

## **Understanding Color Tuning and Reversible Oxidation of Conjugated Azomethines**

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### **ELECTRONIC SUPPORTING INFORMATION**

## Experimental Details

All chemicals and solvents were used as received, unless otherwise stated. NMR measurements were done on a 400 MHz ( $^1\text{H}$ ) spectrometer, unless otherwise stated. The absorption measurements were done on a combined UV-vis-NIR spectrometer. Samples were dissolved in anhydrous dichloromethane, unless otherwise stated. Fluorescence measurements were done on a combined steady-state/time-resolved emission spectrometer. Samples were dissolved in dichloromethane and degassed with nitrogen for 20 minutes before each measurement to remove the dissolved oxygen. The samples were then sealed to prevent ambient oxygen diffusion.

Electrochemical measurements were done with a multi-channel potentiostat connected to a three electrodes system using a platinum wire counter-electrode, a silver wire pseudo-reference electrode, and a polished platinum working electrode. Ferrocene was used as an internal reference for calibrating the measured potentials against SCE. The redox potential,  $E = \frac{1}{2} (E_{\text{forward wave}} + E_{\text{backward wave}})$ , for the reversible  $\text{Fc}/\text{Fc}^+$  couple was taken as +460 mV vs. SCE.<sup>1</sup> Samples were degassed for 20 minutes with nitrogen before each measurement in order to eliminate the dissolved oxygen. Samples were prepared at a 1 mM concentration in a 0.10 M solution of tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) in dichloromethane, unless otherwise described. Additional details and analyses of the compounds can be found elsewhere.<sup>2</sup> The HOMO and LUMO energy levels were calculated from the onset of the forward electrochemical waves for the oxidation ( $E_{\text{ox}}^{\text{onset}}$ ) and reduction ( $E_{\text{red}}^{\text{onset}}$ ) processes according to:  $\text{HOMO} = -e(E_{\text{ox}}^{\text{onset}})$

(SCE) + 4.4), LUMO =  $-e(E_{\text{red}}^{\text{onset}}(\text{SCE}) + 4.4)$ .<sup>3</sup> The electrochemical energy gap ( $E_g^{\text{EC}}$ ) was calculated as the difference between the two calculated energy levels.

The optimized geometries and corresponding energy levels were theoretically calculated using Gaussian 09 at the DFT level.<sup>4</sup> The geometries were optimized using the same theoretical level: B3LYP hybrid functional with 6-31G(d) basis set.<sup>5-9</sup> Optimized geometries were confirmed by frequency calculations with no negative frequencies being calculated. The time-dependent density functional theory (TD-DFT) was used to calculate the optical transitions using the 6-31G(d) basis set. The first six lowest transitions were calculated.

## Synthesis

2,5-Diaminothiophene-3,4-dicarboxylic acid diethyl ester,<sup>10</sup> 3,4-dibutylthiophene,<sup>11</sup> (E)-1,2-di(thiophen-2-yl)ethene,<sup>12</sup> 3,4-dibutylthiophene-2-carbaldehyde,<sup>11</sup> 3,4-dibutylthiophene-2,5-dicarbaldehyde,<sup>11</sup> 2,5-dibromo-3,4-dibutylthiophene,<sup>13</sup> [2,2'-bithiophene]-5,5'-dicarbaldehyde,<sup>14</sup> [2,2':5',2''-terthiophene]-5,5''-dicarbaldehyde,<sup>15</sup> (E)-5,5'-(ethene-1,2-diyl)bis(thiophene-2-carbaldehyde),<sup>12</sup> and (5-(diethyl-5-amino-thiophen-3,4-dicarboxylate-2-ylimino)-methyl)((thiophen-2-yl)methylene)-diethylthiophene-3,4-dicarboxylate-2,5-diamine<sup>16</sup> were prepared according to known methods. 3,4-Dibromothiophene, bithiophene, terthiophene and 2,5-thiophenedicarboxaldehyde were commercially available and they were used without further purification.

**5-Bromo-3,4-dibutylthiophene-2-carboxaldehyde.**

3,4-Dibutylthiophene-2-

carbaldehyde (70 mg, 3.1 mmol) was transferred to a 25 mL round bottom flask equipped with a stir bar using a 1:1 (v/v) ethyl acetate/chloroform mixture (7 mL). *N*-bromosuccinimide (60 mg, 3.4 mmol) was added and the mixture was stirred at room temperature for 16 h under a N<sub>2</sub> atmosphere. The contents of the flask were then poured into cold distilled water (25 mL), transferred into a separatory funnel, and extracted with dichloromethane (3 x 20 mL). The organic fraction was washed with distilled water (1 x 20 mL), a saturated aqueous NaHCO<sub>3</sub> solution (1 x 25 mL), and a saturated aqueous NaCl solution (1 x 25 mL). It was then dried with anhydrous MgSO<sub>4</sub>. The solid was removed by filtering and the filtrate was evaporated in vacuo. The resulting oil was purified by silica gel column chromatography (74 mg, 79%). <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ = 10.02 (s, 1H), 3.02 (t, 2H, *J* = 8.0 Hz), 2.63 (t, 2H, *J* = 7.8 Hz), 1.65–1.41 (m, 8H), 0.96 (dt, 6H, *J* = 7.2 Hz, 2.4 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 180.9, 151.0, 143.5, 138.2, 122.1, 34.2, 27.4, 27.2, 13.6, 13.5. HRMS(+) calculated for [C<sub>13</sub>H<sub>19</sub>BrOS]<sup>+</sup>: 303.0413, found: 303.0409.

**3,3',4,4'-Tetrabutyl-[2,2'-bithiophene]-5,5'-dicarboxaldehyde.**

5-Bromo-3,4-

dibutylthiophene-2-carboxaldehyde (0.74 g, 2.4 mmol) was transferred into a 50 mL double-necked round bottom flask equipped with a magnetic stirrer and a condensing tube using anhydrous toluene (3 mL). Diisopropylethylamine (40 μL, 0.42 mmol), tetrabutylammonium bromide (37 mg, 0.11 mmol), and palladium (II) acetate (1.3 mg, 0.006 mmol) were added. The mixture was stirred and three vacuum–N<sub>2</sub> cycles were completed before refluxing in an oil bath at 105 °C for 4 h. The reaction mixture was

then heated at 77 °C for 15.5 h, followed by heating at 105 °C for 3.5 h. Afterwards, the contents of the flask were poured into cold distilled water (10 mL) before being transferred to a separatory funnel, and extracted with dichloromethane (3 x 10 mL). The organic fraction was washed with distilled water (10 mL) and a saturated aqueous NaCl solution (2 x 10 mL). It was then dried with anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed in vacuo. The resulting oil was purified by silica gel column chromatography (6.8 mg, 1.2%). <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ = 10.15 (s, 2H), 3.06 (t, 4H, *J* = 8.0 Hz), 2.59 (t, 4H, *J* = 4.0 Hz), 1.71–1.63 (m, 4H), 1.51–1.41 (m, 8H), 1.33 – 1.23 (m, 4H), 0.97 (t, 6H, *J* = 7.8 Hz), 0.82 (t, 6H, *J* = 7.6 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 182.3, 151.9, 144.2, 138.4, 138.2, 34.6, 32.8, 27.2, 26.9, 22.8, 22.7, 13.8, 13.6. HRMS(+) calculated for [C<sub>26</sub>H<sub>38</sub>O<sub>2</sub>S<sub>2</sub>]<sup>+</sup>H<sup>+</sup>: 447.2386, found: 447.2396.

**3,3',3'',4,4',4''-Hexabutyl-[2,2':5',2''-terthiophene]-5,5''-dicarboxaldehyde.**

Phosphoryl chloride (0.31 mL, 3.4 mmol) was combined with dichloroethane (10 mL) in a 25 mL Schlenk tube equipped with a stir bar. The solution was then cooled to 0 °C in an ice bath and anhydrous *N,N*-dimethylformamide (0.26 mL, 3.4 mmol) was added. The solution was then warmed to room temperature. After 45 min., 3,3',3'',4,4',4''-hexabutyl-2,2':5',2''-terthiophene (0.25 g, 0.43 mmol) was added, followed by heating in an oil bath at 65 °C for 15 h. The mixture was poured into distilled water, transferred into a separatory funnel and extracted with dichloromethane (3 x 25 mL). The organic fraction was washed with distilled water (1 x 50 mL), dried with anhydrous MgSO<sub>4</sub>, filtered, and the solvent was then removed in vacuo. The resulting orange oil was purified by silica gel column chromatography (0.22 g, 80%). <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ = 10.14 (s, 2H), 3.05 (t,

4H,  $J = 7.6$  Hz), 2.62 (q, 8H,  $J = 8.0$  Hz), 1.71–1.64 (m, 4H), 1.53–1.43 (m, 12H), 1.36–1.24 (m, 8H), 0.97 (t, 6H,  $J = 7.2$  Hz), 0.84 (dt, 12H,  $J = 7.4$  Hz, 3.0 Hz).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta = 184.2, 153.6, 145.8, 144.6, 140.2, 140.0, 131.3, 36.4, 34.6, 34.5, 29.3, 28.6, 24.4, 24.3, 15.1, 15.02, 15.01$ . HRMS(+) calculated for  $[\text{C}_{38}\text{H}_{56}\text{O}_2\text{S}_3]^+\text{H}^+$ : 641.3515, found 641.3504.

#### **Representative procedure for the synthesis of 1B–4.**

**Tetraethyl-5,5'-((1*E*,1'*E*)-((3,4-dibutylthiophene-2,5-diyl)bis(methanylylidene))bis-(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (1B).** 3,4-Dibutylthiophene-2,5-dicarbaldehyde (0.11 g, 0.45 mmol) and 2,5-diaminothiophene-3,4-dicarboxylic acid diethyl ester (0.45 g, 1.7 mmol) were combined in a test tube equipped with a stir bar. The reagents were dissolved in anhydrous ethanol (2 mL) followed by the addition of a catalytic amount of trifluoroacetic acid. The mixture was then stirred for 2.5 h. The solvent was removed in vacuo and the resulting solid was dissolved in a minimal amount of acetone (1 mL) before precipitating in cold hexane (25 mL). The precipitate was filtered and washed with cold hexane (3 x 5 mL) before purifying by silica gel column chromatography that was pre-rinsed with 1% triethylamine (0.27 g, 81%).  $^1\text{H}$ -NMR (acetone- $d_6$ ):  $\delta = 8.17$  (s, 2H), 7.51 (br, 2H), 4.35 (q, 4H,  $J = 7.2$  Hz), 4.21 (q, 4H,  $J = 7.2$  Hz), 1.60–1.39 (m, 14H), 1.27 (t, 10H,  $J = 7.2$  Hz), 0.97 (t, 6H,  $J = 7.2$  Hz).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 165.2, 164.5, 159.5, 146.5, 144.5, 140.1, 134.6, 129.7, 103.4, 61.6, 60.3, 33.9, 26.5, 22.6, 14.5, 14.2, 13.9$ . HRMS(+) calculated for  $[\text{C}_{34}\text{H}_{44}\text{N}_4\text{O}_8\text{S}_3]^+\text{H}^+$ : 733.2394, found 733.2370.

**Tetraethyl-5,5'-((1*E*,1'*E*)-([2,2'-bithiophene]-5,5'-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (2A).** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 8.21 (s, 2H), 7.95 (br, 4H), 7.54 (d, 2H, *J* = 3.6 Hz), 7.48 (d, 2H, *J* = 3.6 Hz), 4.28 (q, 4H, *J* = 7.2 Hz), 4.14 (q, 4H, *J* = 7.2 Hz), 1.33 (t, 6H, *J* = 7.0 Hz), 1.20 (t, 6H, *J* = 7.2 Hz). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 164.6, 163.1, 161.0, 145.3, 141.9, 139.3, 133.4, 131.5, 129.7, 126.2, 100.1, 60.7, 59.5, 14.1, 14.0. HRMS(+) calculated for [C<sub>30</sub>H<sub>30</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>]<sup>+</sup>H<sup>+</sup>: 703.1019, found 703.1009.

**Tetraethyl-5,5'-((1*E*,1'*E*)-((3,3',4,4'-tetrabutyl-[2,2'-bithiophene]-5,5'-diyl)bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (2B).** <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 8.08 (s, 2H), 6.24 (br, 4H), 4.39–4.32 (m, 4H), 4.22 (q, 4H, *J* = 7.0 Hz), 2.74–2.69 (m, 4H), 2.51–2.42 (m, 4H), 1.41–1.36 (m, 14H), 1.30–1.23 (m, 14H), 0.95 (t, 6H, *J* = 7.2 Hz), 0.84–0.79 (m, 6H). HRMS(+) calculated for [C<sub>46</sub>H<sub>62</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>]<sup>+</sup>H<sup>+</sup>: 927.3523, found 927.3530.

**Tetraethyl-5,5'-((1*E*,1'*E*)-([2,2':5',2''-terthiophene]-5,5''-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (3A).** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 8.21 (s, 2H), 7.93 (br, 4H), 7.54 (d, 2H, *J* = 4.2 Hz), 7.45 (s, 2H), 7.43 (d, 2H, *J* = 4.2 Hz), 4.28 (q, 4H, *J* = 7.0 Hz), 4.14 (q, 4H, *J* = 7.0 Hz), 1.33 (t, 6H, *J* = 7.0 Hz), 1.20 (t, 6H, *J* = 7.0 Hz). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 164.6, 163.2, 161.0, 145.5, 141.3, 139.2, 136.0, 133.5, 131.7, 129.5, 126.7, 125.6, 100.1, 60.8, 59.5, 14.2, 14.1. HRMS(+) calculated for [C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>S<sub>5</sub>]<sup>+</sup>H<sup>+</sup>: 785.0896, found 785.0898.

**Tetraethyl-5,5'-((1*E*,1'*E*)-((3,3',3'',4,4',4''-hexabutyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (3B).** <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 8.12 (s, 2H), 6.27 (s, 4H), 4.38 (q, 4H,  $J$  = 7.2 Hz), 4.24 (q, 4H,  $J$  = 7.2 Hz), 2.74 (t, 4H,  $J$  = 8.0 Hz), 2.53–2.46 (m, 8H), 1.57–1.51 (m, 8H), 1.46–1.36 (m, 18H), 1.30 (t, 10H,  $J$  = 7.2 Hz), 0.97 (t, 6H,  $J$  = 7.2 Hz), 0.84 (dt, 12H,  $J$  = 7.2 Hz, 4.0 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  = 165.3, 164.5, 159.0, 146.3, 145.2, 142.8, 142.1, 136.5, 135.0, 134.7, 129.8, 128.4, 103.2, 61.5, 60.2, 34.2, 32.9, 32.8, 29.9, 27.7, 27.2, 27.1, 22.8, 22.7, 14.4, 14.1, 13.9, 13.8, 13.7. HRMS(+) calculated for [C<sub>58</sub>H<sub>80</sub>N<sub>4</sub>O<sub>8</sub>S<sub>5</sub>]<sup>+</sup>H<sup>+</sup>: 1121.4653, found 1121.4639.

