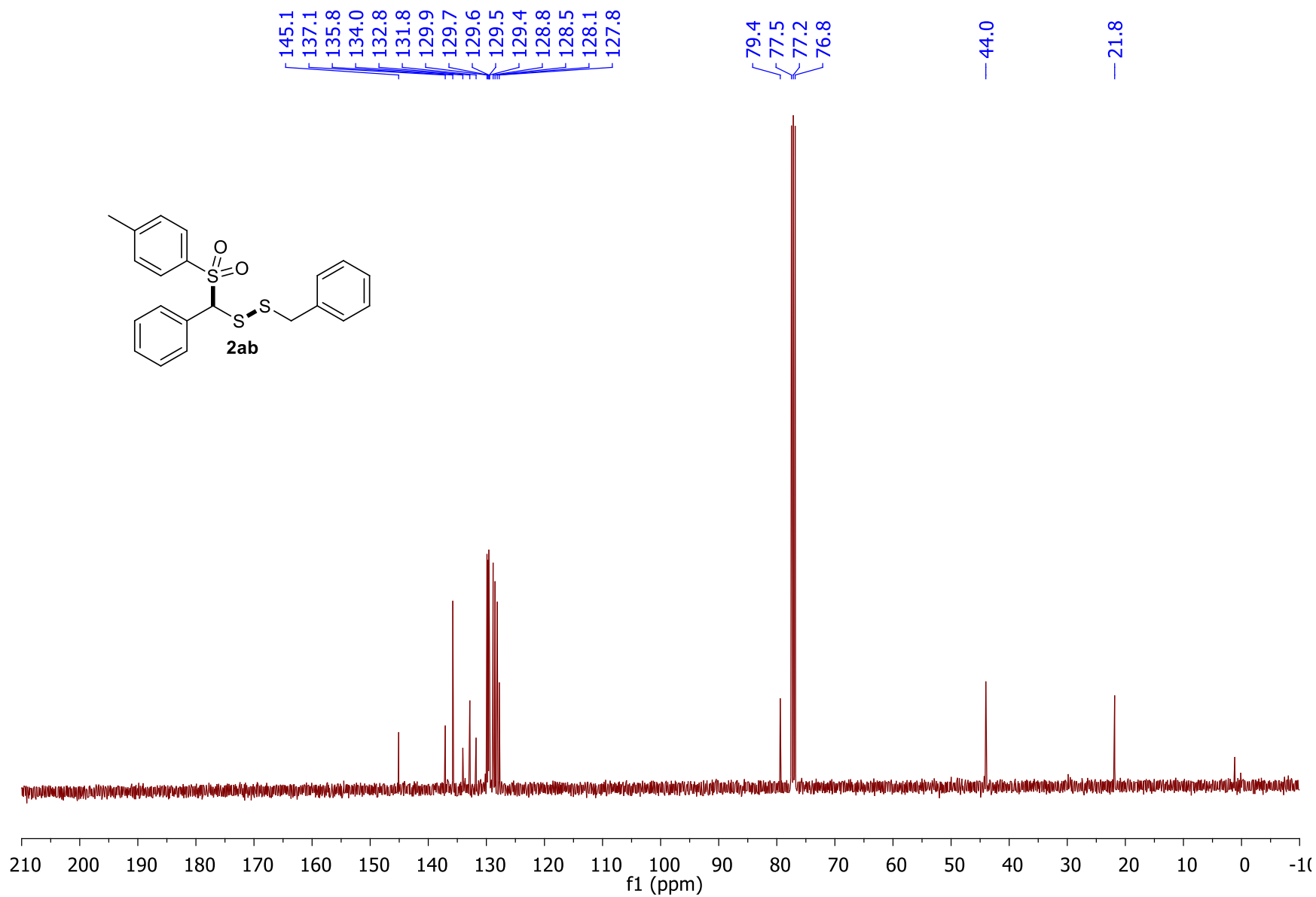
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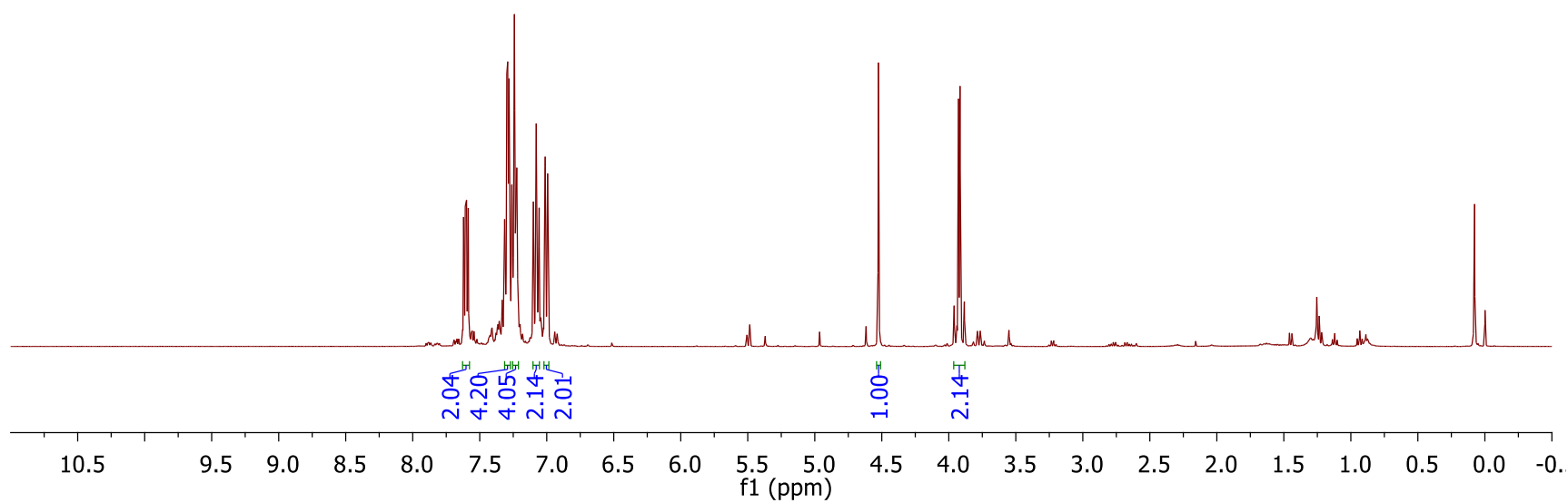
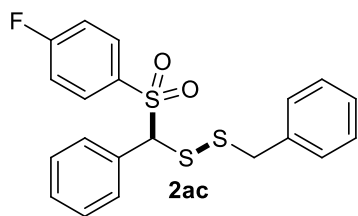


Supplementary Information.....

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0.08

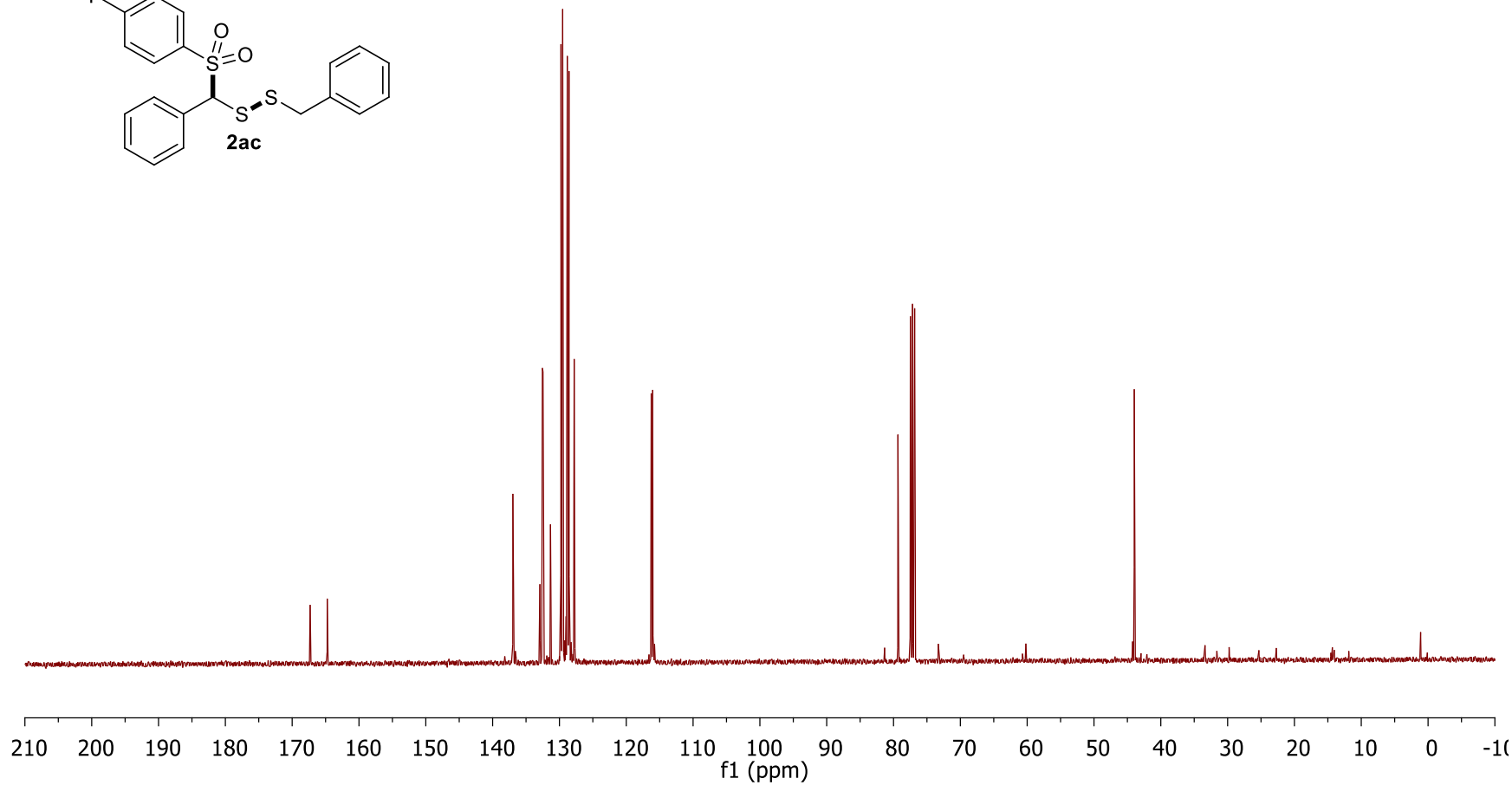
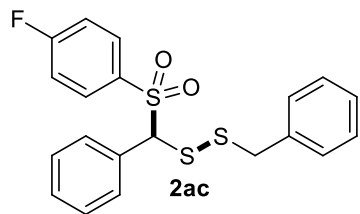


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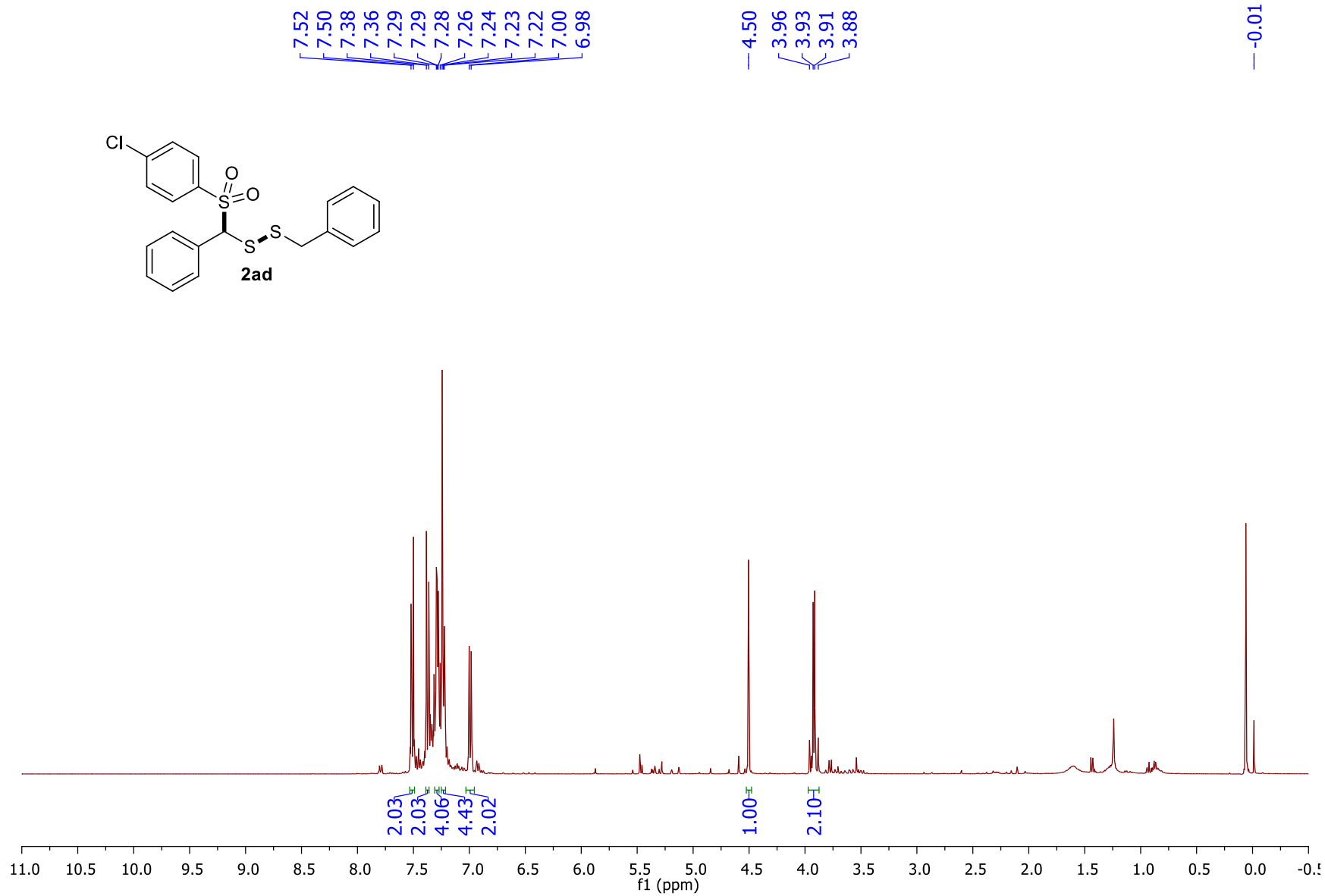
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116.0

79.3  
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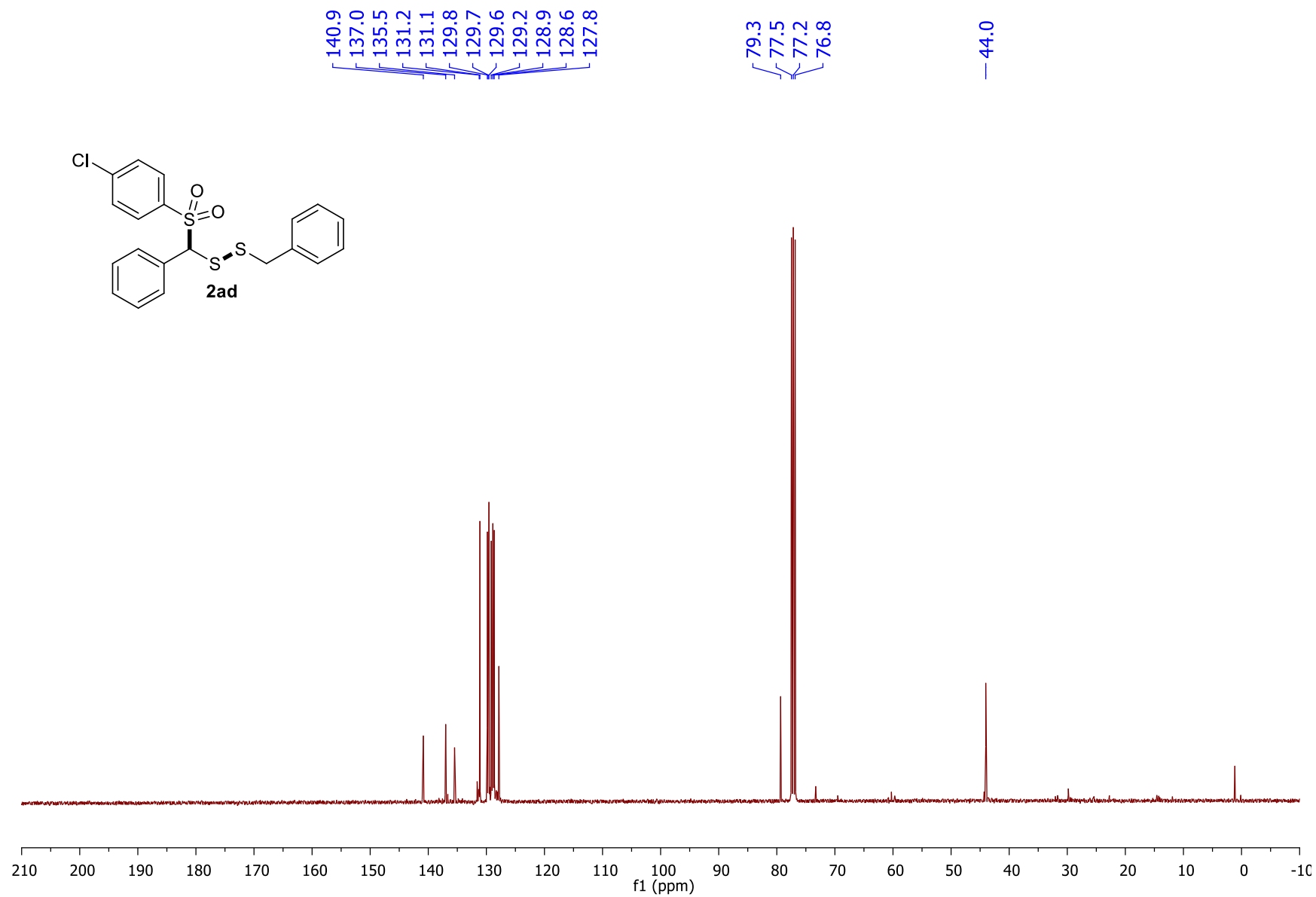
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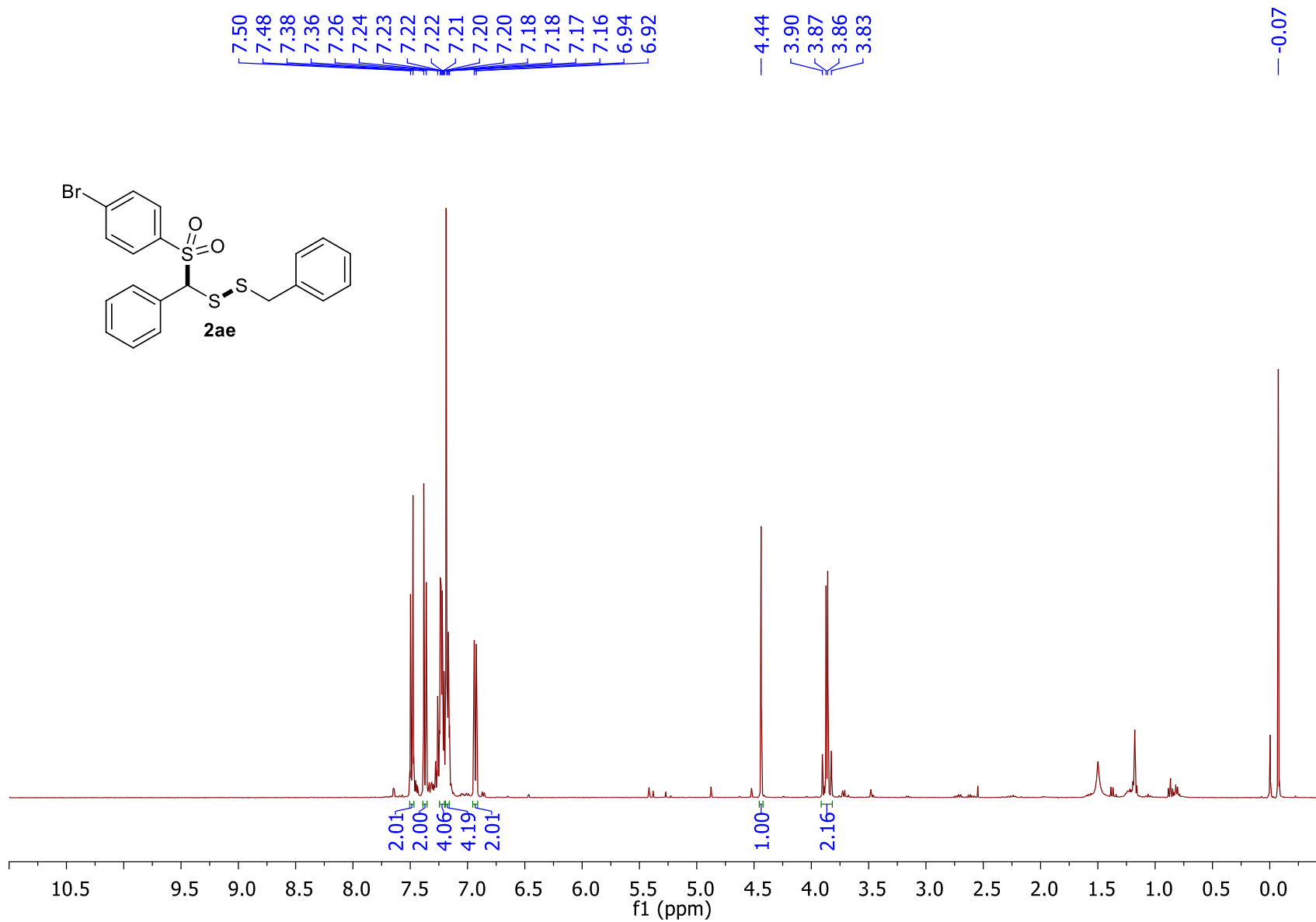
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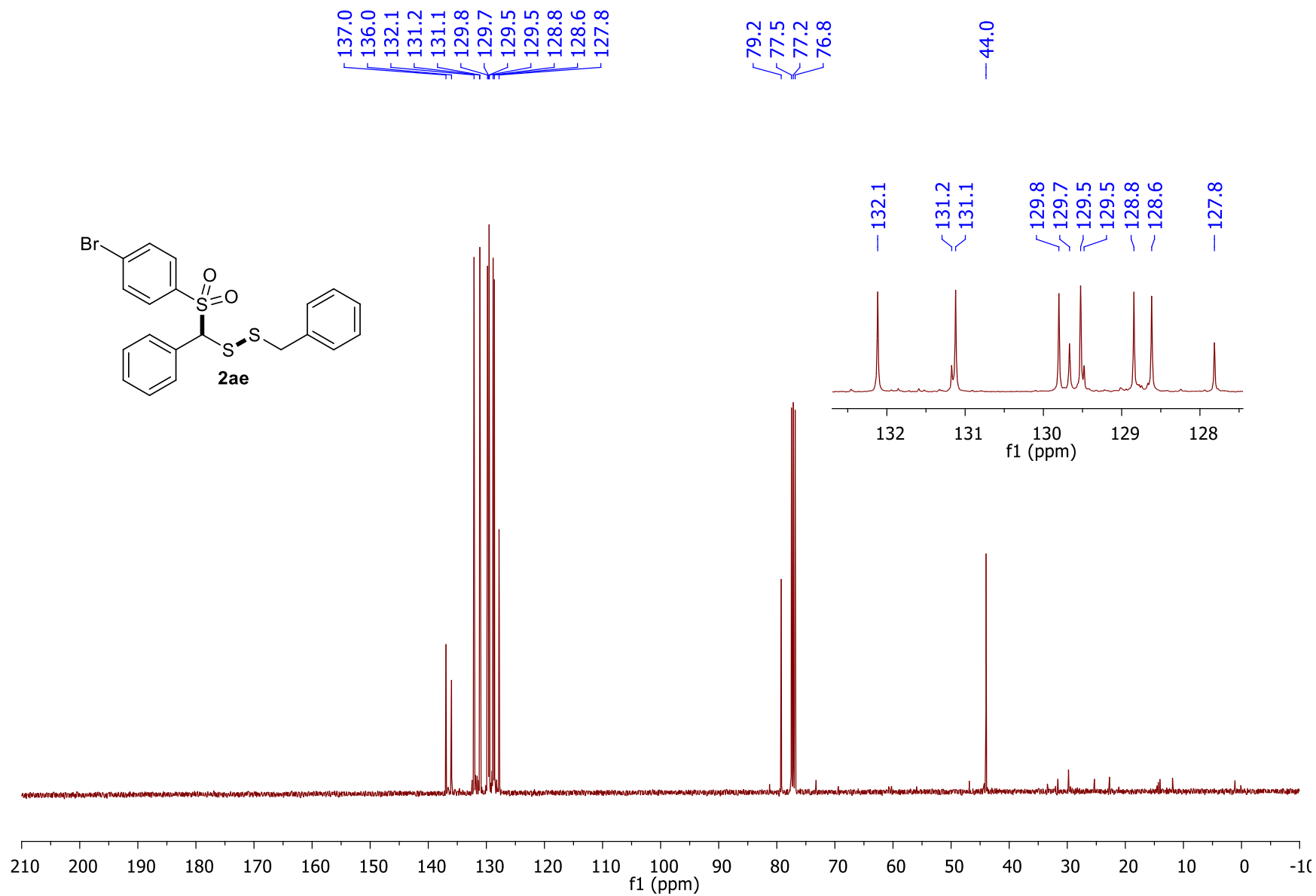


