

## Supplementary Material

### The synthesis of thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acids using the Fischer indolization reaction

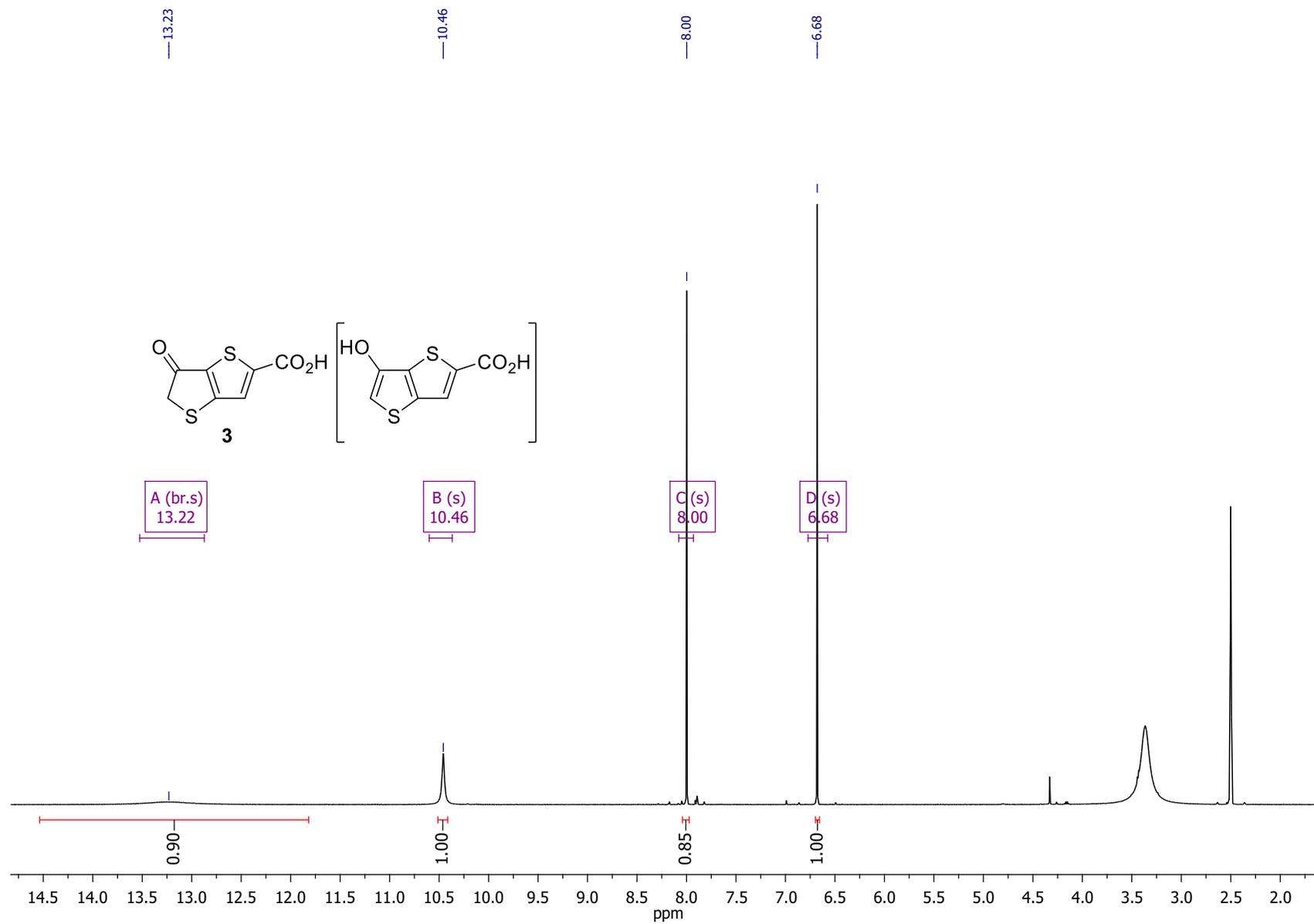
Roman A. Irgashev,\* Alexander S. Steparuk and Nikita A. Kazin

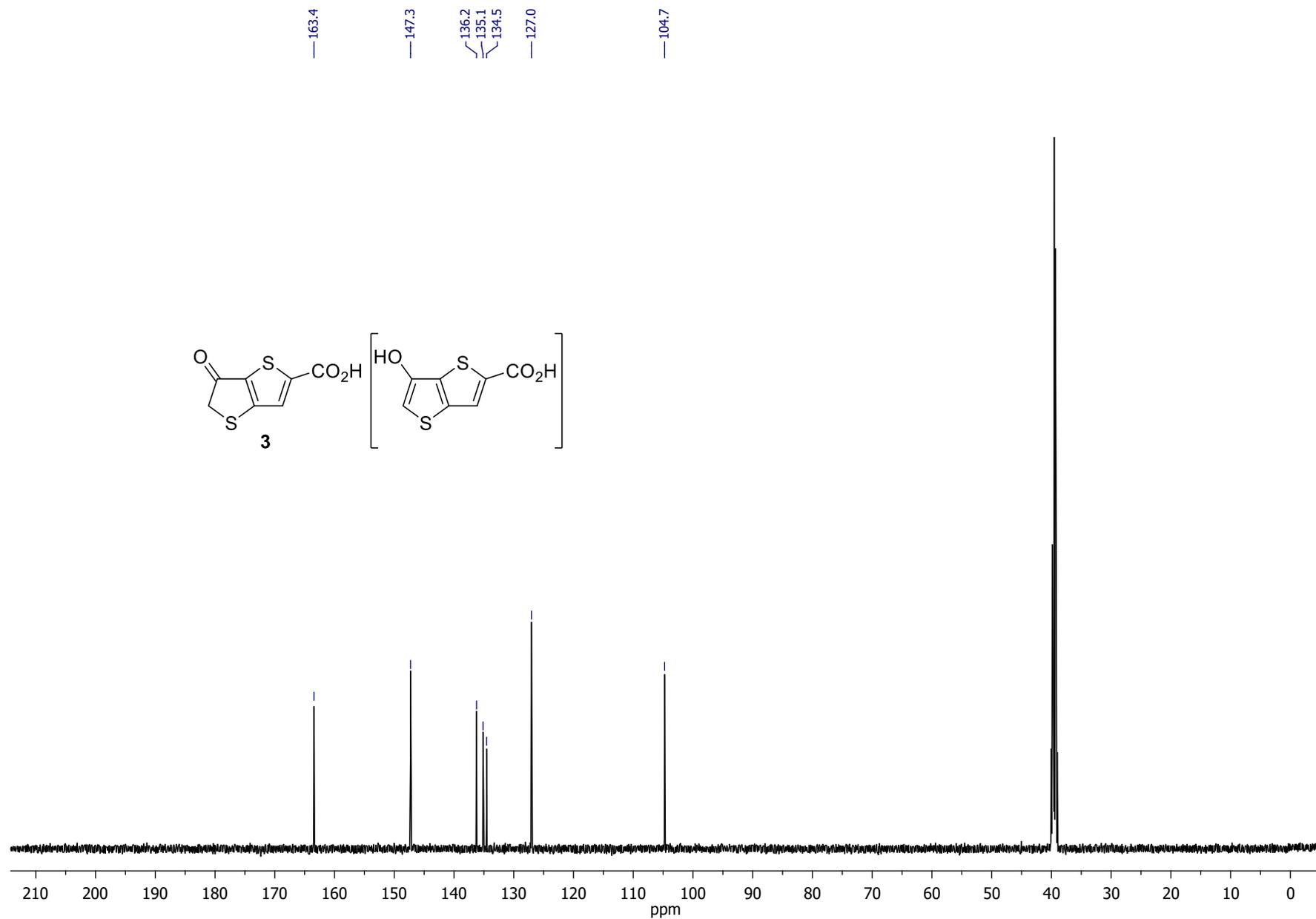
*Postovsky Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences,  
Ekaterinburg, 620990, Russia*

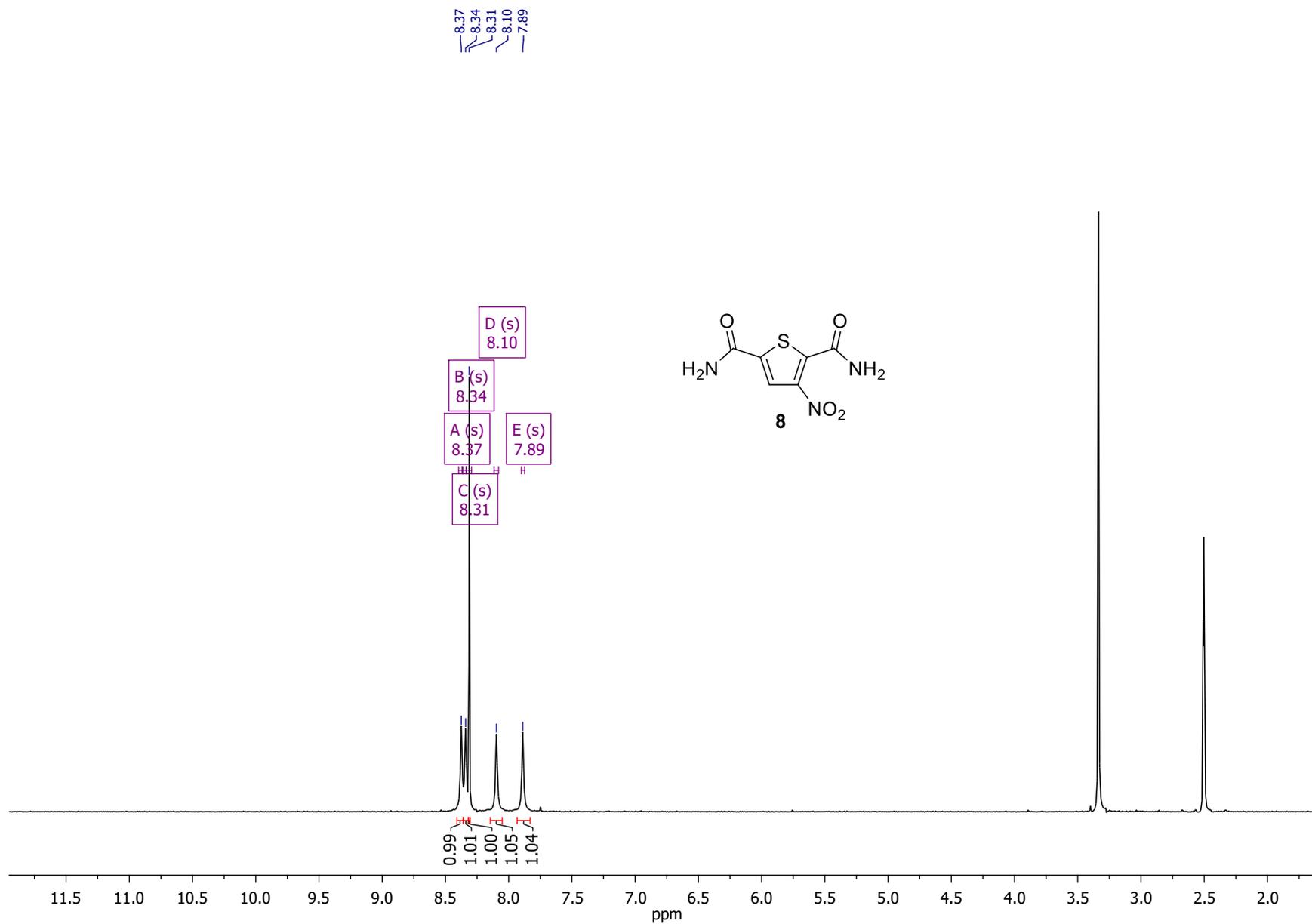
\*Email: [irgashev\\_ra@mail.ru](mailto:irgashev_ra@mail.ru), [irgashev@ios.uran.ru](mailto:irgashev@ios.uran.ru)

