

# A Modular Approach to Highly Functionalized 3-Sulfonylfurans *via* Conjugate Addition of 3-Cyclopropylideneprop-2-en-1-ones with Sodium Sulfinates and Sequential 5-*Endo*-trig Iodocyclization

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## Supporting Information

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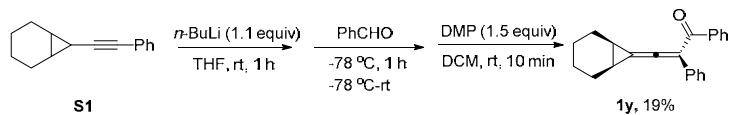
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## 1. General Methods.

NMR spectra were recorded on a Bruker AV-400 MHz spectrometer. The <sup>1</sup>H NMR (400 MHz) chemical shifts were reported in parts per million ( $\delta$ ) relative to internal standard TMS (0 ppm). The coupling constants,  $J$  values are reported in Hertz (Hz). The <sup>13</sup>C NMR (100 MHz) chemical shifts were referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl<sub>3</sub>). High-resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected. All commercial reagents and solvents were used without additional purification. Petroleum ether refers to the fraction with boiling point in the range 60–90 °C. All reactions were monitored by TLC with GF 254 silica gel coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel. The 3-cyclopropylideneprop-2-en-1-ones<sup>1</sup> **1** and sodium sulfinate<sup>2</sup> **2** were prepared according to the literature procedure.

## 2. Procedure and additional experiment data for material **1y** and MCPs **3**<sup>3</sup>

Method for the synthesis of cyclohexyl fused substrate **1y**



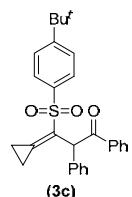
To a solution of 7-(phenylethynyl)bicyclo[4.1.0]heptane **S1** synthesized according to the reported procedure<sup>4</sup> (2.87 g, 14.6 mmol) in 15 mL of anhydrous THF was added *n*-BuLi (6.42 mL, 2.5 M in hexane, 1.1 equiv) at room temperature; the resulting mixture was stirred for 20 min, and cooled to -78 °C. Then PhCHO (1.55 g, 14.6 mmol, 1.0 equiv) was added with a syringe to this mixture at -78 °C. After being stirred for 15 min, the mixture was allowed to warm up to room temperature, quenched with water, extracted with ethyl acetate, dried over MgSO<sub>4</sub>, filtered, and evaporated. The residue was chromatographed through a silica gel column (petroleum ether/ethyl acetate 4:1 v/v) to afford the mixture of cyclopropyl allenol as yellow oil. To a solution of the mixture of cyclopropyl allenol (7.00 mmol, 2.10 g) in 10 mL of DCM were added 1.2 equiv of DMP. After being stirred for 10 min, silica gel 10 g was added and the solvent was evaporated. The solid residue was purified by column chromatography (petroleum ether/ethyl acetate 50:1 v/v) on a silica gel column to give the starting material **1y** (815 mg, 19%) as yellow solid: M.p. 84–86 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91–7.86 (m, 2H), 7.58–7.53 (m, 2H), 7.48 (t,  $J$  = 7.6 Hz, 1H),

7.41-7.34 (m, 4H), 7.27 (t,  $J$  = 6.4 Hz, 1H), 2.31-2.25 (m, 2H), 2.00-1.92 (m, 4H), 1.51-1.30 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.0, 194.7, 139.4, 135.0, 131.8, 129.2, 128.3, 128.2, 127.8, 127.0, 110.0, 89.0, 25.7, 23.4, 20.9; HRMS (ES<sup>+</sup>-TOF): calcd for  $\text{C}_{22}\text{H}_{21}\text{O}$  ( $[\text{M}+\text{H}]^+$ ): 301.1592, Found 301.1594.

MCPs **3a-l**, **3n-o**, **3q-u**, **3w-x** were synthesized according to the known procedure as following:

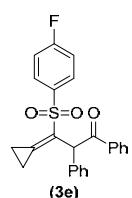
3-Cyclopropylideneprop-2-en-1-ones **1** (0.2 mmol, 1.0 equiv), sodium sulfinates **2** (0.4 mmol, 2.0 equiv), and AcOH (0.4 mmol, 2.0 equiv) were dissolved in 2 mL of MeOH in sequence. The mixture was then stirred at rt under ambient atmosphere for 10 min-20 min. After completion of the reaction, the solvent was removed *in vacuo*, and the residue was purified with flash silica gel chromatography to afford **3**.

Additional experiment data for **3c**, **3e**, **3i**, **3k**, **3r**, **3s**, **3t**, **3u**:



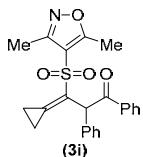
### **3-((4-(tert-butyl)phenyl)sulfonyl)-3-cyclopropylidene-1,2-diphenylpropan-1-one (3c)**

A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2mmol, 1.0 equiv), sodium 4-(*tert*-butyl)benzenesulfinate **2c** (89 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 10 min to afford **3c** (86 mg, 95%) as a yellow solid; M.p. 129-130 °C (Petroleum ether/EtOAc);  $R_f$  = 0.15 (Petroleum ether/EtOAc = 10/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J$  = 7.2 Hz, 2H), 7.62 (d,  $J$  = 8.4 Hz, 2H), 7.51 (t,  $J$  = 7.2 Hz, 1H), 7.40 (t,  $J$  = 7.6 Hz, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 7.19-7.14 (m, 3H), 7.08-7.02 (m, 2H), 6.13 (s, 1H), 1.44-1.33 (m, 2H), 1.27 (s, 9H), 1.03 (dd,  $J_1$  = 19.8 Hz,  $J_2$  = 9.8 Hz, 1H), 0.91 (dd,  $J_1$  = 19.8 Hz,  $J_2$  = 10.2 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.9, 156.9, 141.5, 137.2, 135.8, 135.5, 133.2, 130.7, 129.3, 128.8, 128.6, 128.4, 128.0, 127.4, 125.7, 53.6, 35.0, 31.0, 5.1, 4.6; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{28}\text{H}_{29}\text{O}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 445.1837, found 445.1834.



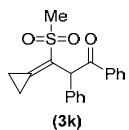
**3-cyclopropylidene-3-((4-fluorophenyl)sulfonyl)-1,2-diphenylpropan-1-one (3e)**

A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2mmol, 1.0 equiv), sodium 4-fluorobenzenesulfinate **2e** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 15 min to afford **3e** (79 mg, 96%) as white solid; M.p. 106-107 °C (Petroleum ether/EtOAc);  $R_f$  = 0.33 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (d,  $J$  = 7.6 Hz, 2H), 7.75-7.69 (m, 2H), 7.52 (t,  $J$  = 7.4 Hz, 1H), 7.41 (t,  $J$  = 7.4 Hz, 2H), 7.23-7.17 (m, 3H), 7.12-7.16 (m, 2H), 7.01 (t,  $J$  = 8.4 Hz, 2H), 6.15 (s, 1H), 1.44-1.24 (m, 2H), 1.03 (dd,  $J_1$  = 19.4 Hz,  $J_2$  = 10.2 Hz, 1H), 0.87 (dd,  $J_1$  = 19.6 Hz,  $J_2$  = 10.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.0, 165.3 (d,  $J$  = 254.4 Hz), 142.3, 136.5 (d,  $J$  = 3.3 Hz), 135.7, 135.2, 133.3, 130.88, 130.86 (d,  $J$  = 9.4 Hz), 129.4, 128.73, 128.67, 128.5, 127.6, 115.9 (d,  $J$  = 21.7 Hz), 53.8, 5.0, 4.8; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{24}\text{H}_{20}\text{FO}_3\text{S}$  ([M+H]<sup>+</sup>): 407.1117, found 407.1111.



**3-cyclopropylidene-3-((3,5-dimethylisoxazol-4-yl)sulfonyl)-1,2-diphenylpropan-1-one (3i)**

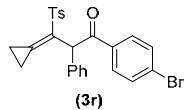
A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (49 mg, 0.2mmol, 1.0 equiv), sodium 3,5-dimethylisoxazole-4-sulfinate **2i** (74 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 30 min to afford **3i** (66 mg, 82%) as white solid; M.p. 138-139 °C (Petroleum ether/EtOAc);  $R_f$  = 0.29 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 7.2 Hz, 2H), 7.46 (t,  $J$  = 7.2 Hz, 1H), 7.34 (t,  $J$  = 7.6 Hz, 2H), 7.24-7.15 (m, 3H), 7.09-7.04 (m, 2H), 5.93 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H), 1.45-1.33 (m, 2H), 1.06 (dd,  $J_1$  = 19.6 Hz,  $J_2$  = 10.8 Hz, 1H), 0.83 (dd,  $J_1$  = 19.6 Hz,  $J_2$  = 10.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.5, 174.3, 157.9, 142.4, 135.5, 135.3, 133.5, 129.7, 128.83, 128.78, 128.7, 128.6, 127.9, 115.6, 53.1, 12.4, 10.5, 5.3, 4.4; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}_4\text{S}$  ([M+H]<sup>+</sup>): 408.1270, found 408.1268.



**3-cyclopropylidene-3-(methylsulfonyl)-1,2-diphenylpropan-1-one (3k)**

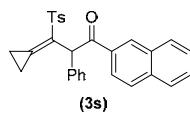
A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv),

sodium methanesulfinate **2k** (42 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 10 min to afford **3k** (64 mg, 97%) as white solid; M.p. 55-56 °C (Petroleum ether/EtOAc);  $R_f$  = 0.20 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J$  = 7.6 Hz, 2H), 7.51 (t,  $J$  = 7.4 Hz, 1H), 7.41 (t,  $J$  = 7.6 Hz, 2H), 7.36-7.28 (m, 3H), 7.25 (d,  $J$  = 7.6 Hz, 2H), 6.16 (s, 1H), 2.87 (s, 3H), 1.50-1.43 (m, 2H), 0.99 (dd,  $J_1$  = 19.8 Hz,  $J_2$  = 10.2 Hz, 1H), 0.80 (dd,  $J_1$  = 20.0 Hz,  $J_2$  = 10.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.0, 141.9, 135.6, 135.2, 133.4, 131.0, 129.6, 129.0, 128.8, 128.7, 127.9, 54.6, 43.0, 4.6; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_3\text{S}$  ([M+H]<sup>+</sup>): 327.1055, found 327.1053.



### **1-(4-bromophenyl)-3-cyclopropylidene-2-phenyl-3-tosylpropan-1-one (3r)**

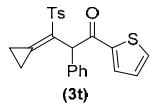
A mixture of 1-(4-bromophenyl)-3-cyclopropylidene-2-phenylprop-2-en-1-one **1r** (66 mg, 0.2mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 10 min to afford **3r** (88 mg, 90%) as white solid; M.p. 113-114 °C (Petroleum ether/EtOAc);  $R_f$  = 0.27 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (d,  $J$  = 8.8 Hz, 2H), 7.60 (d,  $J$  = 8.0 Hz, 2H), 7.54 (d,  $J$  = 8.4 Hz, 2H), 7.23-7.14 (m, 5H), 7.09-7.03 (m, 2H), 6.06 (s, 1H), 2.36 (s, 3H), 1.36-1.28 (m, 2H), 1.00 (dd,  $J_1$  = 19.8 Hz,  $J_2$  = 9.8 Hz, 1H), 0.83 (dd,  $J_1$  = 19.6 Hz,  $J_2$  = 9.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.2, 144.1, 141.6, 137.3, 135.1, 134.6, 131.9, 130.9, 130.3, 129.4, 129.3, 128.5, 128.4, 128.1, 127.5, 53.7, 21.5, 5.0, 4.6; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{25}\text{H}_{22}\text{BrO}_3\text{S}$  ([M+H]<sup>+</sup>): 481.0473, found 481.0499.



### **3-cyclopropylidene-1-(naphthalen-2-yl)-2-phenyl-3-tosylpropan-1-one (3s)**

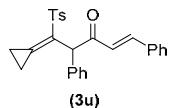
A mixture of 3-cyclopropylidene-1-(naphthalen-2-yl)-2-phenylprop-2-en-1-one **1s** (60 mg, 0.2mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 10 min to afford **3s** (83 mg, 91%) as white solid; M.p. 111-112 °C (Petroleum ether/EtOAc);  $R_f$  = 0.29 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (s, 1H), 8.00 (d,  $J$  = 8.4 Hz, 1H), 7.94 (d,  $J$  = 8.0 Hz, 1H), 7.84 (d,  $J$  = 8.8 Hz, 2H), 7.65-7.50 (m, 4H), 7.24-7.11 (m, 7H), 6.30 (s, 1H),

2.33 (s, 3H), 1.41-1.29 (m, 2H), 1.04 (dd,  $J_1 = 19.2$  Hz,  $J_2 = 10.0$  Hz, 1H), 0.89 (dd,  $J_1 = 19.2$  Hz,  $J_2 = 10.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.1, 144.0, 141.5, 137.4, 135.6, 135.5, 133.2, 132.4, 131.1, 130.7, 129.8, 129.40, 129.39, 128.6, 128.5, 128.4, 128.2, 127.6, 127.4, 126.7, 124.3, 53.7, 21.5, 5.0, 4.7; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{29}\text{H}_{25}\text{O}_3\text{S}$  ([M+H]<sup>+</sup>): 453.1524, found 453.1539.



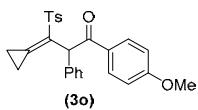
**3-cyclopropylidene-2-phenyl-1-(thiophen-2-yl)-3-tosylpropan-1-one (3t)**

A mixture of 3-cyclopropylidene-2-phenyl-1-(thiophen-2-yl)prop-2-en-1-one **1t** (51 mg, 0.2mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 20 min to afford **3t** (74 mg, 90%) as white solid; M.p. 131-132 °C (Petroleum ether/EtOAc);  $R_f = 0.19$  (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 3.6$  Hz, 1H), 7.53 (d,  $J = 8.0$  Hz, 3H), 7.15-7.69 (m, 8H), 6.91 (s, 1H), 2.29 (s, 3H), 1.32-1.24 (m, 2H), 1.05 (dd,  $J_1 = 20.2$  Hz,  $J_2 = 9.8$  Hz, 1H), 0.84 (dd,  $J_1 = 19.8$  Hz,  $J_2 = 9.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.8, 144.0, 143.0, 141.5, 137.2, 135.4, 134.2, 133.1, 130.7, 129.3, 129.2, 128.35, 128.27, 128.1, 127.4, 54.5, 21.5, 5.0, 4.7; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_3\text{S}_2$  ([M+H]<sup>+</sup>): 409.0932, found 409.0941.



**(E)-5-cyclopropylidene-1,4-diphenyl-5-tosylpent-1-en-3-one (3u)**

A mixture of (E)-1-cyclopropylidene-2,5-diphenylpenta-1,4-dien-3-one **1u** (55 mg, 0.2mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeOH at rt under ambient atmosphere for 10 min to afford **3u** (76 mg, 88%) as white solid; M.p. 192-193 °C (Petroleum ether/EtOAc);  $R_f = 0.24$  (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69-7.61 (m, 3H), 7.50-7.46 (m, 2H), 7.39-7.33 (m, 3H), 7.25-7.19 (m, 5H), 7.11-7.06 (m, 2H), 6.73 (d,  $J = 16.0$  Hz, 1H), 5.51 (s, 1H), 2.37 (s, 3H), 1.41-1.30 (m, 2H), 1.16 (dd,  $J_1 = 19.2$  Hz,  $J_2 = 10.4$  Hz, 1H), 0.91 (dd,  $J_1 = 19.8$  Hz,  $J_2 = 9.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.2, 144.1, 143.7, 141.3, 137.5, 135.3, 134.2, 130.74, 130.67, 129.5, 128.9, 128.5, 128.4, 128.2, 127.5, 124.6, 56.9, 21.5, 5.1, 4.7; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{27}\text{H}_{25}\text{O}_3\text{S}$  ([M+H]<sup>+</sup>): 429.1524, found 429.1522.



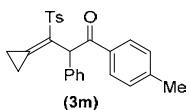
**3-cyclopropylidene-1-(4-methoxyphenyl)-2-phenyl-3-tosylpropan-1-one (3o)**

A mixture of 3-cyclopropylidene-1-(4-methoxyphenyl)-2-phenylprop-2-en-1-one **1o** (54 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at rt under ambient atmosphere for 5 h to afford **3o** (69 mg, 82%) as white solid; M.p. 118-119 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.13 (Petroleum ether/EtOAc = 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96 (d, J = 9.2 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.20-7.05 (m, 7H), 6.88 (d, J = 8.8 Hz, 2H), 6.09 (s, 1H), 3.83 (s, 3H), 2.35 (s, 3H), 1.37-1.30 (m, 2H), 1.02 (dd, J<sub>1</sub> = 19.6 Hz, J<sub>2</sub> = 10.0 Hz, 1H), 0.86 (dd, J<sub>1</sub> = 19.8 Hz, J<sub>2</sub> = 9.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 195.4, 158.9, 143.9, 141.2, 137.5, 135.9, 133.1, 131.4, 130.5, 129.3, 128.8, 128.6, 128.2, 127.4, 113.8, 55.2, 53.0, 21.5, 4.9, 4.6; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>26</sub>H<sub>25</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 433.1474, found 433.1481.

MCPs **3m**, **3p**, **3v**, **3y** were synthesized according to the following procedure:

3-Cyclopropylideneprop-2-en-1-ones **1** (0.2 mmol, 1.0 equiv), sodium sulfinates **2** (0.4 mmol, 2.0 equiv), and AcOH (0.4 mmol, 2.0 equiv) were dissolved in 2 mL of DMSO in sequence. The mixture was then stirred at rt under ambient atmosphere for 2-4 min. After completion of the reaction, the mixture was quenched by 10 mL of H<sub>2</sub>O and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with H<sub>2</sub>O (3 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **3**.

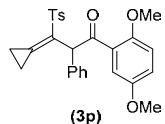
Additional experiment data for **3m**, **3p**, **3v**, **3y**:



**3-cyclopropylidene-2-phenyl-1-(p-tolyl)-3-tosylpropan-1-one (3m)**

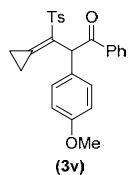
A mixture of 3-cyclopropylidene-2-phenyl-1-(p-tolyl)prop-2-en-1-one **1b** (52 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of DMSO at rt under ambient atmosphere for 2 min to afford **3m** (80 mg, 96%) as white solid; M.p. 122-123 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.24 (Petroleum ether/EtOAc = 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.88 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H),

7.23-7.12 (m, 7H), 7.10-7.05 (m, 2H), 6.12 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.37-1.29 (m, 2H), 1.01 (dd,  $J_1 = 19.6$  Hz,  $J_2 = 9.6$  Hz, 1H), 0.85 (dd,  $J_1 = 19.8$  Hz,  $J_2 = 10.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.6, 144.0, 143.9, 141.4, 137.4, 135.6, 133.3, 131.0, 129.33, 129.30, 129.29, 128.9, 128.3, 128.1, 127.3, 53.5, 21.6, 21.5, 4.9, 4.6; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{26}\text{H}_{25}\text{O}_3\text{S}$  ([M+H]<sup>+</sup>): 417.1524, found 417.1527.



**3-cyclopropylidene-1-(2,5-dimethoxyphenyl)-2-phenyl-3-tosylpropan-1-one (3p)**

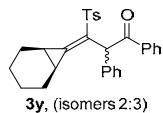
A mixture of 3-cyclopropylidene-1-(2,5-dimethoxyphenyl)-2-phenylprop-2-en-1-one **1p** (61 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of DMSO at rt under ambient atmosphere for 4 min to afford **3p** (78 mg, 85%) as yellow oil;  $R_f = 0.13$  (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 8.4$  Hz, 2H), 7.29 (d,  $J = 2.8$  Hz, 1H), 7.22-7.17 (m, 3H), 7.13-7.07 (m, 4H), 7.02-6.98 (m, 1H), 6.84 (d,  $J = 8.8$  Hz, 1H), 6.35 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 2.34 (s, 3H), 1.40-1.20 (m, 2H), 1.09 (dd,  $J_1 = 18.4$  Hz,  $J_2 = 10.4$  Hz, 1H), 0.88 (dd,  $J_1 = 18.6$  Hz,  $J_2 = 10.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.7, 153.2, 153.1, 143.6, 140.1, 137.9, 136.1, 131.9, 129.7, 129.1, 128.0, 127.9, 127.0, 126.5, 120.8, 114.7, 113.2, 57.5, 55.9, 55.7, 21.4, 4.9, 4.8; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{27}\text{H}_{27}\text{O}_5\text{S}$  ([M+H]<sup>+</sup>): 463.1579, found 463.1577.



**3-cyclopropylidene-2-(4-methoxyphenyl)-1-phenyl-3-tosylpropan-1-one (3v)**

A mixture of 3-cyclopropylidene-2-(4-methoxyphenyl)-1-phenylprop-2-en-1-one **1v** (55 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of DMSO at rt under ambient atmosphere for 4 min to afford **3v** (80 mg, 93%) as white solid; M.p. 99-100 °C (Petroleum ether/EtOAc);  $R_f = 0.18$  (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 7.6$  Hz, 2H), 7.60 (d,  $J = 8.4$  Hz, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.40 (t,  $J = 7.8$  Hz, 2H), 7.16 (d,  $J = 7.6$  Hz, 2H), 7.01 (d,  $J = 8.4$  Hz, 2H), 6.74 (d,  $J = 8.4$  Hz, 2H), 6.08 (s, 1H), 3.75 (s, 3H), 2.37 (s, 3H), 1.38-1.28 (m, 2H), 1.02 (dd,  $J_1 = 19.8$

Hz,  $J_2$  = 9.8 Hz, 1H), 0.88 (dd,  $J_1$  = 19.6 Hz,  $J_2$  = 10.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.4, 159.0, 144.0, 141.2, 137.6, 136.0, 133.2, 131.4, 130.6, 129.4, 128.8, 128.7, 128.2, 127.4, 113.9, 55.3, 53.1, 21.6, 5.0, 4.7; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{26}\text{H}_{25}\text{O}_4\text{S}$  ([M+H]<sup>+</sup>): 433.1474, found 433.1467.



**(Z)-3-(cis-bicyclo[4.1.0]heptan-7-ylidene)-1,2-diphenyl-3-tosylpropan-1-one (3y)**

A mixture of 3-(cis-bicyclo[4.1.0]heptan-7-ylidene)-1,2-diphenylprop-2-en-1-one **1y** (61 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of DMSO at rt under ambient atmosphere for 8 min to afford **3y** (88 mg, 94%, isomers 2:3) as a foam;  $R_f$  = 0.48 (Petroleum ether/EtOAc = 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99-7.90 (m, 2H), 7.66-7.47 (m, 3H), 7.44-7.35 (m, 2H), 7.23-6.97 (m, 7H), 6.14-6.04 (m, 1H), 2.37-2.31 (m, 3H), 2.06-1.73 (m, 2H), 1.62-1.42 (m, 2H), 1.40-0.80 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.5, 195.2, 152.3, 152.1, 143.83, 143.80, 137.5, 137.4, 136.4, 136.0, 135.6, 135.4, 133.2, 133.1, 131.1, 131.0, 129.5, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 128.3, 128.2, 128.0, 127.4, 127.1, 54.1, 53.8, 22.3, 22.0, 21.8, 21.51, 21.47, 21.4, 21.10, 21.03, 21.02, 20.96, 16.0, 15.9, 15.4, 15.0; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{29}\text{H}_{29}\text{O}_3\text{S}$  ([M+H]<sup>+</sup>): 457.1837, found 457.1834.

### 3. Procedure and experiment data for synthesis of 3-sulfonylfurans 4

One-pot Procedure for the synthesis of 3-sulfonylfurans **4** from materials **1** (*Condition A*):

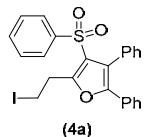
3-Cyclopropylideneprop-2-en-1-ones **1** (0.2 mmol, 1.0 equiv), sodium sulfinates **2** (0.4 mmol, 2.0 equiv) and AcOH (0.4 mmol, 2.0 equiv) were dissolved in 2 mL of MeCN in sequence. The mixture was then stirred at rt for 1.5-20 h under ambient atmosphere till complete consumption of **1**, followed by adding  $I_2$  (254 mg, 1 mmol, 5.0 equiv) and stirred at 100 °C for 10-72 h. After completion of the reaction, the mixture was quenched by 10 mL of saturated  $\text{Na}_2\text{S}_2\text{O}_3$  and extracted with EtOAc (3 × 10 mL). The combined organic phase was concentrated *in vacuo*, and the residue was purified with flash silica gel chromatography to afforded **4**.

Single-step Procedure for the synthesis of 3-sulfonylfurans **4** from MCPs **3** (*Condition B*):

MCPs **3** (0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN in a sealed tube, followed by addition of  $I_2$  (0.6 mmol, 3.0 equiv). The mixture was then stirred at 100 °C for 7.5-43 h under ambient atmosphere. After completion of the reaction, the mixture was quenched by 10 mL of saturated

$\text{Na}_2\text{S}_2\text{O}_3$  and extracted with EtOAc ( $3 \times 10$  mL). The combined organic phase was concentrated *in vacuo*, and the residue was purified with flash silica gel chromatography to afford **4**.

Experiment data for 3-sulfonylfurans **4**:

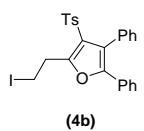


**2-(2-iodoethyl)-4,5-diphenyl-3-(phenylsulfonyl)furan (4a)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate **2a** (66 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2.5 h, then  $\text{I}_2$  (255 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 22 h to afford **4a** (72 mg, 69%).

**Condition B:** 3-Cyclopropylidene-1,2-diphenyl-3-(phenylsulfonyl)propan-1-one **3a** (77 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then  $\text{I}_2$  (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 22 h to afford **4a** (79 mg, 75%).

White solid; M.p. 150-151 °C (Petroleum ether/EtOAc);  $R_f = 0.41$  (Petroleum ether/EtOAc 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 (t,  $J = 7.2$  Hz, 1H), 7.40-7.33 (m, 3H), 7.30-7.21 (m, 6H), 7.20-7.15 (m, 3H), 7.02 (d,  $J = 7.2$  Hz, 2H), 3.90 (t,  $J = 7.4$  Hz, 2H), 3.62 (t,  $J = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.6, 149.0, 141.0, 132.9, 130.9, 130.0, 129.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.5, 125.5, 124.9, 120.2, 31.8, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{24}\text{H}_{20}\text{IO}_3\text{S}$  ([M+H]<sup>+</sup>): 515.0178, found 515.0178.



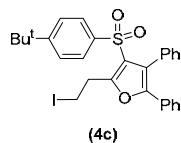
**2-(2-iodoethyl)-4,5-diphenyl-3-tosyloxymethylfuran (4b)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2.5 h, then  $\text{I}_2$  (255 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 23.5 h to afford **4b** (72 mg, 67%).

**Condition B:** 3-Cyclopropylidene-1,2-diphenyl-3-tosyloxymethylpropan-1-one **3b** (80 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then  $\text{I}_2$  (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 23.5 h to afford **4b** (79 mg, 75%).

White solid; M.p. 144-145 °C (Petroleum ether/EtOAc);  $R_f = 0.47$  (Petroleum ether/EtOAc 5/1);  $^1\text{H}$

NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39-7.34 (m, 1H), 7.30-7.22 (m, 6H), 7.20-7.15 (m, 3H), 7.07-7.02 (m, 4H), 3.88 (t, J = 7.4 Hz, 2H), 3.61 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.4, 149.0, 143.8, 138.3, 130.9, 130.2, 129.2, 129.1, 128.35, 128.27, 128.2, 128.1, 127.5, 125.5, 125.2, 120.3, 31.8, 21.5, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>22</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 529.0334, found 529.0335.

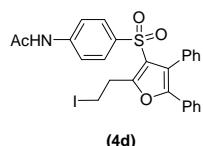


### **3-((4-(tert-butyl)phenyl)sulfonyl)-2-(2-iodoethyl)-4,5-diphenylfuran (4c)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv), 4-(*tert*-butyl)benzenesulfinate **2c** (89 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 12 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 16 h to afford **4c** (75 mg, 66%).

**Condition B:** 3-((4-(*Tert*-butyl)phenyl)sulfonyl)-3-cyclopropylidene-1,2-diphenylpropan-1-one **3c** (89 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 7.5 h to afford **4c** (73 mg, 64%).

White solid; M.p. 126-127 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.53 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37-7.21 (m, 9H), 7.19-7.15 (m, 3H), 7.00 (d, J = 7.6 Hz, 2H), 3.89 (t, J = 7.2 Hz, 2H), 3.62 (t, J = 7.4 Hz, 2H), 1.27 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.7, 156.3, 149.0, 138.0, 130.9, 130.2, 129.2, 128.34, 128.25, 128.1, 127.3, 125.52, 125.45, 125.3, 120.3, 35.0, 31.8, 31.0, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>28</sub>H<sub>28</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 571.0804, found 571.0807.

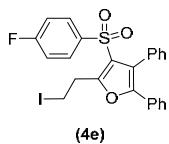


### **N-(4-((2-(2-iodoethyl)-4,5-diphenylfuran-3-yl)sulfonyl)phenyl)acetamide (4d)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (51 mg, 0.2 mmol, 1.0 equiv), sodium 4-acetamidobenzenesulfinate **2d** (89 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 20 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 48 h to afford **4d** (60 mg, 51%).

**Condition B:** N-(4-(1-cyclopropylidene-3-oxo-2,3-diphenylpropylsulfonyl)phenyl)acetamide **3d** (89 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 7.5 h to afford **4d** (67 mg, 59%).

White solid; M.p. 168-169 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.39 (Petroleum ether/EtOAc 1/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 1H), 7.43-7.32 (m, 3H), 7.30-7.21 (m, 6H), 7.20-7.15 (m, 3H), 7.05 (d, J = 7.2 Hz, 2H), 3.87 (t, J = 7.4 Hz, 2H), 3.59 (t, J = 7.4 Hz, 2H), 2.15 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.9, 156.4, 149.1, 142.4, 135.4, 130.9, 130.0, 129.0, 128.7, 128.4, 128.2, 125.5, 125.0, 120.1, 118.6, 31.8, 24.7, 0.0; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>26</sub>H<sub>23</sub>INO<sub>4</sub>S ([M+H]<sup>+</sup>): 572.0392, found 572.0393.

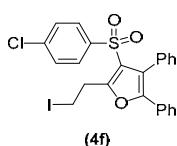


### 3-((4-fluorophenyl)sulfonyl)-2-(2-iodoethyl)-4,5-diphenylfuran (**4e**)

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (51 mg, 0.2 mmol, 1.0 equiv), sodium 4-fluorobenzenesulfinate **2e** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 4 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 24 h to afford **4e** (83 mg, 75%).

**Condition B:** 3-Cyclopropylidene-3-((4-fluorophenyl)sulfonyl)-1,2-diphenylpropan-1-one **3e** (81 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (153 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4e** (72 mg, 68%).

White solid; M.p. 134-135 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.47 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.15 (m, 10H), 7.05 (d, J = 7.2 Hz, 2H), 6.90 (t, J = 8.0 Hz, 2H), 3.90 (t, J = 6.8 Hz, 2H), 3.62 (t, J = 7.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.2 (d, J = 253.9 Hz), 156.6, 149.2, 137.1 (d, J = 3.0 Hz), 130.9, 130.4 (d, J = 9.4 Hz), 130.1, 129.0, 128.4, 128.3, 128.2, 125.6, 124.9, 120.0, 115.7 (d, J = 22.5 Hz), 31.7, 0.0; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>24</sub>H<sub>19</sub>FO<sub>3</sub>S ([M+H]<sup>+</sup>): 533.0084, found 533.0086.

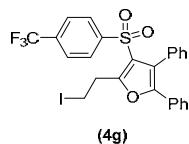


### **3-((4-chlorophenyl)sulfonyl)-2-(2-iodoethyl)-4,5-diphenylfuran (4f)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (51 mg, 0.2 mmol, 1.0 equiv), sodium 4-chlorobenzenesulfinate **2f** (80 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 47 h to afford **4f** (74 mg, 66%).

**Condition B:** 3-((4-Chlorophenyl)sulfonyl)-3-cyclopropylidene-1,2-diphenylpropan-1-one **3f** (85 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4f** (80 mg, 73%).

White solid; M.p.139-140 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.53 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39 (t, J = 7.4 Hz, 1H), 7.33-7.16 (m, 11H), 7.05 (d, J = 7.2 Hz, 2H), 3.89 (t, J = 7.2 Hz, 2H), 3.62 (t, J = 7.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.7, 149.2, 139.5, 139.4, 130.9, 130.0, 129.0, 128.9, 128.7, 128.44, 128.41, 128.38, 128.3, 125.6, 124.7, 119.9, 31.7, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>24</sub>H<sub>19</sub>ClIO<sub>3</sub>S ([M+H]<sup>+</sup>): 548.9788, found 548.9792.



(4g)

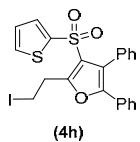
### **2-(2-iodoethyl)-4,5-diphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)furan (4g)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv), sodium 4-(trifluoromethyl)benzenesulfinate **2g** (93 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 8 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4g** (80 mg, 68%).

**Condition B:** 3-Cyclopropylidene-1,2-diphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)propan-1-one **3g** (91 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (153 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4g** (86 mg, 74%).

White solid; M.p. 137-138 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.60 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51-7.48 (m, 4H), 7.37 (t, J = 7.2 Hz, 1H), 7.29-7.17 (m, 7H), 7.01 (d, J = 7.2 Hz, 2H), 3.92 (t, J = 7.2 Hz, 2H), 3.64 (t, J = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.1, 149.4, 144.3, 134.4 (q, J = 32.6 Hz), 130.9, 129.8, 128.8, 128.5, 128.44, 128.37, 128.1, 125.6, 125.5, 124.3,

123.1 (d,  $J$  = 271.3 Hz), 119.9, 31.7, -0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>19</sub>F<sub>3</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 583.0052, found 583.0050.

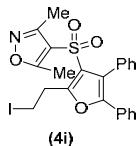


**2-(2-iodoethyl)-4,5-diphenyl-3-(thiophen-2-ylsulfonyl)furan (4h)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (49 mg, 0.2 mmol, 1.0 equiv), sodium thiophene-2-sulfinate **2h** (68 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 1.5 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 48 h to afford **4h** (36 mg, 35%).

**Condition B:** 3-Cyclopropylidene-1,2-diphenyl-3-(thiophen-2-ylsulfonyl)propan-1-one **3h** (79 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 24 h to afford **4h** (64 mg, 62%).

Yellow solid; M.p. 137-138 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.55 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 (dd,  $J$  = 5.2 Hz, 1.2 Hz, 1H), 7.42-7.30 (m, 3H), 7.29-7.24 (m, 2H), 7.22-7.14 (m, 5H), 6.93 (dd,  $J$  = 3.6 Hz, 1.2 Hz, 1H), 6.84-6.80 (m, 1H), 3.85 (t,  $J$  = 7.4 Hz, 2H), 3.59 (t,  $J$  = 7.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 149.1, 142.7, 133.7, 133.5, 130.9, 130.1, 129.1, 128.4, 128.3, 128.2, 127.1, 125.6, 125.5, 120.2, 31.9, -0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>22</sub>H<sub>18</sub>IO<sub>3</sub>S<sub>2</sub> ([M+H]<sup>+</sup>): 520.9742, found 520.9743.



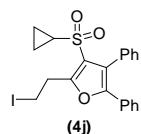
**4-((2-(2-iodoethyl)-4,5-diphenylfuran-3-yl)sulfonyl)-3,5-dimethylisoxazole (4i)**

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (49 mg, 0.2 mmol, 1.0 equiv), sodium 3,5-dimethylisoxazole-4-sulfinate **2i** (74 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 72 h to afford **4i** (41 mg, 39%).

**Condition B:** 3-Cyclopropylidene-3-((3,5-dimethylisoxazol-4-yl)sulfonyl)-1,2-diphenylpropan-1-one

**3i** (82 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 22 h to afford **4i** (48 mg, 45%).

White solid; M.p. 184-185 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.24 (Petroleum ether/EtOAc 10/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43-7.34 (m, 3H), 7.24-7.18 (m, 5H), 7.11-7.06 (m, 2H), 3.87 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 7.2 Hz, 2H), 2.15 (s, 3H), 1.90 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.6, 157.1, 156.9, 149.6, 130.6, 129.9, 129.0, 128.84, 128.75, 128.52, 128.46, 125.4, 124.2, 119.6, 116.8, 32.0, 11.8, 10.4, -1.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>23</sub>H<sub>21</sub>INO<sub>4</sub>S ([M+H]<sup>+</sup>): 534.0236, found 534.0226.

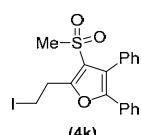


### 3-(cyclopropylsulfonyl)-2-(2-iodoethyl)-4,5-diphenylfuran (**4j**)

**Condition A:** A mixture of 3-cyclopropylidene-1,2-diphenylprop-2-en-1-one **1a** (50 mg, 0.2 mmol, 1.0 equiv), sodium cyclopropanesulfinate **2j** (52 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 1.5 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 72 h to afford **4j** (30 mg, 31%).

**Condition B:** 3-Cyclopropylidene-3-(cyclopropylsulfonyl)-1,2-diphenylpropan-1-one **3j** (71 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 43 h to afford **4j** (41 mg, 42%).

Yellow solid; M.p. 151-152 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.55 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47-7.42 (m, 5H), 7.33-7.28 (m, 2H), 7.25-7.21 (m, 3H), 3.72 (t, J = 7.2 Hz, 2H), 3.52 (t, J = 7.4 Hz, 2H), 2.12-2.04 (m, 1H), 1.00-0.94 (m, 2H), 0.81-0.74 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 149.1, 131.0, 130.9, 129.2, 128.7, 128.6, 128.4, 128.2, 125.7, 124.8, 120.1, 33.1, 31.6, 5.5, 0.2; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>21</sub>H<sub>20</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 479.0178, found 479.0179.

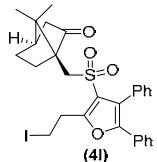


### 2-(2-iodoethyl)-3-(methylsulfonyl)-4,5-diphenylfuran (**4k**)

**Condition B:** 3-Cyclopropylidene-3-(methylsulfonyl)-1,2-diphenylpropan-1-one **3k** (65 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The

mixture was stirred at 100 °C for 17 h to afford **4k** (40 mg, 44%).

White solid; M.p. 162-163 °C (Petroleum ether/EtOAc);  $R_f$  = 0.31 (Petroleum ether/EtOAc 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47-7.44 (m, 5H), 7.33-7.22 (m, 5H), 3.77 (t,  $J$  = 7.2 Hz, 2H), 3.54 (t,  $J$  = 7.2 Hz, 2H), 2.74 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.8, 149.3, 130.9, 130.3, 129.0, 128.9, 128.8, 128.5, 128.4, 125.8, 124.5, 119.8, 44.7, 31.3, 0.4; HRMS (ES $^+$ -TOF) calcd for  $\text{C}_{19}\text{H}_{18}\text{IO}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 453.0021, found 453.0024.

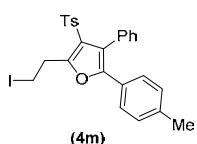


**(1*S*,4*R*)-1-((2-(2-iodoethyl)-4,5-diphenylfuran-3-yl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (4l)**

**Condition B:**

(1*S*,4*R*)-1-((1-cyclopropylidene-3-oxo-2,3-diphenylpropylsulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one **3l** (93 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then  $\text{I}_2$  (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 28 h to afford **4l** (52 mg, 44%).

White solid; M.p. 133-134 °C (Petroleum ether/EtOAc);  $R_f$  = 0.14 (Petroleum ether/EtOAc 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50-7.42 (m, 5H), 7.34-7.29 (m, 2H), 7.25-7.20 (m, 3H), 3.83-3.70 (m, 2H), 3.57-3.51 (m, 2H), 3.35 (d,  $J$  = 14.4 Hz, 1H), 2.60 (d,  $J$  = 14.8 Hz, 1H), 2.45-2.36 (m, 1H), 2.27 (d,  $J_1$  = 18.4 Hz,  $J_2$  = 3.8 Hz, 1H), 2.01-1.81 (m, 3H), 1.61-1.53 (m, 1H), 1.39-1.31 (m, 1H), 0.85 (s, 3H), 0.57 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  214.3, 156.8, 149.2, 131.2, 130.6, 129.2, 128.8, 128.7, 128.4, 128.2, 125.8, 125.3, 119.9, 58.9, 52.8, 47.6, 42.4, 42.3, 31.6, 26.9, 24.5, 19.8, 19.4, 0.2; HRMS (ES $^+$ -TOF) calcd for  $\text{C}_{28}\text{H}_{30}\text{IO}_4\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 589.0909, found 589.0909.



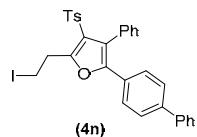
**2-(2-iodoethyl)-4-phenyl-5-(*p*-tolyl)-3-tosylfuran (4m)**

**Condition A:** A mixture of 3-cyclopropylidene-2-phenyl-1-(*p*-tolyl)prop-2-en-1-one **1b** (52 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 5 h, then  $\text{I}_2$  (255 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 12 h to afford **4m**

(63 mg, 58%).

**Condition B:** 3-Cyclopropylidene-2-phenyl-1-(*p*-tolyl)-3-tosylpropan-1-one **3m** (83 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 10 h to afford **4m** (82 mg, 76%).

White solid; M.p. 165-166 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.48 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 (t, J = 7.4 Hz, 1H), 7.30-7.22 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.07-7.02 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 3.87 (t, J = 7.4 Hz, 2H), 3.60 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.1, 149.2, 143.8, 138.2, 138.1, 131.0, 130.3, 129.09, 129.06, 128.2, 128.1, 127.5, 126.4, 125.5, 125.1, 119.5, 31.8, 21.5, 21.2, 0.2; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>26</sub>H<sub>24</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 543.0491, found 543.0487.

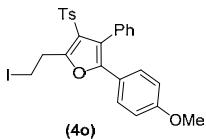


### 2-((1,1'-biphenyl)-4-yl)-5-(2-iodoethyl)-3-phenyl-4-tosylfuran (**4n**)

**Condition A:** A mixture of 1-((1,1'-biphenyl)-4-yl)-3-cyclopropylidene-2-phenylprop-2-en-1-one **1c** (64 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 9 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 10 h to afford **4n** (40 mg, 33%).

**Condition B:** 1-((1,1'-Biphenyl)-4-yl)-3-cyclopropylidene-2-phenyl-3-tosylpropan-1-one **3n** (96 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 10 h to afford **4n** (101mg, 86%).

White solid; M.p. 151-152 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.48 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.51 (d, J = 7.6 Hz, 2H), 7.44-7.36 (m, 5H), 7.34-7.24 (m, 7H), 7.10-7.03 (m, 4H), 3.90 (t, J = 7.4 Hz, 2H), 3.62 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 148.9, 143.9, 140.7, 140.1, 138.3, 131.0, 130.3, 129.1, 128.8, 128.34, 128.26, 128.1, 127.6, 127.0, 126.8, 125.9, 125.4, 120.4, 31.9, 21.5, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>31</sub>H<sub>25</sub>IO<sub>3</sub>S ([M]<sup>+</sup>): 604.0569, found 604.0577.

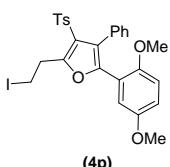


**2-(2-iodoethyl)-5-(4-methoxyphenyl)-4-phenyl-3-tosylfuran (4o)**

**Condition A:** A mixture of 3-cyclopropylidene-1-(4-methoxyphenyl)-2-phenylprop-2-en-1-one **1d** (55 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 6 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 14 h to afford **4o** (75 mg, 67%).

