

## Supplementary Information

### Task-specific design of a hierarchical porous aromatic framework as an ultrastable platform for large-sized catalytic active site binding

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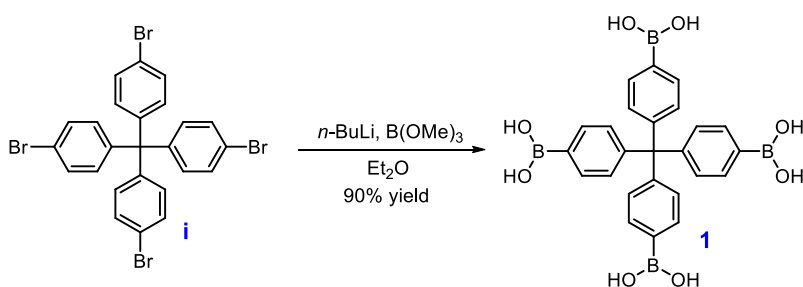
## General

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven or heat-dried flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: Et<sub>2</sub>O (Na), THF (Na). All reactions were monitored by thin-layer chromatography (TLC) on gel F<sub>254</sub> plates using UV light as visualizing agent (if applicable), and a solution of ammonium molybdate tetrahydrate (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Qingdao Marine Chemical Factory in China.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> solution on a Varian 300 MHz instrument (300 MHz for <sup>1</sup>H NMR, 75 MHz for <sup>13</sup>C NMR) or a Bruker 500 MHz instrument (500 MHz for <sup>1</sup>H NMR, 125 MHz for <sup>13</sup>C NMR). Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent (CHCl<sub>3</sub> (7.26 ppm), DMSO-*d*<sub>5</sub> (2.50 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for <sup>1</sup>H NMR and the deuterated solvent (CDCl<sub>3</sub> (77.00 ppm) or DMSO-*d*<sub>6</sub> (39.51 ppm)) or tetramethylsilane (0.00 ppm) as internal standard for <sup>13</sup>C NMR. Coupling constants reported in Hz constitute <sup>3</sup>*J* (H, H) and <sup>4</sup>*J* (H, H) coupling constants, unless otherwise noted. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on an Agilent 1290-microTOF Q II by means of the ESI technique. FT-IR spectra were recorded on a Bruker IFS 66v/S Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA) was performed using a Netzsch Sta 449c thermal analyzer system at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C in an air atmosphere. The N<sub>2</sub> adsorption-desorption isotherms were measured on a Quantachrome Autosorb-iQ2 analyzer. Powder X-ray diffraction (PXRD) was performed by a Rigaku D/MAX2550 diffractometer using Cu-Kα radiation, 40 kV, 200 mA with a scanning rate of 1° min<sup>-1</sup> (2θ). Transmission electron microscopy (TEM) was recorded using a JEOL JEM 3010 instrument with an acceleration voltage of 300 kV. Scanning electron Microscopy (SEM) analysis was performed on a JEOS JSM 6700 system.

## 1. Synthesis of the Monomers

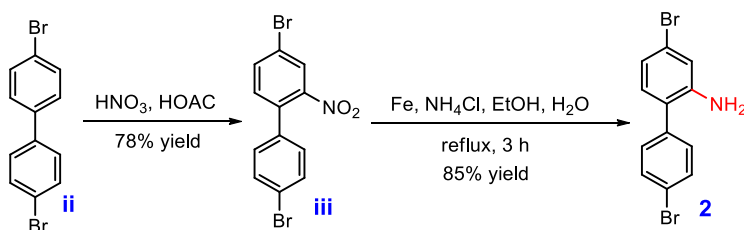
### ■ Synthesis of the monomer 1:



To a suspension of tetra(4-bromophenyl)methane **i** (2.0 g, 3.14 mmol) in Et<sub>2</sub>O (150 mL) was added a solution of *n*-BuLi in hexane (2.5 M, 7.5 mL, 18.9 mmol, 6.0 equiv.) via cannula at -78 °C. The resultant reaction mixture was then allowed to warm to room temperature and stirred for 10 h. After cooling to -78 °C again, B(OMe)<sub>3</sub> (2.61 g, 25.2 mmol, 8.0 equiv.) was added to the reaction mixture, and the resultant reaction mixture was then allowed to warm to room temperature and stirred for 3 h. After removing the solvent by evaporation, to the resulting residue was added aqueous HCl solution (2.4 M, about 60 mL) and the resultant mixture was filtrated. To the resulting solid was added aqueous NaOH solution (1 M, 10 mL) and the resultant mixture was filtrated. Then the pH value of the filtrate was adjusted to <6 by adding aqueous HCl solution (1 M, about 10 mL). After filtration, the resultant solid was washed with H<sub>2</sub>O (2 × 15 mL) and dried in vacuo to give **1** (1.41 g, 2.84 mmol, 90% yield).

**1**: <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ = 8.00 (brs, 8H), 7.68 (d, *J* = 8.4 Hz, 8H), 7.14 ppm (d, *J* = 8.4 Hz, 8H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 148.2, 133.5, 131.8, 129.6, 65.0 ppm.

## ■ Synthesis of the monomer **2**:



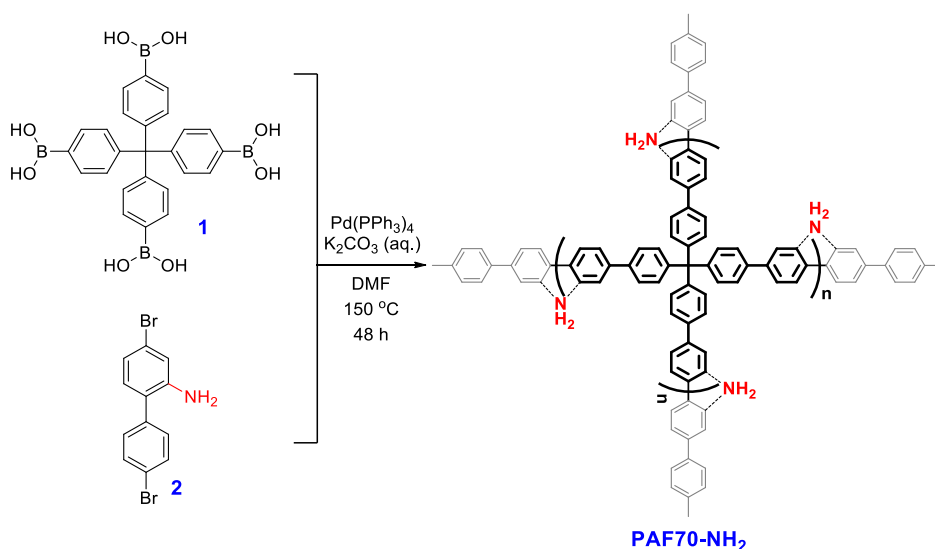
4,4'-Dibromobiphenyl **ii** (8.0 g, 25.6 mmol) was dissolved in glacial acetic acid (120 mL) at 100 °C. Then fuming nitric acid (36 mL) was added dropwise via cannula and the resultant reaction mixture was stirred at 100 °C for 2 h. Then the reaction mixture was poured into 200 mL cold water (0 °C). After filtration under reduced pressure, the resultant solid was washed with H<sub>2</sub>O (3 × 15 mL) and dried in vacuo. The obtained crude product was dissolved in 150 mL boiling EtOH at 90 °C. The mixed solution was stood at room temperature for crystallization for 12 h. Following the filtration under reduced pressure, the solid was isolated and dried in vacuo to give **iii** (7.14 g, 20.0 mmol, 78% yield).

**iii**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.03 (d, *J* = 1.8 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.16 ppm (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 149.3, 135.5, 135.3, 134.1, 133.0, 132.0, 129.4, 127.2, 123.1, 121.8 ppm.

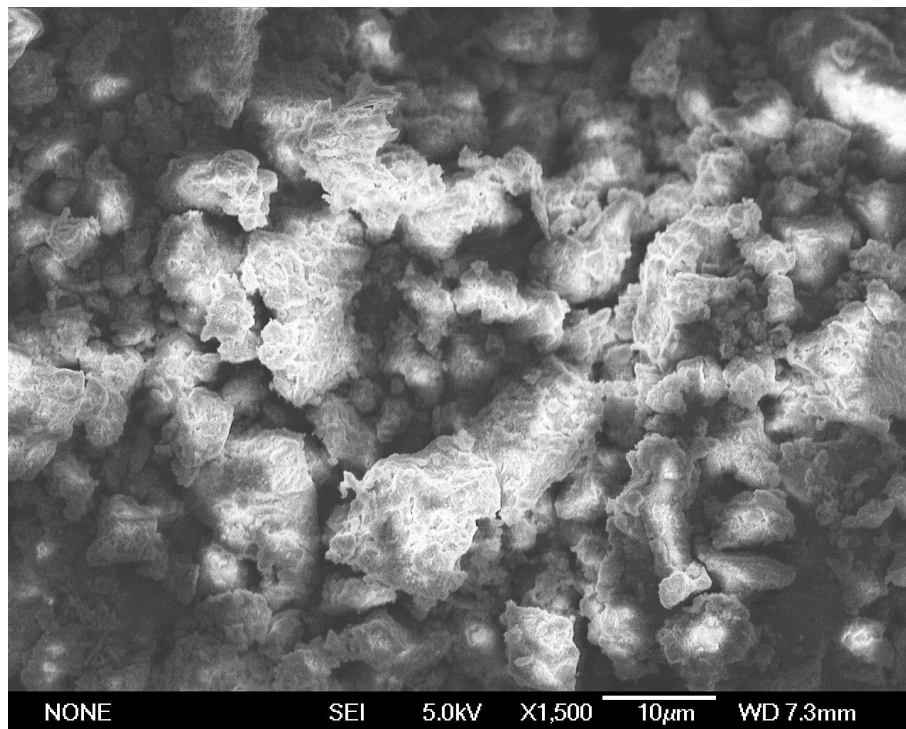
To **iii** (5.15 g, 14.4 mmol) obtained above was sequentially added Fe powder (2.42 g, 43.3 mmol, 3 equiv.), NH<sub>4</sub>Cl (1.54 g, 28.8 mmol, 2 equiv.), 120 mL EtOH and 30 mL H<sub>2</sub>O. The obtained mixture was stirred and refluxed at 90 °C for 3 h. After cooling to room temperature, the pH value of the mixture was adjusted to 7 by adding saturated aqueous NaHCO<sub>3</sub> solution (about 100 mL). Following the filtration under reduced pressure, EtOH was removed from the obtained filtrate by evaporation. The resultant residue was extracted by CH<sub>2</sub>Cl<sub>2</sub> (4 × 100 mL) and the combined organic solution was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under vacuum, the crude product was dissolved in 50 mL boiling CH<sub>2</sub>Cl<sub>2</sub> at 70 °C. The mixed solution was stood at room temperature for crystallization for 12 h. Following the filtration under reduced pressure, the solid was isolated and dried in vacuo to give **2** (4.01 g, 12.3 mmol, 85% yield).

**2**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.94–6.90 (m, 3H), 3.84 ppm (brs, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 144.7, 137.3, 132.1, 131.5, 130.6, 125.1, 122.4, 121.60, 121.56, 118.2 ppm.

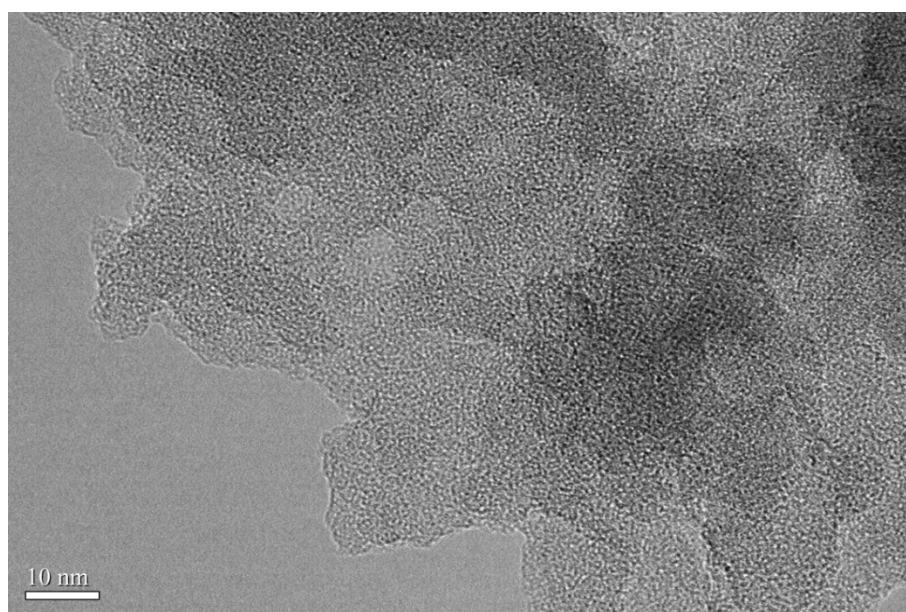
## 2. Synthesis of PAF70-NH<sub>2</sub>



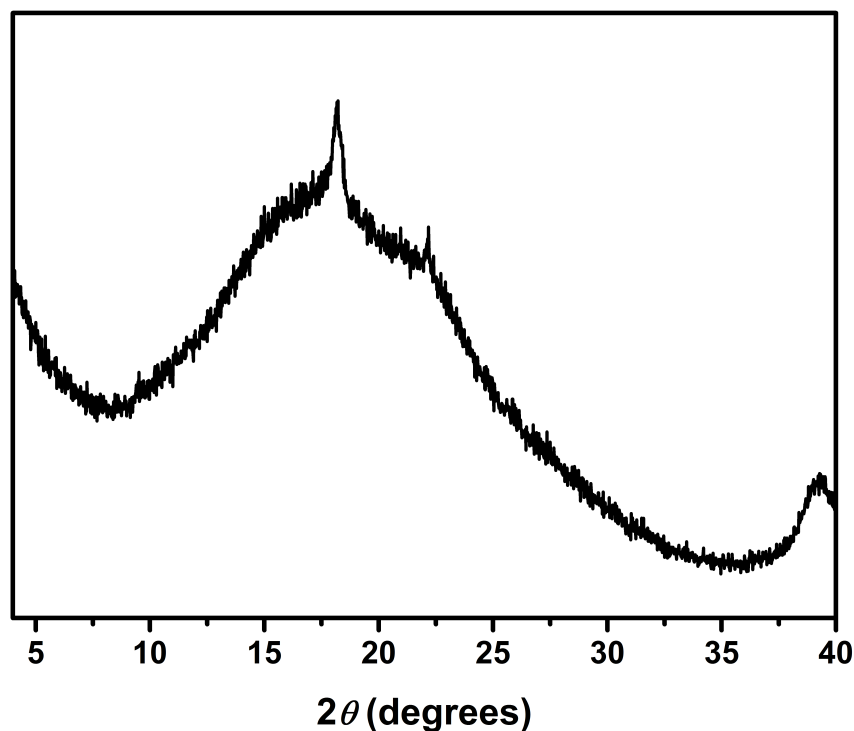
To an oven-dried 100-mL Schlenk tube were sequentially added **1** (100 mg, 0.20 mmol), **2** (132 mg, 0.40 mmol, 2 equiv.), 6.2 mL DMF and 0.8 mL aqueous K<sub>2</sub>CO<sub>3</sub> solution (2.0 M). The mixture was degassed by three freeze–pump–thaw cycles. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (23mg, 0.02mmol, 0.1 equiv.) was added to the system quickly under argon and the resultant reaction mixture was stirred and refluxed for 48 h at 150 °C. After cooling to room temperature, the mixture was filtrated under reduced pressure and the obtained solid was washed with H<sub>2</sub>O (4 × 20 mL), THF (4 × 20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4 × 20 mL), dried in vacuo at 100 °C, yielding the desired **PAF70-NH<sub>2</sub>** (130mg, 99% yield).



