Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Metal-free *S*-arylation of 5-mercaptotetrazoles and 2-mercaptopyridine with Unsymmetrical Diaryliodonium Salts

Raktim Abha Saikia,[a] Nitumoni Hazarika,[b] Nishant Biswakarma,[a] Ramesh Chandra Deka[a] and Ashim Jyoti Thakur*[a]

[a]Department of Chemical Sciences, Tezpur University, Napaam-784028, India.
[b]Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati-781039, India.

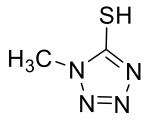
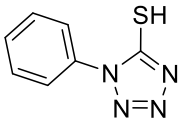
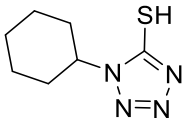
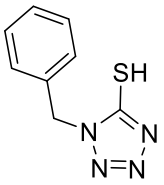
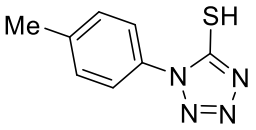
*E-mail: ashim@tezu.ernet.in

CONTENTS:

1. GENERAL EXPERIMENTAL INFORMATION

All reactions were performed in oven-dried Schlenk-tubes or round bottom flasks under ambient conditions, unless otherwise is stated. Dichloromethane (DCM), 1,2-dichloroethane (DCE) and acetonitrile (ACN) were dried by refluxing over CaH_2 under nitrogen condition and stored over 4Å molecular sieves. Toluene and 1,4-dioxane were dried utilising conventional drying procedures using sodium/benzophenone as indicator and stored over 4Å molecular sieves. All chemicals were purchased from commercial suppliers and used as received unless otherwise is stated. NaOH, Cs_2CO_3, K_3PO_4 and ^{t}BuOK were stored in a desiccator. The diaryliodonium salts were synthesized according to procedures described below. *M*-CPBA (Aldrich, 77% active oxidant) was dried at room temperature over high vacuum for 1 hour and titrated by iodometric titration[1] prior to use in the synthesis of diaryliodonium salts. Thin Layer Chromatography (TLC) analyses were performed on pre-coated Merck silica gel $60F_{254}$ plates using UV (254 nm) light and/or with $KMnO_4$-stain. Column chromatography was performed on 100-200 mesh silica gel using the gradient system, freshly distilled ethyl acetate-hexane mixture. All NMR data were recorded in a 400 MHz instrument at 298 K using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26 and sometimes δ 1.56 ($CDCl_3$-water) and in DMSO-d_6 δ 2.50 and δ 3.3 (DMSO-water); ^{13}C NMR: $CDCl_3$ δ 77.16, DMSO-d_6 δ 39.52) with multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, sex=sextet, sep=septet, m=multiplet, app=apparent), coupling constants (in Hz) and integration. Chemical shifts for ^{19}F-NMR are given in ppm relative to monofluorobenzene (-113.15 ppm) used as internal standard. The raw NMR data were processed by MestReNova software.

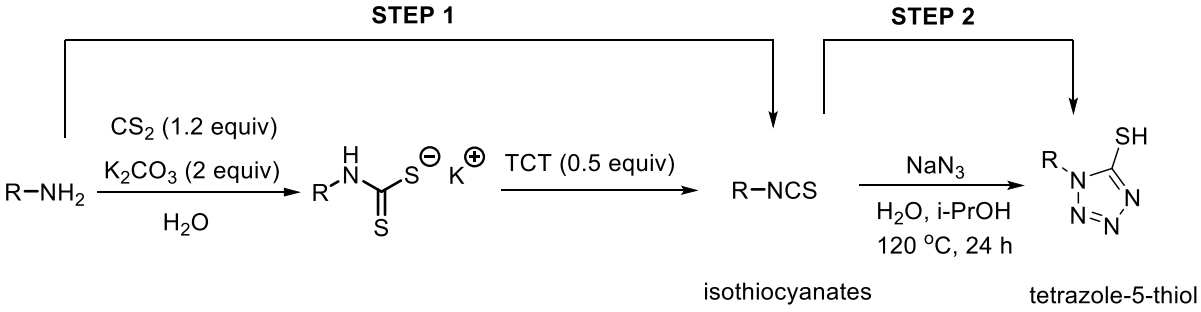
2. SYNTHESIS OF TETRAZOLE-5-THIOL

1a	1b	1c	1d	1e
				

1-methyl-1*H*-tetrazole-5-thiol (**1a)** is commercially available but, other tetrazole-5-thiols (**1b-1e)** are known compounds and were prepared by literature procedures.[2,3]

2.1. General procedure for the alkyl/aryl isothiocyante and its corresponding tetrazole-5-thiol:

Scheme S1:



Step 1[2]: To a mixture of amine (20 mmol) and K_2CO_3 (5.52 g, 40 mmol) in 20 mL of water, 1.82 g of CS_2 (24 mmol) was added drop-wise in a period of 20–30 min at room temperature (rt). After the addition was complete, the mixture was stirred for several hours until complete conversion was determined by TLC. Then, the reaction mixture was cooled to 0 °C and a solution of 1.85 g of 2,4,6-trichloro-1,3,5-triazine (TCT) (10 mmol) in 15 mL of CH_2Cl_2 was added dropwise. After the addition was complete, the mixture was stirred for another 0.5 h to finish the reaction. The reaction mixture was then basified to pH >11 with 6N NaOH to obtain a clear solution. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residual was purified by chromatography through a short silica column using petroleum ether as eluent to obtain the isothiocyanates.

Step 2[3]: To a solution of NaN_3 (2.5 mmol) and H_2O (3 mL) was added a solution of isothiocyanate (5 mmol) in *i*-PrOH (2 mL) at 120 °C using oil bath and the resulting mixture was refluxed for 24 h. The mixture was treated with conc. HCl (1 mL) at 0 °C and then extracted twice with ethyl acetate (10 mL and 5 mL). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated to crude product. Further, the crude product was purified by column chromatography to get the pure product.

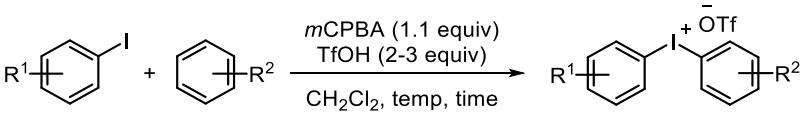
3. SYNTHESIS OF DIARYLIODONIUM SALTS

3.1 Various methods for diaryliodonium salts possessing different counter-anions

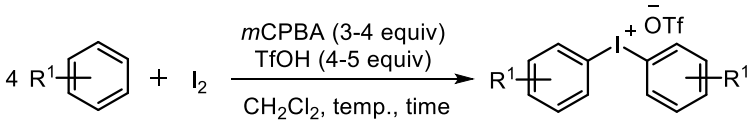
Most of the diaryliodonium salts used in this project were synthesized according to one-pot reported procedure. These reactions were run without precautions to avoid air or moisture.

Olofsson's protocol:

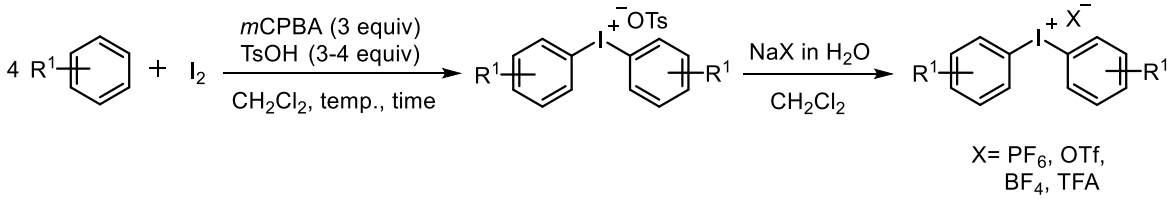
Method I[4]



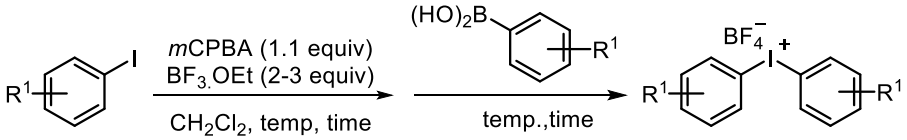
Method II[4]



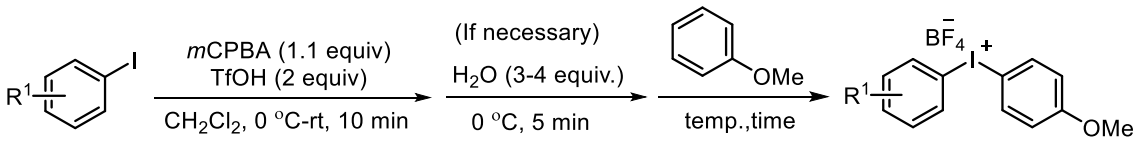
Method III[5]



Method IV[6]

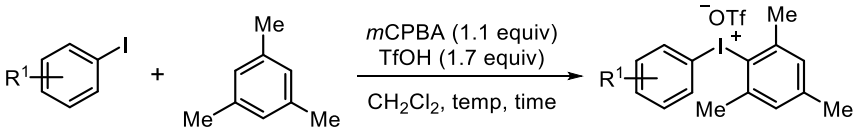


Method V[7]



Gaunt's modified protocol:

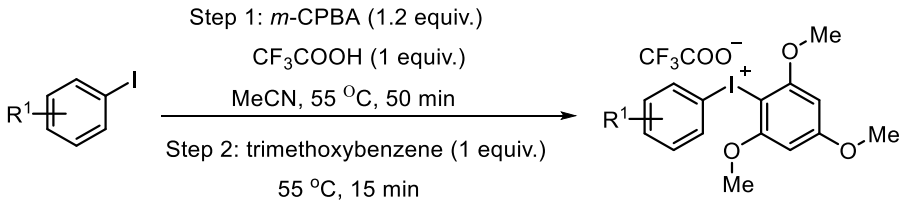
Method VI[8]



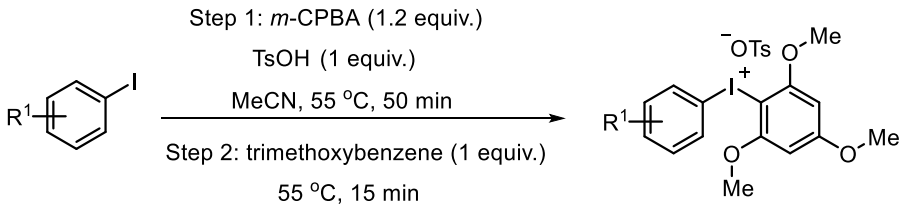
R^1= EDG or EWG

Stuart's protocol:

Method VII[9]

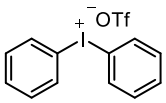
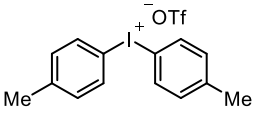
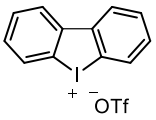
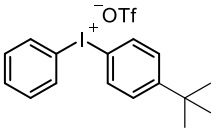
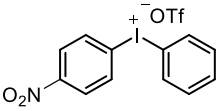
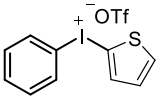
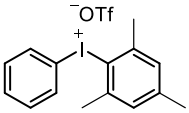
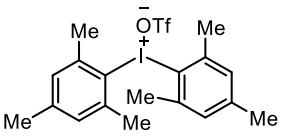
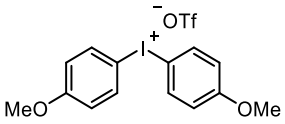
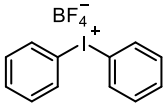
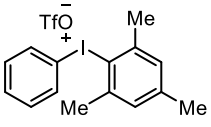


Method VIII[10]

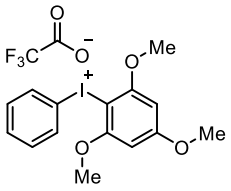


3.2 Diaryliodonium salts synthesized in this work

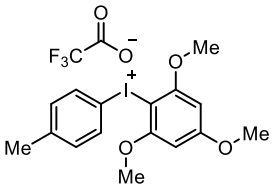
Table S1. Synthesis of various diaryliodonium salts according to above mentioned procedures:

Method I	 **2a-OTf**  **2b-OTf**  **2c-OTf**  **2d-OTf**  **2e-OTf**  **2f-OTf**  **2g-OTf**
Method II	 **2g-OTf**
Method III	 **2i-An**
Method IV	 **2a-BF_4**
Method VI	 **2a-Mes**

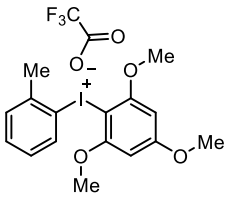
Method VII: Prepared Aryl-TMP-iodonium-trifluoroacetate



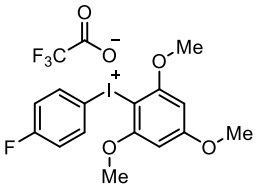
2a-TMP



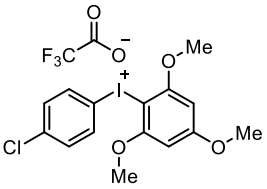
2b-TMP



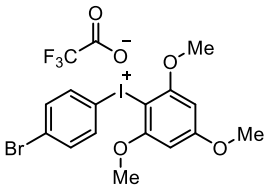
2c-TMP



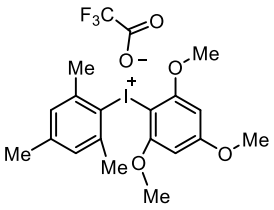
2d-TMP



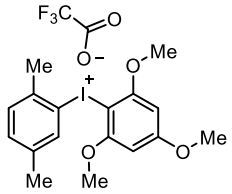
2e-TMP



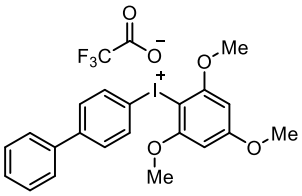
2f-TMP



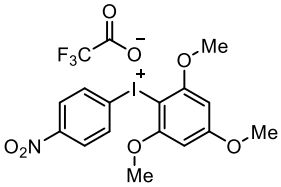
2g-TMP



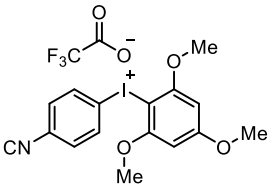
2h-TMP



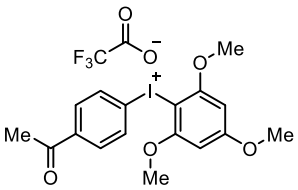
2i-TMP



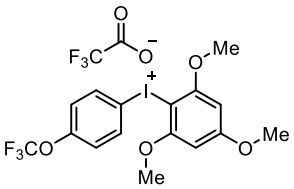
2j-TMP



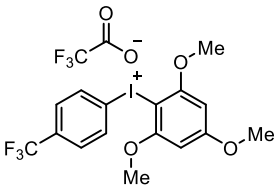
2k-TMP



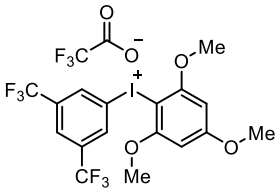
2l-TMP



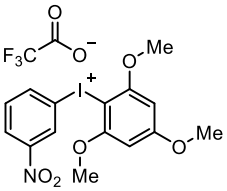
2m-TMP



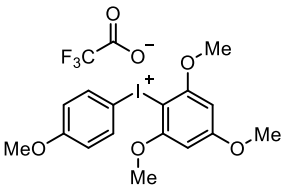
2n-TMP



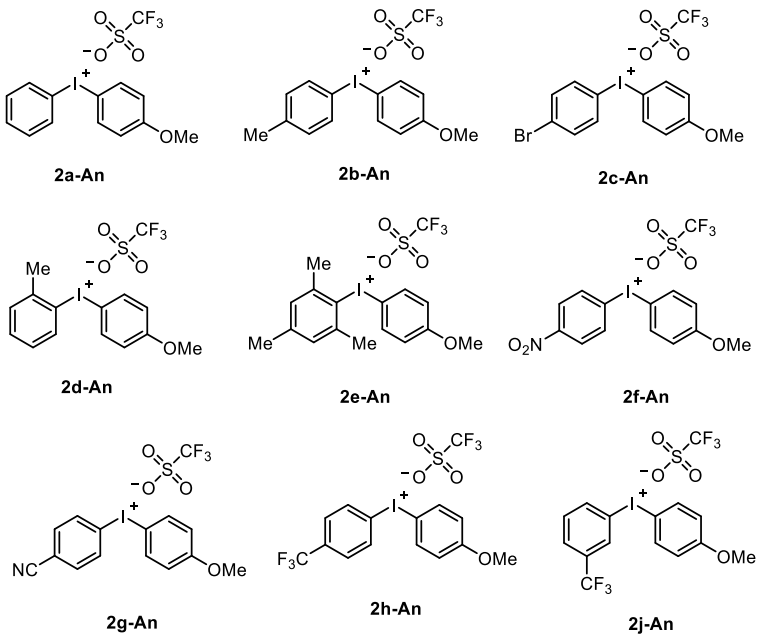
2o-TMP



2p-TMP



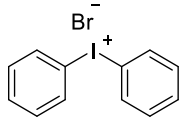
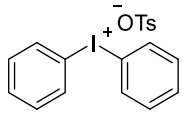
2q-TMP

Method V: Prepared Aryl-anisyl-iodonium-trifluorosulfonate	

All diaryliodonium salts were prepared according to above mentioned procedures. Characterization data of these compounds were matched with those previously reported in the literature.

3.3 Synthesis of other counter-anion diaryliodonium salts

Table S2. Diaryliodonium salts synthesized by other methods

 **2a-Br**	Diphenyliodonium bromide was prepared in 72% yield according to literature report.[11]
 **2a-OTs**	Diphenyliodonium tosylate was prepared in 65% yield *via* anion exchange method from **2a** according to literature report.[5]

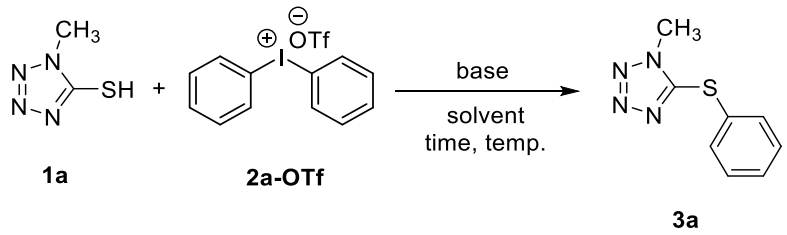
4. OPTIMIZATION ON THE *S*-ARYLATION OF TETRAZOLE-5-THIOLS

4.1 Optimisation for phenylation

The arylation was tried with 1-methyltetrazol-5-thiol **1a** (0.1 mmol) and diphenyliodonium triflate **2a-OTf** (0.1 mmol) in toluene at room temperature (Scheme S2), delivering no *S*-arylated product **3a** (Table S3). In order to maintain the metal-free prospect, various organic and inorganic bases with varying time and temperature were optimized (Entries 1-26, Table S3).

Table S3: **Initial optimization with diphenyliodonium salts**[a]

Scheme S2:



1a **2a-OTf** **3a**

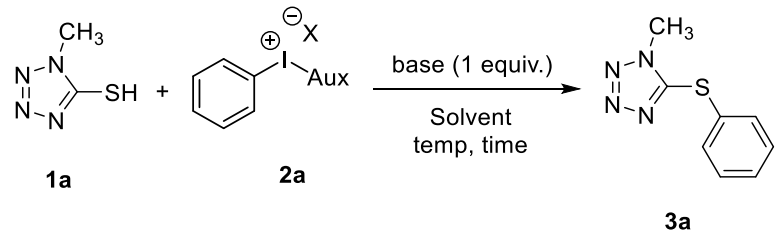
Entry	1a (eq.)	2a (eq.)	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)
1	1	1	Toluene	-	rt	24	n.r.
2	1	1	Toluene	-	45	24	n.r.
3	1	1	Toluene	-	60	24	n.r.
4	1	1	Toluene	-	100	24	n.r.
5	1	1	Toluene	Na_2CO_3 (1.1)	rt	24	n.r.
6	1	1	DCE	Na_2CO_3 (1.1)	45	24	Trace
7	1	1	Toluene	Na_2CO_3 (1.1)	60	24	65
8	1	1	Toluene	Na_2CO_3 (1.1)	80	10	72
9	1	1	Toluene	Na_2CO_3 (1.1)	80	24	71
9	1	1	Toluene	Na_2CO_3 (1.1)	100	10	72
10	1	1	Toluene	$NaHCO_3$ (1.1)	80	12	60
11	1	1	Toluene	K_2CO_3 (1.1)	80	12	62
12	1	1	Toluene	Et_3N (1.1)	80	10	70
13	1	1	Toluene	*t*BuOK (1.1)	80	12	48
14	1	1	Toluene	DABCO (1.1)	80	12	52
15	1	1	Toluene	DBU (1.1)	80	10	70
16	1	1	Toluene	NaOH (1.1)	80	12	trace
17	1	1	Toluene	Pyridine (1.1)	80	12	50
18	1	1	Toluene	K_3PO_4 (1.1)	80	12	45
19	1	1	1,4-dioxane	Na_2CO_3 (1.1)	80	12	54
20	1	1	DMF	Na_2CO_3 (1.1)	80	12	trace
21	1	1	DMSO	Na_2CO_3 (1.1)	80	12	trace
22	1	1	CH_3CN	Na_2CO_3	80	12	70

23	1	1	DCM	(Na_2CO_3 (1.1)	80	12	56
24	1	1	DCE	(Na_2CO_3 (1.1)	80	5	54
25	1	1	MeOH	(Na_2CO_3 (1.1)	80	24	trace
26	2	1	EtOH	(Na_2CO_3 (1.1)	80	24	trace

[a]Reaction conditions: **1a** (0.1 mmol), diphenyliodonium triflate (0.1 mmol), base (1.1 equiv.) and solvent (0.1 M) were added in a Schlenk tube. Yields based on ^{1}H NMR spectra.

Table S4: Investigation for unsymmetrical iodonium salt[a]

Scheme S3:



1a **2a** **3a**

Entry	1a (eq.)	2a (eq.)	Aux	X	Base	Temp. (°C)	Time (h)	Yield (%)
1	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	80	12	72
2	1	**2a-OTs** (1.0)	Ph	OTs	Na_2CO_3 (1.1)	80	12	trace
3	1	**2a-Br** (1.0)	Ph	Br	Na_2CO_3 (1.1)	80	12	56
4	1	**2a-BF_4** (1.0)	Ph	BF_4	Na_2CO_3 (1.1)	80	112	75
5	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.1)	80	5	85 (77)[b]
6	1	**2a-Mes** (1.0)	Mes	OTf	Na_2CO_3 (1.1)	80	12	trace
7	1	**2a-An** (1.0)	Anisyl	OTf	Na_2CO_3 (1.1)	80	12	60
8	1	**2a-TMP** (1.0)	TMP	OTs	Na_2CO_3 (1.1)	80	24	trace
9	1	**2a-TMP** (1.0)	TMP	OTf	Na_2CO_3 (1.1)	80	24	trace
10	1	**2a-TMP** (1.2)	TMP	TFA	Na_2CO_3 (1.1)	80	10	82
11	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (0.5)	80	12	65
12	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.5)	80	12	78
13	1.2	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.1)	80	12	75

14	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.1)	100	12	80
15	1	**2a-TMP** (1.0)	TMP	TFA	Et_3N (1.1)	80	10	72
16	1	**2a-TMP** (1.0)	TMP	TFA	K_3PO_4 (1.1)	80	12	68

[a]Reaction conditions: **1a** (0.1 mmol), **2a** salts (0.1 mmol), base (1.1 equiv.) and solvent (0.1 M) were added in a Schlenk tube. Yields based on ^{1}H NMR spectra. [b]CH_3CN as solvent.

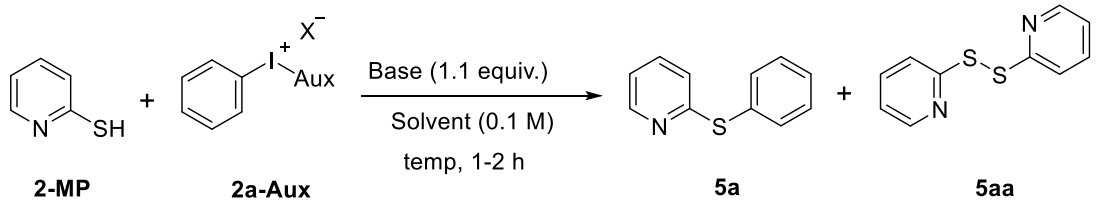
5. OPTIMIZATION ON THE *S*-ARYLATION OF 2-MERCAPTOPYRIDINE (2-MP)

5.1 Initial optimization

As we tried to implement our protocol into *S*-phenylation of 2-mercaptopyridine, we were surprised that the reaction did not work and showed a prominent side product. Initially, we suspected that the side product would be *N*-arylated product of 2-MP. But, later it was confirmed from ^{1}H NMR spectrum that it was disulphide compound of 2-MP (Scheme S4). As a result, we further optimized on the factors by varying of temperature, bases and proper auxiliary selection of iodonium salt (Table S5).

Table S5: Variation of factors on *S*-phenylation of 2-mercaptopyridine[a]

Scheme S4:

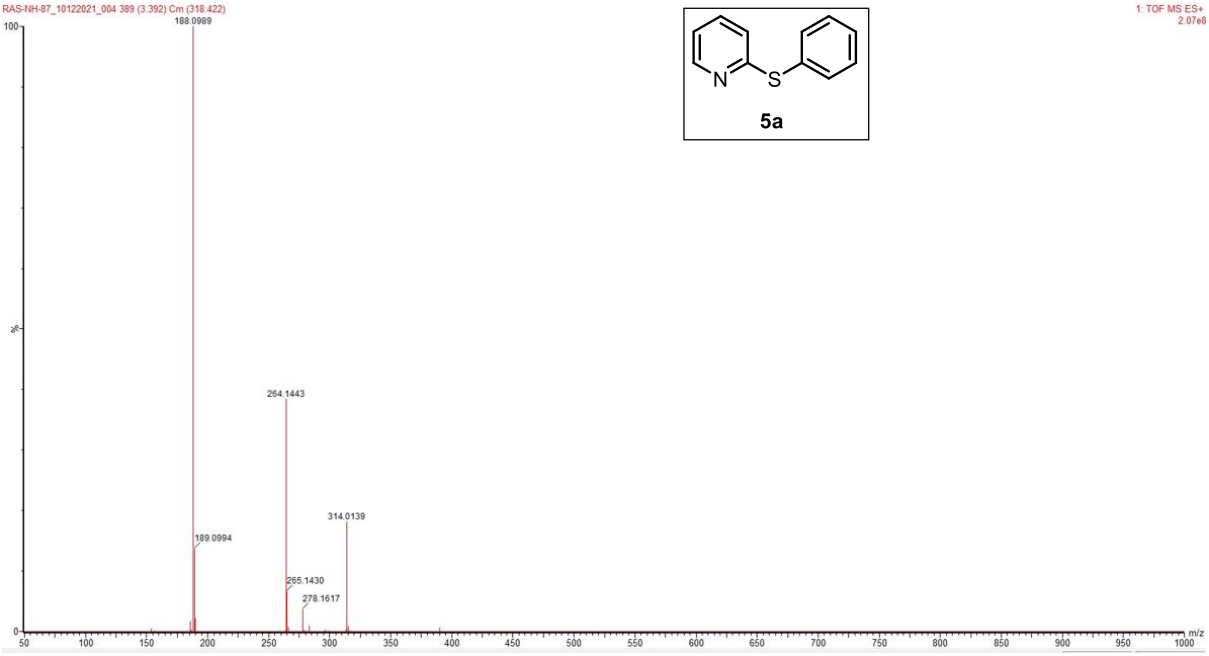


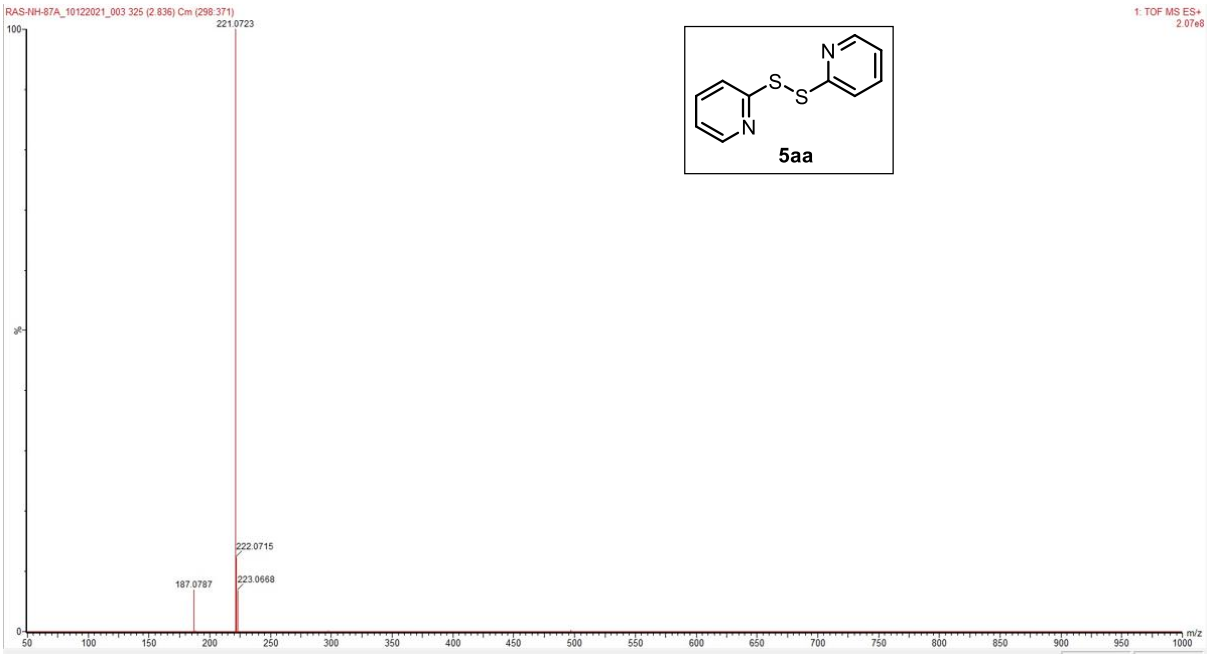
Entry	2-MP (eq.)	2a (equiv.)	Aux	X	Base	Solvent	T (°C)	t (h)	Yield (%) 5a	5aa
1	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.1)	Toluene	80	3	Trace	-
2	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	Toluene	rt	2	0	100
3	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	Toluene	45	3	Trace	100
4	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	Toluene	60	3	15	75
5	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	Toluene	80	3	36	68

6	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	Toluene	100	2	78	-
7	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	ACN	100	3	72	trace
8	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	DMF	100	5	46	-
9	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.0)	MeOH	100	5	28	-
10	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	DCE	100	5	65	-
11	1	**2a-OTf** (1.0)	Ph	OTf	Na_2CO_3 (1.1)	1,4-dioxane	100	5	68	-
12	1	**2a-OTf** (1.0)	Ph	OTf	Et_3N (1.0)	Toluene	100	3	75	trace
13	1	**2a-OTf** (1.0)	Ph	OTf	K_3PO_4 (1.1)	Toluene	100	5	46	trace
14	1	**2a-OTf** (1.0)	Ph	OTf	K_2CO_3 (1.1)	Toluene	100	5	68	trace
15	1	**2a-OTf** (1.0)	Ph	OTf	DABCO (1.1)	Toluene	100	5	55	30
16	1	**2a-OTf** (1.0)	Ph	OTf	DBU (1.0)	Toluene	100	3	72	trace
17	1.2	**2a-OTf** (1.0)	Ph	OTf	K^{t}BuO (1.0)	Toluene	100	2	45	trace
18	1	**2a-TMP** (1.0)	TMP	TFA	Na_2CO_3 (1.0)	Toluene	100	5	48	trace
19	1	**2a-TMP** (1.0)	TMP	OTs	Na_2CO_3 (1.0)	Toluene	100	5	trace	-
20	1	**2a-TMP** (1.0)	TMP	OTf	Na_2CO_3 (1.0)	Toluene	100	5	-	trace
21	1	**2a-Mes** (1.0)	Mes	OTf	Na_2CO_3 (1.0)	Toluene	100	3	trace	-
22	1	**2a-An** (1.0)	anisyl	OTf	Na_2CO_3 (1.0)	Toluene	100	2	78	-

[a]Reaction conditions: **2-MP** (0.1 mmol), **2a** salts (0.1 mmol), base (1.1 equiv.) and solvent (0.1 M) were added in a Schlenk tube. Yields based on ^{1}H NMR spectra. Toluene was degassed before use.

5.2 Validation of 4a and 4aa by HRMS

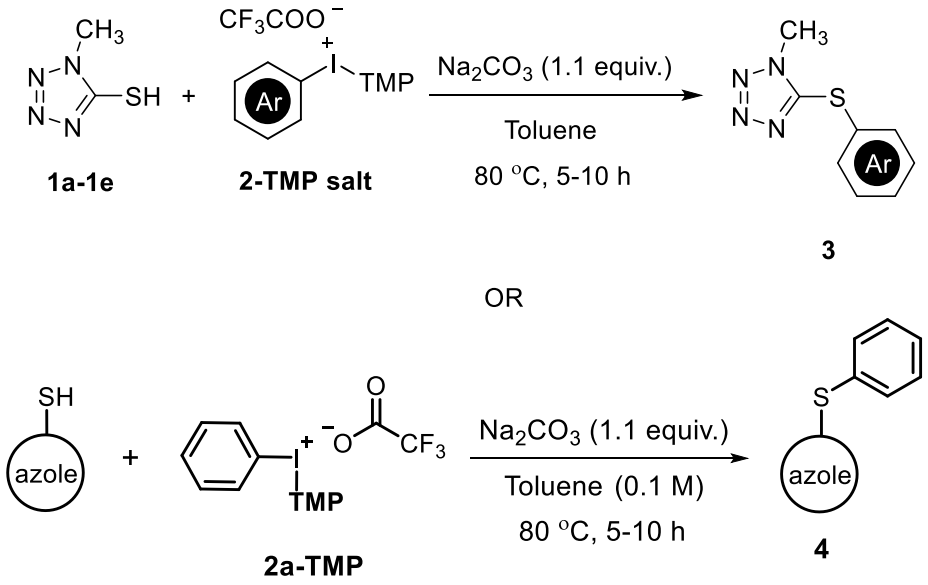




6. PROCEDURES

6.1 General procedure A: *S*-arylation of tetrazole-5-thiols or other azoles

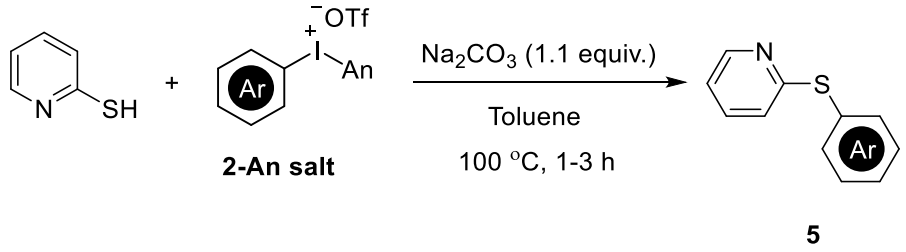
Scheme S5



To an oven-dried Schlenck-tube, tetrazole-5-thiol **1** or **azole** (0.35 mmol), diaryliodonium salt **2-TMP** (0.35 mmol, 1 equiv.), and Na_2CO_3 (0.385 mmol, 1.1 equiv.) were added. After adding toluene (3.5 mL, 0.1 M), the tube was sealed and placed on a pre-heated oil bath at 80 °C. The reaction mixture was stirred till indicated time period. After removing from heat, the reaction was cooled to room temperature and performed work-up with EtOAc and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude product was purified using column-chromatography to obtain the desired product.

6.2 General procedure B: *S*-arylation of 2-mercaptopyridine

Scheme S6



To an oven-dried Schlenck-tube, 2-mercaptopyridine (0.25 mmol), diaryliodonium salt **2-An** (0.25 mmol, 1 equiv.), and Na_2CO_3 (0.275 mmol, 1.1 equiv.) were added. After adding toluene (3.5 mL, 0.1 M), the tube was sealed and placed on a pre-heated oil bath at 100 °C. After removing from heat, the reaction was cooled to room temperature and performed work-up with EtOAc and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude product was purified using column-chromatography to obtain the desired product.

7. DFT STUDIES

Geometry optimizations, ground state energies and vibrational frequencies of the species in interest are obtained using Gaussian 09 program.[12] A popular and reliable Becke-3-parameter-Lee-Yang-Parr B3LYP functional along with LANL2DZ basis set is chosen for the geometry optimizations. B3LYP functional is chosen as it gives accurate structures and energies for the reactions including aryl iodonium salts.[13,14] Vibrational frequency calculations are done in order to distinguish between a minima (No imaginary frequency) and a transition state (One imaginary frequency). Berny algorithm[15] is carried out for the geometry optimization of a transition state structure. IRC calculations[16] have been performed for each TS in order to confirm the reaction path where it connects the transition state with its two neighbouring minima.

6.1 Cartesian coordinates of all the optimized intermediates and transition states

Species	Z	x	y	z
2a-An	6	4.618164000	3.317509000	0.679257000
	6	3.931871000	2.612760000	1.688121000
	6	2.709491000	1.974378000	1.402078000
	6	2.194235000	2.044115000	0.095173000
	6	2.866298000	2.744997000	-0.922623000
	6	4.086097000	3.385094000	-0.621975000
	1	5.559075000	3.811677000	0.906964000
	1	4.339712000	2.562106000	2.694156000
	1	2.182272000	1.434844000	2.184026000
	1	2.459327000	2.800762000	-1.929060000
	1	4.611956000	3.930051000	-1.401448000
	53	0.290859000	1.112161000	-0.364604000
	6	2.285770000	-1.179382000	-0.974681000
	6	2.807671000	-2.476578000	-0.904128000
	6	2.154327000	-3.463647000	-0.129872000
	6	0.978079000	-3.146931000	0.581885000
	6	0.445183000	-1.843727000	0.523599000

	6	1.115431000	-0.893087000	-0.250638000
	1	2.790719000	-0.427402000	-1.572591000
	1	3.708113000	-2.746558000	-1.446177000
	1	0.455999000	-3.890188000	1.174532000
	1	-0.476618000	-1.613849000	1.056073000
	8	2.752579000	-4.714505000	-0.139781000
	6	2.118236000	-5.809064000	0.591889000
	1	2.754541000	-6.677141000	0.413025000
	1	2.077815000	-5.592835000	1.667717000
	1	1.107310000	-6.002944000	0.210420000
	16	-3.052263000	-0.676049000	-0.090952000
	8	-2.433778000	-1.020558000	1.384887000
	8	-3.986347000	-1.775282000	-0.823263000
	8	-1.906727000	0.049235000	-1.062796000
	6	-4.244370000	0.906461000	0.271366000
	9	-3.464106000	1.976293000	0.706954000
	9	-5.171747000	0.611902000	1.254450000
	9	-4.914621000	1.293498000	-0.875566000
2-MP	6	0.573757000	-0.034144000	-0.000042000
	6	-0.175872000	1.200427000	-0.000046000
	6	-1.572584000	1.201815000	0.000023000
	6	-2.272936000	-0.032382000	0.000033000
	6	-1.488617000	-1.201991000	-0.000009000
	7	-0.134139000	-1.230392000	-0.000020000
	1	-2.117782000	2.147064000	0.000060000
	1	0.386994000	2.129819000	-0.000121000
	1	-3.359845000	-0.083625000	0.000063000
	1	-1.973398000	-2.181860000	-0.000035000
	16	2.351282000	-0.012562000	0.000026000

IM1	6	-0.137979000	4.252717000	0.873682000
	6	-1.193924000	3.373676000	1.181026000
	6	-1.203529000	2.055120000	0.678016000
	6	-0.124306000	1.663724000	-0.119189000
	6	0.948912000	2.503735000	-0.442489000
	6	0.930309000	3.819273000	0.064713000
	1	-0.147227000	5.269157000	1.259679000
	1	-2.018322000	3.703779000	1.807799000
	1	-2.013673000	1.361372000	0.901761000
	1	1.777850000	2.162894000	-1.054025000
	1	1.746515000	4.494467000	-0.179321000
	53	-0.139621000	-0.377338000	-0.919706000
	6	2.970748000	-0.675184000	-1.428300000
	6	4.325289000	-0.872811000	-1.118840000
	6	4.731503000	-0.970981000	0.229732000
	6	3.779404000	-0.873940000	1.268006000
	6	2.420973000	-0.678861000	0.947275000
	6	2.018876000	-0.572257000	-0.393139000
	1	2.669439000	-0.604514000	-2.471280000
	1	5.077979000	-0.953368000	-1.897290000
	1	4.073612000	-0.949835000	2.310042000
	1	1.692916000	-0.605133000	1.751641000
	8	6.096339000	-1.164798000	0.429564000
	6	6.598804000	-1.285520000	1.792868000
	1	7.675727000	-1.429788000	1.689374000
	1	6.401545000	-0.372472000	2.371298000
	1	6.156639000	-2.151891000	2.303648000
	6	-3.781512000	-0.692886000	-0.153463000
	6	-4.981954000	-1.446354000	-0.288854000
	6	-5.613669000	-1.951547000	0.854883000

	6	-5.042036000	-1.715174000	2.125489000
	6	-3.855391000	-0.968363000	2.178598000
	7	-3.238348000	-0.461515000	1.078887000
	1	-6.532511000	-2.525856000	0.760349000
	1	-5.387693000	-1.619609000	-1.279857000
	1	-5.497006000	-2.094085000	3.035722000
	1	-3.372863000	-0.756988000	3.130962000
	16	-2.984276000	-0.010401000	-1.636557000
IM2	6	-2.621469000	-1.260912000	1.571311000
	6	-2.343936000	-1.587057000	0.231755000
	6	-3.302516000	-2.232569000	-0.569170000
	6	-4.564256000	-2.548801000	-0.021012000
	1	-5.827393000	-2.464562000	1.737402000
	1	-4.106369000	-1.323855000	3.145345000
	1	-1.876916000	-0.763216000	2.187980000
	1	-3.084201000	-2.489270000	-1.603861000
	1	-5.310349000	-3.045475000	-0.636975000
	53	-0.309110000	-1.209398000	-0.633016000
	6	-1.864233000	1.482500000	-0.801683000
	6	-2.050561000	2.864998000	-0.664905000
	6	-1.020661000	3.667590000	-0.125125000
	6	0.197809000	3.085094000	0.282921000
	6	0.396319000	1.696595000	0.143665000
	6	-0.639890000	0.929945000	-0.391512000
	1	-2.660366000	0.867134000	-1.207836000
	1	-2.977371000	3.337844000	-0.973709000
	1	0.999460000	3.685585000	0.699903000
	1	1.334323000	1.229990000	0.445577000
	8	-1.310707000	5.026494000	-0.038874000
	6	-0.289617000	5.931623000	0.475832000

	1	-0.738136000	6.925633000	0.429161000
	1	-0.032724000	5.689389000	1.516156000
	1	0.614972000	5.902659000	-0.146493000
	6	3.375759000	-0.723108000	-0.299799000
	6	4.678221000	-1.291076000	-0.389819000
	6	5.487101000	-1.350679000	0.752387000
	6	4.991789000	-0.856948000	1.980340000
	6	3.697033000	-0.316465000	1.991834000
	7	2.906325000	-0.239819000	0.889130000
	1	6.484219000	-1.780845000	0.691414000
	1	5.022730000	-1.672798000	-1.344966000
	1	5.583876000	-0.890814000	2.889935000
	1	3.266161000	0.076436000	2.910805000
	16	2.344223000	-0.617450000	-1.791979000
TS1	6	-0.978538000	3.709436000	1.613247000
	6	-1.271958000	2.439289000	2.148051000
	6	-1.204343000	1.281441000	1.343356000
	6	-0.860601000	1.459258000	0.000492000
	6	-0.540530000	2.694534000	-0.575615000
	6	-0.617615000	3.832062000	0.256846000
	1	-1.031085000	4.592615000	2.244485000
	1	-1.558767000	2.334839000	3.192053000
	1	-1.460647000	0.299947000	1.727295000
	1	-0.280603000	2.789499000	-1.624329000
	1	-0.396678000	4.808587000	-0.168145000
	53	0.141776000	-0.477408000	-1.057460000
	6	3.191252000	0.204066000	-1.313274000
	6	4.543040000	0.218831000	-0.945629000
	6	4.959918000	-0.429295000	0.238675000
	6	4.018817000	-1.093237000	1.054564000

	6	2.661260000	-1.104751000	0.678834000
	6	2.247664000	-0.464766000	-0.502498000
	1	2.880739000	0.705918000	-2.225662000
	1	5.287966000	0.722089000	-1.554231000
	1	4.320286000	-1.595934000	1.967857000
	1	1.939831000	-1.616241000	1.310321000
	8	6.322403000	-0.353983000	0.510891000
	6	6.837515000	-0.991348000	1.717155000
	1	7.911025000	-0.794778000	1.708552000
	1	6.387931000	-0.554319000	2.619225000
	1	6.659329000	-2.075257000	1.699838000
	6	-3.694461000	-0.626588000	-0.241180000
	6	-5.115721000	-0.585784000	-0.169988000
	6	-5.780409000	-1.348584000	0.799032000
	6	-5.025054000	-2.131588000	1.700631000
	6	-3.626286000	-2.098290000	1.584662000
	7	-2.966864000	-1.372147000	0.643613000
	1	-6.866468000	-1.333882000	0.854463000
	1	-5.662281000	0.032956000	-0.873834000
	1	-5.500840000	-2.740988000	2.463327000
	1	-2.998605000	-2.676068000	2.260704000
	16	-2.838759000	0.315778000	-1.529571000
TS2	6	5.519235000	-0.281192000	-1.219257000
	6	4.476408000	-0.634626000	-2.097879000
	6	3.190434000	-0.917344000	-1.595375000
	6	2.961555000	-0.848234000	-0.207200000
	6	3.995983000	-0.490266000	0.679251000
	6	5.278412000	-0.209370000	0.166761000
	1	6.509734000	-0.062851000	-1.610873000
	1	4.658728000	-0.690695000	-3.168316000

	1	2.387846000	-1.189241000	-2.275545000
	1	3.815071000	-0.433586000	1.749313000
	1	6.080734000	0.063740000	0.847844000
	53	0.961519000	-1.269971000	0.572757000
	6	0.124341000	1.742975000	1.617520000
	6	-0.107972000	3.109022000	1.387005000
	6	-0.682479000	3.542666000	0.171817000
	6	-1.030777000	2.606135000	-0.823282000
	6	-0.802838000	1.228188000	-0.608748000
	6	-0.252774000	0.842771000	0.611067000
	1	0.546112000	1.408624000	2.558945000
	1	0.143535000	3.847949000	2.141817000
	1	-1.479820000	2.916761000	-1.761386000
	1	-1.096559000	0.487379000	-1.344589000
	8	-0.861105000	4.924636000	0.055493000
	6	-1.479881000	5.445690000	-1.154737000
	1	-1.528643000	6.526891000	-1.011061000
	1	-0.873267000	5.218260000	-2.042874000
	1	-2.494393000	5.044313000	-1.287757000
	6	-2.962277000	-1.384686000	0.314535000
	6	-4.376142000	-1.440748000	0.471766000
	6	-5.180757000	-1.760904000	-0.629511000
	6	-4.573657000	-2.004041000	-1.882087000
	6	-3.175747000	-1.901779000	-1.963802000
	7	-2.380375000	-1.603116000	-0.902708000
	1	-6.260960000	-1.819185000	-0.517458000
	1	-4.807618000	-1.240661000	1.446845000
	1	-5.159990000	-2.260799000	-2.759433000
	1	-2.660229000	-2.070455000	-2.907523000
	16	-1.919731000	-1.029924000	1.752120000

5a	6	-3.756913000	0.935631000	-0.000734000
	6	-3.166871000	0.548692000	-1.219699000
	6	-1.988424000	-0.222304000	-1.221372000
	6	-1.404770000	-0.602392000	0.000347000
	6	-1.988313000	-0.220424000	1.221530000
	6	-3.166751000	0.550569000	1.218774000
	1	-4.667533000	1.530354000	-0.001149000
	1	-3.618479000	0.844192000	-2.163623000
	1	-1.526879000	-0.521307000	-2.157916000
	1	-1.526698000	-0.518024000	2.158487000
	1	-3.618293000	0.847503000	2.162281000
	6	1.477511000	-0.442457000	0.000312000
	6	2.798283000	-0.949490000	-0.000323000
	6	3.858474000	-0.030384000	-0.000795000
	6	3.575621000	1.353038000	-0.000646000
	6	2.229613000	1.754119000	-0.000013000
	7	1.196844000	0.871364000	0.000477000
	1	4.885771000	-0.385378000	-0.001279000
	1	2.980687000	-2.019906000	-0.000470000
	1	4.369636000	2.093320000	-0.000989000
	1	1.954188000	2.805618000	0.000131000
	16	0.099058000	-1.676469000	0.001057000
An-I	53	-2.342741000	-0.079020000	0.000002000
	6	0.406757000	1.345213000	0.000004000
	6	1.805275000	1.444735000	-0.000005000
	6	2.599516000	0.278011000	-0.000014000
	6	1.987395000	-0.991963000	-0.000019000
	6	0.580685000	-1.088526000	-0.000010000
	6	-0.204745000	0.074332000	0.000005000
	1	-0.194757000	2.248796000	0.000017000

	1	2.297131000	2.412501000	-0.000001000
	1	2.576641000	-1.903272000	-0.000040000
	1	0.115621000	-2.069535000	-0.000018000
	8	3.977930000	0.491077000	-0.000020000
	6	4.864845000	-0.664764000	0.000032000
	1	5.875295000	-0.251739000	0.000092000
	1	4.716717000	-1.279758000	0.898624000
	1	4.716824000	-1.279756000	-0.898581000
5i	6	-1.064002000	0.821774000	1.276543000
	6	-2.342790000	0.267276000	1.413615000
	6	-3.063533000	-0.129876000	0.266429000
	6	-2.501053000	0.031252000	-1.016951000
	6	-1.214083000	0.589254000	-1.141639000
	6	-0.495388000	0.984184000	-0.003346000
	1	-0.506901000	1.124614000	2.158133000
	1	-2.799021000	0.131405000	2.389259000
	1	-3.039308000	-0.268599000	-1.910302000
	1	-0.773513000	0.710940000	-2.126892000
	8	-4.326797000	-0.669933000	0.510844000
	6	-5.129383000	-1.113051000	-0.620851000
	1	-6.054838000	-1.494867000	-0.185321000
	1	-5.356713000	-0.278633000	-1.298933000
	1	-4.624070000	-1.914613000	-1.177367000
	6	2.318134000	0.338469000	-0.076113000
	6	3.703054000	0.618760000	-0.149079000
	6	4.600351000	-0.457092000	-0.071300000
	6	4.097770000	-1.768345000	0.077001000
	6	2.705311000	-1.940775000	0.140381000
	7	1.829180000	-0.905154000	0.064256000
	1	5.671018000	-0.277305000	-0.124111000

	1	4.055843000	1.639615000	-0.261121000
	1	4.761221000	-2.625195000	0.141667000
	1	2.263907000	-2.927520000	0.255000000
	16	1.157886000	1.776545000	-0.185294000
Ph-I	6	3.382579000	0.000005000	-0.000262000
	6	2.675664000	-1.217527000	-0.000070000
	6	1.266134000	-1.224680000	0.000240000
	6	0.573228000	-0.000007000	0.000520000
	6	1.266123000	1.224676000	0.000250000
	6	2.675655000	1.217532000	-0.000064000
	1	4.469658000	0.000010000	-0.000562000
	1	3.212341000	-2.163092000	-0.000192000
	1	0.726482000	-2.166602000	0.000352000
	1	0.726472000	2.166599000	0.000347000
	1	3.212326000	2.163100000	-0.000239000
	53	-1.573275000	0.000000000	-0.000064000
OTf	16	1.013955000	0.000007000	-0.000016000
	8	1.336722000	1.294572000	-0.944333000
	8	1.336855000	0.170555000	1.593242000
	8	1.336798000	-1.465091000	-0.648936000
	6	-1.033812000	0.000002000	0.000011000
	9	-1.559381000	-0.138319000	-1.291392000
	9	-1.559408000	1.187535000	0.525953000
	9	-1.559367000	-1.049261000	0.765484000

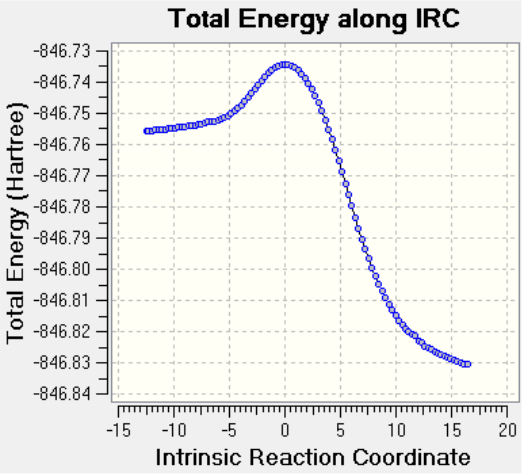
6.2 Absolute and Relative Gibbs free energies for reaction pathway at B3LYP/LANL2DZ level

Species	**G (in a.u.)**	**Relative G (in kcal/mol)**
2a-An+2-MP (deprotonated)	-1419.761809	0.00

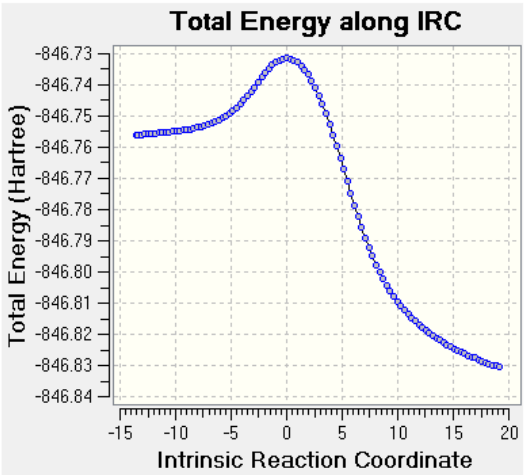
IM1+OTf	-1419.795936	-21.41499964
TS1+OTf	-1419.772011	-6.401846818
5a+An-I+OTf	-1419.895501	-83.89293323

2a-An+2-MP (deprotonated)		-1419.761809	0.00
IM2+OTf	-1419.796404	-21.70867386	
TS2+OTf	-1419.769484	-4.816131575	
5i+Ph-I+OTf	-1419.896029	-84.22425798	

6.3 Intrinsic reaction co-ordinate (IRC) plots of all transition states



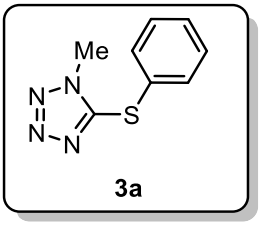
IM1-TS1-5a



IM2-TS2-5i

8. SYNTHESIS AND CHARACTERIZATION OF *S*-ARYL PRODUCTS

1-methyl-5-(phenylthio)-1*H*-tetrazole



3a

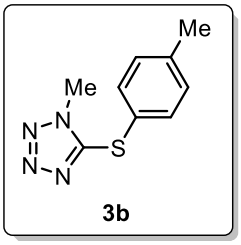
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2a-TMP** (169.5 mg, 0.35 mmol). The reaction was stirred for 5 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3a** (55 mg, 0.285 mmol, 82%) as yellowish liquid. R_f 0.3 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.52 (m, 2H), 7.39-7.41 (m, 3H), 3.96 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 132.5, 130, 129.6, 127.8, 34.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_8N_4S$ 192.0470; found 193.0939

1-methyl-5-(*p*-tolylthio)-1*H*-tetrazole



3b

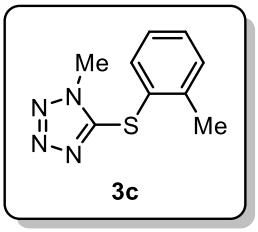
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2b-TMP** (174.38 mg, 0.35 mmol). The reaction was stirred for 5 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3b** (65 mg, 0.318 mmol, 91%) as colourless liquid. R_f 0.4 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, *J*=8 Hz, 2H), 7.18 (d, *J*=8 Hz, 2H), 3.95 (s, 3H), 2.36 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.0, 140.2, 133.1, 130.7, 123.8, 34.17, 21.34

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_{10}N_4S$ 206.0626; found 207.1145

1-methyl-5-(*o*-tolylthio)-1*H*-tetrazole



3c

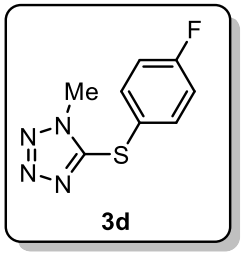
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2c-TMP** (174.3 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3a** (56 mg, 0.35 mmol, 78%) as yellowish oil. R_f 0.35 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J*=8 Hz, 2H), 7.31-7.36 (m, 2H), 7.20-7.23 (m, 1H) 3.96 (s, 3H), 2.46 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.6, 141.3, 134.3, 131.5, 130.4, 127.5, 126.6, 34.0, 20.8

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_{10}N_4S$ 206.0626; found 207.0917

5-((4-fluorophenyl)thio)-1-methyl-1*H*-tetrazole



3d

Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2d-TMP** (175.7 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3d** (56 mg, 0.26 mmol, 76%) as yellowish oil. R_f 0.3 (AcOEt /Hexane: 30/70).

