Supporting Information

Copper-catalyzed arylation/nucleophilic addition/fragmentation/ C−S bond formation cascade: synthesis of bis(arylthio)imines

Wei-Si Guo, Yuan-Chao Wang, Qian Dou, Li-Rong Wen* and Ming Li*

State Key Laboratory Base of Eco-Chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

wenlirong@qust.edu.cn, liming928@qust.edu.cn

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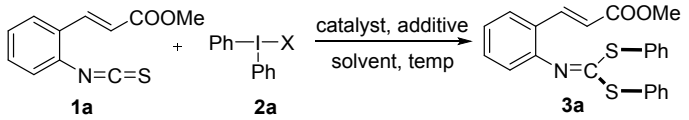
General methods

All reactions were carried out using standard Schlenk technique under nitrogen. DCE was distilled from CaH_2. Unless noted, all commercial reagents were used without further purification. Melting points were recorded on a RY-1 microscopic melting apparatus and uncorrected. ^1H NMR spectra were recorded on 500 MHz and ^{13}C NMR spectra were recorded on 125 MHz by using a Bruker Avance 500 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). Mass spectra were obtained on an Ultima Global spectrometer with an ESI source. Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China).

Optimization of the reaction conditions[a]

Table S1



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

entry	catalyst (mol %)	X	additive[b]	solvent	*T* [°C]	yield [%][c]
1	CuCl (10)	OTf		DCE	80	35
2	CuBr (10)	OTf		DCE	80	32
3	CuTc (10)	OTf		DCE	80	trace
4	$Cu(OTf)_2$ (10)	OTf		DCE	80	43(6)[d]
5	**$Cu(OTf)_2$ (10)**	OTf	**H_2O**	**DCE**	**80**	**77**
6	$Cu(OTf)_2$ (10)	OTf	H_2O (0.2 eq)	DCE	80	68
7	$Cu(OTf)_2$ (10)	OTf	H_2O (1.0 eq)	DCE	80	64
8	$Cu(OTf)_2$ (5)	OTf	H_2O	DCE	80	46
9	$Cu(OTf)_2$ (10)	OTf	H_2O	THF	80	10
10	$Cu(OTf)_2$ (10)	OTf	H_2O	toluene	80	42
11	$Cu(OTf)_2$ (10)	OTf	H_2O	DCM	60	34
12	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	60	53
13	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	100	62
14[e]	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	80	45
15[f]	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	80	56
16	$Cu(OTf)_2$ (10)	PF_6	H_2O	DCE	80	50
17	$Cu(OTf)_2$ (10)	BF_4	H_2O	DCE	80	36
18[g]	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	80	38
19[h]	$Cu(OTf)_2$ (10)	OTf	H_2O	DCE	80	32
20	none	OTf	H_2O	DCE	80	trace

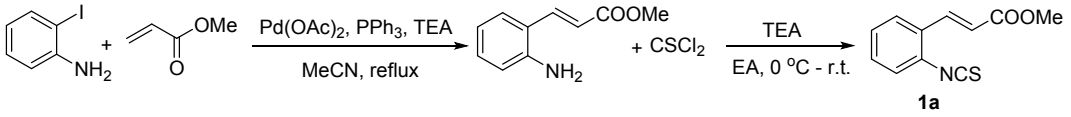
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), solvent (1.5 mL), 3 h, N_2. [b] 0.5 equiv. [c] The isolated yield of **3a** was based on dividing the amount of **1a** by two (theoretical yield 0.15 mmol). [d] The reaction was performed under rigorously anhydrous conditions. [e] 1.0 equiv. of $Ph_2I(OTf)$ was used, 20% of **1a** was recovered after 12h. [f] 1.2 equiv. of $Ph_2I(OTf)$ was used, 13% of **1a** was recovered after 12h. [g] Mesitylphenyliodonium salt was instead of **2a**. [h] Under an air atmosphere.

To optimize the reaction conditions, different copper catalysts were initially screened using isothiocyanate **1a** and diphenyliodonium triflate **2a** (entries 1-4, Table 1). The result showed that $Cu(OTf)_2$ was superior to CuCl, CuBr, and CuTc, and providing **3a** in 43% yield (entry 4). The yield of **3a** was decreased to 6% when the reaction was performed under rigorously anhydrous conditions. Considering incidental water in the reaction system must serve as a nucleophile to attack the imidoyl carbocation, small amount of water was added to facilitate the reaction (entries 5-7). The results indicated 0.5 equiv water was the best choice (77%, entry 5). The yield of **3a** dropped to 46% when catalyst loading was reduced to 5 mol % (entry 8). Moreover, further solvent screening identified DCE as the best one, while THF, toluene, and DCM exhibited lower yields (entries 9-11). Diminished yields were obtained when the reaction was performed at elevated or decreased temperature (entries 12 and 13). When 1.0 equiv or 1.2 equiv diphenyliodonium triflate was used to react with **1a**, product **3a** was obtained in 45% or 56% yields after 12 h, and 20% or 13% of **1a** was recovered (entries 14 and 15). The yield of **3a** was reduced to 50% and 36% when hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-) were used as the counterion of the diphenyliodonium salt (entries 16 and 17). When mesitylphenyliodonium salt was instead of **2a** also exhibited lower yield (entry 18). Carrying out the reaction under air resulted in lower yield (entry 19), whereas without $Cu(OTf)_2$ only a trace amount of **3a** was formed (entry 20). Careful optimization revealed that the reaction performed best at 80 °C in DCE with $Cu(OTf)_2$ (0.1 equiv) as the catalyst (entry 5).

Preparation of starting materials

Diaryliodonium salts[1] and isothiocyanates[2] were prepared according to the literatures.

Methyl (*E*)-3-(2-isothiocyanatophenyl)acrylate **1a**[3] was prepared from the corresponding 2-iodoaniline.

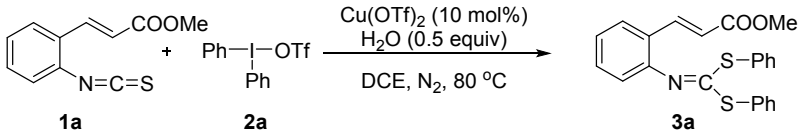


1a

Under nitrogen atmosphere, a round-bottom flask was charged with a mixture of 2-iodoaniline (1.42 g, 6.5 mmol), methyl acrylate (0.78 g, 1.4 equiv), PPh_3 (0.21 g, 12 mol%), $Pd(OAc)_2$ (88 mg, 6 mol%), Et_3N (0.79 g, 1.2 equiv) and acetonitrile (30 mL). The mixture was stirred for 24 h at 85 °C. The reaction was monitored by TLC. After completion, the inorganic precipitate was filtered through a celite pad. The filtrate was concentrated at the reduced pressure. Then, H_2O (20 mL) was added to the reaction mixture and extracted with ethyl acetate (3 × 20 mL). The combined organic solution was washed with saturated NaCl solution, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate = 5:1) to give methyl (*E*)-3-(2-aminophenyl)acrylate (829 mg, 72%).

Thiophosgene (1.67 g, 5.6 mmol) diluted in a dry ethyl acetate was added dropwise to the solution of methyl (*E*)-3-(2-aminophenyl)acrylate and Et_3N (1.18 g, 2.1 equiv) in cool-bath at least 5 min and the mixture was stirred at room temperature for 12 h. After completion, the inorganic salts were filtered, and the filtrate was concentrated at the reduced pressure. The crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate = 30:1) to give methyl (*E*)-3-(2-isothiocyanatophenyl) acrylate **1a** (800 mg, 78%).

General procedure for the synthesis of compounds 3 (3a for example)



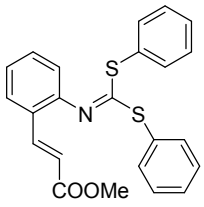
1a **2a** **3a**

Under nitrogen atmosphere, a mixture of methyl (*E*)-3-(2-isothiocyanatophenyl) acrylate **1a** (110 mg, 0.50 mmol), diphenyliodonium triflate **2a** (323 mg, 0.75 mmol), $Cu(OTf)_2$ (18 mg, 0.05 mmol), H_2O (4.5 mg, 0.25 mmol) and DCE (2.5 mL) was added to a dry Schlenk tube. The mixture was allowed to stir at 80 °C for 3 h. After completion, the mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous $MgSO_4$. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to afford methyl (*E*)-3-(2-((bis(phenylthio)methylene)amino) phenyl)acrylate **3a** as a light yellow solid (78 mg, 77%).

Procedure under rigorously anhydrous conditions (Table 1, entry 4)

The flask was flame-dried, the starting materials and solvent were dried under the standard conditions, and the reaction mixture was degassed by freeze-pump-thaw procedure.

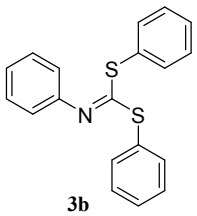
Methyl (*E*)-3-(2-((bis(phenylthio)methylene)amino)phenyl)acrylate (3a)



3a

Light yellow solid, 78 mg, 77% yield, m.p. 114-116 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 30:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.85 (s, 3H), 6.33 (d, J = 16.1 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 8.5 Hz, 1H), 7.39 (app s, 6H), 7.49 (d, J = 7.7 Hz, 1H), 7.58-7.59 (m, 4H), 7.67 (d, J = 16.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 51.6, 118.0, 120.5, 124.4, 125.5, 127.6, 129.1 (6C), 129.8 (2C), 130.5, 136.1 (4C), 141.4, 148.9, 162.9, 167.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{23}H_{20}NO_2S_2^+$: 406.0935, found: 406.0942.

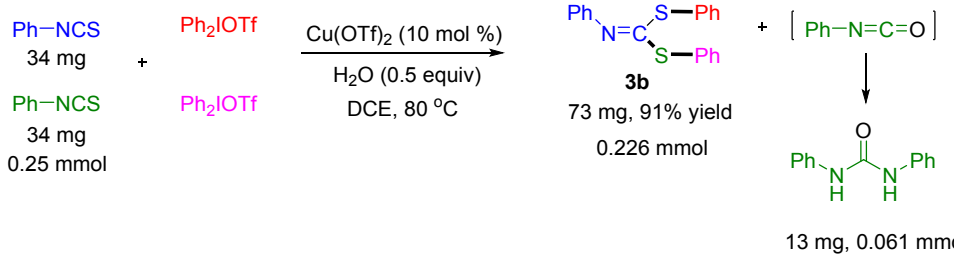
***N*-Phenylbis(phenylthio)methanimines (3b)**



3b

White solid, 73 mg, 91% yield, m.p. 115-117 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.88 (d, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.38-7.39 (m, 6H), 7.58 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.2 (2C), 124.0, 128.8 (2C), 129.0 (2C), 129.5 (6C), 135.7 (4C), 149.7, 160.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{16}NS_2^+$: 322.0724, found: 322.0719.

A mass balance of the reaction 1b with 2a

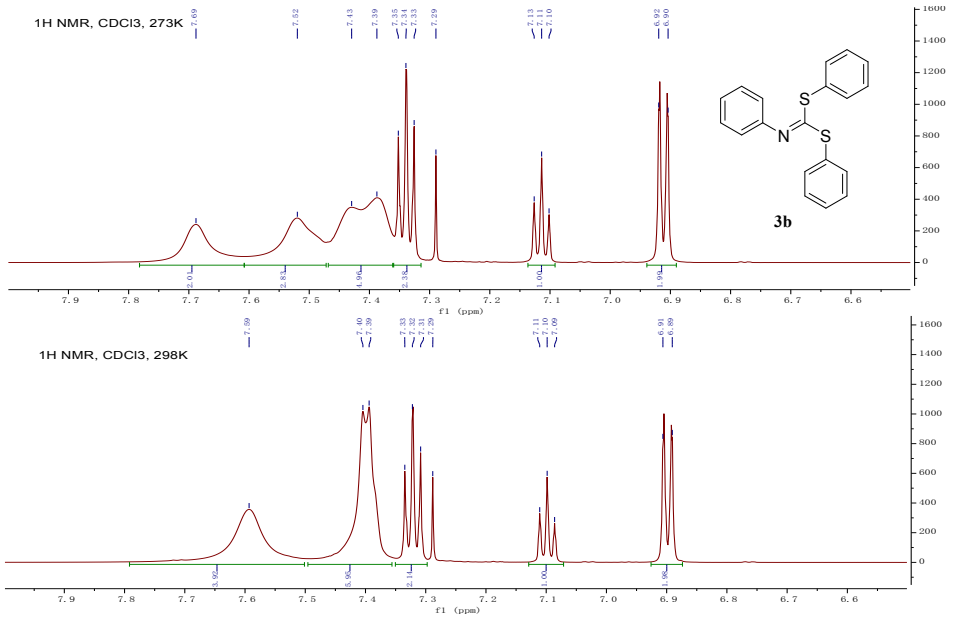


Under nitrogen atmosphere, a mixture of isothiocyanatobenzene **1b** (68 mg, 0.50 mmol), diaryiodonium salt **2a** (323 mg, 0.75 mmol), $Cu(OTf)_2$ (18 mg, 0.05 mmol), H_2O (4.5 mg, 0.25 mmol) and DCE (2.5 mL) was added to a dry Schlenk tube. The mixture was allowed to stir at 80 °C for 3 h. After completion, the mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous $MgSO_4$. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 150:1 to 5:1) to afford *N*-phenylbis(phenylthio)methanimine **3b** (73 mg, 91%), and diphenylurea (13 mg) as a white solid.

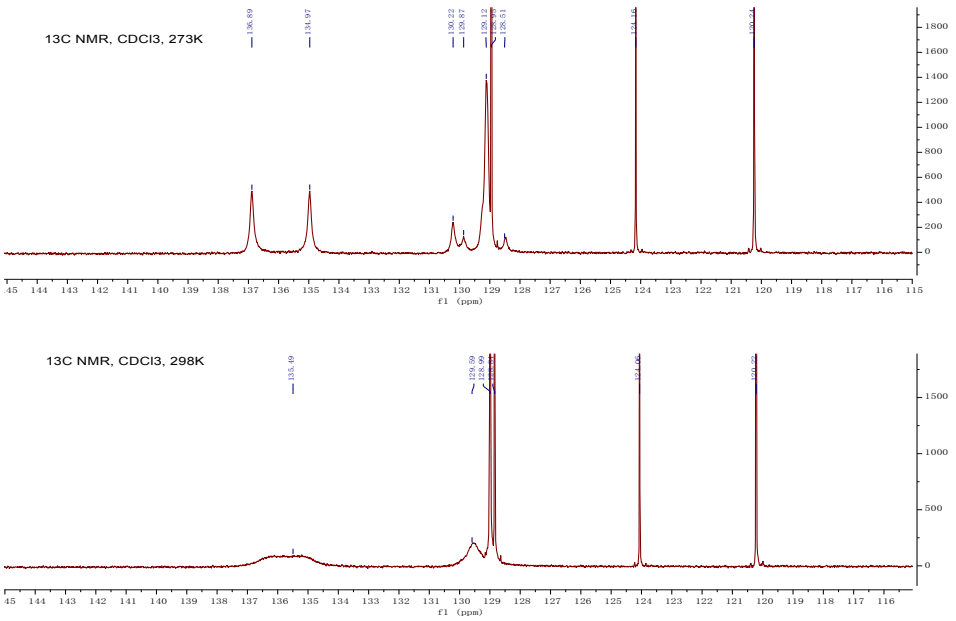
*Note: As shown in the above scheme, this is actually a four component reaction (A_2B_2 type), compound **3b** (shown by four different colors) contains the pieces of all "four starting materials". Only a small amount of urea was isolated as a byproduct, and no isocyanate intermediate was isolated or detected. The process to generate urea from isocyanate was supported by previous reports.*[4] *The isocyanate decomposed to aniline, which provided the N-source to generate urea.*

Variable-temperature NMR experiments

The products are pure according to the NMR spectra, but the peaks of –SAr show unusual shapes (broad singlets). The broad peaks are caused by C-S bond rotation. The NMR spectra of **3b** were improved when decreased the temperature to 273K to prevent the C-S bond rotation, e.g. the broad peak in 7.59 splits into two peaks 7.69 and 7.52 in ^{1}H NMR, and the broad peak in 135.5 splits into two peaks 136.9 and 134.9 in ^{13}C NMR.

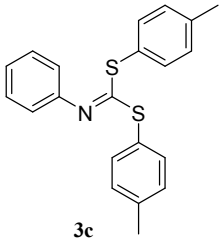


Compared ^{1}H NMR at 273 and 298K



Compared ^{13}C NMR at 273 and 298K

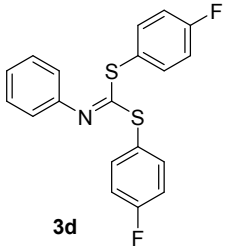
***N*-(Phenyl)bis(p-tolylthio)methanimine (3c)**



3c

White solid, 83 mg, 95% yield, m.p. 152-154 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.38 (br s, 6H), 6.87 (d, J = 7.8 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.19-7.20 (m, 4H), 7.30 (t, J = 7.7 Hz, 2H), 7.47 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.3 (2C), 120.2 (2C), 123.9, 126.0 (2C), 128.7 (4C), 129.8 (2C), 135.9 (4C), 139.8 (2C), 149.9, 161.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{21}H_{20}NS_2^+$: 350.1037, Found: 350.1045.

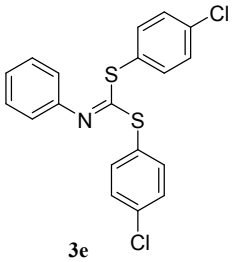
***N*-(Phenyl)bis(4-fluorophenylthio)methanimine (3d)**



3d

White solid, 63 mg, 71% yield, m.p. 93-95 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.85 (d, J = 7.9 Hz, 2H), 7.07-7.10 (m, 5H), 7.31 (t, J = 7.8 Hz, 2H), 7.55 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 116.3 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, 4C), 120.1 (2C), 124.2, 128.9 (4C), 138.4 (4C), 149.4, 160.7. 163.8 (d, $^1J_{C\text{-}F}$ = 257.5 Hz, 2C). HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{14}F_2NS_2^+$: 358.0536, found: 358.0529.

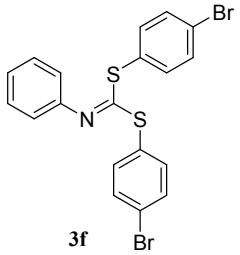
***N*-(Phenyl)bis(4-chlorophenylthio)methanimine (3e)**



3e

White solid, 73 mg, 75% yield, m.p.: 130-132 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, J = 7.8 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 7.27-7.34 (m, 6H), 7.47 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.1 (2C), 124.4, 129.0 (2C), 129.3 (6C), 136.5 (6C), 149.2, 159.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{14}Cl_2NS_2^+$: 389.9939, found: 389.9950.

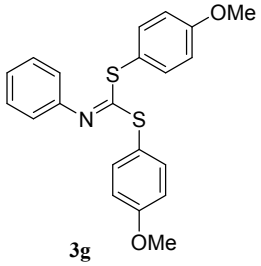
***N*-(Phenyl)bis(4-bromophenylthio)methanimine (3f)**



3f

White solid, 84 mg, 70% yield, m.p. 155-157 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.84 (d, J = 6.7 Hz, 2H), 7.10 (t, J = 6.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.42-7.52 (m, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.1 (2C), 124.4, 128.9 (4C), 132.3 (6C), 137.2 (4C), 149.2, 159.3. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{14}Br_2NS_2^+$: 477.8934, found: 477.8942.

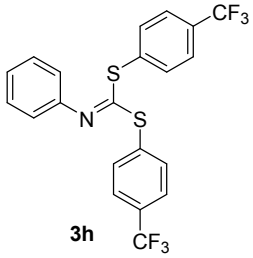
***N*-(Phenyl)bis(4-methoxyphenylthio)methanimine (3g)**



3g

Yellow solid, 53 mg, 56% yield, m.p. 63-65°C. R_f = 0.25 (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.81 (br s, 6H), 6.84-6.90 (m, 6H), 7.05 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.8 Hz, 2H), 7.46 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.3 (2C), 114.6, 120.2, 123.8 (6C), 128.8 (2C), 137.6, 150.0 (2C), 160.9 (4C), 162.9 (2C). HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{21}H_{20}NO_2S_2^+$: 382.0930, found: 382.0930.

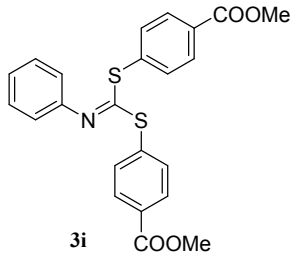
***N*-(Phenyl)bis(4-(trifluoromethyl)phenylthio)methanimine (3h)**



3h

White solid, 98 mg, 86% yield, m.p. 102-104 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.83 (d, J = 7.7 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.7 Hz, 2H), 7.59-7.66 (m, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.1 (2C), 122.7, 124.7 (4C), 125.9 (2C), 129.0 (4C), 131.6 (q, J = 33.2 Hz, 2C), 134.1 (2C), 135.4 (2C), 148.9, 157.5. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{21}H_{14}F_6NS_2^+$: 458.0472, found: 458.0485.

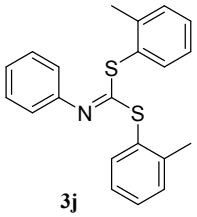
Di-methyl-4,4'-(((phenylimino)methylene)bis(sulfanediyl))dibenzoate (3i)



3i

White solid, 79 mg, 72% yield, m.p. 168-170 °C. R_f = 0.22 (petroleum ether/ethyl acetate = 40:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.92 (s, 6H), 6.84 (d, J = 7.8 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.8 Hz, 2H), 7.60-7.61 (m, 4H), 8.01 (d, J = 8.2 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 52.3 (2C), 120.1 (2C), 124.5, 128.9 (2C), 130.0 (4C), 130.9 (2C), 135.4 (6C), 149.0, 158.1, 166.3 (2C). HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{23}H_{20}NO_4S_2^+$: 438.0828, found: 438.0838.

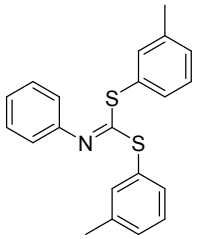
***N*-(Phenyl)bis(*o*-tolylthio)methanimine (3j)**



3j

Yellow oil, 47 mg, 53% yield. R_f = 0.25 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.52 (br s, 6H), 6.86 (d, J = 7.8 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 7.20 (app s, 2H), 7.28-7.31 (m, 6H), 7.53 (app s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.0 (2C), 120.1 (2C), 123.9, 126.5 (2C), 128.8 (2C), 130.6 (2C), 136.2 (2C), 137.7 (2C), 143.1 (4C), 150.1, 160.4. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{21}H_{20}NS_2^+$: 350.1037, found: 350.1043.

***N*-(Phenyl)bis(*m*-tolylthio)methanimine (3k)**

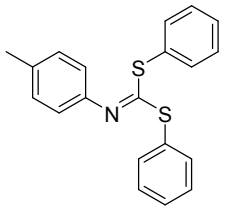


3k

White solid, 61 mg, 70% yield, m.p. 110-112 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.35 (br s, 6H), 6.87 (d, J = 7.9 Hz, 2H), 7.06 (t, J = 7.3 Hz, 1H), 7.19 (app s, 2H), 7.24-7.31 (m, 4H), 7.37 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.2 (2C), 120.2 (2C), 123.9, 128.7 (2C), 129.2 (4C), 130.3 (2C), 132.7 (2C), 136.1 (2C), 138.7 (2C),

149.8, 161.1. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{21}H_{20}NS_2^+$: 350.1037, found: 350.1042.

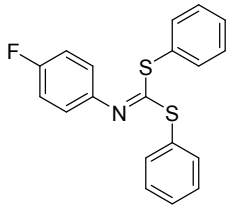
***N*-(*p*-Tolyl)bis(phenylthio)methanimine (3l)**



3l

White solid, 66 mg, 79% yield, m.p. 127-129 °C. R_f = 0.22 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.30 (s, 3H), 6.77 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 7.35 (app s, 6H), 7.54 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.0, 120.1 (4C), 129.0 (4C), 129.4 (4C), 133.6, 135.0 (2C), 136.3 (2C), 147.1, 160.3. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{20}H_{18}NS_2^+$: 336.0881, found: 336.0892.

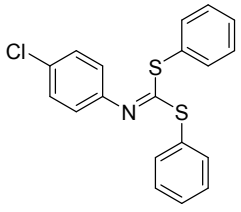
***N*-(4-Fluorophenyl)bis(phenylthio)methanimine (3m)**



3m

White solid, 68 mg, 80% yield, m.p. 73-75 °C. R_f = 0.20 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.80-6.83 (m, 2H), 6.97 (t, J = 8.6 Hz, 2H), 7.37 (app s, 6H), 7.54 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 115.5 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, 2C), 121.6 (2C), 121.7 (2C), 129.1 (4C), 129.8, 135.1 (2C), 136.5 (2C), 145.6, 145.7, 159.7 (d, $^1J_{C\text{-}F}$ = 242.5 Hz), 161.8. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{15}FNS_2^+$: 340.0625, found: 340.0622.

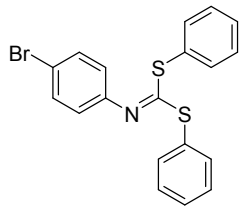
***N*-(4-Chlorophenyl)bis(phenylthio)methanimine (3n)**



3n

White solid, 63 mg, 71% yield, m.p. 83-85 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.79 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.37-7.39 (m, 6H), 7.55 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 121.7 (2C), 128.9, 129.1 (2C), 129.3 (2C), 129.7 (6C), 135.8 (4C), 148.1, 162.2. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{15}ClNS_2^+$: 356.0329, found: 356.0336.

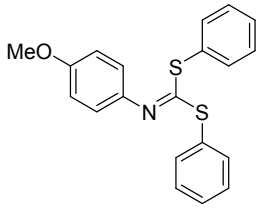
***N*-(4-Bromophenyl)bis(phenylthio)methanimine (3o)**



3o

White solid, 67 mg, 67% yield, m.p. 105-106 °C. R_f = 0.24 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.74 (d, J = 8.5 Hz, 2H), 7.38-7.39 (m, 8H), 7.55 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 117.1, 122.1 (2C), 129.1 (2C), 129.7 (6C), 131.8 (2C), 135.7 (4C), 148.6, 162.1. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{15}BrNS_2^+$: 399.9824, Found: 399.9831.

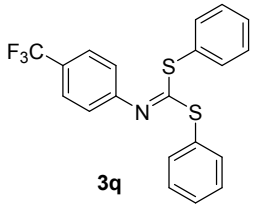
***N*-(4-Methoxyphenyl)bis(phenylthio)methanimine (3p)**



3p

White solid, 78 mg, 89% yield, m.p. 102-104 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.77 (s, 3H), 6.81-6.85 (m, 4H), 7.35 (app s, 6H), 7.54 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.5, 114.1 (2C), 121.8 (2C), 128.9 (4C), 134.7 (4C), 136.3 (4C), 142.9, 156.5, 160.3. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{20}H_{18}NOS_2^+$: 352.0830, found: 352.0832.

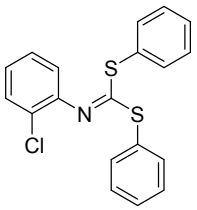
***N*-(4-(Trifluoromethyl)phenyl)bis(phenylthio)methanimine (3q)**



3q

White solid, 65 mg, 67% yield, m.p. 83-85 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90 (d, J = 8.2 Hz, 2H), 7.35-7.37 (m, 6H), 7.49-7.53 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.3 (3C), 125.8 (4C), 129.1 (4C), 129.8 (3C), 135.8 (4C), 152.7, 162.9. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{20}H_{15}F_3NS_2^+$: 390.0593, found: 390.0603.

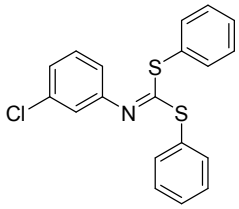
***N*-(2-Chlorophenyl)bis(phenylthio)methanimine (3r)**



3r

Light yellow oil, 49 mg, 55% yield. R_f = 0.24 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.86 (d, J = 7.8 Hz, 1H), 6.96-6.99 (m, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.32-7.37 (m, 7H), 7.59 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 121.3, 124.8, 127.0, 129.0 (6C), 129.7 (4C), 135.7 (4C), 146.7, 163.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{15}ClNS_2^+$: 356.0328, found: 356.0329.

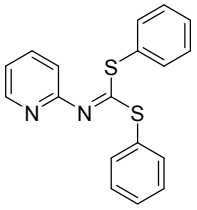
***N*-(3-Chlorophenyl)bis(phenylthio)methanimine (3s)**



3s

White solid, 65 mg, 73% yield, m.p. 98-100 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.74 (d, J = 7.9 Hz, 1H), 6.85 (s, 1H), 7.02 (d, J = 7.9 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.37-7.38 (m, 6H), 7.55 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 118.5, 120.5, 123.9, 129.1 (6C), 129.8 (3C), 134.3, 136.0 (4C), 150.7, 162.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{15}ClNS_2^+$: 356.0328, found: 356.0329.

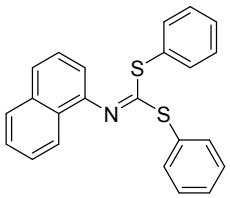
***N*-Pyridin-2-ylbis(phenylthio)methanimine (3t)**



3t

Light yellow solid, 26 mg, 32% yield, m.p. 98-100 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 30:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.82 (d, J = 8.0 Hz, 1H), 6.97-6.99 (m, 1H), 7.36-7.38 (m, 6H), 7.58-7.61 (m, 5H), 8.41 (d, J = 4.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 117.9, 119.7, 129.0 (2C), 129.6 (6C), 136.0 (4C), 137.7, 148.0, 160.0, 165.4. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{18}H_{15}N_2S_2^+$: 323.0671, found: 323.0678.

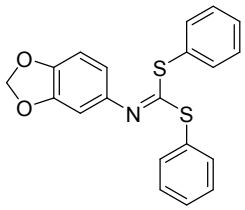
***N*-Naphthalen-1-ylbis(phenylthio)methanimine (3u)**



3u

Yellow solid, 62 mg, 67% yield, m.p. 115-117 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 40:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.97 (d, J = 7.3 Hz, 1H), 7.37-7.46 (m, 9H), 7.55-7.60 (m, 5H), 7.69 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 114.9, 123.5, 124.2, 125.4, 125.5, 126.1 (2C), 126.5, 127.8 (2C), 129.0 (4C), 129.9 (2C), 134.2, 136.0 (4C), 145.8, 161.7. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{23}H_{18}NS_2^+$: 372.0881, found: 372.0892.

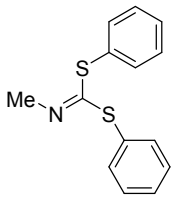
***N*-Benzo[*d*][1,3]dioxol-5-ylbis(phenylthio)methanimine (3v)**



3v

White solid, 75 mg, 82% yield, m.p. 105-107 °C. R_f = 0.23 (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.91 (s, 2H), 6.32-6.33 (m, 1H), 6.41-6.42 (m, 1H), 6.72 (d, J = 8.2 Hz, 1H), 7.36 (app s, 6H), 7.53 (app s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 101.1, 102.3 (2C), 108.2, 112.8 (2C), 129.1 (4C), 129.9 (2C), 134.9 (2C), 136.5 (2C), 144.0, 144.2, 147.8, 161.1. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{20}H_{16}NO_2S_2^+$: 366.0617, found: 366.0628.

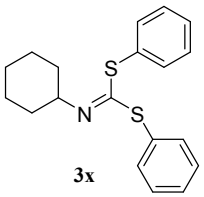
***N*-Methylbis(phenylthio)methanimine (3w)**



3w

Light yellow solid, 36 mg, 56% yield, m.p. 70-72 °C, R_f = 0.21 (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.29 (s, 3H), 7.30-7.32 (m, 3H), 7.37-7.43 (m, 5H), 7.59 (d, J = 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 41.4, 128.8, 129.1 (2C), 129.2 (2C), 129.6, 130.7, 134.6, 135.2 (2C), 135.5 (2C), 157.1. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{14}H_{14}NS_2^+$: 260.0562, found: 260.0562.

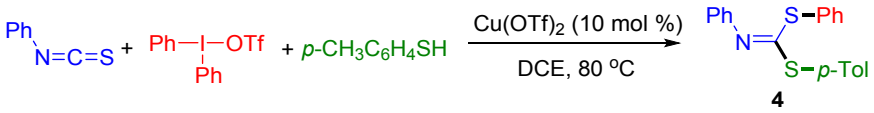
***N*-Cyclohexylbis(phenylthio)methanimine (3x)**



3x

White solid, 58 mg, 71% yield, m.p. 76-78 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.20-1.67 (m, 10H), 3.76-3.80 (m, 1H), 7.25 (s, 3H), 7.30-7.42 (m, 5H), 7.50-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.1 (2C), 25.7, 33.0 (2C), 62.5, 128.1, 128.4, 128.9 (2C), 129.4, 130.6, 131.6, 134.0, 135.0 (2C), 135.4 (2C), 151.8. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{22}NS_2^+$: 328.1188, found: 328.1190.

Phenyl *p*-tolyl (*E*)-phenylcarbonimidodithioate (4)

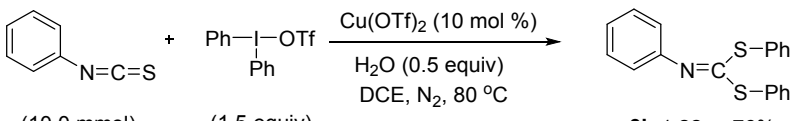


4

Under nitrogen atmosphere, a mixture of isothiocyanatobenzene **1b** (68 mg, 0.50 mmol), diaryiodonium salt **2a** (323 mg, 0.75 mmol), $Cu(OTf)_2$ (18 mg, 0.05 mmol) and DCE (2.0 mL) was added to a dry Schlenk tube, after stirring at 80 °C for 10 minute, *p*-toluenethiol (62 mg, 0.5 mmol) dissolved in DCE (0.5 mL) was added dropwise to the mixture. The mixture was stirring for 3 h. After completion, the mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with saturated NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 150:1) to afford compound **4** as a white solid.

White solid, 104 mg, 62% yield, m.p. 85-87 °C. R_f = 0.25 (petroleum ether/ethyl acetate = 150:1, v/v). ^{1}H NMR (DMSO, 500 MHz): δ 2.31 (s, 3H), 6.70 (t, J = 6.6 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 7.24-7.31 (m, 4H), 7.42-7.55 (m, 7H). ^{13}C NMR (DMSO, 125 MHz): δ 21.3, 120.2 (2C), 124.5, 129.5 (3C), 129.7 (3C), 130.5 (3C), 135.9 (4C), 140.4, 149.6, 160.8. HRMS (ESI-TOF [M + H]$^+$), m/z calcd for $C_{19}H_{22}NS_2^+$: 336.0875, found: 336.0876.

