Supporting Information

"Push Effect" of Sulfur Coordination: Promoting the Breaking of C(sp^2)-I bonds by Pincer Thioimido-Pd(II) Complexes

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Experiment Details

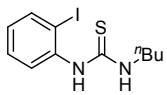
Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled prior to use. Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. N-(2-iodophenyl)ethanethioamide (**2d**),[1] N-(2-iodophenyl)-N-methylacetamide,[2] 2-iodo-4-methylaniline,[3] 4-chloro-2-iodoaniline,[3] 4-bromo-2-iodoaniline,[4] ethyl 4-amino-3-iodobenzoate[5] were prepared according to the previously reported methods.

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel or neutral alumina with 200-300 mesh in petroleum (boiling point is between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios.

^{1}H and ^{13}C NMR data were recorded with a Varian Mercury VX300 (300 MHz) spectrometer or a Varian Mercury VX600 (600 MHz). All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) relative to the internal standard or external standard. Coupling constants are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion (M^{+}). For the ReactIR kinetic experiments, the reaction spectra were recorded using a ReactIR 4000 fitted with a diamond-tipped probe. Data manipulation was carried out using the iC IR software, version 1. 05.

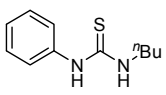
1. Synthesis of substrates

1.1 2a (1-butyl-3-(2-iodophenyl)thiourea)[6]



To a MeOH solution (5 mL) of 2-iodoaniline (2.19 g, 10 mmol) in round-bottom flask was added 1-isothiocyanatobutane (1.152g, 10 mmol). The reaction mixture was heated at 60 ºC for 15 h. White precipitate appeared and the reaction system became cloudy. The solid was filtered and washed with a mixture of petroleum ether and ethyl acetate (5/1) to furnish the product as white solid. (1.492g, yield: 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 7.8 Hz, 1 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.05 (t, J = 8.2 Hz, 1 H), 5.74 (br, 1 H), 3.52-3.70 (m, 2 H), 1.64-1.48 (m, 2 H), 1.42-1.22 (m, 2H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 180.14, 139.98, 138.16, 129.34, 129.00, 127.70, 97.82, 45.01, 30.78, 19.88, 13.60;

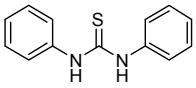
1.2 2b (1-butyl-3-(2-iodophenyl)thiourea)[7]



2b was synthesized following procedure similar to **1.1** from aniline (275.6 mg, 3 mmol) and 1-isothiocyanatobutane (345 mg, 3 mmol). Product, white solid. (547 mg, yield: 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (m, 1 H), 7.43 (t, J = 7.4 Hz, 2 H), 7.30 (d, J = 6.9 Hz, 1 H), 7.22 (d, J = 7.5 Hz, 2 H), 6.16-5.98 (br, 1 H), 3.70-3.54 (m , 2 H), 1.63-1.47 (m, 2H), 1.41-1.22 (m, 2H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 180.18,

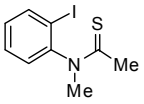
136.12, 130.06, 127.02, 125.05, 45.14, 30.93, 19.98, 13.67;

1.3 2c (1,3-diphenylthiourea)[8]



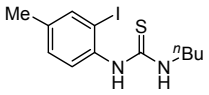
2c was synthesized following procedure similar to **1.1** from aniline (0.93 g, 10 mmol) and isothiocyanatobenzene (1.50 g, 11.1 mmol). Product, white solid. (2.216 g, yield: 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (br, 2 H), 7.46-7.34 (m, 8 H), 7.32-7.25 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 179.69, 137.04, 129.49, 126.98, 125.22;

1.4 2e (N-(2-iodophenyl)-N-methylethanethioamide)[1]



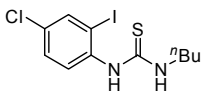
A mixture of N-(2-iodophenyl)-N-methylacetamide[2] (575.7 mg, 2 mmol) and Lawesson's reagent (499.2 mg, 1.23 mmol) in toluene was refluxed for 5 h. The solution was evaporated to dryness and purified by column chromatography (neutral alumina; 10% ethyl acetate in petroleum ether). The product was isolated as yellow solid (516 mg, yield: 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, J = 7.8 Hz, 1 H), 7.47 (t, J = 7.8 Hz, 1 H), 7.26 (t, J = 7.8 Hz, 1 H), 7.13 (t, J = 7.8 Hz, 1 H), 3.64 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 201.62, 148.04, 140.16, 130.12, 129.92, 126.70, 95.93, 44.01, 33.67;

1.5 2f (1-butyl-3-(2-iodo-4-methylphenyl)thiourea)



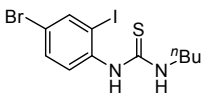
2f was synthesized following procedure similar to **1.1** from 2-iodo-4-methylaniline[3] (4.66 g, 20 mmol) and 1-isothiocyanatobutane (2.3 g, 20 mmol). Product, grey solid. (4.29 g, yield: 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1 H), 7.34 (br, 1 H), 7.26-7.15 (m, 2 H), 5.63 (br, 1 H), 3.68-3.55 (m, 2H), 2.35 (s , 3 H), 1.59-1.50 (m. 2 H), 1.38-1.29 (m, 2H), 0.92 (*t*, J = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 180.48, 140.52, 139.85, 135.43, 130.38, 127.55, 98.08, 45.14, 30.94, 20.46, 19.97, 13.68; HRMS (EI): *m/z* calcd. for $C_{12}H_{17}IN_2S$ (M^+): 348.0157; found: 348.0162.

1.6 2g (1-butyl-3-(4-chloro-2-iodophenyl)thiourea)



2g was synthesized following procedure similar to **1.1** from 4-chloro-2-iodoaniline[3] (3.80 g, 15 mmol) and 1-isothiocyanatobutane (1.72 g, 15 mmol). Product, purple solid. (2.89 g, yield: 52%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.98 (s, 1 H), 7.92 (br, 1 H), 7.85 (br, 1 H), 7.43 (br, 2 H), 3.56-3.37 (m, 2 H), 1.6-1.43 (m, 2 H), 1.38-1.22 (m, 2 H), 0.90 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 181.04, 140.01, 137.34, 130.70, 130.15, 128.22, 99.43, 43.64, 30.53, 19.47, 13.61; HRMS (EI): *m/z* calcd. for $C_{11}H_{14}ClIN_2S$ (M^+): 367.9611; found: 367.9614.

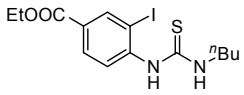
1.7 2h (1-butyl-3-(4-bromo-2-iodophenyl)thiourea)



2h was synthesized following procedure similar to **1.1** from 4-bromo-2-iodoaniline[4] (5.757 g, 19 mmol) and 1-isothiocyanatobutane (2.43

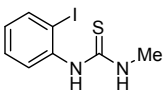
g, 21 mmol). Product, light purple solid. (1.60 g, yield: 20%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.96 (s, 1 H), 8.03 (d, J = 1.8 Hz, 1 H), 7.86 (br, 1 H), 7.56 (dd, J = 8.6 Hz, 1.8 Hz, 1 H), 7.37 (d, J = 7.8 Hz, 1 H), 3.54-3.37 (m, 2 H), 1.59-1.45 (m ,2 H), 1.39-1.23 (m , 2 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 180.96, 140.38, 140.06, 131.21, 130.62, 119.02, 100.06, 43.72, 30.58, 19.54, 13.70; HRMS (EI): *m/z* calcd. for $C_{11}H_{14}BrIN_2S$ (M^+): 411.9106; found: 411.9102.

1.8 2i (ethyl 4-(3-butylthioureido)-3-iodobenzoate)



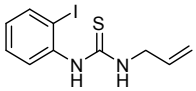
A THF solution (5 mL) of ethyl 4-amino-3-iodobenzoate[5] (1.169 g, 4 mmol) in schlenk tube was cooled to 0 ^{o}C under N_2 atmosphere. Then NaH (176 mg, 4.4 mmol) was added and the reaction mixture was stirred at 0 ^{o}C for 30 min. 1-isothiocyanatobutane (506.8 mg, 4.4 mmol) was added via syringe dropwise, and the reaction mixture was allowed to gradually come to room temperature under stirring. The reaction was tested with TLC and quenched with NH_4Cl (aqueous solution) after ethyl 4-amino-3-iodobenzoate disappeared. The resulted yellow solution was extracted with ether (10 mL * 3) and the organic phase was combined and dried over Na_2SO_4. After filtration, the filtrate was concentrated and washed with a mixture of petroleum ether and ethyl acetate (5/1) to furnish the product as white solid. (666.2 g, yield: 41%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.55 (s, 1 H), 8.06 (d, J = 8.4 Hz, 1 H), 7.66-7.52 (m, 1 H), 7.47 (br, 1 H), 4.34 (t, J = 7.2 Hz, 2 H), 3.78-3.52 (m, 2 H), 1.66-1.56 (m, 2 H), 1.52-1.30 (m, 5 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 180.23, 164.28, 142.19, 141.43, 130.69, 129.65, 124.52, 94.45, 61.57, 45.45, 30.83, 20.13, 14.33, 13.76; HRMS (EI): *m/z* calcd. for $C_{14}H_{19}IN_2O_2S$ (M^+): 406.0212; found: 406.0204.

1.9 2j (1-(2-iodophenyl)-3-methylthiourea)[6]



2i was synthesized following procedure similar to **1.1** from 2-iodoaniline (876 mg, 4 mmol) and isothiocyanatomethane (319.9 mg, 4.4 mmol). Product, white solid. (960 mg, yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 1 H), 7.57 (br, 1 H), 7.48-7.32 (m, 2 H), 7.06 (t, J = 8.2 Hz, 1 H), 5.86 (br, 1 H), 3.14 (d, J = 4.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 181.50, 140.38, 138.09, 129.74, 129.30, 127.53, 97.72, 32.18;

1.10 2k (1-allyl-3-(2-iodophenyl)thiourea)[6]

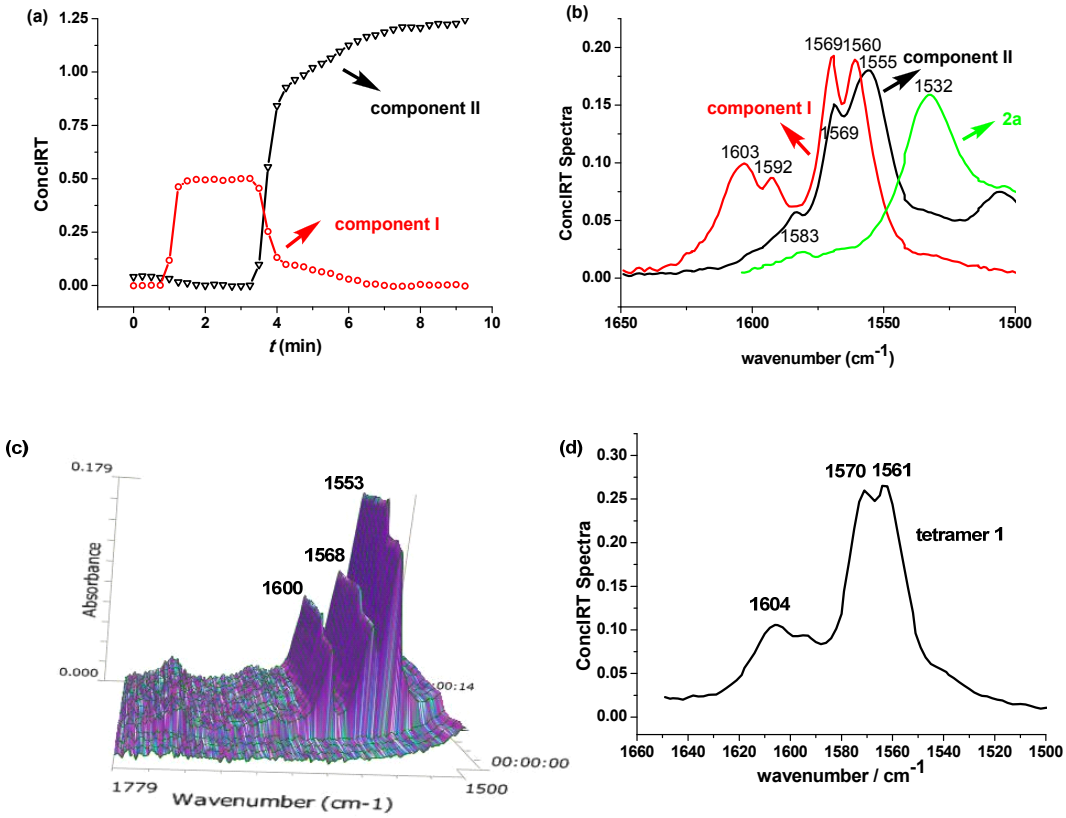


2k was synthesized following procedure similar to **1.1** from 2-iodoaniline (1.098 g, 5 mmol) and 3-isothiocyanatoprop-1-ene (565.3 mg, 5.7 mmol). Product, white solid. (1.0235 g, yield: 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1 H), 7.55 (br, 1 H), 7.44 (t, J = 7.2 Hz, 1 H), 7.42-7.32 (br, 1 H), 7.07 (t, J = 7.8 Hz, 1 H), 5.96-5.85 (m, 1 H), 5.80 (br, 1 H), 5.32-5.06 (m ,2 H), 4.29 (br, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.59, 140.13, 138.06, 132.99, 129.55, 129.28, 127.84, 117.17, 97.91, 47.58;

2. Stoichiometric reaction of complex 1 with different substrates

2.1 Stoichiometric reaction of complex 1 with 2a monitored by ReactIR

The spectra were acquired in 8 scans at a gain of one using system ReactIR 3.0 software. The reaction was carried out as follows: To a three necked reaction vessel fitted with a magnetic stirring bar was added **1** (82.6 mg, 0.2 mmol). Then the IR probe was inserted through an adapter into the middle neck; the other two necks were capped by rubber septums. The reaction vessel was charged with 0.8 mL THF, when the data collection was started. The resulted mixture was stirred at 16 ^{o}C for 3 min, then **2a** (70.2 mg, 0.21 mmol) was added to initiate the reaction, and the data collection was continued until the reaction was finished.



***S Figure 1* (a).** Reaction of **1** (82.6 mg, 0.2 mmol) with **2a** (70.2 mg, 0.21 mmol) in THF at 16 ^{o}C monitored by ReactIR. Component **I**: tetramer **1**. Component **II**: **3a**. **(b).** The ConcIRT spectrum of component **I**, **II** and **2a. (c).** The characteristic peaks of **4a**. **(d).** The ConcIRT spectrum of tetramer **1**.

2.2 stoichiometric reactions monitored by ^{1}HNMR

- **Complex 1** and **2a**

1 (5.2 mg, 0.012 mmol) and **2a** (4.2 mg, 0.012 mmol) was put into NMR tube, followed by addition of 0.4 mL CD_2Cl_2. A clear orange solution was gained. Then sample was characterized by ^{13}H NMR. Disappearance of the two characteristic peaks of complex **1** at 3.92-3.79 ppm and 3.36-3.28 ppm and appearance of the peak at 3.58 ppm indicated the dissociation of tetramer **1** by compound **2a**.

- **Complex 1** and **2b**

1 (5.2 mg, 0.012 mmol) and **2b** (2.6 mg, 0.012 mmol) was put into NMR tube, followed by addition of 0.4 mL CD_2Cl_2. A clear orange solution was gained. Then sample was characterized by ^{13}H NMR. Disappearance of the two characteristic peaks of complex **1** at 3.92-3.79 ppm and 3.36-3.28 ppm and appearance of the peak at 3.58 ppm indicated the dissociation of tetramer **1** by compound **2b**.

- **Complex 1** and **2c**

1 (5.2 mg, 0.012 mmol) and **2c** (2.8 mg, 0.012 mmol) was put into NMR tube, followed by addition of 0.4 mL CD_2Cl_2. A clear orange solution was gained. Then sample was characterized by ^{13}H NMR. Disappearance of the two characteristic peaks of complex **1** at 3.92-3.79 ppm and 3.36-3.28 ppm and appearance of the peak at 3.58 ppm indicated the dissociation of tetramer **1** by compound **2c**.

- **Complex 1** and **2e**

1 (5.2 mg, 0.012 mmol) and **2e** (3.5 mg, 0.012 mmol) was put into NMR tube, followed by addition of 0.4 mL $CDCl_3$. A clear orange solution was gained. Then sample was characterized by ^{13}H NMR. Partial disappearance of the two characteristic peaks of complex **1** at 3.92-3.79 ppm and 3.36-3.28 ppm and appearance of the peak at 3.70 ppm indicated the partial dissociation of tetramer **1** by compound **2e**.

2.3 Representative procedure for stoichiometric reactions of complex 1 with different substrates at high temperatures

- **Complex 1** and **2a**

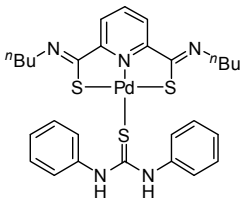
A mixture of complex **1** (10.3 mg, 0.025 mmol) and **2a** (8.4 mg, 0.025 mmol) in DME was stirred at room temperature for 5 min to prepare complex **3a** in situ. The reaction system was then heated at 70 ^oC for 2 h. The initial orange solution was changed to dark red cloudy mixture. The mixture was evaporated to dryness and washed with ether (1 mL * 5). The brown residue was dried under vacuum to furnish complex **5**. (10.4 mg, yield: 77%). The ether solution was concentrated and the yield of **4a** was determined to be 95% by ^1H NMR with CH_2Br_2 as the internal standard.

