Electronic Supplementary Material (ESI) for Chemical Communications.

Chemoselective Arylation of Phenols with Bromo-nitroarenes: Synthesis of Nitro-biaryl-ols and Their Conversion into Benzofurans and Carbazoles

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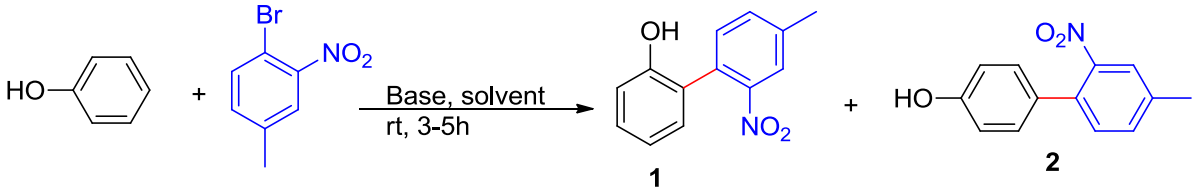
Content

General Experimental Details

All NMR experiments were carried out on 400 MHz spectrometer and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$, (7.26 ppm for ^1H and 77.16 (± 0.06) ppm for ^{13}C, respectively), DMSO-d_6 (3.31 ppm for H_2O, 2.47 ppm for DMSO, 39.9 for carbon) Acetone-d_6, (2.79 for water, 2.03 acetone, ^{13}C 210 (C=O), 34.1 ppm). High resolution mass analysis is performed on quadruple-time of flight (Q-TOF) mass spectrometer equipped with an ESI source (+ve). DMF, DMSO, phenols, and potassium *tert*-butoxide (98% purity) was purchased from SPECTROCHEM Pvt. Ltd. and used as purchased.4-Bromonitrobenzene from SPECTROCHEM Pvt. Ltd., 2-bromonitrobenzene from Alfa Aesar and rest of the halonitrobenzenes were purchased from Aldrich. Silica gel (100-200 mesh size) was used for column chromatography. Room temperature means 25 ^oC. TLC analysis of reaction mixtures was performed using silica gel plates. Nitro-biaryl-ols **30**,[1] **31**,[2] **43**,[3] **45**,[4] benzofurans **48**,[5] **49**,[6] **50**,[7] **51**,[8] and carbazole **56**,[9] are known.

Table S1. Optimization for the Synthesis of Nitro-biaryl-ols[a]



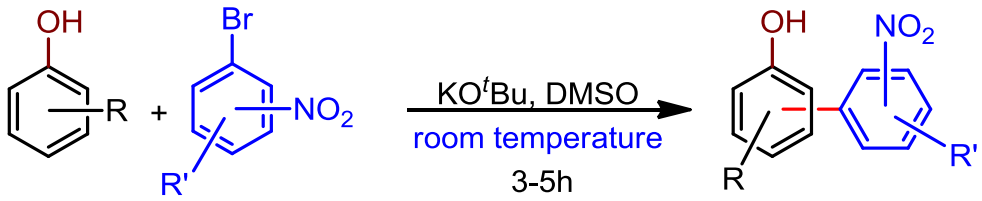
Entry	Base	Solvent	T (°C)	**1** (%)[b]	**2** (%)[b]
1	NaH	DMSO	25	trace	30
2[c]	Cs_2CO_3	DMSO	25	ND	trace
3[c]	K_2CO_3	DMSO	25	ND	trace
4	NaOH	DMSO	25	14	48
5	KOH	DMSO	25	10	42
6	**KO^{t}Bu**	**DMSO**	**25**	**18**	**65**
7	NaO^{t}Bu	DMSO	25	22	46
8	LiO^{t}Bu	DMSO	25	9	40
9	KO^{t}Bu	DMF	25	26	54
10[d]	KO^{t}Bu	Benzene	25	ND	ND
11[d]	KO^{t}Bu	THF	25	ND	ND
12[d]	KO^{t}Bu	Dioxane	25	ND	ND
13[e]	KO^{t}Bu	DMSO	25	-	53
14	KO^{t}Bu	DMSO	110	-	71

[a] Reactions were carried out using 1.0 mmol of 1-bromo-4-methyl-2-nitrobenzene, 1.2 mmol of phenol, and 2.5 mmol of base in four mL of solvent unless otherwise stated. [b] Isolated yield. [c] Reaction stirred for 24 h. [d] Seven mL of solvent was used. Solvents such as benzene, dioxane, and THF were taken nearly double volume as compared to that of DMSO (4 mL) for optimization due to poor solubility of KO^{t}Bu in those solvents. [e] AgOAc used as an additive, reaction was stirred for 12h. ND = Not detected

Optimization of reaction conditions was carried out using phenol and 1-bromo-4-methyl-2-nitrobenzene coupling partners, and results are summarized in Table 1. First various bases were screened to obtain high yield of carbon-carbon coupled nitro-biaryl-ols **1** and **2**. Bases such as NaH, Cs_2CO_3, and K_2CO_3 afforded only traces of nitro-biaryl-ols **1** and **2** (entries 2-3, Table 1). Strong bases NaOH and KOH provided better yields of **1** and **2** (entries 4-5, Table 1). Butoxide

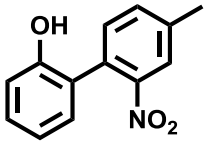
salts of potassium, sodium and lithium offered good yields of nitro-biaryl-ols **1** and **2** (Table 1, entries 6-8). After obtaining nitro-biaryl-ol **1** chemoselectively, we sought for better regioselectivity as the reaction gave two regioisomers, 2'-nitro-biaryl-4-ol **2** and nitro-biaryl-ol **1** in 70:30 ratio, respectively (entry 6, Table 1). For this purpose, a series of solvents were screened in the reaction. The use of DMF as solvent also gave comparable yield and similar regioselective ratio of **1** and **2** (Table1, entry 9). Benzene, THF, and 1,4-dioxane as solvents were found unsuitable as traces of nitro-biaryl-ols **1** and **2** were noticed. The addition of silver acetate as an additive to the reaction mixture provided 2'-nitro-biaryl-4-ol **2** exclusively, albeit in low 53% yield (Table 1, entry 13) and seems due to the highly ionic reaction mixture. Interestingly, reaction at a high temperature (110 ^{o}C) gave 2'-nitro-biaryl-4-ol **2** exclusively in 2 h (Table 1, entry14). Carbon-carbon bond is favorable at high temperature compare to oxygen-carbon bond. The exclusive formation of 2'-nitro-biaryl-4-ol **2** could be due to high delocalization of electronic into benzene ring.

Scheme S1 General Procedure for the Synthesis of Nitrobiarylols.

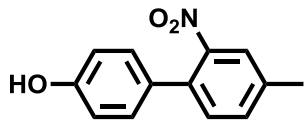


To a single neck flask, phenol (113 mg, 1.2 mmol) and 1-bromo-4-methyl-2-nitrobenzene (216 mg, 1.0 mmol) were added in DMSO (4 mL) and resulted reaction mixture was stirred for 5 min at room temperature. After this, KO^{t}Bu (281 mg, 2.5 mmol) was added portion wise. After complete addition of KO^{t}Bu, the resulted reaction mixture stirred at room temperature. Progress

of the reaction was monitored by TLC. After completion of the reaction (3-5 h), the mixture was poured into 10 N aqueous solution of HCl, 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 under vacuo and the residue was purified by column chromatography (silica gel, eluent: hexane/ ethyl acetate). Two fractions were obtained. First fraction, 4'-Methyl-2'-nitro-[1,1'-biphenyl]-2-ol **1** and second fraction, 4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol **2**.



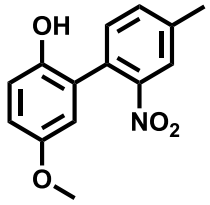
4'-Methyl-2'-nitro-[1,1'-biphenyl]-2-ol (**1**). R_f = 0.5 (ethyl acetate: hexane 1:9), yellow liquid, yield 39 mg (18%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.45 (d, J = 7.5Hz, 1H), 7.30 (d, J = 8.0Hz, 1H), 7.24 (m, 1H), 7.19 (dd, J = 7.7, 1.5Hz, 1H), 7.00 (t, J = 7.6Hz, 1H), 6.82 (d, J = 8.0Hz, 1H), 5.00 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.5, 139.1, 133.6, 132.5, 129.9, 129.7, 129.5, 125.0, 124.6, 121.3, 115.7, 20.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_3$ [M+Na] 252.0636, found 252.0653.



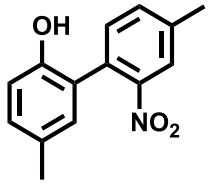
4'-Methyl-2'-nitro-[1,1'-biphenyl]-4-ol (**2**). R_f = 0.4 (ethyl acetate: hexane 1:9), yellow solid, yield 151 mg (65%), Mp 80-81^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.37 (d, J = 7.8Hz, 1H), 7.28 (d, J = 7.8Hz, 1H), 7.16 (d, J = 8.8Hz, 2H), 6.84 (d, J = 8.3Hz, 2H), 5.13 (bs, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 149.1, 138.3, 133.0, 131.7, 129.7, 129.3, 124.3, 115.7, 100.0, 20.8. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_3$ [M+Na] 252.0636, found 252.0653.

Regioselective Synthesis of 4'-Methyl-2'-nitro-[1,1'-biphenyl]-4-ol (2) at 110 ^{o}C. Reaction was carried by following standard procedure as mentioned above. After addition of KO^{t}Bu to the phenol and 1-bromo-4-methyl-2-nitrobenzene, the resulted reaction mixture was heated at 110 ^{o}C for 2 h. Workup and purification procedure are similar as described above. Yield 163 mg (71%).

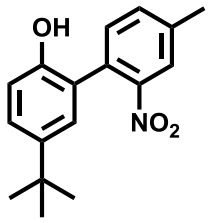
Regioselective Synthesis of 4'-Methyl-2'-nitro-[1,1'-biphenyl]-4-ol (2) using AgOAc Additive. To the stirred mixture of phenol (132 mg, 1.4 mmol) and 1-bromo-4-methyl-2-nitrobenzene (238 mg, 1.1 mmol) in DMSO (6 mL), AgOAc (237 mg, 1.4 mmol) was added. After this, KO^{t}Bu (314 mg, 2.8 mmol) was added and resulted reaction mixture was stirred for 12 h at room temperature. After this, reaction mixture was poured over water (100 mL) and extracted with ethyl acetate (25 mL x 4), dried over Na_2SO_4, concentrated under vacuo, purification by column chromatography gave **2** (138 mg, 54 %).



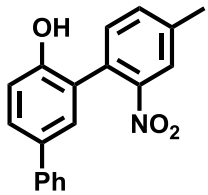
5-Methoxy-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (**3**). Rf = 0.5 (ethyl acetate: hexane 1.5:8.5), yellow solid; yield: 142 mg (55%), Mp 150-151 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.3 (d, J = 7.7 Hz, 1H), 6.79-6.74 (m, 3H), 4.71 (bs, 1H), 3.77 (s, 3H), 2.46 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 149.4, 146.4, 139.2, 133.6, 132.4, 129.4, 125.8, 124.6, 116.5, 115.3, 114.6, 55.8, 20.9; HRMS (EI) *m/z* calcd for $C_{13}H_{14}NO_4$ [M –H] 258.0761, found 258.0736.



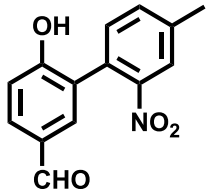
4',5-Dimethyl-2'-nitro-[1,1'-biphenyl]-2-ol (4). Rf = 0.5 (ethyl acetate: hexane 1.5:8.5) yellow semisolid, yield: 148 mg (61%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s,1H), 7.43 (d, J = 8.14 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1Hz), 7.04 (dd, J = 8.14,1.9 Hz, 1H), 6.99 (d, J = 1.9 Hz, 1H), 6.72 (d, J = 8.16 Hz, 1H), 4.98 (bs,1H), 2.45 (s, 3H), 2.30 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ150.25, 149.5, 138.9, 133.5, 132.5, 130.4, 130.3, 130.1, 129.7, 124.8, 124.5, 115.5, 20.9, 20.5; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_3$ [M-H] 282.0817, found 282.0832



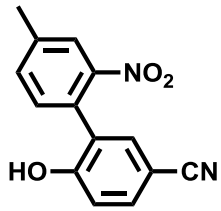
5-(*tert*-Butyl)-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (**5**). R_f = 0.5 (hexane), yellow solid, yield 212 mg (73%), Mp 70-71 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76(s, 1H), 7.42(d, J = 6.8Hz, 1H), 7.32(d, J = 8.4Hz, 1H), 7.27-7.24(m, 1H), 7.17(d, J = 2.3Hz, 1H), 6.76(d, J = 8.9Hz, 1H), 4.84(bs, 1H), 2.46(s, 3H), 1.30(s, 9H),^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.6, 144.0, 138.9, 133.5, 132.6, 130.0, 126.8, 126.5, 124.5, 124.2, 115.2, 34.2, 31.5, 29.7(grease), 20.9; HRMS (APCI) *m/z* calcd for $C_{17}H_{19}NO_3$ [M+H] 285.1359, found 285.1344.



4''-Methyl-2''-nitro-[1,1':3',1''-terphenyl]-4'-ol (**6**). Rf = 0.5 (ethyl acetate: hexane 1:9), yellow semisolid and solidified on cooling, yield 156 mg (51%), Mp 161-162 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (s,1H), 7.55 (d, J = 7.5 Hz, 2H), 7.48-7.44 (m, 3H), 7.40 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 5.43 (bs, 1H), 2.47 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 149.4, 140.4, 139.2, 134.4, 133.7, 132.6, 129.6, 128.7, 128.6, 128.2, 126.9, 126.8, 125.4, 124.6, 116.0, 20.9; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_3$ [M-H] 304.0968, found 304.0986

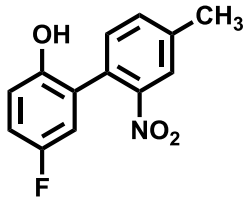


6-Hydroxy-4'-methyl-2'-nitro-[1,1'-biphenyl]-3-carbaldehyde (7). Rf = 0.5 (ethyl acetate: hexane 1.5:8.5), brown solid, yield 105 mg (41%), Mp 226-227 ^{o}C, ^{1}H NMR (400 MHz, DMSO-d_6) δ10.97 (s, 1H), 9.83 (s, 1H), 7.80-7.76 (m, 3H), 7.57 (d, J = 7.8 Hz 1H), 7.38 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 2.41 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.4, 160.3, 149.4, 139.6, 134.5, 132.7, 132.3, 132.0, 129.3, 129.2, 126.3, 124.6, 115.9, 20.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}NO_4$ [M-H] 256.0604, found 256.0628.

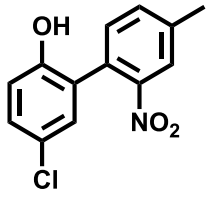


6-Hydroxy-4'-methyl-2'-nitro-[1,1'-biphenyl]-3-carbonitrile (8). Rf = 0.5 (ethyl acetate: hexane 1.5:8.5), white solid, yield 142 mg (56%), Mp 240-241 ^{o}C, ^{1}H NMR (400 MHz, DMSO-

d_6) δ 11.0 (bs, 1H), 7.85 (s,1H), 7.74 (d, J = 2.1 Hz, 1H), 7.67 (dd, J = 8.4, 2.11 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 2.44 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.8, 149.2, 139.8, 134.5, 134.4, 134.2, 132.9, 128.3, 127.0, 124.6, 119.7, 116.3, 102.1, 20.75; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}N_2O_3$ [M+Na] 277.0584, found 277.0583.

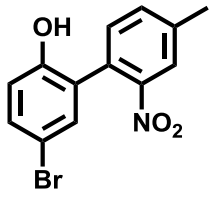


5-Fluoro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (9). Rf = 0.5 (ethyl acetate: hexane 1:9) yellow semisolid, yield 151 mg (61%), Mp 140-141 ^{o}C,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 6.94-6.90 (m, 2H), 6.77-6.74 (m, 1H), 4.04 (bs, 1H), 2.45 (s, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 155.8, 149.2, 148.8(d, J = 2.2Hz), 139.5, 133.8, 132.3, 128.7(d, J = 1.7Hz), 126.3, 126.2, 124.7, 116.5, 116.4, 116.4, 116.2, 115.9, 115.7, 20.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}FNO_3$ [M-H] 246.0566, found 246.0563.

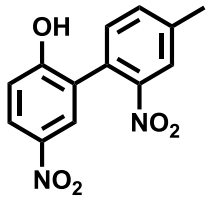


5-Chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (10). Rf = 0.5 (ethyl acetate: hexane 1:9) yellow solid, yield 242 mg (92%), Mp 150-151 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$+one drop DMSO-d_6) δ 9.19 (bs, 1H), 7.65 (s, 1H),7.35 (d, J = 7.3 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 2.5 Hz 1H), 7.04 (dd, J = 8.5,2.5 Hz, 1H), 6.73 (d, J = 8.5 Hz 1H), 2.35 (s, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.2, 138.7, 133.6, 132.2, 129.4, 129.0, 128.8, 126.8, 124.4, 124.1,

116.5, 20.8; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClNO_3$ [M-H] 262.0271, found 262.0281. X-ray quality crystals were obtained by dissolving **10** in CH_2Cl_2 / hexane. Crystals of **10** were grown by cooling at -35 ^oC. Optical rotation of **10** was recorded by dissolving crystals in $CHCl_3$. [α] = 24.04±0.4 (c = 0.3, $CHCl_3$).

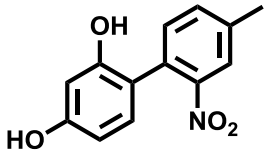


5-Bromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (11). Rf = 0.6 (ethyl acetate: hexane 1:9) yellow solid, yield 178 mg (58%), Mp 148-149 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.32-7.29 (m, 2H), 7.26 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 8.89 Hz, 1H), 5.72 (s, 1H), 2.45 (s, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 149.1, 139.6, 133.9, 132.35, 132.50, 132.20, 128.4, 127.3, 124.7, 117.3, 112.8, 20.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}BrNO_3$ [M+Na] 329.9741, found 329.9733. X-ray quality crystals were obtained by dissolving **11** in CH_2Cl_2 / hexane. Crystals of **11** were grown by cooling at -35 ^oC.

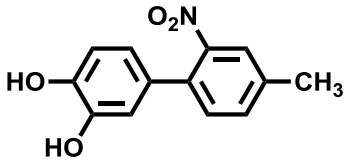


4'-Methyl-2',5-dinitro-[1,1'-biphenyl]-2-ol (12). Rf = 0.6 (ethyl acetate: hexane 1.5:8.5), yellow solid, yield137 mg (50%), Mp 130-131 ^oC, ^1H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 8.15-8.10 (m, 2H), 7.85 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 8.9 Hz, 1H), 2.42 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.0, 149.2, 140.3, 140.1, 134.7,

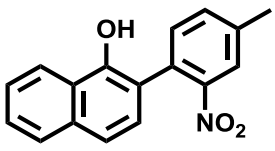
132.8, 128.2, 126.5, 126.2, 125.9, 124.8, 115.7, 20.7; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}N_2O_5$ [M+Na] 297.0487, found 297.0468.



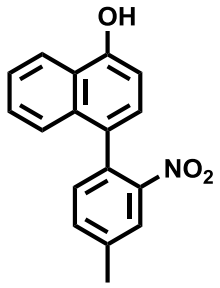
4'-Methyl-2'-nitro-[1,1'-biphenyl]-2,6-diol (13). Rf = 0.6 (ethyl acetate: hexane 2.5:7.5), brown semisolid, yield 164 mg (67%), ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 9.46 (s, 1H), 7.66 (s, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 8.13 Hz, 1H), 6.30-6.26 (m, 2H), 2.37 (s, 3H),^{13}C NMR (100 MHz, DMSO-d_6) δ 159.0, 155.4, 149.6, 137.8, 133.8, 132.7, 130.67, 130.61, 124.3, 116.3, 107.4, 102.6, 20.6; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_4$ [M-H] 244.0609, found 244.0620.



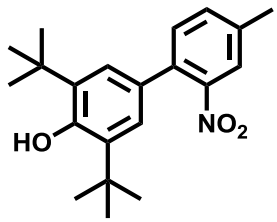
4'-Methyl-2'-nitro-[1,1'-biphenyl]-3,4-diol (14). R_f = 0.4 (ethyl acetate: hexane 3:7), liquid, yield 163 mg (67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 7.8Hz, 1H), 6.85 (d, J = 8.0Hz, 1H), 6.80 (d, J = 1.9Hz, 1H), 6.71 (dd, J = 8.0, 1.9Hz, 1H), 5.62 (bs, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 143.8, 143.7, 138.4, 133.0, 132.8, 131.7, 130.1, 124.2, 120.8, 115.7, 115.2, 20.8; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_4$ [M+Na] 268.0585, found 268.0580.



2-(4-Methyl-2-nitrophenyl)naphthalen-1-ol (15). R_f = 0.4 (ethyl acetate: hexane 2:8), yellow liquid, yield 41 mg (13%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 1H), 7.83 (m, 2H), 2.53-5.46 (m, 4H), 7.38 (d, J = 7.9Hz, 1H), 7.17 (d, J = 8.2Hz, 1H), 5.36 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.2, 139.8, 134.5, 133.8, 132.9, 128.9, 127.8, 126.8(d), 125.9, 125.0, 124.0, 121.7, 120.8, 118.1, 21.0. HRMS (ESI) *m/z* calcd for $C_{17}H_{13}NO_3$ [M+Na] 302.0793, found 302.0784.

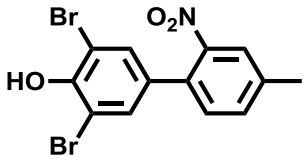


4-(4-Methyl-2-nitrophenyl)naphthalen-1-ol (16). R_f = 0.3(ethyl acetate: hexane 2:8), yellow solid, yield 171 mg (60%), Mp 140-141 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.8 Hz, 1H), 7.83 (s, 1H), 7.45 (m, 4H), 7.30 (d, J = 7.2Hz, 1H), 7.12 (d, J = 7.6Hz, 1H), 6.73 (d, J = 7.5Hz, 1H), 5.68 (bs, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.0, 138.9, 133.3, 132.8, 132.3, 127.9, 127.0, 126.3, 125.3, 124.9, 124.6, 124.5, 124.4, 122.0, 108.1, 21.0; HRMS (ESI) *m/z* calcd for $C_{17}H_{13}NO_3$ [M+Na] 302.0793, found 302.0781.

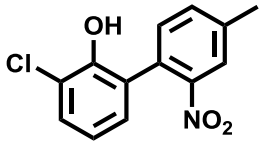


3,5-Di-tert-butyl-4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (17). Rf = 0.6 (hexane), yellow solid, yield 252 mg (74%), Mp 135-136 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.37-7.31 (m,

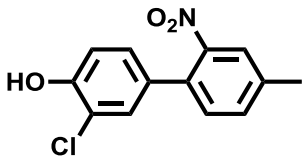
2H), 7.10 (s, J = 7.8, 2H), 5.28 (s, 1H), 2.43 (s, 3H), 1.43 (s, 18 H),^{13}C NMR (100 MHz, $CDCl_3$) δ153.9, 149.6, 137.7, 136.1, 133.8, 132.5, 131.6, 127.9, 124.8, 124.0, 34.4, 30.2, 20.8; HRMS (ESI) *m/z* calcd for $C_{21}H_{27}NO_3$ [M-H] 340.1912, found 340.1920.



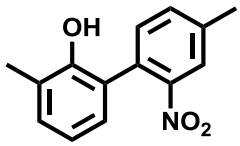
3,5-Dibromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (18). R_f = 0.5 (ethyl acetate: hexane, 1:9), yellow solid, yield 259 mg (67%), Mp 178-179 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.40 (d, J = 7.7Hz, 1H), 7.37 (s, 2H), 7.24 (s, 1H), 5.94 (s, 1H), 2.46 (s, 3),^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 148.6, 139.6, 133.3, 132.2, 131.7, 131.6, 130.5, 124.5, 109.9, 20.9; HRMS (APCI) *m/z* calcd for $C_{13}H_9Br_2NO_3$ [M+H] 385.9007, found 385.9035.



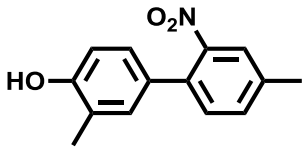
3-Chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (19). R_f = 0.46 (ethyl acetate: hexane 1:9), yellow solid, yield 32 mg (12%), Mp 108-109 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.44 (d, J = 7.8Hz, 1H), 7.34 (dd, J = 8.1, 1.5 Hz, 1H), 7.27 (d, J = 8.1Hz, 1H), 7.16 (dd, J = 7.6, 1.5Hz, 1H), 6.95 (t, J = 7.8Hz, 1H), 5.64(s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.3, 139.3, 133.6, 132.2, 129.1, 128.9, 128.6, 126.4, 124.7, 121.4, 120.0, 20.9, HRMS (APCI) *m/z* calcd for $C_{13}H_{10}ClNO_3$ [M+H] 264.0427, found 264.0432.



3-**Chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (20).** R_f = 0.4 (ethyl acetate: hexane 1:9), yellow solid, yield 169 mg (64%), Mp 95-96 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.38 (d, J = 7.8Hz, 1H), 7.26 (s, 2H), 7.08 (dd, J = 8.4, 2.0 Hz, 1H), 7.02 (m, 1H), 5.68 (s, 1H), 2.44 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 148.9, 139.0, 133.1, 131.8, 131.7, 130.8, 128.5, 128.2, 124.5, 120.1, 116.4, 20.9; HRMS (APCI) *m/z* calcd for $C_{13}H_{10}ClNO_3$ [M+H]264.0427, found 264.0428

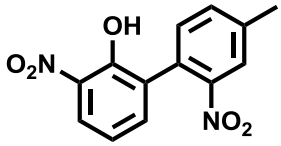


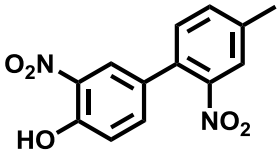
3,4'-dimethyl-2'-nitro-[1,1'-biphenyl]-2-ol (21). Rf = 0.6 (ethyl acetate: hexane 1.5:8.5), yellow solid, yield 27 mg (11%), Mp 100-101 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (d, J = 7.67 Hz, 1H), 7.29 (d, J = 7.85Hz, 1H), 7.14 (d, J = 7.28 Hz, 1H), 7.01 (dd, J = 7.6, 1.23 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 4.74 (bs, 1H), 2.46 (s, 3H), 2.26 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.78, 149.7, 149.6, 139.2, 133.5, 132.5, 131.0, 129.5, 127.5, 124.6, 123.6, 120.8, 20.9, 15.9; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_3$ [M-H] 242.0817, found 242.0810.



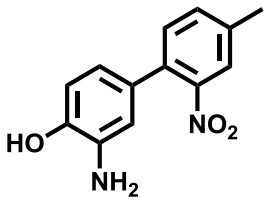
3,4'-Dimethyl-2'-nitro-[1,1'-biphenyl]-4-ol (22). R_f = 0.4(ethyl acetate: hexane 1:9); yellow solid, yield 156 mg (64%), Mp 120-121 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 1.7Hz,

1H), 7.28 (d, J = 8.6Hz, 1H), 7.10 (dd, J = 8.6, 1.7Hz, 1H), 7.02 (d, J = 1.9Hz, 1H), 6.96 (dd, J = 8.1, 1.9Hz, 1H), 6.75 (d, J = 8.1Hz, 1H), 5.28 (s, 1H), 3.87 (s, 3H), 2.24 (s, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.8, 149.6, 132.6, 130.6, 129.5, 128.4, 126.7, 124.3, 118.6, 115.2, 108.8, 55.9, 15.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_3$ [M+ Na] 266.0793, found 266.0764.



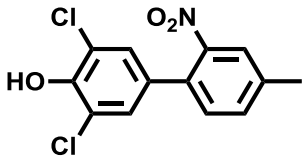


4'-Methyl-2',3-dinitro-[1,1'-biphenyl]-2-ol and 4'-Methyl-2',3-dinitro-[1,1'-biphenyl]-4-ol (23a&23b). Rf = 0.5 (ethyl acetate: hexane 0.5 : 9.5), yellow solid, yield 131 mg (48%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84-10.61 (m, 1H), 8.15-8.04 (m, 1H), 7.89-7.75 (m, 1H), 7.58-7.44 (m, 2H), 7.29-7.24 (m, 1H),7.18-7.06 (m, 1H), 2.49-2.47 (m, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 152.3, 148.8, 148.5, 140.1, 139.9, 137.4, 137.1, 134.0, 133.68, 133.62, 133.4, 132.1, 131.7, 130.9, 130.21, 130.18, 127.8, 125.0, 124.9, 124.8, 124.2, 120.3, 120.1, 21.0, 20.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}N_2O_5$ [M – H] 273.0511, found 273.0527.

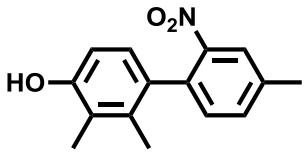


3-Amino-4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (**24**). Rf = 0.3 (ethyl acetate: hexane 1.5: 8.5) brown semisolid, yield 110 mg (45%), ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 7.60 (s, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.50 (d, J = 2.1 Hz, 1H), 6.29 (dd, J = 8.0, 2.0 Hz, 1H), 4.67 (bs, 2H), 2.35 (s, 3H), ^{13}C NMR (100 MHz,

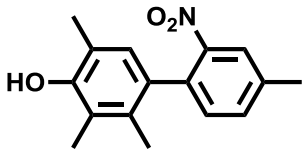
DMSO-d_6) δ 149.5, 144.7, 138.1, 137.3, 133.26, 133.21, 131.6, 128.7, 124.0, 116.3, 114.9, 113.9, 20.6; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_2O_3$ [M+H] 245.0926, found 245.0950.



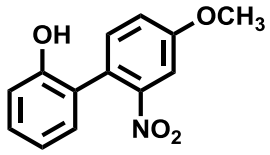
3,5-Dichloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (25). R_f = 0.4 (ethyl acetate: hexane 1:9); yellow solid, yield 200 mg (67%), Mp 155-156 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.41 (d, J = 7.7Hz, 1H), 7.25 (s, 1H), 7.18 (s, 2H), 5.95 (s, 1H), 2.45 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ148.6, 147.7, 139.6, 133.3, 131.7, 130.9, 130.8, 127.9, 124.7, 121.2, 20.9; HRMS (ESI) *m/z* calcd for $C_{13}H_9Cl_2NO_3$ [M- H] 295.9881, found 295.9902.



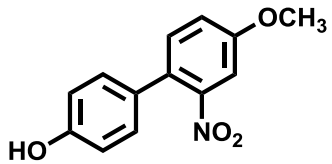
2,3,4'-Trimethyl-2'-nitro-[1,1'-biphenyl]-4-ol (26). Rf = 0.4(ethyl acetate: hexane 1:9) yellow solid, yield 149 mg (58%), Mp 115-116 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.39 (d, J = 7.6Hz, 1H), 7.17 (d, J = 7.6Hz, 1H), 6.79 (d, J = 8.2Hz, 1H), 6.62 (d, J = 8.2Hz, 1H), 4.92 (s, 1H), 2.46 (s, 3H), 2.19 (s, 3H), 1.99 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 149.4, 138.3, 136.2, 134.2, 133.1, 132.5, 130.1, 126.6, 124.1, 122.9, 112.3, 20.9, 17.2, 12.0, HRMS (ESI) *m/z* calcd for $C_{15}H_{15}NO_3$ [M+Na] 280.0949, found 280.0971.



2,3,4',5-Tetramethyl-2'-nitro-[1,1'-biphenyl]-4-ol (27). Rf = 0.4 (ethyl acetate: hexane 1:9), yellow solid, yield 174 mg (64%), Mp 105-106 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 6.72 (s, 1H), 4.72 (s, 1H), 2.46 (s, 3 H), 2.20-2.19 (m, 6H), 1.97 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 149.4, 138.2, 134.2, 133.4, 133.0, 132.5, 129.5, 127.9, 124.0, 122.2, 119.9, 20.9, 17.1, 15.8, 12.1; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO_3$ [M+K] 310.0845, found 310.0829. X-ray quality crystals were obtained by dissolving **27** in CH_2Cl_2 / hexane. Crystals of **27** were grown by cooling at -35 ^{o}C.



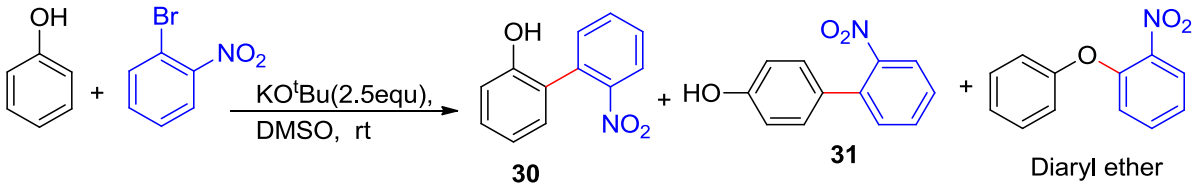
4'-Methoxy-2'-nitro-[1,1'-biphenyl]-2-ol (28). Rf = 0.4 (ethyl acetate: hexane 2:8) yellow solid, yield 25 mg (10%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48(d, J = 2.5Hz, 1H), 7.33 (d, J = 8.6Hz, 1H), 7.26-7.22(m, 1H), 7.19-7.17(m, 2H), 6.99(t, J = 7.4Hz, 1H), 6.81(d, J = 8.4Hz, 1H), 5.07(bs, 1H), 3.89(s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 152.5, 150.1, 133.6, 130.0, 129.6, 124.9, 124.5, 121.2, 119.3, 115.6, 109.3, 55.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_4$ [M+Na] 268.0585, found 268.0566.

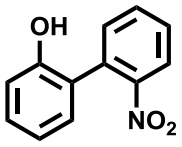


4'-Methoxy-2'-nitro-[1,1'-biphenyl]-4-ol (29). Rf = 0.3 (ethyl acetate: hexane 2:8); yellow solid, yield 123mg (50%), Mp 110-111 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2H), 7.15-7.10 (m, 3H), 6.83 (d, J = 8.6Hz, 2H), 5.12 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz,

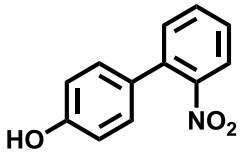
$CDCl_3$) δ 158.8, 155.4, 149.7, 132.8, 129.6, 129.4, 128.2, 118.7, 115.6, 108.9, 55.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO4$ [M+Na] 268.0585, found 268.0566.

Reaction of 2-Bromonitrobenzene with Phenols



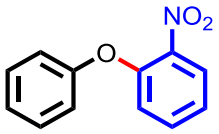


2'-Nitro-[1,1'-biphenyl]-2-ol (30).[1] Rf = 0.37 (ethyl acetate: hexane 1:9); yellow oil, yield 49 mg (23%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2Hz, 1H), 7.64 (td, J = 7.5, 1.1Hz, 1H), 7.49 (td, J = 7.5, 1.1Hz, 1H), 7.43 (dd, J = 7.5, 1.1Hz, 1H), 7.27-7.22 (m, 2H), 7.02 (t, J = 7.3Hz, 1H), 6.81 (d, J = 7.8Hz, 1H), 5.14 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 149.6, 132.9, 132.7, 132.6, 129.9, 129.8, 128.5, 125.0, 124.2, 121.3, 115.7. HRMS (ESI) *m/z* calcd for $C_{12}H_9NO_3$ [M+Na] 238.0480, found 238.0468.

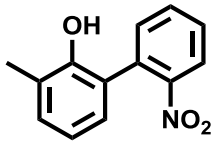


2'-Nitro-[1,1'-biphenyl]-4-ol **(31).**[2] Rf = 0.3 (ethyl acetate: hexan 1:9), yellow solid, yield:97 mg (45%), Mp 100-101 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1Hz, 1H), 7.58 (td, J = 7.5, 1.1Hz, 1H), 7.45-7.40 (m, 2H), 7.19 (d, J = 8.5Hz, 2H), 6.86 (d, J = 8.5Hz, 2H), 5.04 (s,

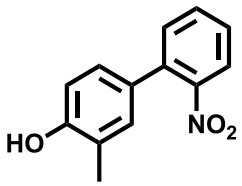
1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 149.4, 135.8, 132.2, 131.9, 129.7, 129.4, 127.8, 124.0, 115.7; HRMS (ESI) *m/z* calcd for $C_{12}H_9NO_3$ [M+Na] 238.0480, found 238.0475.



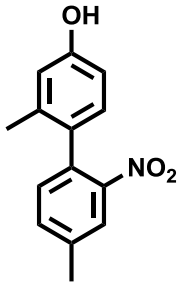
1-Nitro-2-phenoxybenzene: First Fraction, R_f 0.43 (hexane), yellow solid**,** yield 26 g (12%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.50-7.46 (m, 1H), 7.37 (t, *J* = 8.4Hz, 2H), 7.19 – 7.16 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 150.8, 134.1, 130.1, 125.7, 124.6, 123.11, 120.5, 119.3, 111.8; GC/MS (EI): rt = 7.28 min, *m/z* = 215. (reference: Kumar, A.; Bahkuni, B. S.; Prasad, C. D.; Kumar, S.; Kumar, S. *Tetrahedron*, **2013**, *69*, 5383.)



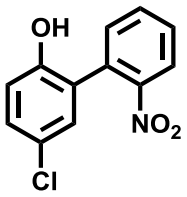
3-Methyl-2'-nitro-[1,1'-biphenyl]-2-ol (32). Rf = 0.4 (ethyl acetate: hexane 1.5 : 8.5), yellow solid, yield 18 mg (8%), Mp 60-61 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.2, 1.1Hz, 1H), 7.64 (td, J = 7.6, 1.1Hz, 1H), 7.50 (td, J = 8.0, 1.3Hz, 1H), 7.42 (dd, J = 7.4, 1.3Hz, 1H), 7.16 (d, J = 7.4Hz, 1H), 7.02 (d, J = 7.6Hz, 1H), 6.92 (t, J = 7.6Hz, 1H), 4.75 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 149.8, 132.8, 132.7, 132.6, 131.2, 128.5, 127.6, 124.7, 124.2, 123.6, 120.9, 15.8. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_3$ [M+Na] 252.0636, found 252.0649.



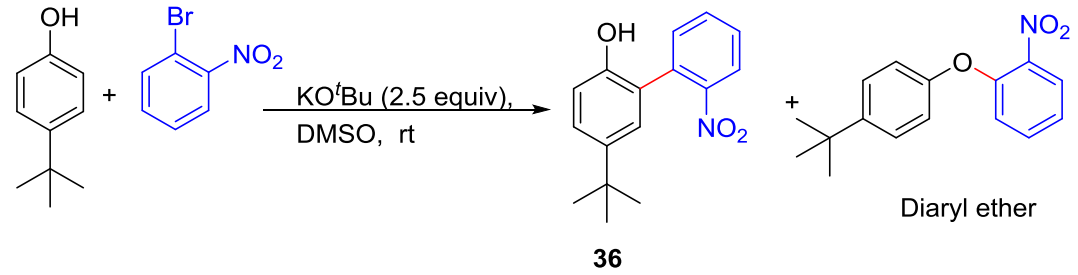
3-Methyl-2'-nitro-[1,1'-biphenyl]-4-ol (33). Rf = 0.3(ethyl acetate: hexane 2:8), yellow solid, yield 123 mg (54%), Mp 109-110 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8Hz, 1H), 7.56 (t, J = 8.0Hz, 1H), 7.41 (t, J = 7.6Hz, 2H), 7.08 (s, 1H), 7.02 (dd, J = 8.0, 2.0Hz, 1H), 6.78 (d, J = 8.1Hz, 1H), 4.99 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.4, 136.0, 132.1, 131.9, 130.6, 129.6, 127.7, 126.7, 124.4, 124.0, 115.3, 15.8. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_3$ [M+Na] 252.0636, found 252.0644. X-ray quality crystals were obtained by dissolving **33** in CH_2Cl_2 / hexane. Crystals of **33** were grown by cooling at -35 ^{o}C.



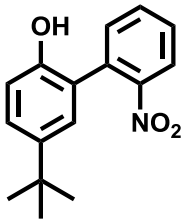
2,4'-Dimethyl-2'-nitro-[1,1'-biphenyl]-4-ol (34). Rf = 0.4 (ethyl acetate: hexane 1.5:8.5), yellow solid, yield 122 mg (50%), Mp 110-111 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.71 (d, J = 2.3 Hz, 1H), 6.65 (dd, J = 8.2, 2.3 Hz, 1H), 5.02 (s, 1H), 2.45 (s, 3H), 2.03 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 149.3, 138.5, 137.6, 133.2, 133.1, 132.4, 129.8, 129.7, 124.3, 116.8, 112.6, 20.7, 19.9; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_3$ [M-H] 242.0817, found 242.0825.



5-Chloro-2'-nitro-[1,1'-biphenyl]-2-ol (35). R_f = 0.5 (ethyl acetate: hexane 1:9), yellow solid,yield 137 mg (55%), Mp 108-109 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ7.89 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.22-7.19 (m, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.37 (bs, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 149.3, 133.2, 132.5, 131.4, 129.53, 129.50, 129.0, 126.7, 125.9, 124.4, 116.9; HRMS (ESI) *m/z* calcd for $C_{12}H_8ClNO_3$ [M-H] 248.0114, found 248.0086.

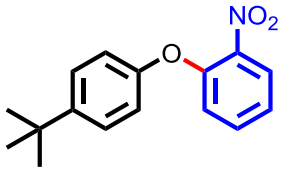


36

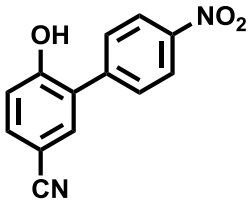


5-(*tert*-Butyl)-2'-nitro-[1,1'-biphenyl]-2-ol (36). R_f = 0.5 (ethyl acetate: hexane 1:9), yellow solid, yield 165 mg (61%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.1, 1.0Hz, 1H), 7.64 (dt, J = 7.5, 1.0Hz, 1H), 7.50-7.44 (m, 2H), 7.27 (dd, J = 8.4, 2.4Hz, 1H), 7.21 (d, J = 2.4Hz, 1H), 6.75 (d, J = 8.4Hz, 1H), 4.97 (s, 1H), 1.31(s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 149.7,

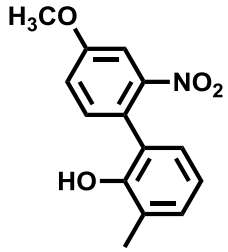
144.1, 133.1, 132.8, 132.7, 128.3, 126.8, 126.7, 124.2, 124.1, 115.2, 34.2, 31.5; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO_3$ [M+Na] 294.1106, found 294.1112.



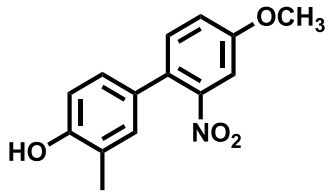
1-(4-(*tert*-Butyl)phenoxy)-2-nitrobenzene. First Fraction, R_f 0.5 (hexane), yellow solid**,** yield 30 mg (11%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 1.6Hz, 1H), 7.46 (dt, J = 7.1, 1.6 Hz, 1H), 7.38 (d, 8.7Hz, 2H), 7.14 (dt, J = 8.2, 1.1Hz,1H), 6.98 (t, J = 8.6Hz, 3H), 1.32 (s, 9H). (reference: Hui, X.; Fei, Y.; Ling, D. H.; *Chin. J. Chem.* **2008**, *26*, 1465.)



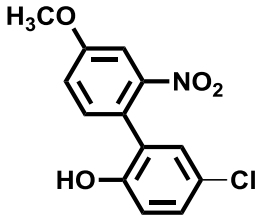
6-Hydroxy-4'-nitro-[1,1'-biphenyl]-3-carbonitrile (37). Rf = 0.5 (ethyl acetate: hexane 2:8) yellow solid, yield 146 mg (61%), Mp 198-199 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (bs, 1H), 8.24 (d, J = 8.7 Hz, 2H), 7.85-7.82 (m, 3H), 6.69 (dd, J = 8.5, 2.1 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 5.71 (CH_2Cl_2), 3.30 (H_2O), 2.46 (DMSO), ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 146.9, 143.6, 135.2, 134.7, 130.9, 127.1, 123.6, 119.5, 117.7, 102.4; HRMS (ESI) *m/z* calcd for $C_{13}H_8N_2O_3$[M-H^+] 239.0451, found 239.0424.



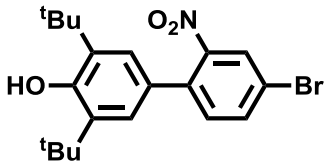
4'-Methoxy-3-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (38). R_f = 0.54 (ethyl acetate: hexane, 2:8); yellow solid, yield 44 mg (17%), Mp 78-79 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 2.6Hz, 1H), 7.31 (d, J = 8.4Hz, 1H), 7.17 (dd, J = 8.4, 2.6Hz, 1H), 7.13 (d, J = 7.5Hz, 1H), 6.99(d, J = 8.1Hz, 1H), 6.89 (t, J = 7.3Hz, 1H), 4.74 (bs, 1H), 3.89 (s, 3H), 2.21 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 150.9, 150.3, 133.6, 131.0, 127.7, 124.5, 124.4, 123.7, 120.7, 119.2, 109.3, 55.9, 15.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{14}NO_4$ [M+Na] 282.0742, found 282.0738.



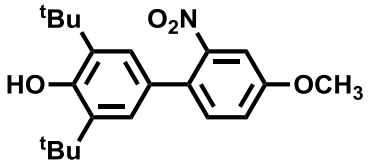
4'-Methoxy-3-methyl-2'-nitro-[1,1'-biphenyl]-4-ol (39). R_f = 0.5 (ethyl acetate: hexane, 2:8), yellow solid, yield 134 mg (52%), Mp 102-103 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 1.7Hz, 1H), 7.28 (d, J = 8.6Hz, 1H), 7.10 (dd, J = 8.6, 1.7Hz, 1H), 7.02(d, J = 1.9Hz, 1H), 6.96 (dd, J = 8.1, 1.9Hz, 1H), 6.75 (d, J = 8.1Hz, 1H), 5.28 (s, 1H), 3.87 (s, 3H), 2.24 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.8, 149.6, 132.6, 130.6, 129.5, 128.4, 126.7, 124.3, 118.6, 115.2, 108.8, 55.9, 15.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_4$ [M+Na] 282.0742, found 282.0731.



5-Chloro-4'-methoxy-2'-nitro-[1,1'-biphenyl]-2-ol (40). R_f = 0.5(ethylacetate: hexane 2:8), yellow solid,yield: 142 mg (51%), Mp 130-131 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 2.6Hz, 1H), 7.29 (d, J = 8.6Hz, 1H), 7.20 (m, 1H), 7.18-7.16(m, 2H), 6.76(dd, J = 8.4Hz, 0.5Hz, 1H), 5.16 (bs, 1H), 3.90(s, 3H),^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 151.3, 149.9, 133.4, 129.6, 129.2, 126.6, 125.8, 123.2, 119.4, 116.8, 109.5, 56.0; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClNO_3$ [M+Na] 302.0196, found 302.0182.

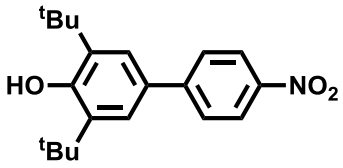


4'-Bromo-3,5-di-tert-butyl-2'-nitro-[1,1'-biphenyl]-4-ol (41). 0.5 (hexane), yellow solid, yield 203 mg (50%), Mp 138-139 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 1.9 Hz, 1H), 7.67 (dd, J = 8.3, 1.9 Hz, 1H), 7.32 (d, J = 8.3, 1H), 7.07 (s, 2H), 5.33 (s, 1H), 1.42 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 149.9, 136.3, 135.6, 134.8, 133.1, 126.8, 126.6, 124.7, 120.2, 34.4, 30.2; HRMS (ESI) *m/z* calcd for $C_{20}H_{24}BrNO_3$ [M–H] 404.0861, found 404.0867.

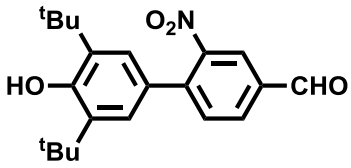


3,5-Di-tert-butyl-4'-methoxy-2'-nitro-[1,1'-biphenyl]-4-ol (42) 0.5 (ethyl acetate: hexane, 1:9), yellow solid, yield 250 mg (70%), Mp 84-85 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J =

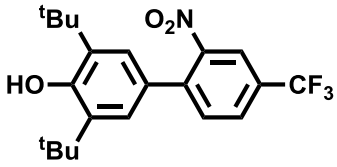
8.6Hz, 1H), 7.26 (d, J= 2.6Hz, 1H), 7.10 (dd, J = 8.6, 2.6 Hz, 1H), 7.08 (s, 2H), 5.27 (s, 1H), 3.87 (s, 3H), 1.43 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 153.8, 150.0, 136.1, 132.7, 129.1, 127.8, 124.8, 118.3, 108.6, 55.9, 34.4, 30.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{27}NO_4$ [M] 357.1940, found 357.1934.



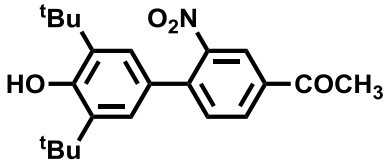
3,5-Di-tert-butyl-4'-nitro-[1,1'-biphenyl]-4-ol (43).[3] R_f = 0.56 (hexane), yellow solid, yield 196 mg (60%), Mp 138-139 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8Hz, 2H), 7.42 (s, 2H), 5.43(s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 148.6, 136.7, 130.1, 130.0, 127.2, 124.3, 124.0, 34.5, 30.2; LRMS (ESI) *m/z* 328.1 [M+H].



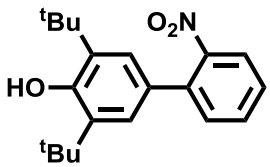
3',5'-Di-tert-butyl-4'-hydroxy-2-nitro-[1,1'-biphenyl]-4-carbaldehyde (44). Rf = 0.5 (ethyl acetate: hexane 2:8) yellow solid, yield 220 mg (62%), Mp 130-131 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.20 (d, J = 1.5Hz, 1H), 8.04 (dd, J = 8.1, 1.4Hz, 1H), 7.65 (d, J = 8.1Hz, 1H), 7.16 (s, 2H), 5.44 (s, 1H), 1.44 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 155.1, 150.1, 142.2, 136.6, 135.1, 132.7, 131.8, 126.7, 124.9, 124.8, 34.5, 30.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{25}NO_4$ [M+Na] 378.1681, found 378.1671.



3,5-Di-tert-butyl-2'-nitro-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (45).[4] R_f = 0.5 (hexane) yellow solid, yield 256 mg (65%), Mp 85-86 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.80 (d, J = 8.1Hz, 1H), 7.60 (d, J = 8.1Hz, 1H), 7.12 (s, 2H), 5.39 (s, 1H), 1.44 (s, 18H),^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 149.5, 140.2, 136.5, 132.6, 129.9, 129.6, 128.3(q, J = 3.6Hz), 126.5, 124.8, 124.1, 34.5, 30.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{24}F_3NO_3$ [M+Na] 418.1606, found 418.1614.

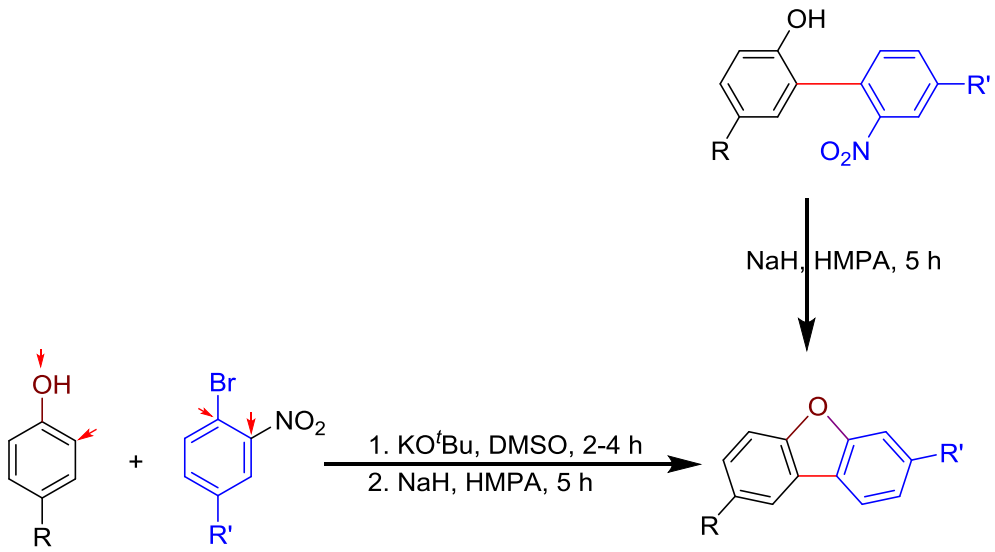


1-(3',5'-Di-tert-butyl-4'-hydroxy-2-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one (46). R_f = 0.6 (ethyl acetate: hexane 1:9), yellow solid, yield 370 mg (74%), Mp85-86^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 1.6Hz, 1H), 8.11 (dd, J = 8.1, 1.6Hz, 1H), 7.57 (d, J = 7.9Hz, 1H), 7.14 (s, 2H), 5.40 (s, 1H), 2.65 (s, 3H), 1.44 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 154.9, 149.8, 140.9, 136.5, 135.8, 132.2, 131.0, 126.8, 124.8, 123.8, 34.5, 30.2, 26.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{27}NO_4$ [M+Na] 392.1837, found 392.1809.



3,5-Di-tert-butyl-2'-nitro-[1,1'-biphenyl]-4-ol (47). 0.5 (hexane), yellow solid, yield 221 mg (68%), Mp 62-63 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0Hz, 1H), 7.55 (t, J = 7.5Hz, 1H), 7.46 (d, J = 7.8Hz, 1H), 7.40 (t, J = 8.1Hz, 1H), 7.13 (s, 2H), 5.32(s, 1H), 1.45 (s, 18H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.8, 136.7, 136.2, 131.9, 131.8, 127.9, 127.3, 124.8, 123.7, 34.4, 30.3; HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NO_3$ [M] 327.1834, found 327.1819.

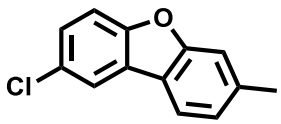
Scheme S2. Synthesis of Dibenzofurans



General Method for the Synthesis of Dibenzofurans from Nitrobiarylols: Hexamethyl phosphoramide, HMPA (1 mL) was added to a single neck flask (5 mL) containing stirrer bar. To this flask, compounds **1, 10, 36**, and **4** (0.5 mmol) and sodium hydride (42 mg, 1.0 mmol,

60% in mineral oil) was added, resulted reaction mixture was stirred at 80 ^{o}C. Progress of reaction was monitored by TLC. Upon completion, the reaction (4-6 h) was cooled to room temperature and poured into 3 N aqueous HCl solution, extracted four times with 15 mL of ethyl acetate. The combined organic layer was dried over Na_2SO_4, and filtered. The solvent was removed *in vacuum* and the residue was purified by column chromatography (silica gel, eluent: hexane/ ethyl acetate) to afford the dibenzofurnas **48-51**.

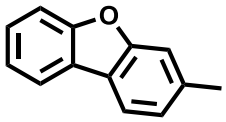
Synthesis of Dibenzofuran from *para*-Substituted Phenol and Bromonitrobenzene in One Pot. To a single neck flask, para-chloro phenol (154 mg, 1.2 mmol) and 1-bromo-4-methyl-2-nitrobenzene (216 mg, 1.0 mmol) were added in DMSO (2 mL) and resulted reaction mixture was stirred for 5 min at room temperature. After this, KO^{t}Bu (281 mg, 2.5 mmol) was added portion wise. After complete addition of KO^{t}Bu, the resulted reaction mixture stirred at room temperature. Progress of reaction was monitored by TLC. After completion of the reaction (2-4 h), HMPA (3mL) and sodium hydride (84 mg, 2.1 mmol, 60% in mineral oil) were added, resulted reaction mixture was stirred at 80 ^{o}C. Progress of reaction was monitored by TLC. Upon completion, the reaction (4-6 h) was cooled to room temperature and poured into 4N aqueous HCl solution, 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 vacuum* and the residue was purified by column chromatography (silica gel, eluent: hexane/ ethyl acetate) to afford the dibenzofurnas **48** (yield 48%), **50** (yield 56%), and **51** (yield 47%).



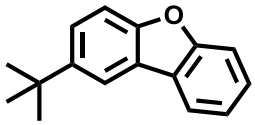
2-Chloro-7-methyldibenzo[b,d]furan (48).[5] R_f = 0.5 (hexane), white solid, yield 65 mg (60%), Mp 92-93 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 2.1HZ, 1H), 7.74 (d, J = 7.9Hz, 1H),

7.43 (d, J = 8.8Hz, 1H), 7.36-7.33 (m, 2H), 7.5 (d, J = 7.9Hz, 1H), 2.51 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.5, 138.6, 128.1, 126.5, 125.8, 124.3, 120.8, 120.3, 120.2, 112.5, 112.1, 22.0.

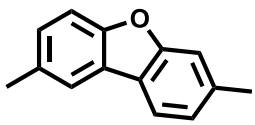
48) LRMS (ESI) m/z 217.0.