Scale-up reaction and synthetic transformation:

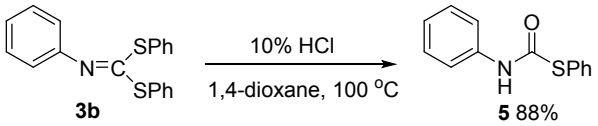


(10.0 mmol) (1.5 equiv) **3b** 1.22 g, 76%

Under N_2, to a dry Schlenk tube was charged with a mixture of isothiocyanatobenzene **1b** (1.35 g, 10.0 mmol), diphenyliodonium salt **2a** (6.45 g, 15.0 mmol), $Cu(OTf)_2$ (0.36 g, 1.0 mmol), H_2O (90

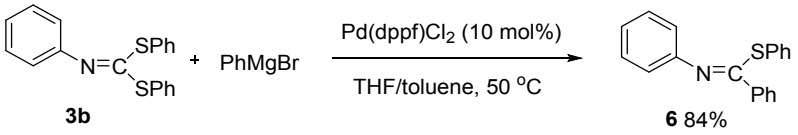
mg, 5.0 mmol) and DCE (50 mL) . The mixture was allowed to stir at 80 °C for 3 h. After completion, the mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous $MgSO_4$. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 150:1) to afford *N*-phenylbis(phenylthio)methanimine **3b** as a white solid (1.22 g, 76%).

_S_-Phenyl phenylcarbamothioate (5)[5]



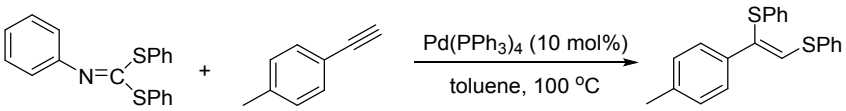
N-Phenylbis(phenylthio)methanimine **3b** (129 mg, 0.4 mmol) and 10% HCl (0.4 mL) was dissolved in 1,4-dioxane (2.0 mL) and the reaction temperature was heated to 100 °C for 3 h. After completion, the mixture was cooled to room temperature, poured into ice-cold diluted saturated $NaHCO_3$, and extracted with ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous $MgSO_4$. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel to afford **5** as a pale yellow solid (81 mg, 88%), m.p. 123-125 °C. R_f = 0.2 (petroleum ether/ethyl acetate = 20:1, v/v). IR (KBr, *v*, cm^{-1}): 3252 (NH), 3191, 3127, 3050, 3014, 1661 (C=O), 1597, 1538, 1500, 1442, 749, 690, 643.

Phenyl (*Z*)-*N*-phenylbenzimidothioate (6)[6]



Under nitrogen atmosphere, phenylmagnesium bromide[7] (0.8 mmol, 1.0 M, 0.8 mL) was added to a mixture of **3b** (129 mg, 0.4 mmol) and $Pd(dppf)Cl_2$ (29 mg, 0.04 mmol) in dry toluene (0.8 mL) at room temperature. The reaction mixture was stirred at 50 °C for 5 h. After completion, the mixture was quenched with water (10.0 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products **6** as a yellow solid (97 mg, 84%), m.p. 70-72 °C, R_f = 0.21 (petroleum ether/ethyl acetate = 60:1, v/v). ^1H NMR ($CDCl_3$, 500 MHz): δ 6.99 (s, 2H), 7.07 (s, 3H), 7.14 (s, 3H), 7.21-7.27 (m, 3H), 7.35-7.44 (m, 2H), 7.67 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 29.4, 119.9, 124.3, 127.6, 127.9, 128.3, 128.7, 128.8, 129.2, 130.0, 132.3, 133.3, 137.5, 150.3, 163.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{19}H_{16}NS^+$: 290.0998, found: 290.0996.

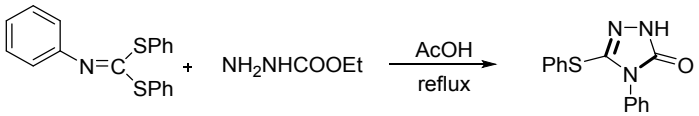
(*Z*)-(1-(*p*-Tolyl)ethene-1, 2-diyl)bis(phenylsulfane) (7)[8]



3b **7** 72%

Under N_2, 1-ethynyl-4-methylbenzene (93 mg, 0.8 mmol) was added dropwise to a mixture of **3b** (129 mg, 0.4 mmol) and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) in dry toluene (1.5 mL) at room temperature. The reaction mixture was carried out at 100 °C for 3 h. After completion, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel to afford **7** as a light yellow oil (96 mg, 72%), R_f = 0.3 (petroleum ether/ethyl acetate = 100:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.28 (s, 3H), 7.05 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.7 Hz, 2H), 7.21 (s, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.1, 125.8, 126.6, 127.4, 128.1, 128.8, 129.1, 129.2, 129.3, 130.5, 134.8, 135.3, 135.5, 135.9, 137.5. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{21}H_{19}S_2^+$: 335.0923, found: 335.0923.

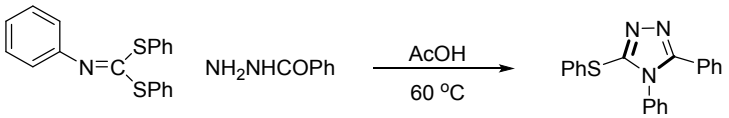
4-Phenyl-5-(phenylthio)-2,4-dihydro-3H-1,2,4-triazol-3-one (8)



3b **8** 60%

A mixture of **3b** (129 mg, 0.4 mmol), ethyl hydrazinecarboxylate (107 mg, 1.0 mmol) and acetic acid (2.0 mL) was stirred at 120 °C for 24 h. After completion, the mixture was cooled to room temperature, quenched with saturated $NaHCO_3$, extracted with ethyl acetate (3 × 10 mL) and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products **8** as a white solid (65 mg, 60%), m.p. 157-158 °C. R_f = 0.15 (petroleum ether/ethyl acetate = 3:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18-7.21 (m, 2H), 7.24-7.28 (m, 5H), 7.39-7.40 (m, 3H), 10.31 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 127.3, 128.7, 128.8, 129.1, 129.2, 129.3 132.1, 132.3, 143.2, 155.0. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{14}H_{12}N_3OS^+$: 270.0696, found: 270.0695.

3,4-Diphenyl-5-(phenylthio)-4H-1,2,4-triazole (9)[9]



3b **9** 58%

A mixture of **3b** (129 mg, 0.4 mmol), benzohydrazide (136 mg, 1.0 mmol) and acetic acid (2.0 mL) was stirred at 60 °C for 8 h. After cooled to room temperature, the mixture was quenched with saturated $NaHCO_3$, extracted with ethyl acetate and concentrated. The residue was purified by

flash chromatography on silica gel to afford the desired products **9** as a white solid (76 mg, 58%), m.p. 167-169 ^{o}C. R_f = 0.12 (petroleum ether/ethyl acetate = 5:1, v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.01 (d, J = 7.6 Hz, 2H), 7.21-7.27 (m, 7H), 7.31-7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 126.5, 127.6, 128.1, 128.3, 128.4, 129.2, 129.5, 129.7, 129.9, 131.0, 131.4, 134.4, 150.3, 155.7. HRMS (ESI-TOF $[M + H]^+$), m/z calcd for $C_{20}H_{16}N_3S^+$: 330.1059, found: 330.1059.

References

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3. (a) Shuhei Fukamachi; Hisatoshi Konishi and Kazuhiro Kobayashi. *Synthesis* 2010, ***10***, 1593; (b) W. Y. Hao, J. Huang, S. S. Jie and M. Z. Cai, *Eur. J. Org. Chem.* 2015, 6655.
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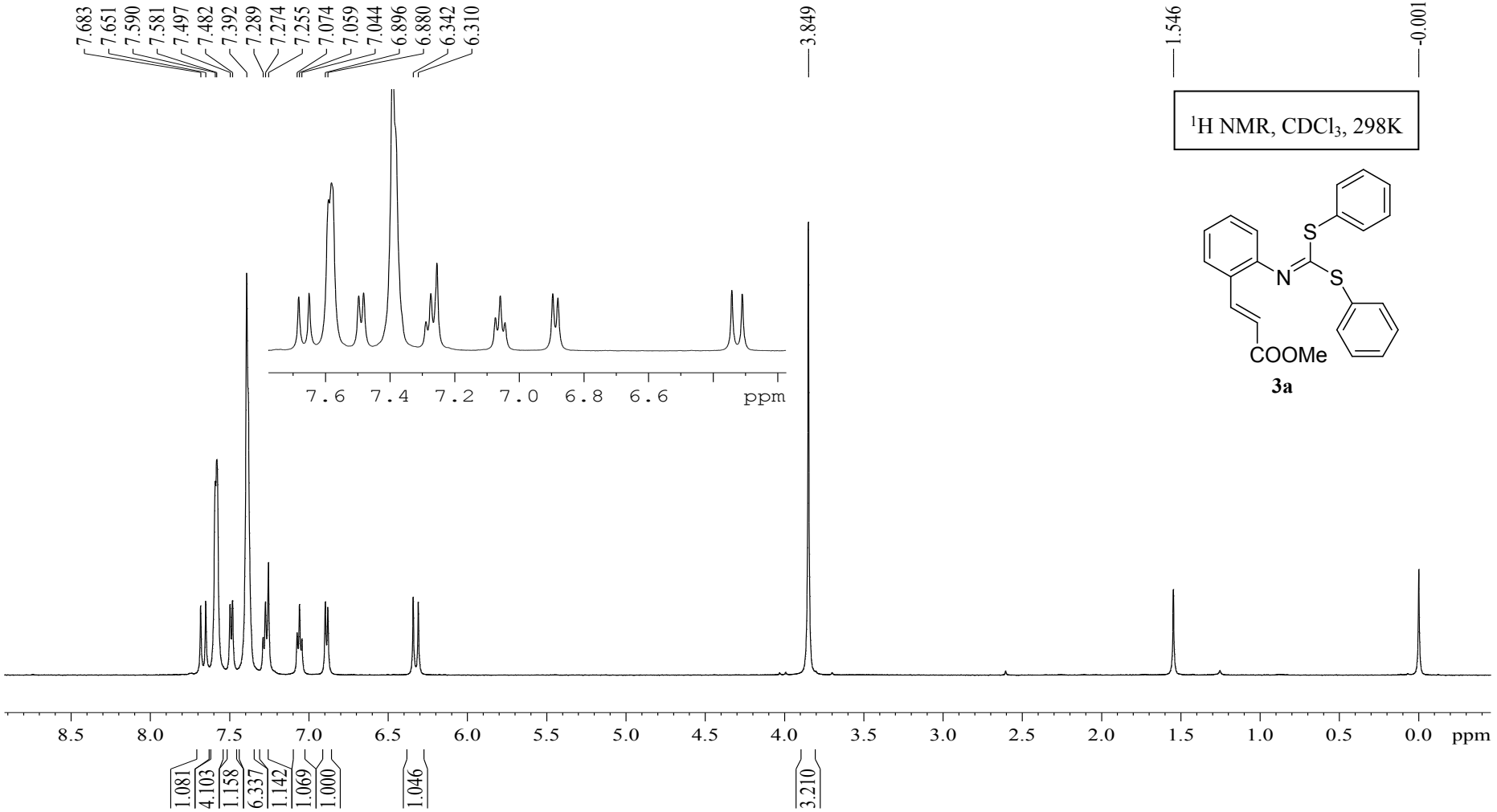
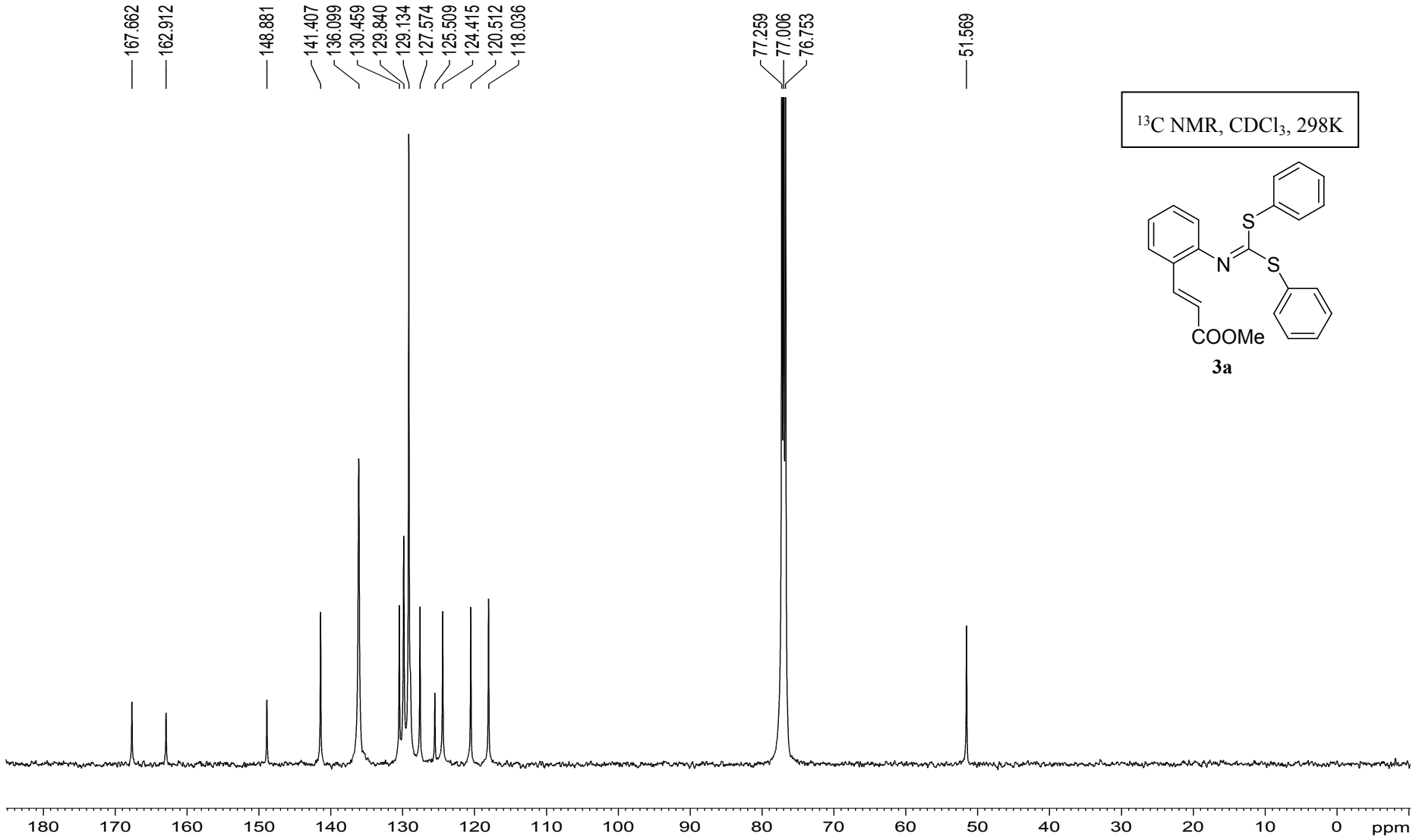
9. L. F. Niu, Y. Cai, C. Liang, X. P. Hui and P. F. Xu, *Tetrahedron* 2011, ***67,*** 2878.

^{1}H NMR and ^{13}C NMR spectra of carbonimidodithioate

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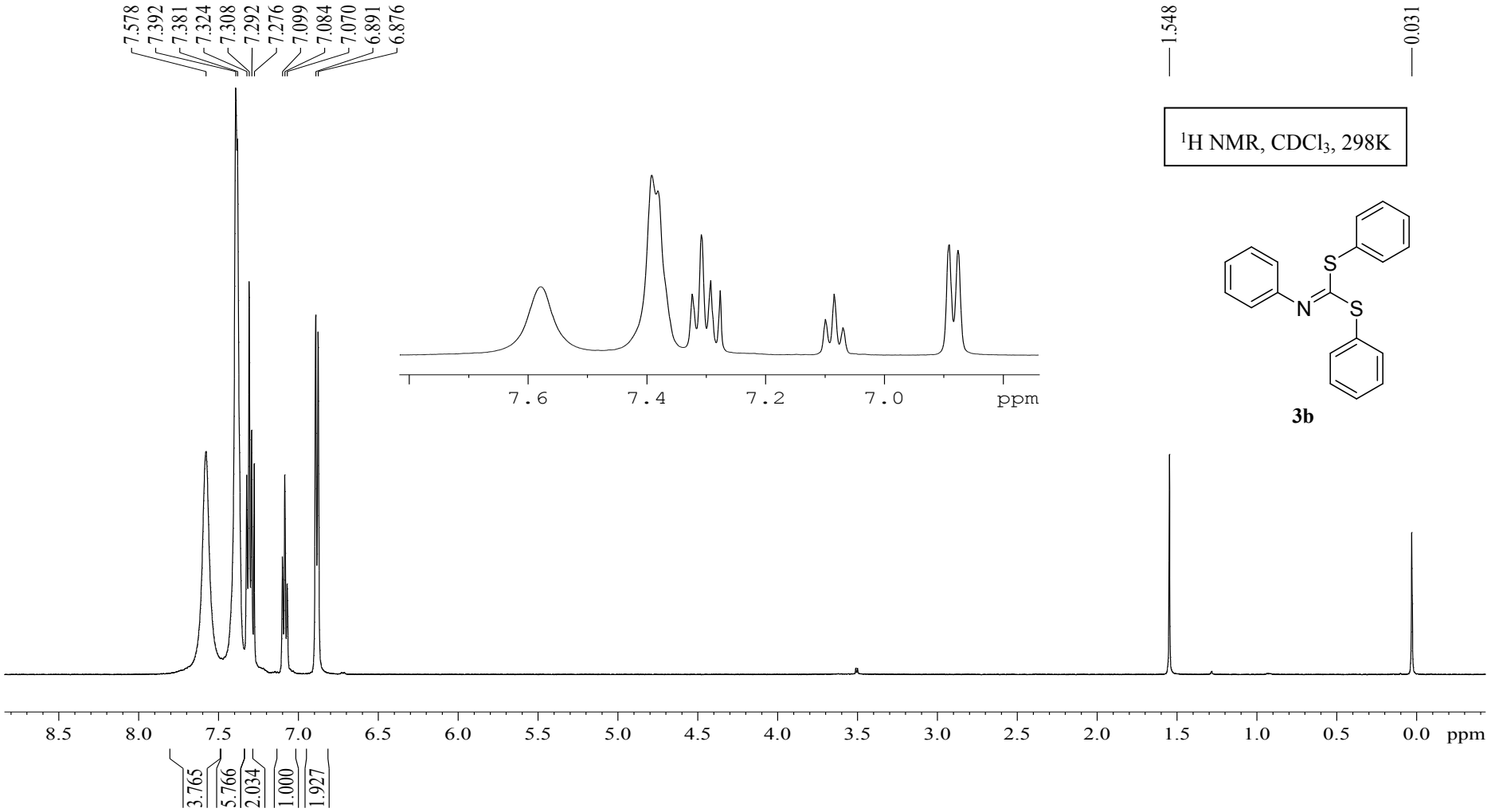
141.407
136.099
130.459
129.840
129.134
127.574
125.509
124.415
120.512
118.036
77.259
77.006
76.753
51.569
^{13}C NMR, $CDCl_3$, 298K
S
N
S
COOMe
3a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.392
7.381
7.324
7.308
7.292
7.276
7.099
7.084
7.070
6.891
6.876
1.548
0.031
^{1}H NMR, $CDCl_3$, 298K
7.6
7.4
7.2
7.0
ppm
S
N
S
3b
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
ppm
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5.766
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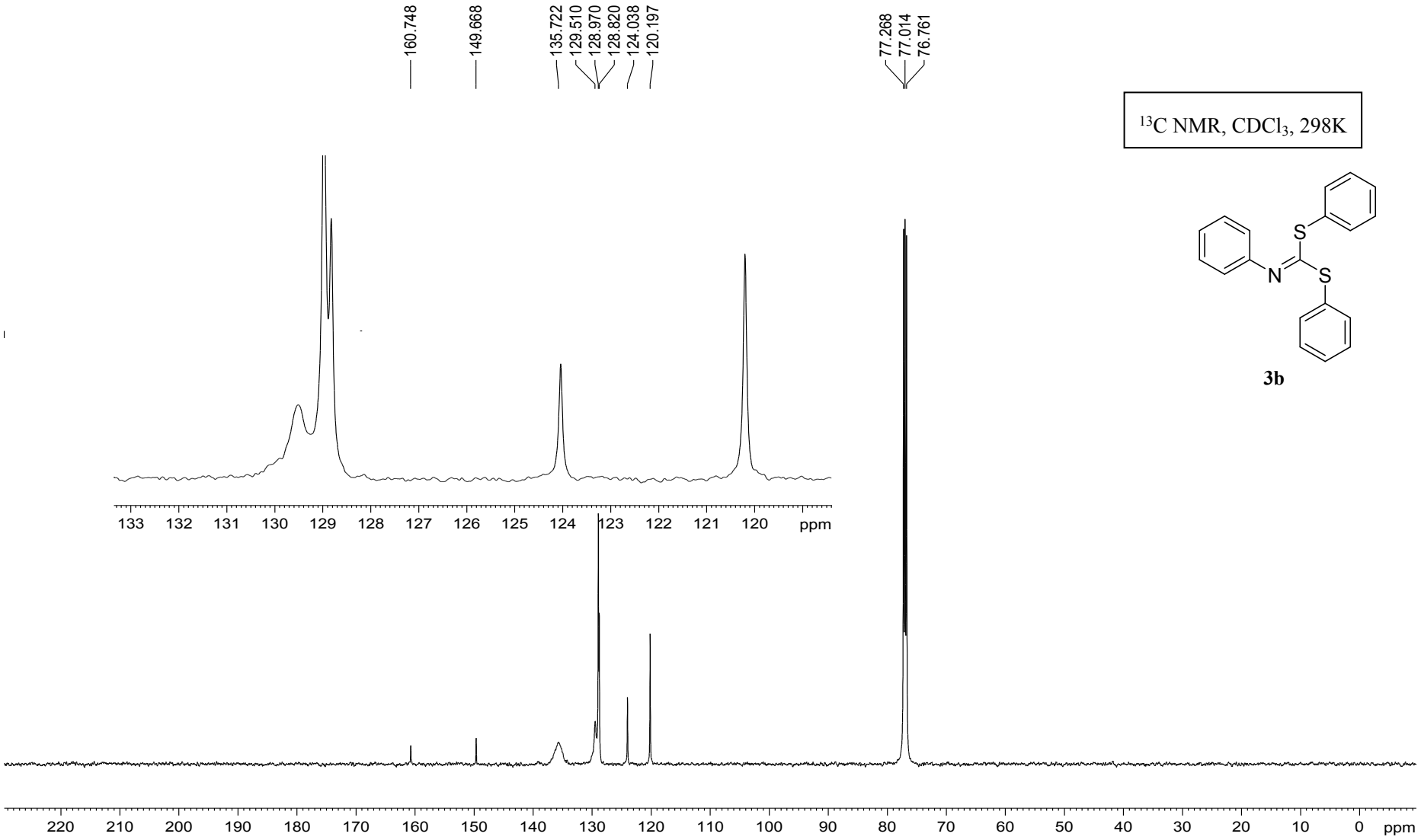
1.000
1.927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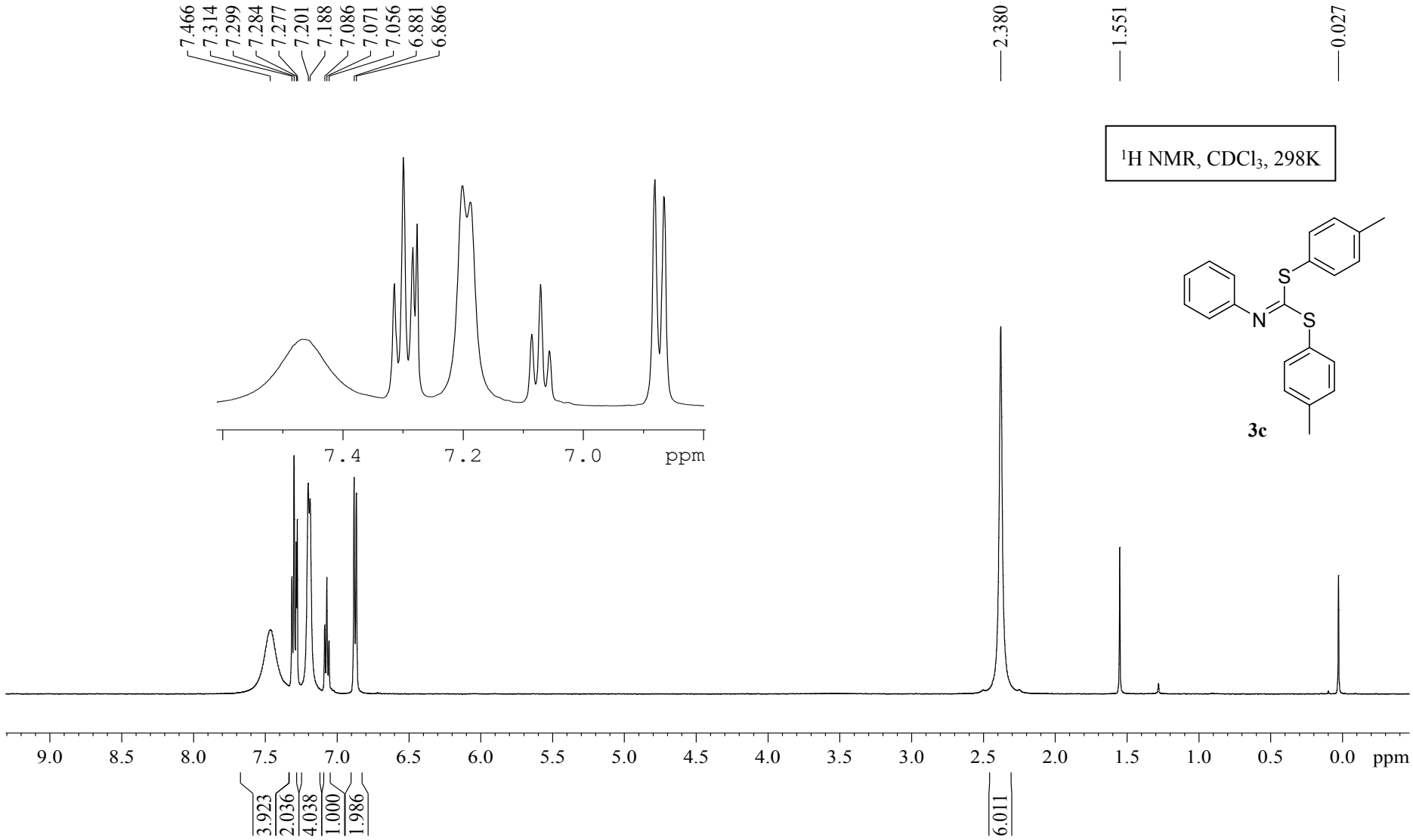
149.668
135.722
129.510
128.970
128.820
124.038
120.197
77.268
77.014
76.761
^{13}C NMR, $CDCl_3$, 298K
S
N
S
3b
133 132 131 130 129 128 127 126 125 124 123 122 121 120 ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.314
7.299
7.284
7.277
7.201
7.188
7.086
7.071
7.056
6.881
6.866
2.380
1.551
0.027
^{1}H NMR, $CDCl_3$, 298K
S
N
S
3c
7.4
7.2
7.0
ppm
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
ppm
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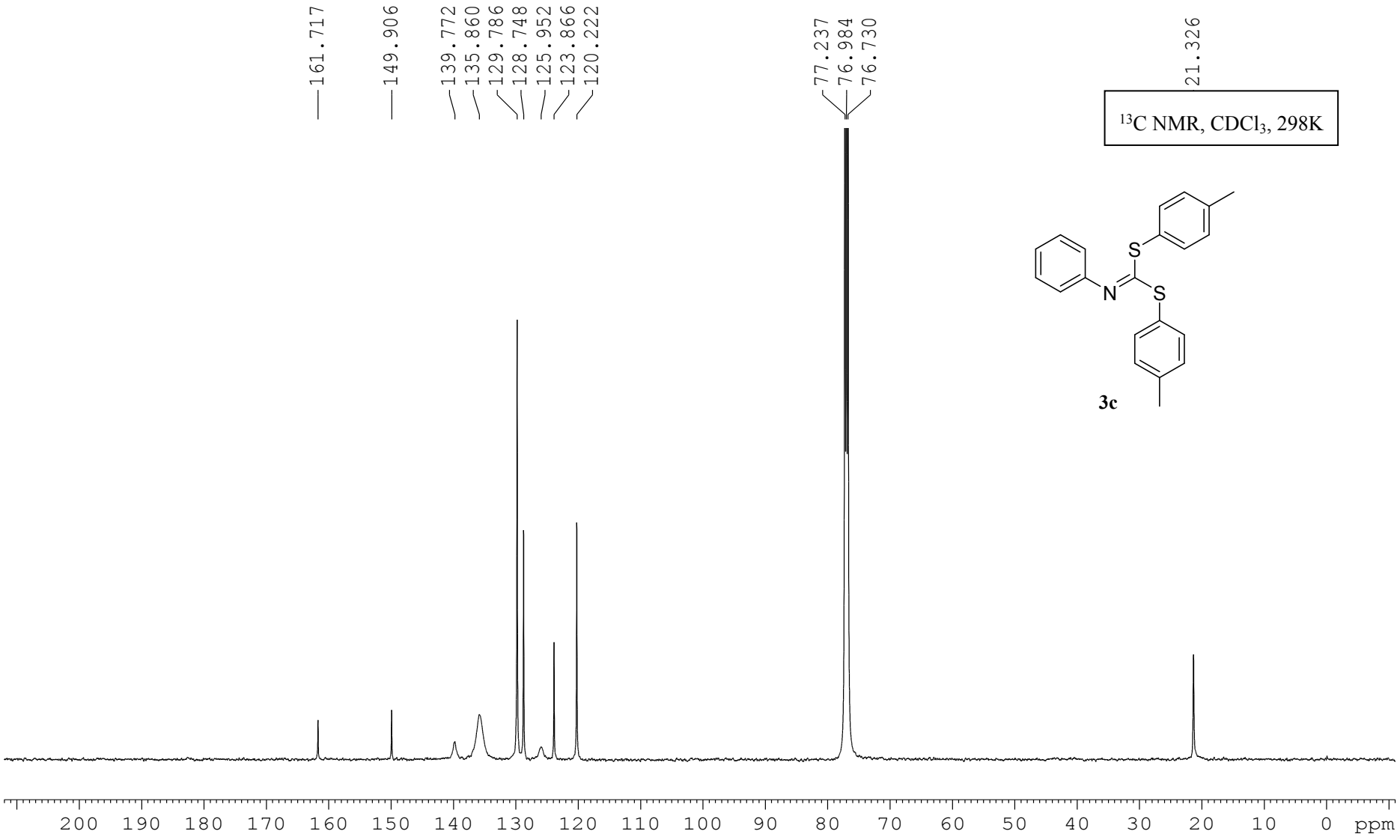
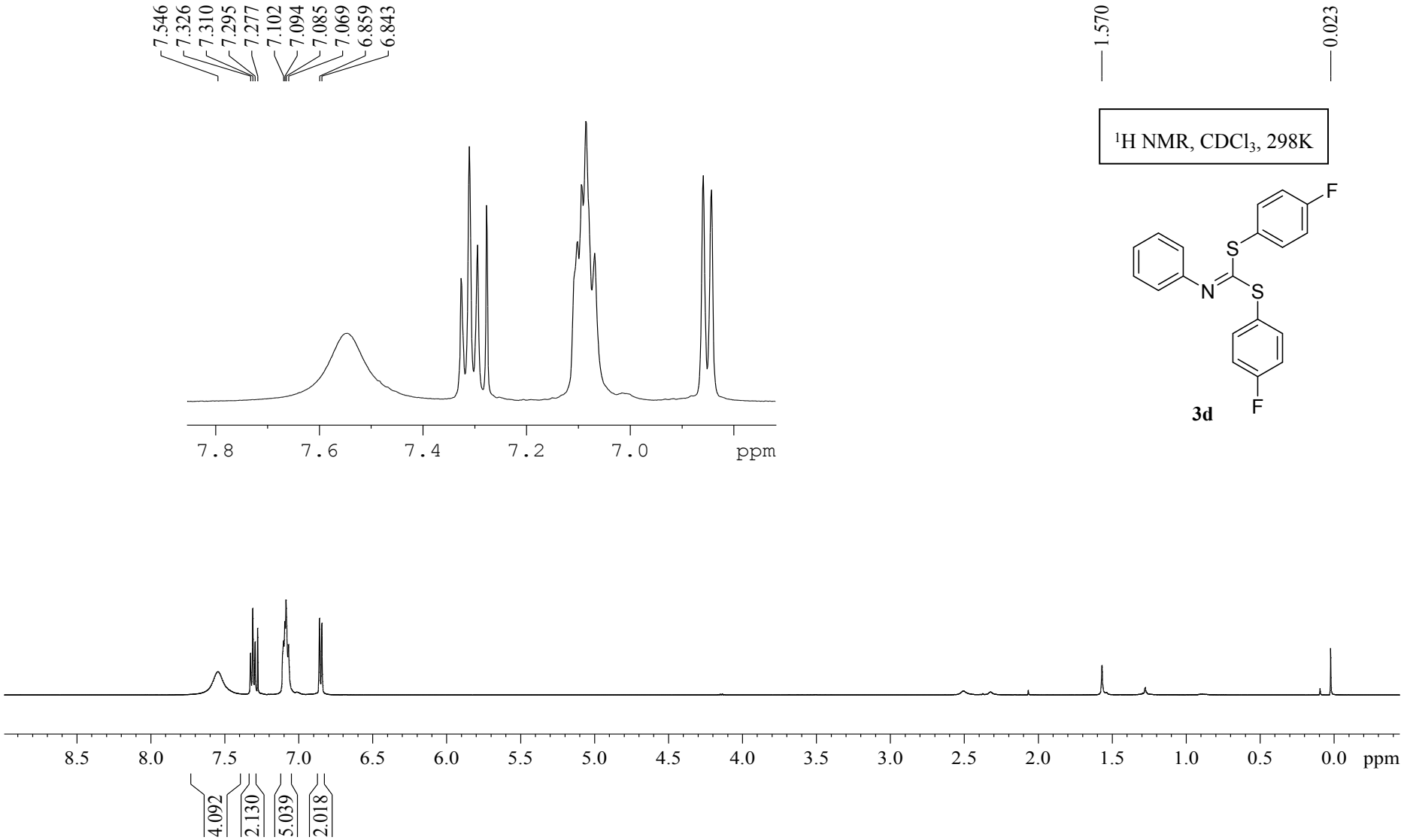
1.000
1.986
6.011