- **Complex 1** and **2d**

The stoichiometric reaction of complex **1** and **2d** was carried out following procedure similar to that of complex **1** and **2a**, and 87% of **5** and 80% of **4d** were gained. **4d**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 1 H), 7.44 (t, J = 7.8 Hz, 1 H), 7.34 (t, J = 7.5 Hz, 1 H), 2.83(s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 166.75, 153.36, 135.60, 125.81, , 124.61, 122.32, 121.28, 19.99.

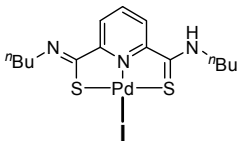
2.4 Preparation of single crystals

2.4.1 Synthesis of 3c

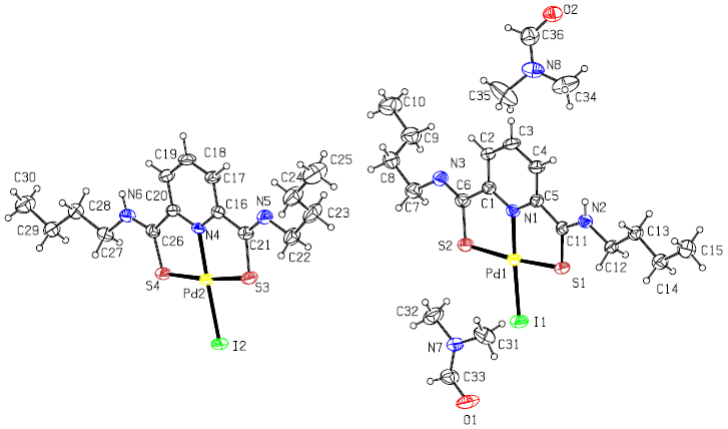


1 (10.3 mg, 0.025 mmol) and **2c** (5.7 mg, 0.025 mmol) was put into a round-bottom flask, followed by addition of 0.5 mL THF. A clear orange solution was gained. The reaction mixture was stirred at room temperature for 10 min, and then was evaporated to dryness. Re-crystallization from DMF / CH_3OH gave red block crystals of **3c** suitable for X-ray diffraction.

2.4.2 Synthesis of 5



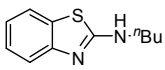
The brown residue gained from the stoichiometric reaction of **1** and **2a** in section **2.3** was recrystalized from DMF / CH_3OH to give orange block crystals of **5** suitable for X-ray diffraction and the structure was as follows.



S Figure 2 The single crystal structure of complex **5**.

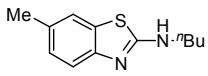
2.5 Representative procedure for complex 1 catalyzed reactions to afford thiazoles

2.5.1 Reaction of 2a to afford 4a (N-butylbenzo[d]thiazol-2-amine)[9]



Complex **1** (1.0 mg, 0.5 mol %), **2a** (167.1 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) were added to a test tube, followed by addition of DME (3 mL). The reaction system was then heated at 80 ^oC for 10 h till **2a** disappeared as tested by TLC. The reaction system changed from a clear orange solution to red cloudy mixture. Water (5 mL) was added and the system was extracted with ether (5 mL * 5). The combined organic phase was dried over Na_2SO_4 and filtered. The filtrate was evaporated to dryness and purified by silica gel column chromatography (20% ethyl acetate in petroleum ether). The product **4a**[9] was isolated as white solid (98.1 mg, yield: 95%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 7.5 Hz, 1 H), 7.50 (d, J = 8.1 Hz, 1 H), 7.27 (t, J = 7.8 Hz, 1 H), 7.05 (t, J = 7.5 Hz, 1 H), 6.89 (br, 1 H), 3.38 (t, J = 6.9 Hz, 2 H), 1.74-1.58 (m, 2 H), 1.51-1.32 (m, 2 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 168.38, 152.38, 130.11, 125.81, 121.08, 120.72, 118.30, 45.49, 31.55, 20.00, 13.68;

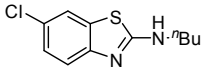
2.5.2 Reaction of 2f to afford 4f (N-butyl-6-methylbenzo[d]thiazol-2-amine)



The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2f** (174.1 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME (3 mL) at 80 ^oC. Purification by silica gel column chromatography

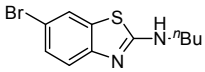
(20% ethyl acetate in petroleum ether) furnished the product **4f** as white solid (104.7 mg, yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.33 (m, 2 H), 7.08 (d, *J* = 8.1 Hz, 1 H), 6.39 (br, 1 H), 3.36 (t, *J* = 7.0 Hz, 2 H), 2.38 (s, 3 H), 1.75-1.57 (m, 2 H), 1.51-1.32 (m, 2 H), 0.93 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.46, 150.15, 130.84, 130.18, 126.95, 120.79, 118.03, 45.39, 31.58, 21.15, 19.99, 13.71; HRMS (EI): *m/z* calcd. for $C_{12}H_{16}N_2S$ (M^+): 220.1034; found: 220.1035.

2.5.3 Reaction of 2g to afford 4g (N-butyl-6-chlorobenzo[d]thiazol-2-amine)



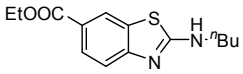
The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2g** (184.3 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME at 80 °C. Purification by silica gel column chromatography (15% ethyl acetate in petroleum ether) furnished the product **4g** as white solid (115.3 mg, yield: 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.8 Hz, 1 H), 7.40 (d, *J* = 8.7 Hz, 1 H), 7.24 (dd, *J* = 8.7 Hz, 1.8 Hz, 1 H), 5.83 (br, 1 H), 3.39 (t, *J* = 7.0 Hz, 2 H), 1.77-1.59 (m, 2 H), 1.52-1.35 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.14, 151.05, 131.40, 126.29, 120.42, 119.06, 45.46, 31.51, 19.98, 13.66; HRMS (EI): *m/z* calcd. for $C_{11}H_{13}ClN_2S$ (M^+): 240.0488; found: 240.0491.

2.5.4 Reaction of 2h to afford 4h (6-bromo-N-butylbenzo[d]thiazol-2-amine)



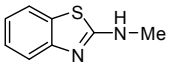
The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2h** (206.6 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME at 80 °C. Purification by silica gel column chromatography (10% ethyl acetate in petroleum ether) furnished the product **4h** as white solid (125.3 mg, yield: 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.8 Hz, 1 H), 7.36 (dd, *J* = 8.4 Hz, 1.8 Hz, 1 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 6.69 (br, 1 H), 3.35 (t, *J* = 7.2 Hz, 2 H), 1.70-1.61 (m, 2 H), 1.46-1.35 (m, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.37, 151.29, 131.74, 128.99, 123.17, 119.35, 113.33, 45.49, 31.42, 19.96, 13.68; HRMS (EI): *m/z* calcd. for $C_{11}H_{13}BrN_2S$ (M^+): 283.9983; found: 283.9986.

2.5.5 Reaction of 2i to afford 4i (ethyl 2-(butylamino)benzo[d]thiazole-6-carboxylate)



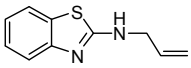
The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2i** (203.1 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME at 80 °C. Purification by silica gel column chromatography (15% ethyl acetate in petroleum ether) furnished the product **4i** as white solid (133.3 mg, yield: 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 8.00 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 6.95 (br, 1 H), 4.38 (q, *J* = 7.0 Hz, 2 H), 3.42 (t, *J* = 6.9 Hz, 2 H), 1.74-1.63 (m, 2 H), 1.49-1.34 (m, 5 H), 0.94 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.78, 166.38, 156.03, 129.81, 127.67, 122.82, 122.60, 117.19, 60.64, 45.49, 31.25, 19.88, 14.20, 13.52; HRMS (EI): *m/z* calcd. for $C_{14}H_{18}N_2O_2S$ (M^+): 278.1089; found: 278.1091.

2.5.6 Reaction of 2j to afford 4j (N-methylbenzo[d]thiazol-2-amine)[10]



The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2j** (146.1 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME at 80 ^oC. Purification by silica gel column chromatography (10% ethyl acetate in petroleum ether) furnished the product **4j**[10] as white solid (76.7 mg, yield: 93%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.18 (br, 1 H), 7.06 (t, *J* = 7.8 Hz, 1 H), 3.06 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.22, 152.29, 130.07, 125.86, 121.07, 120.80, 118.22, 31.58;

2.5.7 Reaction of 2k to afford 4k (N-allylbenzo[d]thiazol-2-amine)



The reaction was carried out following procedure similar to **2.5.1** with Complex **1** (1.0 mg, 0.5 mol %), **2k** (159.1 mg, 0.5 mmol) and NMe_4OAc (133.2 mg, 1 mmol) in DME at 80 ^oC. Purification by silica gel column chromatography (10% ethyl acetate in petroleum ether) furnished the product **4k** as white solid (86.8 mg, yield: 91%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 7.22-7.10 (br, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.09-5.86 (m, 1 H), 5.35 (d, *J* = 17.1 Hz, 1 H), 5.21 (d, *J* = 10.2 Hz, 1 H), 4.03 (d, *J* = 4.5 Hz, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.20, 152.09, 133.46, 130.12, 125.84, 121.31, 120.77, 118.50, 117.16, 47.86; HRMS (EI): *m/z* calcd. for $C_{10}H_{10}N_2S$ (M^+): 190.0565; found: 190.0566.

Reference:

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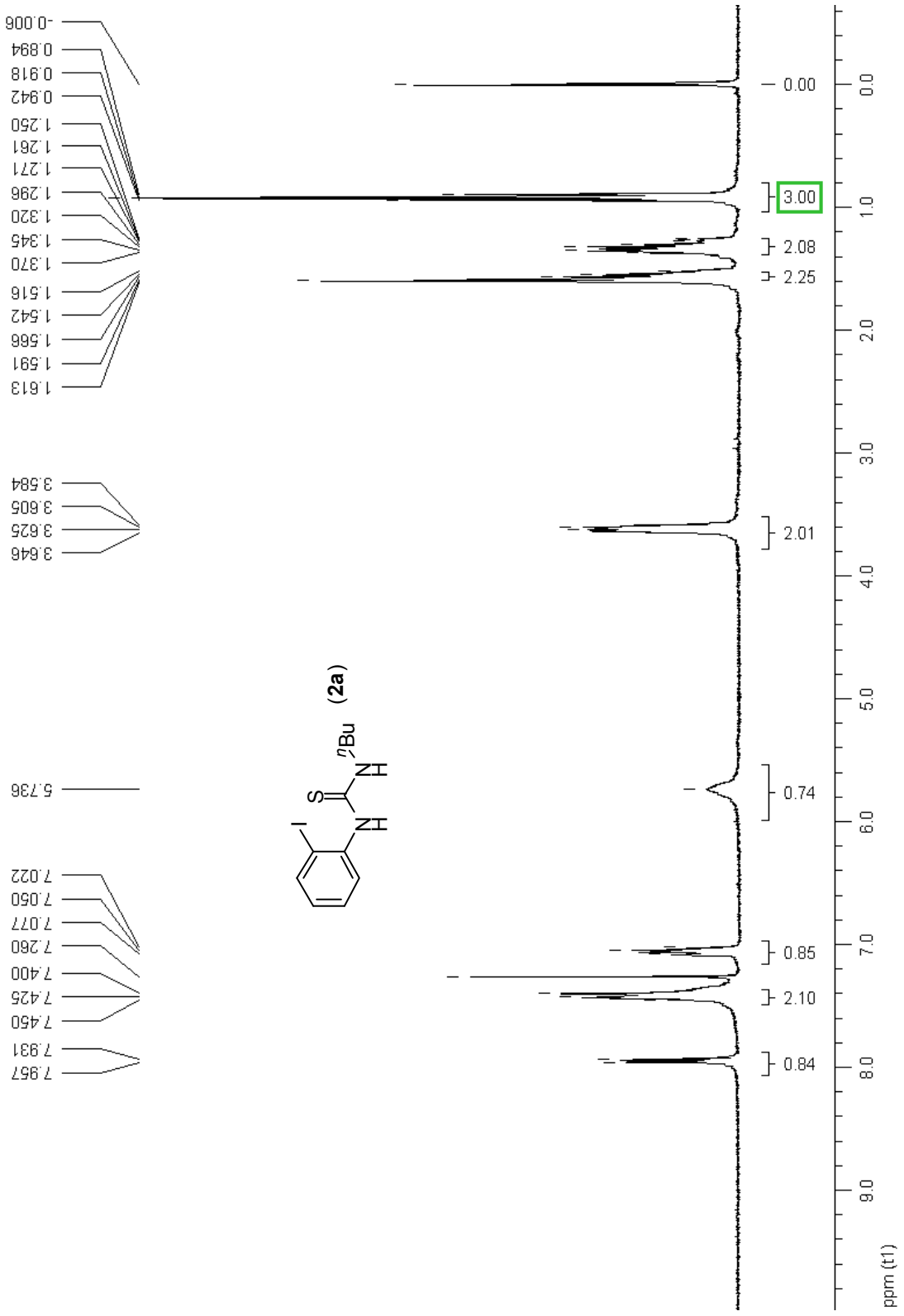

