

## Cation- $\pi$ Interactions Secure Aggregation Induced Emission of Planar Organic Luminophores

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## General considerations

Column chromatography was performed using reversed phase C18-silica gel columns (RP18 25-40  $\mu\text{m}$ ) and direct phase silica gel columns.

Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies:  $^1\text{H}$ , 400 MHz;  $^{13}\text{C}\{^1\text{H}\}$ , 100.6 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS (ESI-TOF)) were recorded on a mass spectrometer with a time-of-flight (TOF) mass analyzer using the ESI technique. Melting points are uncorrected.

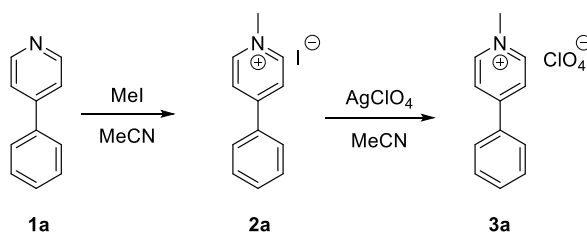
Unless otherwise noted, all chemicals were used as received from commercial sources. Anhydrous THF, diethyl ether and  $\text{CH}_2\text{Cl}_2$  were obtained by passing commercially available solvents through activated alumina columns.

The luminescence data was collected with Edinburgh Instruments *FS5* Spectrofluorometer; photoluminescence quantum yields (PLQY) were measured using an integrating sphere.

Single-crystal X-ray diffraction analyses were performed on Rigaku *XtaLAB Synergy S, Dualflex* apparatus with HyPix6000 detector and  $\text{CuK}\alpha/\text{MoK}\alpha$  radiation type. Single crystals of pyridinium salts **3a**, **6a** and **7a** suitable for X-ray crystallography were obtained by  $\text{Et}_2\text{O}$  vapor diffusion into the corresponding MeCN solutions.

## Experimental procedures for synthesis of luminophores

### Synthesis of **2a** and **3a**



**1-Methyl-4-phenylpyridin-1-ium iodide (2a).** To a clear solution of 4-phenylpyridine (**1a**; 0.50 g, 3.22 mmol, 1.00 equiv) in anhydrous acetonitrile (3 mL) was added iodomethane (0.69 g, 4.83 mmol, 1.50 equiv) and the resulting pale green suspension was stirred in a pressure vial at 80 °C for 16h. The reaction mixture was cooled in an ice bath, then EtOAc (50 mL) was

added to form precipitate. The precipitate was filtered, washed with EtOAc and dried *in vacuo* to afford the title compound **2a** as green crystals (0.92 g, 3.10 mmol, 96%).

Mp 166–168 °C (recrystallized from MeCN/EtOAc).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 8.93-8.89 (m, 2H), 8.44-8.39 (m, 2H), 8.04-8.00 (m, 2H), 7.67-7.59 (m, 3H), 4.31 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 154.8, 145.8, 133.8, 132.5, 130.1, 128.3, 124.5, 47.5 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>12</sub>H<sub>12</sub>N: 170.0970; Found: 170.0968.

IR (KBr, cm<sup>-1</sup>) 3437, 3115, 3016, 1949, 1637.

**1-Methyl-4-phenylpyridin-1-ium perchlorate (3a).** To a suspension of **2a** (0.30 g, 1.01 mmol, 1.00 equiv) in MeCN (3 mL) was added a solution of AgClO<sub>4</sub> (0.27 g, 1.30 mmol, 1.30 equiv) in MeCN (2 mL). The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite, and the pad was washed with MeCN. The filtrate was evaporated to give an off-white solid, which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **3a** as off-white plates (0.19 g, 0.70 mmol, 70%).

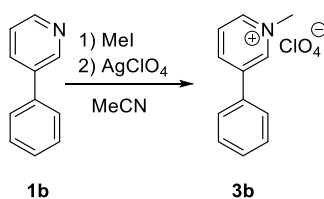
Mp 134–136 °C (recrystallized from *i*-PrOH).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 8.91-8.86 (m, 2H), 8.42-8.38 (m, 2H), 8.04-7.98 (m, 2H), 7.67-7.59 (m, 3H), 4.30 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 154.8, 145.8, 133.9, 132.5, 130.2, 128.4, 124.5, 47.5 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>12</sub>H<sub>12</sub>N: 170.0970; Found: 170.0970.

IR (KBr, cm<sup>-1</sup>) 3420, 3139, 3062, 1988, 1103.

Synthesis of **3b**

**1-Methyl-3-phenylpyridin-1-ium perchlorate (3b).** To a clear solution of 3-phenylpyridine (**1b**; 0.17 g, 1.09 mmol, 1.00 equiv) in anhydrous acetonitrile (2 mL) was added iodomethane (0.23 g, 1.64 mmol, 1.50 equiv) and the resulting pale green solution was stirred in a pressure vial at 80 °C for 16h. After cooling in an ice bath, EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt a solution of AgClO<sub>4</sub> (0.29 g, 1.42 mmol, 1.30 equiv) in MeCN (2 mL) was added. The resulting suspension was stirred at room temperature for 30 minutes, filtered through a pad of Celite, and the pad was washed with acetonitrile. The filtrate was evaporated to give a white solid, which was suspended in *i*-PrOH (20 mL), sonified, and left to stand at -15 °C for 2h. Filtration and washing with *i*-PrOH afforded the title compound **3b** as a white powder (0.18 g, 0.67 mmol, 61%).

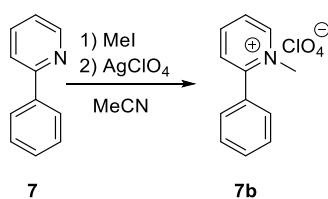
Mp 127–129 °C (recrystallized from *i*-PrOH).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 9.31-9.28 (m, 1H), 8.88-8.80 (m, 2H), 8.16-8.10 (m, 1H), 7.87-7.81 (m, 2H), 7.64-7.53 (m, 3H), 4.38 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 144.0, 143.9, 142.6, 139.8, 133.5, 130.6, 130.0, 128.1, 127.7, 48.5 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>12</sub>H<sub>12</sub>N: 170.0970; Found: 170.0969.

IR (KBr, cm<sup>-1</sup>) 3429, 3086, 2005, 1090.

Synthesis of **3c**

**1-Methyl-2-phenylpyridin-1-ium perchlorate (3c).** To a clear solution of 2-phenylpyridine (**1c**; 0.17 g, 1.09 mmol, 1.00 equiv) in anhydrous acetonitrile (2 mL) was added iodomethane (0.23 g, 1.64 mmol, 1.50 equiv). The resulting pale green solution was stirred in a pressure vial at 80 °C for 16h. The clear green solution was cooled in an ice bath and EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt a solution of AgClO<sub>4</sub> (0.29 g, 1.42 mmol, 1.30 equiv) in MeCN (2 mL) was added. The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad washed with acetonitrile. The filtrate was evaporated to give white solid which was suspended in *i*-PrOH (20 mL), sonified, let to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **3c** as a white powder (0.26 g, 0.96 mmol, 88%).

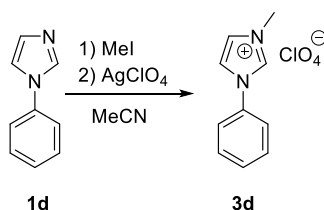
Mp 135–137 °C (recrystallized from *i*-PrOH).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 9.04-9.00 (m, 1H), 8.61-8.55 (m, 1H), 8.11-8.06 (m, 1H), 8.04-8.00 (m, 1H), 7.70-7.60 (m, 5H), 4.09 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 155.4, 146.9, 145.8, 132.1, 131.6, 130.2, 129.5, 129.4, 127.0, 47.4 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>12</sub>H<sub>12</sub>N: 170.0970; Found: 170.0969.

IR (KBr, cm<sup>-1</sup>) 3065, 2025, 1630, 1093.

Synthesis of **3d**

**3-Methyl-1-phenyl-1H-imidazol-3-ium perchlorate (3d).** To a clear solution of 1-phenyl-1H-imidazole (**1d**; 0.16 g, 1.09 mmol, 1.00 equiv) in anhydrous acetonitrile (2 mL) was added iodomethane (0.23 g, 1.64 mmol, 1.50 equiv) and the resulting colorless solution was stirred in a pressure vial at 80 °C for 16h. The colorless solution was cooled in an ice bath and EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt a solution of AgClO<sub>4</sub> (0.29 g, 1.42 mmol, 1.30 equiv) in MeCN (2 mL) was added. The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad was washed with acetonitrile. The filtrate was evaporated to give white solid which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **3d** as an off-white powder (0.18 g, 0.70 mmol, 64%).

Mp 101–103 °C (recrystallized from *i*-PrOH).

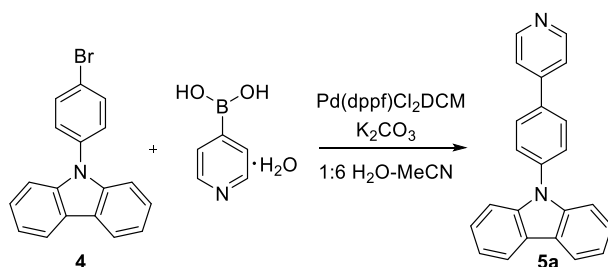
<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 9.60-9.57 (m, 1H), 8.20-8.16 (m, 1H), 7.86-7.82 (m, 1H), 7.74-7.69 (m, 2H), 7.67-7.55 (m, 3H), 3.92 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 136.0, 135.1, 130.7, 130.3, 124.8, 122.2, 121.4, 36.5 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for Mass for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>: 159.0922; Found: 159.0918.

IR (KBr, cm<sup>-1</sup>) 3144, 3084, 1576, 1095.

## Synthesis of 5a



**9-(4-(Pyridin-4-yl)phenyl)-9H-carbazole (5a).** 9-(4-Bromophenyl)-9H-carbazole (**4**) (1.00 g, 3.10 mmol, 1.00 equiv), pyridin-4-ylboronic acid hydrate (0.46 g, 3.26 mmol, 1.05 equiv), K<sub>2</sub>CO<sub>3</sub> (1.29 g, 9.31 mmol, 3.00 equiv) and Pd(dppf)Cl<sub>2</sub> × CH<sub>2</sub>Cl<sub>2</sub> (0.13 g, 0.16 mmol, 0.05 equiv) were combined in a 50 mL round-bottom flask. Acetonitrile (24 mL) and water (4 mL) were added, the flask was sealed and the formed suspension was stirred at room temperature. A stream of argon was passed through a vigorously stirred suspension for 10 minutes, and the formed black suspension was stirred at 90 °C for 1h whereupon the suspension turned brown. The reaction mixture was cooled and partitioned between water (100 mL) and DCM (100 mL). Layers were separated, and the water layer was washed with DCM (50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The black oily residue was purified by column chromatography on silica gel using 50% of EtOAc in petroleum ether as a mobile phase. The crude product was recrystallized from EtOAc to afford the title compound **5a** as pale green needles (0.75 g, 2.34 mmol, 75%).

Mp 248–250 °C (recrystallized from EtOAc).

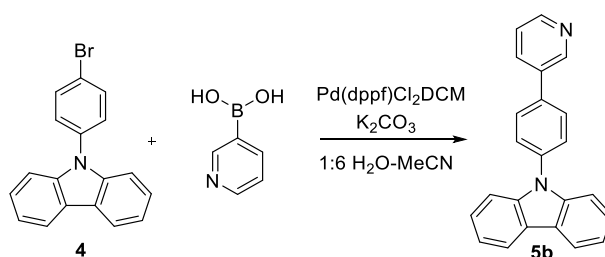
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.76-8.72 (m, 2H), 8.20-8.14 (m, 2H), 7.90-7.85 (m, 2H), 7.74-7.69 (m, 2H), 7.62-7.59 (m, 2H), 7.50-7.41 (m, 4H), 7.35-7.30 (m, 2H) ppm.

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ): 150.6, 147.5, 140.8, 138.8, 137.2, 128.6, 127.7, 126.2, 123.7, 121.7, 120.6, 120.4, 109.9 ppm.

Anal. Calcd for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>: C, 86.22; H, 5.03; N, 8.74. Found: C, 86.30; H, 5.02; N, 8.62.

HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calc for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>: 321.1392; Found: 321.1397.

IR (KBr, cm<sup>-1</sup>) 3462, 3058, 1593, 1451.

Synthesis of **5b**

**9-(4-(Pyridin-3-yl)phenyl)-9H-carbazole (5b).** 9-(4-Bromophenyl)-9H-carbazole **4** (1.00 g, 3.10 mmol, 1.00 equiv), pyridin-3-ylboronic acid (0.37 g, 3.01 mmol, 0.97 equiv), K<sub>2</sub>CO<sub>3</sub> (1.29 g, 9.31 mmol, 3.00 equiv) and Pd(dppf)Cl<sub>2</sub> × CH<sub>2</sub>Cl<sub>2</sub> (0.13 g, 0.16 mmol, 0.05 equiv) were combined in a 50 mL round bottom flask. Acetonitrile (24 mL) and water (4 mL) were added, the flask sealed and the formed suspension was stirred at room temperature. A stream of argon was passed through a vigorously stirred suspension for 10 minutes, and the formed black suspension was stirred at 90 °C for 1h. The brown reaction mixture was cooled and partitioned between water (100 mL) and DCM (100 mL). Layers were separated and the water layer was washed with DCM (50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The black oily residue was purified by column chromatography on silica gel using 50% of EtOAc in petroleum ether as a mobile phase. The crude product was recrystallized from EtOAc/Hexane to afford the title compound **5b** as brown crystals (0.72 g, 2.25 mmol, 72%).

Mp 168–170 °C (recrystallized from EtOAc/Hexane).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 9.00-8.96 (m, 1H), 8.69-8.65 (m, 1H) 8.20-8.14 (m, 2H), 8.00-7.95 (m, 1H), 7.85-7.79 (m, 2H), 7.73-7.67 (m, 2H), 7.51-7.41 (m, 5H), 7.35-7.30 (m, 2H) ppm.

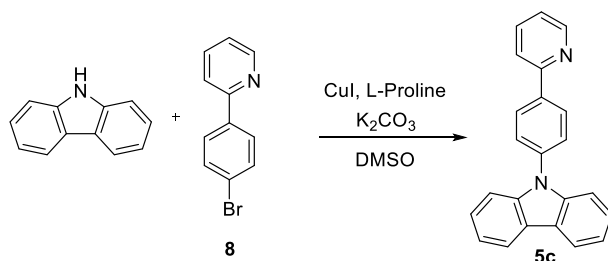
<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ): 149.0, 148.5, 140.8, 137.9, 137.0, 135.9, 134.4, 128.7, 127.7, 126.2, 123.8, 123.6, 120.5, 120.3 109.9 ppm.

HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calc for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>: 321.1392; Found: 321.1389.

IR (KBr, cm<sup>-1</sup>) 3055, 1603, 1520, 1452.



## Synthesis of 5c



**9-(4-(Pyridin-2-yl)phenyl)-9H-carbazole (5c).** Carbazole (0.90 g, 5.38 mmol, 1.00 equiv), 2-(4-bromophenyl)pyridine (**8**; 1.26 g, 5.38 mmol, 1.00 equiv), K<sub>2</sub>CO<sub>3</sub> (2.23 g, 16.14 mmol, 3.00 equiv), copper (I) iodide (0.15 g, 0.81 mmol, 0.15 equiv) and L-Proline (0.19 g, 1.61 mmol, 0.30 equiv) were combined in a 20 mL pressure vial, and the vial was flushed with argon and sealed. Anhydrous DMSO (15 mL) was added under inert atmosphere and the reaction mixture was stirred for 15 min until a black suspension is formed. The reaction mixture was stirred at 120 °C for 16h, then cooled, diluted with water (150 mL) and aqueous saturated ammonia (50 mL), and extracted with DCM (3x50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The brown oily residue was purified by column chromatography on silica gel using 5% of EtOAc in hexane as a mobile phase. The crude product was recrystallized from Et<sub>2</sub>O to afford the title compound **5c** as pale green powder (0.38 g, 1.20 mmol, 22%).

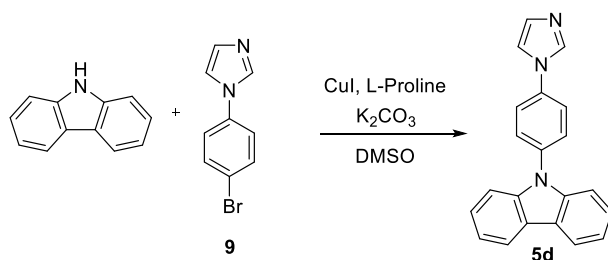
Mp 173–175 °C (recrystallized from Et<sub>2</sub>O).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.80-8.73 (m, 1H), 8.28-8.22 (m, 2H), 8.20-8.15 (m, 2H), 7.85-7.79 (m, 2H), 7.73-7.67 (m, 2H), 7.53-7.41 (m, 4H), 7.36-7.27 (m, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ): 156.7, 150.0, 140.9, 138.6, 138.5, 137.0, 128.5, 127.3, 126.1, 123.6, 122.5, 120.7, 120.5, 120.2 110.0 ppm.

HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calc for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>: 321.1392; Found: 321.1396.

IR (KBr, cm<sup>-1</sup>) 3055, 1605, 1452.

Synthesis of imidazole **5d**

**9-(4-(1H-Imidazol-1-yl)phenyl)-9H-carbazole (5d).** Carbazole (0.90 g, 5.38 mmol, 1.20 equiv), 1-(4-bromophenyl)-1H-imidazole (**9**; 1.00 g, 4.48 mmol, 1.00 equiv), K<sub>2</sub>CO<sub>3</sub> (1.86 g, 13.45 mmol, 3.00 equiv), copper (I) iodide (0.13 g, 0.67 mmol, 0.15 equiv) and L-Proline (0.16 g, 1.35 mmol, 0.30 equiv) were combined in a 20 mL pressure vial. The vial was flushed with argon and sealed. Anhydrous DMSO (15 mL) was added under inert atmosphere and the reaction mixture was stirred for 15 min until a black suspension is formed. The reaction mixture was stirred at 140 °C for 72h, the resulting brown suspension was cooled, diluted with water (150 mL), aqueous saturated ammonia (50 mL) and extracted with DCM (3x50 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The brown oily residue was purified by column chromatography on silica gel using 50% of EtOAc in hexane as a mobile phase. The crude product was recrystallized from *i*-PrOH to afford the title compound **5d** as colorless crystals (0.65 g, 2.09 mmol, 47%).

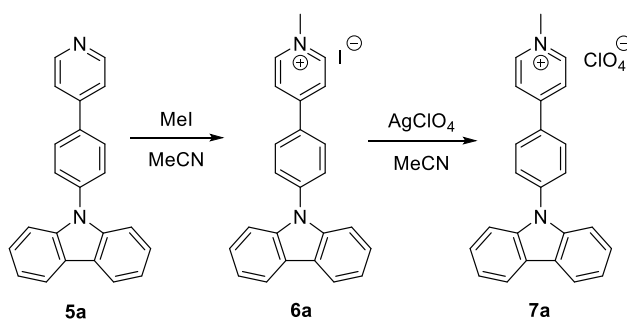
Mp 222–224 °C; (recrystallized from *i*-PrOH).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.19-8.15 (m, 2H), 7.98-7.95 (m, 1H) 7.72-7.67 (m, 2H), 7.65-7.60 (m, 2H), 7.47-7.41 (m, 4H), 7.40-7.37 (m, 1H), 7.36-7.28 (m, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ): 140.8, 137.1, 136.3, 135.8, 131.0, 128.7, 126.3, 123.7, 123.0, 120.6, 120.5, 118.4, 109.6 ppm.

HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> calc for C<sub>21</sub>H<sub>16</sub>N<sub>3</sub>: 310.1344; Found: 310.1344.

IR (KBr, cm<sup>-1</sup>) 3049, 1520, 1450.

Synthesis of **6a** and **7a**

**4-(4-(9H-Carbazol-9-yl)phenyl)-1-methylpyridin-1-ium iodide (6a).** To a clear solution of pyridine **5a** (0.40 g, 1.25 mmol, 1.0 equiv) in anhydrous acetonitrile (10 mL) was added iodomethane (0.23 g, 1.62 mmol, 1.3 equiv) and the resulting colorless suspension was stirred in a pressure vial at 80 °C for 16h. The reaction mixture was cooled in an ice bath and EtOAc (100 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and dried *in vacuo* to afford the title compound **6a** as pale green powder (0.54 g, 1.17 mmol, 94%).

Mp 270–280 °C (dec.); recrystallized from MeCN/Et<sub>2</sub>O.

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 9.00-8.95 (m, 2H), 8.56-8.51 (m, 2H), 8.37-8.32 (m, 2H), 8.29-8.24 (m, 2H), 7.94-7.89 (m, 2H), 7.54-7.45 (m, 4H), 7.36-7.31 (m, 2H), 4.35 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 153.7, 145.9, 140.6, 139.8, 132.4, 130.3, 127.5, 126.9, 124.4, 123.5, 121.1, 121.0, 110.1, 47.5 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>: 335.1548; Found: 335.1549.

IR (KBr, cm<sup>-1</sup>) 3208, 3003, 1942.

**4-(4-(9H-Carbazol-9-yl)phenyl)-1-methylpyridin-1-ium perchlorate (7a).** To a solution of **6a** (0.21 g, 0.45 mmol, 1.0 equiv) in MeCN (10 mL) was added a solution of AgClO<sub>4</sub> (0.14 g, 0.68 mmol, 1.5 equiv) in MeCN (2 mL). The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad was washed with MeCN. The filtrate was evaporated to give an off-white solid which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **7a** as a pale yellow powder (0.19 g, 0.44 mmol, 98%).

Mp 299–301 °C (dec.); recrystallized from *i*-PrOH.

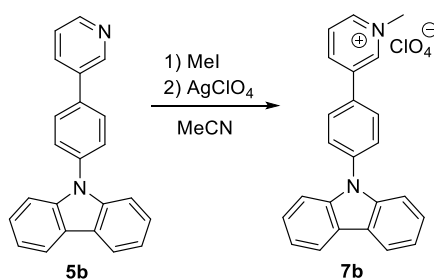
$^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $\delta$ ): 9.00-8.95 (m, 2H), 8.56-8.50 (m, 2H), 8.37-8.31 (m, 2H), 8.29-8.23 (m, 2H), 7.94-7.88 (m, 2H), 7.54-7.45 (m, 4H), 7.36-7.29 (m, 2H), 4.34 (s, 3H) ppm.

$^{13}\text{C}$  NMR (100.6 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $\delta$ ): 153.7, 145.9, 140.6, 139.9, 132.4, 130.3, 127.6, 126.9, 124.4, 123.5, 121.1, 121.0, 110.1, 47.5 ppm.

HRMS (ESI-TOF)  $m/z$ :  $[\text{M}]^+$  calc for  $\text{C}_{24}\text{H}_{19}\text{N}_2^+$ : 335.1548; Found: 335.1551.

IR (KBr,  $\text{cm}^{-1}$ ) 3430, 3057, 1602, 1084.

### Synthesis of **7b**



**3-(4-(9H-Carbazol-9-yl)phenyl)-1-methylpyridin-1-ium perchlorate (7b)**. To a suspension of pyridine **5b** (0.11 g, 0.35 mmol, 1.00 equiv) in anhydrous acetonitrile (3 mL) was added iodomethane (0.07 g, 0.52 mmol, 1.50 equiv) and the resulting green suspension was stirred in a pressure vial at 80 °C for 16h. The resulting clear green solution was cooled in an ice bath and EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt was added a solution of  $\text{AgClO}_4$  (0.09 g, 0.46 mmol, 1.30 equiv) in MeCN (2 mL). The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad was washed with acetonitrile. The filtrate was evaporated to give a white solid which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **2b** as a white powder (0.14 g, 0.33 mmol, 94%).

Mp 247–249 °C (recrystallized from *i*-PrOH).

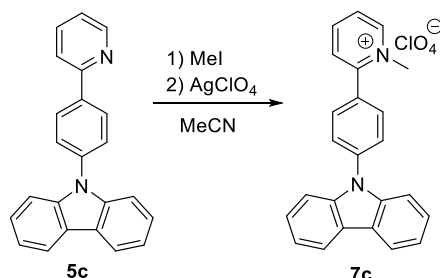
$^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $\delta$ ): 9.44-9.40 (m, 1H), 8.95 -8.89 (m, 2H), 8.27-8.22 (m, 2H), 8.21-8.12 (m, 3H), 7.88-7.83 (m, 2H), 7.50-7.43 (m, 4H), 7.36-7.28 (m, 2H), 4.42 (s, 3H) ppm.

$^{13}\text{C}$  NMR (100.6 MHz,  $(\text{CD}_3)_2\text{SO}$ ,  $\delta$ ): 144.2, 144.0, 142.6, 140.1, 139.0, 138.9, 132.4, 129.7, 128.2, 127.7, 126.9, 123.4, 121.1, 121.0, 110.0, 48.6 ppm.

HRMS (ESI-TOF)  $m/z$ :  $[M]^+$  calc for  $C_{24}H_{19}N_2^+$ : 335.1548; Found: 335.1545.

IR (KBr,  $cm^{-1}$ ) 3075, 1607, 1101.

### Synthesis of **7c**



**2-(4-(9H-Carbazol-9-yl)phenyl)-1-methylpyridin-1-ium perchlorate (7c)**. To a suspension of pyridine **5c** (0.11 g, 0.35 mmol, 1.00 equiv) in anhydrous acetonitrile (3 mL) was added iodomethane (0.07 g, 0.52 mmol, 1.50 equiv) and the resulting pale green suspension was stirred in a pressure vial at 80 °C for 16h. The reaction mixture was cooled in an ice bath and EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt was added a solution of AgClO<sub>4</sub> (0.09 g, 0.46 mmol, 1.30 equiv) in MeCN (2 mL). The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad washed with acetonitrile. The filtrate was evaporated to give white solid which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **7c** as a white powder (0.08 g, 0.19 mmol, 54%).

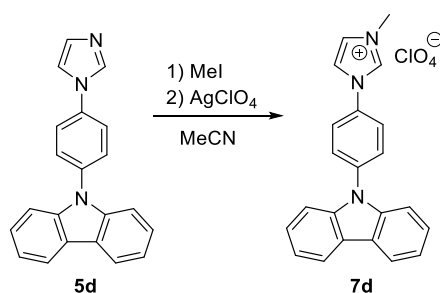
Mp 227–229 °C (recrystallized from *i*-PrOH).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO,  $\delta$ ): 9.10-9.06 (m, 1H), 8.68-8.62 (m, 1H), 8.28-8.23 (m, 2H), 8.20-8.11 (m, 2H), 7.98-7.87 (m, 4H), 7.57-7.52 (m, 2H), 7.51-7.45 (m, 2H), 7.37-7.29 (m, 2H), 4.24 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO,  $\delta$ ): 154.8, 147.1, 145.9, 140.0, 139.7, 131.7, 130.6, 130.3, 127.2, 126.9, 123.5, 121.1, 121.0, 110.2, 47.6 ppm.