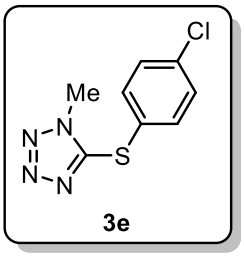
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53-7.56 (m, 2H), 7.08-7.10 (m, 2H), 3.96 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.75 (d, J_{C-F} = 250 Hz), 152.95, 135.76, 122.38, 117.3 (d, J_{C-F} = 25 Hz), 34

^{19}F NMR (376 MHz, $CDCl_3$) δ = -109.7

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_4FS$ 210.0375; found 211.0917

5-((4-chlorophenyl)thio)-1-methyl-1*H*-tetrazole



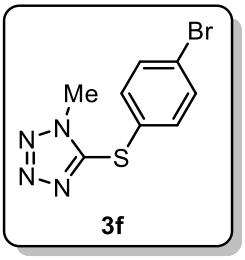
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2c-TMP** (181.5 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3e** (65 mg, 0.28 mmol, 82%) as white solid. R_f 0.35 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J*=8 Hz, 2H), 7.41 (d, *J*=8 Hz, 2H), 3.99 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 134.1, 133.1, 126.7, 124.3, 34.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_4SCl$ 226.0080; found 227.0622

5-((4-bromophenyl)thio)-1-methyl-1*H*-tetrazole



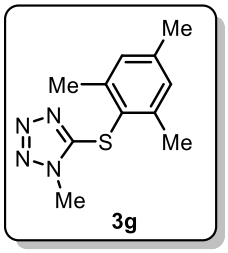
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2f-TMP** (197 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3f** (76 mg, 0.283 mmol, 81%) as white solid. R_f 0.4 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J*=8 Hz, 2H), 7.33 (d, *J*=8 Hz, 2H), 3.95 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.2, 136.2, 134.1, 130.1, 125.9, 34.0

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_4SBr$ 269.9575; found 272.9648

5-(mesitylthio)-1-methyl-1*H*-tetrazole



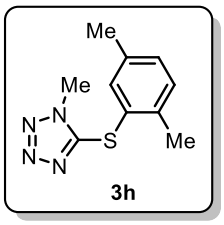
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2g-TMP** (184 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3g** (53 mg, 0.227 mmol, 65%) as yellowish liquid. R_f 0.45 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (s, 2H), 3.93 (s, 3H), 2.39 (s, 6H), 2.28 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 143.2, 141.1, 130.0, 121.6, 33.82, 21.91, 21.16

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{11}H_{14}N_4S$ 234.0939; found 235.1013

5-((2,5-dimethylphenyl)thio)-1-methyl-1*H*-tetrazole



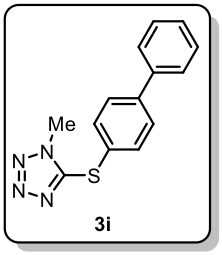
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2h-TMP** (179 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3h** (55 mg, 0.252 mmol, 72%) as white solid. R_f 0.4 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (s, 1H), 7.16 (d, *J*=8 Hz, 1H), 7.10 (d, *J*=8 Hz, 1H), 3.91 (s, 3H), 2.36 (s, 3H), 2.25 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.7, 138.0, 137.2, 134.6, 131.1, 126.2, 33.8, 20.8, 20.3

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{12}N_4S$ 220.0783; found 221.0857

5-([1,1'-biphenyl]-4-ylthio)-1-methyl-1*H*-tetrazole



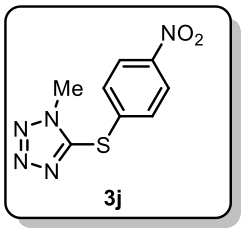
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2i-TMP** (196 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3i** (61.9 mg, 0.231 mmol, 66%) as white solid. R_f 0.45 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54-7.61 (m, 6H), 7.43 (t, *J*=8 Hz, 2H), 7.36 (t, *J*=8 Hz, 2H), 7.10 (d, *J*=8 Hz, 1H), 3.97 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.5, 142.7, 139.6, 133.0, 129.0, 128.6, 128.1, 127.1, 34.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{12}N_4S$ 268.0783; found 269.0859

1-methyl-5-((4-nitrophenyl)thio)-1*H*-tetrazole



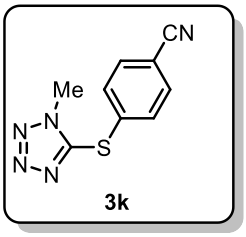
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2j-TMP** (185 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3j** (61.4 mg, 0.259 mmol, 74%) as brownish solid. R_f 0.2 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J*=8 Hz, 2H), 7.64 (d, *J*=8 Hz, 1H), 4.07 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.2, 147.8, 137.0, 131.0, 124.8, 34.2

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_5O_2S$ 237.0320; found 238.0398

4-((1-methyl-1*H*-tetrazol-5-yl)thio)benzonitrile



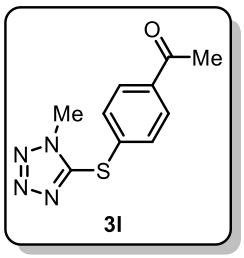
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2k-TMP** (178 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3k** (54.7 mg, 0.252 mmol, 74%) as white solid. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J*=8 Hz, 2H), 7.55 (d, *J*=8 Hz, 1H), 4.01 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.4, 134.8, 133.3, 131.2, 117.7, 112.8, 34.2

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_7N_5S$ 217.0422; found 218.0499

1-(4-((1-methyl-1*H*-tetrazol-5-yl)thio)phenyl)ethan-1-one



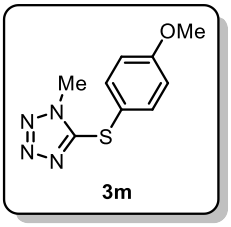
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2l-TMP** (184 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3l** (59 mg, 0.252 mmol, 72%) as white solid. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J*=8 Hz, 2H), 7.50 (d, *J*=8 Hz, 1H), 3.98 (s, 3H), 2.56 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.9, 137.2, 134.2, 130.9, 129.6, 34.3, 26.7

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_{10}N_4OS$ 234.0575; found 235.0835

5-((4-methoxyphenyl)thio)-1-methyl-1*H*-tetrazole



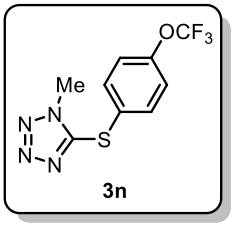
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2i-An** (171 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3m** (68.5 mg, 0.308 mmol, 88%) as yellowish liquid. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J*=8 Hz, 2H), 6.89 (d, *J*=8 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.2, 153.8, 135.7, 117.0, 115.6, 55.5, 33.8

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_{10}N_4OS$ 222.0575; found 223.0851

1-methyl-5-((4-(trifluoromethoxy)phenyl)thio)-1*H*-tetrazole



Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2m-An** (198 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3n** (71.4 mg, 0.259 mmol, 74%) as colourless oil. R_f 0.35 (AcOEt /Hexane: 30/70).

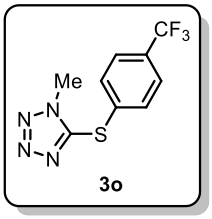
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J*=8 Hz, 2H), 7.23 (d, *J*=8 Hz, 1H), 3.99 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.2, 150.2, 134.4, 125.9, 122.2, 121.6, 119.0, 34.0

^{19}F NMR (376 MHz, $CDCl_3$) δ = -58.2

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_7N_4OF_3S$ 276.0293; found 277.0368

1-methyl-5-((4-(trifluoromethyl)phenyl)thio)-1*H*-tetrazole



Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2n-An** (193 mg, 0.35 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3o** (74.6 mg, 0.287 mmol, 82%) as colourless oil. R_f 0.4 (AcOEt /Hexane: 30/70).

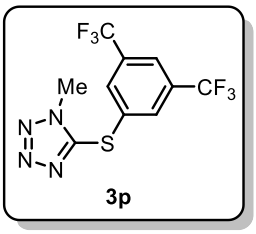
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J*=8 Hz, 2H), 7.58 (d, *J*=8 Hz, 1H), 4.00 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 132.9, 131.6, 131.5, 127.6, 126.8, 124.9, 122.2, 34.3

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.5

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_7N_4F_3S$ 260.0344; found 261.0419

5-((3,5-bis(trifluoromethyl)phenyl)thio)-1-methyl-1*H*-tetrazole



Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2o-TMP** (217 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3p** (75 mg, 0.227 mmol, 65%) as white solid. R_f 0.35 (AcOEt /Hexane: 30/70).

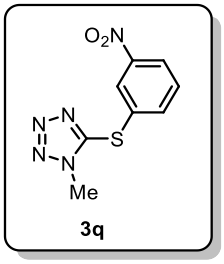
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 2H), 7.90 (s, 1H), 4.07 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.8, 133.7, 133.4, 133.0, 132.7, 132.2, 131.1, 126.6, 123.9, 123.4, 121.2, 118.5, 34.1

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.9

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_6N_4F_6S$ 328.0217; found 329.0878

1-methyl-5-((3-nitrophenyl)thio)-1*H*-tetrazole



3q

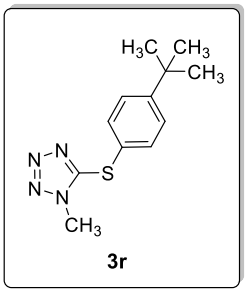
Synthesized following **general procedure A** starting from **1a** (40.6 mg, 0.35 mmol) and **2p-TMP** (285 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3p** (62 mg, 0.262 mmol, 75%) as yellowish oil. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (t, *J* = 2.2 Hz, 1H), 8.21 (dq, *J* = 8 and 1 Hz, 1H), 7.86 (dq, *J* = 8 and 1 Hz, 1H), 7.60 (t, *J*=8 Hz, 1H), 4.04 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.3, 148.7, 138.2, 130.9, 130.1, 127.0, 124.4, 34.2

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_5O_2S$ 237.0320; found 238.0401

5-((4-(tert-butyl)phenyl)thio)-1-methyl-1*H*-tetrazole



3r

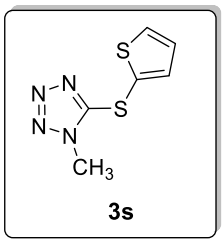
Synthesized following **general procedure A** starting from **1a** (58 mg, 0.5 mmol) and **2d-OTf** (244 mg, 0.5 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3r** (59 mg, 0.24 mmol, 48%) as colourless oil. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 3.96 (s, 3H), 1.31 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 152.9, 132.7, 129.5, 127.0, 123.8, 120.2, 115.4, 34.8, 34.1, 31.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_{16}N_4S$ 248.1096; found 249.1565

1-methyl-5-(thiophen-2-ylthio)-1*H*-tetrazole



3s

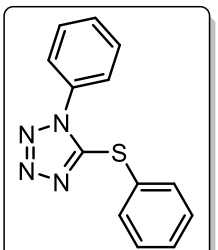
Synthesized following **general procedure A** starting from **1a** (58 mg, 0.5 mmol) and **2f-OTf** (218 mg, 0.5 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3s** (24 mg, 0.12 mmol, 24%) as black oil. R_f 0.25 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (dd, *J* = 8 & 1 Hz, 1H), 7.45 (dd, *J* = 8 & 1 Hz, 1H), 7.10 (dd, *J* = 8 & 1 Hz, 1H), 4.04 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.7, 137.5, 133.0, 128.2, 122.9, 115.4, 34.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_6H_6N_4S_2$ 198.0034; found 200.0472

1-phenyl-5-(phenylthio)-1*H*-tetrazole



3ba

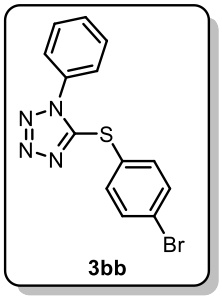
Synthesized following **general procedure A** starting from **1b** (44.5 mg, 0.25 mmol) and **2a-OTf** (121 mg, 0.25 mmol). The reaction was stirred for 6 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3ba** (48 mg, 0.190 mmol, 75%) as white solid. R_f 0.5 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54-7.58 (m, 7H), 7.37-7.43 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.7, 134.0, 133.6, 130.4, 126.8, 124.5

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_{10}N_4S$ 254.0626; found 255.1227

5-((4-bromophenyl)thio)-1-phenyl-1*H*-tetrazole



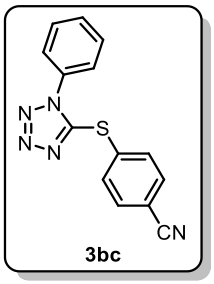
Synthesized following **general procedure A** starting from **1b** (44.5 mg, 0.25 mmol) and **2f-TMP-TFA** (141 mg, 0.25 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3bb** (59 mg, 0.18 mmol, 72%) as yellow solid. R_f 0.5 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.55 (m, 7H), 7.42 (d, *J*=8 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.2, 135.6, 133.5, 133.1, 130.6, 129.9, 125.8, 125.0, 124.5

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_9N_4BrS$ 331.9731; found 332.9808

4-((1-phenyl-1*H*-tetrazol-5-yl)thio)benzonitrile



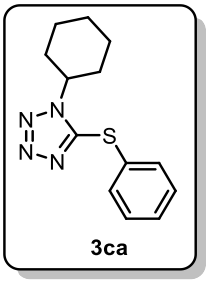
Synthesized following **general procedure A** starting from **1b** (44.5 mg, 0.25 mmol) and **2k-TMP-TFA** (127 mg, 0.25 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3bc** (45.3 mg, 0.162 mmol, 65%) as off-white solid. R_f 0.45 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (m, 5H), 7.54-7.58 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.6, 133.8, 133.1, 133.0, 130.9, 124.5, 117.8, 113.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_9N_5S$ 279.0579; found 280.0652

1-cyclohexyl-5-(phenylthio)-1*H*-tetrazole



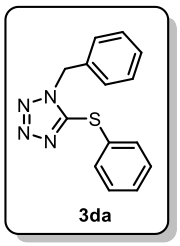
Synthesized following **general procedure A** starting from **1c** (46 mg, 0.25 mmol) and **2a-TMP-TFA** (121 mg, 0.25 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→30/70) to afford **3ca** (40 mg, 0.155 mmol, 62%) as yellowish liquid. R_f 0.5 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.54 (m, 2H), 7.38-7.40 (m, 3H), 1.90-1.93 (m, 6H), 1.28-1.39 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 132.6, 129.9, 129.5, 128.4, 58.6, 32.4, 25.3, 24.8

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_{16}N_4S$ 260.1096; found 261.1117

1-benzyl-5-(phenylthio)-1*H*-tetrazole



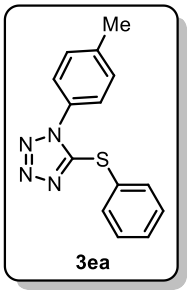
Synthesized following **general procedure A** starting from **1d** (48 mg, 0.25 mmol) and **2a-TMP-TFA** (121 mg, 0.25 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→0/70) to afford **3da** (44.2 mg, 0.165 mmol, 66%) as yellowish liquid. R_f 0.5 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.46 (m, 2H), 7.32-7.35 (m, 6H), 7.22-7.24 (m, 2H), 5.50 (s, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 133.0, 132.7, 129.9, 129.6, 129.18, 129.06, 128.1, 127.8, 51.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{12}N_4S$ 268.0763; found 269.0655

5-(phenylthio)-1-(*p*-tolyl)-1*H*-tetrazole



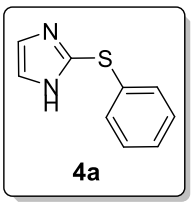
Synthesized following **general procedure A** starting from **1d** (48 mg, 0.25 mmol) and **2a-TMP-TFA** (121 mg, 0.25 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90→20/80) to afford **3ea** (55 mg, 0.205 mmol, 82%) as white solid. R_f 0.45 (AcOEt /Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J*= 8 Hz, 2H), 7.35-7.43 (m, 7H), 2.46 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 140.9, 134.0, 131.1, 130.3, 129.8, 127.0, 21.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{12}N_4S$ 268.0763; found 269.1367

2-(phenylthio)-1*H*-imidazole



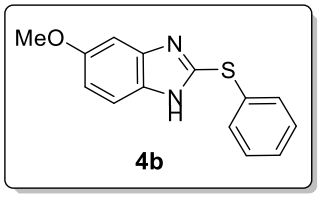
Synthesized following **general procedure A** starting from 1*H*-imidazole-2-thiol (35 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→20/95) to afford **4a** (42 mg, 0.238 mmol, 68%) as white solid. R_f 0.25 (AcOEt /Hexane: 10/90).

^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.03 (t, *J*= 8 Hz, 2H), 6.91-6.95 (m, 3H), 6.83 (d, *J*= 8 Hz, 2H)

^{13}C NMR (150 MHz, DMSO-d_6) δ = 134.9, 133.6, 128.3, 126.3, 125.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_9H_8N_2S$ 176.0408; found 177.0862

5-methoxy-2-(phenylthio)-1*H*-benzo[d]imidazole



4b

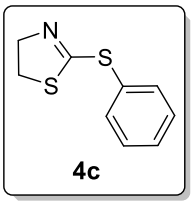
Synthesized following **general procedure A** starting from 5-methoxy-1*H*-benzo[d]imidazole-2-thiol (63 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→20/95) to afford **4b** (64 mg, 0.252 mmol, 72%) as yellow solid. R_f 0.3 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.45 (m, 2H), 7.38 (d, *J*= 8 Hz, 1H), 7.21-7.23 (m, 3H), 6.76 (d, *J*= 4 Hz, 1H), 6.83 (q, *J*= 8 Hz, 1H), 3.75 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.5, 147.1, 139.3, 134.4, 132.2, 131.0, 129.6, 128.5, 115.8, 112.3, 97.1, 55.8

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{12}N_2OS$ 256.0670; found 257.1184

2-(phenylthio)-4,5-dihydrothiazole[17]



4c

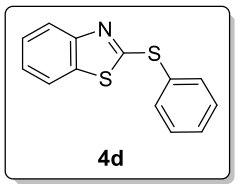
Synthesized following **general procedure A** starting from 4,5-dihydrothiazole-2-thiol (38.9 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→10/95) to afford **4c** (52 mg, 0.266 mmol, 76%) as colourless liquid. R_f 0.4 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63-7.65 (m, 2H), 7.40-7.44 (m, 3H), 4.26 (t, *J*= 8 Hz, 2H), 3.30 (t, *J*= 8 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.7, 135.6, 130.0, 129.2, 65.4, 35.0

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{11}H_9NS$ 196.0176; found 196.0710

2-(phenylthio)benzo[*d*]thiazole[17]



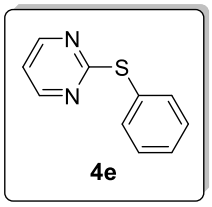
Synthesized following **general procedure A** starting from benzo[*d*]thiazole-2-thiol (58.5 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→10/95) to afford **4d** (75.8 mg, 0.3115 mmol, 89%) as colourless liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J*= 8 Hz, 1H), 7.73 (d, *J*= 8 Hz, 2H), 7.64 (d, *J*= 8 Hz, 1H), 7.41-7.49 (m, 3H) 7.40 (t, *J*= 8 Hz, 1H), 7.26 (t, *J*= 8 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.7, 153.9, 135.5, 135.4, 130.5, 129.9, 126.2, 124.3, 121.9, 120.8

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{13}H_9NS_2$ 243.0176; found 244.0624

2-(phenylthio)pyrimidine[17]



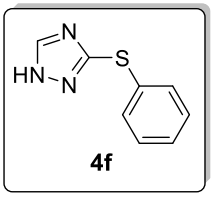
Synthesized following **general procedure A** starting from pyrimidine-2-thiol (40 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→10/95) to afford **4e** (50.7 mg, 0.269 mmol, 77%) as yellow liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, *J*= 8 Hz, 2H), 7.62-7.65 (m, 2H), 7.45 (t, *J*= 4 Hz, 1H), 6.95 (t, *J*= 4 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.8, 157.6, 135.3, 129.3, 117.0

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{10}H_8N_2S$ 188.0408; found 189.0922

3-(phenylthio)-1*H*-1,2,4-triazole[17]



4f

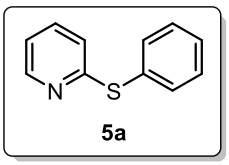
Synthesized following **general procedure A** starting from pyrimidine-2-thiol (40 mg, 0.35 mmol) and **2a-TMP** (170 mg, 0.35 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/98→10/95) to afford **4f** (44 mg, 0.245 mmol, 70%) as colourless liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (s, 1H), 7.52-7.53 (m, 2H), 7.34-7.37 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 147.4, 132.5, 130.4, 129.6, 128.7, 125.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_8H_7N_3S$ 177.0361; found 178.0844

2-(phenylthio)pyridine[17]



5a

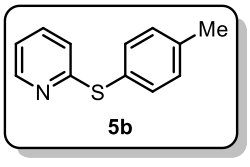
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2a-An** (161 mg, 0.35 mmol). The reaction was stirred for 2 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5a** (49 mg, 0.262 mmol, 75%) as colourless liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39-8.41 (m, 1H), 7.56-7.59 (m, 2H), 7.39-7.45 (m, 4H), 6.95-6.98 (m, 1H), 6.87 (dt, J= 8 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 149.6, 136.8, 135.0, 131.1, 129.7, 129.2, 121.4, 120.02

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{11}H_9NS$ 187.0456; found 188.0989

2-(*p*-tolylthio)pyridine[18]



5b

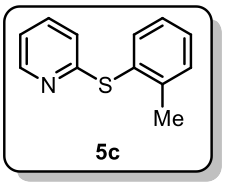
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2b-An** (166 mg, 0.35 mmol). The reaction was stirred for 2 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5b** (57.8 mg, 0.287 mmol, 82%) as white solid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, *J*= 8 Hz, 1H), 7.47 (d, *J*= 8 Hz, 2H), 7.41 (dt, *J*= 8 & 1 Hz, 1H), 7.22 (d, *J*= 8 Hz, 2H), 6.95 (dq, *J*= 5 & 1 Hz, 1H), 6.82 (t, *J*= 8 Hz, 1H), 2.38 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.3, 149.6, 139.5, 136.7, 135.3, 130.6, 127.3, 120.9, 119.6, 21.3

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_{11}NS$ 201.0612; found 202.0758

2-(*o*-tolylthio)pyridine[17]



5c

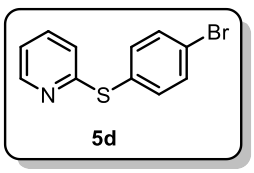
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2b-An** (166 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5c** (57.8 mg, 0.287 mmol, 72%) as colourless liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, *J*= 8 Hz, 1H), 7.59 (d, *J*= 8 Hz, 1H), 7.39 (dt, *J*= 8 & 1 Hz, 1H), 7.33-7.34 (m, 2H), 7.21-7.25 (m, 1H), 6.95 (dq, *J*= 5 & 1 Hz, 1H), 6.82 (t, *J*= 8 Hz, 1H), 2.39 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.3, 149.7, 142.8, 136.8, 131.1, 129.9, 127.2, 120.4, 119.6, 20.9

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_{11}NS$ 201.0612; found 202.0758

2-((4-bromophenyl)thio)pyridine[18]



5d

Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2b-An** (188.6 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction

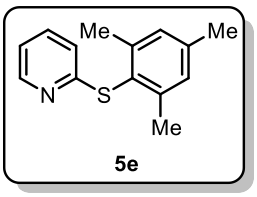
mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5d** (72.6 mg, 0.273 mmol, 78%) as yellow solid. R_f 0.5 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (d, *J*= 8 Hz, 1H), 7.42-7.54 (m, 5H), 7.01 (dq, *J*= 5 & 1 Hz, 1H), 6.84 (t, *J*= 8 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 149.8, 136.9, 136.3, 132.8, 130.4, 123.5, 121.8, 120.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{11}H_8NSBr$ 264.9561; found 266.0168

2-(mesitylthio)pyridine



5e

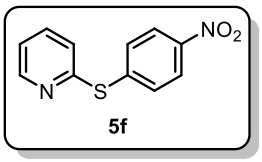
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2b-An** (175.8 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5e** (57.8 mg, 0.287 mmol, 72%) as light-yellow liquid. R_f 0.6 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, J= 8 Hz, 1H), 7.33-7.37 (m, 1H), 7.01 (s, 2H), 6.90-6.93 (m, 1H), 6.53 (d, J= 8 Hz, 1H), 2.38 (s, 6H), 2.31 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 149.6, 143.8, 139.8, 136.7, 129.5, 125.8, 119.0, 21.7, 21.4

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{15}NS$ 229.0925; found 230.0946

2-((4-nitrophenyl)thio)pyridine[17]



5f

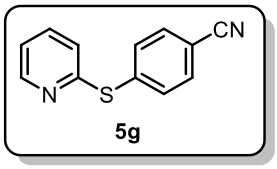
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2f-An** (176 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→10/90) to afford **5f** (71.5 mg, 0.308 mmol, 88%) as yellow solid. R_f 0.3 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, J= 8 Hz, 1H), 8.16 (d, J= 8 Hz, 2H), 7.58 (d, J= 8 Hz, 2H), 7.29 (d, J= 8 Hz, 1H), 7.15-7.19 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.6, 150.5, 147.0, 142.5, 137.5, 131.9, 125.0, 124.2, 122.1

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{15}NS$ 232.0306; found 233.0462

4-(pyridin-2-ylthio)benzonitrile[17]



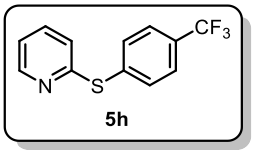
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2g-An** (169 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→10/90) to afford **5g** (61.6 mg, 0.308 mmol, 83%) as colourless liquid. R_f 0.35 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.47 (d, J= 8 Hz, 1H), 7.53-7.61 (m, 5H), 7.21 (d, J= 8 Hz, 1H), 7.11-7.15 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.4, 139.7, 137.4, 132.7, 132.5, 124.5, 121.8, 118.5, 11.3

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_8N_2S$ 212.0408; found 213.0408

2-((4-(trifluoromethyl)phenyl)thio)pyridine[18]



Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2h-An** (184 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98→5/95) to afford **5h** (69.6 mg, 0.273 mmol, 78%) as colourless liquid. R_f 0.5 (AcOEt /Hexane: 10/90).

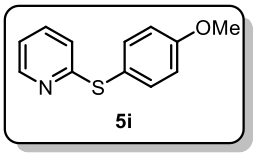
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (d, J= 8 Hz, 1H), 7.60-7.65 (m, 4H), 7.53 (t, J= 8 Hz, 1H), 7.06-7.10 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.8, 150.1, 137.1, 133.6, 130.4 (q, $J_{C\text{-}F}$ = 40 Hz), 129.9, 126.2, 125.3, 123.1, 122.6, 121.1

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.7

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_8NSF_3$ 255.0330; found 258.0262

2-((4-methoxyphenyl)thio)pyridine[18]



5i

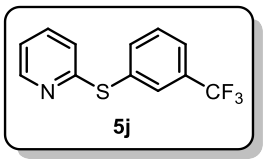
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2i-An** (171 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98 → 10/90) to afford **5i** (49 mg, 0.227 mmol, 65%) as colourless liquid. R_f 0.35 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, J= 8 Hz, 1H), 7.52 (d, J= 8 Hz, 2H), 7.40 (t, J= 8 Hz, 1H), 6.92-6.96 (m, 3H), 6.76 (d, J= 8 Hz, 1H), 3.83 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 160.7, 149.5, 137.3, 136.6, 121.1, 120.4, 119.5, 115.3, 55.5

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_8NSF_3$ 255.0330; found 256.0330

2-((3-(trifluoromethyl)phenyl)thio)pyridine



5j

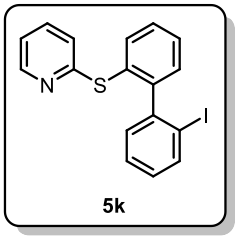
Synthesized following **general procedure B** starting from 2-mercaptopyridine (38.9 mg, 0.35 mmol) and **2j-An** (185 mg, 0.35 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98 → 10/90) to afford **5j** (64 mg, 0.252 mmol, 72%) as yellow liquid. R_f 0.45 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, J= 8 Hz) 1H), 7.82 (s, 1H), 7.73 (d, J= 8 Hz, 1H), 7.62 (d, J= 8 Hz, 1H), 7.51 (t, J= 8 Hz, 2H), 7.03-7.07 (m, 1H), 7.01 (d, J= 8 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.4, 150.0, 137.5, 137.1, 133.6, 133.1, 132.4, 132.1, 131.7, 131.4, 130.9, 129.9, 125.5, 125.1, 122.3, 120.7

HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{12}H_8NSF_3$ 255.0330; found 256.0334

2-((2'-iodo-[1,1'-biphenyl]-2-yl)thio)pyridine



Synthesized following **general procedure B** starting from 2-mercaptopyridine (27.7 mg, 0.25 mmol) and **2c-OTf** (108 mg, 0.25 mmol). The reaction was stirred for 3 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 2/98 → 10/90) to afford **5k** (64 mg, 0.165 mmol, 66%) as yellow liquid. R_f 0.3 (AcOEt /Hexane: 10/90).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.33 (d, J= 8 Hz, 1H), 7.55 (dd, J= 8 & 1 Hz, 1H), 7.66-7.68 (m, 1H), 7.28 (dd, J= 8 & 1 Hz, 1H), 7.21-7.25 (m, 1H), 7.12 (d, J= 8 Hz, 1H) 6.91-6.99 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7, 149.5, 148.2, 145.3, 138.8, 136.5, 135.7, 131.1, 130.1, 128.9, 127.6, 122.5, 120.1, 100.1

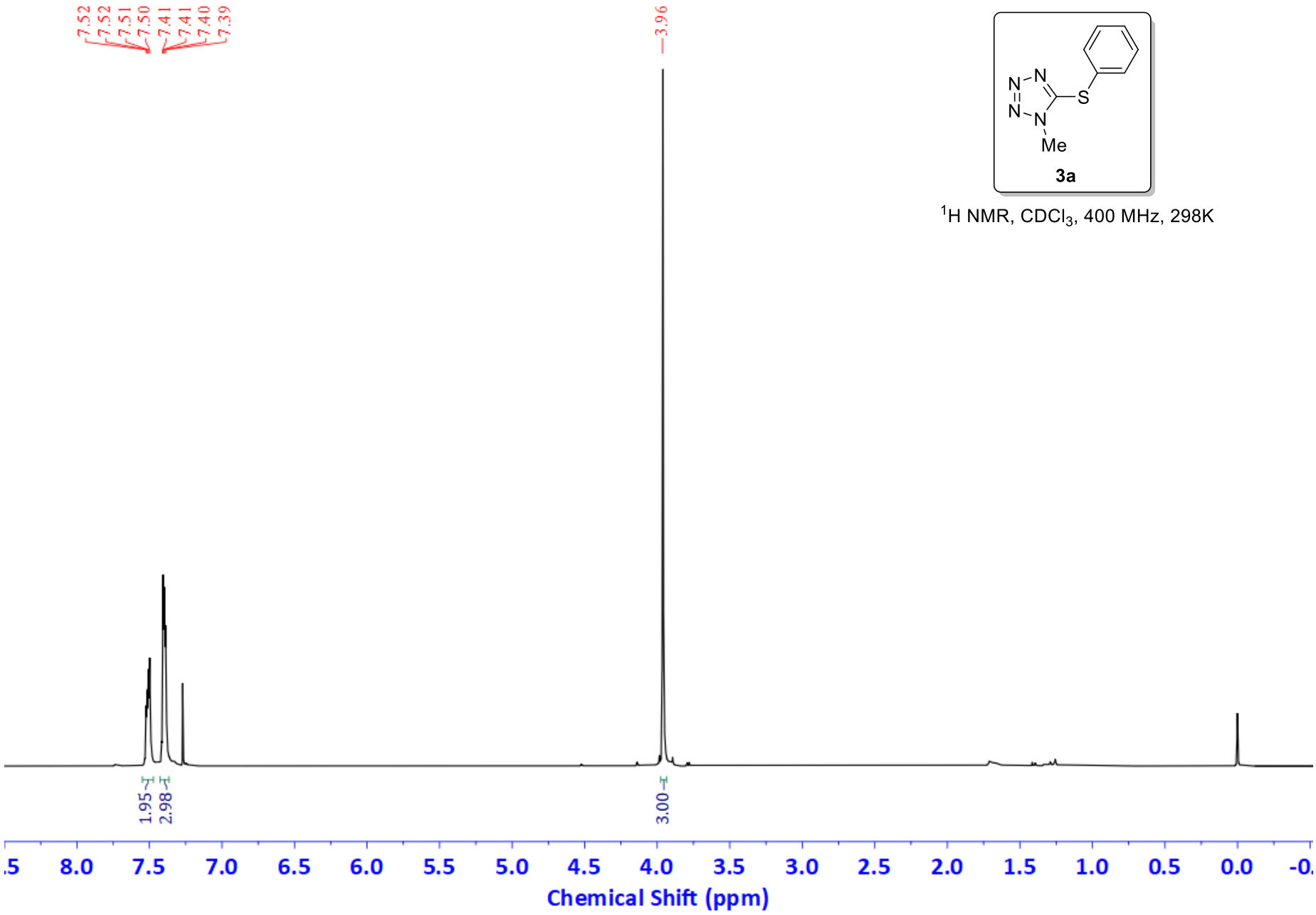
HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{12}NSI$ 388.9735; found 389.9735

9. REFERENCES

1. I. Vogel, B. S. Furnis, A. J. Hannaford, V. Rogers, P. W. G. Smith, A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 1978.
2. N. Sun, B. Li, J. Shao, W. Mo, B. Hu, Z. Shen and X. Hu, *Beilstein J. Org. Chem.*, 2012, **8**, 61–70.
3. K. Ando and D. Takama, *Org. Lett.*, 2020, **22**, 6907–6910.
4. M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal.*, 2007, **349** (17–18), 2610–2618.
5. M. Zhu, N. Jalalian and B. Olofsson, *Synlett*, 2008, **4**, 592–596.
6. M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.*, 2008, **73** (12), 4602–4607.
7. G. Kervefors, L. Kersting and B. Olofsson, *Chem. - A Eur. J.*, 2021, **27**, 5790–5795.
8. R. J. Phipps, N. P. Grimster and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130** (26), 8172–8174.
9. V. Carreras, A. H. Sandtorv and D. R. Stuart, *J. Org. Chem.*, 2017, **82**, 1279–1284.
10. T. L. Seidl, S. K. Sundalam, B. McCullough and D. R. Stuart, *J. Org. Chem.*, 2016, **81**, 1998–2009.
11. N. Soldatova, P. Postnikov, O. Kukurina, V. V. Zhdankin, A. Yoshimura, T. Wirth and M. S. Yusubov, *Beilstein J. Org. Chem.*, 2018, **14**, 849–855.

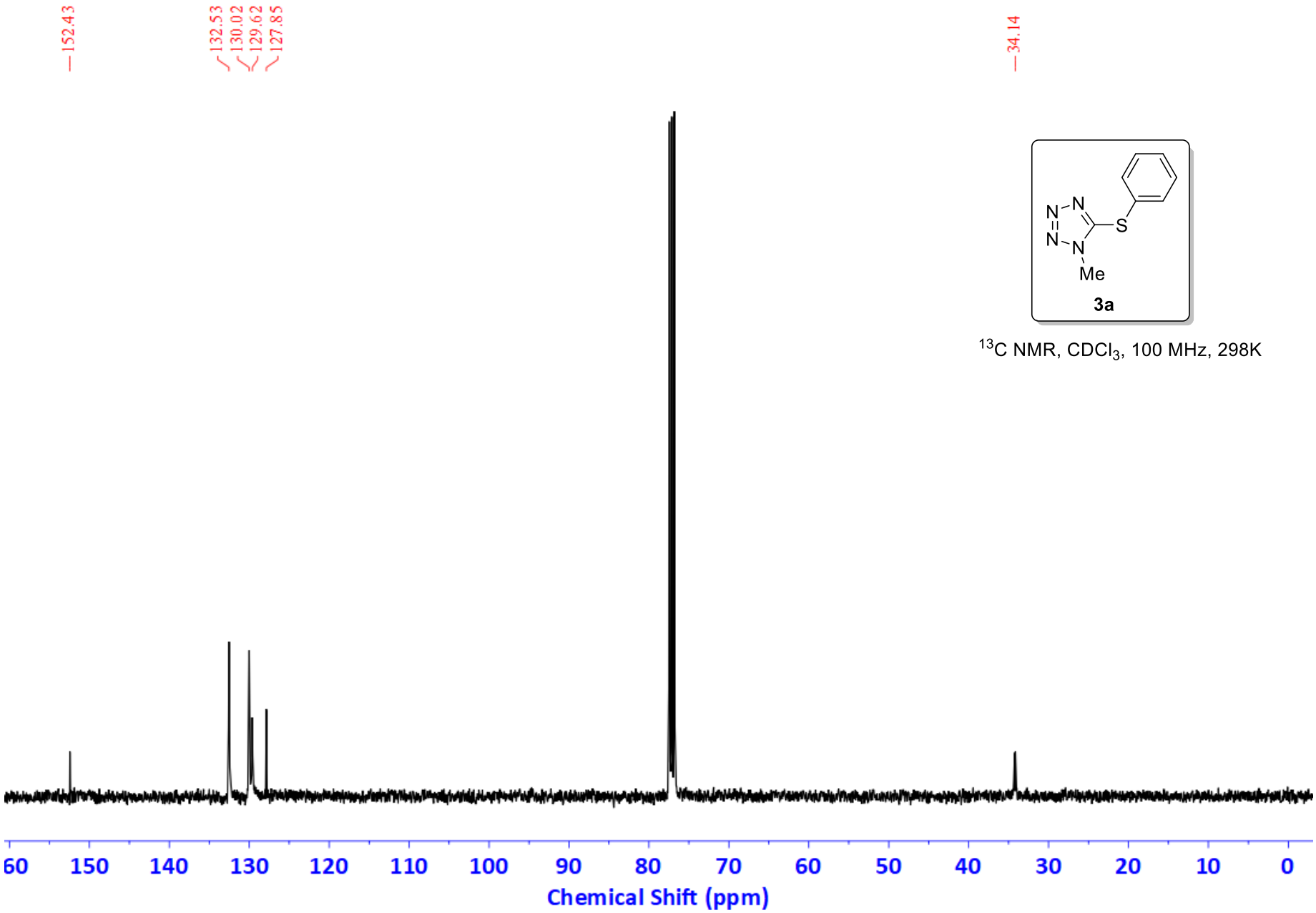
12. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
13. S. Roshandel, M. J. Lunn, G. Rasul, D. S. Muthiah Ravinson, S. C. Suri and G. K. S. Prakash, *Org. Lett.*, 2019, **21**, 6255–6258.
14. S. Prasad, D. D. Rodene, M. B. Burkholder, K. J. Donald and B. F. Gupton, *ACS Omega*, 2021, **6**, 27216–27224.
15. H. B. Schlegel, *Adv. Chem. Phys.*, 2007, **67**, 249–286.
16. C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1991, **95(8)**, 5853-5860.
17. X. Ma, Q. Liu, X. Jia, C. Su and Q. Xu, *RSC Adv.*, 2016, **6**, 56930–56935.
18. A. García-Rubia, M. Ú. Fernández-Ibáñez, R. Gõmez Arrayás and J. C. Carretero, *Chem. Eur. J.*, 2011, **17**, 3567–3570.

10. COPIES OF ^{1}H, ^{13}C and ^{19}F NMR SPECTRA

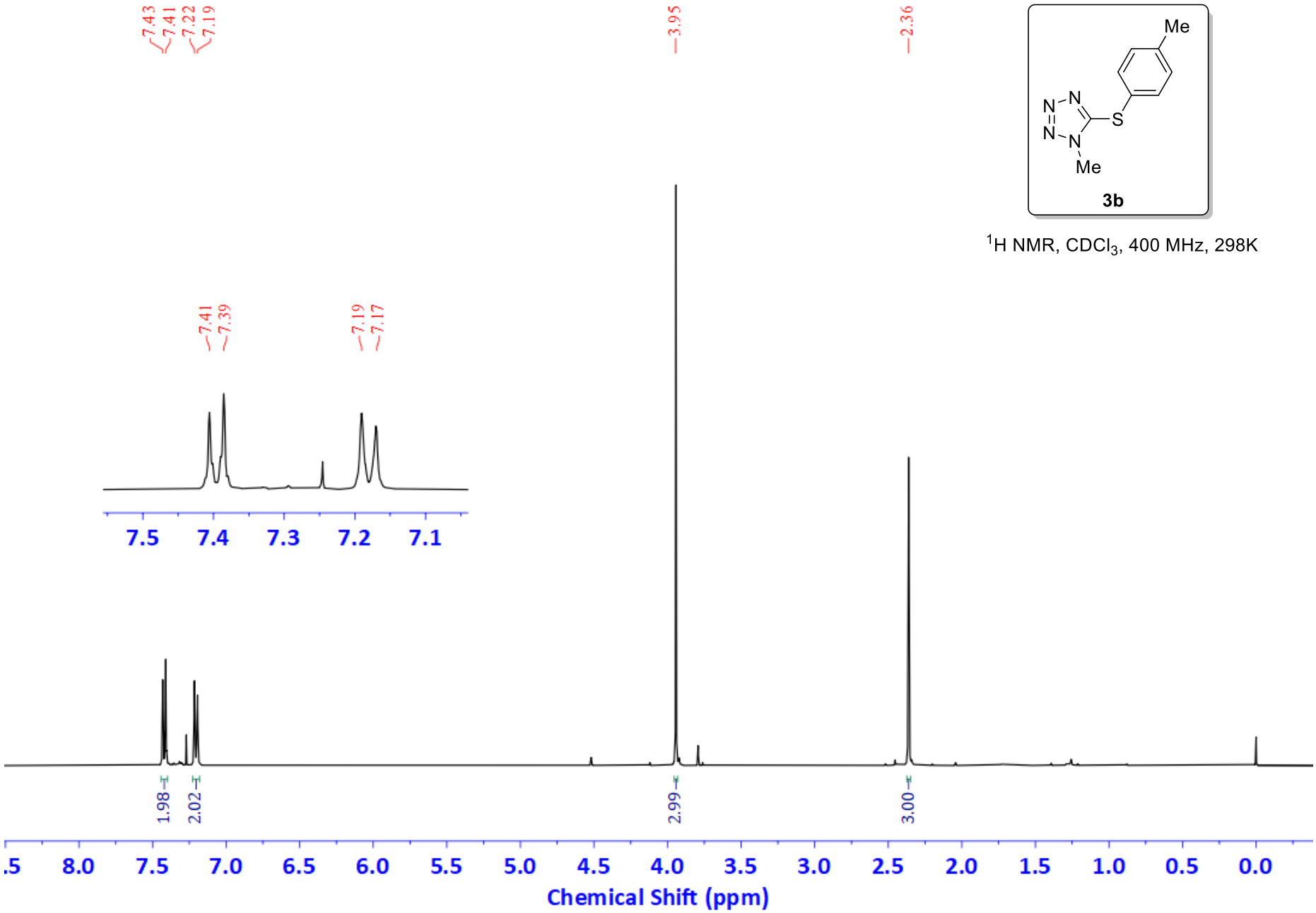


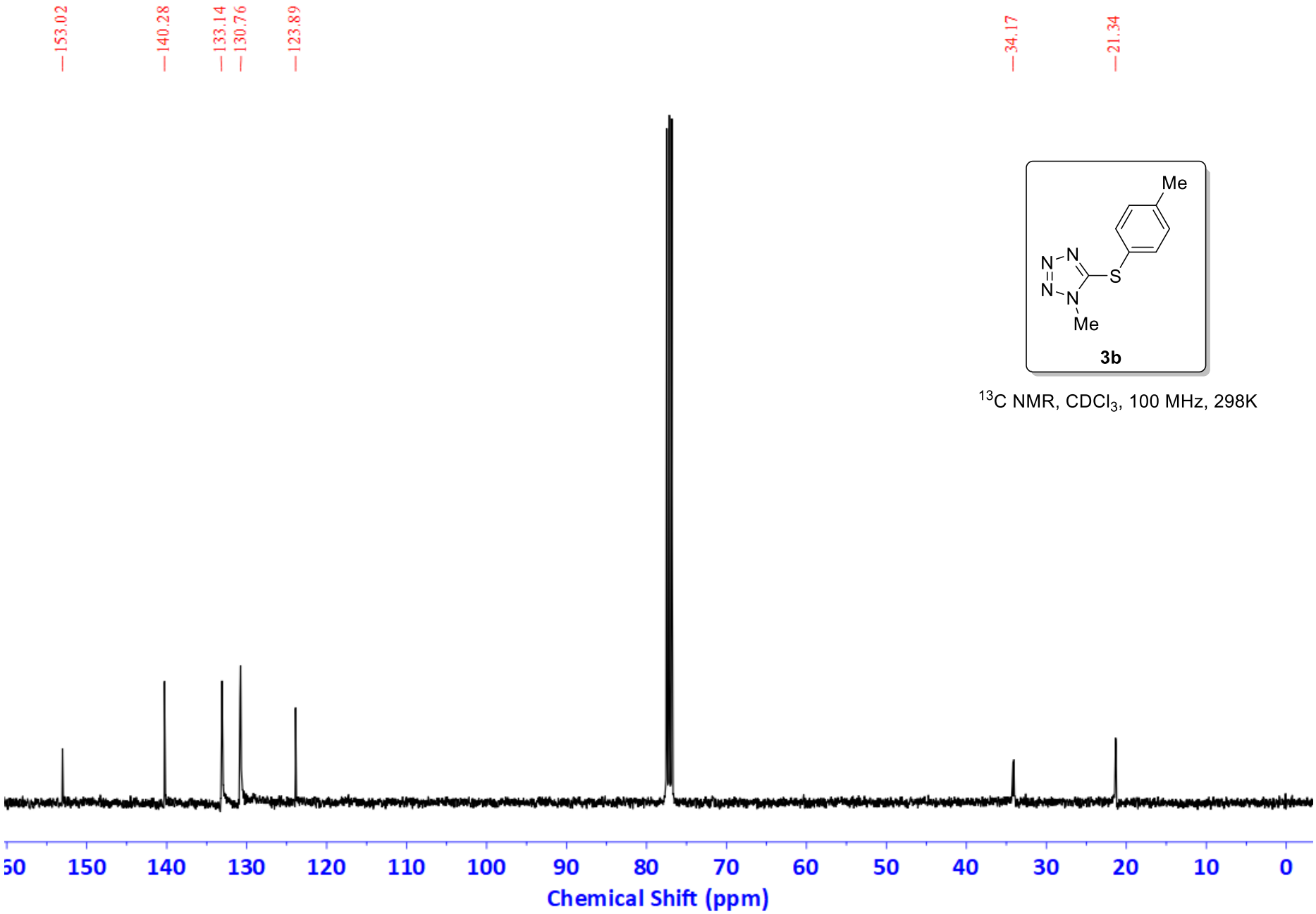
3a

^{1}H NMR, $CDCl_3$, 400 MHz, 298K

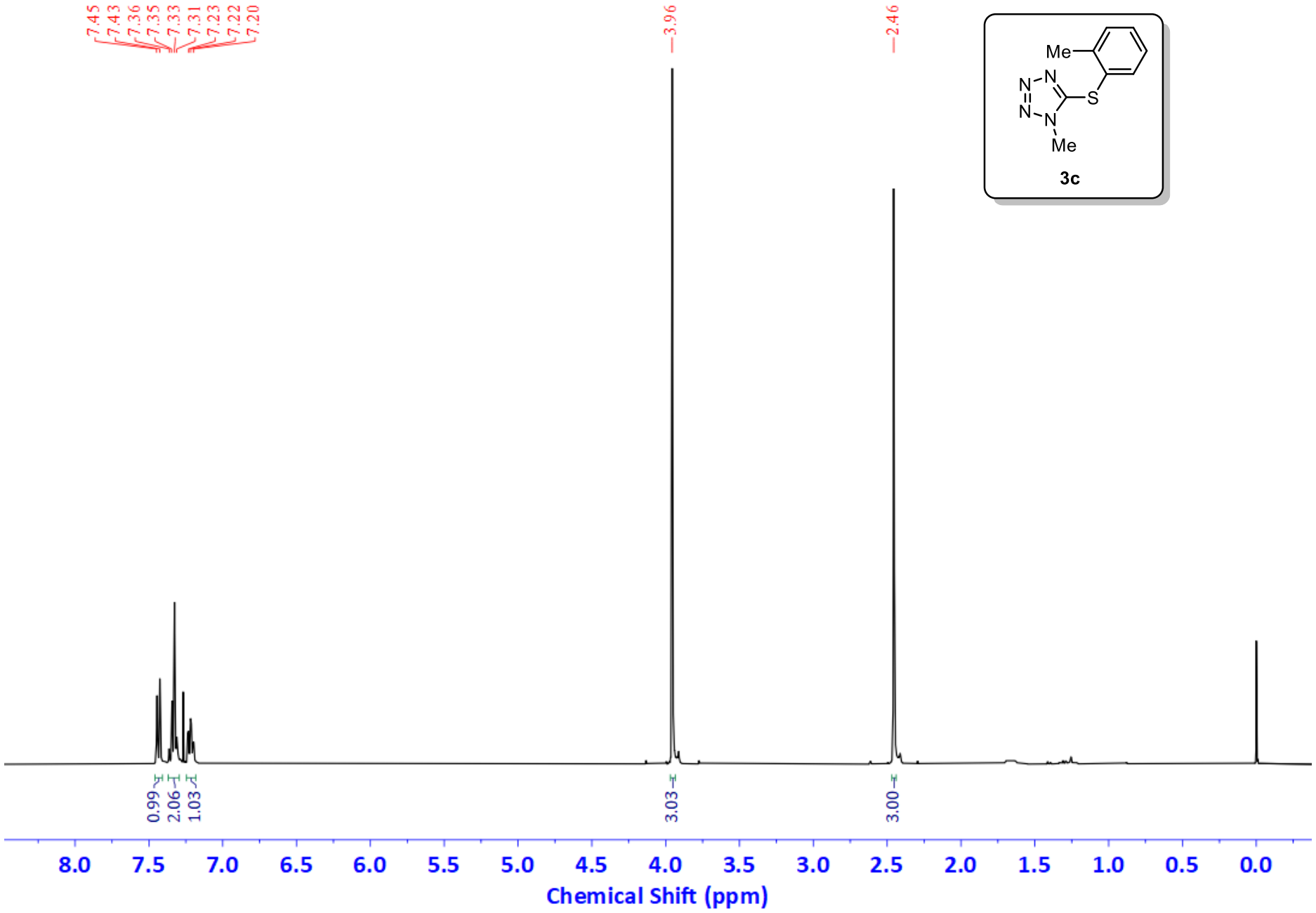


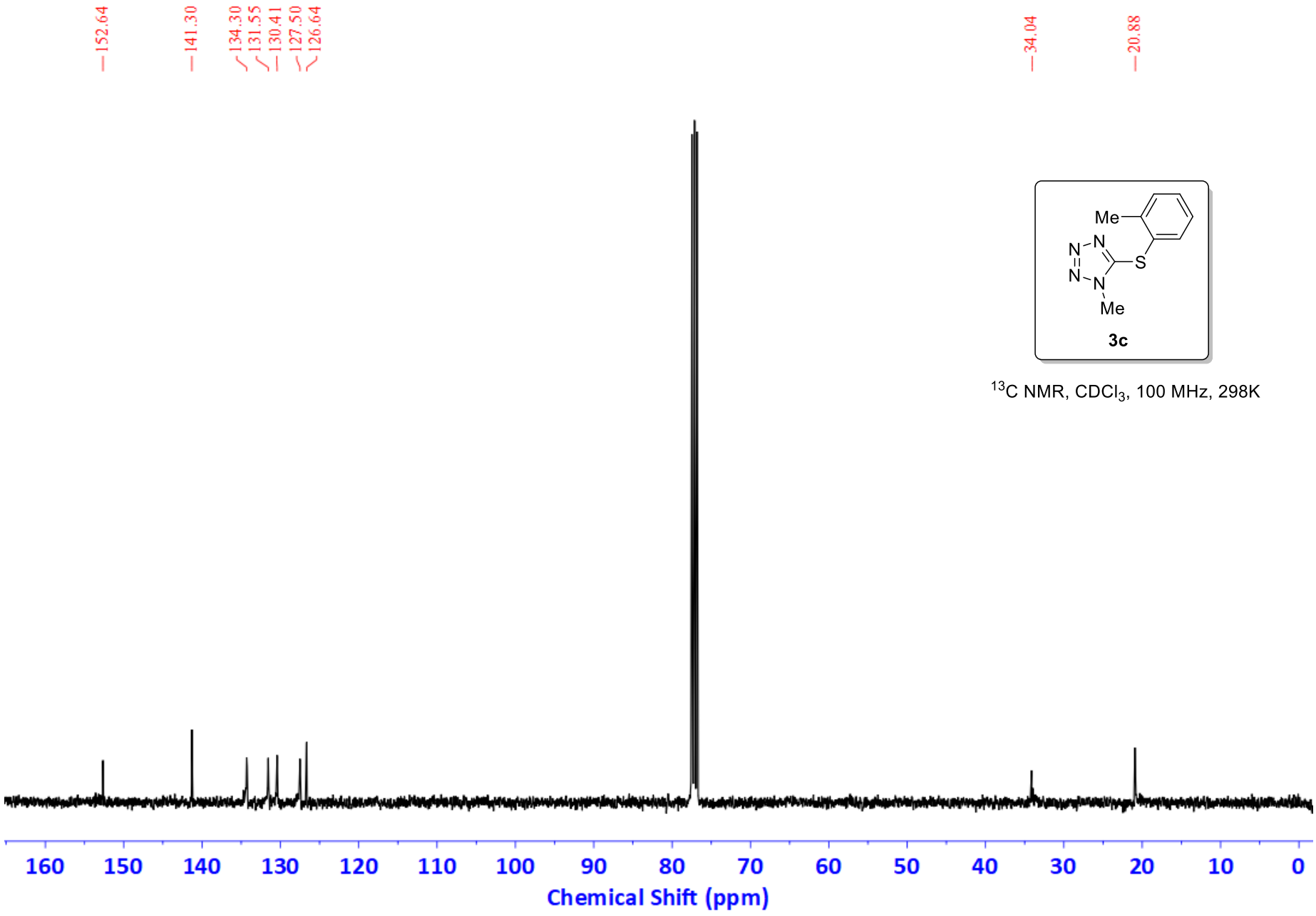
^{13}C NMR, $CDCl_3$, 100 MHz, 298K


7.43
7.41
7.22
7.19
3.95
2.36
Me
N
N
S
N
N
Me
3b
^{1}H NMR, CDCl$_3$, 400 MHz, 298K
7.41
7.39
7.19
7.17
7.5
7.4
7.3
7.2
7.1
1.98
2.02
2.99
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