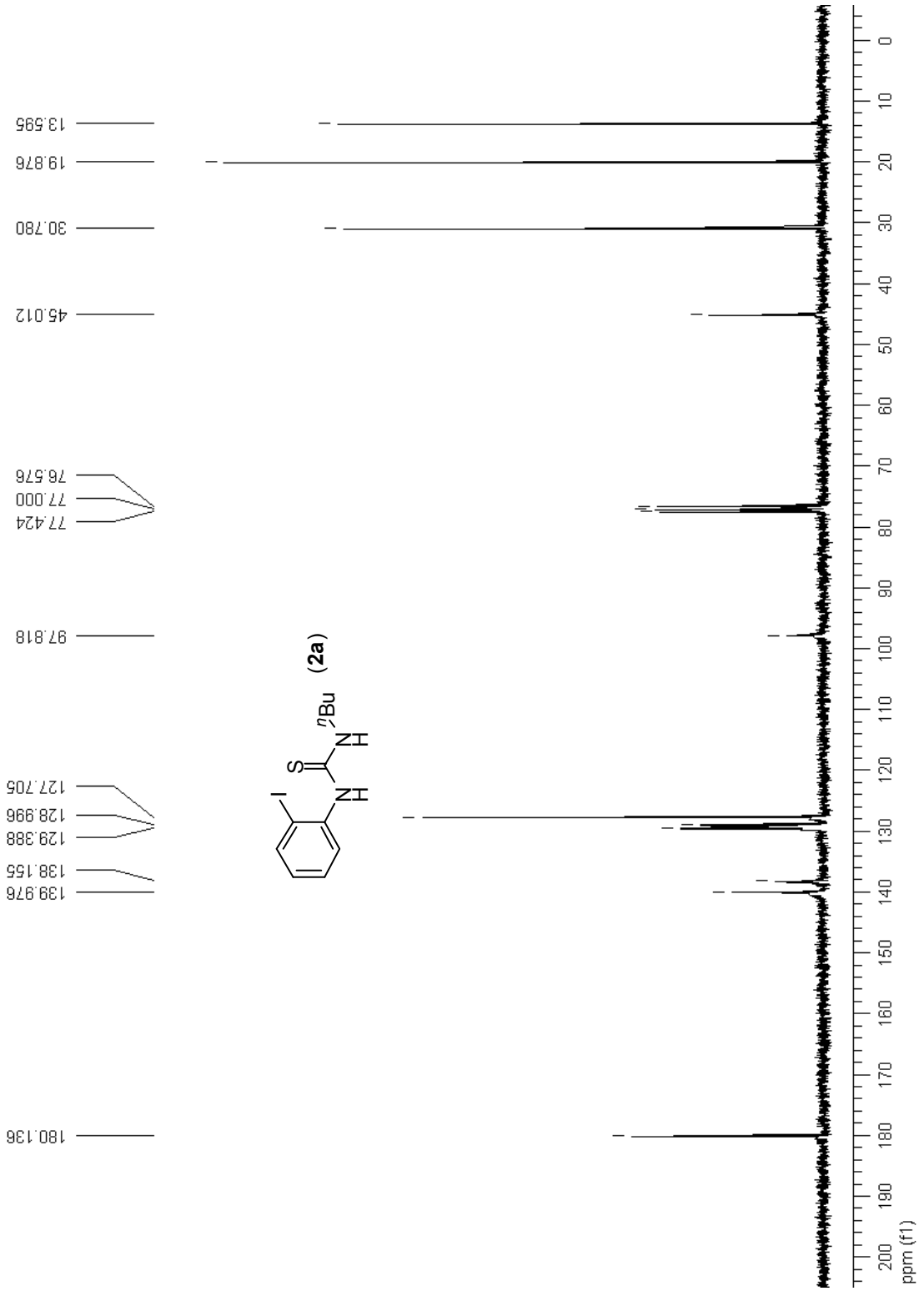
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77.000
77.424
97.818
127.705
128.996
129.388
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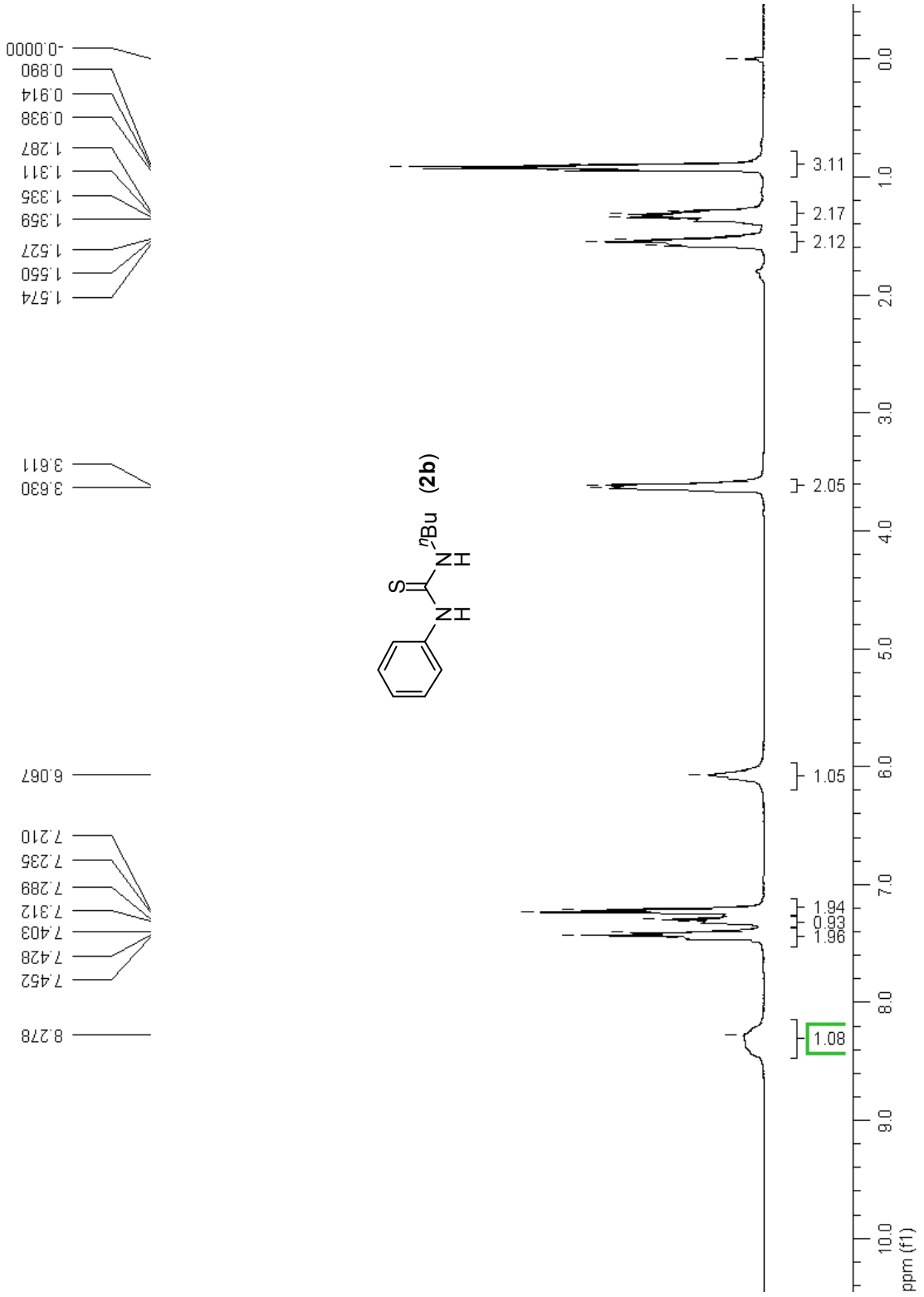
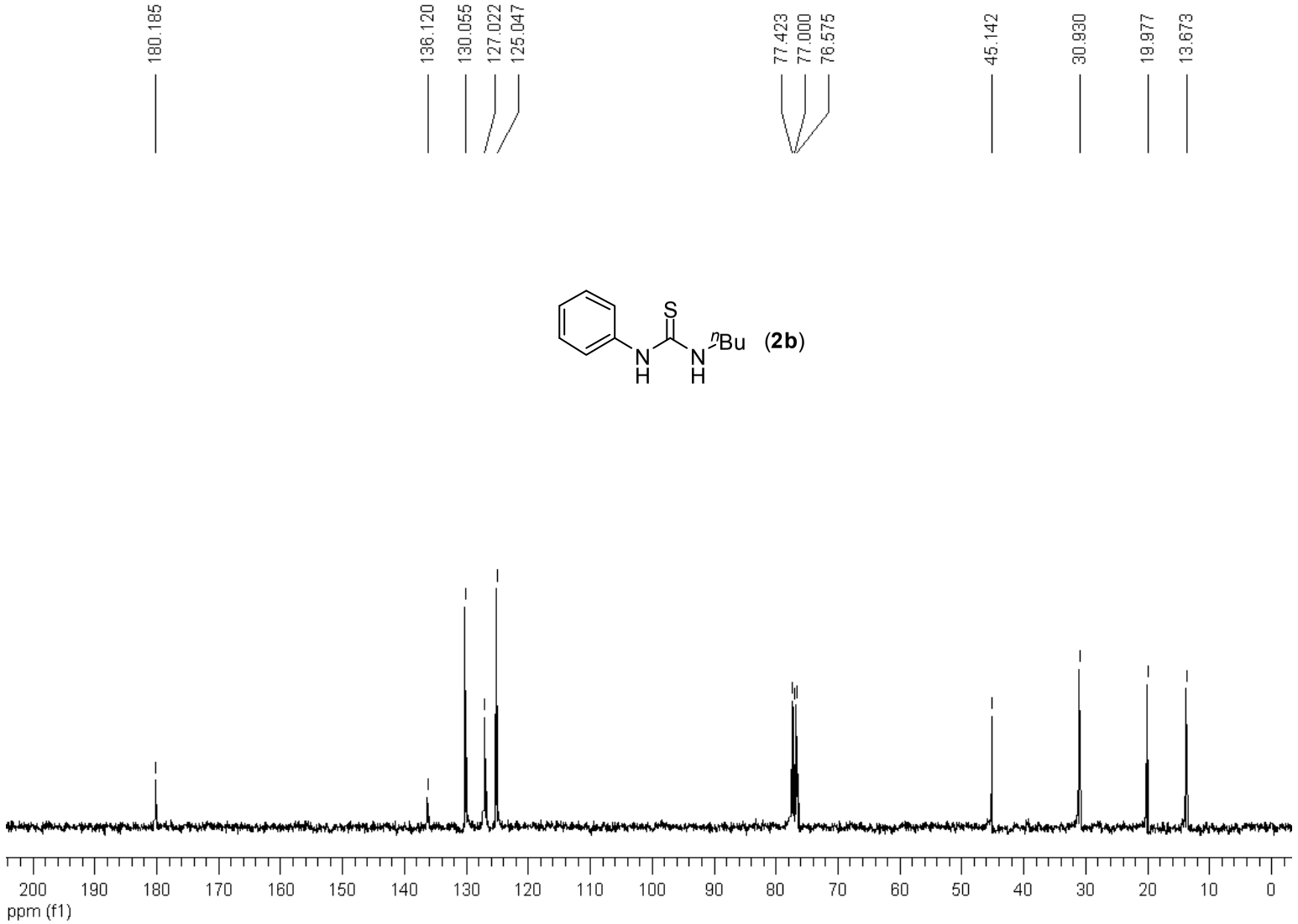
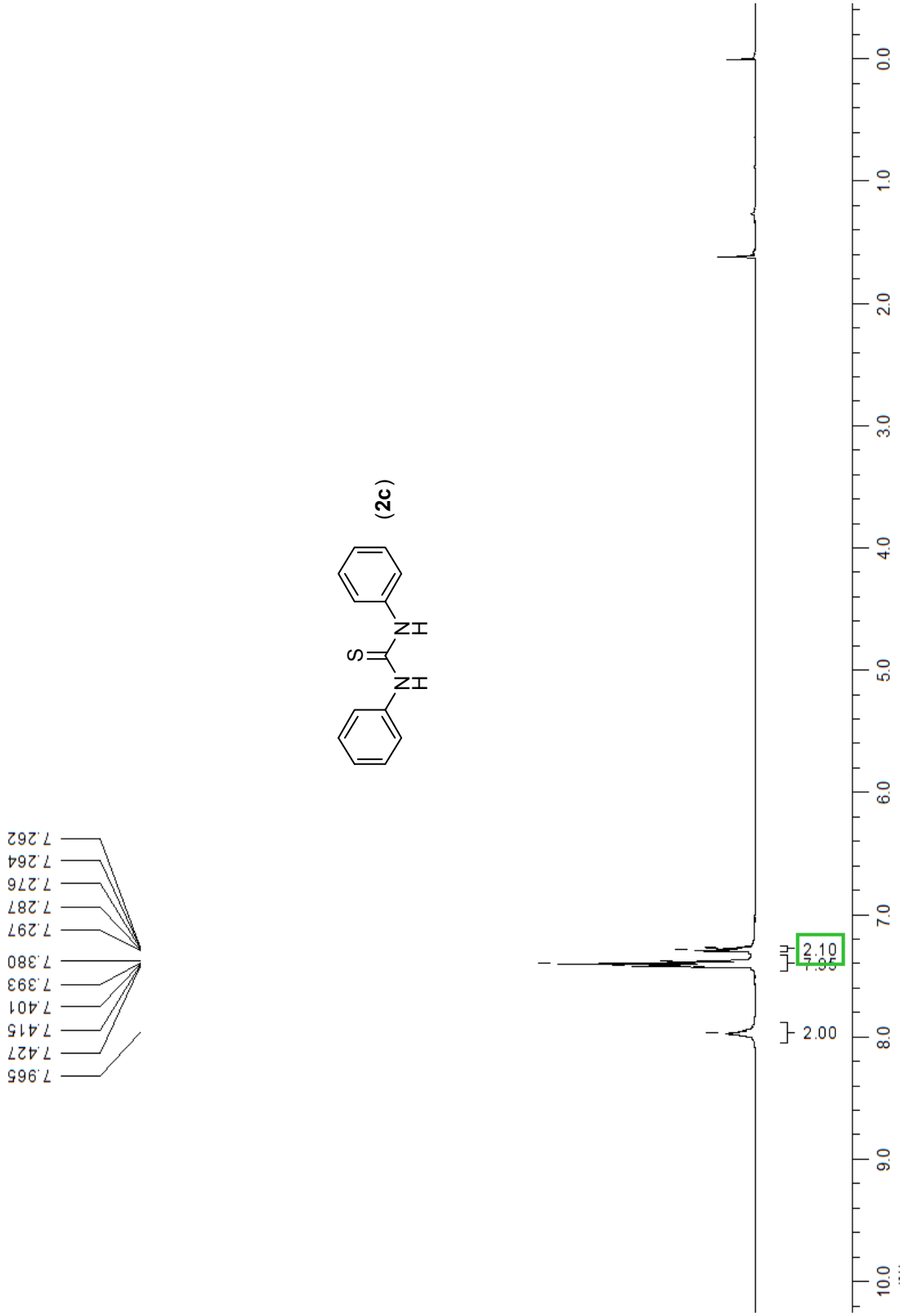
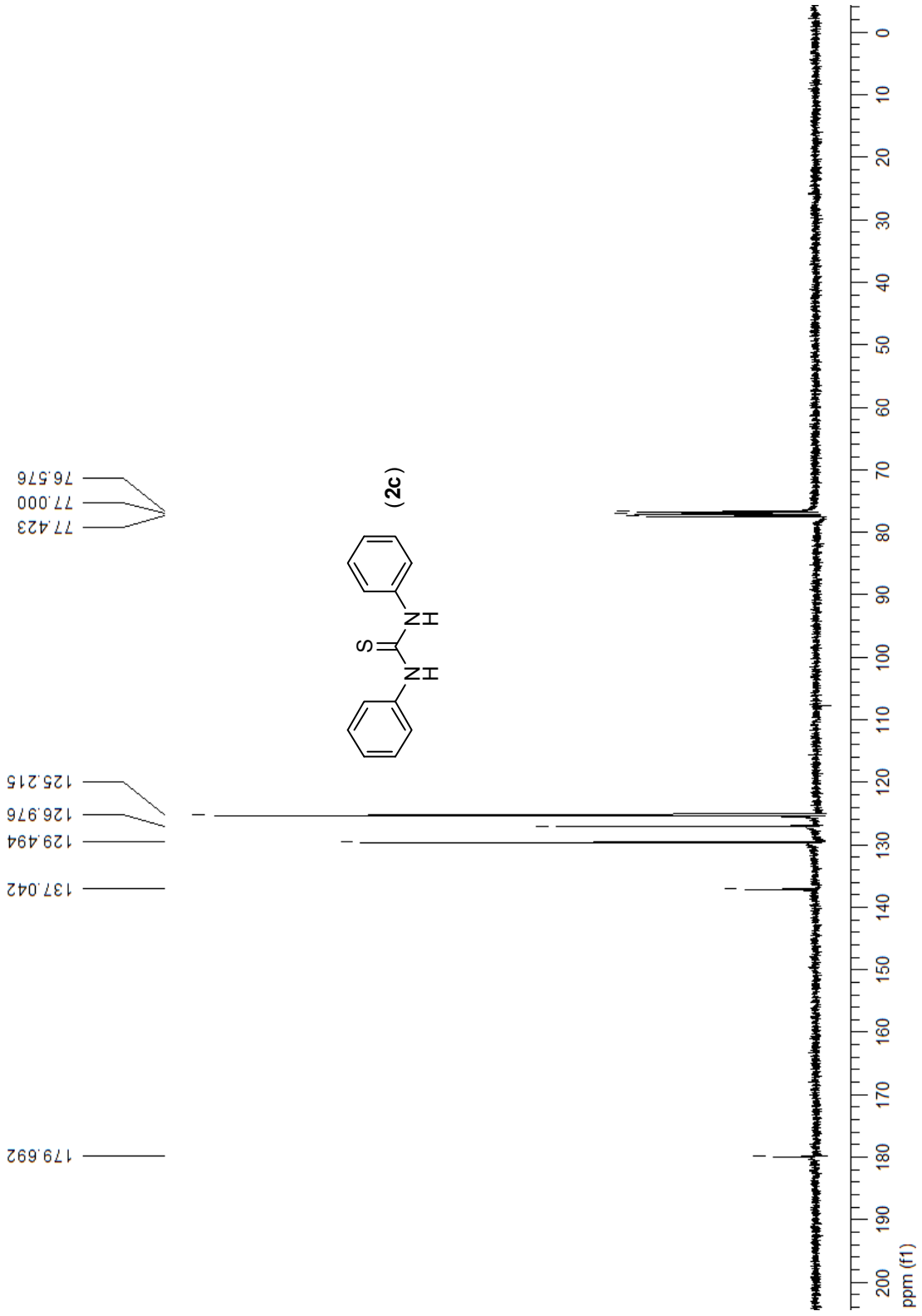
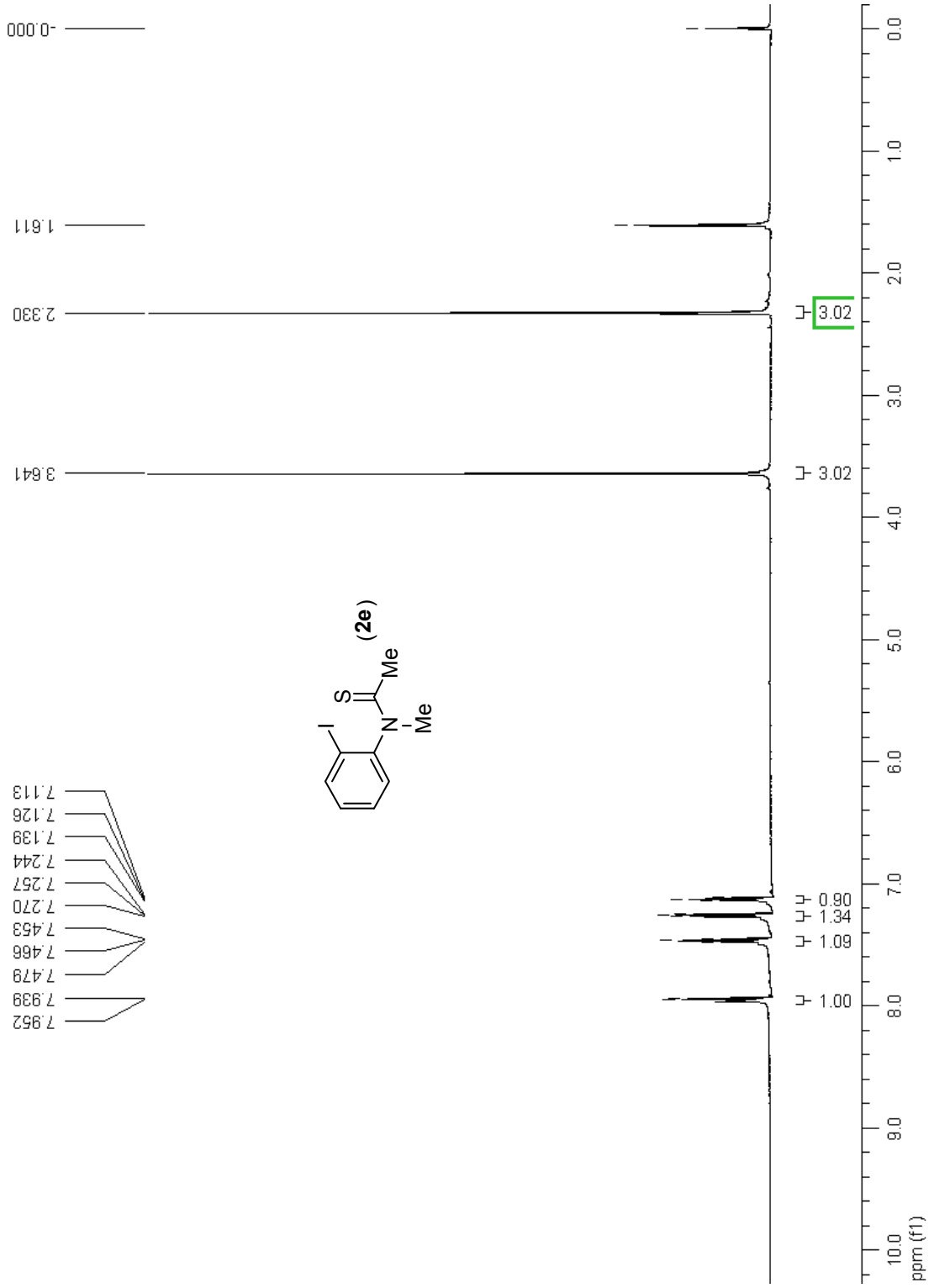
139.976
180.136
(2a)
nBu
NH
NH
S
I
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
ppm (f1)