HRMS (ESI-TOF)  $m/z$ :  $[M]^+$  calc for  $C_{24}H_{19}N_2$ : 335.1548; Found: 335.1546.

IR (KBr,  $cm^{-1}$ ) 3451, 3051, 1605, 1085.

Synthesis of **7d**

**1-(4-(9H-Carbazol-9-yl)phenyl)-3-methyl-1H-imidazol-3-ium perchlorate (7d).** To a clear solution of imidazole **5d** (0.11 g, 0.35 mmol, 1.00 equiv) in anhydrous acetonitrile (2 mL) was added iodomethane (0.07 g, 0.52 mmol, 1.50 equiv) and the resulting colorless suspension was stirred in a pressure vial at 80 °C for 16h. The pale green solution was cooled in an ice bath and EtOAc (50 mL) was added to form precipitate. The precipitate was filtered, washed with EtOAc and redissolved in acetonitrile (10 mL). To the MeCN solution of the iodide salt was added a solution of AgClO<sub>4</sub> (0.09 g, 0.46 mmol, 1.30 equiv) in MeCN (2 mL). The resulting suspension was stirred at room temperature for 30 minutes, then filtered through a pad of Celite and the pad was washed with acetonitrile. The filtrate was evaporated to give a white solid, which was suspended in *i*-PrOH (20 mL), sonified, left to stand at -15 °C for 2h, filtered and washed with *i*-PrOH to afford the title compound **7d** as a white powder (0.14 g, 0.33 mmol, 94%).

Mp 143–145 °C (*i*-PrOH).

<sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 9.72-9.69 (m, 1H), 8.31-8.28 (m, 1H), 8.26-8.23 (m, 2H), 8.05-7.99 (m, 2H), 7.94-7.87 (m, 3H), 7.50-7.41 (m, 4H), 7.35-7.29 (m, 2H), 3.97 (s, 3H) ppm.

<sup>13</sup>C NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, δ): 140.2, 138.4, 136.3, 133.8, 128.6, 127.0, 124.9, 124.2, 123.4, 121.5, 121.1, 109.9, 36.6 ppm.

HRMS (ESI-TOF) *m/z*: [M]<sup>+</sup> calc for C<sub>22</sub>H<sub>18</sub>N<sub>3</sub>: 324.1501; Found: 324.1508.

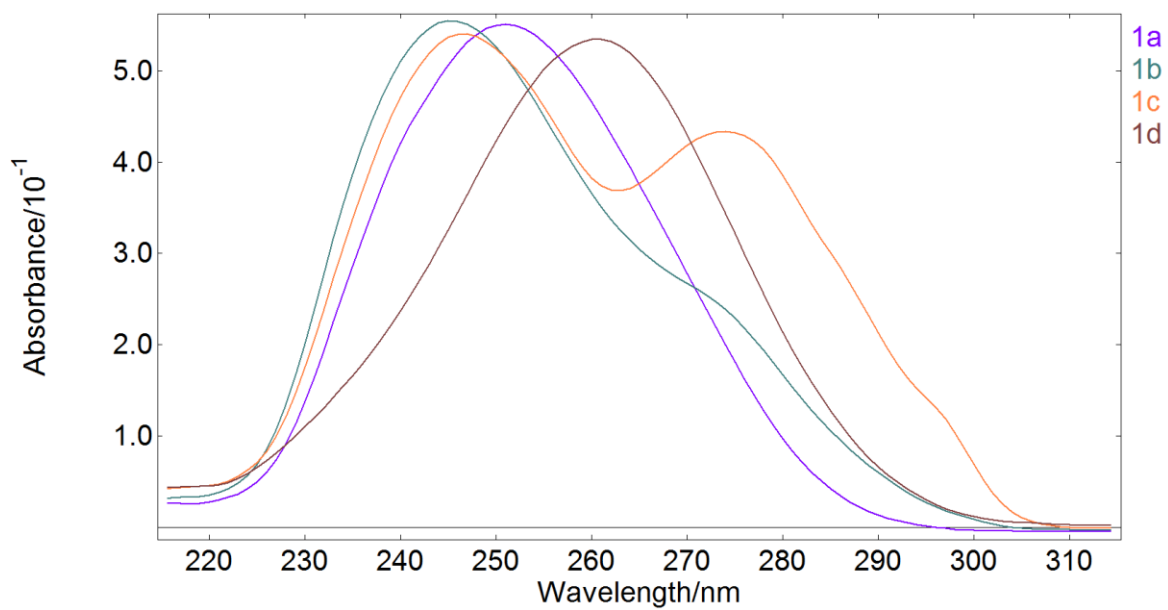
IR (KBr, cm<sup>-1</sup>) 3519, 3160, 3083, 2964, 1083.

**Absorption spectra for 1a–d, 2a, 3a–d, 5a–d, 6a and 7a–d in MeCN**

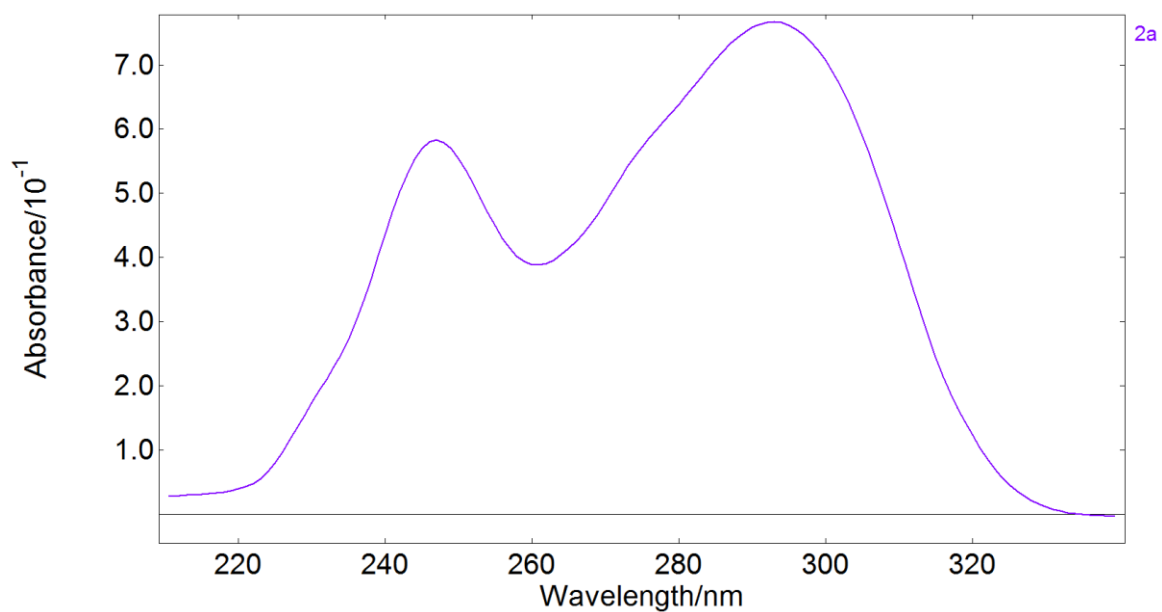
UV-vis spectra of all synthesized quaternary heteroaromatic salts and parent heterocycles were measured in MeCN solutions (at *ca.*  $10^{-5}$  mol L<sup>-1</sup> concentration) at room temperature and under ambient atmosphere. The absorption spectra of the phenyl-substituted pyridines and imidazole **1a–d** displayed 1 or 2 absorption bands in the range of 241–274 nm. The corresponding *N*-alkylated pyridinium and imidazolium salts **2a** and **3a–d** featured wider absorption range from 231 nm to 294 nm with 1 to 3 absorption bands (entries 1–5, Table S1). The attachment of carbazole moiety in **1a–d** afforded luminophores **5a–d**, respectively, with absorption bands in the 238–274 nm region (similar to those for **1a–d**) and with additional absorption bands in the range from 290 to 339 nm (entries 6–9, Table S1). Carbazole-containing quaternary heteroarene salts **7b** and **7d** displayed similar absorption to the parent **5b** and **5d**, whereas pyridinium salts **6a**, **7a** and **7c** featured 22–57 nm red-shift of absorption at 376, 379 and 337 nm respectively (entries 10,11,13, Table S1).

**Table S1.** Absorption data of luminophores **2a–7d**

entry	compound	$\lambda_{\text{abs}}$ , nm
1	<b>2a</b>	247, 293
2	<b>3a</b>	231, 294
3	<b>3b</b>	237, 257, 292
4	<b>3c</b>	239, 282
5	<b>3d</b>	235
6	<b>5a</b>	238, 292, 322
7	<b>5b</b>	240, 292, 338
8	<b>5c</b>	240, 292, 315
9	<b>5d</b>	240, 292, 326, 339
10	<b>6a</b>	237, 282, 376
11	<b>7a</b>	239, 282, 379
12	<b>7b</b>	236, 289, 339
13	<b>7c</b>	237, 279, 337
14	<b>7d</b>	241, 291, 336

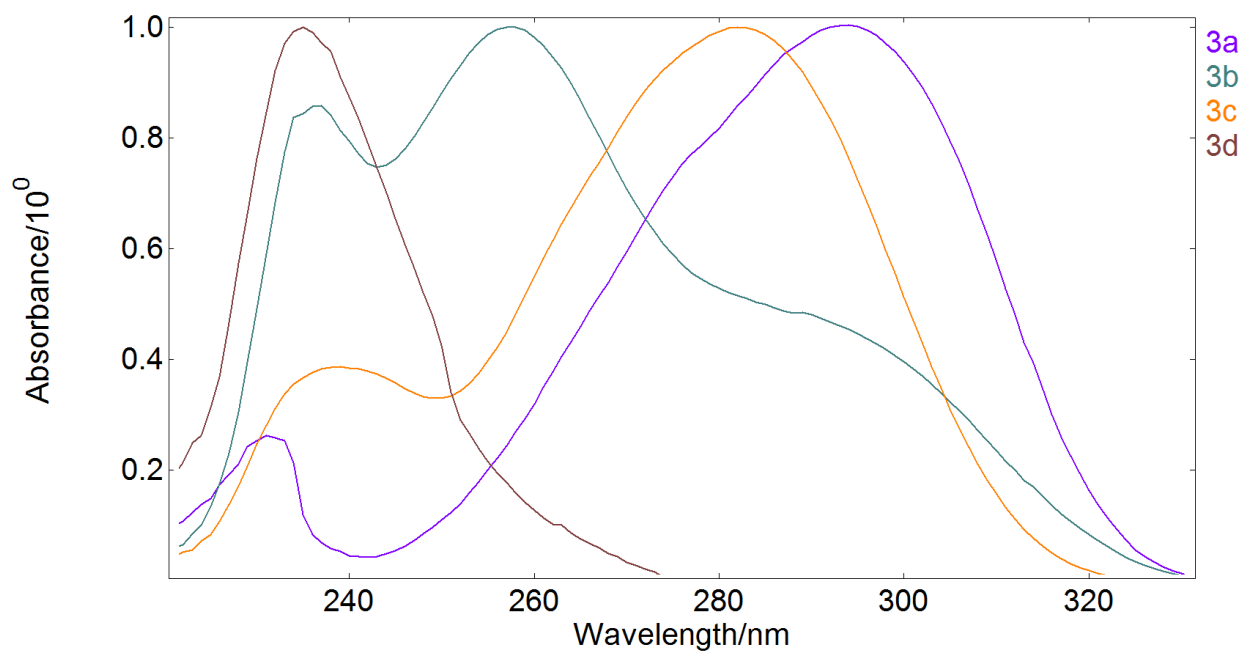


**Fig. S1.** Absorption of **1a–d** in MeCN solution (at 10<sup>-5</sup> mol/L)

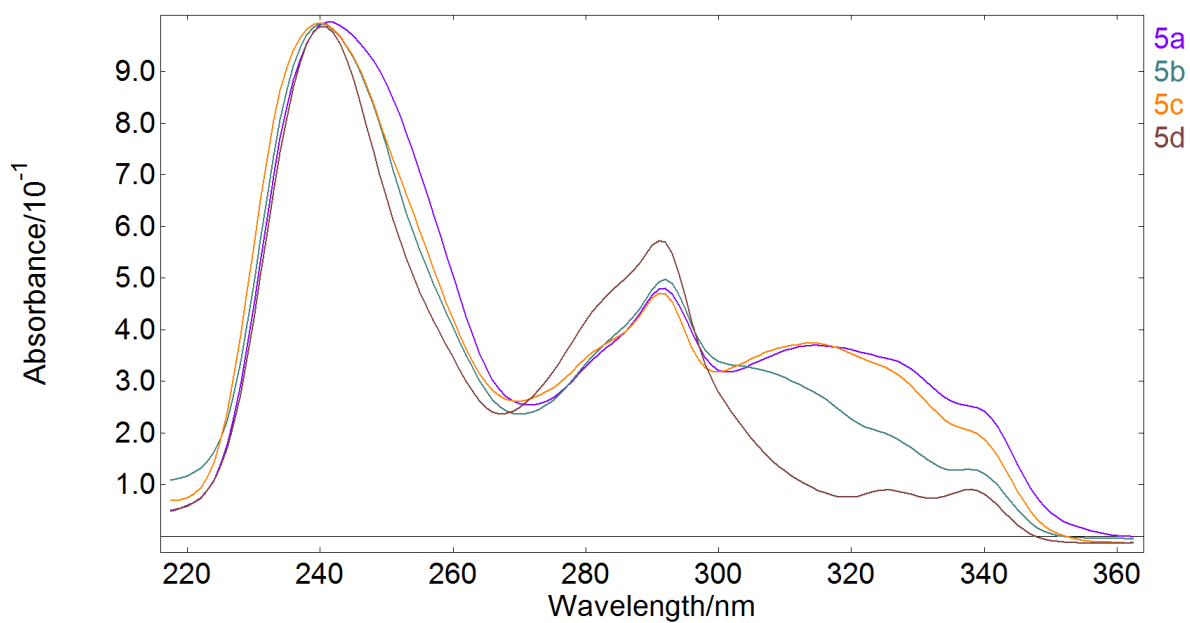


**Fig. S2.** Absorption of **2a** in MeCN solution (at 10<sup>-5</sup> mol/L)

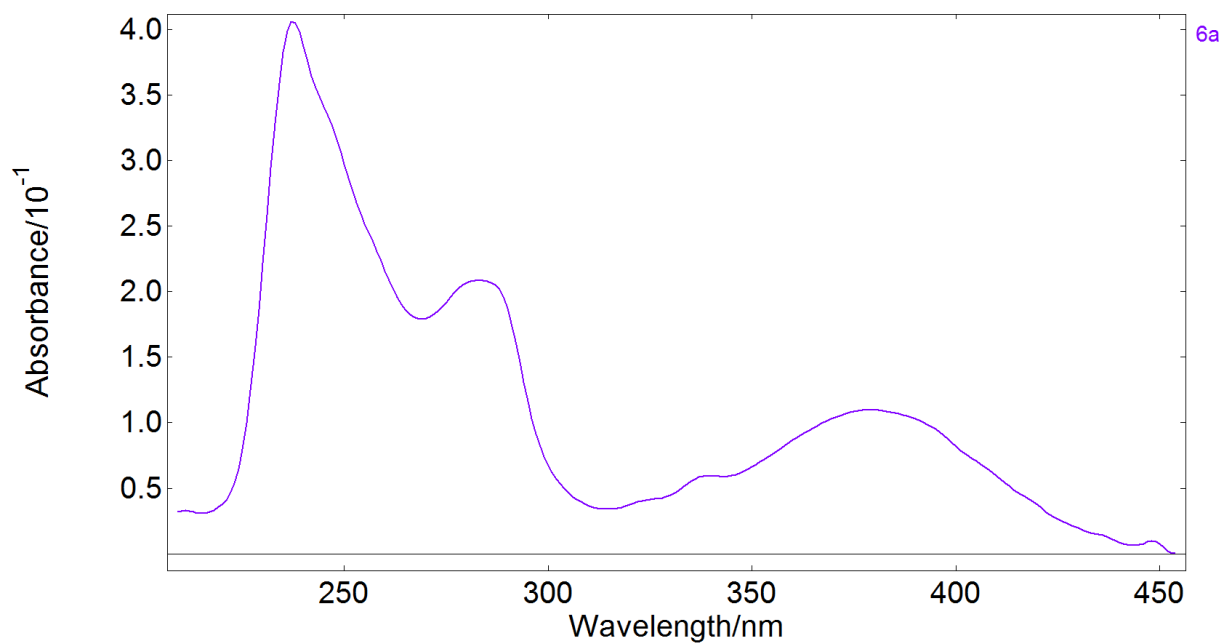




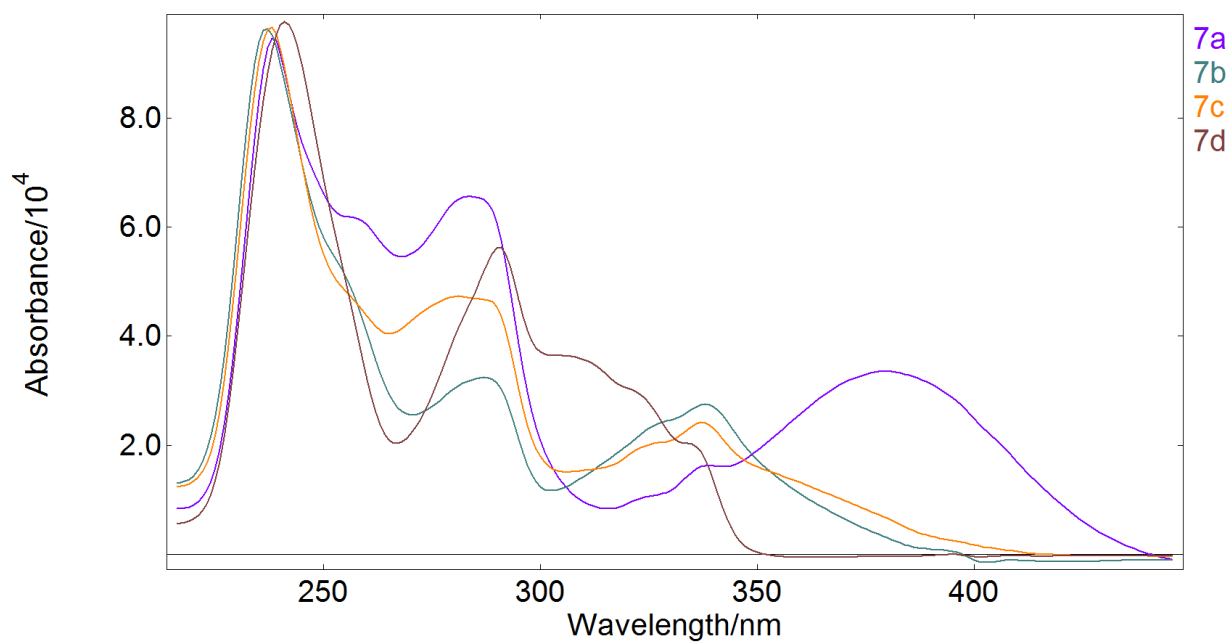
**Fig. S3.** Absorption of **3a–d** in MeCN solution (at  $10^{-5}$  mol/L)



**Fig. S4.** Absorption of **5a–d** in MeCN solution (at  $10^{-5}$  mol/L)

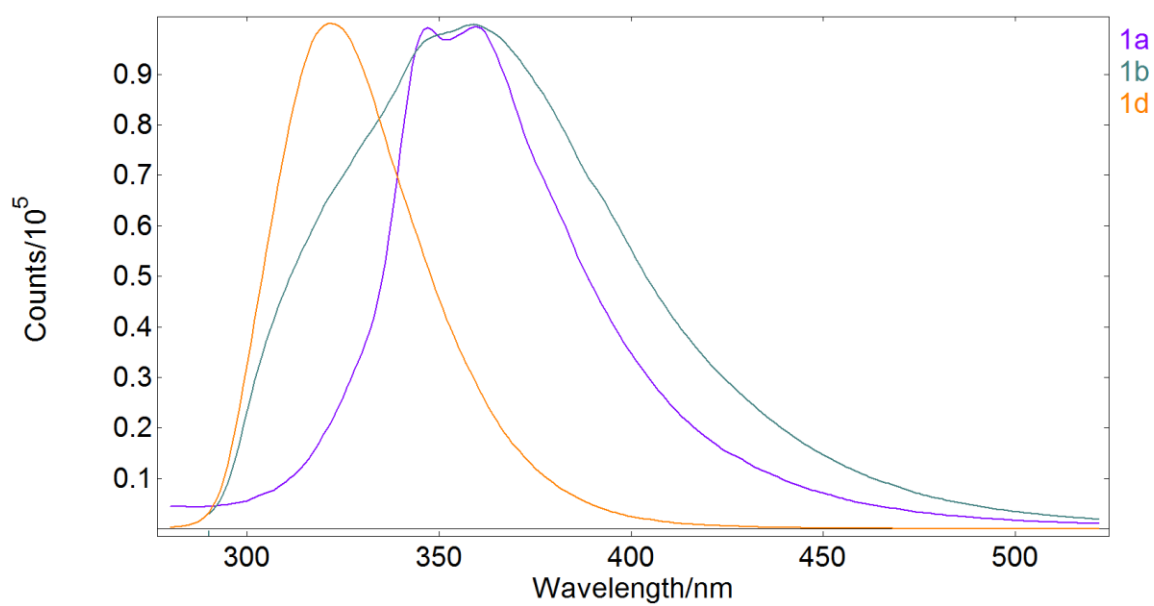
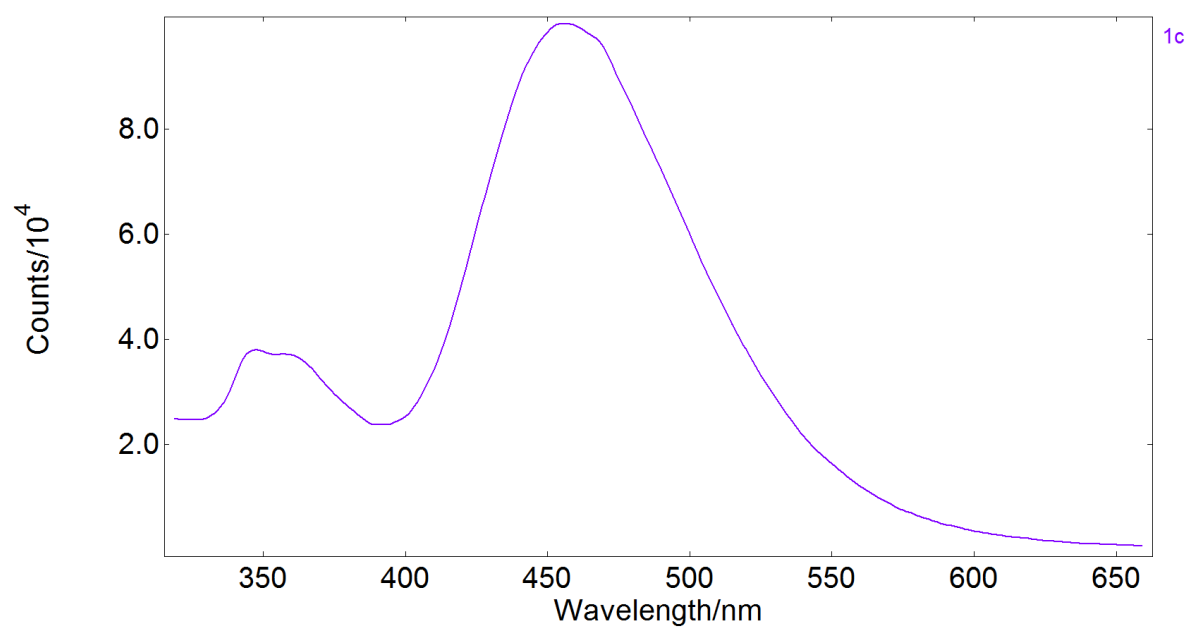


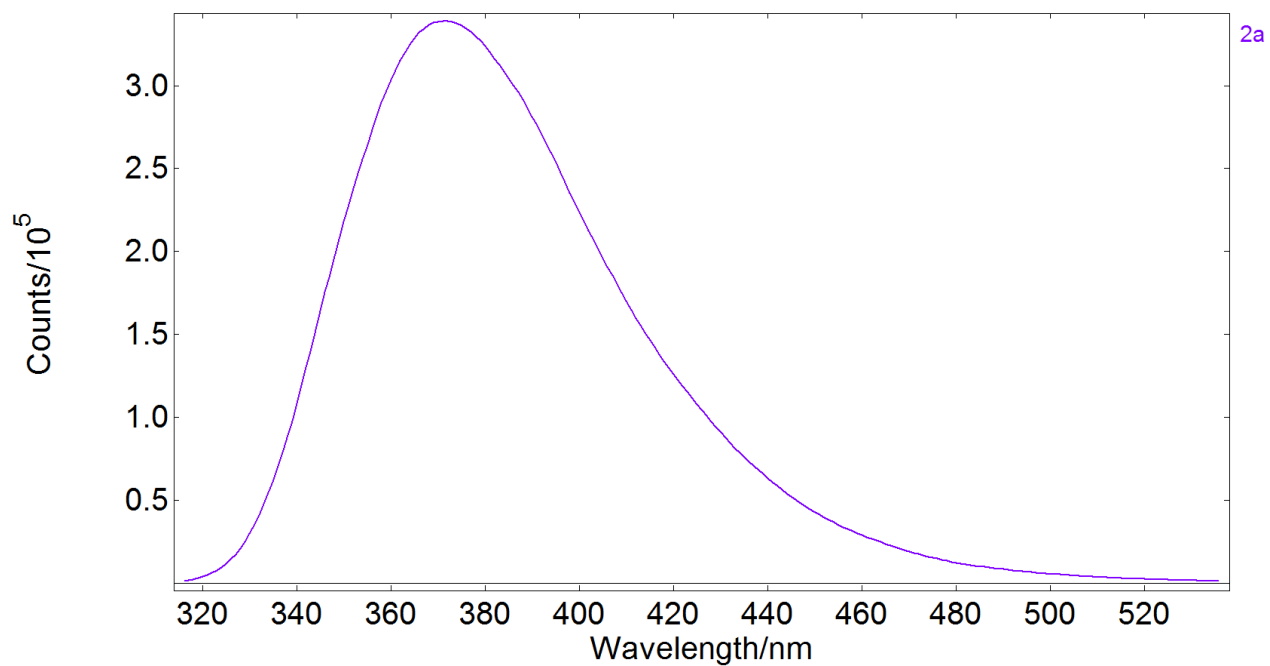
**Fig. S5.** Absorption of **6a** in MeCN solution (at 10<sup>-5</sup> mol/L)