**Tetraethyl-5,5'-((1*E*,1'*E*)-((5,5'-((*E*)-ethene-1,2-diyl)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (4).** <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 8.18 (s, 2H), 7.95 (br, 4H), 7.51 (d, 2H,  $J$  = 4.0 Hz), 7.31 (d, 2H,  $J$  = 4.0 Hz), 7.27 (s, 2H), 4.27 (q, 4H,  $J$  = 7.2 Hz), 4.14 (q, 4H,  $J$  = 7.2 Hz), 1.34 (t, 12H,  $J$  = 7.0 Hz). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 164.9, 163.4, 161.1, 145.5, 141.6, 133.7, 132.1, 129.5, 129.1, 125.1, 123.1, 100.4, 61.0, 59.8, 14.4, 14.3. HRMS(+) calculated for [C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>S<sub>5</sub>]<sup>+</sup>H<sup>+</sup>: 729.1176, found 729.1160.



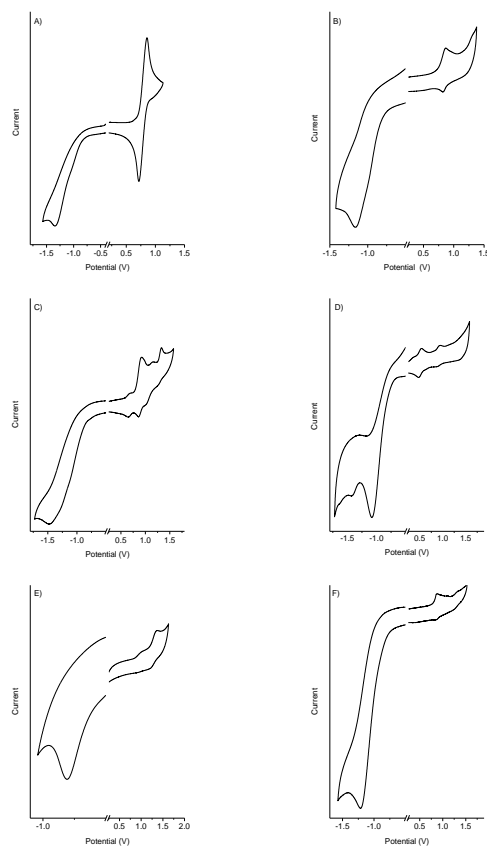


Figure S1. Cyclic voltammograms of **1B** (A), **2A** (B), **2B** (C), **3A** (D), **3B** (E), and **4** (F) measured at 100 mV/sec in dichloromethane with 0.1 M TBAPF<sub>6</sub> vs. Ag<sup>0</sup>.

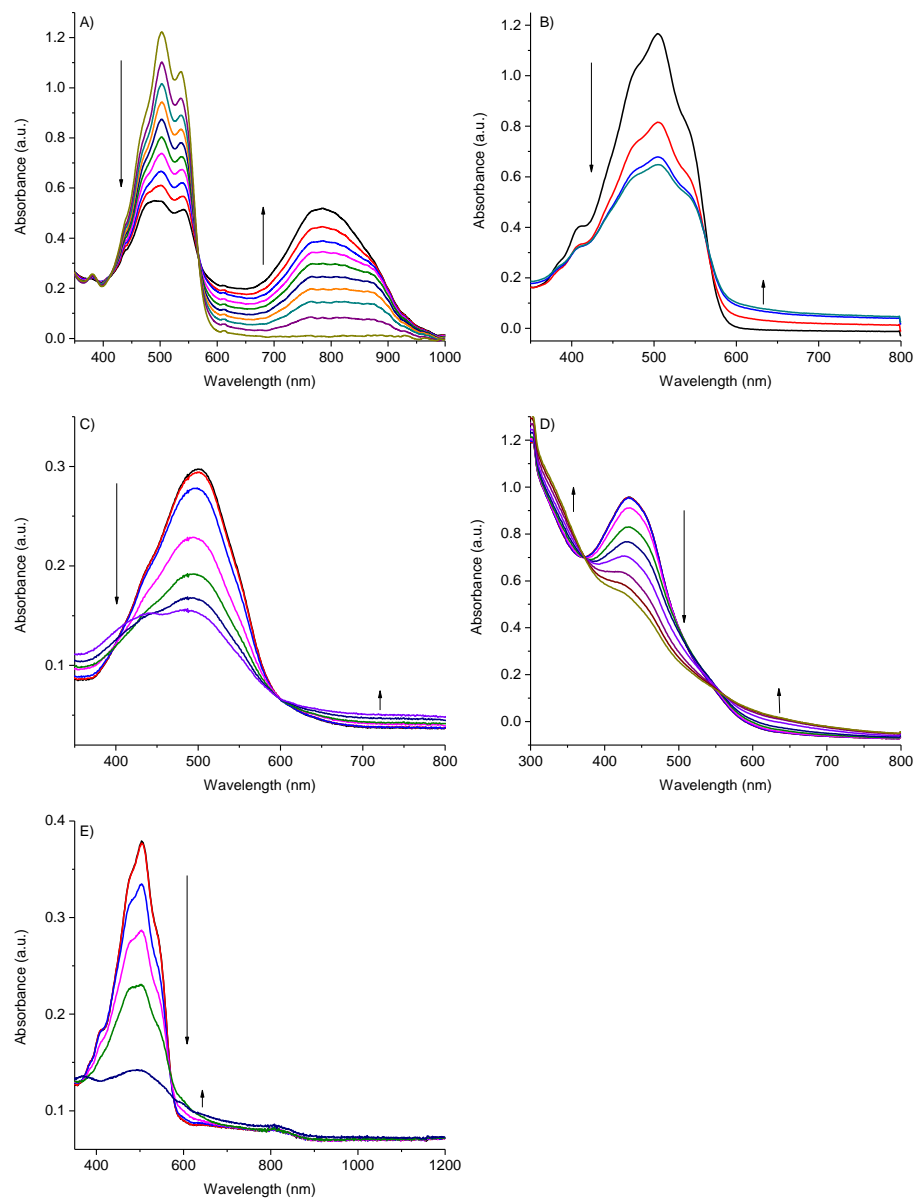


Figure S2. Spectroelectrochemistry measured in 0.1 M TBAPF<sub>6</sub> in dichloromethane: A) **1B** from 0 mV to 900 mV, B) **2A** from 0 mV to 1.0 V, C) **3A** between 0 mV and 1.5 V, D) **3B** between 0 mV and 1.2 V, and E) **4** between 0 mV and 1.1 V.

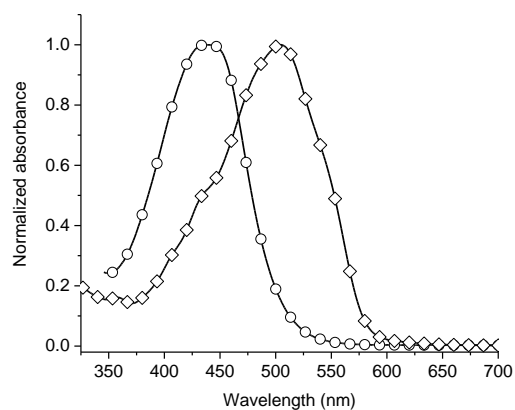


Figure S3. Normalized absorption spectra of **2B** (○) and **3A** (◇).

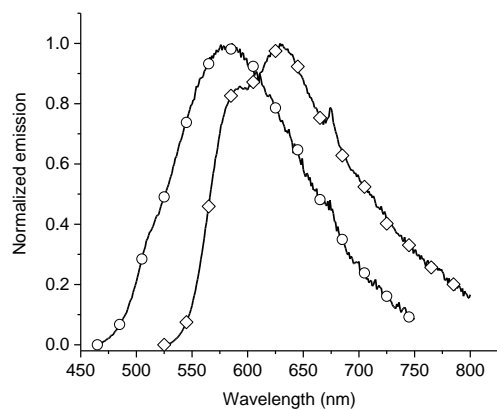


Figure S4. Normalized emission spectra of **2B** (○) and **3A** (◇).

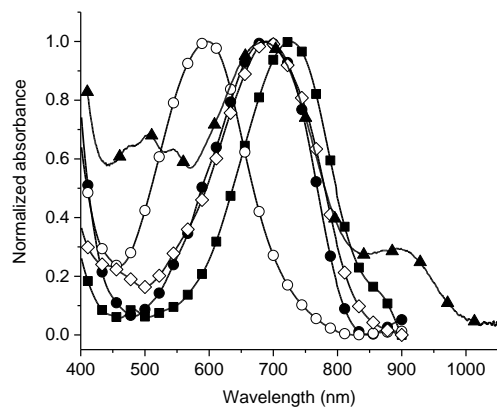


Figure S5. Normalized absorption spectra of **1B** (■), **2A** (●), **2B** (○), **3A** (◇), **3B** (◆), and **4** (▲) in dichloromethane with FeCl<sub>3</sub> added.

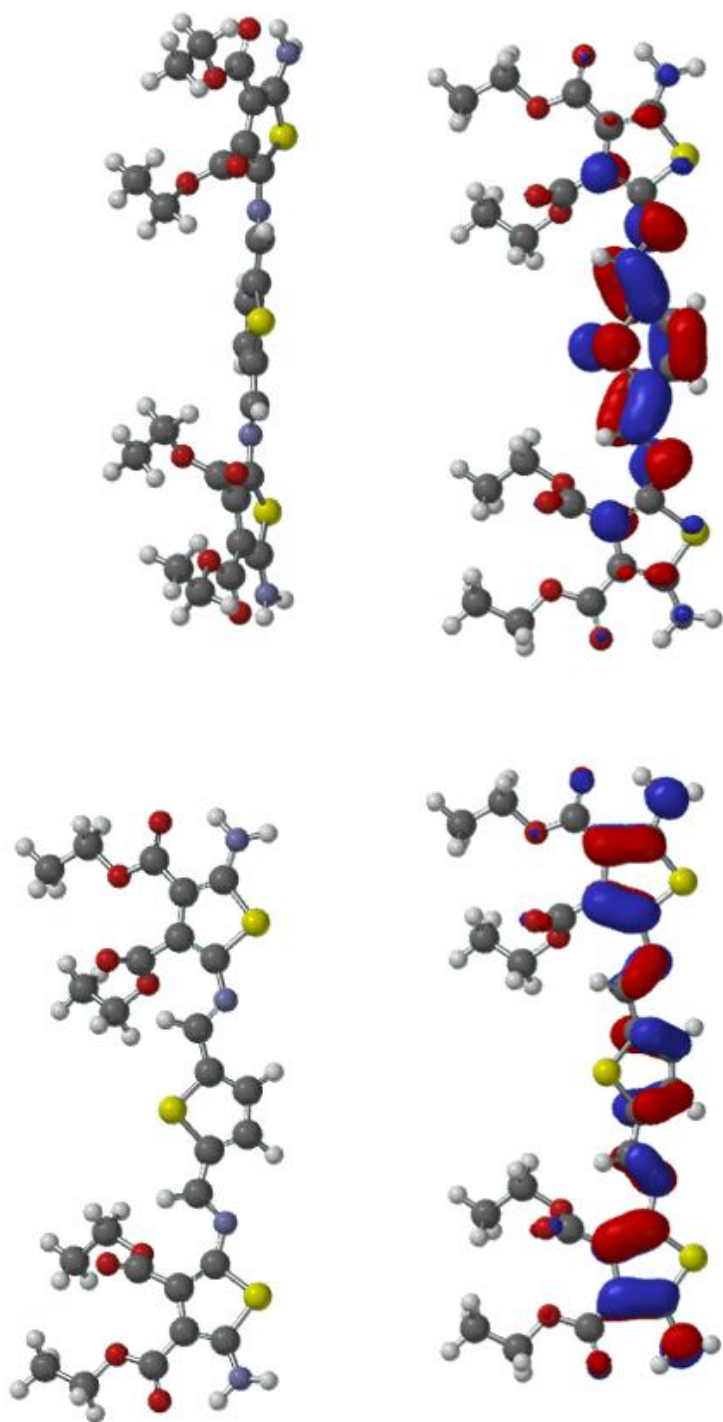


Figure S6. Top down view (top left) and side-on view (top right) of the calculated geometry of **1A** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

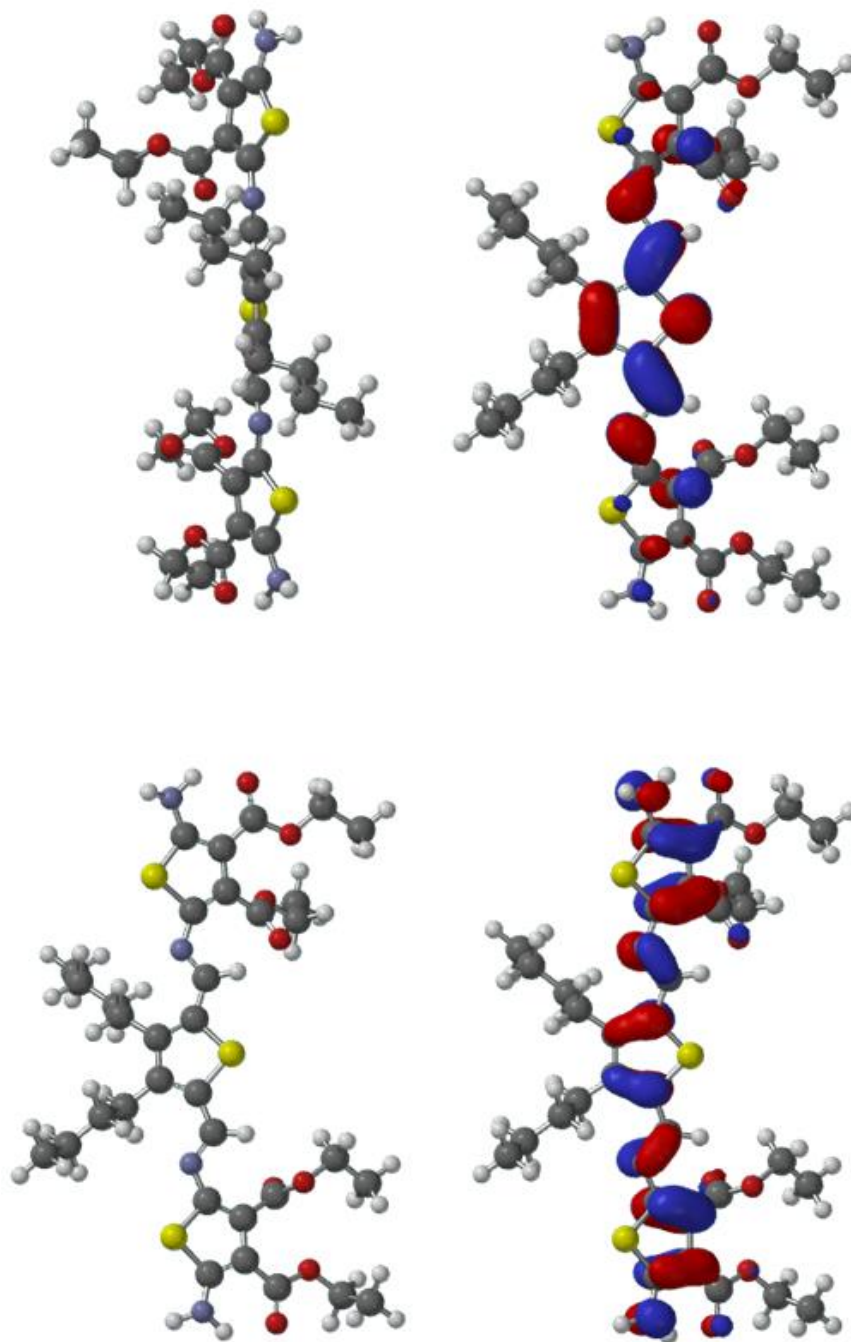


Figure S7. Top down view (top left) and side-on view (top right) of the calculated geometry of **1B** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