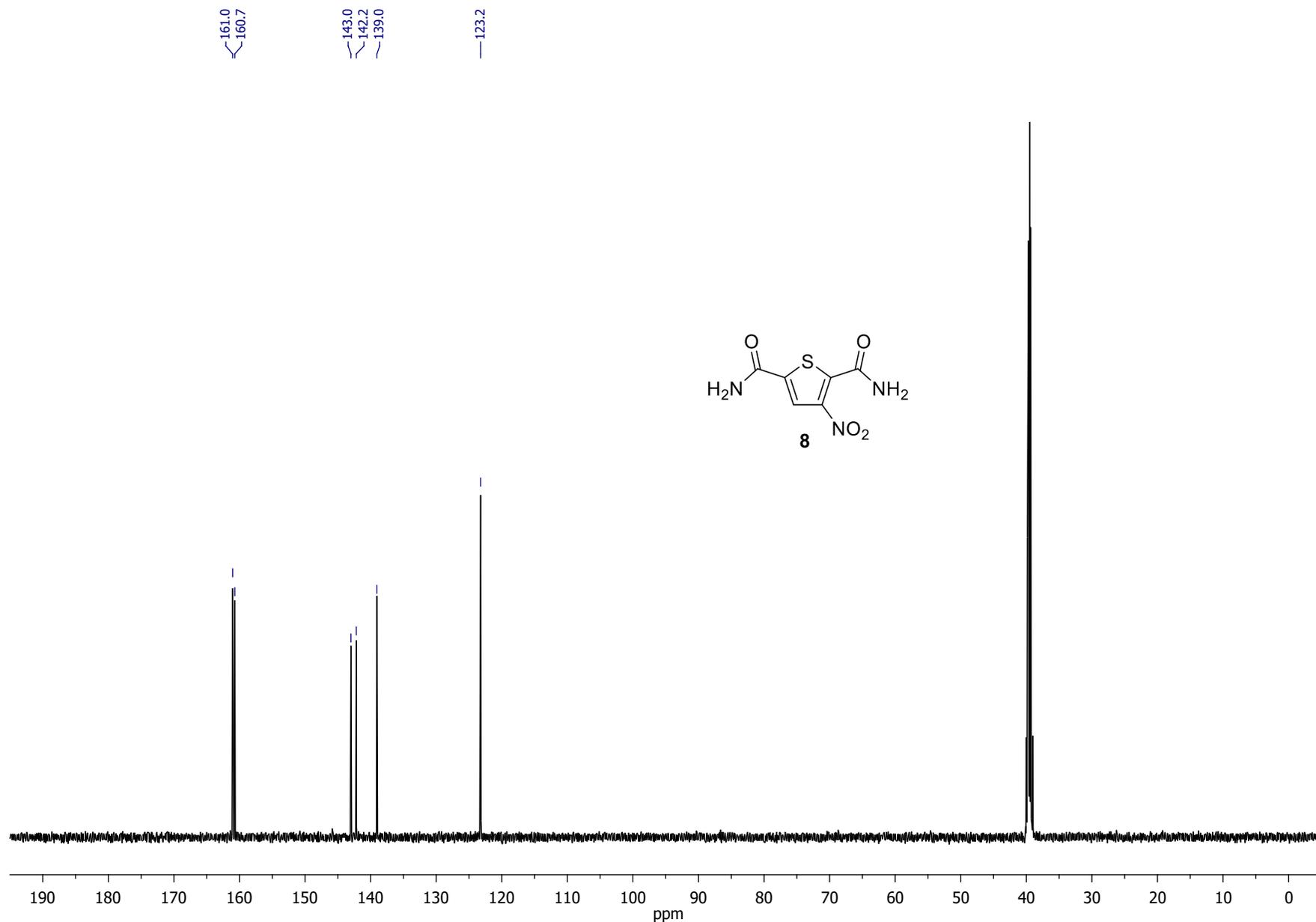
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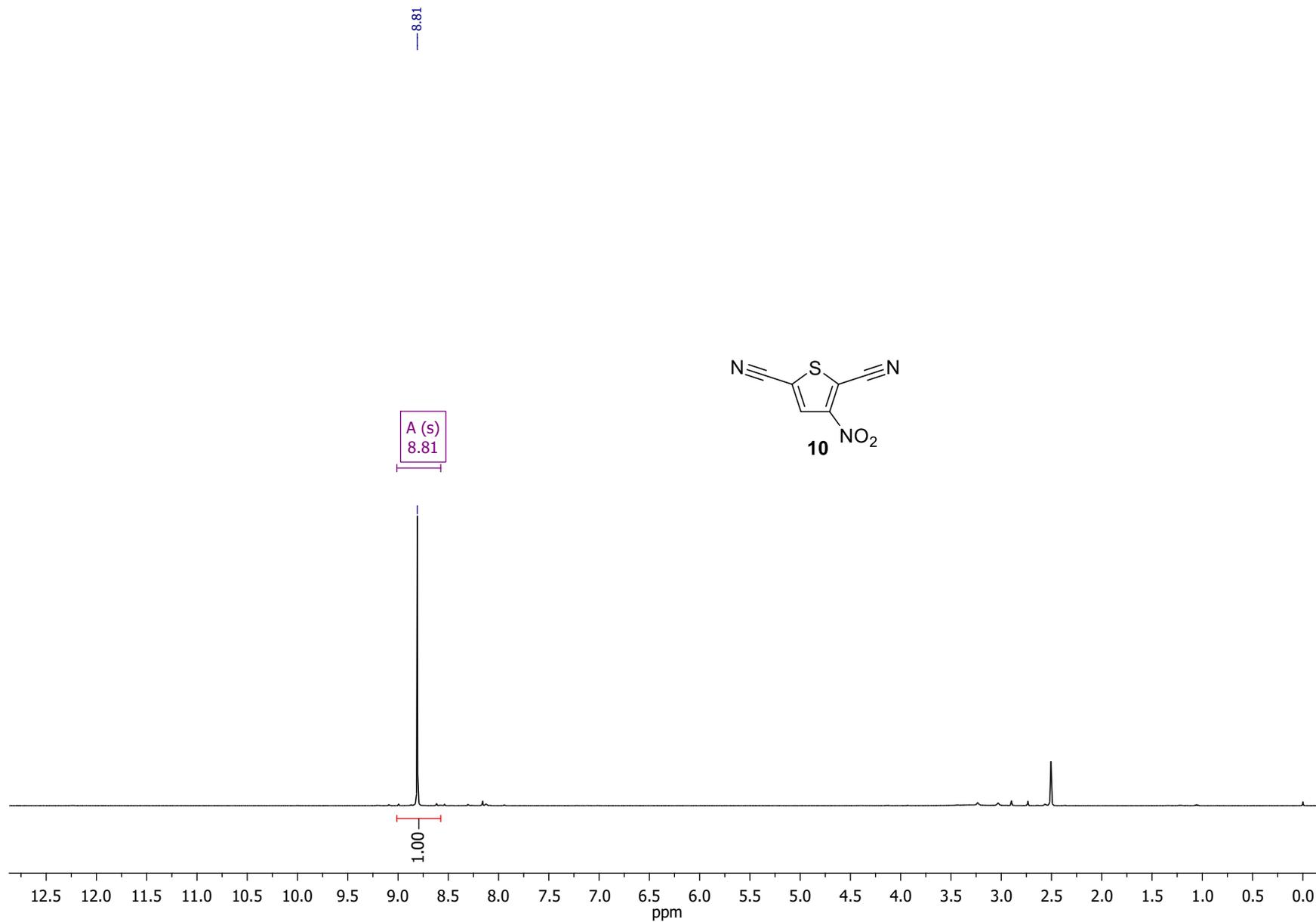
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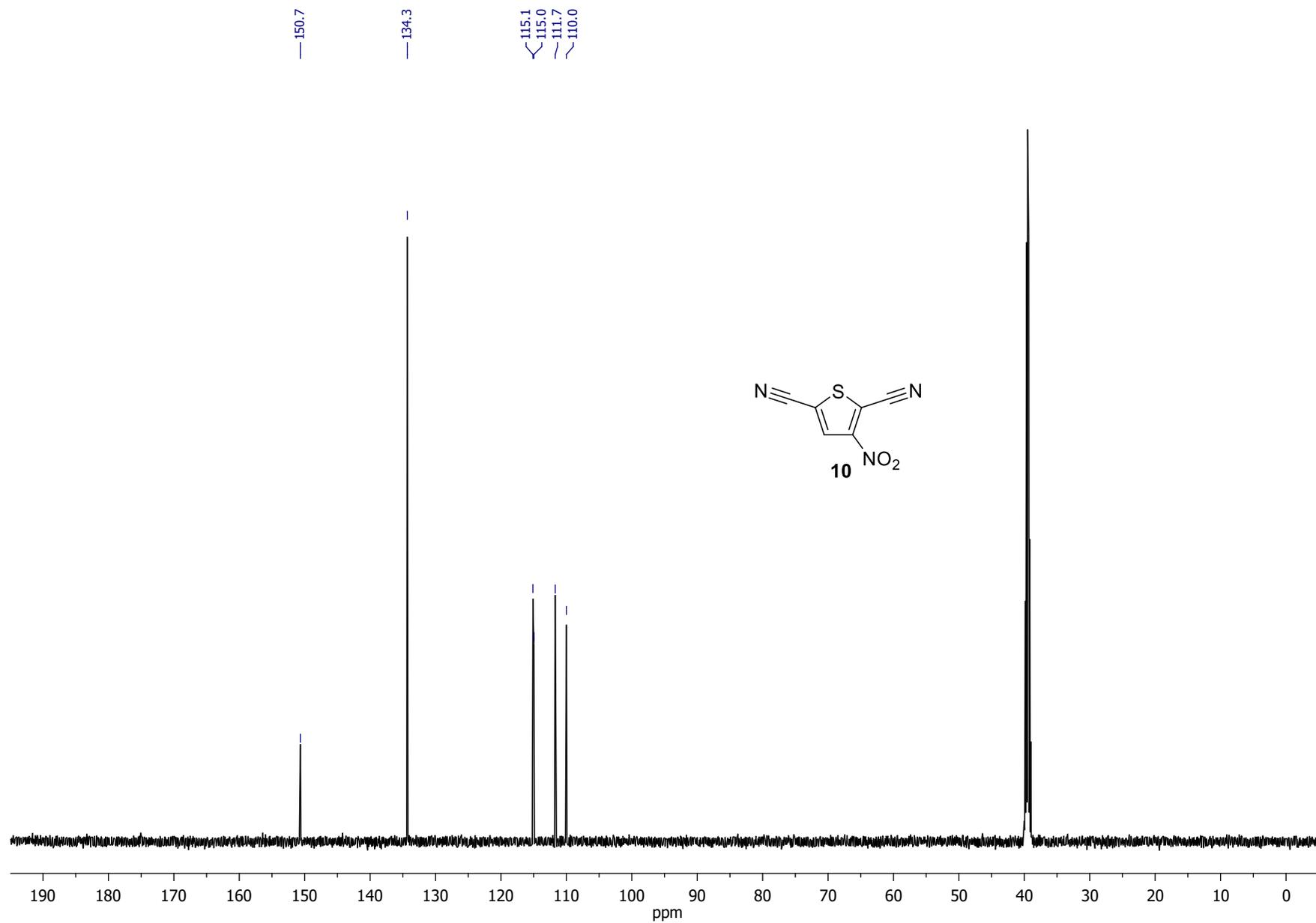
**6-Oxo-5,6-dihydrothieno[3,2-*b*]thiophene-2-carboxylic acid [6-hydroxythieno[3,2-*b*]thiophene-2-carboxylic acid] (3).** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

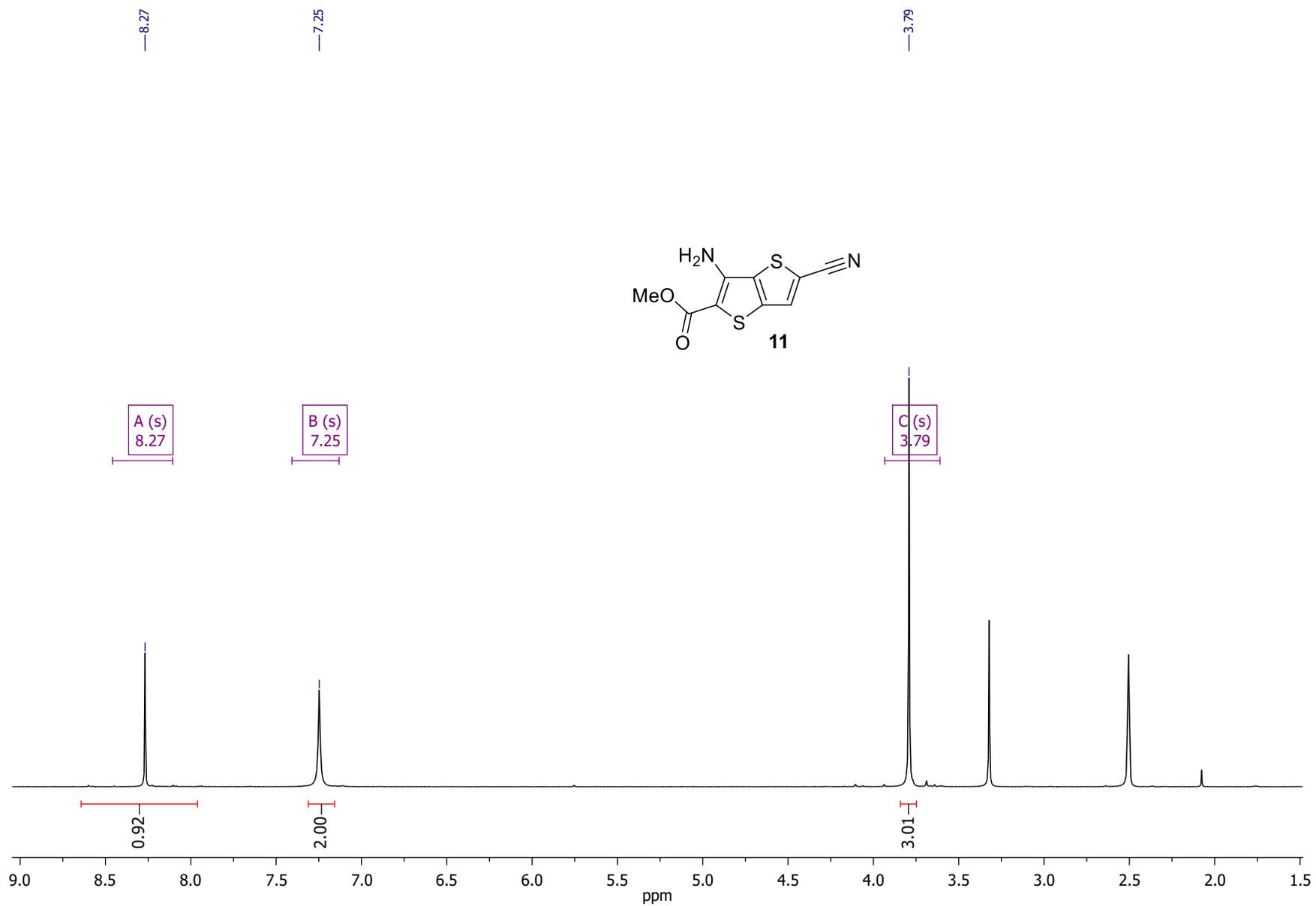
**6-Oxo-5,6-dihydrothieno[3,2-*b*]thiophene-2-carboxylic acid [6-hydroxythieno[3,2-*b*]thiophene-2-carboxylic acid] (3).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

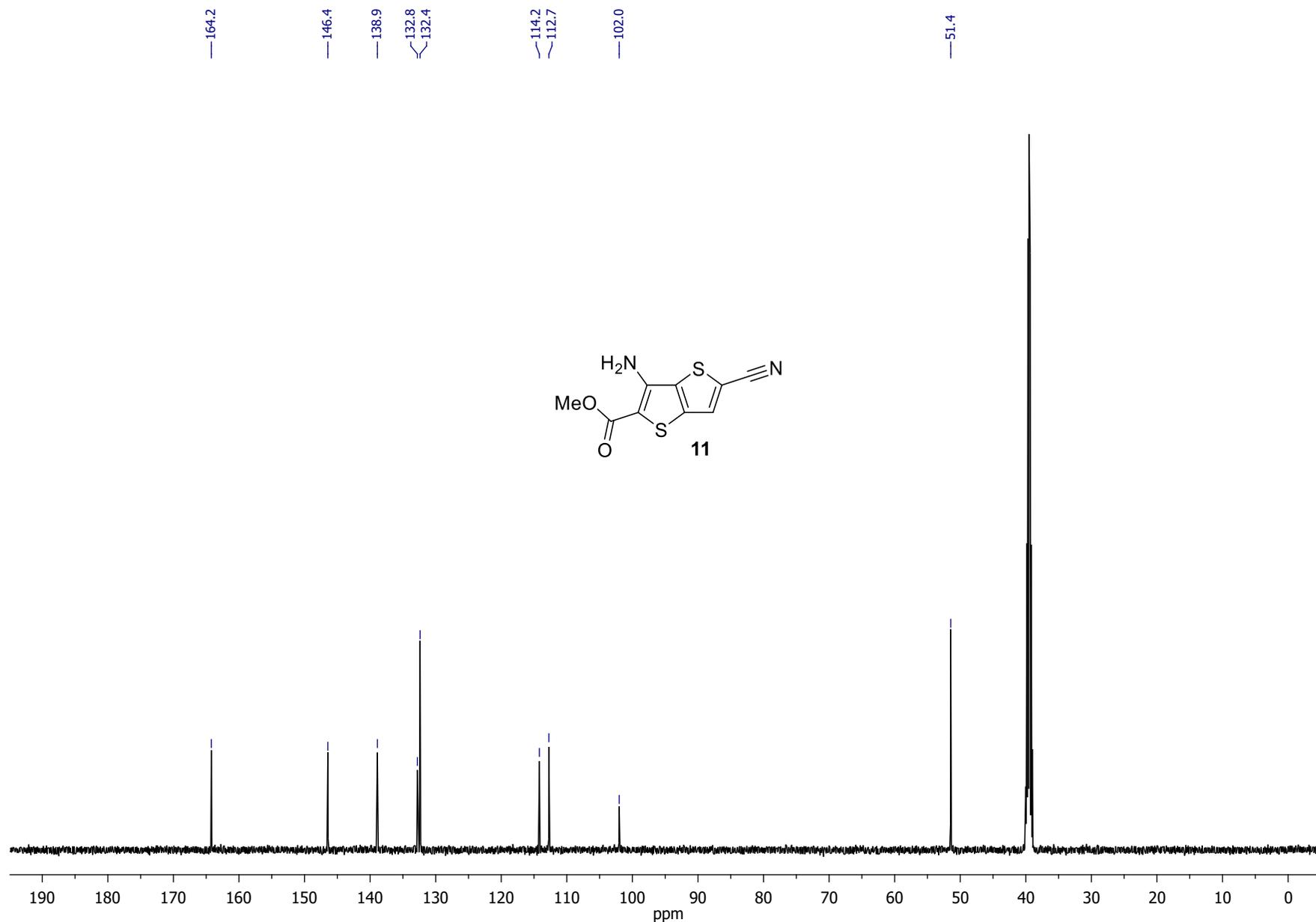
**3-Nitrothiophene-2,5-dicarboxamide (8).**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )

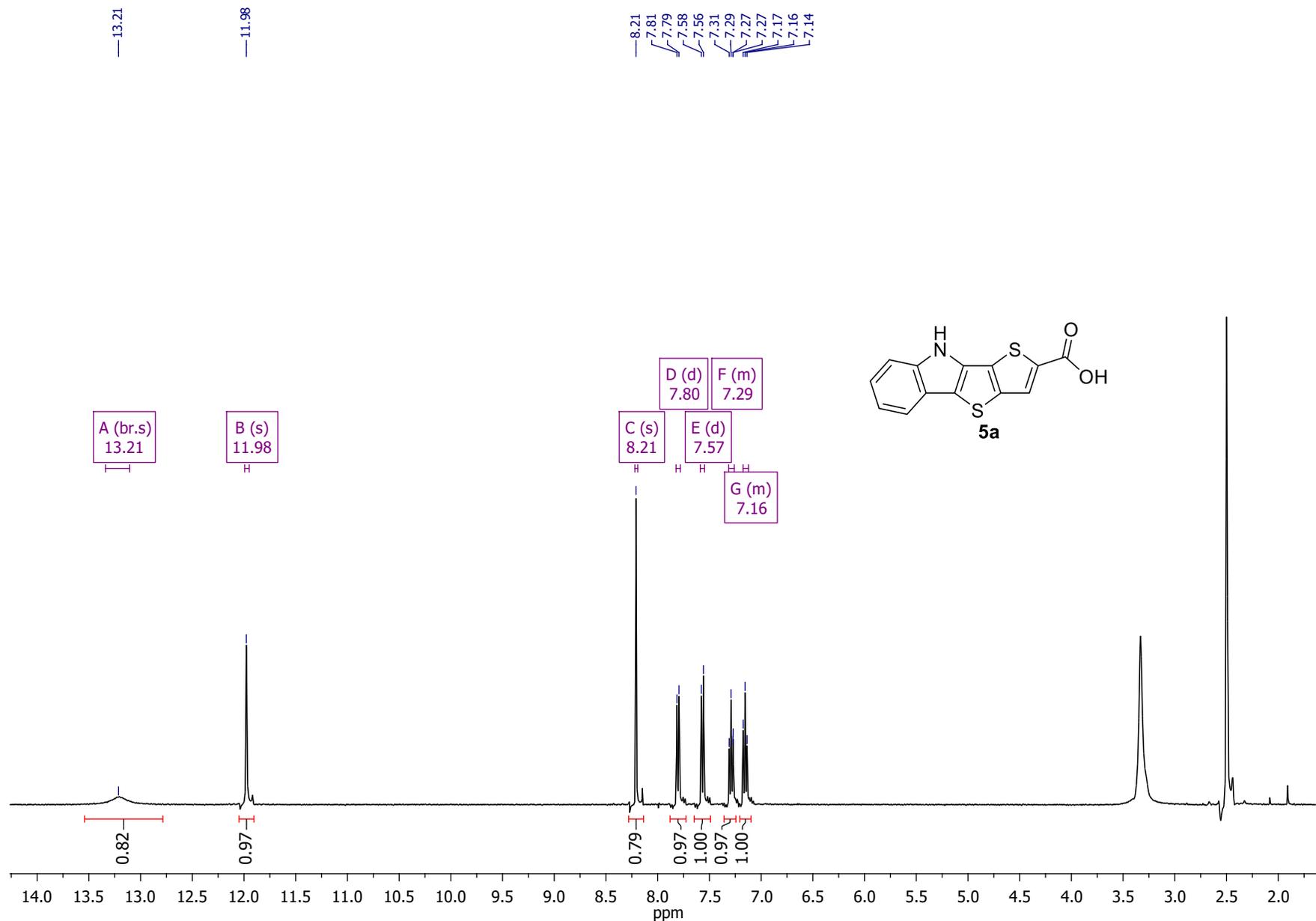
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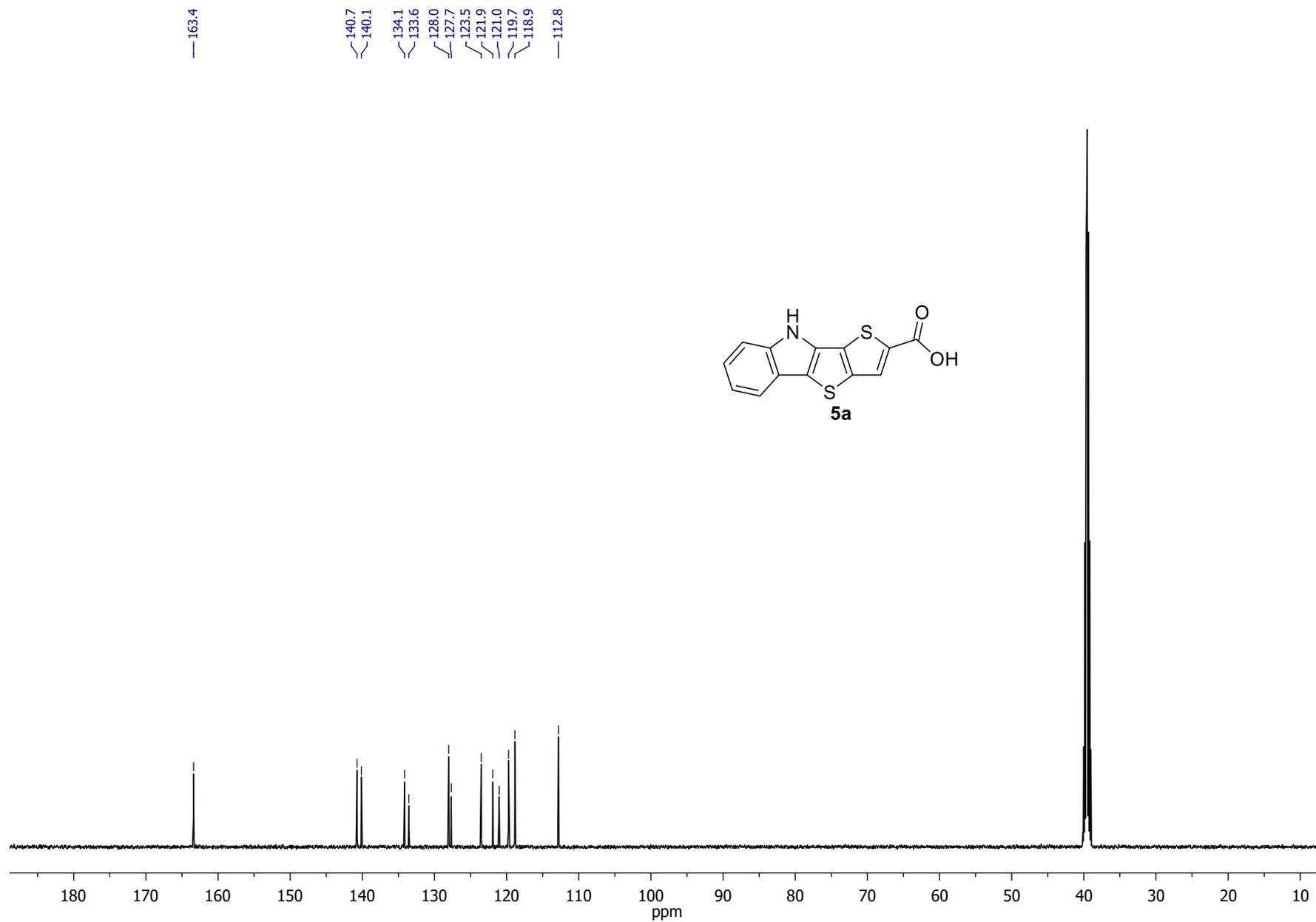
**3-Nitrothiophene-2,5-dicarbonitrile (10).**  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )

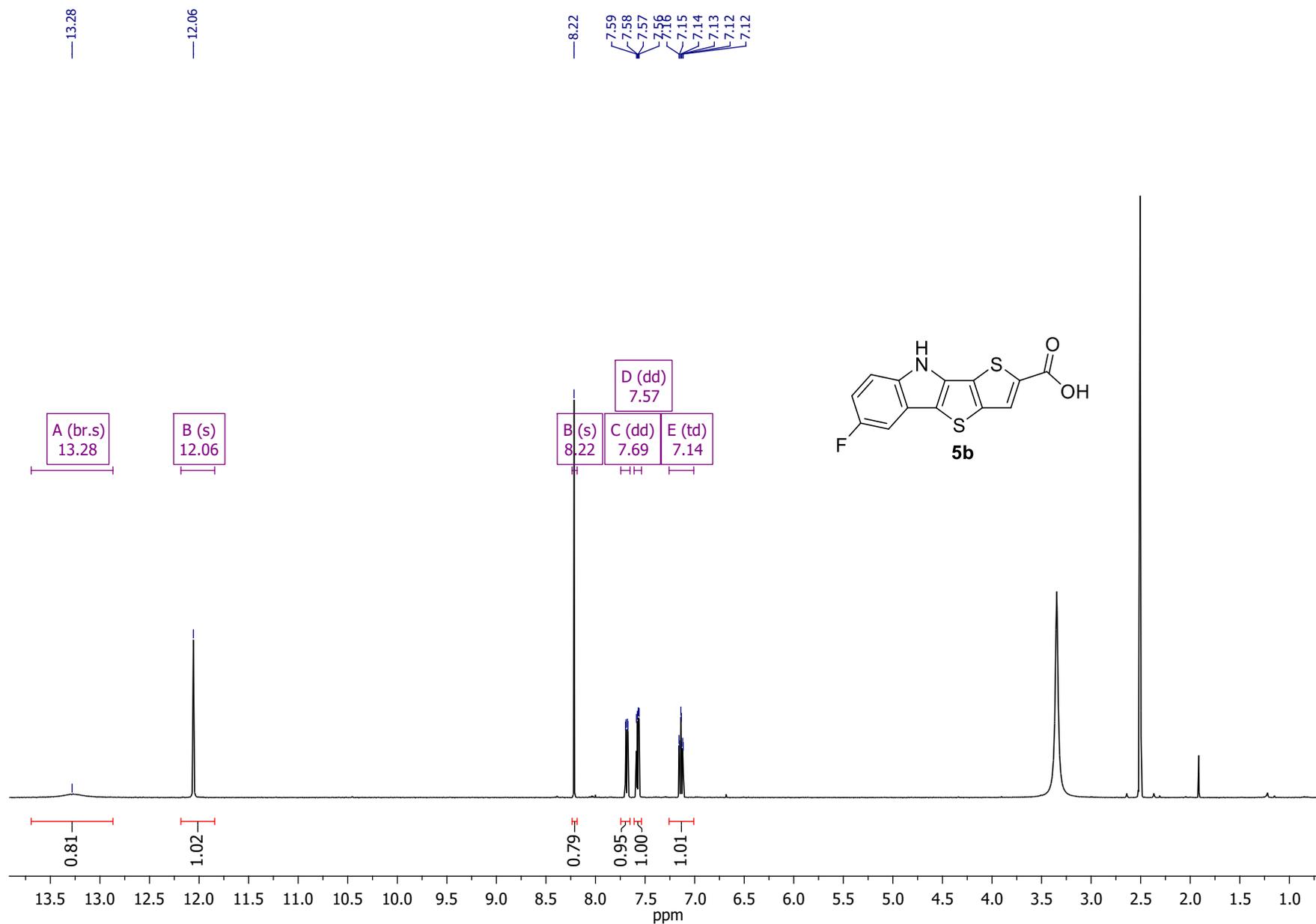
**3-Nitrothiophene-2,5-dicarbonitrile (10).**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

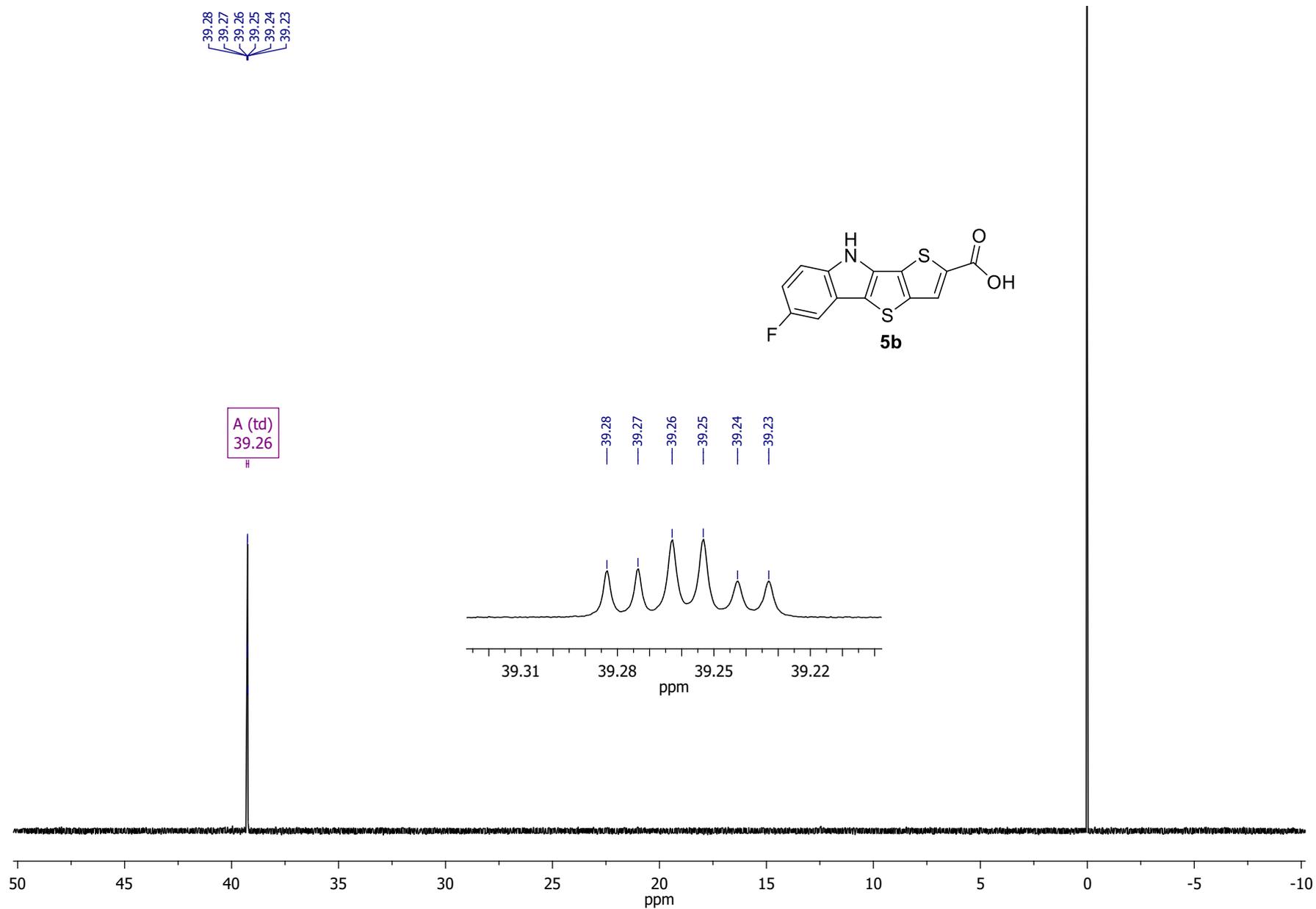
Methyl 3-amino-5-cyanothieno[3,2-*b*]thiophene-2-carboxylate (**11**).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )

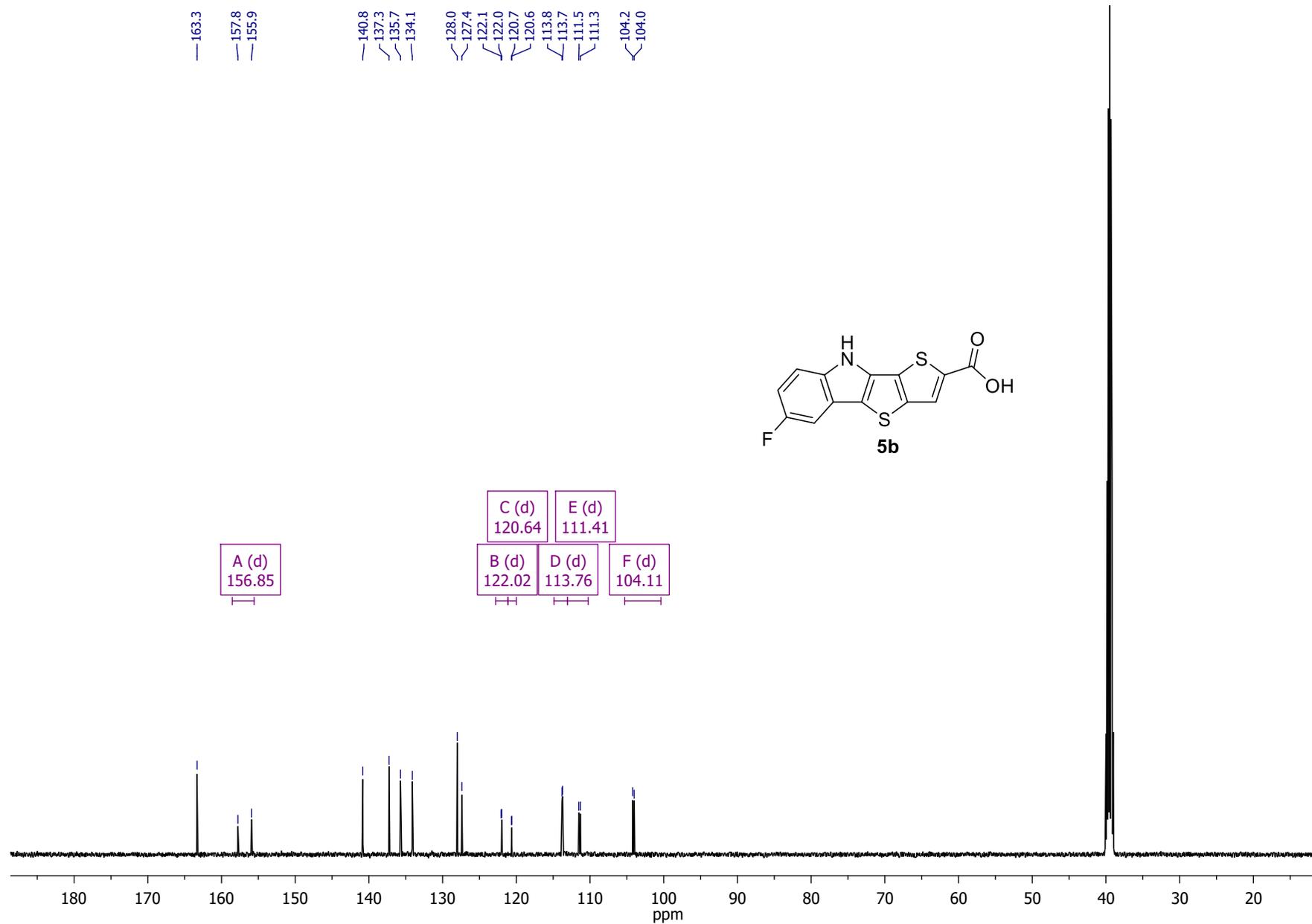
Methyl 3-amino-5-cyanothieno[3,2-*b*]thiophene-2-carboxylate (**11**).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

**9H-Thieno[2',3':4,5]thieno[3,2-b]indole-2-carboxylic acid (5a).** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

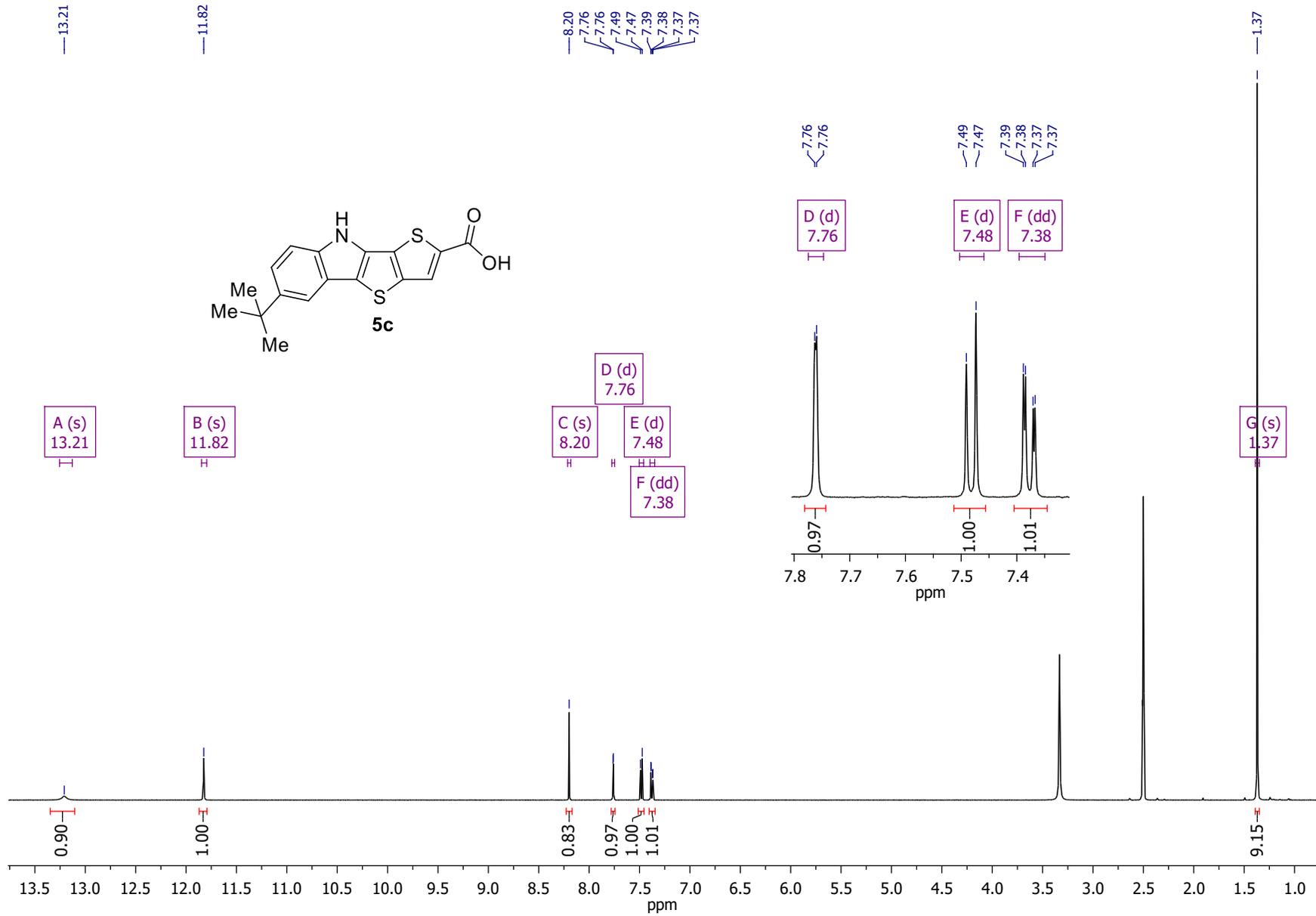
**9H-Thieno[2',3':4,5]thieno[3,2-b]indole-2-carboxylic acid (5a).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

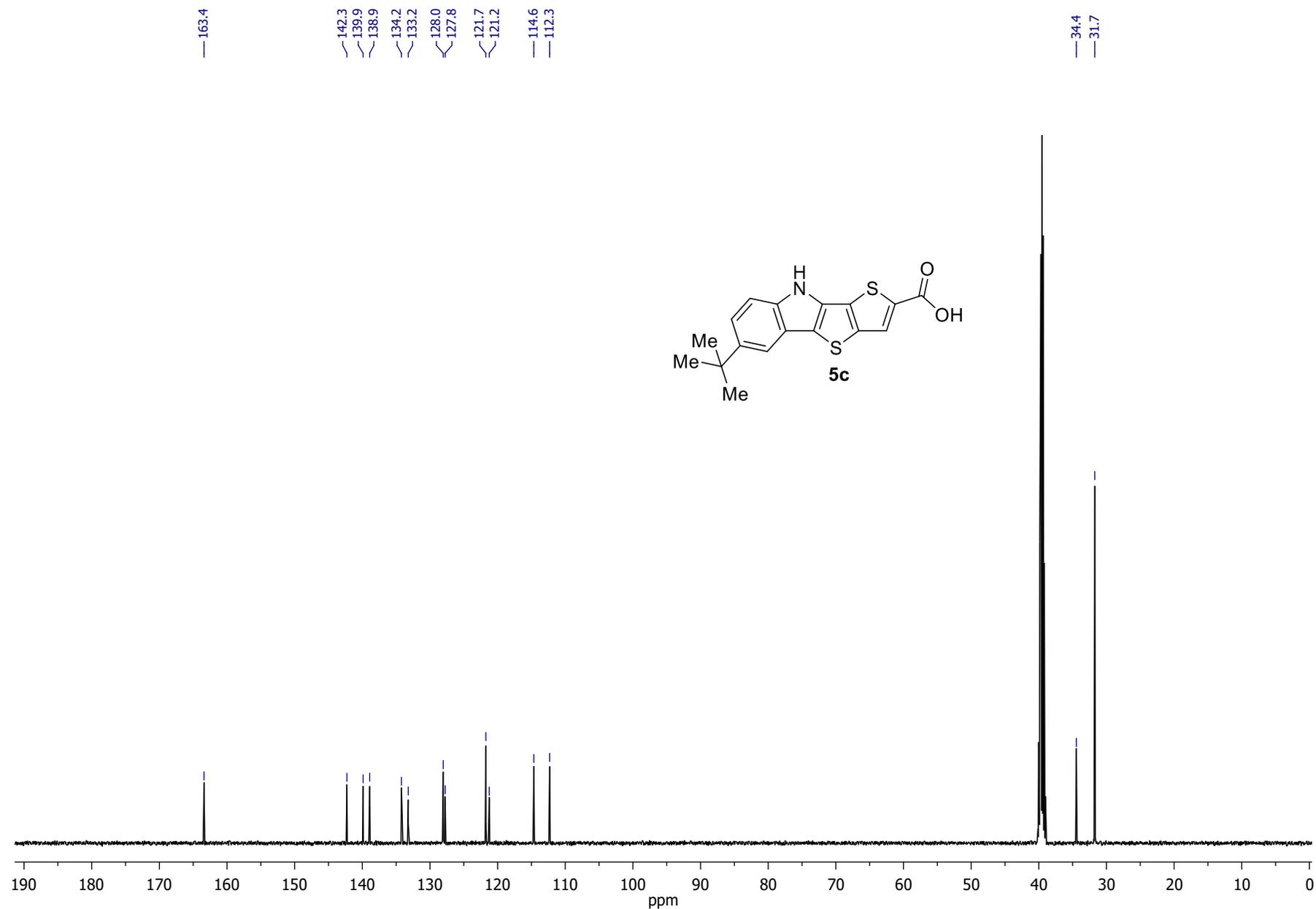
**6-Fluoro-9H-thieno[2',3':4,5]thieno[3,2-b]indole-2-carboxylic acid (5b).**  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )

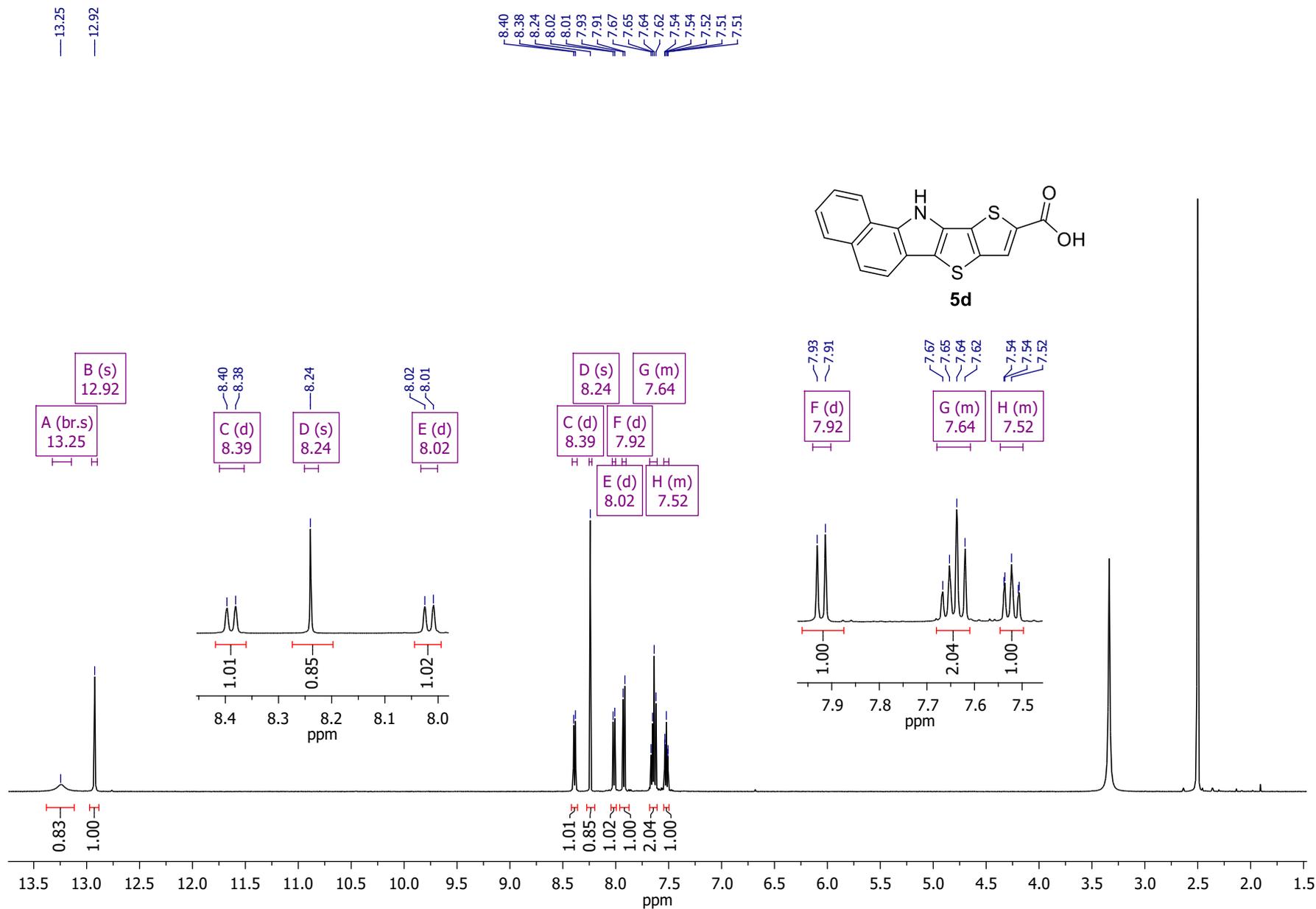
6-Fluoro-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (**5b**).  $^{19}\text{F}$  NMR (471 MHz,  $\text{DMSO-}d_6$ )