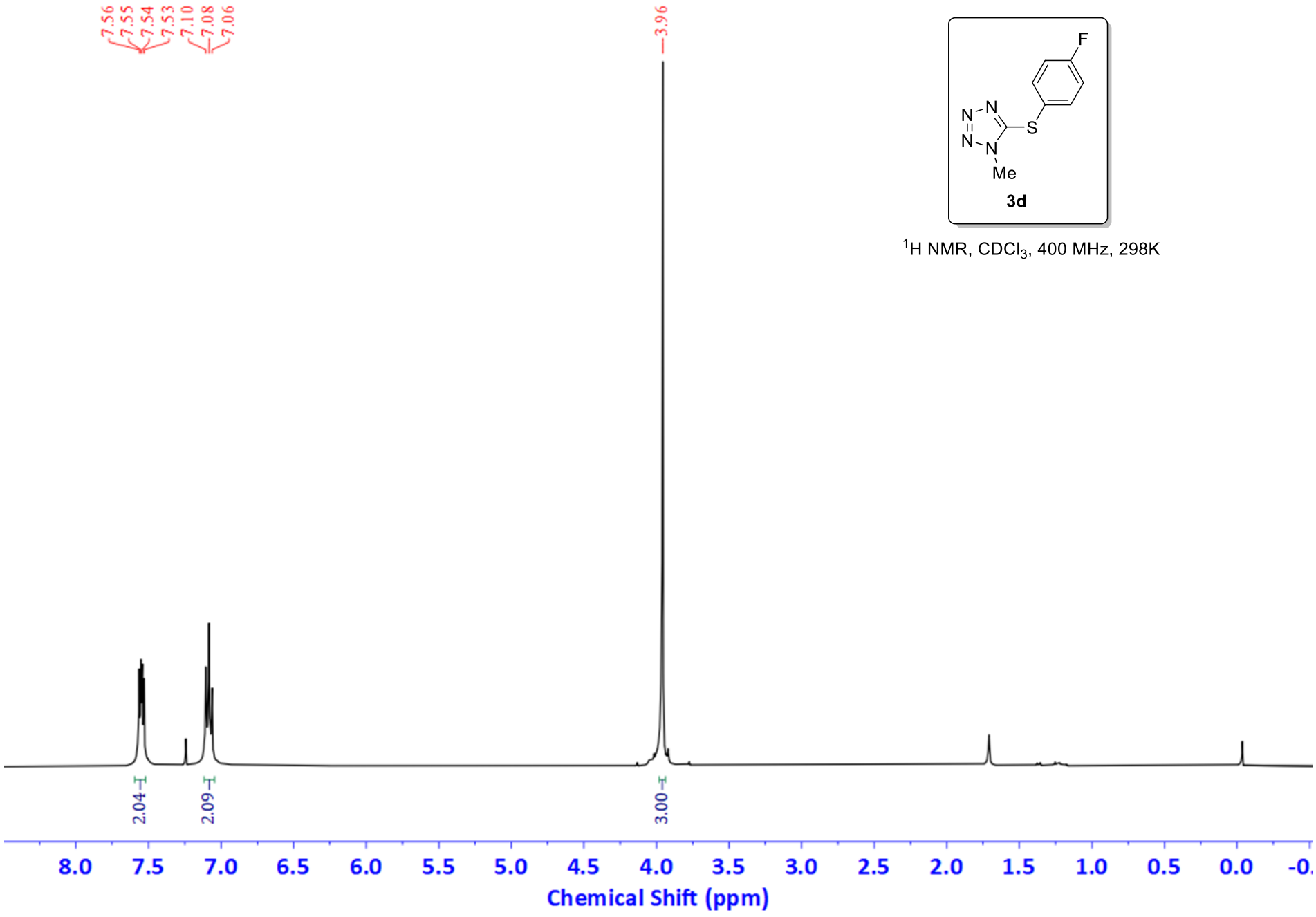


^{13}C NMR, $CDCl_3$, 100 MHz, 298K

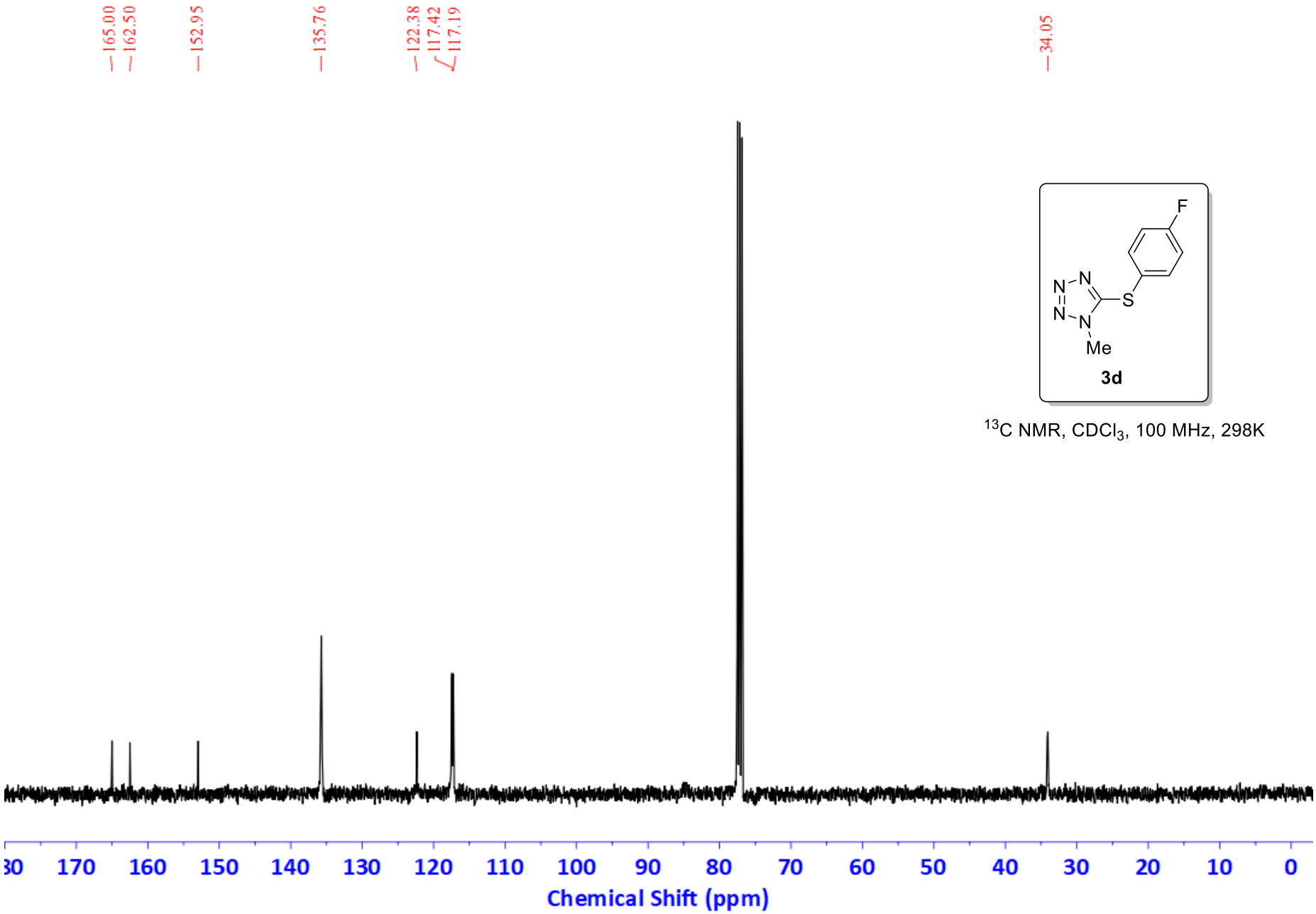

7.45
7.43
7.36
7.35
7.33
7.31
7.23
7.22
7.20
3.96
2.46
Me
N
N
N
S
N
Me
3c
0.99
2.06
1.03
3.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)



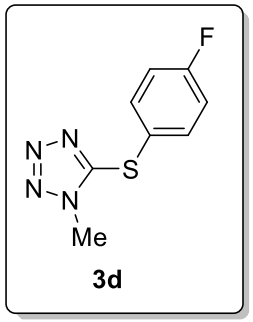
^{13}C NMR, $CDCl_3$, 100 MHz, 298K



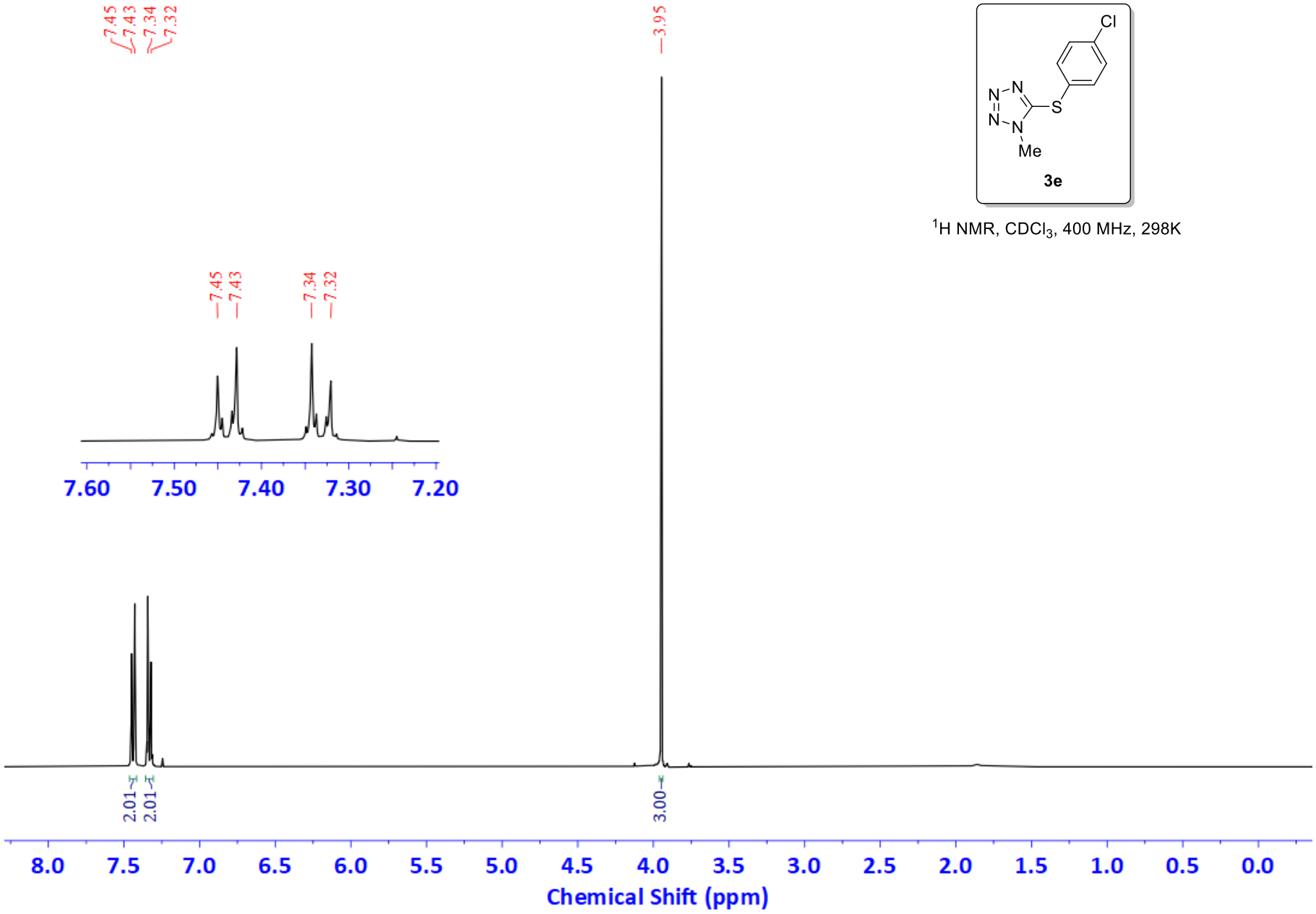
^{1}H NMR, $CDCl_3$, 400 MHz, 298K



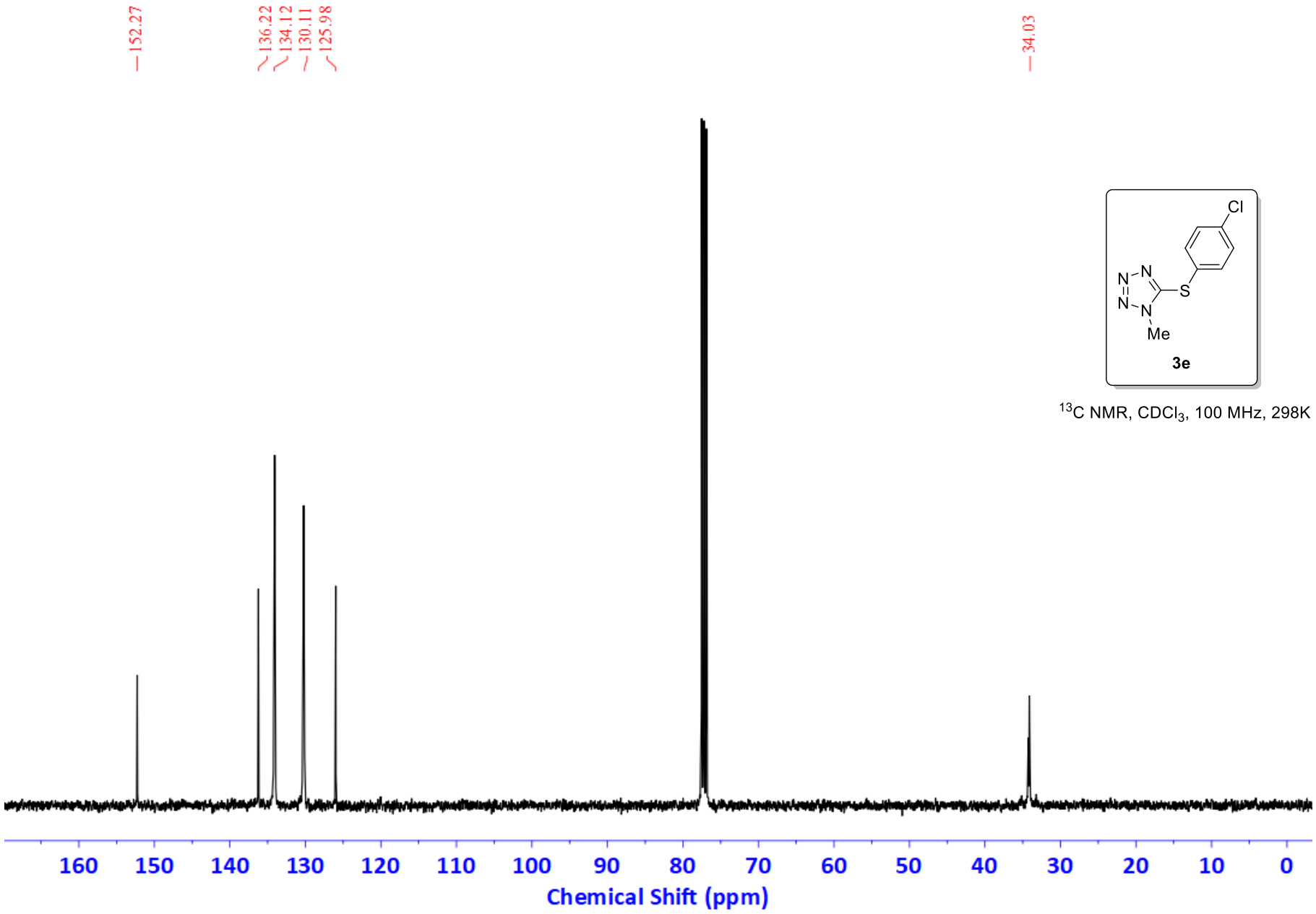
^{13}C NMR, $CDCl_3$, 100 MHz, 298K



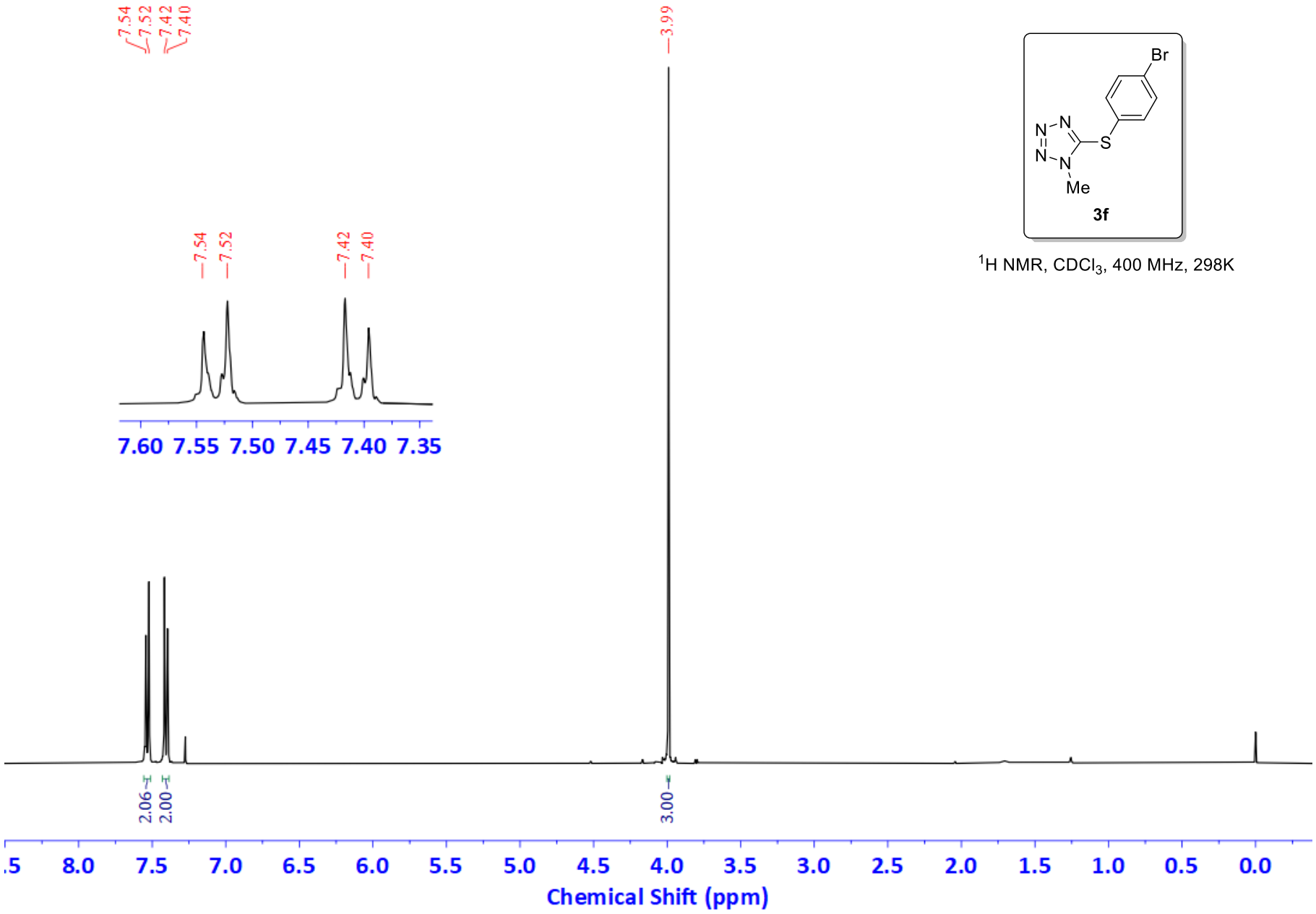
^{19}F NMR, $CDCl_3$, 376 MHz, 298K



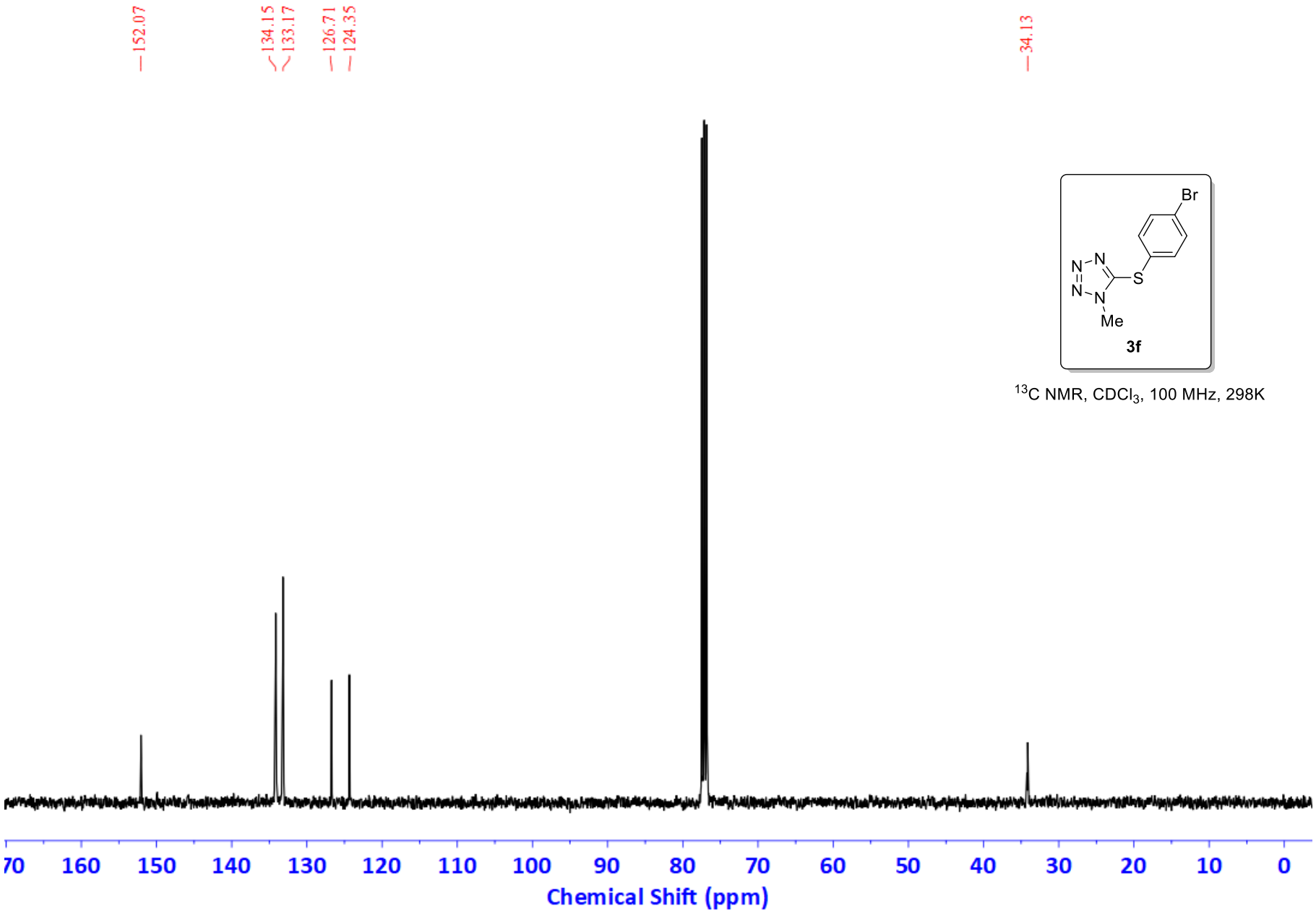
^{1}H NMR, $CDCl_3$, 400 MHz, 298K



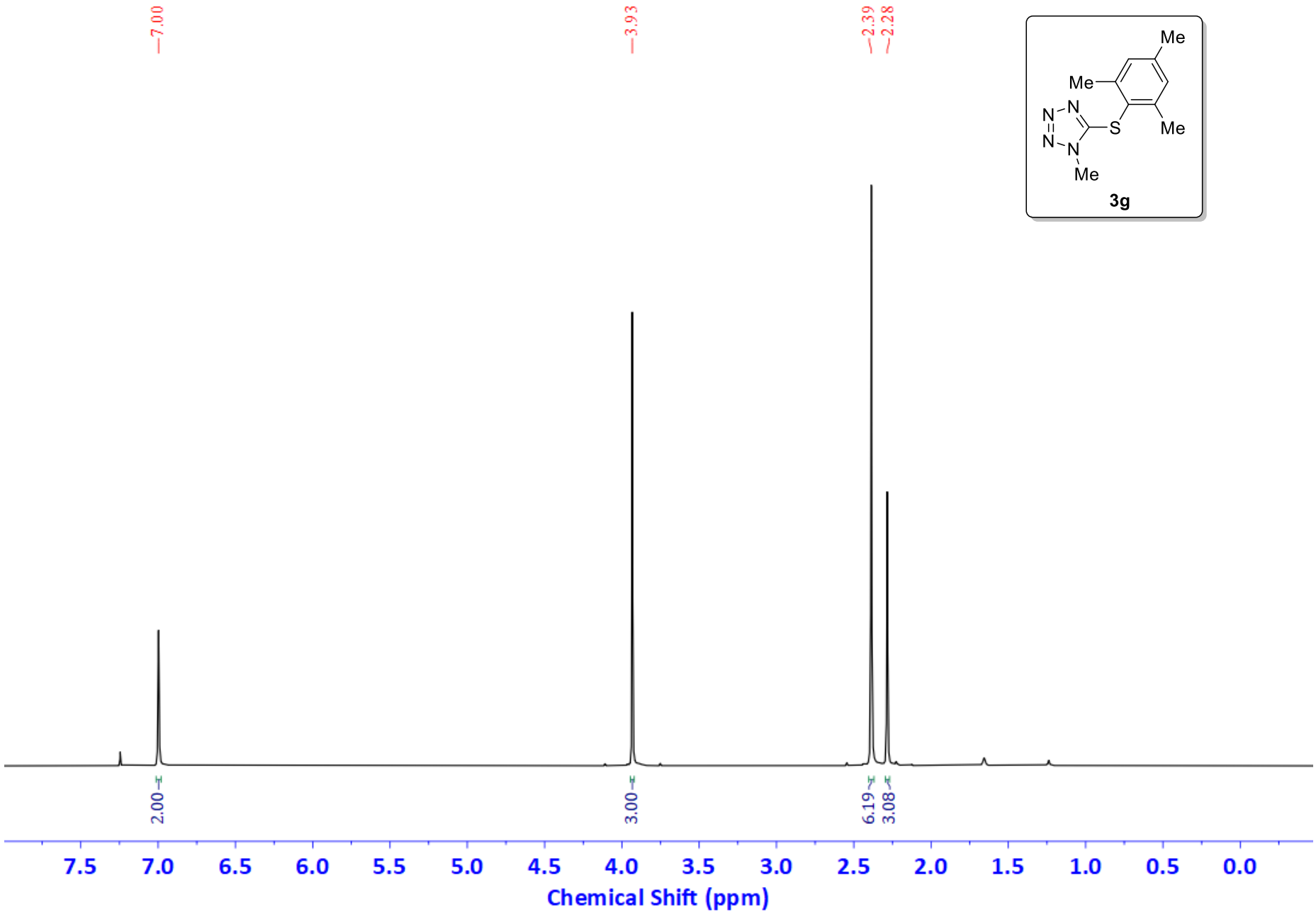
^{13}C NMR, $CDCl_3$, 100 MHz, 298K

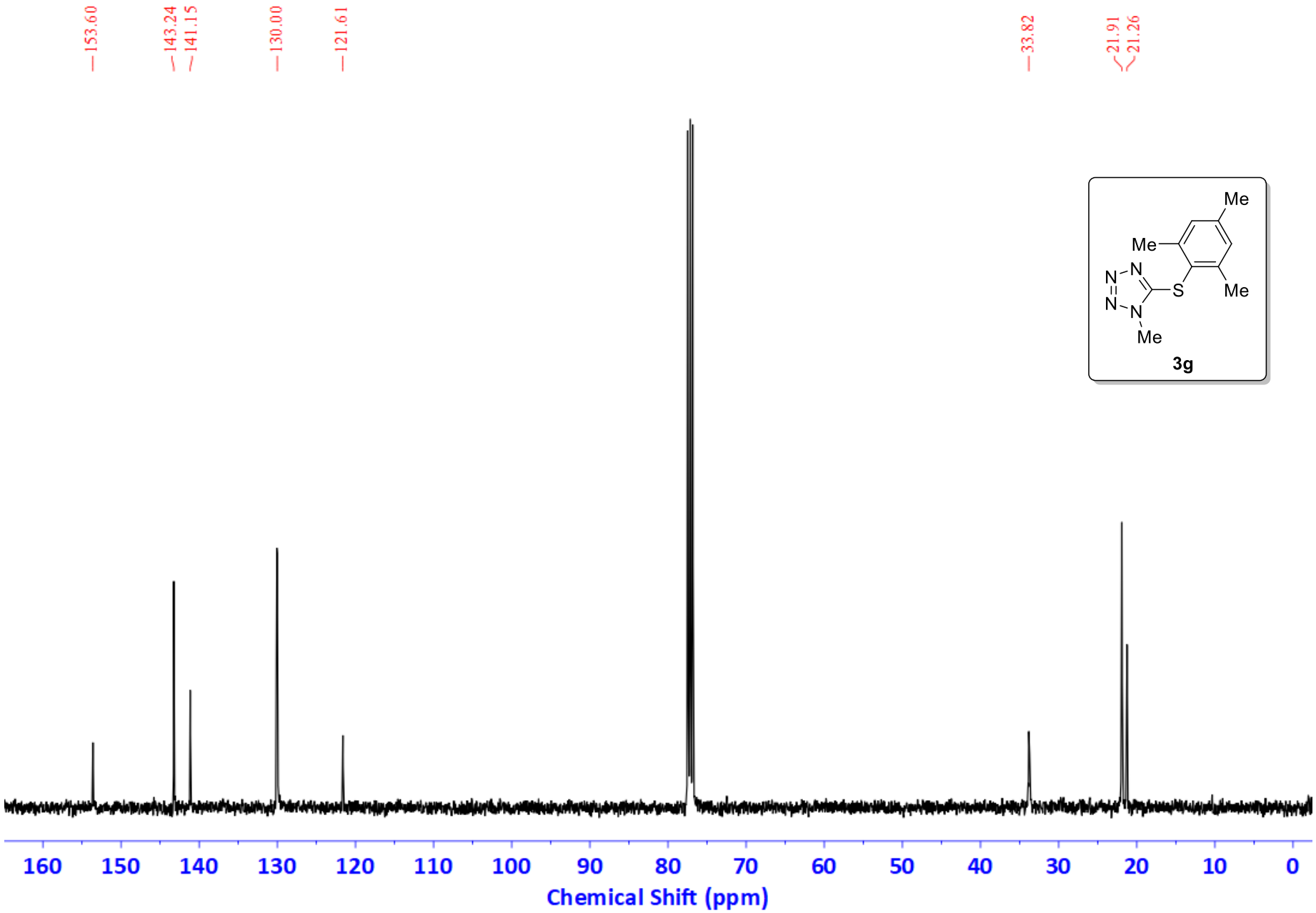


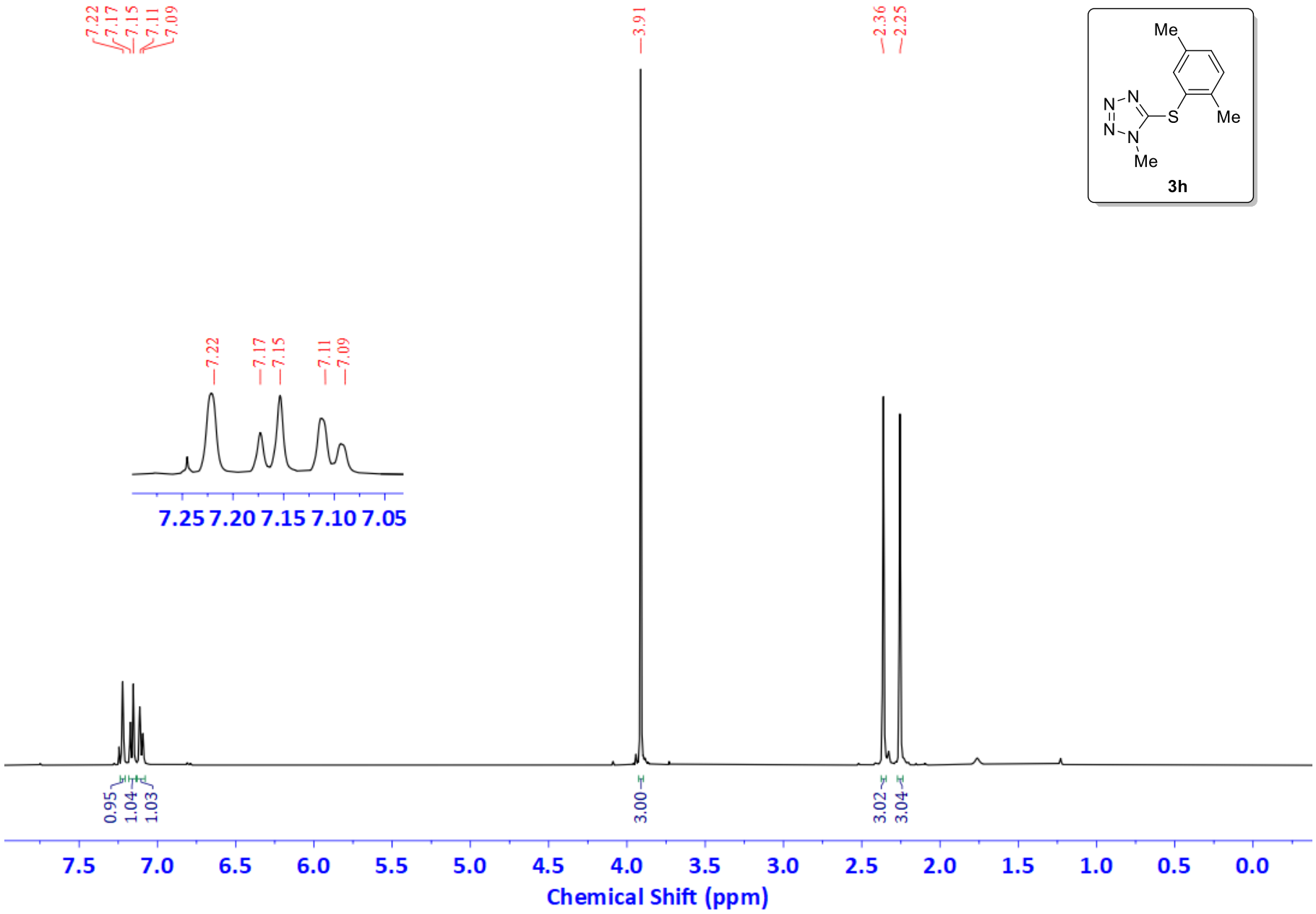
^{1}H NMR, $CDCl_3$, 400 MHz, 298K

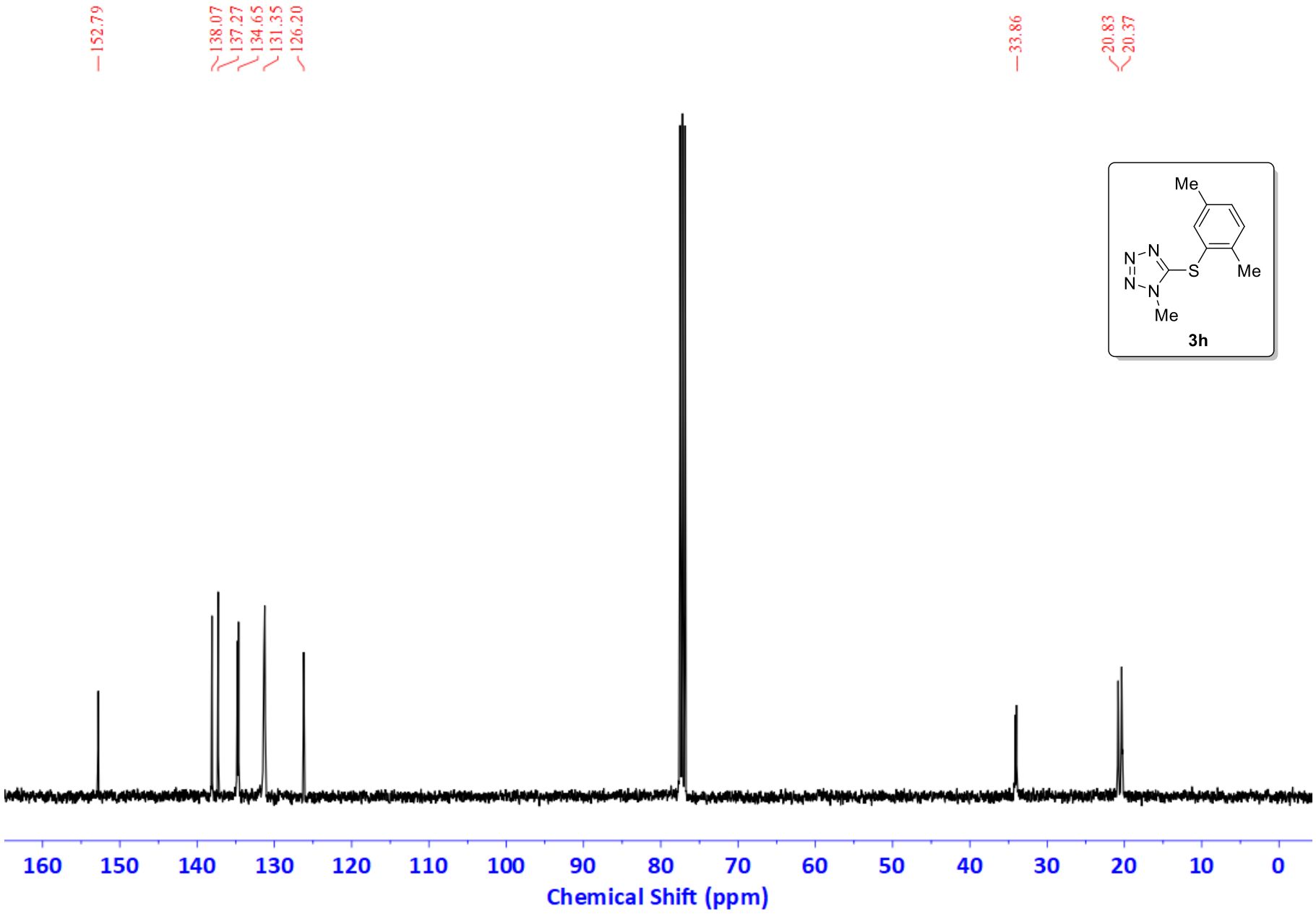


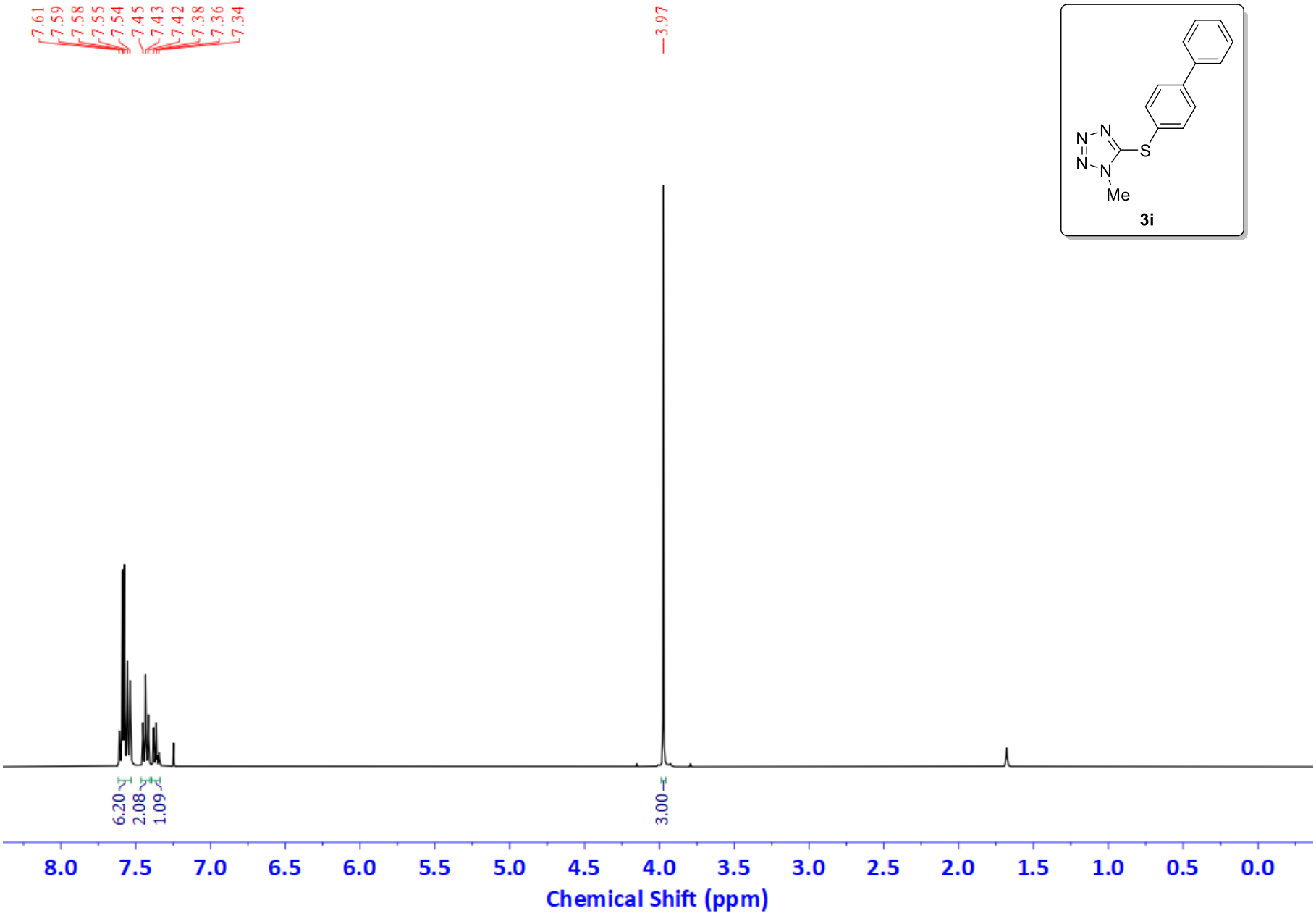
^{13}C NMR, $CDCl_3$, 100 MHz, 298K

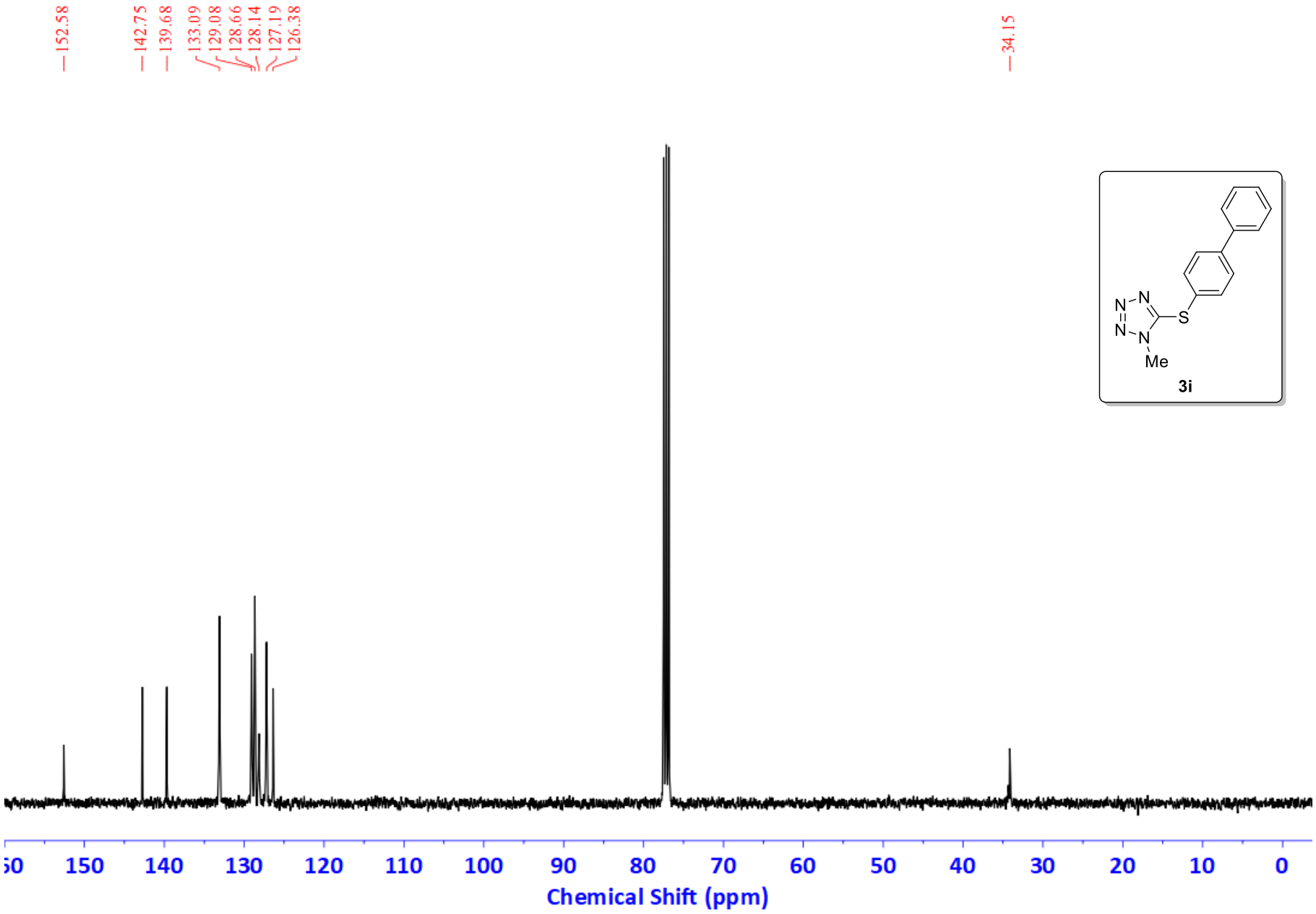

7.00
3.93
2.39
2.28
Me
Me
Me
N
N
N
S
Me
3g
2.00
3.00
6.19
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