**Fig. S1** SEM image of PAF70-NH<sub>2</sub>.



**Fig. S2** TEM image of PAF70-NH<sub>2</sub>.



**Fig. S3** The PXRD pattern of PAF70-NH<sub>2</sub>.

### 3. The Chemical Stability of PAF70-NH<sub>2</sub>

The experimental procedure for testing chemical stability of PAF70-NH<sub>2</sub> was described as follows:

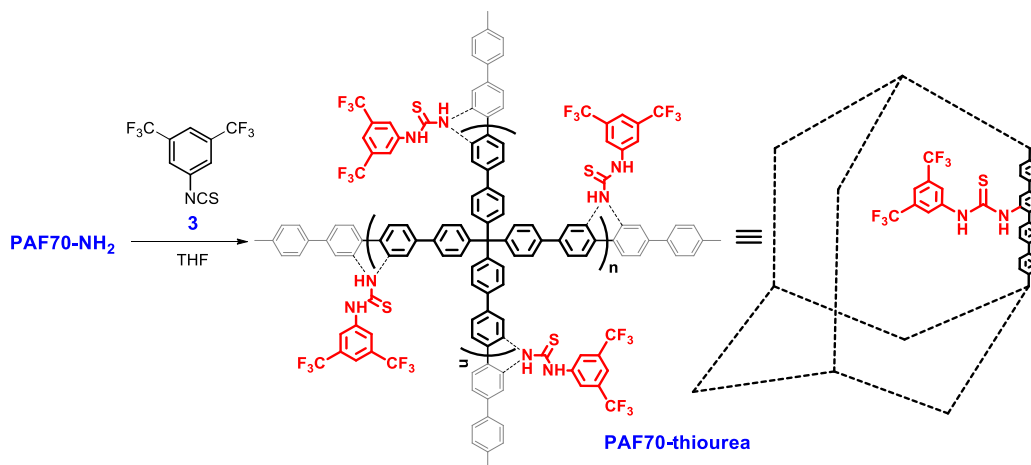
Step 1: 20 mg PAF70-NH<sub>2</sub> was dispersed in 20 mL different solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, EtOAc, toluene, MeOH, EtOH, DMSO, DMF, water, boiling water, boiling DMF, 12 mol/L HCl aqueous solution, and 14 mol/L NaOH aqueous solution) for one week. Then the mixture was filtrated under reduced pressure.

Step 2: In the event that the used solvent was THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, EtOAc, MeOH or EtOH, the resultant solid from Step 1 was directly dried in vacuo for 18 h at 100 °C, affording the desired PAF70-NH<sub>2</sub>.

In the event that the the used solvent was toluene, water or boiling water, the resultant solid from Step 1 was washed with EtOH (3 × 30 mL), dried in vacuo for 18 h at 100 °C, affording the desired PAF70-NH<sub>2</sub>.

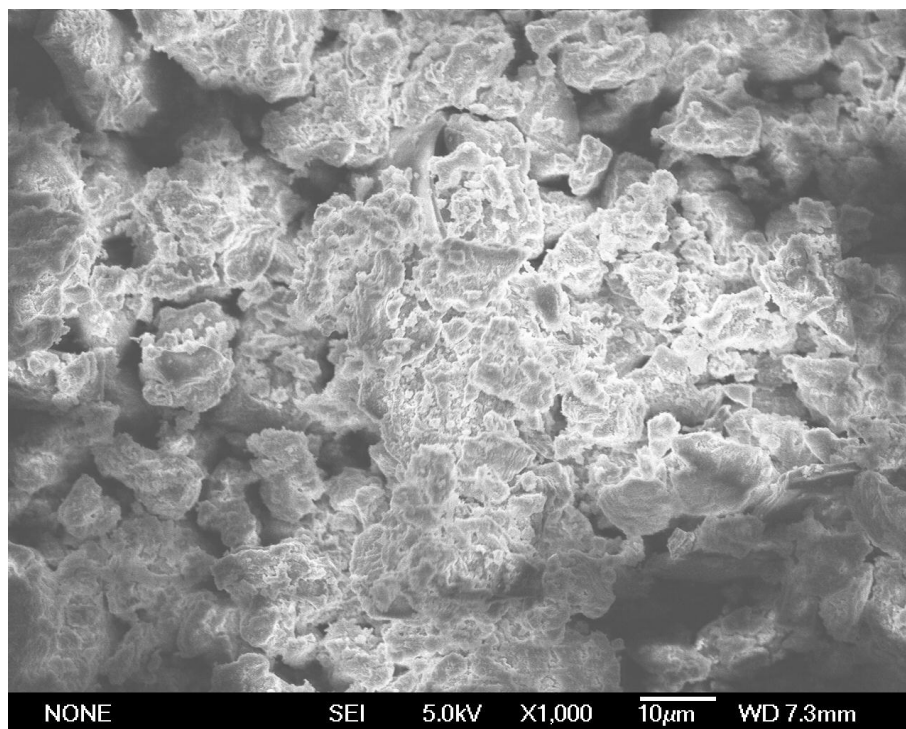
In the event that the the used solvent was DMSO, DMF, boiling DMF, 12 mol/L HCl aqueous solution, or 14 mol/L NaOH aqueous solution, the resultant solid from Step 1 was washed with H<sub>2</sub>O (3 × 30 mL) and EtOH (3 × 30 mL), dried in vacuo for 18 h at 100 °C, affording the desired PAF70-NH<sub>2</sub>.

### 4. Synthesis of PAF70-thiourea

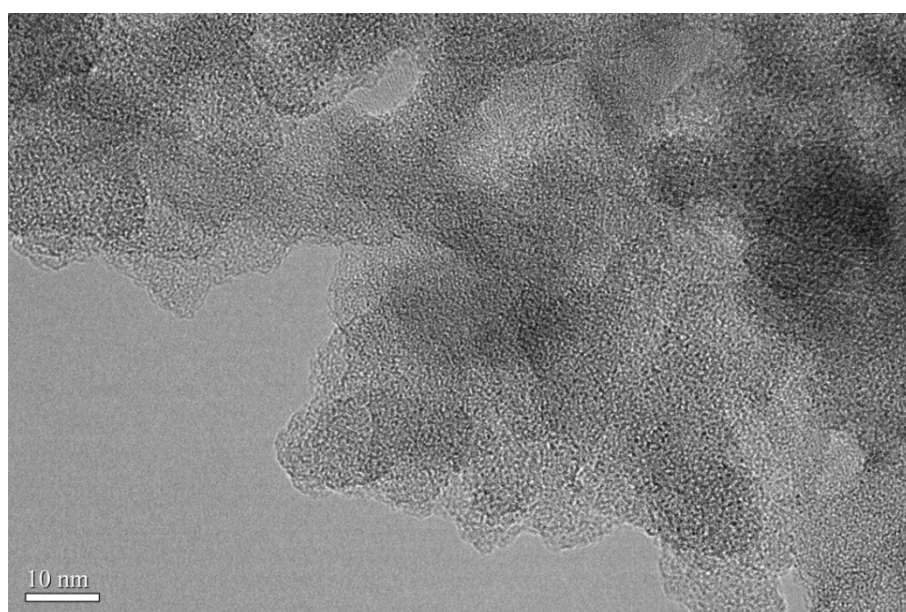




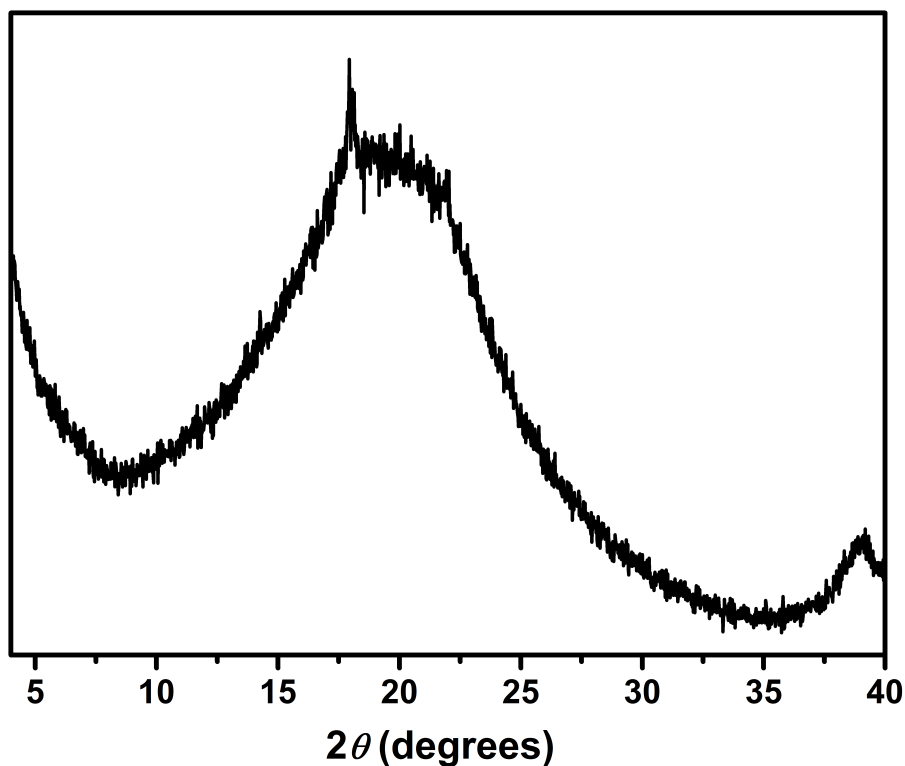
To **PAF70-NH<sub>2</sub>** (600 mg) obtained above was added a solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate **3** (1.02 g, 3.76 mmol) in THF (60 mL) and the resulting mixture was stirred for 4 days at room temperature. Then the reaction mixture was filtrated under reduced pressure. The resultant solid was washed with H<sub>2</sub>O (4 × 40 mL), THF (4 × 40 mL) and CH<sub>2</sub>Cl<sub>2</sub> (4 × 40 mL), dried in vacuo for 18 h at 60 °C, yielding the desired **PAF70-thiourea** (804mg).



**Fig. S4** SEM image of **PAF70-thiourea**.



**Fig. S5** TEM image of **PAF70-thiourea**.



**Fig. S6** The PXRD pattern of PAF70-thiourea.

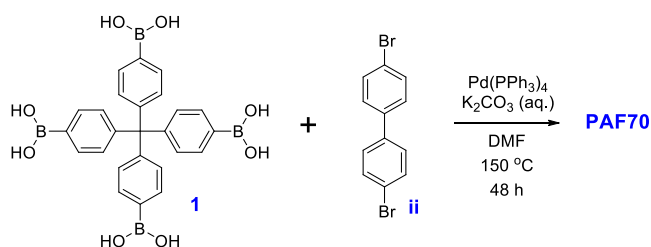
## 5. Control Experiments for the NBS-mediated Oxidation of Alcohols

**Table S1.** The control experiments for the NBS-mediated oxidation of alcohols<sup>a</sup>

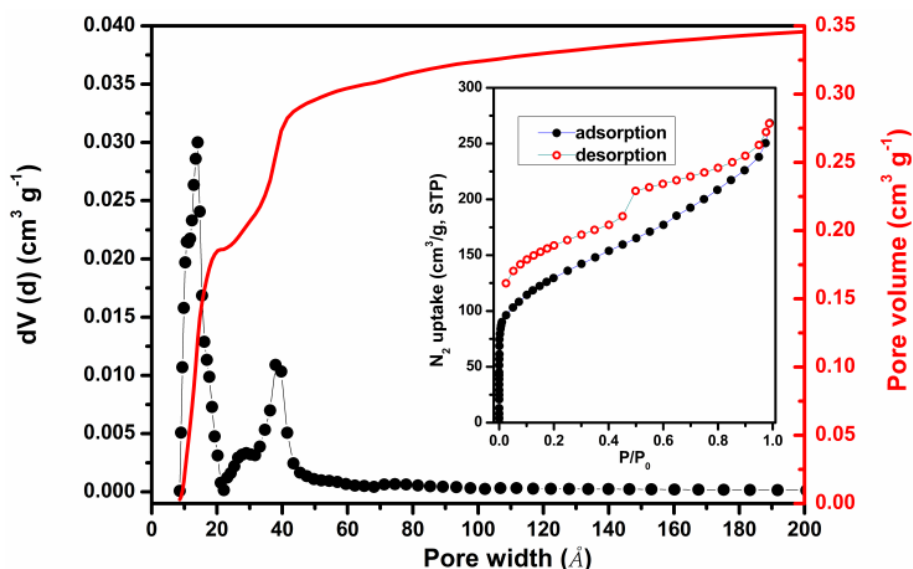
entry	catalyst (catalyst loading)	conversion <sup>b</sup>
1	PAF70-thiourea (5 mol%)	71%
2	No catalyst	0
3	PAF70 <sup>c</sup>	0
4	PAF70-NH <sub>2</sub> (5 mol%)	PAF70-NH <sub>2</sub> reacts with NBS
5		4 reacts with NBS
6	 Homogeneous Catalyst (5 mol%)	60%
7	PAF70-thiourea (10 mol%)	79%
8	The supernatant liquid of the CH <sub>2</sub> Cl <sub>2</sub> suspension of PAF70-thiourea <sup>d</sup>	0

<sup>a</sup> Reaction condition: a solution of 0.335 mmol **1a**, 0.50 mmol NBS and the catalysts (for entry 1, no catalyst was added; for entry 3, 18 mg PAF70 was added as catalyst; for other entries the catalysts were added at the indicated loadings) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was stirred at -35 °C for 48 h. <sup>b</sup> Conversion was determined by <sup>1</sup>H NMR of the crude reaction mixture obtained under the optimized condition. <sup>c</sup> PAF70 was synthesized as followed which has a 4.6 wt% palladium oxide residue. <sup>d</sup> 35 mg PAF70-thiourea was immersed in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> for 48 h at -35 °C, after centrifugation, to the supernatant liquid was added 0.335 mmol **1a** and 0.50 mmol NBS and the resulted mixture was stirred at -35 °C for 48 h.