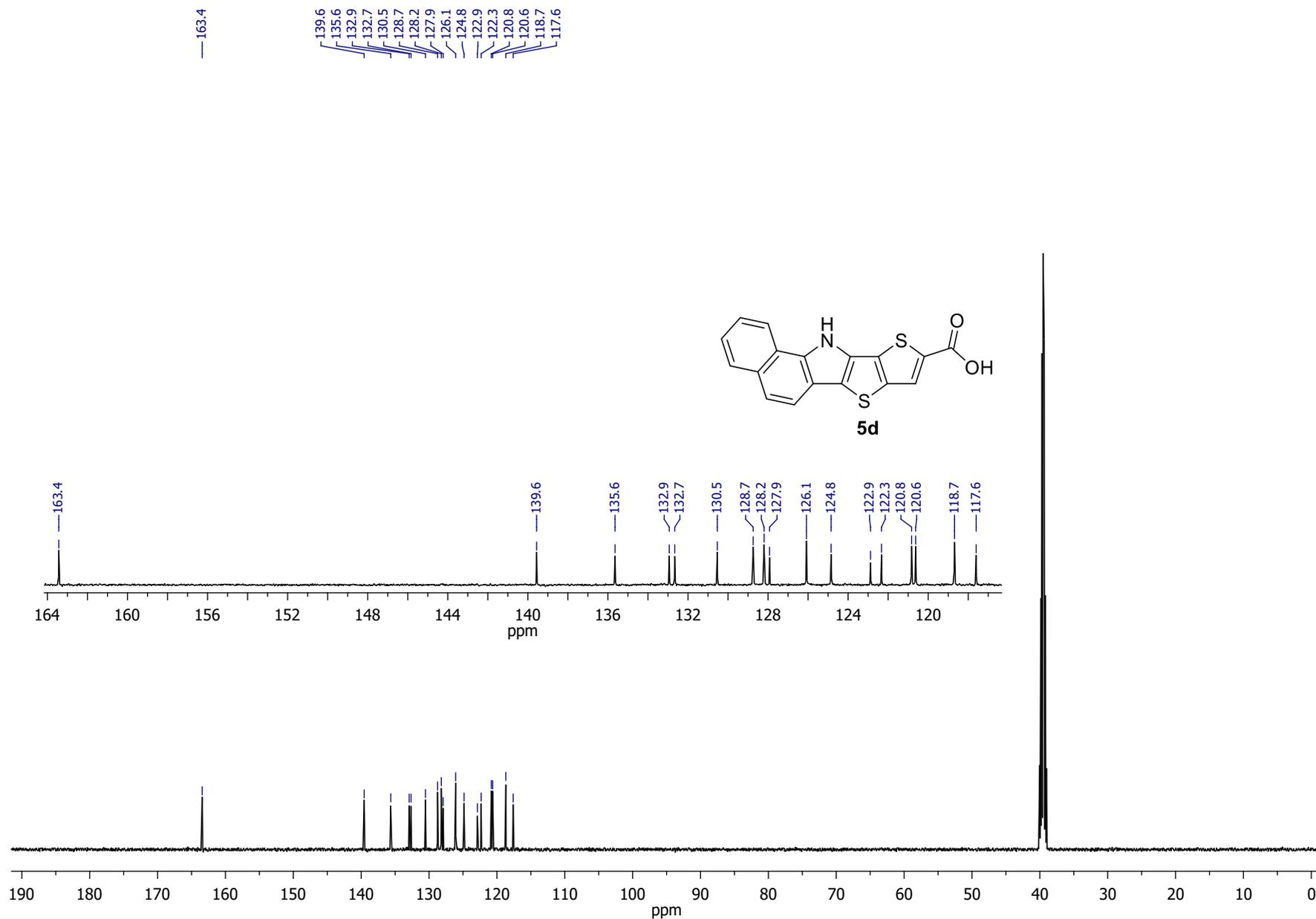
**6-Fluoro-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (5b).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

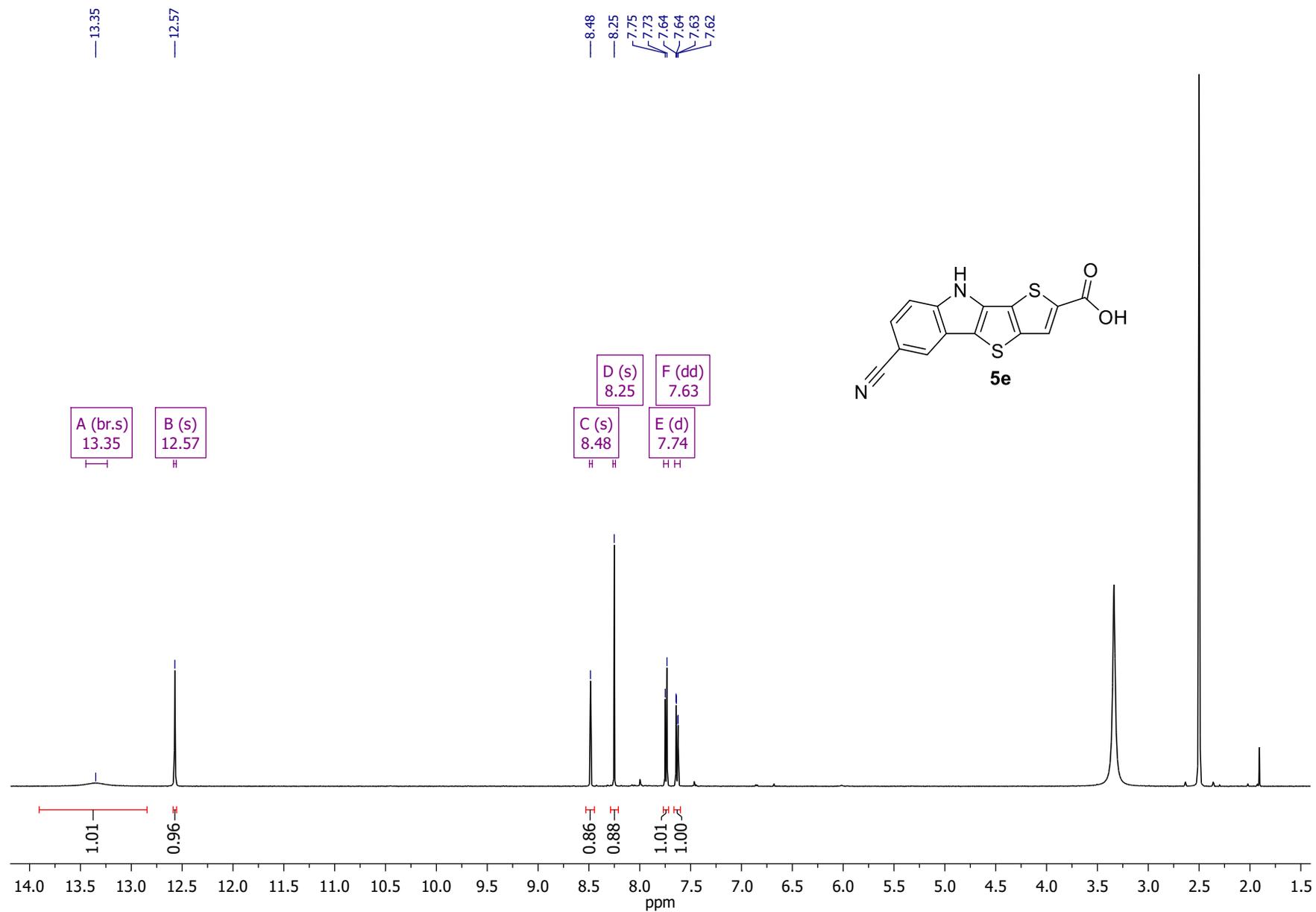
6-(*tert*-Butyl)-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (**5c**). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

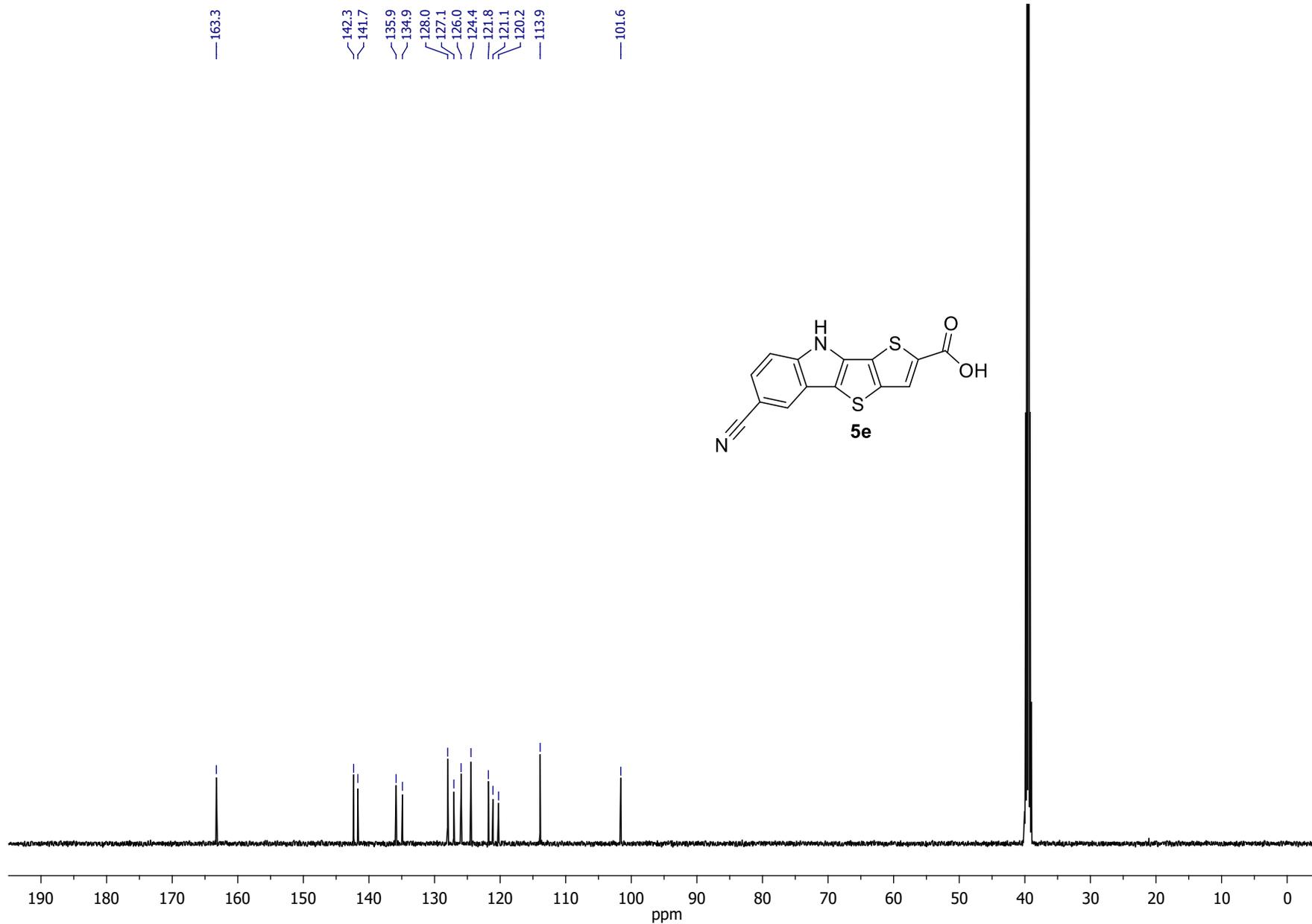


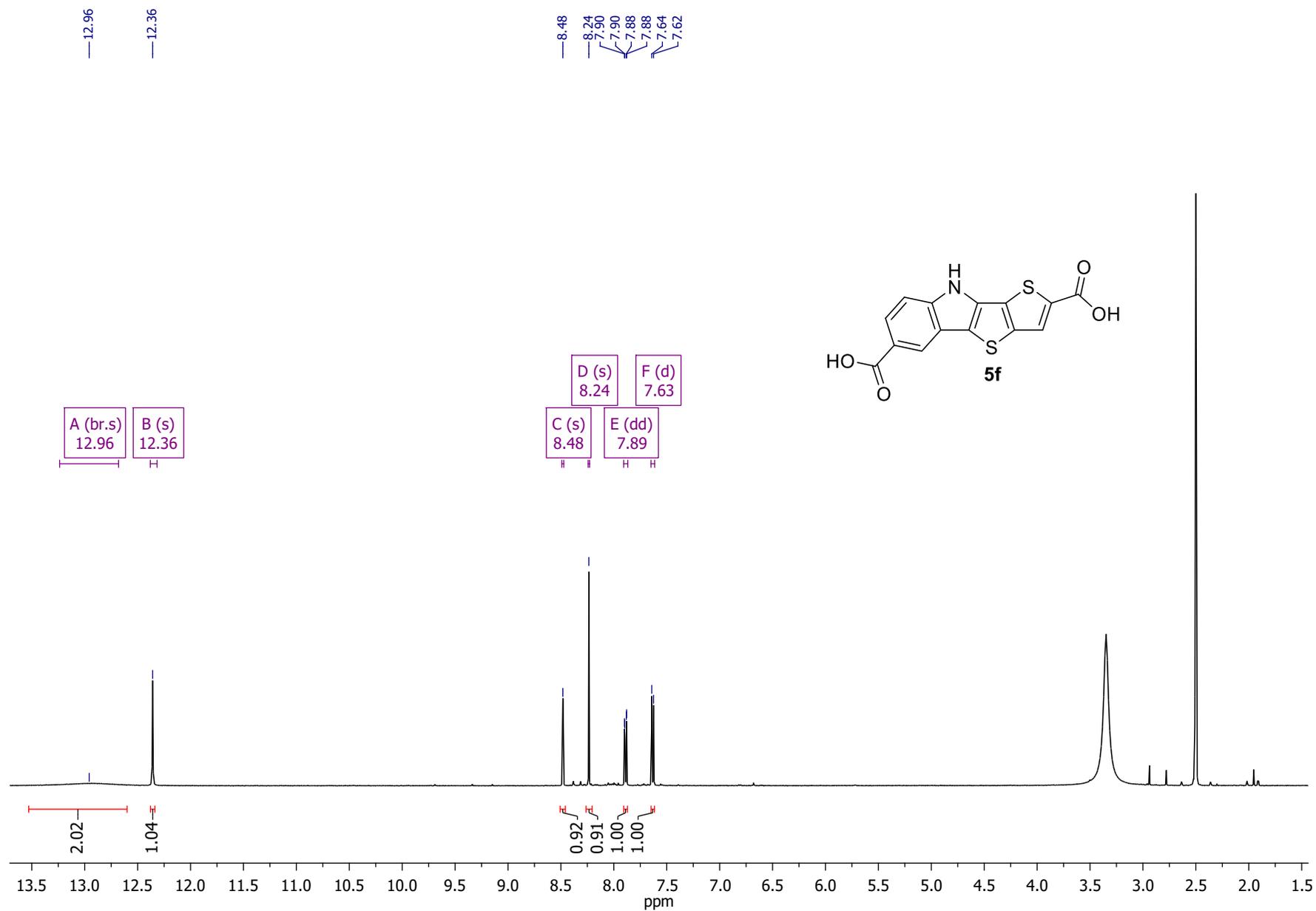
6-(*tert*-Butyl)-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (**5c**).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

