

SUPPORTING INFORMATION

## ***cine*-Substitutions at 5-membered Hetarenes enabled by Sulfonium Salts**

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## MATERIALS AND METHODS

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 25–40 °C at an appropriate pressure. Purified compounds were further dried under vacuum ( $10^{-6}$  –  $10^{-3}$  bar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated. Reactions that require heating were performed in sealed glass vials placed inside an aluminium heating block, unless otherwise stated. Temperatures refer to the temperature of the aluminium heating block.

### Solvents

Dichloromethane, and methanol were purchased from *Sigma-Aldrich* and used as received. Anhydrous solvents were obtained from *Phoenix Solvent Drying Systems*. All deuterated solvents were purchased from *Euriso-Top*. Anhydrous acetonitrile- $d_3$  was dried by storage over molecular sieves. The term “hexanes” refers to a mixture of volatile saturated hydrocarbons, mostly 2-methylpentane.

### Chromatography

Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250  $\mu\text{m}$  thickness silica gel 60 F<sub>254</sub> plates and visualized by irradiation UV light or by dipping the TLC plate into a dilute, alkaline, aqueous  $\text{KMnO}_4$ -solution. Flash chromatography was performed on an *Isolera Four* from *Biotage* using silica gel (40–63  $\mu\text{m}$  particle size) purchased from *Geduran*.

### NMR Spectroscopy

NMR spectra were recorded on a *Bruker Ascend™ 500* spectrometer operating at 500 MHz, 471 MHz, 203 MHz, and 126 MHz, for  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  acquisitions, respectively. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For  $^1\text{H}$  NMR:  $\text{CDCl}_3$ ,  $\delta$  7.260;  $\text{CD}_3\text{CN}$ ,  $\delta$  1.940;  $\text{DMSO}-d_6$ ,  $\delta$  2.500; For  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ ,  $\delta$  77.16;  $\text{CD}_3\text{CN}$ ,  $\delta$  1.32;  $\text{DMSO}-d_6$ ,  $\delta$  39.52.  $^{19}\text{F}$  NMR spectra were referenced using a unified chemical shift scale based on the  $^1\text{H}$  resonance of tetramethylsilane (1% v/v solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration. Multiplets resulting from coupling to several magnetically non identical atoms with a coincidentally equal (within the limits of detection) coupling constant are indicated with  $\psi$  as well as splittings not resulting from a coupling to another spin.

### Massspectrometry

High-resolution mass spectra were acquired using a *Q Exactive Plus Orbitrap* manufactured by *Thermo Scientific*, Bremen, Germany or a *Q Exactive GC Orbitrap* manufactured by *Thermo Scientific*, Bremen, Germany in combination with the gas-chromatograph *Trace 1310* manufactured by *Thermo Scientific*, Bremen, Germany.

**Starting materials**

All substrates were used as received from commercial suppliers, unless otherwise stated. Chemicals were purchased from *Sigma-Aldrich*, *Chempur*, *TCI*, or *Alfa Aesar*.

## EXPERIMENTAL DATA

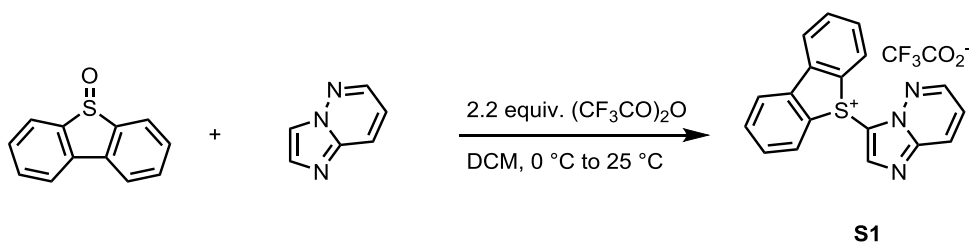
## Experimental procedures and compound characterization

## Thianthrene-S-oxide

Thianthrene-S-oxide was prepared as described previously.<sup>4a</sup>

## Dibenzothiophene-S-oxide

Dibenzothiophene-S-oxide was prepared as described previously.<sup>4e</sup>

Imidazopyridazine-derived dibenzothiophenium salt **S1** (CCDC 1987149)

Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with imidazopyridazine (1.07 g, 9.00 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (1.80 g, 9.00 mmol, 1.0 equiv.), and DCM (60 ml,  $c = 0.15$  M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (2.77 mL, 4.16 g, 19.8 mmol, 2.2 eq.) was added. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 1.5 h. Subsequently, the reaction mixture was diluted with water (20 ml). The layers were separated. The aqueous layer was extracted with DCM (20 ml). The combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 1) to afford 2.88 g (77 %) of compound **S1** as brown foam.

$R_f = 0.24$  (DCM / MeOH, 9 / 1 (v/v)).

## NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.81 (s, 1H), 8.34 (dd,  $J = 7.8, 1.1$  Hz, 2H), 8.16 – 8.07 (m, 4H), 7.87 (td,  $J = 7.7, 1.0$  Hz, 2H), 7.61 (td,  $J = 7.7, 1.2$  Hz, 2H), 7.34 (dd,  $J = 9.1, 4.8$  Hz, 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (128 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 160.6 (q,  $J = 32$  Hz), 147.4, 146.5, 146.4, 141.6, 135.1, 132.0, 128.9, 128.2, 128.0, 124.9, 123.4, 118.6 (q,  $J = 299$  Hz), 102.5.

**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): –75.4.

**HRMS-ESI (m/z)** calc'd for  $\text{C}_{18}\text{H}_{12}\text{N}_3\text{S}^+$  [ $\text{M-TFA}$ ] $^+$ , 302.0746; found 302.0744; deviation 0.8 ppm.

## X-ray crystallography:

Sample preparation: In a 2 mL GC-vial, a small portion of compound **S1** (approx. 5 mg) was dissolved in 0.5 mL chloroform. It was then placed in a 20 mL glass vial filled with 2 mL hexanes. The larger vial was capped

and the cap was stabbed with a syringe needle. The system was left on a shelf at 20 °C until the formed crystals had sufficient size (approx. one week).

X-ray measurement:

device: Bruker-AXS Kappa Mach3 APEX-II

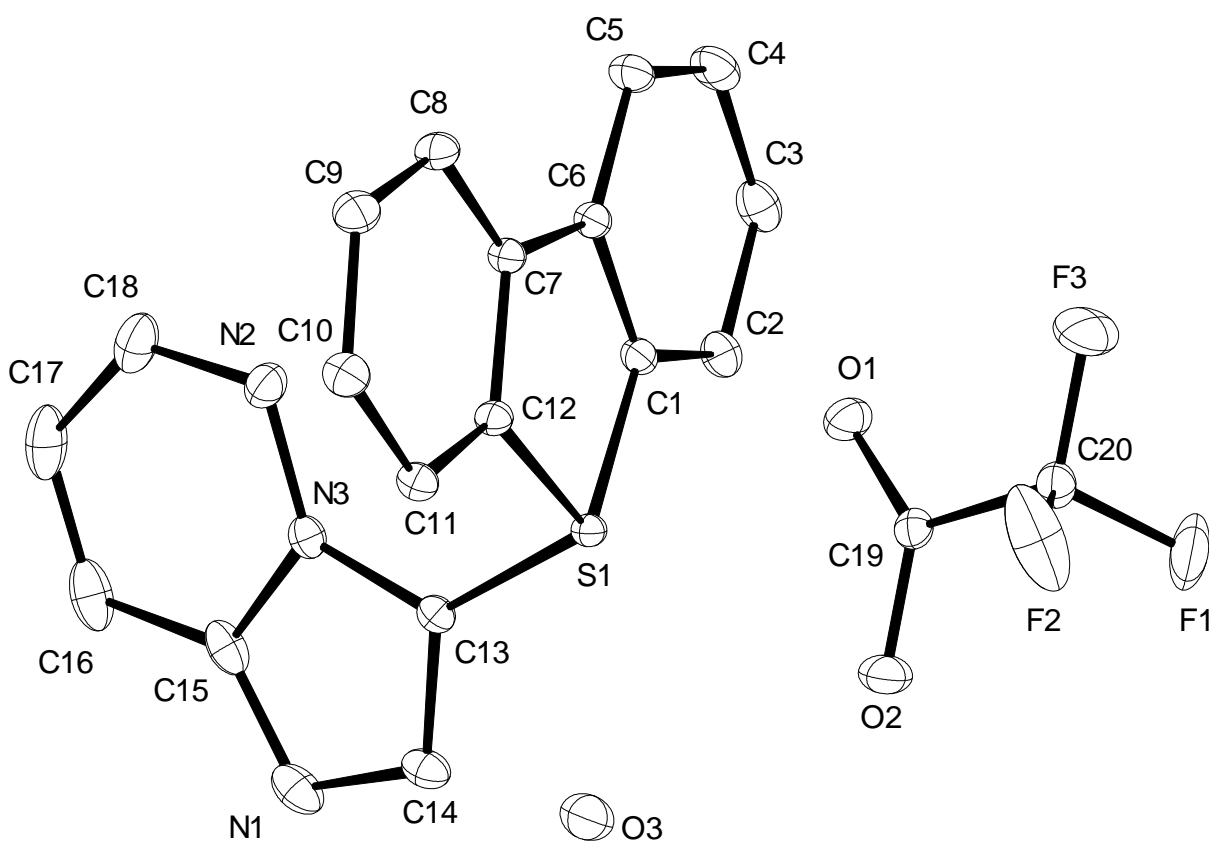
method: f- and w-scans

radiation: Mo-K $\alpha$

wavelength: 0.71073 Å

radiation source: 1\mS

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.



**Fig. S1:** Crystal structure of compound **S1**. The nonhydrogen atoms are depicted with 50 % probability ellipsoids.

**Table S1. Crystal data and structure refinement.**

Identification code	12795
Empirical formula	C <sub>20</sub> H <sub>14</sub> F <sub>3</sub> N <sub>3</sub> O <sub>3</sub> S
Color	colourless

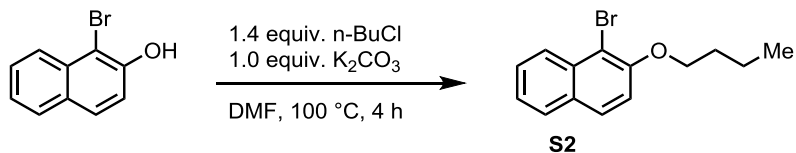
Formula weight	433.40 g · mol <sup>-1</sup>	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	<b>P1, (no. 2)</b>	
Unit cell dimensions	a = 7.7627(3) Å	α = 100.4140(10)°.
	b = 9.9150(3) Å	β = 106.2760(10)°.
	c = 13.0037(5) Å	γ = 91.2600(10)°.
Volume	942.12(6) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.528 Mg · m <sup>-3</sup>	
Absorption coefficient	0.230 mm <sup>-1</sup>	
F(000)	444 e	
Crystal size	0.118 x 0.075 x 0.054 mm <sup>3</sup>	
θ range for data collection	2.742 to 34.845°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	
Reflections collected	37409	
Independent reflections	8122 [R <sub>int</sub> = 0.0214]	
Reflections with I > 2σ(I)	6938	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8122 / 0 / 327	
Goodness-of-fit on F <sup>2</sup>	1.030	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0346	wR <sup>2</sup> = 0.0888
R indices (all data)	R <sub>1</sub> = 0.0433	wR <sup>2</sup> = 0.0943
Largest diff. peak and hole	0.7 and -0.5 e · Å <sup>-3</sup>	

**Table S2. Bond lengths [Å] and angles [°].**

S(1)-C(1)	1.7811(8)	S(1)-C(12)	1.7837(8)
S(1)-C(13)	1.7337(8)	N(1)-C(14)	1.3564(13)
N(1)-C(15)	1.3389(13)	N(2)-N(3)	1.3509(11)
N(2)-C(18)	1.3145(13)	N(3)-C(13)	1.3787(11)
N(3)-C(15)	1.3865(11)	C(1)-C(2)	1.3842(12)
C(1)-C(6)	1.3991(11)	C(2)-H(2)	0.941(15)
C(2)-C(3)	1.3949(13)	C(3)-H(3)	0.961(16)
C(3)-C(4)	1.3920(14)	C(4)-H(4)	0.970(15)
C(4)-C(5)	1.3941(13)	C(5)-H(5)	0.960(15)
C(5)-C(6)	1.3936(12)	C(6)-C(7)	1.4628(12)
C(7)-C(8)	1.3950(12)	C(7)-C(12)	1.3994(11)
C(8)-H(8)	0.957(14)	C(8)-C(9)	1.3929(13)
C(9)-H(9)	0.960(14)	C(9)-C(10)	1.3966(13)
C(10)-H(10)	0.959(14)	C(10)-C(11)	1.3981(12)
C(11)-H(11)	0.926(14)	C(11)-C(12)	1.3815(12)
C(13)-C(14)	1.3868(11)	C(14)-H(14)	0.965(14)
C(15)-C(16)	1.4095(15)	C(16)-H(16)	0.940(17)
C(16)-C(17)	1.3593(18)	C(17)-H(17)	0.943(18)
C(17)-C(18)	1.4230(16)	C(18)-H(18)	0.976(16)
F(1)-C(20)	1.3423(11)	F(2)-C(20)	1.3240(12)
F(3)-C(20)	1.3262(11)	O(1)-C(19)	1.2334(11)
O(2)-C(19)	1.2557(10)	C(19)-C(20)	1.5491(12)
O(3)-H(3A)	0.828(19)	O(3)-H(3B)	0.846(19)
C(1)-S(1)-C(12)	91.59(4)	C(13)-S(1)-C(1)	104.65(4)
C(13)-S(1)-C(12)	104.75(4)	C(15)-N(1)-C(14)	105.51(7)
C(18)-N(2)-N(3)	113.51(8)	N(2)-N(3)-C(13)	126.42(7)
N(2)-N(3)-C(15)	127.11(8)	C(13)-N(3)-C(15)	106.43(7)
C(2)-C(1)-S(1)	124.60(6)	C(2)-C(1)-C(6)	124.07(8)
C(6)-C(1)-S(1)	111.24(6)	C(1)-C(2)-H(2)	121.1(9)
C(1)-C(2)-C(3)	116.61(8)	C(3)-C(2)-H(2)	122.3(9)
C(2)-C(3)-H(3)	117.2(9)	C(4)-C(3)-C(2)	120.69(8)
C(4)-C(3)-H(3)	122.1(9)	C(3)-C(4)-H(4)	118.6(9)

C(3)-C(4)-C(5)	121.67(8)	C(5)-C(4)-H(4)	119.7(9)
C(4)-C(5)-H(5)	121.4(9)	C(6)-C(5)-C(4)	118.68(8)
C(6)-C(5)-H(5)	119.9(9)	C(1)-C(6)-C(7)	112.90(7)
C(5)-C(6)-C(1)	118.29(8)	C(5)-C(6)-C(7)	128.82(8)
C(8)-C(7)-C(6)	128.66(7)	C(8)-C(7)-C(12)	118.28(8)
C(12)-C(7)-C(6)	113.05(7)	C(7)-C(8)-H(8)	120.2(9)
C(9)-C(8)-C(7)	118.76(8)	C(9)-C(8)-H(8)	121.0(9)
C(8)-C(9)-H(9)	119.3(9)	C(8)-C(9)-C(10)	121.49(8)
C(10)-C(9)-H(9)	119.3(9)	C(9)-C(10)-H(10)	120.4(8)
C(9)-C(10)-C(11)	120.74(8)	C(11)-C(10)-H(10)	118.8(8)
C(10)-C(11)-H(11)	121.5(9)	C(12)-C(11)-C(10)	116.47(8)
C(12)-C(11)-H(11)	122.1(9)	C(7)-C(12)-S(1)	111.10(6)
C(11)-C(12)-S(1)	124.67(6)	C(11)-C(12)-C(7)	124.23(7)
N(3)-C(13)-S(1)	126.89(6)	N(3)-C(13)-C(14)	105.67(7)
C(14)-C(13)-S(1)	127.13(7)	N(1)-C(14)-C(13)	111.15(8)
N(1)-C(14)-H(14)	123.7(8)	C(13)-C(14)-H(14)	125.2(8)
N(1)-C(15)-N(3)	111.23(8)	N(1)-C(15)-C(16)	131.67(9)
N(3)-C(15)-C(16)	117.09(9)	C(15)-C(16)-H(16)	118.8(10)
C(17)-C(16)-C(15)	117.59(9)	C(17)-C(16)-H(16)	123.6(10)
C(16)-C(17)-H(17)	122.5(11)	C(16)-C(17)-C(18)	119.56(10)
C(18)-C(17)-H(17)	118.0(11)	N(2)-C(18)-C(17)	125.03(10)
N(2)-C(18)-H(18)	114.1(9)	C(17)-C(18)-H(18)	120.9(9)
O(1)-C(19)-O(2)	130.34(8)	O(1)-C(19)-C(20)	116.84(7)
O(2)-C(19)-C(20)	112.81(8)	F(1)-C(20)-C(19)	110.82(7)
F(2)-C(20)-F(1)	106.19(9)	F(2)-C(20)-F(3)	108.28(9)
F(2)-C(20)-C(19)	111.47(7)	F(3)-C(20)-F(1)	105.64(8)
F(3)-C(20)-C(19)	113.98(8)	H(3A)-O(3)-H(3B)	105.4(17)

### Bromobutoxynaphthalene S2



Under an ambient atmosphere, a 250 ml round bottom flask equipped with a teflon coated stir bar and a reflux condenser was charged with hydroxybromonaphthalene (3.00 g, 13.4 mmol, 1.0 equiv.), chlorobutane (2.0 ml, 1.8 g, 19 mmol, 1.4 equiv.), potassium carbonate (1.9 g, 13 mmol, 1.0 equiv.), and DMF (100 ml, c = 0.13 M). The mixture was heated to 100 °C and stirred for 4 h. After cooling to 25 °C, the mixture was diluted

with water (75 ml) and EtOAc (50 ml). The layers were separated. The aqueous layer was extracted with EtOAc (2 × 50 ml). The combined organic layers were washed with water (2 × 50 ml), dried over MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography and on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 10 / 1) to afford 2.06 g (55 %) of compound **S2** as yellowish liquid.

$R_f$  = 0.73 (hexanes / EtOAc, 4 / 1 (v/v)).

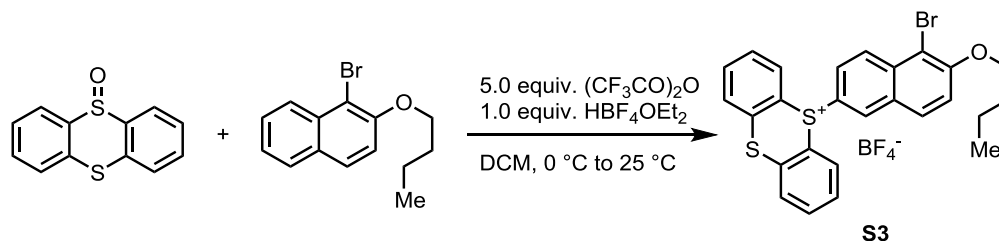
#### NMR Spectroscopy:

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, 298 K,  $\delta$ ): 8.27 (dd,  $J$  = 8.6, 2.7 Hz, 1H), 7.81 (d,  $J$  = 9.1 Hz, 2H), 7.59 (ddt,  $J$  = 8.5, 7.0, 1.6 Hz, 1H), 7.42 (ddt,  $J$  = 8.3, 6.8, 1.4 Hz, 1H), 7.27 (d,  $J$  = 9.0 Hz, 1H), 4.21 (t,  $J$  = 6.5 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.71 – 1.56 (m, 2H), 1.05 (td,  $J$  = 7.4, 2.5 Hz, 3H).

**<sup>13</sup>C {<sup>1</sup>H} NMR** (128 MHz, CDCl<sub>3</sub>, 298 K,  $\delta$ ): 153.5, 133.3, 129.9, 128.9, 128.1, 127.7, 126.3, 124.4, 115.3, 109.6, 70.0, 31.6, 19.4, 14.0.

**HRMS-EI (m/z)** calc'd for C<sub>14</sub>H<sub>15</sub>OBr<sup>+</sup> [M]<sup>+</sup>, 278.0301; found 278.0297; deviation 1.2 ppm.

#### Bromobutoxynaphthalin-derived diphenylsulfonium salt **S3**



Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with bromobutoxynaphthalene (1.02 g, 3.65 mmol, 1.0 equiv.), thianthrene-S-oxide (849 mg, 3.65 mmol, 1.0 equiv.), and DCM (50 ml,  $c$  = 0.073 M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (2.5 mL, 3.8 g, 18 mmol, 5.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.5 ml, 0.60 g, 3.7 mmol, 1.0 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 5 h. Subsequently, the reaction mixture was poured onto aqueous NaHCO<sub>3</sub> solution (saturated, 50 ml). The layers were separated. The organic layer was washed with aqueous NaBF<sub>4</sub> solution (20 % (w/w), 3 × 20 ml), and water (20 ml), and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc / DCM / MeOH (2 / 1 / 0 / 0, then 0 / 0 / 2 / 1) to afford 828 mg (39 %) of compound **S3** as dark purple solid.

$R_f$  = 0.52 (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

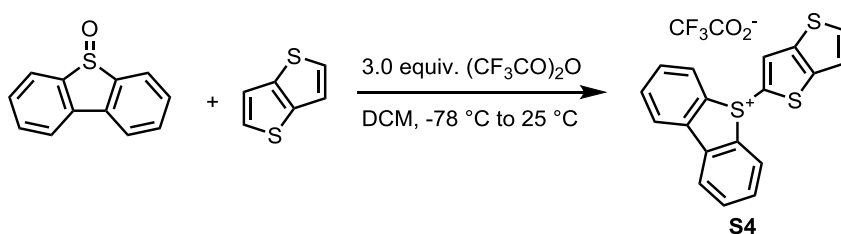
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, 298 K, δ): 8.60 (dd, *J* = 7.5, 1.4 Hz, 2H), 8.18 (d, *J* = 9.3 Hz, 1H), 7.99 (d, *J* = 2.3 Hz, 1H), 7.89 – 7.72 (m, 7H), 7.30 (d, *J* = 9.1 Hz, 1H), 7.14 (dd, *J* = 9.3, 2.3 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.62 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C {<sup>1</sup>H} NMR** (128 MHz, CDCl<sub>3</sub>, 298 K, δ): 156.5, 136.4, 135.5, 134.91, 134.86, 131.4, 130.6, 130.5, 130.2, 129.5, 129.0, 123.6, 119.3, 118.9, 116.7, 108.8, 69.9, 31.3, 19.3, 13.9.

**<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>, 298 K, δ): –150.6, –150.7.

**HRMS-ESI(m/z)** calc'd for C<sub>26</sub>H<sub>22</sub>OS<sub>2</sub>Br<sup>+</sup> [M-BF<sub>4</sub>]<sup>+</sup>, 493.0290; found 493.0285; deviation 1.1 ppm.

#### Thienothiophene-derived dibenzothiophenium salt **S4**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene (400 mg, 2.85 mmol, 1.00 equiv.), thianthrene-S-oxide (571 mg, 2.85 mmol, 1.0 equiv.), and DCM (11 ml, *c* = 0.26 M). The mixture was cooled to –78 °C, subsequently trifluoroacetic acid anhydride (1.21 ml, 1.80 g, 8.56 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was stirred at –78 °C for 30 min, then allowed to warm to 25 °C, over a period of approximately 1 h. The reaction mixture was stirred at 25 °C for 12 h. Subsequently, the reaction mixture was diluted with DCM (25 ml). The organic phase was washed with aqueous NaHCO<sub>3</sub> solution (saturated, 30 ml). The aqueous layer was extracted with DCM (2 × 20 ml). The combined organic layers were dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 620 mg (51 %) of compound **S4** as green-brown solid.

*R<sub>f</sub>* = 0.50 (DCM / MeOH, 10 / 1 (v/v)).

#### NMR Spectroscopy:

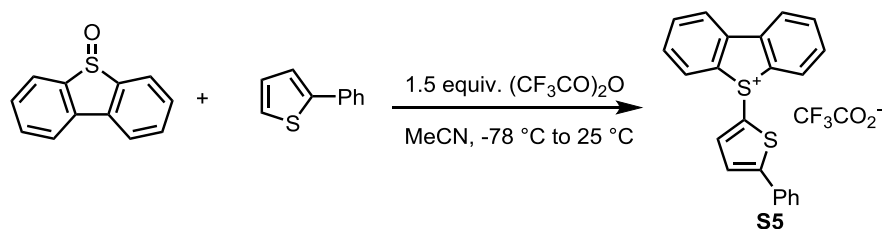
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, 298 K, δ): 9.31 (s, 1H), 8.41 (d, *J* = 8.0 Hz, 2H), 8.11 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.84 (t, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 5.3 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 5.3 Hz, 1H).

**<sup>13</sup>C {<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>, 298 K, δ): 145.8, 139.3, 138.2, 137.0, 134.7, 134.4, 134.1, 131.8, 129.4, 123.6, 121.5, 119.5. C-atoms of trifluoroacetate ion were not detected.

**<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>, 298 K, δ): –75.3 (s).

**HRMS-ESI(m/z)** calc'd for C<sub>18</sub>H<sub>11</sub>S<sub>3</sub><sup>+</sup> [M-TFA]<sup>+</sup>, 323.0017; found 323.0015; deviation 0.8 ppm.

### 2-Phenylthiophene-derived dibenzothiophenium salt **S5**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with dibenzothiophene-S-oxide (0.50 g, 2.5 mmol, 1.0 equiv.), 2-phenylthiophene (0.40 g, 2.5 mmol, 1.0 equiv.), and MeCN (5 ml,  $c = 0.5$  M). The mixture was cooled to  $-78$  °C, subsequently trifluoroacetic acid anhydride (0.53 mL, 3.8 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to  $25$  °C, over a period of 20 min. Subsequently, the mixture was stirred for 1 h at  $25$  °C. Subsequently, the reaction mixture was diluted with DCM (30 ml) and washed with water ( $3 \times 30$  ml). The organic layer was dried with  $\text{MgSO}_4$ . The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 17 / 3) to afford 1.01 g (89 %) of compound **S5** as pale yellow, highly viscous oil.

$R_f = 0.33$  (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

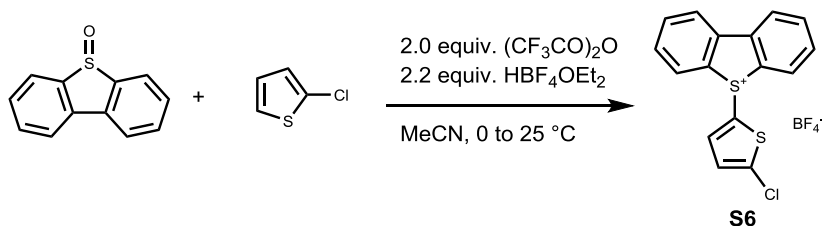
**$^1\text{H}$  NMR** (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.35 – 8.30 (m, 3H), 8.21 (d,  $J = 8.1$  Hz, 2H), 7.94 (wt,  $J = 7.6$  Hz, 2H), 7.73 (t,  $J = 7.8$  Hz, 2H), 7.51 (d,  $J = 4.0$  Hz, 1H), 7.49 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 157.9, 144.5, 139.5, 135.7, 134.6, 132.7, 132.5, 131.2, 130.4, 129.0, 127.2, 126.2, 125.5, 120.6. C-atoms of the trifluoroacetate ion were not detected.

**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ):  $-76.3$  (s).

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{22}\text{H}_{15}\text{S}_2^+$  [M-TFA] $^+$ , 343.0610; found 343.0606; deviation 1.0 ppm.

### 2-Chlorothiophene-derived dibenzothiophenium salt **S6**



Dibenzothiophene-S-oxide (0.50 g, 2.5 mmol, 1.0 equiv.) and 2-chlorothiophene (0.70 ml, 7.5 mmol, 3.0 equiv.) were suspended in acetonitrile (5 ml,  $c = 0.5$  M). At  $0$  °C, tetrafluoroboric acid diethyl ether complex (0.37 ml, 2.7 mmol, 1.1 equiv.) and trifluoroacetic acid anhydride (0.70 mL, 5.0 mmol, 2.0 eq.) were added dropwise. Subsequently, the reaction mixture was allowed to warm to  $25$  °C, and was stirred for 2 h. Subsequently, EtOAc (10 ml) and aqueous  $\text{NaHCO}_3$  solution (saturated, 10 ml) were added under vigorous stirring. The organic phase was separated, and the aqueous layer was extracted with EtOAc ( $2 \times 20$  ml). The

combined organic layers were washed with aqueous NaBF<sub>4</sub> solution (10 % (w/w), 2 × 20 mL), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The resulting solid was washed with DCM (2 ml) to afford 610 mg (63 %) of dibenzothiophenium salt **S6** as colorless crystals.

R<sub>f</sub> = 0.36 (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

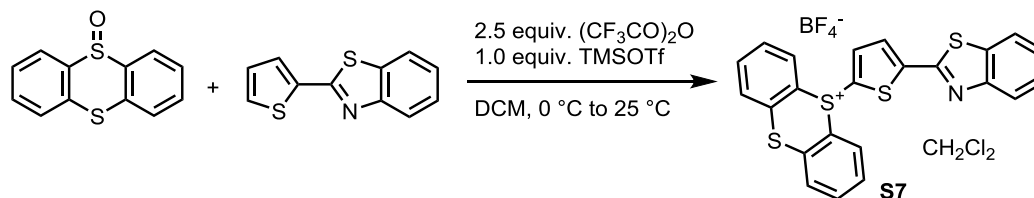
**<sup>1</sup>H NMR** (500 MHz, CD<sub>3</sub>CN, 298 K, δ): 8.31 (dd, *J* = 7.9, 1.2 Hz, 2H), 8.17 – 8.11 (m, 3H), 7.96 (ψtd, *J* = 7.7, 1.1 Hz, 2H), 7.75 (ddd, *J* = 8.4, 7.6, 1.2 Hz, 2H), 7.21 (d, *J* = 4.3 Hz, 1H).

**<sup>13</sup>C {<sup>1</sup>H} NMR** (126 MHz, CD<sub>3</sub>CN, 298 K, δ): 143.8, 143.3, 139.5, 136.0, 133.8, 132.9, 130.4, 129.0, 125.7, 120.9.

**<sup>19</sup>F NMR** (471 MHz, CD<sub>3</sub>CN, 298 K, δ): –151.2, –151.3.

**HRMS-ESI (m/z)** calc'd for C<sub>16</sub>H<sub>10</sub>S<sub>2</sub>Cl<sup>+</sup> [M-BF<sub>4</sub>]<sup>+</sup>, 300.9907; found 300.9904; deviation 1.0 ppm.

#### Benzothiazol-substituted thiophene-derived thianthrenium salt **S7**



Under an atmosphere of argon, a 50 ml round bottom flask equipped with a teflon coated stir bar was charged with benzothiazolylthiophene (1.00 g, 4.60 mmol, 1.0 equiv.), thianthrene-S-oxide (1.07 g, 4.60 mmol, 1.0 equiv.), and DCM (10 ml, c = 0.46 M). The mixture was cooled to 0 °C, subsequently trimethylsilyltriflate (0.83 ml, 1.0 g, 4.6 mmol, 1.0 equiv.) and trifluoroacetic acid anhydride (1.6 ml, 2.4 g, 11.5 mmol, 2.5 eq.) were added dropwise. Subsequently, the reaction mixture was allowed to warm to 25 °C over a period of approximately 30 min. The reaction mixture was stirred at 25 °C. Subsequently, the reaction mixture was washed with aqueous NaHCO<sub>3</sub> solution (saturated, 15 ml), washed with water (15 ml), and washed with aqueous NaBF<sub>4</sub> solution (10 % (w/w), 2 × 15 ml). The resulting precipitate was dissolved by addition of approx. 0.3 L of DCM. The organic layer was washed with aqueous NaBF<sub>4</sub> solution (10 % (w/w), 50 ml). The organic phase was dried over MgSO<sub>4</sub>, and loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 2.65 g (95 %) of compound **S7**·CH<sub>2</sub>Cl<sub>2</sub> as yellow crystals.

R<sub>f</sub> = 0.59 (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

**<sup>1</sup>H NMR** (500 MHz, CD<sub>3</sub>CN, 298 K, δ): 8.34 (dd, *J* = 8.1, 1.3 Hz, 2H), 8.02 – 7.95 (m, 3H), 7.94 – 7.86 (m, 3H), 7.78 (ddd, *J* = 8.0, 7.4, 1.3 Hz, 2H), 7.66 (d, *J* = 4.2 Hz, 1H), 7.63 (d, *J* = 4.2 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.45 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 5.44 (s, 2H).

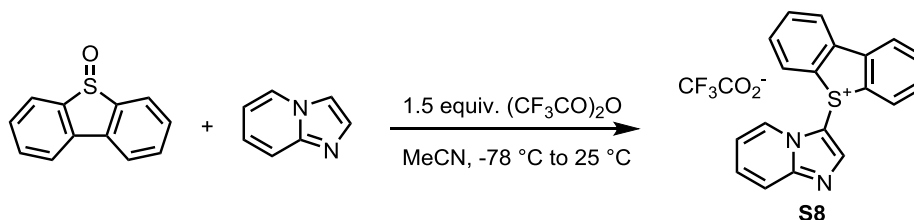
**<sup>13</sup>C {<sup>1</sup>H} NMR** (126 MHz, CD<sub>3</sub>CN, 298 K, δ): 159.6, 154.0, 147.5, 139.7, 136.9, 136.4, 136.3, 135.0,

131.5, 131.2, 129.6, 128.2, 127.6, 125.5, 124.2, 123.3, 120.5, 55.3.

$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ):  $-151.46$ ,  $-151.52$ .

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{23}\text{H}_{14}\text{NS}_4^+$  [M-TFA] $^+$ , 432.0004; found 432.0003; deviation 0.1 ppm.

#### Imidazopyridine-derived dibenzothiophenium salt **S8**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine (590 mg, 5.0 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (1.0 g, 5.0 mmol, 1.0 equiv.), and MeCN (15 ml,  $c = 0.33$  M). The mixture was cooled to  $-78$  °C, subsequently trifluoroacetic acid anhydride (1.0 ml, 1.6 g, 7.5 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to  $25$  °C, over a period of 1 h. The reaction mixture was stirred at  $25$  °C for 24 h. Subsequently, the reaction mixture was diluted with DCM (15 ml) and washed with water (30 ml). The organic layer was dried with  $\text{MgSO}_4$ . The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 4 / 1) to afford 1.50 g (72 %) of compound **S8** as colorless crystals.

$R_f = 0.21$  (DCM / MeOH, 10 / 1 (v/v)).

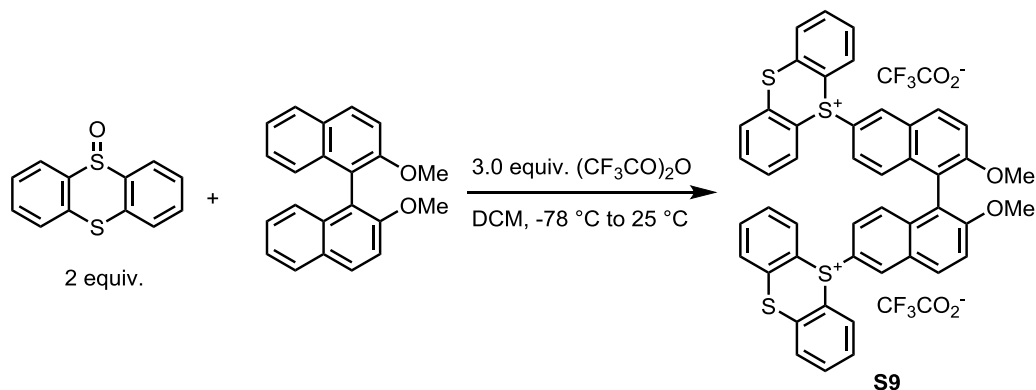
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.75 (s, 1H), 8.43 (dd,  $J = 8.1$ , 1.3 Hz, 2H), 8.08 (dd,  $J = 8.1$ , 0.8 Hz, 2H), 7.95 ( $\psi$ td,  $J = 7.6$ , 1.0 Hz, 2H), 7.79 (d,  $J = 9.0$  Hz, 1H), 7.69 (ddd,  $J = 8.4$ , 7.4, 1.2 Hz, 2H), 7.54 (ddd,  $J = 9.0$ , 7.0, 1.2 Hz, 1H), 7.06 (d,  $J = 7.0$  Hz, 1H), 6.87 (td,  $J = 6.9$ , 1.2 Hz, 1H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 160.30 (q,  $J = 31$  Hz), 152.7, 150.6, 140.1, 135.5, 132.6, 131.7, 129.1, 127.8, 126.3, 125.8, 120.0, 118.65 (q,  $J = 298$  Hz), 117.6, 95.3.

$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ):  $-75.3$  (s).

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{19}\text{H}_{13}\text{N}_2\text{S}^+$  [M-TFA] $^+$ , 301.0794; found 301.0792; deviation 0.8 ppm.

BINOL-dimethylether-derived thianthrenium salt **S9**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with BINOL-dimethylether (250 mg, 0.80 mmol, 1.0 equiv.), thianthrene-*S*-oxide (365 mg, 1.6 mmol, 2.0 equiv.), and DCM (3 ml,  $c = 0.27\text{ M}$ ). The mixture was cooled to  $-78\text{ }^\circ\text{C}$ , subsequently trifluoroacetic acid anhydride (0.37 ml, 0.50 g, 2.4 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 30 min, then allowed to warm to  $25\text{ }^\circ\text{C}$ , over a period of approximately 1 h. The reaction mixture was stirred at  $25\text{ }^\circ\text{C}$  for 12 h. Subsequently, the reaction mixture was diluted with DCM (10 ml). The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 320 mg (45 %) of compound **S9** as brown solid.

$R_f = 0.67$  (DCM / MeOH, 4 / 1 (v/v)).

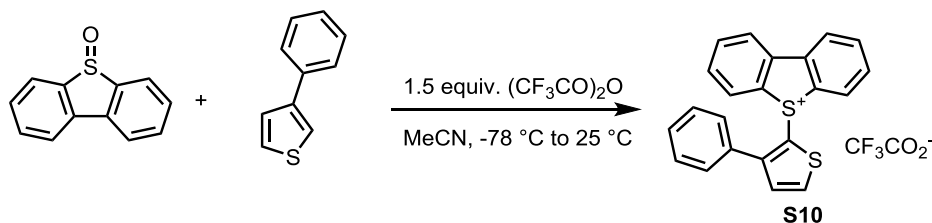
## NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.67 (ddd,  $J = 8.2, 6.6, 1.7\text{ Hz}$ , 4H), 8.05 (s, 2H), 7.98 (d,  $J = 9.2\text{ Hz}$ , 2H), 7.80 – 7.67 (m, 12H), 7.44 (d,  $J = 9.3\text{ Hz}$ , 2H), 6.90 (d,  $J = 1.5\text{ Hz}$ , 4H), 3.70 (s, 6H).

**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 157.8, 136.5, 135.5, 135.4, 135.3, 134.68, 134.66, 131.7, 131.3, 130.3, 130.21, 130.18, 130.1, 128.4, 127.9, 123.1, 119.5, 119.3, 118.3, 117.9, 115.5, 56.6. C-atoms of the trifluoroacetate anion were not detected.

**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ):  $-74.8$  (s).

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{46}\text{H}_{32}\text{O}_2\text{S}_4^{2+}$   $[\text{M}-2\text{TFA}]^{2+}$ , 372.0637; found 372.0630; deviation 1.8 ppm.

3-Phenylthiophen-derived dibenzothiophenium salt **S10**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 3-phenylthiophene (0.50 g, 3.1 mmol, 1.0 equiv.), dibenzothiophene-S-oxide (0.76 g, 82 % dibenzothiophene-S-oxide, rest sulfone, 3.1 mmol, 1.0 equiv.), and MeCN (5 ml,  $c = 0.6$  M). The mixture was cooled to  $-78$  °C, subsequently trifluoroacetic acid anhydride (1.3 mL, 2.0 g, 9.4 mmol, 3.0 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to  $25$  °C, over a period of 1 h. Subsequently, the reaction mixture was diluted with DCM (10 ml) and washed with water ( $2 \times 30$  ml). The organic layer was dried with  $\text{MgSO}_4$ . The organic phase was directly loaded onto a silica column and eluted with DCM / MeOH (1 / 0 gradient to 4 / 1) to afford 1.17 g (82 %) of compound **S10** as pale yellow highly viscous oil.

$R_f = 0.14$  (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

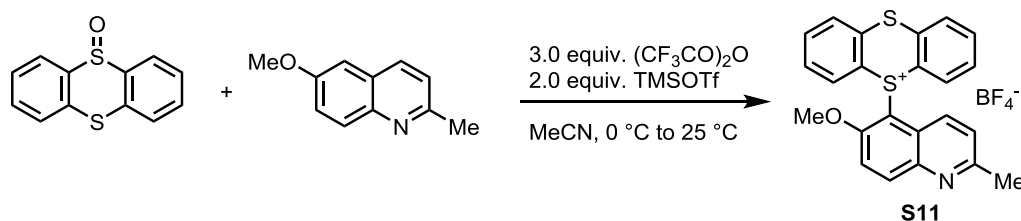
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.07 (d,  $J = 7.7$  Hz, 2H), 7.99 (d,  $J = 8.1$  Hz, 2H), 7.81 – 7.75 (m, 3H), 7.71 (d,  $J = 6.8$  Hz, 2H), 7.57 (wt,  $J = 7.8$  Hz, 2H), 7.55 – 7.47 (m, 3H), 7.21 (d,  $J = 5.2$  Hz, 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 154.4, 138.4, 136.2, 134.5, 132.9, 131.7, 131.6, 131.5, 129.9, 129.7, 129.2, 128.4, 124.2, 117.1. C-atoms of trifluoroacetate ion were not detected.

$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ):  $-74.8$  (s).

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{22}\text{H}_{15}\text{S}_2^+$  [M-TFA] $^+$ , 343.0610; found 343.0606; deviation 1.2 ppm.

#### Methoxyquinolin-derived thianthrenium salt **S11**



A flame-dried, argon-filled Schlenk-tube equipped with a magnetic stir bar was charged with methoxy methyl quinoline (866 mg, 5.00 mmol, 1.00 equiv.), thianthrene S-oxide (1.16 g, 5.00 mmol, 1.00 equiv.), and dry MeCN (20 mL,  $c = 0.25$  M). After cooling to  $0$  °C, trifluoroacetic anhydride (2.09 mL, 3.16 g, 15.0 mmol, 3.00 equiv.) was added while stirring. Trimethylsilyl trifluoromethanesulfonate (1.81 mL, 2.22 g, 10.0 mmol, 2.00 equiv.) was added dropwise. The mixture was stirred at  $0$  °C for 1 h, then at ambient temperature for 14 h. The reaction mixture was diluted with DCM. The solution was washed with aqueous  $\text{NaHCO}_3$  solution, and subsequently with aqueous  $\text{NaBF}_4$  solution. The organic phase was dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM / MeOH (47:3 (v/v)) to afford 1.558 g (66%) of **S11** as colorless solid.

$R_f = 0.58$  (DCM / MeOH, 10 / 1 (v/v)).

#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 298 K,  $\delta$ ): 8.66 (d,  $J = 9.5$  Hz, 1H), 8.59 (d,  $J = 8.6$  Hz, 1H), 8.10 (d,  $J =$

9.6 Hz, 1H), 8.04 (dd,  $J = 7.9, 1.3$  Hz, 2H), 7.76 (ψtd,  $J = 7.6, 1.2$  Hz, 2H), 7.66 (d,  $J = 8.8$  Hz, 1H), 7.54 (ddd,  $J = 8.5, 7.3, 1.3$  Hz, 2H), 7.40 (dd,  $J = 8.3, 1.2$  Hz, 2H), 3.81 (s, 3H), 2.72 (s, 3H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz, DMSO- $d_6$ , 298 K,  $\delta$ ): 160.8, 158.7, 143.4, 140.4, 132.8, 131.6, 130.8, 129.8, 129.7, 128.1, 127.9, 125.0, 123.1, 118.4, 96.0, 57.7, 24.4.

$^{19}\text{F}$  NMR (471 MHz, DMSO- $d_6$ , 298 K,  $\delta$ ): -148.2, -148.3.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{23}\text{H}_{18}\text{NOS}_2^+ [\text{M}-\text{BF}_4]^+$ , 388.0824; found 388.0825; deviation 0.3 ppm.

### Methoxynaphthalin-derived diphenylsulfonium salt **S12**



Under an ambient atmosphere, a 100 ml round bottom flask equipped with a teflon coated stir bar was charged with 2-methoxynaphthalene (1.58 g, 10.0 mmol, 1.0 equiv.), diphenylsulfoxide (2.02 g, 10.0 mmol, 1.0 equiv.), and DCM (40 ml,  $c = 0.25$  M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (2.82 mL, 4.20 g, 20.0 mmol, 2.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.68 ml, 0.81 g, 5.0 mmol, 0.50 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 1 h. Subsequently, the reaction mixture was poured onto aqueous  $\text{NaHCO}_3$  solution (saturated, 120 ml). The reaction mixture was stirred for 5 min. The organic layer was separated and subsequently washed with  $\text{NaBF}_4$  solution (10 % (w/w),  $3 \times 50$  ml). The organic layer was dried with  $\text{MgSO}_4$ . The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 1 / 1) to afford 2.27 g (53 %) of compound **S12** as colorless solid.

$R_f = 0.47$  (DCM / MeOH, 9 / 1 (v/v)).

### NMR Spectroscopy:

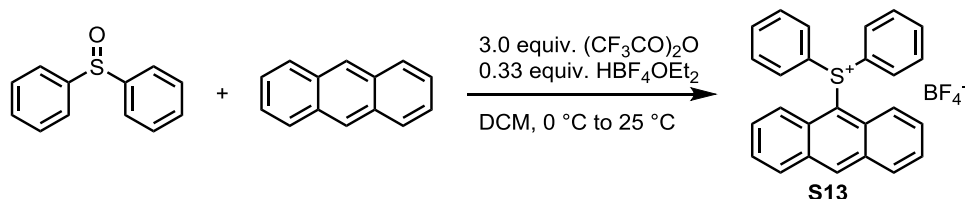
$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.52 – 8.46 (m, 2H), 8.09 (ddd,  $J = 8.2, 1.4, 0.7$  Hz, 1H), 7.82 (ddd,  $J = 8.4, 7.0, 1.4$  Hz, 1H), 7.79 – 7.75 (m, 2H), 7.74 – 7.72 (m, 3H), 7.69 – 7.65 (m, 3H), 7.63 (ddd,  $J = 8.1, 7.0, 1.0$  Hz, 1H), 7.58 (d,  $J = 9.2$  Hz, 1H), 3.74 (s, 3H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (128 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 161.7, 140.7, 134.8, 134.7, 131.9, 131.6, 131.2, 130.6, 130.4, 126.8, 124.8, 122.5, 115.8, 101.4, 57.6.

$^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): -151.7, -151.8.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{23}\text{H}_{19}\text{OS}^+ [\text{M}-\text{BF}_4]^+$ , 343.1151; found 343.1148; deviation 0.7 ppm.

### Anthracen-derived diphenylsulfonium salt **S13**



Under an ambient atmosphere, a 250 ml round bottom flask equipped with a teflon coated stir bar was charged with anthracene (2.00 g, 11.2 mmol, 1.0 equiv.), diphenylsulfoxide (2.27 g, 11.2 mmol, 1.0 equiv.), and DCM (100 ml,  $c = 0.11$  M). The mixture was cooled to 0 °C, subsequently, trifluoroacetic acid anhydride (4.7 mL, 7.1 g, 33.7 mmol, 3.0 eq.) was added. Subsequently, tetrafluoroboric acid diethylether complex (0.5 ml, 0.60 g, 3.7 mmol, 0.33 equiv.) was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and stirred at 25 °C for 5 h. Subsequently, the reaction mixture was poured onto aqueous  $\text{NaHCO}_3$  solution (saturated, 100 ml), and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography and on silica gel eluting with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 3 / 2). The product containing solutions were washed with aqueous  $\text{NaBF}_4$  solution (20 % (w/w), 3  $\times$  25 ml). The organic layer was dried with  $\text{MgSO}_4$ . The solvent was removed to afford 1.86 g (37 %) of compound **S13** as yellow solid.

$R_f = 0.55$  (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

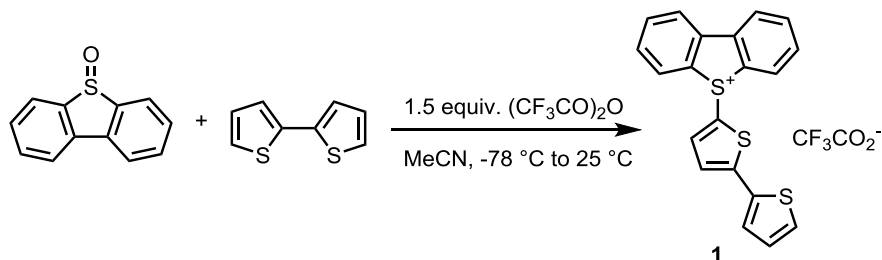
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 9.12 (s, 1H), 8.44 (d,  $J = 9.0$  Hz, 2H), 8.28 (d,  $J = 7.8$  Hz, 2H), 7.82 – 7.61 (m, 14H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (128 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 139.6, 134.3, 134.1, 132.1, 131.83, 131.76, 131.0, 129.6, 127.1, 123.4, 122.8, 109.5.

$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): –152.91, –152.95.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{26}\text{H}_{19}\text{S}^+ [\text{M}-\text{BF}_4]^+$ , 363.1202; found 363.1197; deviation 1.4 ppm.

### Bithiophen-derived dibenzothiophenium salt **1**



Under an ambient atmosphere, a 50 ml round bottom flask equipped with a teflon coated stir bar was charged with dibenzothiophene-S-oxide (2.44 g, 82 % (w/w) rest dibenzothiophene sulfone, 10 mmol, 1.0 equiv.),

bithiophene (1.746 g, 10.5 mmol, 1.05 equiv.), and MeCN (15 ml,  $c = 0.67$  M). The mixture was cooled to  $-78$  °C, subsequently trifluoroacetic acid anhydride (2.09 mL, 15 mmol, 1.5 eq.) was added dropwise. Subsequently, the reaction mixture was allowed to warm to  $25$  °C, over a period of approximately 20 min, and subsequently stirred for 1 h at  $25$  °C. Subsequently, the reaction mixture was diluted with DCM (30 ml) and washed with water ( $2 \times 50$  ml). The organic layer was dried with  $\text{MgSO}_4$ . The organic phase was directly loaded onto a silica column and eluted with EtOAc / DCM / MeOH (1 / 0 / 0, then 0 / 1 / 0 gradient to 0 / 4 / 1) to afford 4.05 g (88 %) of compound **1** as a brown solid.

$R_f = 0.34$  (DCM / MeOH, 9 / 1 (v/v)).

#### NMR Spectroscopy:

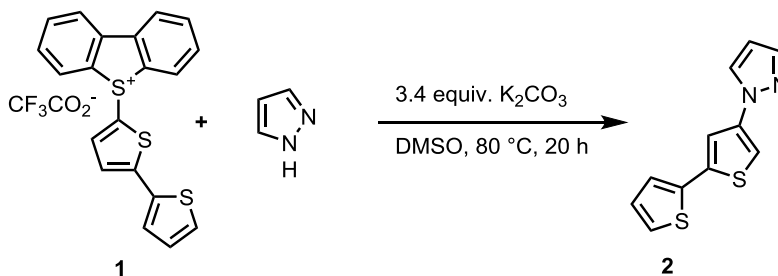
**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.78 (d,  $J = 4.1$  Hz, 1H), 8.43 – 8.39 (m, 2H), 8.11 (dd,  $J = 7.8$ , 1.1 Hz, 2H), 7.84 (ψtd,  $J = 7.6$ , 1.1 Hz, 2H), 7.67 (ddd,  $J = 8.5$ , 7.5, 1.2 Hz, 2H), 7.31 (dd,  $J = 5.0$ , 1.2 Hz, 1H), 7.18 (d,  $J = 4.2$  Hz, 1H), 7.09 (dd,  $J = 3.7$ , 1.2 Hz, 1H), 6.97 (dd,  $J = 5.1$ , 3.7 Hz, 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 149.6, 144.9, 138.2, 134.42, 134.38, 134.2, 131.8, 129.2, 128.5, 128.0, 126.8, 125.1, 123.7, 118.7. C-atoms of the trifluoroacetate ion were not detected.

**$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ):  $-75.0$  (s).

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{20}\text{H}_{13}\text{S}_3^+$   $[\text{M-TFA}]^+$ , 349.0144; found 349.0171; deviation 1.0 ppm.

#### Pyrazole-substituted bithiophene **2**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (250 mg, 0.54 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (250 mg, 1.81 mmol, 3.4 equiv.), pyrazole (100 mg, 1.47 mmol, 2.7 equiv.), and DMSO (10 ml,  $c = 0.054$  M). The vial was sealed, and subsequently stirred for 20 h at  $80$  °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 4 / 1 (v/v)) to afford 117 mg (94 %) of compound **2** as yellowish oil.

$R_f = 0.92$  (hexanes / EtOAc, 1 / 1 (v/v)).

#### NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.82 (dd,  $J = 2.5, 0.5$  Hz, 1H), 7.69 (d,  $J = 1.8$  Hz, 1H), 7.48 (d,  $J = 1.6$  Hz, 1H), 7.27 (dd,  $J = 5.2, 1.2$  Hz, 1H), 7.24 (dd,  $J = 3.6, 1.2$  Hz, 1H), 7.21 (d,  $J = 1.6$  Hz, 1H), 7.04 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.43 (dd,  $J = 2.4, 1.9$  Hz, 1H).

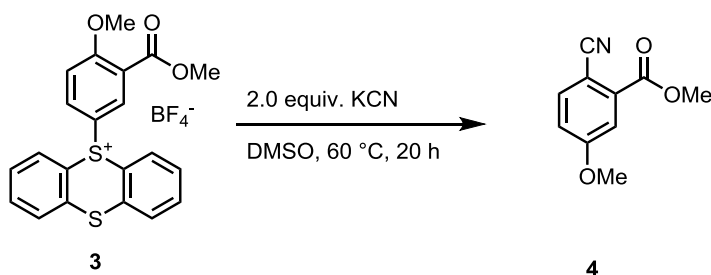
**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 140.7, 139.6, 138.2, 136.6, 127.9, 127.4, 125.2, 124.3, 116.6, 108.9, 107.2.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{S}_2^+ [\text{M}+\text{H}]^+$ , 223.0202; found 223.0200; deviation 0.9 ppm.

### Methoxymethylbenzoate-derived thianthrenium salt **3**

Methoxymethylbenzoate-derived thianthrenium salt was prepared as described previously.<sup>4b</sup>

### Side reaction with the methoxymethylbenzoate-derived thianthrenium salt, compound **4**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 2-methoxymethylbenzoate-derived thianthrenium salt **3** (375 mg, 0.80 mmol, 1.0 equiv.), KCN (104 mg, 1.60 mmol, 2.0 equiv.), and DMSO (10 ml,  $c = 0.08$  M). The vial was sealed, and the reaction mixture was subsequently stirred for 20 h at 60 °C. Subsequently, the reaction mixture was diluted aqueous  $\text{Fe}(\text{OAc})_2$  solution (200 mg  $\text{Fe}(\text{OAc})_2$  in 5 ml  $\text{H}_2\text{O}$ ). The mixture was stirred for 10 min at ambient temperature, and subsequently poured onto a biphasic mixture of EtOAc (150 ml) and water (150 ml). The layers were separated. The aqueous layer was extracted with EtOAc (2  $\times$  50 ml). The combined organic layers were washed with water (50 ml) and subsequently dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (19 / 1 gradient to 3 / 2 (v/v)) to afford 32 mg (21 %) of compound **4** as colorless oil.

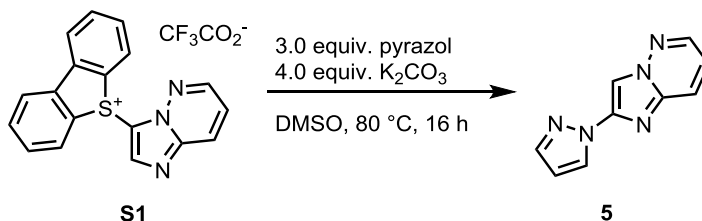
$R_f = 0.41$  (hexanes / EtOAc, 7 / 3 (v/v)).

### NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.70 (d,  $J = 8.6$  Hz, 1H), 7.59 (d,  $J = 2.7$  Hz, 1H), 7.11 (dd,  $J = 8.6, 2.7$  Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H).

**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 164.5, 162.5, 136.4, 134.4, 118.5, 118.0, 116.6, 104.5, 56.0, 53.0.

NMR data of compound **4** match with the NMR data reported in the literature.<sup>18</sup>

**Pyrazol-substituted imidazopyridazine 5 (CCDC 1987150)**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridazine-derived dibenzothiophenium salt **S1** (200 mg, 0.48 mmol, 1.0 equiv.),  $K_2CO_3$  (266 mg, 1.93 mmol, 4.0 equiv.), pyrazol (98 mg, 1.44 mmol, 3.0 equiv.), and DMSO (10 ml,  $c = 0.05$  M). The vial was sealed and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with water (10 ml). The reaction mixture was extracted with EtOAc (4 × 20 ml). The combined organic layers were dried with  $MgSO_4$ , filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 3 (v/v)) to afford 72 mg (80 %) of compound **5** as colorless solid.

$R_f = 0.48$  (hexanes / EtOAc, 4 / 1 (v/v)).

**NMR Spectroscopy:**

**$^1H$  NMR** (500 MHz,  $CDCl_3$ , 298 K,  $\delta$ ): 8.34 (dd,  $J = 2.6, 0.7$  Hz, 1H), 8.31 (dd,  $J = 4.5, 1.6$  Hz, 1H), 8.23 (d,  $J = 0.6$  Hz, 1H), 7.87 (ddd,  $J = 9.2, 1.7, 0.7$  Hz, 1H), 7.75 – 7.72 (m, 1H), 7.06 (dd,  $J = 9.1, 4.5$  Hz, 1H), 6.46 (dd,  $J = 2.5, 1.7$  Hz, 1H).

**$^{13}C$  { $^1H$ } NMR** (126 MHz,  $CDCl_3$ , 298 K,  $\delta$ ): 144.4, 143.2, 142.1, 137.2, 127.4, 124.5, 117.4, 107.5, 104.6.

**HRMS-ESI ( $m/z$ )** calc'd for  $C_9H_8N_5$  [ $M+H$ ] $^+$ , 186.0774; found 186.0773; deviation 0.4 ppm.

**X-ray crystallography:**

Sample preparation: Vapor diffusion technique was used to grow the crystals. Compound **5** (approx. 5mg) was dissolved in 1.5 mL DCM in a 4 mL glass vial. The vial with the solution was placed inside a 20 mL glass vial filled with 3 mL pentane. The 20 ml vial was sealed and the vials were left at ambient temperature for three days to yield the crystals that were used for the analysis.

X-ray measurement:

device: Bruker AXS Enraf-Nonius KappaCCD

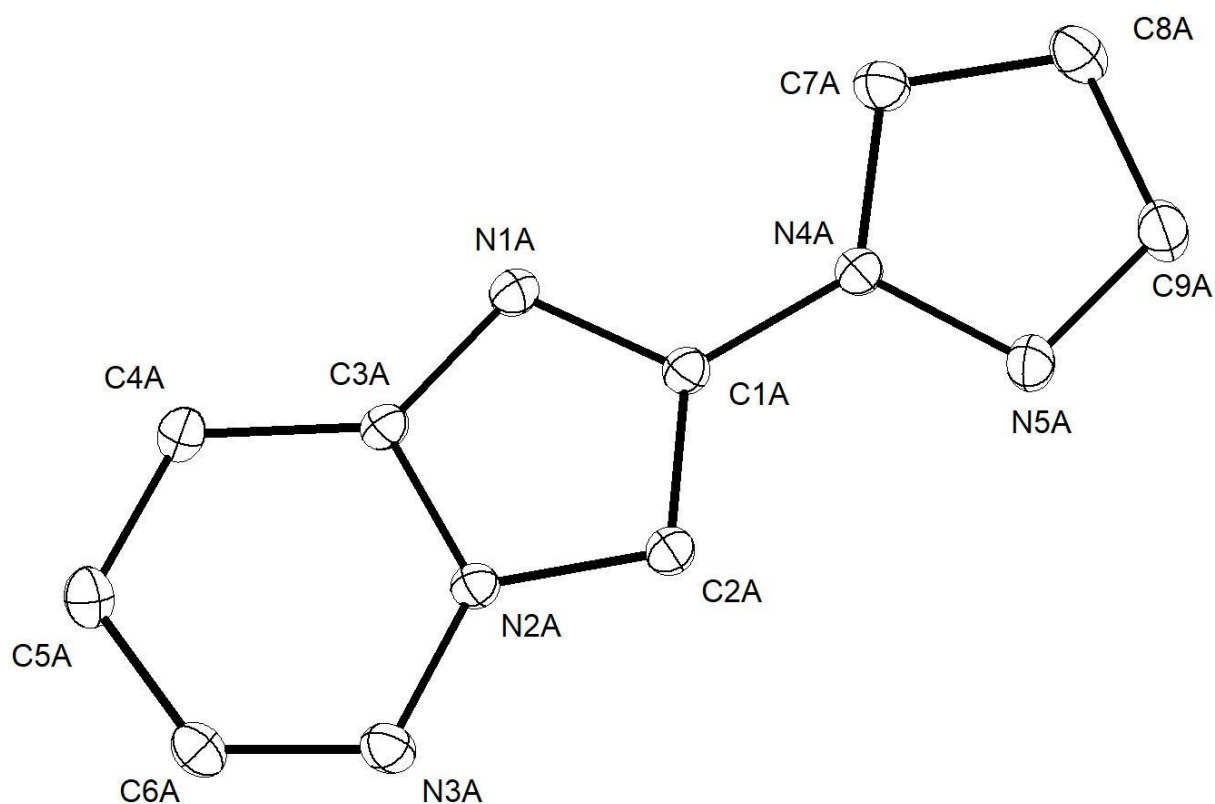
method: CCD f- and w-scans

radiation: Mo-K $\alpha$

wavelength: 0.71073 Å

radiation source: 0.2 × 2 mm $^2$  focus rotating anode

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.