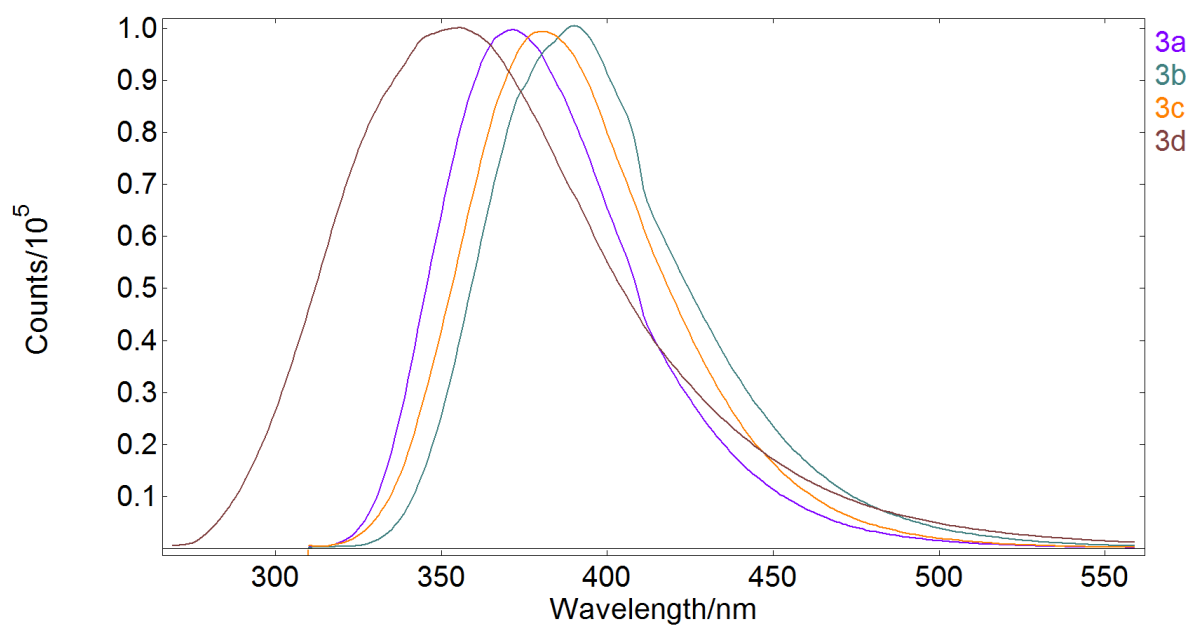
**Fig. S6.** Absorption of **7a–d** in MeCN solution (at 10<sup>-5</sup> mol/L)

## Emission spectra for 1a–d, 2a, 3a–d

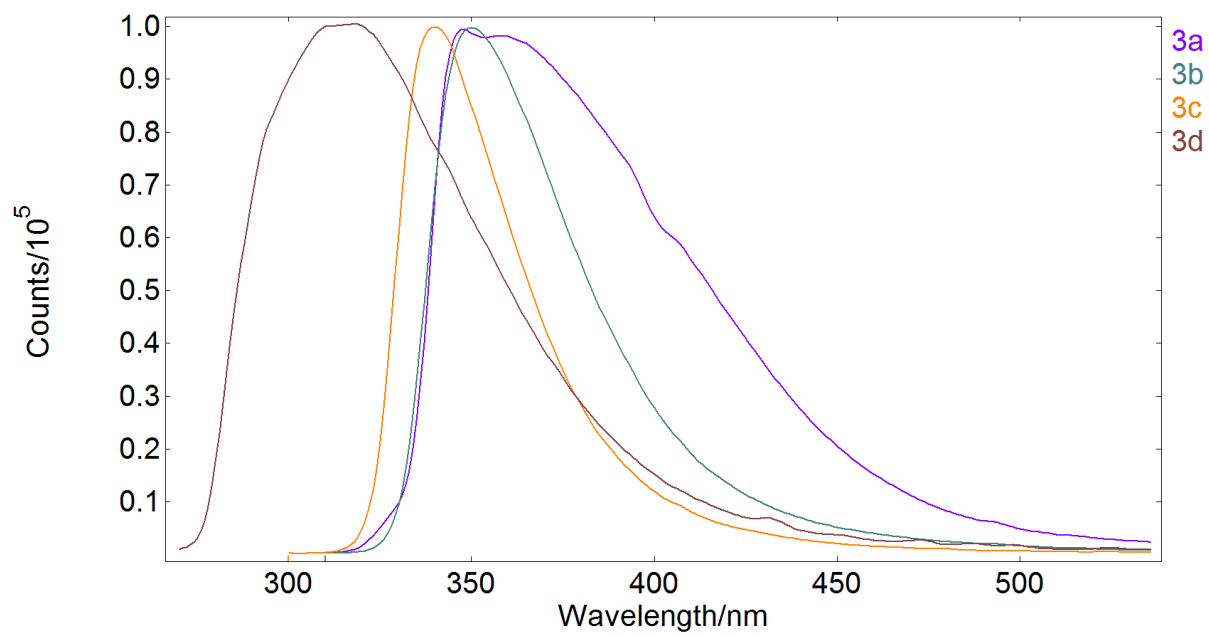
**Fig. S7.** Emission of **1a**, **1b** and **1d** in MeCN solution (at  $10^{-5}$  mol/L)**Fig. S8.** Emission of **1c** in MeCN solution (at  $10^{-5}$  mol/L)



**Fig. S9.** Emission of **2a** in MeCN solution (at  $10^{-5}$  mol/L)



**Fig. S10.** Emission of **3a–d** in MeCN solution (at  $10^{-5}$  mol/L)



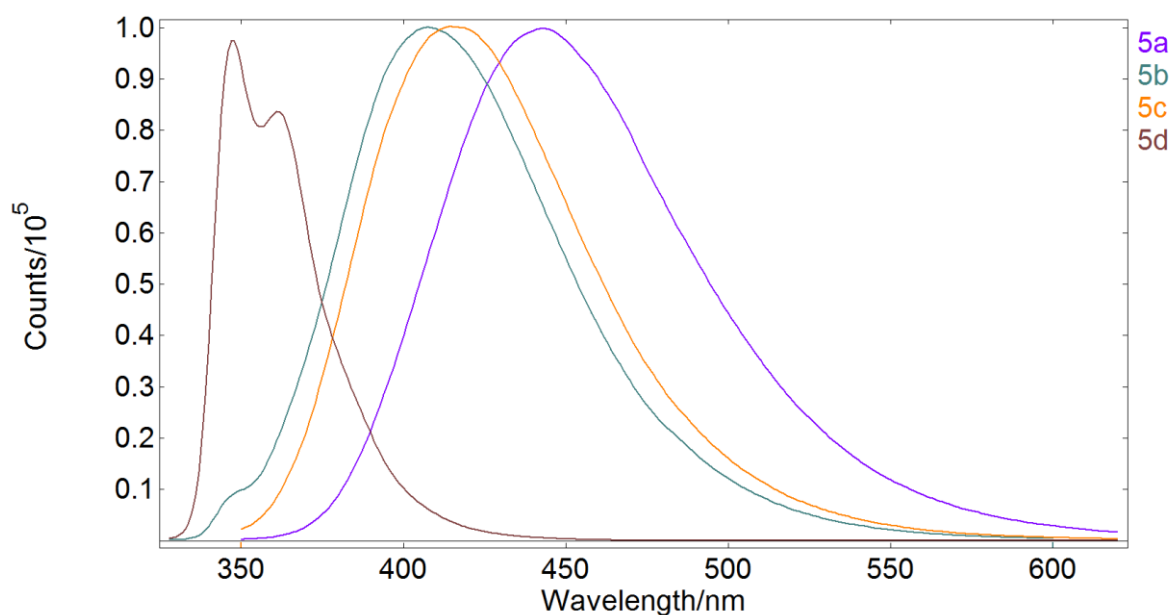
**Fig. S11.** Emission of **3a–d** in the solid state

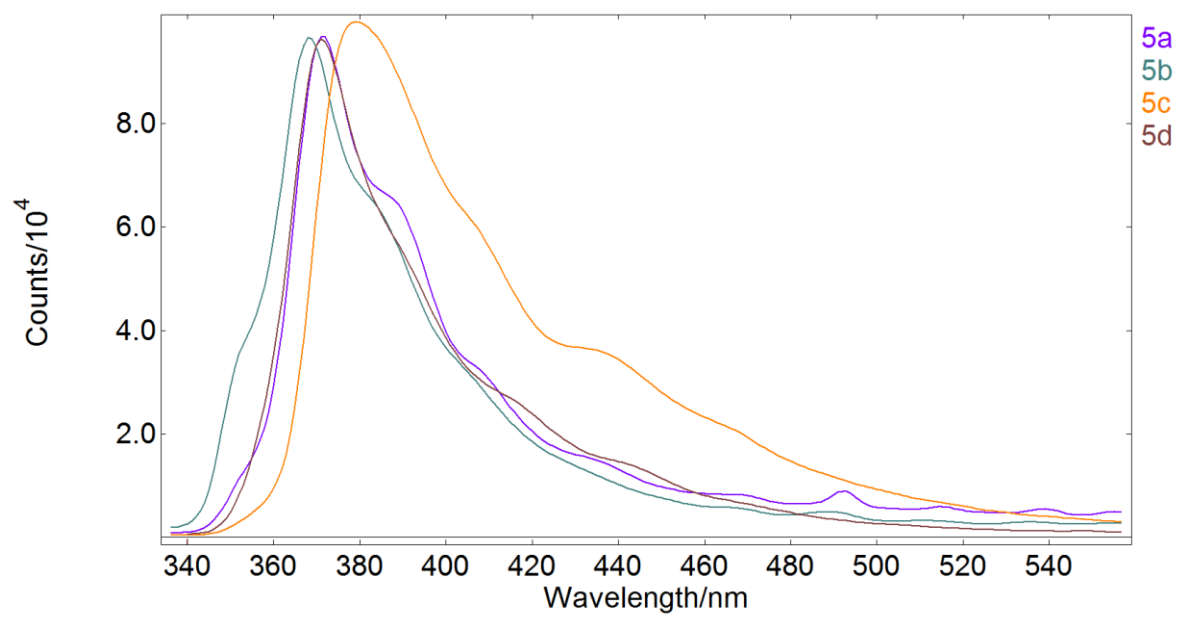
**Emission spectra for 5a–d**

The presence of strong intermolecular interactions leading to the pronounced ACQ effect in **5a,b** is also supported by the observed hypsochromic shift of the solid-state emission (entries 1-2, Table S2). Interestingly, **5c** featured only a partial hypsochromic character of the emission as a new red-shifted solid-state emission peak at 436 nm was observed (entry 3, Table S2). Likewise, lack of the change in the emission spectra when going from the solution to the solid state was observed for **5d**. These observations correlated well with the less-pronounced ACQ effect for both **5c** and **5d**.

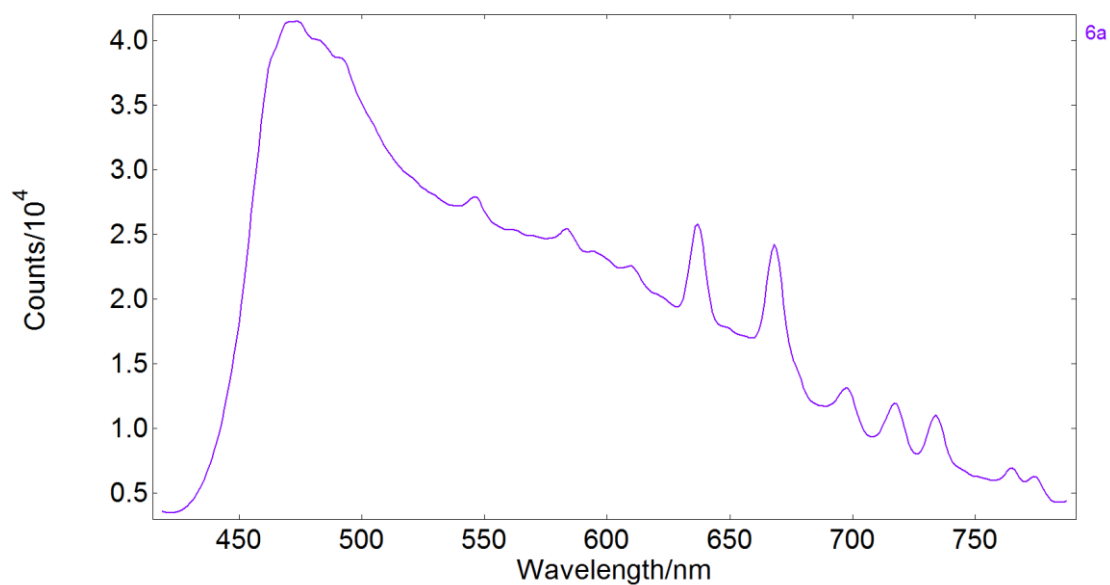
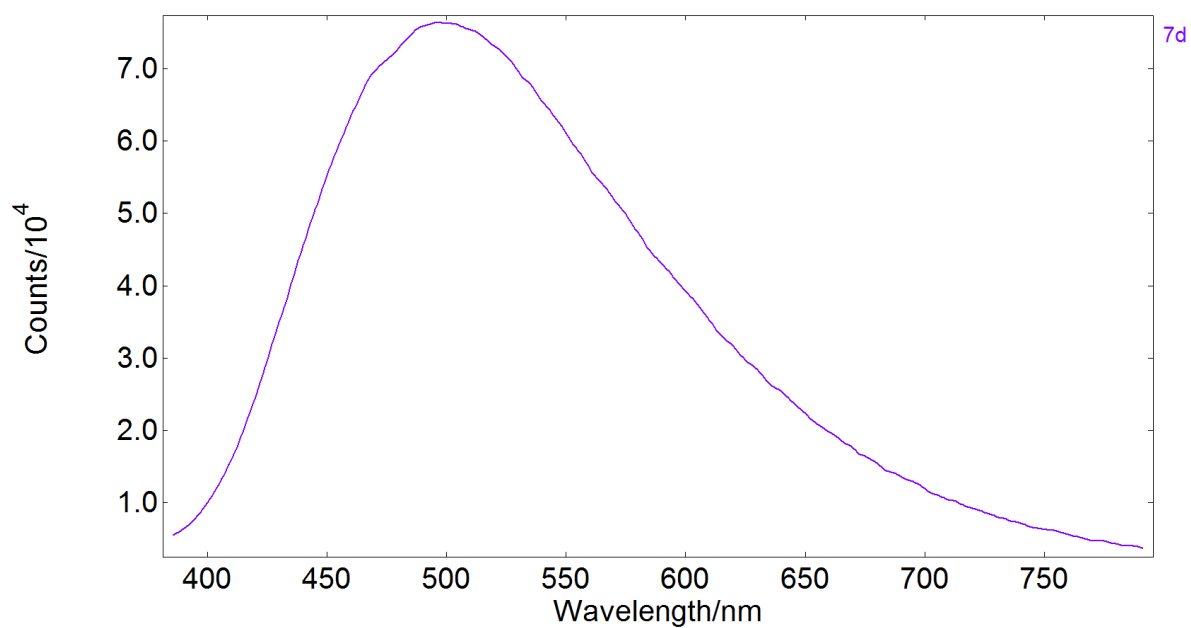
**Table S2.** Photoluminescence emission data for luminophores **5a–d**

entry	compound	Solution $\lambda_{em}$ , nm	Solid $\lambda_{em}$ , nm	Solution, $\phi$ (%)	Solid, $\phi$ (%)	$\alpha_{AIE}$
1	<b>5a</b>	442	371, 387, 407	73.1	5.7	0.1
2	<b>5b</b>	408	368	46.5	0.6	<0.1
3	<b>5c</b>	416	378, 436	74.6	16.8	0.2
4	<b>5d</b>	347, 361	371	33.2	17.8	0.5

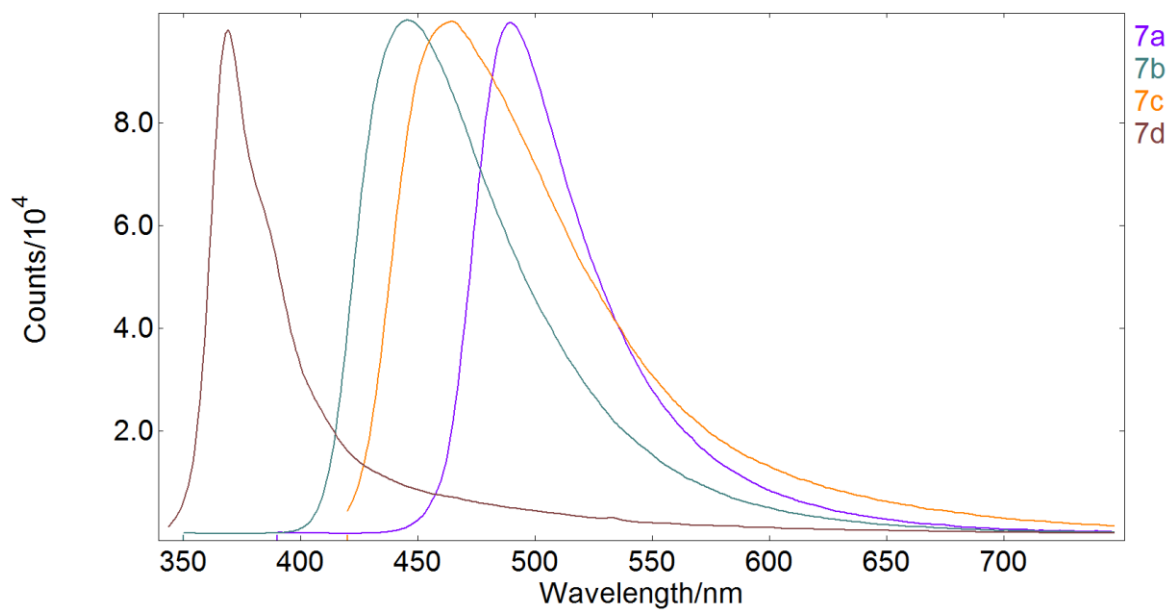
**Fig. S12.** Emission of **5a–d** in MeCN solution (at  $10^{-5}$  mol/L)



**Fig. S13.** Emission of **5a–d** in the solid state

**Emission spectra for 6a and 7a–d****Fig. S14.** Emission of **6a** in the solid state**Fig. S15.** Emission of **7d** in MeCN solution (at 10<sup>-5</sup> mol/L)

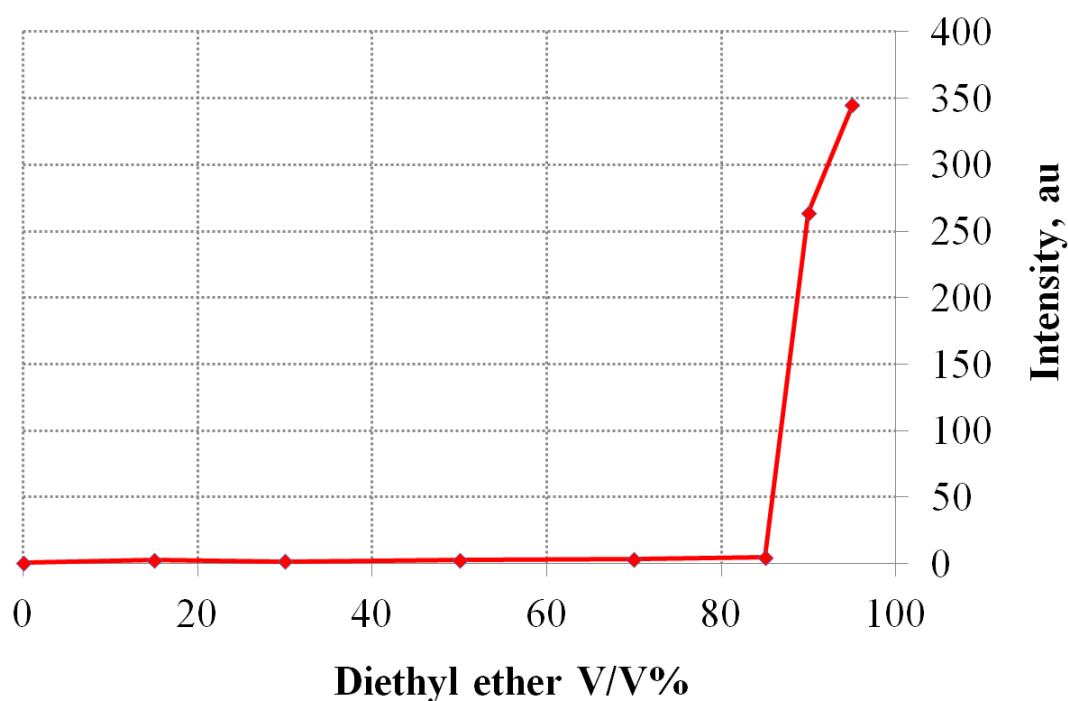




**Fig. S16.** Emission of **7a–d** in the solid state

**Correlation between the solid state emission and aggregation for 7a**

Solid state photoluminescence behavior of the most efficient luminophore **7a** was further investigated in various mixtures of MeCN (good solvent) and Et<sub>2</sub>O (poor solvent) to get an additional insight into the AIE properties of quaternary heteroaromatic salts **7a–d**. Lack of the emission for **7a** was observed in solvent mixtures containing up to 90% Et<sub>2</sub>O, whereas intense emission was observed in mixtures containing high fraction (90-95% v/v) of Et<sub>2</sub>O in MeCN (Fig S1). Importantly, dynamic light scattering (DLS) measurements indicated formation of aggregates in solvent mixtures with more than 90% v/v of Et<sub>2</sub>O in acetonitrile (Fig. S2). The formed aggregates displayed Gaussian distribution with the average particle size of 540 nm (Fig. S3). The apparent correlation between the emission and formation of aggregates provided an additional support to AIE properties of perchlorate salts **7a–d**.



**Fig. S1.** Emission of **7a** in Et<sub>2</sub>O/MeCN mixtures

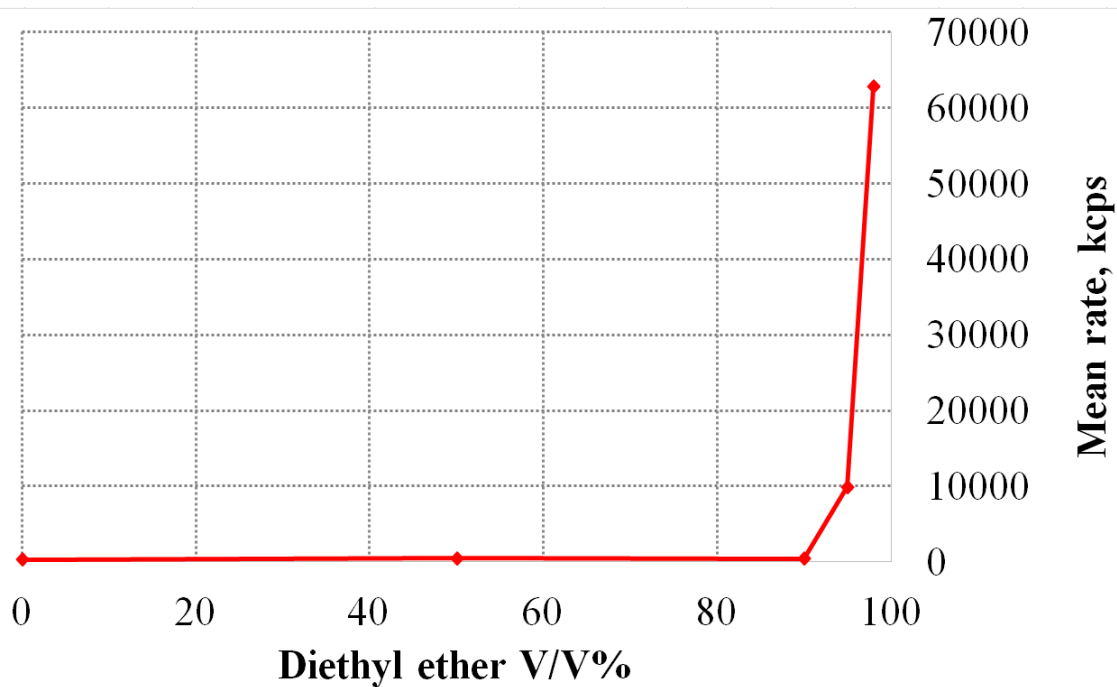


Fig. S2. DLS values of **7a** in Et<sub>2</sub>O/MeCN mixtures

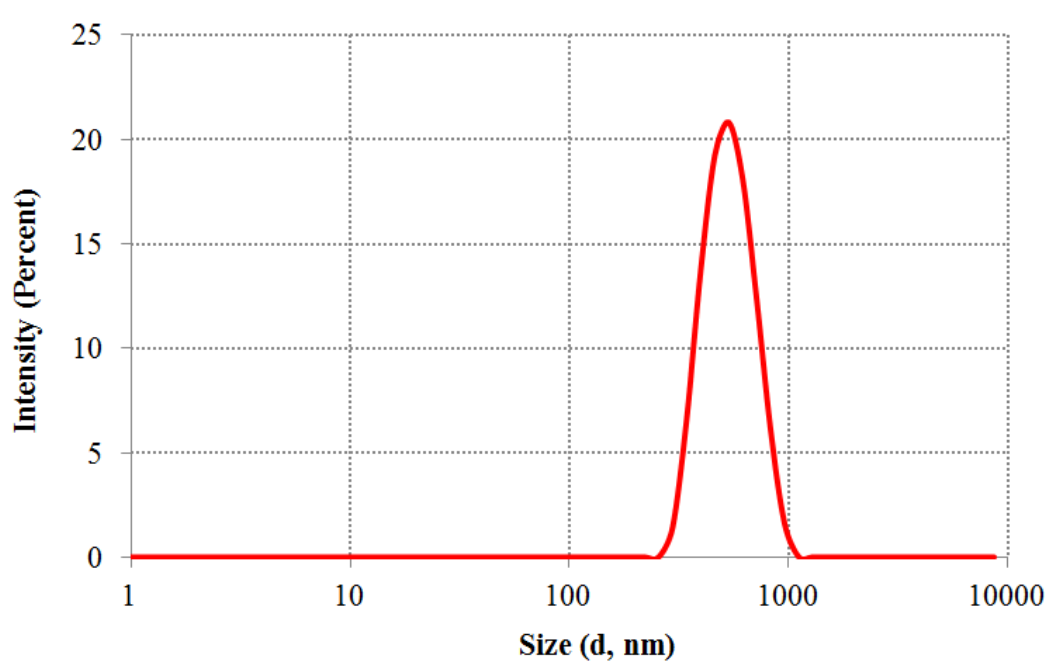
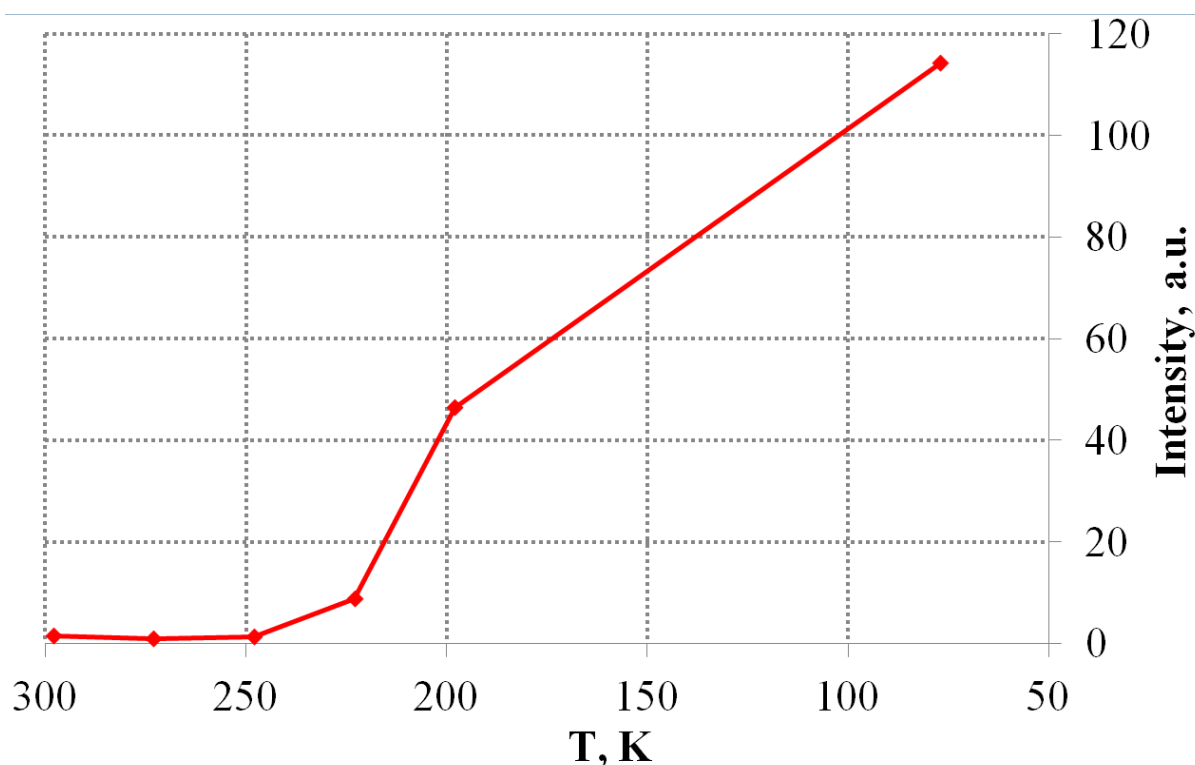