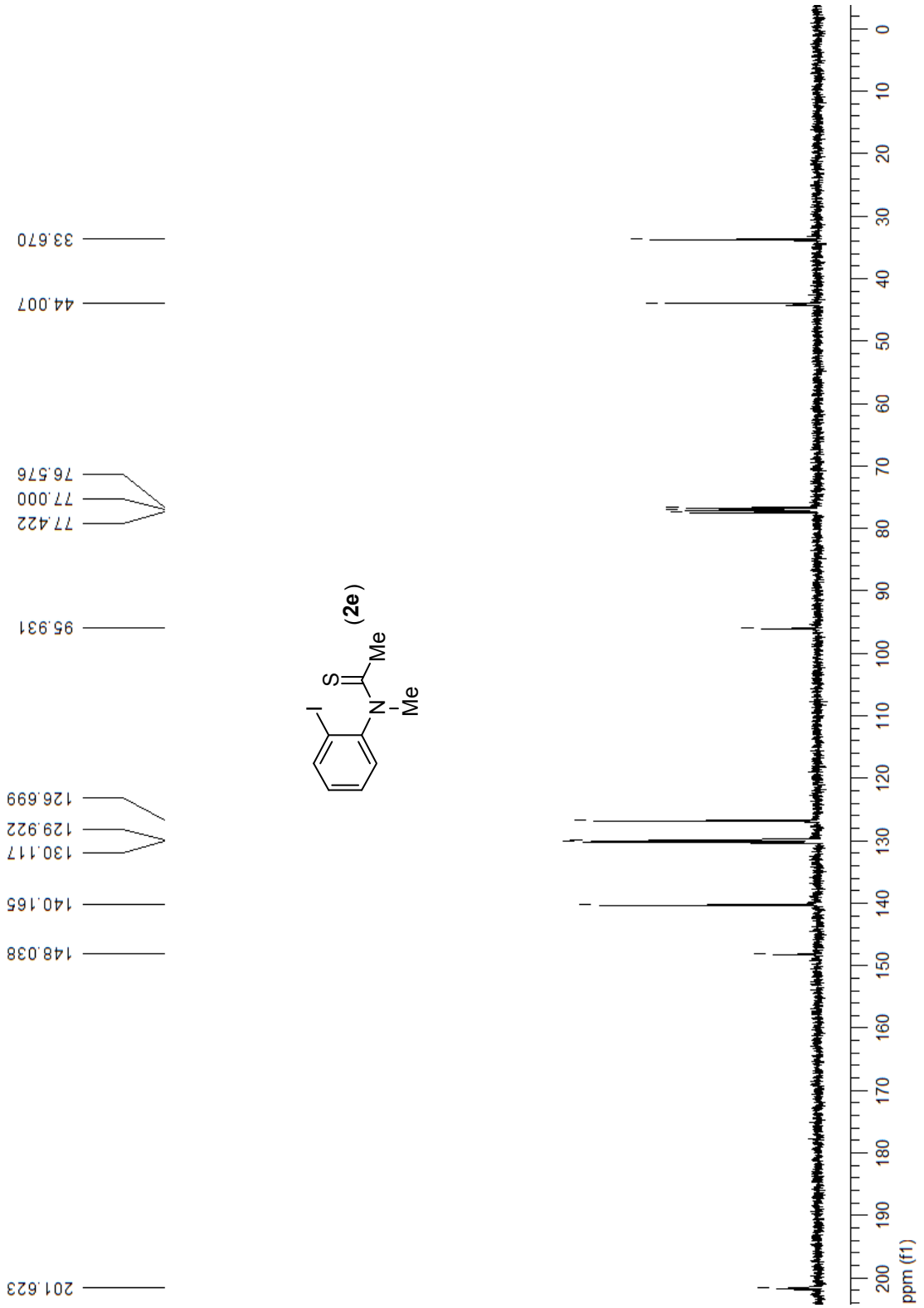


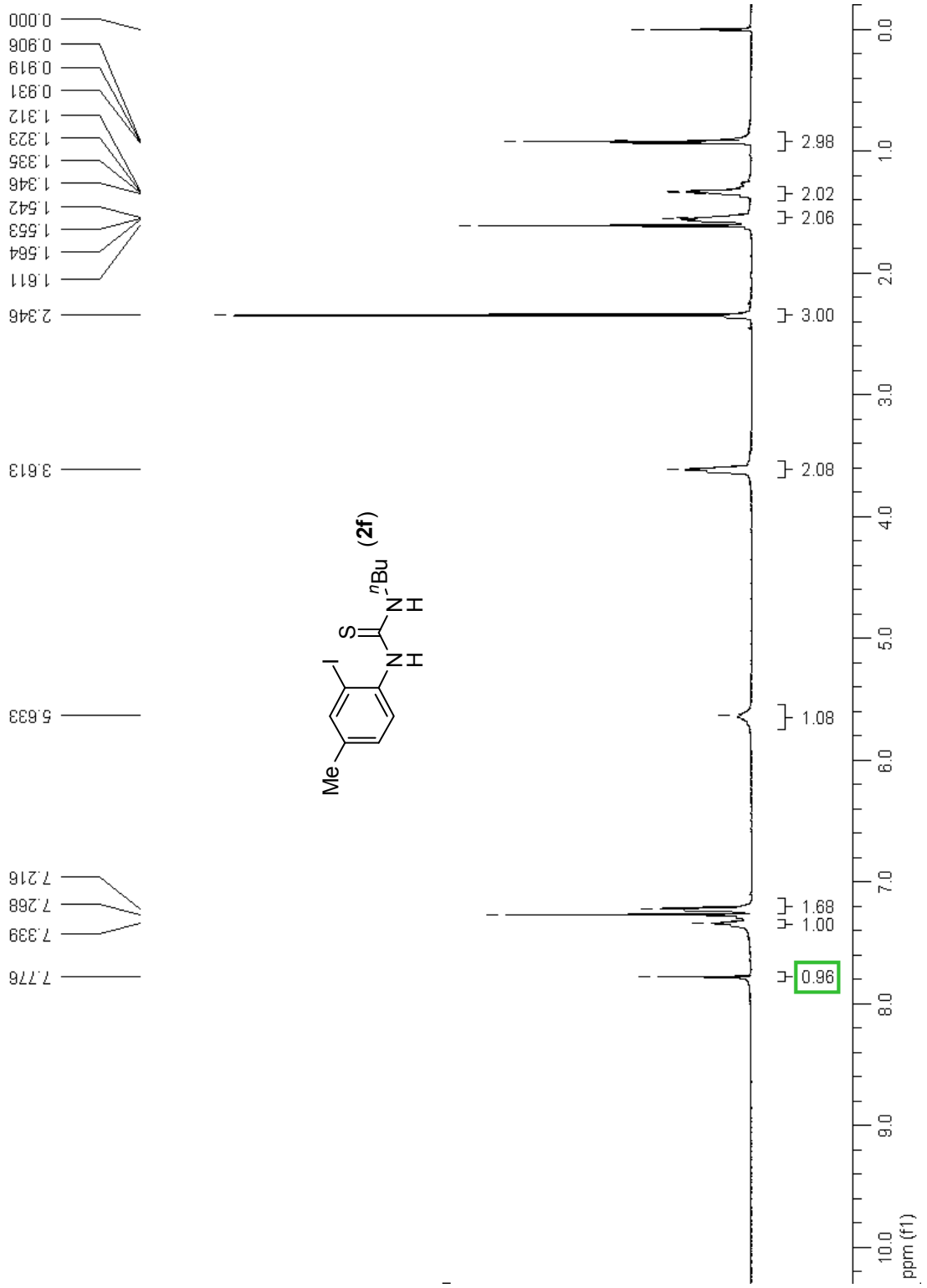


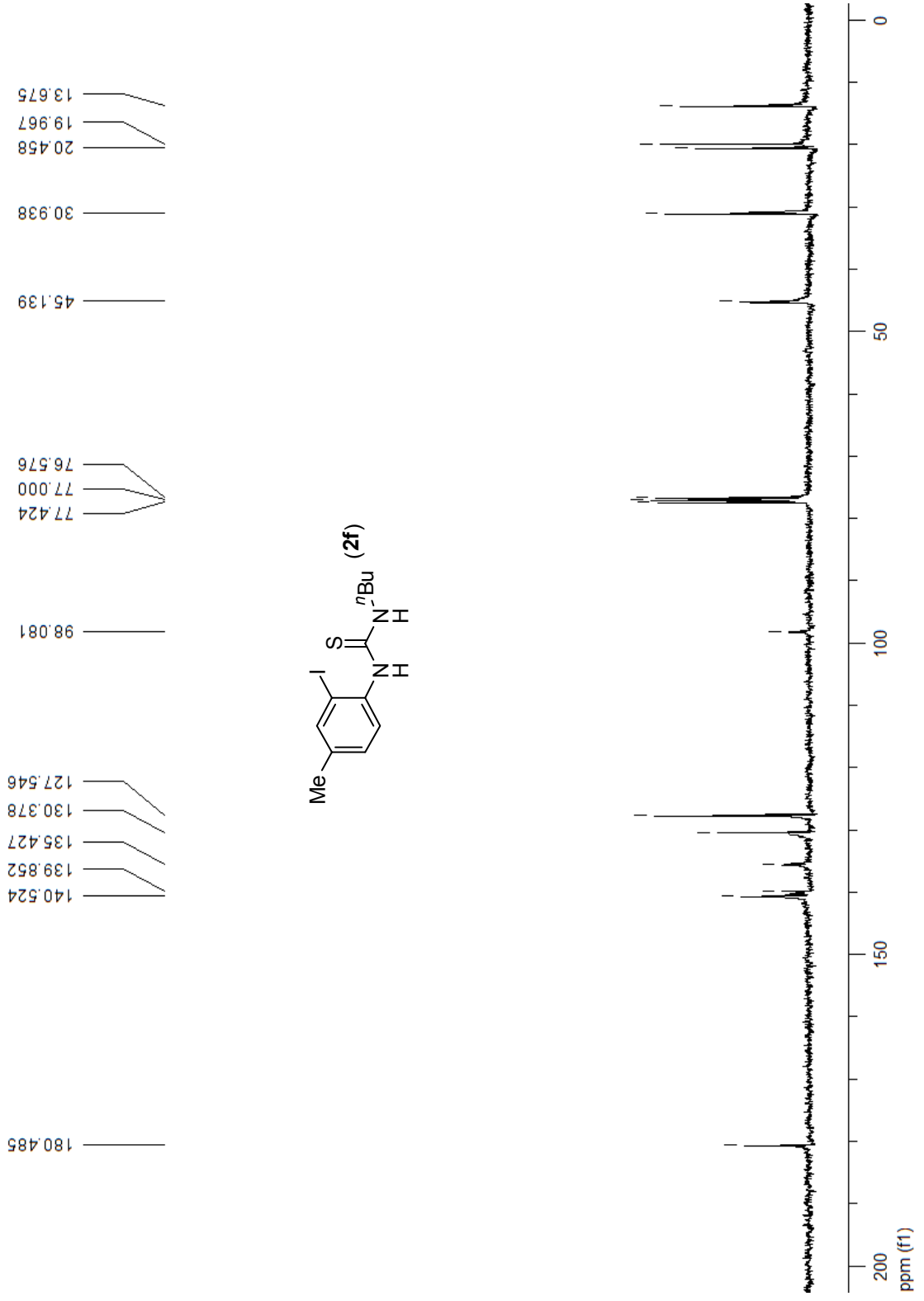


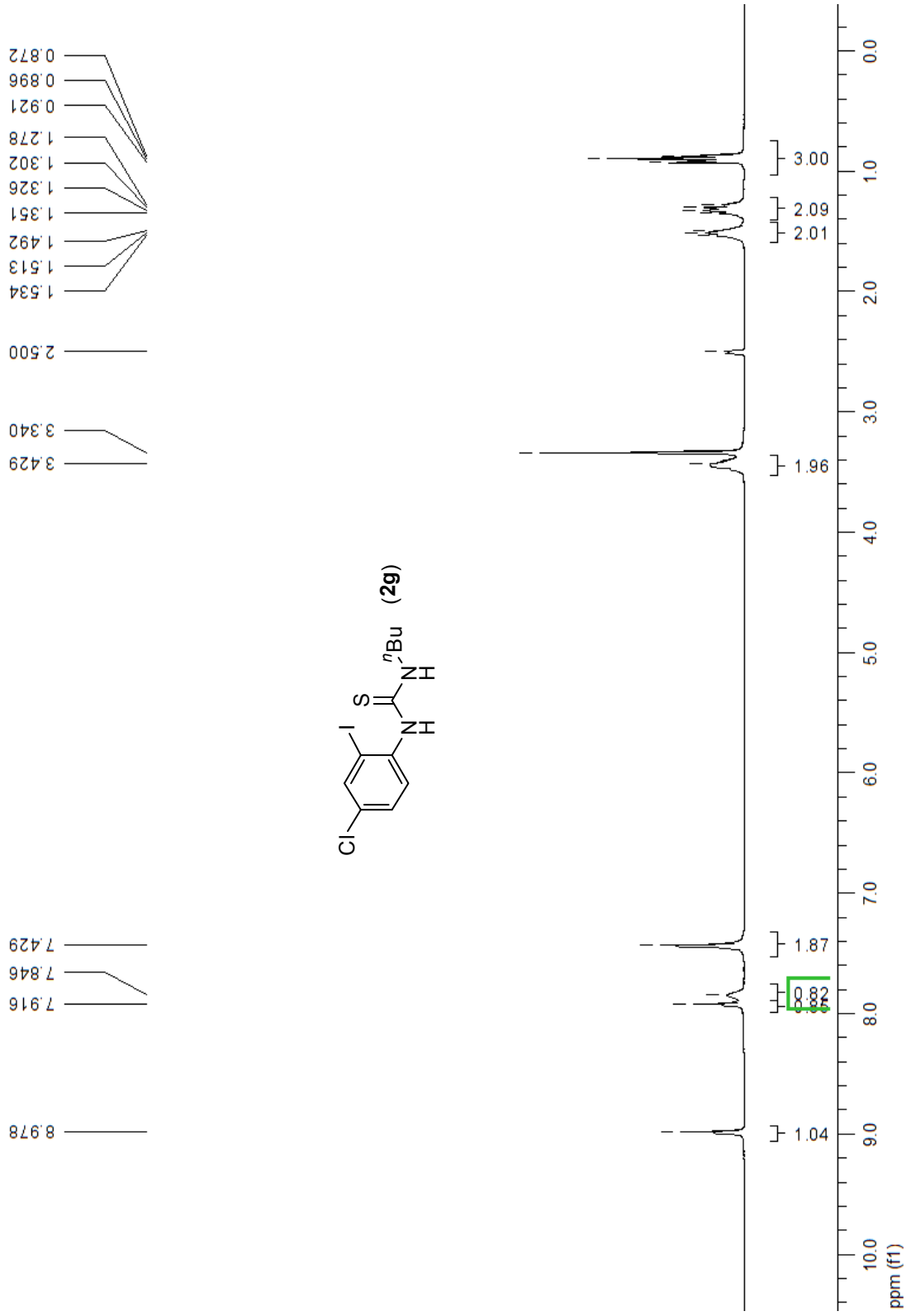


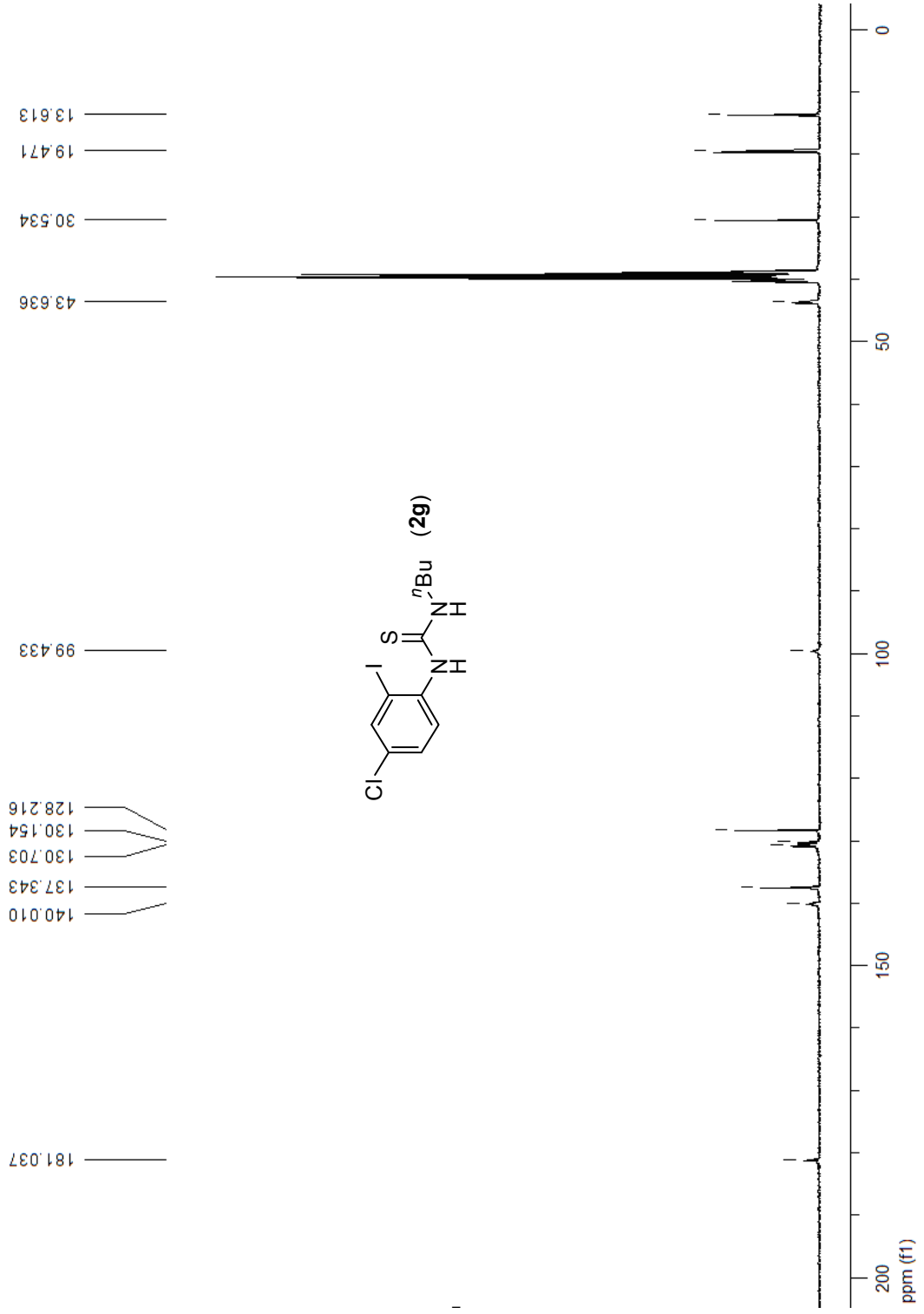


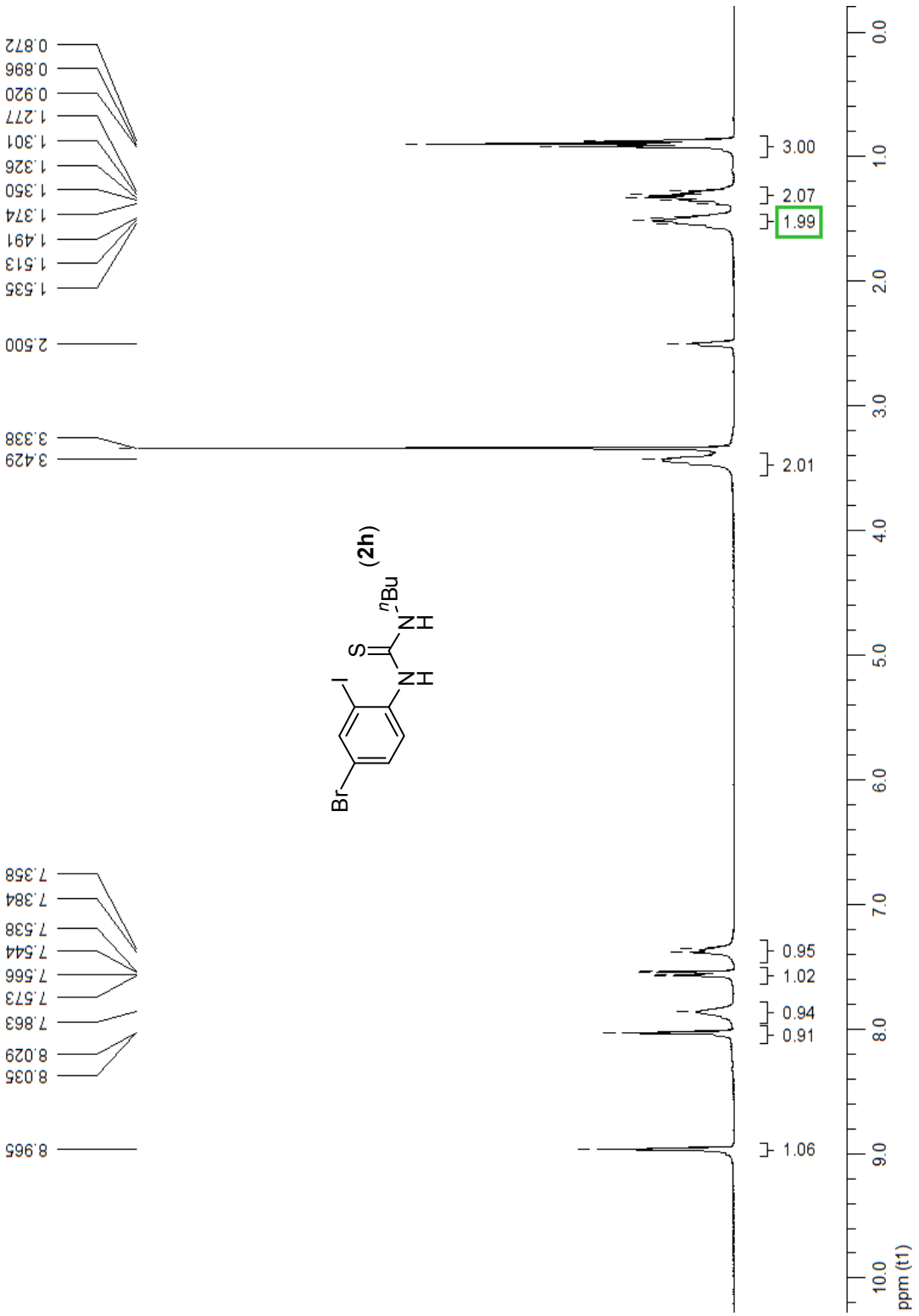


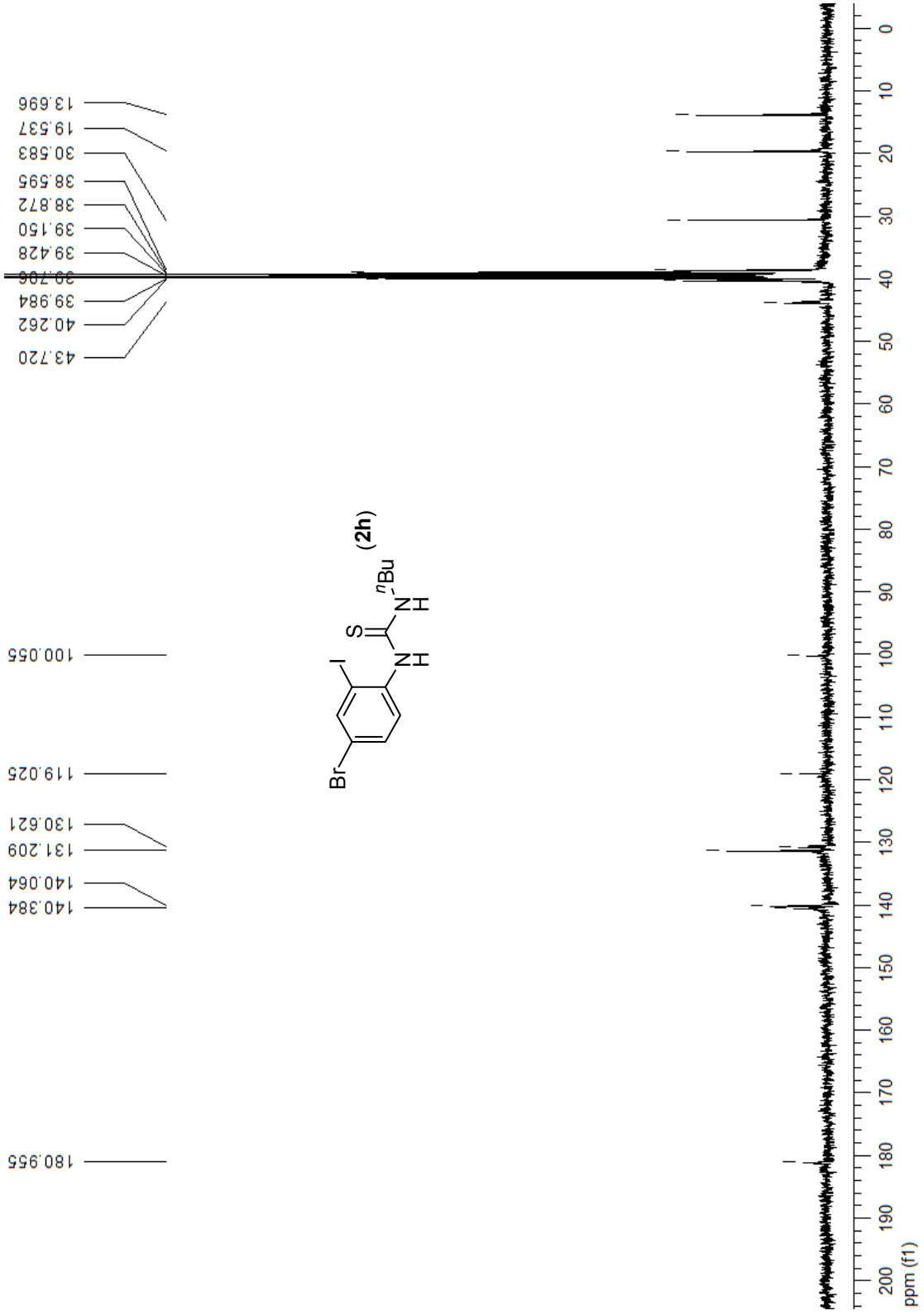


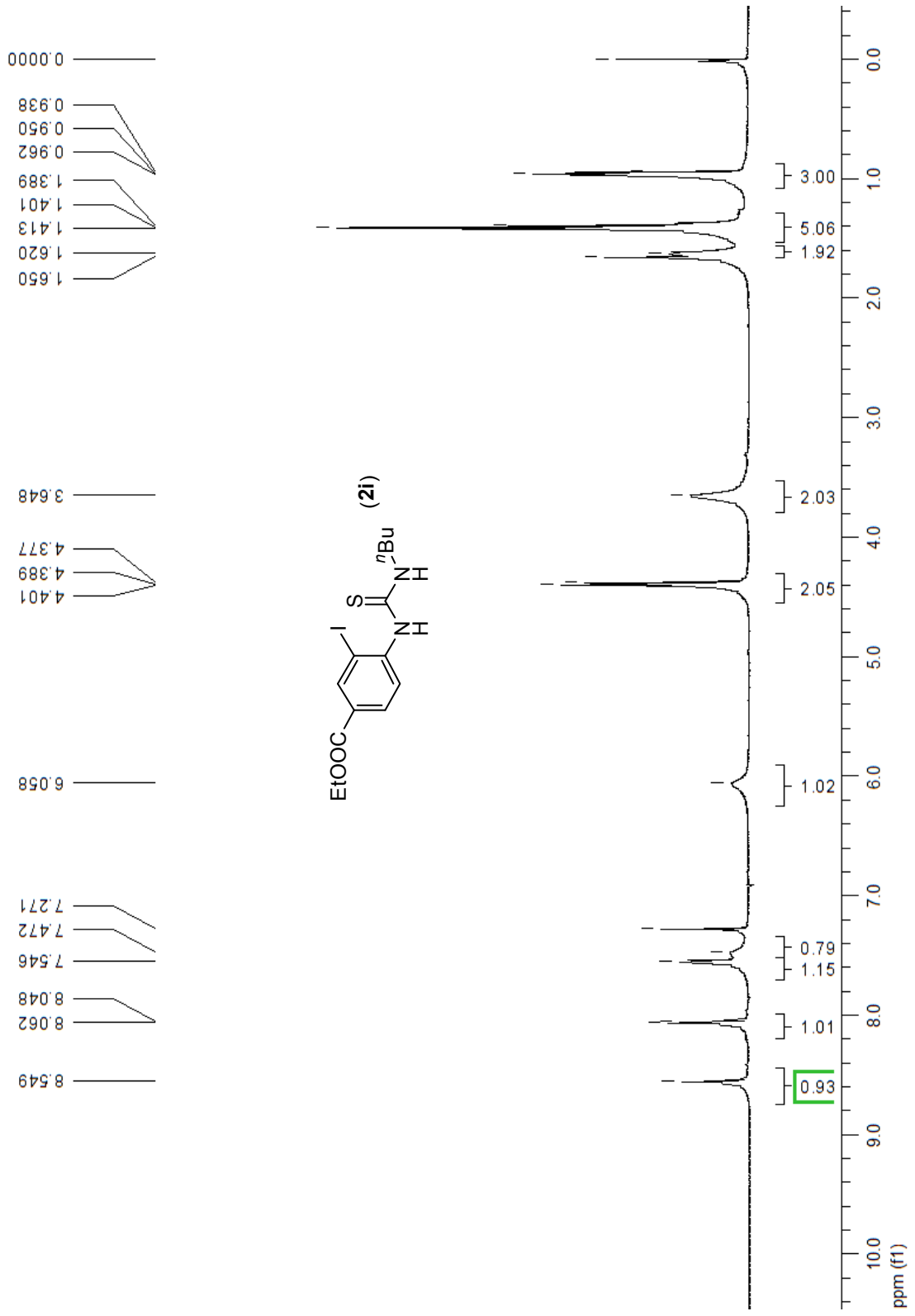