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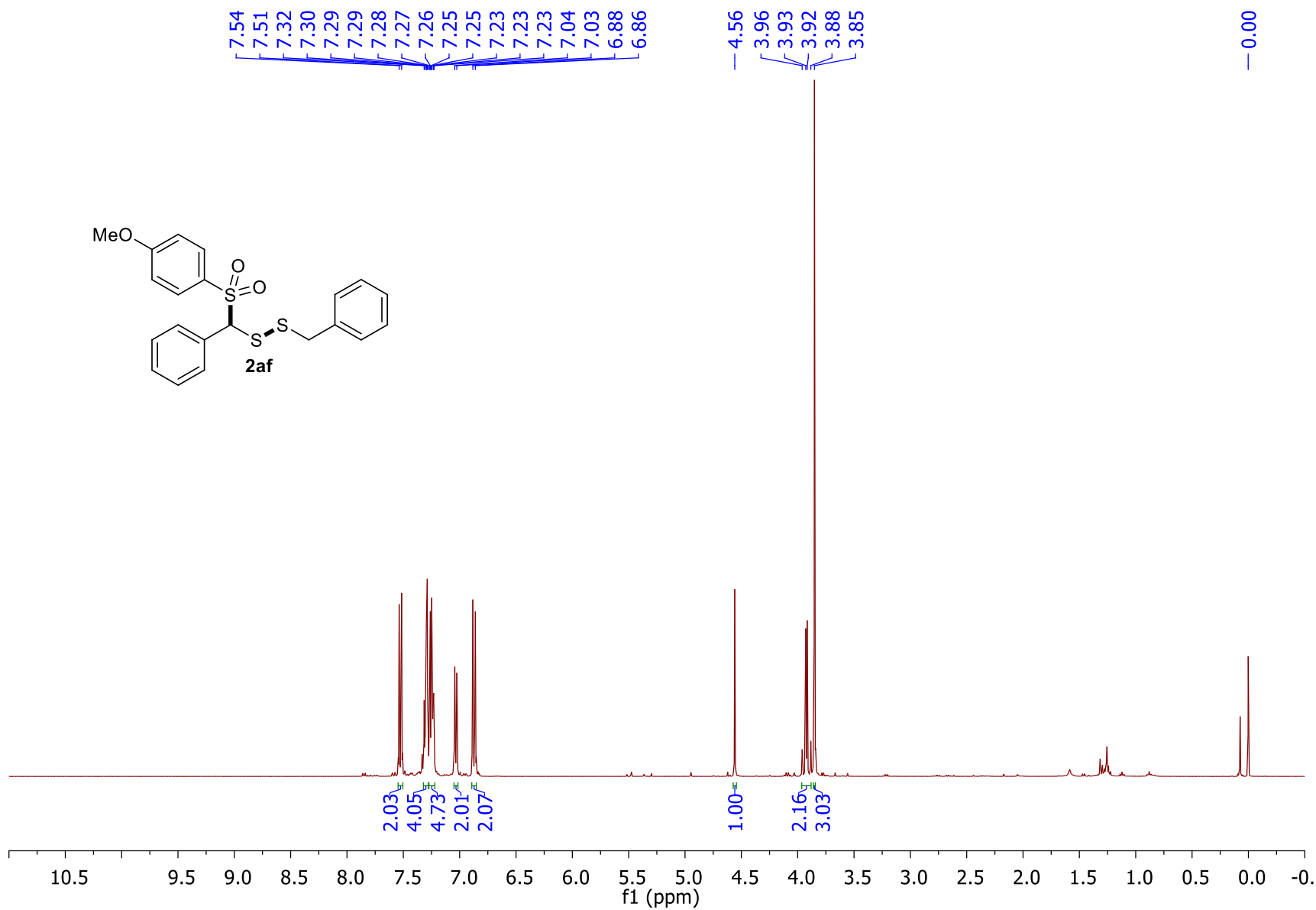




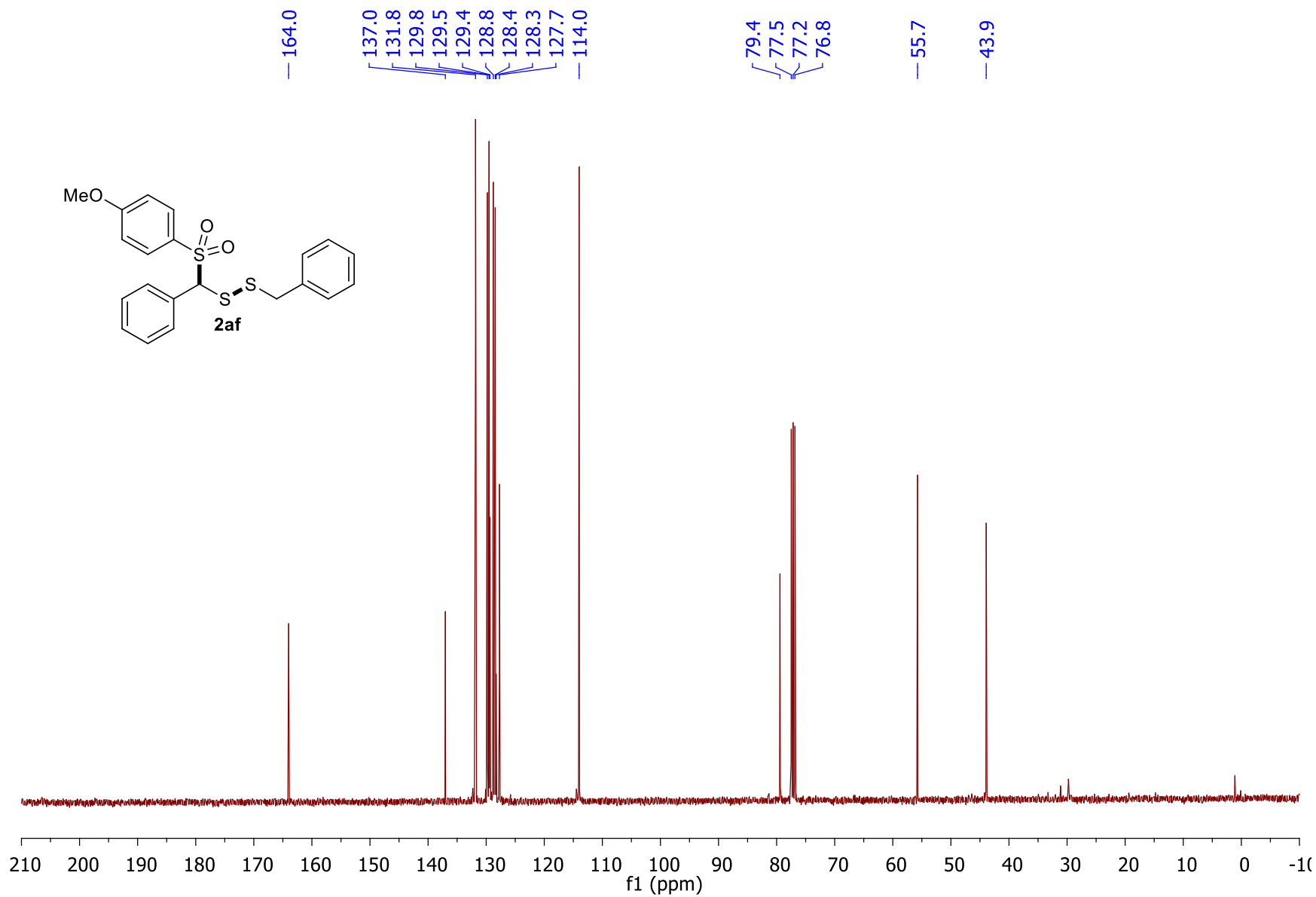
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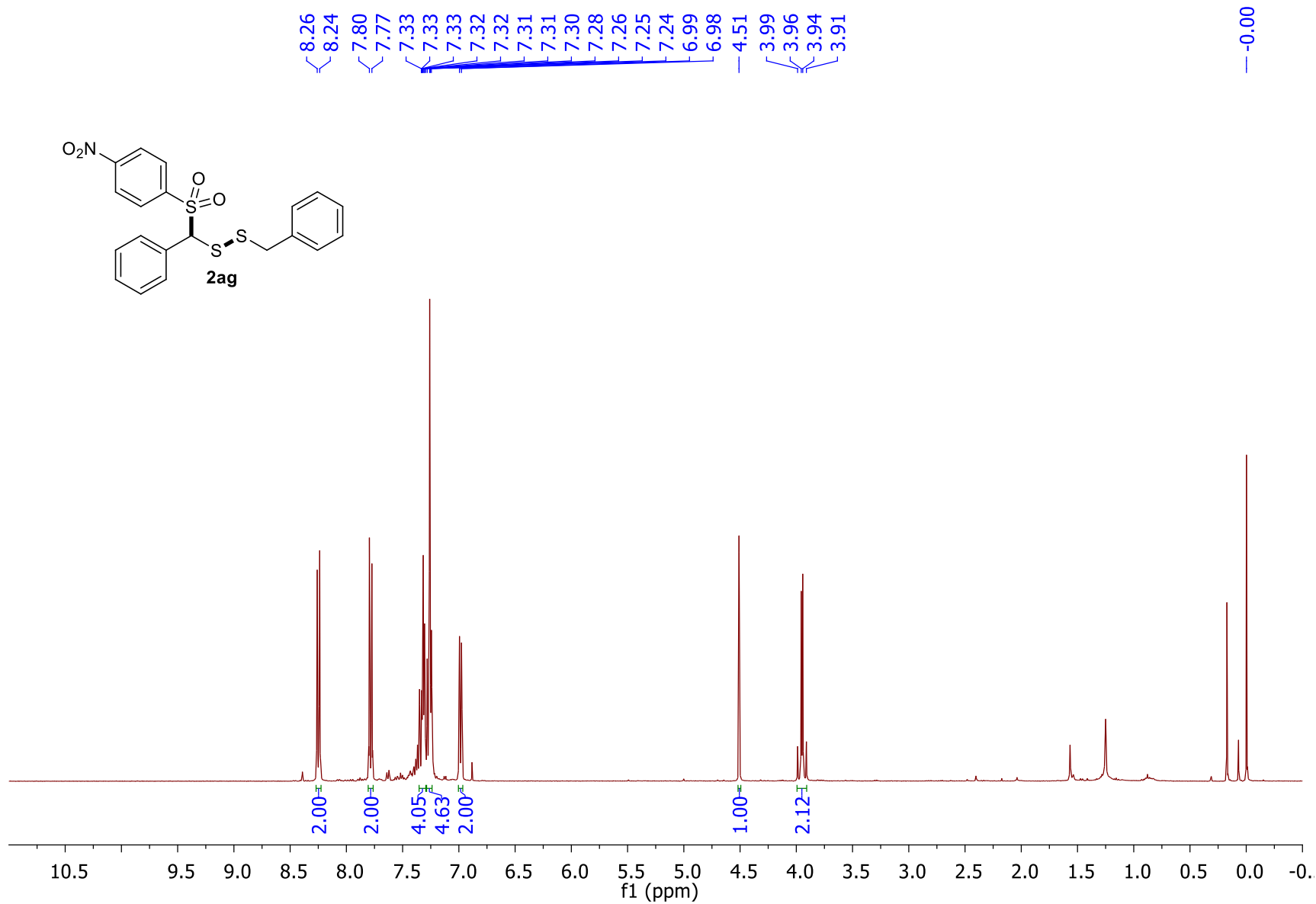
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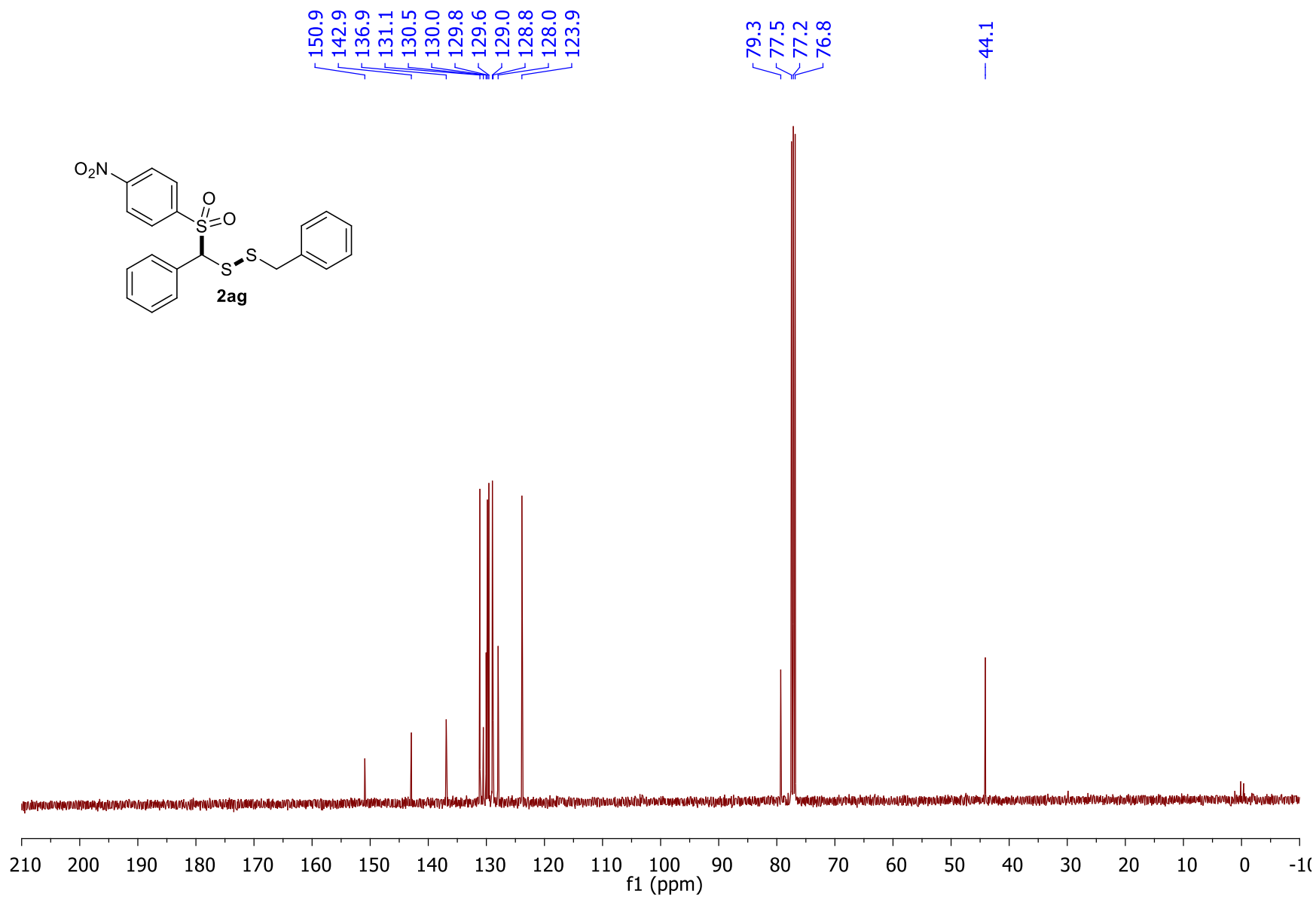
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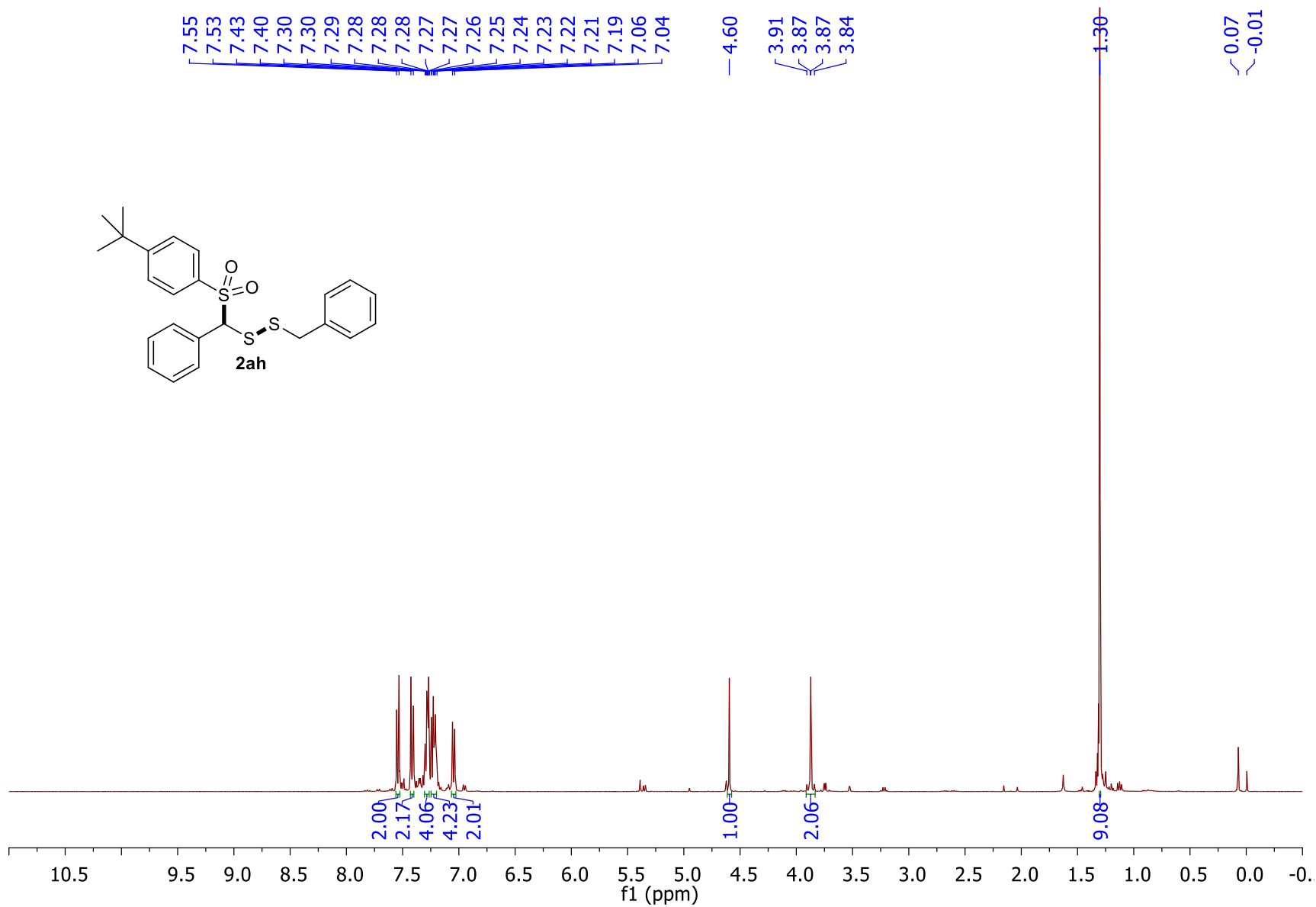
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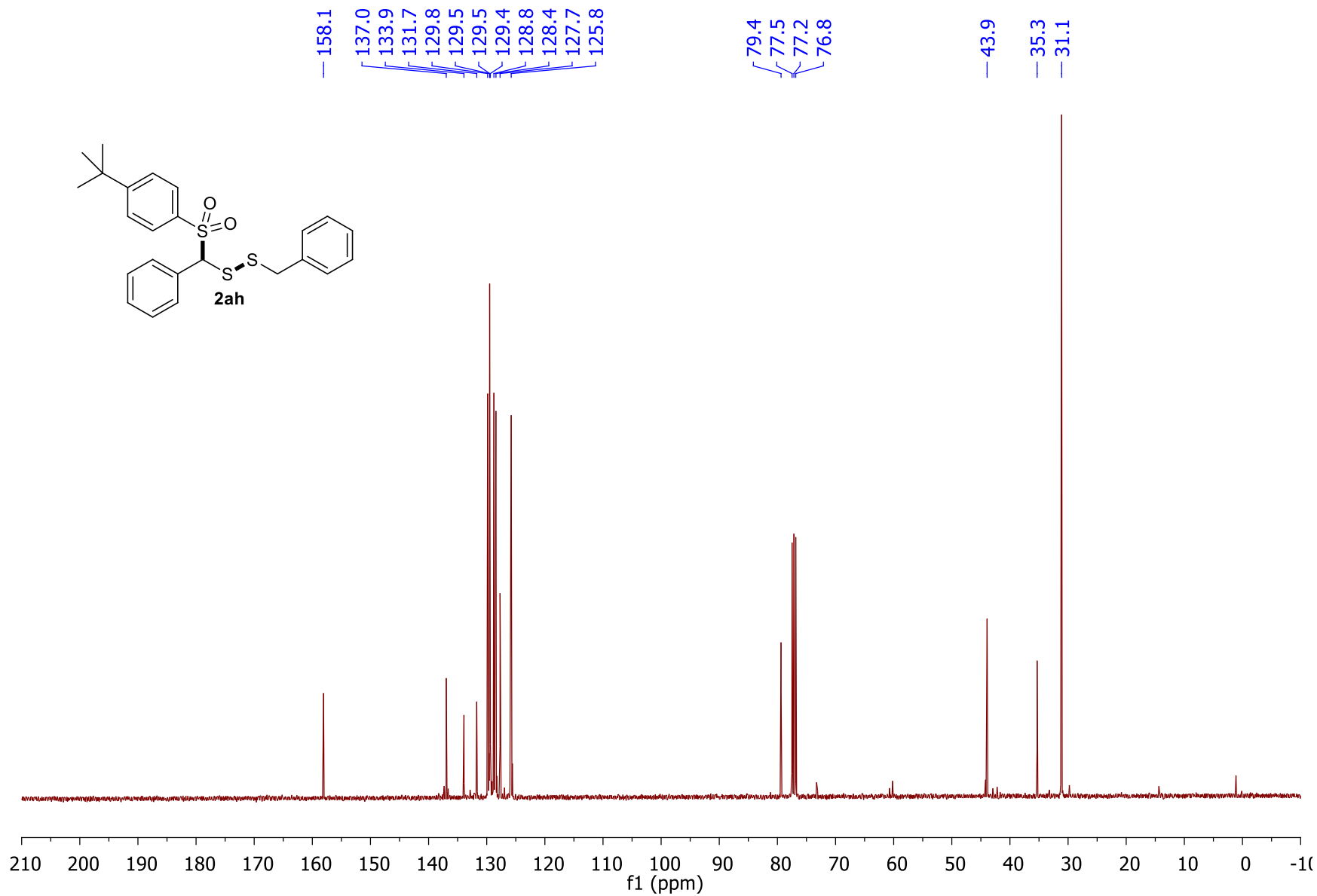
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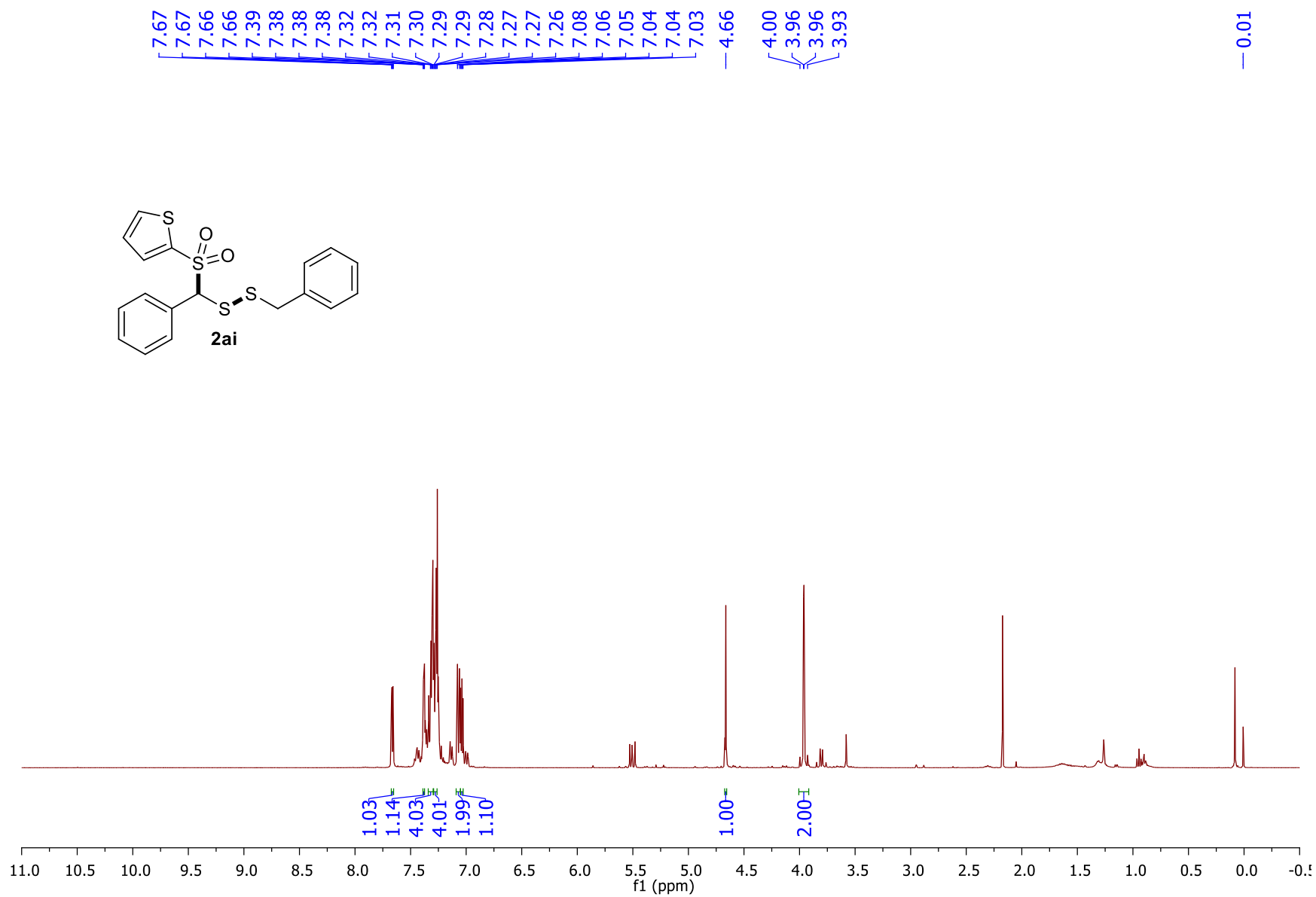
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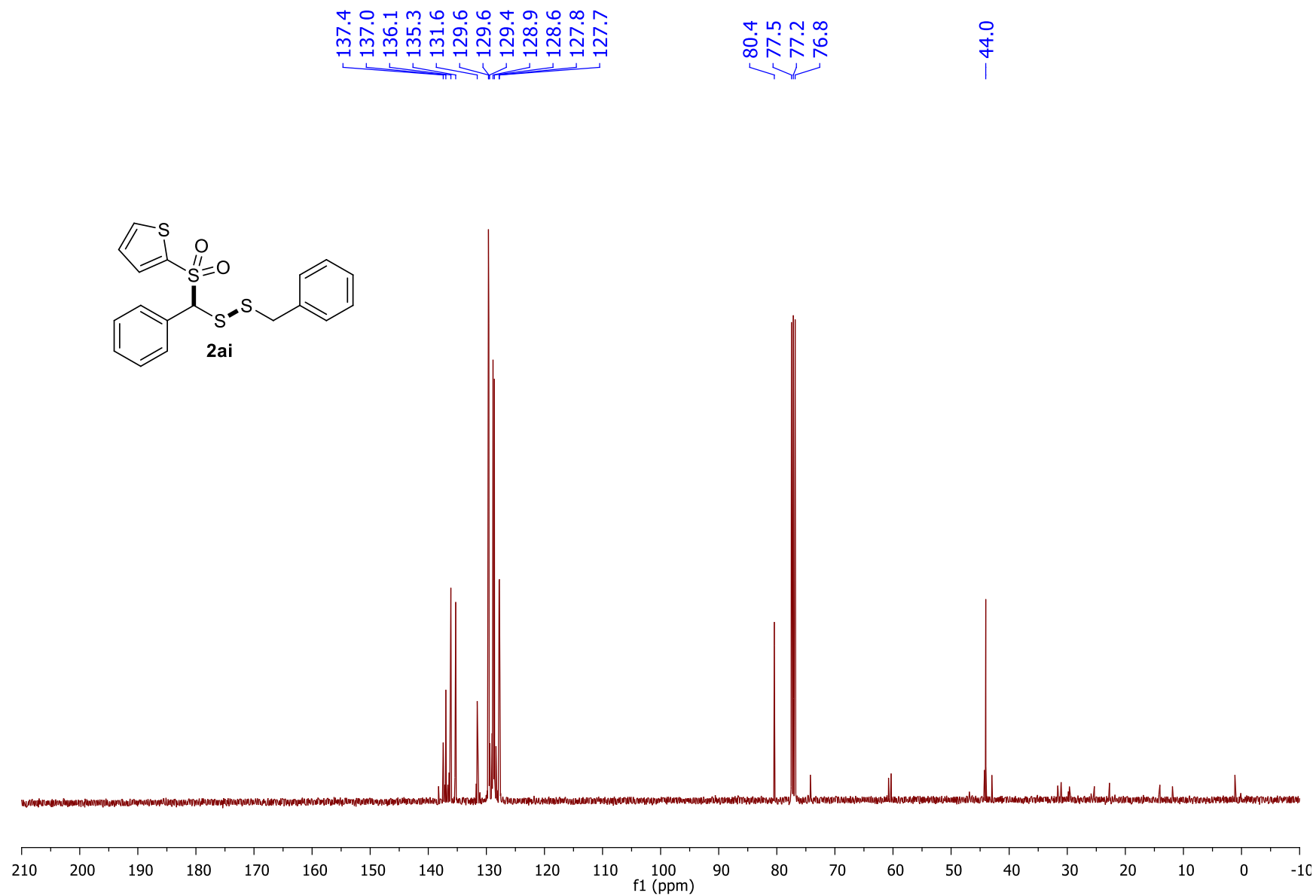