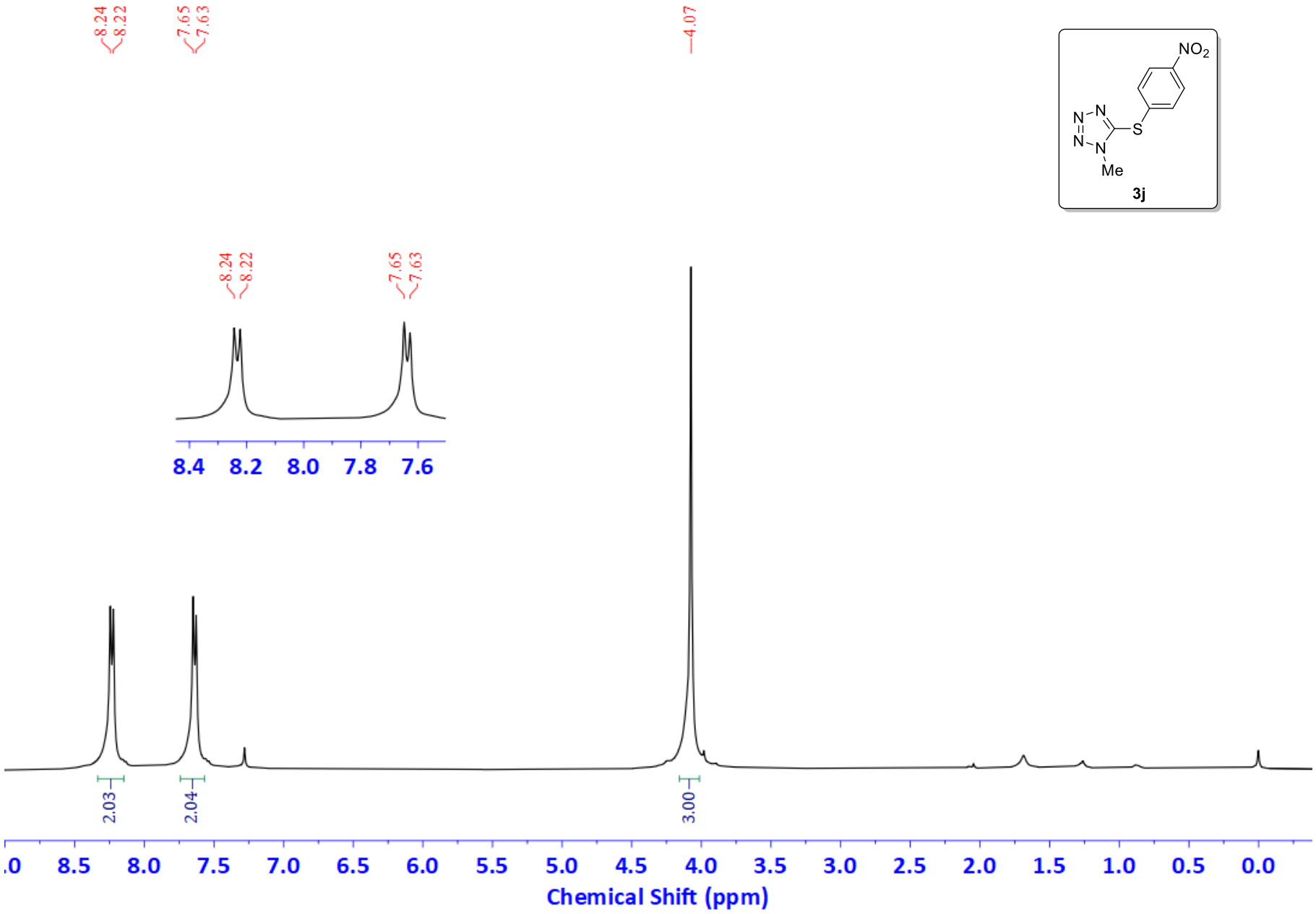

153.60
143.24
141.15
130.00
121.61
33.82
21.91
21.26
Me
Me
Me
Me
N
N
N
S
3g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

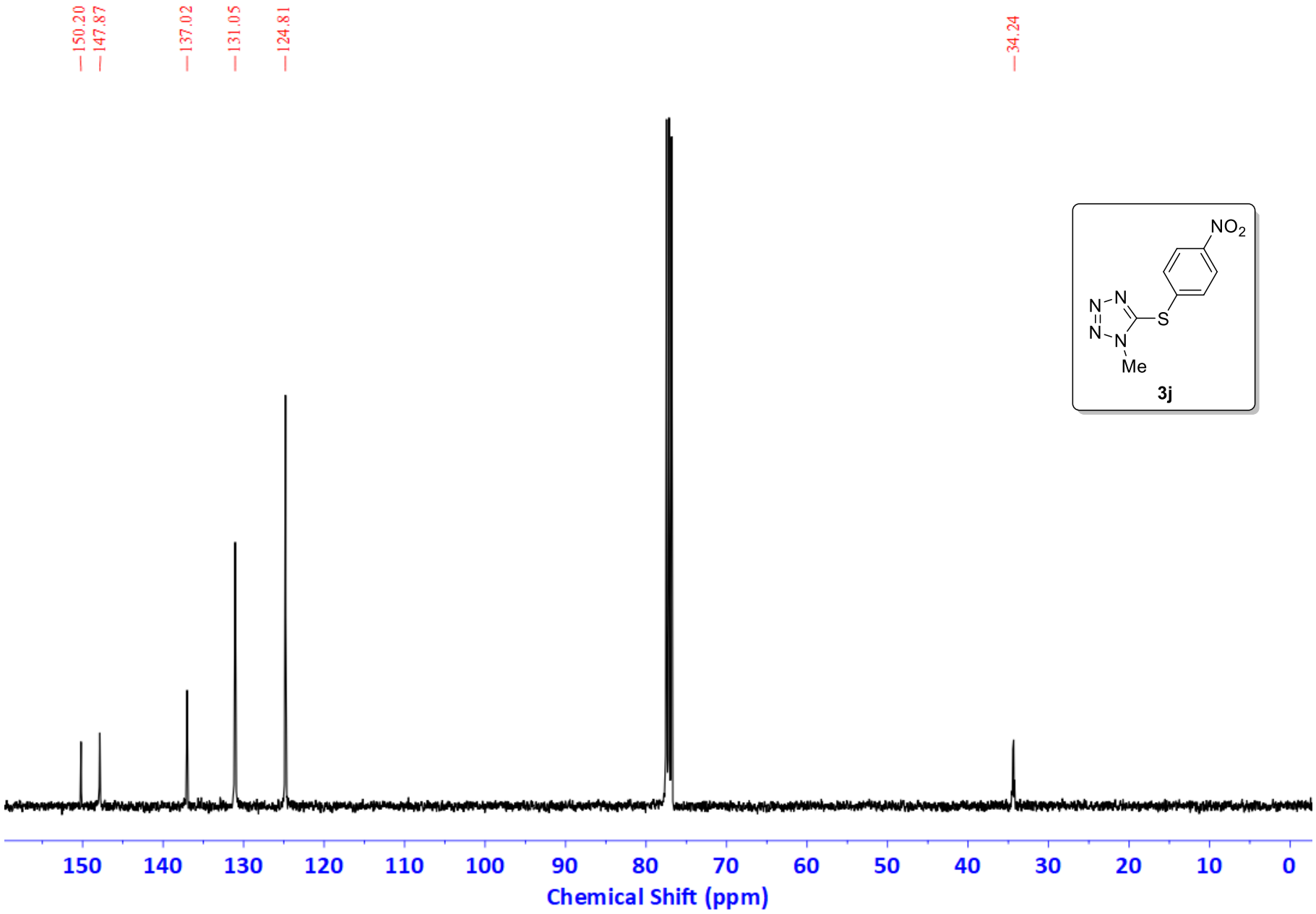

7.22
7.17
7.15
7.11
7.09
3.91
2.36
2.25
Me
N
N
N
S
Me
N
Me
3h
7.22
7.17
7.15
7.11
7.09
7.25 7.20 7.15 7.10 7.05
0.95
1.04
1.03
3.00
3.02
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

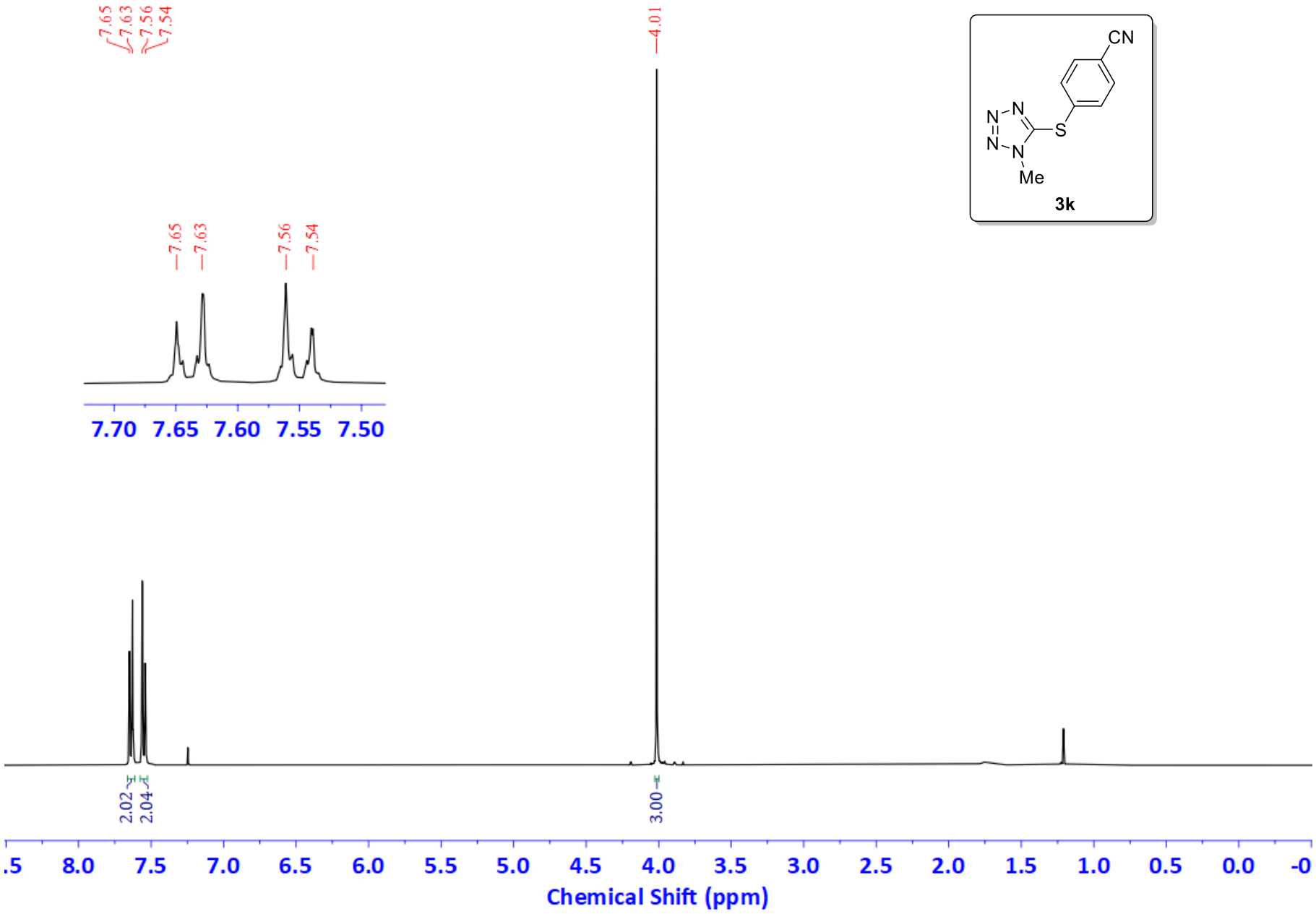

152.79
138.07
137.27
134.65
131.35
126.20
33.86
20.83
20.37
Me
N
N
S
Me
N
Me
3h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

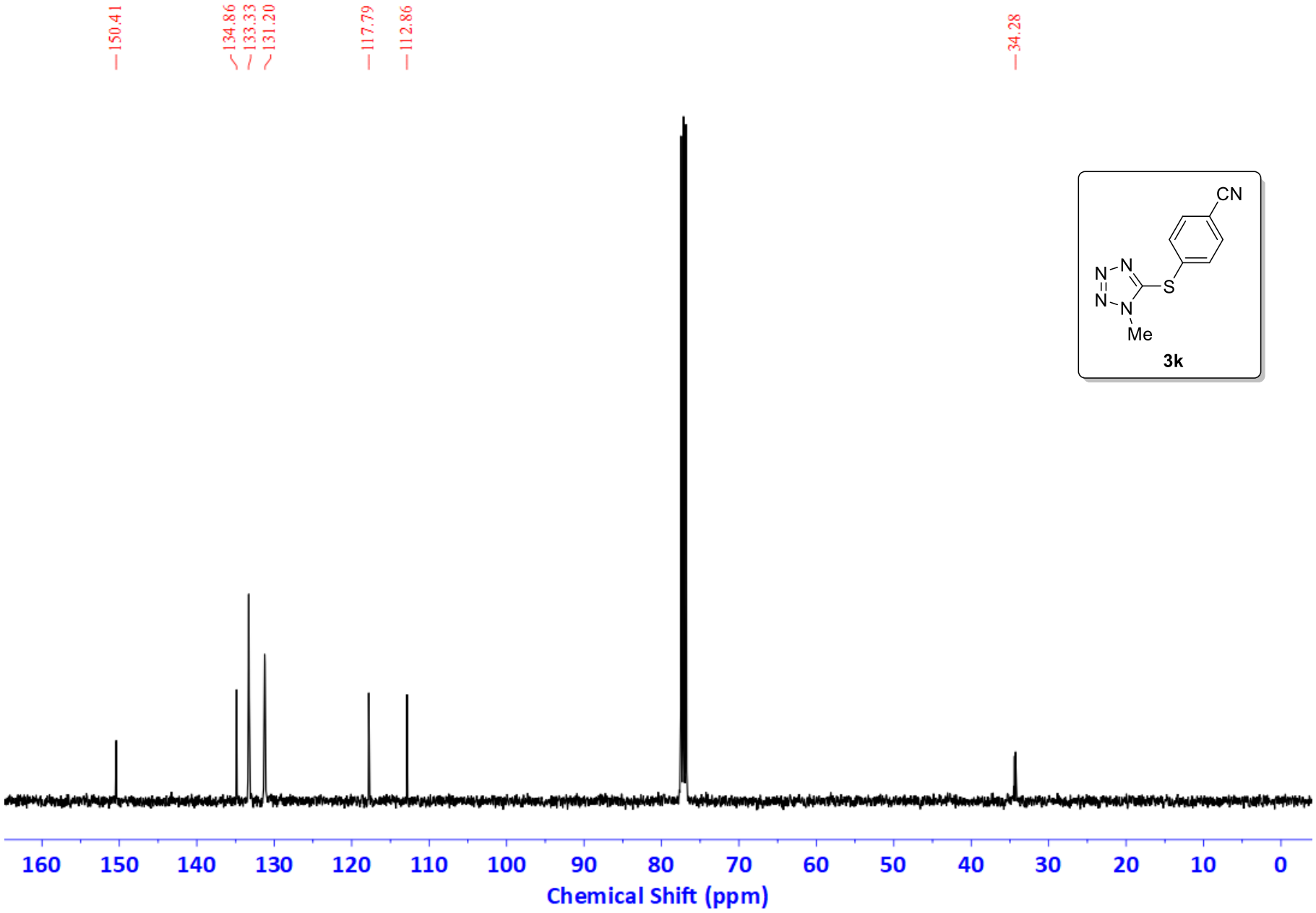

7.61
7.59
7.58
7.55
7.54
7.45
7.43
7.42
7.38
7.36
7.34
3.97
N
N
N
N
S
Me
3i
6.20
2.08
1.09
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

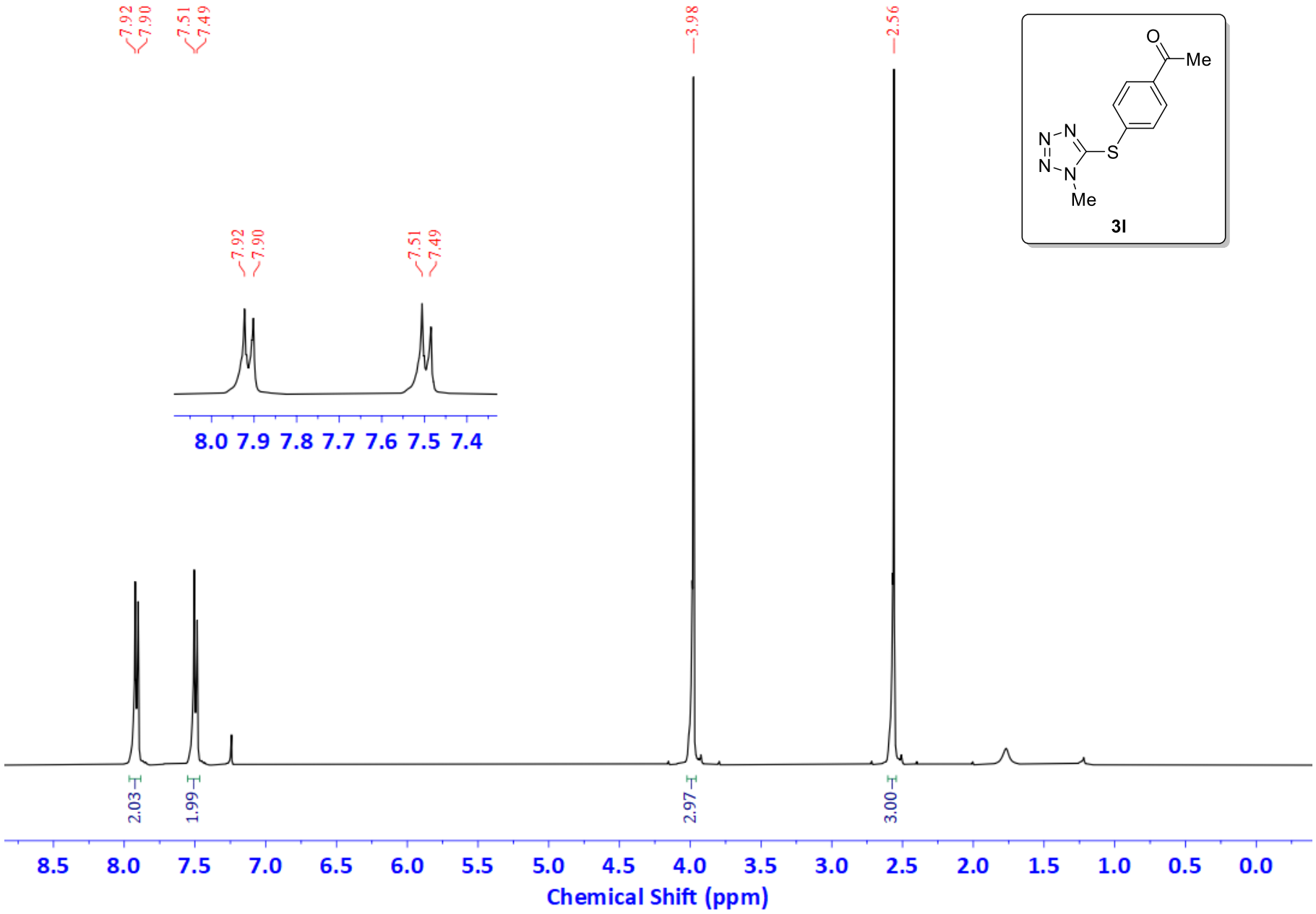

152.58
142.75
139.68
133.09
129.08
128.66
128.14
127.19
126.38
34.15
N
N
N
N
S
Me
3i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

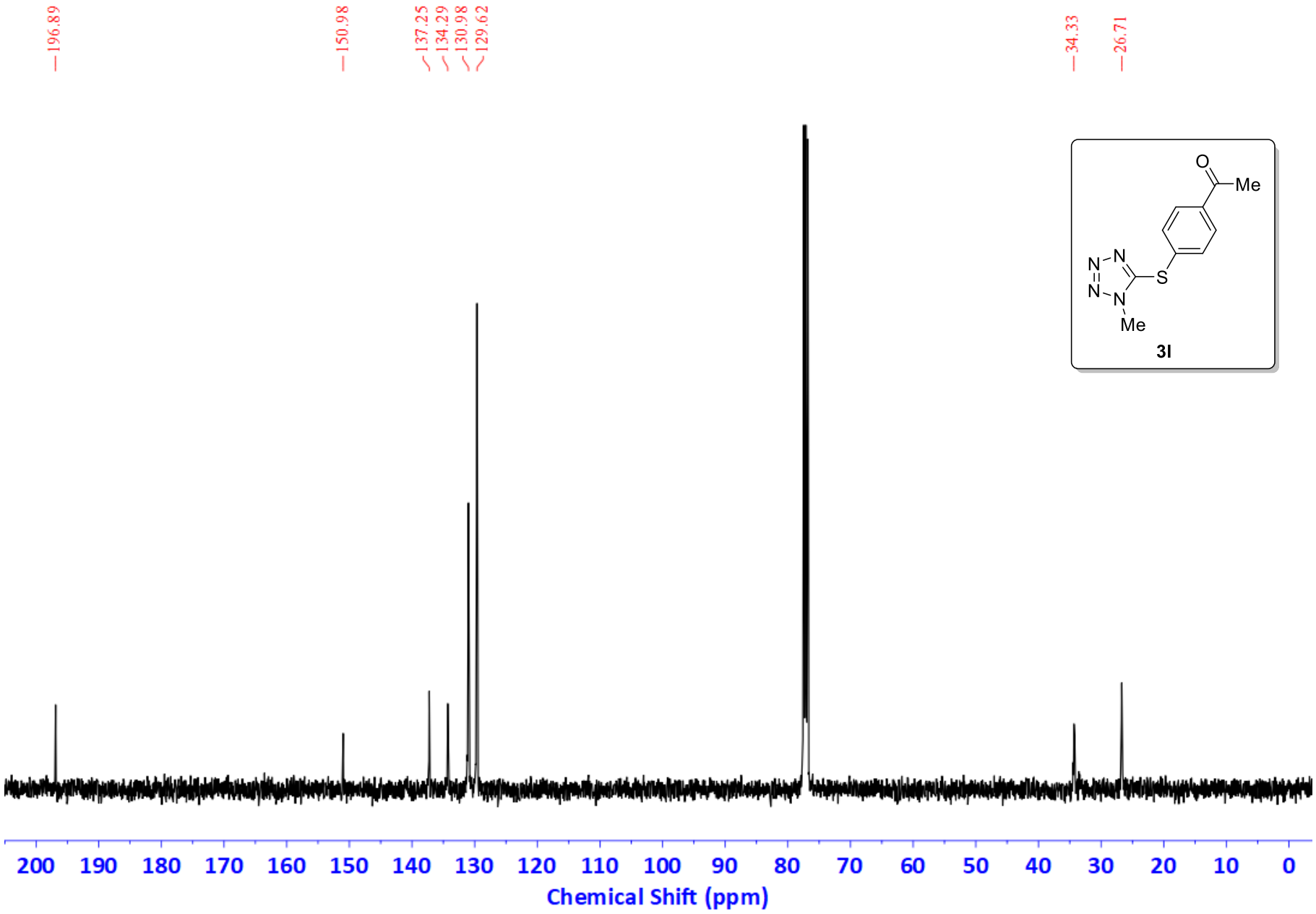

8.24
8.22
7.65
7.63
4.07
NO2
N
N
N
S
Me
3j
8.4
8.2
8.0
7.8
7.6
2.03
2.04
3.00
Chemical Shift (ppm)

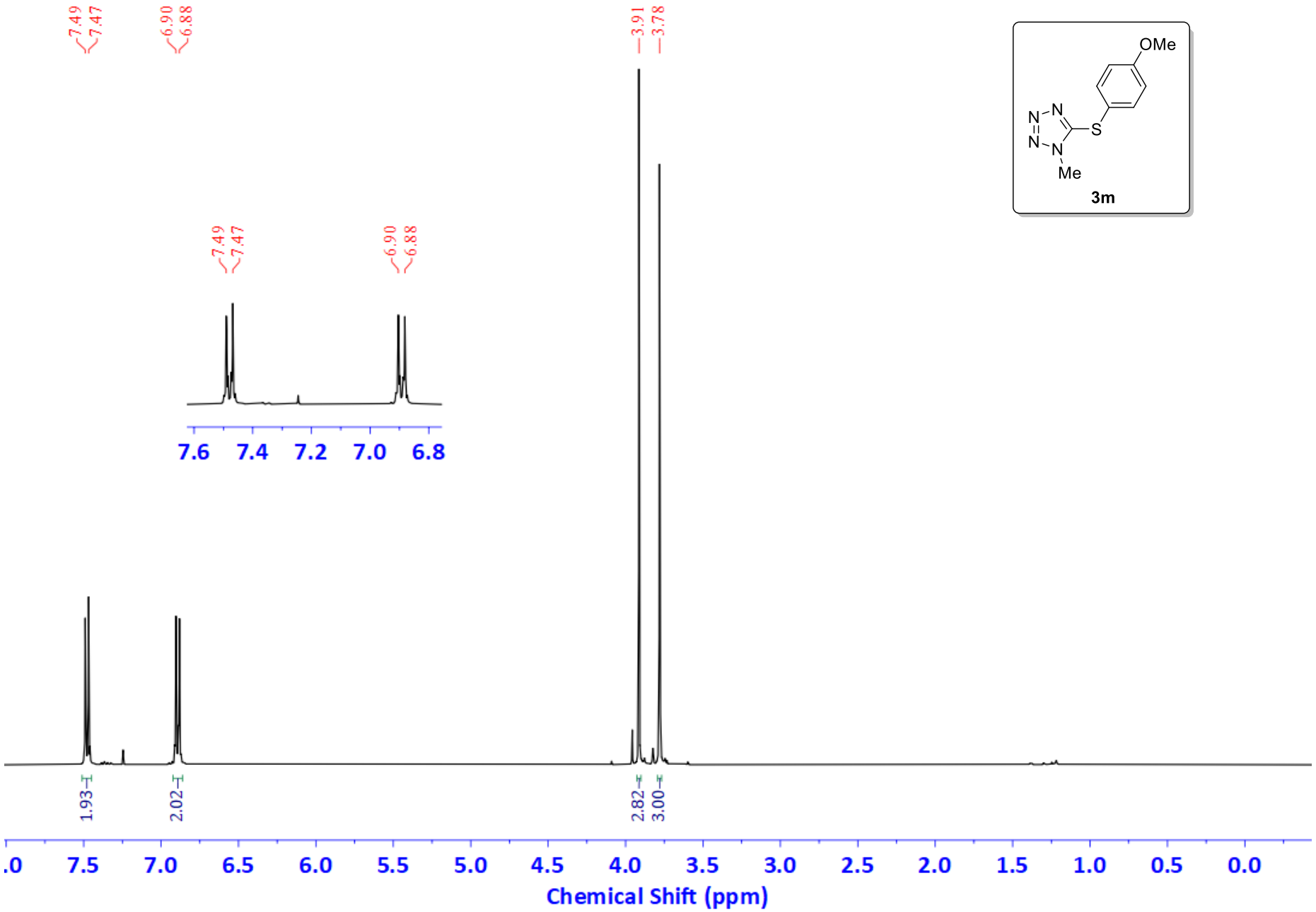

150.20
147.87
137.02
131.05
124.81
34.24
NO2
N
N
N
N
S
Me
3j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

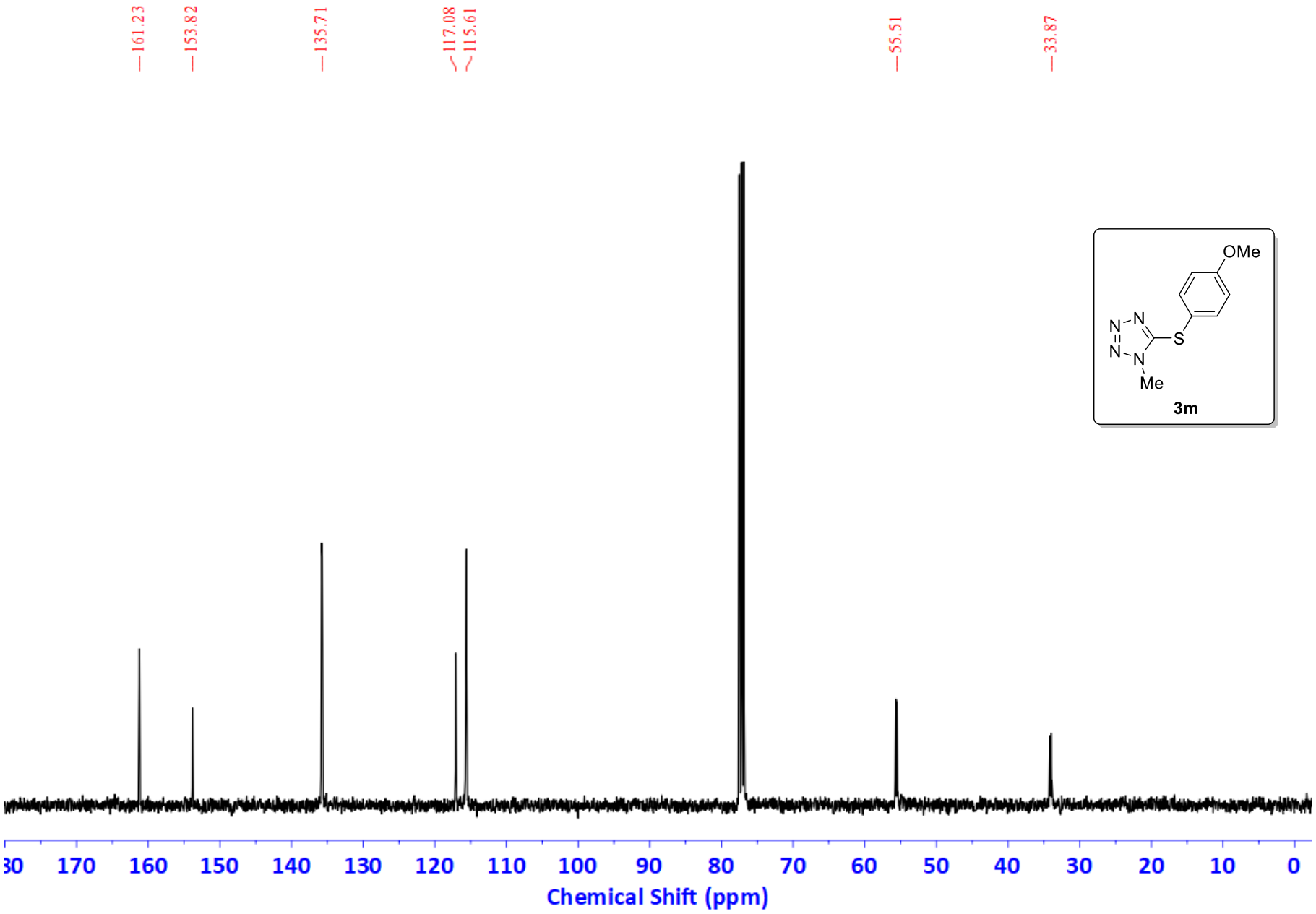

7.65
7.63
7.56
7.54
4.01
CN
N
N
N
S
Me
3k
7.65
7.63
7.56
7.54
7.70 7.65 7.60 7.55 7.50
2.02
2.04
3.00
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
Chemical Shift (ppm)

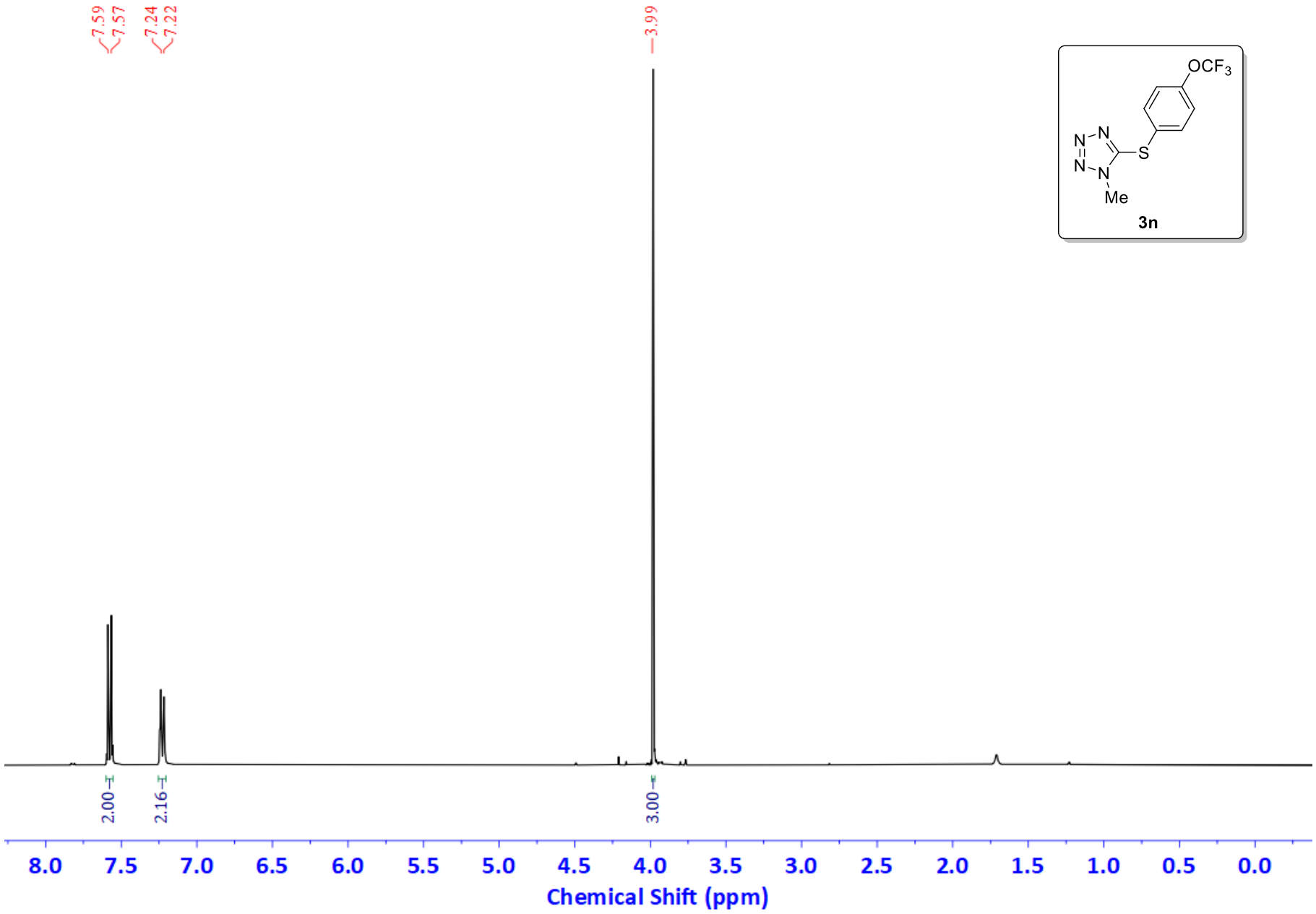

150.41
134.86
133.33
131.20
117.79
112.86
34.28
CN
N
N
N
N
S
Me
3k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

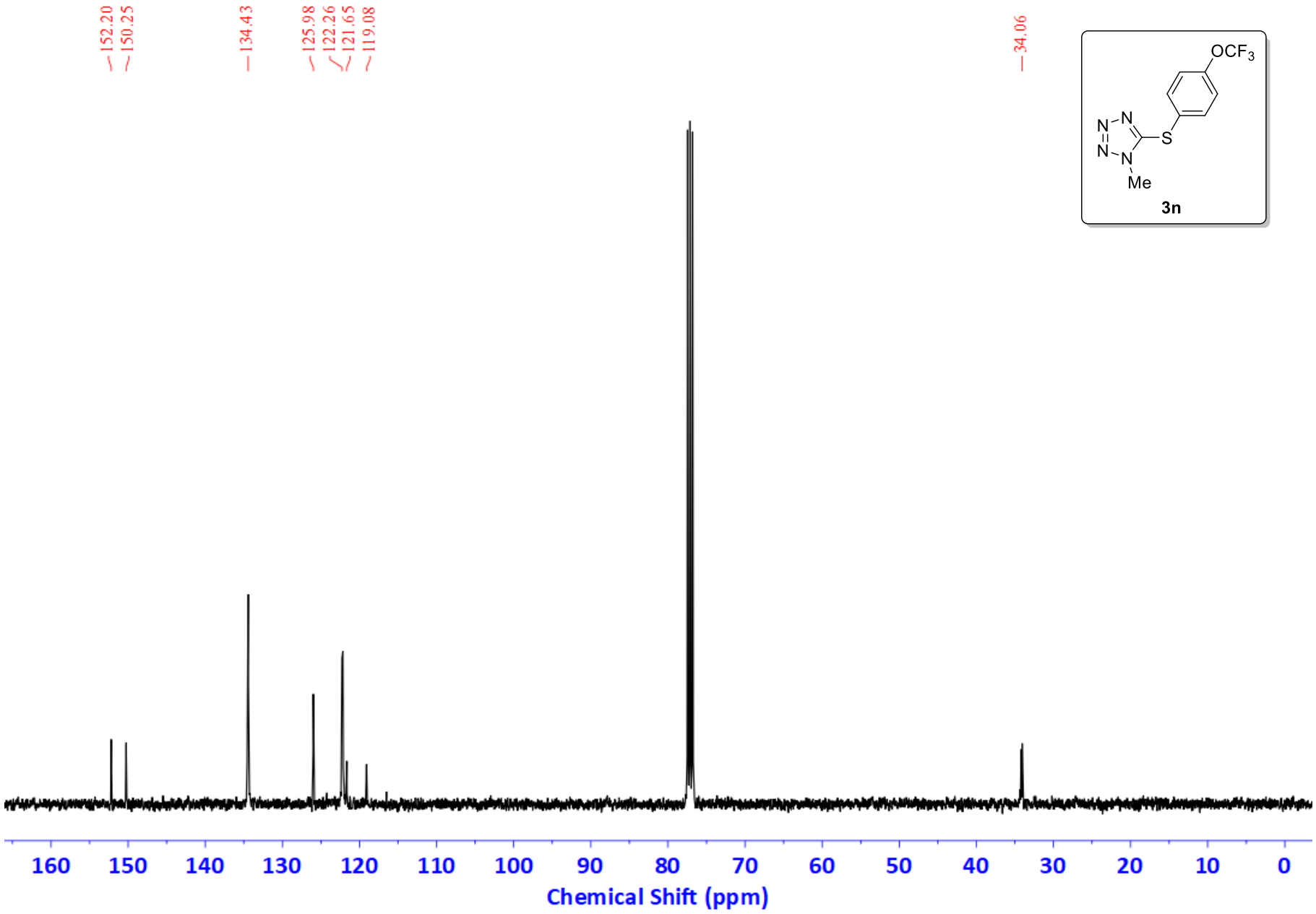

7.92
7.90
7.51
7.49
3.98
2.56
O
Me
N
N
N
N
S
Me
3l
7.92
7.90
7.51
7.49
8.0 7.9 7.8 7.7 7.6 7.5 7.4
2.03
1.99
2.97
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

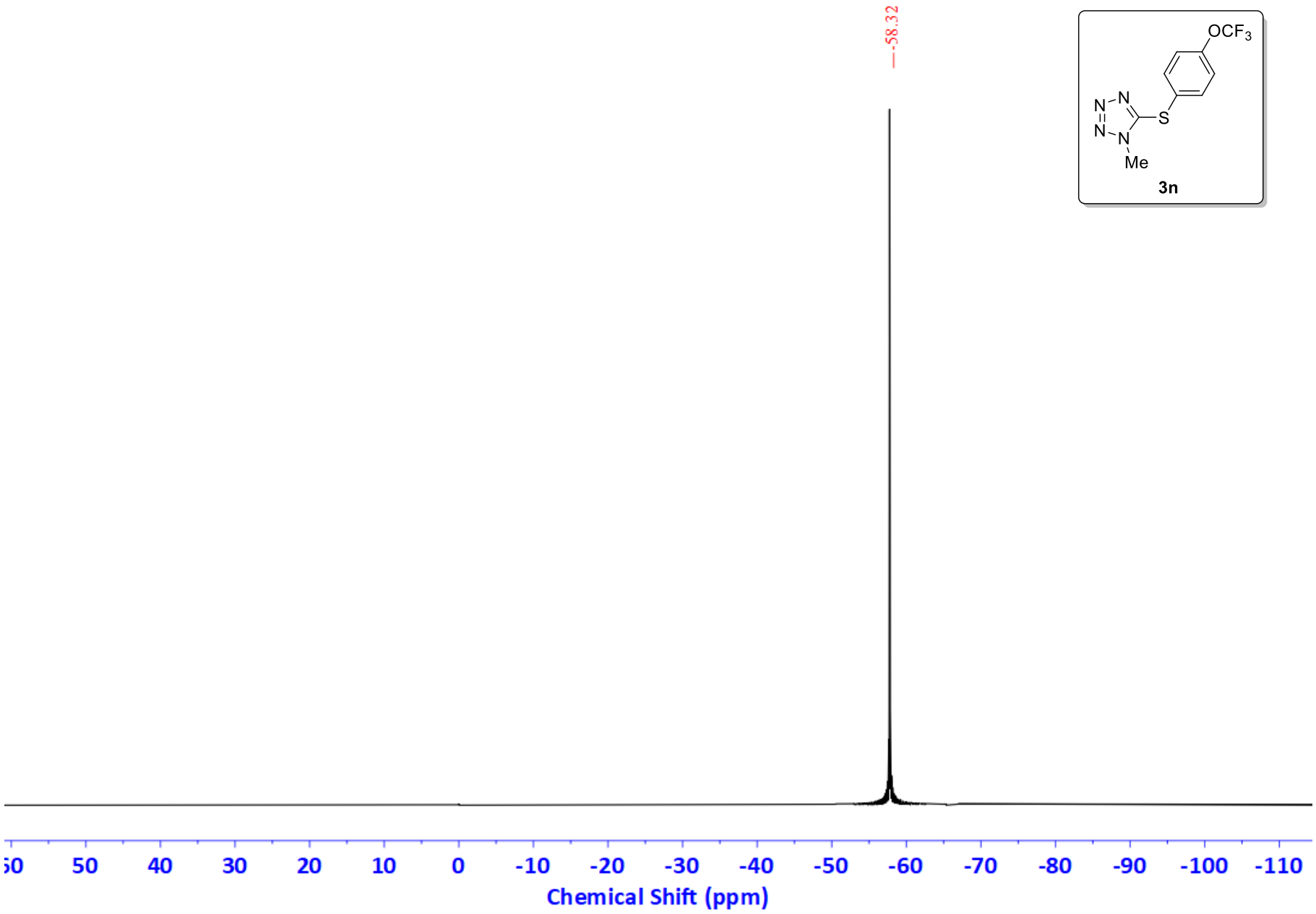

196.89
150.98
137.25
134.29
130.98
129.62
34.33
26.71
O
Me
N
N
N
S
N
Me
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

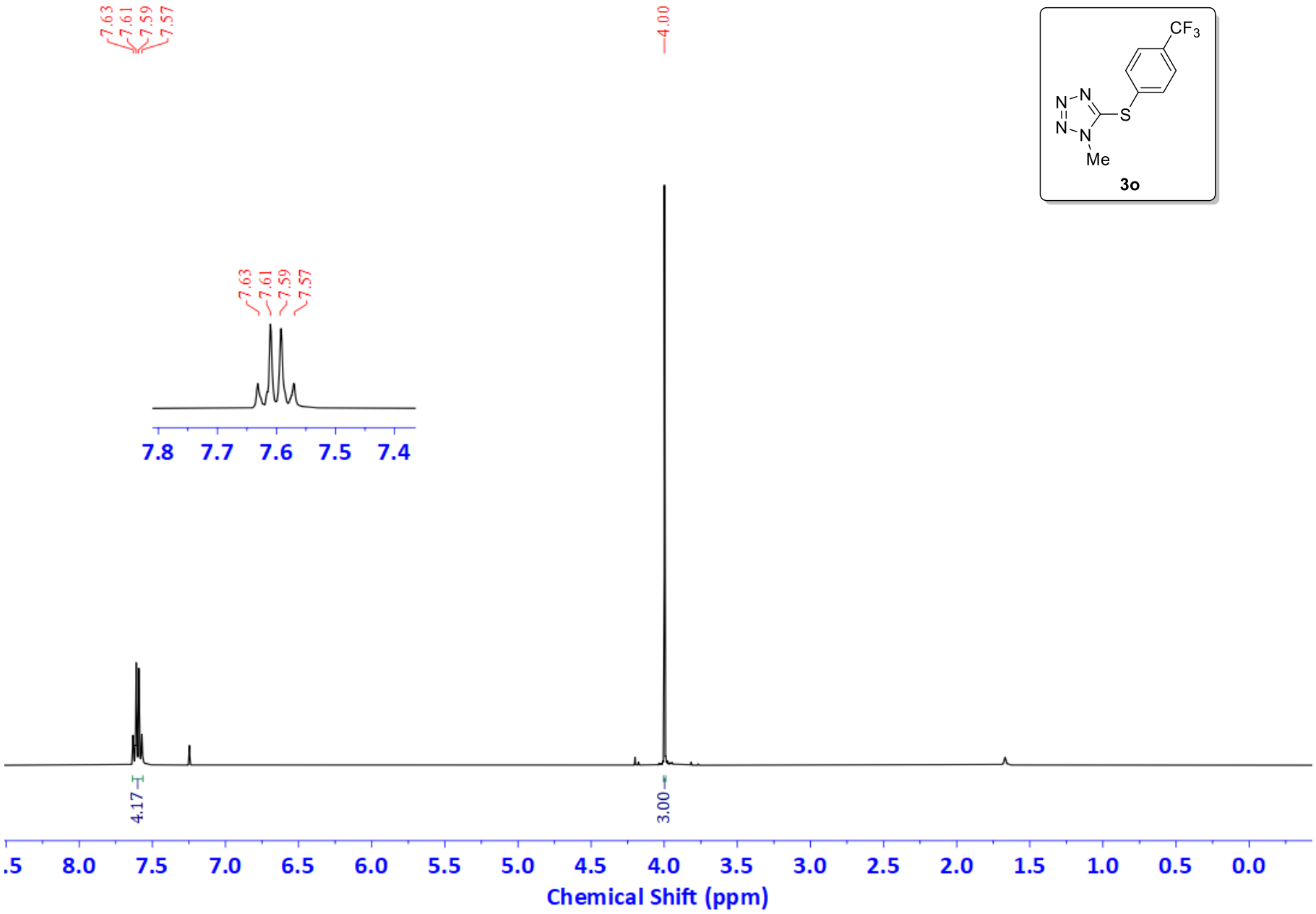

7.49
7.47
6.90
6.88
3.91
3.78
OMe
N
N
N
N
S
Me
3m
7.6
7.4
7.2
7.0
6.8
1.93
2.02
2.82
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

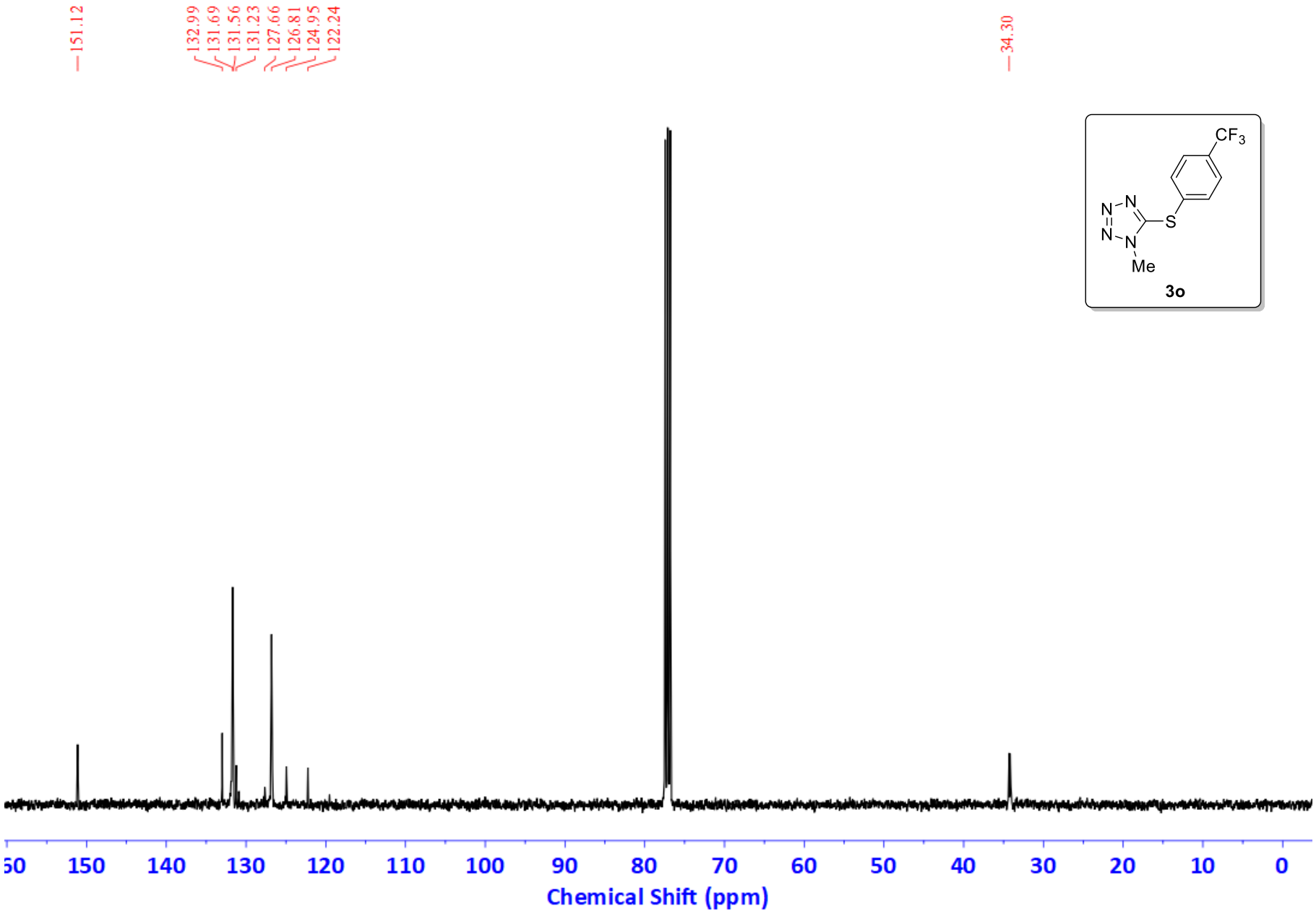

161.23
153.82
135.71
117.08
115.61
55.51
33.87
OMe
N
N
N
S
Me
3m
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

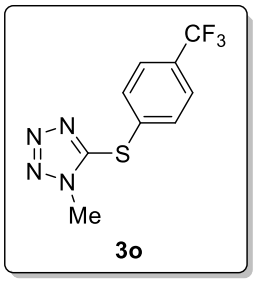

7.59
7.57
7.24
7.22
3.99
OCF3
N
N
N
N
S
Me
3n
2.00
2.16
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


152.20
150.25
134.43
125.98
122.26
121.65
119.08
34.06
OCF3
N
N
N
S
Me
3n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


-58.32
OCF3
N
N
N
N
S
Me
3n
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
Chemical Shift (ppm)