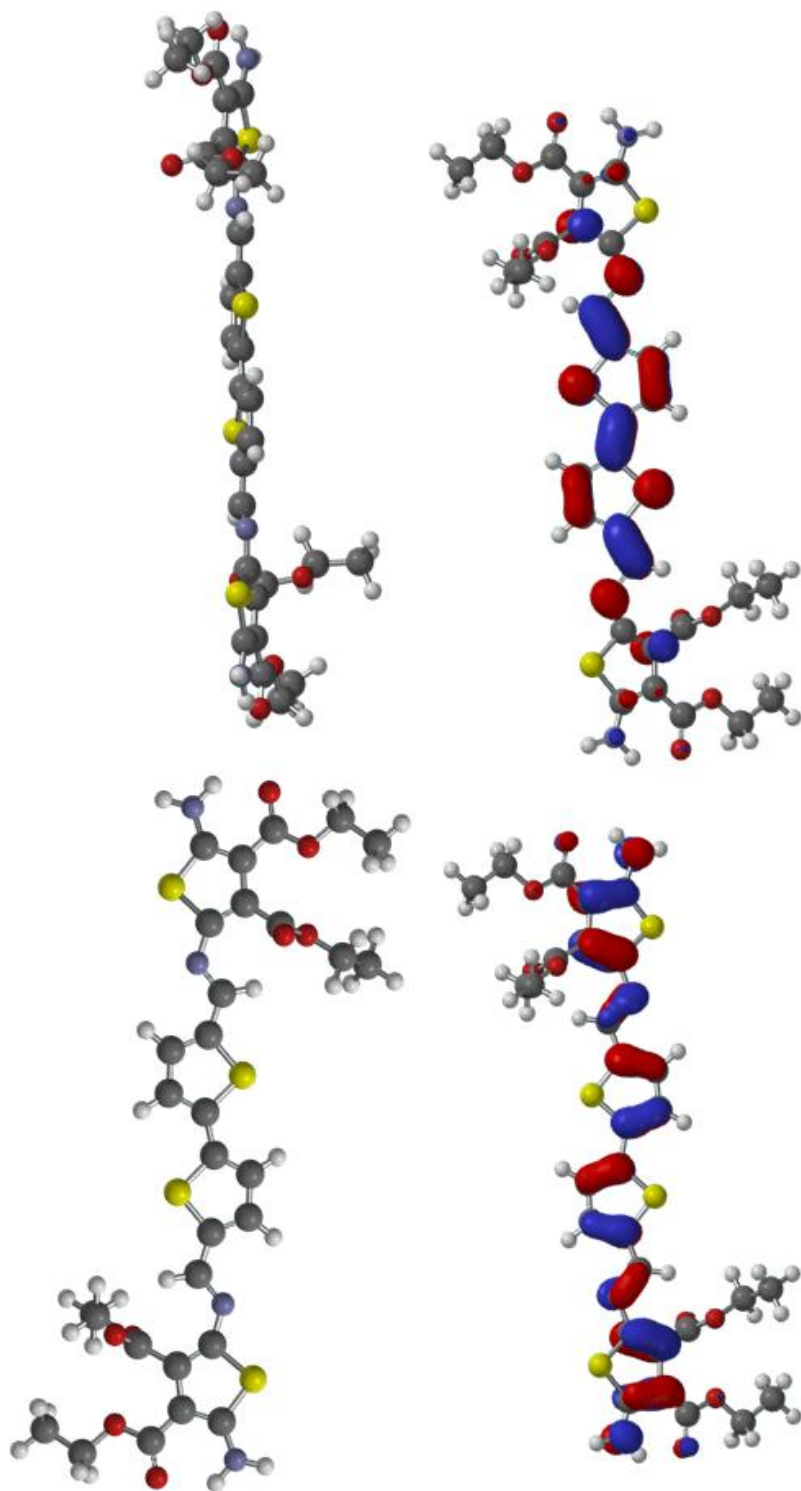


Figure S8. Top down view (top left) and side-on view (top right) of the calculated geometry of **2A** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

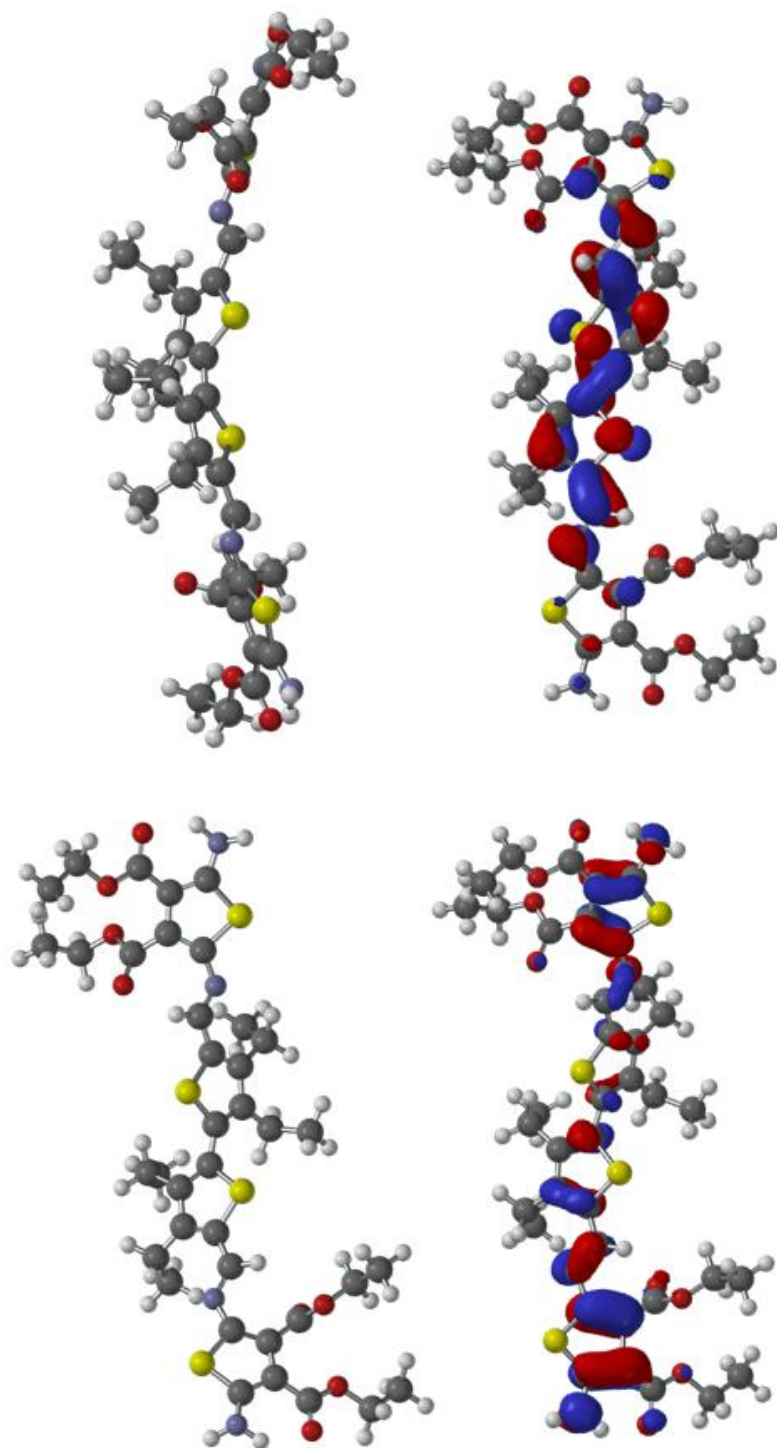


Figure S9. Top down view (top left) and side-on view (top right) of the calculated geometry of the ethylated derivative of **2B** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

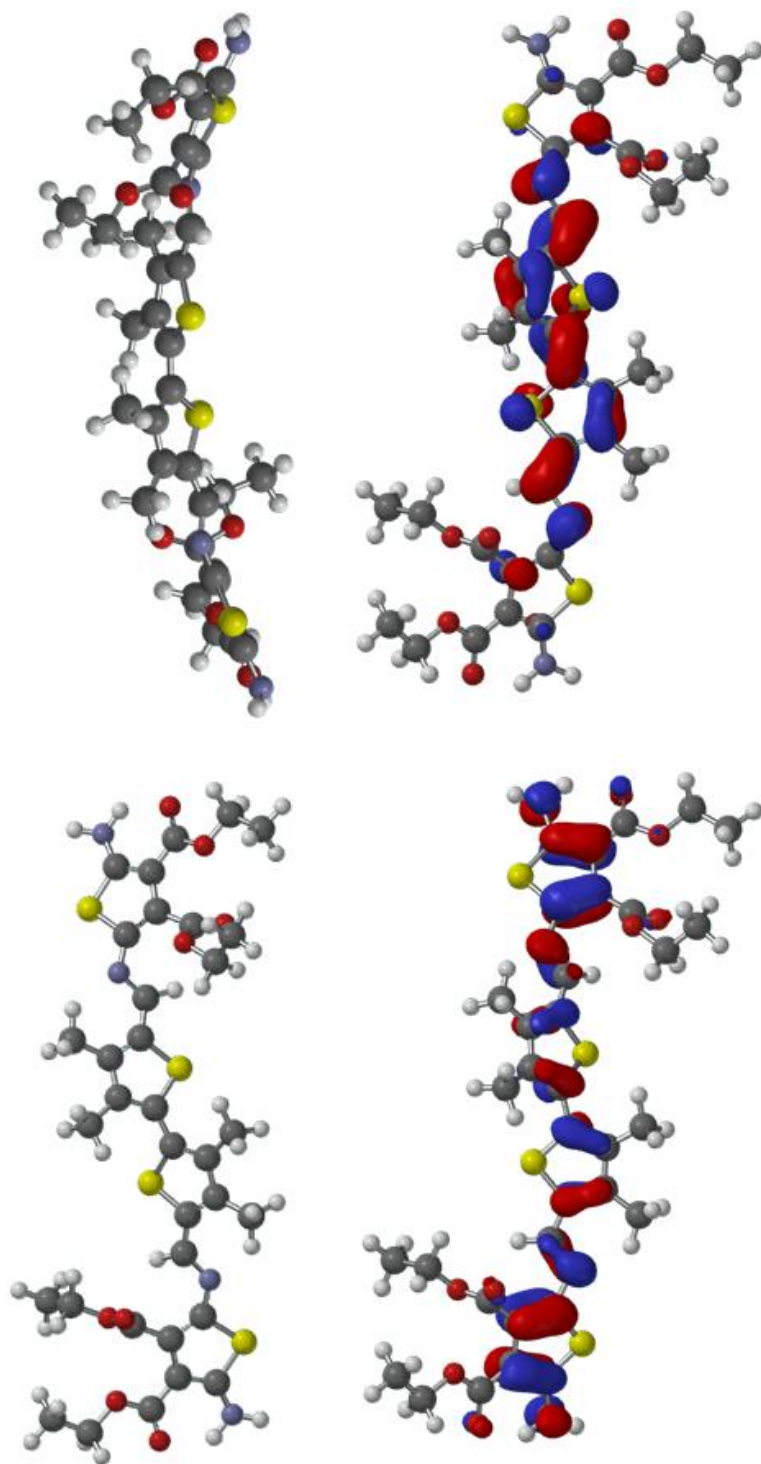


Figure S10. Top down view (top left) and side-on view (top right) of the calculated geometry of the methylated derivative of **2B** and the HOMO (bottom left) and LUMO (bottom right) orbitals.



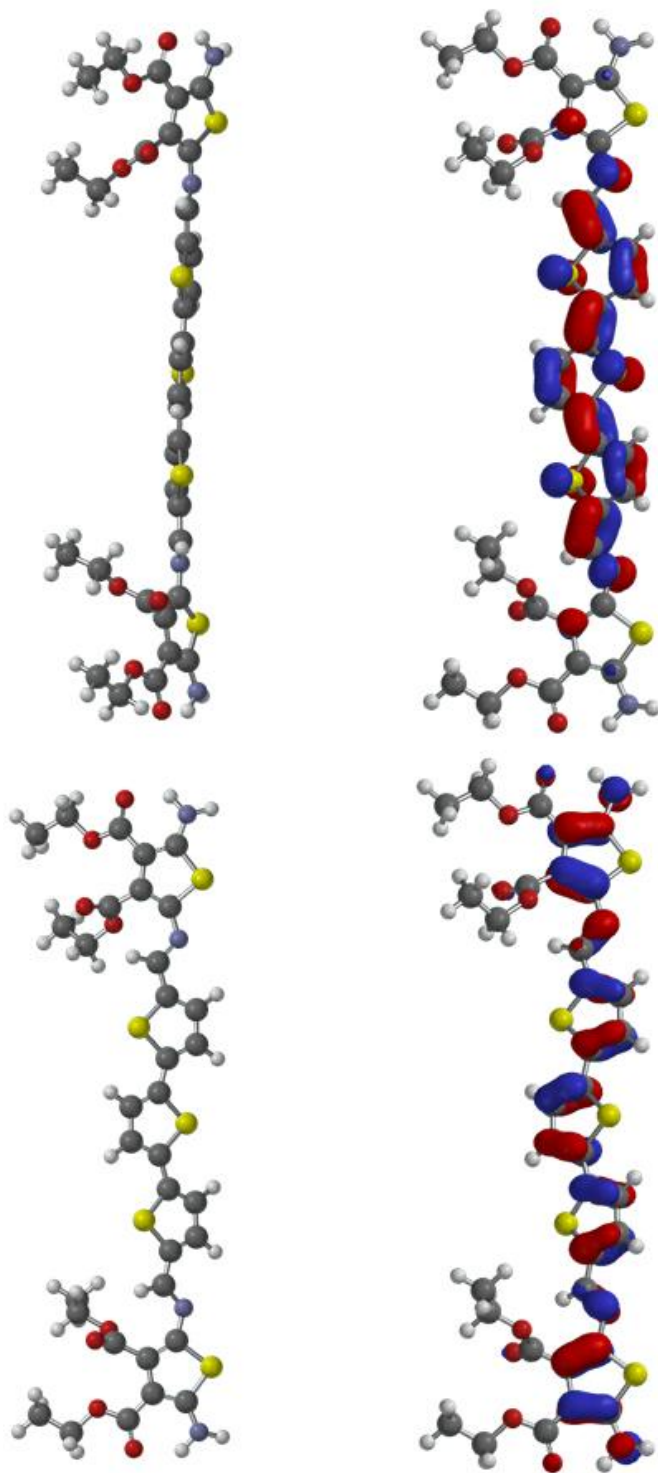


Figure S11. Top down view (top left) and side-on view (top right) of the calculated geometry of **3A** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