**Fig. S2:** Crystal structure of compound **5**. The nonhydrogen atoms are depicted with 50 % probability ellipsoids.

**Table S3. Crystal data and structure refinement.**

Identification code	12857	
Empirical formula	C <sub>9</sub> H <sub>7</sub> N <sub>5</sub>	
Color	colourless	
Formula weight	185.20 g·mol <sup>-1</sup>	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 <sub>1</sub> /n, (No. 14)	
Unit cell dimensions	<i>a</i> = 5.4868(3) Å	$\alpha = 90^\circ$ .
	<i>b</i> = 13.7279(12) Å	$\beta = 99.788(5)^\circ$ .
	<i>c</i> = 11.0932(7) Å	$\gamma = 90^\circ$ .
Volume	823.40(10) Å <sup>3</sup>	
<i>Z</i>	4	

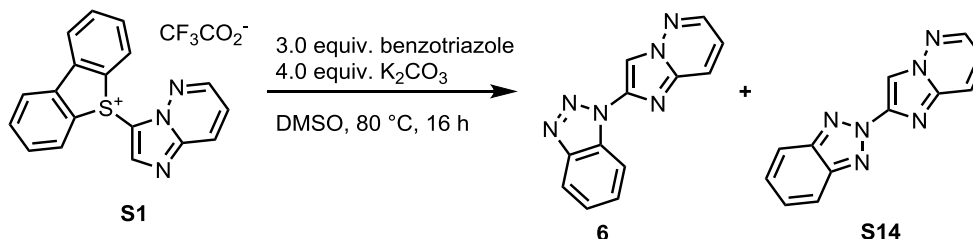
Density (calculated)	1.494 Mg·m <sup>-3</sup>	
Absorption coefficient	0.100 mm <sup>-1</sup>	
F(000)	384 e	
Crystal size	0.37 x 0.3 x 0.17 mm <sup>3</sup>	
θ range for data collection	2.968 to 48.137°.	
Index ranges	-11 ≤ h ≤ 11, -28 ≤ k ≤ 28, -23 ≤ l ≤ 23	
Reflections collected	54162	
Independent reflections	7910 [R <sub>int</sub> = 0.0402]	
Reflections with I>2σ(I)	5629	
Completeness to θ = 25.242°	99.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98426 and 0.96449	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7910 / 0 / 149	
Goodness-of-fit on F <sup>2</sup>	1.049	
Final R indices [I>2σ(I)]	R <sub>1</sub> = 0.0396	wR <sup>2</sup> = 0.1074
R indices (all data)	R <sub>1</sub> = 0.0669	wR <sup>2</sup> = 0.1157
Extinction coefficient	n/a	
Largest diff. peak and hole	0.544 and -0.285 e·Å <sup>-3</sup>	

**Table S4. Bond lengths [Å] and angles [°].**

N(4A)-N(5A)	1.3613(6)	N(4A)-C(7A)	1.3619(6)
N(4A)-C(1A)	1.3942(6)	N(2A)-N(3A)	1.3508(6)
N(2A)-C(3A)	1.3903(6)	N(2A)-C(2A)	1.3718(6)
N(3A)-C(6A)	1.3147(7)	N(5A)-C(9A)	1.3272(7)
N(1A)-C(3A)	1.3369(6)	N(1A)-C(1A)	1.3583(6)
C(6A)-C(5A)	1.4186(7)	C(3A)-C(4A)	1.4096(6)
C(7A)-C(8A)	1.3758(7)	C(5A)-C(4A)	1.3686(7)
C(9A)-C(8A)	1.4134(8)	C(1A)-C(2A)	1.3783(6)
C(1B)-C(2B)	1.330(18)	C(1B)-N(4B)	1.300(14)
C(1B)-N(1B)	1.340(16)	C(3B)-N(2B)	1.3900
C(3B)-C(4B)	1.3900	C(3B)-N(1B)	1.319(13)
N(2B)-N(3B)	1.3900	N(2B)-C(2B)	1.325(15)
N(3B)-C(6B)	1.3900	C(6B)-C(5B)	1.3900
C(5B)-C(4B)	1.3900	N(4B)-C(7B)	1.4200
N(4B)-N(5B)	1.4200	C(7B)-C(8B)	1.4200
C(8B)-C(9B)	1.4200	C(9B)-N(5B)	1.4200
N(5A)-N(4A)-C(7A)	112.70(4)	N(5A)-N(4A)-C(1A)	119.31(4)
C(7A)-N(4A)-C(1A)	127.99(4)	N(3A)-N(2A)-C(3A)	126.50(4)
N(3A)-N(2A)-C(2A)	125.43(4)	C(2A)-N(2A)-C(3A)	108.07(4)
C(6A)-N(3A)-N(2A)	114.07(4)	C(9A)-N(5A)-N(4A)	104.04(4)
C(3A)-N(1A)-C(1A)	104.01(4)	N(3A)-C(6A)-C(5A)	124.95(4)
N(2A)-C(3A)-C(4A)	117.60(4)	N(1A)-C(3A)-N(2A)	110.78(4)
N(1A)-C(3A)-C(4A)	131.60(4)	N(4A)-C(7A)-C(8A)	106.34(5)
C(4A)-C(5A)-C(6A)	119.69(5)	N(5A)-C(9A)-C(8A)	112.20(5)
C(5A)-C(4A)-C(3A)	117.18(5)	N(1A)-C(1A)-N(4A)	120.60(4)
N(1A)-C(1A)-C(2A)	113.67(4)	C(2A)-C(1A)-N(4A)	125.72(4)
N(2A)-C(2A)-C(1A)	103.47(4)	C(7A)-C(8A)-C(9A)	104.73(5)
C(2B)-C(1B)-N(1B)	113.3(12)	N(4B)-C(1B)-C(2B)	123.0(12)
N(4B)-C(1B)-N(1B)	123.8(11)	N(2B)-C(3B)-C(4B)	120.0
N(1B)-C(3B)-N(2B)	107.2(7)	N(1B)-C(3B)-C(4B)	132.8(7)
N(3B)-N(2B)-C(3B)	120.0	C(2B)-N(2B)-C(3B)	109.8(8)
C(2B)-N(2B)-N(3B)	130.2(8)	N(2B)-N(3B)-C(6B)	120.0
C(5B)-C(6B)-N(3B)	120.0	C(6B)-C(5B)-C(4B)	120.0
C(5B)-C(4B)-C(3B)	120.0	N(2B)-C(2B)-C(1B)	104.0(11)

C(1B)-N(4B)-C(7B)	125.2(9)	C(1B)-N(4B)-N(5B)	126.6(9)
C(7B)-N(4B)-N(5B)	108.0	C(8B)-C(7B)-N(4B)	108.0
C(7B)-C(8B)-C(9B)	108.0	N(5B)-C(9B)-C(8B)	108.0
N(4B)-N(5B)-C(9B)	108.0	C(3B)-N(1B)-C(1B)	105.6(10)

### Benzotriazol-substituted imidazopyridazine **6** (CCDC 1987148)



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridazine-derived dibenzothiophenium salt **S1** (200 mg, 0.48 mmol, 1.0 equiv.),  $K_2CO_3$  (266 mg, 1.93 mmol, 4.0 equiv.), benzotriazol (172 mg, 1.44 mmol, 3.0 equiv.), and DMSO (10 ml,  $c = 0.05$  M). The vial was sealed and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with water (10 ml). The reaction mixture was extracted with EtOAc (4 × 20 ml). The combined organic layers were dried with  $MgSO_4$ , filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 7 / 13 (v/v)) to afford 75 mg (66 %) of compound **6** as colorless solid and 10 mg (9 %) of compound **S14** as colorless solid.

Compound **S14**:

$R_f = 0.37$  (hexanes / EtOAc, 4 / 1 (v/v)).

#### NMR Spectroscopy:

$^1H$  NMR (500 MHz,  $CDCl_3$ , 298 K,  $\delta$ ): 8.62 (d,  $J = 0.6$  Hz, 1H), 8.42 (dd,  $J = 4.5, 1.6$  Hz, 1H), 8.08 – 8.03 (m, 1H), 7.96 (dd,  $J = 6.6, 3.1$  Hz, 2H), 7.45 (dd,  $J = 6.7, 3.0$  Hz, 2H), 7.18 (dd,  $J = 9.2, 4.5$  Hz, 1H).

$^{13}C$  { $^1H$ } NMR (126 MHz,  $CDCl_3$ , 298 K,  $\delta$ ): 145.3, 144.2, 137.8, 127.7, 125.9, 118.6, 118.4, 107.8. One C-atom not detected.

HRMS-ESI ( $m/z$ ) calc'd for  $C_{12}H_9N_6$   $[M+H]^+$ , 237.0883; found 237.0881; deviation 0.8 ppm.

Compound **6**:

$R_f = 0.73$  (hexanes / EtOAc, 4 / 1 (v/v)).

#### NMR Spectroscopy:

$^1H$  NMR (500 MHz,  $CDCl_3$ , 298 K,  $\delta$ ): 8.57 (d,  $J = 0.6$  Hz, 1H), 8.55 (dt,  $J = 8.4, 1.0$  Hz, 1H), 8.43 (dd,  $J = 4.5, 1.6$  Hz, 1H), 8.15 (dt,  $J = 8.4, 1.0$  Hz, 1H), 8.04 (ddd,  $J = 9.2, 1.7, 0.7$  Hz, 1H), 7.64 (ddd,  $J = 8.2, 7.0, 1.0$  Hz, 1H), 7.47 (ddd,  $J = 8.1, 7.0, 1.0$  Hz, 1H), 7.18 (dd,  $J = 9.2, 4.5$  Hz, 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 146.2, 143.7, 141.9, 137.3, 131.7, 128.8, 125.1, 124.9, 119.8, 117.7, 113.0, 106.2.

**HRMS-EI (m/z)** calc'd for  $\text{C}_{12}\text{H}_9\text{N}_6$   $[\text{M}+\text{H}]^+$ , 237.0883; found 237.0880; deviation 1.4 ppm.

**X-ray crystallography:**

Sample preparation: Vapor diffusion technique was used to grow the crystals. Compound **6** (approx. 5mg) was dissolved in 1.5 mL DCM in a 4 mL glass vial. The vial with the solution was placed inside a 20 mL glass vial filled with 3 mL pentane. The 20 mL vial was sealed and the vials were left at ambient temperature for three days to yield the crystals that were used for the analysis.

X-ray measurement:

device: Bruker AXS Enraf-Nonius KappaCCD

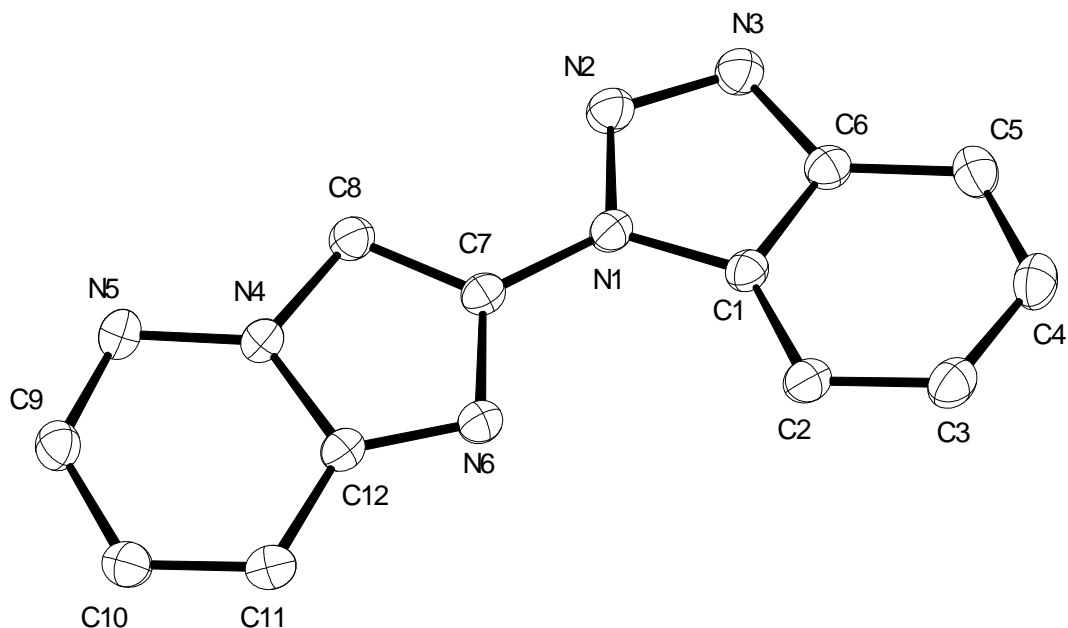
method: CCD f- and w-scans

radiation: Mo-K $\alpha$

wavelength: 0.71073 Å

radiation source: 0.2 x 2 mm<sup>2</sup> focus rotating anode

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.



**Fig. S3:** Crystal structure of compound **6**. The nonhydrogen atoms are depicted with 50 % probability ellipsoids.

**Table S5. Crystal data and structure refinement.**

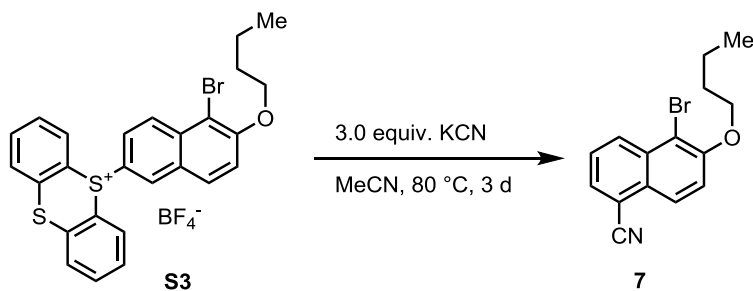
Identification code	12856
Empirical formula	C <sub>12</sub> H <sub>8</sub> N <sub>6</sub>
Color	colourless
Formula weight	236.24 g · mol <sup>-1</sup>
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	MONOCLINIC
Space group	<b>P2<sub>1</sub>/n, (no. 14)</b>
Unit cell dimensions	$a = 8.5333(6)$ Å $\alpha = 90^\circ$ .

	$b = 11.275(3) \text{ \AA}$	$\beta = 90.422(10)^\circ$ .
	$c = 10.7791(16) \text{ \AA}$	$\gamma = 90^\circ$ .
Volume	$1037.1(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.513 \text{ Mg} \cdot \text{m}^{-3}$	
Absorption coefficient	$0.101 \text{ mm}^{-1}$	
F(000)	488 e	
Crystal size	$0.40 \times 0.33 \times 0.16 \text{ mm}^3$	
$\theta$ range for data collection	$2.614$ to $33.203^\circ$ .	
Index ranges	$-13 \leq h \leq 12$ , $-17 \leq k \leq 17$ , $-16 \leq l \leq 16$	
Reflections collected	22379	
Independent reflections	3956 [ $R_{\text{int}} = 0.0646$ ]	
Reflections with $I > 2\sigma(I)$	3019	
Completeness to $\theta = 25.242^\circ$	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.96	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3956 / 0 / 164	
Goodness-of-fit on $F^2$	1.057	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0487$	$wR^2 = 0.1343$
R indices (all data)	$R_1 = 0.0683$	$wR^2 = 0.1453$
Extinction coefficient	$0.054(11)$	
Largest diff. peak and hole	$0.5$ and $-0.5 \text{ e} \cdot \text{\AA}^{-3}$	

**Table S6. Bond lengths [Å] and angles [°].**

N(1)-N(2)	1.3712(11)	N(1)-C(1)	1.3746(12)
N(1)-C(7)	1.4040(13)	N(2)-N(3)	1.3021(12)
N(3)-C(6)	1.3828(13)	N(4)-N(5)	1.3572(12)
N(4)-C(8)	1.3728(13)	N(4)-C(12)	1.3908(12)
N(5)-C(9)	1.3153(14)	N(6)-C(7)	1.3611(13)
N(6)-C(12)	1.3393(13)	C(1)-C(2)	1.4023(14)
C(1)-C(6)	1.4026(14)	C(2)-C(3)	1.3808(15)
C(3)-C(4)	1.4142(16)	C(4)-C(5)	1.3829(16)
C(5)-C(6)	1.4063(14)	C(7)-C(8)	1.3778(14)
C(9)-C(10)	1.4161(15)	C(10)-C(11)	1.3679(15)
C(11)-C(12)	1.4121(14)		
N(2)-N(1)-C(1)	110.16(8)	N(2)-N(1)-C(7)	119.05(8)
C(1)-N(1)-C(7)	130.77(8)	N(3)-N(2)-N(1)	108.97(8)
N(2)-N(3)-C(6)	108.26(8)	N(5)-N(4)-C(8)	125.15(9)
N(5)-N(4)-C(12)	126.82(9)	C(8)-N(4)-C(12)	108.02(8)
C(9)-N(5)-N(4)	113.41(9)	C(12)-N(6)-C(7)	103.85(8)
N(1)-C(1)-C(2)	133.99(9)	N(1)-C(1)-C(6)	103.51(8)
C(2)-C(1)-C(6)	122.49(9)	C(3)-C(2)-C(1)	115.60(10)
C(2)-C(3)-C(4)	122.70(10)	C(5)-C(4)-C(3)	121.43(10)
C(4)-C(5)-C(6)	116.72(10)	N(3)-C(6)-C(1)	109.10(9)
N(3)-C(6)-C(5)	129.86(10)	C(1)-C(6)-C(5)	121.04(9)
N(6)-C(7)-N(1)	120.61(9)	N(6)-C(7)-C(8)	113.71(9)
C(8)-C(7)-N(1)	125.67(9)	N(4)-C(8)-C(7)	103.54(9)
N(5)-C(9)-C(10)	125.50(10)	C(11)-C(10)-C(9)	119.60(10)
C(10)-C(11)-C(12)	117.30(10)	N(4)-C(12)-C(11)	117.36(9)
N(6)-C(12)-N(4)	110.86(8)	N(6)-C(12)-C(11)	131.76(9)

### Cyano-substituted bromobutoxynaphthalene **7**



Under an ambient atmosphere, a 25 ml round bottom flask equipped with a teflon coated stir bar and a reflux condenser was charged with bromobutoxynaphthalene-derived thianthrenium salt **S3** (200 mg, 0.34 mmol, 1.0 equiv.), KCN (67 mg, 1.0 mmol, 3.0 equiv.), and MeCN (5 ml,  $c = 0.05$  M). The reaction mixture was stirred at 80 °C for 3 d. The solvent was removed under reduced pressure. The residue was dissolved in a biphasic mixture of water (5 ml) and EtOAc (5 ml). The layers were separated. The organic layer was washed with aqueous  $\text{FeSO}_4$  solution (10 ml, 0.1 M). The organic layer was dried with  $\text{MgSO}_4$ , filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 10 / 1 (v/v)) to afford 75.5 mg (72 %) of compound **7** as colorless solid.

$R_f = 0.37$  (hexanes / EtOAc, 10 / 1 (v/v)).

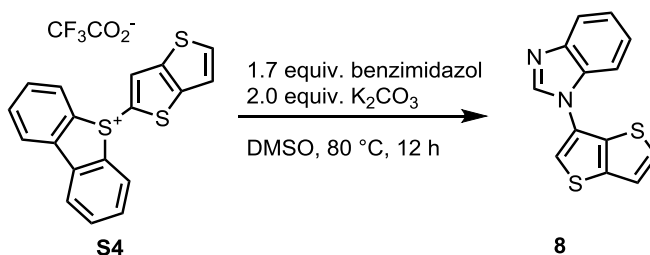
#### NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.48 (dt,  $J = 8.7, 1.0$  Hz, 1H), 8.19 (dd,  $J = 9.1, 0.9$  Hz, 1H), 7.81 (dd,  $J = 7.1, 1.1$  Hz, 1H), 7.58 (dd,  $J = 8.7, 7.1$  Hz, 1H), 7.43 (d,  $J = 9.1$  Hz, 1H), 4.23 (t,  $J = 6.4$  Hz, 2H), 1.94 – 1.84 (m, 2H), 1.67 – 1.54 (m, 3H), 1.02 (t,  $J = 7.4$  Hz, 3H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 154.8, 133.1, 131.7, 131.0, 128.5, 126.7, 126.1, 117.8, 117.1, 110.5, 110.0, 70.0, 31.5, 19.4, 14.0.

**HRMS-Cl** ( $m/z$ ) calc'd for  $\text{C}_{15}\text{H}_{14}\text{NOBr}$  [ $\text{M}]^+$ , 303.0253; found 303.0257; deviation 1.1 ppm.

### Benzimidazol-substituted thienothiophene **8** (CCDC 1987147)



Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt **S4** (100 mg, 0.229 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (63 mg, 0.46 mmol, 2.0 equiv.), benzimidazol (47 mg, 0.40 mmol, 1.7 equiv.), and DMSO (1.5 ml,  $c = 0.15$  M). The

vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was directly loaded onto a column of silica gel and purified by chromatography eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 45 mg (78 %) of compound **8** as colorless solid.

$R_f = 0.39$  (hexanes / EtOAc, 1 / 1 (v/v)).

**NMR Spectroscopy:**

**$^1\text{H}$  NMR** (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.30 (s, 1H), 7.83 – 7.78 (m, 1H), 7.72 (d,  $J = 1.6$  Hz, 1H), 7.61 (dd,  $J = 5.2, 1.5$  Hz, 1H), 7.58 – 7.53 (m, 1H), 7.45 (d,  $J = 5.2$  Hz, 1H), 7.39 – 7.33 (m, 2H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 144.7, 143.7, 140.7, 135.0, 134.4, 129.9, 128.0, 124.7, 123.9, 121.7, 121.5, 121.2, 112.1.

**HRMS-EI (m/z)** calc'd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{S}_2^+$  [ $\text{M}$ ] $^+$ , 256.0123; found 256.0125; deviation 0.5 ppm.

**X-ray crystallography:**

Sample preparation: Compound **8** was dissolved in warm acetone in a 4 ml vial. The open vial was left standing for 1 d at ambient temperature, resulting in the formation of colorless crystals.

X-ray measurement:

device: Bruker-AXS Kappa Mach3 APEX-II

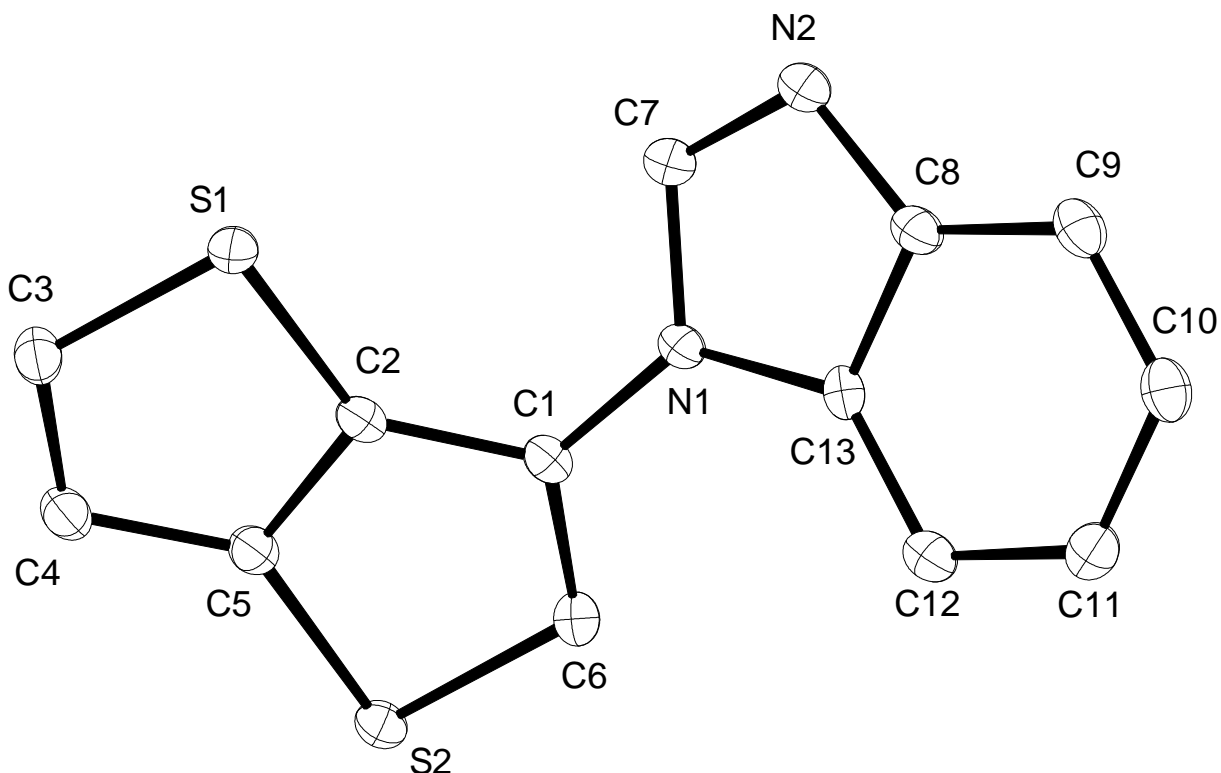
method: 'CCD f- and w-scans

radiation: Cu-K $\alpha$

wavelength: 1.54178 Å

radiation source: 0.2 x 2 mm $^2$  focus rotating anode

Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75.



**Fig. S4:** Crystal structure of compound **8**. The nonhydrogen atoms are depicted with 50 % probability ellipsoids.

**Table S7. Crystal data and structure refinement.**

Identification code	12773
Empirical formula	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>
Color	colourless
Formula weight	256.33 g · mol <sup>-1</sup>
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	TRICLINIC
Space group	<b>P1, (no. 2)</b>
Unit cell dimensions	$a = 3.86470(10)$ Å $\alpha = 89.7700(10)^\circ$ .

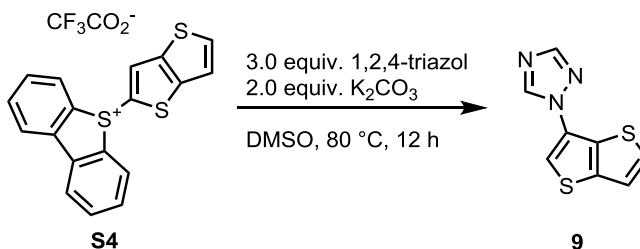
	$b = 9.8913(3) \text{ \AA}$	$\beta = 87.9850(10)^\circ$ .
	$c = 14.0495(4) \text{ \AA}$	$\gamma = 85.984(2)^\circ$ .
Volume	$535.42(3) \text{ \AA}^3$	
Z	2	
Density (calculated)	$1.590 \text{ Mg} \cdot \text{m}^{-3}$	
Absorption coefficient	$4.281 \text{ mm}^{-1}$	
F(000)	264 e	
Crystal size	$0.183 \times 0.101 \times 0.031 \text{ mm}^3$	
$\theta$ range for data collection	$3.147$ to $72.410^\circ$ .	
Index ranges	$-4 \leq h \leq 4$ , $-12 \leq k \leq 11$ , $-17 \leq l \leq 17$	
Reflections collected	19864	
Independent reflections	1985 [ $R_{\text{int}} = 0.0399$ ]	
Reflections with $I > 2\sigma(I)$	1740	
Completeness to $\theta = 67.679^\circ$	95.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.90 and 0.62	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	1985 / 0 / 154	
Goodness-of-fit on $F^2$	1.218	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0364$	$wR^2 = 0.0947$
R indices (all data)	$R_1 = 0.0414$	$wR^2 = 0.0963$
Largest diff. peak and hole	$0.4$ and $-0.4 \text{ e} \cdot \text{\AA}^{-3}$	

**Table S8. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].**

S(1)-C(2)	1.726(2)	S(1)-C(3)	1.730(2)
S(2)-C(5)	1.729(2)	S(2)-C(6)	1.724(2)
N(1)-C(1)	1.411(3)	N(1)-C(7)	1.381(3)

N(1)-C(13)	1.396(3)	N(2)-C(7)	1.303(3)
N(2)-C(8)	1.396(3)	C(1)-C(2)	1.426(3)
C(1)-C(6)	1.362(3)	C(2)-C(5)	1.385(3)
C(3)-C(4)	1.356(3)	C(4)-C(5)	1.427(3)
C(8)-C(9)	1.393(3)	C(8)-C(13)	1.406(3)
C(9)-C(10)	1.386(3)	C(10)-C(11)	1.402(3)
C(11)-C(12)	1.388(3)	C(12)-C(13)	1.395(3)
C(2)-S(1)-C(3)	90.93(10)	C(6)-S(2)-C(5)	91.34(10)
C(7)-N(1)-C(1)	125.40(18)	C(7)-N(1)-C(13)	105.65(17)
C(13)-N(1)-C(1)	128.76(17)	C(7)-N(2)-C(8)	104.54(17)
N(1)-C(1)-C(2)	122.89(18)	C(6)-C(1)-N(1)	125.56(19)
C(6)-C(1)-C(2)	111.54(19)	C(1)-C(2)-S(1)	136.07(17)
C(5)-C(2)-S(1)	110.78(16)	C(5)-C(2)-C(1)	113.12(19)
C(4)-C(3)-S(1)	113.84(17)	C(3)-C(4)-C(5)	110.6(2)
C(2)-C(5)-S(2)	110.98(16)	C(2)-C(5)-C(4)	113.87(19)
C(4)-C(5)-S(2)	135.12(17)	C(1)-C(6)-S(2)	113.01(16)
N(2)-C(7)-N(1)	114.33(19)	N(2)-C(8)-C(13)	110.36(18)
C(9)-C(8)-N(2)	129.31(19)	C(9)-C(8)-C(13)	120.33(19)
C(10)-C(9)-C(8)	118.0(2)	C(9)-C(10)-C(11)	121.0(2)
C(12)-C(11)-C(10)	122.0(2)	C(11)-C(12)-C(13)	116.5(2)
N(1)-C(13)-C(8)	105.11(17)	C(12)-C(13)-N(1)	132.7(2)
C(12)-C(13)-C(8)	122.15(19)		

### Triazol-substituted thienothiophene **9**



Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt **S4** (100 mg, 0.229 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (63 mg, 0.46 mmol, 2.0 equiv.), 1,2,4-triazol (48 mg, 0.69 mmol, 3.0 equiv.), and DMSO (1.5 ml,  $c = 0.15 \text{ M}$ ). The vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was directly loaded onto a column of silica gel and purified by chromatography eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 34 mg (72 %) of compound **9** as green solid.

$R_f = 0.36$  (hexanes / EtOAc, 1 / 1 (v/v)).

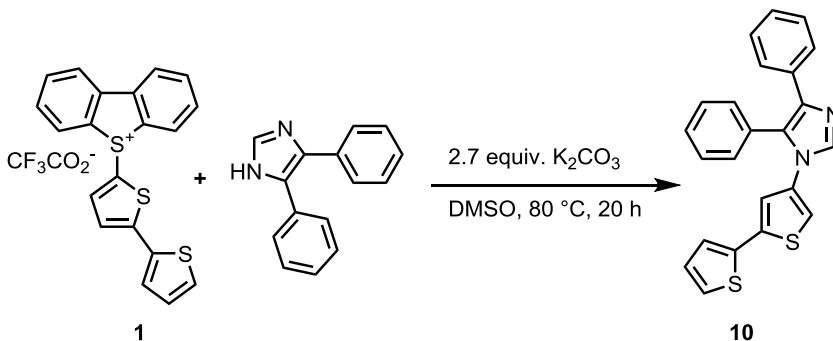
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.83 (s, 1H), 8.12 (s, 1H), 7.71 (d,  $J = 1.5$  Hz, 1H), 7.62 (dd,  $J = 5.3, 1.6$  Hz, 1H), 7.38 (d,  $J = 5.3$  Hz, 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 152.7, 142.9, 140.4, 132.4, 131.0, 129.5, 121.0, 118.3.

HRMS-EI ( $m/z$ ) calc'd for  $\text{C}_8\text{H}_5\text{N}_3\text{S}_2^+ [\text{M}]^+$ , 206.9919; found 206.9923; deviation 1.9 ppm.

#### Diphenylimidazole-substituted bithiophene 10



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (250 mg, 0.54 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (200 mg, 1.45 mmol, 2.7 equiv.), diphenylimidazole (250 mg, 1.14 mmol, 2.1 equiv.), and DMSO (10 ml,  $c = 0.054$  M). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (7 / 3 gradient to 0 / 1 (v/v)) to afford 189 mg (91 %) of compound **10** as colorless solid.

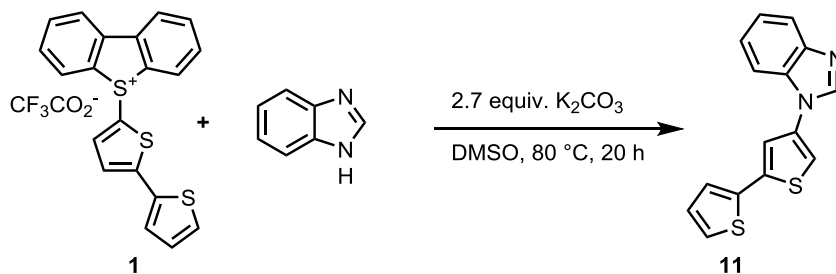
$R_f = 0.51$  (hexanes / EtOAc, 1 / 1 (v/v)).

#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.13 (s, 1H), 7.52 (dd,  $J = 5.1, 1.2$  Hz, 1H), 7.47 – 7.40 (m, 5H), 7.34 – 7.30 (m, 3H), 7.27 – 7.22 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 (d,  $J = 1.6$  Hz, 1H), 7.07 (dd,  $J = 5.1, 3.6$  Hz, 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 138.3, 137.9, 136.8, 136.0, 134.84, 134.81, 131.3, 130.5, 129.31, 129.26, 129.0, 128.9, 128.64, 128.55, 127.0, 126.8, 125.1, 121.5, 118.6.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{S}_2^+ [\text{M}+\text{H}]^+$ , 385.0828; found 385.0825; deviation 0.8 ppm.

Benzimidazole-substituted bithiophene **11**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (250 mg, 0.54 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (200 mg, 1.45 mmol, 2.7 equiv.), benzimidazole (200 mg, 1.69 mmol, 3.1 equiv.), and DMSO (10 ml,  $c = 0.054 \text{ M}$ ). The vial was sealed, and subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (20 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). Subsequently, the combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (7 / 3 gradient to 0 / 1 (v/v)) to afford 133 mg (88 %) of compound **11** as yellowish oil.

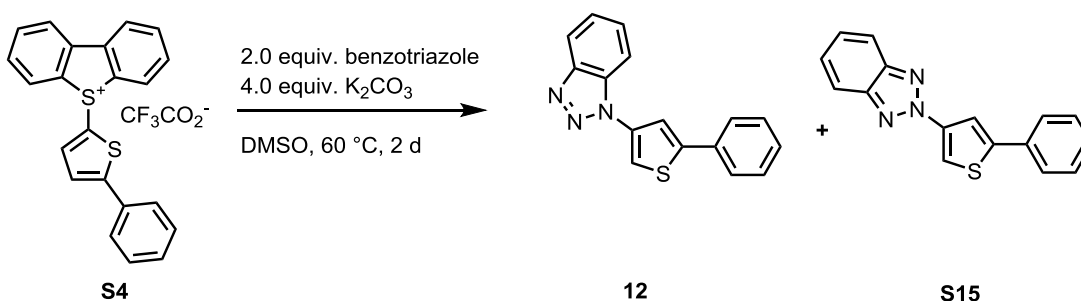
$R_f = 0.39$  (hexanes / EtOAc, 1 / 1 (v/v)).

## NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.19 (s, 1H), 7.91 – 7.86 (m, 1H), 7.62 – 7.57 (m, 1H), 7.38 – 7.35 (m, 2H), 7.35 (d,  $J = 1.6 \text{ Hz}$ , 1H), 7.31 (dd,  $J = 5.1, 1.2 \text{ Hz}$ , 1H), 7.29 – 7.27 (m, 2H), 7.07 (dd,  $J = 5.1, 3.6 \text{ Hz}$ , 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 143.3, 142.1, 139.2, 136.2, 134.7, 133.6, 128.2, 125.8, 124.9, 124.2, 123.3, 120.6, 119.2, 115.3, 110.8.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{15}\text{H}_{11}\text{N}_2\text{S}_2^+$  [ $\text{M}+\text{H}$ ] $^+$ , 283.0358; found 283.0357; deviation 0.5 ppm.

Benzotriazole-substituted 2-phenylthiophene **12**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 2-phenylthiophene-derived dibenzothiophenium salt **S4** (150 mg, 0.33 mmol, 1.0 equiv.), benzotriazole (78 mg,

0.66 mmol, 2.0 equiv.),  $\text{K}_2\text{CO}_3$  (132 mg, 1.31 mmol, 4.0 equiv.), and DMSO (5 ml,  $c = 0.07 \text{ M}$ ). The vial was sealed, and subsequently stirred for 2 d at  $60^\circ\text{C}$ . Subsequently, the reaction mixture was diluted with EtOAc (30 ml) and washed with water (70 ml). The aqueous layer was extracted with EtOAc ( $2 \times 10 \text{ ml}$ ). The combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 4 / 1 (v/v)) to afford 50 mg (55 %) of compound **12** as colorless crystals. A second fraction, which based on  $^1\text{H}$  NMR spectroscopy is assumed to be 2-(5-phenylthiophen-3-yl)-2H-benzo[d][1,2,3]triazole (**S15**), was also obtained, but not in pure form.

$R_f = 0.65$  (hexanes / EtOAc, 7 / 3 (v/v)).

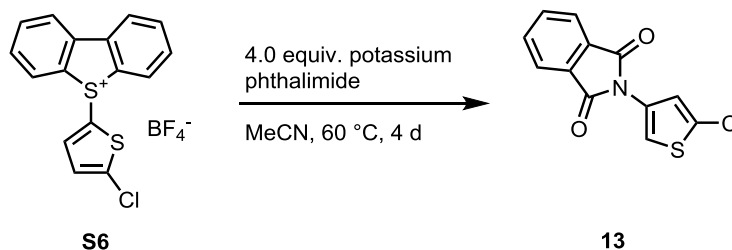
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.16 (d,  $J = 8.4 \text{ Hz}$ , 1H), 7.84 – 7.78 (m, 2H), 7.71 – 7.67 (m, 2H), 7.63 – 7.56 (m, 2H), 7.49 – 7.42 (m, 3H), 7.40 – 7.35 (m, 1H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 146.3, 146.0, 135.8, 133.4, 132.2, 129.3, 128.7, 128.6, 126.0, 124.6, 120.6, 118.1, 114.3, 110.5.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{16}\text{H}_{12}\text{N}_3\text{S}^+ [\text{M}+\text{H}]^+$ , 278.0746; found 278.0743; deviation 1.4 ppm.

#### Phthalimide-substituted 2-chlorothiophene 13



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with chlorothiophene-derived dibenzothiophenium salt **S6** (200 mg, 0.51 mmol, 1.0 equiv.), potassium phthalimide (381 mg, 2.06 mmol, 4.0 equiv.), and MeCN (5 ml,  $c = 0.1 \text{ M}$ ). The vial was sealed, and subsequently the mixture was stirred for 4 d at  $60^\circ\text{C}$ . Subsequently, the reaction mixture diluted with EtOAc (35 ml) and washed with water ( $2 \times 20 \text{ ml}$ ) and brine ( $1 \times 10 \text{ ml}$ ). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 7 / 3 (v/v)) to afford 80 mg (59 %) of compound **13** as colorless crystals.

$R_f = 0.66$  (hexanes / EtOAc, 7 / 3 (v/v)).

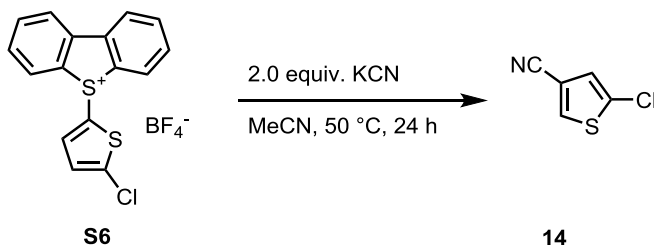
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.93 (dd,  $J = 5.5, 3.0 \text{ Hz}$ , 2H), 7.79 (dd,  $J = 5.5, 3.0 \text{ Hz}$ , 2H), 7.50 (d,  $J = 1.8 \text{ Hz}$ , 1H), 7.47 (d,  $J = 1.8 \text{ Hz}$ , 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 166.5, 134.8, 131.6, 130.2, 128.8, 124.0, 122.4, 116.1.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{12}\text{H}_6\text{NO}_2\text{SClNa}^+$   $[\text{M}+\text{Na}]^+$ , 285.97000; found 285.9698; deviation 0.9 ppm.

#### Cyano-substituted 2-chlorothiophene 14



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with chlorothiophene-derived dibenzothiophenium salt **S6** (500 mg, 1.29 mmol, 1.00 equiv.), KCN (168 mg, 2.57 mmol, 2.00 equiv.), and MeCN (10 ml,  $c = 0.13$  M). The vial was sealed, and stirred for 24 h at 50 °C. Subsequently, the reaction mixture was poured onto an aqueous solution of iron(II) acetate (0.2 g in 100 ml water). The mixture was extracted with EtOAc (30 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 3 / 1 (v/v)) to afford 111 mg (60 %) of compound **14** as colorless oil, which crystallized after several days.

$R_f = 0.79$  (hexanes / EtOAc, 7 / 3 (v/v)).

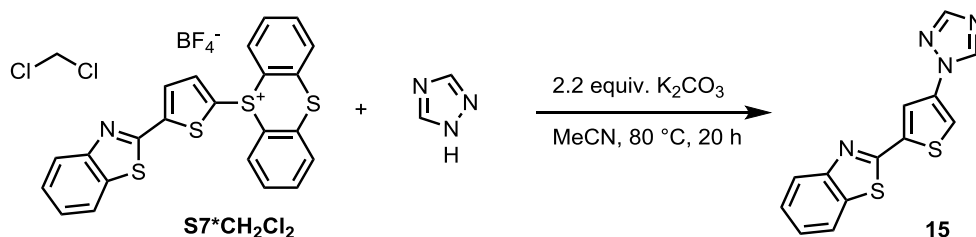
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.72 (d,  $J = 1.5$  Hz, 1H), 7.12 (d,  $J = 1.5$  Hz, 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 134.2, 132.7, 127.1, 114.2, 110.5.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_5\text{H}_2\text{NSClNa}^+$   $[\text{M}+\text{Na}]^+$ , 165.9489; found 165.9490; deviation 0.7 ppm.

#### Triazol-substituted 2-benzothiazolo thiophene 15



Under an ambient atmosphere, a 20 ml glass-vial was charged with thianthrenium salt **S7\*CH<sub>2</sub>Cl<sub>2</sub>** (200 mg, 0.33 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (100 mg, 0.72 mmol, 2.2 equiv.), 1,2,4-triazole (50 mg, 0.72 mmol, 2.2 equiv.), and MeCN (10 ml,  $c = 0.033$  M). The vial was sealed, and the reaction mixture was subsequently stirred for 20 h at 80 °C. Subsequently, the reaction mixture was allowed to cool to 25 °C, and filtered through a thin layer of silica gel. The solvent was removed, and the residue was purified by column chromatography on

silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 7 / 13 (v/v)) to afford 84 mg (89 %) of compound **15** as yellow solid.

$R_f = 0.22$  (hexanes / EtOAc, 1 / 1 (v/v)).

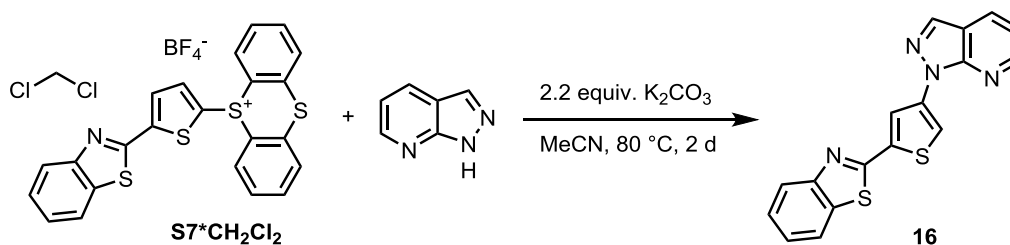
#### NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.54 (s, 1H), 8.11 (s, 1H), 8.06 (dt,  $J = 8.3, 0.8$  Hz, 1H), 7.92 – 7.87 (m, 2H), 7.63 (d,  $J = 1.5$  Hz, 1H), 7.52 (ddd,  $J = 8.3, 7.1, 1.2$  Hz, 1H), 7.42 (ddd,  $J = 8.2, 7.1, 1.2$  Hz, 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 159.9, 153.6, 152.6, 141.3, 139.0, 136.1, 135.0, 127.0, 126.0, 123.5, 121.8, 120.6, 116.5.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{13}\text{H}_9\text{N}_4\text{S}_2^+$  [ $\text{M}+\text{H}$ ] $^+$ , 285.0263; found 285.0260; deviation 1.2 ppm.

#### Pyrazolopyridinyl-substituted 2-benzothiazolo thiophene **16**



Under an ambient atmosphere, a 20 ml glass-vial was charged with thianthrenium salt **S7\*CH<sub>2</sub>Cl<sub>2</sub>** (200 mg, 0.33 mmol, 1.0 equiv.),  $\text{K}_2\text{CO}_3$  (100 mg, 0.72 mmol, 2.2 equiv.), pyrazolopyridine (100 mg, 0.84 mmol, 2.5 equiv.), and MeCN (10 ml,  $c = 0.033$  M). The vial was sealed, and the reaction mixture was subsequently stirred for 2 d at 80 °C. Subsequently, the reaction mixture was allowed to cool to 25 °C, and filtered through a thin layer of silica gel. The solvent was removed, and the residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 4 / 1 (v/v)) to afford 29 mg (26 %) of compound **16** as yellow solid (> 95 % purity). A sample was further purified by column chromatography on silica gel eluting with DCM / EtOAc, which was used for the acquisition of the  $^1\text{H}$  NMR spectrum.

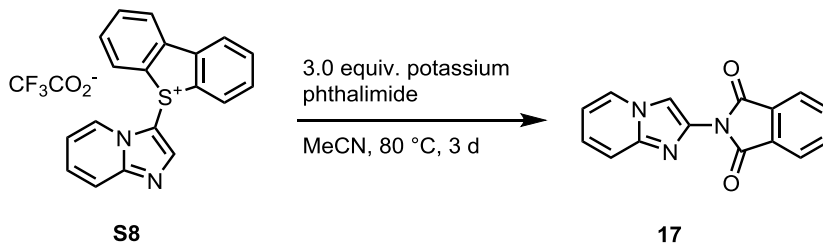
$R_f = 0.66$  (hexanes / EtOAc, 1 / 1 (v/v)).

#### NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.68 (dd,  $J = 4.5, 1.6$  Hz, 1H), 8.51 (d,  $J = 1.4$  Hz, 1H), 8.33 (d,  $J = 1.5$  Hz, 1H), 8.18 (s, 1H), 8.14 (dd,  $J = 8.0, 1.6$  Hz, 1H), 8.14 (dd,  $J = 8.0, 1.6$  Hz, 1H), 8.06 (d,  $J = 8.3$  Hz, 1H), 7.88 (ddd,  $J = 8.0, 1.2, 0.6$  Hz, 1H), 7.49 (ddd,  $J = 8.3, 7.2, 1.2$  Hz, 1H), 7.39 (ddd,  $J = 8.2, 7.2, 1.2$  Hz, 1H), 7.25 (dd,  $J = 8.0, 4.5$  Hz, 1H).

**$^{13}\text{C}$  { $^1\text{H}$ } NMR** (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 161.3, 153.6, 149.71, 149.65, 138.4, 136.7, 135.0, 134.1, 130.5, 126.7, 125.6, 123.2, 122.3, 121.7, 118.1, 116.9, 114.8.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{17}\text{H}_{11}\text{N}_4\text{S}_2^+$  [ $\text{M}+\text{H}$ ] $^+$ , 335.0420; found 335.0415; deviation 1.3 ppm.

Phthalimide-substituted imidazopyridine **17**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine-derived dibenzothiophenium salt **S8** (200 mg, 0.48 mmol, 1.0 equiv.), potassium phthalimide (268 mg, 1.45 mmol, 3.0 equiv.), and MeCN (10 ml,  $c = 0.05$  M). The vial was sealed, and subsequently stirred for 3 d at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (60 ml) and washed with water (50 ml). The aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 3 / 2 (v/v)) to afford 37 mg (29 %) of compound **17** as yellow crystals.

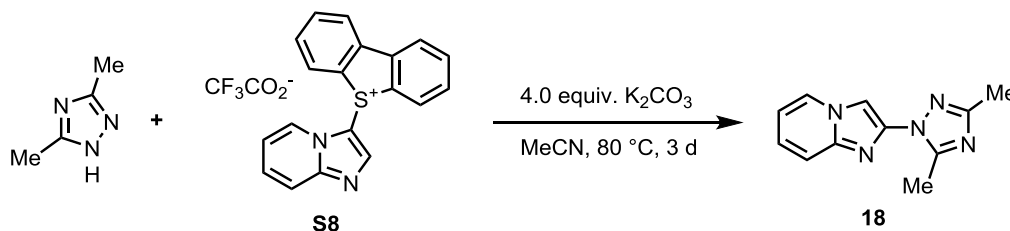
$R_f = 0.50$  (EtOAc).

## NMR Spectroscopy:

**$^1\text{H}$  NMR** (500 MHz,  $\text{DMSO}-d_6$ , 298 K,  $\delta$ ): 8.66 (d,  $J = 6.7$  Hz, 1H), 8.14 (s, 1H), 8.00 (dd,  $J = 5.5, 3.0$  Hz, 2H), 7.93 (dd,  $J = 5.5, 3.1$  Hz, 2H), 7.62 (d,  $J = 9.0$  Hz, 1H), 7.35 (ddd,  $J = 9.1, 6.8, 1.3$  Hz, 1H), 7.01 ( $\psi$ td,  $J = 6.8, 0.9$  Hz, 1H).

**$^{13}\text{C}$   $\{^1\text{H}\}$  NMR** (126 MHz,  $\text{DMSO}-d_6$ , 298 K,  $\delta$ ): 166.6, 143 (only visible in HMBC spectrum), 135.0, 133.9, 131.4, 127.2, 125.4, 123.6, 116.8, 112.8, 109.2.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{15}\text{H}_{10}\text{N}_3\text{O}_2^+$   $[\text{M}+\text{H}]^+$ , 264.0768; found 264.0765; deviation 1.1 ppm.

Dimethyltriazol-substituted imidazopyridine **18**

Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with imidazopyridine-derived dibenzothiophenium salt **S8** (200 mg, 0.48 mmol, 1.0 equiv.), potassium carbonate (266 mg, 1.93 mmol, 4.0 equiv.), dimethyltriazol (141 mg, 1.45 mmol, 3.0 equiv.), and MeCN (10 ml,  $c = 0.05$  M). The vial was sealed, and subsequently stirred for 3 d at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (30 ml) and washed with water (100 ml). The aqueous layer was extracted with EtOAc (2

× 20 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 1 gradient to 0 / 1 (v/v)) to afford 69 mg (67 %) of compound **18** as light green solid.

$R_f = 0.17$  (EtOAc).

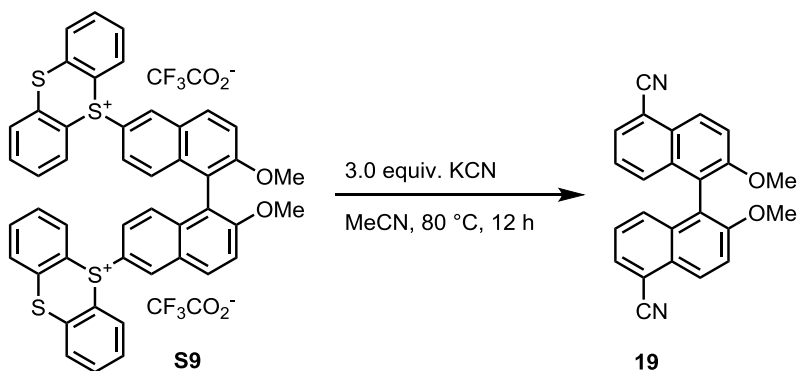
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 8.13 (d,  $J = 6.7$  Hz, 1H), 7.78 (bs, 1H), 7.59 (dd,  $J = 9.0, 1.0$  Hz, 1H), 7.25 (ddd,  $J = 9.1, 6.8, 1.2$  Hz, 1H), 6.87 (ψtd,  $J = 6.8, 1.1$  Hz, 1H), 2.82 (s, 3H), 2.41 (s, 3H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 160.5, 153.6, 143.2, 142.0, 125.9, 125.4, 117.7, 113.4, 102.7, 14.1, 13.9.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{11}\text{H}_{12}\text{N}_5^+$   $[\text{M}+\text{H}]^+$ , 214.1087; found 214.1085; deviation 1.2 ppm.

#### Cyano BINOL-dimethylether **19**



Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with BINOL-dimethylether-derived thianthrenium salt **S9** (120 mg, 0.124 mmol, 1.0 equiv.), KCN (24 mg, 0.37 mmol, 3.0 equiv.), and MeCN (0.5 ml,  $c = 0.25$  M). The vial was sealed and the reaction mixture was stirred at 80 °C for 12 h. Subsequently, the reaction mixture was poured onto a mixture of EtOAc (10 ml) and water (15 ml). The aqueous layer was extracted with EtOAc (3 × 10 ml). Subsequently, the combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (4 / 1 gradient to 1 / 1 (v/v)) to afford 23 mg (51 %) of compound **19** as colorless oil.

$R_f = 0.56$  (EtOAc / hexanes, 1 / 1 (v/v)).

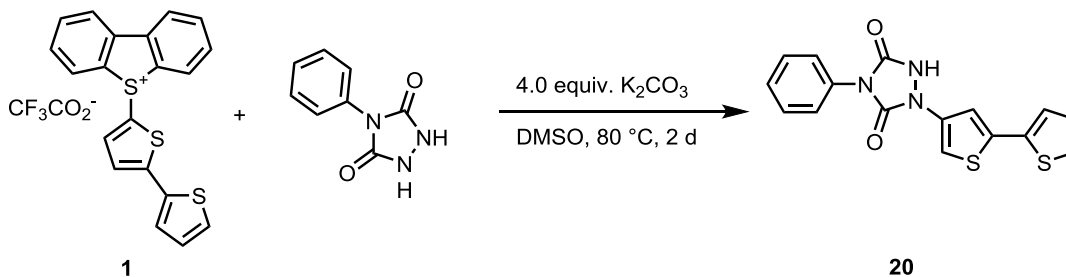
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.38 (d,  $J = 9.3$  Hz, 1H), 7.85 (d,  $J = 6.9$  Hz, 1H), 7.79 (d,  $J = 9.3$  Hz, 1H), 7.33 (dd,  $J = 8.7, 6.8$  Hz, 1H), 7.28 (d,  $J = 8.5$  Hz, 1H), 3.77 (s, 2H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 157.2, 134.3, 131.7, 131.0, 128.4, 127.9, 127.0, 119.8, 118.7, 117.4, 111.0, 57.2.

**HRMS-ESI (m/z)** calc'd for  $C_{24}H_{16}N_2O_2Na^+$   $[M+Na]^+$ , 387.1104; found 387.1100; deviation 1.0 ppm.

### Phenylurazole-substituted bithiophene **20**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (200 mg, 0.43 mmol, 1.0 equiv.), potassium carbonate (239 mg, 1.73 mmol, 4.0 equiv.), phenylurazole (230 mg, 1.30 mmol, 3.0 equiv.), and DMSO (10 ml,  $c = 0.04$  M). The vial was sealed, and subsequently stirred for 2 d at 80 °C. Subsequently, the reaction mixture was poured onto a biphasic mixture of EtOAc (50 ml), water (50 ml) and sulfuric acid (1M, 10 ml). The layers were separated, and the aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (10 ml), and subsequently dried over  $MgSO_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 6 / 4 (v/v)) to afford 100 mg (68 %) of compound **20** as colorless solid.

$R_f = 0.48$  (hexanes / EtOAc, 1 / 1 (v/v)).

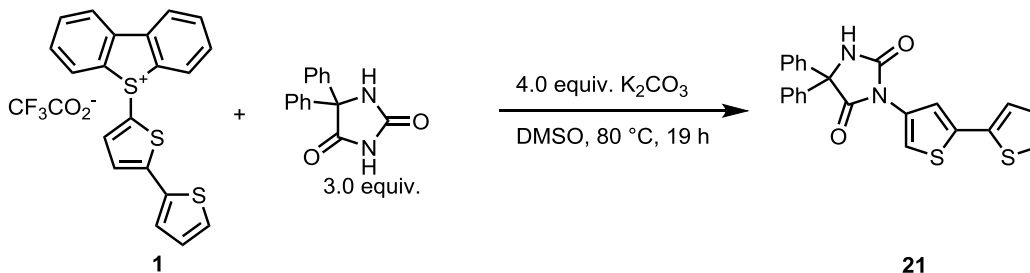
### NMR Spectroscopy:

**$^1H$  NMR** (500 MHz,  $DMSO-d_6$ , 298 K,  $\delta$ ): 11.66 (bs, 1H), 7.58 – 7.56 (m, 2H), 7.54 – 7.51 (m, 4H), 7.47 – 7.42 (m, 1H), 7.36 (dd,  $J = 3.6, 1.2$  Hz, 1H), 7.31 (d,  $J = 1.6$  Hz, 1H), 7.12 (dd,  $J = 5.1, 3.6$  Hz, 1H).

**$^{13}C$  { $^1H$ } NMR** (126 MHz,  $DMSO-d_6$ , 298 K,  $\delta$ ): 152.5, 149.2, 137.1, 136.3, 134.9, 131.9, 129.4, 129.0, 128.7, 127.0, 126.6, 125.0, 116.5, 108.6.

**HRMS-ESI (m/z)** calc'd for  $C_{16}H_{12}N_3O_2S_2^+$   $[M+H]^+$ , 342.0366; found 342.0363; deviation 0.8 ppm.

### Diphenylhydantoin-substituted bithiophene **21**



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (250 mg, 0.54 mmol, 1.0 equiv.), potassium carbonate (299

mg, 2.16 mmol, 4.0 equiv.), diphenylhydantoin (409 mg, 1.62 mmol, 3.0 equiv.), and DMSO (10 ml,  $c = 0.05$  M). The vial was sealed, and subsequently stirred for 19 h at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (40 ml) and washed with water (100 ml). The aqueous layer was extracted with EtOAc ( $2 \times 40$  ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 7 / 3 (v/v)). The resulting solid was dissolved in 100 ml EtOAc and washed with dilute aqueous NaOH solution ( $3 \times 50$  ml), followed by washing with water ( $2 \times 30$  ml). Subsequently, the solvent was removed to afford 185 mg (82 %) of compound **21** as colorless crystals.

$R_f = 0.71$  (hexanes / EtOAc, 1 / 1 (v/v)).

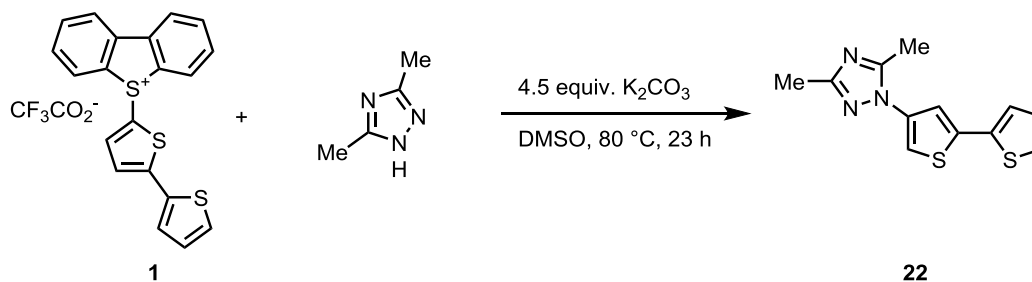
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 298 K,  $\delta$ ): 10.05 (s, 1H), 7.74 (d,  $J = 1.5$  Hz, 1H), 7.60 (d,  $J = 1.5$  Hz, 1H), 7.54 (dd,  $J = 5.1, 1.2$  Hz, 1H), 7.48 – 7.34 (m, 11H), 7.10 (dd,  $J = 5.1, 3.6$  Hz, 1H).

$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO}-d_6$ , 298 K,  $\delta$ ): 171.6, 153.5, 139.4, 135.8, 135.6, 129.6, 128.7, 128.42, 128.38, 126.8, 126.0, 124.5, 120.2, 118.3, 69.0.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{23}\text{H}_{15}\text{N}_2\text{O}_2\text{S}_2^+ [\text{M}-\text{H}]^+$ , 415.0581; found 415.0582; deviation 0.3 ppm.