161.717
149.906
139.772
135.860
129.786
128.748
125.952
123.866
120.222
77.237
76.984
76.730
21.326
^{13}C NMR, $CDCl_3$, 298K
S
N
S
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.326
7.310
7.295
7.277
7.102
7.094
7.085
7.069
6.859
6.843
1.570
0.023
^{1}H NMR, $CDCl_3$, 298K
F
S
N
S
F
3d
7.8
7.6
7.4
7.2
7.0
ppm
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
ppm
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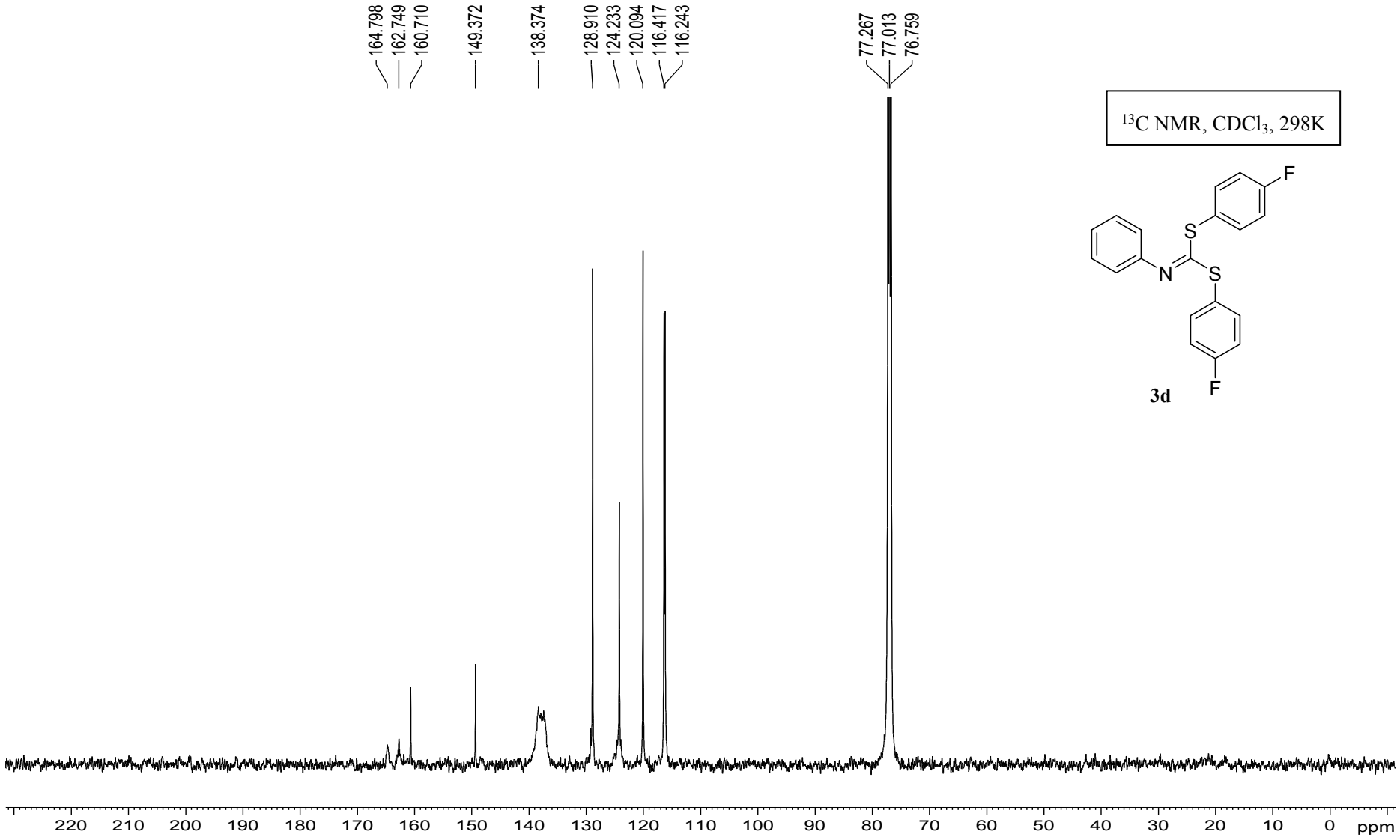
2.130
5.039
2.018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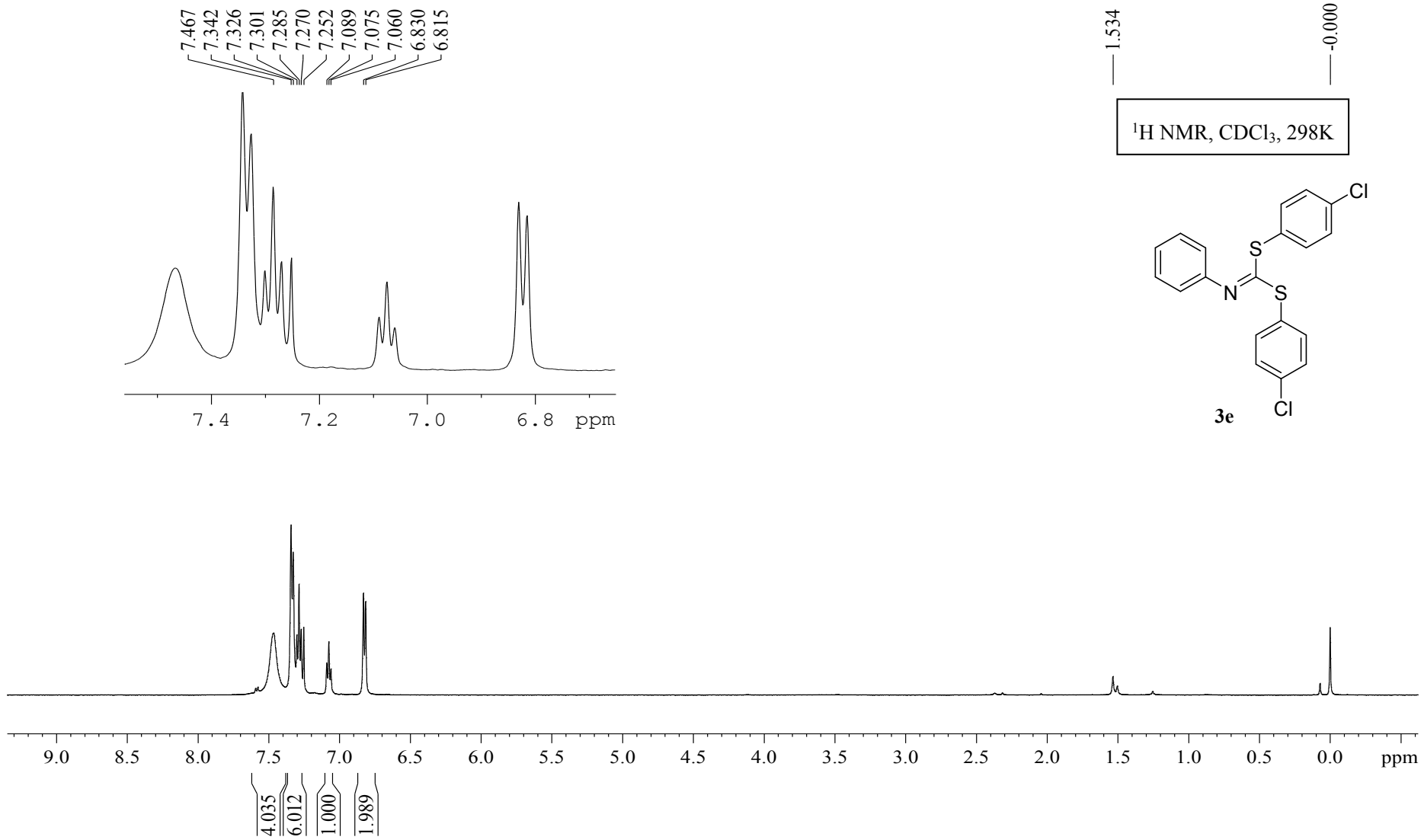
162.749
160.710
149.372
138.374
128.910
124.233
120.094
116.417
116.243
77.267
77.013
76.759
^{13}C NMR, $CDCl_3$, 298K
F
S
N
S
F
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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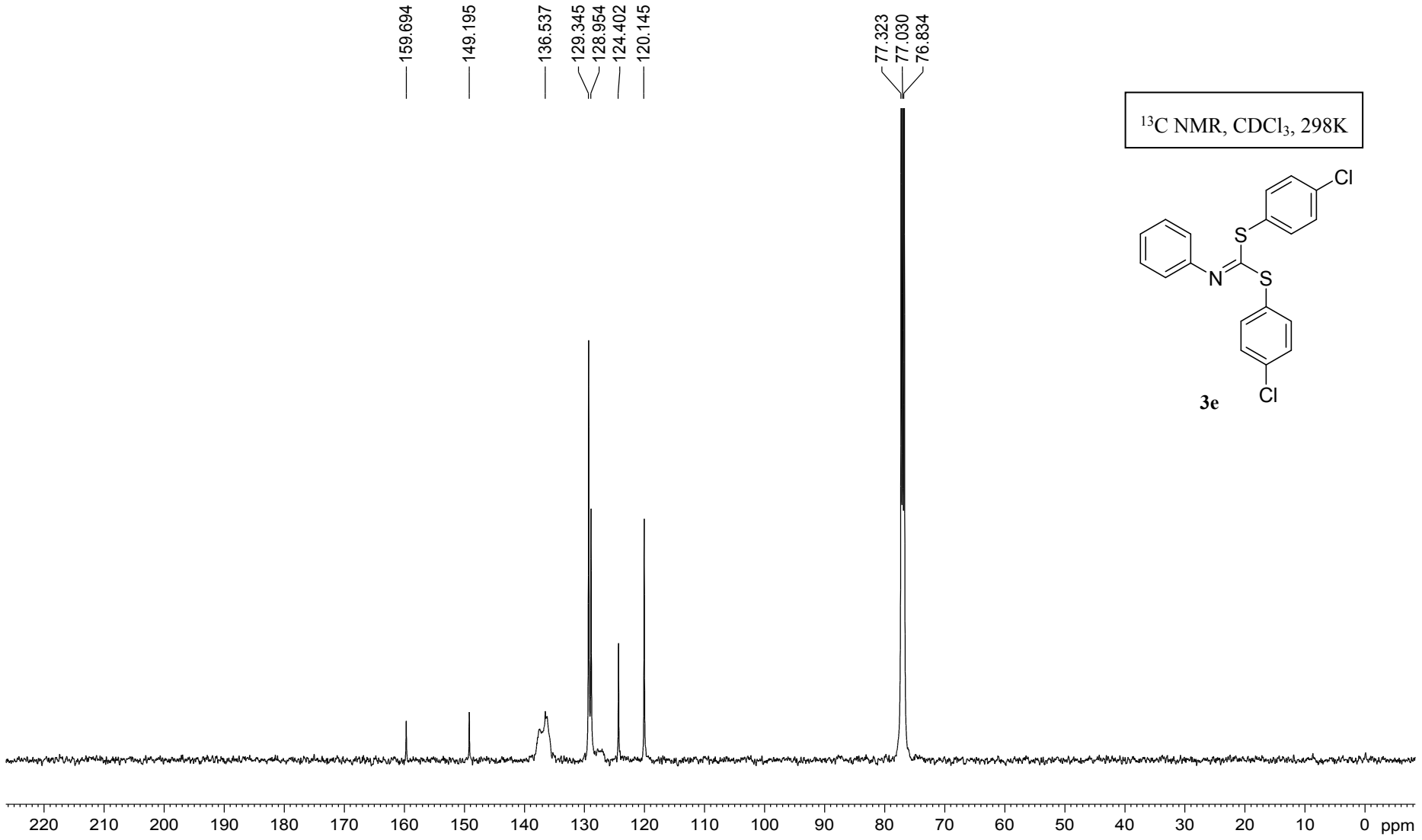
7.342
7.326
7.301
7.285
7.270
7.252
7.089
7.075
7.060
6.830
6.815
7.4
7.2
7.0
6.8
ppm
1.534
-0.000
^{1}H NMR, CDCl$_3$, 298K
Cl
S
N
S
Cl
3e
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.035
6.012
1.000
1.989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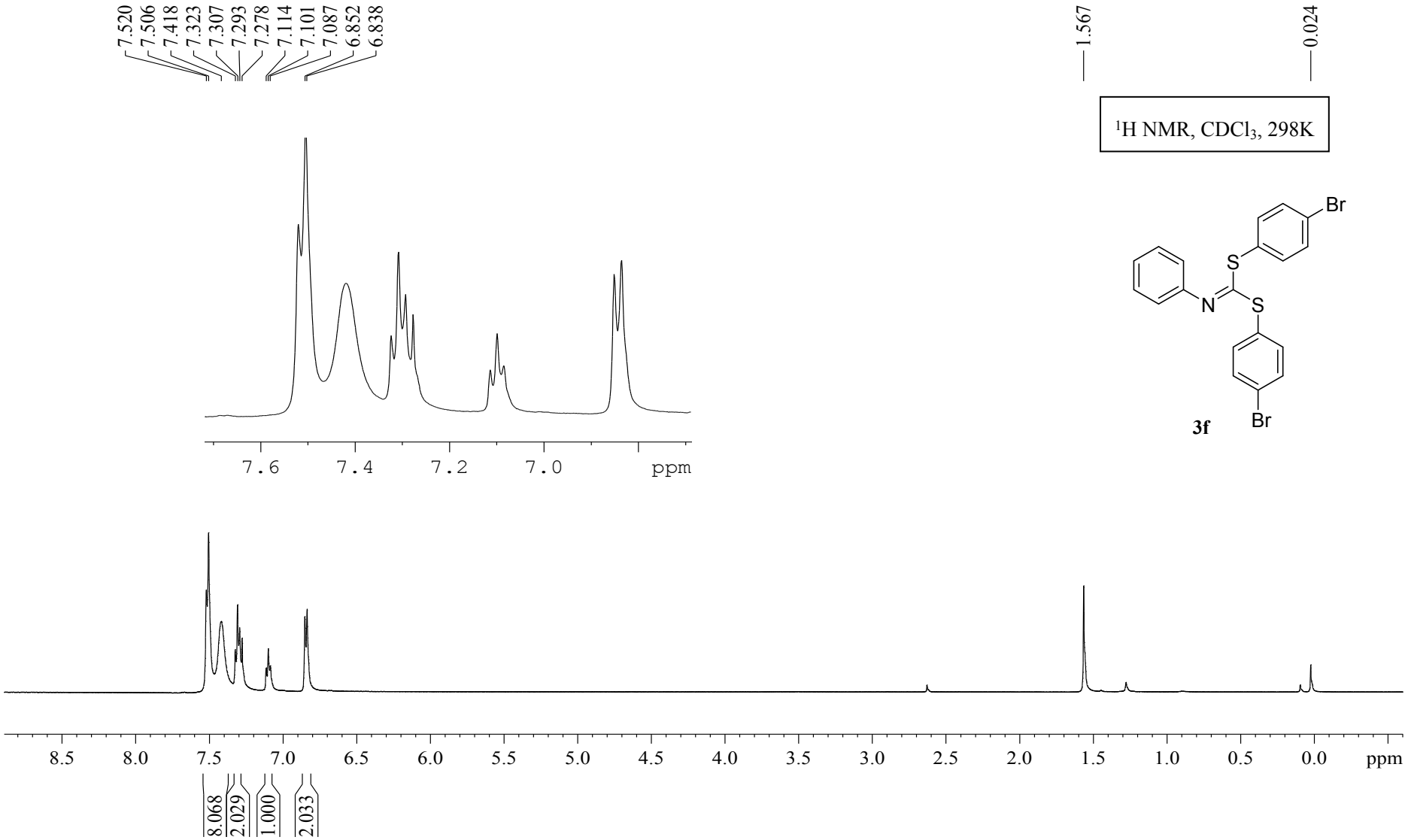
149.195
136.537
129.345
128.954
124.402
120.145
77.323
77.030
76.834
^{13}C NMR, $CDCl_3$, 298K
Cl
S
N
S
Cl
3e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.293
7.278
7.114
7.101
7.087
6.852
6.838
1.567
0.024
^{1}H NMR, $CDCl_3$, 298K
Br
S
N
S
Br
3f
7.6
7.4
7.2
7.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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ppm
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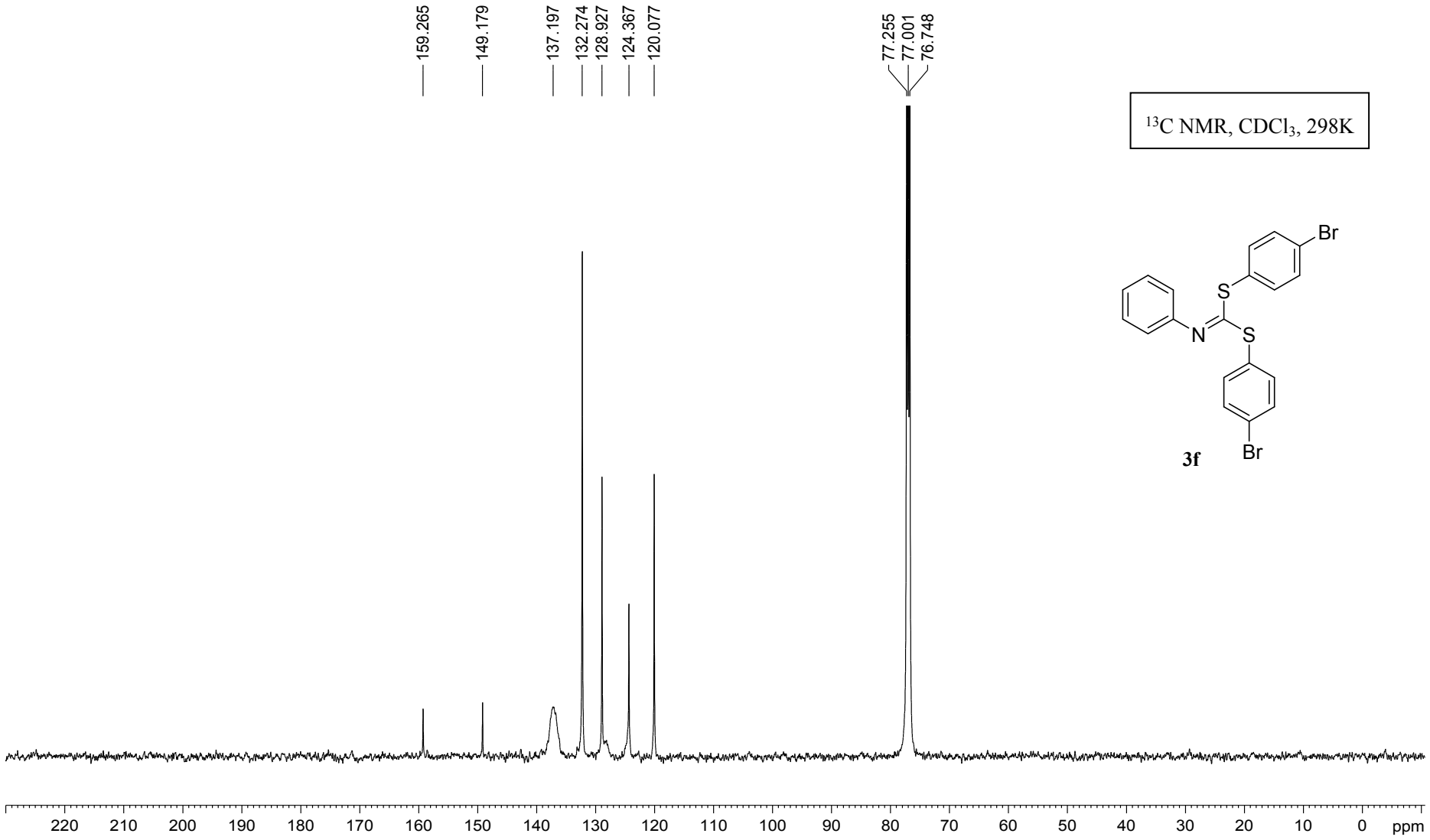
2.029
1.000
2.033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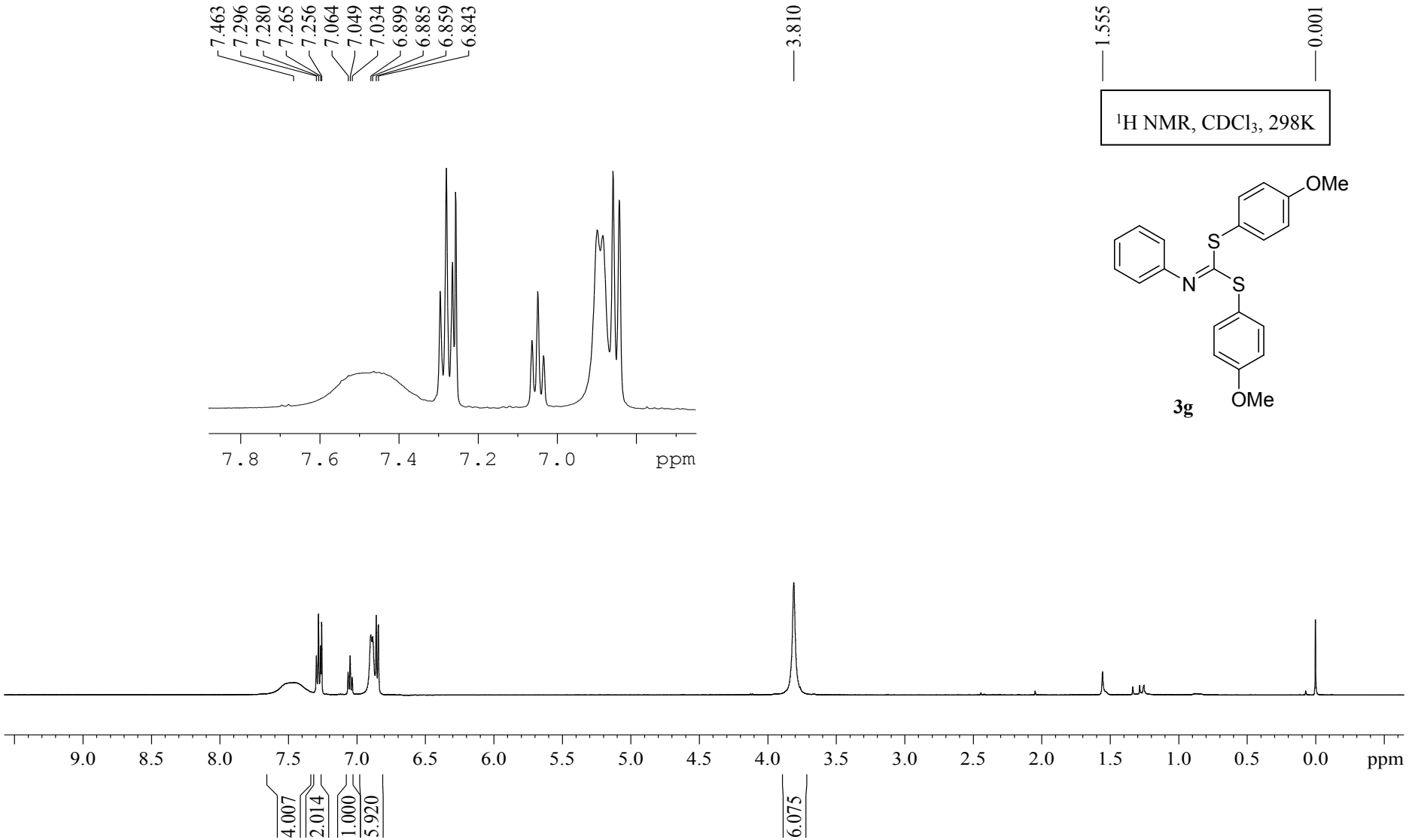
137.197
132.274
128.927
124.367
120.077
77.255
77.001
76.748
^{13}C NMR, $CDCl_3$, 298K
Br
S
N
S
Br
3f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.034
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6.859
6.843
3.810
1.555
0.001
^{1}H NMR, $CDCl_3$, 298K
OMe
S
N
S
OMe
3g
7.8
7.6
7.4
7.2
7.0
ppm
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