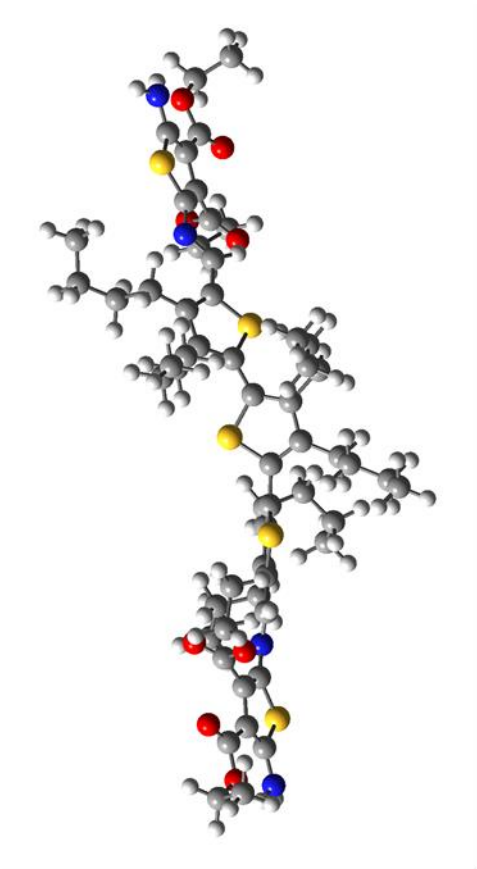
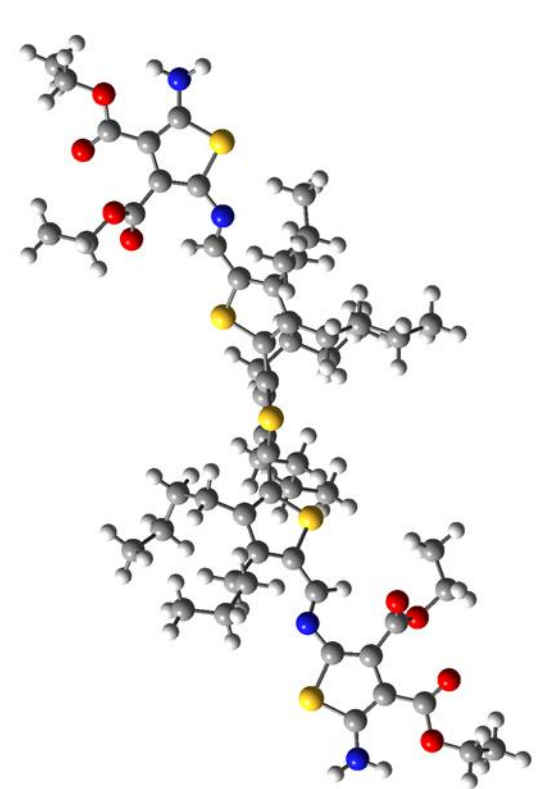


Figure S12. Top down view (left) and side-on view (right) of the calculated geometry of **3B**.

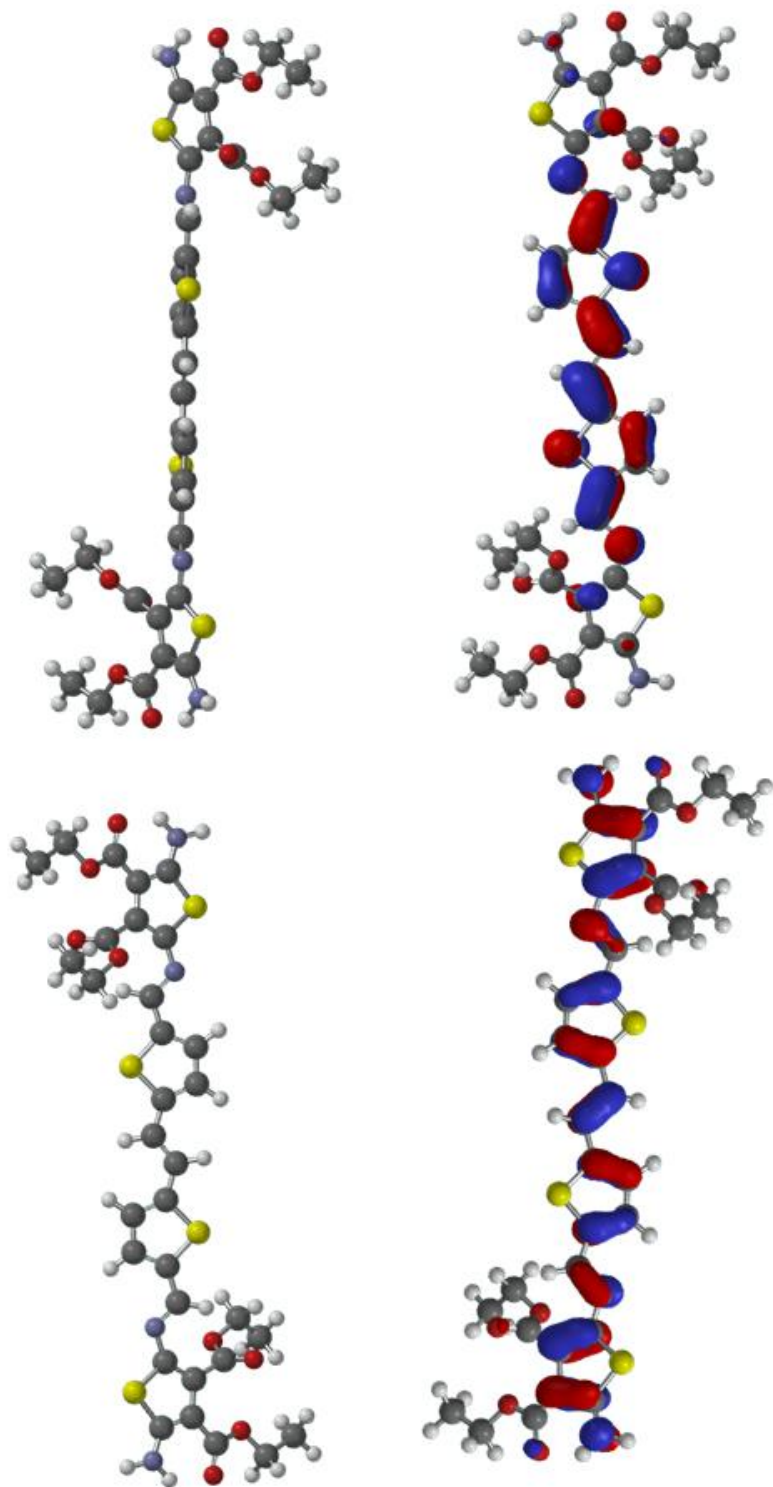


Figure S13. Top down view (top left) and side-on view (top right) of the calculated geometry of **4** and the HOMO (bottom left) and LUMO (bottom right) orbitals.

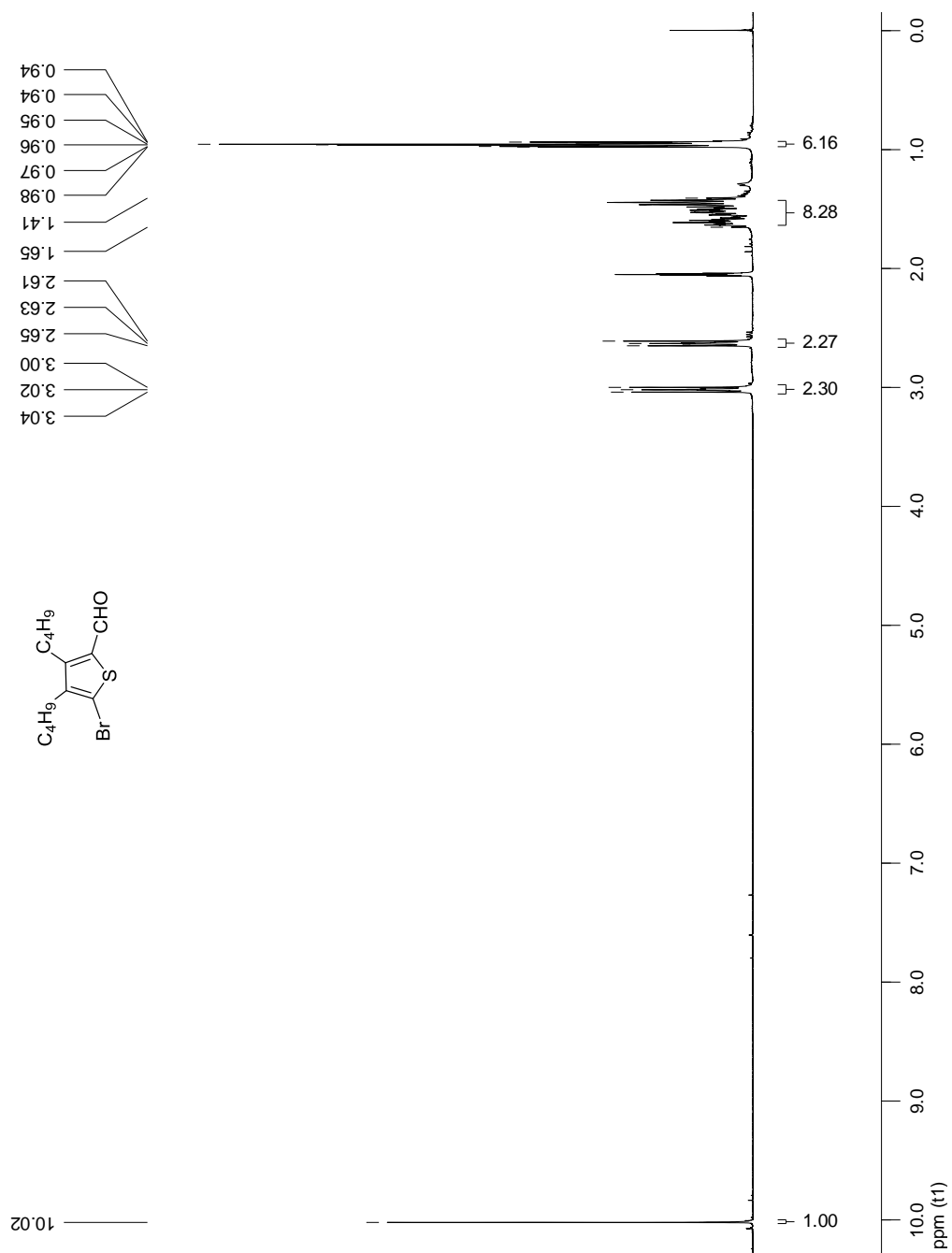


Figure S14. <sup>1</sup>H NMR spectrum of 5-bromo-3,4-dibutylthiophene-2-carboxaldehyde recorded in acetone-d<sub>6</sub>.

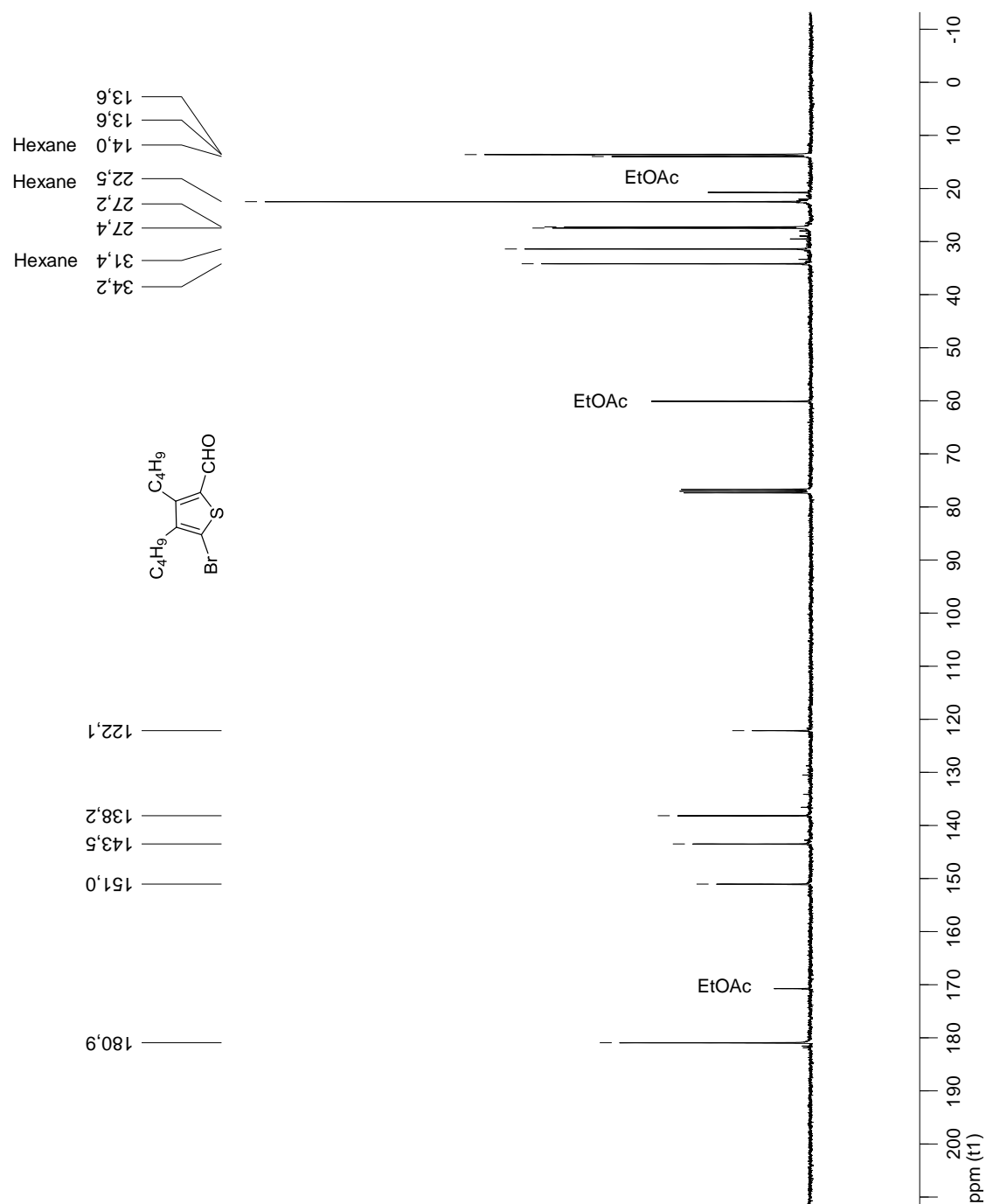


Figure S15. <sup>13</sup>C NMR spectrum of 5-bromo-3,4-dibutylthiophene-2-carboxaldehyde recorded in CDCl<sub>3</sub>.