#### Dimethyltriazol-substituted bithiophene **22**



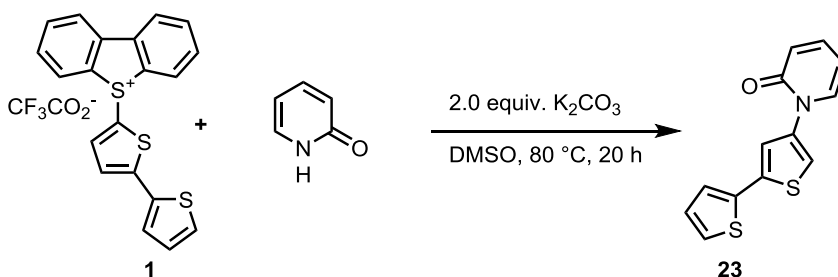
Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with bithiophene-derived dibenzothiophenium salt **1** (250 mg, 0.54 mmol, 1.0 equiv.), potassium carbonate (338 mg, 2.45 mmol, 4.5 equiv.), dimethyltriazole (178 mg, 1.84 mmol, 3.4 equiv.), and DMSO (10 ml,  $c = 0.05$  M). The vial was sealed, and subsequently stirred for 23 h at 80 °C. Subsequently, the reaction mixture diluted with EtOAc (50 ml) and washed with water (50 ml). The aqueous layer was extracted with EtOAc (30 ml). The combined organic layers were washed with water (20 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 1 / 4 (v/v)) to afford 125 mg (88 %) of compound **22** as colorless solid.

$R_f = 0.19$  (hexanes / EtOAc, 1 / 1 (v/v)).

#### NMR Spectroscopy:

**<sup>13</sup>C {<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>, 298 K, δ): 160.0, 152.4, 138.5, 136.2, 136.0, 128.1, 125.7, 124.8, 119.6, 115.7, 13.8, 13.4.

### Pyridone-substituted bithiophene 23

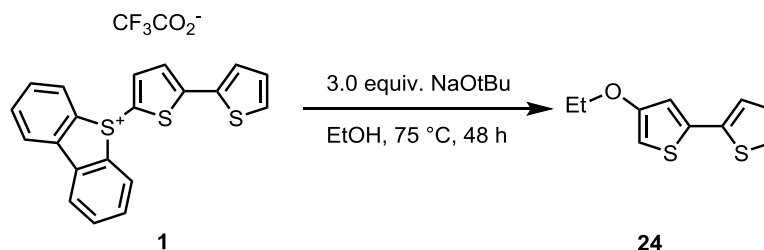


**R<sub>f</sub>** = 0.27 (hexanes / EtOAc, 1 / 1 (v/v)).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, 298 K, δ): 7.43 (ddd, *J* = 6.9, 2.1, 0.8 Hz, 1H), 7.38 (ddd, *J* = 9.2, 6.6, 2.1 Hz, 1H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 7.25 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.21 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.67 (d<sub>ψt</sub>, *J* = 9.3, 1.1 Hz, 1H), 6.24 (ψtd, *J* = 6.7, 1.4 Hz, 1H).

**HRMS-ESI (m/z)** calc'd for  $C_{13}H_9NOS_2Na^+$   $[M+Na]^+$ , 282.0018; found 282.0016; deviation 0.7 ppm.

### Ethoxybithiophene 24



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with thienothiophene-derived dibenzothiophenium salt **1** (200 mg, 0.43 mmol, 1.0 equiv.), NaOtBu (125 mg, 1.29 mmol, 3.0 equiv.), and EtOH (10 ml,  $c = 0.04$  M). The vial was sealed and the reaction mixture was stirred at 75 °C for 40 h. Subsequently, the solvent was removed under reduced pressure. The residue was dissolved in a biphasic mixture of EtOAc (10 ml) and aqueous HBr solution (0.1 M, 10 ml), and the layers were separated. The organic layer was washed with water ( $2 \times 10$  ml), and dried over  $\text{MgSO}_4$ , filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes to afford 67 mg (74 %) of compound **24** as yellowish oil.

$R_f = 0.62$  (hexanes / EtOAc, 9 / 1 (v/v)).

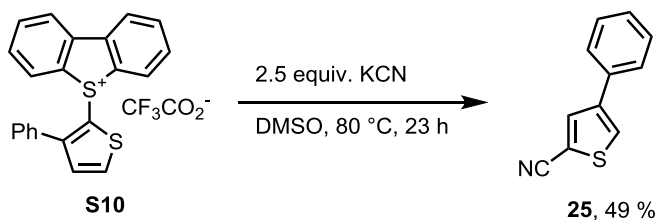
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.21 (dd,  $J = 5.1, 1.2$  Hz, 1H), 7.15 (dd,  $J = 3.6, 1.2$  Hz, 1H), 7.00 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.86 (d,  $J = 1.3$  Hz, 1H), 6.13 (d,  $J = 1.8$  Hz, 1H), 4.02 (q,  $J = 7.0$  Hz, 2H), 1.41 (t,  $J = 7.0$  Hz, 3H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 157.5, 137.7, 136.0, 127.9, 124.7, 123.7, 116.2, 96.4, 65.7, 14.9.

HRMS-EI ( $m/z$ ) calc'd for  $\text{C}_{10}\text{H}_{10}\text{OS}^+ [\text{M}]^+$ , 210.0168; found 210.0171; deviation 1.8 ppm.

### Cyano-substituted 3-phenylthiophene 25



Under an ambient atmosphere, a 20 ml glass vial equipped with a teflon coated stir bar was charged with 3-phenylthiophene-derived dibenzothiophenium salt **S10** (200 mg, 0.44 mmol, 1.0 equiv.), KCN (71 mg, 1.1 mmol, 2.5 equiv.), and DMSO (9 ml,  $c = 0.05$  M). The vial was sealed, and subsequently stirred for 23 h at 80 °C. Subsequently, the reaction mixture was diluted with EtOAc (10 ml) and washed with water (40 ml). The aqueous layer was extracted with EtOAc (20 ml). The combined organic layers were washed with aqueous  $\text{Fe}(\text{OAc})_2$  solution (5 ml). Subsequently, the organic layer was dried over  $\text{MgSO}_4$ . The solvent was

removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 17 / 3 (v/v)) to afford 40 mg (49 %) of compound **25** as colorless oil, which crystallized after several hours.

$R_f$  = 0.85 (hexanes / EtOAc, 7 / 3 (v/v)).

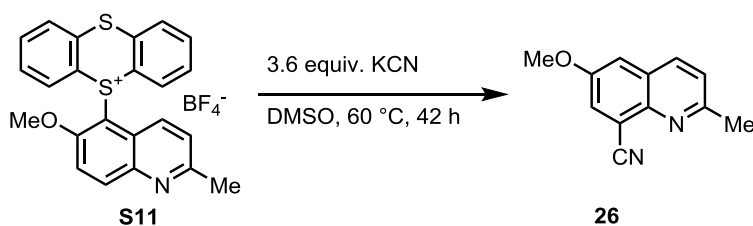
#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.87 (d,  $J$  = 1.4 Hz, 1H), 7.66 (d,  $J$  = 1.5 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.44 (wt,  $J$  = 7.5 Hz, 2H), 7.41 – 7.33 (m, 1H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 143.3, 136.4, 133.8, 129.3, 128.5, 127.0, 126.6, 114.7, 110.8.

HRMS-EI ( $m/z$ ) calc'd for  $\text{C}_{11}\text{H}_7\text{NS}^+ [\text{M}]^+$ , 185.0294; found 185.0296; deviation 1.4 ppm.

#### Cyano-substituted 6-methoxy-2-methylquinoline 26



Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with methoxymethylquinoline-derived thianthrenium salt **S11** (98 mg, 0.18 mmol, 1.0 equiv.), KCN (43 mg, 0.66 mmol, 3.6 equiv.), and DMSO (3 ml,  $c$  = 0.06 M). The vial was sealed, and the reaction mixture was subsequently stirred for 42 h at 60 °C. Subsequently, the reaction mixture was poured onto a mixture of aqueous  $\text{Fe}(\text{OAc})_2$  solution (120 mg  $\text{Fe}(\text{OAc})_2$  in 20 ml  $\text{H}_2\text{O}$ ) and 20 ml EtOAc. The aqueous layer was extracted with EtOAc (3  $\times$  20 ml). The combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (9 / 1 gradient to 3 / 2 (v/v)) to afford 6 mg (16 %) of compound **26** as colorless crystals.

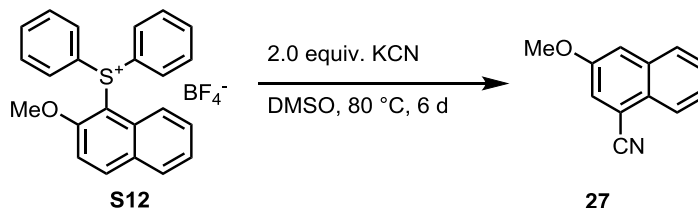
$R_f$  = 0.67 (hexanes / EtOAc, 7 / 3 (v/v)).

#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 7.98 (d,  $J$  = 8.5 Hz, 1H), 7.71 (d,  $J$  = 2.8 Hz, 1H), 7.35 (d,  $J$  = 8.4 Hz, 1H), 7.28 (d,  $J$  = 2.8 Hz, 1H), 3.94 (s, 3H), 2.77 (s, 3H).

$^{13}\text{C}$  { $^1\text{H}$ } NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ ): 159.3, 156.0, 143.2, 135.2, 127.5, 127.3, 124.0, 117.2, 113.6, 111.1, 56.1, 25.4.

HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{12}\text{H}_{11}\text{NO}^+ [\text{M}+\text{H}]^+$ , 199.0866; found 199.0865; deviation 0.5 ppm.

Cyano-substituted methoxy-naphthalin **27**

Under an ambient atmosphere, a 4 ml glass vial equipped with a teflon coated stir bar was charged with methoxynaphthalene-derived diphenylsulfonium salt **S12** (250 mg, 0.50 mmol, 1.0 equiv.), KCN (66 mg, 1.0 mmol, 2.0 equiv.), and MeCN (3 ml,  $c = 0.17 \text{ M}$ ). The vial was sealed, and the reaction mixture was subsequently stirred for 6 d at 80 °C. Subsequently, the reaction mixture was diluted with water (50 ml) and extracted with EtOAc (3 × 20 ml). The combined organic layers were washed with aqueous  $\text{FeSO}_4$  solution (approx. 20 %, 10 ml). The organic layer was dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 9 / 1 (v/v)) to afford 34 mg (37 %) of compound **27** as colorless crystals.

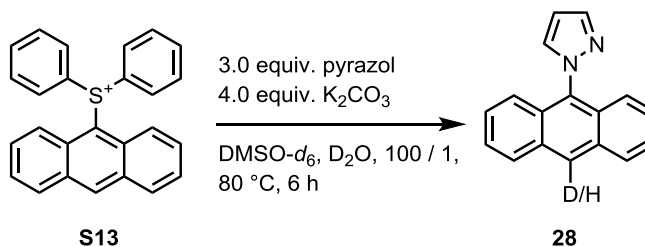
$R_f = 0.46$  (hexanes / EtOAc, 4 / 1 (v/v)).

## NMR Spectroscopy:

$^1\text{H NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.09 – 8.06 (m, 1H), 7.92 – 7.89 (m, 1H), 7.67 (d,  $J = 2.6 \text{ Hz}$ , 1H), 7.63 – 7.55 (m, 3H), 3.93 (s, 3H).

$^{13}\text{C} \{^1\text{H}\} \text{NMR}$  (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 157.3, 135.4, 129.0, 128.6, 128.4, 127.2, 126.1, 125.4, 118.0, 113.1, 111.9, 56.6.

**HRMS-ESI ( $m/z$ )** calc'd for  $\text{C}_{12}\text{H}_9\text{NONa}^+ [\text{M}+\text{Na}]^+$ , 206.0576; found 206.0575; deviation 0.6 ppm.

Pyrazol-substituted anthracen **28**

Under an atmosphere of argon, a flame dried *Schlenk* tube equipped with a teflon coated stir bar was charged with pyrazol (102 mg, 1.5 mmol, 3.0 equiv.), and  $\text{K}_2\text{CO}_3$  (276 mg, 2.0 mmol, 4.0 equiv.) and deuterium oxide (2 ml). The mixture was stirred at 25 °C for 45 min. The solvent was removed under reduced pressure and the residue was dried in vacuo. Subsequently, anthracene-derived diphenylsulfonium salt **S13** (225 mg, 0.50 mmol, 1.0 equiv.),  $\text{DMSO-}d_6$  (5 ml,  $c = 0.1 \text{ M}$ ), and  $\text{D}_2\text{O}$  (50  $\mu\text{l}$ ) were added. The reaction mixture was stirred at 80 °C for 6 h. The mixture was diluted with water (30 ml). The mixture was extracted with EtOAc (5 × 40 ml). The combined organic layers were washed with water (30 ml). The organic layer was

dried with  $\text{MgSO}_4$ , filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexanes / EtOAc (1 / 0 gradient to 17 / 3 (v/v)) to afford 110 mg (90 %) of compound **28** as yellow solid with a deuterium incorporation of 77 % by  $^1\text{H}$  NMR by integration of the  $^1\text{H}$ -signal at 8.73 ppm.

$R_f = 0.37$  (hexanes / EtOAc, 5 / 1 (v/v)).

#### NMR Spectroscopy:

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 8.73 (s, 0.23H), 8.17 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.96 – 7.94 (m, 2H), 7.61 – 7.49 (m, 4H), 7.34 (d,  $J = 8.6$  Hz, 2H), 6.73 (t,  $J = 2.1$  Hz, 1H).

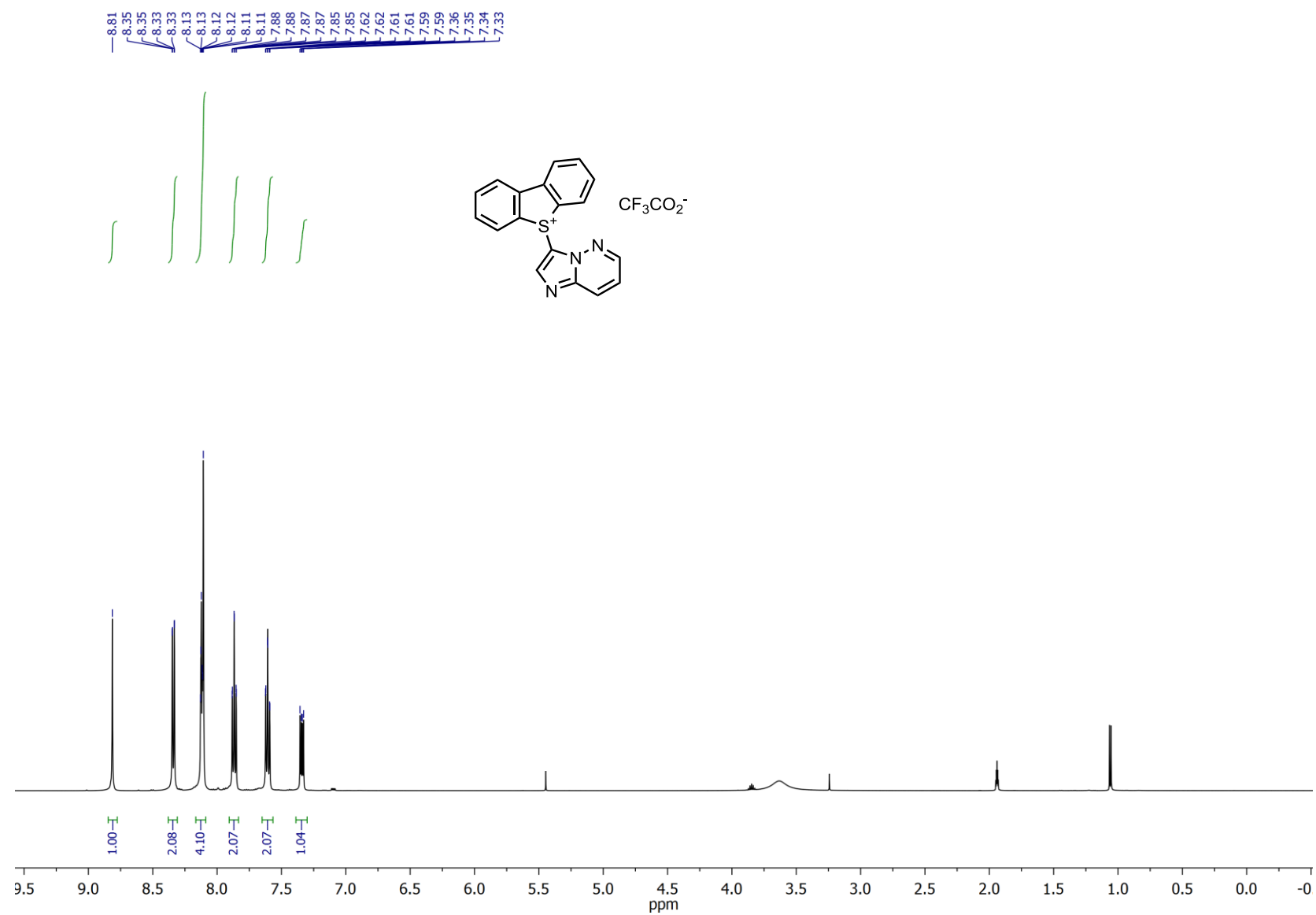
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ , 298 K,  $\delta$ ): 141.5, 134.7, 133.5, 132.3, 132.2, 129.9, 129.5, 129.3, 129.22, 129.17 (t,  $J = 24$  Hz), 128.4, 126.8, 123.5, 107.3.

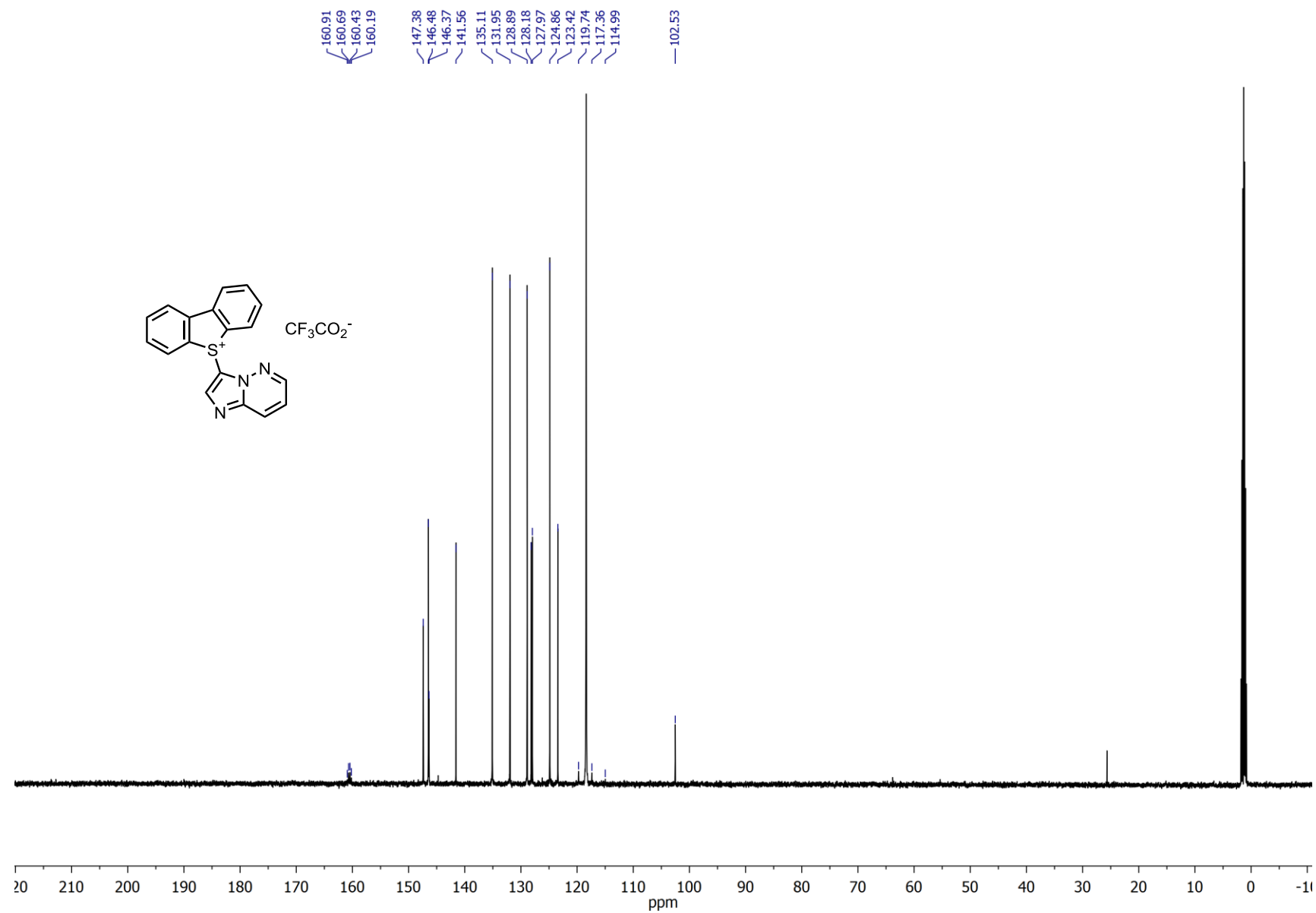
HRMS-ESI ( $m/z$ ) calc'd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{D}$   $[\text{M}+\text{H}]^+$ , 246.1136; found 246.1137; deviation 0.5 ppm.

## REFERENCES

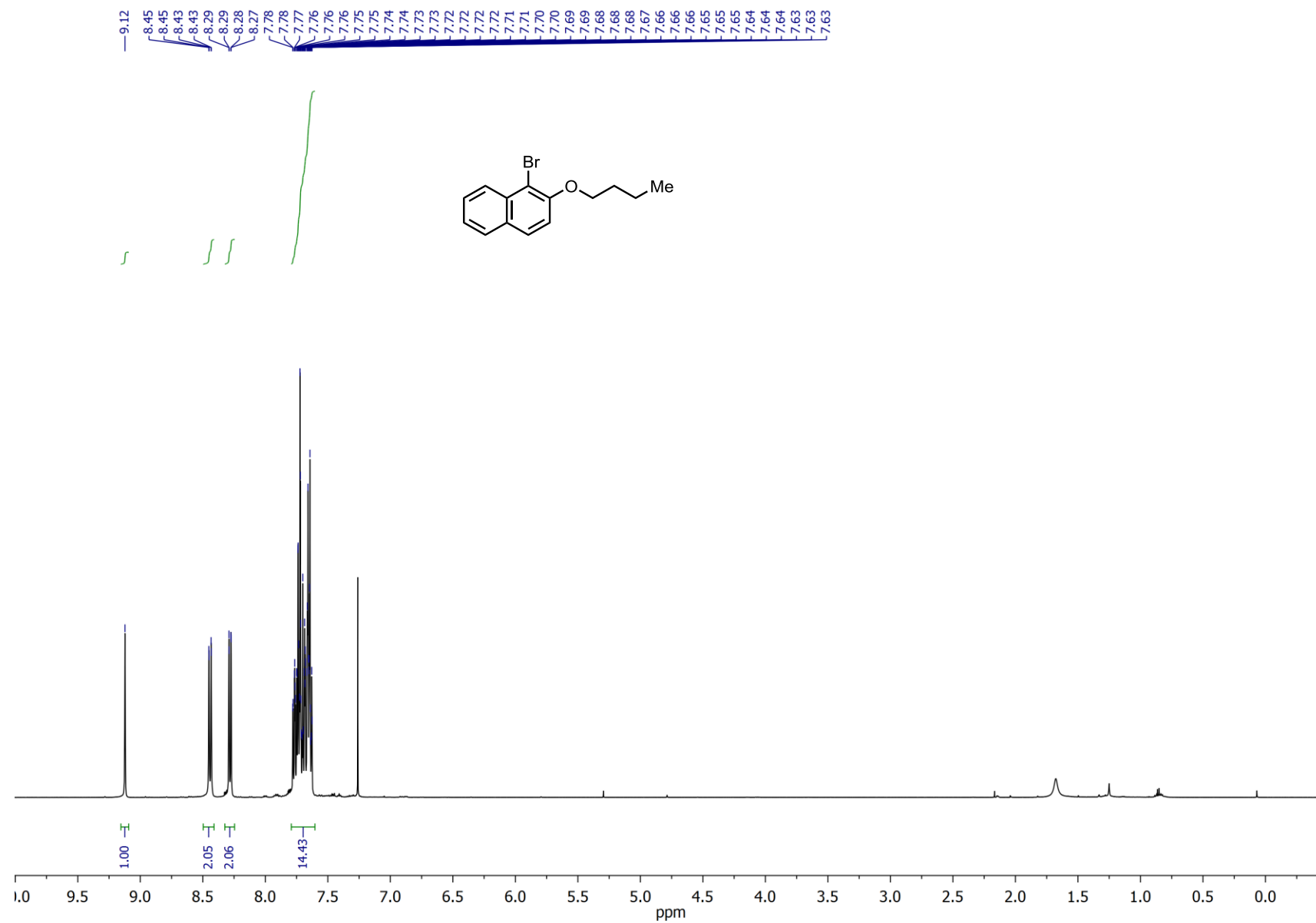
(18) S. Zheng, C. Yu, Z. Shen *Org. Lett.* **2012**, *14*, 3644-3647.

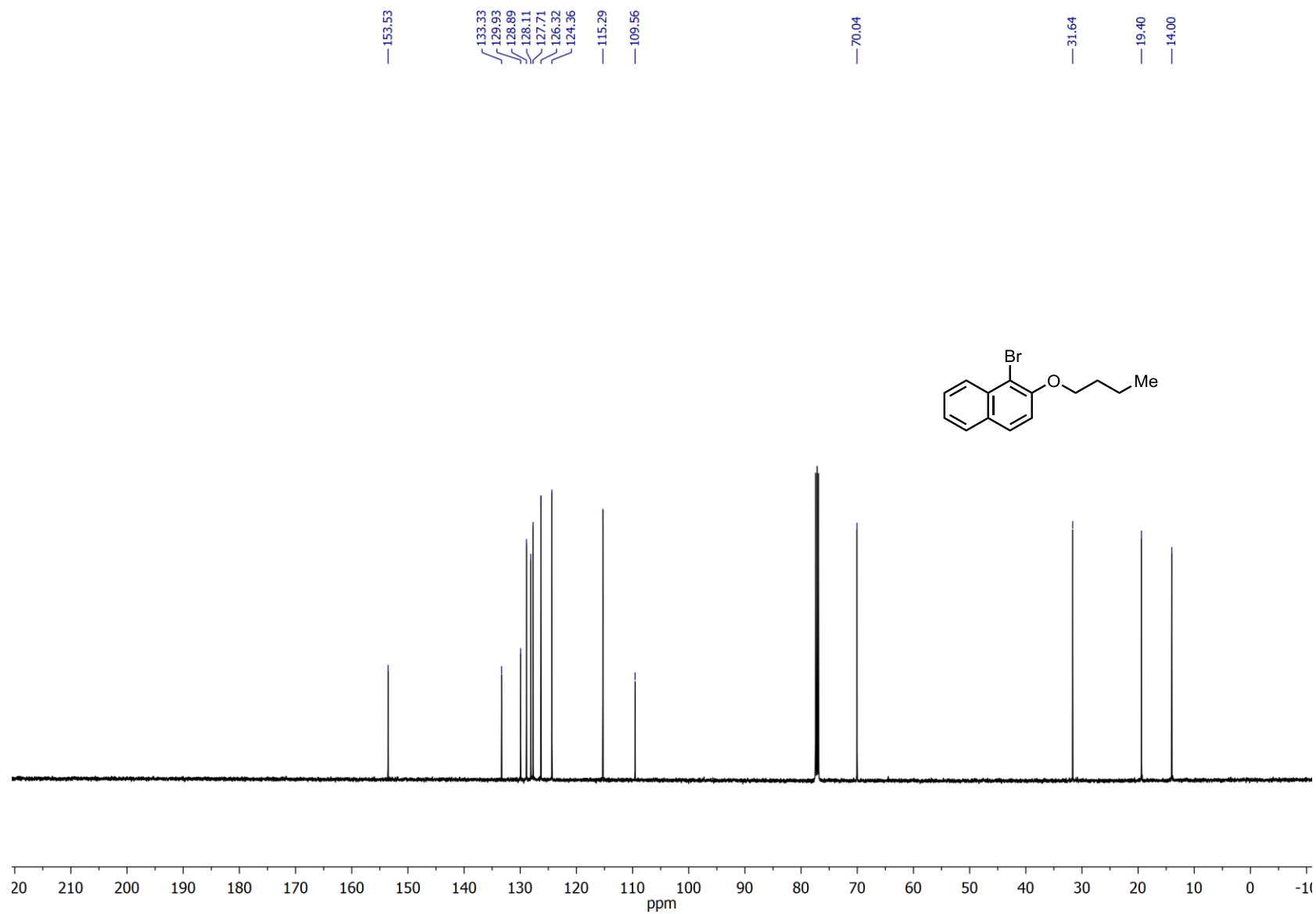
## SPECTROSCOPIC DATA

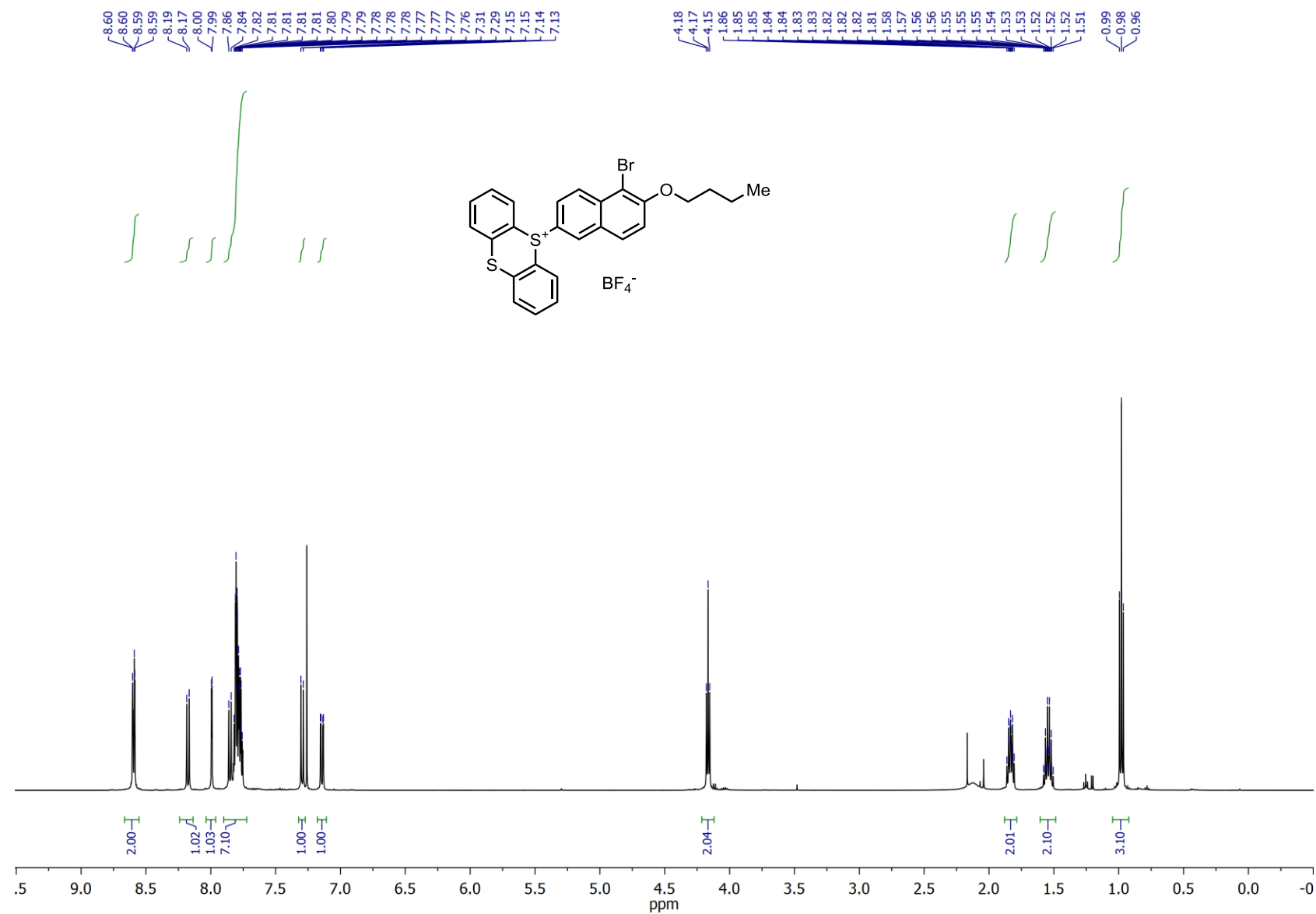
 **$^1\text{H}$  NMR of imidazopyridazine-derived dibenzothiophenium salt S1**CDCl<sub>3</sub>, 500 MHz, 298 K

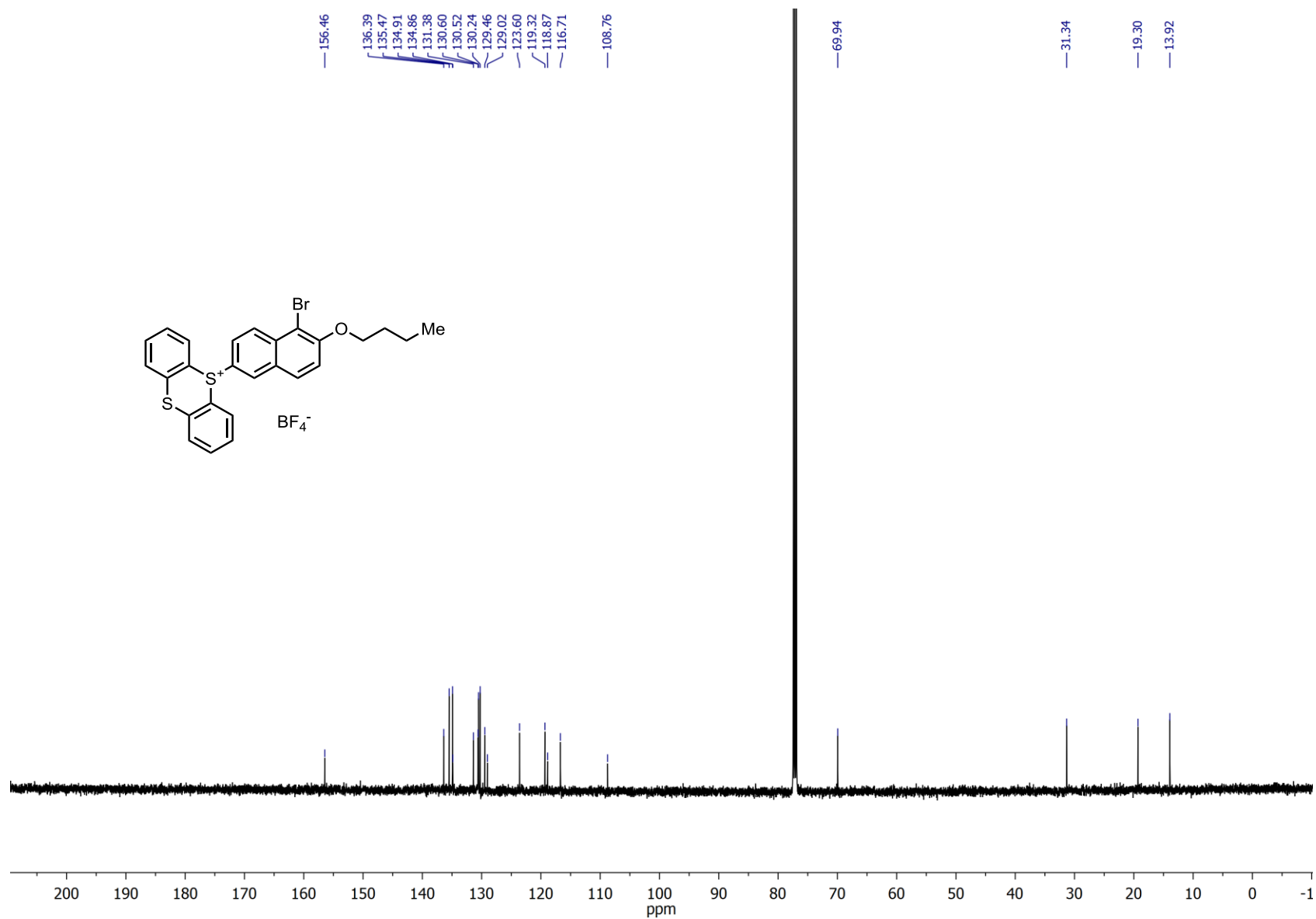
**$^{13}\text{C}$  NMR of imidazopyridazine-derived dibenzothiophenium salt S1**CDCl<sub>3</sub>, 126 MHz, 298 K

**$^{19}\text{F}$  NMR of imidazopyridazine-derived dibenzothiophenium salt S1**CDCl<sub>3</sub>, 471 MHz, 298 K

**$^1\text{H}$  NMR of bromobutoxy naphthalene S2**CDCl<sub>3</sub>, 500 MHz, 298 K

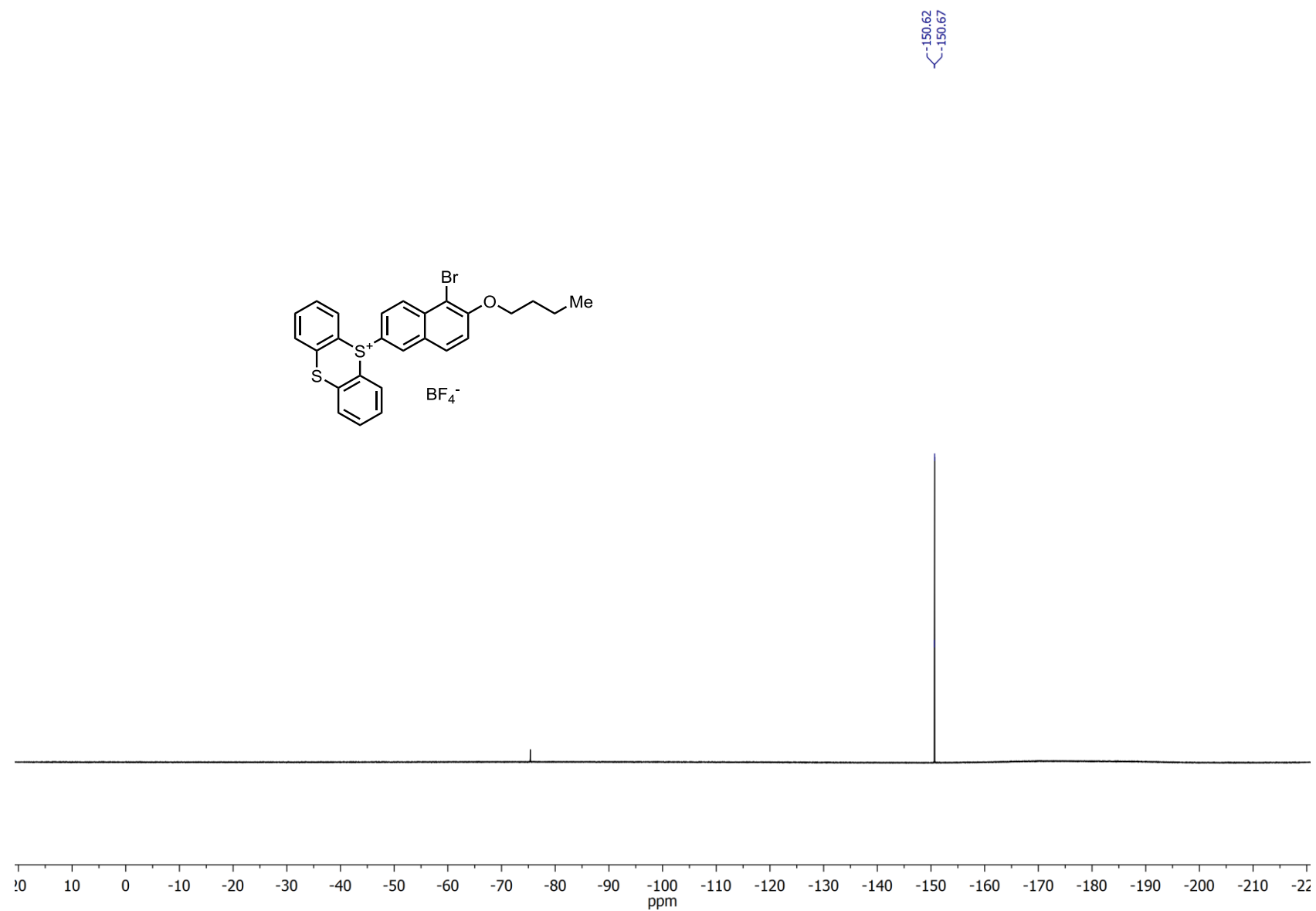
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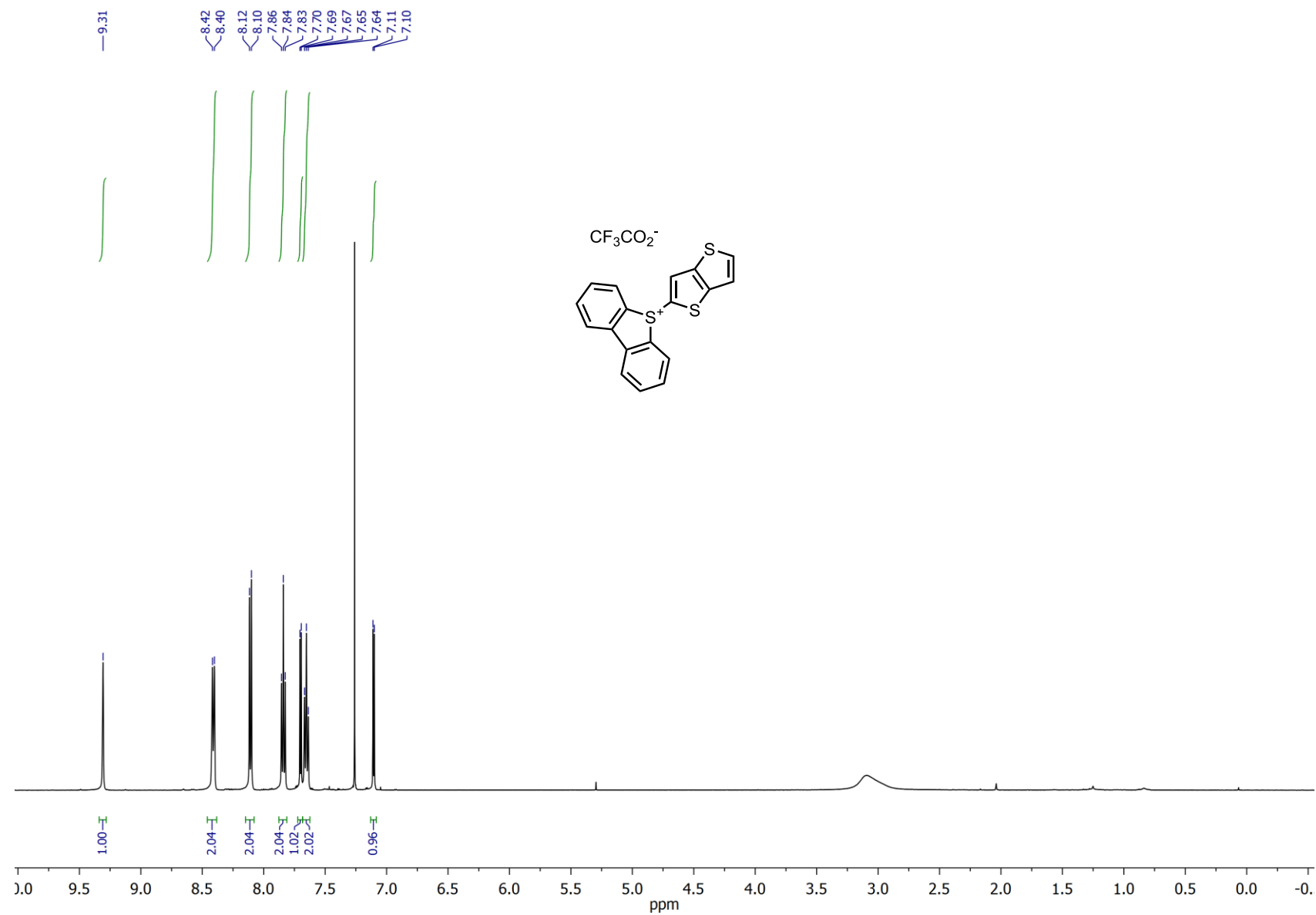
**$^1\text{H}$  NMR of bromobutoxynaphthalene-derived thianthrenium salt S3**CDCl<sub>3</sub>, 500 MHz, 298 K

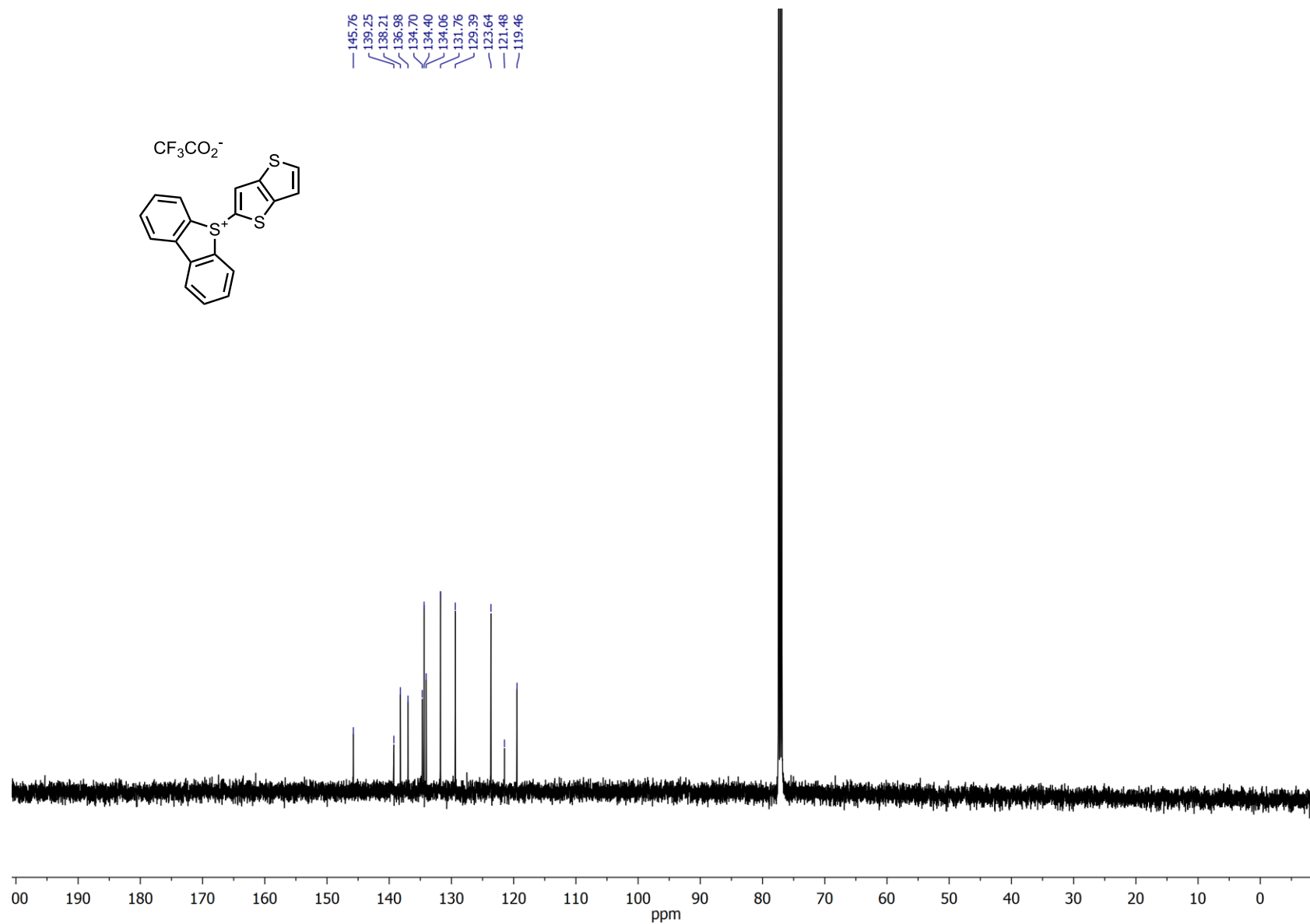
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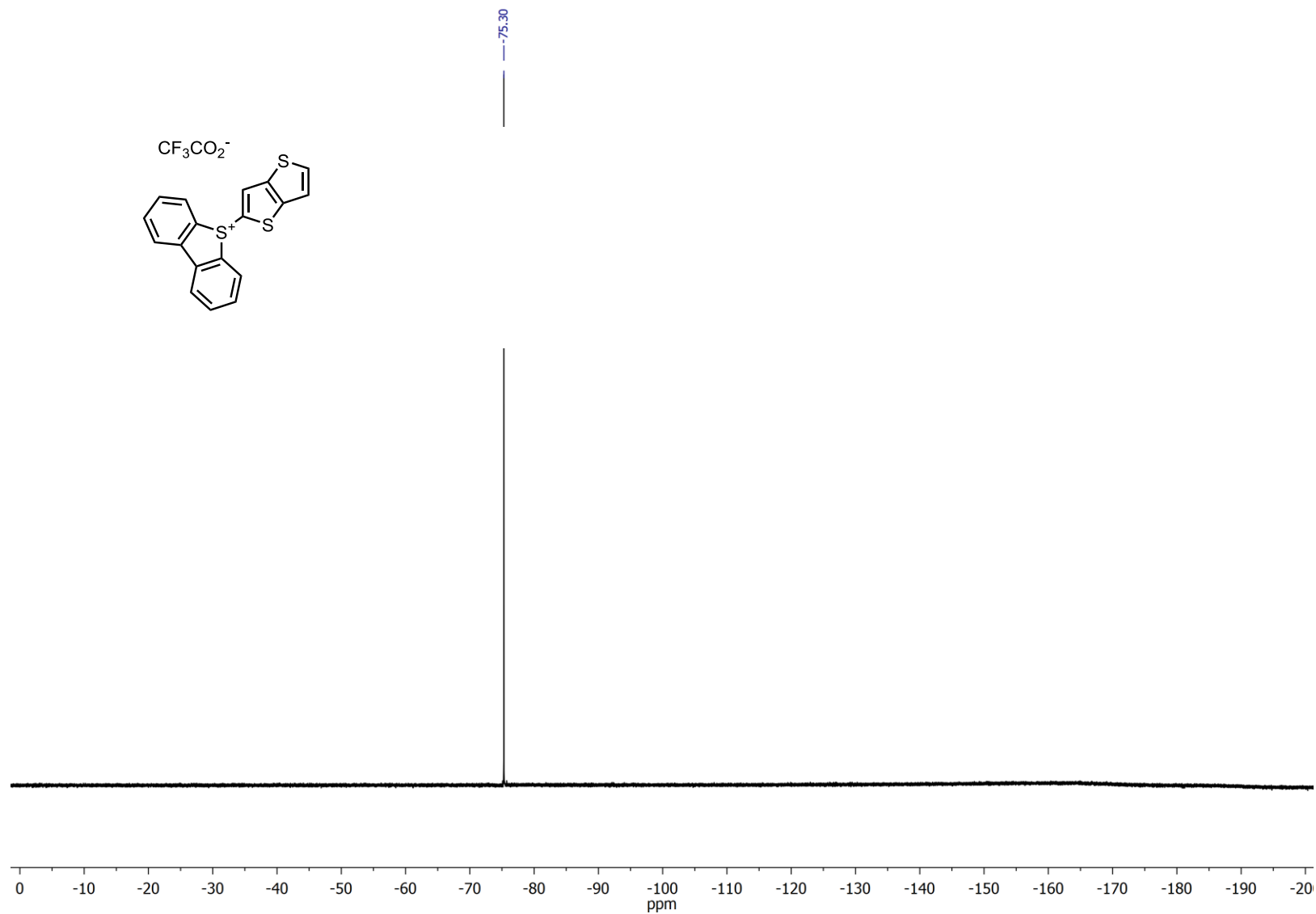
**$^{19}\text{F}$  NMR of bromobutoxynaphthalene-derived thianthrenium salt S3**

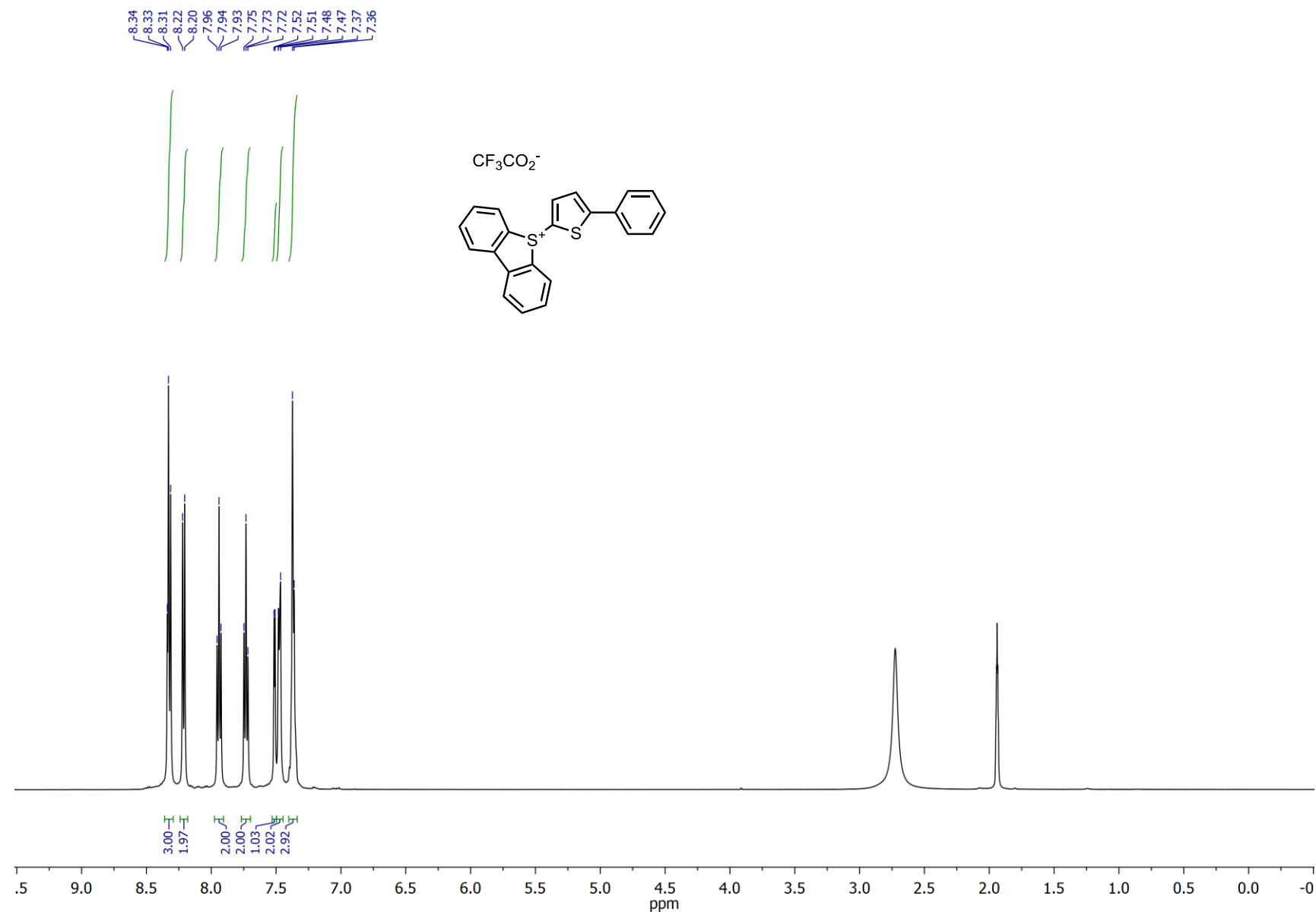
$\text{CDCl}_3$ , 471 MHz, 298 K, an impurity of trifluoroacetate ions was detected.