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1.5
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0.5
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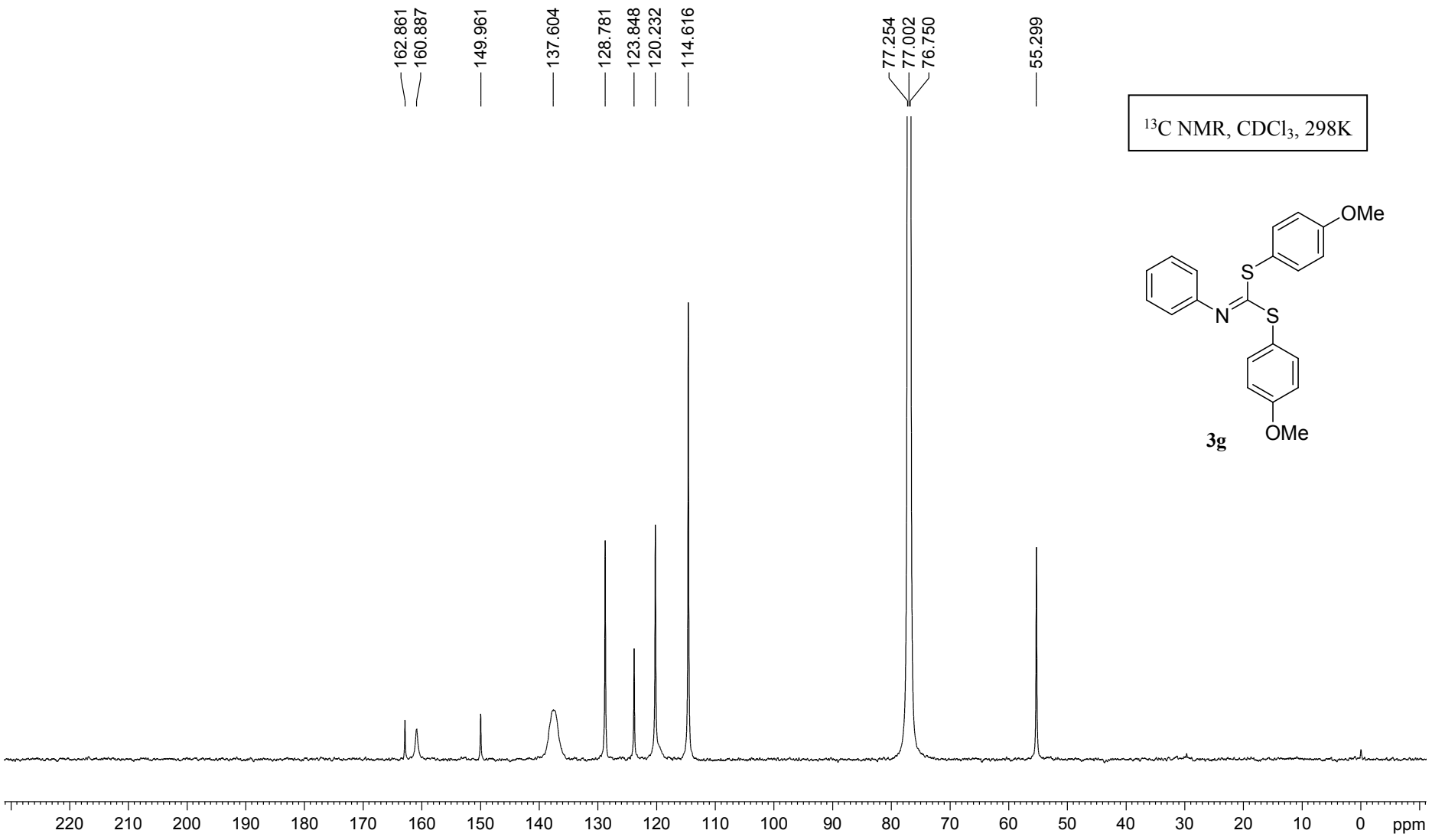
6.075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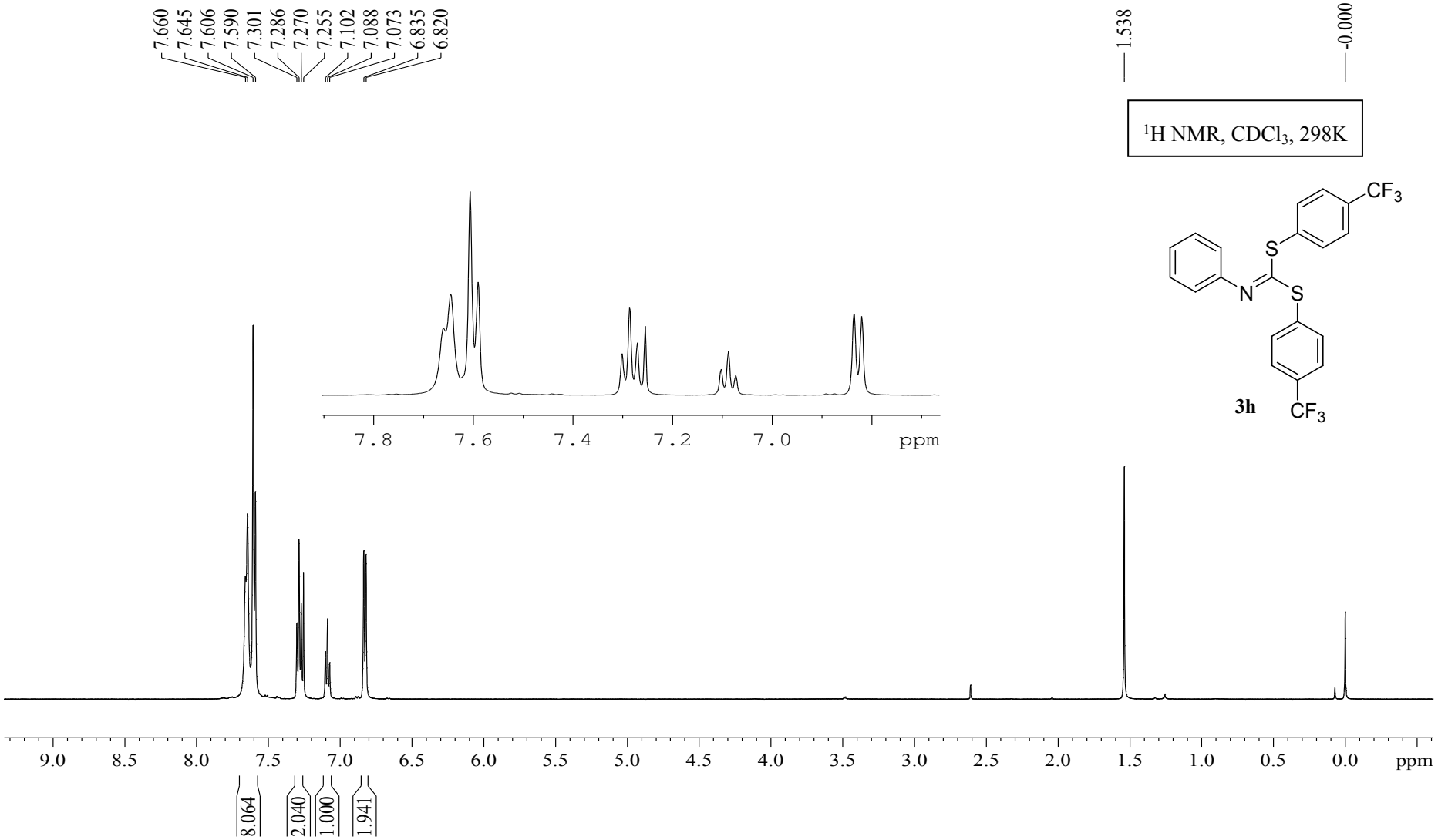
77.002
76.750
55.299
^{13}C NMR, $CDCl_3$, 298K
OMe
S
N
S
OMe
3g
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.286
7.270
7.255
7.102
7.088
7.073
6.835
6.820
1.538
-0.000
^{1}H NMR, $CDCl_3$, 298K
CF_3
S
N
S
CF_3
3h
7.8
7.6
7.4
7.2
7.0
ppm
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
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2.0
1.5
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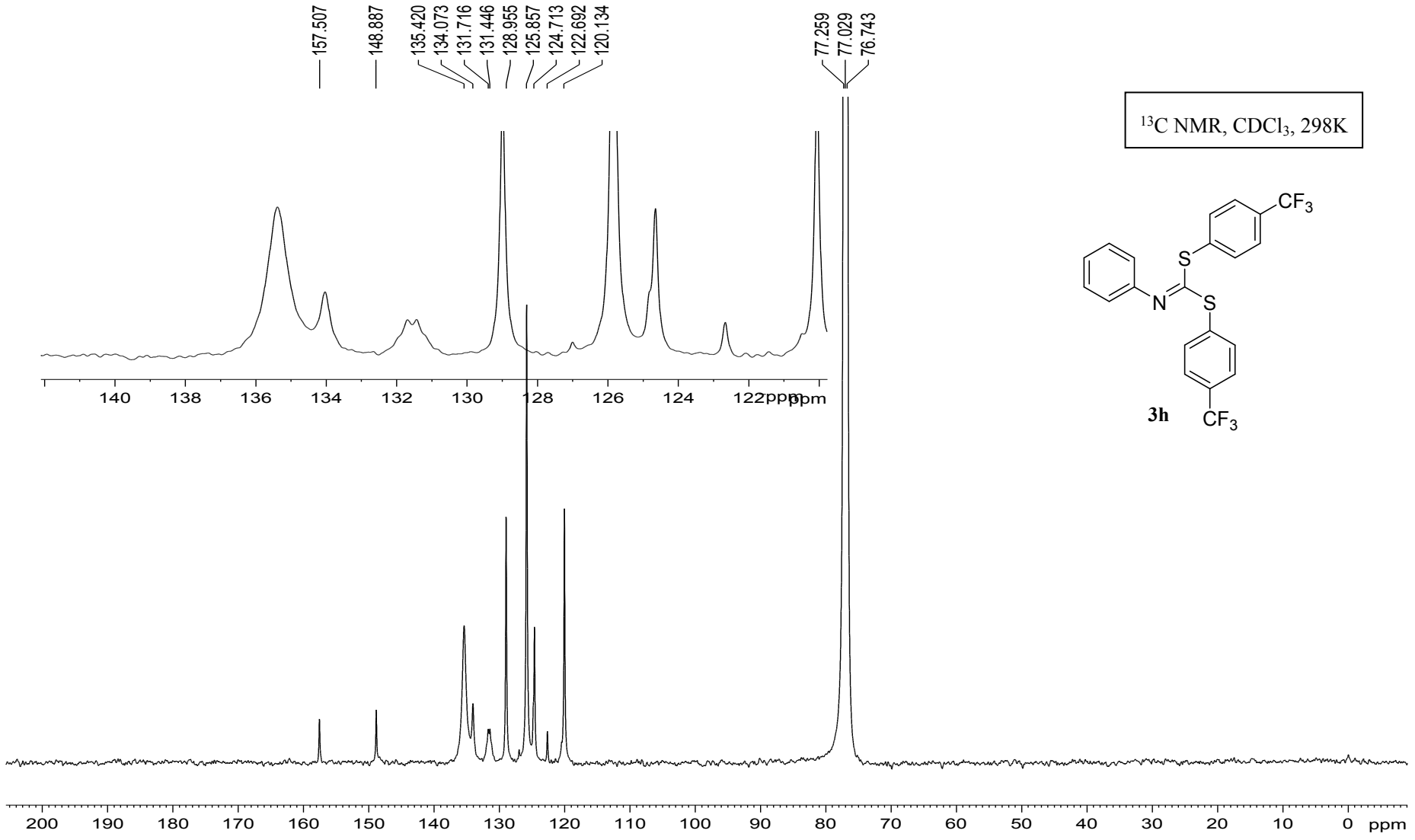
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131.446
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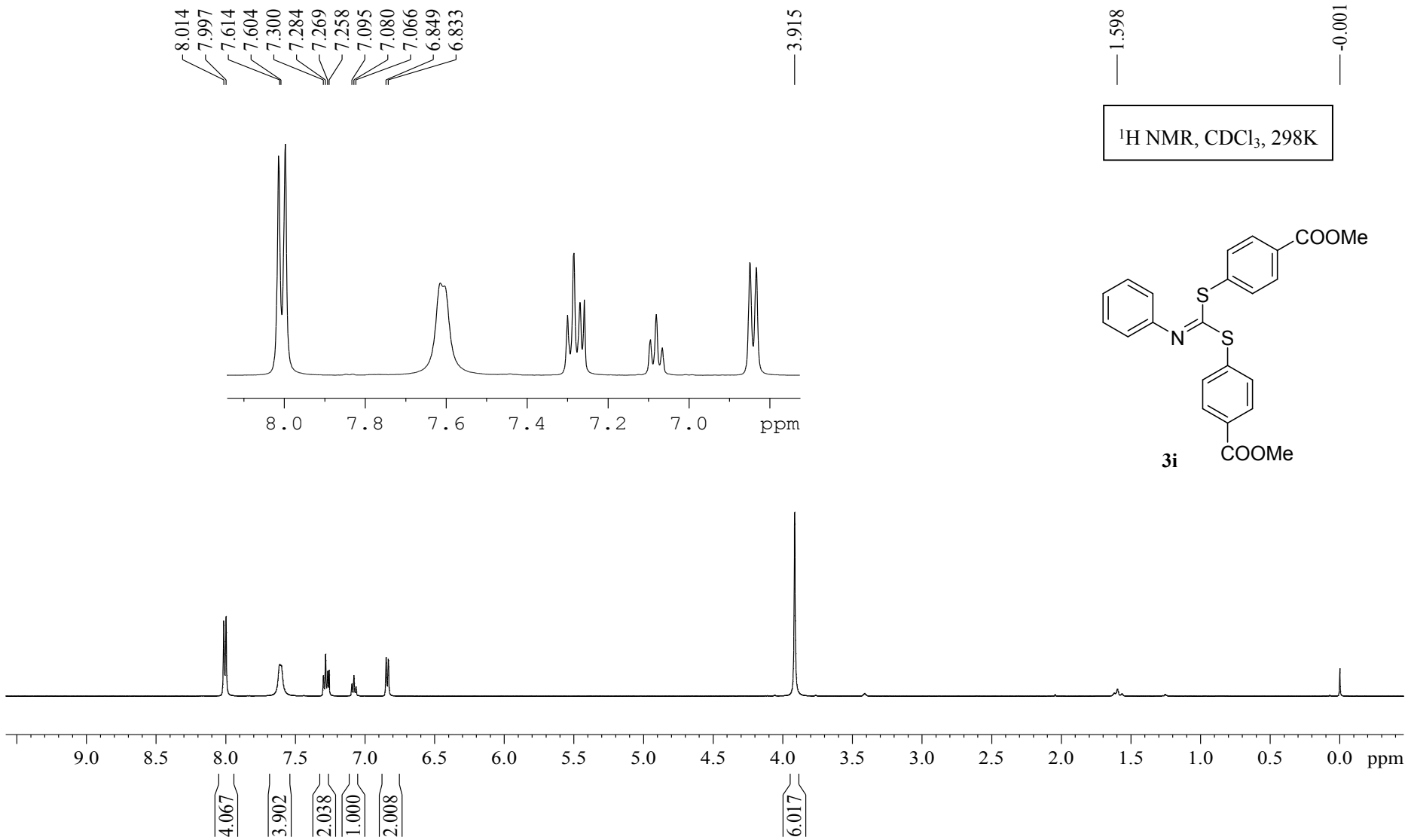
125.857
124.713
122.692
120.134
77.259
77.029
76.743
^{13}C NMR, $CDCl_3$, 298K
CF_3
S
N
S
CF_3
3h
140 138 136 134 132 130 128 126 124 122 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.833
3.915
1.598
-0.001
^{1}H NMR, $CDCl_3$, 298K
COOMe
S
N
S
COOMe
3i
8.0
7.8
7.6
7.4
7.2
7.0
ppm
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
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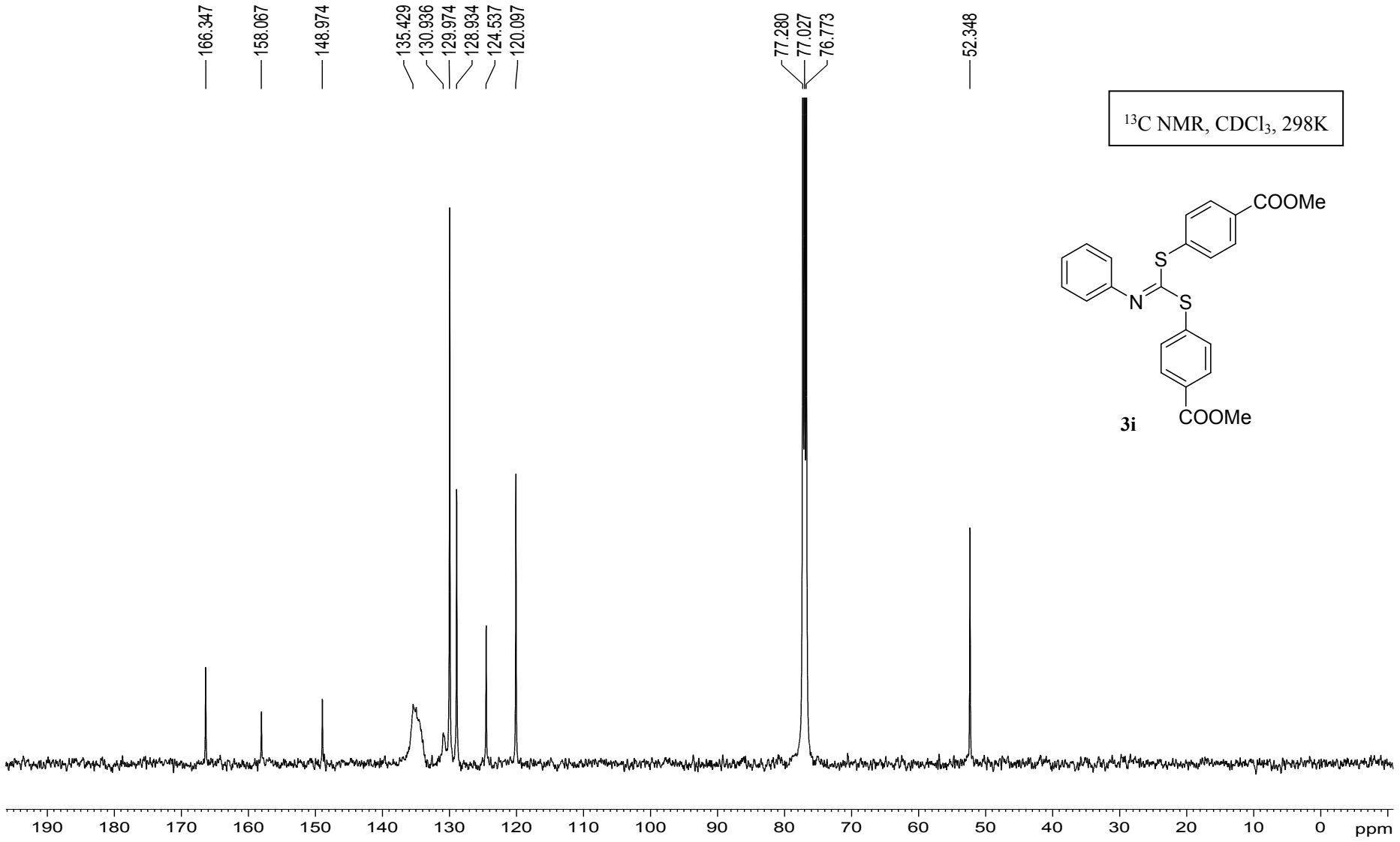
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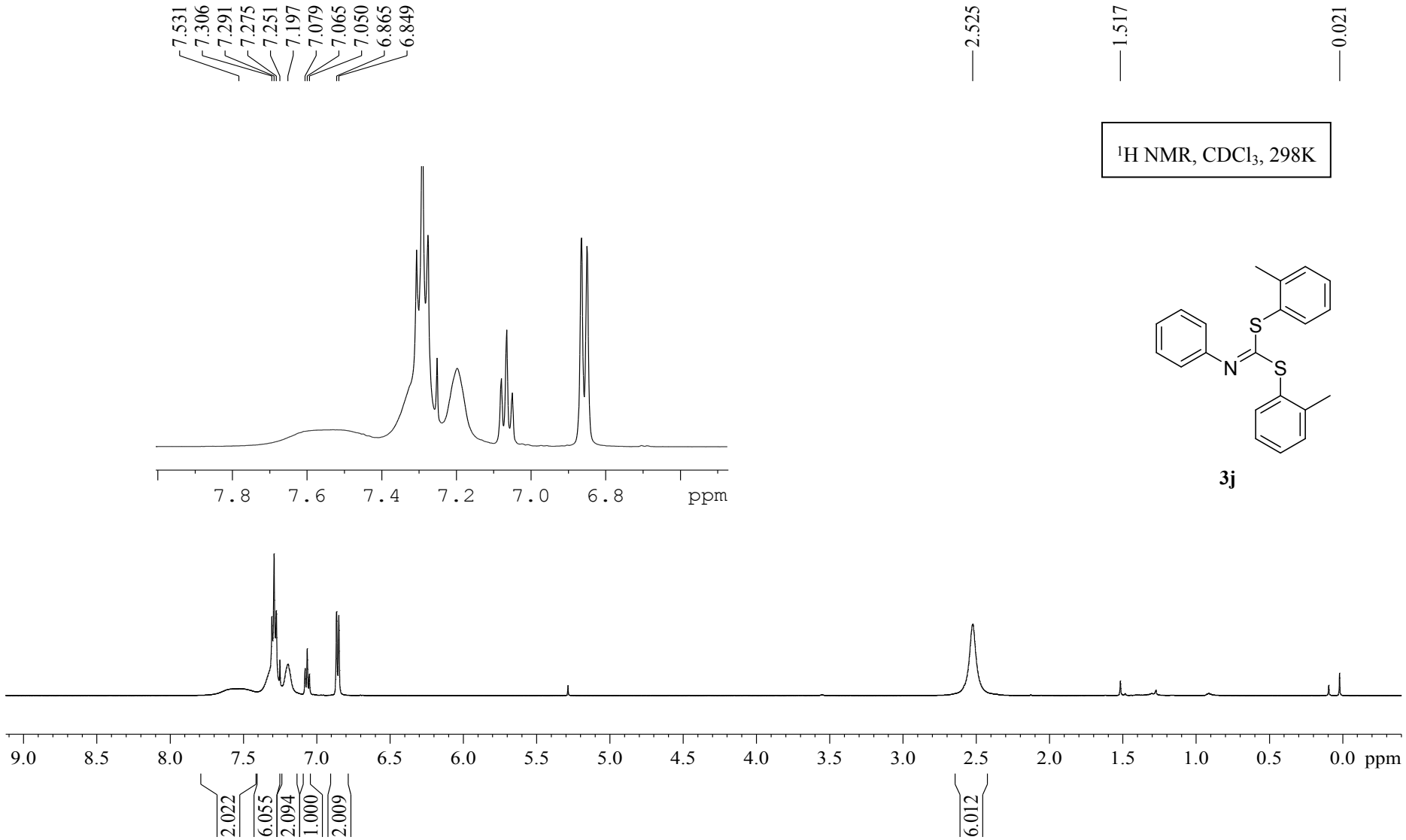
135.429
130.936
129.974
128.934
124.537
120.097
77.280
77.027
76.773
52.348
^{13}C NMR, $CDCl_3$, 298K
COOMe
S
N
S
COOMe
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.251
7.197
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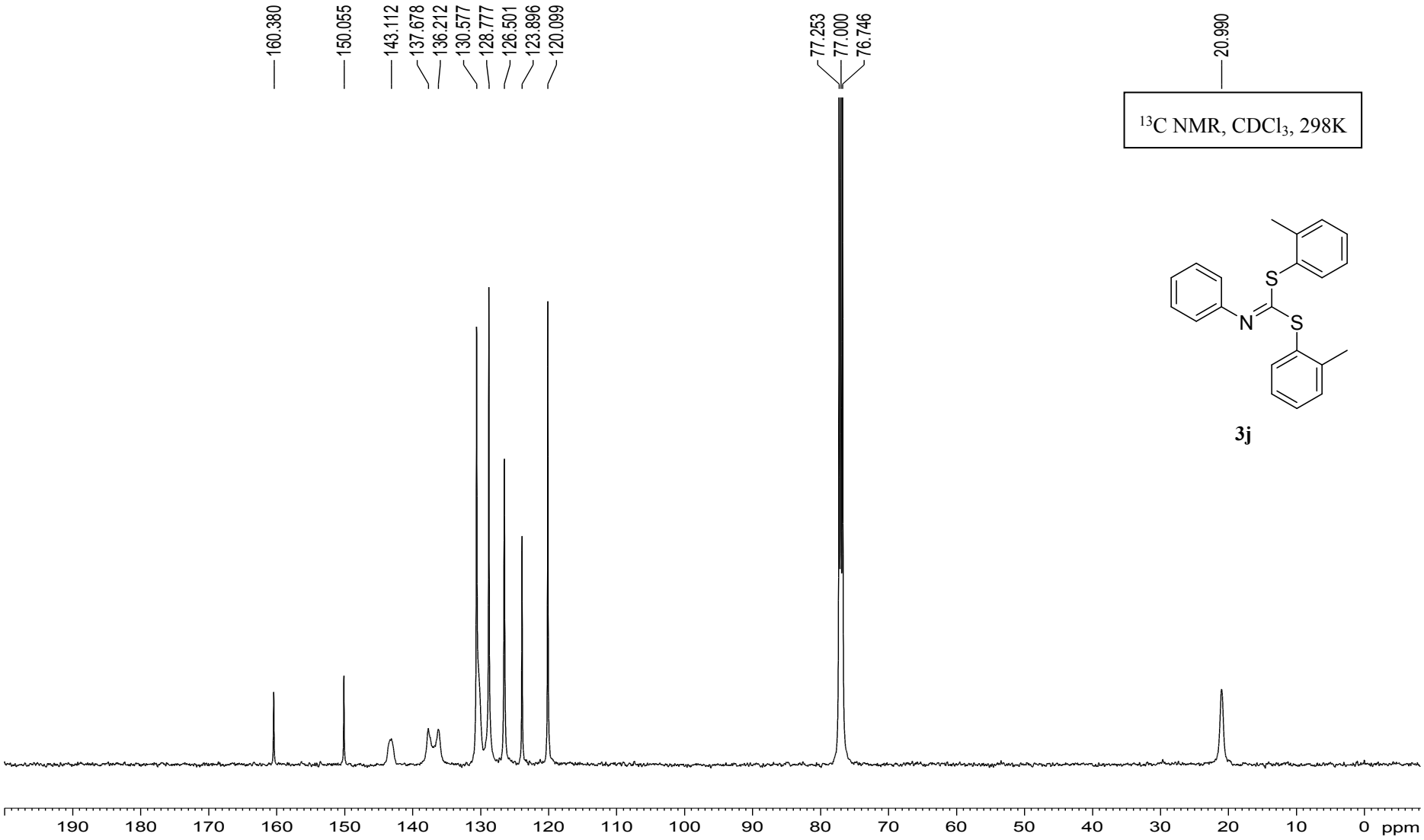
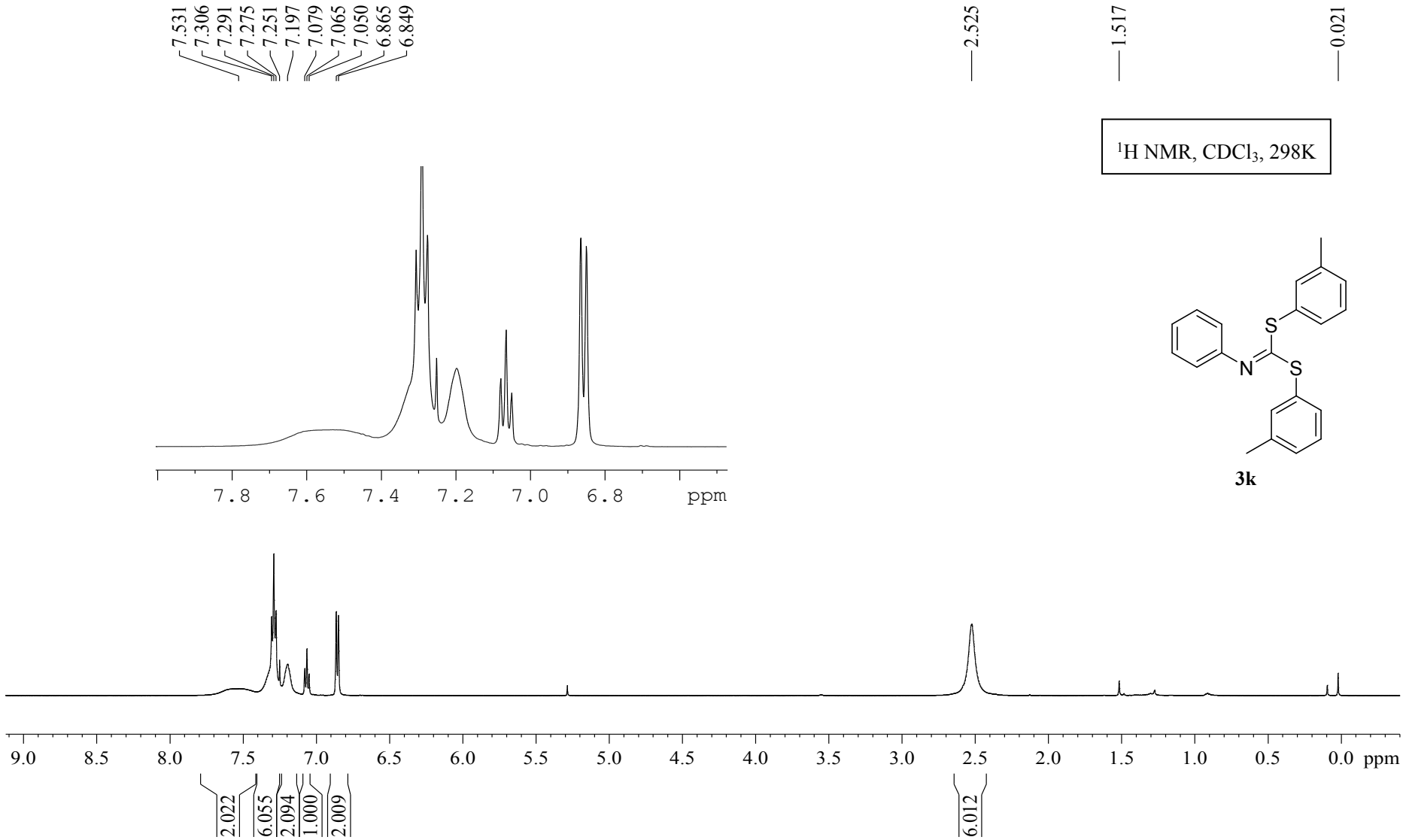
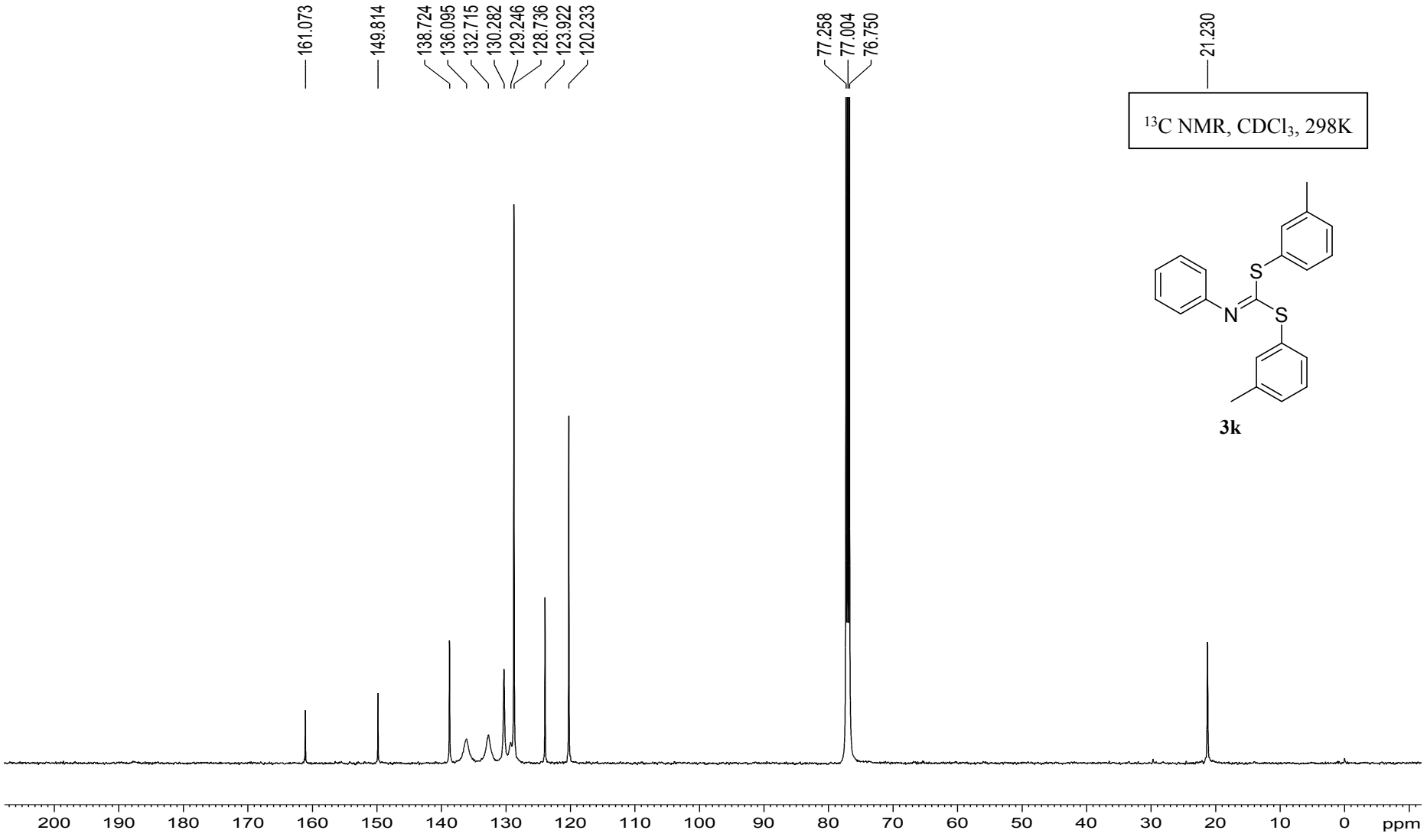
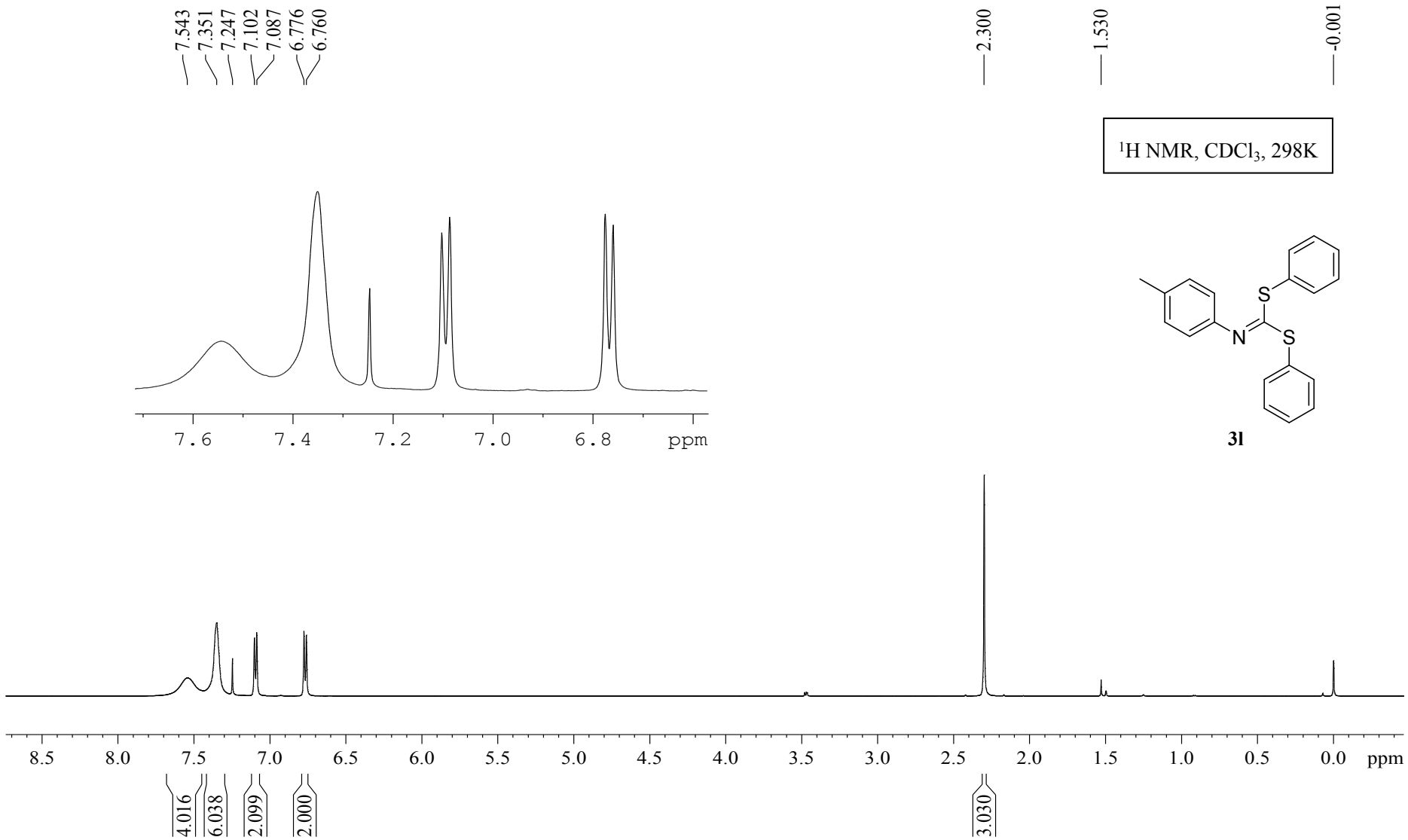
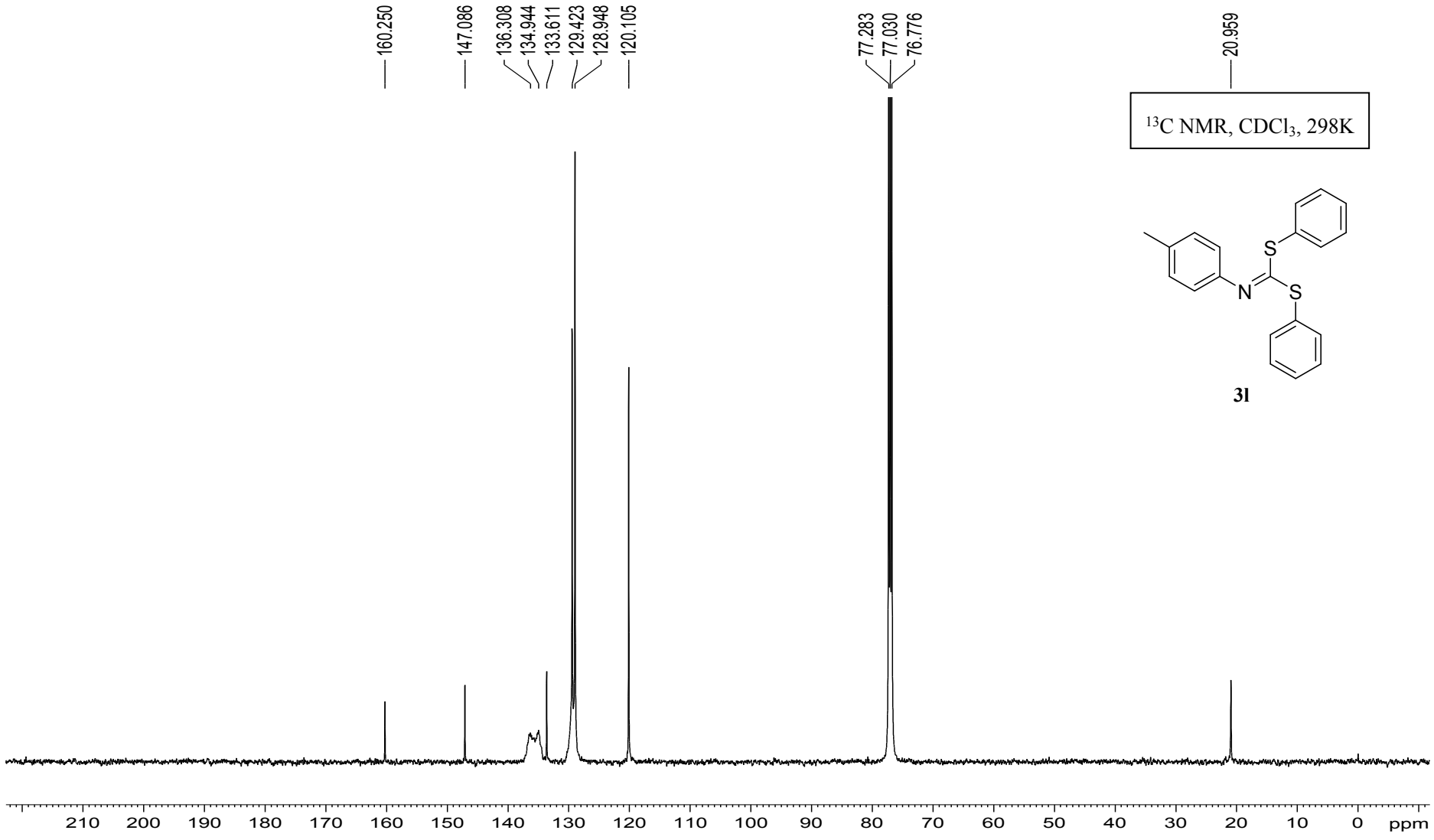
7.050
6.865
6.849
2.525
1.517
0.021
1H NMR, CDCl3, 298K
3j
7.8
7.6
7.4
7.2
7.0
6.8
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.022
6.055
2.094
1.000
2.009
6.012