3-Methyldibenzo[b,d]furan (49).[6] R_f = 0.5 (hexane), white solid, yield, 64 mg (70%); Mp 63-64 ^{o}C (62-63)[6], ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6Hz, 1H), 7.83 (d, J = 7.8Hz, 1H), 7.58 (d, J = 8.2Hz, 1H), 7.44 (t, J = 7.5Hz, 1H), 7.40 (s, 1H), 7.34 (t, J = 7.4Hz, 1H), 7.18 (d, J = 7.8Hz, 1H), 2.54(s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.2, 137.7, 126.6, 124.4, 124.0, 122.6, 121.7, 120.4, 120.2, 112.0, 111.6, 22.0. LRMS (ESI) m/z 183.1 ($M + H^+$).

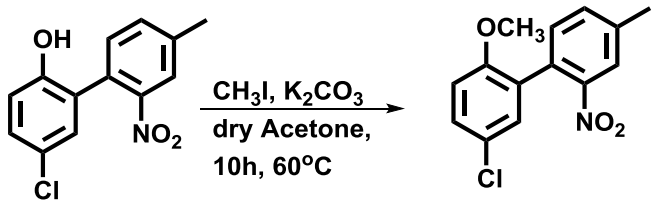


2-(*tert*-Butyl)dibenzo[b,d]furan (50).[7] R_f = 0.6 (hexane), white solid, yield 90 mg (80%), Mp 55-56 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.96 (m, 2H), 7.56 (d, J = 8.3Hz, 1H), 7.52-7.50 (m, 2H), 7.44 (dt, J = 7.1, 1.0Hz, 1H), 7.33 (t, J = 7.4, 1Hz, 1H), 1.44 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.4, 145.9, 126.8, 124.9, 124.6, 123.8, 122.5, 120.5, 116.9, 111.6, 110.9, 34.8, 31.9. LRMS (ESI) m/z 225.1 ($M + H^+$).



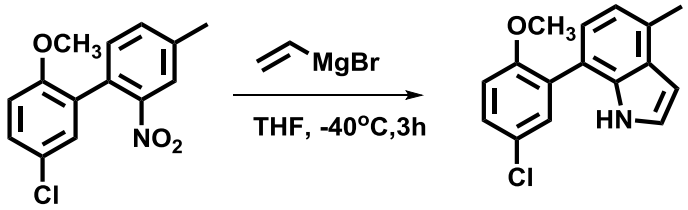
2,7-Dimethyldibenzo[b,d]furan (51).[8] 0.6 (hexane), white solid, yield 69 mg (70%), Mp 72-73 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8Hz, 1H), 7.69 (s, 1H), 7.42 (d, J = 8.4Hz, 1H), 7.35 (s, 1H), 7.22 (d, J = 8.3Hz, 1H), 7.14 (d, J = 7.8Hz, 1H), 2.52 (s, 3H), 2.50 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 154.5, 137.5, 132.1, 127.6, 124.3, 123.8, 121.7, 120.4, 120.1, 111.9, 111.0, 22.0, 21.4. LRMS (ESI) m/z 197.0 ($M + H^+$).

Preparation of Biaryl Indole 52



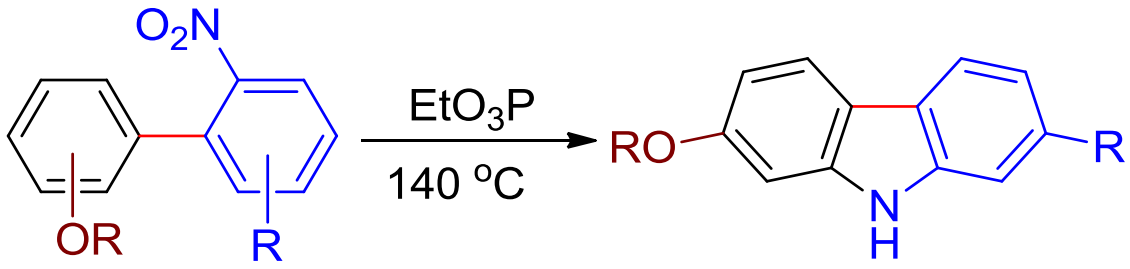
Preparation of 5'-Chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl from 5-Chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol (10). To a single neck flask, 5-Chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **10** (1 mmol, 265 mg), methyl iodide (5 mmol, 713mg), and potassium carbonate (8 mmol, 1.11 g) were added in dry acetone (10 mL) and resulted reaction mixture was stirred for 10 hours at 60 ^{o}C temperature. Progress of reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and poured into water, 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 vacuum* and the residue was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate) to afford 5'-Chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl. Rf = 0.4 (hexane: ethyl acetate 9:1), yellow solid, yield:253 mg (91%), Mp 125-126 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.29(dd, J = 8.6, 2.6Hz, 1H), 7.26 – 7.23 (m, 2H), 6.80 (d, J = 8.6Hz, 1H), 3.66 (s, 3H), 2.45 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 149.2, 139.2, 133.6, 132.1, 129.4, 129.1, 128.9,

128.8, 125.9, 124.4, 111.8, 55.5, 20.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{12}ClNO_3$ [M+H] 278.0584, found 278.0564.

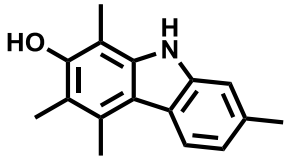


Synthesis of 7-(5-Chloro-2-methoxyphenyl)-4-methyl-1H-indole (52) from 5'-Chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl. 5'-Chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl (138 mg, 0.5 mmol) was dissolved in THF (5 mL) and the solution cooled to –40 ^{o}C. Then vinylmagnesium bromide (1.6 mL, 1.0 M in THF, 3.0 equiv) was added dropwise over 15 min. After completion of the addition, the reaction mixture was stirred at –40 ^{o}C. The progress of reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with ethyl acetate (3×15 mL), the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane: ethyl acetate) to give the substituted indole **52** with 45% yield. Rf: 0.4 (hexane: ethyl acetate 8:2), solid, yield 61 mg (45%), Mp 110-111 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (bs, 1H), 7.43 (d, J = 2.7Hz, 1H), 7.34 (dd, J = 8.8, 2.6Hz, 1H), 7.19 (t, J = 2.6Hz, 1H), 7.12 (d, J = 7.3Hz, 1H), 7.02 (d, J 7.4Hz, 1H), 6.98 (d, J = 8.8Hz, 1H), 6.63-6.62 (m, 1H), 3.77 (s, 3H), 2.63 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 133.8, 131.5, 130.3, 130.0, 128.3, 127.9, 126.2, 123.8, 123.4, 120.2, 118.9, 113.0, 101.2, 56.3, 18.8. HRMS (ESI) m/z calcd. for $C_{16}H_{14}ClNO$ [M+H] 208.0842, found 208.0848.

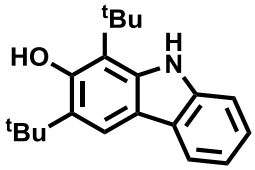
General Method for the Synthesis of Carbazoles



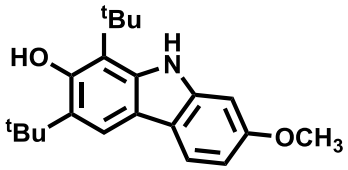
Triethyl phosphite $P(OC_2H_5)_3$ (1 mL) was added to a sealed tube (10 mL) containing stirrer bar. To this, compound **27** (0.5 mmol) was added and resulted reaction mixture was stirred at 140 ^oC. Progress of reaction was monitored by TLC. Upon completion of the reaction (24-28 h), the mixture was cooled to room temperature, poured into 5N HCl and extracted four times with 15 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).



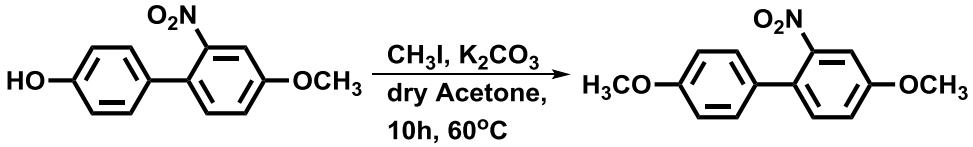
1,3,4,7-Tetramethyl-9H-carbazol-2-ol (52). R_f = 0.5 (hexane: ethyl acetate 8:2), reddish liquid, yield 62 mg (52%), Mp 157-158 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1Hz, 1H), 7.68 (s, 1H), 7.19 (s, 1H), 7.00 (d, J = 8.1Hz, 1H), 4.73 (s, 1H), 2.76 (s, 3H), 2.49 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 140.2, 138.0, 133.8, 129.1, 122.6, 121.5, 120.7, 115.8, 114.2, 1110.4, 101.6, 21.8, 16.7, 11.8, 10.1; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}NO$ [M+H] 240.1388, found 240.1383.



1,3-Di-tert-butyl-9H-carbazol-2-ol (54). R_f = 0.3 (hexane), brown viscous solid, yield: 81 mg (55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.96 (d, J = 7.7Hz, 1H), 7.89 (s, 1H), 7.35 (d, J = 7.6Hz, 1H), 7.30 (d, J = 7.9Hz, 1H), 7.16 (t, J = 7.2Hz, 1H), 5.46 (s, 1H), 1.77 (s, 9H), 1.57 (s, 9H),^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 139.1, 137.3, 129.6, 124.3, 123.3, 119.1, 118.7, 117.7, 117.6, 115.9, 109.9, 36.8, 34.3, 31.6, 30.8; HRMS (ESI) *m/z* calcd for $C_{20}H_{25}NO$ [M+H] 296.2014, found 296.2016.

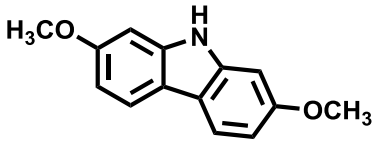


1,3-Di-tert-butyl-7-methoxy-9H-carbazol-2-ol (55). R_f = 0.3 (hexane), brown viscous liquid, yield 92 mg (57%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.80 (d, J = 8.5Hz, 1H), 7.78 (s, 1H), 6.87 (d, J = 1.9Hz, 1H), 6.78 (dd, J = 8.5, 1.2 Hz, 1H), 5.35 (s, 1H), 3.88 (s, 3H), 1.75 (s, 9H), 1.55 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 152.3, 140.3, 137.1, 129.5, 119.4, 117.4, 117.8, 117.2, 115.1, 107.6, 94.4, 55.6, 36.8, 34.3, 31.6, 30.8.



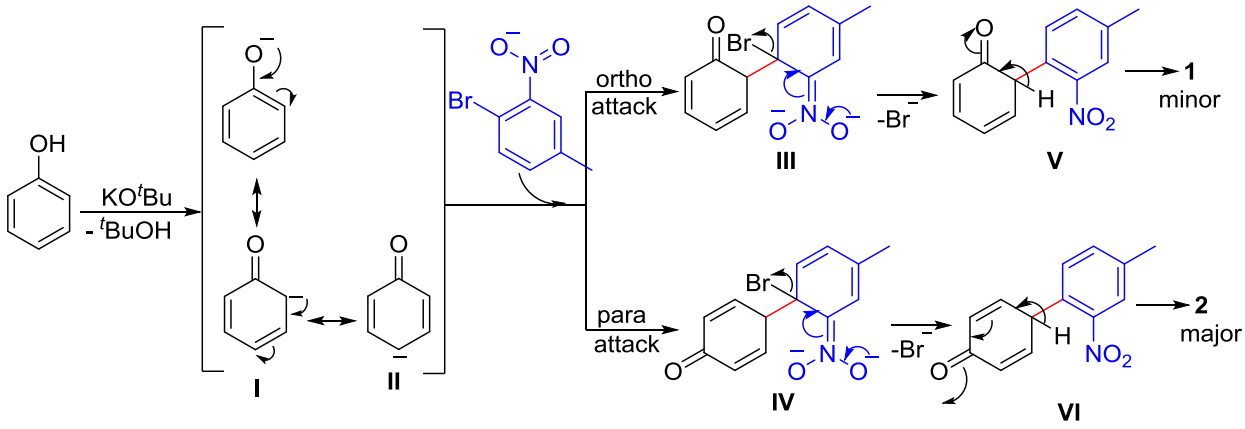
4,4'-Dimethoxy-2-nitro-1,1'-biphenyl (Substrate for 56).[9] This substrate was synthesized by following procedure as described above for the substrate of **52**. R_f 0.4 (hexane: ethyl acetate 9:1),

yellow solid, yield 123 mg (95%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.19 (d, J = 8.6Hz, 2H), 7.11 (dd, J = 8.7, 2.5Hz, 1H), 6.92 (d, J = 8.6Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 158.8, 149.7, 132.8, 129.4, 129.2, 128.2, 118.6, 114.1, 108.9, 55.9, 55.3. LRMS (ESI) m/z 260.1 (M+H).



2,7-Dimethoxy-9H-carbazole (56)[9] from 4,4'-Dimethoxy-2-nitro-1,1'-biphenyl. Rf = 0.4 (hexane: ethyl acetate 8:2), brown solid, yield, 68 mg (60%), Mp 231-232°C (229-230)[9], ^{1}H NMR (400 MHz, Acetone) δ 10.02 (bs, 1H), 7.82 (d, J = 8.5Hz, 2H), 6.96 (d, J = 2.1Hz, 2H), 6.74 (dd, J = 8.5, 2.1Hz, 2Hz), 3.82 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5(Acetone), 163.8, 146.4, 122.4, 122.2, 112.7, 99.9, 60.0, 34.1 (septet).

Scheme S3. Mechanism for C-H Arylation of Phenol



To understand the mechanistic part of the reaction, several control experiments were carried out. 2-Nitrobromobenzene with phenol gave exclusively C-O coupled diaryl ether when reaction was performed in anhydrous DMSO at 45-50 °C.[10,11] Reactions in DMSO (2% H_2O) gave biaryls as

the major the product at 25 ^{o}C.[12] Contrarily, nitroaryl bromide substituted with electron rich CH_3 or OCH_3 group gave exclusively nitrobiarylols under both anhydrous or hydrous conditions. Next, reactions of fluoro, chloro, and iodonitrobenzenes were tested with phenol under optimized reaction conditions. Iodonitrobenzene afforeded only deiodinated nitrobenzene. Fluoro and chloro-nitrobenzenes noticed to be poorly reactive and gave 5, 10% yield, respectively, of nitrobiarylol **31**. Based on the above experiments, and regioselectivity in the synthesized nitro-biarylols, a plausible mechanism has been depicted in Scheme 2. The reaction seems following a traditional nucleophilic aromatic substitution S_NAr pathway. Worth mentioning, although, S_NAr has been established more than100 years ago, however, its use in the biaryl coupling reactions has not been established under mild conditions.[3] Here, the addition of KO^{t}Bu to phenol generates a phenoxide ion, which subsequently gave carboanion **I** and **II**. The addition of **I** and **II** bromonitroarene to lead to intermediates **III** and **IV**, respectively. Nitro group in these intermediates facilitates the elimination of bromide ion to form arylated species **V** and **VI**, which undergo rearomatization to give desired nitro-biaryl-ols**1** and **2**.