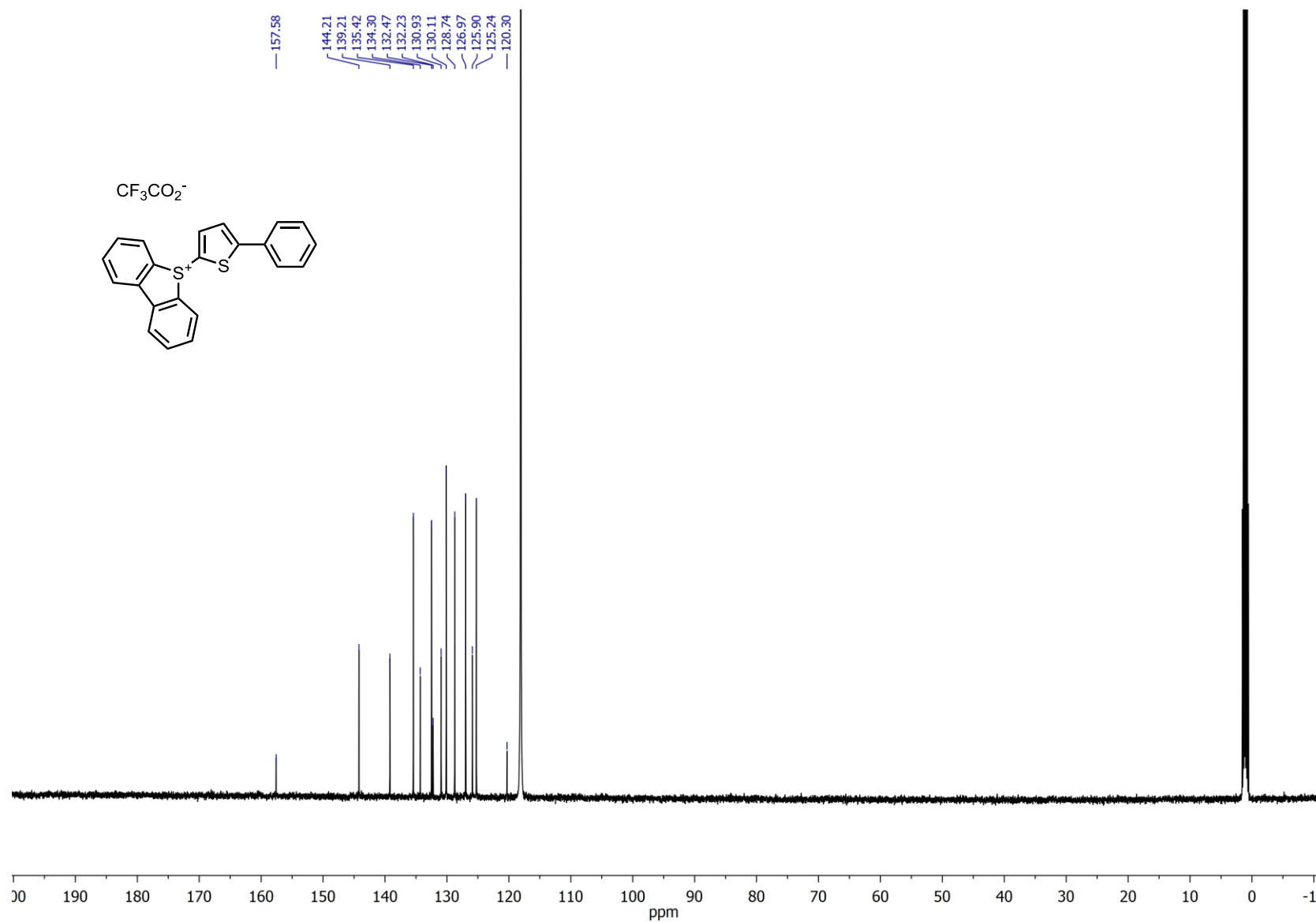


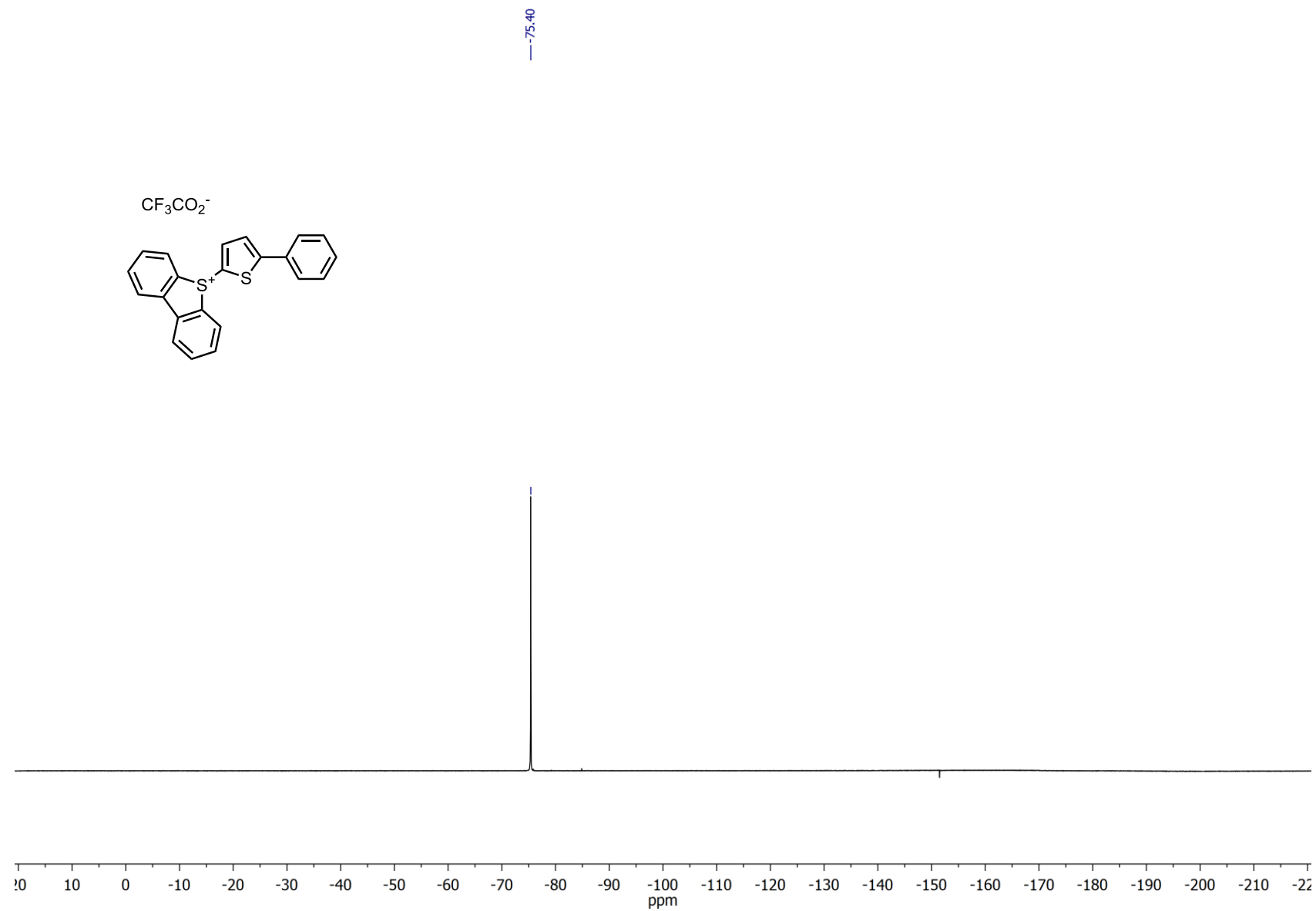
**$^1\text{H}$  NMR of thienothiophen-derived dibenzothiophenium salt S4** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

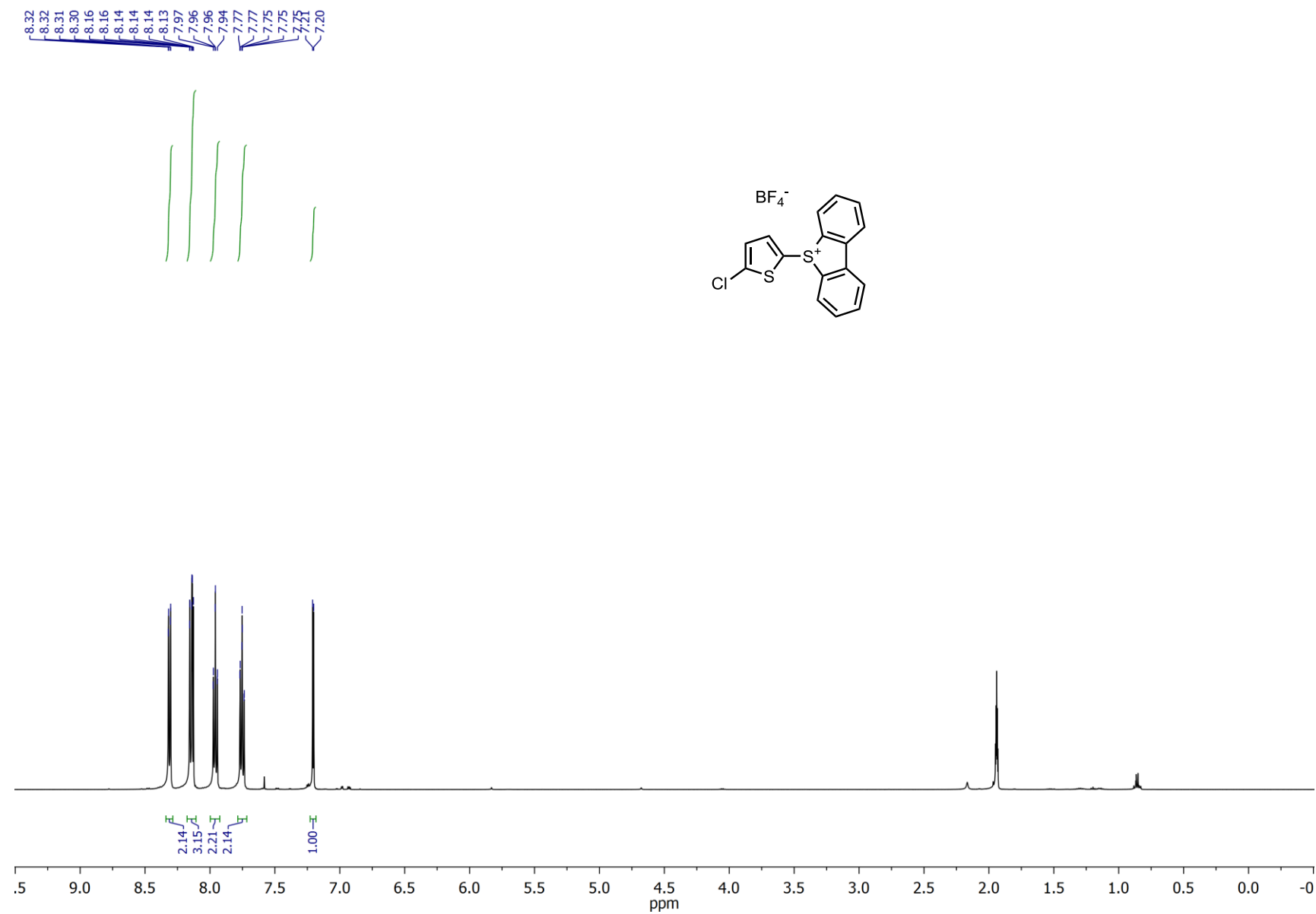
**$^{13}\text{C}$  NMR of thienothiophen-derived dibenzothiophenium salt S4** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

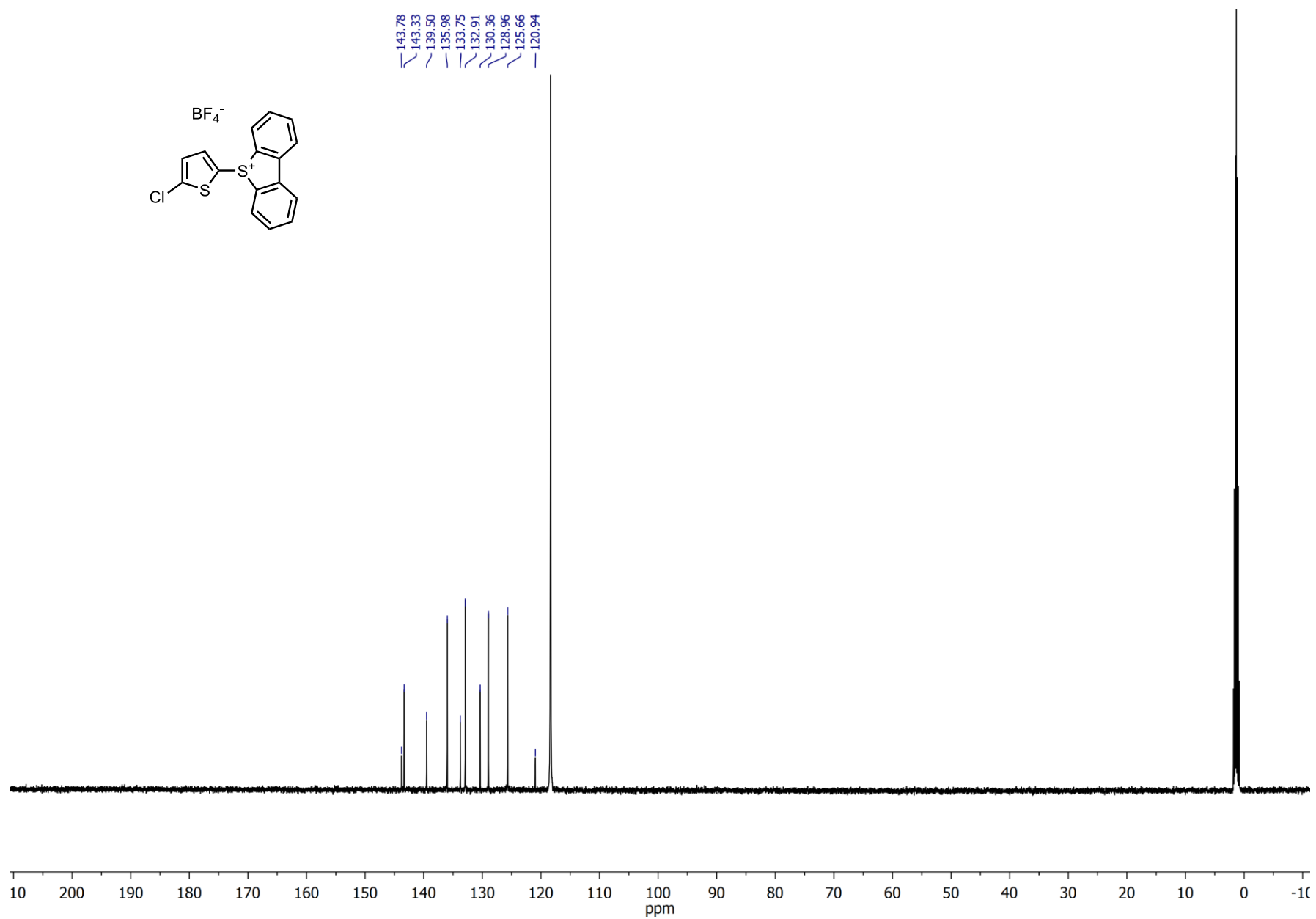
**$^{19}\text{F}$  NMR of thienothiophen-derived dibenzothiophenium salt S4** $\text{CD}_3\text{CN}$ , 471 MHz, 298 K

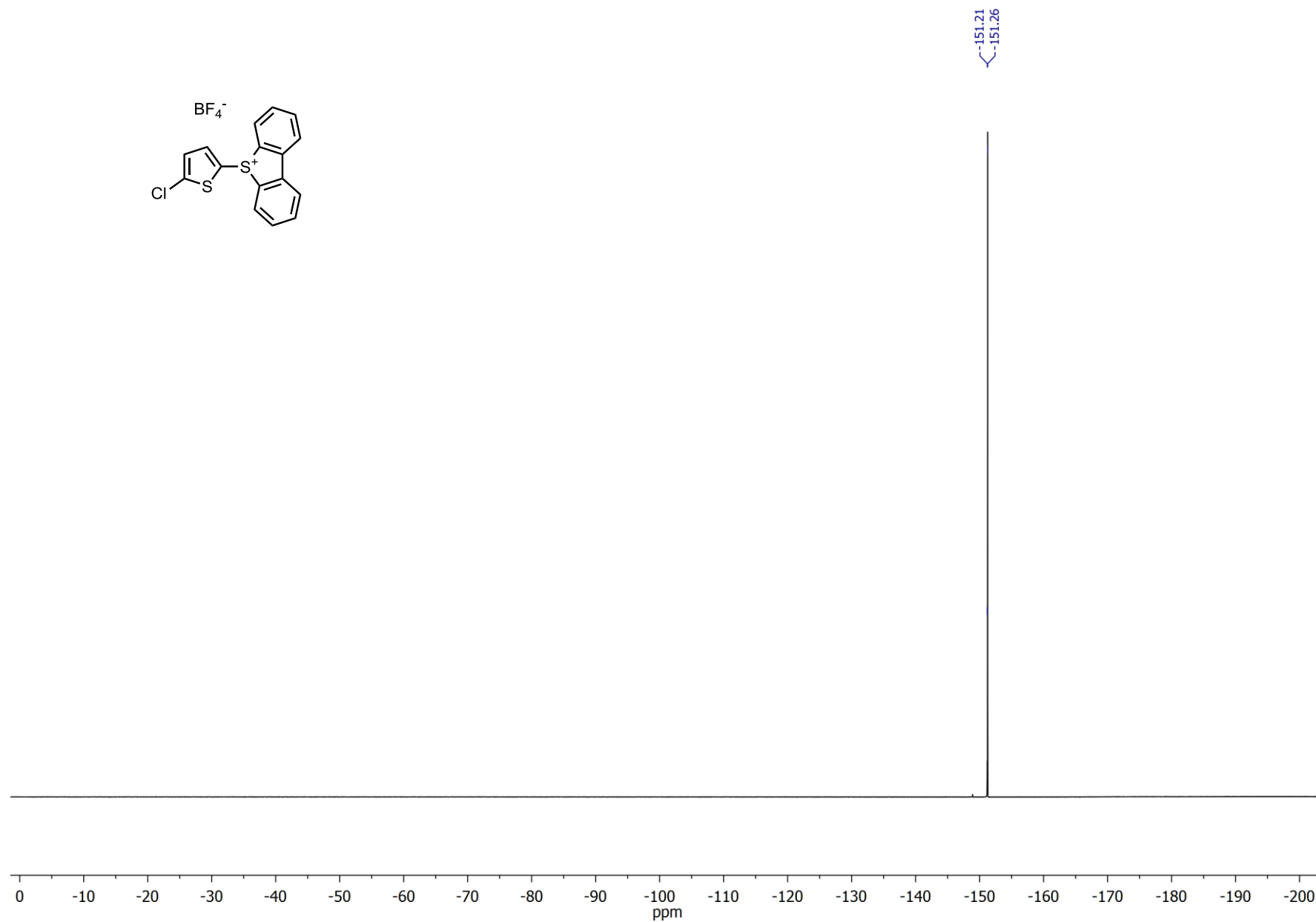
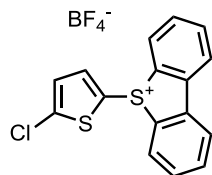
**$^1\text{H}$  NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

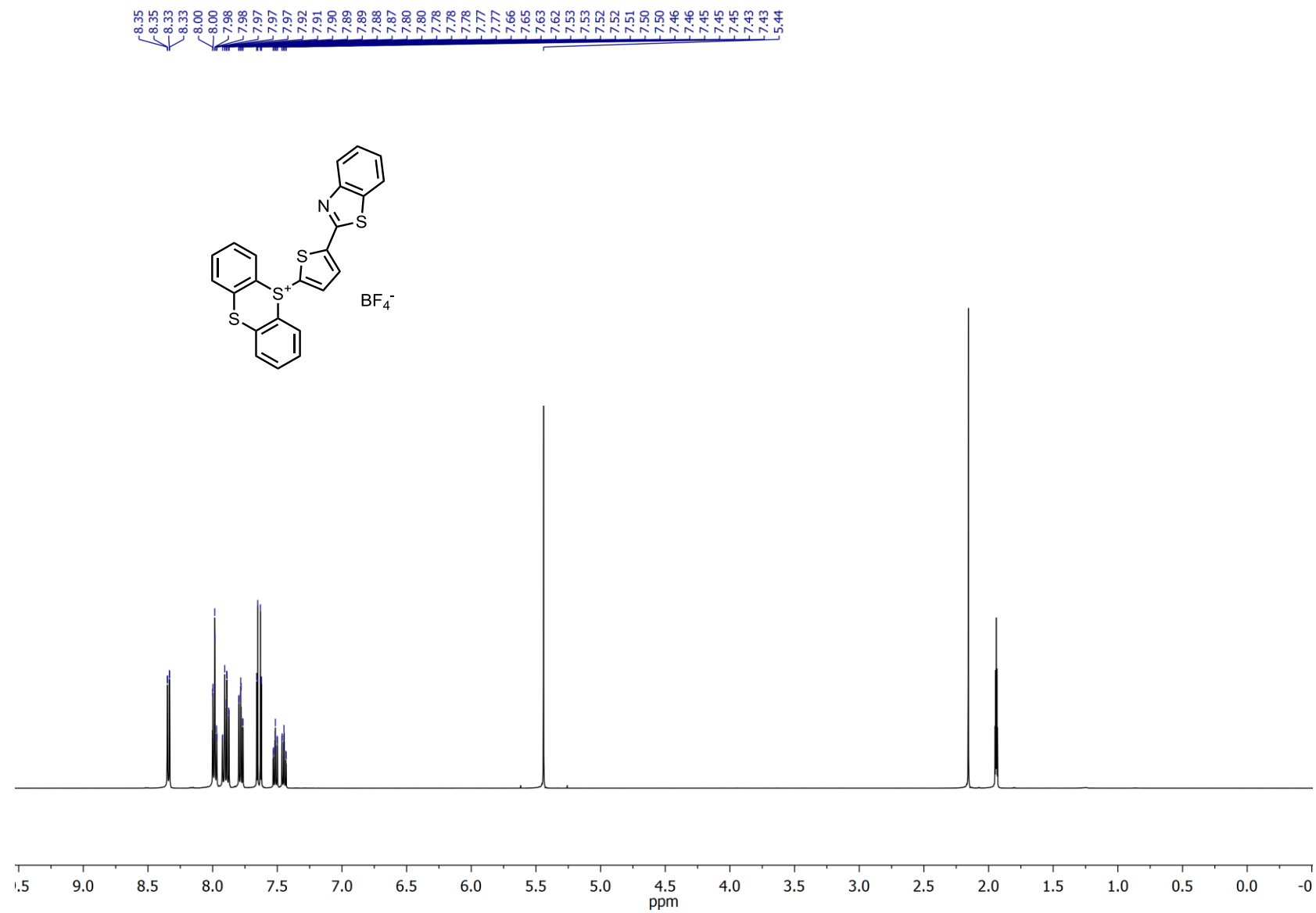
**$^{13}\text{C}$  NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

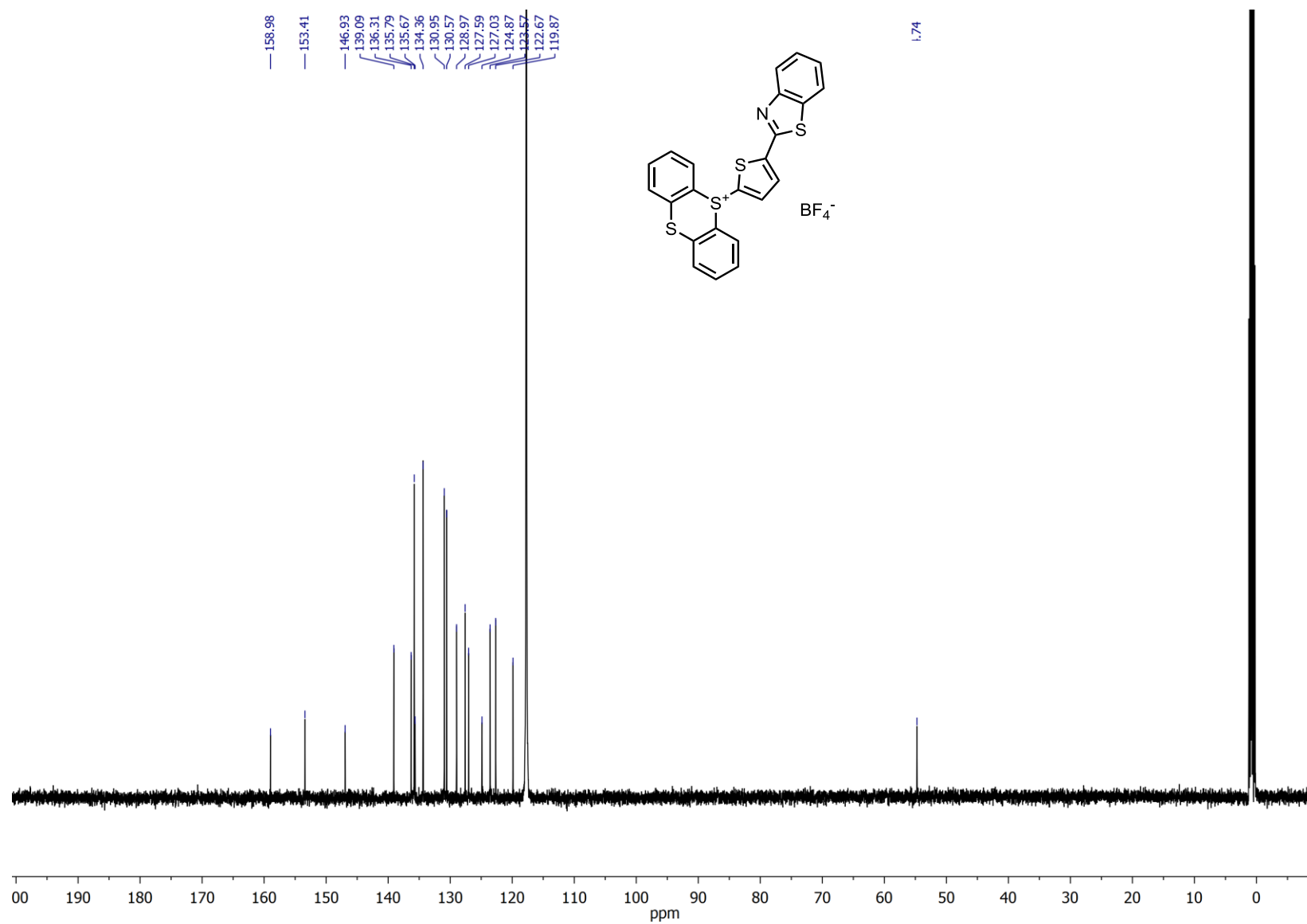
**$^{19}\text{F}$  NMR of 2-phenylthiophen-derived dibenzothiophenium salt S5** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

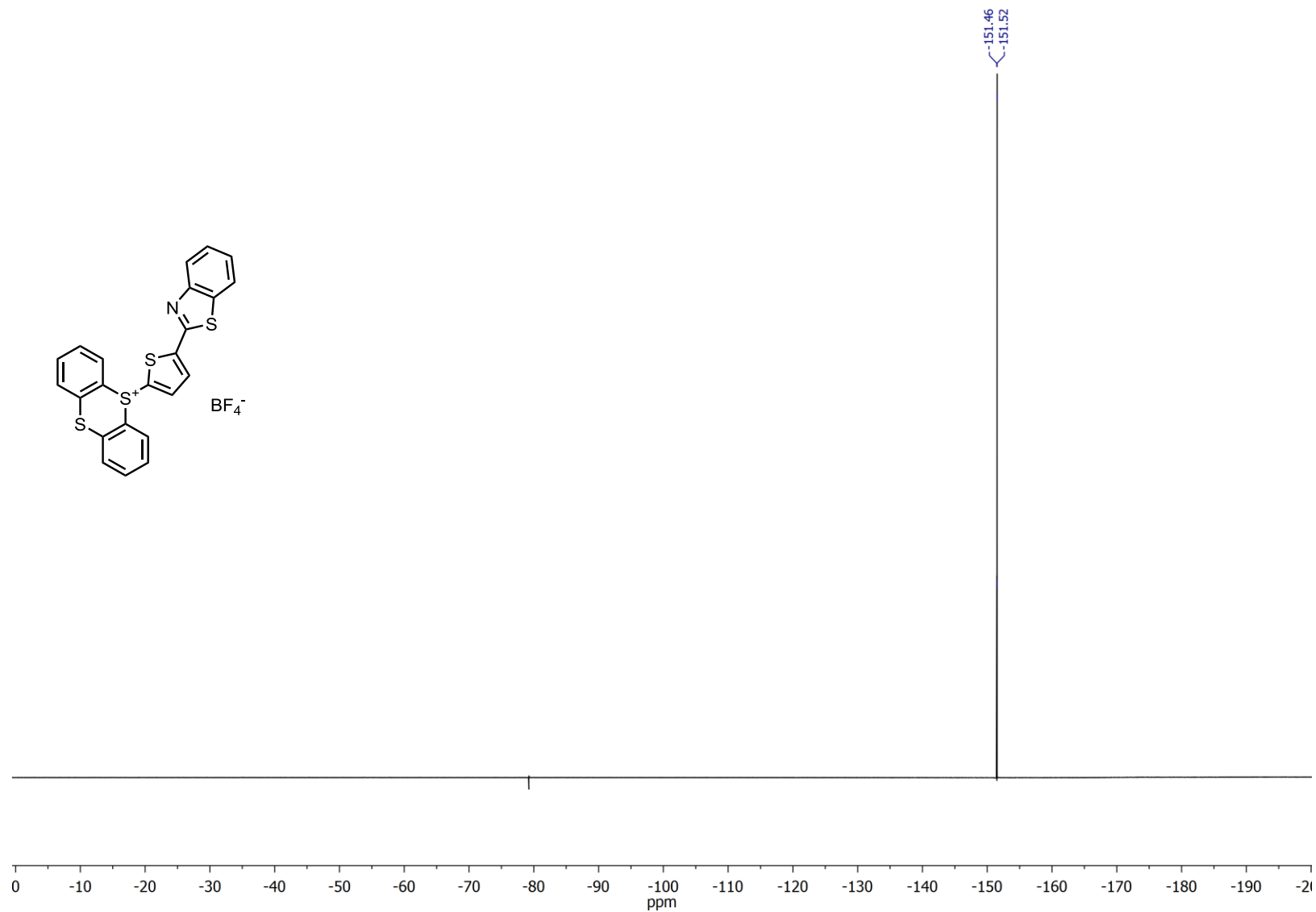
**$^1\text{H}$  NMR of 2-chlorothiophen-derived dibenzothiophenium salt S6** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

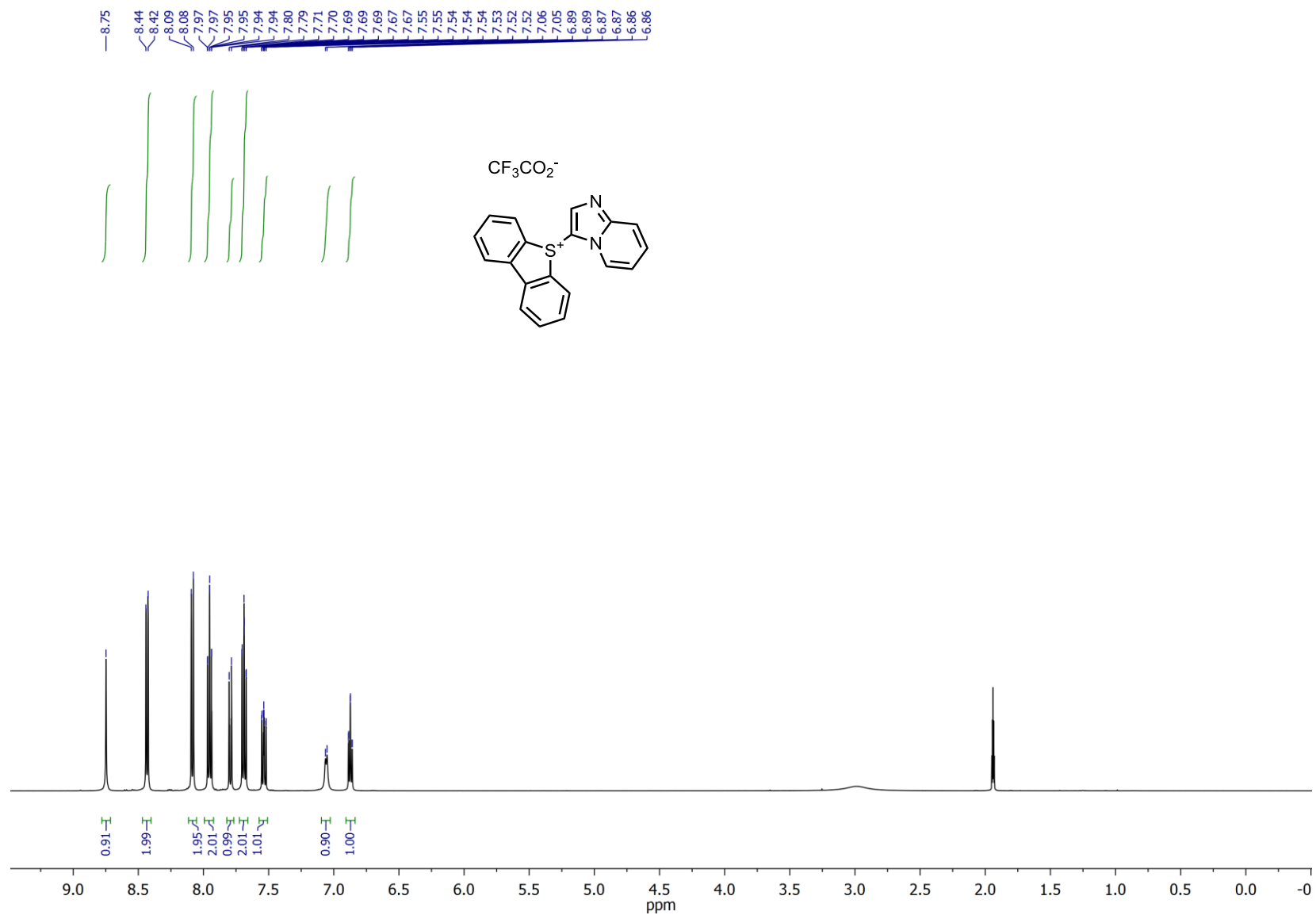
**$^{13}\text{C}$  NMR of 2-chlorothiophen-derived dibenzothiophenium salt S6** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

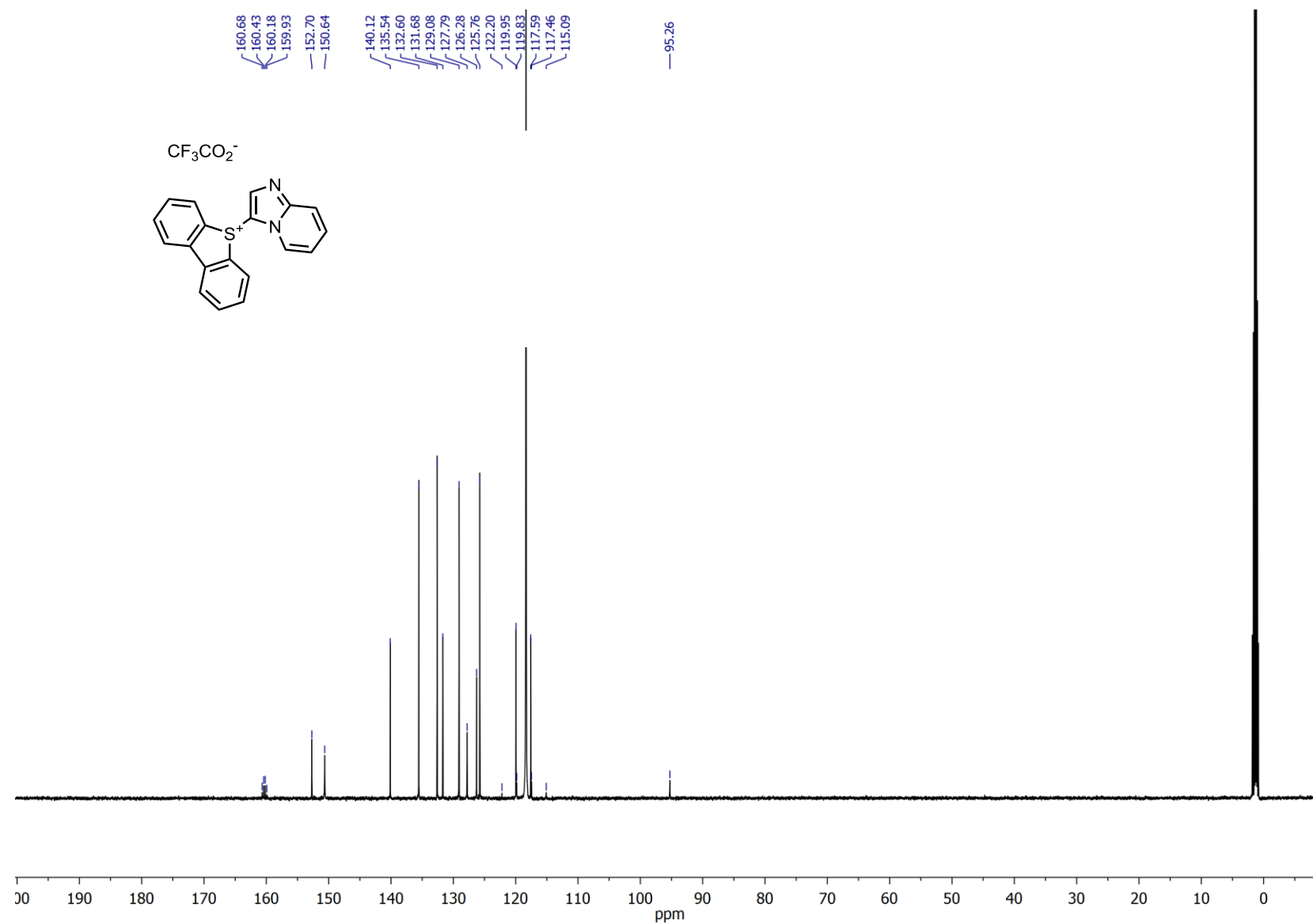
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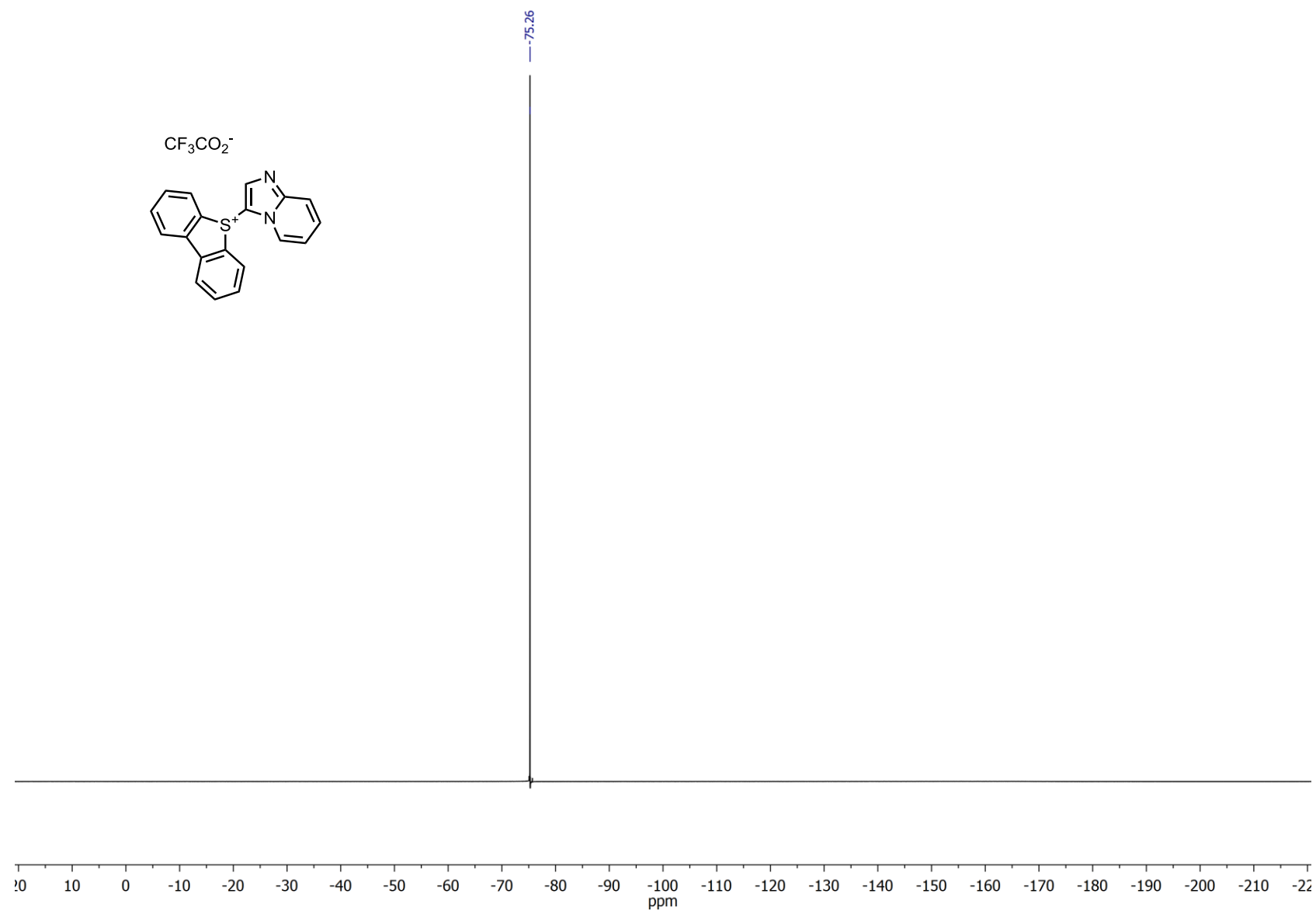
**$^1\text{H}$  NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

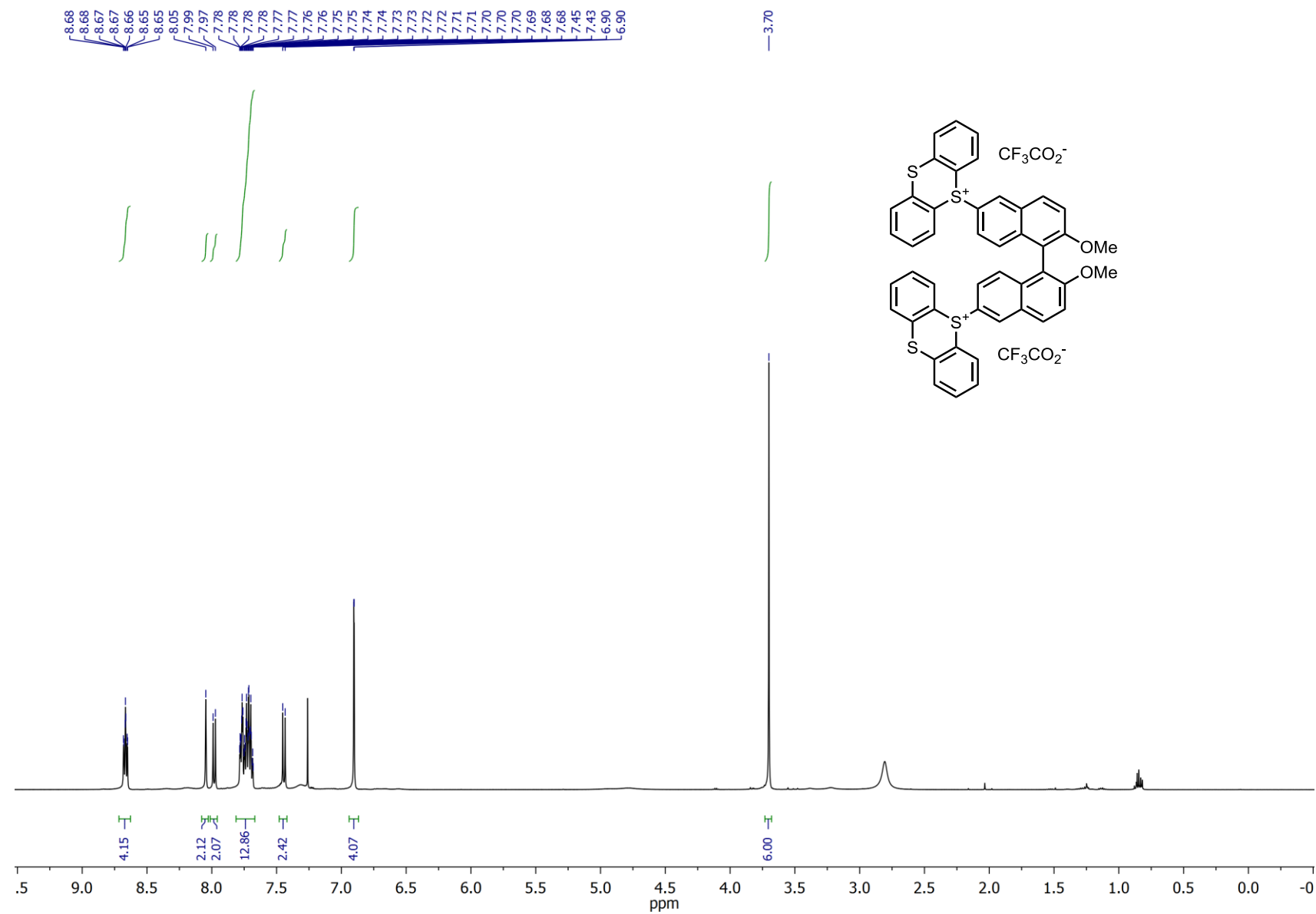
**$^{13}\text{C}$  NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

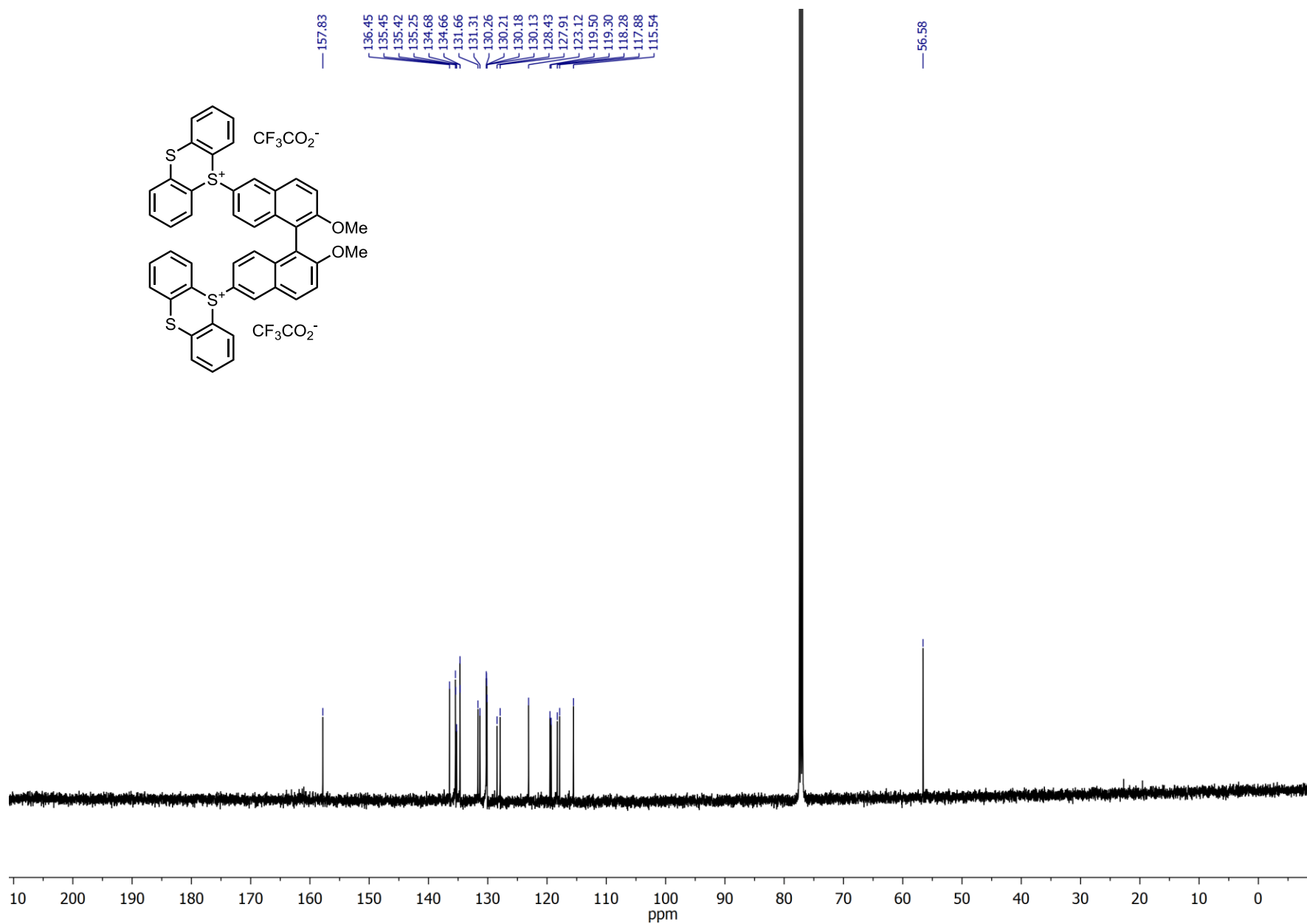
**$^{19}\text{F}$  NMR of benzothiazol-substituted thiophene-derived thianthrenium salt S7** $\text{CD}_3\text{CN}$ , 471 MHz, 298 K

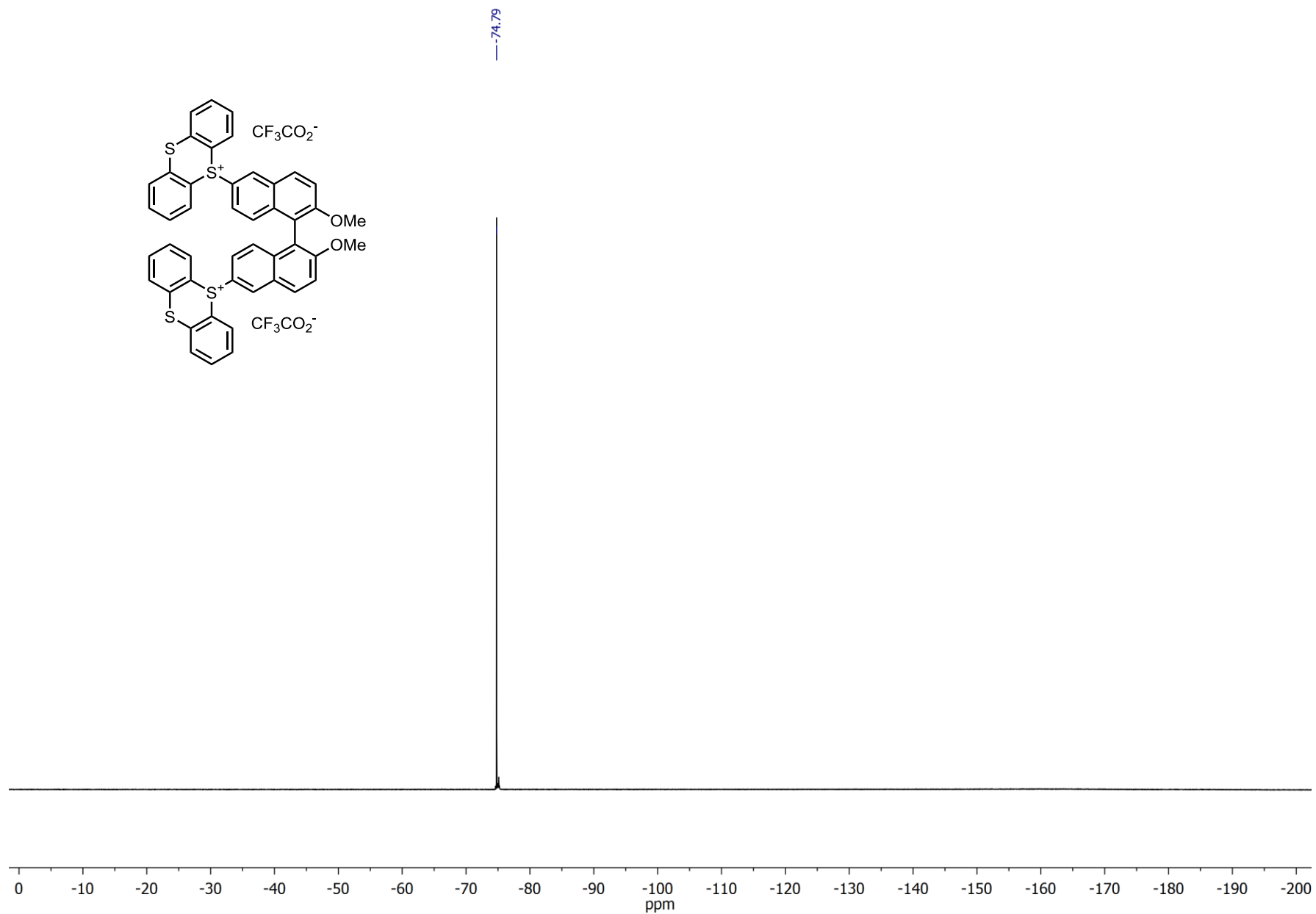
**$^1\text{H}$  NMR of imidazopyridine-derived dibenzothiophenium salt S8** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

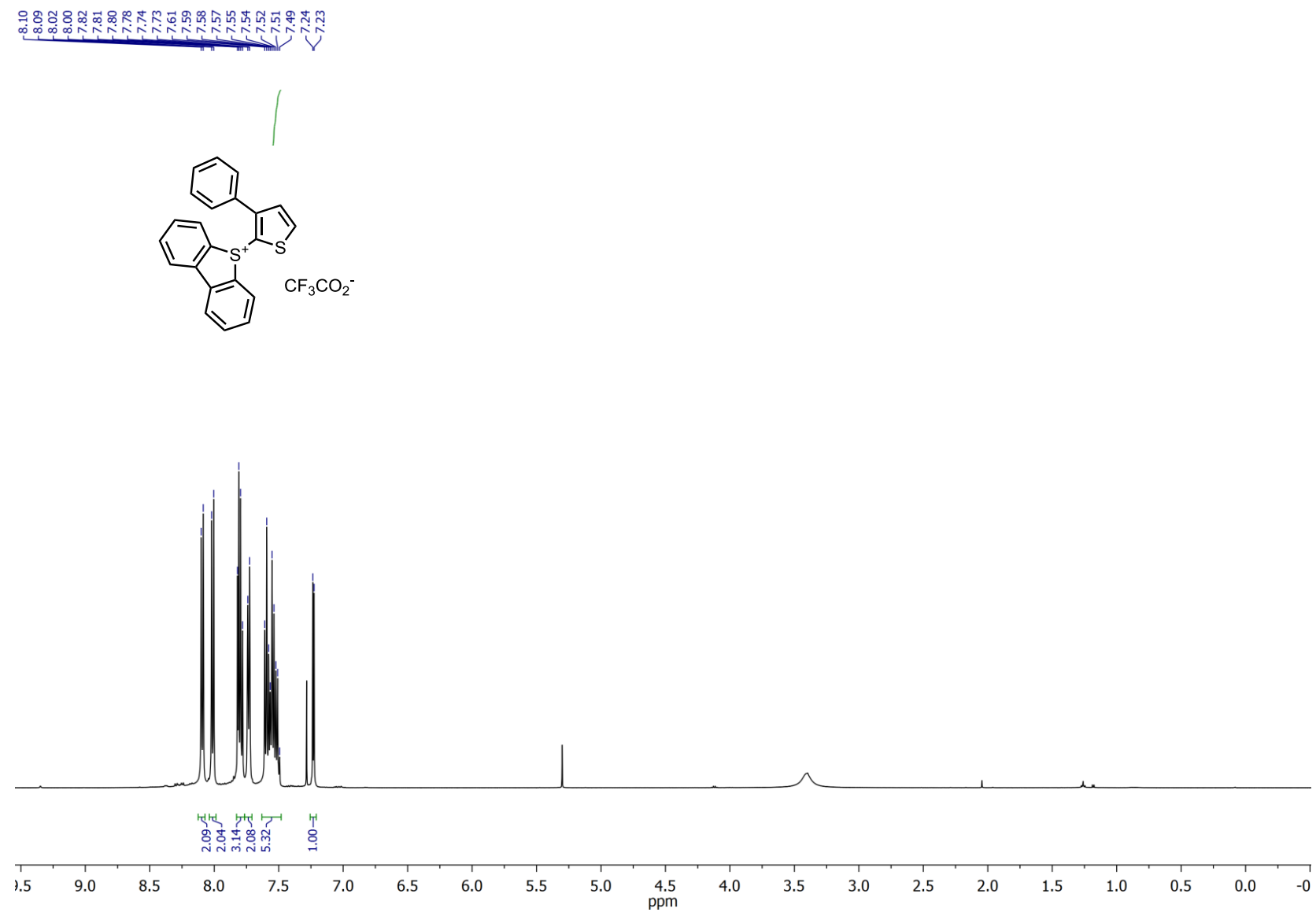
**$^{13}\text{C}$  NMR of imidazopyridine-derived dibenzothiophenium salt S8** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

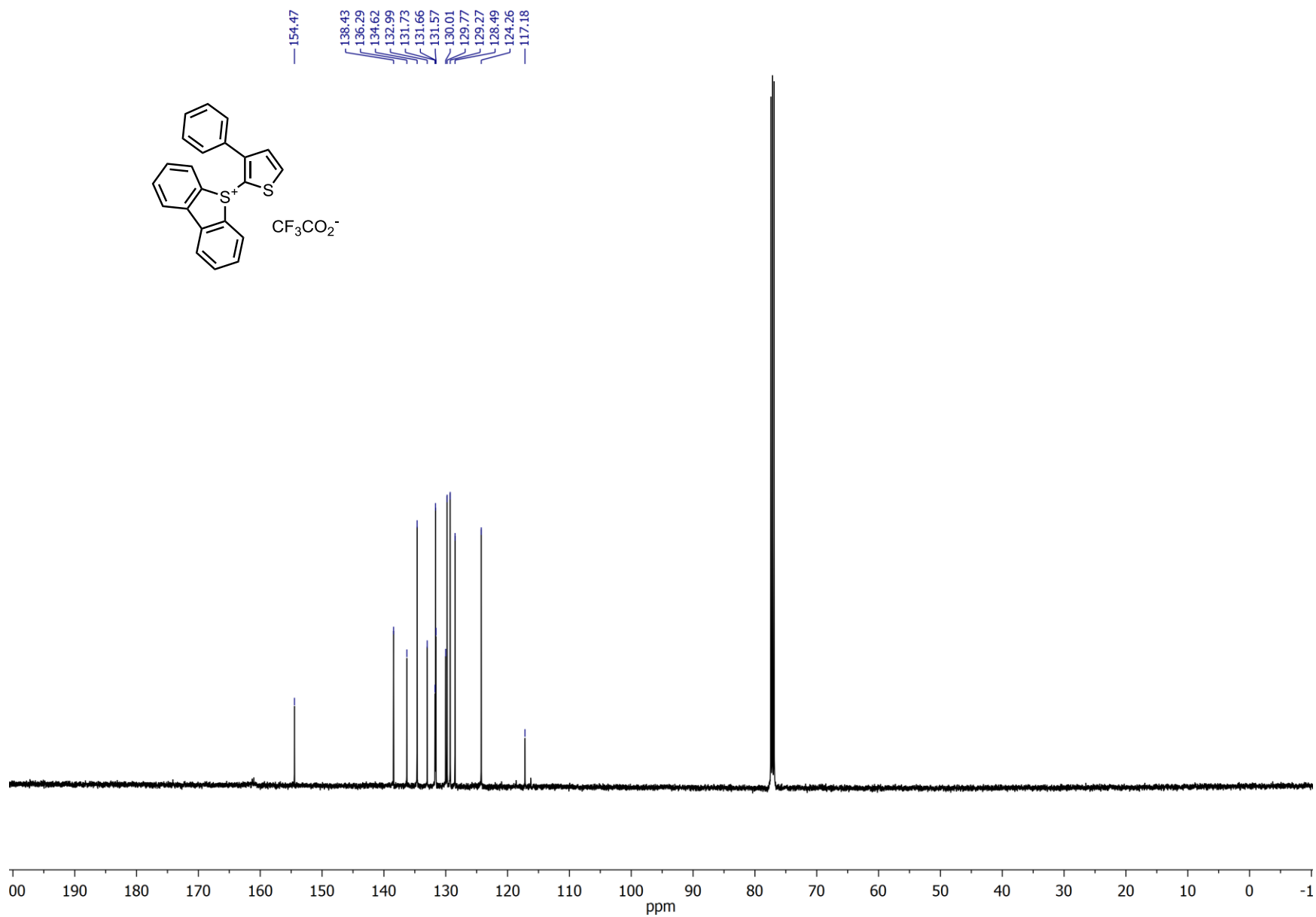
**$^{19}\text{F}$  NMR of imidazopyridine-derived dibenzothiophenium salt S8** $\text{CD}_3\text{CN}$ , 471 MHz, 298 K

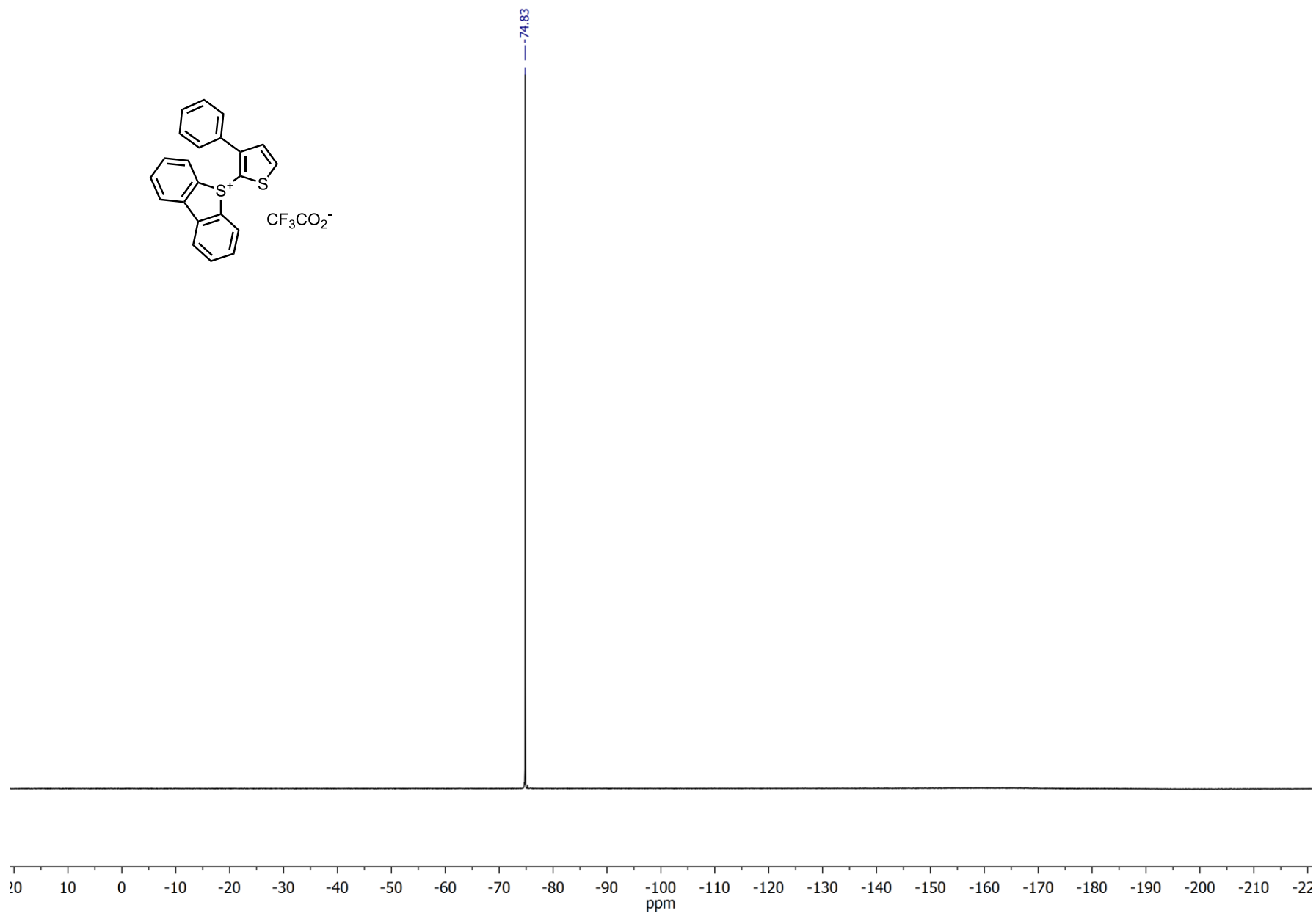
**$^1\text{H}$  NMR of BINOL dimethylether-derived thianthrenium salt S9**CDCl<sub>3</sub>, 500 MHz, 298 K