## ■ Synthesis of PAF70:

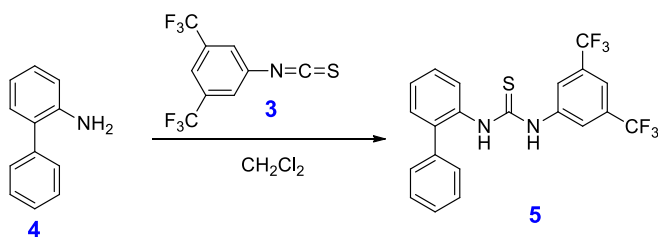


To an oven-dried 100-mL Schlenk tube were sequentially added **1** (100 mg, 0.20 mmol), **ii** (125 mg, 0.40 mmol, 2 equiv.), 6.2 mL DMF and 0.8 mL aqueous  $K_2CO_3$  solution (2.0 M). The mixture was degassed by three freeze–pump–thaw cycles. Then  $Pd(PPh_3)_4$  (23mg, 0.02mmol, 0.1 equiv.) was added to the system quickly under argon and the resultant reaction mixture was stirred and refluxed for 48 h at 150 °C. After cooling to room temperature, the mixture was filtrated under reduced pressure and the obtained solid was washed with  $H_2O$  ( $4 \times 20$  mL), THF ( $4 \times 20$  mL) and  $CH_2Cl_2$  ( $4 \times 20$  mL), dried in vacuo at 100 °C, yielding the desired **PAF70** (123mg, 99% yield).



**Fig. S7** Pore size distribution calculated from NLDFT ( $N_2$  at 77K on carbon (slit pore)) of **PAF70**. Insert: nitrogen adsorption (solid symbols)–desorption (open symbols) isotherms measured at 77 K for **PAF70**.

■ The experimental procedure for preparation of the monomer catalyst **5** was described as follows:



To a solution of 2-biphenylamine **4** (200 mg, 1.18 mmol) in  $CH_2Cl_2$  (30 mL) was added 3,5-bis(trifluoromethyl)phenyl isothiocyanate **3** (481 mg, 1.77 mmol, 1.5 equiv.) and the resulting mixture was stirred for 1 day at room temperature. Then the reaction mixture was concentrated under reduced pressure. The resultant residue was then directly subjected to the flash column chromatography purification on silica gel, affording the monomer catalyst **5** (490 mg, 1.11 mmol, 94% yield).

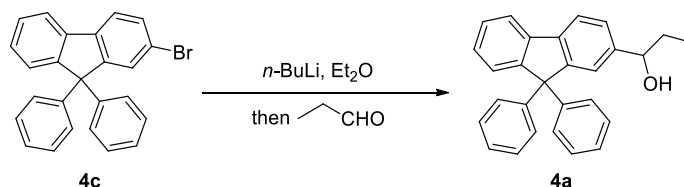
**5**:  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 8.73 (s, 1H), 7.63 (s, 2H), 7.54–7.38 ppm (m, 11H);  $^{13}C$  NMR (125 MHz,



CDCl<sub>3</sub>):  $\delta$  = 179.5, 139.3, 138.2, 137.6, 133.0, 131.9 (q,  $J$  = 34 Hz), 131.6, 129.2, 129.0, 128.8, 128.6, 128.4, 127.2, 125.16 (q,  $J$  = 3.0 Hz), 122.8 (q,  $J$  = 271 Hz), 119.6 (m) ppm; HRMS (ESI):  $m/z$  calcd for C<sub>21</sub>H<sub>15</sub>F<sub>6</sub>N<sub>2</sub>S: 441.0855; found: 441.0851 [ $M+H$ ]<sup>+</sup>.

## 6. PAF70-thiourea Catalyzed NBS-mediated Oxidation of Alcohols

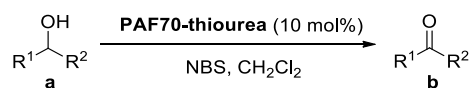
■ The experimental procedure for preparation of the large-size substrate **4a** was described as follows:



To a solution of **4c** (993 mg, 2.50 mmol) in Et<sub>2</sub>O (50 mL) was added *n*-BuLi (2.5 M in hexane, 2.0 mL, 5.0 mmol, 2.0 equiv) at -78 °C. Then the reaction temperature was allowed to naturally increase to room temperature, and the reaction mixture was stirred totally for 3 h during this manipulation. After that, propionaldehyde (436 mg, 7.5 mmol, 3.0 equiv) was added to this resulting mixture at -78 °C. Following naturally warming up to room temperature, the mixture was stirred at this temperature for 5 h. Then H<sub>2</sub>O (20 mL) was added to quench the reaction, and the resulting mixture was extracted with AcOEt (3 × 50 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue obtained was purified by flash column chromatography on silica gel to afford **4a** (565 mg, 1.50 mmol, 60% yield).

**4a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.76–7.71 (m, 2H), 7.40–7.24 (m, 5H), 7.23–7.16 (m, 10H), 4.58 (t,  $J$  = 6.6 Hz, 1H), 1.84–1.65 (m, 3H), 0.88 ppm (t,  $J$  = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.35, 151.31, 145.9, 144.4, 139.9, 139.6, 128.2, 128.1, 127.6, 127.4, 126.6, 126.2, 125.3, 123.9, 120.1, 76.1, 65.5, 32.0, 10.1 ppm; HRMS (ESI):  $m/z$  calcd for C<sub>28</sub>H<sub>24</sub>NaO: 399.1719; found: 399.1713 [ $M+Na$ ]<sup>+</sup>.

■ General experimental procedure for **PAF70-thiourea** catalyzed NBS-mediated oxidation of alcohols in Table 1 of the paper was described as follows:



To an oven-dried 10-mL Schlenk tube at the indicated temperature were sequentially added alcohol **1–4a** (0.335 mmol, 1 equiv.), *N*-bromosuccinimide (NBS, 89 mg, 0.503 mmol, 1.5 equiv.), the catalyst **PAF70-thiourea** (0.97 mmol g<sup>-1</sup> of thiourea unit based on the elemental analysis of sulfur, 35 mg, 0.034 mmol thiourea unit, 0.1 equiv) and CH<sub>2</sub>Cl<sub>2</sub> (pre-cooled to the indicated temperature, 1.0 mL). The reaction mixture was stirred at this temperature for the indicated time. Then saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (1.5 mL) and brine (1.5 mL) was added to the mixture. After centrifugation, the solid was washed with H<sub>2</sub>O (1 × 5 mL) and AcOEt (5 × 5 mL). The combined solution was extracted with AcOEt (70 mL) and the organic phase was washed with H<sub>2</sub>O (2 × 15 mL) and brine (20 mL). The combined organic solution was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under vacuum at 0 °C, the crude product was purified by flash chromatography over silica gel to give the product **1–4b**.

**1b**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.99–7.94 (m, 2H), 7.57 (t,  $J$  = 7.5 Hz, 1H), 7.46 (t,  $J$  = 7.5 Hz, 2H), 2.61 ppm (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.9, 137.0, 132.9, 128.4, 128.1, 26.4 ppm.

**2b**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.04 (d,  $J$  = 8.2 Hz, 2H), 7.69 (d,  $J$  = 8.2 Hz, 2H), 7.64 (dd,  $J$  = 6.9, 1.5 Hz, 2H), 7.51–7.38 (m, 3H), 2.64 ppm (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 197.6, 145.7, 139.8, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6 ppm.

**3b:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.99–7.95 (m, 2H), 7.59–7.52 (m, 1H), 7.49–7.43 (m, 2H), 3.01 (q,  $J$  = 7.2 Hz, 2H), 1.23 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 200.6, 136.8, 132.7, 128.4, 127.8, 31.6, 8.1 ppm.

**4b:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.03 (s, 1H), 7.99 (d,  $J$  = 8.0 Hz, 1H), 7.81 (d,  $J$  = 7.5 Hz, 2H), 7.43 (d,  $J$  = 7.5 Hz, 1H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 7.32 (t,  $J$  = 7.5 Hz, 1H), 7.26–7.16 (m, 10H), 2.95 (q,  $J$  = 7.2 Hz, 2H), 1.18 ppm (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 200.1, 152.4, 151.6, 145.2, 144.8, 138.9, 136.4, 128.9, 128.4, 128.1, 128.0, 127.7, 126.9, 126.4, 125.9, 121.0, 120.0, 65.6, 31.9, 8.3 ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{23}\text{O}$ : 375.1743; found: 375.1732 [ $M+\text{H}$ ] $^+$ .

## 7. Recyclability of PAF70-thiourea for Catalyzing NBS-mediated Oxidation of Alcohols

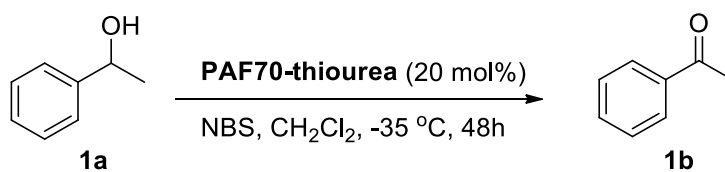
■ General experimental procedure for the recycle test of **PAF70-thiourea** catalyzed NBS-mediated oxidation of alcohols in Table S2 was described as follows:

The experimental procedure for cycle 1: To an oven-dried 10-mL Schlenk tube at  $-35\text{ }^\circ\text{C}$  were sequentially added alcohol **1a** (59 mg, 0.485 mmol, 1 equiv.), *N*-bromosuccinimide (NBS, 129 mg, 0.728 mmol, 1.5 equiv.), the catalyst **PAF70-thiourea** (0.97 mmol  $\text{g}^{-1}$  of thiourea unit based on the elemental analysis of sulfur, 100 mg, 0.097 mmol thiourea unit, 0.2 equiv) and  $\text{CH}_2\text{Cl}_2$  (pre-cooled to  $-35\text{ }^\circ\text{C}$ , 1.5 mL). The reaction mixture was stirred at  $-35\text{ }^\circ\text{C}$  for 2 days. Then saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution (2 mL) and brine (2 mL) were added to the mixture. After centrifugation, the solid was washed with  $\text{H}_2\text{O}$  ( $1 \times 5\text{ mL}$ ) and  $\text{AcOEt}$  ( $5 \times 5\text{ mL}$ ). The combined solution was extracted with  $\text{AcOEt}$  (70 mL) and the organic phase was washed with  $\text{H}_2\text{O}$  ( $2 \times 15\text{ mL}$ ) and brine (20 mL). The combined organic solution was dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent under vacuum at  $0\text{ }^\circ\text{C}$ , the conversion of **1a** was measured by  $^1\text{H}$  NMR spectrum of the crude product through calculating the ratio of the peak area integral for the methyl groups in **1b** (the signal of methyl group in **1b** is a singlet-peak at 2.61 ppm) and **1a** (the signal of methyl group in **1a** is a doublet-peak at 1.50 ppm). In addition, the crude product could be further purified by flash chromatography over silica gel to give the pure product **1b**.

The recovery procedure of catalyst: The solid obtained from centrifugation above was washed with  $\text{H}_2\text{O}/\text{EtOH}$  ( $v/v = 1:1$ ) ( $2 \times 5\text{ mL}$ ) and  $\text{EtOH}$  ( $2 \times 5\text{ mL}$ ). Then, the obtained solid was dried in vacuo at  $60\text{ }^\circ\text{C}$ , providing the recovered catalyst **PAF70-thiourea**.

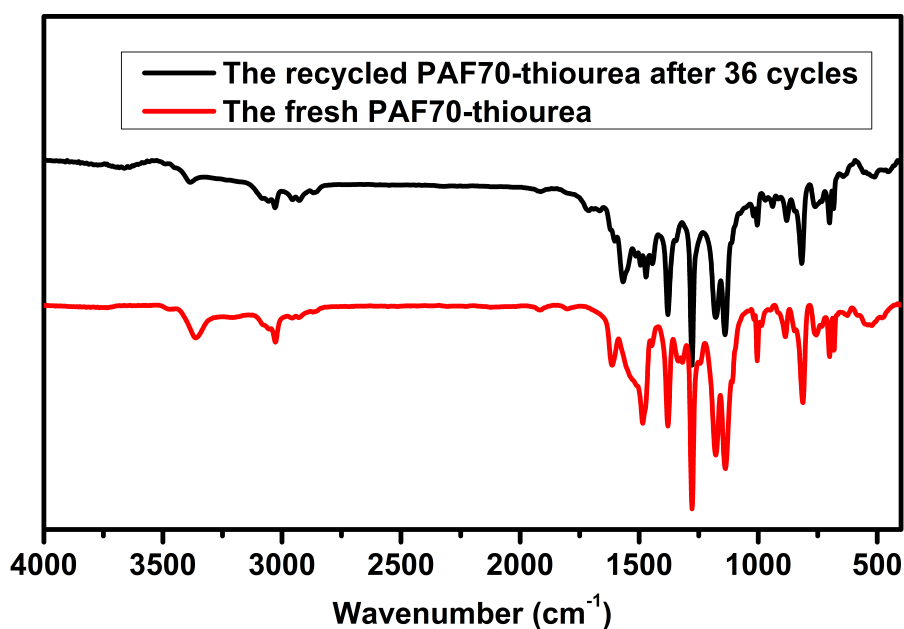
The experimental procedure for cycles 2-36: The above-mentioned recovered catalyst **PAF70-thiourea** was reused in the same reaction and the other substrates in the reaction were correspondingly decreased based on the actual mass of the recovered **PAF70-thiourea**, making sure that the mole ratios of all the reactants were the same as that in cycle 1.