**Condition B:** 3-Cyclopropylidene-1-(4-methoxyphenyl)-2-phenyl-3-tosylpropan-1-one **3o** (86 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 10 h to afford **4o** (88 mg, 80%).

White solid; M.p. 119-120 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.33 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 (t, J = 7.4 Hz, 1H), 7.30-7.22 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 7.07-7.02 (m, 4H), 6.71(d, J = 8.4 Hz, 2H), 3.86 (t, J = 7.4 Hz, 2H), 3.73 (s, 3H), 3.59 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.4, 155.8, 149.2, 143.7, 138.4, 131.1, 130.5, 129.1, 128.2, 128.0, 127.5, 127.1, 125.0, 121.9, 118.6, 113.8, 55.2, 31.8, 21.5, 0.2; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>26</sub>H<sub>24</sub>IO<sub>4</sub>S ([M+H]<sup>+</sup>): 559.0440, found 559.0436.

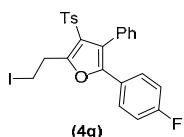


**2-(2,5-dimethoxyphenyl)-5-(2-iodoethyl)-3-phenyl-4-tosylfuran (4p)**

**Condition A:** A mixture of 3-cyclopropylidene-1-(2,5-dimethoxyphenyl)-2-phenylprop-2-en-1-one **1e** (61 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 5 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 13 h to afford **4p** (67 mg, 57%).

**Condition B:** 3-Cyclopropylidene-1-(2,5-dimethoxyphenyl)-2-phenyl-3-tosylpropan-1-one **3p** (92 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 11 h to afford **4p** (81 mg, 69%).

Yellow solid; M.p. 117-118 °C (Petroleum ether/EtOAc);  $R_f$  = 0.20 (Petroleum ether/EtOAc 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30-7.26 (m, 2H), 7.25-7.15 (m, 3H), 7.06-7.00 (m, 4H), 6.81-6.67 (m, 3H), 3.87 (t,  $J$  = 7.4 Hz, 2H), 3.62-3.56 (m, 5H), 3.37 (s, 3H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.0, 153.0, 150.9, 147.6, 143.6, 138.5, 131.0, 130.7, 129.0, 127.51, 127.48, 124.4, 122.2, 118.7, 115.9, 115.6, 112.8, 55.6, 32.0, 21.5, 0.2; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{27}\text{H}_{26}\text{IO}_5\text{S}$  ([M+H]<sup>+</sup>): 589.0546, found 589.0554.

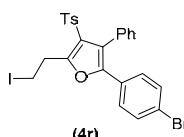


### **2-(4-fluorophenyl)-5-(2-iodoethyl)-3-phenyl-4-tosylfuran (4q)**

**Condition A:** A mixture of 3-cyclopropylidene-1-(4-fluorophenyl)-2-phenylprop-2-en-1-one **1f** (53 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 5 h, then  $\text{I}_2$  (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4q** (56 mg, 51%).

**Condition B:** 3-Cyclopropylidene-1-(4-fluorophenyl)-2-phenyl-3-tosylpropan-1-one **3q** (84 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then  $\text{I}_2$  (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 16 h to afford **4q** (79 mg, 75%).

White solid; M.p. 150-151 °C (Petroleum ether/EtOAc);  $R_f$  = 0.35 (Petroleum ether/EtOAc 5/1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38 (t,  $J$  = 7.4 Hz, 1H), 7.32-7.18 (m, 6H), 7.07-7.01 (m, 4H), 6.87 (t,  $J$  = 8.6 Hz, 2H), 3.88 (t,  $J$  = 7.2 Hz, 2H), 3.60 (t,  $J$  = 7.6 Hz, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.3 (d,  $J$  = 248.2 Hz), 156.4, 148.2, 143.9, 138.2, 130.9, 130.0, 129.1, 128.4, 128.3, 127.51, 127.47 (d,  $J$  = 7.6 Hz), 125.4 (d,  $J$  = 3.8 Hz), 125.3, 119.9, 115.5 (d,  $J$  = 22.1 Hz), 31.8, 21.5, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for  $\text{C}_{25}\text{H}_{21}\text{FO}_3\text{S}$  ([M+H]<sup>+</sup>): 547.0240, found 547.0249.



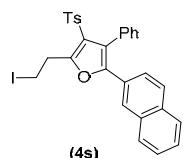
### **2-(4-bromophenyl)-5-(2-iodoethyl)-3-phenyl-4-tosylfuran (4r)**

**Condition A:** A mixture of 1-(4-bromophenyl)-3-cyclopropylidene-2-phenylprop-2-en-1-one **1g** (65 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv), and

AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 4 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 21 h to afford **4r** (74 mg, 61%).

**Condition B:** 1-(4-Bromophenyl)-3-cyclopropylidene-2-phenyl-3-tosylpropan-1-one **3r** (96 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 23 h to afford **4r** (89 mg, 74%).

White solid; M.p. 167-168 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.42 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.38 (t, J = 7.4 Hz, 1H), 7.32-7.21 (m, 6H), 7.11-7.00 (m, 6H), 3.88 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 7.0 Hz, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.6, 148.0, 143.9, 138.1, 131.6, 130.8, 129.9, 129.1, 128.4, 128.0, 127.5, 126.9, 125.4, 122.2, 120.9, 31.8, 21.5, 0.0; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>21</sub>BrIO<sub>3</sub>S ([M+H]<sup>+</sup>): 606.9439, found 606.9445.

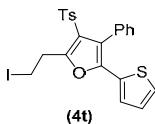


### **2-(2-iodoethyl)-5-(naphthalen-2-yl)-4-phenyl-3-tosylfuran (4s)**

**Condition A:** A mixture of 3-cyclopropylidene-1-(naphthalen-2-yl)-2-phenylprop-2-en-1-one **1h** (59 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 12 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 24 h to afford **4s** (68 mg, 59%).

**Condition B:** 3-Cyclopropylidene-1-(naphthalen-2-yl)-2-phenyl-3-tosylpropan-1-one **3s** (90 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 12 h to afford **4s** (93 mg, 81%).

White solid; M.p. 204-205 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.44 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.77-7.58 (m, 4H), 7.44-7.37 (m, 3H), 7.33-7.27 (m, 4H), 7.26-7.24 (m, 1H), 7.12-7.03 (m, 4H), 3.93 (t, J = 7.6 Hz, 2H), 3.65 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.7, 149.2, 143.9, 138.3, 132.9, 132.7, 131.1, 130.3, 129.2, 128.34, 128.29, 128.0, 127.58, 127.56, 126.6, 126.5, 126.4, 125.4, 125.0, 123.1, 120.7, 32.0, 21.5, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>29</sub>H<sub>24</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 579.0491, found 579.0487.

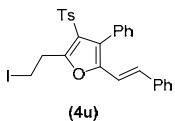


**2-(2-iodoethyl)-4-phenyl-5-(thiophen-2-yl)-3-tosylfuran (4t)**

**Condition A:** A mixture of 3-cyclopropylidene-2-phenyl-1-(thiophen-2-yl)prop-2-en-1-one **1i** (51 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 3 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 20 h to afford **4t** (76 mg, 65%).

**Condition B:** 3-Cyclopropylidene-2-phenyl-1-(thiophen-2-yl)-3-tosylpropan-1-one **3t** (82 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 12 h to afford **4t** (74 mg, 69%).

Yellow solid; M.p. 101-102 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.46 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40 (t, J = 7.4 Hz, 1H), 7.34-7.25 (m, 4H), 7.13-7.04 (m, 5H), 6.92-6.84 (m, 2H), 3.85 (t, J = 7.4 Hz, 2H), 3.58 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.0, 145.8, 144.0, 138.2, 131.1, 131.0, 129.4, 129.2, 128.5, 128.3, 127.6, 127.1, 125.7, 125.2, 124.7, 119.1, 31.7, 21.5, -0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>23</sub>H<sub>20</sub>IO<sub>3</sub>S<sub>2</sub> ([M+H]<sup>+</sup>): 534.9899, found 534.9900.



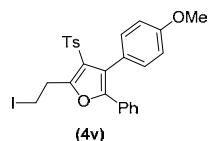
**(E)-2-(2-iodoethyl)-4-phenyl-5-styryl-3-tosylfuran (4u)**

**Condition A:** A mixture of (E)-1-cyclopropylidene-2,5-diphenylpenta-1,4-dien-3-one **1j** (54 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 4 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 11 h to afford **4u** (30 mg, 27%).

**Condition B:** (E)-5-cyclopropylidene-1,4-diphenyl-5-tosylpent-1-en-3-one **3u** (86 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 26 h to afford **4u** (29 mg, 26%).

White solid; M.p. 175-176 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.48 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41-7.25 (m, 9H), 7.24-7.18 (m, 1H), 7.16-7.01 (m, 5H), 6.48 (d, J = 16.4 Hz, 1H), 3.85 (t, J = 7.4 Hz, 2H), 3.59 (t, J = 7.4 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ

156.9, 149.5, 143.9, 138.2, 136.2, 131.1, 129.5, 129.4, 129.1, 128.7, 128.2, 128.1, 127.9, 127.4, 126.5, 124.8, 122.2, 113.5, 32.0, 21.5, -0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>27</sub>H<sub>24</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 555.0491, found 555.0491.

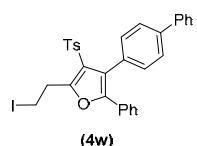


**2-(2-iodoethyl)-4-(4-methoxyphenyl)-5-phenyl-3-tosylfuran (4v)**

**Condition A:** A mixture of 3-cyclopropylidene-2-(4-methoxyphenyl)-1-phenylprop-2-en-1-one **1k** (55 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (71 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 12 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 24 h to afford **4v** (67 mg, 60%).

**Condition B:** 3-Cyclopropylidene-2-(4-methoxyphenyl)-1-phenyl-3-tosylpropan-1-one **3v** (86 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 10 h to afford **4v** (83 mg, 75%).

White solid; M.p. 136-137 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.35 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31-7.24 (m, 4H), 7.21-7.16 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.90-3.84 (m, 5H), 3.60 (t, J = 7.2 Hz, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.5, 156.3, 149.0, 143.8, 138.3, 132.1, 129.2, 129.1, 128.3, 128.0, 127.5, 125.4, 125.3, 122.1, 120.0, 113.7, 55.2, 31.8, 21.5, 0.2; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>26</sub>H<sub>24</sub>IO<sub>4</sub>S ([M+H]<sup>+</sup>): 559.0440, found 559.0442.

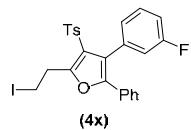


**3-([1,1'-biphenyl]-4-yl)-5-(2-iodoethyl)-2-phenyl-4-tosylfuran (4w)**

**Condition A:** A mixture of 2-([1,1'-biphenyl]-4-yl)-3-cyclopropylidene-1-phenylprop-2-en-1-one **1l** (64 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (72 mg, 0.4 mmol, 2.0 equiv), and AcOH (25 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2.5 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 18 h to afford **4w** (31 mg, 26%).

**Condition B:** 2-([1,1'-Biphenyl]-4-yl)-3-cyclopropylidene-1-phenyl-3-tosylpropan-1-one **3w** (98 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 30 h to afford **4w** (78 mg, 65%).

White solid; M.p. 177-178 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.42 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (d, J = 6.8 Hz, 2H), 7.55-7.46 (m, 4H), 7.40 (t, J = 6.8 Hz, 1H), 7.33-7.26 (m, 4H), 7.22-7.16 (m, 3H), 7.12 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 3.90 (t, J = 7.0 Hz, 2H), 3.62 (t, J = 7.0 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 149.1, 143.9, 140.8, 140.4, 138.2, 131.4, 129.22, 129.17, 129.1, 128.9, 128.4, 128.2, 127.6, 127.0, 126.8, 125.6, 125.4, 119.9, 31.9, 21.5, 0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>31</sub>H<sub>26</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 605.0647, found 605.0644.



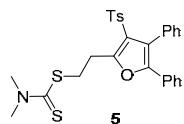
### 3-(3-fluorophenyl)-5-(2-iodoethyl)-2-phenyl-4-tosylfuran (4x)

**Condition A:** A mixture of 3-cyclopropylidene-2-(3-fluorophenyl)-1-phenylprop-2-en-1-one **1m** (53 mg, 0.2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2b** (73 mg, 0.4 mmol, 2.0 equiv) was stirred in 2 mL of MeCN at rt under ambient atmosphere for 2.5 h, then I<sub>2</sub> (254 mg, 1 mmol, 5.0 equiv) was added. The mixture was stirred at 100 °C for 22 h to afford **4x** (59 mg, 54%).

**Condition B:** 3-Cyclopropylidene-2-(3-fluorophenyl)-1-phenyl-3-tosylpropan-1-one **3x** (84 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of MeCN, then I<sub>2</sub> (154 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at 100 °C for 12 h to afford **4x** (85 mg, 78%).

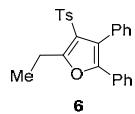
White solid; M.p. 130-131 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.47 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.33-7.18 (m, 8H), 7.12-7.03 (m, 3H), 6.92 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 9.6 Hz, 1H), 3.89 (t, J = 7.2 Hz, 2H), 3.61 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.5 (d, J = 246.0 Hz), 156.6, 149.2, 144.2, 138.2, 132.4 (d, J = 8.5 Hz), 129.9 (d, J = 9.4 Hz), 129.2, 128.8, 128.5, 128.4, 127.5, 127.0 (d, J = 2.5 Hz), 125.6, 125.2, 118.9 (d, J = 1.4 Hz), 117.9 (d, J = 21.6 Hz), 115.2 (d, J = 21.1 Hz), 31.8, 21.5, -0.1; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>21</sub>FO<sub>3</sub>S ([M+H]<sup>+</sup>): 547.0240, found 547.0244.

### 3. Transformation of 3-sulfonylfuran 4b to other functionalized furans 5-10



#### **2-(4,5-diphenyl-3-tosyloxymethyl)ethyl dimethylcarbamodithioate (5)**

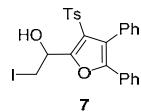
2-(2-iodoethyl)-4,5-diphenyl-3-tosyloxymethylfuran **4b** (106 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of DMF, and dimethyldithiocarbamic acid sodium salt dihydrate (72 mg, 0.4 mmol, 2.0 equiv) was added, the mixture was then stirred at 150 °C for 0.5 h under ambient atmosphere. After completion of the reaction, the mixture was quenched by 10 mL of H<sub>2</sub>O and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with H<sub>2</sub>O (3 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **5** (94 mg, 90%) as a white solid; M.p. 126-127 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.14 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 (t, J = 7.6 Hz, 1H), 7.32-7.22 (m, 6H), 7.19-7.15 (m, 3H), 7.08-7.03 (m, 4H), 3.83 (t, J = 7.4 Hz, 2H), 3.70 (t, J = 7.4 Hz, 2H), 3.59 (s, 3H), 3.42 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 196.3, 156.5, 148.7, 143.6, 138.6, 130.9, 130.5, 129.3, 129.0, 128.23, 128.17, 128.1, 127.8, 127.4, 125.4, 124.8, 120.1, 45.3, 41.4, 35.2, 27.2, 21.4; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>27</sub>H<sub>24</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 522.1231, found 522.1236.



#### **2-ethyl-4,5-diphenylfuran (6)**

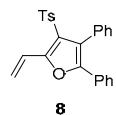
To a solution of 2-(2-iodoethyl)-4,5-diphenyl-3-tosyloxymethylfuran **4b** (106 mg, 0.2 mmol, 1.0 equiv) in 2 mL of AcOH was added zinc power (131 mg, 2 mmol, 10.0 equiv) in portions at 65 °C. The mixture was stirred at 65 °C for 1 h. After completion of the reaction, zinc power was filtered off, the filtrate was diluted with EtOAc and neutralized by the addition of aq 70% NaHCO<sub>3</sub> (10 mL), was extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified with flash silica gel chromatography to afford **6** (69 mg, 86%) as a white solid; M.p. 131-132 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.31 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.36 (t, J = 7.4 Hz, 1H), 7.31-7.20 (m, 6H), 7.19-7.14 (m, 3H), 7.08-7.03 (m, 4H), 3.30 (q, J = 7.6 Hz, 2H), 2.34 (s, 3H), 1.46 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.5, 148.1, 143.5, 139.0, 131.0, 130.7, 129.5, 129.1, 128.3, 128.2, 128.0, 127.7, 127.3, 125.3, 123.2, 120.2, 21.5,

21.2, 12.9; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>22</sub>NaO<sub>3</sub>S ([M+Na]<sup>+</sup>): 403.1368, found 403.1362.



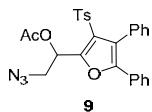
### 1-(4,5-diphenyl-3-tosylfuran-2-yl)-2-iodoethan-1-ol (7)

A solution of cerium (IV) ammonium nitrate (CAN) (274 mg, 0.5 mmol, 2.5 equiv) in water (2 mL) was added dropwise to a stirring solution of the **4b** (106 mg, 0.2 mmol, 1.0 equiv) in acetonitrile (6 mL), the mixture was stirred at room temperature for 20 min, then added 10 mL of H<sub>2</sub>O and extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated *in vacuo*. The residue was purified with flash silica gel chromatography to afford **7** (46 mg, 42%) as a white solid; M.p. 176-177 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.31 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37 (t, *J* = 7.4 Hz, 1H), 7.30-7.23 (m, 6H), 7.21-7.15 (m, 3H), 7.08-6.99 (m, 4H), 5.58 (t, *J* = 6.8 Hz, 1H), 4.02 (br, 1H), 3.88-3.75 (m, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.6, 149.4, 144.3, 137.4, 130.9, 129.6, 129.2, 128.8, 128.43, 128.41, 128.35, 128.3, 127.6, 125.8, 120.6, 67.8, 21.6, 7.3; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>25</sub>H<sub>21</sub>INaO<sub>4</sub>S ([M+Na]<sup>+</sup>): 567.0103, found 567.0106.



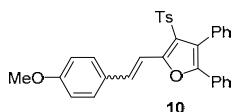
### (E)-2-(2-iodoethyl)-4-phenyl-5-styryl-3-tosylfuran (8)

2-(2-iodoethyl)-4,5-diphenyl-3-tosylfuran **4b** (106 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of THF, and Et<sub>3</sub>N (204 mg, 2 mmol, 10.0 equiv) was added, the mixture was then stirred at 80 °C for 0.5 h under ambient atmosphere. After completion of the reaction, the solvent was removed *in vacuo*, and the residue was purified with flash silica gel chromatography to afford **8** (73 mg, 91%) as a white solid; M.p. 184-185 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.25 (Petroleum ether/EtOAc 20/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 (dd, *J*<sub>1</sub> = 17.4 Hz, *J*<sub>2</sub> = 11.4 Hz, 1H), 7.38 (*J* = 7.4 Hz, 1H), 7.33-7.23 (m, 6H), 7.20-7.15 (m, 3H), 7.09-7.03 (m, 4H), 6.21-6.14 (m, 1H), 5.66-5.60 (m, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 152.7, 149.0, 143.7, 138.7, 130.9, 130.2, 129.2, 129.1, 128.34, 128.27, 128.2, 127.4, 125.7, 124.7, 123.4, 121.3, 119.1, 21.5; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>27</sub>H<sub>24</sub>IO<sub>3</sub>S ([M+H]<sup>+</sup>): 401.1211, found 401.1216.



### **2-azido-1-(4,5-diphenyl-3-tosylfuran-2-yl)ethyl acetate (9)**

2-(2-iodoethyl)-4,5-diphenyl-3-tosylfuran **4b** (106 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of THF, and Et<sub>3</sub>N (204 mg, 2 mmol, 10.0 equiv) was added, the mixture was then stirred at 80 °C for 0.5 h under ambient atmosphere. After completion of the reaction, THF and Et<sub>3</sub>N were removed *in vacuo*, the mixture was directly used in the next step. To a suspension of NaN<sub>3</sub> (39 mg, 0.6 mmol, 3.0 equiv) and KI (34 mg, 0.2 mmol, 1.0 equiv) in AcOH (2 mL) at room temperature under N<sub>2</sub> atmosphere was added NaIO<sub>4</sub> (43 mg, 0.2 mmol, 1.0 equiv) and the reaction mixture was stirred for 5 min when a dark brown color was observed. This was followed by the addition of the crude product prepared and the entire reaction mixture was stirred at rt for 24 h. After completion of the reaction, the mixture was quenched by adding 10 mL of H<sub>2</sub>O and extracted with EtOAc (3 × 10 mL). The combine organic layers were washed with sat. aq NaHCO<sub>3</sub> (5 mL), aq 5% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure. The residue was purified with flash silica gel chromatography to afford **9** (54mg, 54%) as a white solid; M.p. 125-126 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.13 (Petroleum ether/EtOAc 10/1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.42-7.34 (m, 3H), 7.30 (t, J = 7.6 Hz, 2H), 7.25-7.18 (m, 5H), 7.09 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 6.86 (dd, J<sub>1</sub> = 7.2 Hz, J<sub>2</sub> = 4.4 Hz, 1H), 3.95-3.81 (m, 2H), 2.35 (m, 3H), 2.26 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.8, 151.0, 150.3, 144.2, 137.7, 130.9, 129.6, 129.2, 128.8, 128.5, 128.4, 128.3, 127.8, 125.7, 120.3, 67.7, 53.0, 21.6, 20.8; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>27</sub>H<sub>23</sub>N<sub>3</sub>NaO<sub>5</sub>S ([M+Na]<sup>+</sup>): 502.1437, found 524.1264.



### **2-(4-methoxystyryl)-4,5-diphenyl-3-tosylfuran (10)**

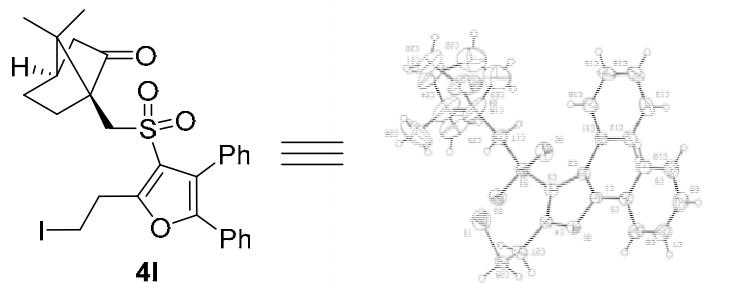
2-(2-iodoethyl)-4,5-diphenyl-3-tosylfuran **4b** (106 mg, 0.2 mmol, 1.0 equiv) was dissolved in 2 mL of CH<sub>3</sub>CN, and Et<sub>3</sub>N (204 mg, 2 mmol, 10.0 equiv) was added, the mixture was then stirred at 80 °C for 0.5 h under N<sub>2</sub> atmosphere. After completion of the reaction, 4-iodoanisole (57 mg, 0.24 mmol, 1.2 equiv) and Pd(OAc)<sub>2</sub> (5 mg, 0.02 mmol, 0.1 equiv) were added and the entire reaction mixture was stirred at the same temperature for 24 h, the solvent was removed *in vacuo*, and the residue was purified with flash silica gel chromatography to afford **10** (61 mg, 60%) as a yellow solid (E/Z =6:1); M.p. 190-191 °C (Petroleum ether/EtOAc); R<sub>f</sub> = 0.34 (Petroleum ether/EtOAc 5/1); <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>): δ 7.84-7.28 (m, 5H), 7.33-7.27 (m, 6H), 7.22-7.18 (m, 2H), 7.10-6.86 (m, 7H), 3.88-3.84 (m, 3H), 2.36-2.33 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.3, 153.7, 148.5, 143.6, 138.9, 133.2, 131.0, 130.4, 129.3, 129.1, 129.0, 128.8, 128.35, 128.27, 128.2, 128.1, 127.4, 125.7, 123.5, 121.6, 114.3, 112.1, 55.4, 21.5; HRMS (ES<sup>+</sup>-TOF) calcd for C<sub>32</sub>H<sub>27</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 507.1630, found 507.1631.

#### 4. X-ray diffraction analysis of **3I**

Crystallographic structure analysis of **3I**: A suitable single crystal was mounted on a *Xcalibur, Atlas, Gemini ultra* at 296(2) using Mo K $\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). The intensity data were collected with *CrysAlisPro* program and reduced by *CrysAlisPro* program. The structure was solved by direct methods, expended by difference Fourier syntheses and refined by Full-matrix squares on F<sup>2</sup> using *SHELXL* program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. Details of the X-ray experiments and crystal data are summarized in **Table S1**.

**Figure S1.** ORTEP drawing of **3I** with ellipsoid contour at 30% probability level (CCDC 1543241)

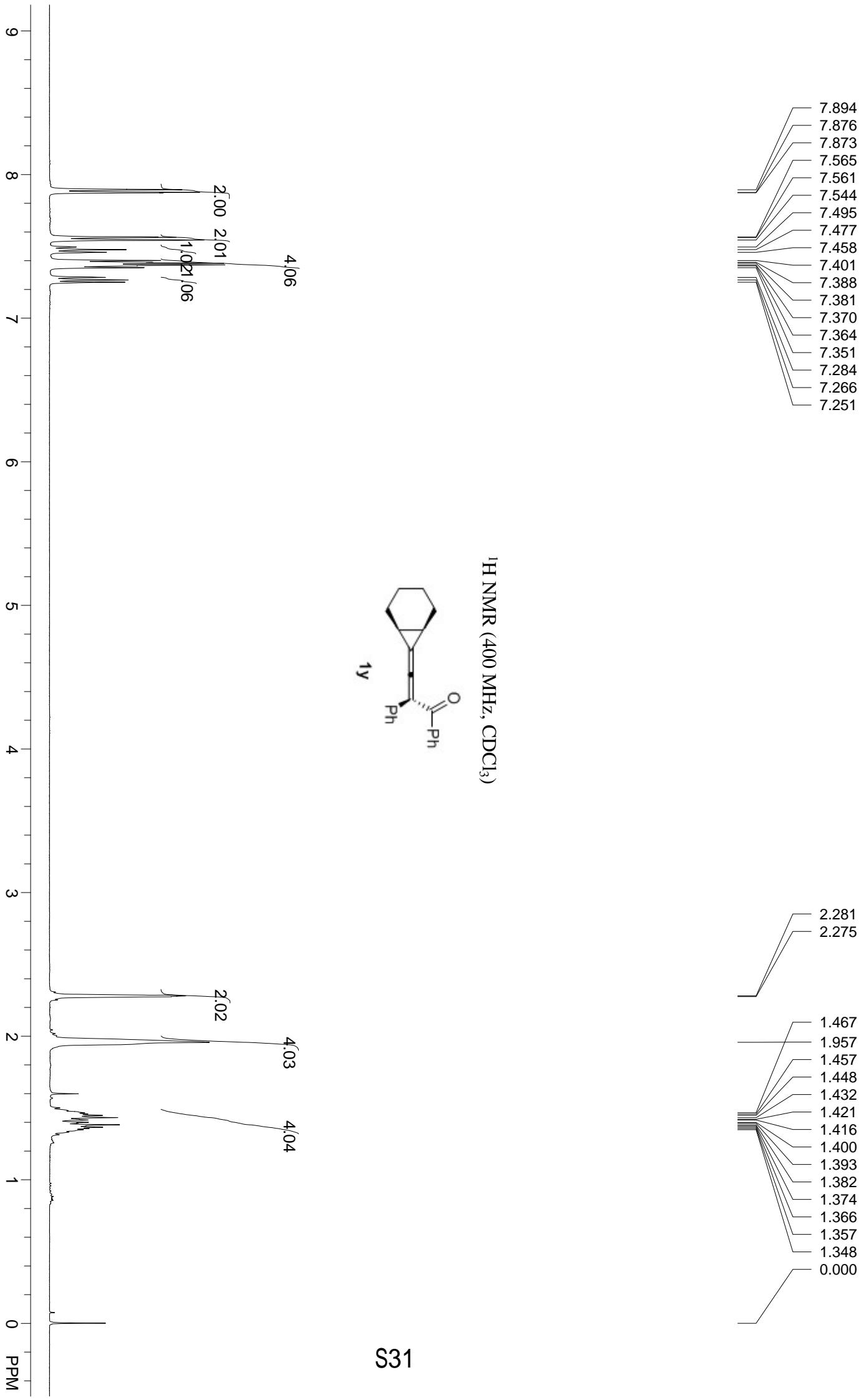


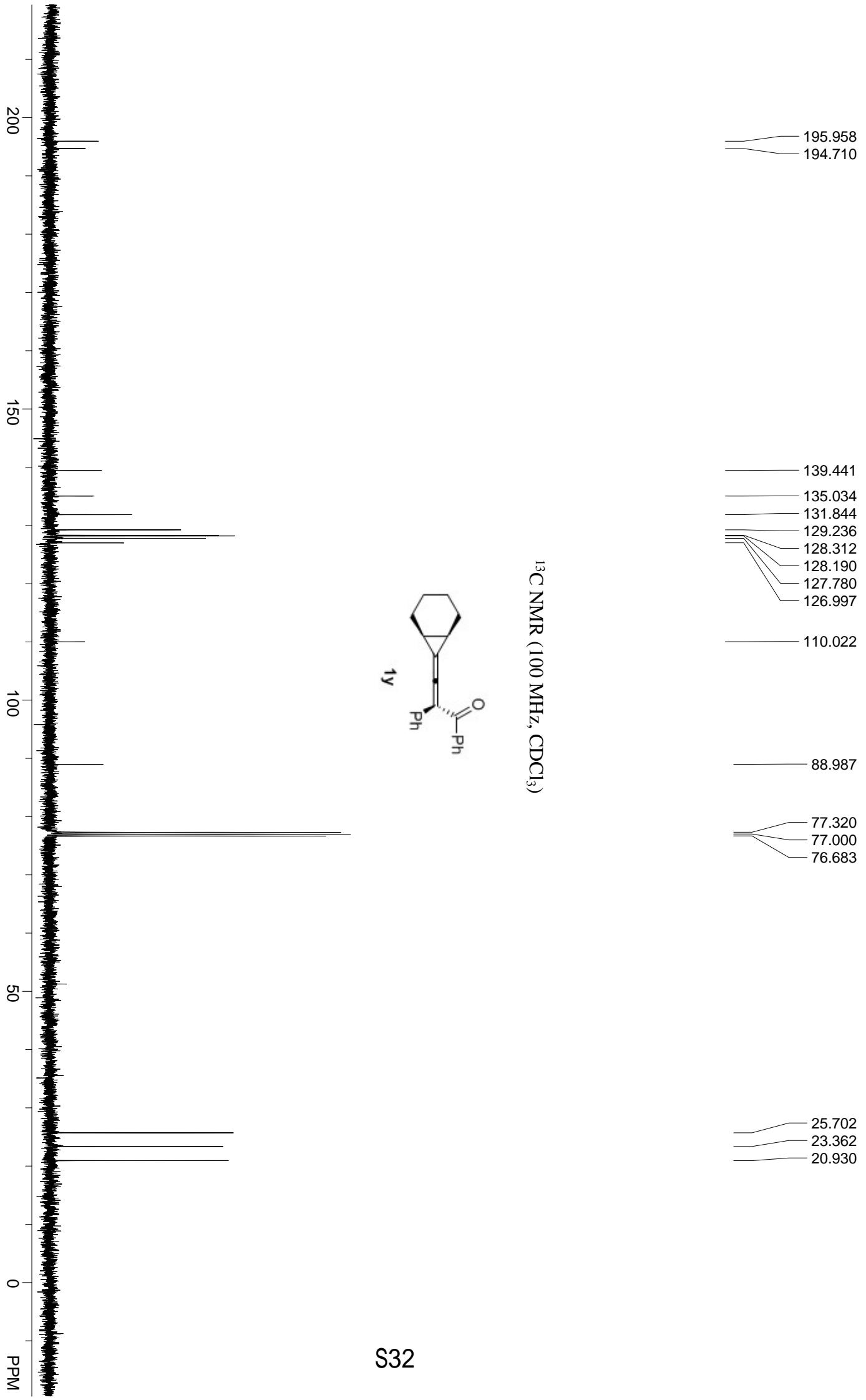
**Table S1.** Crystal data and structure refinement for **3I**.

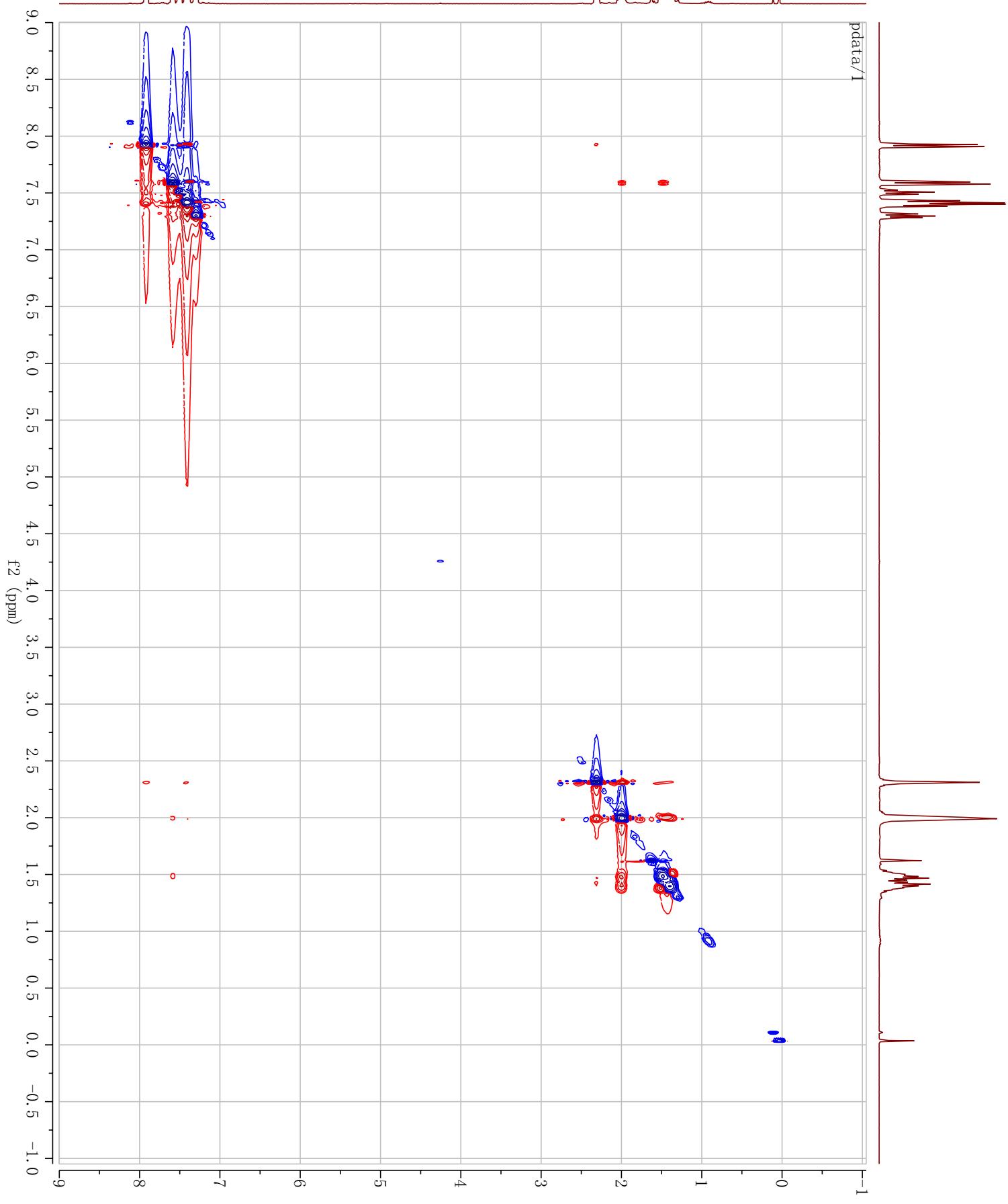
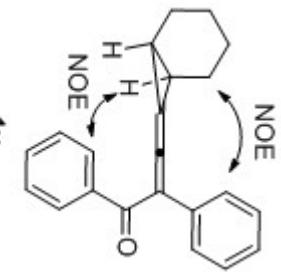
Empirical formula	$C_{28}H_{29}IO_4S$	
Formula weight	588.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, Space group	Monoclinic, P 21/n	
Unit cell dimensions	$a = 12.0087(6)$ Å	$\alpha = 90.00^\circ$
	$b = 17.7464(7)$ Å	$\beta = 103.892(5)^\circ$
	$c = 12.6045(7)$ Å	$\gamma = 90.00^\circ$
Volume	$2607.6(2)$ Å <sup>3</sup>	
Z	4	
Density(calculated)	1.499 Mg/m <sup>3</sup>	
Absorption coefficient	1.339 mm <sup>-1</sup>	
F(000)	1192	
Crystal size	0.49*0.40*0.36 mm <sup>3</sup>	
Theta range for data collection	2.92 to 25.35°.	
Index ranges	-13≤h≤14, -21≤k≤21, -14≤l≤15	
Reflections collected	18518	
Independent reflections	4753 [R(int)= 0.0319]	
Completeness to theta=26.32°	99.75 %	
Absorption correction	Multi-scan from equivalents	
Max. and min. transmission	1.000 and 0.843	
Refinement method	Full-matrix squares on F <sup>2</sup>	
Data/restraints/parameters	4753 / 49 / 328	
Goodness-of-fit on F <sup>2</sup>	1.049	
Final R indices [I>2sigma(I)]	$R_1 = 0.0665$ , $wR_2 = 0.1759$	
R indices(all data)	$R_1 = 0.0879$ , $wR_2 = 0.1906$	
Extinction coefficient	?	
Largest diff.peak and hole	0.776 and -0.469 eÅ <sup>3</sup>	

## References

1. Miao, M.; Cao, J.; Zhang, J.; Huang, X.; Wu, L. *Org. Lett.* **2012**, *14*, 2718;
2. Crowell, T. A.; Halliday, B. D.; McDonald, J. H., III; Indelicato, J. M.; Pasini, C. E.; Wu, E. C. Y. *J. Med. Chem.* **1989**, *32*, 2436;
3. Miao, M.; Luo, Y.; Xu, H.; Chen, Z.; Xu, J.; Ren, H. *Org. Lett.* **2016**, *18*, 4292;
4. Ye, S.; Yu, Z.-X. *Org. Lett.* **2009** *12*, 804.
6. Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR

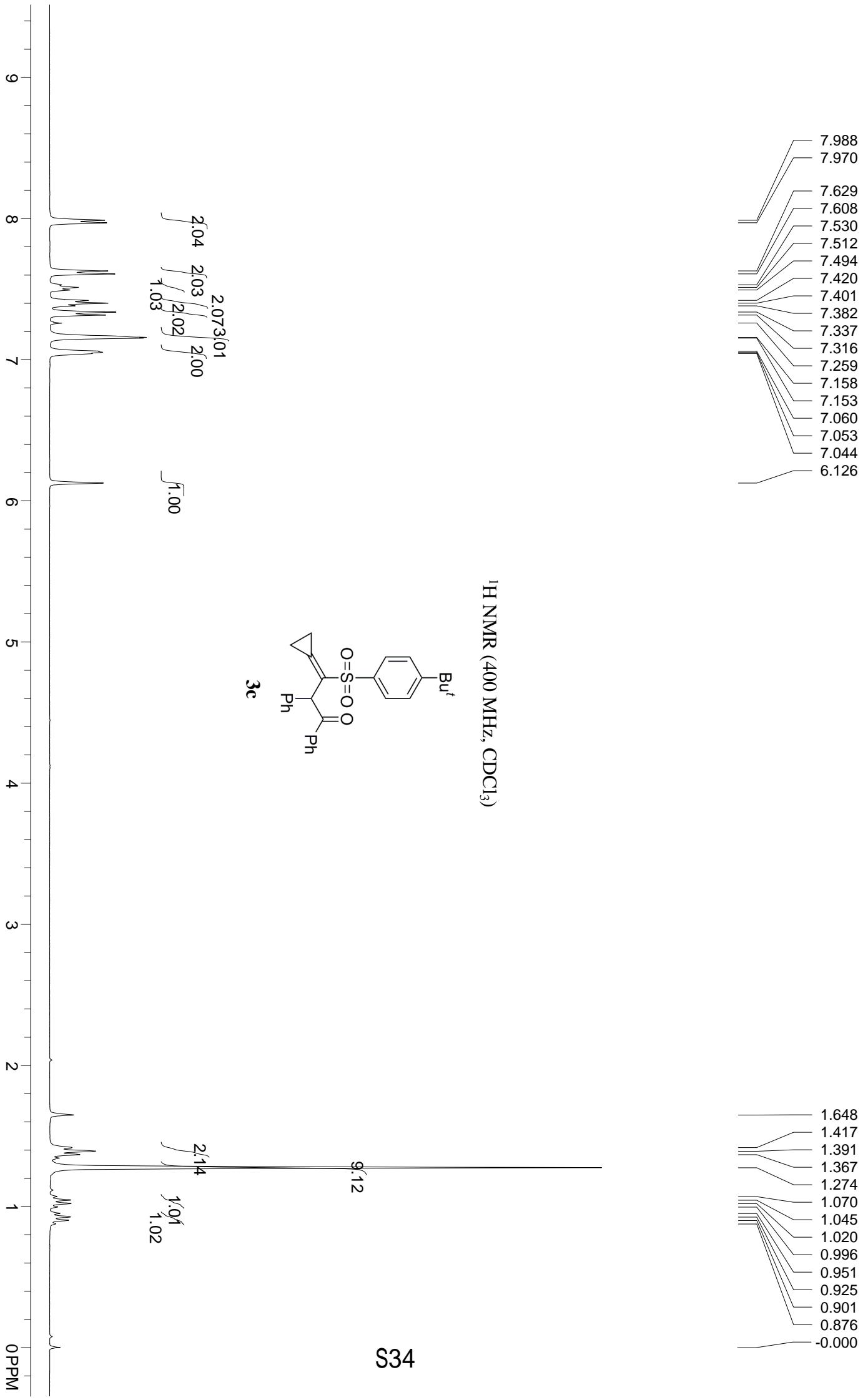


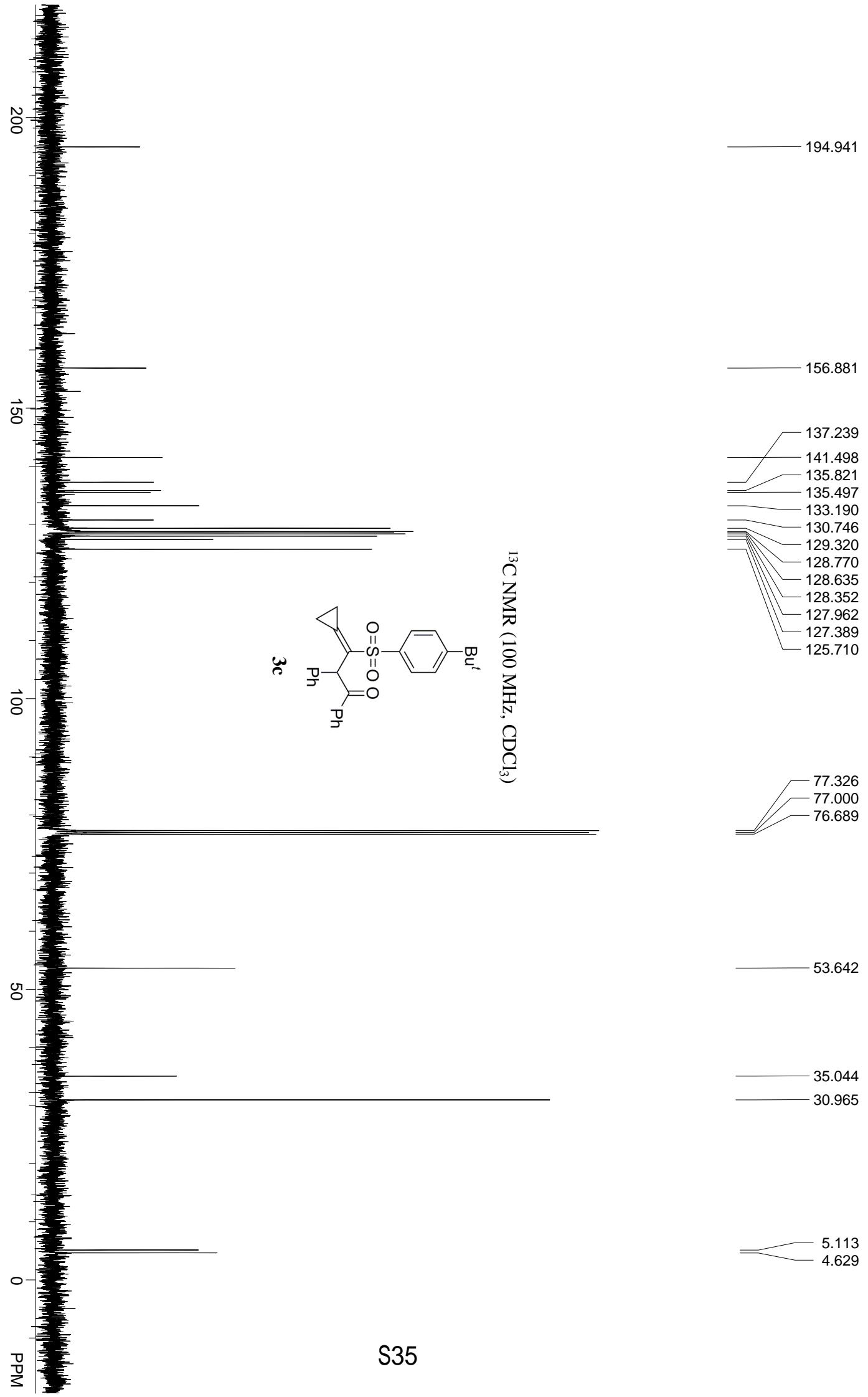




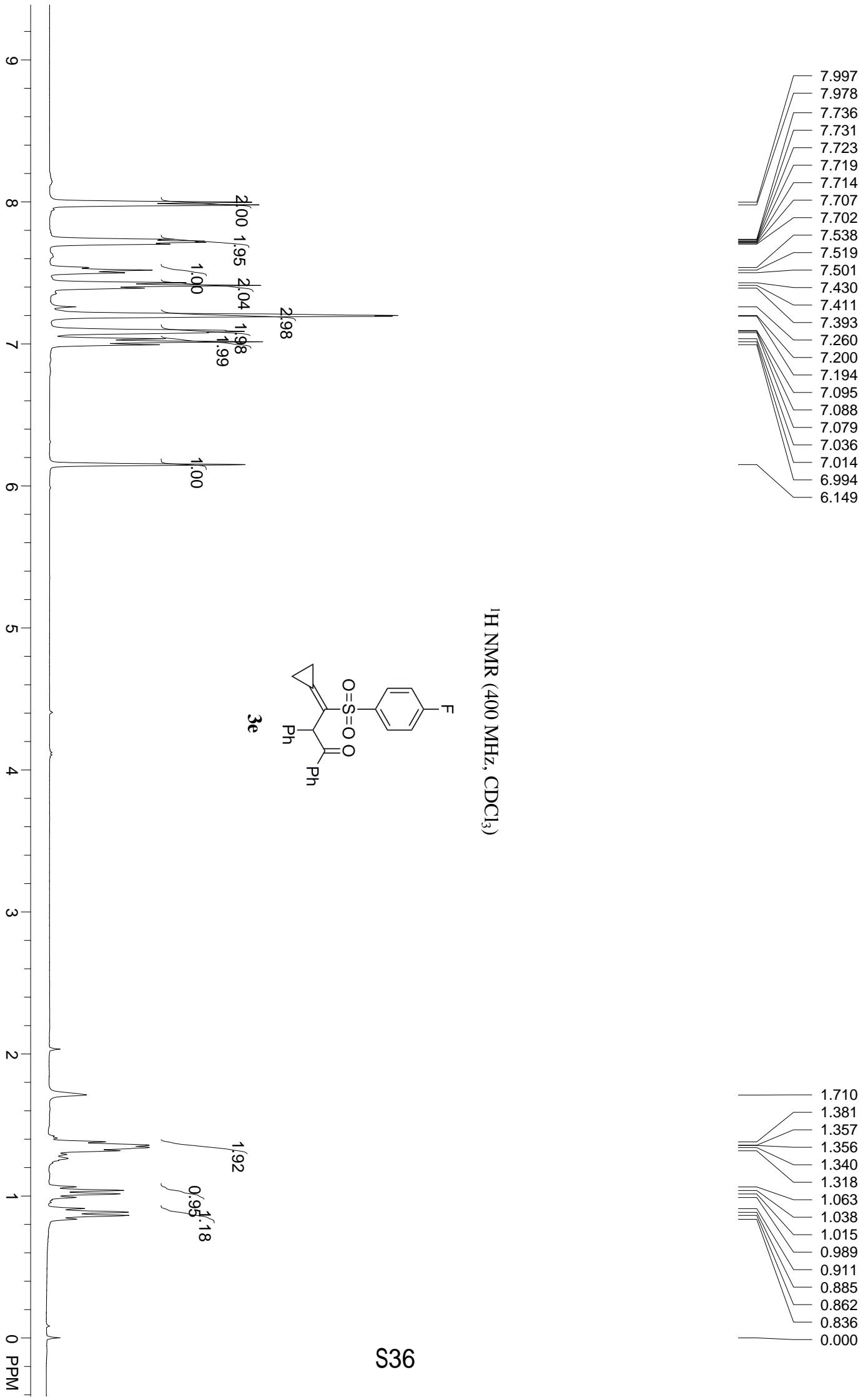
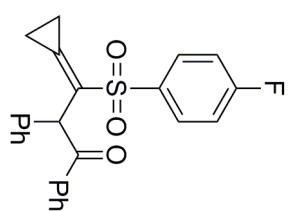
S33

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

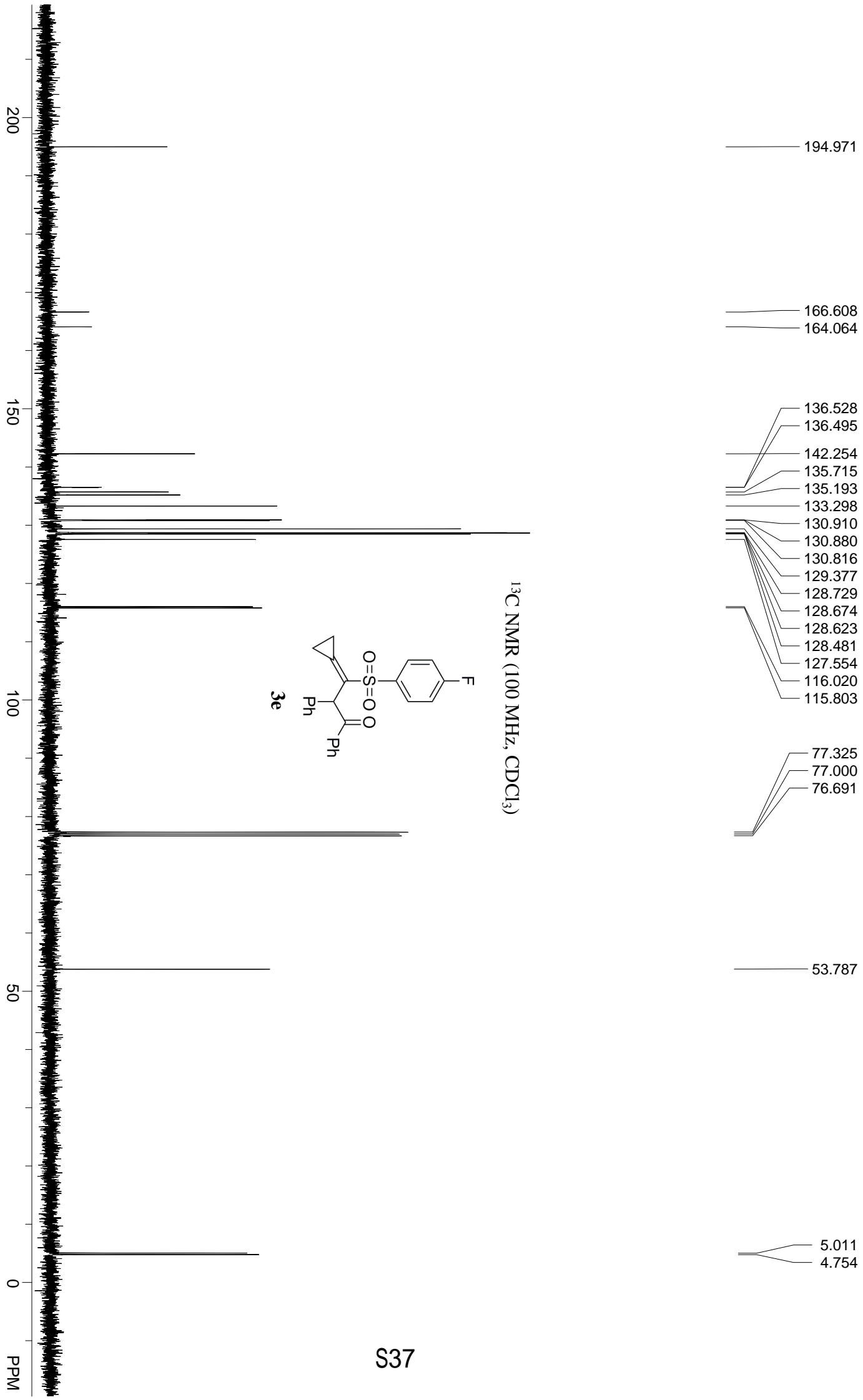
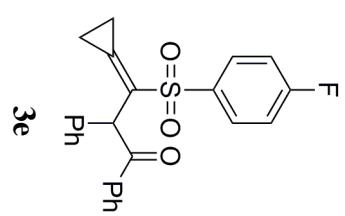


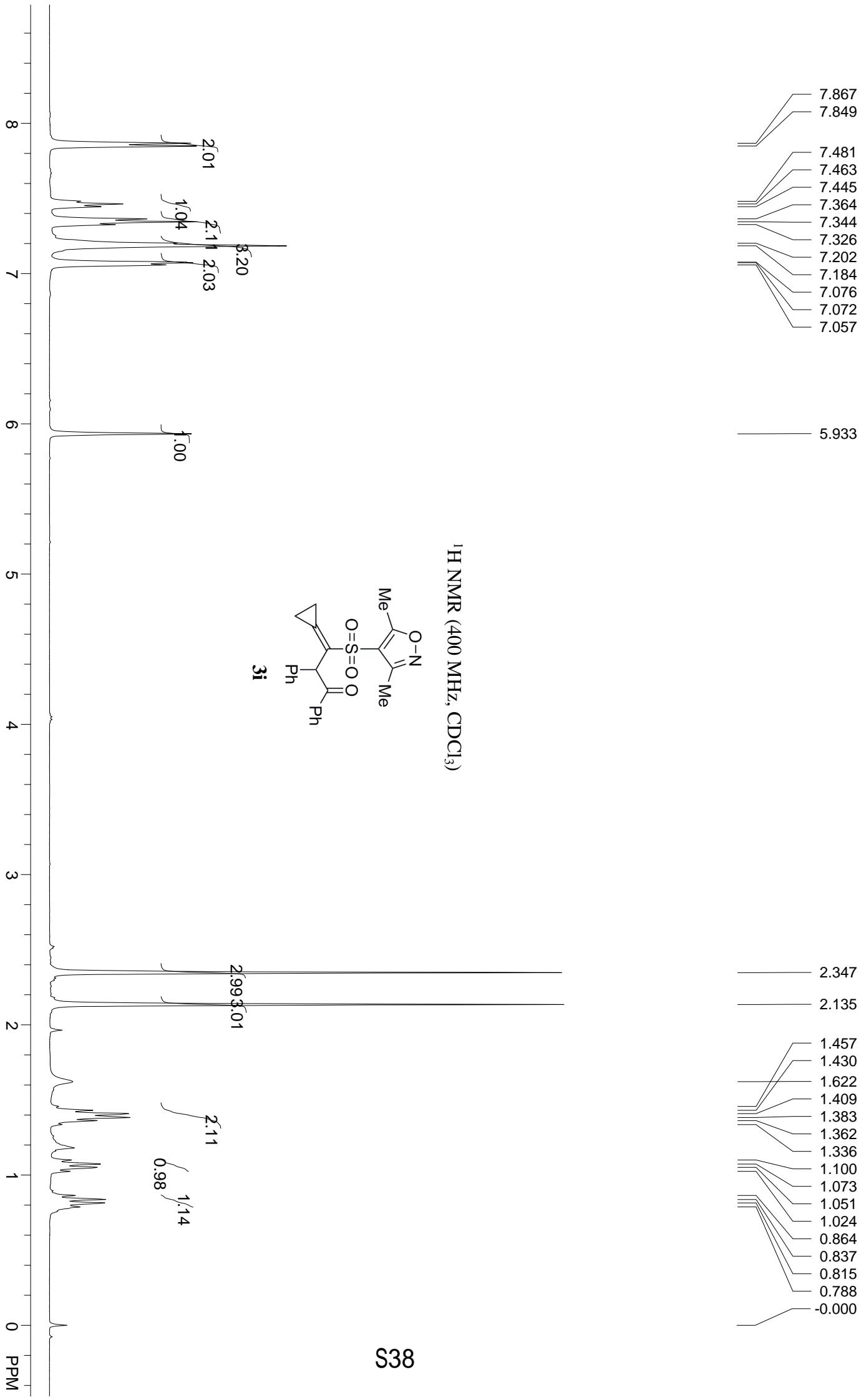


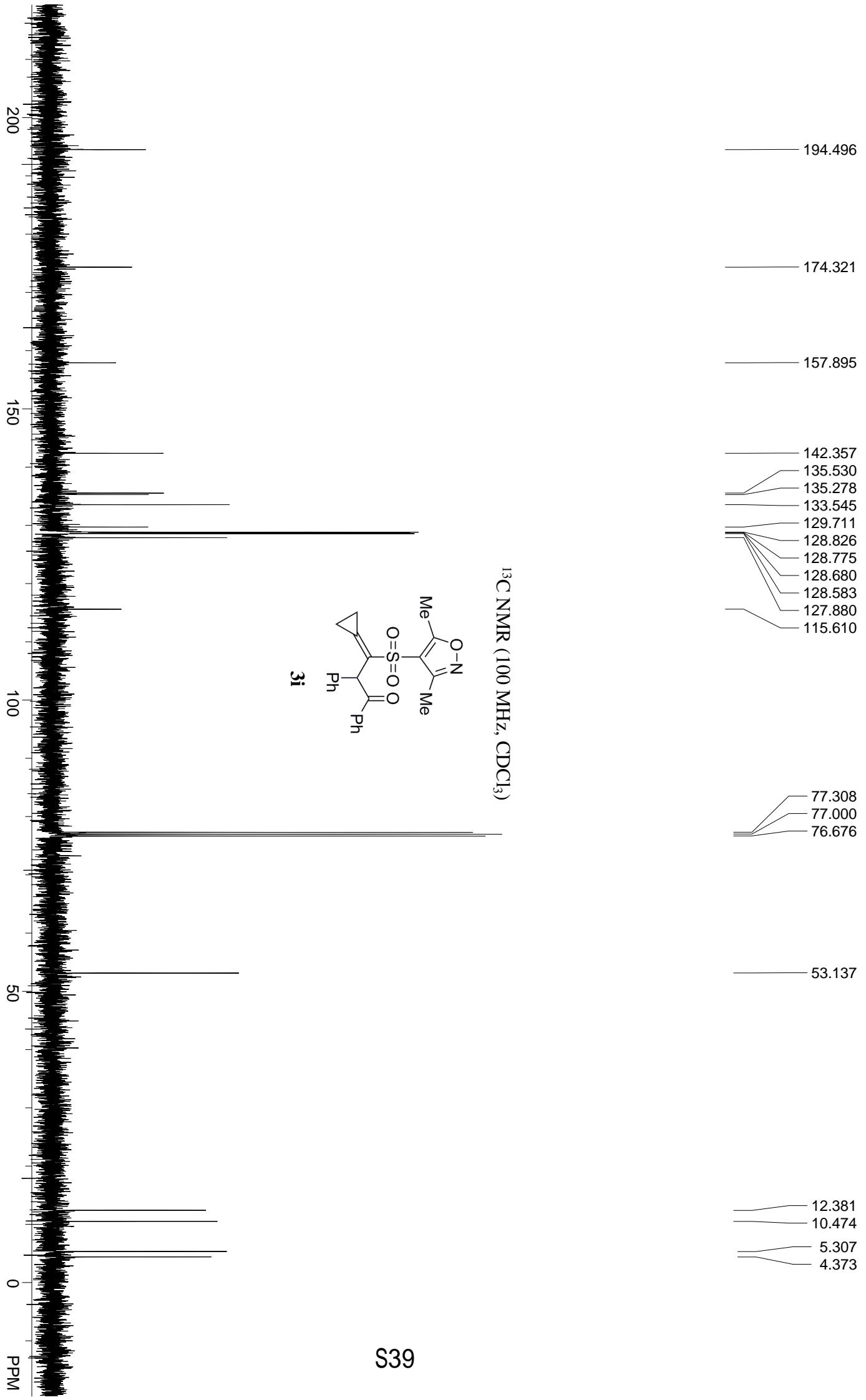
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



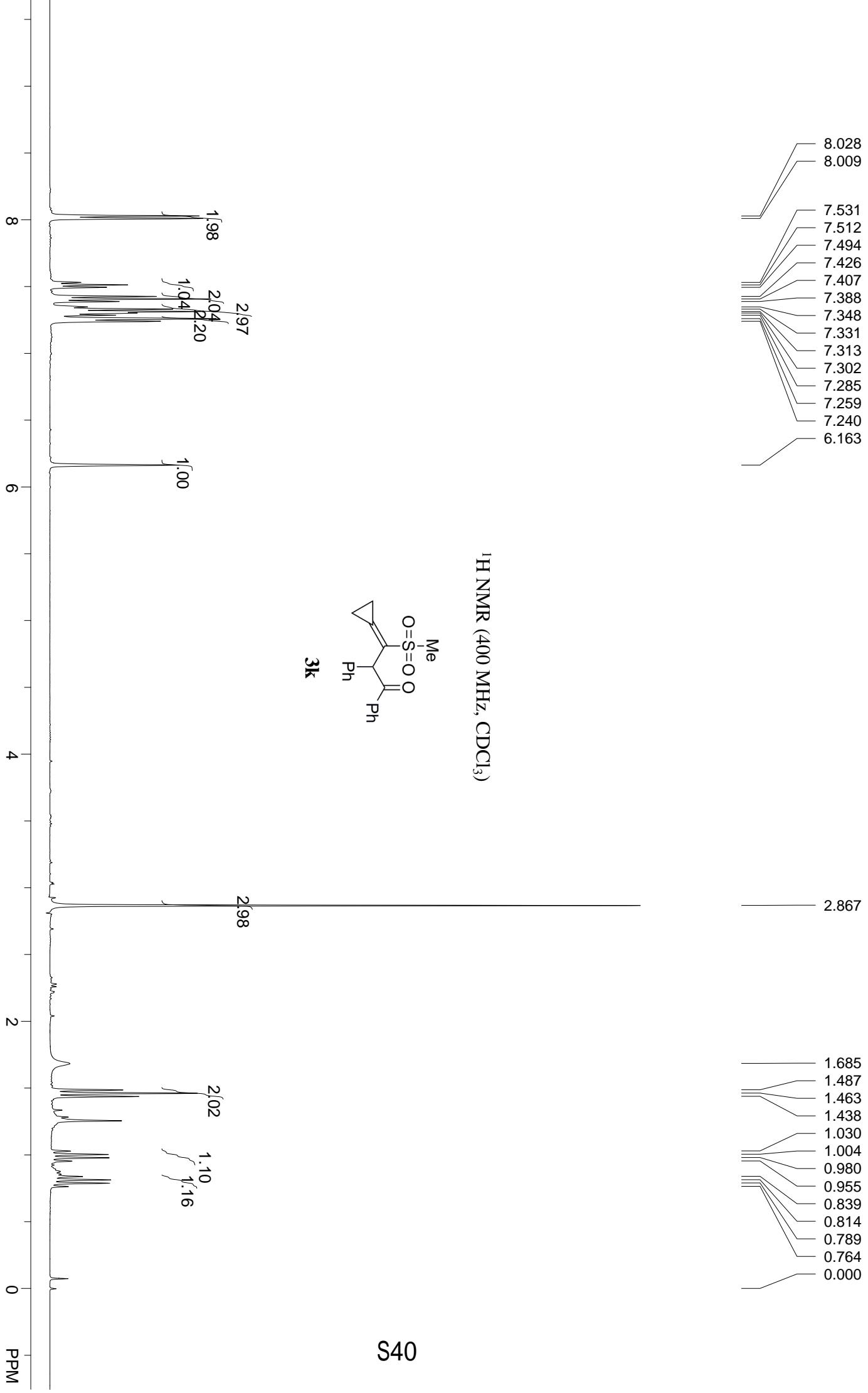
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

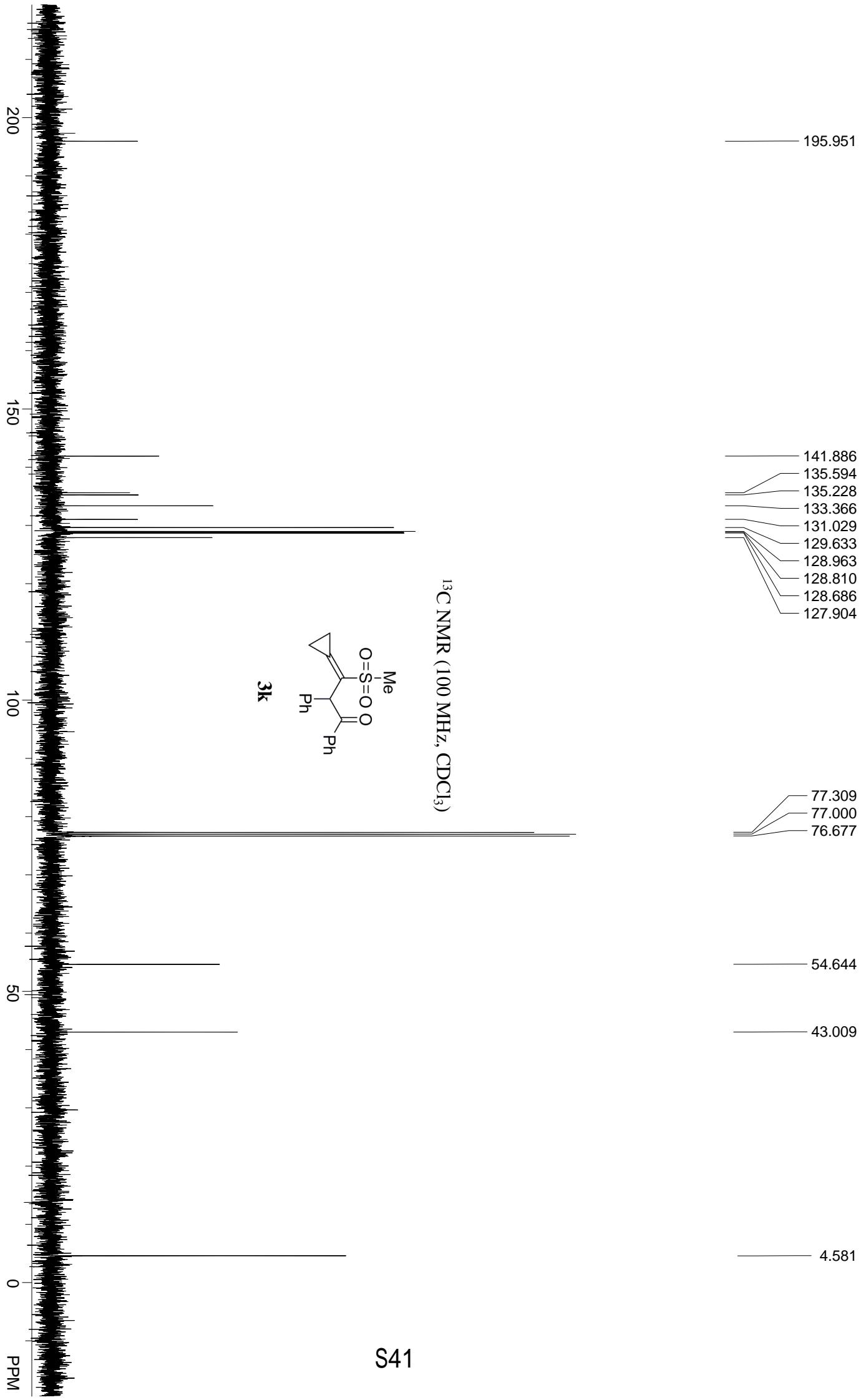




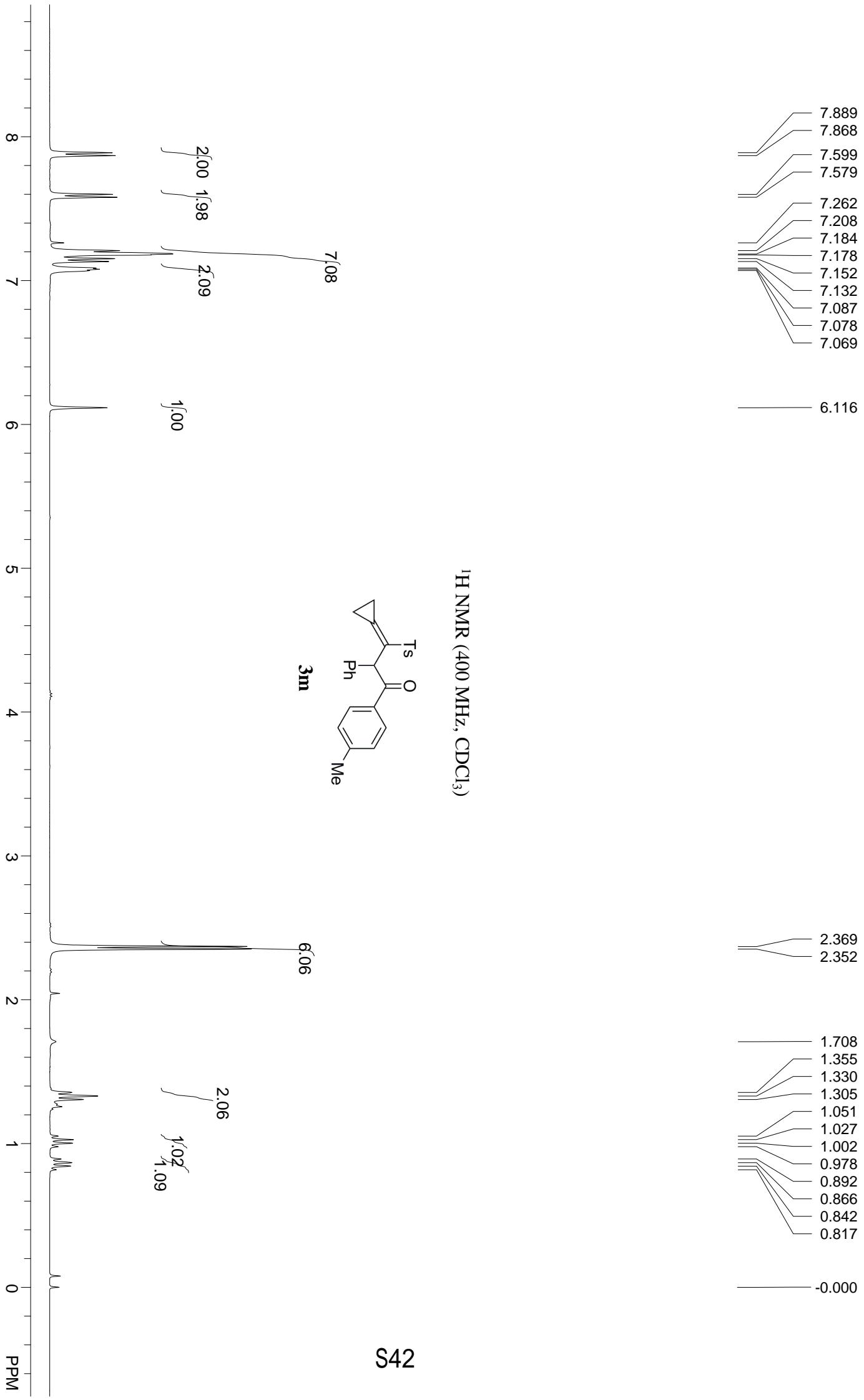
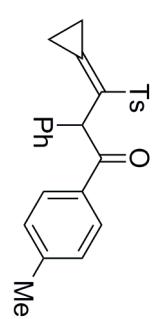


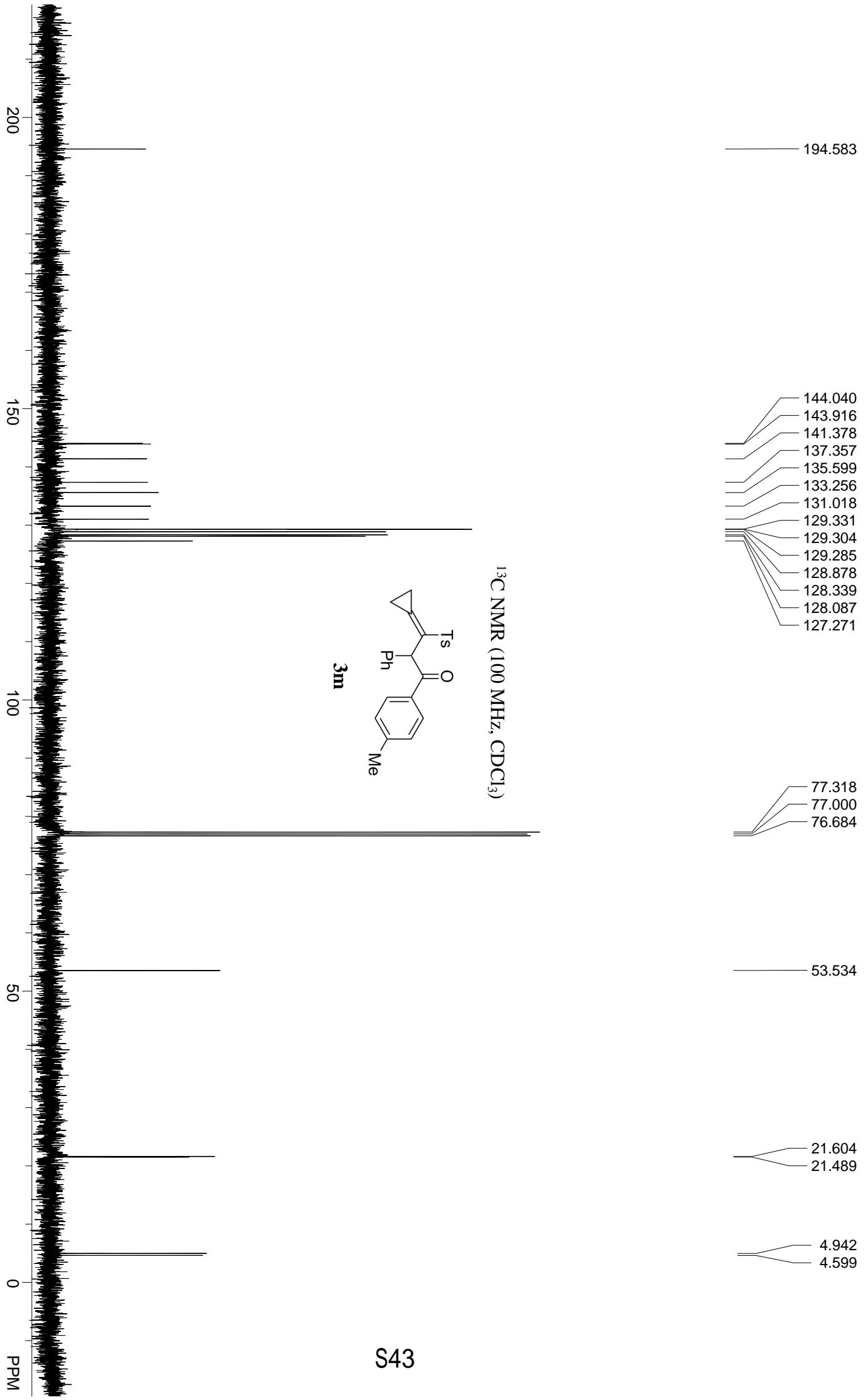
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



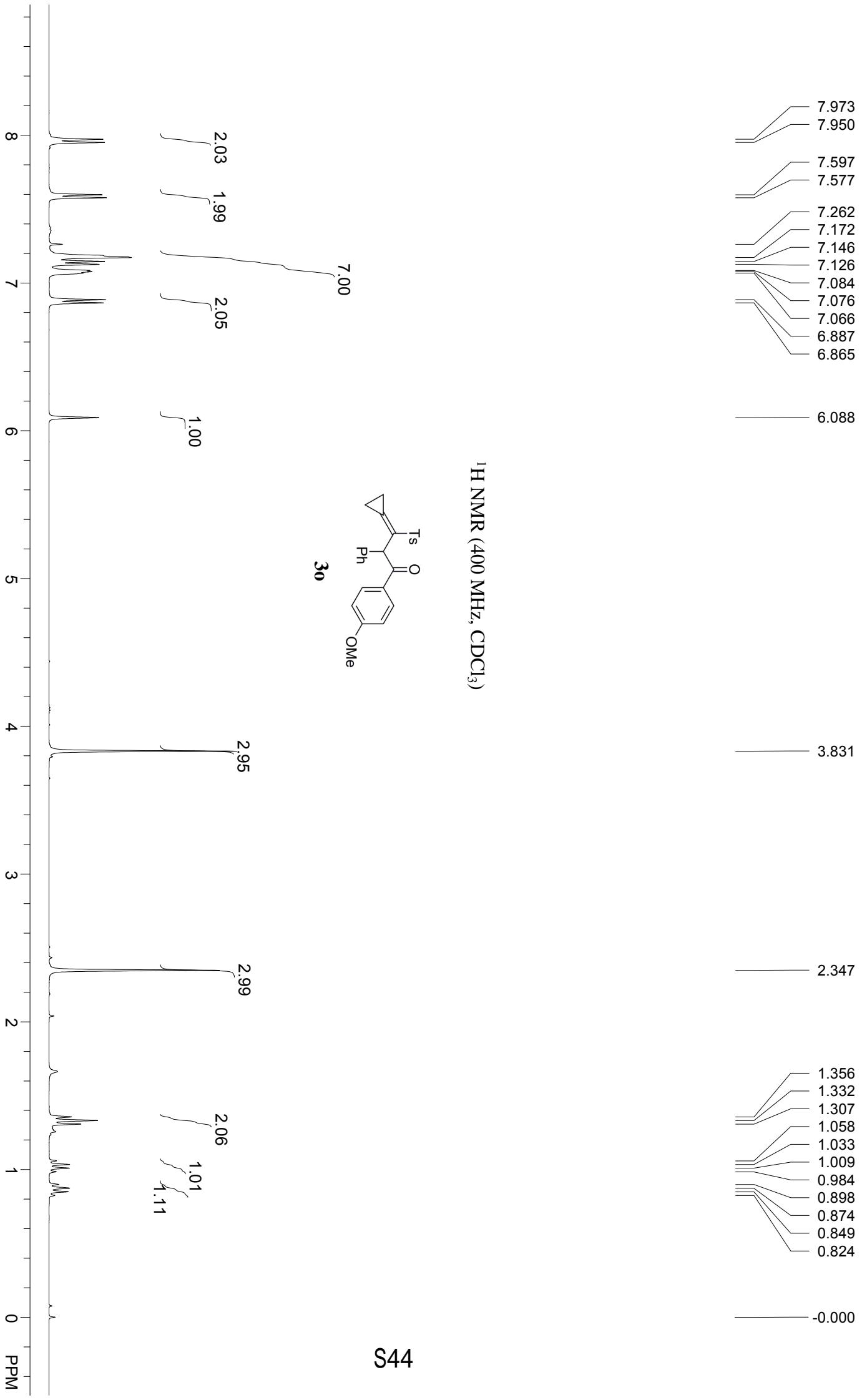
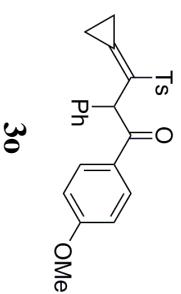


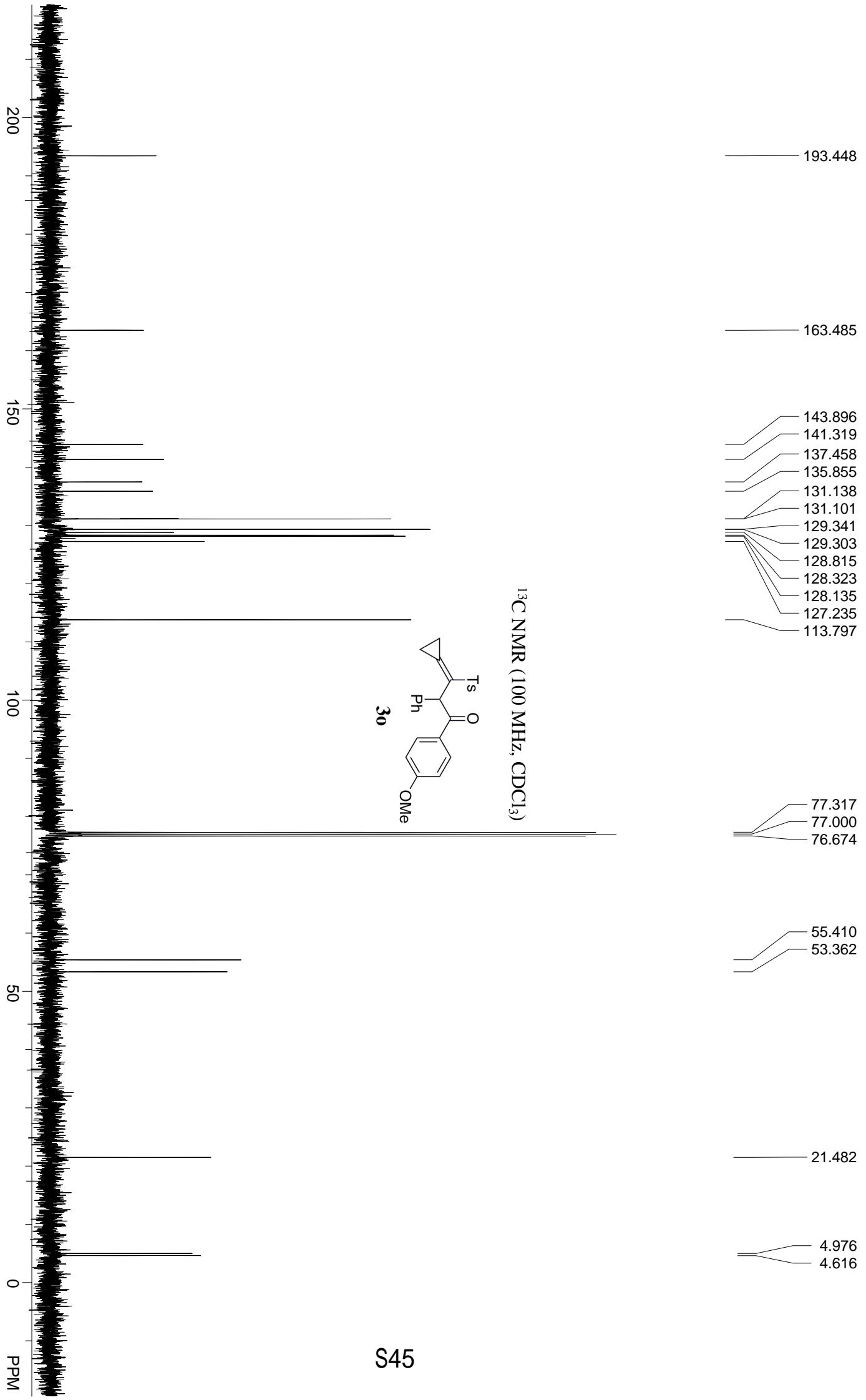
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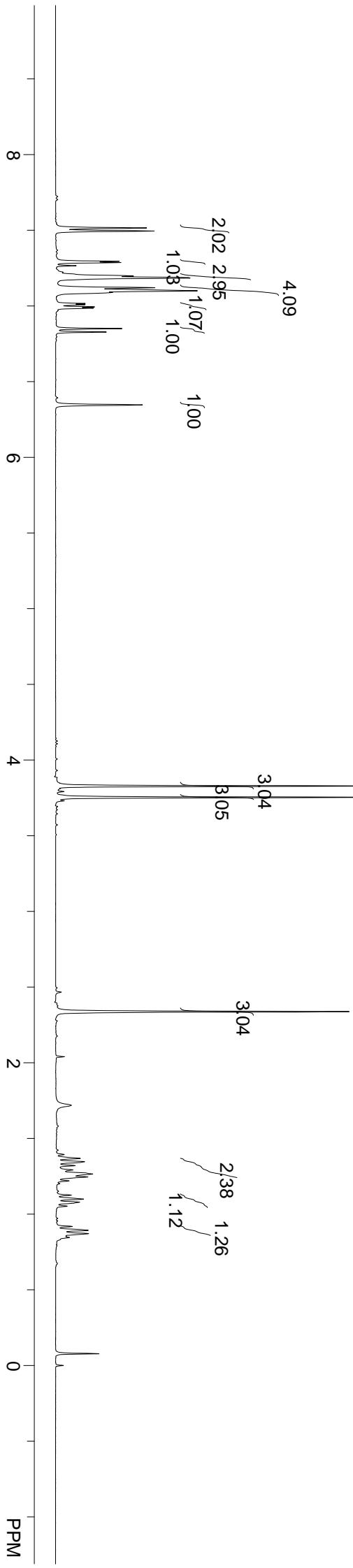
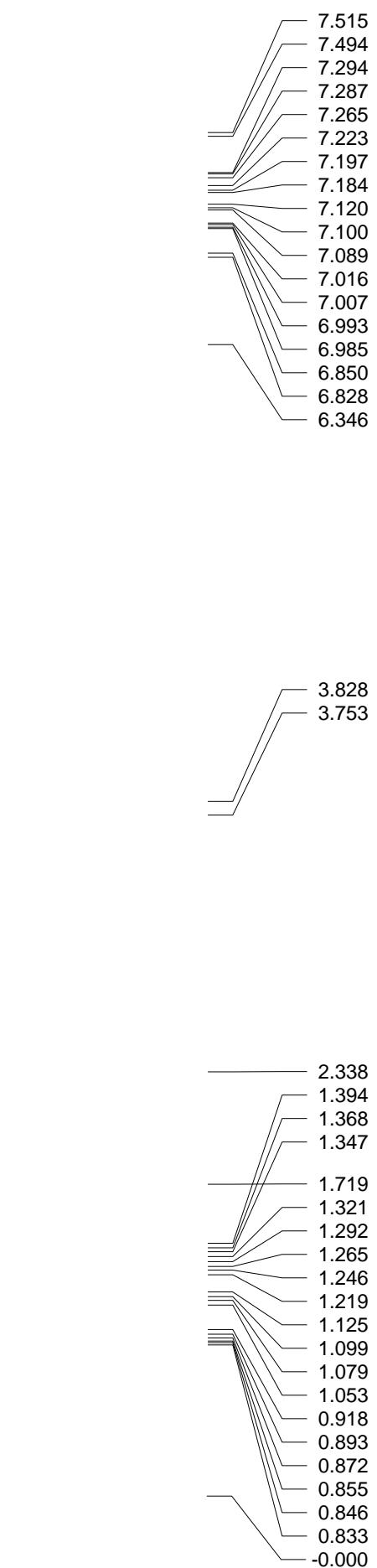