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

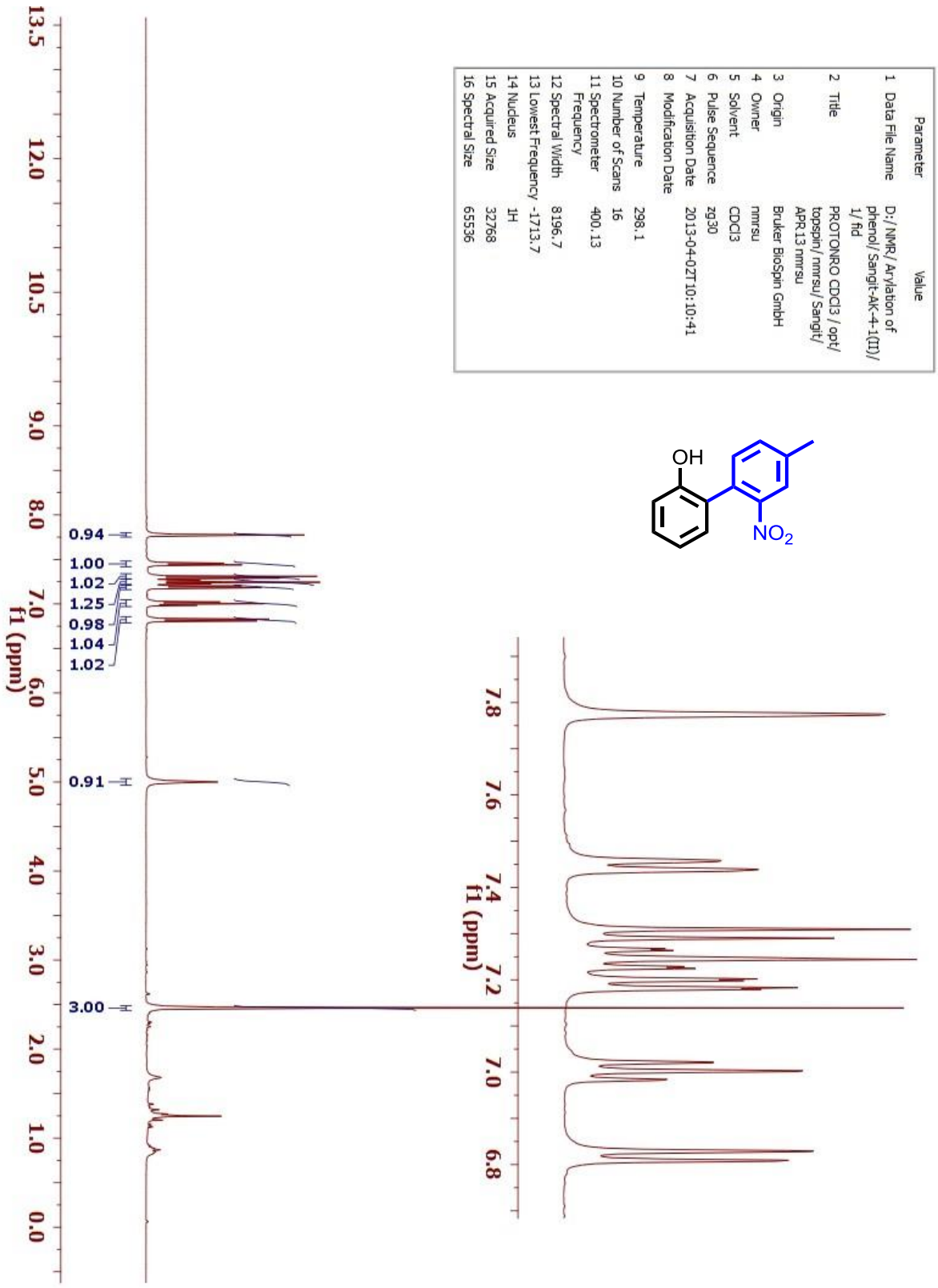


Figure S2 ^{13}C NMR spectrum of 1

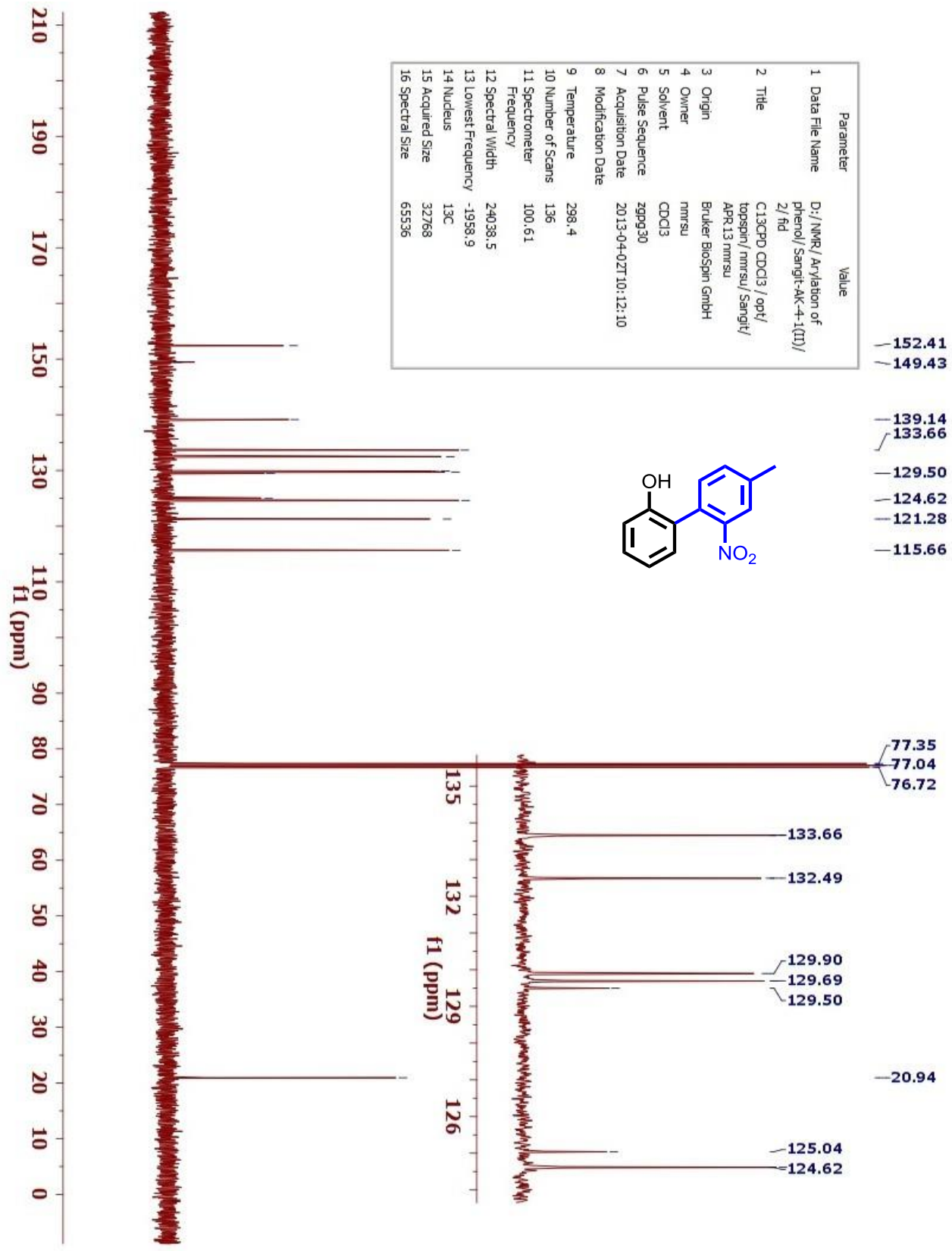


Figure S3 ^{1}H NMR spectrum of **2**

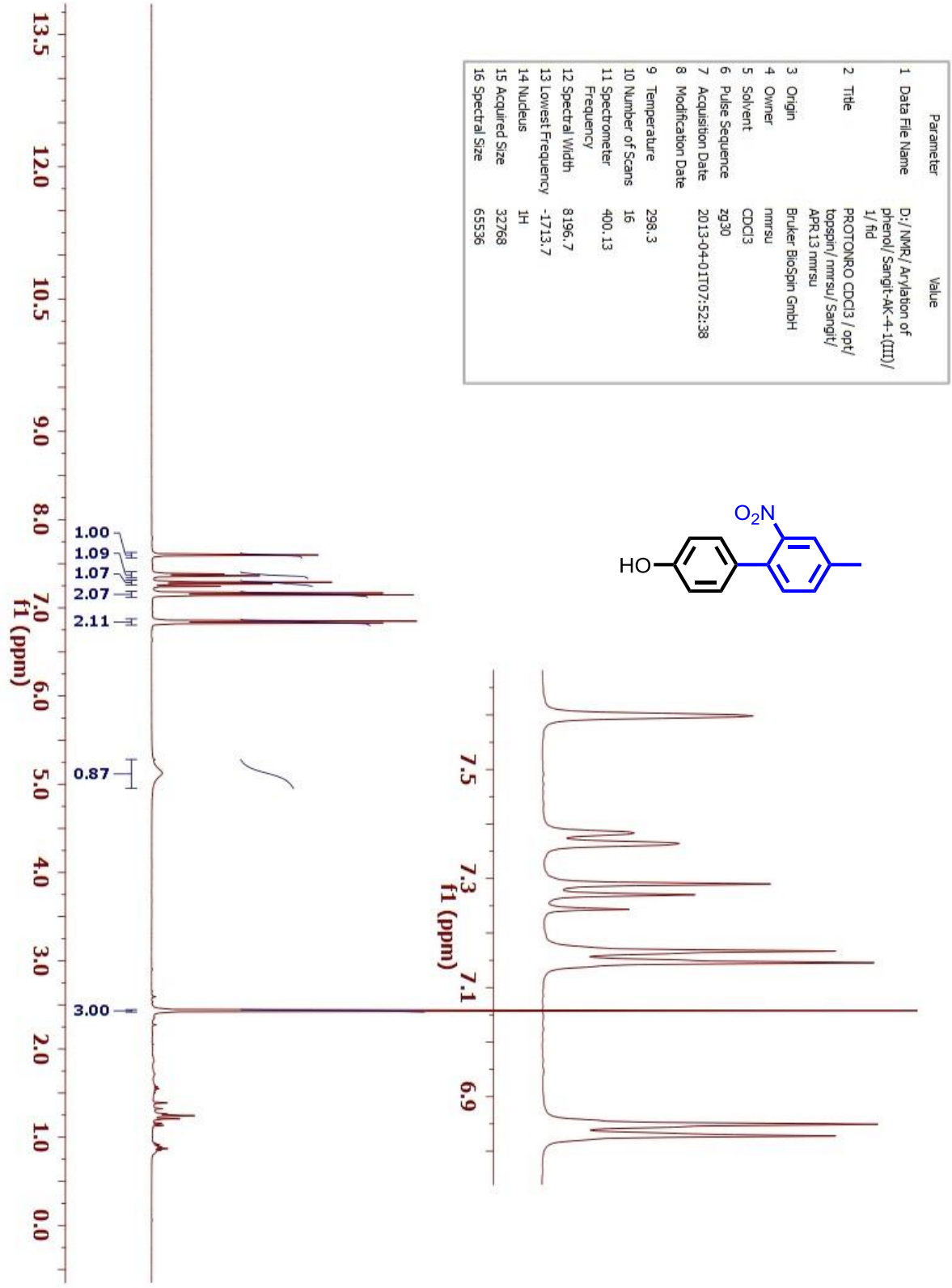


Figure S4 ^{13}C NMR spectrum of **2**

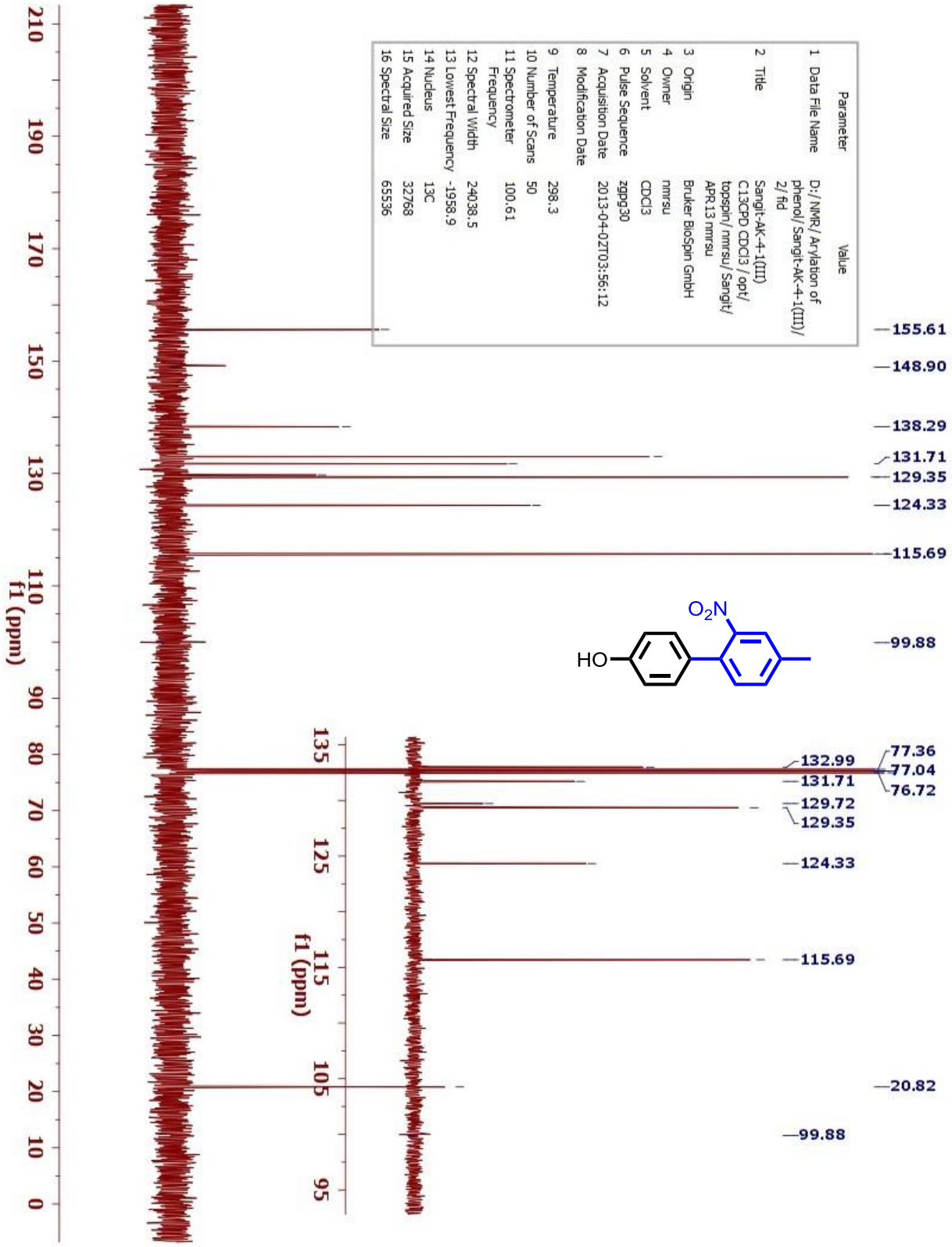


Figure S5 ^{1}H NMR spectrum of **3**

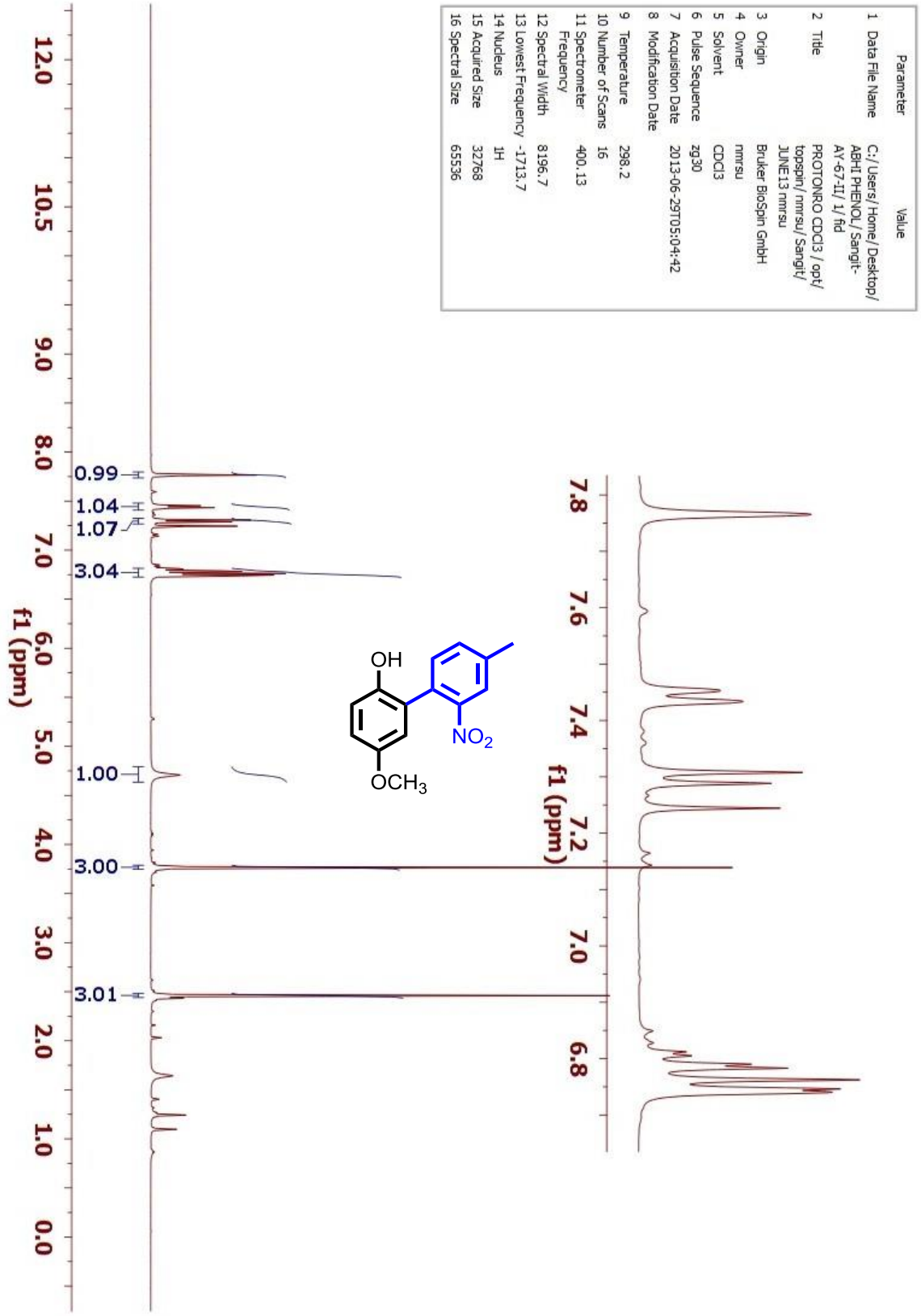


Figure S6 ^{13}C NMR spectrum of **3**

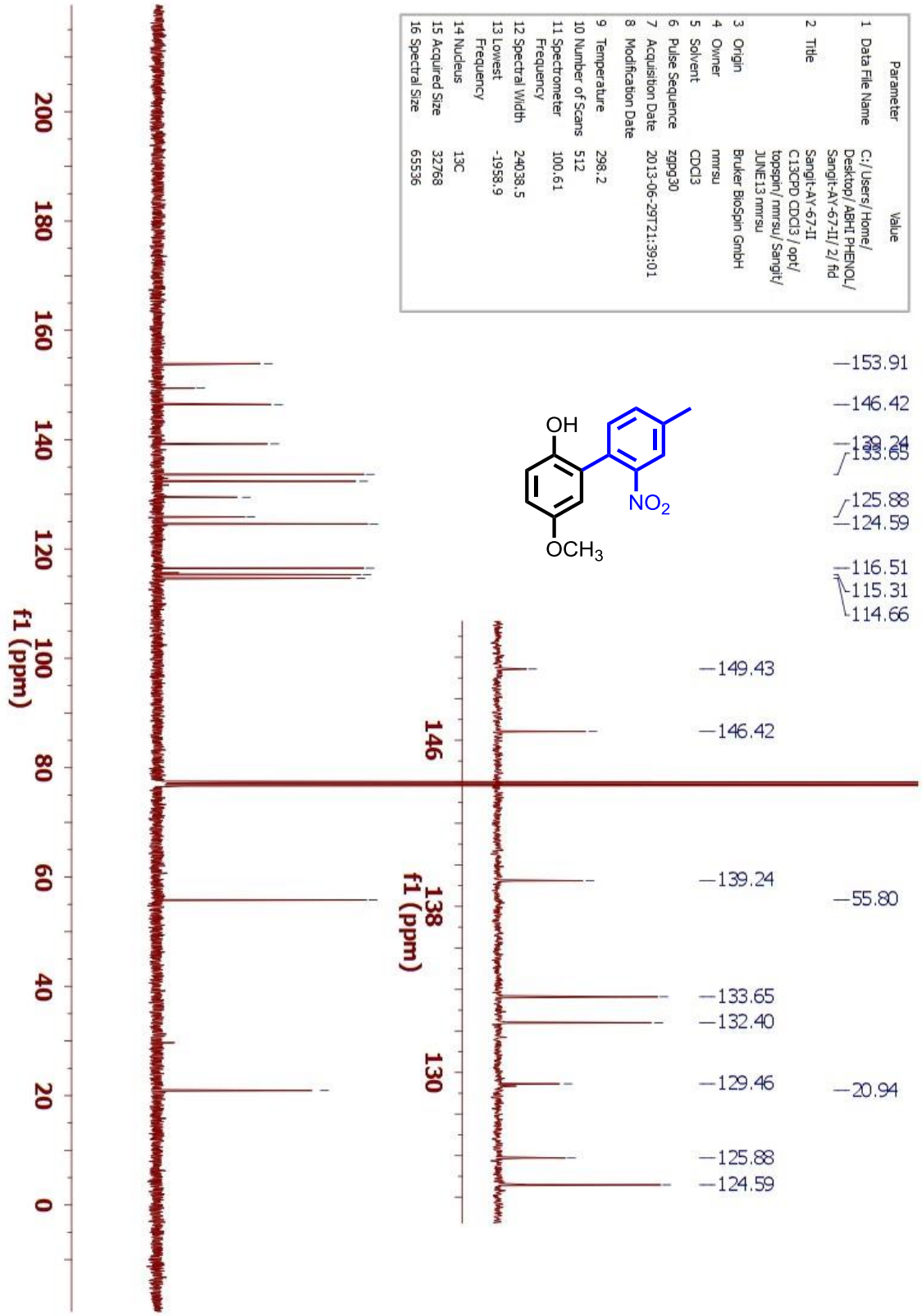


Figure S7 ^{1}H NMR spectrum of **4**

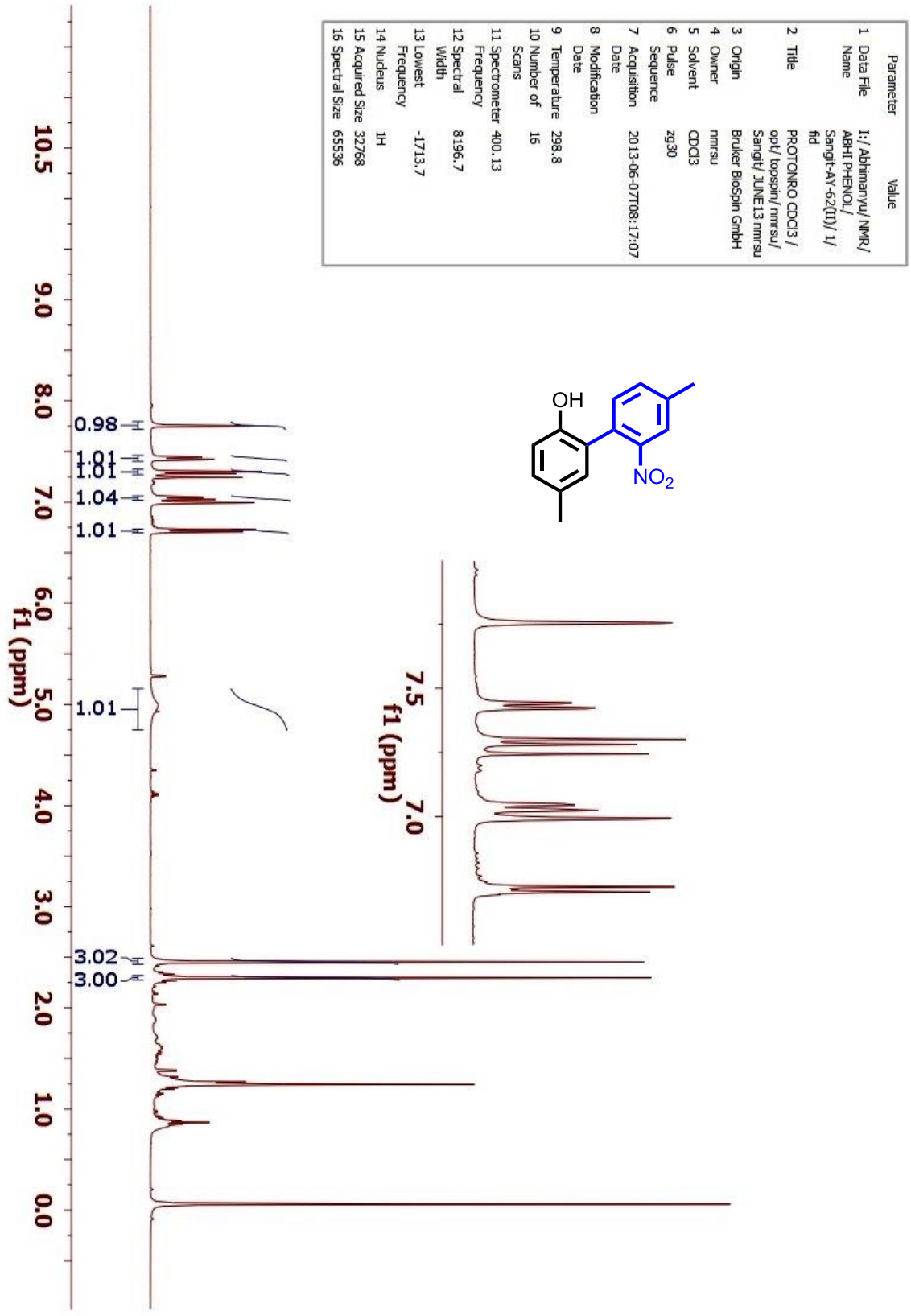


Figure S8 ^{13}C NMR spectrum of **4**

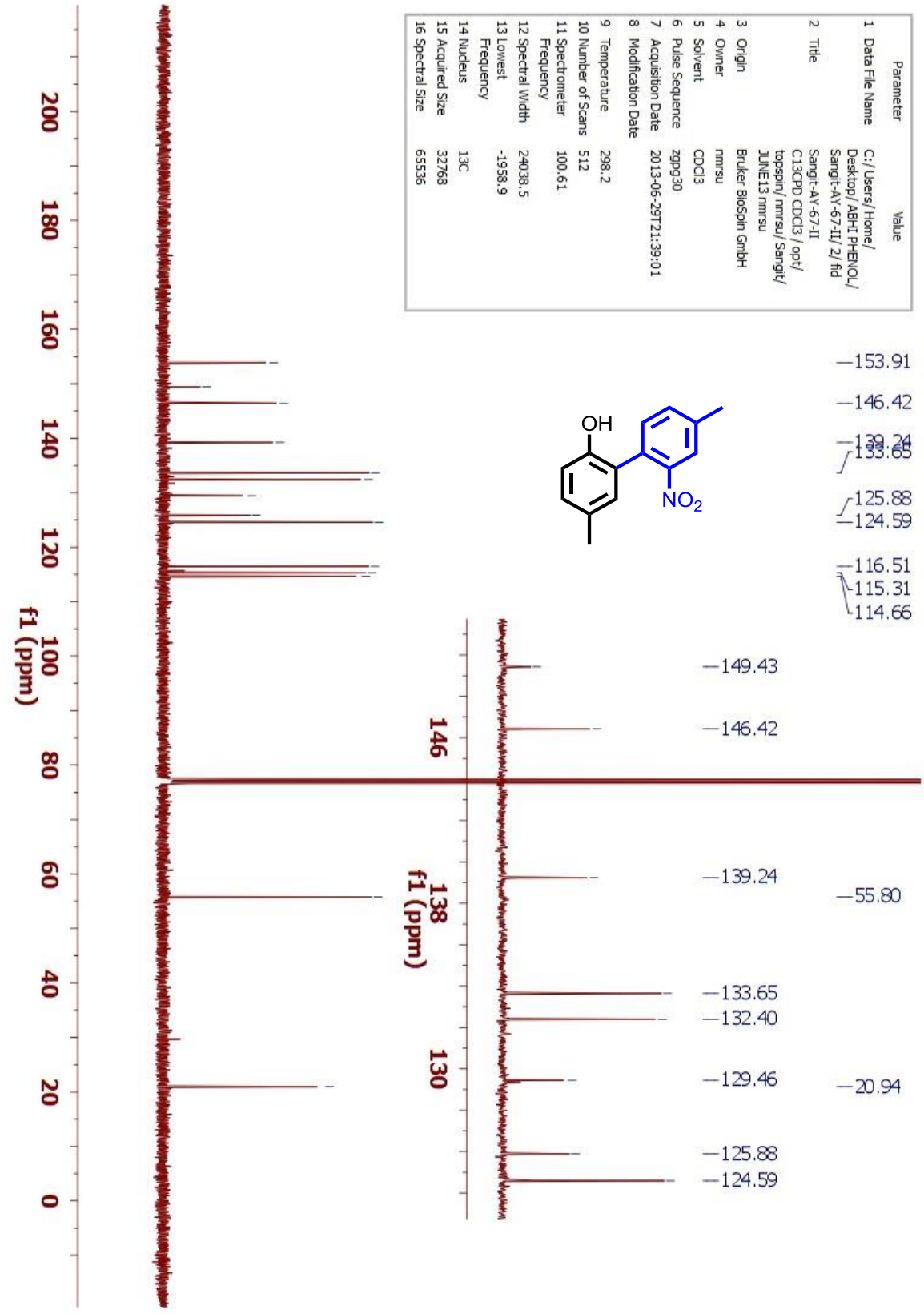


Figure S9 ^{1}H NMR spectrum of **5**

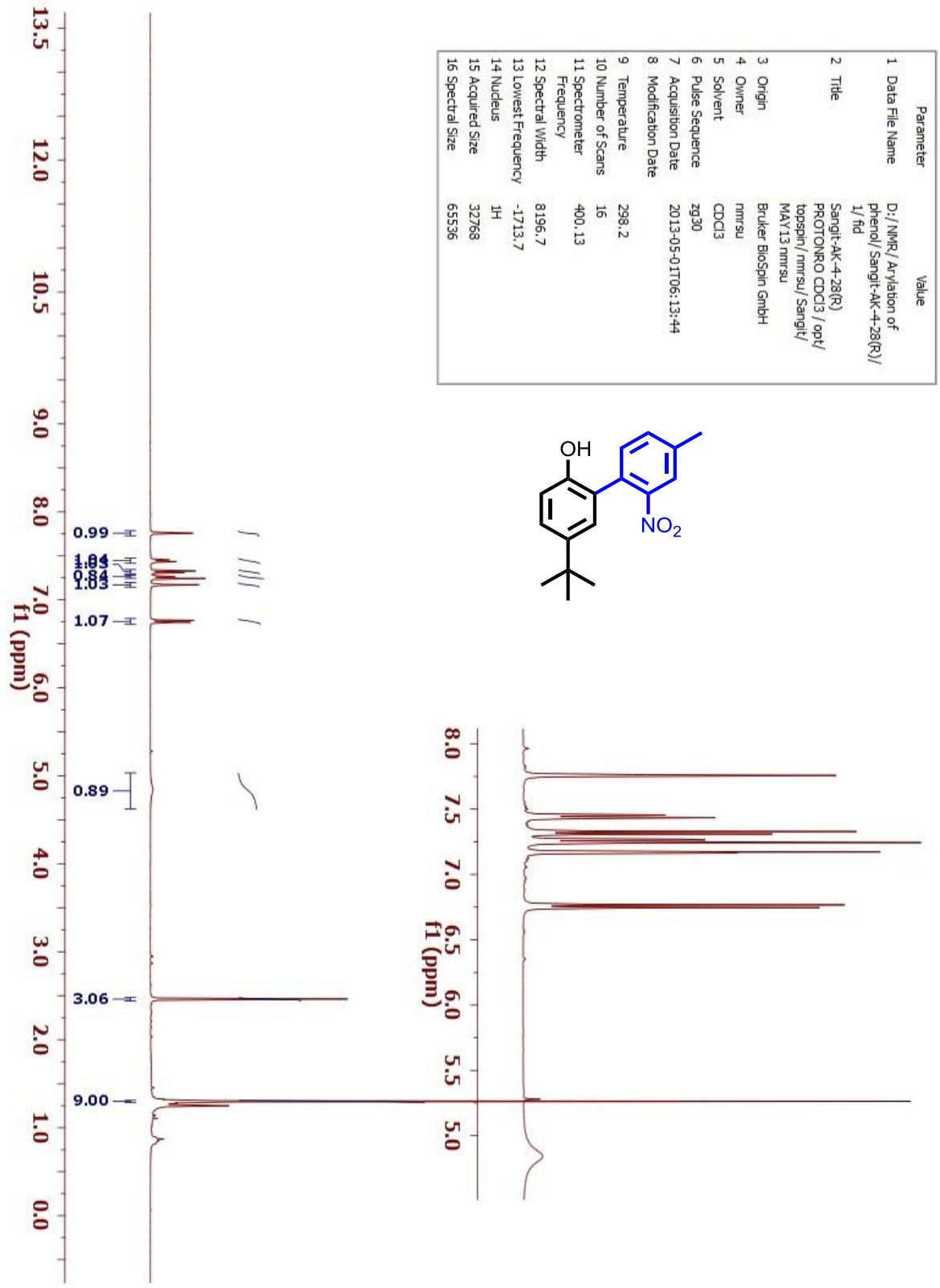


Figure S10 ^{13}C NMR spectrum of **5**

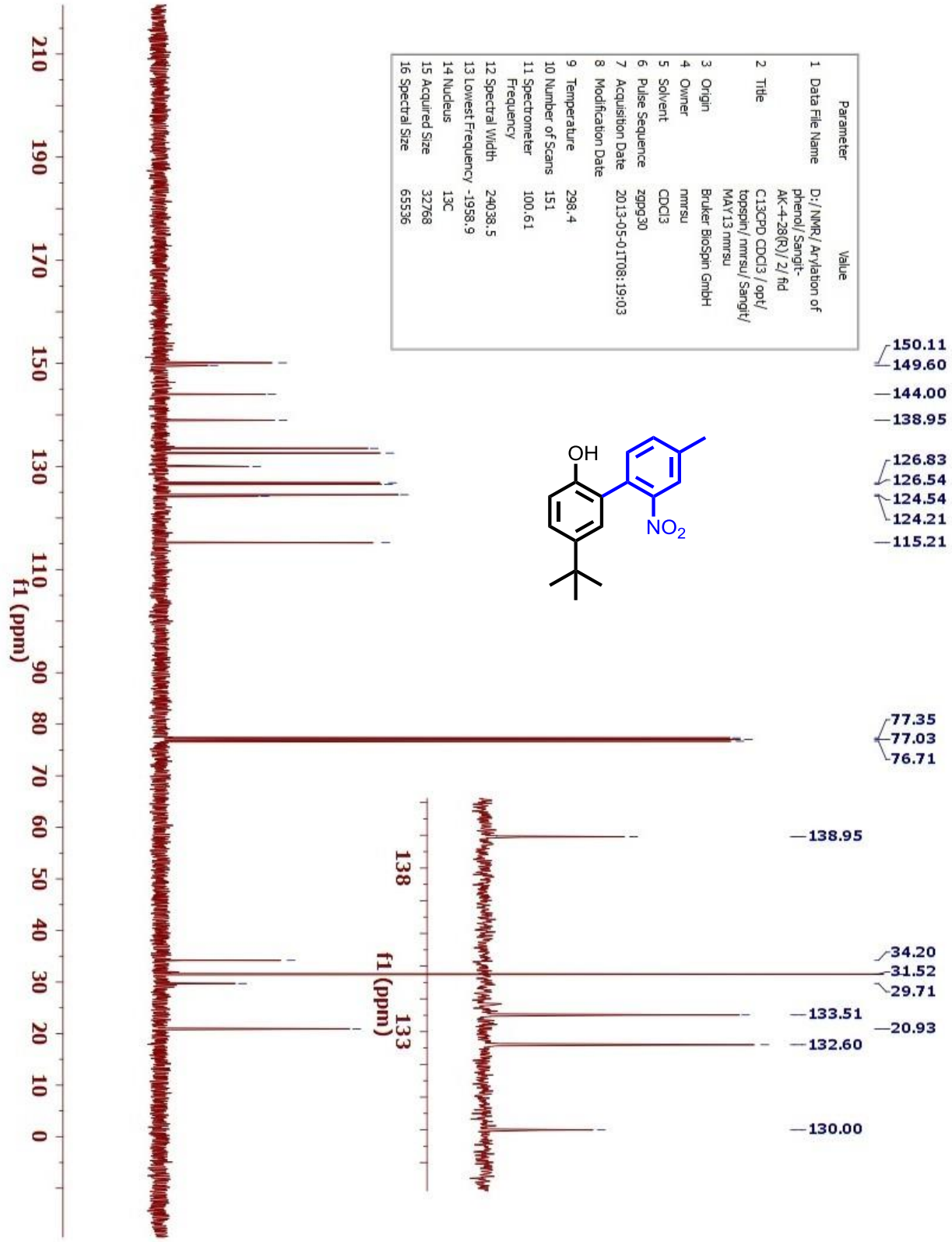


Figure S11 ^{1}H NMR spectrum of **6**

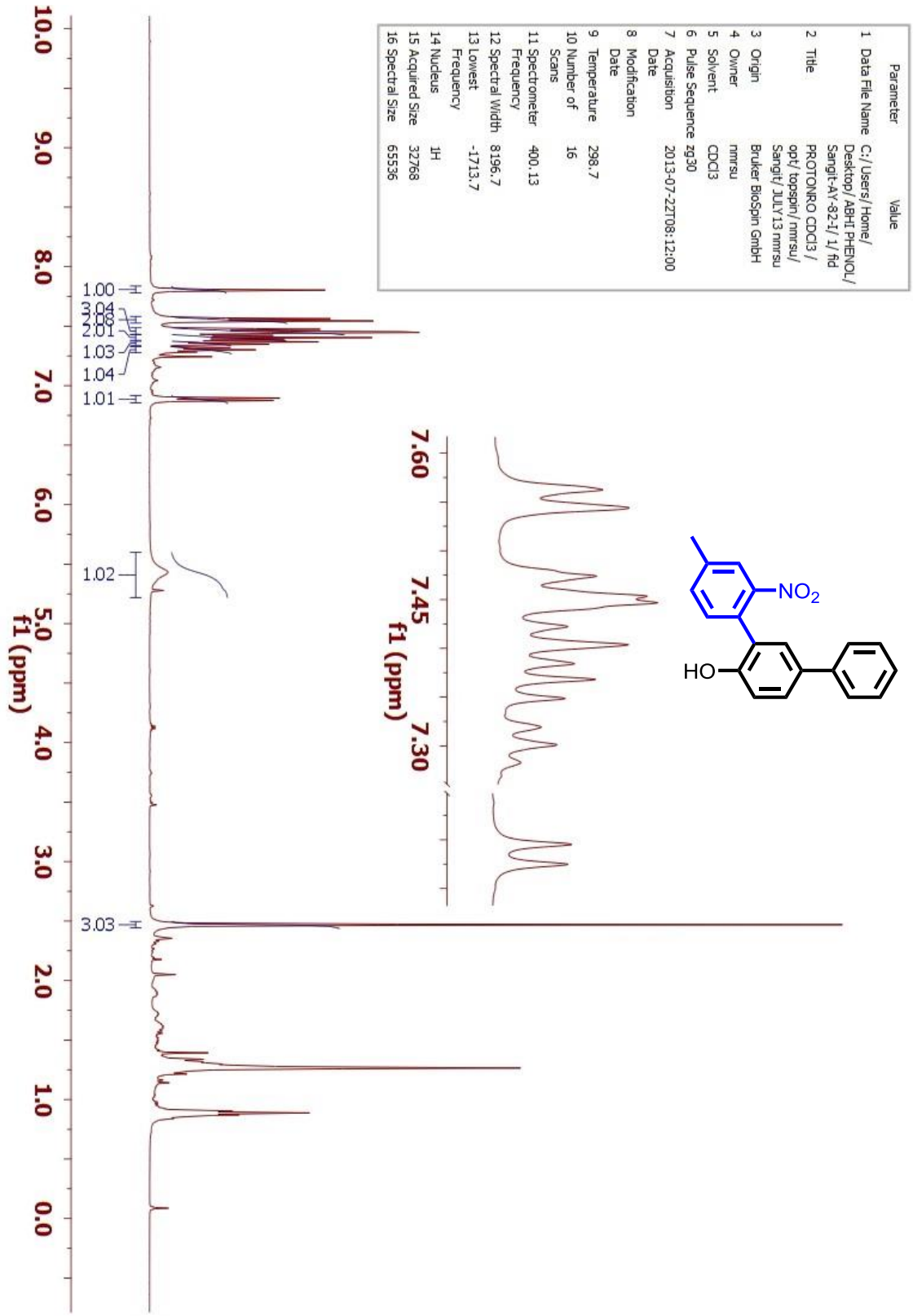


Figure S12 ^{13}C NMR spectrum of **6**

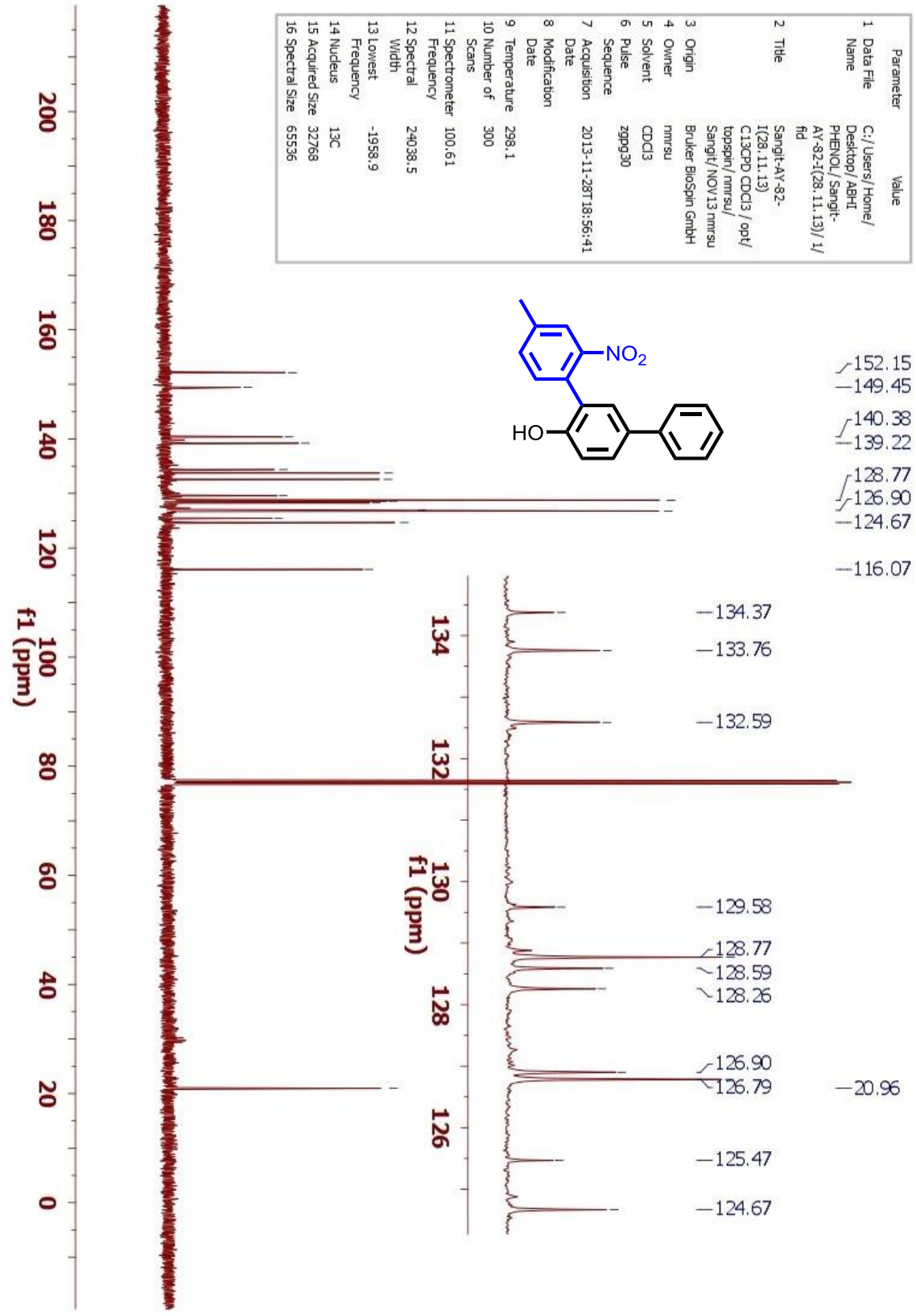


Figure S13 ^{1}H NMR spectrum of **7**

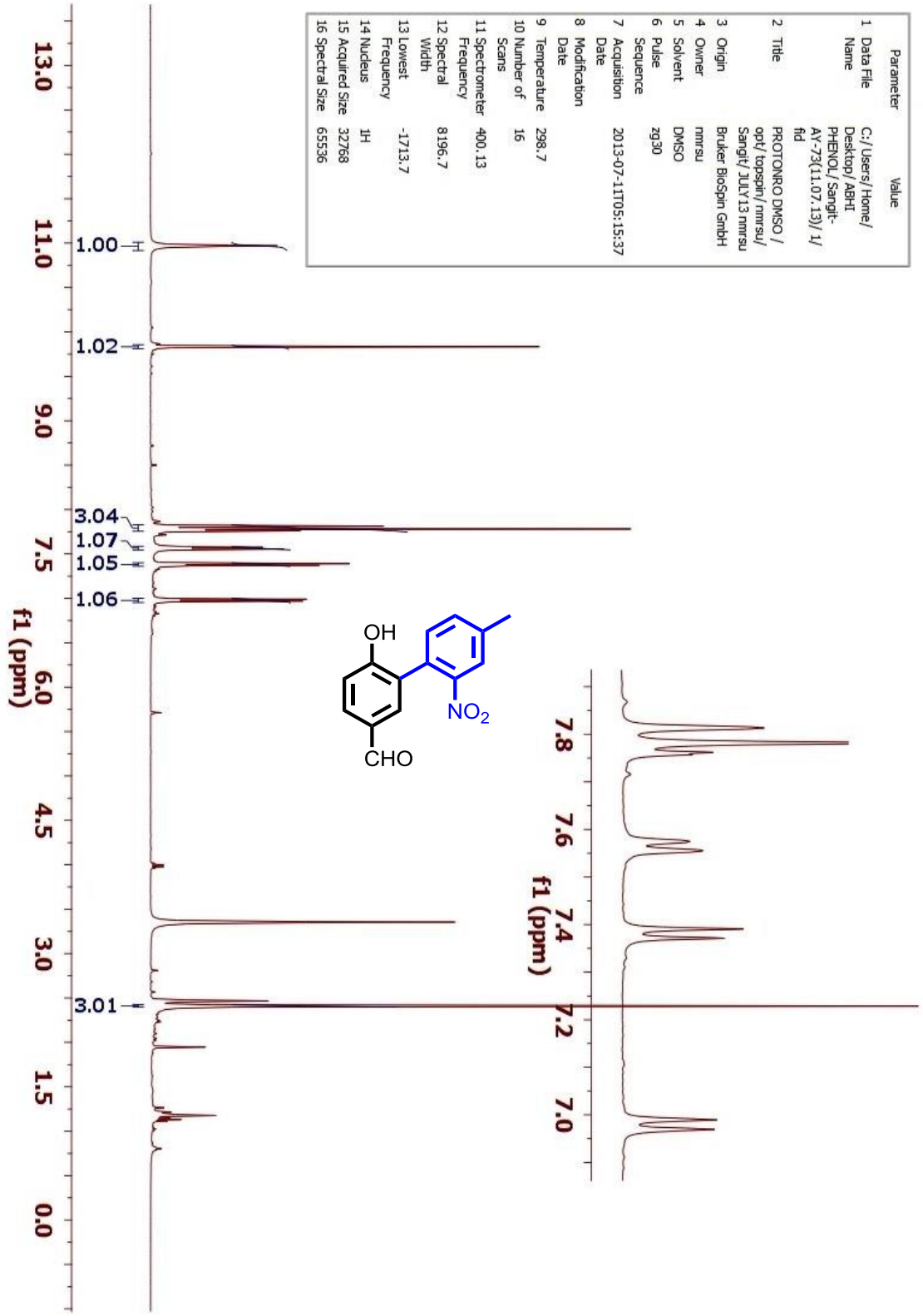


Figure S14 ^{13}C NMR spectrum of **7**

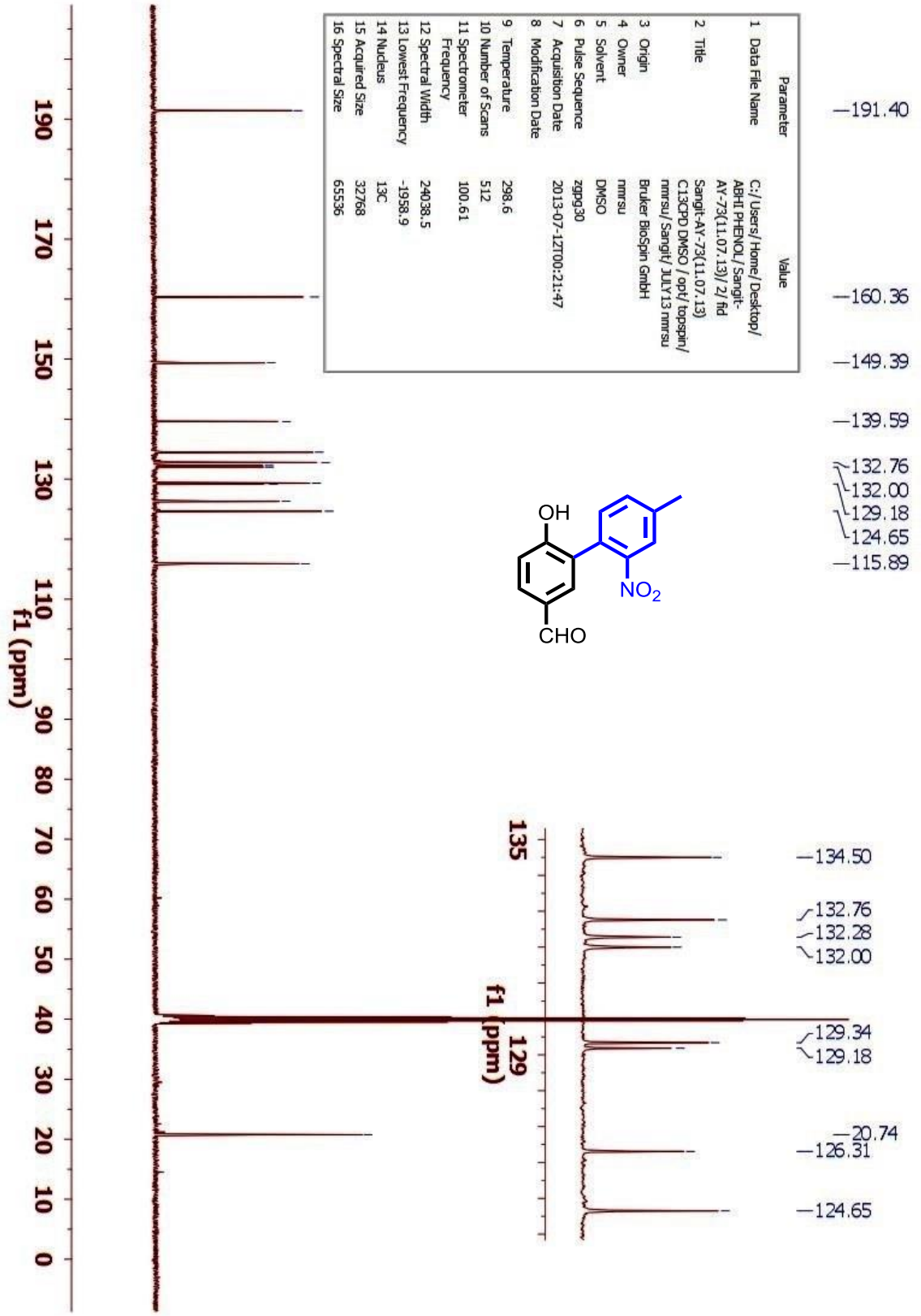


Figure S15 ^{1}H NMR spectrum of **8**

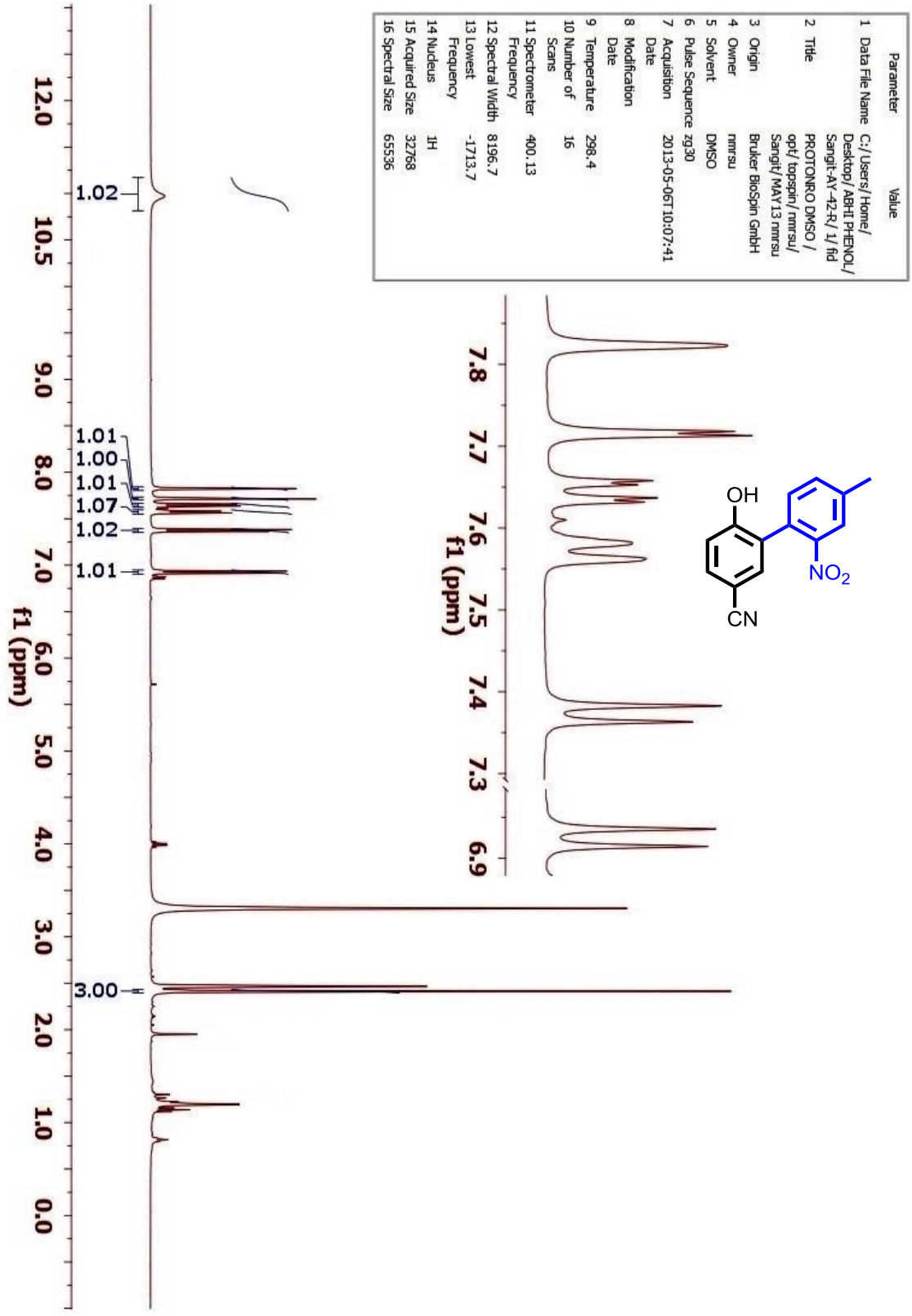


Figure S16 ^{13}C NMR spectrum of **8**

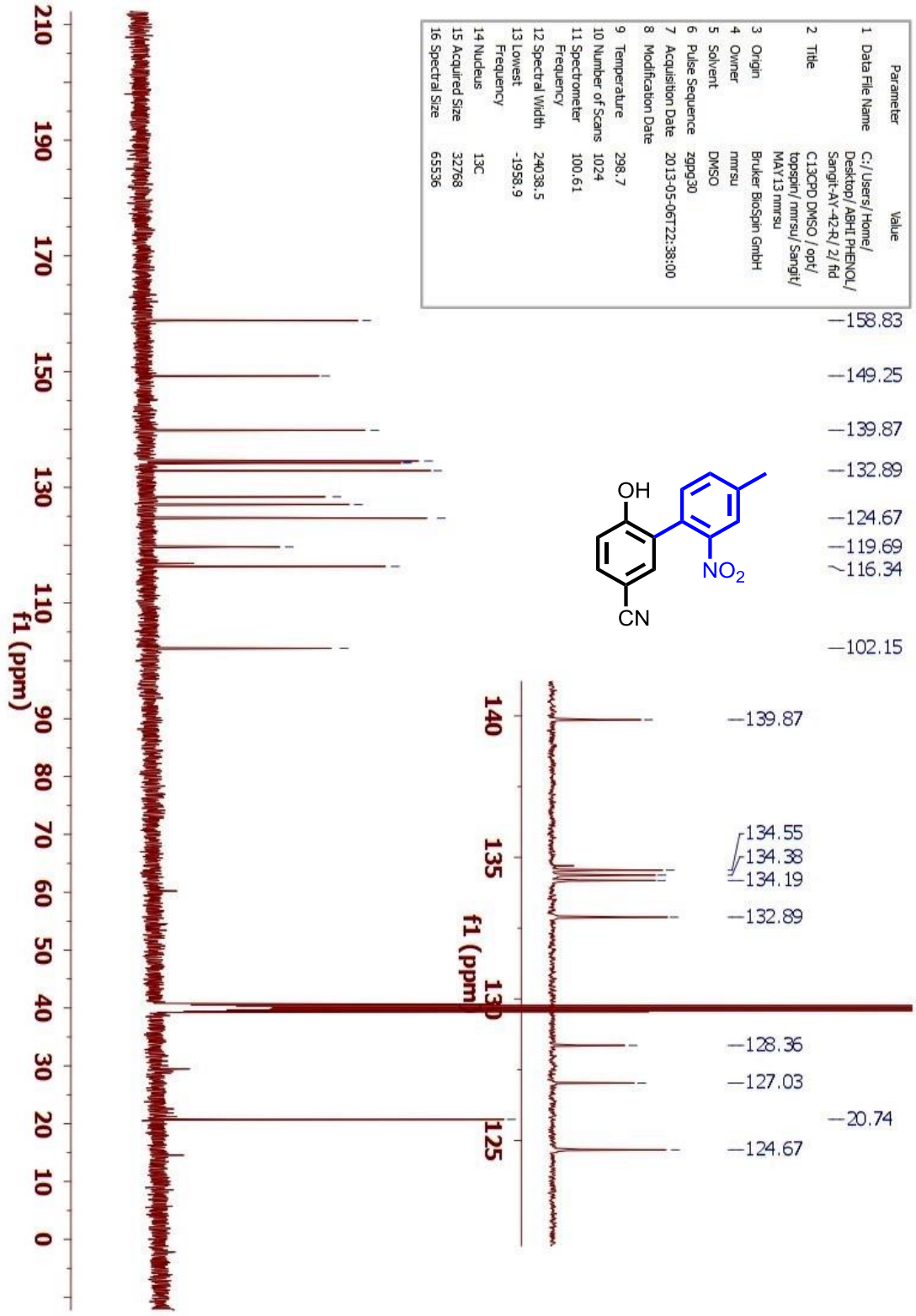


Figure S17 ^{1}H NMR spectrum of **9**

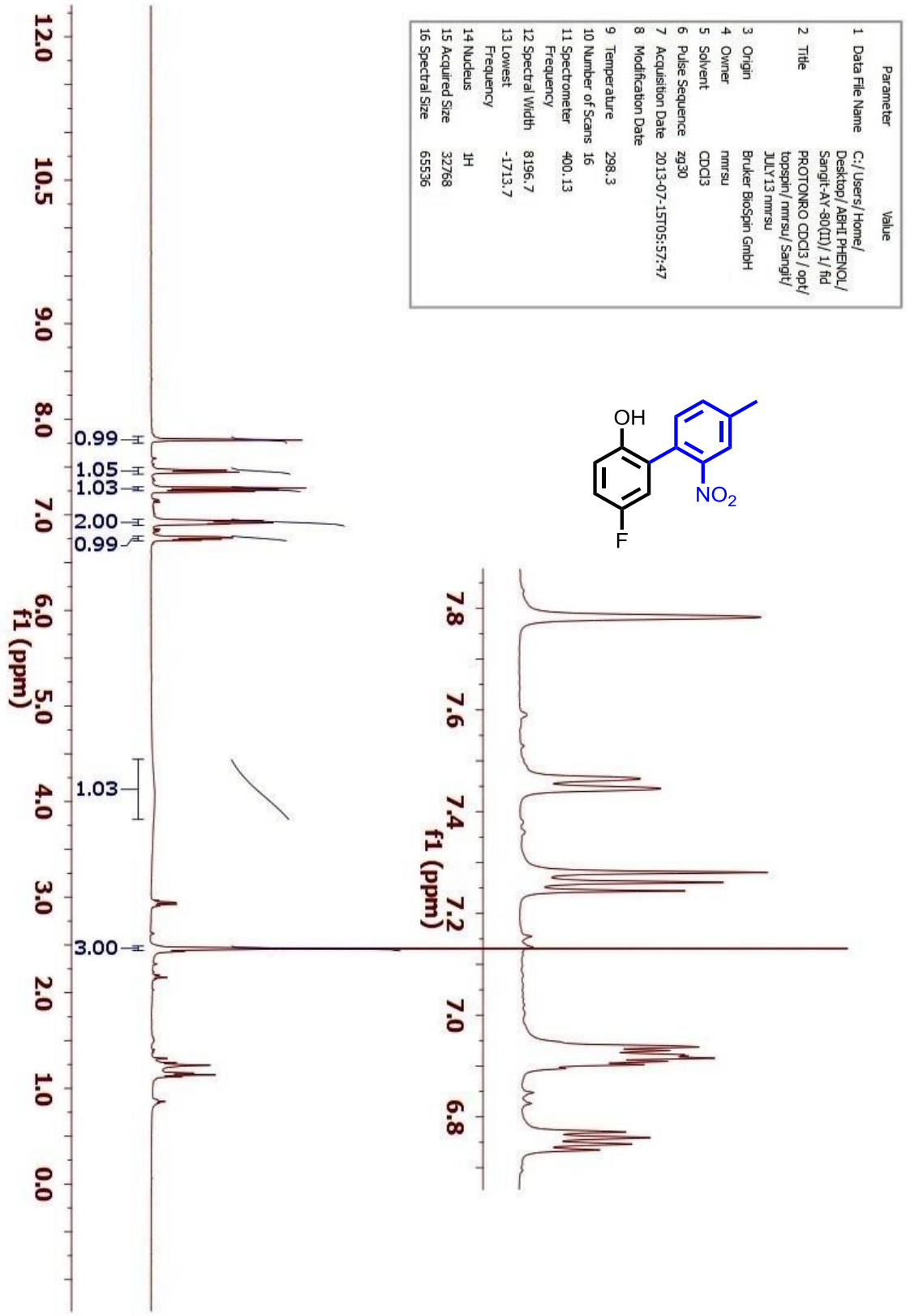