**Table S2.** The recycle test of **PAF70-thiourea** catalyzed NBS-mediated oxidation of alcohols.

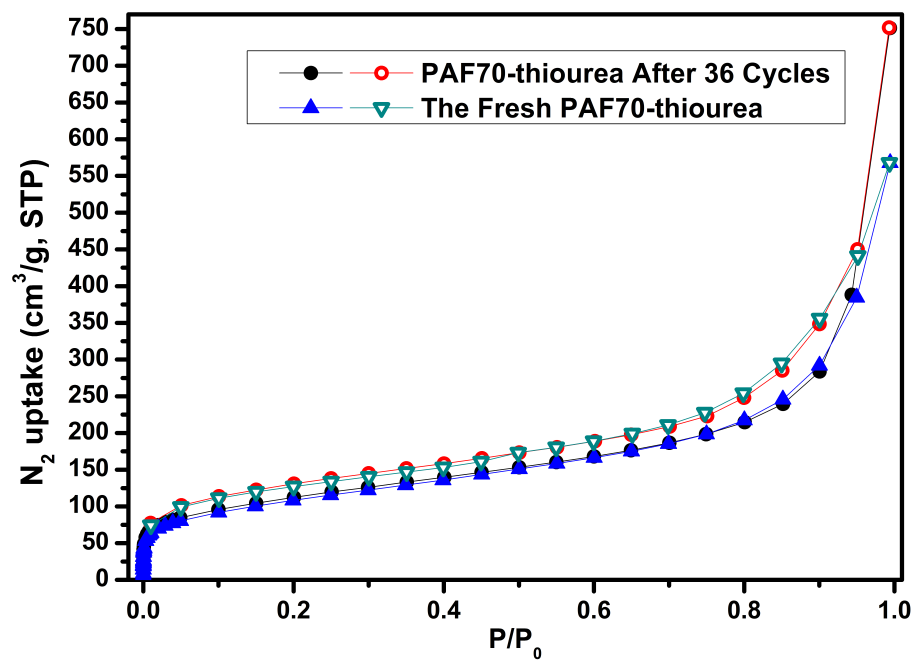


cycle	Conversion <sup>a</sup>	Yield <sup>b</sup>	cycle	Conversion <sup>a</sup>	Yield <sup>b</sup>
1	42%	-	19	88%	-
2	72%	-	20	89%	-
3	79%	72%	21	88%	76%
4	82%	-	22	85%	-
5	87%	-	23	87%	-
6	86%	76%	24	88%	75%
7	86%	-	25	89%	-
8	85%	-	26	88%	-
9	87%	74%	27	88%	77%
10	86%	-	28	86%	-
11	86%	-	29	85%	-
12	86%	77%	30	88%	76%
13	88%	-	31	89%	-
14	86%	-	32	88%	-
15	85%	75%	33	85%	75%
16	89%	-	34	87%	-
17	87%	-	35	88%	-
18	88%	74%	36	86%	74%

<sup>a</sup>Conversion was determined by <sup>1</sup>H NMR of the crude reaction mixture. <sup>b</sup>Isolated yield of **1b**.

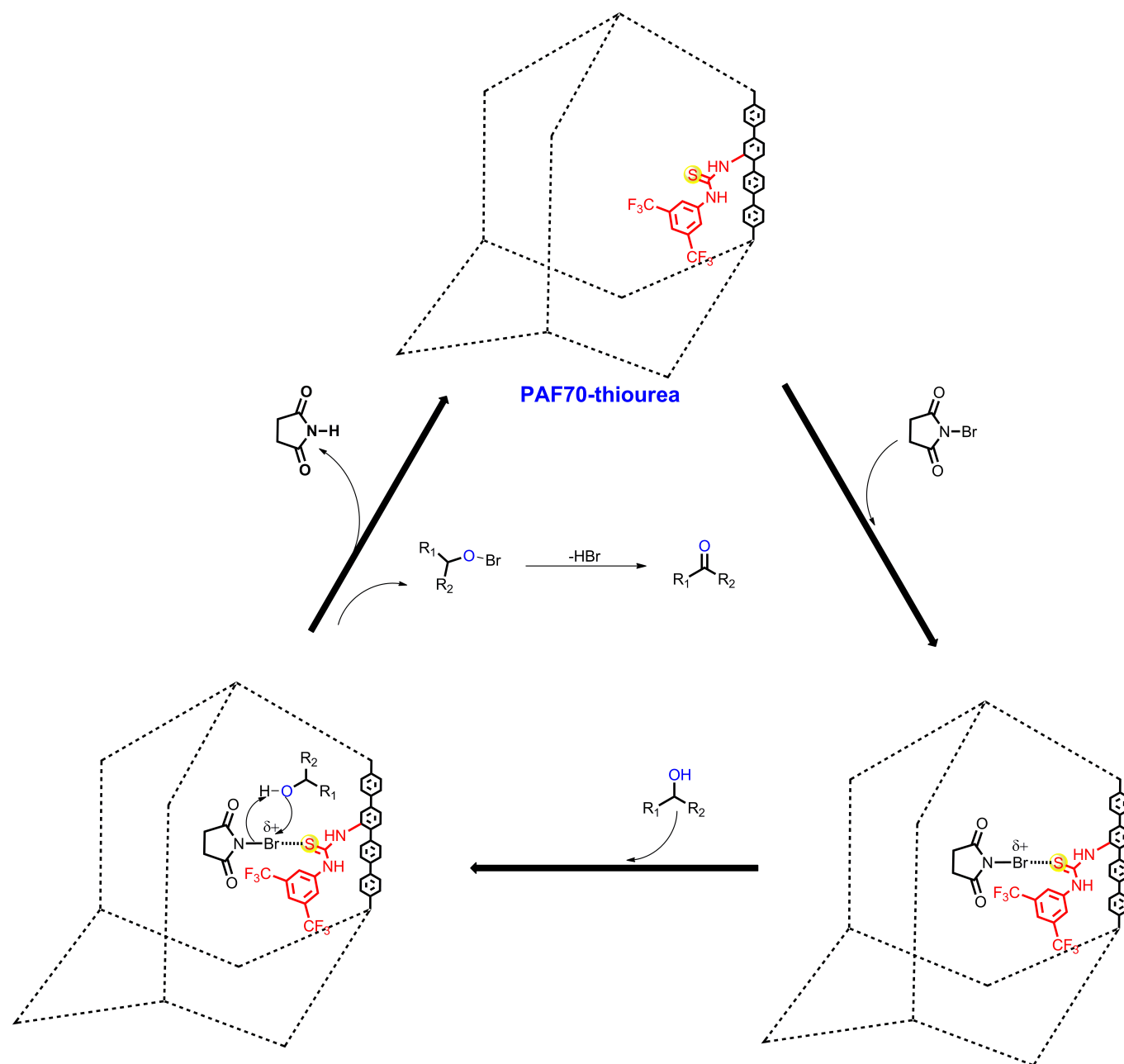


**Fig. S8** FT-IR spectra of the fresh **PAF70-thiourea** (red) and the recycled **PAF70-thiourea** (black) after 36 cycles.



**Fig. S9** Nitrogen adsorption (solid symbols)–desorption (open symbols) isotherms of the fresh **PAF70-thiourea** and the recycled **PAF70-thiourea** after 36 cycles measured at 77 K.

## 8. The Proposed Mechanism of PAF70-thiourea Catalyzed NBS-mediated Oxidation of Alcohols

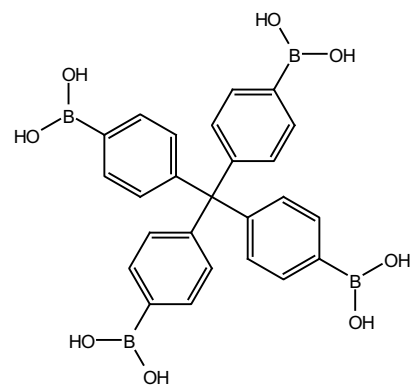


**Fig. S10** The proposed mechanism of PAF70-thiourea catalyzed NBS-mediated oxidation of alcohols.

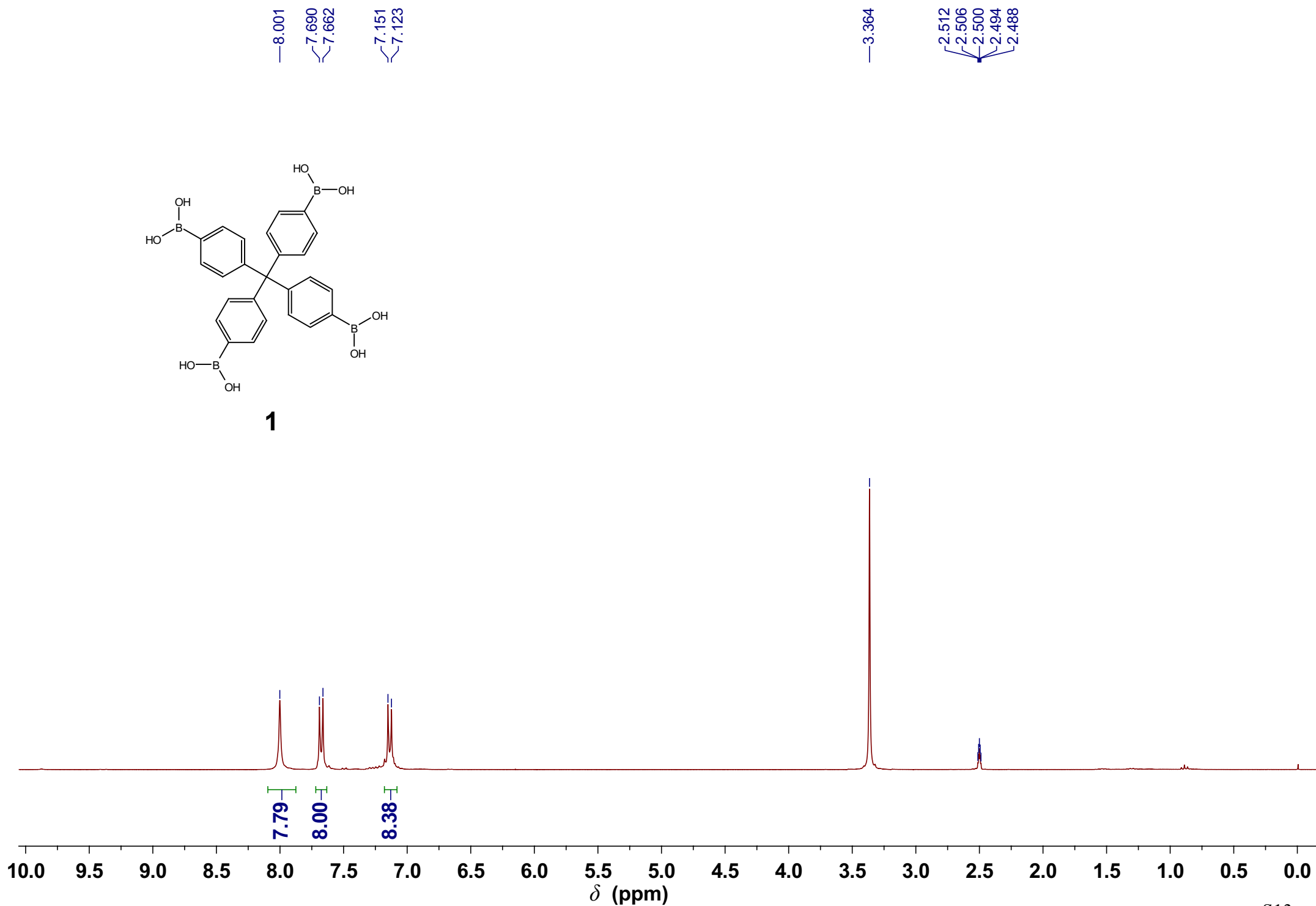
## 9. Copies of NMR Spectra

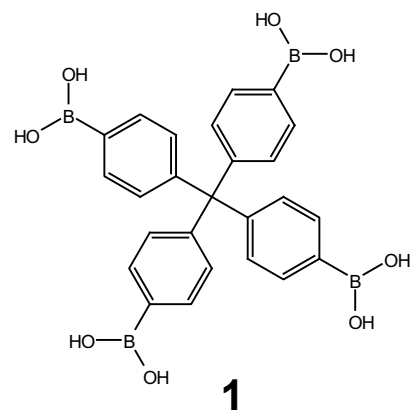
See the next page!





