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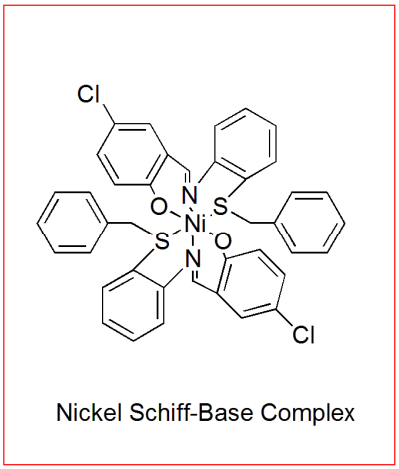

Nickel Schiff-Base Complex

Nickel-Schiff base complex catalyzed C-S cross-coupling of thiols with organic chlorides

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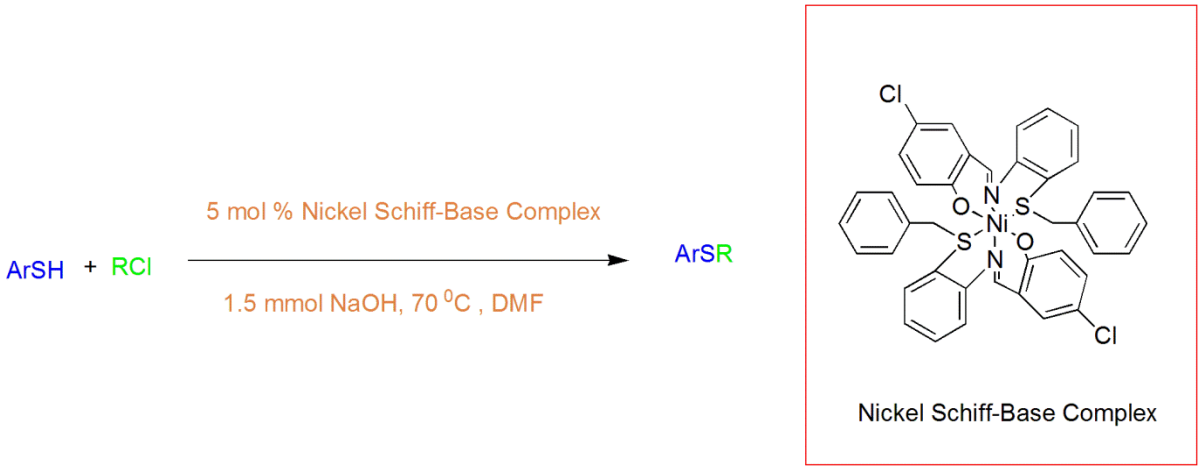
Graphical Abstract:



***Keywords*:** Nickel-Schiff base complex, Thiols, Organic chloride, NaOH

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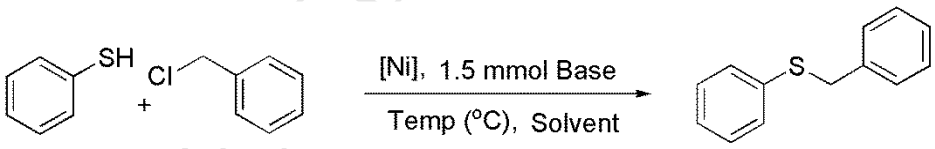
Abstract: We report an efficient, mild and convenient synthetic protocol for the C-S cross-coupling reaction of various aryl, benzyl, allyl chlorides and thiols using 5 mol % Nickel-Schiff base catalyst with NaOH as the base, in DMF at 70 °C. Using this protocol, we have shown that a variety of aryl sulfides can be synthesized in excellent yields from readily available organic chlorides and thiols.

1. Introduction

Sulfides are important compounds in organic synthesis and many of which are biologically and pharmacologically active natural products.[1] The synthesis of this privileged structure has attracted significant interest of synthetic chemist who in recent years have developed numerous synthetic methodologies of organic sulfides. Most of these methods are focused on transition-metal-catalyzed C–S bond formation reactions.[2] The transition metal catalysts used are palladium,[3] nickel,[4] copper,[5] cobalt,[6] zinc,[7] iron,[8] and indium.[9] But almost all of these methods have some inherent shortcomings like harsh reaction conditions, metal toxicity, and high cost of the metal which restrict their applications especially in large scale processes. A few reports on the C-S bond formation using metal-Schiff base complexes[10] are also known. More recently synthesis of diaryl sulfides from thiophenols and aryliodides has been reported by Punniyamurthy et al.[11] albeit in a relatively slow reaction whereas, Peng et al.[12] synthesis of diarylsulfides with electron withdrawing groups in the substrates gives poor yields. In this piece of work we report an efficient Nickel(II)-Schiff base complex mediated C-S cross coupling of thiophenols with organic chlorides (Table 2).

2. Results and discussion

Table 1: Optimization of reaction condition for coupling reaction



Entry	Catalyst (mol %)	Base (Temp °C)	Solvent	Time (h)	Yield (%)[a]
1	----------	NaOH (100)	DMF	3	nr
2	$NiCl_2.6H_2O$ (10)	NaOH (70)	DMF	3	40
3	$NiNO_3.6H_2O$ (10)	NaOH (70)	DMF	5	20
4	$NiNO_3.3H_2O$ (10)	NaOH (70)	DMF	5	19
5	NiL_2 (5)	NaOH (100)	DMF	1	90

6	**NiL_2 (5)**	**NaOH (70)**	**DMF**	**1**	**95**
7	NiL_2 (5)	NaOH (70)	DMSO	3	50
8	NiL_2(5)	Piperidine (70)	DMF	4	12
9	NiL_2 (10)	Triethyl amine (70)	DMF	4	23
10	NiL_2 (10)	Ethylene diammine (70)	DMSO	3	11

[a]Isolated yield

NiL_2 Preparation: The preparation of Nickel-Schiff base complex followed by our earlier work.[13]

In our initial screening experiments we chose thiophenol and benzylchloride as the model substrates (Table 1). Initially we investigated the C-S cross coupling reaction without a catalyst when no reaction took place (entry 1). However, when an equimolar mixture of these substrates was stirred for 3 hr at 70 ^{o}C in DMF and NaOH in presence of Ni-catalyst ($NiCl_2.6H_2O$) C-S bond formation took place to give 40% of the desired organic sulfide (entry 2). The yields were still lower when nickel nitrate hexahydrate and nickel nitrate trihydrate were used as the catalysts under same reaction conditions (entries 3-4). But the yield dramatically increased when nickel-Schiff base complex was used as the catalyst (entry 5). The optimum temperature for the best result was found to be 70 ^{o}C (entry 6) and inorganic base sodium hydroxide was found to give much better yields in comparison with organic bases pyridine, piperidine, triethylamine and ethylene diamine (entries 8-10). DMF was found to be the solvent of choice. The optimized reaction condition, turned out to be using nickel-Schiff base complex NiL_2 (5 mol %), NaOH (1.5 equivalent) in reagent grade DMF at 70 ^{o}C for 1 h.

The structure of 2-nitrophenyl benzyl sulfide, 3o (Fig 2) was characterized by X-ray diffraction.

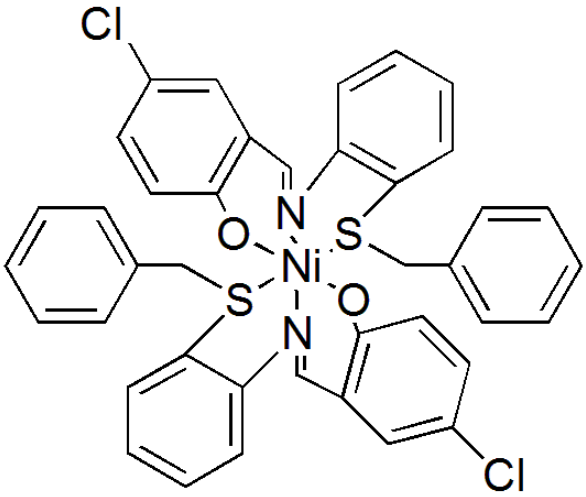


Fig 1: Nickel-Schiff base complex (NiL_2)

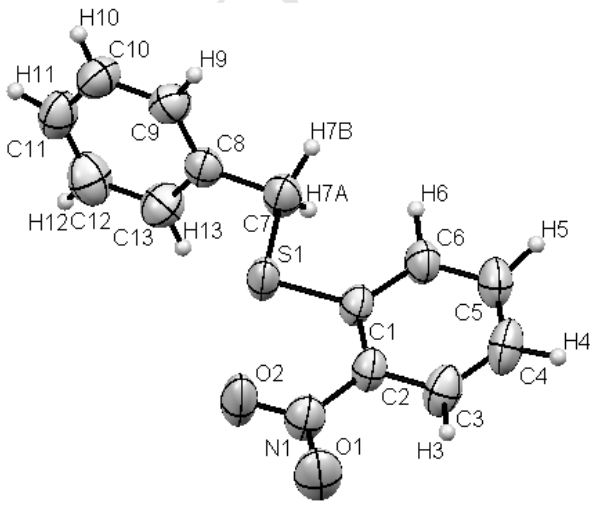
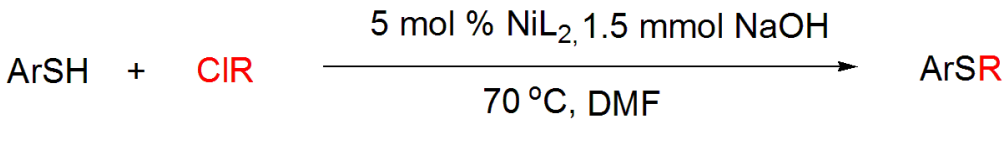
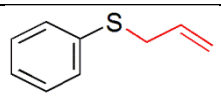
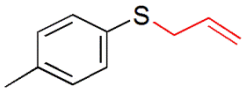
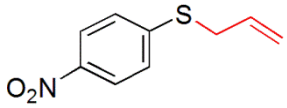
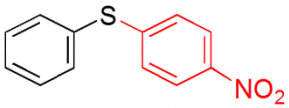
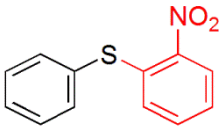
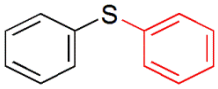
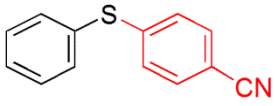
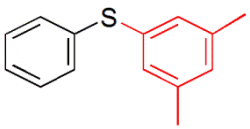
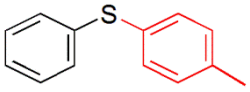
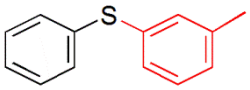


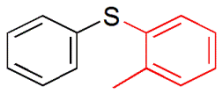
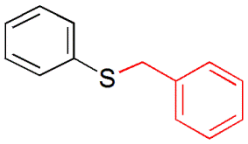
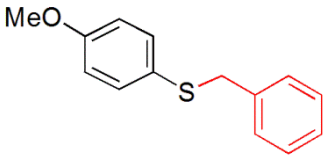
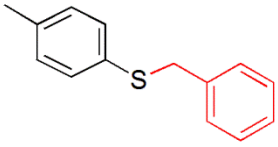
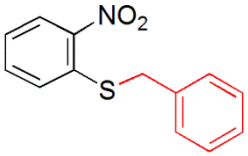
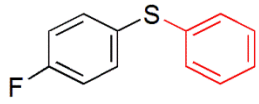
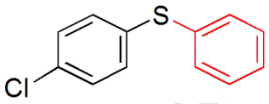
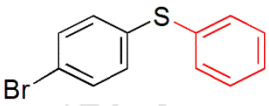
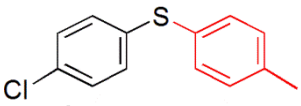
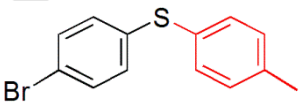
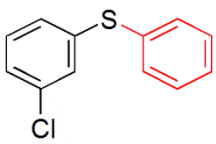
Fig 2: X ray crystal structure analysis of 3o (CCDC **1018005**)

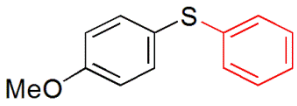
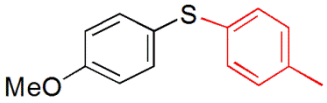
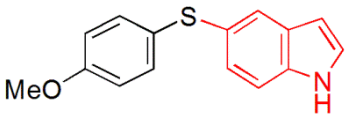
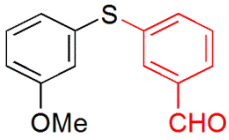
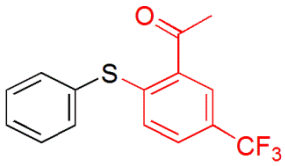
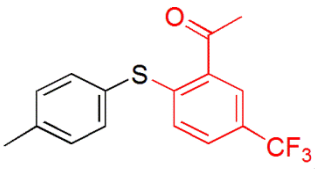
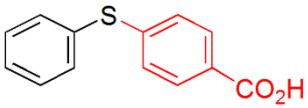
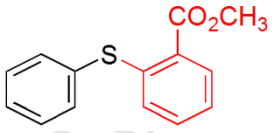
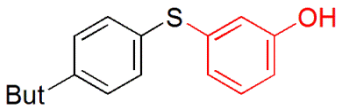
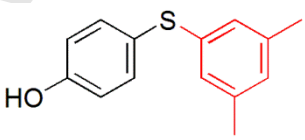
Table 2: C-S cross coupling of Aryl thiols with various organic chloride[a]



3

Entry	Product (3)	Time (h)	Yield (%)[b]
1	 3a	3	82
2	 3b	3	74
3	 3c	3	88
4	 3d	2	99
5	 3e	2	96
6	 3f	2	81
7	 3g	1	93
8	 3h	3	77
9	 3i	3	79
10	 3j	3	76

11	 3k	3	78
12	 3l	1	95
13	 3m	1	78
14	 3n	1	85
15	 3o	1	99
16	 3p	2	89
17	 3q	2	86
18	 3r	2	84
19	 3s	3	77
20	 3t	3	75
21	 3u	2	88

22	 3v	3	74
23	 3w	5	70
24	 3x	4	70
25	 3y	2	73
26	 3z	2	77
27	 3Aa	3	72
28	 3Ab	2	89
29	 3Ac	2	76
30	 3Ad	3	65
31	 3Ae	3	68

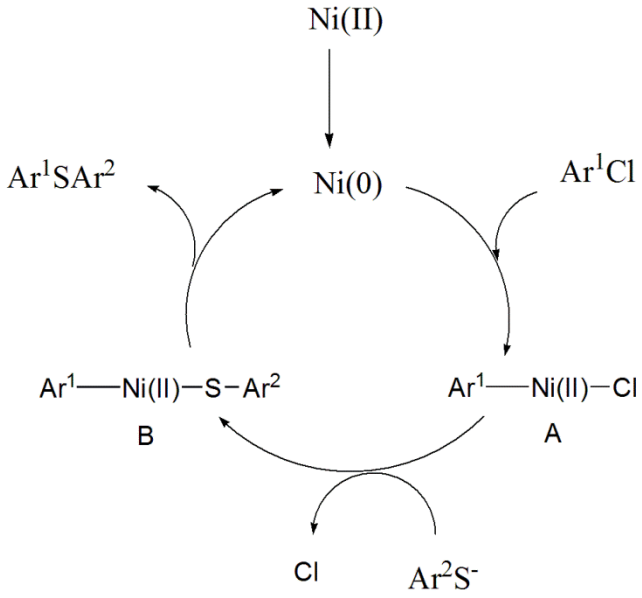
[a]Reaction conditions: NiL_2 (5 mol %), arylthiol (1 mmol), organic chloride (1 mmol), NaOH (1.5 mmol) in DMF (2 mL)

[b]Isolated yield

To determine the scope of this method and to test the generality of the protocol, a range of thiophenols and aryl chlorides were surveyed (Table 2). Various substituents such as Me, NO_2, CN, CF_3, COOH, CHO, CO_2CH_3, $COCH_3$, and OH in the aromatic ring of the aryl chlorides were well tolerated in the reactions to give good to excellent yields of the desired diaryl sulfides (Table 2). The polar effects of the substituent in the aryl halides were found to have very limited influence on the yields of the reaction through electron withdrawing substituents in the aromatic ring gave a little better yields (Table 2, entries 4-5 and 7) than those with electron releasing groups in the ring (Table 2 entries 8-11 and 23).

We consider it to be worth mentioning here that this methodology is quite suitable with different types of organic chlorides such as allyl, aryl, and benzyl chlorides though benzyl chlorides were found to be most reactive of all giving desired sulfides in excellent yields (Table 2, entries 12-15). On the other hand, all types of substituents in the aromatic ring of the other component thiophenol were found to be well tolerated in the reaction giving good to excellent yields of the desired organic sulfides. Polar effects of these substituents on the reactions were found to be minimal (Table 2, entries 22-31).

The proposed mechanism of this C-S bond formation reaction is in the well known line[11,14] of such low valent transition metal mediated reactions. This involved an oxidative addition of a substrate to the Ni(0) to give an intermediate (A) which on ligand substitution reaction with a thiolate anion forms another intermediate (B). The latter undergoes a reductive elimination of a diaryl sulfide molecule to regenerate the catalyst Ni(0) (Scheme 1).



Scheme 1. Outline of a possible reaction pathway

3. Conclusions

In summary, we have developed an efficient catalytic system for the C-S coupling reaction of organic halide with thiols at 70 ^{o}C in DMF. Under optimal conditions, for all aryl halides, allyl halides and benzyl halides the corresponding coupling products can be achieved in good to high yields. This novel method provides a complementary, efficient and easy operational approach to accessing C-S derivatives.

4. Experimental Section

4.1 General Information

All solvents and chemicals were purchased commercially and used without further purification. Column chromatography was generally performed on silca gel (230-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light (254 nm) to visualise the course of reactions. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 400 and 100 MHz respectively. All NMR samples were recorded in deuterated chloroform. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument at NIT Silchar. CCDC number for the compound **3o** is CCDC **1018005.** This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/deposit/, or from the Cambridge Crystallographic Data Centre,

12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

4-Nitrophenyl phenyl sulfide (3d):

A mixture of *p*-nitro-chlorobenzene (157 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 20/1) to give the title compound 3d (228 mg, 99%) as a pale yellow solid; mp 55-56 ^oC; [Found: C, 62.28; H, 3.96; N, 6.09. $C_{12}H_9NO_2S$ requires C, 62.32; H, 3.92; N, 6.06 %]; R*f* = 0.4 (hexane/ethyl acetate = 20/1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J*=7.2 Hz, 2H), 7.67-7.59 (m, 2H), 7.47– 7.42 (m, 3H), 7.07 (d, *J*=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 145.3, 134.8, 130.2, 129.6, 126.7, 124.7, 124.2.

2-Nitrophenyl phenyl sulfide (3e):

A mixture of o-nitro-chlorobenzene (157 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 4/1) to give the title compound 3e (222 mg, 96%) as a orange oil; [Found: C, 62.37; H, 3.91; N, 6.11. $C_{12}H_9NO_2S$ requires C, 62.32; H, 3.92; N, 6.06%]; R*f* = 0.4 (hexane/ethyl acetate = 4/1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J*=7.3 Hz, 2H), 7.58 (d, *J*=7.2 Hz, 2H), 7.47(s, 3H), 7.34-7.18 (m, 1H), 6.83 (d, *J*=7.4 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 139.2, 135.7, 133.4, 131.6, 130.9, 130.2, 130.0, 128.7, 125.3, 124.3.

Diphenyl sulfide (3f):

A mixture of chlorobenzene (112 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column

chromatography (hexane/ethyl acetate = 4/1) to give the title compound 3f (150 mg, 81%) as a colourless oil; [Found C, 77.55; H, 5.47; $C_{12}H_{10}S$ requires C, 77.37; H, 5.41%]; R*f* = 0.4 (hexane/ethyl acetate = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 131.2, 129.2, 127.7.

4-(Phenylthio)benzonitrile (3g):

A mixture of 4-chlorobenzonitrile (137 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 1 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 25/1) to give the title compound 3g (196 mg, 93%) as a colourless oil; [Found: C, 73.93; H, 4.21; N, 6.68. $C_{13}H_9NS$ requires C, 73.90; H, 4.29; N, 6.63%]; R*f* = 0.4 (hexane/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.43 (m, 7H), 7.21-7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 135.5, 132.4, 130.6, 130.1, 129.2, 127.4, 118.9, 109.1.

4-Methylphenyl phenyl sulfide (3i):

A mixture of 1-chloro-4-methyl benzene (126 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 20/1) to give the title compound 3i (158 mg, 79%) as a colorless oil; [Found: C, 77.98; H, 6.11. $C_{13}H_{12}S$ requires C, 77.95; H, 6.04%]; R*f* = 0.4 (hexane/ethyl acetate = 20/1).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.22 (m, 9H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 137.2, 132.4, 131.2, 129.8, 128.1, 126.8, 21.2.

3-Methylphenyl phenyl sulfide (3j):

A mixture of 1-chloro-3-methyl benzene (126 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 10/1) to give the title compound 3j (152 mg, 76%) as a colorless oil; [Found: C, 77.90; H, 6.12. $C_{13}H_{12}S$ requires C, 77.95; H, 6.04%]; R*f* = 0.4 (hexane/ethyl acetate = 10/1).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 9H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 136.2, 135.4, 131.7, 130.4, 129.4, 129.1, 128.4, 128.2, 126.7, 21.4.

2-Methylphenyl phenyl sulfide (3k):

A mixture of 1-chloro-2-methyl benzene (126 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 10/1) to give the title compound 3k (156 mg, 78%) as a colorless oil; [Found: C, 77.96; H, 6.13. $C_{13}H_{12}S$ requires C, 77.95; H, 6.04%]; R*f* = 0.4 (hexane/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.22 (m, 9H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 136.2, 133.4, 131.3, 131.3, 128.4, 127.2, 125.2, 124.7, 123.1, 122.2, 20.5.

Phenyl benzyl sulfide (3l):

A mixture of benzyl chloride (127 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 1 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 4/1) to give the title compound 3l (190 mg, 95%) as a colourless oil; [Found: C, 77.90; H, 6.21. $C_{13}H_{12}S$ requires C, 77.95; H, 6.04%]; R*f* = 0.4 (hexane/ethyl acetate = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.36-7.30 (m, 10 H), 4.06 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 138.8, 129.9, 128.4, 128.3, 127.2, 126.9, 39.3.

Benzyl 2-nitrophenyl sulfide (3o):

A mixture of benzyl chloride (127 mg, 1 mmol), 2-nitrothiophenol (155 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 1 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 8/1) to give the title compound 3o (243 mg, 95%) as a yellow solid; mp 83-84 ^{o}C; [Found: C, 63.61; H, 4.59. $C_{13}H_{11}NO_2S$ requires C, 63.65; H, 4.52%]; R*f* = 0.4 (hexane/ethyl acetate = 8/1). ^{1}H NMR (400 MHz, CDCl3): δ 8.22 (d, *J*=7.2 Hz, 1H), 7.53-7.23 (8H, m), 4.21 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 134.8, 133.4, 128.9, 128.7, 127.6, 126.7, 125.9, 124.6, 37.4.