Figure S18 ^{13}C NMR spectrum of **9**

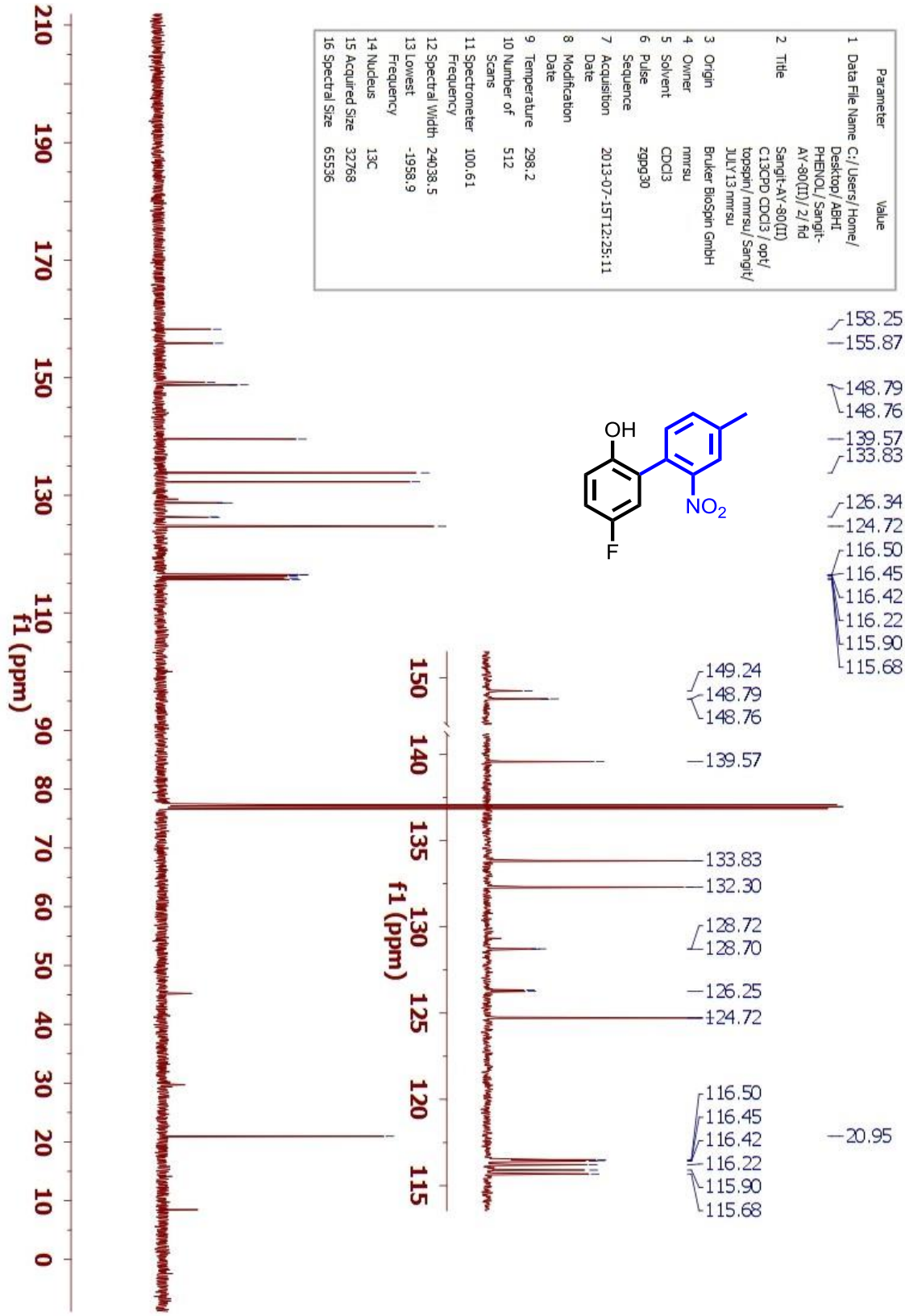


Figure S19 ^{1}H NMR spectrum of **10**

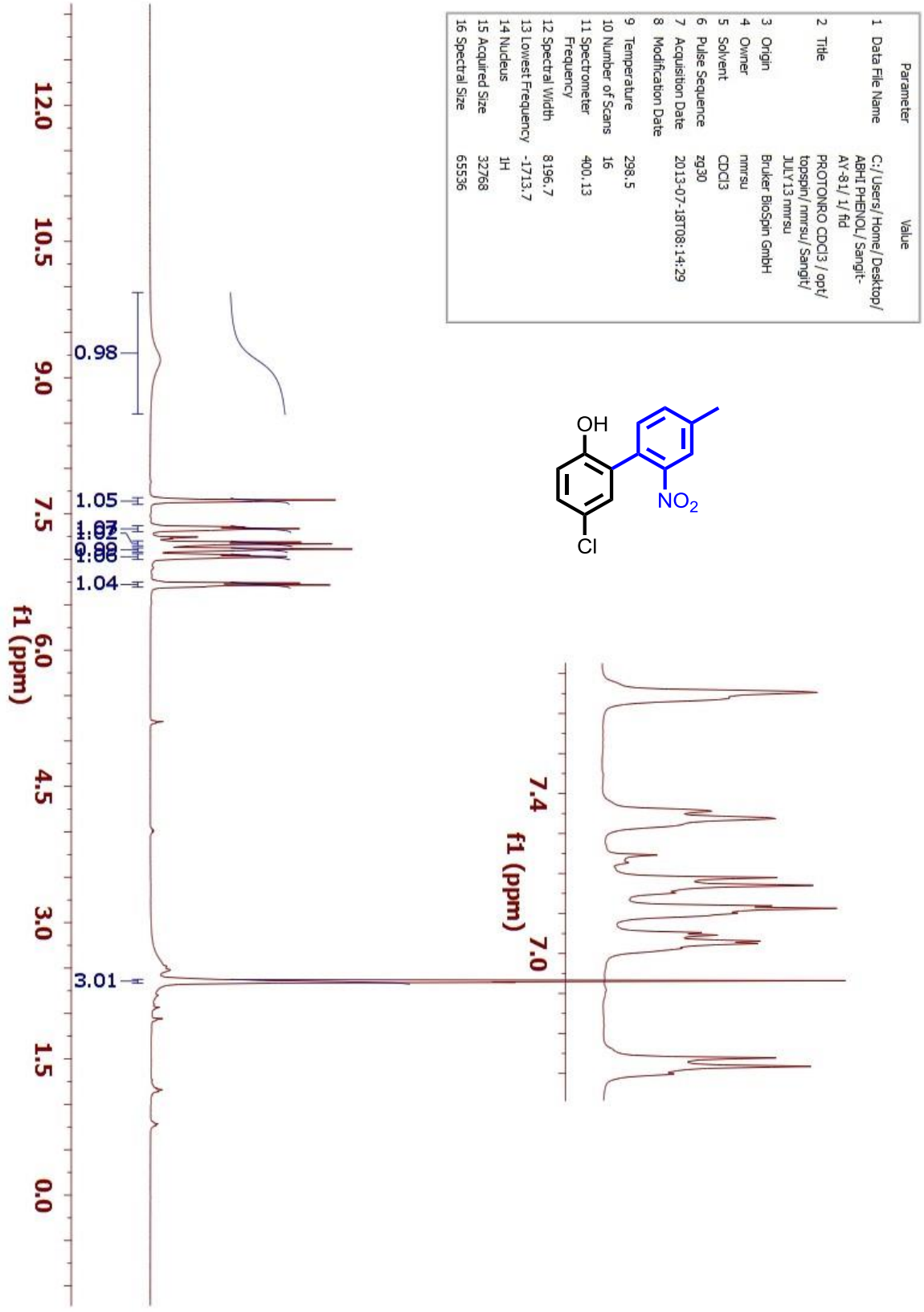


Figure S20 ^{13}C NMR spectrum of **10**

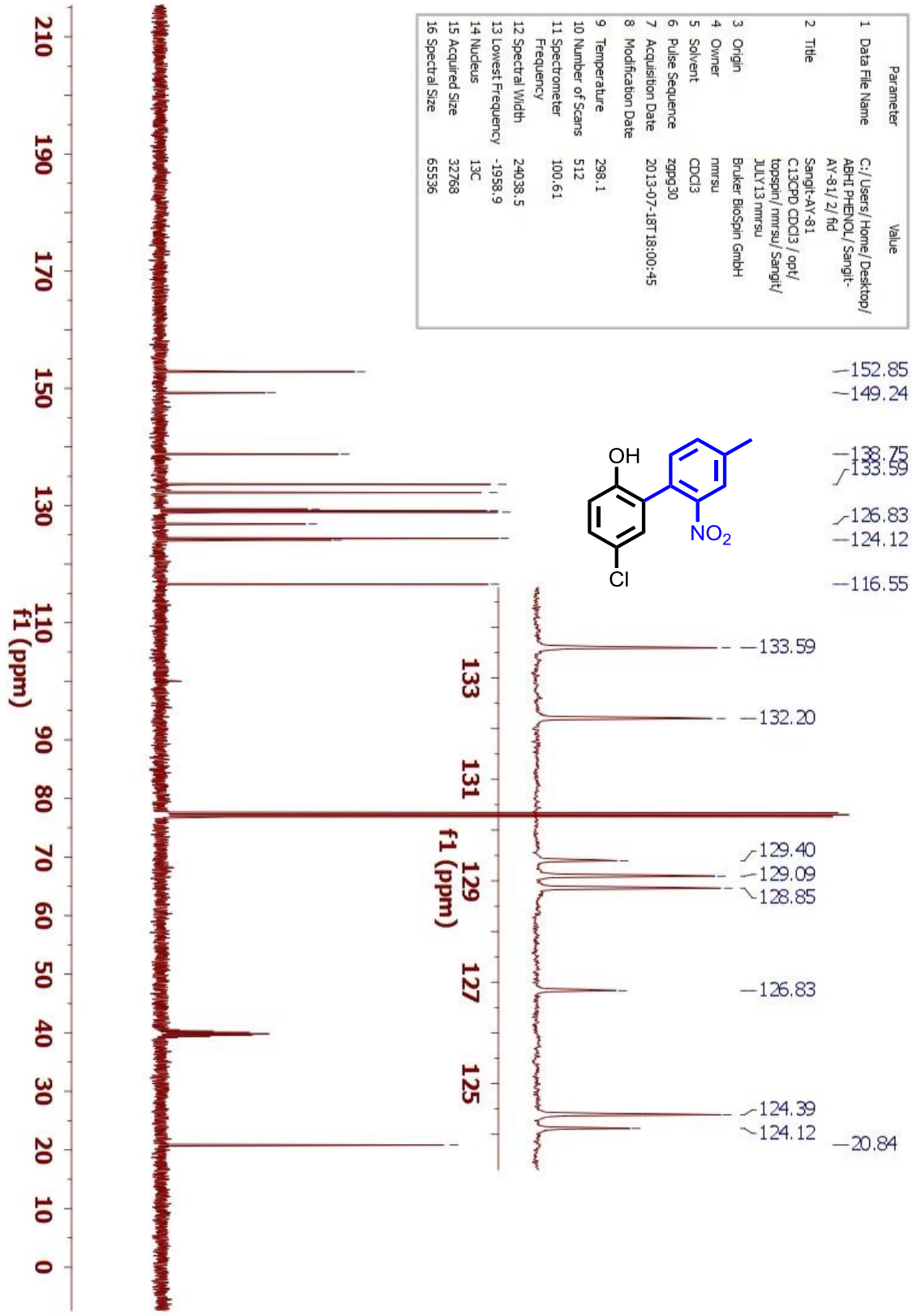


Figure S21 ^{1}H NMR spectrum of **11**

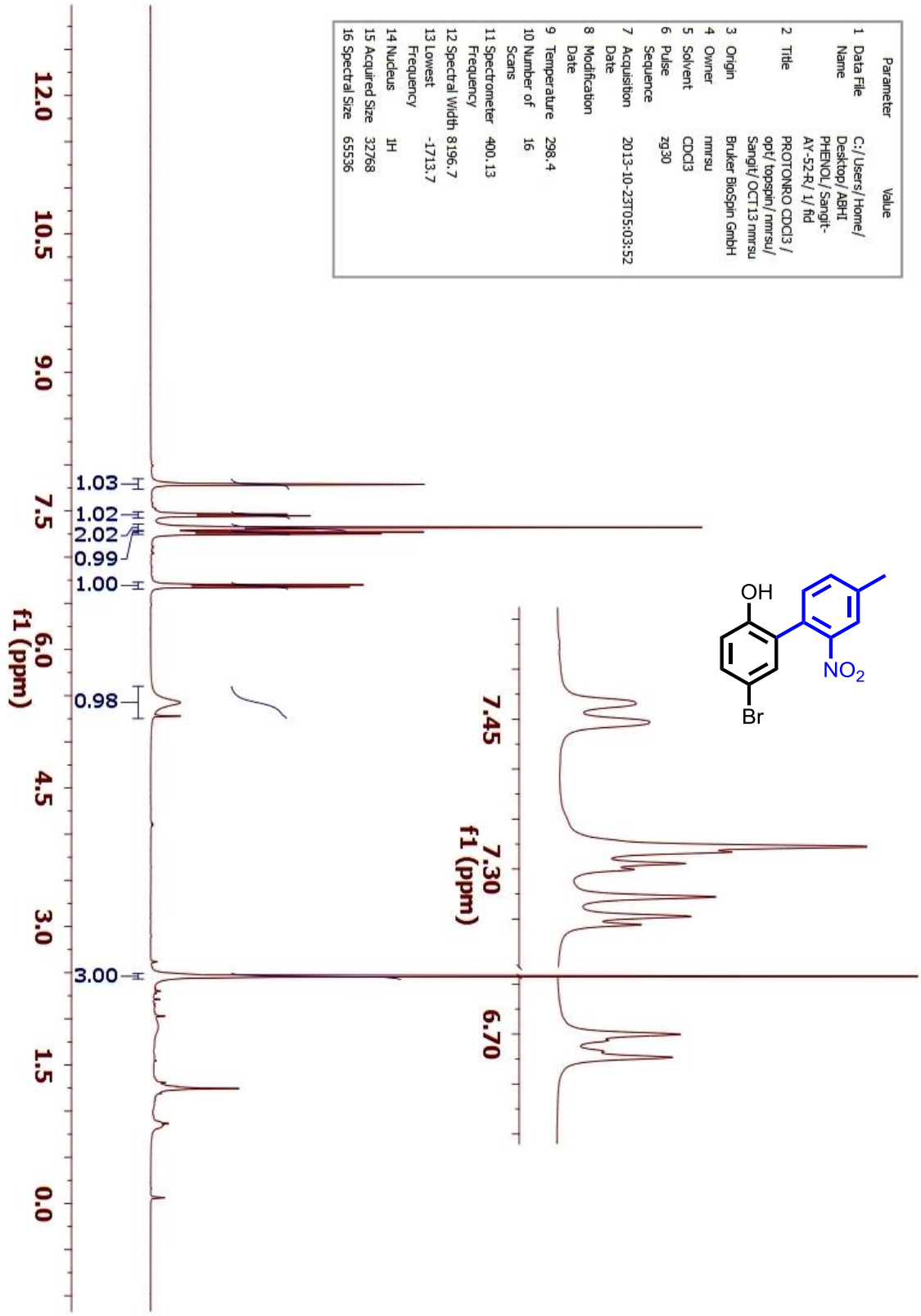


Figure S22 ^{13}C NMR spectrum of **11**

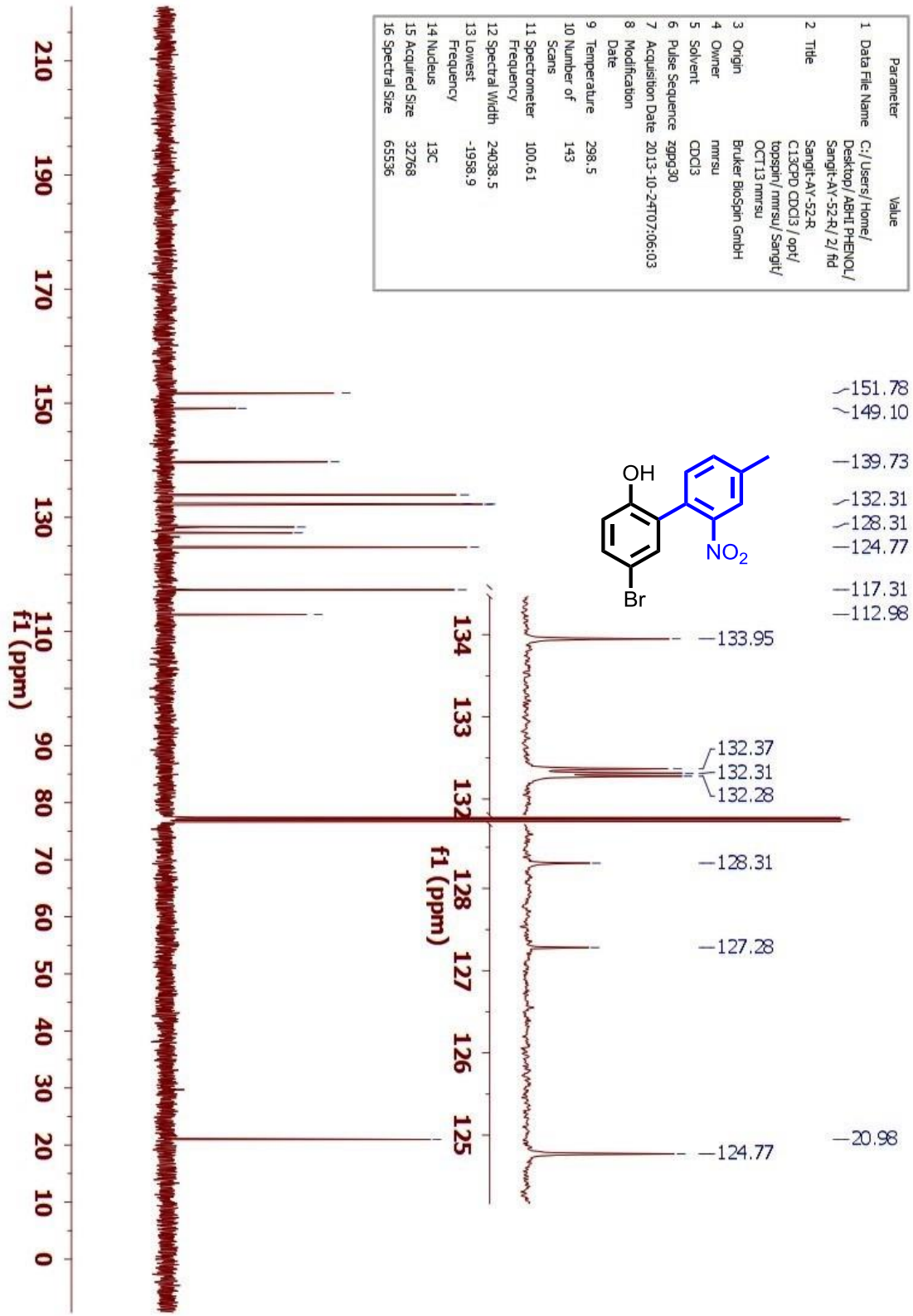


Figure S23 ^{1}H NMR spectrum of **12**

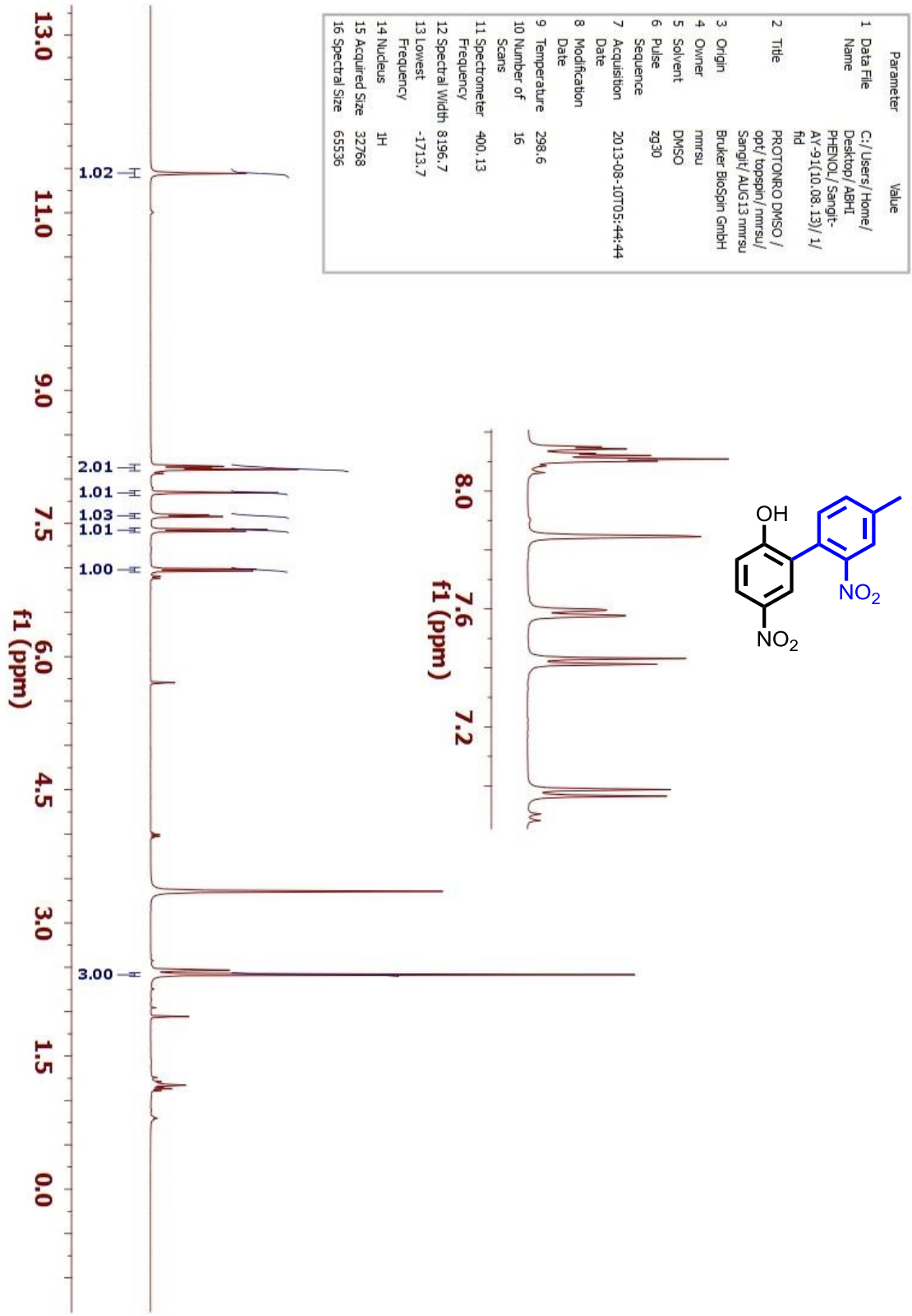


Figure S24 ^{13}C NMR spectrum of **12**

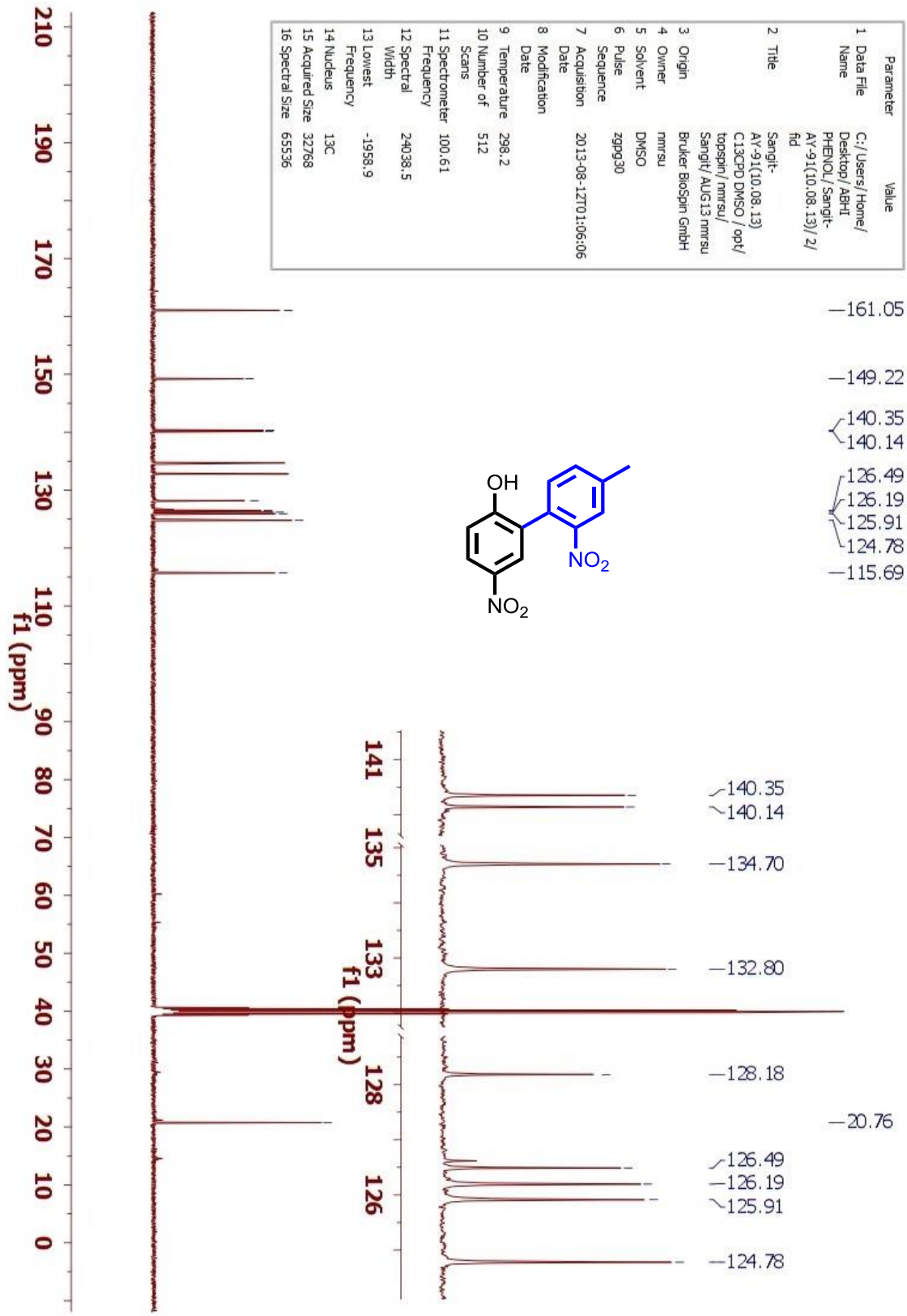


Figure S25 ^{1}H NMR spectrum of **13**

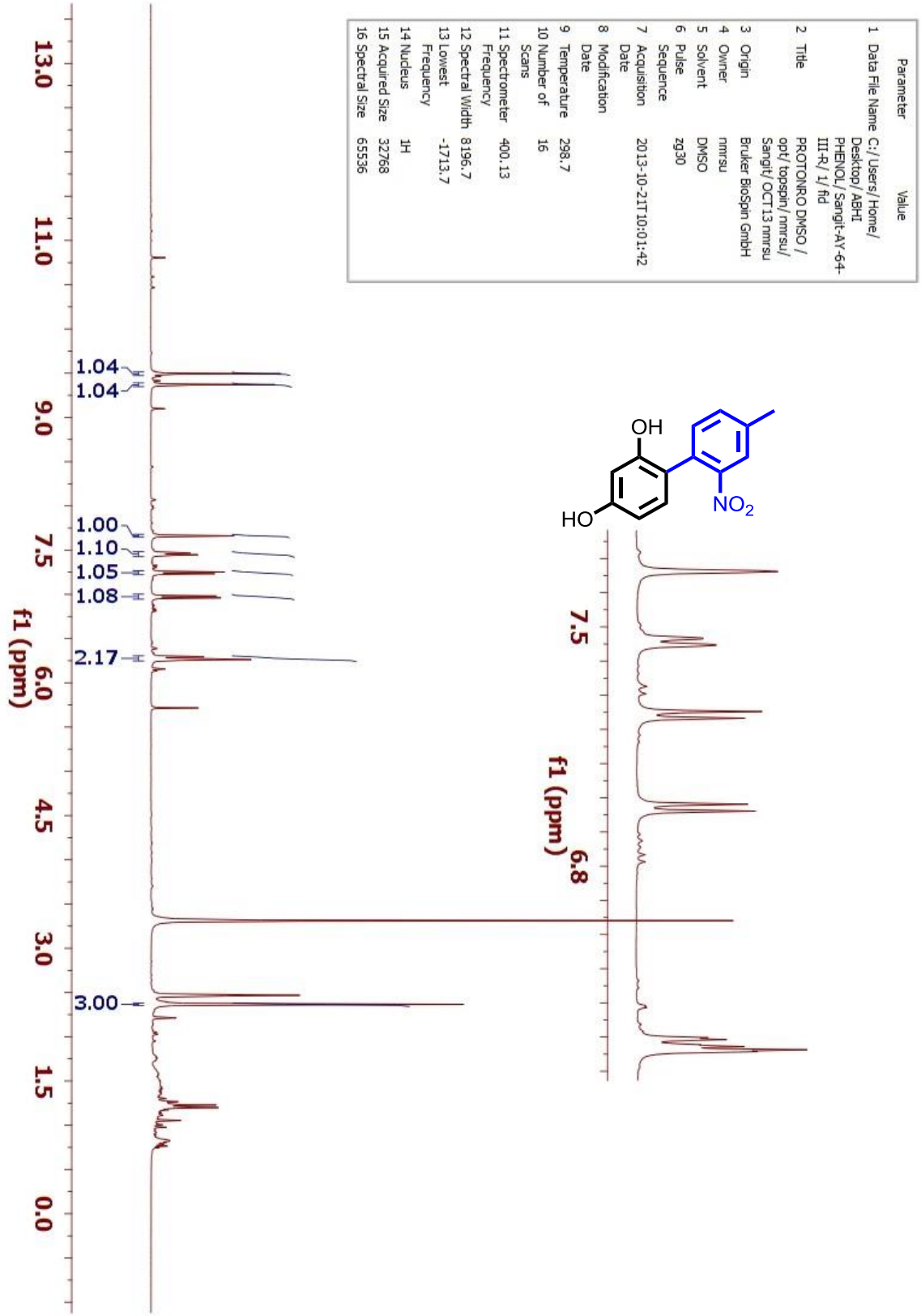


Figure S26 ^{13}C NMR spectrum of **13**

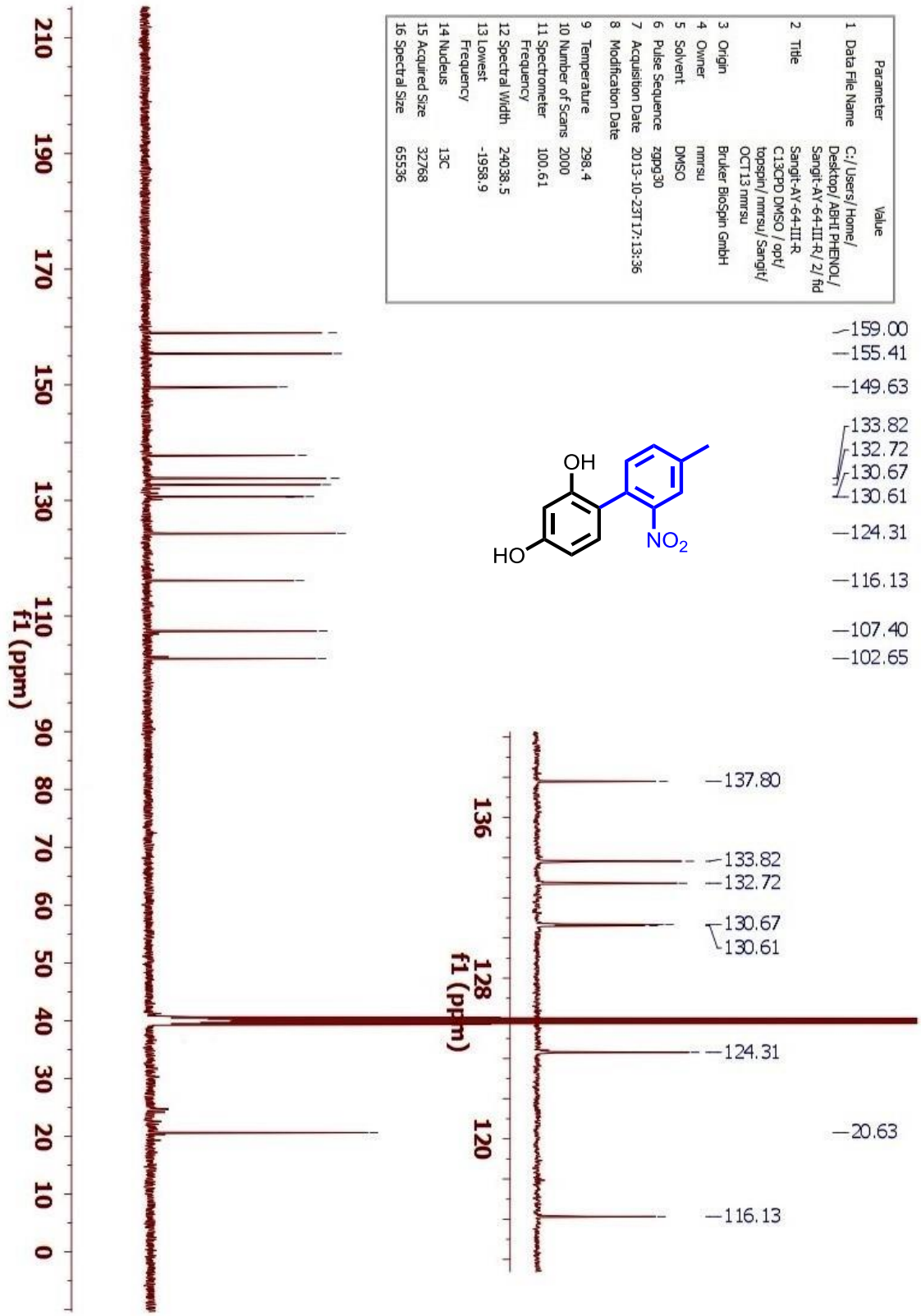


Figure S27 ^{1}H NMR spectrum of **14**

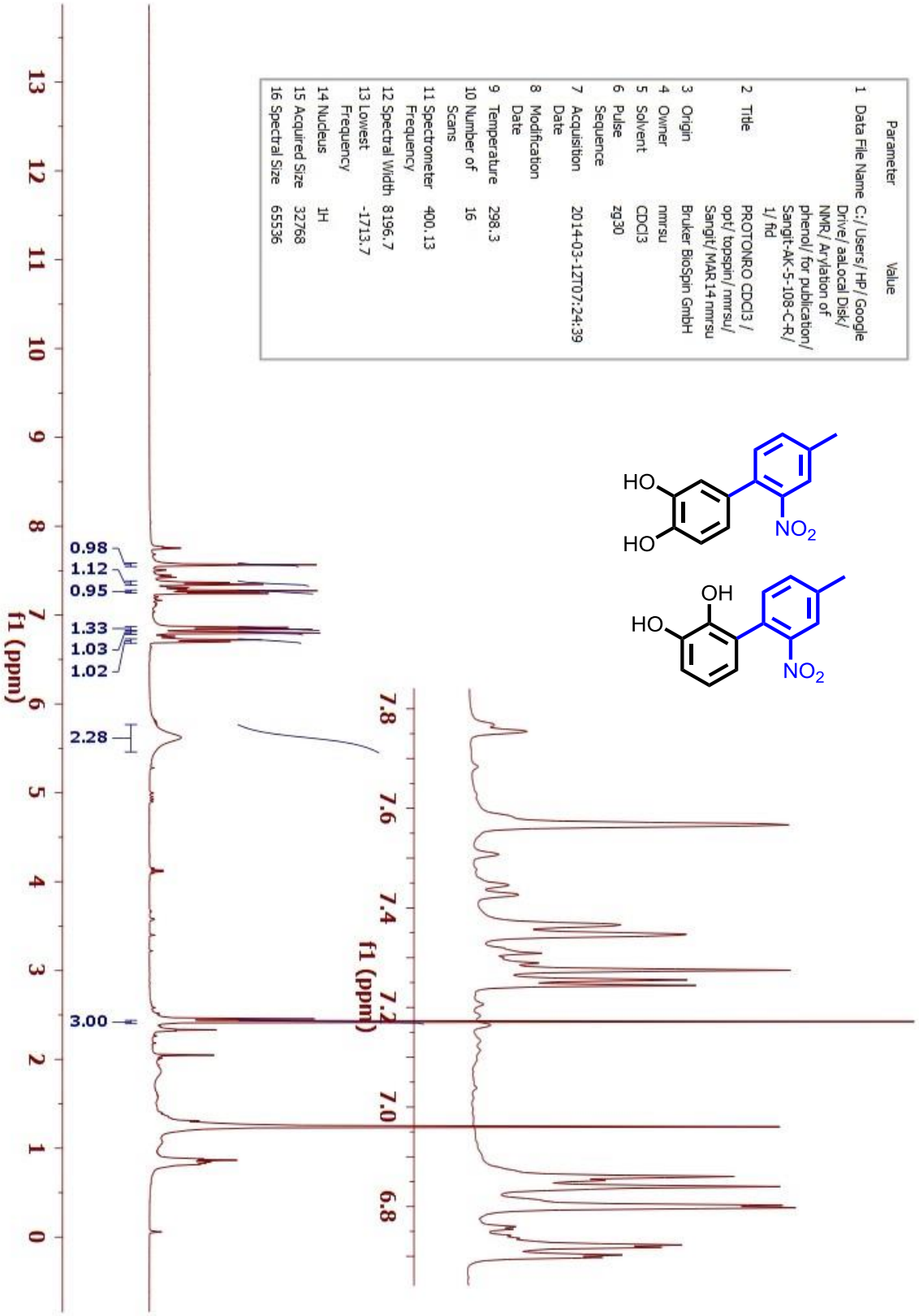


Figure S28 ^{13}C NMR spectrum of **14**

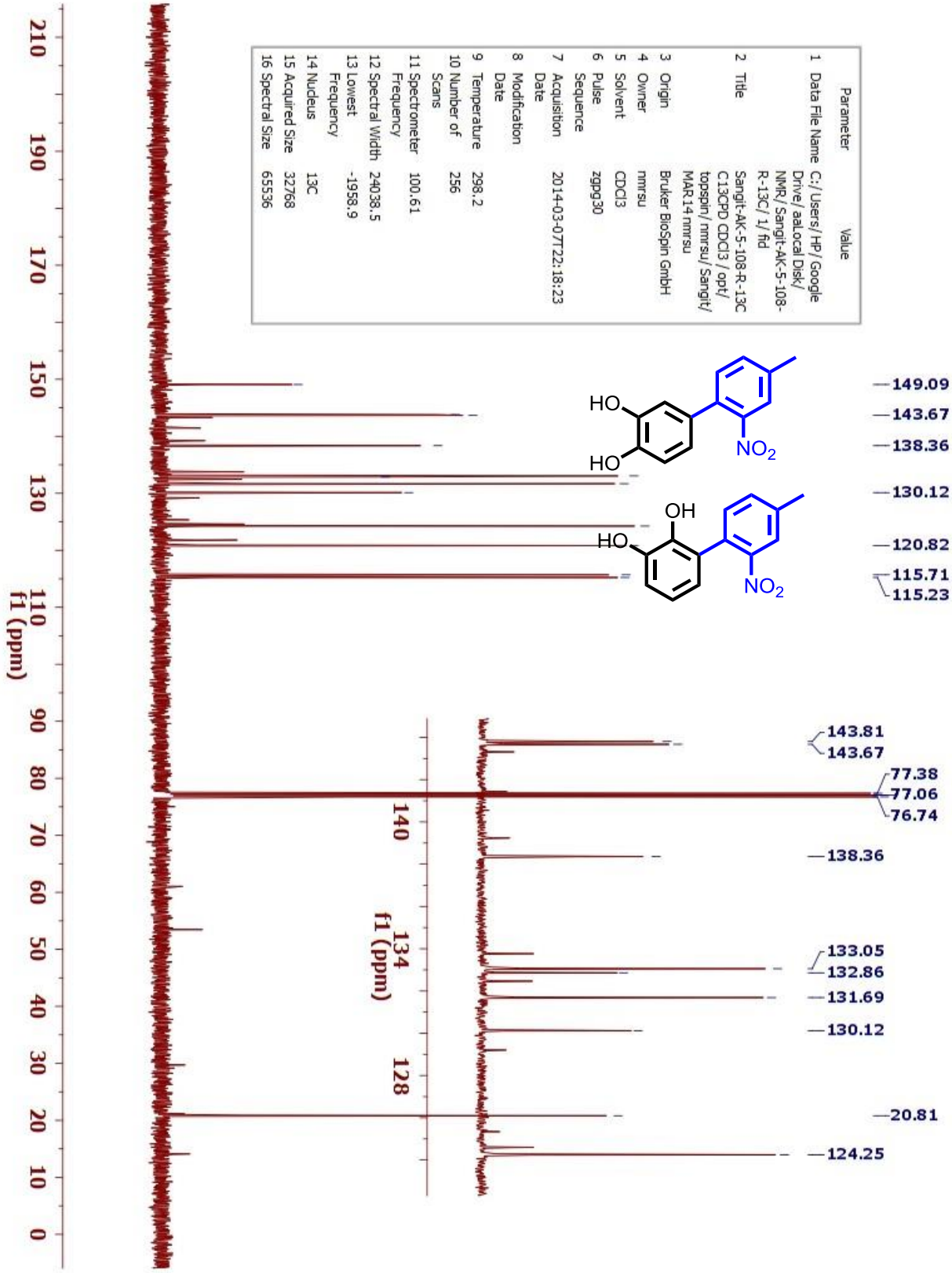


Figure S29 ^{1}H NMR spectrum of **15**

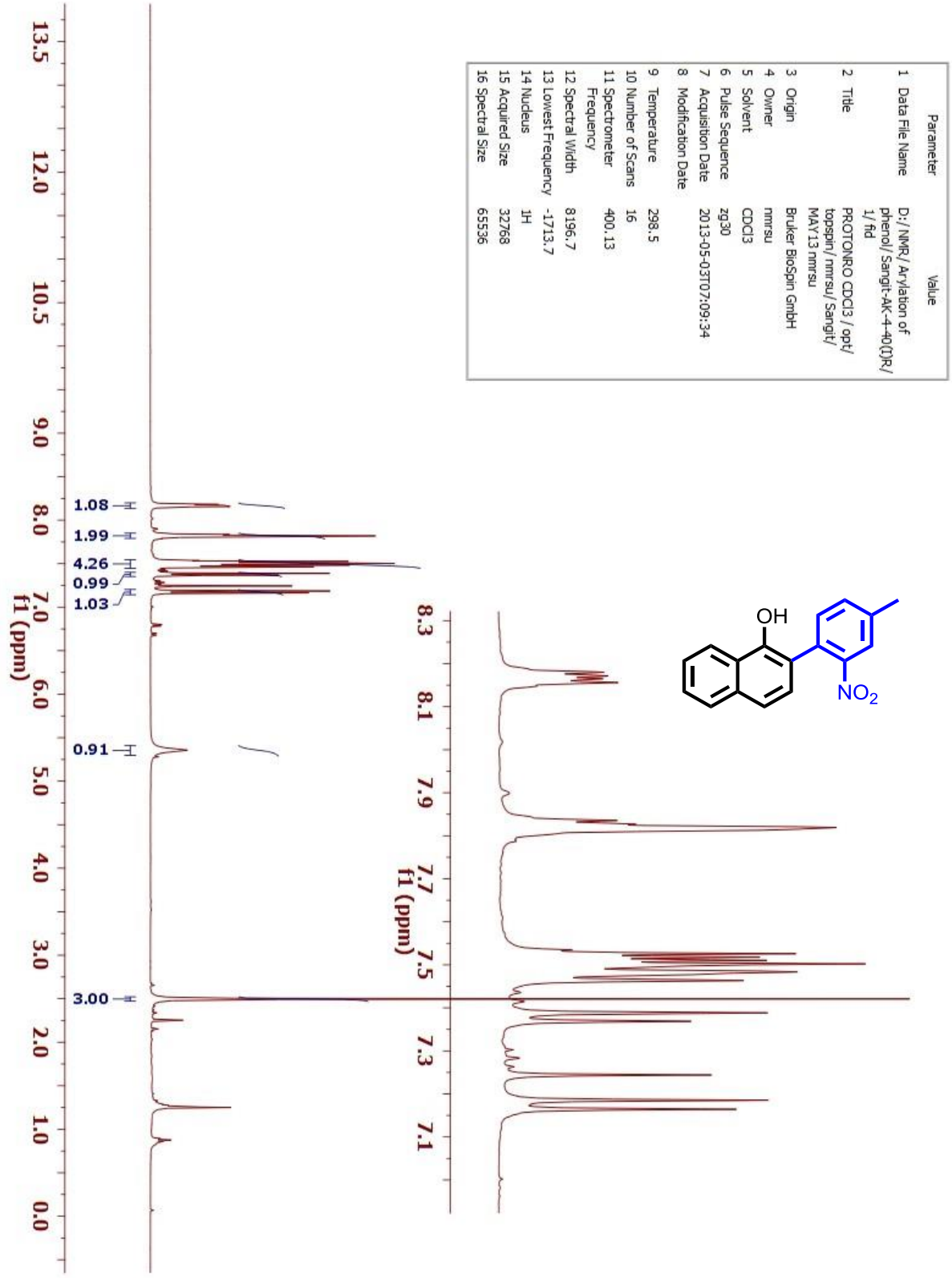


Figure S30 ^{13}C NMR spectrum of **15**

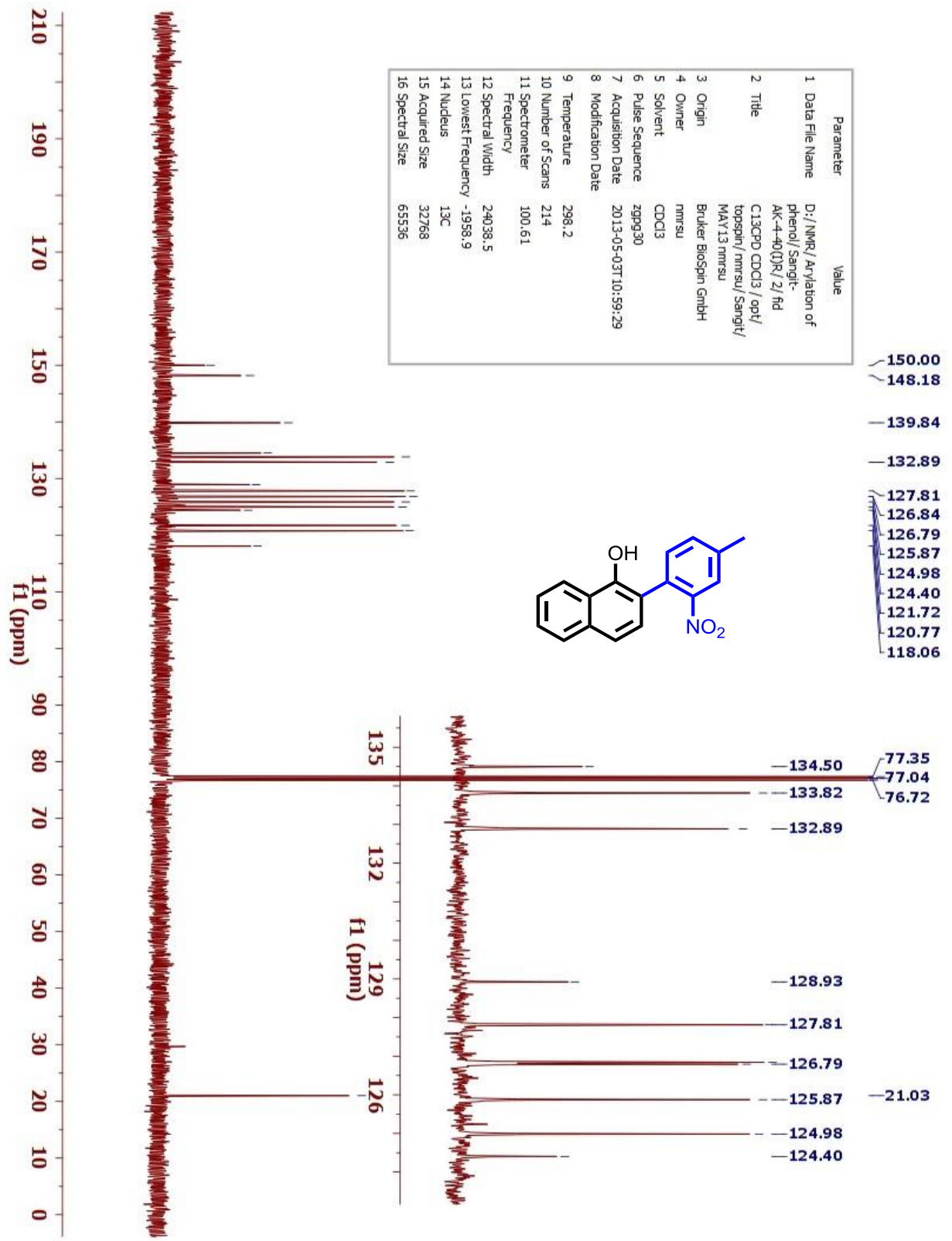


Figure S31 ^{1}H NMR spectrum of **16**

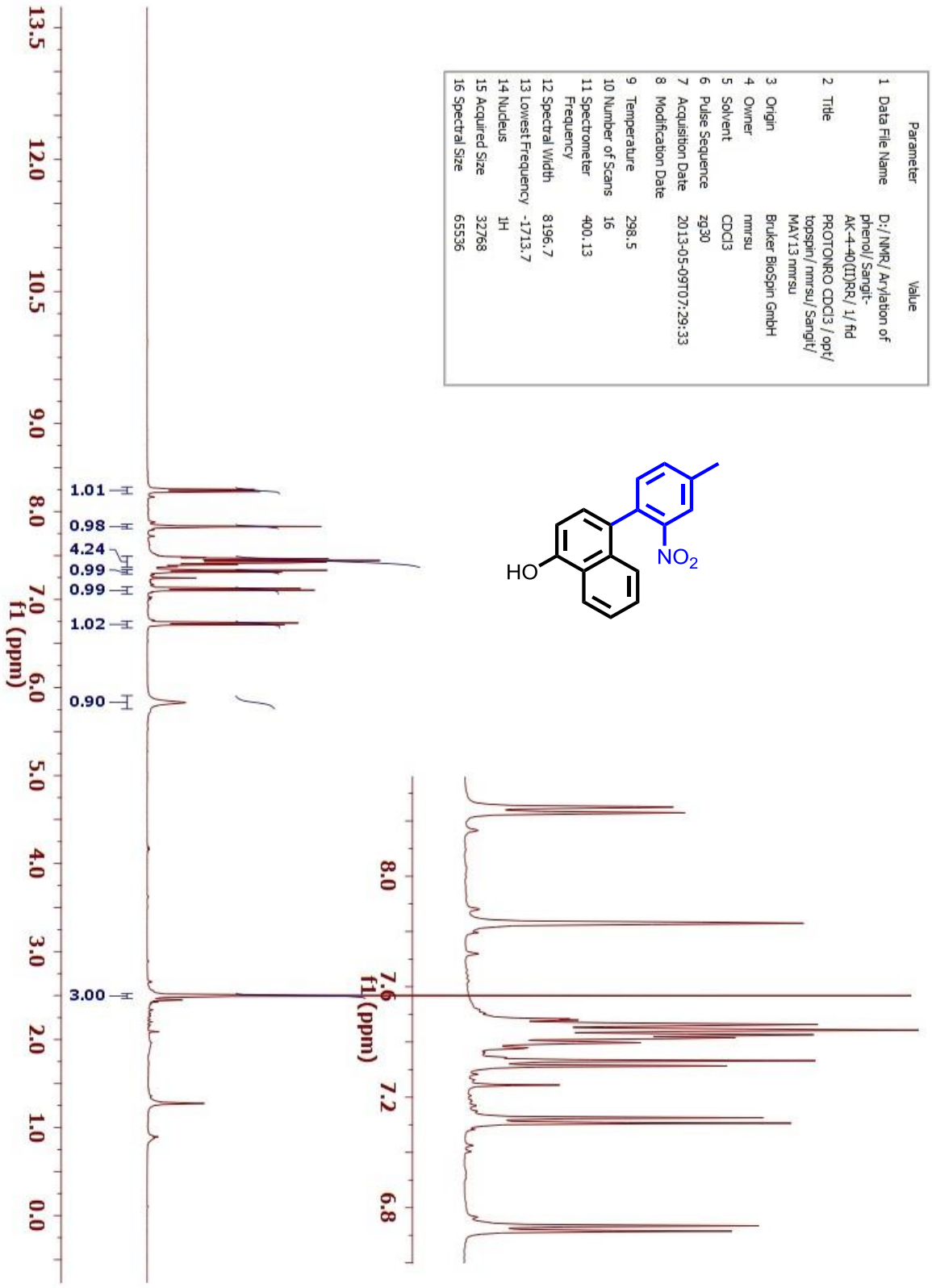


Figure S32 ^{13}C NMR spectrum of **16**

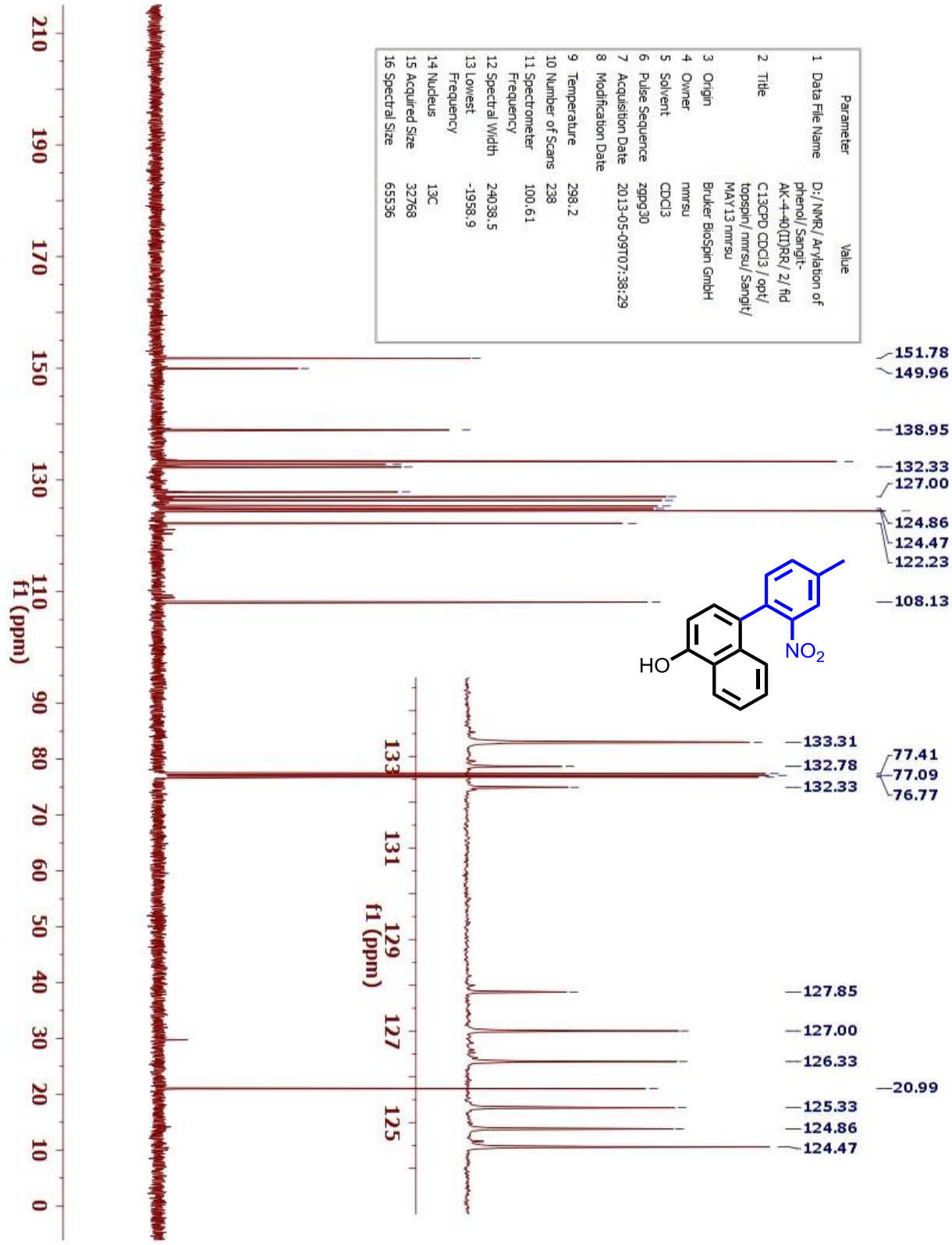


Figure S33 ^{1}H NMR spectrum of **17**

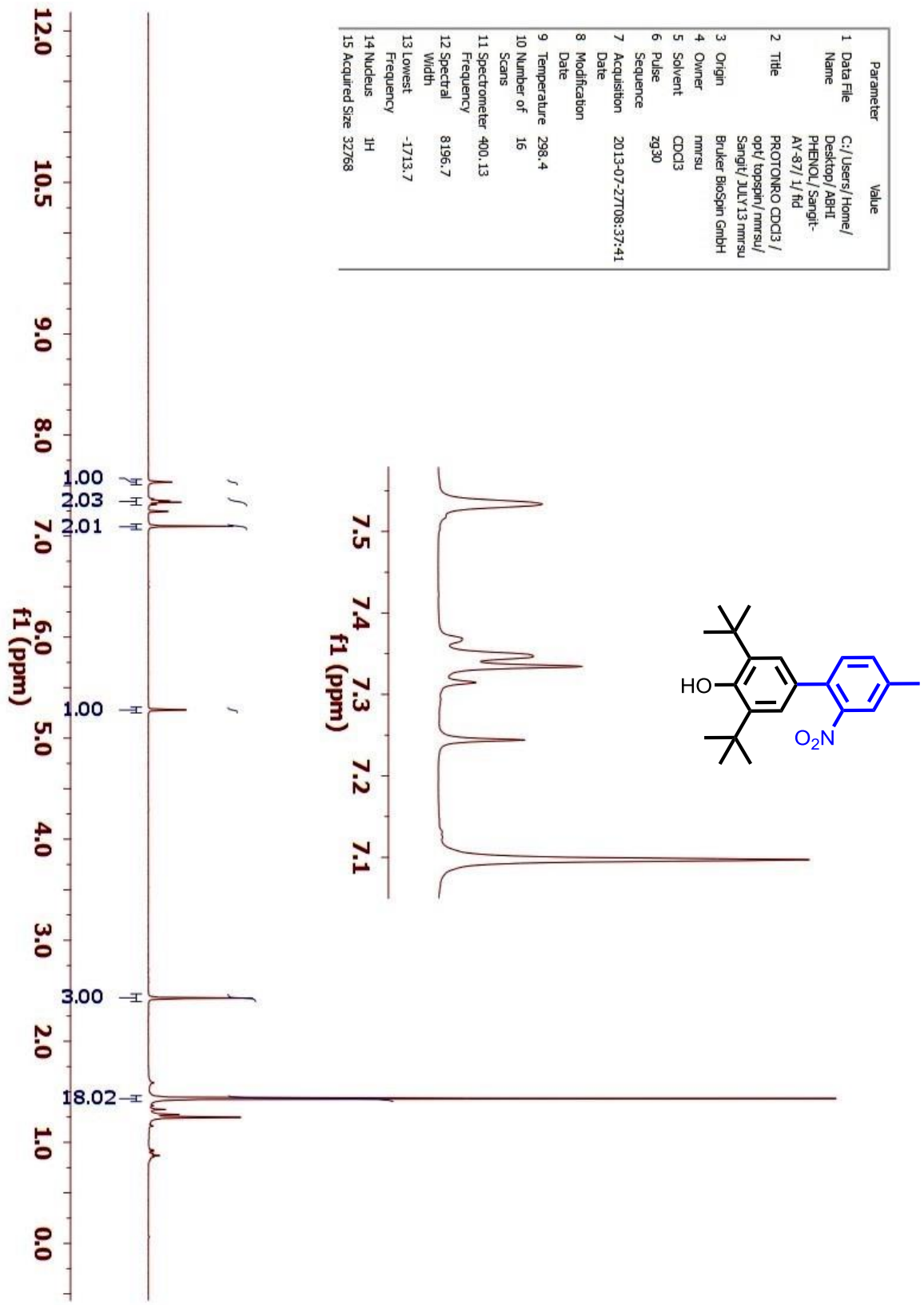


Figure S34 ^{13}C NMR spectrum of **17**

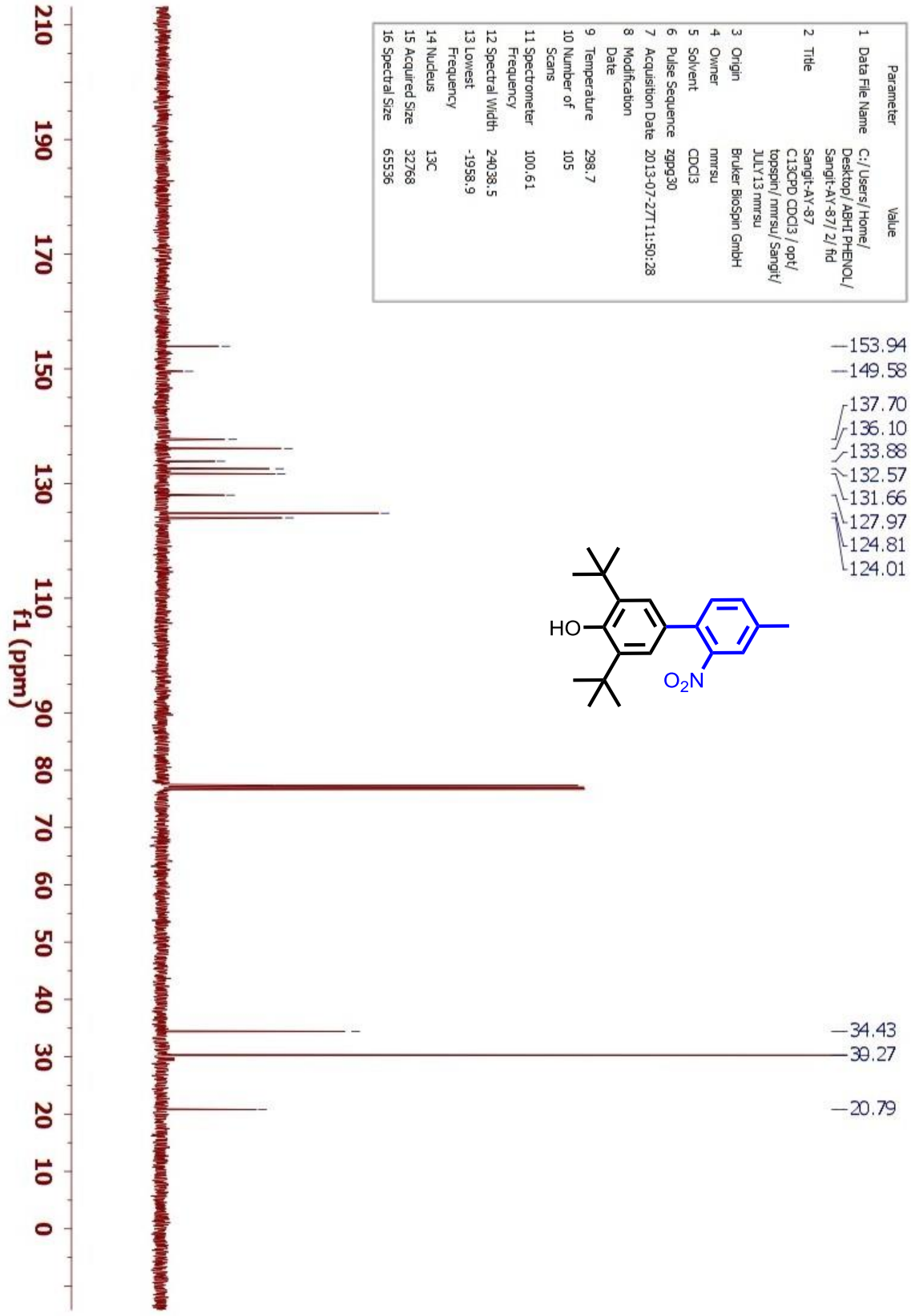