**1**





—148.22

133.51

131.75

129.61

—64.95

40.35

40.07

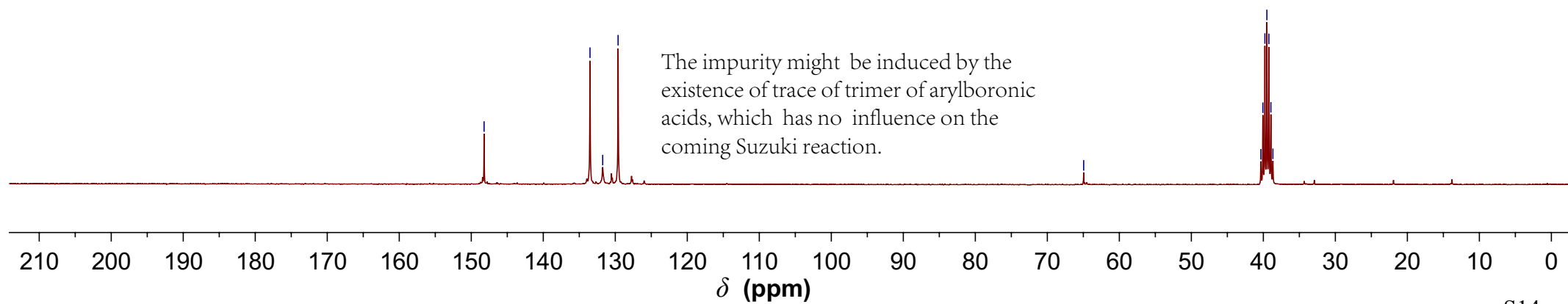
39.79

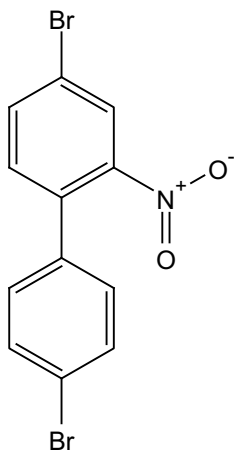
39.51

39.23

38.95

38.67

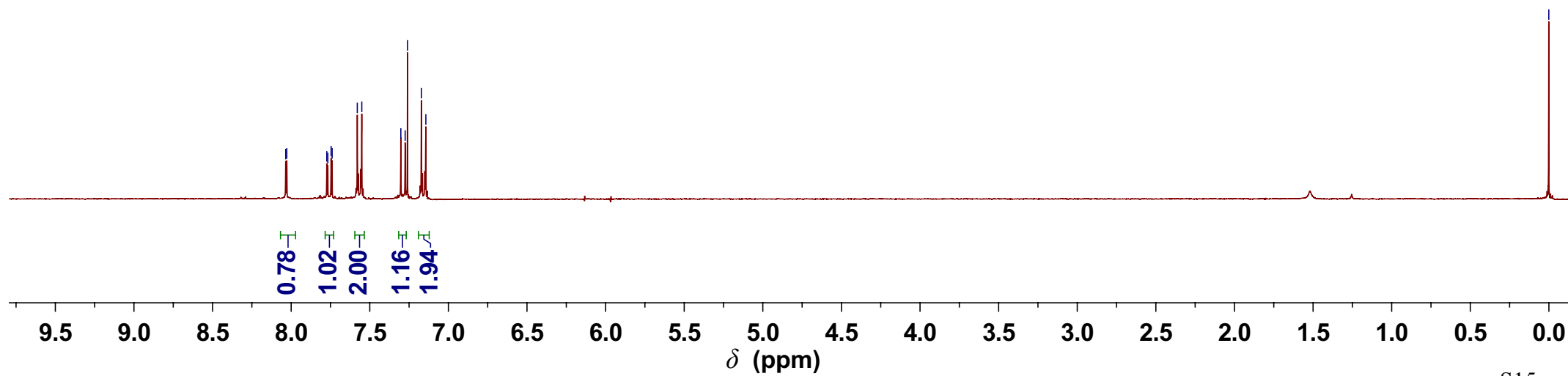


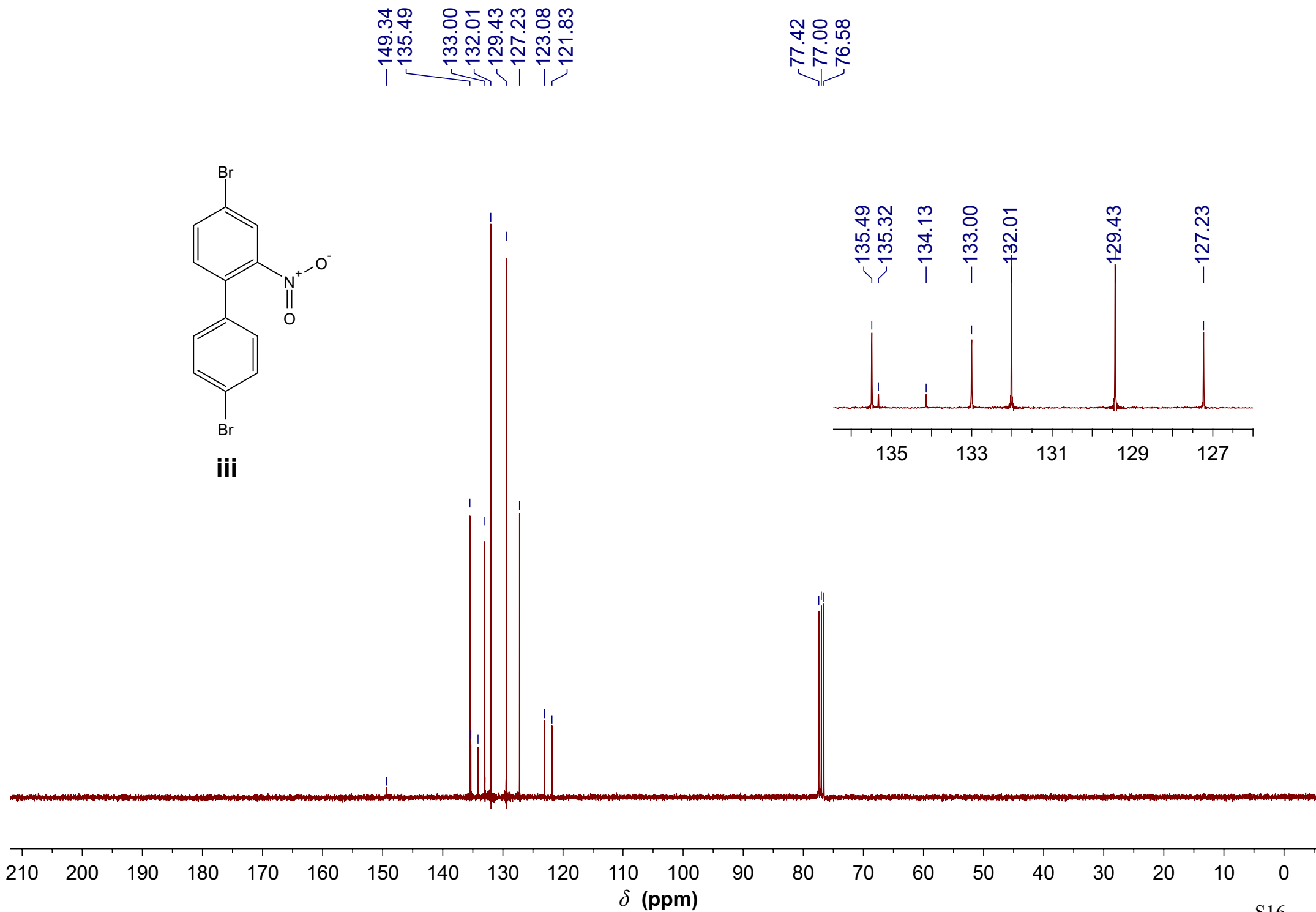
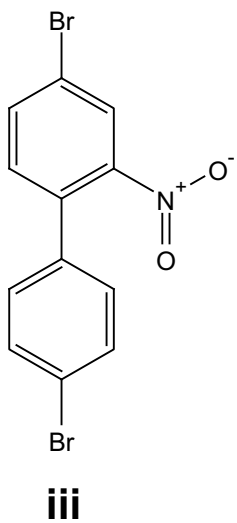


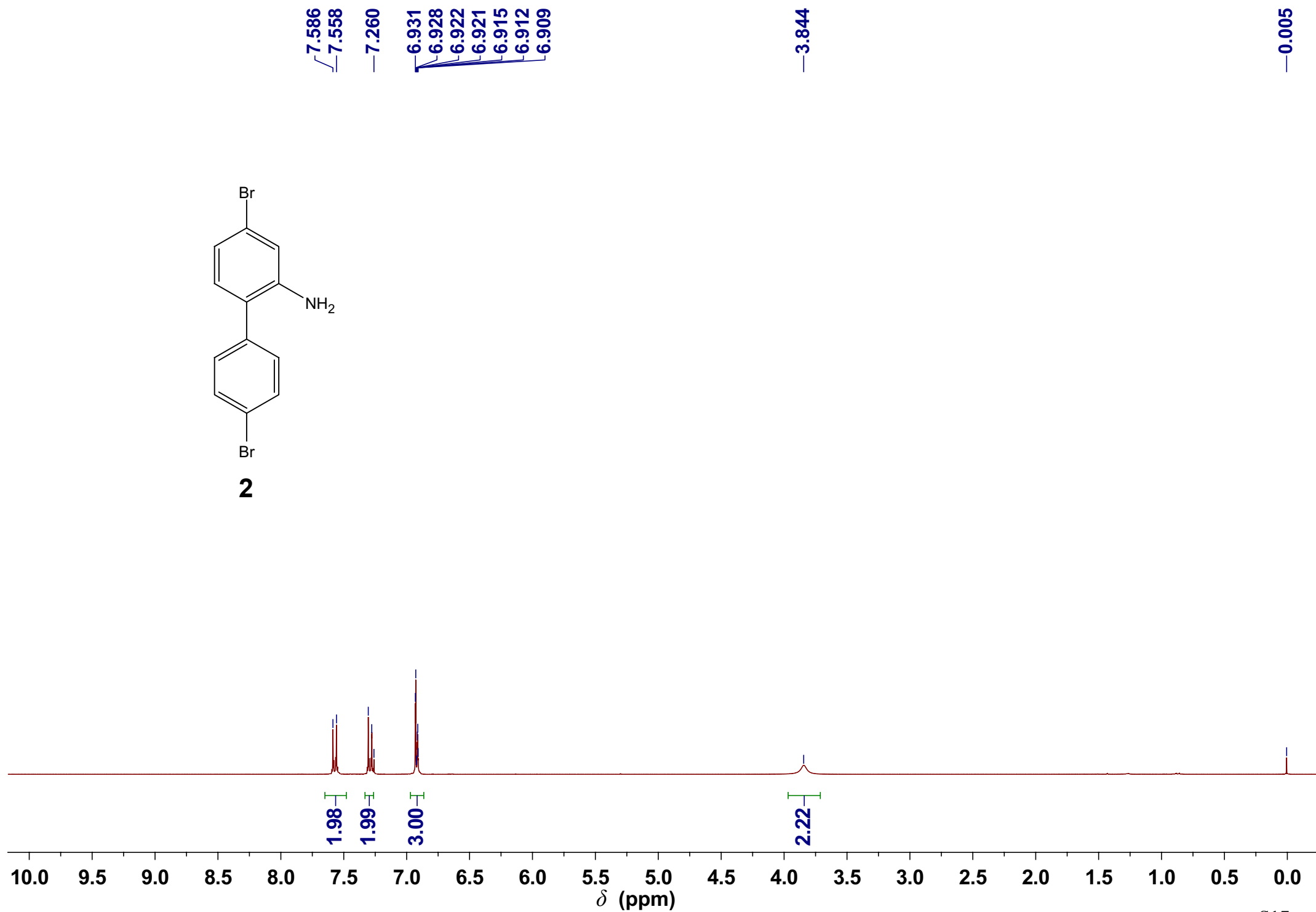
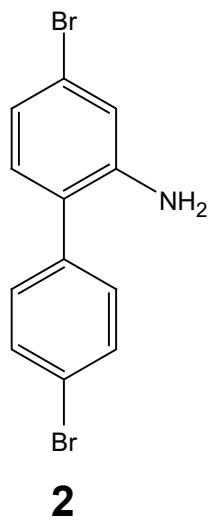
iii