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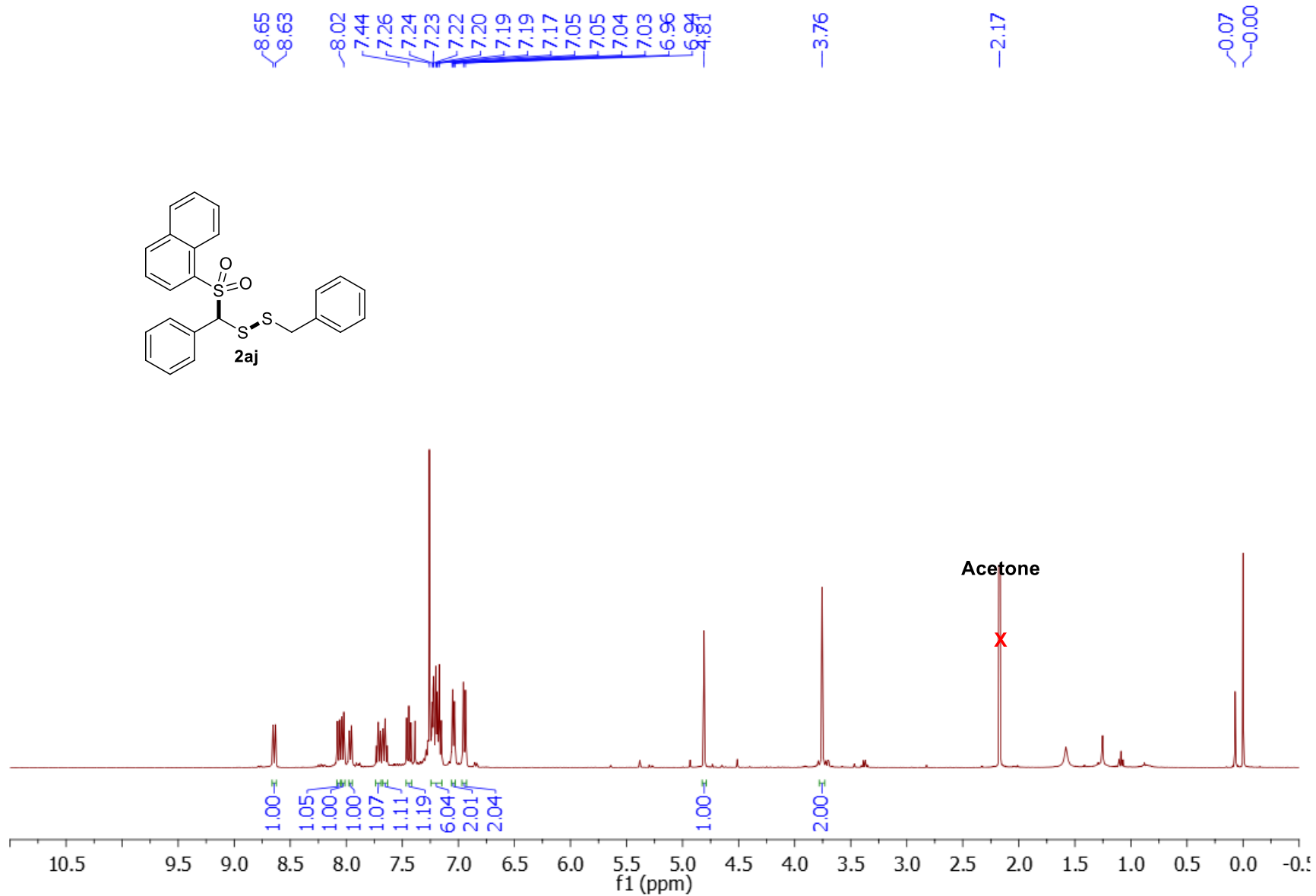