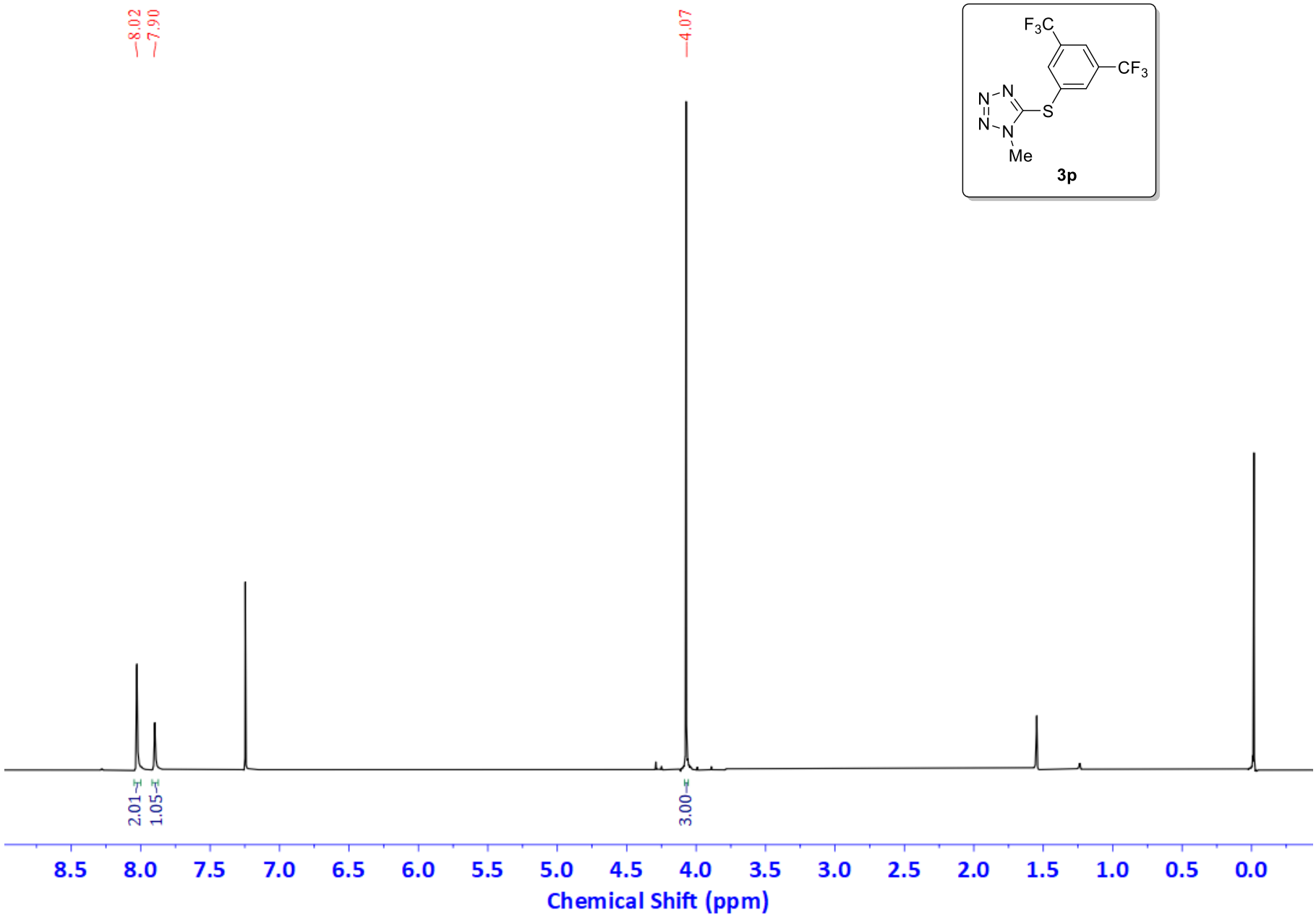

7.63
7.61
7.59
7.57
4.00
CF3
N
N
N
S
Me
3o
7.63
7.61
7.59
7.57
7.8
7.7
7.6
7.5
7.4
4.17
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

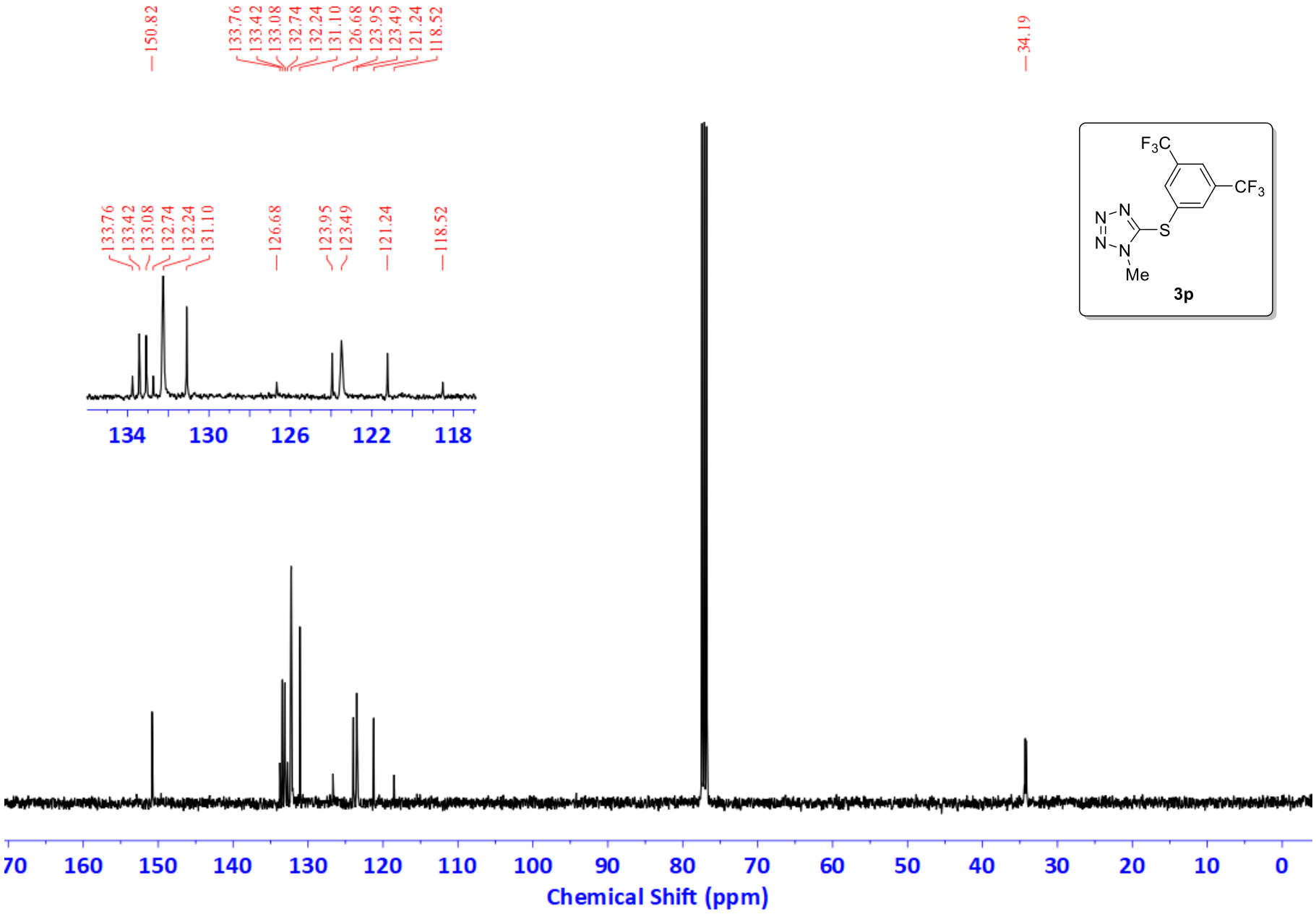

151.12
132.99
131.69
131.56
131.23
127.66
126.81
124.95
122.24
34.30
CF3
N
N
N
N
S
Me
3o
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

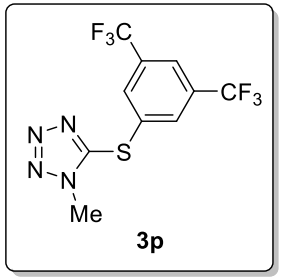

CF3
N
N
N
N
S
Me

3o

-62.52
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Chemical Shift (ppm)

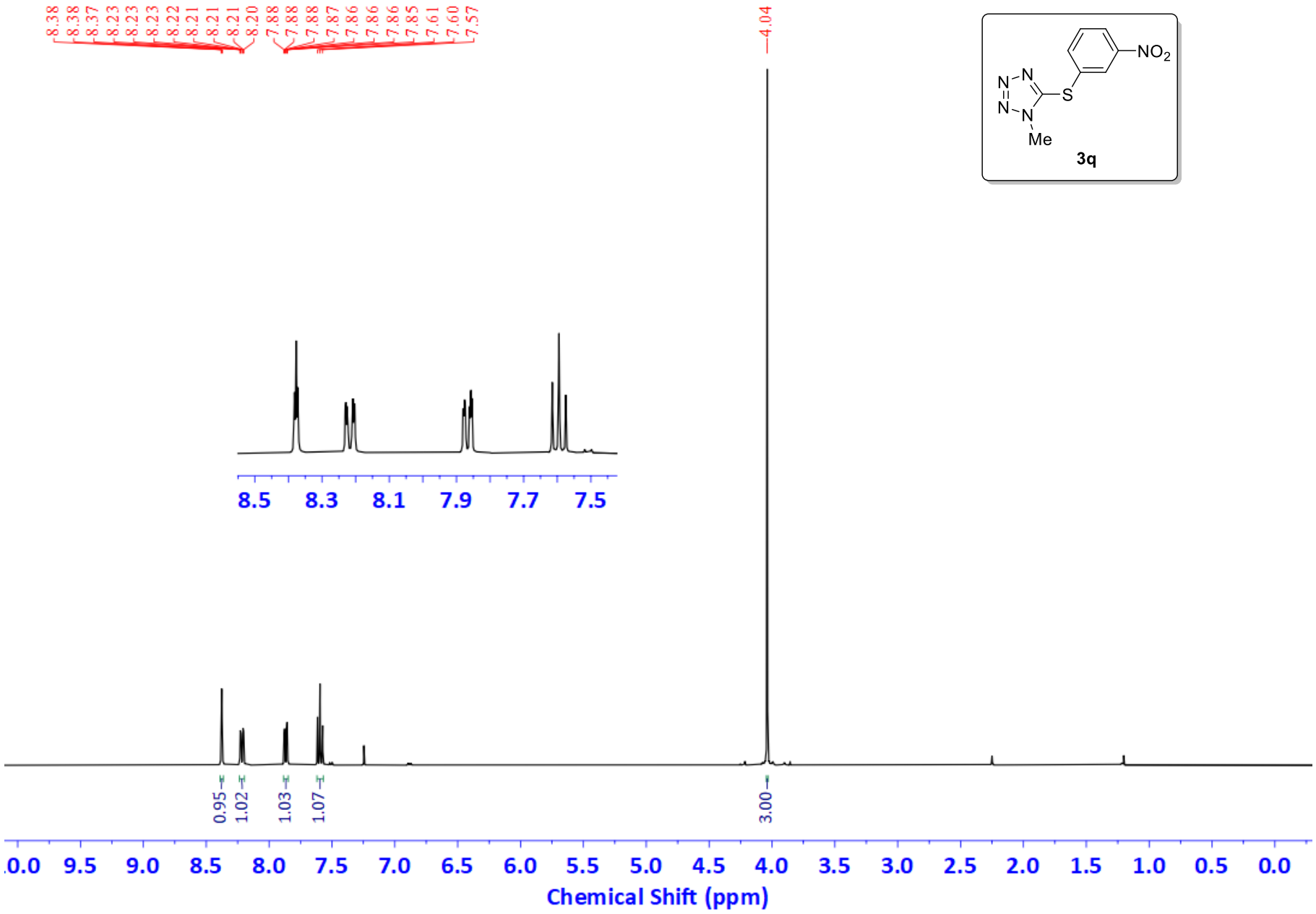

8.02
7.90
4.07
F3C
CF3
N
N
N
S
Me
3p
2.01
1.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

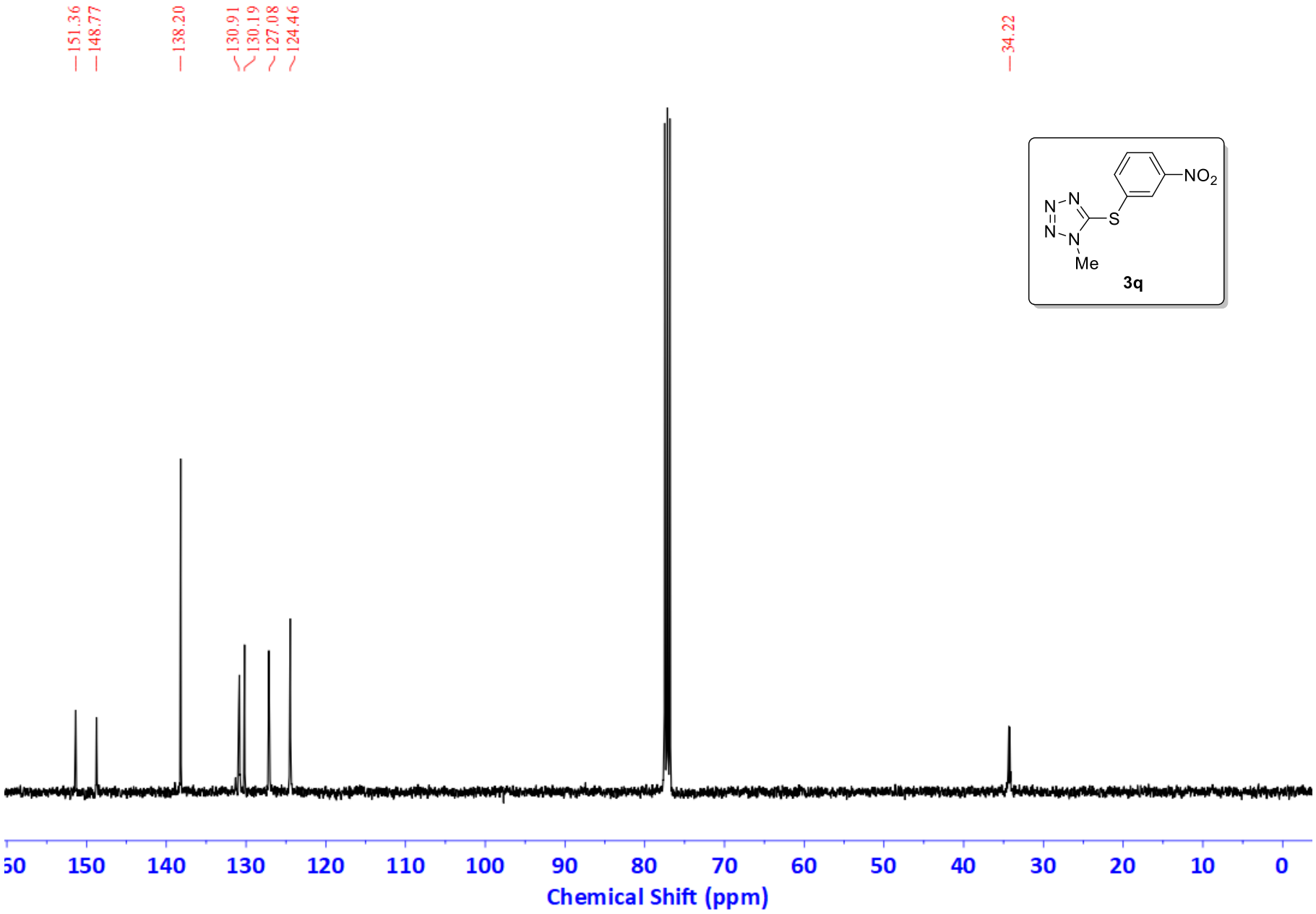

150.82
133.76
133.42
133.08
132.74
132.24
131.10
126.68
123.95
123.49
121.24
118.52
34.19
F3C
CF3
N
N
N
S
Me
3p
134
130
126
122
118
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

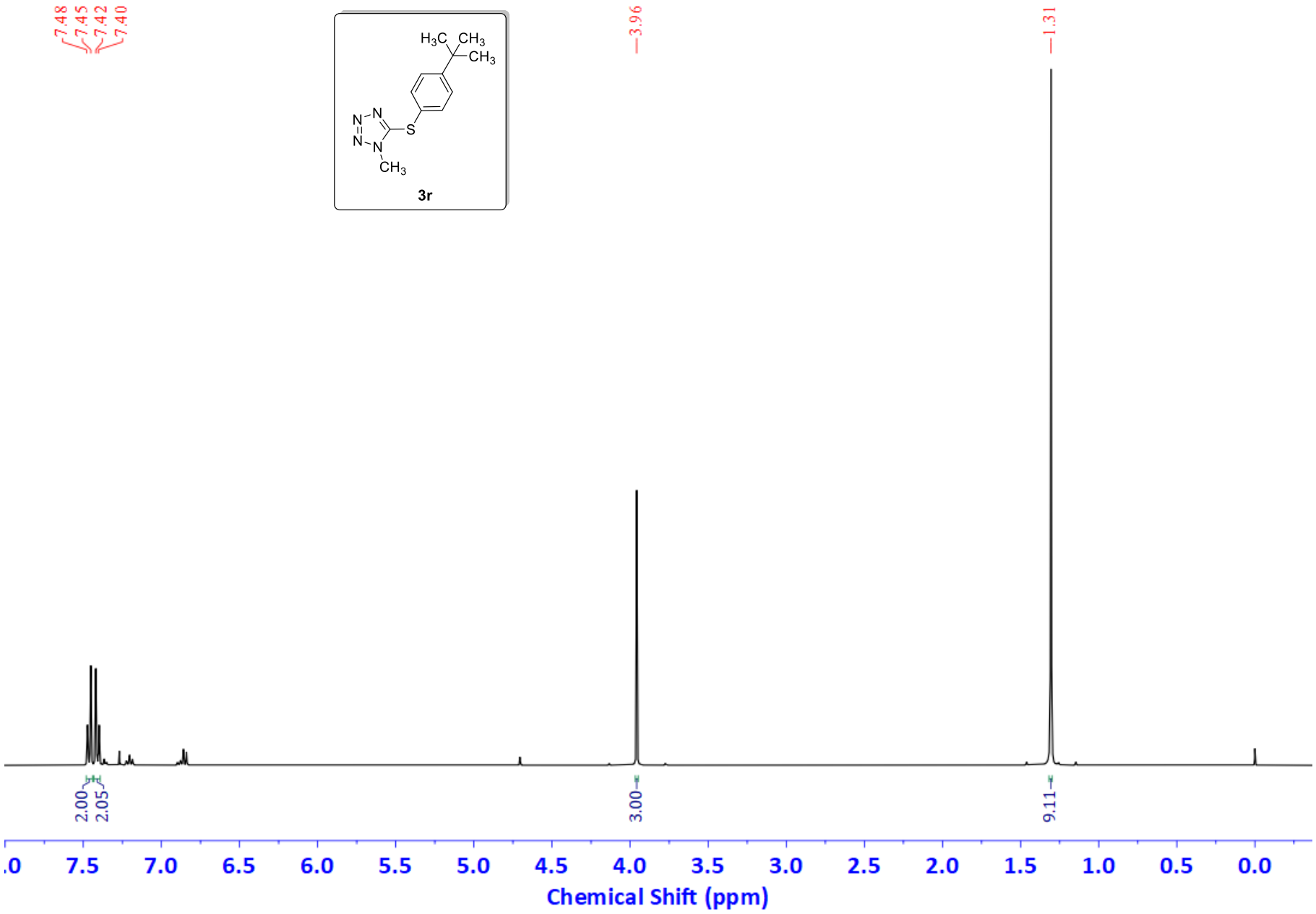

F3C
CF3
N
N
N
N
S
Me

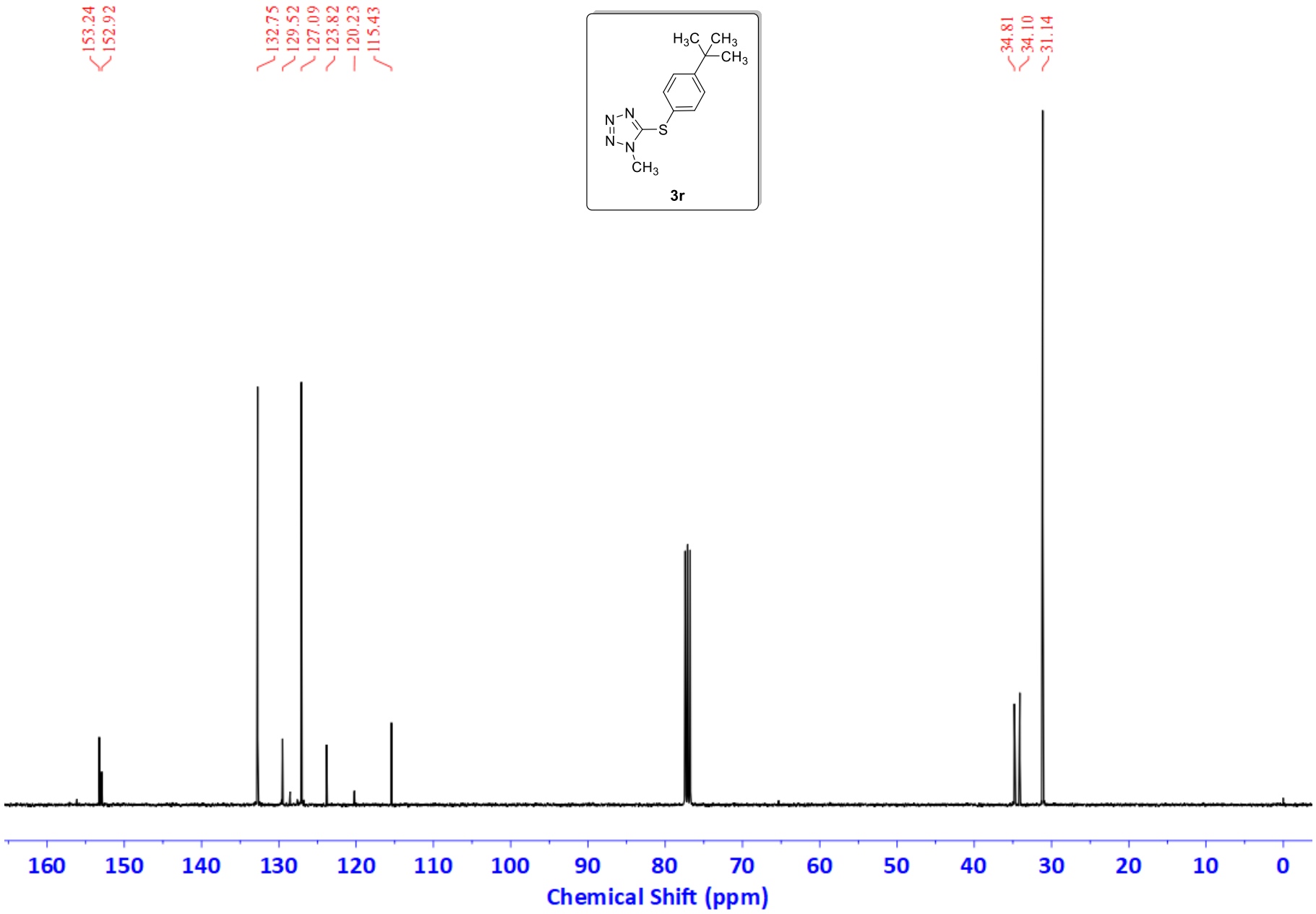
3p

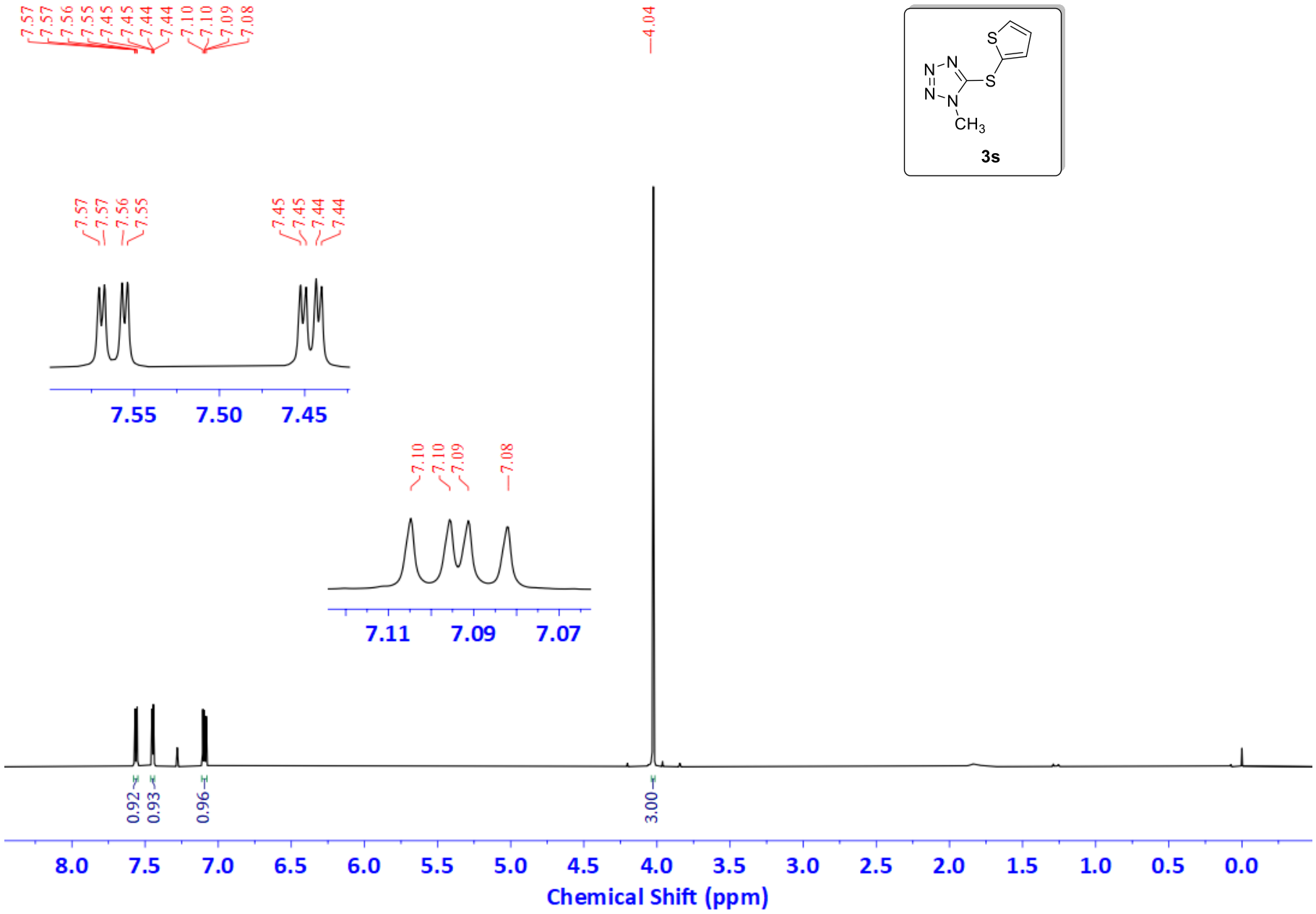
-62.93
0
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-12
Chemical Shift (ppm)

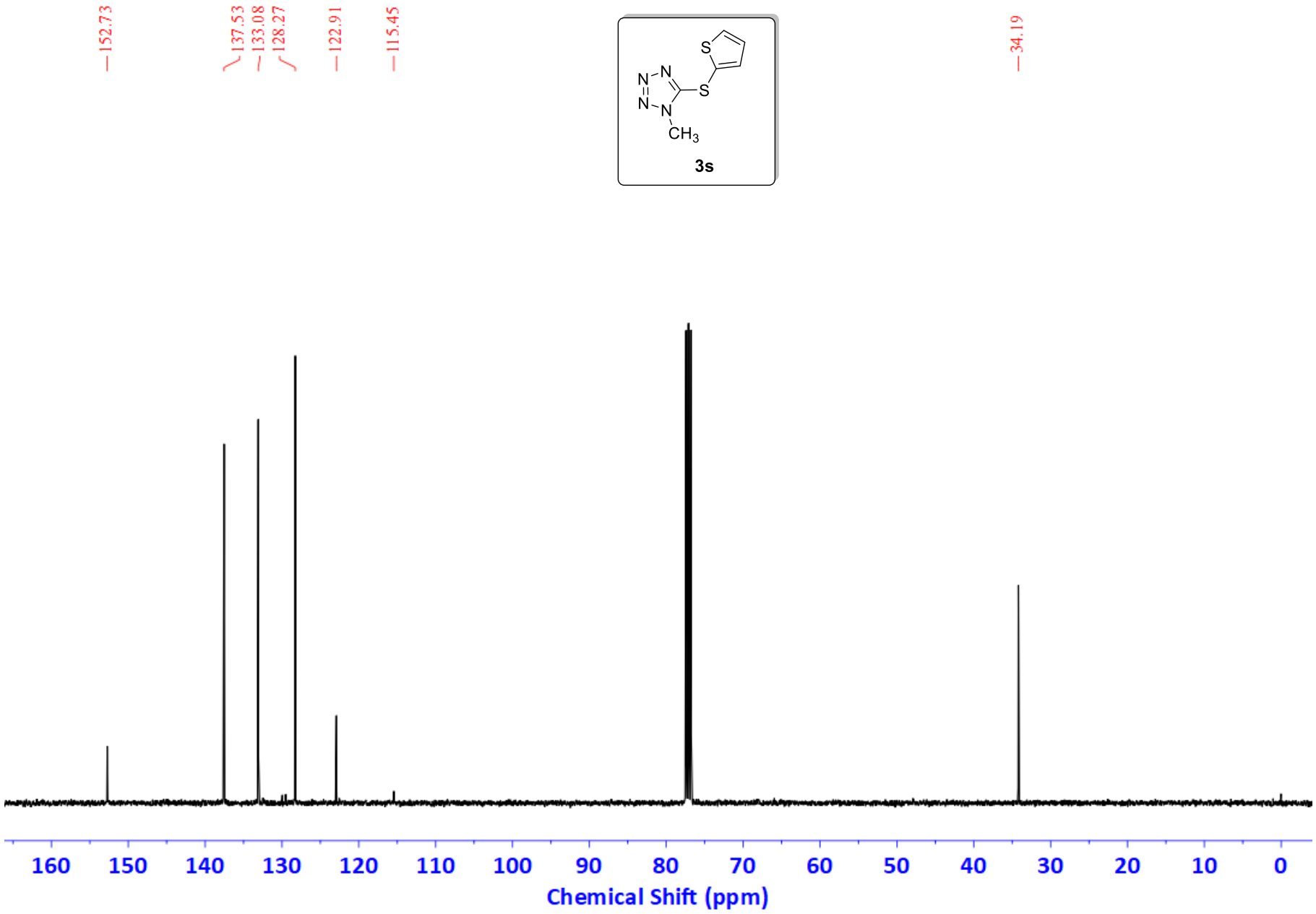

8.38
8.38
8.37
8.23
8.23
8.23
8.22
8.21
8.21
8.21
8.20
7.88
7.88
7.88
7.87
7.86
7.86
7.86
7.85
7.61
7.60
7.57
4.04
NO2
N
N
N
S
Me
3q
8.5
8.3
8.1
7.9
7.7
7.5
0.95
1.02
1.03
1.07
3.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

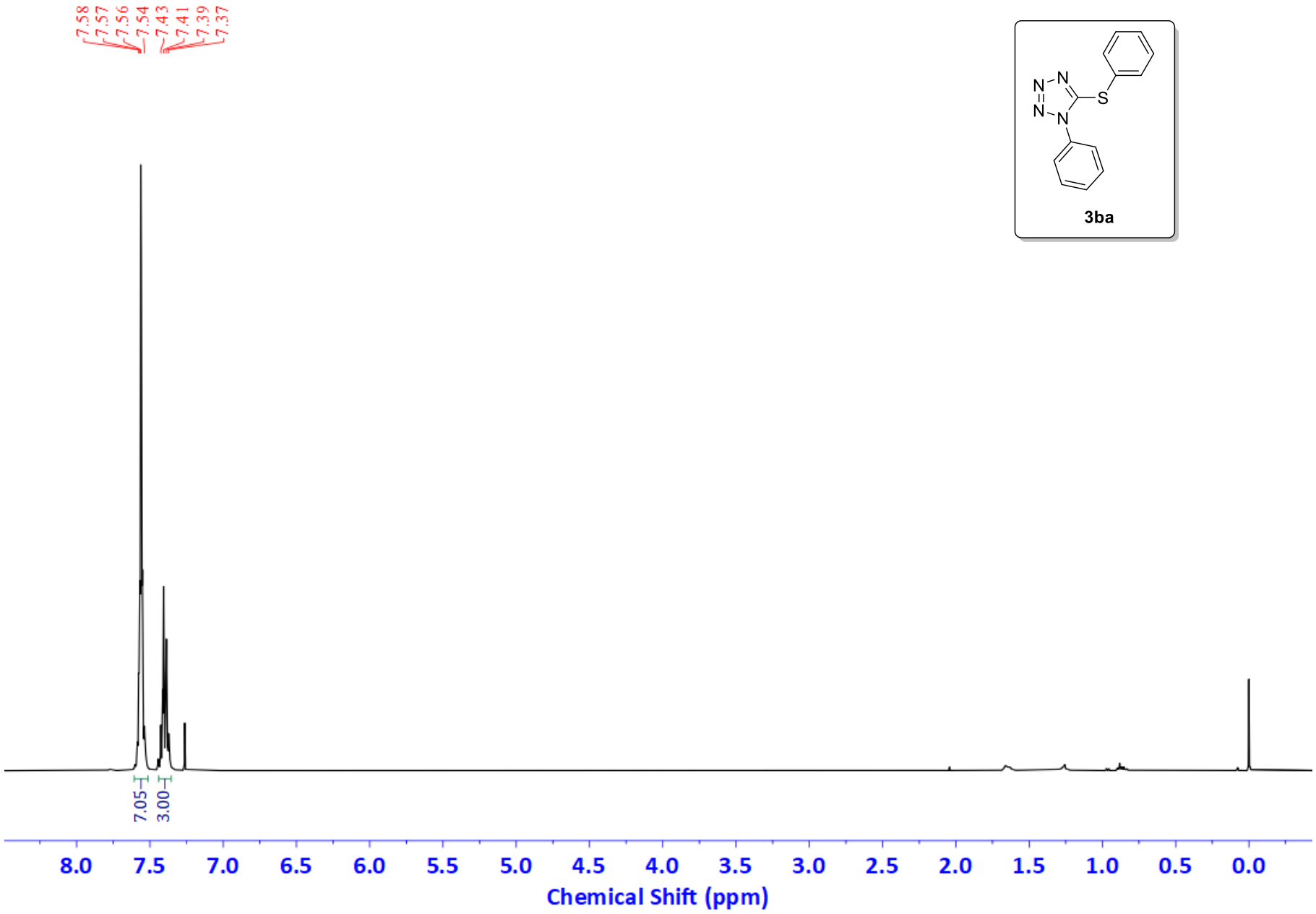

151.36
148.77
138.20
130.91
130.19
127.08
124.46
34.22
NO2
N
N
N
N
S
Me
3q
50
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

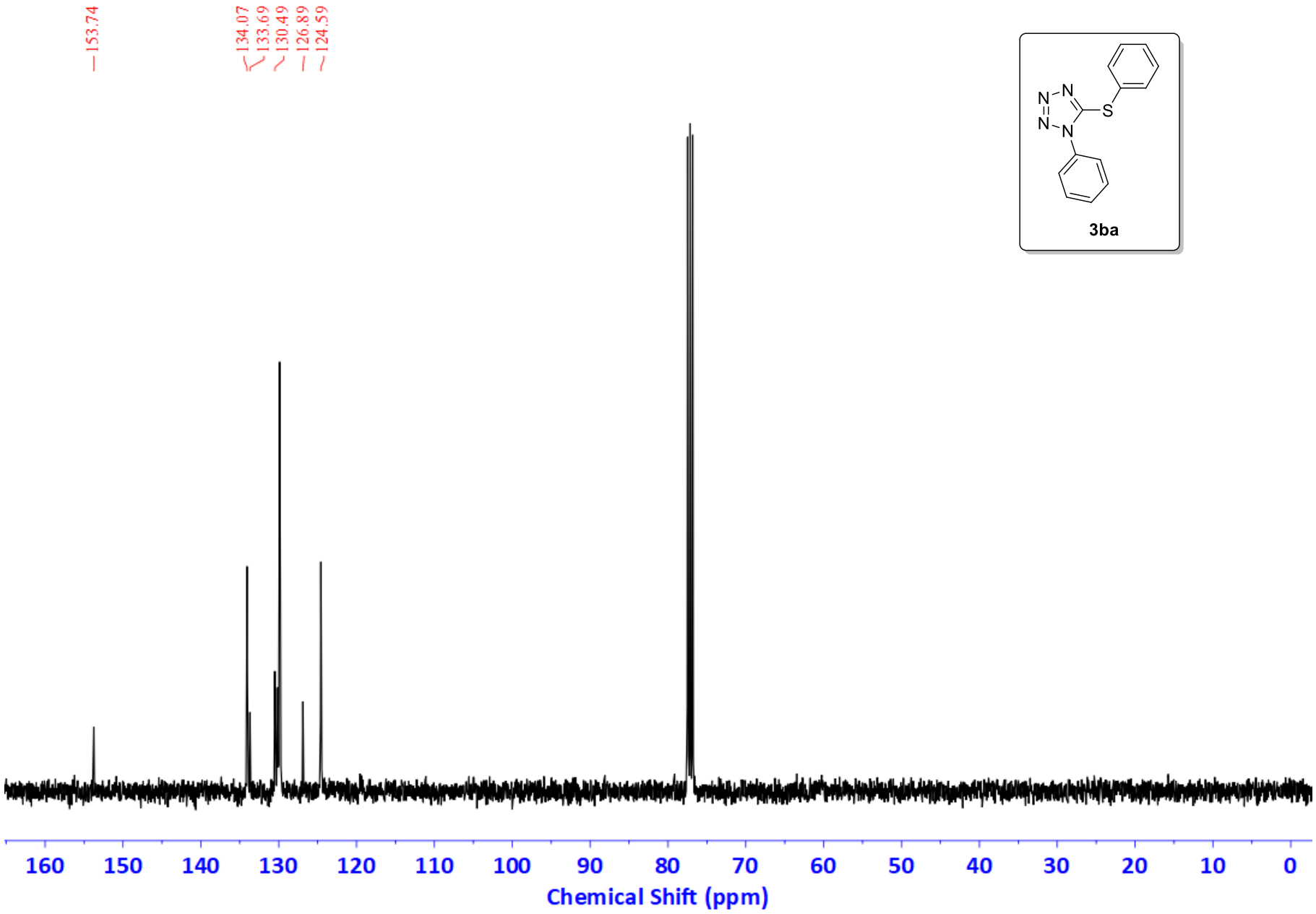

7.48
7.45
7.42
7.40
3.96
1.31
H3C CH3
CH3
N
N
N
S
CH3
3r
2.00
2.05
3.00
9.11
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

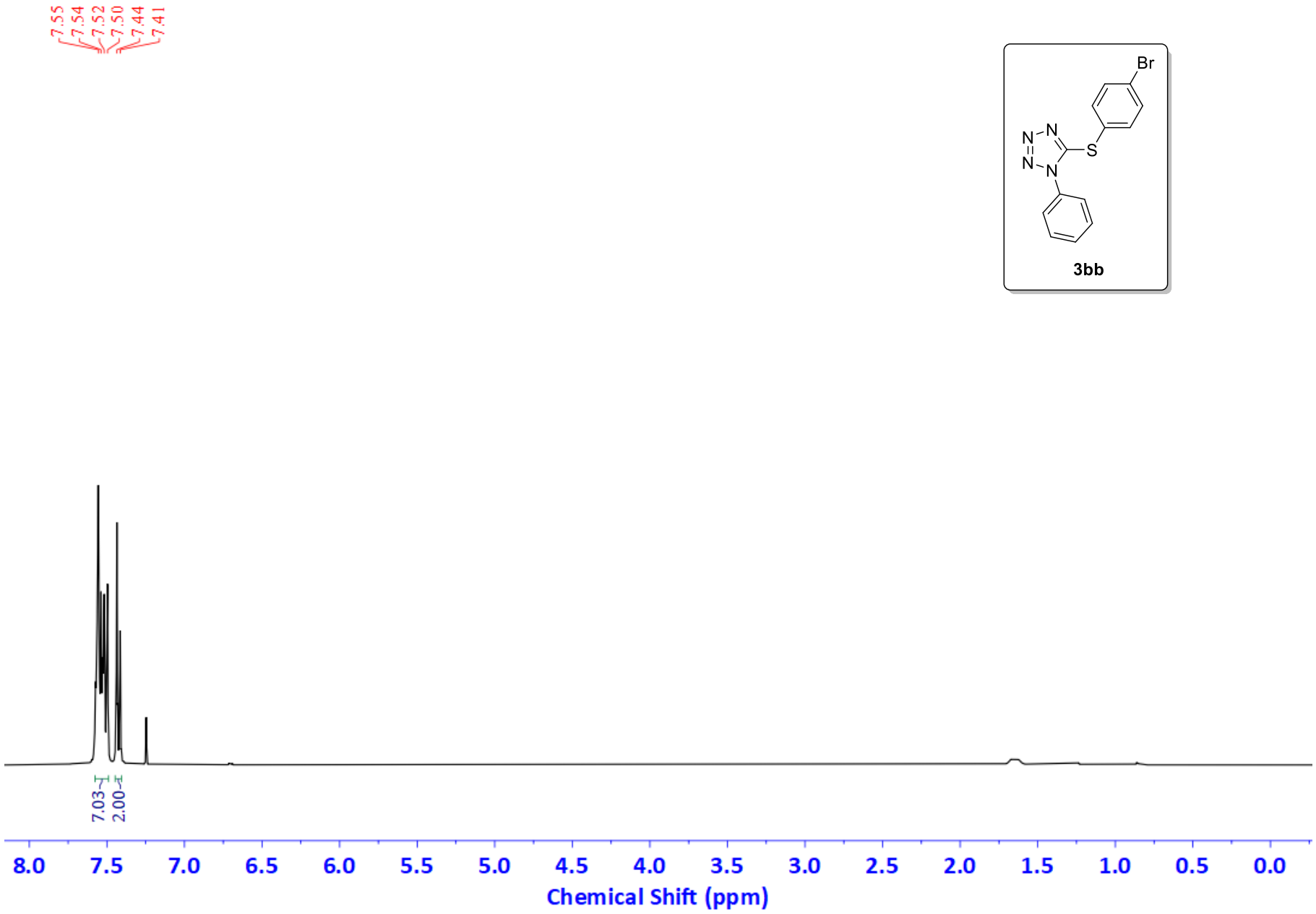

153.24
152.92
132.75
129.52
127.09
123.82
120.23
115.43
34.81
34.10
31.14
H3C CH3
CH3
N
N
N
N
S
CH3
3r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

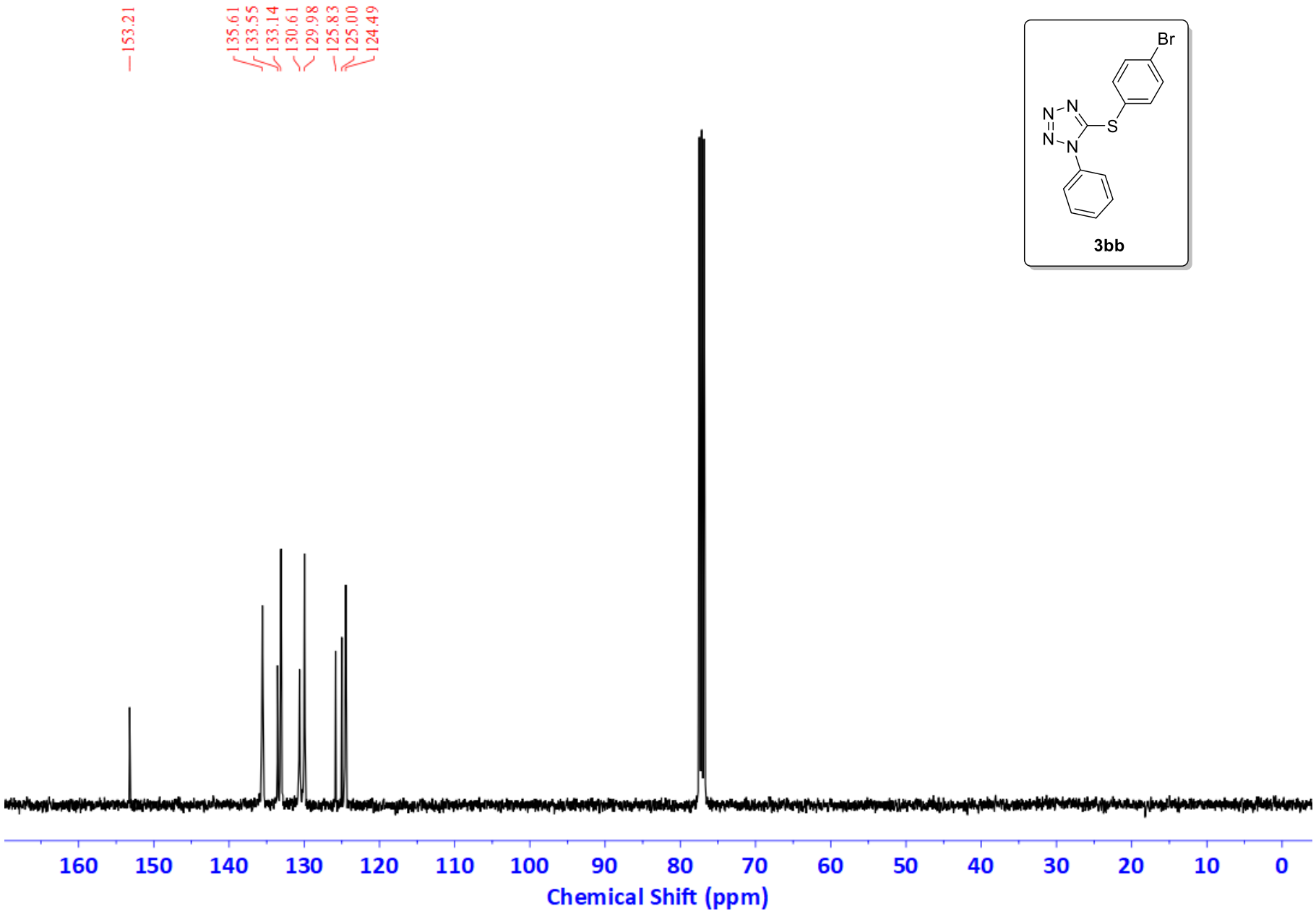

7.57
7.57
7.56
7.55
7.45
7.45
7.44
7.44
7.10
7.10
7.09
7.08
4.04
S
N
N
N
S
CH3
3s
7.55
7.50
7.45
7.11
7.09
7.07
0.92
0.93
0.96
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

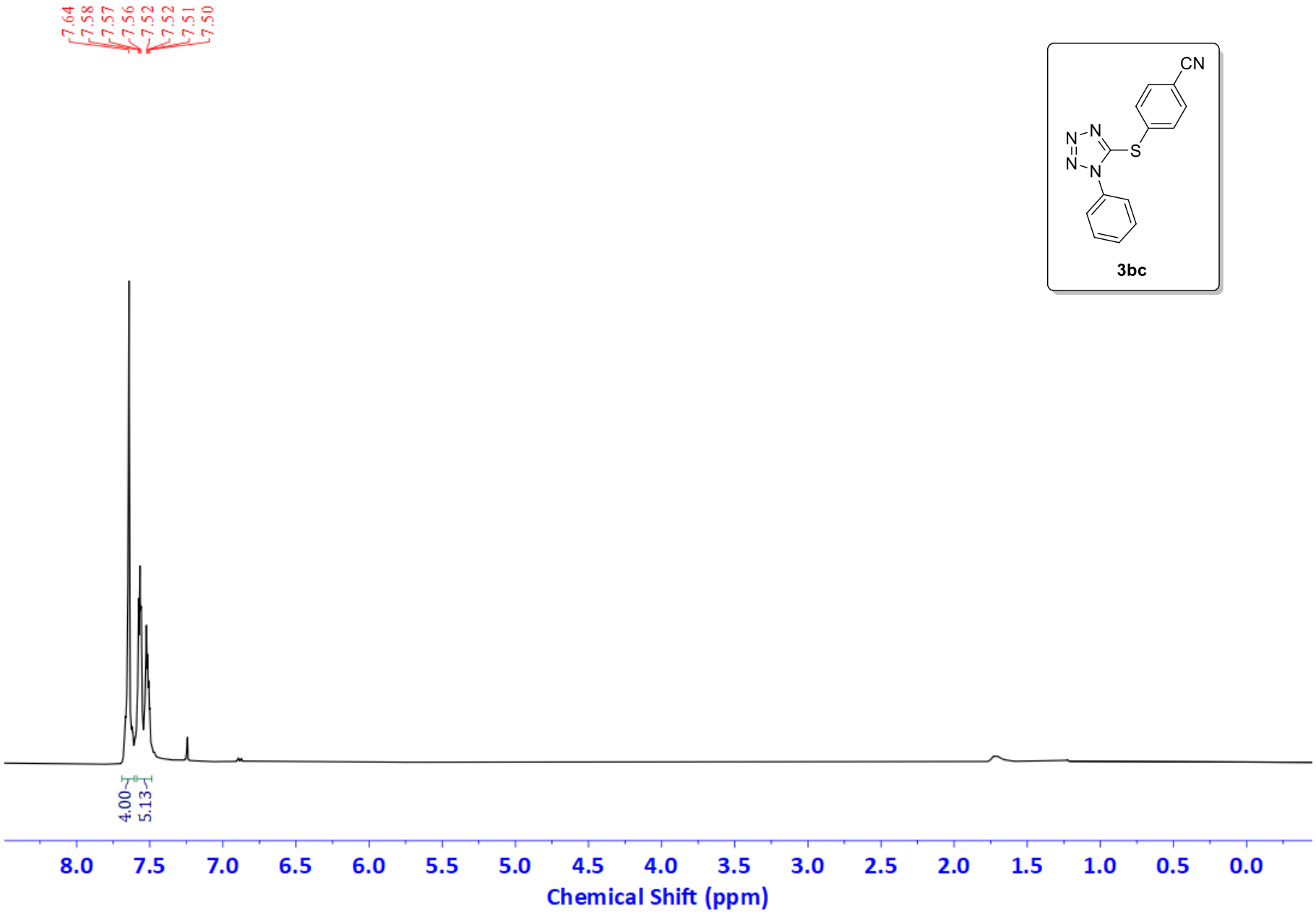

152.73
137.53
133.08
128.27
122.91
115.45
34.19
S
N
N
N
S
CH3
3s
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

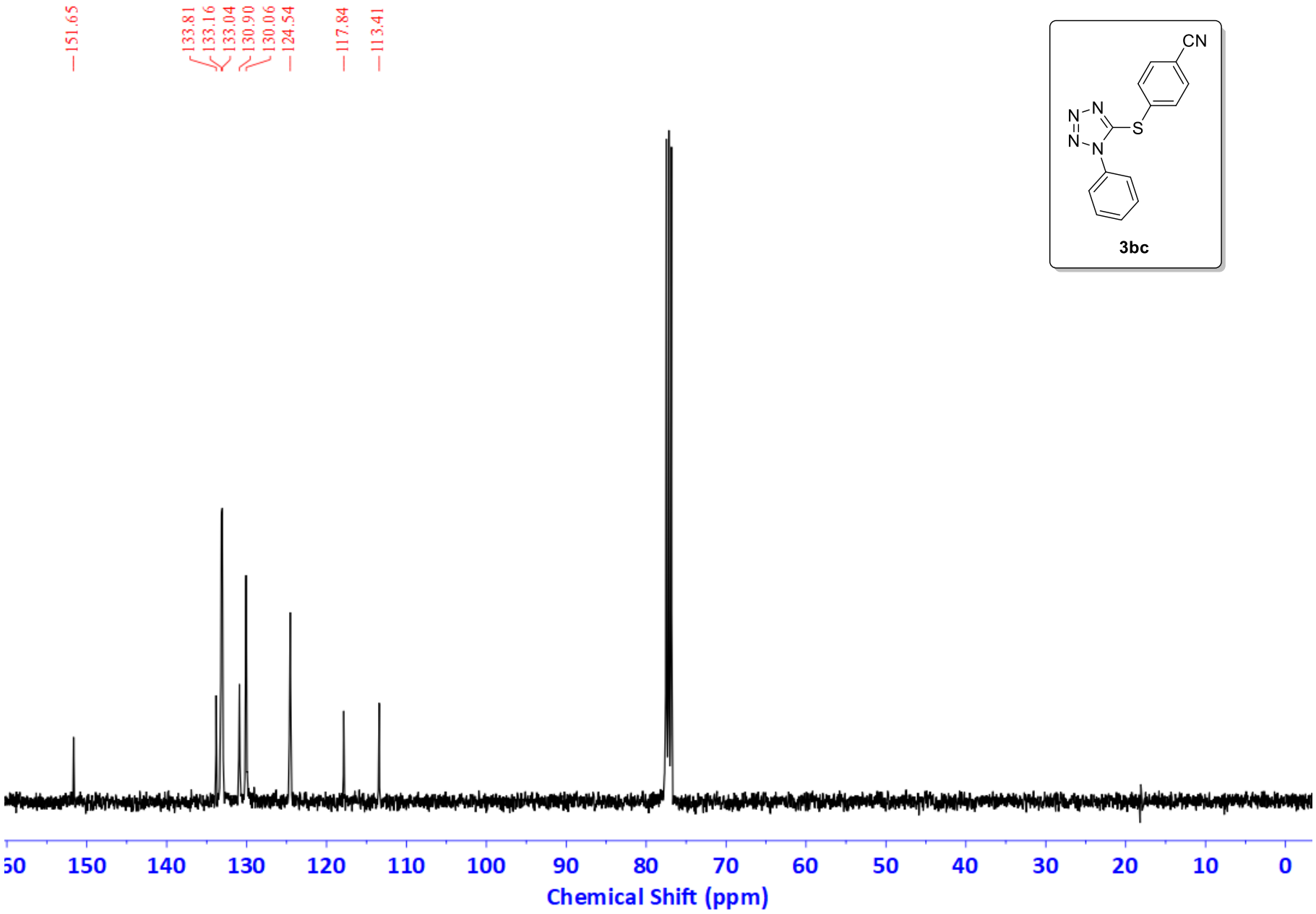

7.58
7.57
7.56
7.54
7.43
7.41
7.39
7.37
3ba
7.05
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