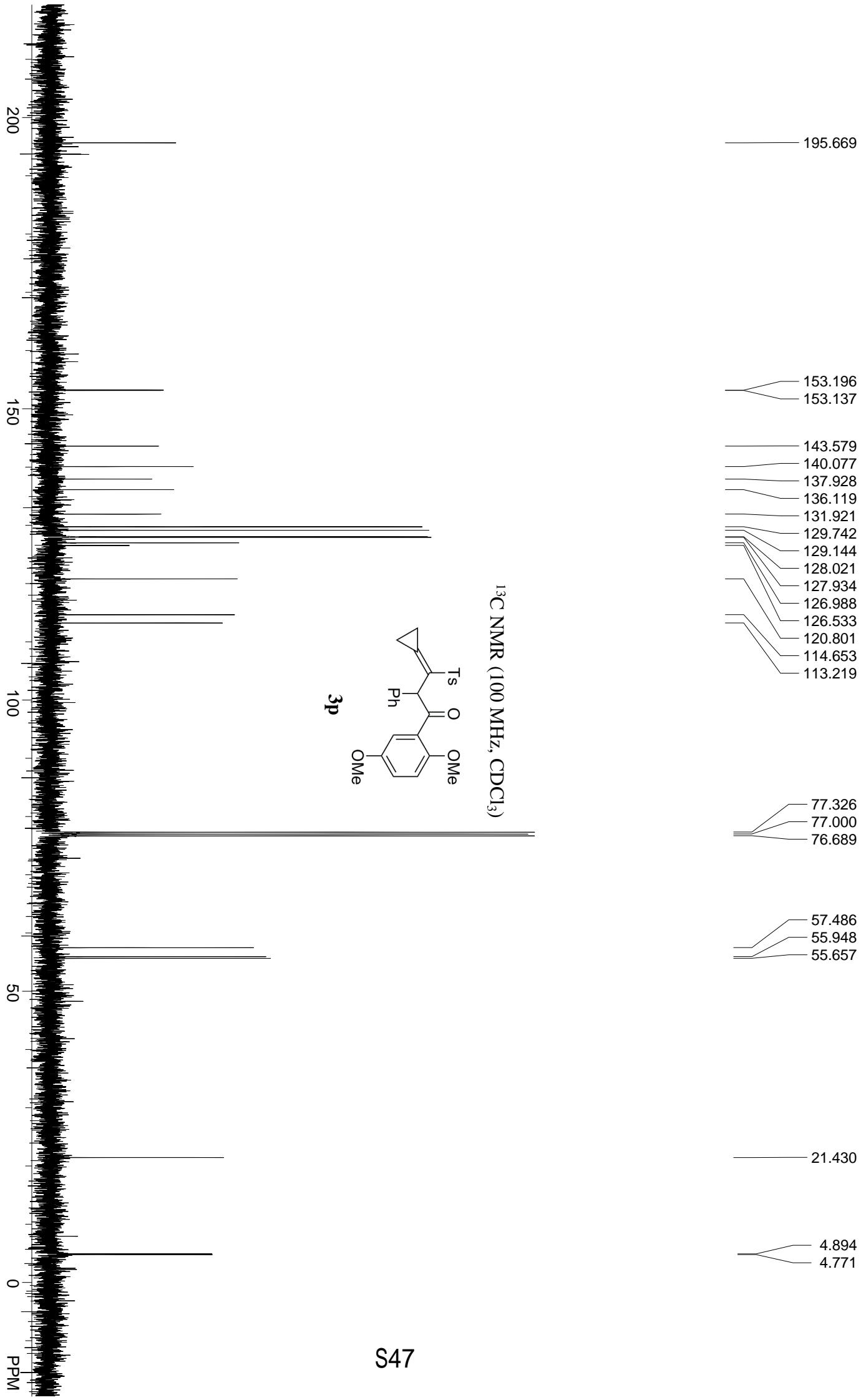
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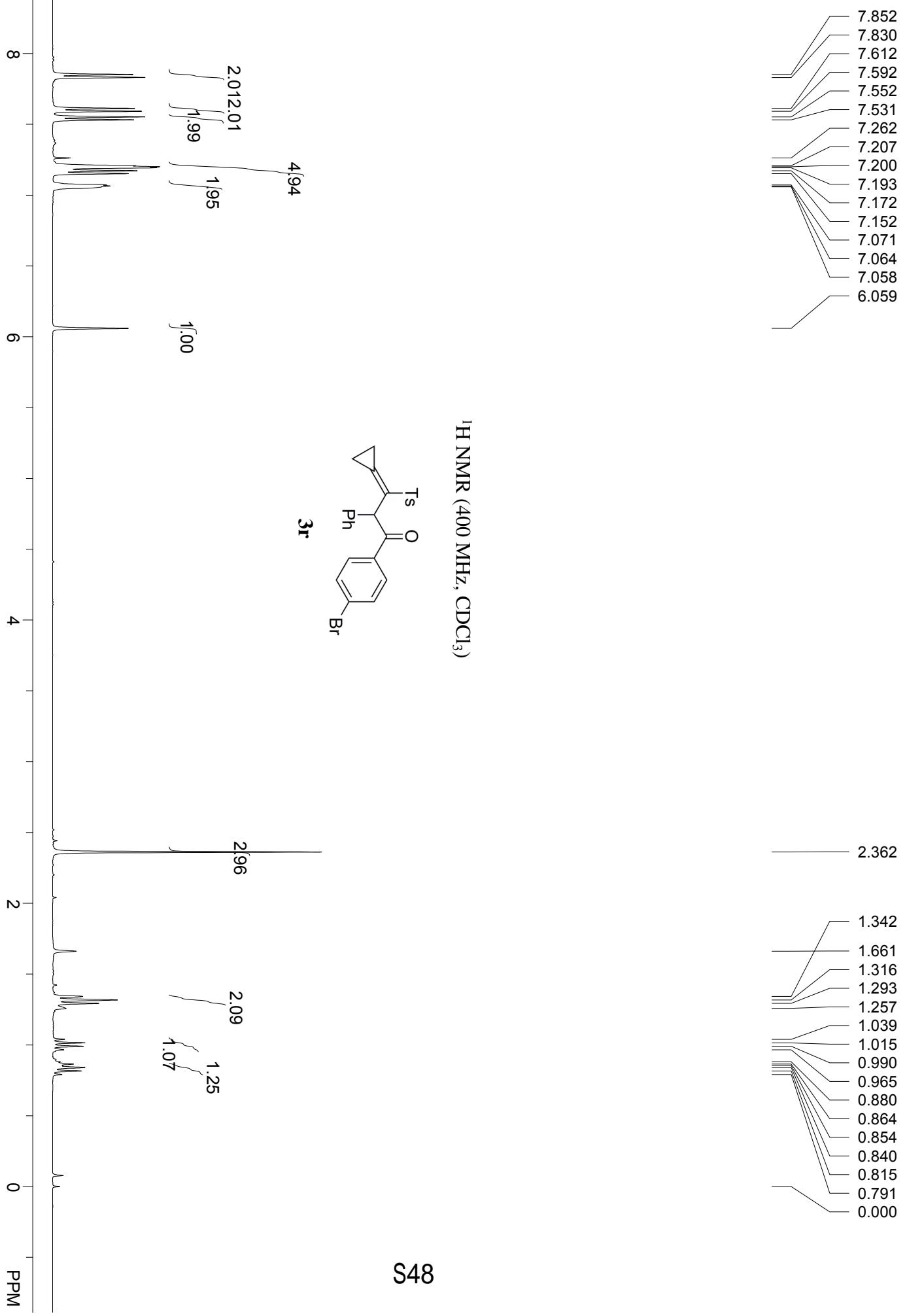


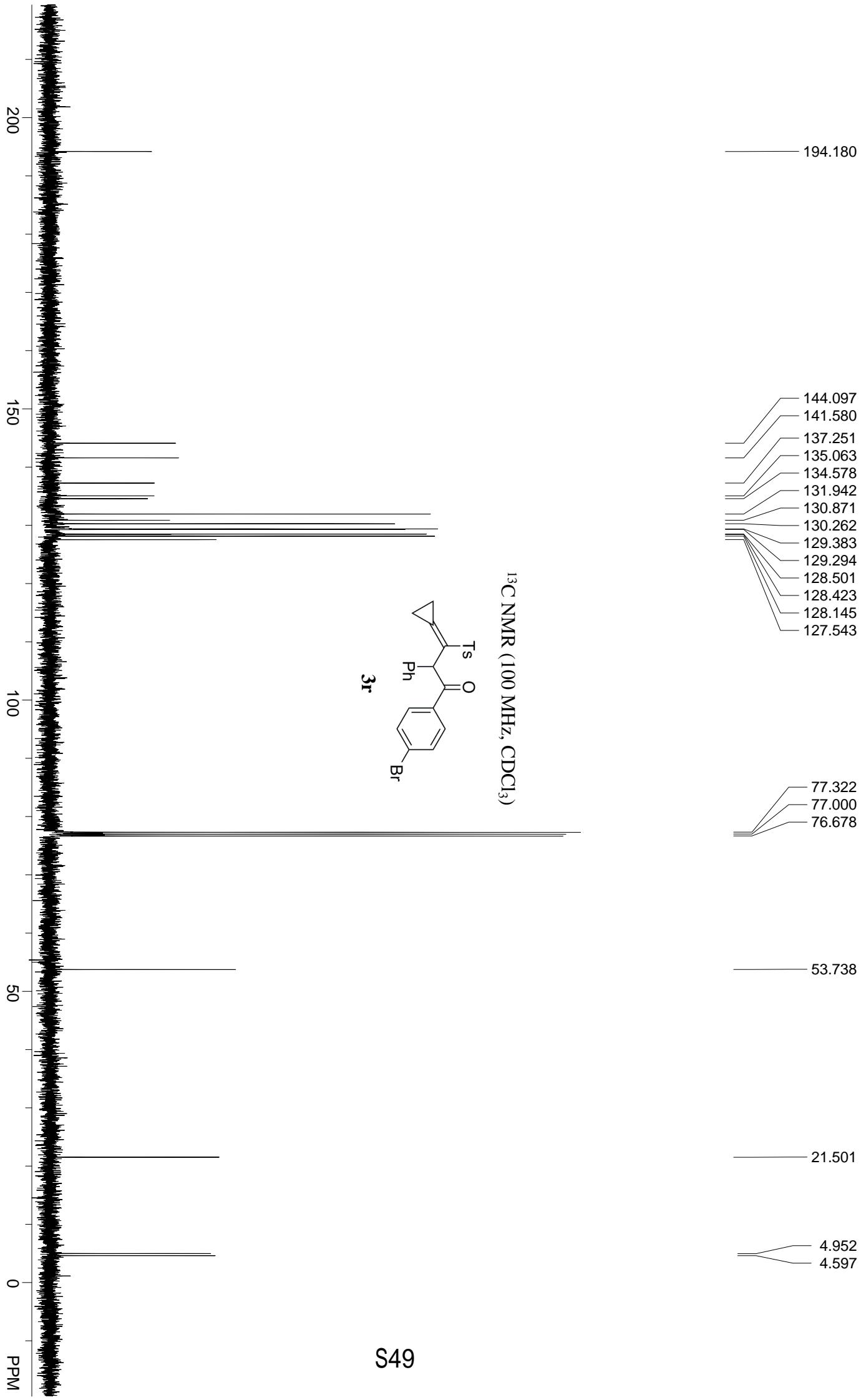


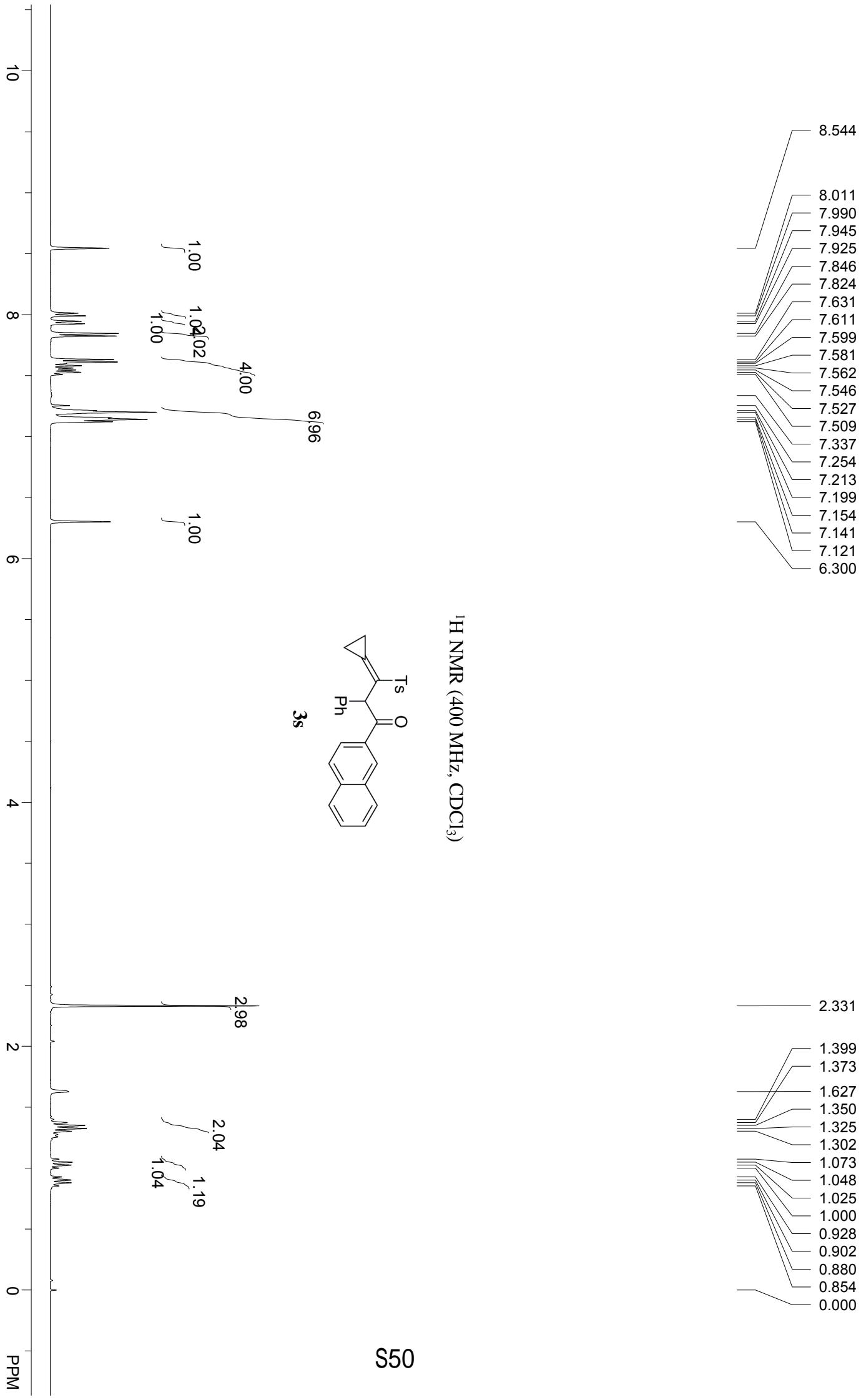
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

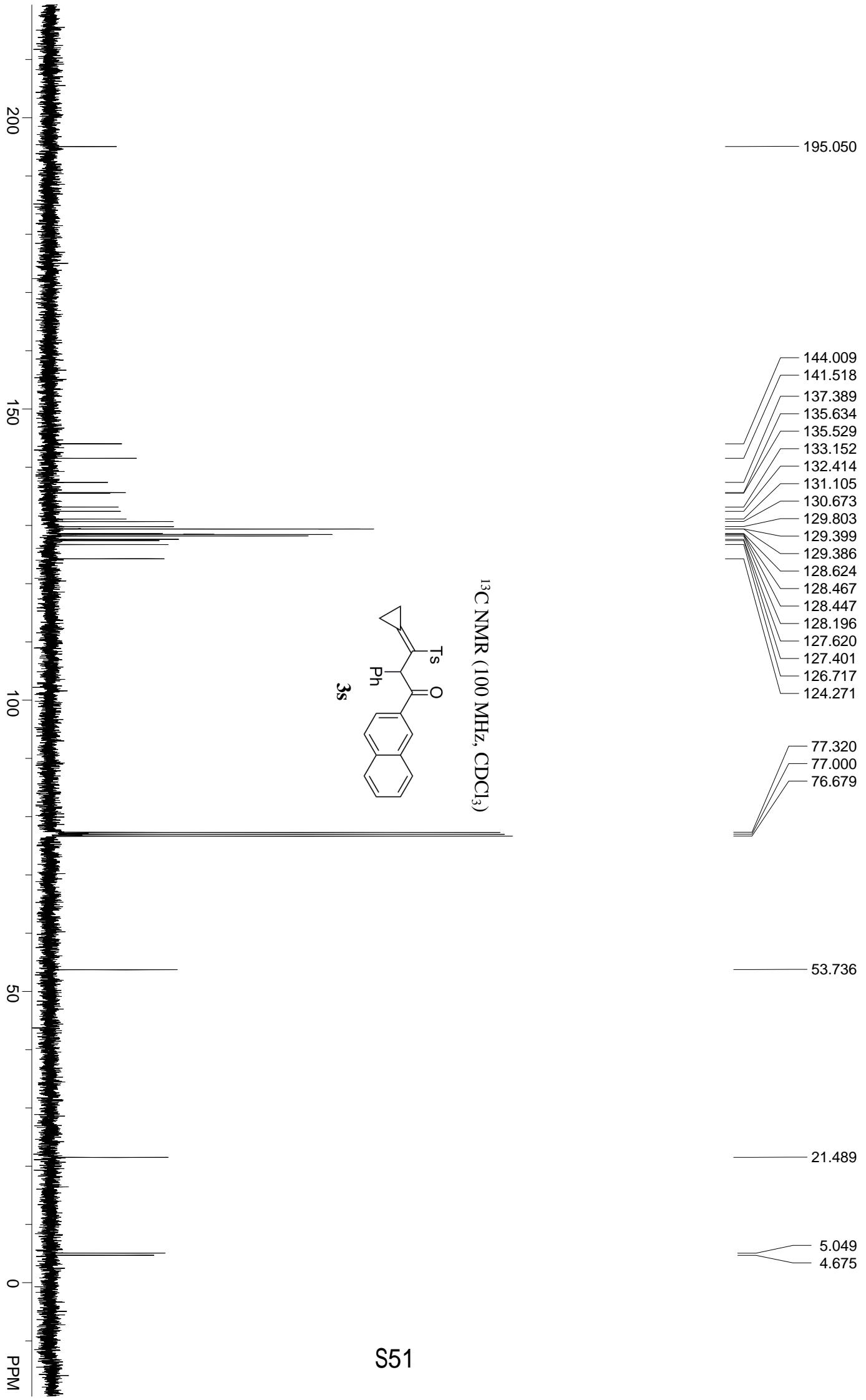


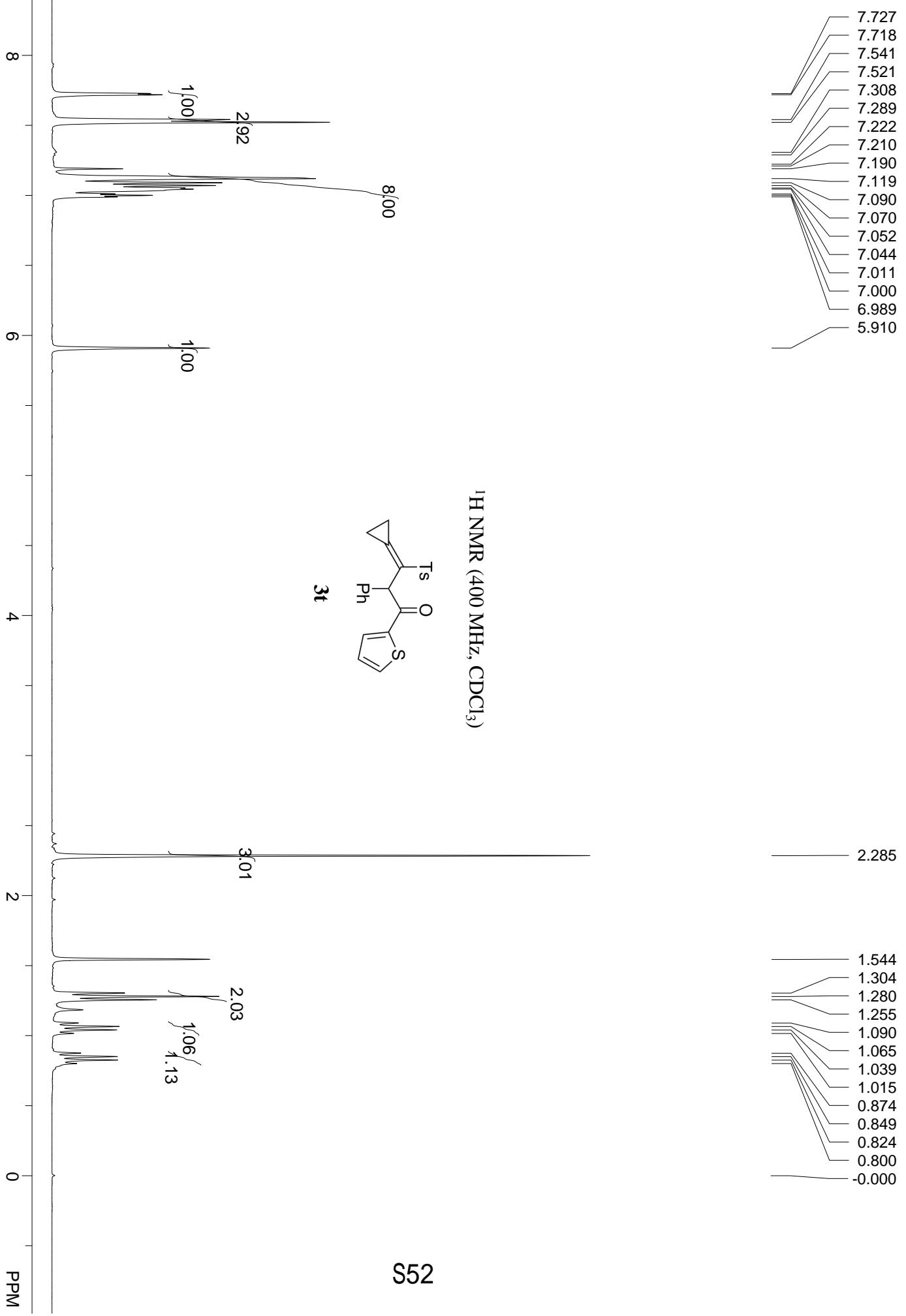


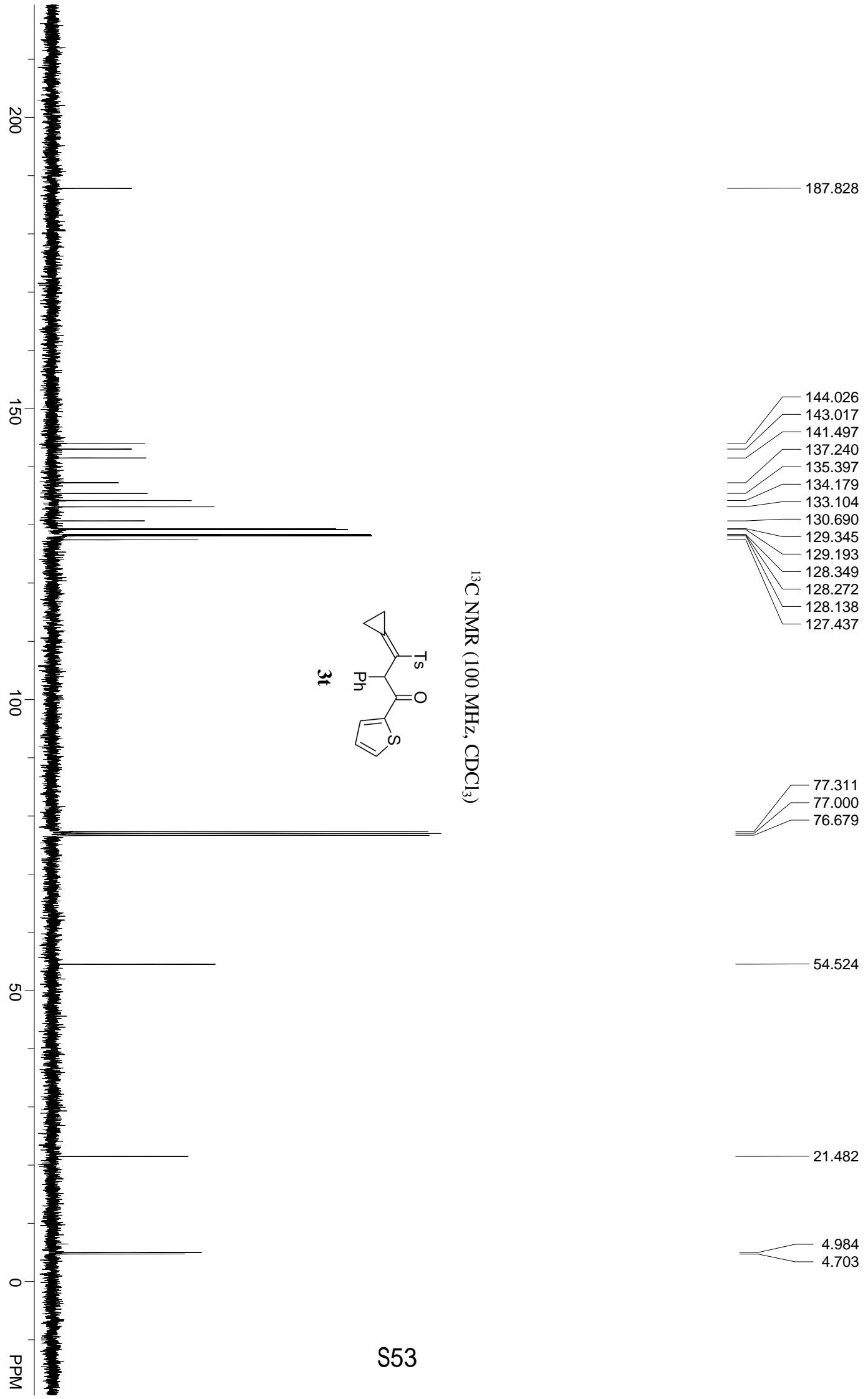




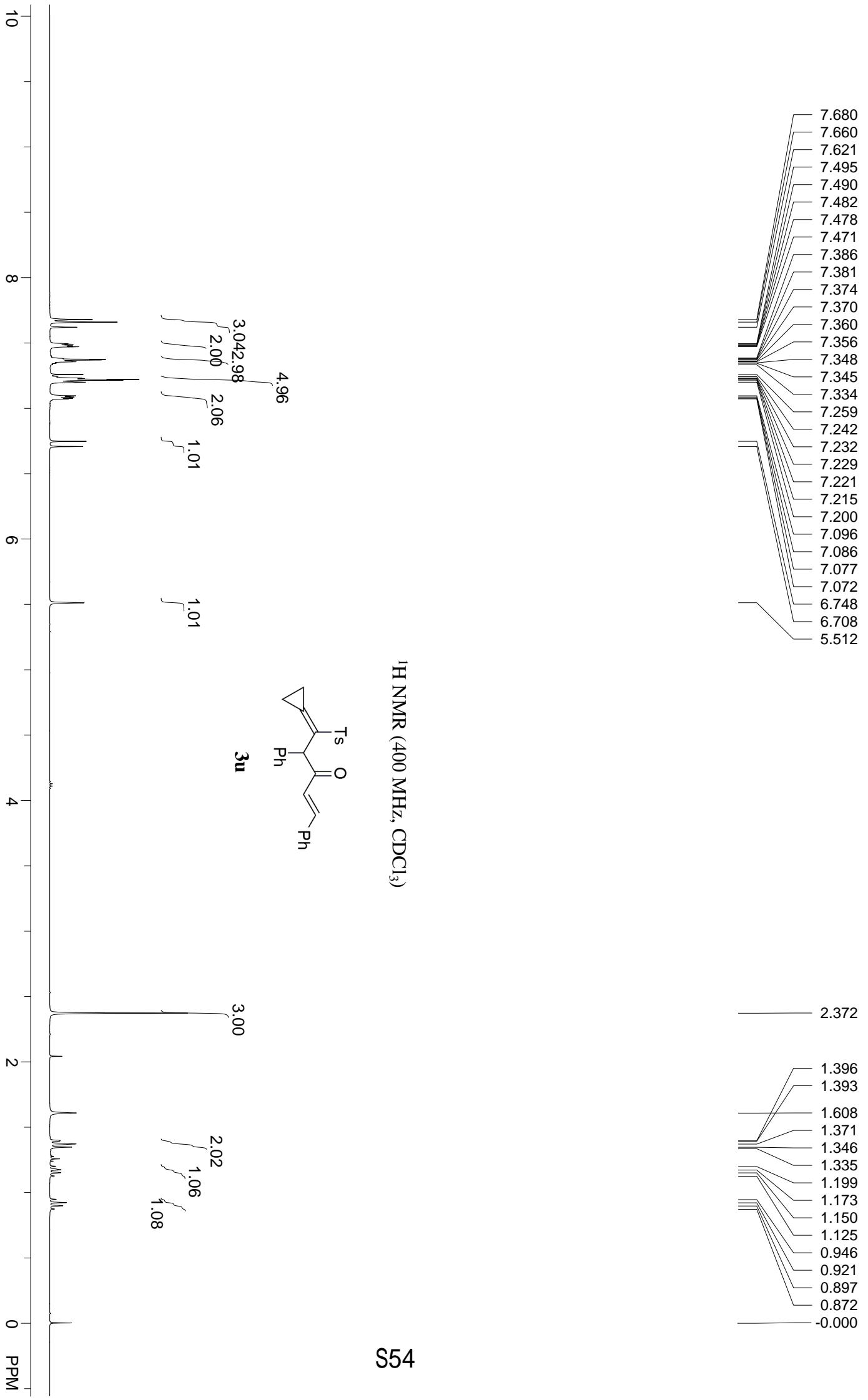


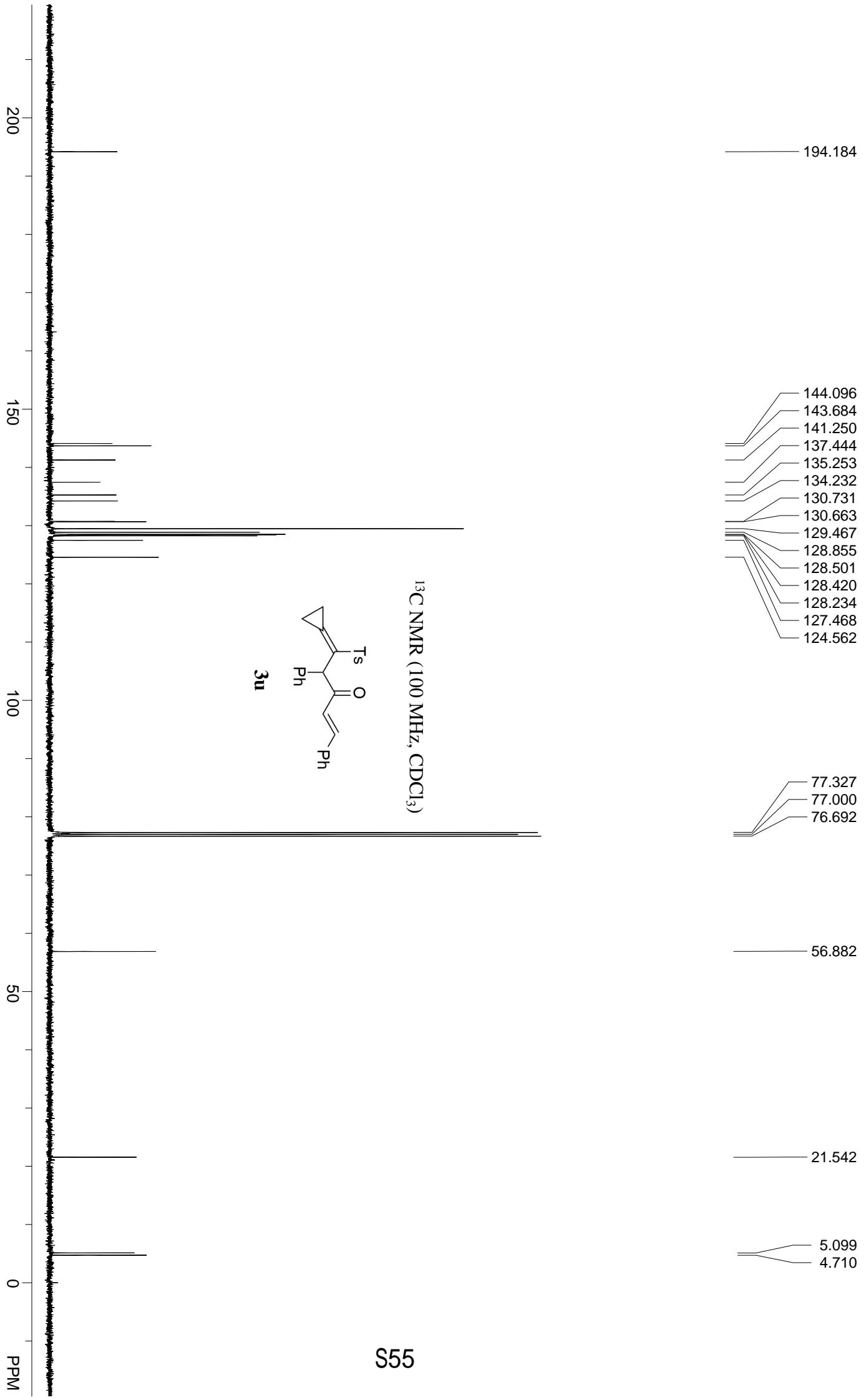


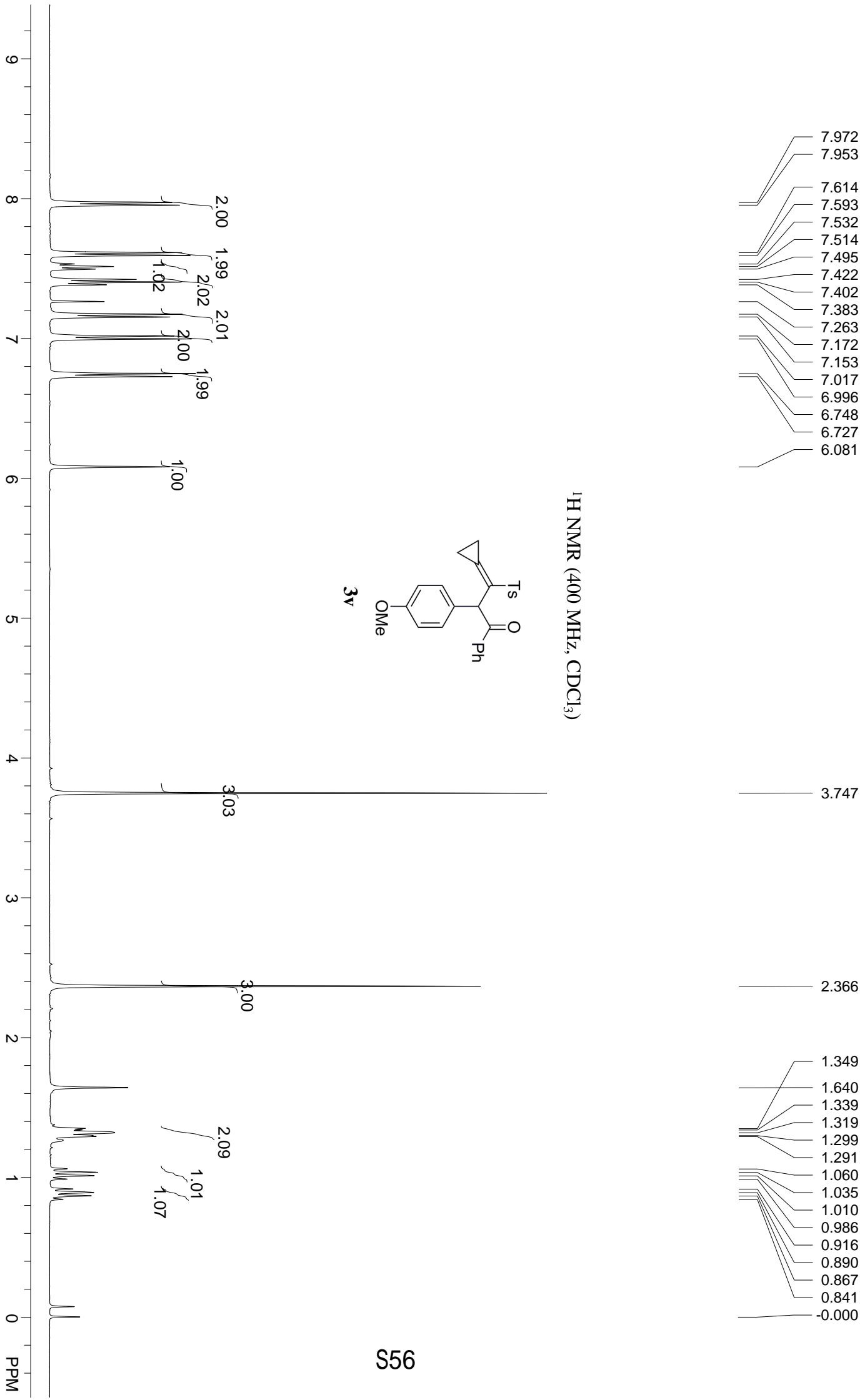


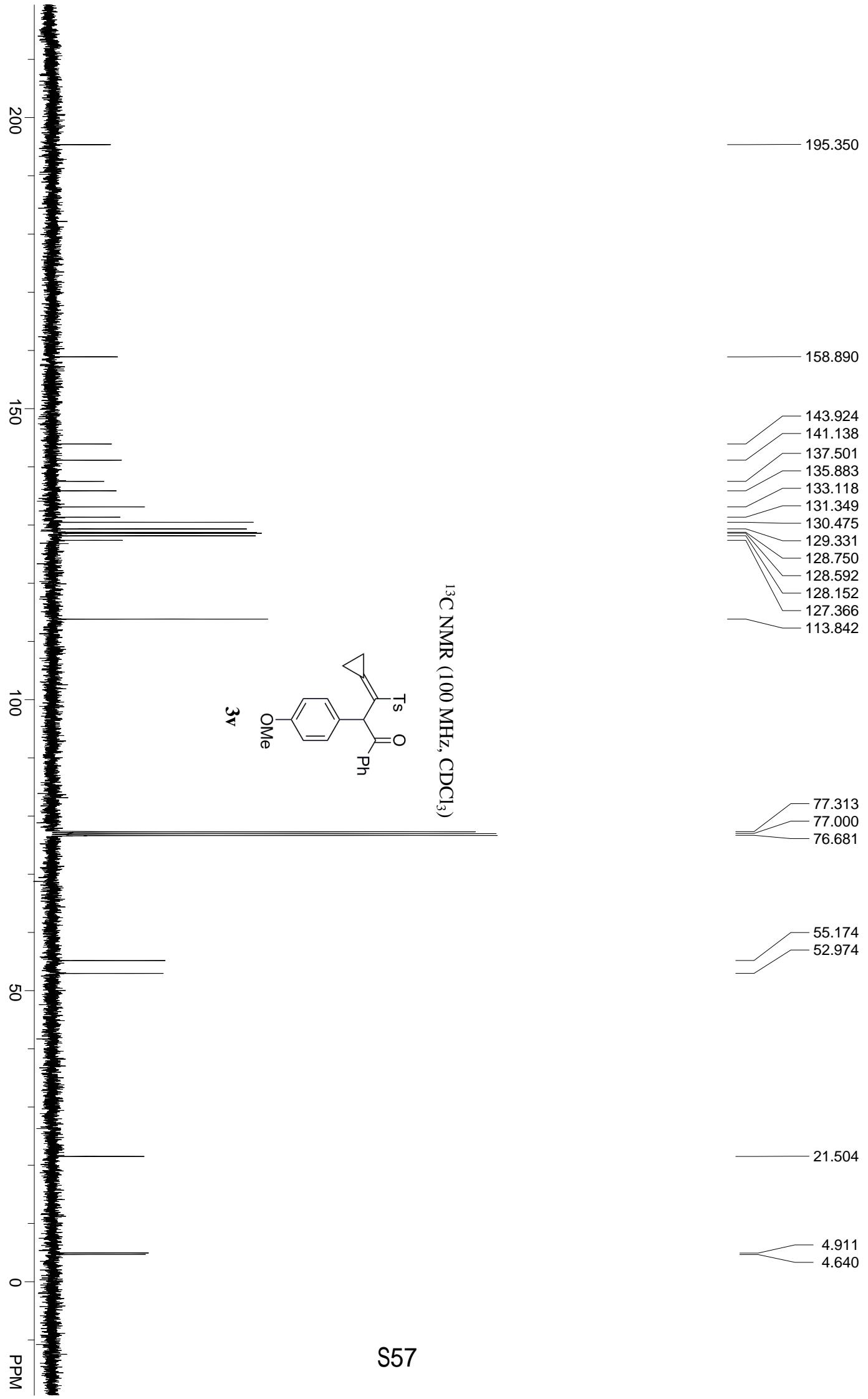


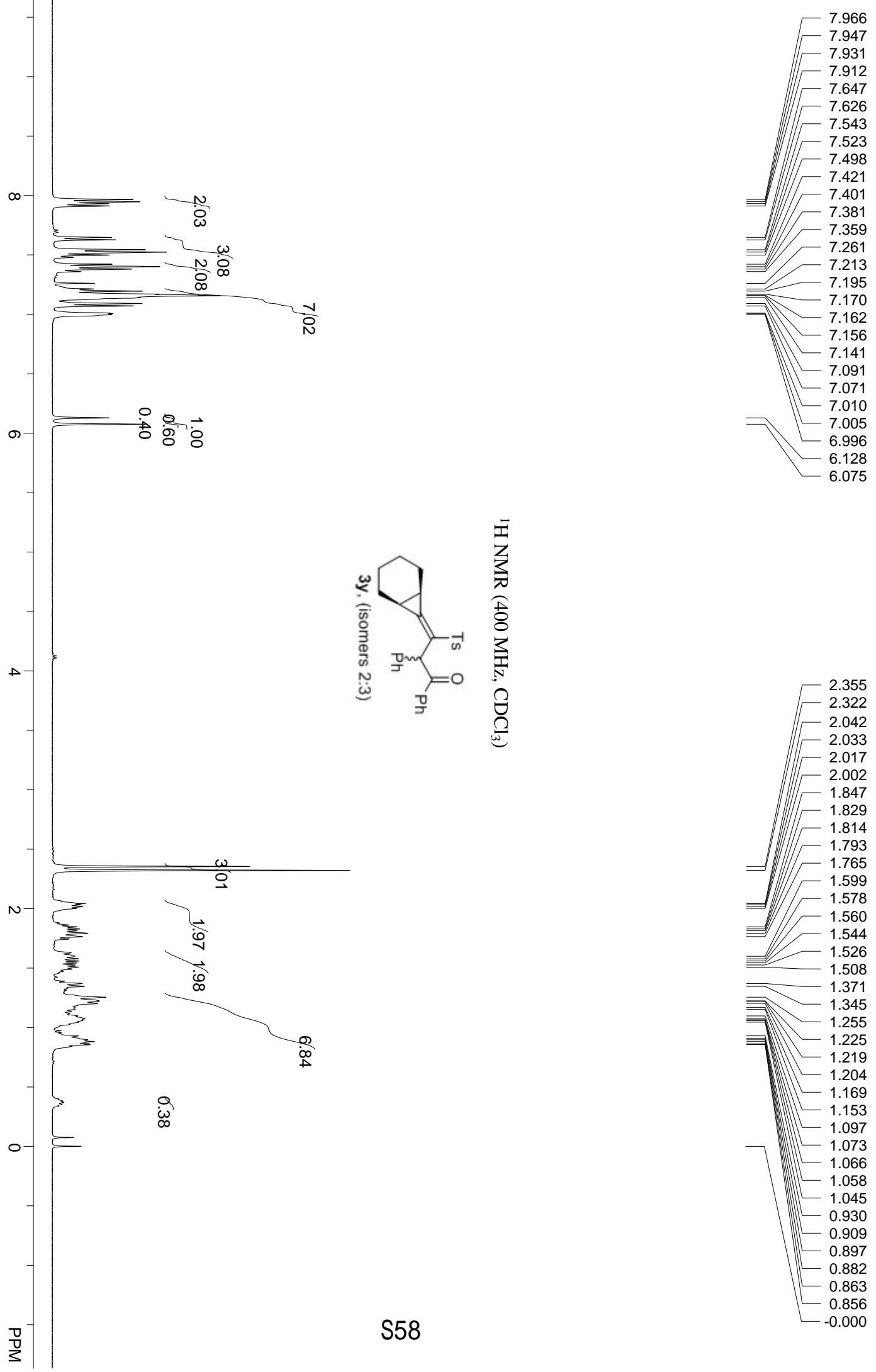
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