Fig. S3. Particle size distribution observed for aggregates of **7a**

**Emission of 7a in DMSO matrix**

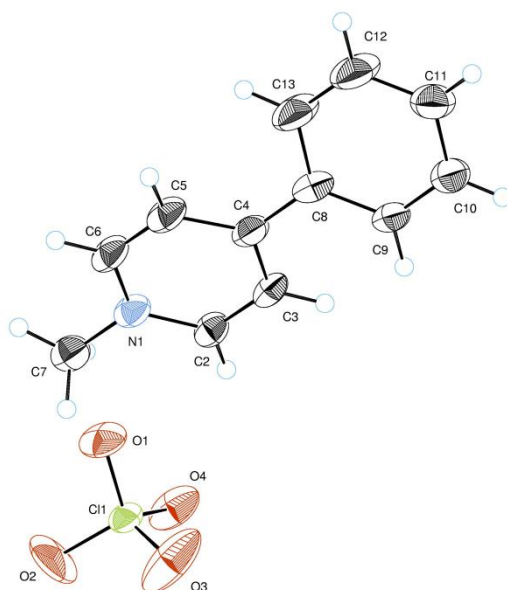
We have also examined whether AIE properties of quaternary heteroaromatic salts **1a–d** and **7a–d** originate from restriction of intramolecular rotation (RIR) phenomena.<sup>1</sup> To this end we measured a relationship between emission of **7a** in DMSO solution and temperature in the range from 77 K to 293 K (Fig. 3D). A solution of **7a** in DMSO did not display observable emission at 293 K. Importantly, the emission increase could not be determined after freezing of the DMSO solution of **7a**, as well as upon further cooling to 248 K. The emission only started to appear at temperatures below 233 K. Lack of the emission for **7a** in the DMSO matrix (at 248 K and 273 K) points against the RIR mechanism as the origin of AIE properties of **7a**, because considerable enhancement of the emission in solid matrices is usually observed for most of AIEgens that benefit from RIR effect.<sup>2</sup>



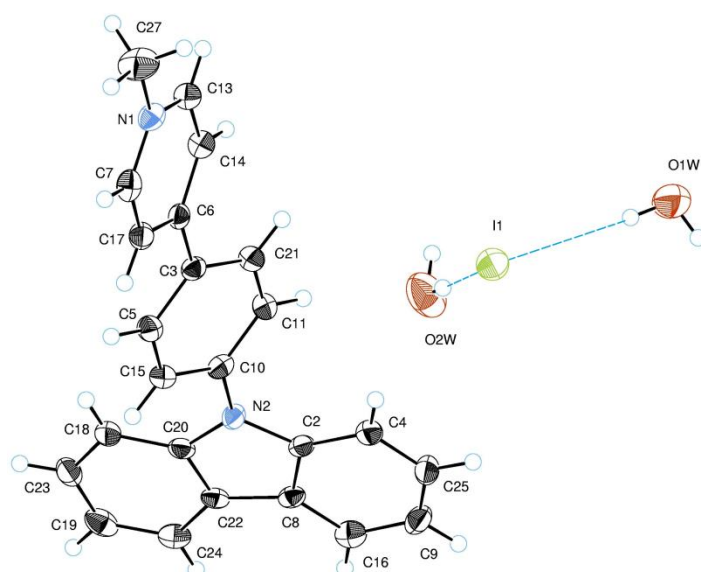
**Fig. S4.** Emission of **7a** in DMSO as a function of temperature.

(1) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater.*, 2003, **15**, 1535–1546.

(2) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, **2009**, 4332–4353.

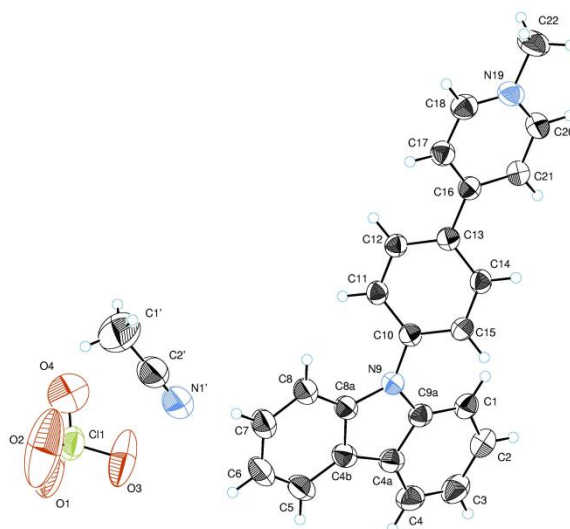
**X-Ray Structure, crystal data and structure refinements for 3a**

Identification code	KL-1256
Empirical formula	$C_{13}H_{17}ClN_2O_2$
Formula weight	269.69
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.7674(10)
$b/\text{\AA}$	5.8992(5)
$c/\text{\AA}$	17.3999(15)
$\alpha/^\circ$	90
$\beta/^\circ$	96.609(8)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	1199.84(18)
$Z$	4
$\rho_{\text{calc}}/\text{cm}^3$	1.4928
$\mu/\text{mm}^{-1}$	2.906
$F(000)$	563.3
Crystal size/ $\text{mm}^3$	$0.12 \times 0.11 \times 0.07$
Radiation	Cu $K\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ max. for data collection/ $^\circ$	157
Index ranges	$-14 \leq h \leq 14, -7 \leq k \leq 7, 0 \leq l \leq 21$
Reflections collected	4414
Independent reflections	2520 [ $R_{\text{int}} = 0.0981, R_{\text{sigma}} = 0.0871$ ]
Data/restraints/parameters	2520/0/164
Goodness-of-fit on $F^2$	1.019
Final $R$ indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0967, wR_2 = 0.2119$

**X-Ray Structure, crystal data and structure refinements for 6a**

Identification code	kl_1203
Empirical formula	C <sub>24</sub> H <sub>23</sub> IN <sub>2</sub> O <sub>2</sub>
Formula weight	498.34
Temperature/K	190(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	10.7797(2)
b/Å	8.0018(2)
c/Å	25.0126(6)
α/°	90
β/°	94.381(1)
γ/°	90
Volume/Å <sup>3</sup>	2151.21(8)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.539
μ/mm <sup>-1</sup>	1.511
F(000)	1000.0
Crystal size/mm <sup>3</sup>	0.12 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ max. for data collection/°	55.0
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 9, -32 ≤ l ≤ 32
Reflections collected	8185
Independent reflections	4877 [R <sub>int</sub> = 0.0451, R <sub>sigma</sub> = 0.0671]
Data/restraints/parameters	4877/6/279
Goodness-of-fit on F <sup>2</sup>	1.018
Final R indexes [I > 2σ(I)]	R <sub>1</sub> = 0.0393, wR <sub>2</sub> = 0.0725
Final R indexes [all data]	R <sub>1</sub> = 0.0732, wR <sub>2</sub> = 0.0827
Largest diff. peak/hole / e Å <sup>-3</sup>	0.44/-0.64

## X-Ray Structure, crystal data and structure refinements for 7a

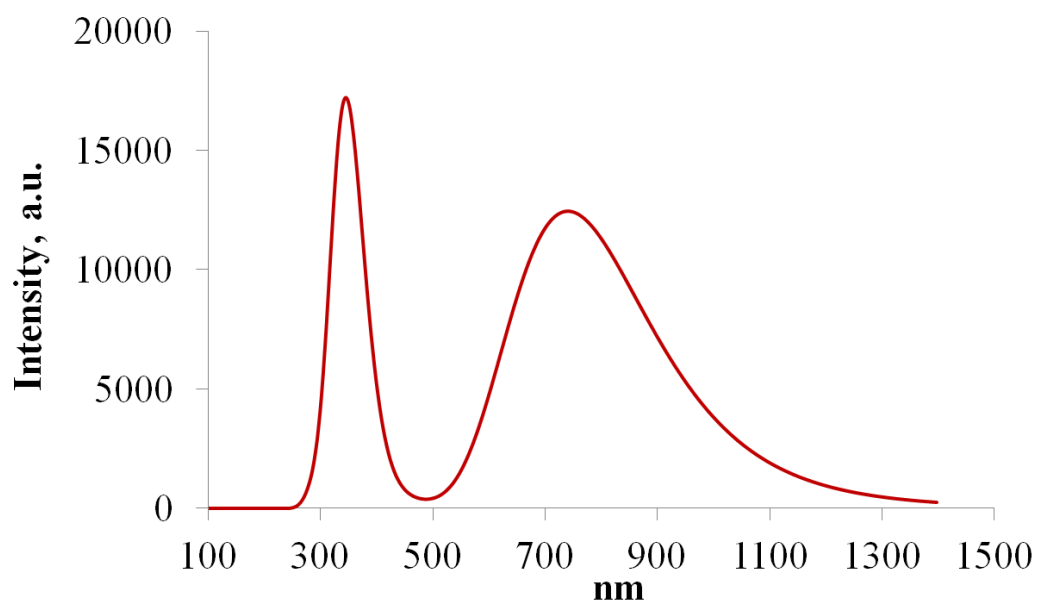


Identification code	KL_1232
Empirical formula	C <sub>26</sub> H <sub>22</sub> ClN <sub>3</sub> O <sub>4</sub>
Formula weight	475.93
Temperature/K	273 K
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	16.36790(12)
<i>b</i> /Å	7.39194(5)
<i>c</i> /Å	19.97192(13)
$\alpha$ /°	90
$\beta$ /°	104.1870(7)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2342.72(3)
<i>Z</i>	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.3493
$\mu$ /mm <sup>-1</sup>	1.763
<i>F</i> (000)	996.6
Crystal size/mm <sup>3</sup>	0.19 × 0.07 × 0.02
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
2 $\theta$ max. for data collection/°	155.0
Index ranges	-20 ≤ <i>h</i> ≤ 20, -9 ≤ <i>k</i> ≤ 8, -25 ≤ <i>l</i> ≤ 24
Reflections collected	21192
Independent reflections	4901 [ <i>R</i> <sub>int</sub> = 0.0154, <i>R</i> <sub>sigma</sub> = 0.0116]
Data/restraints/parameters	4901/0/310
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.042
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0649, <i>wR</i> <sub>2</sub> = 0.2240
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0667, <i>wR</i> <sub>2</sub> = 0.2271
Largest diff. peak/hole / e Å <sup>-3</sup>	0.74/-0.48

## Theoretical calculations

The calculations were performed using Gaussian 09 series of programs. B3LYP/6-31G(d) basis set was used for calculations. The geometry of **7a** was obtained from monocrystal X-Ray data and used without optimization.

### *7a monomer*



**Fig. S17.** The calculated emission of **7a** monomer in the solid state

**Excited State 2: Singlet-A 1.6759 eV 739.82 nm f=0.3063 <S\*\*2>=0.000**

88 -> 89 0.70438

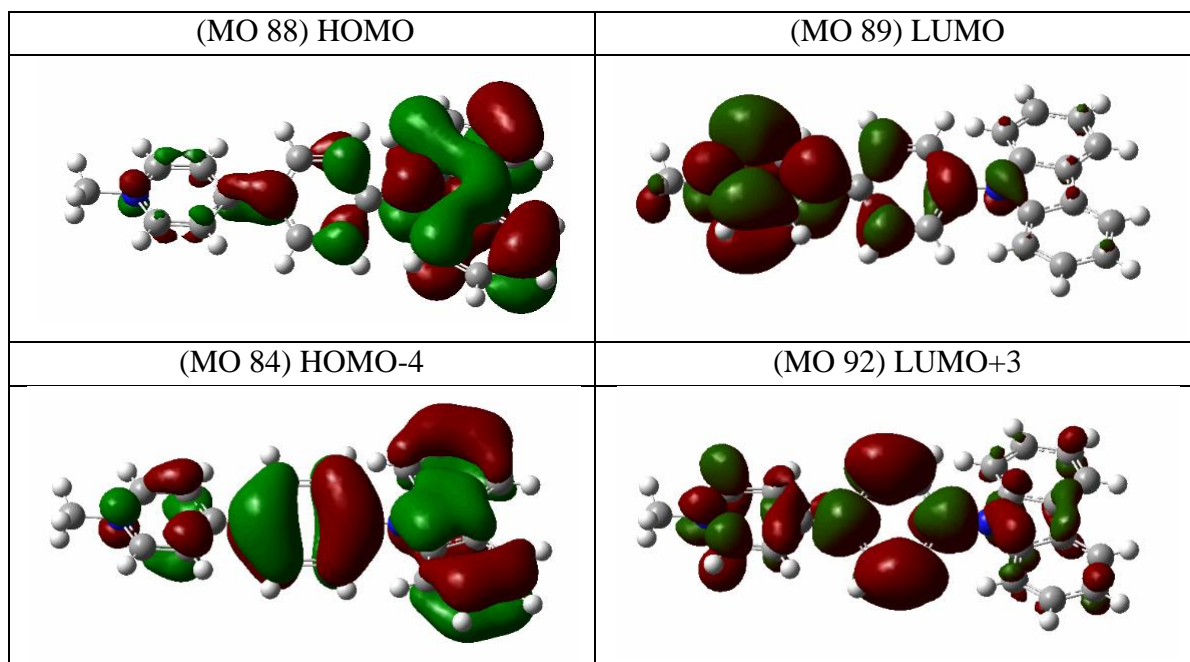
And

**Excited State 9: Singlet-A 3.6357 eV 341.02 nm f=0.3387 <S\*\*2>=0.000**

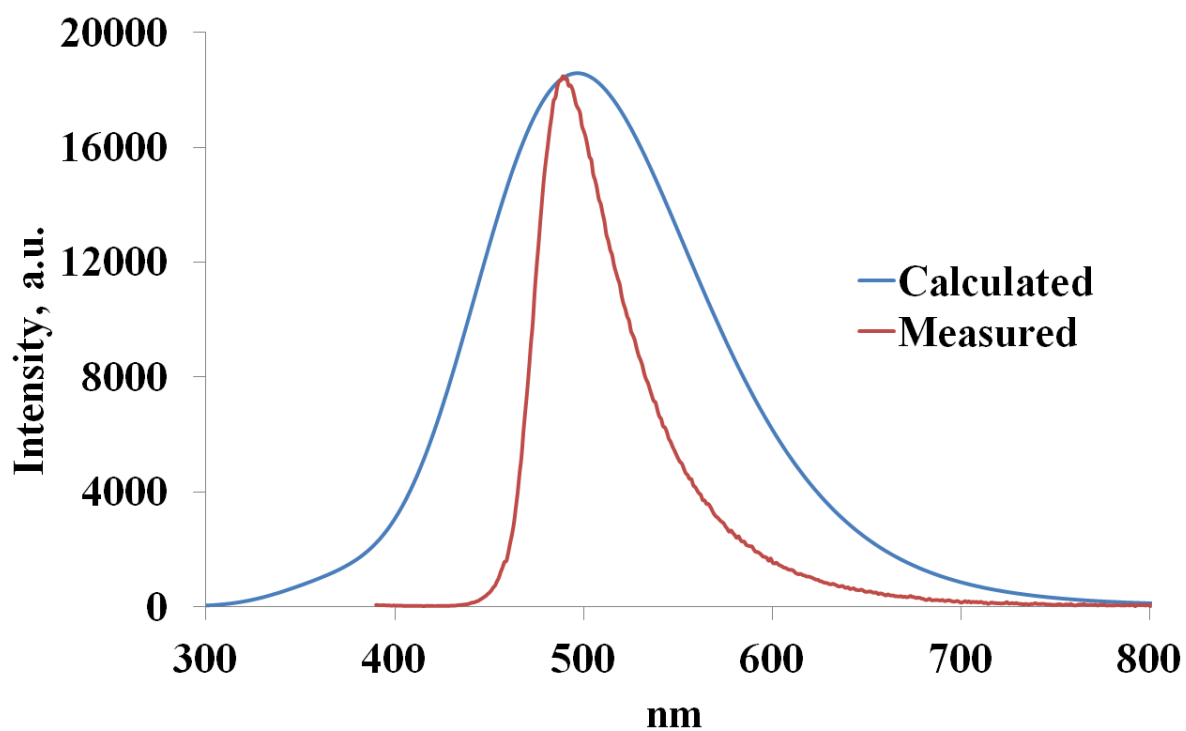
84 -> 89 0.63757

88 -> 92 0.28396





**Fig. S18.** HOMO and LUMO state representations in **7a** monomer

**7a dimer**

**Fig. S19.** The calculated and observed emission of **7a** in the solid state

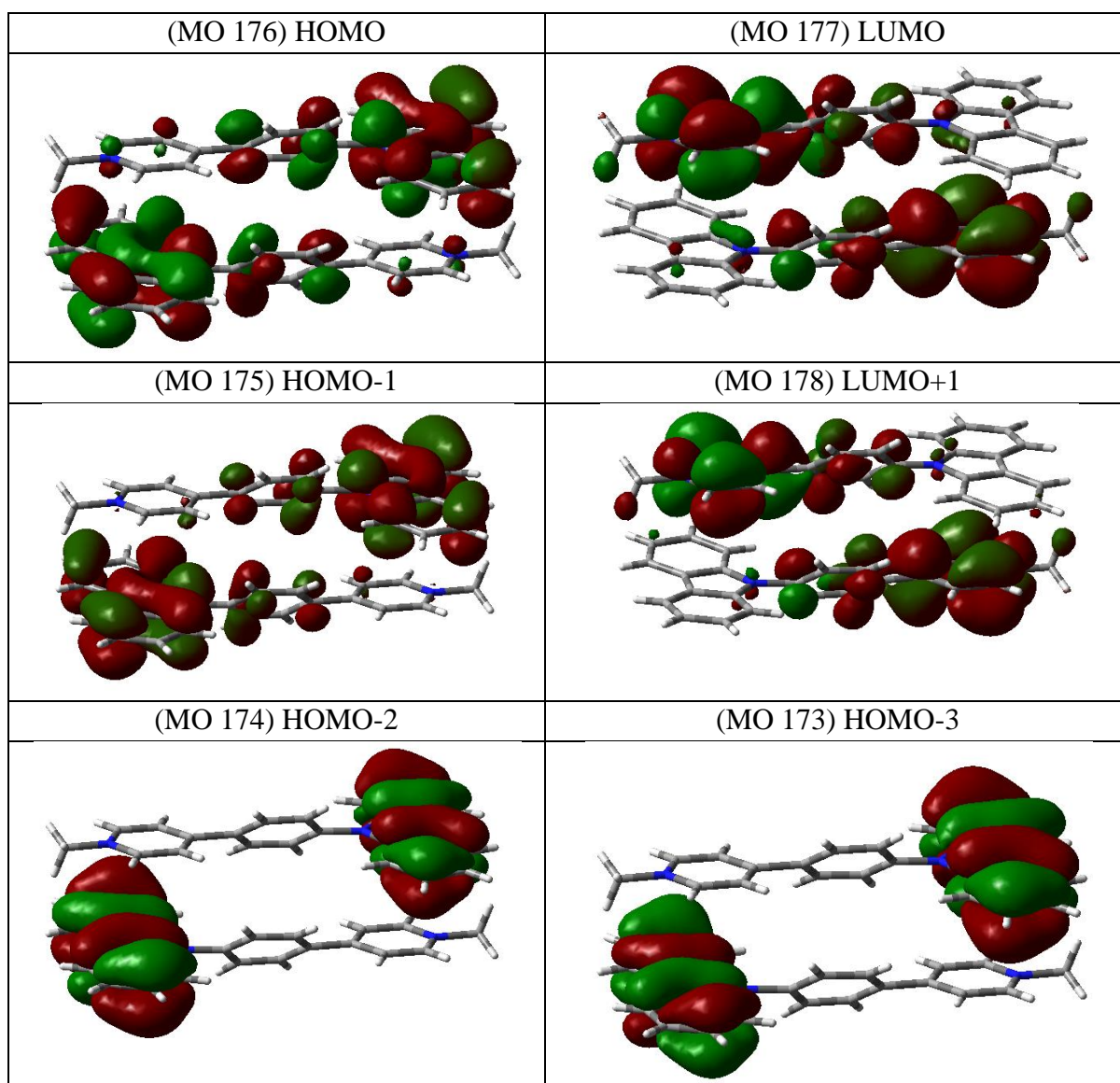
**Excited State 6: Singlet-A 2.5073 eV 494.50 nm f=0.3784 <S\*\*2>=0.000**

173 -> 177 -0.20461

174 -> 178 -0.13765

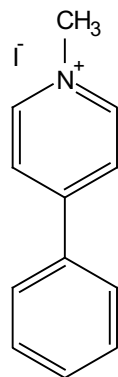
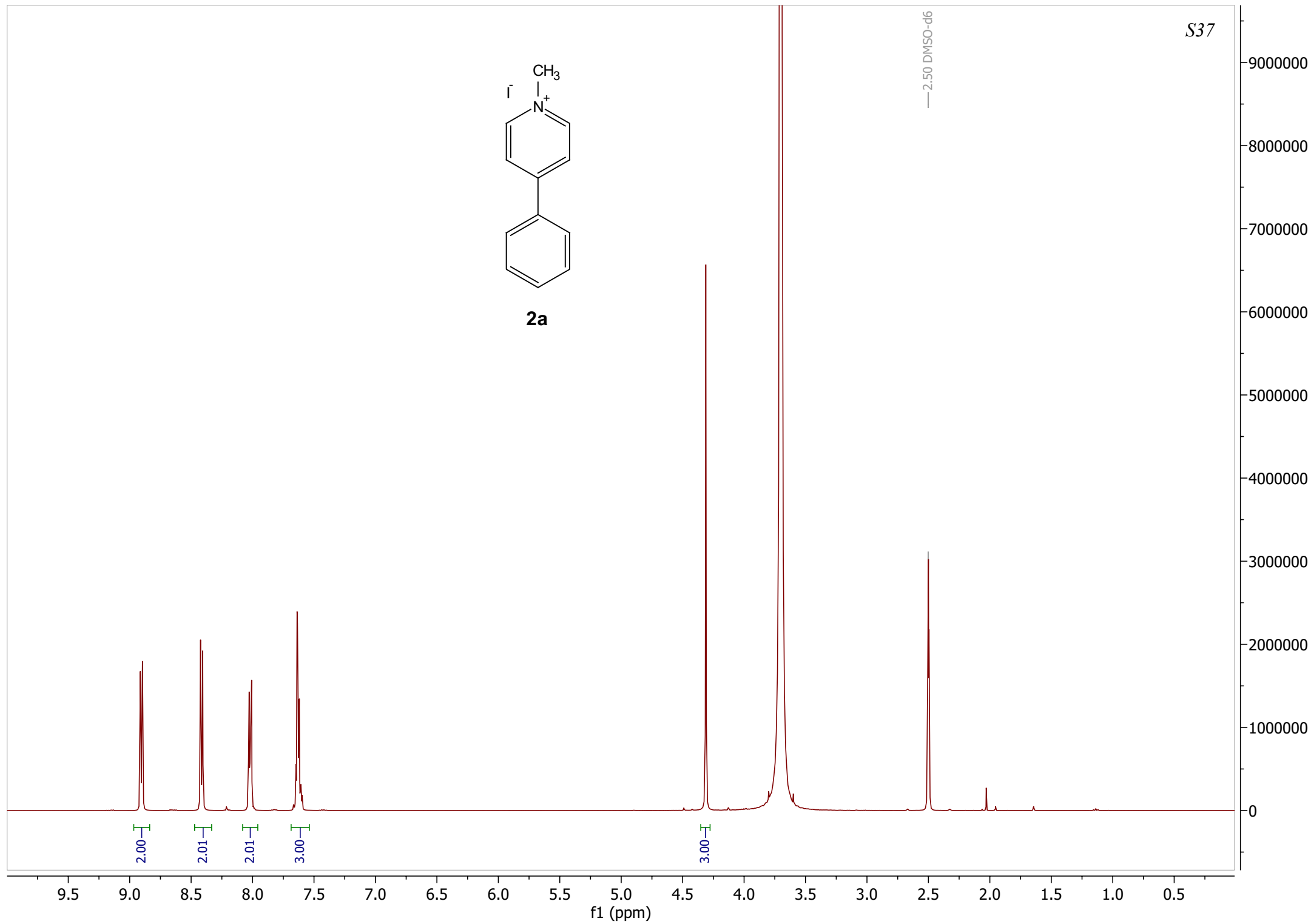
175 -> 177 -0.41195