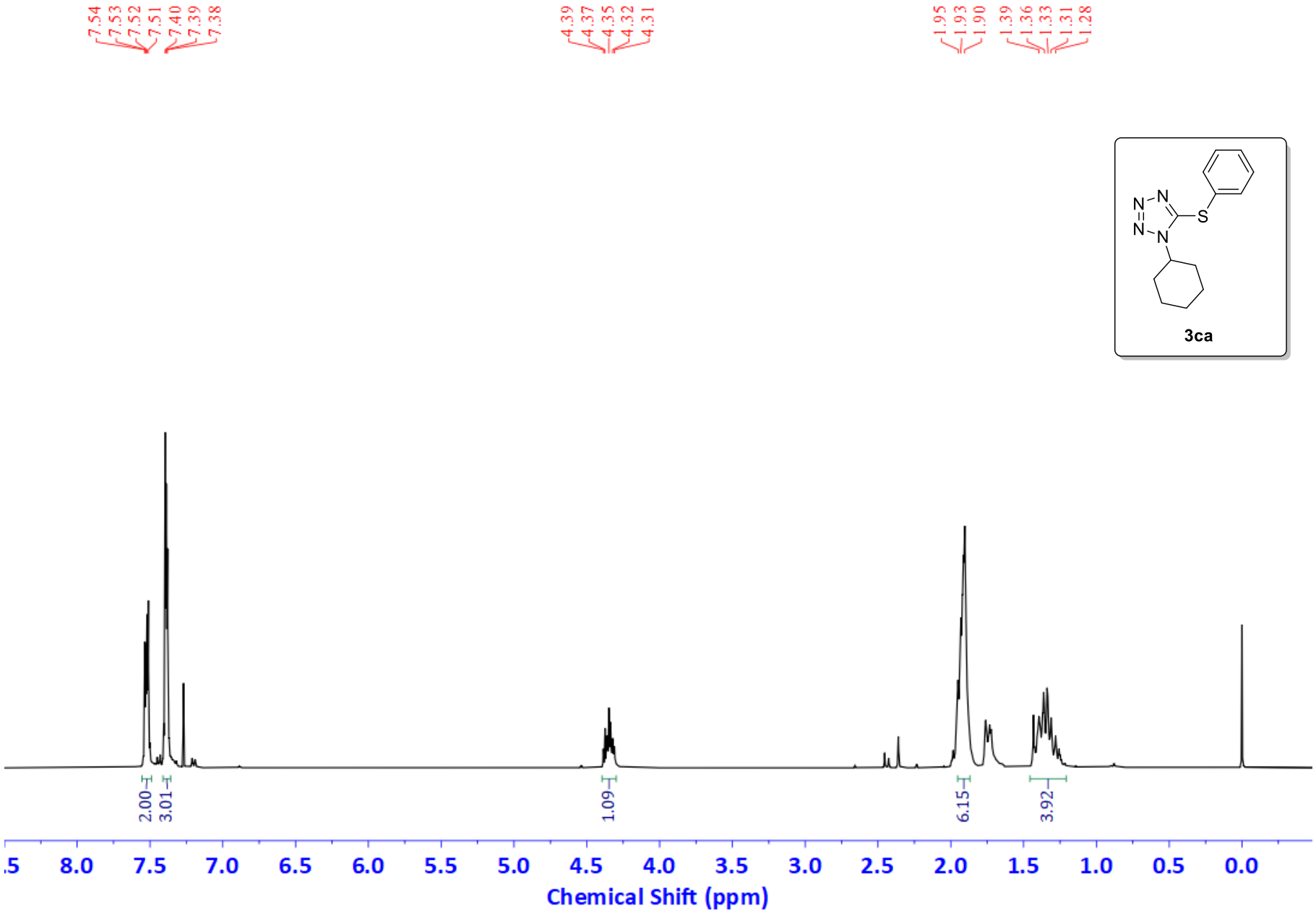

153.74
134.07
133.69
130.49
126.89
124.59
3ba
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

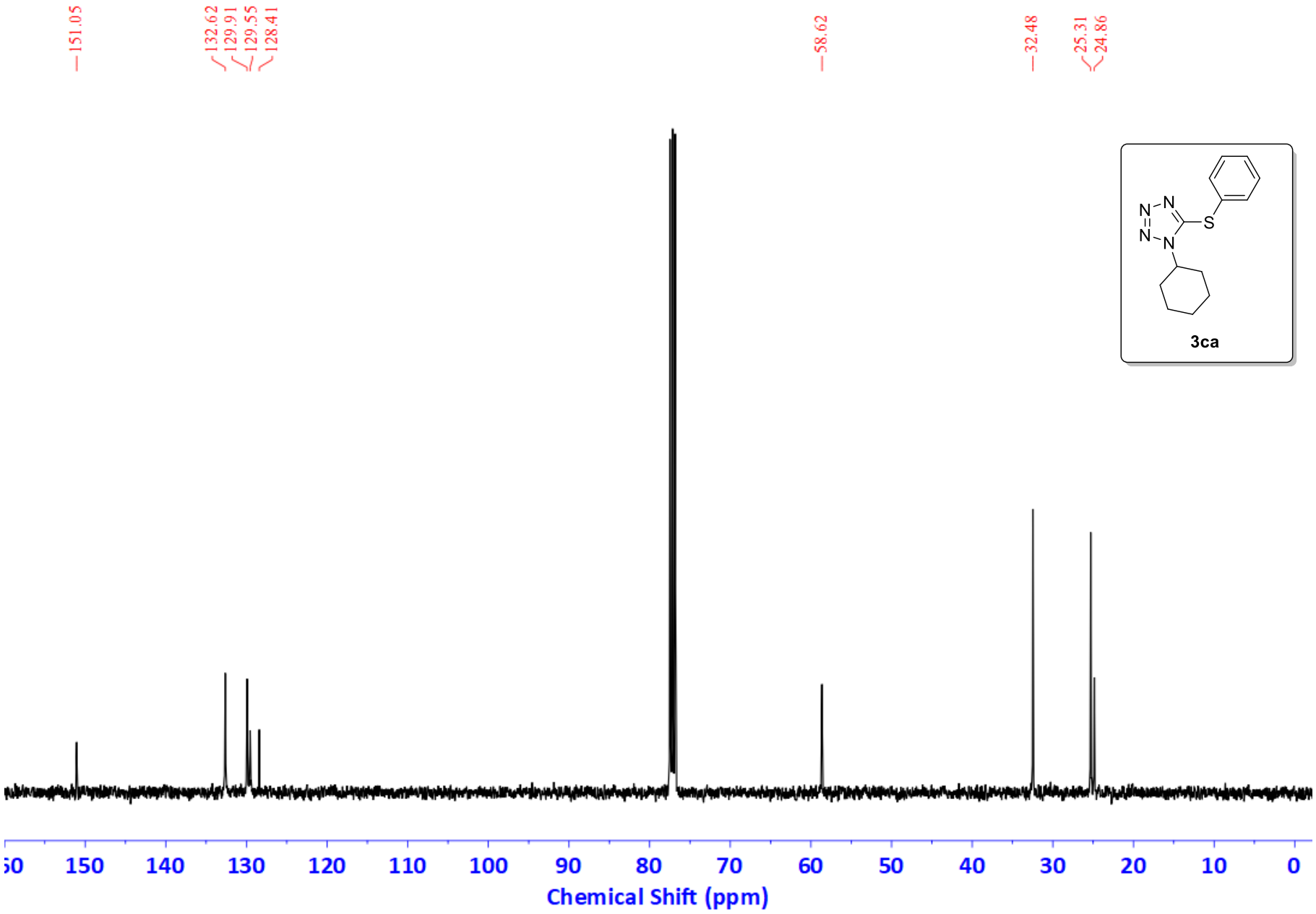

7.55
7.54
7.52
7.50
7.44
7.41
Br
N
N
N
N
S
3bb
7.03
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

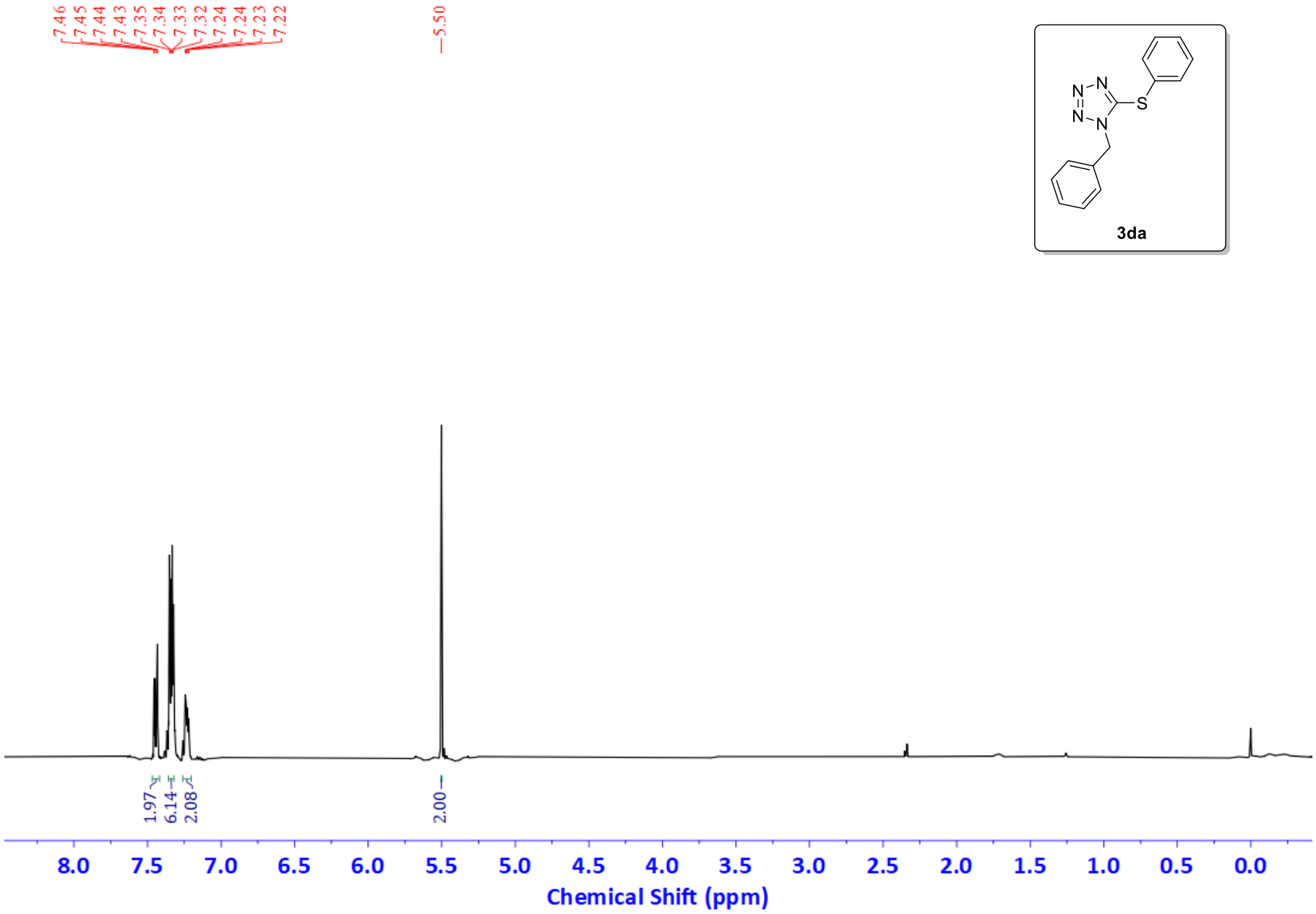

153.21
135.61
133.55
133.14
130.61
129.98
125.83
125.00
124.49
Br
N
N
N
N
S
3bb
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

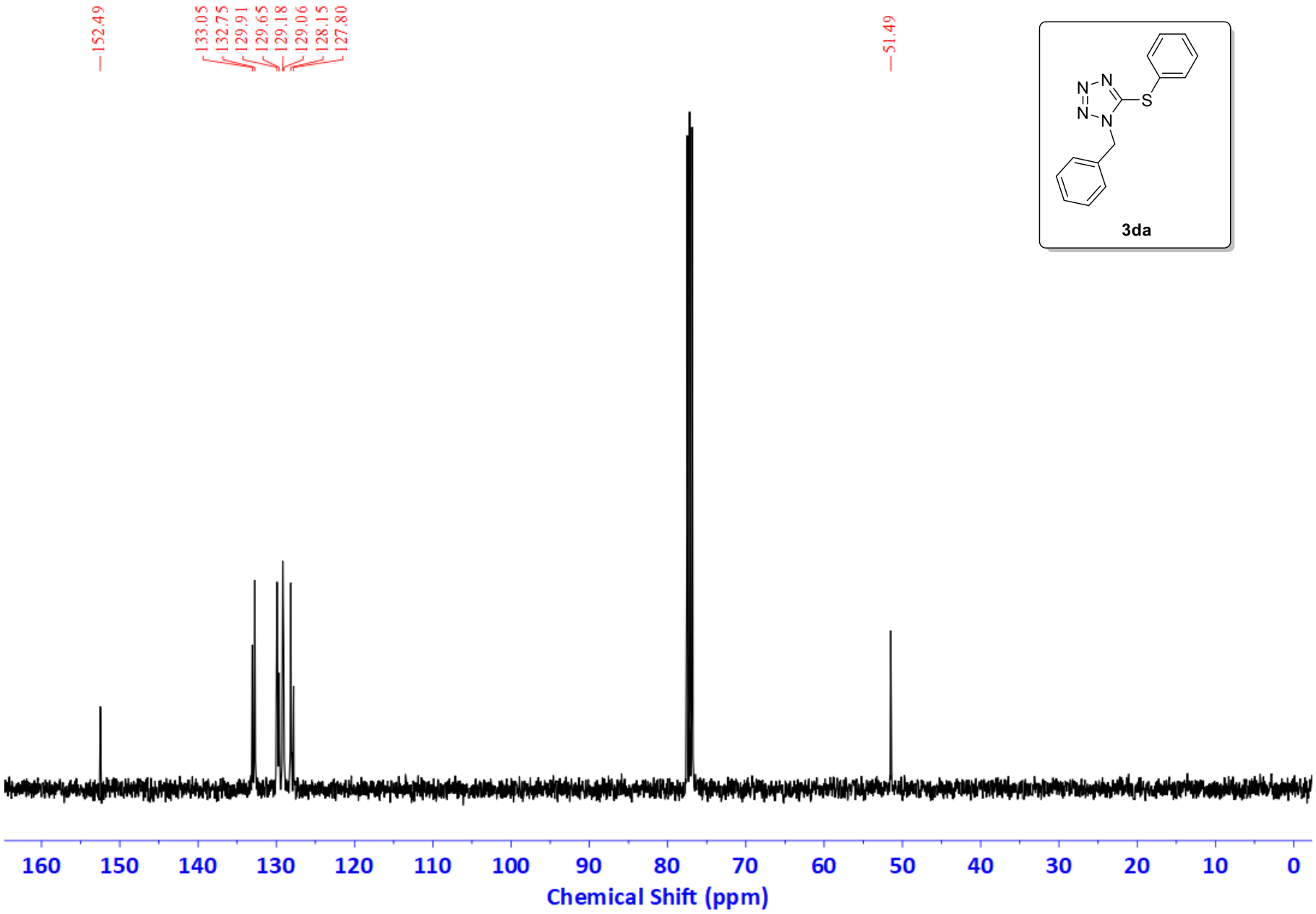

7.64
7.58
7.57
7.56
7.52
7.52
7.51
7.50
CN
N
N
N
S
3bc
4.00
5.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

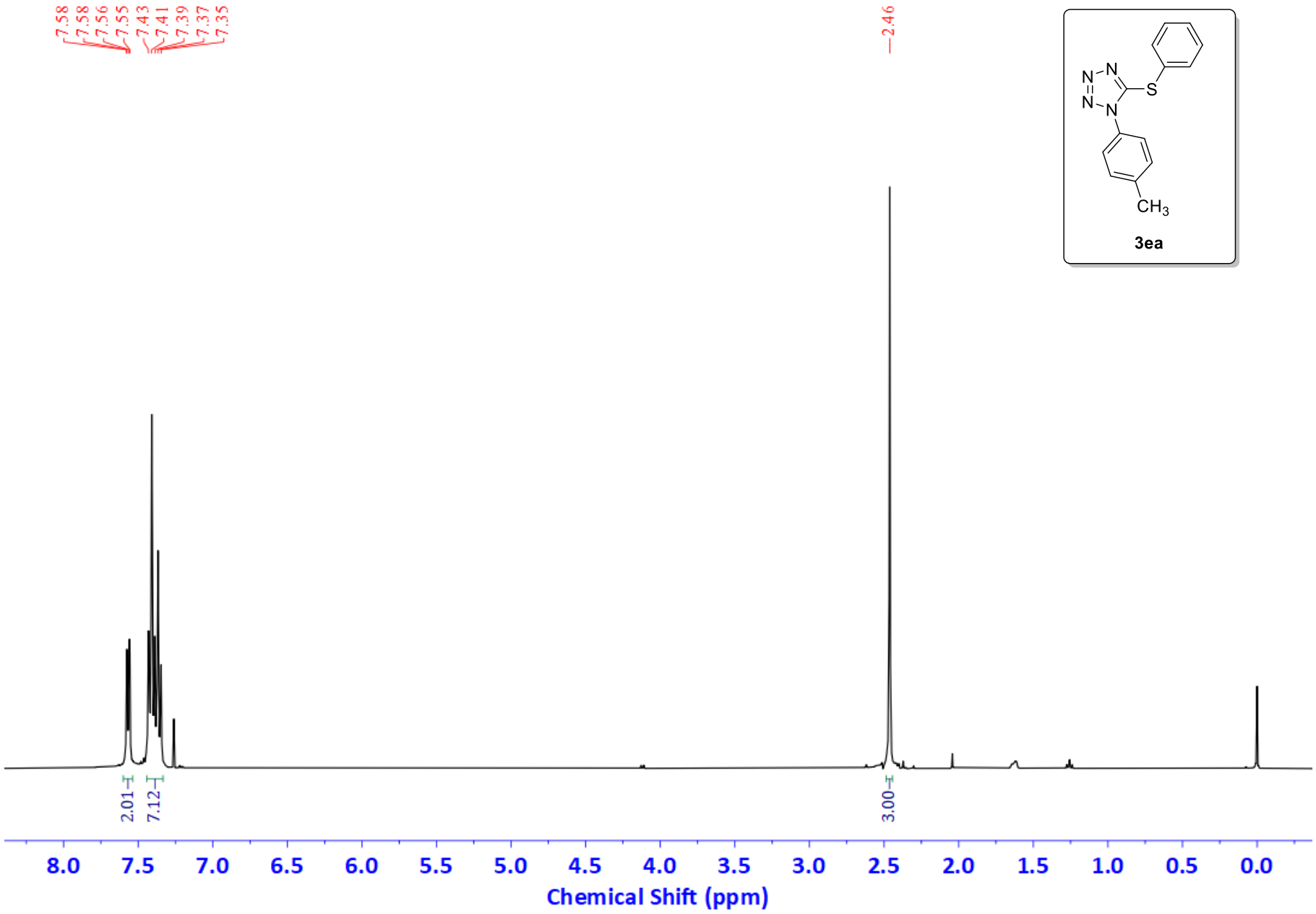

151.65
133.81
133.16
133.04
130.90
130.06
124.54
117.84
113.41
CN
N
N
N
S
3bc
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

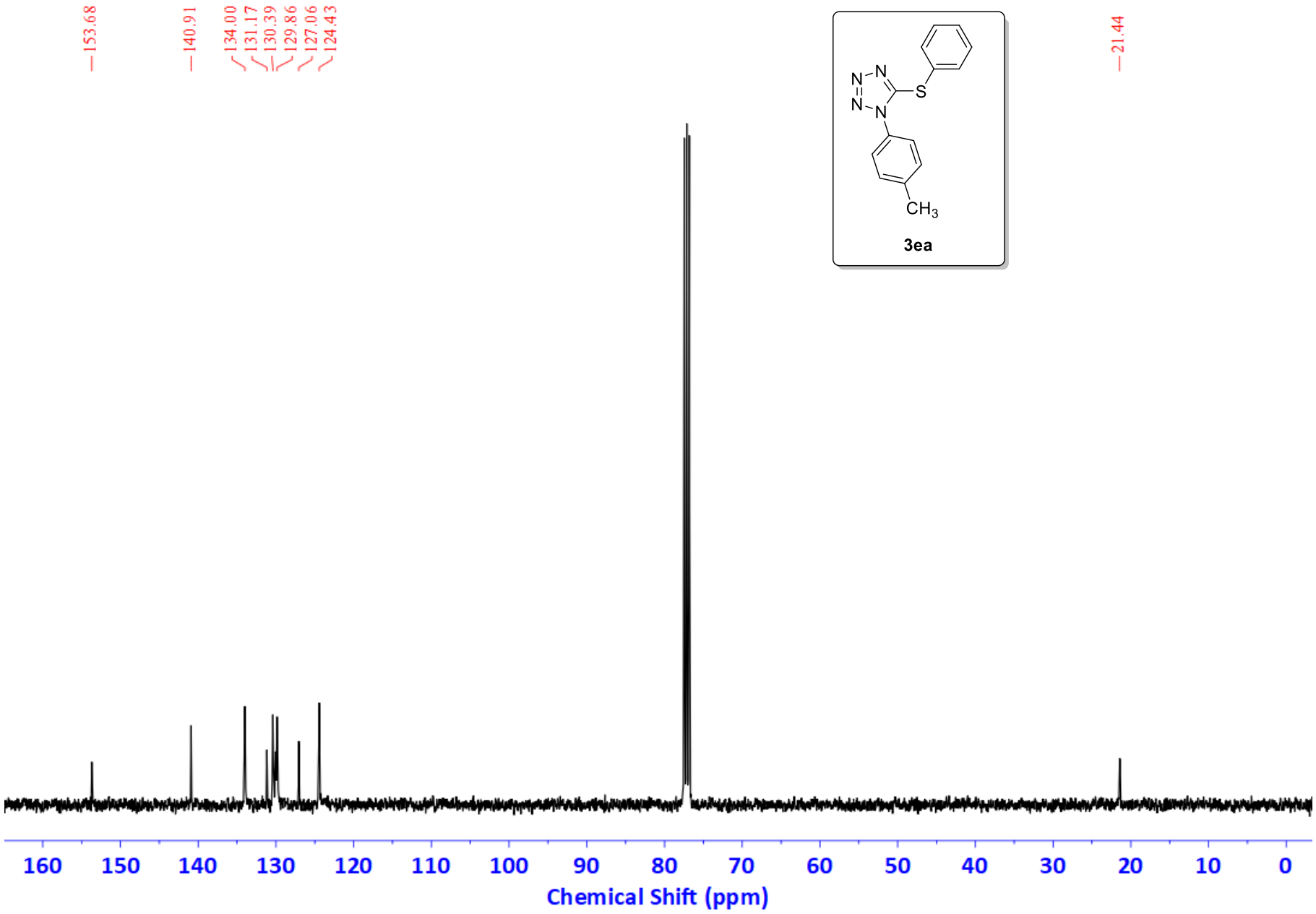

7.54
7.53
7.52
7.51
7.40
7.39
7.38
4.39
4.37
4.35
4.32
4.31
1.95
1.93
1.90
1.39
1.36
1.33
1.31
1.28
3ca
2.00
3.01
1.09
6.15
3.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

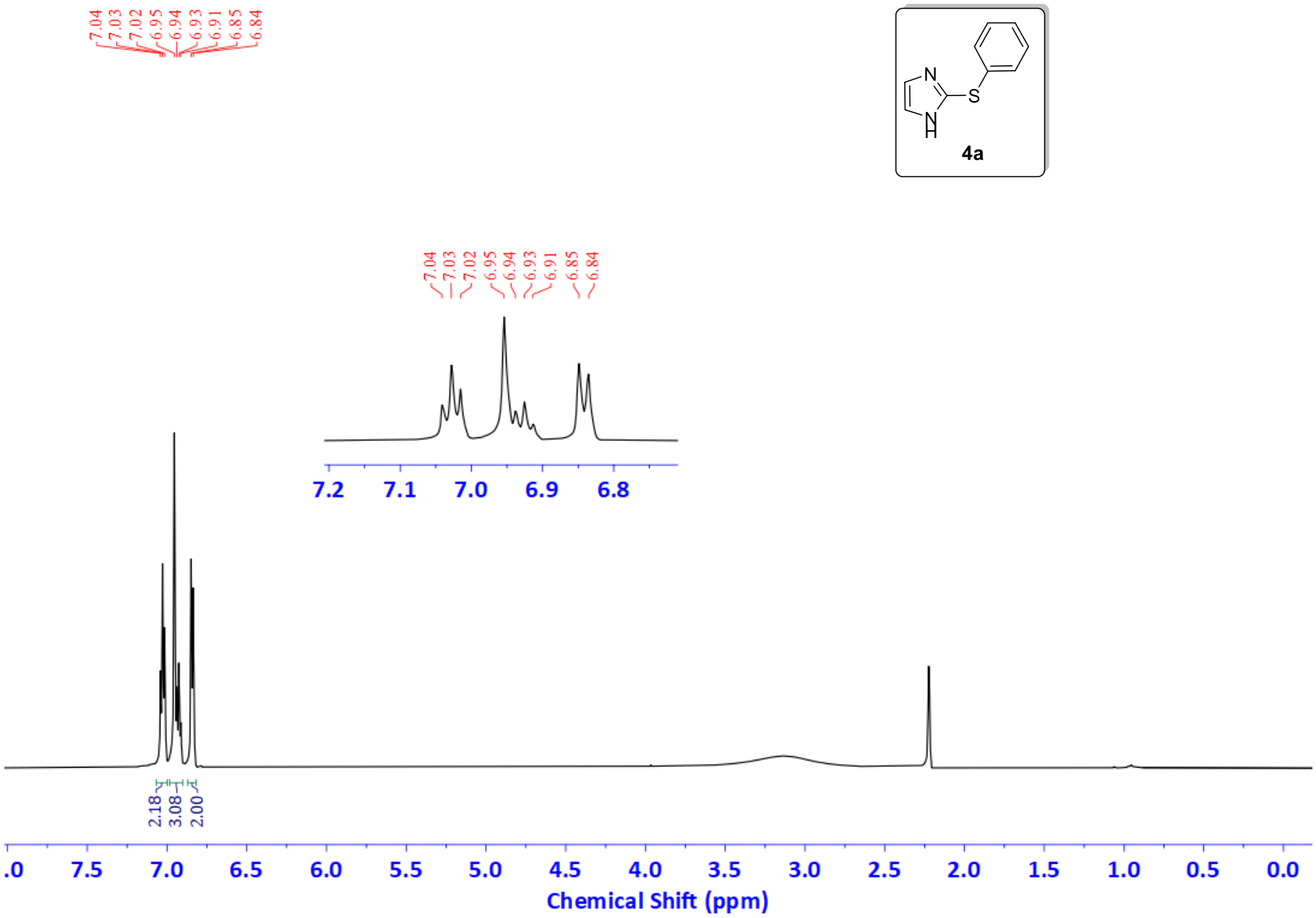

151.05
132.62
129.91
129.55
128.41
58.62
32.48
25.31
24.86
N
N
N
S
3ca
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

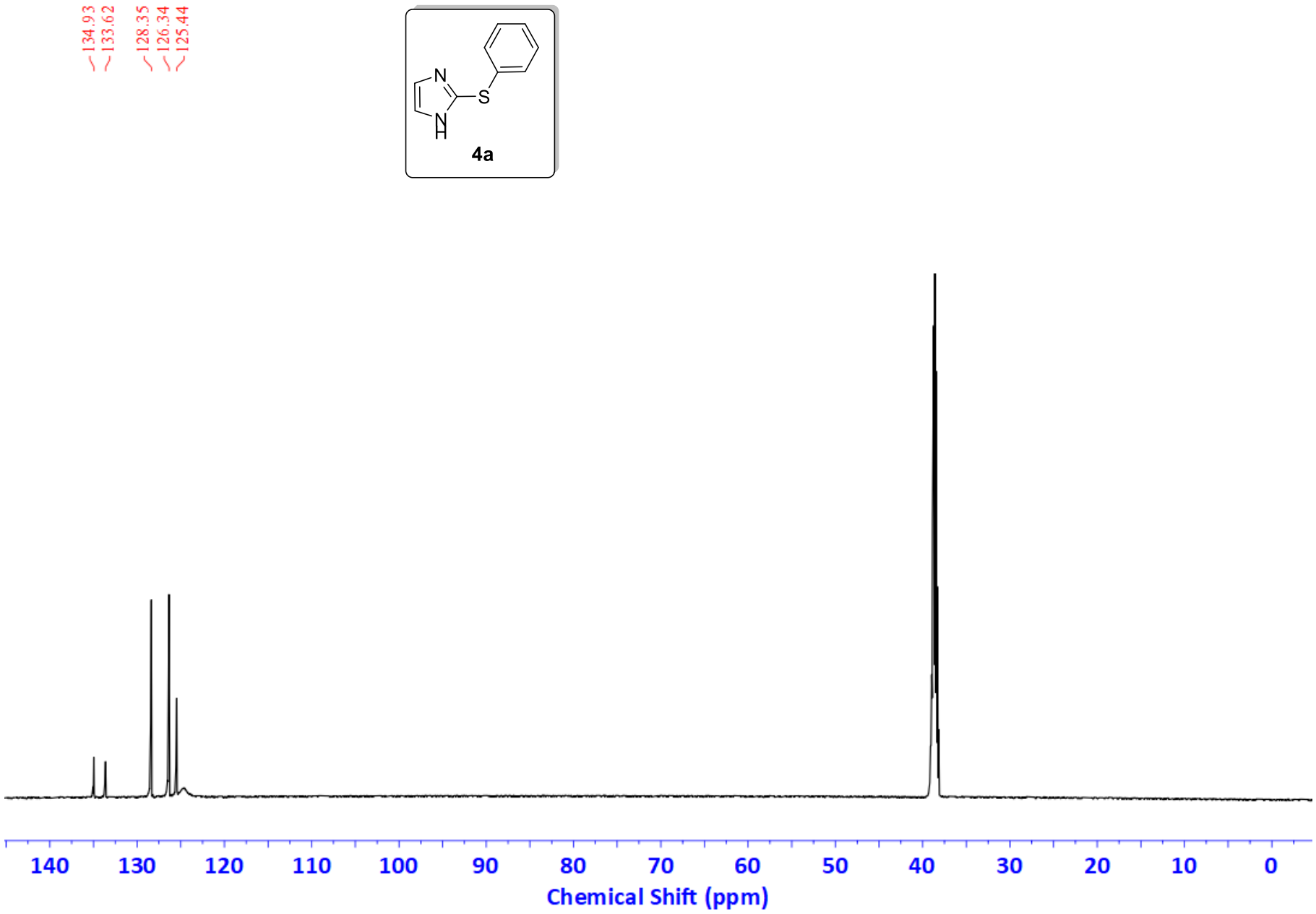

7.46
7.45
7.44
7.43
7.35
7.34
7.33
7.32
7.24
7.24
7.23
7.22
5.50
3da
1.97
6.14
2.08
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

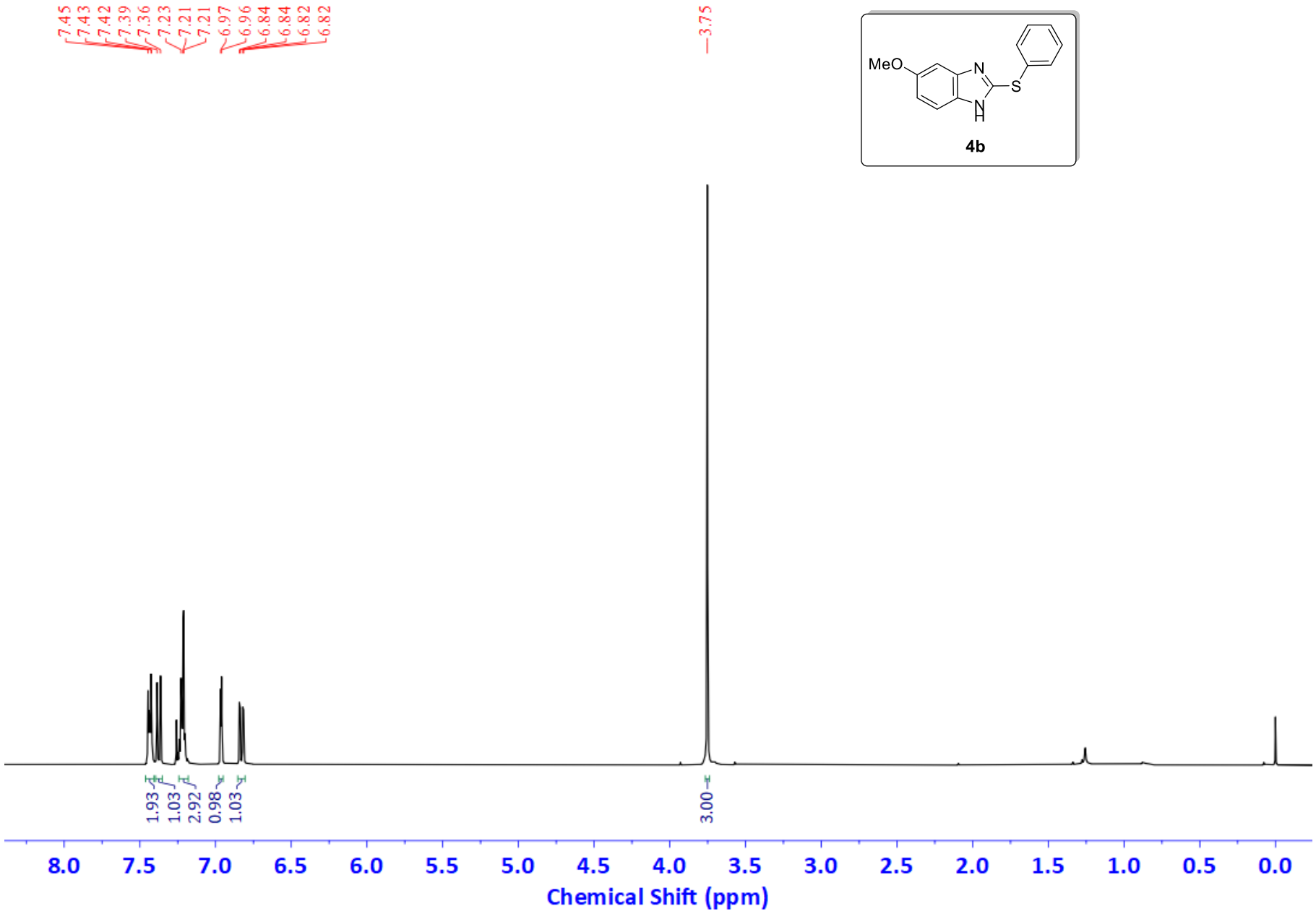

152.49
133.05
132.75
129.91
129.65
129.18
129.06
128.15
127.80
51.49
N
N
N
S
3da
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

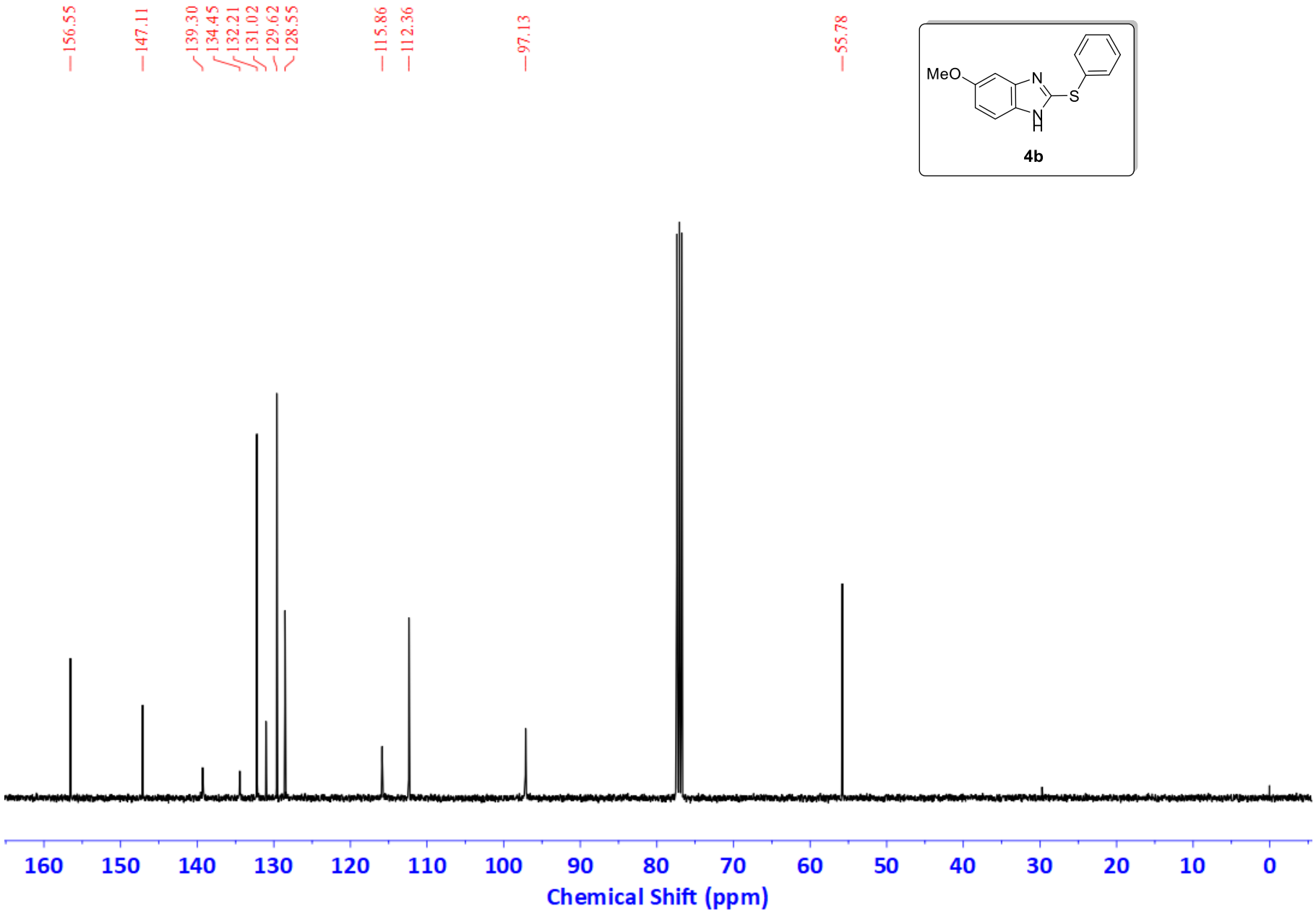

7.58
7.58
7.56
7.55
7.43
7.41
7.39
7.37
7.35
2.46
2.01
7.12
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)
N
N
N
S
CH3
3ea

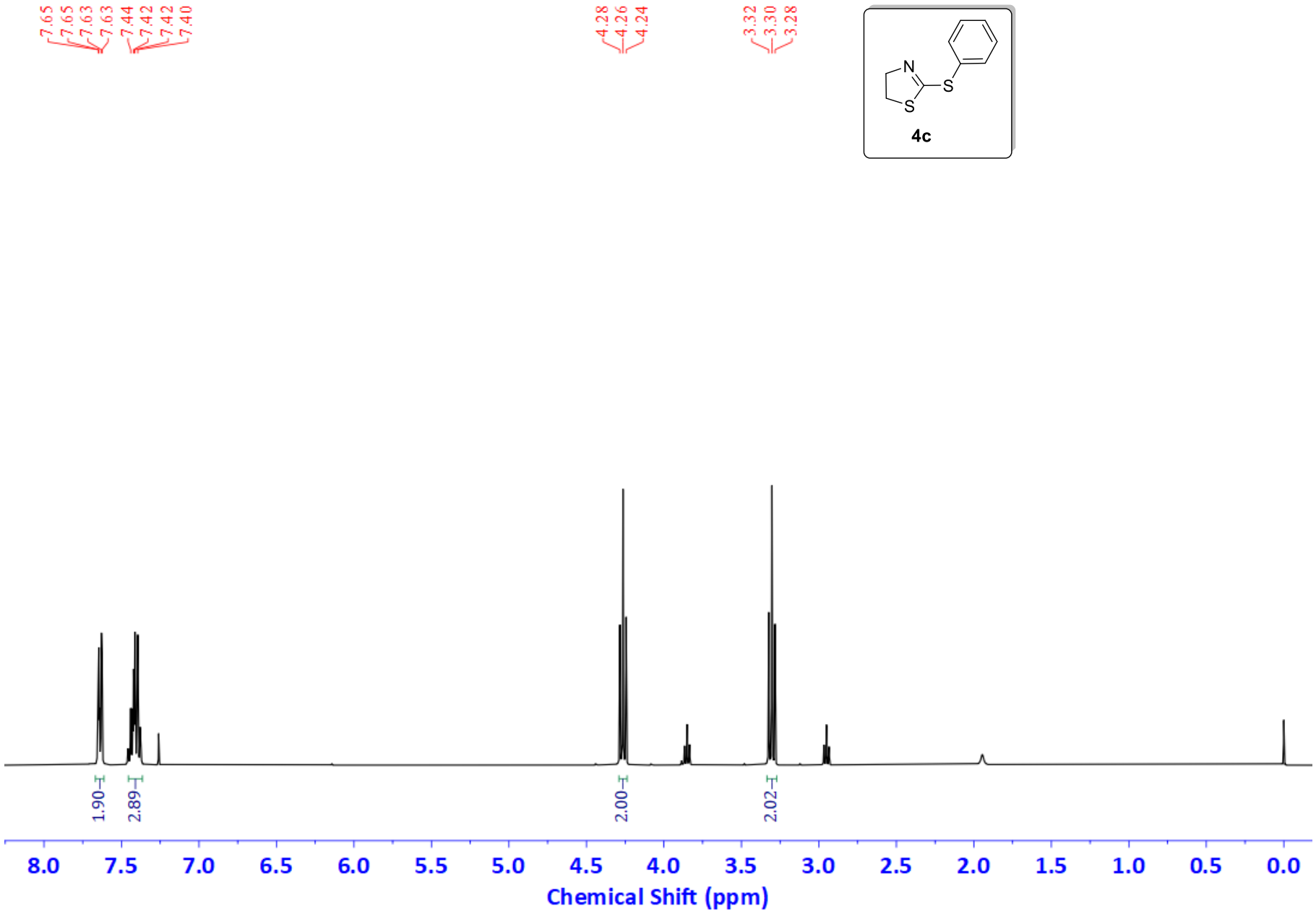

153.68
140.91
134.00
131.17
130.39
129.86
127.06
124.43
21.44
N
N
N
S
CH3
3ea
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

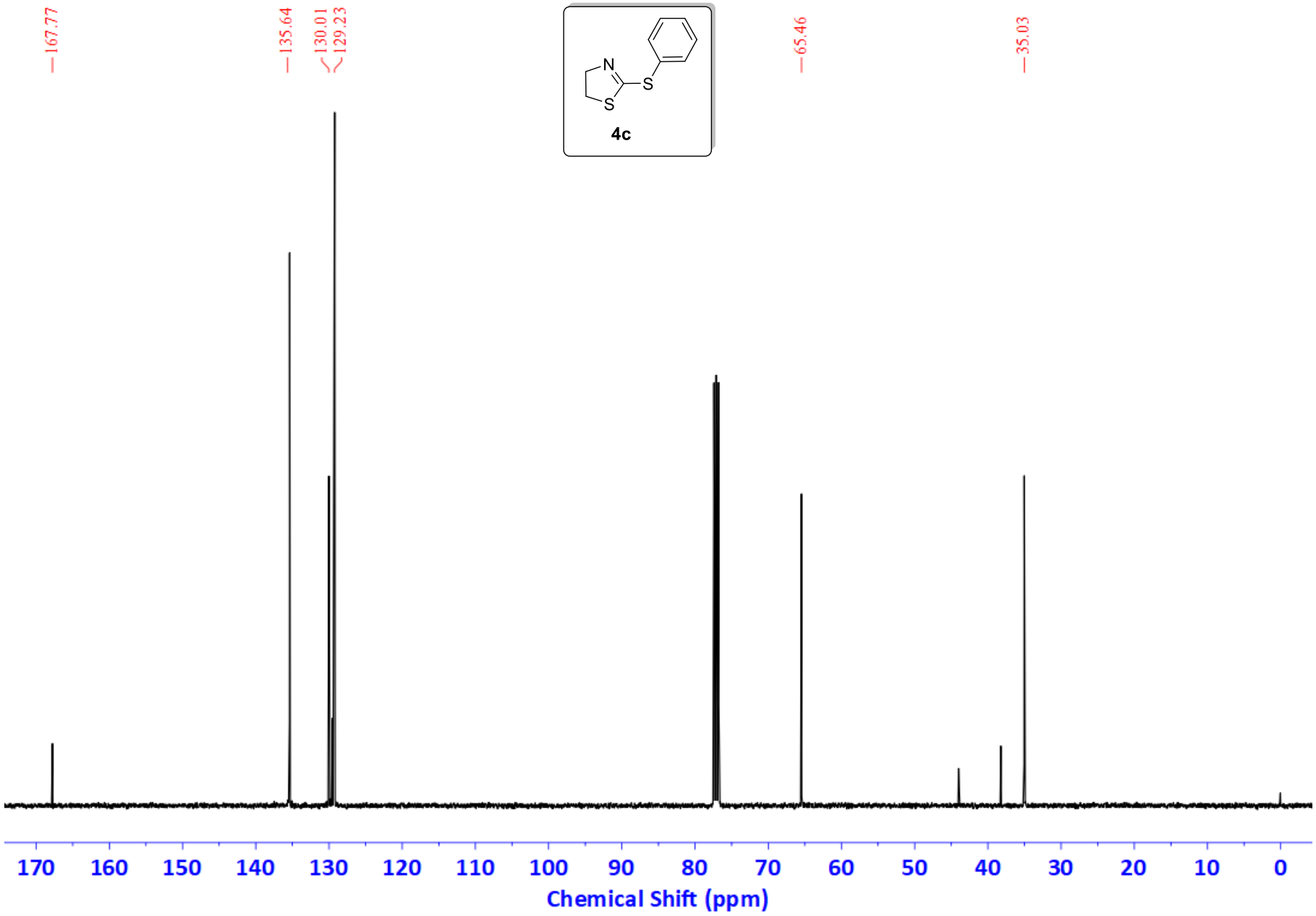

7.04
7.03
7.02
6.95
6.94
6.93
6.91
6.85
6.84
N
S
N
H
4a
7.2
7.1
7.0
6.9
6.8
2.18
3.08
2.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


134.93
133.62
128.35
126.34
125.44
N
S
H
4a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

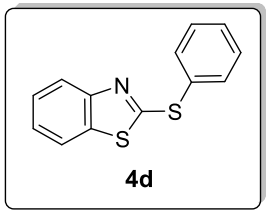

7.45
7.43
7.42
7.39
7.36
7.23
7.21
7.21
6.97
6.96
6.84
6.84
6.82
6.82
3.75
MeO
N
S
N
H
4b
1.93
1.03
2.92
0.98
1.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

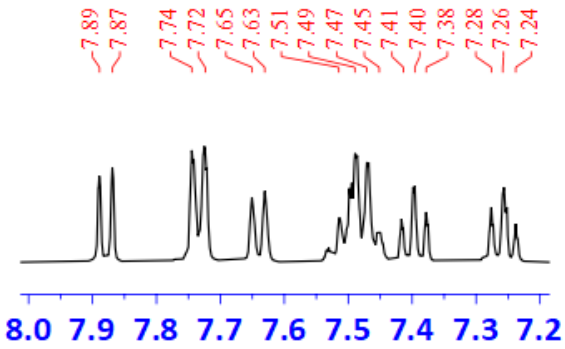

156.55
147.11
139.30
134.45
132.21
131.02
129.62
128.55
115.86
112.36
97.13
55.78
MeO
N
S
N
H
4b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

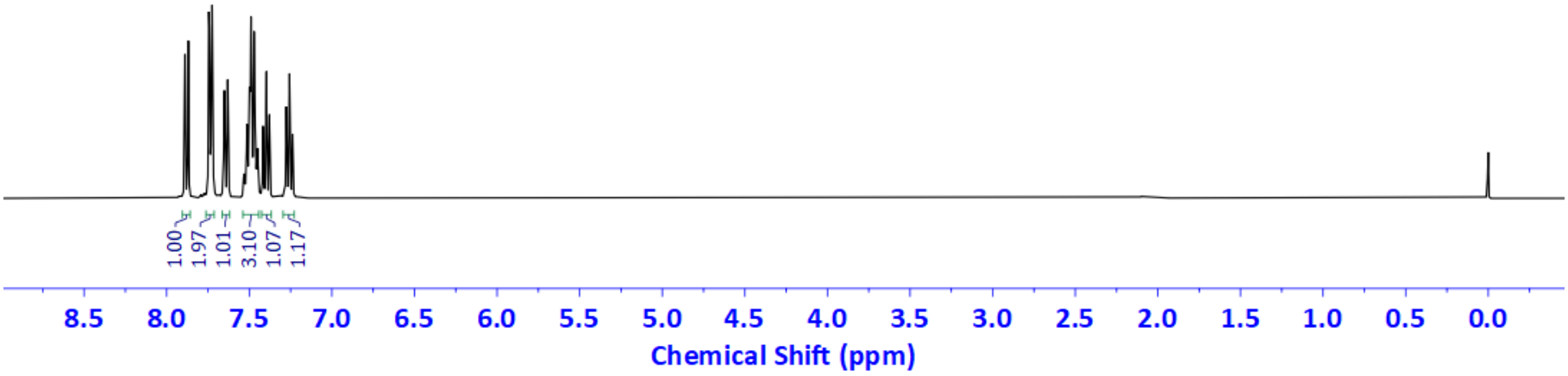

7.65
7.65
7.63
7.63
7.44
7.42
7.42
7.40
4.28
4.26
4.24
3.32
3.30
3.28
N
S
S
4c
1.90
2.89
2.00
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

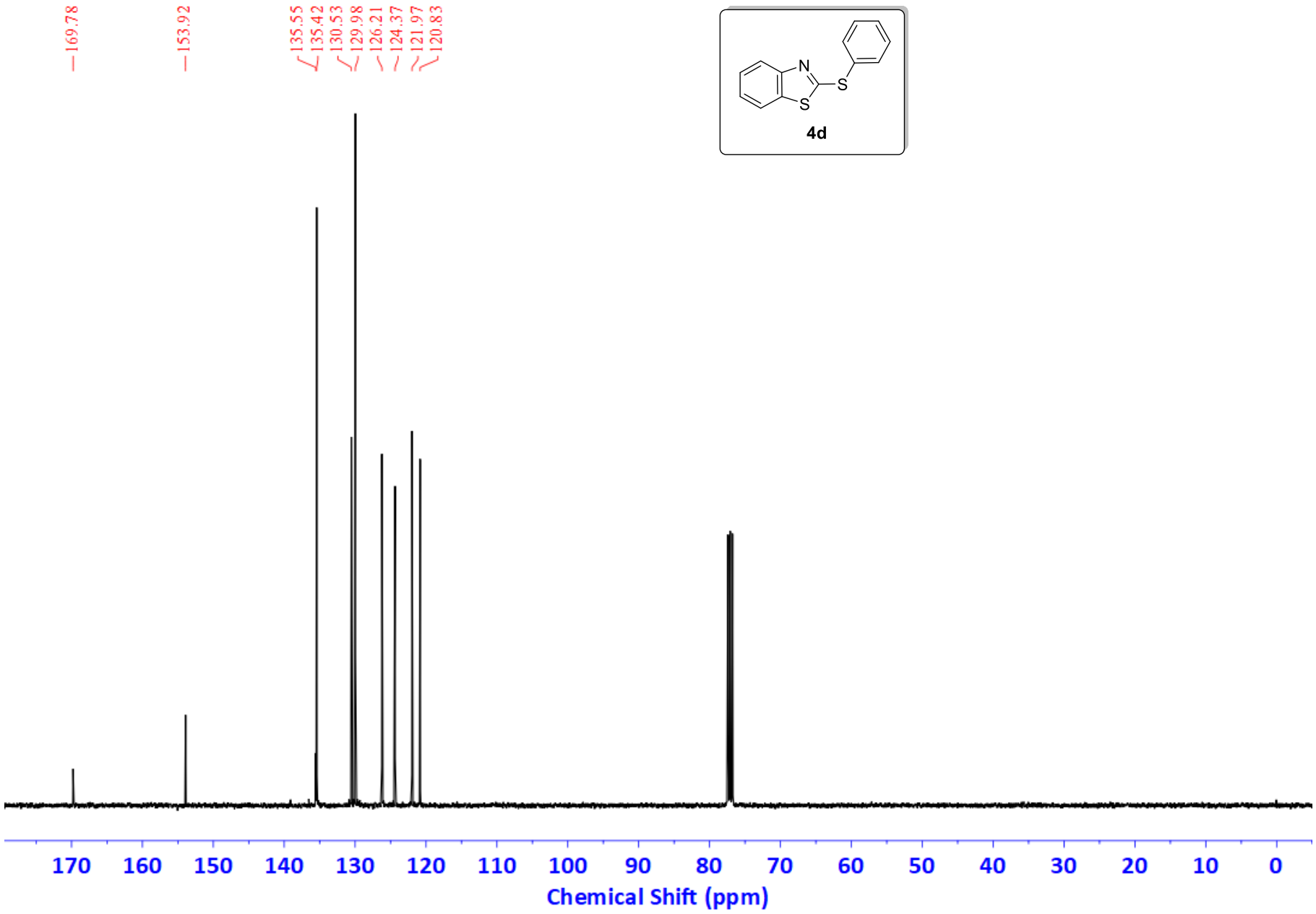

167.77
135.64
130.01
129.23
65.46
35.03
N
S
S
4c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