Figure S35 ^{1}H NMR spectrum of **18**

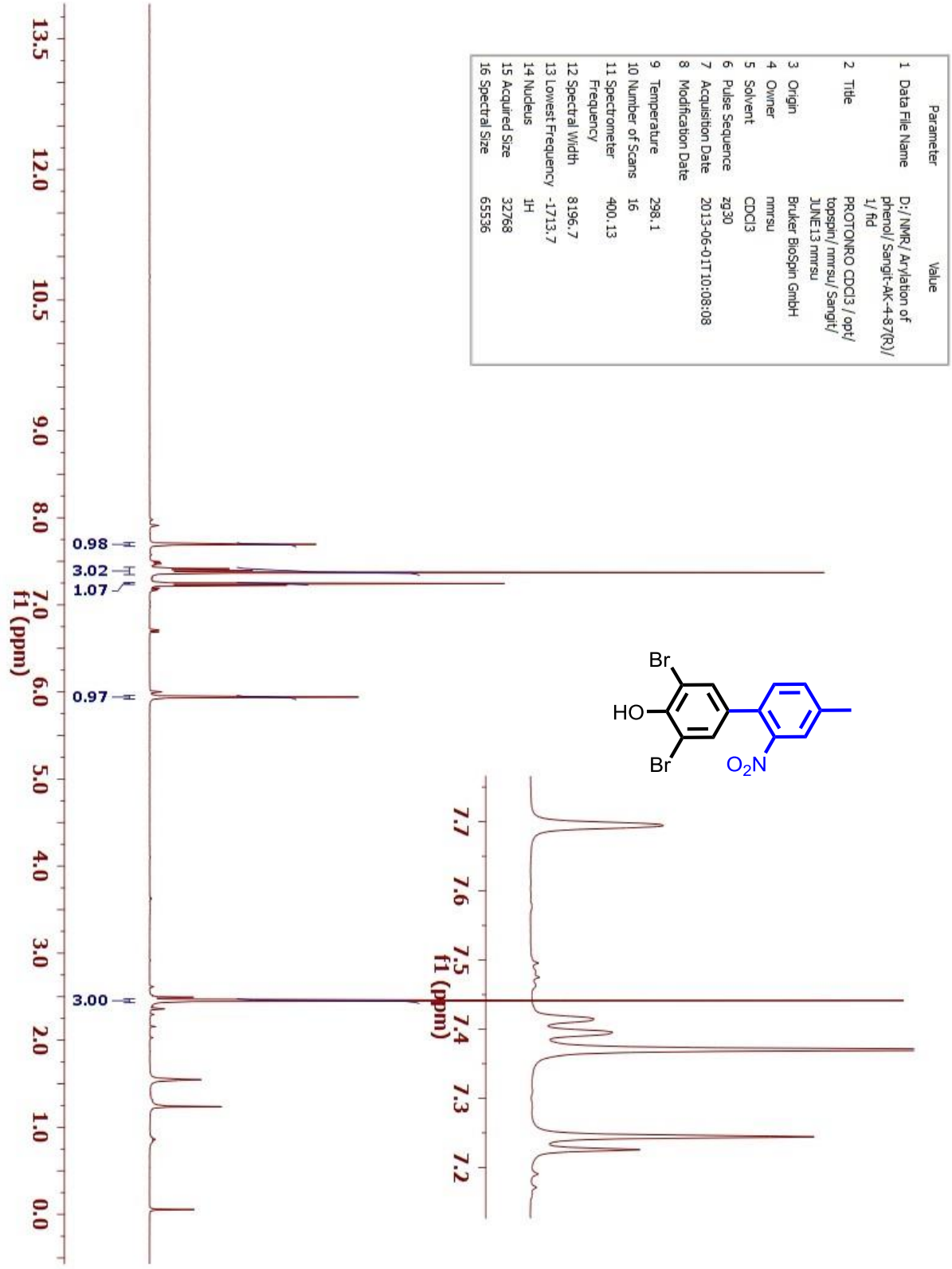


Figure S36 ^{13}C NMR spectrum of **18**

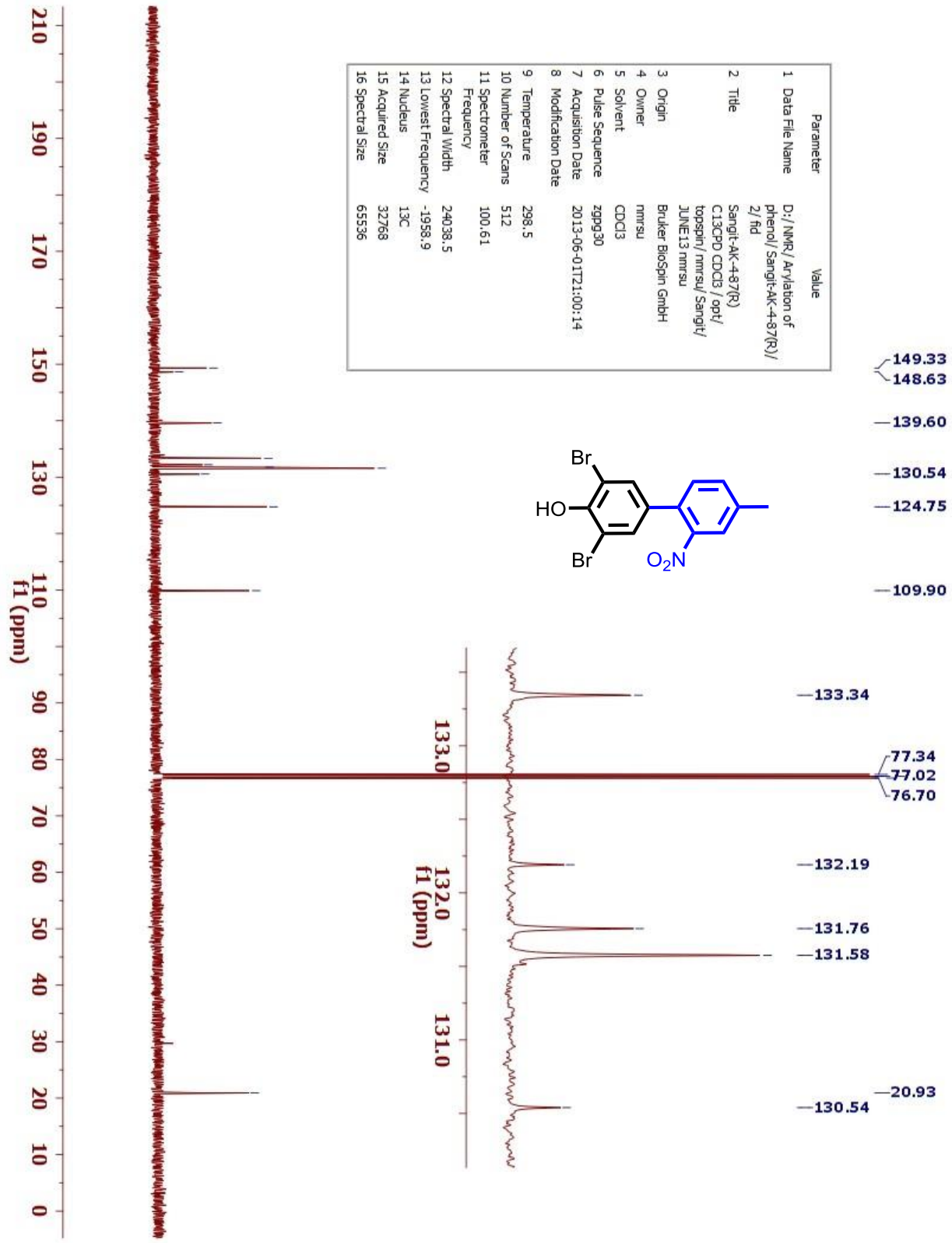


Figure S37 ^{1}H NMR spectrum of **19**

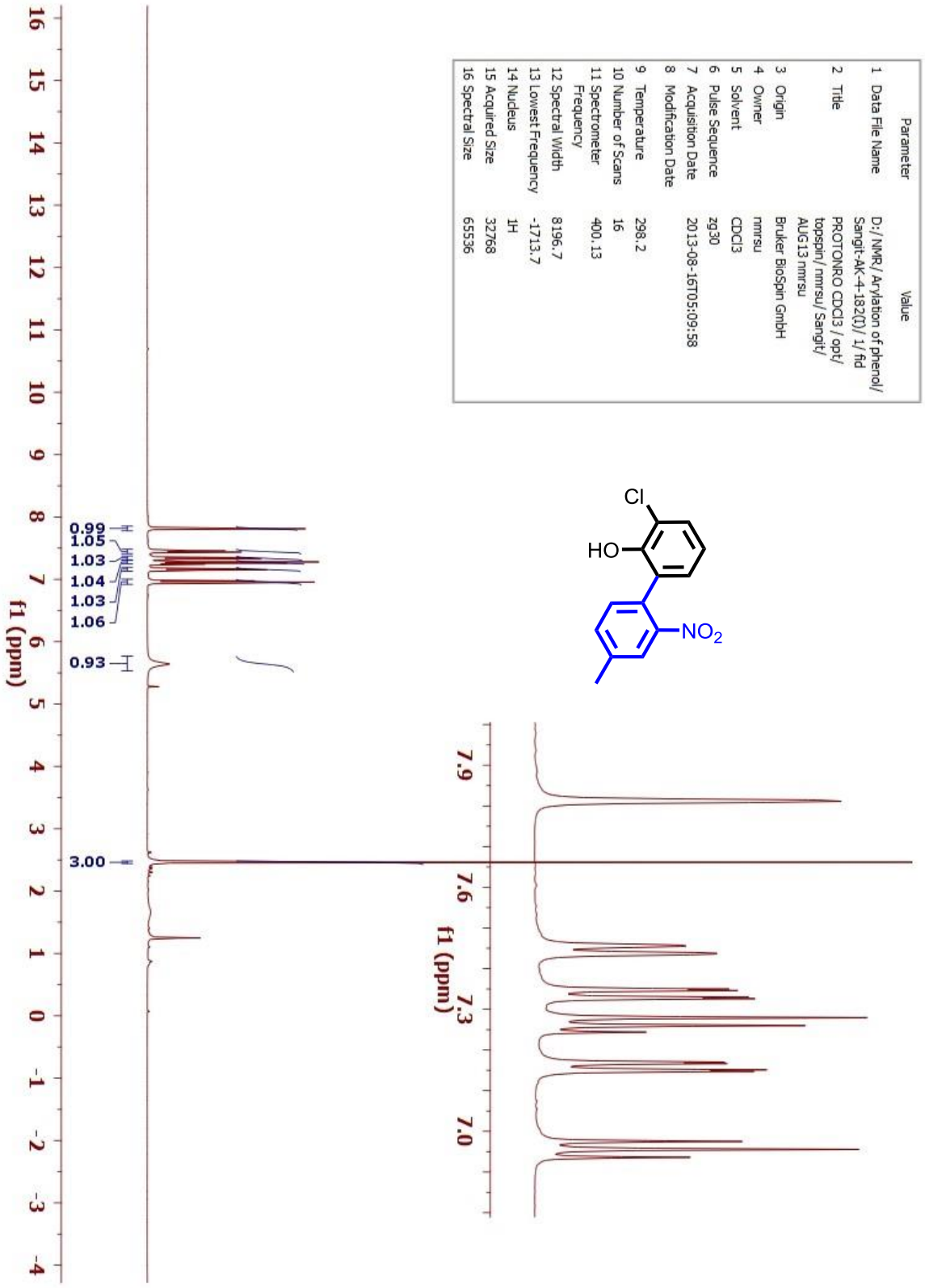


Figure S38 ^{13}C NMR spectrum of **19**

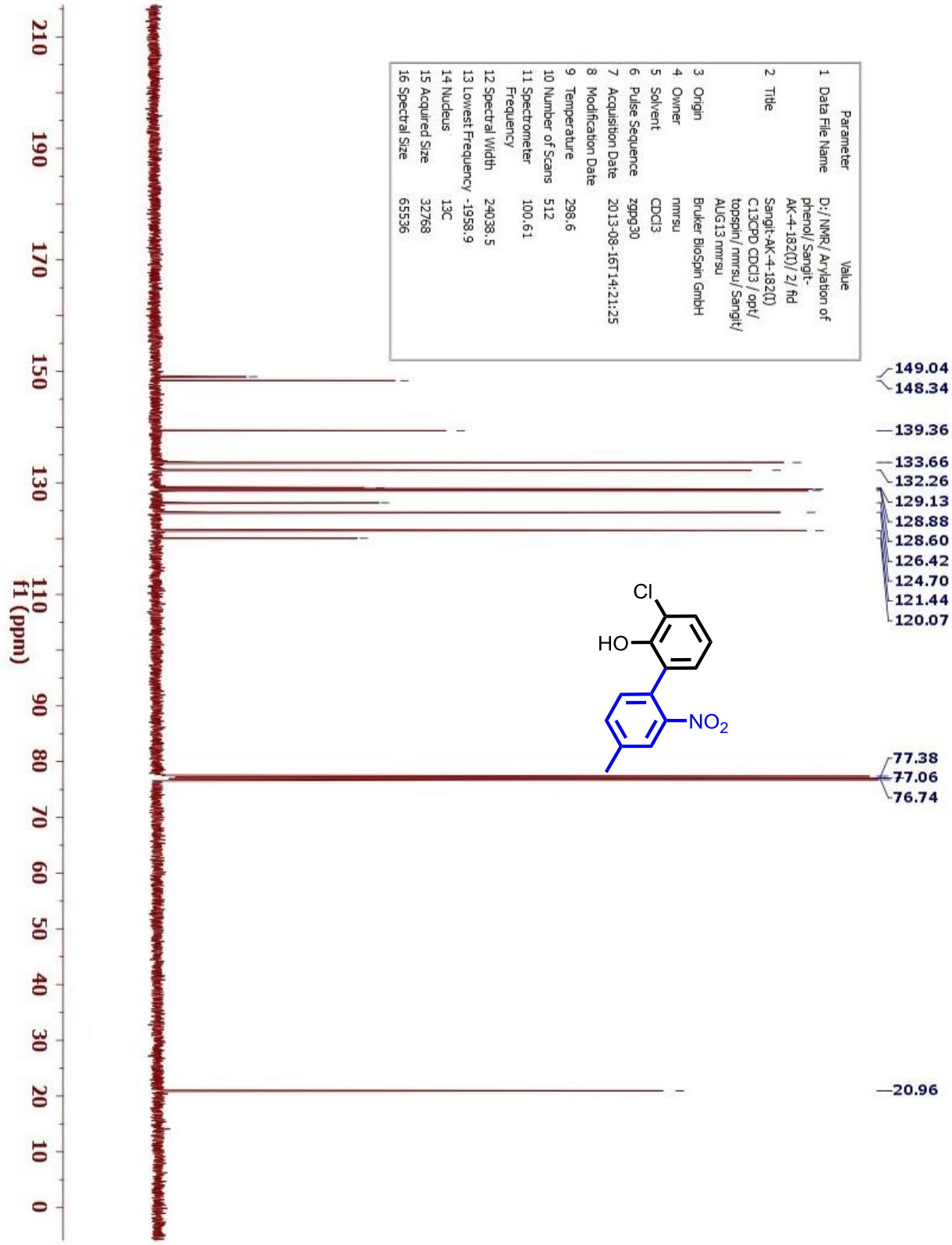


Figure S39 ^{1}H NMR spectrum of **20**

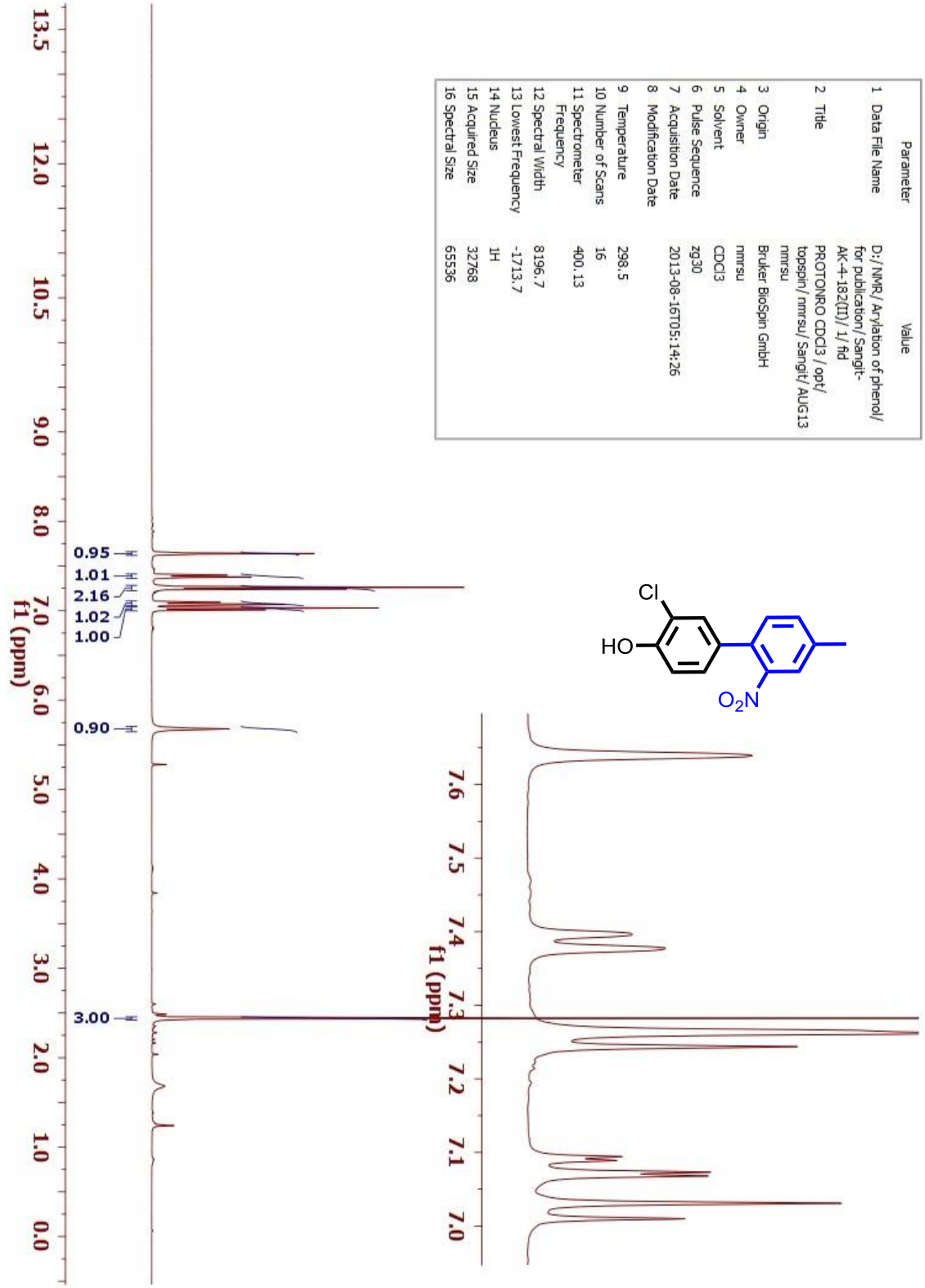


Figure S40 ^{13}C NMR spectrum of **20**

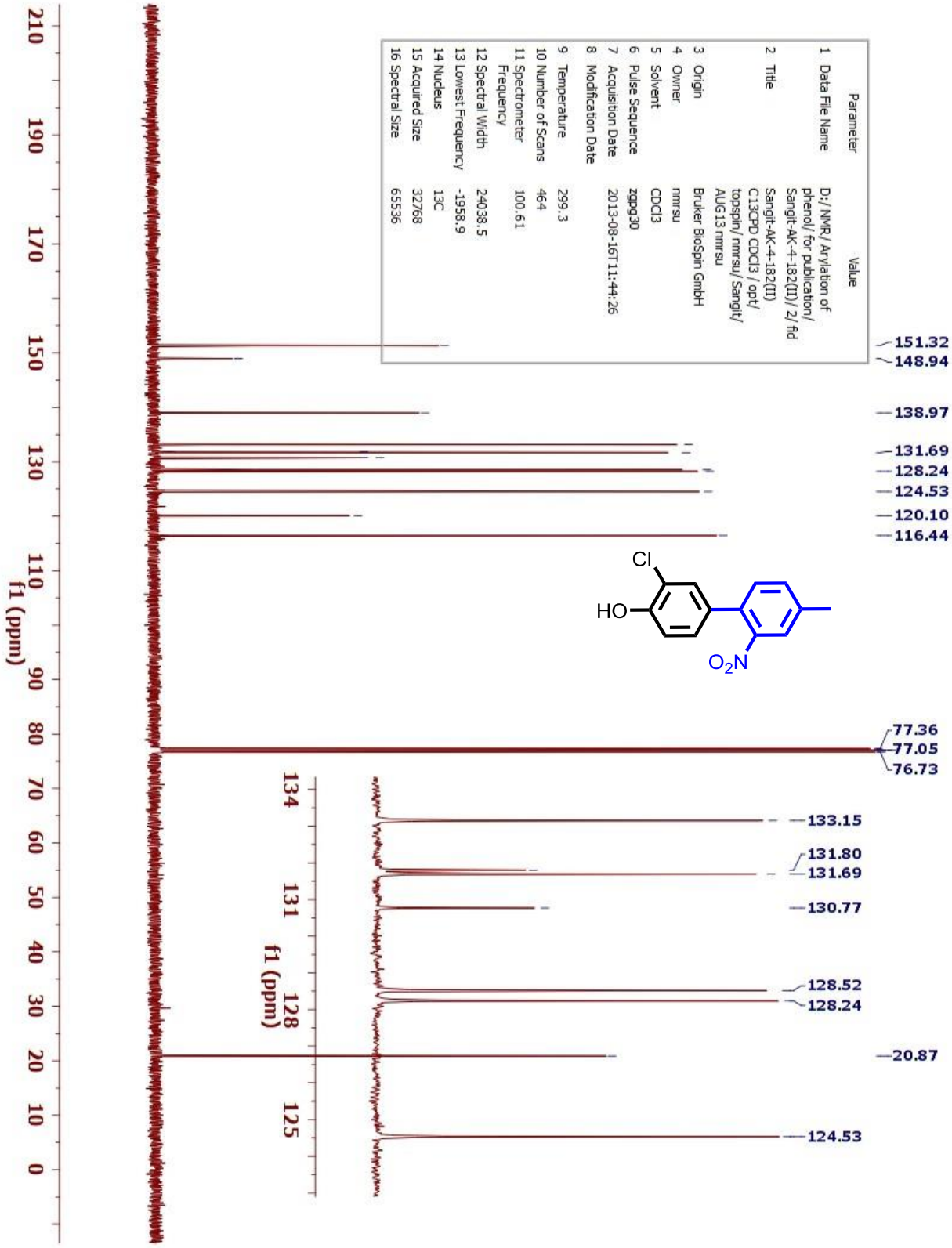


Figure S41 ^{1}H NMR spectrum of **21**

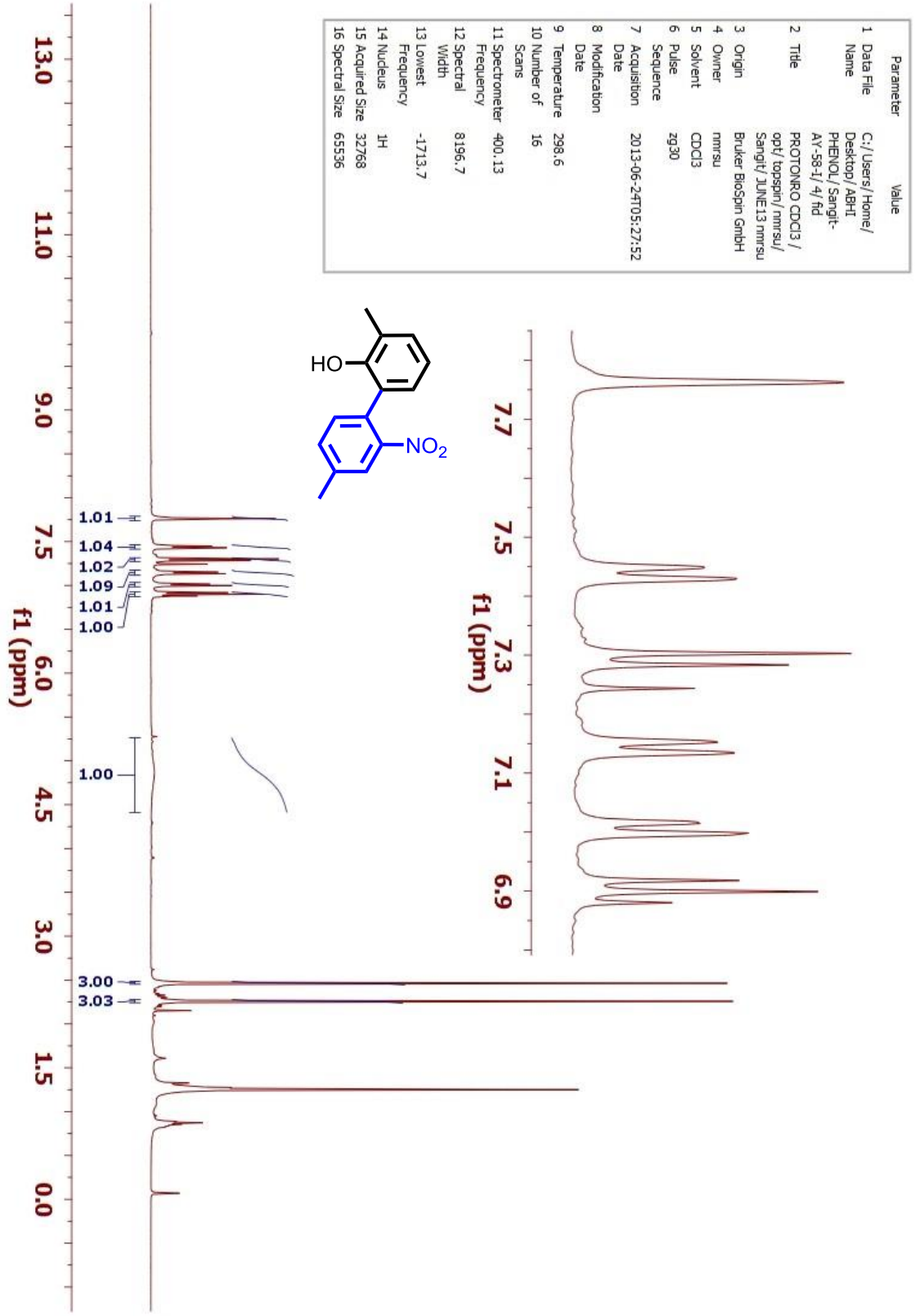


Figure S42 ^{13}C NMR spectrum of **21**

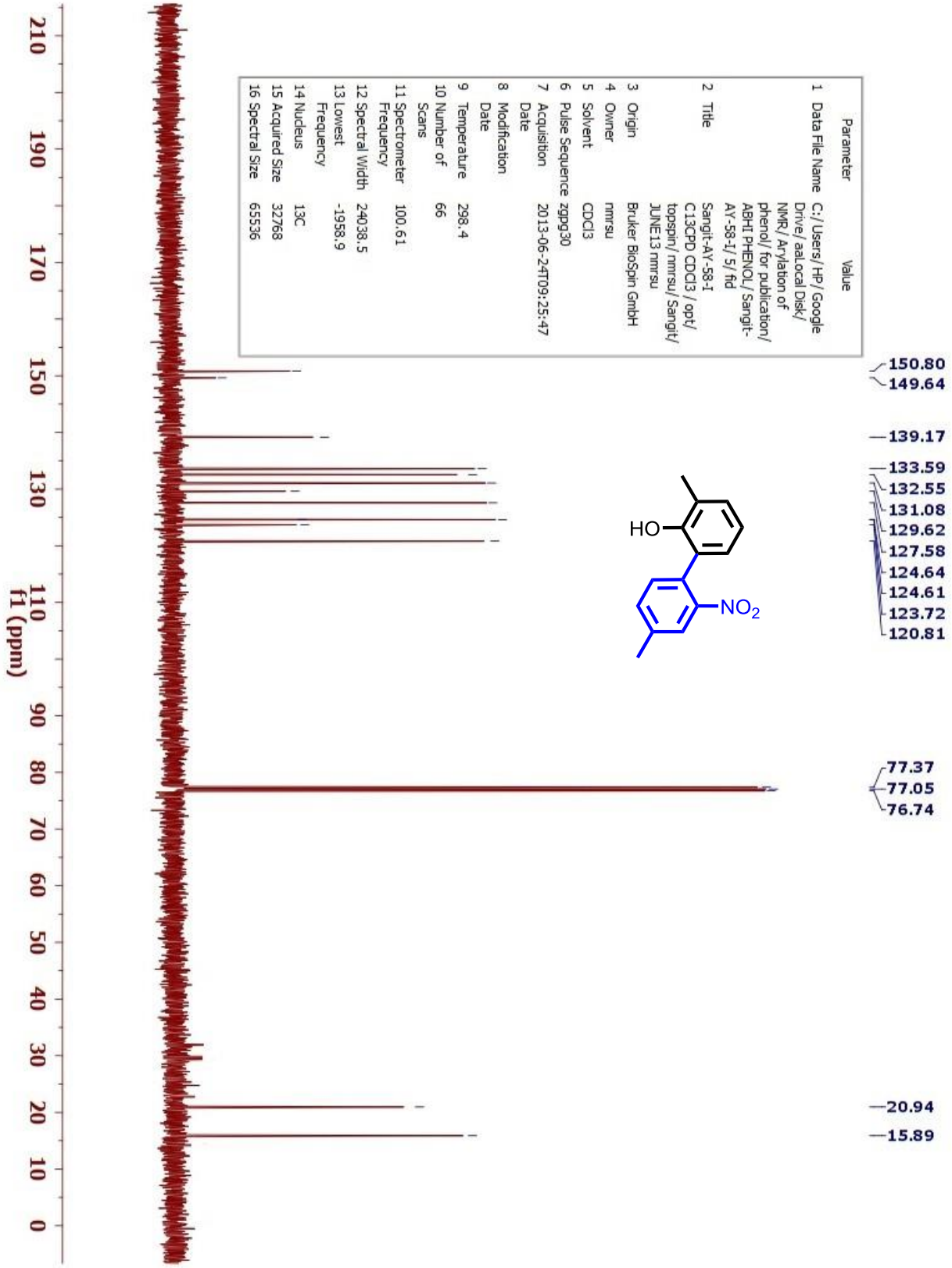


Figure S43 ^{1}H NMR spectrum of **22**

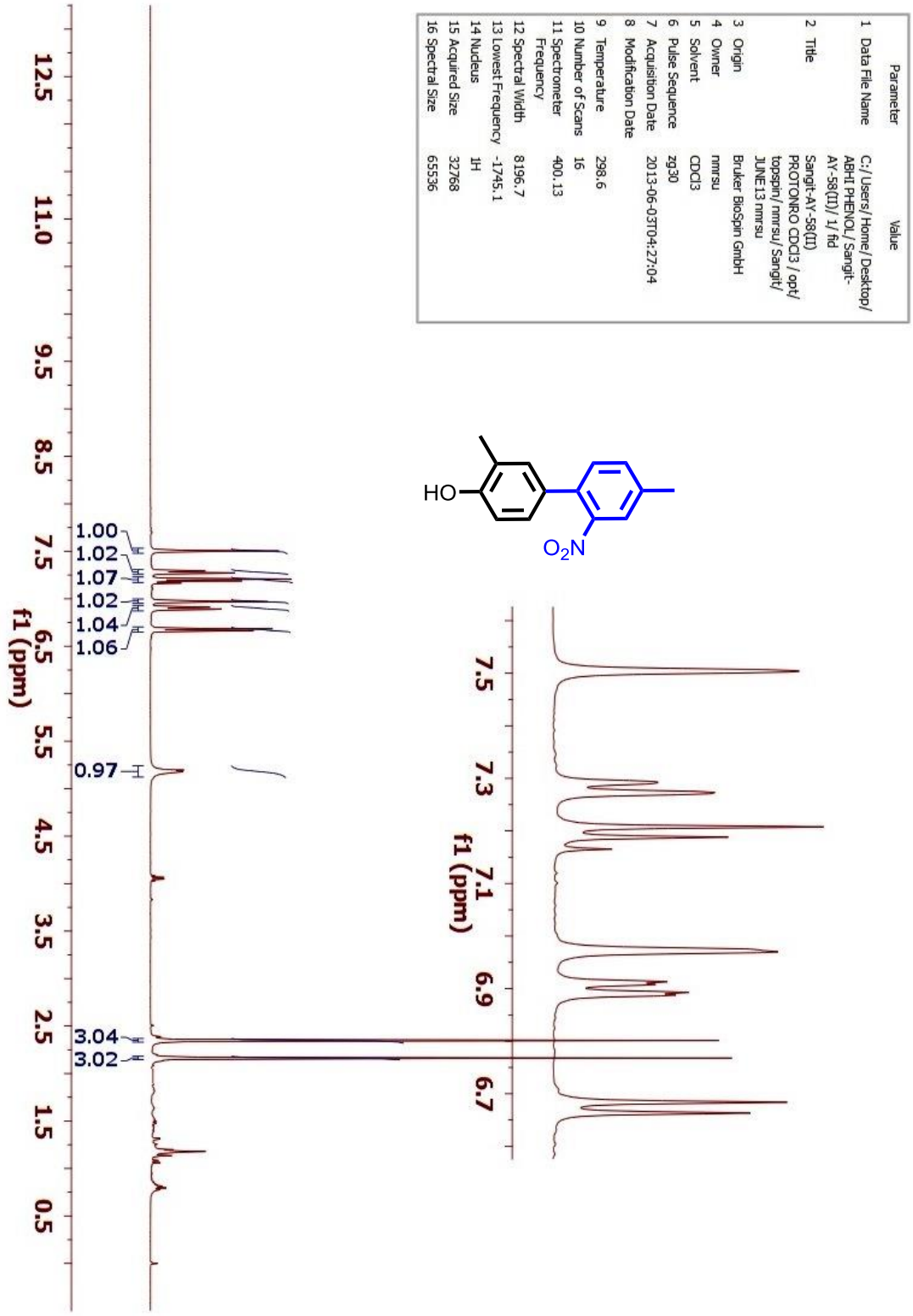


Figure S44 ^{13}C NMR spectrum of **22**

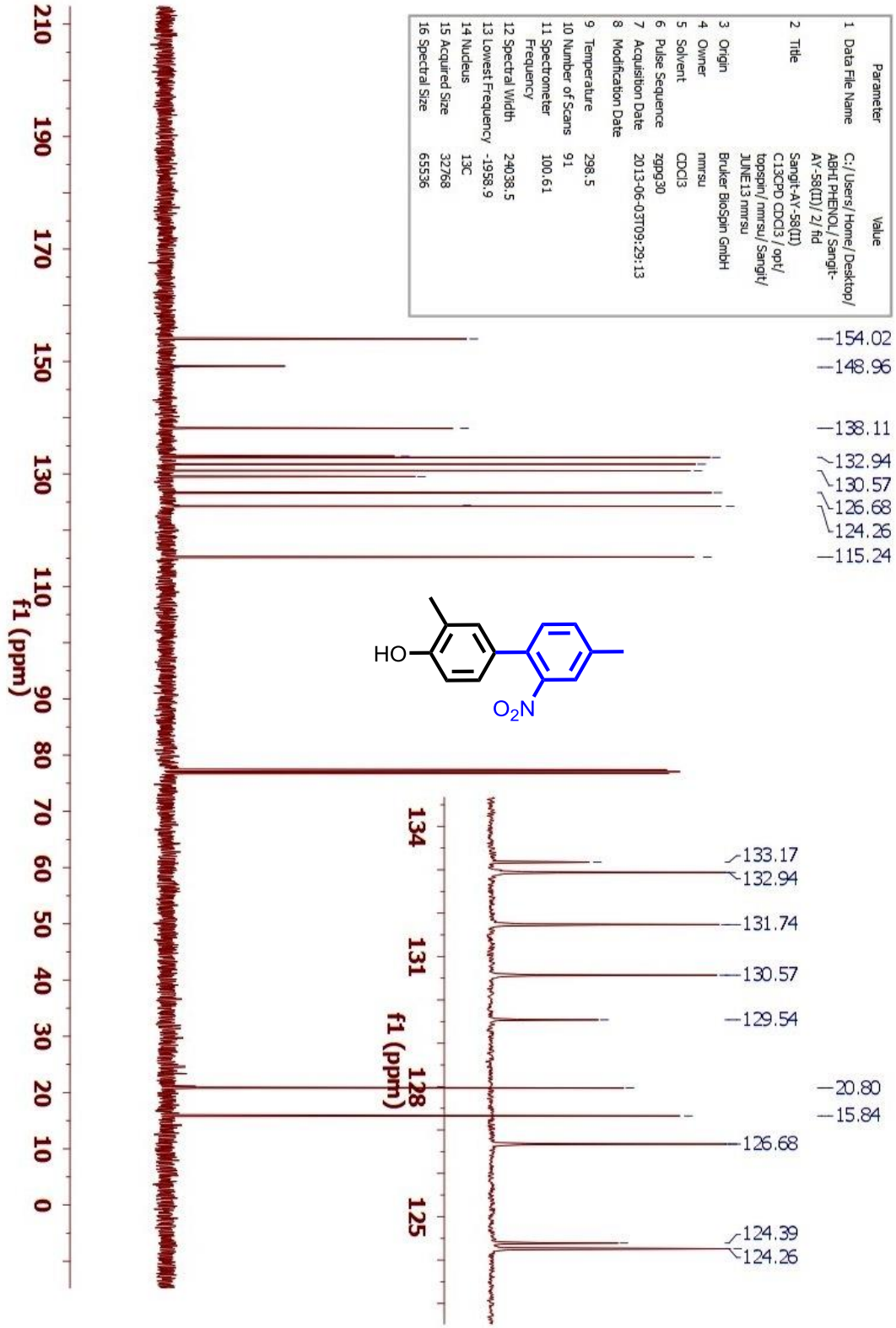


Figure S45 ^{1}H NMR spectrum of **23a&23b**

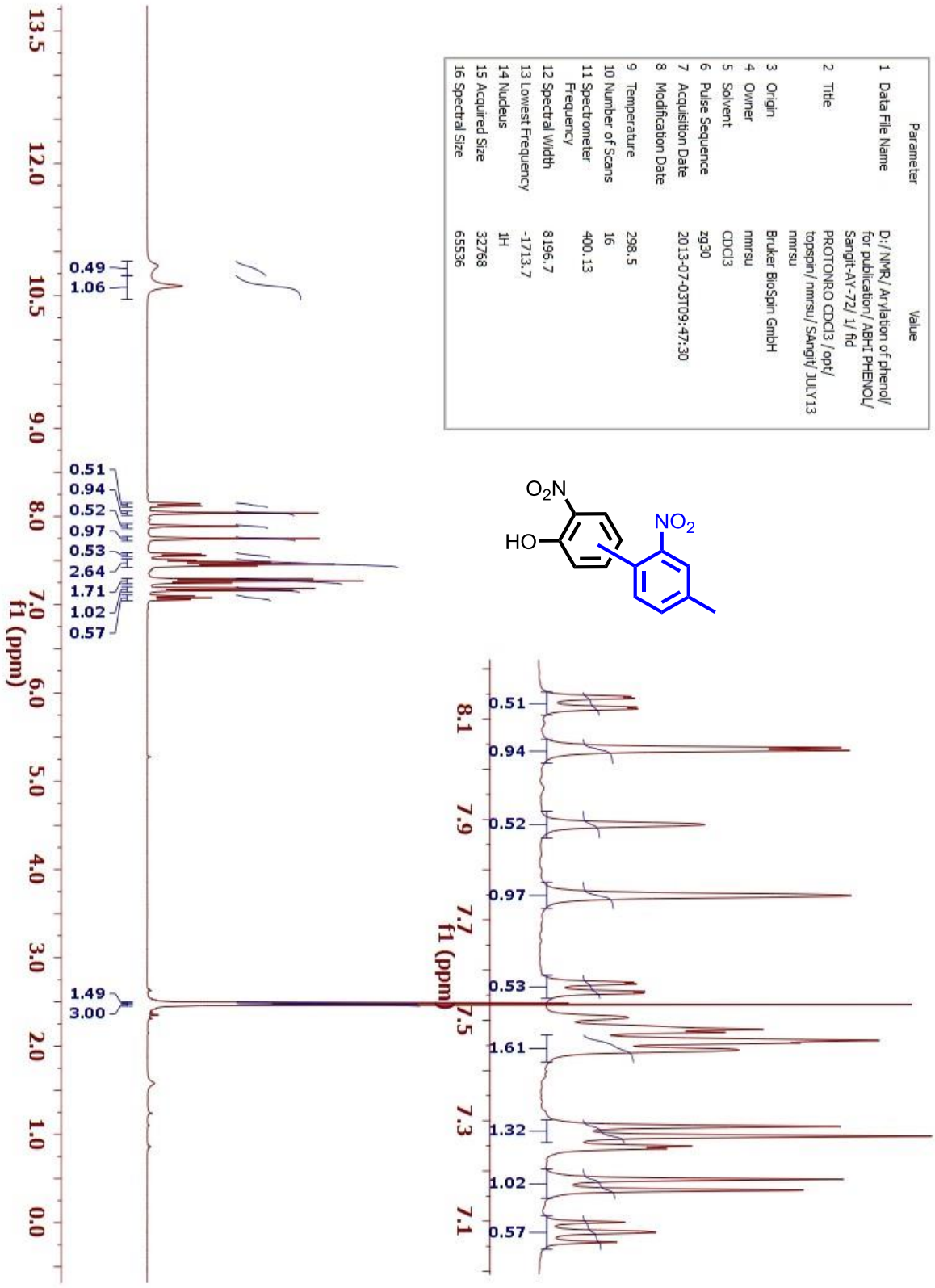


Figure S46 ^{13}C NMR spectrum of **23a&23b**

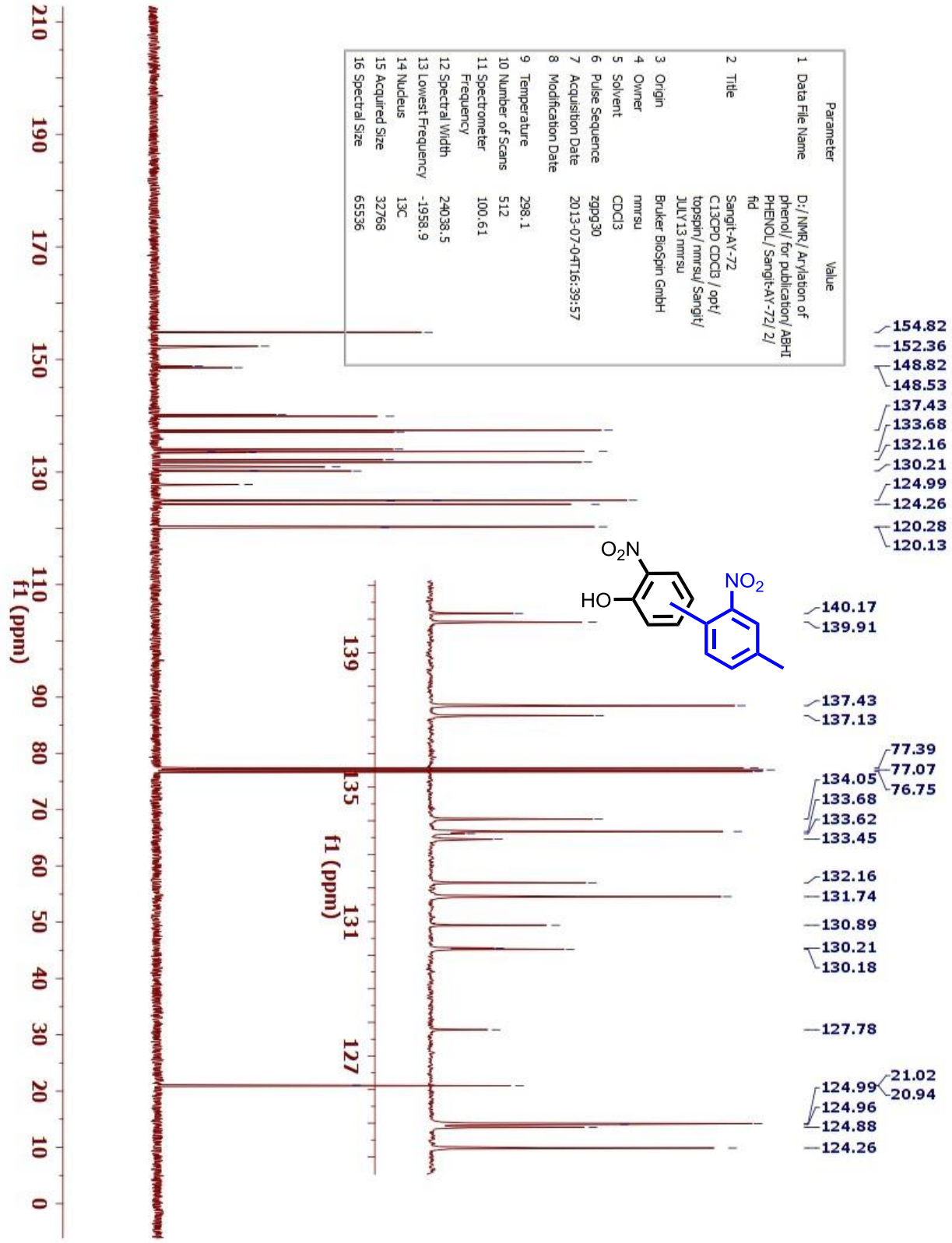


Figure S47 ^{1}H NMR spectrum of **24**

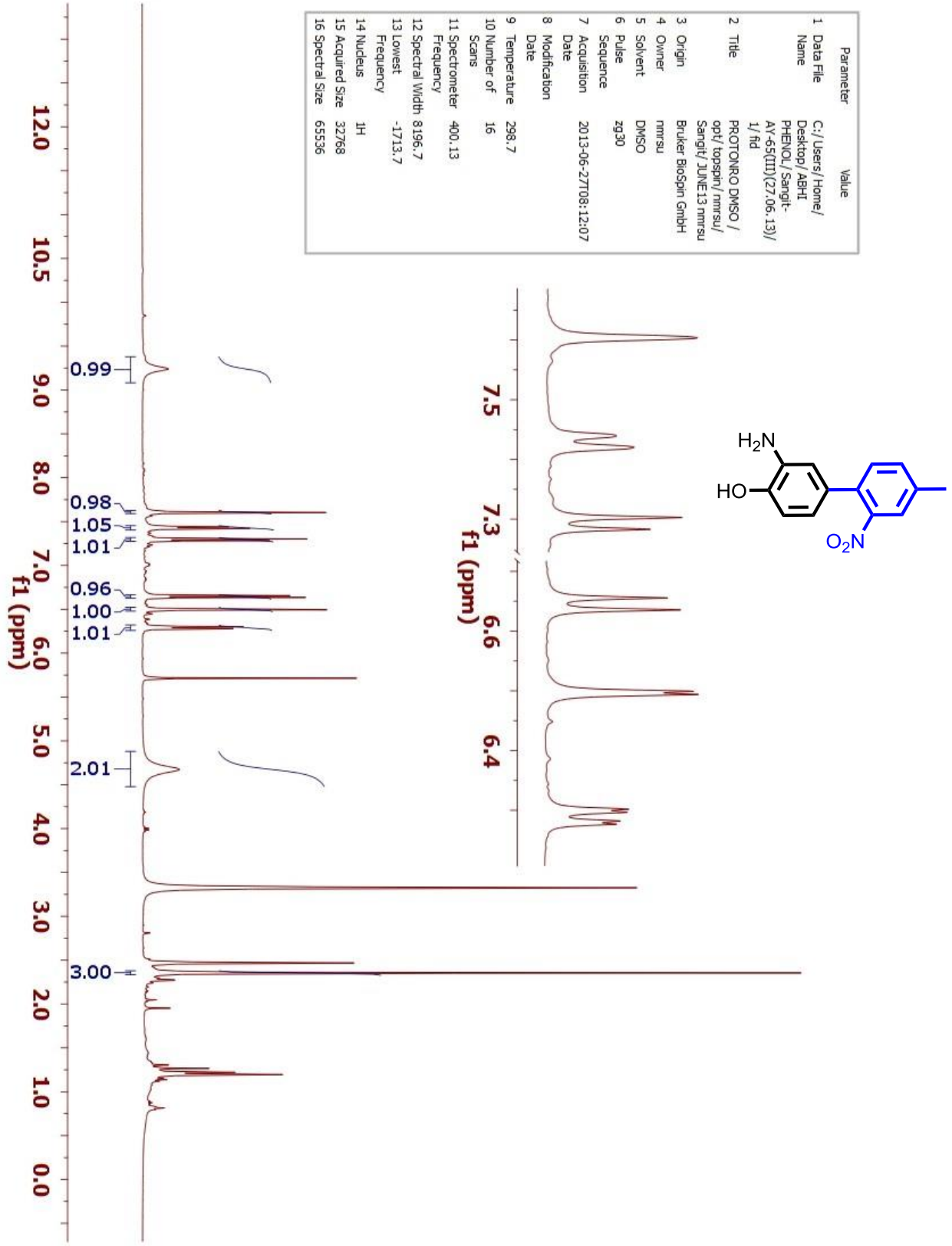


Figure S48 ^{13}C NMR spectrum of **24**

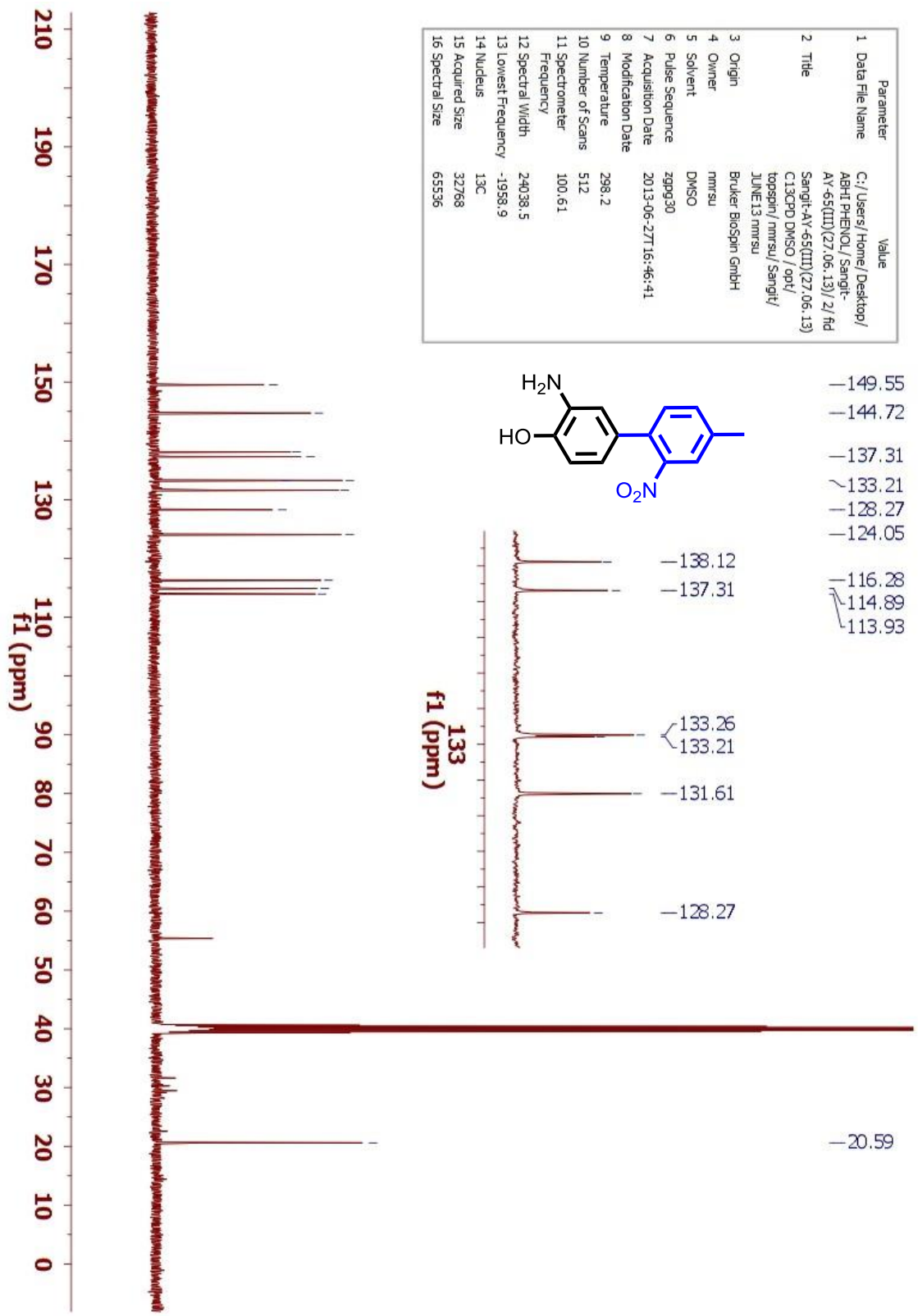


Figure S49 ^{1}H NMR spectrum of **25**

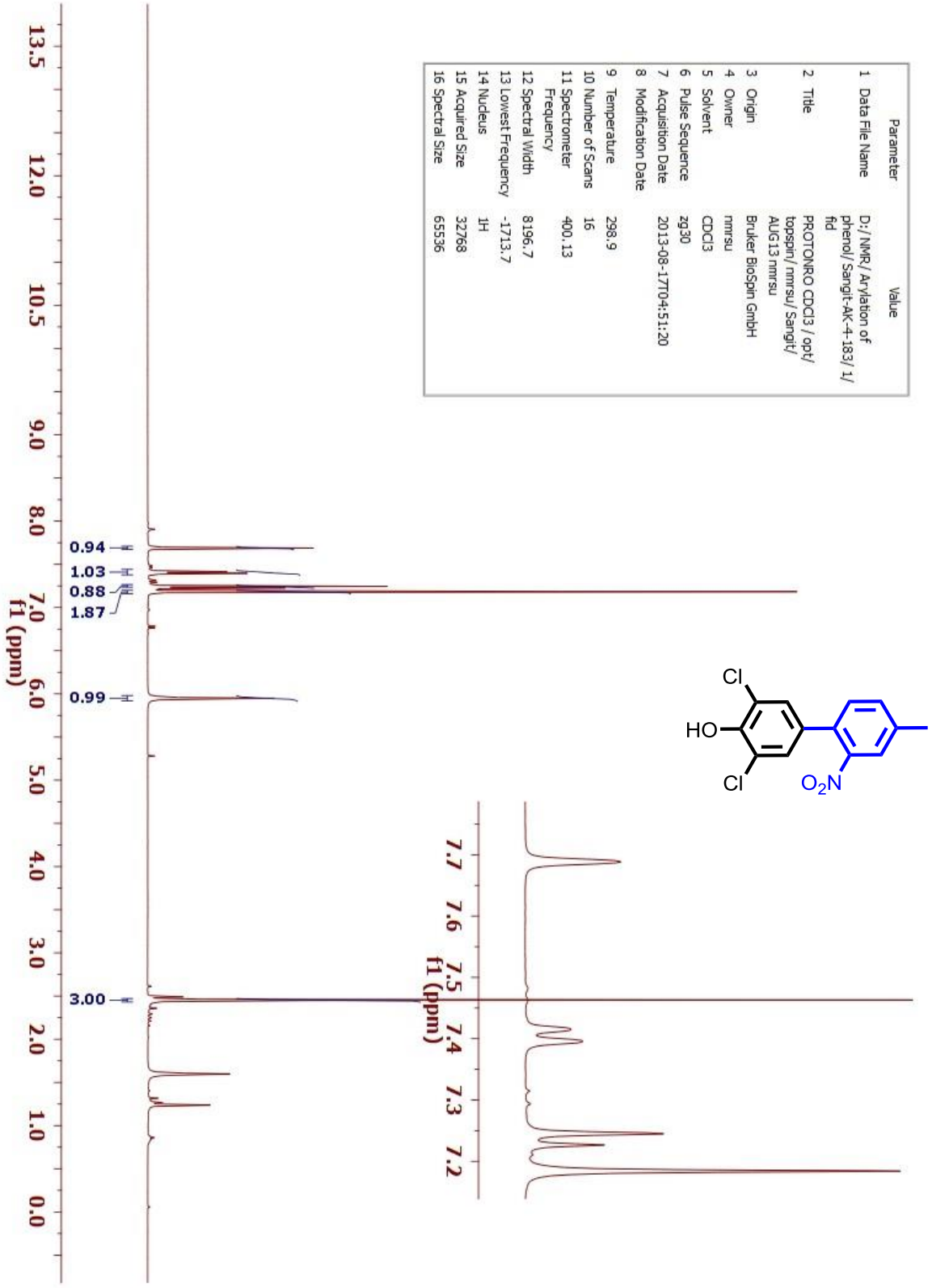


Figure S50 ^{13}C NMR spectrum of **25**

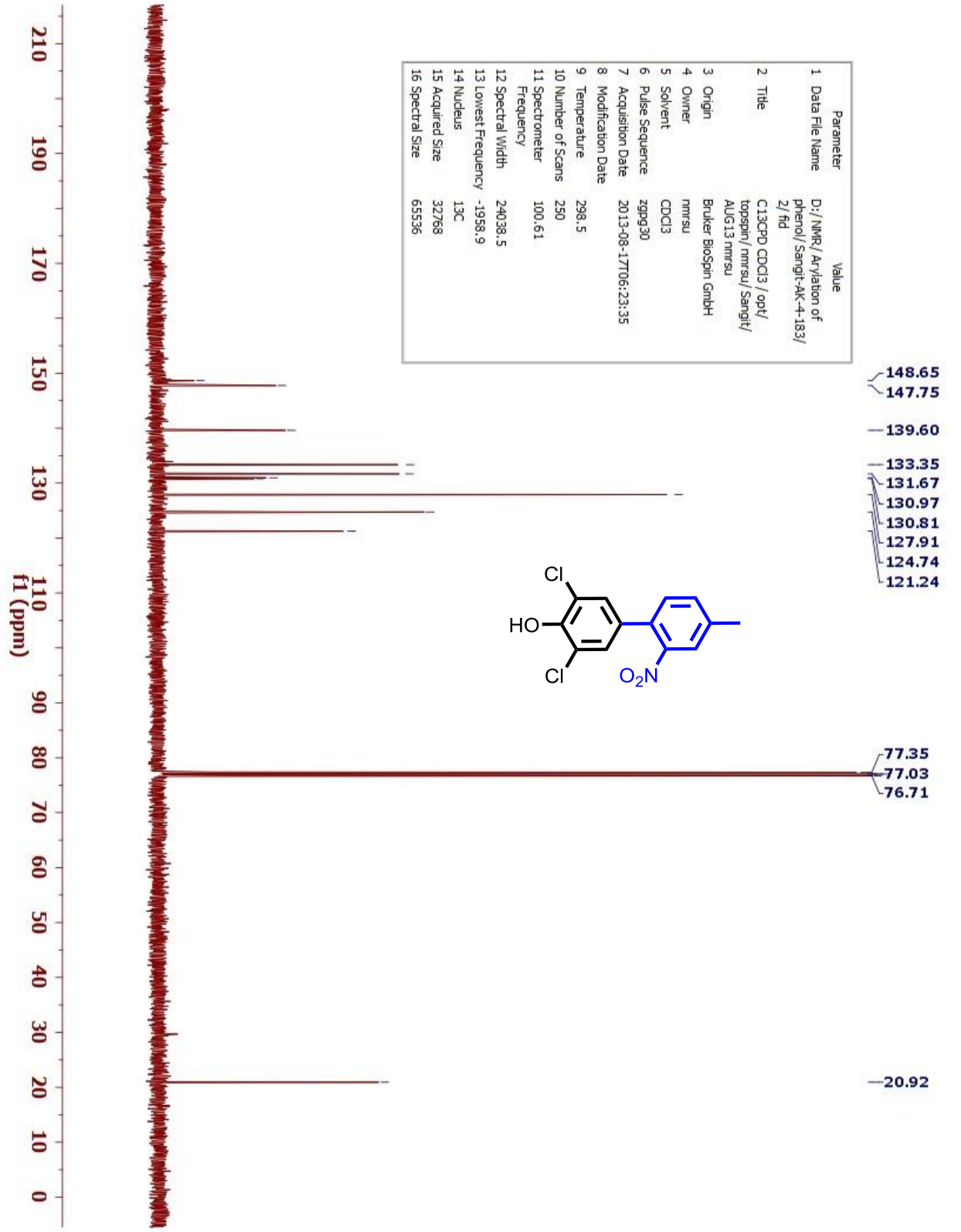


Figure S51 ^{1}H NMR spectrum of **26**