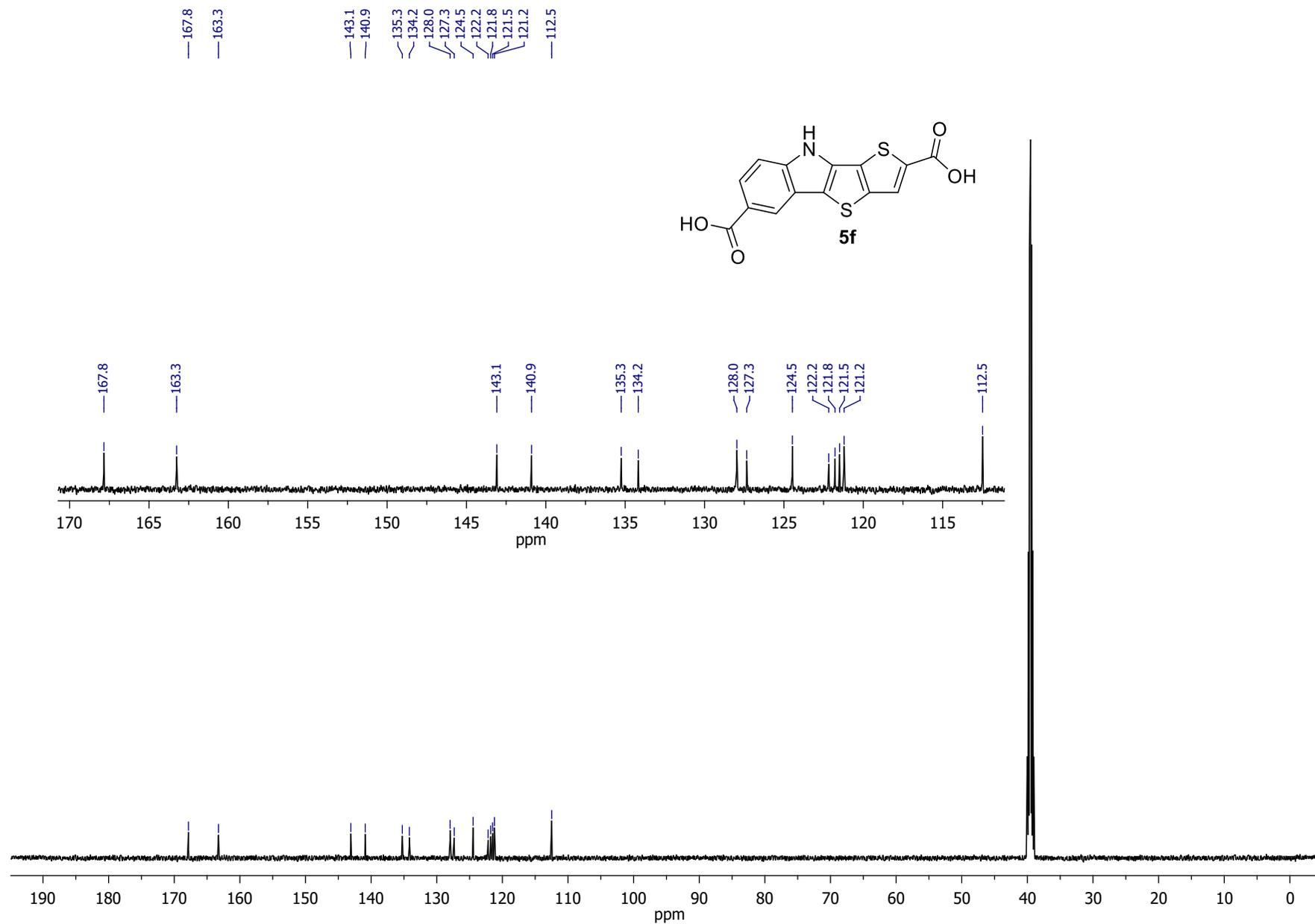
**11H-Benzo[g]thieno[2',3':4,5]thieno[3,2-b]indole-9-carboxylic acid (5d).** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

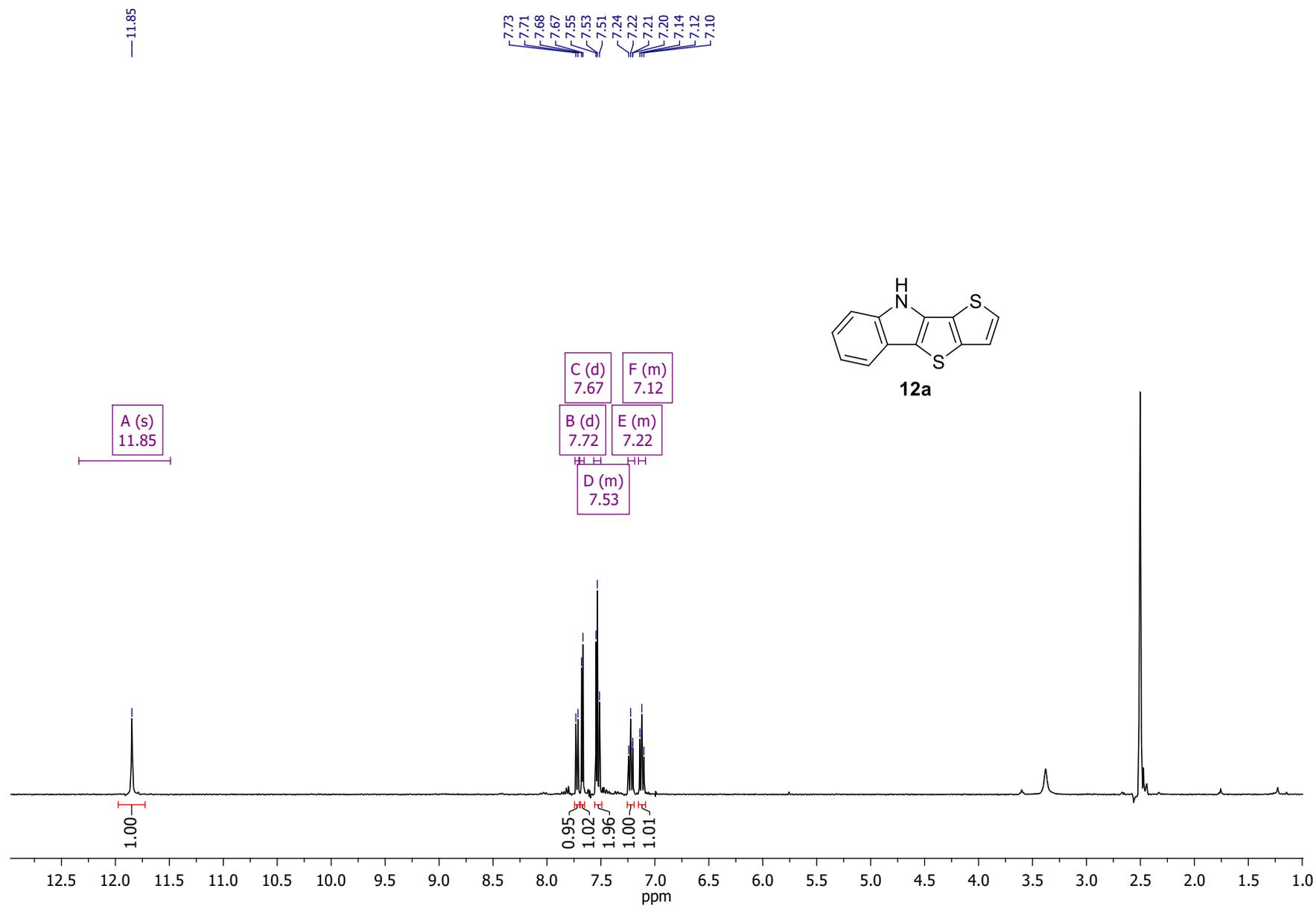
**11H-Benzo[g]thieno[2',3':4,5]thieno[3,2-b]indole-9-carboxylic acid (5d).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

**6-Cyano-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (5e).** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

**6-Cyano-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole-2-carboxylic acid (5e).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

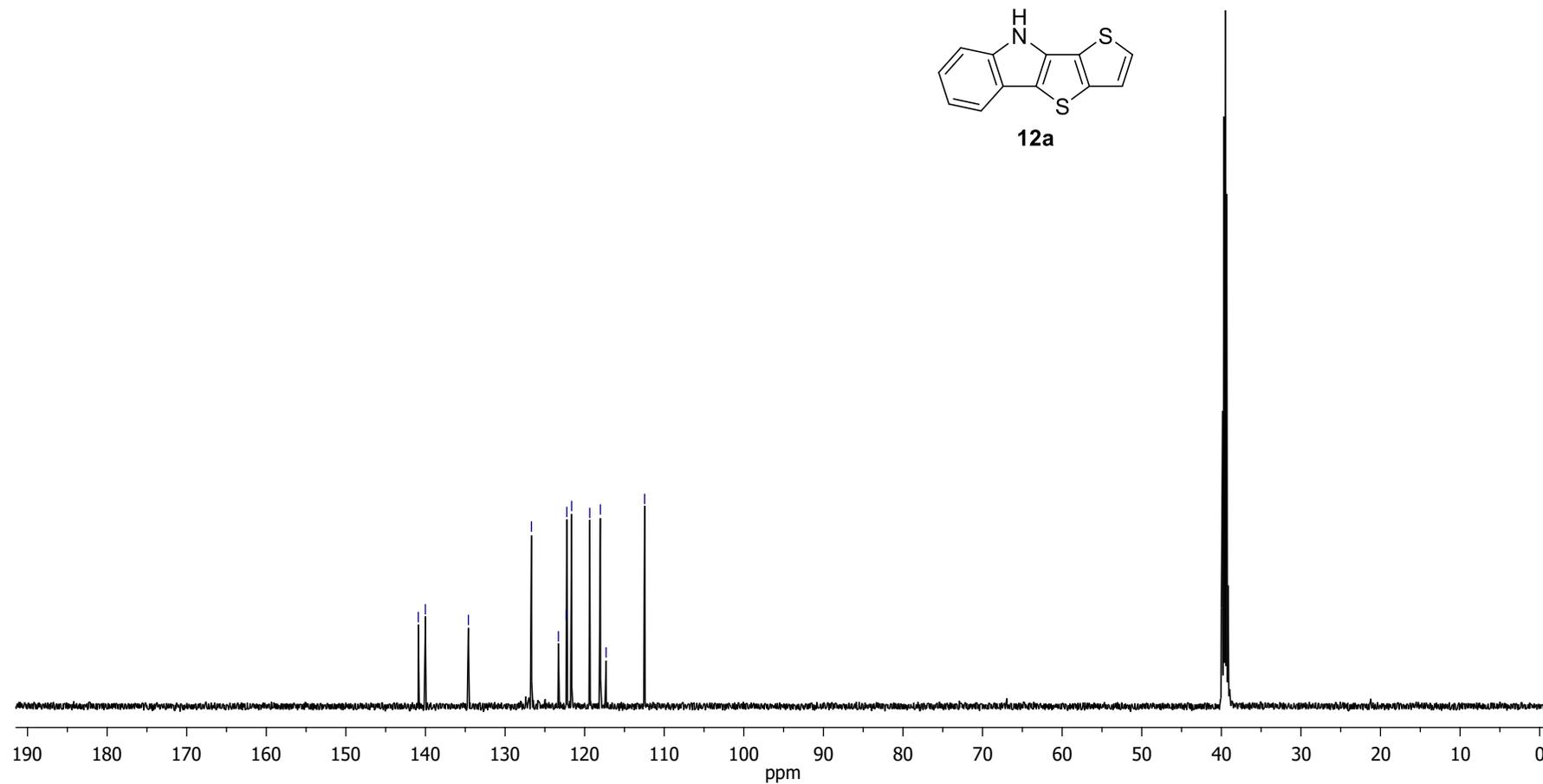
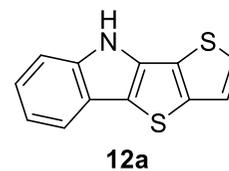
**9H-Thieno[2',3':4,5]thieno[3,2-b]indole-2,6-dicarboxylic acid (5f).** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)