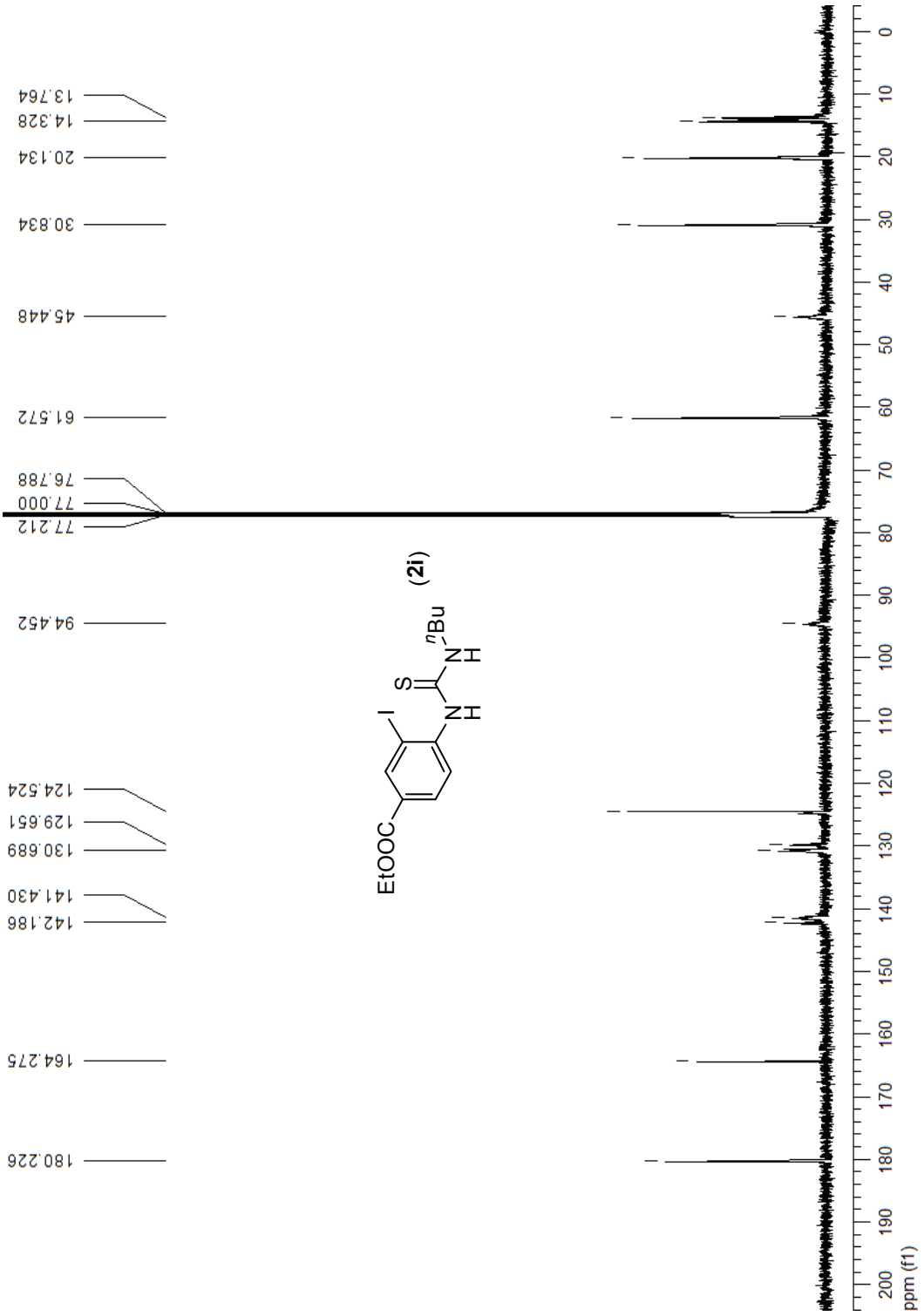








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142.186
164.275
180.226
(2i)
EtOOC
I
S
H
N
H
N
nBu
0
10
20
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40
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70
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90