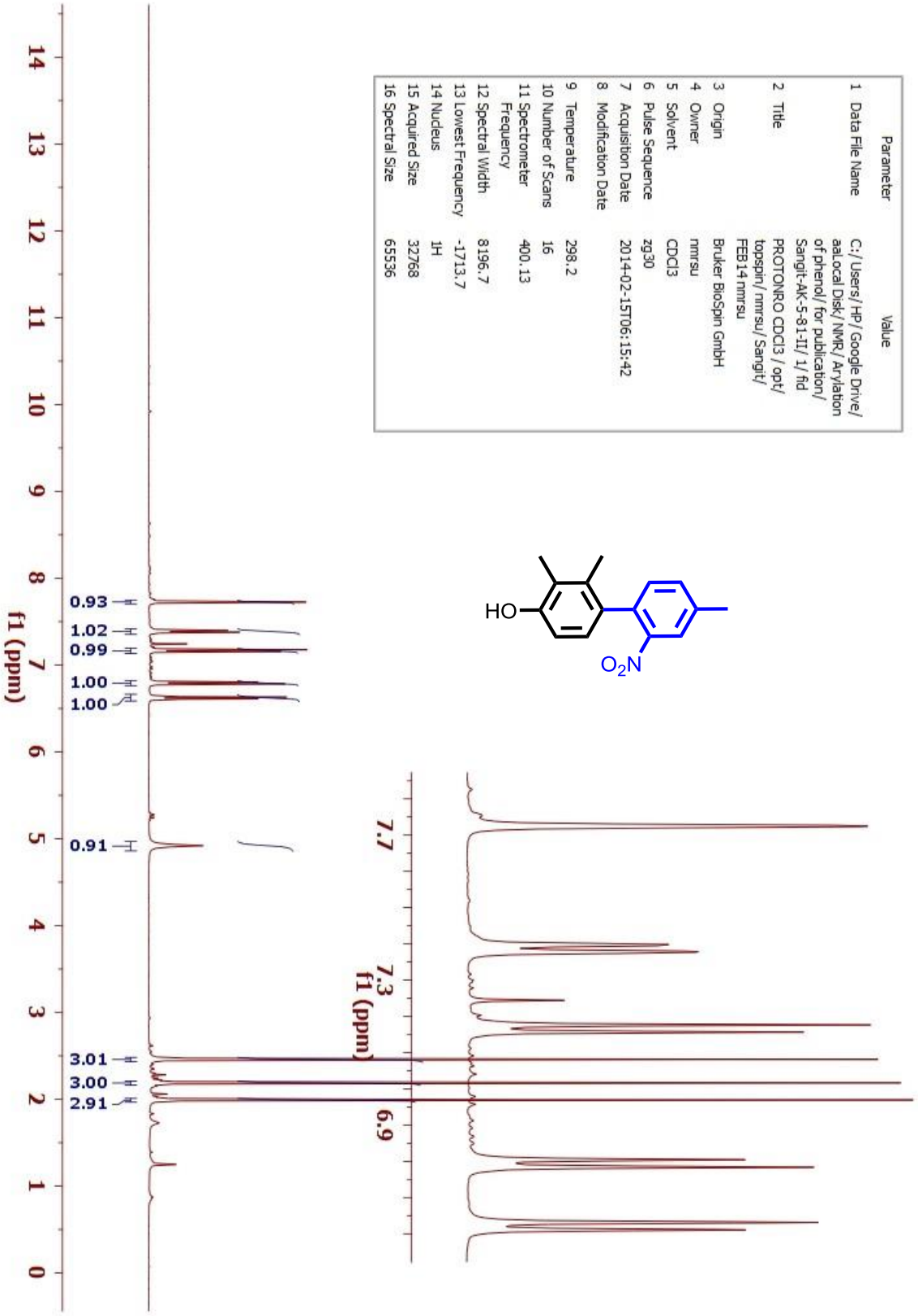


Figure S52 ^{13}C NMR spectrum of **26**

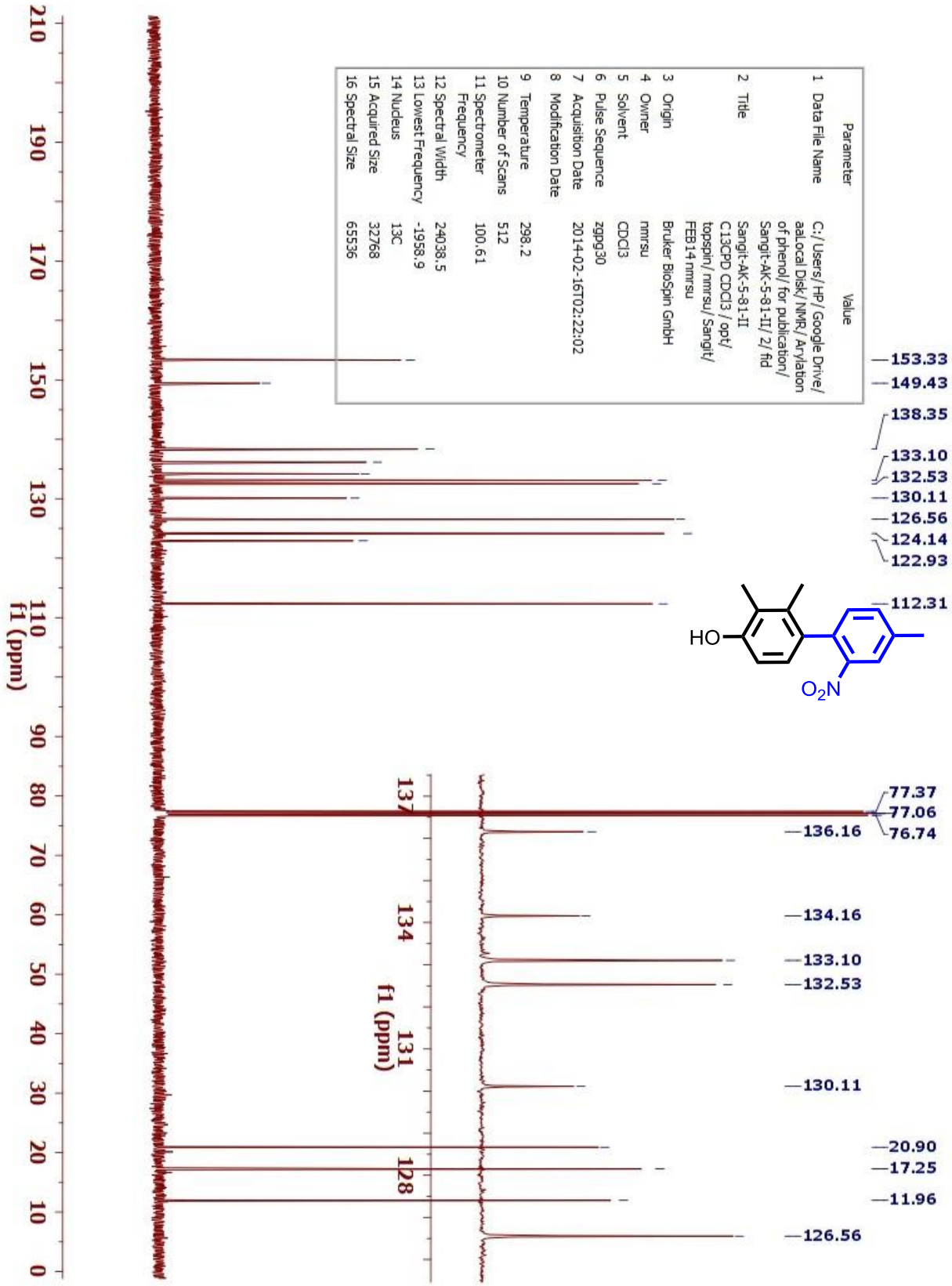


Figure S53 ^{1}H NMR spectrum of **27**

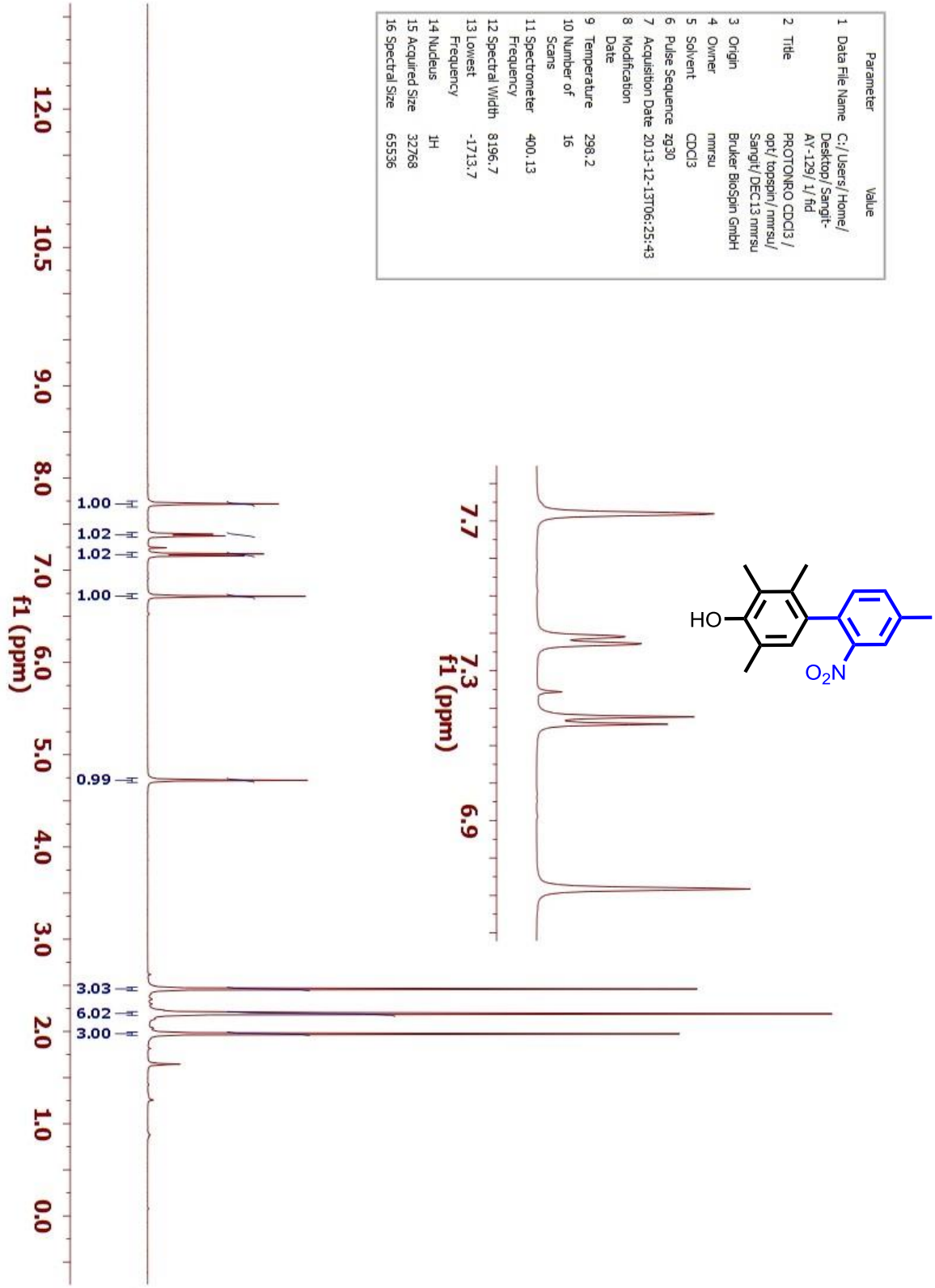


Figure S54 ^{13}C NMR spectrum of **27**

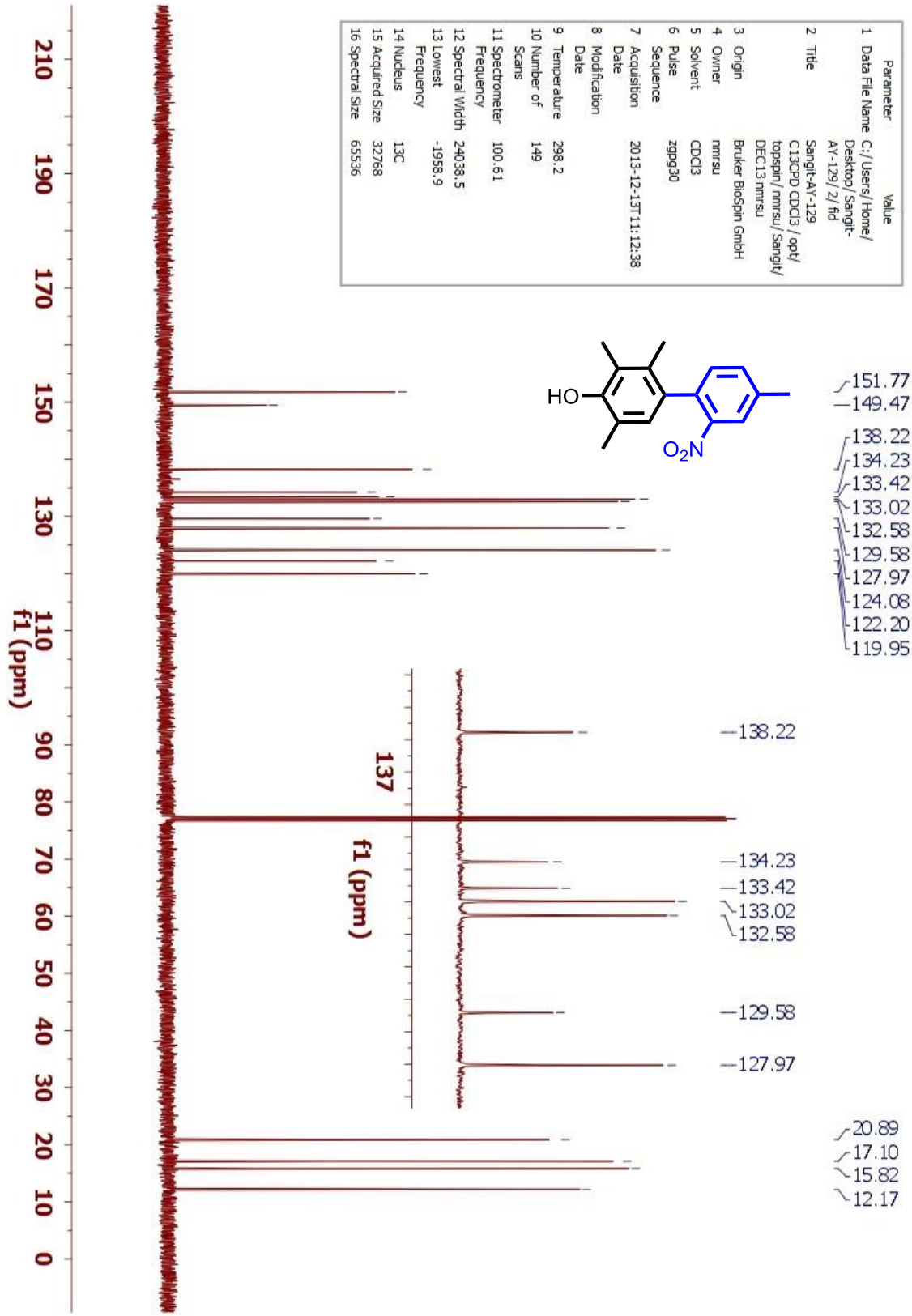


Figure S55 ^{1}H NMR spectrum of **28**

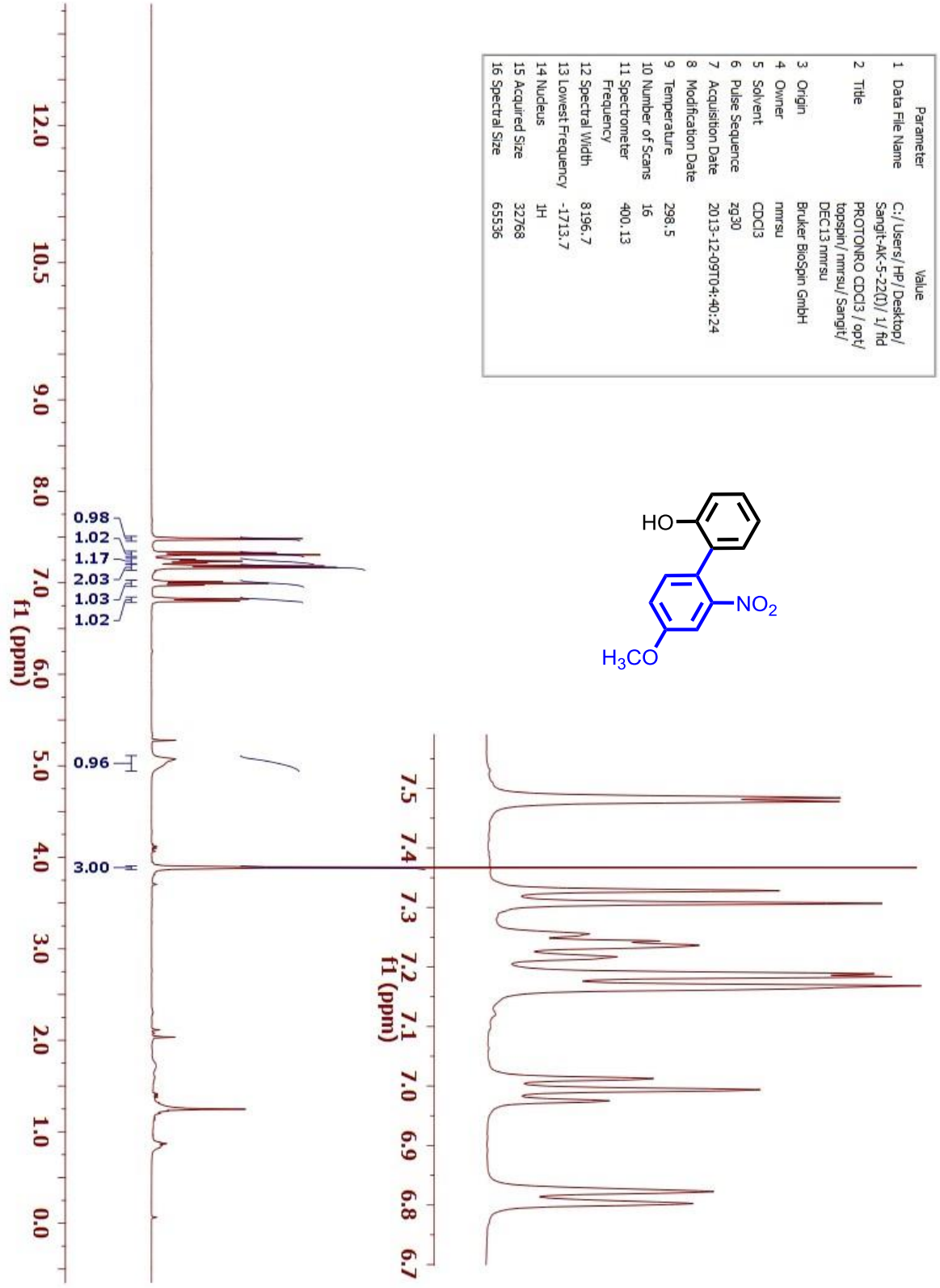


Figure S56 ^{13}C NMR spectrum of **28**

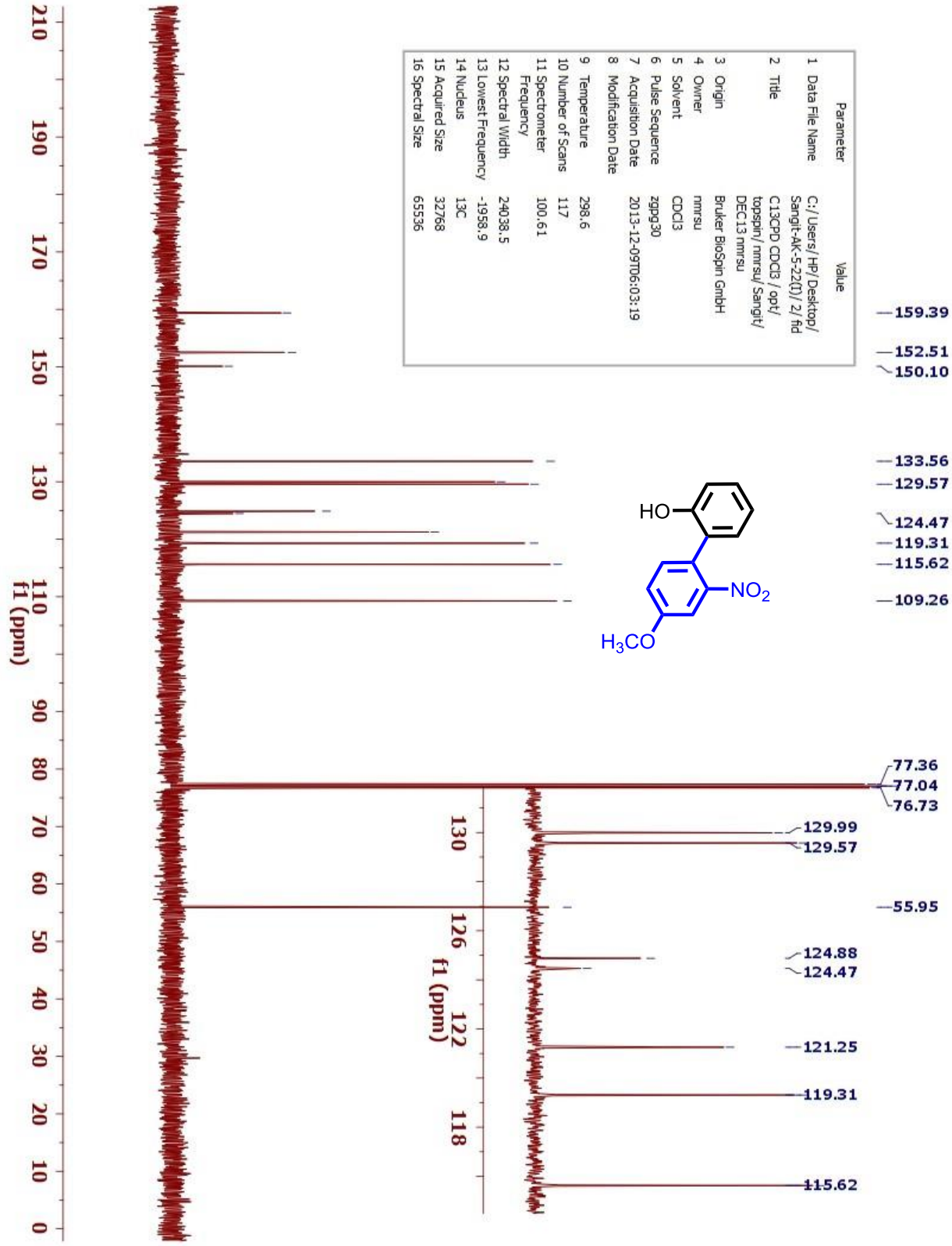


Figure S57 ^{1}H NMR spectrum of **29**

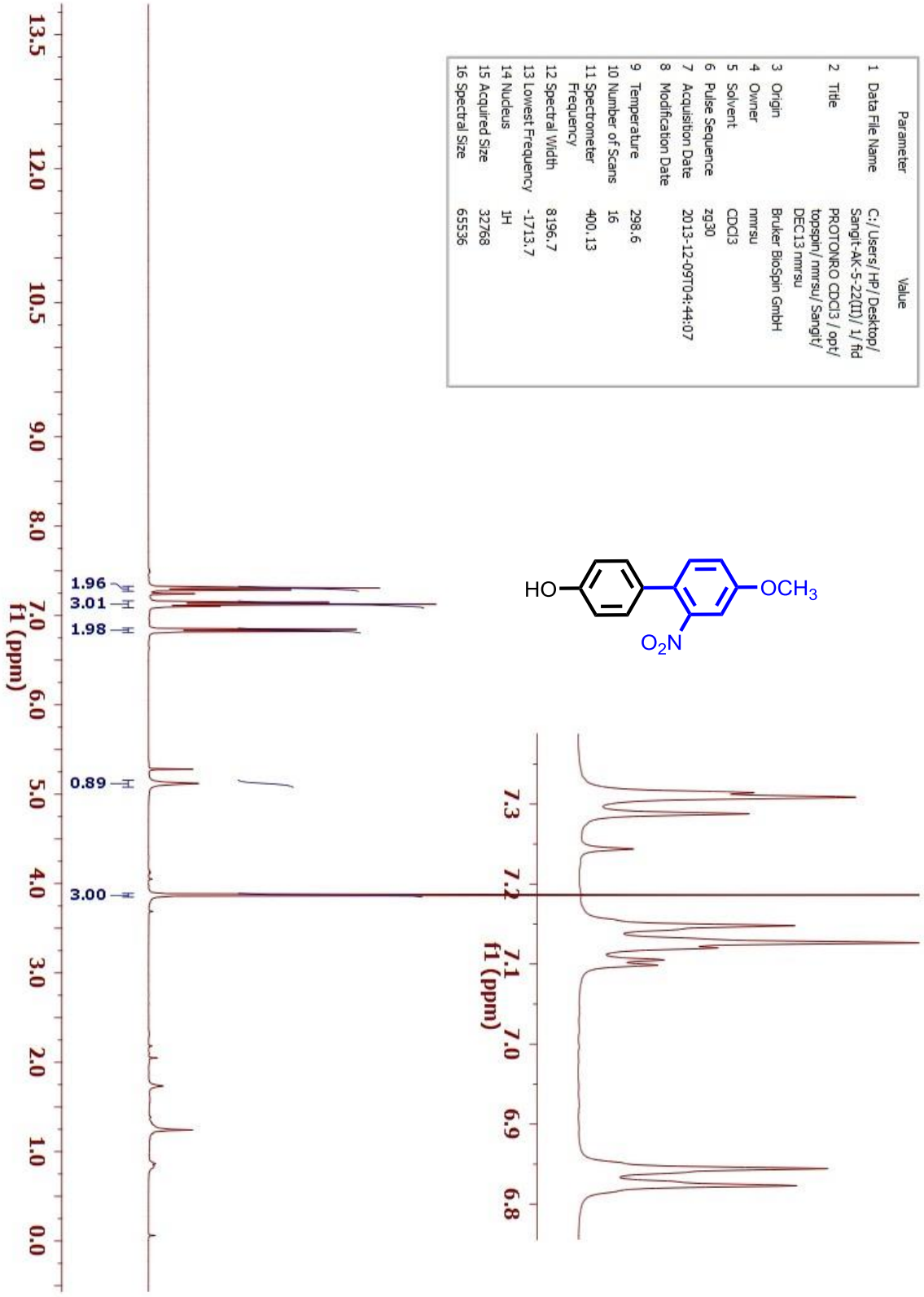


Figure S58 ^{13}C NMR spectrum of **29**

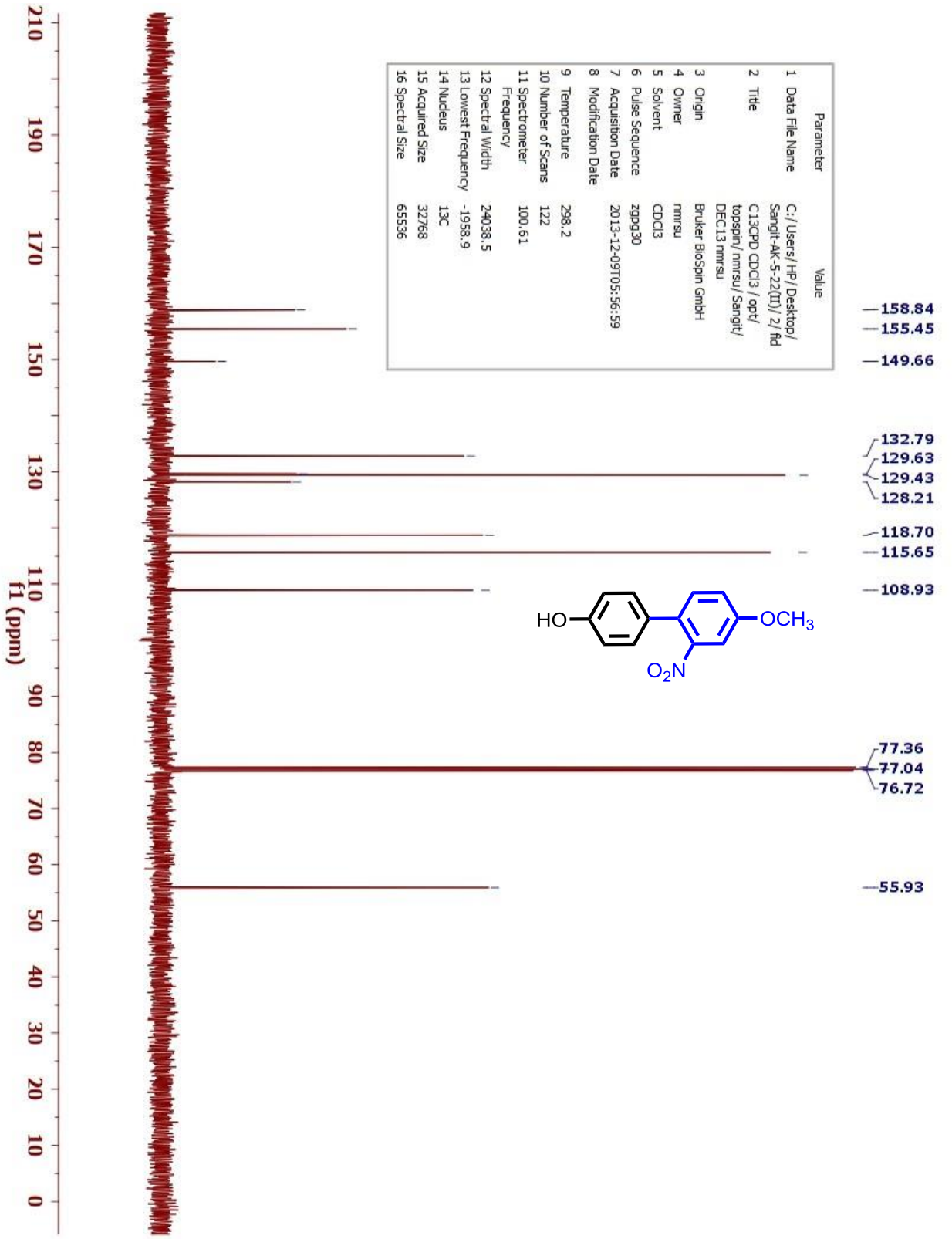


Figure S59 ^{1}H NMR spectrum of **30**

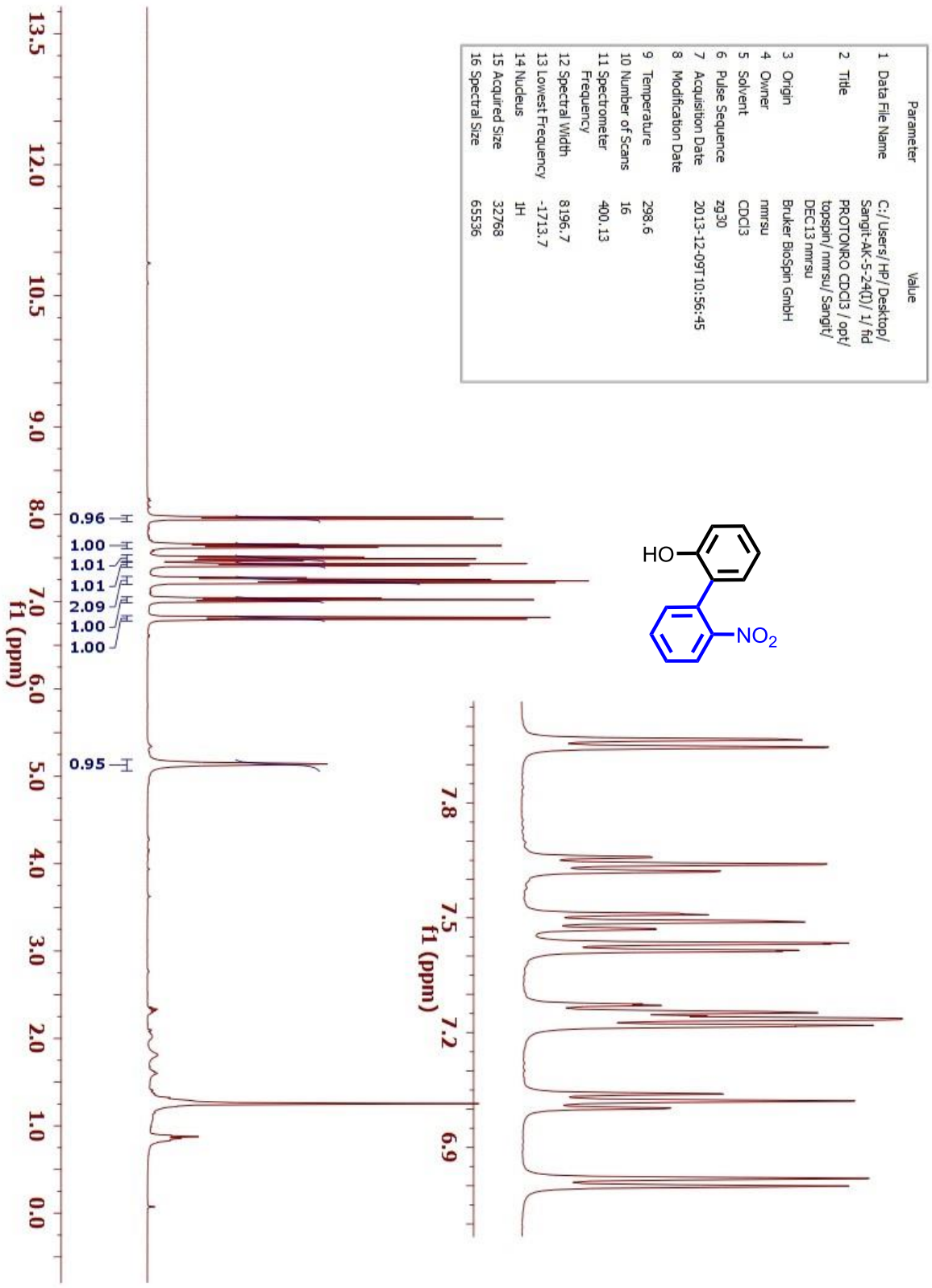


Figure S60 ^{13}C NMR spectrum of **30**

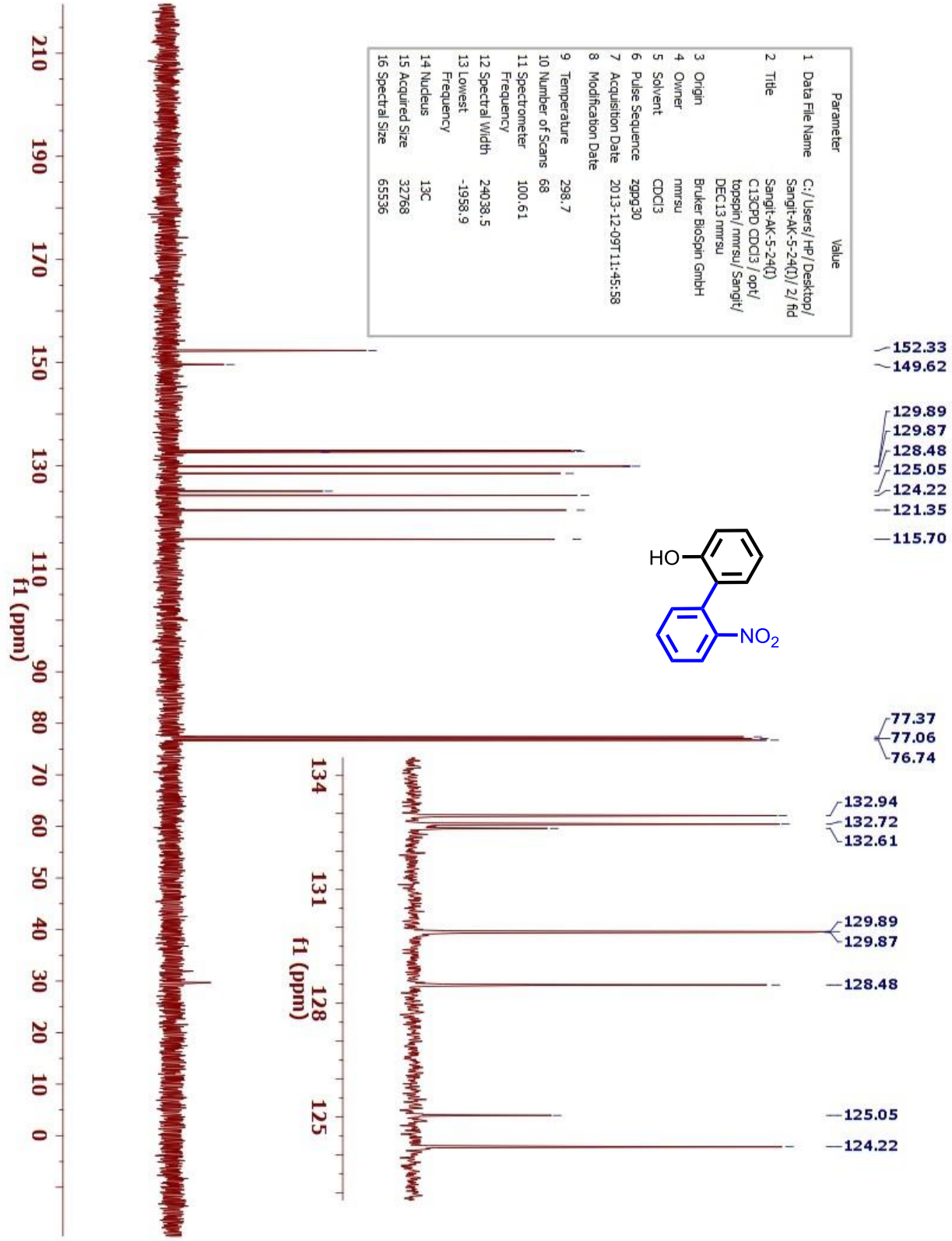


Figure S61 ^{1}H NMR spectrum of **31**

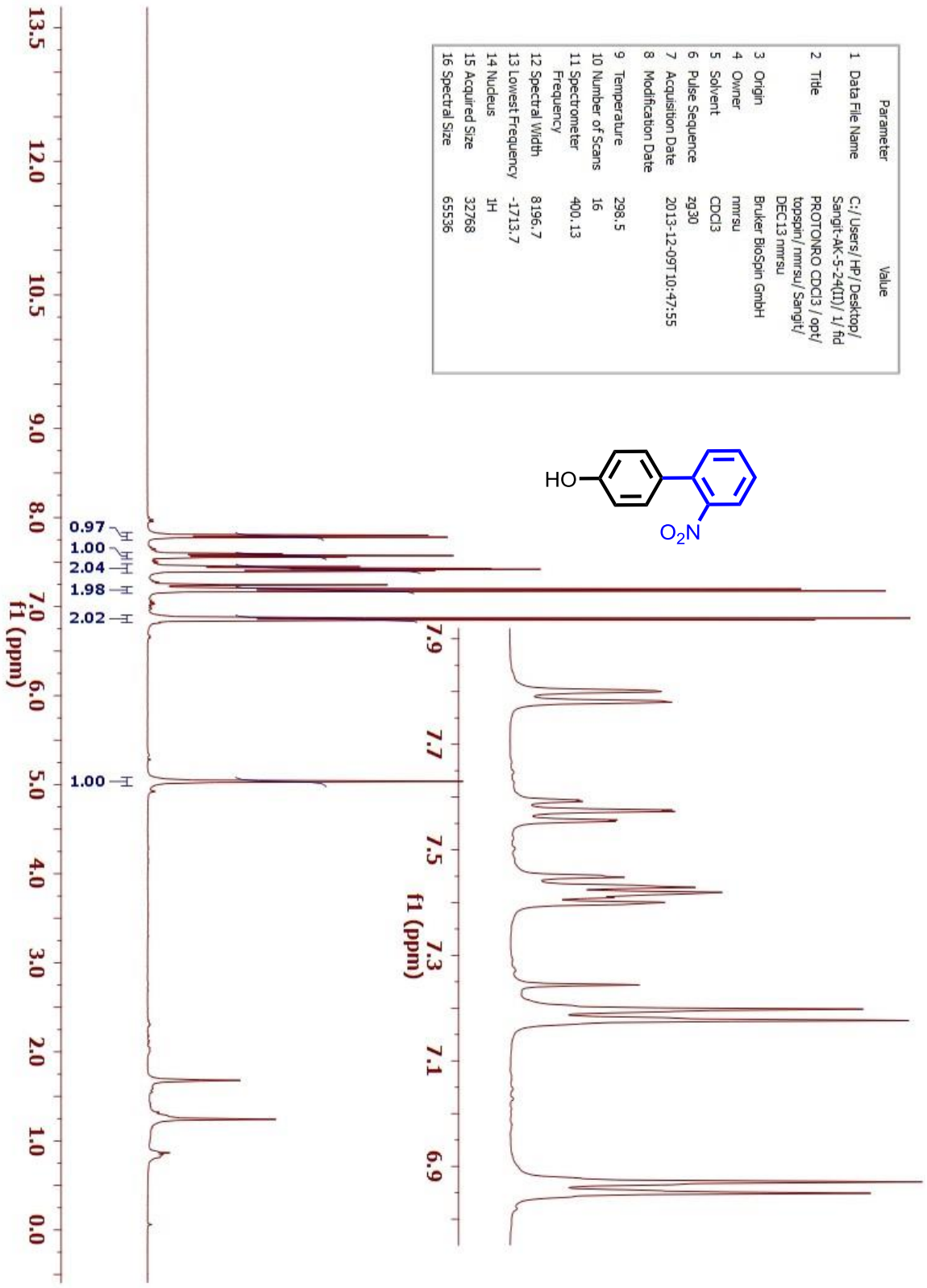


Figure S62 ^{13}C NMR spectrum of **31**

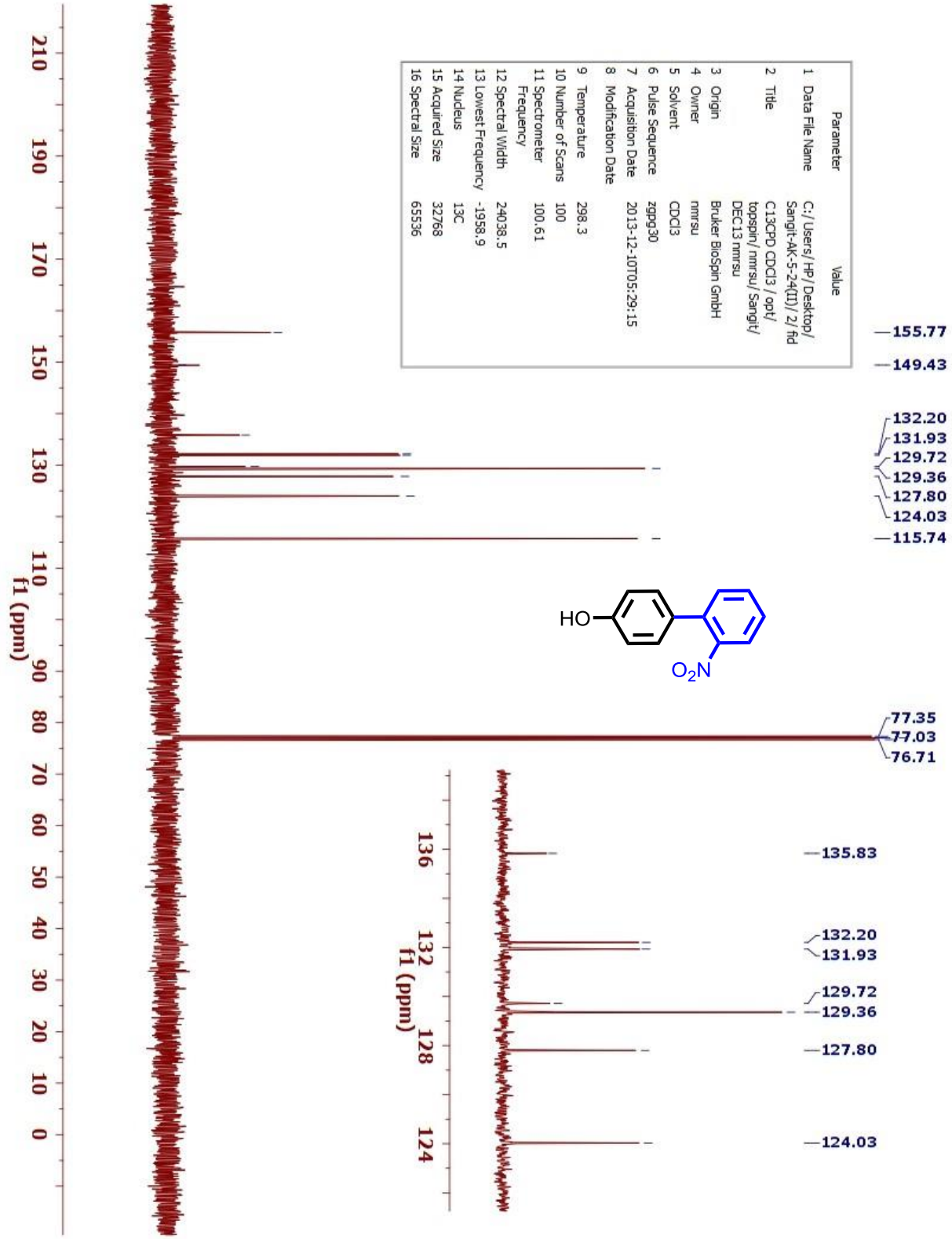


Figure S63 ^{1}H NMR spectrum of **32**

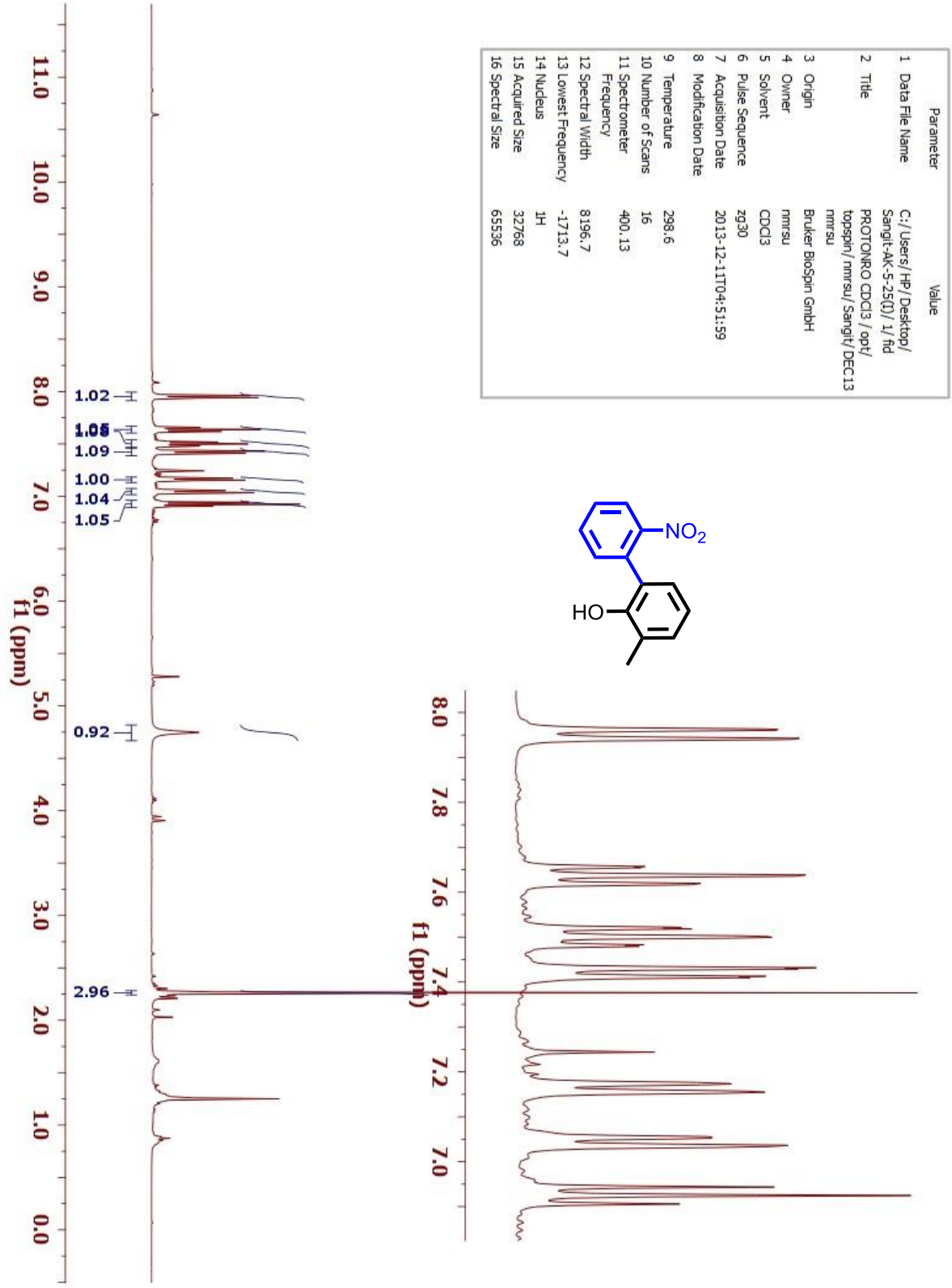


Figure S64 ^{13}C NMR spectrum of **32**

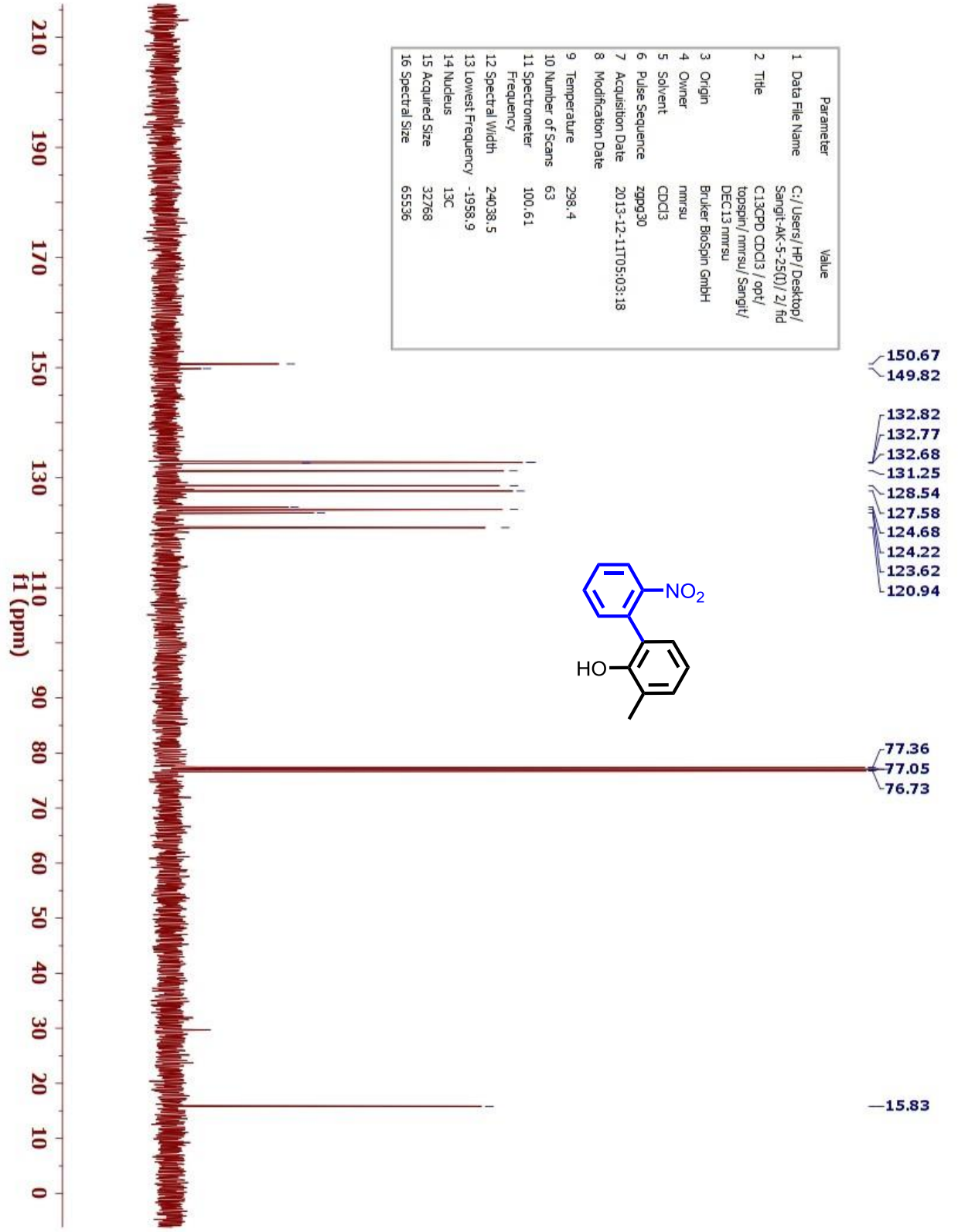


Figure S65 ^{1}H NMR spectrum of **33**

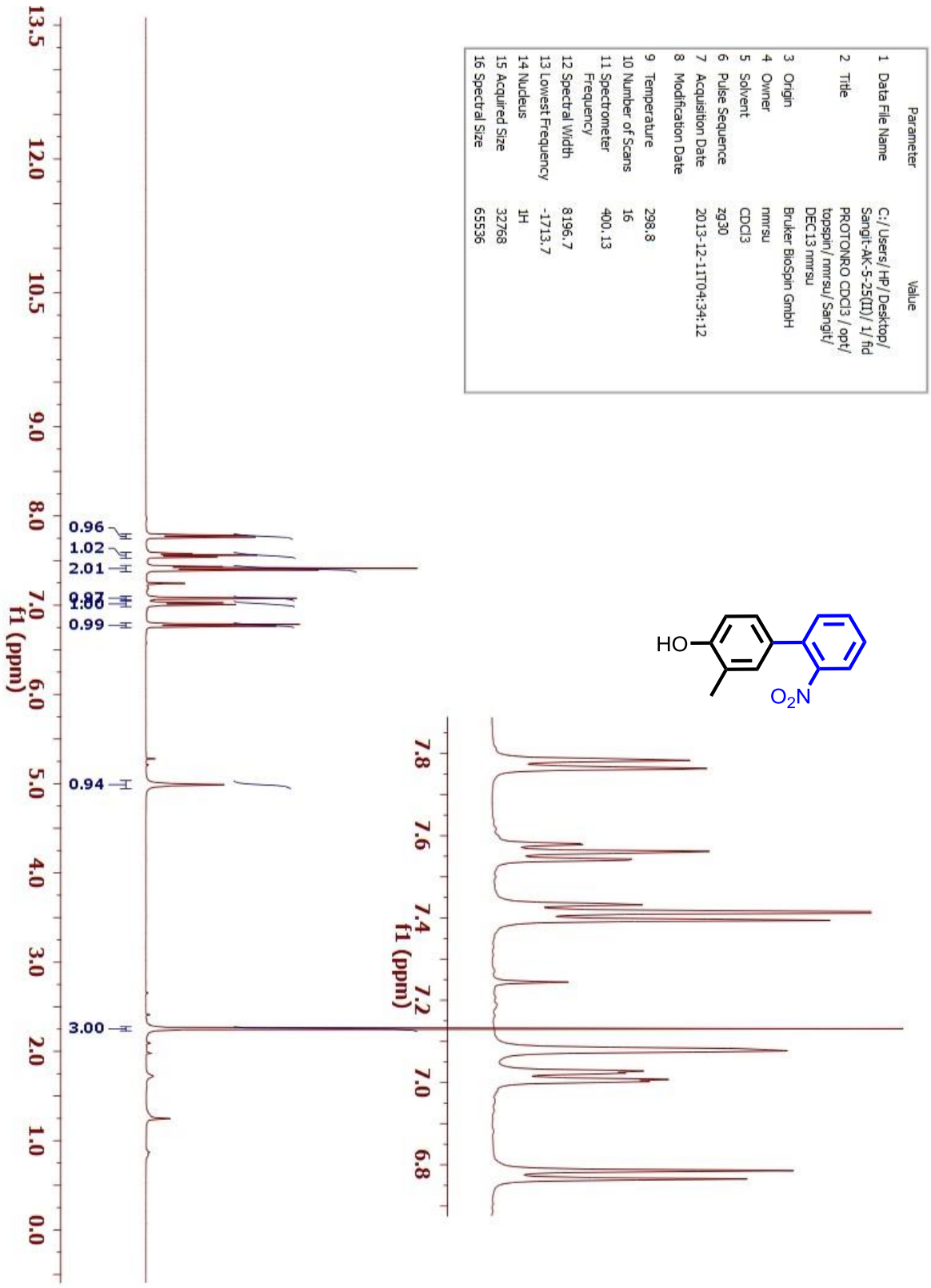


Figure S66 ^{13}C NMR spectrum of **33**

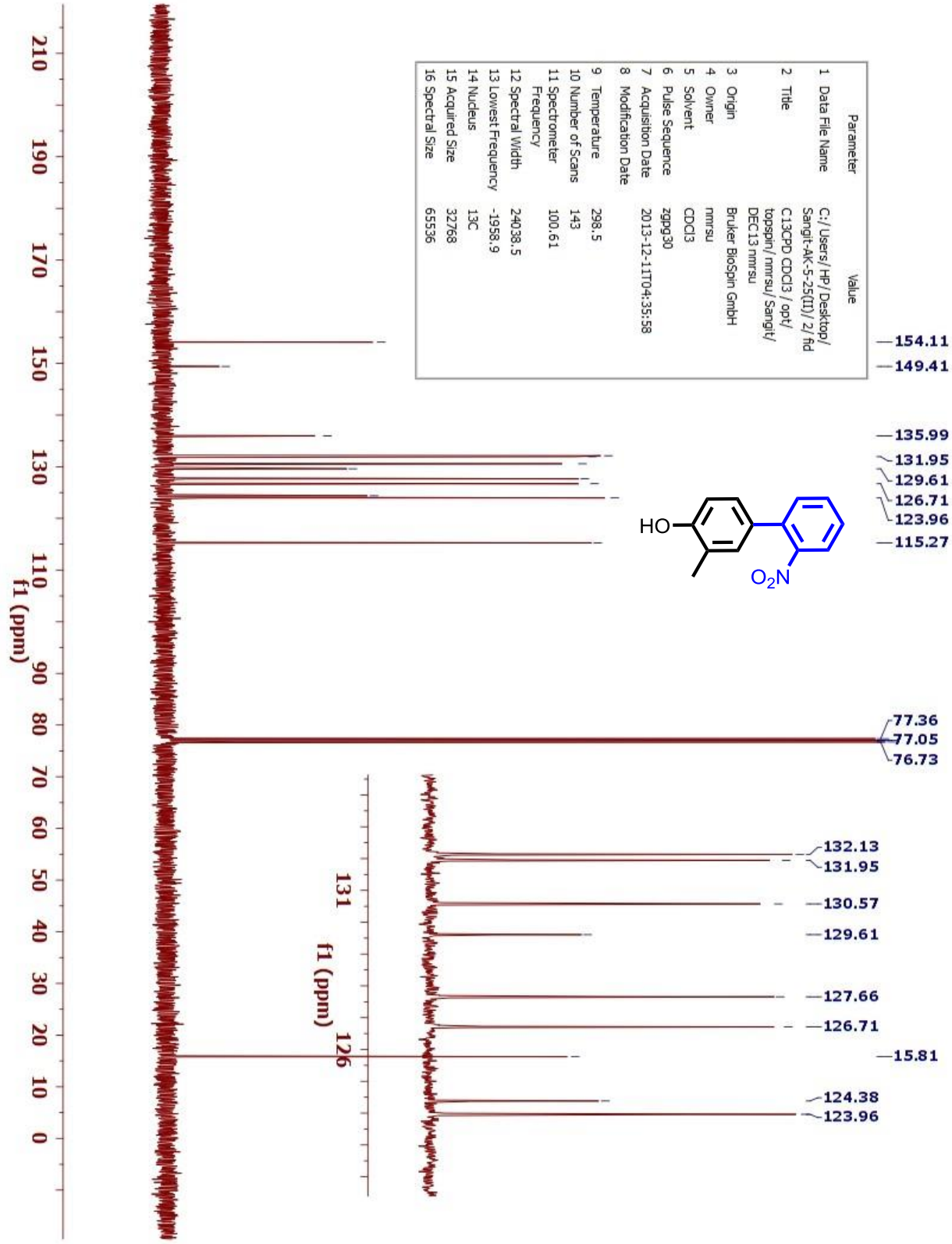


Figure S67 ^{1}H NMR spectrum of **34**

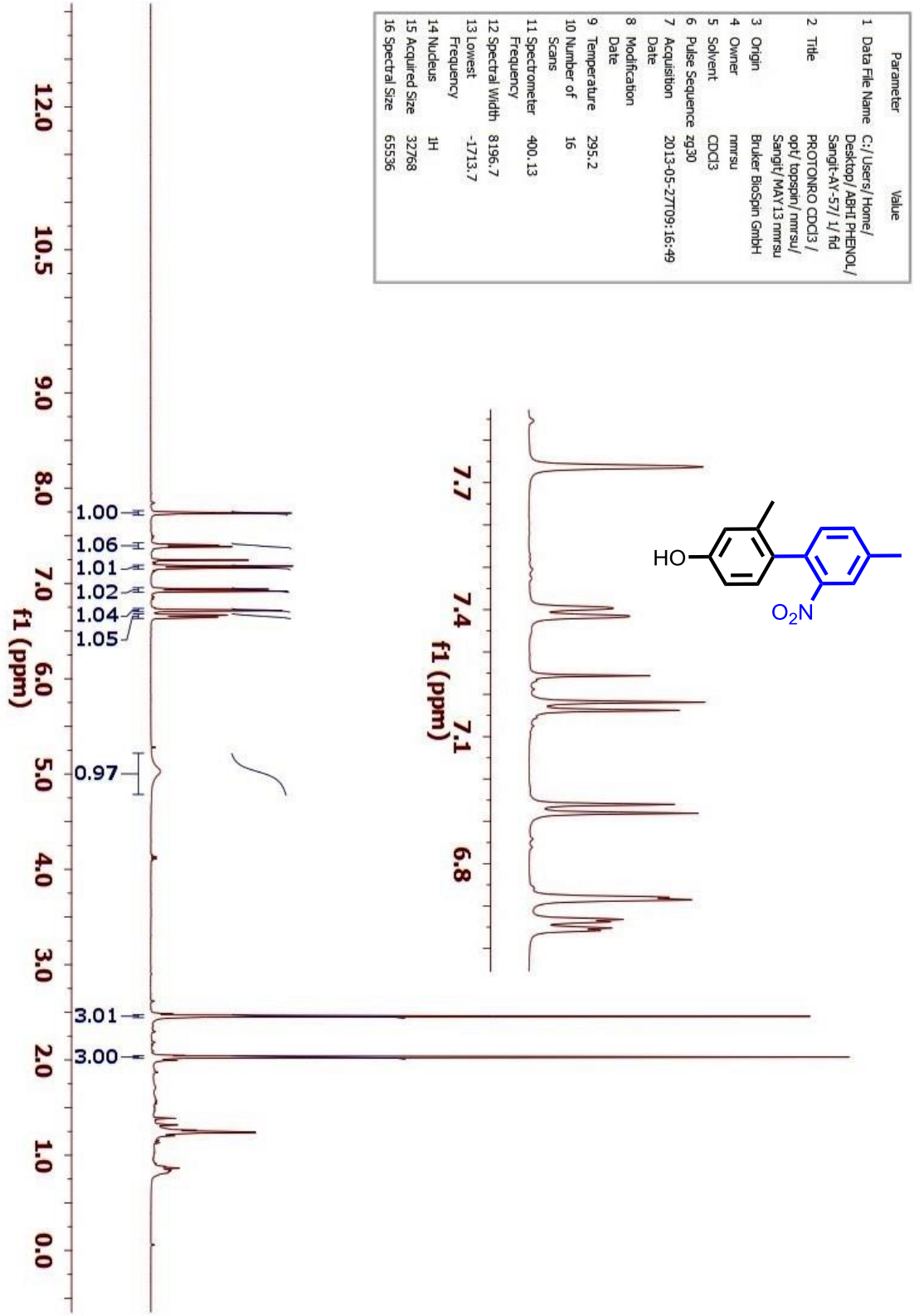
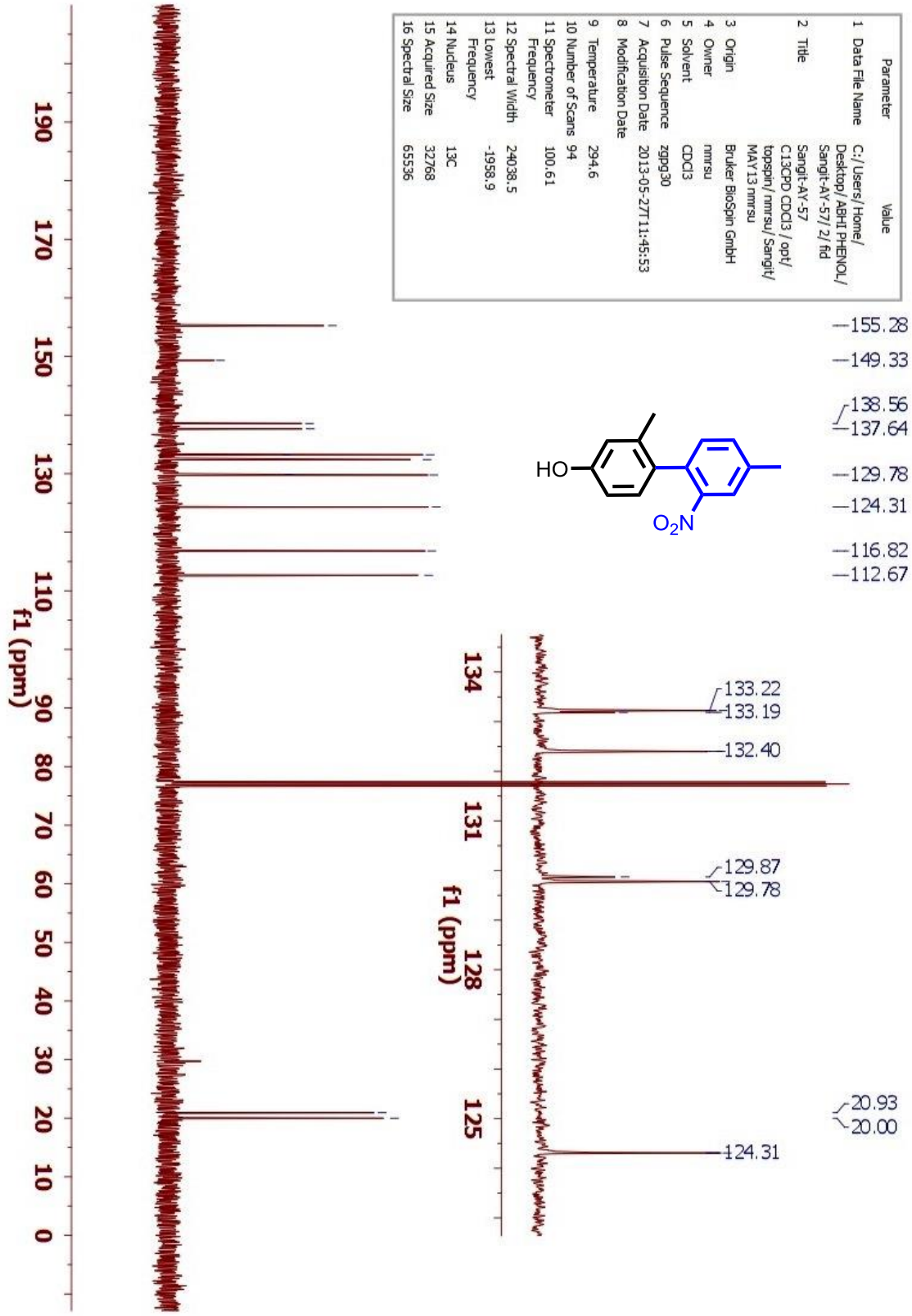