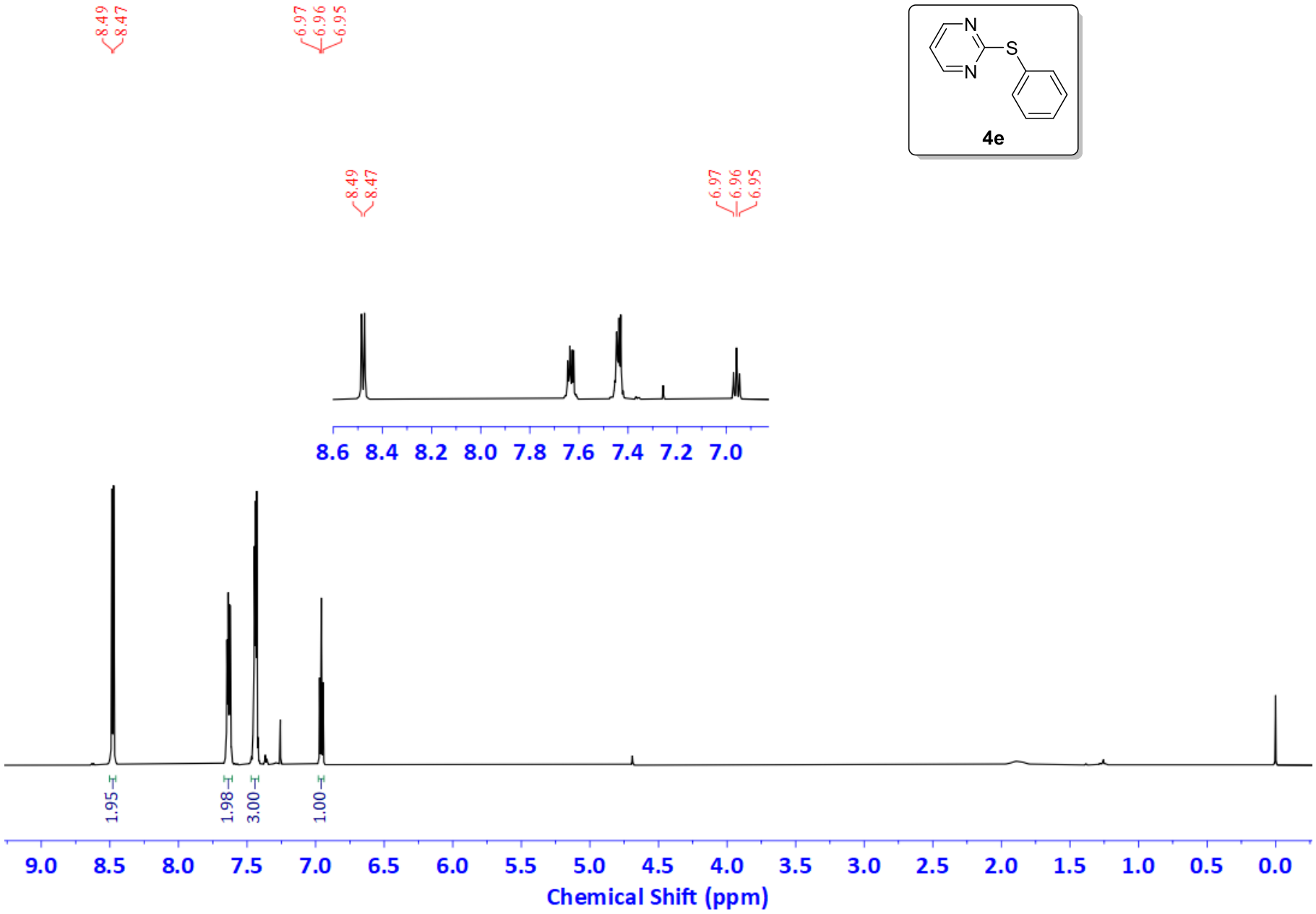

7.89
7.87
7.74
7.72
7.65
7.63
7.51
7.49
7.47
7.45
7.41
7.40
7.38
7.28
7.26
7.24

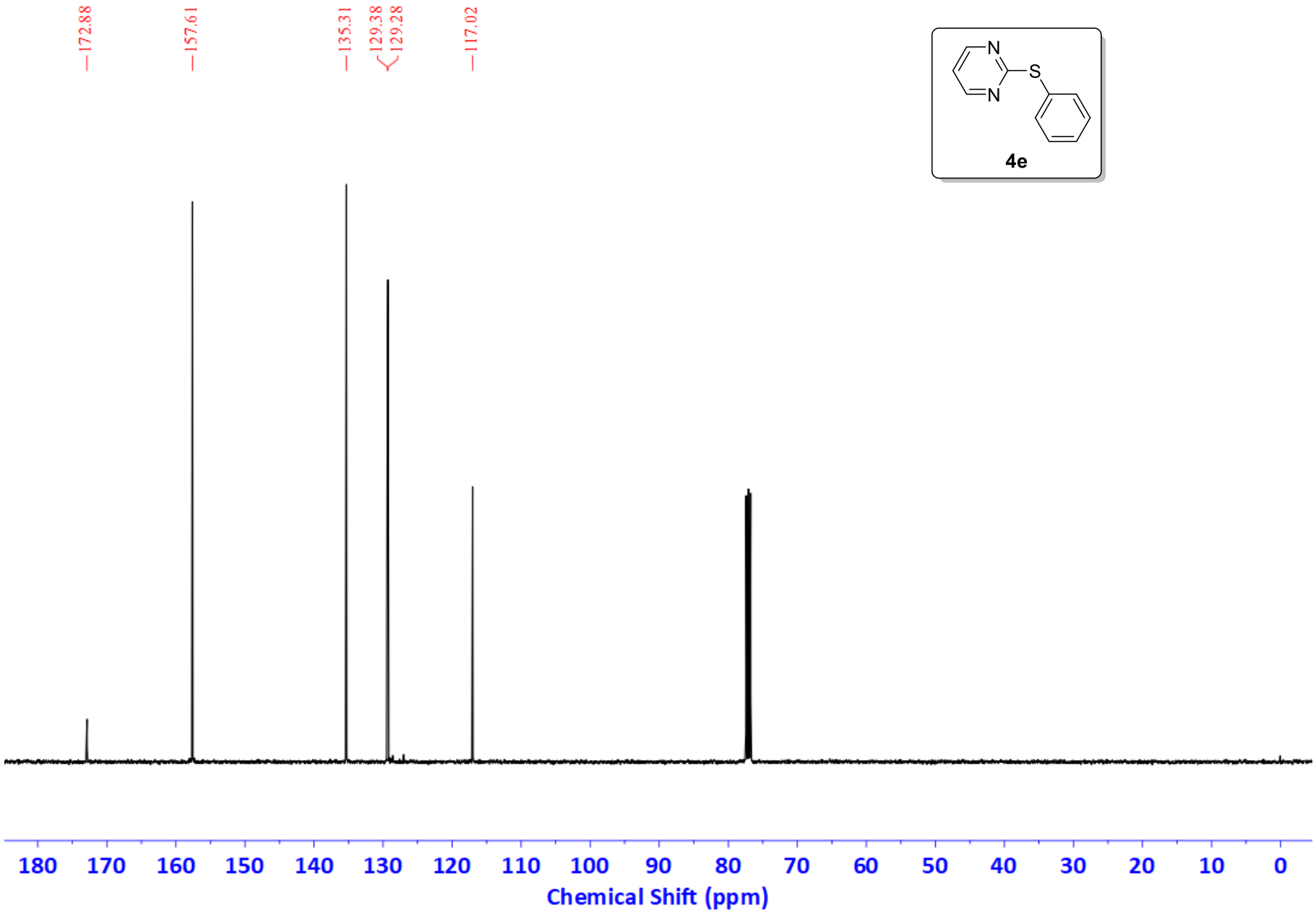

N
S
S
4d

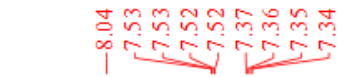

7.89
7.87
7.74
7.72
7.65
7.63
7.51
7.49
7.47
7.45
7.41
7.40
7.38
7.28
7.26
7.24
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2

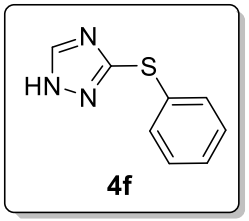

1.00
1.97
1.01
3.10
1.07
1.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)


169.78
153.92
135.55
135.42
130.53
129.98
126.21
124.37
121.97
120.83
N
S
S
4d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

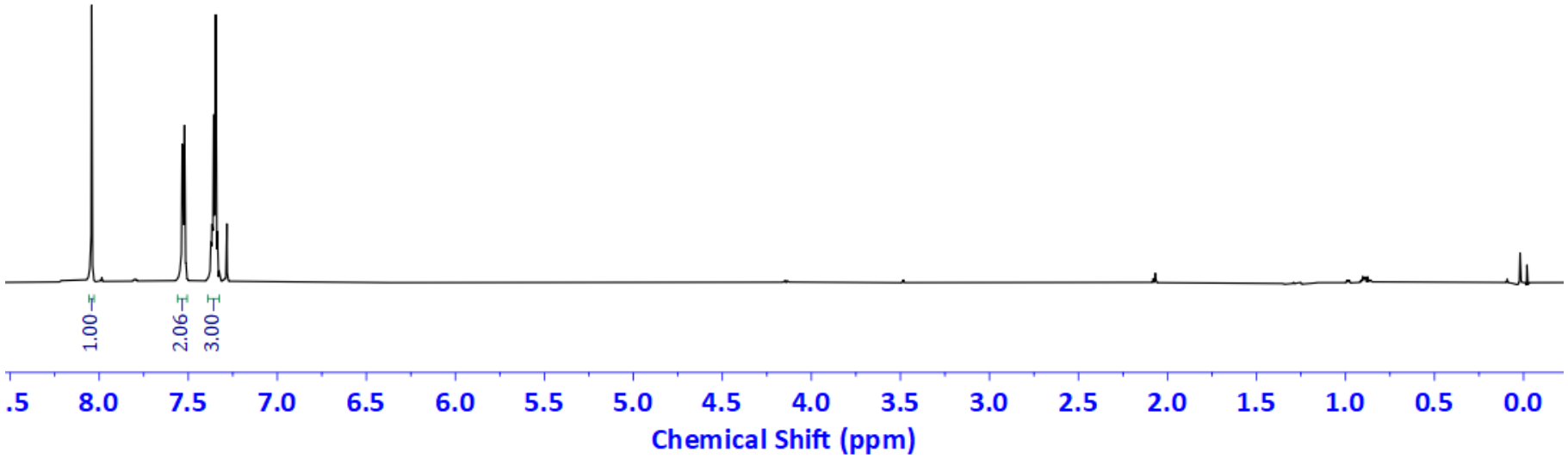

8.49
8.47
6.97
6.96
6.95
N
S
N
4e
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
1.95
1.98
3.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

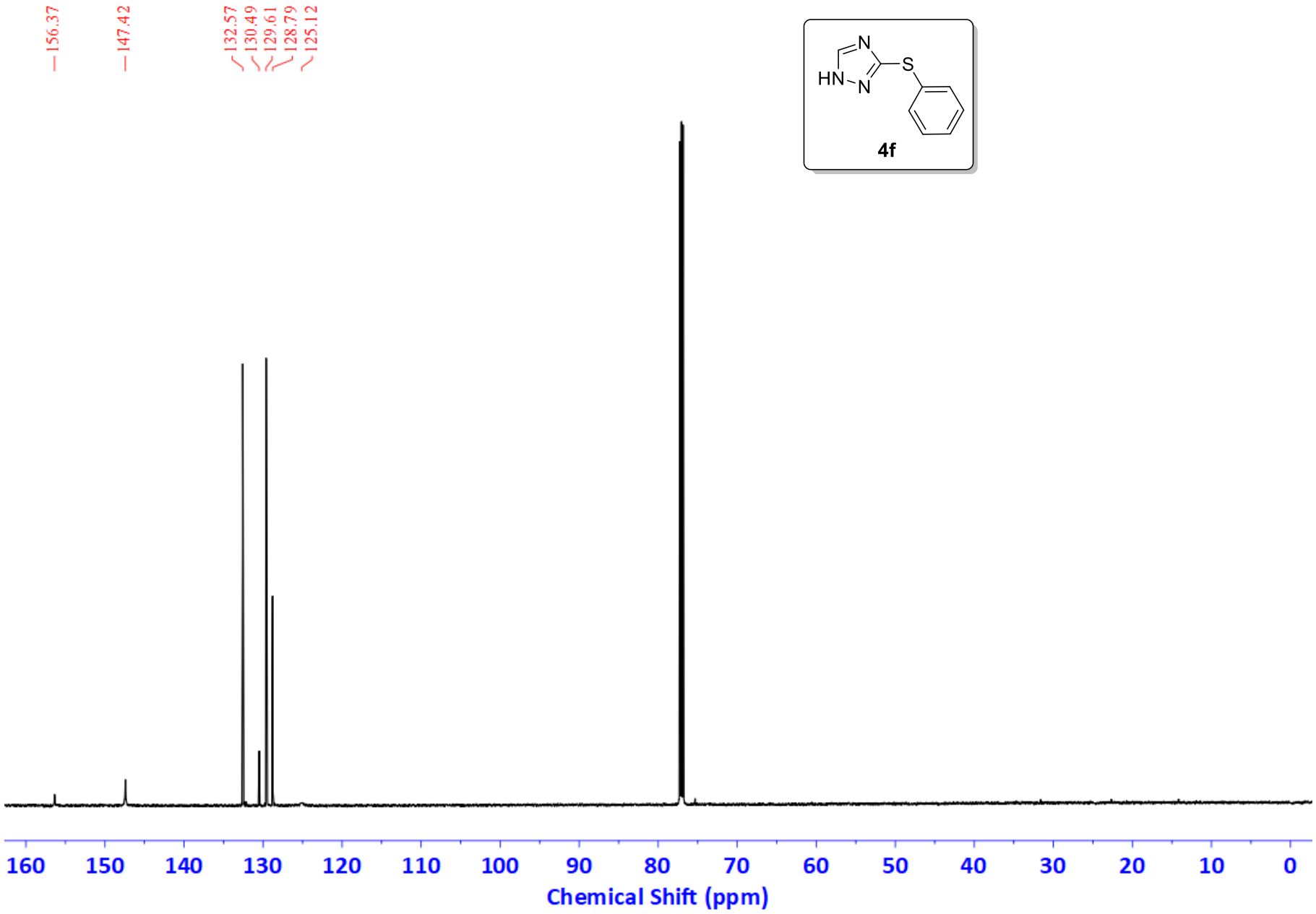

172.88
157.61
135.31
129.38
129.28
117.02
N
S
N
4e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

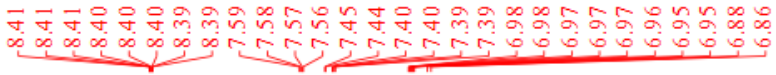

8.04
7.53
7.53
7.52
7.52
7.37
7.36
7.35
7.34

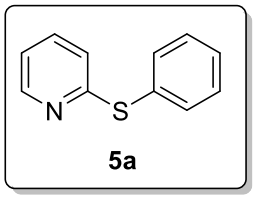

N
HN
N
S

4f


1.00
2.06
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)

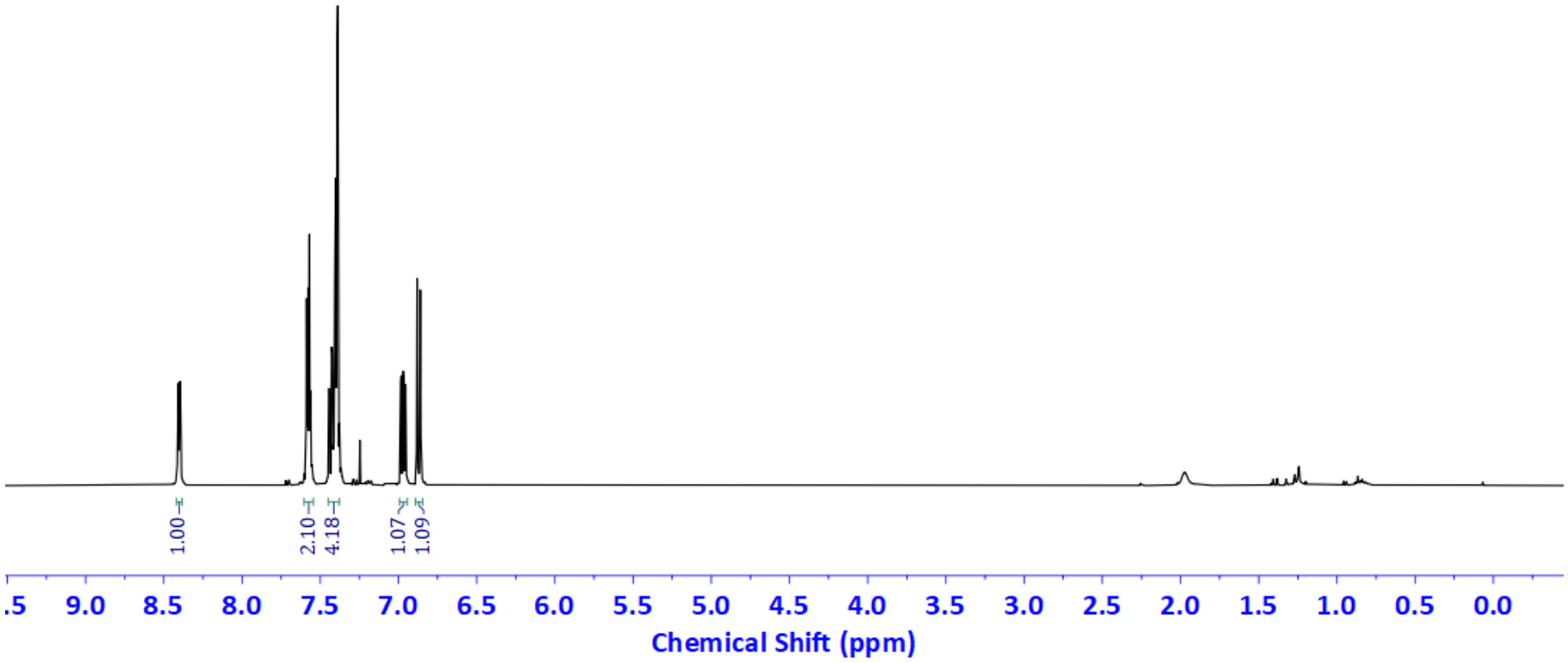

156.37
147.42
132.57
130.49
129.61
128.79
125.12
HN
N
N
S
4f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

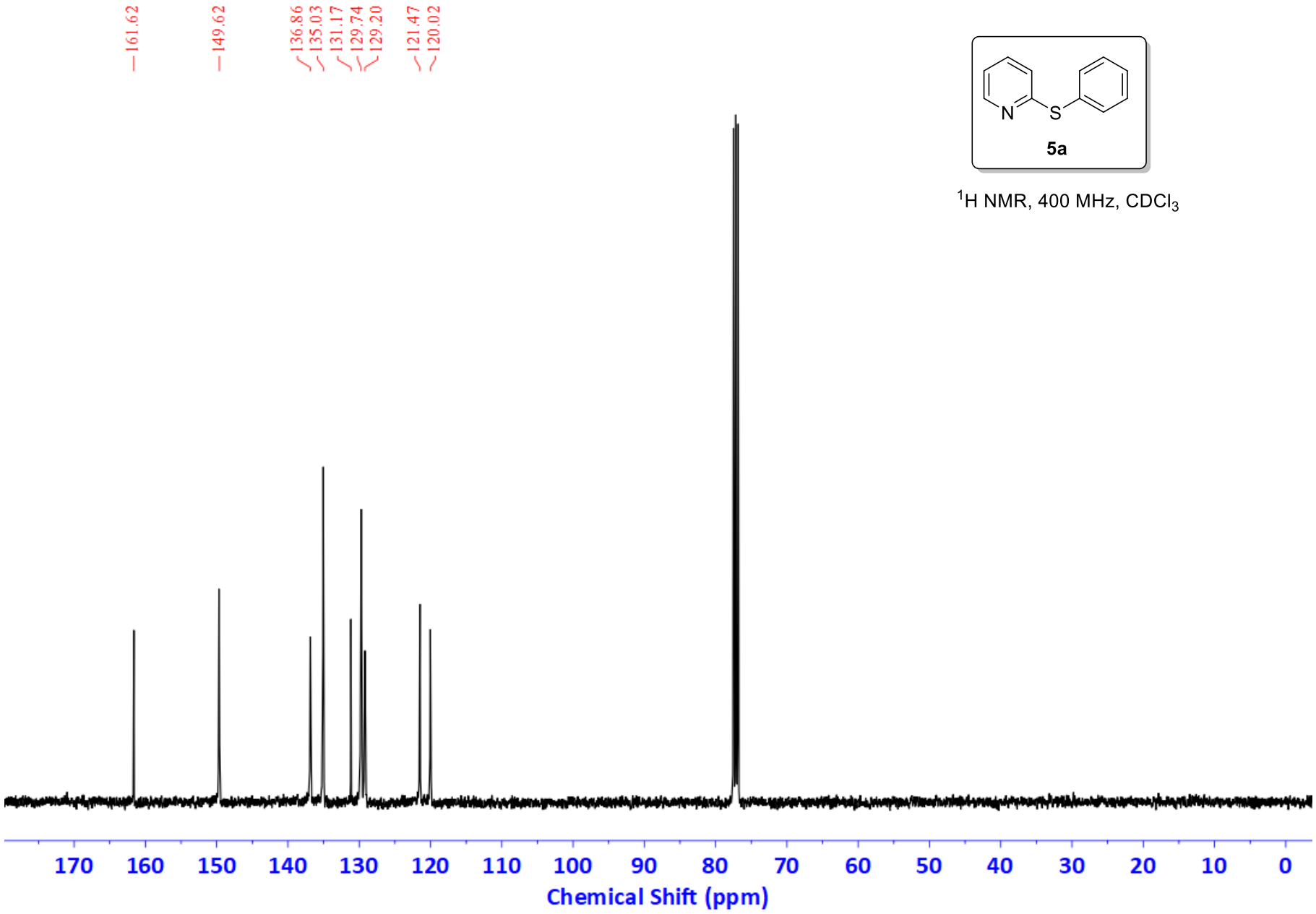




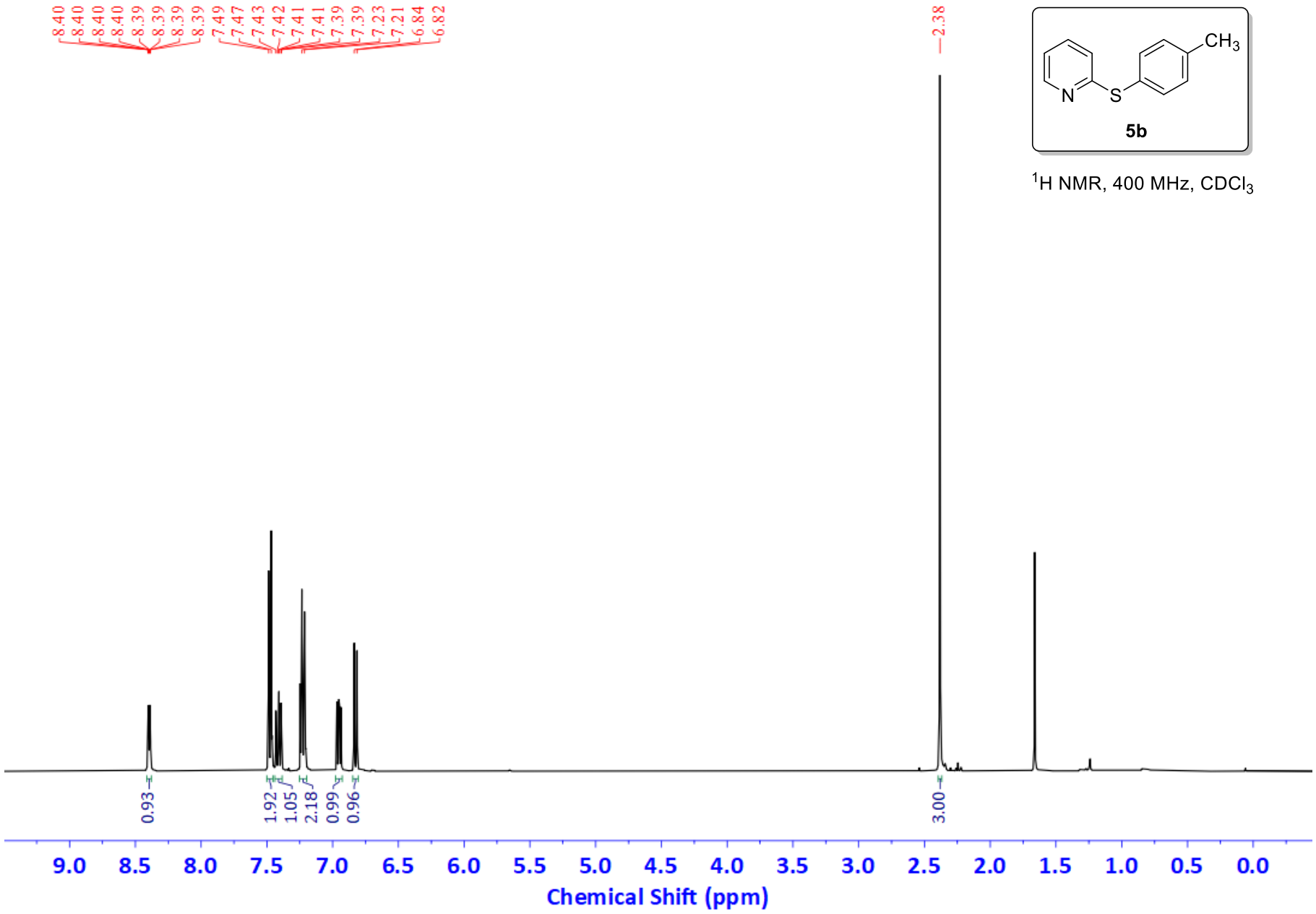
5a

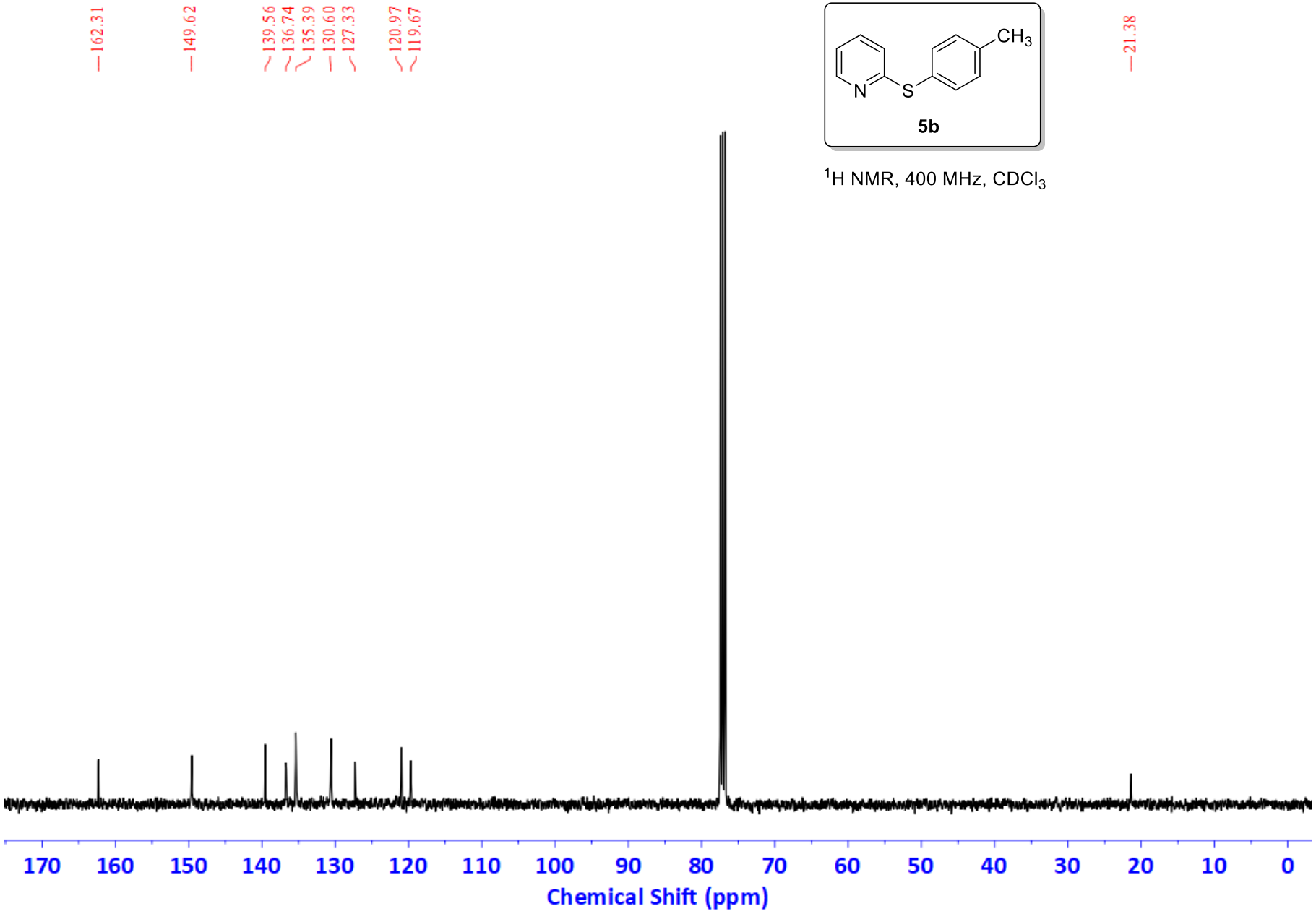
^{1}H NMR, 400 MHz, $CDCl_3$

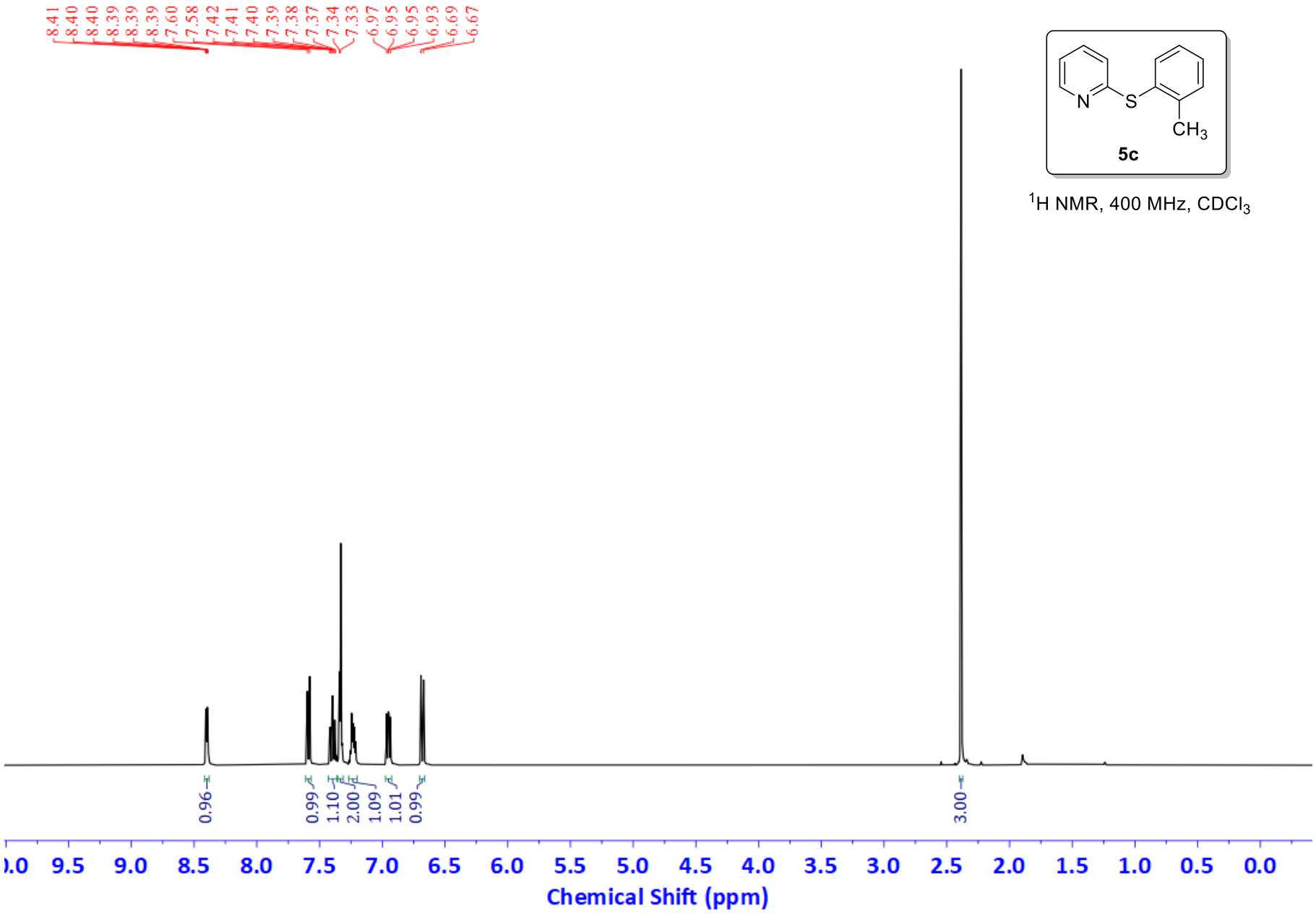


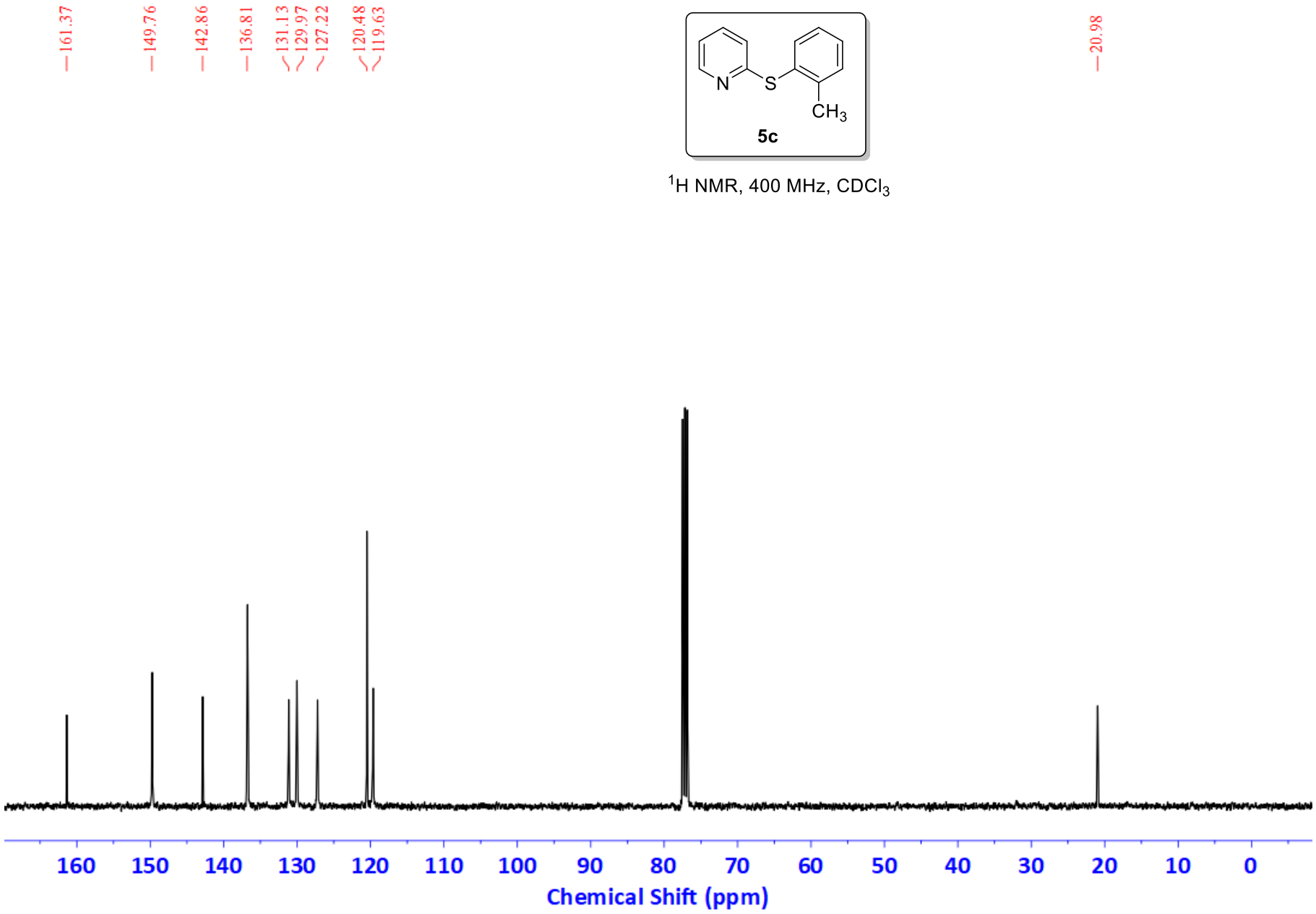


^{1}H NMR, 400 MHz, $CDCl_3$

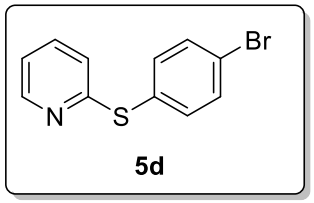

8.40
8.40
8.40
8.40
8.39
8.39
8.39
8.39
7.49
7.47
7.43
7.42
7.41
7.41
7.39
7.39
7.23
7.21
6.84
6.82
2.38
CH3
N
S
5b
1H NMR, 400 MHz, CDCl3
0.93
1.92
1.05
2.18
0.99
0.96
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


162.31
149.62
139.56
136.74
135.39
130.60
127.33
120.97
119.67
21.38
CH3
N
S
5b
1H NMR, 400 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

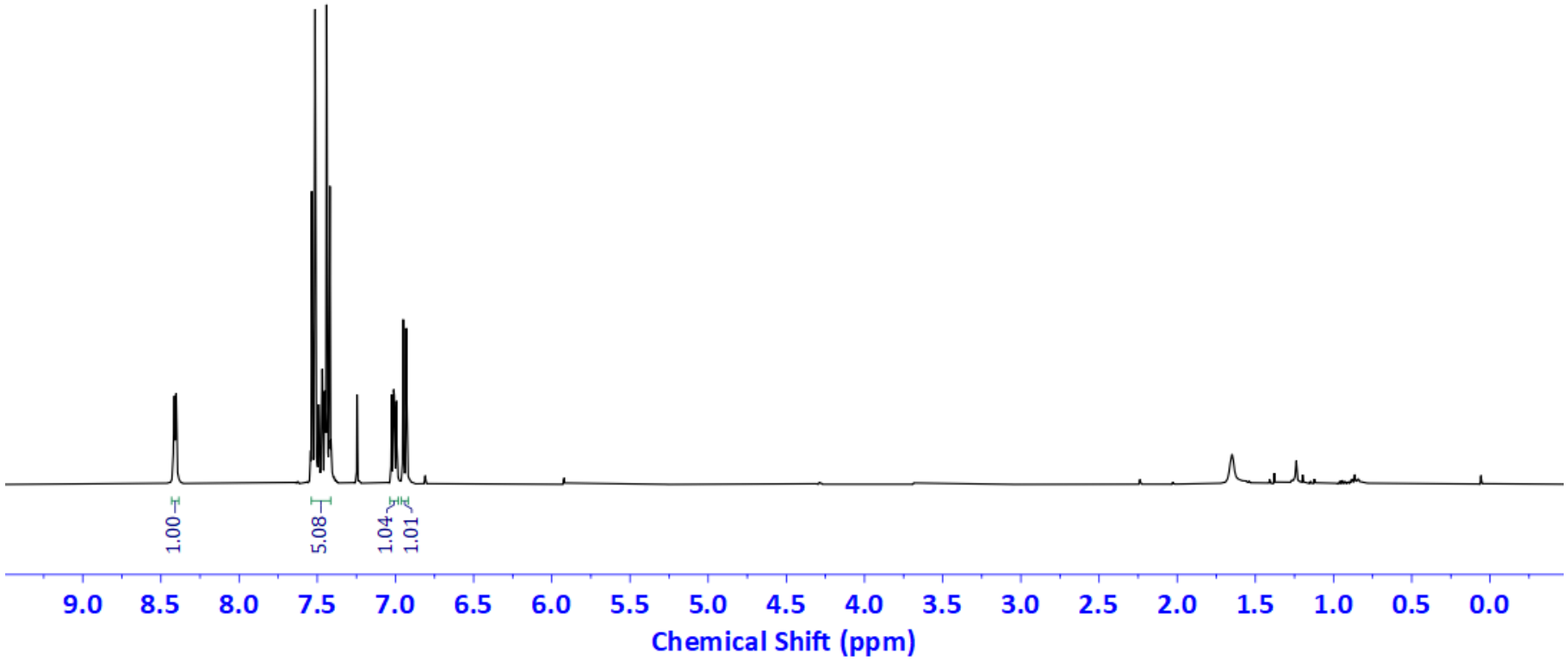

8.41
8.40
8.40
8.39
8.39
8.39
7.60
7.58
7.42
7.41
7.40
7.39
7.38
7.37
7.34
7.33
6.97
6.95
6.95
6.93
6.69
6.67
N
S
CH3
5c
1H NMR, 400 MHz, CDCl3
0.96
0.99
1.10
2.00
1.09
1.01
0.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

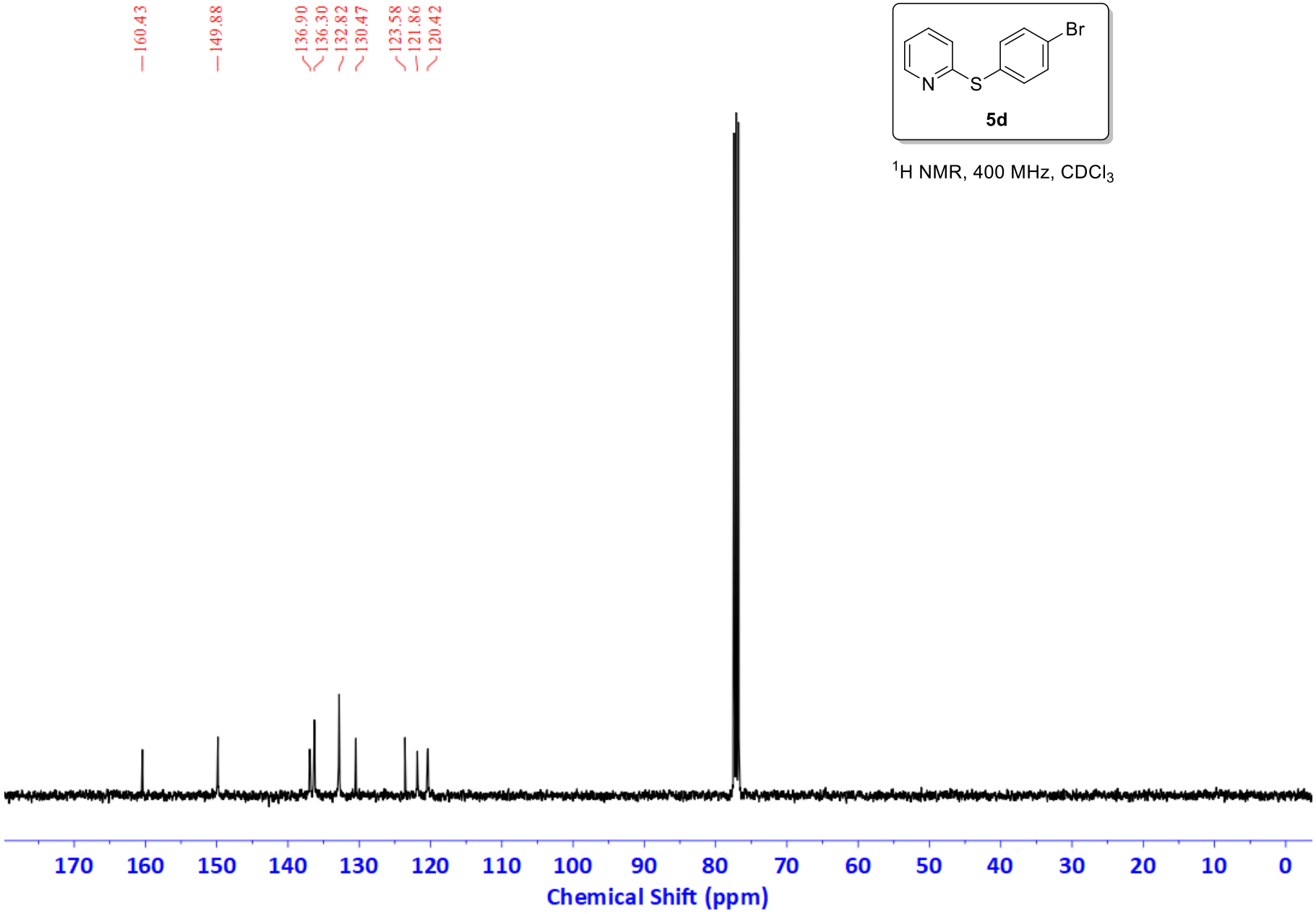


^{1}H NMR, 400 MHz, $CDCl_3$

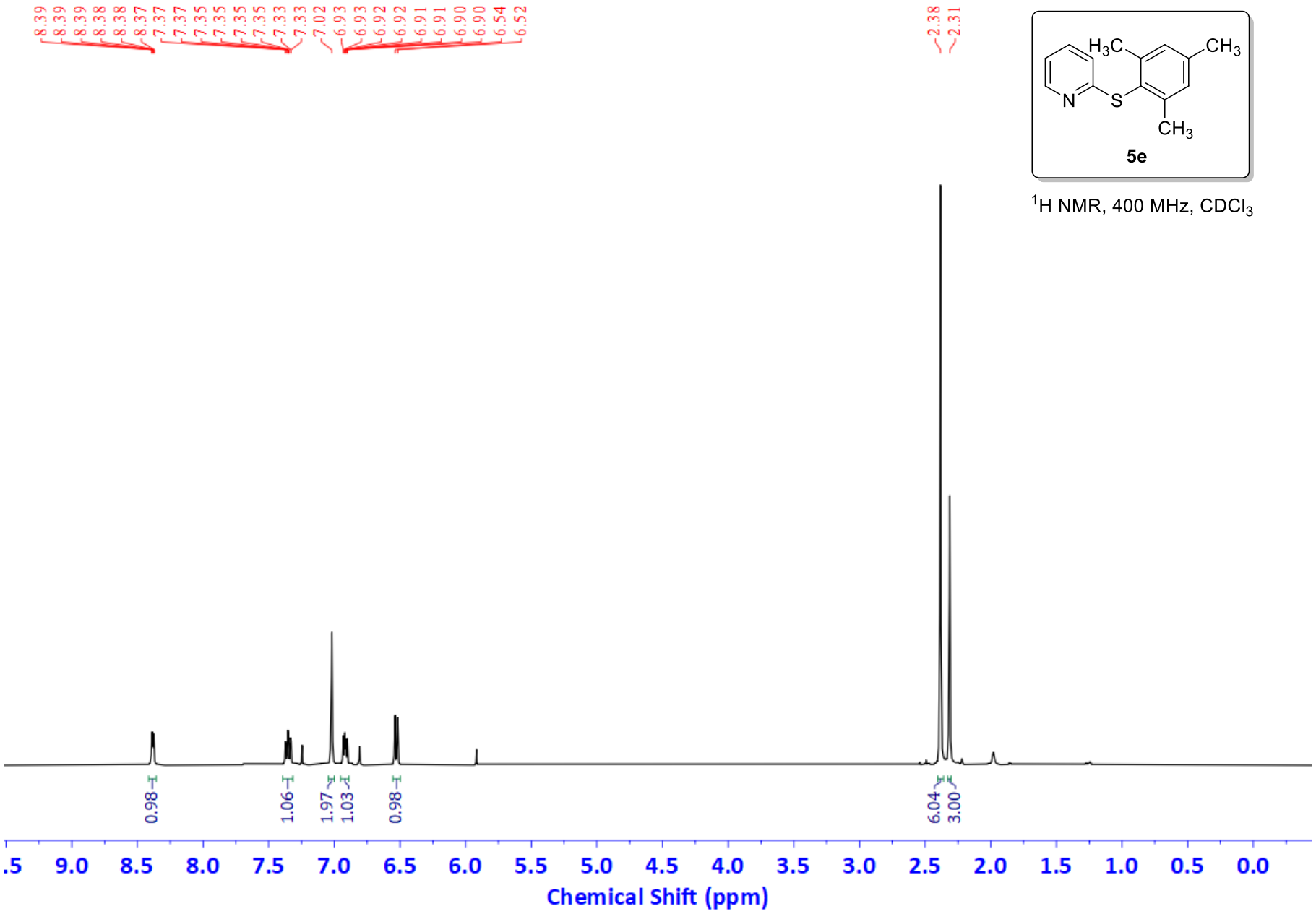


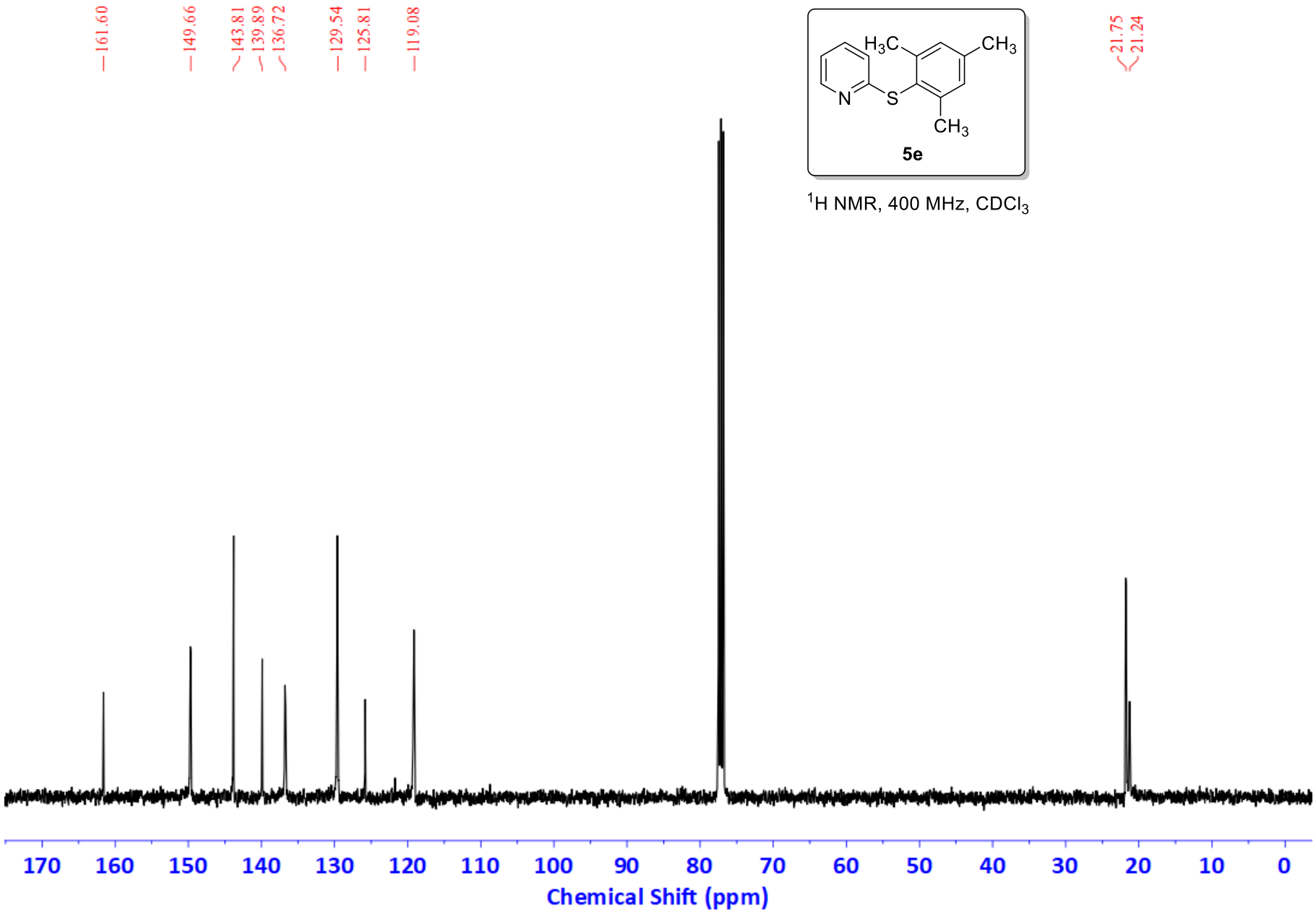
^{1}H NMR, 400 MHz, $CDCl_3$

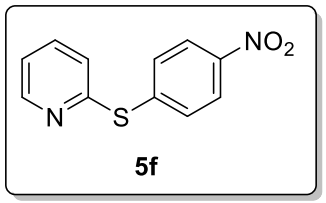




^{1}H NMR, 400 MHz, $CDCl_3$

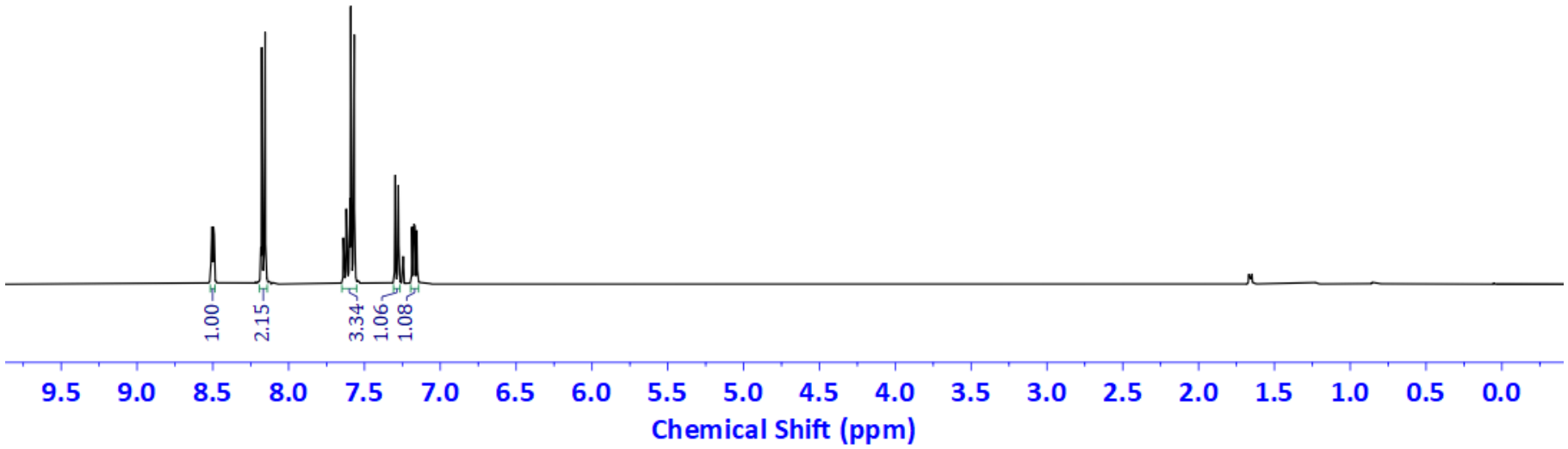

8.39
8.39
8.39
8.38
8.38
8.37
7.37
7.37
7.35
7.35
7.35
7.35
7.33
7.33
7.02
6.93
6.93
6.92
6.92
6.91
6.91
6.90
6.90
6.54
6.52
2.38
2.31
H3C
CH3
N
S
CH3
5e
1H NMR, 400 MHz, CDCl3
0.98
1.06
1.97
1.03
0.98
6.04
3.00
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