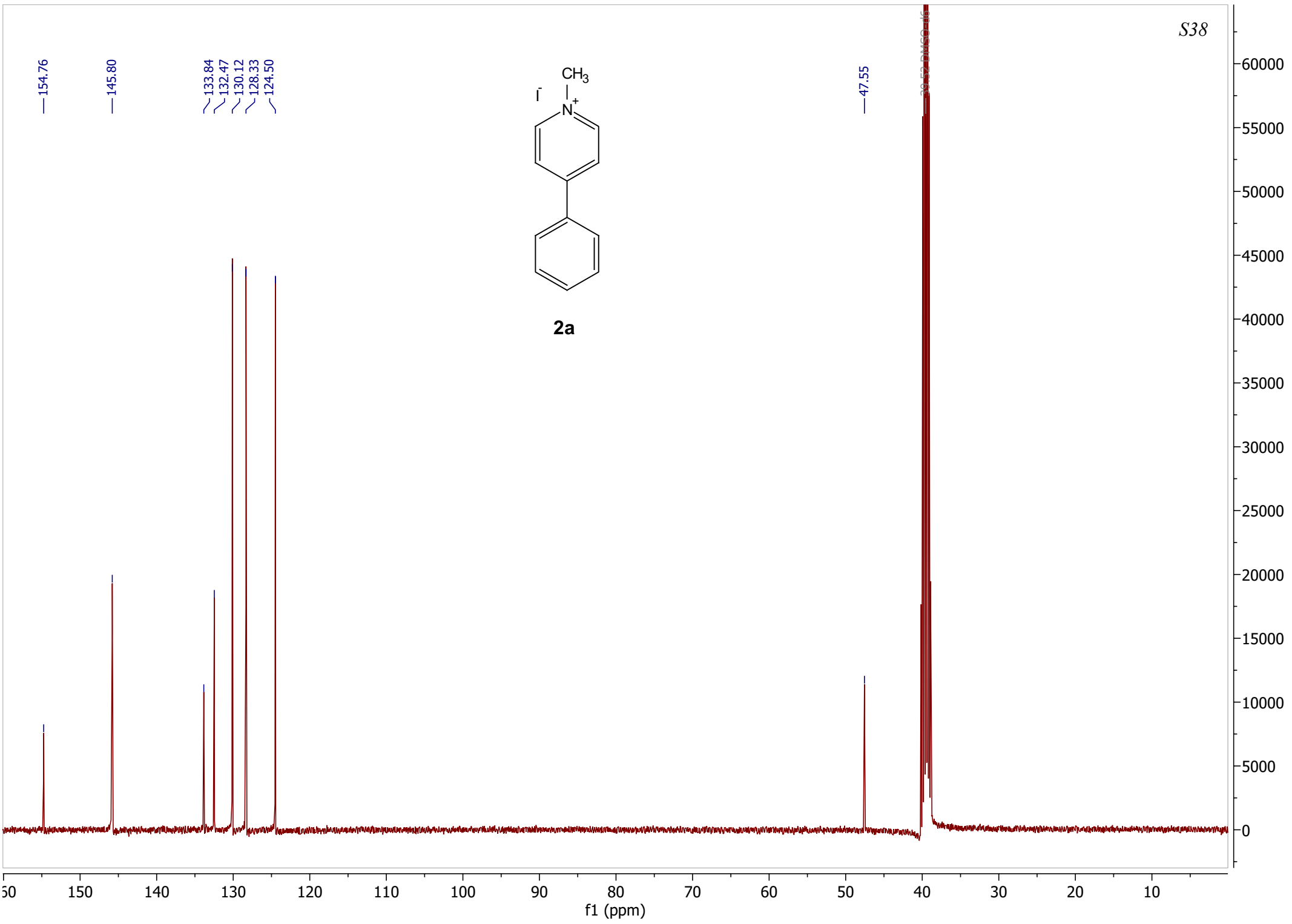
176 -> 178 0.51595

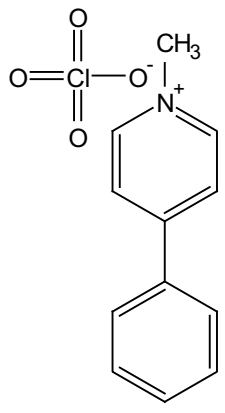


**Fig. S18.** HOMO and LUMO state representations in dimer of **7a**

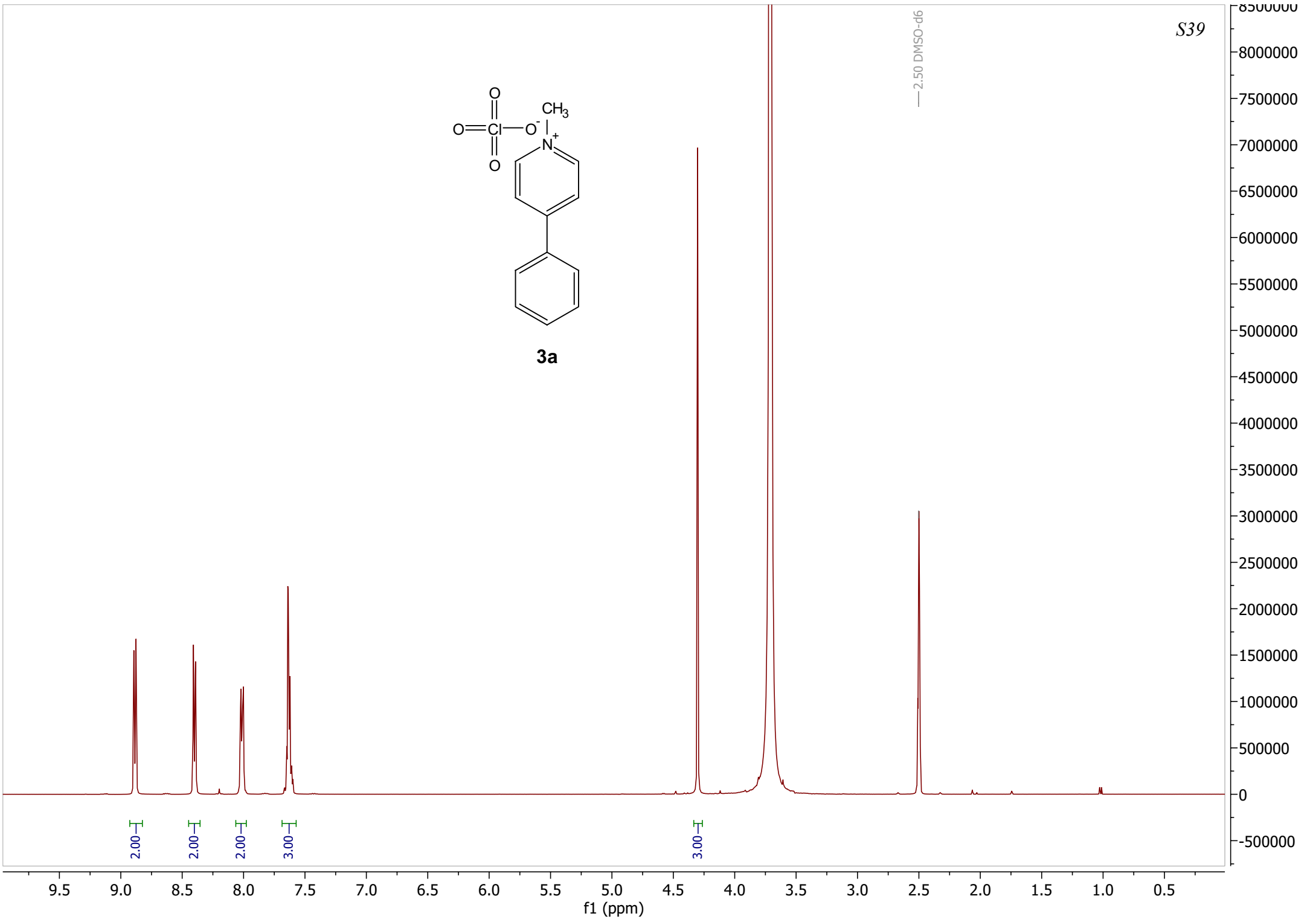
**$^1\text{H}$  and  $^{13}\text{C}$  NMR data**

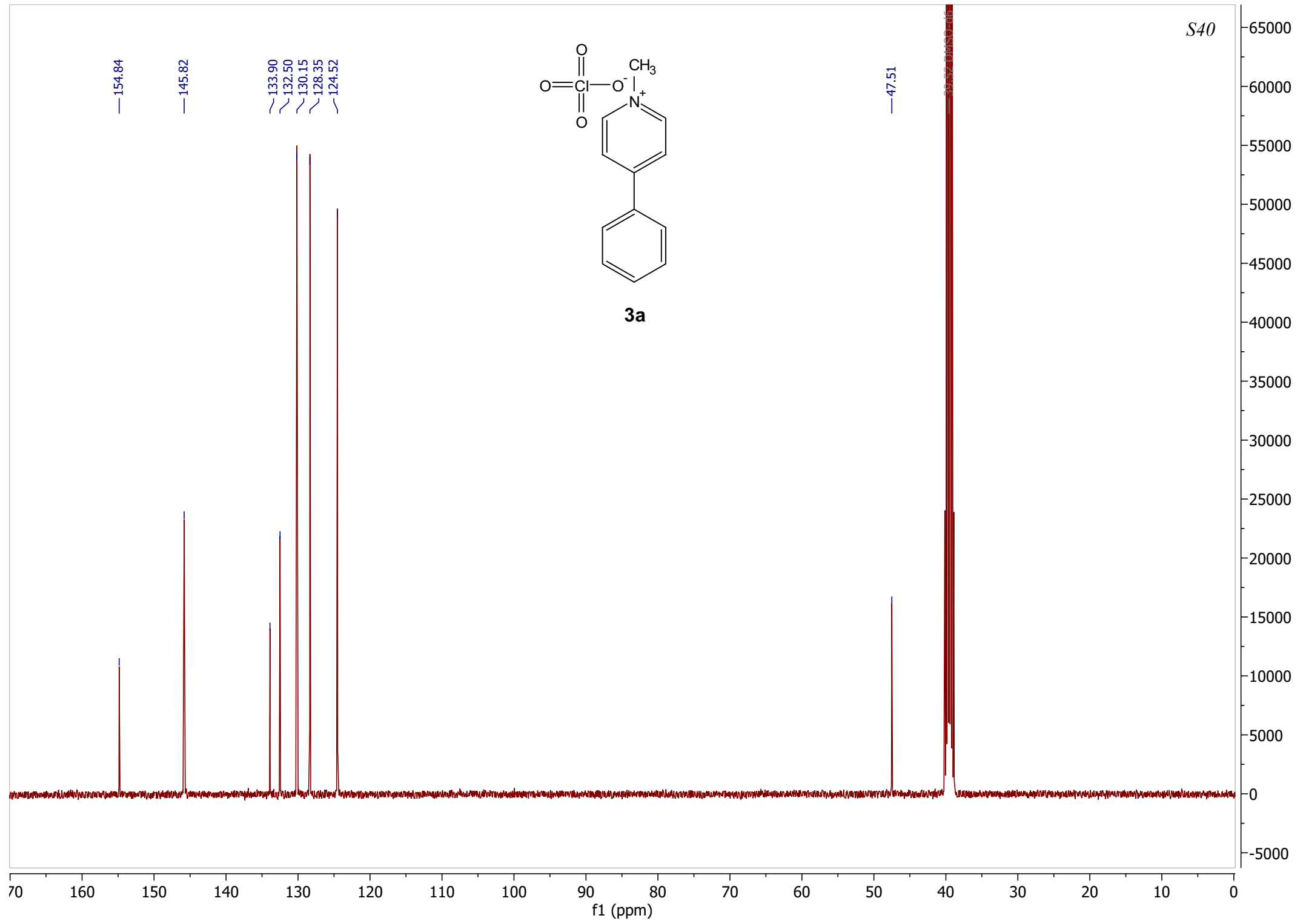
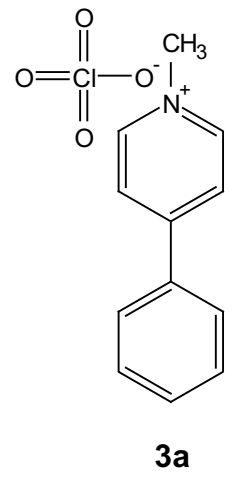
**2a**



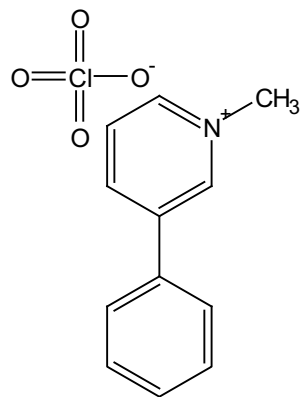
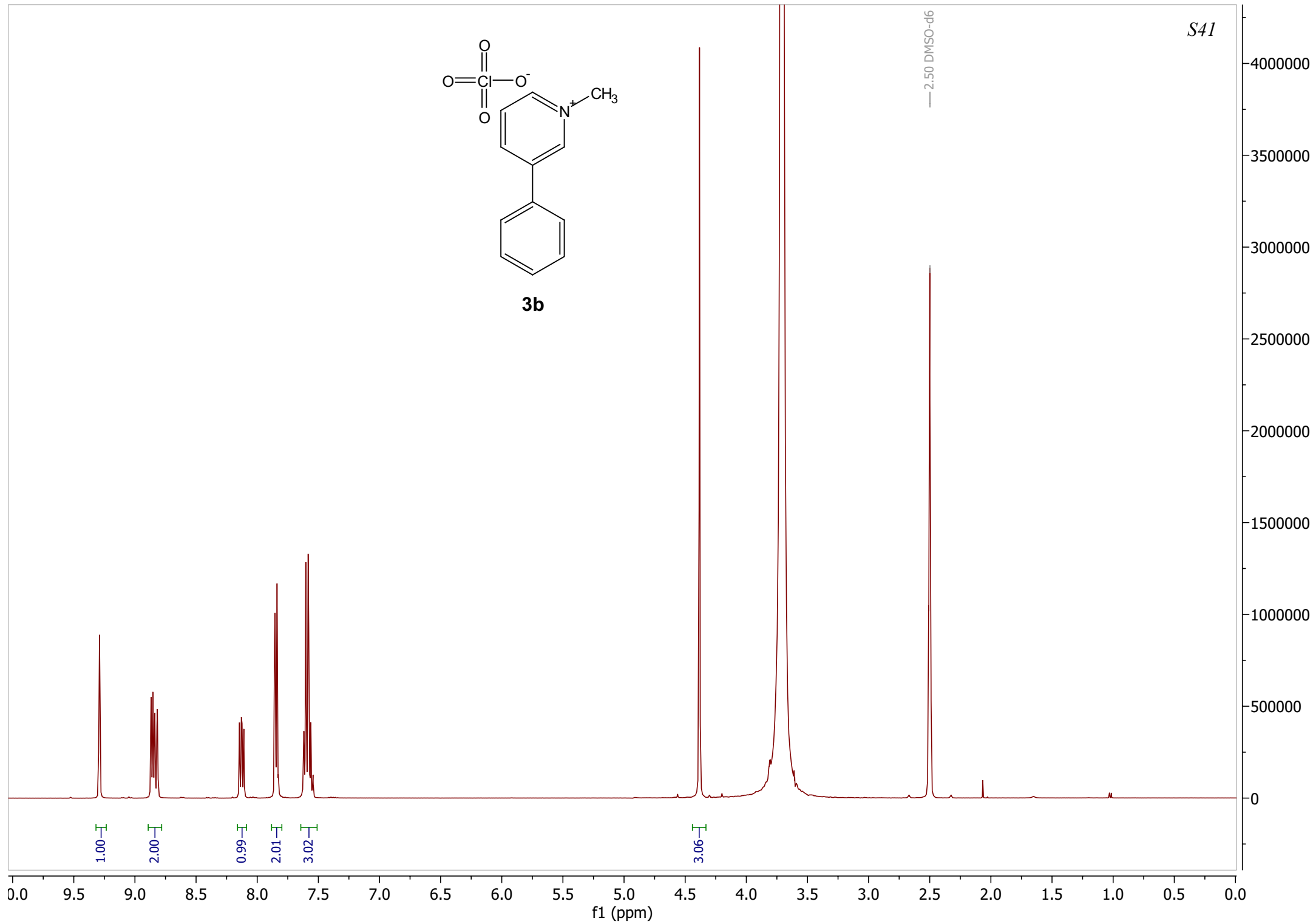


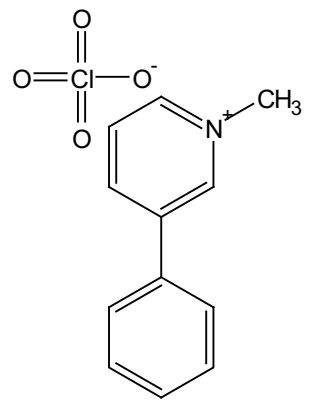
3a



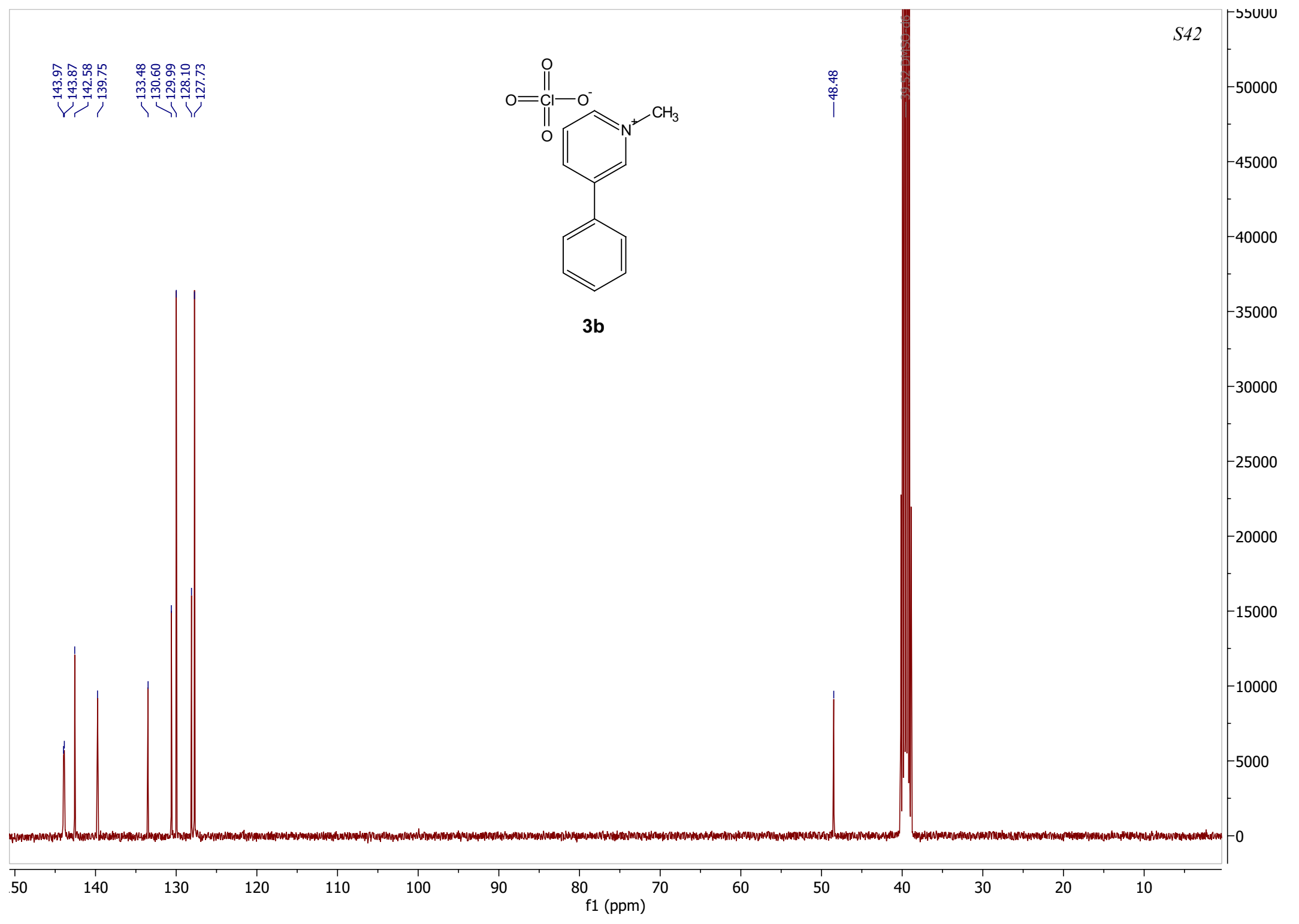


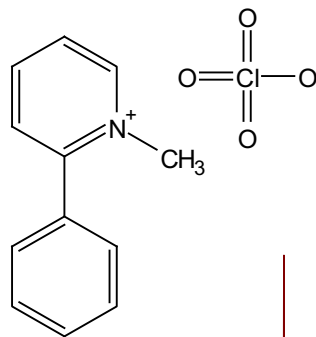
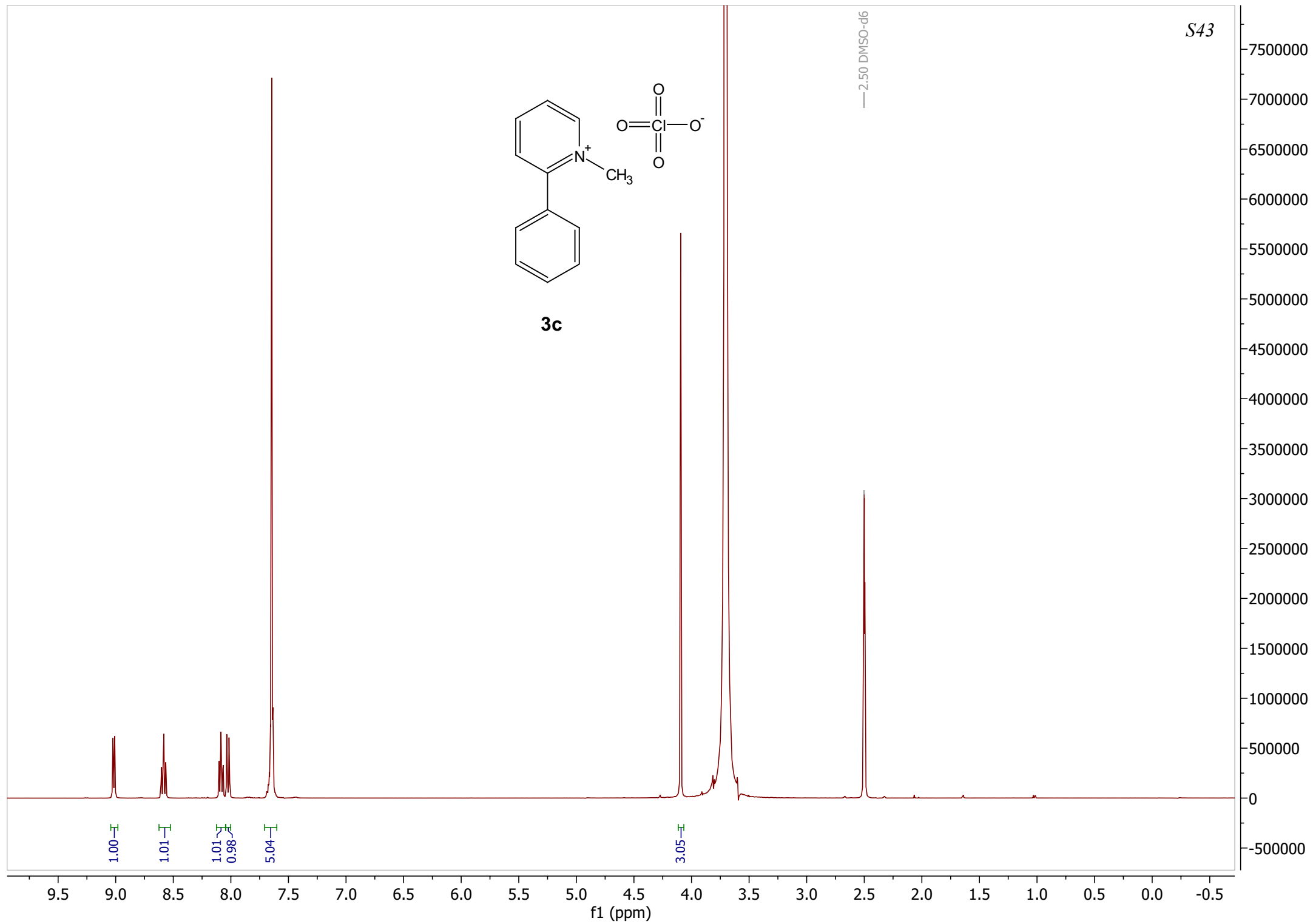