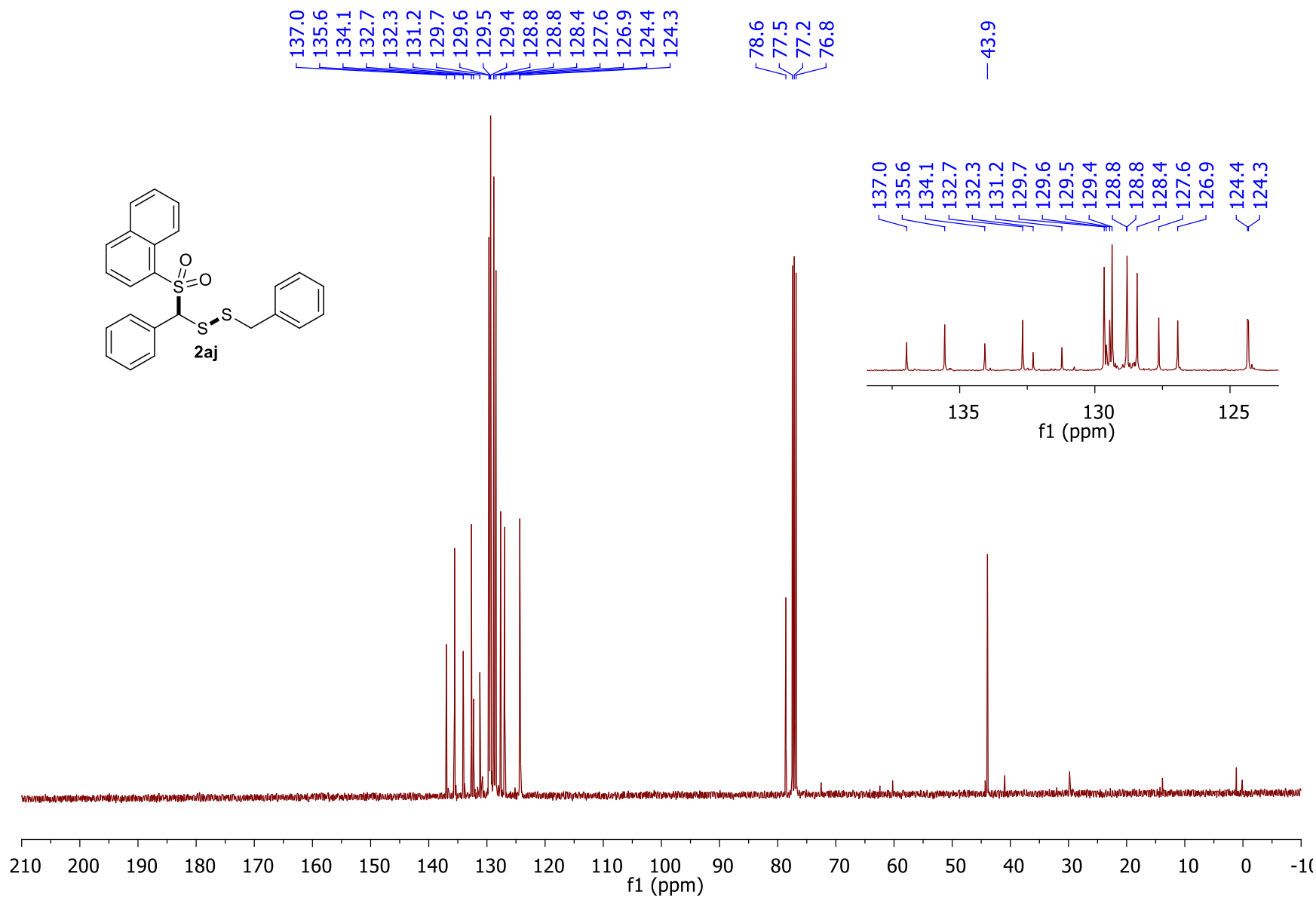
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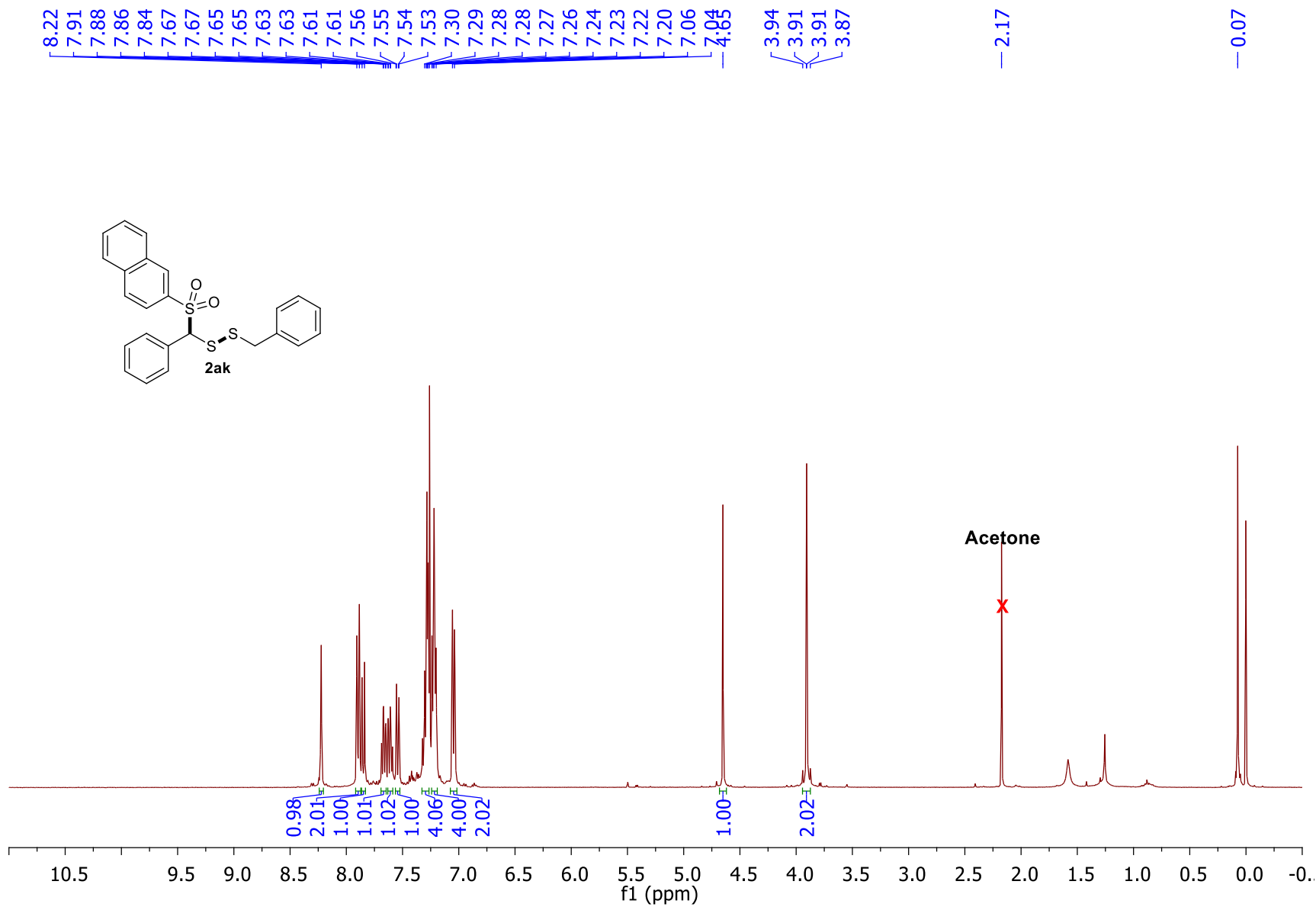
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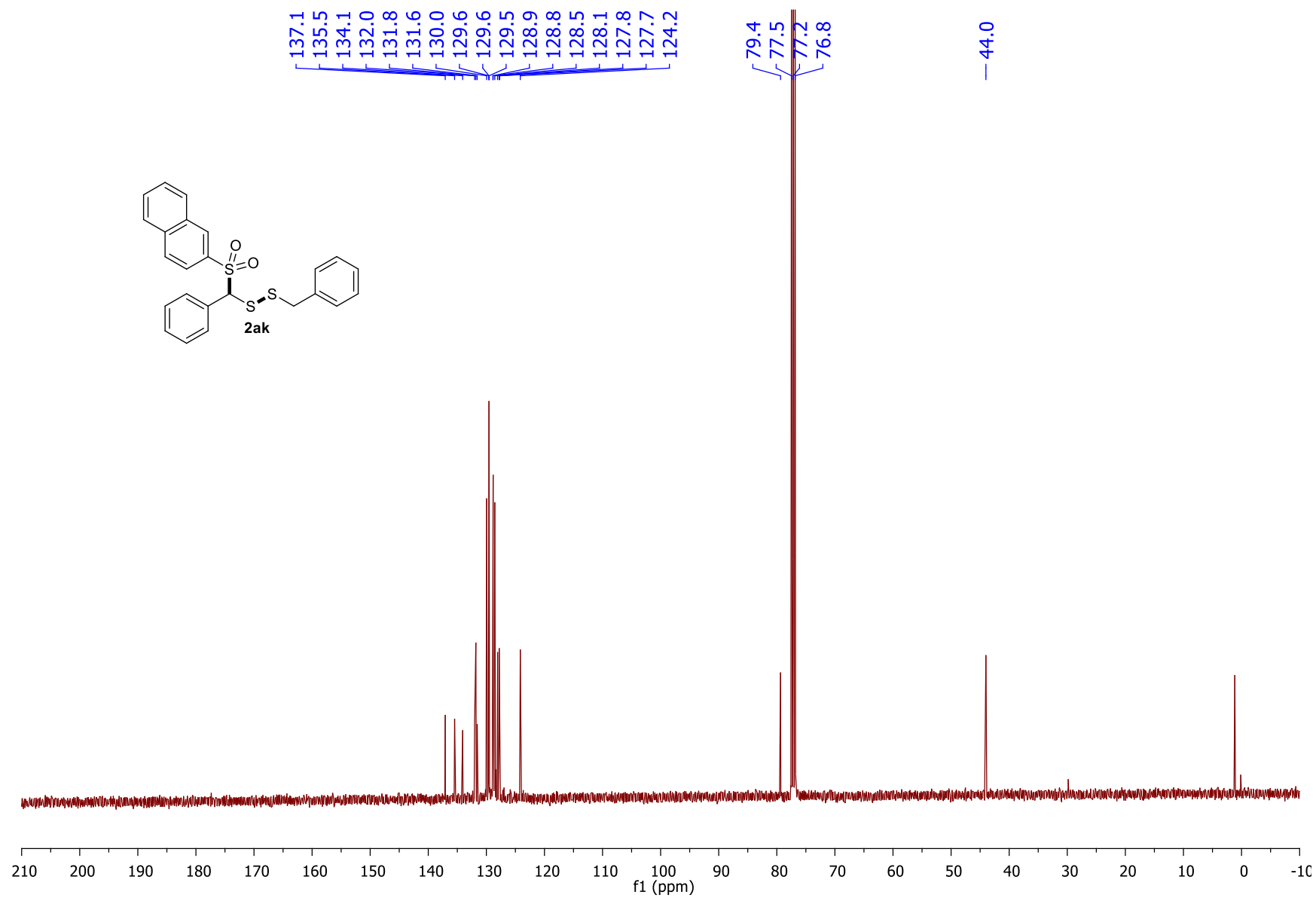
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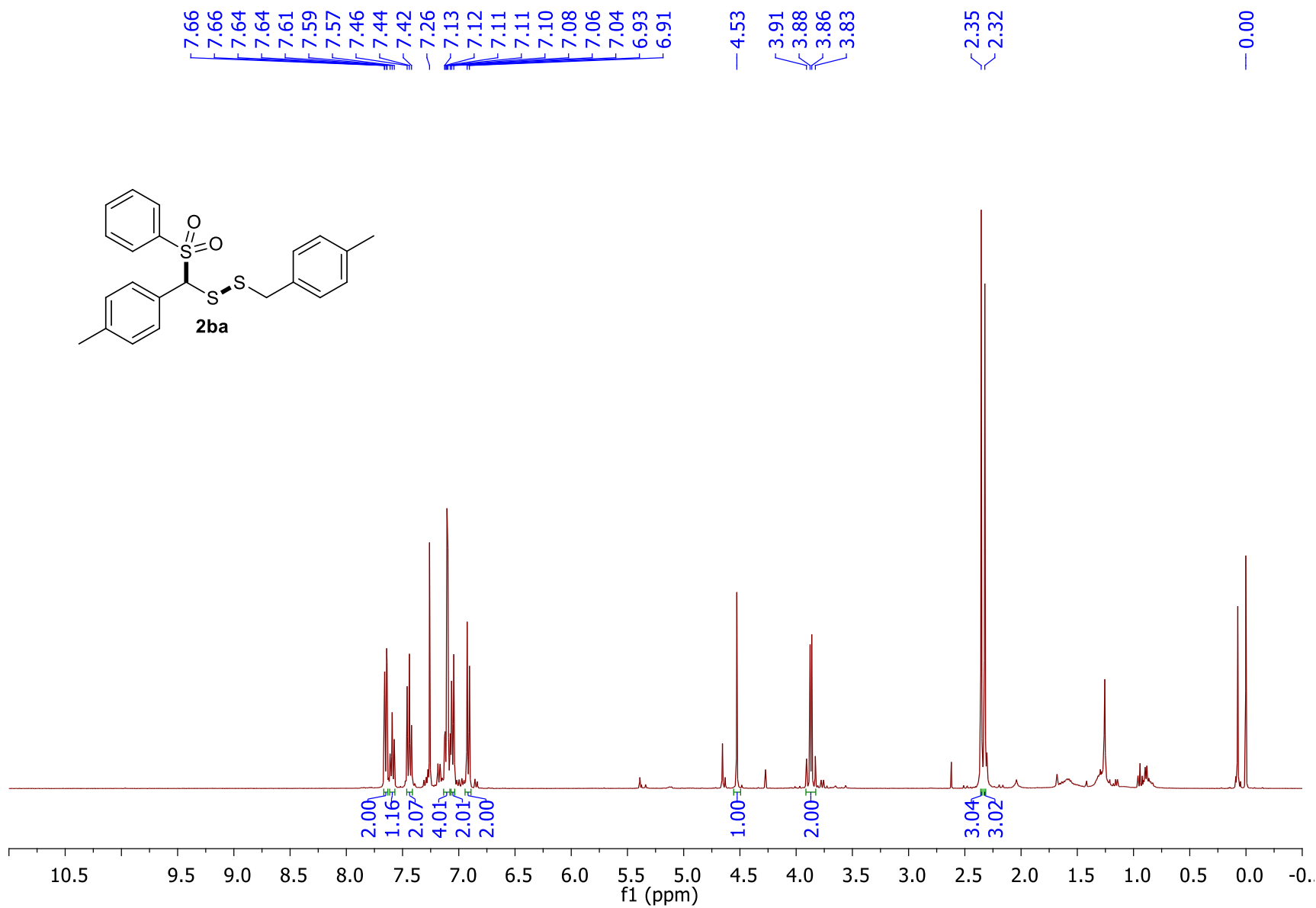
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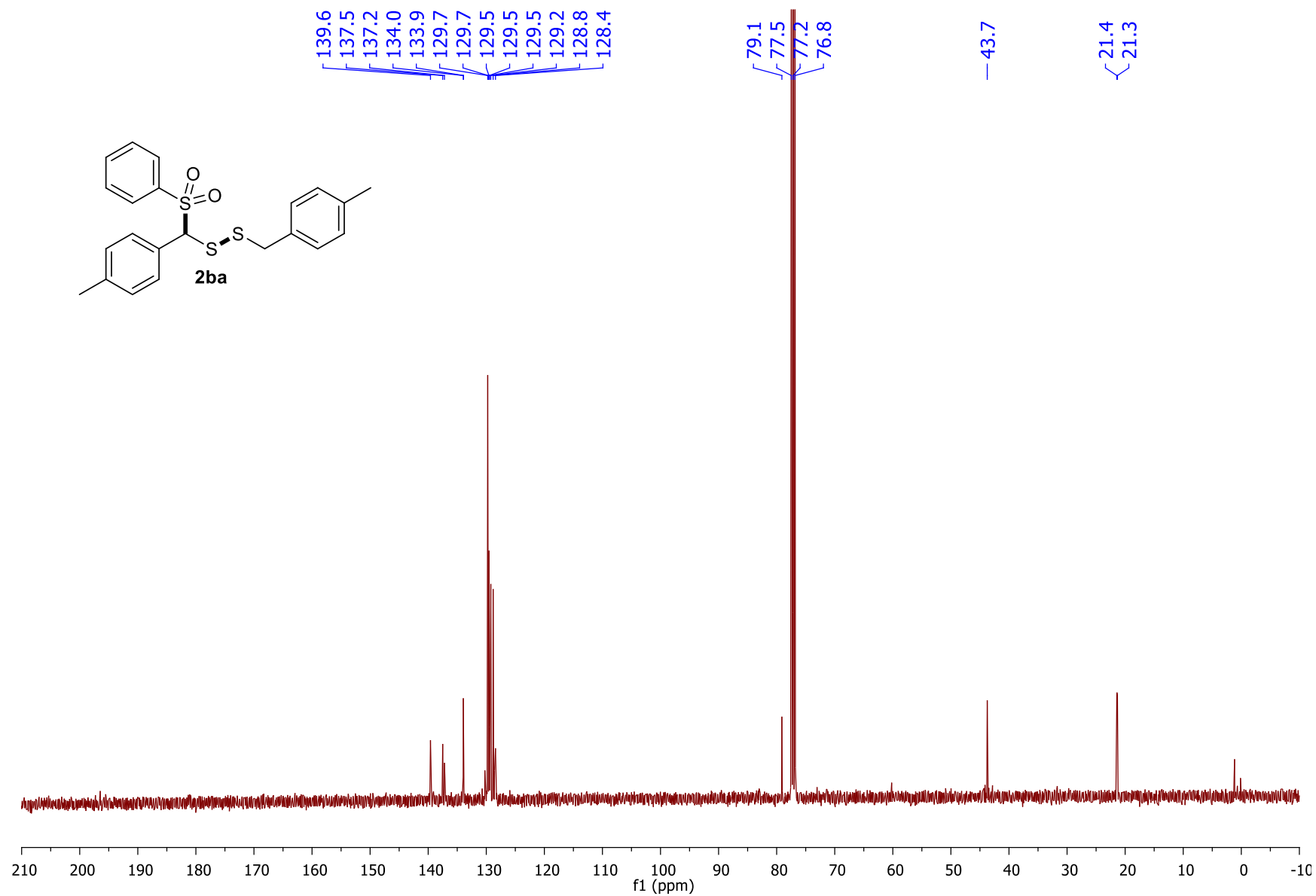
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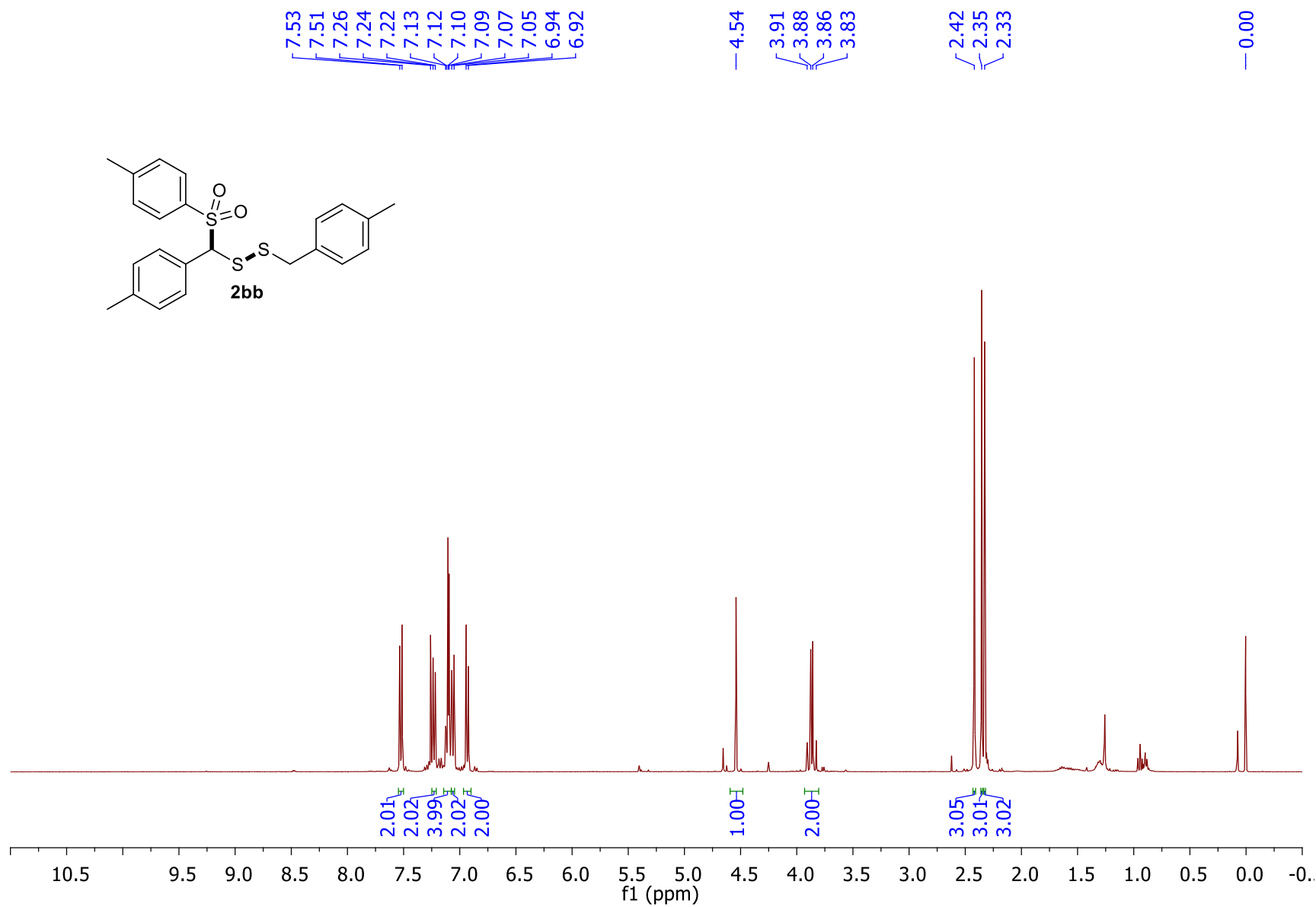
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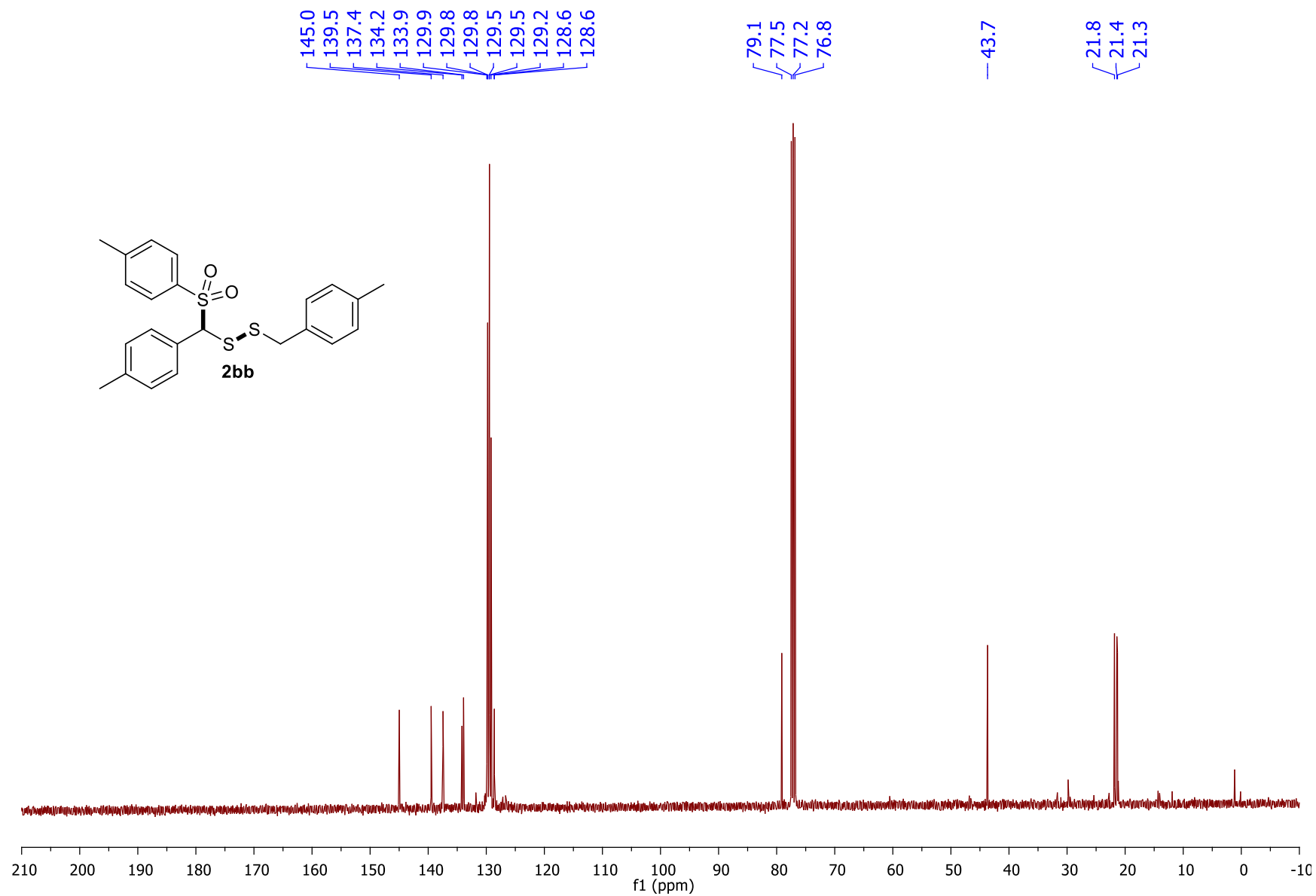


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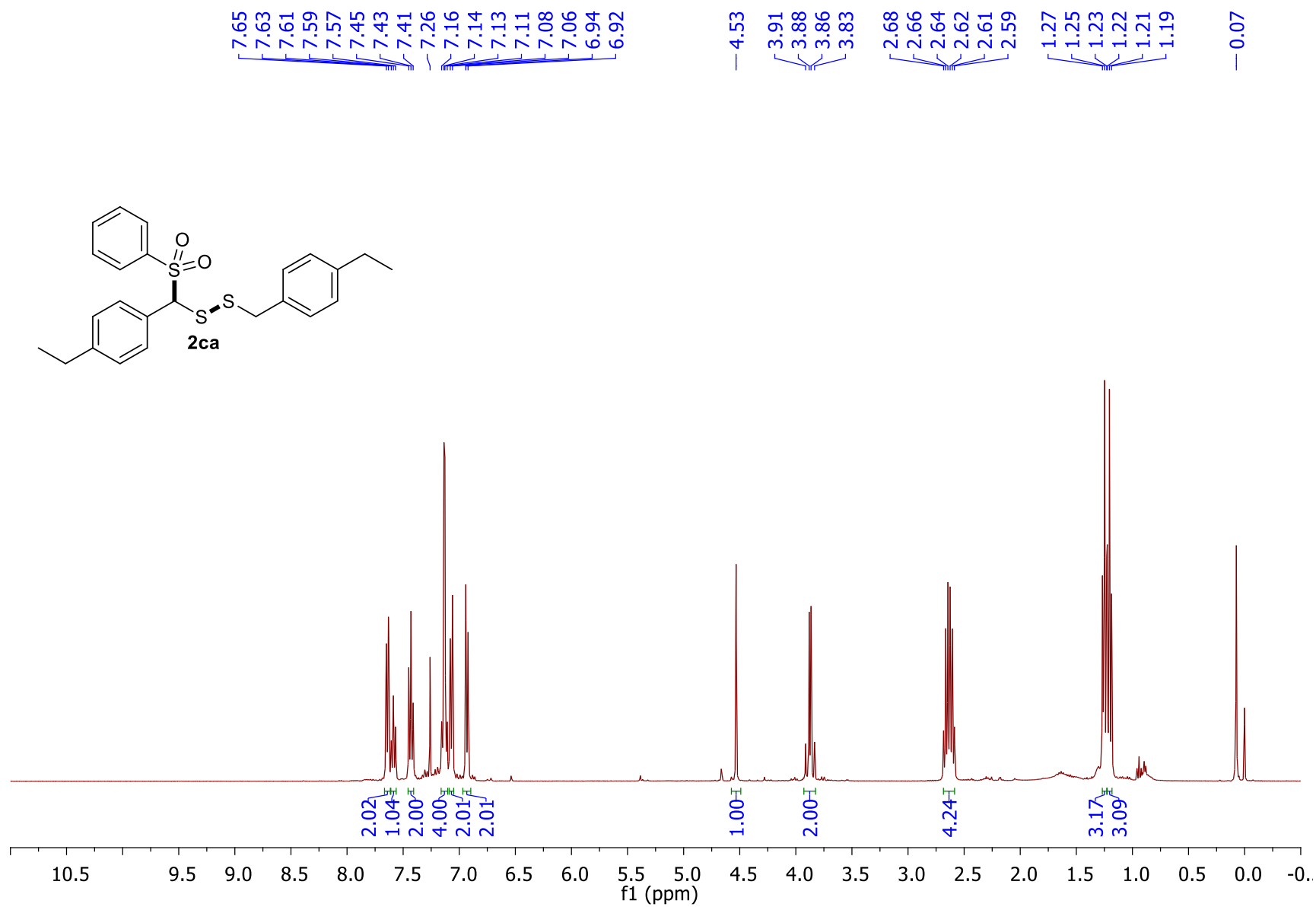