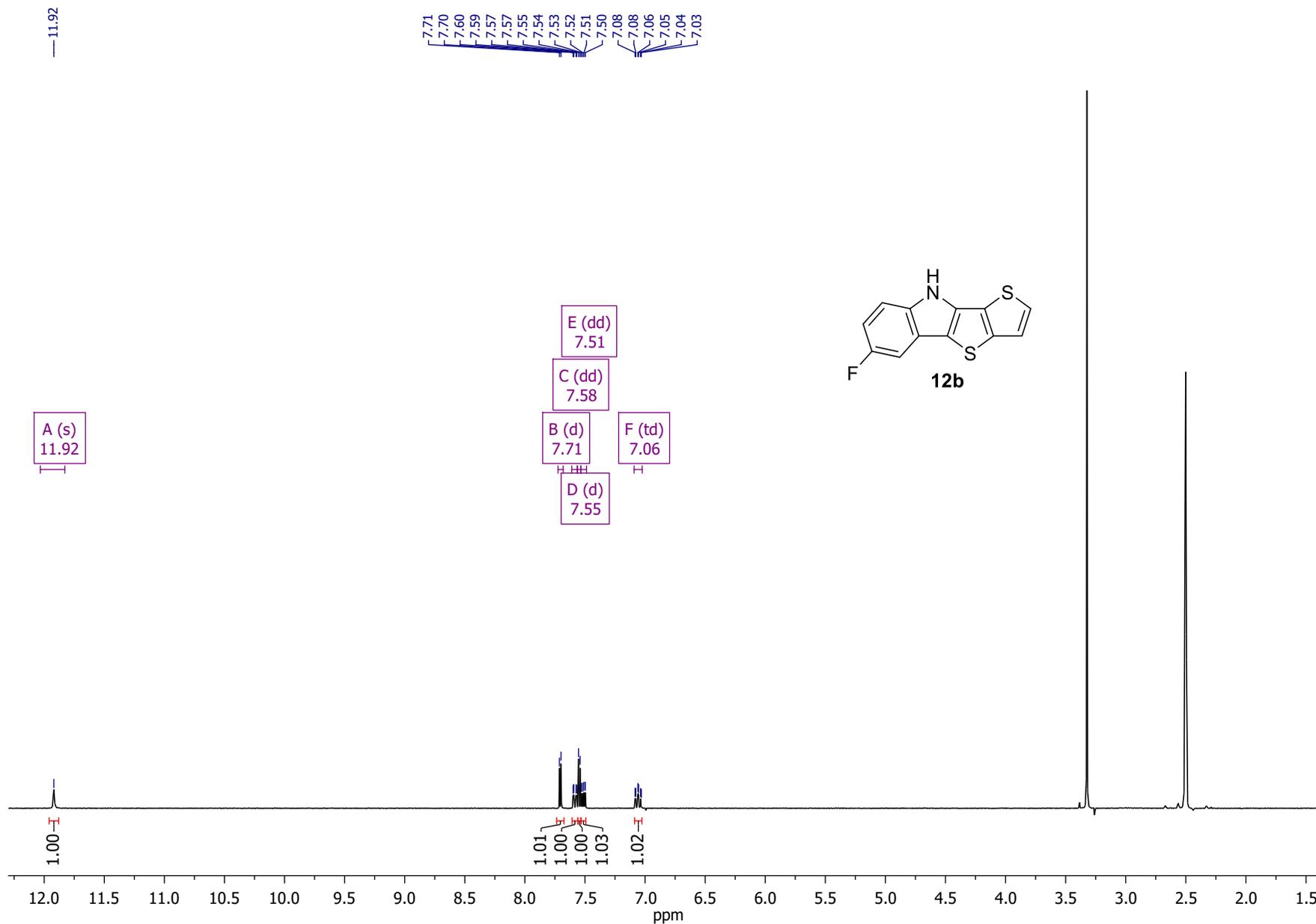
**9H-Thieno[2',3':4,5]thieno[3,2-b]indole-2,6-dicarboxylic acid (5f).**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

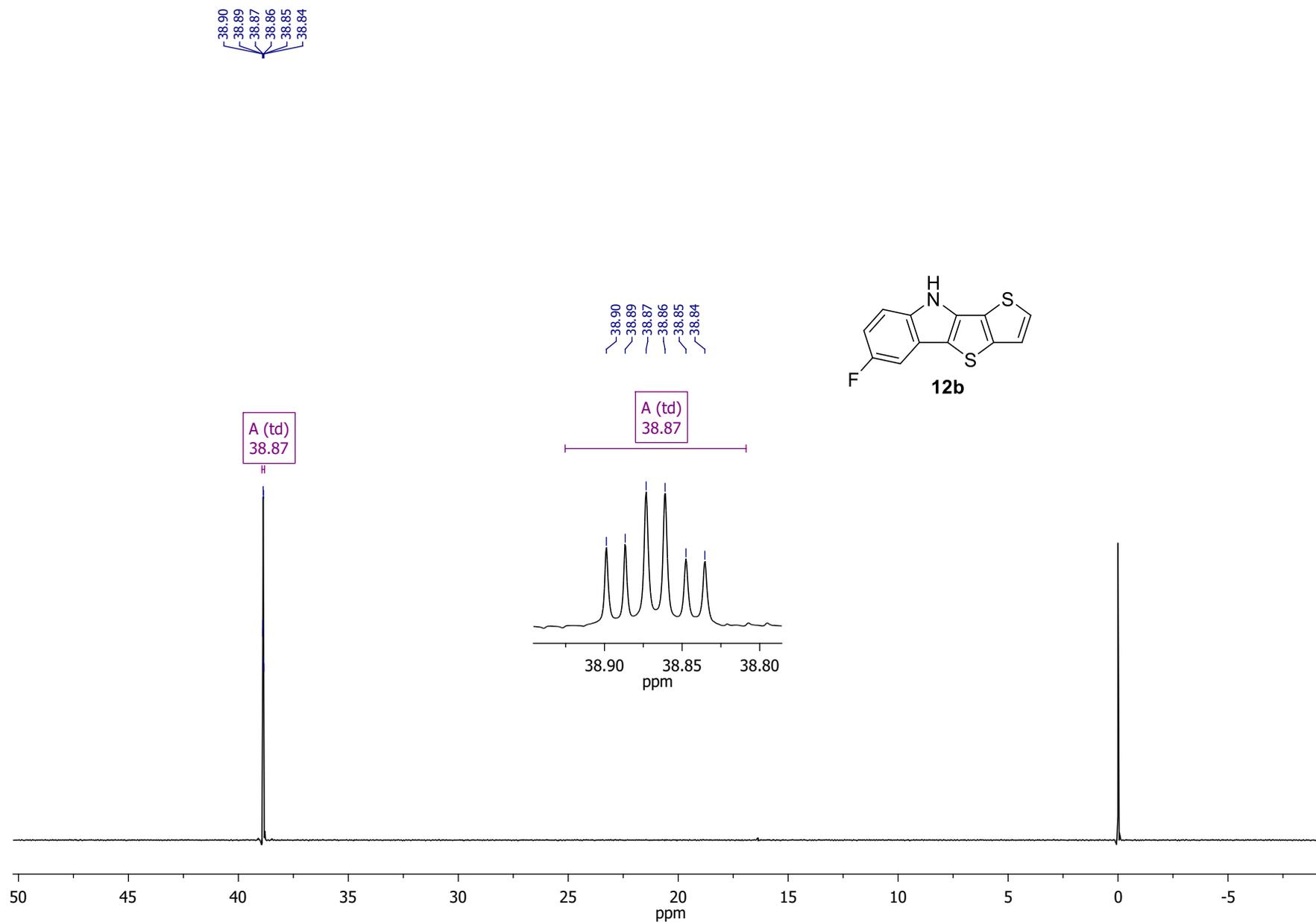
**9H-Thieno[2',3':4,5]thieno[3,2-b]indole (12a).**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )

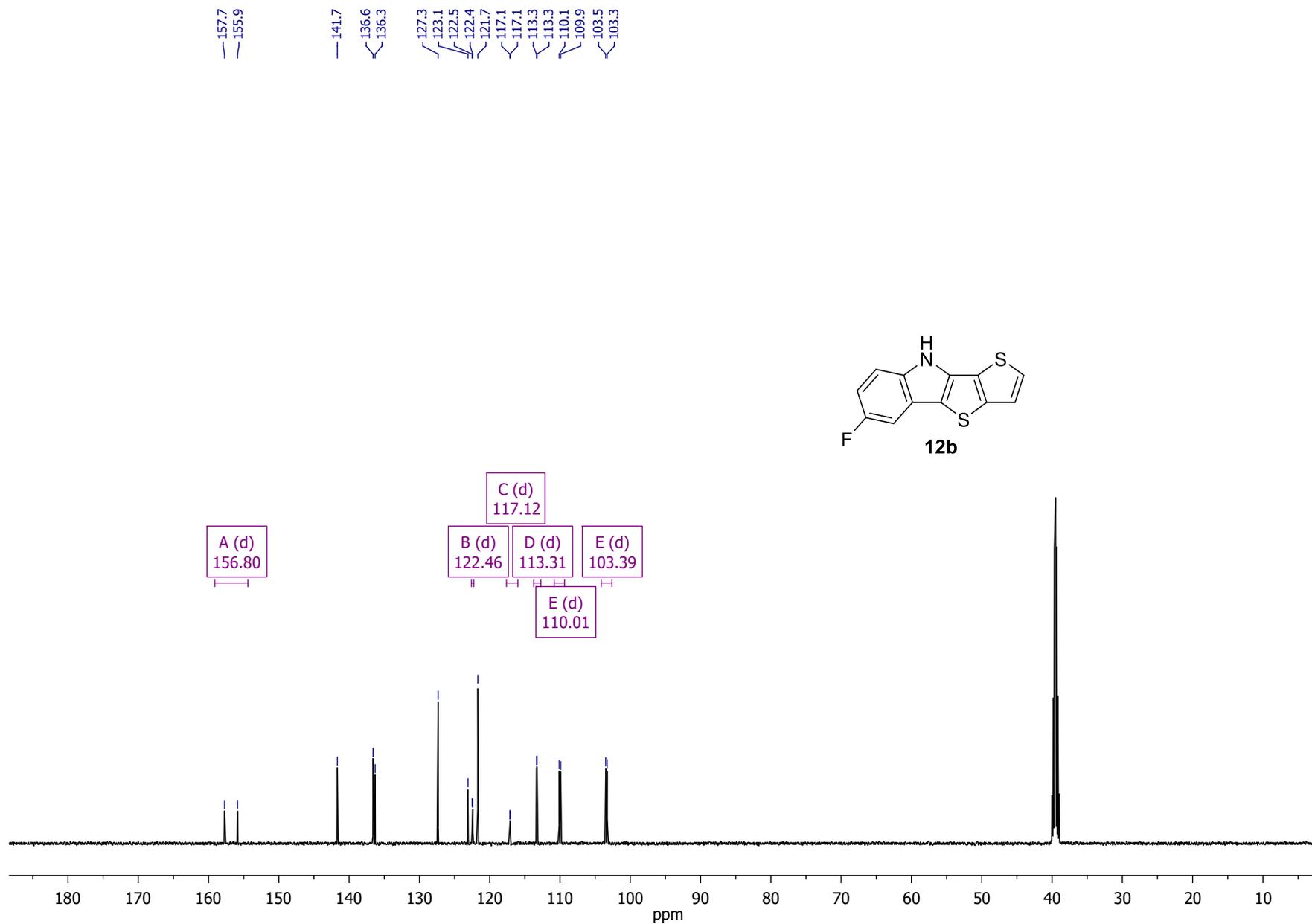
**9H-Thieno[2',3':4,5]thieno[3,2-b]indole (12a).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

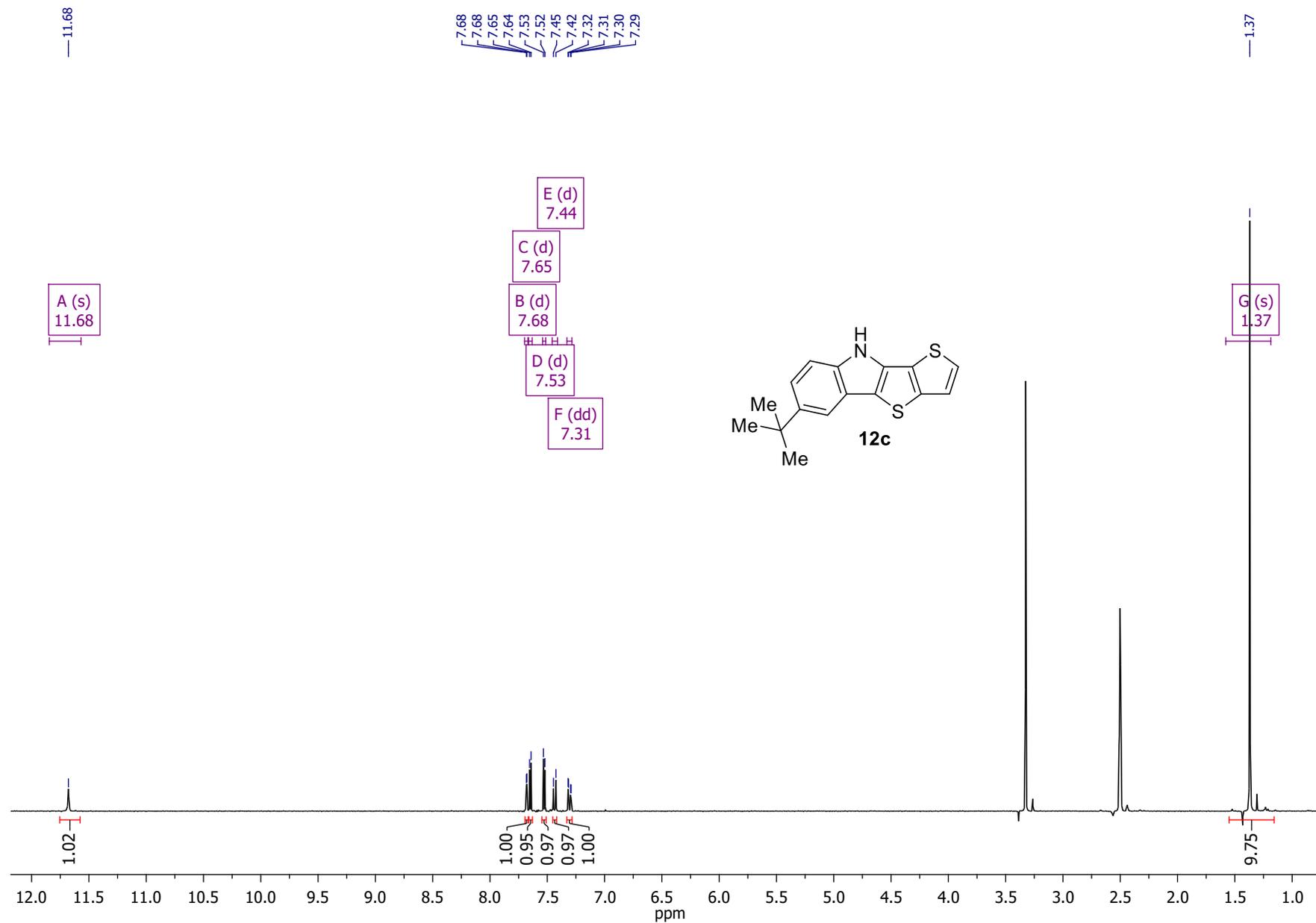
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140.0  
134.6  
126.7  
123.3  
122.3  
122.2  
121.6  
119.4  
118.0  
117.3  
112.5