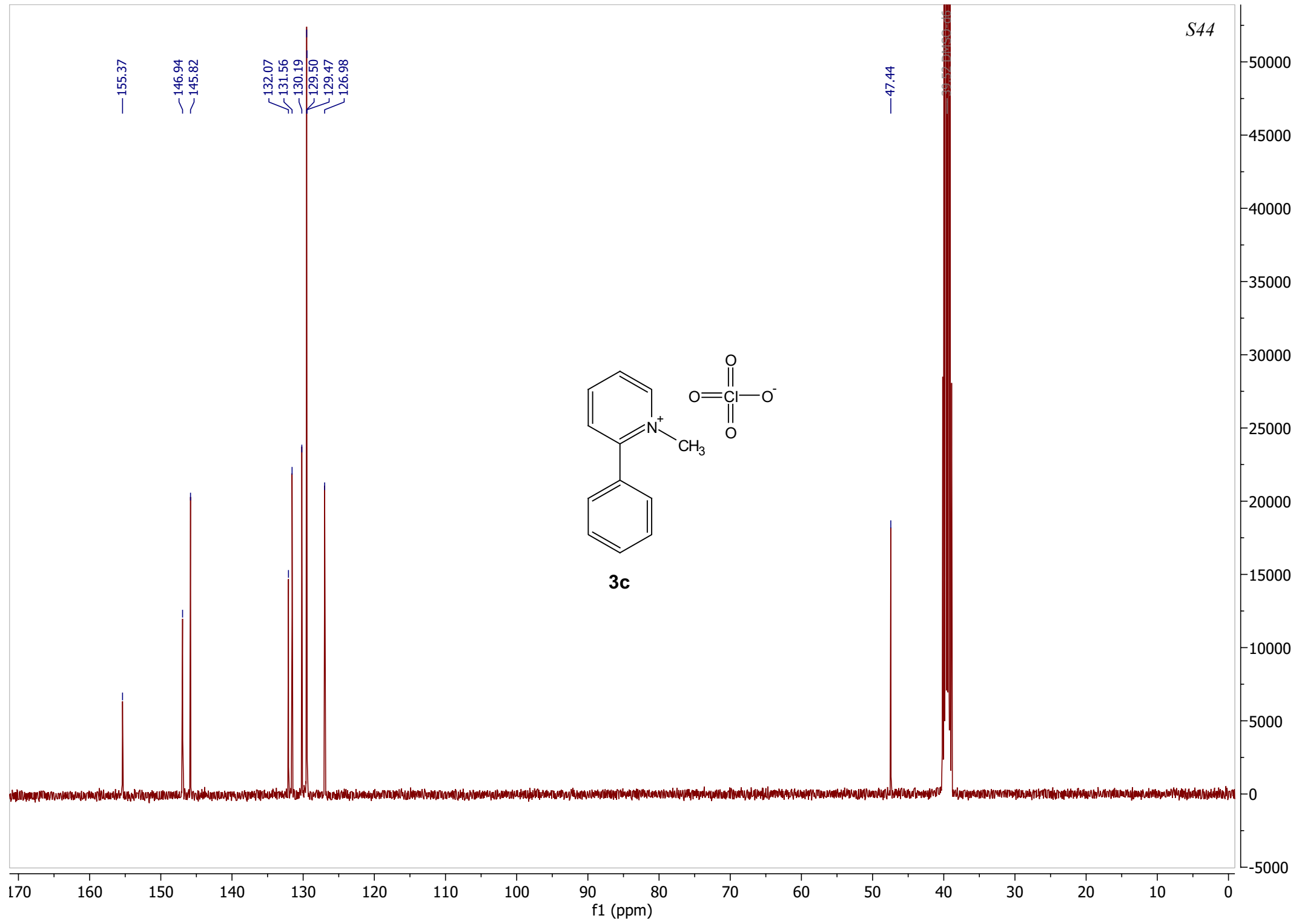
**3b**

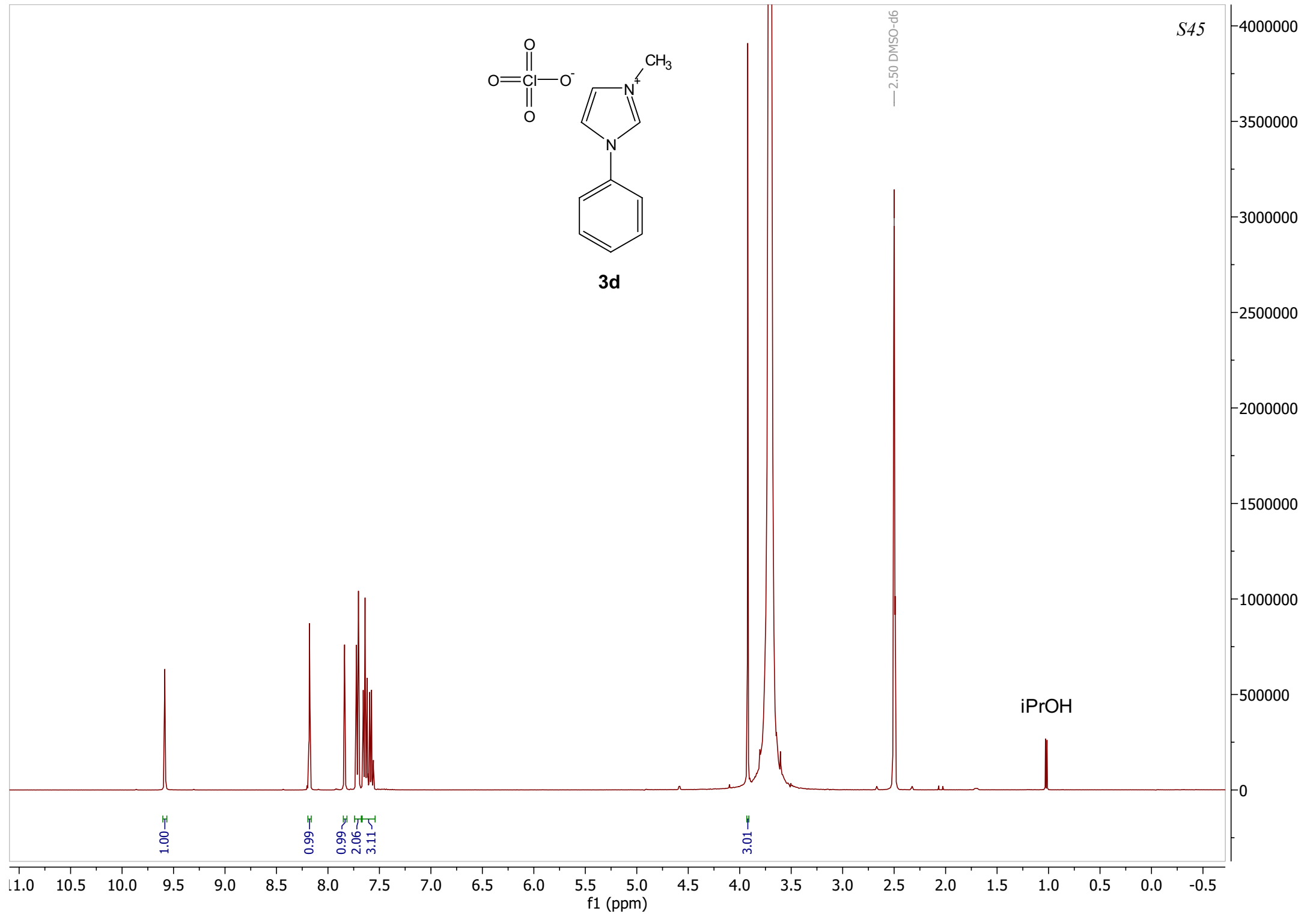
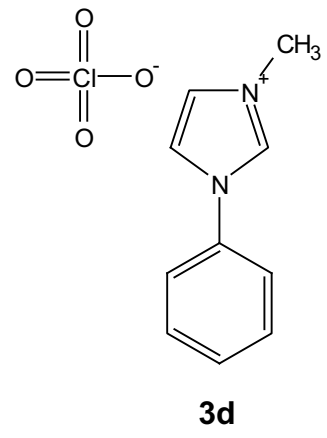


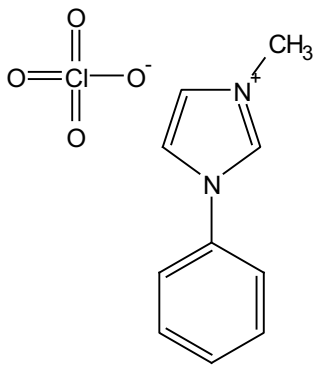
**3b**



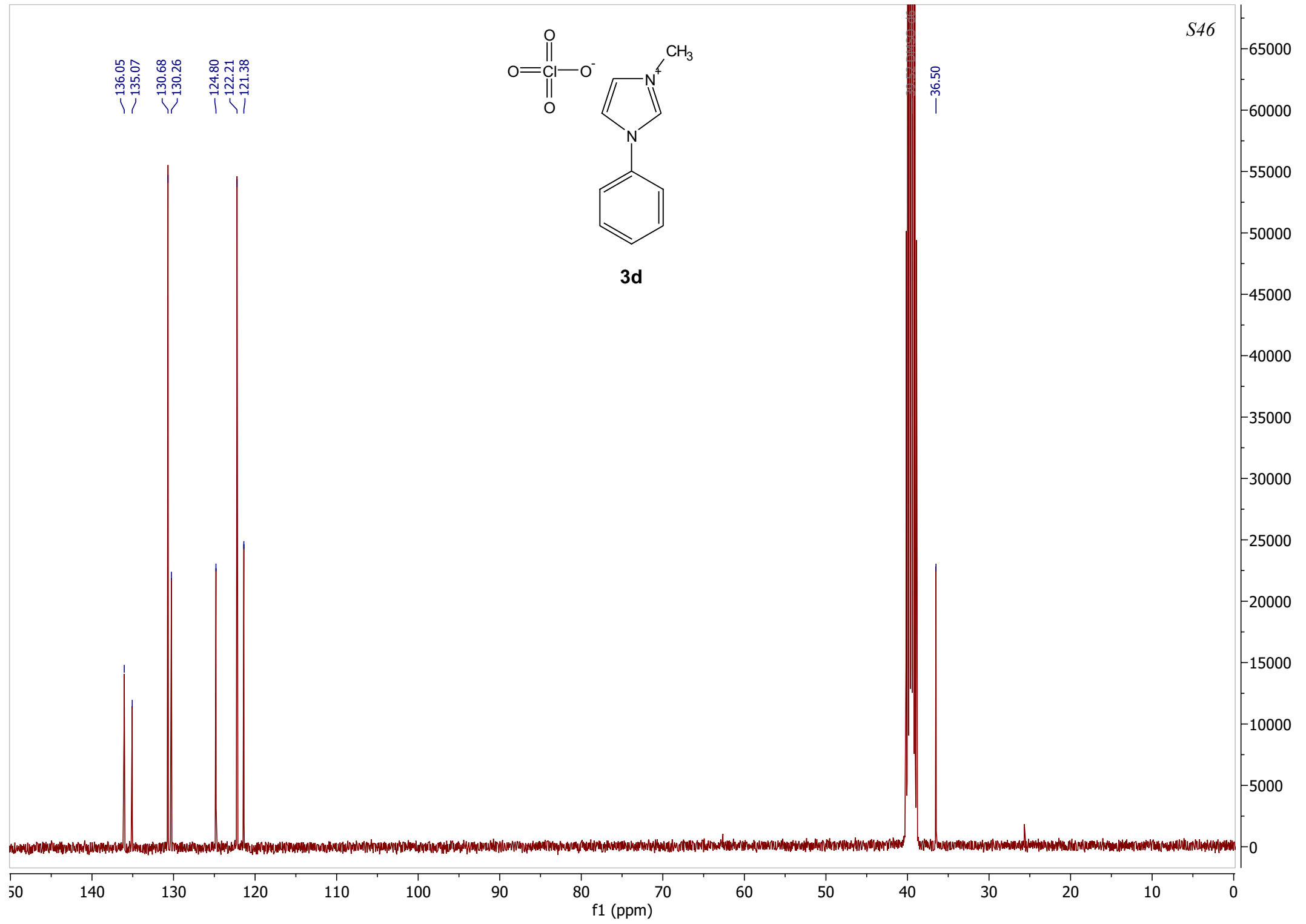
**3c**

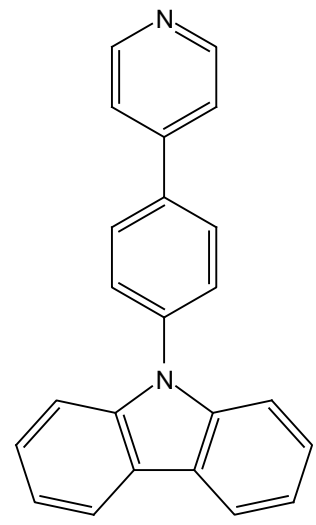
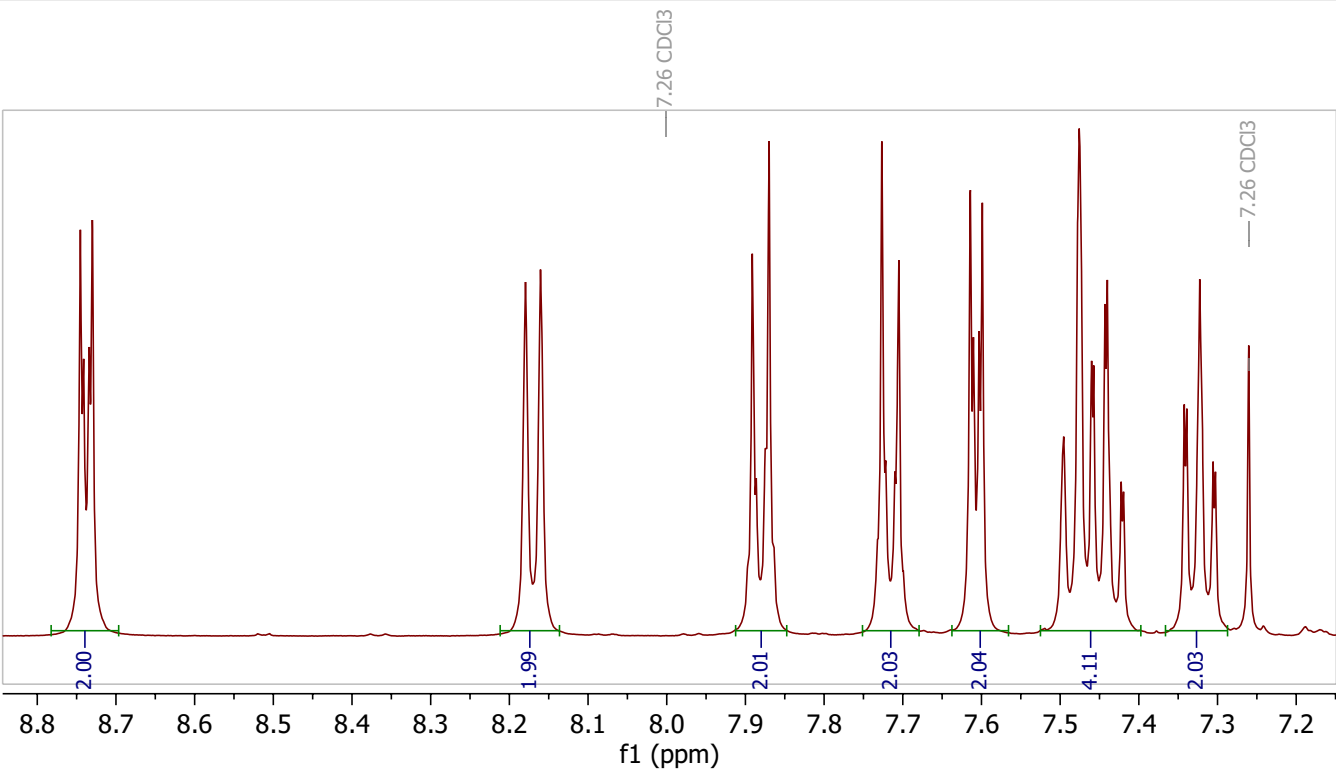




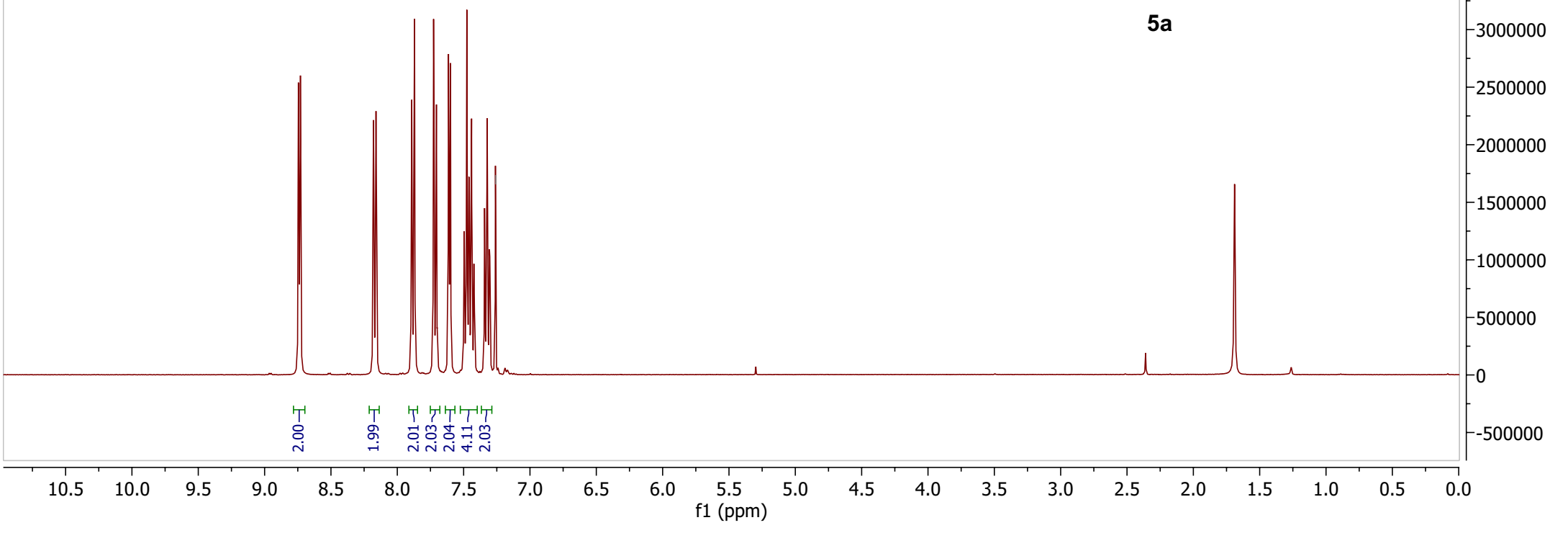


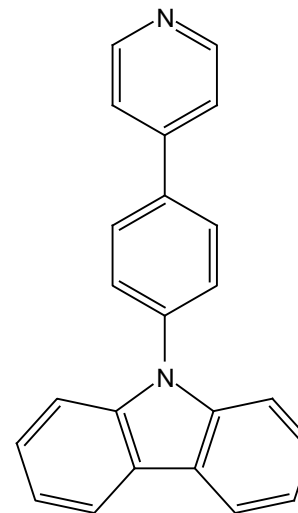
3d



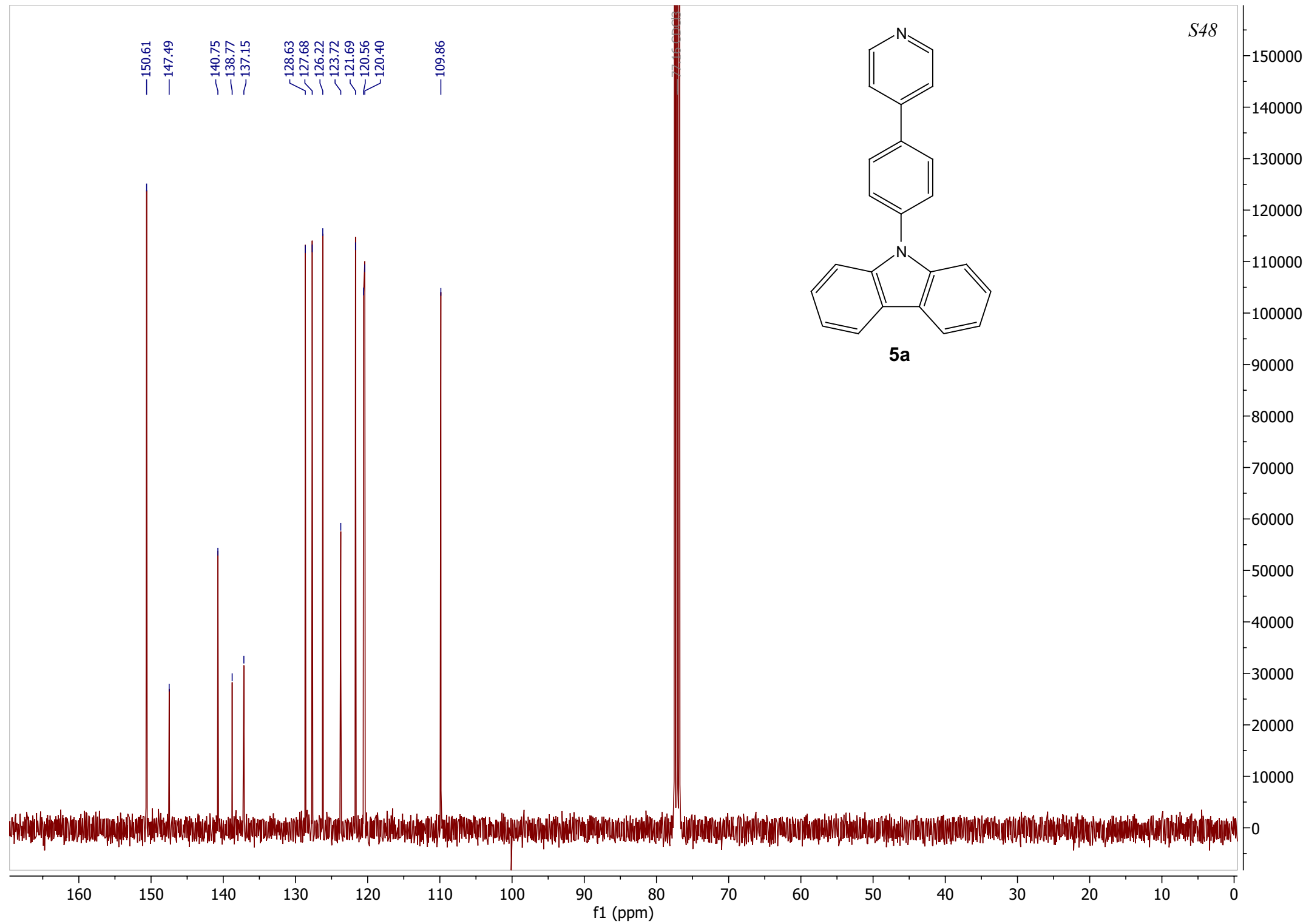


5a



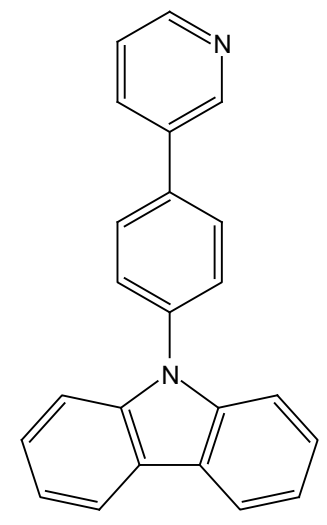
**5a**

— 150.61  
— 147.49  
— 140.75  
— 138.77  
— 137.15  
— 128.63  
— 127.68  
— 126.22  
— 123.72  
— 121.69  
— 120.56  
— 120.40  
— 109.86