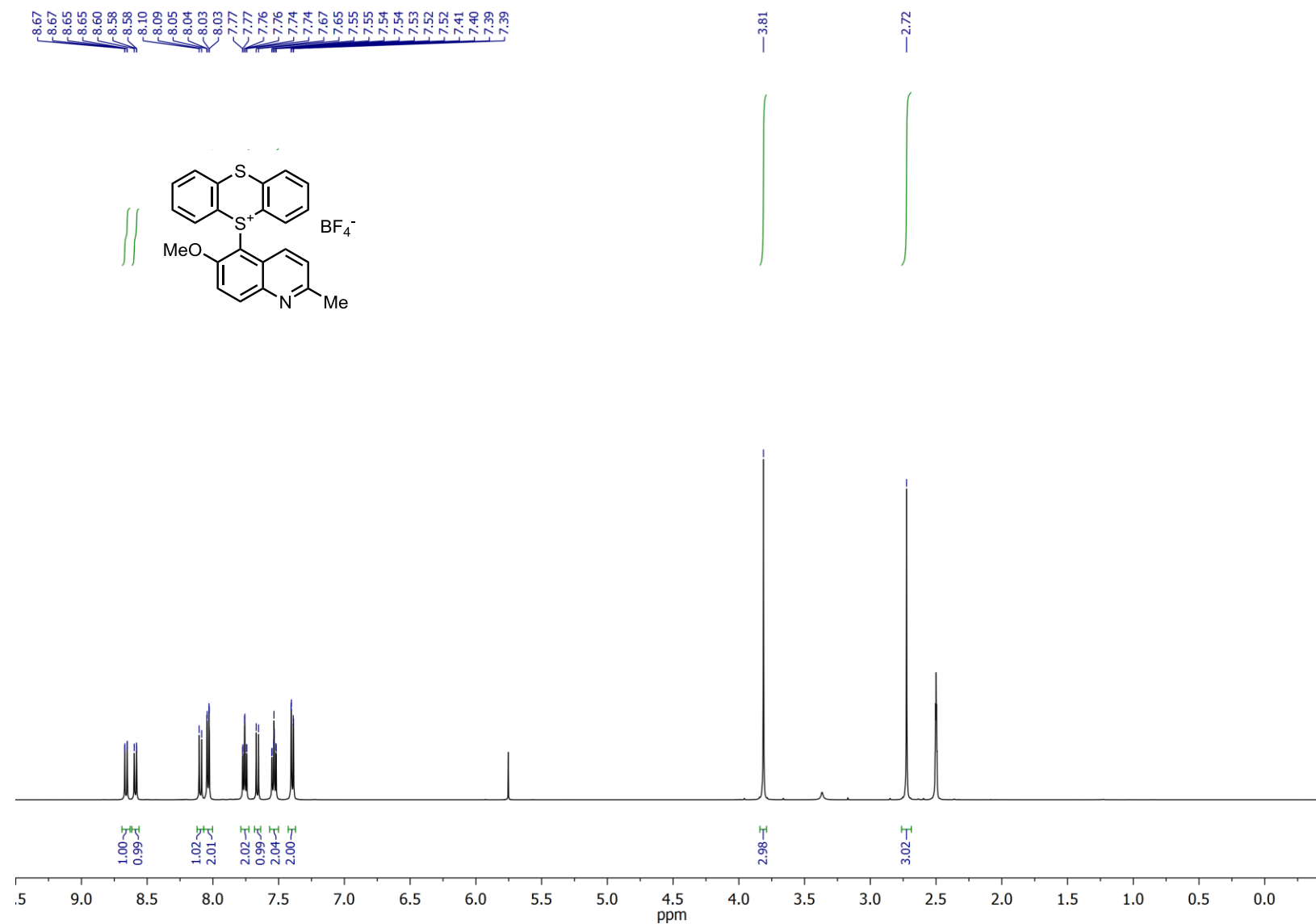
**$^{13}\text{C}$  NMR of BINOL dimethylether-derived thianthrenium salt S9**CDCl<sub>3</sub>, 126 MHz, 298 K

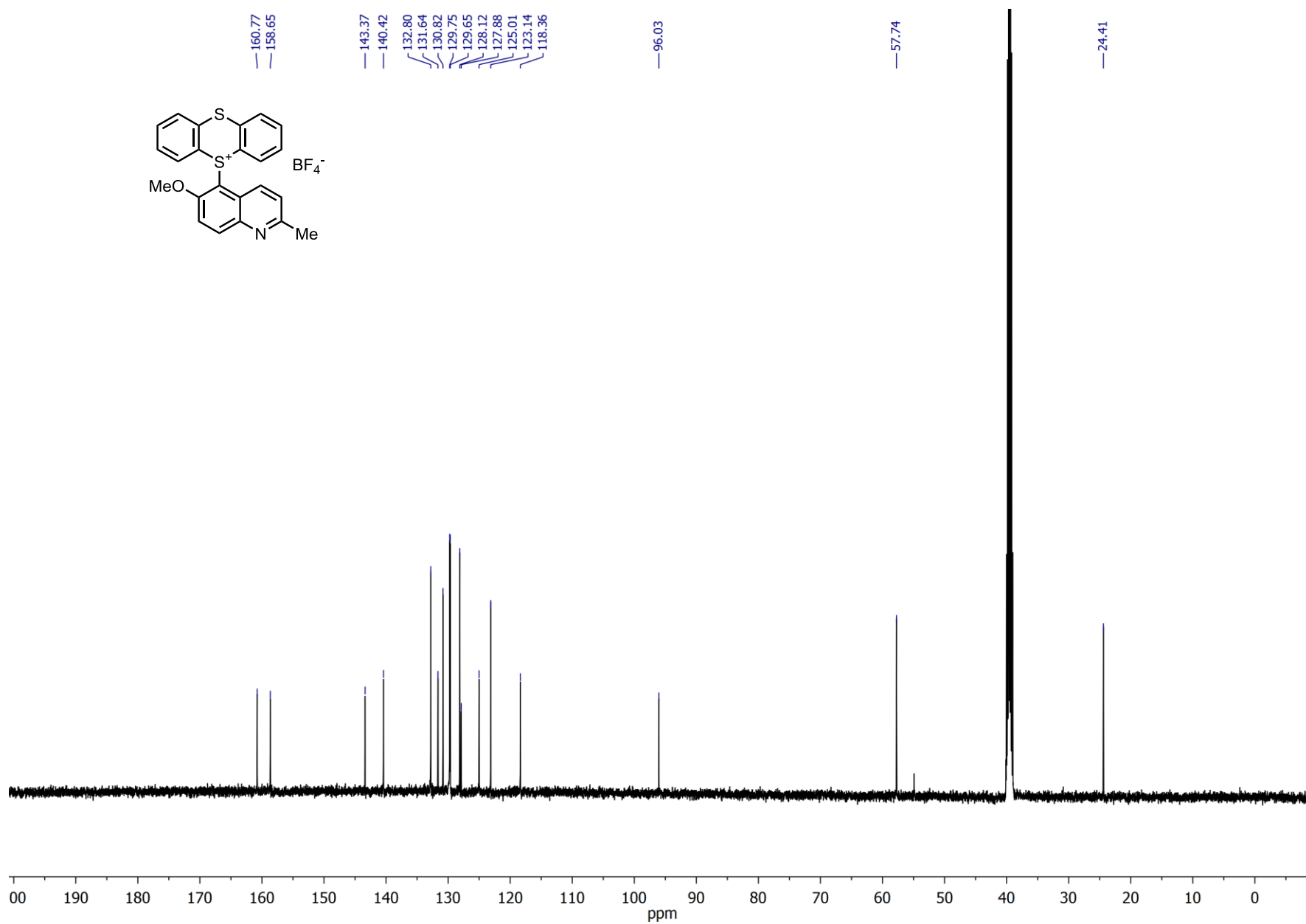
**$^{19}\text{F}$  NMR of BINOL dimethylether-derived thianthrenium salt S9**CDCl<sub>3</sub>, 471 MHz, 298 K

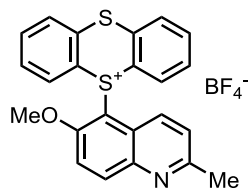
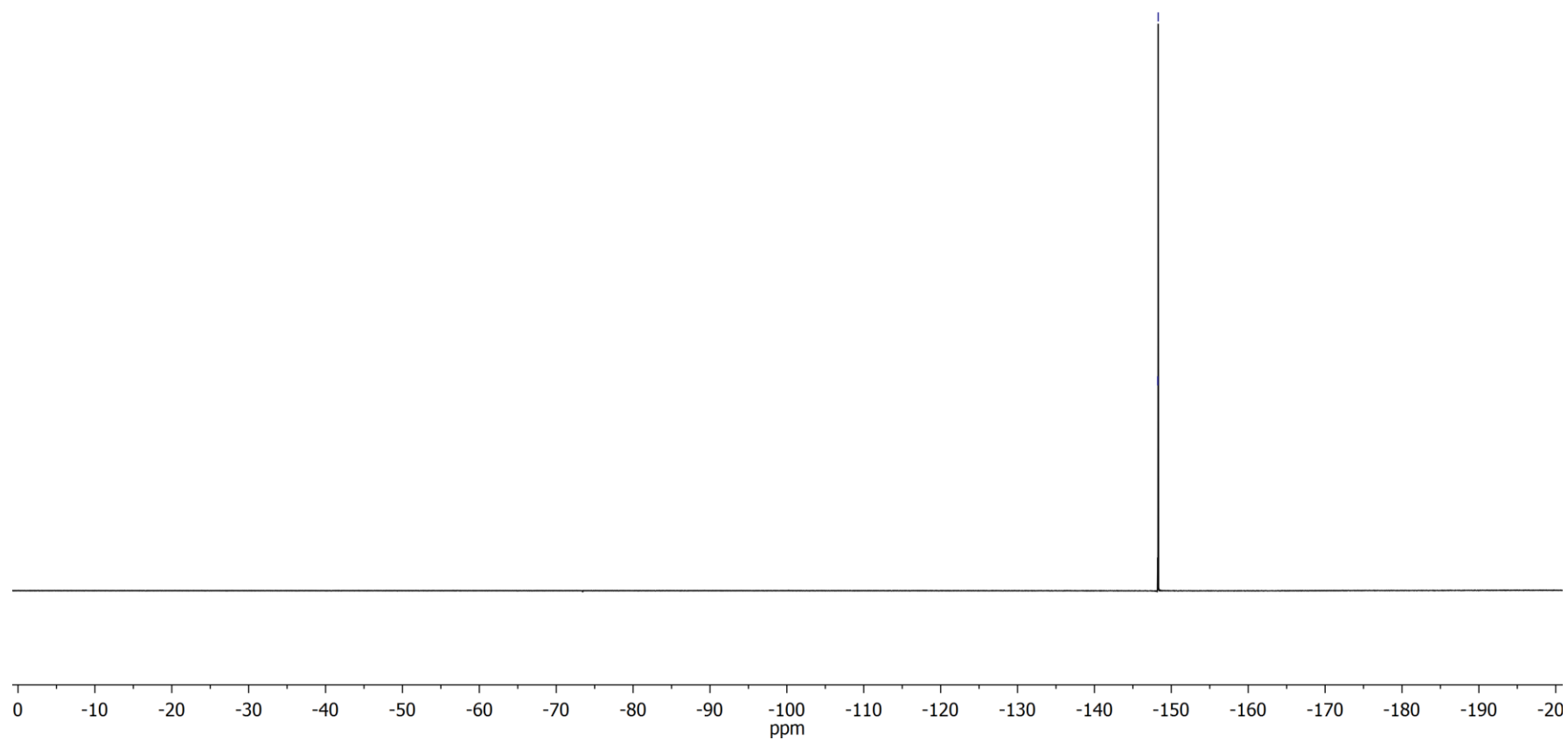
**$^1\text{H}$  NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10**CDCl<sub>3</sub>, 500 MHz, 298 K

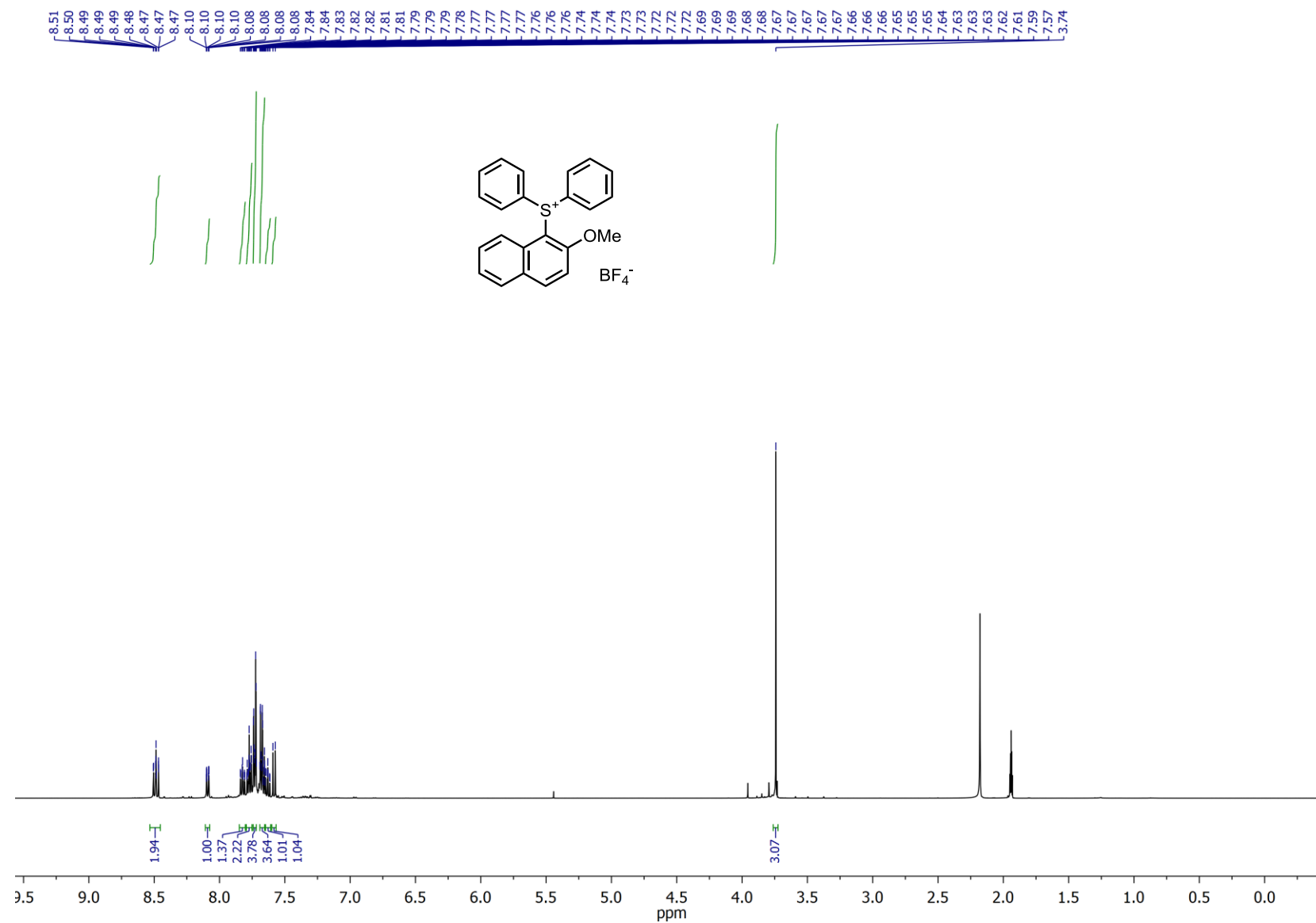
**$^{13}\text{C}$  NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10**CDCl<sub>3</sub>, 126 MHz, 298 K

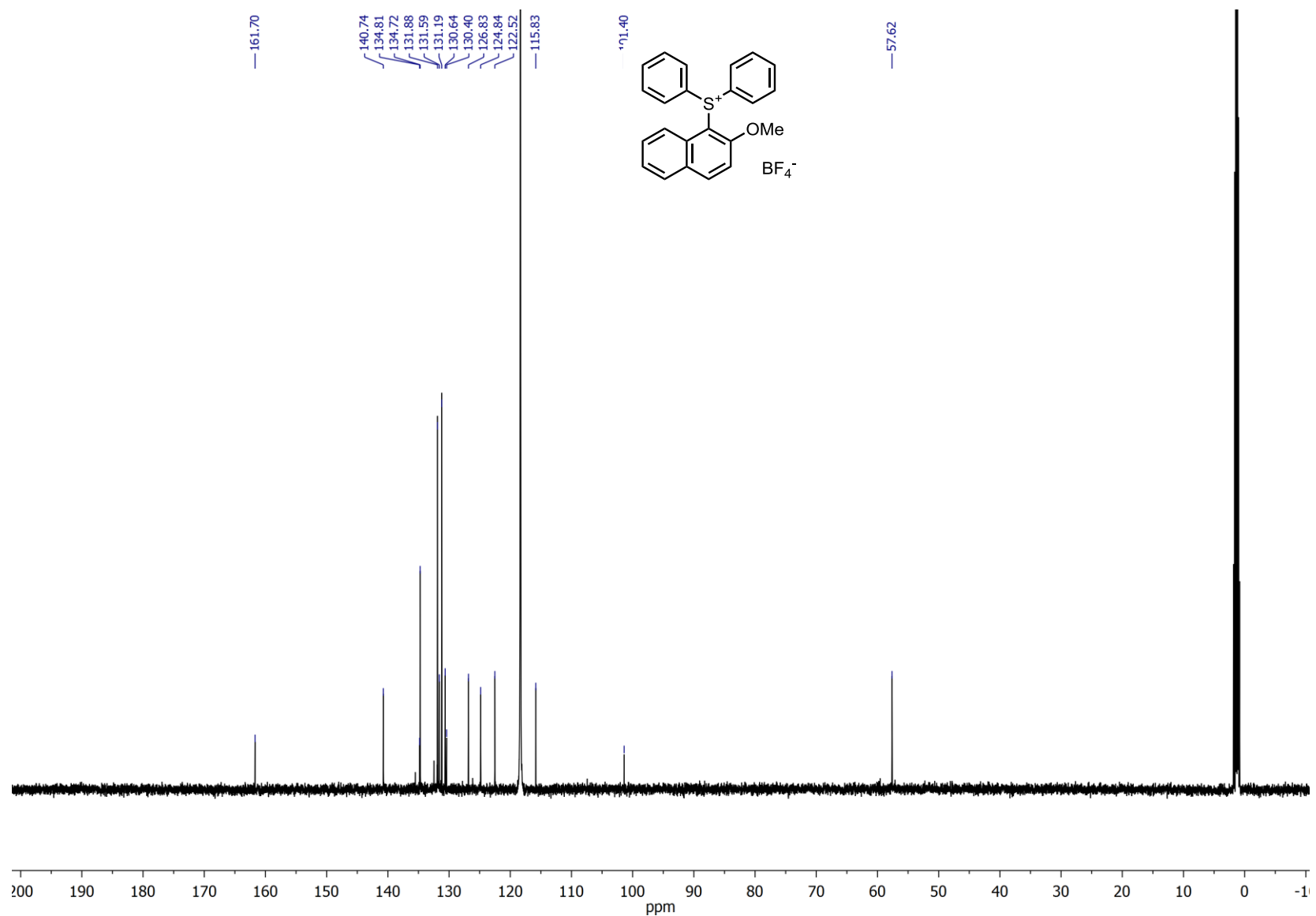
**$^{19}\text{F}$  NMR of 3-phenylthiophene-derived dibenzothiophenium salt S10**CDCl<sub>3</sub>, 471 MHz, 298 K

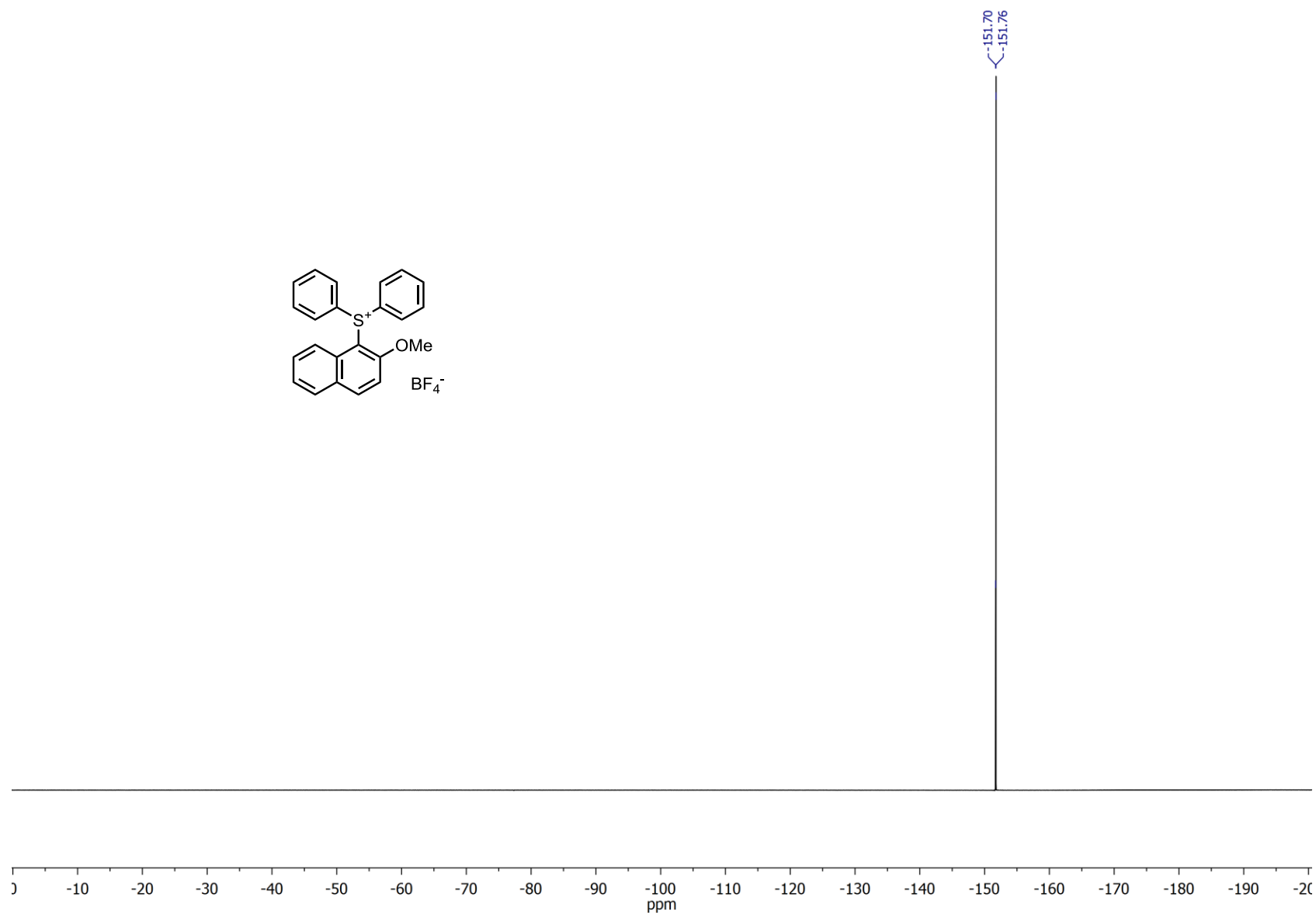
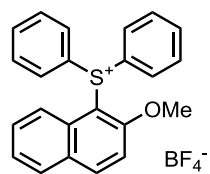
**<sup>1</sup>H NMR of methoxyquinolin-derived thiantrhenium salt S11**DMSO-*d*<sub>6</sub>, 500 MHz, 298 K

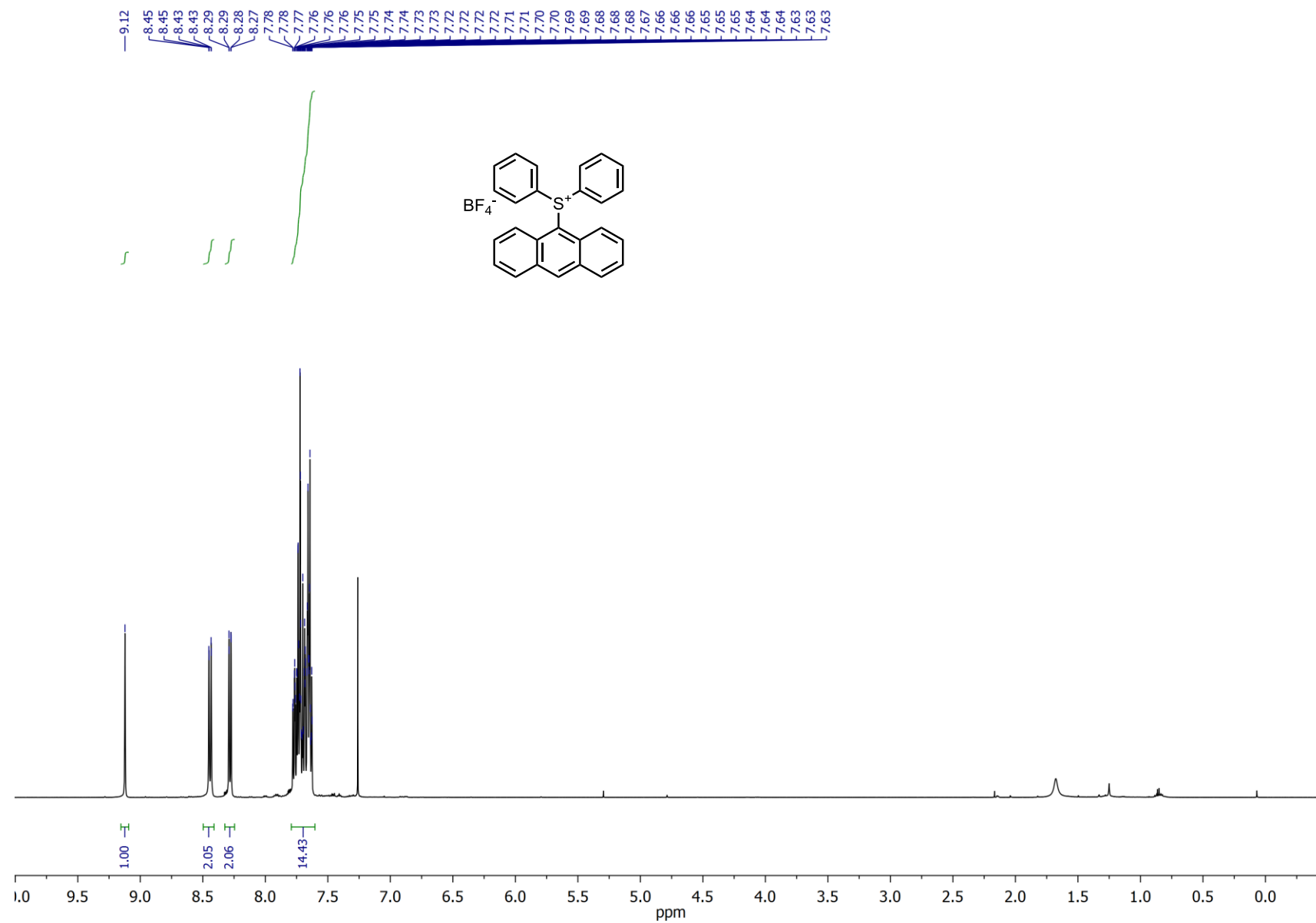
**$^{13}\text{C}$  NMR of methoxyquinolin-derived thiantrhenium salt S11**DMSO- $d_6$ , 126 MHz, 298 K

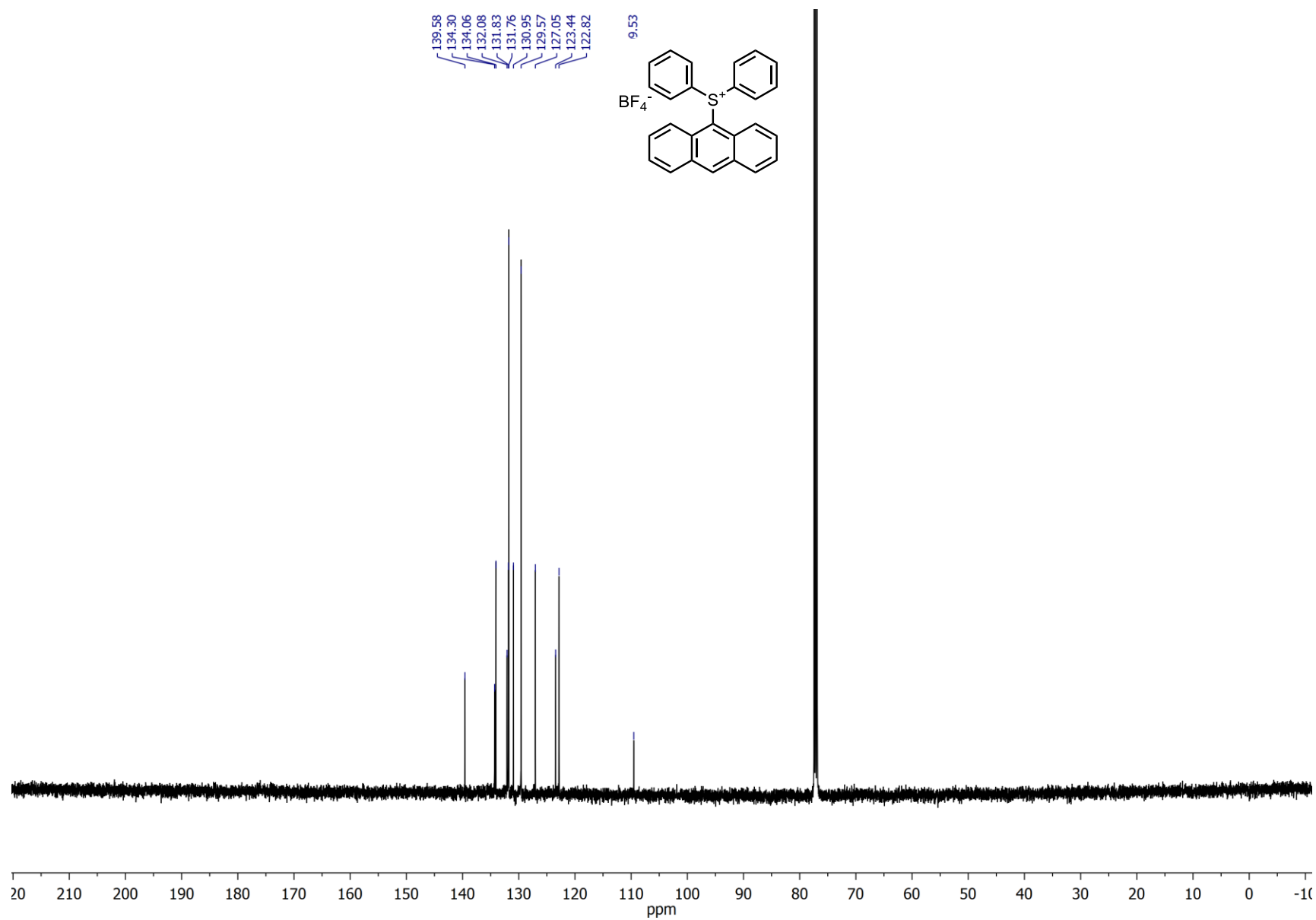
**$^{19}\text{F}$  NMR of methoxyquinolin-derived thiantrhenium salt S11**DMSO- $d_6$ , 471 MHz, 298 K $\sim 148.24$   
 $\sim 148.29$ 

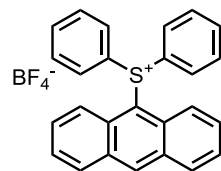
**$^1\text{H}$  NMR of methoxynaphthalin-derived diphenylsulfonium salt S12** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

**$^{13}\text{C}$  NMR of methoxynaphthalin-derived diphenylsulfonium salt S12** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

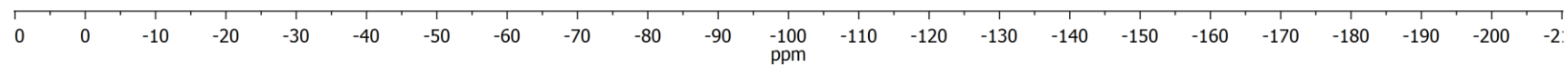
**$^{19}\text{F}$  NMR of methoxynaphthalin-derived diphenylsulfonium salt S12** $\text{CD}_3\text{CN}$ , 471 MHz, 298 K

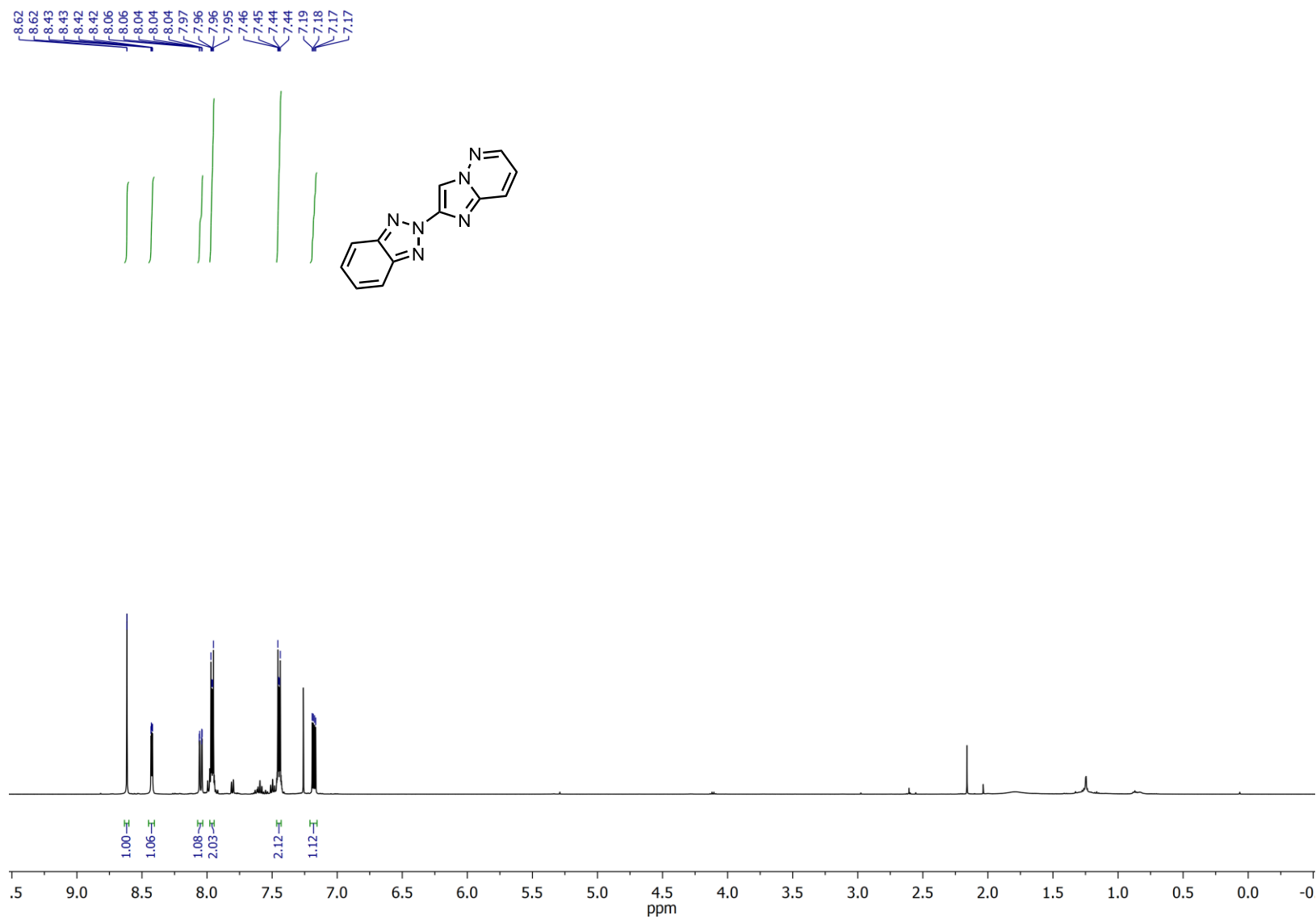
**$^1\text{H}$  NMR of anthracen-derived diphenylsulfonium salt S13**CDCl<sub>3</sub>, 500 MHz, 298 K

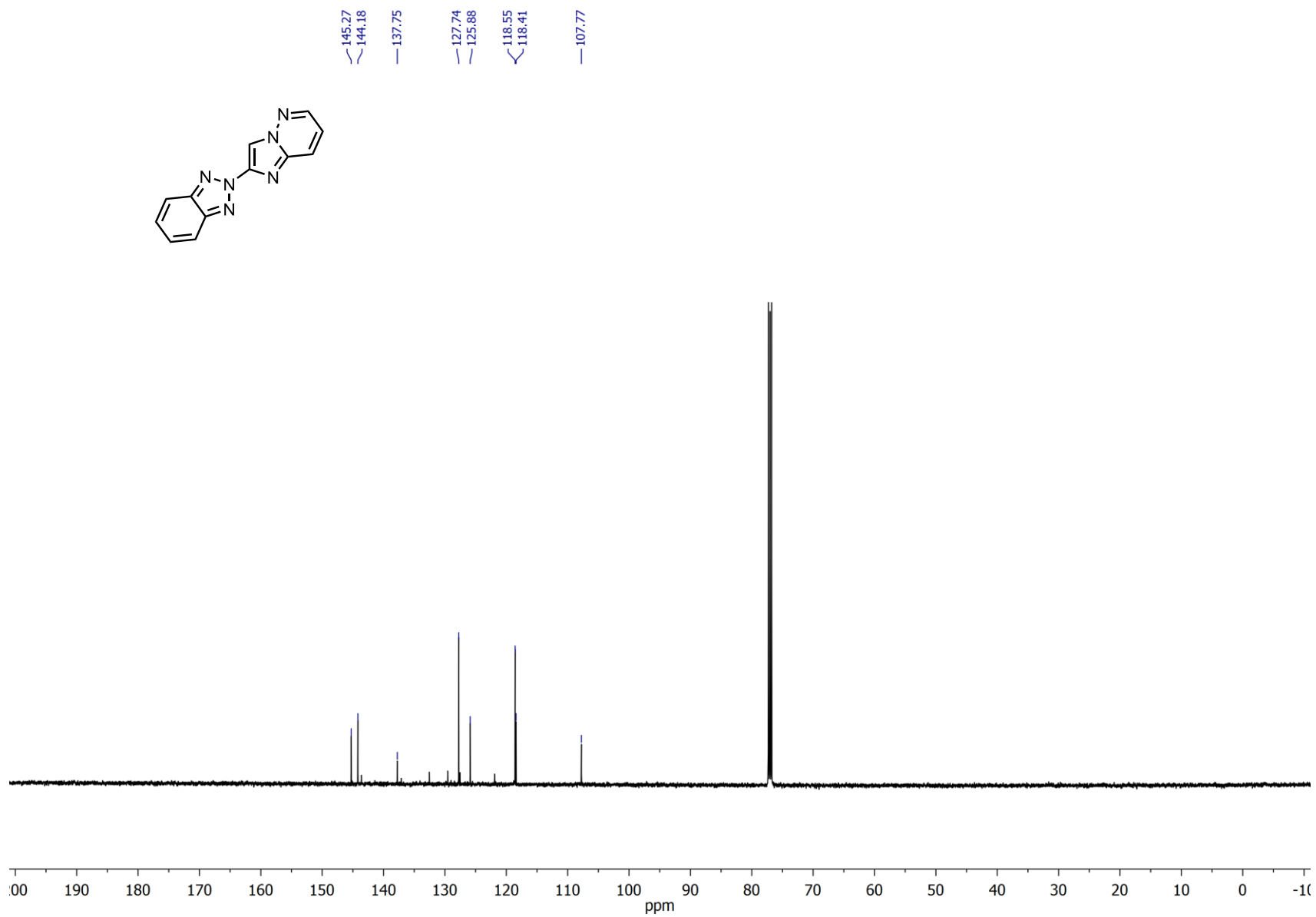
**$^{13}\text{C}$  NMR of anthracen-derived diphenylsulfonium salt S13**CDCl<sub>3</sub>, 126 MHz, 298 K

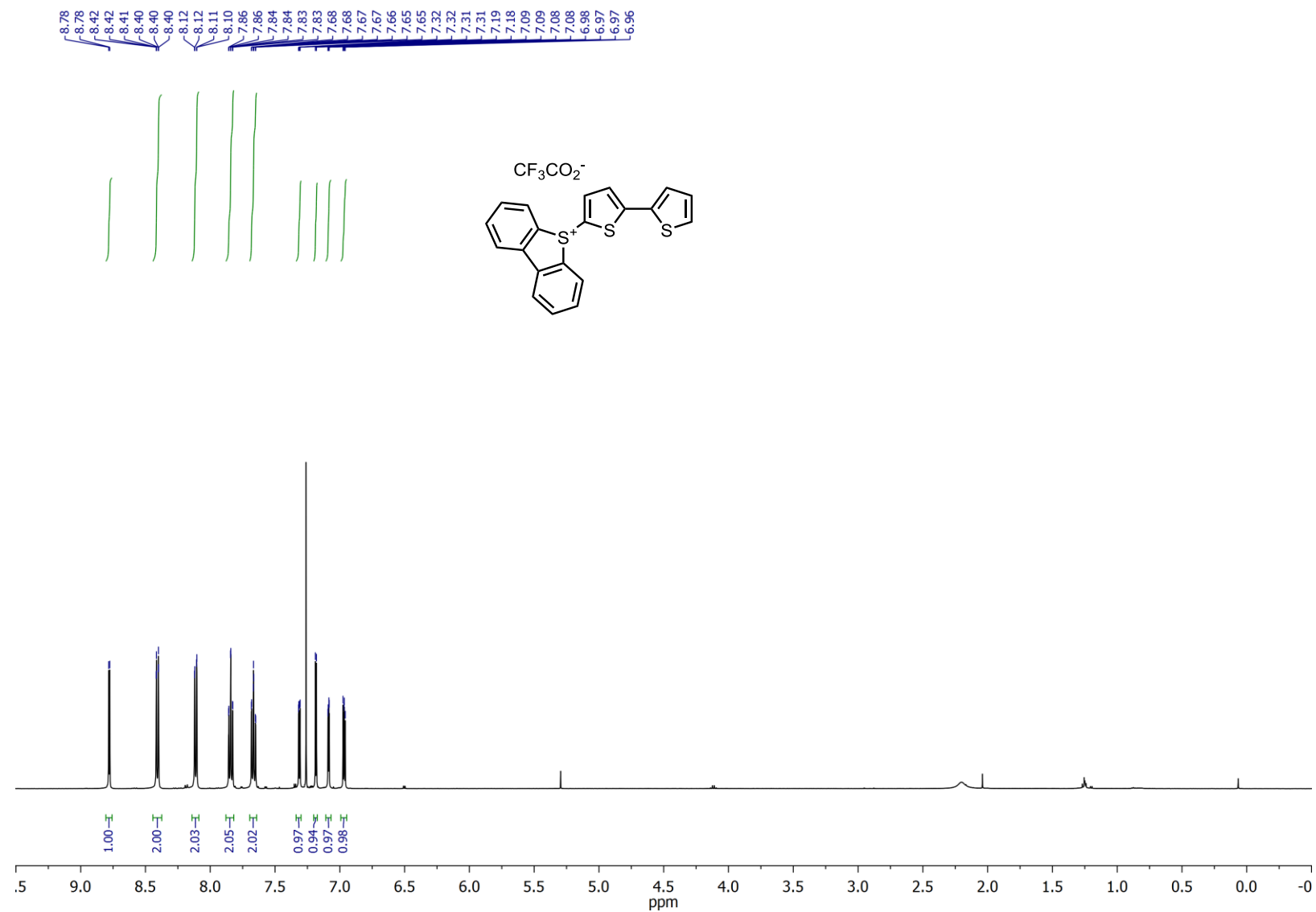
**$^{19}\text{F}$  NMR of anthracen-derived diphenylsulfonium salt S13** $\text{CDCl}_3$ , 471 MHz, 298 K

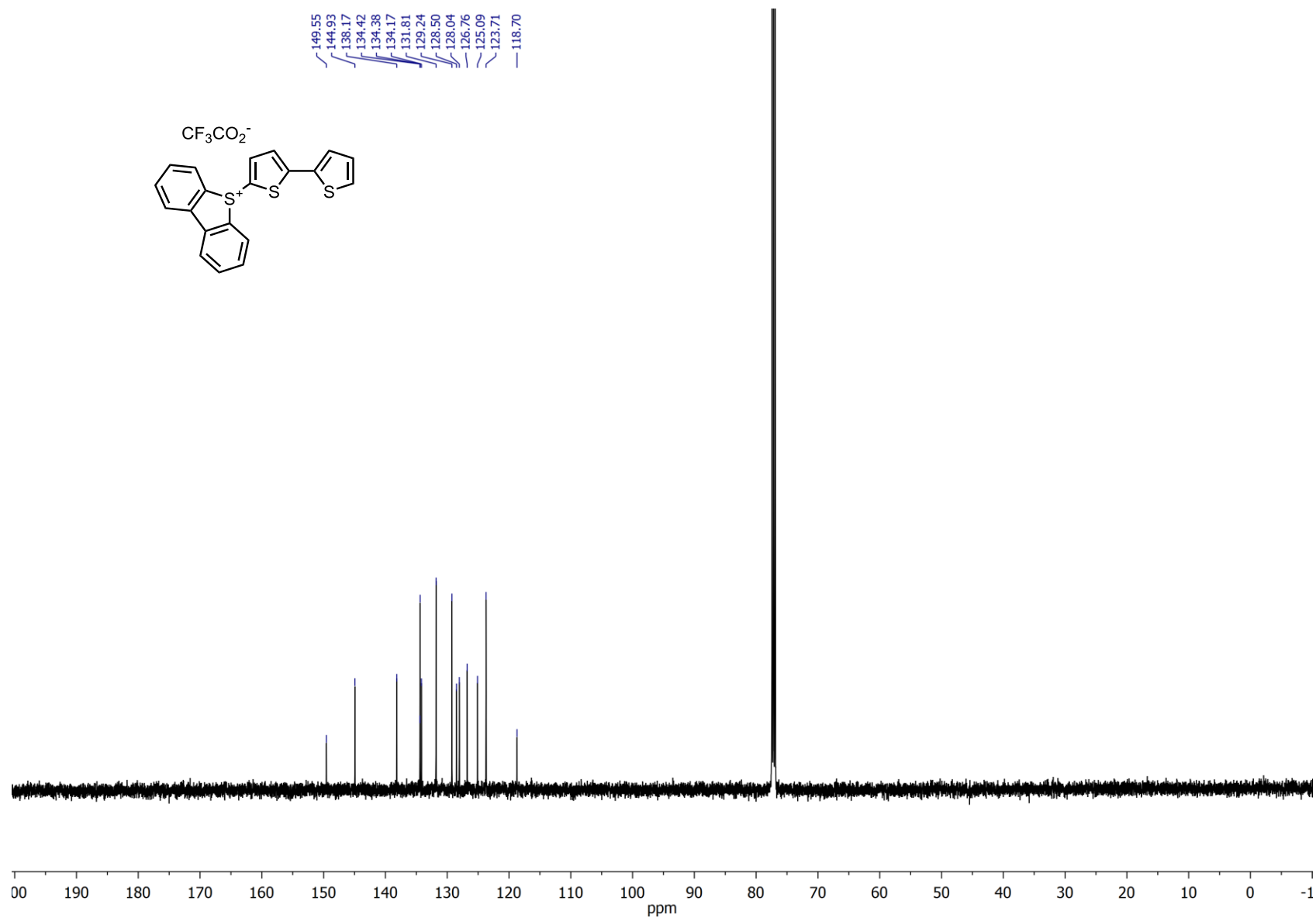
152.91  
152.96

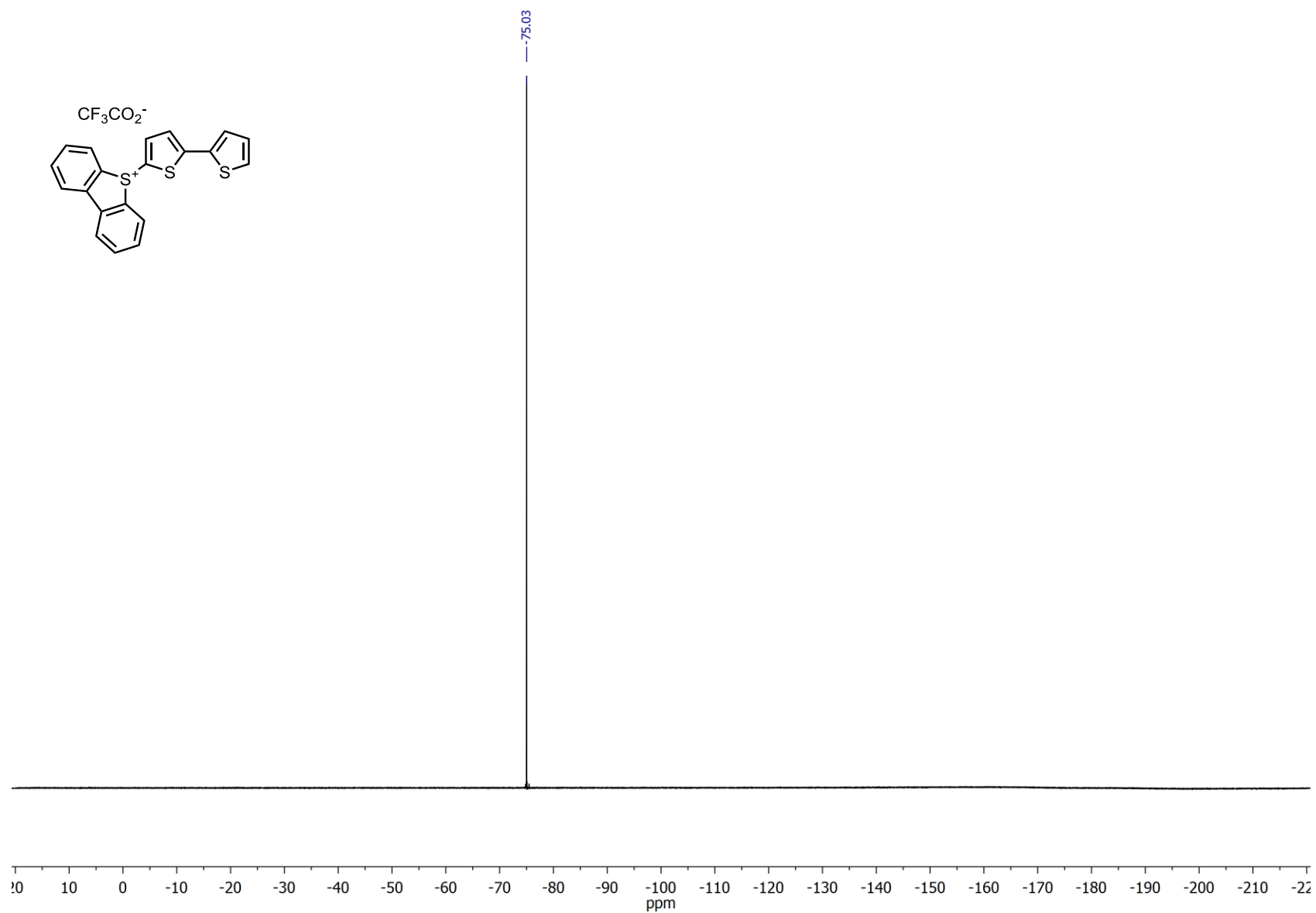


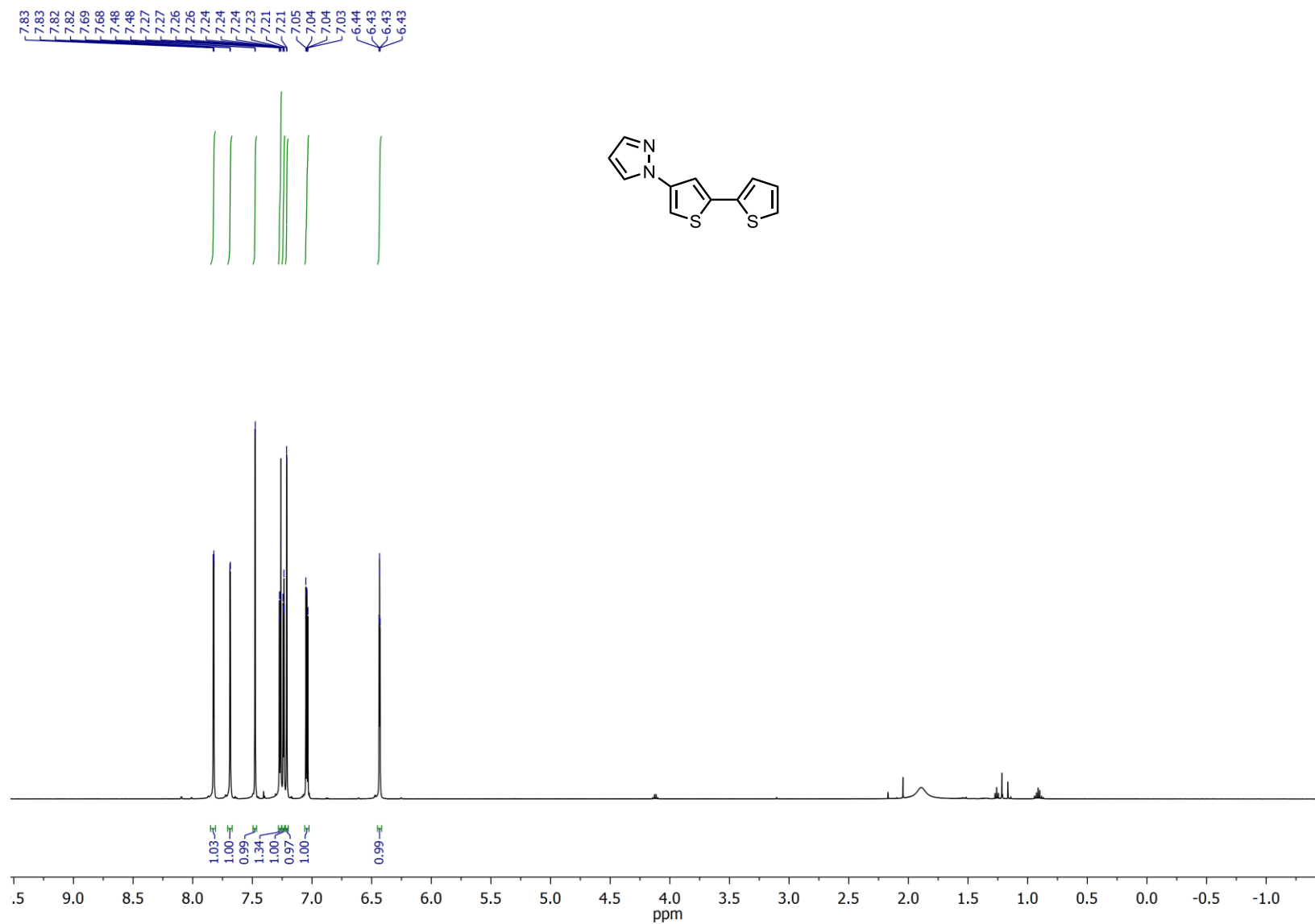
**<sup>1</sup>H NMR of benzotriazol-substituted imidazopyridazine S14**CDCl<sub>3</sub>, 500 MHz, 298 K

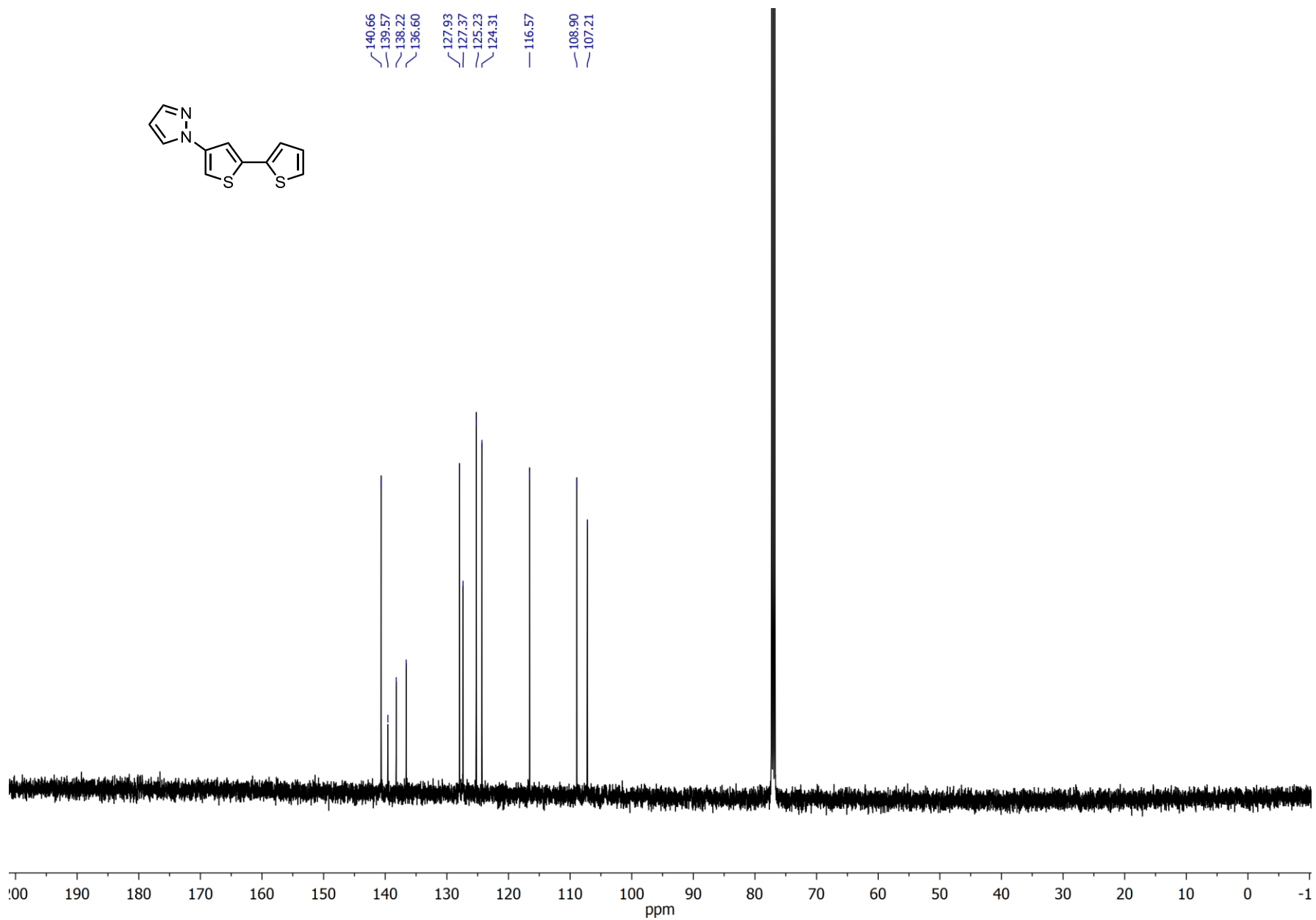
**$^{13}\text{C}$  NMR of benzotriazol-substituted imidazopyridazine S14**CDCl<sub>3</sub>, 126 MHz, 298 K

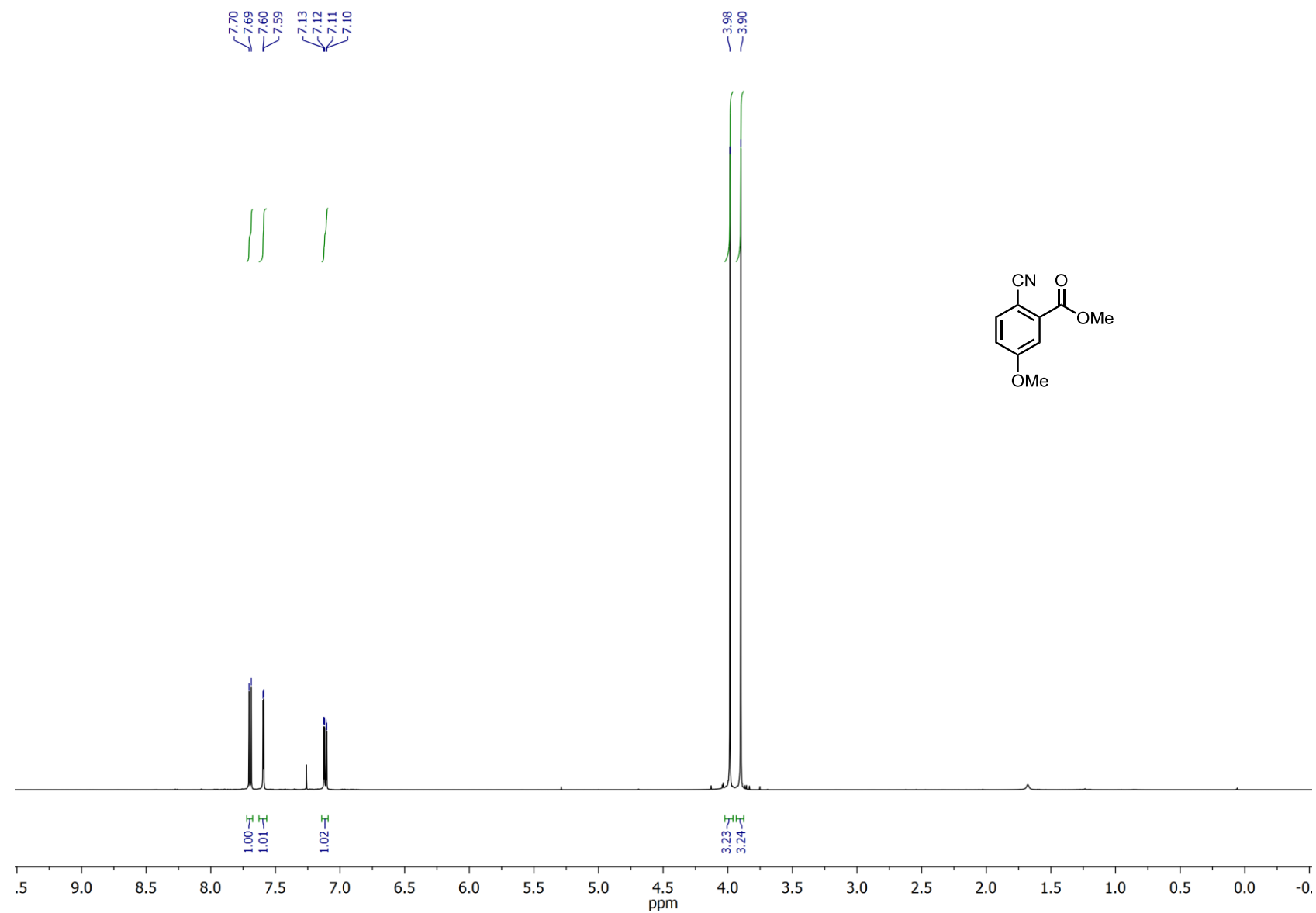
**$^1\text{H}$  NMR of bithiophen-derived dibenzothiophenium salt 1**CDCl<sub>3</sub>, 500 MHz, 298 K