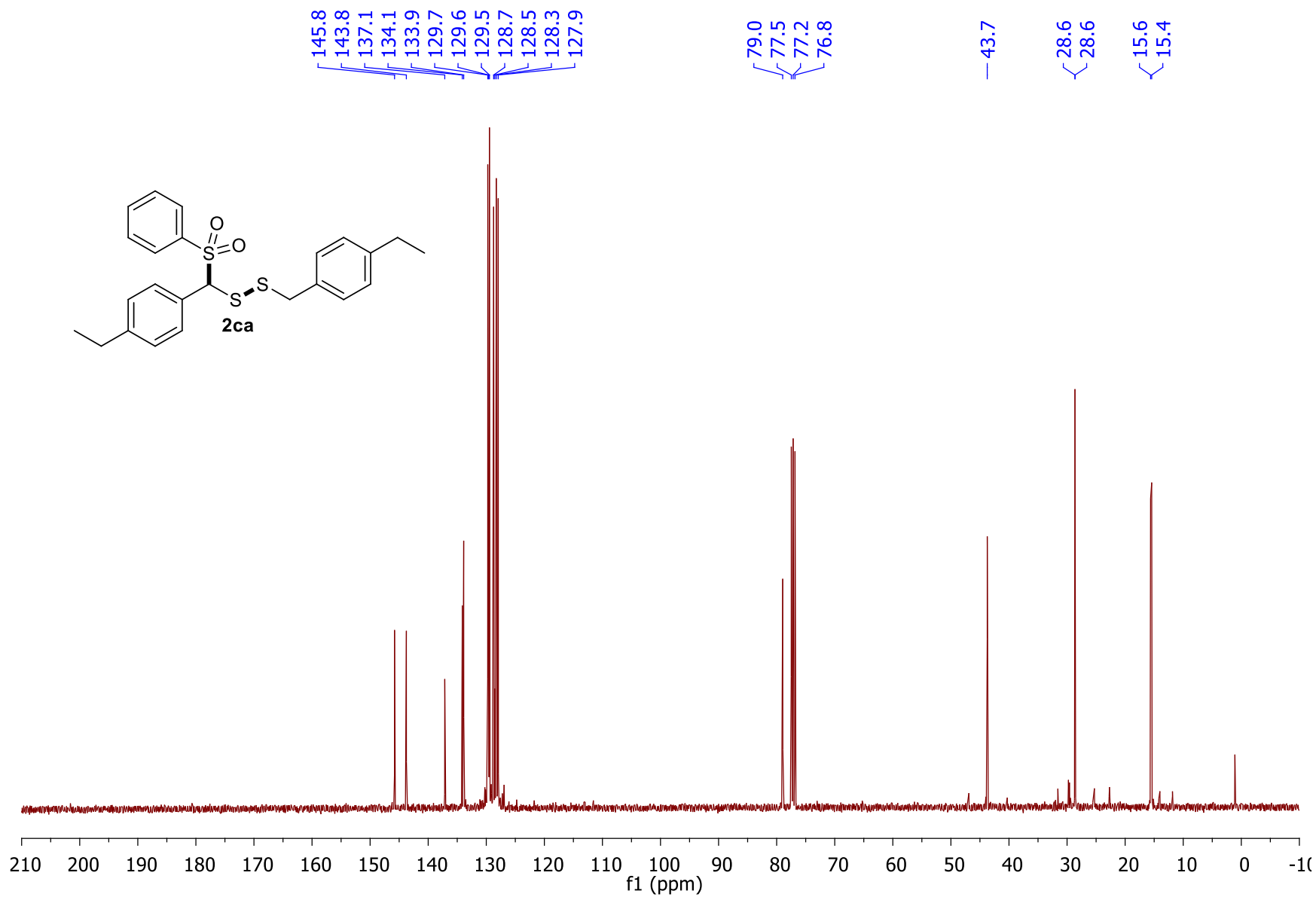
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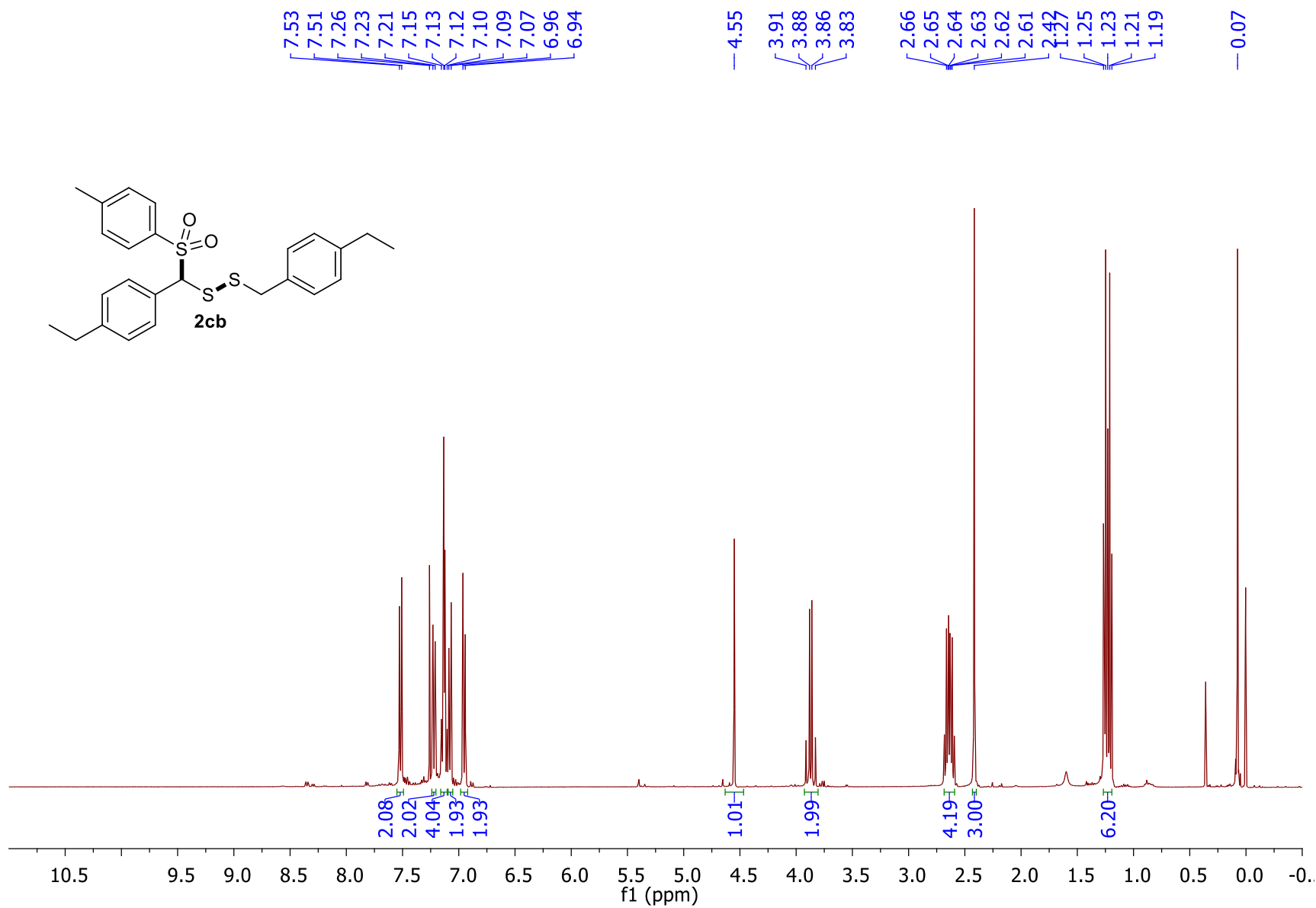
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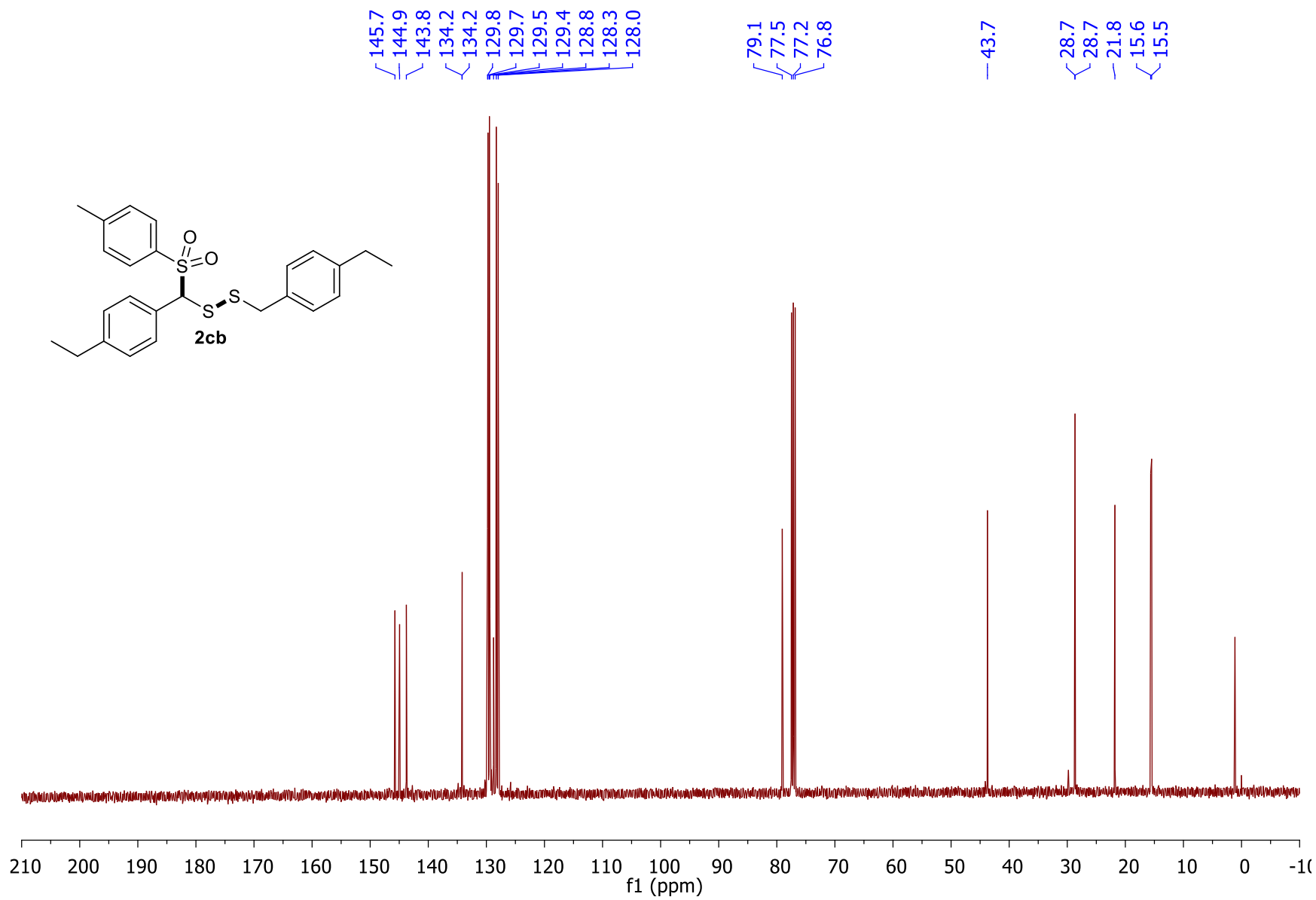
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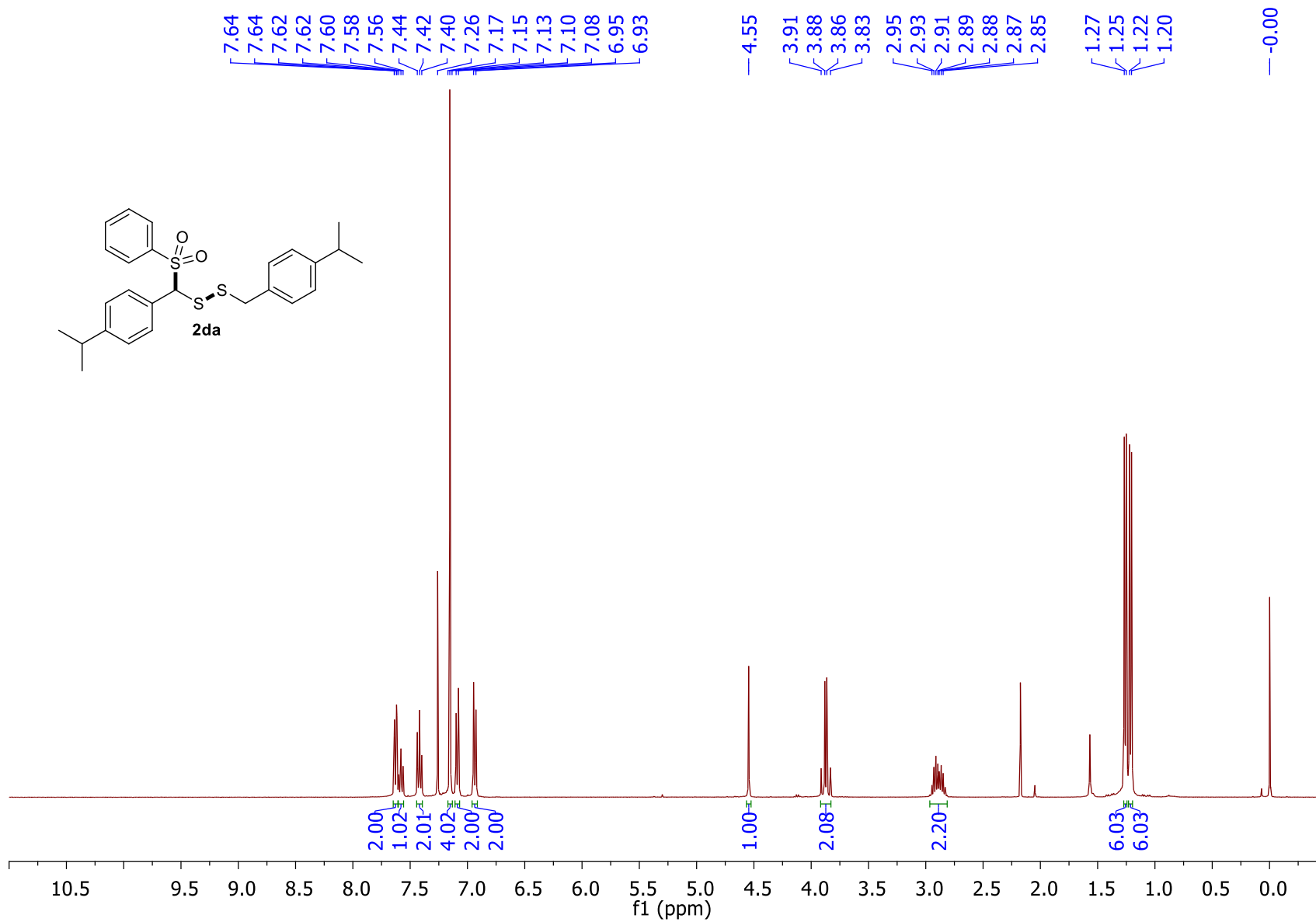
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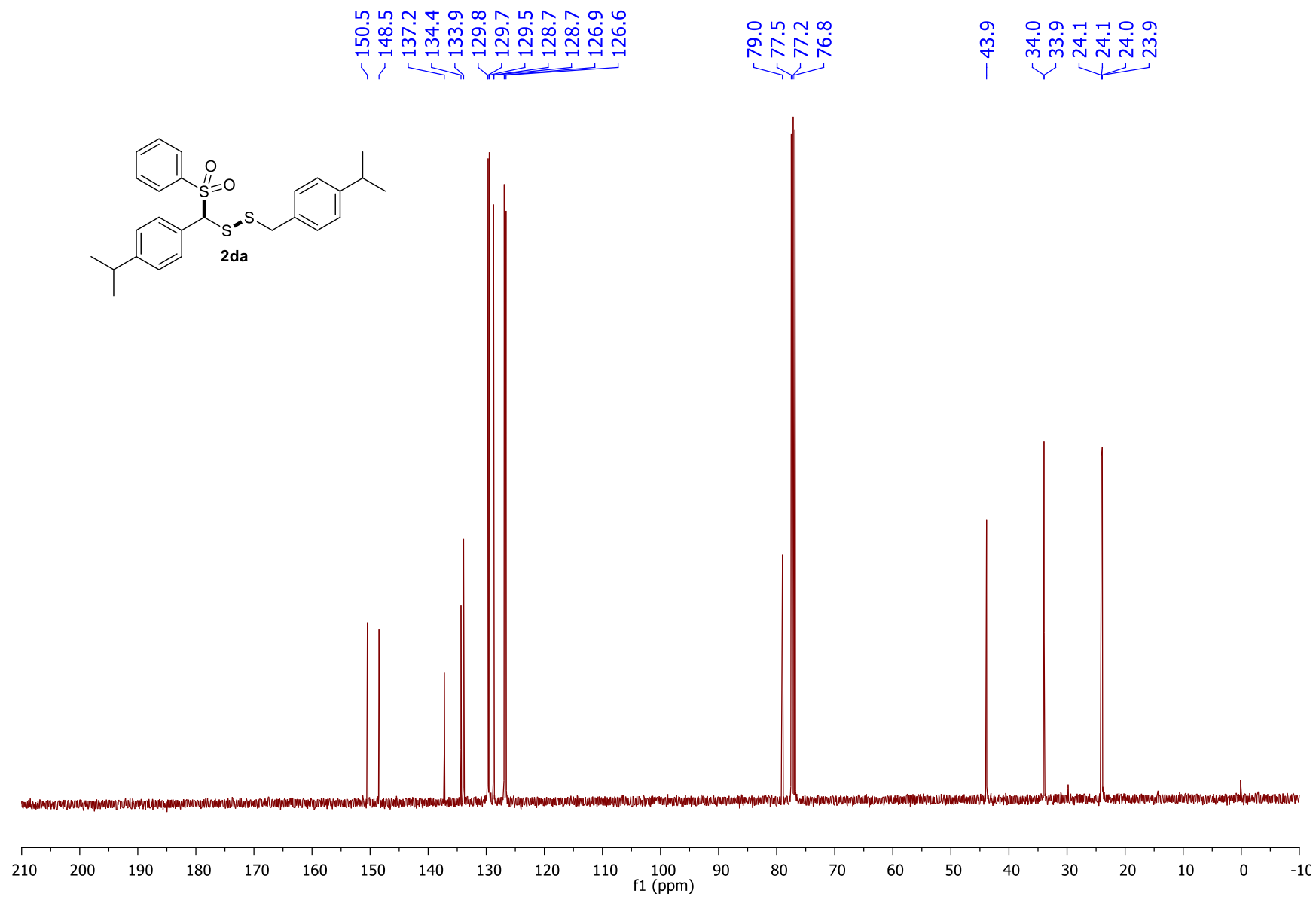
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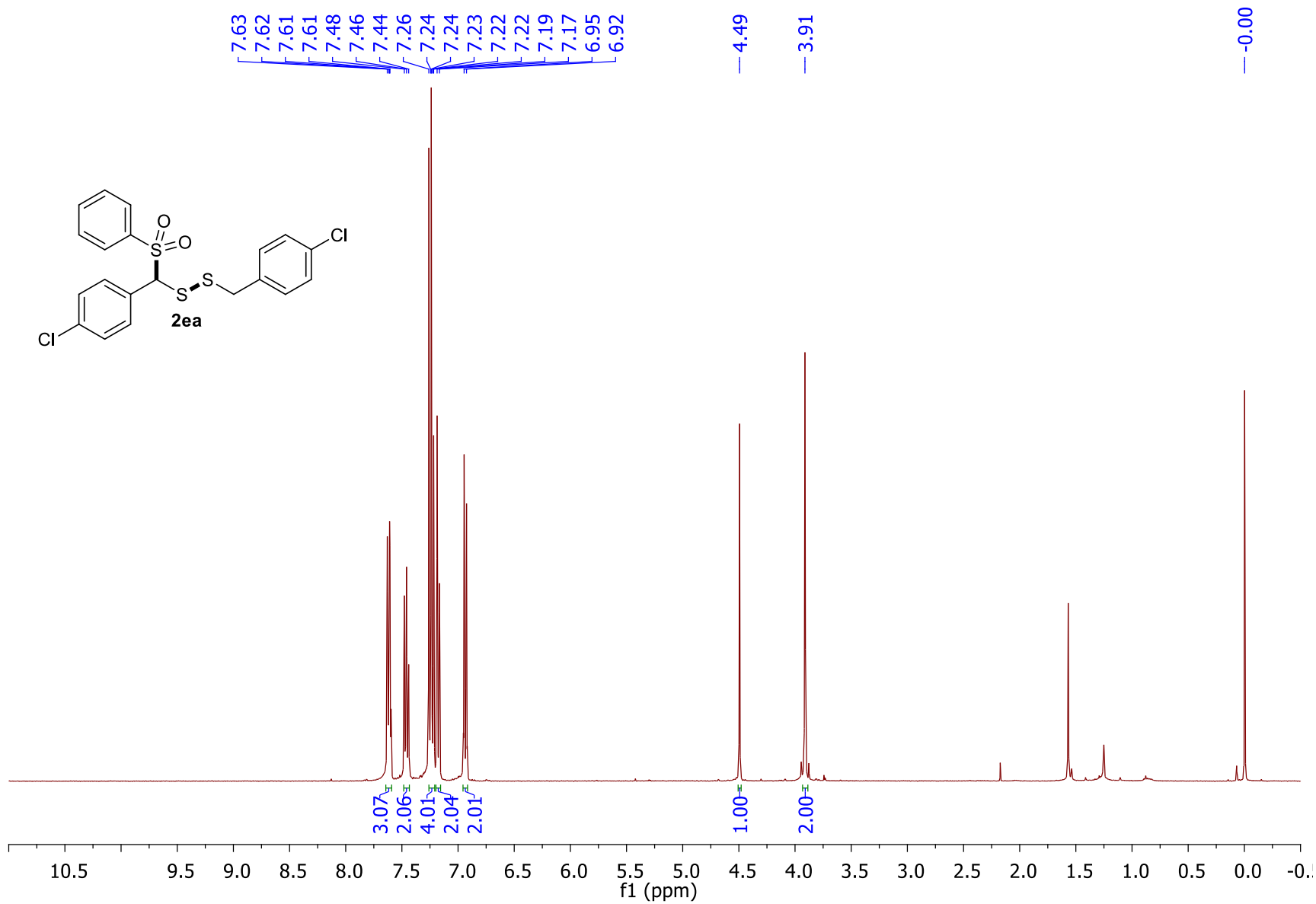
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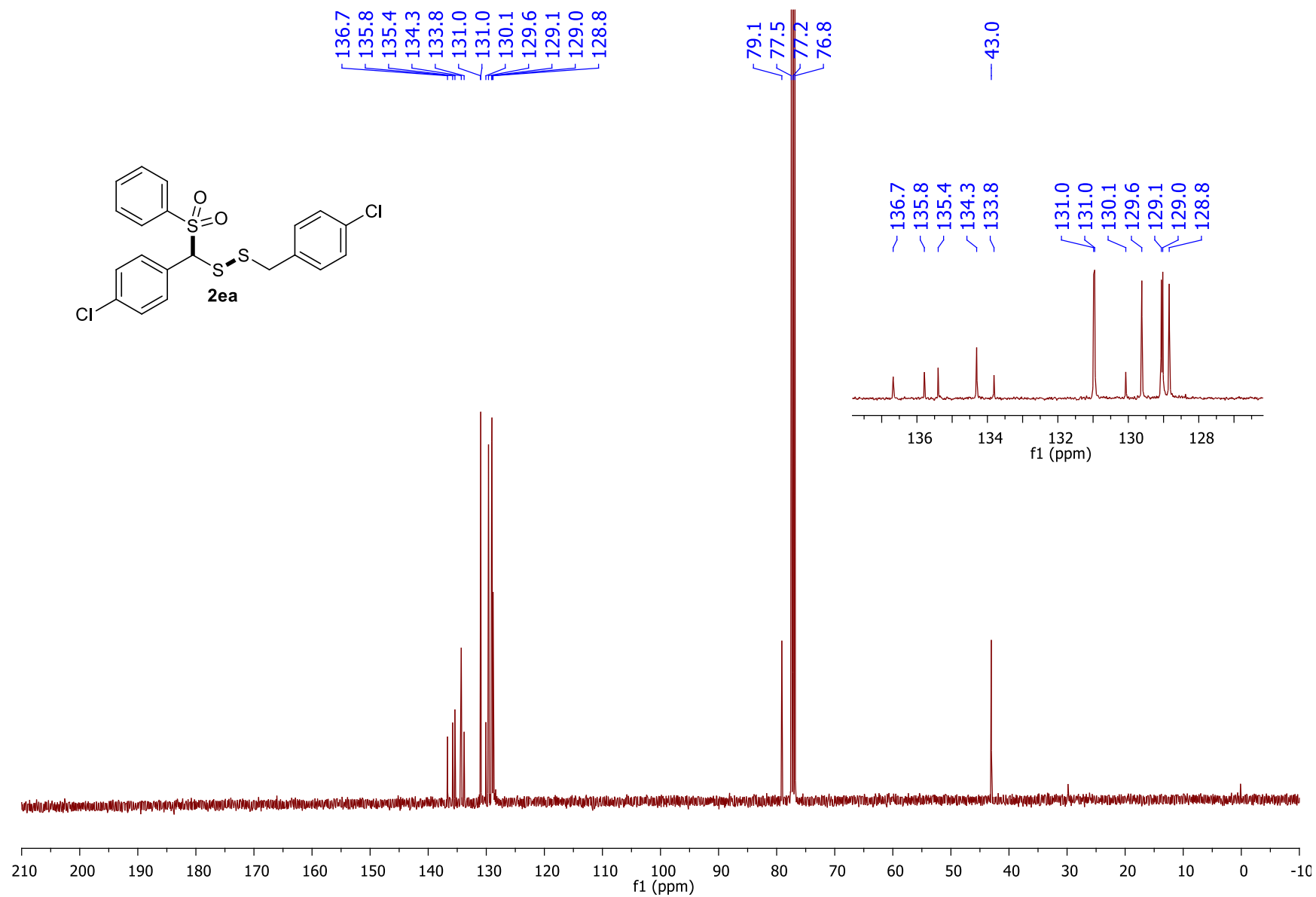