100
110
120
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150
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170
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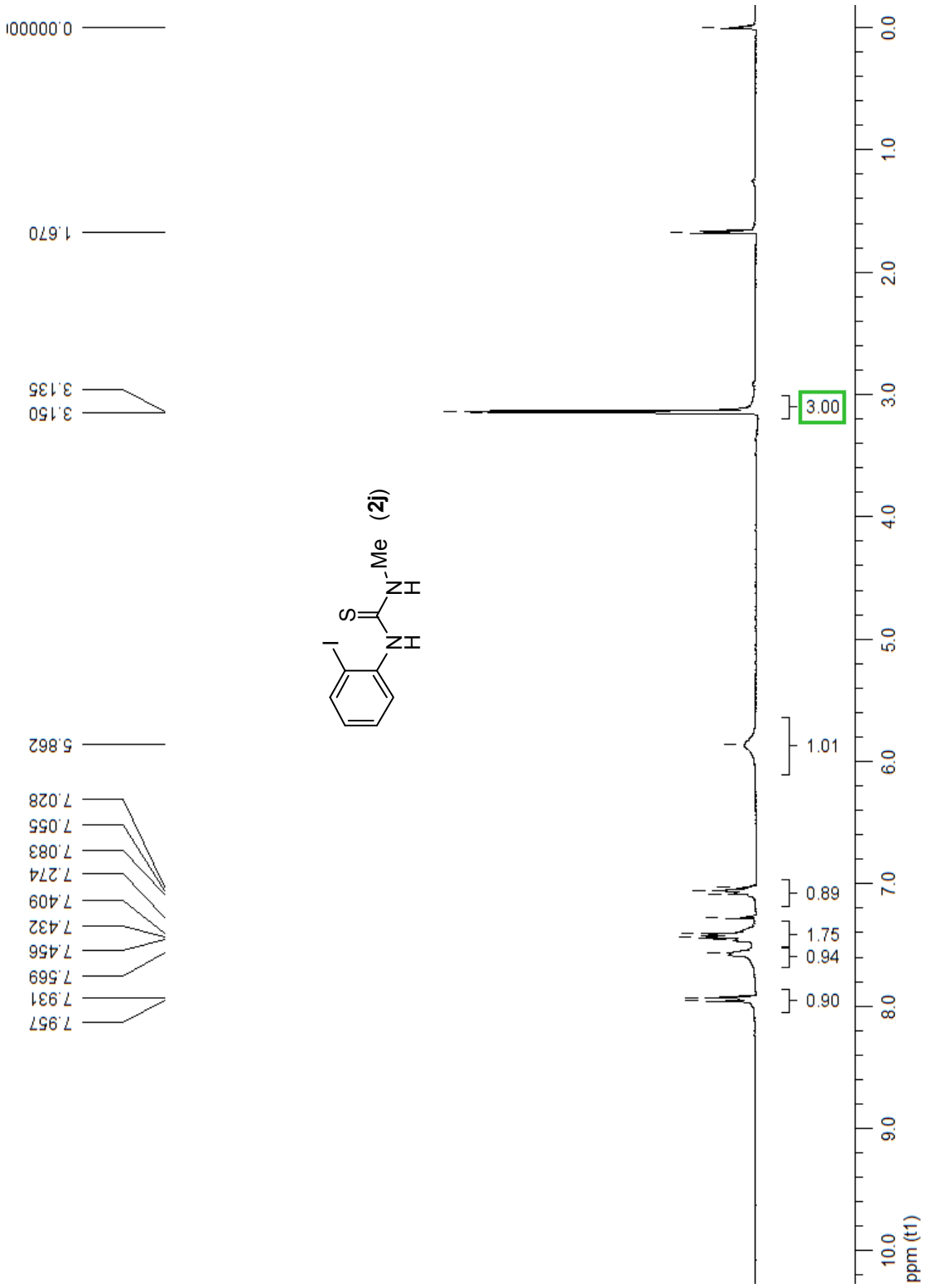
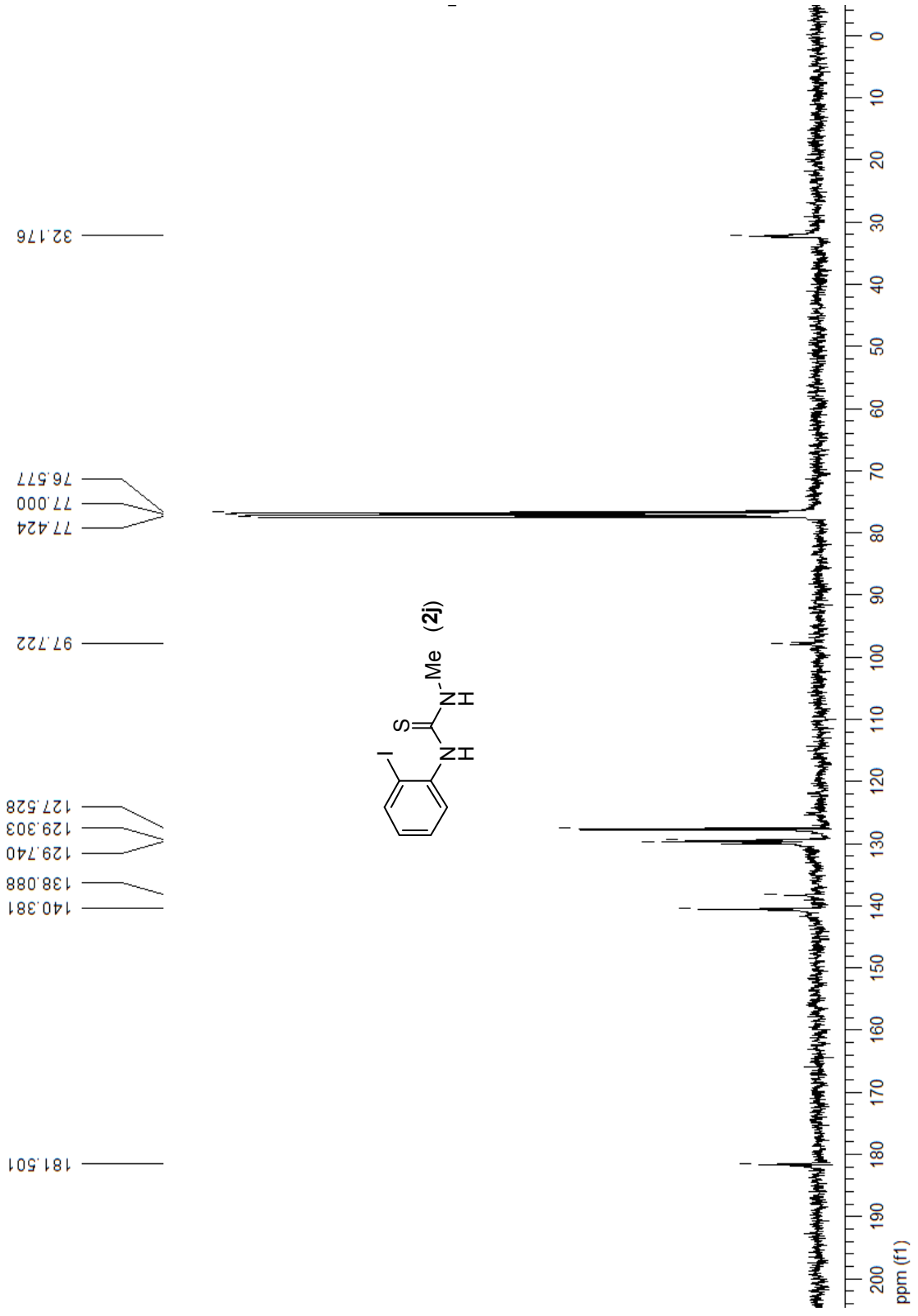
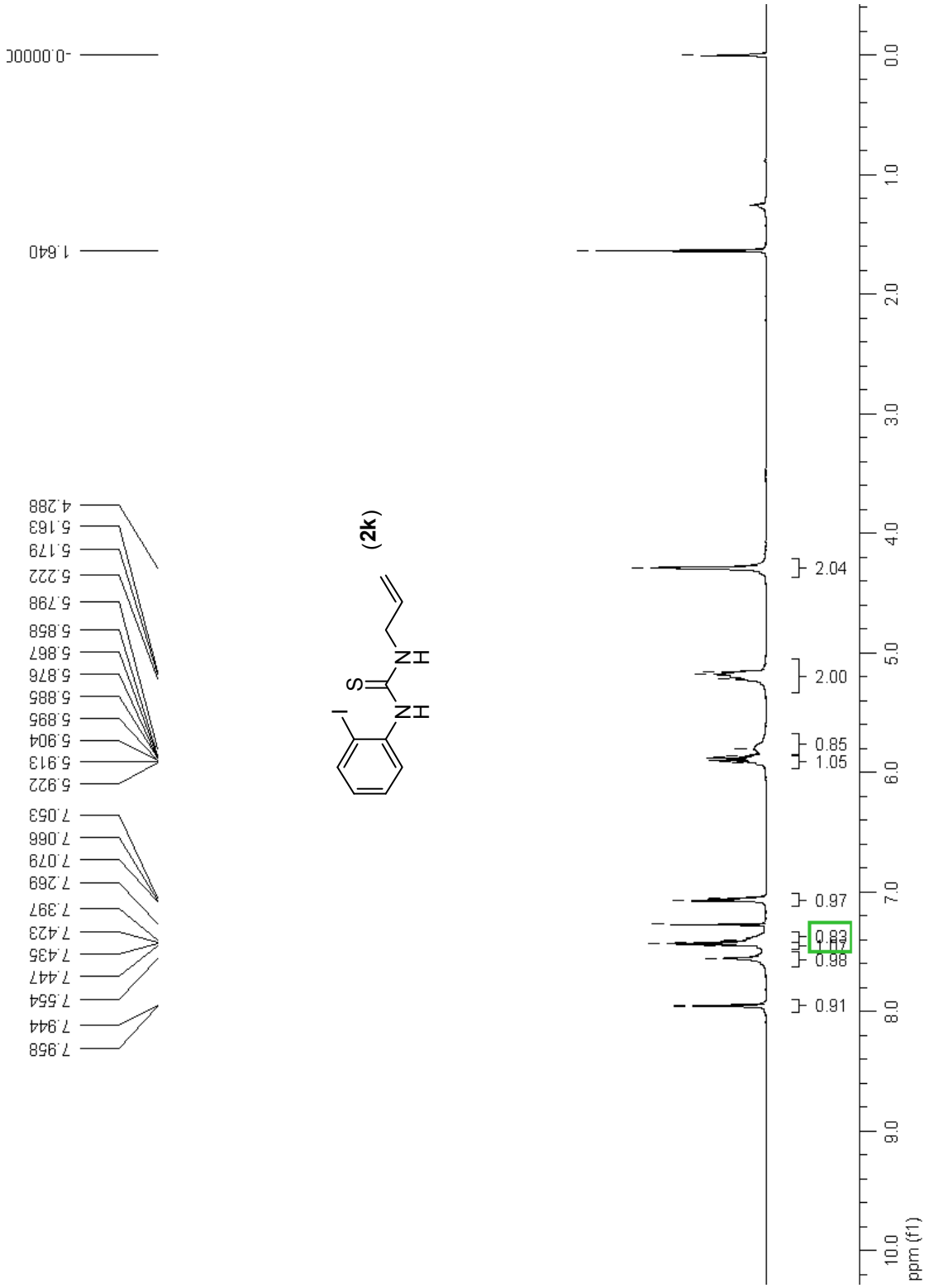
190
200
ppm (f1)