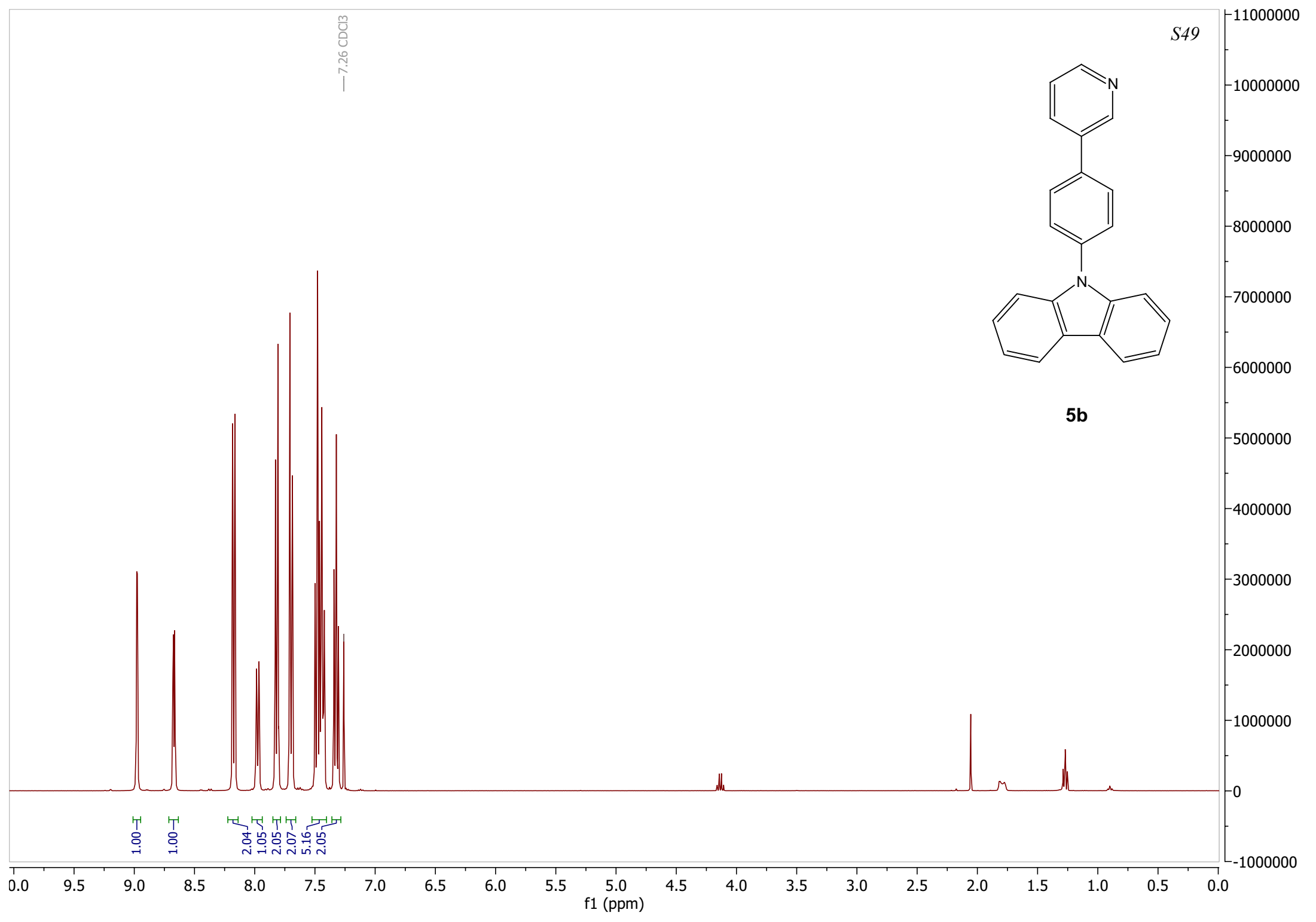


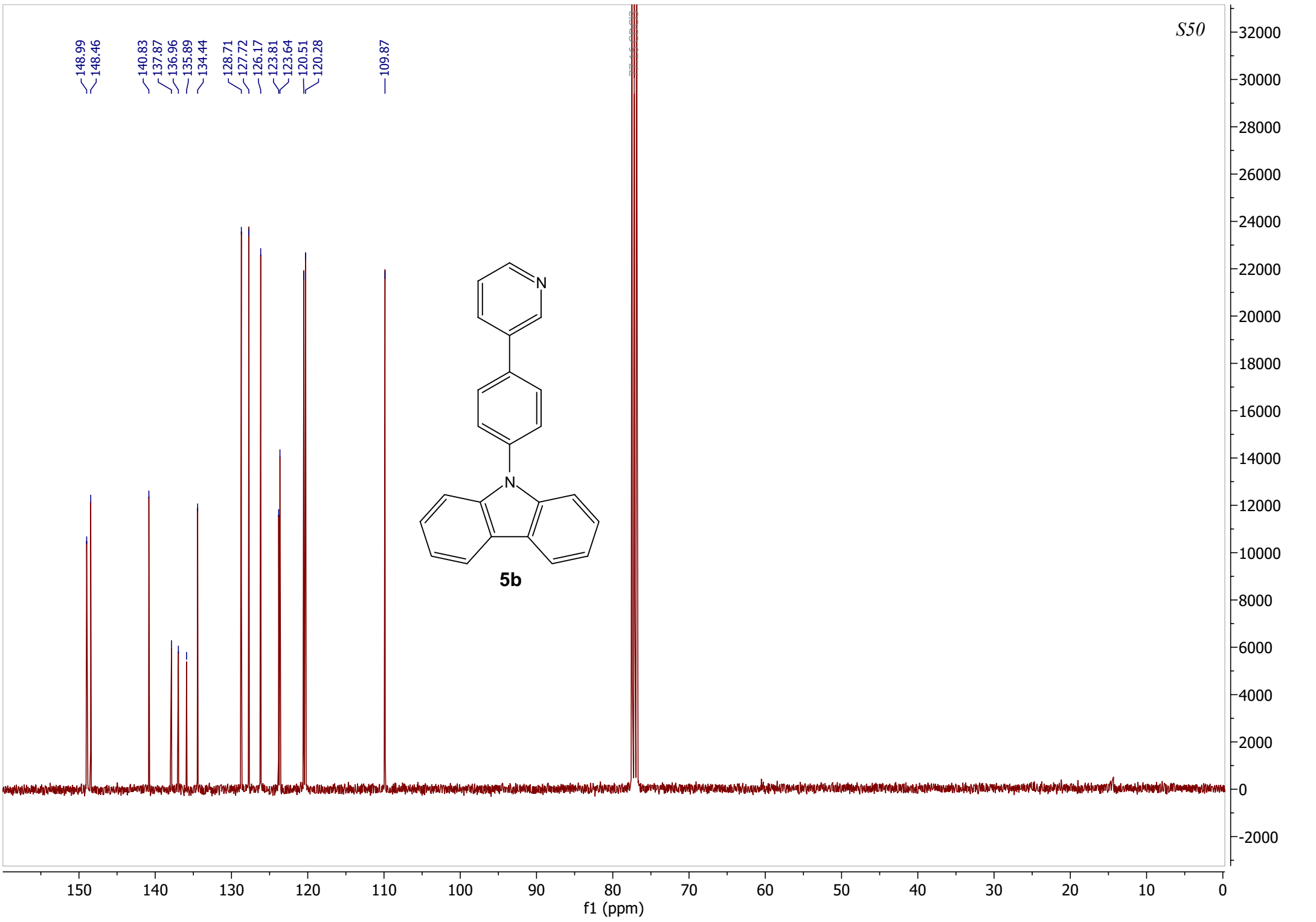
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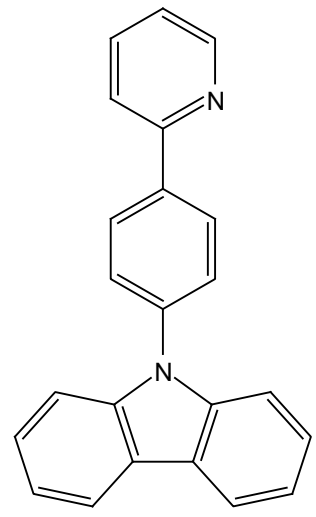
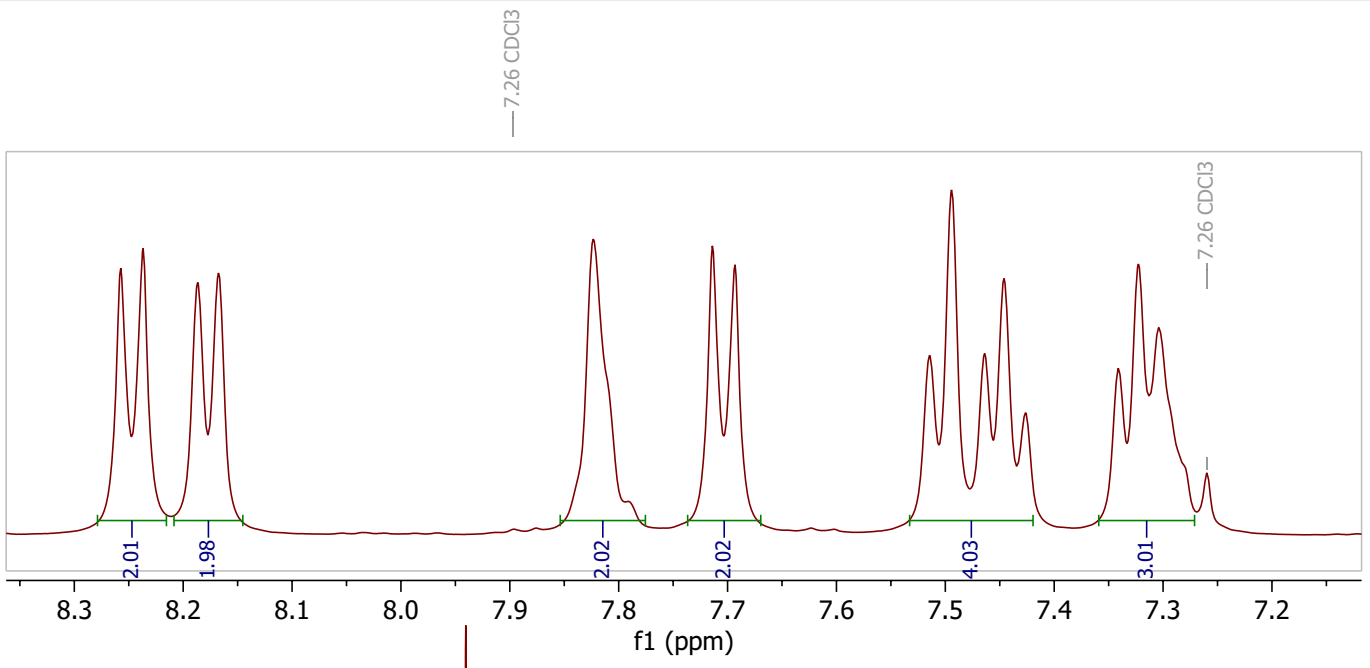


**5b**

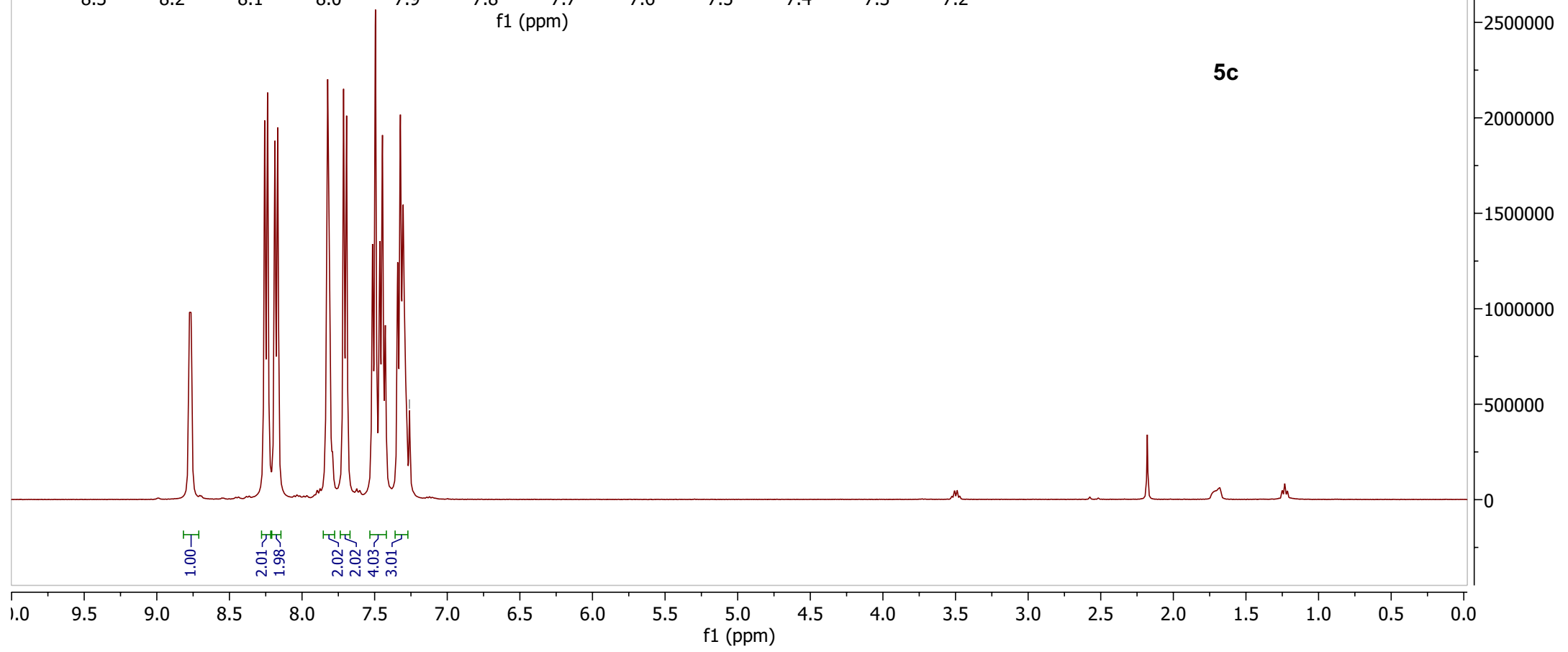
— 7.26 CDCl3

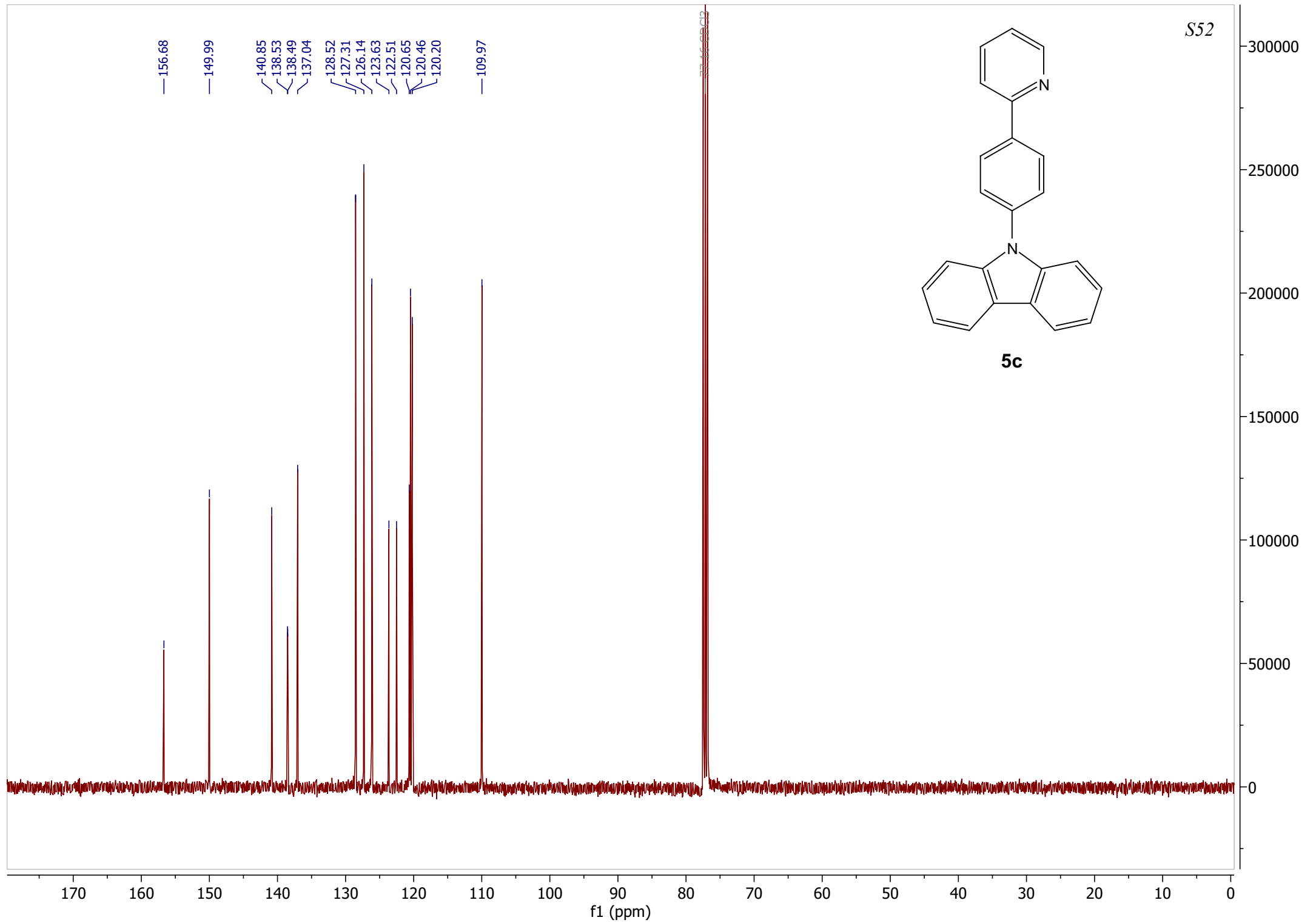


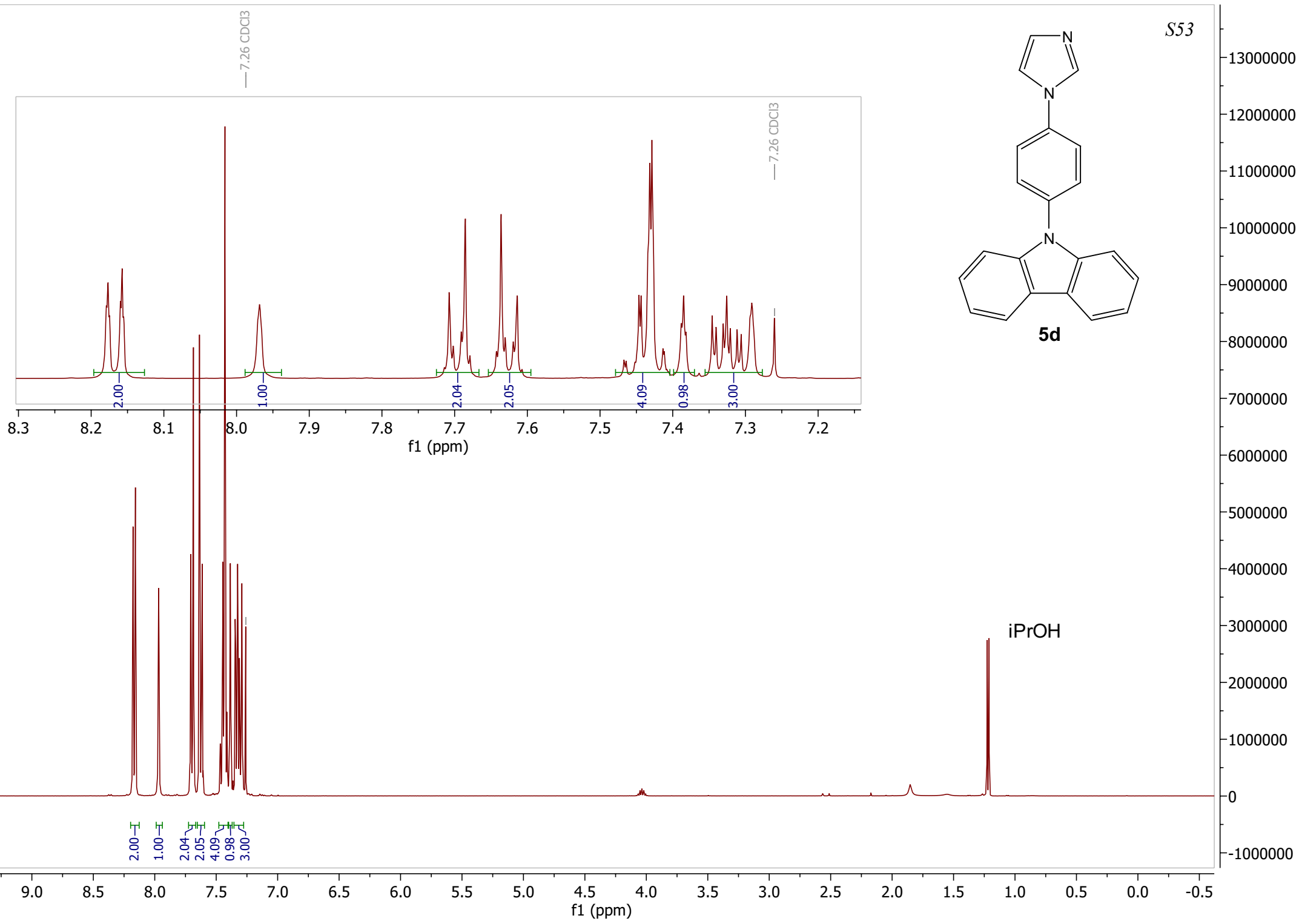
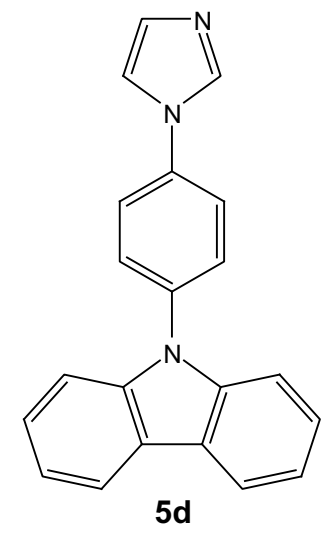




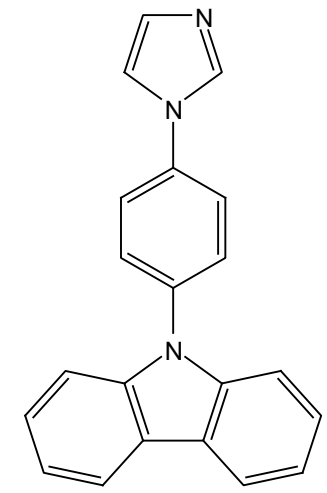
**5c**



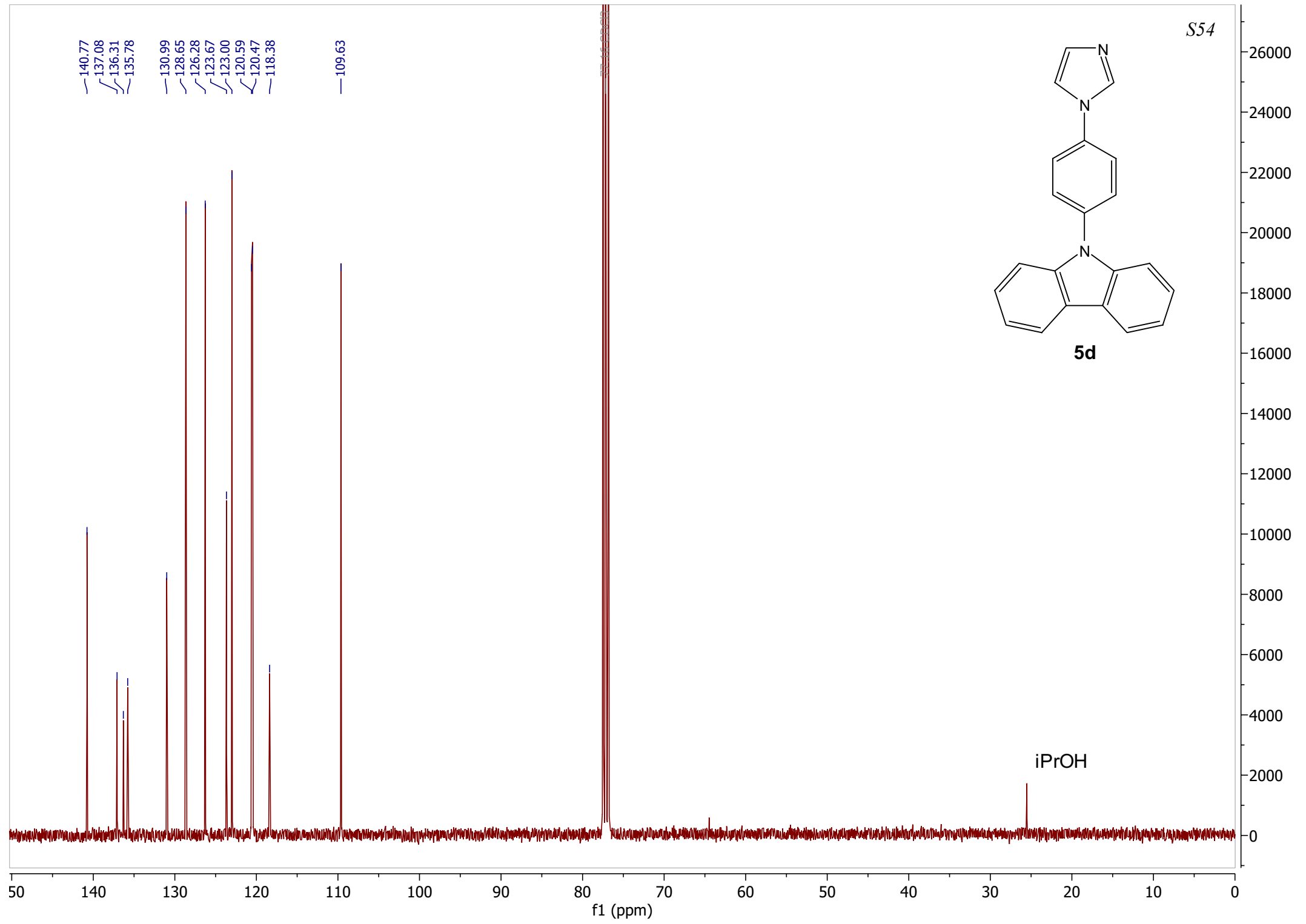




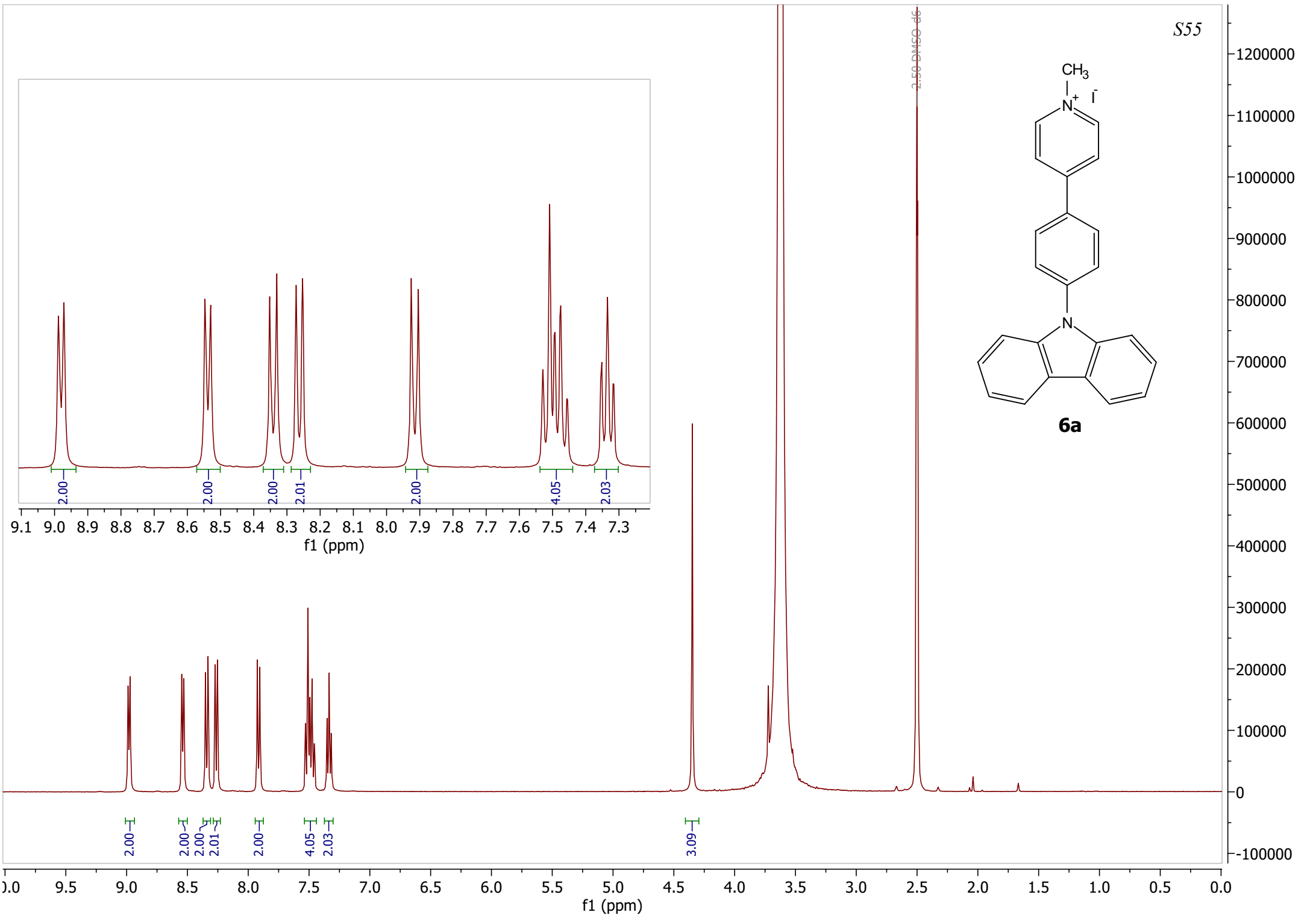
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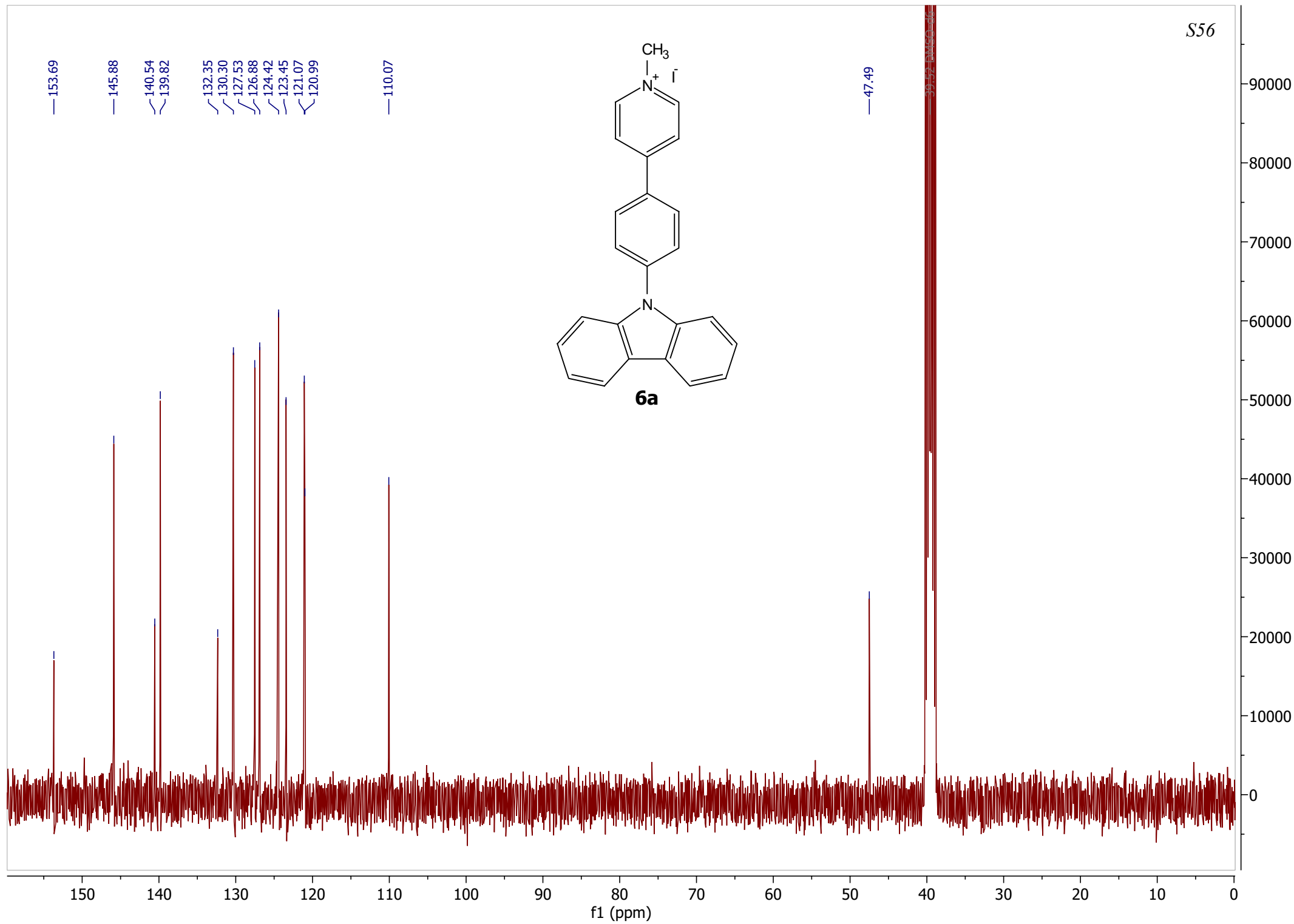
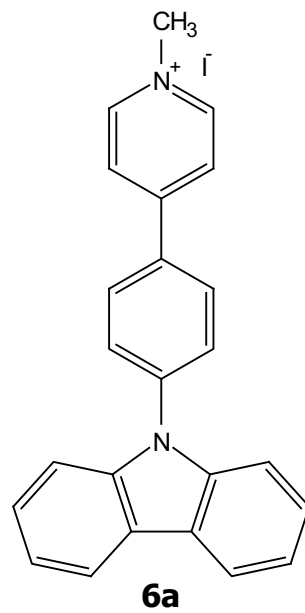