160.380
150.055
143.112
137.678
136.212
130.577
128.777
126.501
123.896
120.099
77.253
77.000
76.746
20.990
^{13}C NMR, $CDCl_3$, 298K
S
N
S
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

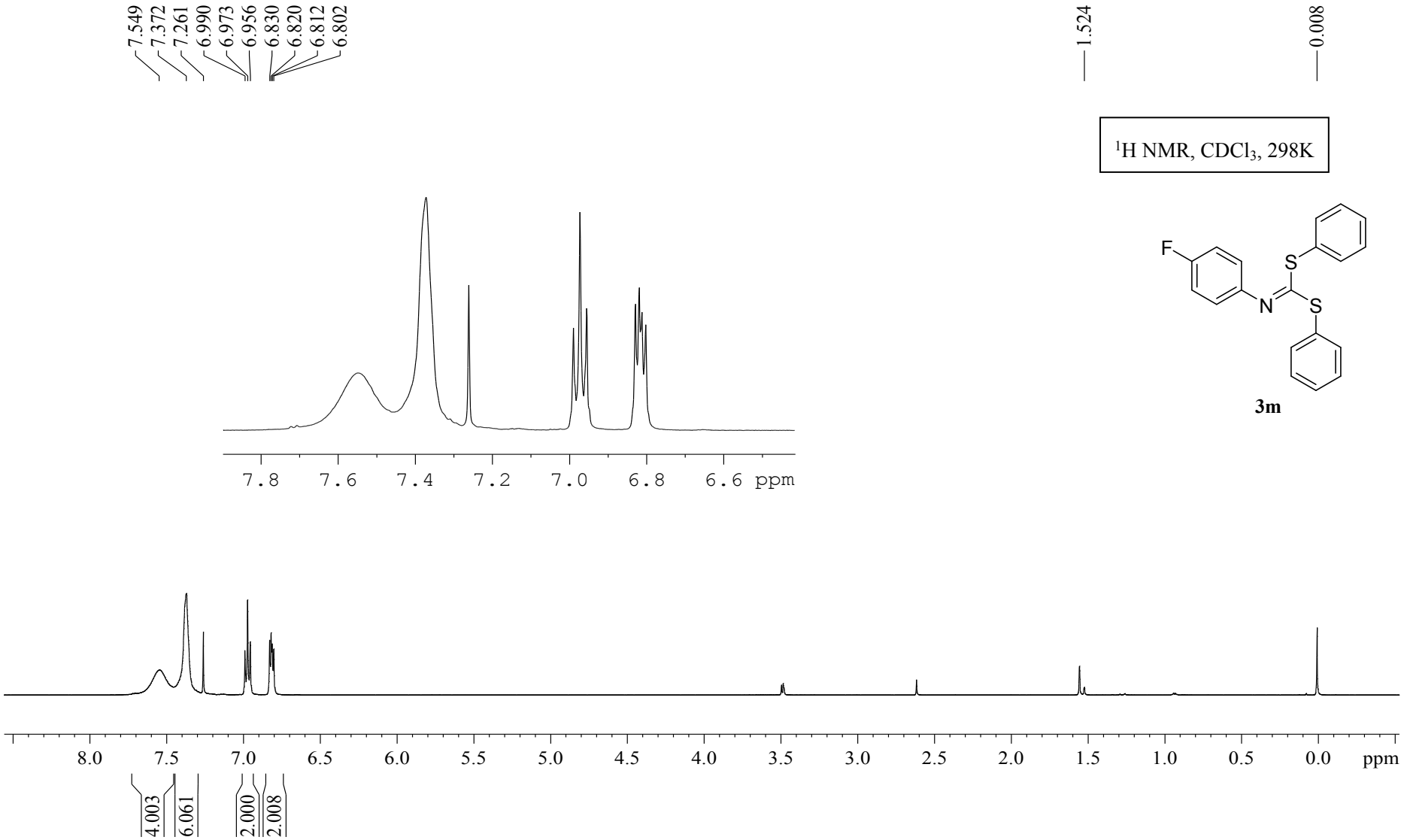

7.531
7.306
7.291
7.275
7.251
7.197
7.079
7.065
7.050
6.865
6.849
2.525
1.517
0.021
^{1}H NMR, $CDCl_3$, 298K
S
N
S
3k
7.8
7.6
7.4
7.2
7.0
6.8
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.022
6.055
2.094
1.000
2.009
6.012

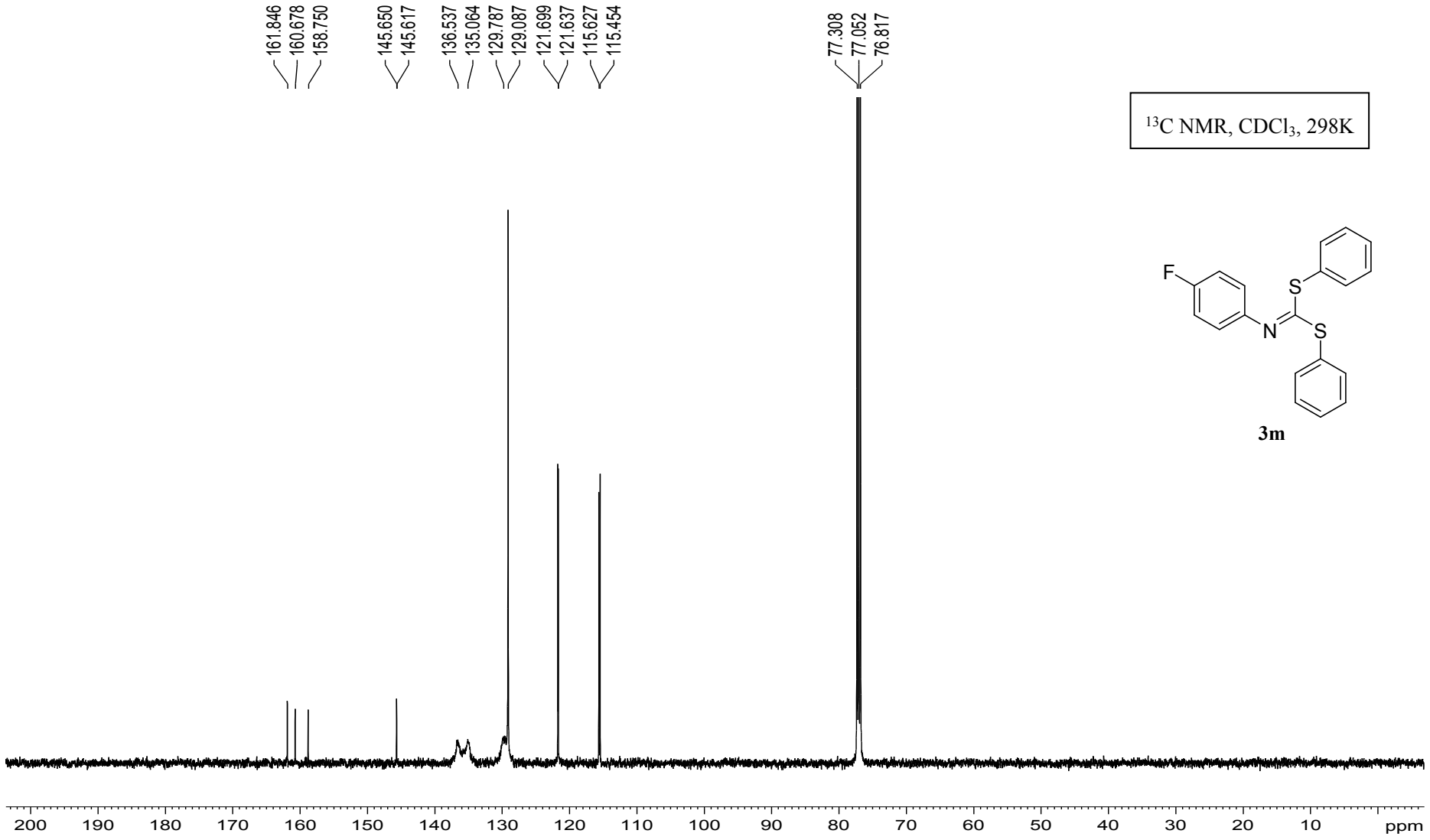

161.073
149.814
138.724
136.095
132.715
130.282
129.246
128.736
123.922
120.233
77.258
77.004
76.750
21.230
^{13}C NMR, $CDCl_3$, 298K
S
N
S
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

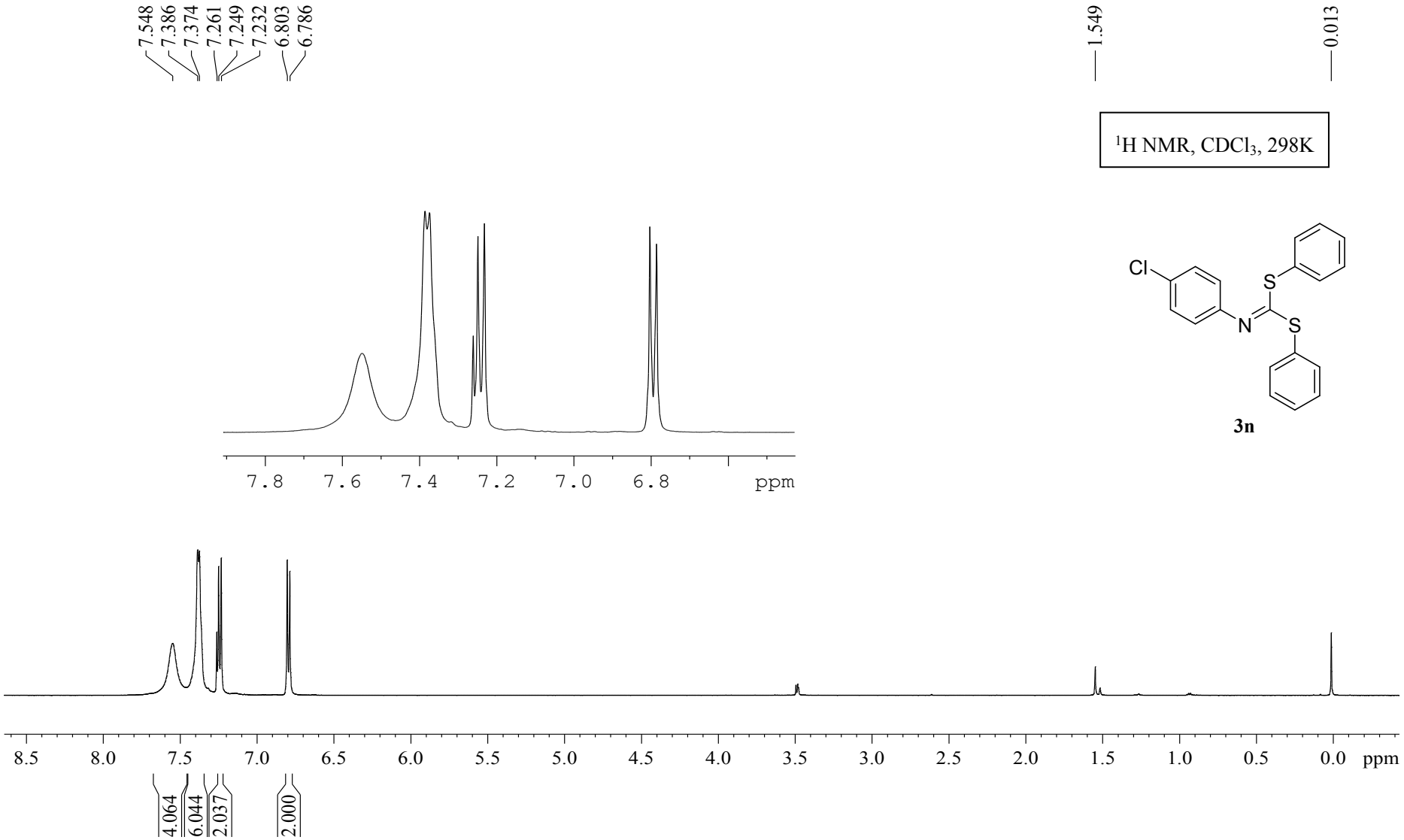

7.543
7.351
7.247
7.102
7.087
6.776
6.760
2.300
1.530
-0.001
^{1}H NMR, $CDCl_3$, 298K
S
N
S
3l
7.6
7.4
7.2
7.0
6.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.016
6.038
2.099
2.000
3.030

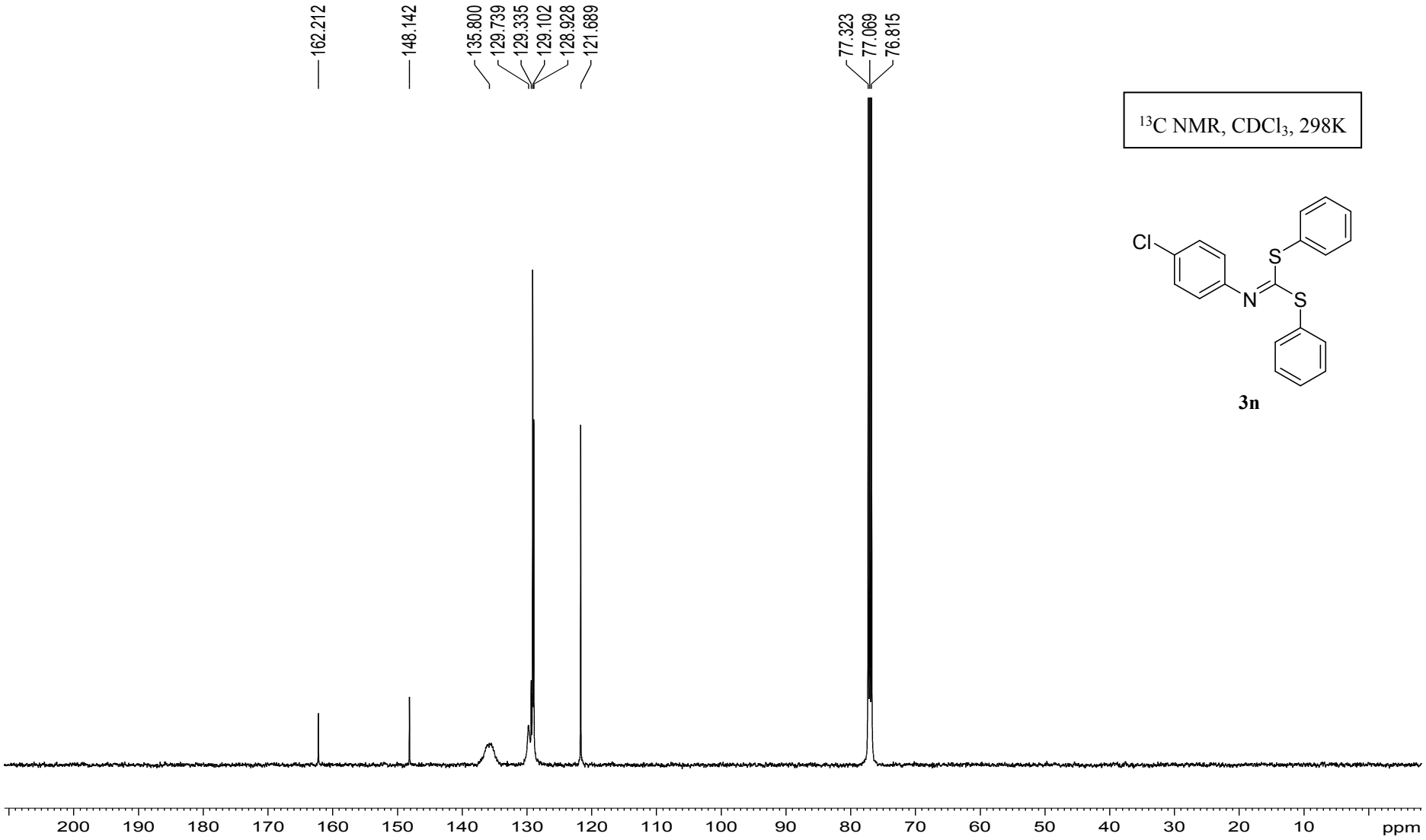

160.250
147.086
136.308
134.944
133.611
129.423
128.948
120.105
77.283
77.030
76.776
20.959
^{13}C NMR, $CDCl_3$, 298K
S
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

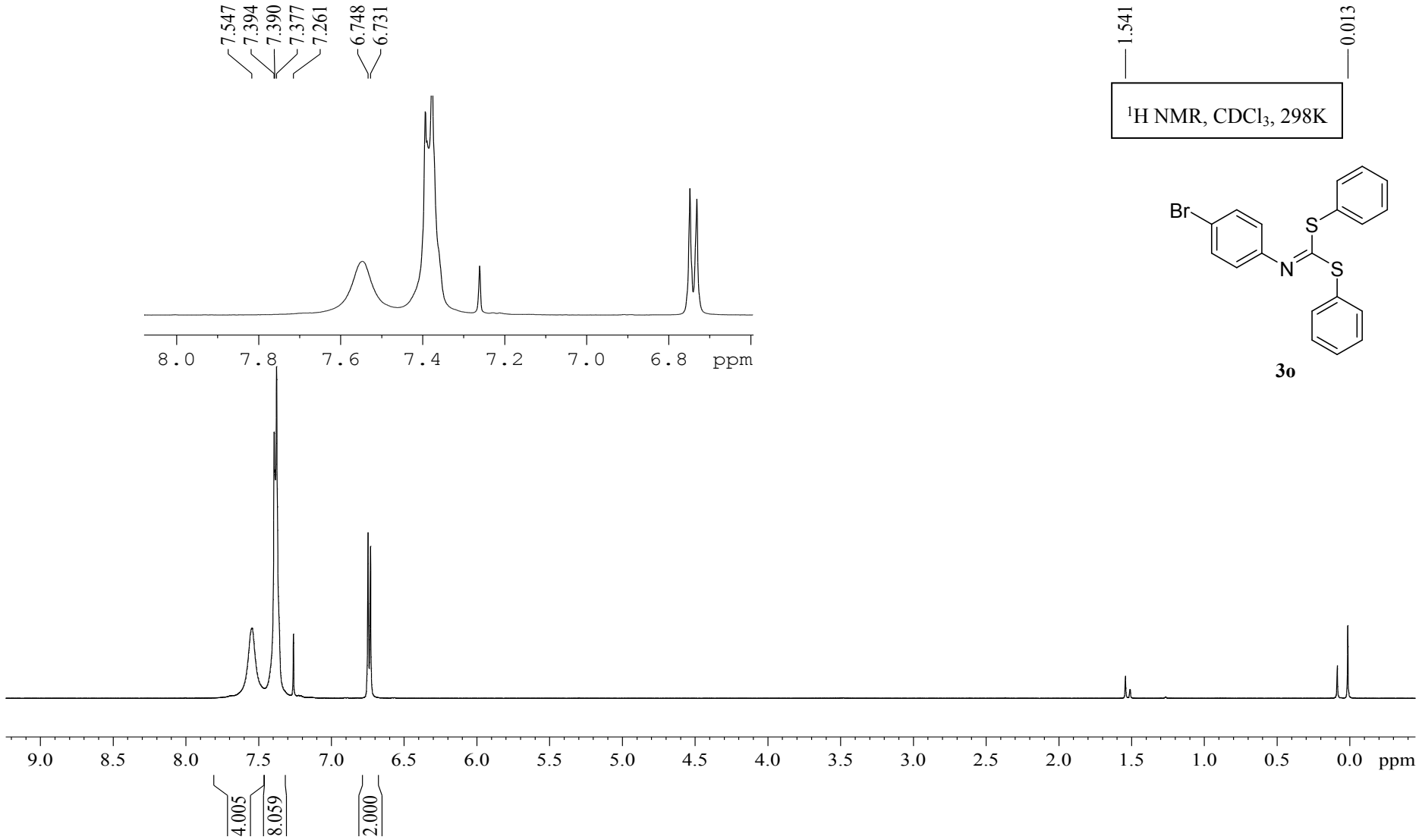
3l

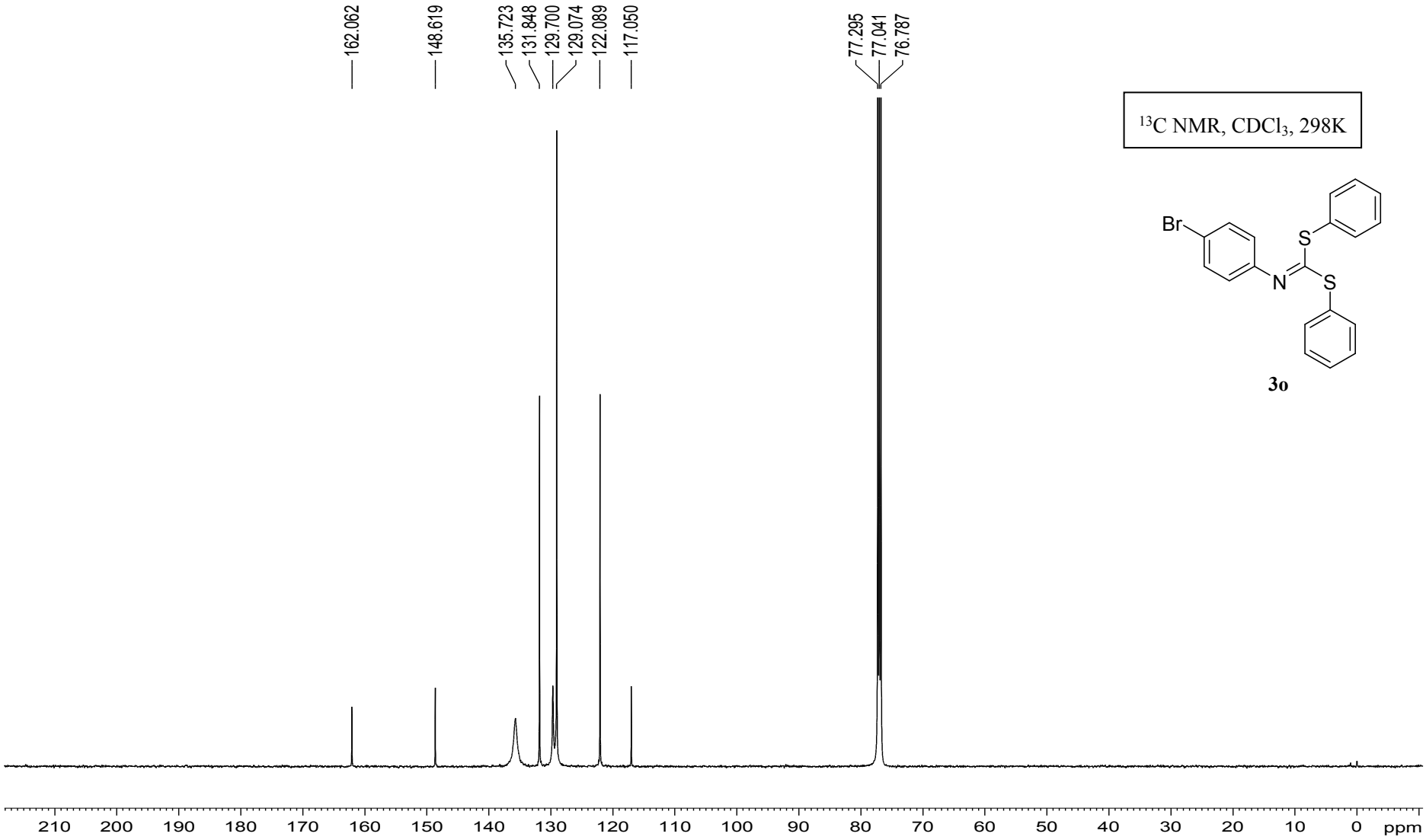

7.549
7.372
7.261
6.990
6.973
6.956
6.830
6.820
6.812
6.802
1.524
0.008
^{1}H NMR, $CDCl_3$, 298K
F
S
N
S
3m
7.8
7.6
7.4
7.2
7.0
6.8
6.6 ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
4.003
6.061
2.000
2.008

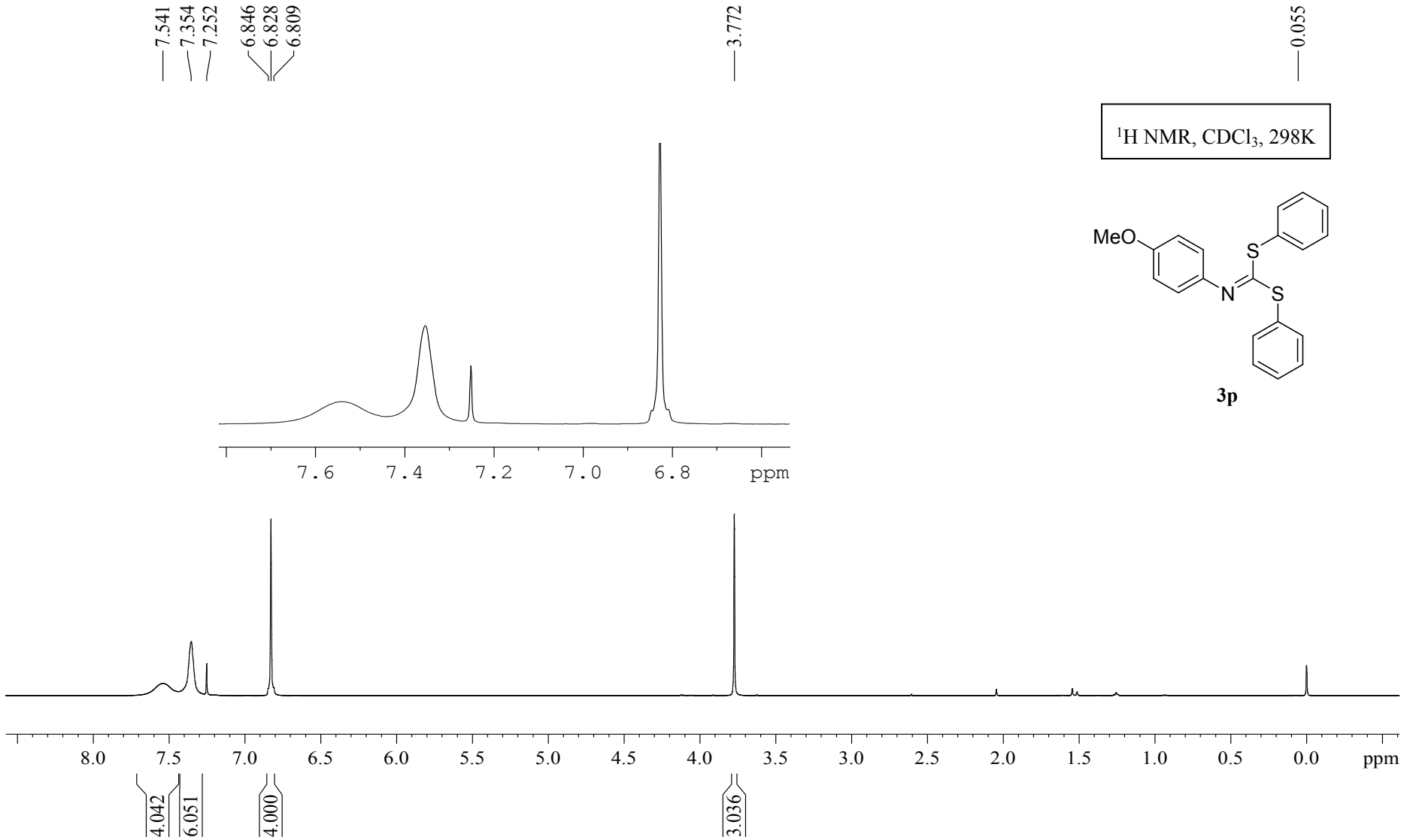

161.846
160.678
158.750
145.650
145.617
136.537
135.064
129.787
129.087
121.699
121.637
115.627
115.454
77.308
77.052
76.817
^{13}C NMR, $CDCl_3$, 298K
F
S
N
S
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

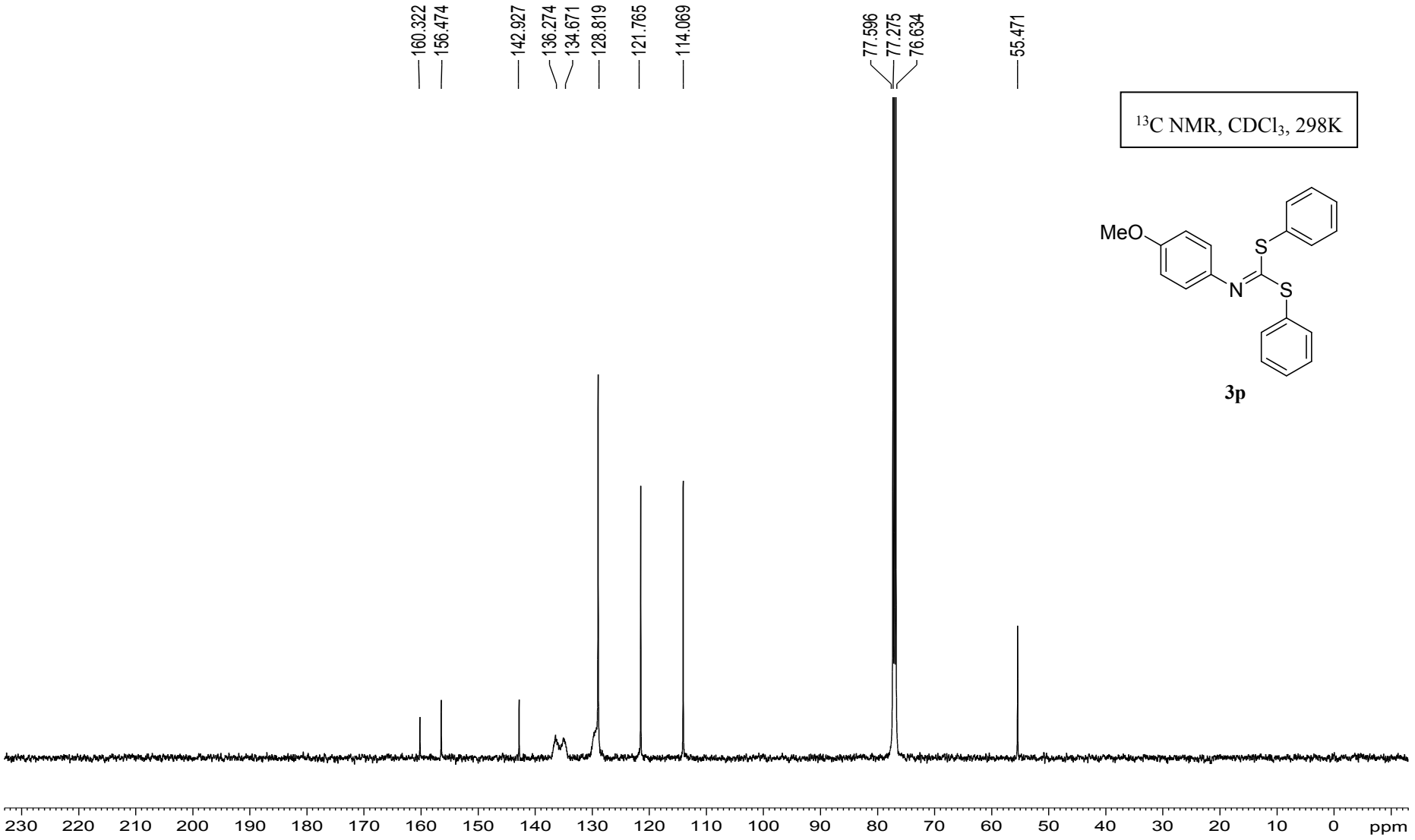

7.548
7.386
7.374
7.261
7.249
7.232
6.803
6.786
1.549
0.013
^{1}H NMR, $CDCl_3$, 298K
Cl
S
N
S
3n
7.8
7.6
7.4
7.2
7.0
6.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.064
6.044
2.037
2.000

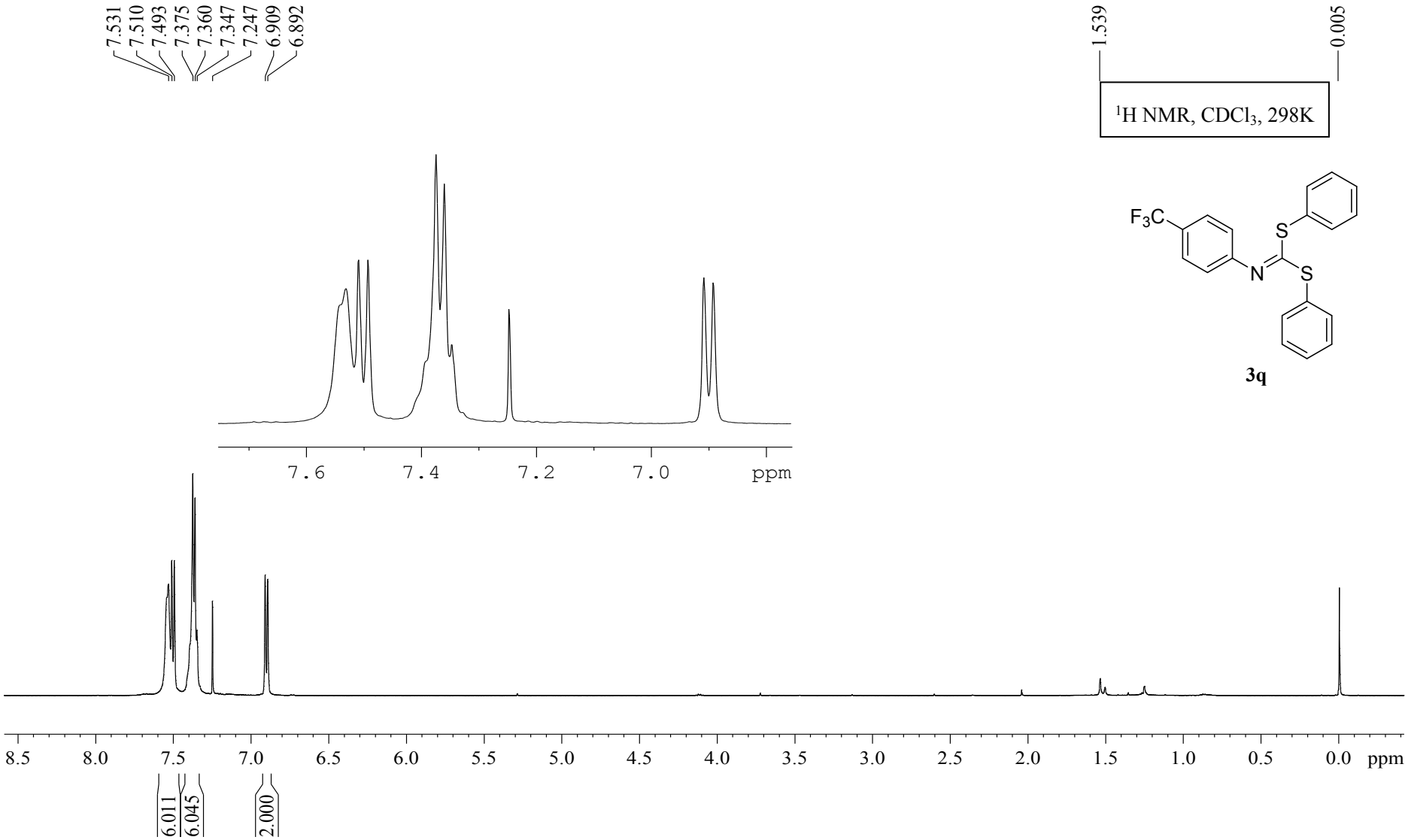

162.212
148.142
135.800
129.739
129.335
129.102
128.928
121.689
77.323
77.069
76.815
^{13}C NMR, $CDCl_3$, 298K
Cl
S
N
S
S
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