4-Fluorophenyl phenyl sulfide (3p):

A mixture of chlorobenzene (112 mg, 1 mmol), 4-fluorothiophenol (128 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 30/1) to give the title compound 3p (181 mg, 89%) as a colourless oil; [Found: C, 70.50; H, 4.41. $C_{12}H_9FS$ requires C, 70.56; H, 4.44%]; R*f* = 0.5 (hexane/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 2H), 7.25–7.18 (m, 5H), 6.96 (t, *J*=8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 160.4, 136.2, 133.9, 130.0, 129.7, 129.1, 126.8, 116.5, 116.3.

4-Chlorophenyl phenyl sulfide (3q):

A mixture of chlorobenzene (112 mg, 1 mmol), 4-chlorothiophenol (144 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 40/1) to give the title compound 3q (189 mg, 86%) as a colourless oil; [Found: C, 65.37; H, 4.16. $C_{12}H_9ClS$ requires C, 65.30; H, 4.11%]; R*f* = 0.5 (hexane/ethyl acetate = 40/1).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.20 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.7, 133.1, 132.2, 131.7, 129.4, 128.0, 127.7.

4-bromophenyl phenyl sulfide (3r):

A mixture of chlorobenzene (112 mg, 1 mmol), 4-bromothiophenol (188 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 8/1) to give the title compound 3r (222 mg, 84%) as a colourless oil; [Found: C, 54.31; H, 3.45. $C_{12}H_9BrS$ requires C, 54.35; H, 3.42%]; R*f* = 0.6 (hexane/ethyl acetate = 8/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.20 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 134.6, 132.4, 132.04, 131.3, 129.04, 127.2.

3-Chlorophenyl phenyl sulfide (3u):

A mixture of chlorobenzene (112 mg, 1 mmol), 3-chlorothiophenol (144 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 40/1) to give the title compound 3u (194 mg, 88%) as a colourless oil; [Found: C, 65.33; H, 4.14. $C_{12}H_9ClS$ requires C, 65.30; H, 4.11%]; R*f* = 0.4 (hexane/ethyl acetate = 40/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.15 (m, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 134.6, 134.3, 132.2, 130.7, 129.7, 129.2, 128.6, 127.3, 126.2.

4-Methoxyphenyl phenyl sulfide (3v):

A mixture of chlorobenzene (112 mg, 1 mmol), 4-mercaptoanisole (140 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 40/1) to give the title compound 3v (160 mg, 74%) as a colorless oil; [Found: C, 72.20; H, 5.66. $C_{13}H_{12}OS$ requires C, 72.19; H, 5.59%]; R*f* = 0.3 (hexane/ethyl acetate = 40/1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J*=7.4 Hz, 2H), 7.48-7.41 (m, 2H), 7.31– 7.23 (m, 3H), 6.94 (d, *J*=7.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 138.7, 135.2, 128.7, 127.8, 125.6, 124.0, 114.8, 55.4.

2-Acetyl-4-trifluoromethylphenylphenylsulfide (3z):

A mixture of 1-(2-chloro-5-(trifluoromethyl)phenyl) ethanone (222 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 10/1) to give the title compound 3z (228 mg, 77%) as a yellow oil; [Found: C, 60.84; H, 3.71. $C_{15}H_{11}F_3OS$ requires C, 60.80; H, 3.74%]; R*f* = 0.3 (hexane/ethyl acetate = 10/1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 6.1 Hz, 1H), 7.74-7.68 (m, 2H), 7.53-7.45 (m, 4H), 6.71 (d, *J*=8.3 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 147.4, 134.6, 133.2, 131.2, 130.8, 130.3, 129.2, 127.6, 126.7, 125.3, 123.4, 28.0.

2-Acetyl-4-trifluoromethylphenyl4-methoxyphenylsulfide (3Aa):

A mixture of 1-(2-chloro-5-(trifluoromethyl)phenyl) ethanone (222 mg, 1 mmol), *p*-thiocresol (124 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography

(hexane/ethyl acetate = 10/1) to give the title compound 3Aa (235 mg, 72%) as a white solid; mp 76-78 ^{o}C; [Found: C, 58.81; H, 4.01. $C_{16}H_{13}F_3O_2S$ requires C, 58.89; H, 4.02%]; R*f* = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.46-7.38 (m, 3H), 7.05 (d, *J*=8.4 Hz, 2H), 6.90 (d, *J*=8.4 Hz, 1H), 3.89 (s, 1H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 161.8, 147.7, 136.9, 131.6, 128.8, 127.5, 126.6, 124.4, 121.7, 120.9, 115.8, 54.8, 28.0.

4-(Phenylthio)benzoic acid (3Ab):

A mixture of 4-chloro-benzoic acid (156 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 4/1) to give the title compound 3Ab (204 mg, 89%) as a yellow solid; mp 173-174 ^{o}C; [Found: C, 67.81; H, 4.31. $C_{13}H_{10}O_2S$ requires C, 67.80; H, 4.38%]; R*f* = 0.2 (hexane/ethyl acetate = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J*=8.4 Hz, 2H), 7.51-7.44 (m, 2H), 7.36– 7.29 (m, 3H), 7.17 (d, *J*=8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 146.0, 134.5, 131.5, 130.8, 129.2, 128.6, 127.0, 126.4.

2-Phenylsulfanylbenzoic acid methyl ester (3Ac):

A mixture of methyl-2-chloro-benzotae (170 mg, 1 mmol), thiophenol (110 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^{o}C for 2 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 20/1) to give the title compound 3Ac (185 mg, 76%) as a white solid; mp 46-48 ^{o}C; [Found: C, 68.81; H, 4.91. $C_{14}H_{12}O_2S$ requires C, 68.83; H, 4.95%]; R*f* = 0.4 (hexane/ethyl acetate = 20/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.92 (m, 1H), 7.68-7.59 (m, 2H), 7.44-7.37 (m, 3H), 7.23-7.15 (m, 1H), 7.06 (t, *J*=7.3 Hz, 1H), 6.85 (d, *J*=8.2 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 166.6, 143.1, 134.8, 134.4, 133.3, 132.8, 128.4, 126.3, 125.1, 124.7, 123.2, 52.8.

3-(4-tert-Butylphenyl)sulfanylphenol (3Ad):

A mixture of 3-chlorophenol (128 mg, 1 mmol), 4-*tert*-butylthiophenol (166 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 10/1) to give the title compound 3Ad (168 mg, 65%) as a colorless oil; [Found: C, 74.41; H, 7.01. $C_{16}H_{18}OS$ requires C, 74.38; H, 7.02%]; R*f* = 0.2 (hexane/ethyl acetate = 10/1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.27 (m, 2H), 7.12 (t, *J*=8.1 Hz, 1H), 7.02 (t, *J*=8.1 Hz, 1H), 6.88-6.79 (m, 1H), 6.69-6.65 (m, 1H), 6.52-6.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 132.5, 131.6, 131.2, 129.4, 128.7, 127.4, 117.7, 114.2, 112.3, 34.5, 31.4.

4-(3,5-Dimethylphenyl)sulfanylphenol (3Ae):

A mixture of 5-chloro-1,3-xylene (140 mg, 1 mmol), 4-mercaptoophenol (126 mg, 1 mmol), NaOH (60 mg, 1.5 mmol) and 5 mol % NiL_2 (38 mg) in DMF was stirred at 70 ^oC for 3 h. The reaction mixture was filtered and the solvent evaporated in vacuo to give the crude product, which was purified by column chromatography (hexane/ethyl acetate = 10/1) to give the title compound 3Ae (156 mg, 68%) as a colorless oil; [Found: C, 73.06; H, 6.11. $C_{14}H_{14}OS$ requires C, 73.01; H, 6.13 %]; R*f* = 0.3 (hexane/ethyl acetate = 10/1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.40 (m, 2H), 6.87-6.79 (m, 5H), 4.81 (s, 1H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 138.1, 134.8, 133.6, 127.8, 126.7, 116.7, 21.3.

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Supplementary data:

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org.....

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SUPPORTING INFORMATION

Nickel-Schiff base complex catalyzed C-S cross-coupling of thiols with organic chlorides

Prasanta Gogoi,[a] Sukanya Hazarika,[a] Manas J. Sarma,[b] Kuladip Sarma,[a] and Pranjit Barman[a]*

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[b]*Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India*

X-ray crystal structure for 3o: (The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and has the deposition number **CCDC 1018005**)

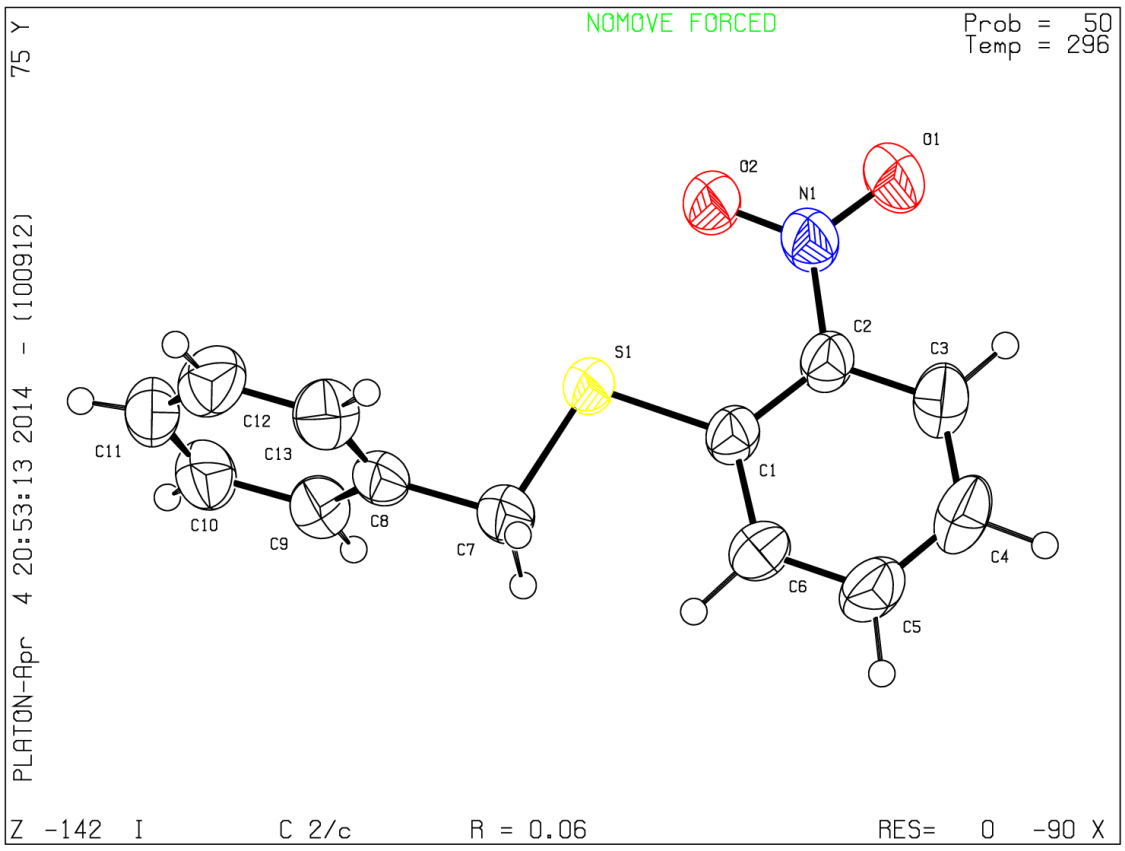

Figure S1. Thermal ellipsoidal plot of compound **3o** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=18.074(2) b=7.8223(10) c=18.038(2)
alpha=90 beta=109.641(8) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	2401.8(5)	2401.9(5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	?
Moiety formula	C13 H11 N O2 S	C13 H11 N O2 S
Sum formula	C13 H11 N O2 S	C13 H11 N O2 S
Mr	245.30	245.29
Dx,g cm-3	1.357	1.357
Z	8	8
Mu (mm-1)	0.257	0.258
F000	1024.0	1256.0
F000'	1025.42	
h,k,lmax	23,10,23	23,10,23
Nref	2935	2869
Tmin,Tmax	0.931,0.952	0.930,0.951
Tmin'	0.881	

Correction method= PSI-SCAN

Data completeness= 0.978 Theta(max)= 28.120

R(reflections)= 0.0607(1993) wR2(reflections)= 0.1818(2869)

S = 1.177 Npar= Npar = 199

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low .......      0.978 Note
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT125_ALERT_4_C No '_symmetry_space_group_name_Hall' Given .....     Please Do !
PLAT351_ALERT_3_C Long    C-H (X0.96,N1.08A) C7     -   H7B    ...      1.12 Ang.
```

Alert level G

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PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF     Please Do !
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

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PUBL004_ALERT_1_A  The contact author's name and address are missing,
           _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
```