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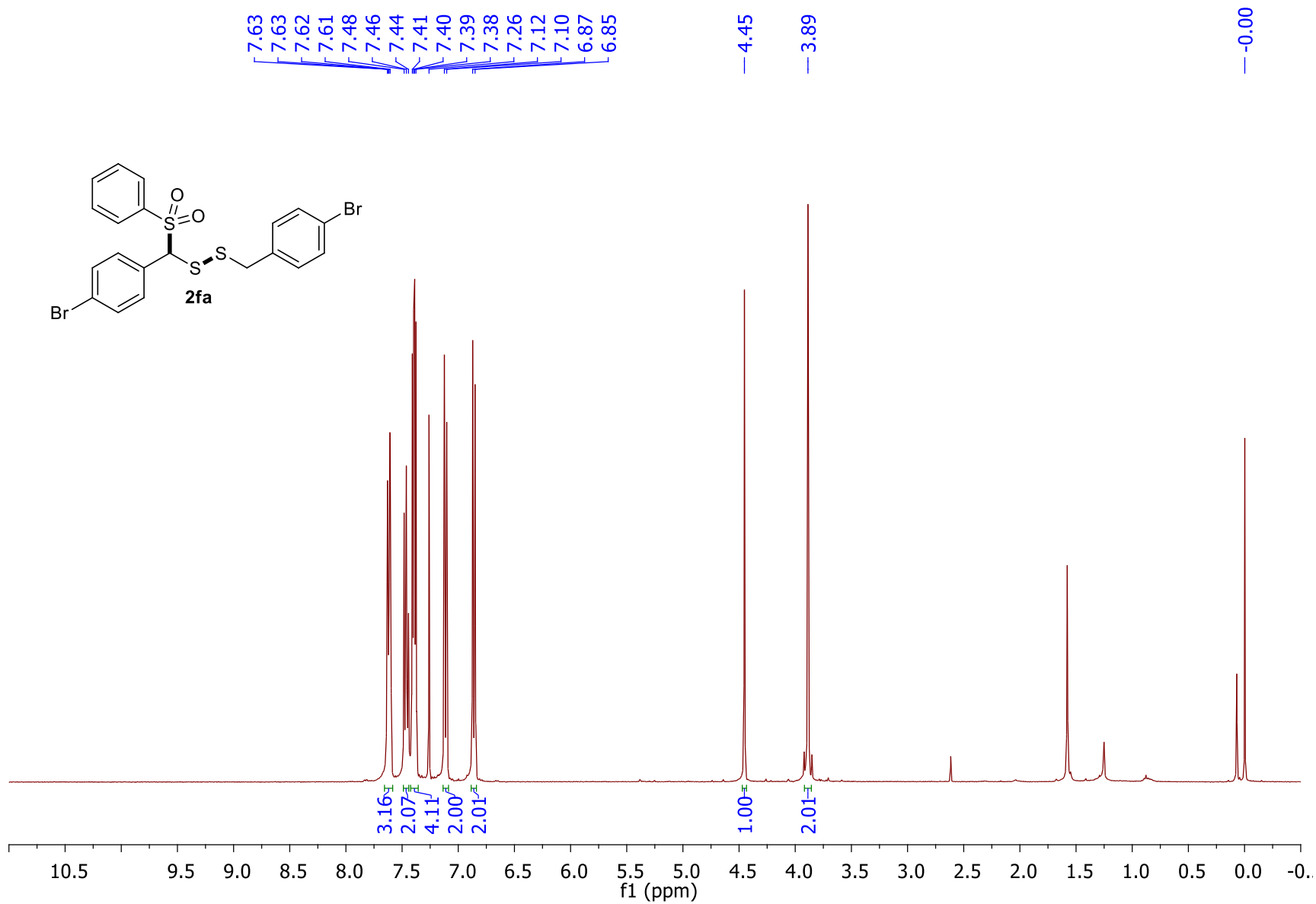




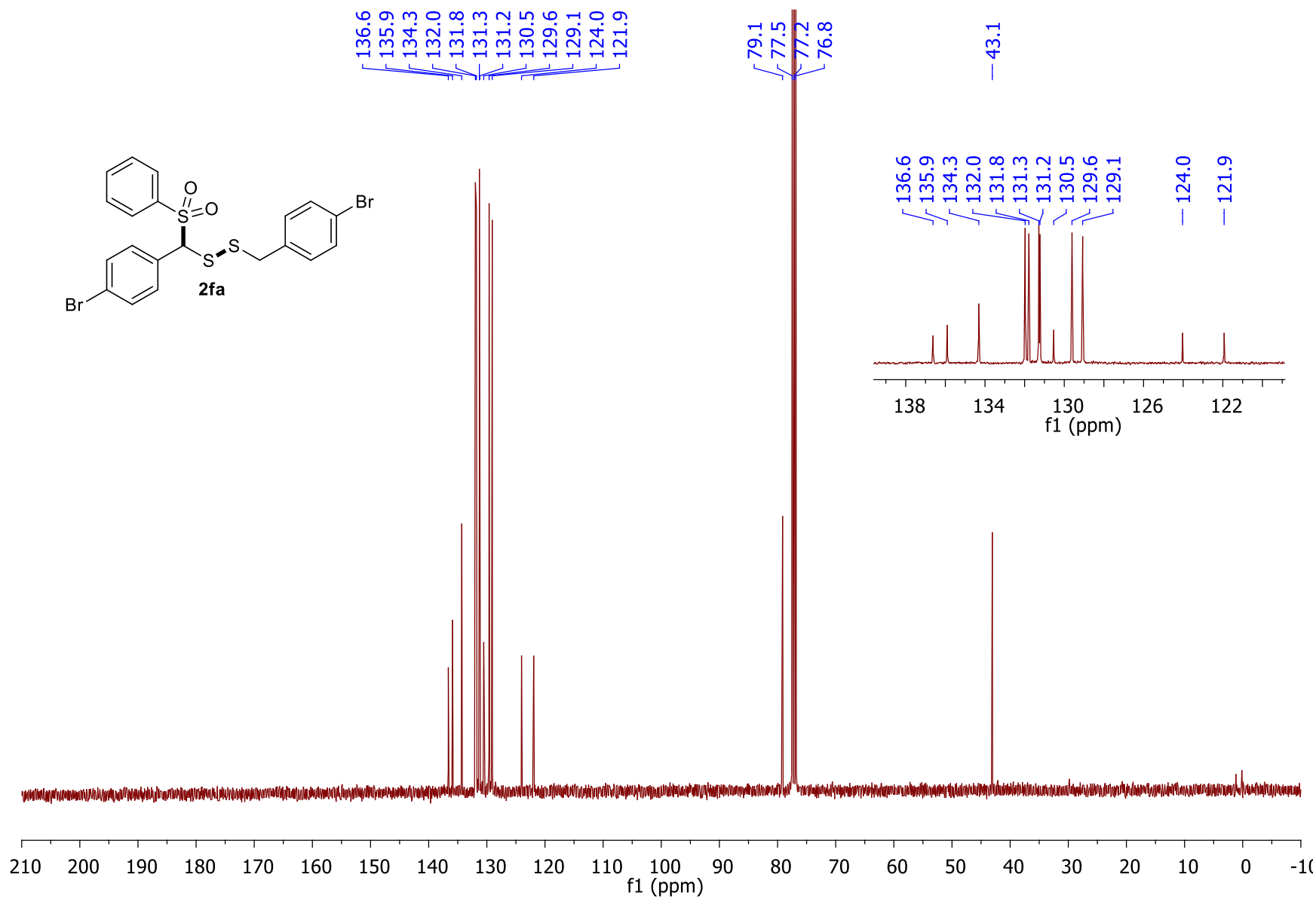
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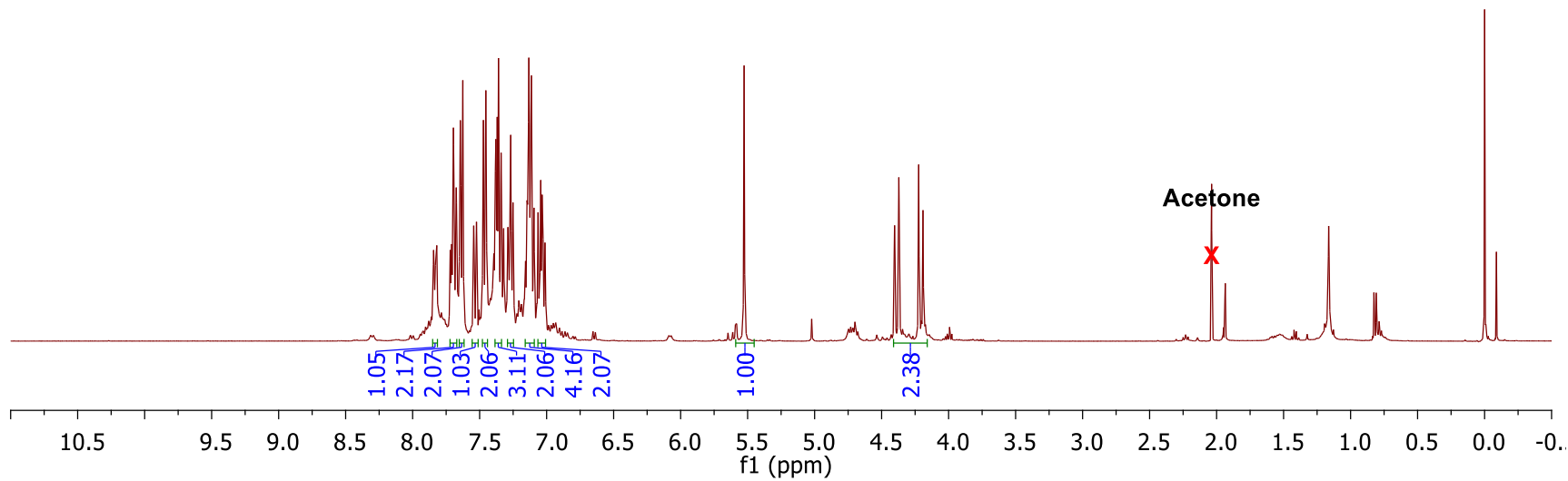
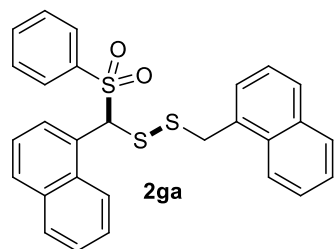