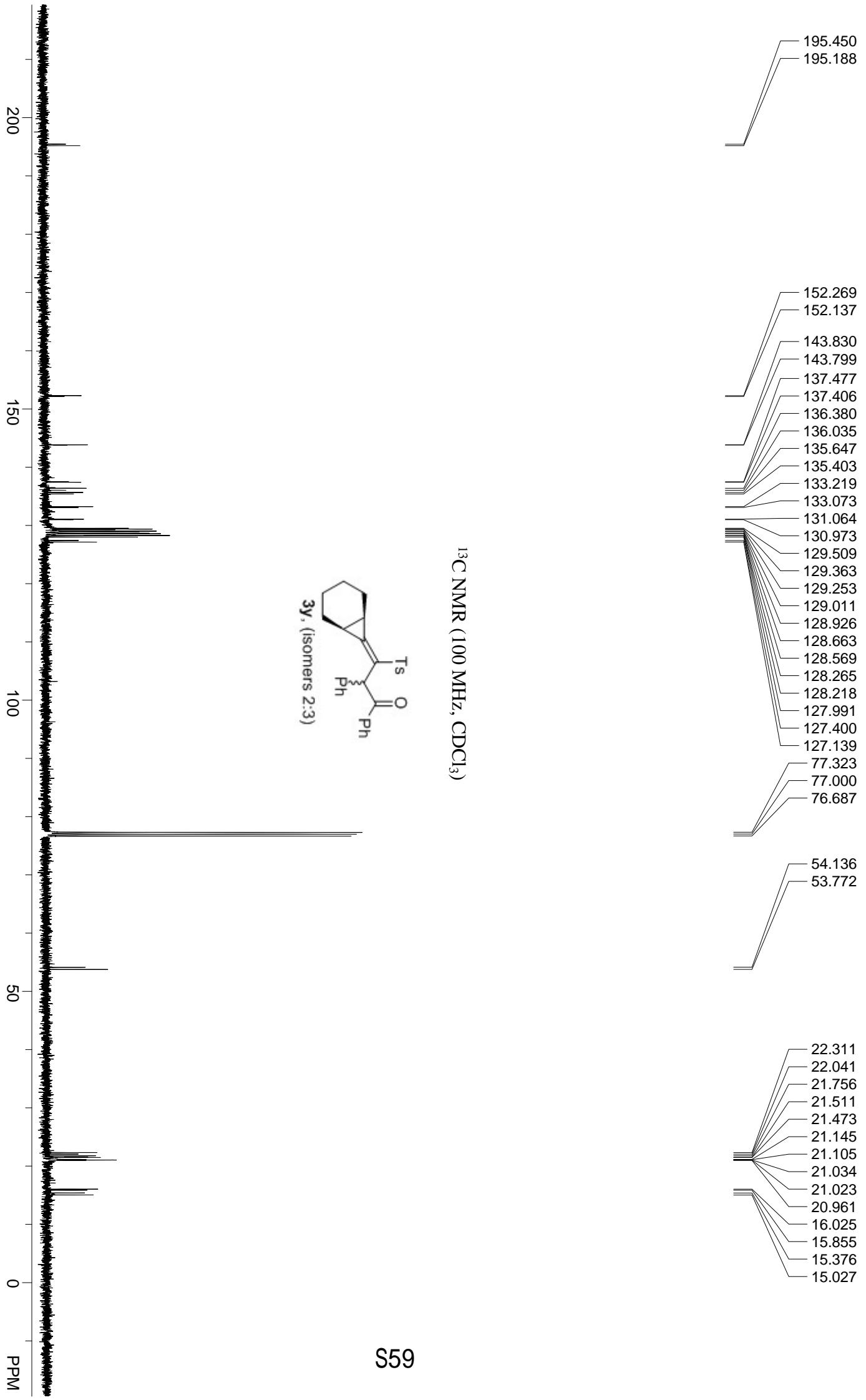




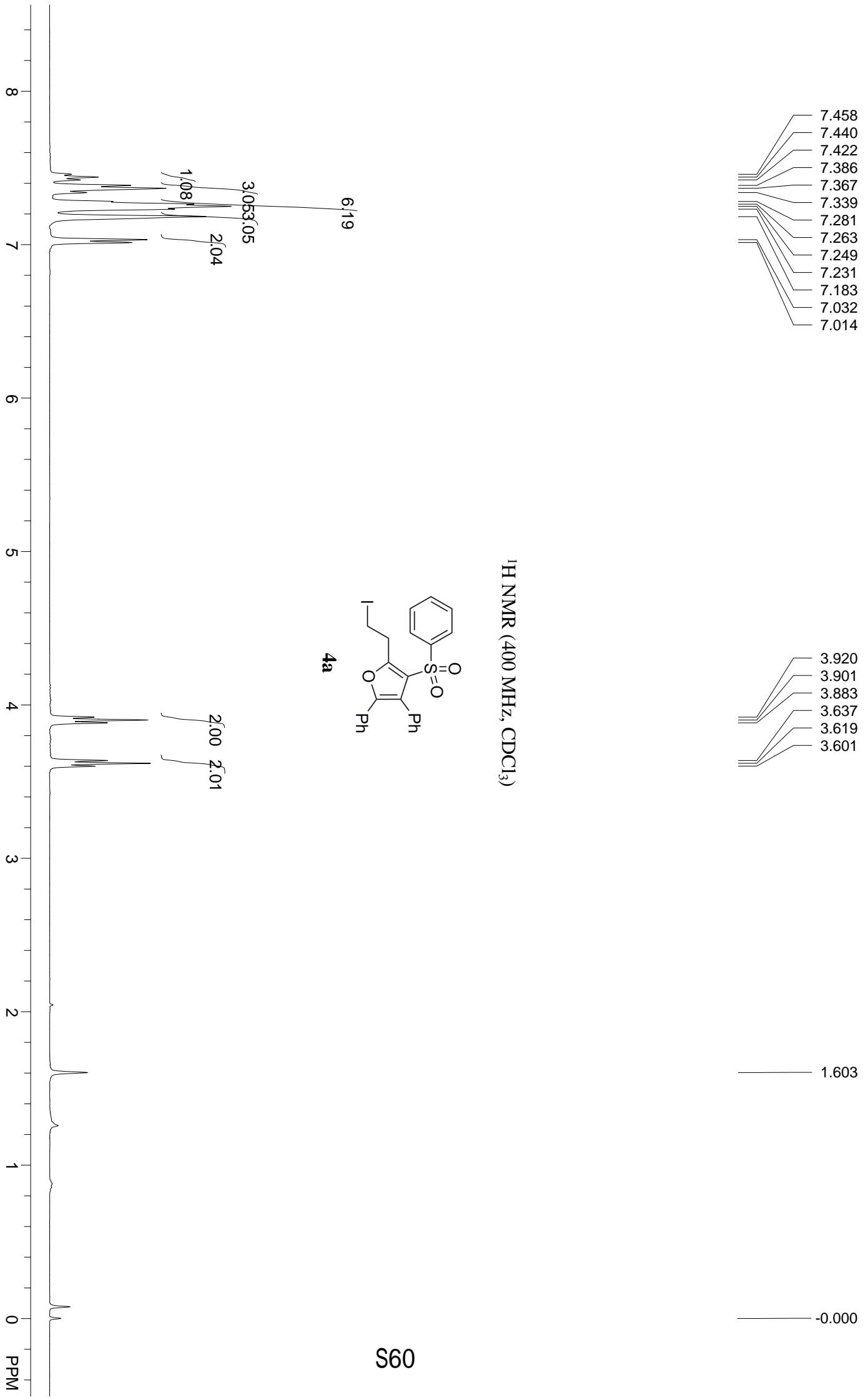


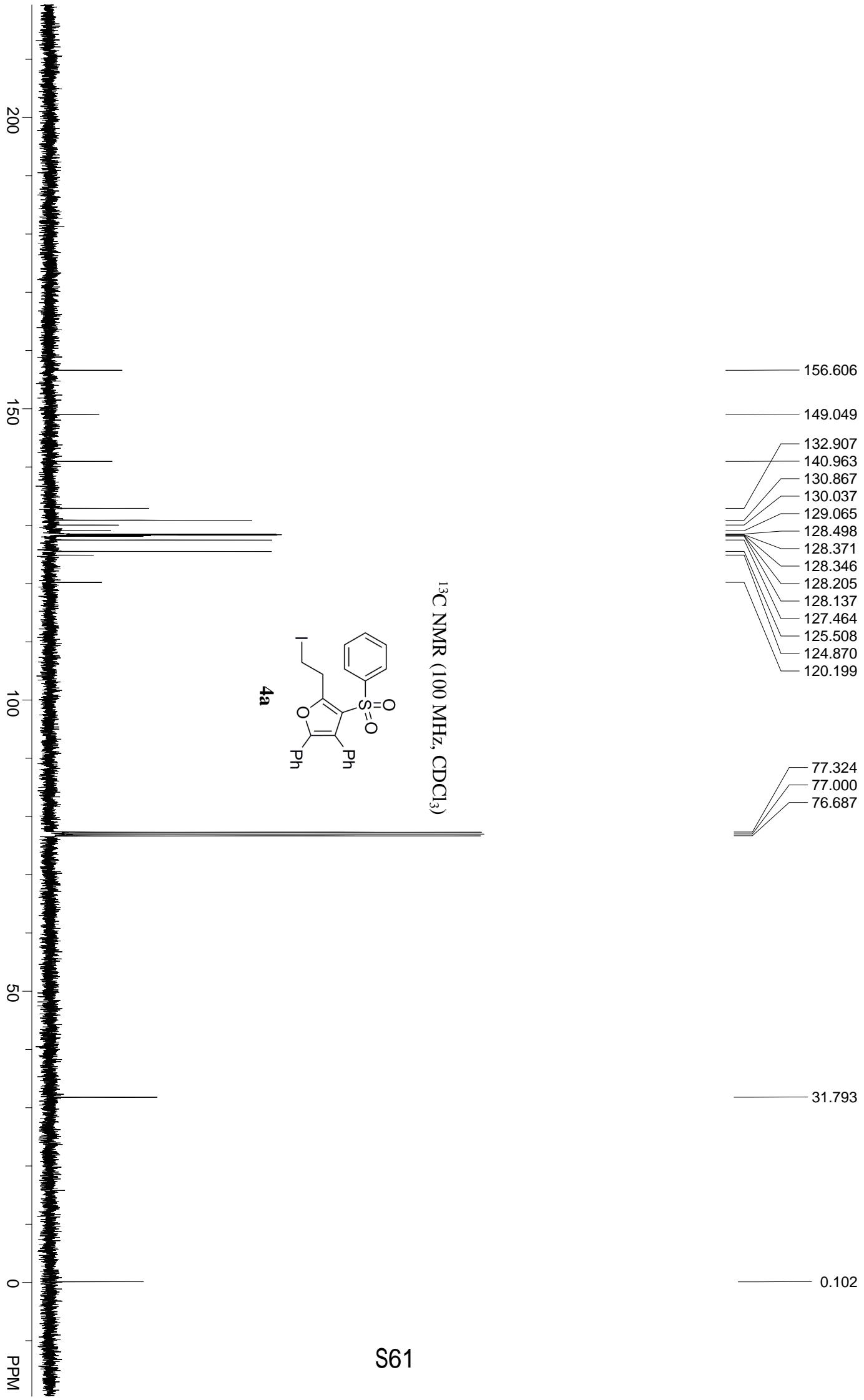


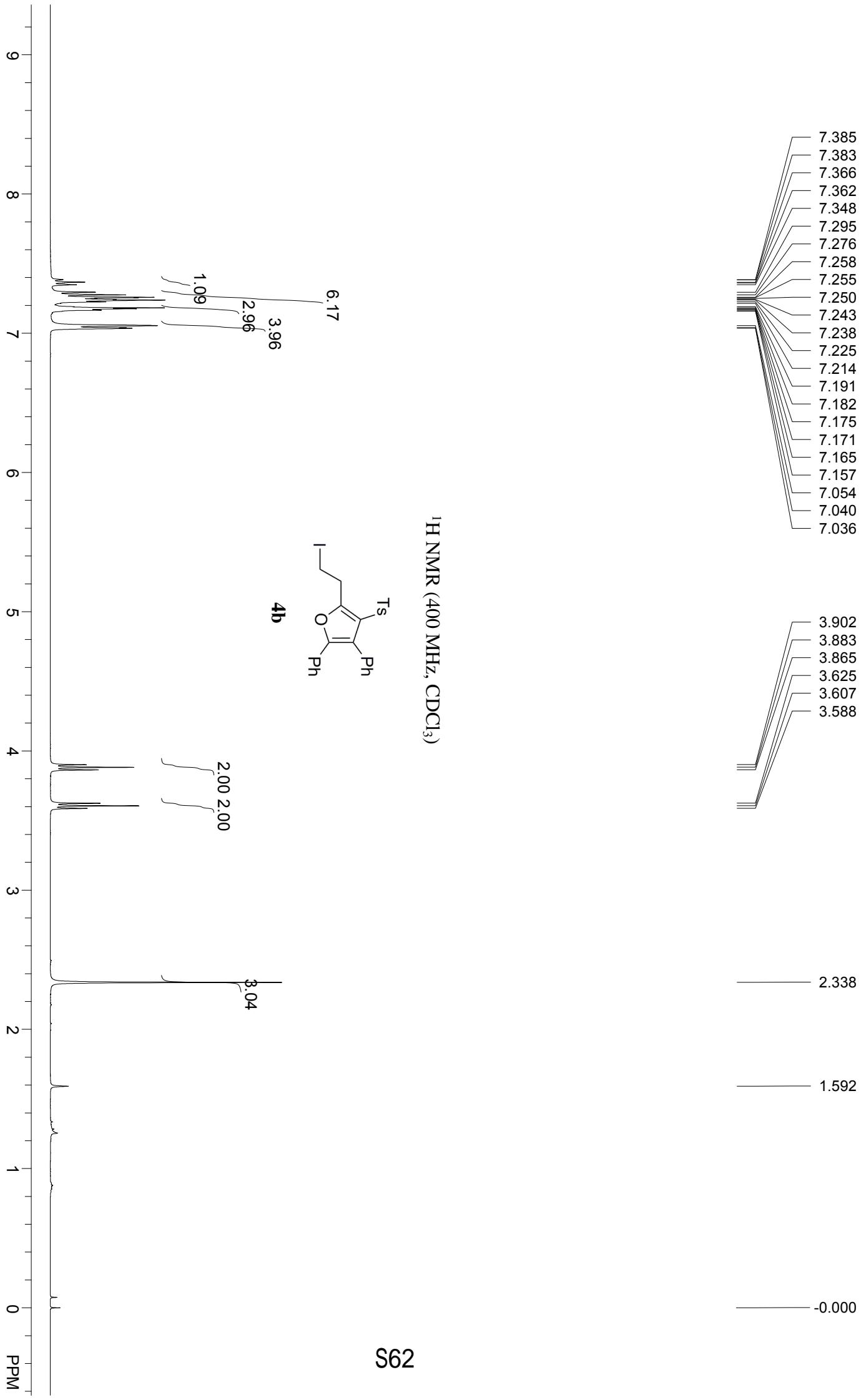


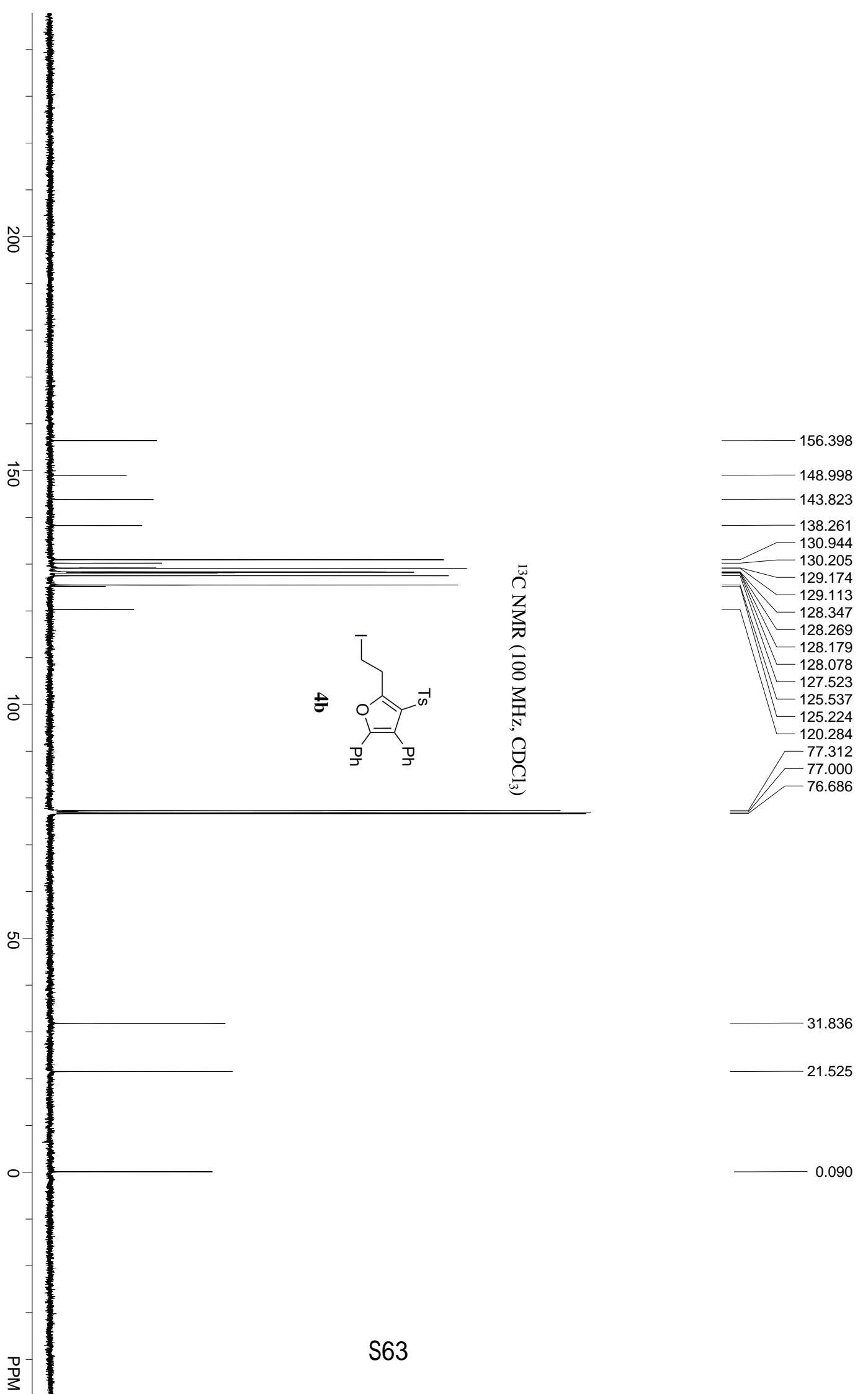


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

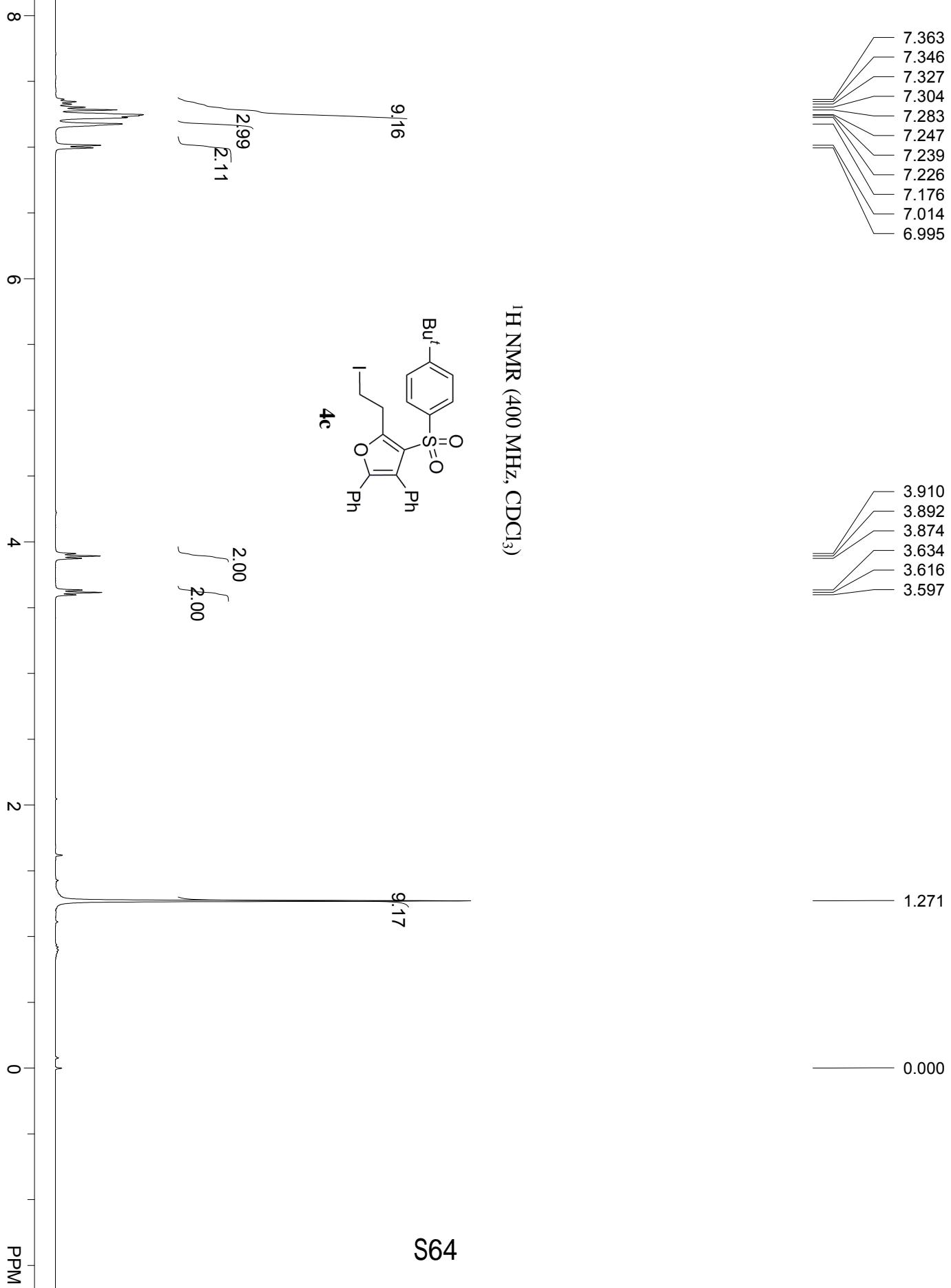


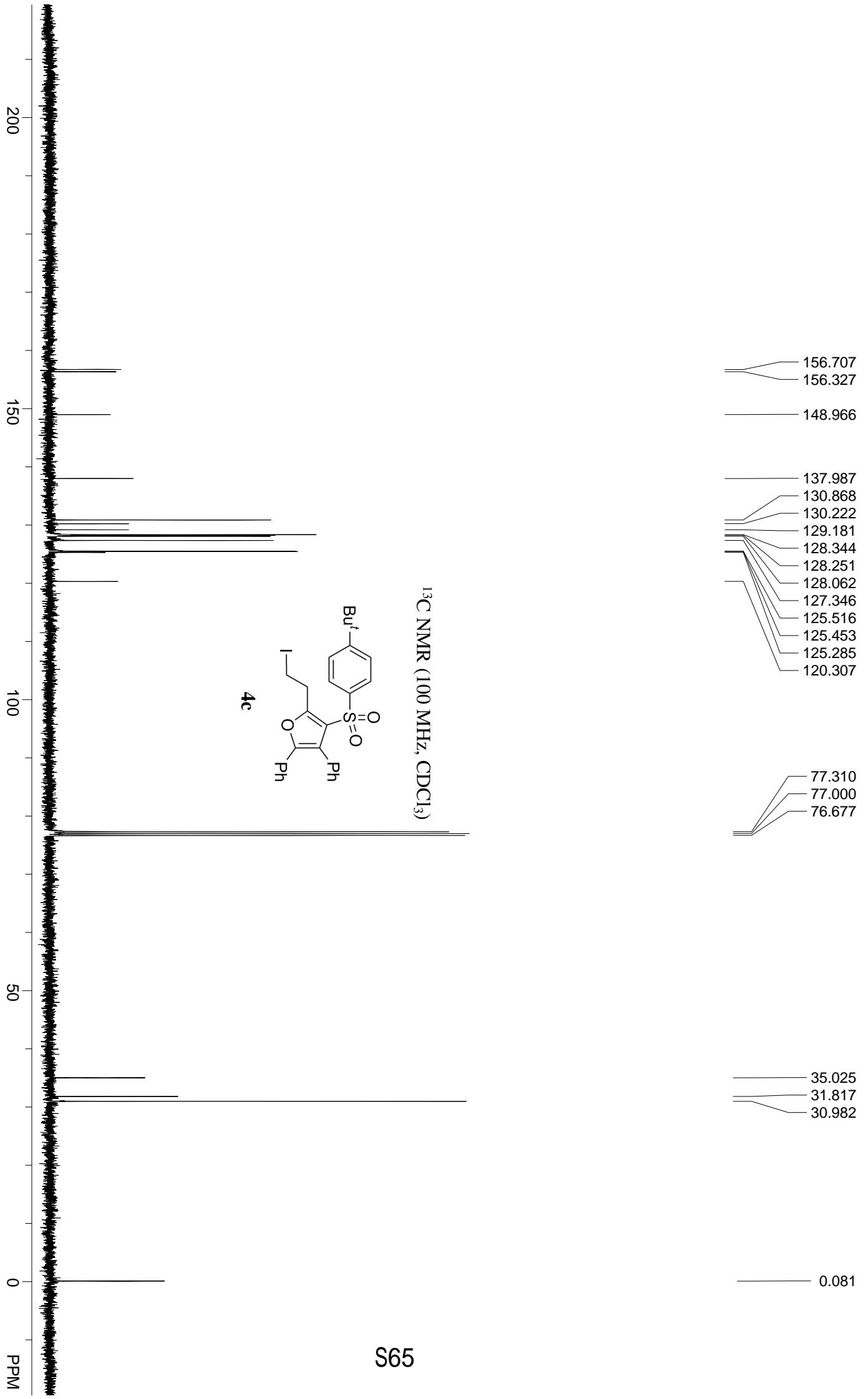




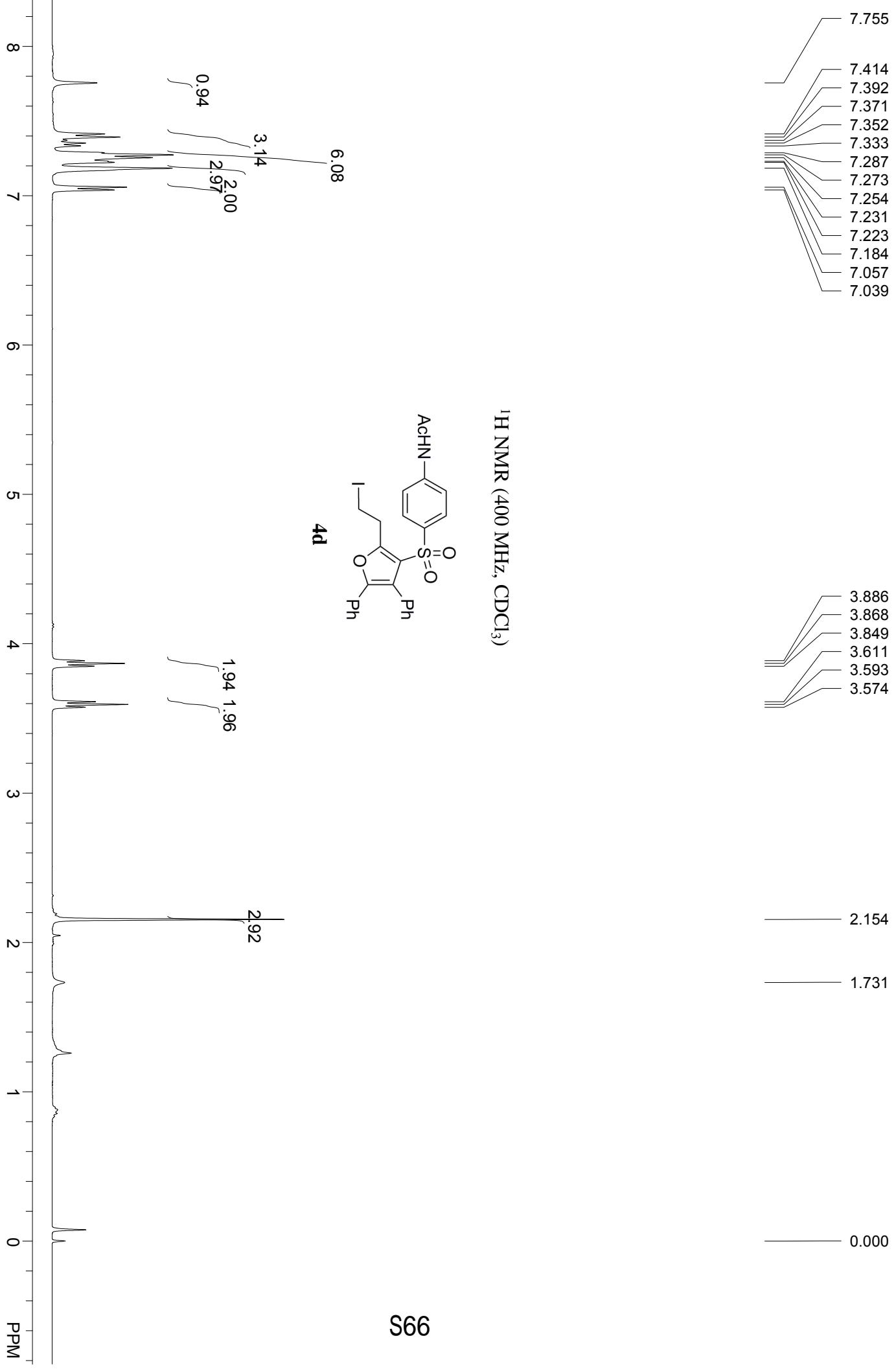


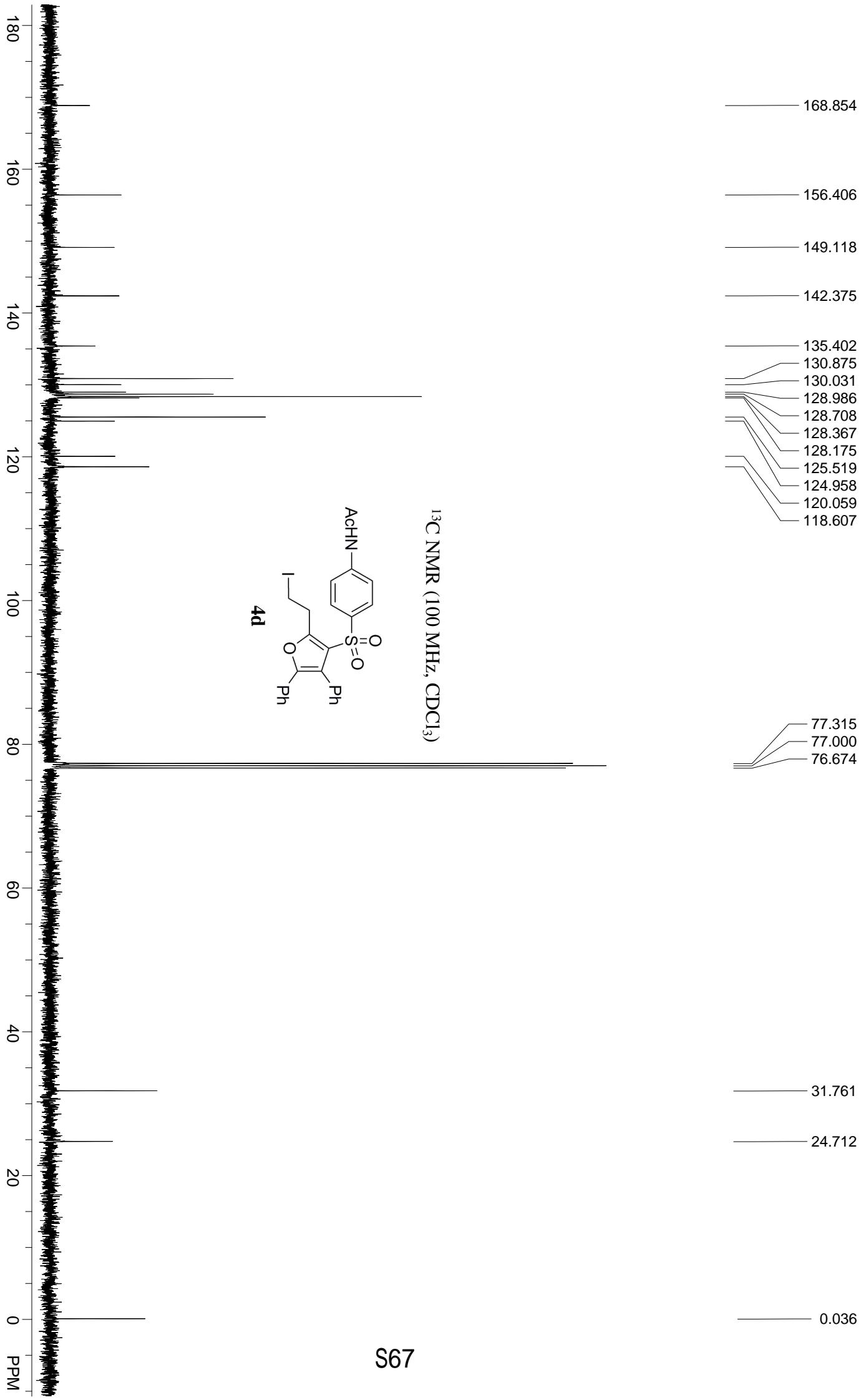
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