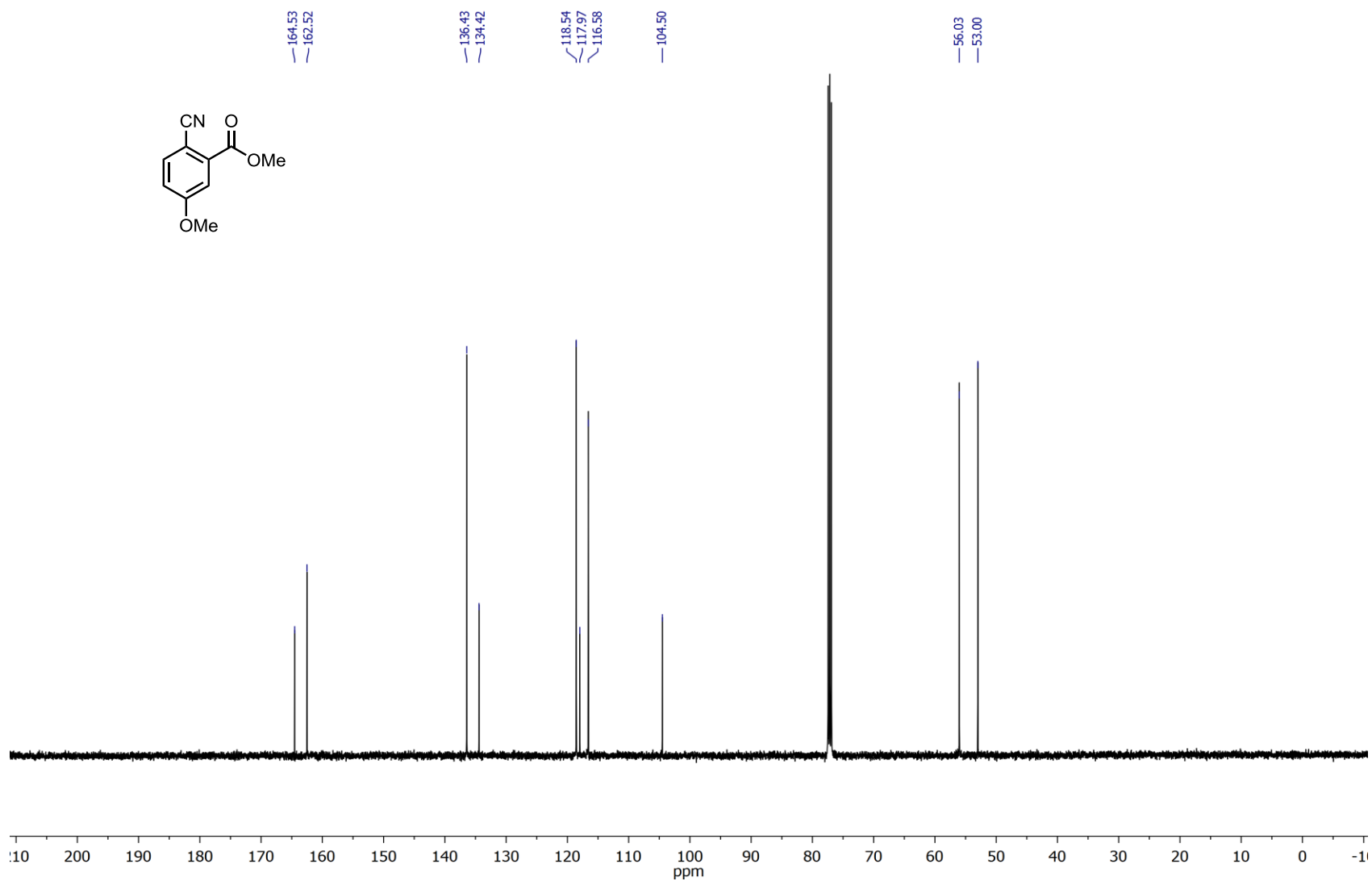
**$^{13}\text{C}$  NMR of bithiophen-derived dibenzothiophenium salt 1**CDCl<sub>3</sub>, 126 MHz, 298 K

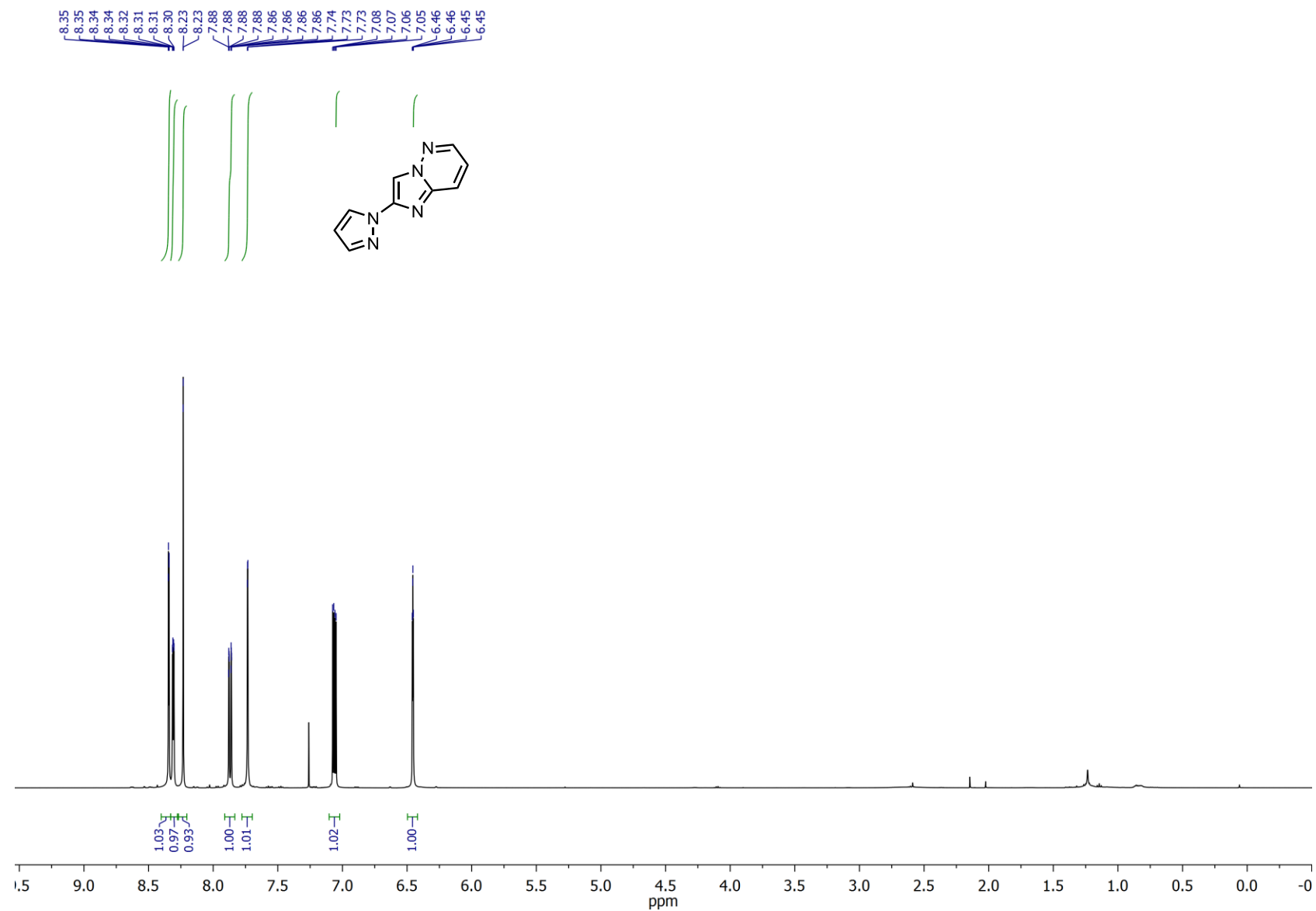
**$^{19}\text{F}$  NMR of bithiophen-derived dibenzothiophenium salt 1** $\text{CDCl}_3$ , 126 MHz, 298 K

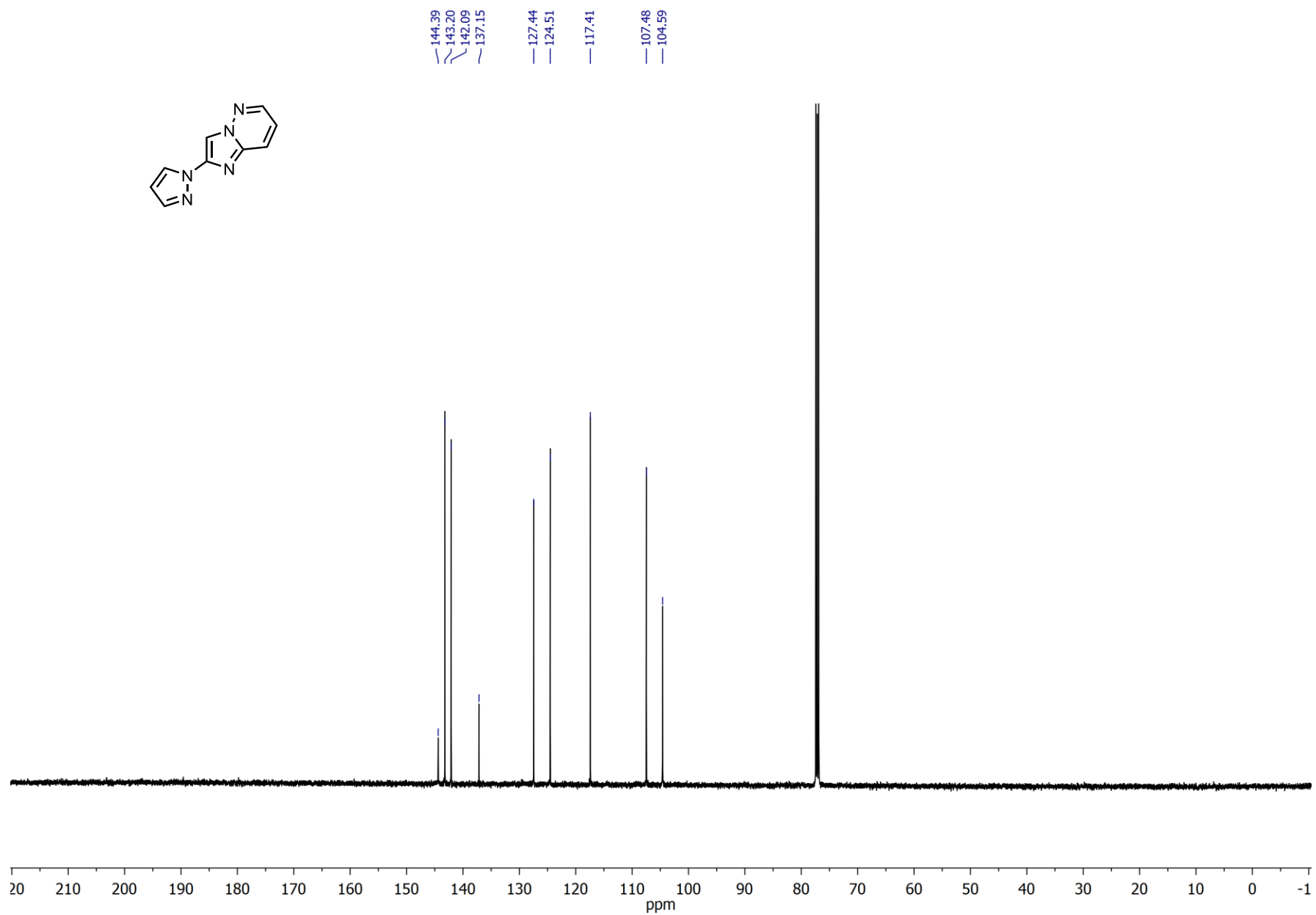
**$^1\text{H}$  NMR of pyrazol-substituted bithiophen 2**CDCl<sub>3</sub>, 500 MHz, 298 K

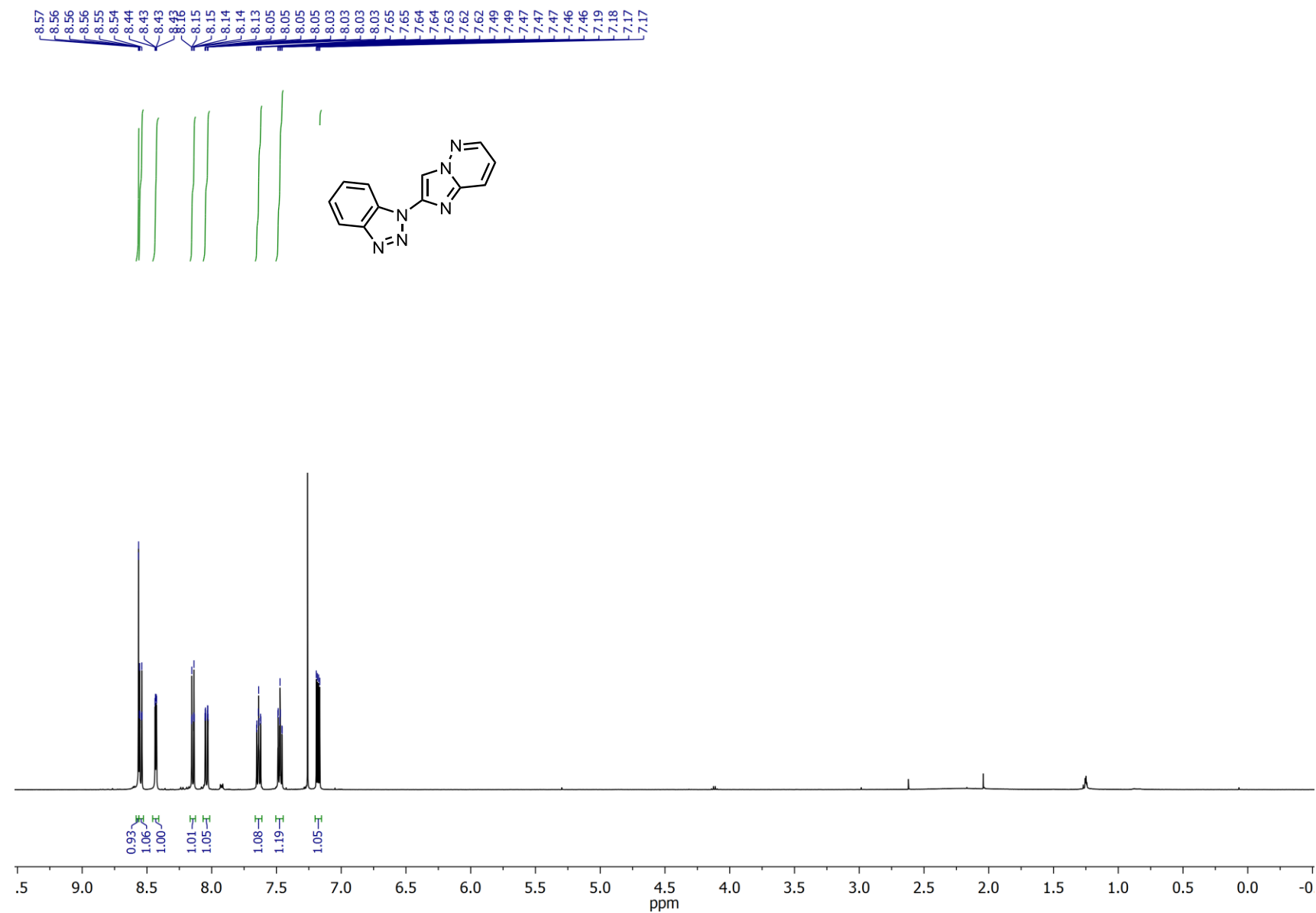
**$^{13}\text{C}$  NMR of pyrazol-substituted bithiophen 2**CDCl<sub>3</sub>, 126 MHz, 298 K

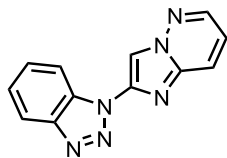
**$^1\text{H}$  NMR of cyano methoxy methylbenzoate 4**CDCl<sub>3</sub>, 500 MHz, 298 K

**$^{13}\text{C}$  NMR of cyano methoxy methylbenzoate 4**CDCl<sub>3</sub>, 126 MHz, 298 K

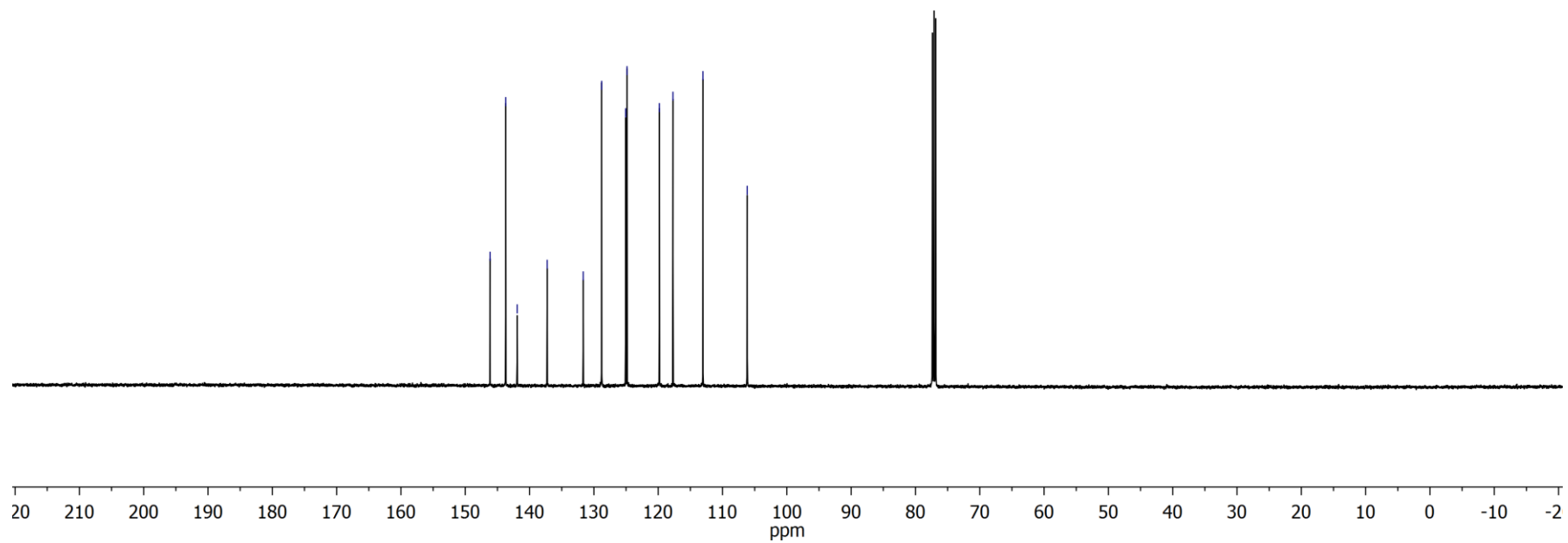
**$^1\text{H}$  NMR of pyrazol-substituted imidazopyridazine 5**CDCl<sub>3</sub>, 500 MHz, 298 K

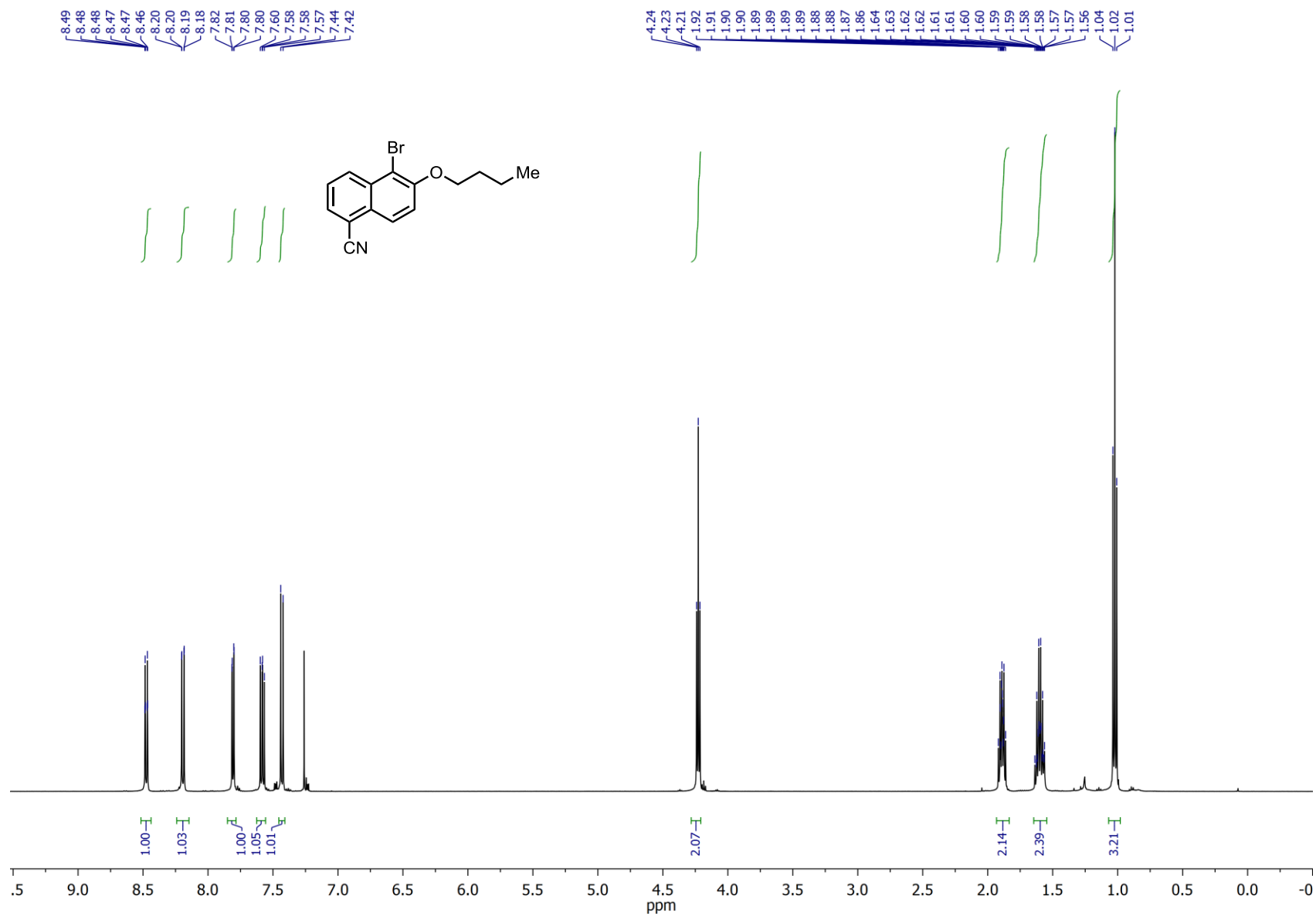
**$^{13}\text{C}$  NMR of pyrazol-substituted imidazopyridazine 5**CDCl<sub>3</sub>, 126 MHz, 298 K

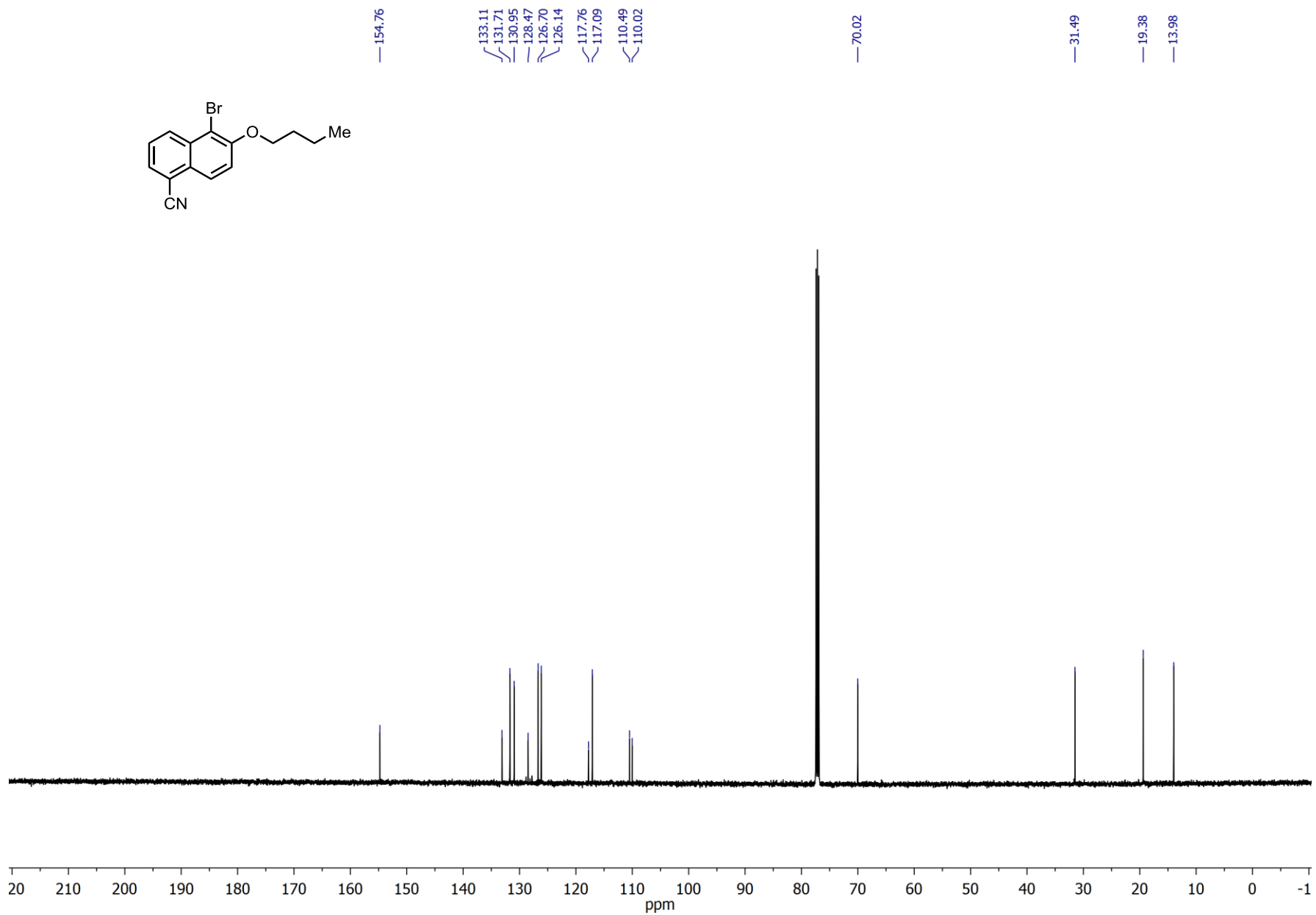
**$^1\text{H}$  NMR of benzotriazol-substituted imidazopyridazine 6**CDCl<sub>3</sub>, 500 MHz, 298 K

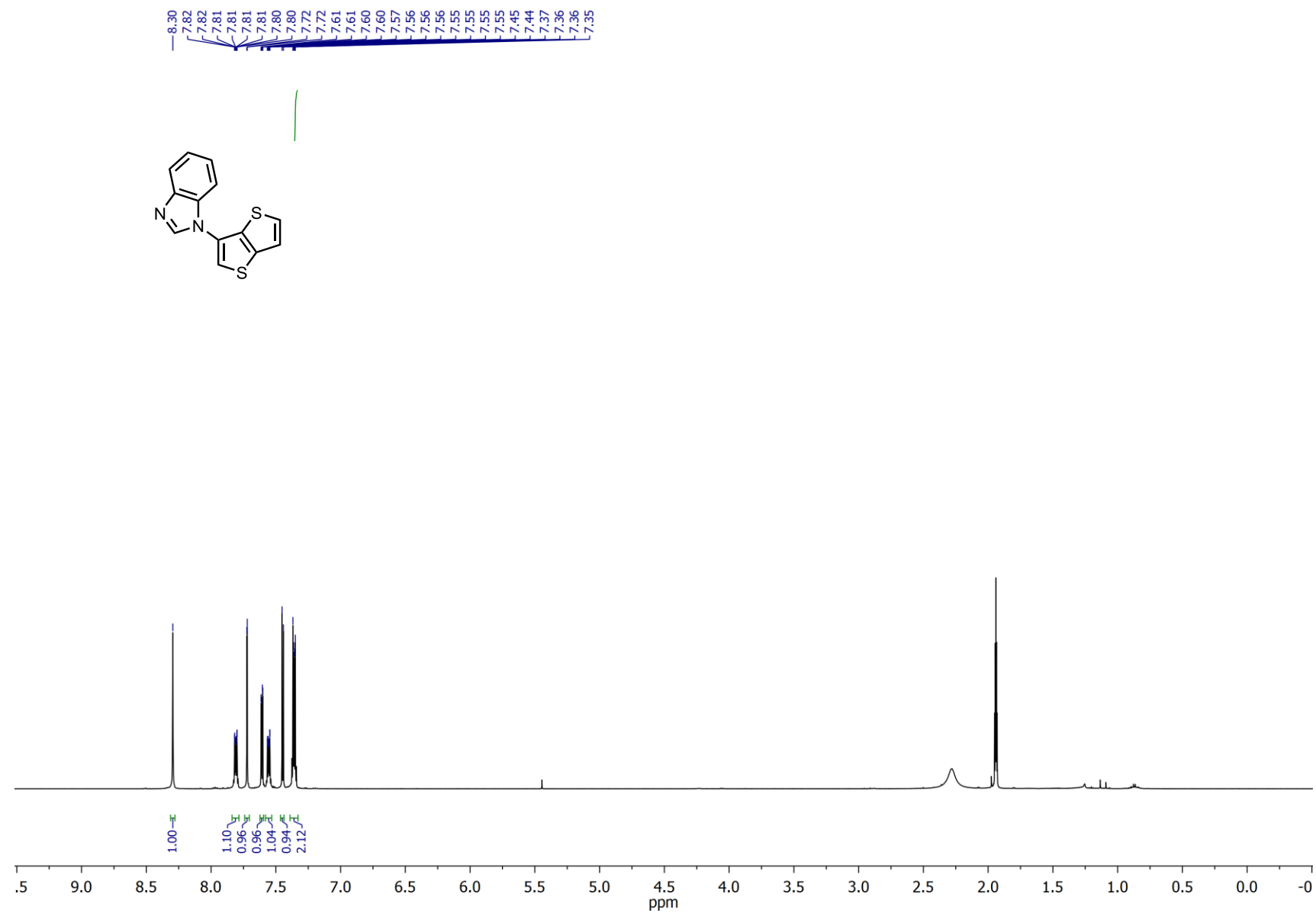
**$^{13}\text{C}$  NMR of benzotriazol-substituted imidazopyridazine 6**CDCl<sub>3</sub>, 126 MHz, 298 K

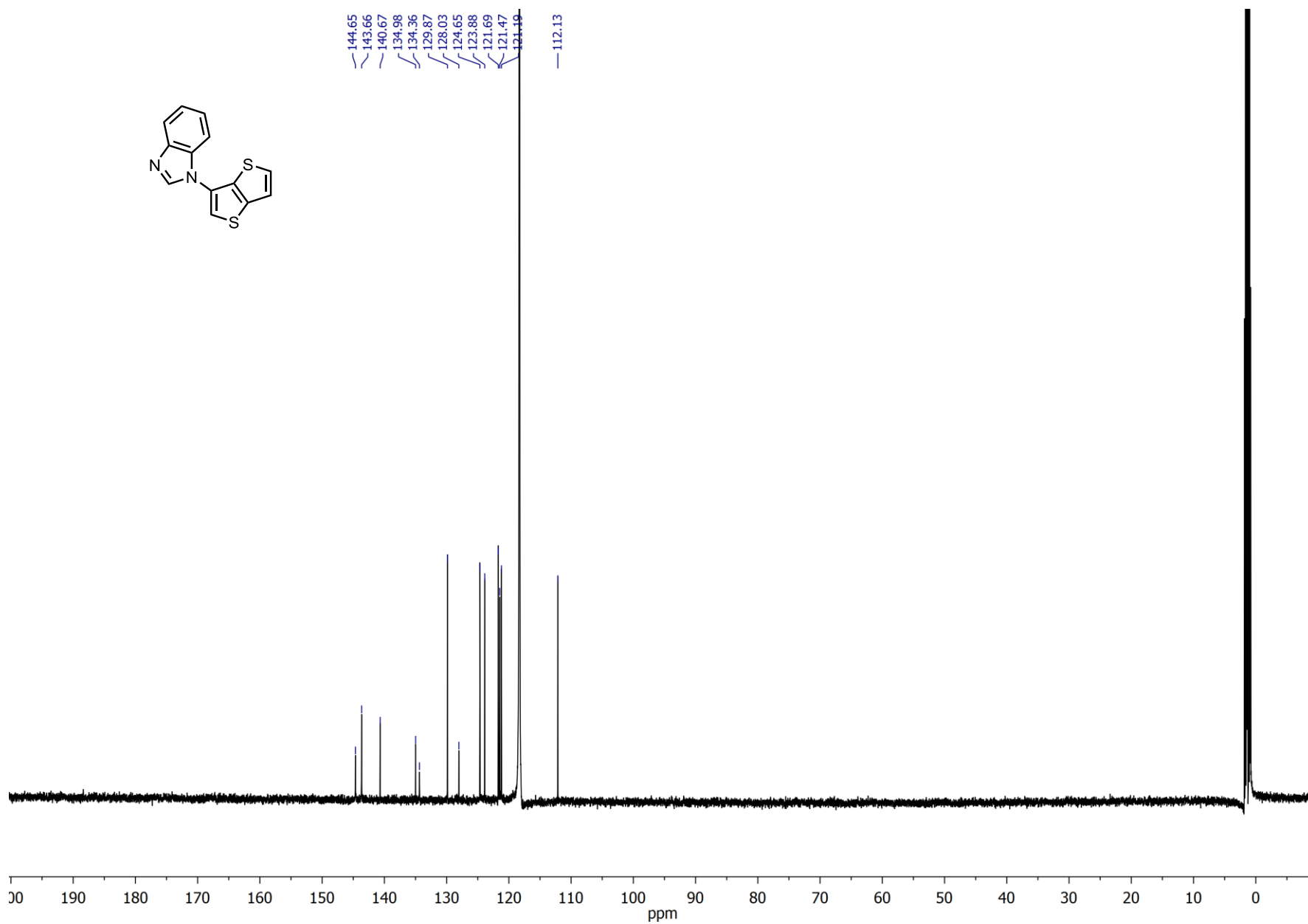
146.15  
143.71  
141.93  
137.26  
131.66  
128.79  
125.06  
124.85  
119.82  
117.71  
113.04  
106.17

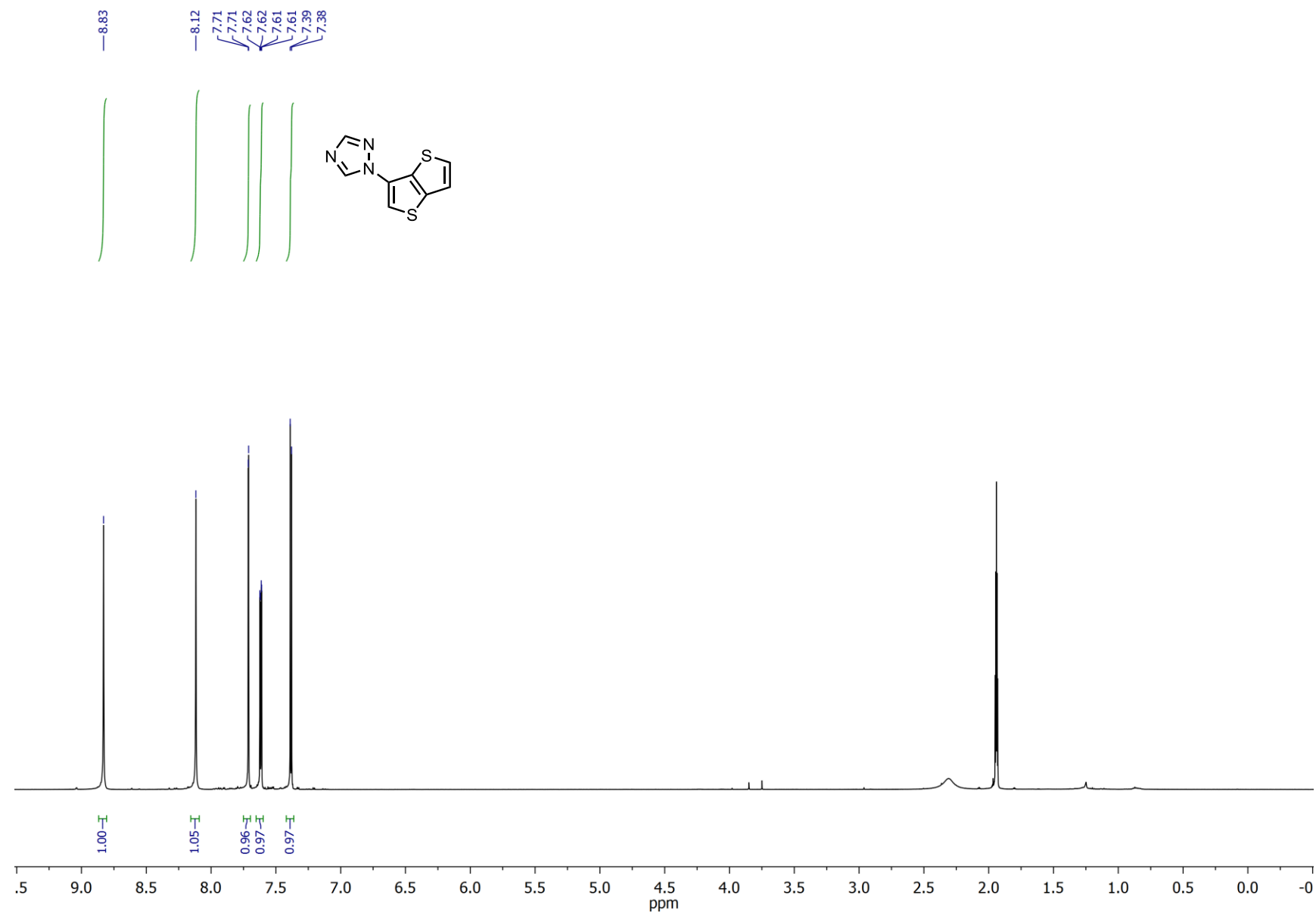


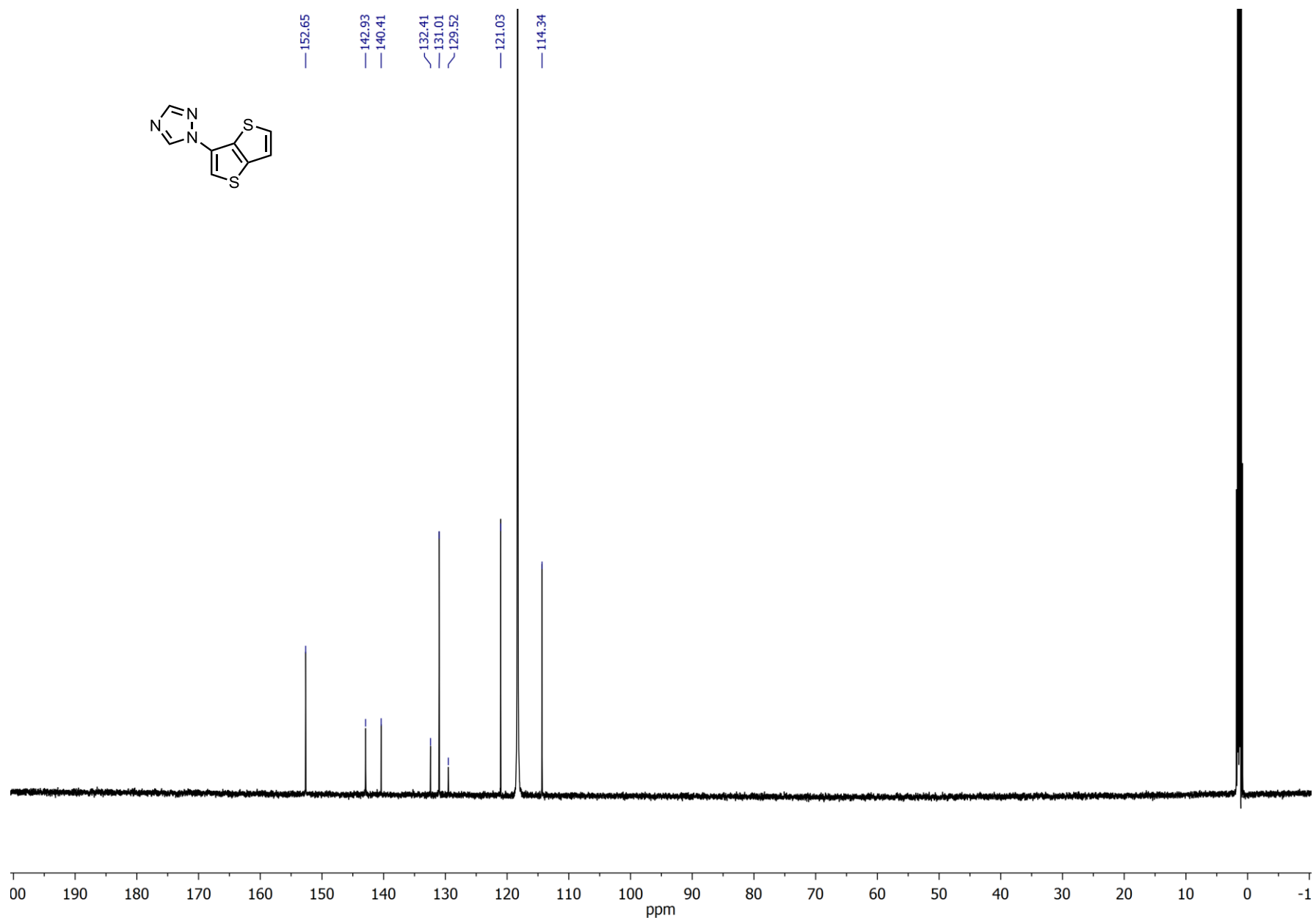
**$^1\text{H}$  NMR of cyano-substituted butoxynaphthalene 7**CDCl<sub>3</sub>, 500 MHz, 298 K

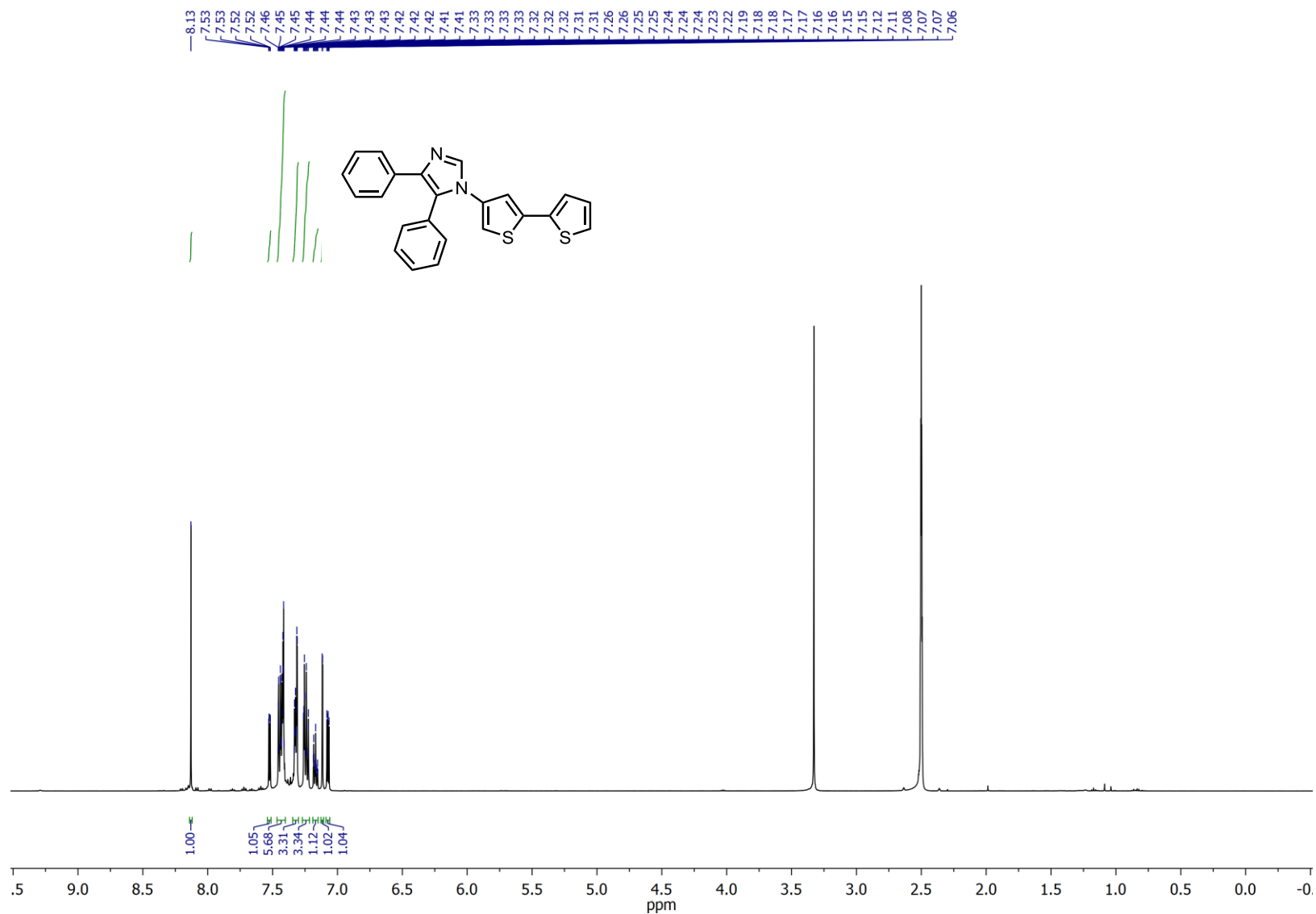
**$^{13}\text{C}$  NMR of cyano-substituted butoxynaphthalene 7**CDCl<sub>3</sub>, 126 MHz, 298 K

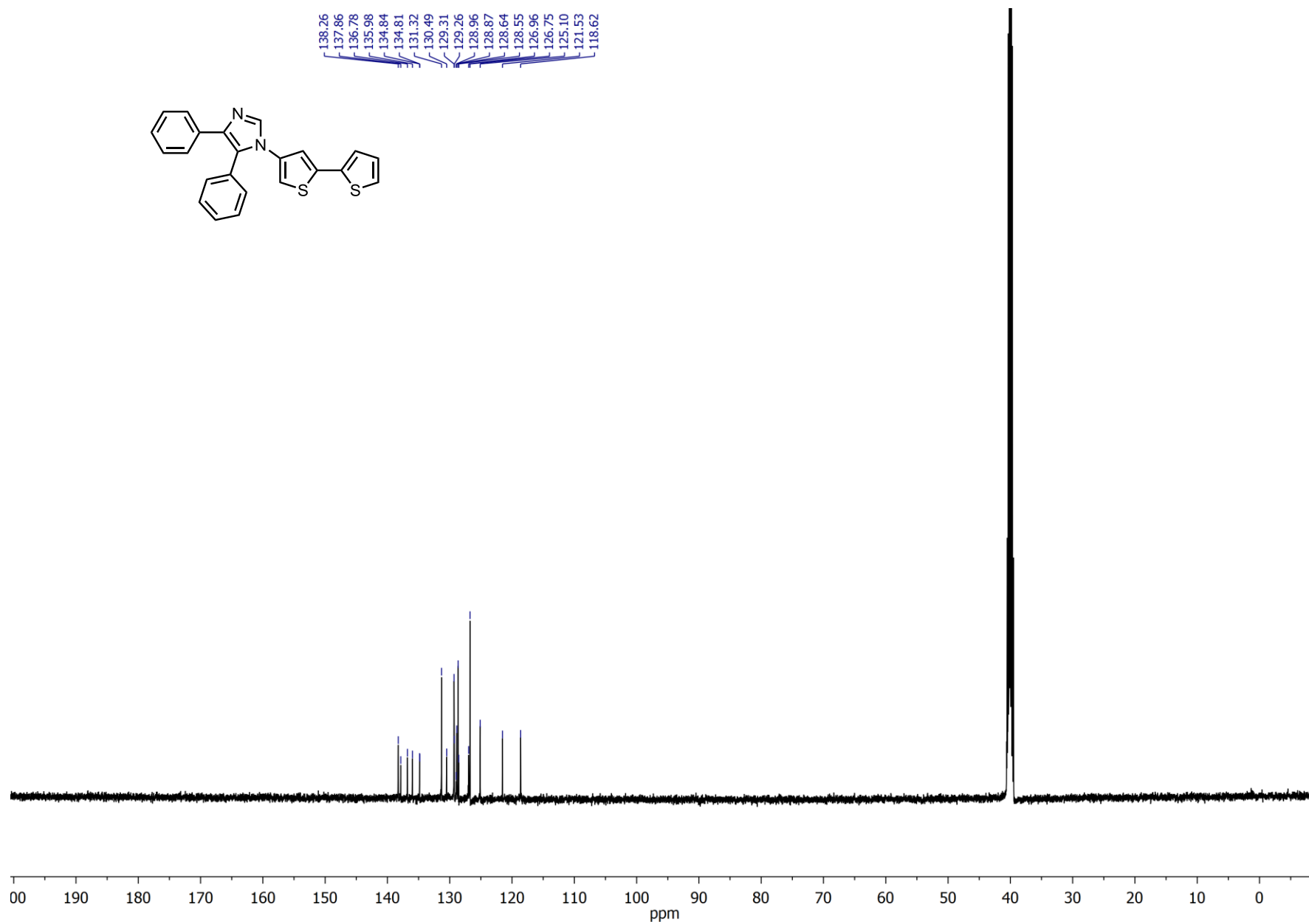
**$^1\text{H}$  NMR of benzimidazol-substituted thienothiophen 8** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

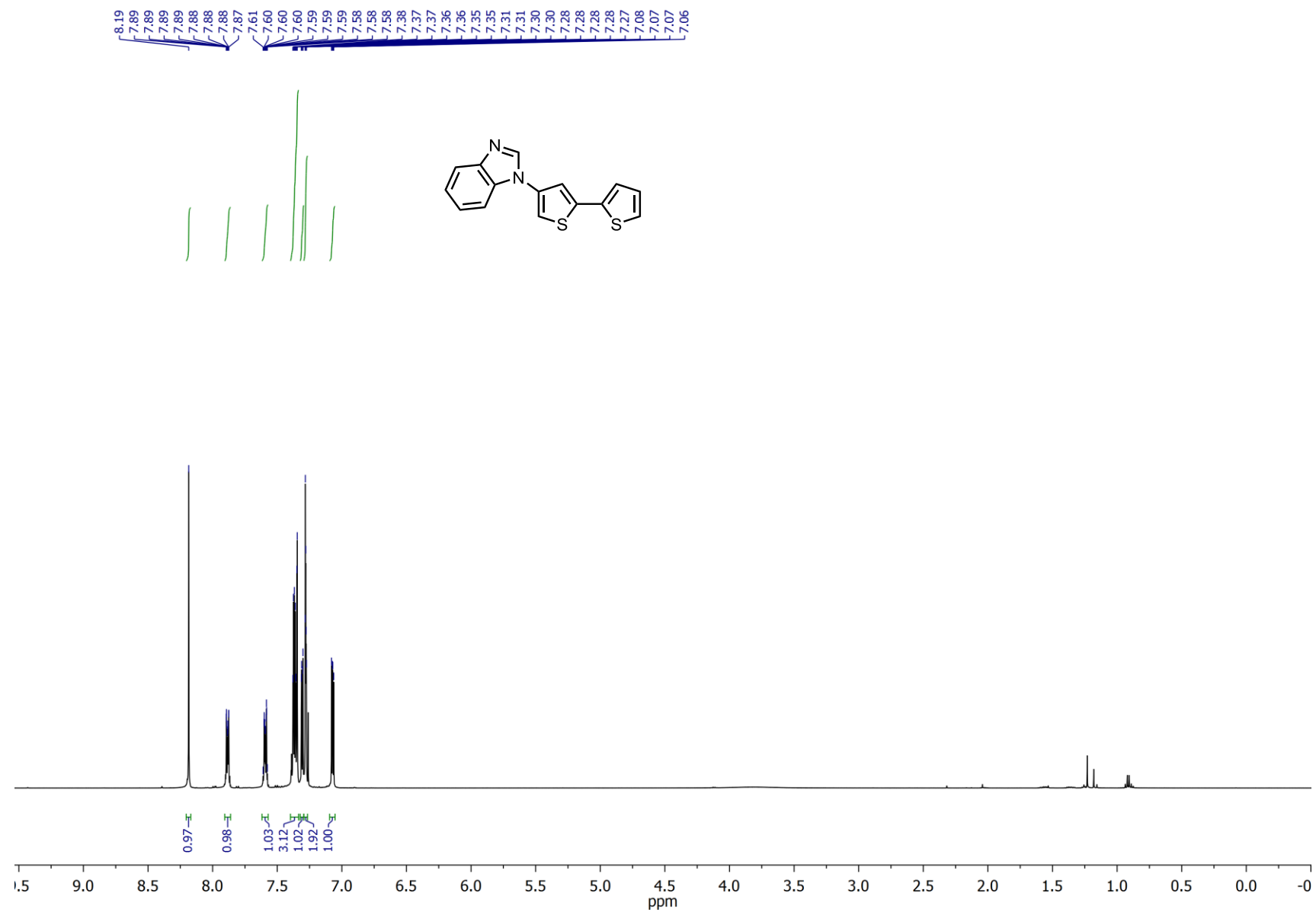
**$^{13}\text{C}$  NMR of benzimidazol-substituted thienothiophen 8** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

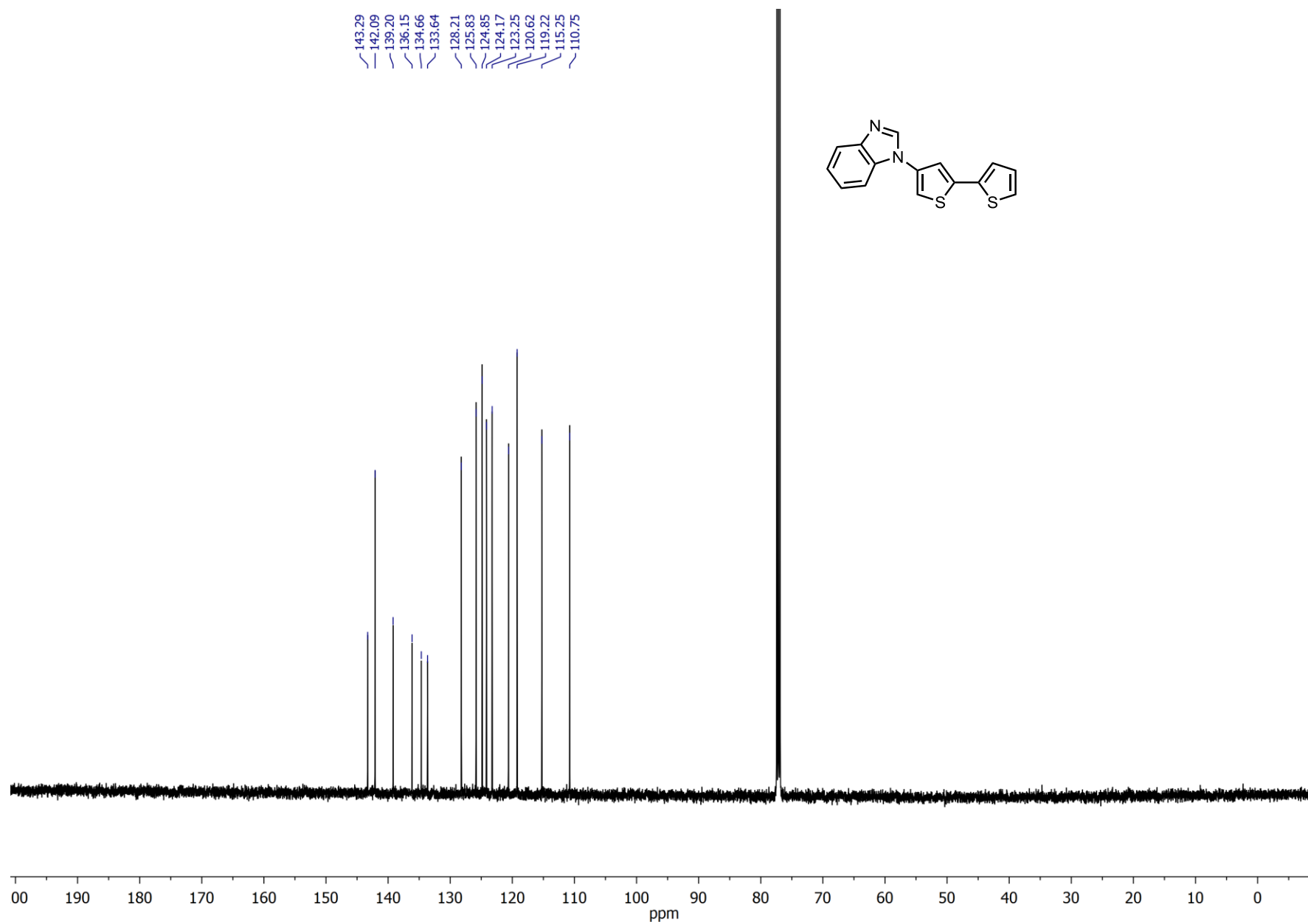
**$^1\text{H}$  NMR of triazol-substituted thienothiophen 9** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

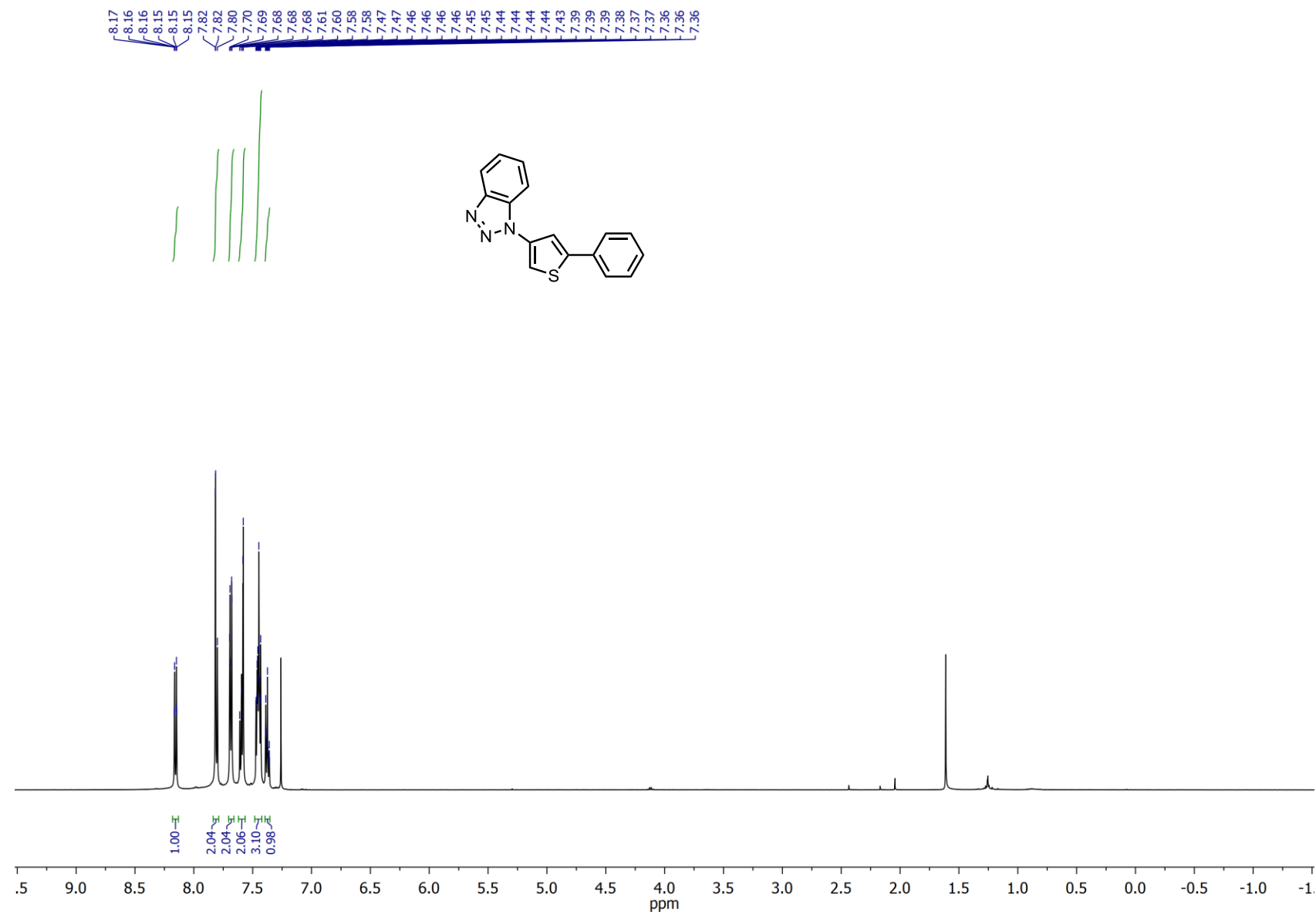
**$^{13}\text{C}$  NMR of triazol-substituted thienothiophen 9** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