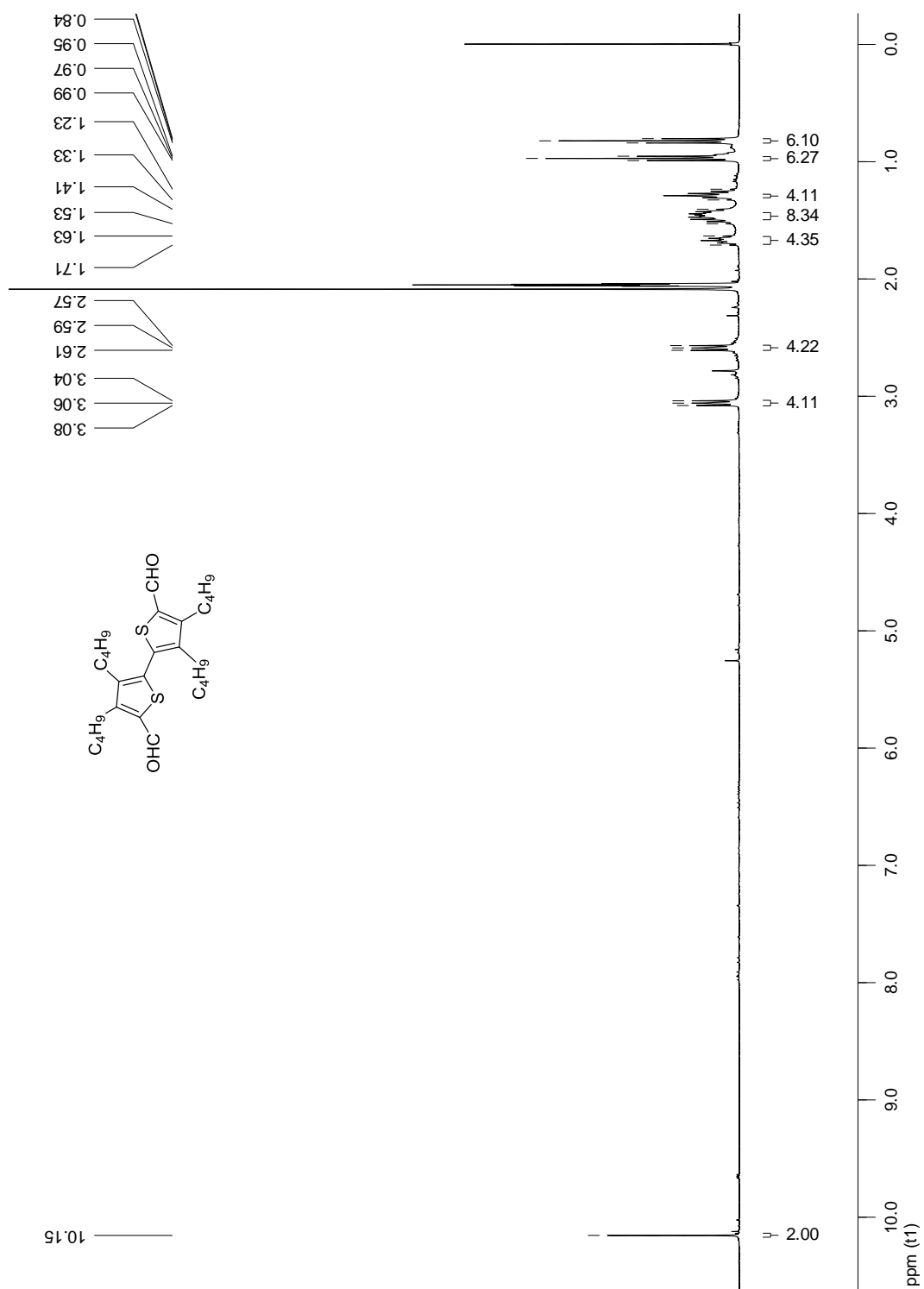


Figure S16. <sup>1</sup>H NMR spectrum of 3,3',4,4'-tetrabutyl-[2,2'-bithiophene]-5,5'-dicarboxaldehyde recorded in acetone-d<sub>6</sub>.

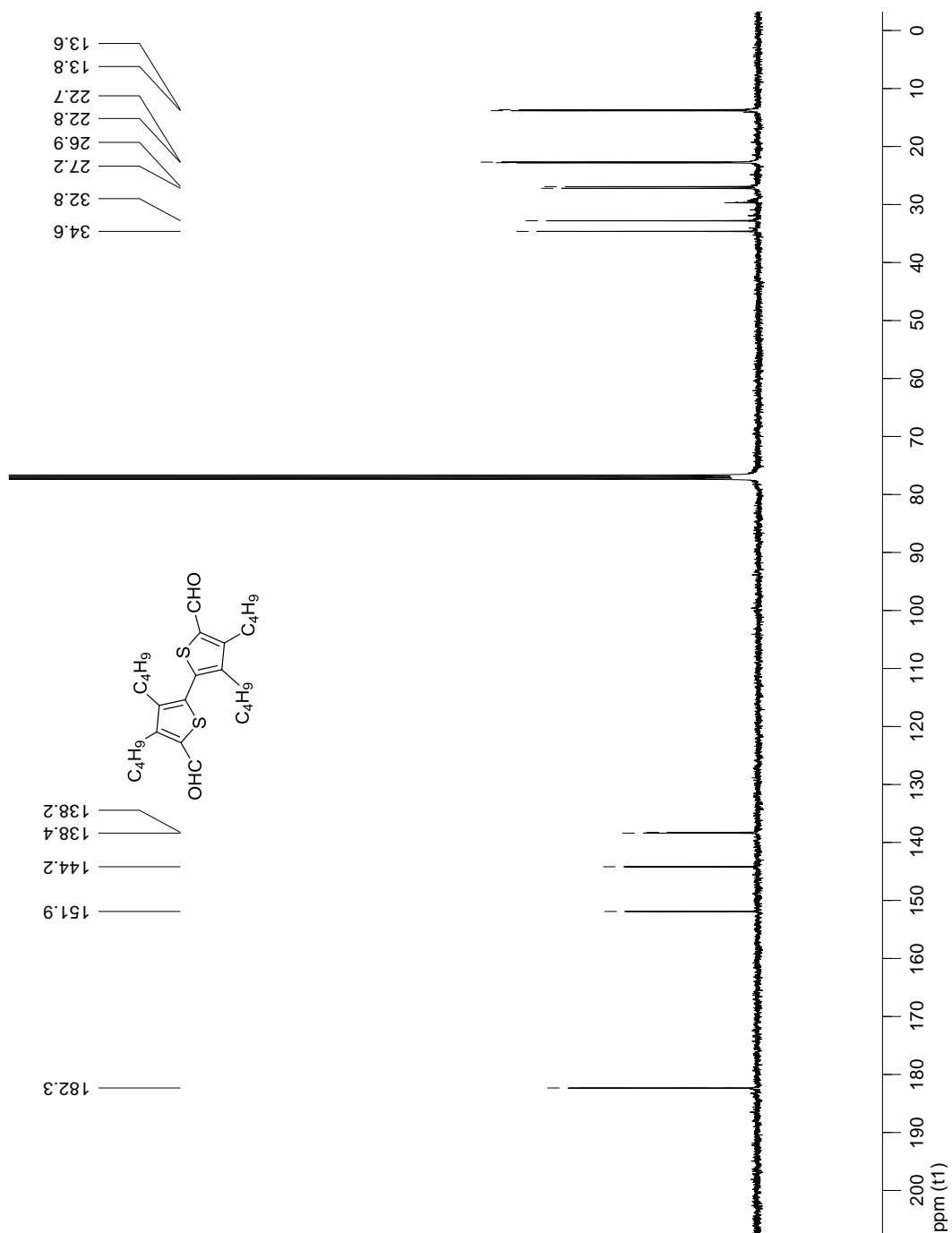


Figure S17.  $^{13}\text{C}$  NMR spectrum of 3,3',4,4'-tetrabutyl-[2,2'-bithiophene]-5,5'-dicarboxaldehyde recorded in  $\text{CDCl}_3$ .

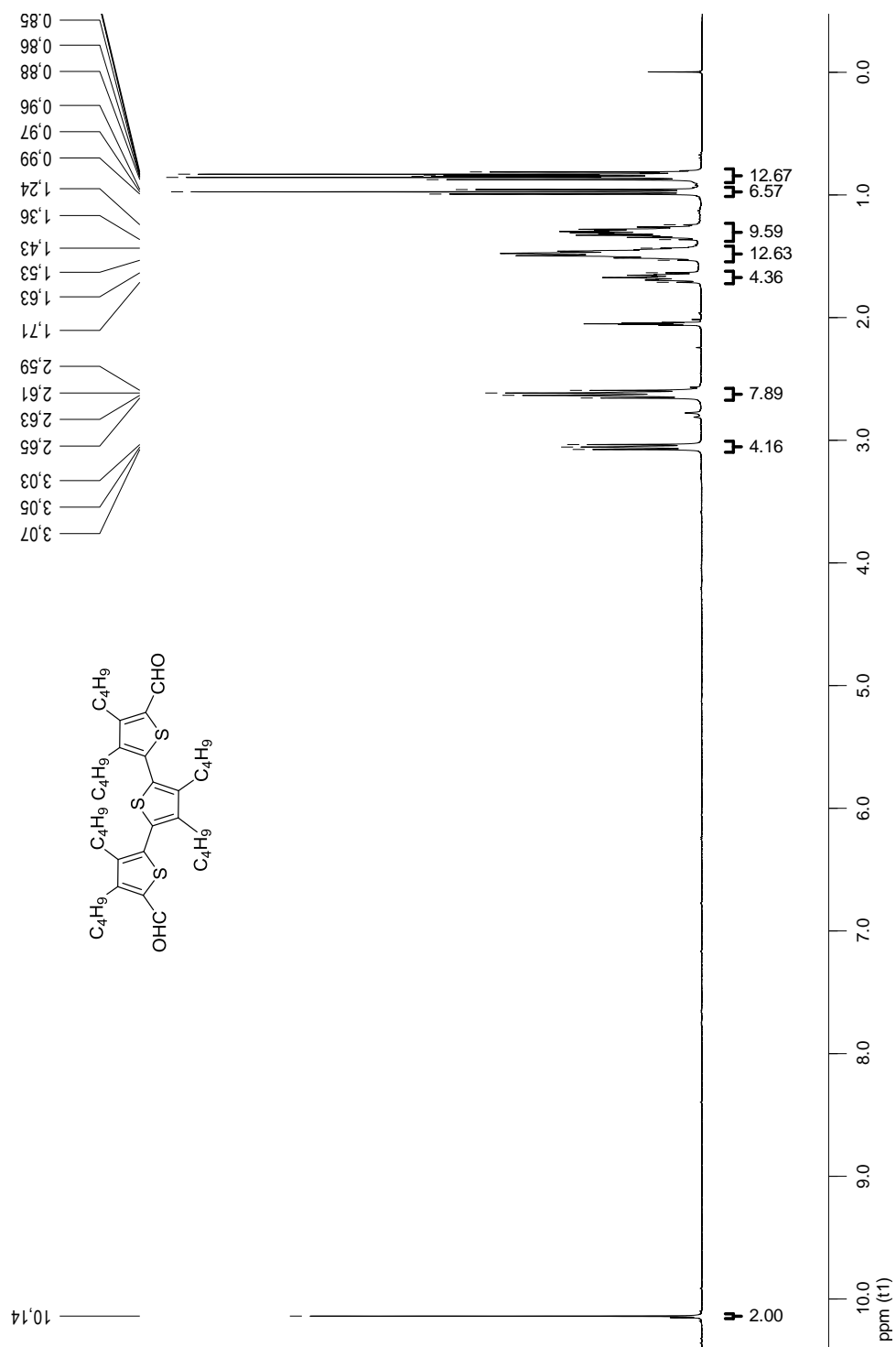


Figure S18.  $^1\text{H}$  NMR spectrum of 3,3',3'',4,4',4''-hexabutyl-[2,2':5',2''-terthiophene]-5,5''-dicarboxaldehyde recorded in acetone- $\text{d}_6$ .



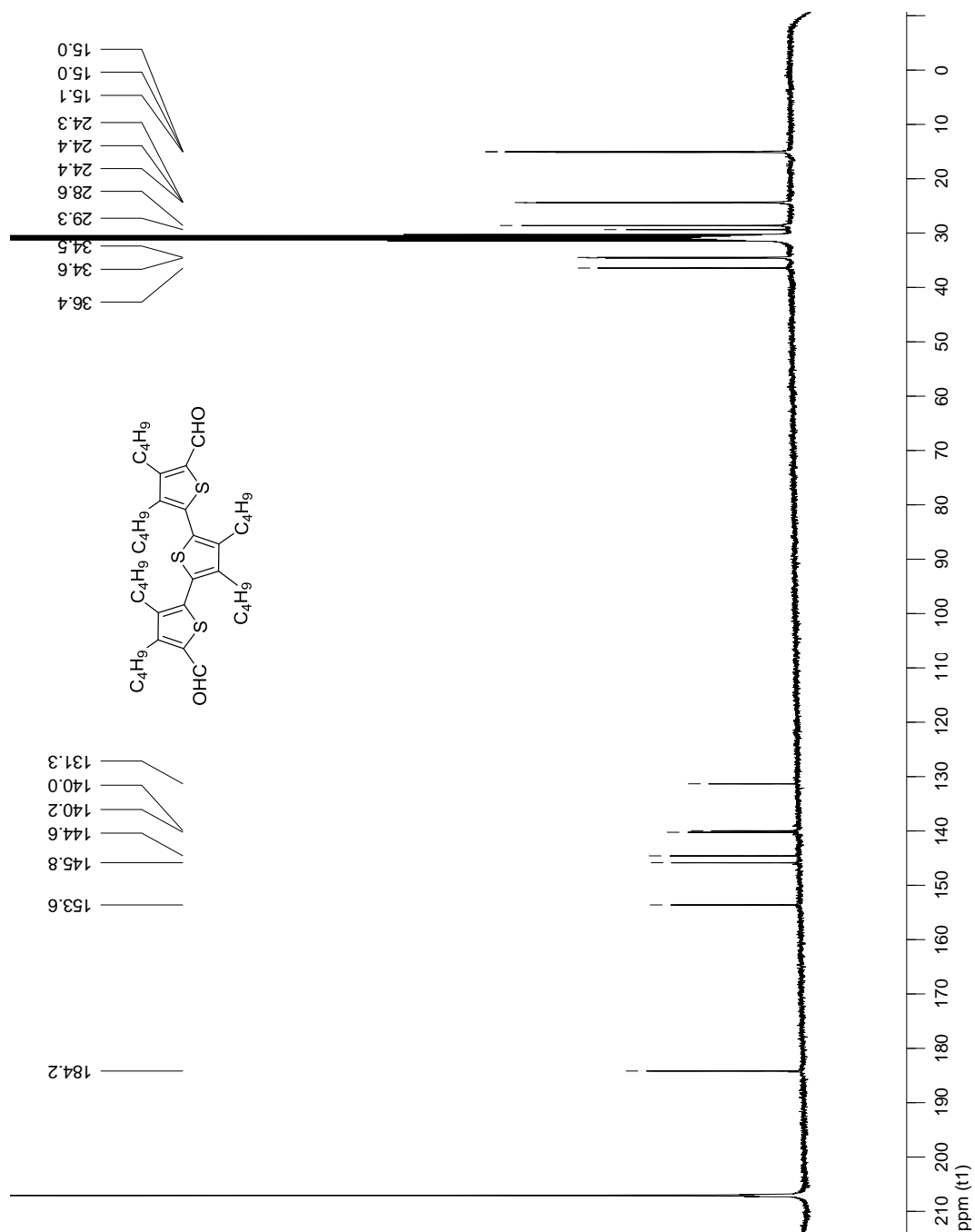


Figure S19.  $^{13}\text{C}$  NMR spectrum of 3,3',3'',4,4',4''-hexabutyl-[2,2':5',2''-terthiophene]-5,5''-dicarboxaldehyde recorded in acetone- $\text{d}_6$ .