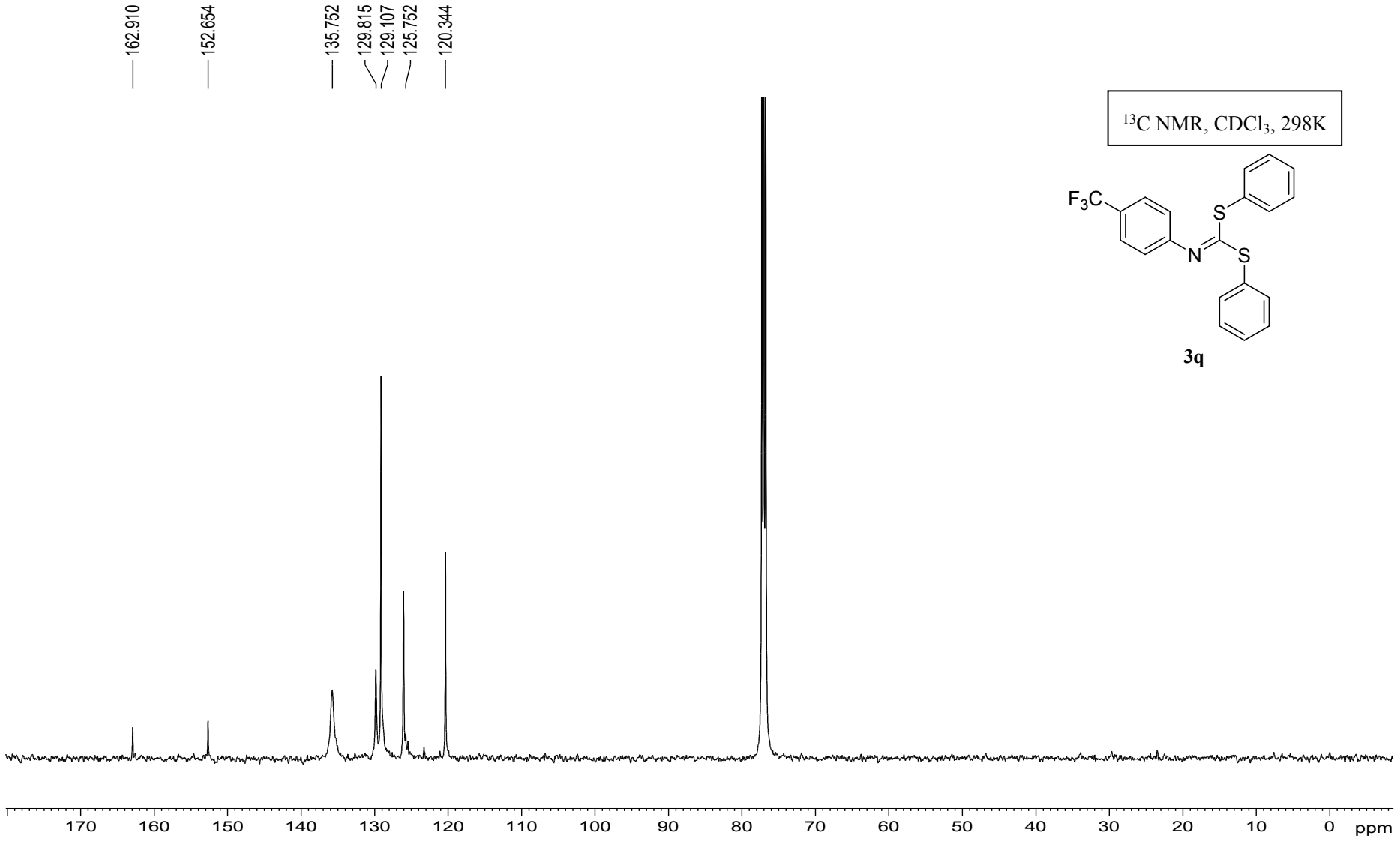

7.547
7.394
7.390
7.377
7.261
6.748
6.731
1.541
0.013
^{1}H NMR, $CDCl_3$, 298K
Br
S
N
S
3o
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.005
8.059
2.000

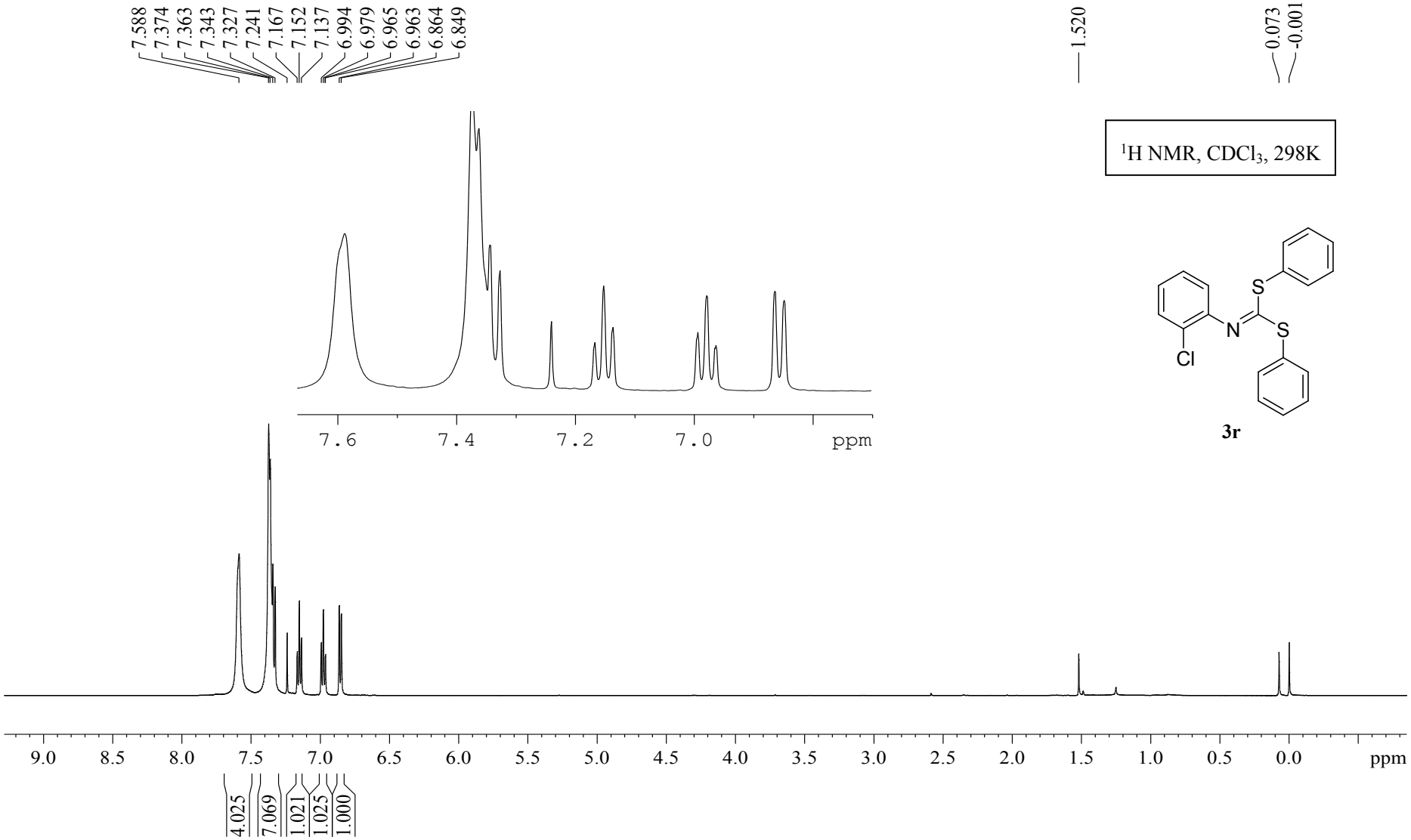

162.062
148.619
135.723
131.848
129.700
129.074
122.089
117.050
77.295
77.041
76.787
^{13}C NMR, $CDCl_3$, 298K
Br
S
N
S
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

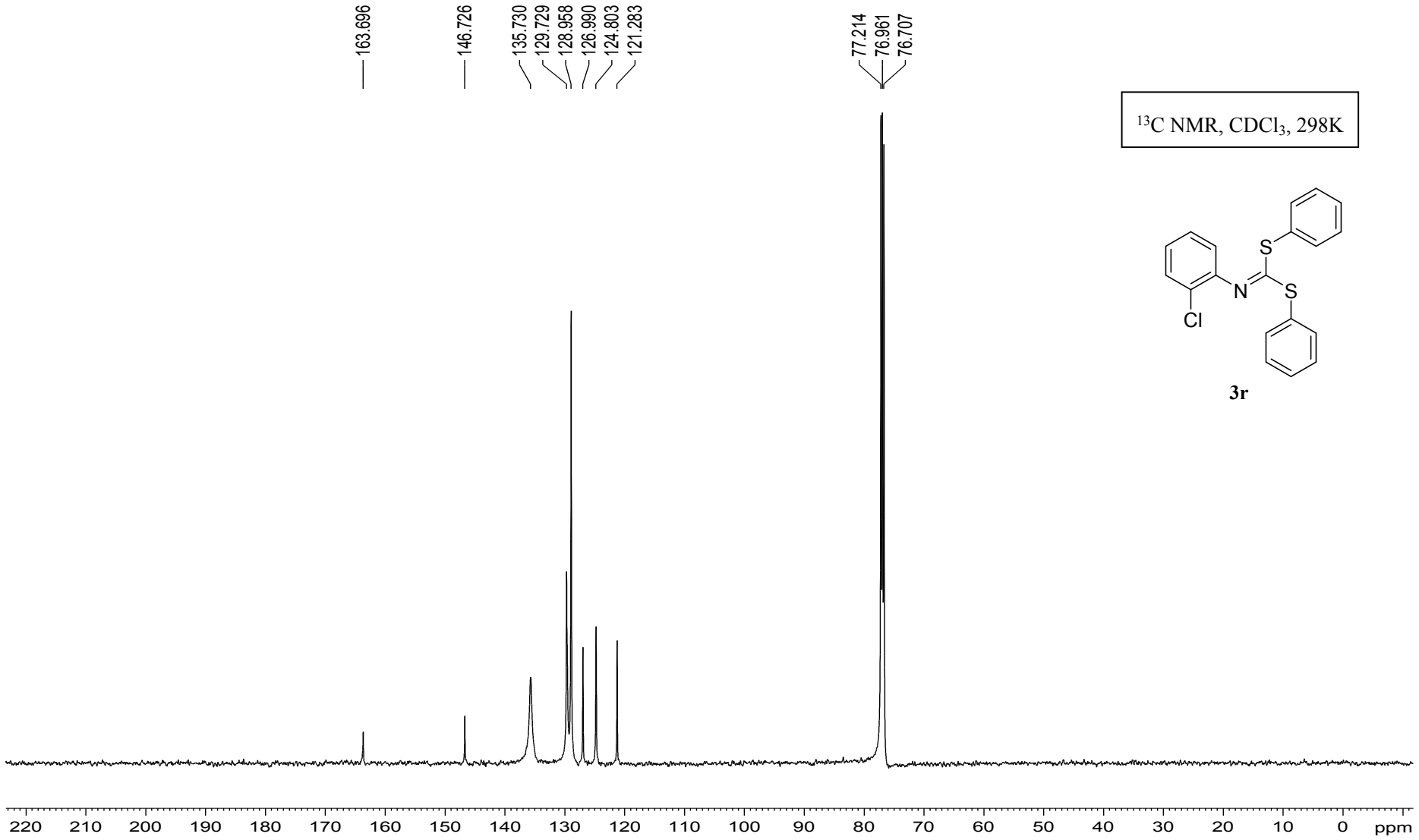

7.541
7.354
7.252
6.846
6.828
6.809
3.772
0.055
^{1}H NMR, $CDCl_3$, 298K
MeO
S
N
S
3p
7.6
7.4
7.2
7.0
6.8
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.042
6.051
4.000
3.036

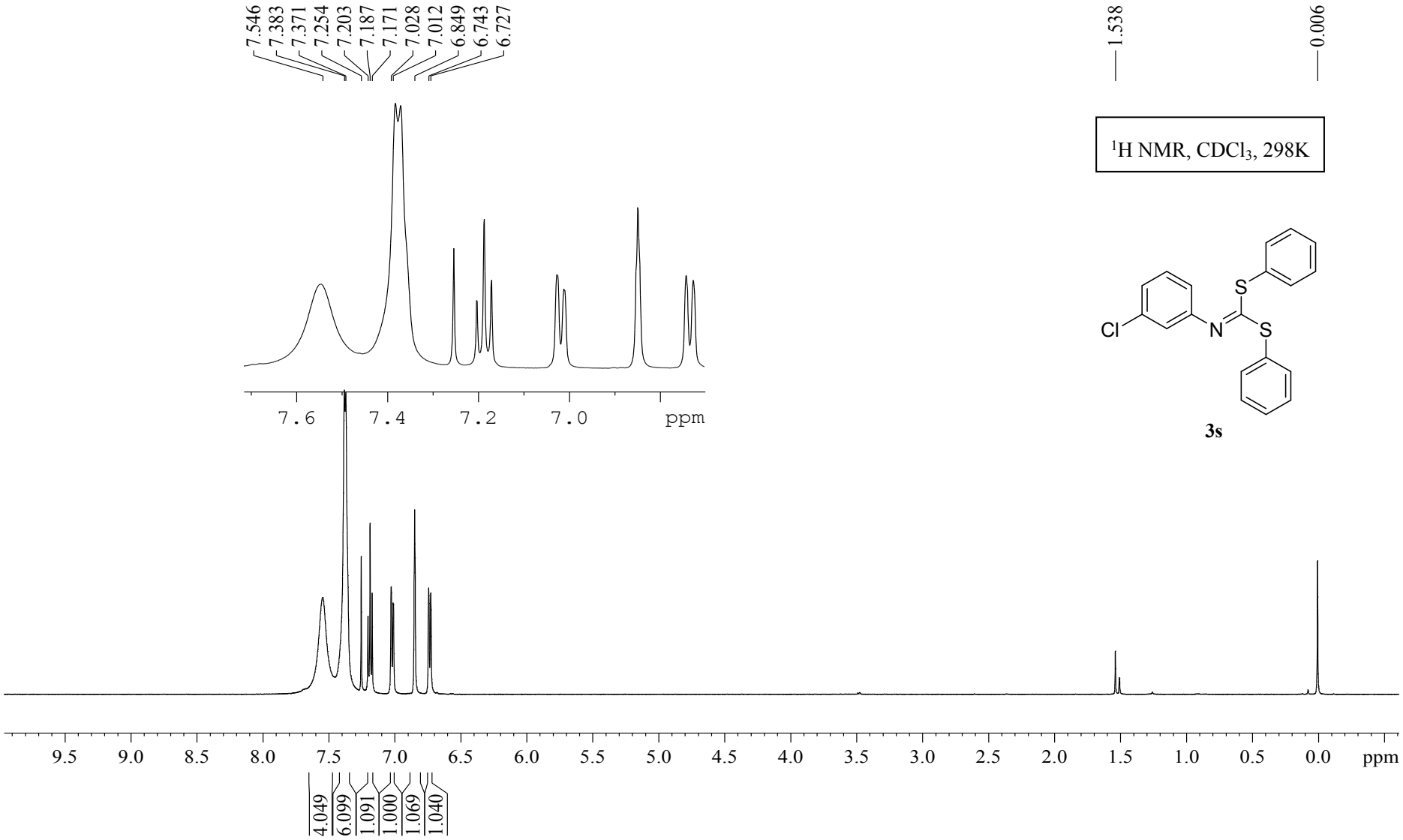

160.322
156.474
142.927
136.274
134.671
128.819
121.765
114.069
77.596
77.275
76.634
55.471
^{13}C NMR, $CDCl_3$, 298K
MeO
S
N
S
3p
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

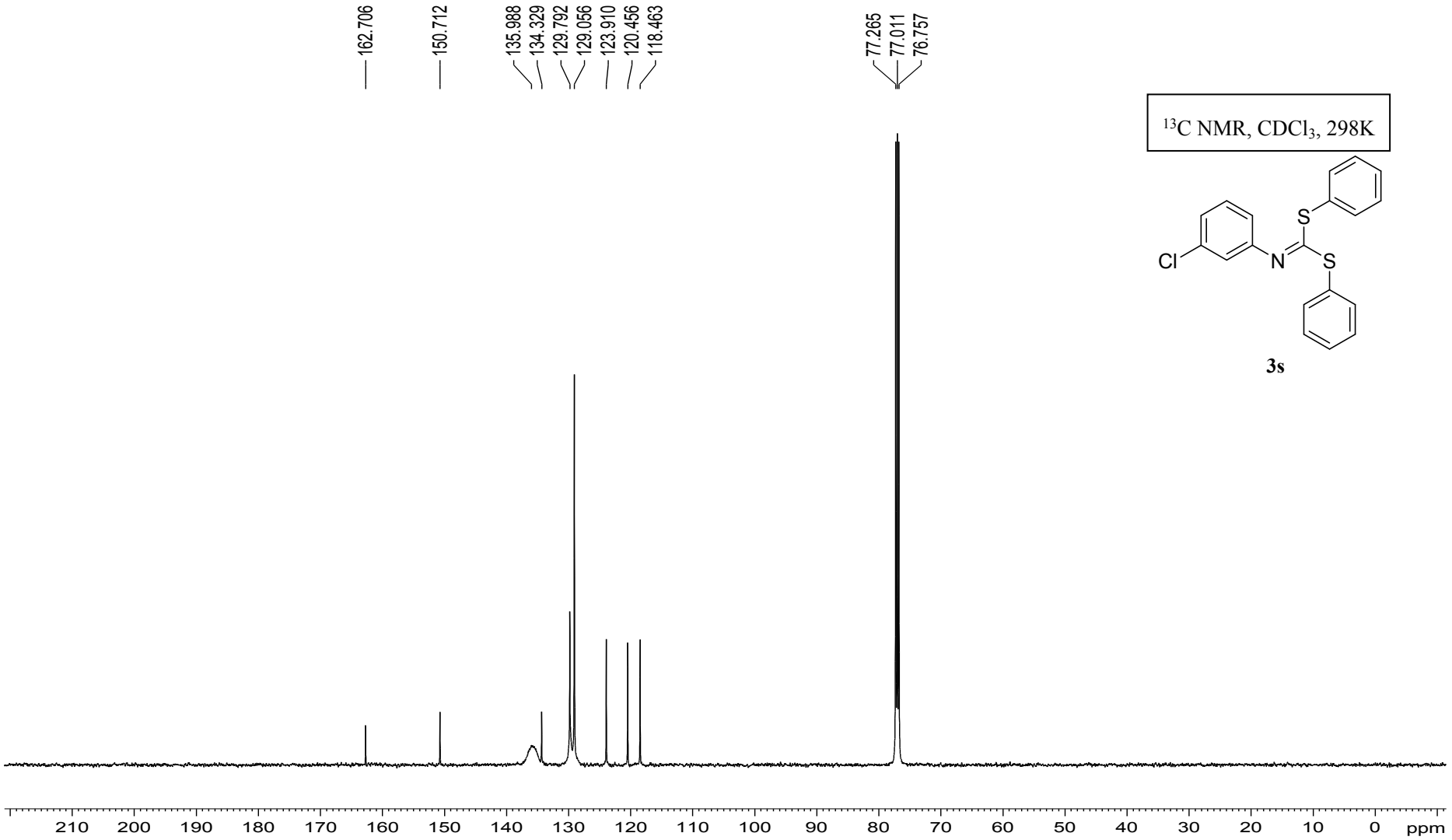

7.531
7.510
7.493
7.375
7.360
7.347
7.247
6.909
6.892
1.539
0.005
^{1}H NMR, $CDCl_3$, 298K
F_3C
S
N
S
3q
7.6
7.4
7.2
7.0
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
6.011
6.045
2.000

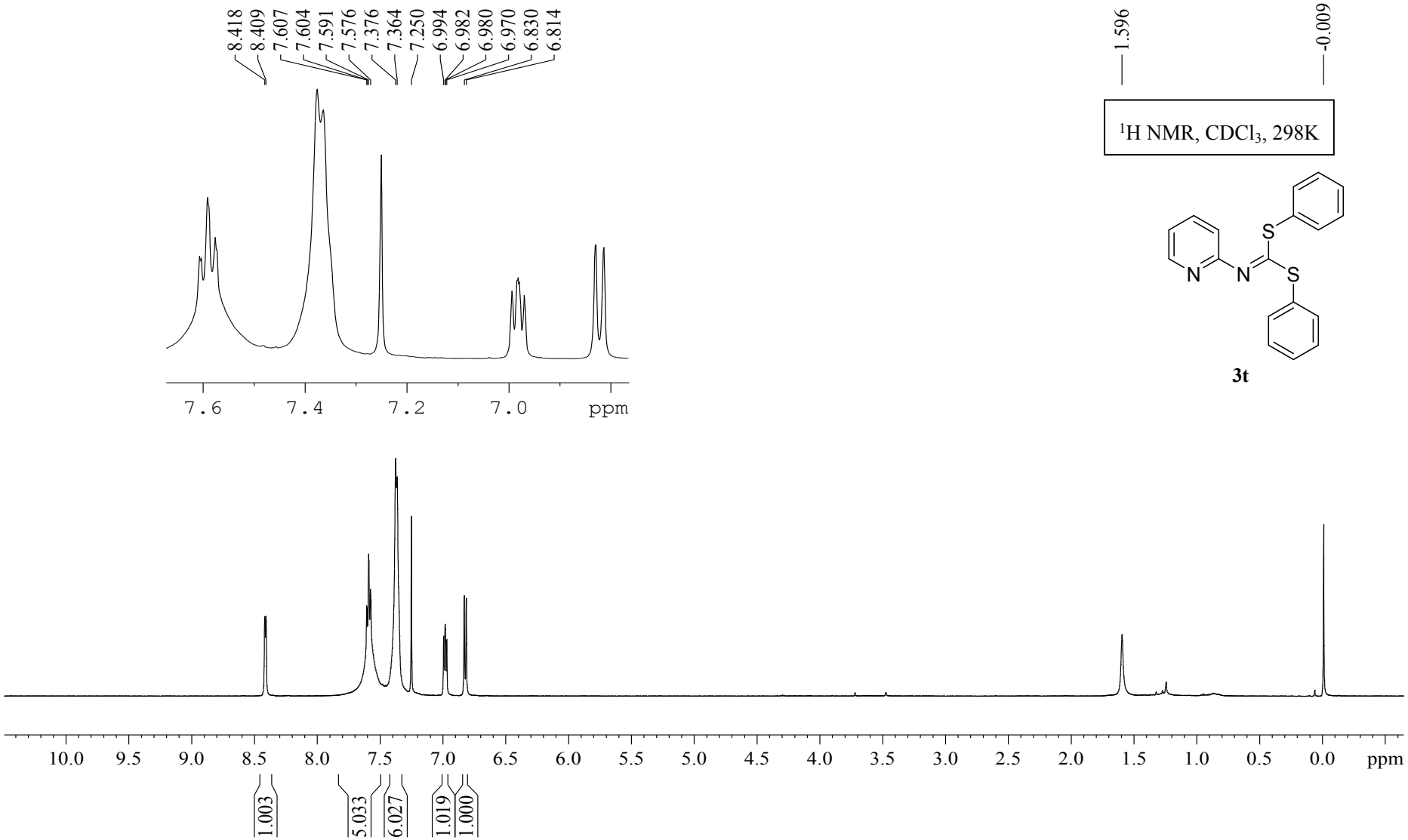

162.910
152.654
135.752
129.815
129.107
125.752
120.344
^{13}C NMR, $CDCl_3$, 298K
F_3C
S
N
S
3q
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

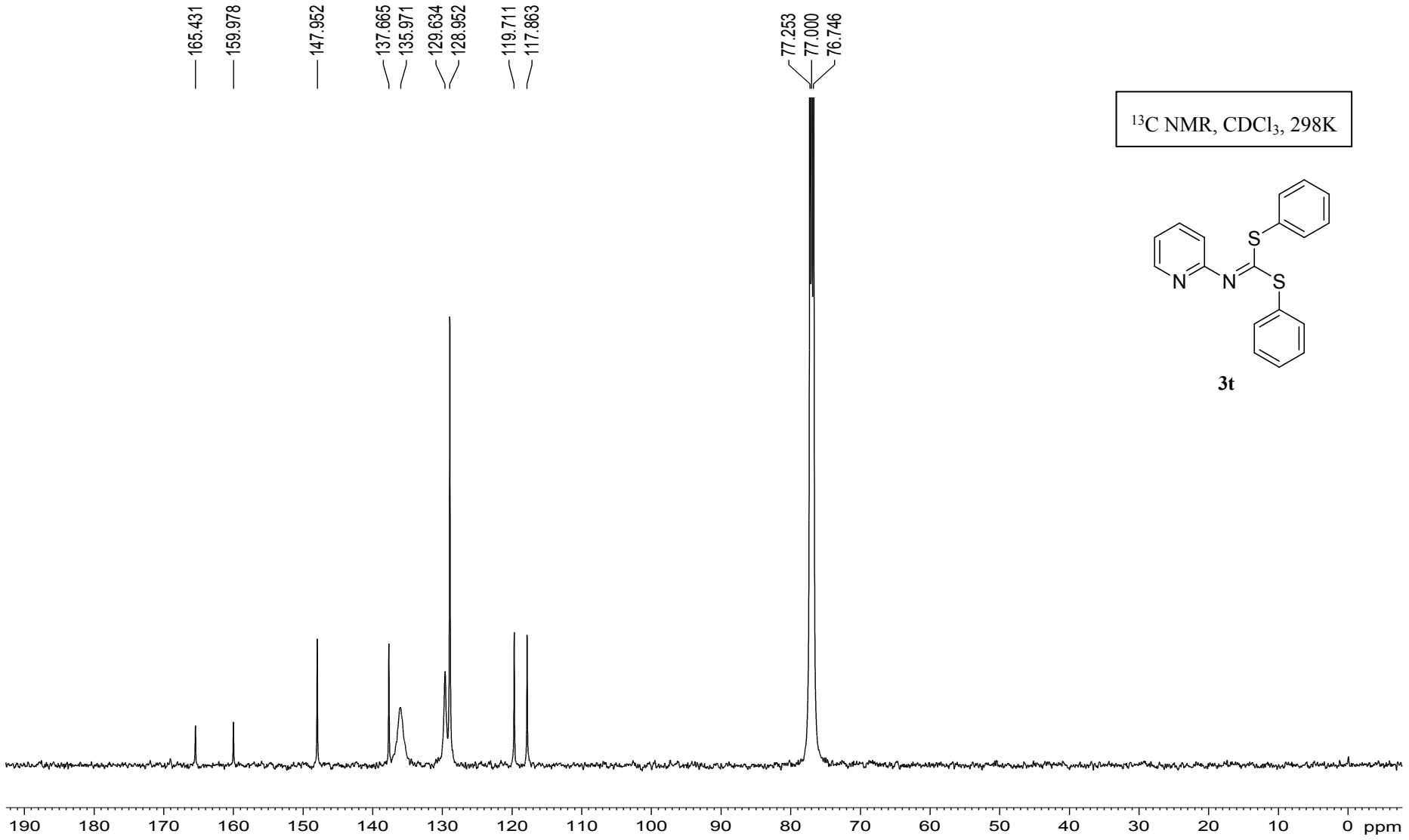

7.588
7.374
7.363
7.343
7.327
7.241
7.167
7.152
7.137
6.994
6.979
6.965
6.963
6.864
6.849
1.520
0.073
-0.001
[1]H NMR, CDCl3, 298K
S
N
S
Cl
3r
7.6
7.4
7.2
7.0
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.025
7.069
1.021
1.025
1.000

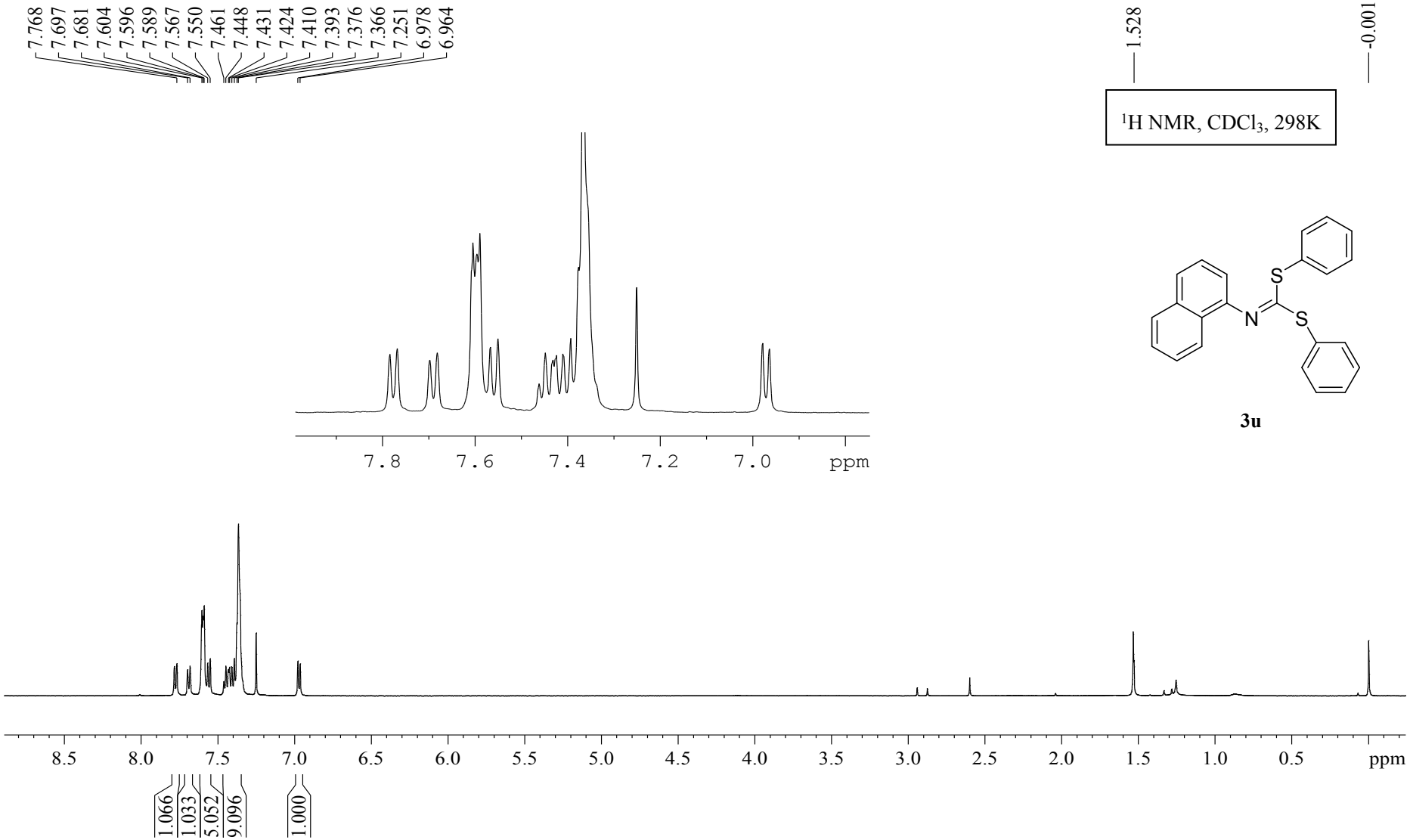

163.696
146.726
135.730
129.729
128.958
126.990
124.803
121.283
77.214
76.961
76.707
^{13}C NMR, $CDCl_3$, 298K
S
N
S
Cl
3r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

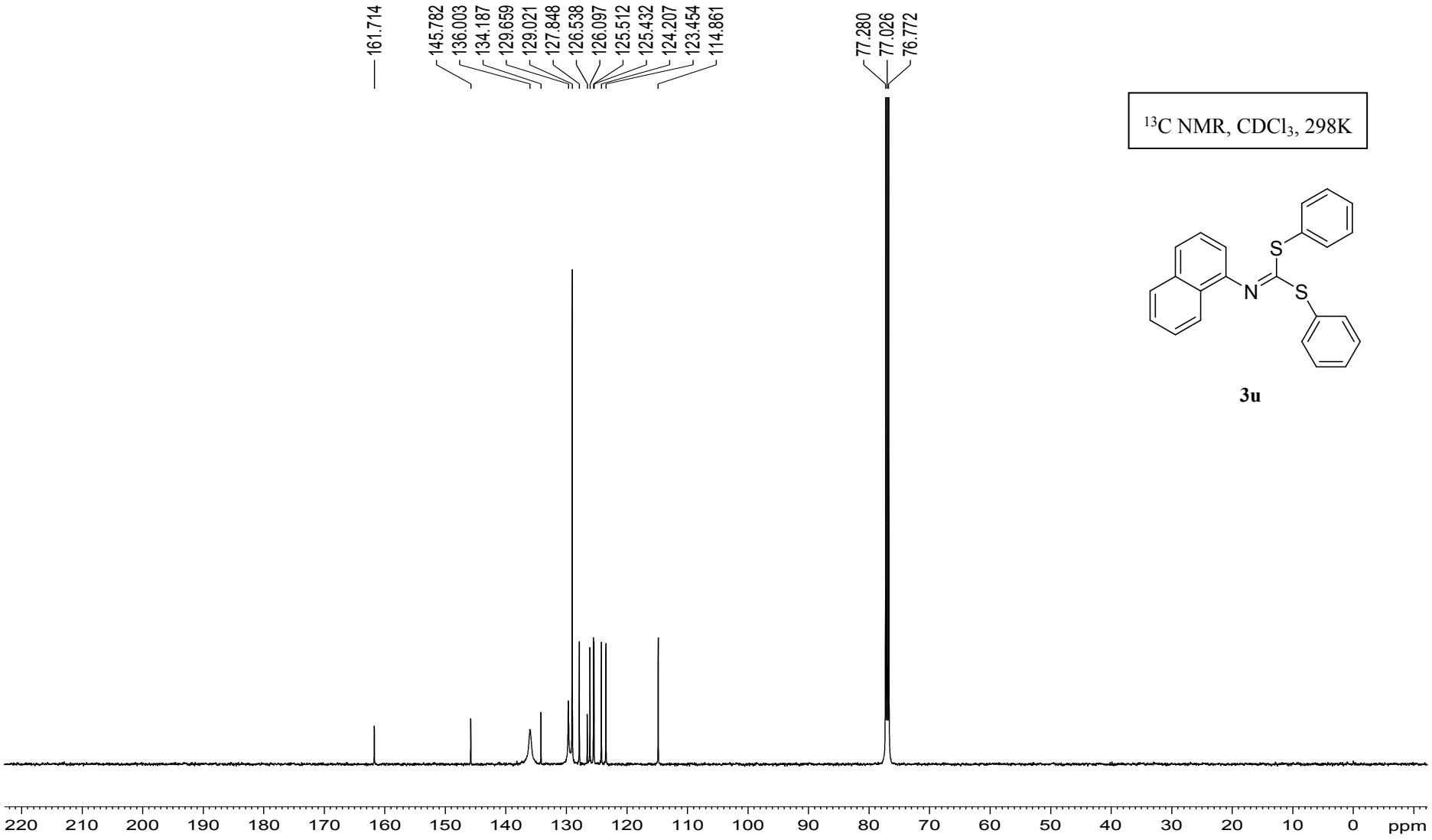

7.546
7.383
7.371
7.254
7.203
7.187
7.171
7.028
7.012
6.849
6.743
6.727
1.538
0.006
^{1}H NMR, $CDCl_3$, 298K
Cl
N
S
S
3s
7.6
7.4
7.2
7.0
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.049
6.099
1.091
1.000
1.069
1.040