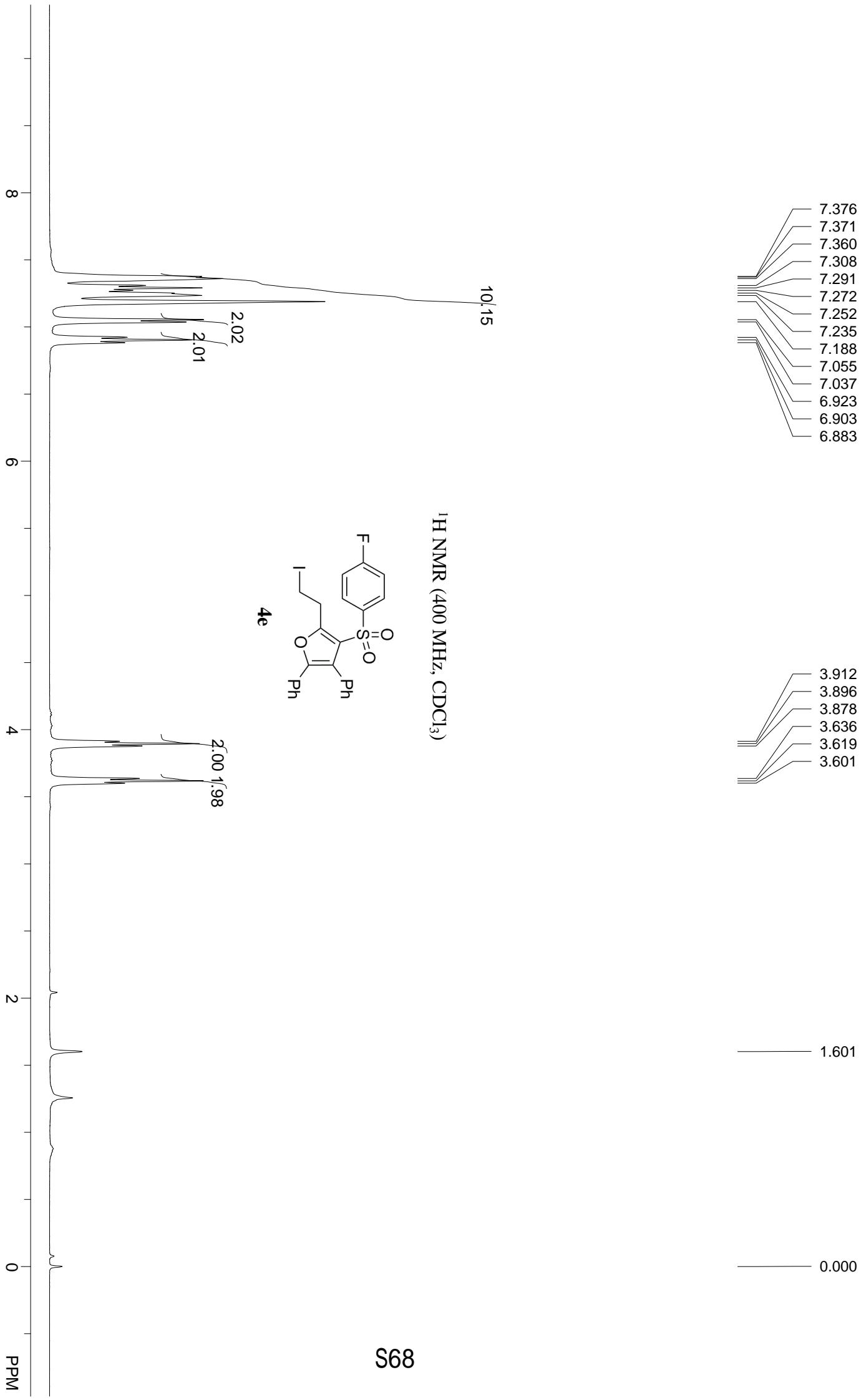


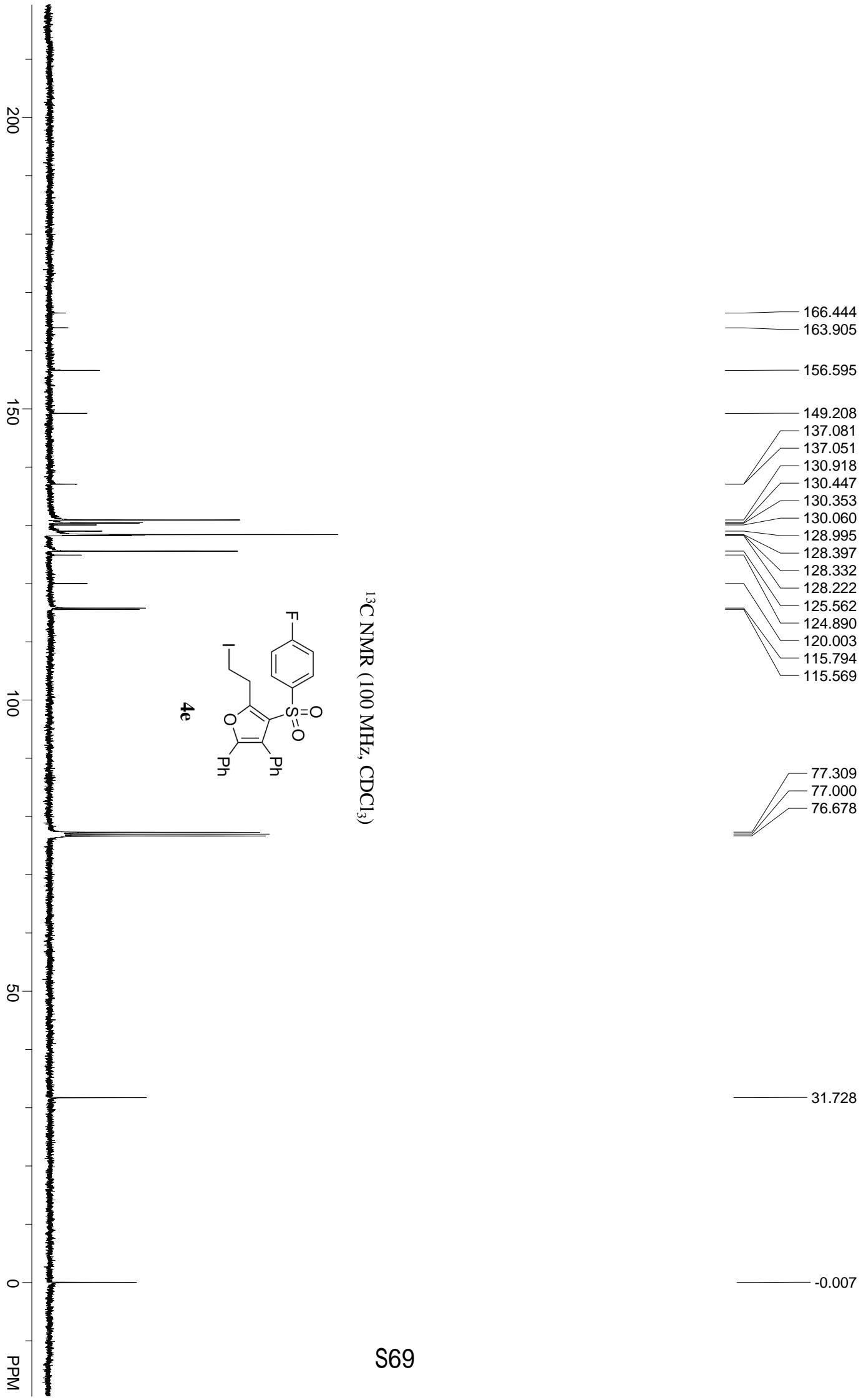


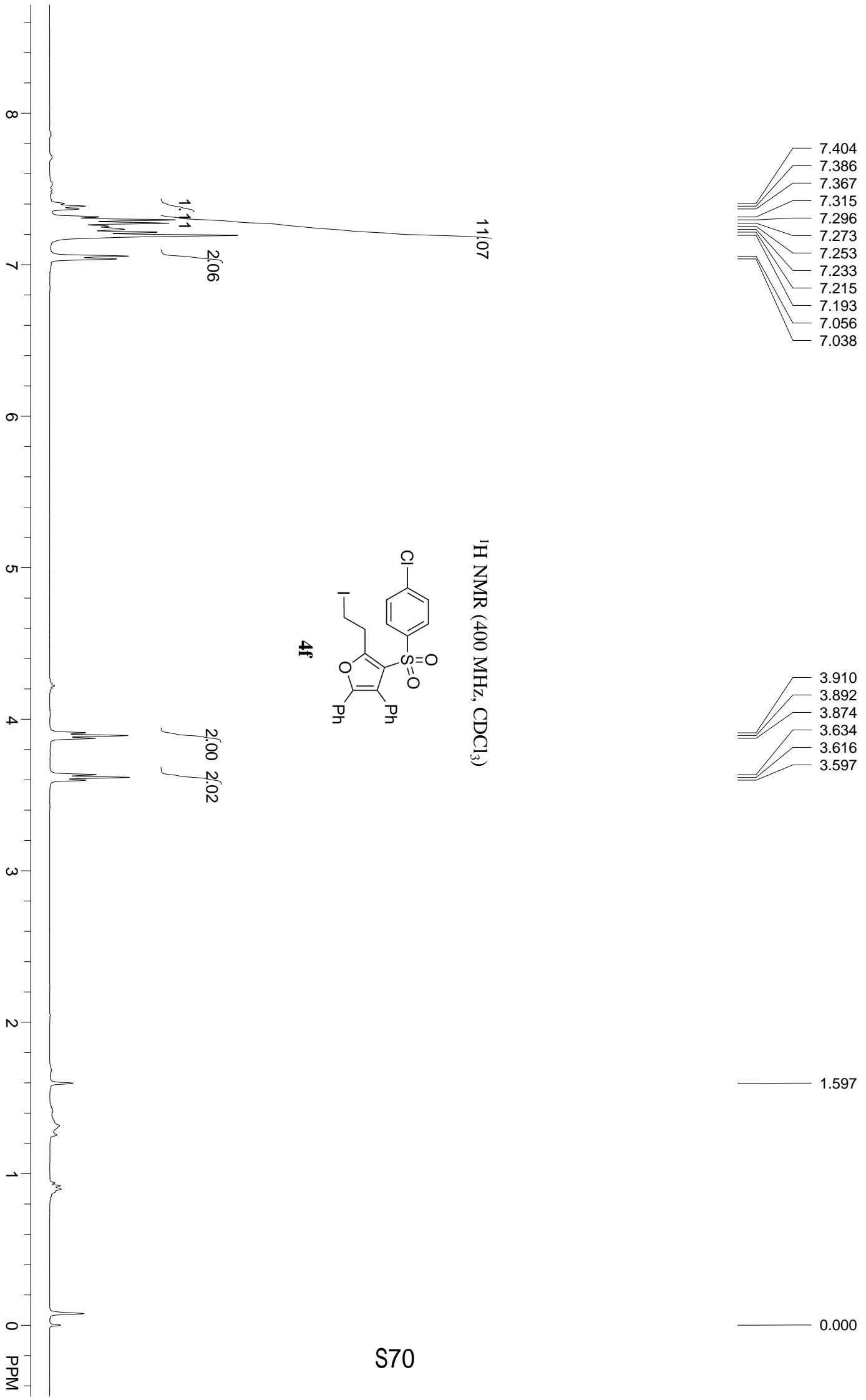
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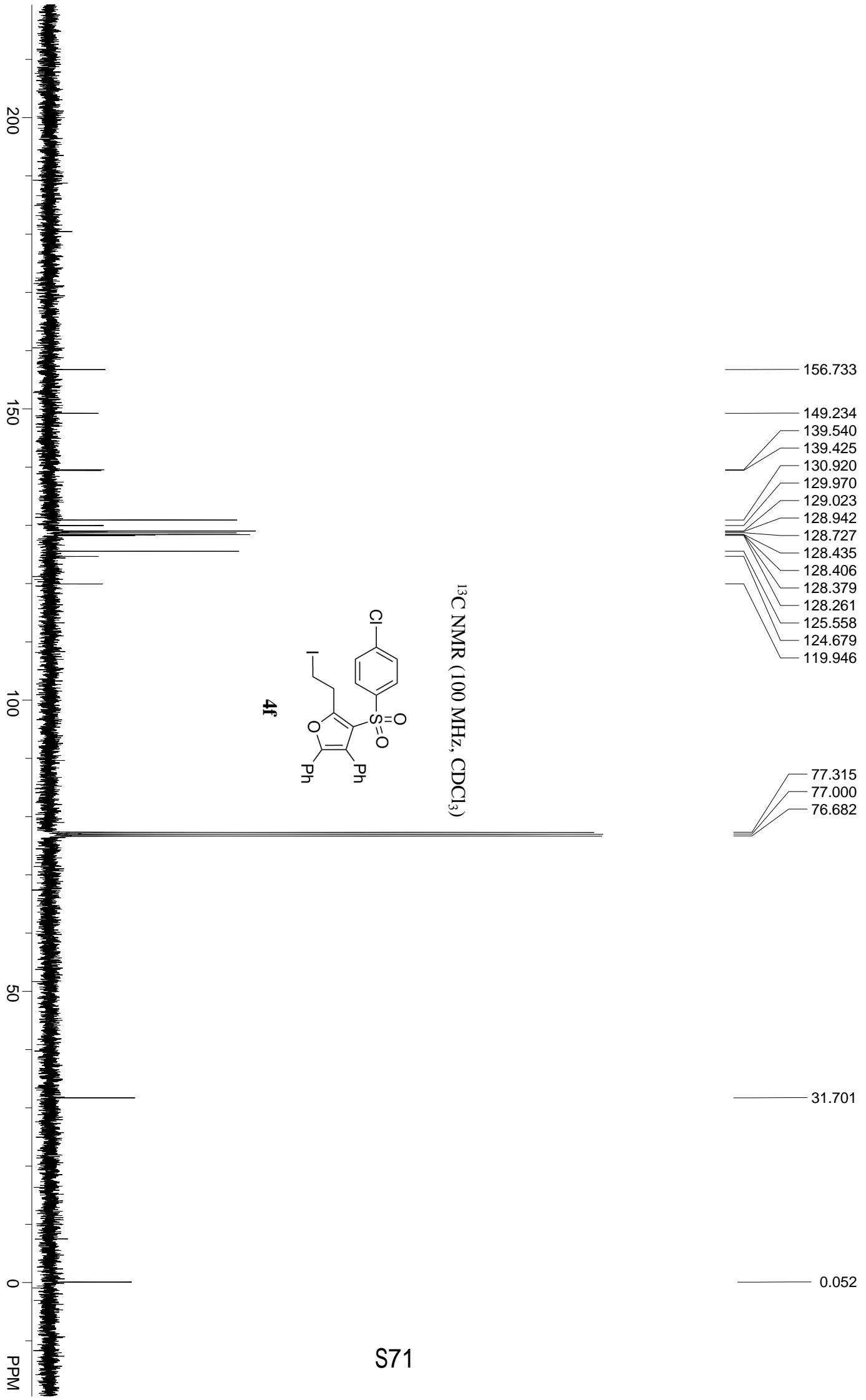


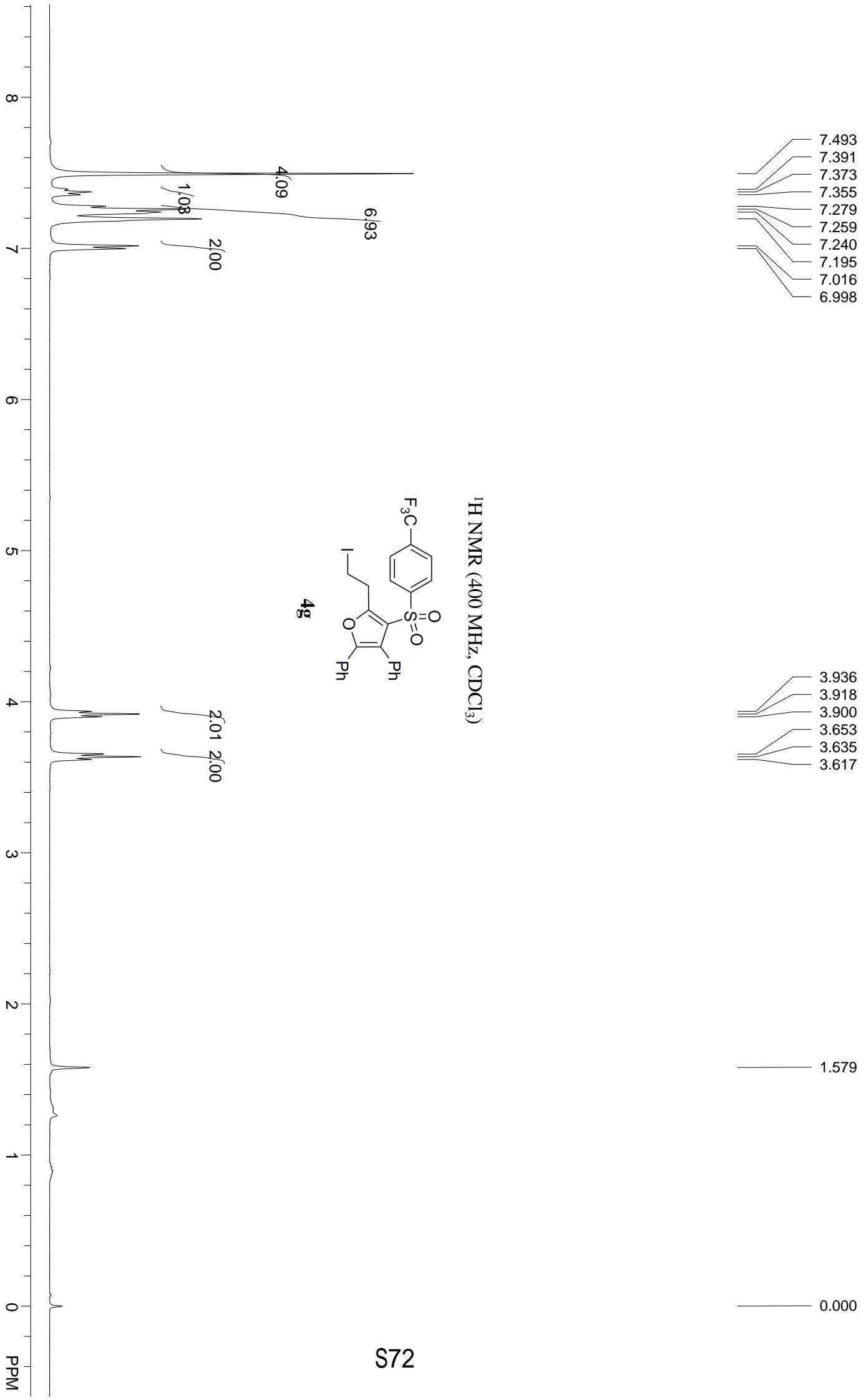


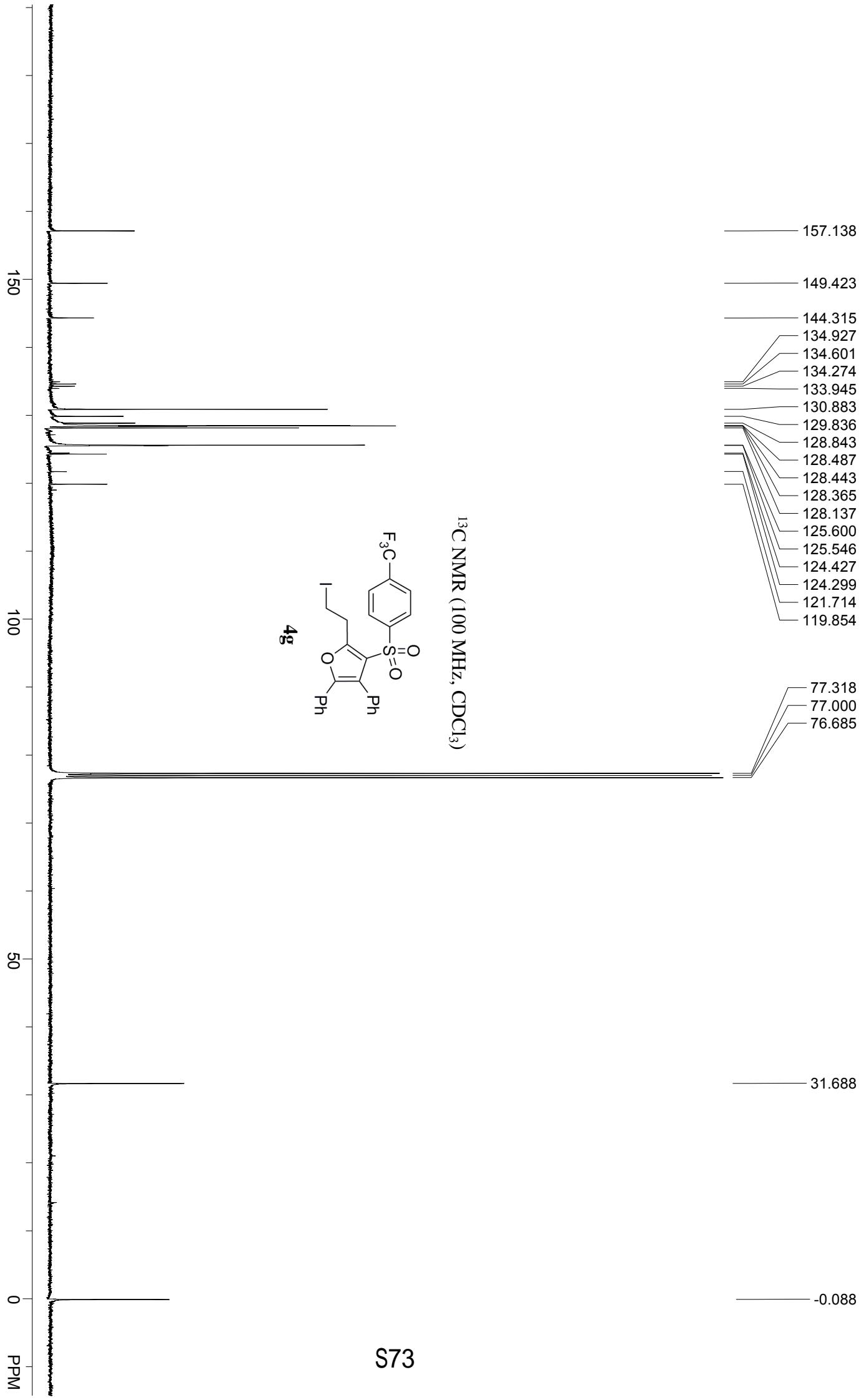


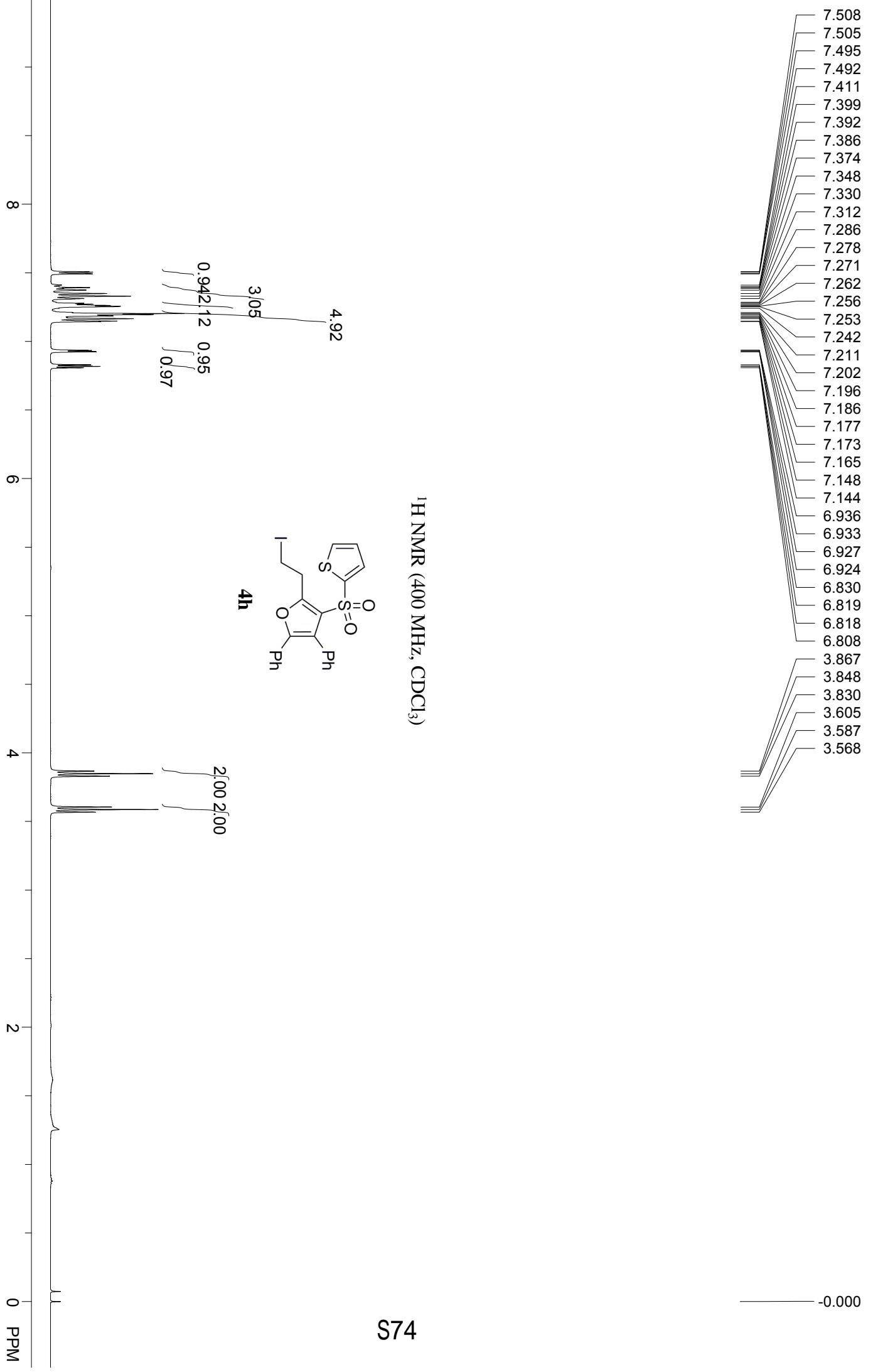




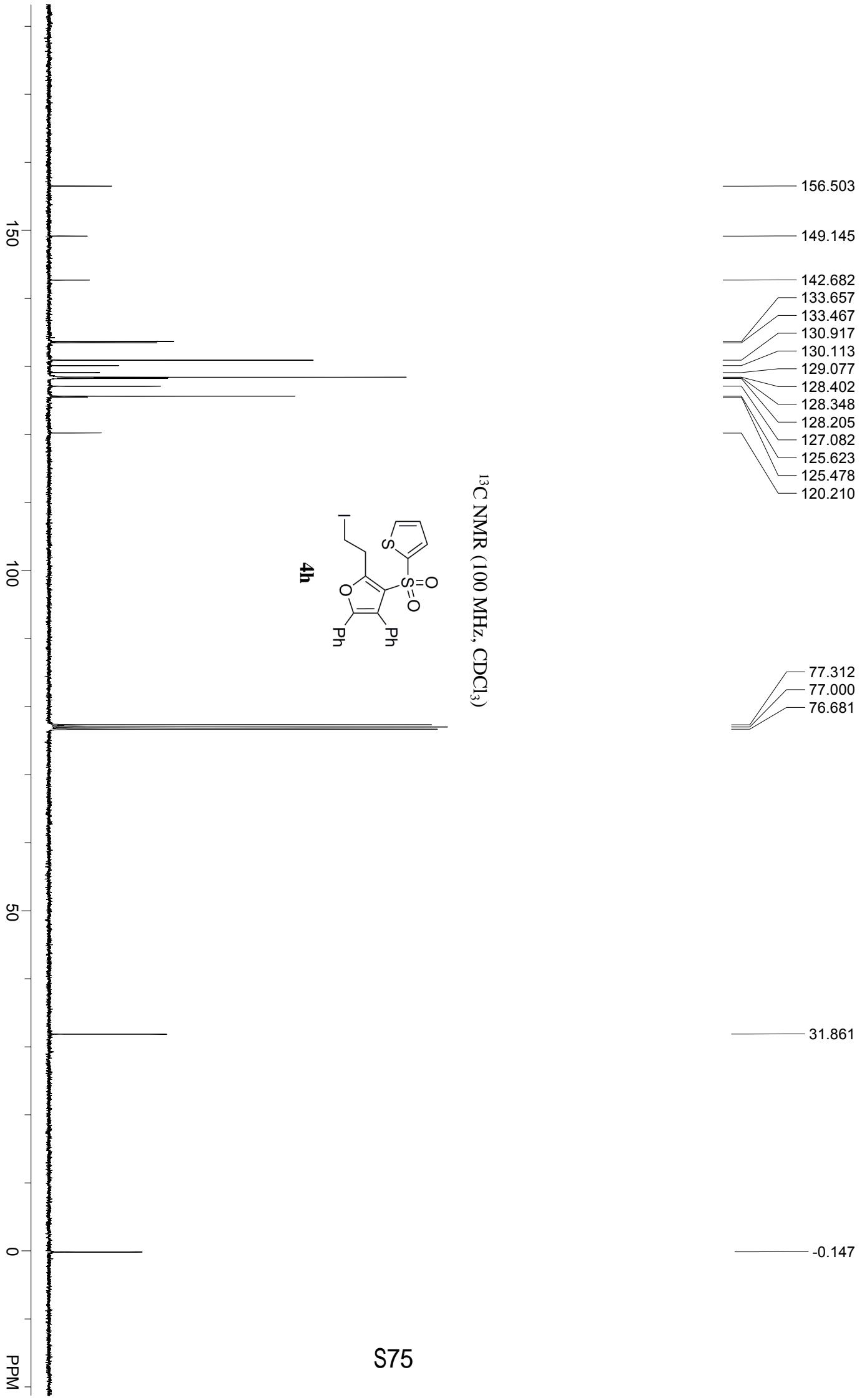


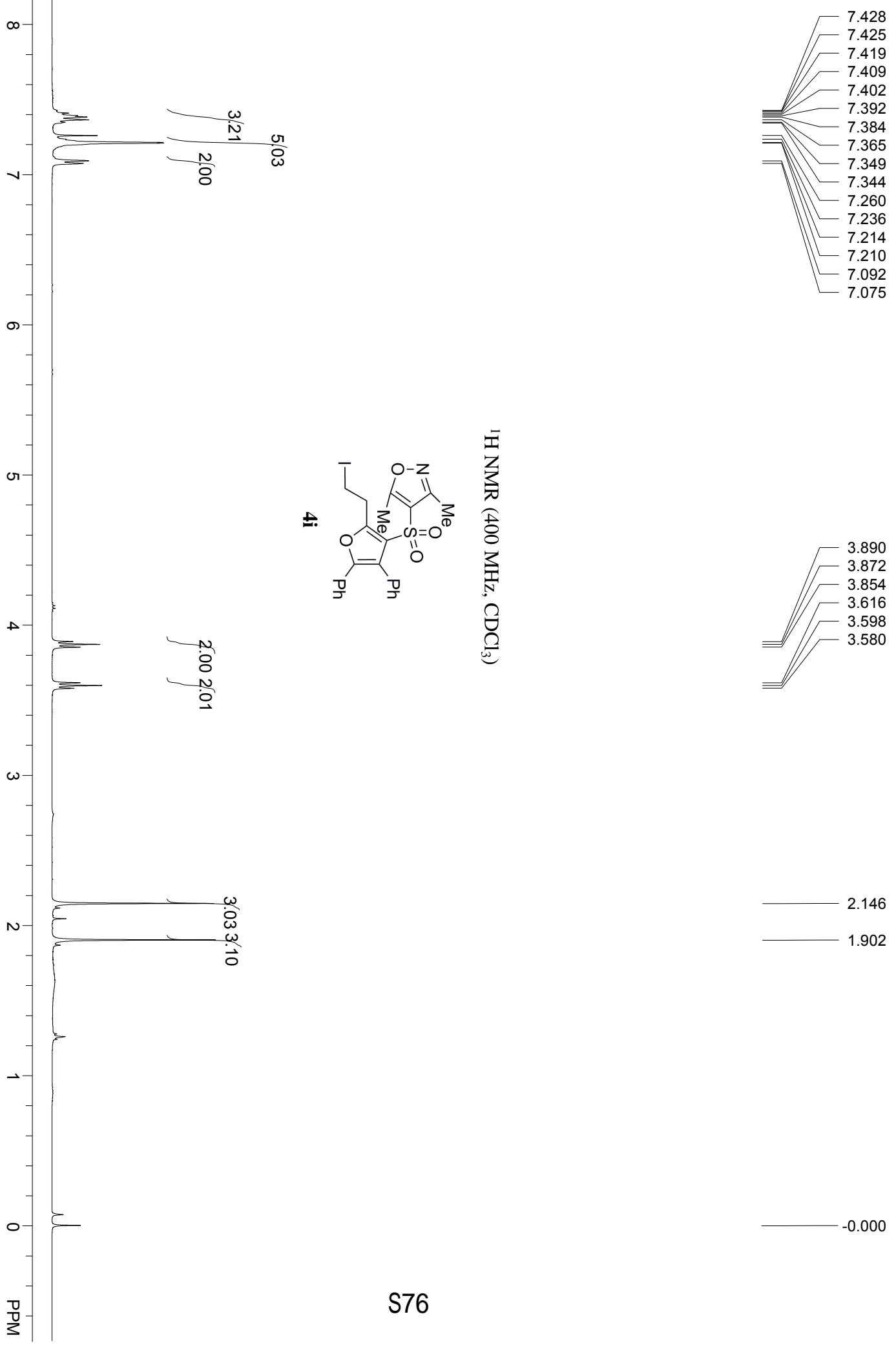


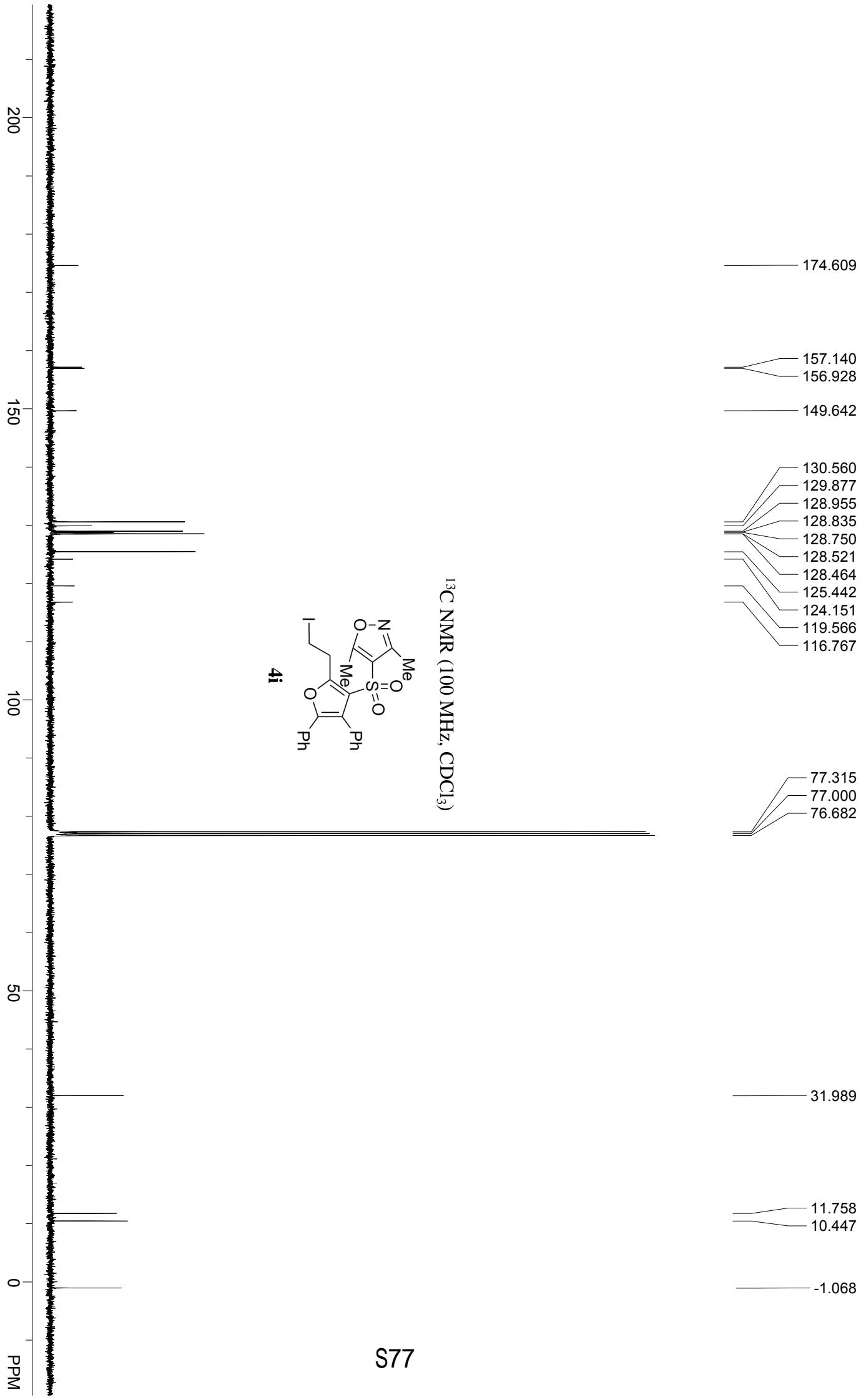


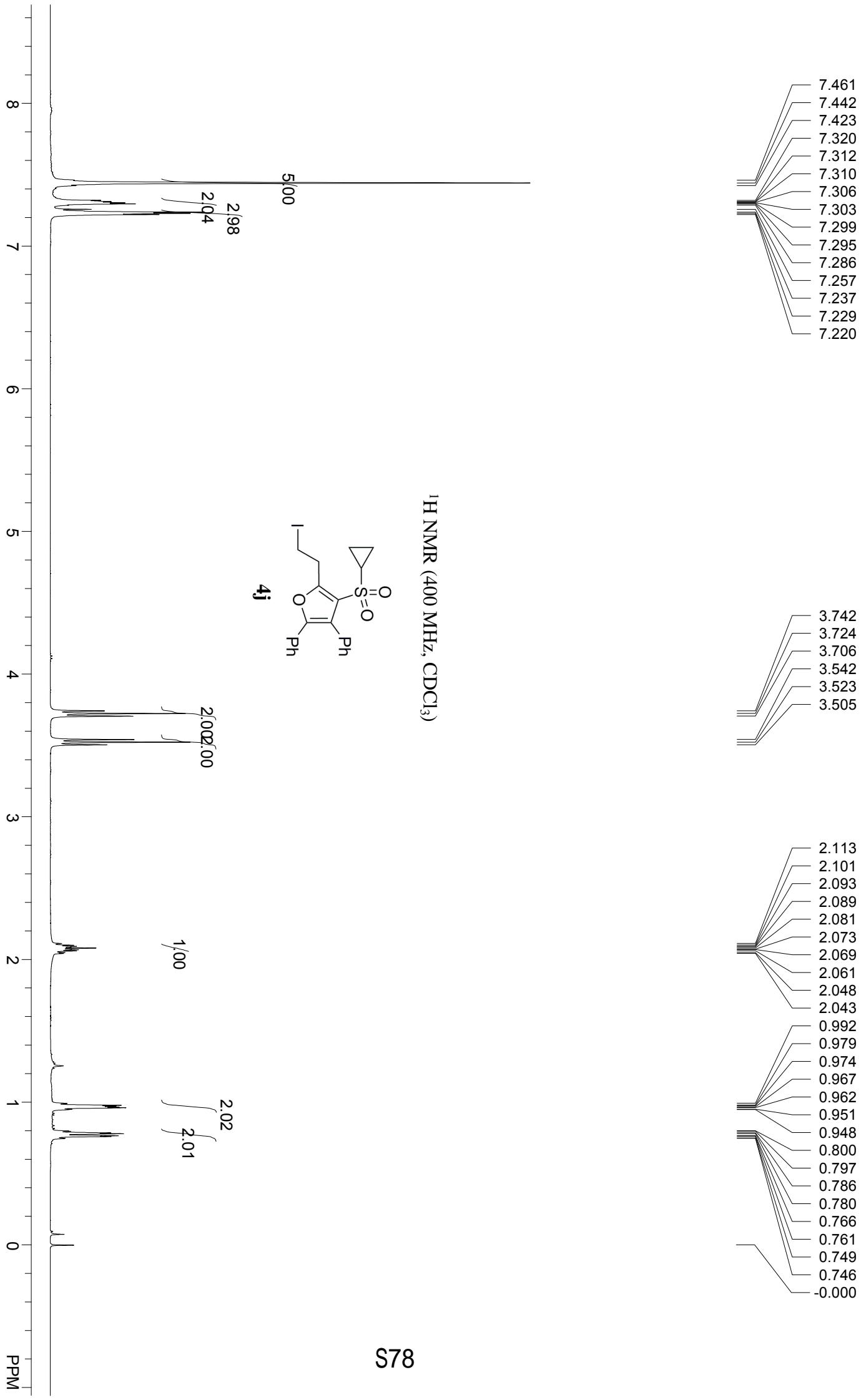


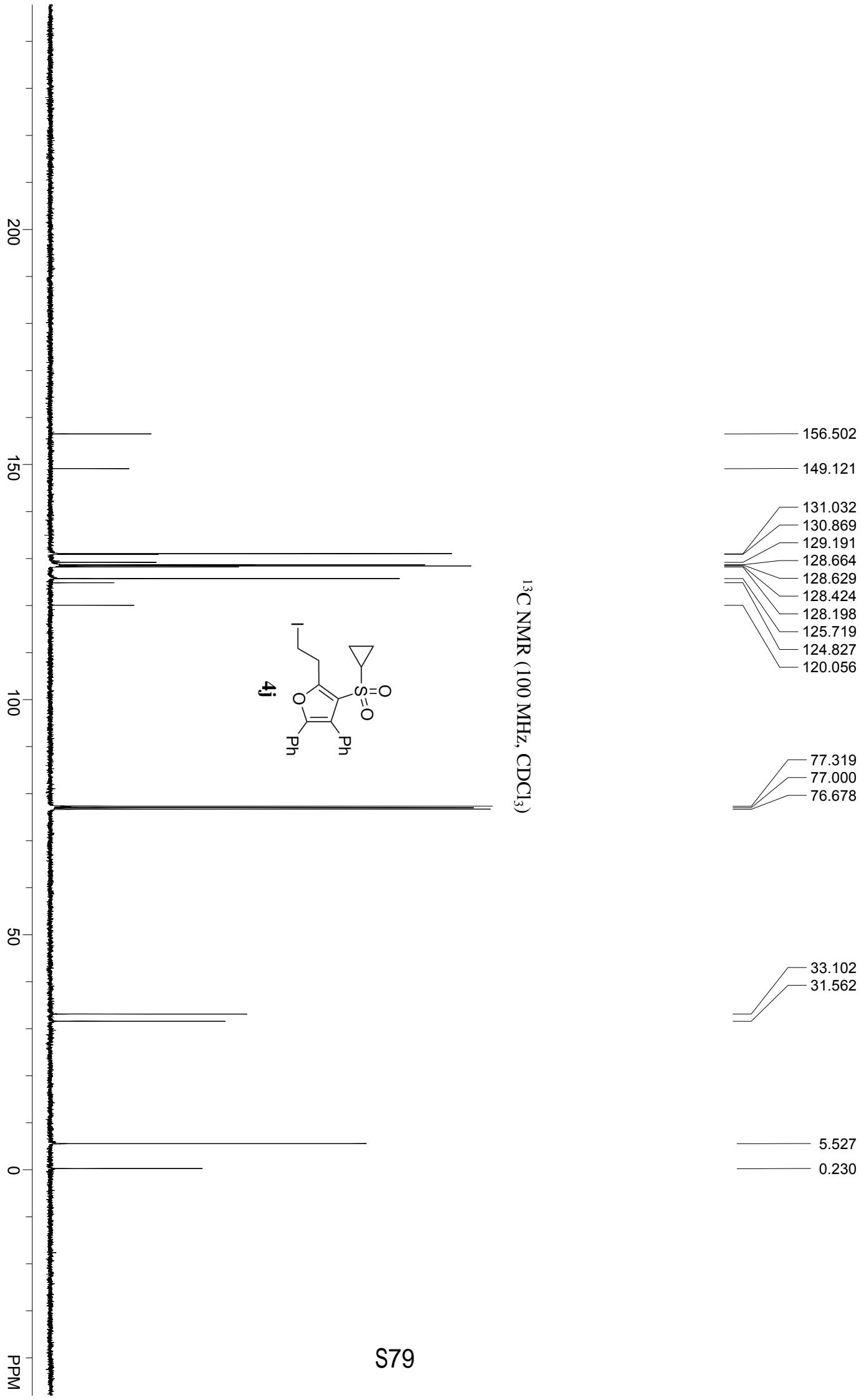
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