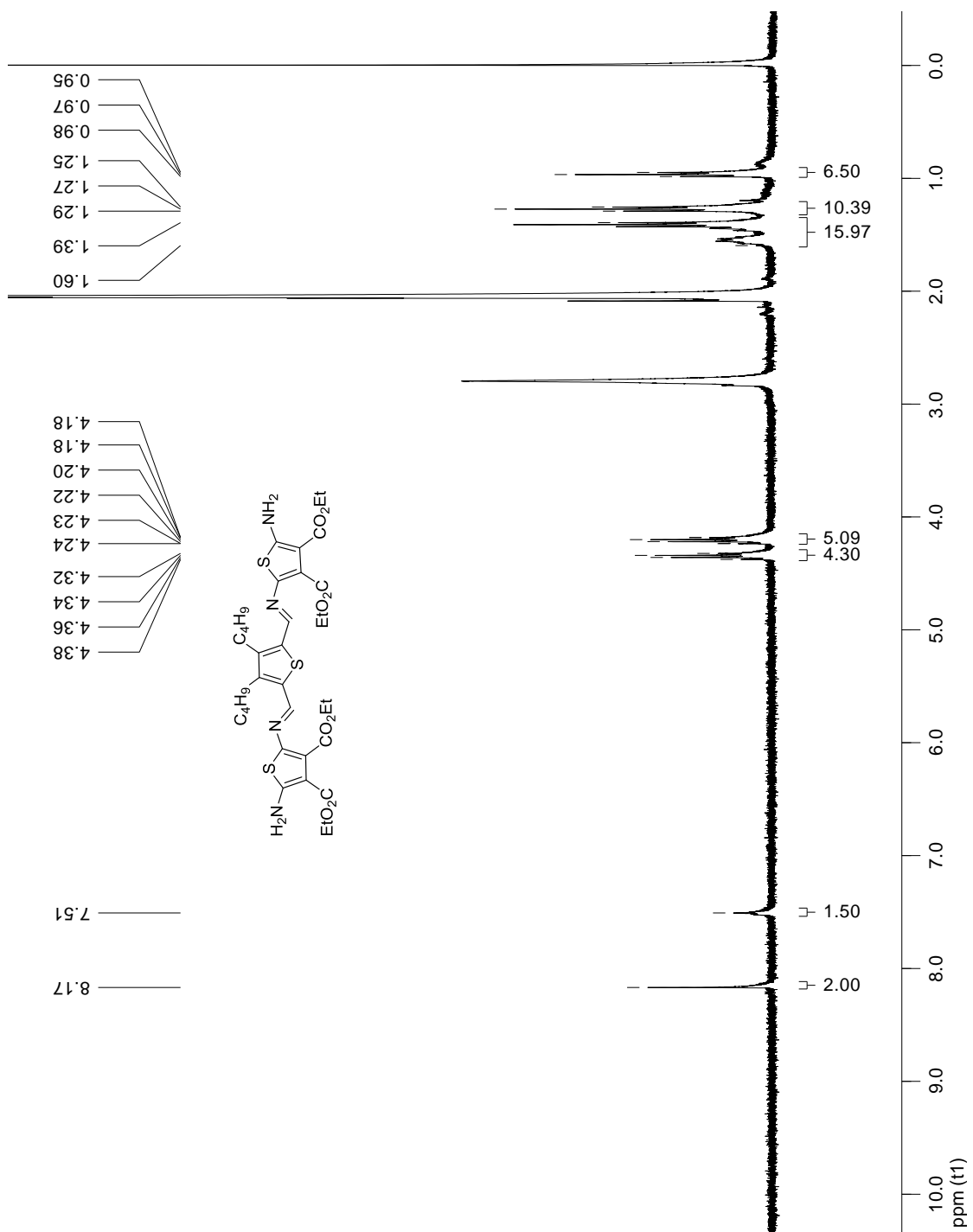


Figure S20.  $^1\text{H}$  NMR spectrum of **1B** recorded in  $\text{acetone-d}_6$ .

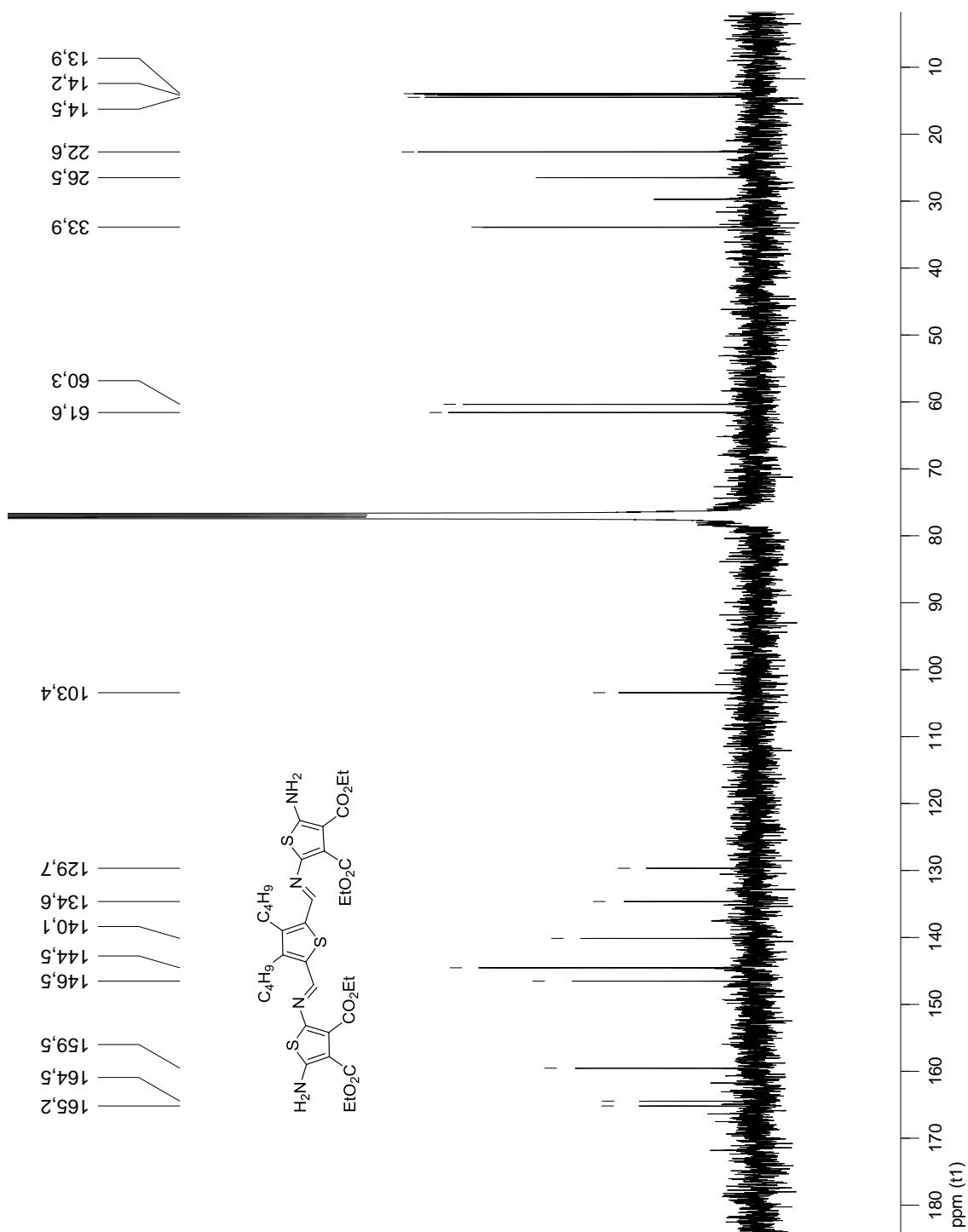


Figure S21. <sup>13</sup>C NMR spectrum of **1B** recorded in CDCl<sub>3</sub>.

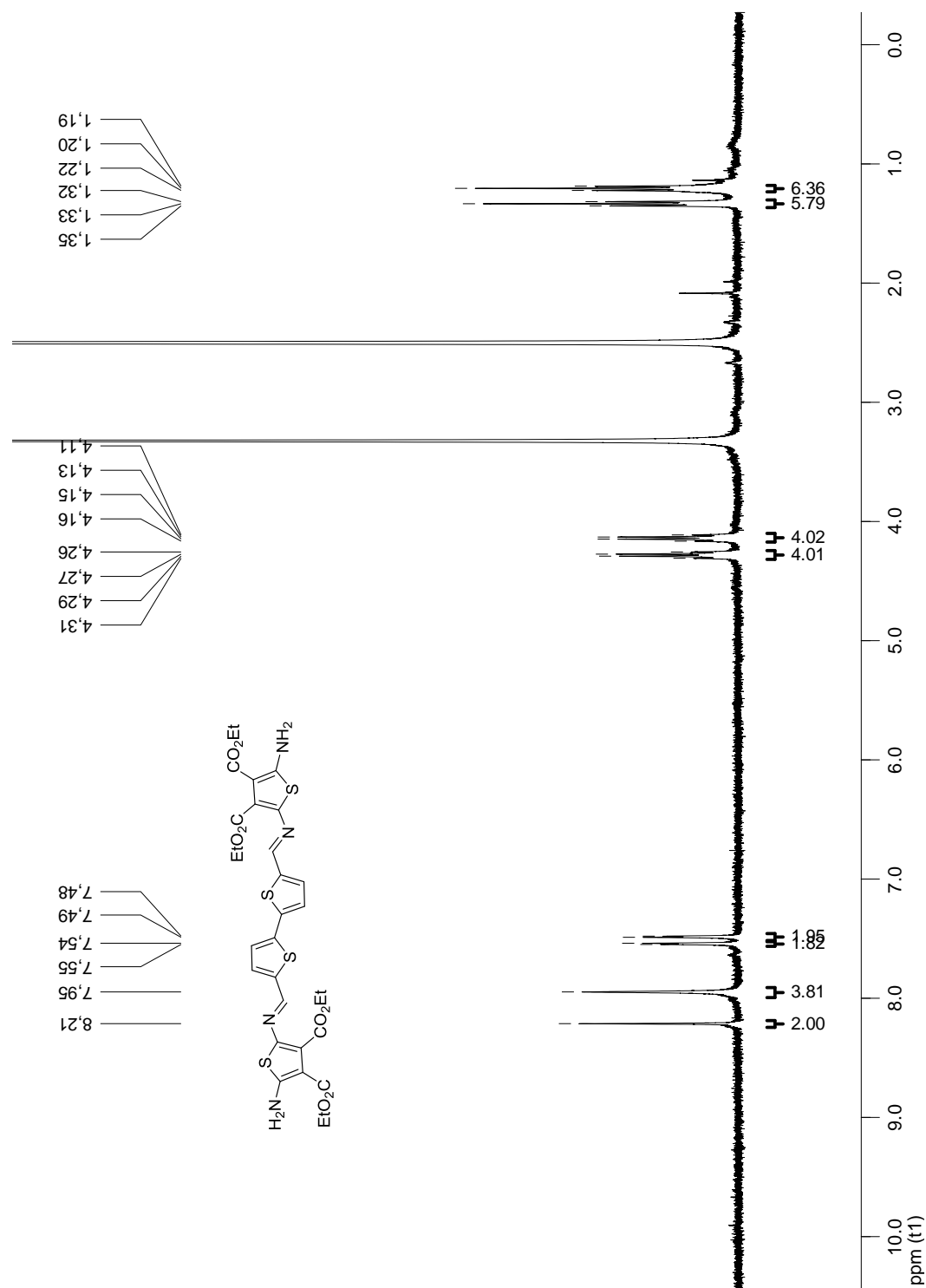


Figure S22.  $^1\text{H}$  NMR spectrum of **2A** recorded in DMSO- $d_6$ .