Figure S68 ^{13}C NMR spectrum of **34**



Figure

Figure S69 ^{1}H NMR spectrum of **35**

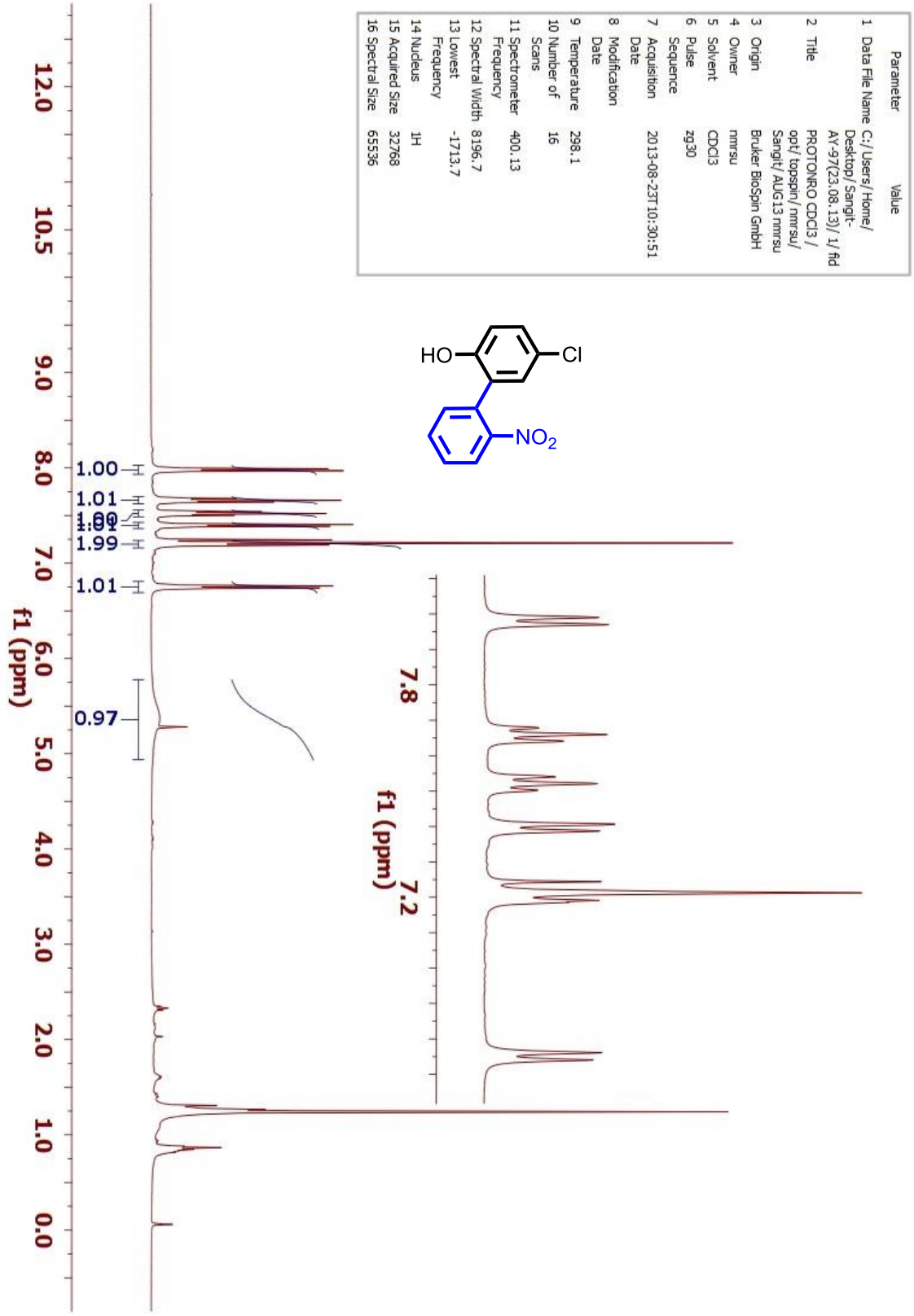


Figure S70 ^{13}C NMR spectrum of **35**

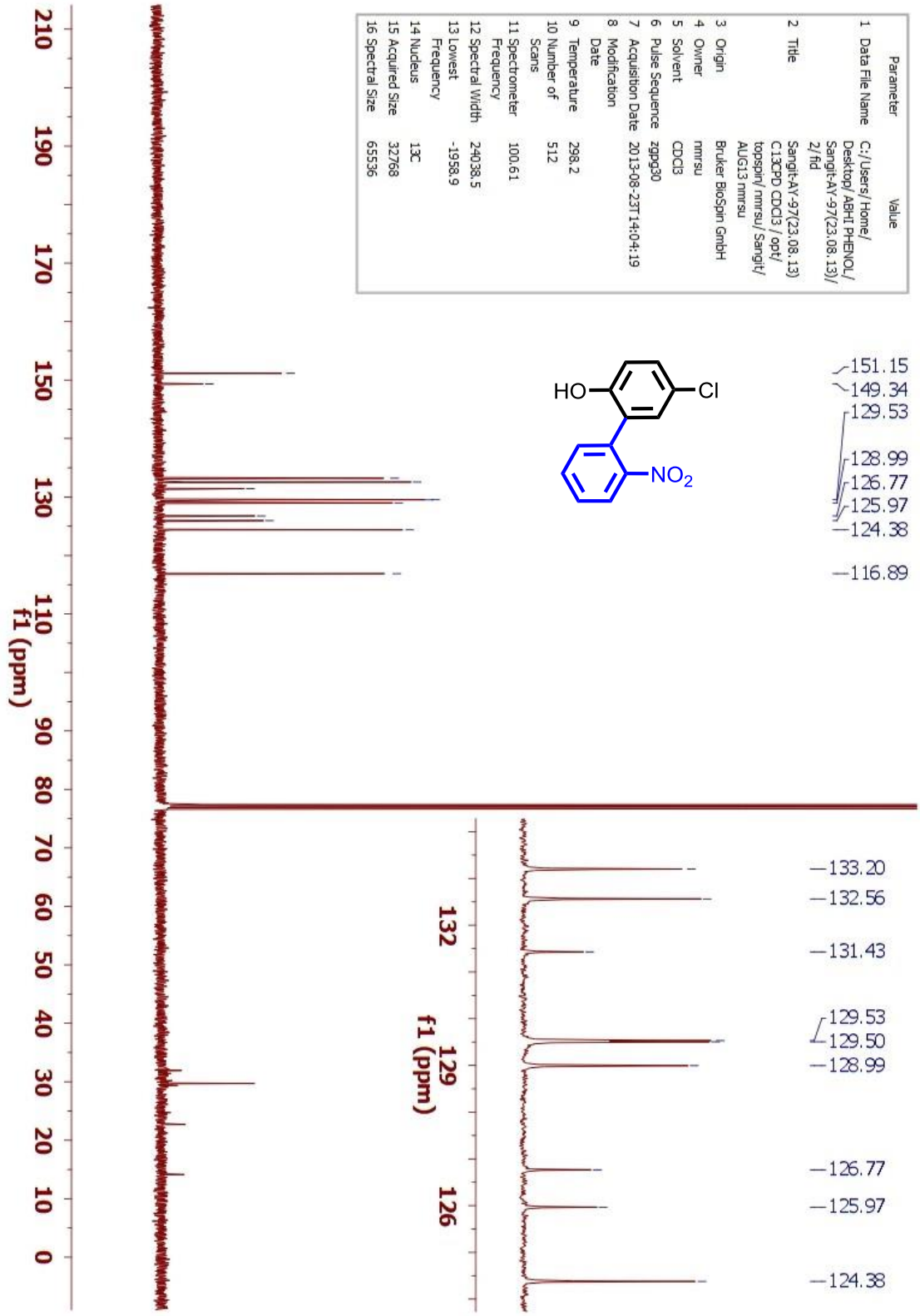


Figure S71 ^{1}H NMR spectrum of **36**

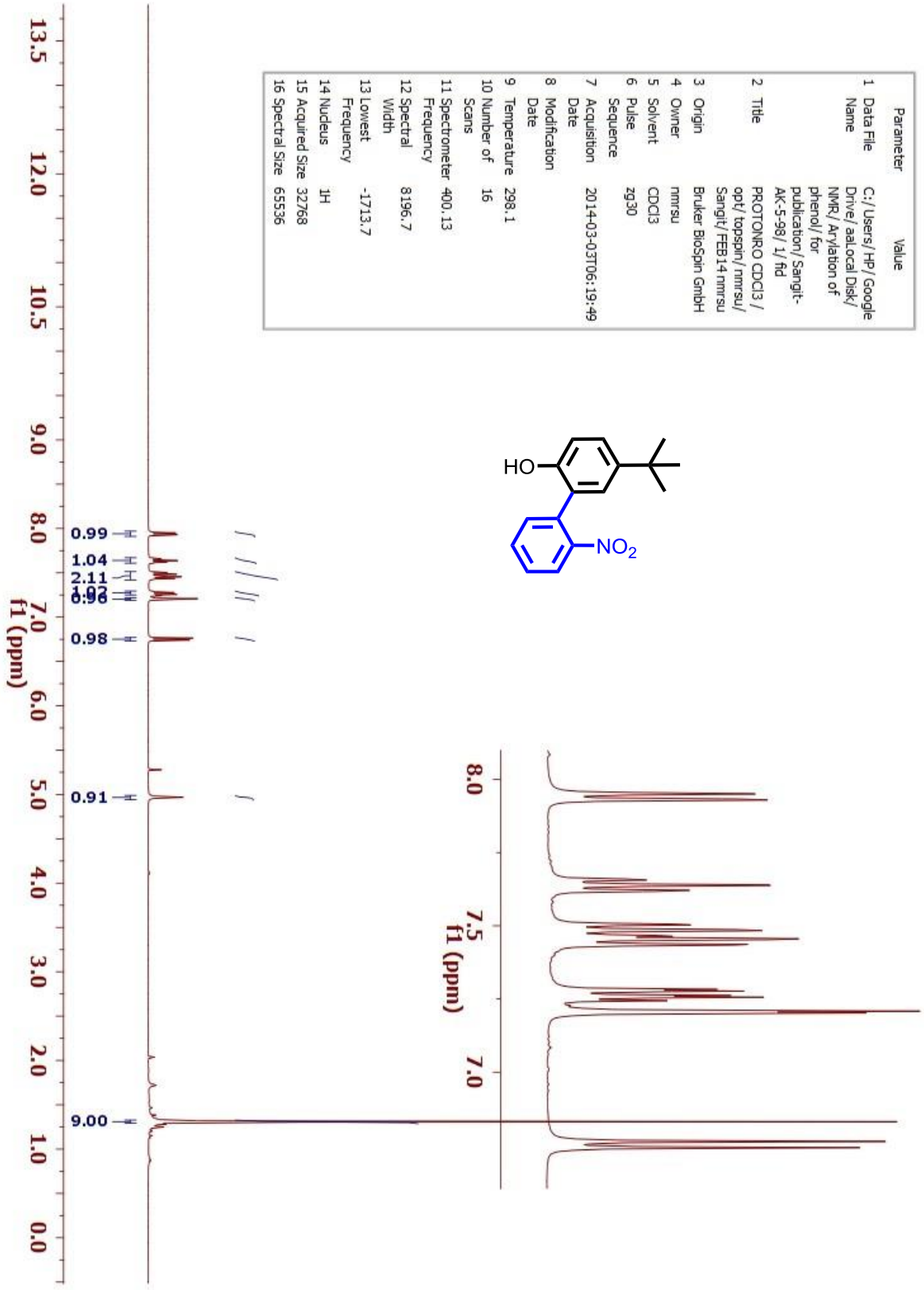


Figure S72 ^{13}C NMR spectrum of **36**

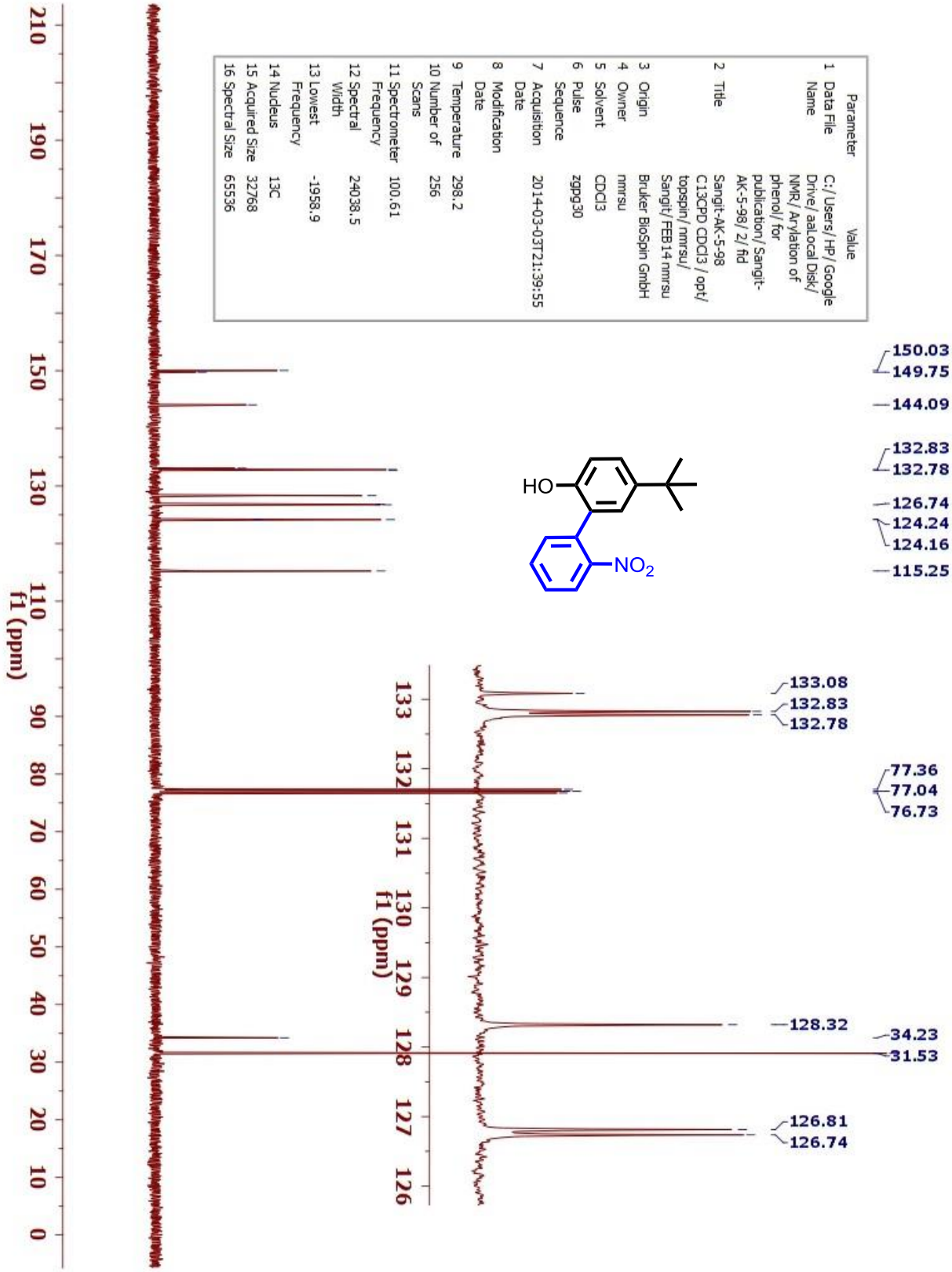


Figure S73 ^{1}H NMR spectrum of **37**

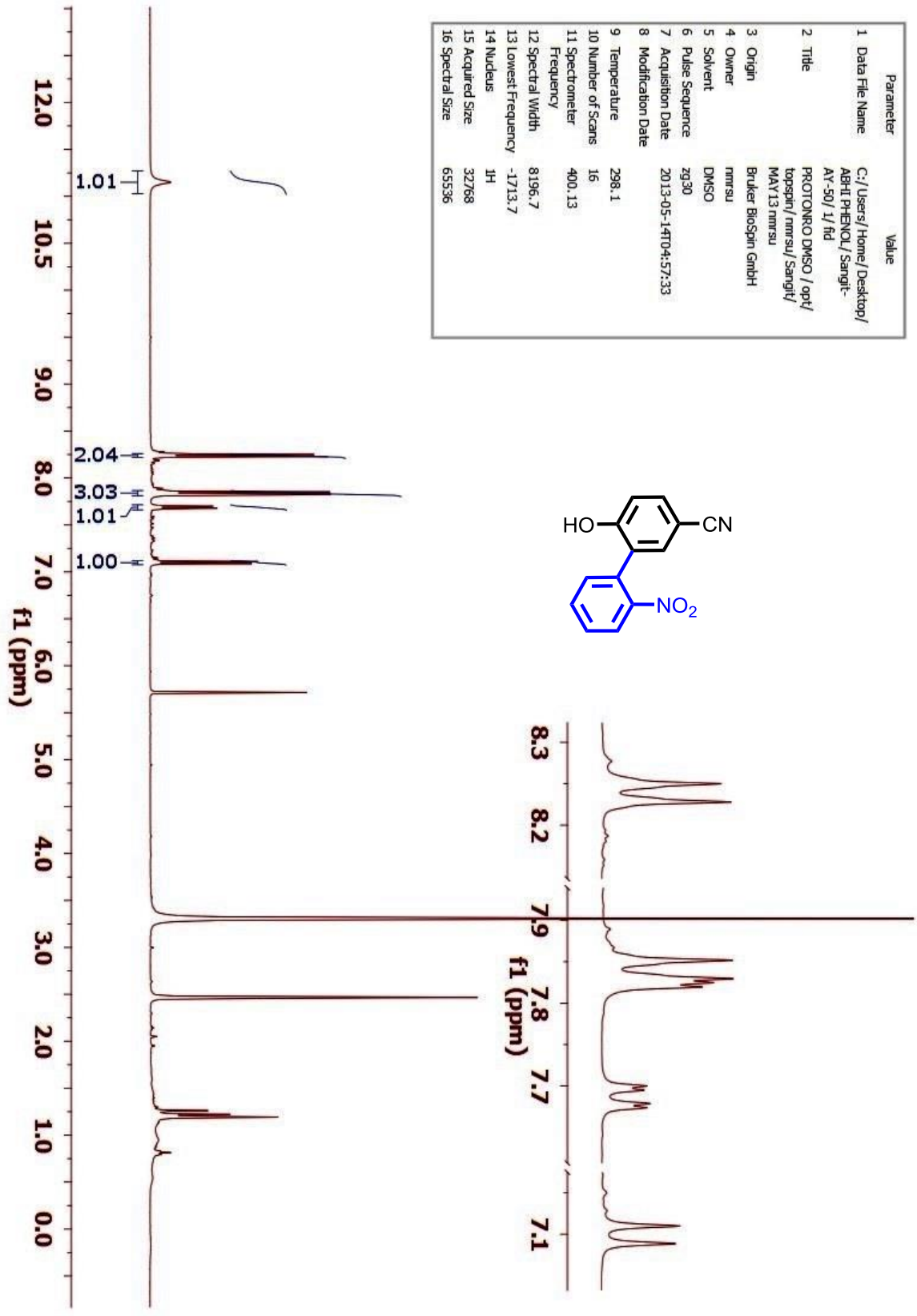


Figure S74 ^{13}C NMR spectrum of **37**

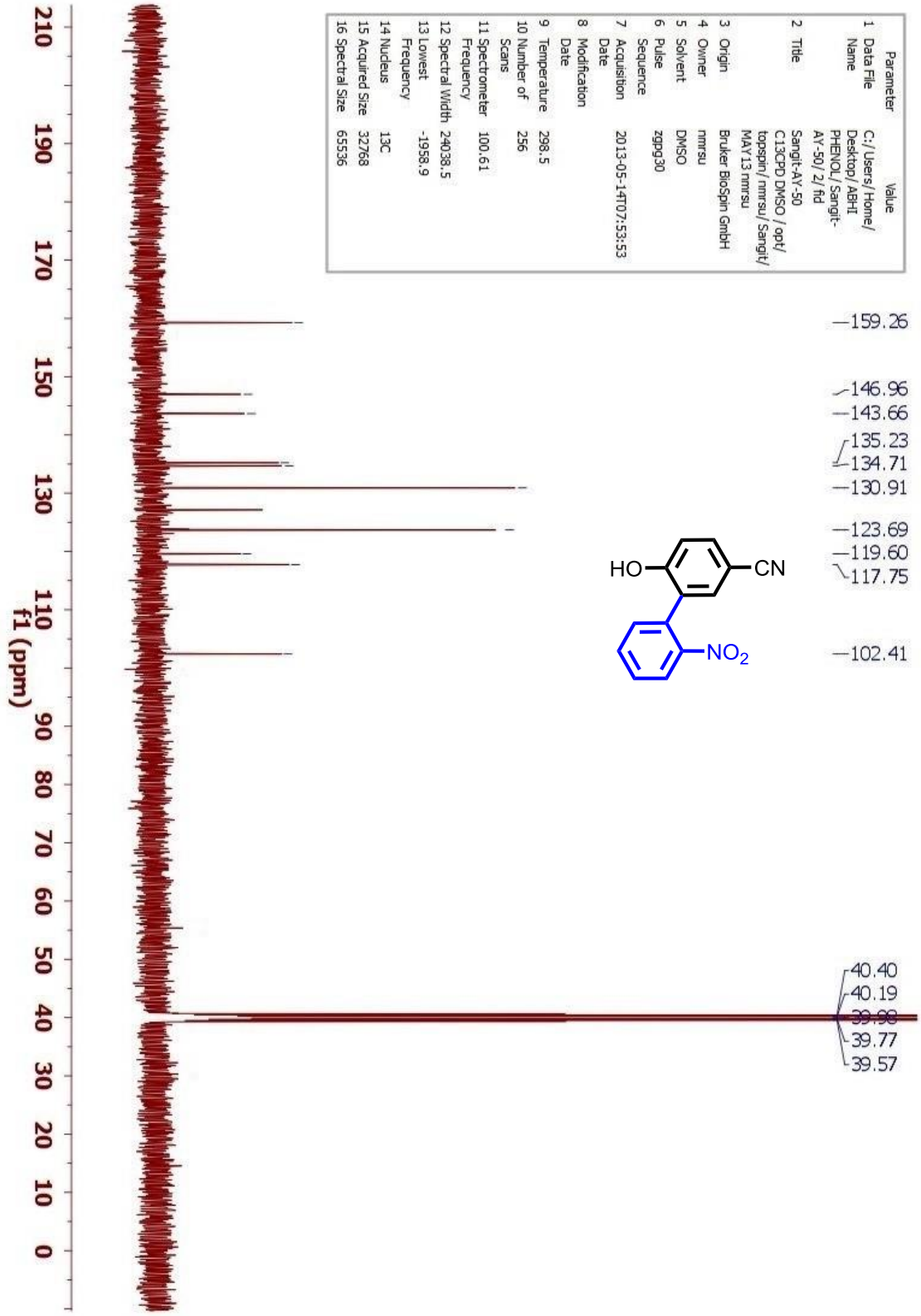


Figure S75 ^{1}H NMR spectrum of **38**

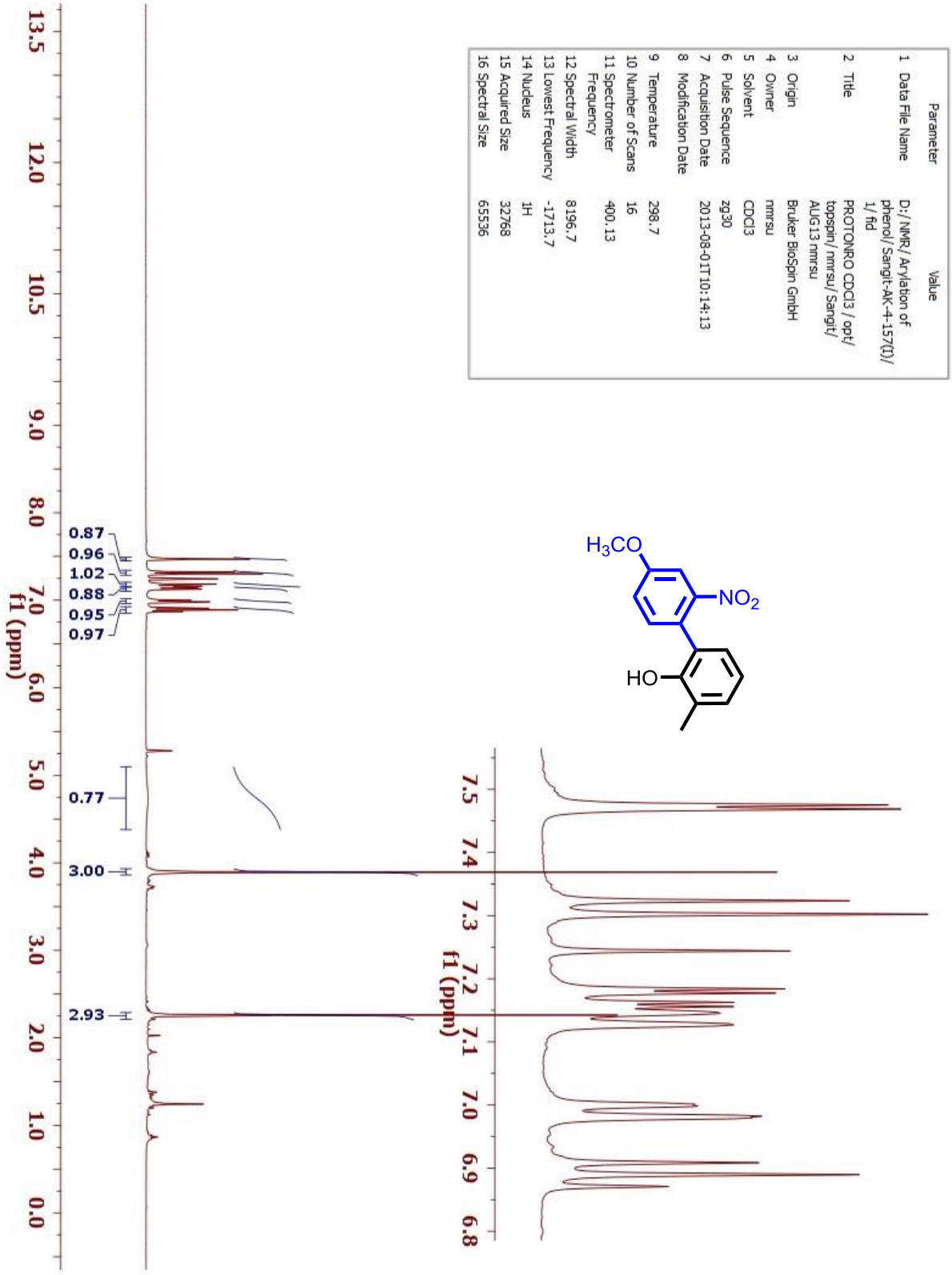


Figure S76 ^{13}C NMR spectrum of **38**

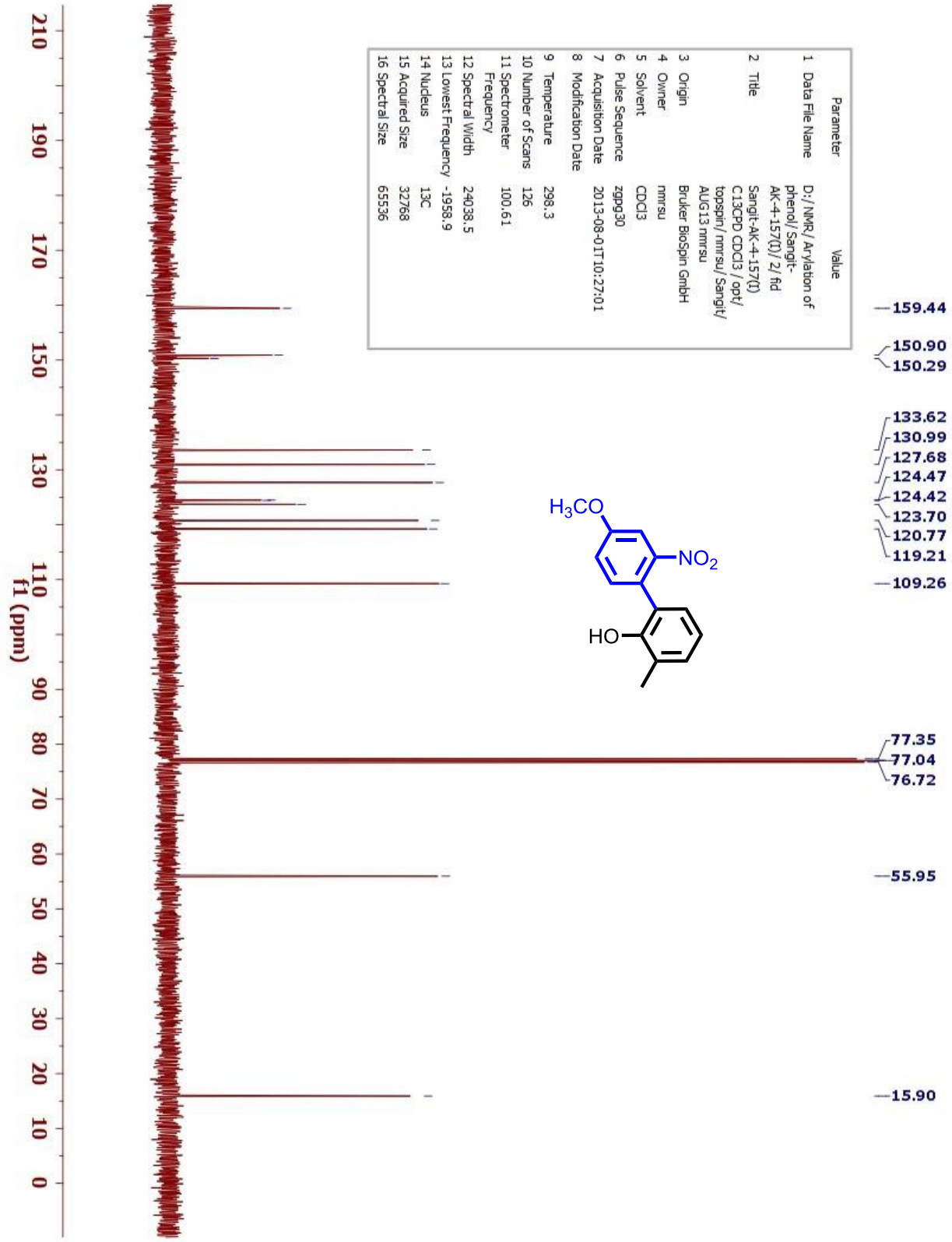


Figure S77 ^{1}H NMR spectrum of **39**

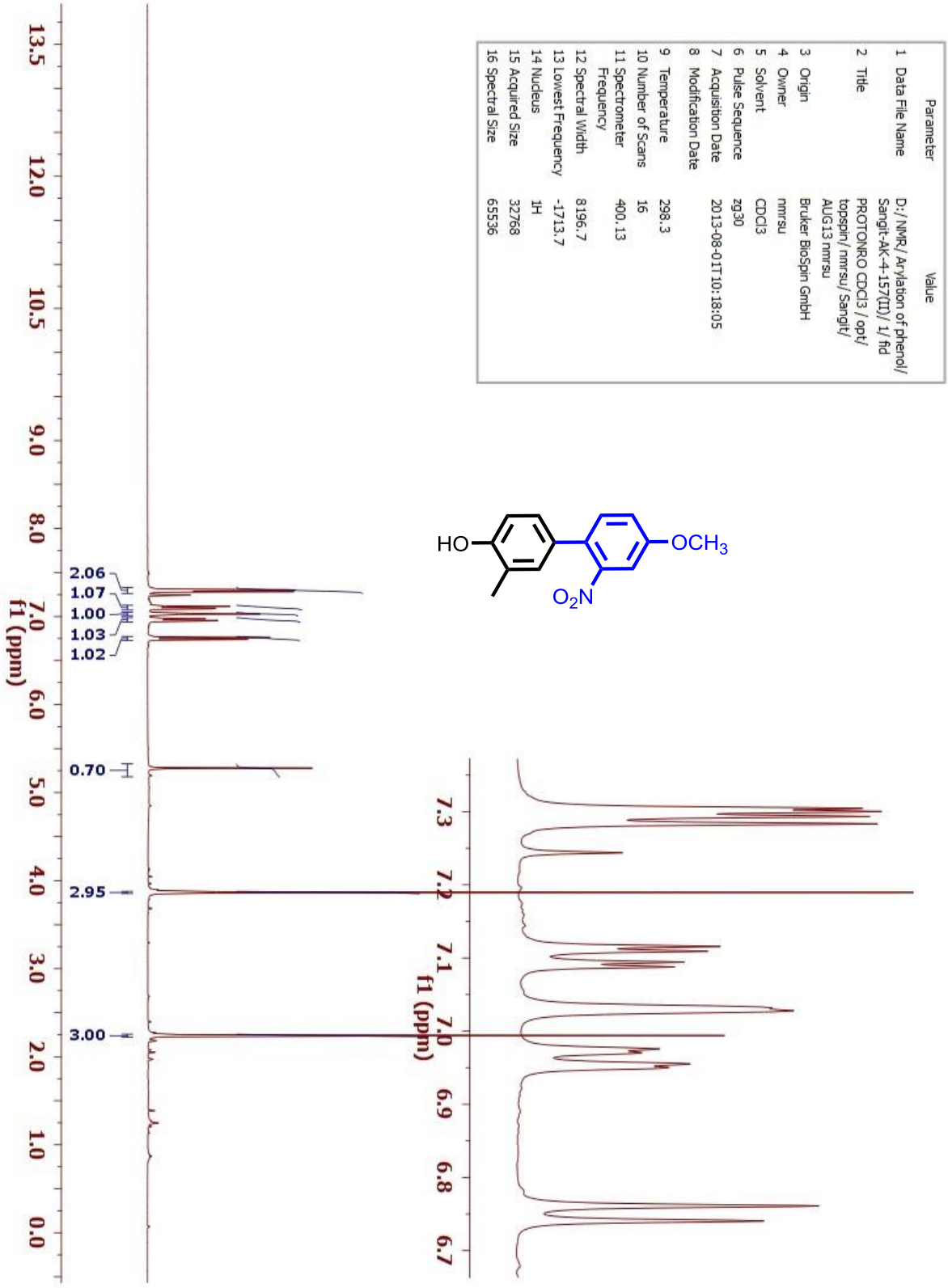


Figure S78 ^{13}C NMR spectrum of **39**

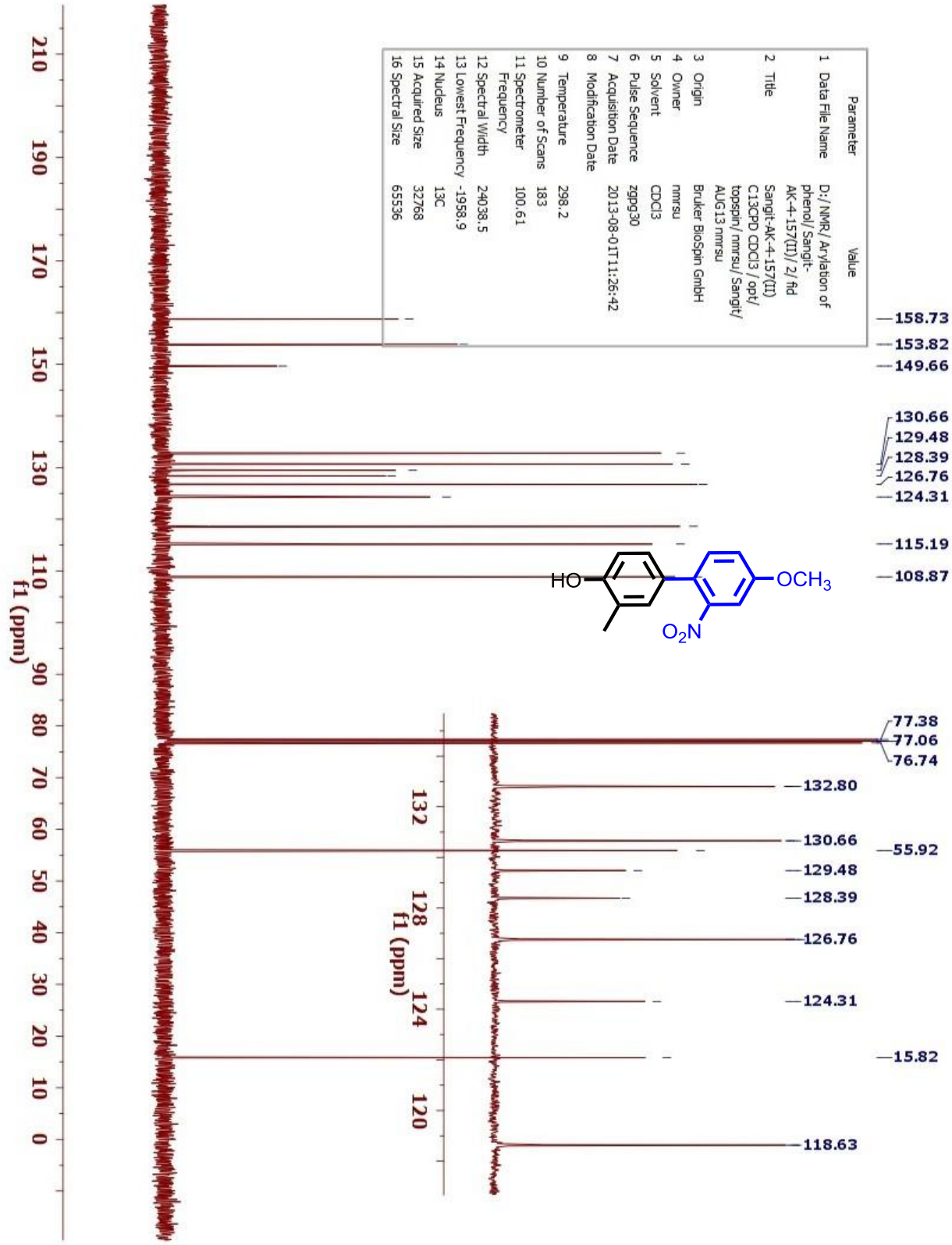


Figure S79 ^{1}H NMR spectrum of **40**

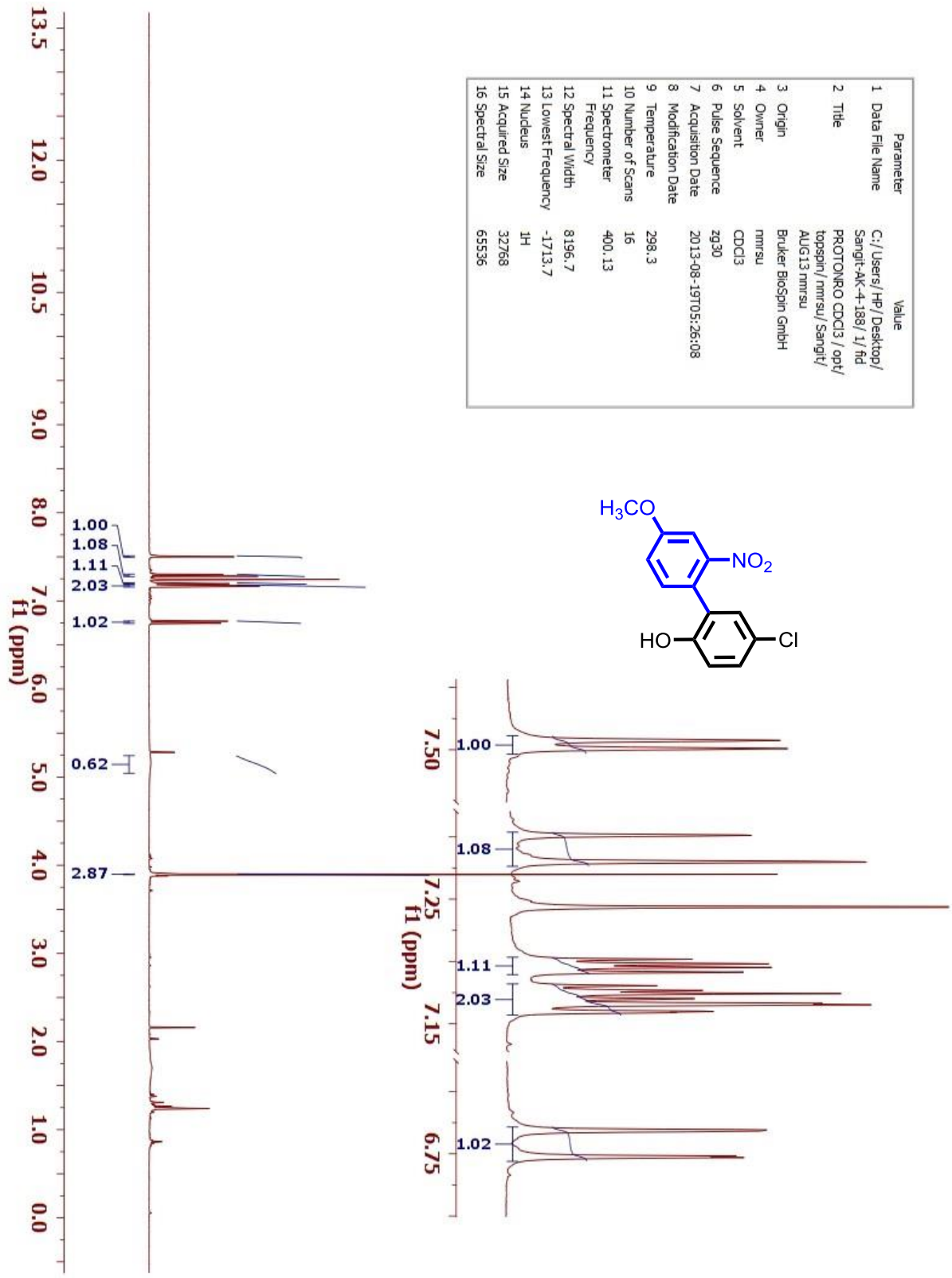


Figure S80 ^{13}C NMR spectrum of **40**

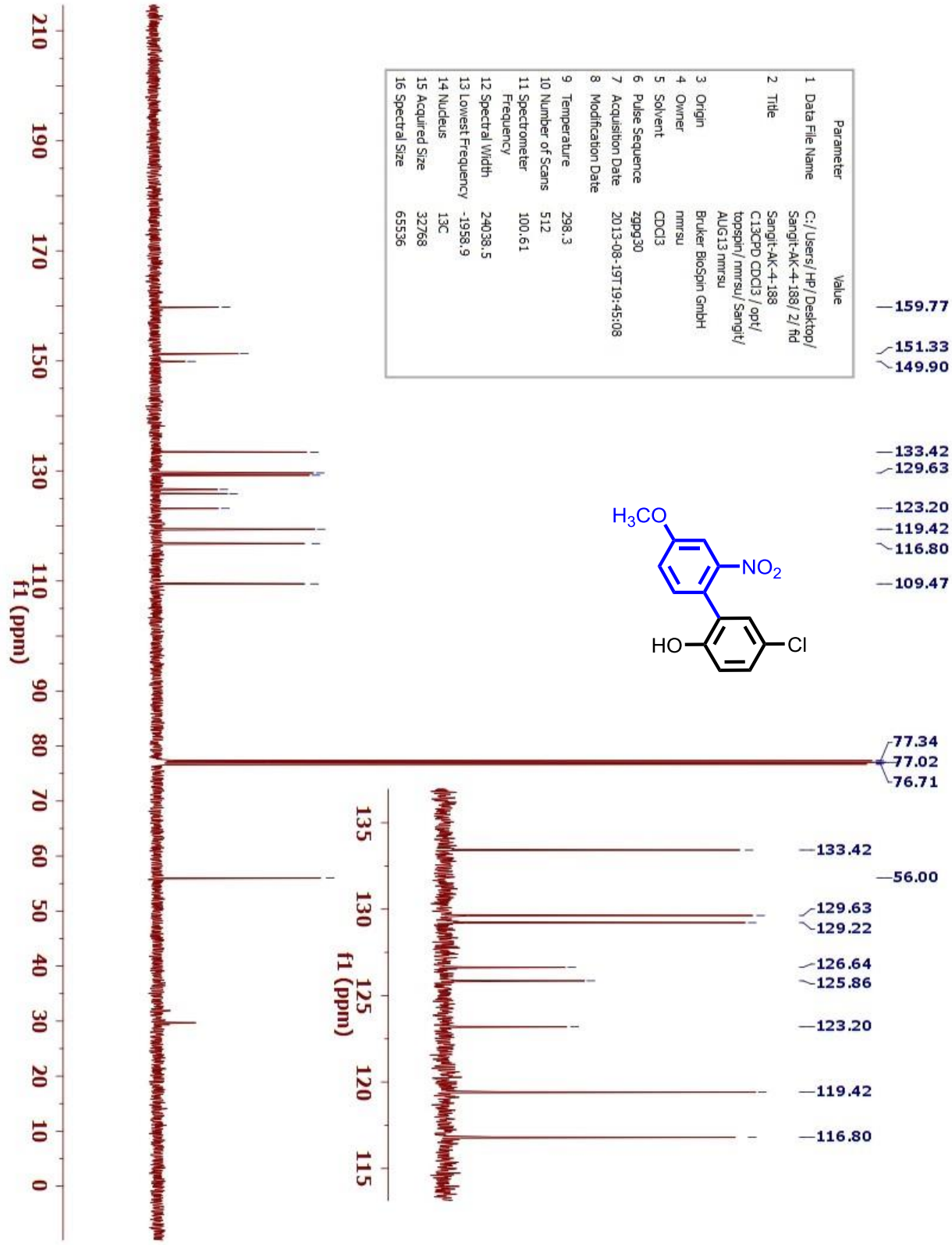


Figure S81 ^{1}H NMR spectrum of **41**

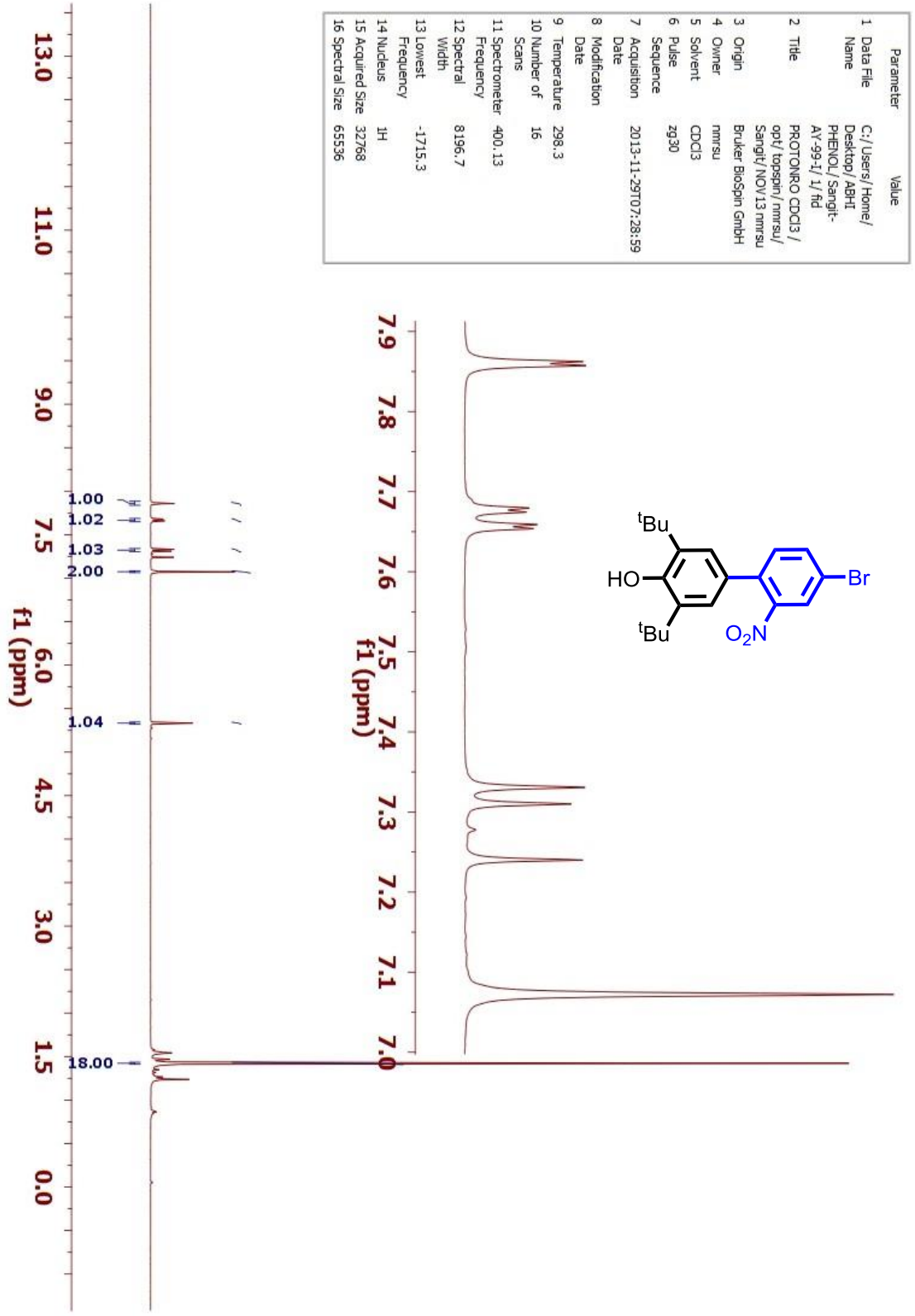


Figure S82 ^{13}C NMR spectrum of **41**

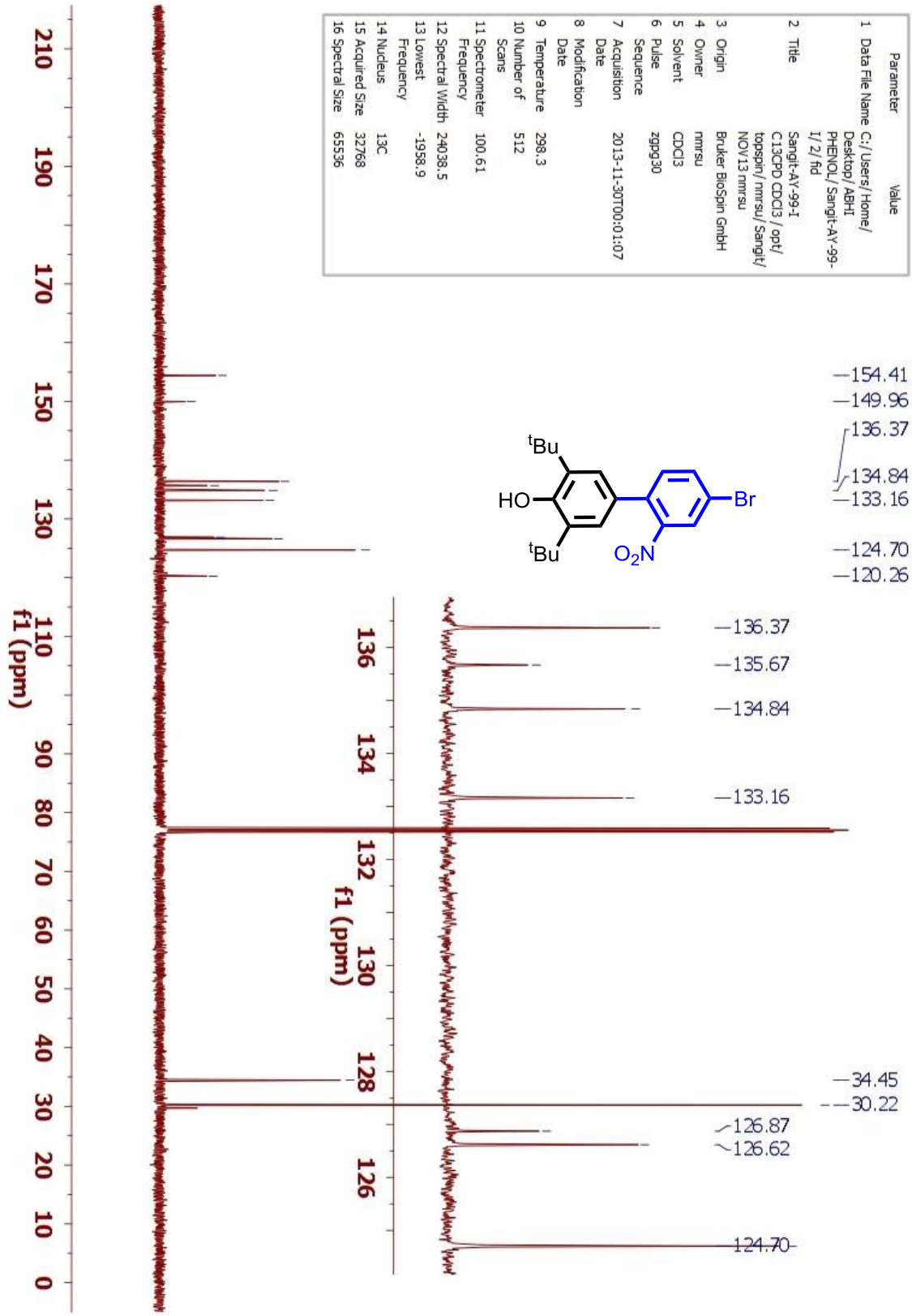


Figure S83 ^{1}H NMR spectrum of **42**

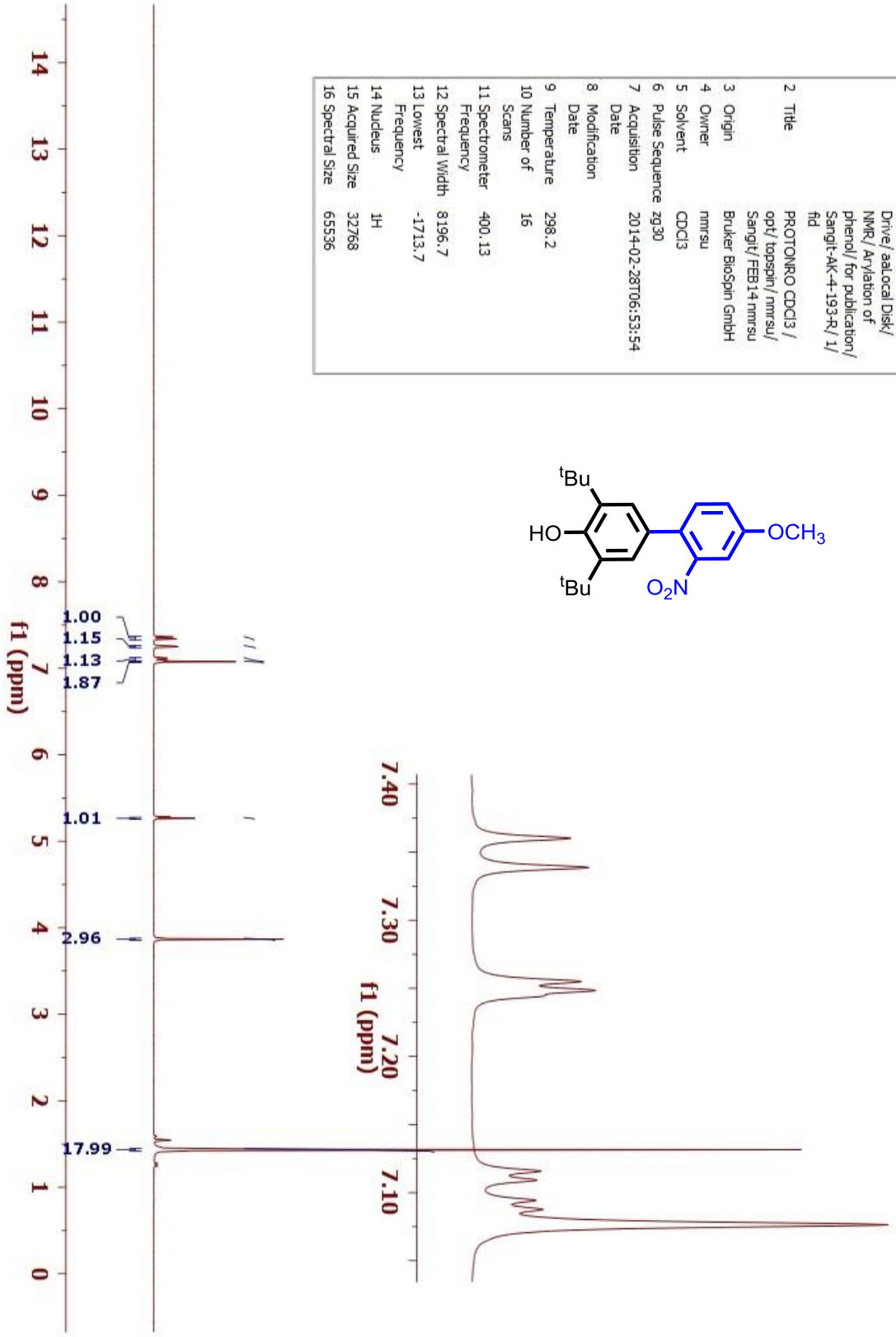


Figure S84 ^{13}C NMR spectrum of **42**

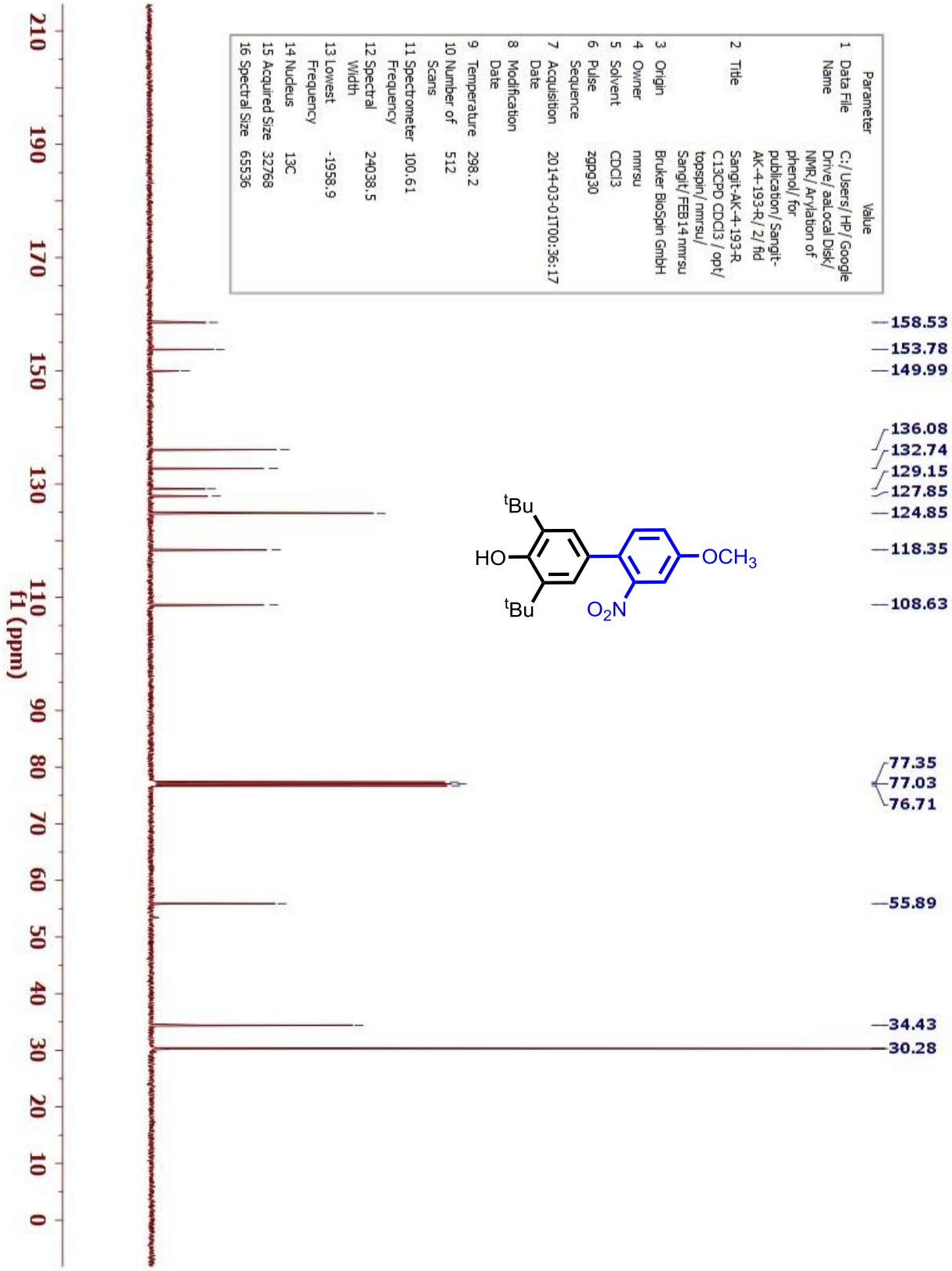


Figure S85 ^{1}H NMR spectrum of **43**

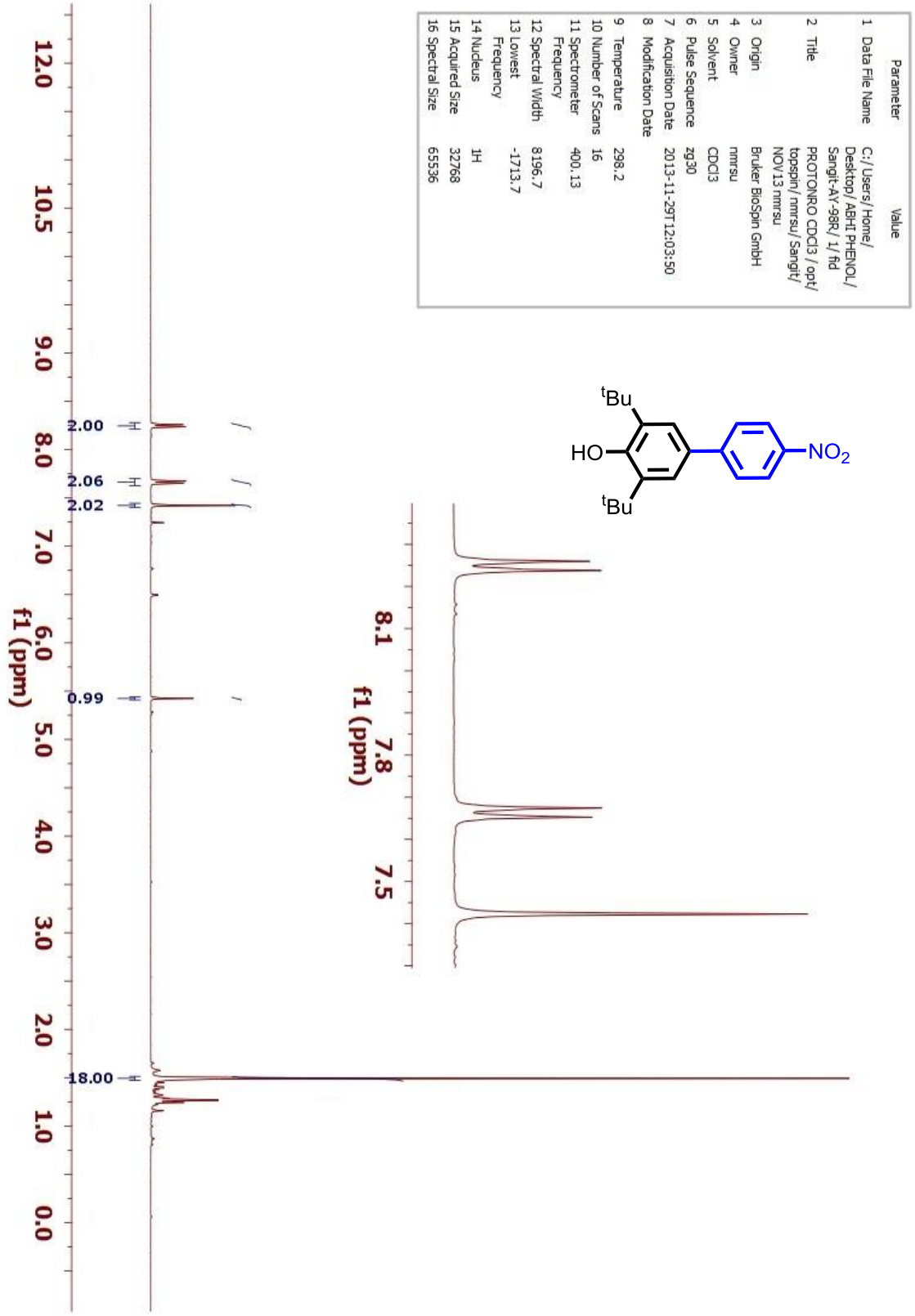


Figure S86 ^{13}C NMR spectrum of **43**