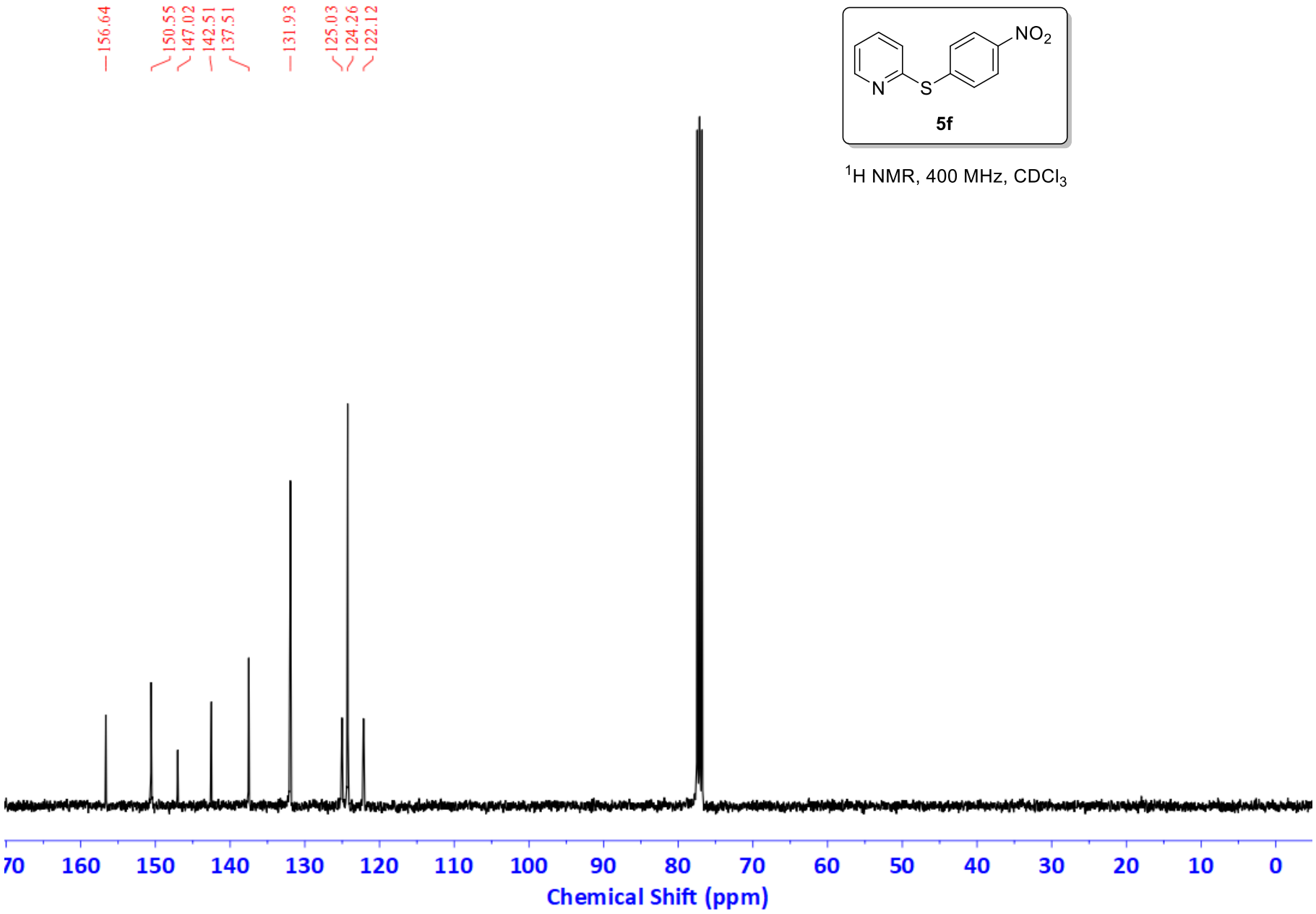

161.60
149.66
143.81
139.89
136.72
129.54
125.81
119.08
21.75
21.24
H3C
CH3
N
S
CH3
5e
1H NMR, 400 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

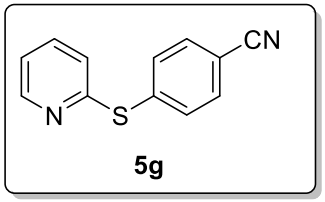


5f

^{1}H NMR, 400 MHz, $CDCl_3$

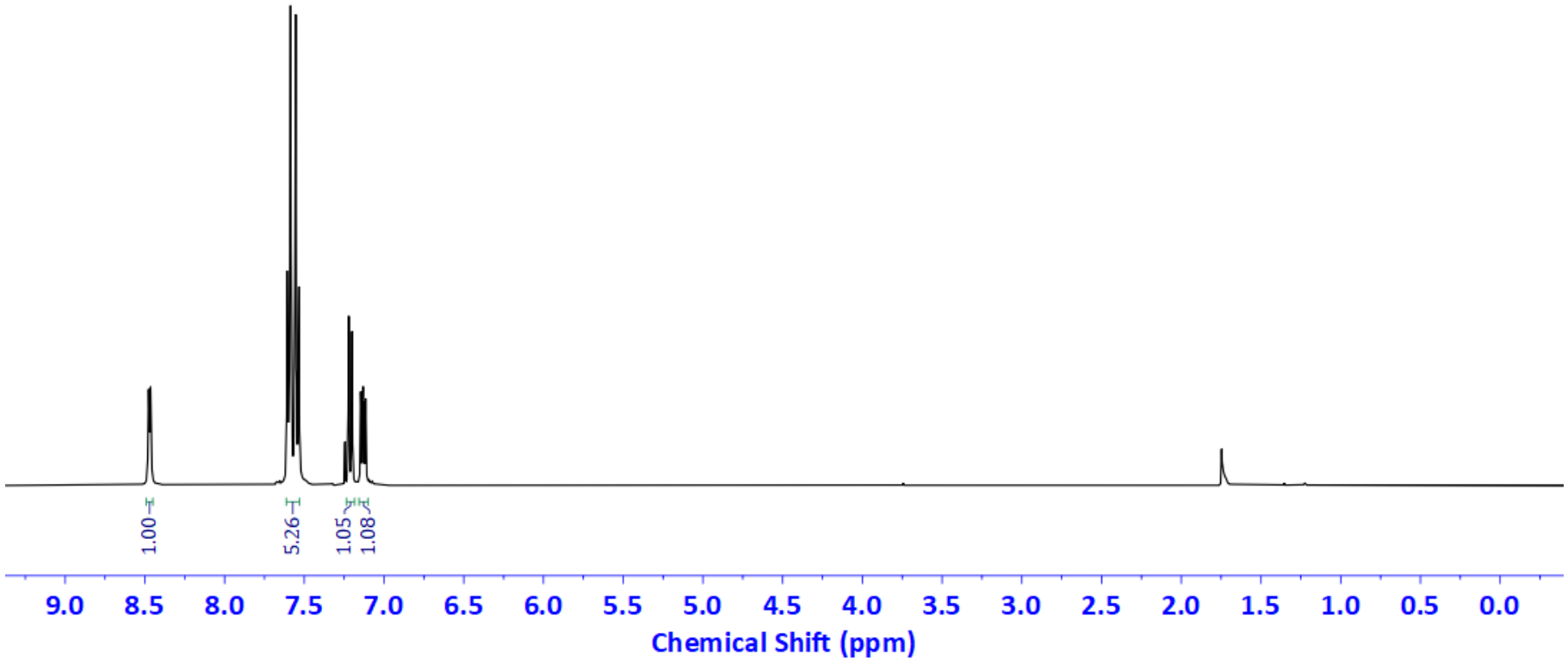


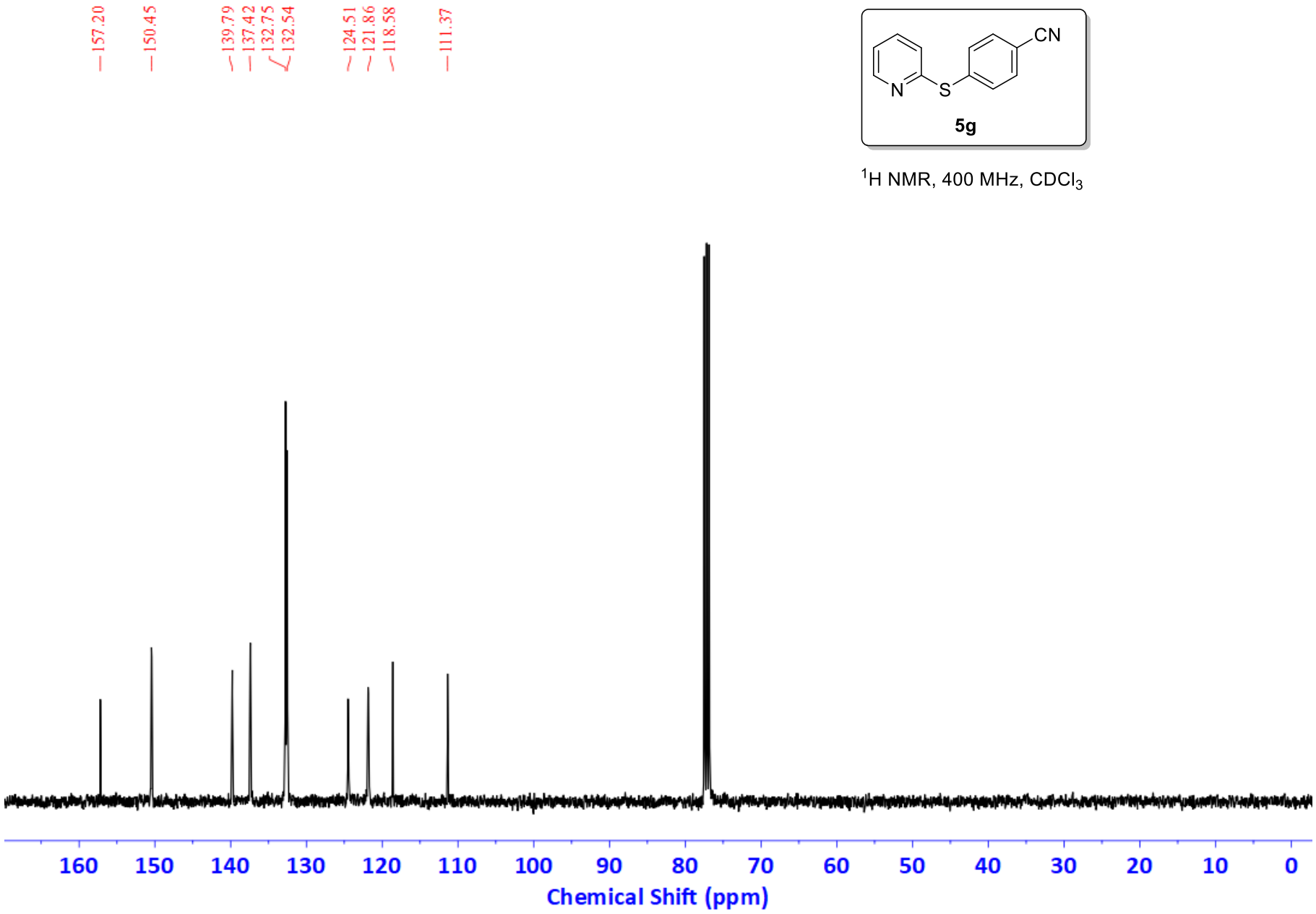

156.64
150.55
147.02
142.51
137.51
131.93
125.03
124.26
122.12
NO2
N
S
5f
1H NMR, 400 MHz, CDCl3
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)



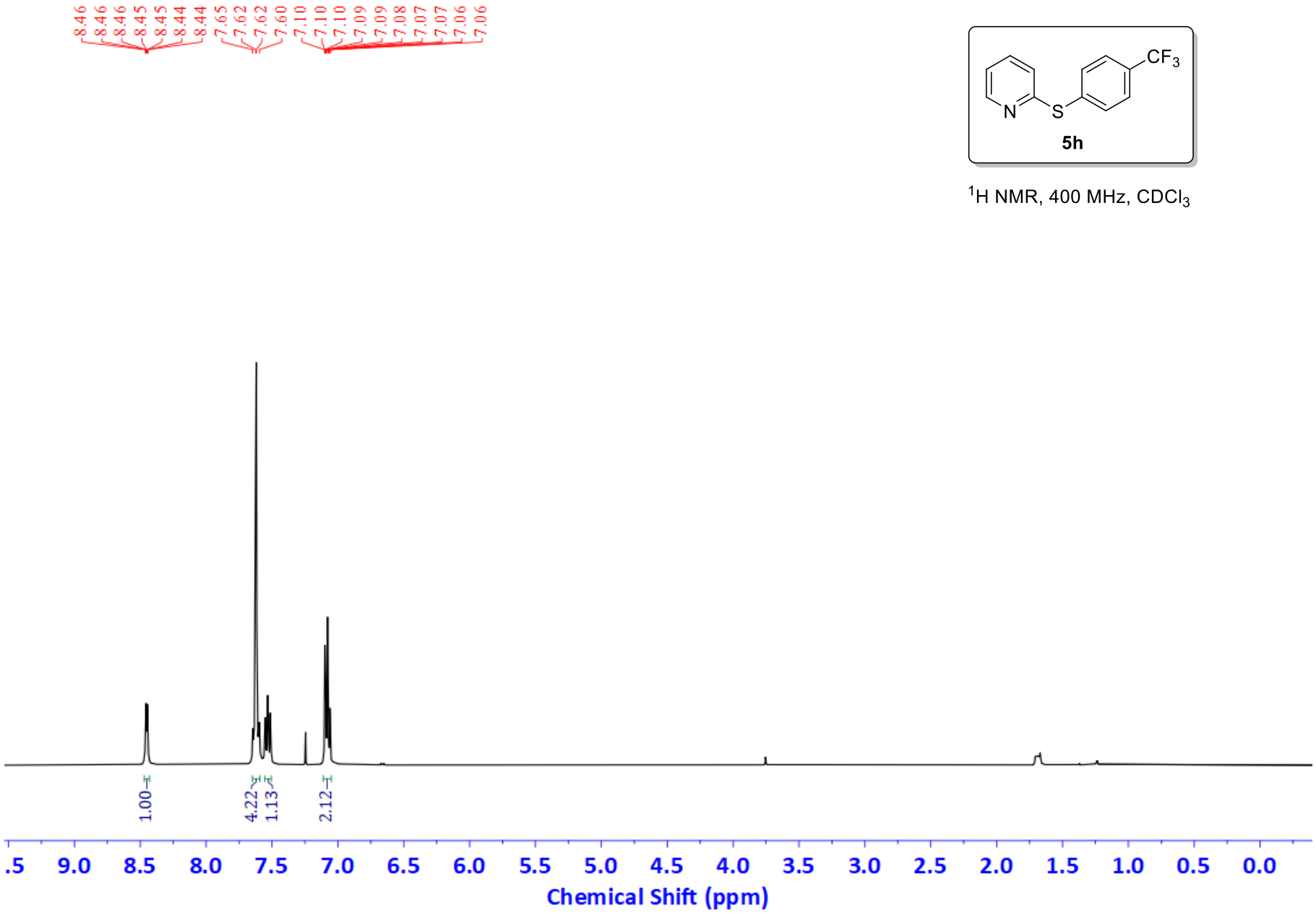
5g

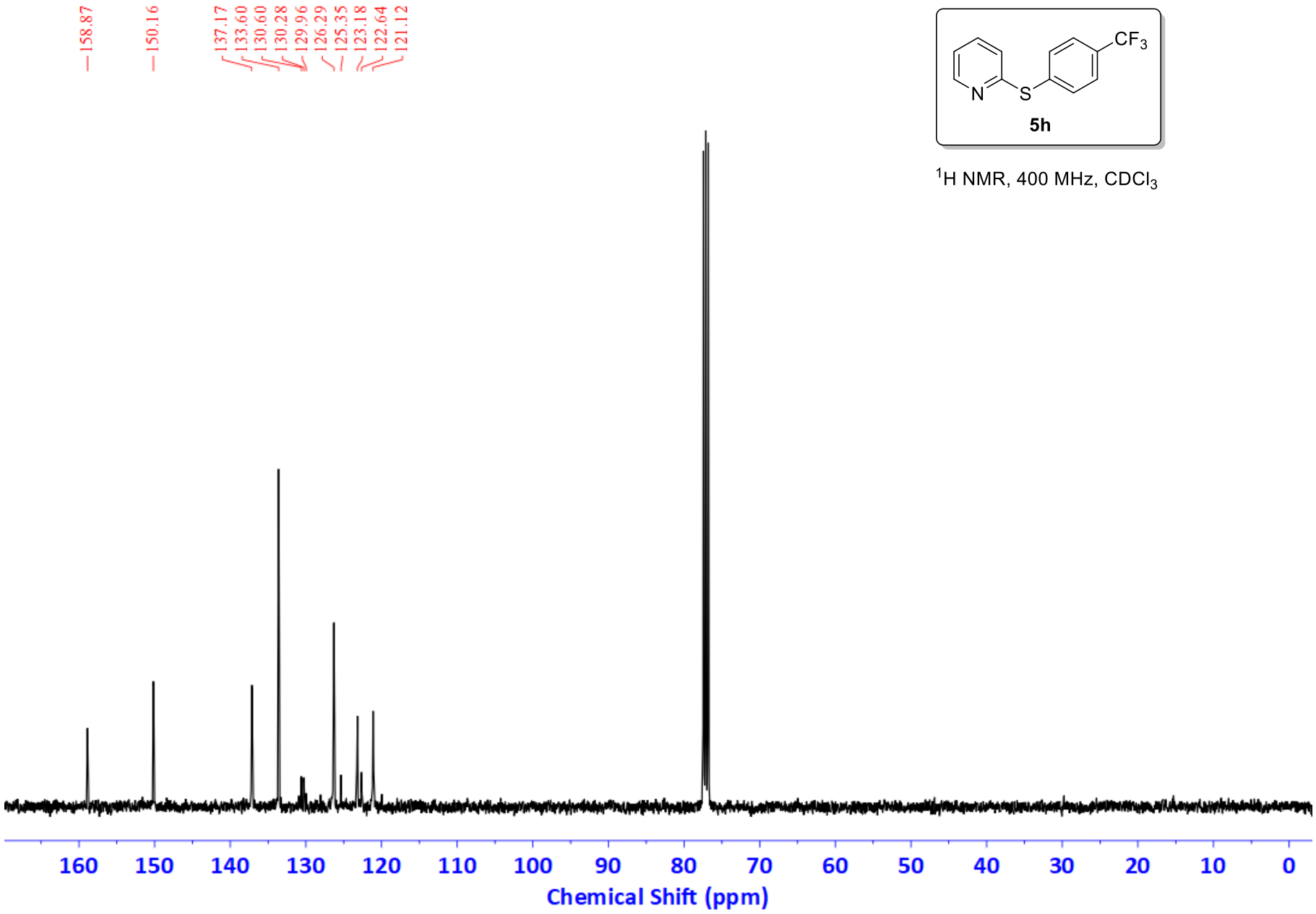
^{1}H NMR, 400 MHz, $CDCl_3$



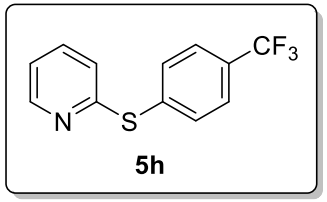


^{1}H NMR, 400 MHz, $CDCl_3$


8.46
8.46
8.46
8.45
8.45
8.44
8.44
7.65
7.62
7.62
7.60
7.10
7.10
7.10
7.09
7.09
7.08
7.07
7.07
7.06
7.06
CF3
N
S
5h
1H NMR, 400 MHz, CDCl3
1.00
4.22
1.13
2.12
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

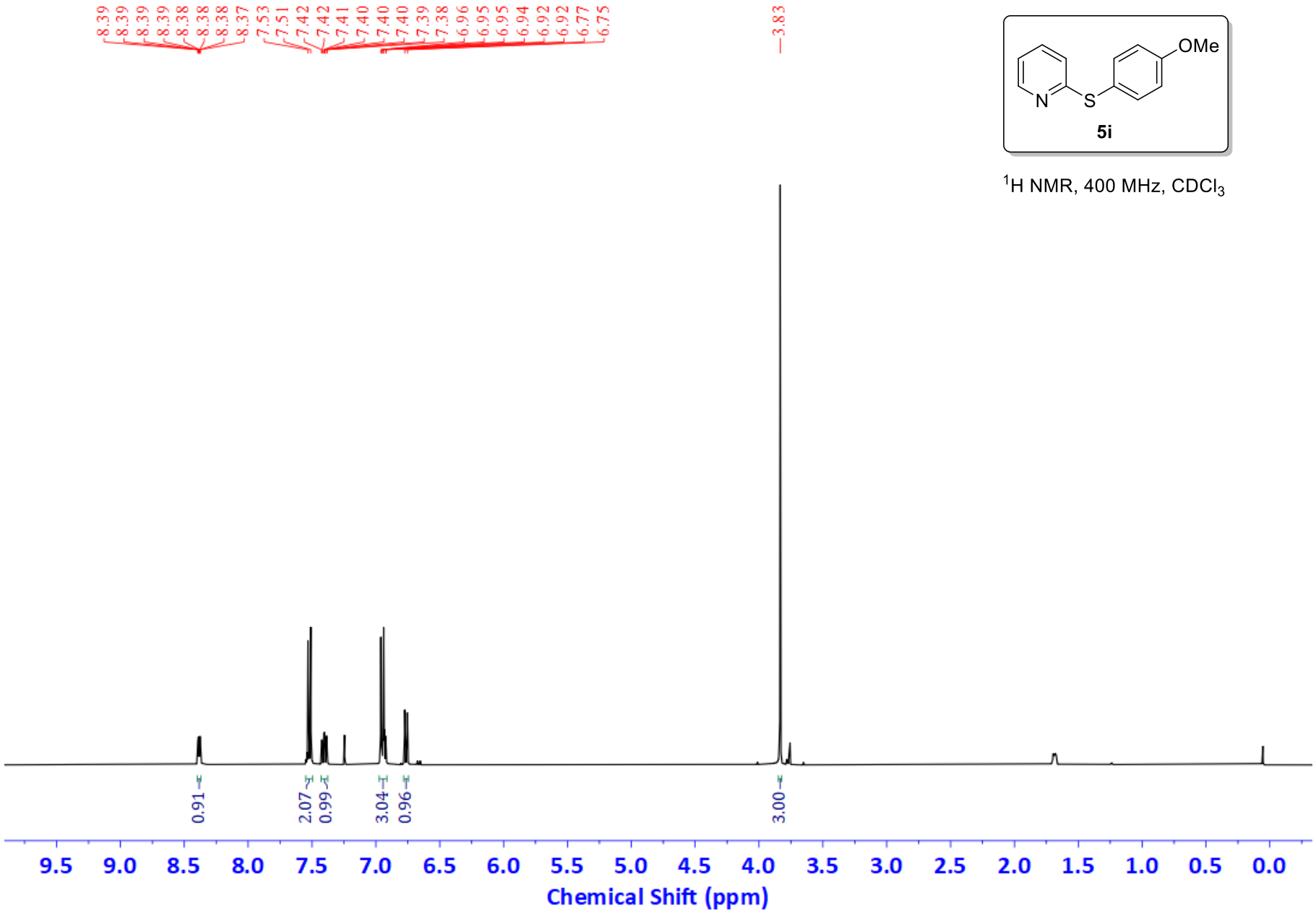


^{1}H NMR, 400 MHz, $CDCl_3$

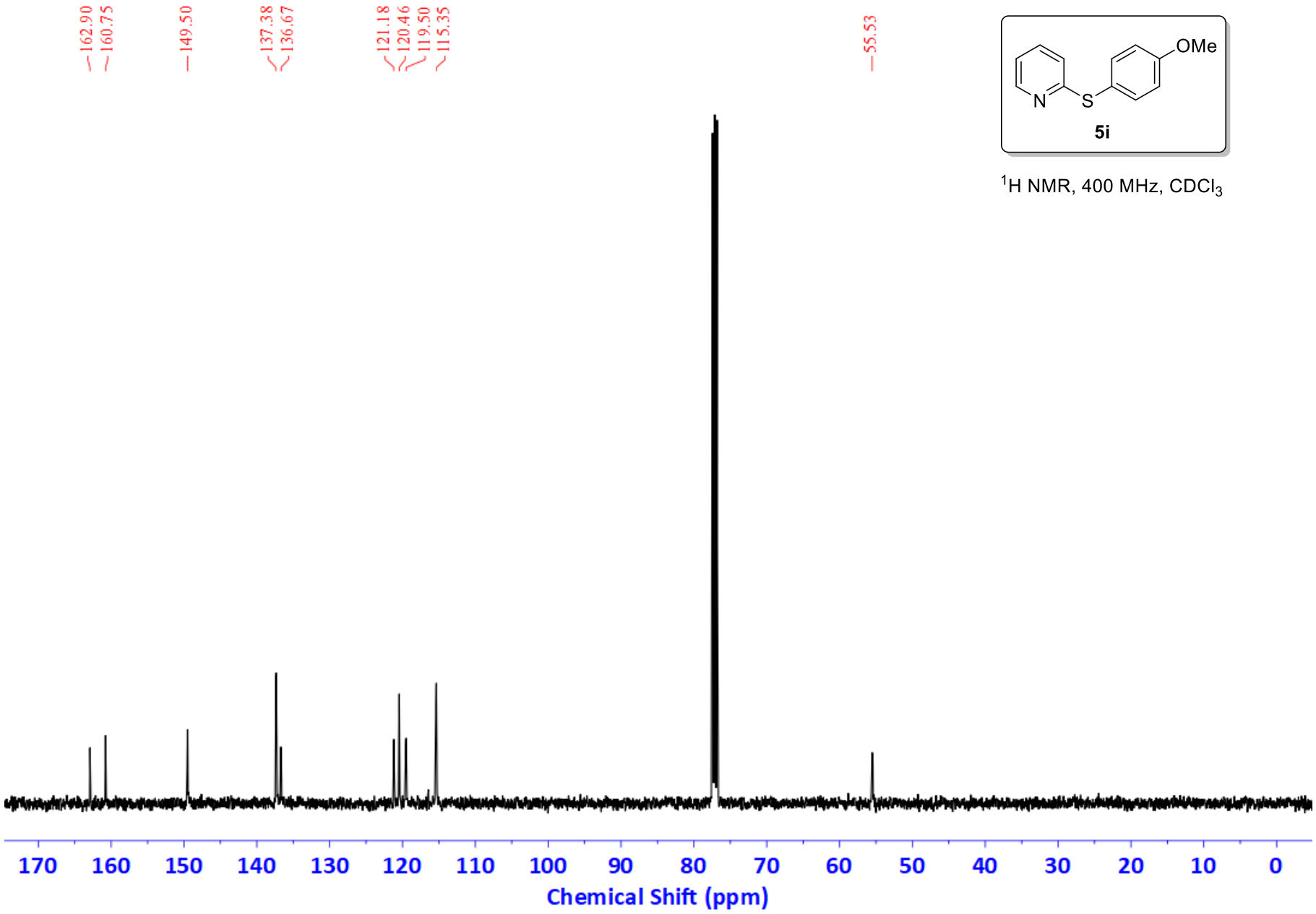


5h

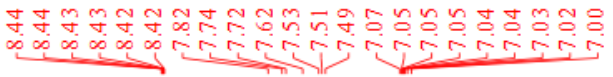
^{19}F NMR, 376 MHz, $CDCl_3$, 298K

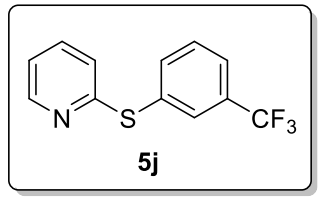


^{1}H NMR, 400 MHz, $CDCl_3$



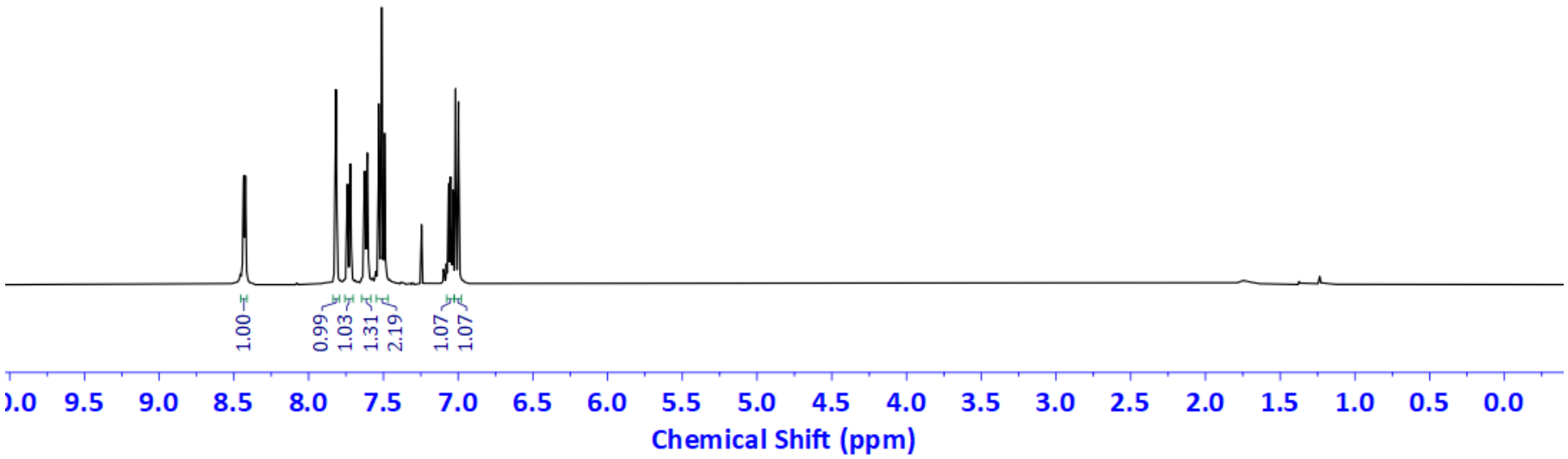
^{1}H NMR, 400 MHz, $CDCl_3$

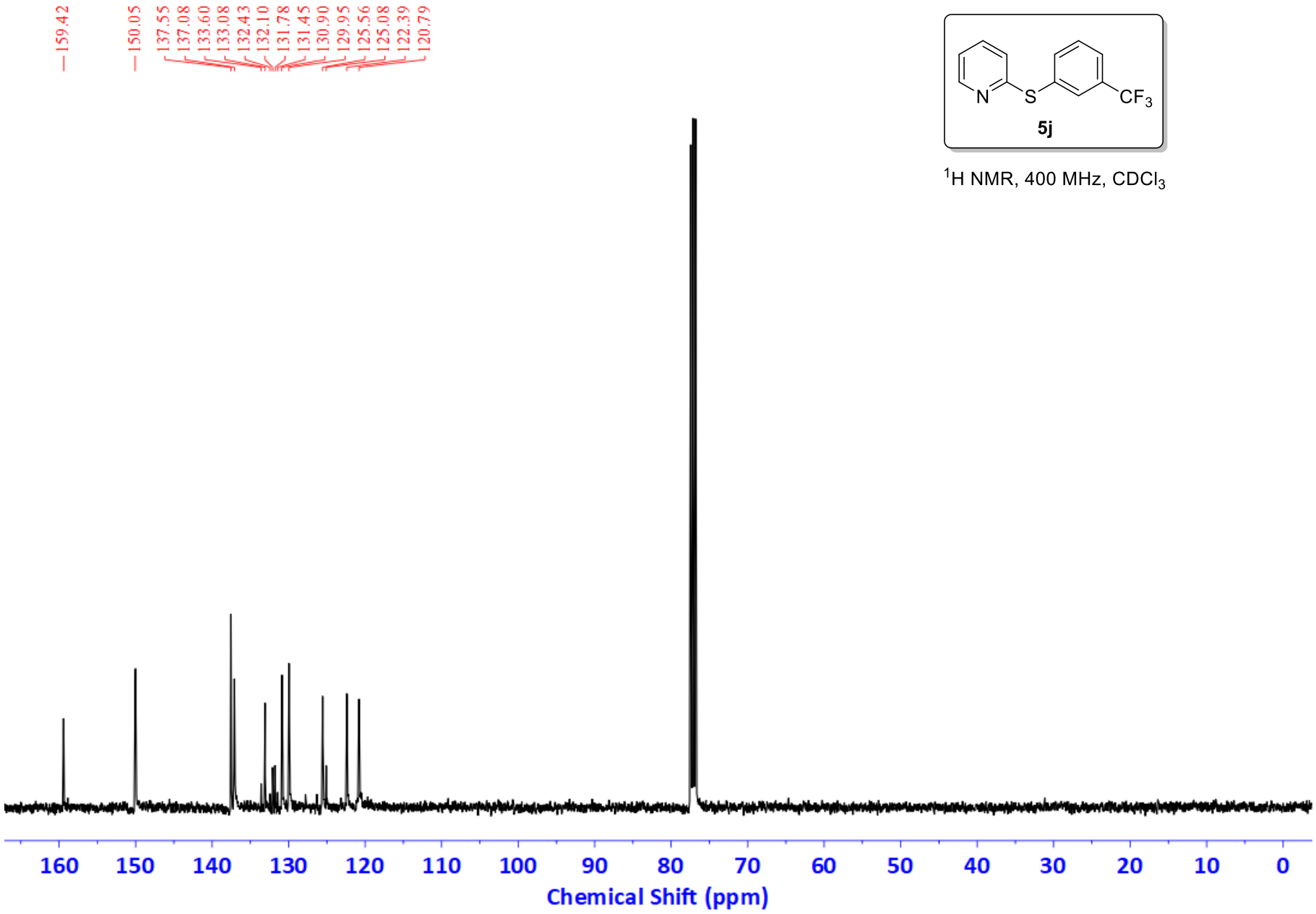




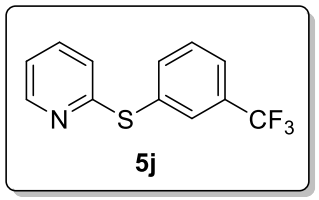
5j

^{1}H NMR, 400 MHz, $CDCl_3$



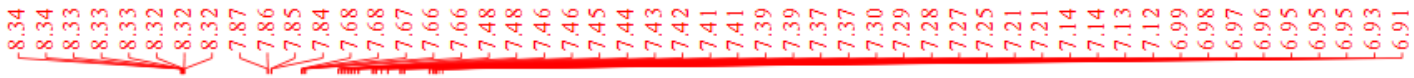


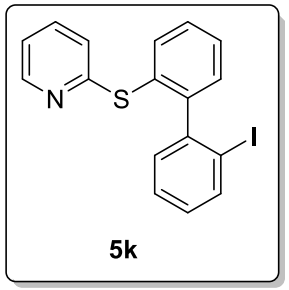
^{1}H NMR, 400 MHz, $CDCl_3$



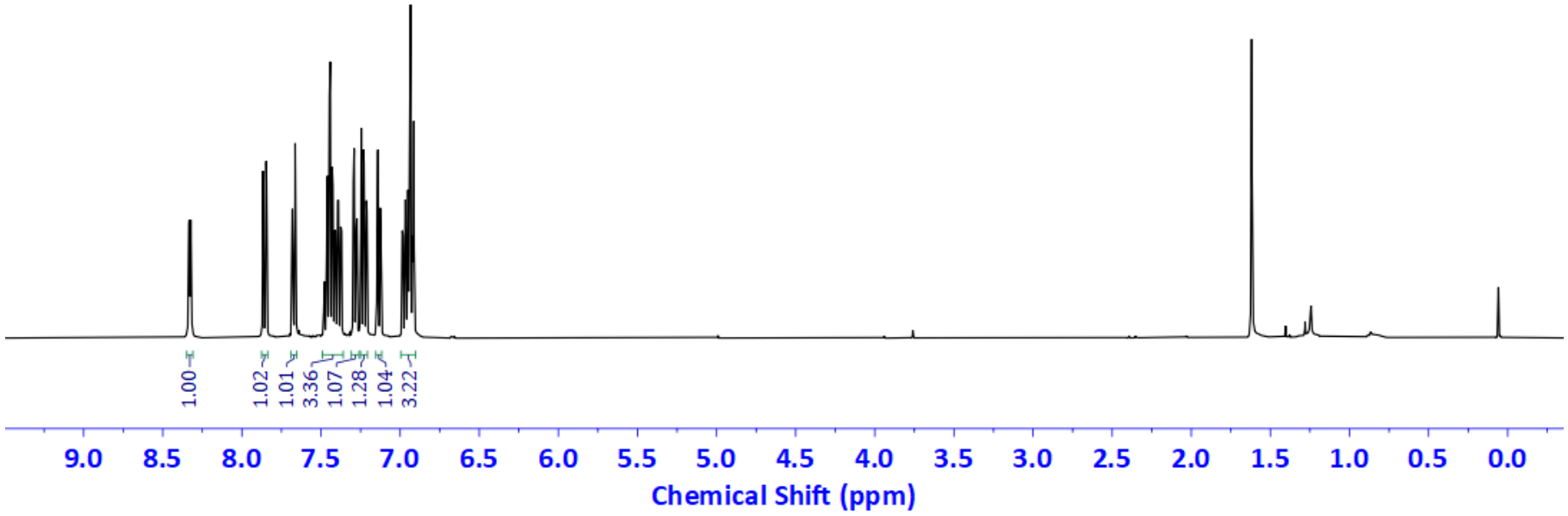
5j

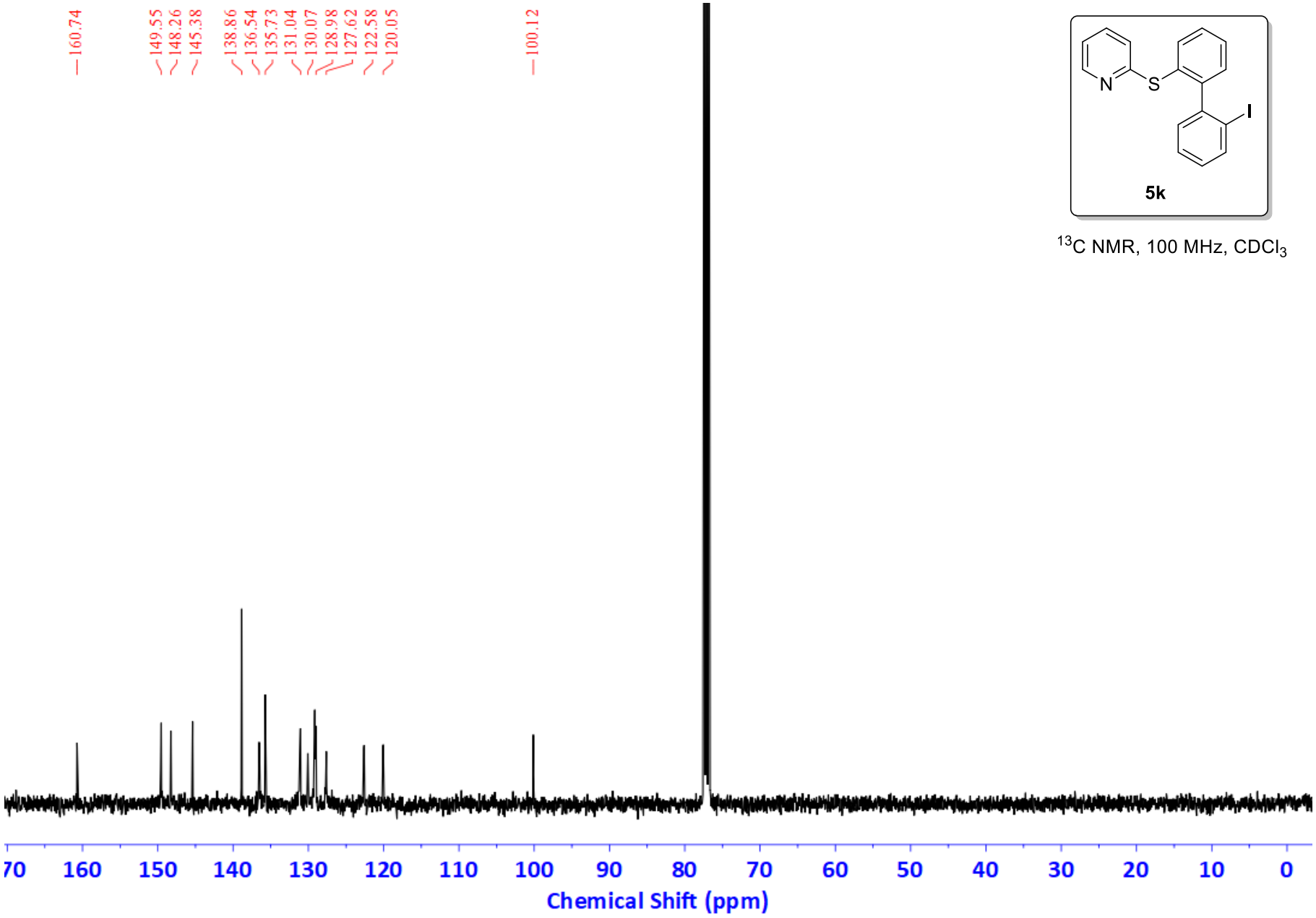
^{19}F NMR, 376 MHz, $CDCl_3$, 298K



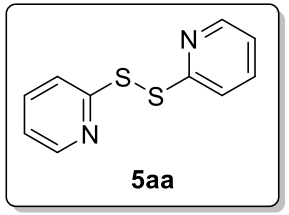


^{1}H NMR, 400 MHz, $CDCl_3$



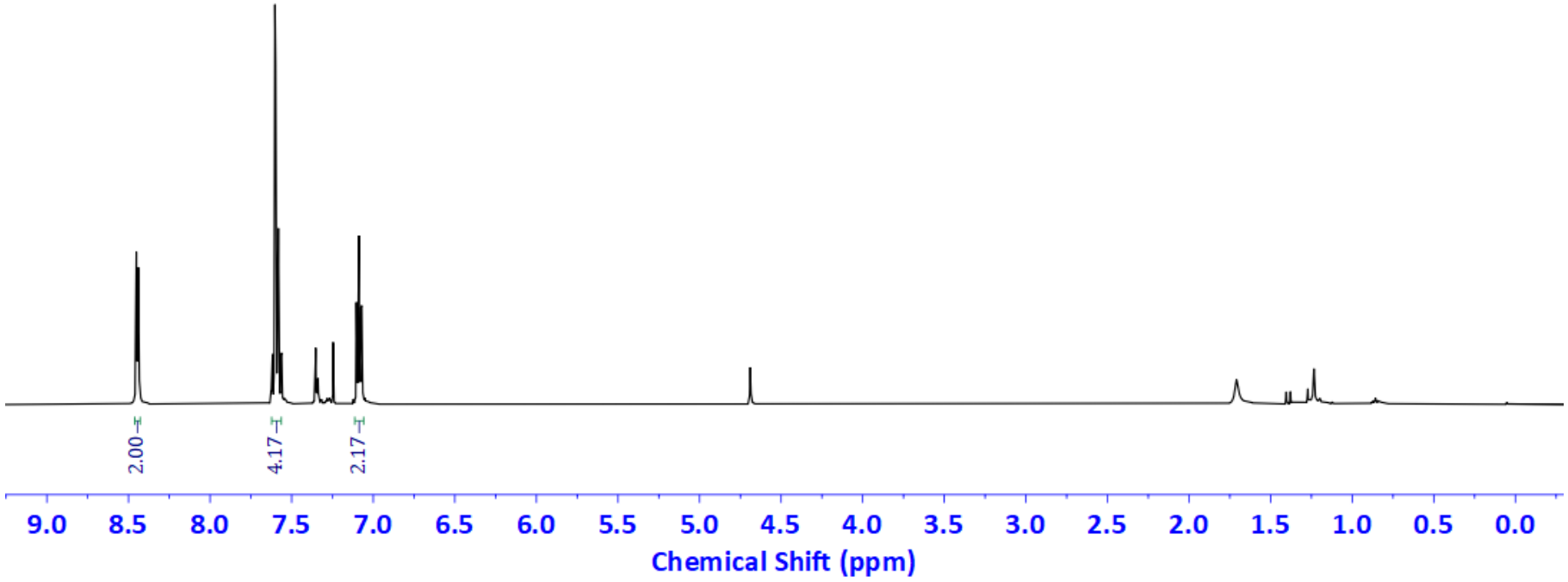


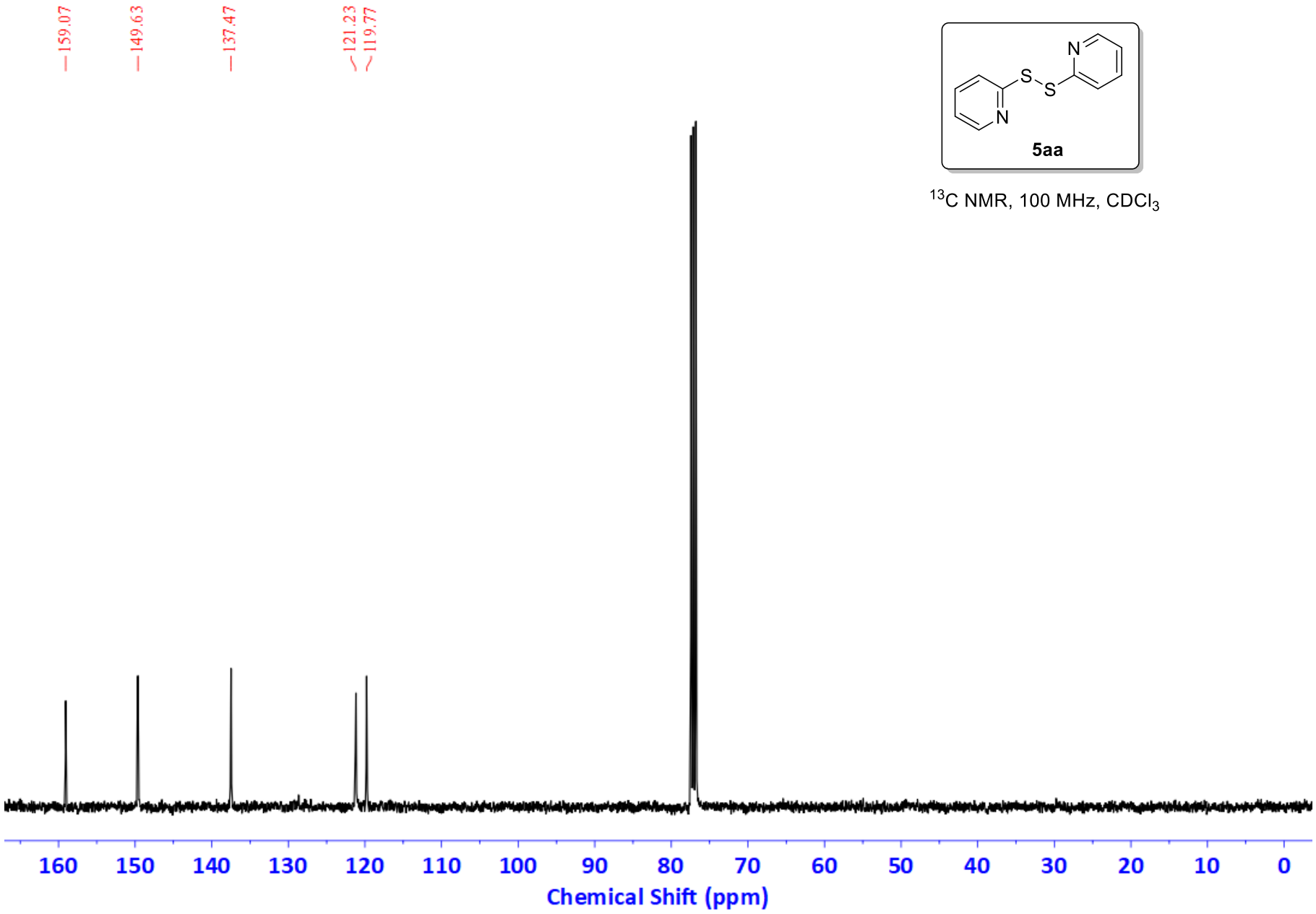
^{13}C NMR, 100 MHz, $CDCl_3$



5aa

^{1}H NMR, 400 MHz, $CDCl_3$





^{13}C NMR, 100 MHz, $CDCl_3$