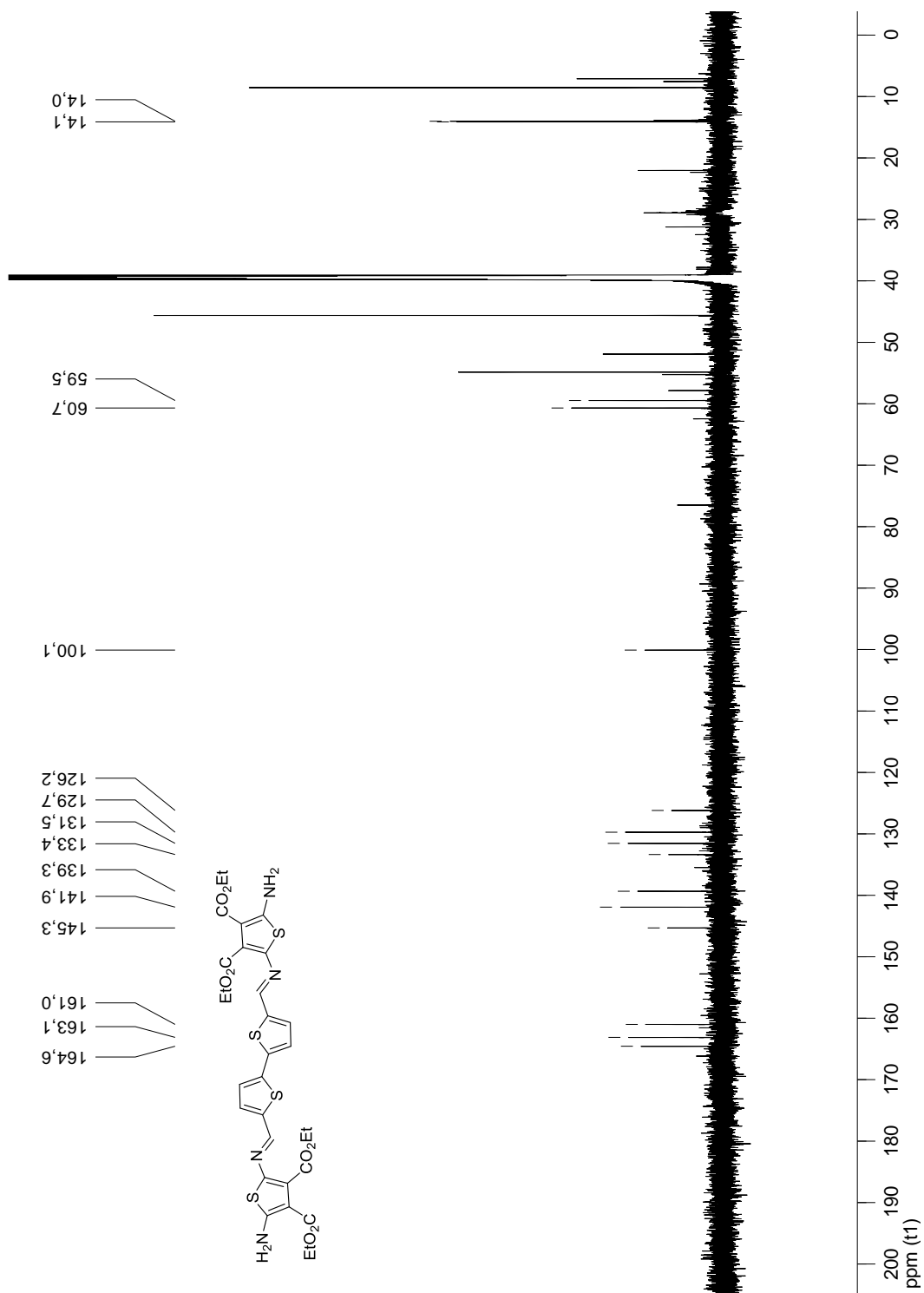


Figure S23. <sup>13</sup>C NMR spectrum of **2A** recorded in DMSO-d<sub>6</sub>.

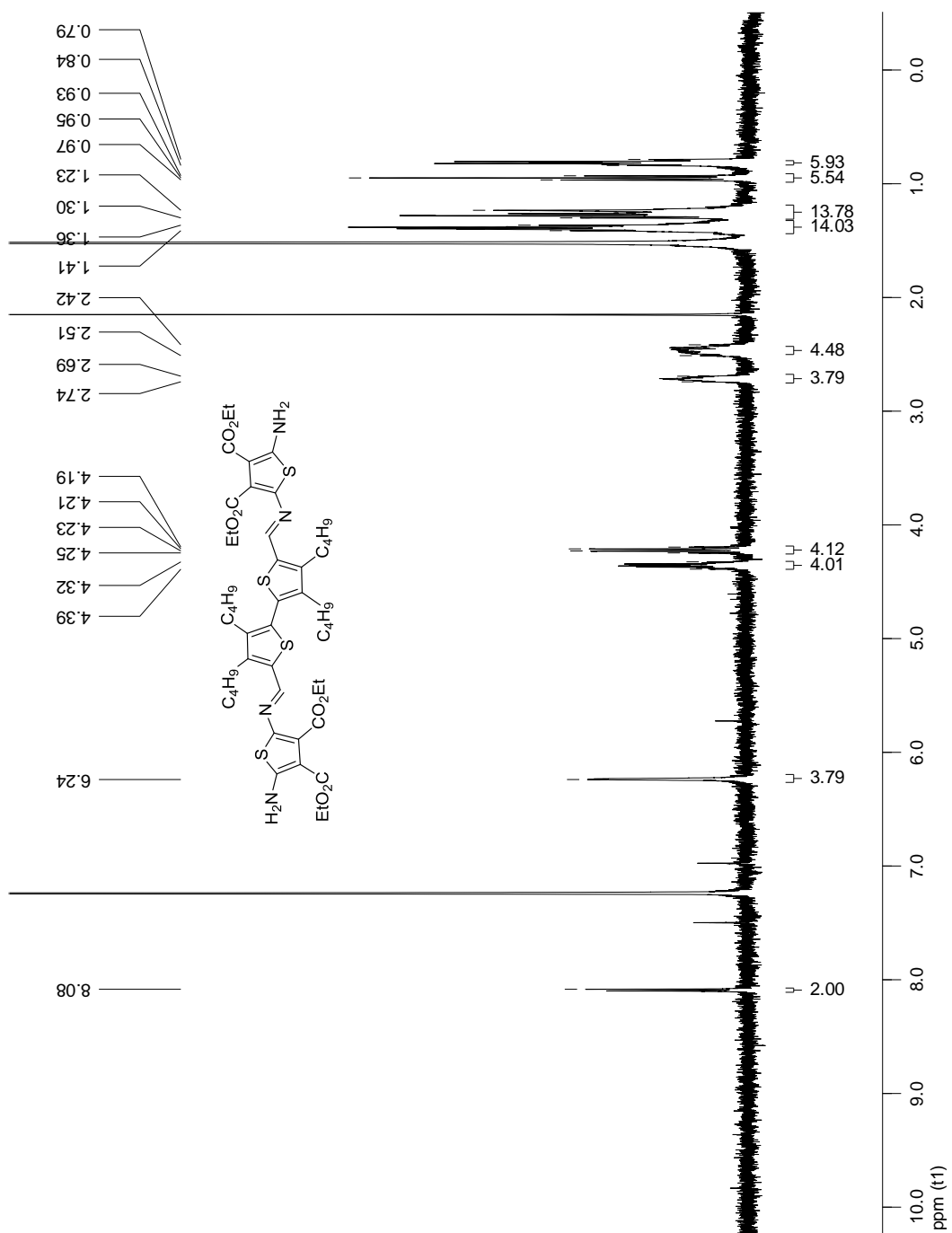


Figure S24. <sup>1</sup>H NMR spectrum of **2B** recorded in CDCl<sub>3</sub>.

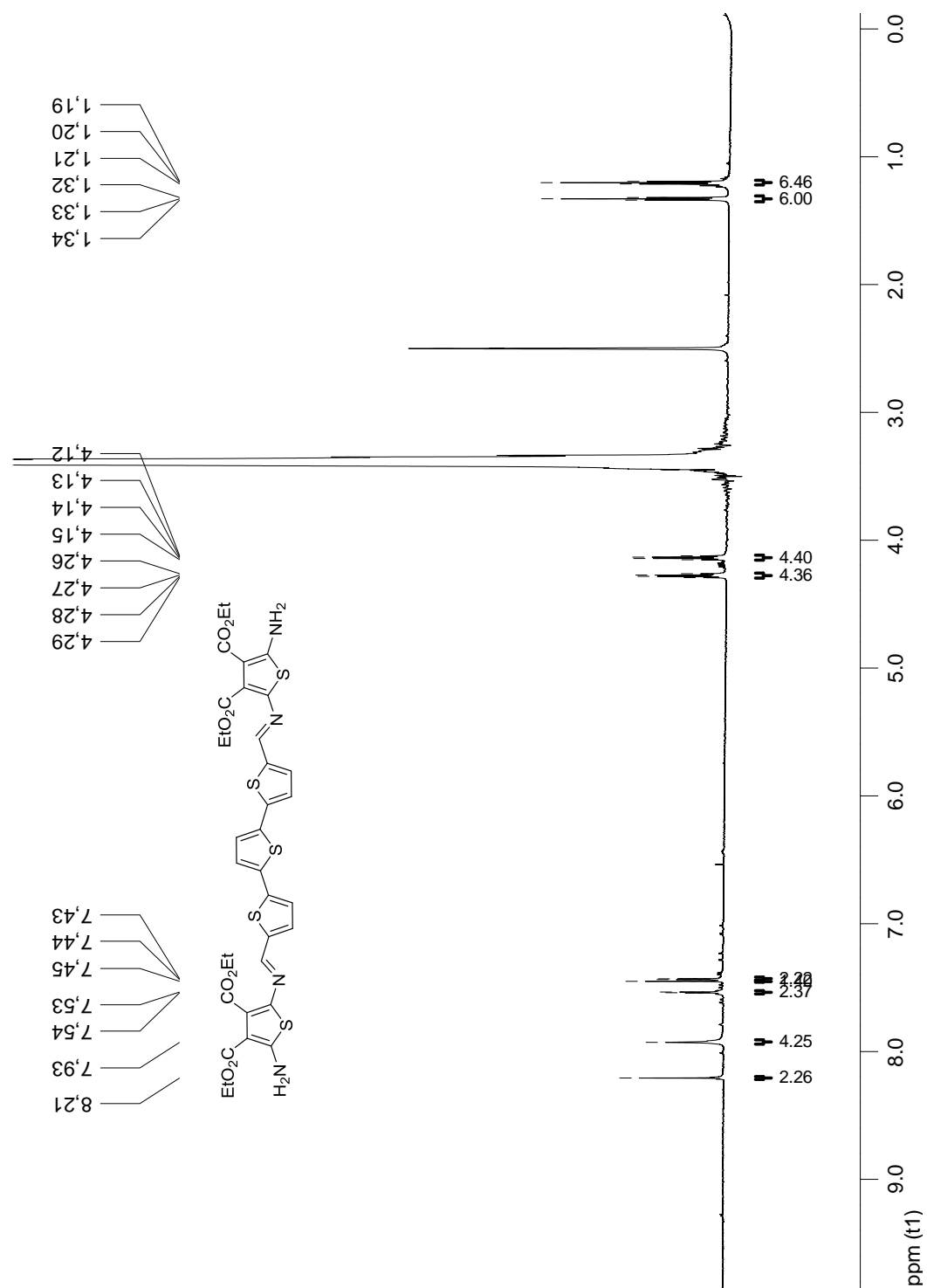


Figure S25. <sup>1</sup>H NMR spectrum of **3A** recorded in DMSO-d<sub>6</sub>.

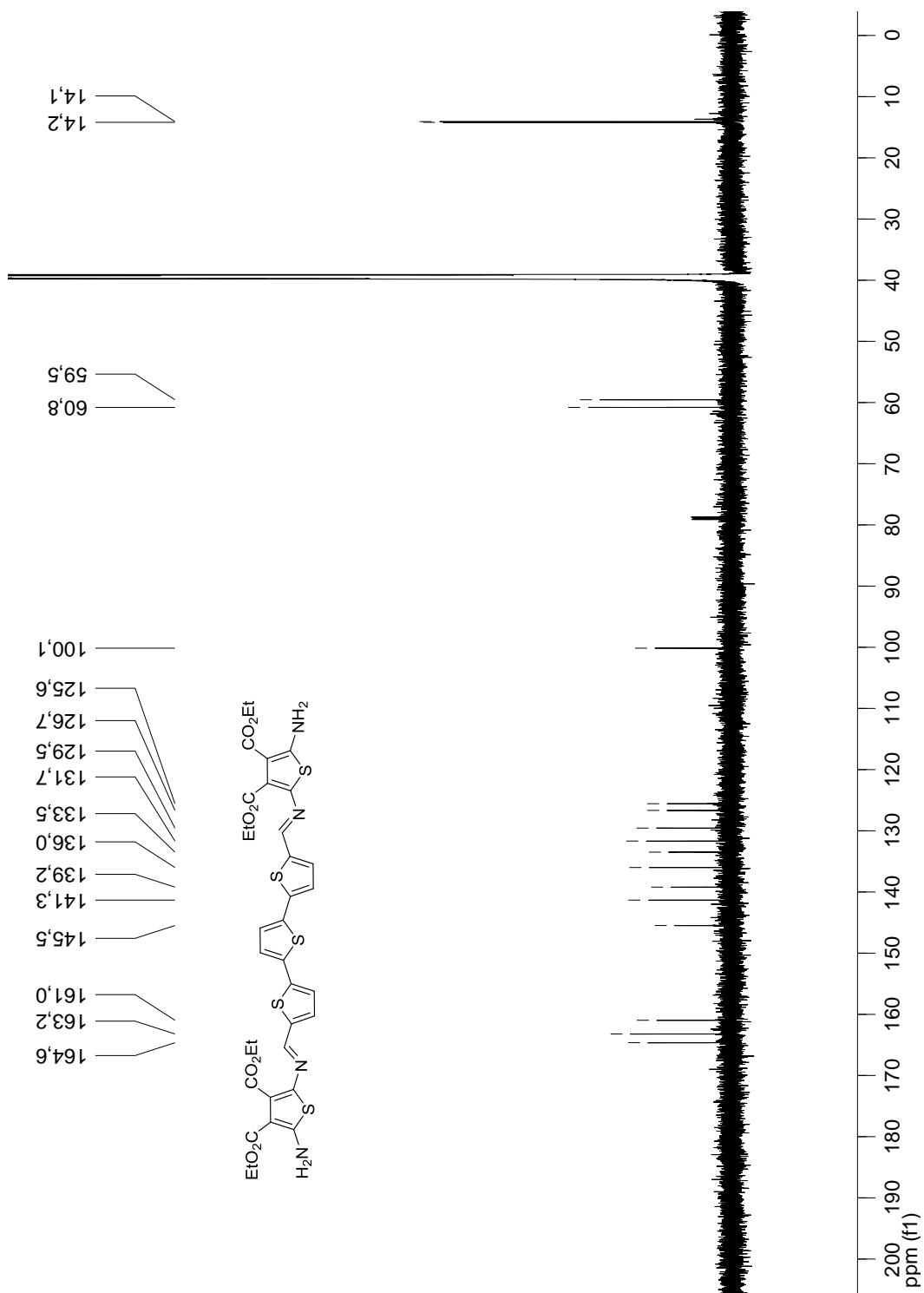


Figure S26.  $^{13}\text{C}$  NMR spectrum of **3A** recorded in  $\text{DMSO-d}_6$ .