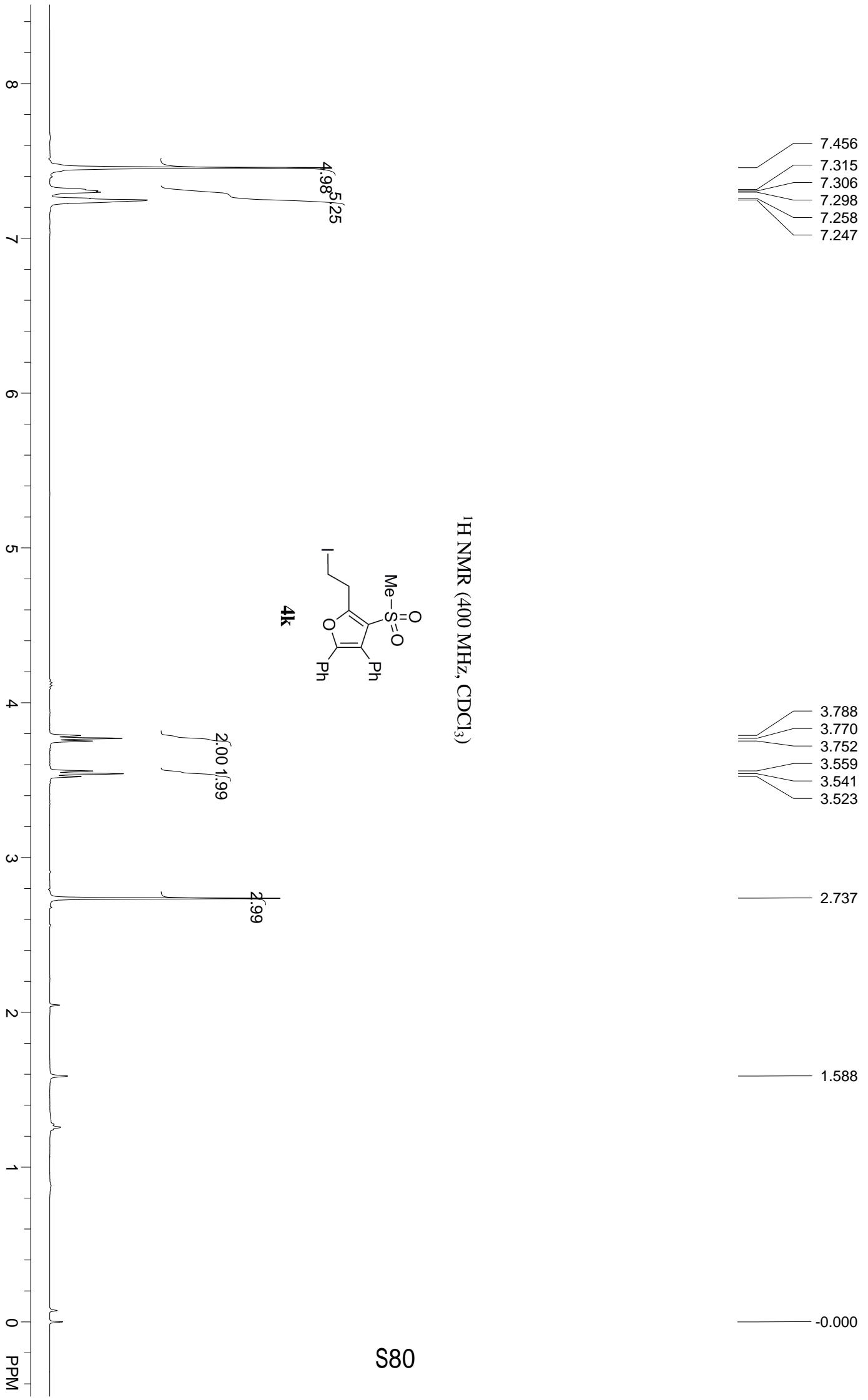


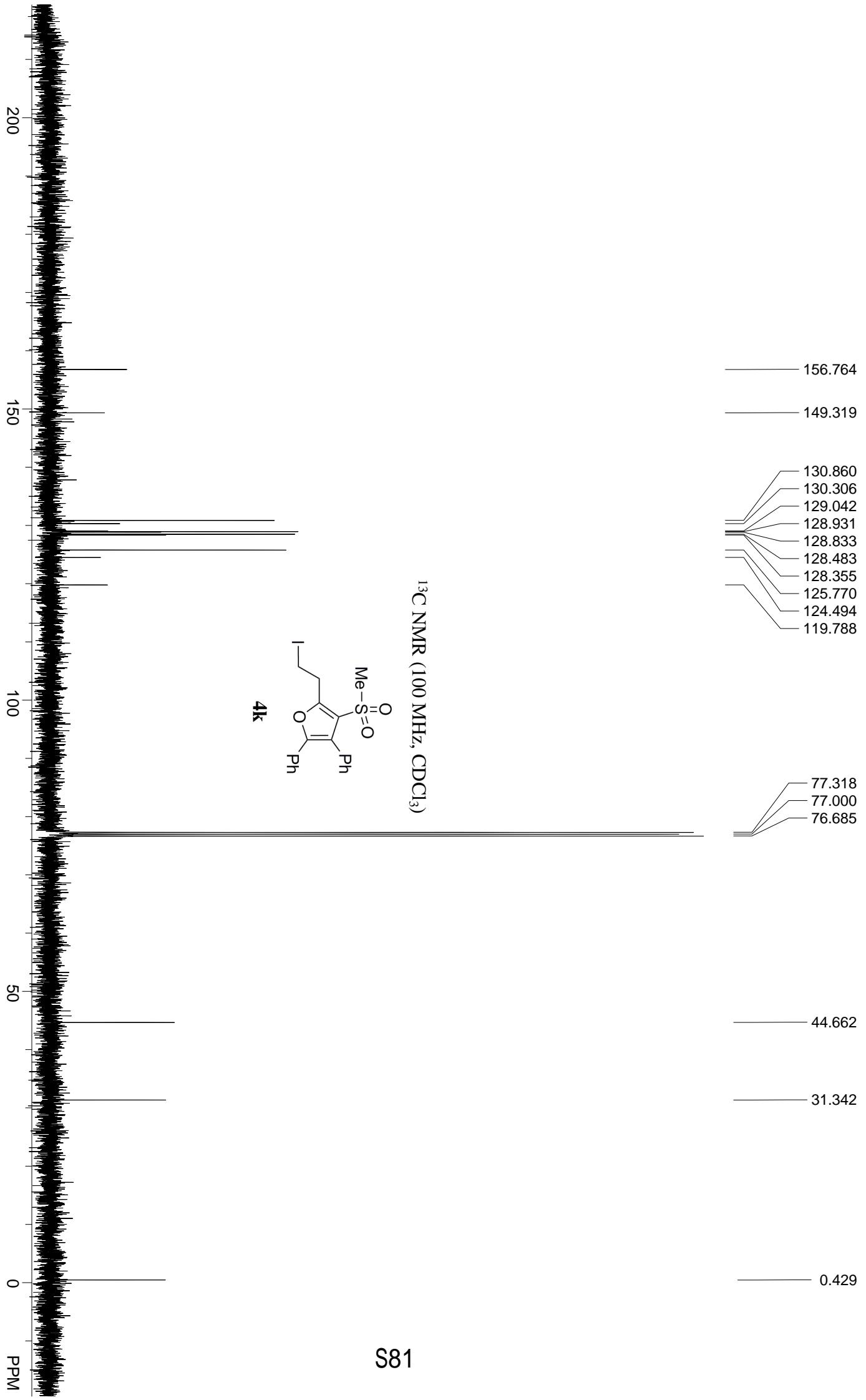




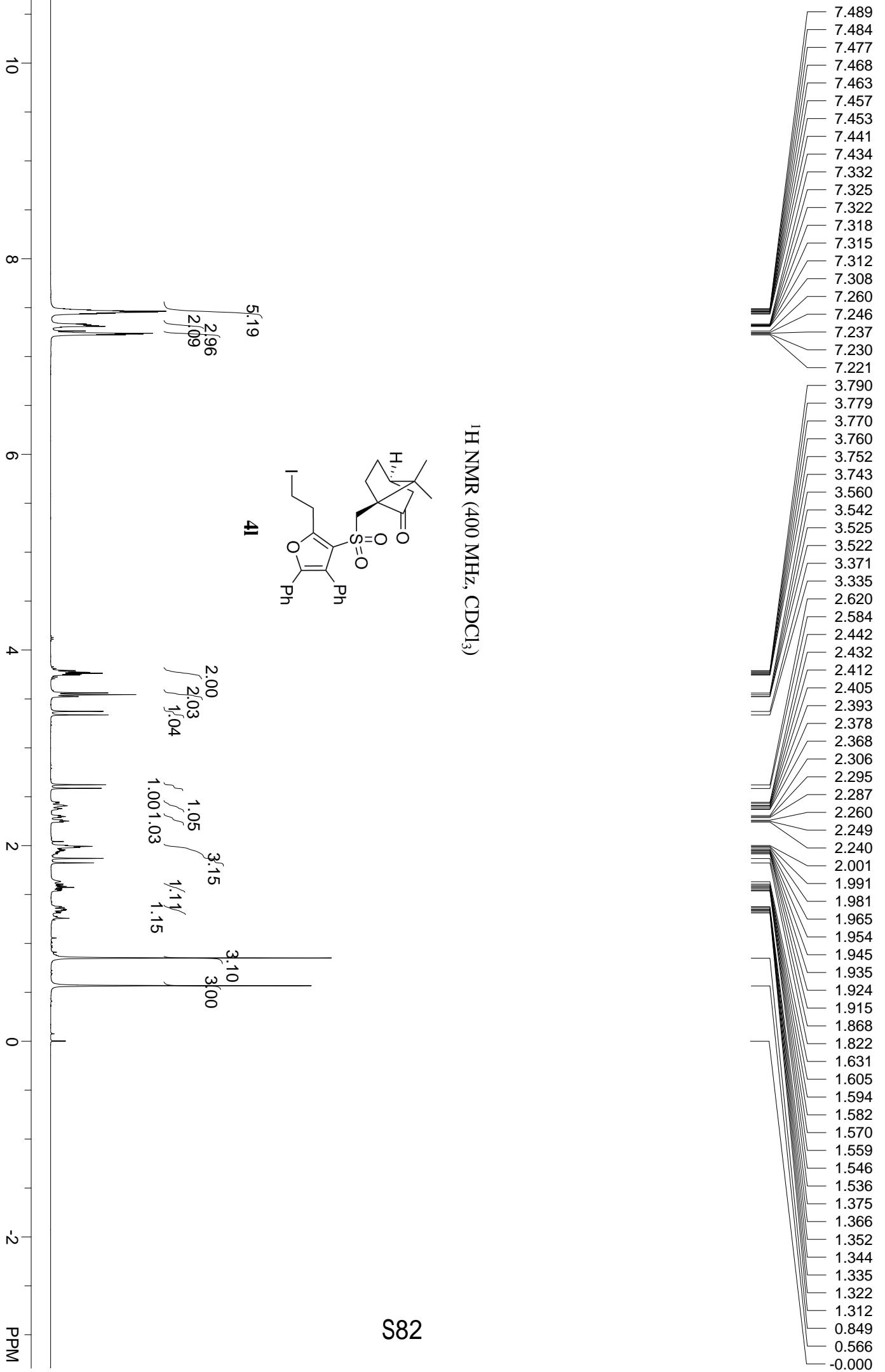


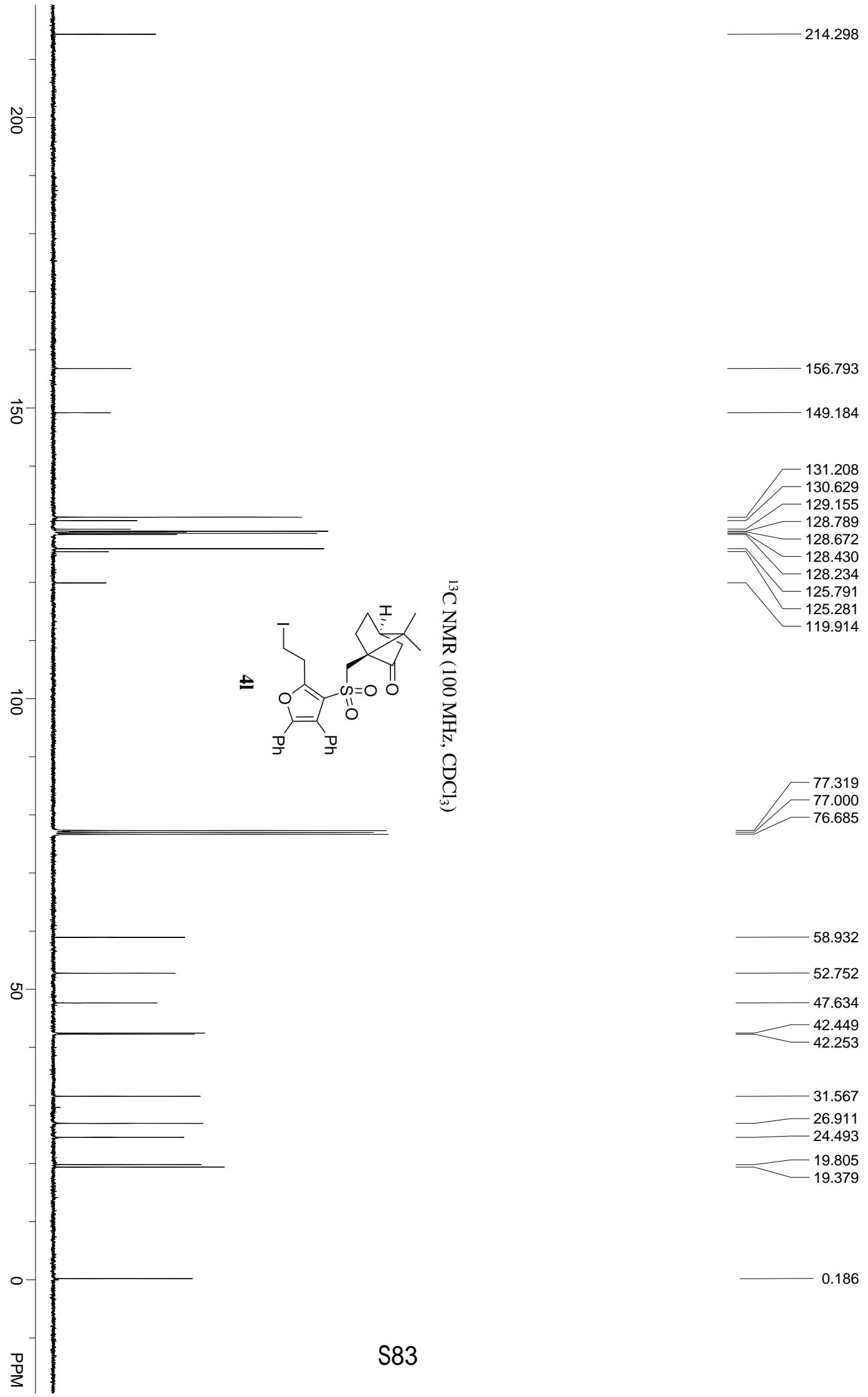
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

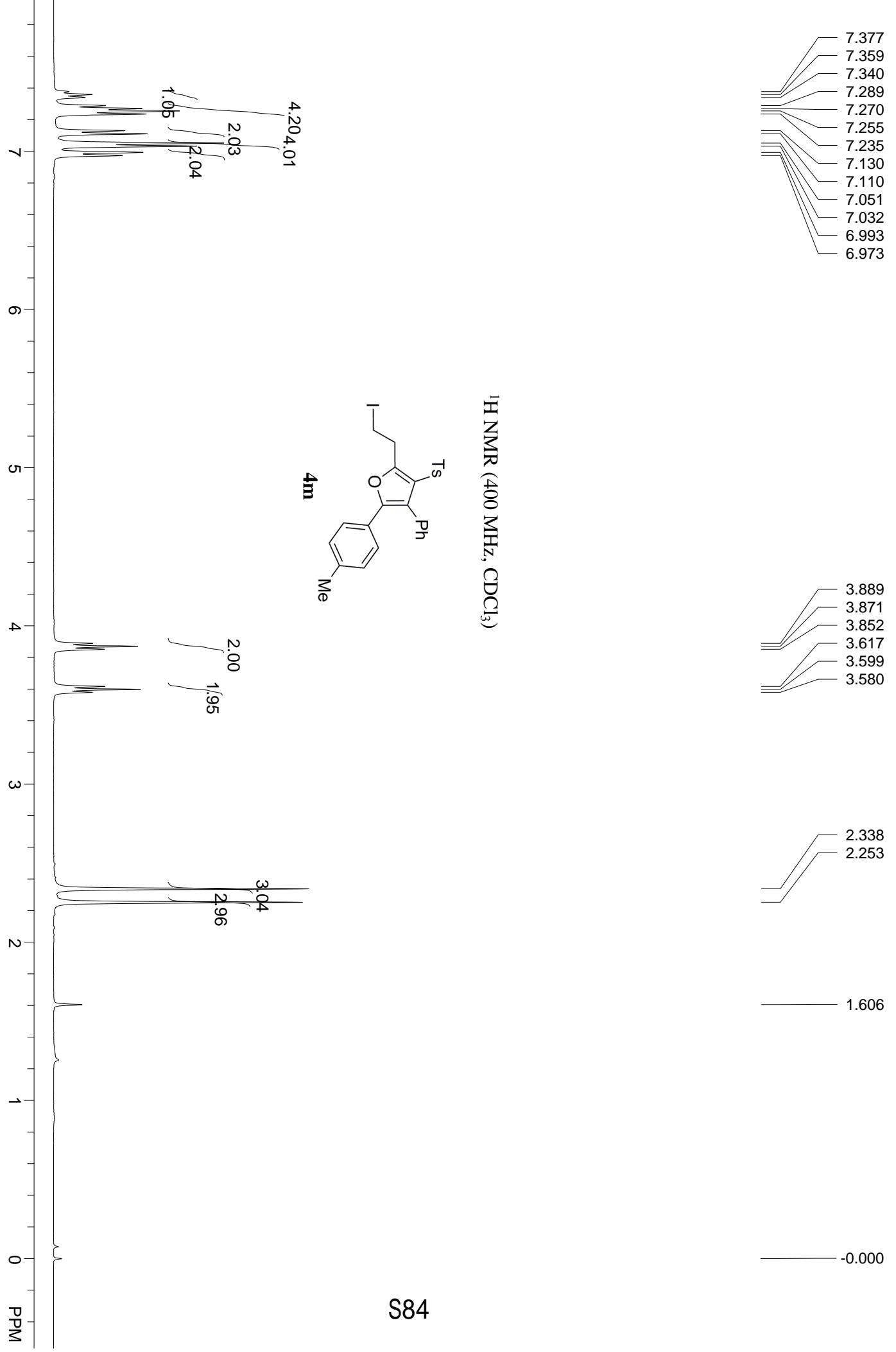


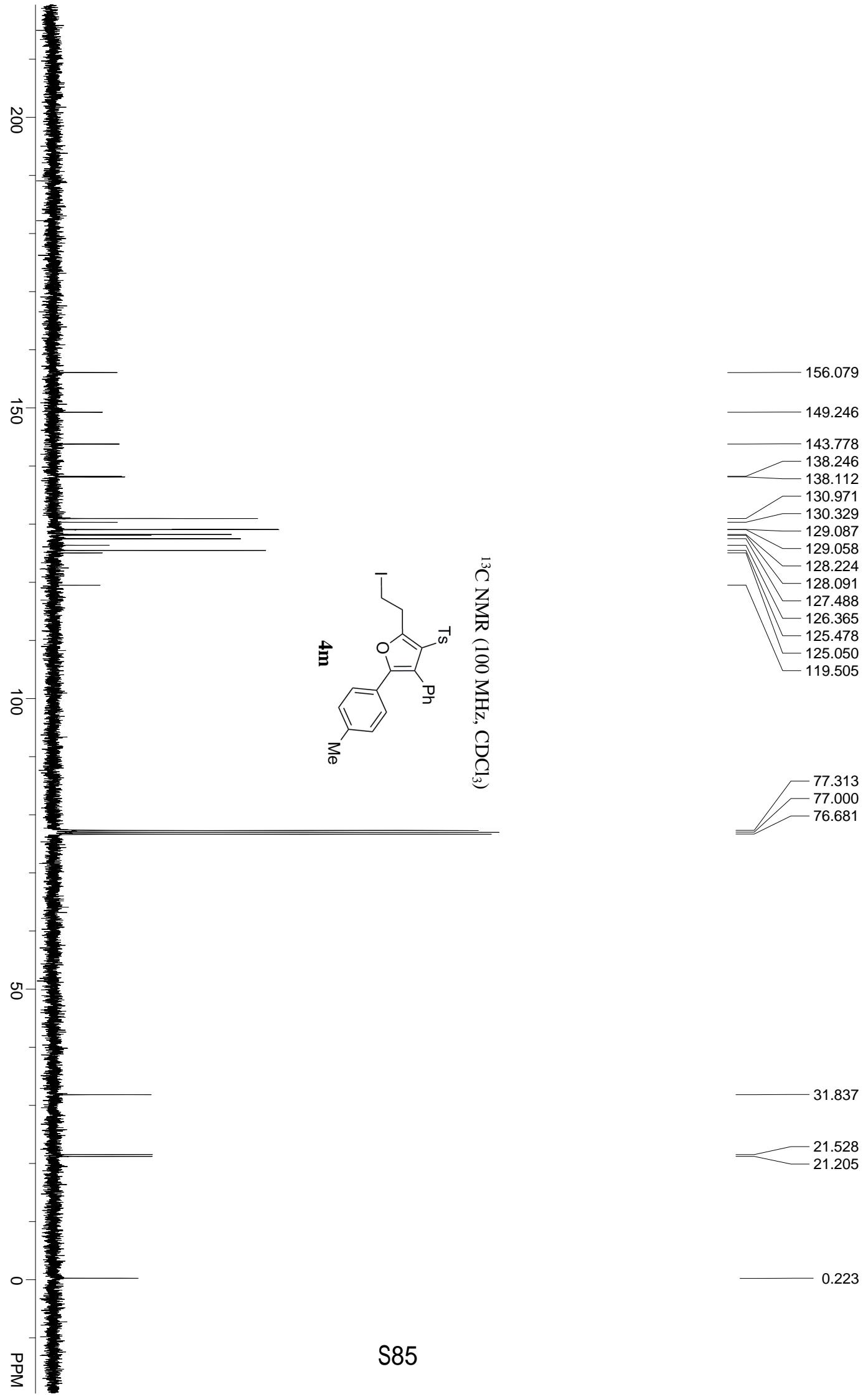


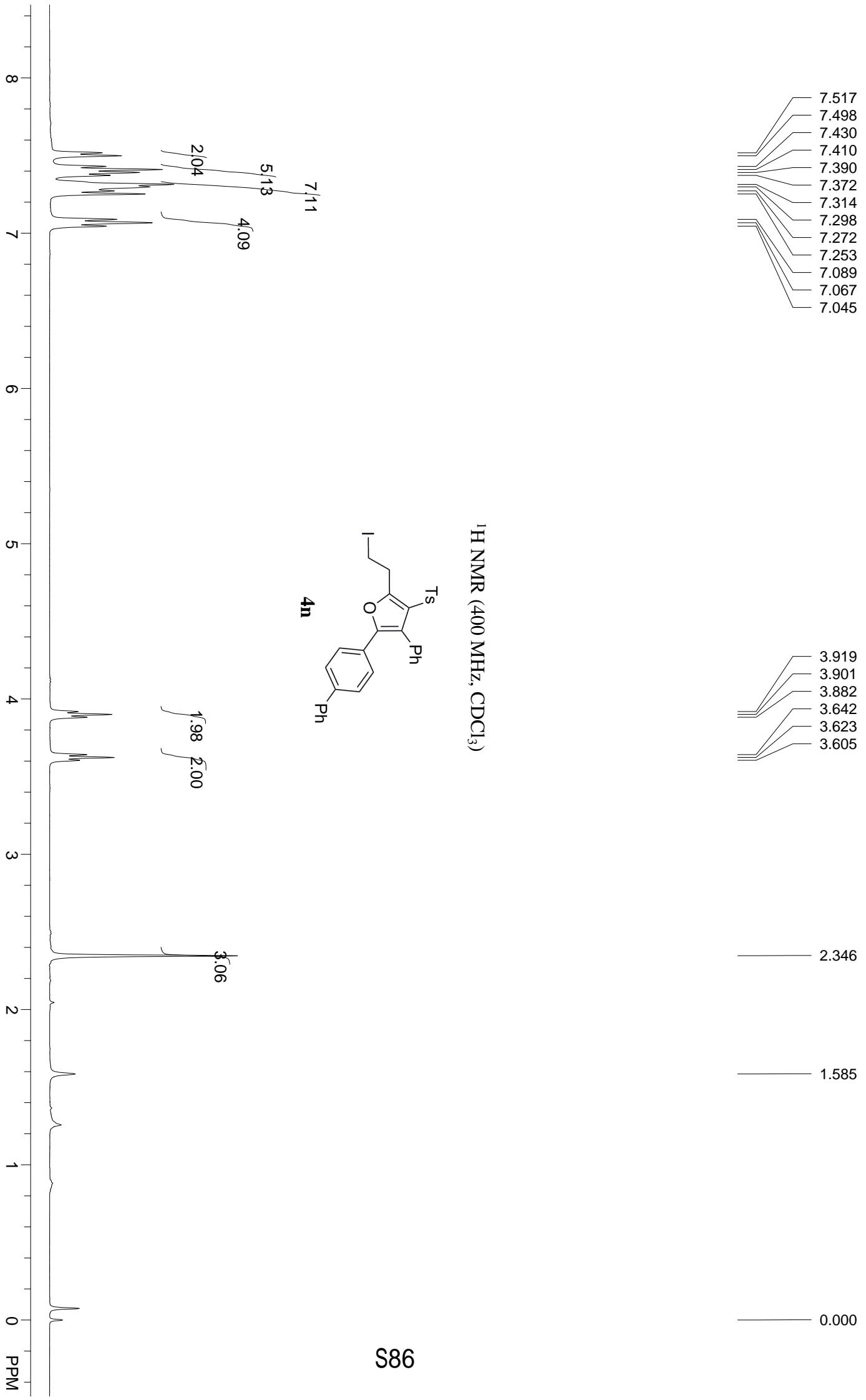
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

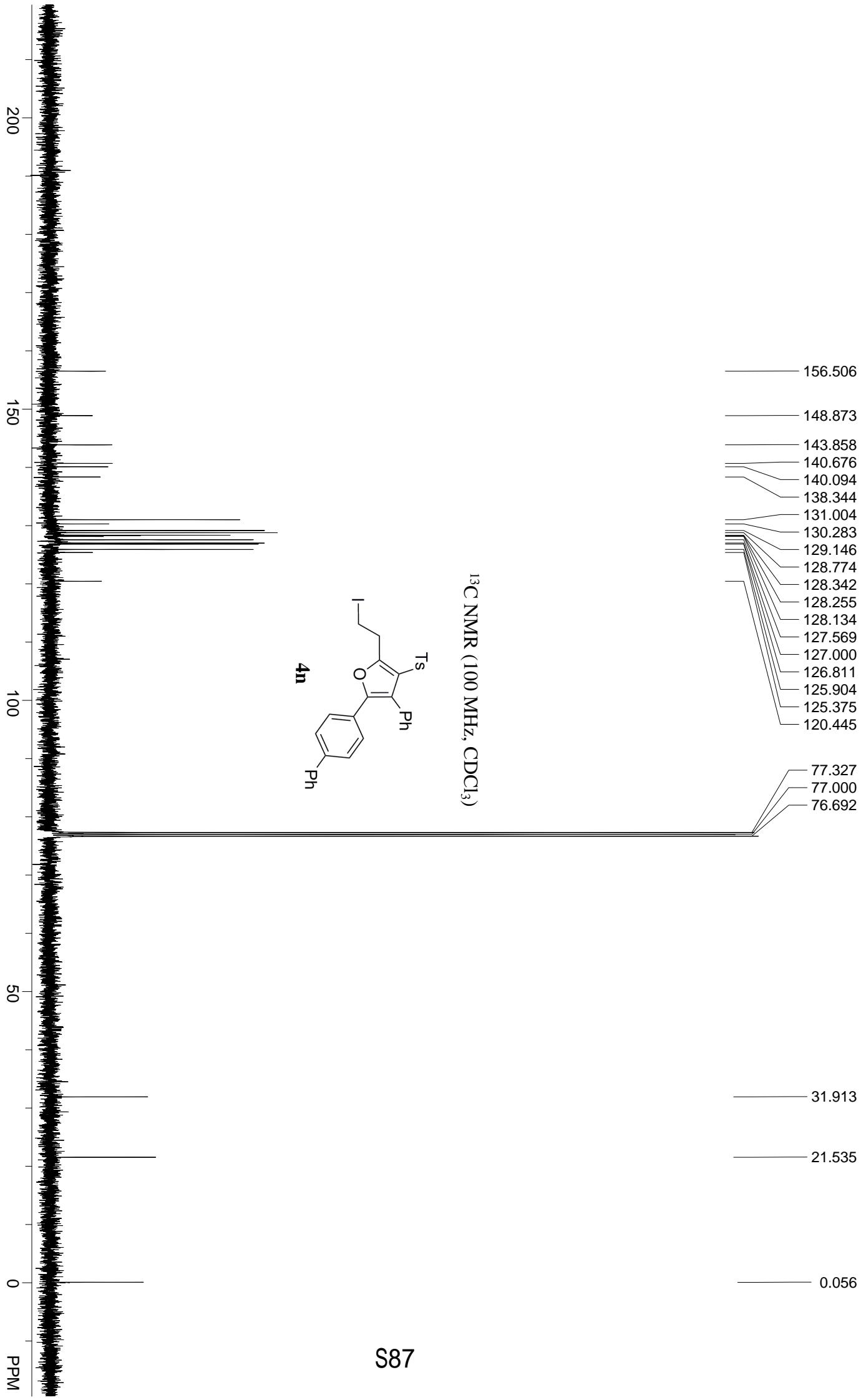




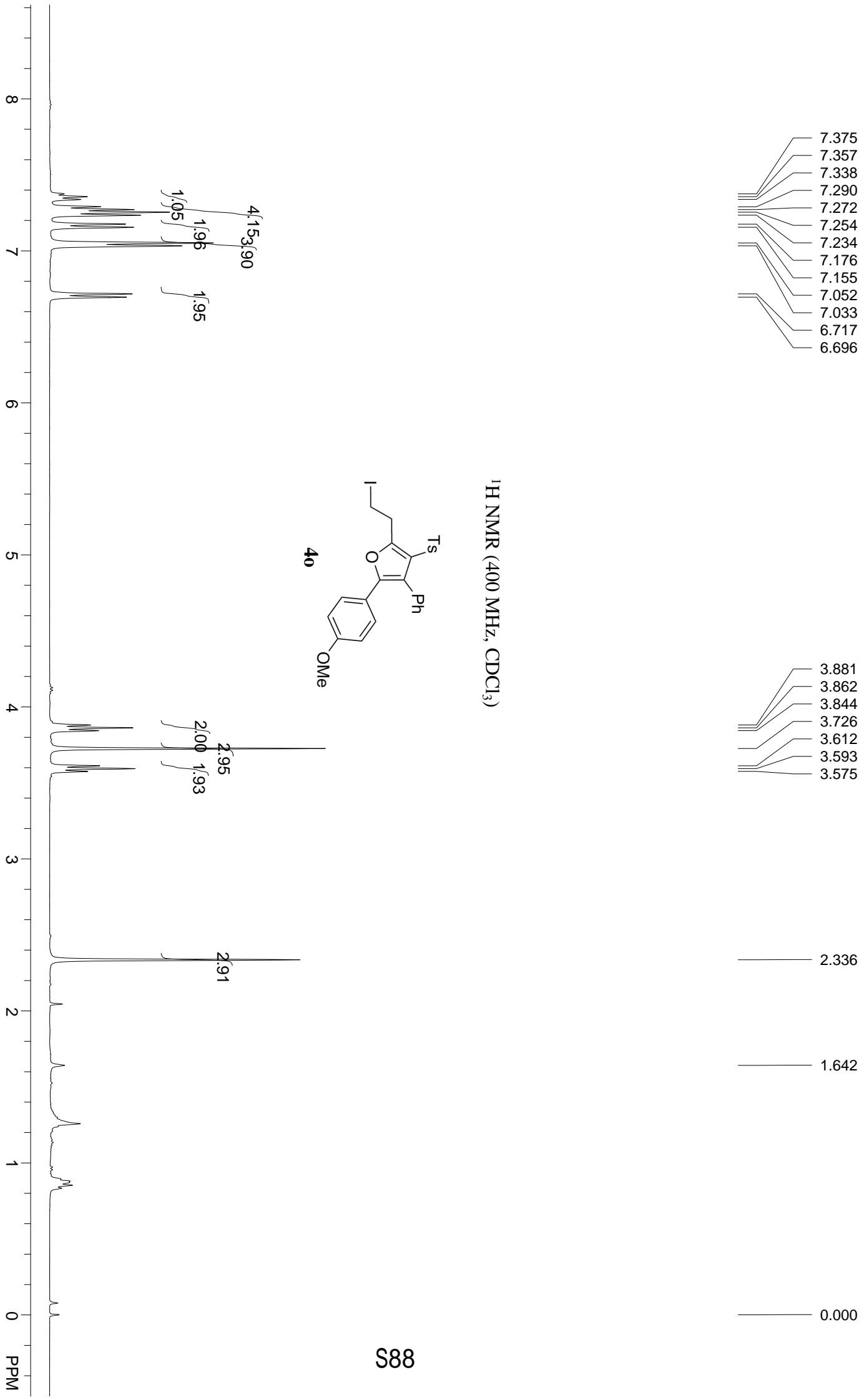


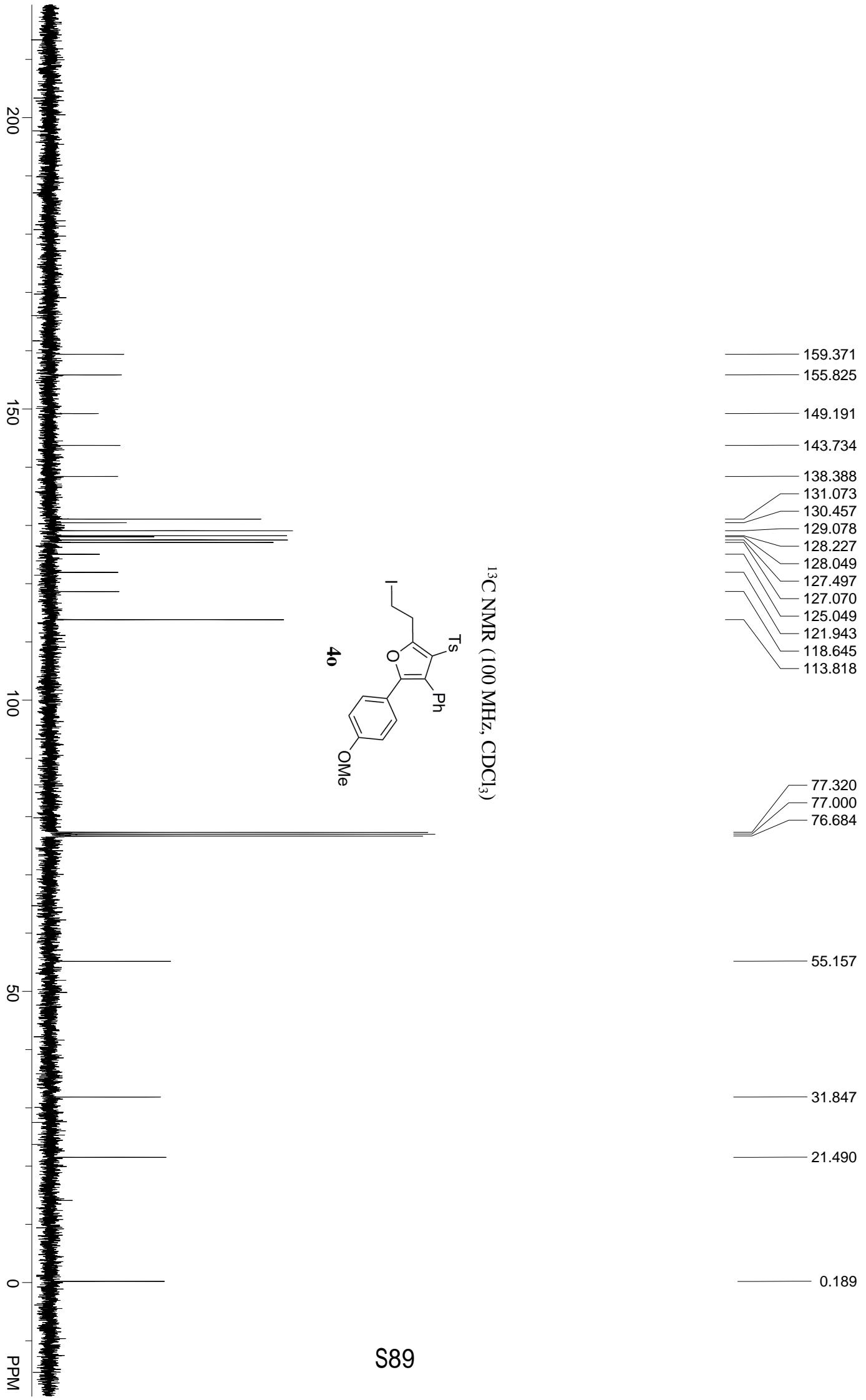


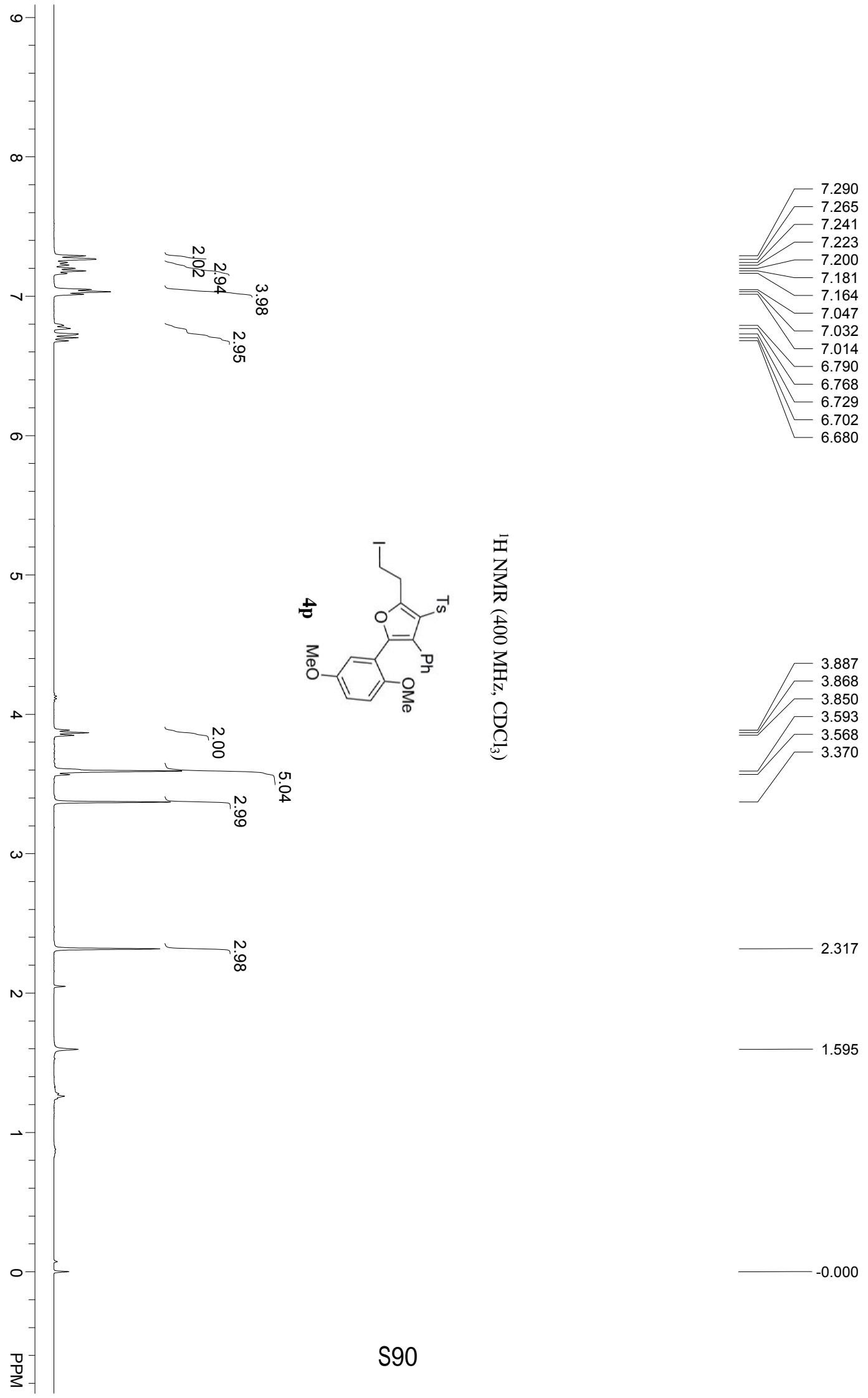


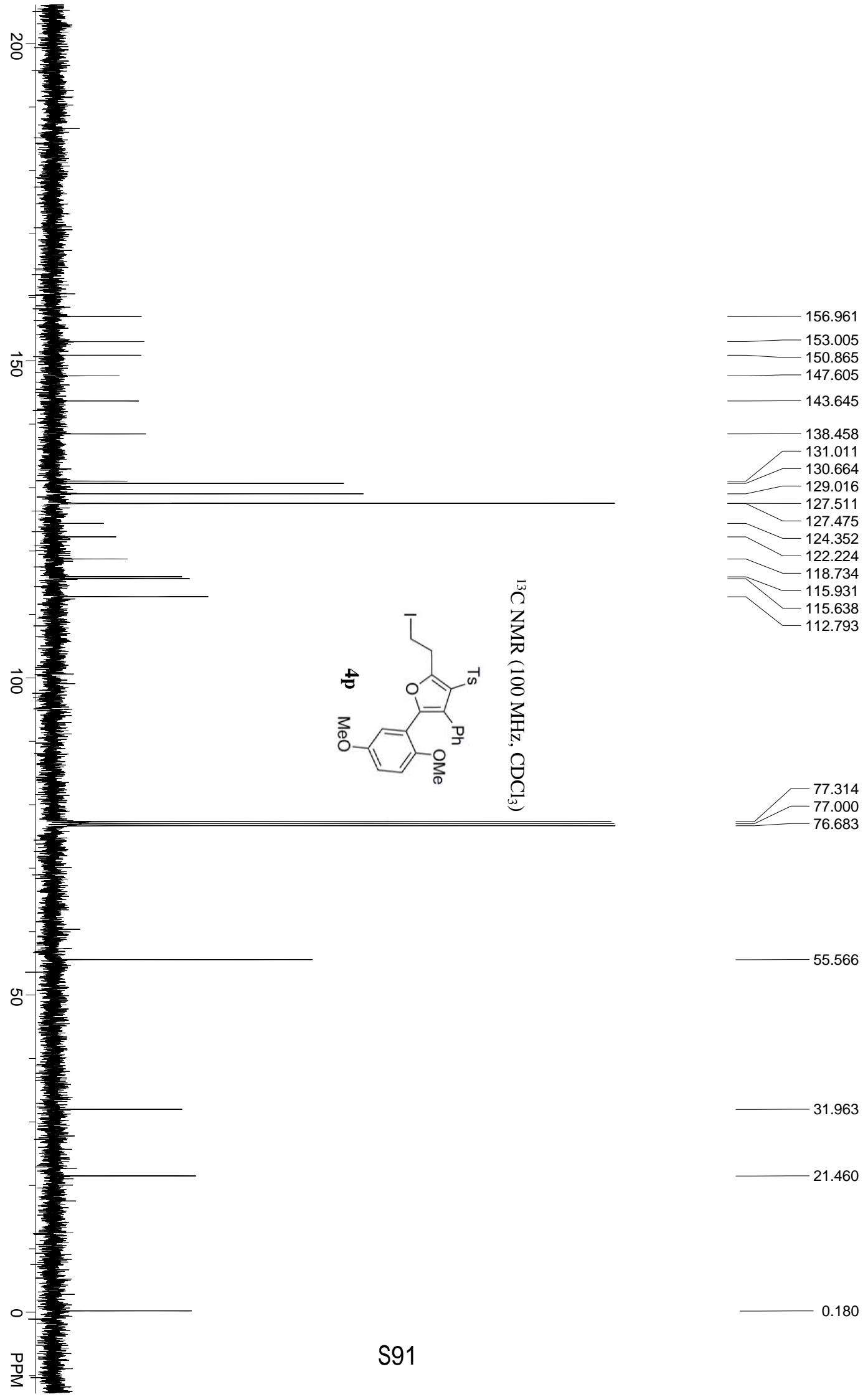


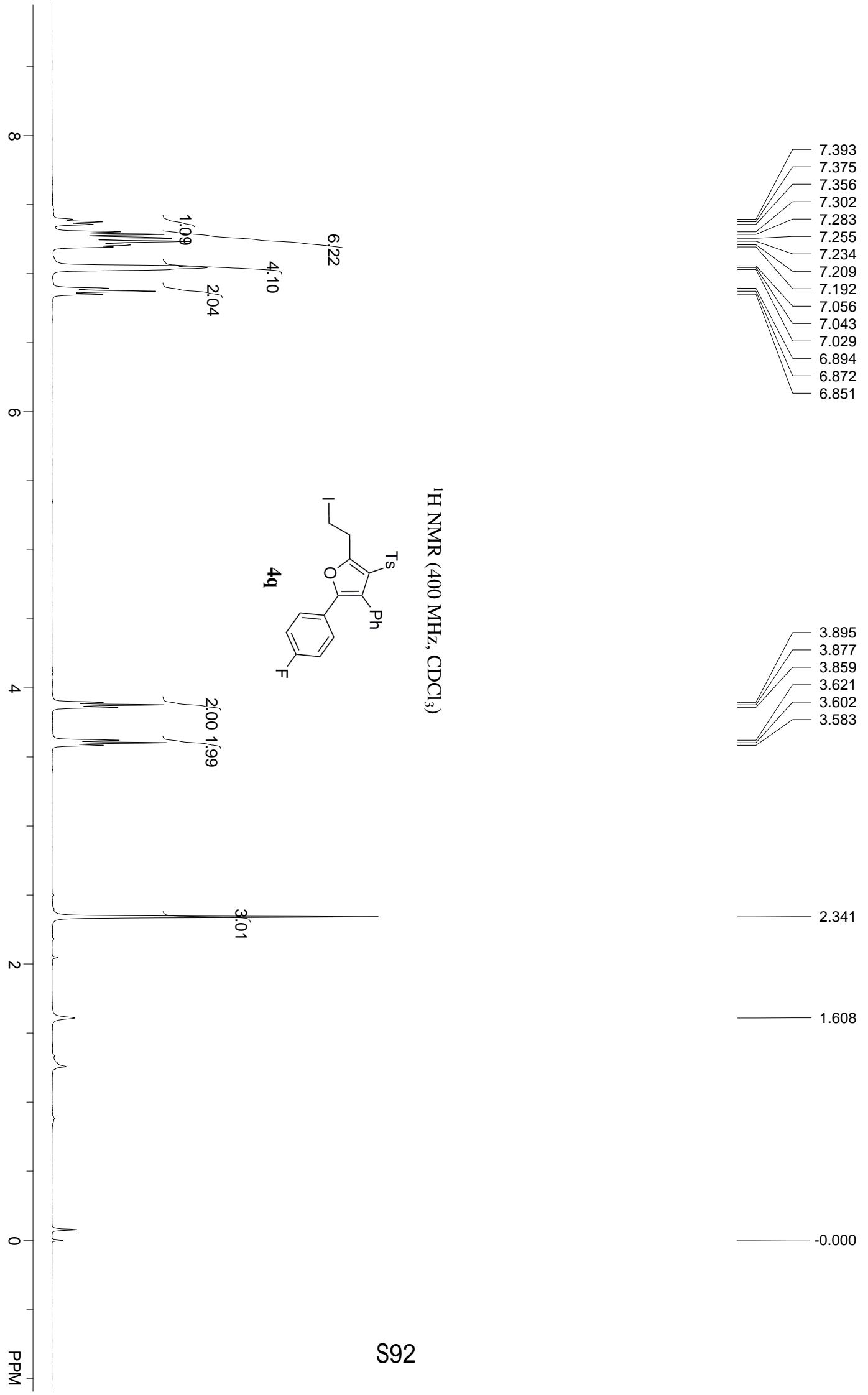
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