5d



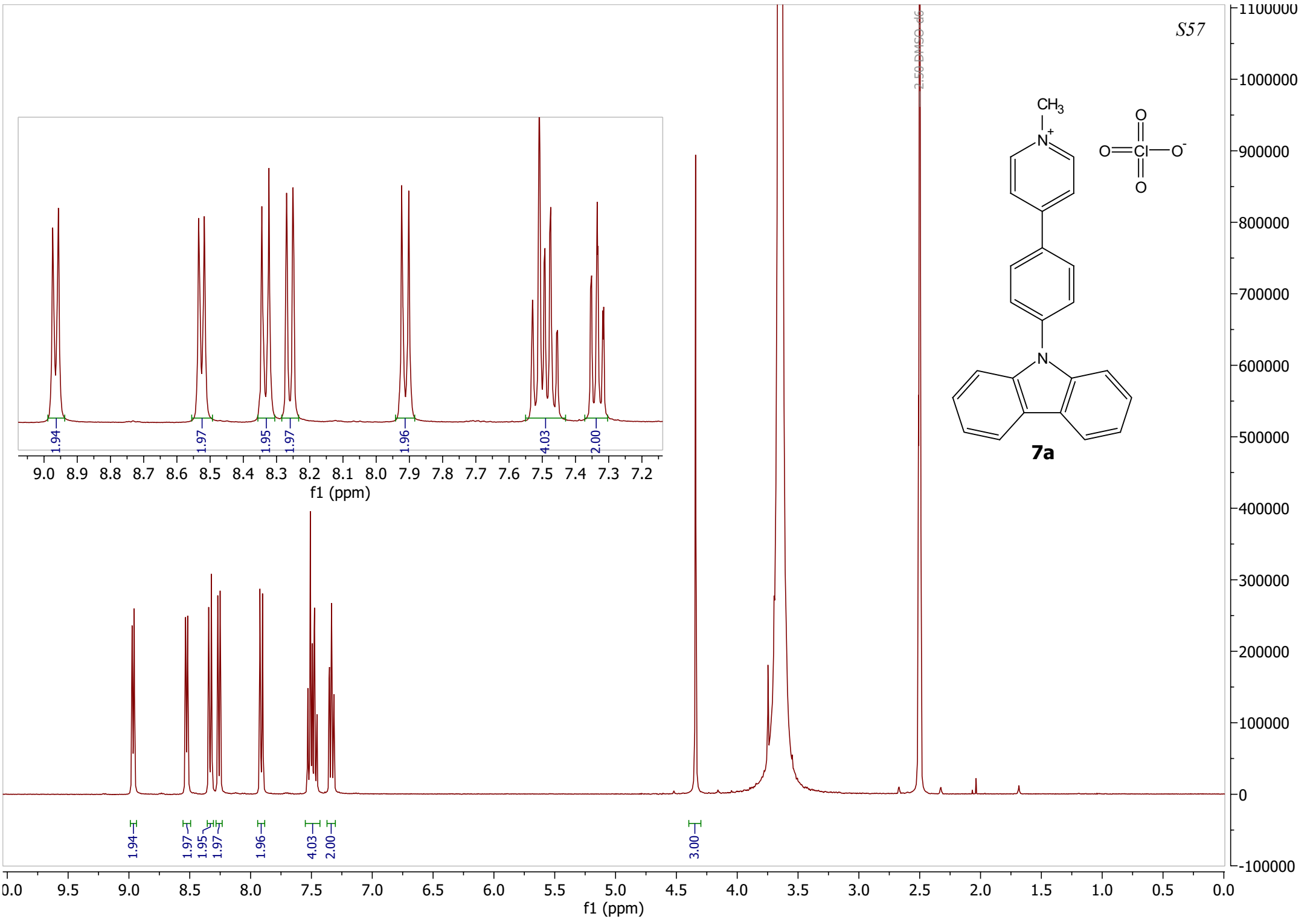
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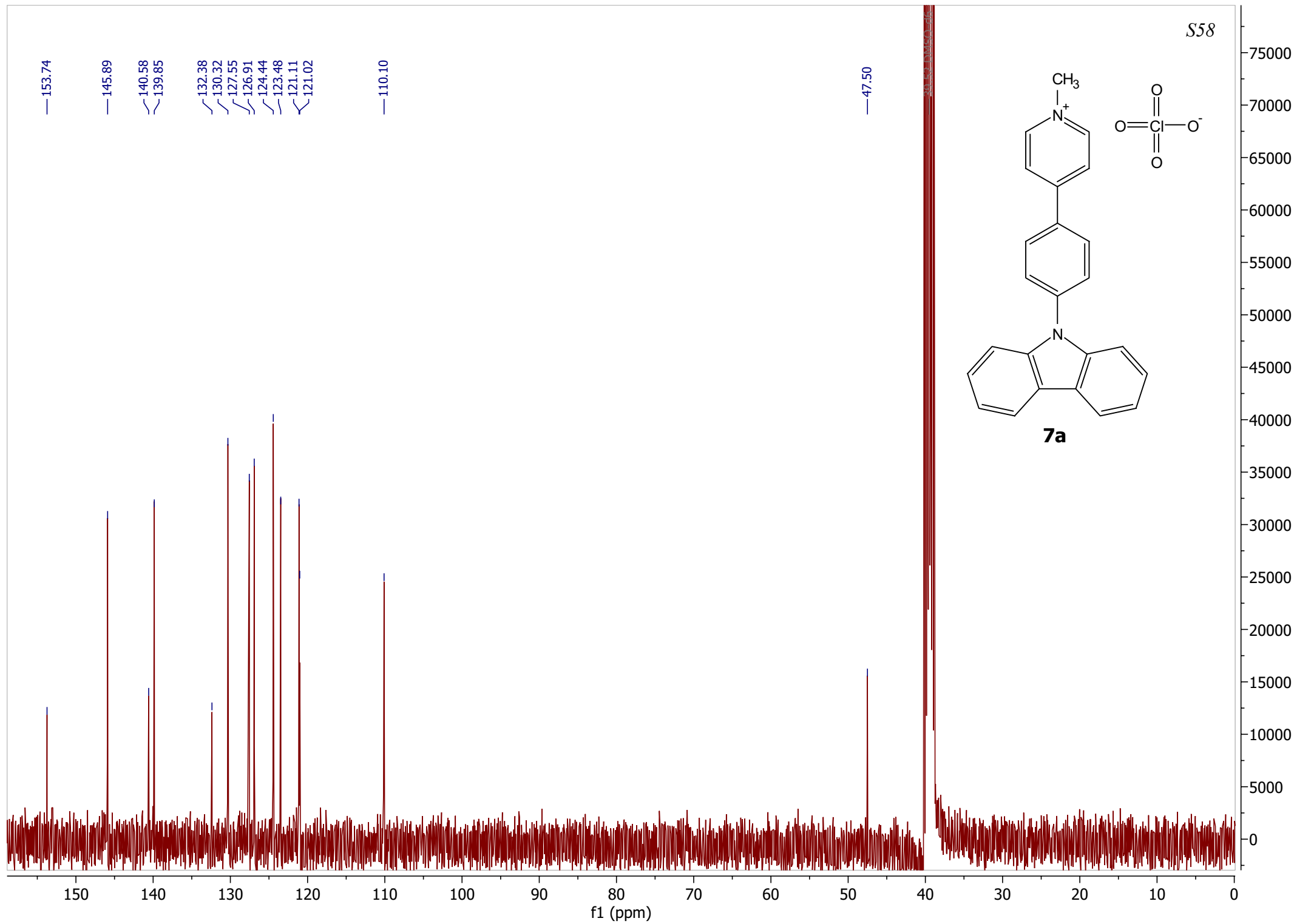




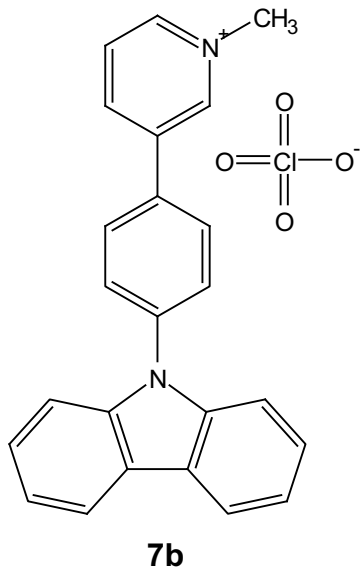
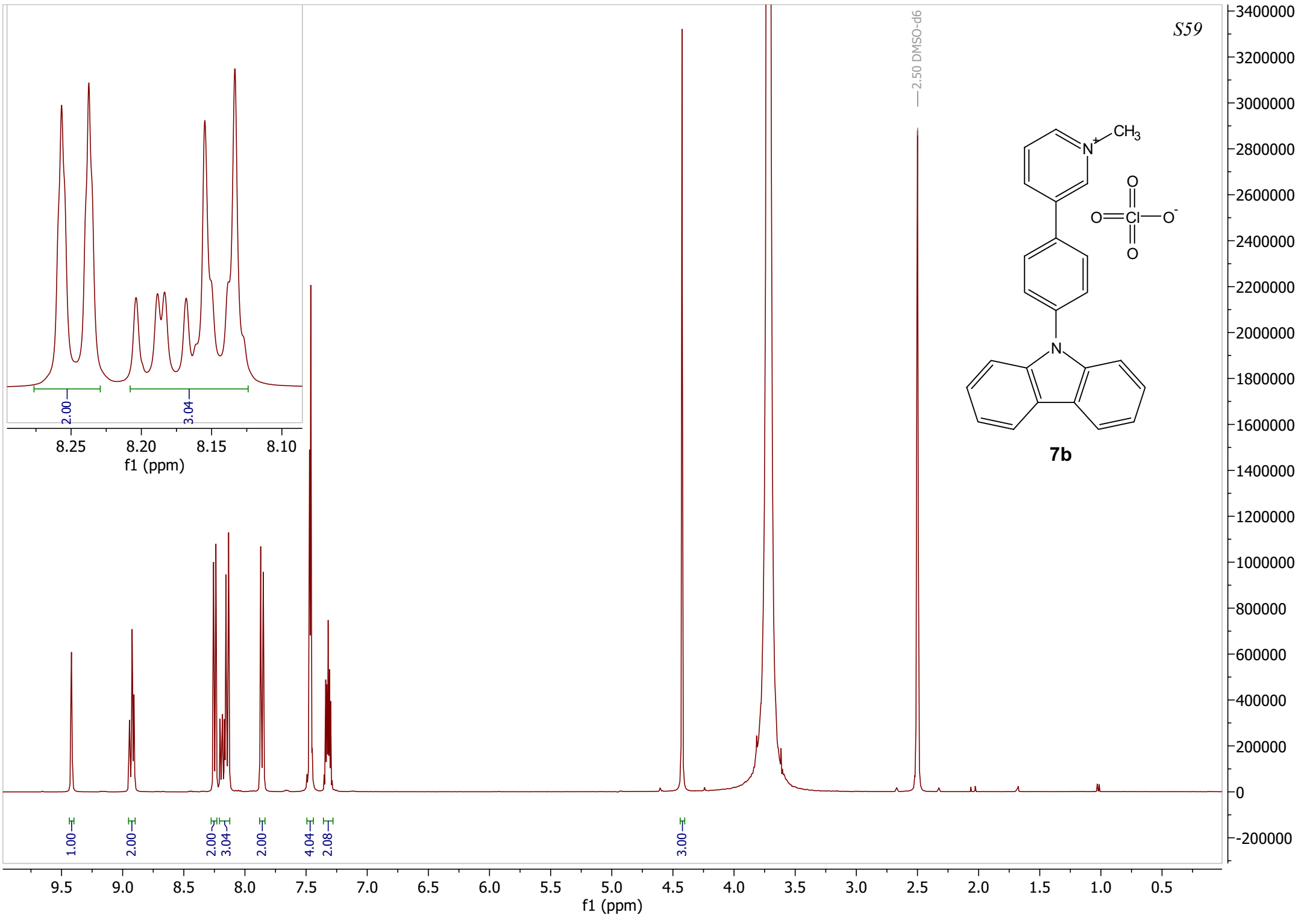


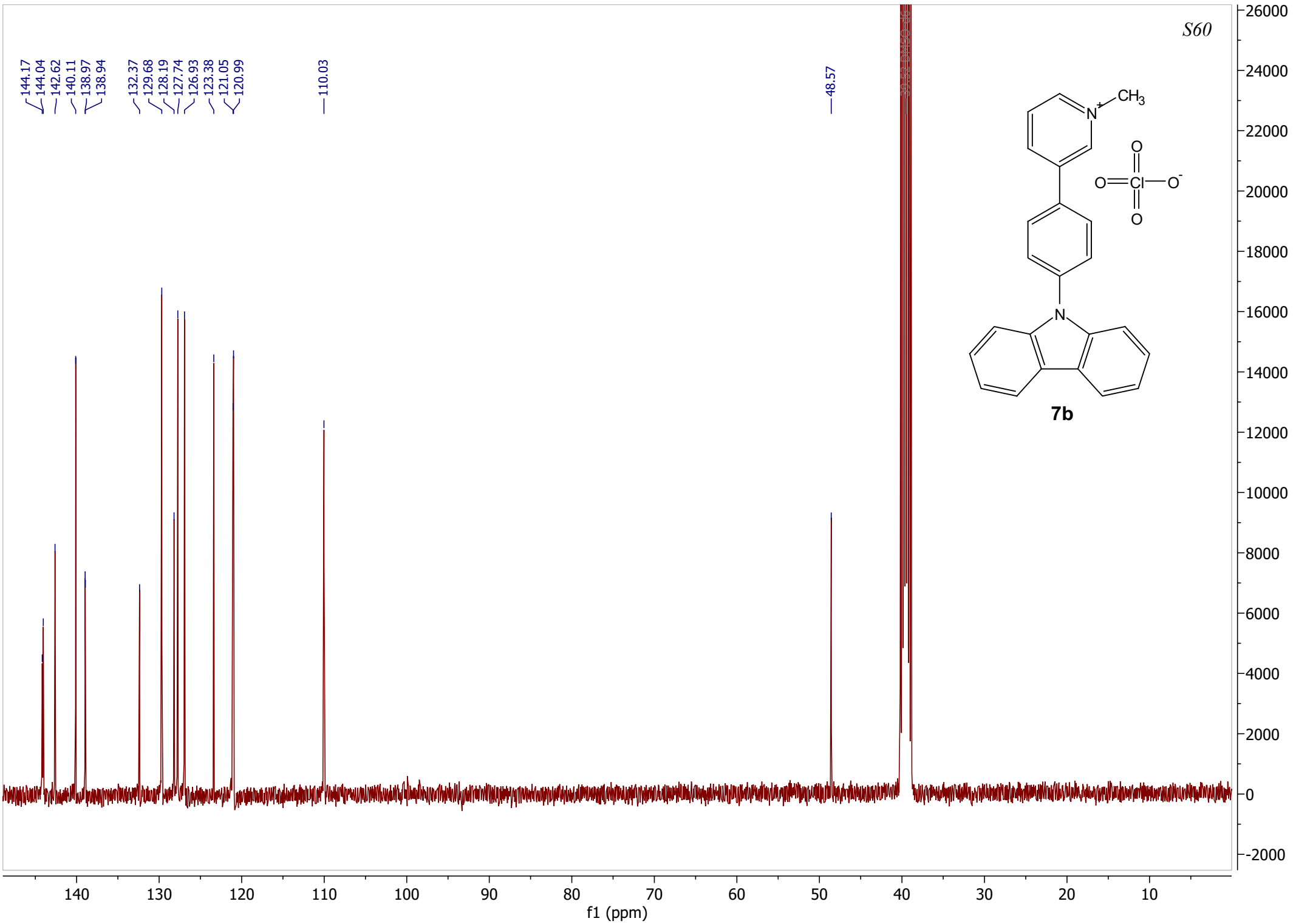
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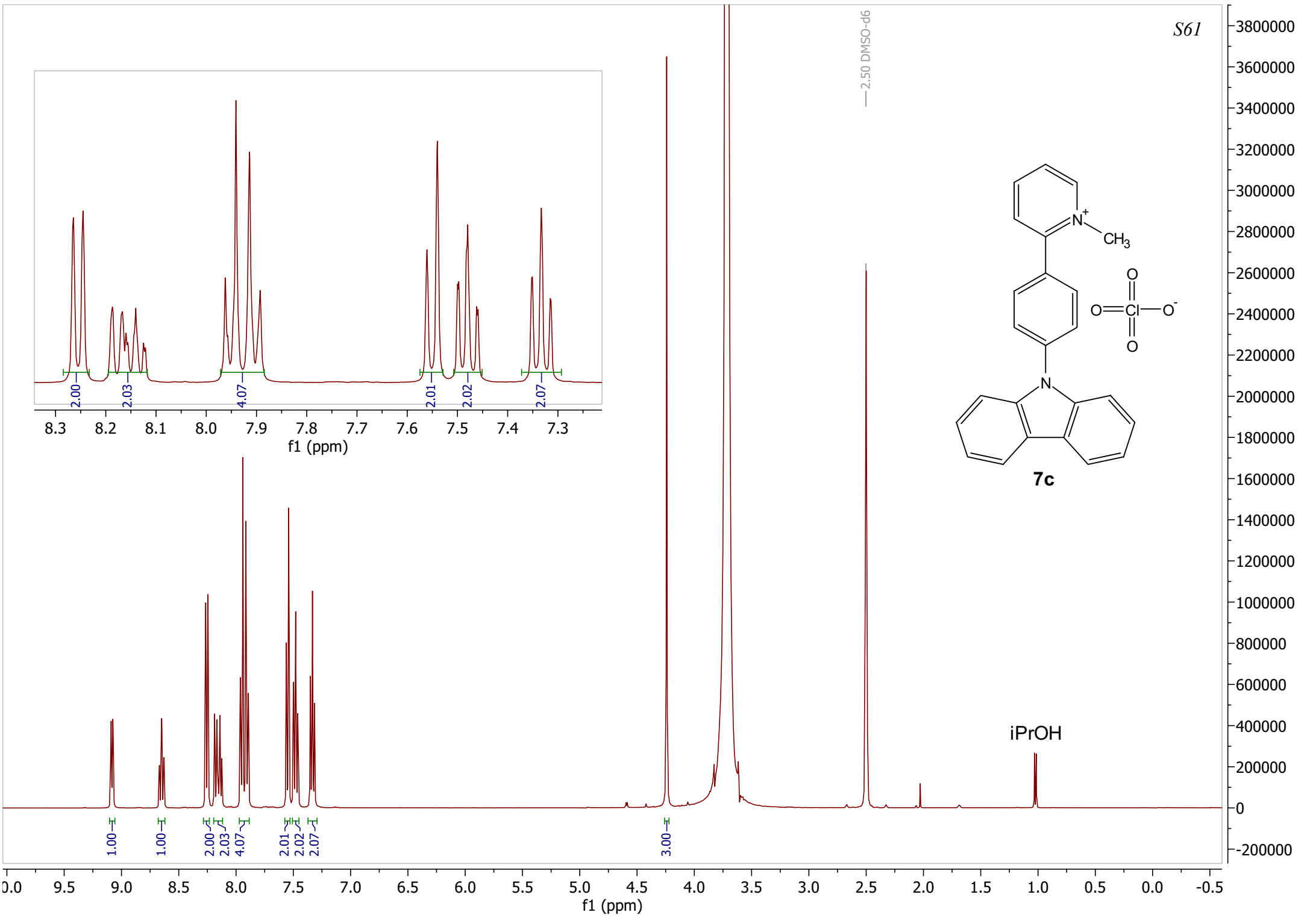


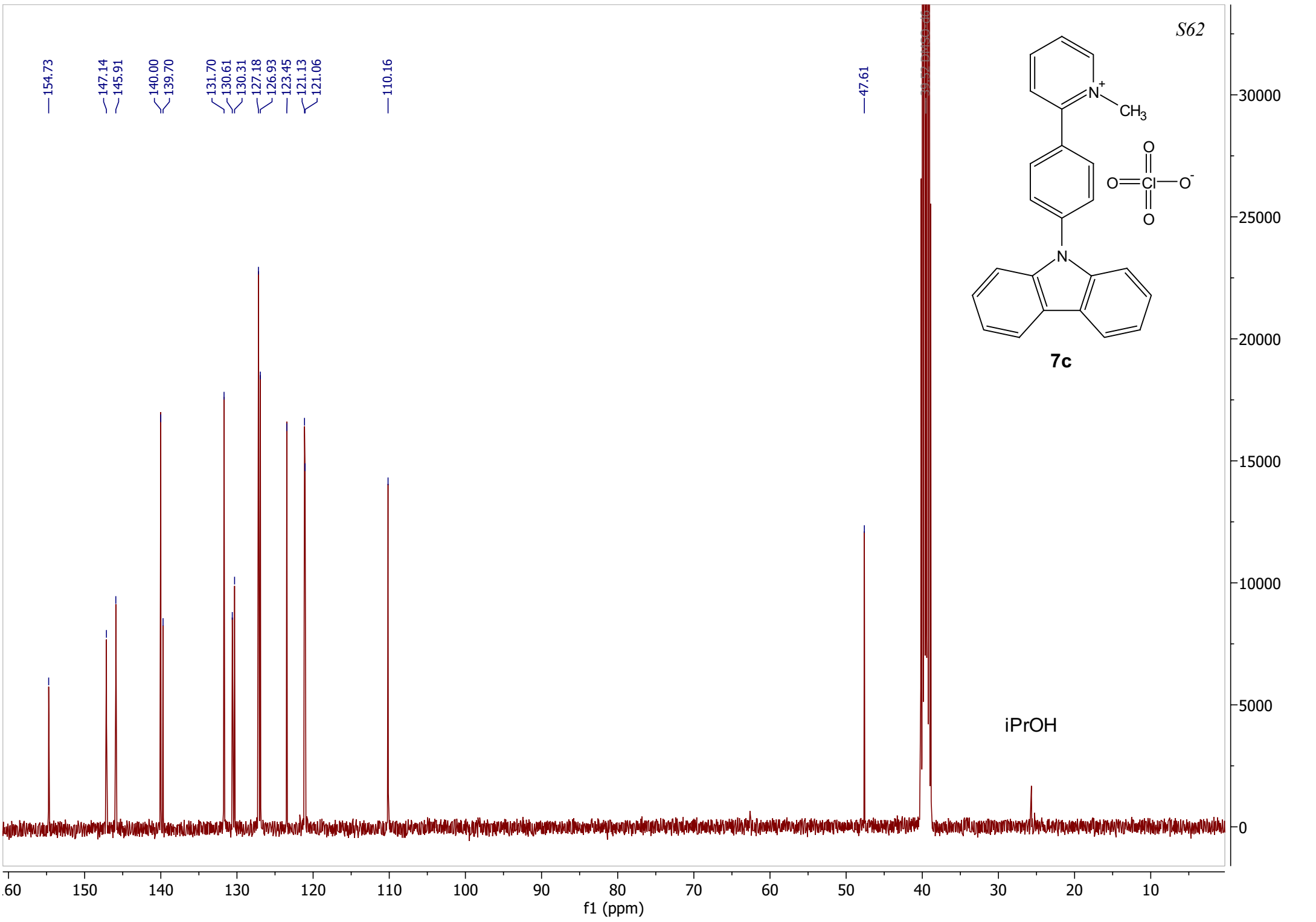


S59



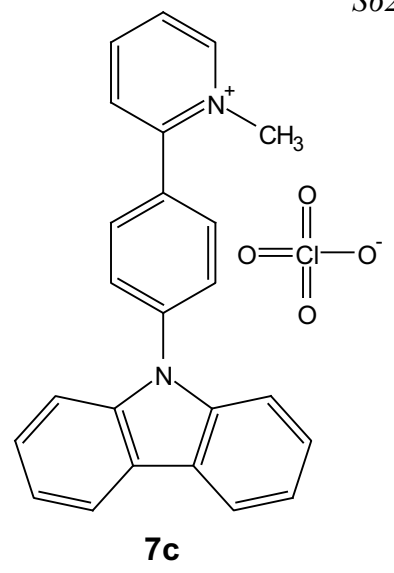






154.73  
147.14  
145.91  
140.00  
139.70  
131.70  
130.61  
130.31  
127.18  
126.93  
123.45  
121.13  
121.06  
110.16

47.61



iPrOH

60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