8.034  
8.028  
7.746  
7.551  
7.302  
7.275  
7.260  
7.172  
7.143

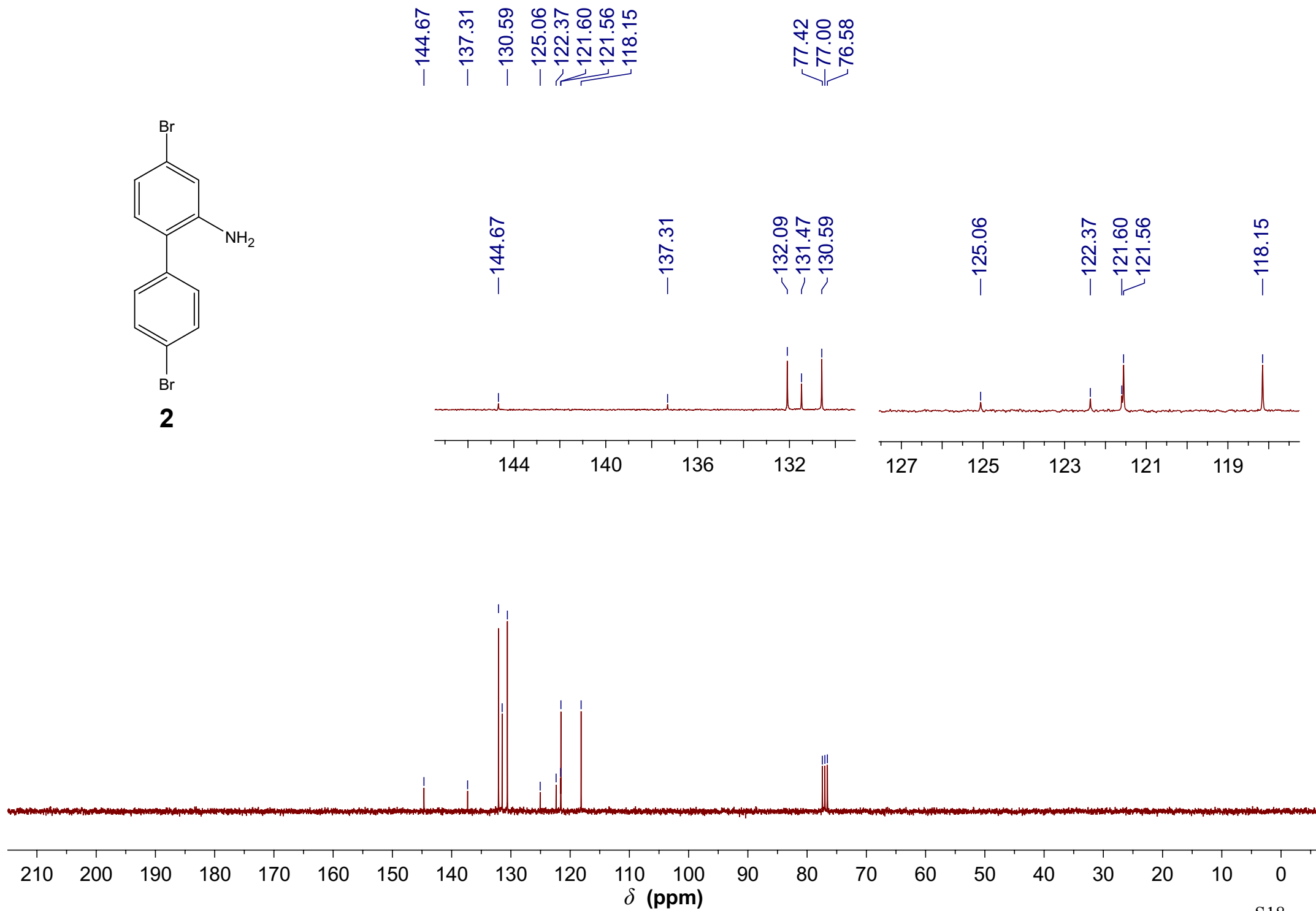
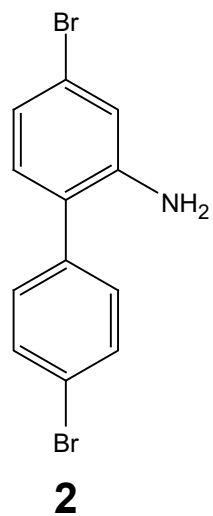
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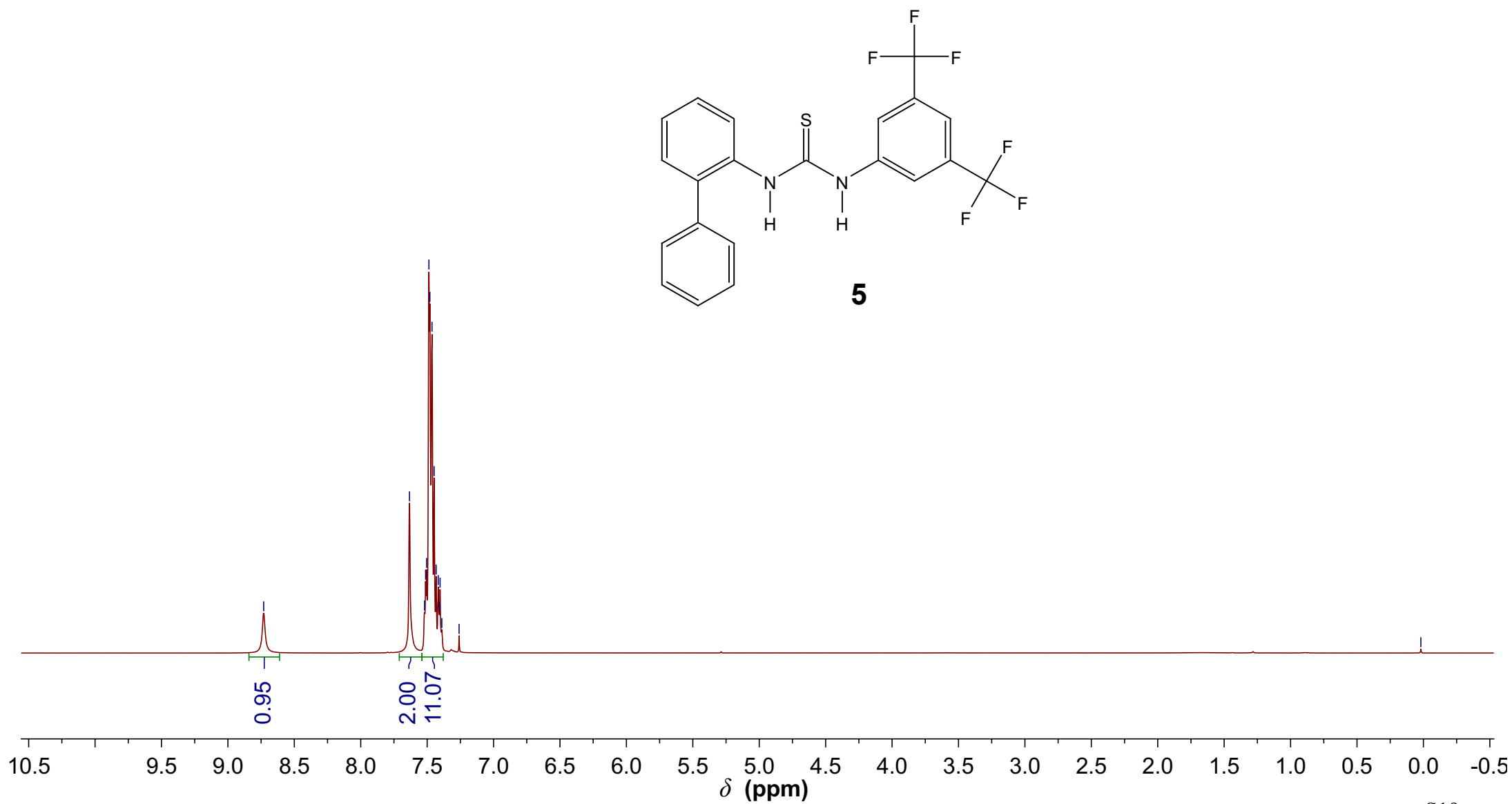


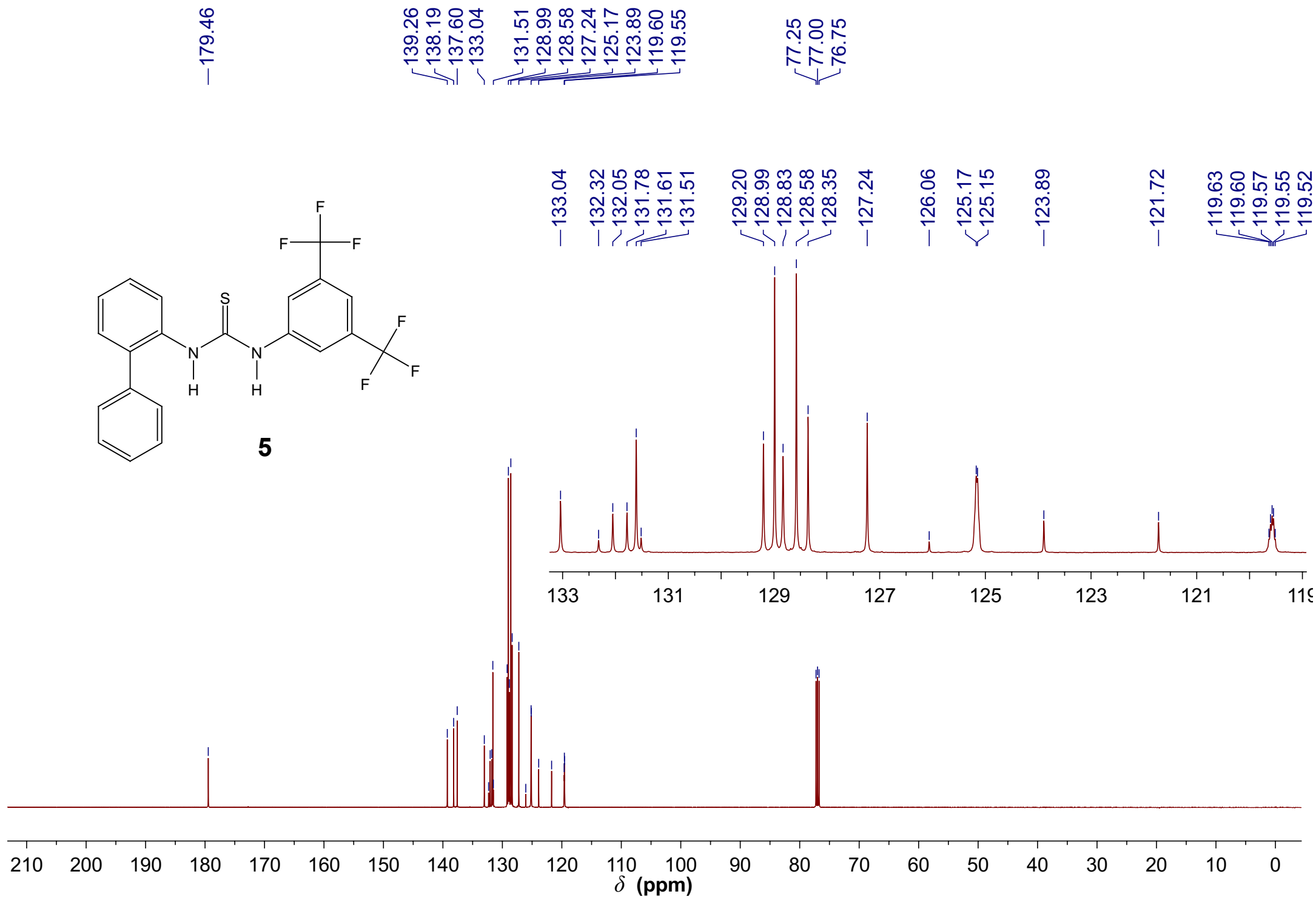
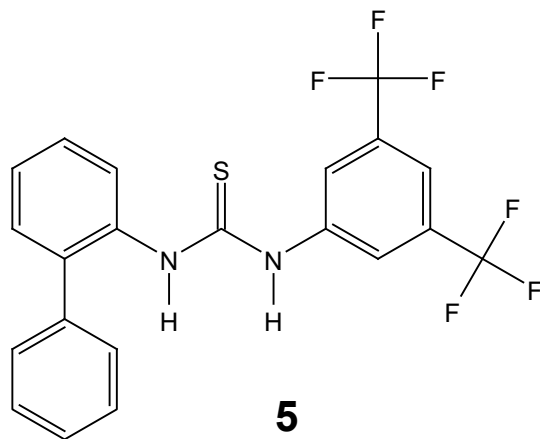