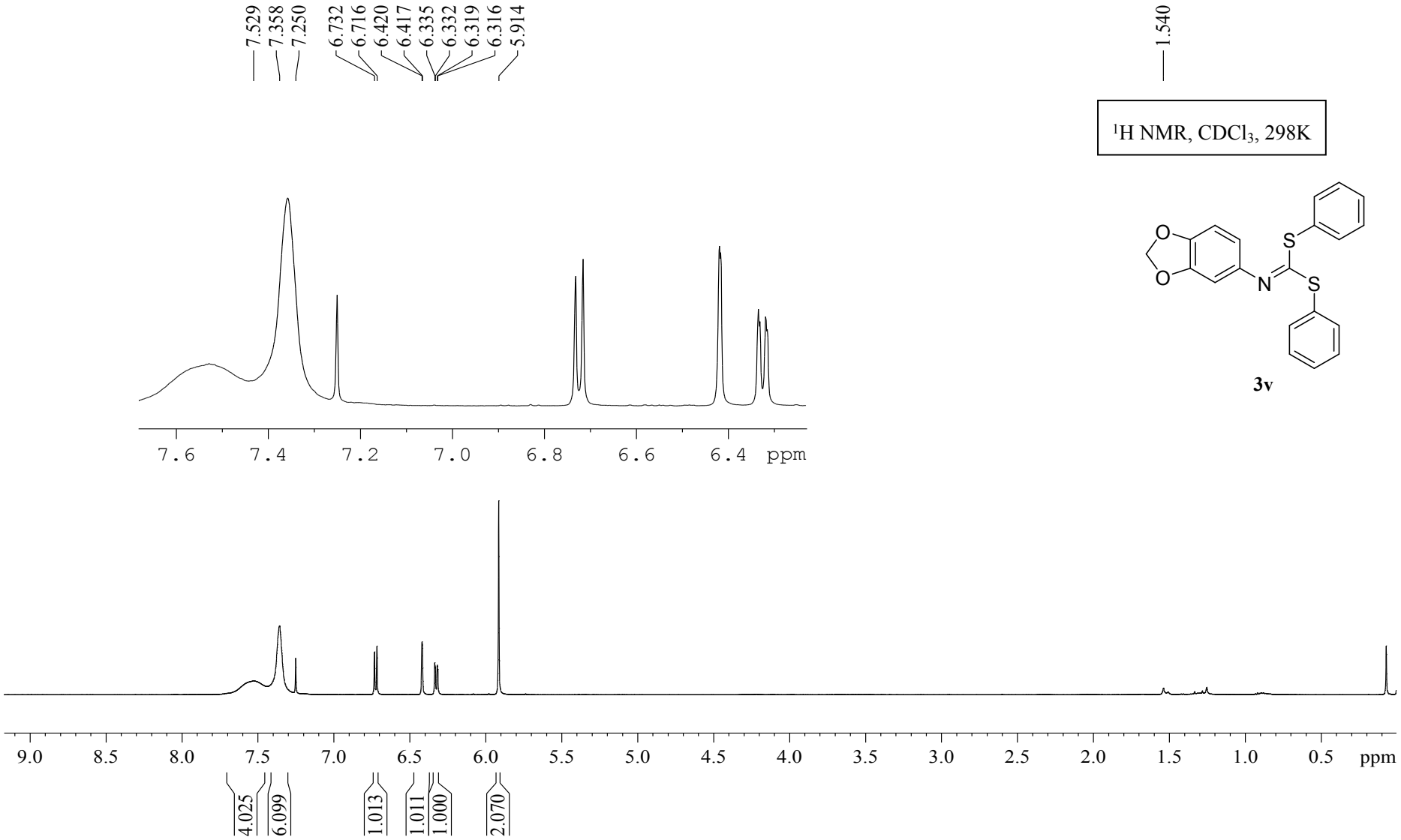

162.706
150.712
135.988
134.329
129.792
129.056
123.910
120.456
118.463
77.265
77.011
76.757
^{13}C NMR, $CDCl_3$, 298K
Cl
N
S
S
3s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

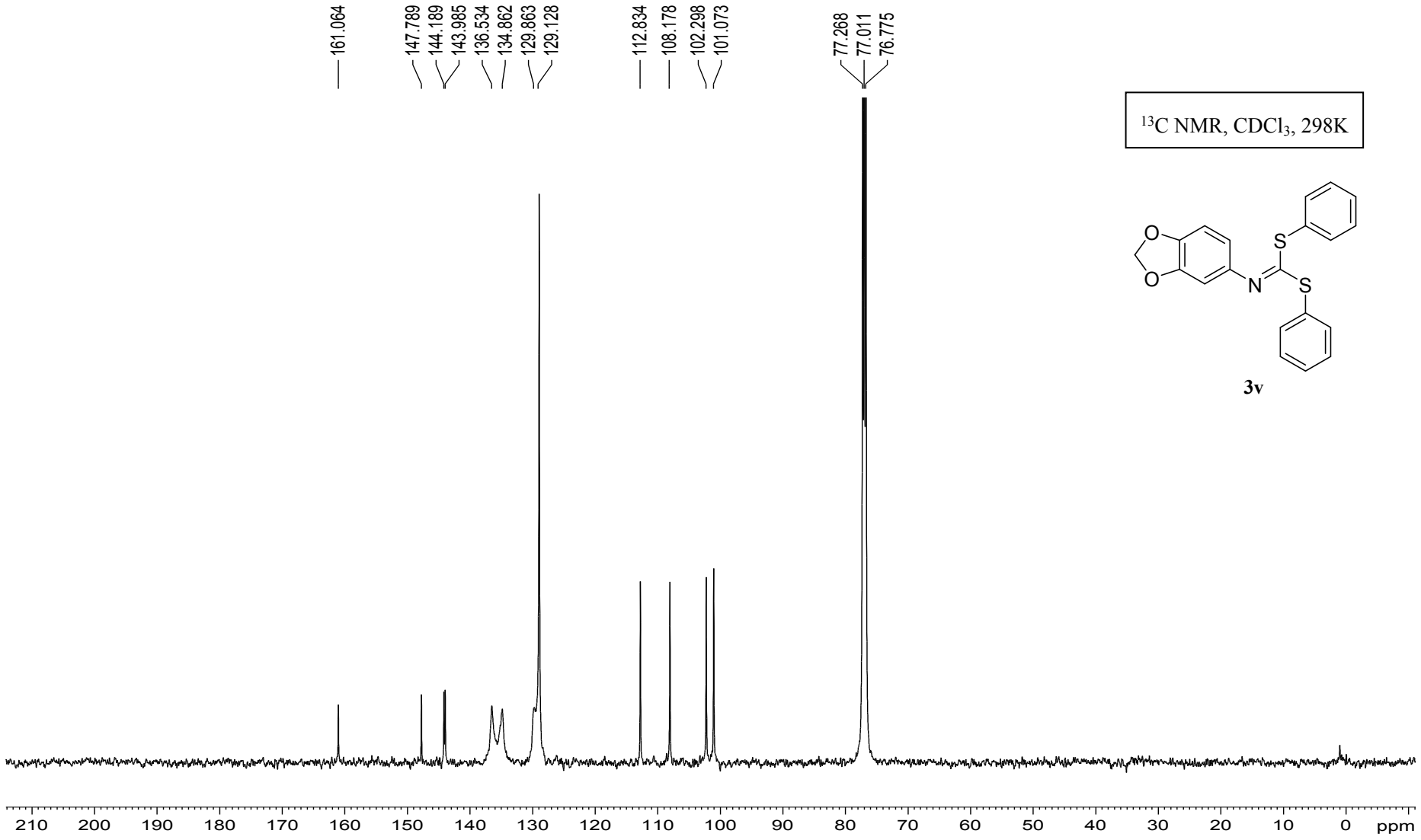

8.418
8.409
7.607
7.604
7.591
7.576
7.376
7.364
7.250
6.994
6.982
6.980
6.970
6.830
6.814
7.6
7.4
7.2
7.0
ppm
1.596
-0.009
^{1}H NMR, $CDCl_3$, 298K
N
N
S
S
3t
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.003
5.033
6.027
1.019
1.000

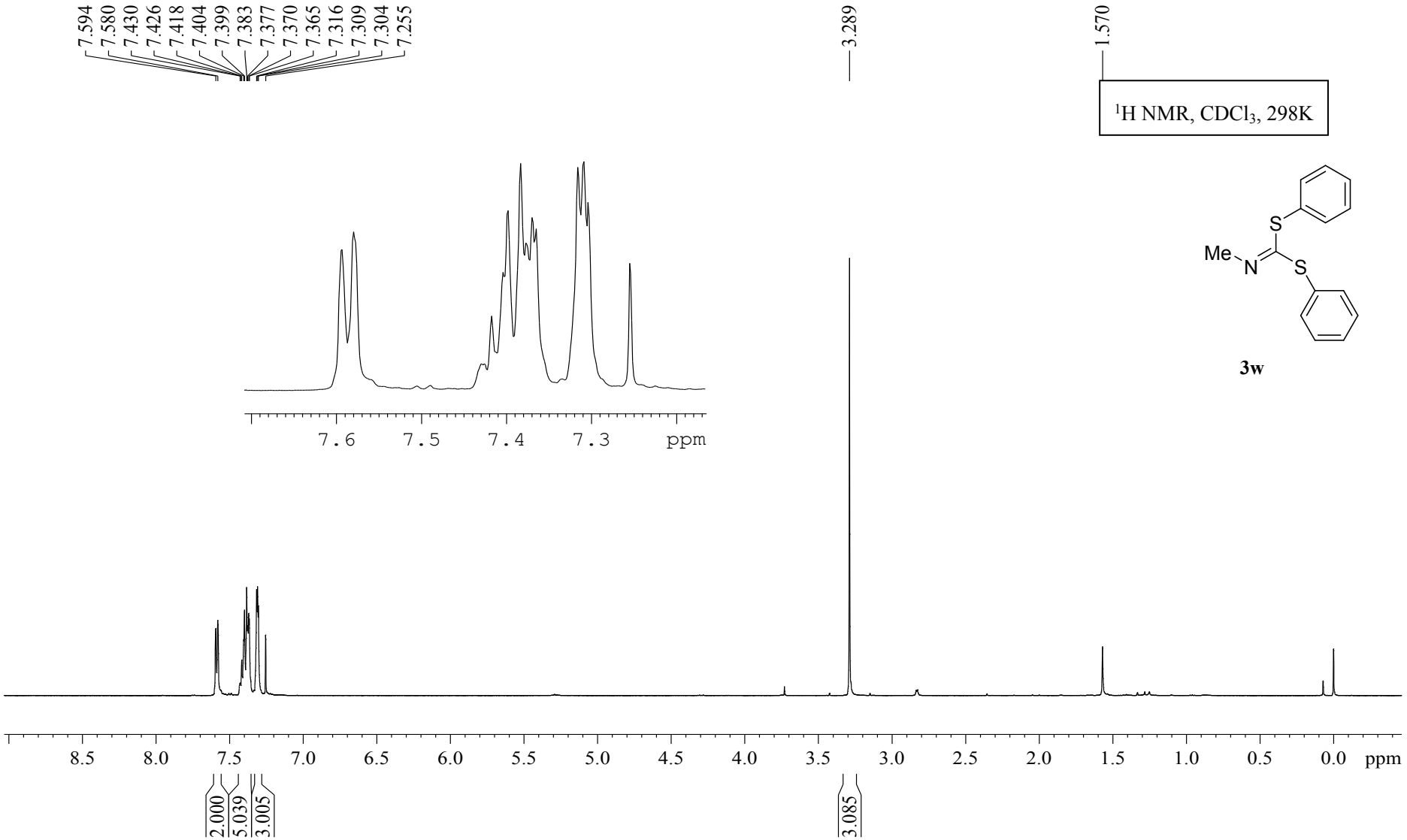

165.431
159.978
147.952
137.665
135.971
129.634
128.952
119.711
117.863
77.253
77.000
76.746
^{13}C NMR, $CDCl_3$, 298K
S
N
N
S
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.768
7.697
7.681
7.604
7.596
7.589
7.567
7.550
7.461
7.448
7.431
7.424
7.410
7.393
7.376
7.366
7.251
6.978
6.964
1.528
-0.001
^{1}H NMR, $CDCl_3$, 298K
S
N
S
3u
7.8
7.6
7.4
7.2
7.0
ppm
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
ppm
1.066
1.033
5.052
9.096
1.000


161.714
145.782
136.003
134.187
129.659
129.021
127.848
126.538
126.097
125.512
125.432
124.207
123.454
114.861
77.280
77.026
76.772
^{13}C NMR, $CDCl_3$, 298K
S
N
S
3u
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.529
7.358
7.250
6.732
6.716
6.420
6.417
6.335
6.332
6.319
6.316
5.914
1.540
^{1}H NMR, $CDCl_3$, 298K
3v
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
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
ppm
4.025
6.099
1.013
1.011
1.000
2.070


161.064
147.789
144.189
143.985
136.534
134.862
129.863
129.128
112.834
108.178
102.298
101.073
77.268
77.011
76.775
^{13}C NMR, $CDCl_3$, 298K
O
O
N
S
S
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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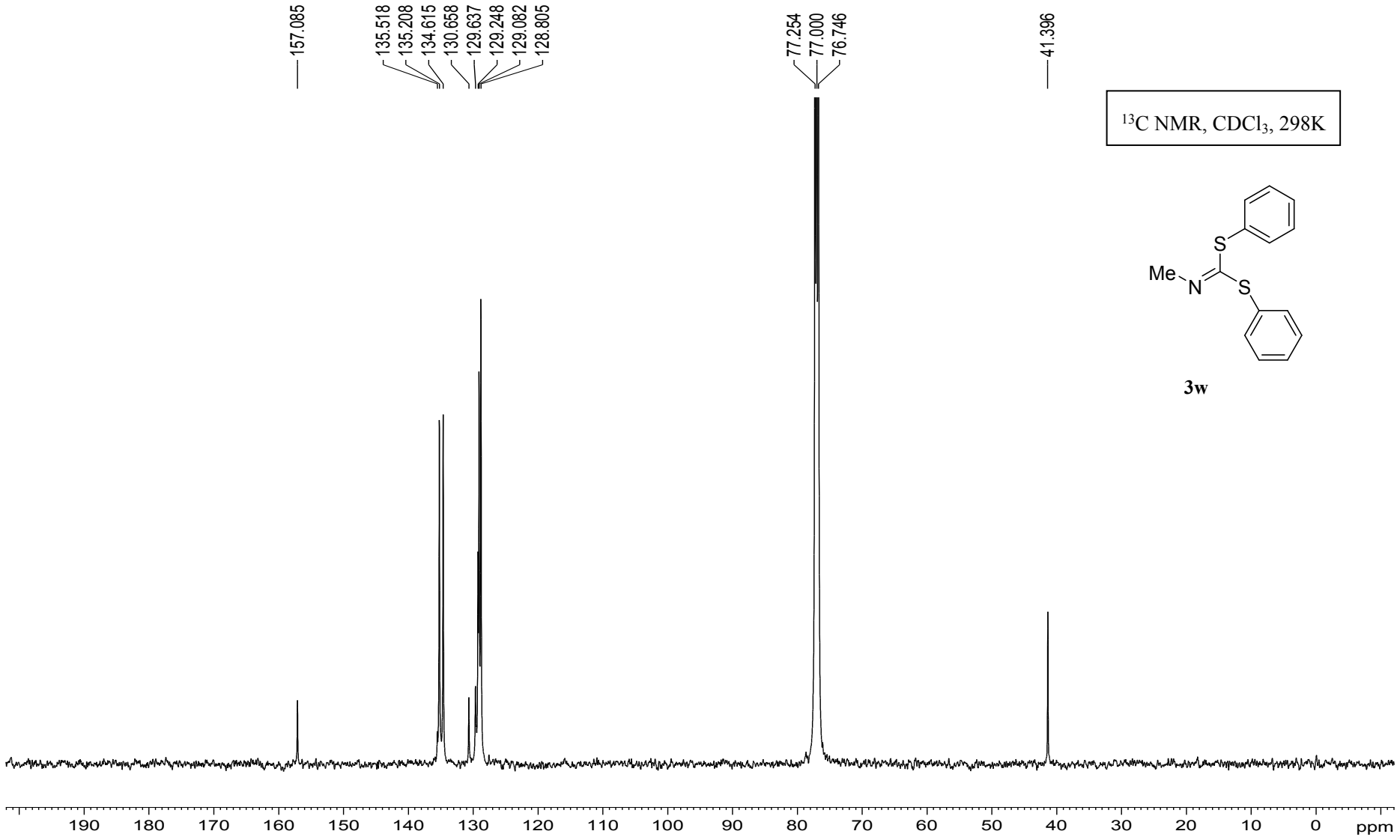
7.580
7.430
7.426
7.418
7.404
7.399
7.383
7.377
7.370
7.365
7.316
7.309
7.304
7.255
3.289
1.570
^{1}H NMR, $CDCl_3$, 298K
S
Me
N
S
3w
7.6
7.5
7.4
7.3
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.000
5.039
3.005
3.085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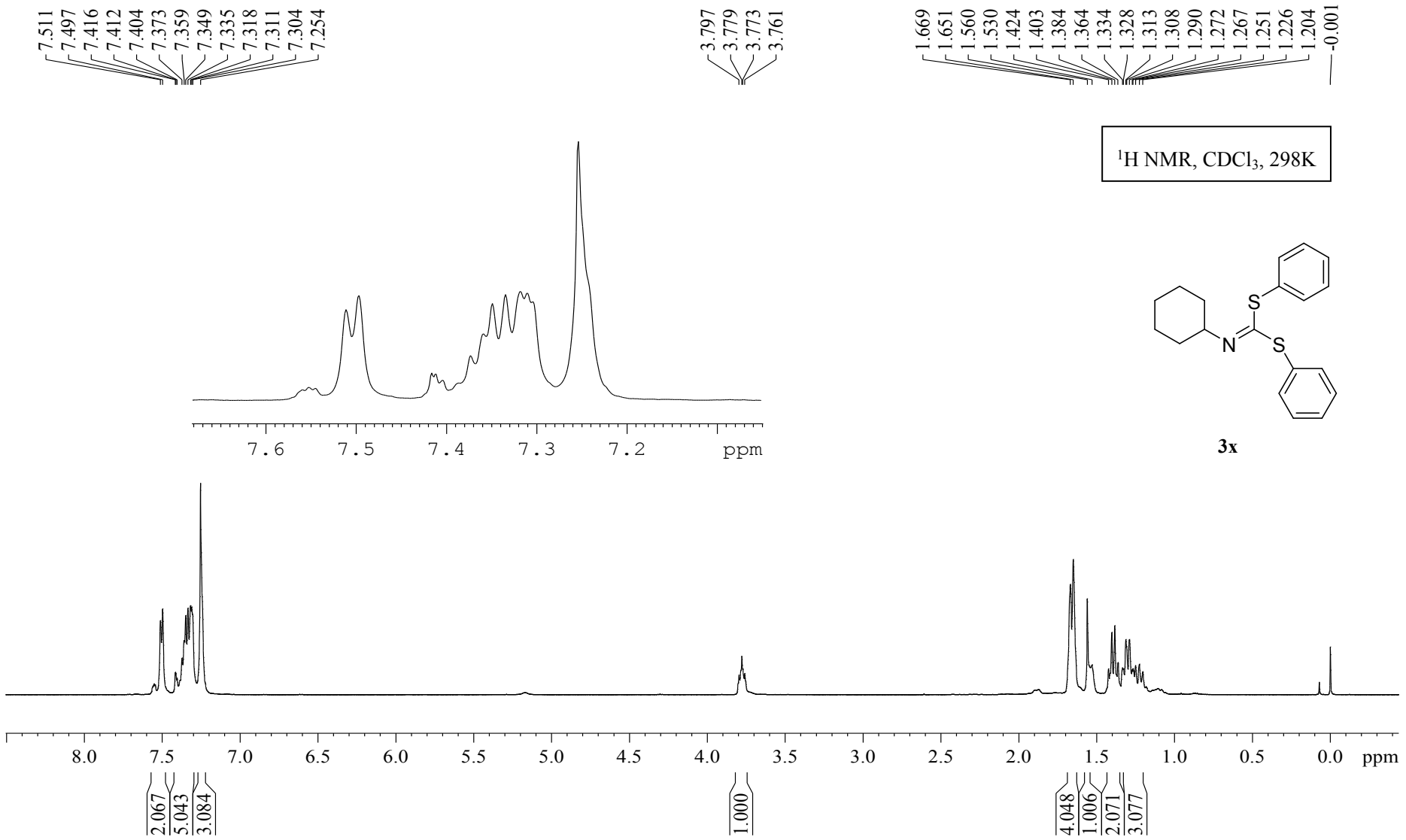
135.518
135.208
134.615
130.658
129.637
129.248
129.082
128.805
77.254
77.000
76.746
41.396
^{13}C NMR, $CDCl_3$, 298K
Me
N
S
S
3w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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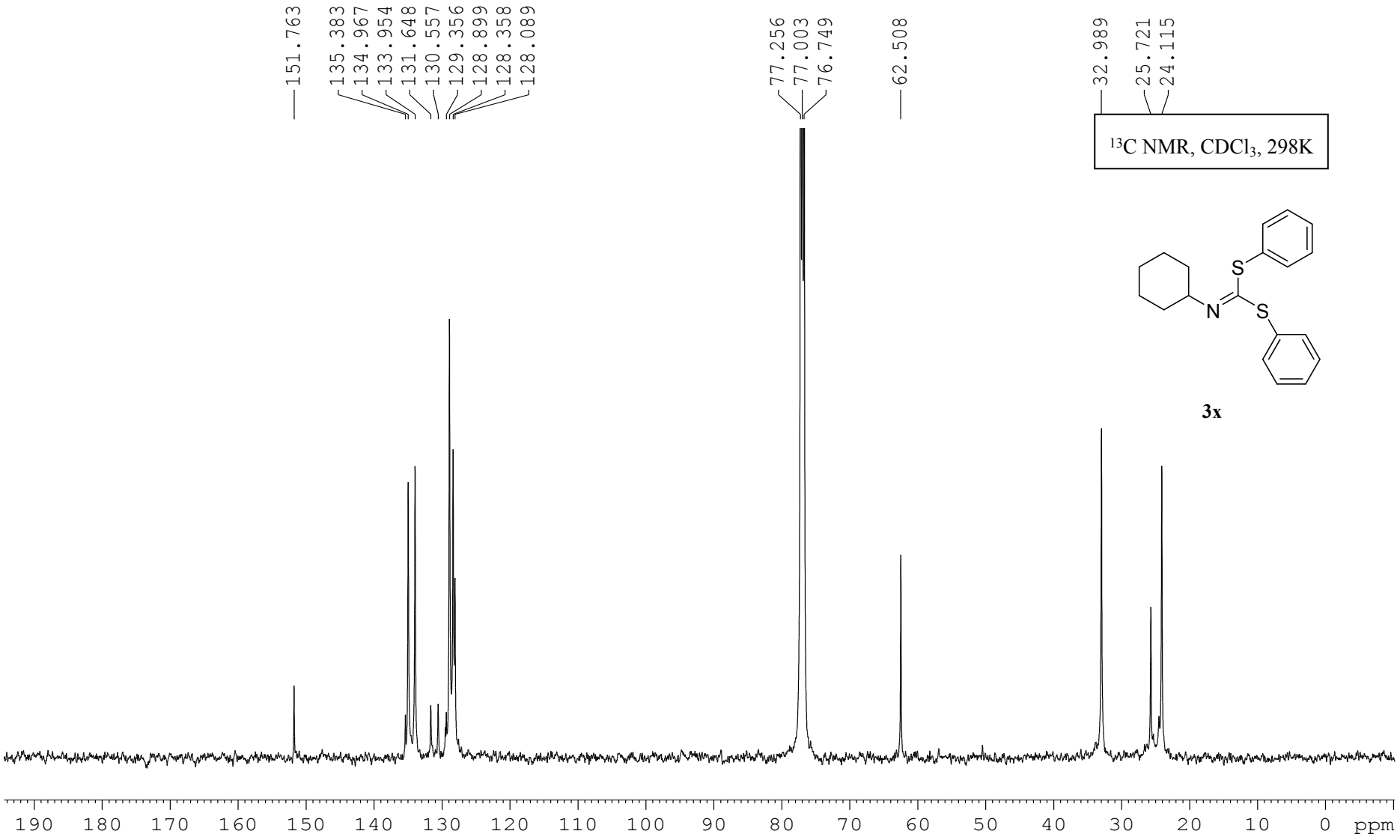
7.497
7.416
7.412
7.404
7.373
7.359
7.349
7.335
7.318
7.311
7.304
7.254
3.797
3.779
3.773
3.761
1.669
1.651
1.560
1.530
1.424
1.403
1.384
1.364
1.334
1.328
1.313
1.308
1.290
1.272
1.267
1.251
1.226
1.204
-0.001
[1]H NMR, CDCl3, 298K
S
N
S
3x
7.6
7.5
7.4
7.3
7.2
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.067
5.043
3.084
1.000
4.048
1.006
2.071
3.077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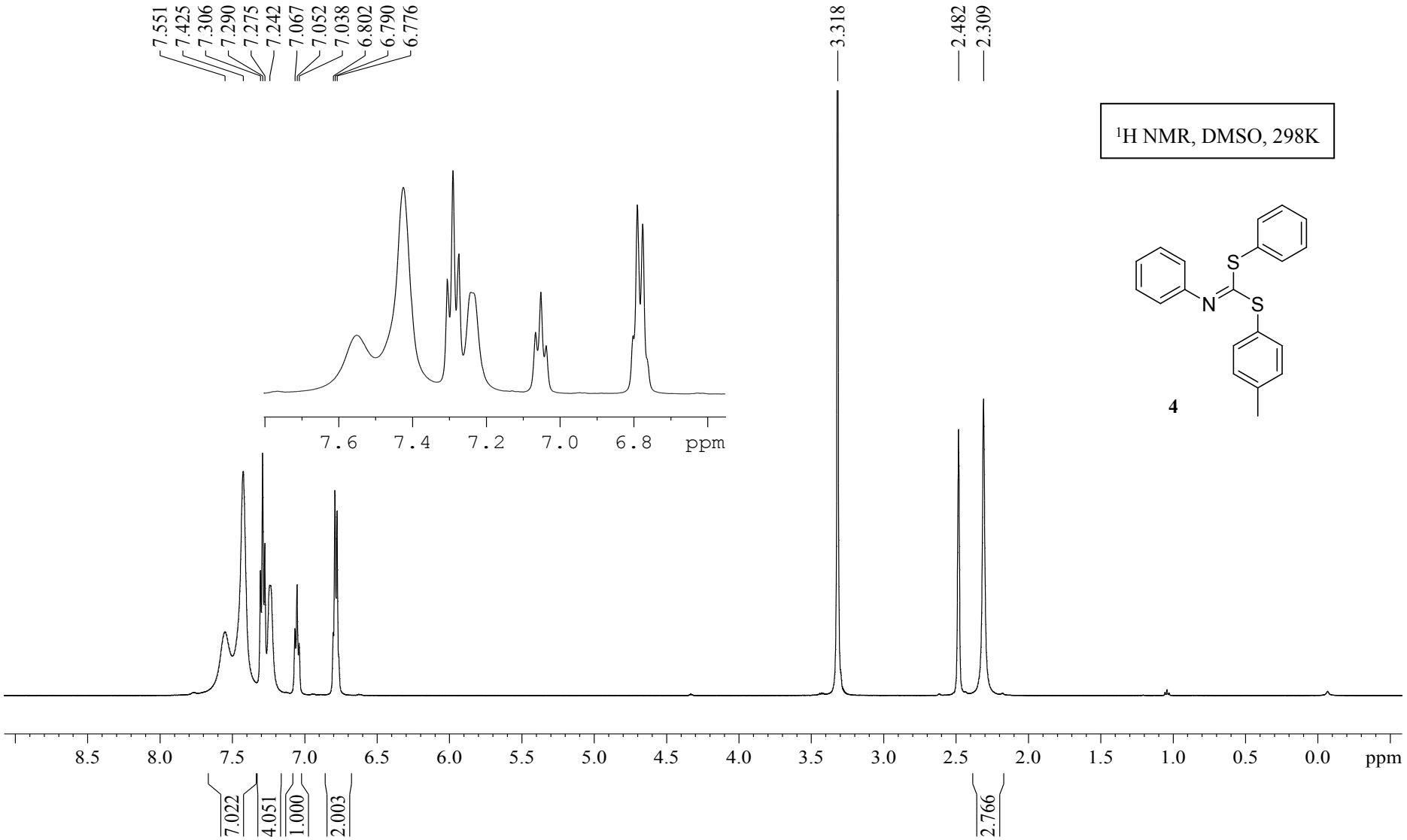
135.383
134.967
133.954
131.648
130.557
129.356
128.899
128.358
128.089
77.256
77.003
76.749
62.508
32.989
25.721
24.115
13C NMR, CDCl3, 298K
S
N
S
3x
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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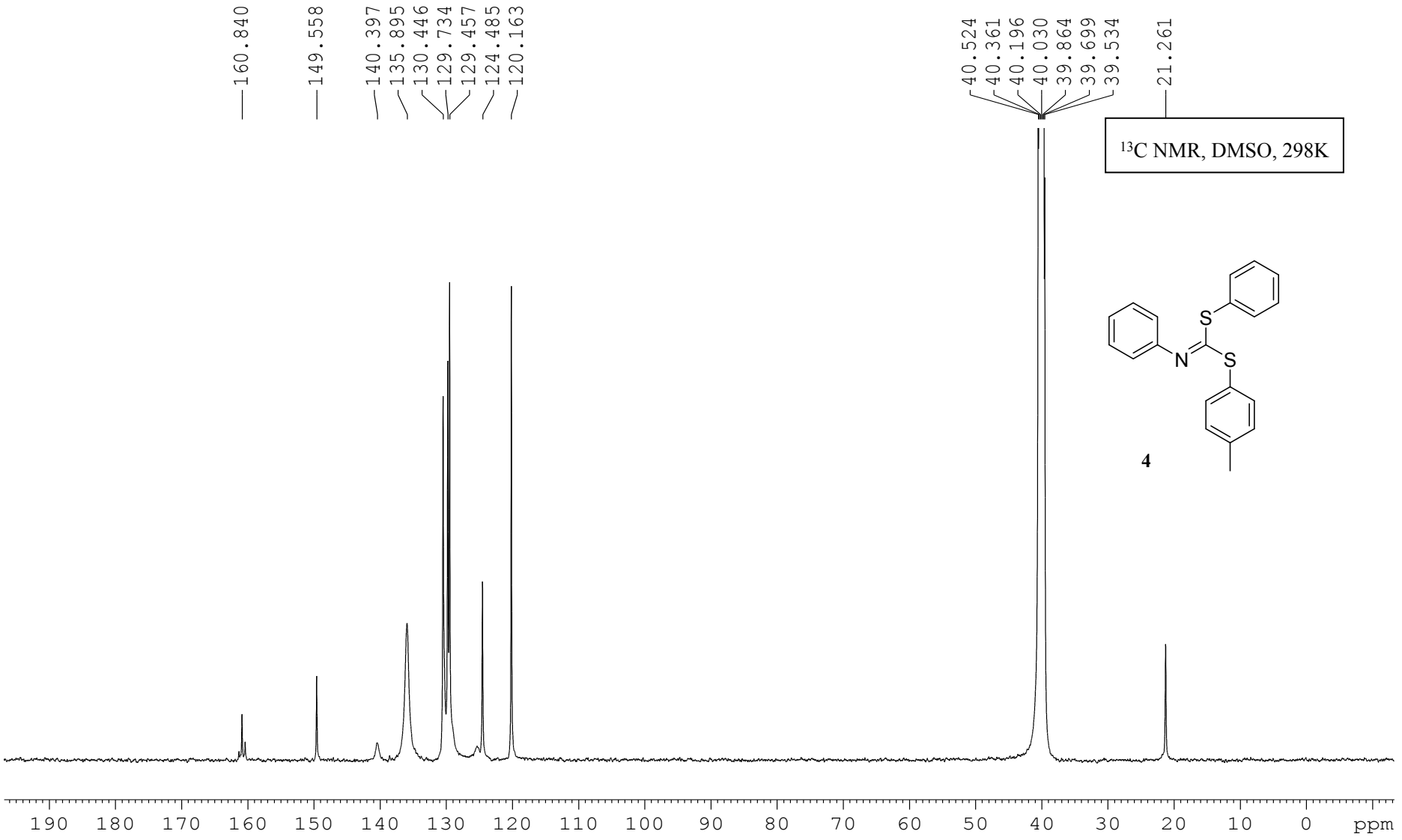
7.425
7.306
7.290
7.275
7.242
7.067
7.052
7.038
6.802
6.790
6.776
3.318
2.482
2.309
1H NMR, DMSO, 298K
S
N
S
4
7.6
7.4
7.2
7.0
6.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.022
4.051
1.000
2.003
2.766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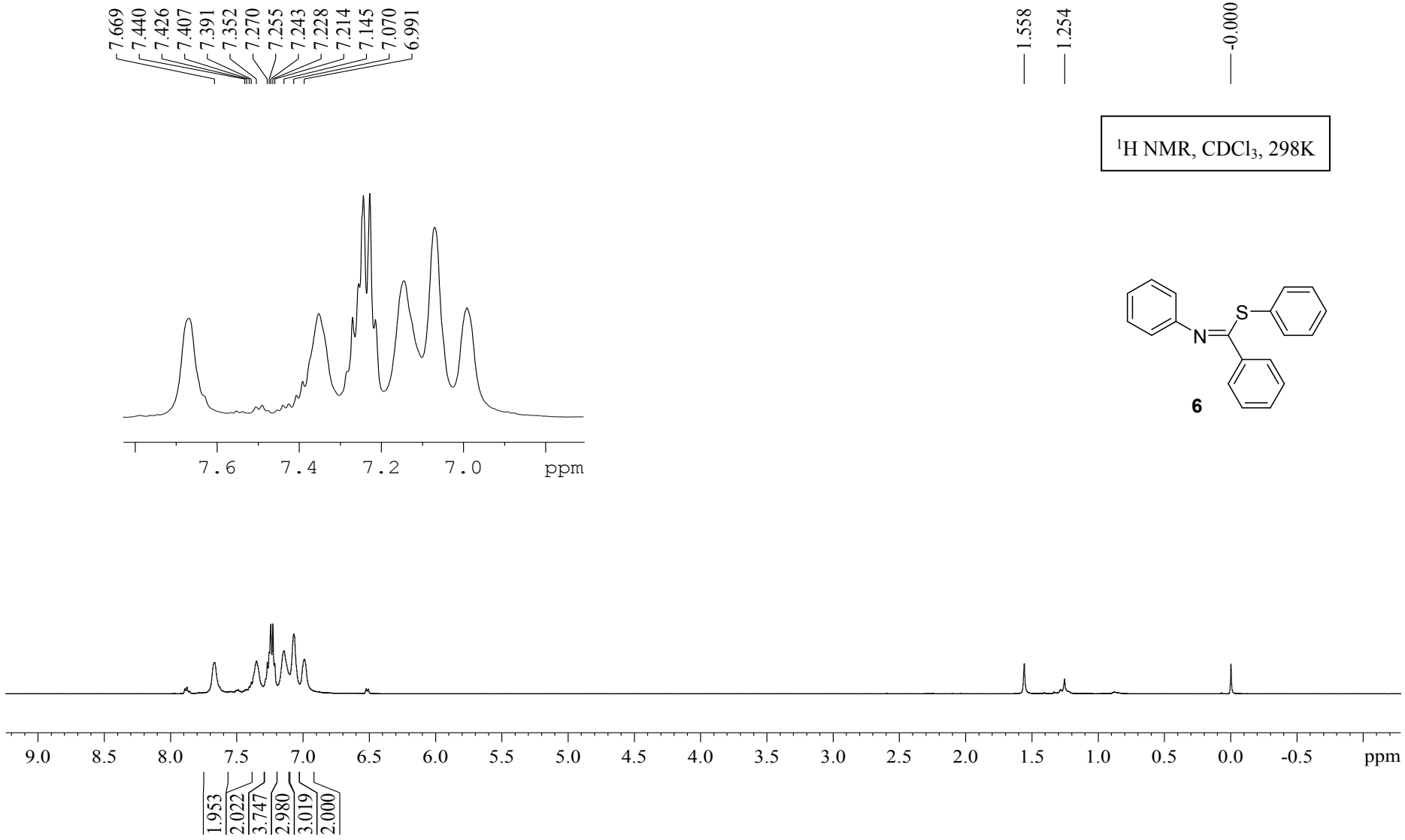
149.558
140.397
135.895
130.446
129.734
129.457
124.485
120.163
40.524
40.361
40.196
40.030
39.864
39.699
39.534
21.261
13C NMR, DMSO, 298K
S
N
S
4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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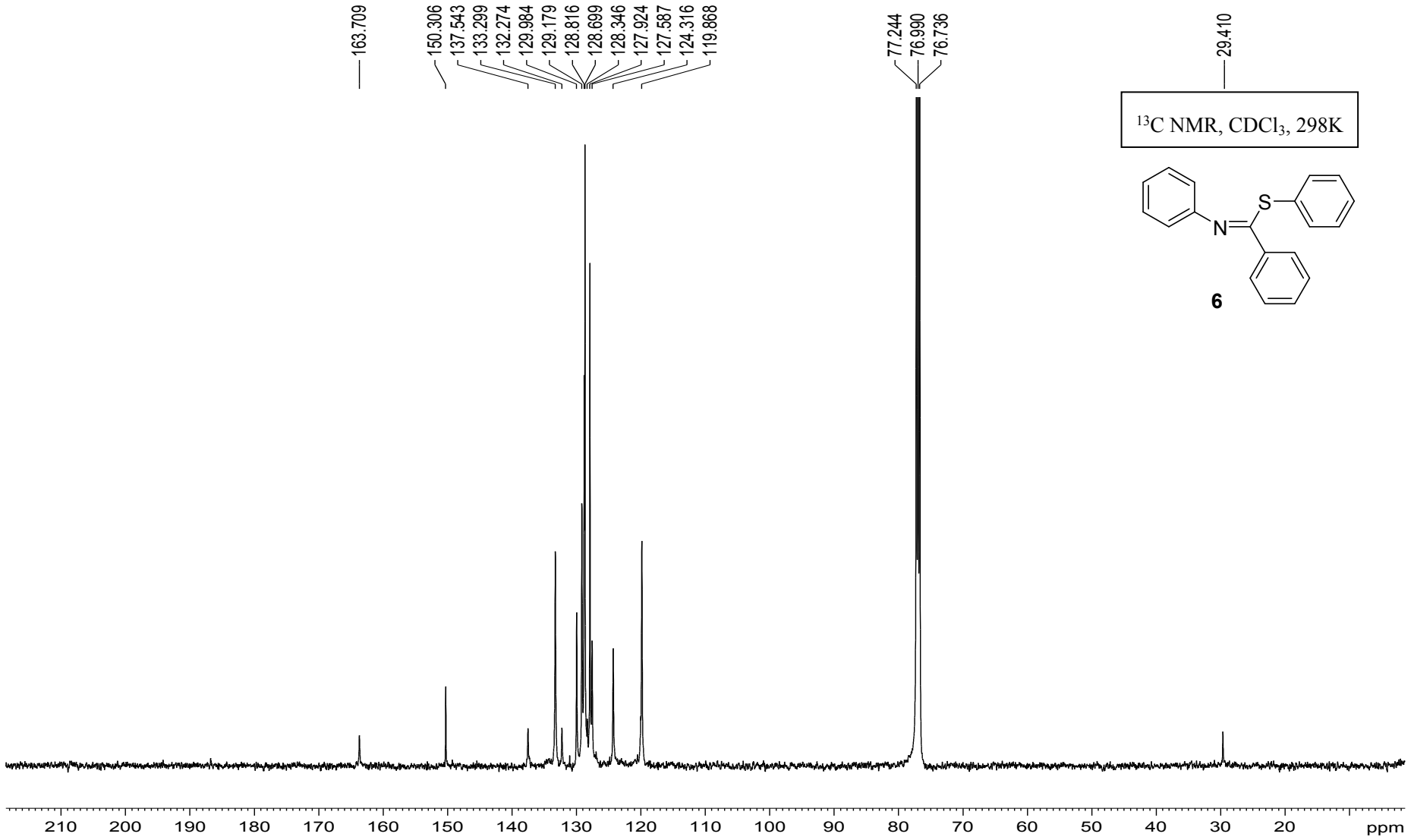
7.440
7.426
7.407
7.391
7.352
7.270
7.255
7.243
7.228
7.214
7.145
7.070
6.991
1.558
1.254
-0.000
^{1}H NMR, $CDCl_3$, 298K
S
N
6
7.6
7.4
7.2
7.0
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.953
2.022
3.747
2.980
3.019
2.000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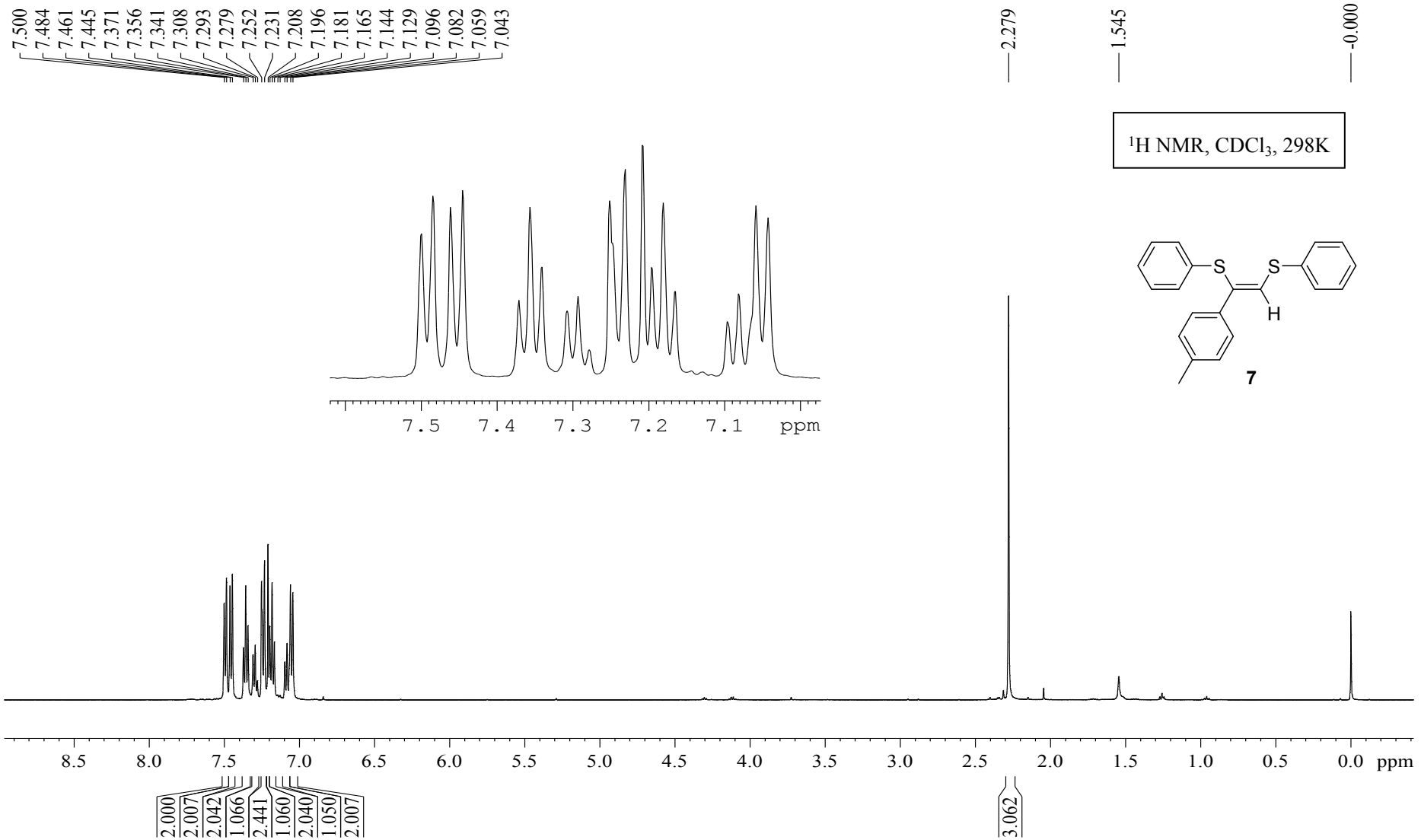
150.306
137.543
133.299
132.274
129.984
129.179
128.816
128.699
128.346
127.924
127.587
124.316
119.868
77.244
76.990
76.736
29.410
^{13}C NMR, $CDCl_3$, 298K
S
N
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.484
7.461
7.445
7.371
7.356
7.341
7.308
7.293
7.279
7.252
7.231
7.208
7.196
7.181
7.165
7.144
7.129
7.096
7.082
7.059
7.043
2.279
1.545
-0.000
^{1}H NMR, $CDCl_3$, 298K
S
S
H
7
7.5
7.4
7.3
7.2
7.1
ppm
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
ppm
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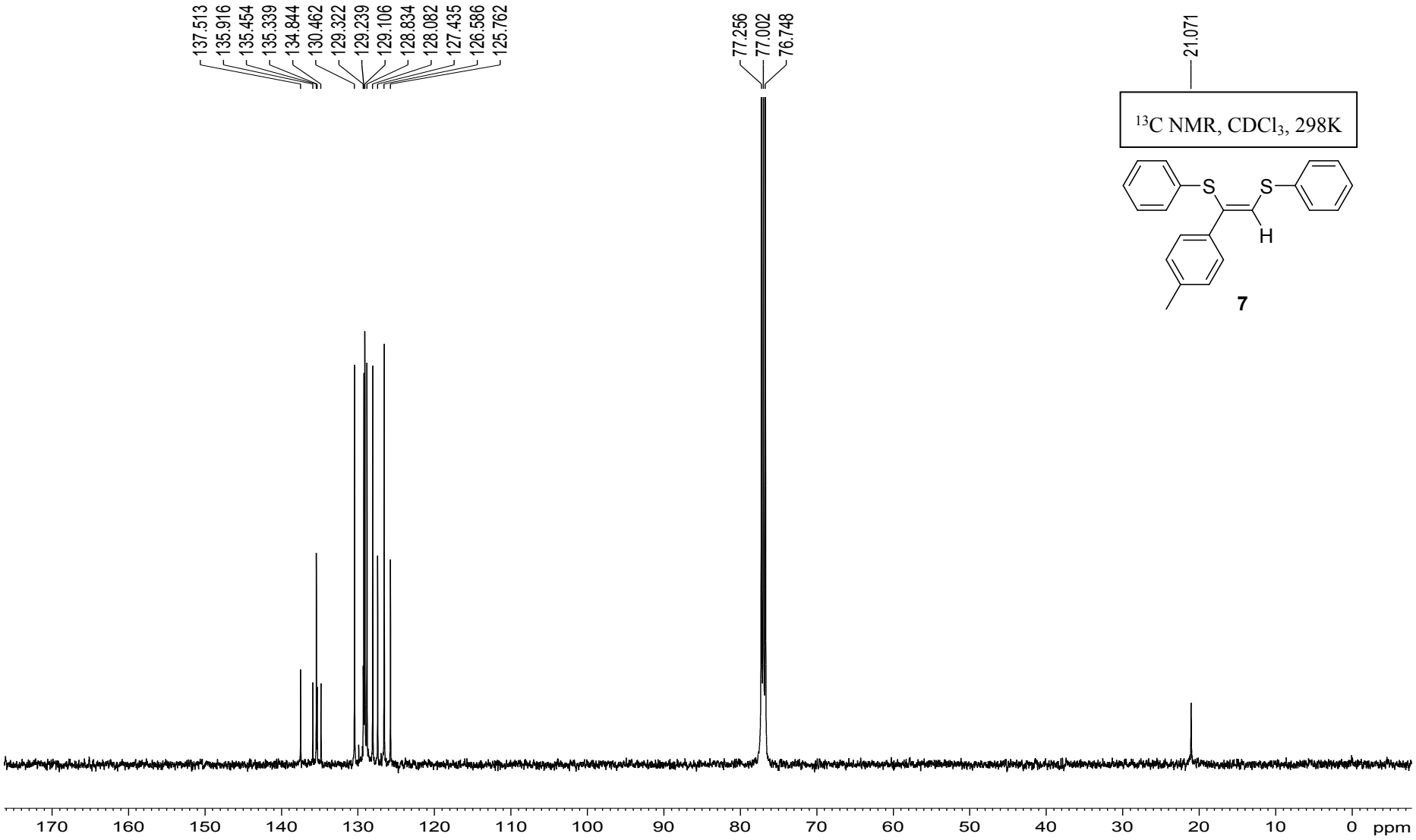
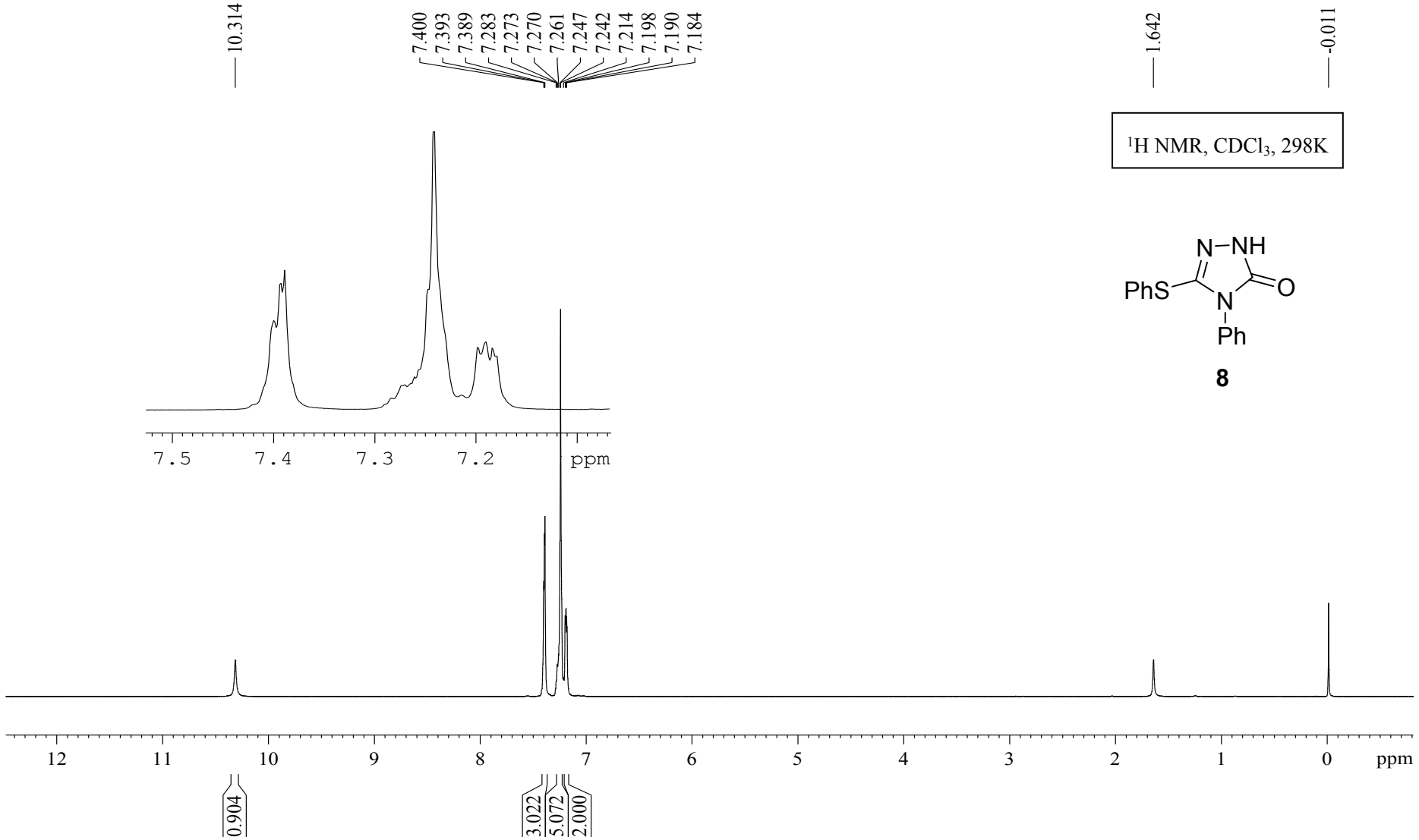
2.007
2.042
1.066
2.441
1.060
2.040
1.050
2.007
3.062