Alert level G

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PUBL017_ALERT_1_G The _publ_section_references section is missing or
           empty.
```

7 **ALERT level A** = Data missing that is essential or data in wrong format
1 **ALERT level G** = General alerts. Data that may be required is missing

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

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PROBLEM: The contact author's name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
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PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
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_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
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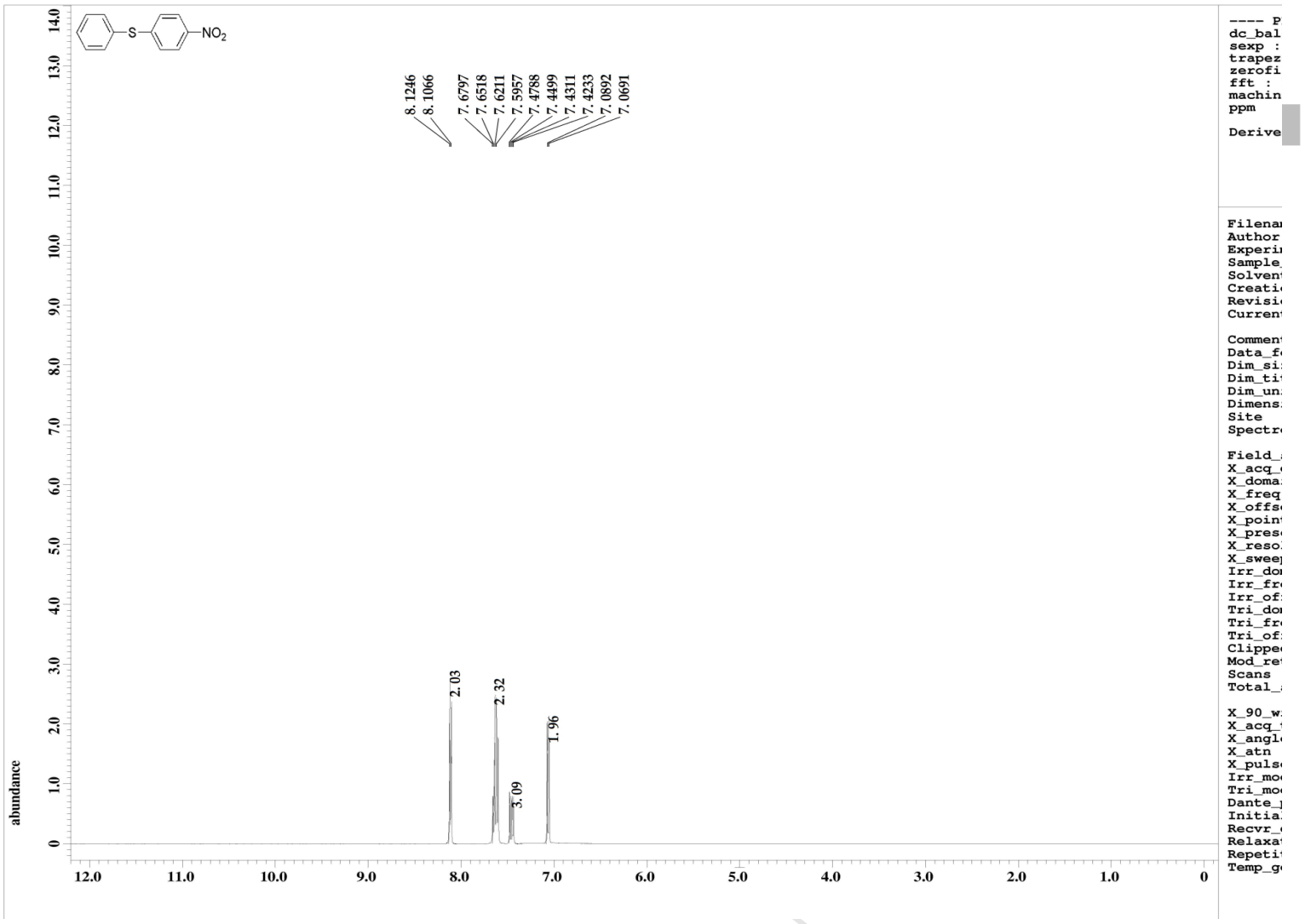
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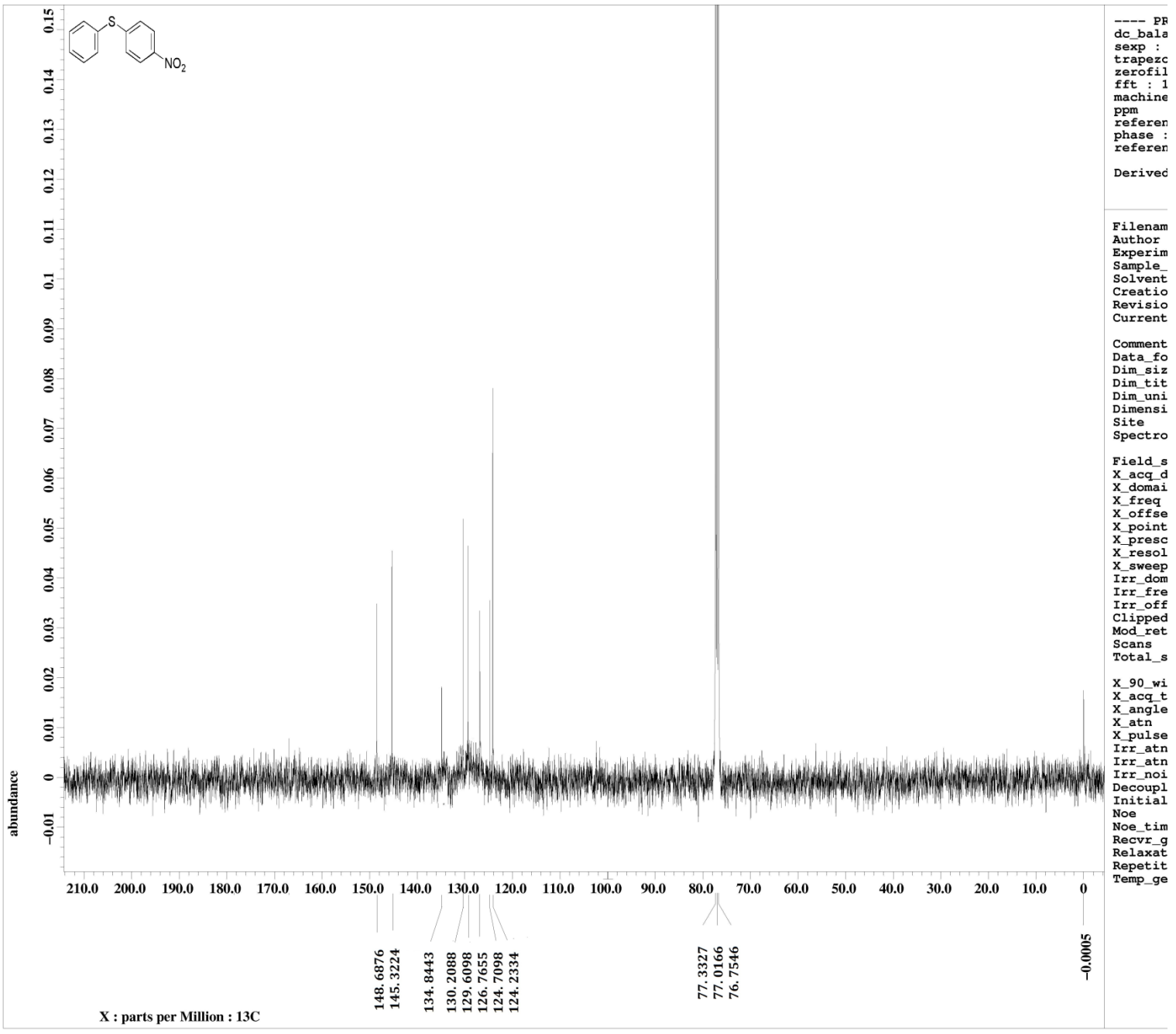
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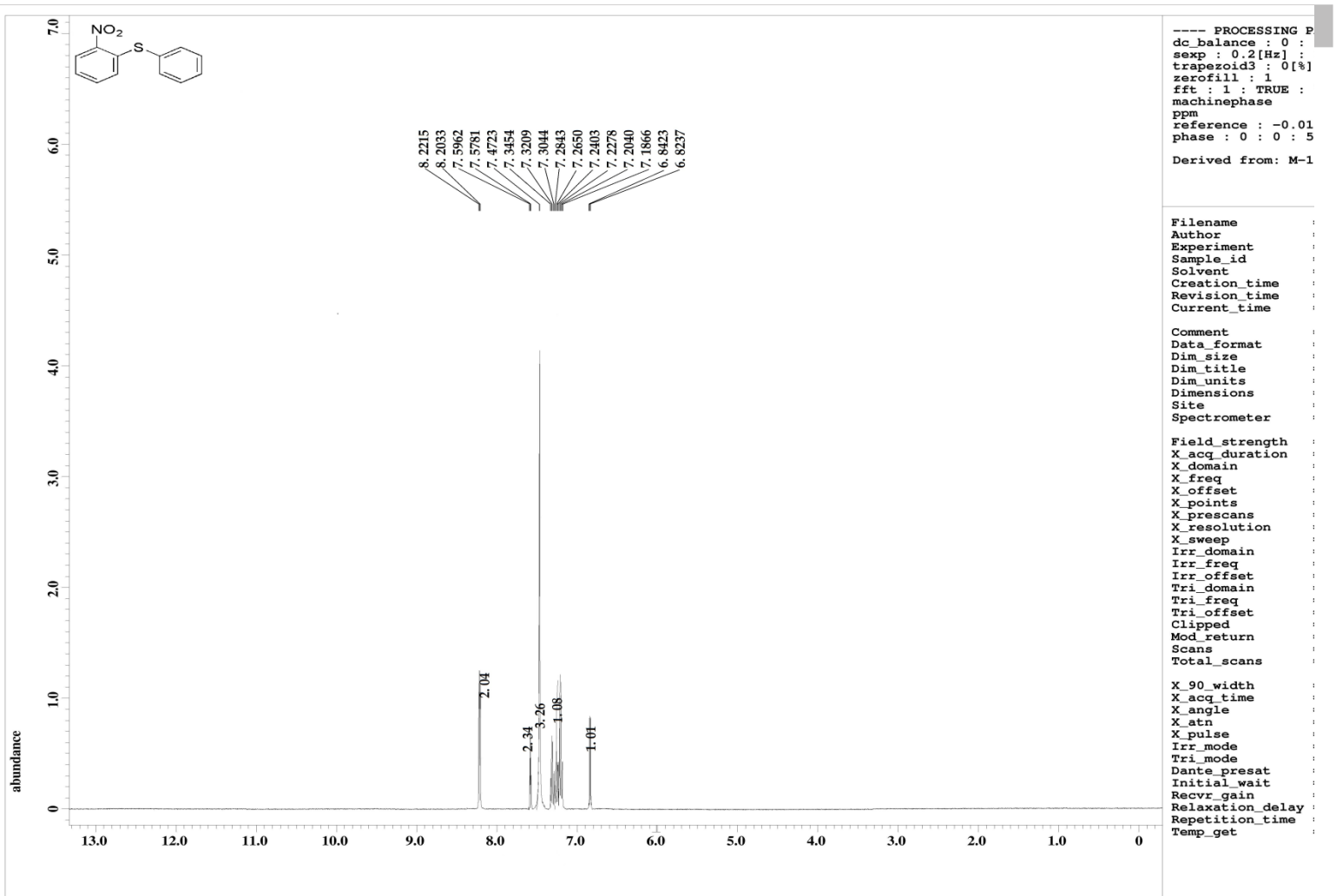
−0.0005
abundance
X : parts per Million : 13C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2.34
3.26
1.08
1.01
abundance
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11.0
10.0
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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fft : 1 : TRUE :
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ppm
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Derived from: M-1
Filename
Author
Experiment
Sample_id
Solvent
Creation_time
Revision_time
Current_time
Comment
Data_format
Dim_size
Dim_title
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Site
Spectrometer
Field_strength
X_acq_duration
X_domain
X_freq
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X_points
X_prescans
X_resolution
X_sweep
Irr_domain
Irr_freq
Irr_offset
Tri_domain
Tri_freq
Tri_offset
Clipped
Mod_return
Scans
Total_scans
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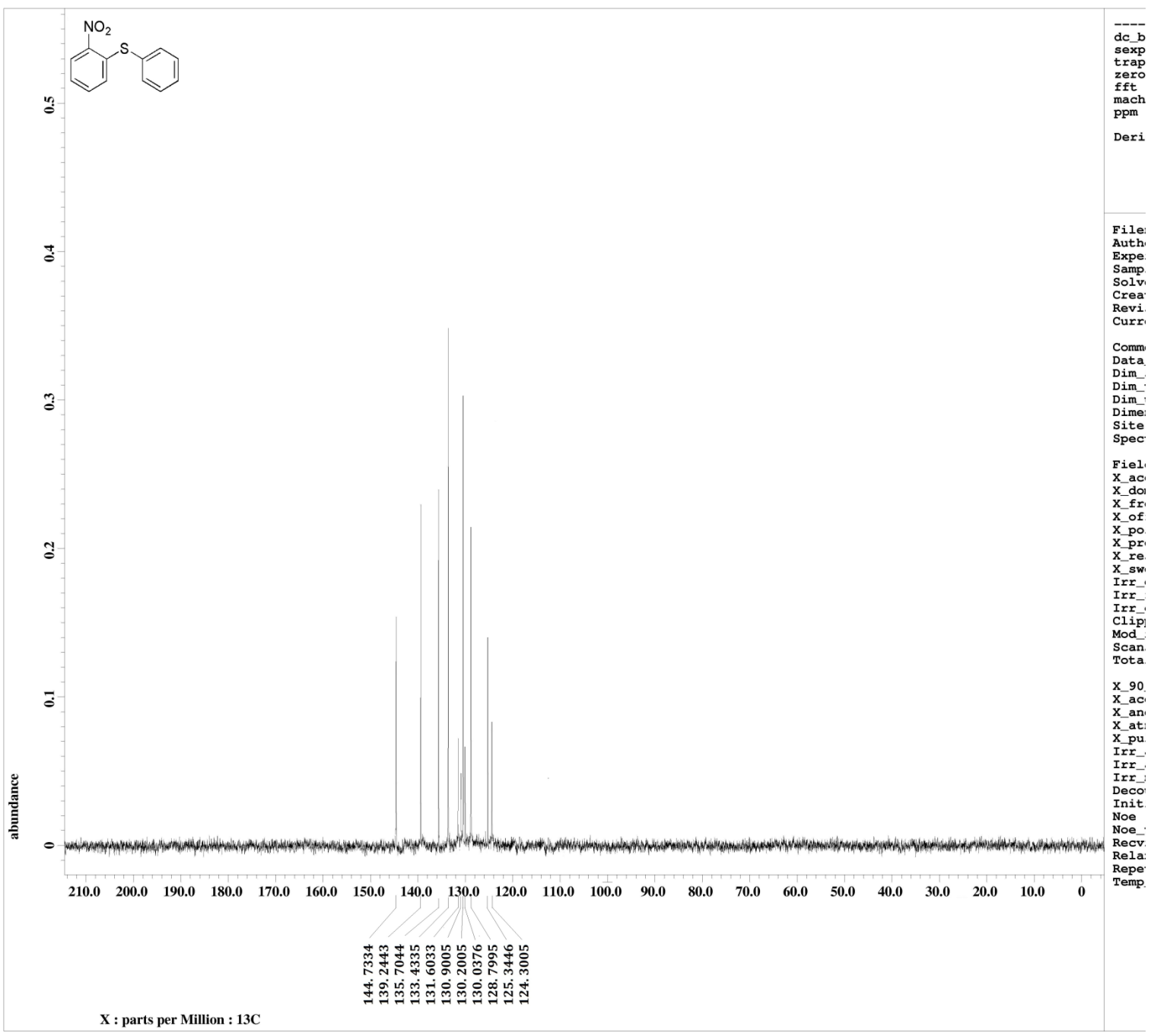
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170.0
160.0
150.0
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110.0
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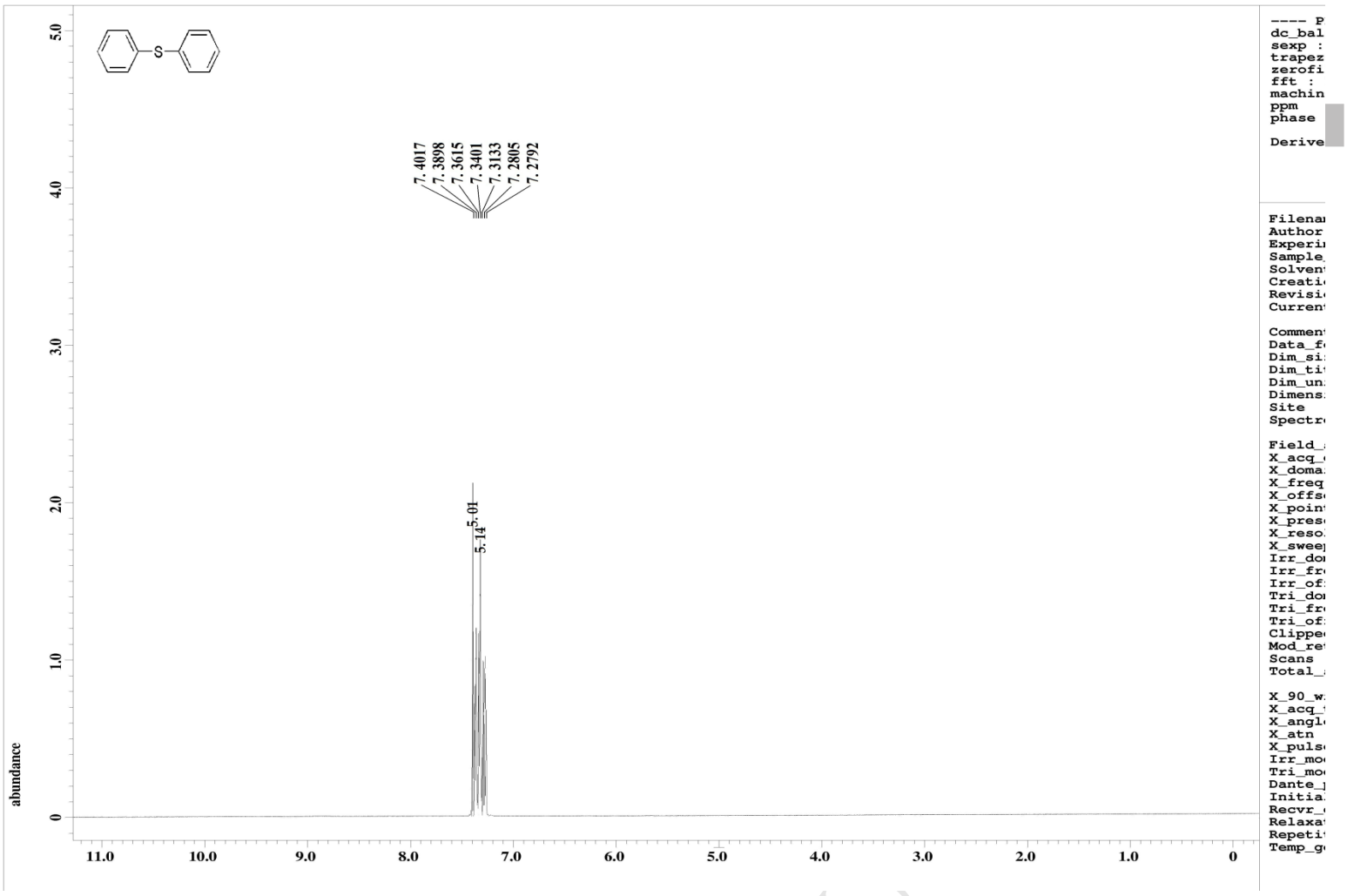
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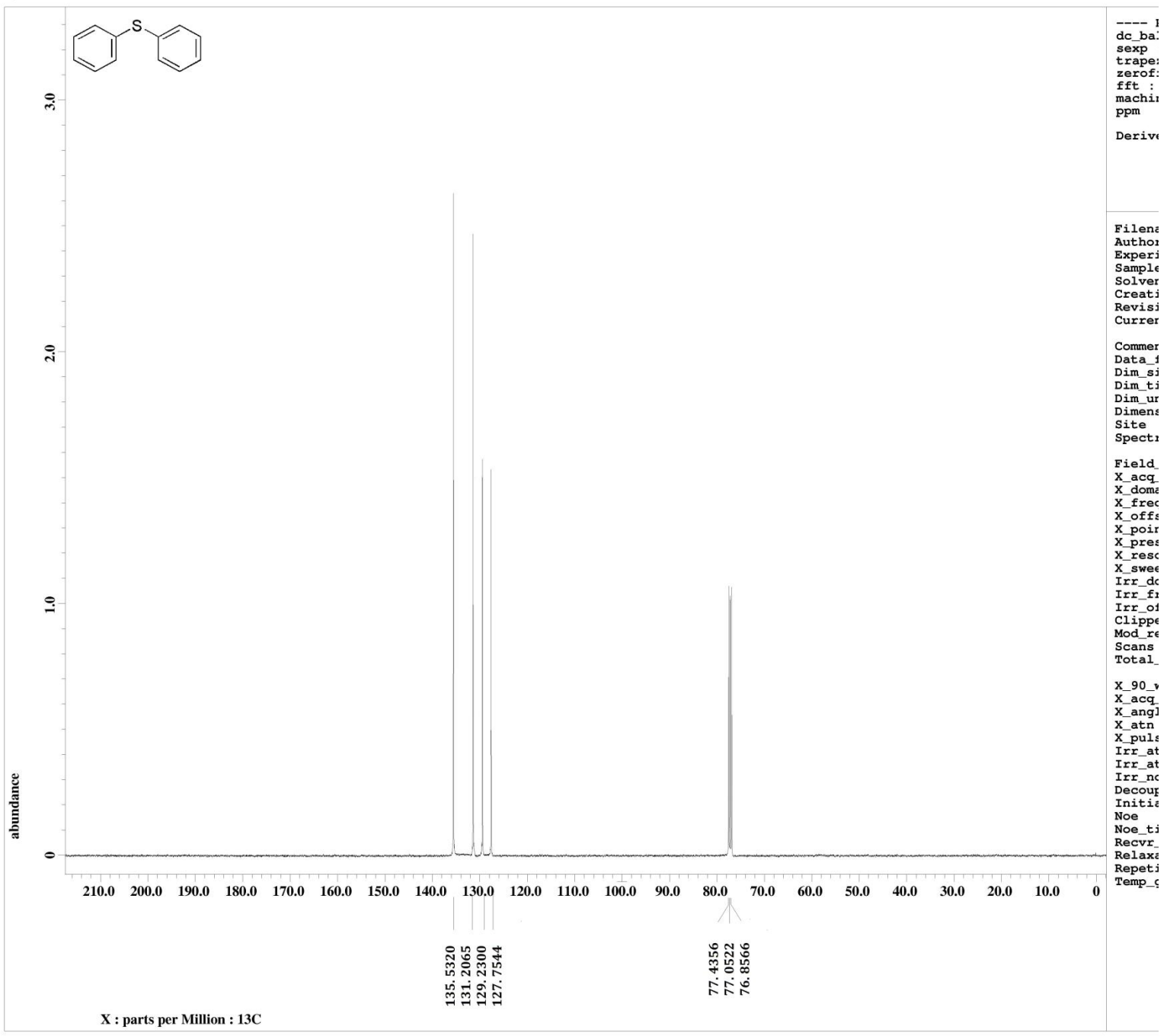
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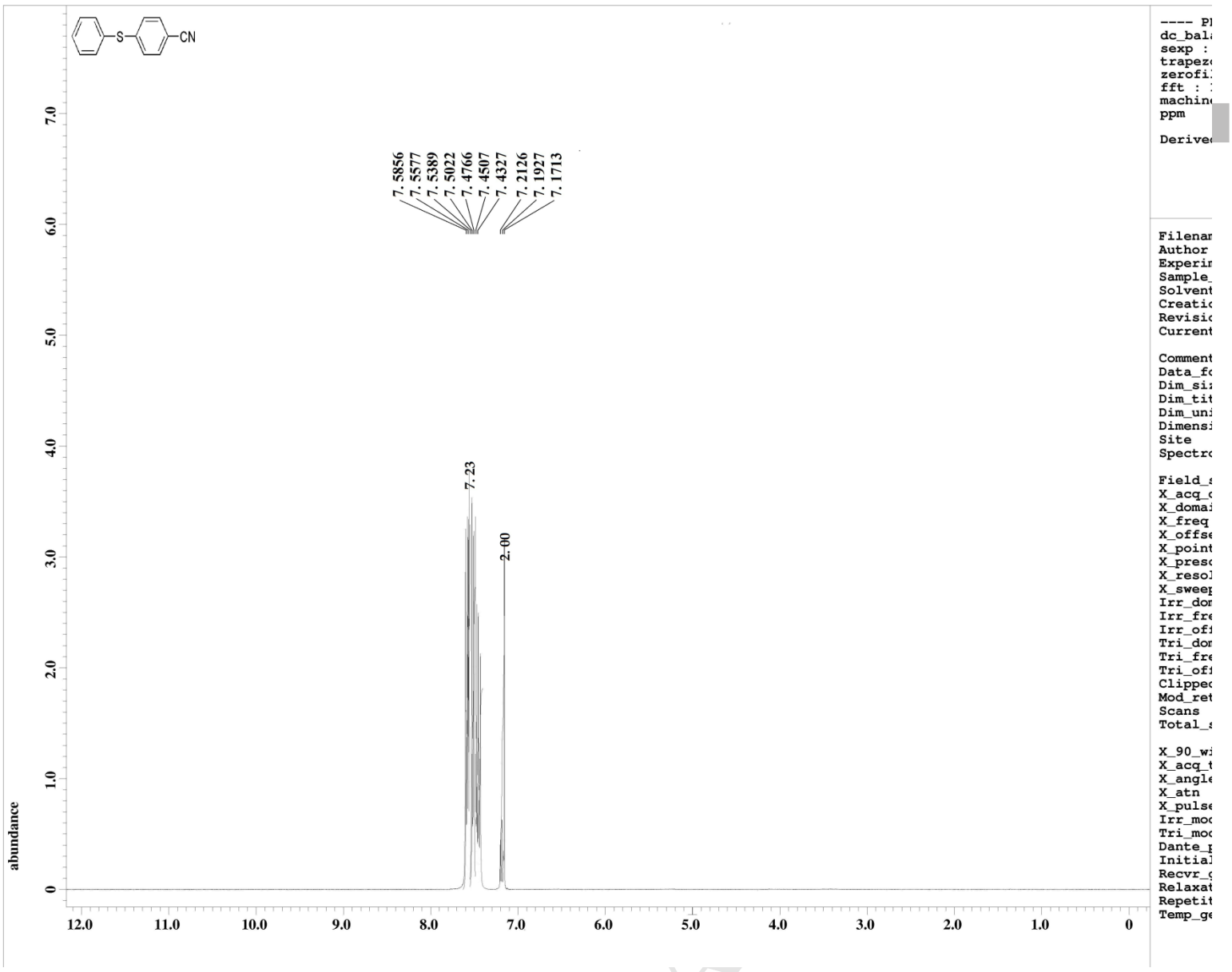
X : parts per Million : 13C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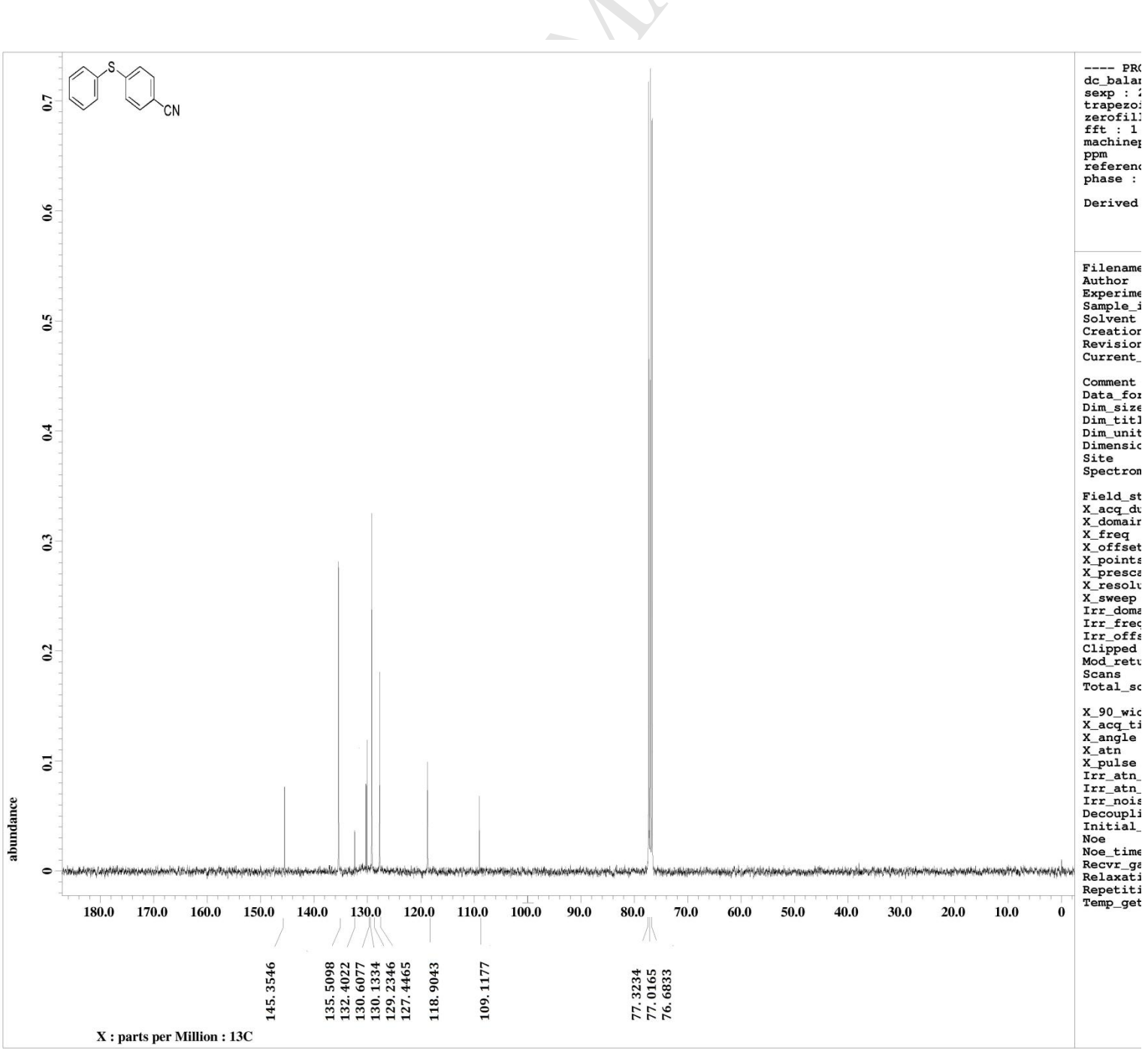
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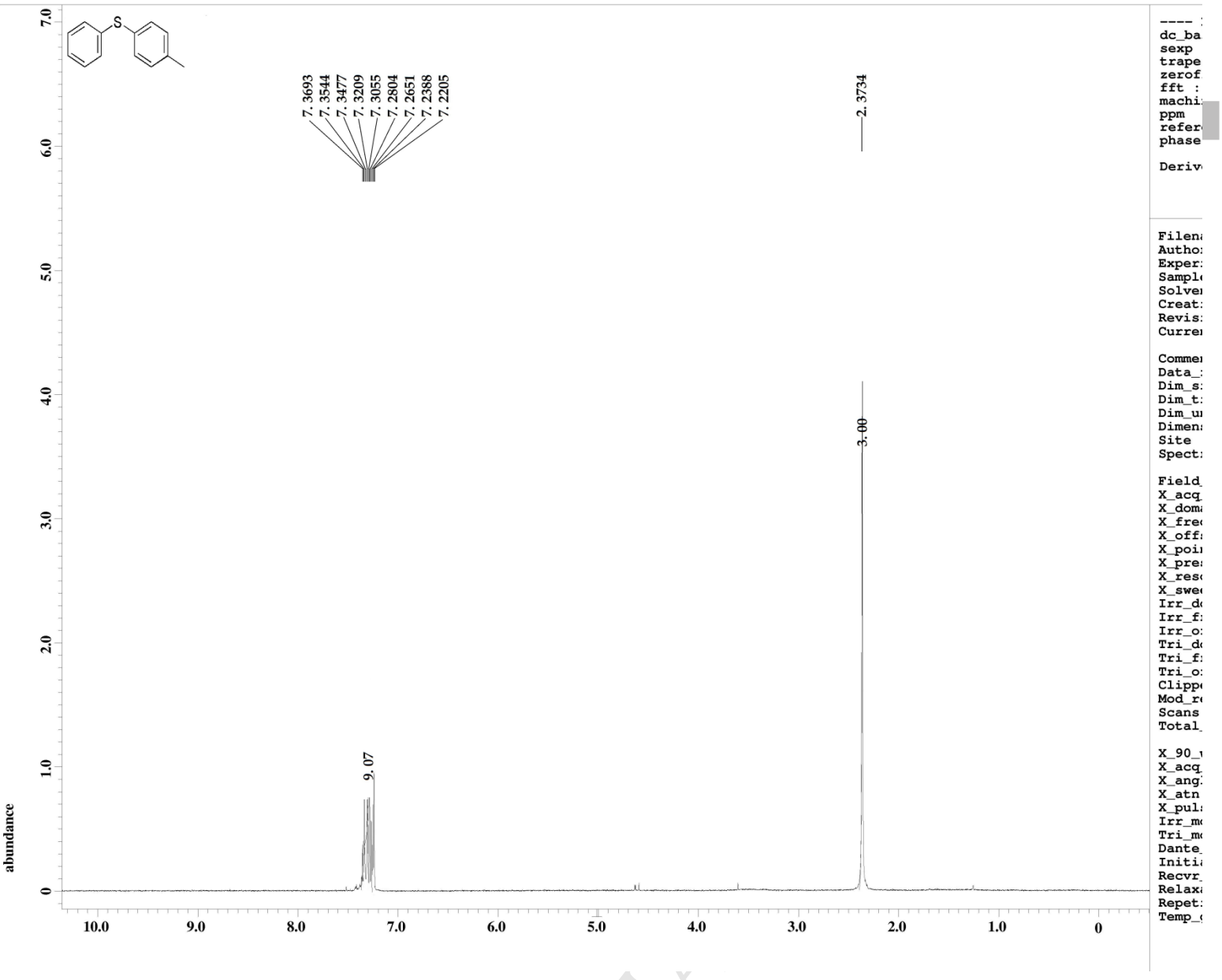
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3.00
9.07
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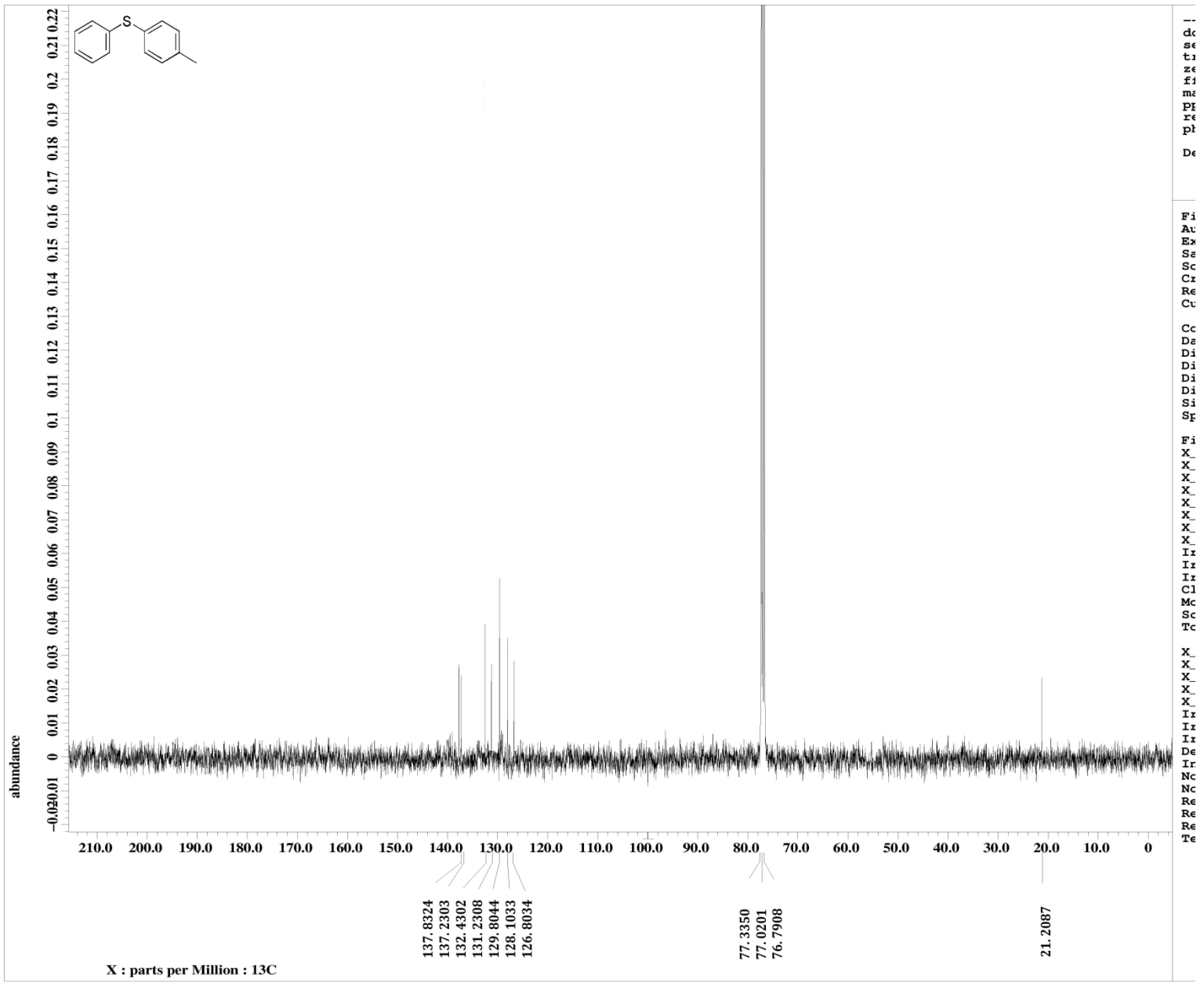
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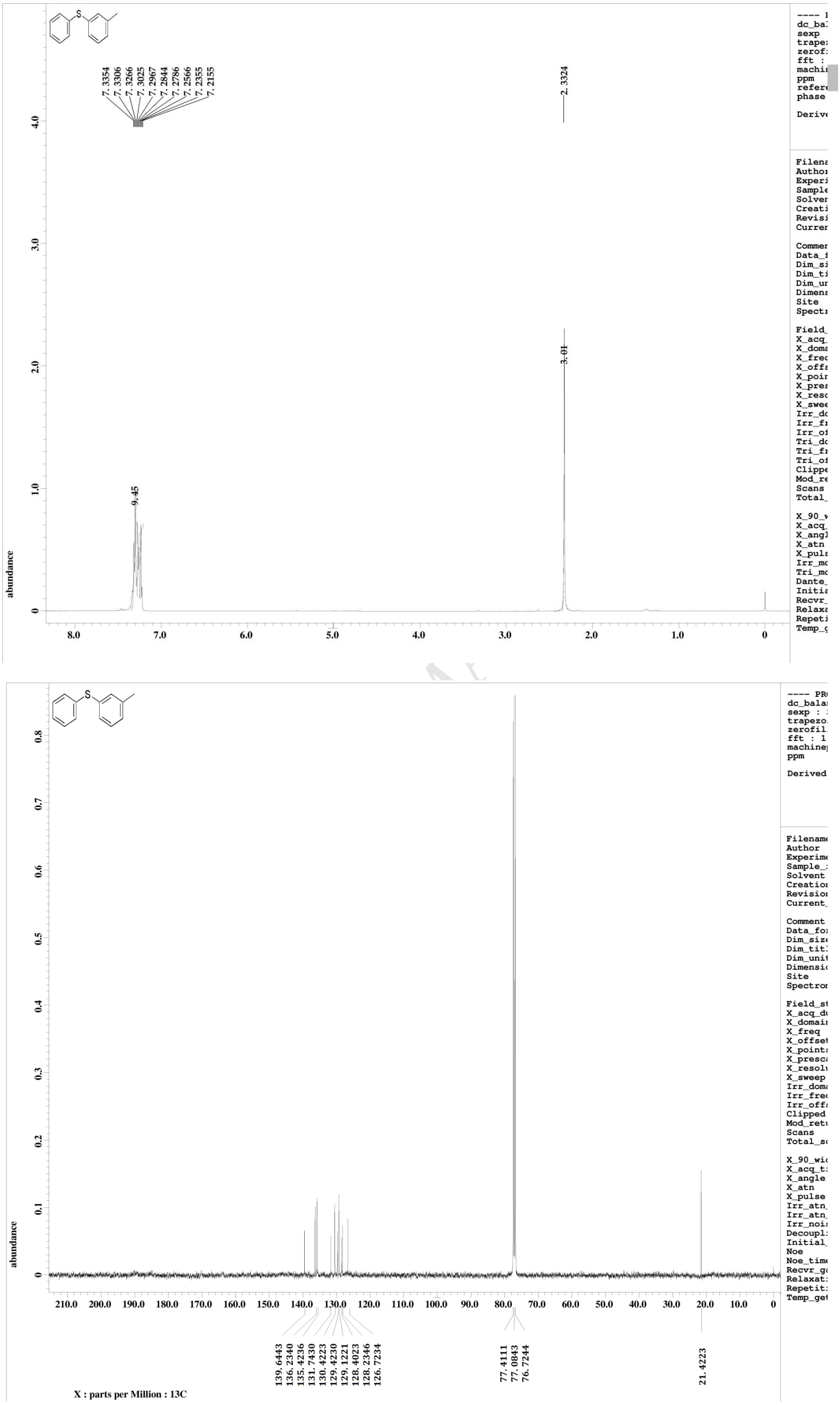
X : parts per Million : 13C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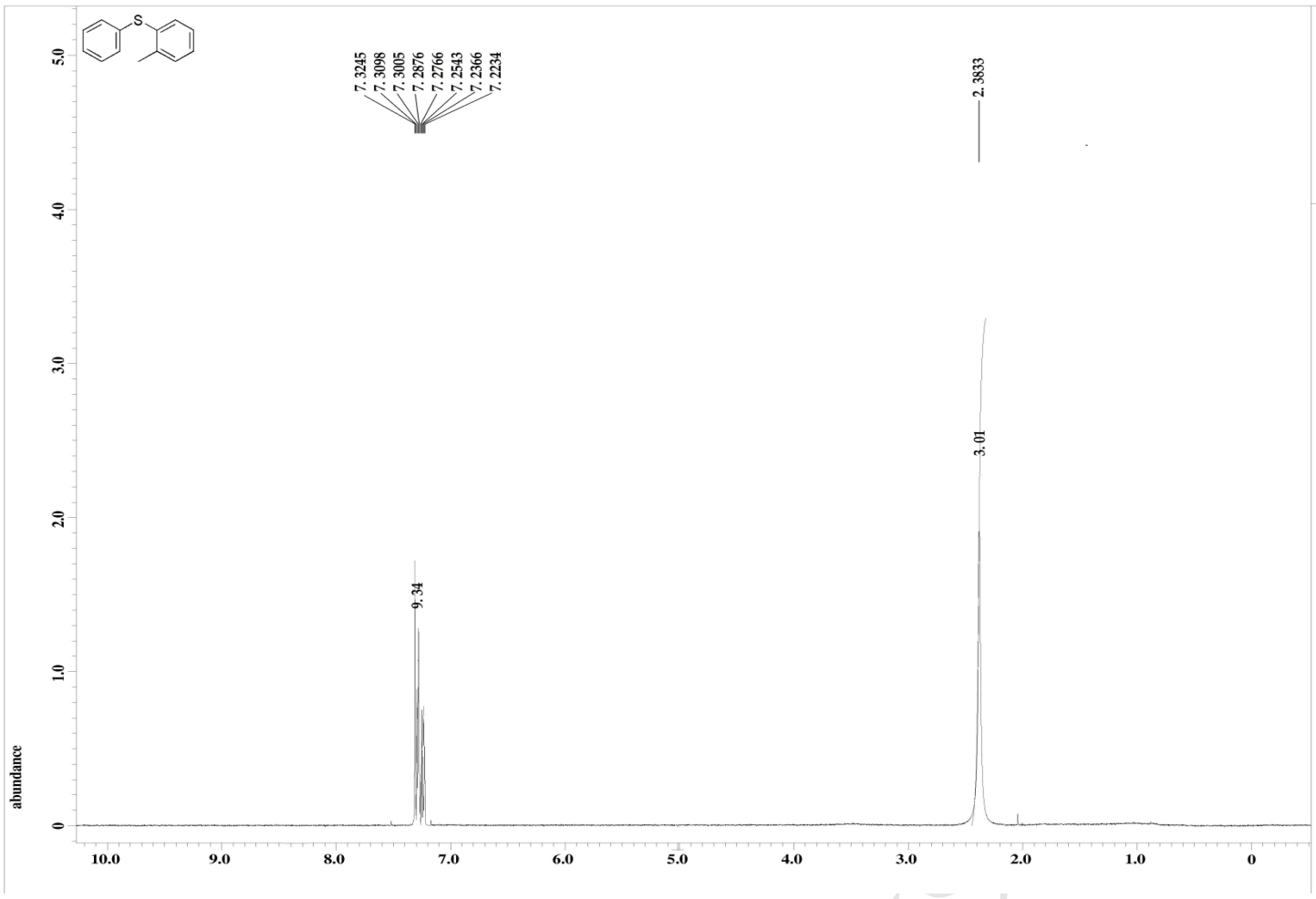
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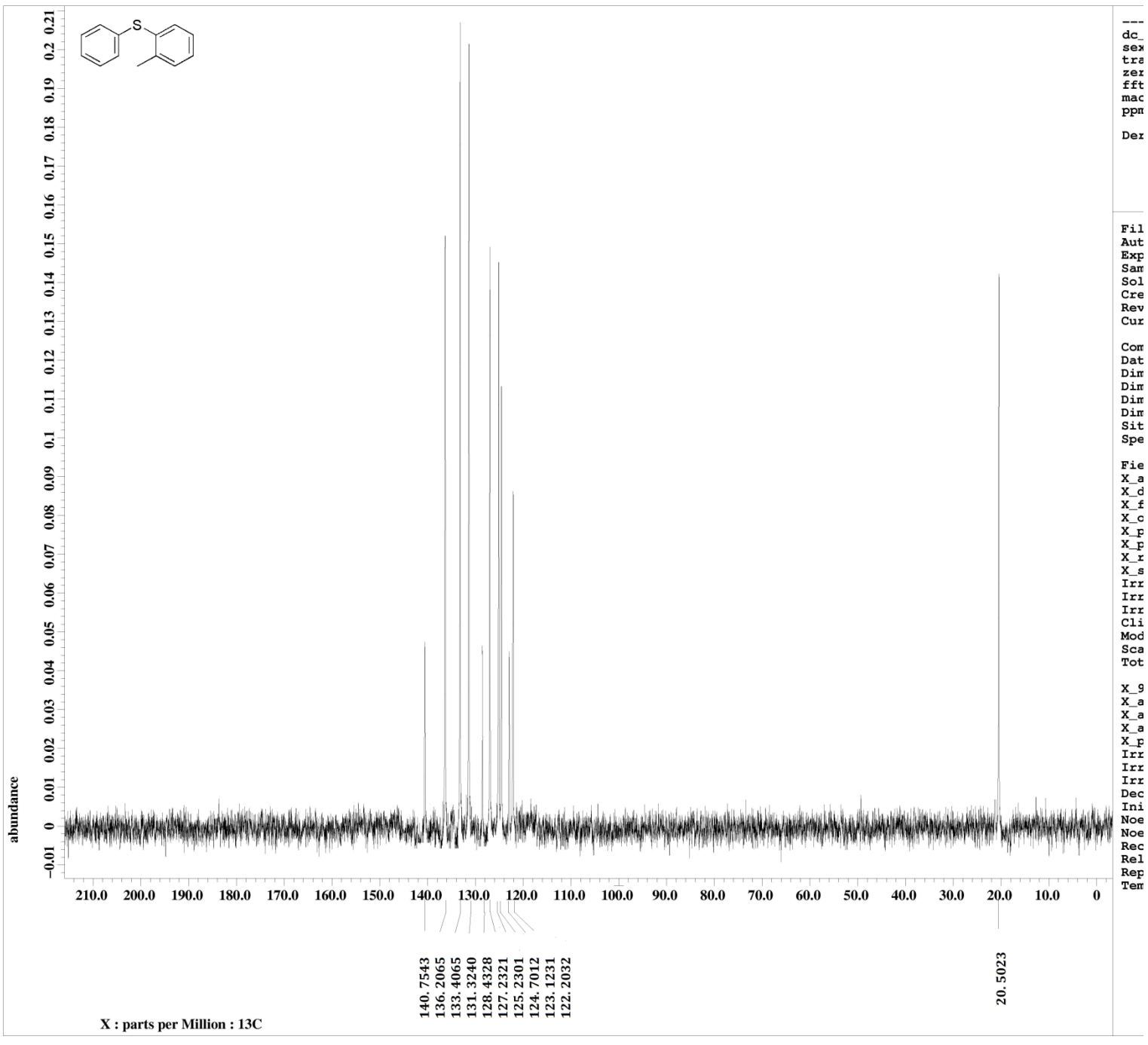
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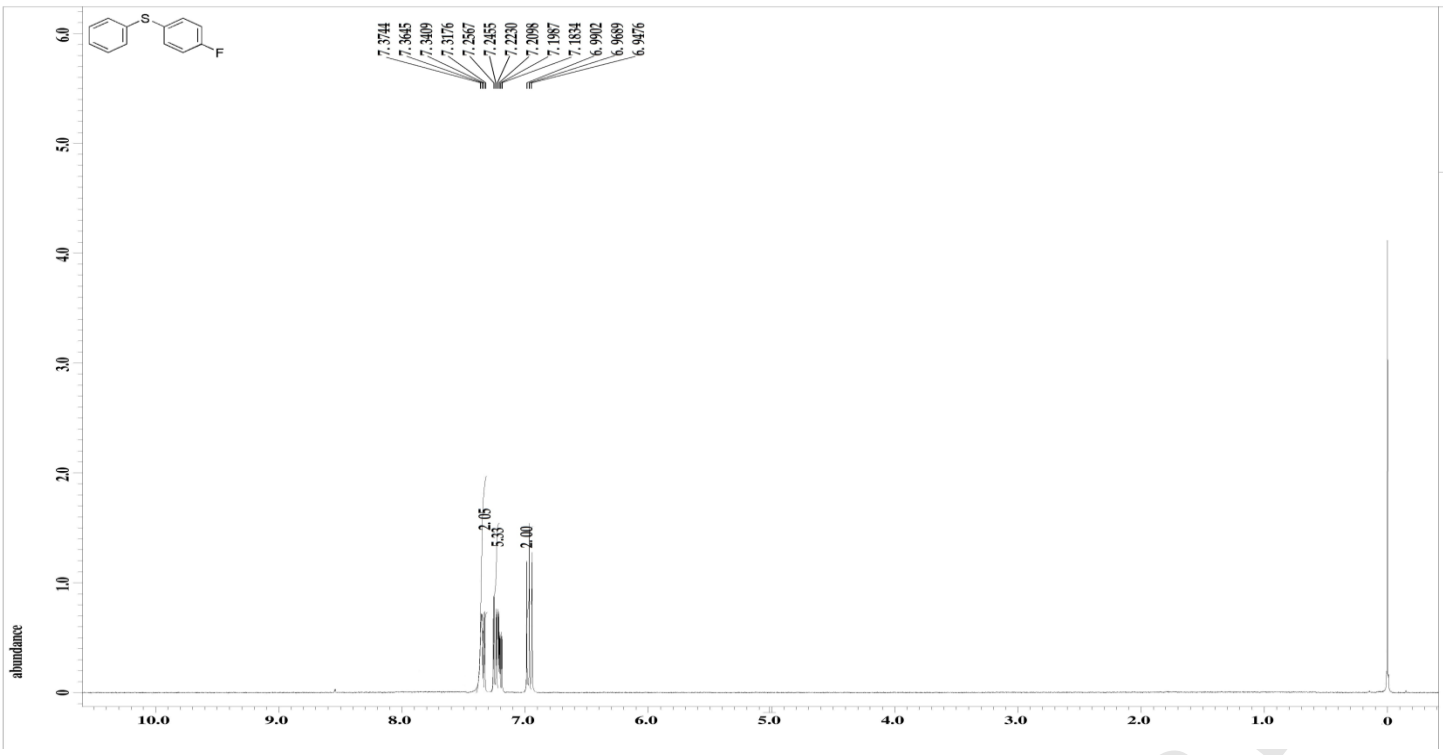
X : parts per Million : 13C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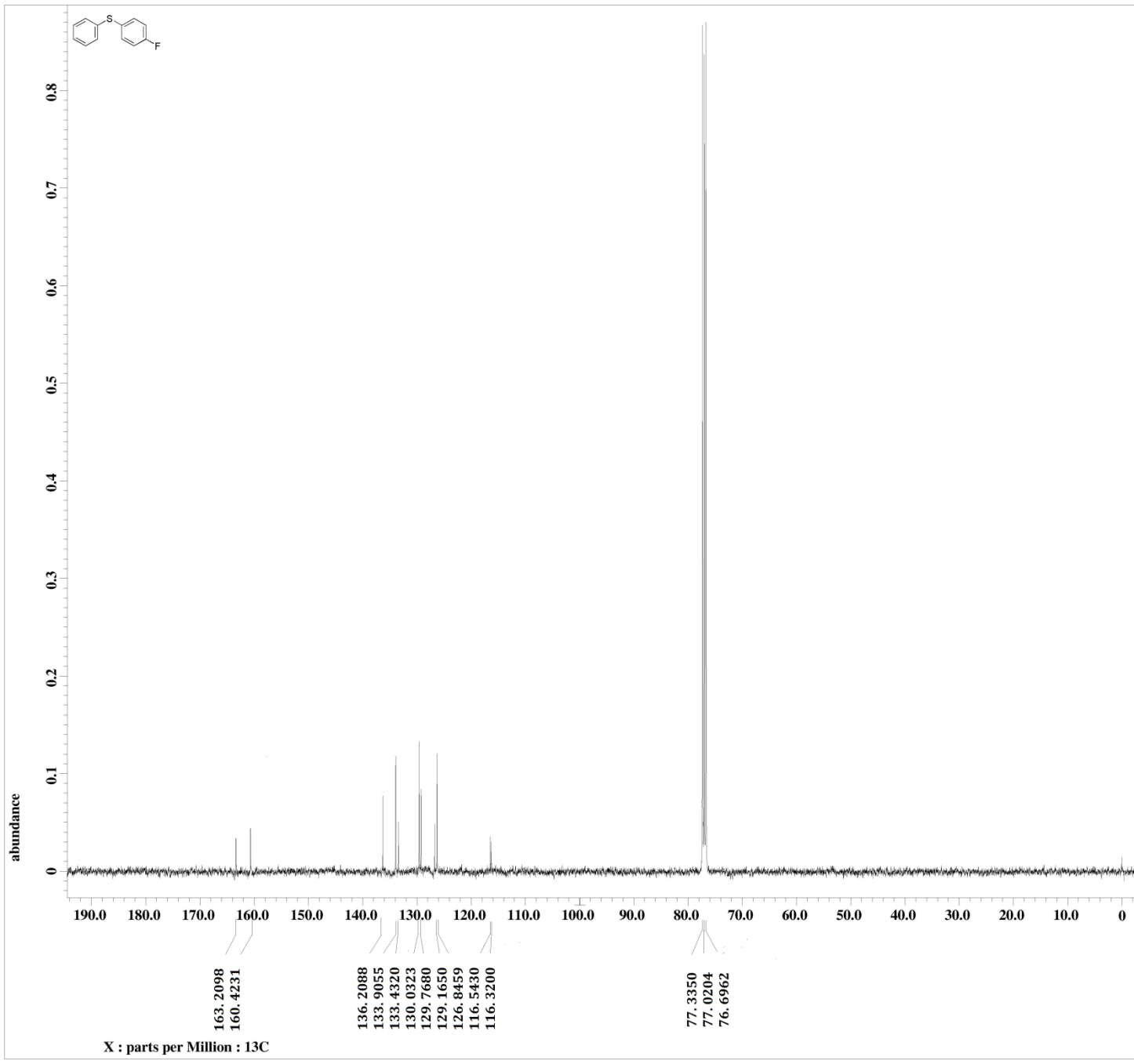
abundance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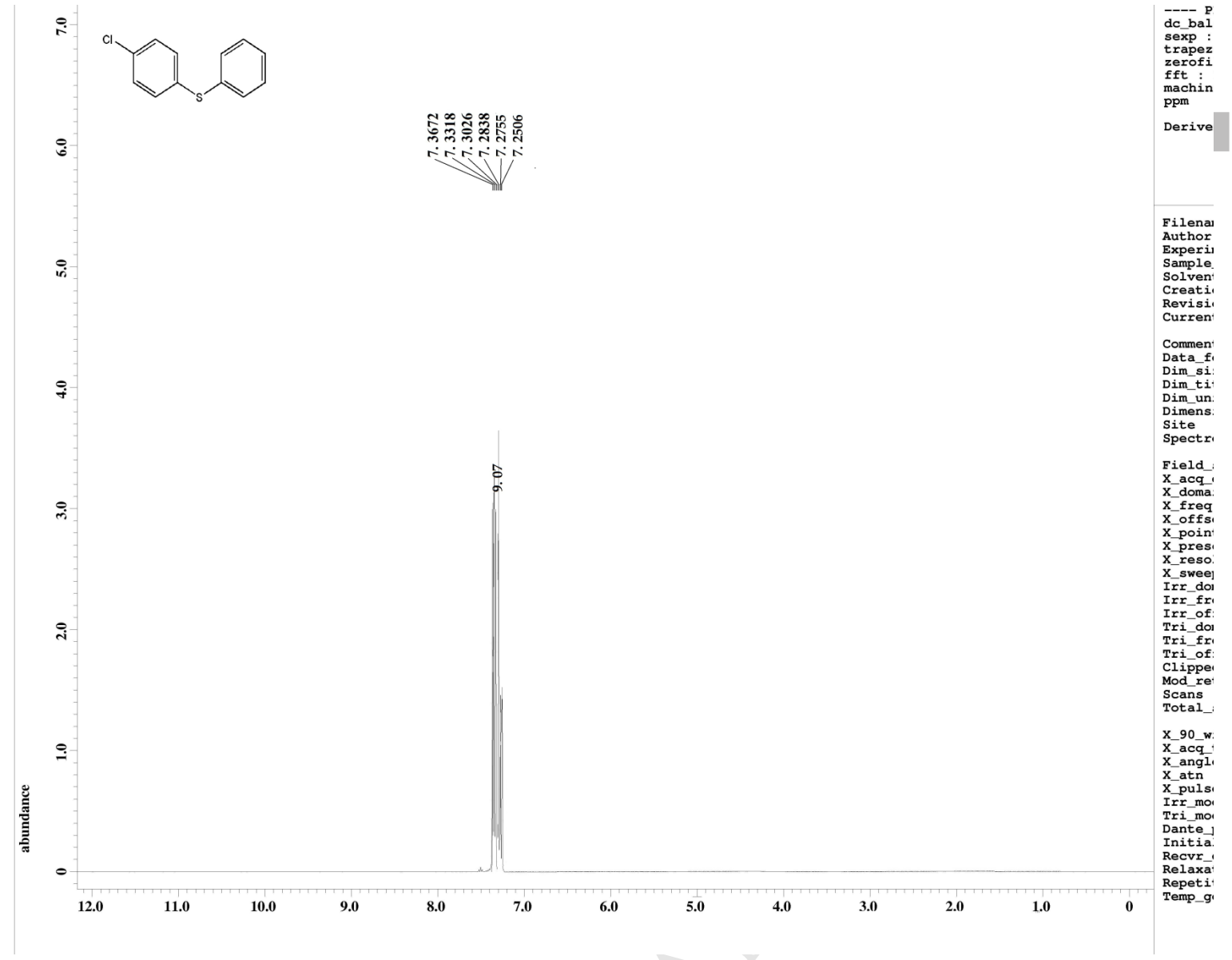
abundance
X : parts per Million : 13C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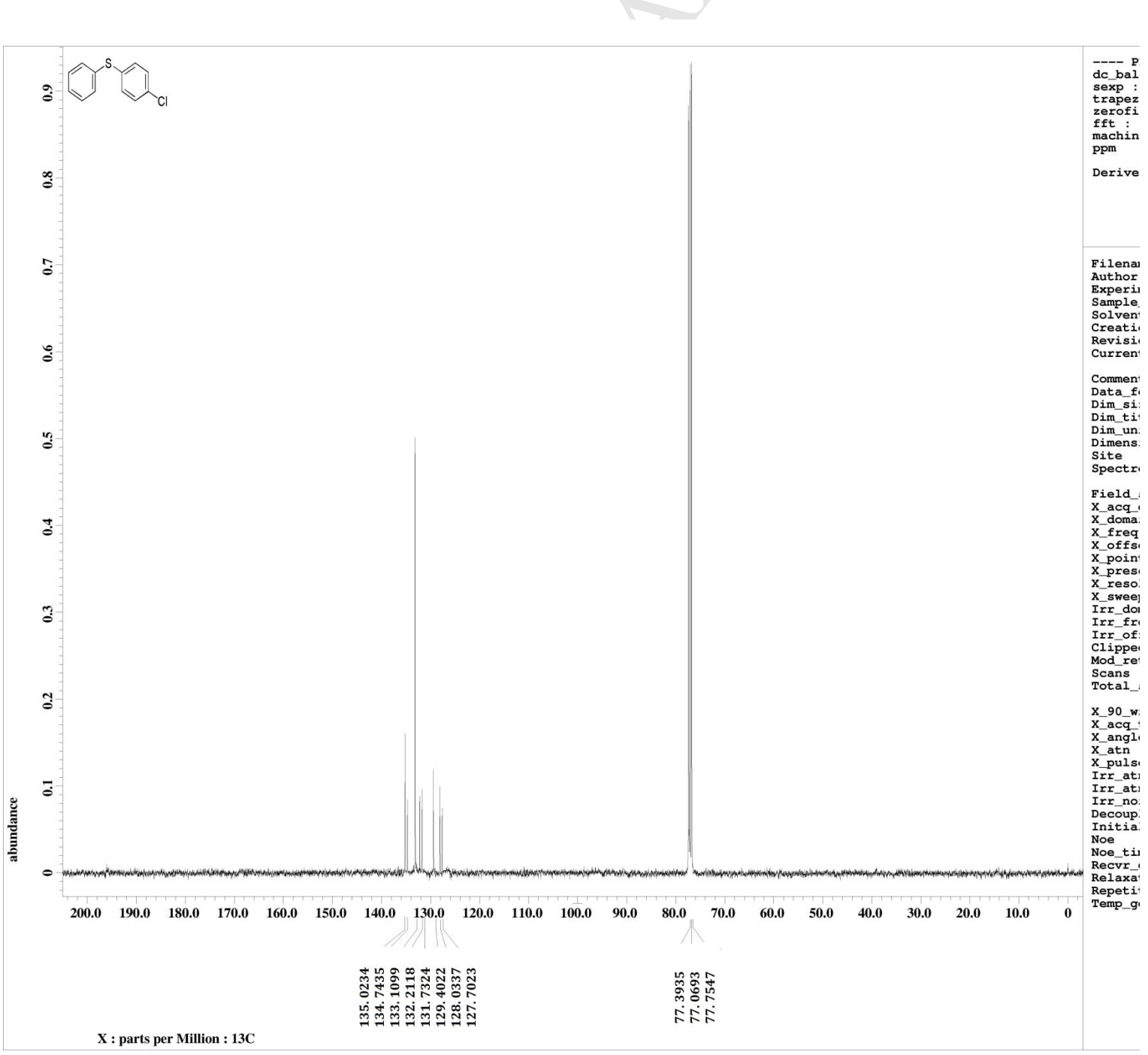
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120.0
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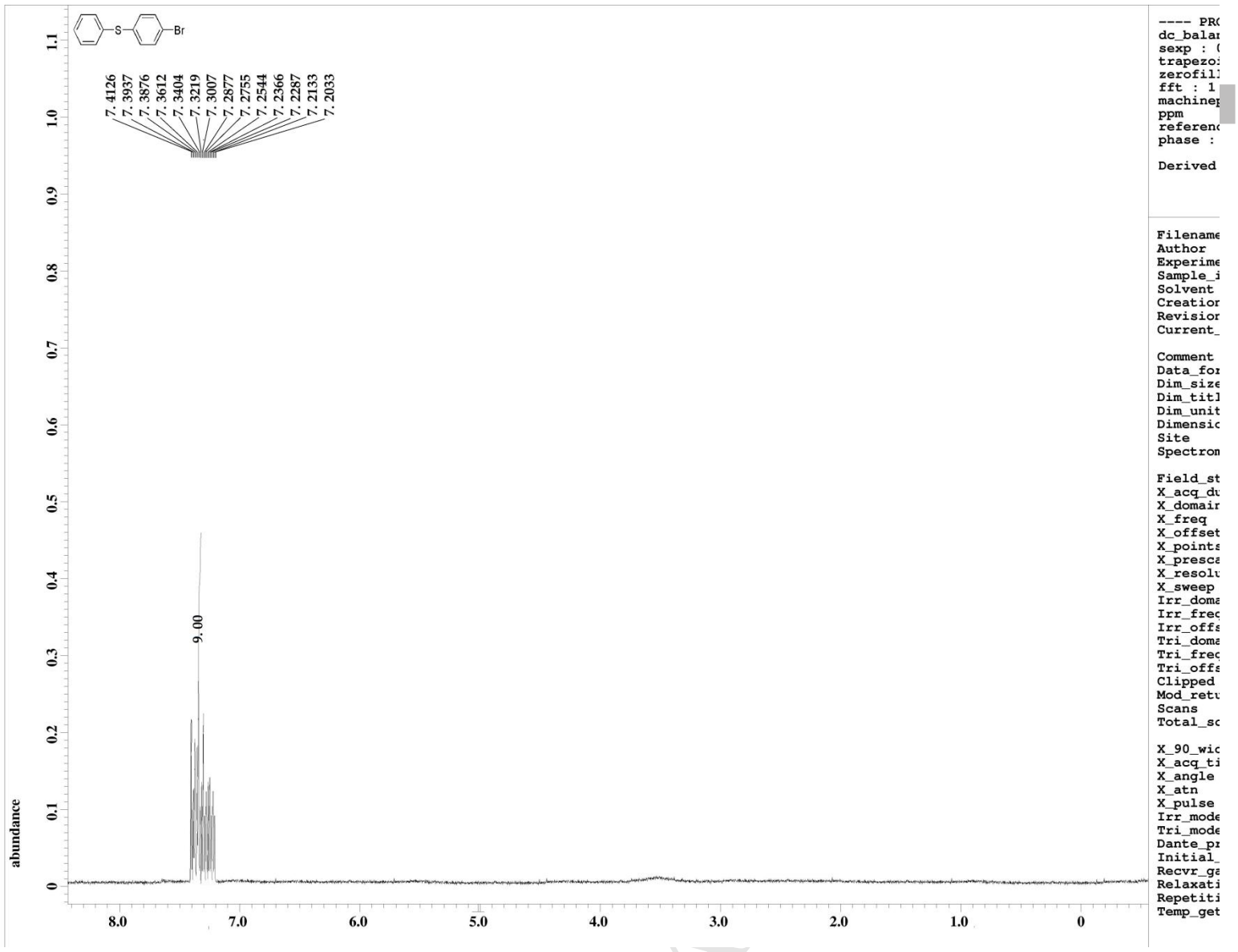
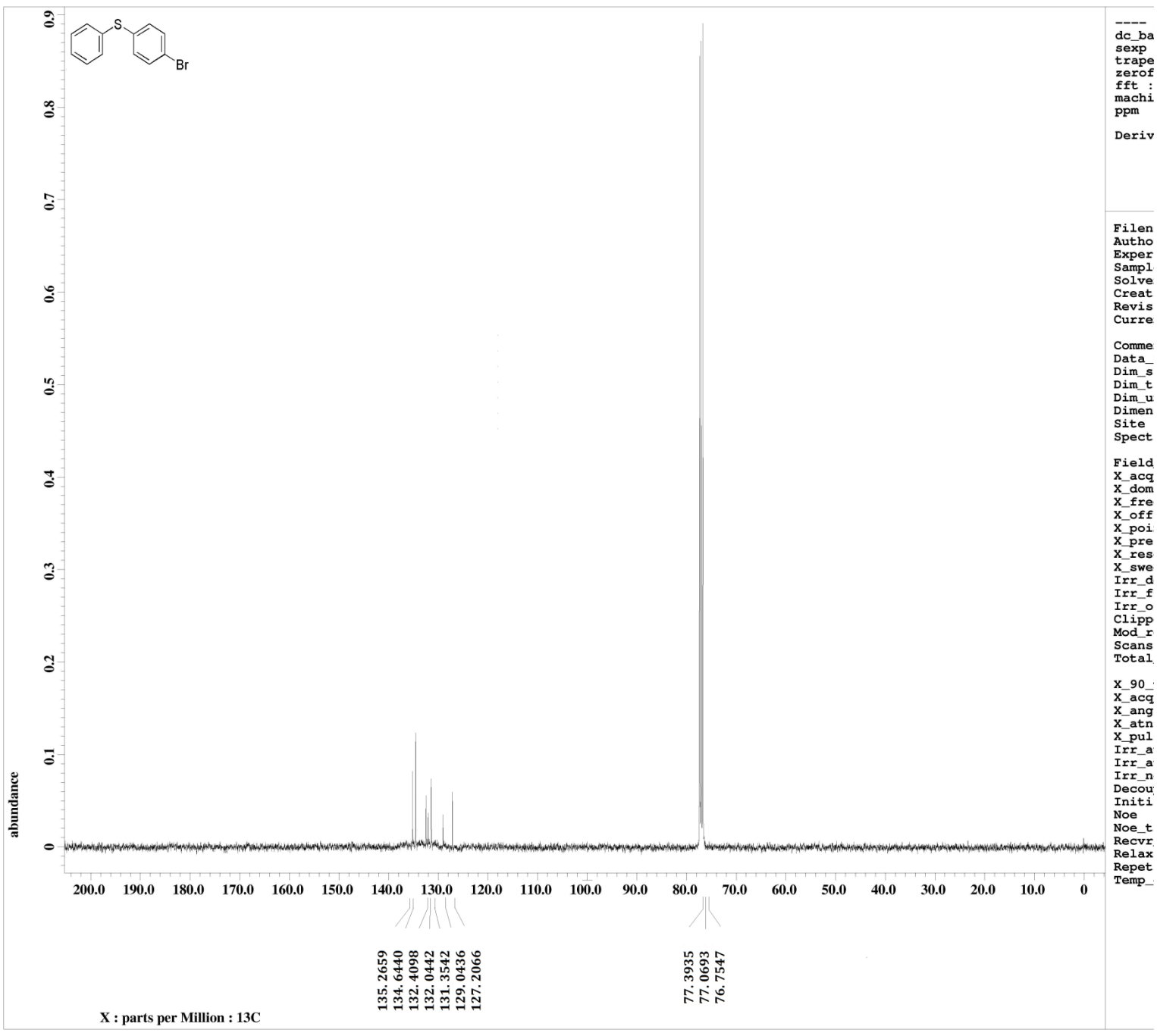
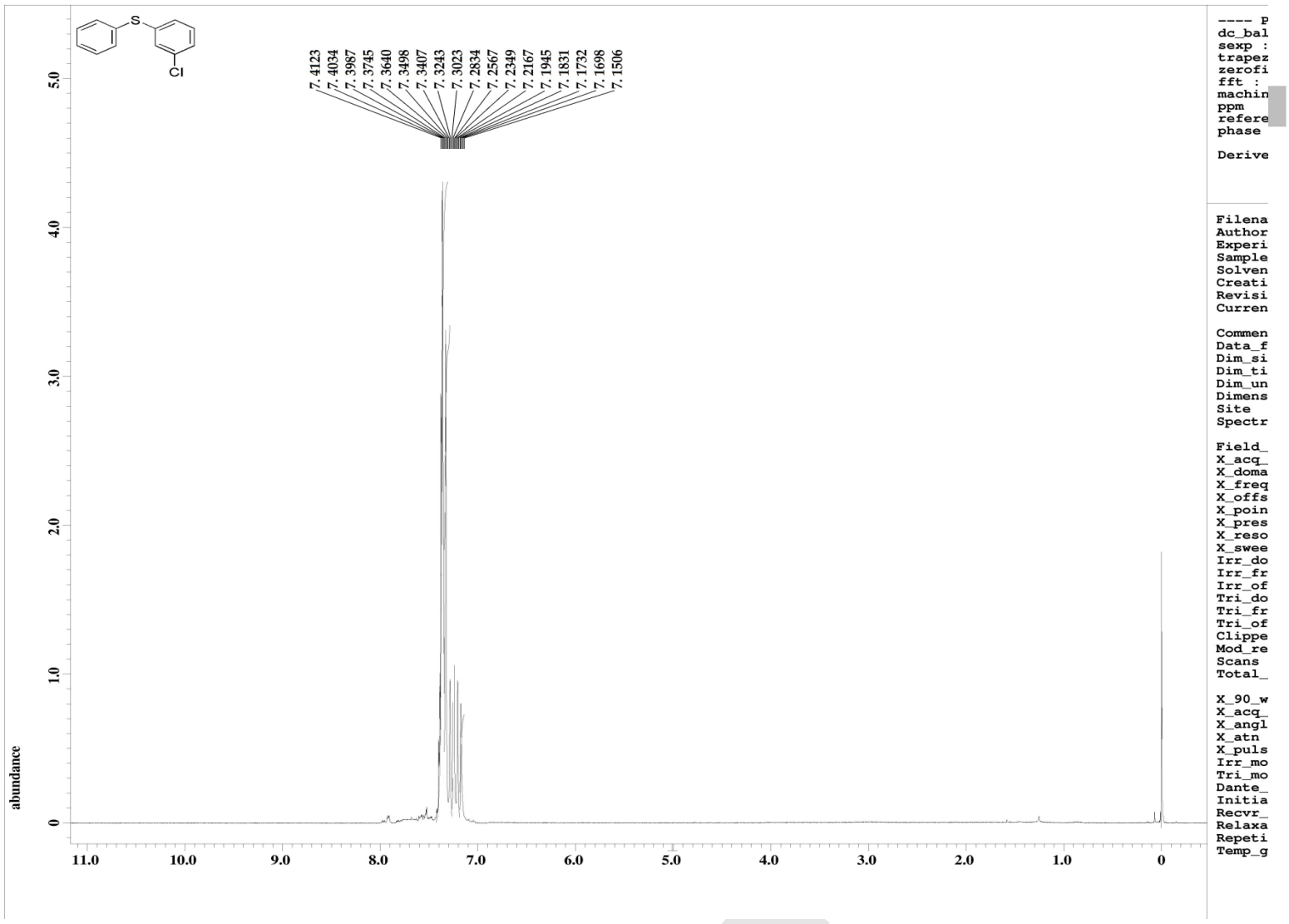
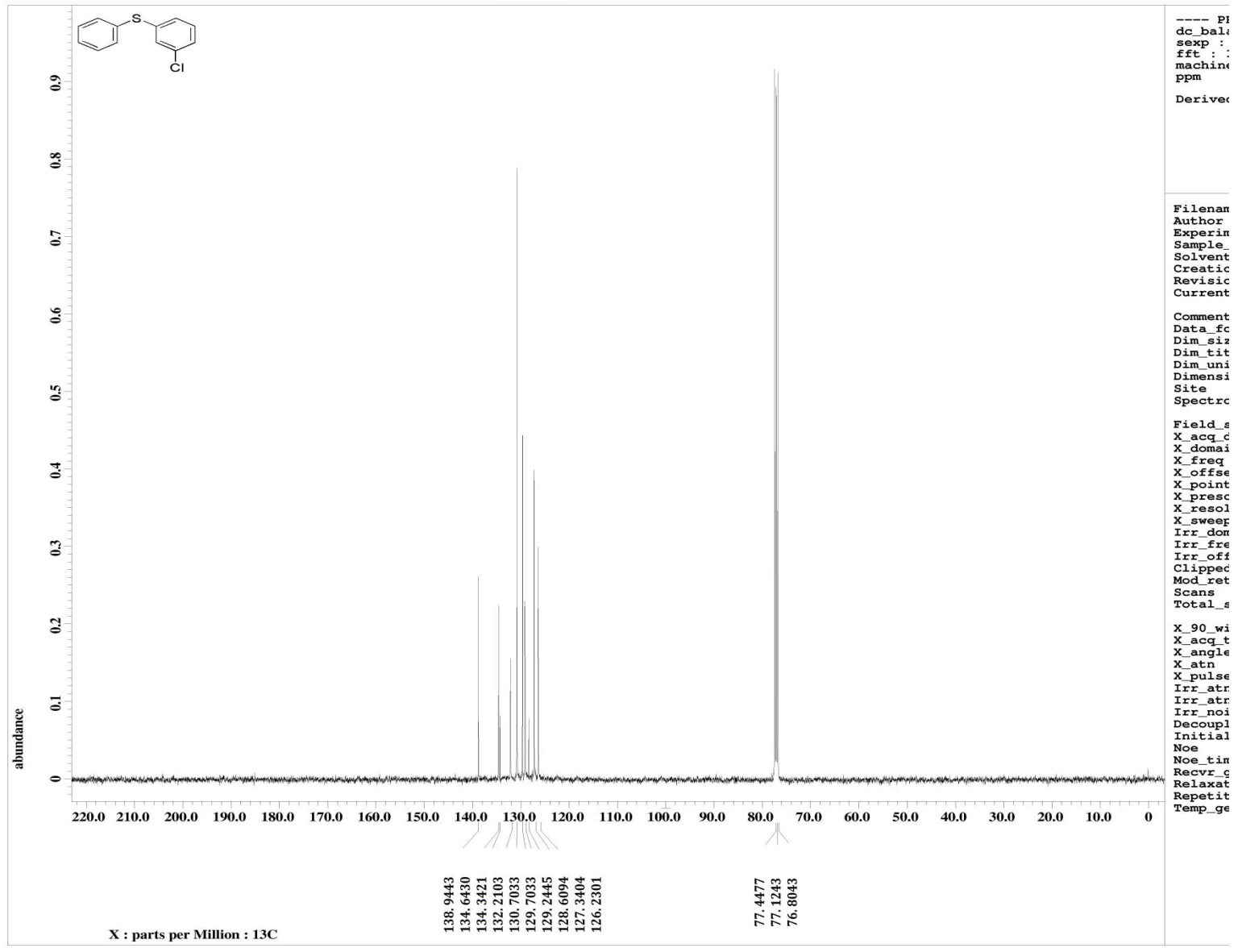
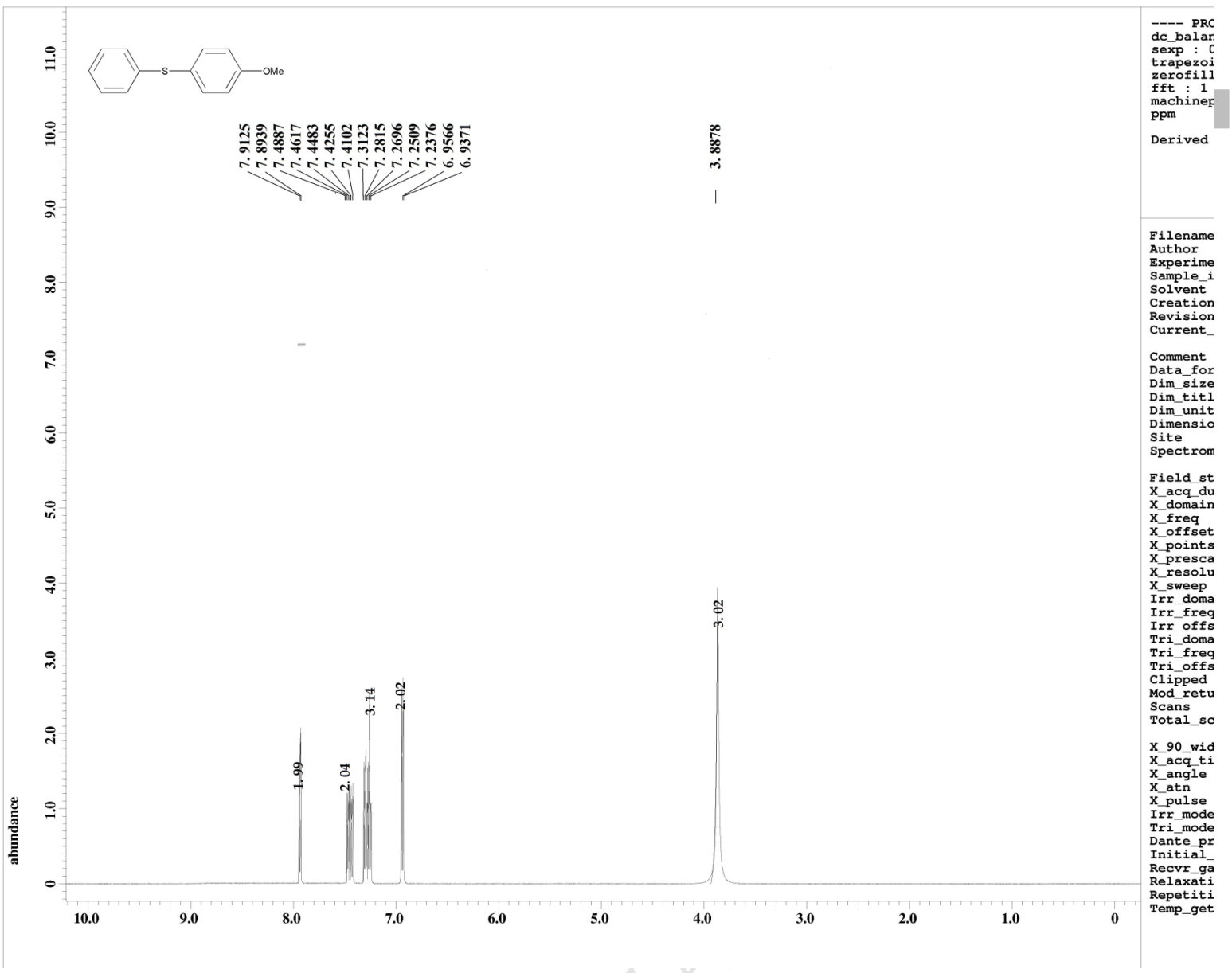
128.0337
127.7023
77.3935
77.0693
77.7547
X : parts per Million : 13C

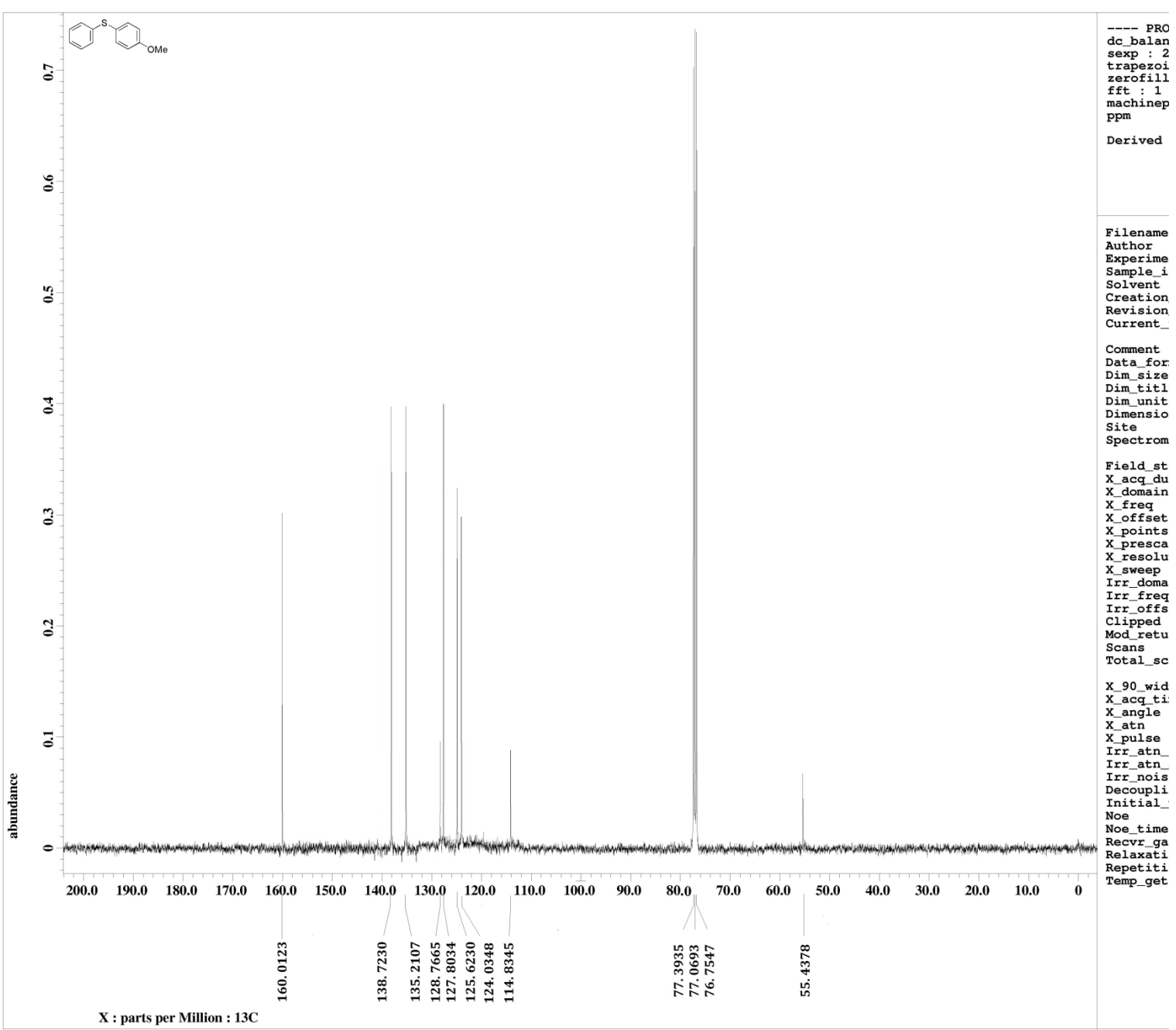

S
Br
7.4126
7.3937
7.3876
7.3612
7.3404
7.3219
7.3007
7.2877
7.2755
7.2544
7.2366
7.2287
7.2133
7.2033
9.00
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

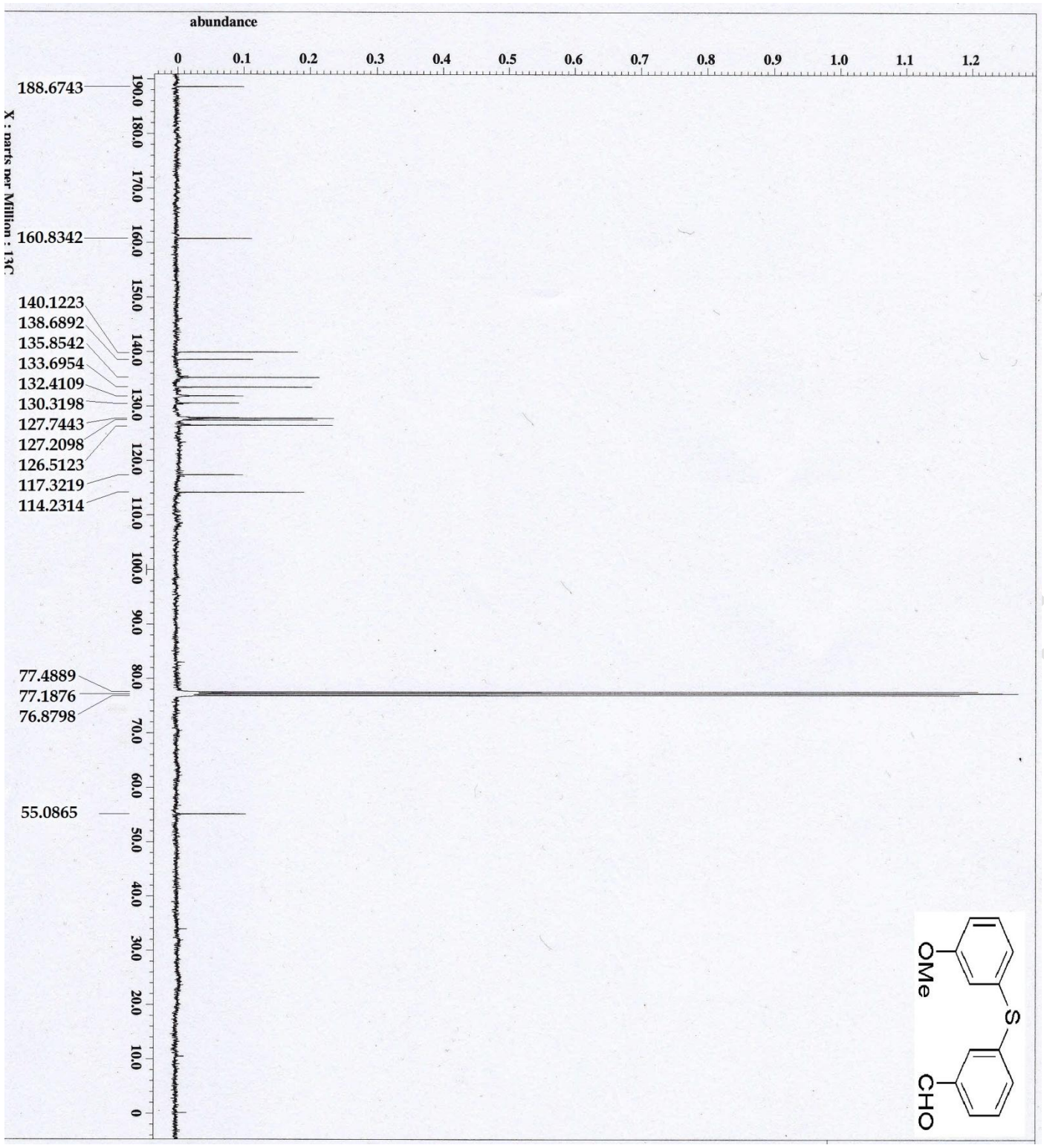

S
Br
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.2659
134.6440
132.4098
132.0442
131.3542
129.0436
127.2066
77.3935
77.0693
76.7547
X : parts per Million : 13C

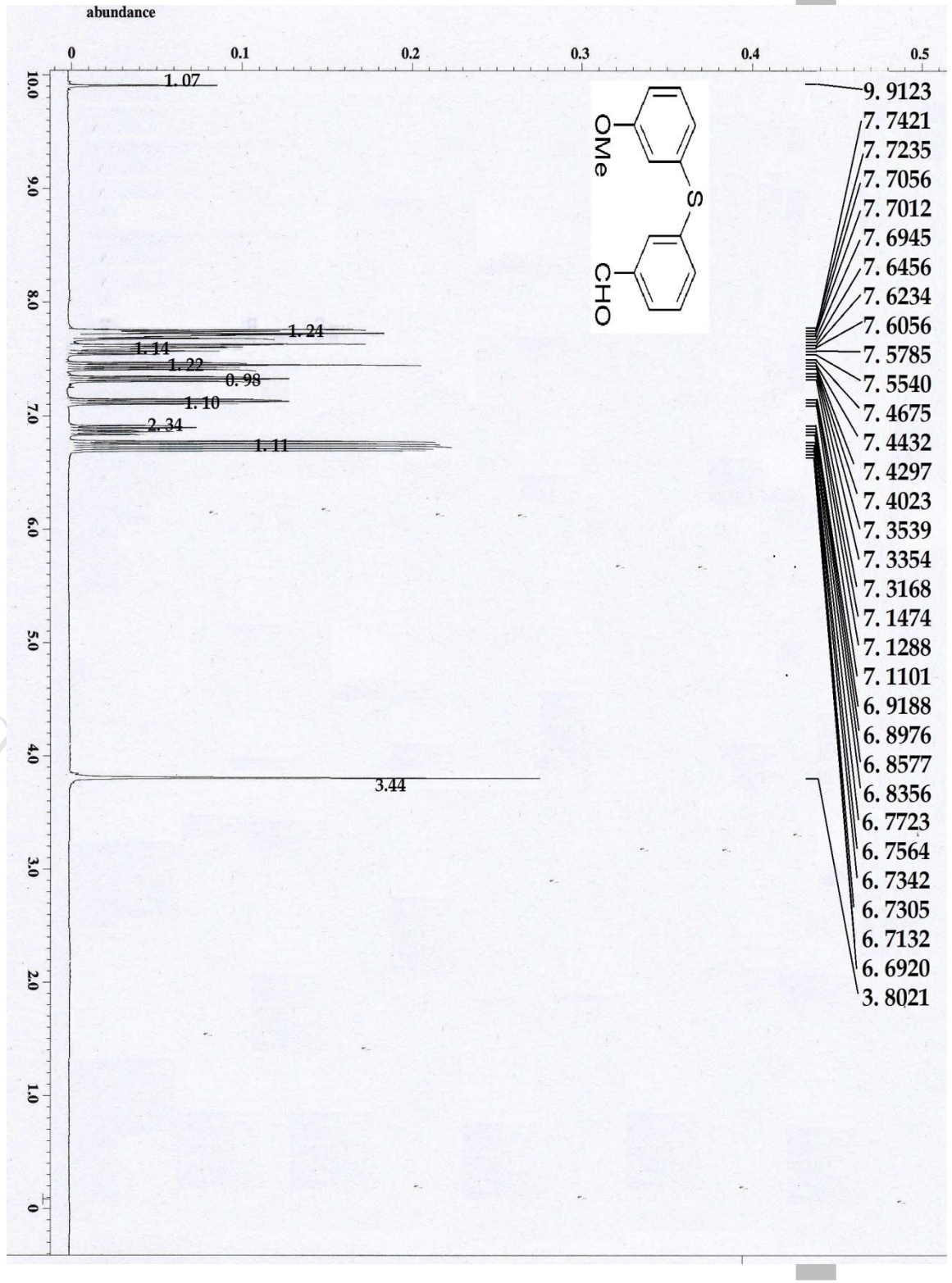

S
Cl
7.4123
7.4034
7.3987
7.3745
7.3640
7.3498
7.3407
7.3243
7.3023
7.2834
7.2567
7.2349
7.2167
7.1945
7.1831
7.1732
7.1698
7.1506
abundance
0
1.0
2.0
3.0
4.0
5.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

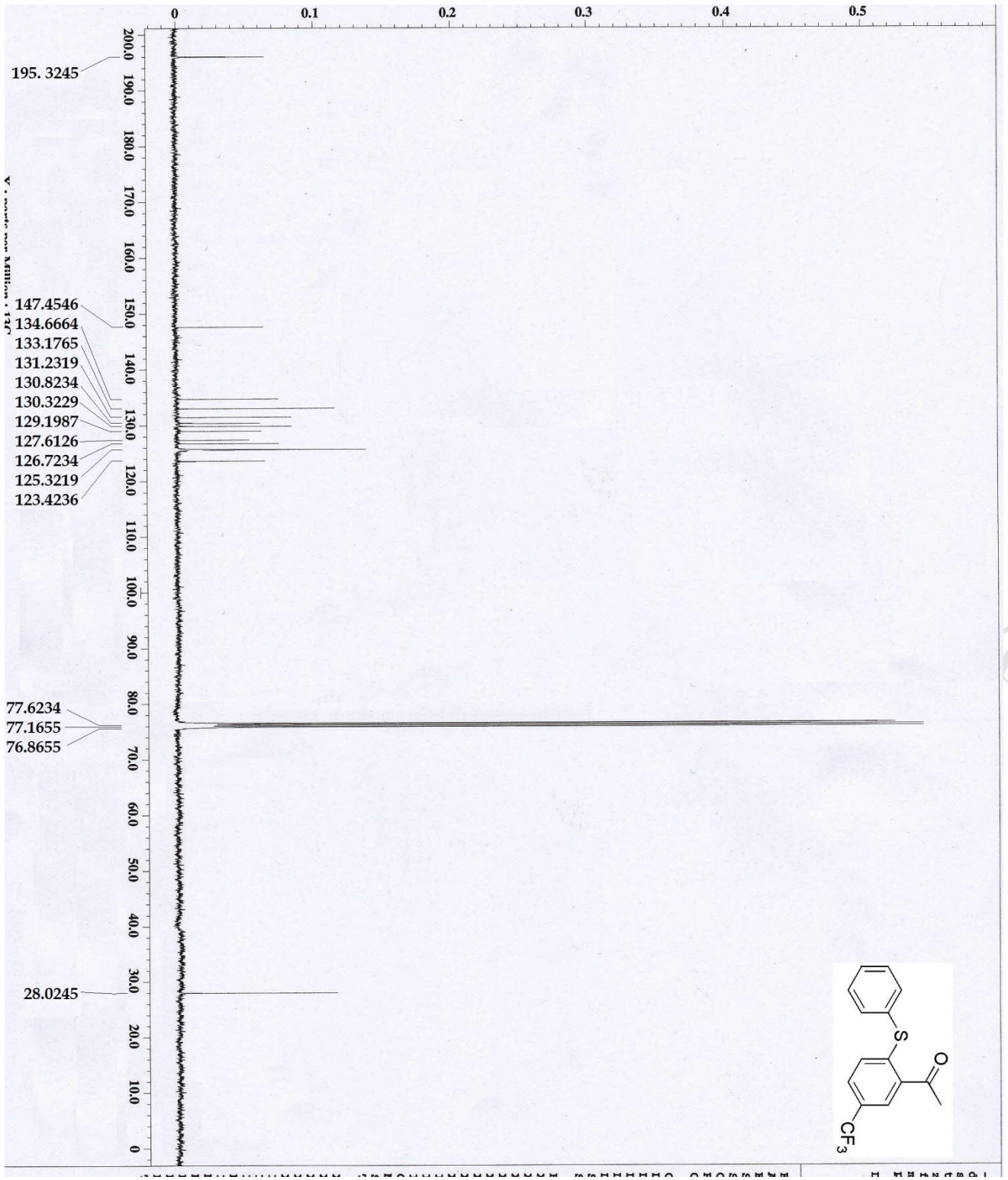

S
Cl
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
138.9443
134.6430
134.3421
132.2103
130.7033
129.7033
129.2445
128.6094
127.3404
126.2301
77.4477
77.1243
76.8043
X : parts per Million : 13C

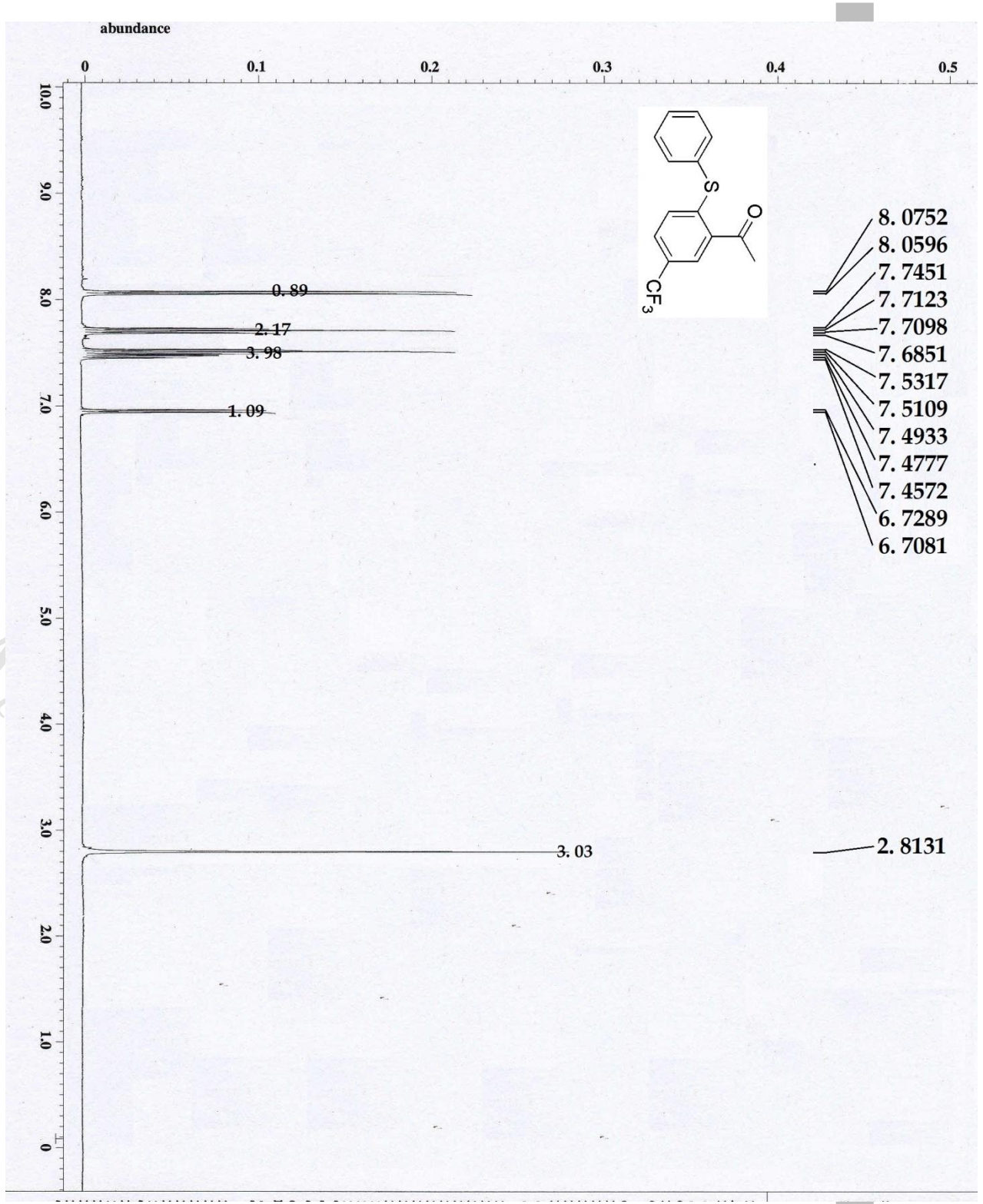

S
OMe
7.9125
7.8939
7.4887
7.4617
7.4483
7.4255
7.4102
7.3123
7.2815
7.2696
7.2509
7.2376
6.9566
6.9371
3.8878
1.99
2.04
3.14
2.02
3.02
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
---- PRO
dc_balan
sexp : 0
trapezoi
zerofill
fft : 1
machinep
ppm
Derived
Filename
Author
Experime
Sample_i
Solvent
Creation
Revision
Current_
Comment
Data_for
Dim_size
Dim_titl
Dim_unit
Dimensio
Site
Spectrom
Field_st
X_acq_du
X_domain
X_freq
X_offset
X_points
X_presca
X_resolu
X_sweep
Irr_doma
Irr_freq
Irr_offs
Tri_doma
Tri_freq
Tri_offs
Clipped
Mod_retu
Scans
Total_sc
X_90_wid
X_acq_ti
X_angle
X_atn
X_pulse
Irr_mode
Tri_mode
Dante_pr
Initial_
Recvr_ga
Relaxati
Repetiti
Temp_get

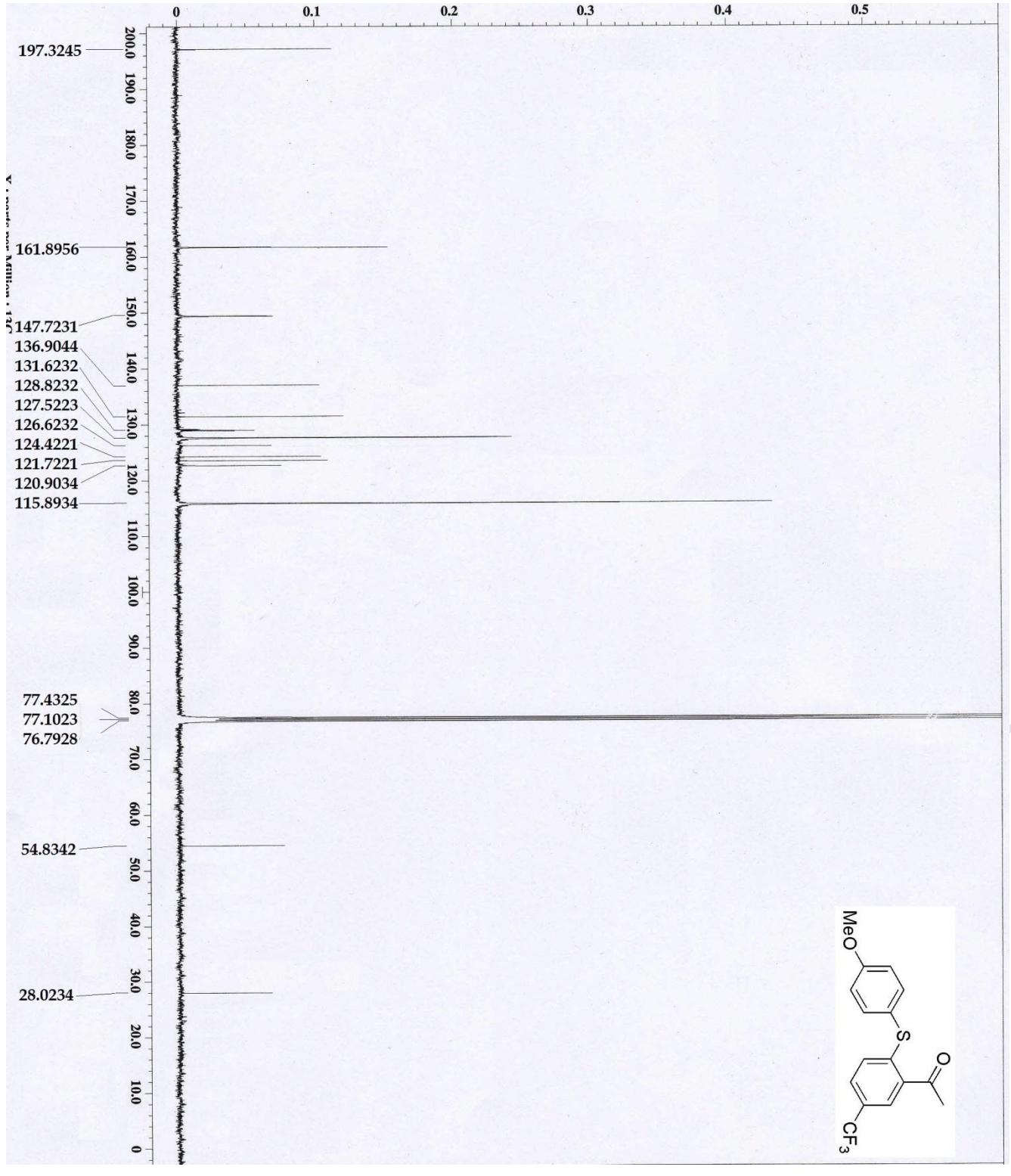

S
OMe
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.0123
138.7230
135.2107
128.7665
127.8034
125.6230
124.0348
114.8345
77.3935
77.0693
76.7547
55.4378
X : parts per Million : 13C
---- PRO
dc_balan
sexp : 2
trapezoi
zerofill
fft : 1
machinep
ppm
Derived
Filename
Author
Experime
Sample_i
Solvent
Creation
Revision
Current_
Comment
Data_for
Dim_size
Dim_titl
Dim_unit
Dimensio
Site
Spectrom
Field_st
X_acq_du
X_domain
X_freq
X_offset
X_points
X_presca
X_resolu
X_sweep
Irr_doma
Irr_freq
Irr_offs
Clipped
Mod_retu
Scans
Total_sc
X_90_wid
X_acq_ti
X_angle
X_atn
X_pulse
Irr_atn_
Irr_atn_
Irr_nois
Decoupli
Initial_
Noe
Noe_time
Recvr_ga
Relaxati
Repetiti
Temp_get

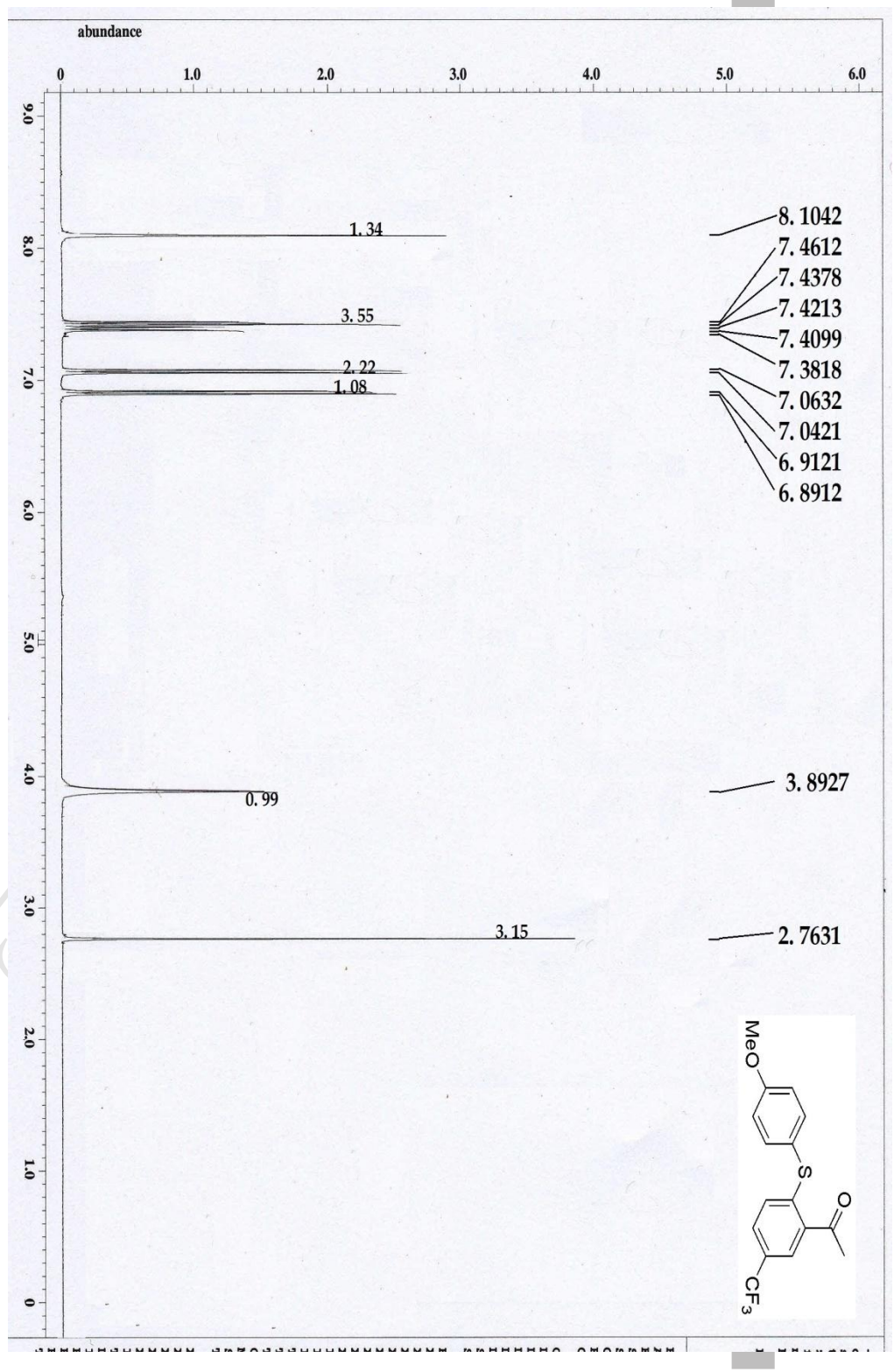

abundance
188.6743
160.8342
140.1223
138.6892
135.8542
133.6954
132.4109
130.3198
127.7443
127.2098
126.5123
117.3219
114.2314
77.4889
77.1876
76.8798
55.0865
OMe
S
CHO

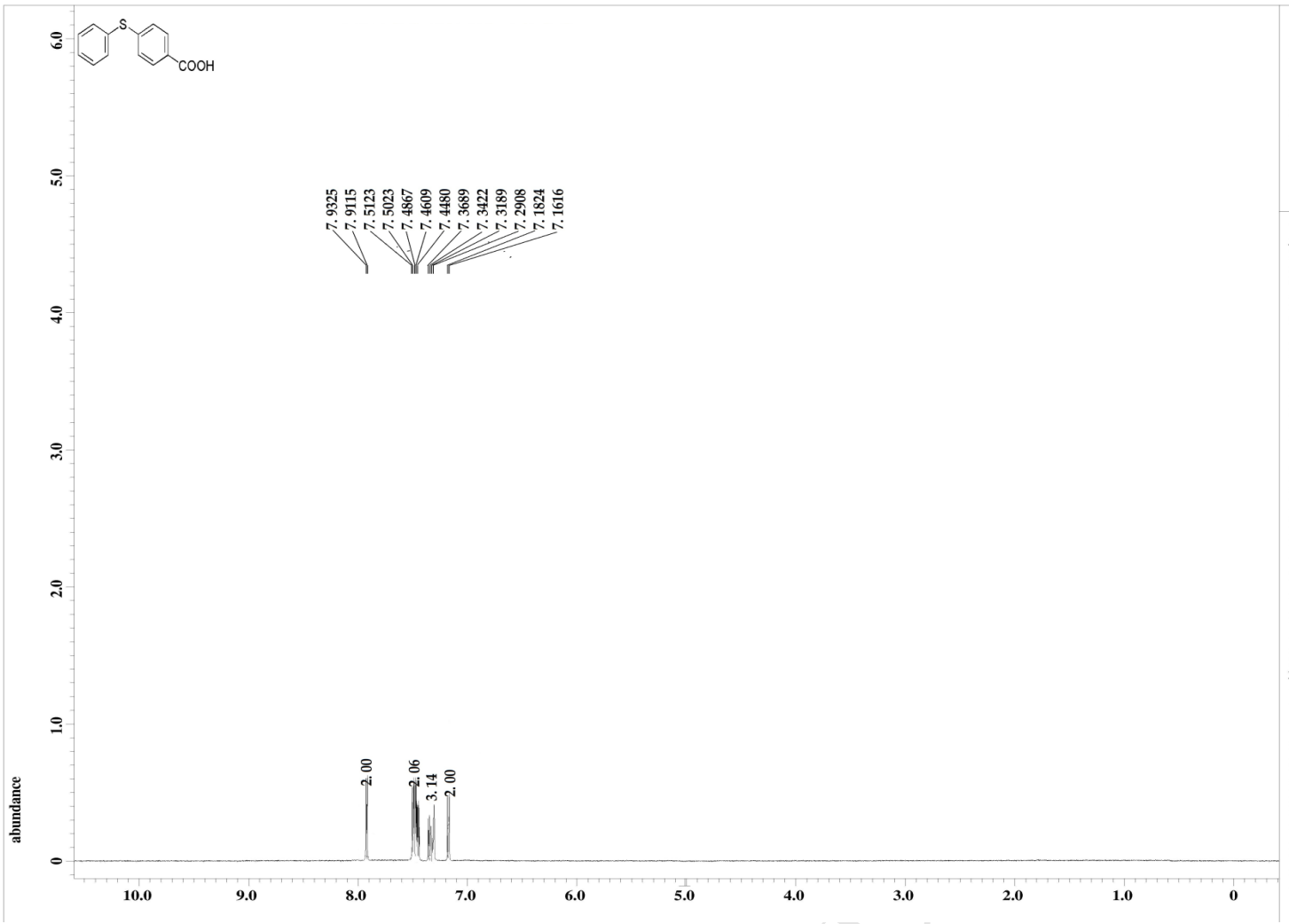

abundance
1.07
1.24
1.14
1.22
0.98
1.10
2.34
1.11
3.44
OMe
S
CHO
9.9123
7.7421
7.7235
7.7056
7.7012
7.6945
7.6456
7.6234
7.6056
7.5785
7.5540
7.4675
7.4432
7.4297
7.4023
7.3539
7.3354
7.3168
7.1474
7.1288
7.1101
6.9188
6.8976
6.8577
6.8356
6.7723
6.7564
6.7342
6.7305
6.7132
6.6920
3.8021

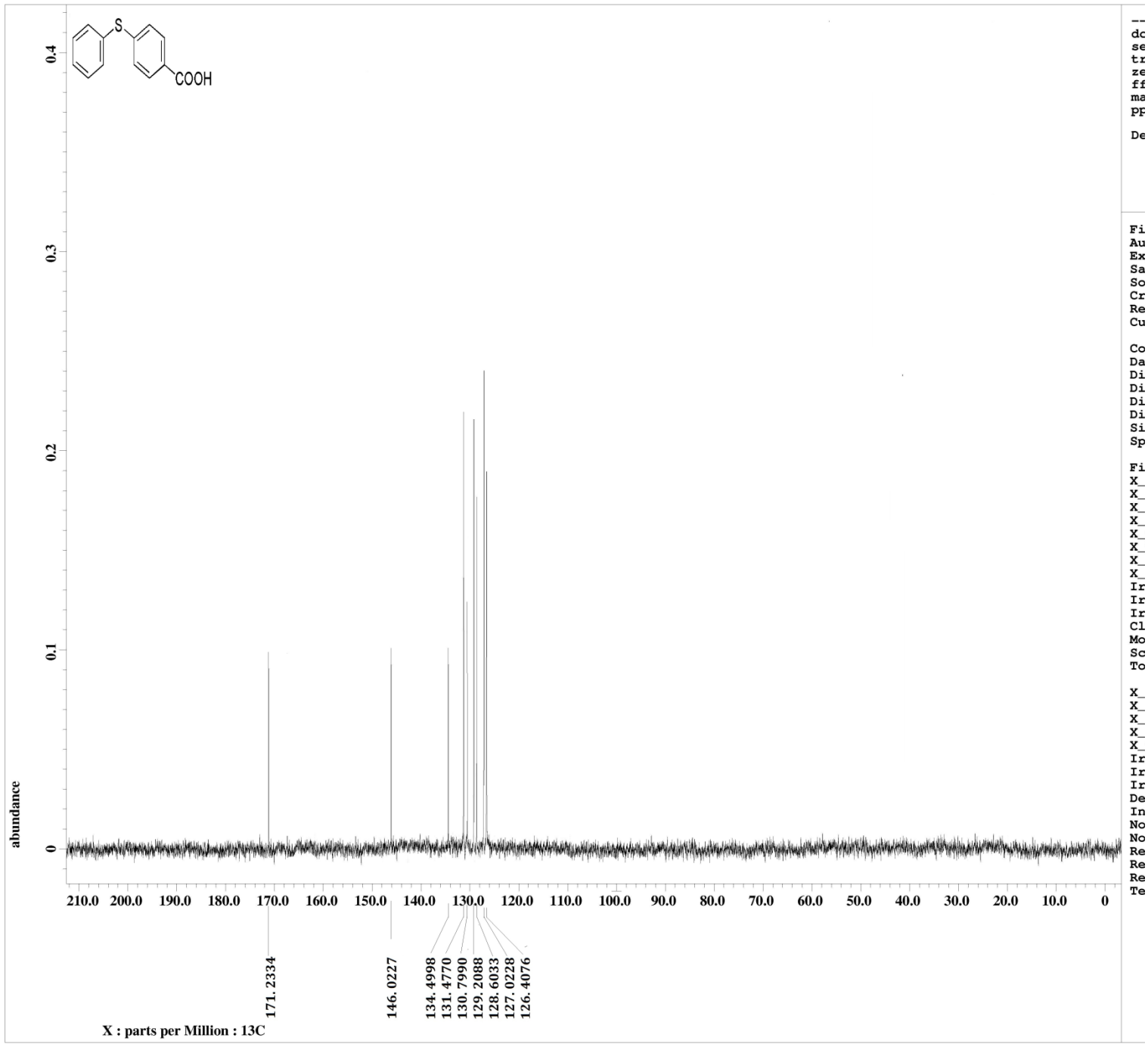

195.3245
147.4546
134.6664
133.1765
131.2319
130.8234
130.3229
129.1987
127.6126
126.7234
125.3219
123.4236
77.6234
77.1655
76.8655
28.0245
S
O
CF3

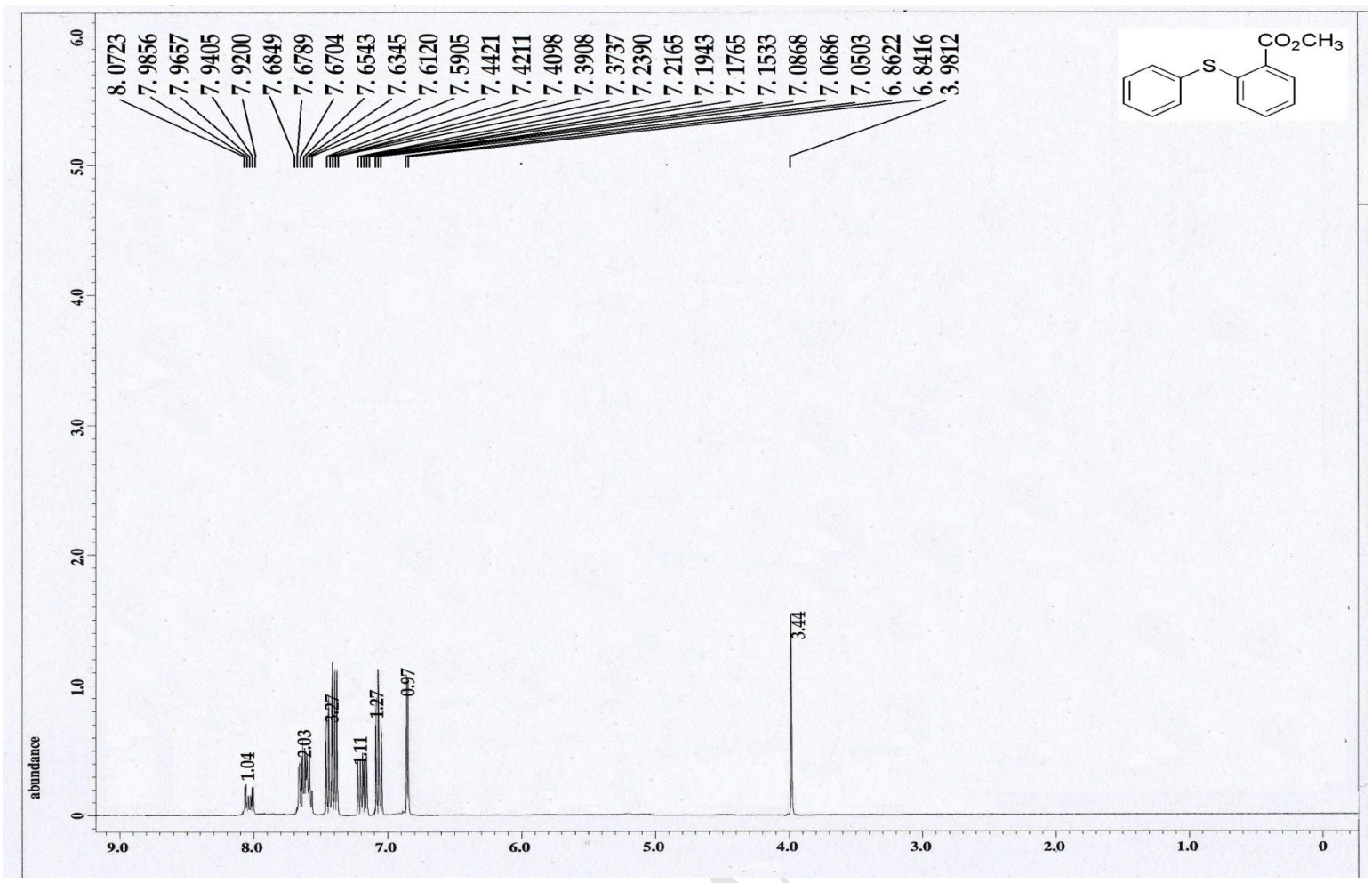

abundance
0.89
2.17
3.98
1.09
3.03
2.8131
8.0752
8.0596
7.7451
7.7123
7.7098
7.6851
7.5317
7.5109
7.4933
7.4777
7.4572
6.7289
6.7081
S
O
CF3

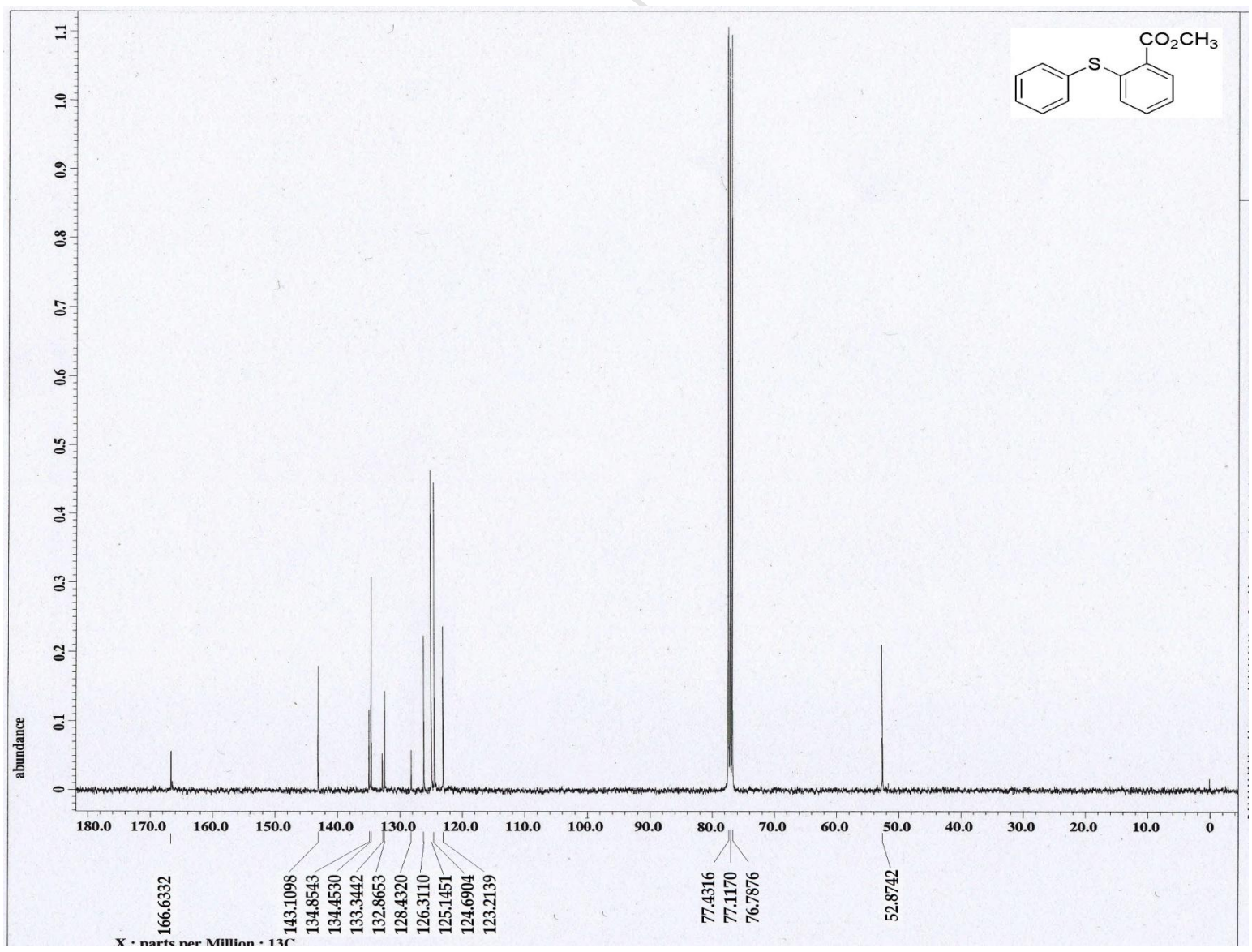

197.3245
161.8956
147.7231
136.9044
131.6232
128.8232
127.5223
126.6232
124.4221
121.7221
120.9034
115.8934
77.4325
77.1023
76.7928
54.8342
28.0234
MeO
S
O
CF3

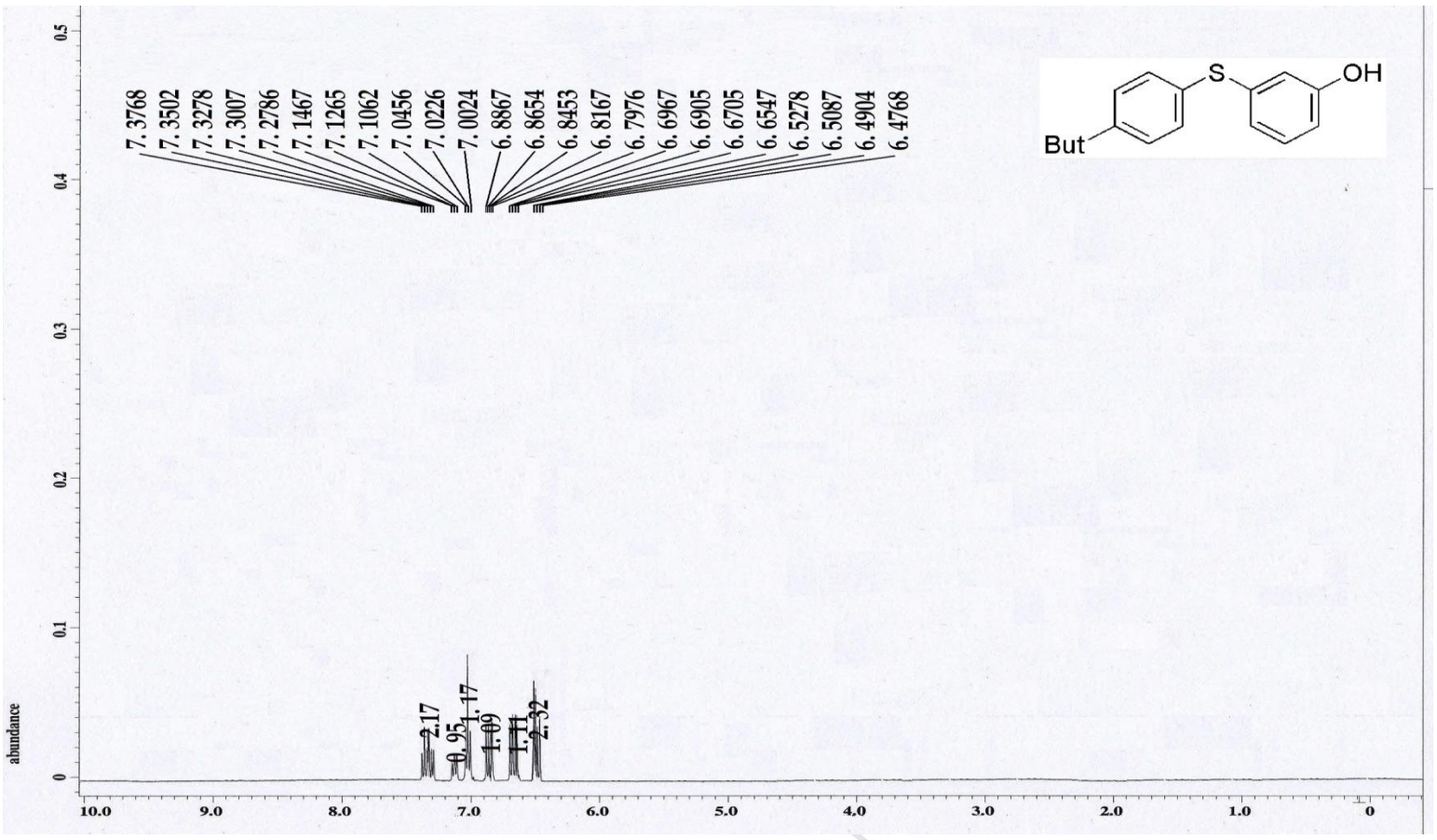

abundance
1.34
3.55
2.22
1.08
0.99
3.15
8.1042
7.4612
7.4378
7.4213
7.4099
7.3818
7.0632
7.0421
6.9121
6.8912
3.8927
2.7631
MeO
S
O
CF3

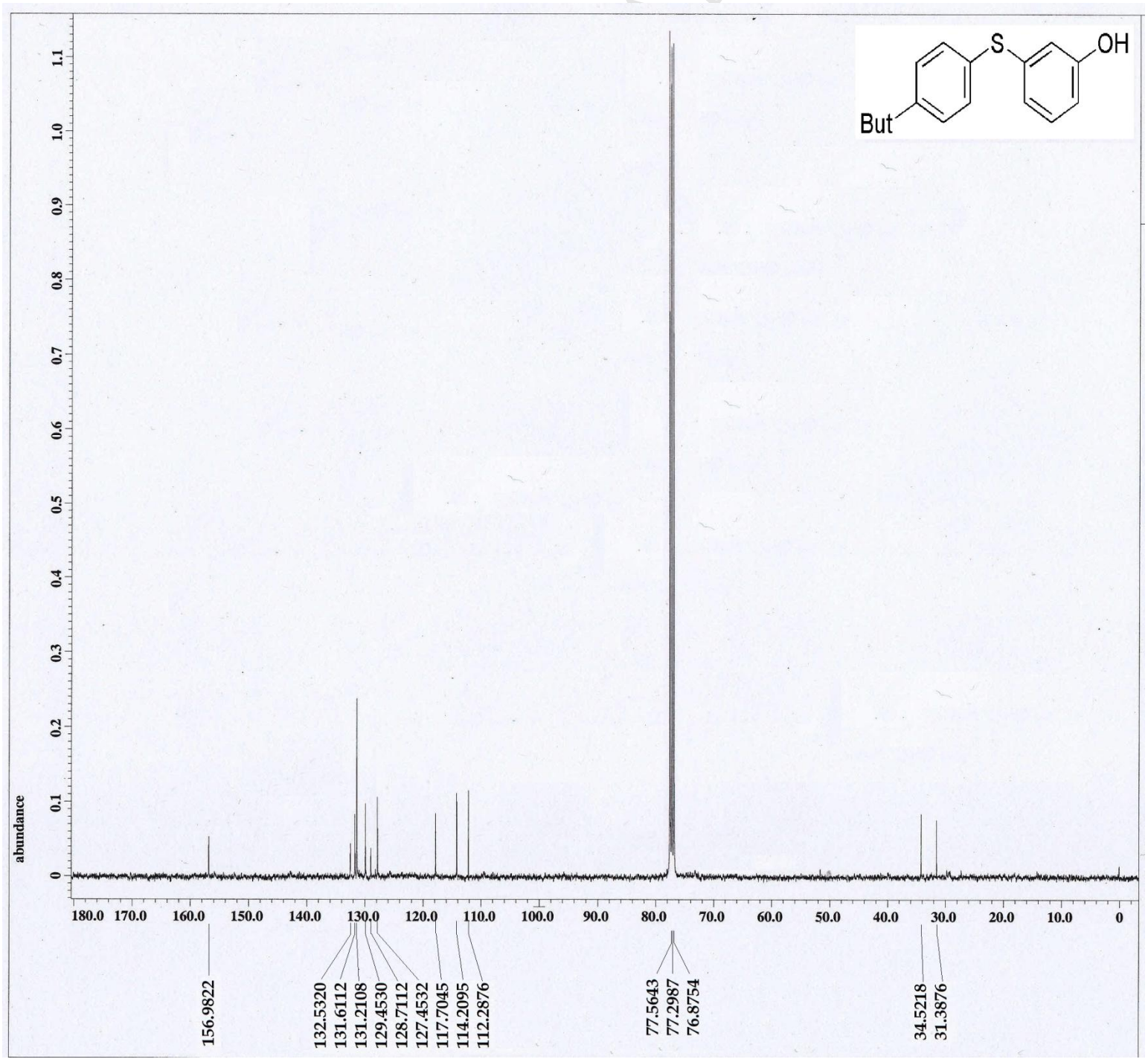

COOH
7.9325
7.9115
7.5123
7.5023
7.4867
7.4609
7.4480
7.3689
7.3422
7.3189
7.2908
7.1824
7.1616
2.00
2.06
3.14
2.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


COOH
171.2334
146.0227
134.4998
131.4770
130.7990
129.2088
128.6033
127.0228
126.4076
abundance
X : parts per Million : 13C


8.0723
7.9856
7.9657
7.9405
7.9200
7.6849
7.6789
7.6704
7.6543
7.6345
7.6120
7.5905
7.4421
7.4211
7.4098
7.3908
7.3737
7.2390
7.2165
7.1943
7.1765
7.1533
7.0868
7.0686
7.0503
6.8622
6.8416
3.9812
CO2CH3
S
abundance
1.04
2.03
3.27
1.11
1.27
0.97
3.44


CO2CH3
S
abundance
166.6332
143.1098
134.8543
134.4530
133.3442
132.8653
128.4320
126.3110
125.1451
124.6904
123.2139
77.4316
77.1170
76.7876
52.8742


7.3768
7.3502
7.3278
7.3007
7.2786
7.1467
7.1265
7.1062
7.0456
7.0226
7.0024
6.8867
6.8654
6.8453
6.8167
6.7976
6.6967
6.6905
6.6705
6.6547
6.5278
6.5087
6.4904
6.4768
2.17
0.95
1.17
1.09
1.11
2.32
abundance
But
S
OH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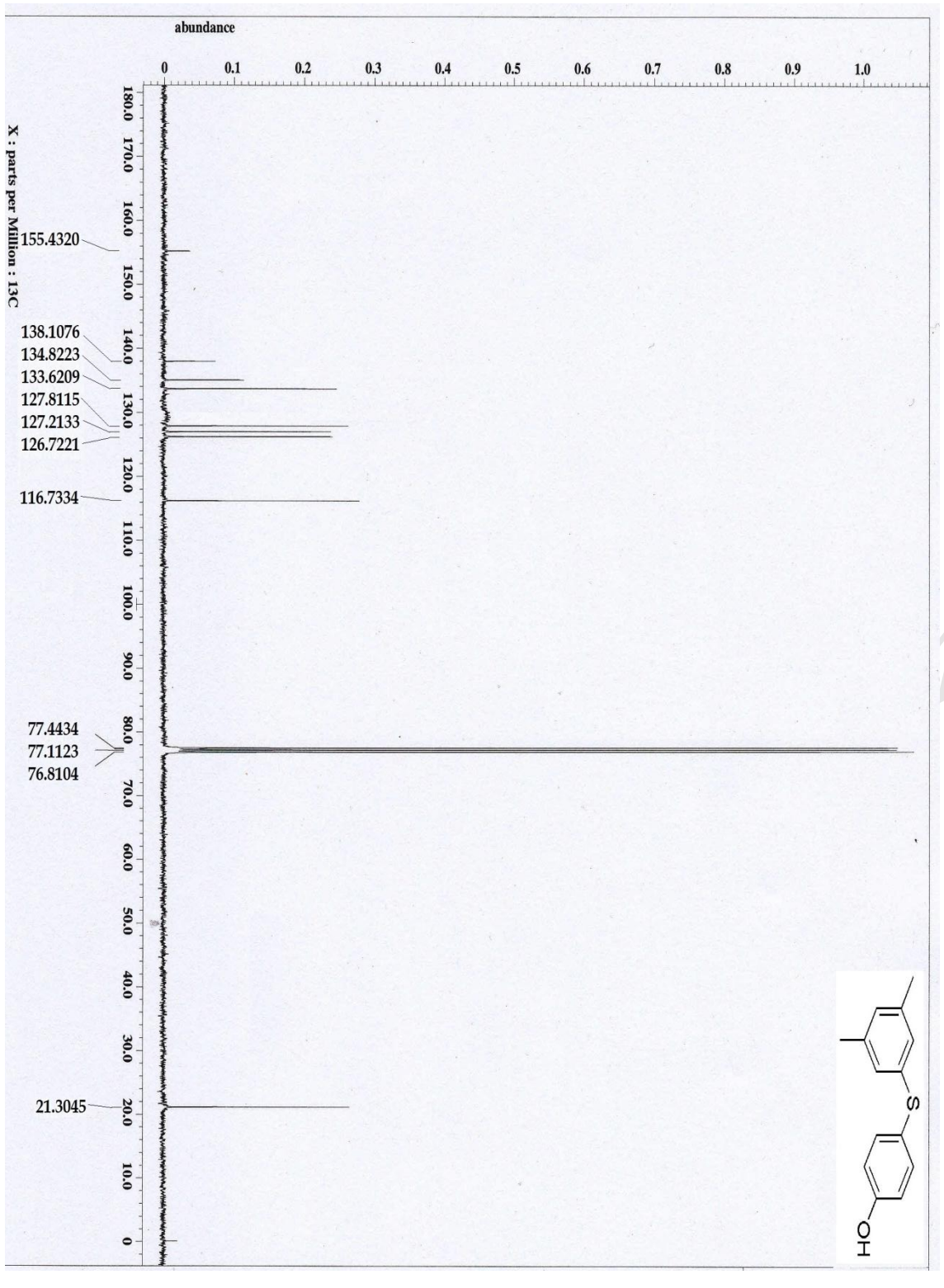
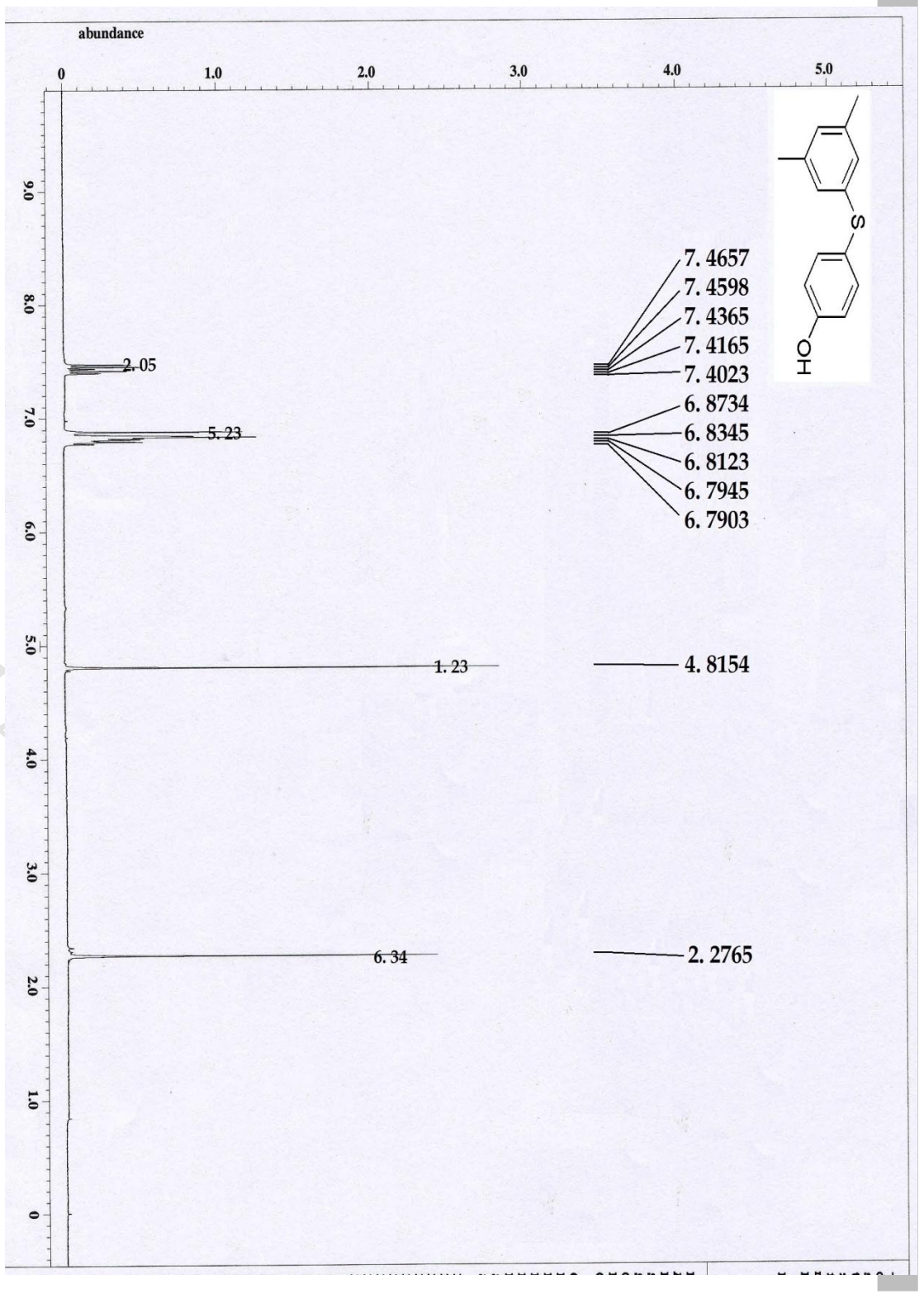
132.5320
131.6112
131.2108
129.4530
128.7112
127.4532
117.7045
114.2095
112.2876
77.5643
77.2987
76.8754
34.5218
31.3876
abundance
But
S
OH


abundance
X : parts per Million : 13C
155.4320
138.1076
134.8223
133.6209
127.8115
127.2133
126.7221
116.7334
77.4434
77.1123
76.8104
21.3045
OH


abundance
7. 4657
7. 4598
7. 4365
7. 4165
7. 4023
6. 8734
6. 8345
6. 8123
6. 7945
6. 7903
2. 05
5. 23
1. 23
4. 8154
6. 34
2. 2765
OH