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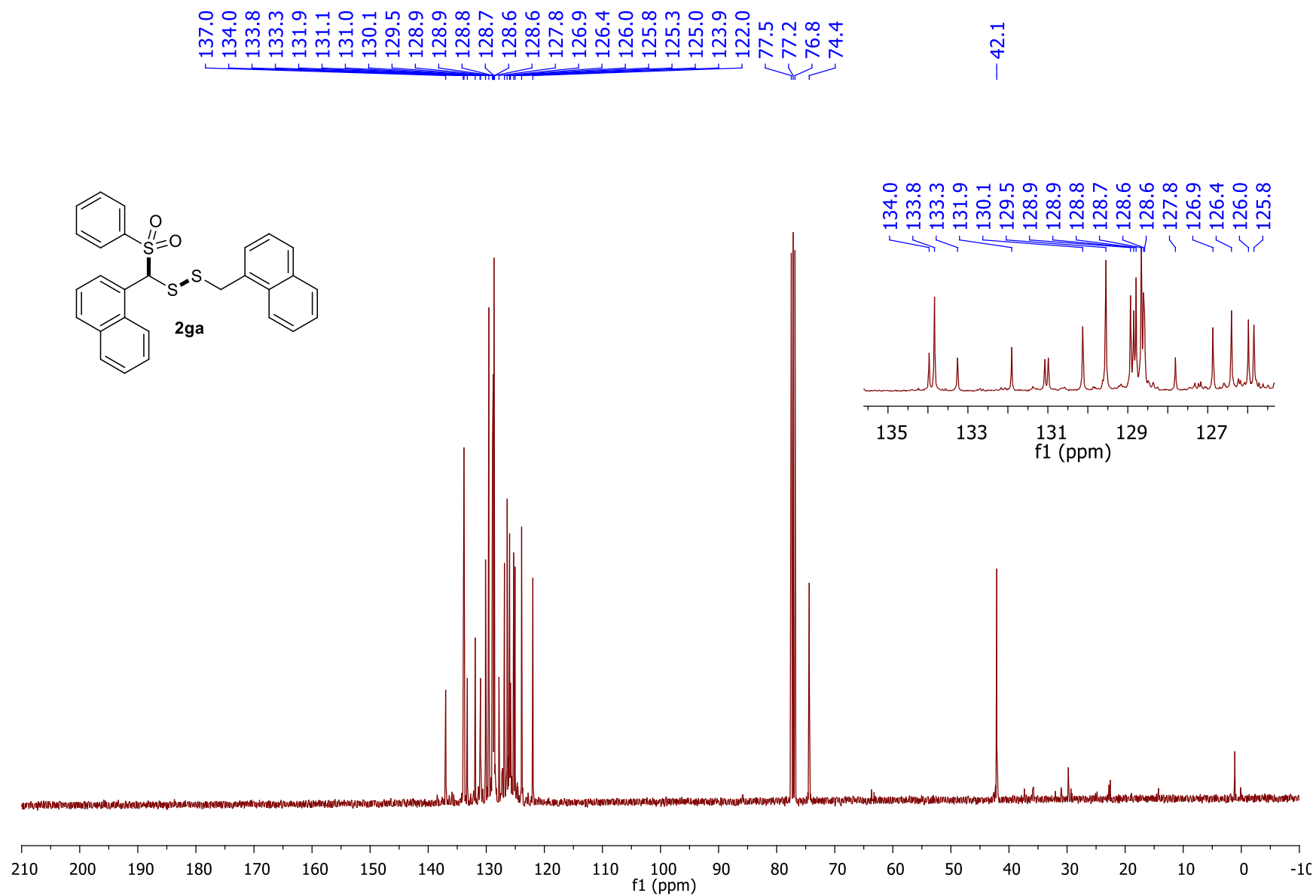
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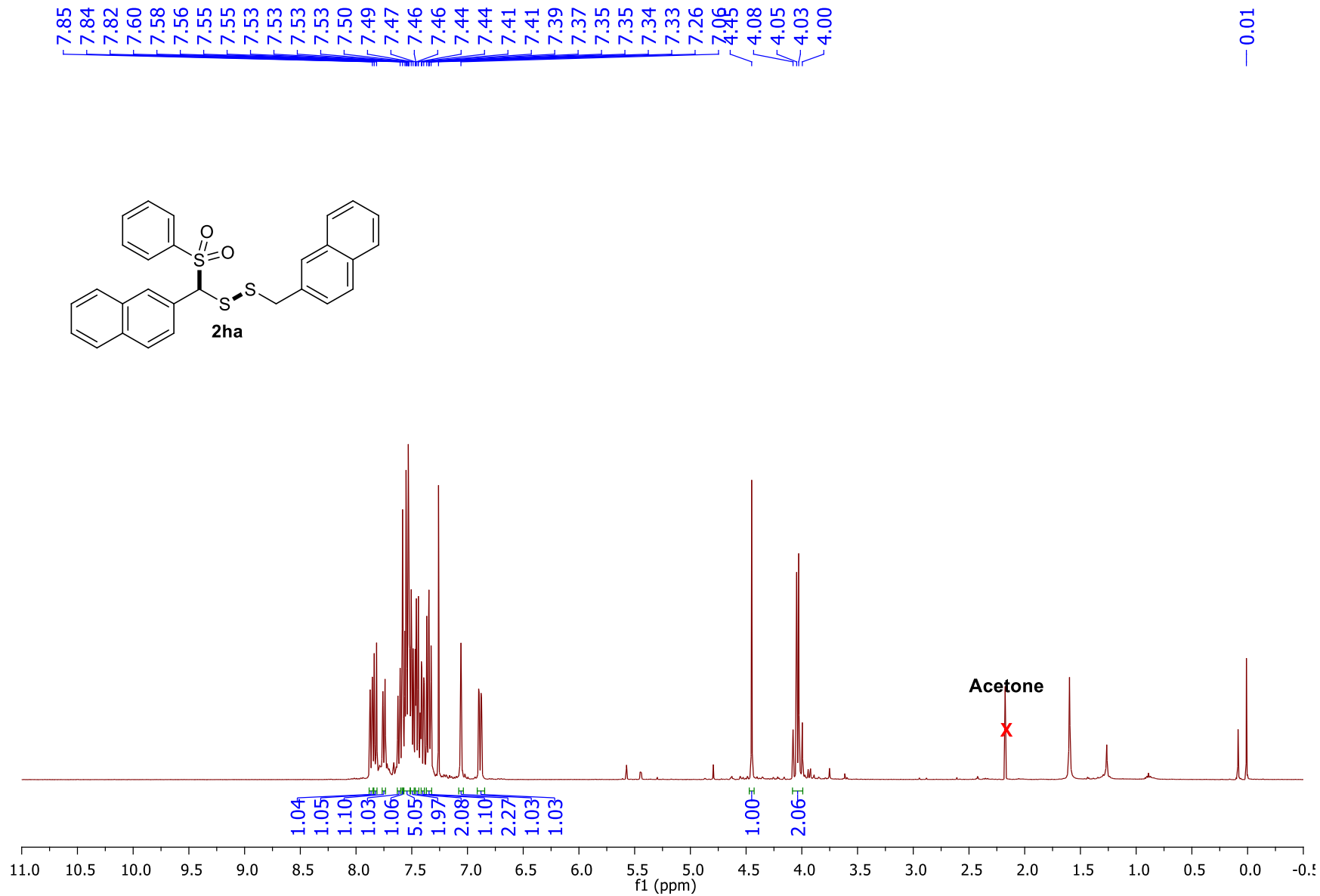
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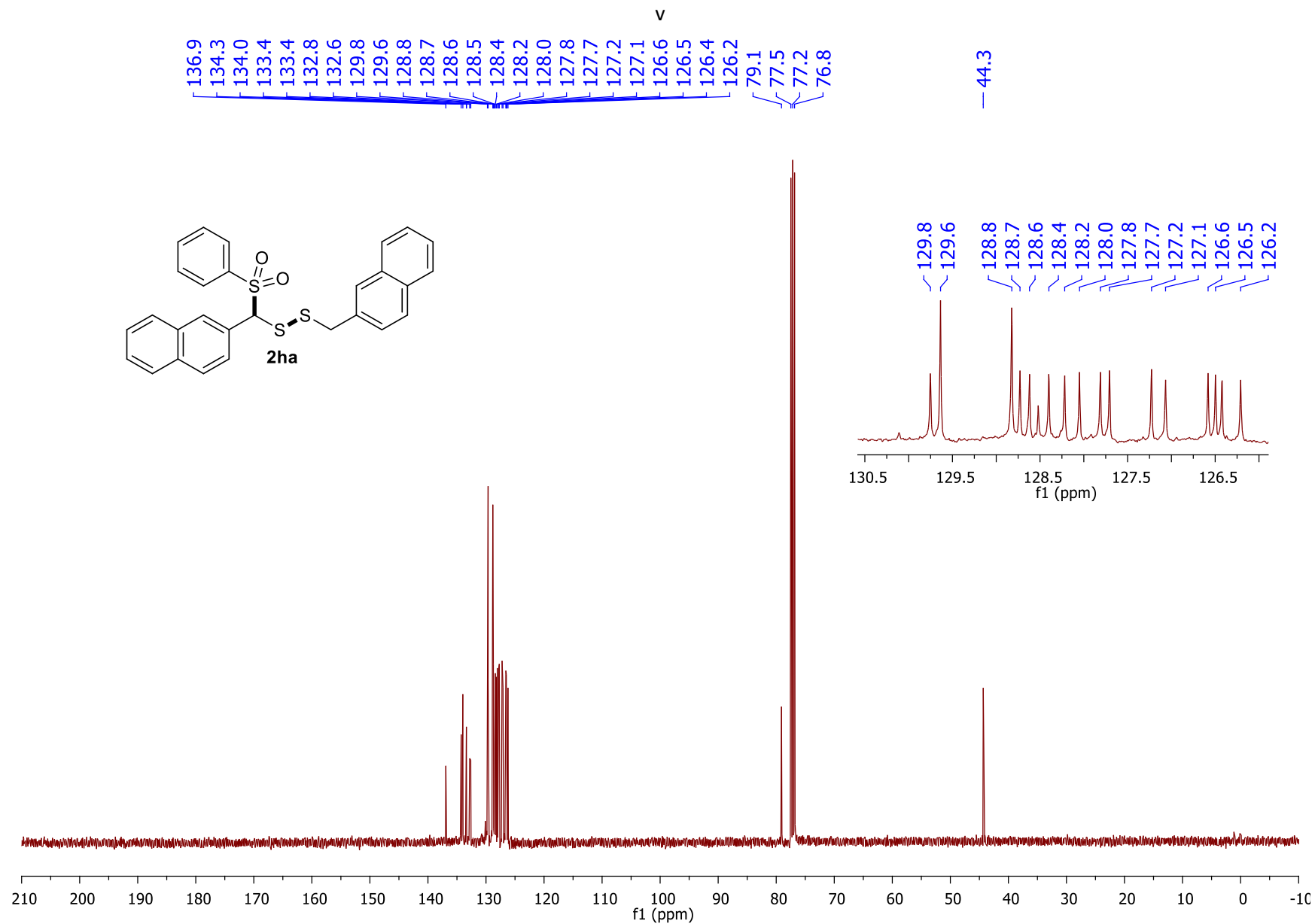
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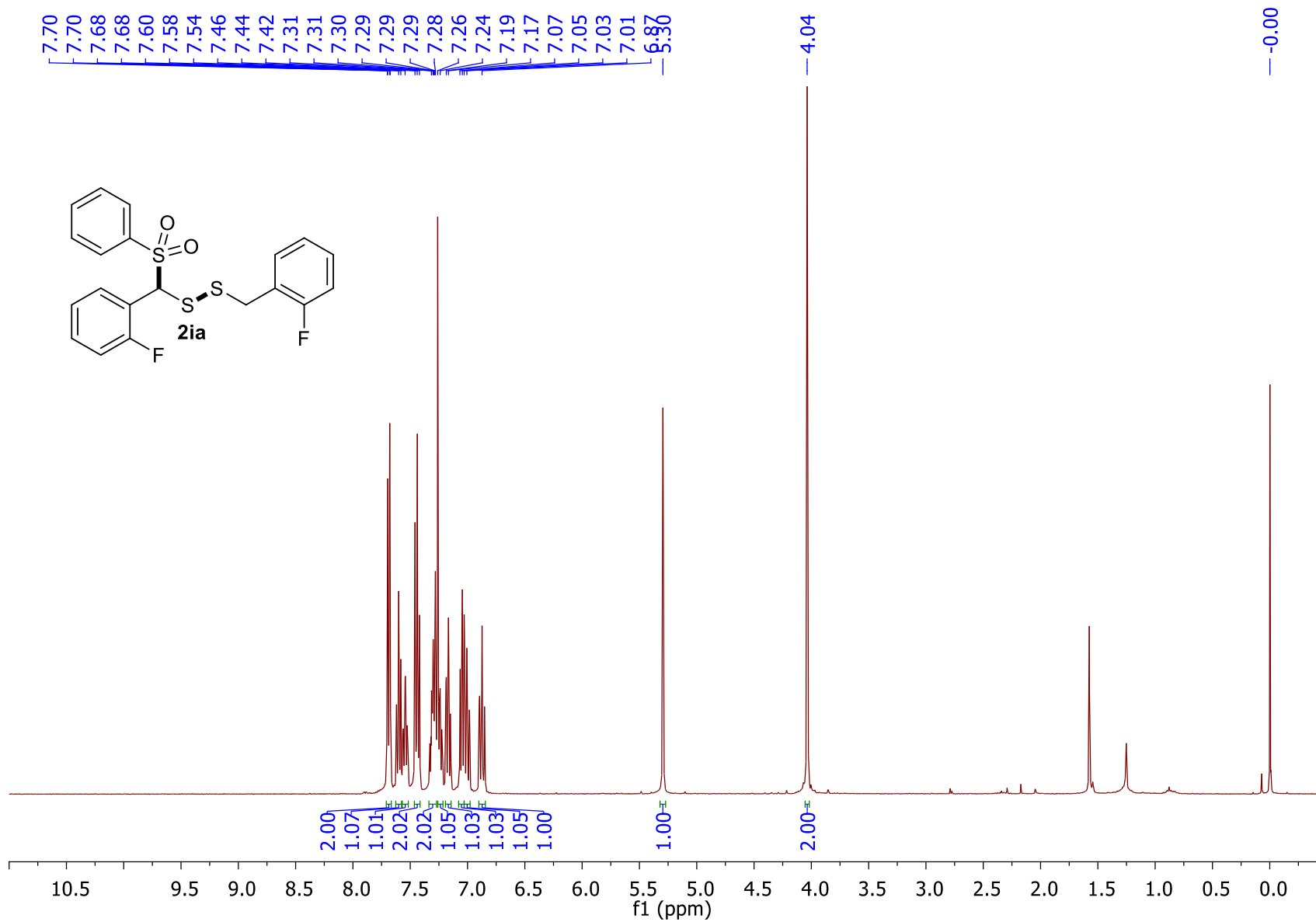
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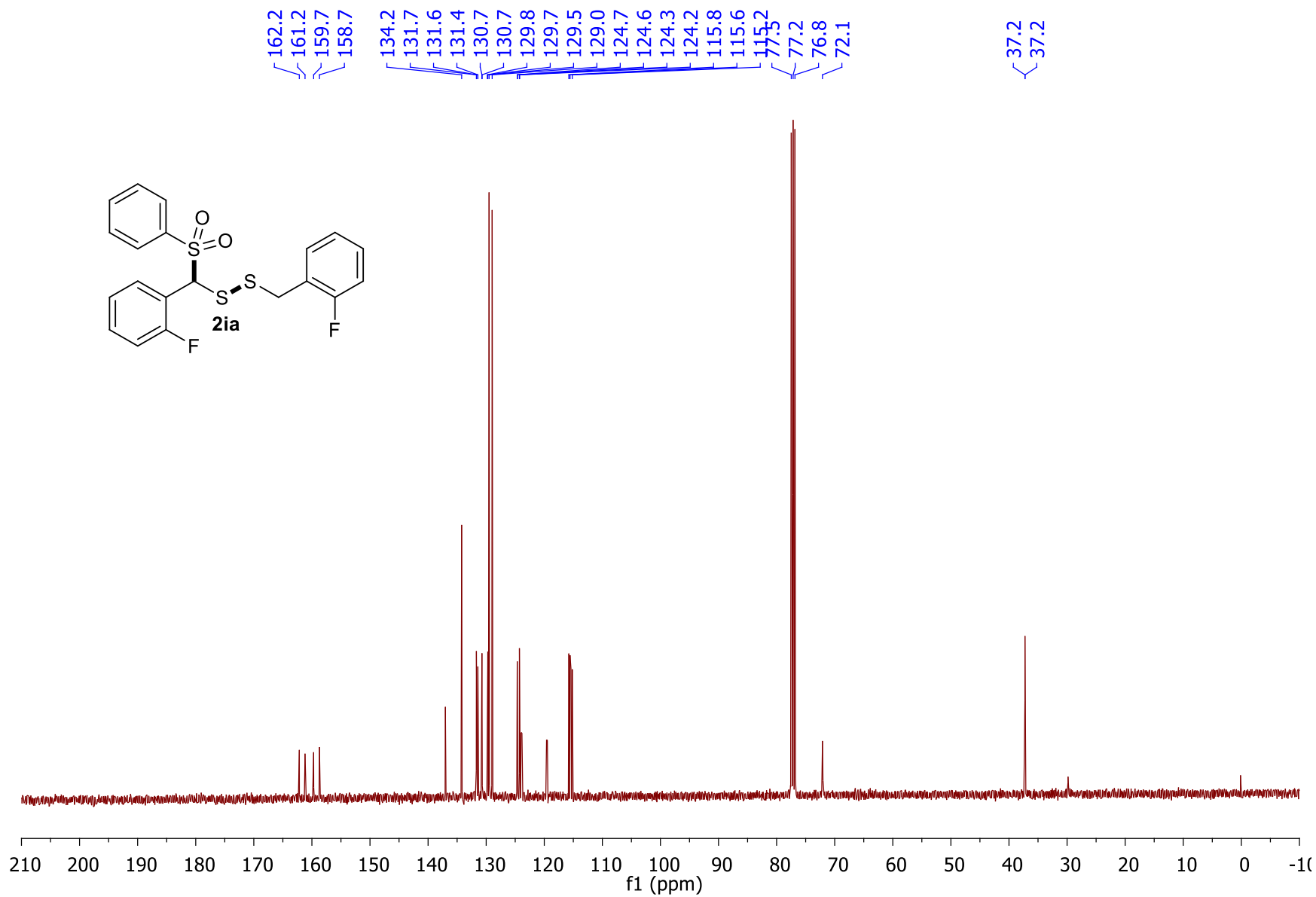


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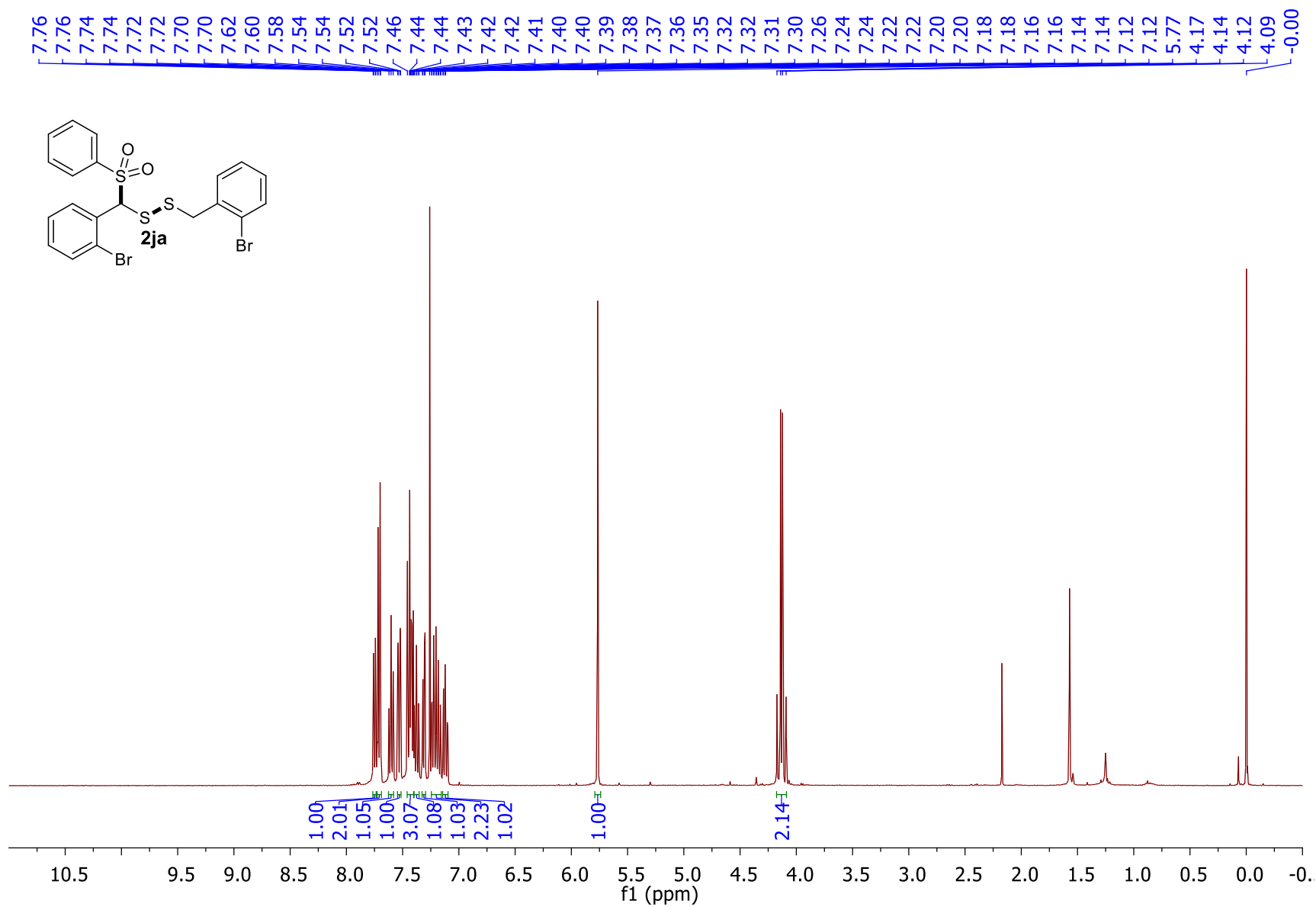