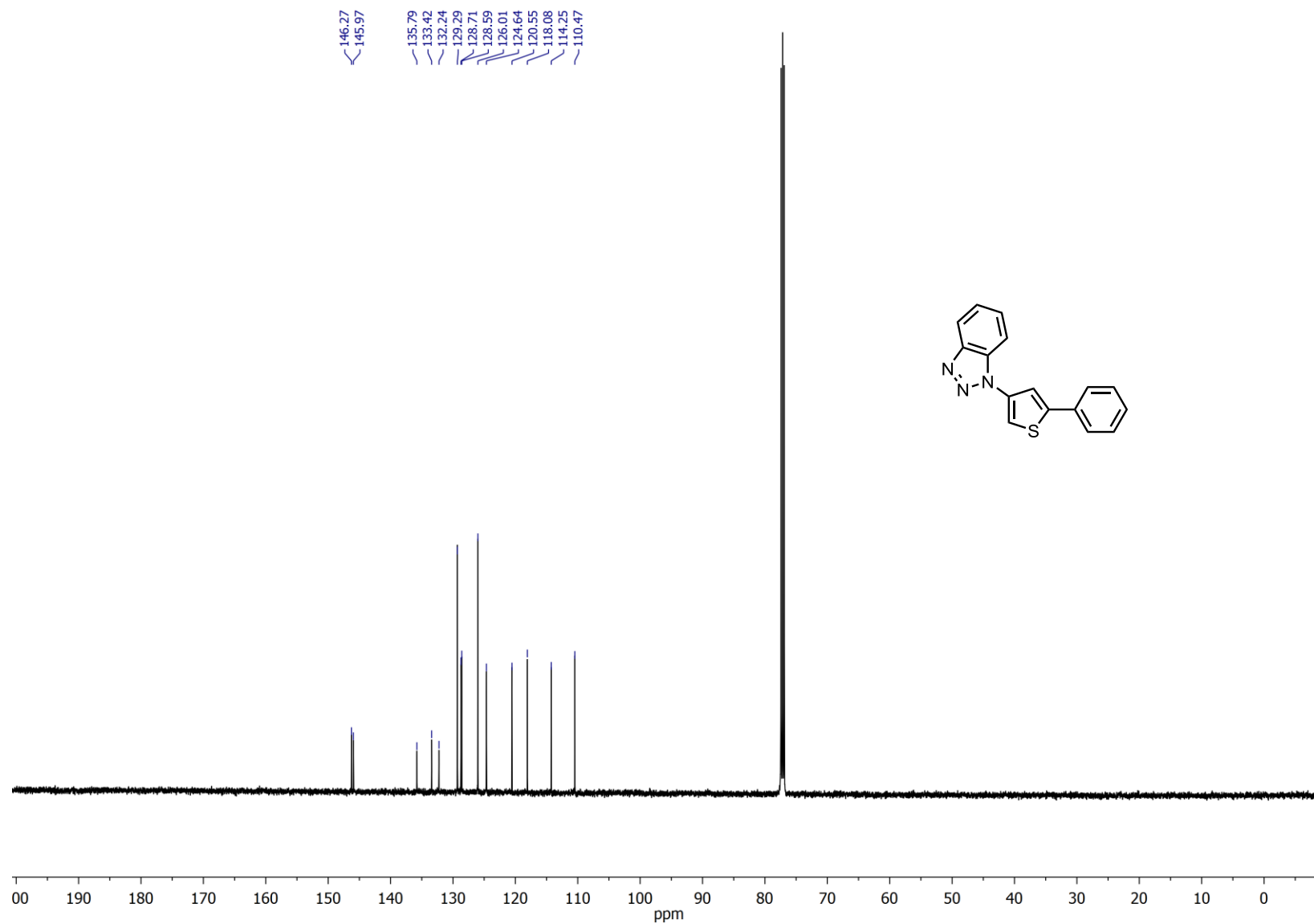
**$^1\text{H}$  NMR of diphenylimidazol-substituted bithiophen 10**DMSO- $d_6$ , 500 MHz, 298 K

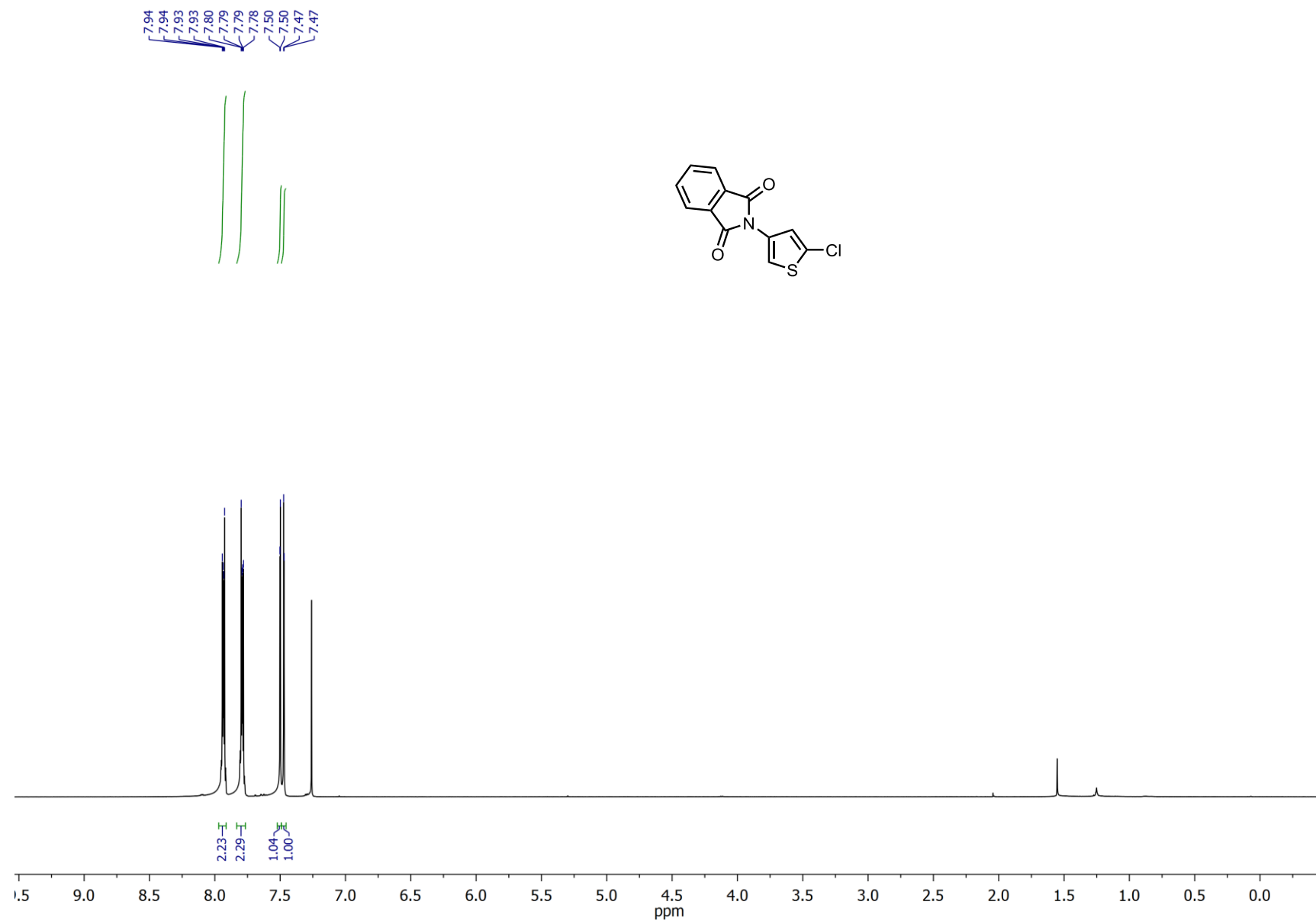
**$^{13}\text{C}$  NMR of diphenylimidazol-substituted bithiophen 10**DMSO- $d_6$ , 126 MHz, 298 K

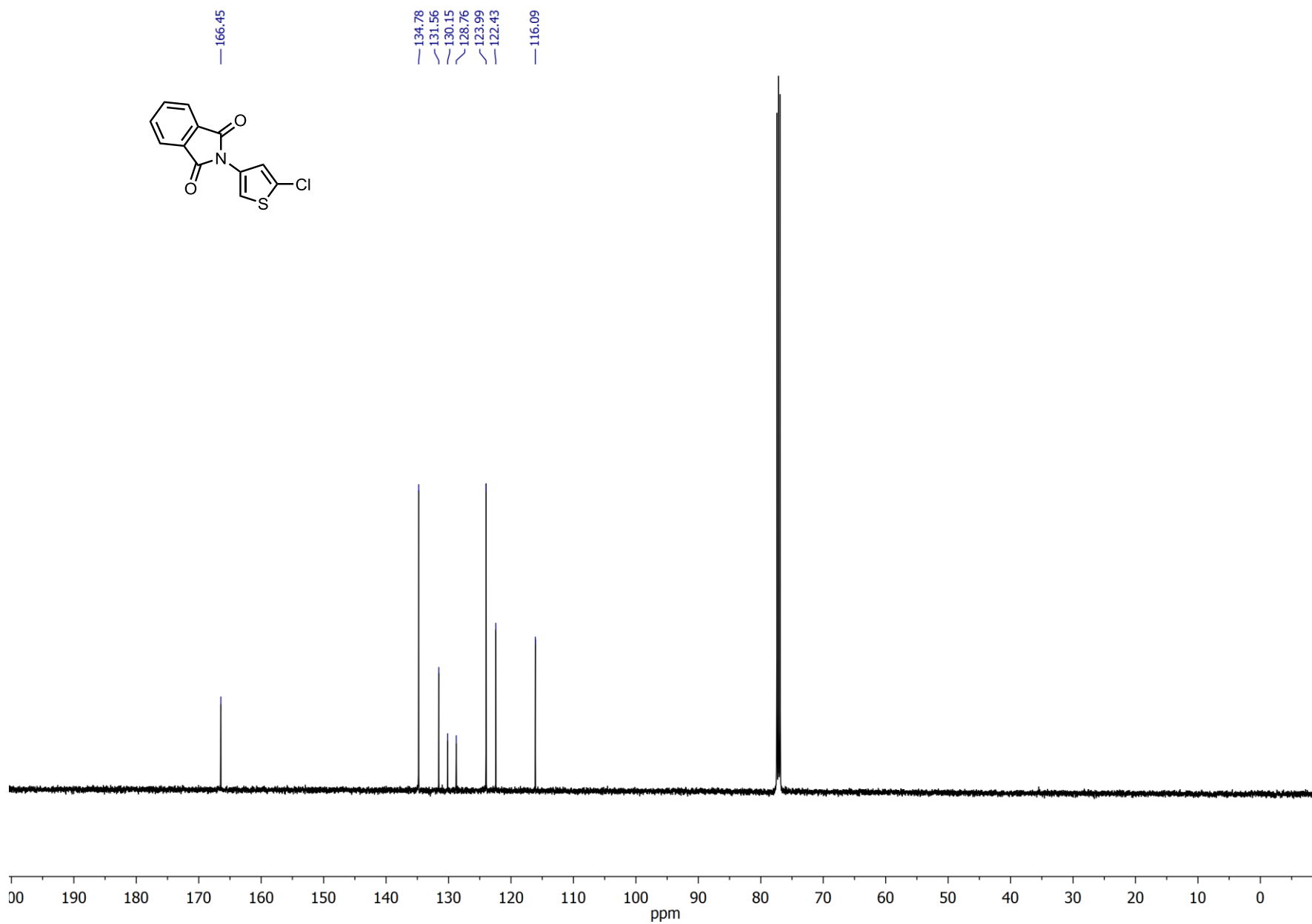
**<sup>1</sup>H NMR of benzimidazol-substituted bithiophen 11**CDCl<sub>3</sub>, 500 MHz, 298 K

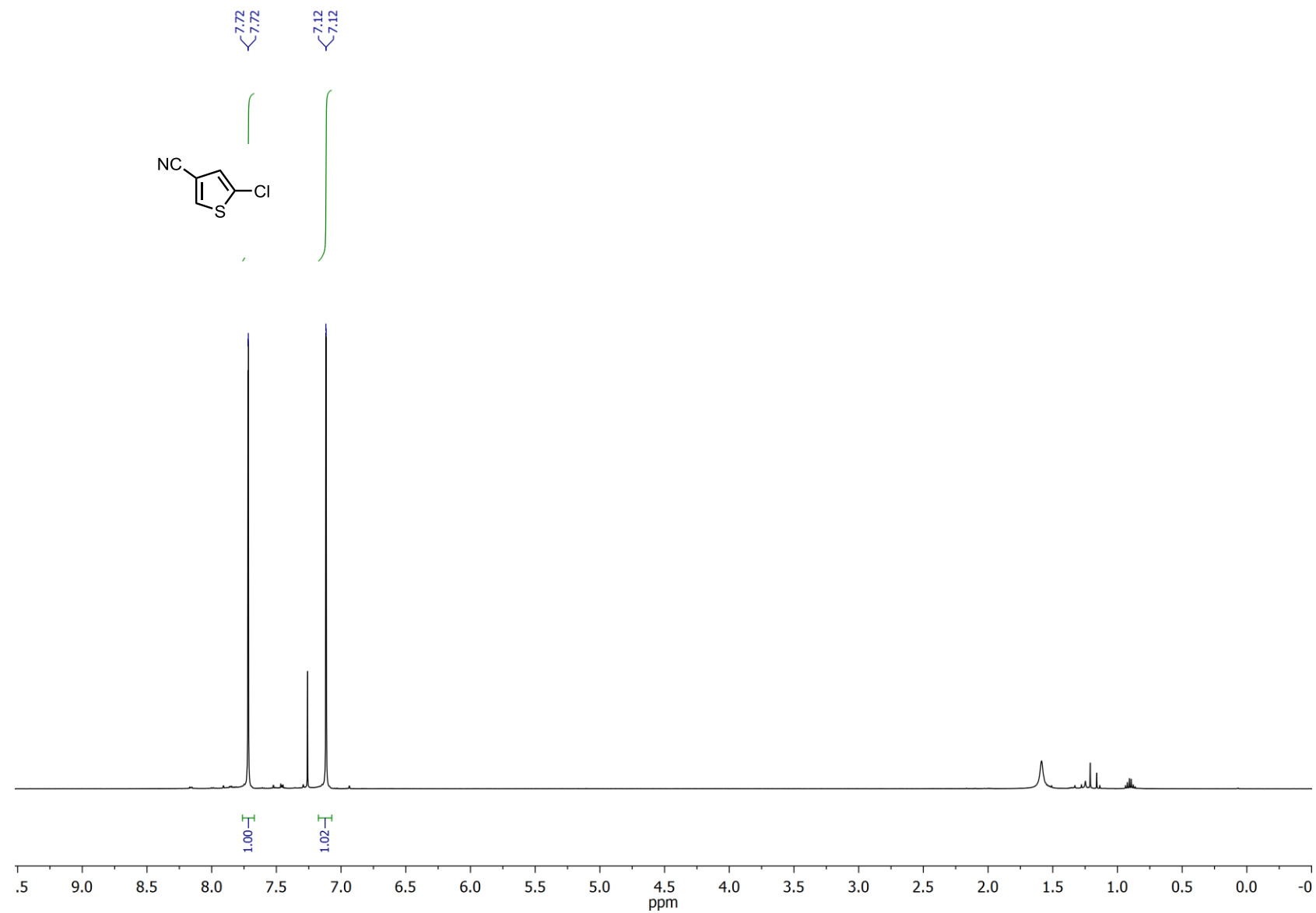
**$^{13}\text{C}$  NMR of benzimidazol-substituted bithiophen 11**CDCl<sub>3</sub>, 126 MHz, 298 K

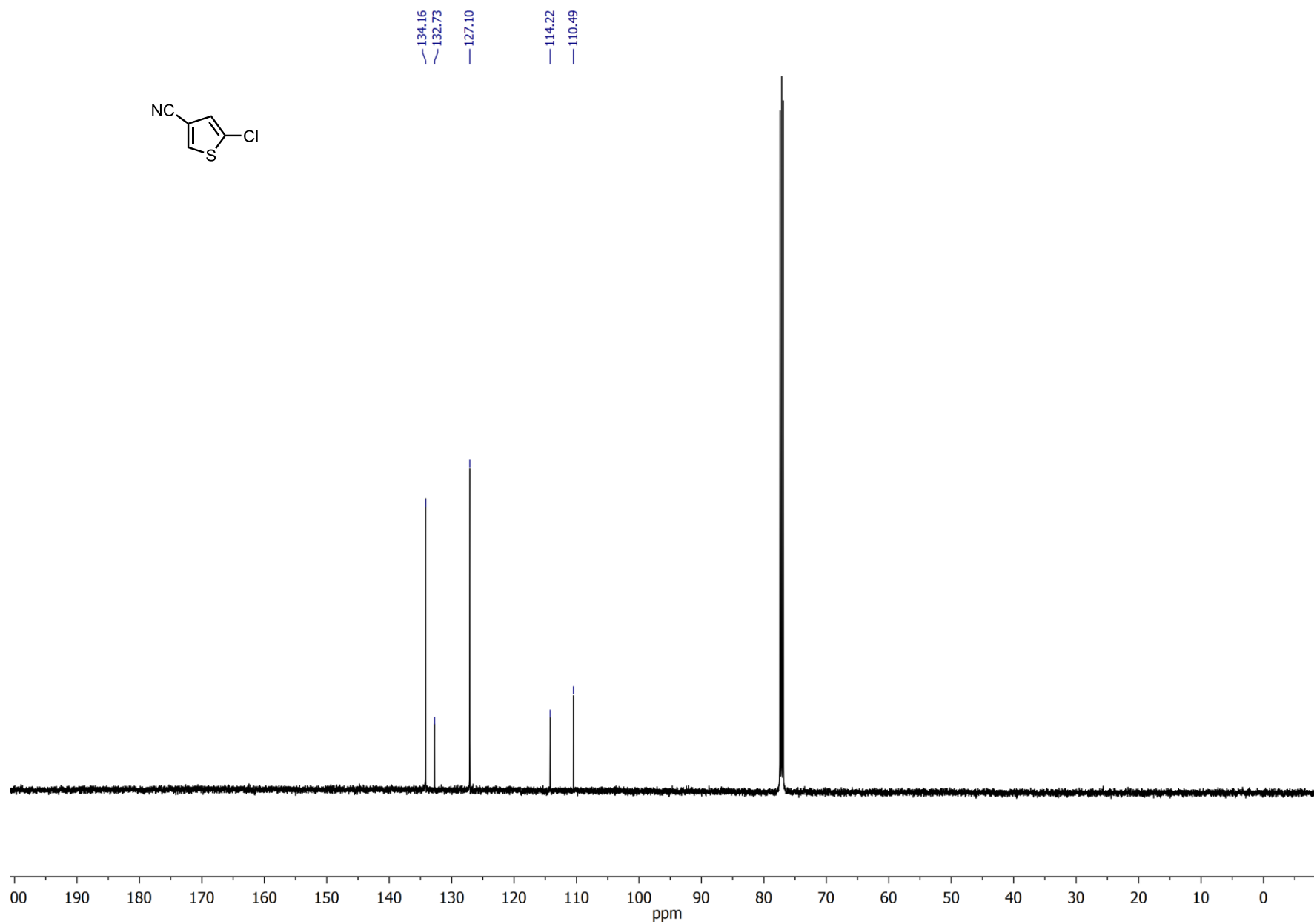
**$^1\text{H}$  NMR of benzotriazol-substituted 2-phenylthiophen 12**CDCl<sub>3</sub>, 500 MHz, 298 K

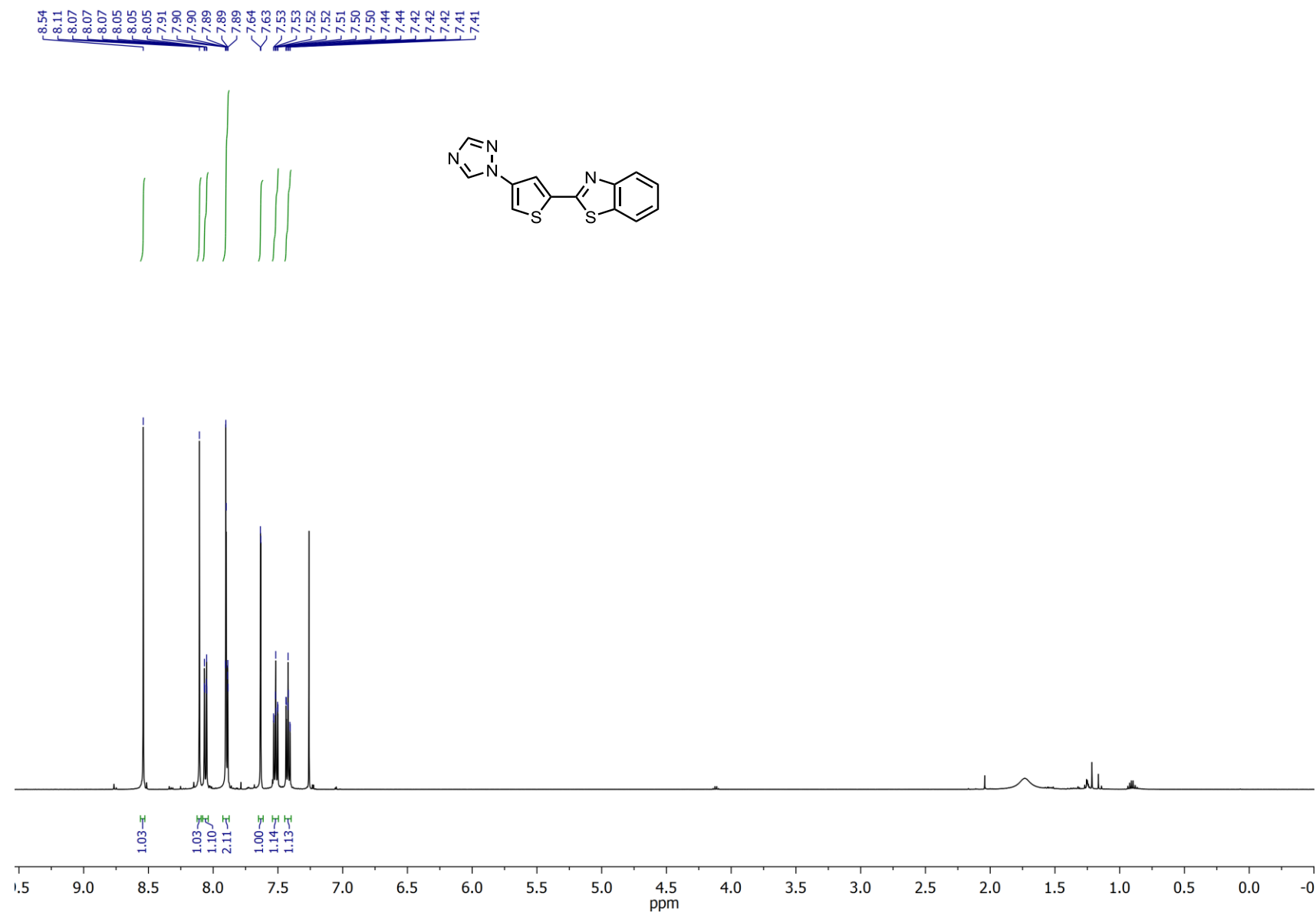
**$^{13}\text{C}$  NMR of benzotriazol-substituted 2-phenylthiophen 12**CDCl<sub>3</sub>, 126 MHz, 298 K

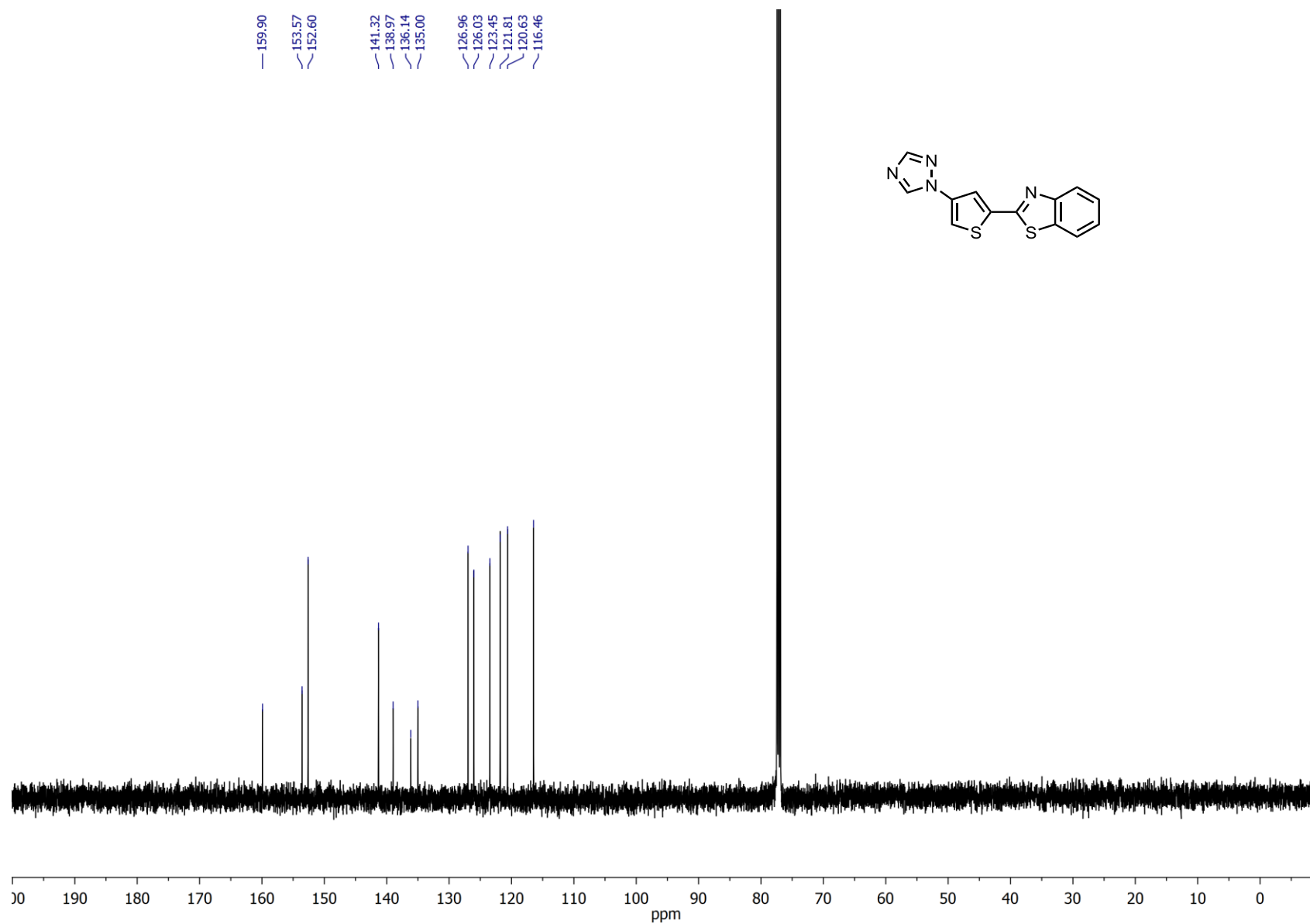
**$^1\text{H}$  NMR of phthalimid-substituted 2-chlorothiophen 13**CDCl<sub>3</sub>, 500 MHz, 298 K

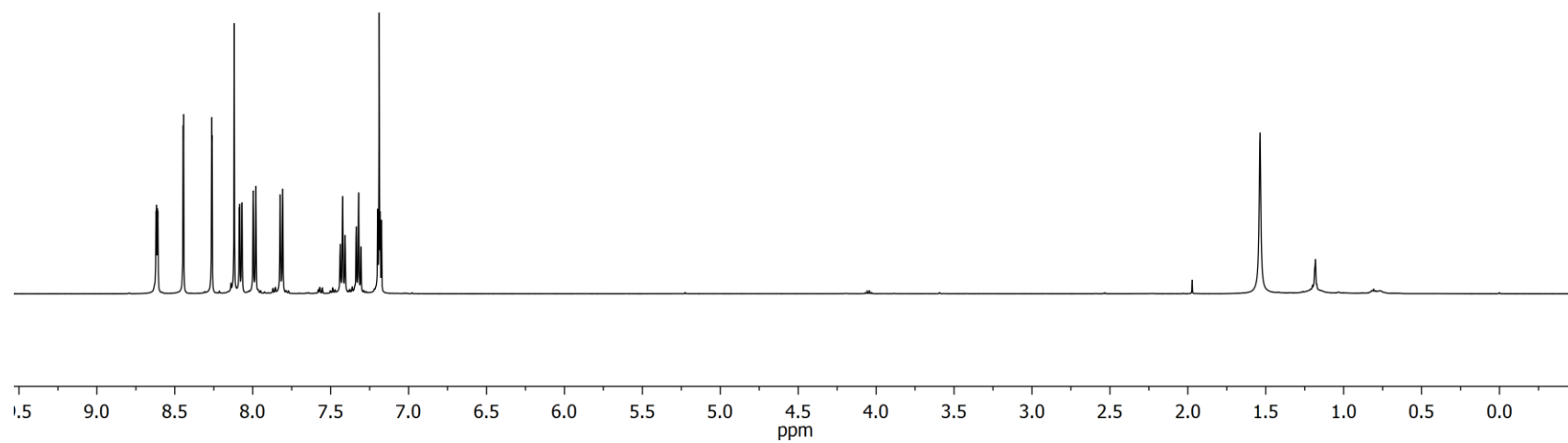
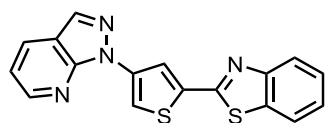
**$^{13}\text{C}$  NMR of phthalimid-substituted 2-chlorothiophen 13**CDCl<sub>3</sub>, 126 MHz, 298 K

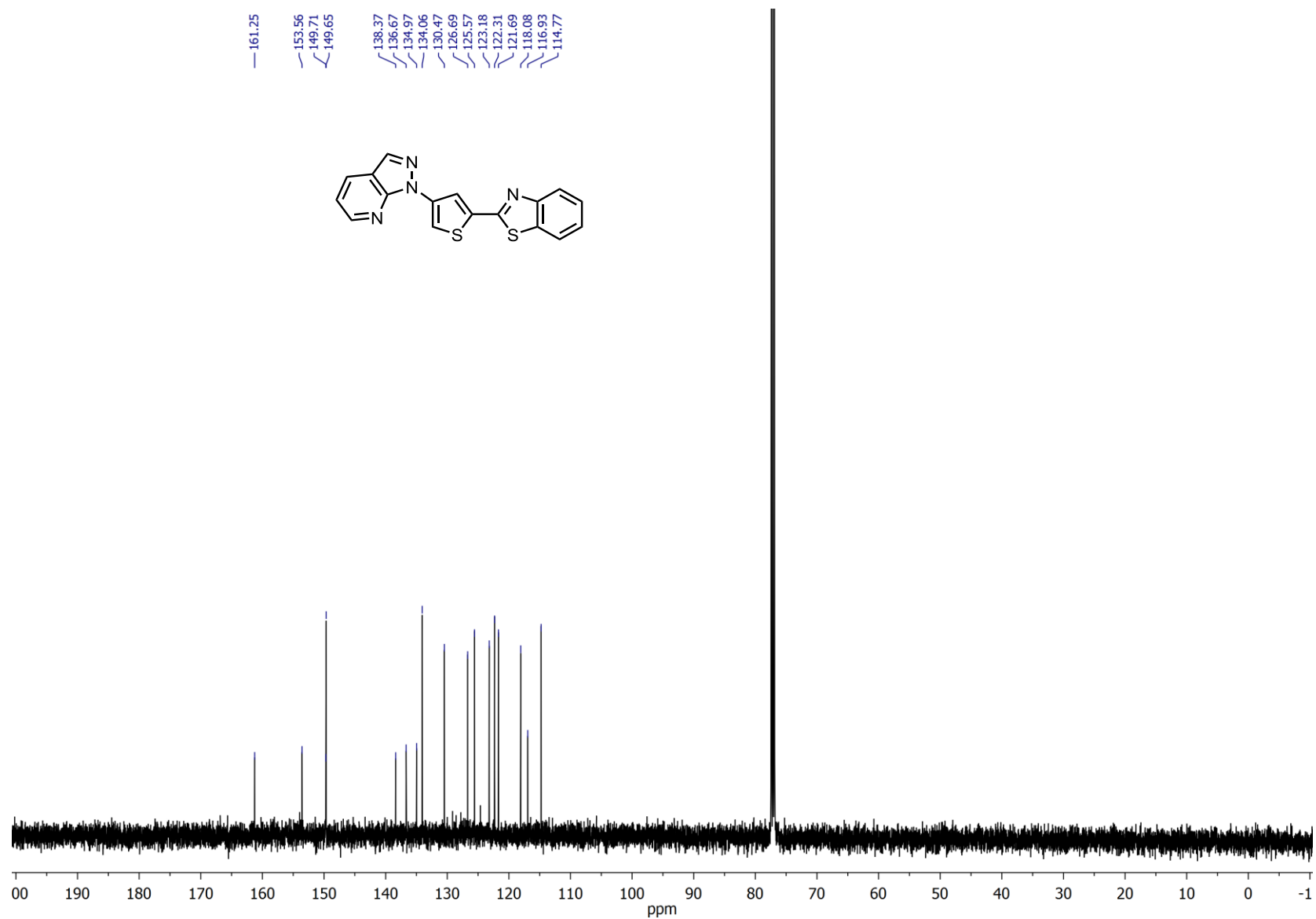
**$^1\text{H}$  NMR of cyano-substituted 2-chlorothiophen 14**CDCl<sub>3</sub>, 500 MHz, 298 K

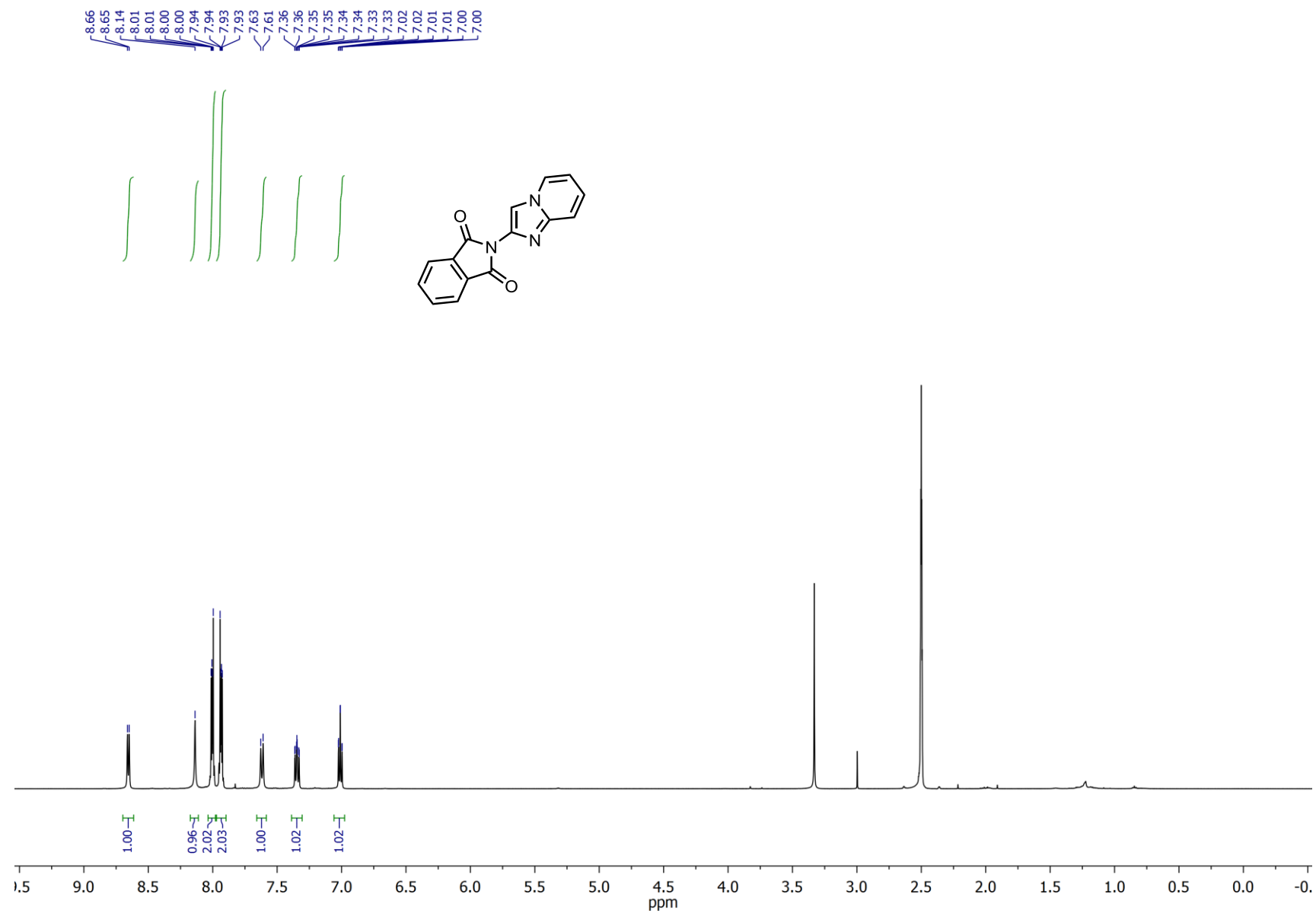
**$^{13}\text{C}$  NMR of phthalimid-substituted 2-chlorothiophen 14**CDCl<sub>3</sub>, 126 MHz, 298 K

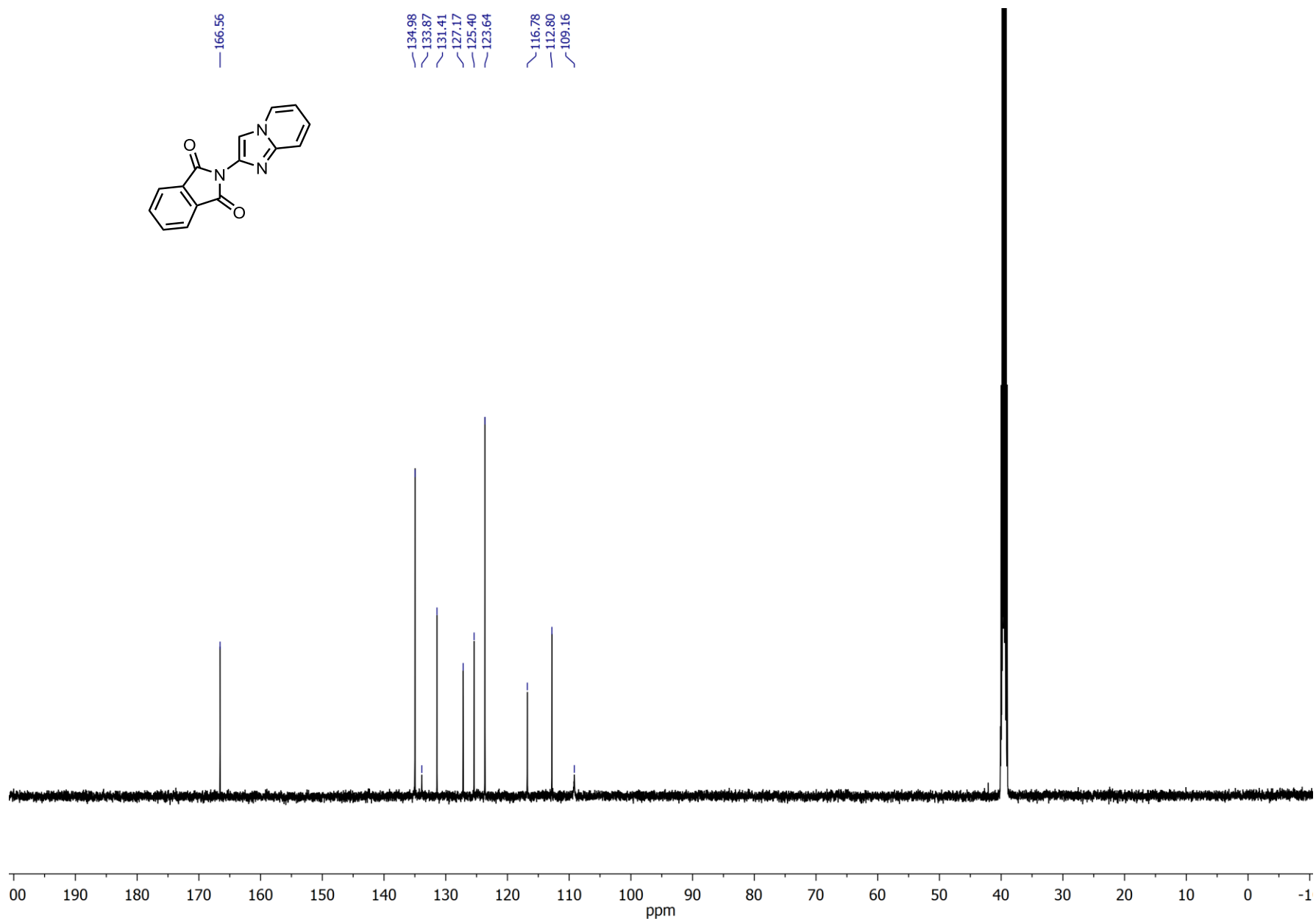
**<sup>1</sup>H NMR of triazol-substituted benzothiazolylthiophen 15**CDCl<sub>3</sub>, 500 MHz, 298 K

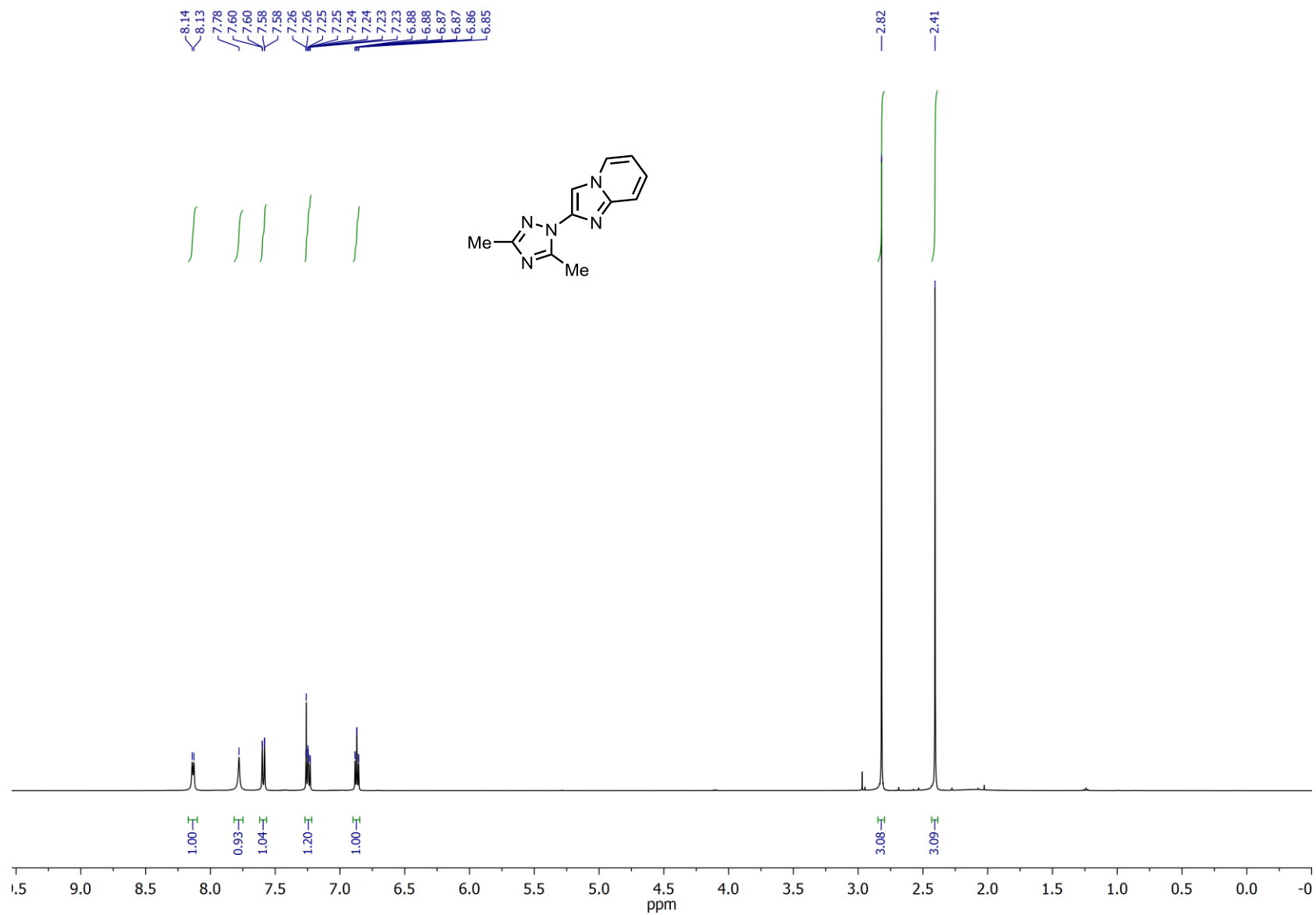
**$^{13}\text{C}$  NMR of triazol-substituted benzothiazolylthiophen 15**CDCl<sub>3</sub>, 126 MHz, 298 K

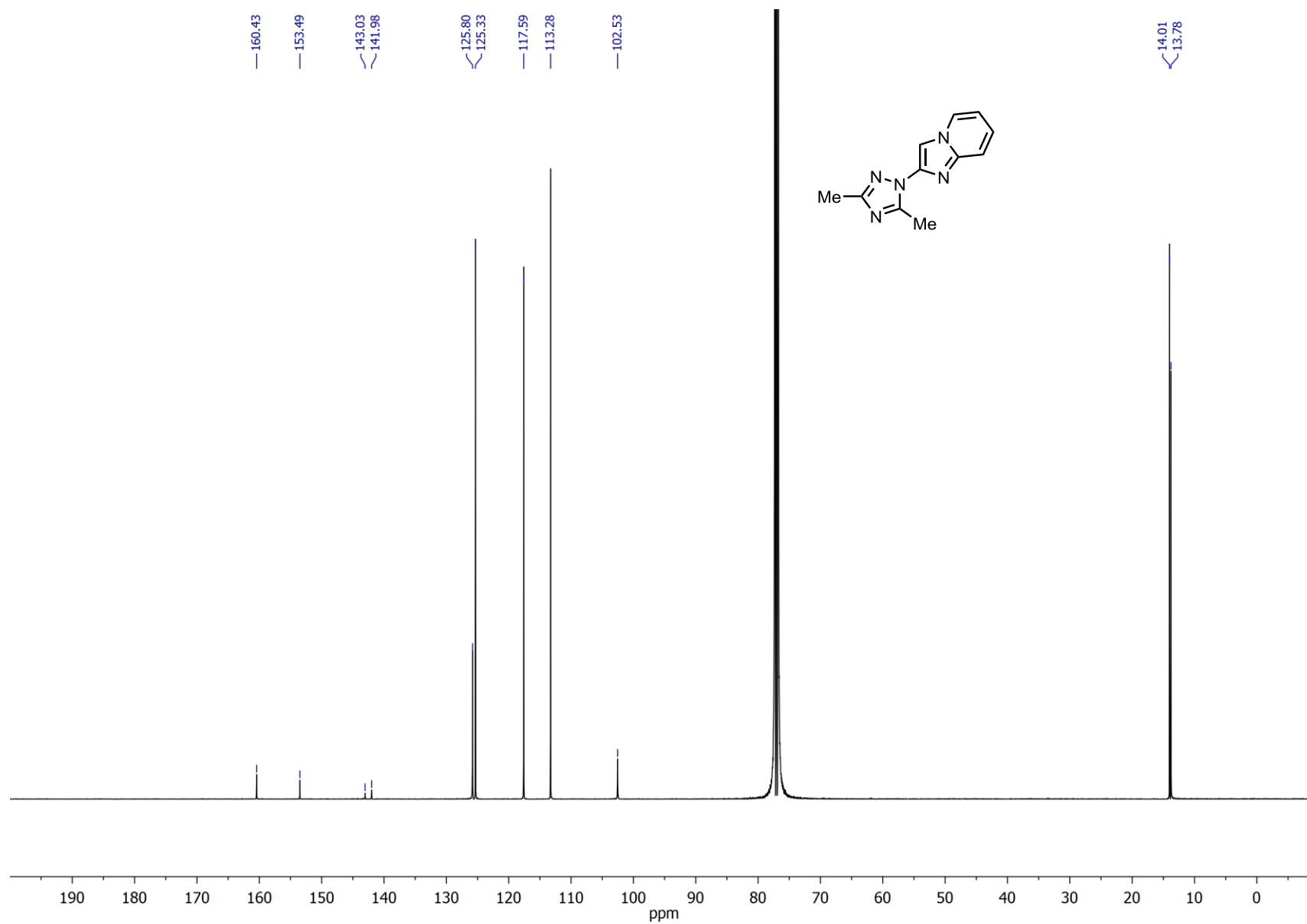
**<sup>1</sup>H NMR of pyrazolopyridine-substituted benzothiazolylthiophen 16**CDCl<sub>3</sub>, 500 MHz, 298 K

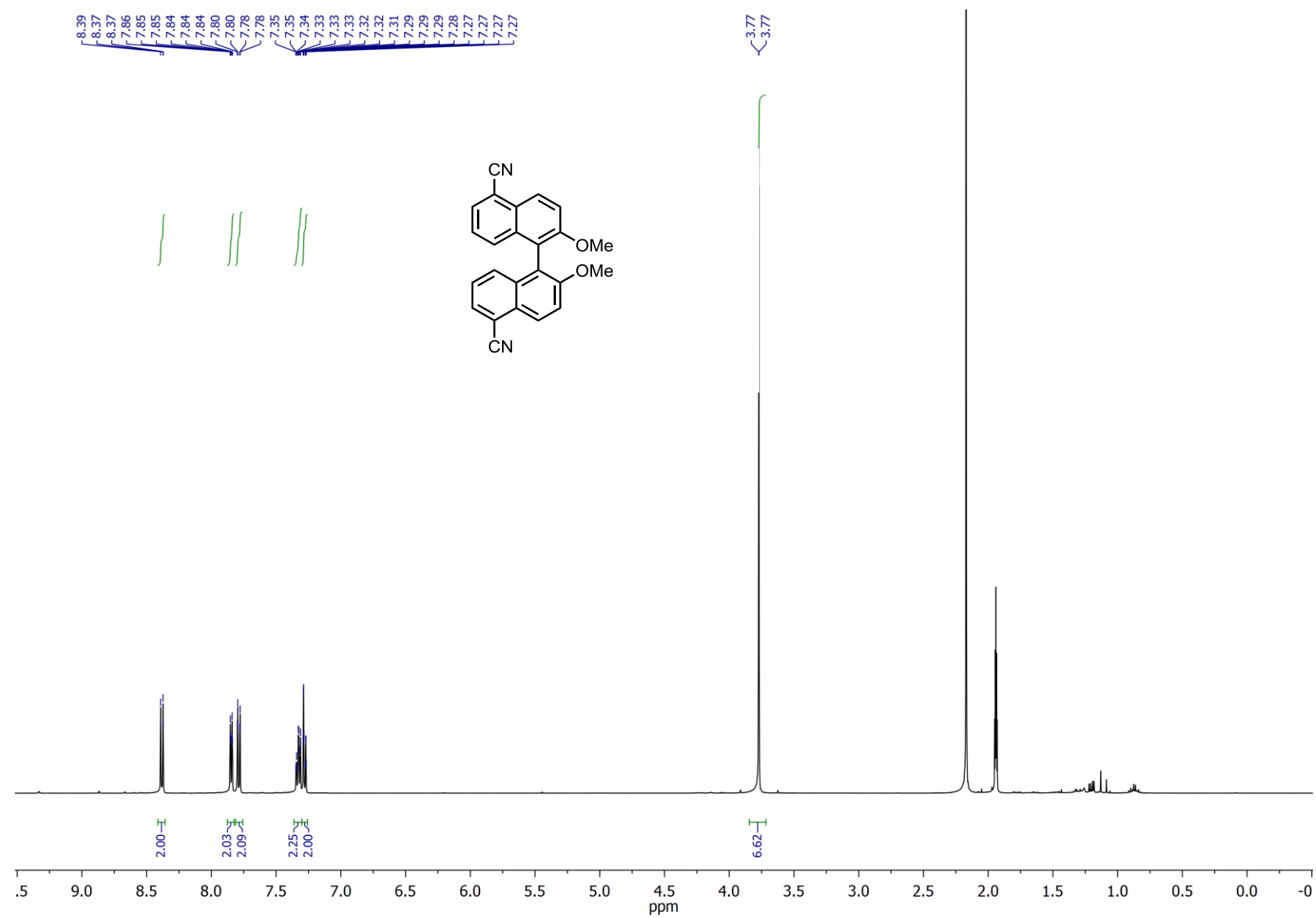
**$^{13}\text{C}$  NMR of pyrazolopyridine-substituted benzothiazolylthiophen 16**CDCl<sub>3</sub>, 500 MHz, 298 K

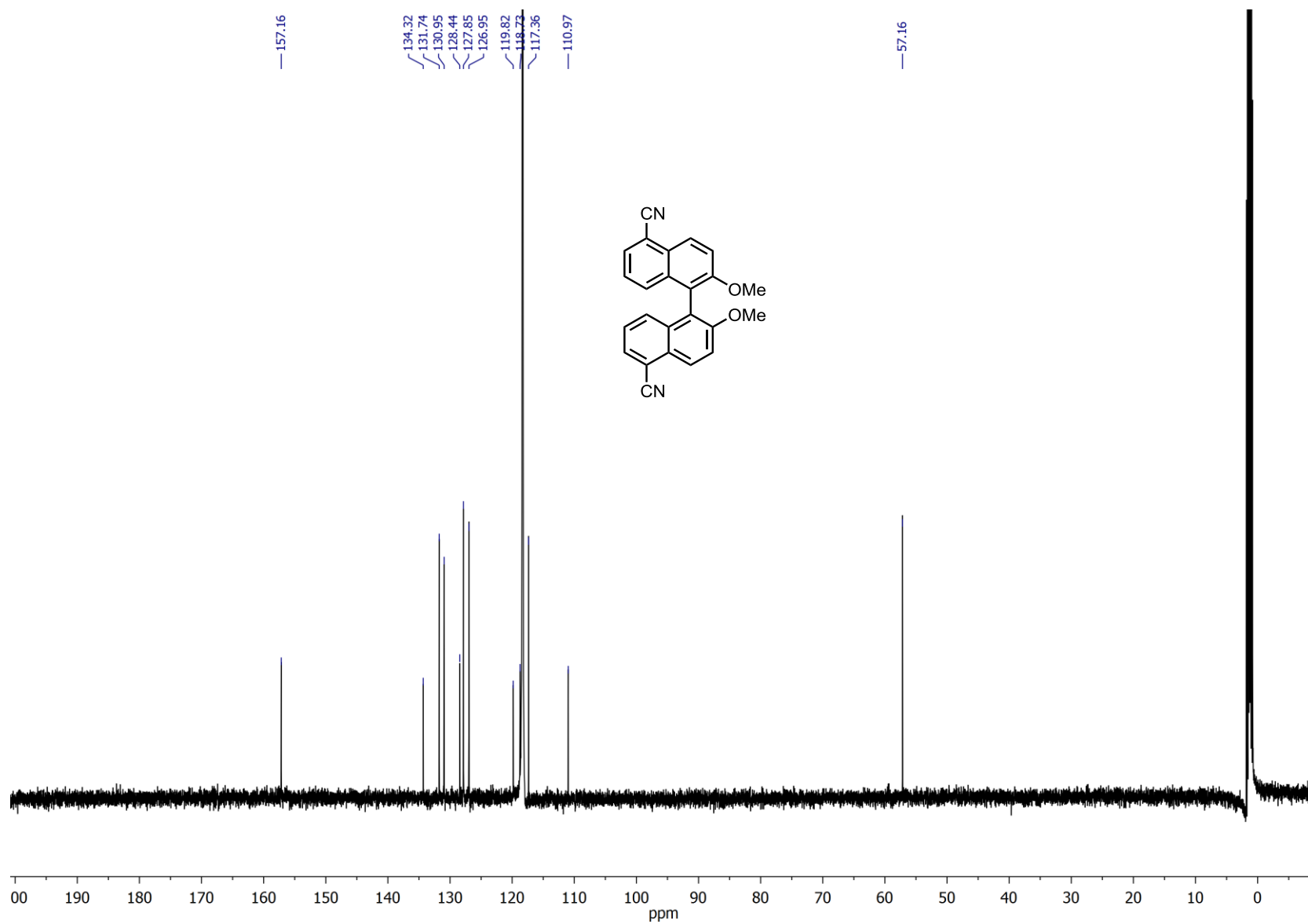
**$^1\text{H}$  NMR of phthalimid-substituted imidazopyridine 17**DMSO- $d_6$ , 500 MHz, 298 K

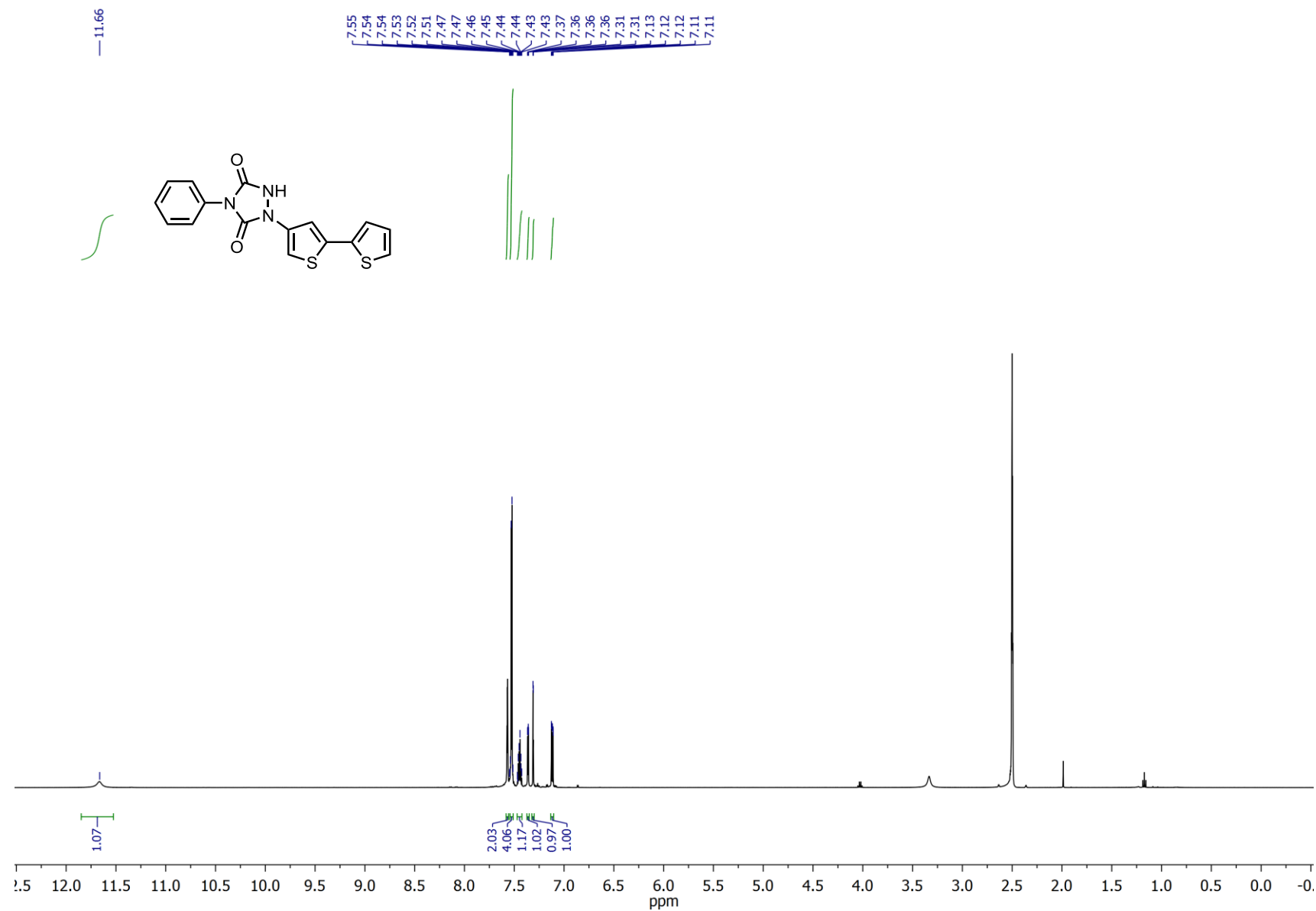
**$^{13}\text{C}$  NMR of phthalimid-substituted imidazopyridine 17**DMSO- $d_6$ , 126 MHz, 298 K