137.513
135.916
135.454
135.339
134.844
130.462
129.322
129.239
129.106
128.834
128.082
127.435
126.586
125.762
77.256
77.002
76.748
21.071
^{13}C NMR, $CDCl_3$, 298K
S
S
H
7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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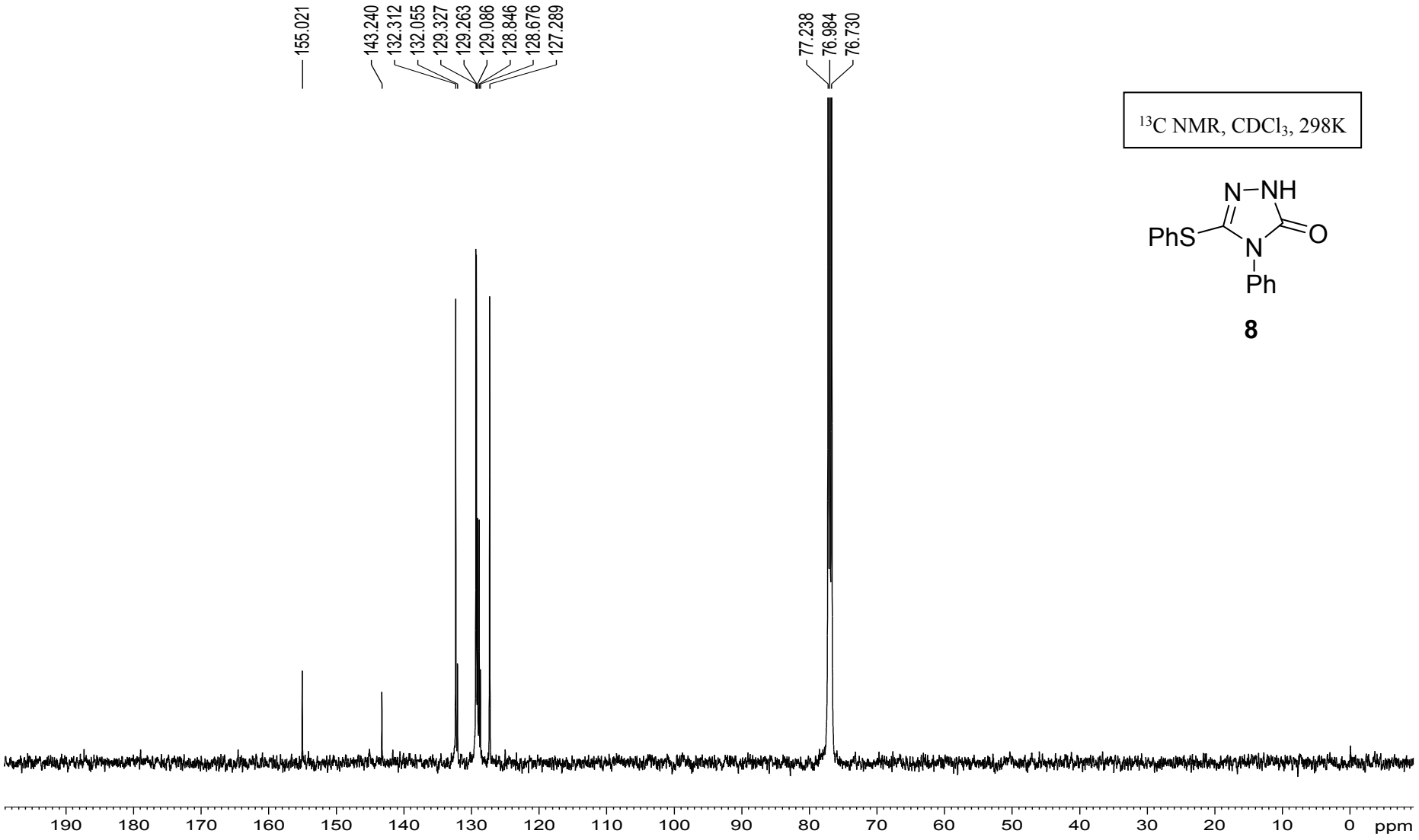
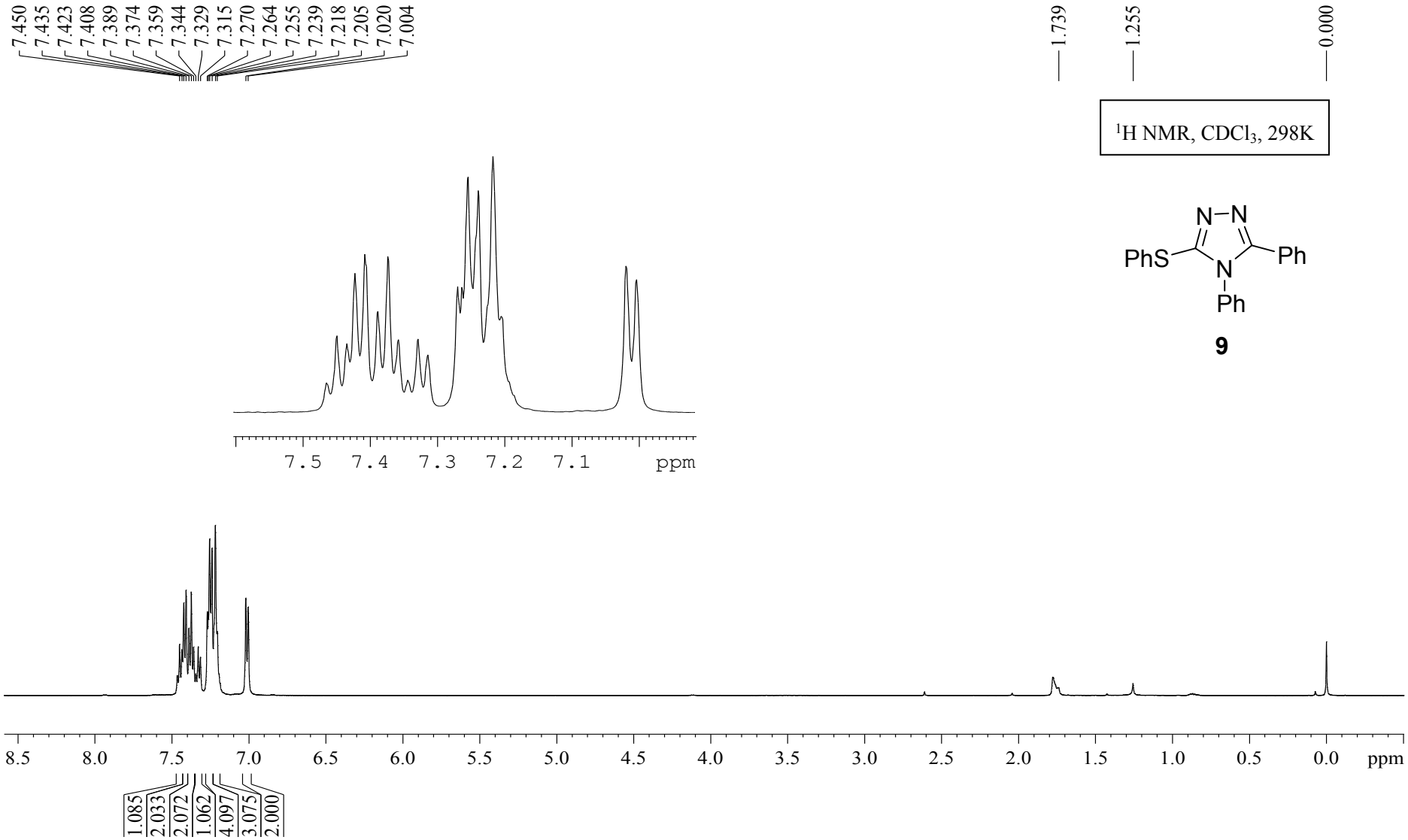
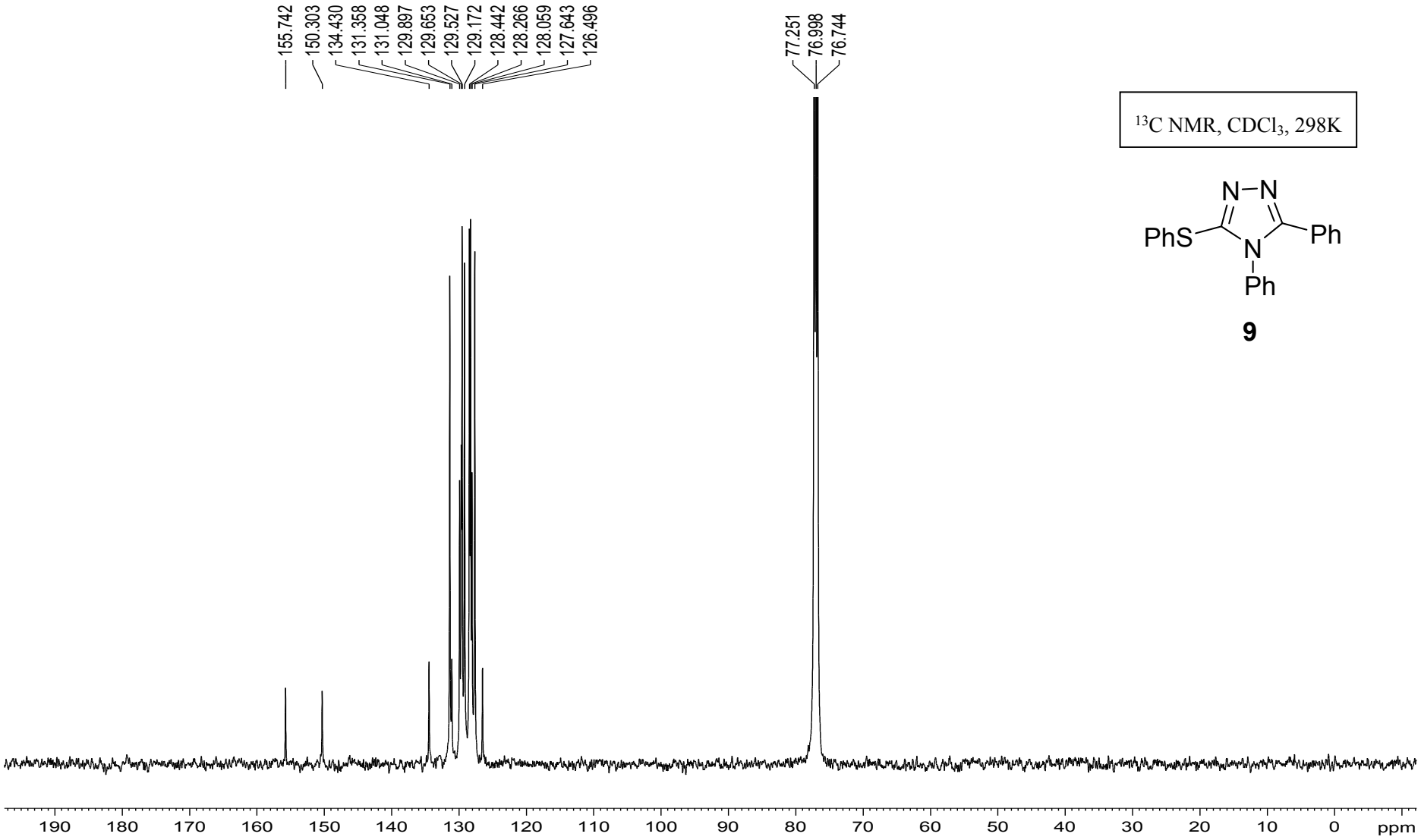
7.400
7.393
7.389
7.283
7.273
7.270
7.261
7.247
7.242
7.214
7.198
7.190
7.184
1.642
-0.011
^{1}H NMR, $CDCl_3$, 298K
N–NH
PhS
O
N
Ph
8
7.5
7.4
7.3
7.2
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.904
3.022
5.072
2.000


155.021
143.240
132.312
132.055
129.327
129.263
129.086
128.846
128.676
127.289
77.238
76.984
76.730
^{13}C NMR, $CDCl_3$, 298K
N–NH
PhS
N
O
Ph
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.450
7.435
7.423
7.408
7.389
7.374
7.359
7.344
7.329
7.315
7.270
7.264
7.255
7.239
7.218
7.205
7.020
7.004
1.739
1.255
0.000
^{1}H NMR, $CDCl_3$, 298K
PhS
Ph
Ph
9
7.5
7.4
7.3
7.2
7.1
ppm
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
ppm
1.085
2.033
2.072
1.062
4.097
3.075
2.000



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

9

Molecular structure and crystallographic data of 3a

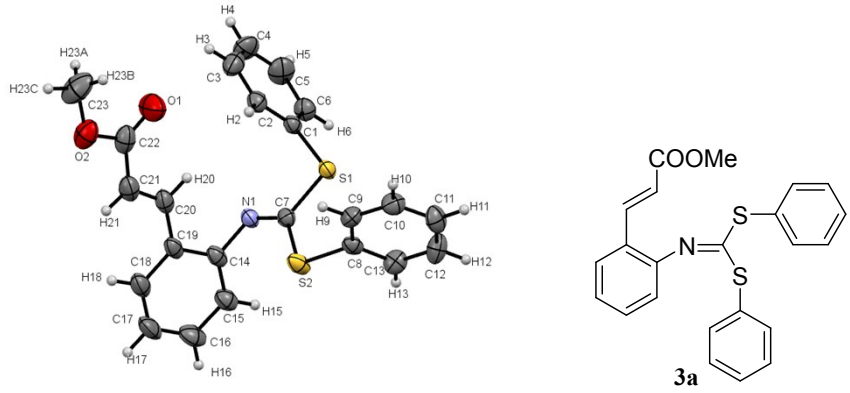


Figure S1 X-ray crystal structure of **3a**

Table S1. Crystal data and structure refinement for **3a**

Formula	$C_{23}H_{19}NO_2S_2$
CCDC number	1423393
Formula weight	405.51
Temperature (K)	173.1500 K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P 21 21 21
a (Å)	8.189(2)
b (Å)	14.782(4)
c (Å)	17.421(5)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2108.7(10)
Z	4
Density (calculated) (Mg/m^3)	1.277
Absorption coefficient (mm^{-1})	0.270
F(000)	848
Crystal size (mm^3)	0.27 x 0.19 x 0.1
Theta range for data collection (°)	2.714 to 27.454
Index ranges	-10<=h<=10, -16<=k<=19, -22<=l<=19
Reflections collected	15230
Independent reflections	4800 [R(int) = 0.0464]
Completeness to theta = 26.000° (%)	99.2
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9006
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4800 / 0 / 254
Goodness-of-fit on F^2	1.150
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.0937
R indices (all data)	R1 = 0.0577, wR2 = 0.0959
Absolute structure parameter	1.01(4)
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å^{-3})	0.188 and -0.209

Molecular structure and crystallographic data of diphenylurea

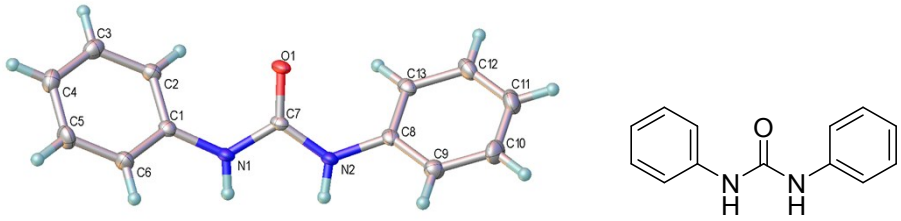


Figure S2 X-ray crystal structure of diphenylurea

Table S2. Crystal data and structure refinement for diphenylurea

Formula	$C_{13}H_{12}N_2O$
CCDC number	1497705
Formula weight	212.25
Temperature (K)	173.1500 K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P n a 21
a (Å)	9.077(4)
b (Å)	10.400(4)
c (Å)	11.750(5)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	1109.3(8)
Z	4
Density (calculated) (Mg/m^3)	1.277
Absorption coefficient (mm^{-1})	0.082
F(000)	448
Crystal size (mm^3)	0.23 x 0.12 x 0.07
Theta range for data collection (°)	2.979 to 27.454
Index ranges	-11<=h<=11, -13<=k<=13, -12<=l<=15
Reflections collected	6686
Independent reflections	2035 [R(int) = 0.0361]
Completeness to theta = 26.000° (%)	99.6
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.73899
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2035 / 1 / 145
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.1194
R indices (all data)	R1 = 0.0383, wR2 = 0.1208
Absolute structure parameter	0.2(10)
Extinction coefficient	n/a
Largest diff. peak and hole ($e.Å^{-3}$)	0.196 and -0.145