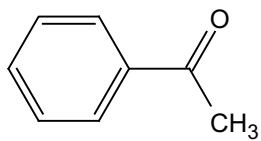




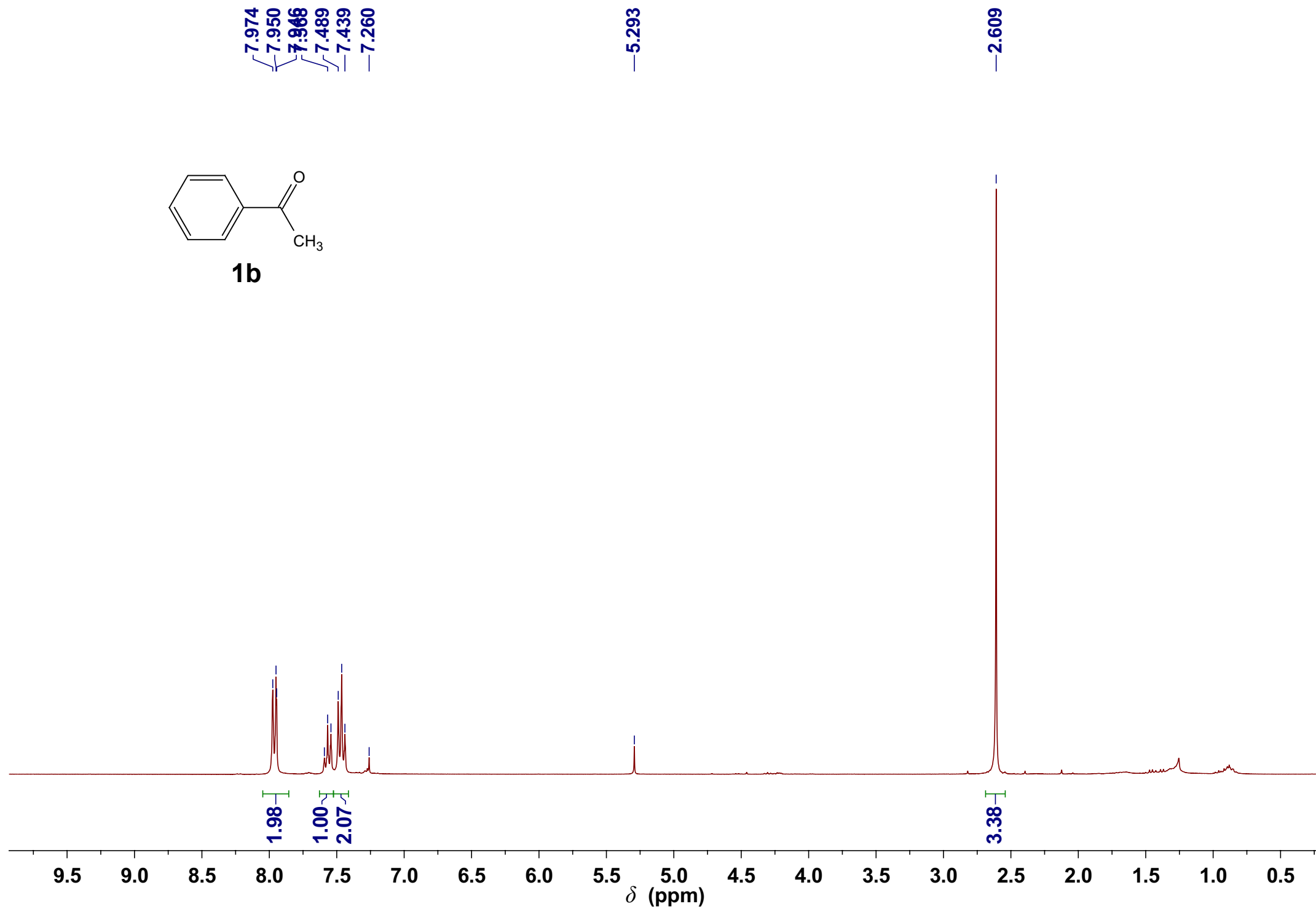


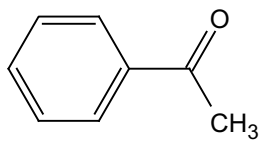




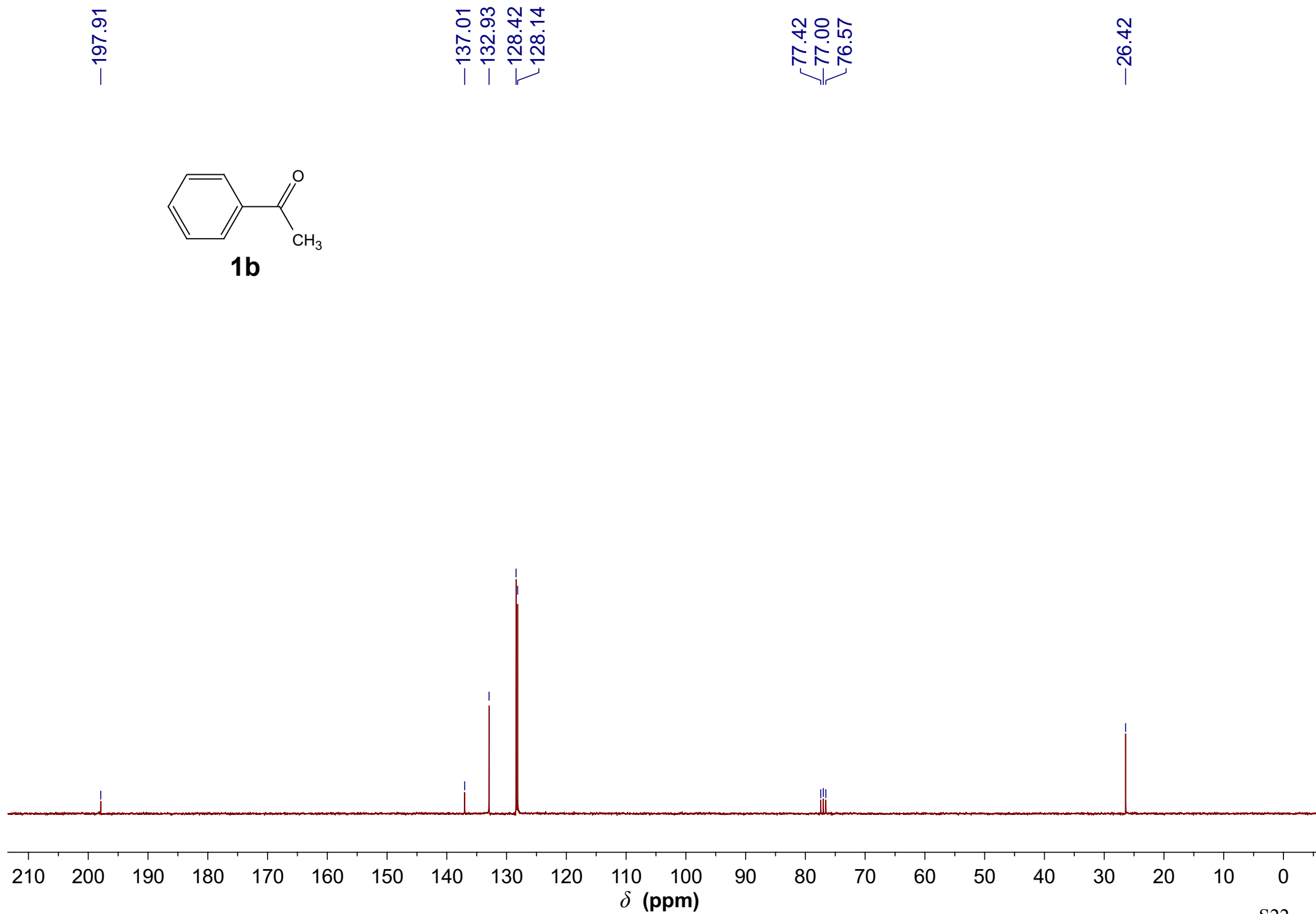


**1b**

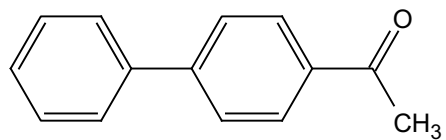




**1b**







**2b**

8.052  
8.025  
7.704  
7.676  
7.650  
7.645  
7.627  
7.622  
7.619  
7.506  
7.501  
7.495  
7.478  
7.473  
7.457  
7.453  
7.432  
7.428  
7.423  
7.412  
7.404  
7.260

2.641

1.99

2.00

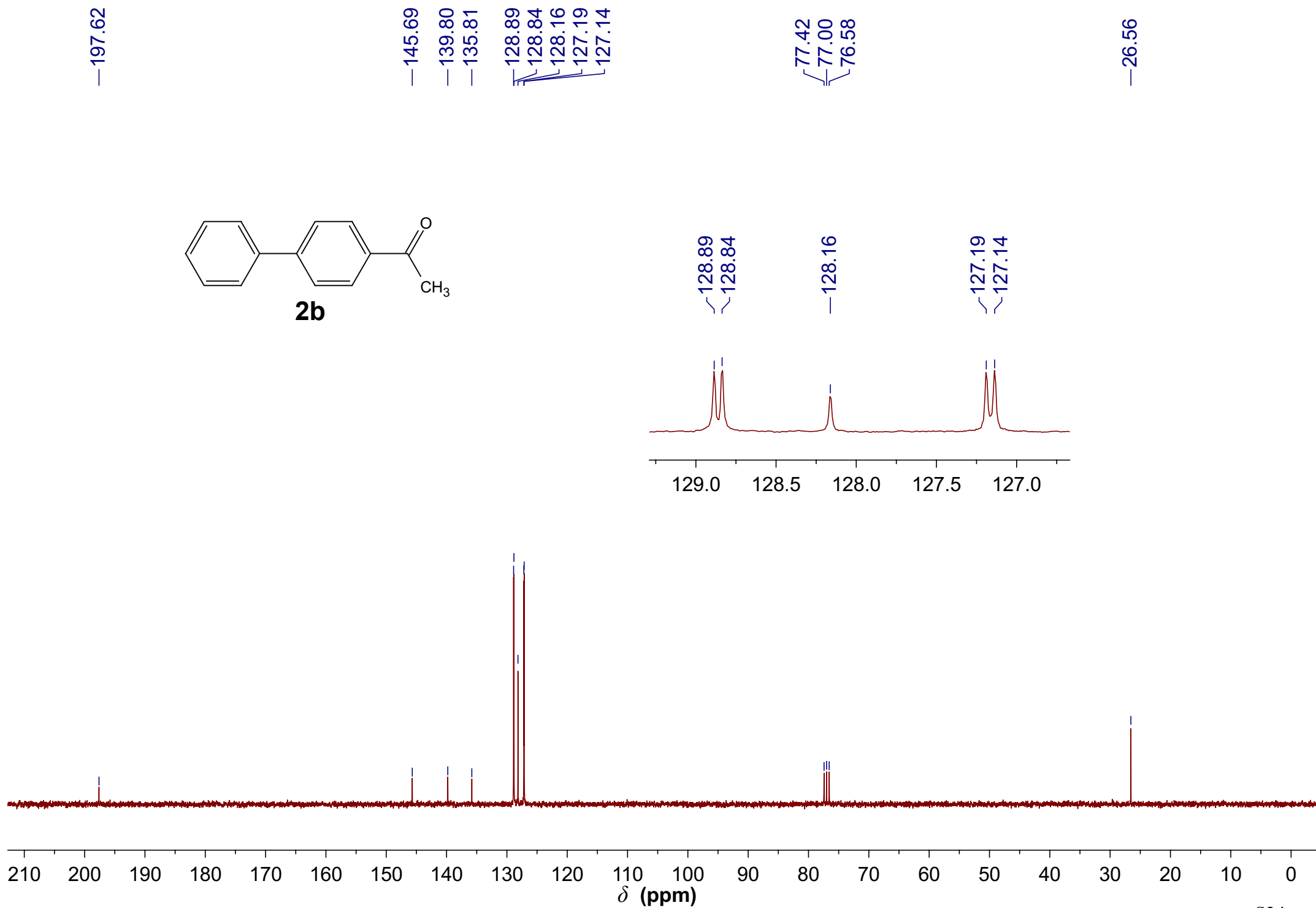
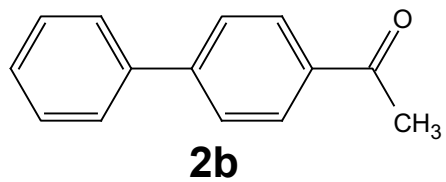
2.01

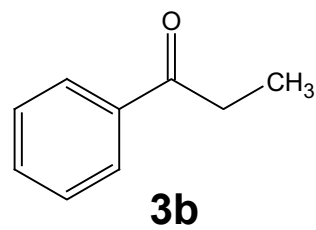
2.87

3.17

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

$\delta$  (ppm)