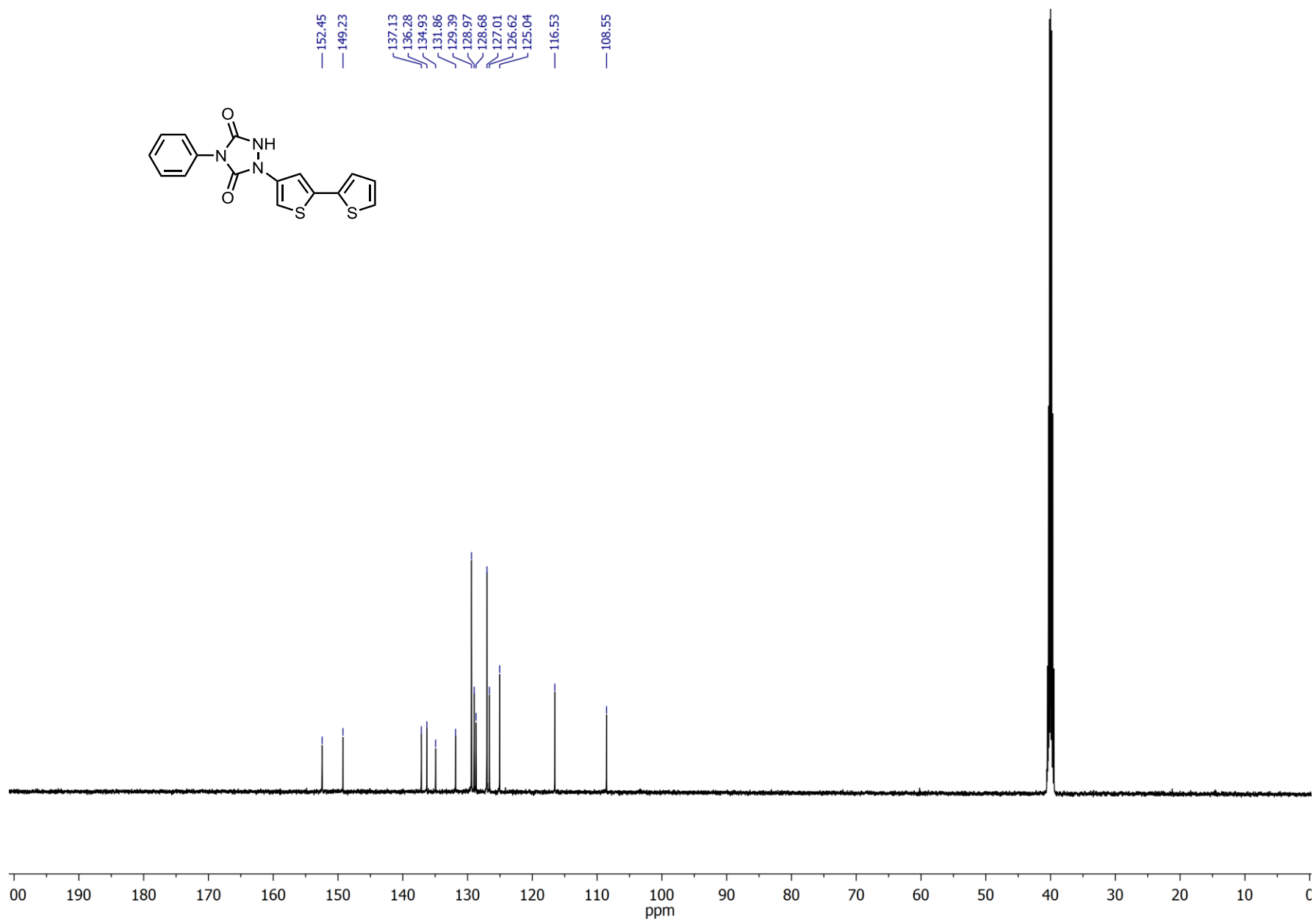
**$^1\text{H}$  NMR of dimethyltriazol-substituted imidazopyridine 18**CDCl<sub>3</sub>, 500 MHz, 298 K

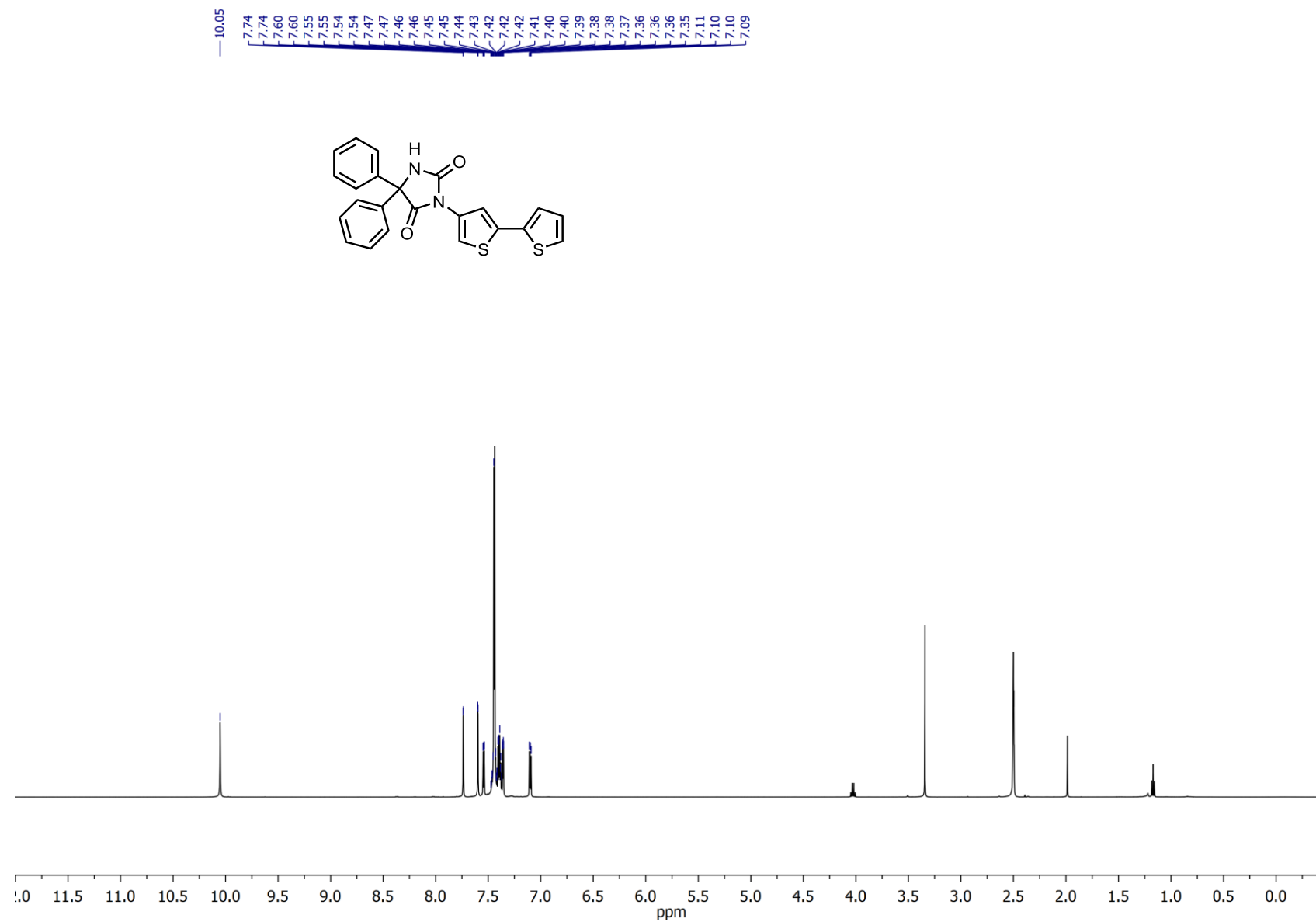
**$^{13}\text{C}$  NMR of dimethyltriazol-substituted imidazopyridine 18**CDCl<sub>3</sub>, 126 MHz, 298 K

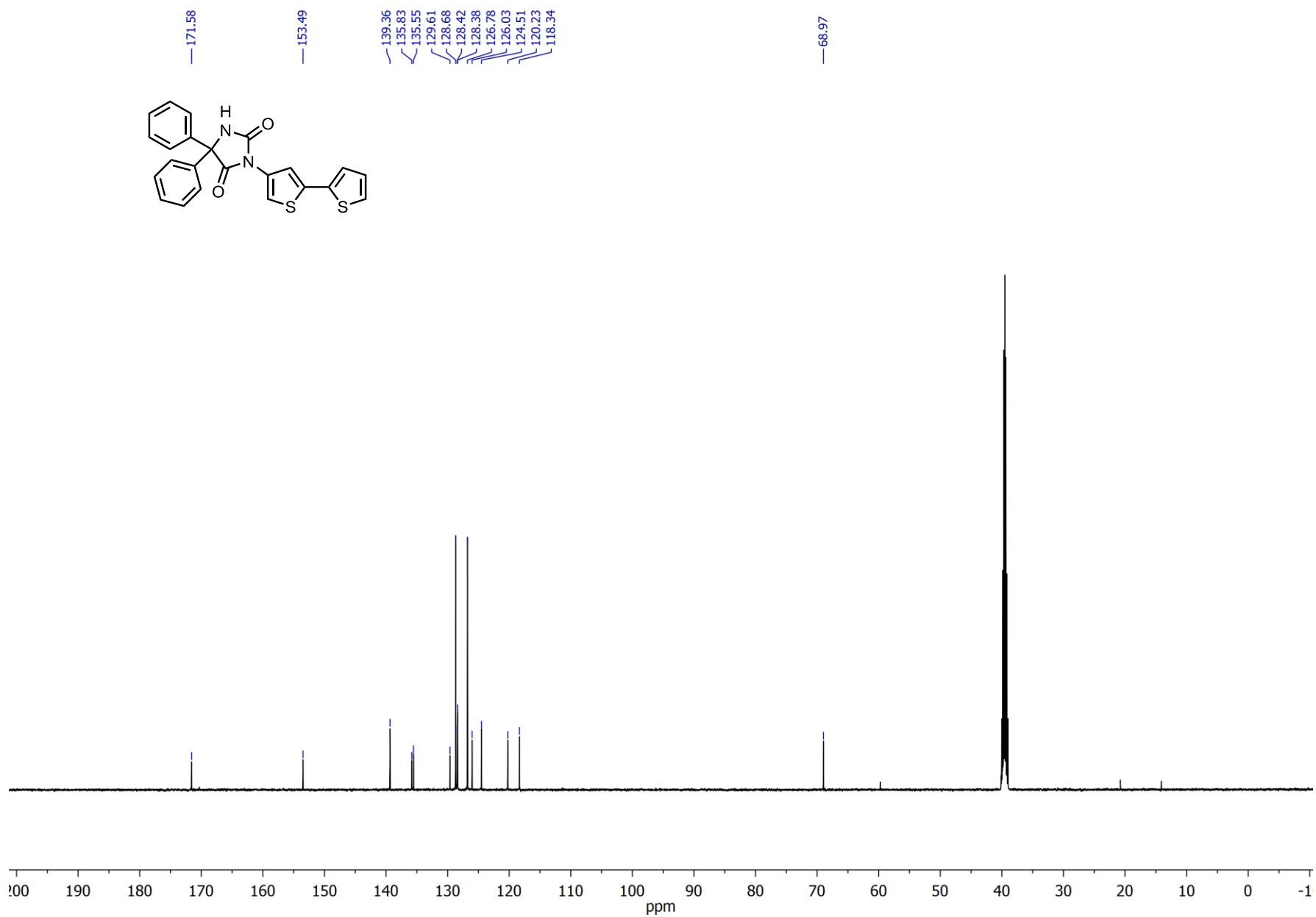
**$^1\text{H}$  NMR of cyano-substituted BINOL diemthylether 19** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

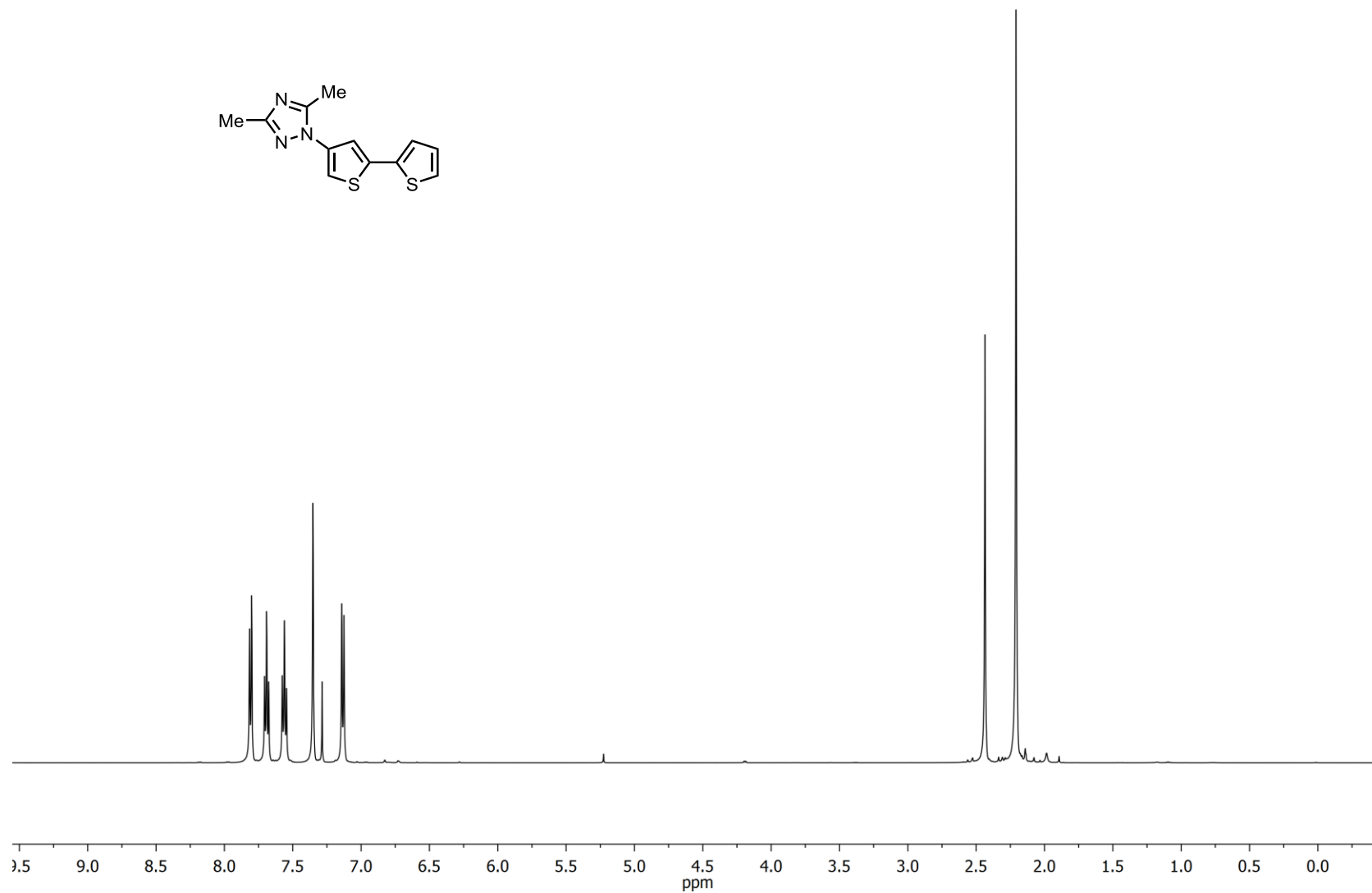
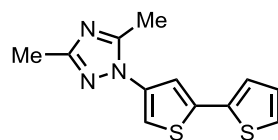
**$^{13}\text{C}$  NMR of cyano-substituted BINOL diemthylether 19** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

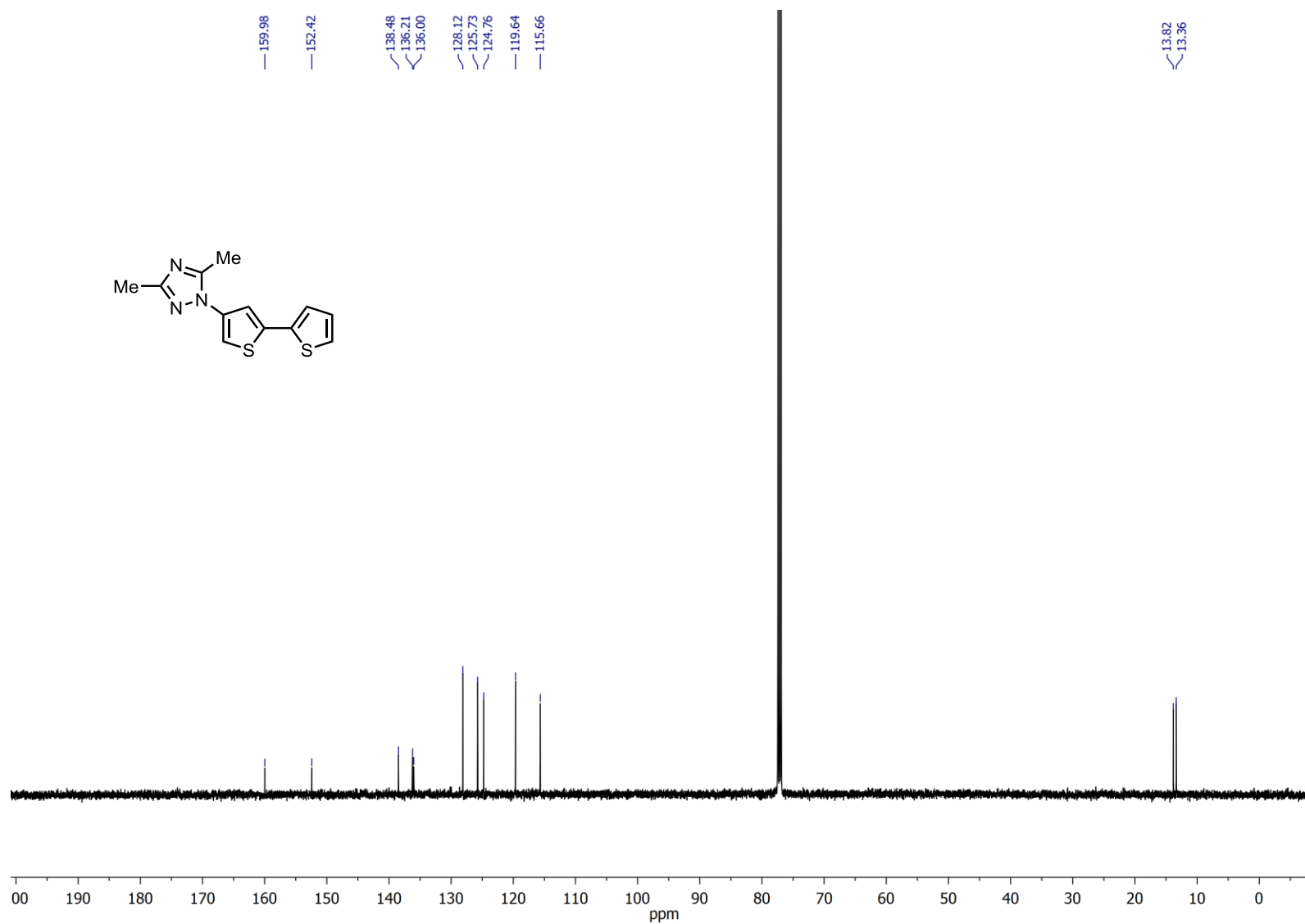
**$^1\text{H}$  NMR of phenylurazol-substituted bithiophen 20**DMSO- $d_6$ , 500 MHz, 298 K

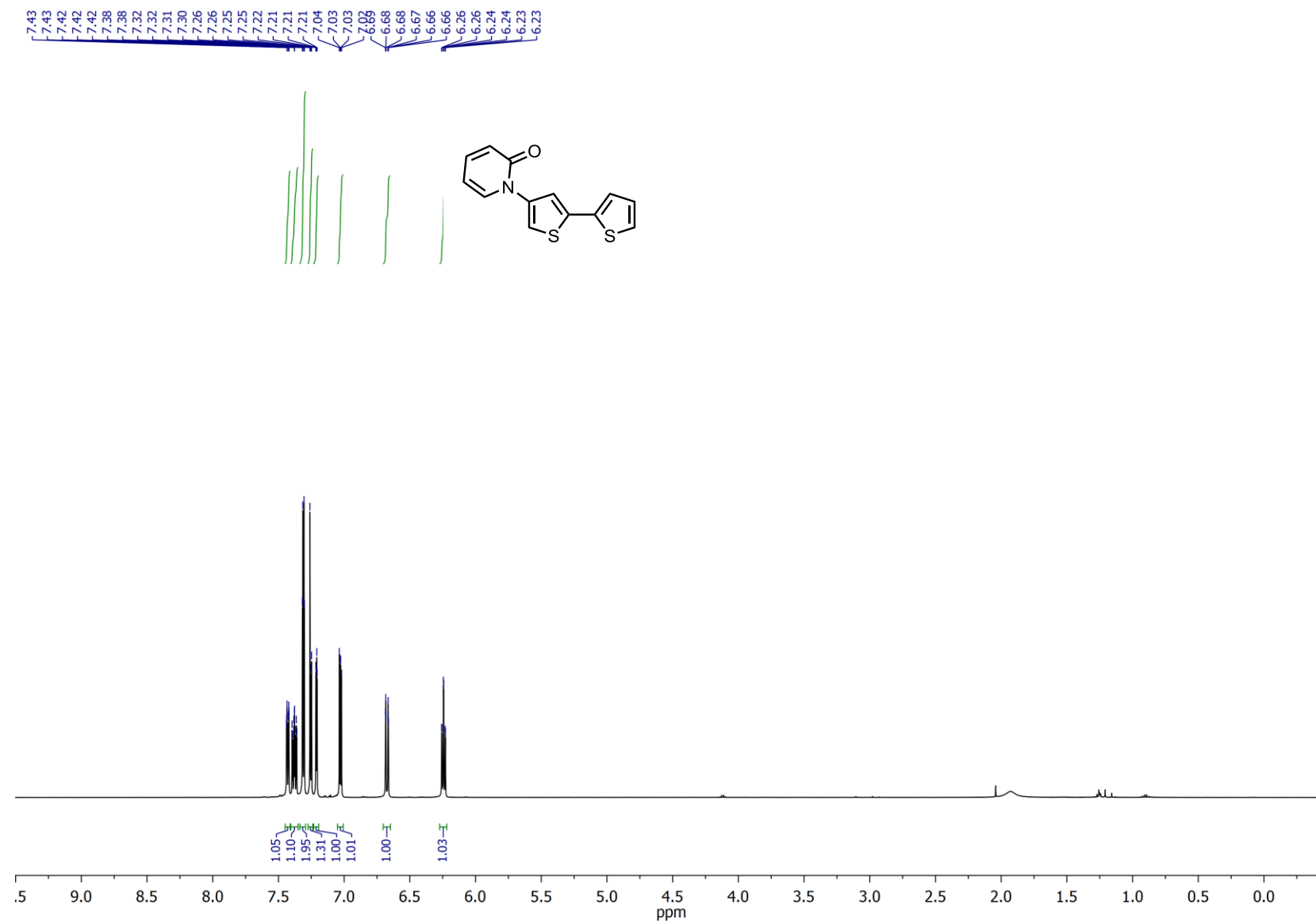
**$^{13}\text{C}$  NMR of phenylurazol-substituted bithiophen 20**DMSO- $d_6$ , 126 MHz, 298 K

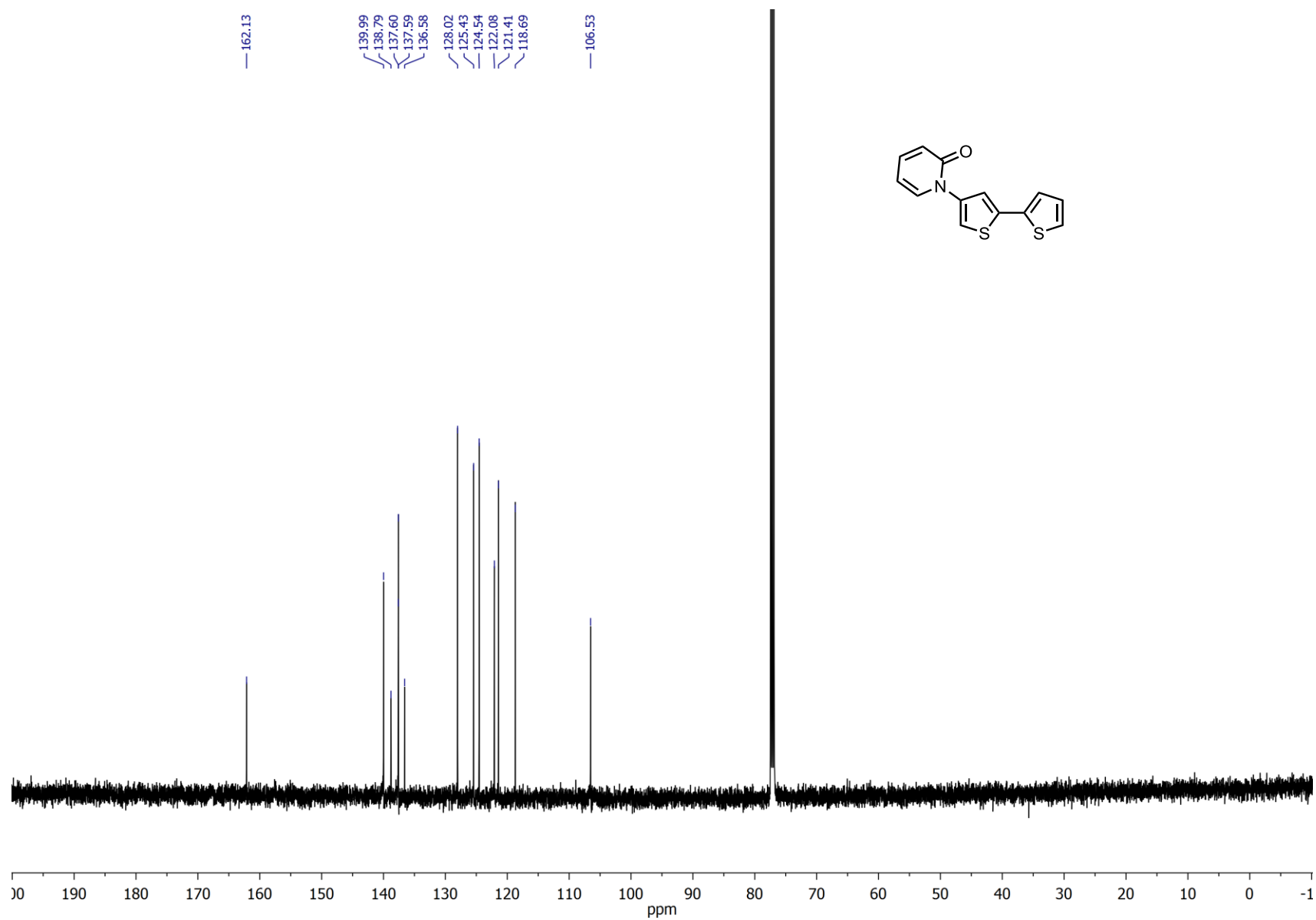
**$^1\text{H}$  NMR of diphenylhydantoin-substituted bithiophen 21**DMSO- $d_6$ , 500 MHz, 298 K

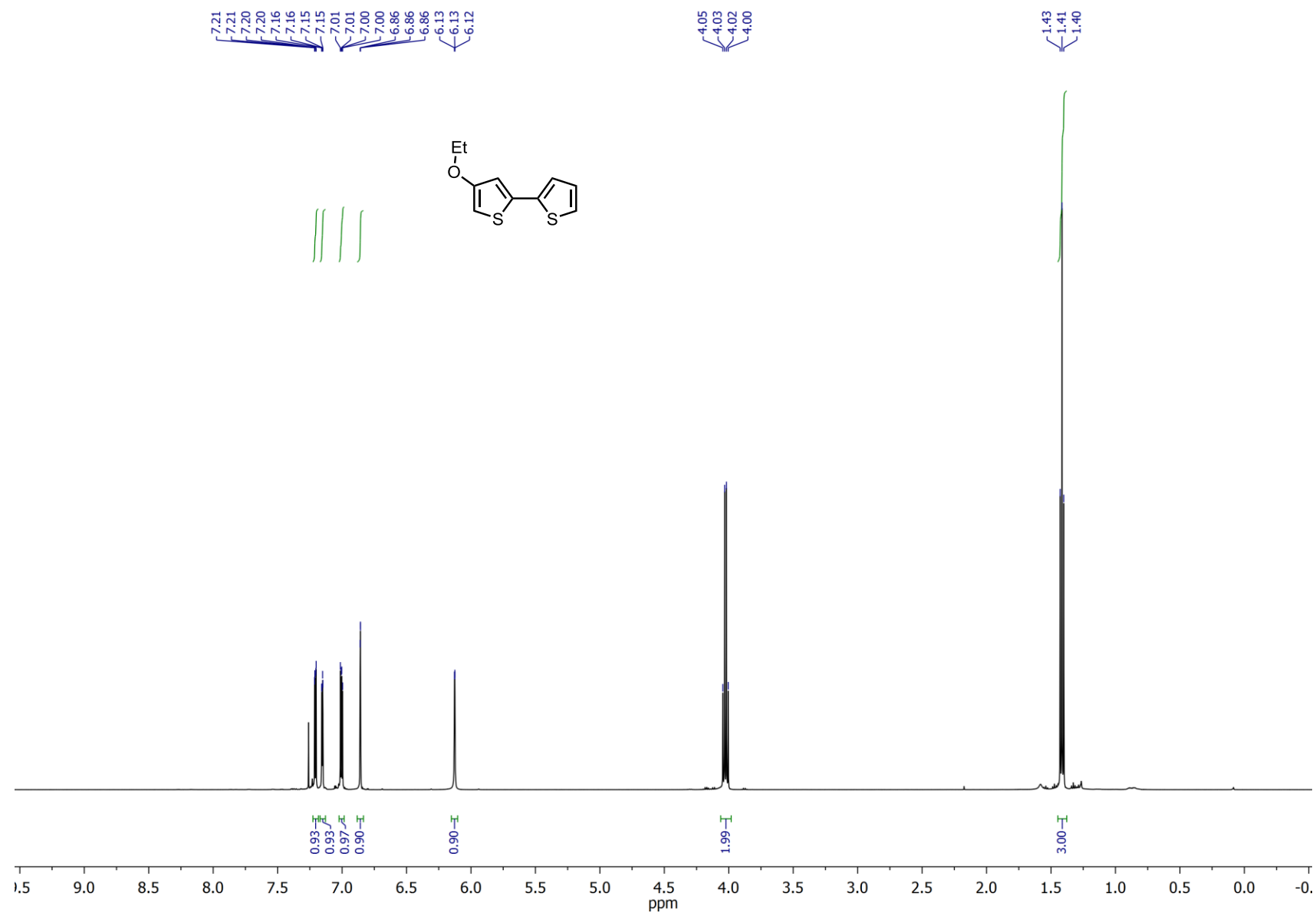
**$^{13}\text{C}$  NMR of diphenylhydantoin-substituted bithiophen 21**DMSO- $d_6$ , 126 MHz, 298 K

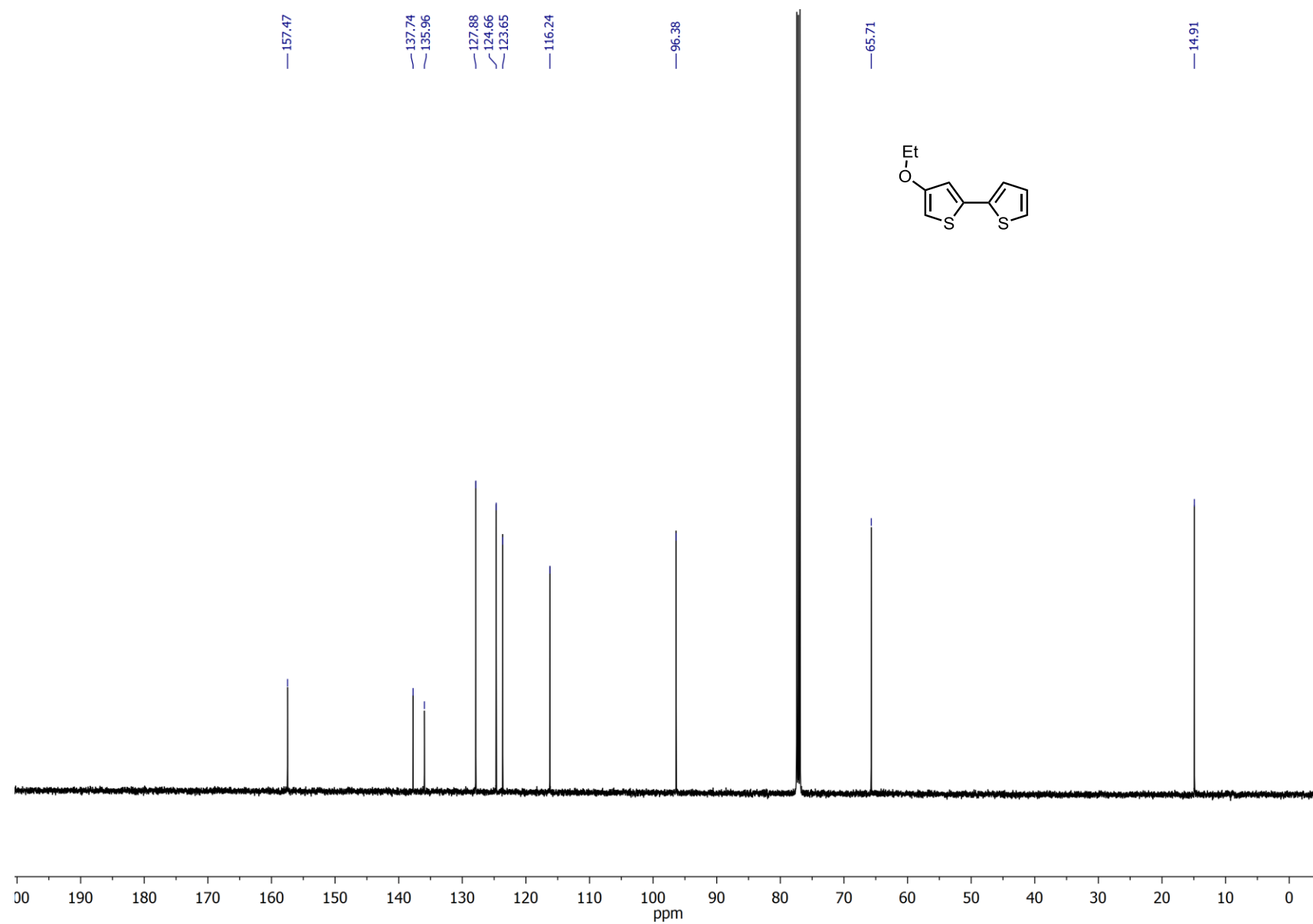
**$^1\text{H}$  NMR of dimethyltriazol-substituted bithiophen 22** $\text{CDCl}_3$ , 500 MHz, 298 K

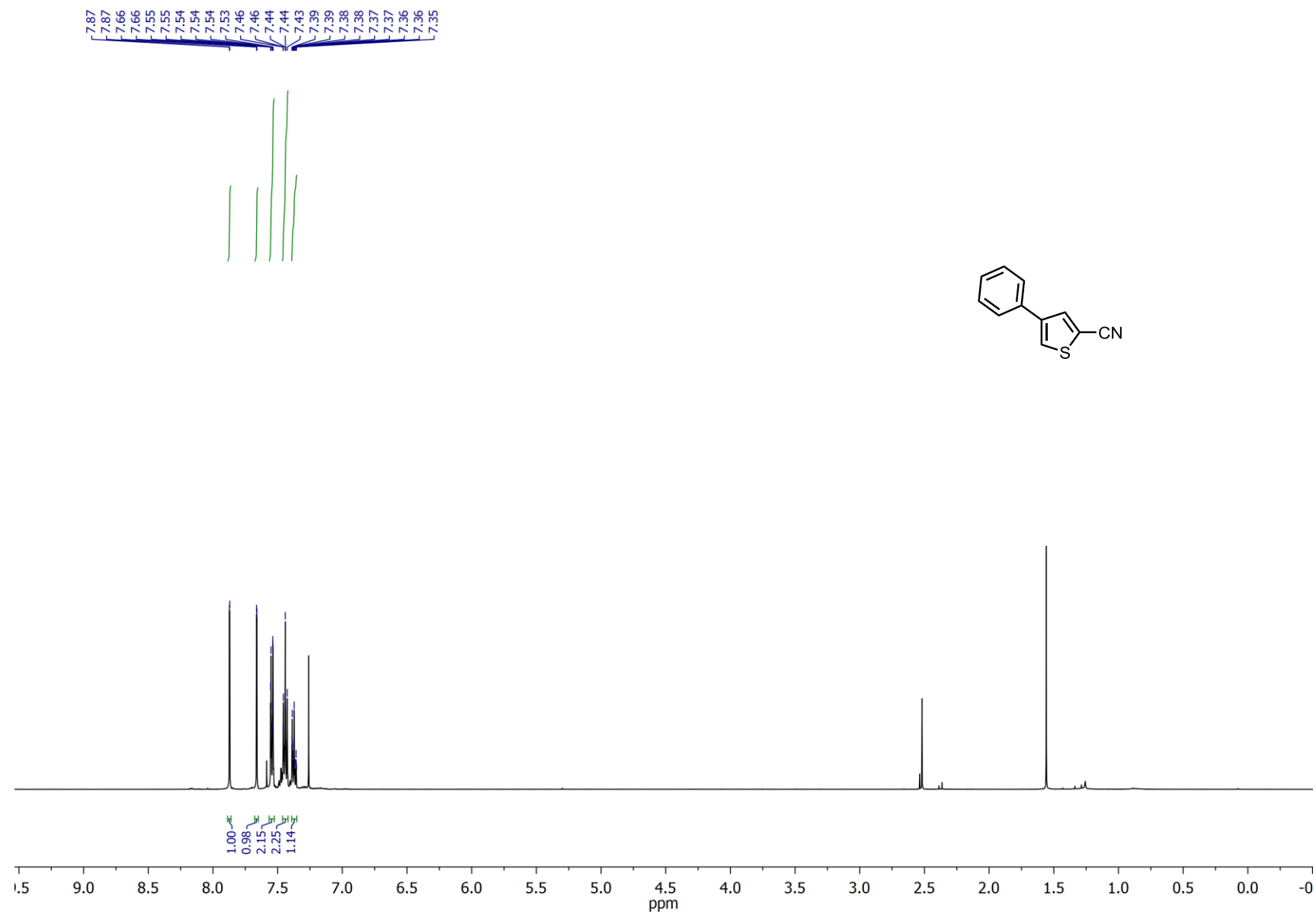
**$^{13}\text{C}$  NMR of dimethyltriazol-substituted bithiophen 22**CDCl<sub>3</sub>, 126 MHz, 298 K

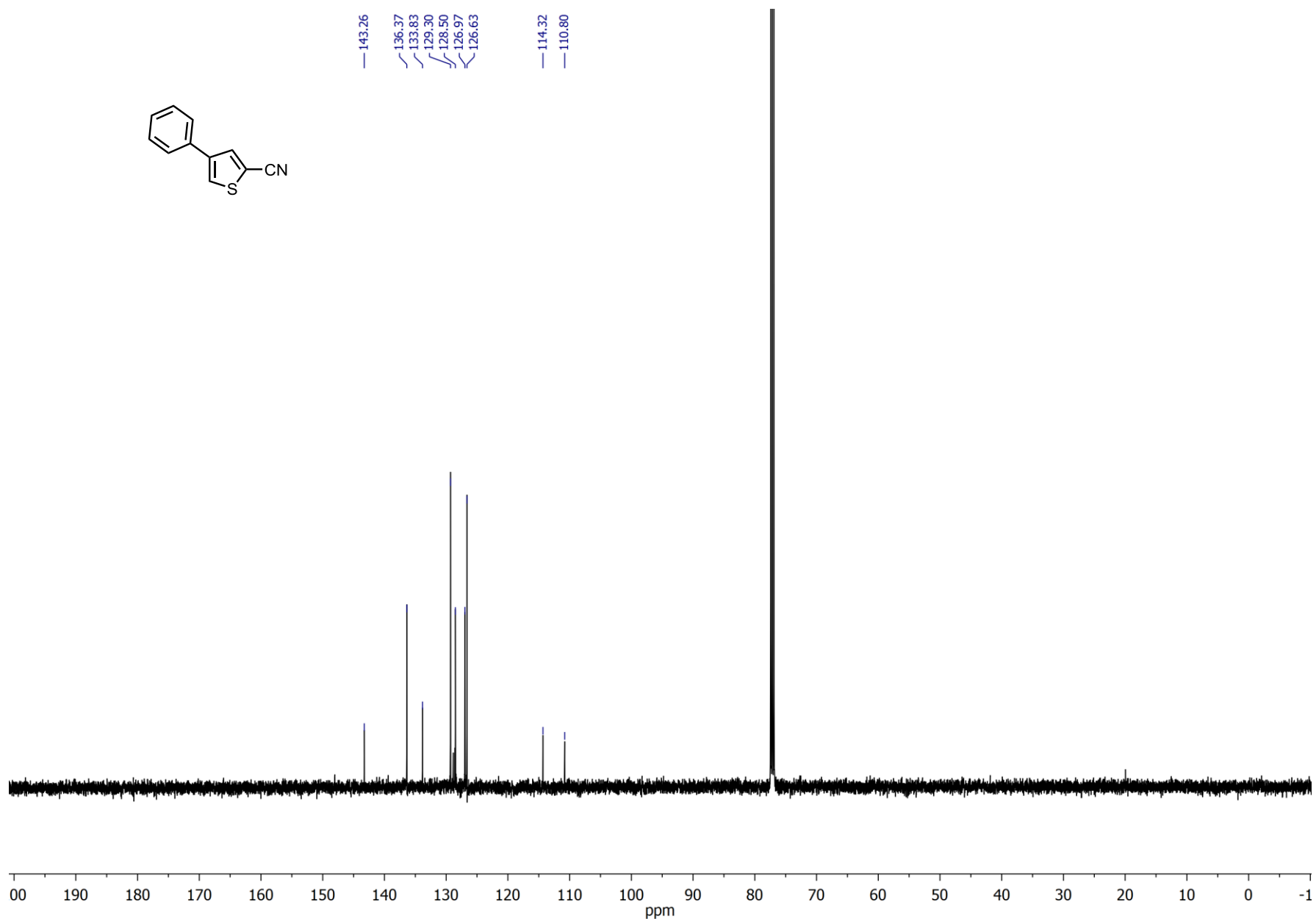
**$^1\text{H}$  NMR of pyridon-substituted bithiophen 23**CDCl<sub>3</sub>, 500 MHz, 298 K

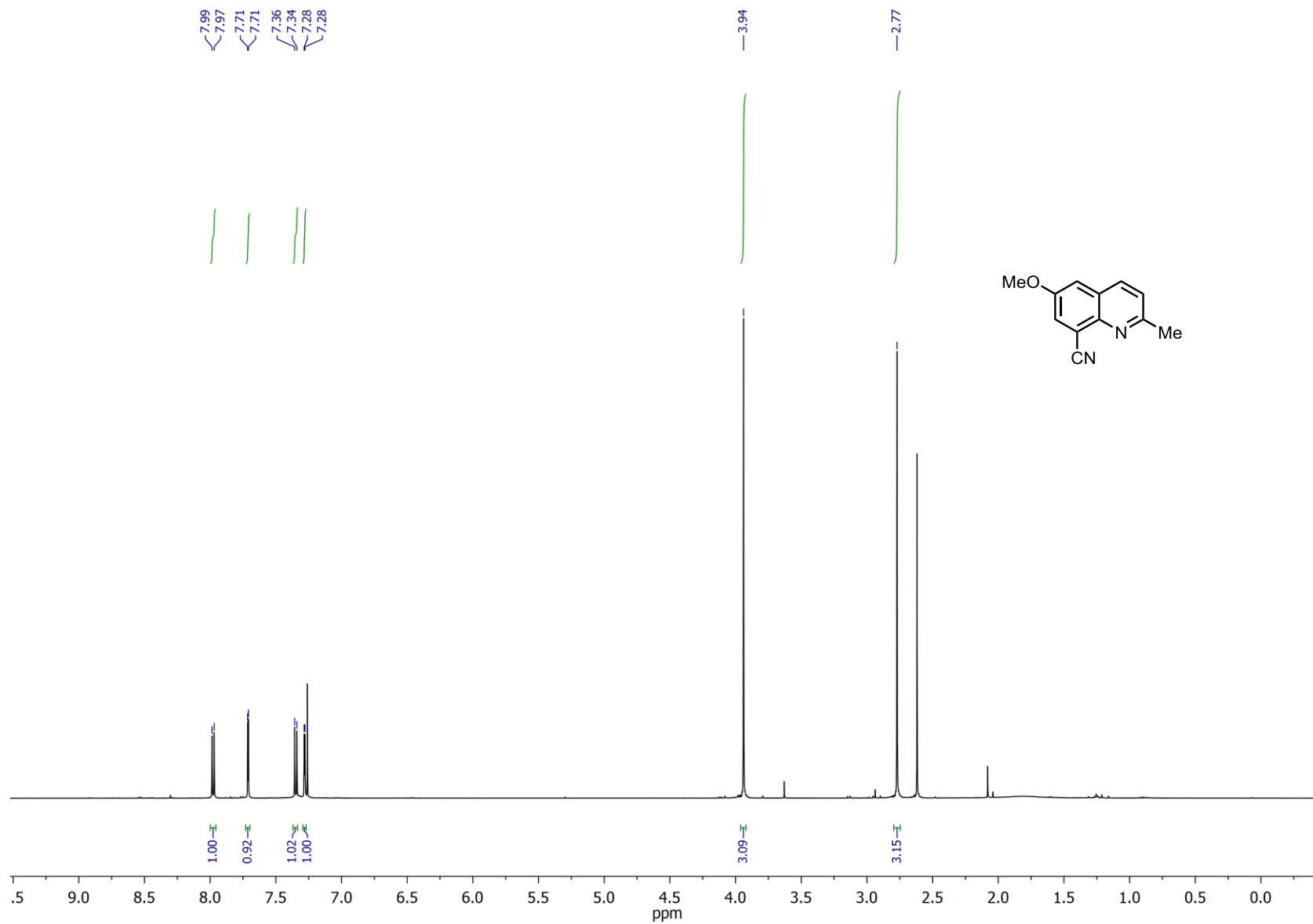
**$^{13}\text{C}$  NMR of pyridon-substituted bithiophen 23**CDCl<sub>3</sub>, 126 MHz, 298 K

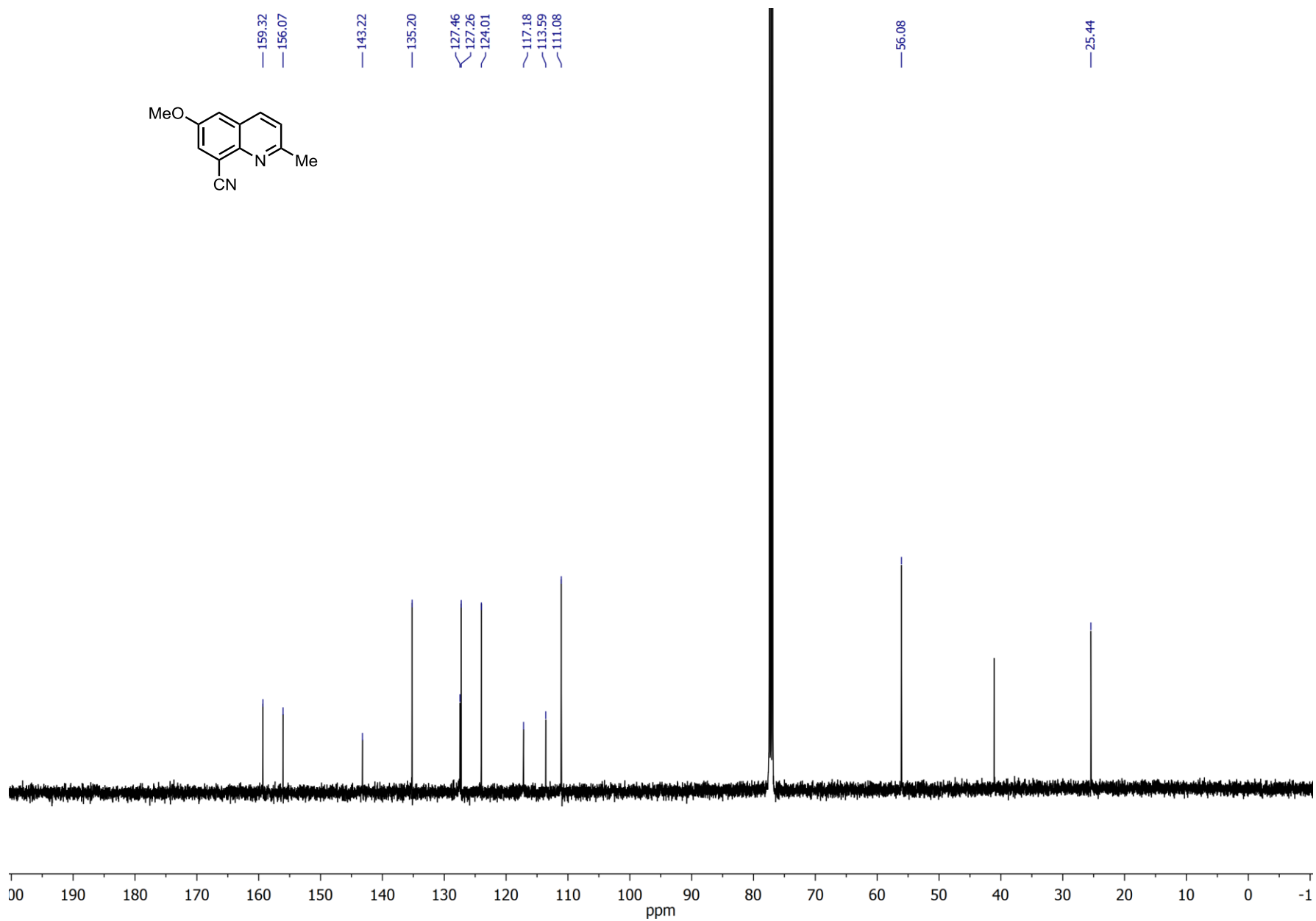
**$^1\text{H}$  NMR of ethoxy-substituted bithiophen 24** $\text{CDCl}_3$ , 500 MHz, 298 K

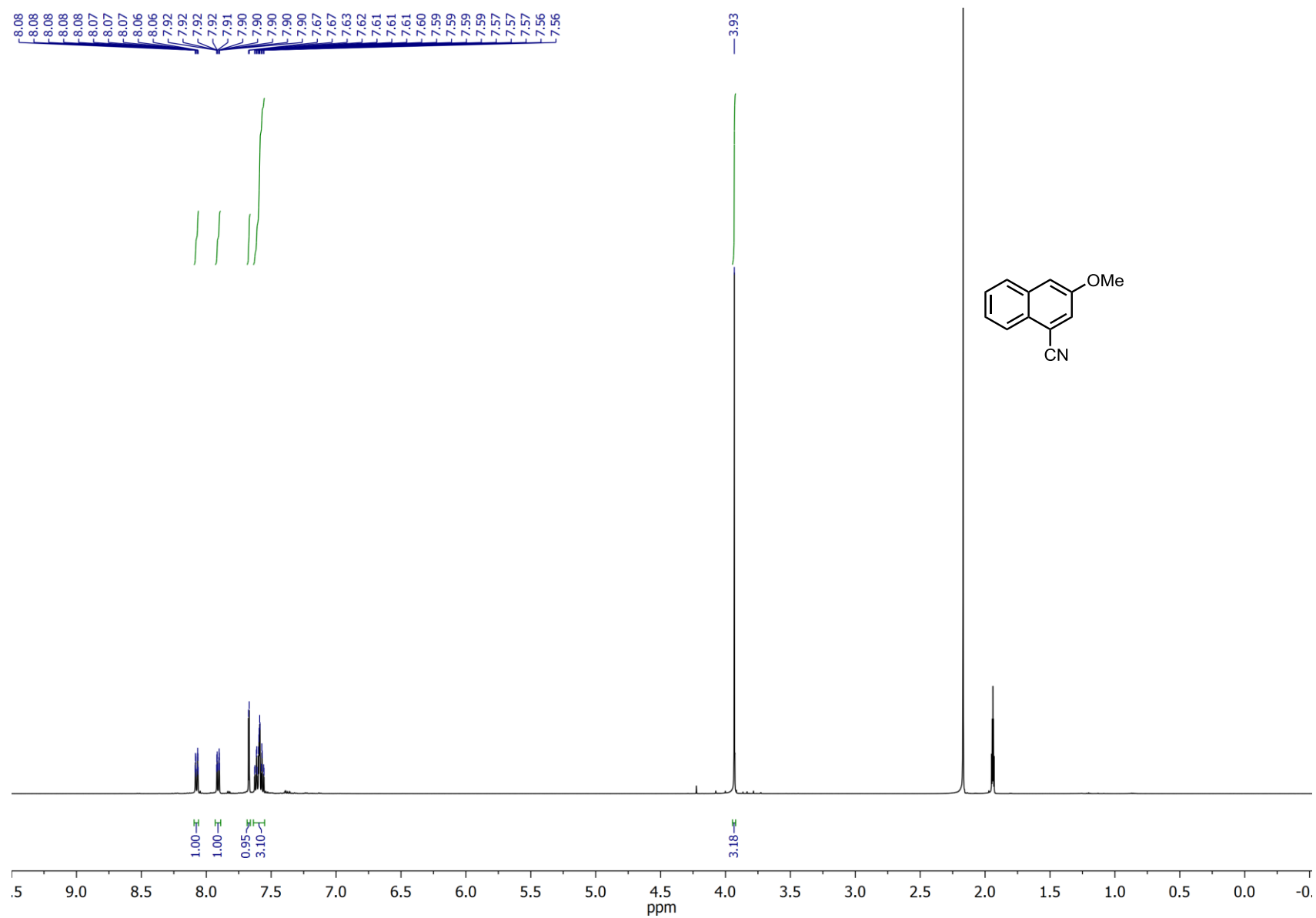
**$^{13}\text{C}$  NMR of ethoxy-substituted bithiophen 24**CDCl<sub>3</sub>, 126 MHz, 298 K

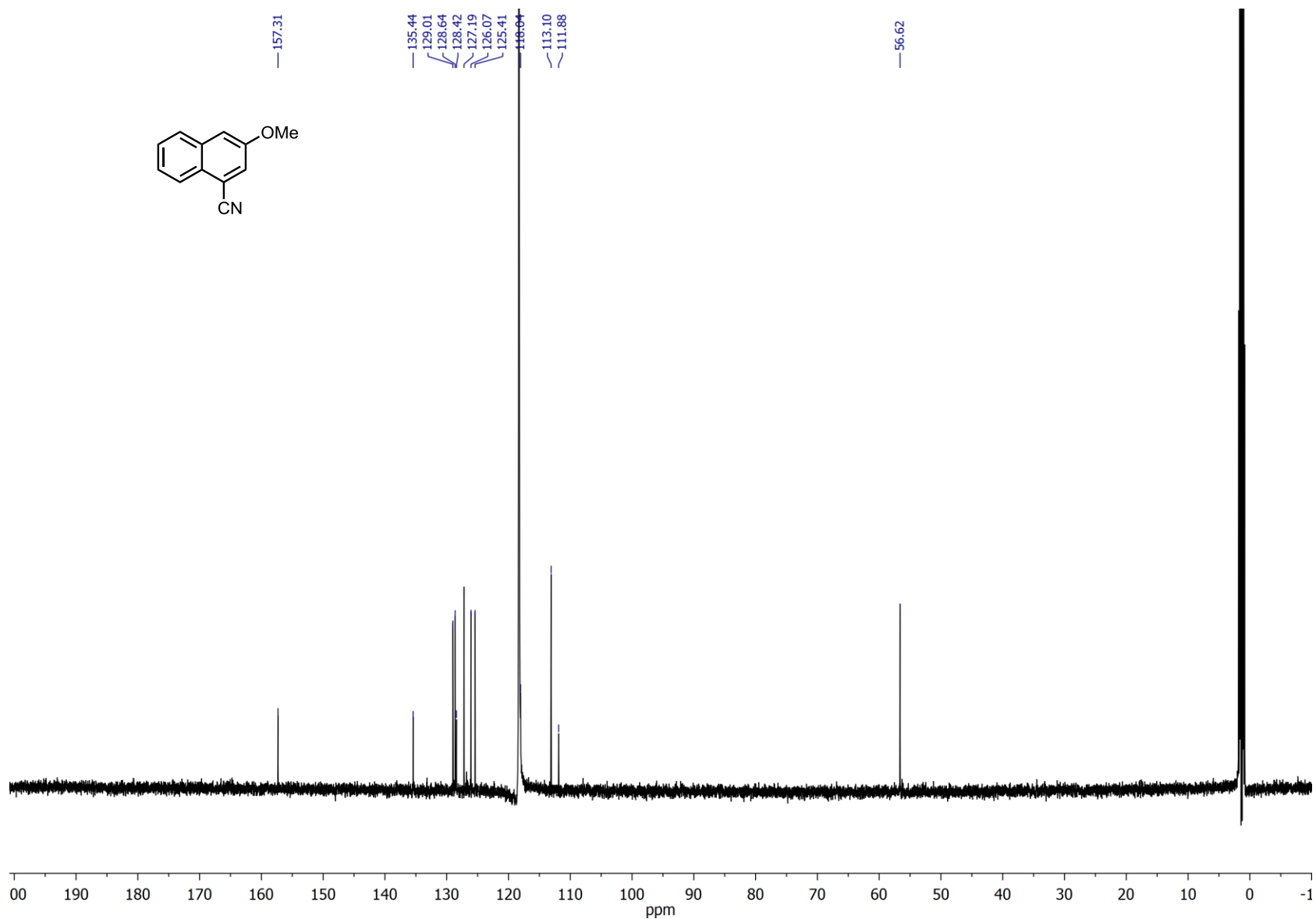
**$^1\text{H}$  NMR of cyano-substituted 3-phenylthiophene 25**CDCl<sub>3</sub>, 500 MHz, 298 K

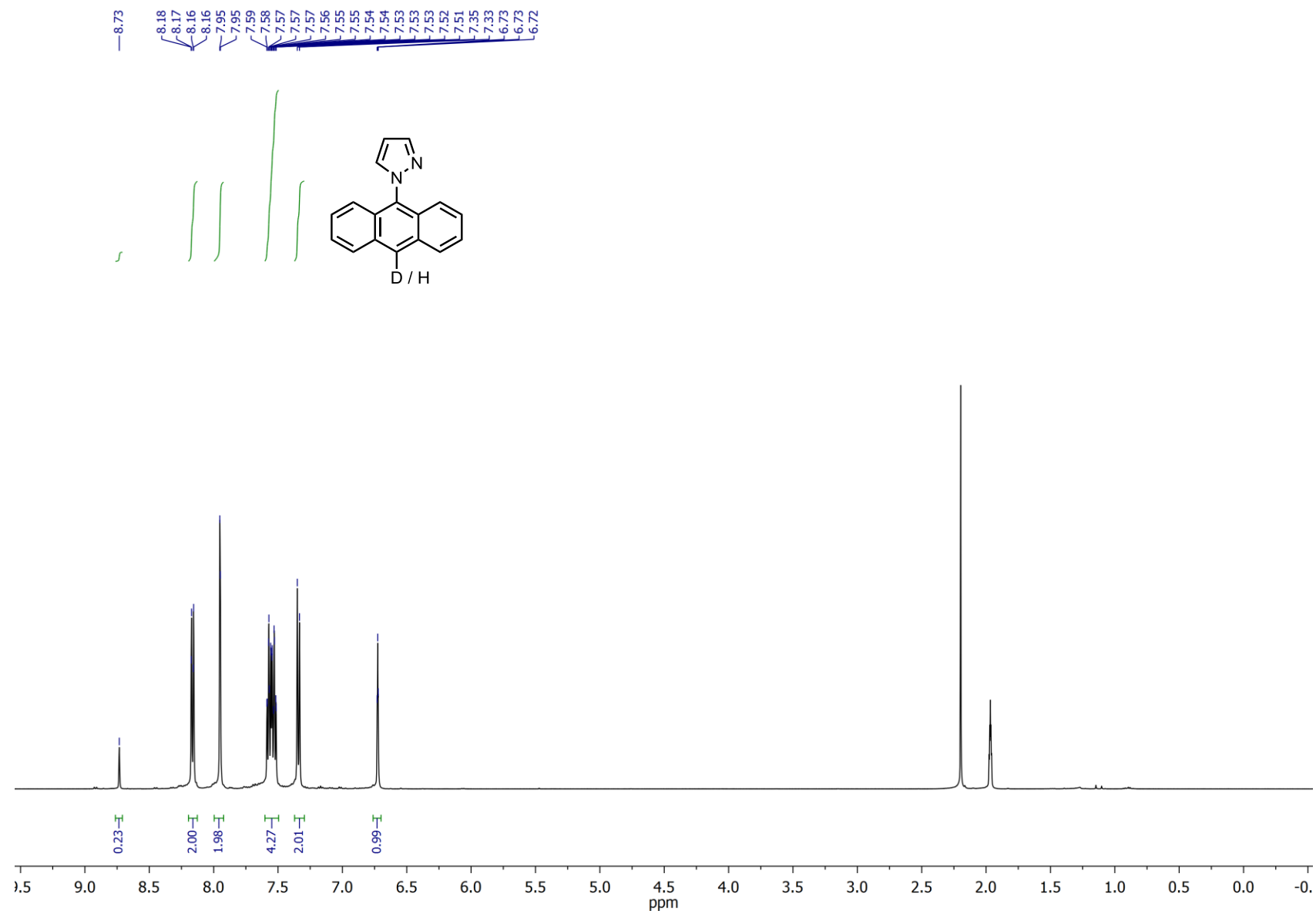
**$^{13}\text{C}$  NMR of cyano-substituted 3-phenylthiophene 25**CDCl<sub>3</sub>, 126 MHz, 298 K

**$^1\text{H}$  NMR of cyano-substituted methoxyquinoline 26**CDCl<sub>3</sub>, 500 MHz, 298 K

**$^{13}\text{C}$  NMR of cyano-substituted methoxyquinoline 26**CDCl<sub>3</sub>, 126 MHz, 298 K

**$^1\text{H}$  NMR of cyano-substituted methoxynaphthalene 27** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

**$^{13}\text{C}$  NMR of cyano-substituted methoxynaphthalene 27** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K

**$^1\text{H}$  NMR of pyrazol-substituted anthracen 28** $\text{CD}_3\text{CN}$ , 500 MHz, 298 K

**$^{13}\text{C}$  NMR of pyrazol-substituted anthracen 28** $\text{CD}_3\text{CN}$ , 126 MHz, 298 K