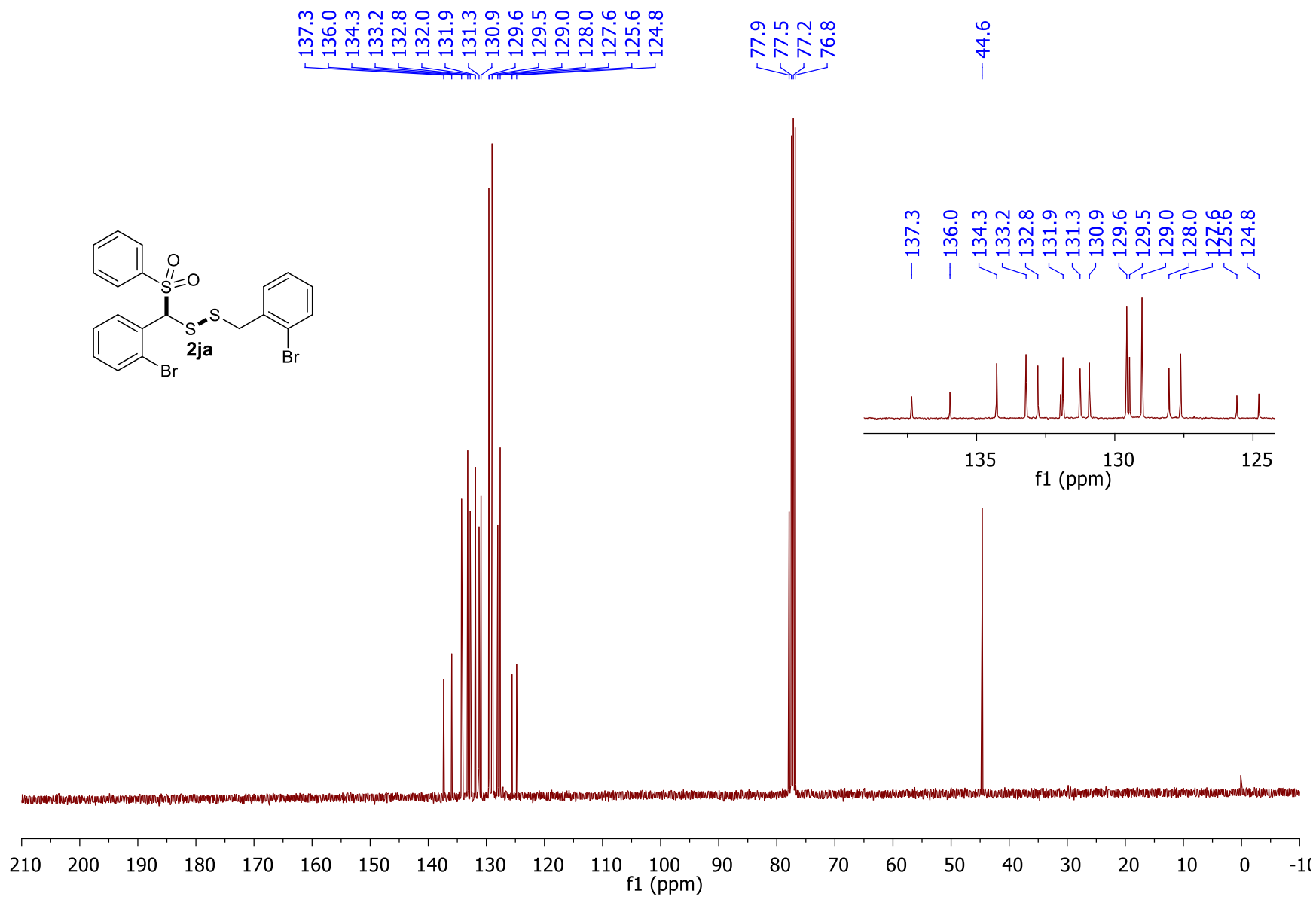
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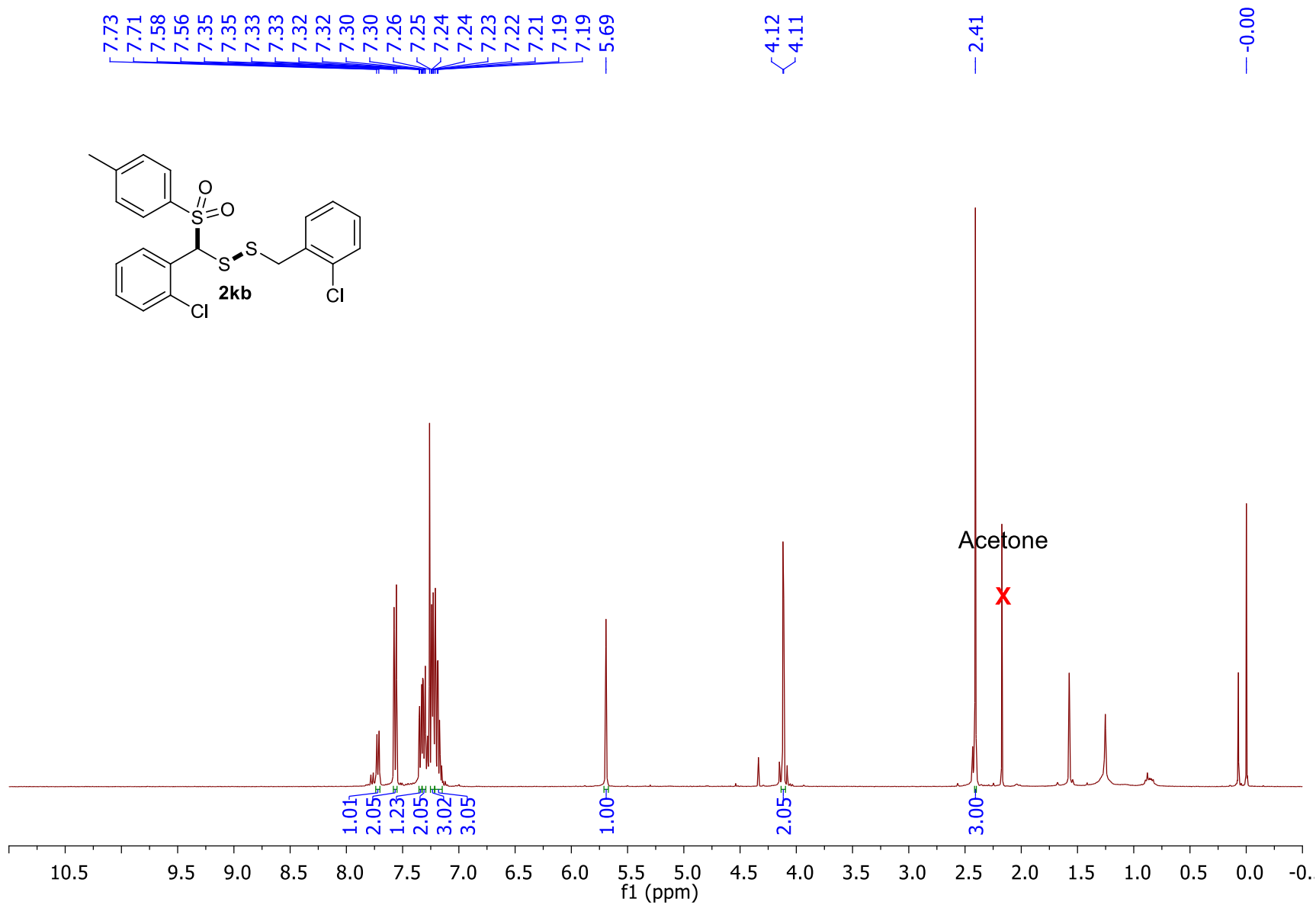
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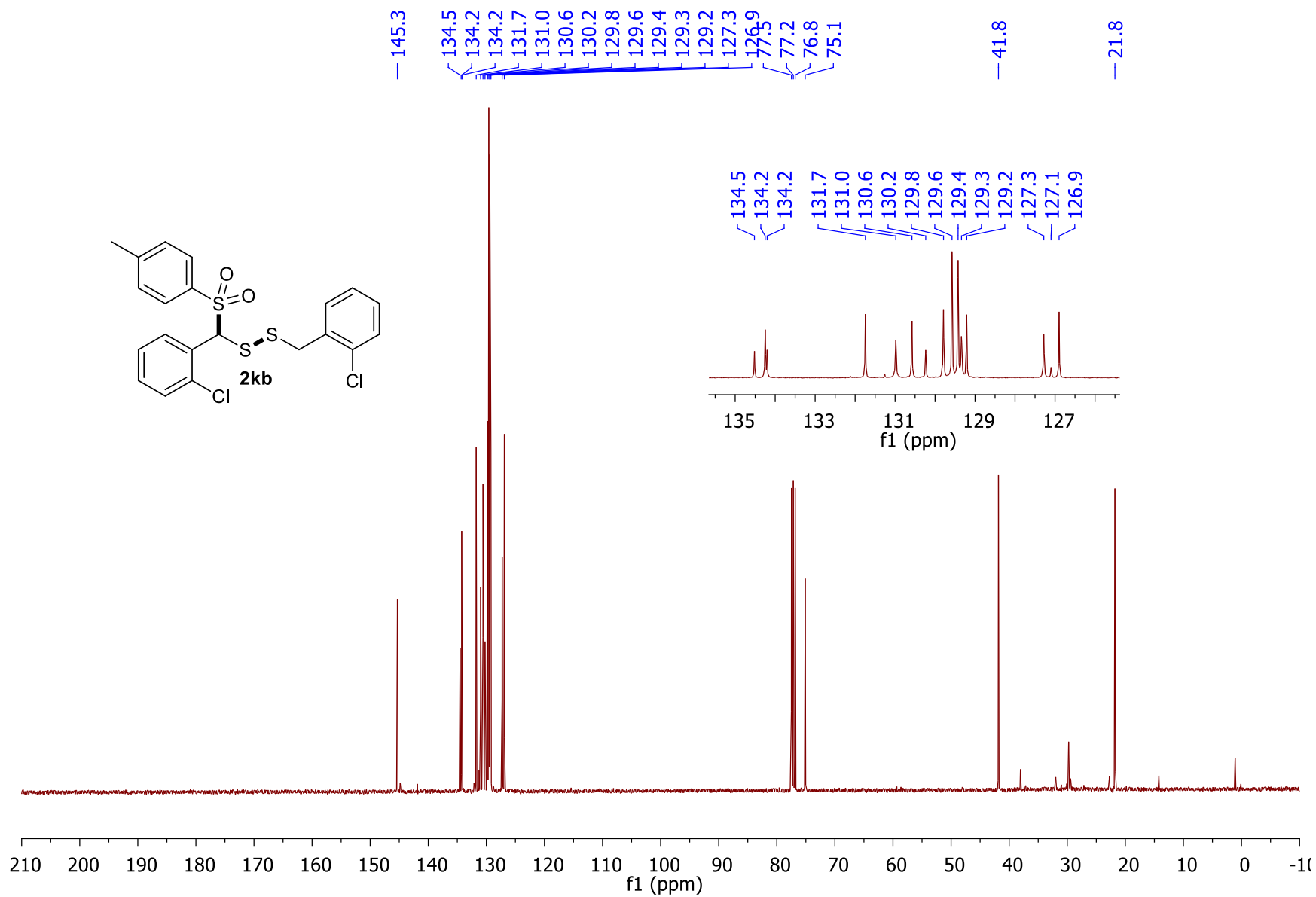
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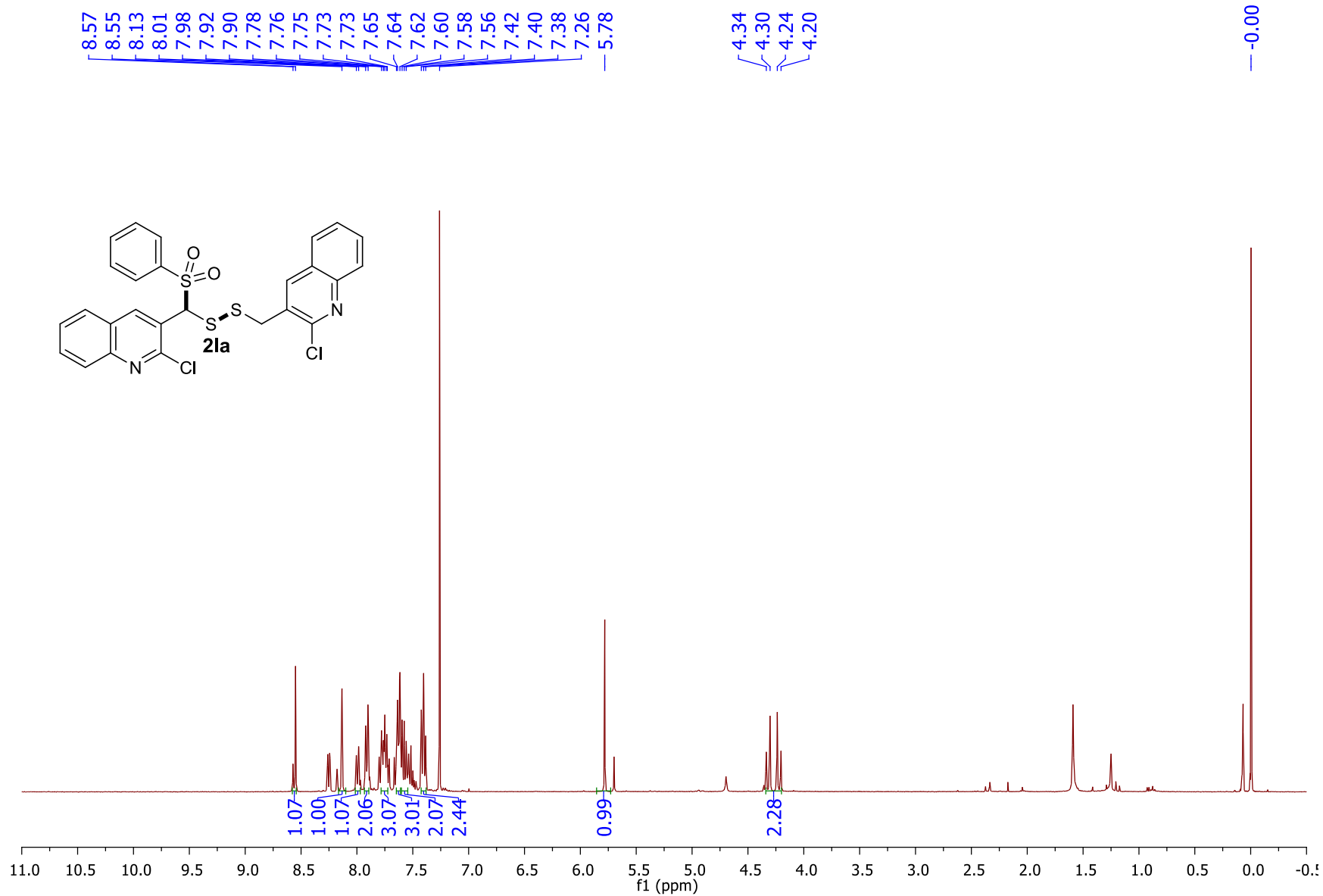
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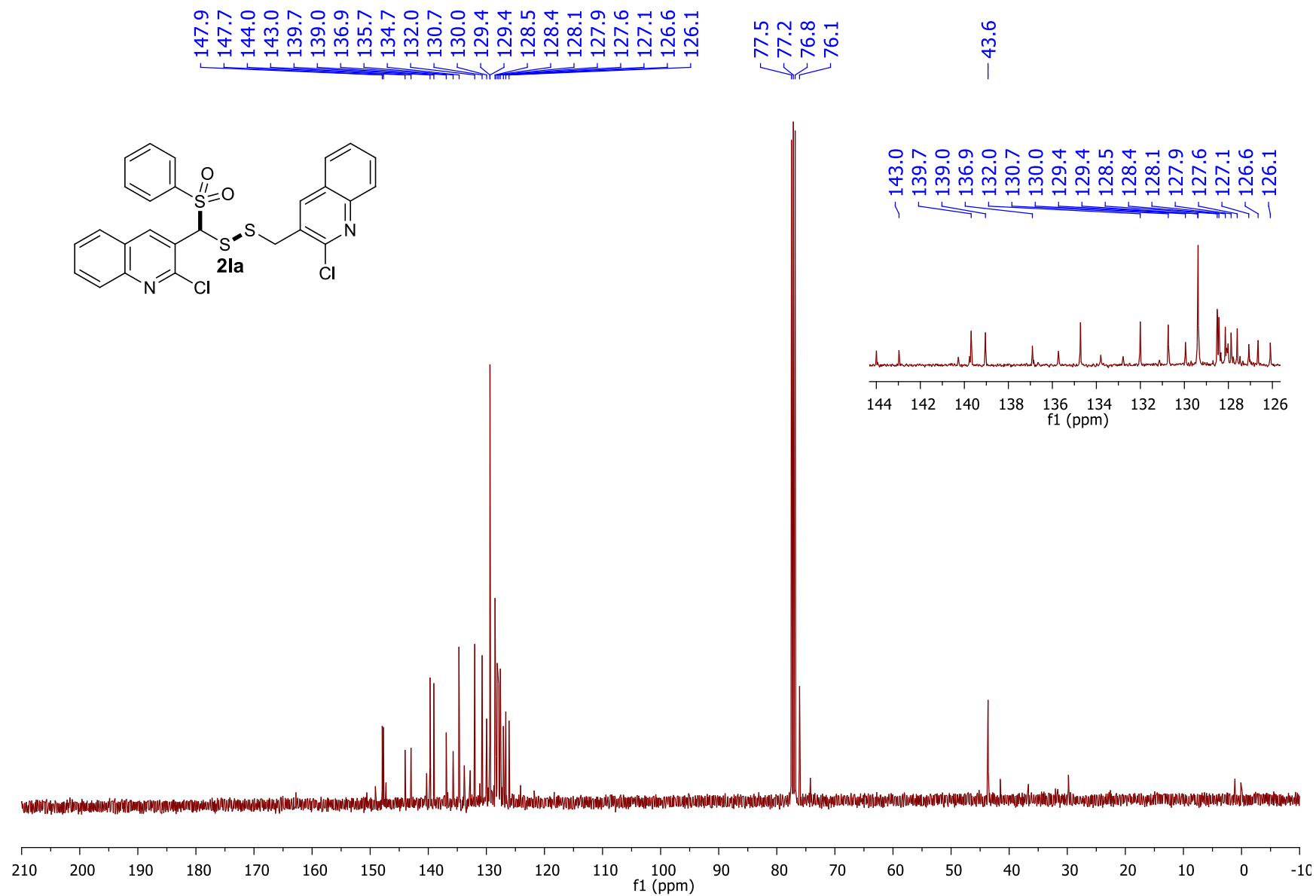
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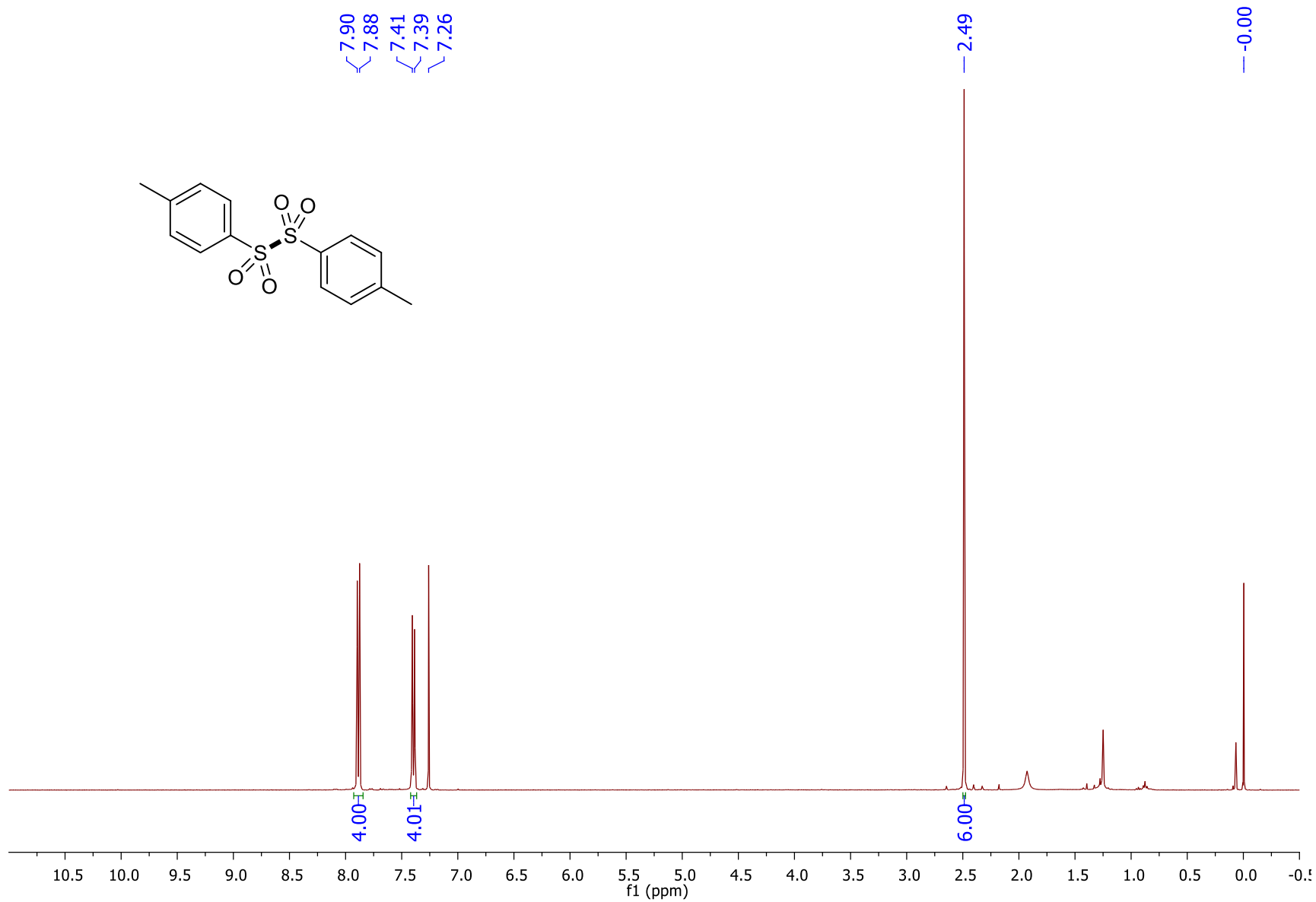
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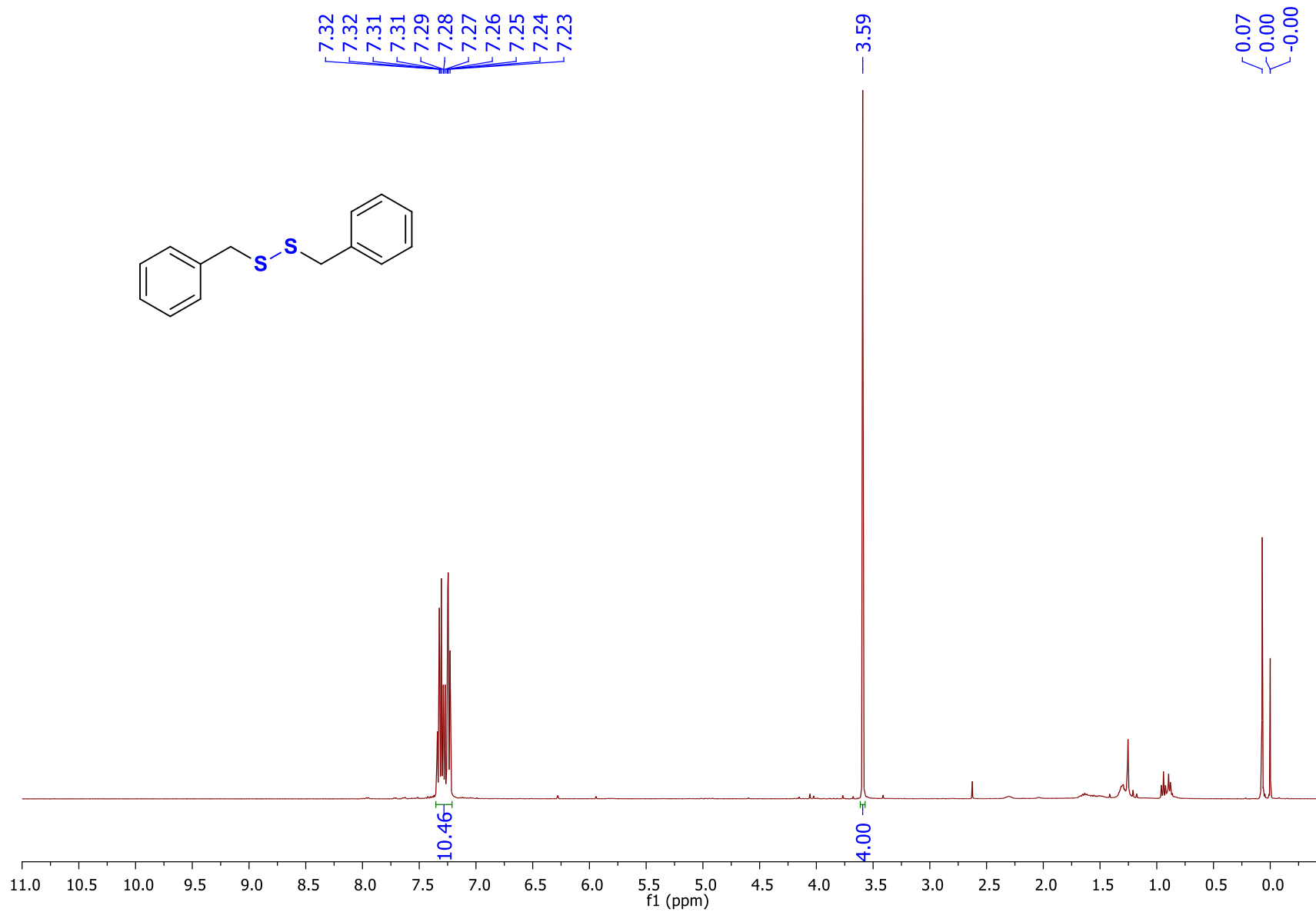


Supplementary Information.....





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