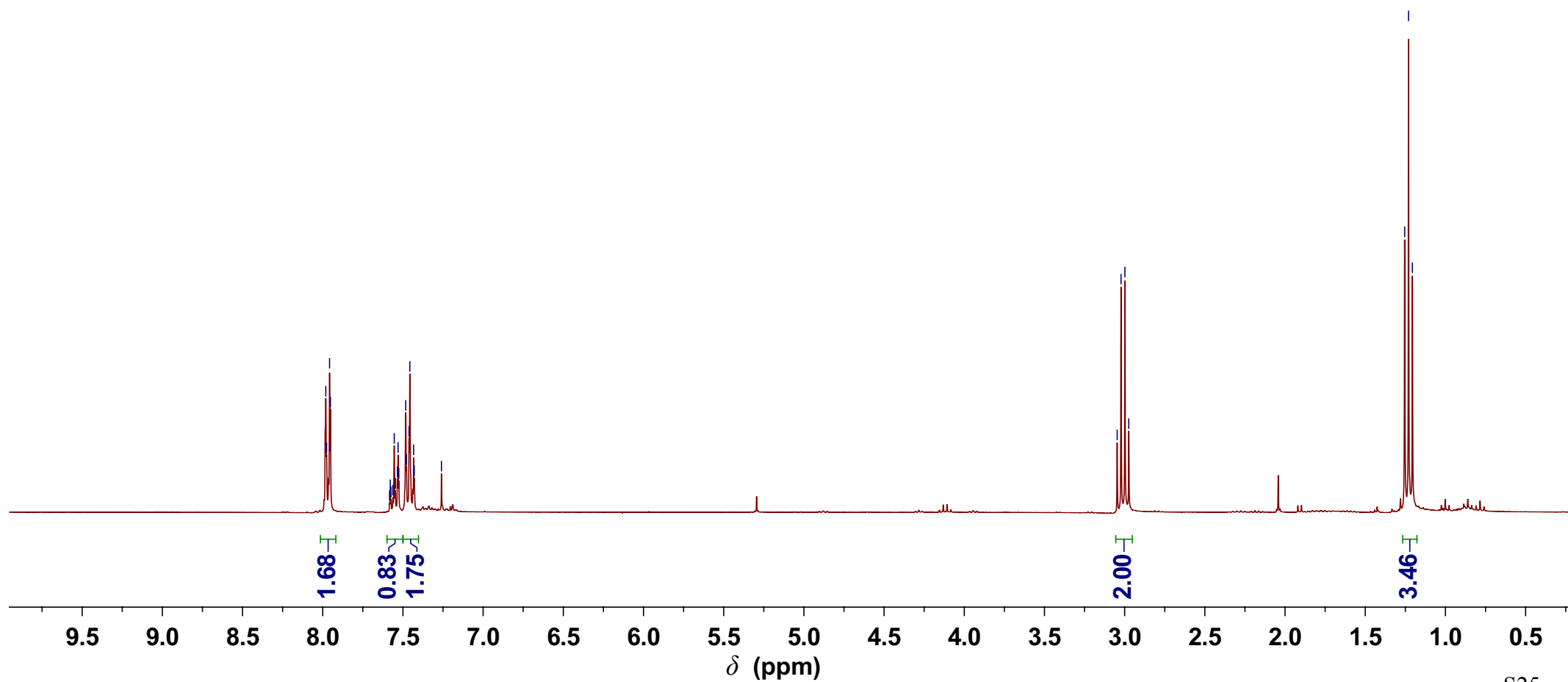


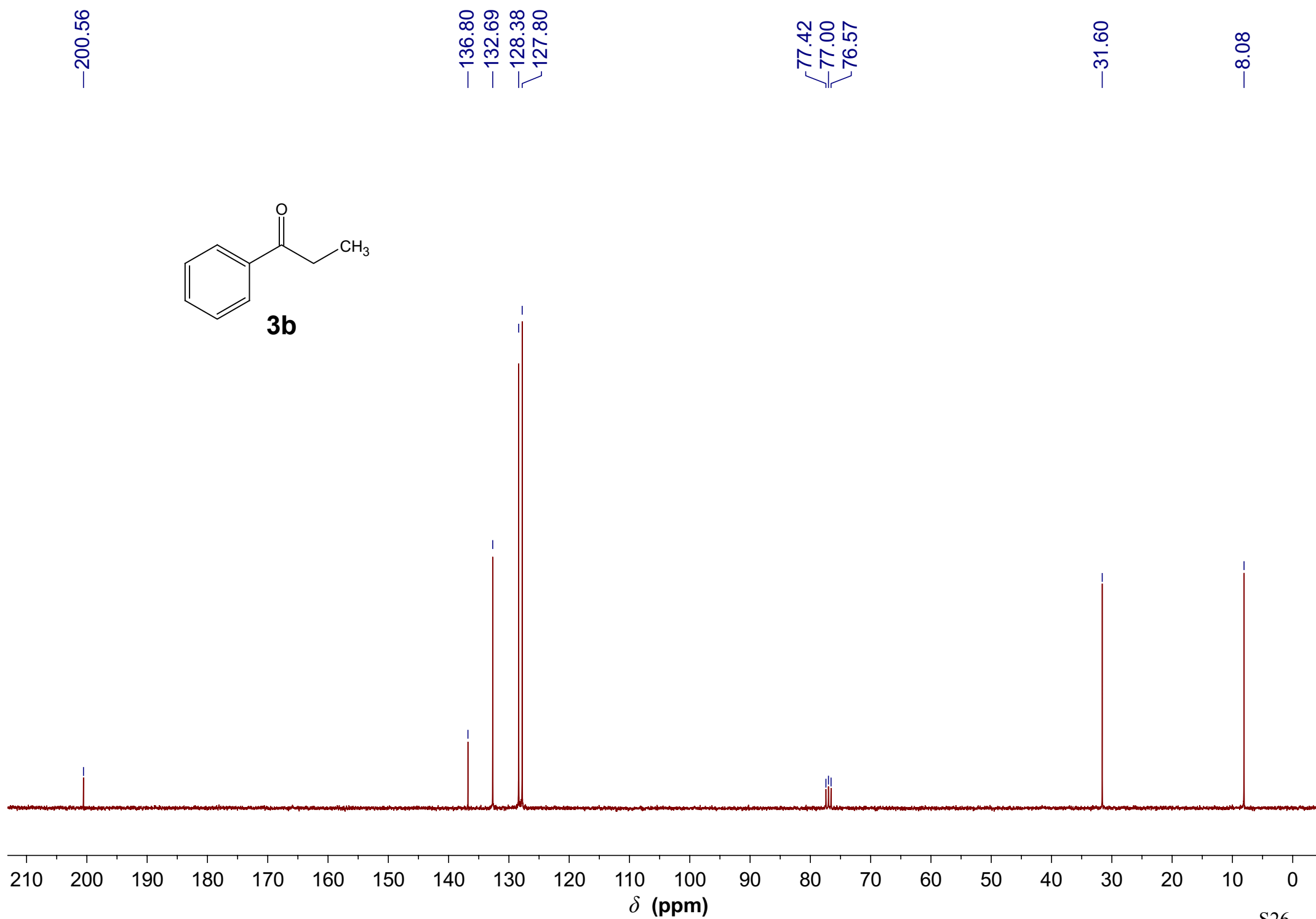
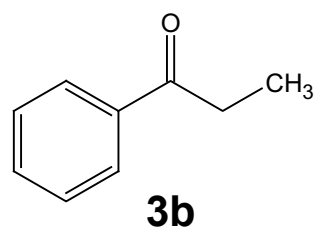


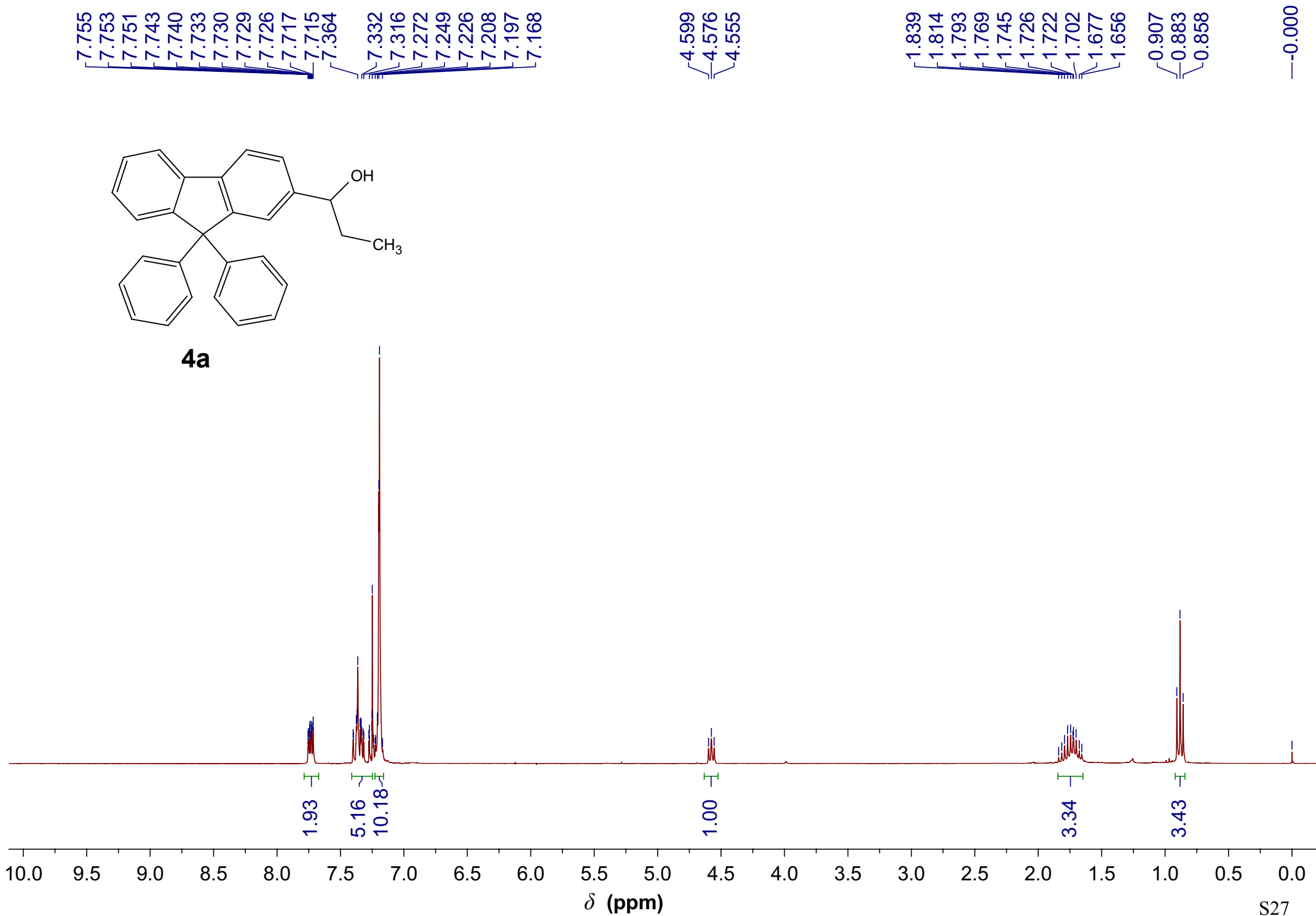
7.981  
 7.976  
 7.957  
 7.952  
 7.482  
 7.430  
 7.260

3.047  
 3.023  
 2.998  
 2.974

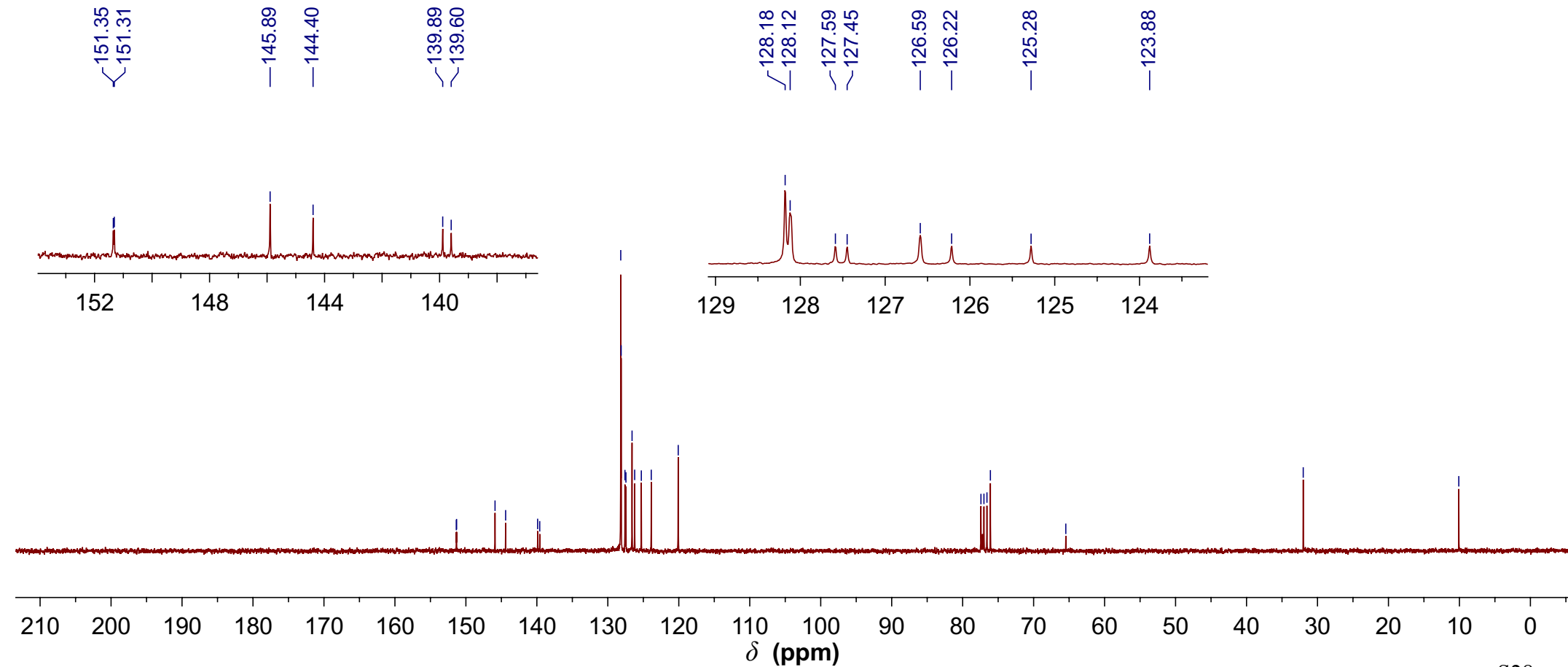
1.254  
 1.230  
 1.206

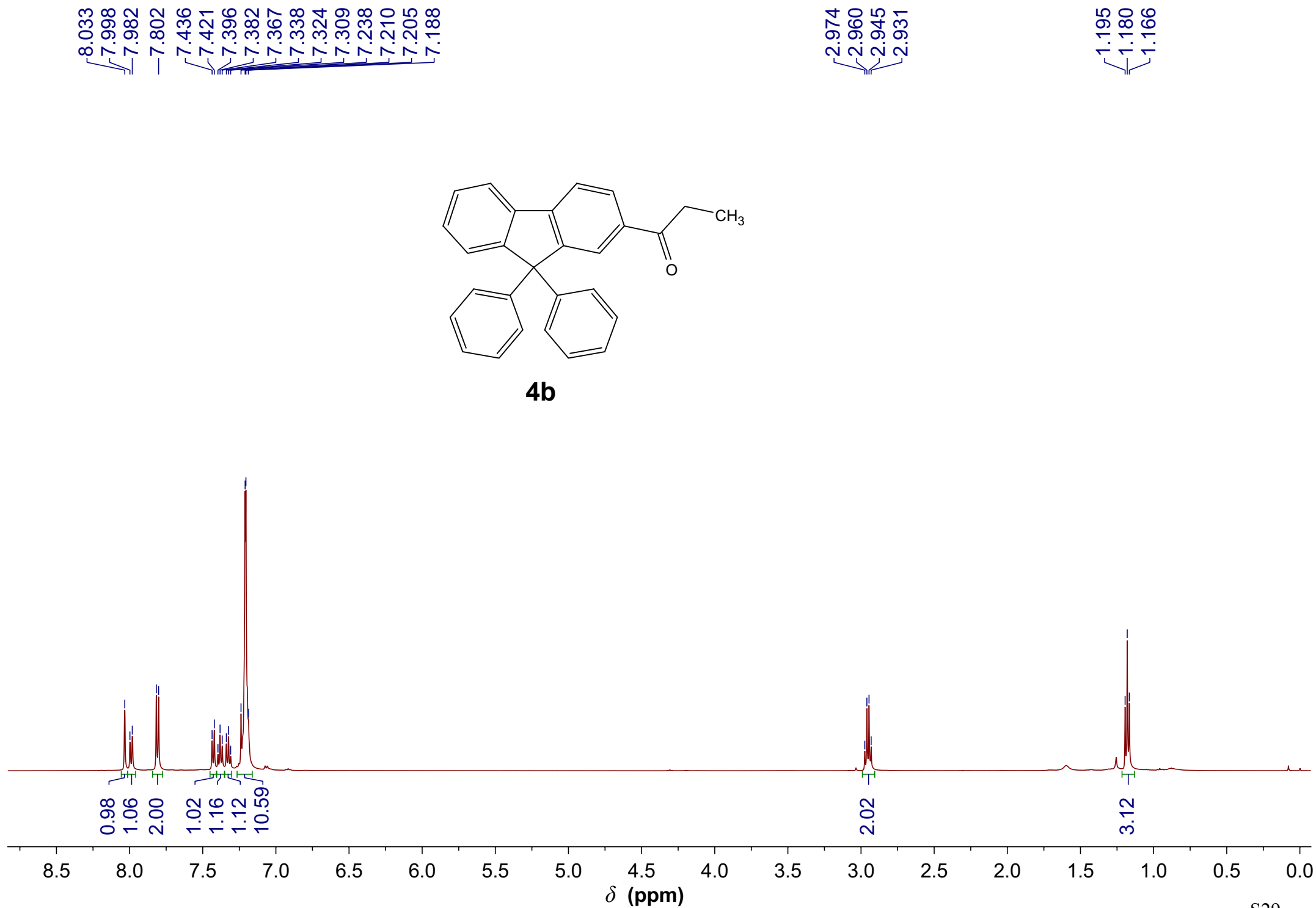


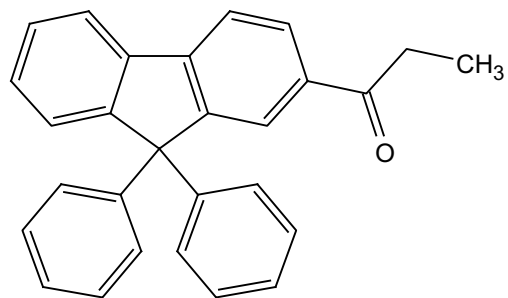












**4b**