(2k)
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5.798
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5.895
5.904
5.913
5.922
7.053
7.066
7.079
7.269
7.397
7.423
7.435
7.447
7.554
7.944
7.958
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2.00
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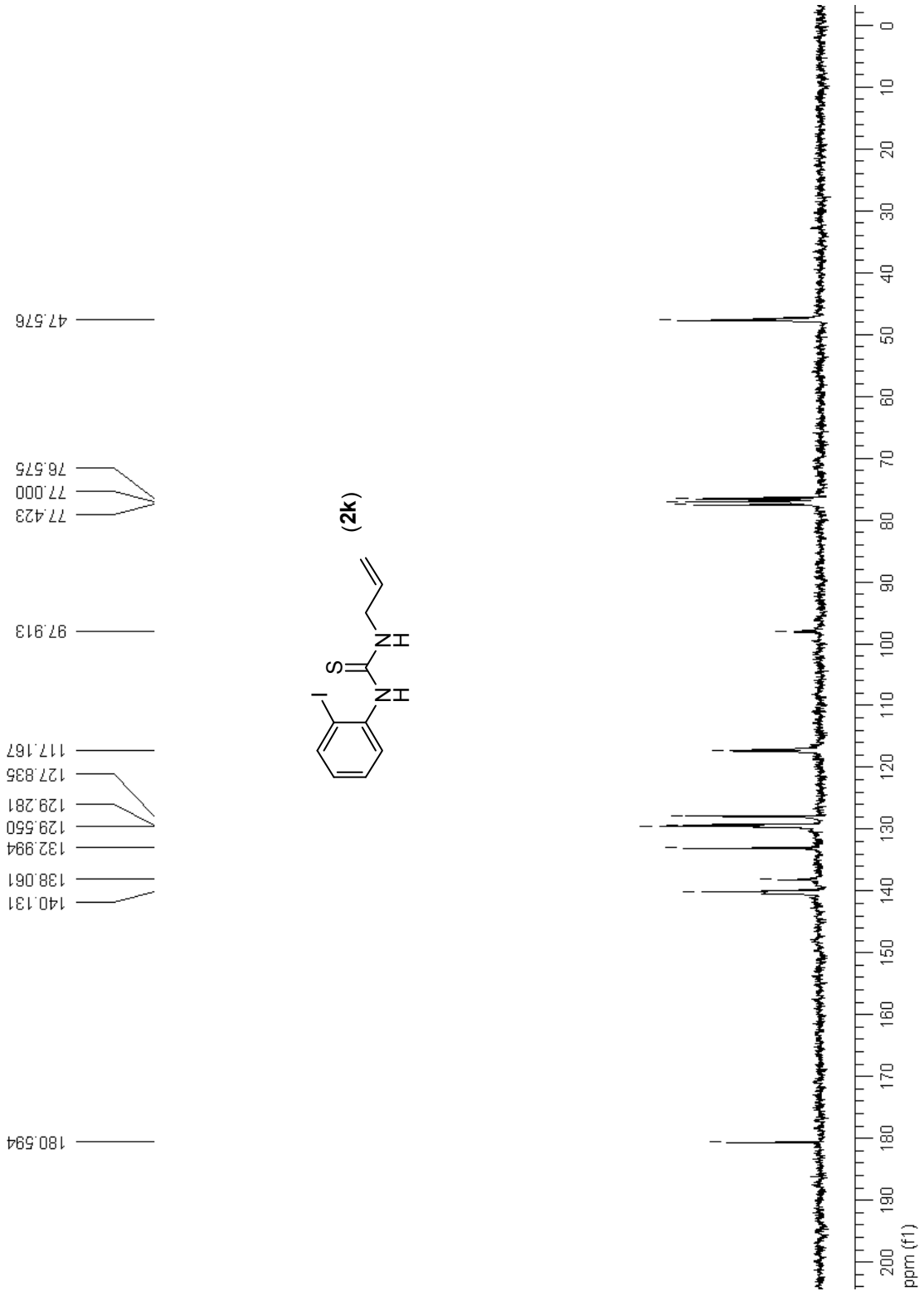
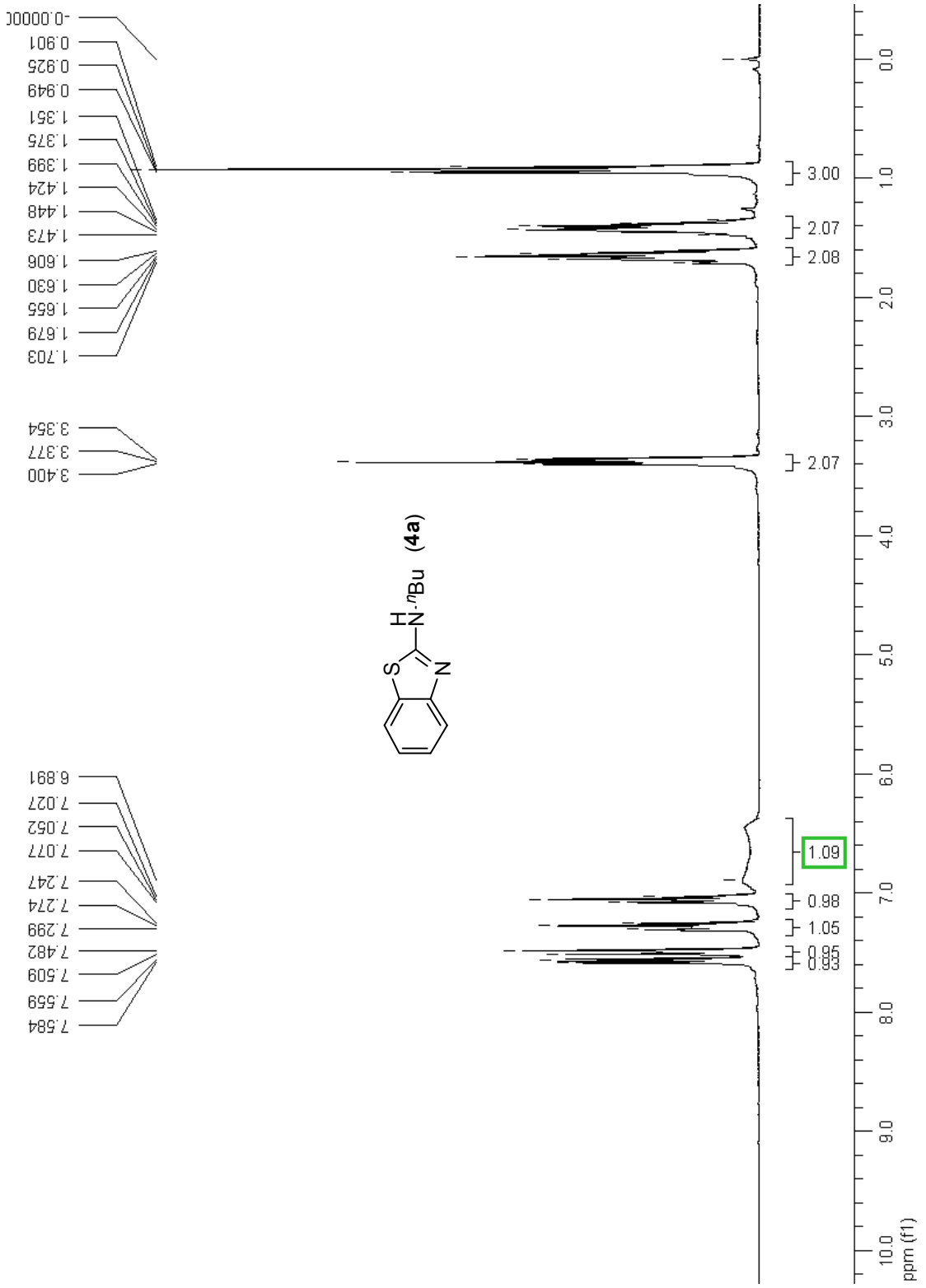
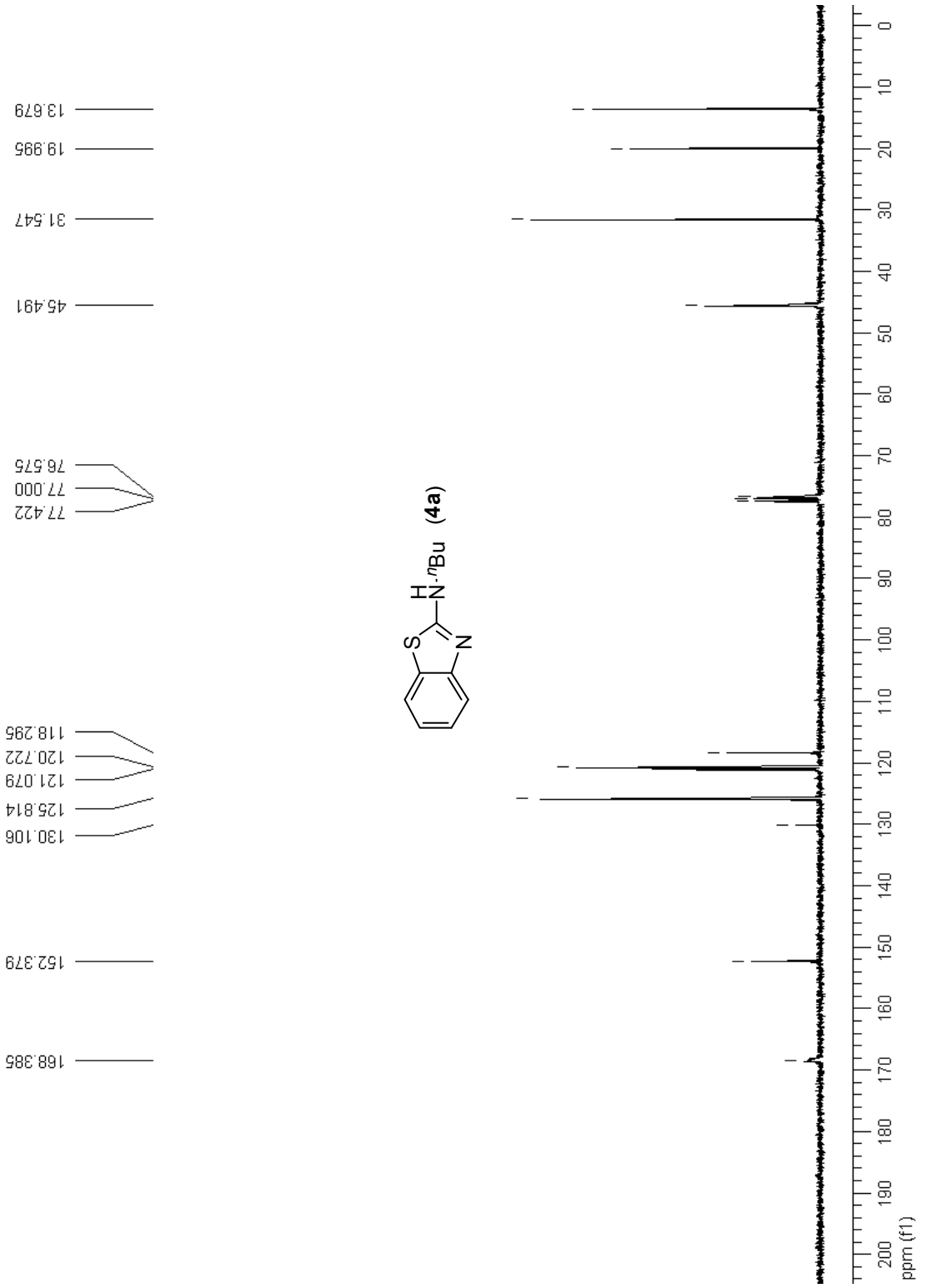
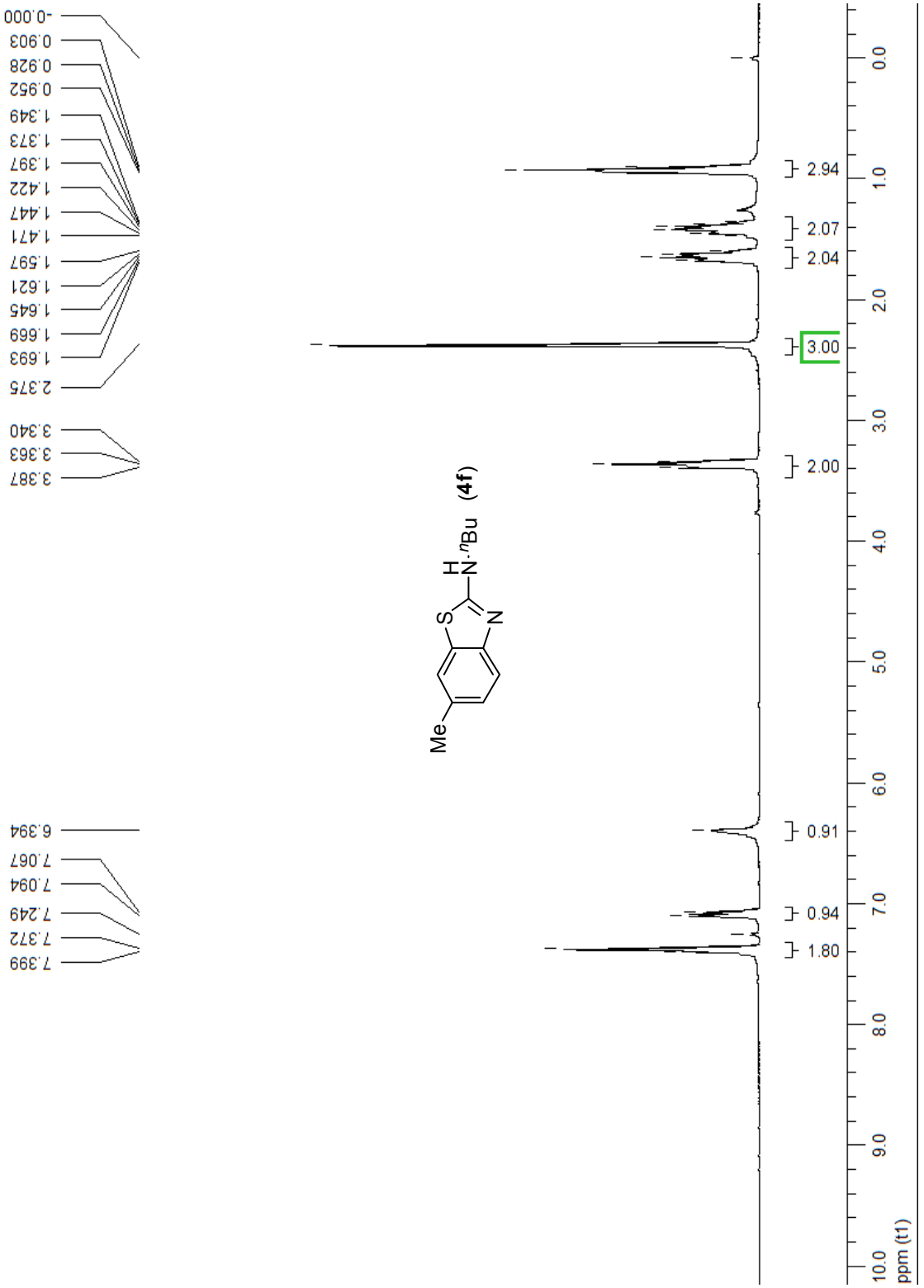
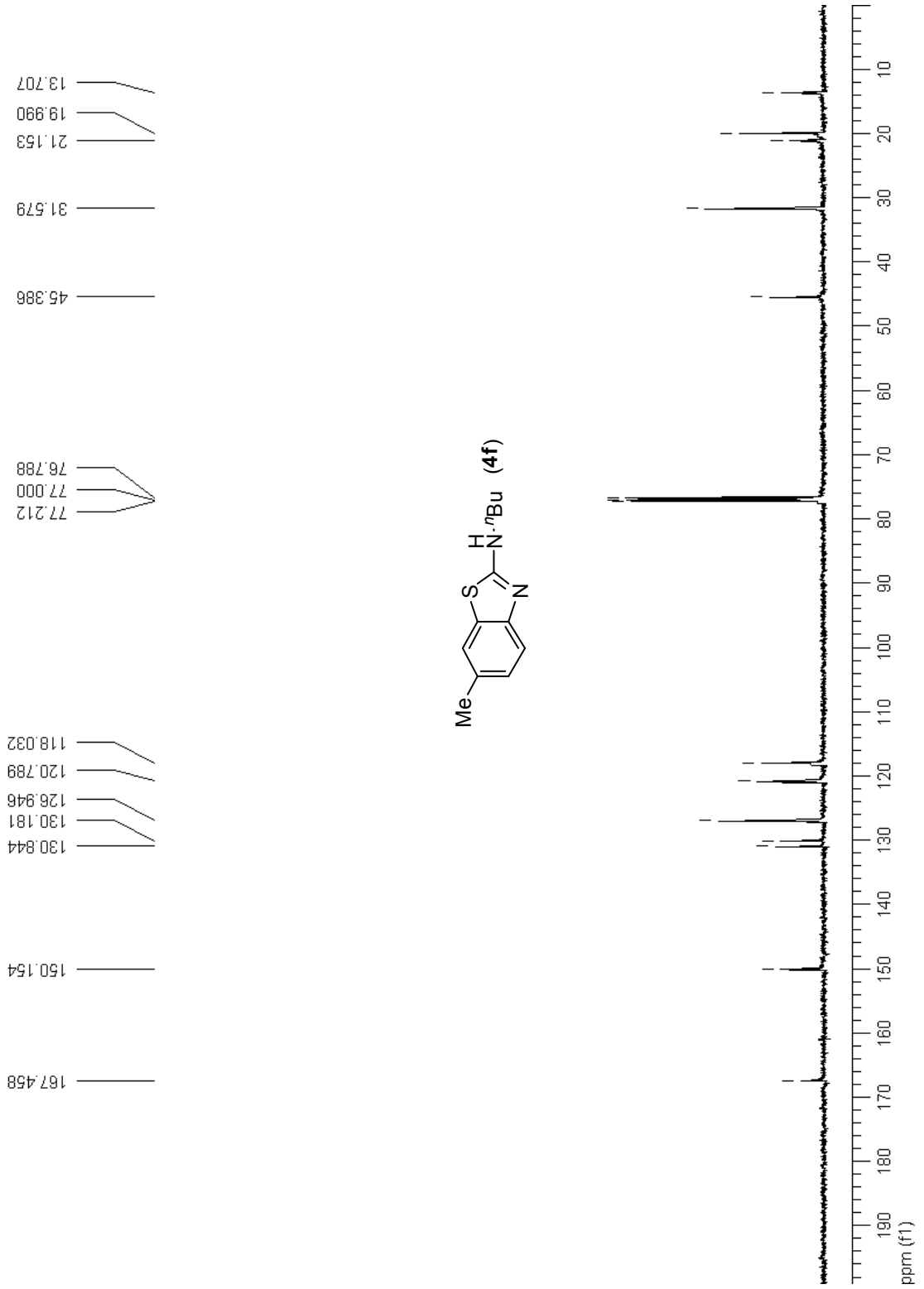
10.0
ppm (f1)