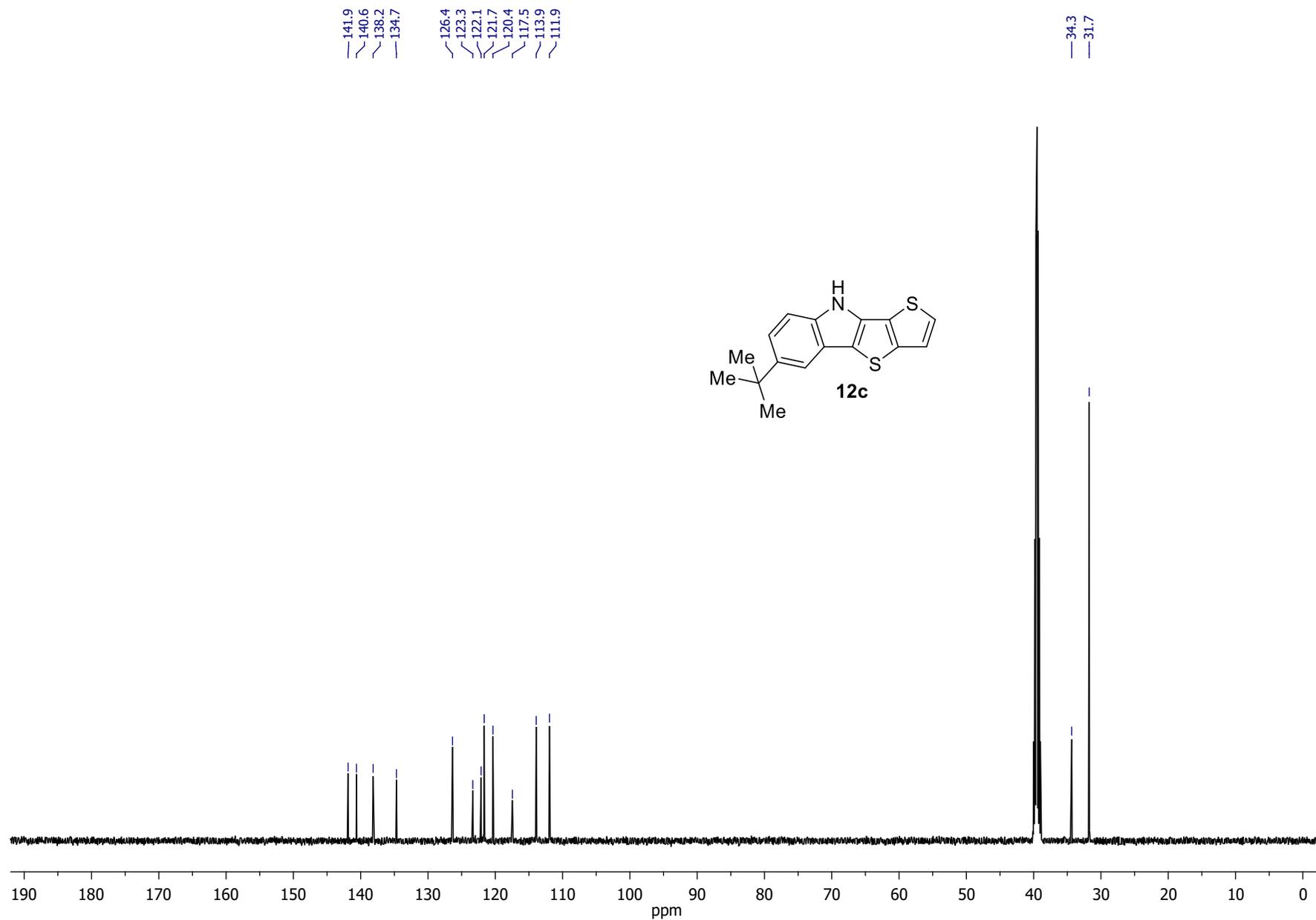


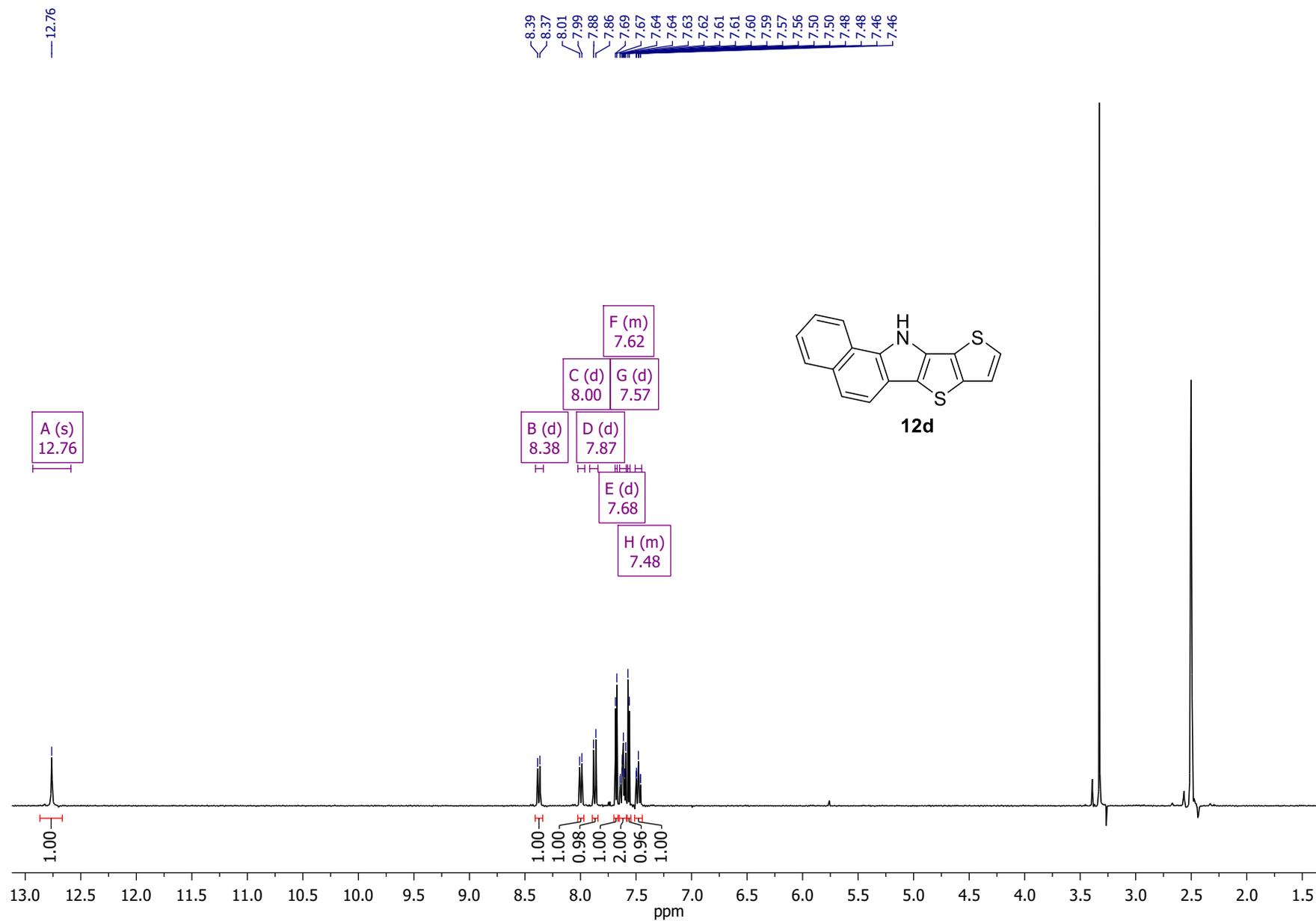
6-Fluoro-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12b). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)

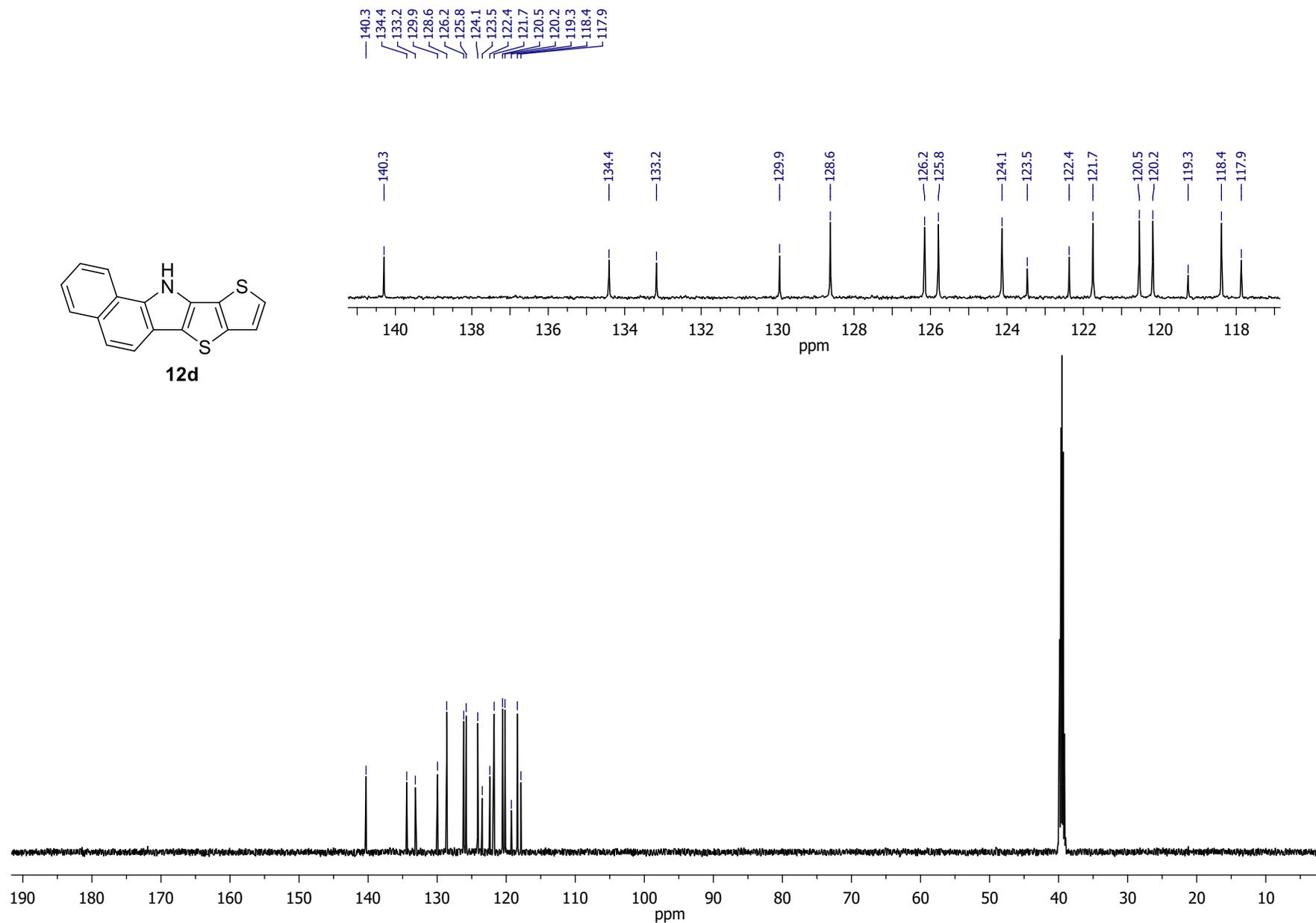
**6-Fluoro-9H-thieno[2',3':4,5]thieno[3,2-b]indole (12b).**  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )

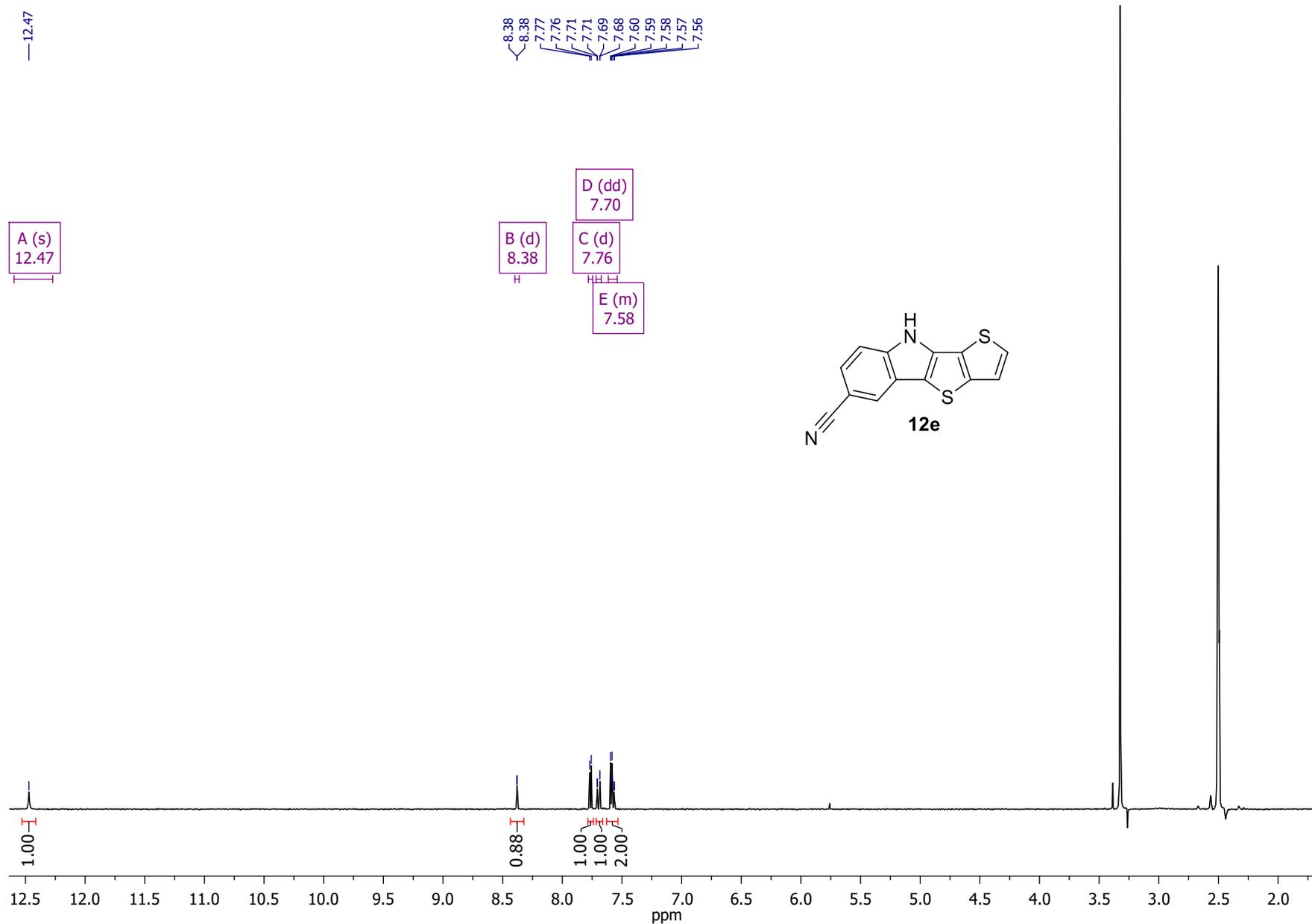
**6-Fluoro-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12b).**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

**6-(*tert*-Butyl)-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12c).**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )

**6-(*tert*-Butyl)-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12c).**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )

**11H-Benzo[g]thieno[2',3':4,5]thieno[3,2-b]indole (12d).**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )

**11H-Benzo[*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole (12d).**  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

6-Cyano-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12e). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)

**6-Cyano-9*H*-thieno[2',3':4,5]thieno[3,2-*b*]indole (12e).**  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )