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Potassium *tert*-Butoxide-Mediated Synthesis of Unsymmetrical Diaryl Ethers, Sulfides, and Selenides from Aryl Bromides

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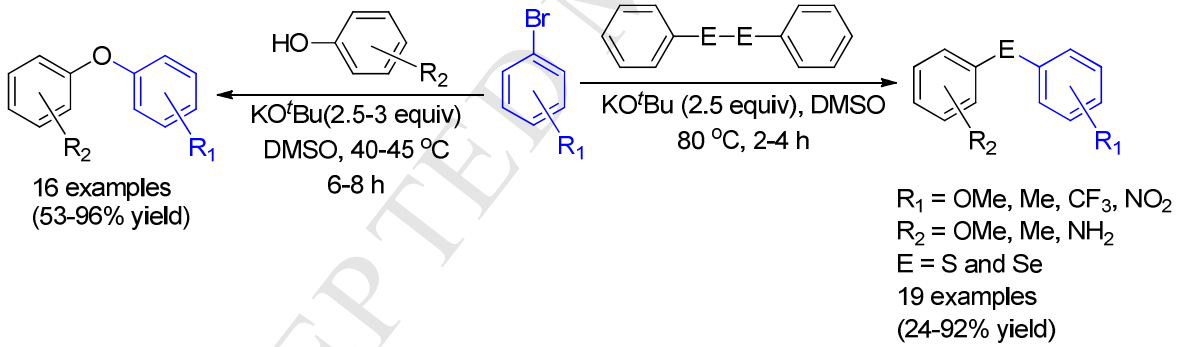
Abstract



Potassium *tert*-butoxide mediated carbon-chalcogen C-E (E = O, S, and Se) coupling reaction has been studied from aryl bromide and phenol/ aryl disulfide/ diselenide substrates. A series of unsymmetrical diaryl chalcogenides were accessed from aryl bromide and diaryl dichalcogenide precursors by using 2.5 equiv of potassium *tert*-butoxide in DMSO at 80 ^{o}C. Unsymmetrical diaryl ethers were also obtained by using phenol precursors at 40-45 ^{o}C. Aryl bromides with methyl, trifluoromethyl, methoxy, and nitro substituents showed compatibility in the carbon-chalcogen bond forming reaction. 4-Methoxy, methyl, trifluoromethyl substituted bromobenzene substrates gave two regio-isomers: 3-substituted and 4-substituted

diaryl chalcogenides when reacted with phenols/ diaryl disulfides/ diselenides. Formation of two regioisomeric diaryl chalcogenides in the reaction mixture suggests that potassium *tert*-butoxide reacts with bromobenzene to produce benzyne intermediate which subsequently reacts with diaryl dichalcogenides and finally give a regioisomeric mixture of 4-substituted and 3-substituted diaryl chalcogenides.

Introduction

Diaryl chalcogenides are an important class of organic compounds which play a significant role in biological, polymer, and material sciences.[1-3] As a consequence, many approaches have been developed for the synthesis of unsymmetrical diaryl chalcogenides. Transition metal catalyzed intermolecular reaction of phenol, diaryl disulfide, and -diselenide with aryl halide is an attractive method for the formation of carbon-chalcogen bond. Palladium, nickel, copper, gold, and iron together with ligands are known to catalyse carbon–chalcogen bond forming reaction.[4-6] Many advances such as reaction in aqueous solvent, low catalyst loading and compatibility with various substrates have been made in this area.

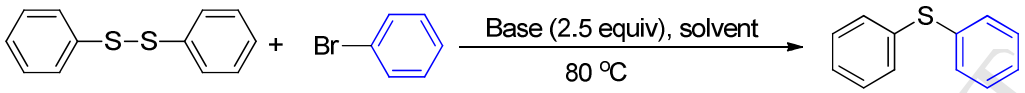
Efforts are also being made to develop transition metal free approaches for the formation of carbon-chalcogen (C-E; E = O, S, Se) bond.[7-9] Recently, potassium *tert*-butoxide mediated carbon-carbon and carbon-heteroatom coupling reactions have been reported for the synthesis of various organic molecules.[10] Out of these the synthesis of diaryl selenides/ sulfides is of particular interest. Although, potassium *tert*-butoxide mediated synthesis of unsymmetrical diaryl ethers[8b] has been described during our investigation on the synthesis of diaryl chalcogenides, however, synthesis of unsymmetrical diaryl sulfides and selenides using potassium *tert*-butoxide has not been reported. Moreover, the synthesis of diaryl ethers was achieved from respective phenol precursors at 120 ^{o}C.[8b] Selenium analogues (ArSeH) of phenols are not readily available. Although, aryl thiols (ArSH) are

commercially available, they possess foul smell. Diaryl disulfides are easily accessible sulfur substrates and also easy to handle due to their low foul smell. Similarly, diaryl diselenides are the only key substrates for the synthesis of unsymmetrical diaryl selenides. Therefore, a method which utilizes diaryl dichalcogenides would be beneficial for the synthesis unsymmetrical diaryl selenides. Hence it is worth studying the reaction of diaryl disulfides and diselenides with aryl halides in the potassium *tert*-butoxide mediated reaction. In continuation of our work on organochalcogen chemistry[11a-c,e-g] and potassium *tert*-butoxide mediated coupling reaction,[11d] herein, we present a potassium *tert*-butoxide mediated synthesis of diaryl sulfides and selenides using diaryl disulfide and diselenide precursors, respectively. Also, the synthesis of diaryl ethers was achieved from phenols and bromoarenes at 40-45 ^{o}C using highly pure DMSO.

Results and discussion

Bromobenzene and diphenyl disulfide were chosen as the substrates for the screening of various reaction conditions in the KO^{t}Bu-mediated reaction (Table 1). As studied earlier by us, we employed five equiv of potassium *tert*-butoxide and 20 mol % of 1,10-phenanthroline or 0.2 equiv of AIBN in solvents such as benzene, toluene, and mesitylene.[11d]

Table 1: Optimization of reaction conditions[a]



Entry	Base	Solvent	T (°C)	Time (h)	Yield (%)
1	K_2CO_3	DMSO	rt	12	nil
2	K_2CO_3	DMSO	80	4	10
3	NaOH	DMF	80	4	nil
4	Cs_2CO_3	DMSO	80	4	13
5	KOH	DMSO	80	8	56
6	KO^{t}Bu	DMSO	rt	24	18
7	**KO^{t}Bu**	**DMSO**	**80**	**2**	**89/ 87[b]**
8	KO^{t}Bu	Benzene	110	24	traces
9	KO^{t}Bu	Mesitylene	110	24	traces
10	KO^{t}Bu	DMF	80	2	65
11	KO^{t}Bu	MeCN	80	2	nil
12	NaH	DMSO	80	2	nil
13	K_3PO_4	DMSO	80	2	10

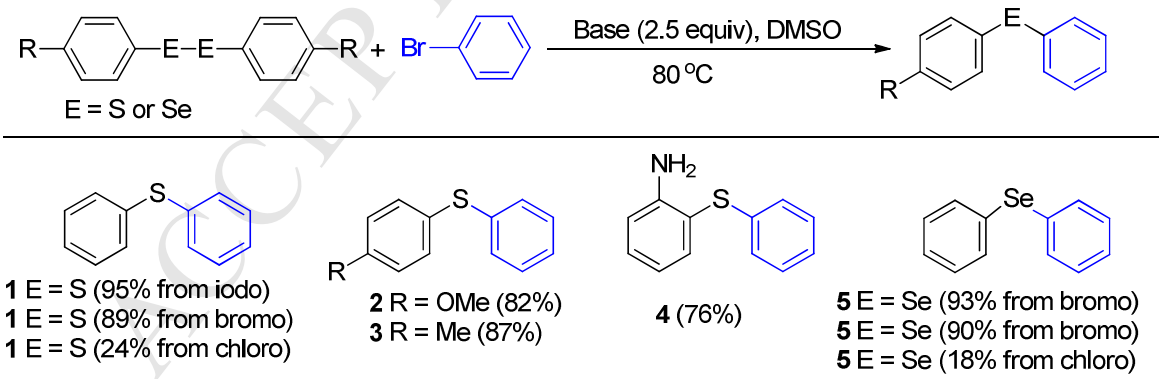
[a] Reactions were carried out at 1 mmol scale using 1.0 mmol of bromobenzene, 0.5 mmol of diphenyl disulfide, and 1.25 mmol of KO^{t}Bu in 1 mL of solvent otherwise stated and isolated yield of 1 was based on the diphenyl disulfide used in the reaction. rt = 40-45 °C. [b] Yield of diaryl sulfide **1** was obtained using KO^{t}Bu of 99.99% purity. Anhydrous DMSO with sure seal septa is important for high yield of the sulfide **1**.

Unfortunately, traces of product, diaryl sulfide **1** were observed under these conditions (entries 8 and 9, Table 1). Yield of diaryl sulfide **1** increased substantially in the solvents DMF and DMSO (entries 1-7, 10, 12-13, Table 1). It was observed that the addition of 1,10-

phenanthroline ligand or radical initiator was ineffective in the formation of diaryl sulfide **1** as the isolated yield remained the same in their presence. Moreover, 2.5 equiv of potassium *tert*-butoxide is enough for the complete conversion of substrate. It is worthy to note that the reaction time is considerably shorter (6 to 8 h) than the copper catalyzed (8-30 h) coupling reactions.[5a,f]

Various other bases K_2CO_3, NaOH, Cs_2CO_3, KOH, NaH, and K_3PO_4 were also screened for the C-S coupling reaction (entries 1-5, 12 and 13, Table 1). None of the base was noticed to be effective for the promotion of C-S coupling reaction and poor yield of C-S coupled product **1** was observed. Next, iodo and chloro benzenes were studied as substrates in the C-S coupling reaction. Iodo benzene gave slightly better yield (95%) than the corresponding bromo substrate (89%) when reacted with diphenyl disulfide. Chlorobenzene reacted sluggishly with diphenyl disulfide and poor yield of product **1** was obtained (Scheme 1, *vide infra*).

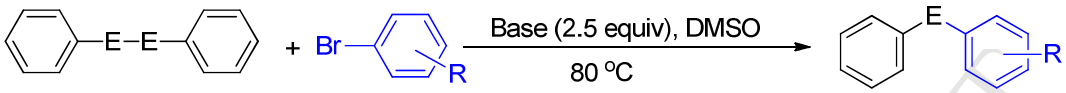
Scheme 1. Synthesis of diaryl sulfides and selenides using various diaryl disulfides and diselenides

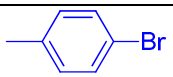
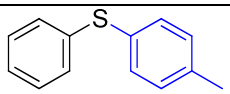
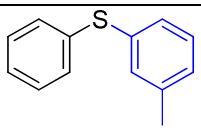
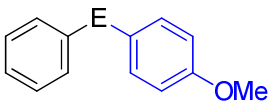
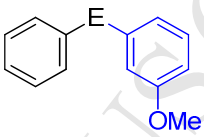
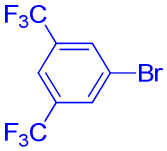
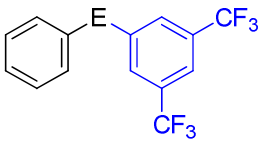
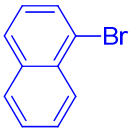
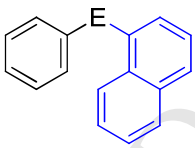
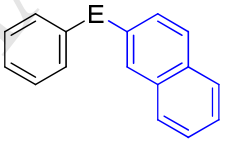
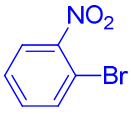
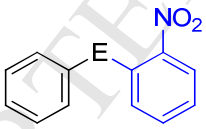
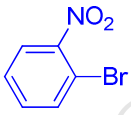
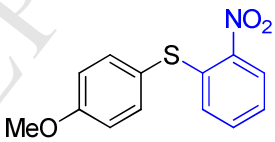
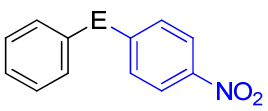
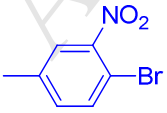
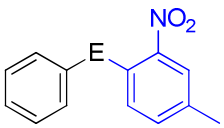


After screening a series of reaction conditions, we used potassium *tert*-butoxide, aryl bromide and DMSO to further study the scope and limitation of this method. The results are

summarized in Scheme 1. First, we studied substituted diphenyl disulfides in the potassium *tert*-butoxide mediated C-S coupling reaction. Para-methoxy and methylphenyl disulfides reacted smoothly with bromobenzene and yielded unsymmetrical diaryl sulfides **2** and **3** in 82 and 87% yield, respectively (Scheme 1). Interestingly, 2-aminophenyl disulfide having acidic $N\underline{H_2}$ proton also coupled with bromobenzene chemo-selectively to give 2-aminophenyl phenyl sulfide **4** in 76% yield. Similarly, diphenyl selenide **5** was obtained in 3.5-4.5 h in 93, 90, and 18% yield from iodo, bromo, and chlorobenzene, respectively. However, the reaction was noticed to be slightly slower as compared to the sulfur analogue **1**.

Table 2. Synthesis of diaryl sulfides and selenides from substituted bromoarenes



Entry	Aryl bromide	Product (**a**)	Product (**b**)	Yield (%)[a]
1				**3/6b** (1:0.9)[b] (79)
2 3				**2/7b** E =S (1:1)[b] (81) **8a/8b** E = Se (0.7:0.3) [b] (81)
4 5			--[c]	**9** E = S (56) **10** E = Se (52)
6 7				**11a/11b** (1:1)[b] E = S (76) **12a/12b** (1:1)[b] E= Se (87)
8			--[c]	**13** E = S (90)
9			--[c]	**14** E = Se (86)
10[d]			--[c]	**15** (79)
11			--[c]	**16** E = S (82)
12			--[c]	**17** E = Se (79)
13			--[c]	**18** E = S (60)
14			--[c]	**19** E= Se (57)

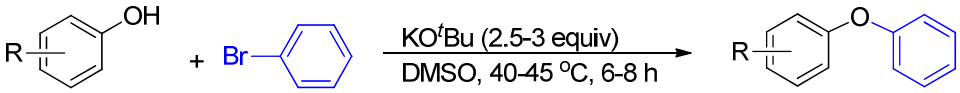
[a] Isolated yields are based on the diaryldisulfide used in the reaction [b] Ratio of regioisomers was determined by ^{1}H NMR. [c] Formation of isomer **b** was not observed. [d] Bis (4-methoxyphenyl) disulfide was used.

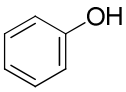
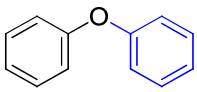
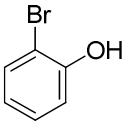
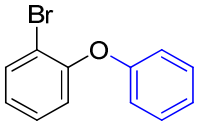
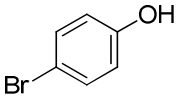
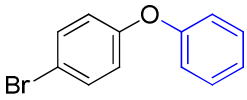
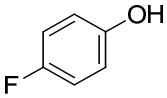
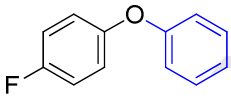
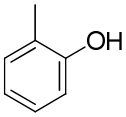
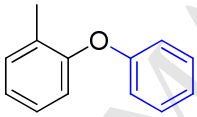
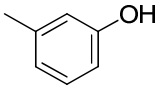
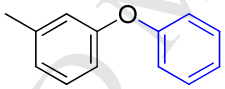
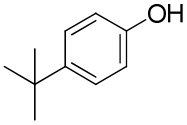
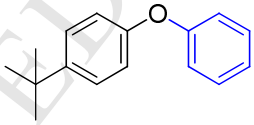
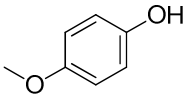
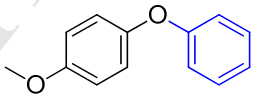
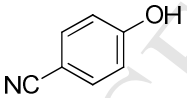
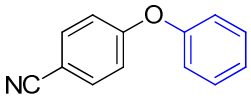
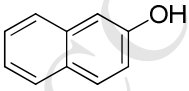
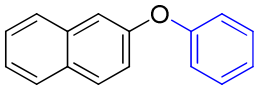
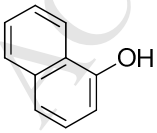
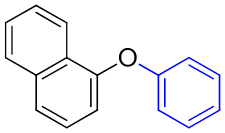
After studying, substituted diaryl disulfides and diphenyl diselenide, we explored substituted bromobenzenes in the potassium *tert*-butoxide mediated C-S coupling reaction and the results are presented in Table 2. 4-Methylbromobenzene reacted completely with diphenyl disulfide in 2.5 h, however, a regioisomeric mixture of 3- and 4-methylphenyl phenyl sulfides **3** and **6b** was observed in the ration of 1:0.9. Similar observation was made with 4-methoxy bromobenzene (entries 2 Table 2), which afforded a mixture of diaryl sulfides (**2** and **7b**). Similar to electron rich substituted bromobenzenes, 1-bromo-naphthalene reacted with diphenyl disulfide in potassium *tert*-butoxide mediated C-S coupling reaction and gave a regioisomeric mixture of 1-naphthyl and 2-naphthyl phenyl sulfides (**11a** and **11b**). We attempted to optimize the formation of one regioisomer by varying the reaction temperature and by adding additives. Lowering the reaction temperature to 40-45 ^{o}C failed to provide any product despite the prolonged (24 h) stirring of reaction mixture. Similarly, addition of radical initiator AIBN to the reaction mixture did not improve the regioselectivity. Additives such as L-proline, 1,10-phenanthrolene, *N,N'*-dimethylethyldiamine (DMEDA) were also failed to provide selective formation of one regioisomer.

Interestingly, trifluoromethyl and nitro substituted bromobenzenes gave only one regioisomeric product in the potassium *tert*-butoxide mediated C-S coupling reaction (entries 4, 8, 10, 11 and 13, Table 2). Also, *ortho* and *para* substituted nitrobromobenzenes gave quantitative yield of *ortho* and *para*-nitrophenyl phenyl sulfides **13**, **15** and **16**, respectively. Moreover, methyl substituted bromobenzene together with nitro group gave regioselectively only one isomer **18** in the C-S coupling reaction. Reaction of substituted bromobenzenes was also studied with diphenyl diselenide. Indeed similar results were obtained as noticed for

sulfur analogues (entries 3, 5, 7, 9, 12, and 14; Table 2). Diphenyl diselenide provided slightly better regioselectivity (0.7:0.3) as compared to sulfur analogue (1:1) when reacted with 4-methoxybromobenzene (entries 2 and 3; Table 2). However, dipehenyl diselenide gave selenides **12a/12b** in poor regioselectivity ration (1:1) when reacted with 1-bromonaphthalene.

Table 3. Coupling of substituted phenol with bromobenzene

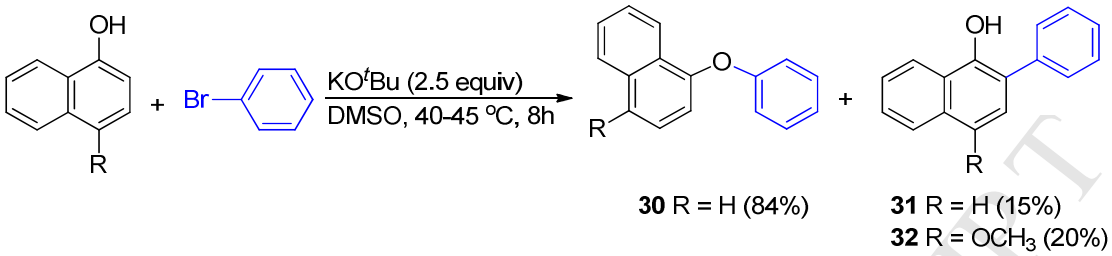


Entry	Phenol	Product	Yield (%)[a]
1			**20** (96)
2			**21** (62)
3			**22** (58)
4			**23** (65)
5			**24** (76)
6			**25** (79)
7			**26** (82)
8			**27** (76)
9			**28** (64)
10			**29** (83)
11			**30** (84)

[a] Isolated yields of ethers are based on the respective phenols used in the reaction.

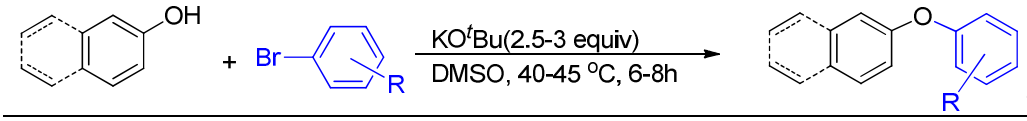
We next turned our attention to the potassium *tert*-butoxide mediated carbon-oxygen coupling reaction using bromobenzene and substituted phenol for the synthesis of unsymmetrical diaryl ethers. Unsymmetrical diaryl ethers are of paramount importance and as a result several methodologies have been developed for the synthesis of diaryl ethers.[7,8,12,13] Yang and Xu et al. have reported KO^{t}Bu mediated C-O and C-N coupling reactions using two equiv of KO^{t}Bu at 120 ^{o}C (*vide supra*).[8b] Potassium hydroxide has also been reported as a super base for Ullmann type of carbon-heteroatom coupling reaction. Nonetheless, high amount of potassium hydroxide (250 mol %) and/ or high temperature (120-135 ^{o}C) were required for smooth formation of the diaryl ethers.[7i,j] To see the compatibility of C-O bond formation in the potassium *tert*-butoxide mediated coupling reaction and also to compare the reactivity with heavy chalcogen (sulfur and selenium) analogues, we studied the synthesis of unsymmetrical diaryl ether. A series of substituted phenols underwent coupling reaction with bromobenzene and produced diaryl ethers **20-30** in 58-96% yield (Table 3). In contrast to diaryl sulfides and selenides, synthesis of unsymmetrical diaryl ethers was achieved at 40 -45 ^{o}C. However, longer reaction time is necessary to achieve the complete conversion of the substrates into diaryl ethers. It seems that the high purity of DMSO solvent and slight excess of potassium *tert*-butoxide may be responsible for milder reaction conditions for the carbon-oxygen bond formation. Under our reaction conditions, a series of unsymmetrical diaryl ethers **20-30** with substituents such as methyl, bromo, fluoro, *tert*-butyl, cyano, and methoxy have been accessed in good to excellent yield at 40-45 ^{o}C.

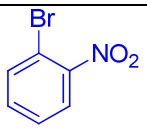
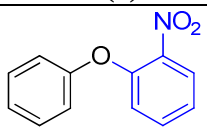
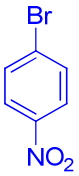
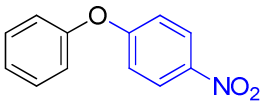
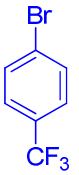
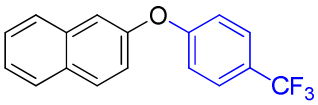
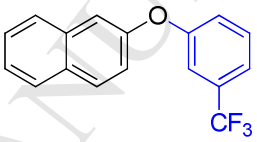
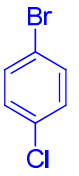
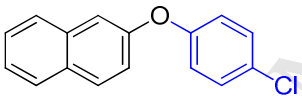
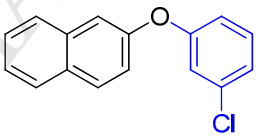
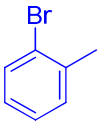
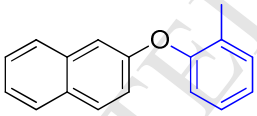
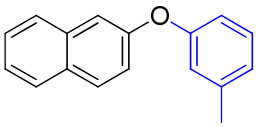
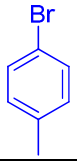
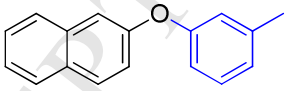
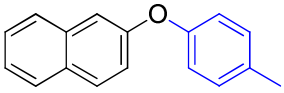
Scheme 2. Synthesis of naphthyl ether **30** and C-C coupled naphtha-2-ols **31** and **32**



α-, β-Naphthols also reacted with bromo benzene in the potassium *tert*-butoxide mediated coupling reaction and produced β and α-naphthyl phenyl ethers **29**-**30** in 84 and 83% yields, respectively. In case of α-naphthol substrates, intermolecular carbon-carbon coupled products **31** and **32** were also observed (Scheme 2). Synthesis of biaryls having various functional groups has been reported using potassium *tert*-butoxide reagent.[10a-n] However, intermolecular carbon-carbon coupling in phenols has not been described using potassium *tert*-butoxide. Here phenyl naphthalenols **31** and **32** are produced in 15 and 20% yields respectively.

Table 4. Coupling of aryl alcohol with substituted bromobenzene



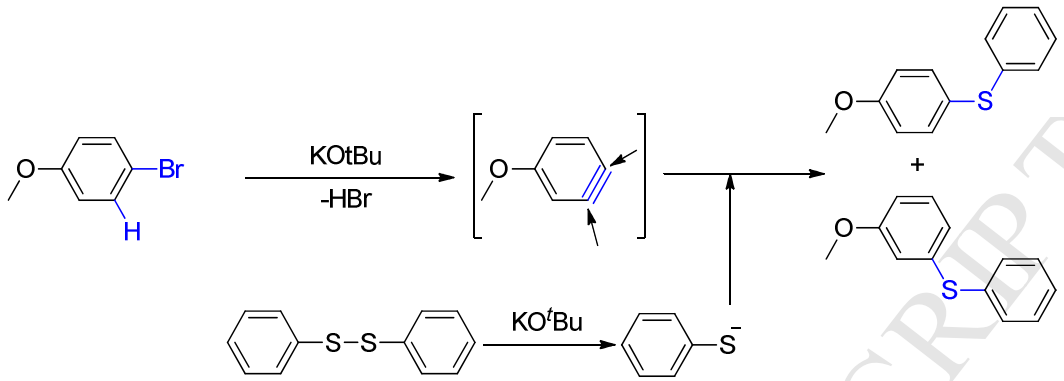
Entry	Bromoarene	Product (**a**)	Product (**b**)	Yield (%)[a]
1[b]			--	**33** (72)
2[b]			--	**34** (80)
3[c]				**35a/35b** (1:1) (59)
4[c]				**36a/36b** (5:3) (53)
5[c]				**37a/37b** (5:3) (56)
6[c]				**37b/38** (5:3) (57)

[a] Isolated yields of ethers are based on the respective phenols used in the reaction. [b] Phenol was used. [c] β-Naphthol was used

After studying various substituted phenols in the potassium *tert*-butoxide mediated carbon-oxygen coupling reaction, we explored substituted bromobenzenes. Nitro-substituted bromobenzenes gave only one product regioselectively and quantitative yields (72 and 80%) of nitro-substituted diphenyl ethers **33** and **34** were obtained (Table 4). Reaction of substituted bromobenzenes such as 4-methoxy-bromobenzene, 1-Bromo-4-(trifluoromethyl)benzene, 1-bromo-4-chlorobenzene, 1-bromo-2-methylbenzene, and 1-bromo-4-methylbenzene gave a mixture of regioisomeric products together with side products when reacted with the phenol. Purification of products was noticed to be difficult despite applying mild reaction conditions when substituted bromobenzenes were used in the C-O coupling reaction with phenol. However, substituted bromobenzens reacted smoothly with β-naphthol and produced a mixture of products and the formation of other side products was not observed (entries 3-6, Table 4).

Mechanism: Recently, a radical mechanism for the KO^{t}Bu mediated carbon-carbon coupling reaction has been suggested by us and others in which carbon-halogen and carbon-hydrogen bonds are involved.[10,11d] In the present C-E coupling reaction, it is very unlikely that reaction proceeds via radical pathway. Instead, reaction proceeds by another pathway in which benzyne intermediate forms in the potassium *tert*-butoxide mediated reaction and is very similar to previously reported mechanism by Yang and Xu et al.[8b] The formation of two regioisomers from para substituted bromobenzene could be well correlated by the formation of benzyne intermediate (Scheme 3).

Scheme 3. Proposed reaction pathway for KO^{t}Bu mediated C-E coupling



It seems that diaryl disulfide/ diselenide is equivalent to phenol in the potassium *tert*-butoxide mediated C-E coupling reaction as both substrates gave respective thioether and selenoether when reacted with bromobenzene.[8b]

It is worth comparing the reactivities of diphenyl disulfide, diselenide, and phenol in the potassium *tert*-butoxide carbon-chalcogen coupling reaction. Diphenyl disulfide and diselenide reacted with bromobenzene at 80 ^{o}C (Scheme 1, Table 2) whereas phenols reacted at 40-45 ^{o}C. Coupling of disulfide and diselenide with bromobenzene was not completed at 40-45 ^{o}C even in the presence of excess of KO^{t}Bu. Also increase in reaction time from 4 to 24 h failed to provide the satisfactory yield of diaryl sulfide and selenide. Although, difference between the reactivities of disulfide and diselenide is not substantial with respect to reaction time, however, disulfide reacts slightly in short time as compared to diselenide.

It may be worth comparing the reactivity of KO^{t}Bu with other bases. Other bases such as K_2CO_3, Cs_2CO_3, and K_3PO_4 were noticed to be ineffective in the C-S coupling reaction. Also sodium and potassium-hydroxides produced less yield of C-S coupled product which could be due to the formation of trace amount of water by the reaction of KOH and bromobenzene. This is well explained by Xu et al.[8b] Another reason could be more solubility of potassium *tert*-butoxide in DMSO.[8b] Another possibility in which methylsulfinylmethyl

anion ($CH_3S(O)CH_2^-$) was formed by the reaction of KO^{t}Bu with DMSO.[14] Methylsulfinylmethyl anion (pKa = 35.1) is a stronger base than the KO^{t}Bu (32.2). This could be another reason for the high reactivity of potassium *tert*-butoxide in DMSO for the formation of carbon-chalcogen bond. Thus, the better solubility of potassium *tert*-butoxide in DMSO, absence of trace of H_2O, and generation of methylsulfinyl anion could make this base superior over the other bases in C-E coupling reactions.

Conclusion

In summary, we have shown that potassium *tert*-butoxide can be used for the synthesis of unsymmetrical diaryl sulfides and selenides by using diaryl disulfides and bromobenzene at 80 ^{o}C. A series of unsymmetrical diaryl sulfides and selenides have been synthesized in 2-4 h without adding any transition metal and or ligand in the reaction. Also the synthesis of unsymmetrical diaryl ethers has been achieved at 40-45 ^{o}C in 4-6 h. It seems that reaction proceeds via the formation of benzyne intermediate from bromobenzene as the reaction gives two regioisomers when studied with substituted bromobenzene. Coupling of benzyne with in-situ formed phenolate, thiolate, and selenolate would lead to the formation carbon-chalcogen bond.

General Methods

Dimethyl formamide and dimethyl sulfoxide with seal septa were used as received from Aldrich. Potassium *tert*-butoxide (98% purity) was purchased from SPECTROCHEM Pvt. Ltd. used as purchased and stored under desiccator. Room temperature refers to 40-45 ^{o}C. Reactions were conducted in 10 mL round bottom flask with glass stopper. Silica gel (100-200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{13}C DEPT-135

(100 MHz), and ^{77}Se NMR (76 MHz) spectra were recorded on a FT NMR spectrometer and referenced to solvent DMSO or $CDCl_3$ peak.

A typical procedure for C-S/ Se coupling: DMSO (1 mL) was added to a single neck flask (10 mL) containing stirrer bar. To this flask, diphenyl disulfide (109 mg, 0.5 mmol) and bromobenzene (157 mg, 1.0 mmol). After this, KO^{t}Bu (140 mg, 1.25 mmol) was added portion wise and resulted reaction mixture was stirred at 40-45 ^{o}C for 15 min and then heated at 80 °C. Progress of reaction was monitored by TLC. Upon completion of the reaction (2-4 h), the mixture was cooled to room temperature, poured into water, and extracted four times with 20 mL of ethyl acetate. The combined organic layers were dried over Na_2SO_4, and filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate) to afford the coupling product.

Diphenylsulfane (1):[5f] R_f 0.60 (100% hexane), colourless oil, yield 0.16 g (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 4 H), 7.4 (t, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 131.2, 129.3, 127.2; IR (film) ν cm^{-1} 3051, 1579, 1467, 1242, 1023, 740; GC/MS (EI): rt = 6.38 min, *m/z* = 186.

4-Methoxyphenyl(phenyl)sulfane (2):[5a] R_f 0.43 (100% hexane), colourless oil, yield 0.17 g (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.17 – 7.11 (m, 3H), 6.88 (sextet, *J* = 1.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 138.6, 135.4, 128.9, 128.2, 125.8, 124.3, 115.0, 55.38; IR (film) ν cm^{-1} 3030, 2948, 1592, 1592, 1493, 1288, 1031, 827, 739, 690; GC/MS (EI): rt = 7.48 min, *m/z* = 216.

Phenyl(p-tolyl)sulfane (3):[5a] R_f 0.61 (100% hexane), colourless oil, yield 0.17 g (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 2H), 7.26 (d, *J* = 1.7 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

137.6, 137.2, 132.3, 131.3, 130.1, 129.8, 129.1, 126.4, 21.2; IR (film) ν cm^{-1} 3059, 3021, 2922, 1582, 1492, 1083, 809, 739, 690; GC/MS (EI): rt = 6.86 min, *m/z* = 200.

2-(Phenylthio)aniline (4):[15] R_f 0.60 (9.5:0.5 hexane: ethyl acetate), dark yellow-green, yield 0.17 (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.25(m, 3H), 7,16 - 7.11 (m, 3H), 6.85 - 6.78 (m, 2H), 4.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.4, 136.7, 131.1, 129.0, 126.6, 125.5, 190.0, 115.6, 114.8; IR (film) ν cm^{-1} 3465, 3367, 3055, 2919, 1607, 1477, 739; HRMS (APCI) *m/z* 202.0685, calcd for $C_{12}H_{11}S$ + H: 202.0679.

Diphenylselane (5):[5f] R_f 0.54 (100% hexane), colourless oil, yield 0.21 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 -7.45 (m, 4H), 7.27 7.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 131.1, 129.3, 127.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 416.3; IR (film) ν cm^{-1} 3052, 2937, 2834, 1590, 1476, 1246, 1033, 828, 739, 689; GC/MS (EI): rt = 6.66 min, *m/z* = 234.

Phenyl(p-tolyl)sulfane (3)[5f] **and Phenyl(m-tolyl)sulfane (6b)**:[16] R_f 0.32 (100% hexane), colourless oil, yield 0.16 g (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m 11H), 7.21-7.11 (m, 6H), 7.06 (d, *J* = 7.1 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.6, 137.2, 136.2, 135.3, 132.3, 131.9, 131.3, 130.8, 130.1, 129.8, 129.2, 129.1, 128.4, 128.1, 127.6, 126.9, 126.4, 21.3, 21.2; IR (film) ν cm^{-1} 3057, 2921, 1582, 1491, 1439, 1082, 739, 689; GC/MS (EI): rt = 6.78, 6.87 min, *m/z* = 200.

(4-Methoxyphenyl)(phenyl)sulfane (2)[5a] **and (3-Methoxyphenyl)(phenyl)sulfane (7b)**:[17] R_f 0.27 (100% hexane), colourless oil, yield 0.17 g (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28-7.13 (m, 7H), 6.94-6.90 (m, 4H), 6.79 (dd, *J* = 8.3, 1.9Hz, 1H), 3.82(s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.9, 138.7, 137.3, 135.4, 135.3, 131.5, 130.0, 129.3, 129.0, 128.3, 127.3, 125.8, 124.4, 123.0,

116.0, 115.1, 112.8, 55.4, 55.3; IR (film) ν cm^{-1} 3052, 2937, 2834, 1590, 1476, 1246, 1033, 828, 739, 689; GC/MS (EI): rt = 7.36, 7.50 min, *m/z* = 216.

4-Methoxyphenyl)(phenyl)selane (8a)[5e] and 3-methoxyphenyl)(phenyl)selane (8b):[18] Ratio of **8a**/**8b** = 2/1, R_f 0.35 (100% hexane), yellow oil, yield 0.21 g (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 3H), 7.38 – 7.36 (m, 1H), 7.33-7.30 (m, 3H), 7.27- 7.20 (m, 3H), 7.07 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.04 (t, *J* = 2.2 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.85-6.82 (m, 1H), 3.84 (s, 1.5 H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.8, 136.6, 133.3, 132.3, 131.5, 130.9, 130.8, 130.1, 129.4, 129.2, 127.5, 126.5, 125.0, 120.0, 118.0, 115.2, 113.2, 55.3, 55.2; ^{77}Se NMR(76 MHz, $CDCl_3$) δ 420.3, 398.9; IR (film) ν cm^{-1} 3057, 3000, 2936, 1587, 1475, 1246, 1039, 826, 736, 688; GC/MS (EI): rt = 7.60, 7.74 min, *m/z* = 264.

Phenyl(3,5-(di-trifluoromethyl)phenyl)sulfane (9):[19] R_f 0.30 (100% hexane), colourless liquid, yield 0.18 g (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.58 (s, 2H), 7.50 (m, 2H), 7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 133.8, 133.5, 133.4, 133.1, 132.8, 132.4, 132.1, 132.0(m), 131.8, 131.2, 130.0, 129.3, 127.8(m), 127.1, 124.4, 123.8, 123.4, 121.6, 121.2(m), 121.1(m), 119.6(m), 118.9; IR (film) ν cm^{-1} 3080, 1793, 1616, 1599, , 1477, 1352, 1278, 1180, 1139, 885, 749; HRMS (APCI) *m/z* 322.0245, calcd for $C_{14}H_8F_6S$: 322.0231.

Phenyl(3,5-(di-trifluoromethyl)phenyl)selane (10):[19] R_f 0.4 (100% hexane), colourless liquid, yield 0.19 g (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.68 (s, 1H), 7.60 – 7.57 (m, 2H), 7.43 – 7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.0(t), 132.7, 132.4, 132.1, 131.7, 130.6(m), 130.1, 129.2, 127.7, 127.0, 124.3, 121.6, 120.4(m), 118.9; 77Se NMR (76 MHz, $CDCl_3$) 438.8; IR (film) ν cm^{-1} 3077, 2927, 2855, 1801, 1617, 1595,

1578, 1477, 1440, 1349, 1278, 1178, 1140, 885, 741; HRMS (APCI) *m/z* 369.9690, calcd for $C_{14}H_8F_6Se$: 369.9682.

Naphthalen-2-yl(phenyl)sulfane (11a)[5a,f] and naphthalen-1-yl(phenyl)sulfane (11b): R_f 0.38 (100% hexane), yellowish oil, yield 0.18 g (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47-8.45 (m, 1H), 7.93-7.72 (m, 7H), 7.57-7.54 (m, 8H), 7.37-7.17 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.0, 134.3, 133.9, 133.7, 133.1, 132.7, 132.4, 131.3, 131.1, 130.0, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.7, 127.9, 127.5, 127.2, 127.1, 126.7, 126.5, 126.3, 126.2, 125.9, 125.7; IR (film) ν cm^{-1} 3055, 1579, 1476, 1256, 1023, 740; GC/MS (EI): rt = 11.42, 11.4 min, *m/z* = 236.

Naphthalen-2-yl(phenyl)selane (12a) and naphthalen-1-yl(phenyl)selane (12b):[5a,f,20] R_f 0.56 (100% hexane), colourless liquid, yield 0.24 g (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.43 (m, 1H), 8.07 (s, 1H), 7.91-7.89 (m, 2H), 7.85 (d, *J* = 6.4Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.61-7.56 (m, 5H), 7.53-7.51 (m, 2H), 7.45-7.40 (m, 3H), 7.33 (t, *J* = 3.0Hz, 2H), 7.25 (t, *J* = 3.2 Hz, 4H); δ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 134.2, 134.1, 134.0, 133.0, 132.5, 132.2, 131.9, 131.8, 131.4, 130.6, 129.6, 129.5, 129.4, 129.3, 128.9, 128.7, 128.6, 127.9, 127.8, 127.6, 127.5, 127.1, 126.9, 126.7, 126.5, 126.4, 126.2; IR (film) ν cm^{-1} 3050, 1579, 1486, 1196, 1033, 742. GC/MS (EI): rt = 9.45, 9.72 min, *m/z* = 283.9.

2-Nitrophenyl)(phenyl)sulfane (13):[5a] R_f 0.50(100% hexane); yellow solid, yield 0.21 g (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.56 (m 2H), 7.50-7.44(m, 3H), 7.32 (m, 1H), 7.19 (m, 1H), 6.85 (dd, *J* = 8.2, 0.9 Hz, 1H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.5, 135.9, 133.4, 131.0, 130.1, 130.0, 128.3, 125.7, 125.0; IR (film) ν cm^{-1} 3061, 1926, 1591, 1567, 1337, 733; GC/MS (EI): rt = 8.38 min, *m/z* = 231.

2-Nitrophenyl)(phenyl)selane (14):[5a] R_f 0.34 (8:2 hexane : ethyl acetate); yellow solid, Yield 0.24 g (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.52 7.43 (m, 3H), 7.31-7.23 (m, 2H), 6.98 (d, *J* = 7.6Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 137.4, 135.9, 133.7, 130.3, 130.1, 129.9, 128.2, 126.1, 125.8. ^{77}Se NMR(76 MHz, $CDCl_3$) δ 485.6; IR (film) ν cm^{-1} 3061, 2926, 1591, 1516, 1475, 1337, 1250, 733; GC/MS (EI): rt = 8.84 min, *m/z* = 278.9.

4-Methoxyphenyl)(2-nitrophenyl)sulfane (15):[21] R_f 0.40 (8:2 hexane : ethyl acetate); yellow solid, yield 0.20 g (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.49-7.45 (m, 2H), 7.33-7.29(m, 1H), 7.18-7.14 (m, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.81 (dd, *J* = 8.2, 1 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 144.6, 140.7, 137.7, 133.4, 127.9, 125.7, 124.7, 121.2, 115.8, 55.5; IR (film) ν cm^{-1} 3020, 2927, 2854, 1592, 1455, 1204, 1036; GC/MS (EI): rt = 10.22 min, *m/z* = 260.9.

4-Nitrophenyl)(phenyl)sulfane (16):[5a] R_f 0.52 (9.5:0.5 hexane : ethyl acetate); yellow oil, yield 0.19 g (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.54-7.51 (m, 2H), 7.46-7.43(m, 3H), 7.16 (d, *J* = 9.0 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 145.4, 134.8, 130.5, 130.1, 129.7, 126.7, 124.0. IR (film) ν cm^{-1} 3063, 2915, 1574, 1515, 1475, 1083, 852, 740, HRMS-APCI *m/z*: 232.0427 (calculated for $C_{12}H_9NO_2S$: 232.0430).

4-Nitrophenyl)(phenyl)selane (17):[5a] R_f 0.50 (9.5:0.5 hexane : ethyl acetate), yellow oil, yield 0.22 g (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.62-7.60 (m, 2H), 7.45-7.35 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 144.0, 135.9(t), 130.1, 129.7(t), 129.4, 127.2, 124.0; ^{77}Se NMR(76 MHz, $CDCl_3$) δ 440.5; IR

(film) ν cm^{-1} 3060, 2923, 1595, 1574, 1060, 850, 737, 691; HRMS-APCI *m/z*: 279.9872 (calculated for $C_{12}H_9NO_2$ ^{80}Se: 279.9854).

2-Nitro-4-methyl-phenyl(phenyl)sulfane (18):[15] R_f 0.48 (9.5:0.5 hexane : ethyl acetate), yellow oil, yield 0.14 g (60%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01(s, 1H), 7.56-7.54 (m, 2H), 7.45-7.43 (m, 3H), 7.13 (dd, *J* = 8.4, 1.4, 1H), 6.75 (d, *J* = 8.4Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 135.8, 135.7, 135.5, 134.5, 131.5, 130.0, 129.7, 128.5, 125.8, 20.4; IR (film) ν cm^{-1} 3054, 2914, 1518, 1329, 1290, 1199, 751; GC/MS (EI): rt = 8.96 min, *m/z* = 244.9

2-Nitro-4-methyl-phenyl(phenyl)selane (19): R_f 0.46 (9.5:0.5 hexane: ethyl acetate), yellow oil, yield 0.16g (57%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.69-6.67 (m, 2H), 7.50-7.41 (m, 3H), 7.11 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.85(d, *J* = 8.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.4, 136.2, 134.9, 132.1, 130.1, 130.0, 129.7, 128.4, 126.1, 20.5; ^{77}Se NMR(76 MHz, $CDCl_3$) δ 478.5; IR (film) ν cm^{-1} 3059, 2918, 1518, 1340, 1199, 1024, 739; HRMS-APCI *m/z*: 292.9950 (calculated for $C_{13}H_{11}NO_2$ ^{80}Se: 292.9938).

A general procedure for C-O coupling: Phenol (94 mg, 1 mmol) and bromobenzene (314 mg, 2.0 mmol) were added to a single necked flask containing DMSO (1 mL) and resulted reaction mixture was stirrer for 5 min. After this potassium *tert*-butoxide (280 mg, 2.5 mmol) was added portion wise and stirring continued for 6-8 h at 40-45 ^oC. The progress of reaction was monitored by TLC. Upon completion of the reaction, mixture poured into water, and extracted four times with 20 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4, and filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, eluent: hexane/ ethyl acetate) to afford the coupling product.

Oxydibenzene (20):[13g] R_f 0.62 (100% hexane), colourless liquid, yield 0.16 g (96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 4H), 7.18-7.14 (m, 2H), 7.09-7.06 (m 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 129.8, 123.2, 118.9; IR (film) ν cm^{-1} 3042, 2960, 1586, 1490, 1012; GC/MS (EI): rt = 5.51 min, *m/z* = 170.1.

1-Bromo-2-phenoxybenzene (21):[22] R_f 0.39 (100% hexane), white solid, yield 0.15 g (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* =7.9 Hz, 1.6 Hz, 1H), 7.39-7.34 (m, 2H), 7.31-7.27 (m, 1H), 7.16-7.12 (m, 1H), 7.05 (dd, *J* = 7.5 Hz, 1.5Hz, 1H), 7.03-6.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 153.7, 133.8, 129.8, 128.7, 125.0, 123.4, 120.6, 118.1, 114.9; IR (film) ν cm^{-1} 2964, 1577, 1261, 1029, 797; GC/MS (EI): rt = 6.66 min, *m/z* = 247.9, 249.9.

1-Bromo-4-phenoxybenzene (22):[23] R_f 0.39 (100% hexane), colourless, yield 0.14 g (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.26-7.21 (m, 2H), 7.04-7.00 (m, 1H), 6.90-6.88 (m, 2H), 6.79-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.4, 132.7, 129.9, 123.7, 120.4, 119.0, 115.6; IR (film) ν cm^{-1} 3067, 2925, 1578, 1481, 1236, 752; GC/MS (EI): rt = 6.79 min, *m/z* = 248, 250.

1-Fluoro-4-phenoxybenzene (23):[13g] R_f 0.38 (100% hexane), colourless dense oil, yield 0.12g (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.16-7.11 (m, 1H), 7.10-7.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.7, 157.6, 153.0, 152.9, 129.8, 123.1, 120.6, 120.5, 118.3, 116.4, 116.2; IR (film) ν cm^{-1} 3060, 2925, 1571, 1481, 1236, 755; GC/MS (EI): rt = 5.47 min, *m/z* = 188.1.

1-Methyl-2-phenoxybenzene (24):[24] R_f 0.40 (100% hexane), colourless liquid, yield 0.14g (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 3H), 7.22-7.18 (m, 1H), 7.127.06 (m,

2H), 6.95-6.93 (m, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9,154.5, 131.4, 130.0, 129.7, 127.1, 124.0, 122.3, 119.8, 117.3, 16.2; IR (film) ν cm^{-1} 3039, 2925, 1583, 1488, 1239, 874; GC/MS (EI): rt = 5.96 min, *m/z* = 184.1.

1-Methyl-3-phenoxybenzene (25):[25] R_f 0.37 (100% hexane), mp = 20 ^oC, colorless liquid which is solid at 0 ^oC, yield 0.14 g (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.16-7.13 (m, 1H), 7.08-7.05 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.90-6.86 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.2, 139.9, 129.7, 129.5, 124.1, 123.1, 119.6, 118.9, 115.9, 21.4; IR (film) ν cm^{-1} 3039, 2920, 1584, 1487, 1256, 1216, 936; GC/MS (EI): rt = 5.94 min, *m/z* = 184.2.

1-(*tert*-Butyl)-4-phenoxybenzene (26):[13g] R_f 0.56 (100% hexane), white solid, yield 0.18 g (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 4H), 7.15-7.11 (m, 1H), 7.08-7.05 (m, 2H), 7.02-6.99 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 154.8, 146.1, 129.7, 126.6, 122.9, 118.7, 118.5, 34.3, 31.5; IR (film) ν cm^{-1} 3040, 2963, 1905, 1589, 1488, 1238, 1170, 753; GC/MS (EI): rt = 6.92 min, *m/z* = 226.2.

1-Methoxy-4-phenoxybenzene (27):[13g] R_f 0.46 (100% hexane), colourless liquid, yield 0.15 g (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.02-6.96 (m, 4H), 6.93-6.89 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5,155.9, 150.1, 129.6, 122.4, 120.8, 117.6, 114.9, 55.7; IR (film) ν cm^{-1} 3040, 2952, 1590, 1505, 1489, 1225, 1186, 841; GC/MS (EI): rt = 6.55 min, *m/z* = 200.1.

4-Phenoxybenzonitrile (28):[13t] R_f 0.40 (100% hexane), white solid, yield 0.12 g (64%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.29 (bs, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.05 (dd, *J* = 29.6, 8.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-

d_6) δ 167.6, 159.9, 156.1, 130.7, 130.1, 129.5, 124.7, 119.9, 117.7; IR (film) ν cm^{-1} 3028, 2974, 2250, 1580, 1470, 1253, 753; GC/MS (EI): rt = 6.99 min, *m/z* = 195.

2-Phenoxynaphthalene (29):[26] R_f 0.48 (9:2 hexane: ethyl acetate), white solid, yield 0.18 g (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.60 (d, *J* = 8.2Hz, 1H), 7.36 (dd, *J* = 6.8 Hz, 1.3 Hz, 1H), 7.32 (dd, *J* = 4.8 Hz, 1.5 Hz, 1H), 7.30-7.28 (m, 1H), 7.27-7.24 (m, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 8.9 Hz, 2.5 Hz, 1H), 7.06-7.02 (m, 1H), 6.99-6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.1, 134.5, 130.2, 129.9, 129.8, 127.7, 127.2, 126.5, 124.7, 123.5, 120.0, 119.2, 114.1; IR (film) ν cm^{-1} 3050, 1588, 1488, 1249, 1222, 807; GC/MS (EI): rt = 8.01 min, *m/z* = 220.1.

1-Phenoxynaphthalene (30):[26] R_f 0.46 (9:2 hexane: ethyl acetate), white solid, yield 0.18 g (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 8.91 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.58-7.50 (m, 2H), 7.43-736 (m, 3H), 7.16-7.13 (m, 1H), 7.08 (dd, *J* = 8.7 Hz, 1 Hz, 2H), 6.99 (d *J* = 7.5Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9,153.0, 135.0, 129.8, 127.8, 126.9, 126.6, 125.9, 125.8, 123.4, 123.1, 122.1, 118.6, 113.5; IR (film) ν cm^{-}1 3055, 2925, 1594, 1574, 1488, 1392, 1210, 772; GC/MS (EI): rt = 8.81 min, *m/z* = 220.1.

2-Phenylnaphthalen-1-ol (31):[27] R_f 0.37 (100% hexane), colourless liquid, yield 30 mg (15%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (t, *J* = 4.9 Hz, 1H), 7.87-7.84(m, 1H), 7.58 (d, *J* = 4.3 Hz, 4H), 7.55- 7.53 (m, 2H), 7.51 (s, 1H), 7.47 (m 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 5.87 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 137.4, 134.2, 129.6,129.4, 127.9, 127.6, 127.5, 126.5, 125.6, 124.3, 122.3, 122.4, 120.2; IR (film) ν cm^{-1} 3560, 3055, 2925, 1594, 1574, 1488, 1392, 1234, 1080, 772; GC/MS (EI): rt = 8.81 min, *m/z* = 220.1.

4-Methoxy-2-phenylnaphthalen-1-ol (32):[28] R_f 0.39 (100% hexane), colourless solid, yield 40 mg (20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (m, 2H), 7.56 – 7.51 (m,6H), 7.44 – 7.41 (m, 1H), 6.69 (s, 1H), 5.46 (bs, 1H) 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 141.5, 137.9, 129.6, 129.4, 127.9, 126.2, 125.9, 126.8, 125.2, 122.2, 121.8, 120.2, 106.6, 55.8; IR (film) ν cm^{-1} 3410, 3068, 2925, 1664, 1597, 1305, 1249, 759; GC/MS (EI): rt = 9.16 min, *m/z* = 249.9.

1-Nitro-2-phenoxybenzene (33):[29] R_f 0.43 (100% hexane), yellow solid**,** yield 0.15 g (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.50-7.46 (m, 1H), 7.37 (t, *J* = 8.4Hz, 2H), 7.19 – 7.16 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.8, 134.1, 130.1, 125.7, 124.6, 123.11, 120.5, 119.3, 111.8; IR (film) ν cm^{-1} 2918, 2852, 1588, 1346, 742; GC/MS (EI): rt = 7.28 min, *m/z* = 215.

1-Nitro-4-phenoxybenzene (34):[13g,t] R_f 0.42 (100% hexane), yellow solid**,** yield 0.17 g, (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 7.44-7.40 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.1 (d, *J* = 7.6 Hz, 2H), 7.01 – 6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 154.7, 142.6, 130.3, 125.9, 125.4, 120.5, 117.1; IR (film) ν cm^{-1} 2956, 2910, 1566, 1408, 846; GC/MS (EI): rt = 7.57 min, *m/z* = 215.

2-(4-(Trifluoromethyl)phenoxy)naphthalene (35a) and 2-(3-(trifluoromethyl)phenoxy)naphthalene (35b). R_f 0.23 (100% hexane), liquid, yield 0.17 g (59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 4H), 7.76 – 7.73 (m, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.51 – 7.42 (m, 6H), 7.37 (m, 2H), 7.31(s, 1H), 7.26 (d, J = 2.3Hz, 1H), 7.24 – 7.20 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.9, 153.9, 153.5, 134.4, 134.3, 130.8, 130.6, 130.3, 127.8 (d), 127.3 (d), 127.2 (d), 126.8 (d), 125.3 (d), 121.8, 120.2, 120.0, 119.8 (d), 118.1, 115.9, 115.5(m), 115.2; IR (film) ν cm^{-1} 3059, 1616,

1596, 1325, 1124, 964, 840; HRMS (GC): rt = 4.387 min, *m/z* = 288.0767 (calculated for $C_{17}H_{11}F_3O$ = 288.0769)

2-(4-Chlorophenoxy)naphthalene (36a) and 2-(3-chlorophenoxy)naphthalene (36b). R_f 0.27 (100% hexane), liquid, yield 0.13 g (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82(m, 4H), 7.72(t, J = 9.1Hz, 2H), 7.43 (m, 4H), 7.37 (d, J = 2.1Hz, 1H), 7.33 – 7.30 (3H), 7.26 – 7.22 (m, 3H), 7.10 (m, 1H), 7.05 (t, J = 2.0Hz, 1H), 7.00 (m, 2H), 6.95 (dd, J = 8.3, 1.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 155.9, 154.7, 154.1, 135.2, 134.3, 130.6, 130.5, 130.3, 130.2, 130.1, 129.8, 128.5, 127.8, 127.7, 127.3, 127.2, 126.7, 125.1, 125.0, 123.4, 120.3, 120.1, 119.8, 119.0, 116.9, 115.1, 114.3; IR (film) ν cm^{-1} 3058, 1633, 1586, 1485, 1248, 963, 810; HRMS (GC): rt =6.673 min, *m/z* = 254.0494 (calculated for $C_{16}H_{11}ClO$ = 2254.0496).

2-(o-Tolyloxy)naphthalene (37a) and 2-(m-tolyloxy)naphthalene (37b). R_f 0.30 (100% hexane), liquid, yield 0.13 g (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81(m, 3H), 7.70 (d, J = 8.6Hz, 1H), 7.64 (d, J = 8.3Hz, 1H), 7.47 – 7.35 (m, 3H), 7.31- 7.19 (m, 5H), 7.13 (d, J = 6.3Hz, 1H), 7.10 (d, J = 2.1Hz, 1H), 7.00 – 6.95 (m, 2H), 6.88 (m, 1H), 2.34 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.9, 155.2, 154.3, 140.0, 134.4, 131.6, 130.2, 130.1, 129.8, 129.7, 129.5, 127.8, 127.7, 127.3, 127.1, 127.0, 126.5(d), 124.6, 124.3, 124.2, 120.2, 120.1, 119.8, 119.1, 116.2, 114.1, 111.7, 21.4, 16.2; IR (film) ν cm^{-1} 3056, 1633, 1584, 1488, 1252, 1229, 963, 748; HRMS (GC): rt = 6.22 min, *m/z* = 234.1041 (calculated for $C_{17}H_{14}O$ = 234.1045).

2-(m-Tolyloxy)naphthalene (37b) and 2-(p-tolyloxy)naphthalene (38).[30] R_f 0.27 (100% hexane), liquid, yield 0.13 g (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 3H), 7.70(t, J = 8.1Hz, 2H), 7.47 – 7.37 (m, 3H), 7.33 (m, 1H), 7.26 (m, 4H), 7.18 (d, J = 8.1Hz, 1H), 7.01 – 6.96(m, 2H), 6.90 (m, 2H), 2.37 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 157.2, 155.2, 154.7, 140.1, 134.4, 133.8, 133.2, 130.4, 130.2, 129.8(d), 129.5, 127.7(d), 127.1(d), 126.5(d), 124.6, 124.5, 124.3, 120.1, 119.8(d), 119.4, 116.2, 114.1, 113.3, 21.4, 20.8; IR (film) ν cm^{-1} 3056, 1585, 1505, 1254, 1169, 963, 748; HRMS (GC): rt = 6.369 min, *m*/*z*:=234.1043 (calculated for $C_{17}H_{14}O$ = 234.1047).

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Graphical Abstract

Potassium *tert*-Butoxide-Mediated Synthesis of Unsymmetrical Diaryl Ethers, Sulfides, and Selenides from Aryl Bromides

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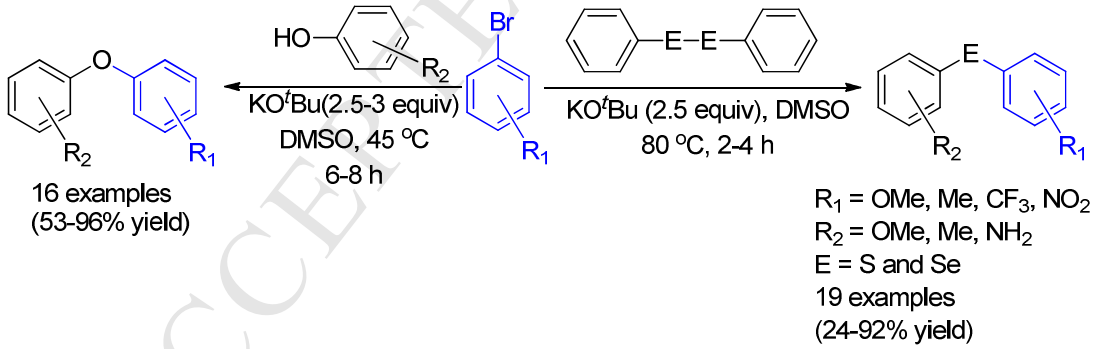
Abstract



Potassium *tert*-butoxide mediated carbon-chalcogen C-E (E = O, S, and Se) coupling reaction has been studied from aryl bromide and phenol/ aryl disulfide/ diselenide substrates. A series of unsymmetrical diaryl chalcogenides were accessed from aryl bromide and diaryl dichalcogenide precursors by using 2.5 equiv of potassium *tert*-butoxide in DMSO at 80 °C. Unsymmetrical diaryl ethers were also obtained by using phenol precursors at 45 °C. Aryl

bromides with methyl, trifluromethyl, methoxy, and nitro substitutents showed compatibility in the carbon-chalcogen bond forming reaction. 4-Methoxy, methyl, trifluoromethyl substituted bromobenzene substrates gave two regio-isomers: 3-substituted and 4-substituted diaryl chalcogenides when reacted with phenols/ diaryl disulfides/ diselenides. Formation of two regioisomeric diaryl chalcogenides in the reaction mixture suggests that potassium *tert*-butoxide reacts with bromobenzene to produce benzyne intermediate which subsequently reacts with diaryl dichalcogenides and finally give a regioisomeric mixture of 4-substituted and 3-substituted diaryl chalcogenides.

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S U P P L E M E N T A R Y M A T E R I A L

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B E L O N G I N G T O T H E P A P E R

Potassium *tert*-Butoxide-Mediated Synthesis of Unsymmetrical Diaryl Ethers, Sulfides, and Selenides from Aryl Bromides

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Figure S1 ^{1}H NMR spectrum of **1**

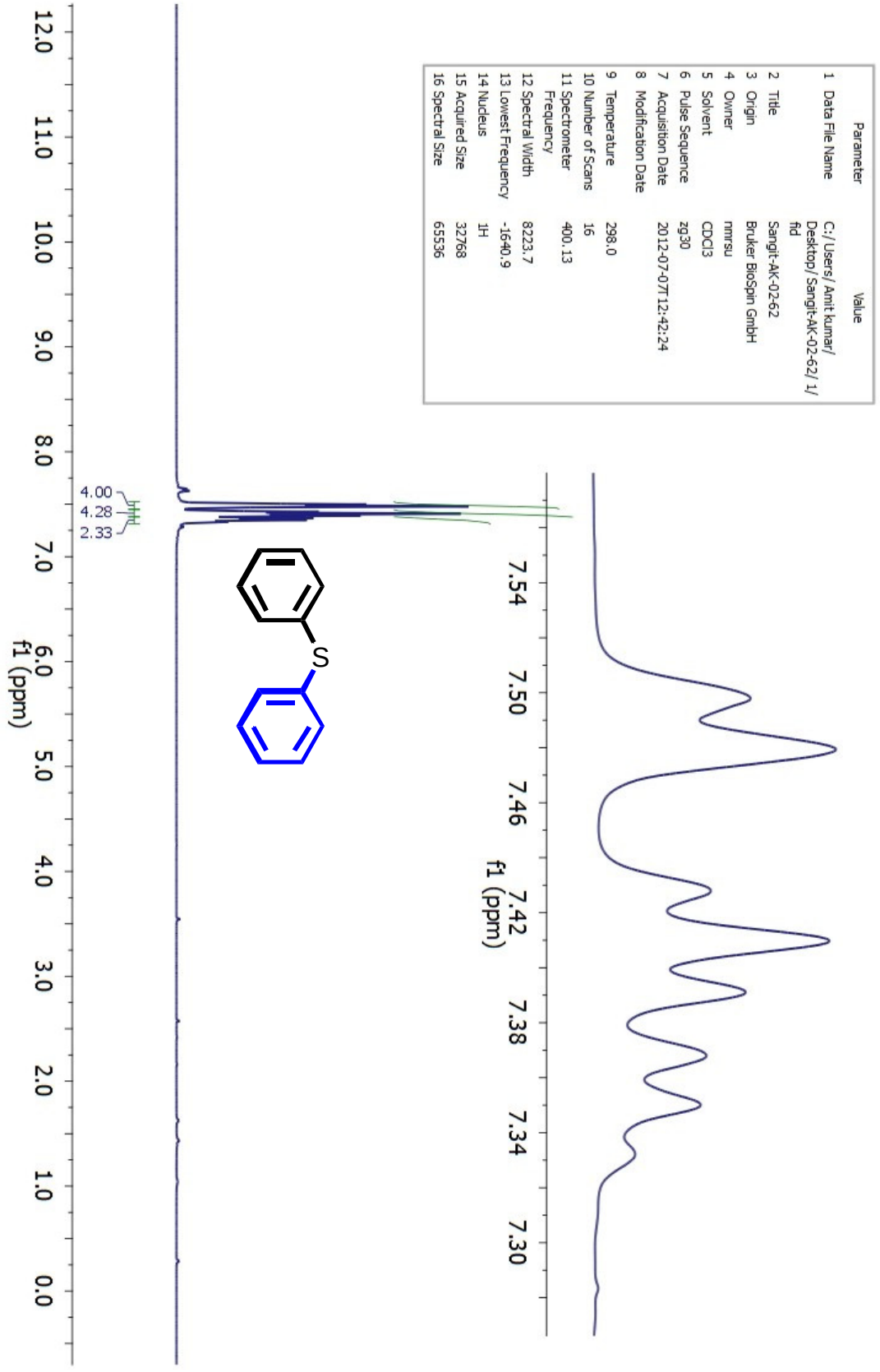

Figure S2 ^{13}C NMR spectrum of **1**

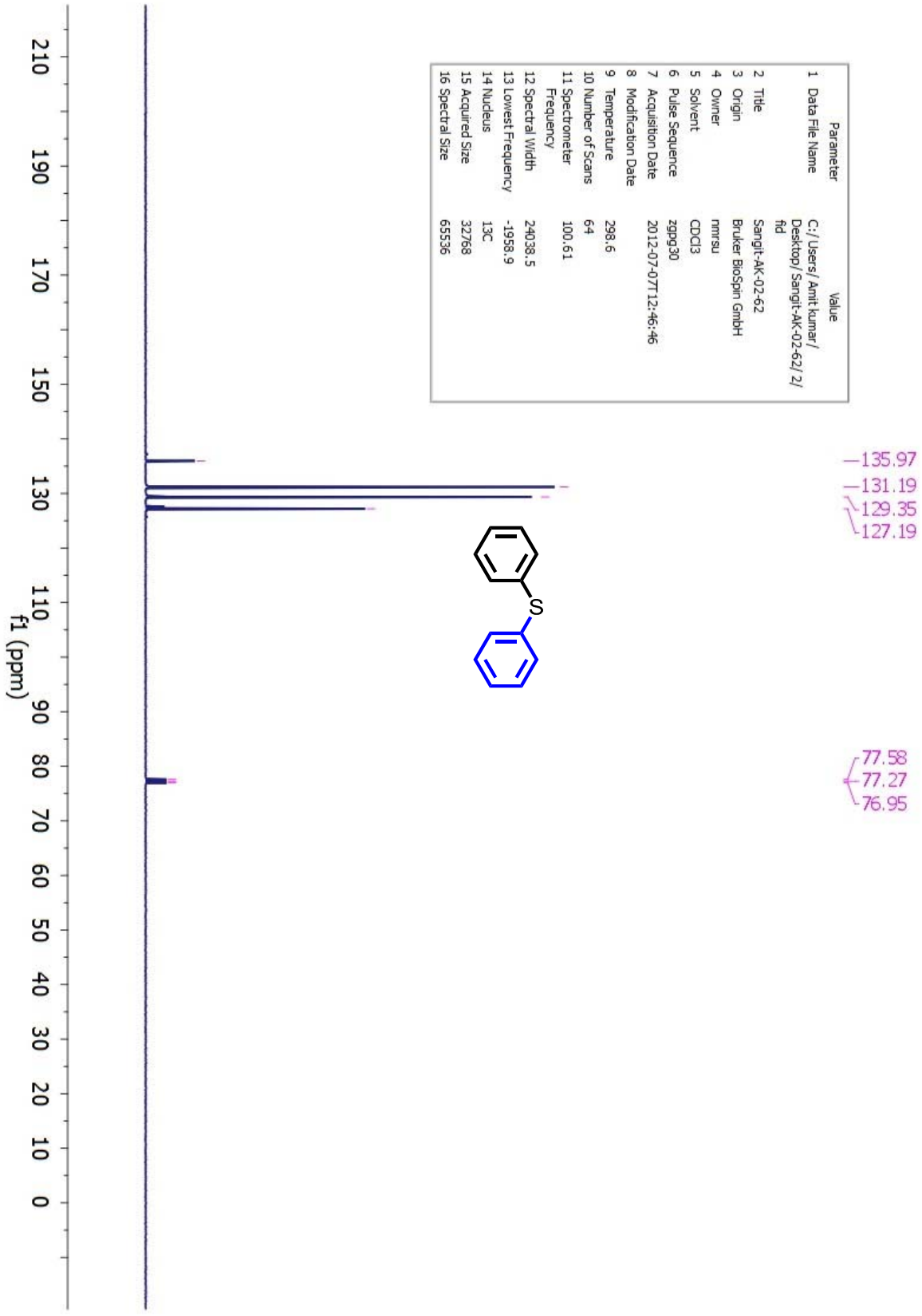

Figure S3 DEPT- 135 NMR spectrum of **1**

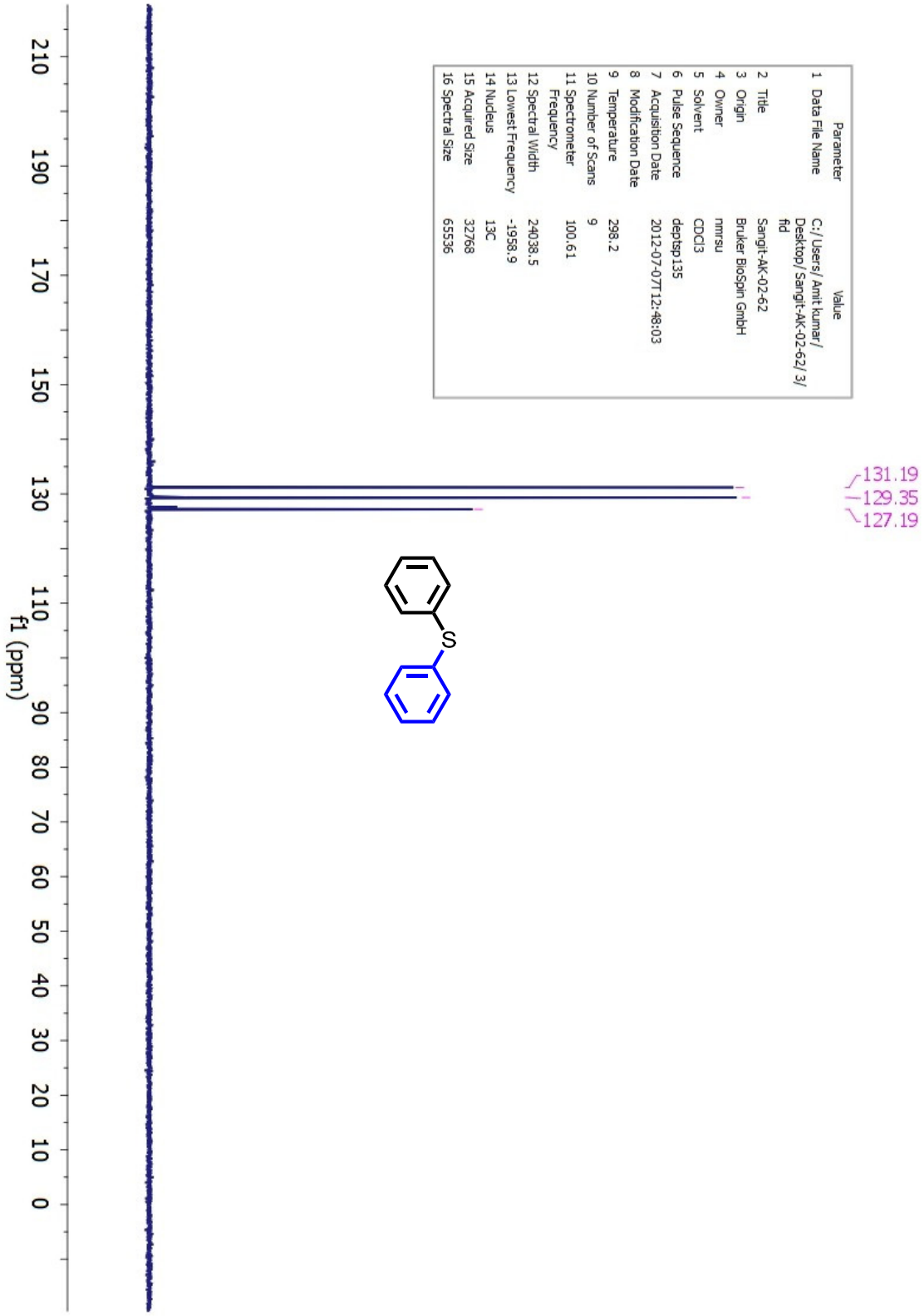

Figure S4 ^{1}H NMR spectrum of **2**

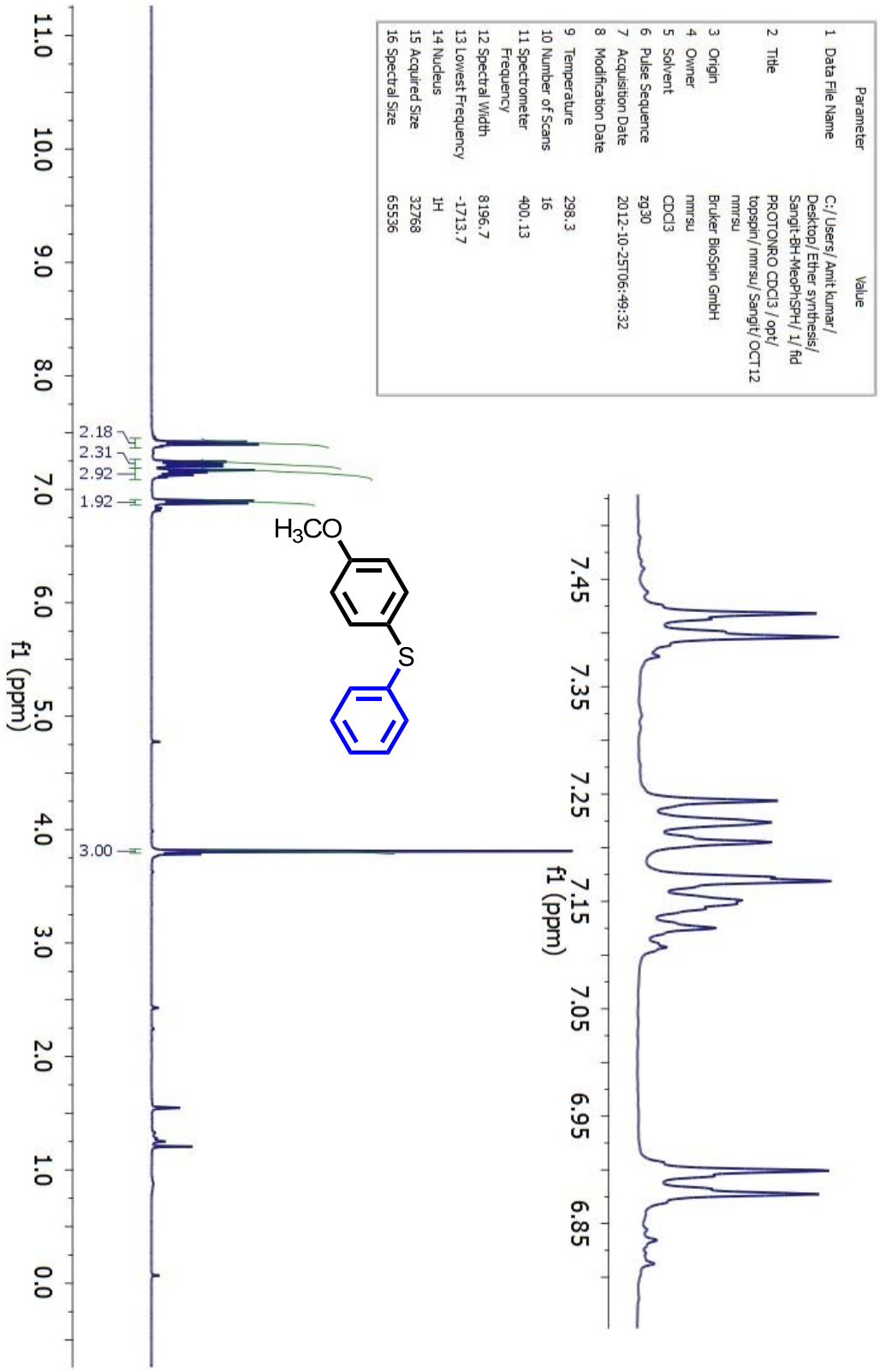

Figure S5 ^{13}C NMR spectrum of **2**

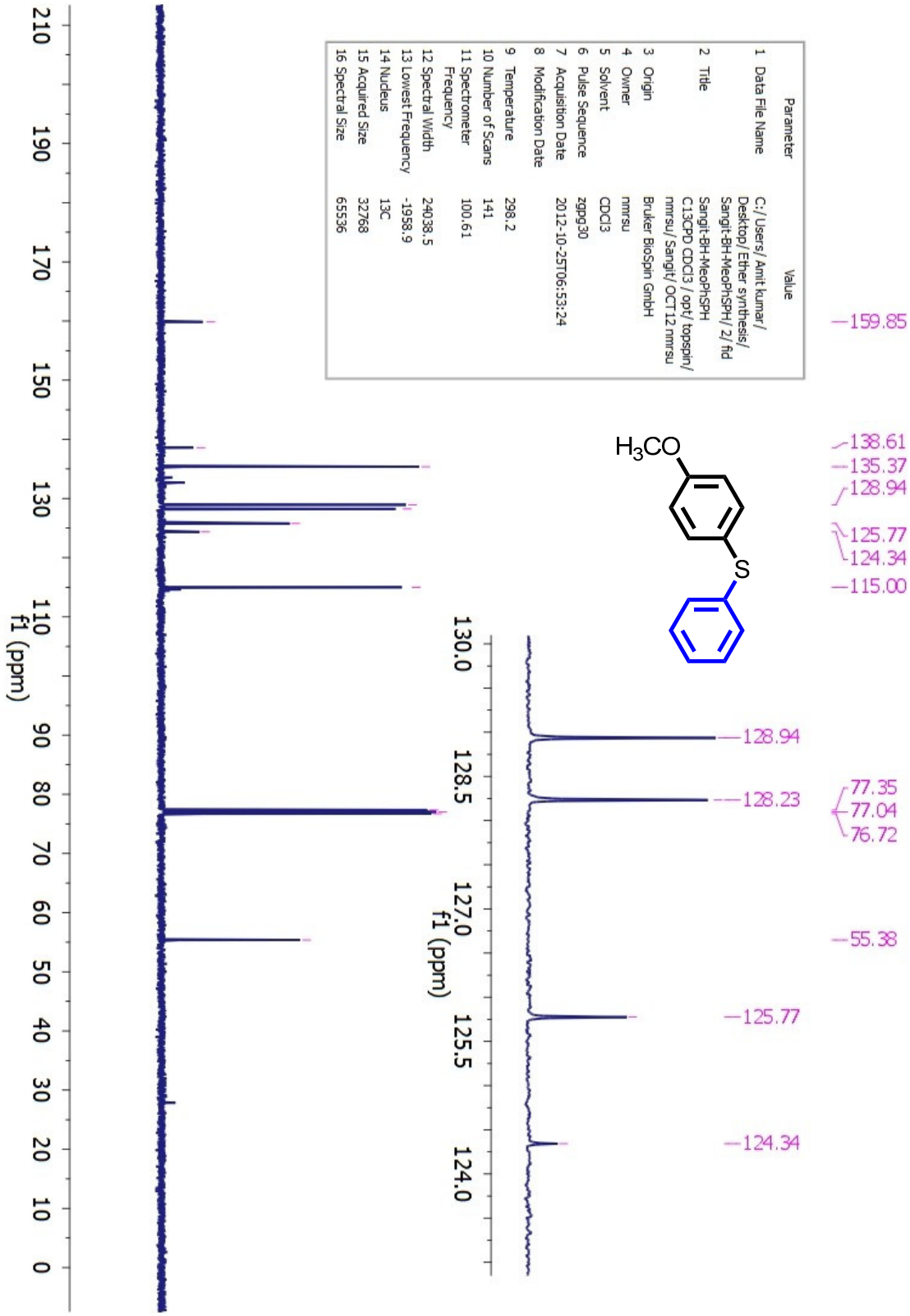

Figure S6 DEPT- 135 NMR spectrum of **2**

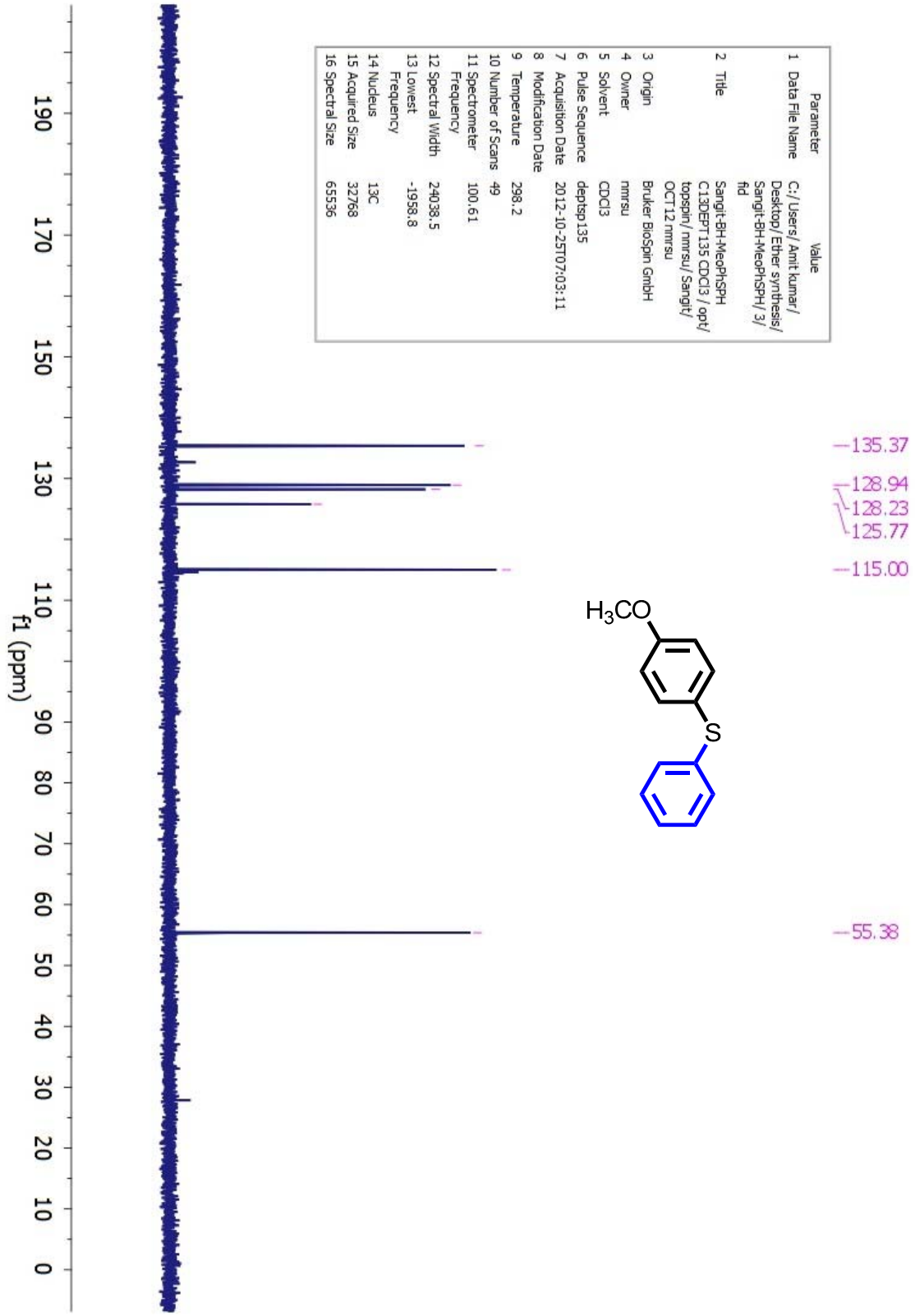

Figure S7 ^{1}H NMR spectrum of **3**

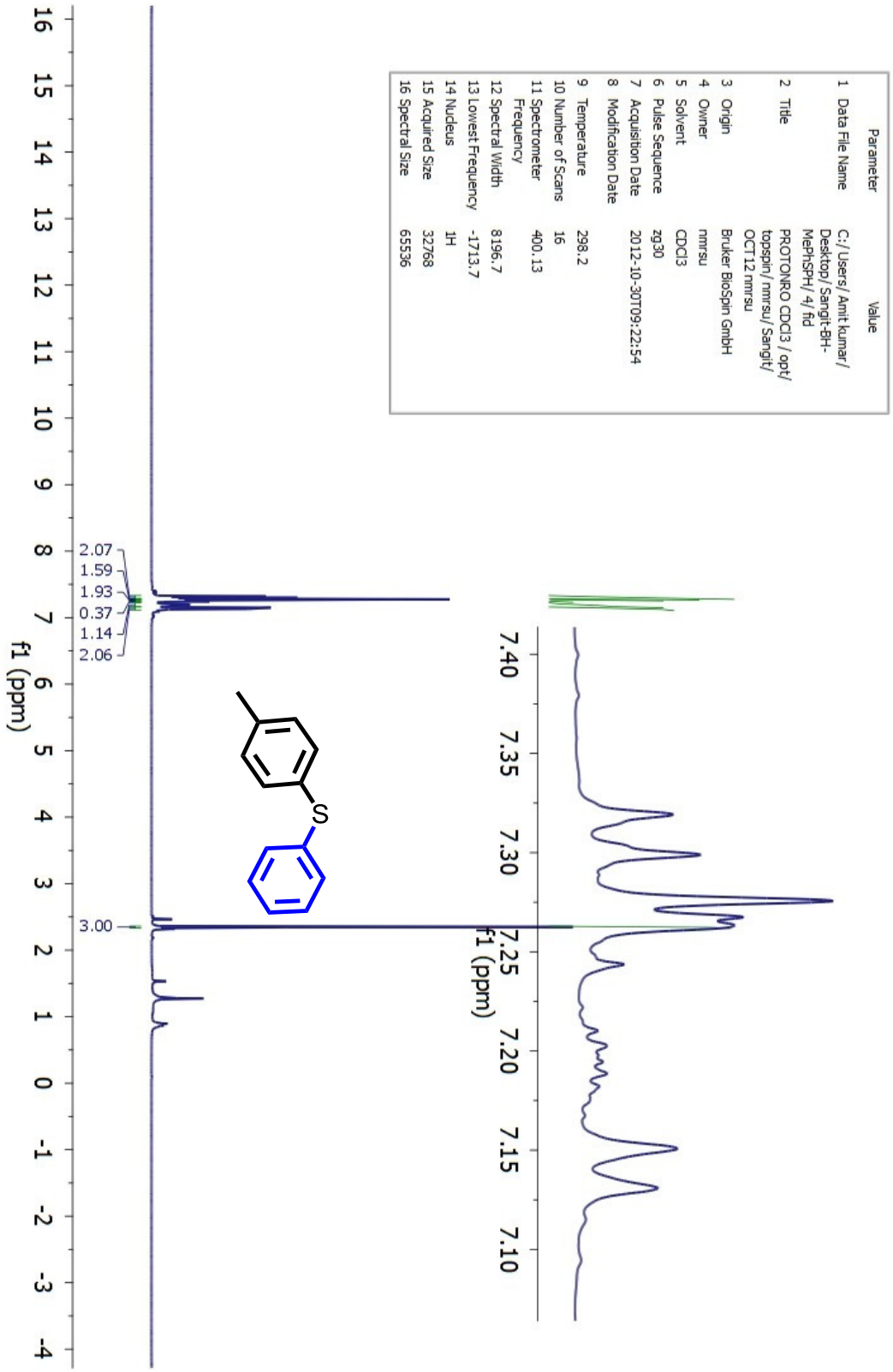

Figure S8 ^{13}C NMR spectrum of **3**

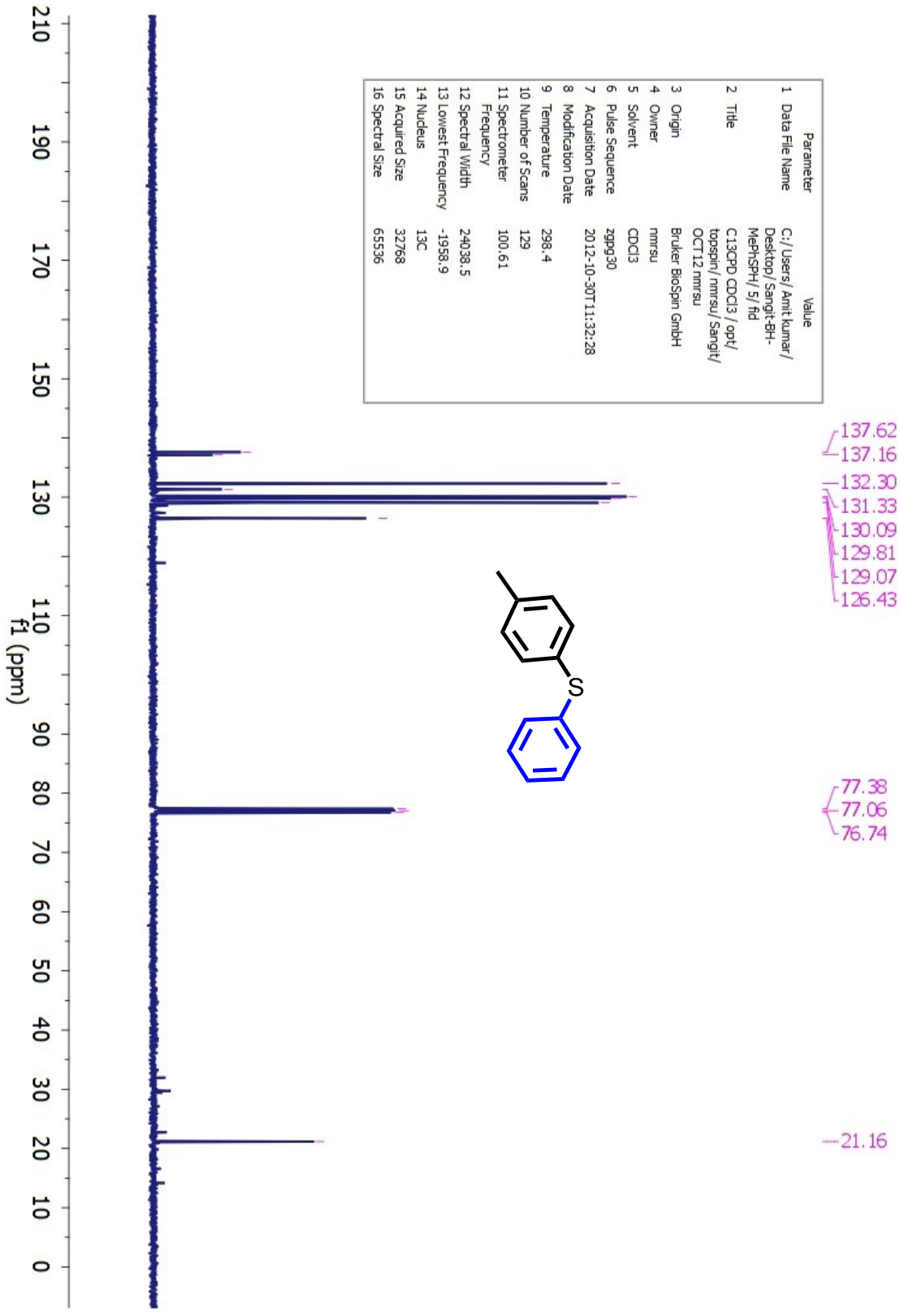

Figure S9 DEPT- 135 NMR spectrum of **3**

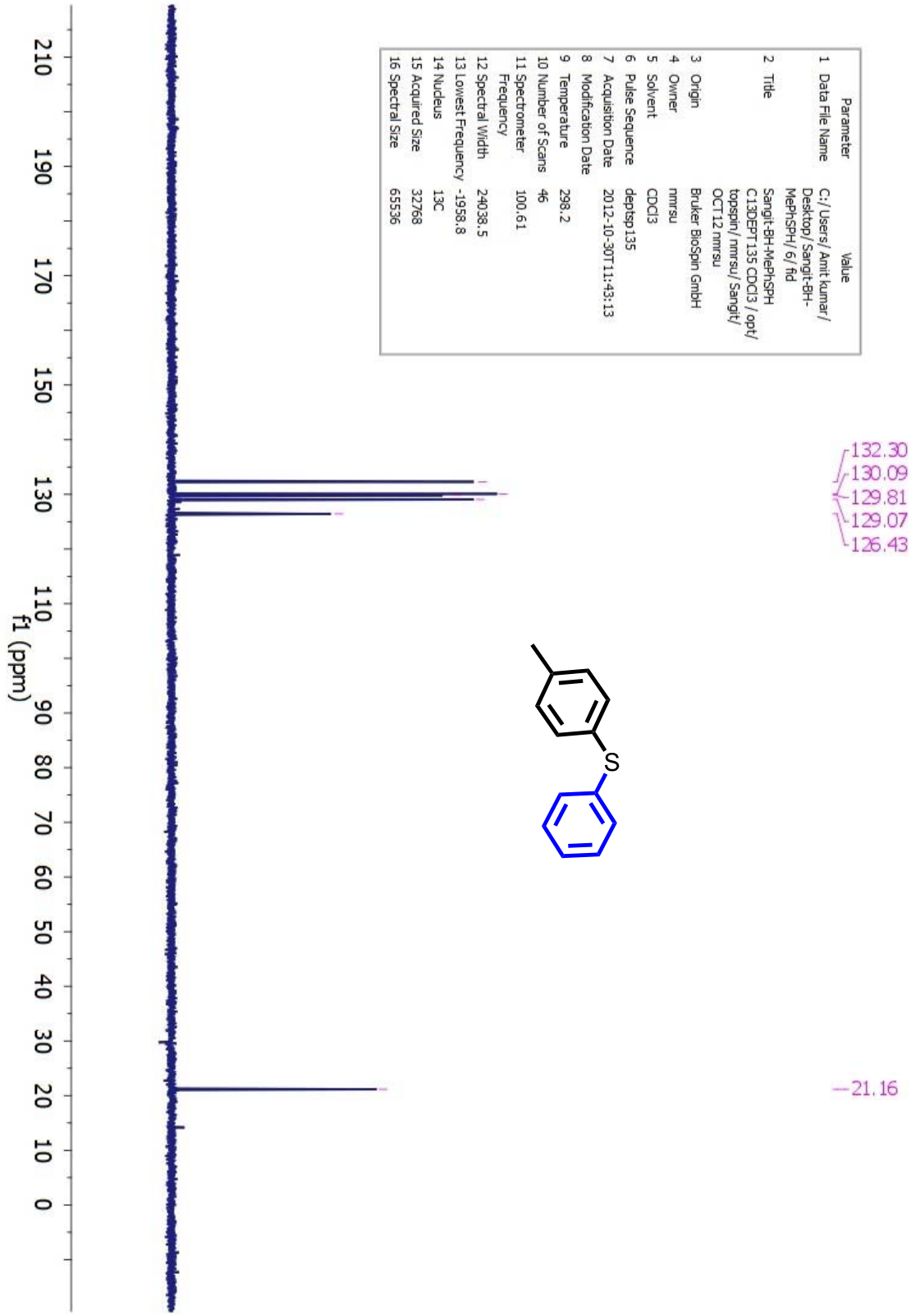

Figure S10 ^{1}H NMR spectrum of **4**

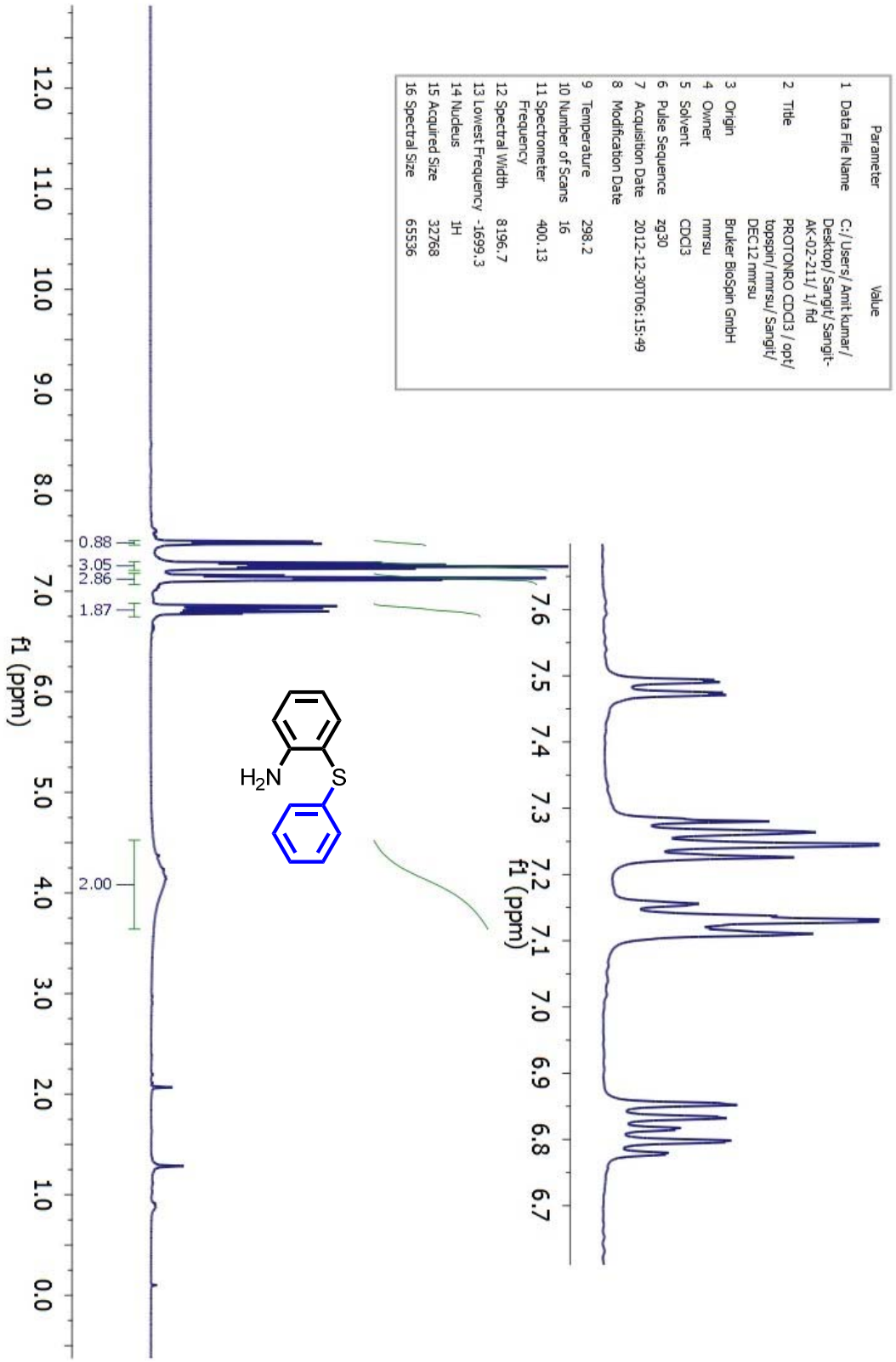

Figure S11 ^{13}C NMR spectrum of **4**

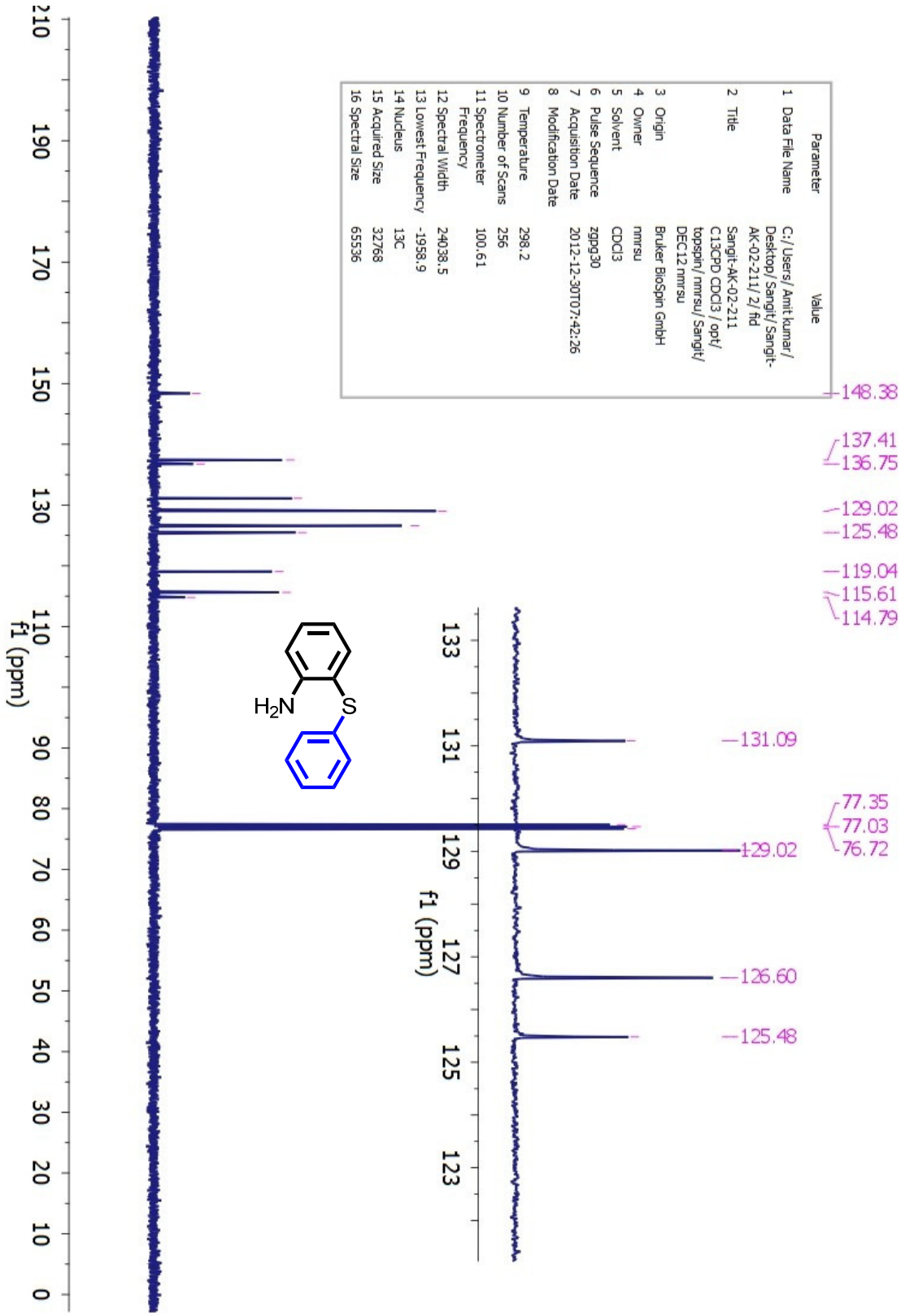

Figure S12 DEPT- 35 NMR spectrum of **4**

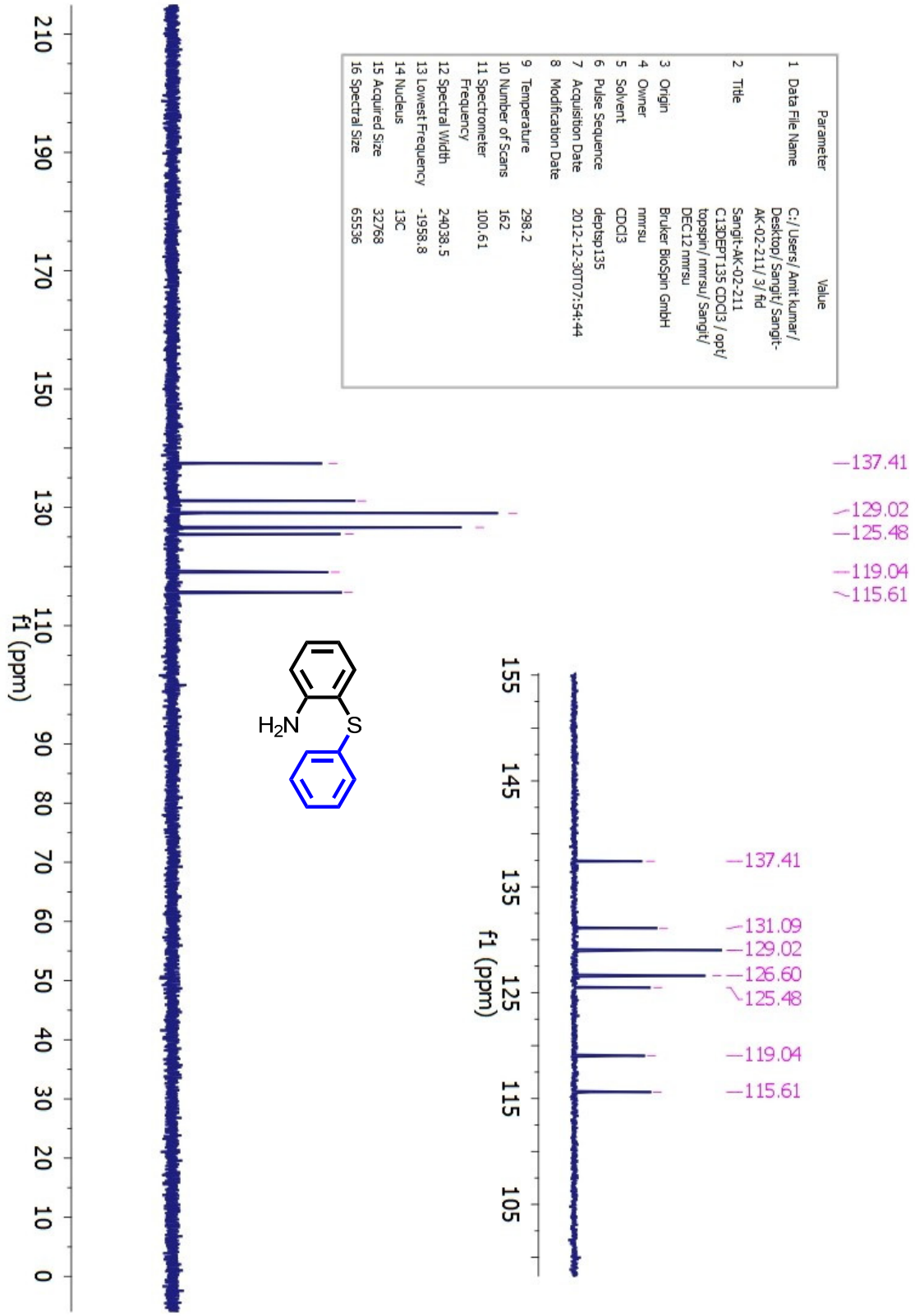

Figure S13 ^{1}H NMR spectrum **5**

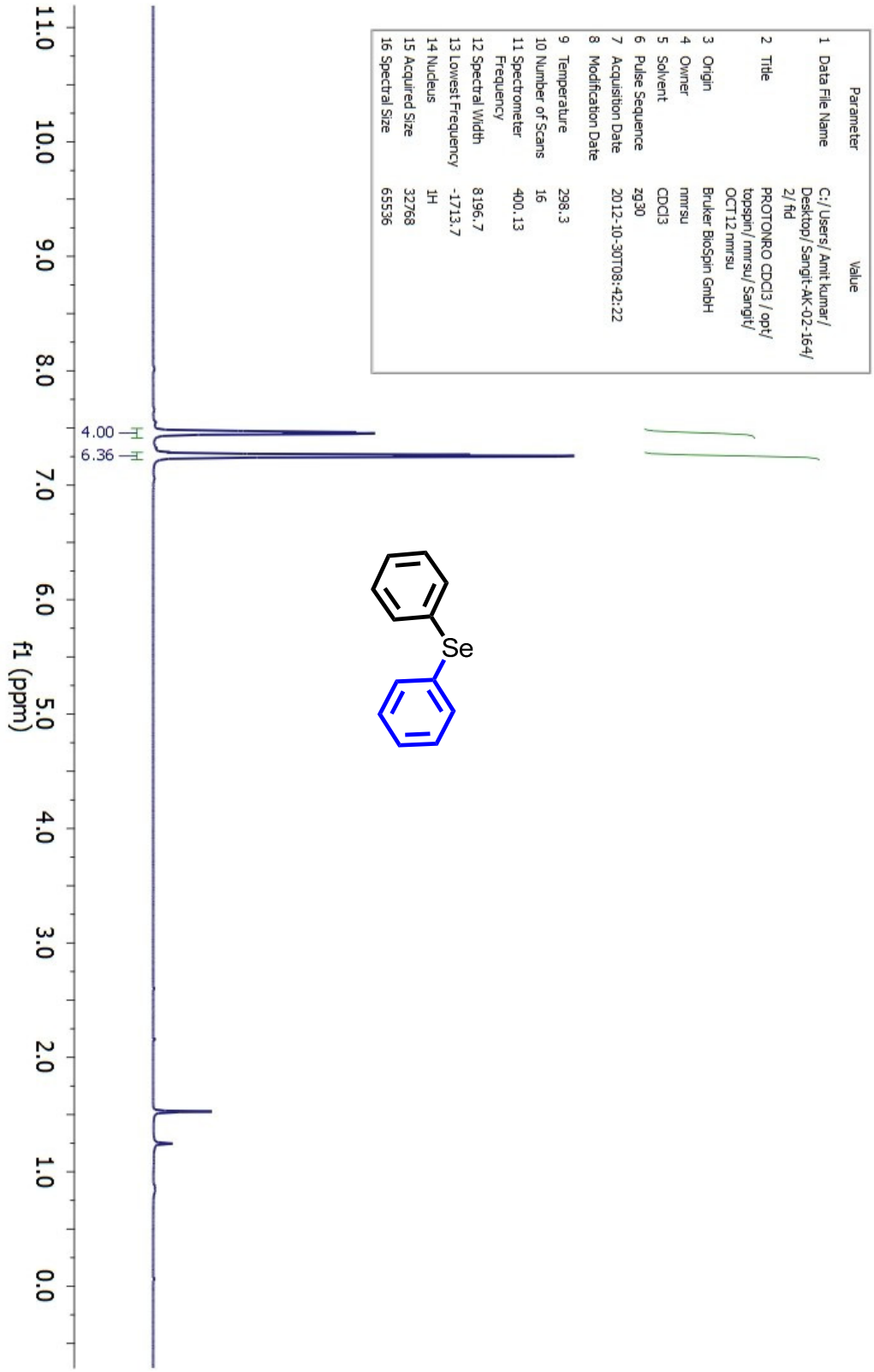

Figure S14 ^{13}C NMR spectrum of **5**

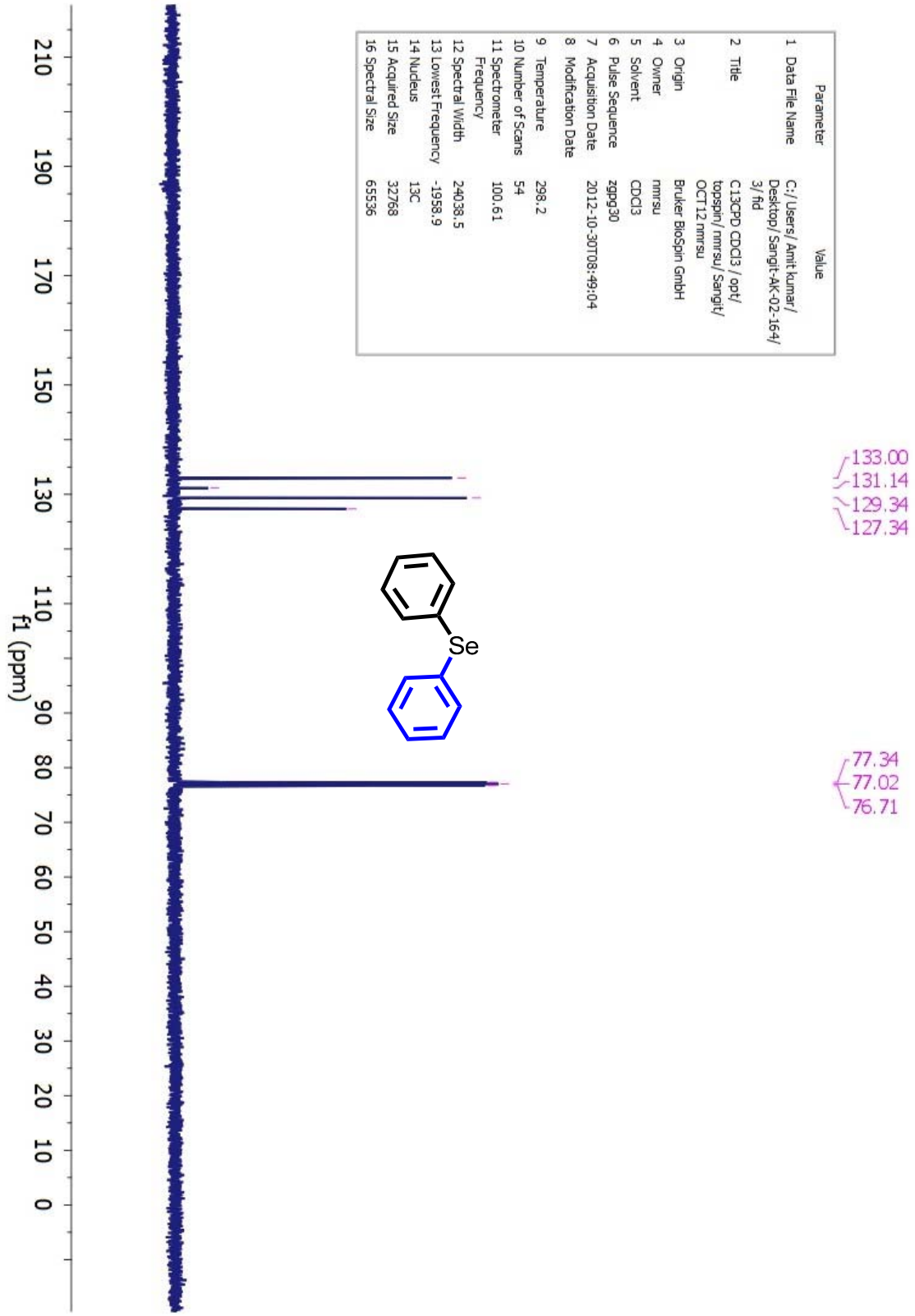

Figure S15 DEPT- 135 NMR spectrum of **5**

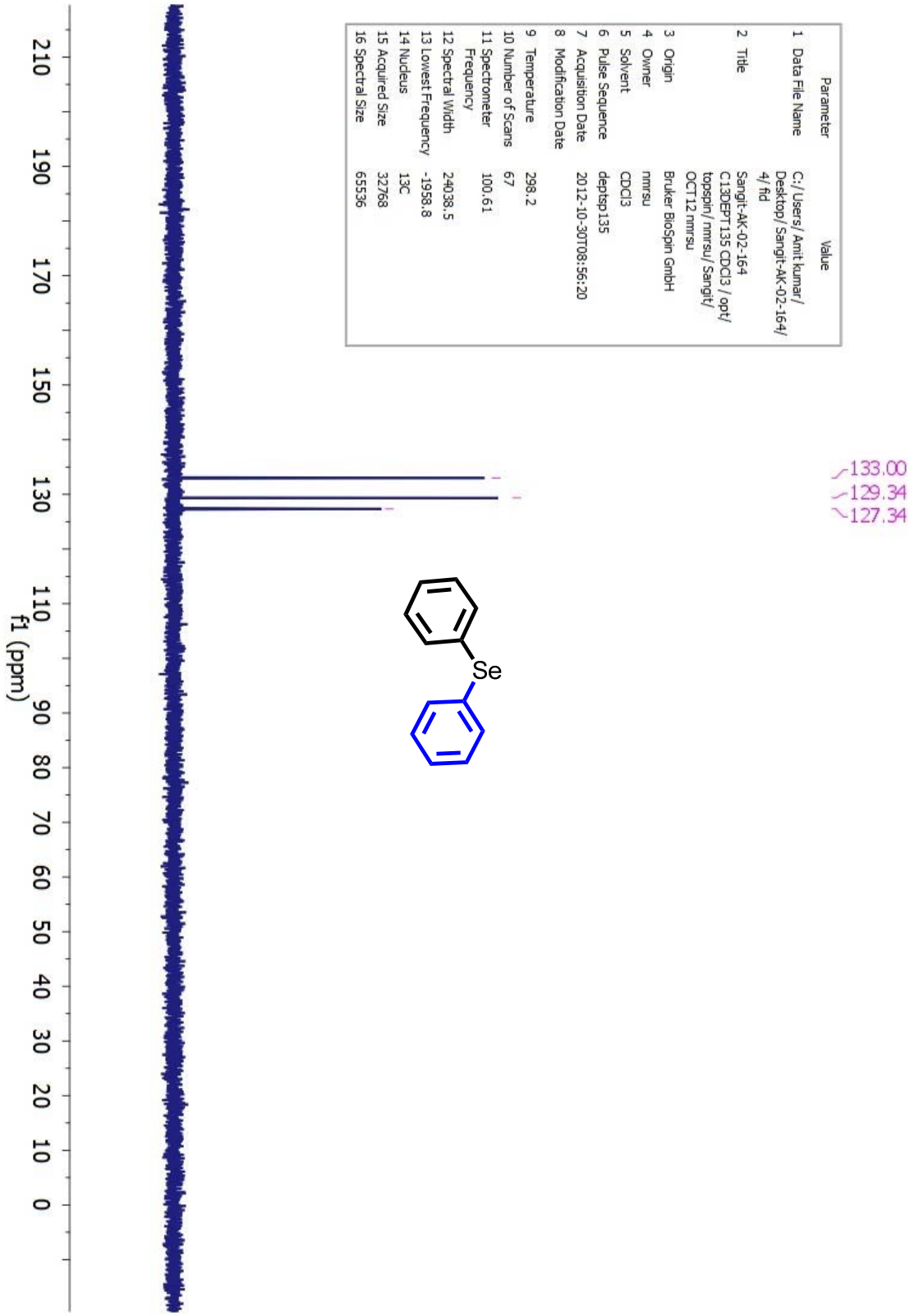

Figure S16 ^{77}Se NMR spectrum of **5**

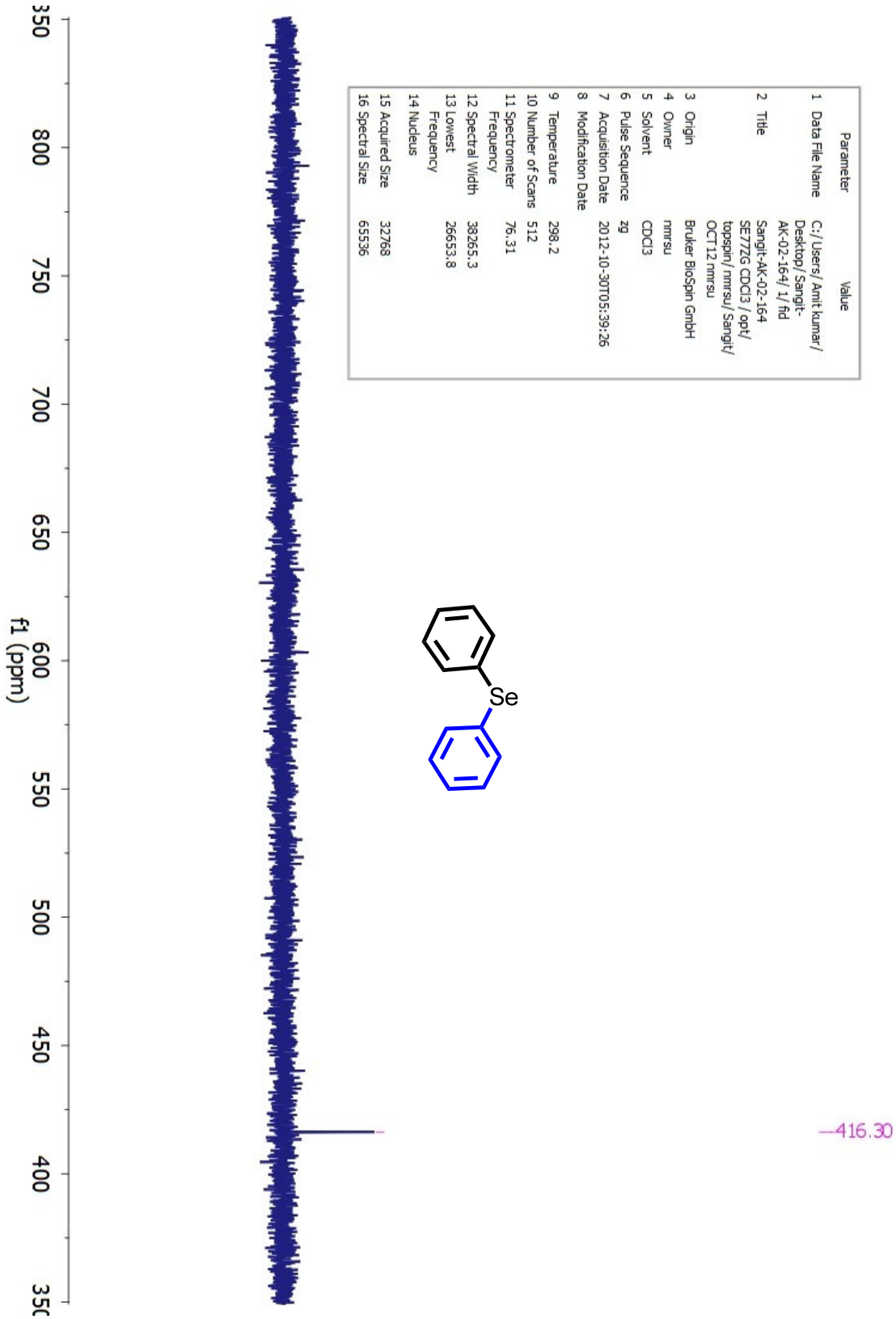

Figure S17 ^{1}H NMR spectrum of **3/6**

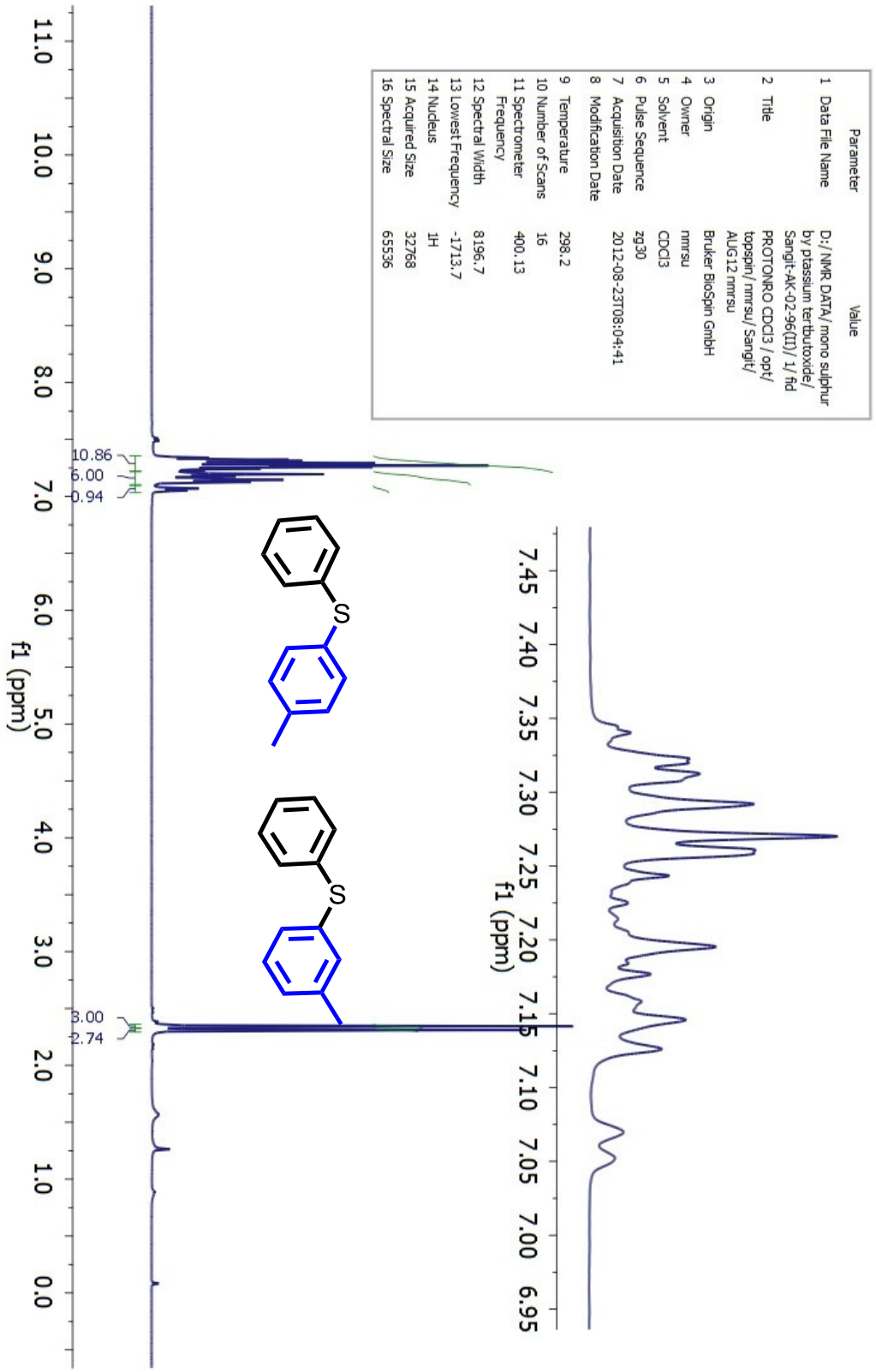

Figure S18 ^{13}C NMR spectrum of **3/6b**

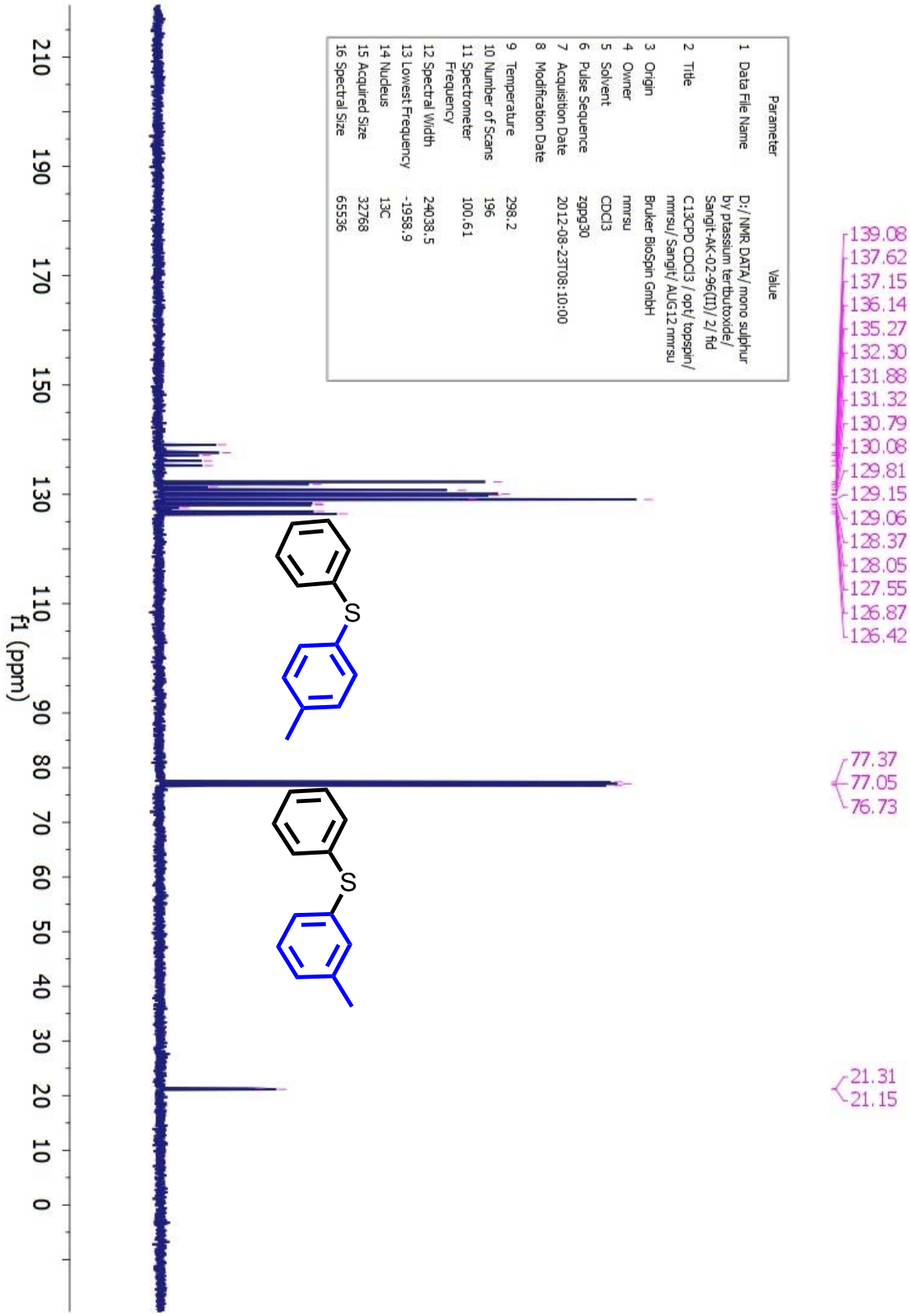

Figure S19 DEPT-135 NMR spectrum of **3/6b**

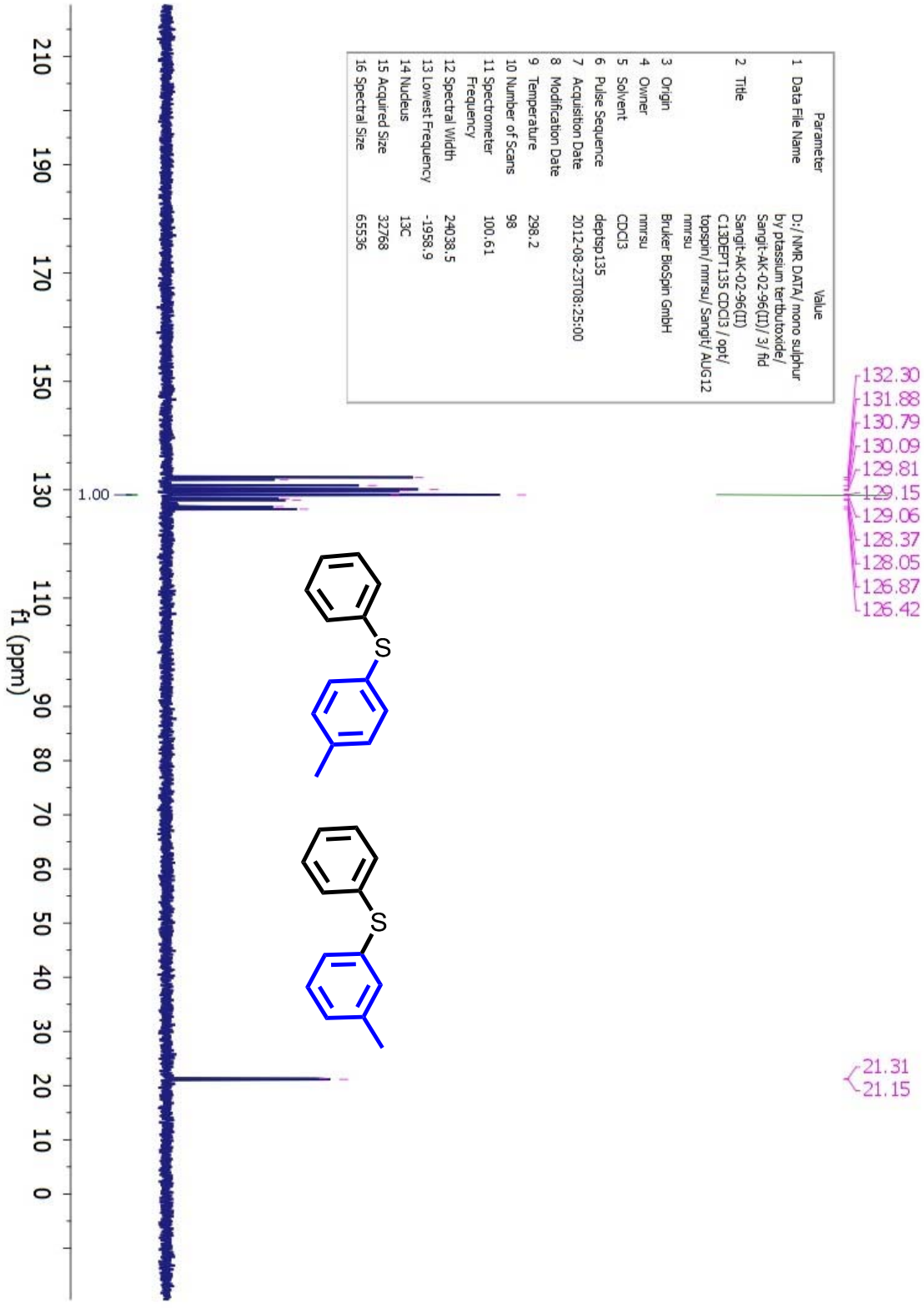

Figure S20 ^{1}H NMR spectrum of **2/7b**

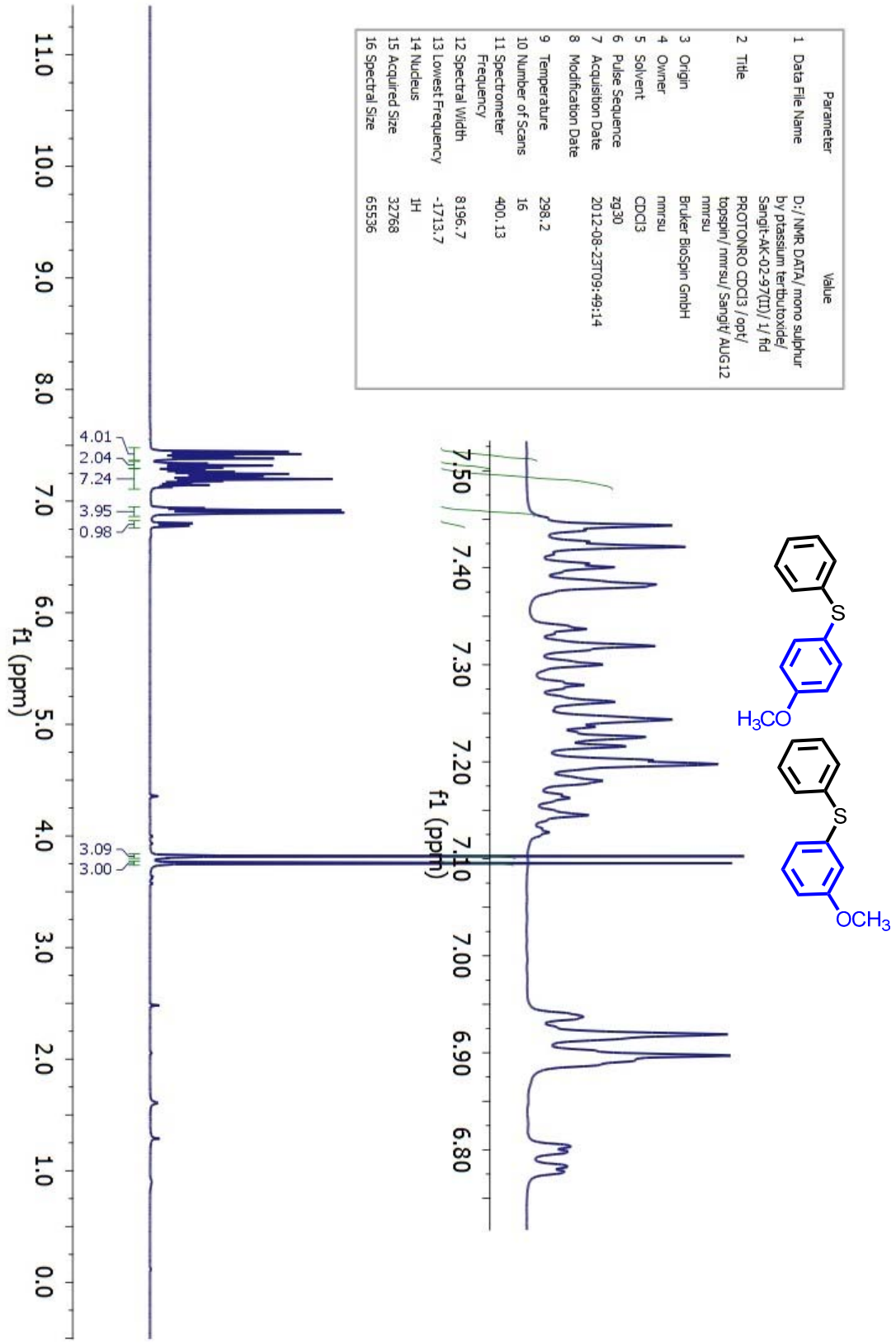

Figure S21 ^{13}C NMR spectrum of **2/7b**

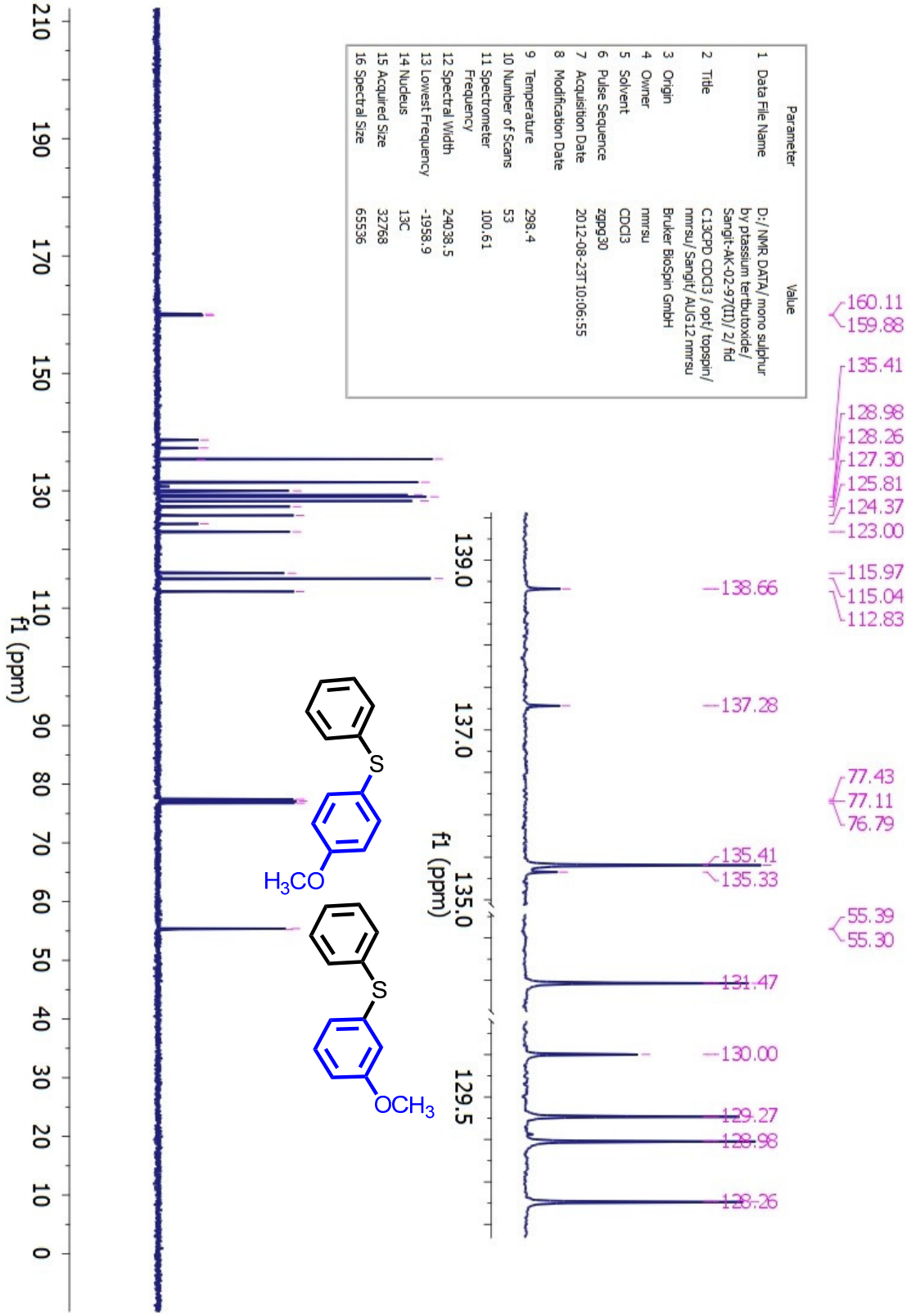

Figure S22 DEPT-135 NMR spectrum of **2/7b**

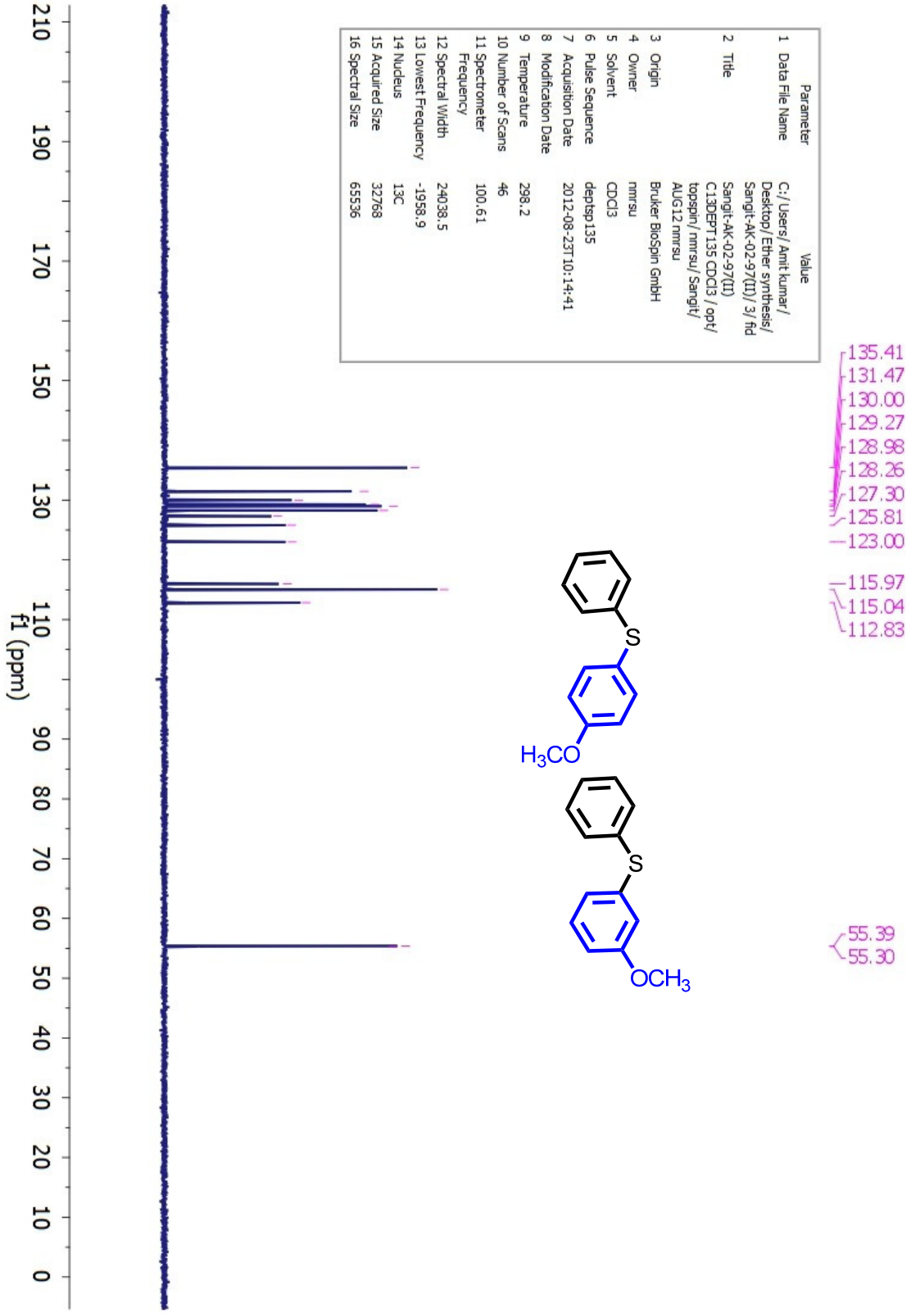

Figure S23 ^{1}H NMR spectrum of **8a/8b**

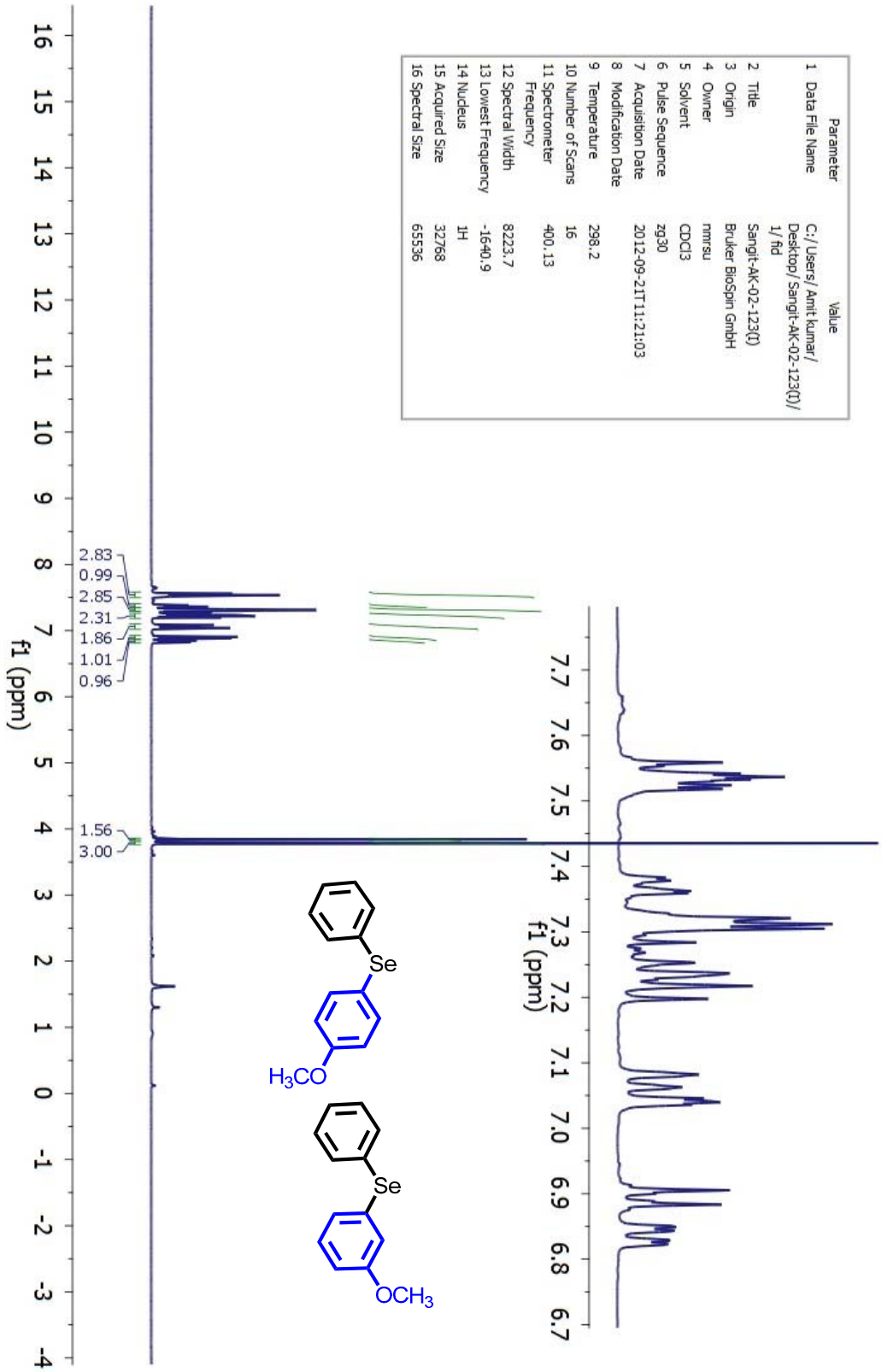

Figure S24 ^{13}C NMR spectrum of **8a/8b**

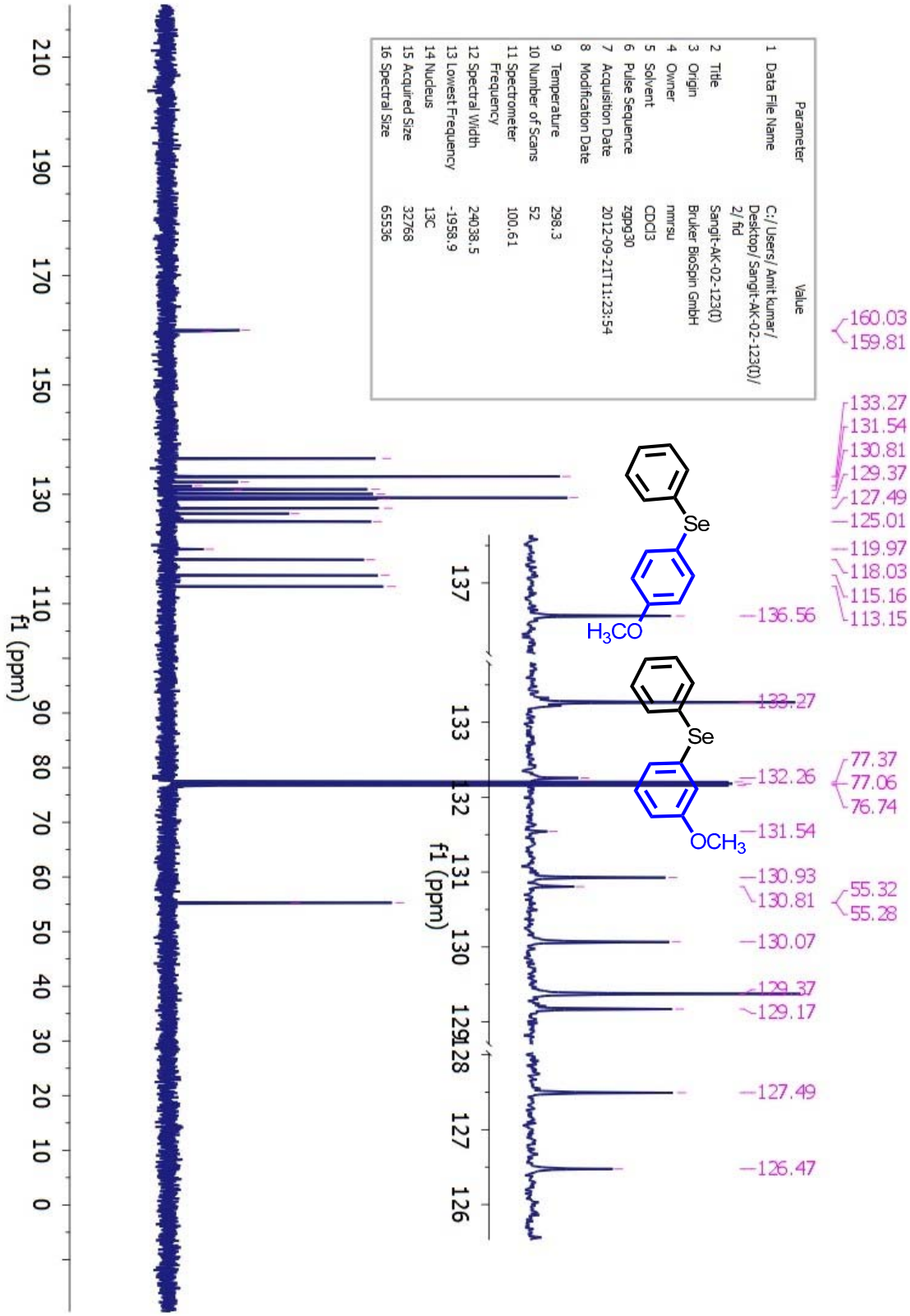

Figure S25 ^{77}Se NMR spectrum of **8a/8b**

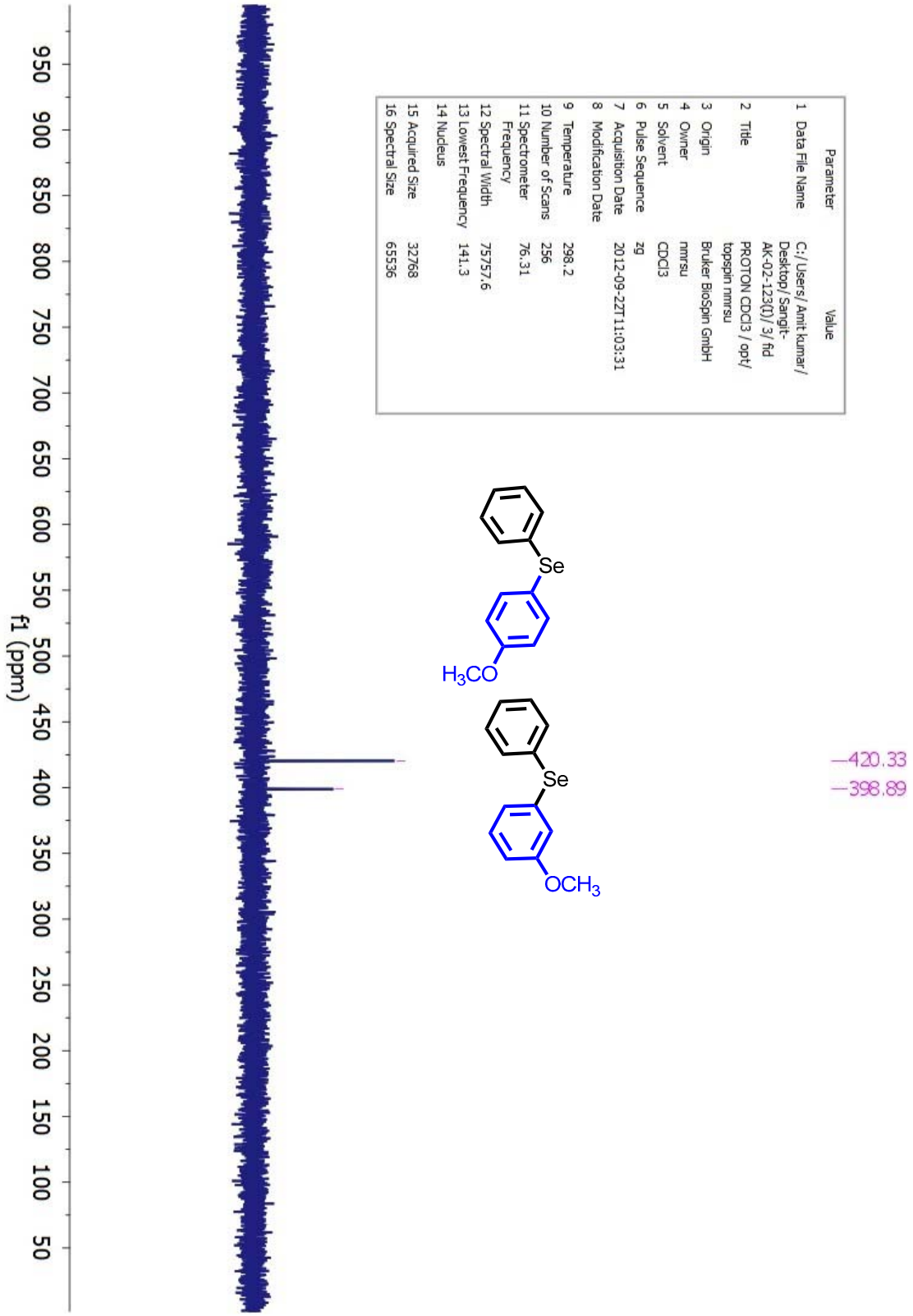

Figure S26 ^{1}H NMR spectrum of **9a/9b**

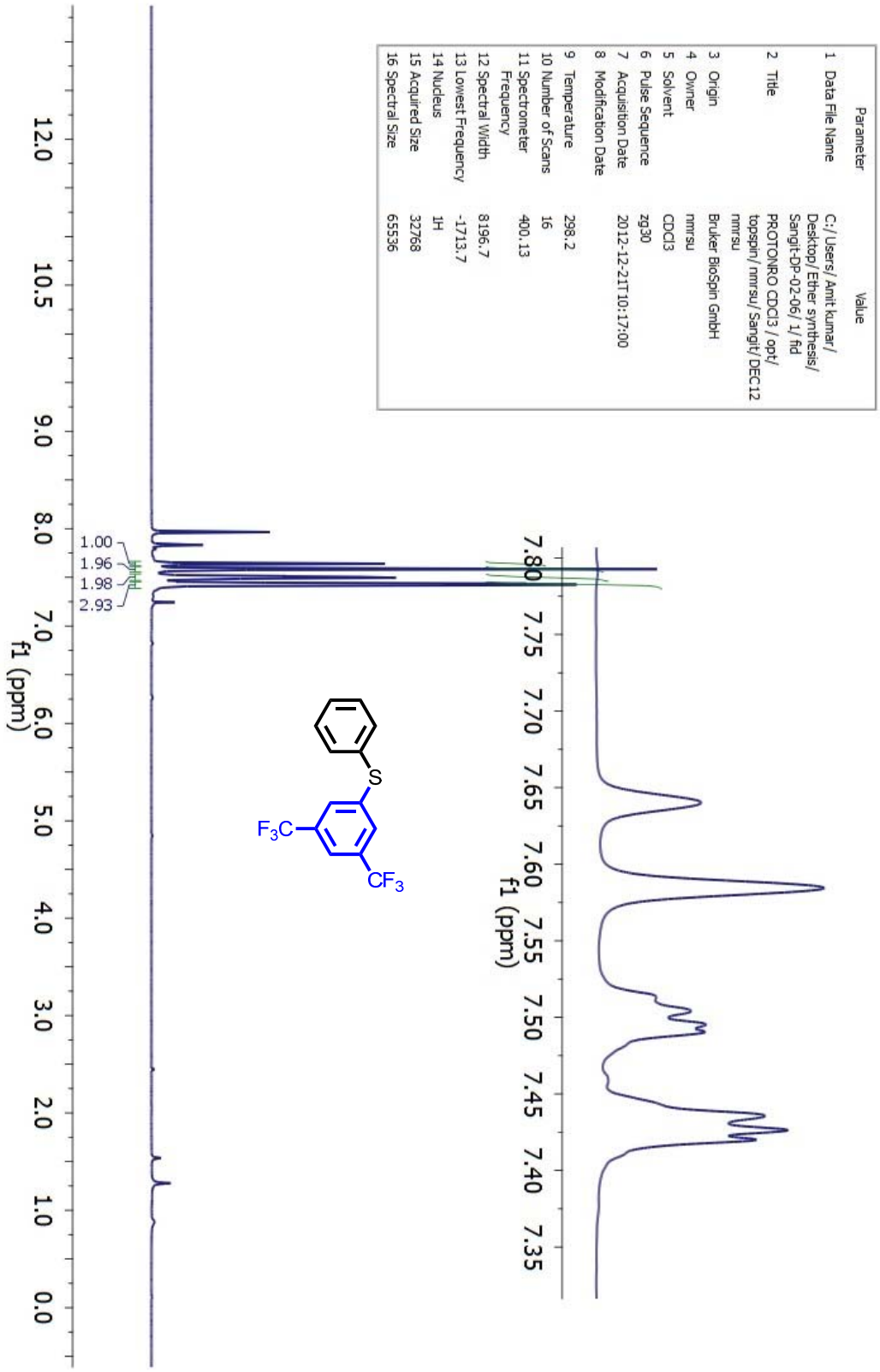

Figure S27 ^{13}C NMR spectrum of **9**

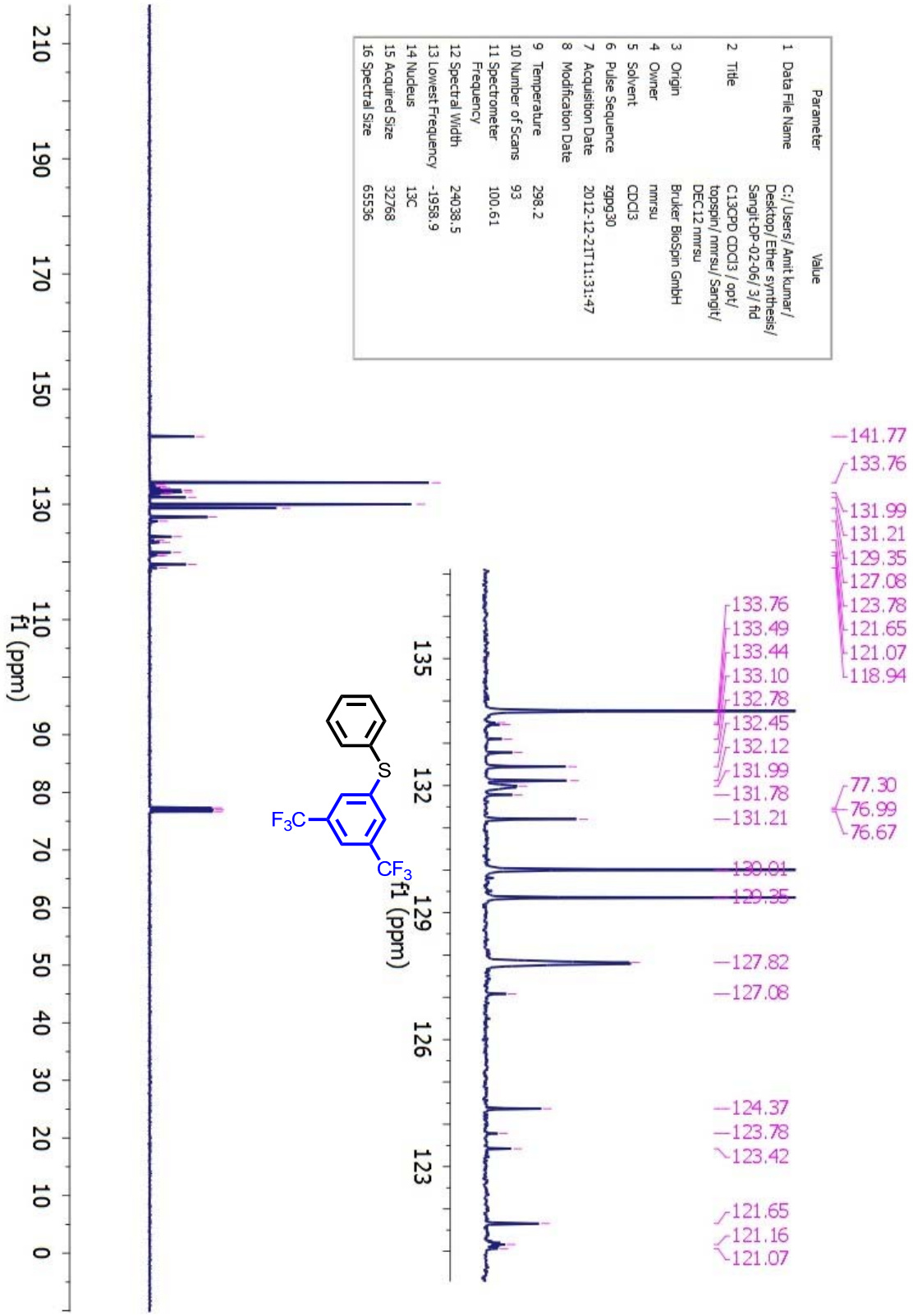

Figure S28 DEPT-135 NMR spectrum of **9**

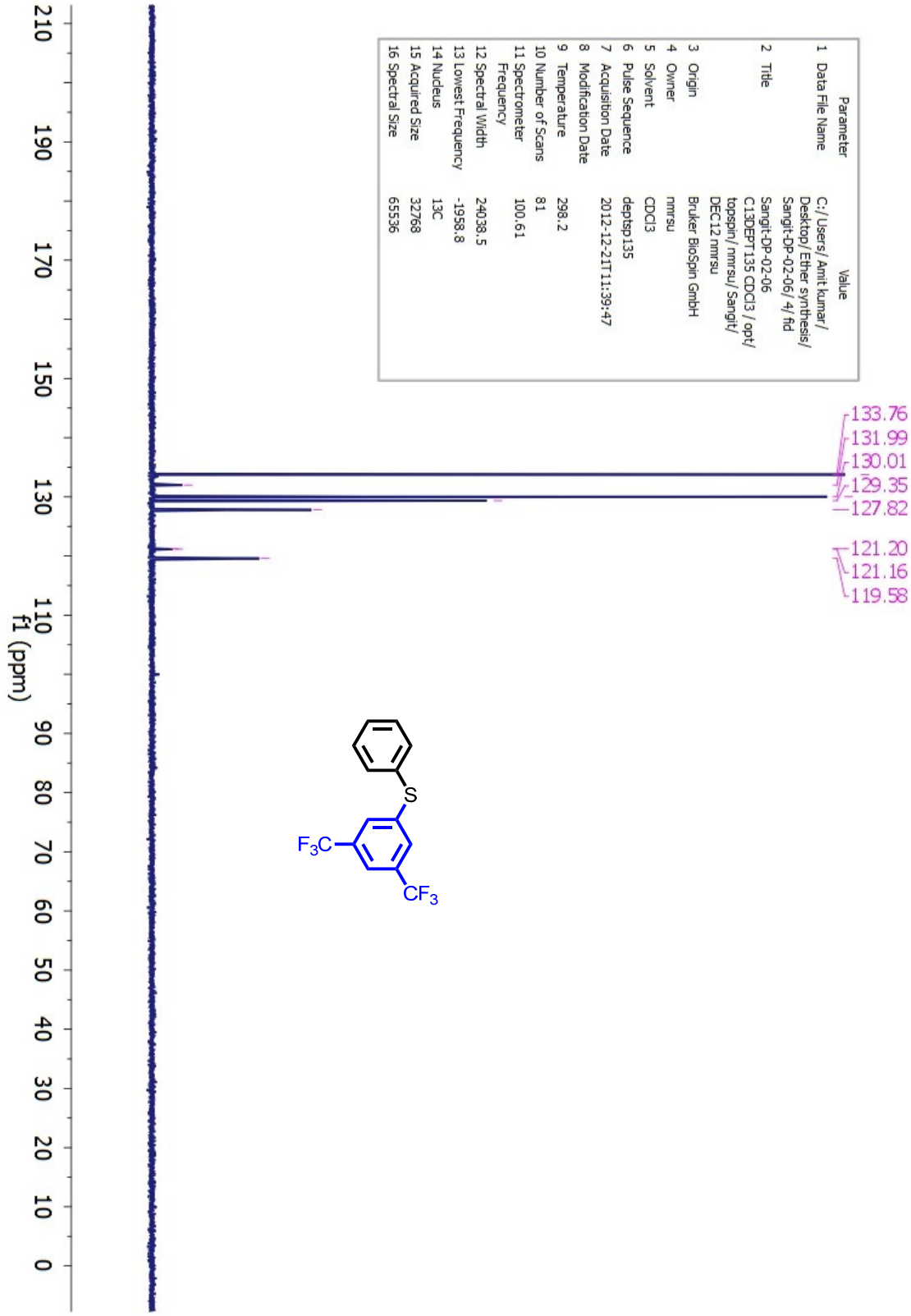

Figure S29 ^{1}H NMR spectrum of **10**

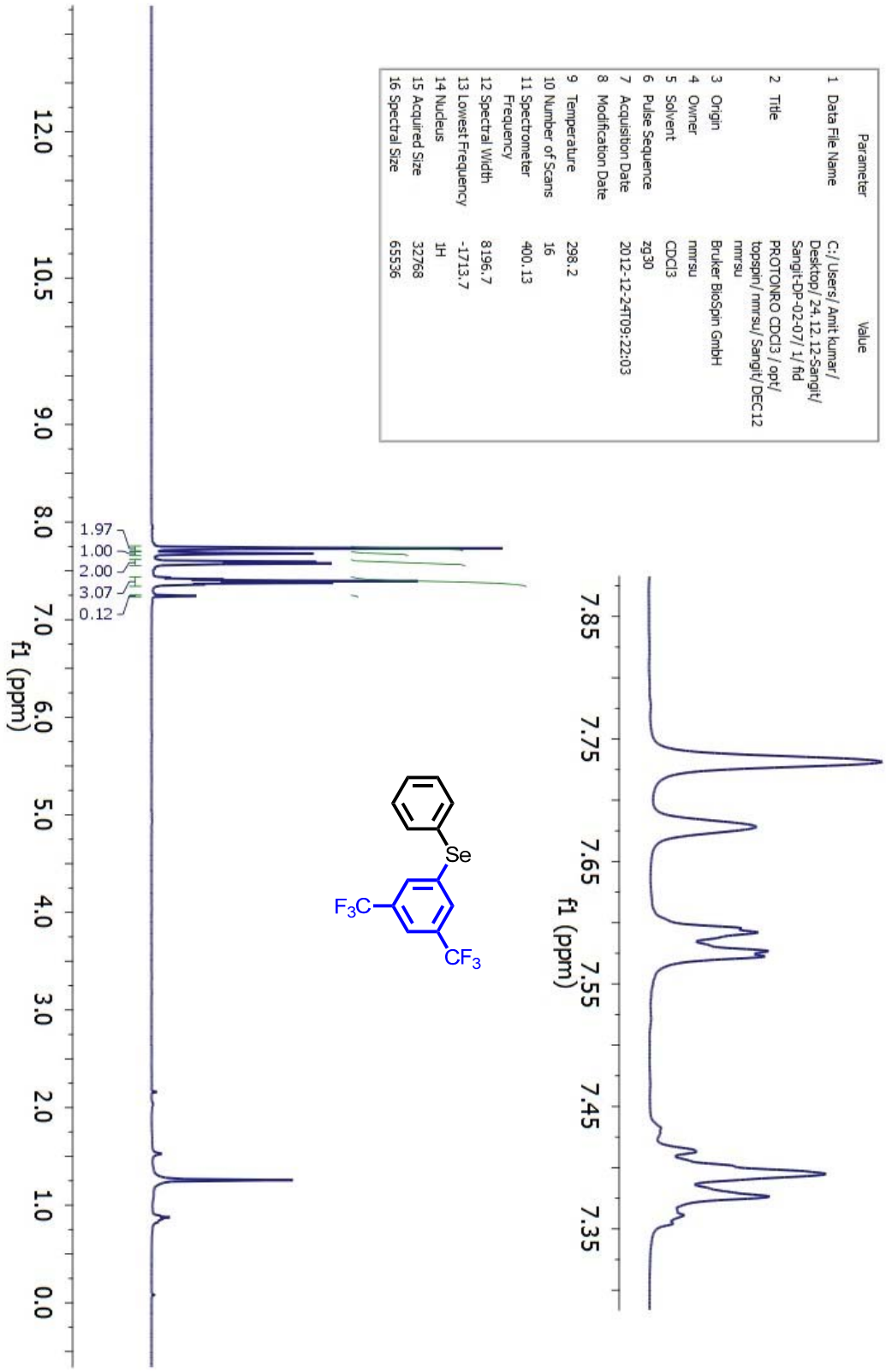

Figure S30 ^{13}C NMR spectrum of **10**

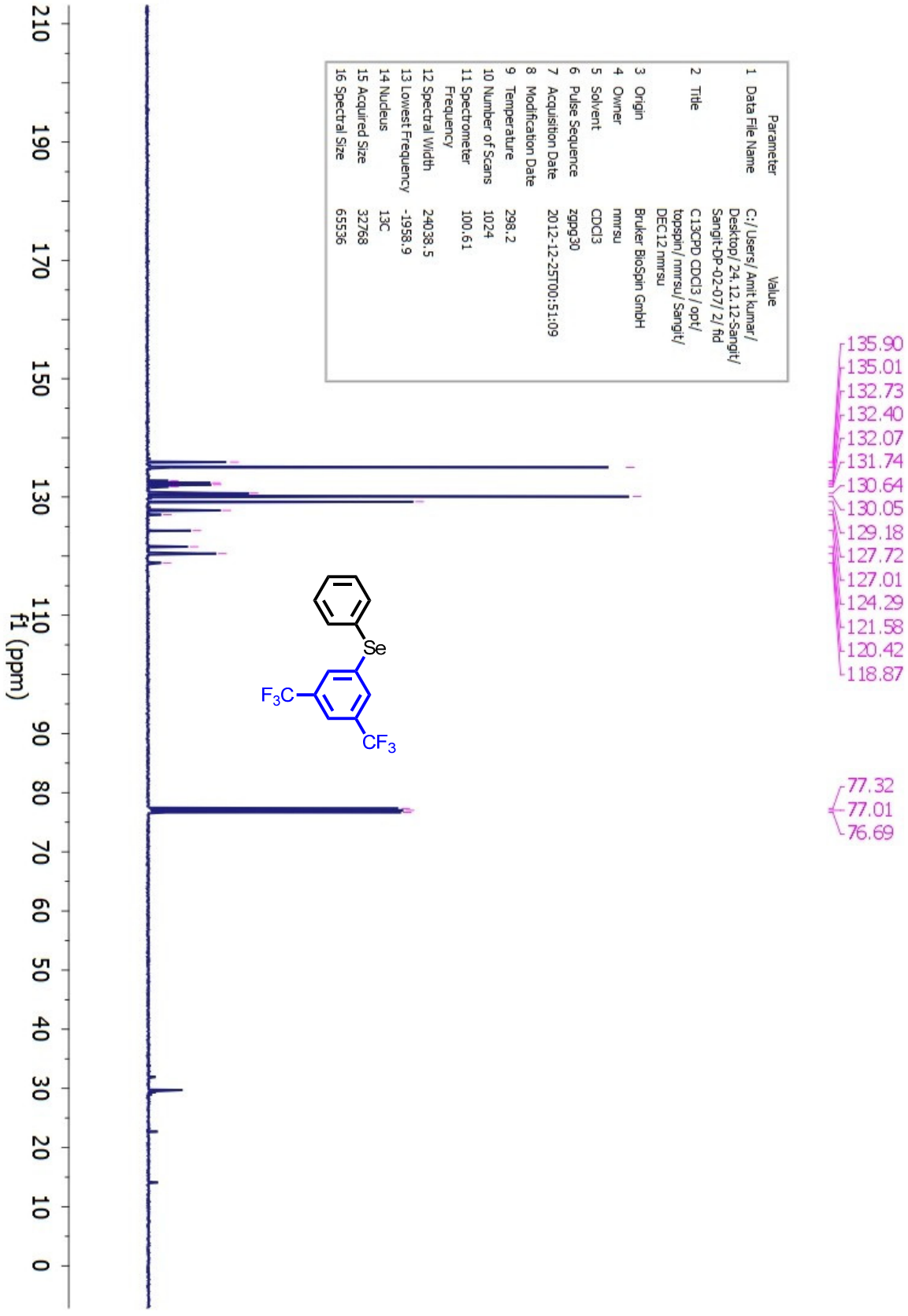

Figure S31 DEPT-135 NMR spectrum of **10**

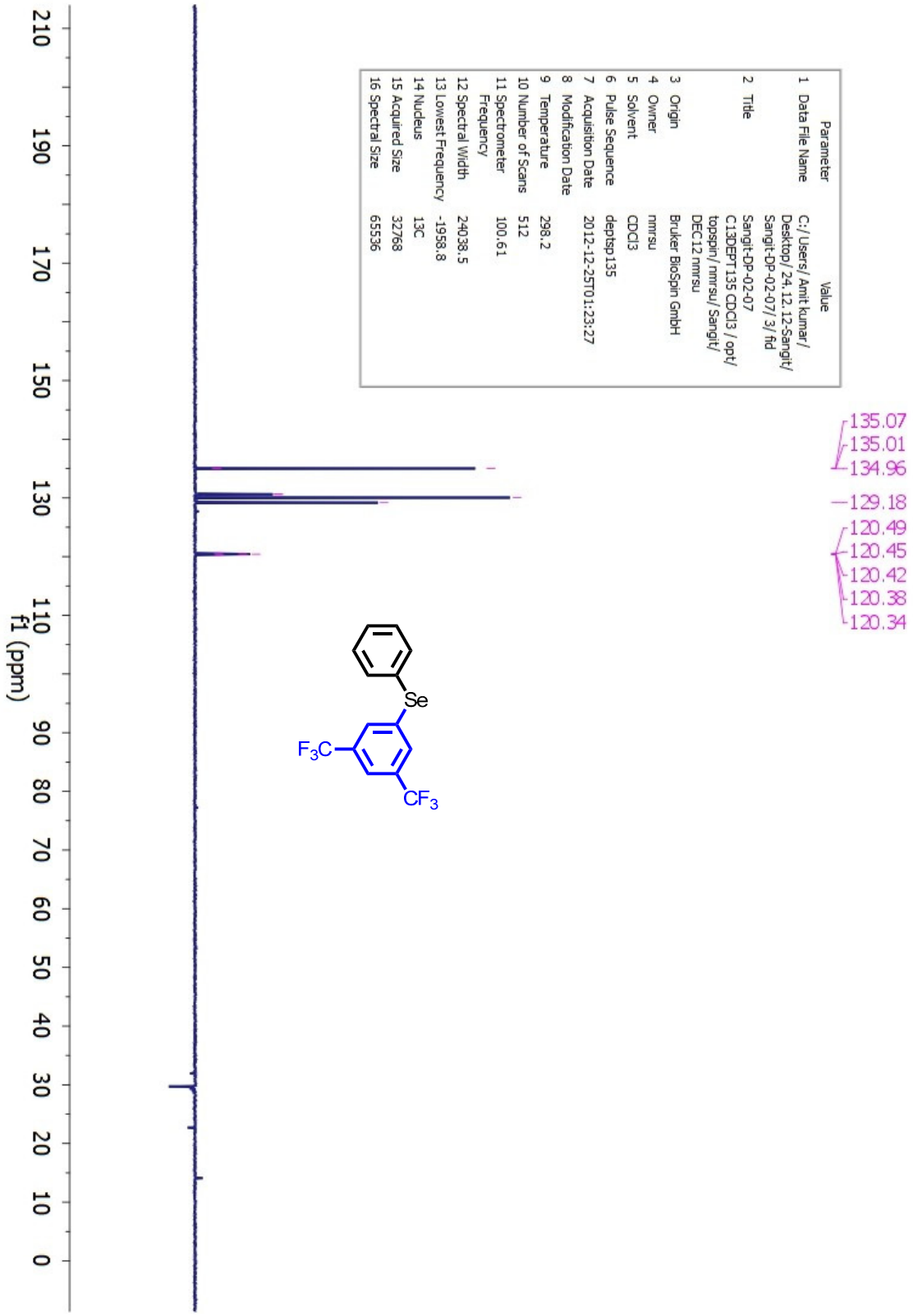

Figure S32 ^{77}Se NMR spectrum of **10**

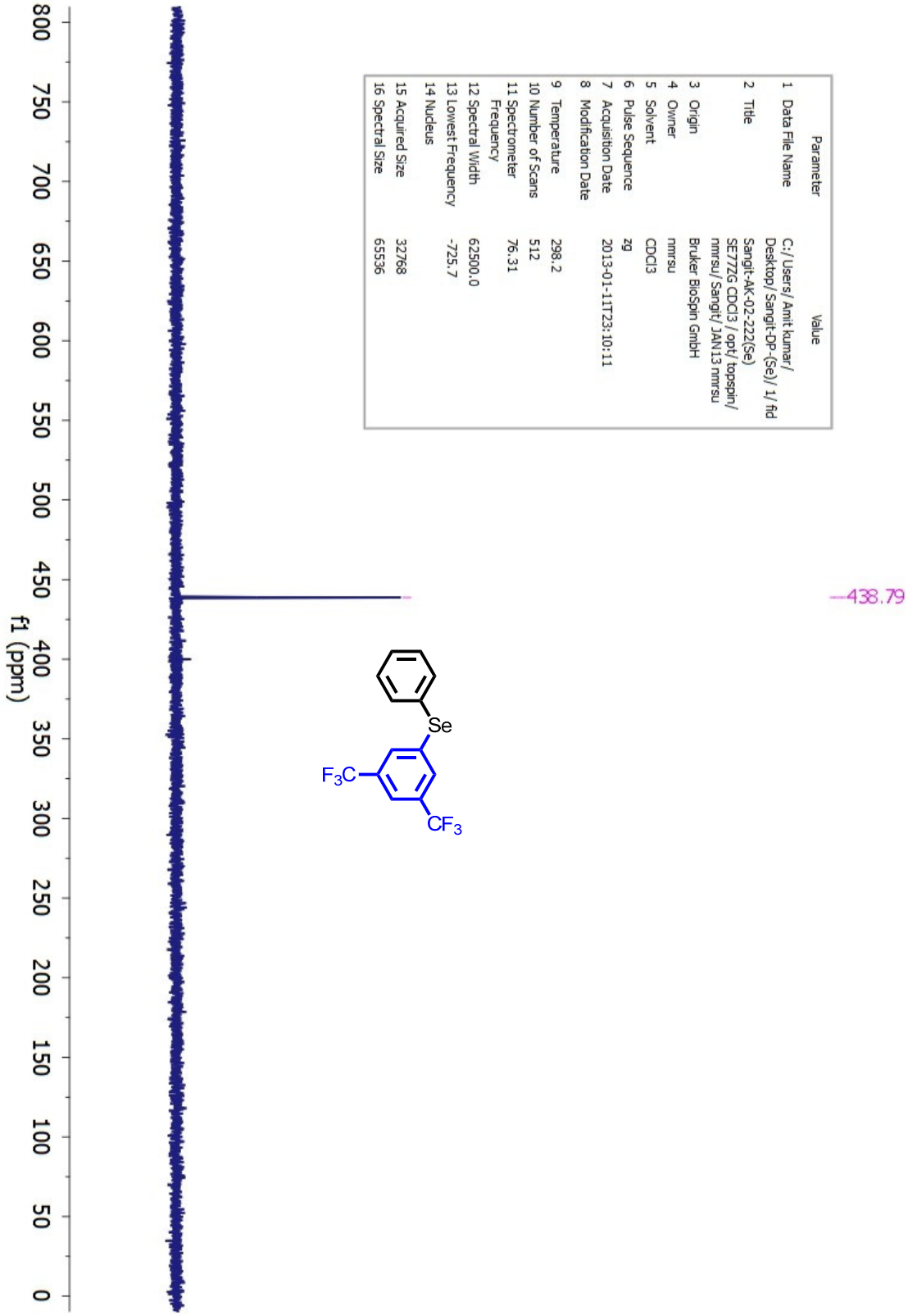

Figure S33 ^{1}H NMR spectrum of **11a/11b**

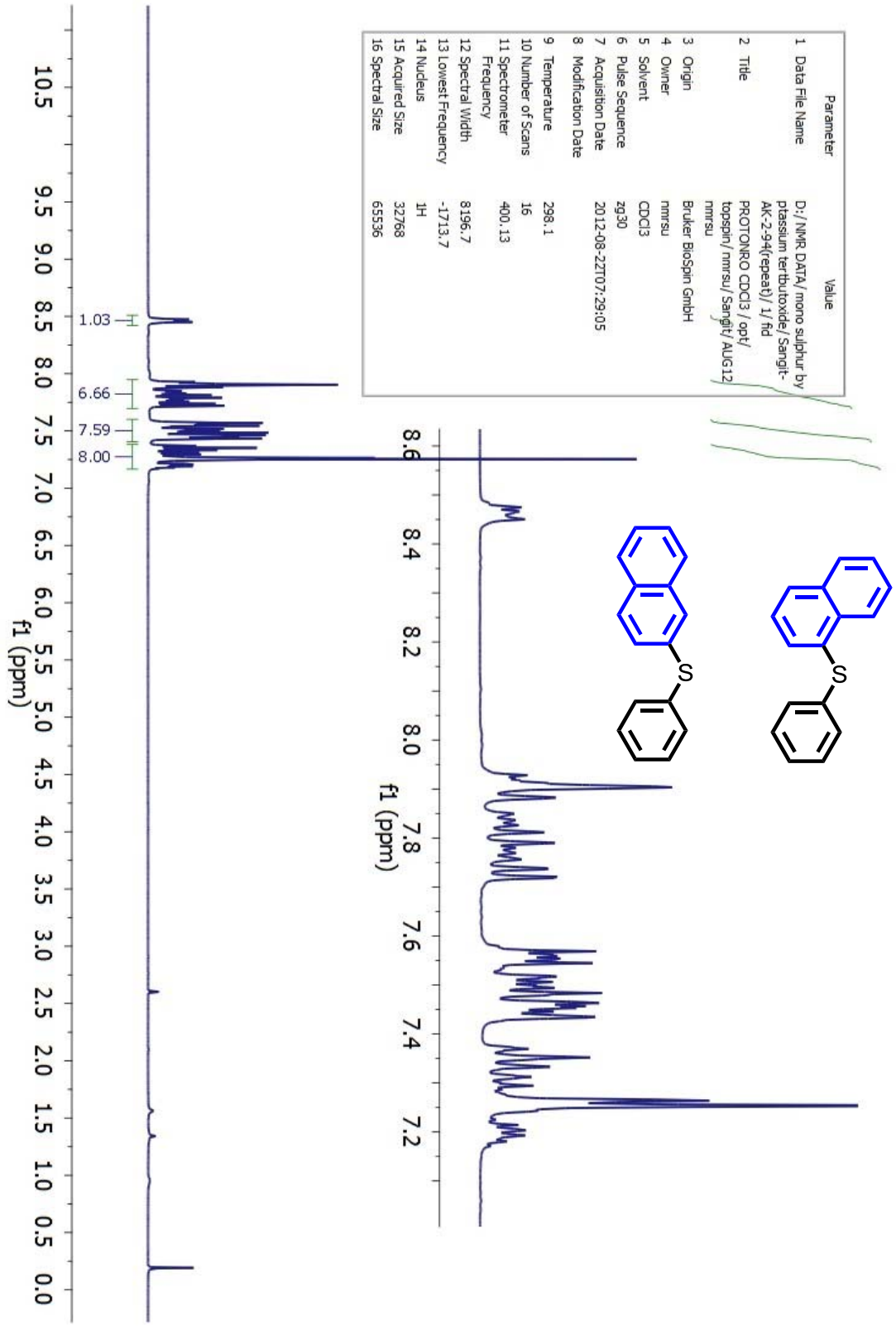

Figure S34 ^{13}C NMR spectrum of **11a/11b**

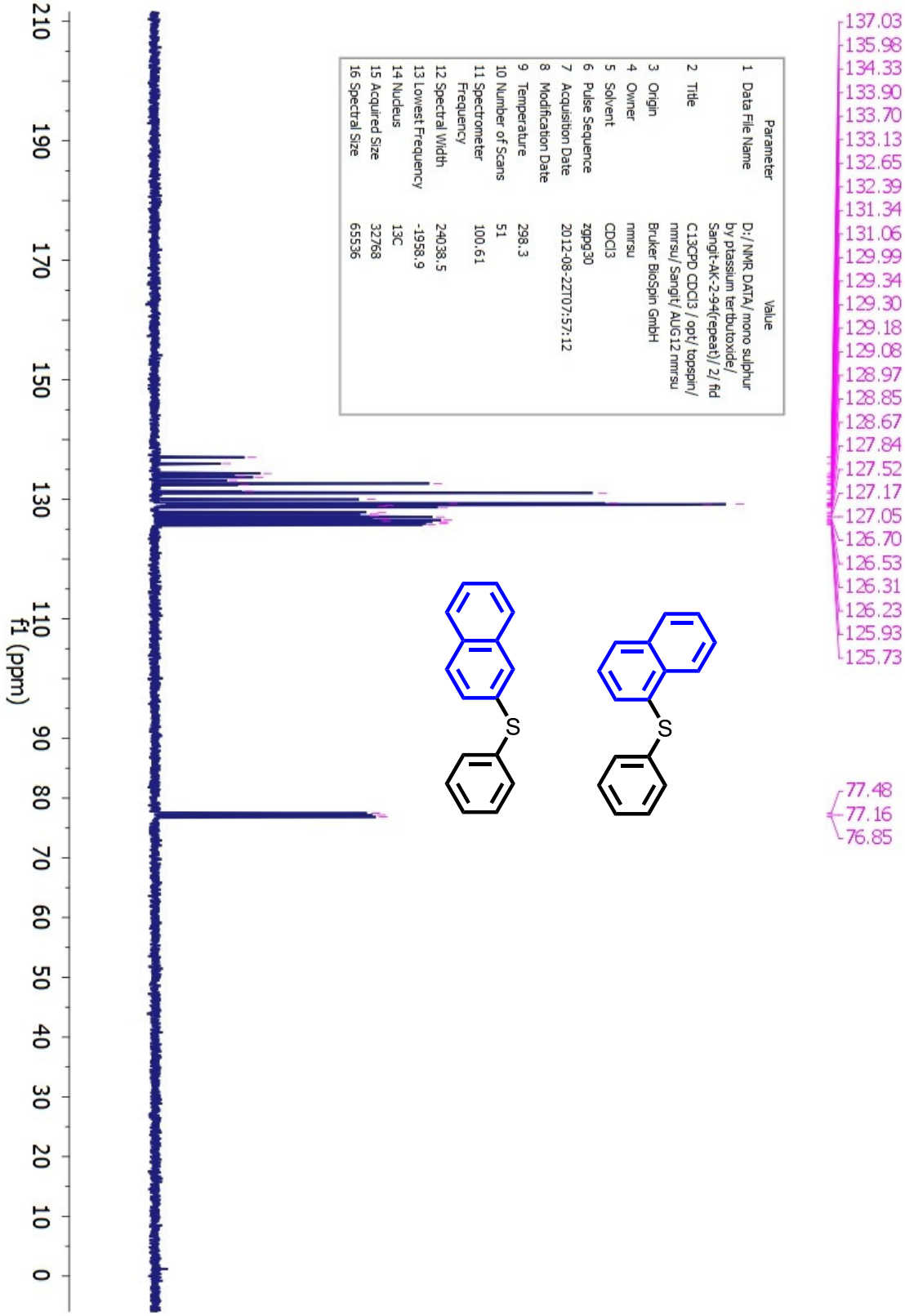

Figure S35 DEPT-135 NMR spectrum of **10a/10b**

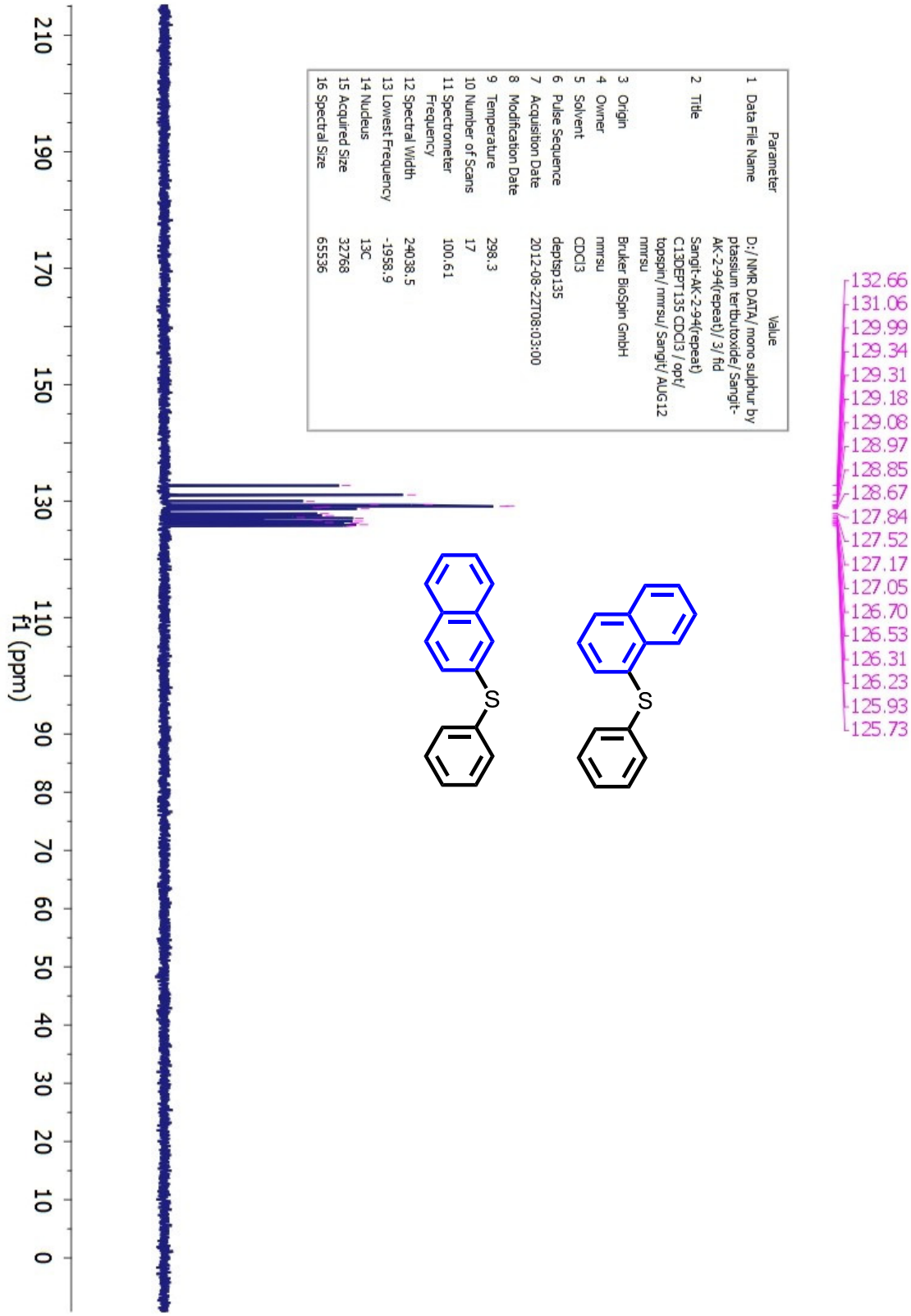

Figure S36 ^{1}H NMR spectrum of **12a/12b**

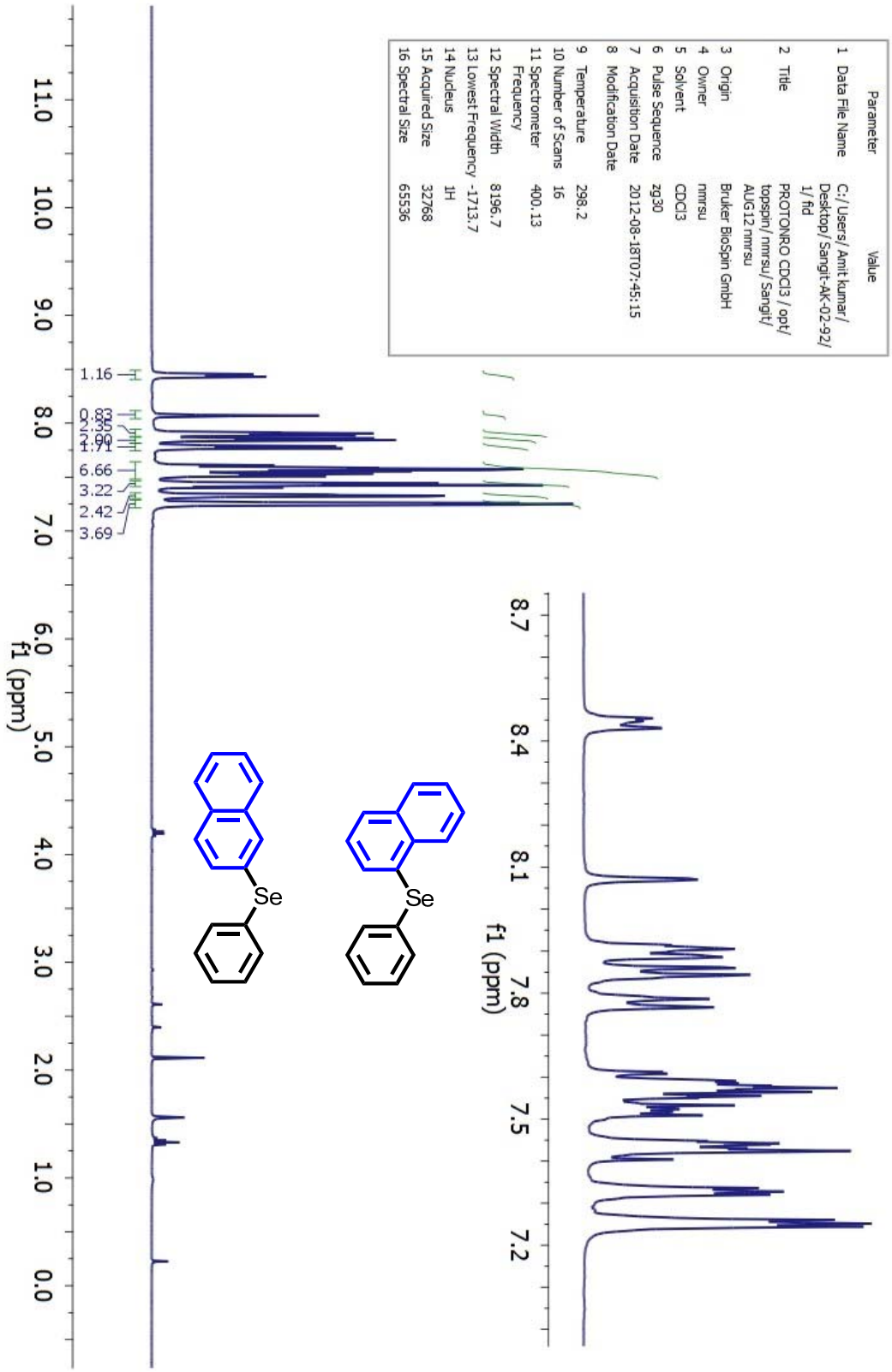

Figure S37 ^{13}C NMR spectrum of **12a/12b**

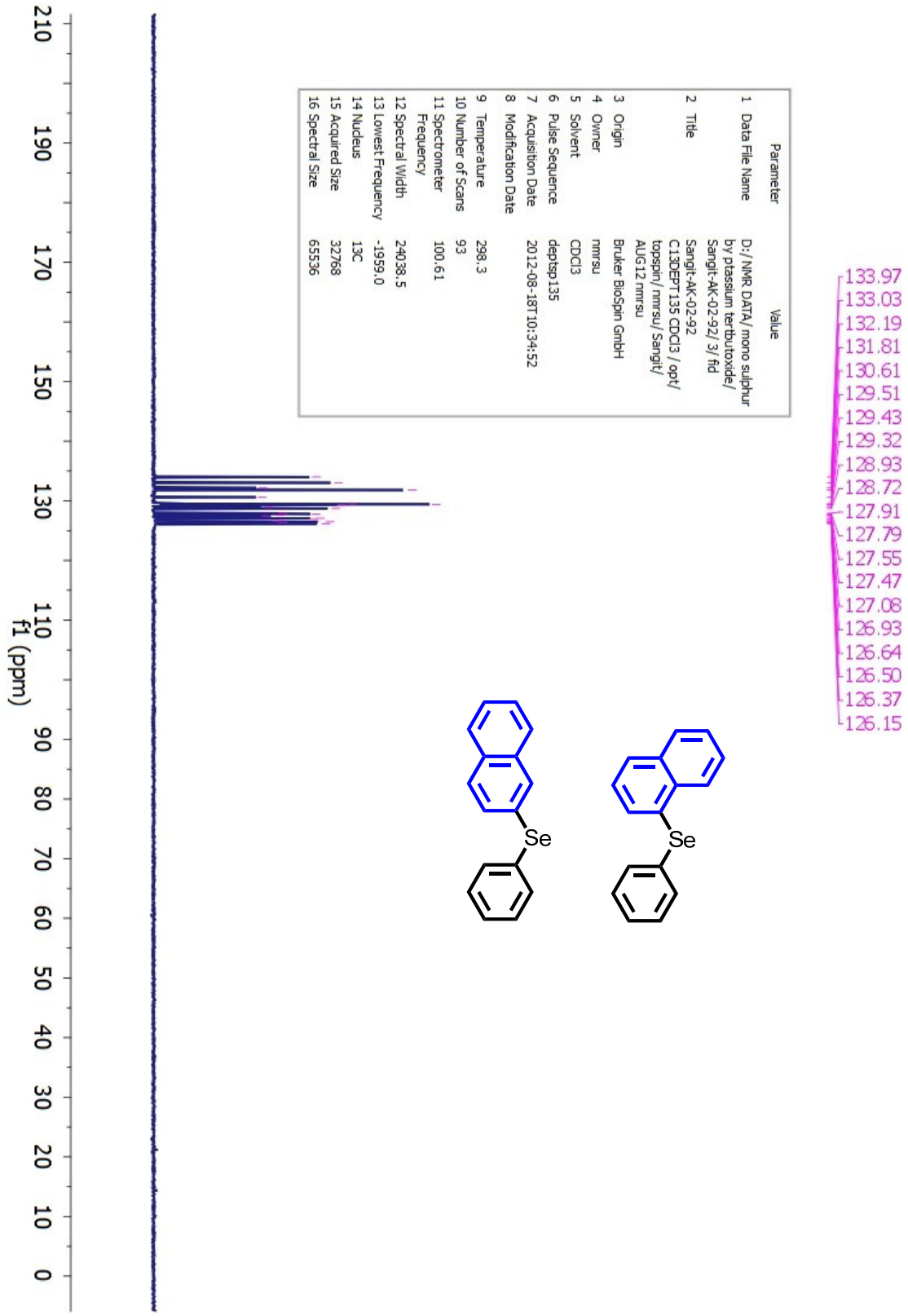

Figure S38 ^{77}Se NMR spectrum of (**12a/12b)**

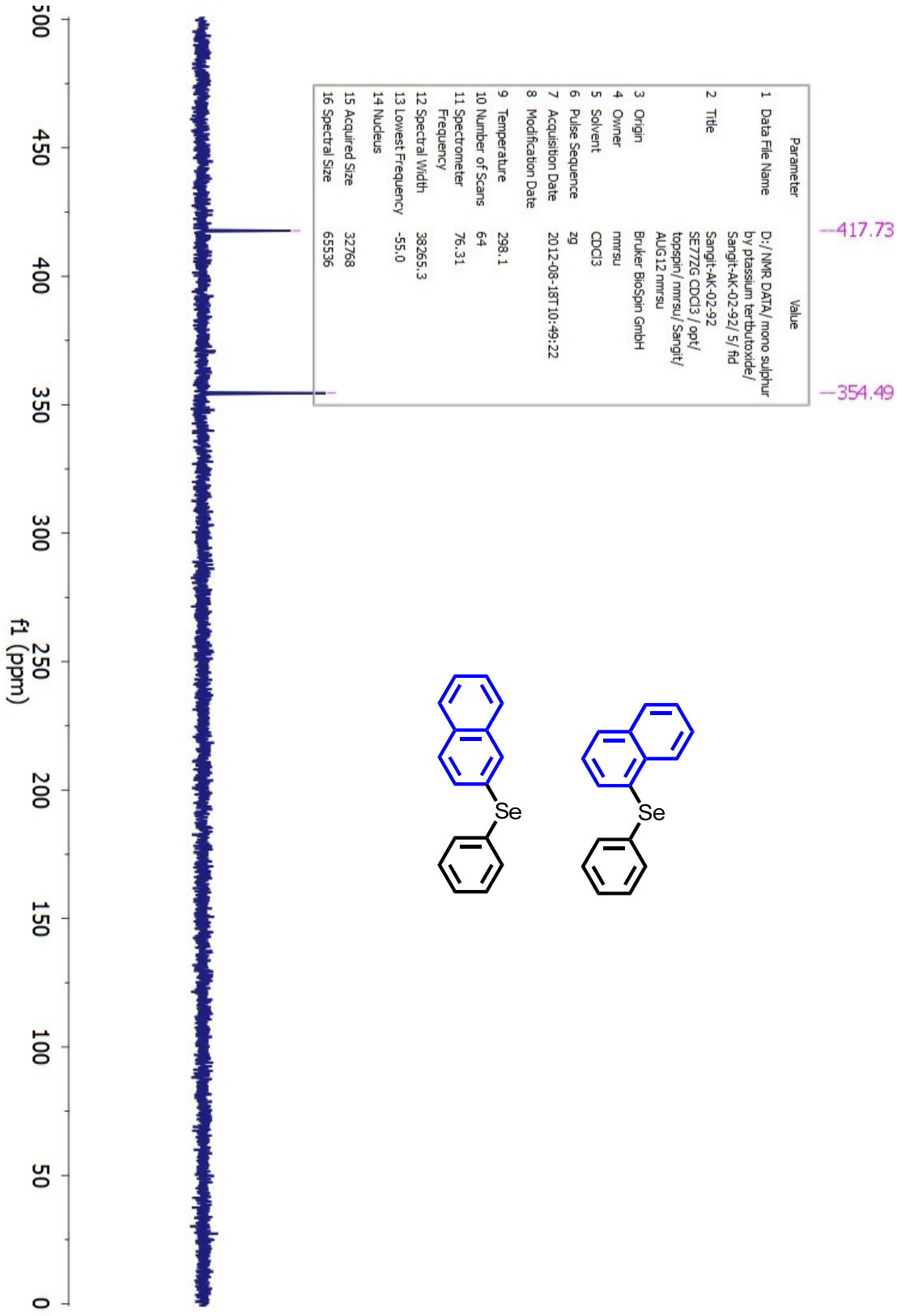

Figure S39 ^{1}H NMR spectrum of **13**

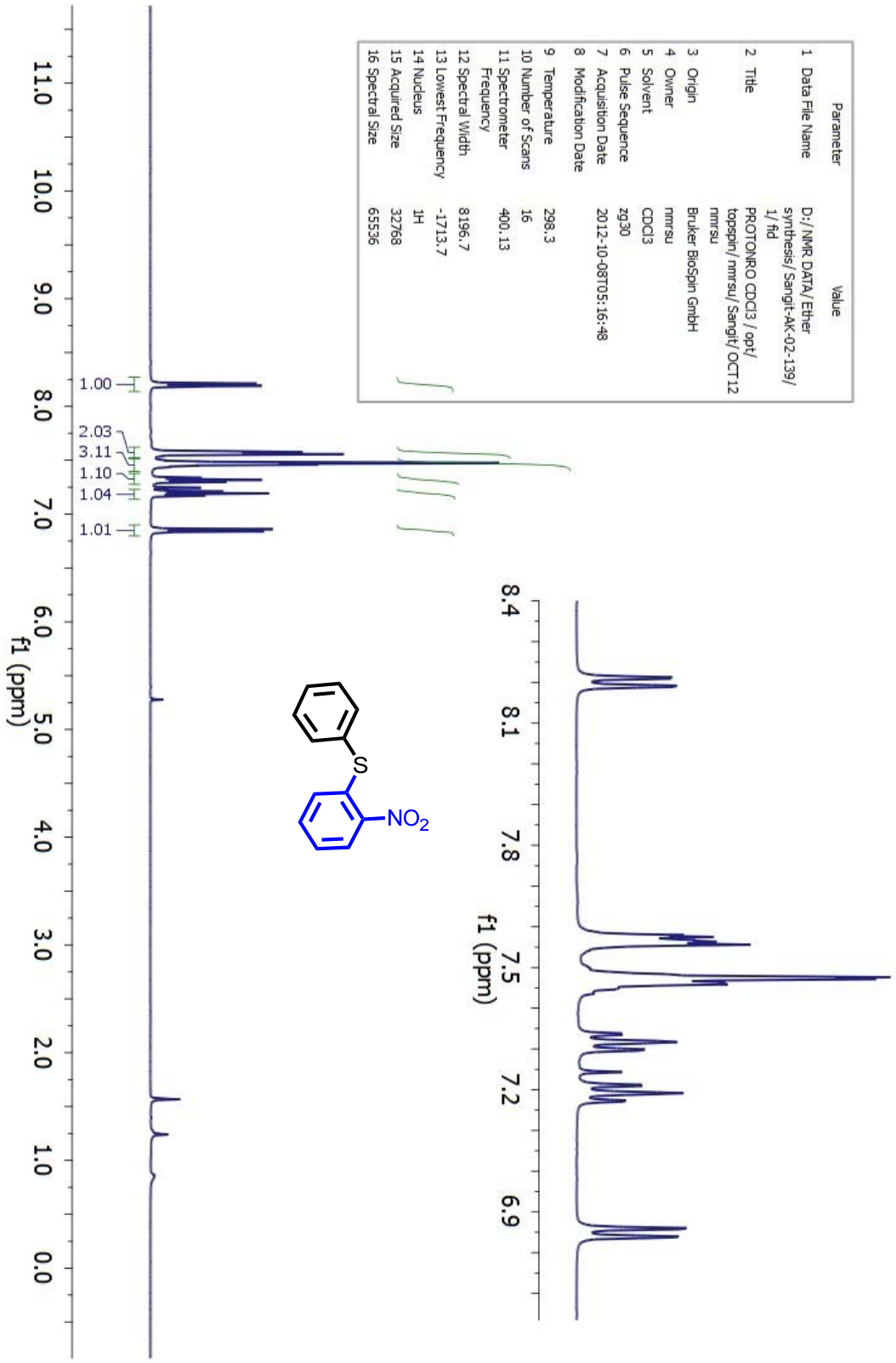

Figure S40 ^{13}C NMR spectrum of **13**

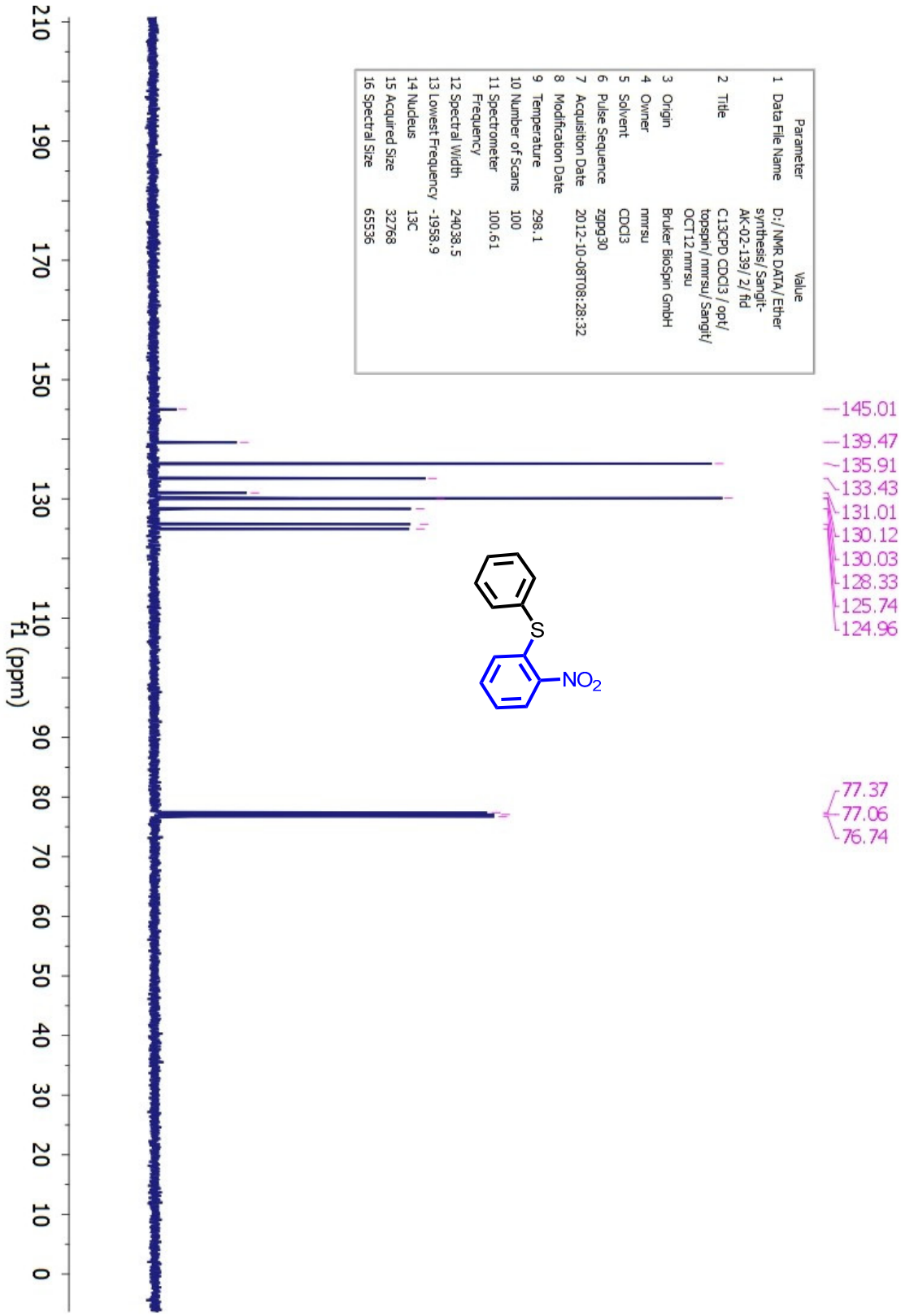

Figure S41 ^{1}H NMR spectrum **14**

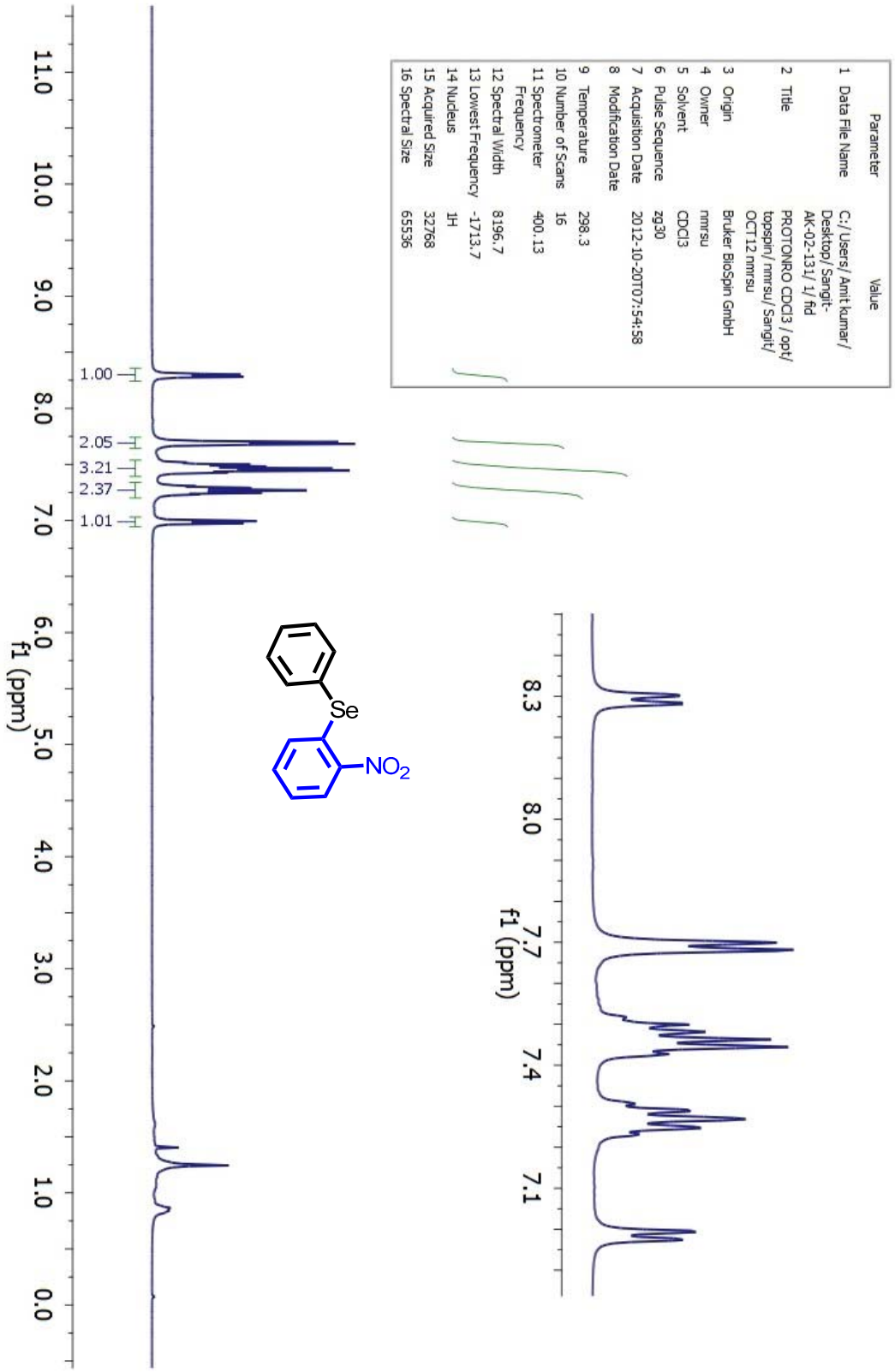

Figure S42 ^{13}C NMR spectrum of **14**

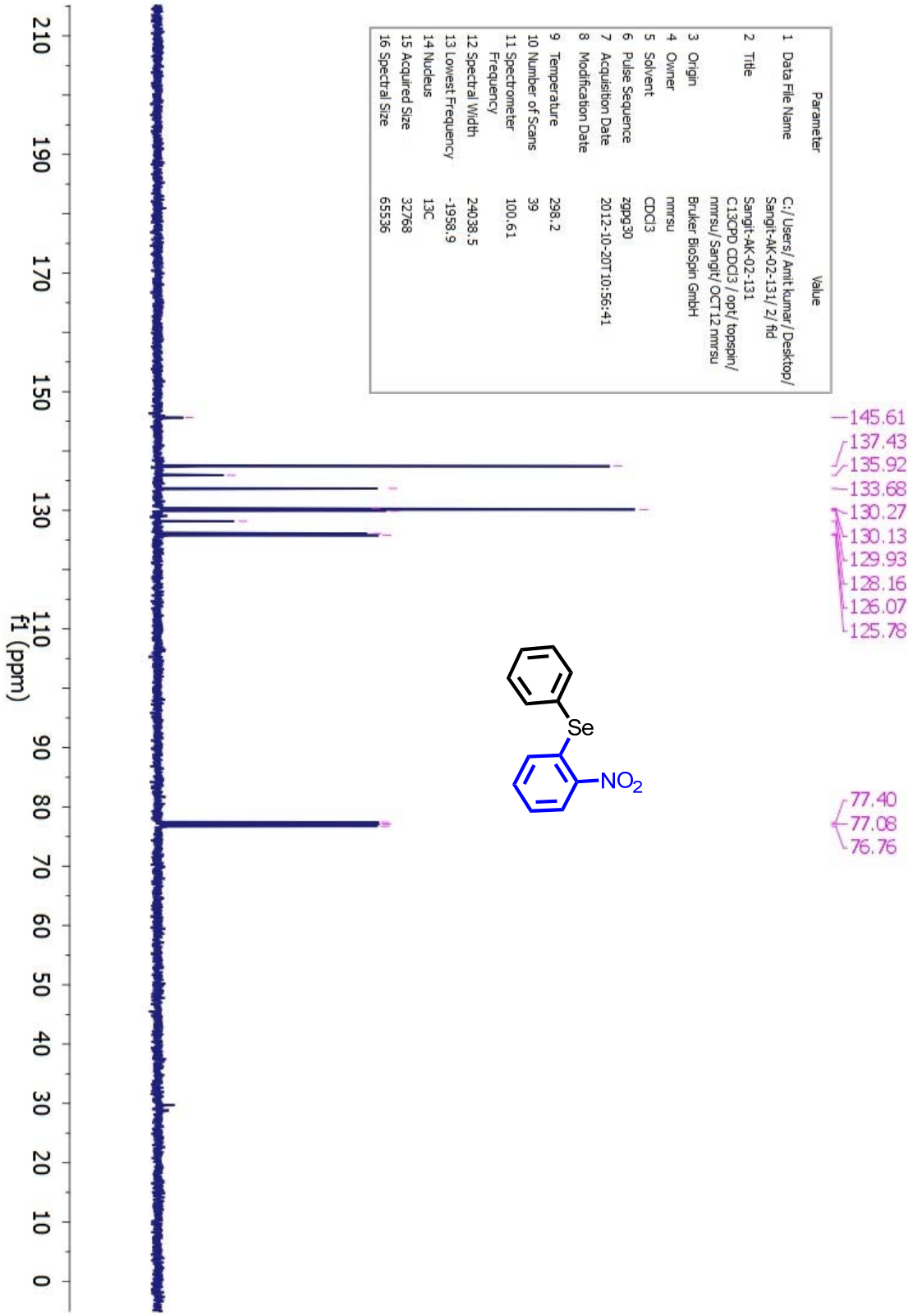

Figure S43 DEPT- 135 NMR spectrum of **14**

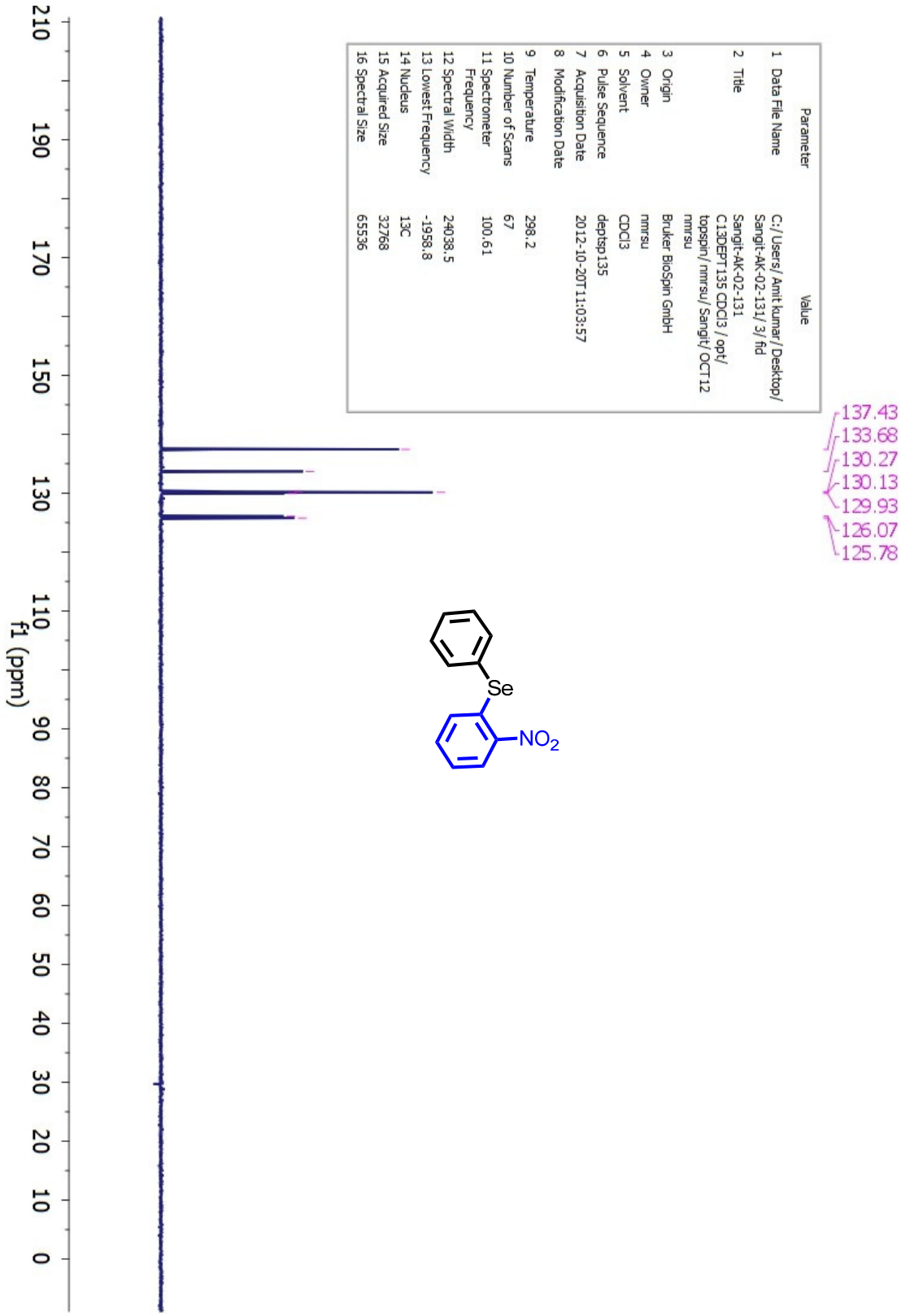

Figure S44 ^{77}Se NMR spectrum of **14**

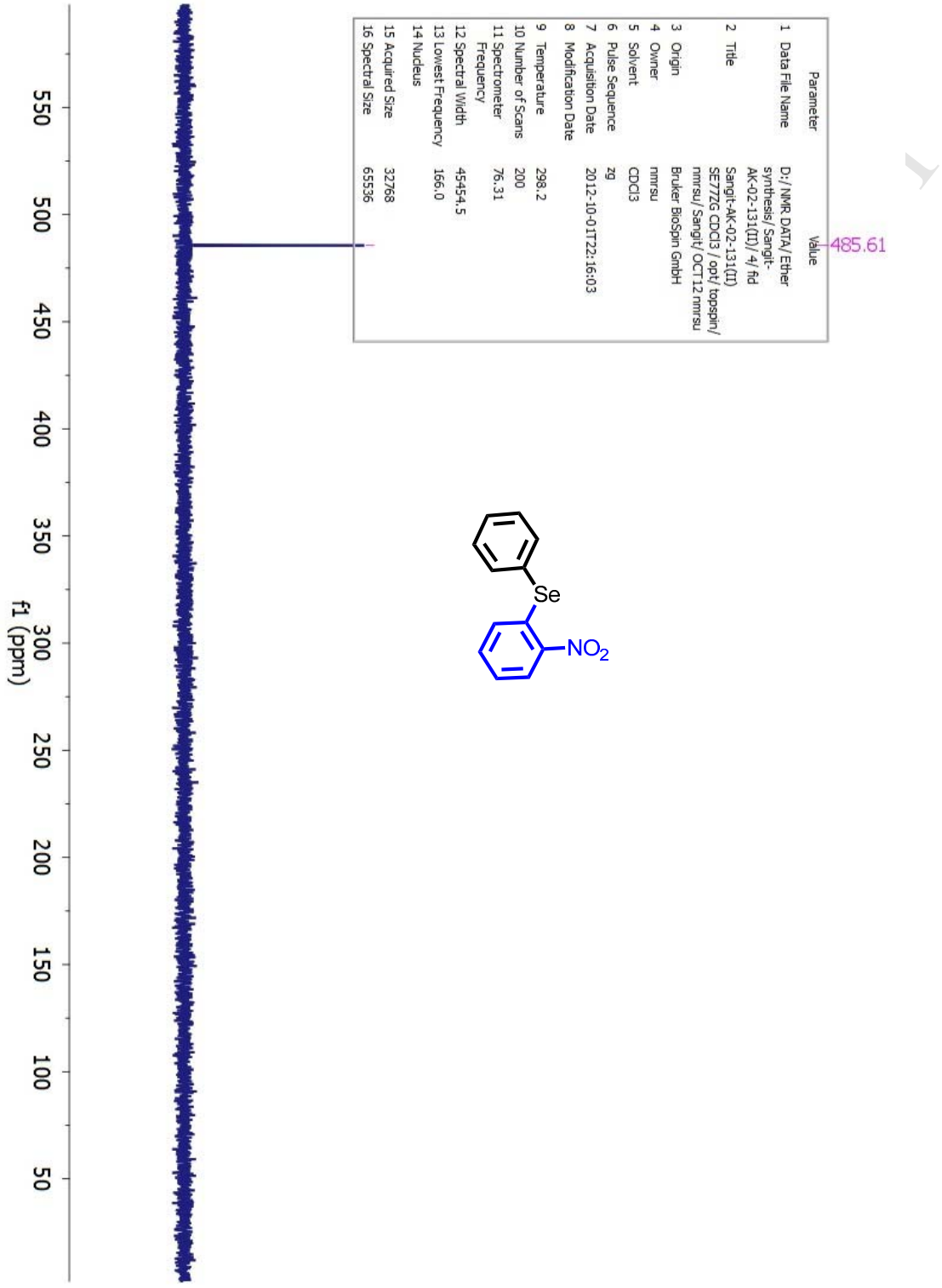

Figure S45 ^{1}H NMR spectrum **15**

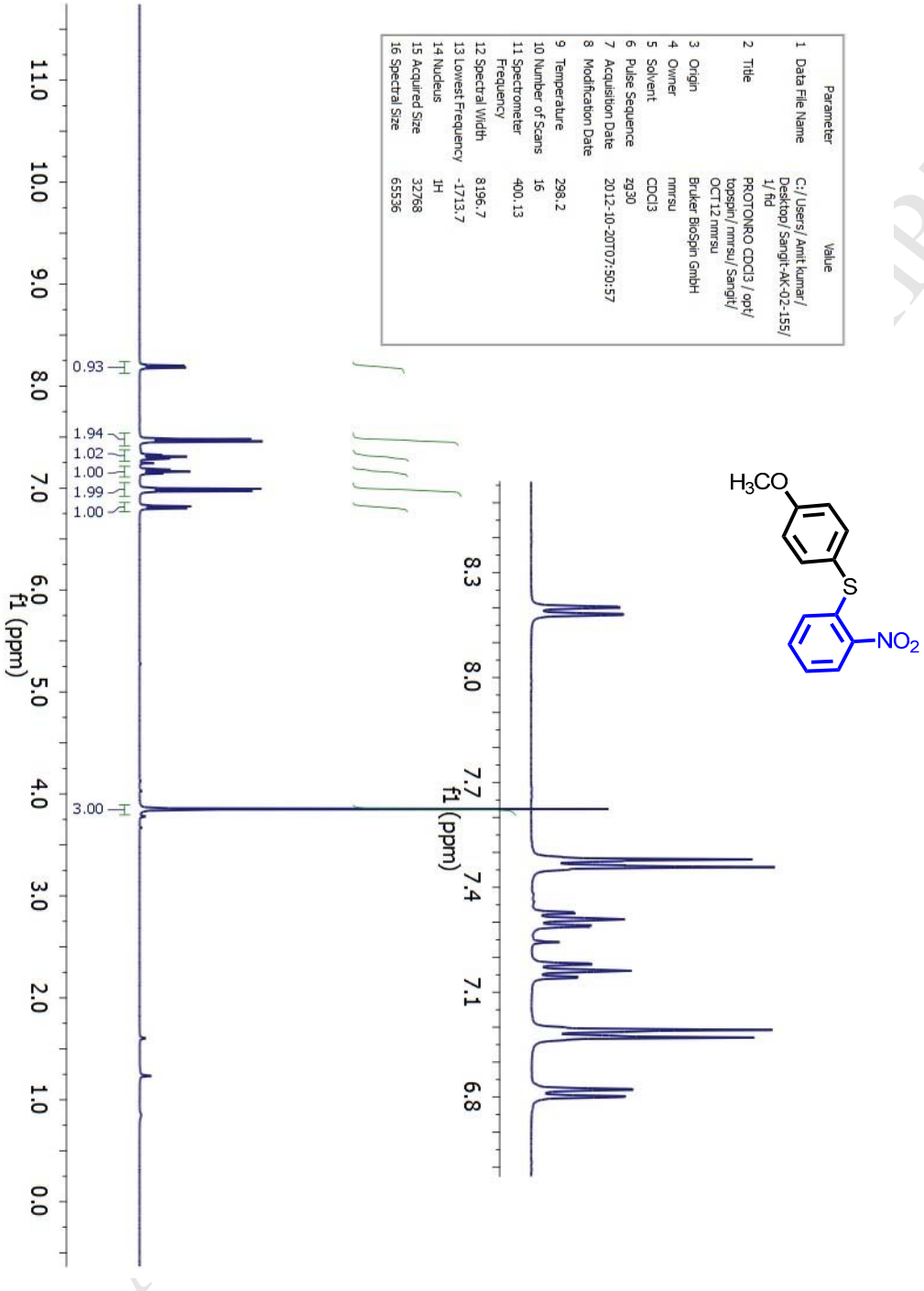

Figure S46 ^{13}C NMR spectrum of **15**

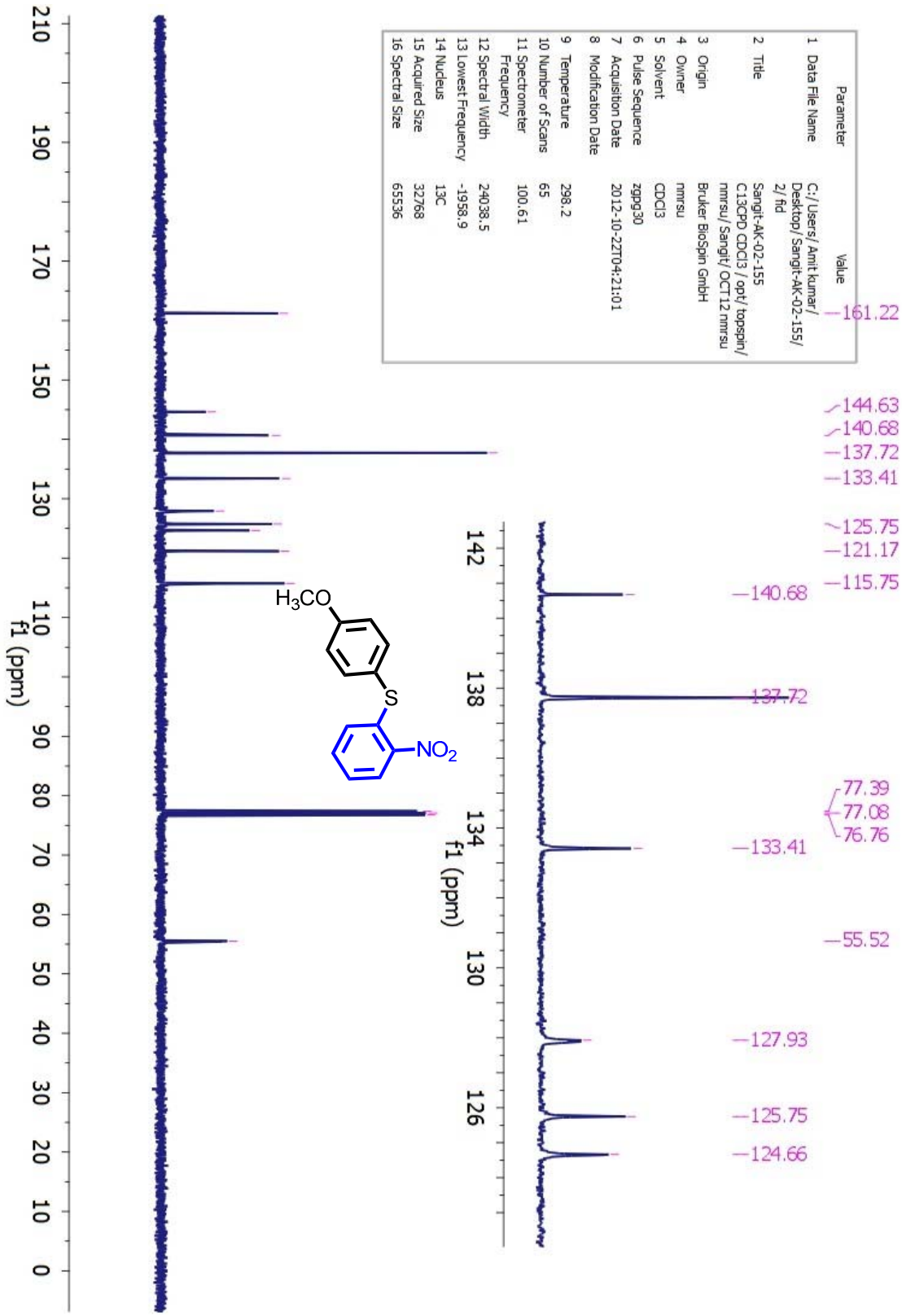

Figure S47 DEPT- 135 NMR spectrum of **15**

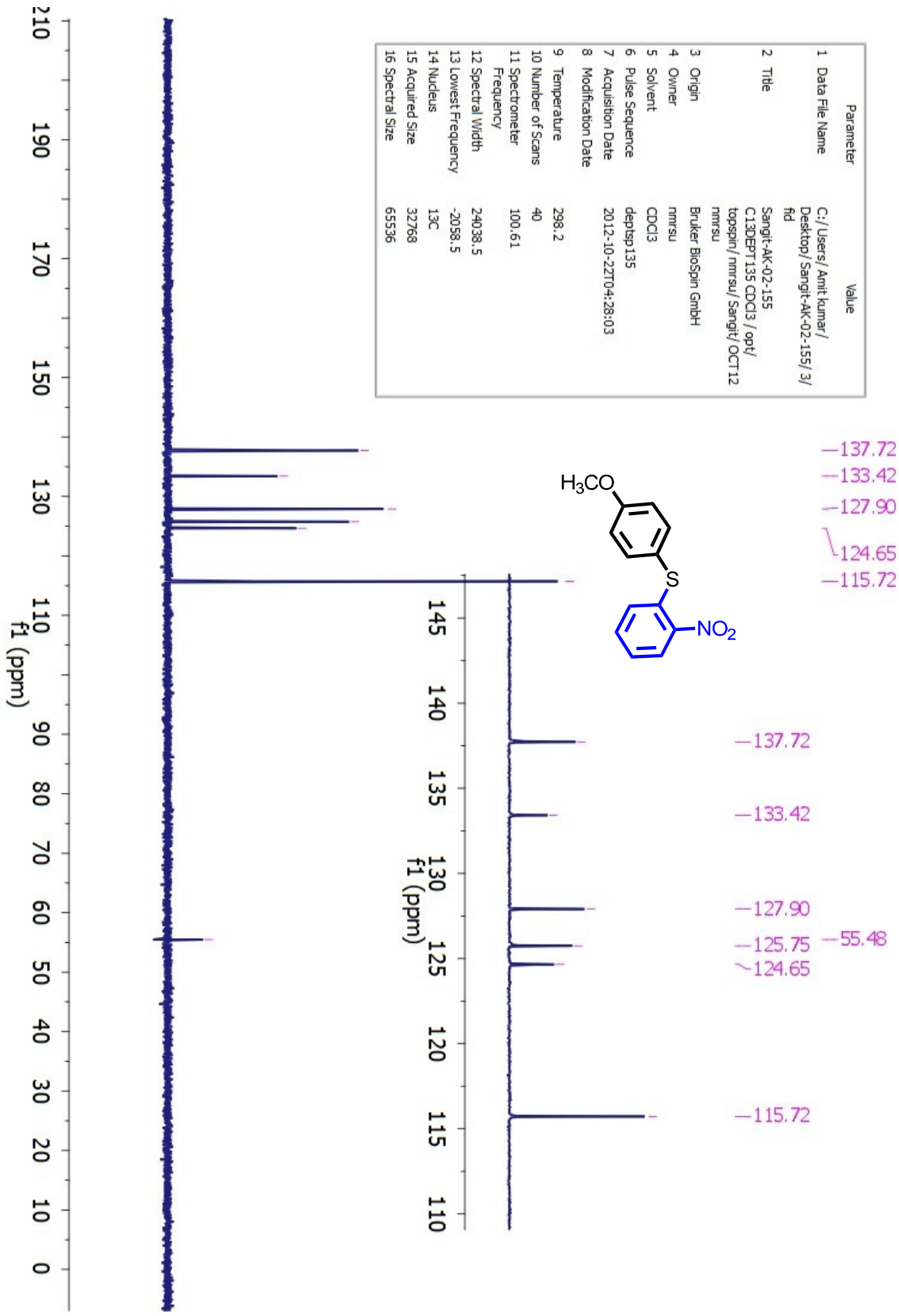

Figure S48 ^{1}H NMR spectrum **16**

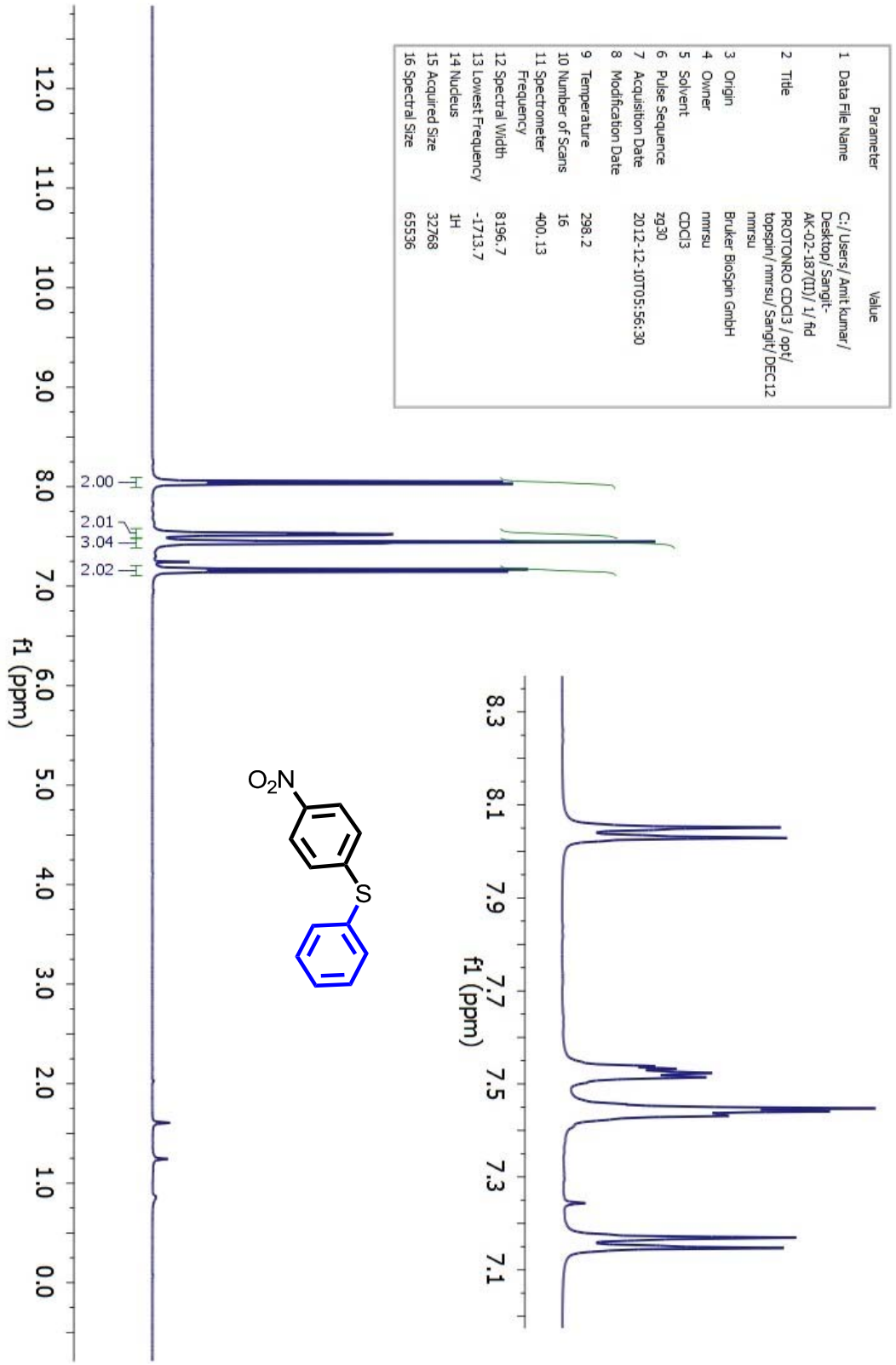

Figure S49 ^{13}C NMR spectrum of **16**

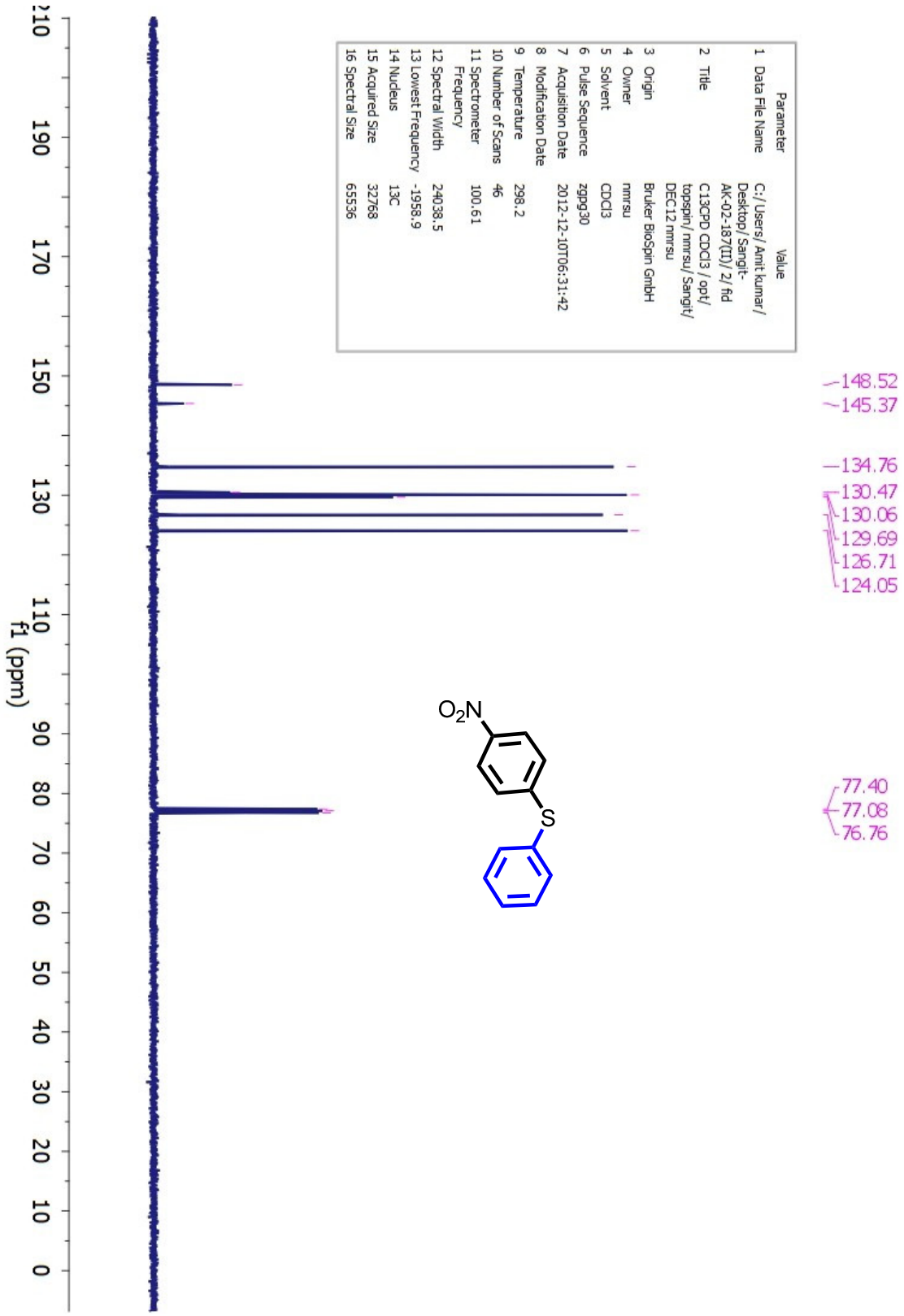

Figure S50 DEPT- 135 NMR spectrum of **16**

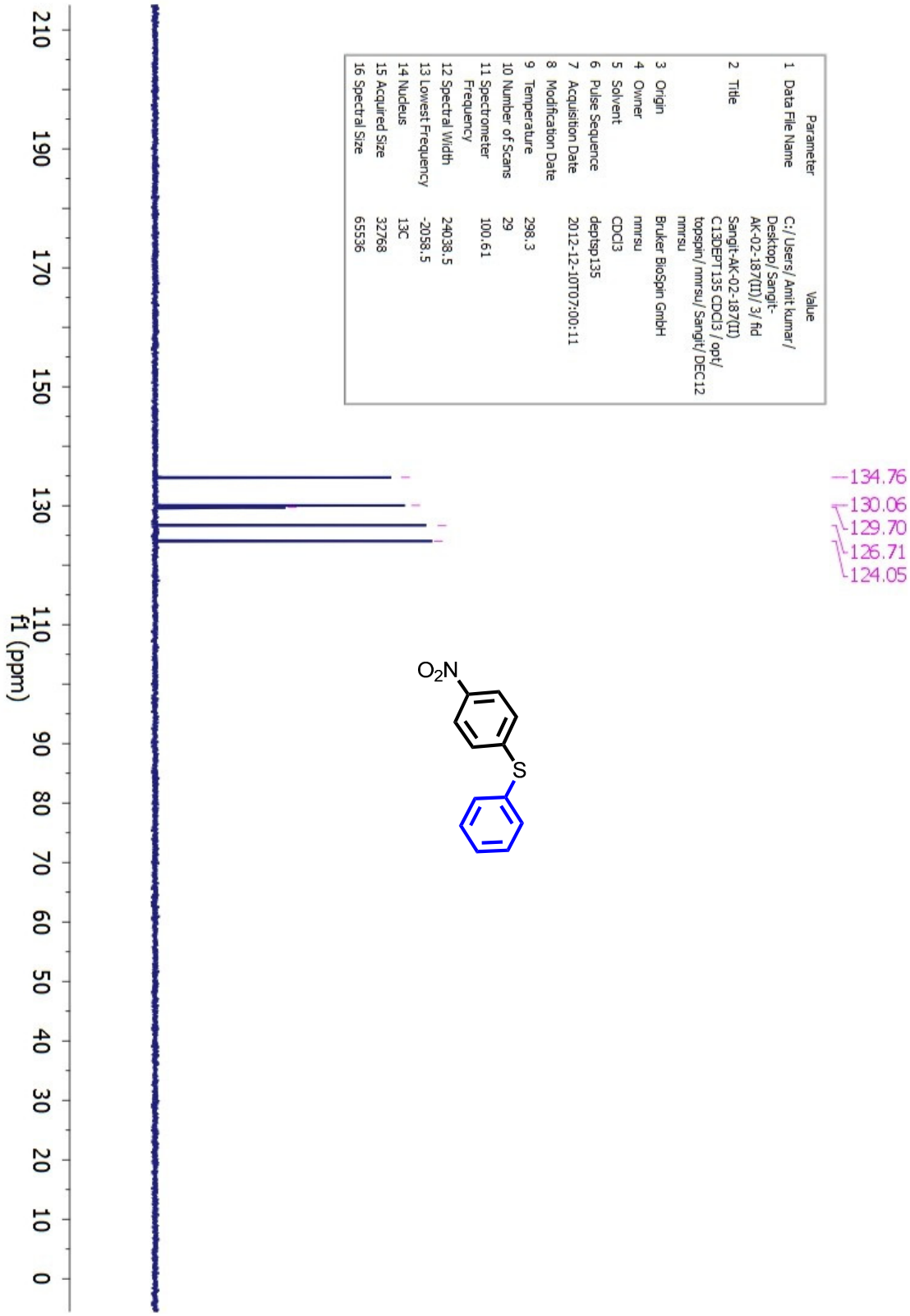

Figure S51 ^{1}H NMR spectrum of **17**

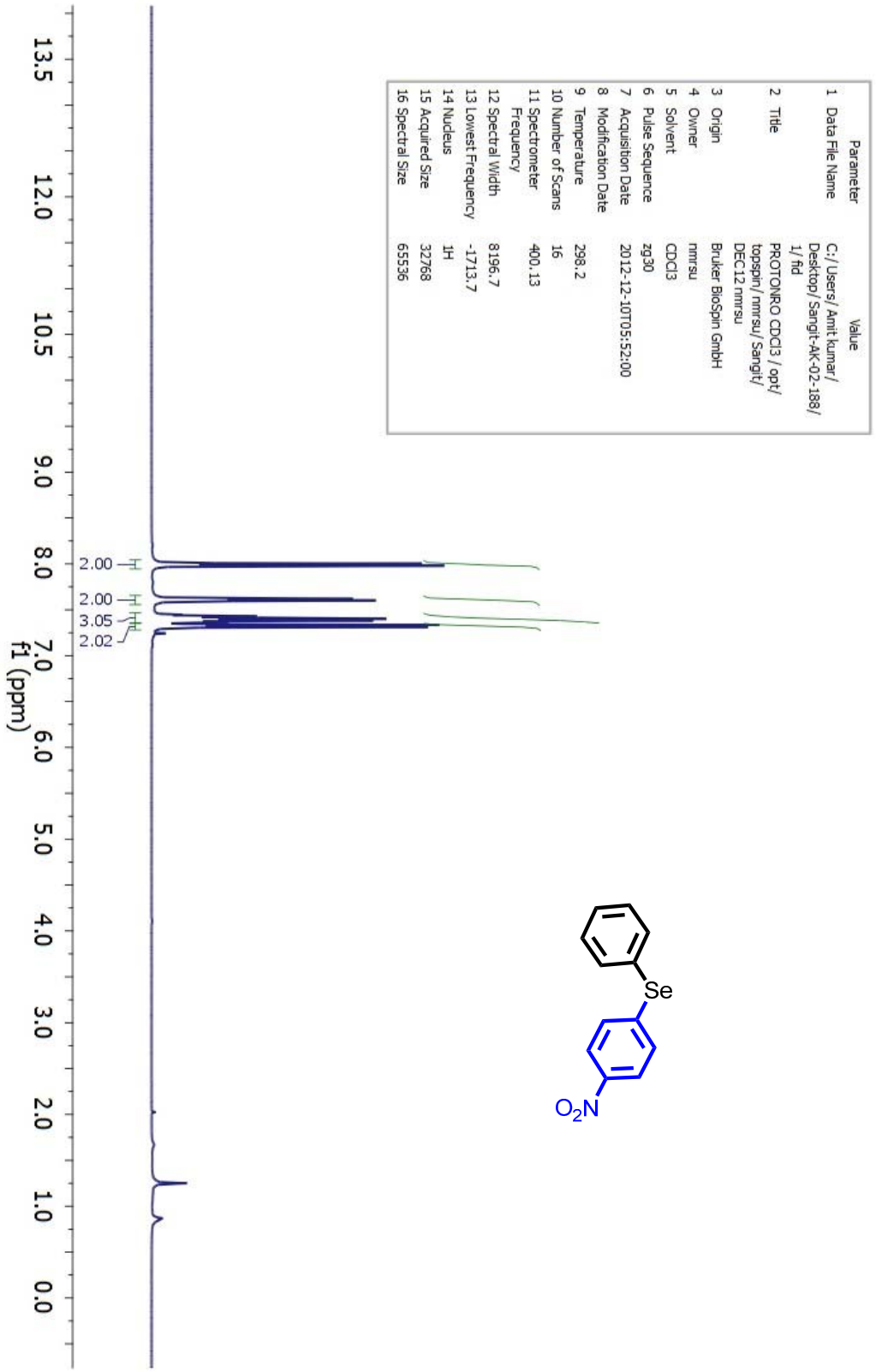

Figure S52 ^{13}C NMR spectrum of **17**

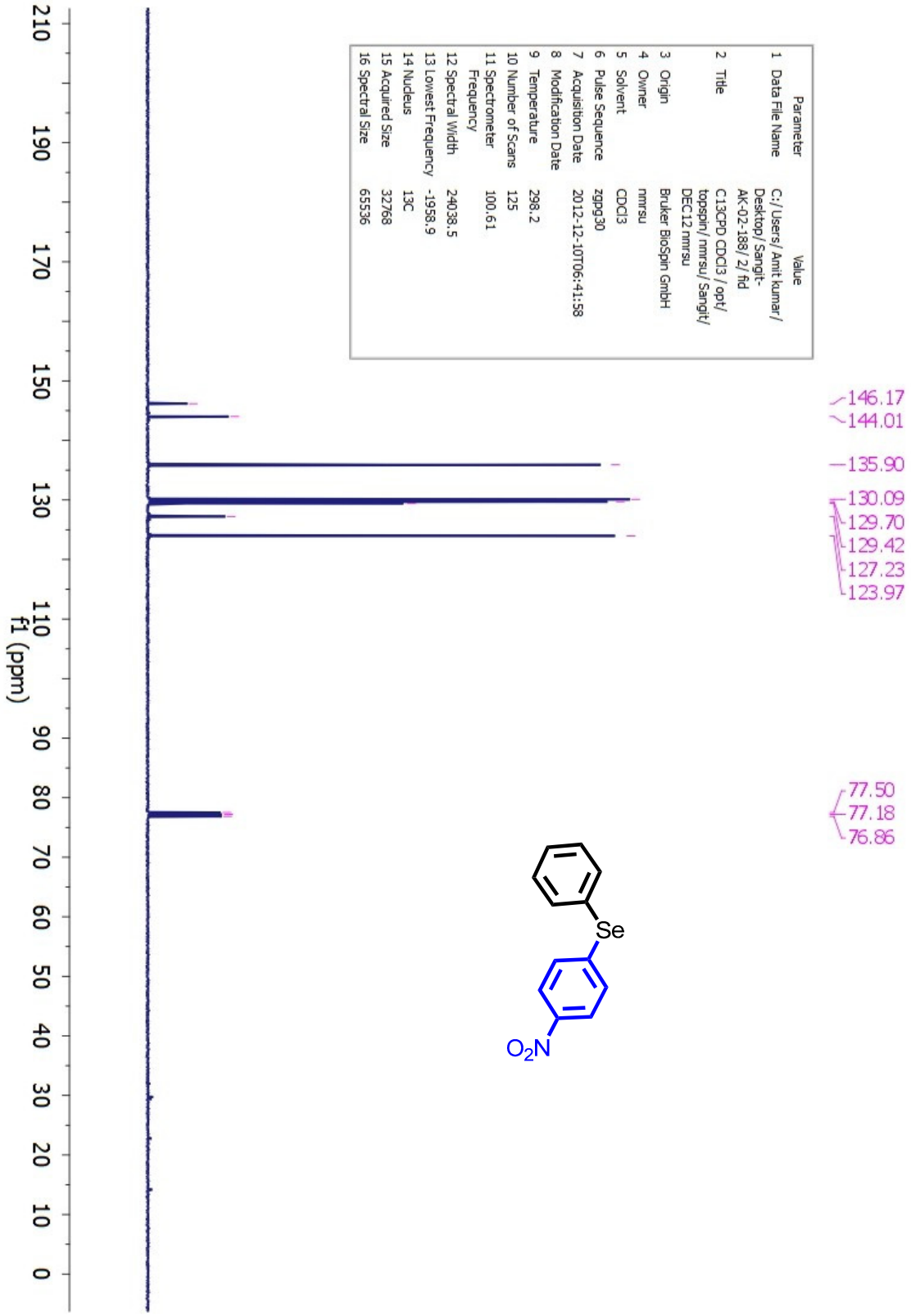

Figure S53 DEPT- 135 NMR spectrum of **17**

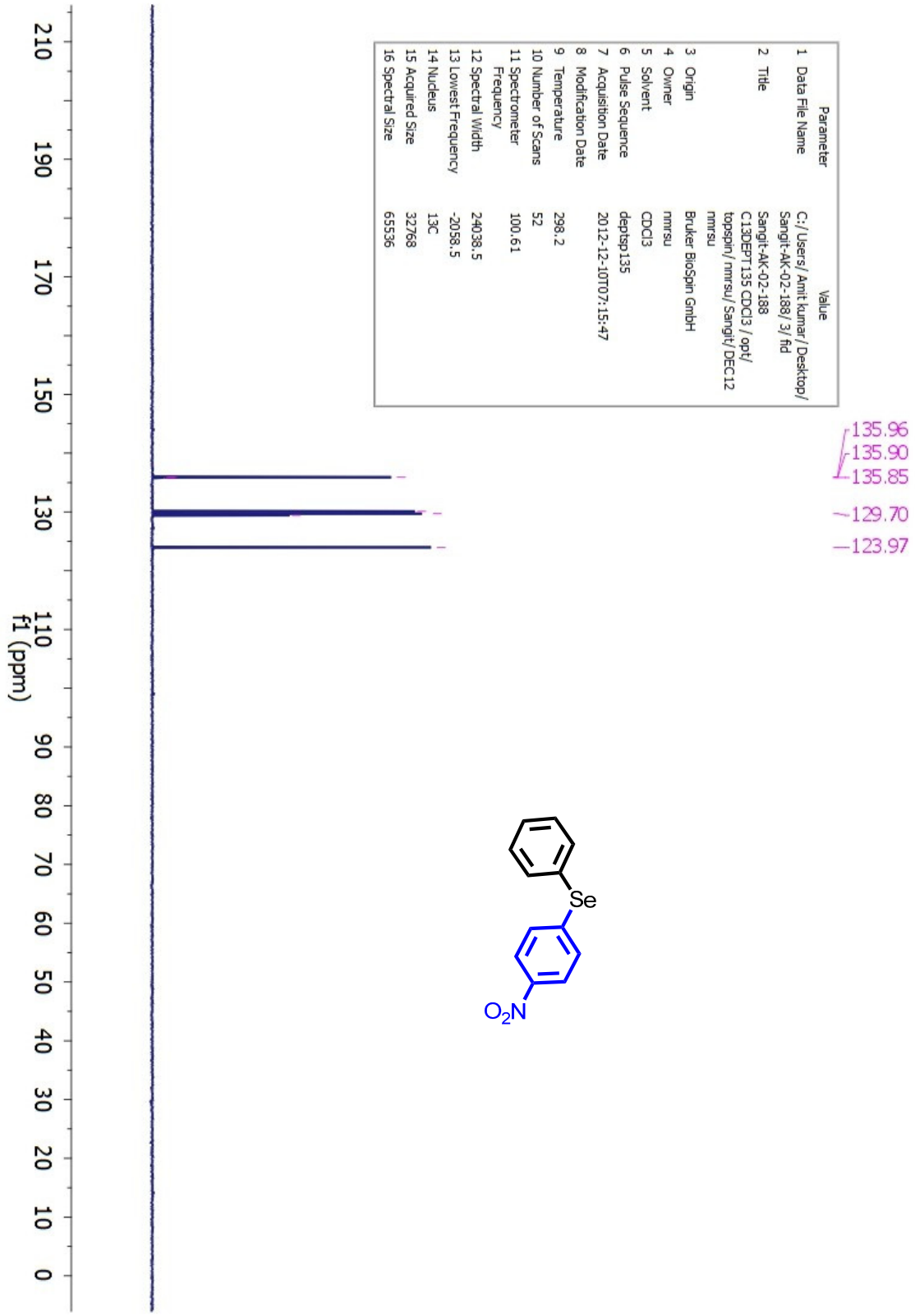

Figure S54 ^{77}Se NMR spectrum of **17**

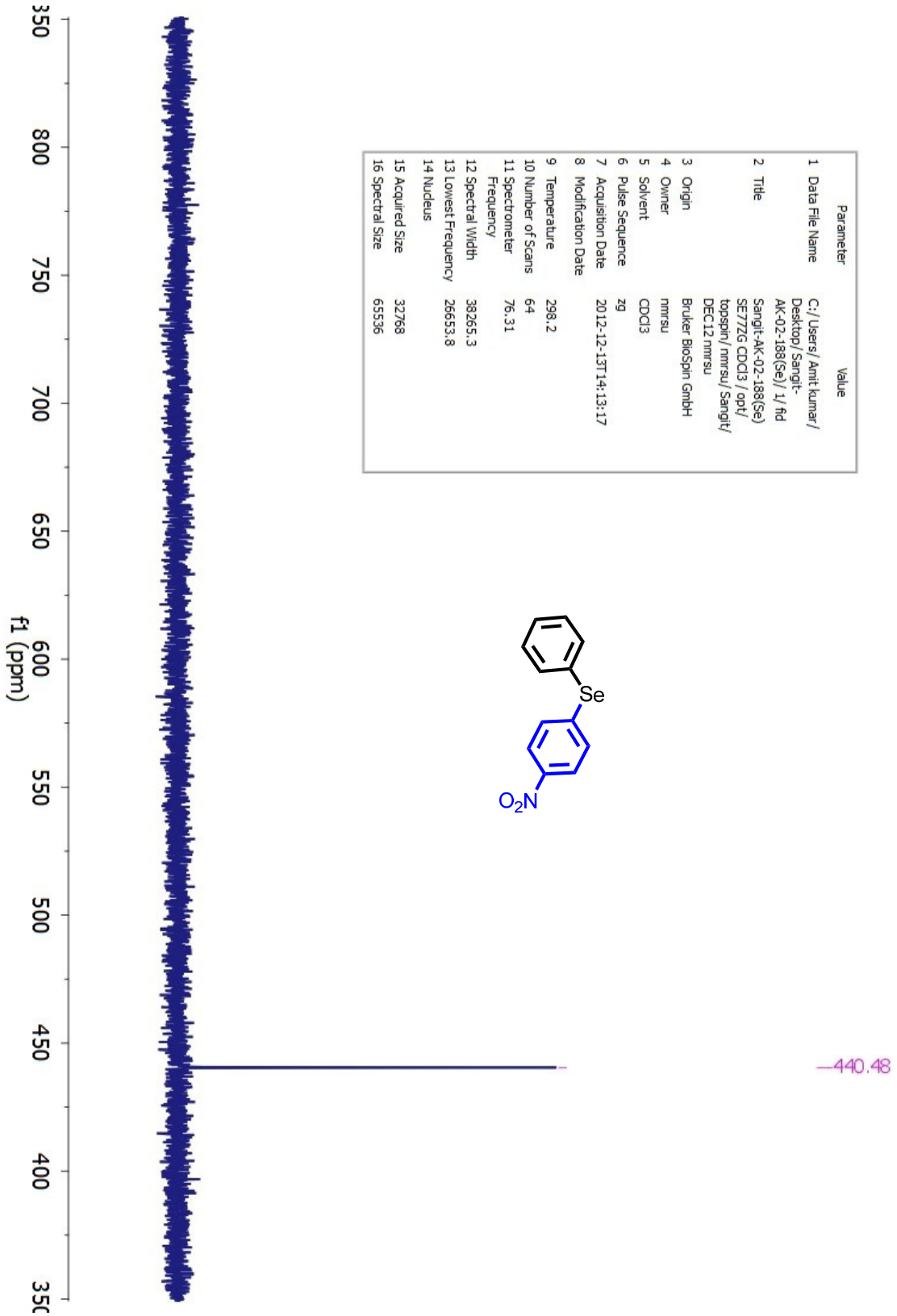

Figure S55 ^{1}H NMR spectrum of **18**

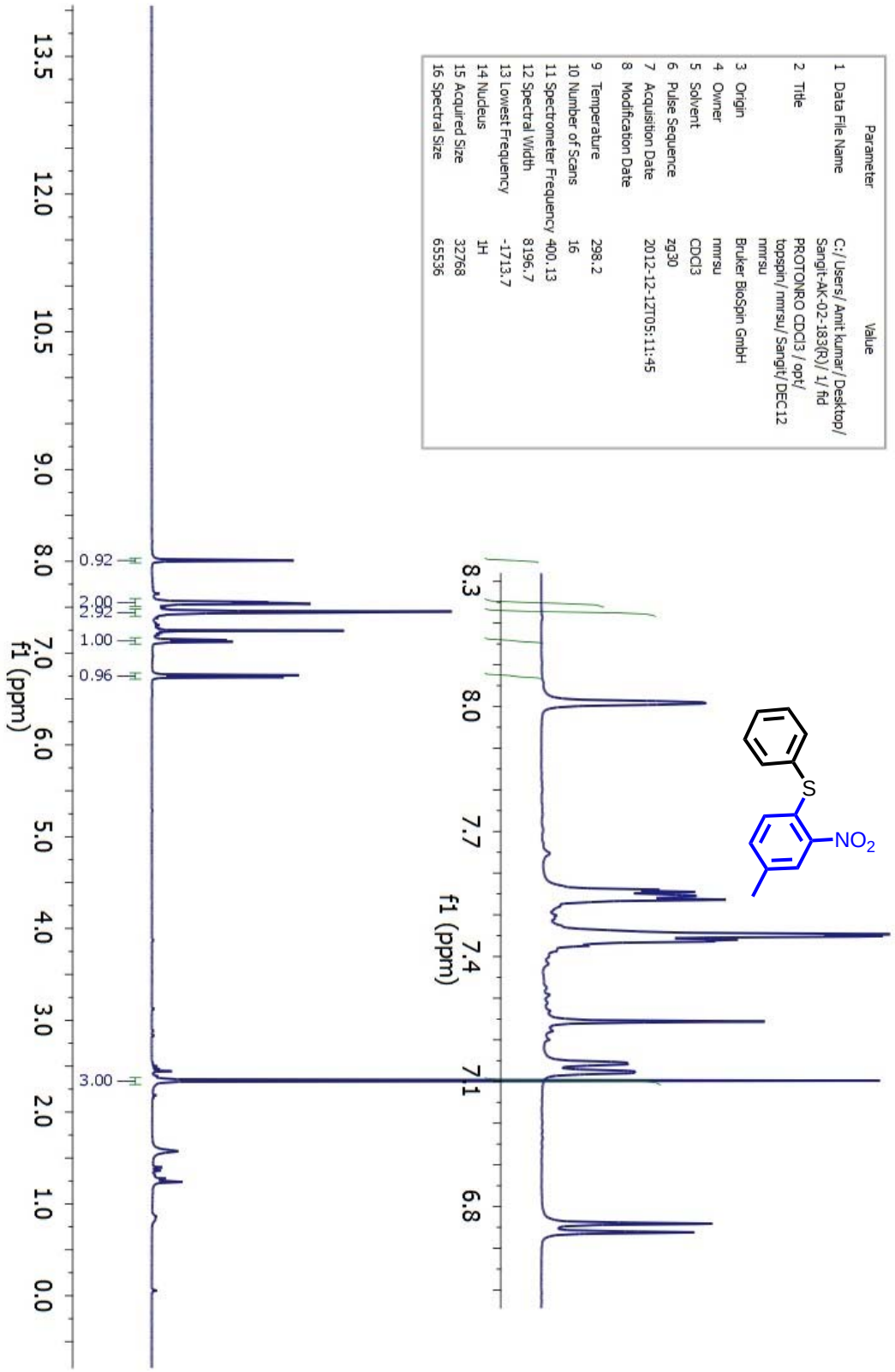

Figure S56 ^{13}C NMR spectrum of**8**

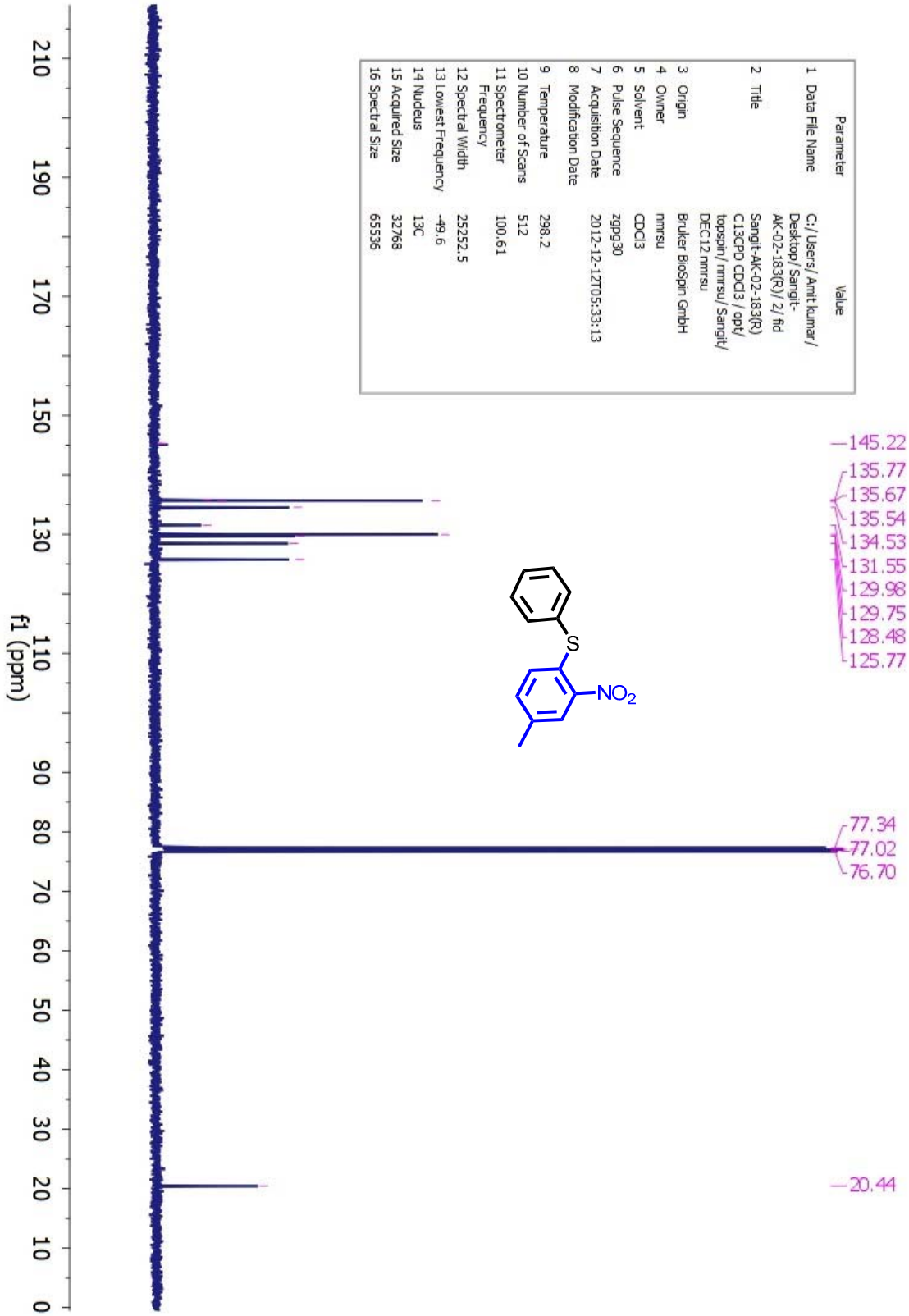

Figure S57 DEPT- 135 NMR spectrum of **18**

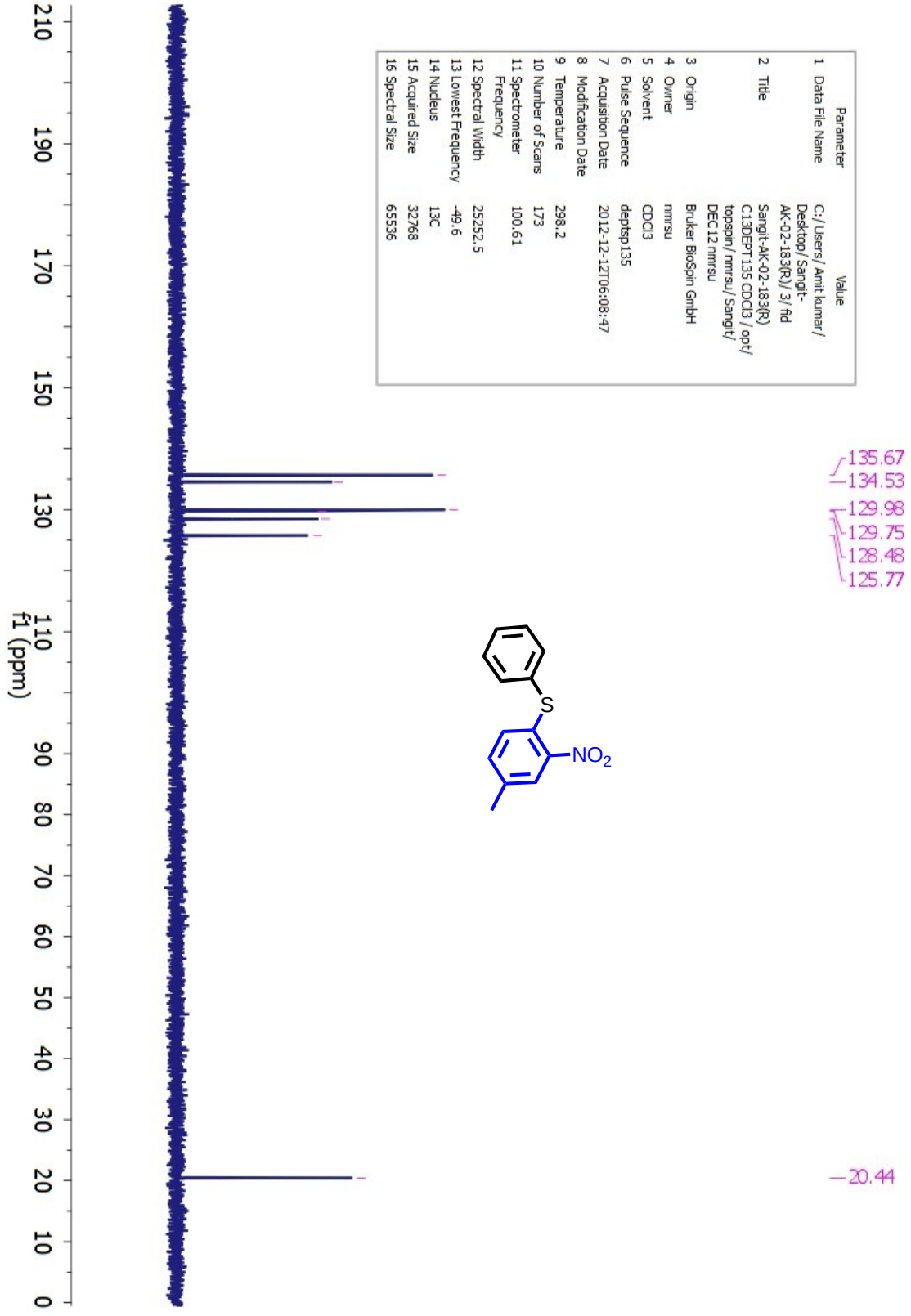

Figure S58 ^{1}H NMR spectrum of **19**

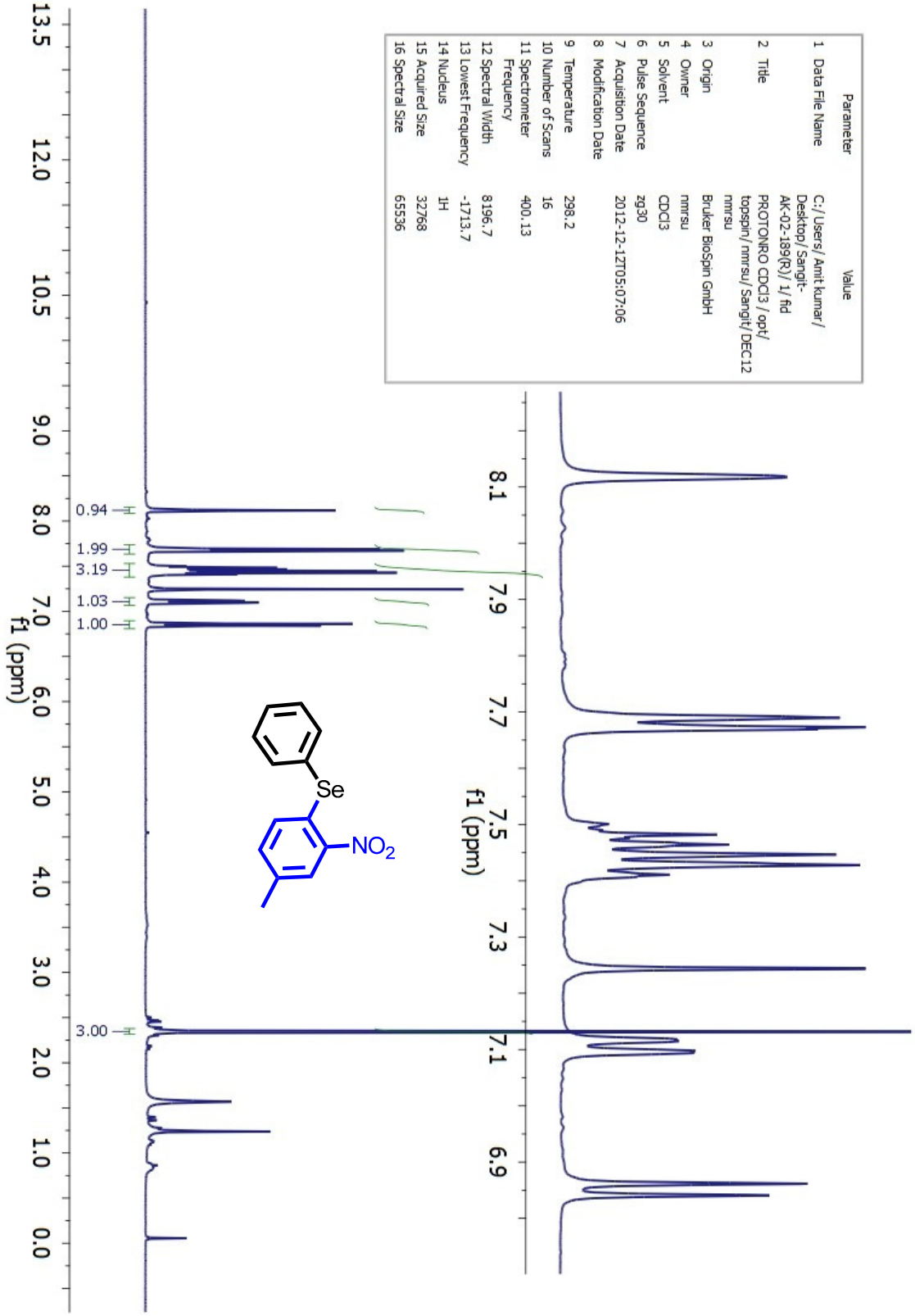

Figure S59 ^{13}C NMR spectrum of **19**

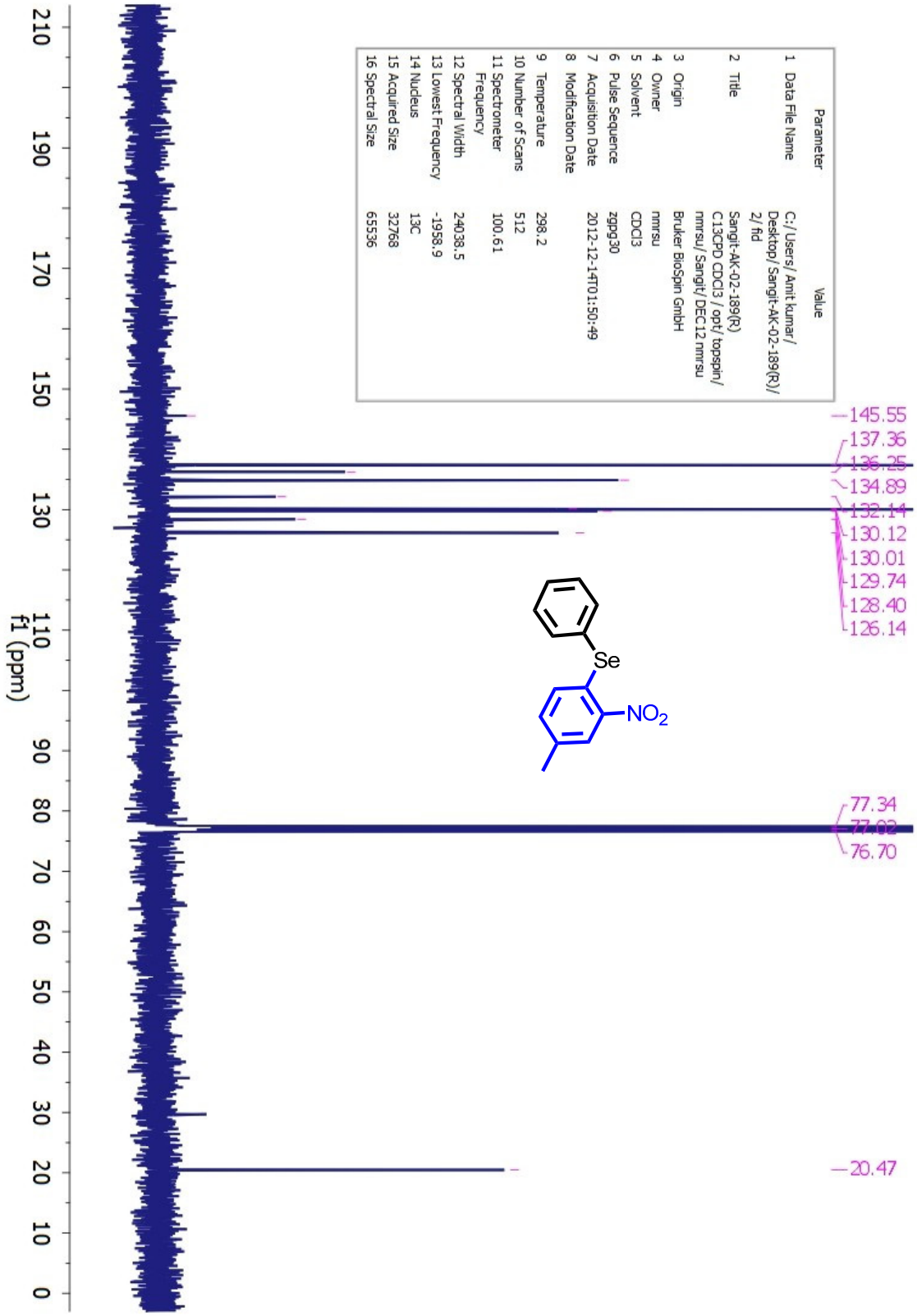

Figure S60 DEPT- 135 NMR spectrum of **19**

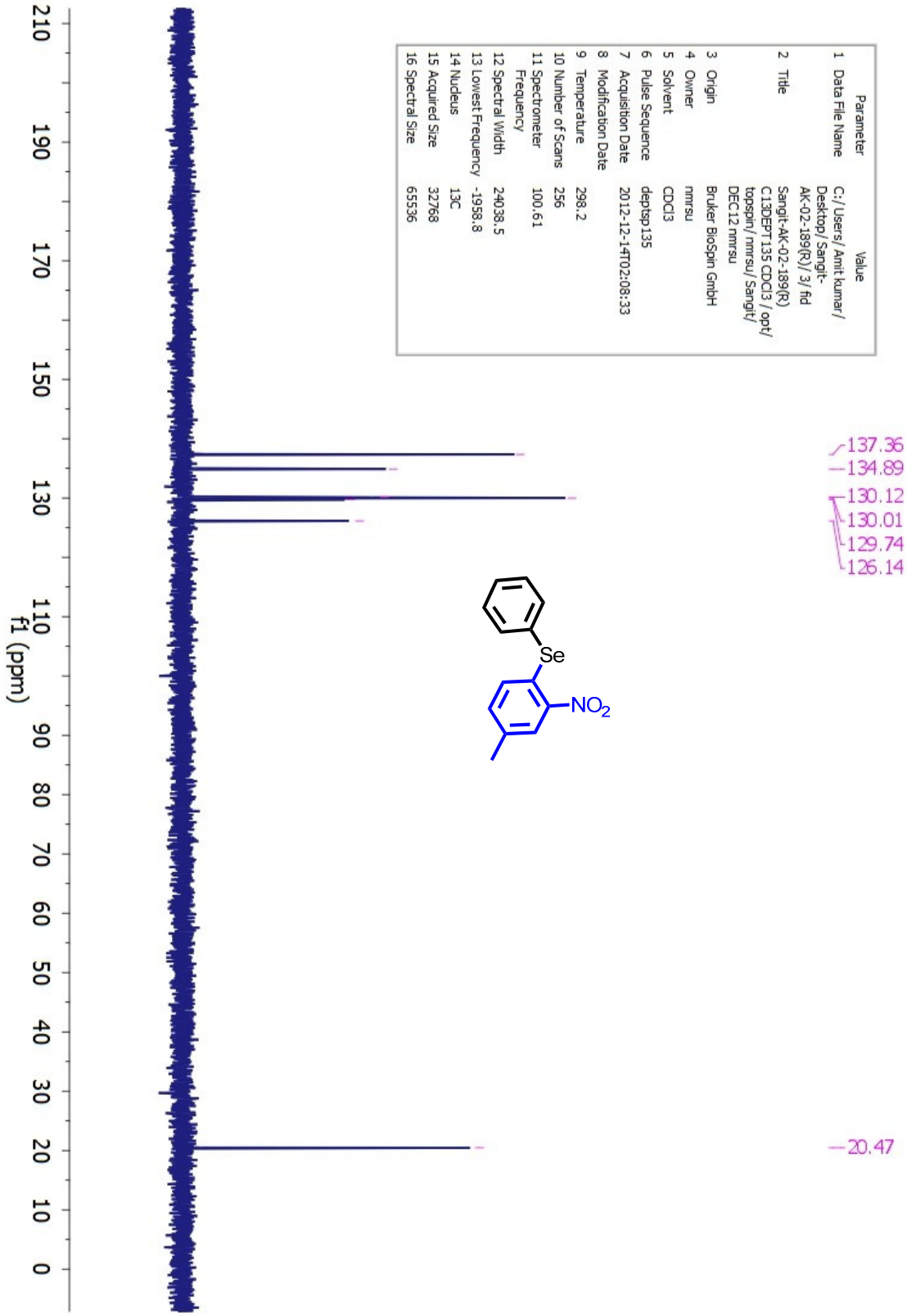

Figure S61 ^{77}Se NMR spectrum of **19**

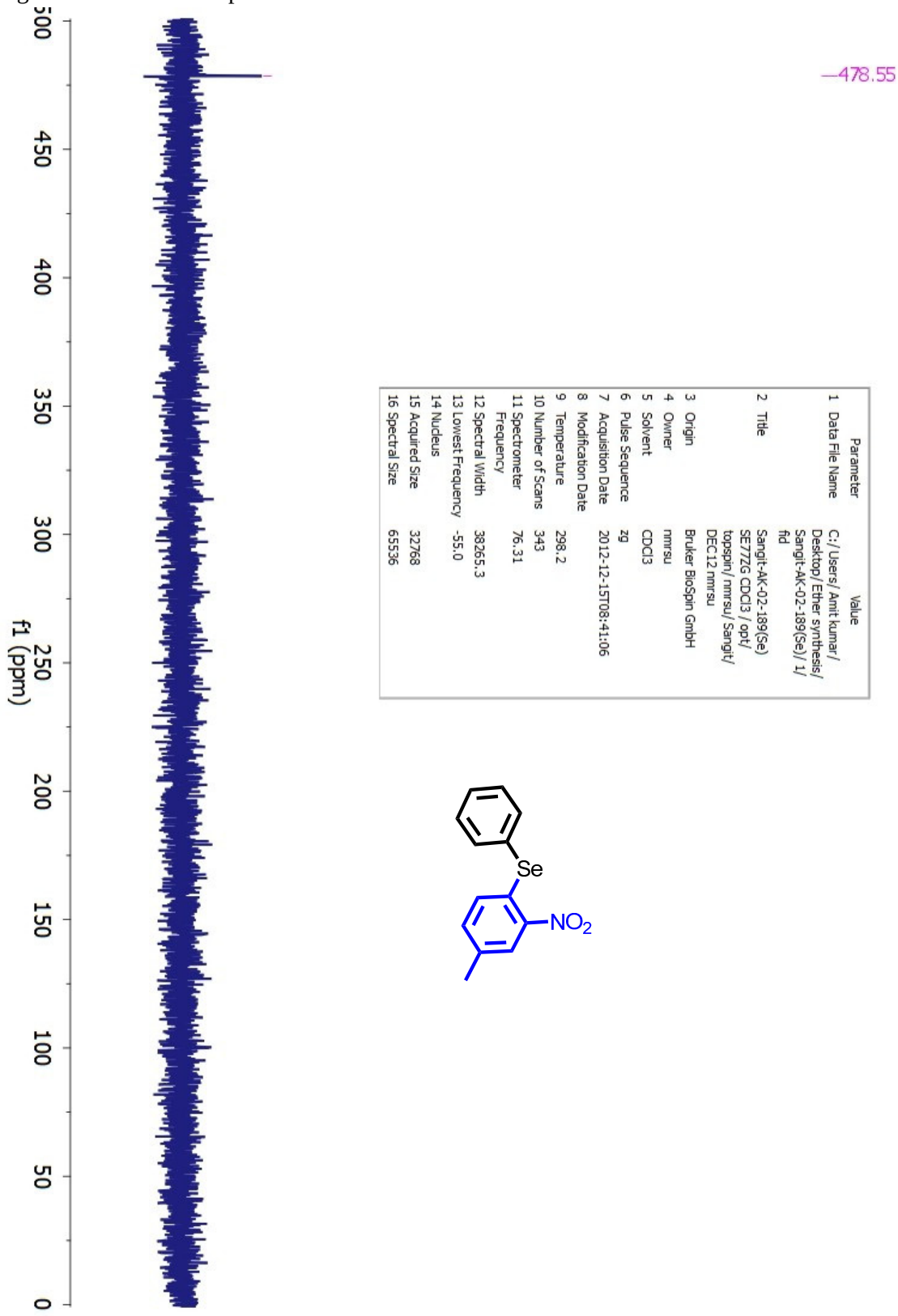

Figure S62 ^{1}H NMR spectrum of **20**

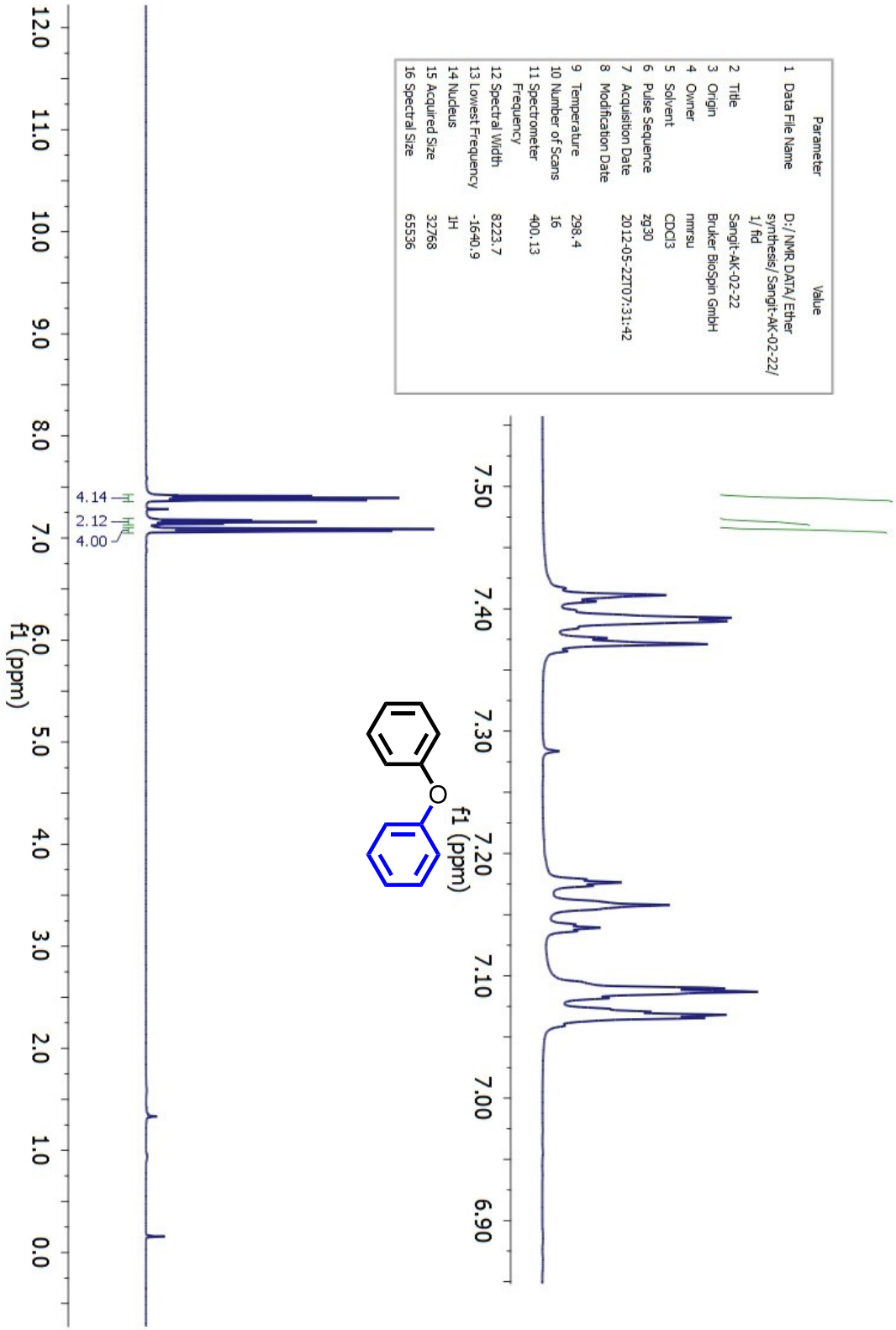

Figure S63 ^{13}C NMR spectrum of **20**

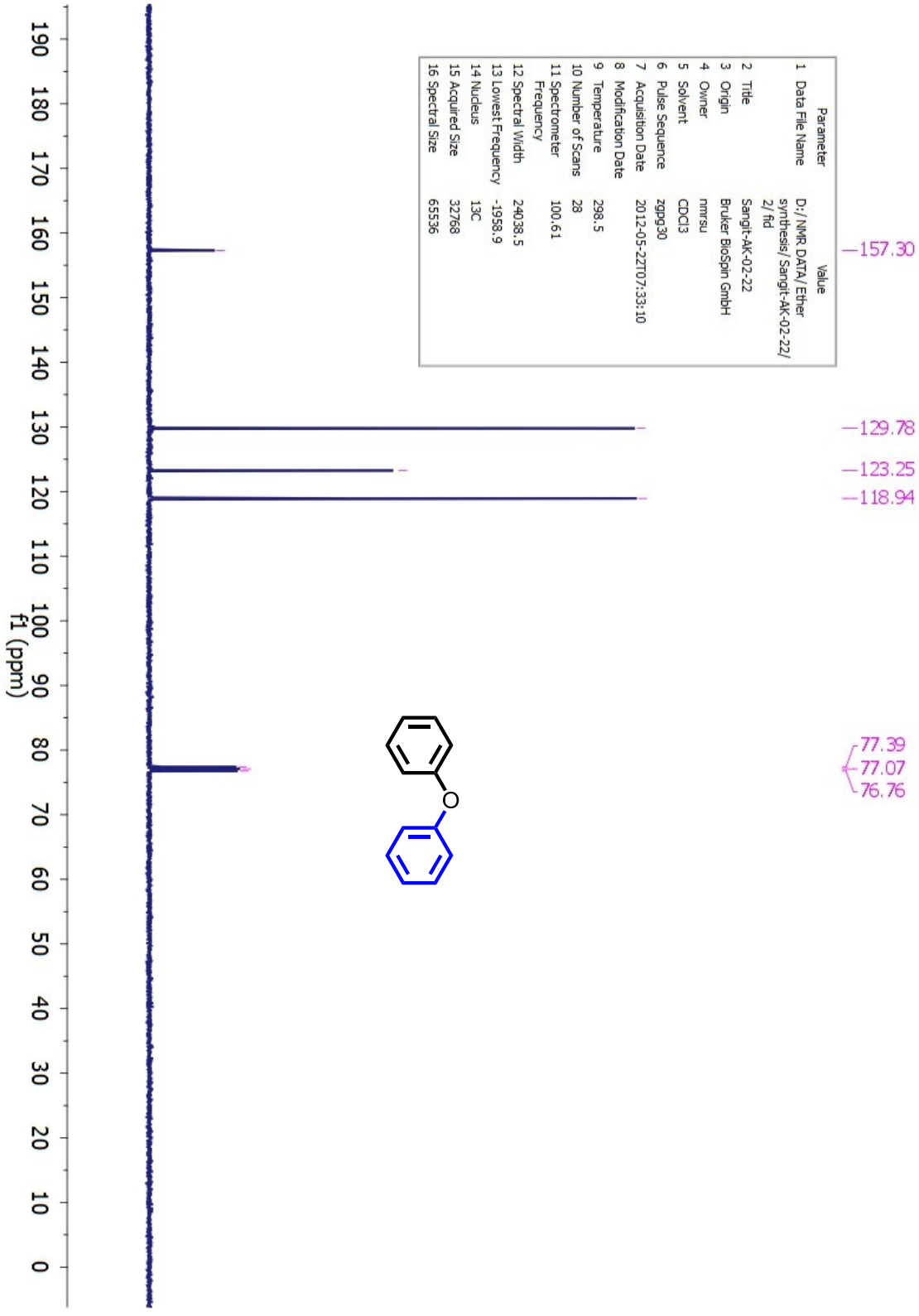

Figure S64 ^{1}H NMR spectrum of **21**

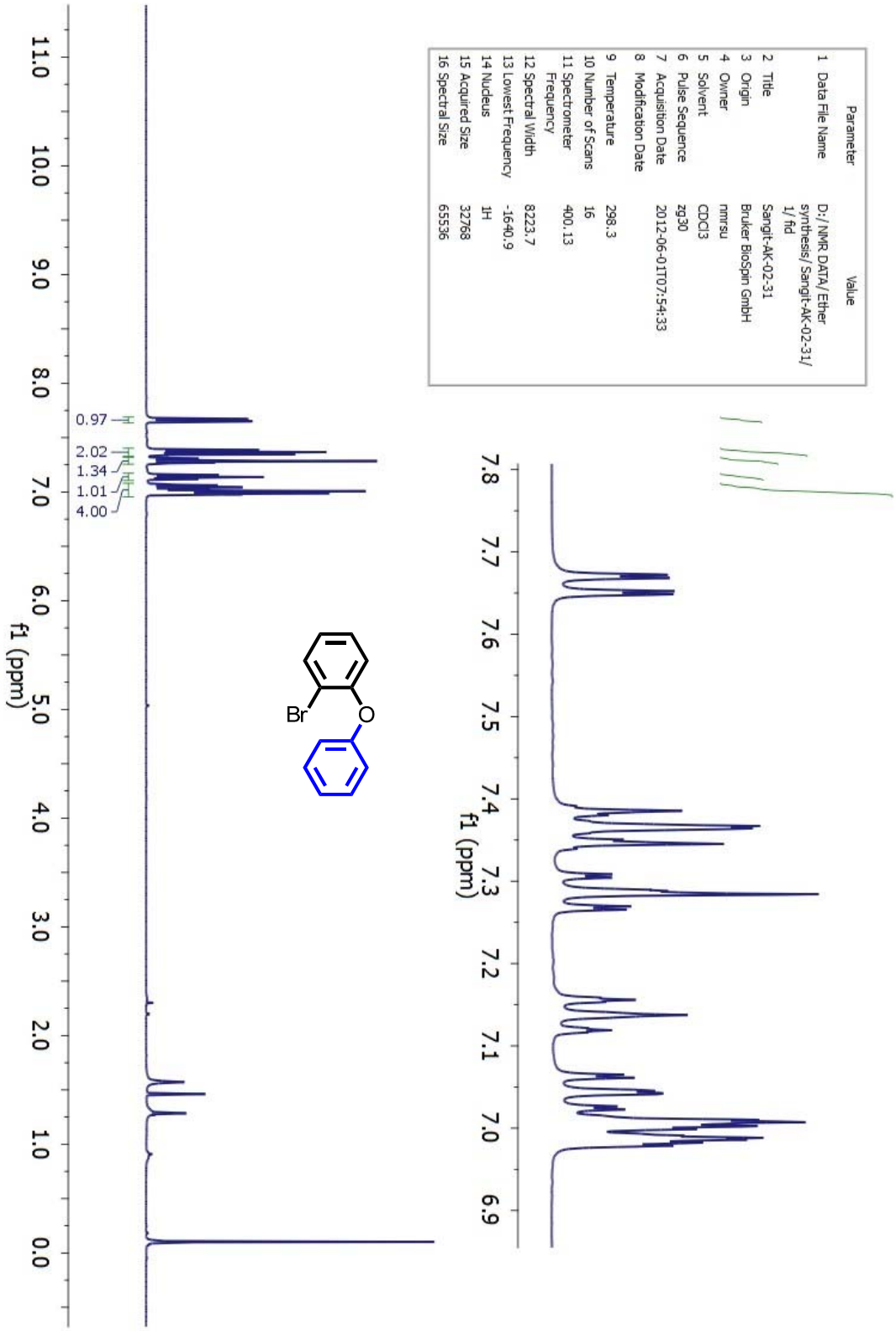

Figure S65 ^{13}C NMR spectrum of **21**

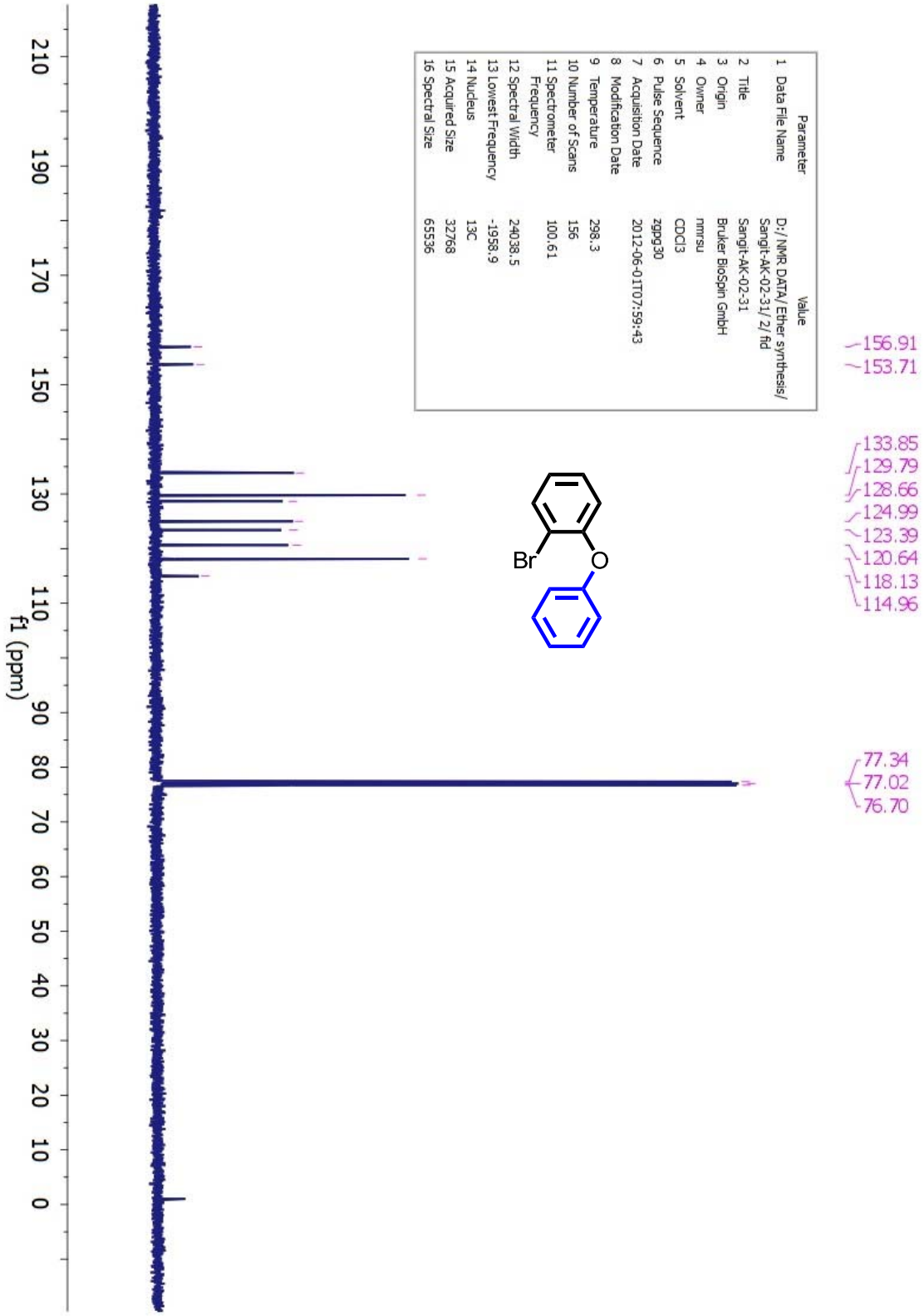

Figure S66 ^{1}H NMR spectrum of **22**

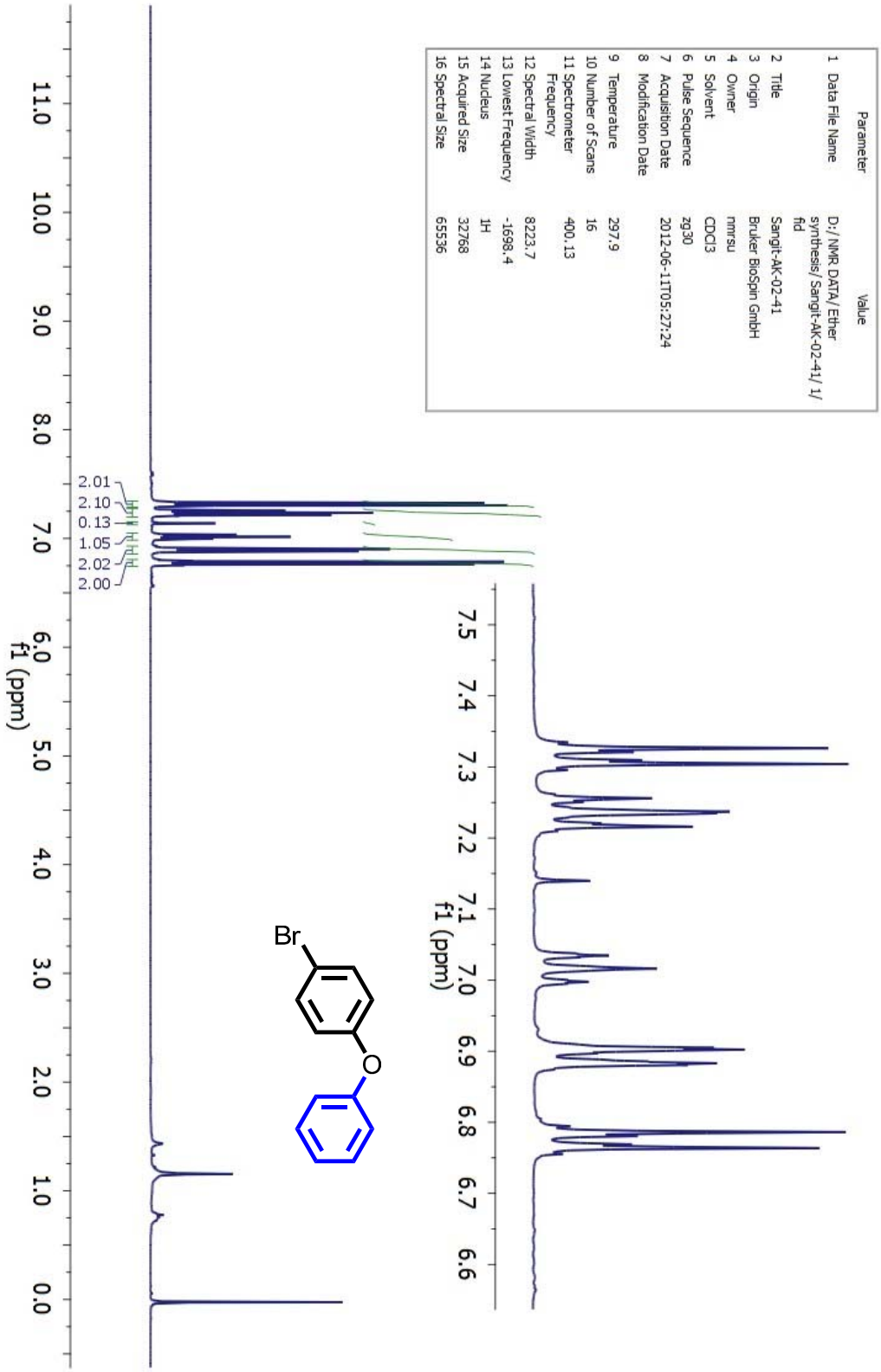

Figure S67 ^{13}C NMR spectrum of **22**

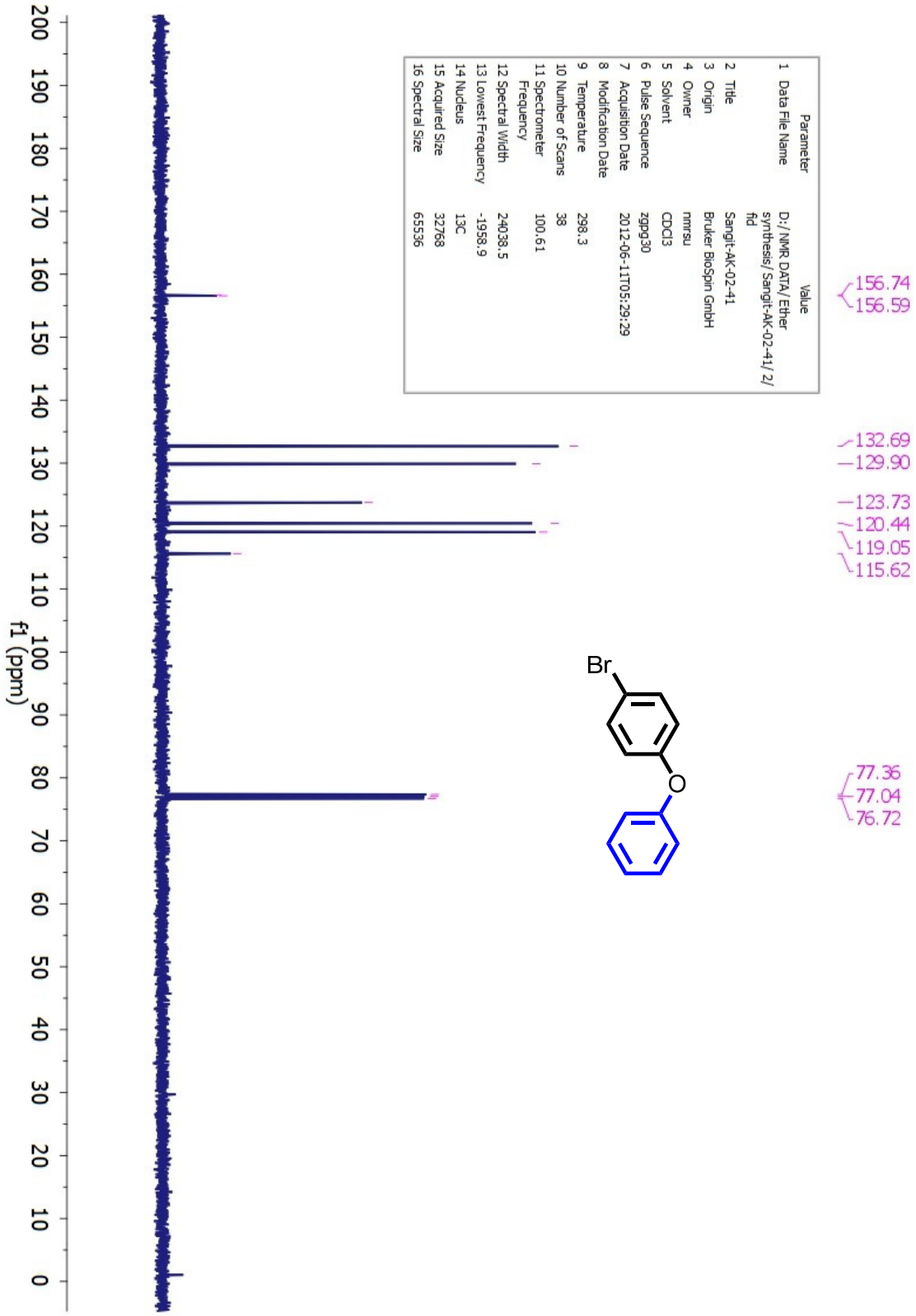

Figure S68 ^{1}H NMR spectrum of **23**

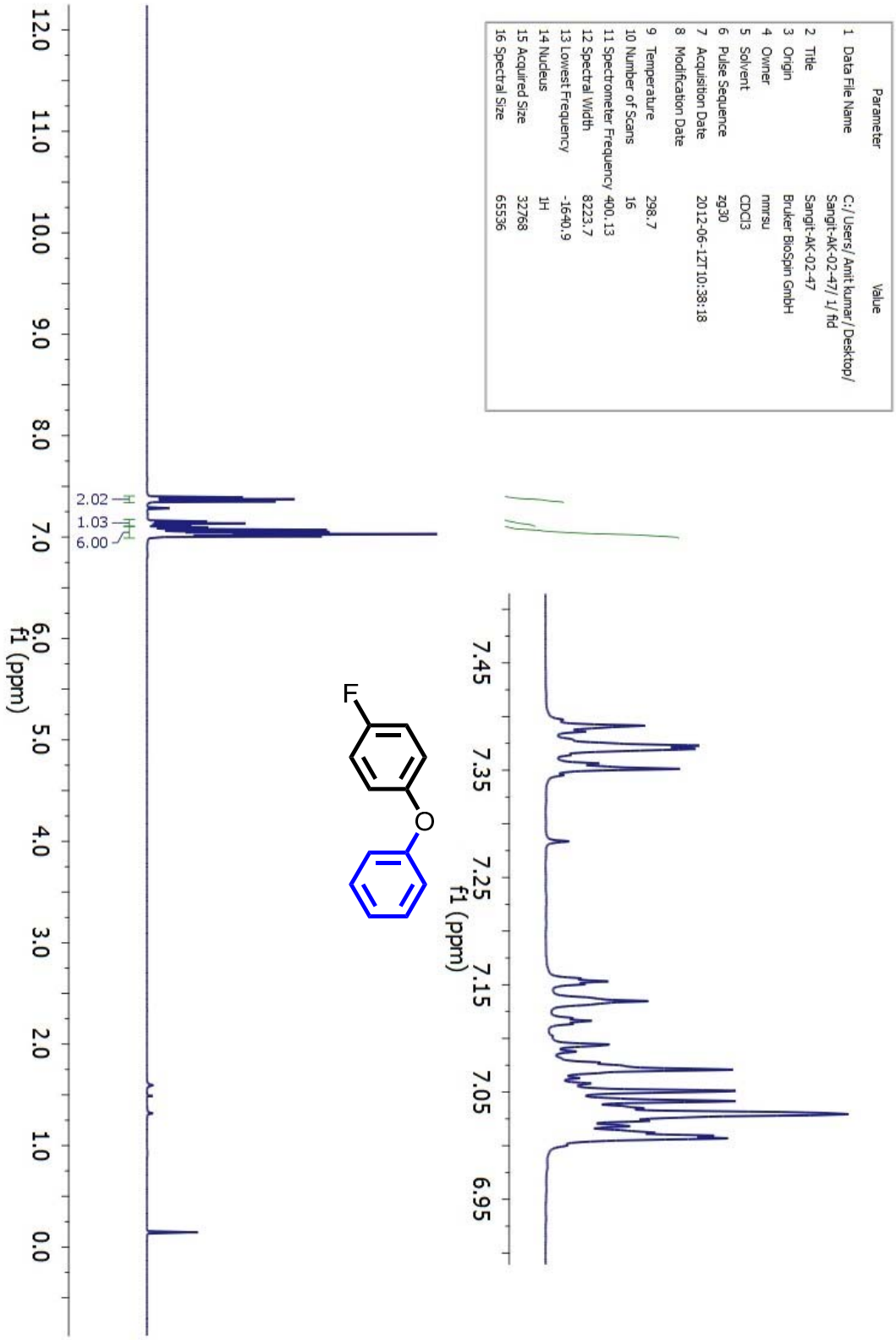

Figure S69 ^{13}C NMR spectrum of **23**

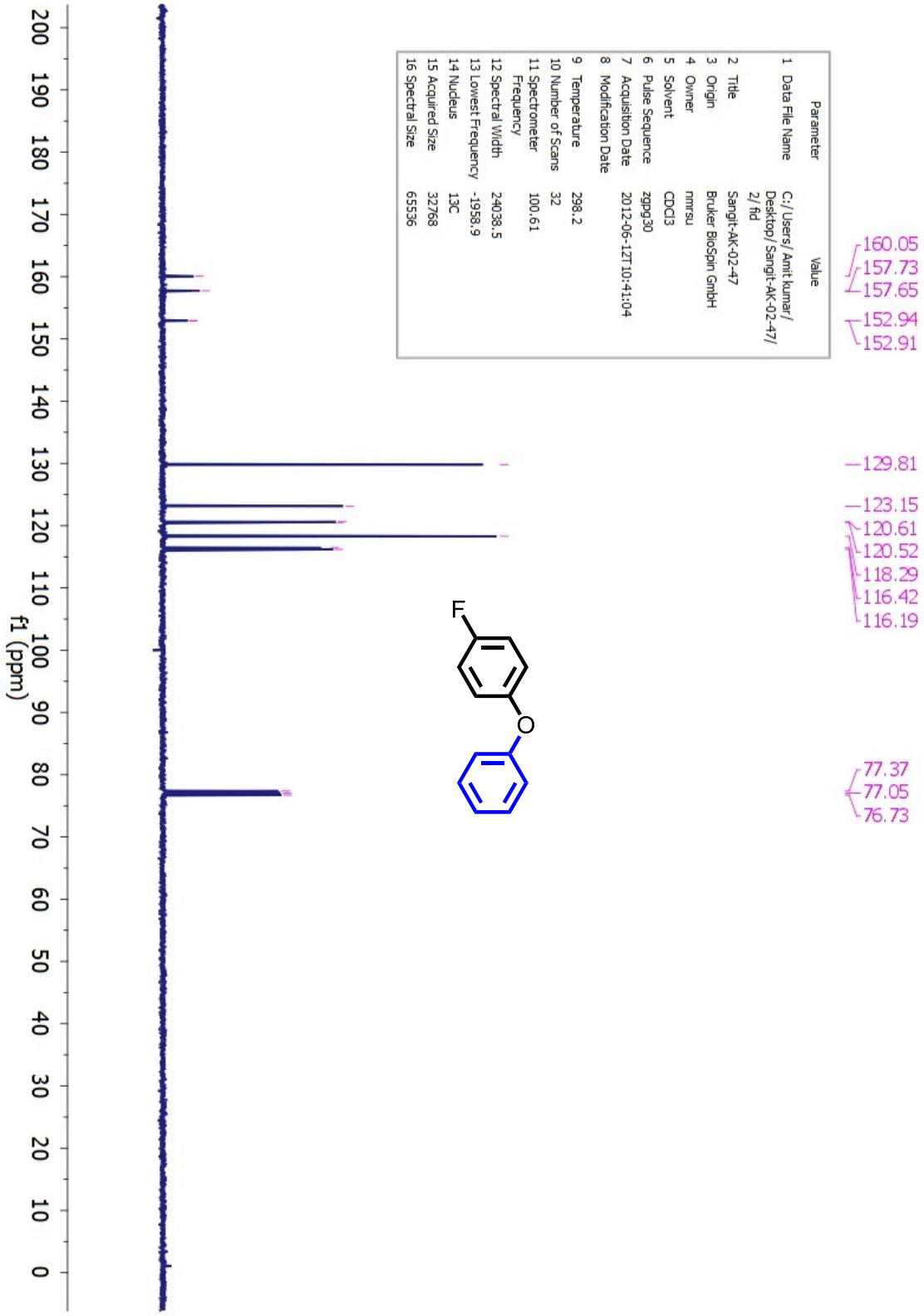

Figure S70 ^{1}H NMR spectrum of **24**

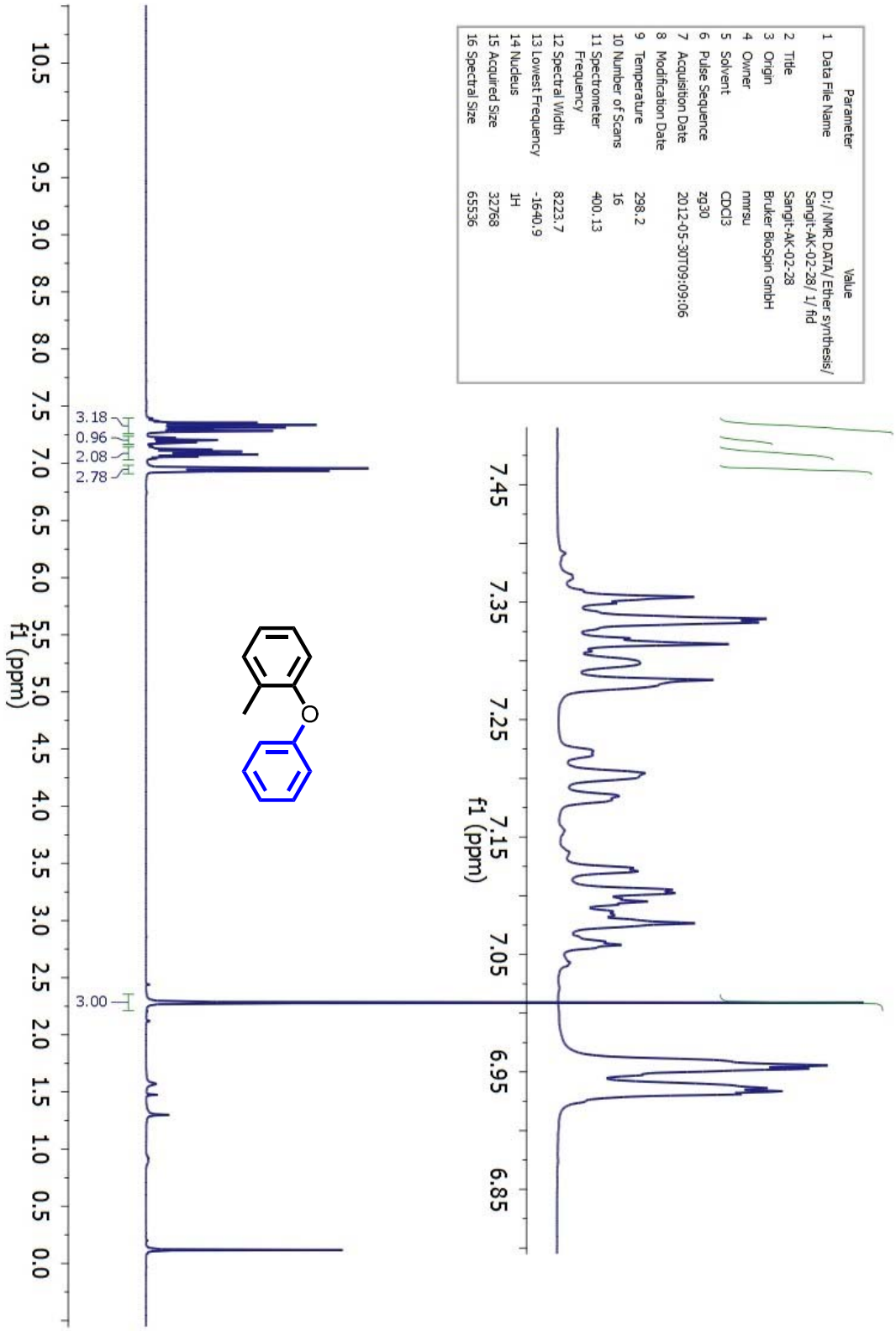

Figure S71 ^{13}C NMR spectrum of **24**

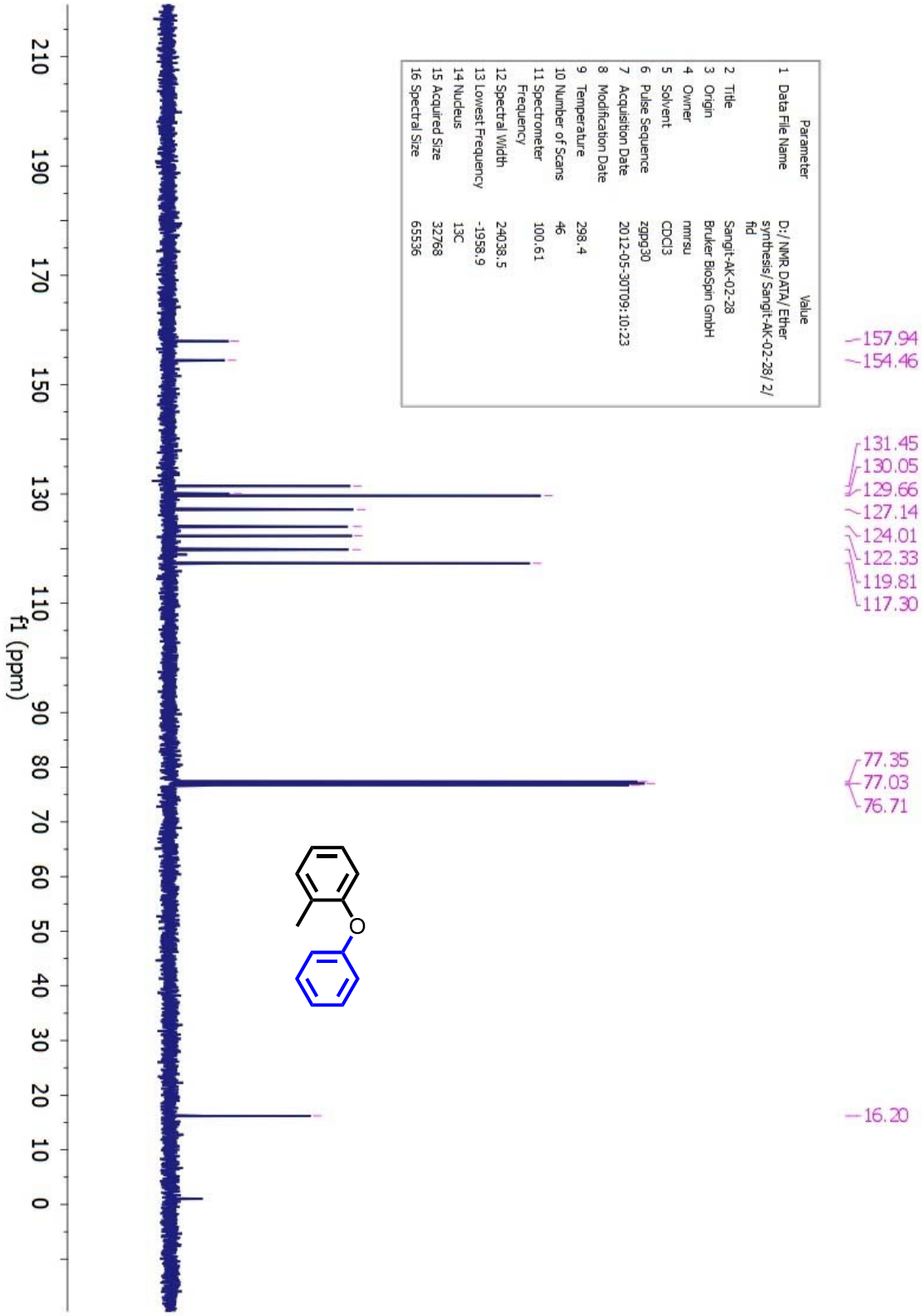

Figure S72[1]H NMR spectrum of **25**

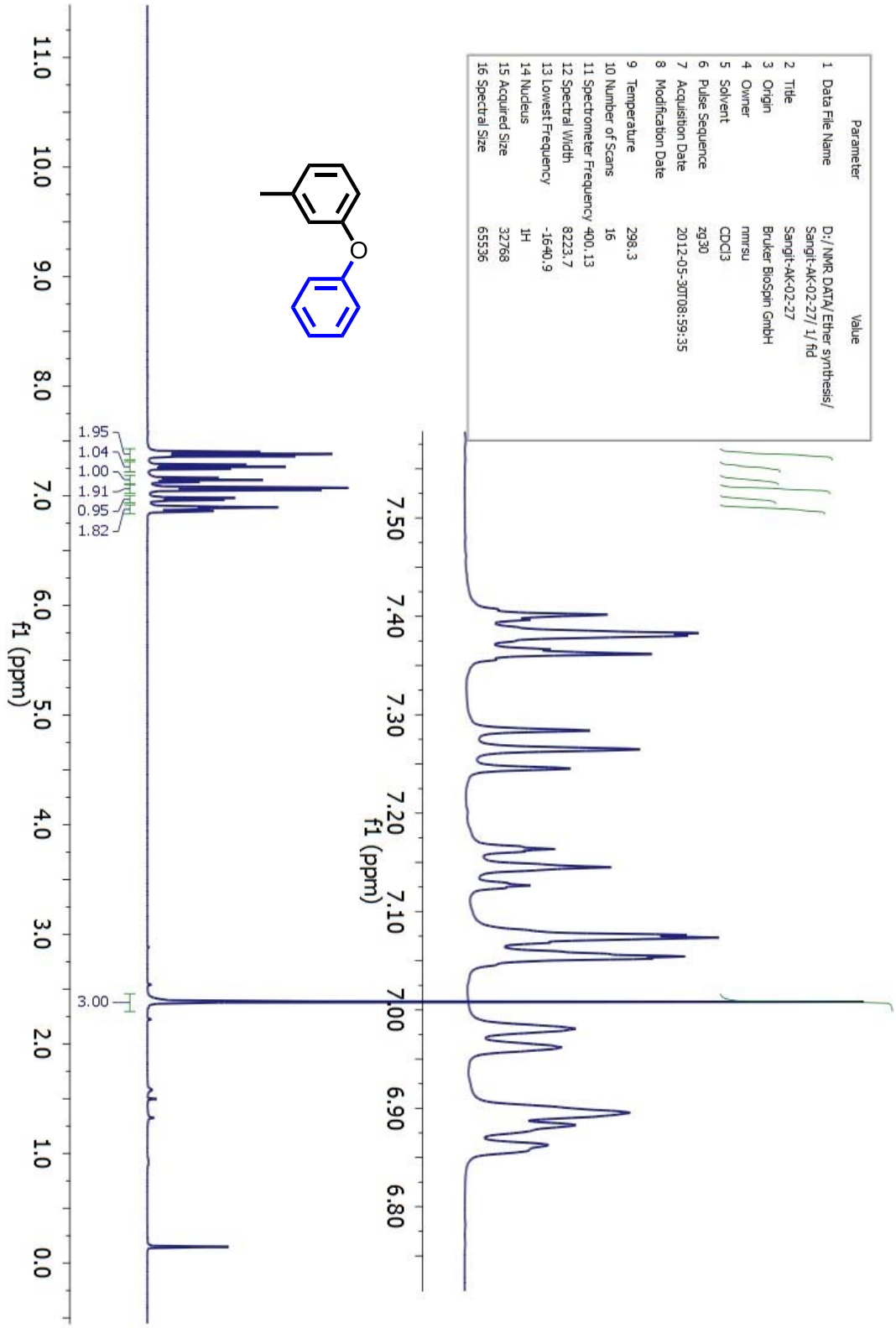

Figure S73 ^{13}C NMR spectrum of **25**

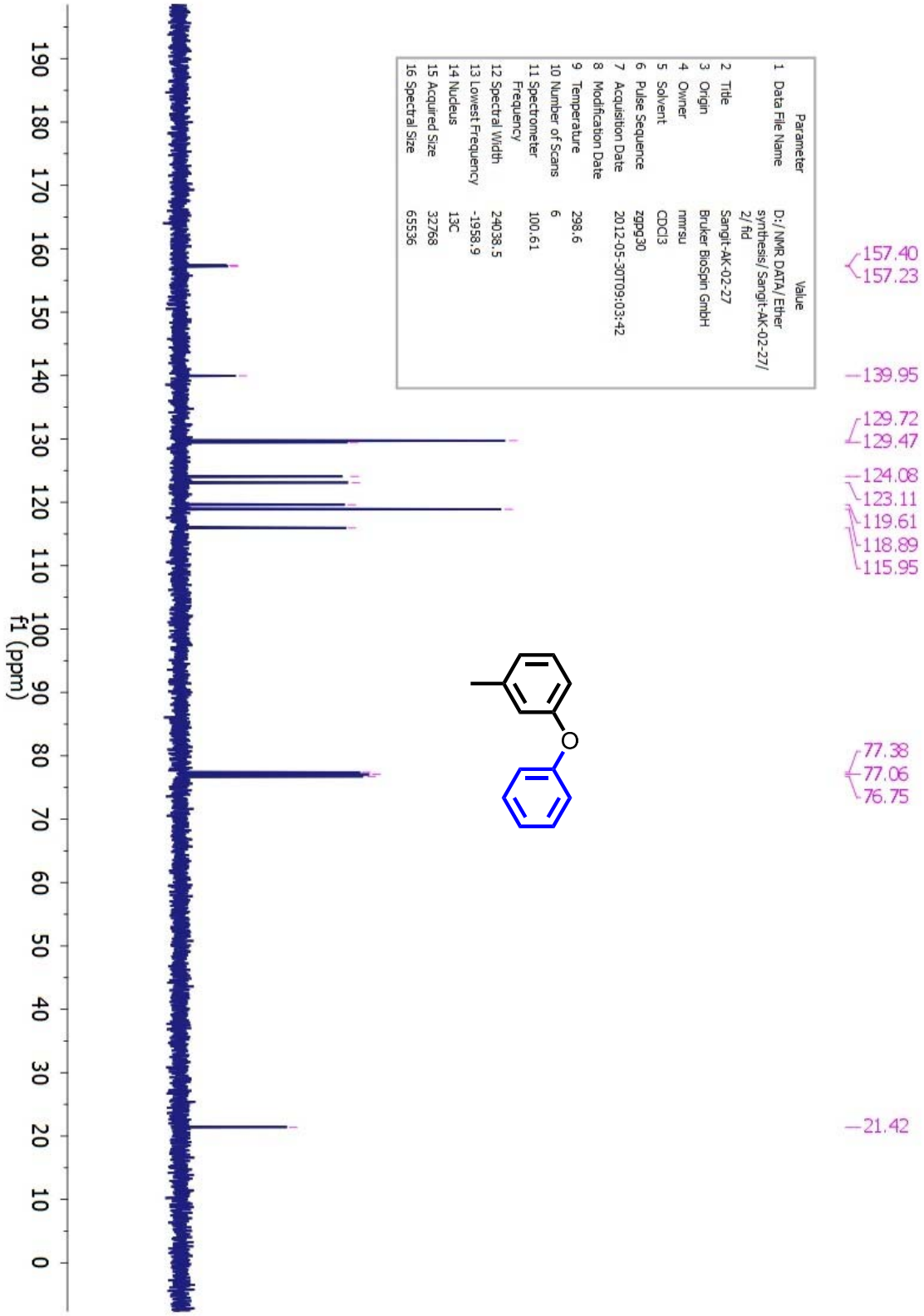

Figure S74 ^{1}H NMR spectrum of **26**

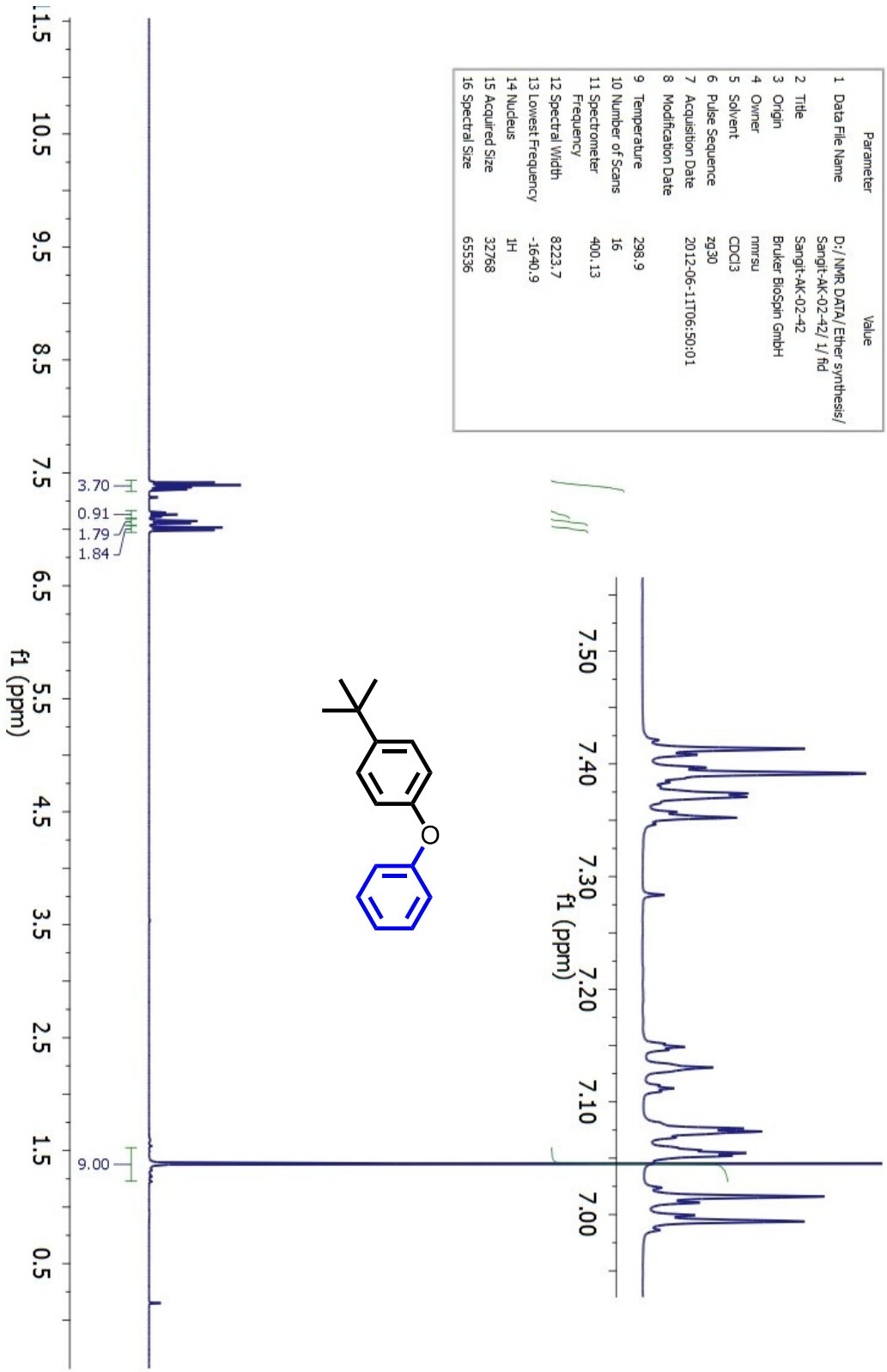

Figure S75 ^{13}C NMR spectrum of **26**

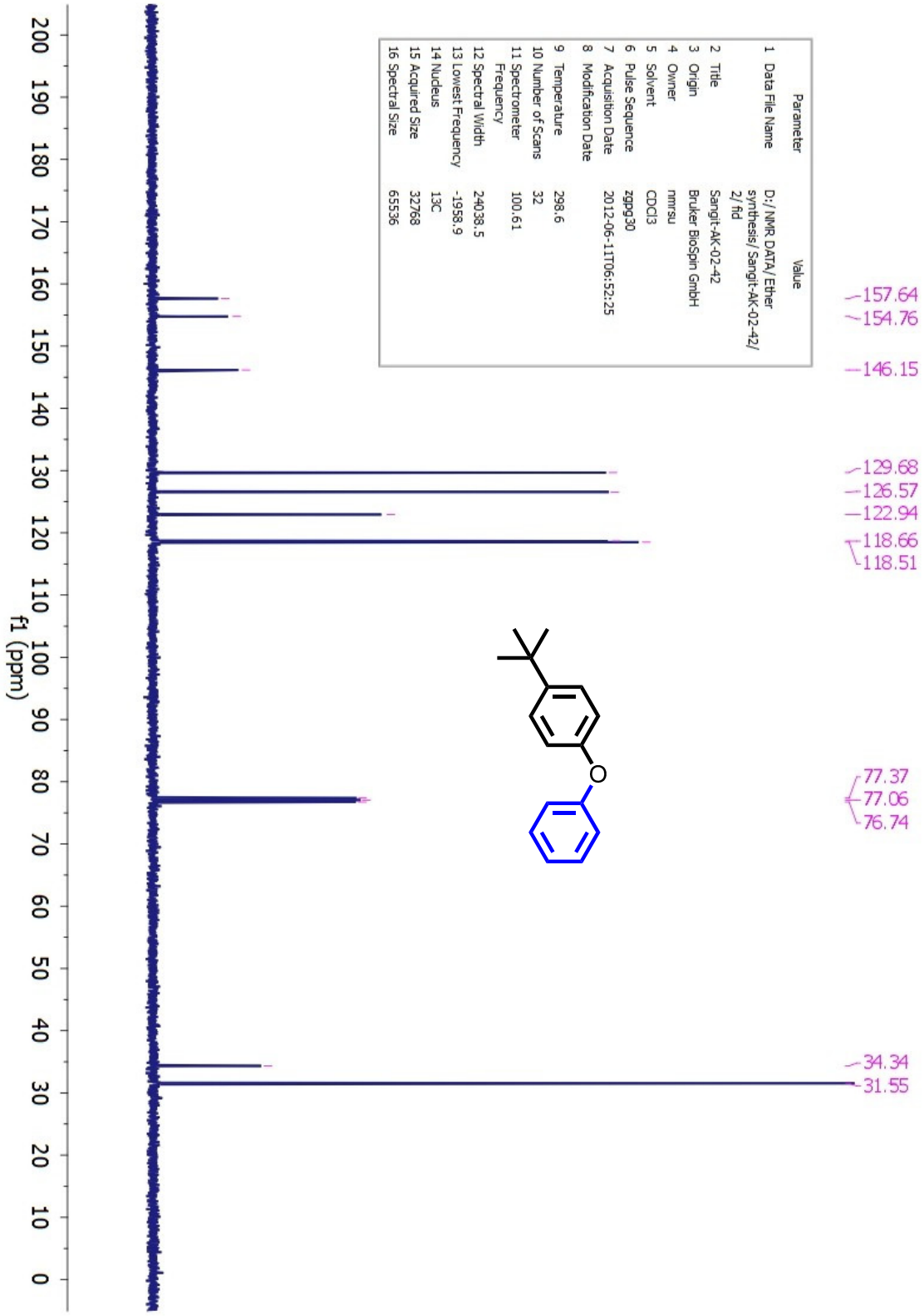

Figure S76 ^{1}H NMR spectrum of **27**

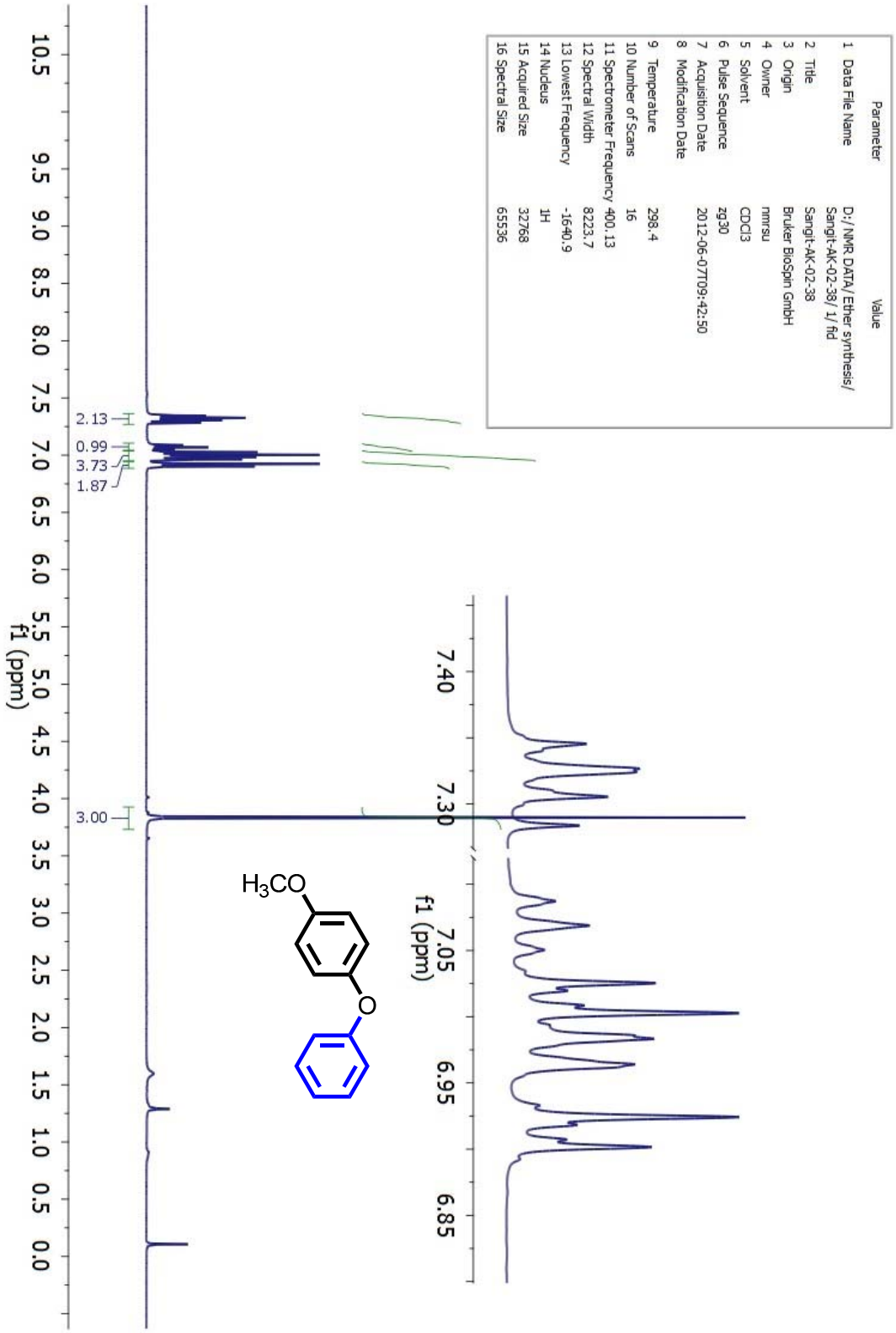

Figure S77 ^{13}C NMR spectrum of **27**

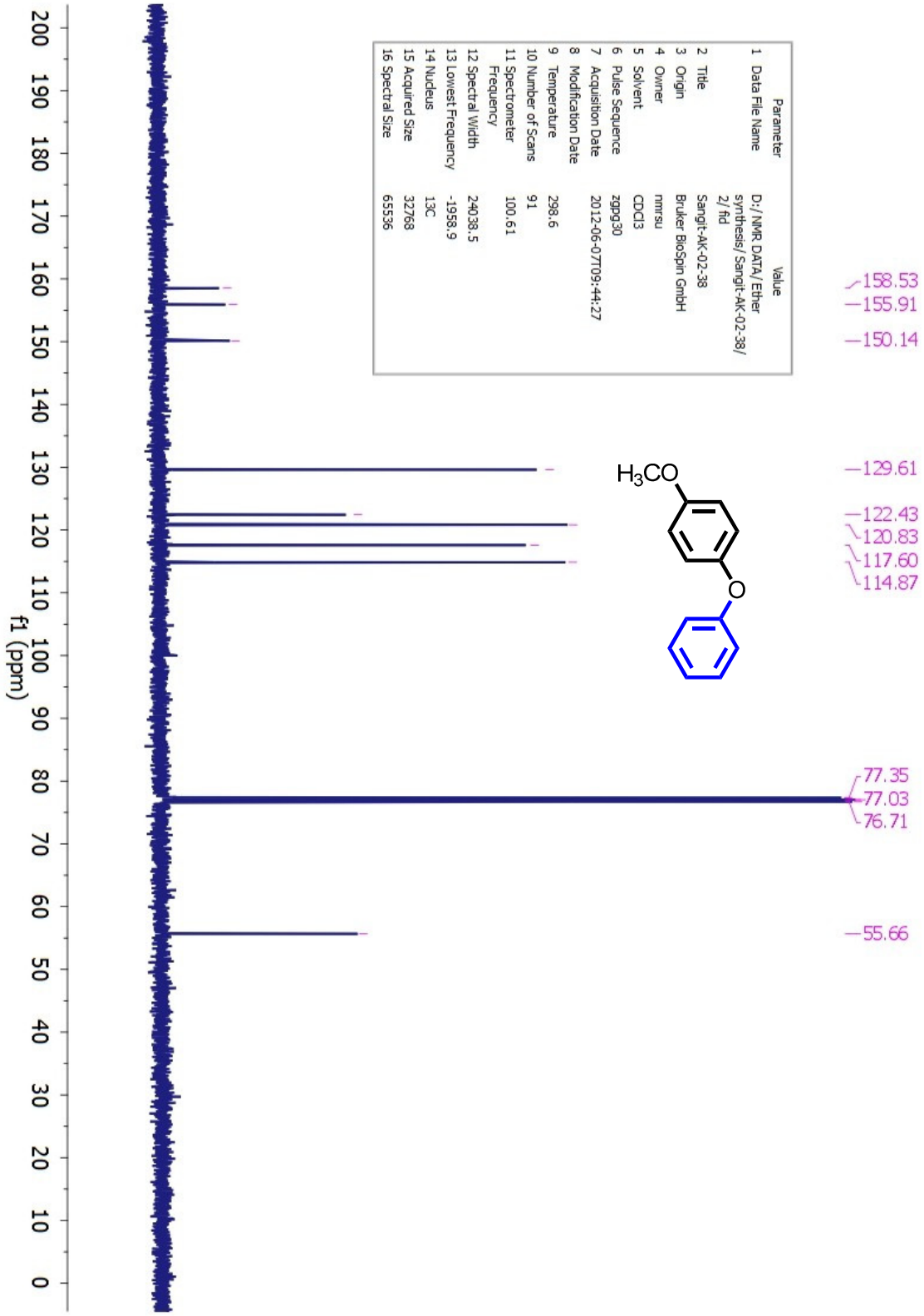

Figure S78 ^{1}H NMR spectrum of **28**

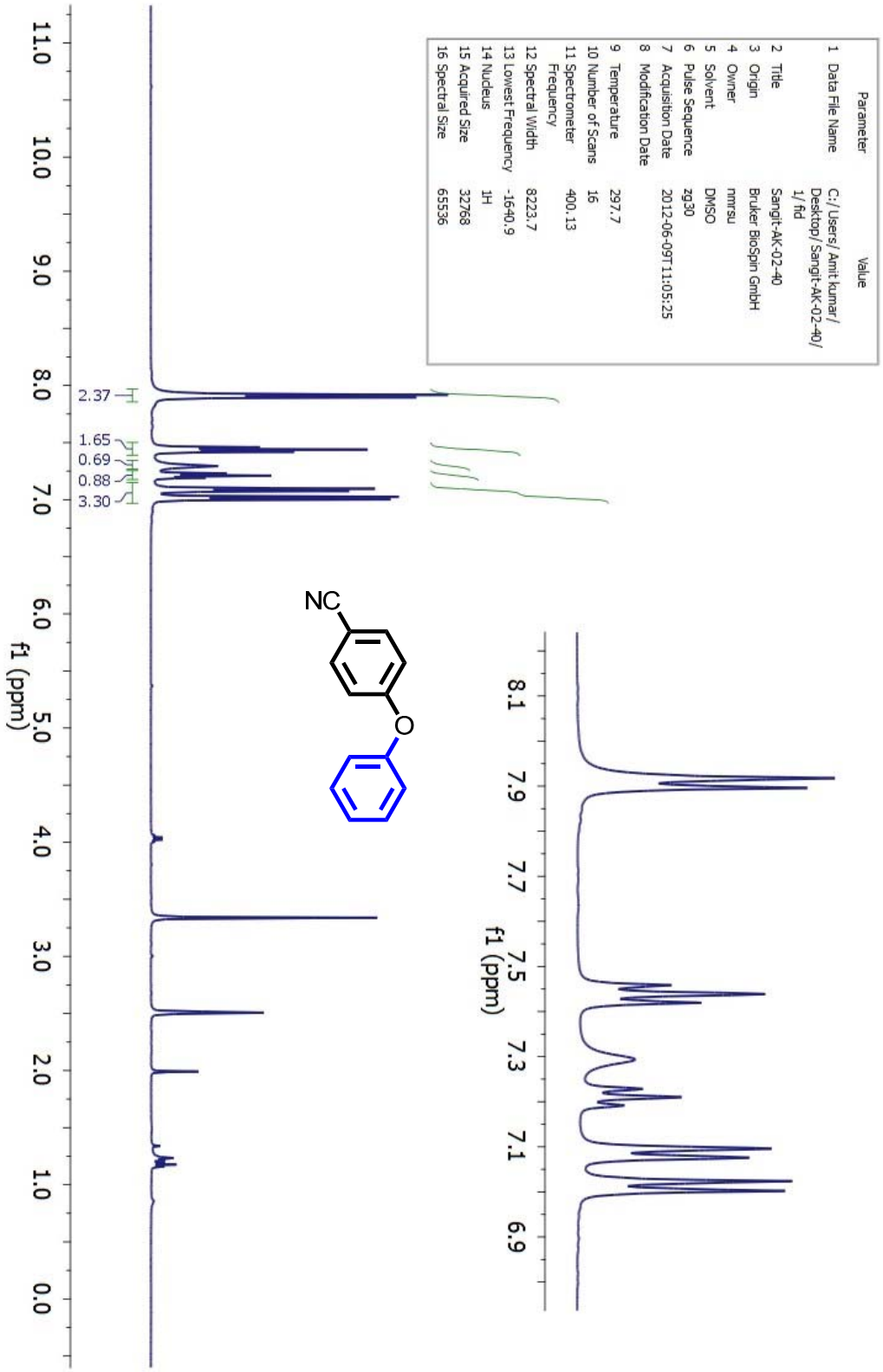

Figure S79 ^{13}C NMR spectrum of **28**

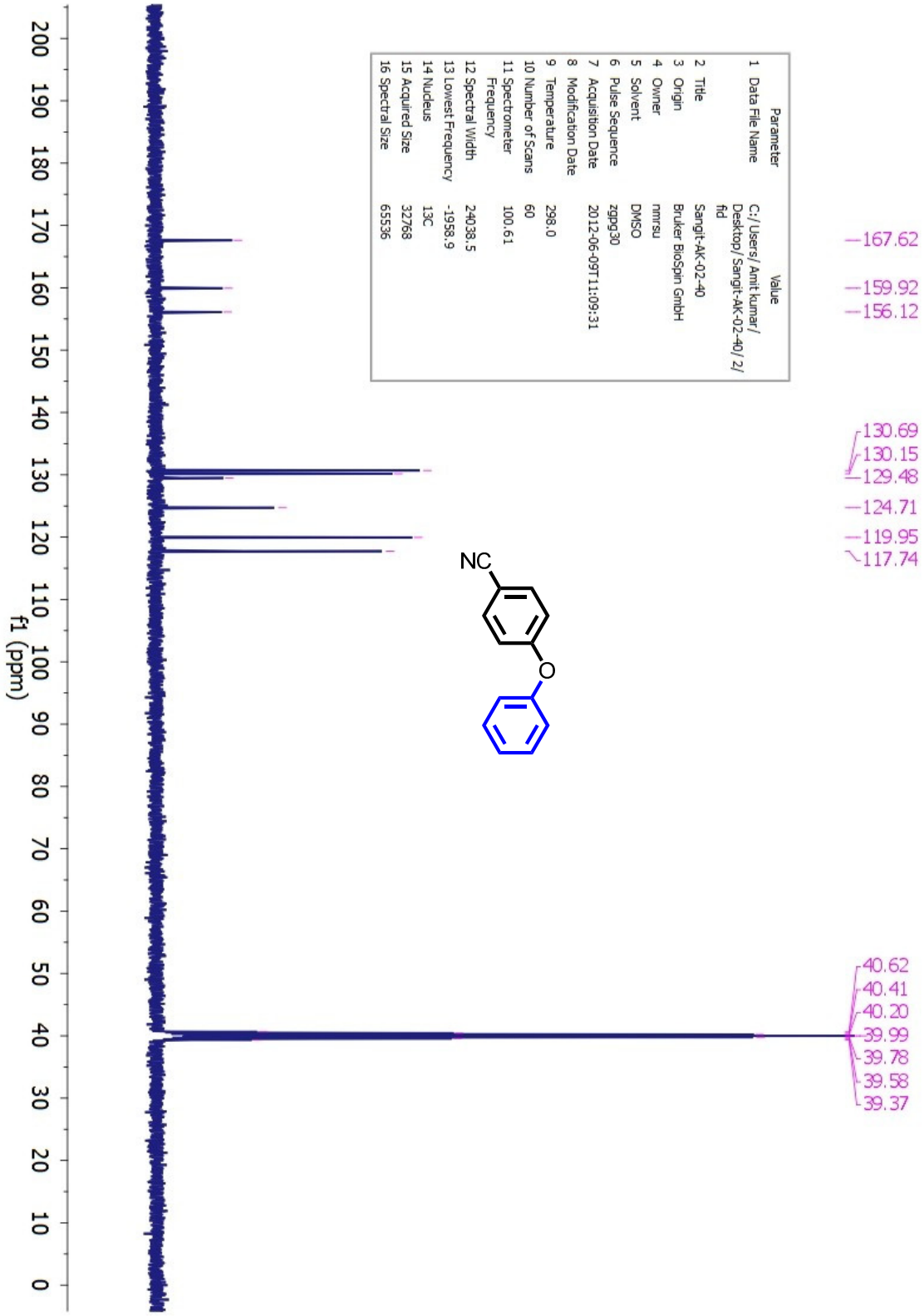

Figure S80 ^{1}H NMR spectrum of **29**

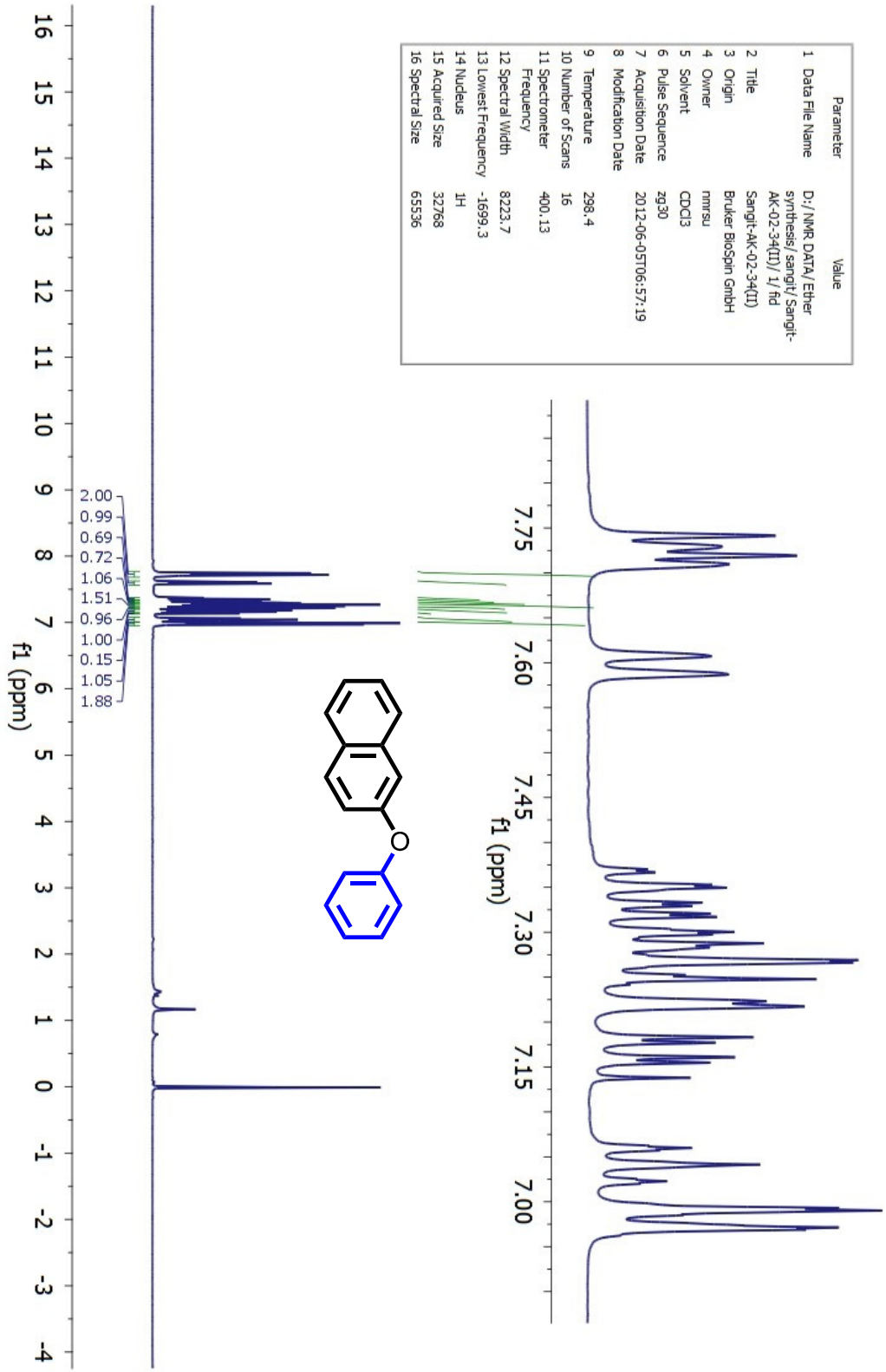

Figure S81 ^{13}C NMR spectrum of **29**

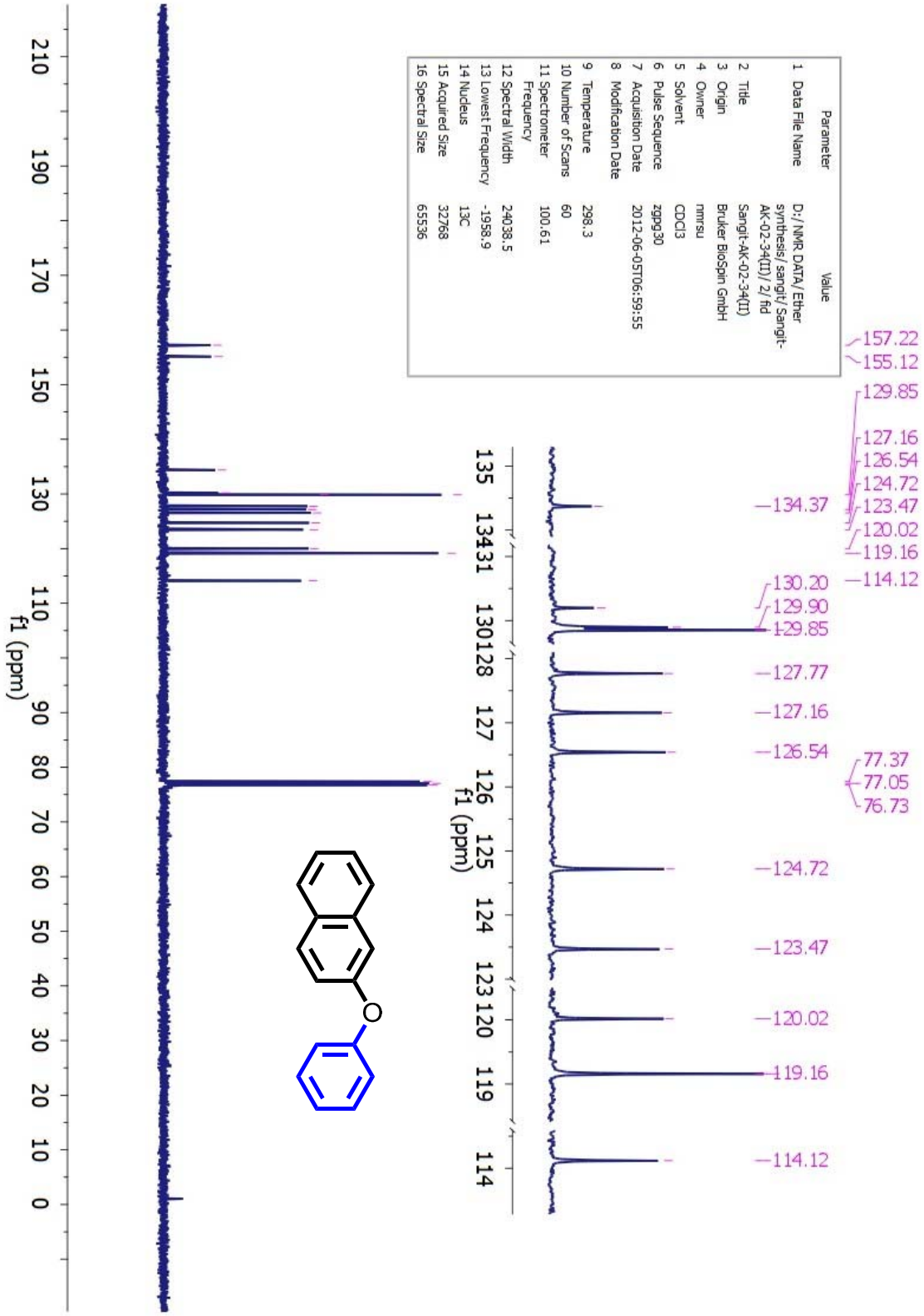

Figure S82 ^{1}H NMR spectrum of **30**

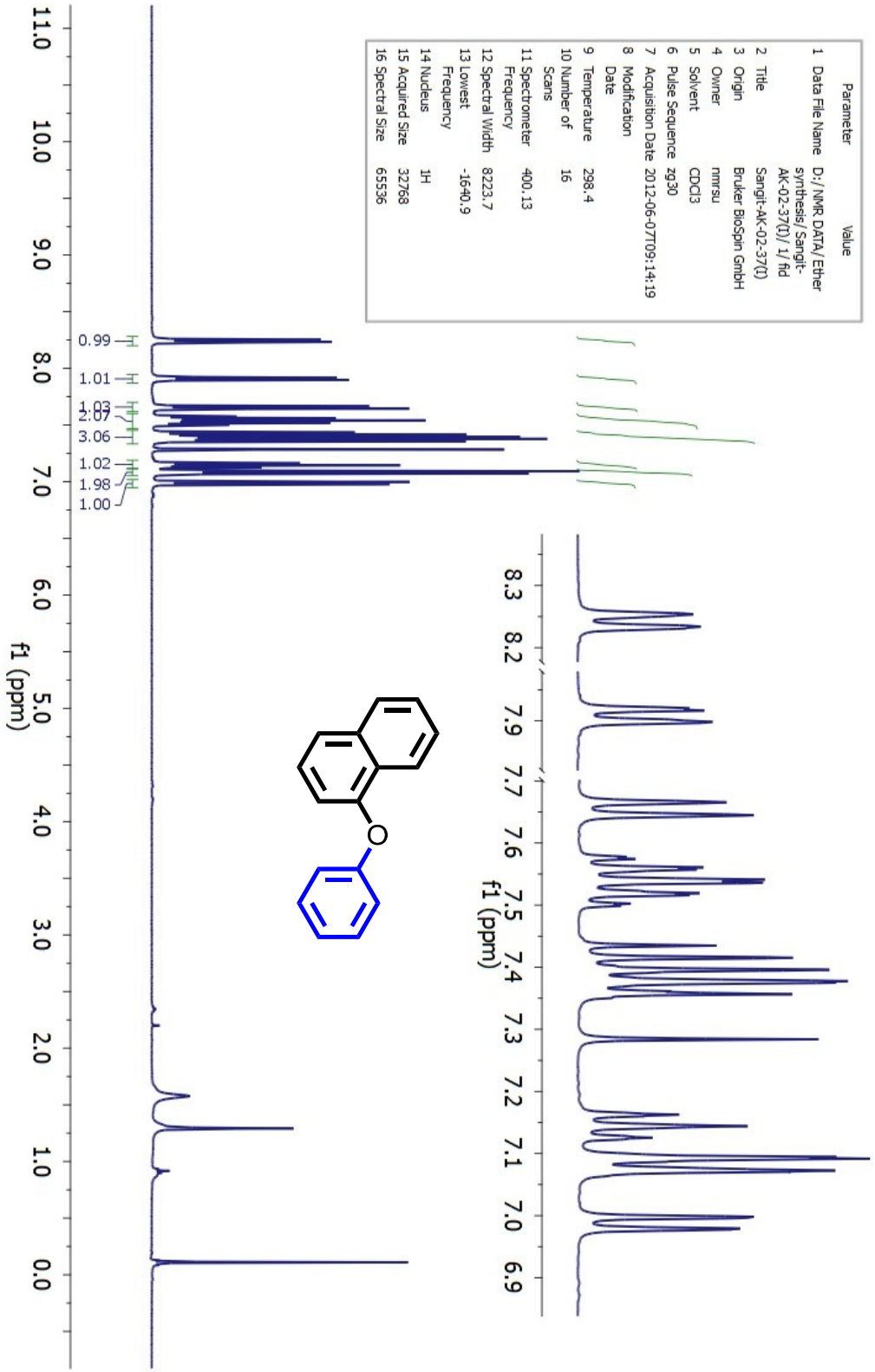

Figure S83 ^{13}C NMR spectrum of **30**

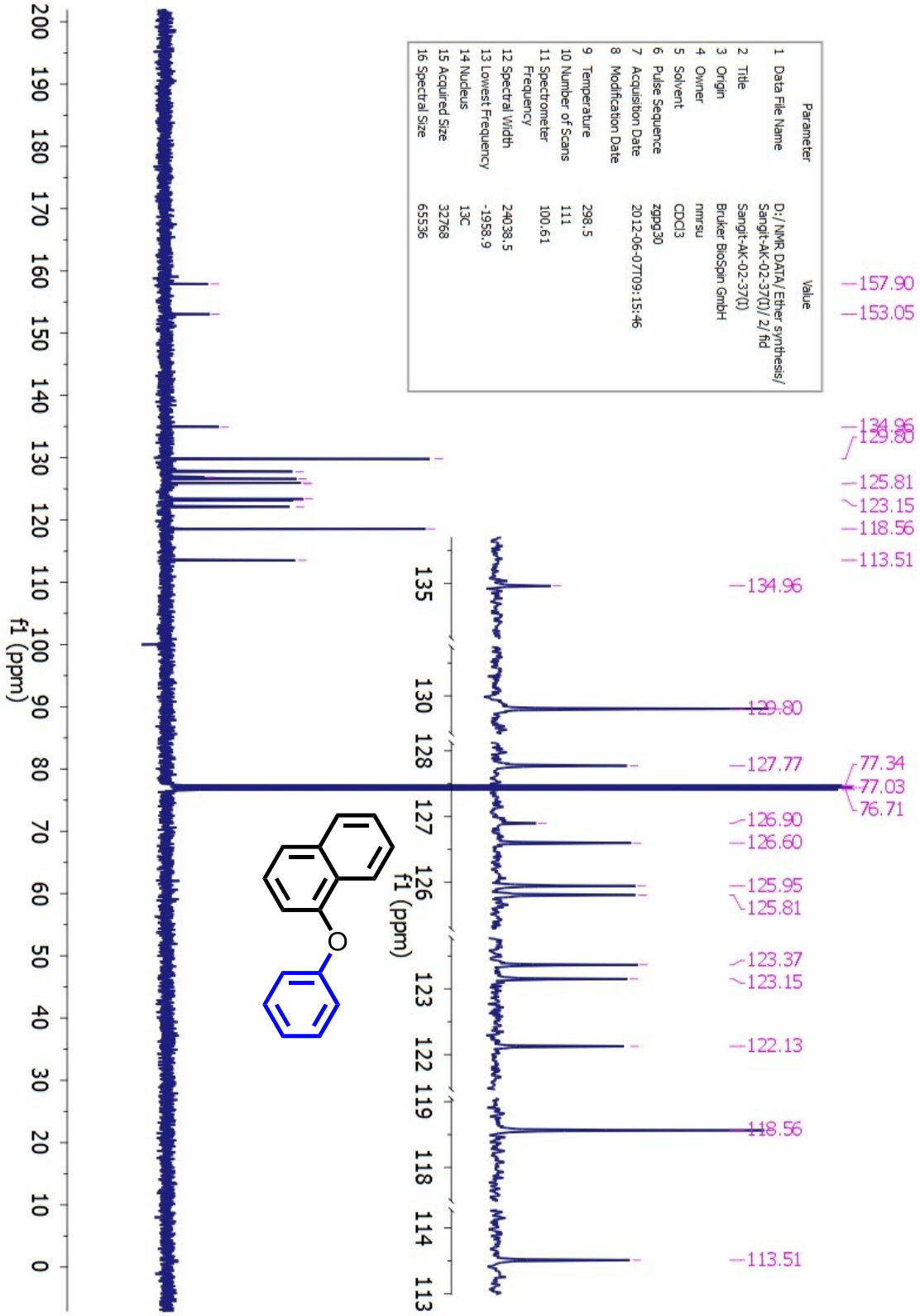

Figure S84 ^{1}H NMR spectrum of **31**

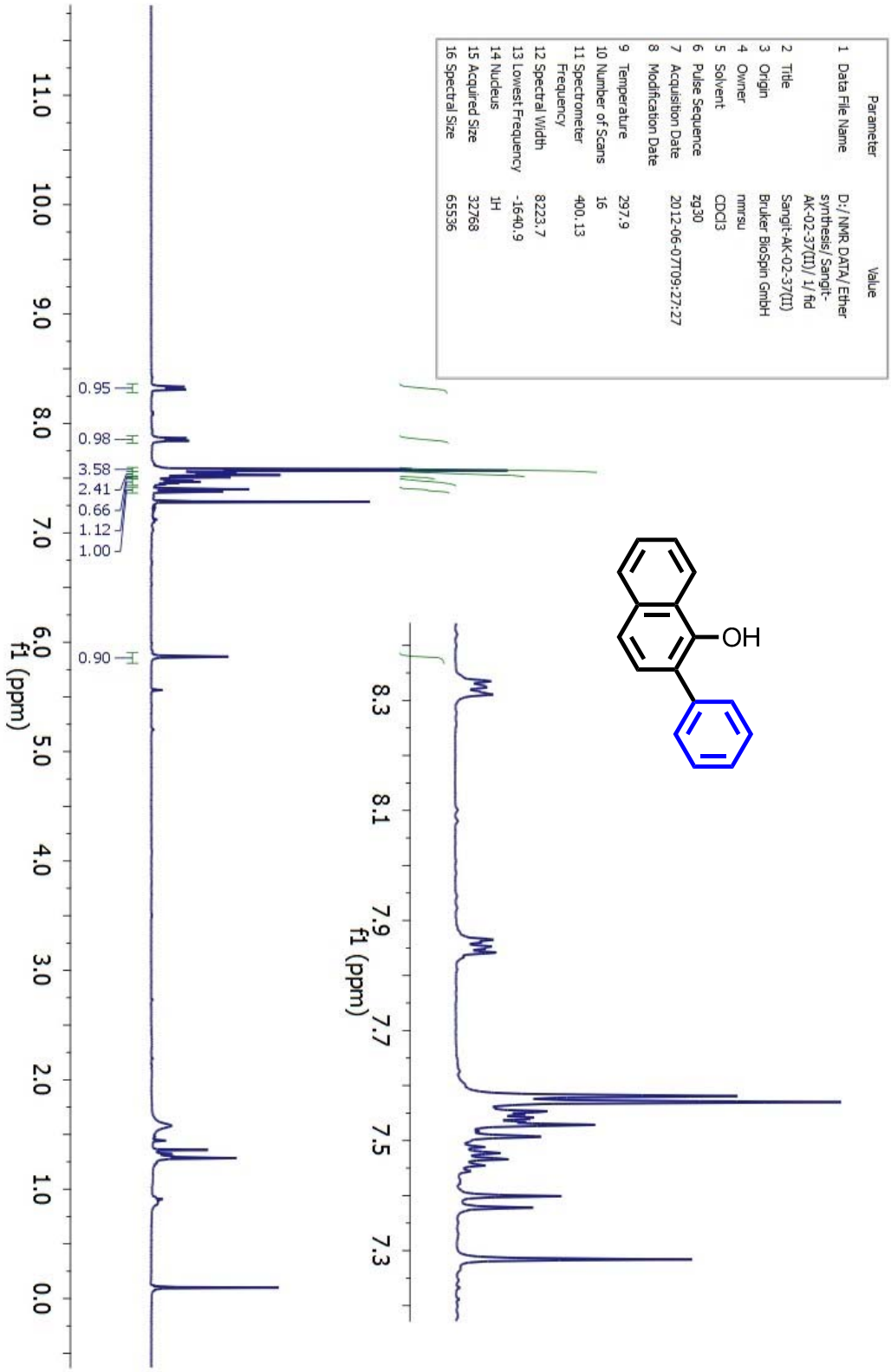

Figure S85 ^{13}C NMR spectrum of **31**

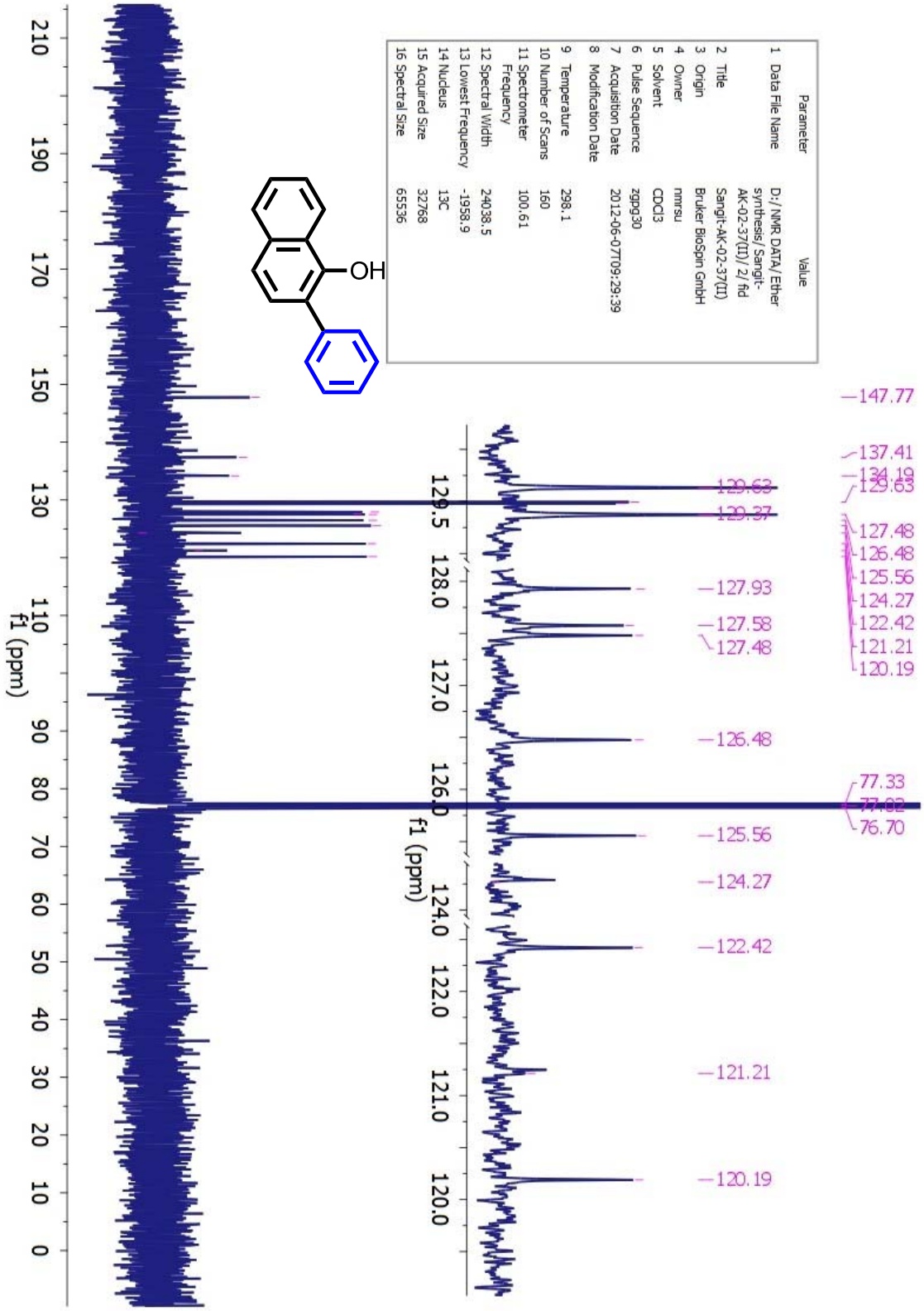

Figure S86 ^{1}H NMR spectrum of **32**

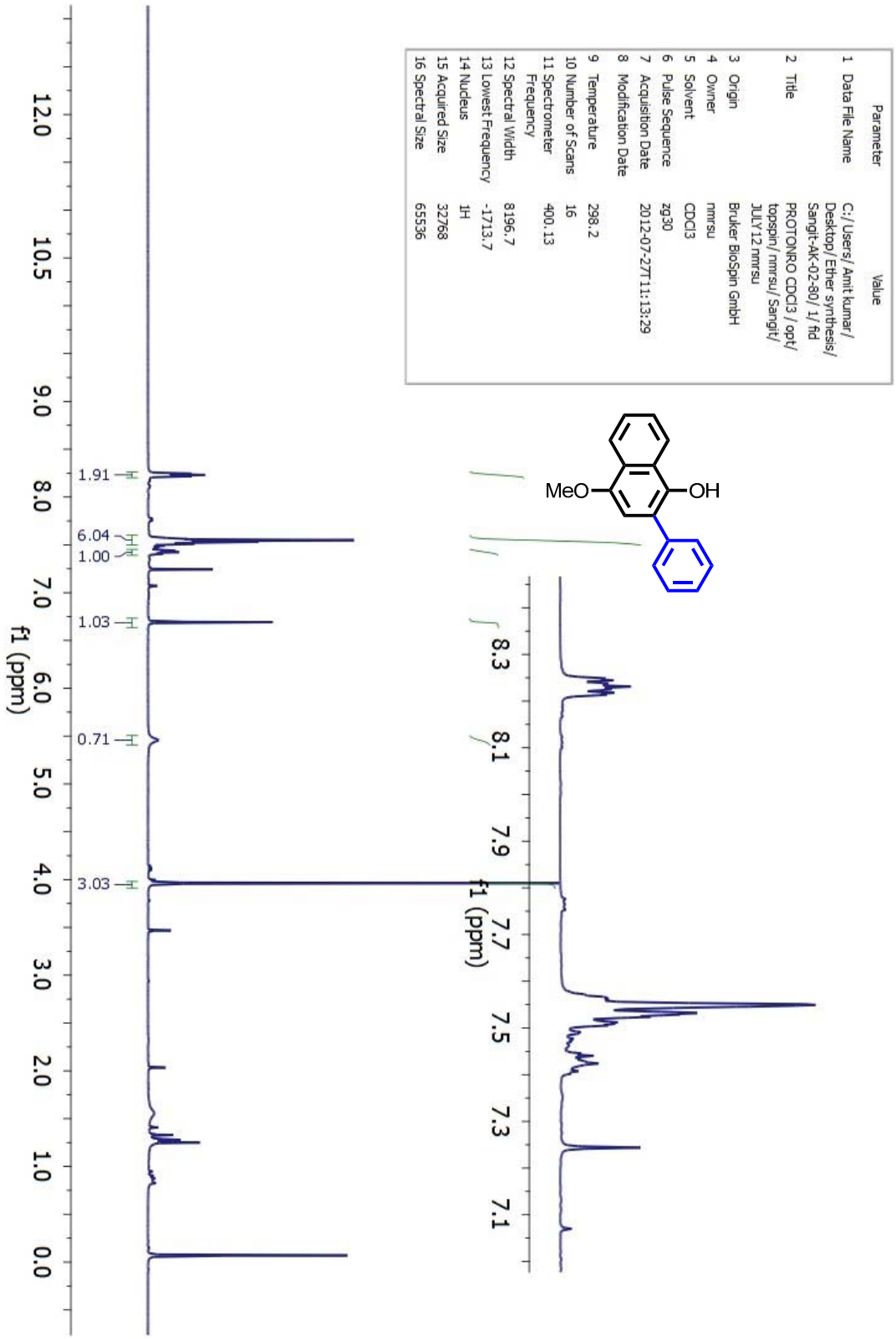

Figure S87 ^{13}C NMR spectrum of **32**

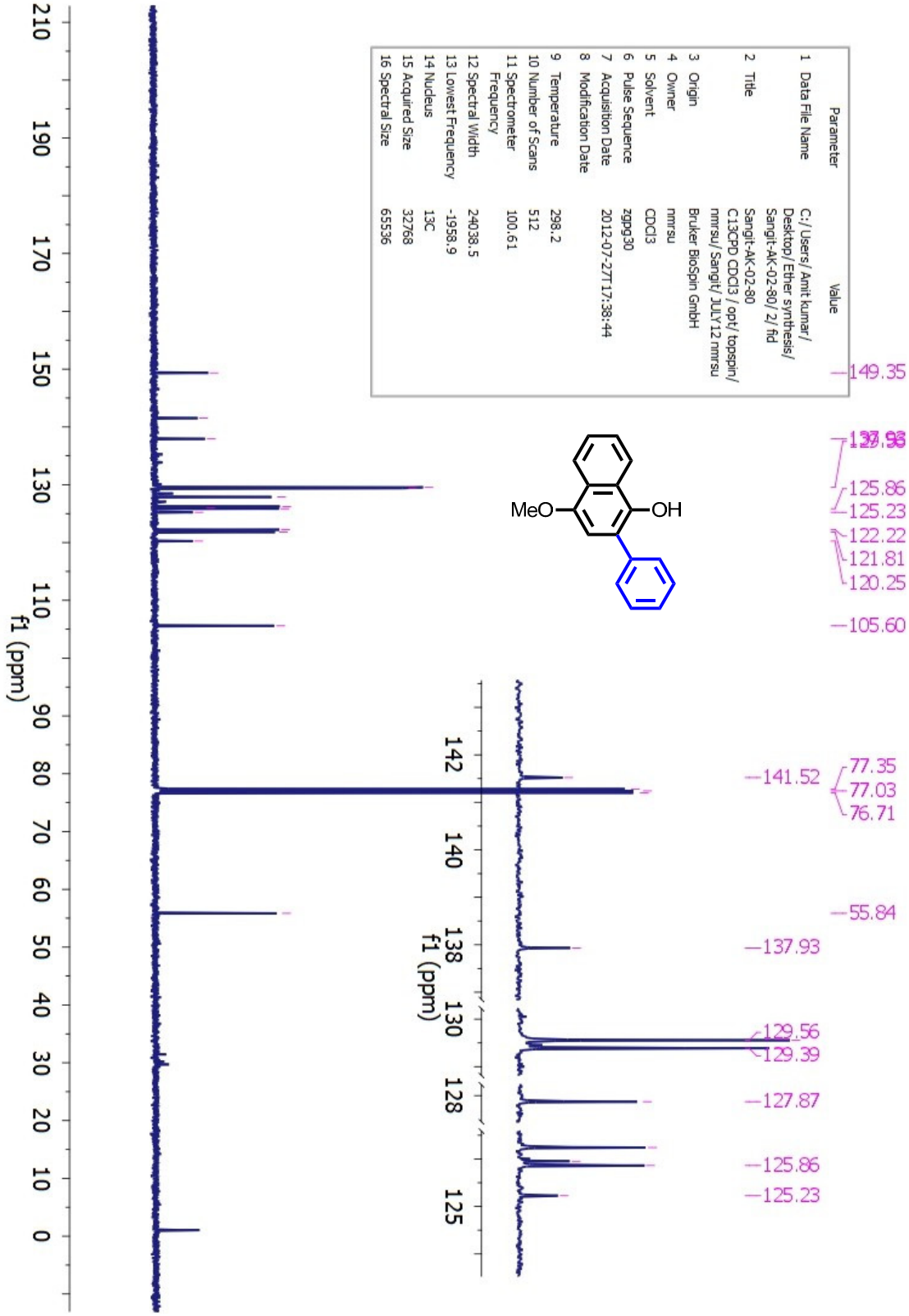

Figure 88 DEPT-135 NMR spectrum of **32**

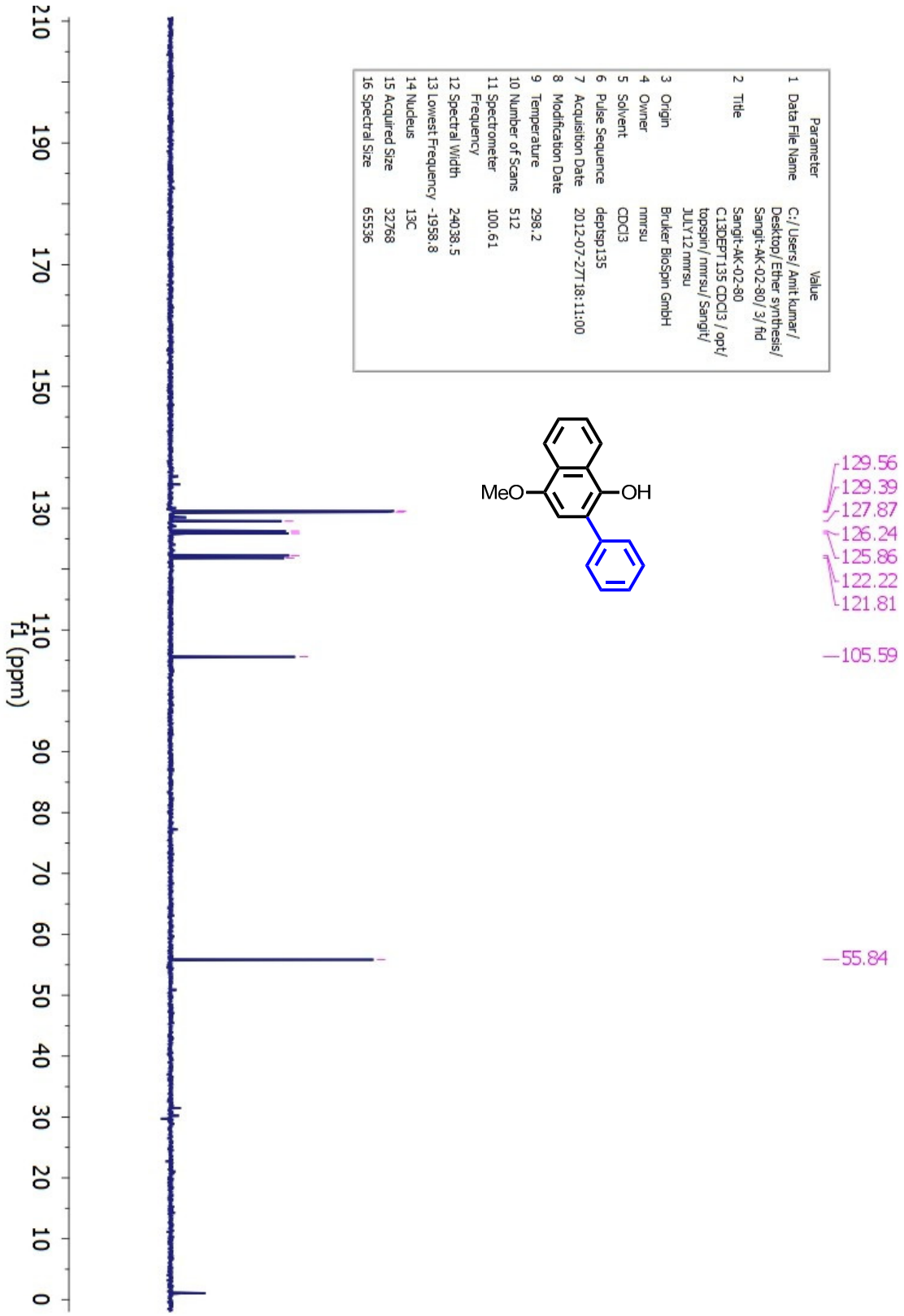

Figure S89 ^{1}H NMR spectrum of **33**

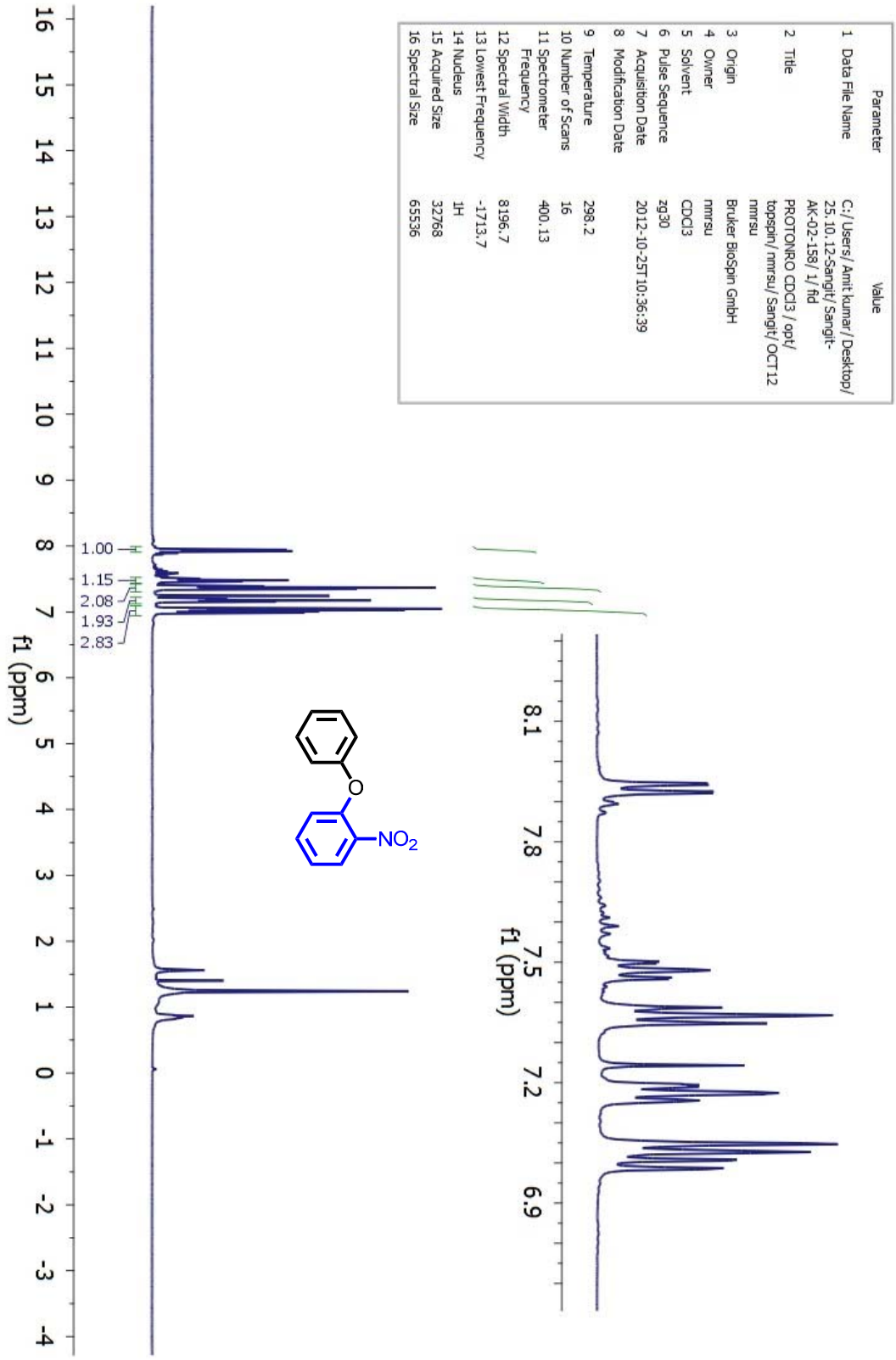

Figure S90 ^{13}C NMR spectrum of **33**

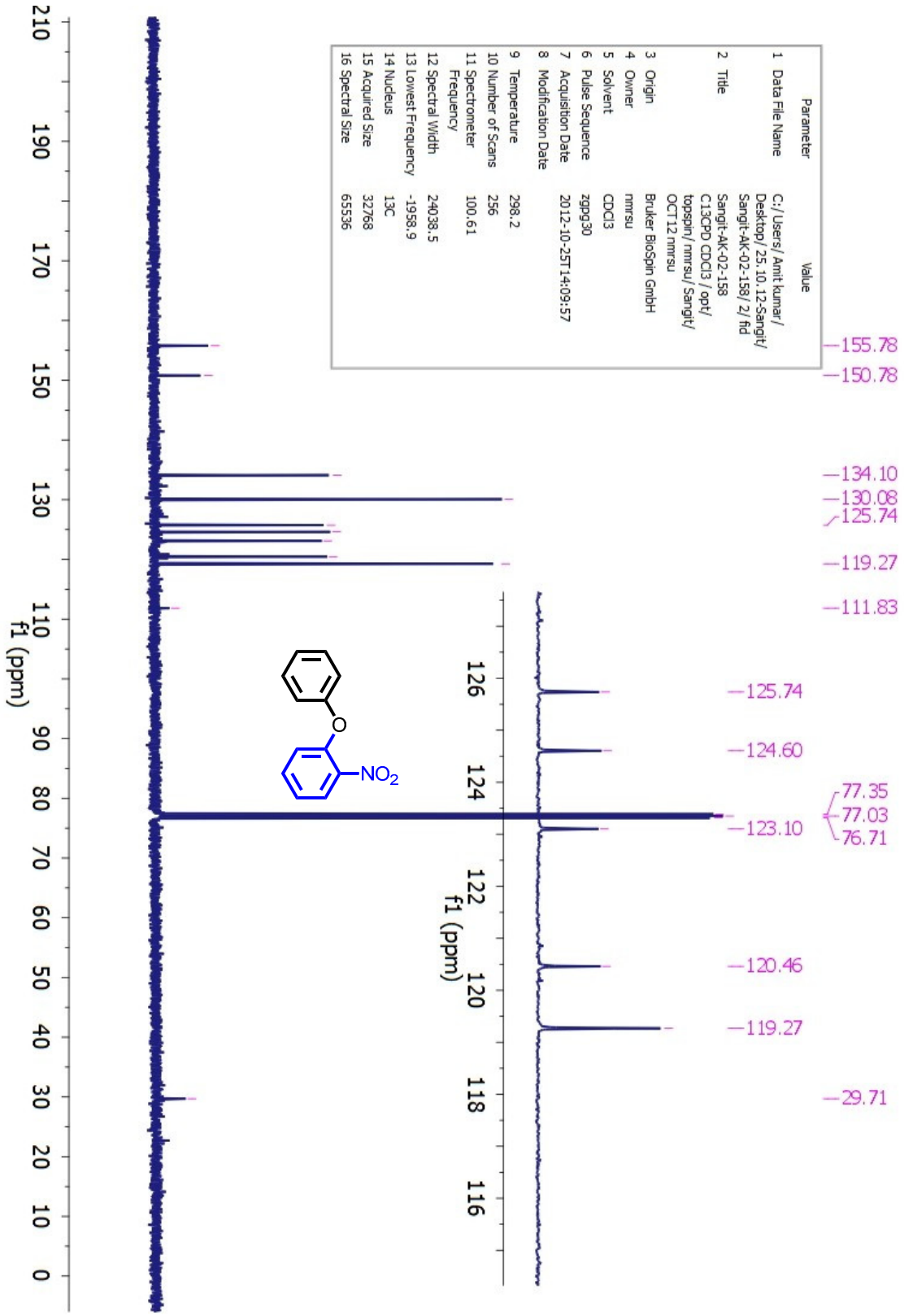

Figure S91 DEPT- 135 NMR spectrum of **33**

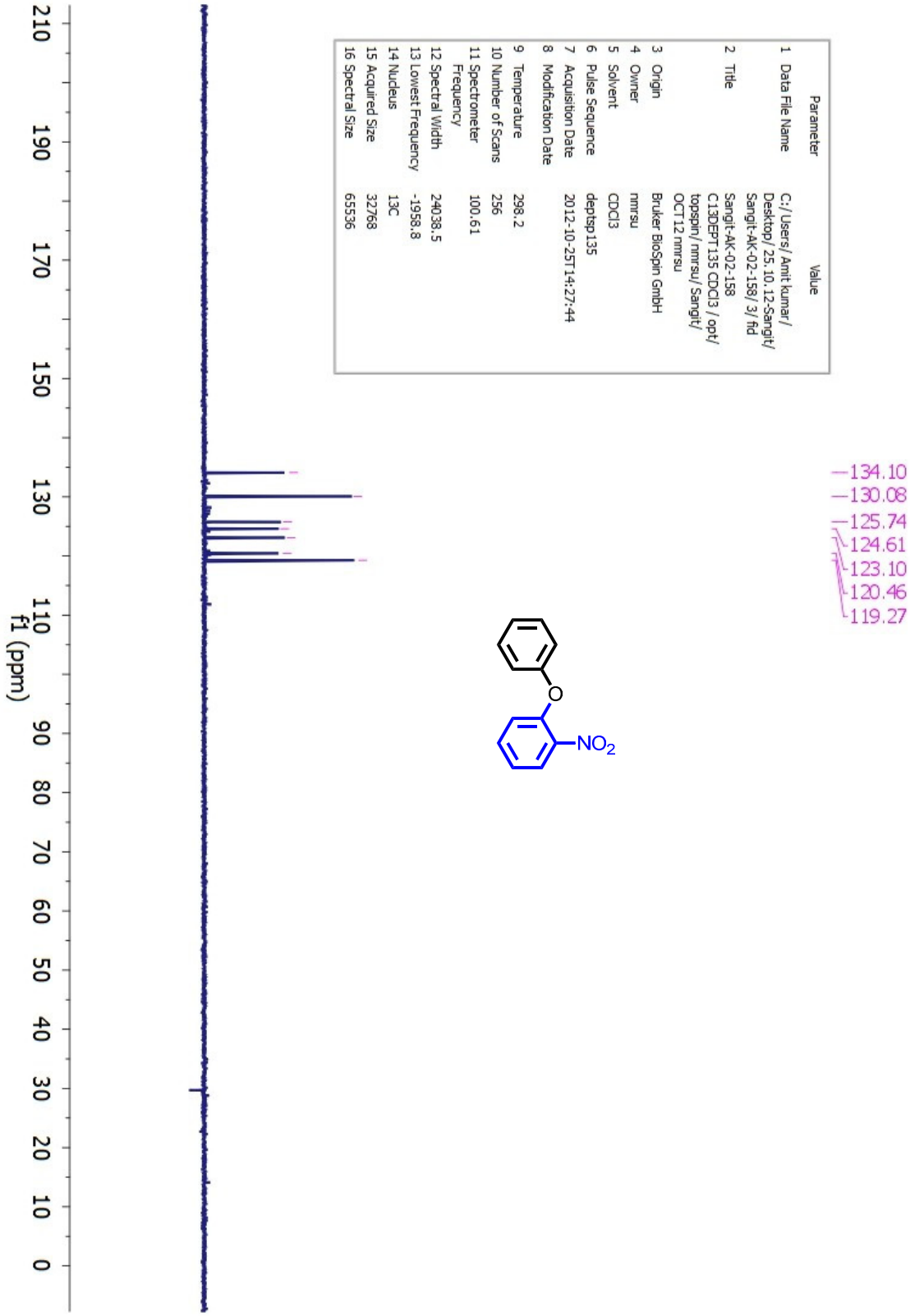

Figure S92 ^{1}H NMR spectrum of **34**

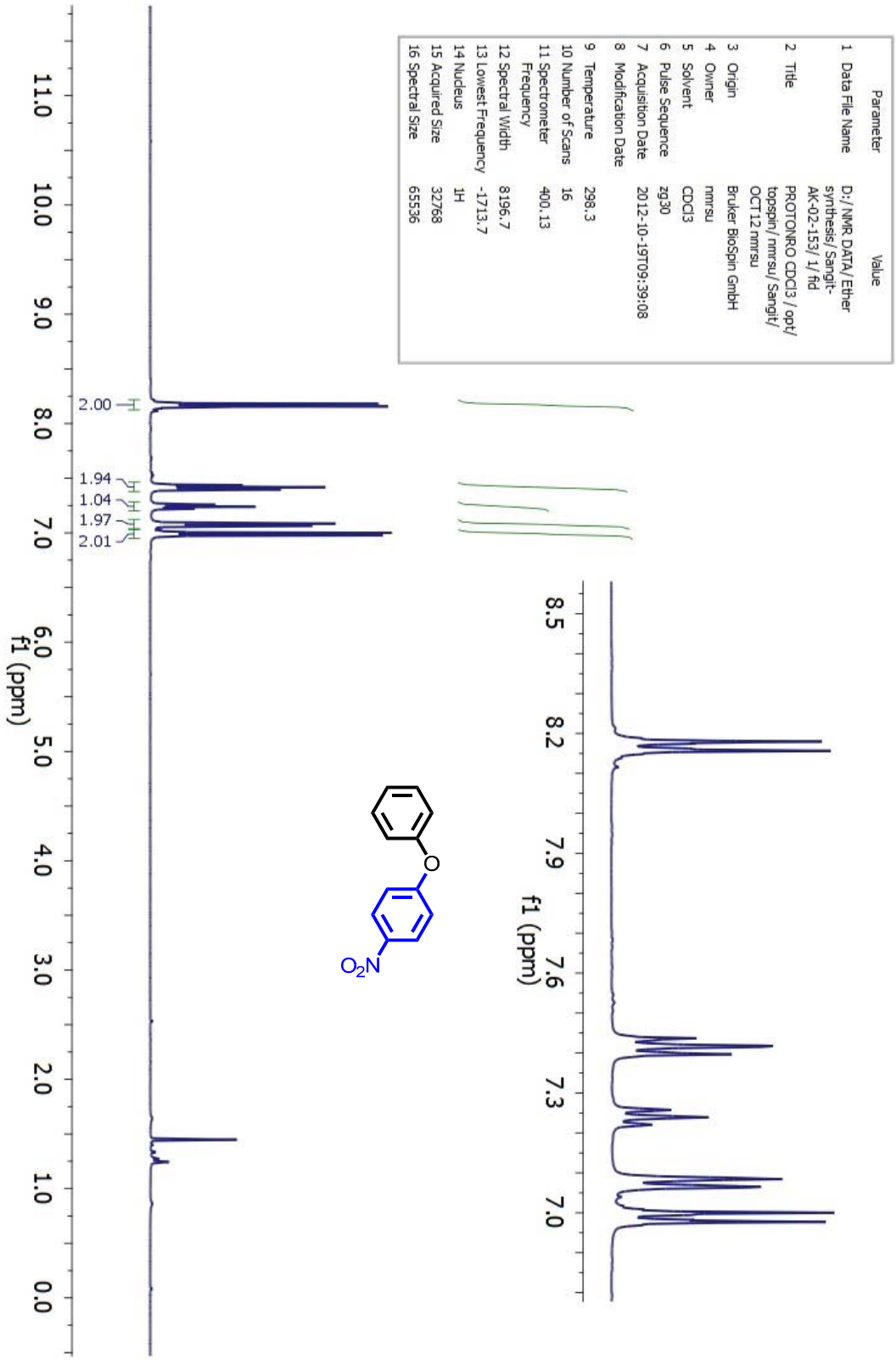

Figure S93 ^{13}C NMR spectrum of **34**

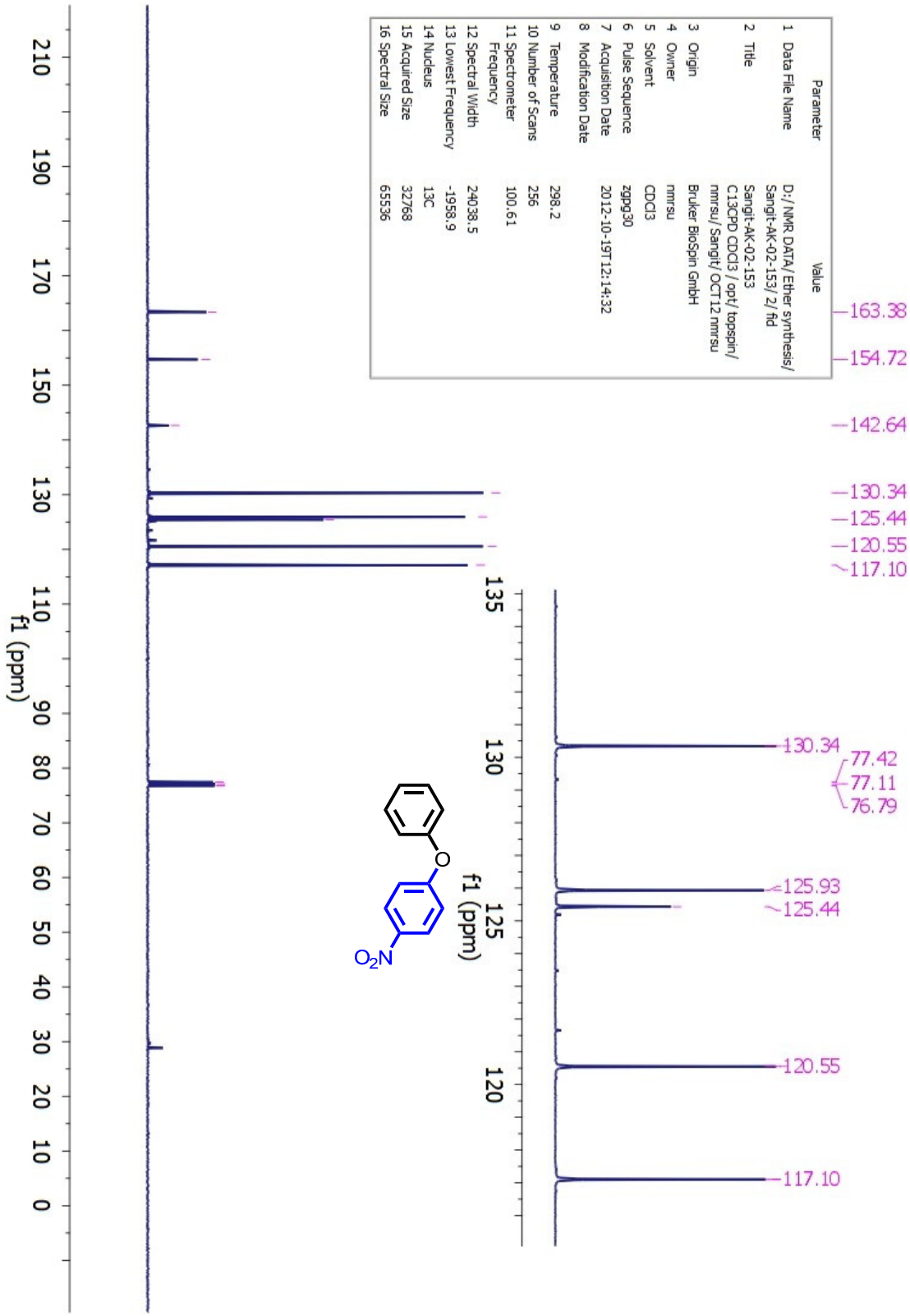

Figure S94 DEPT- 135 NMR spectrum of **34**

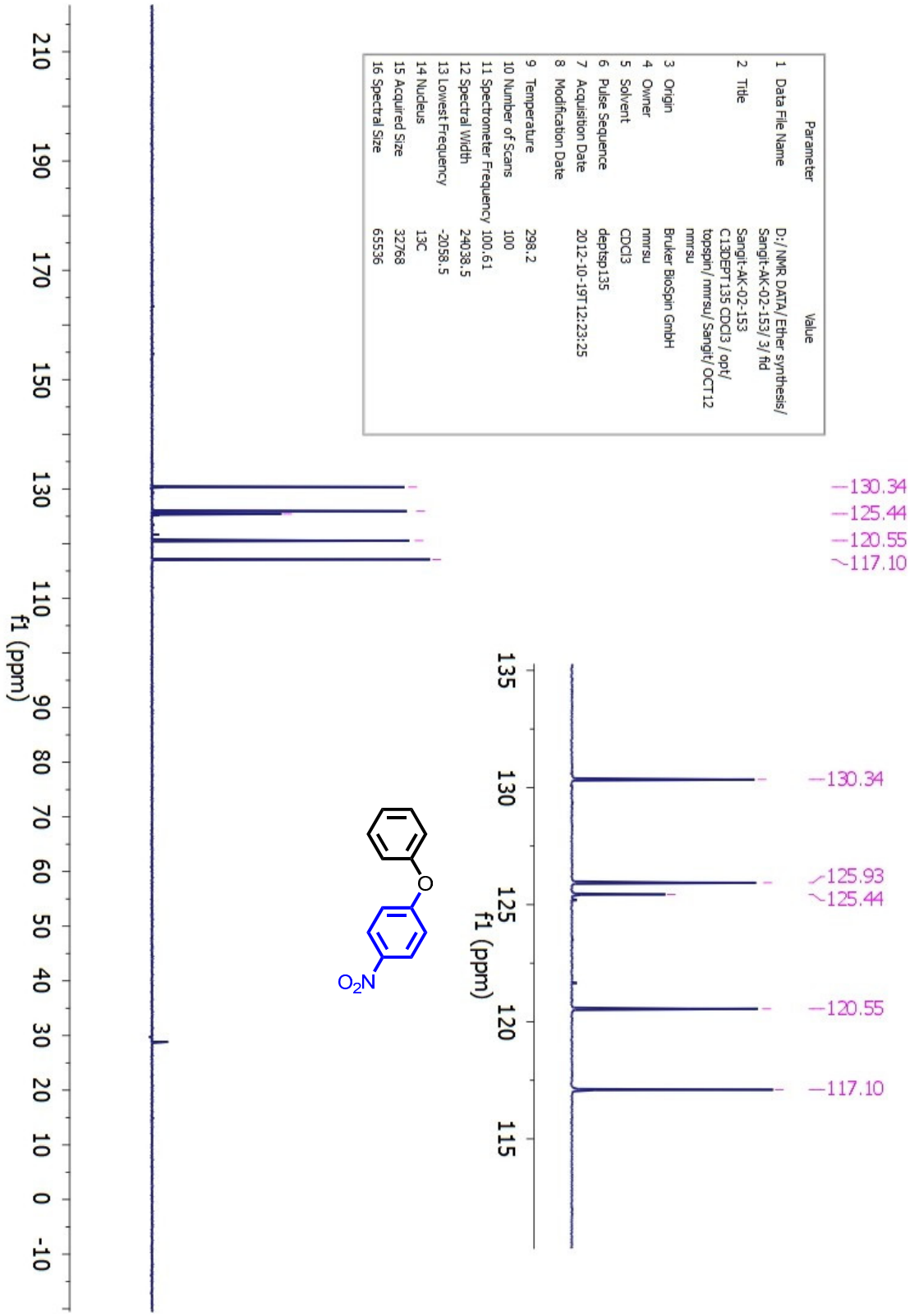

Figure S95 ^{1}H NMR spectrum of **35a** and **35b**

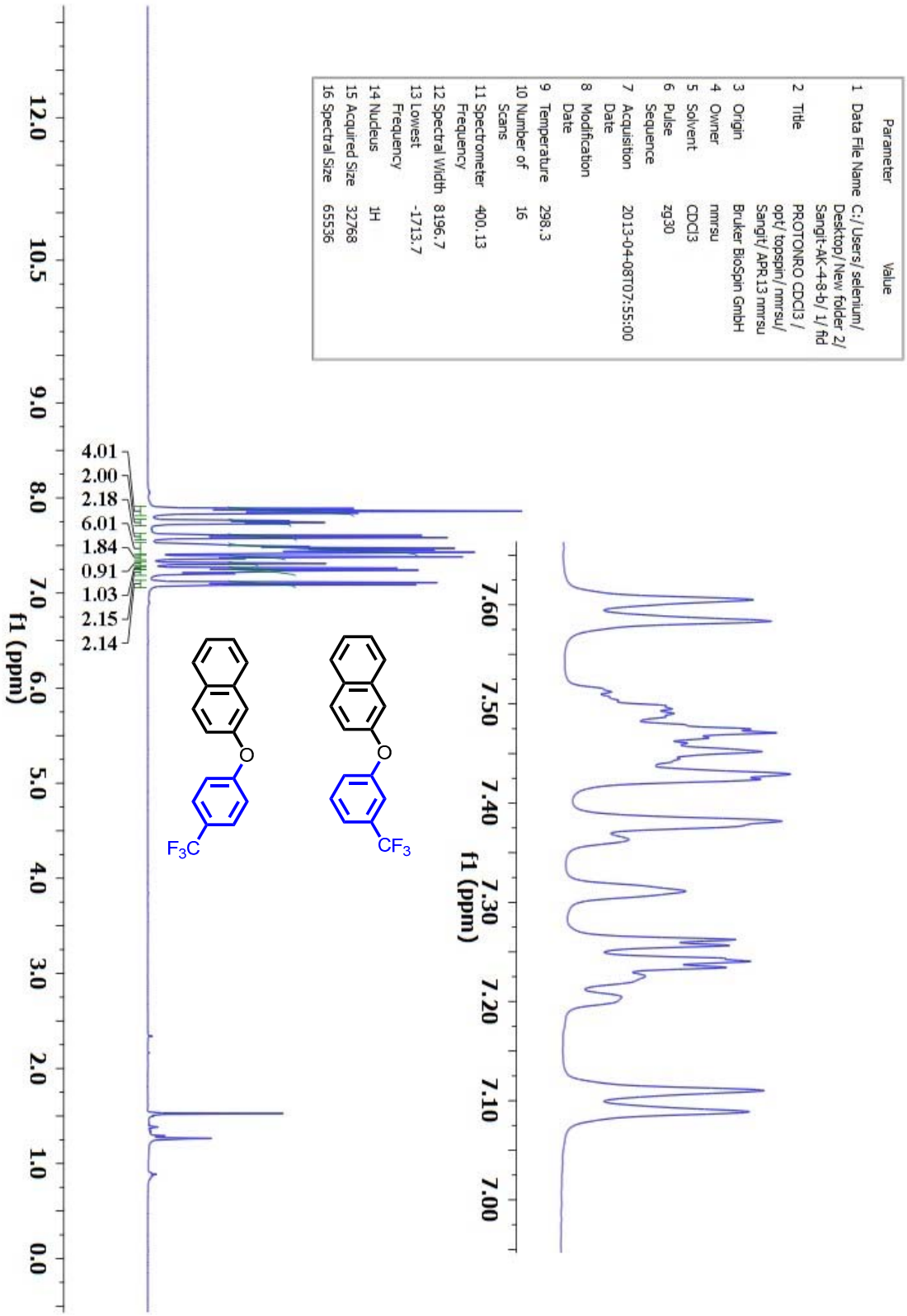

Figure S96 ^{13}C NMR spectrum of **35a** and **35b**

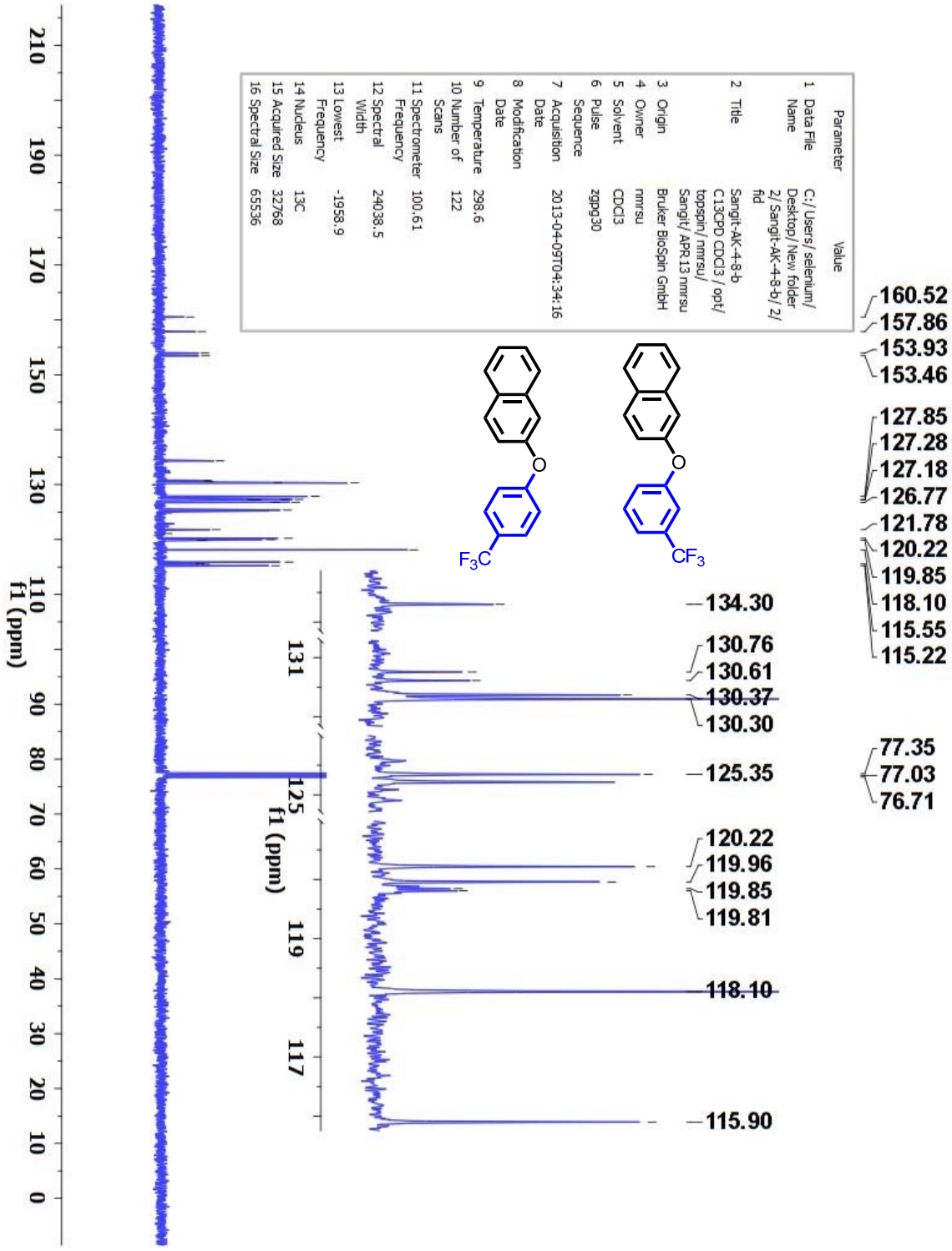

Figure S97 ^{1}H NMR spectrum of **36a** and **36b**

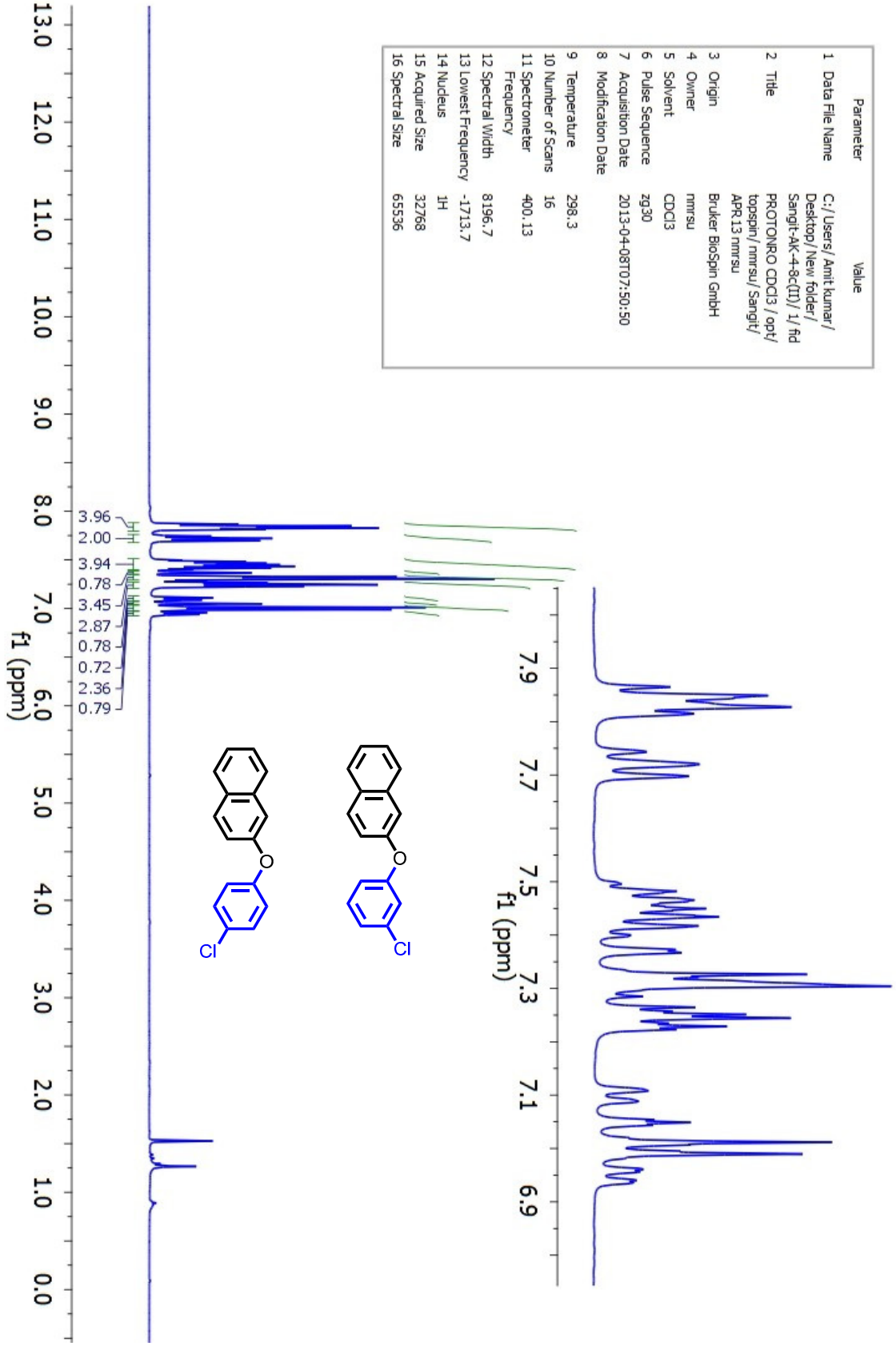

Figure S98 ^{13}C NMR spectrum of **36a** and **36b**

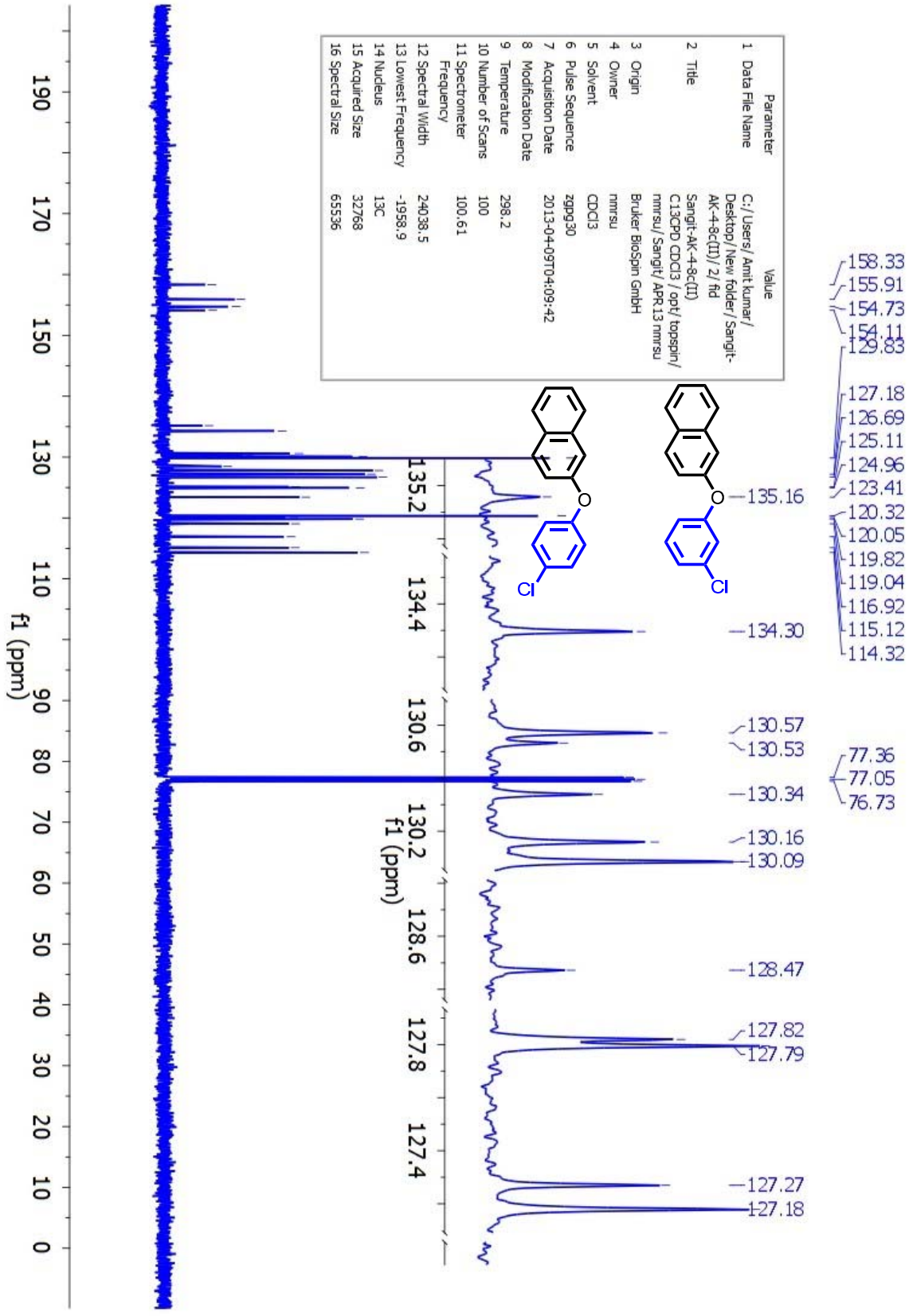

Figure S99 ^{1}H NMR spectrum of **37a** and **37b**

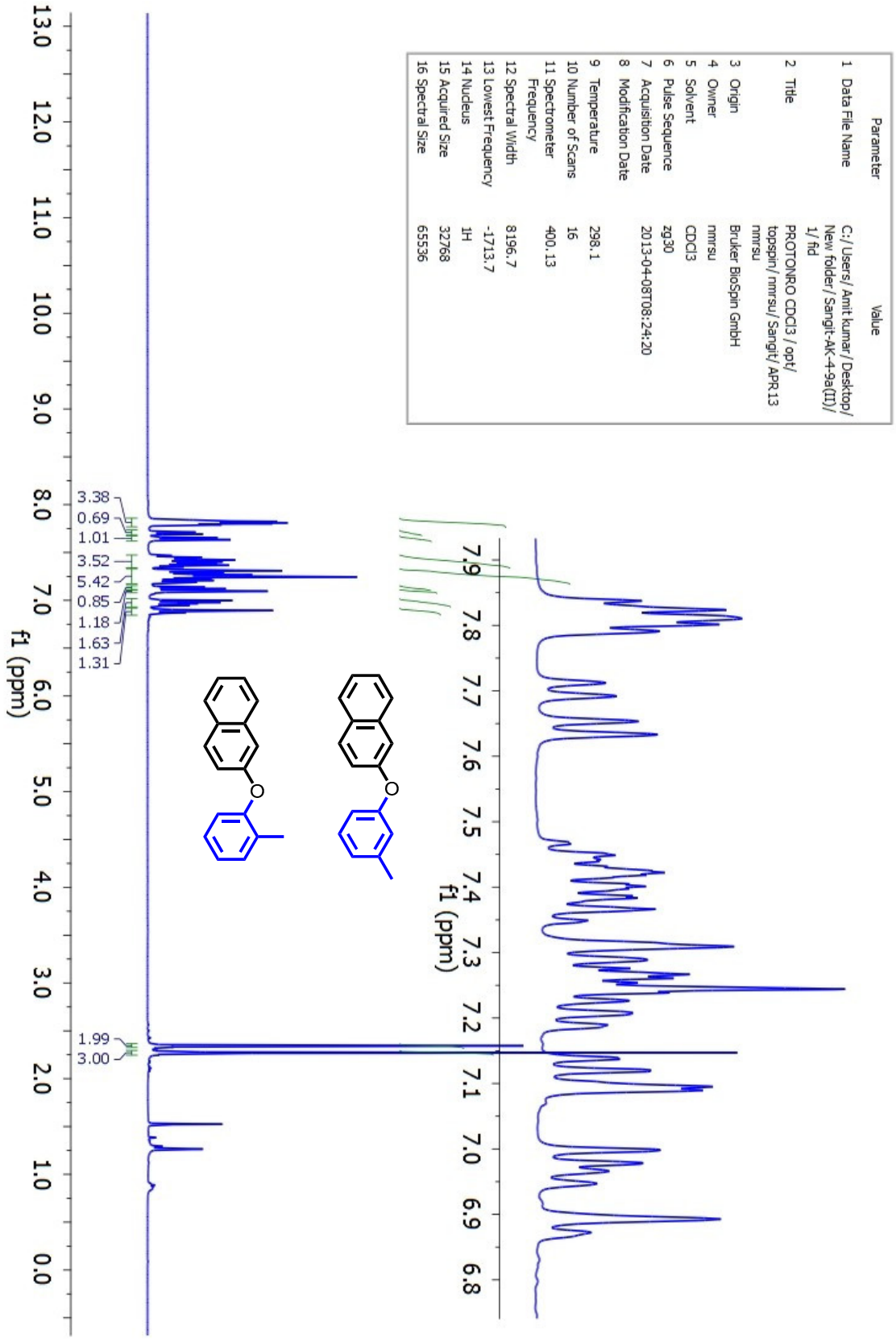

Figure S100 ^{13}C NMR spectrum of **37a** and **37b**

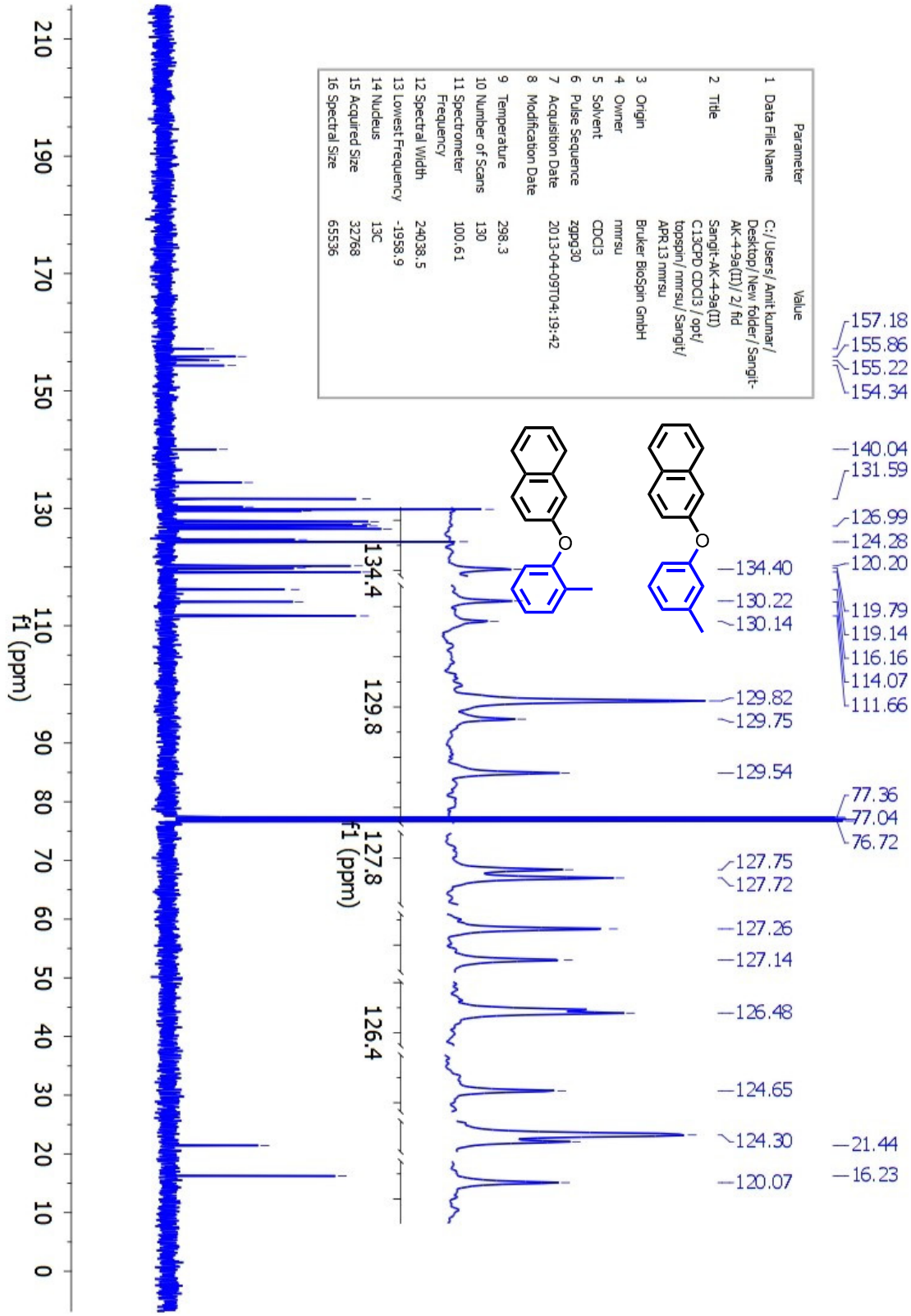

Figure S101 ^{1}H NMR spectrum of **37b** and **38**

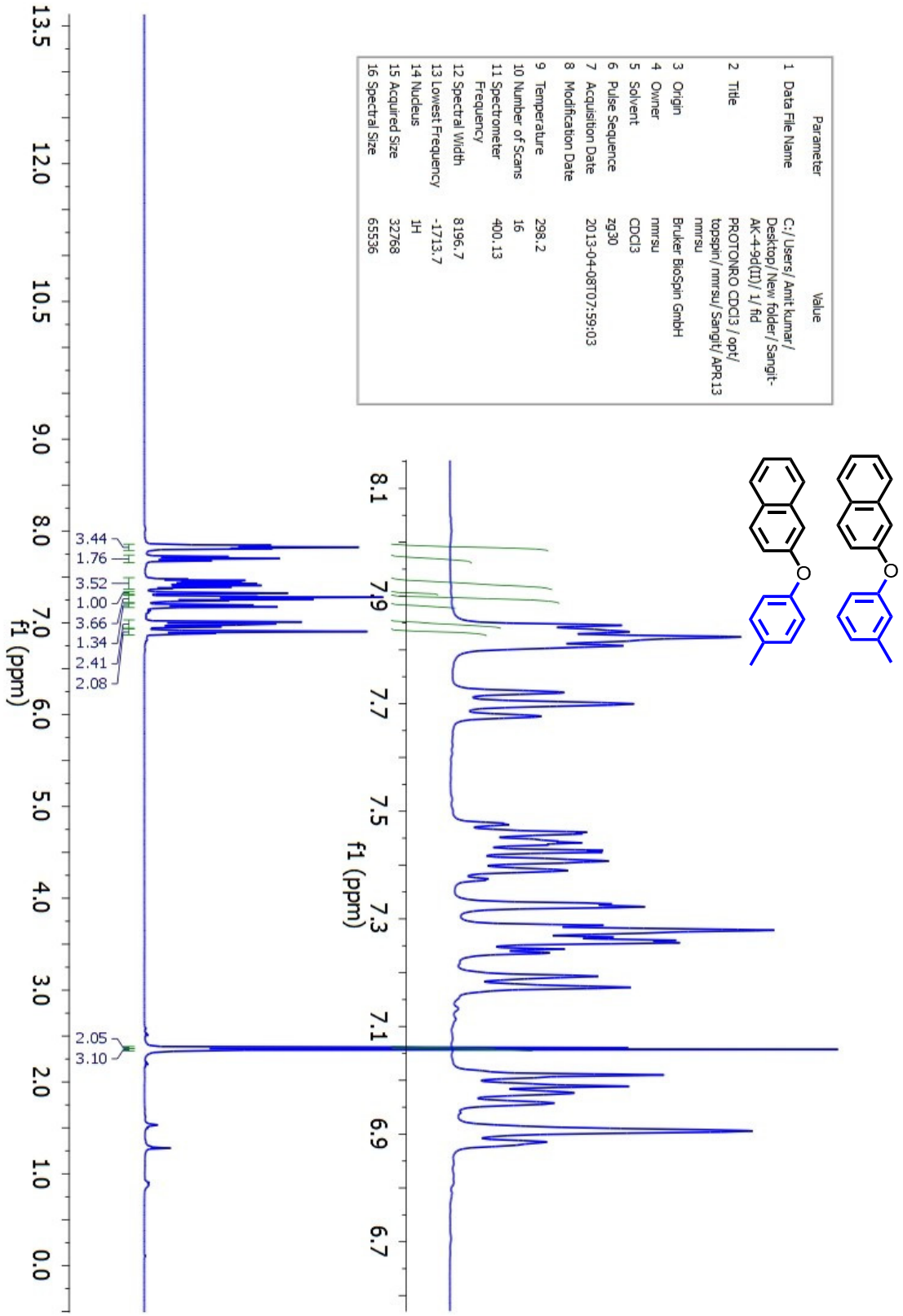

Figure S102 ^{13}C NMR spectrum of **37b** and **38**