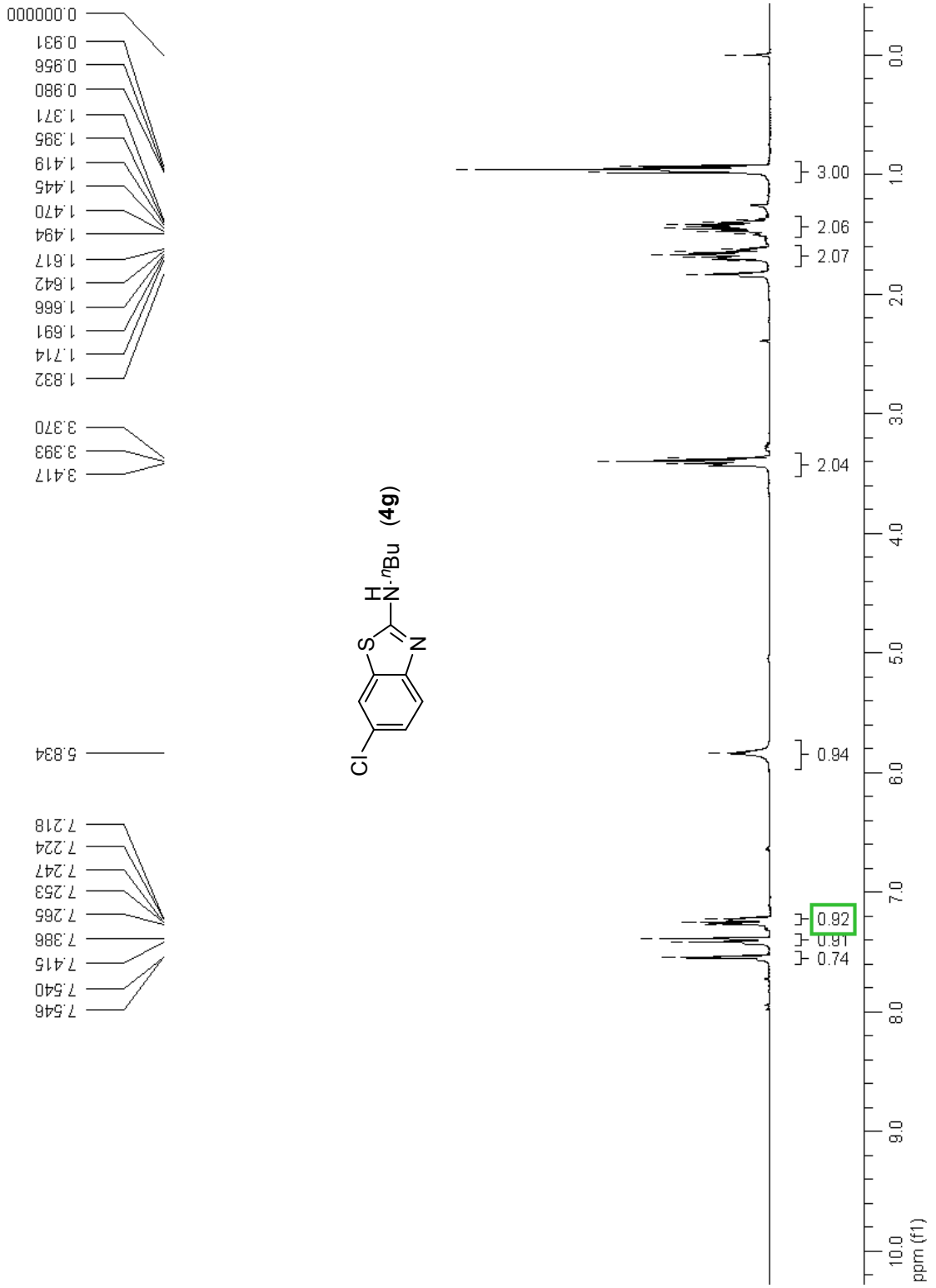


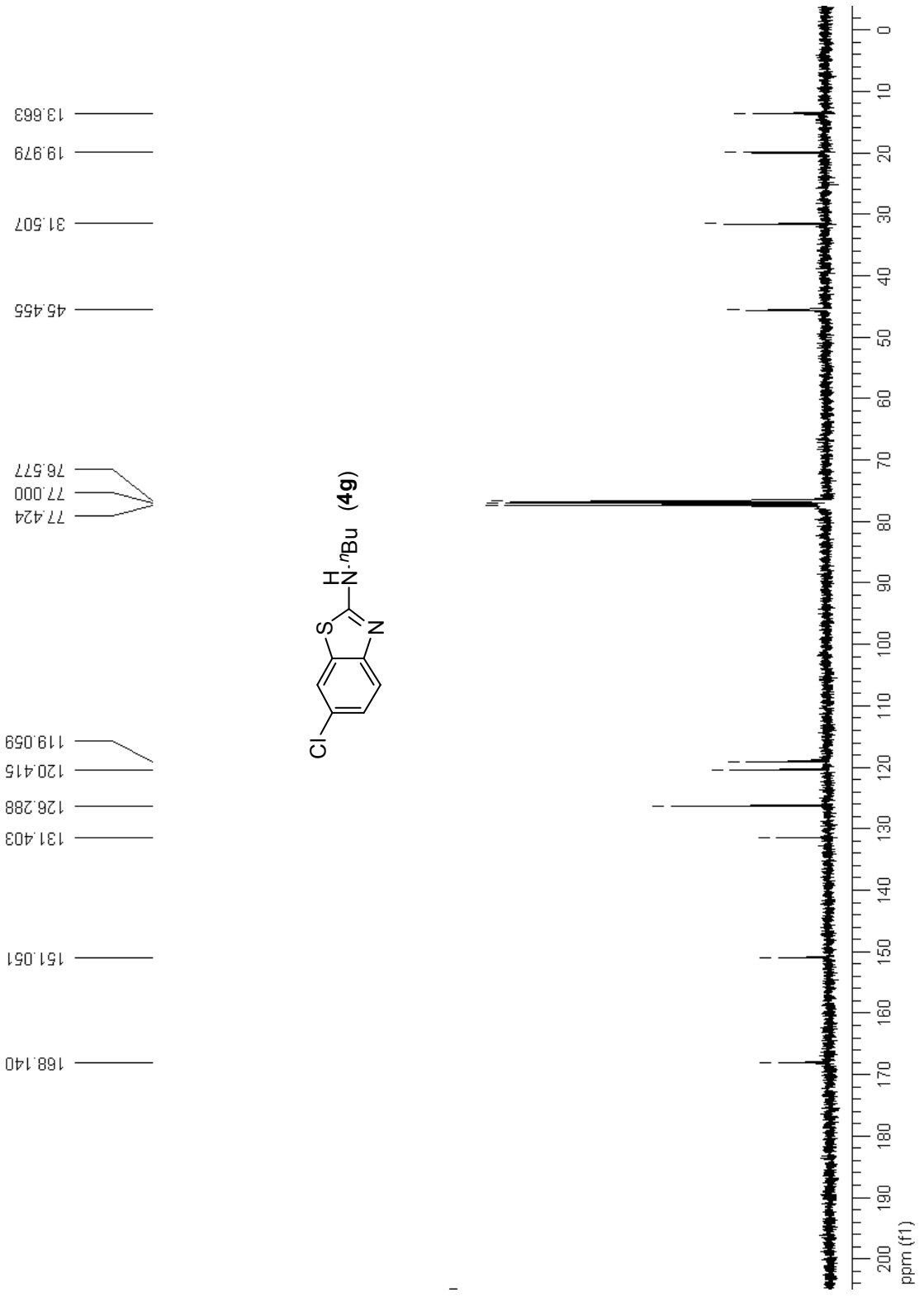


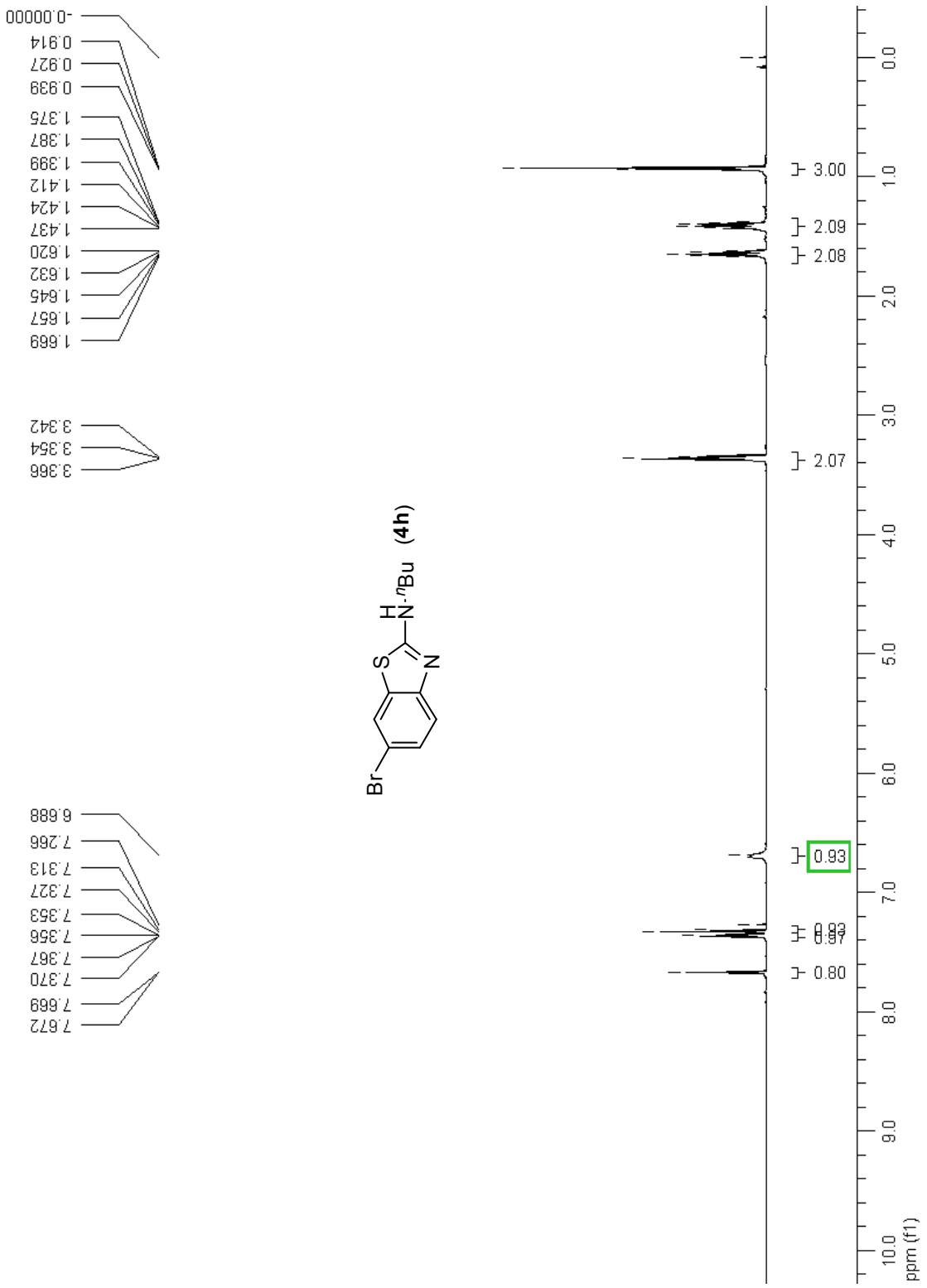


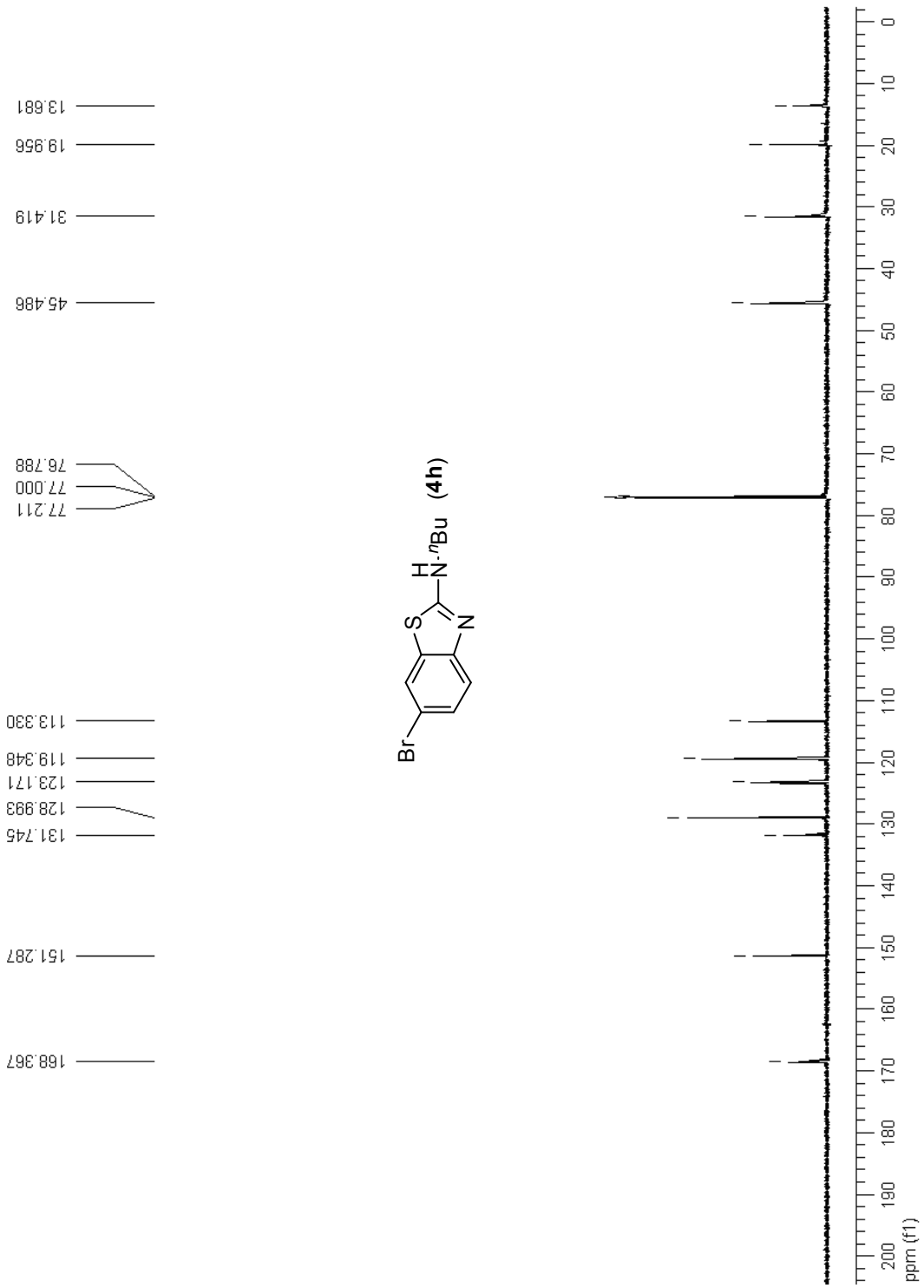


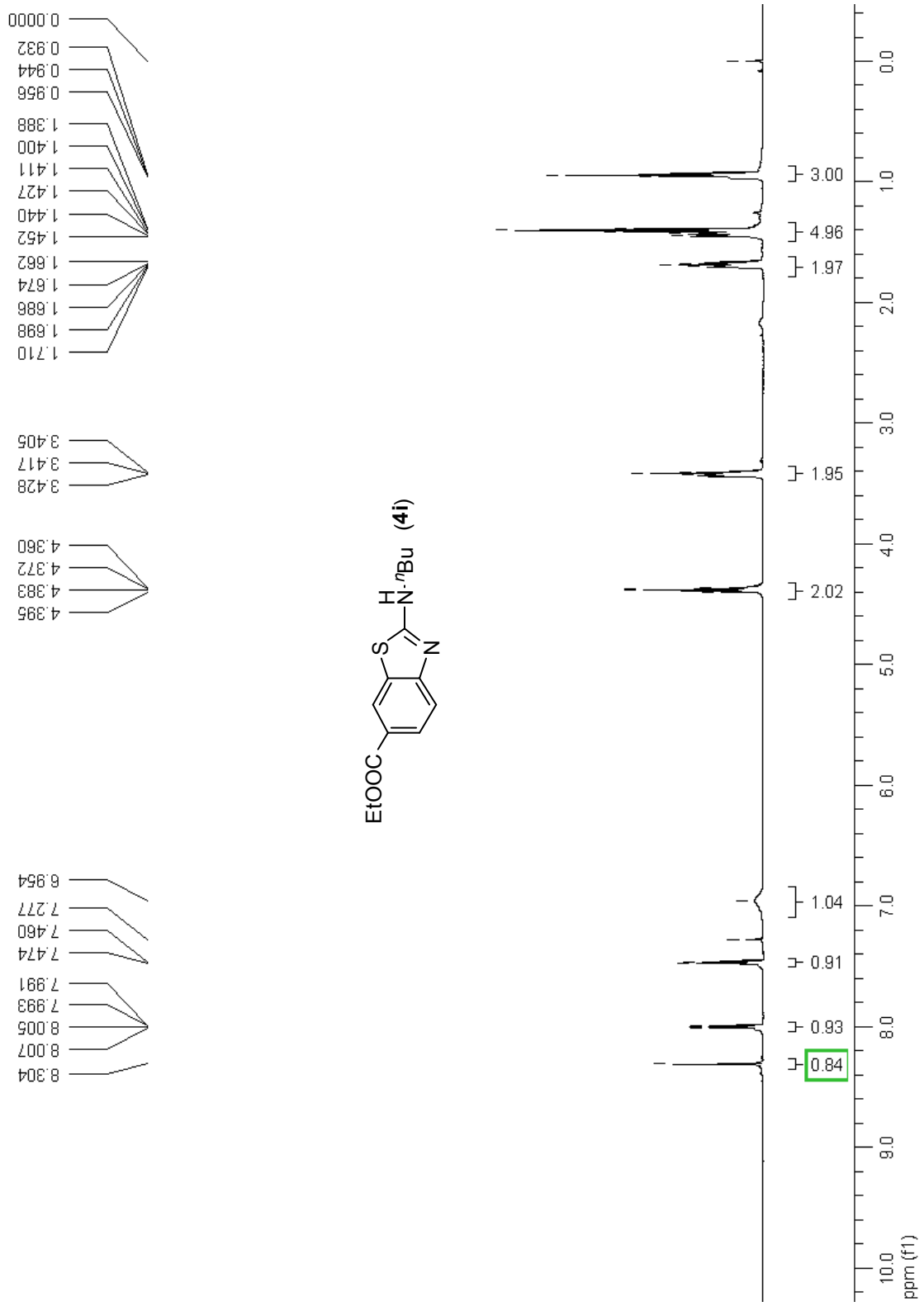


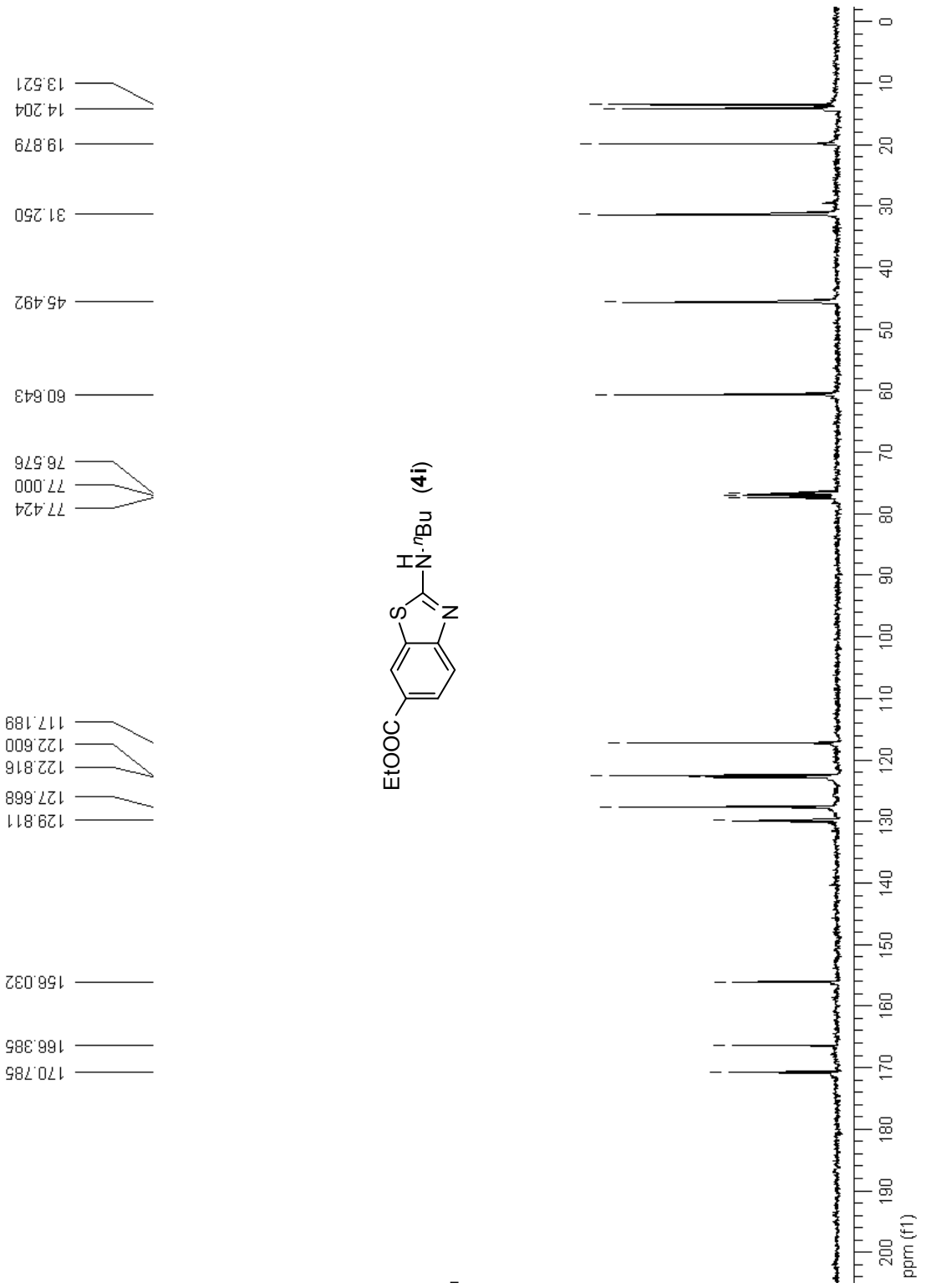








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129.811
156.032
166.385
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EtOOC
S
N
H
N
nBu
(4i)
ppm (f1)