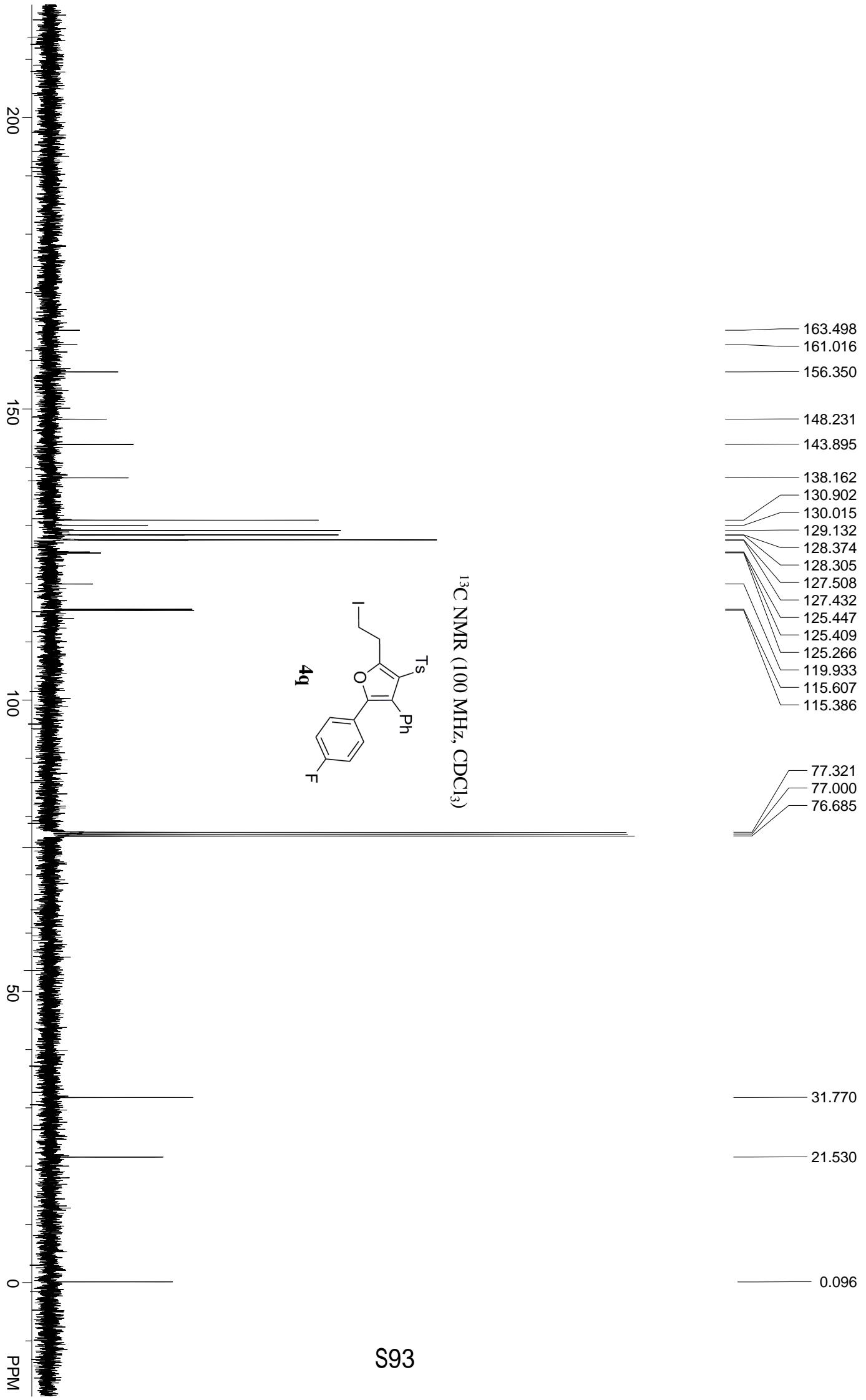


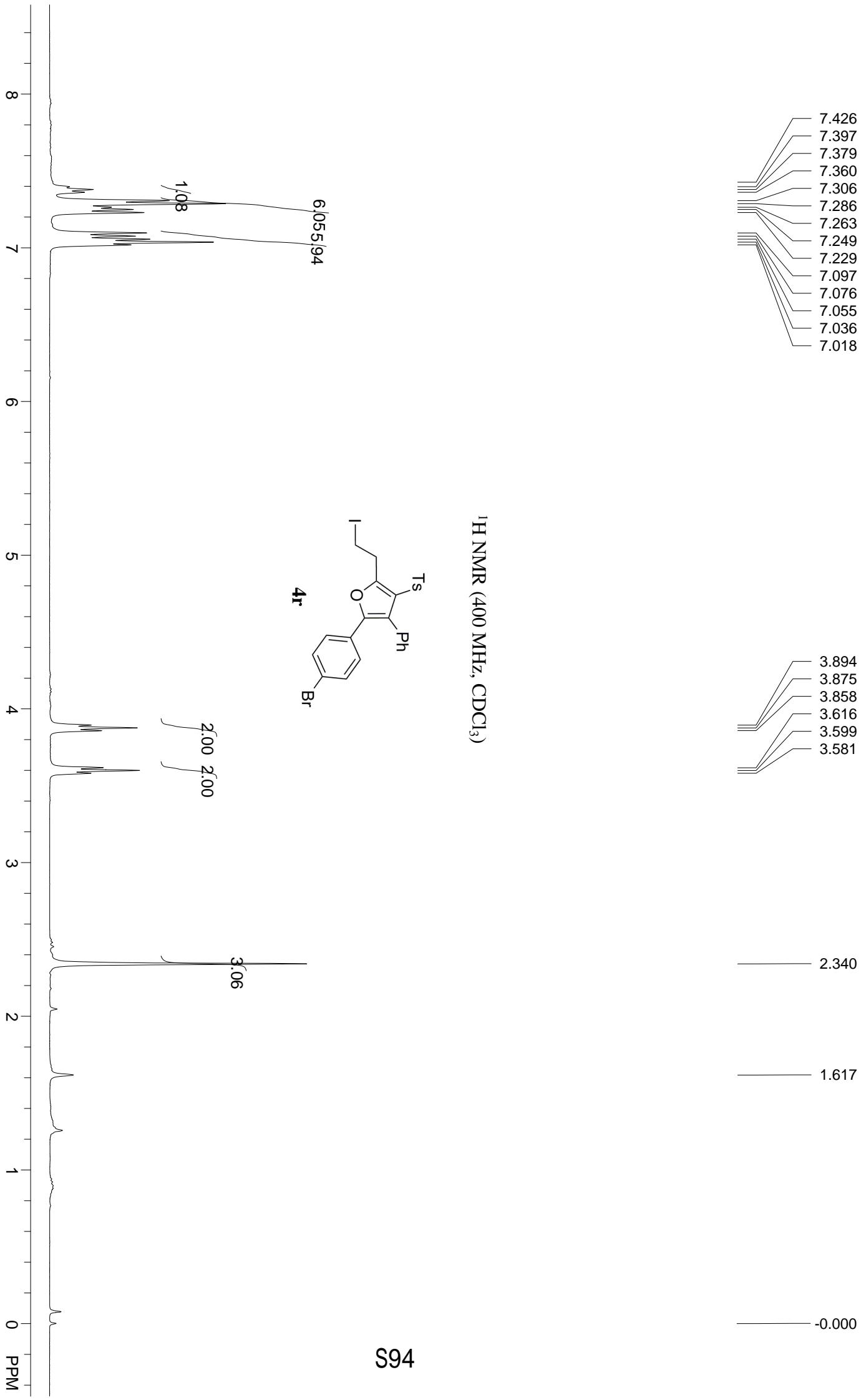


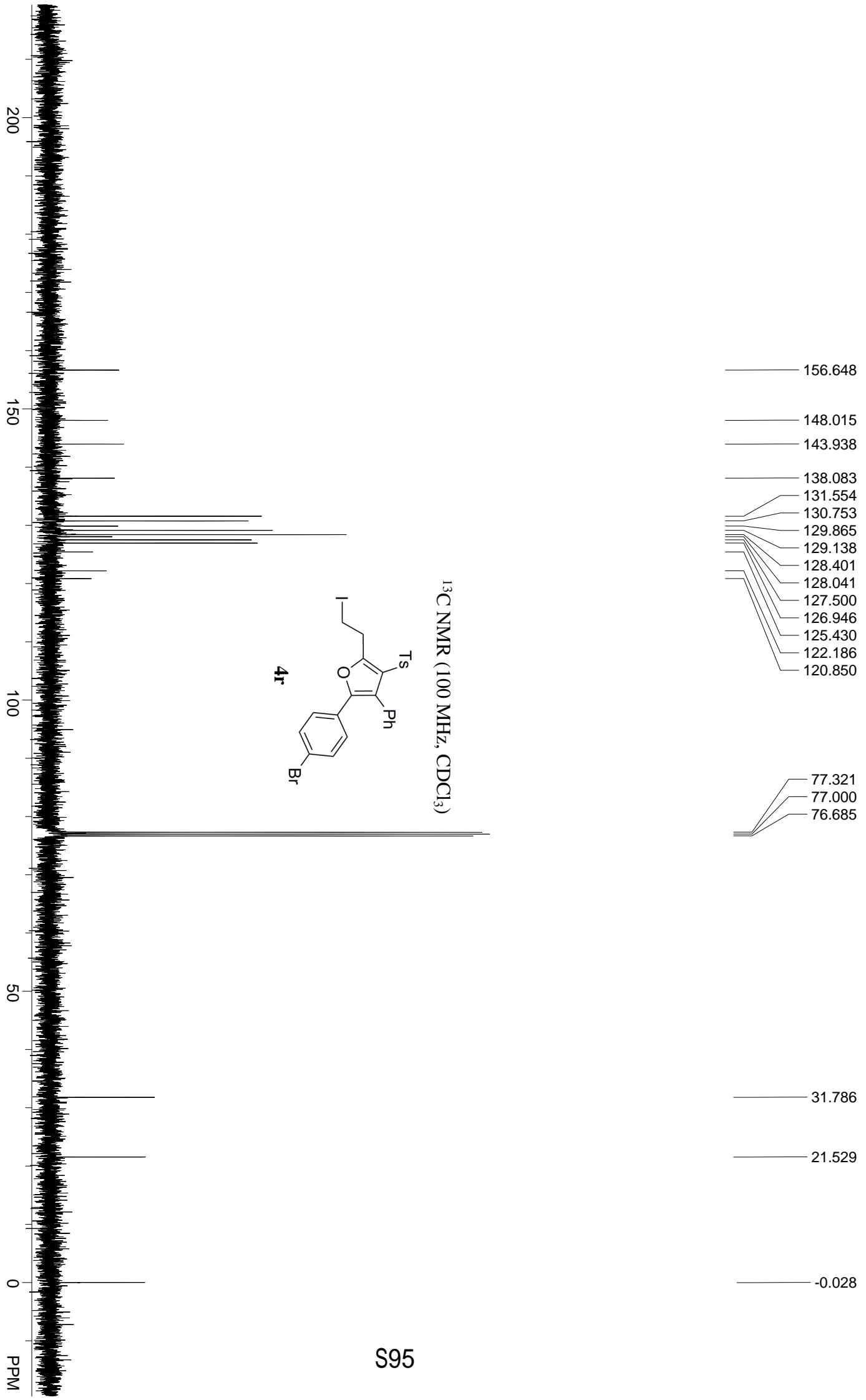


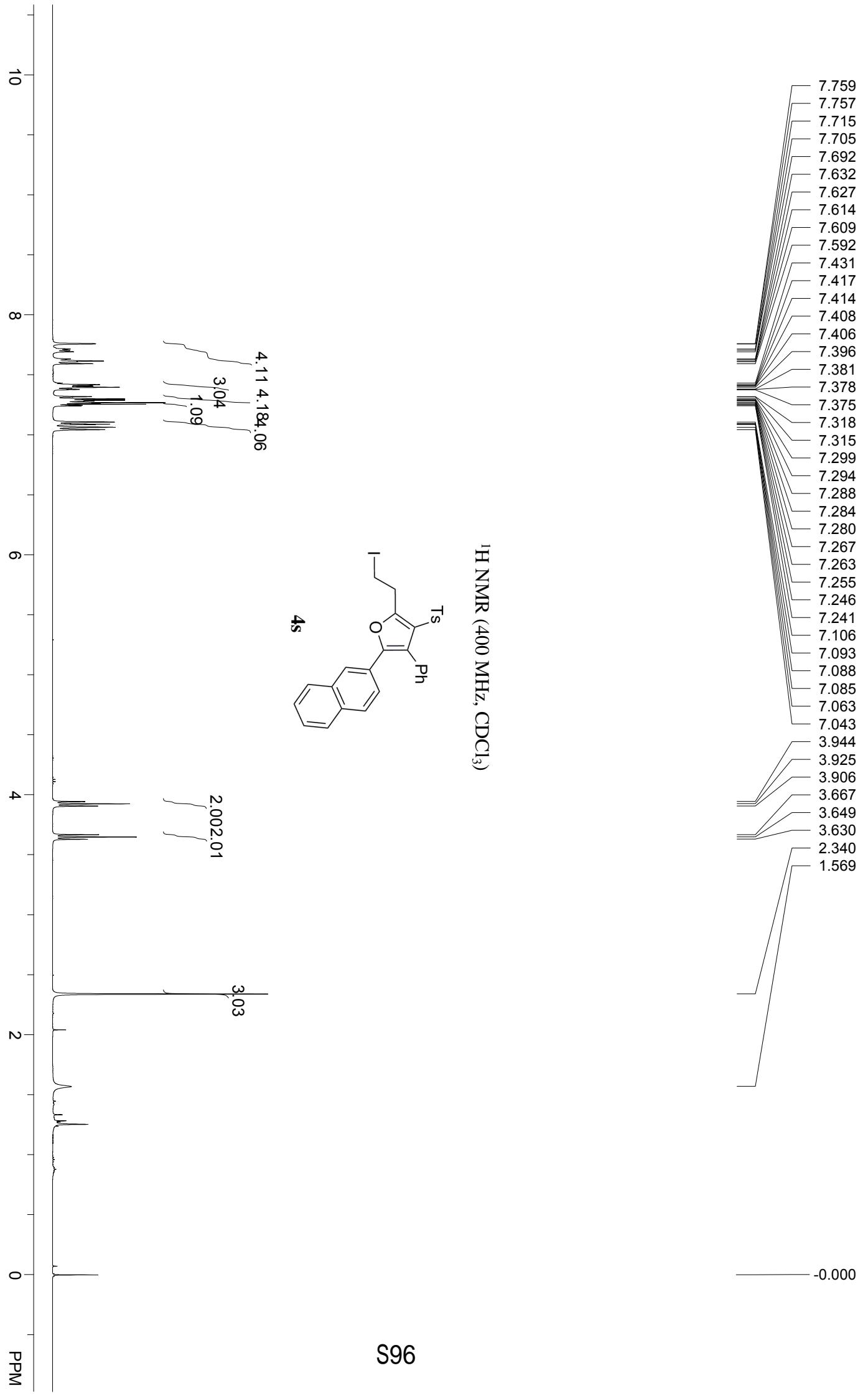


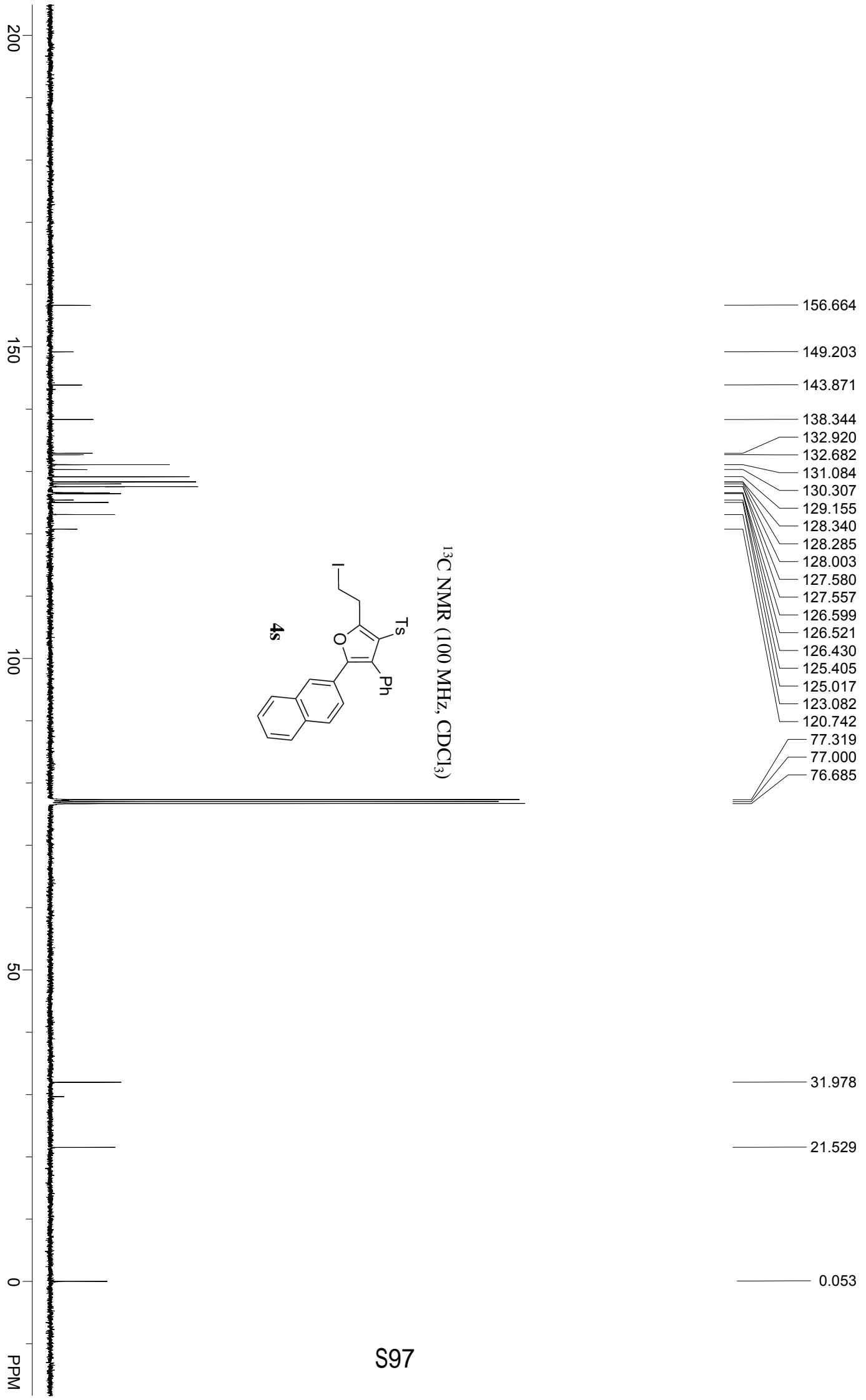


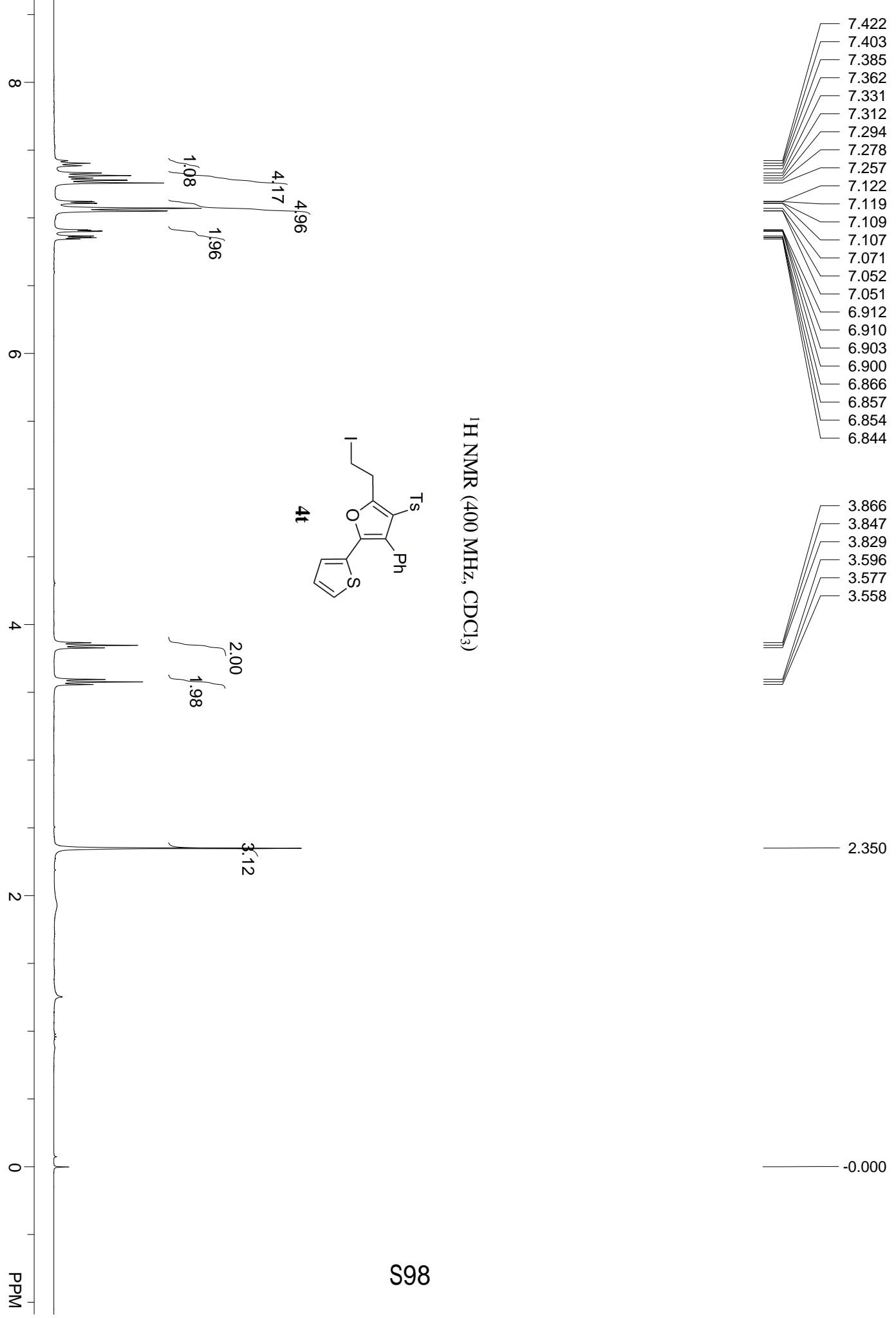




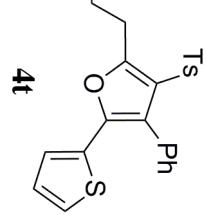








<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



200

150

100

50

0

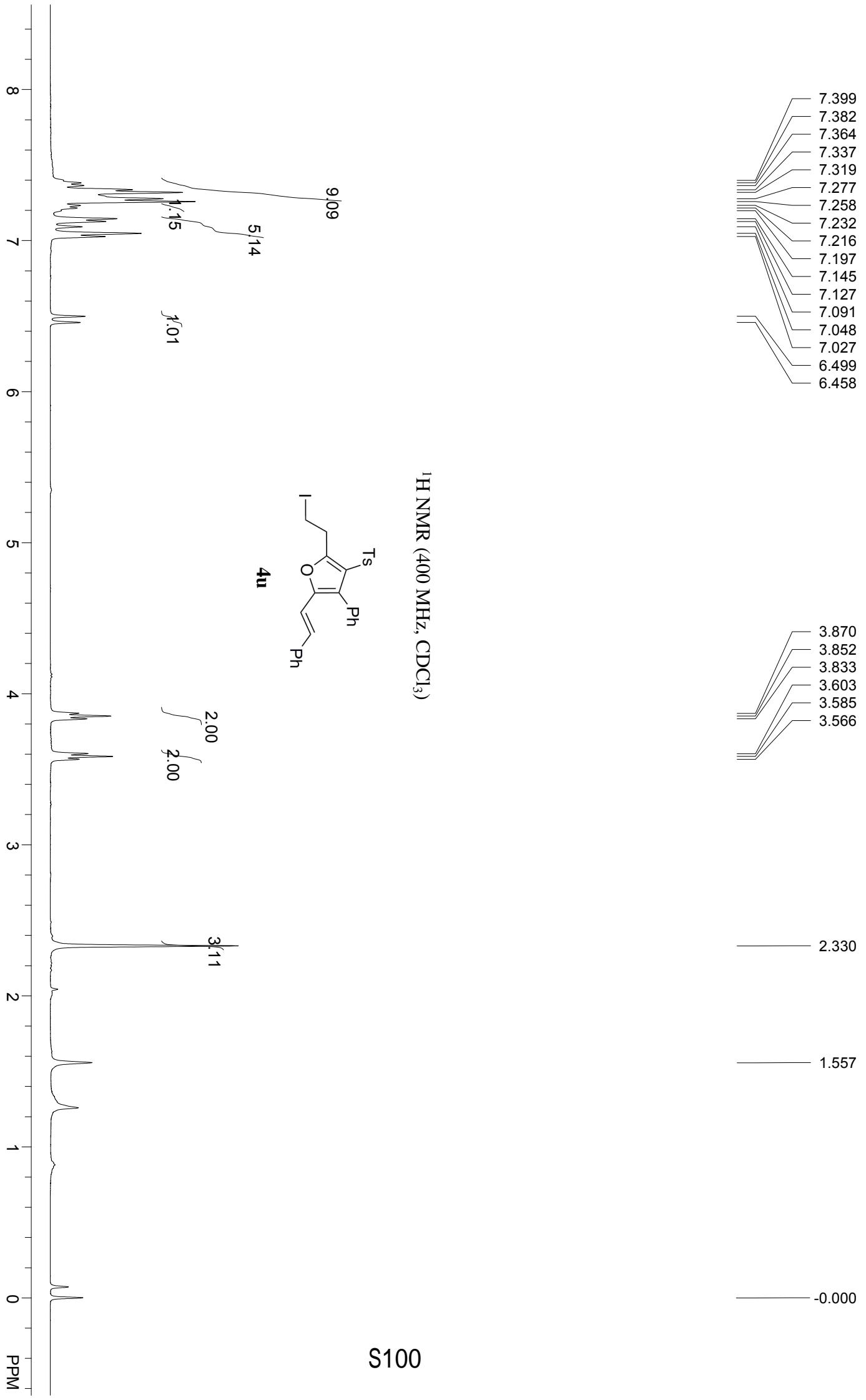
PPM

156.002
145.766
143.965
138.155
131.080
130.955
129.378
129.159
128.539
128.277
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127.135
125.694
125.222
124.679
119.101
77.319
77.000
76.681

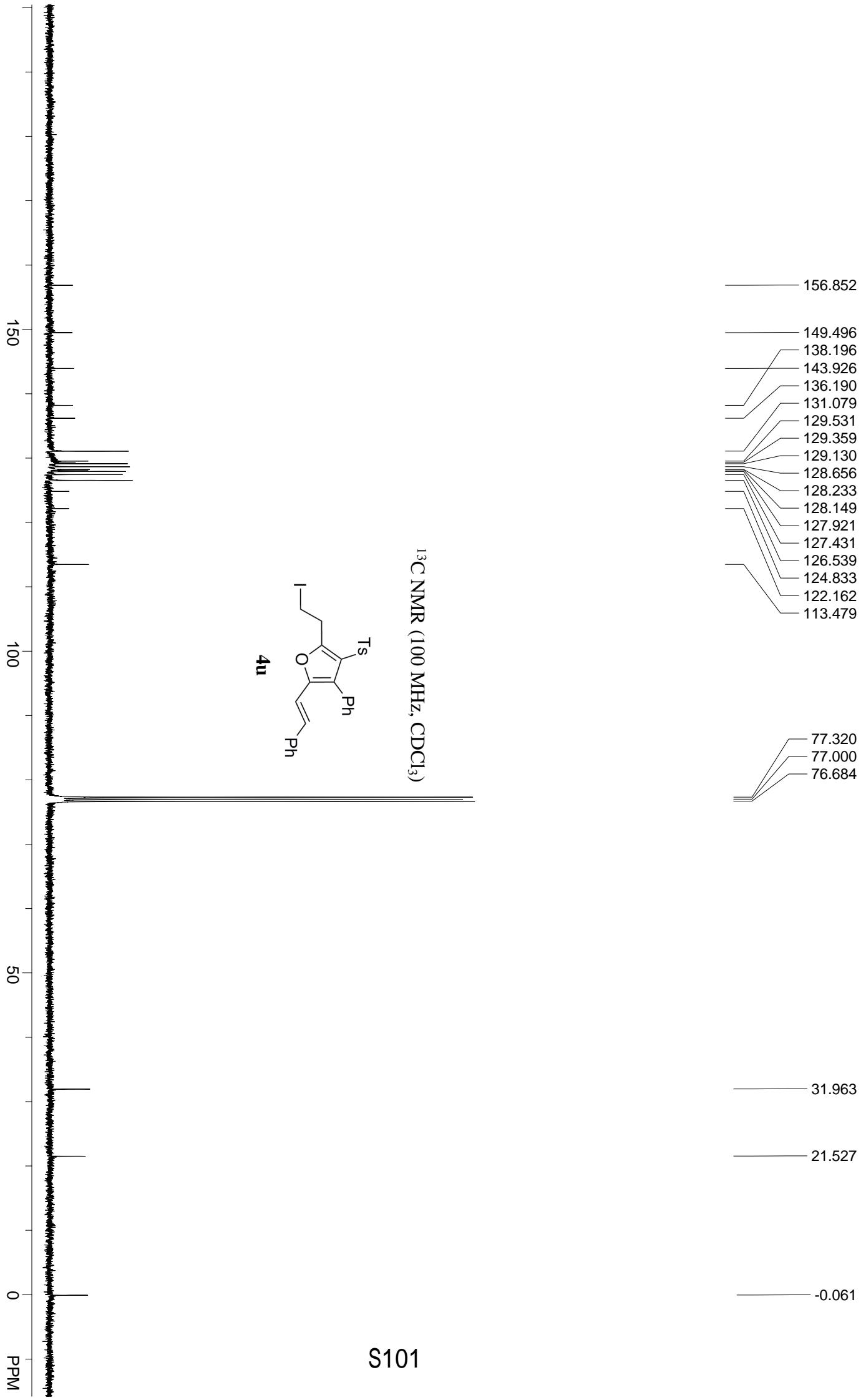
31.739

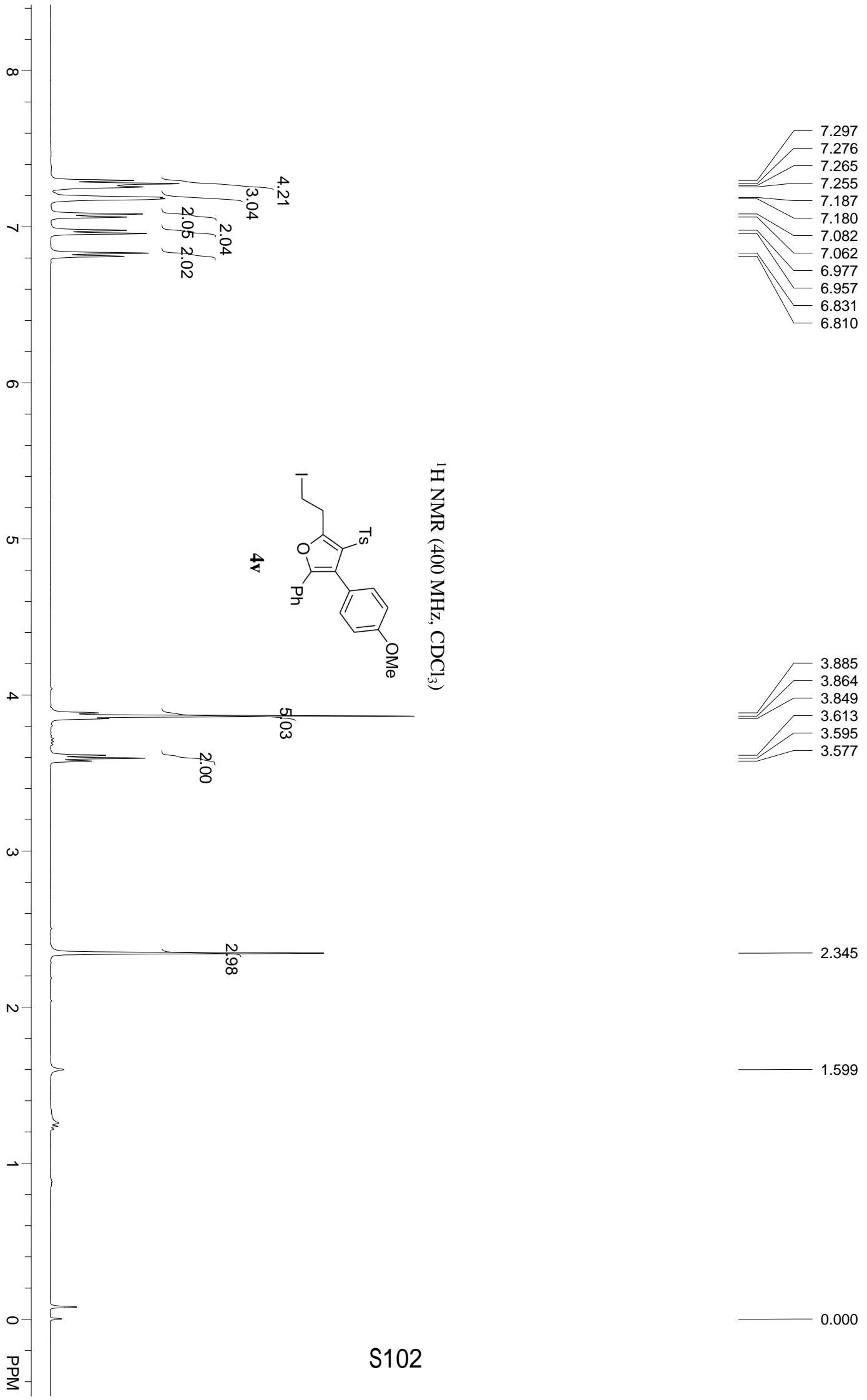
21.531

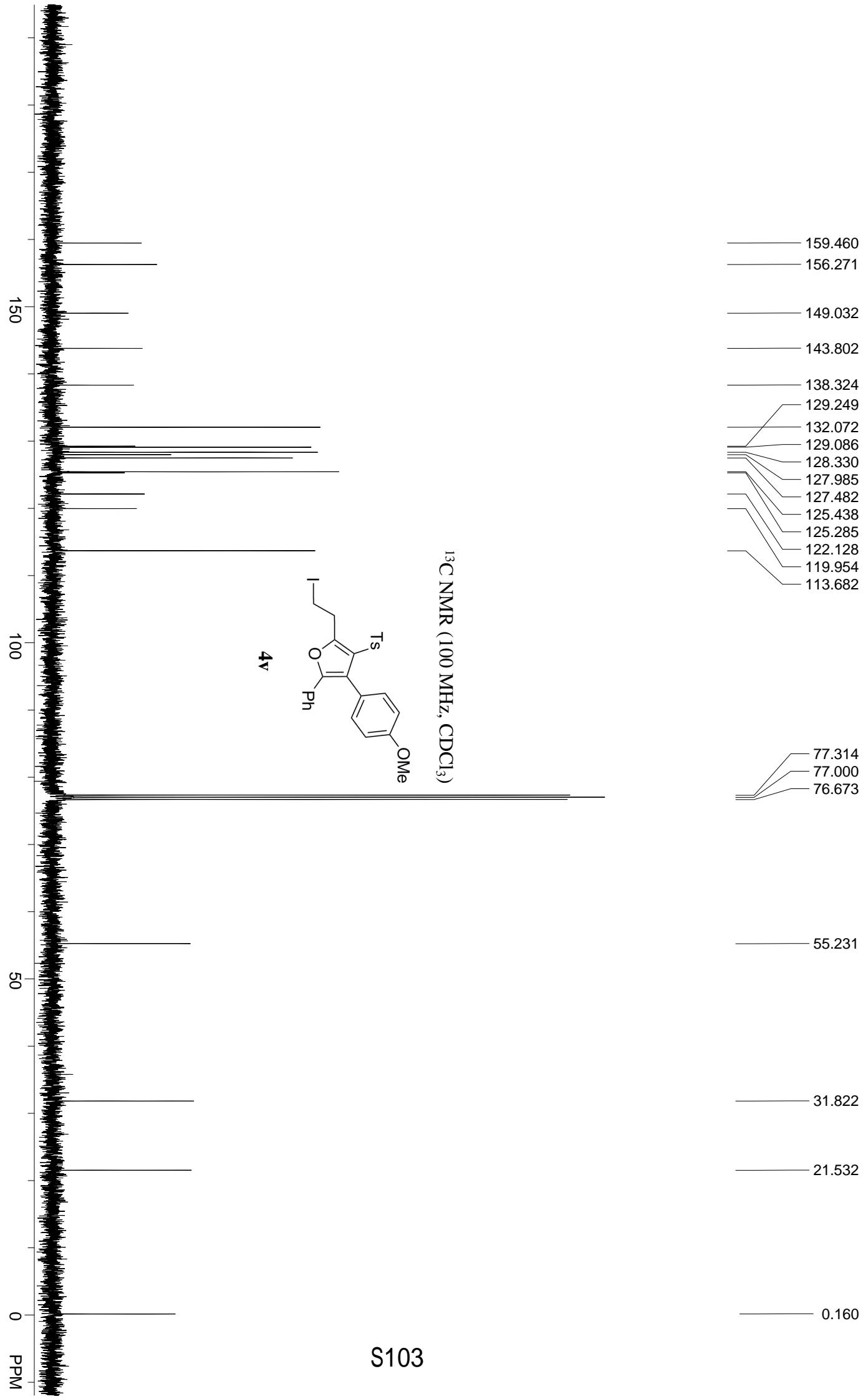
-0.075



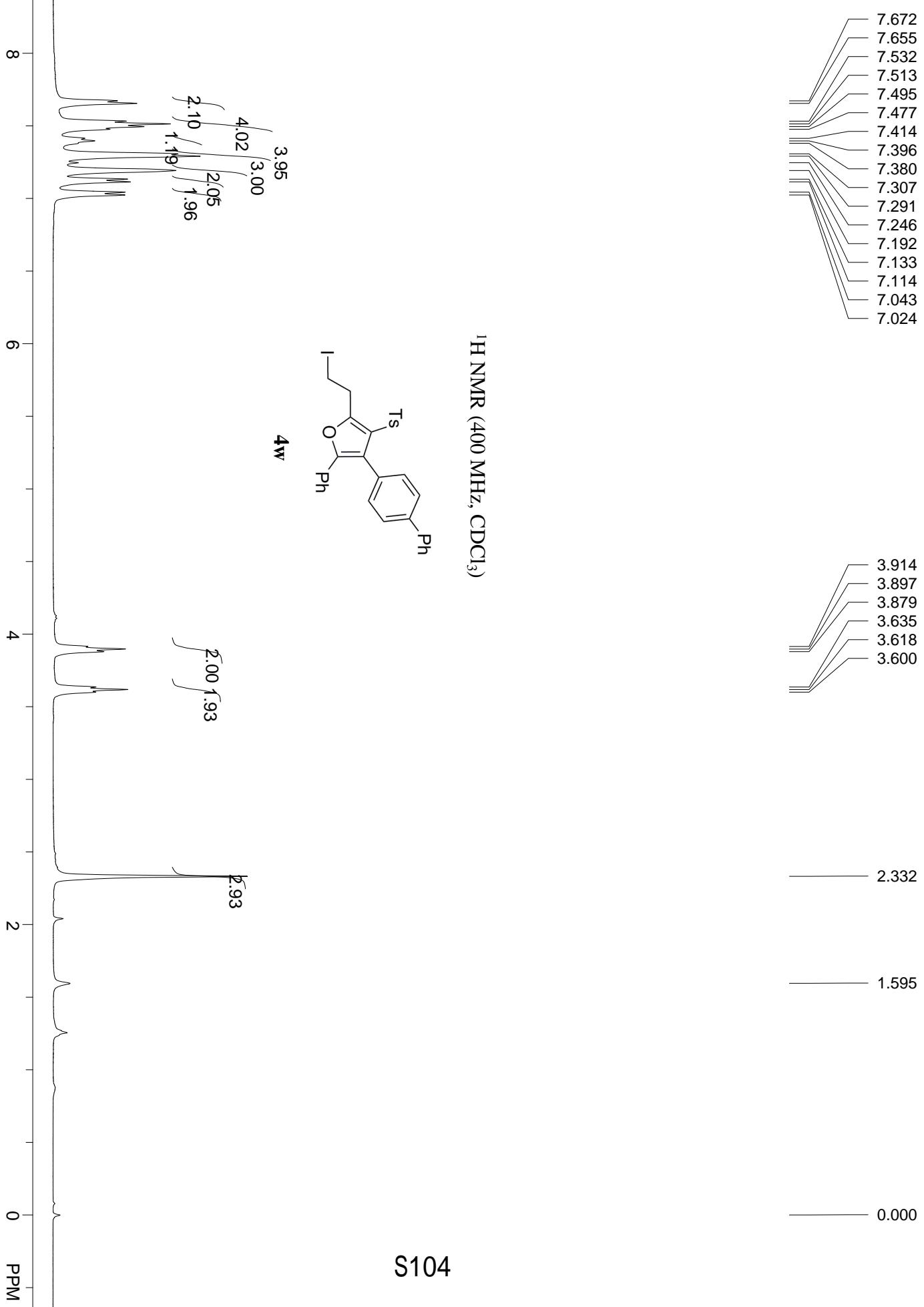
S100

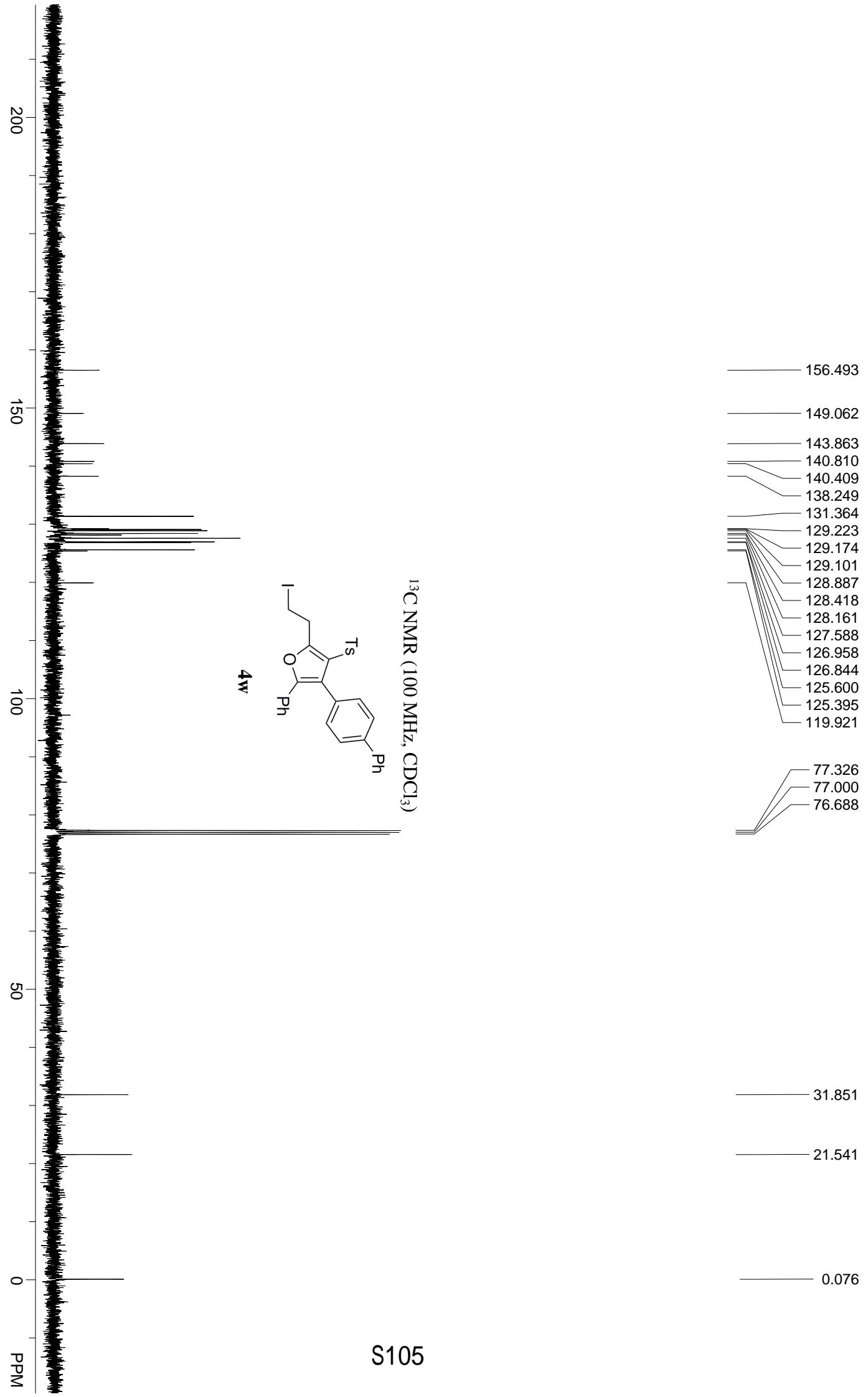






<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