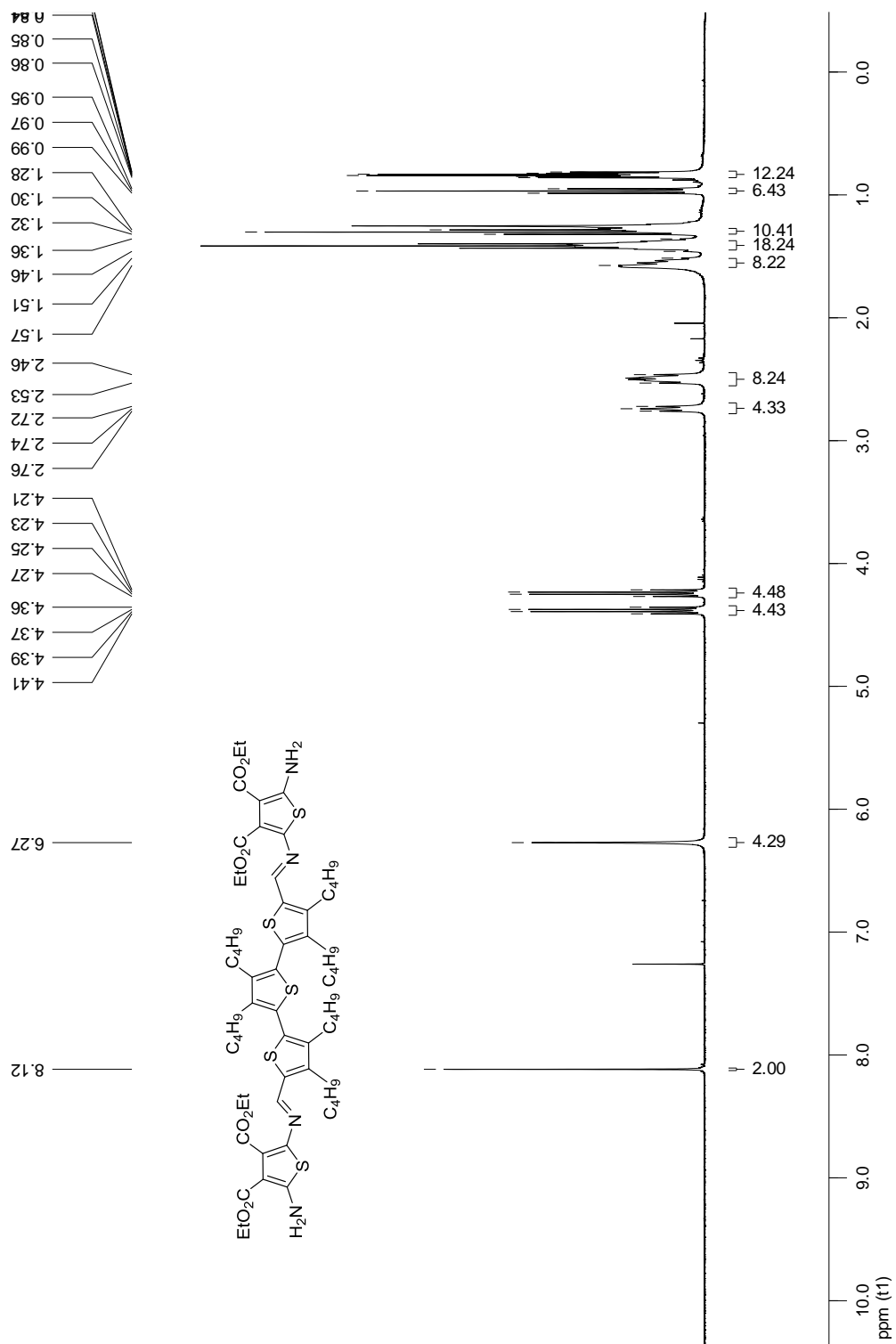


Figure S27.  $^1\text{H}$  NMR spectrum of **3B** recorded in CDCl<sub>3</sub>.

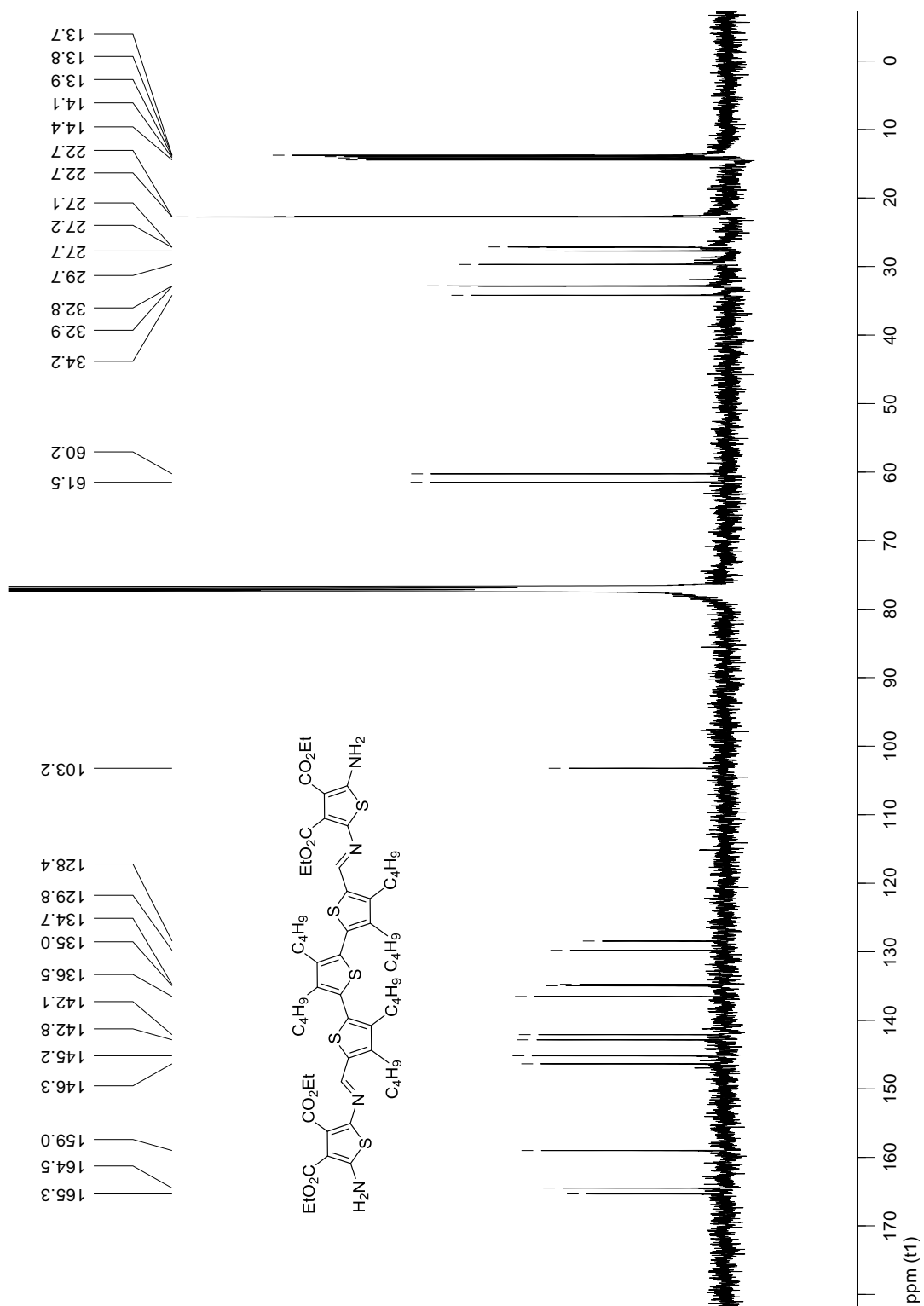


Figure S28. <sup>13</sup>C NMR spectrum of **3B** recorded in CDCl<sub>3</sub>.

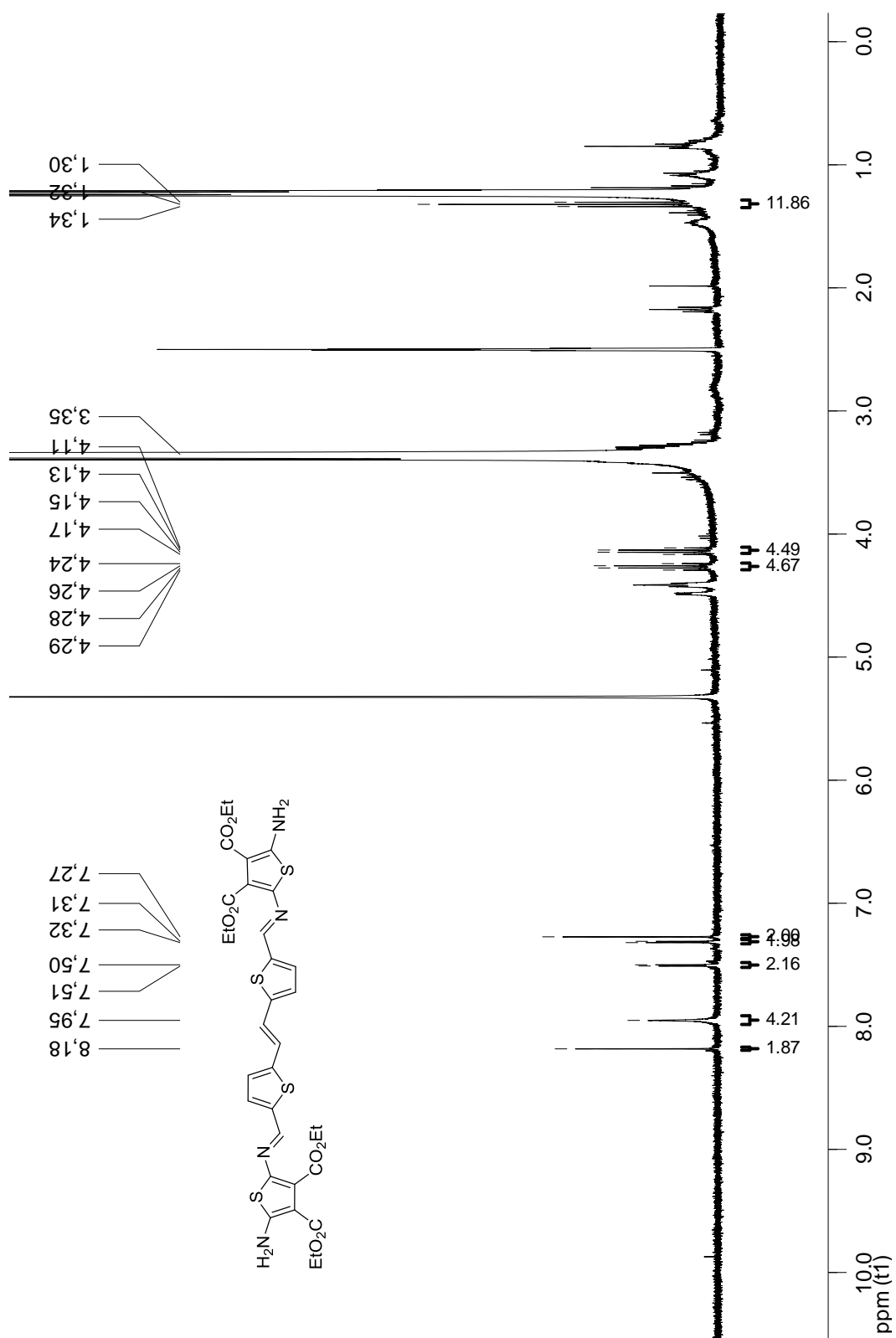


Figure S29. <sup>1</sup>H NMR spectrum of **4** recorded in DMSO-d<sub>6</sub>.

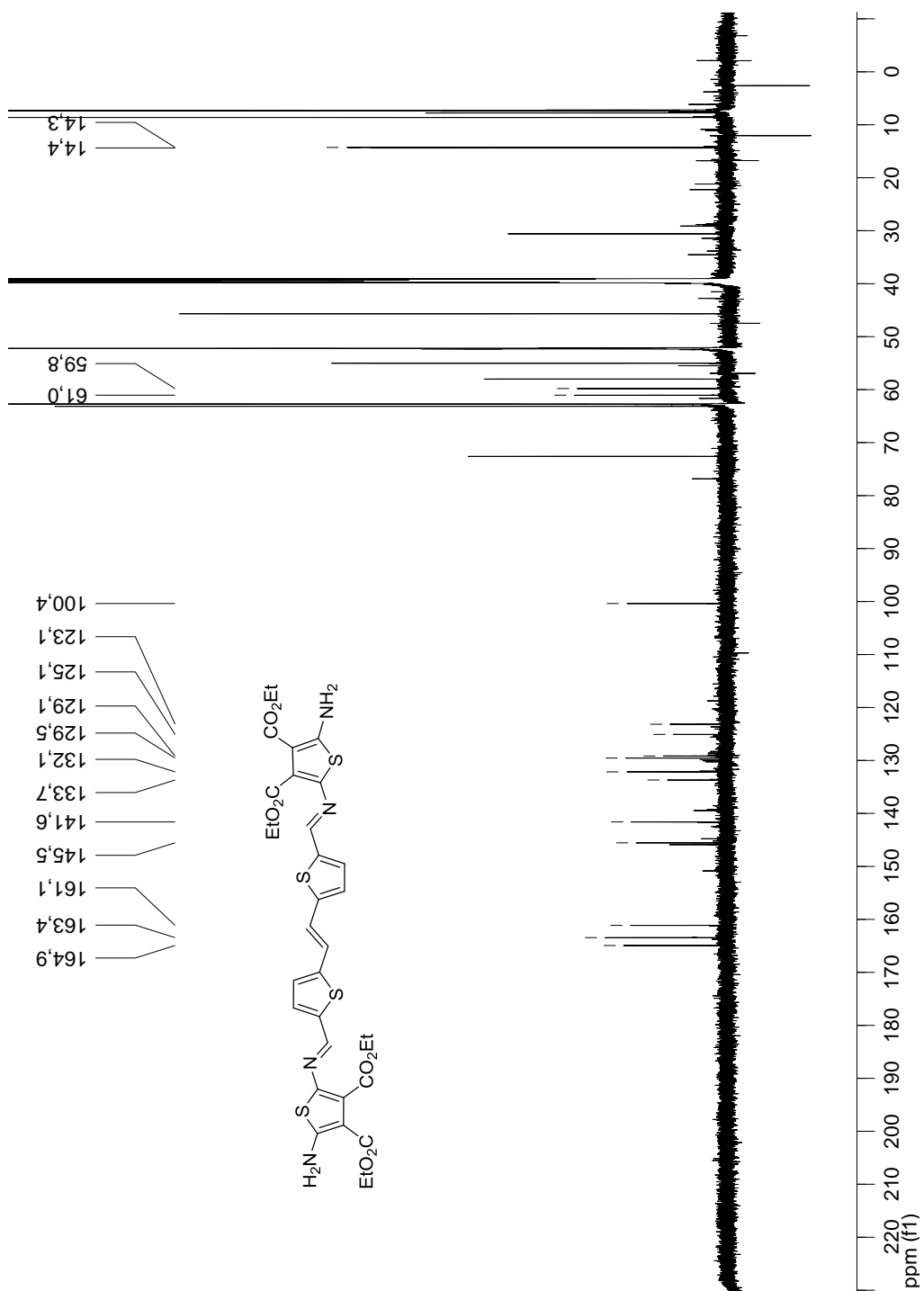


Figure S30.  $^{13}\text{C}$  NMR spectrum of **4** recorded in DMSO- $\text{d}_6$ .

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