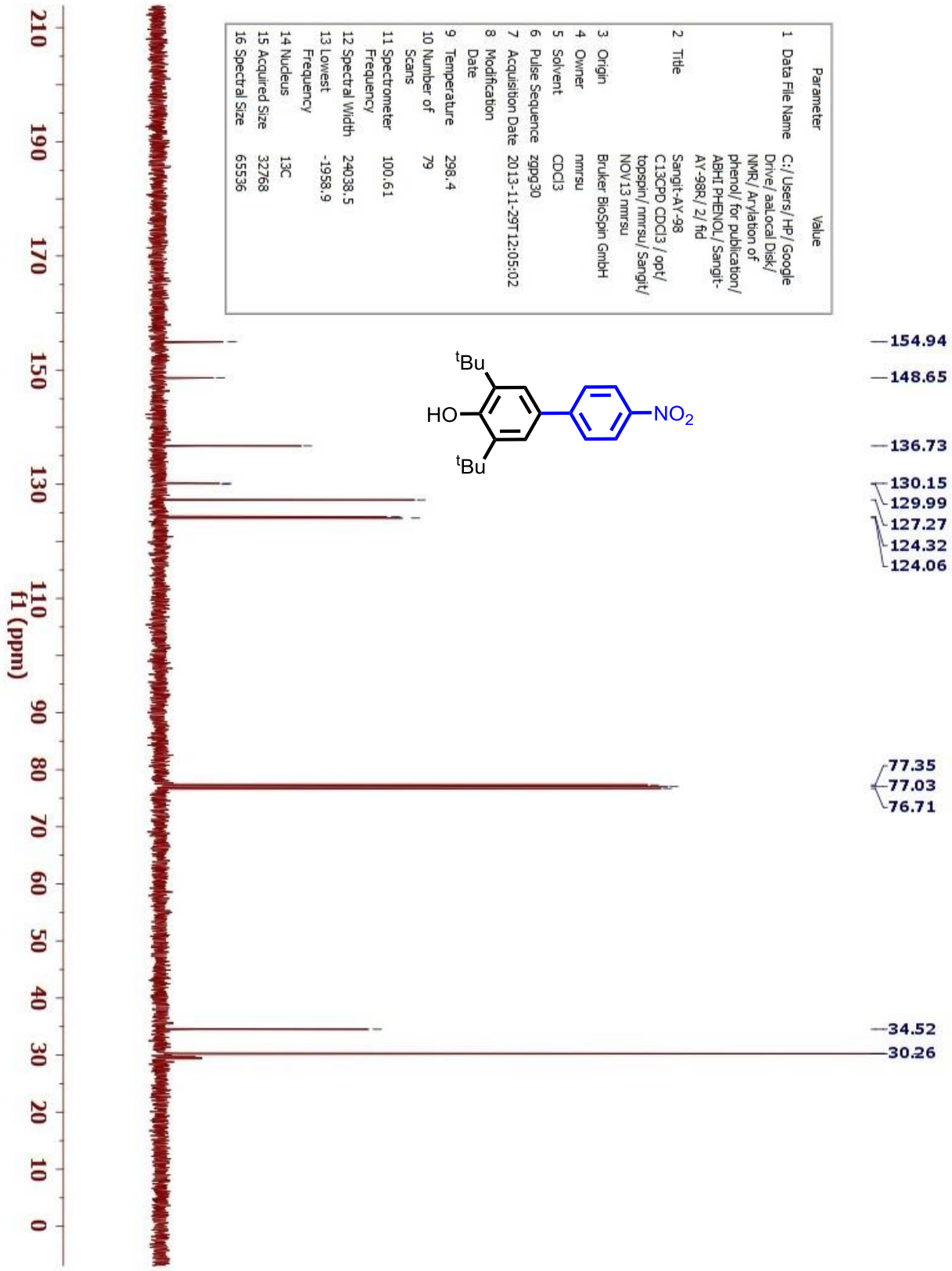


Figure S87 ^{1}H NMR spectrum of **44**

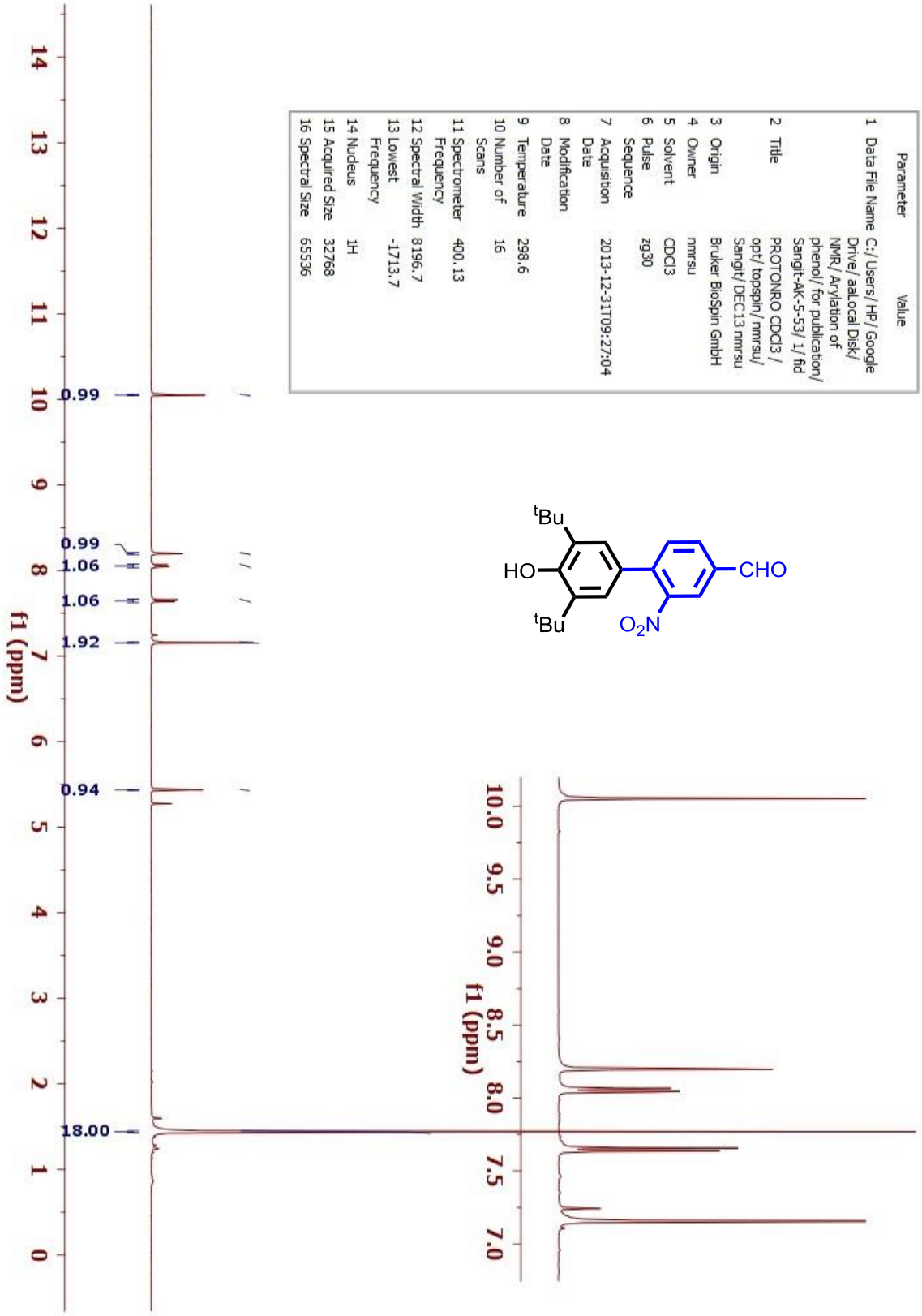


Figure S88 ^{13}C NMR spectrum of **44**

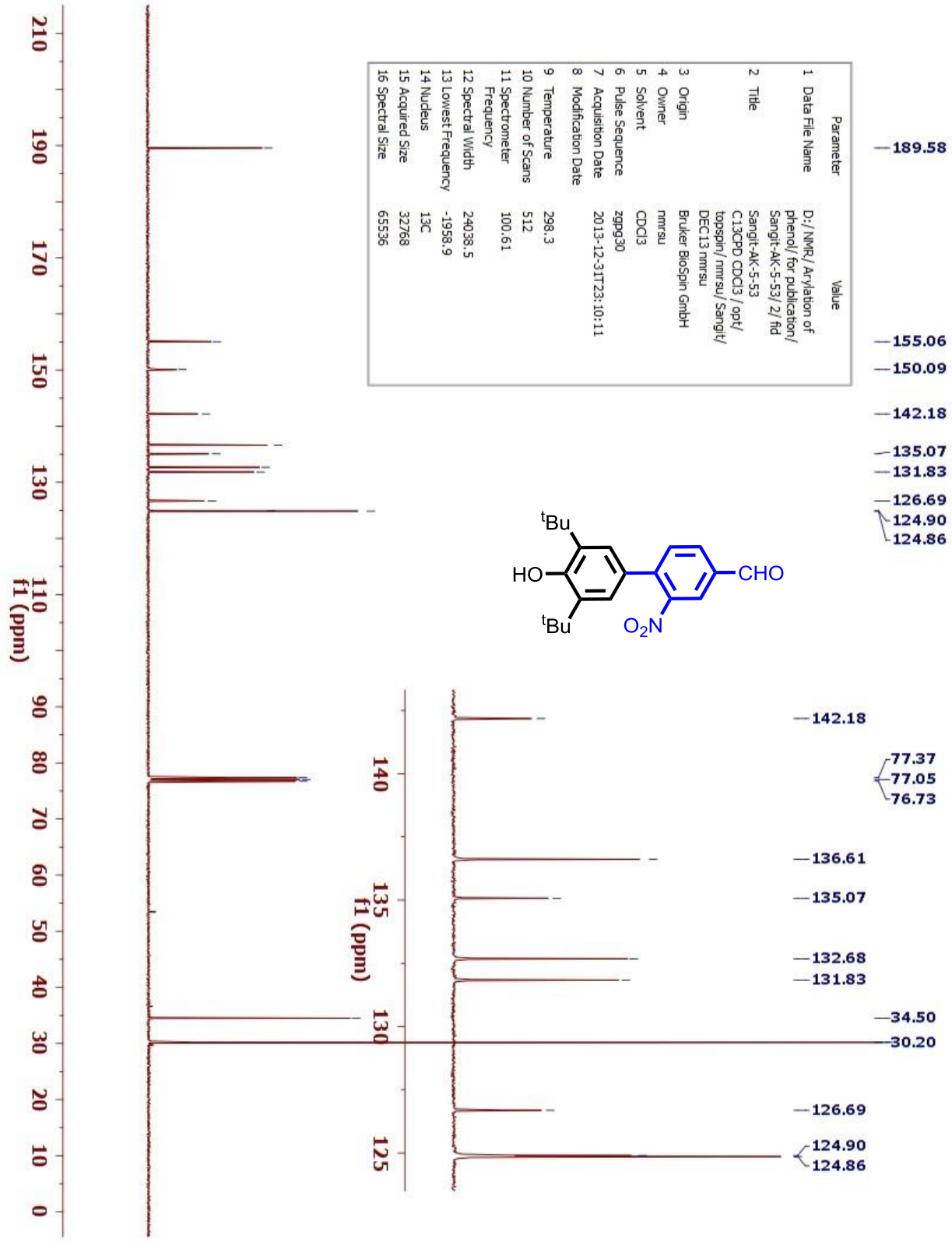


Figure S89 ^{1}H NMR spectrum of **45**

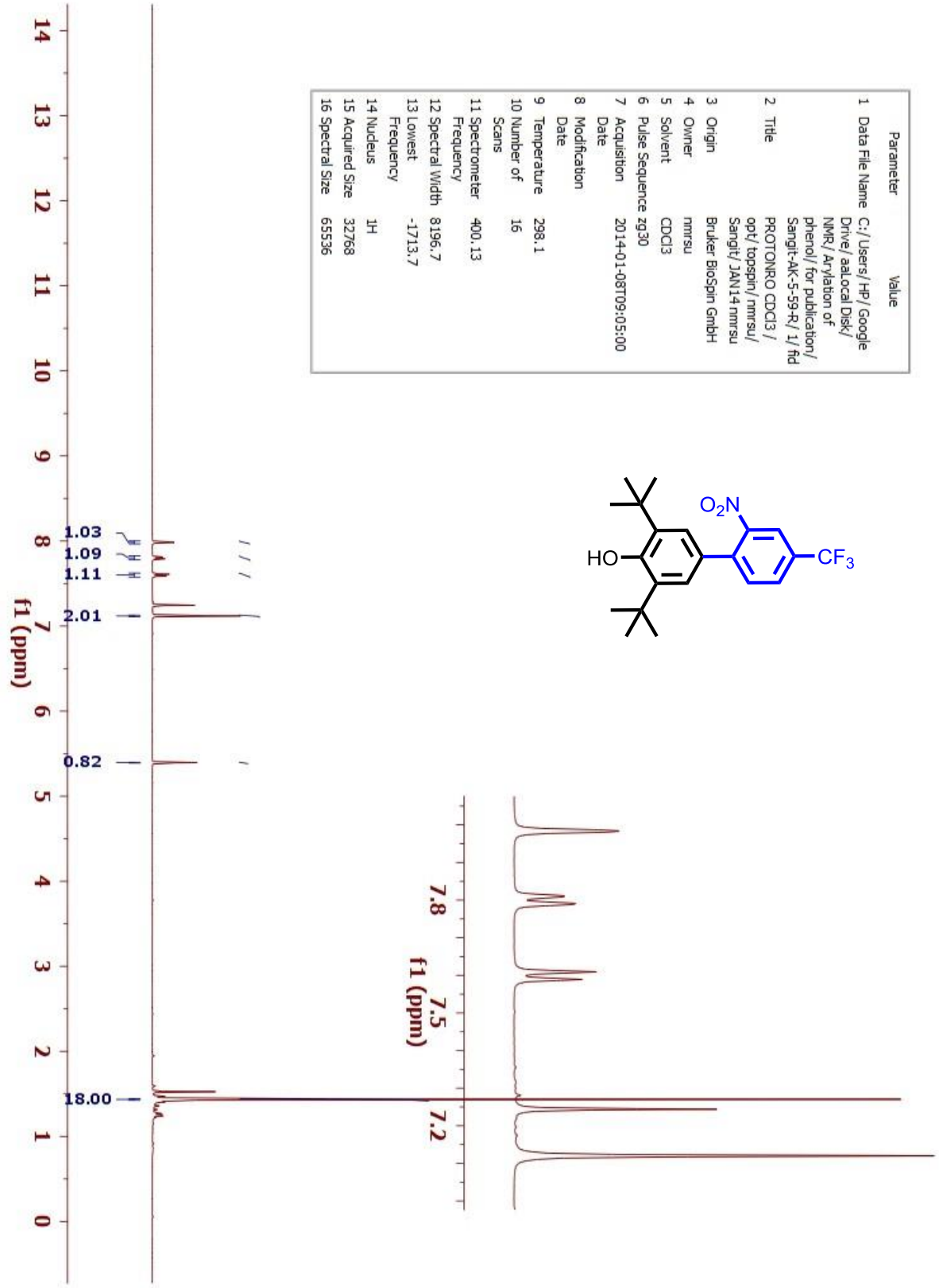


Figure S90 ^{13}C NMR spectrum of **45**

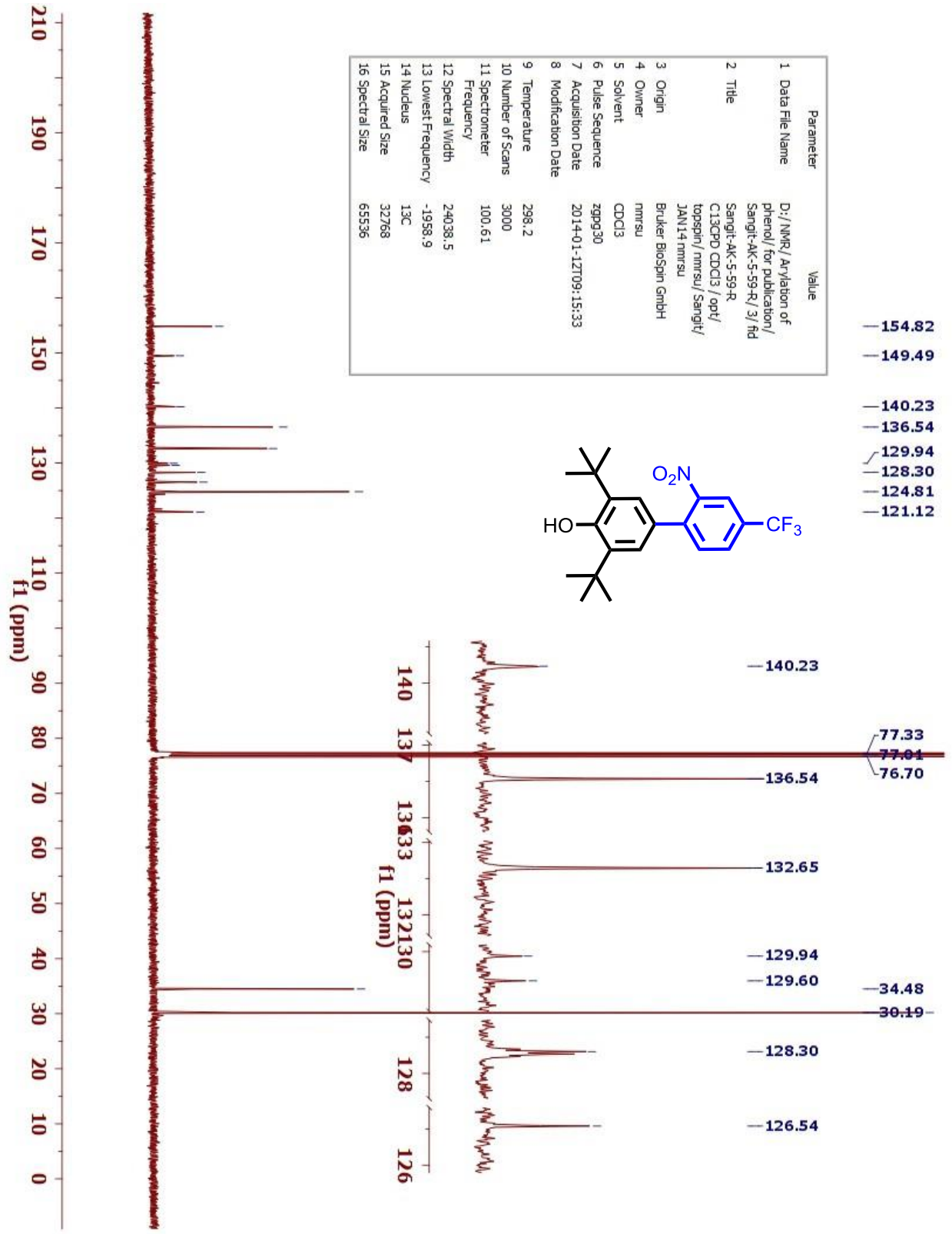


Figure S91 ^{1}H NMR spectrum of **46**

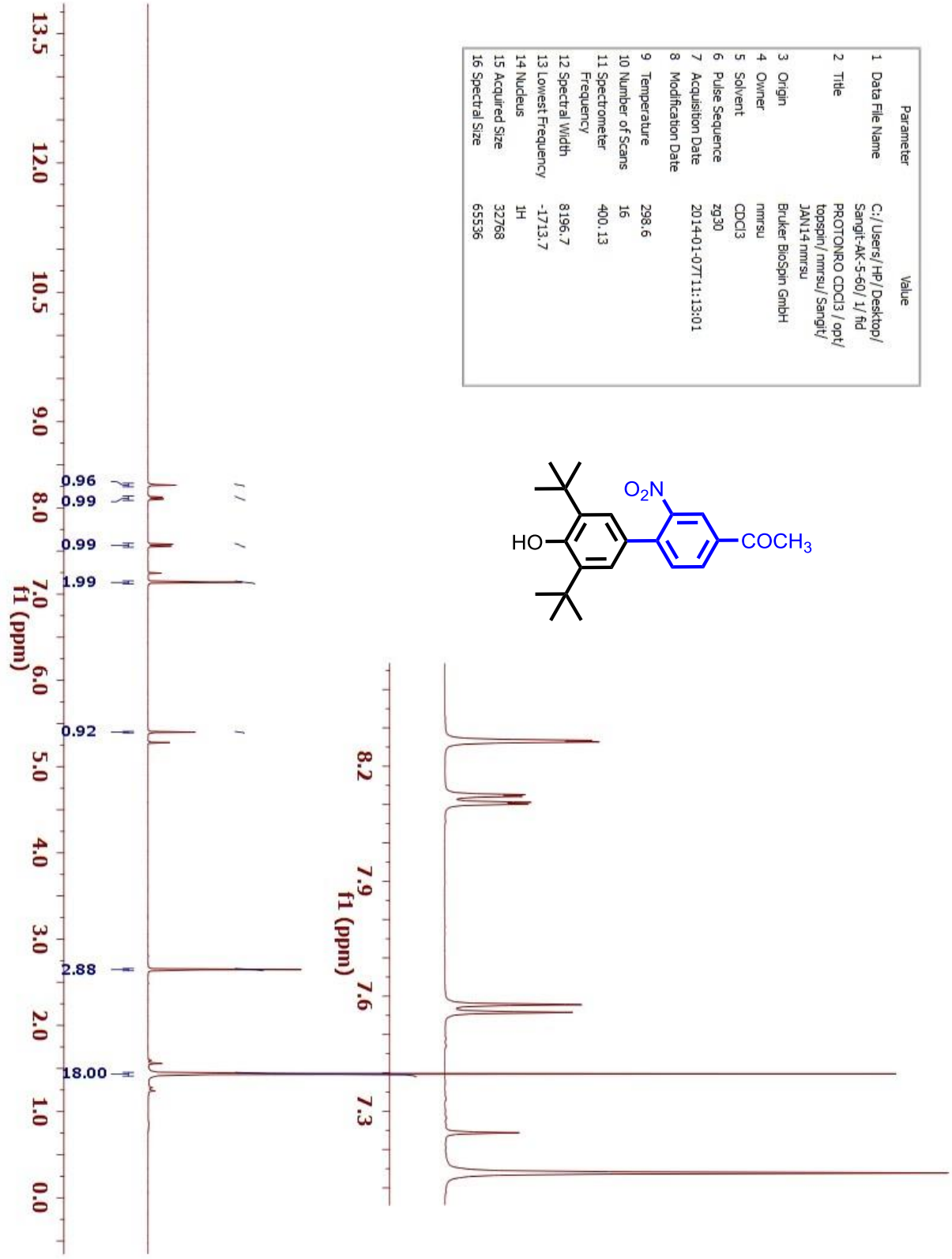


Figure S92 ^{13}C NMR spectrum of **46**

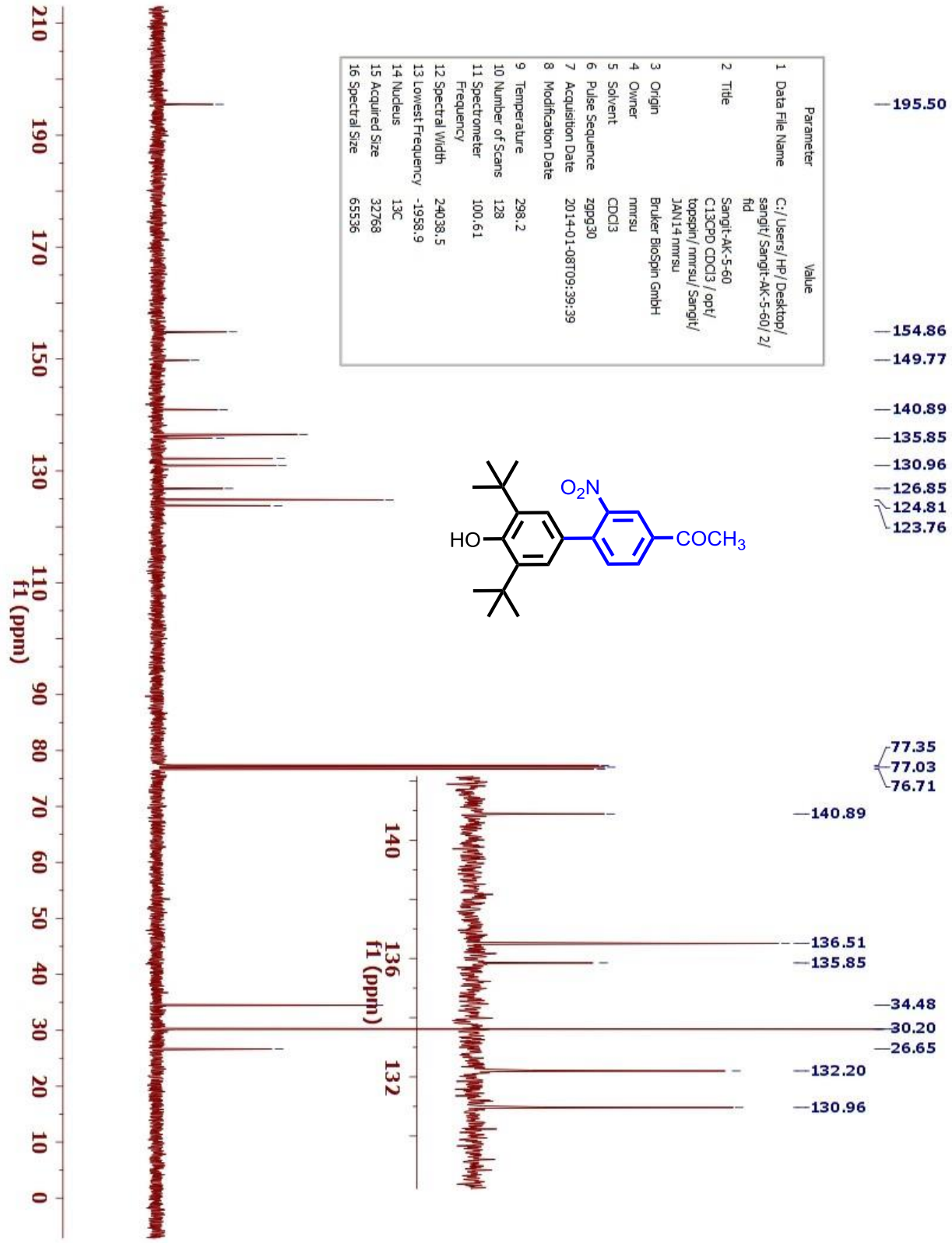


Figure S93 ^{1}H NMR spectrum of **47**

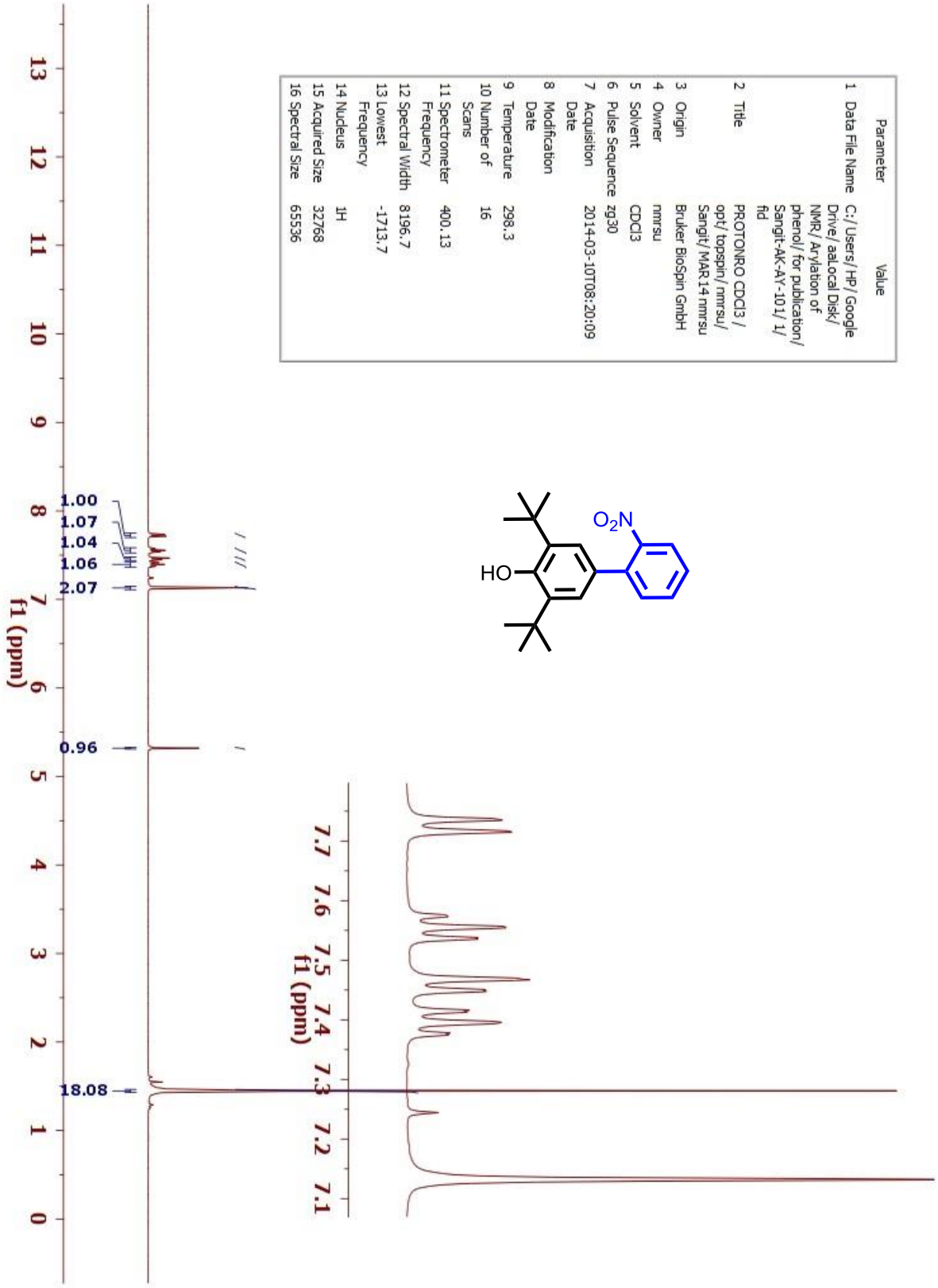


Figure S94 ^{13}C NMR spectrum of **47**

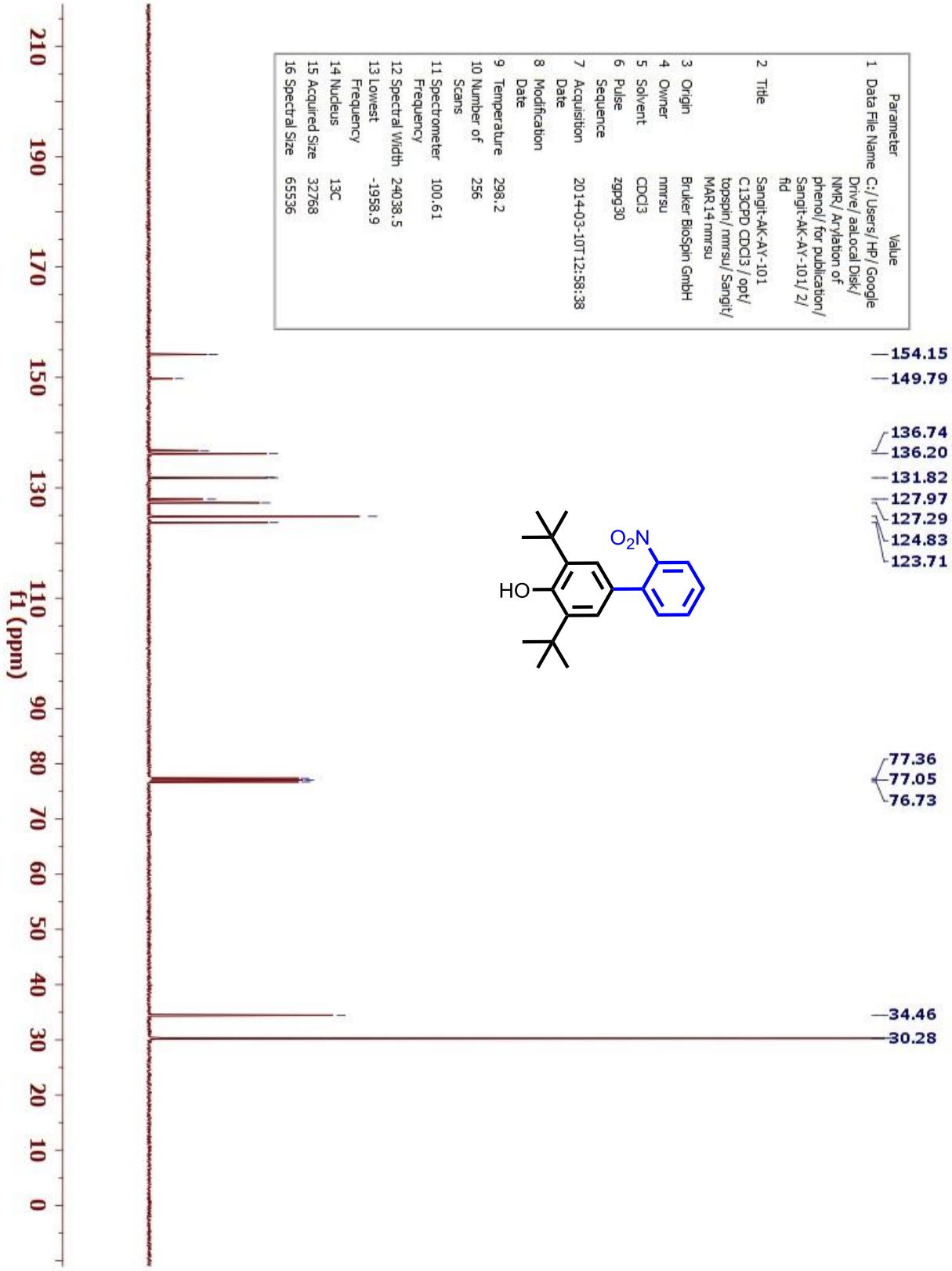


Figure S95 ^{1}H NMR spectrum of **48**

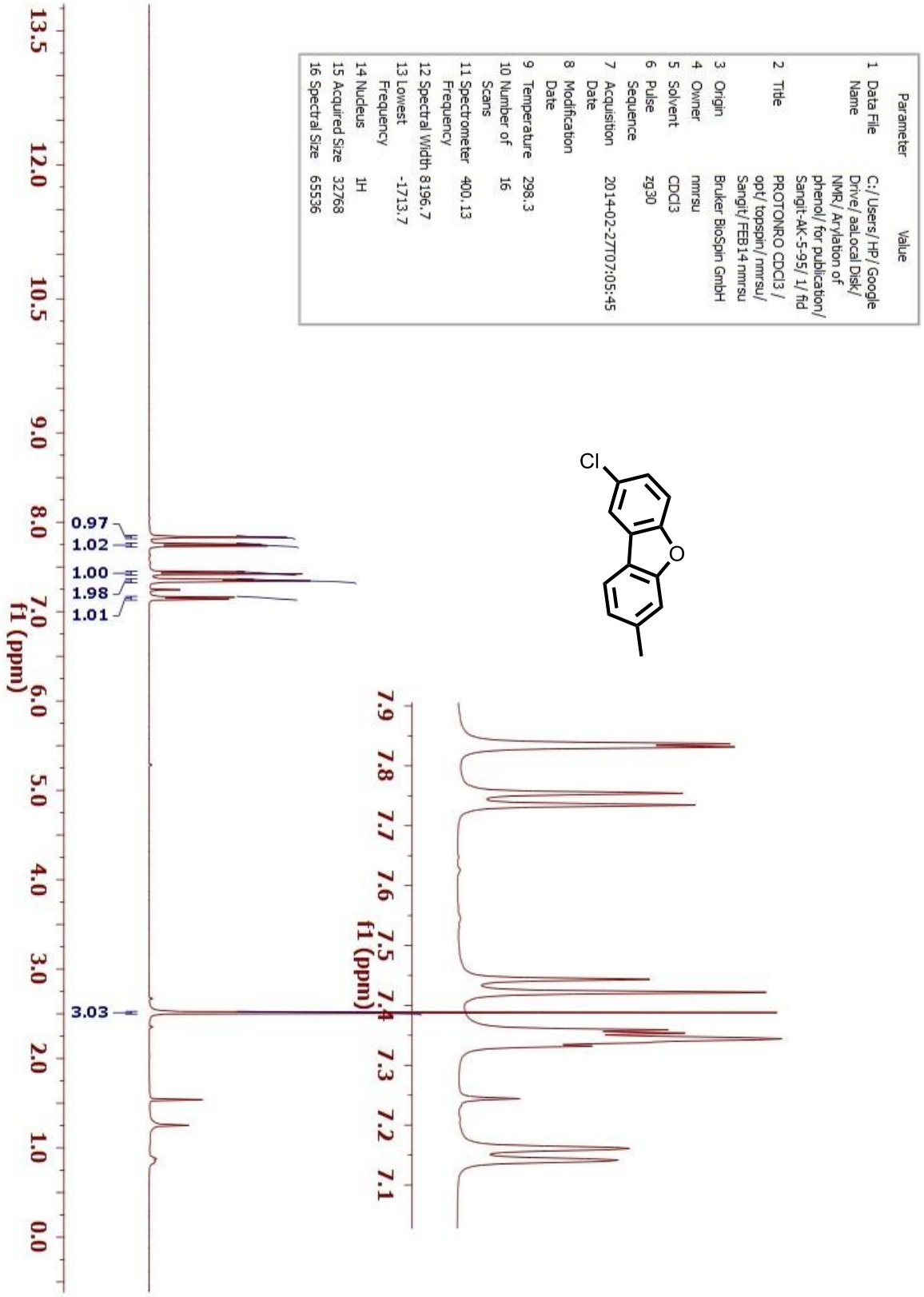


Figure S96 ^{13}C NMR spectrum of **48**

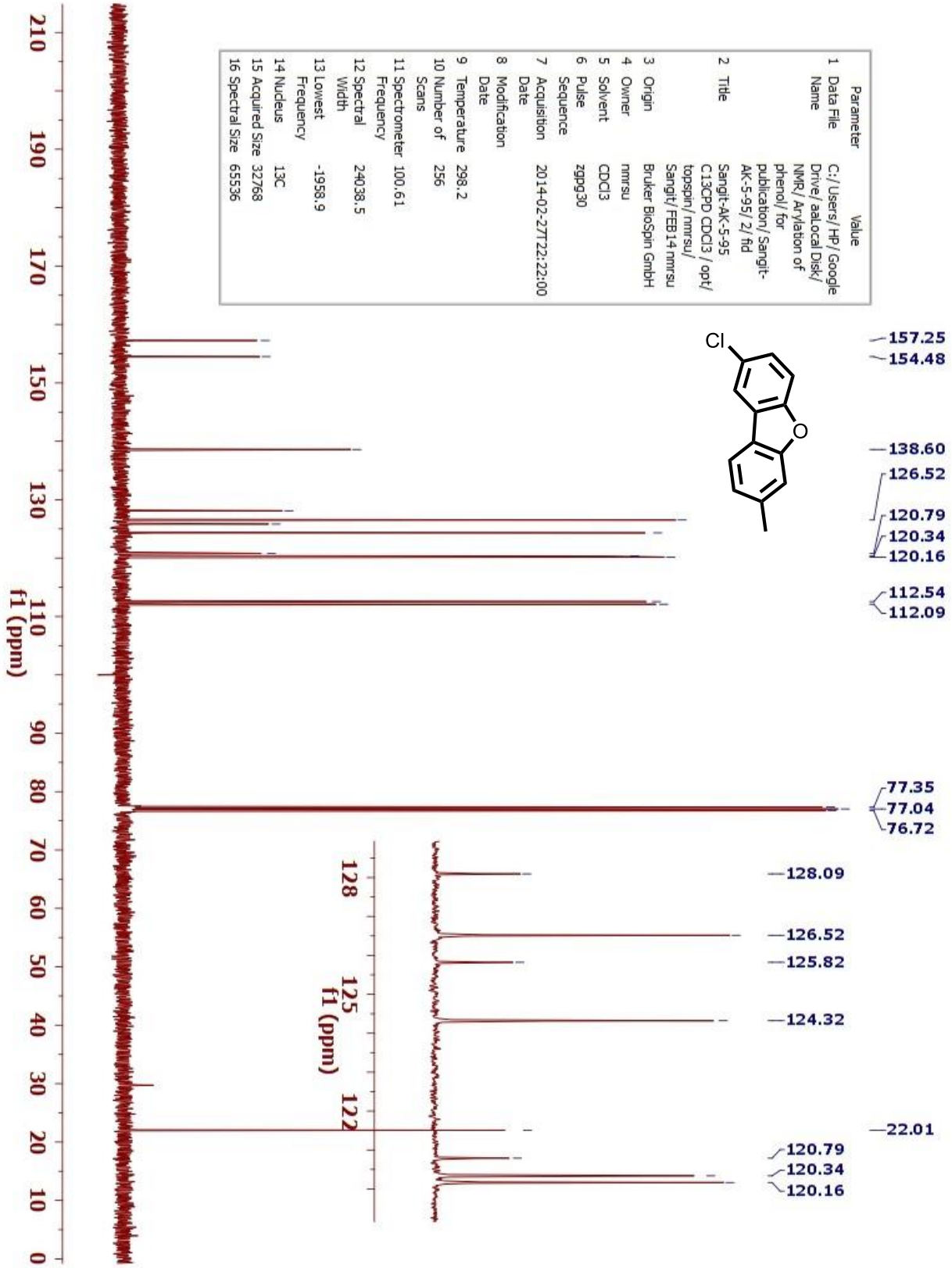


Figure S97 ^{1}H NMR spectrum of **49**

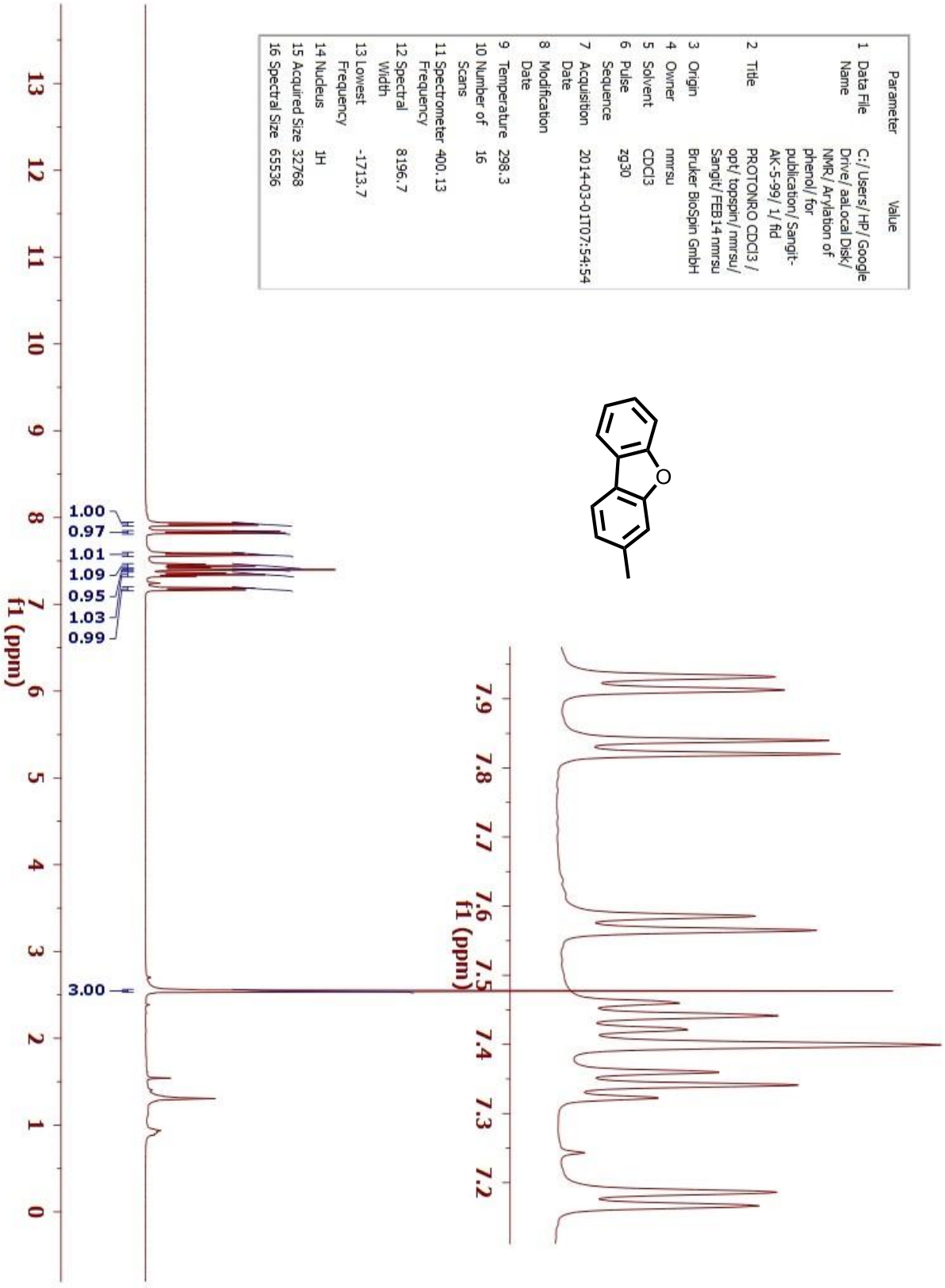


Figure S98 ^{13}C NMR spectrum of **49**

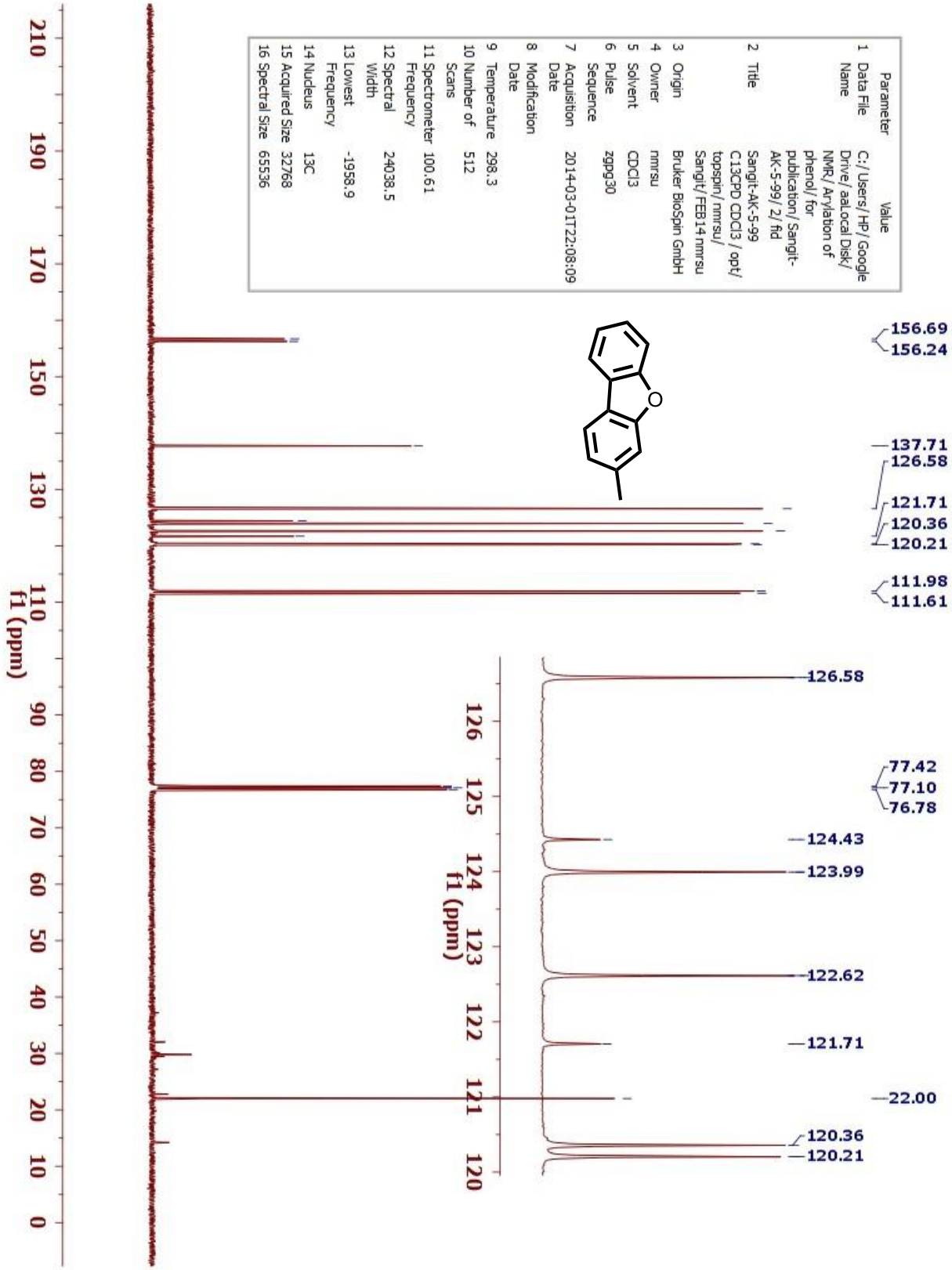


Figure S99 ^{13}C NMR spectrum of **50**

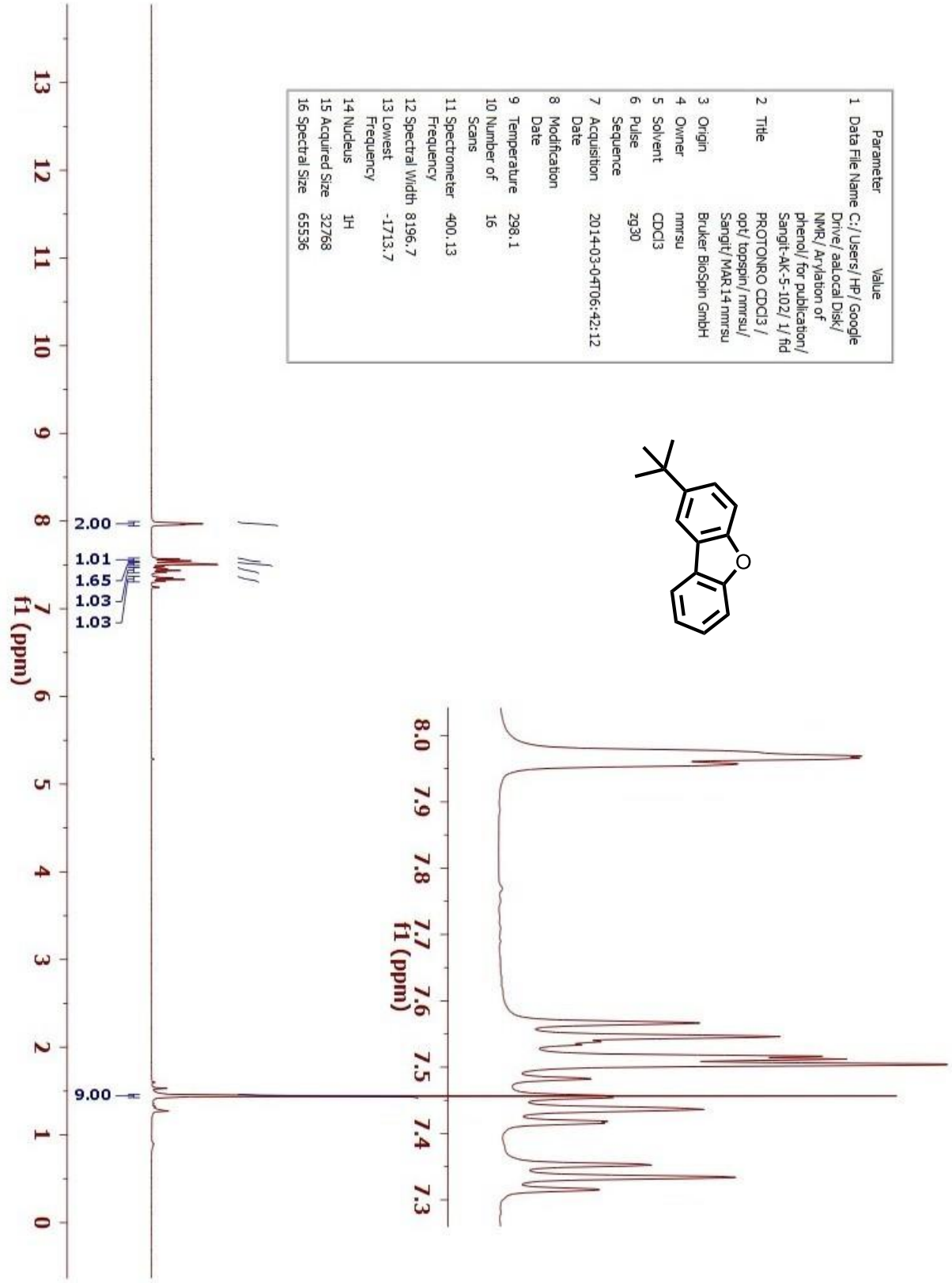


Figure S100 ^{13}C NMR spectrum of **50**

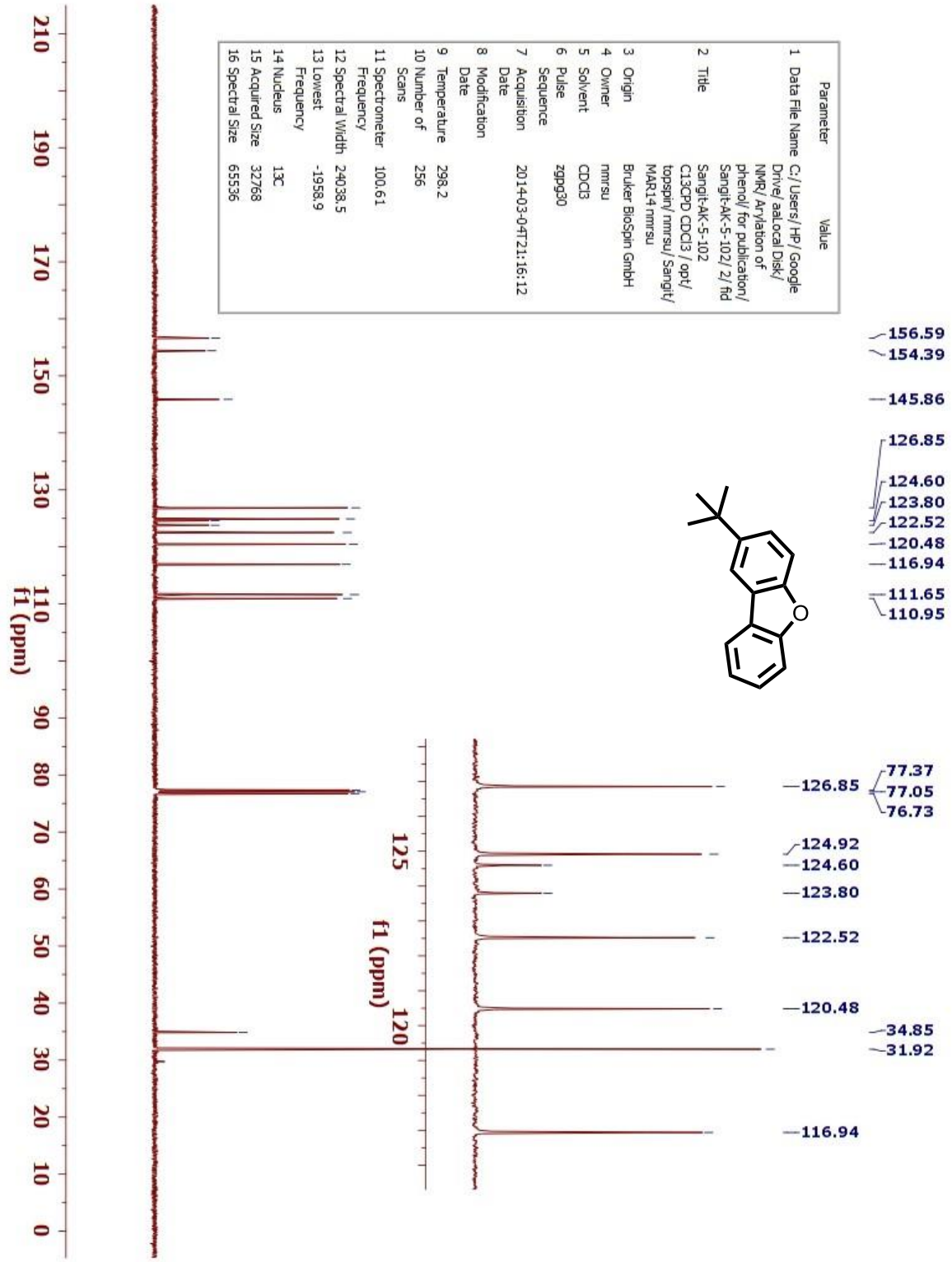


Figure S101 ^{1}H NMR spectrum of **51**

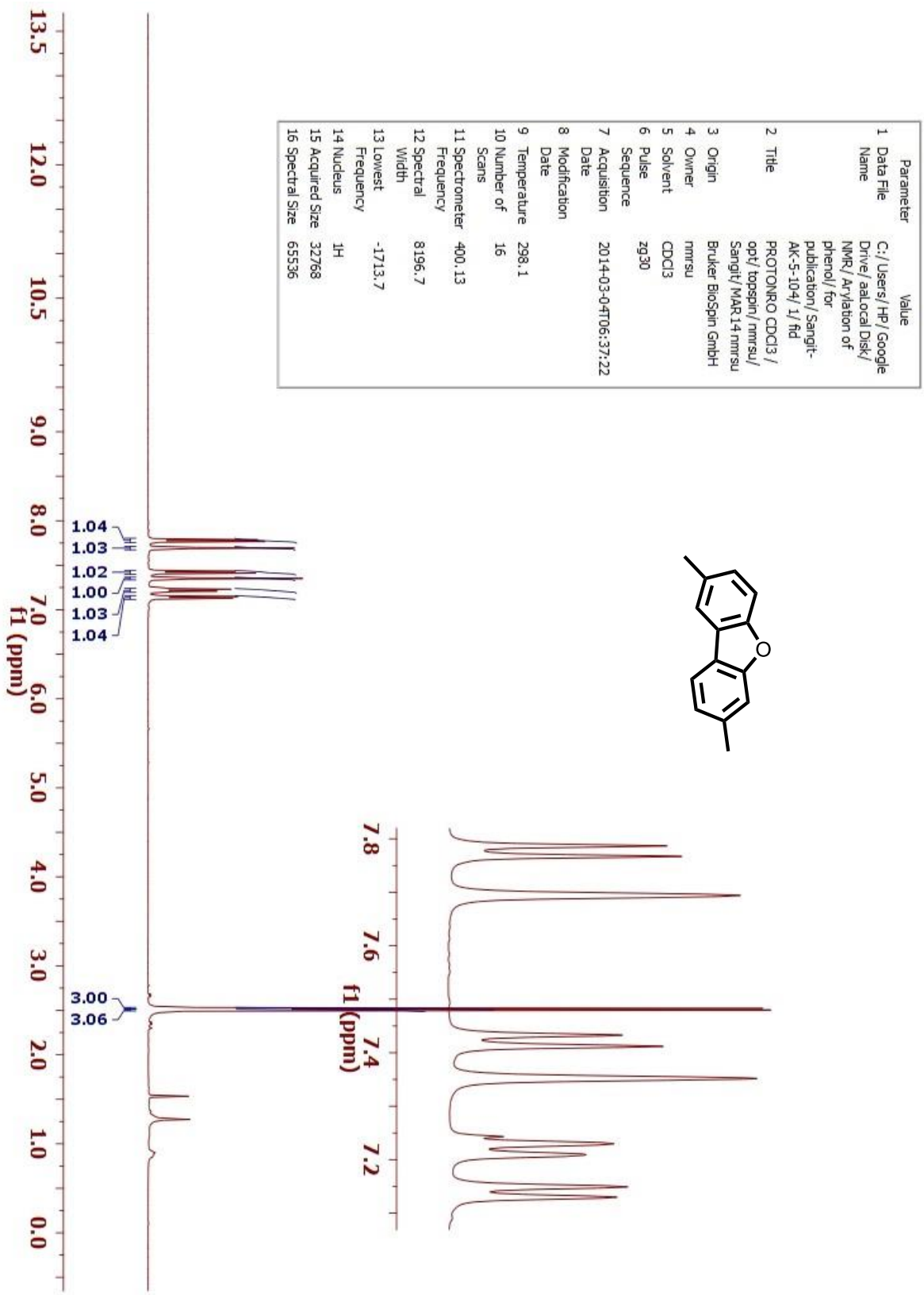


Figure S102 ^{13}C NMR spectrum of **51**

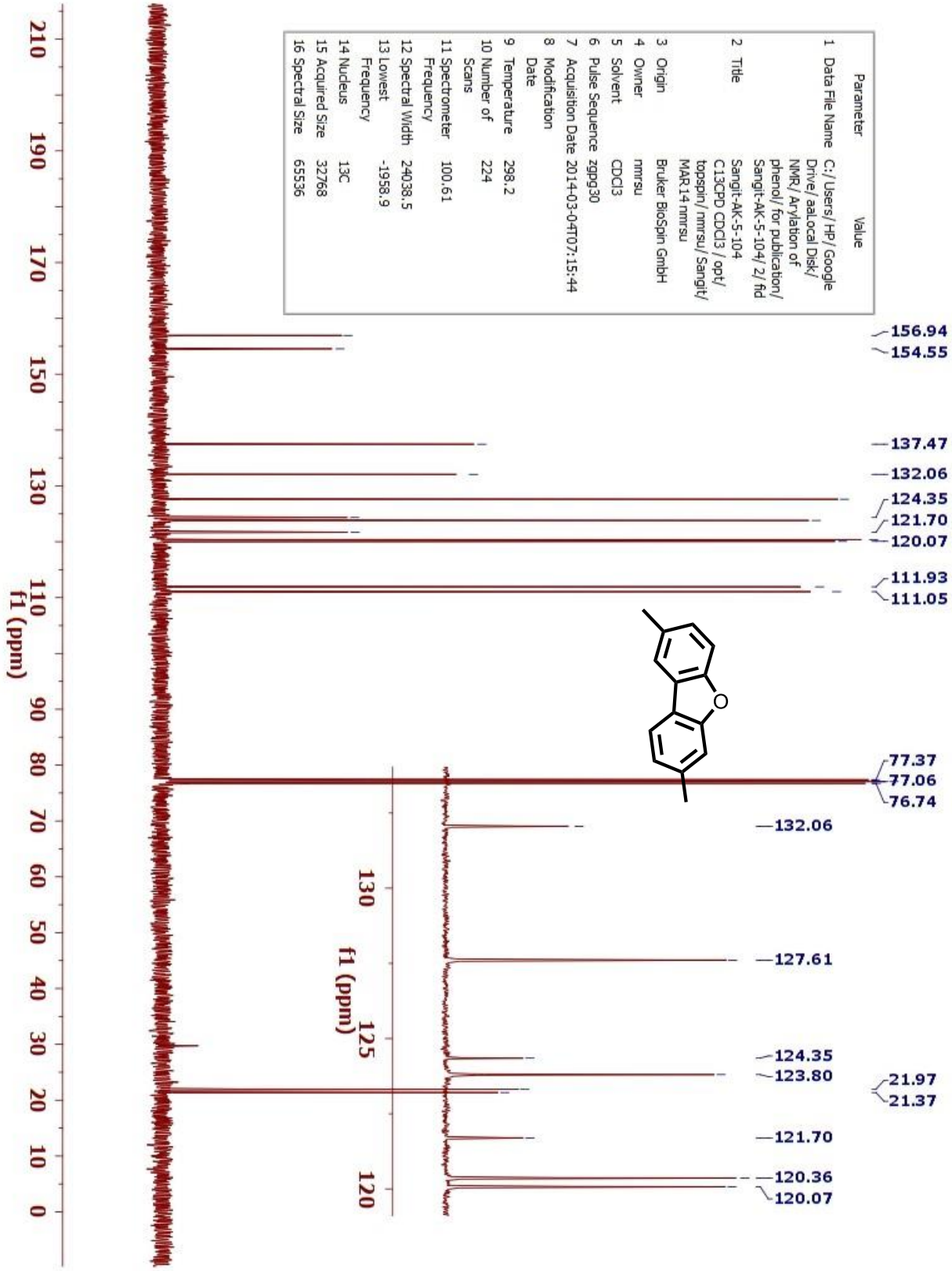


Figure S4 ^{1}H NMR spectrum of 5'-chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl **(substrate for 52)**

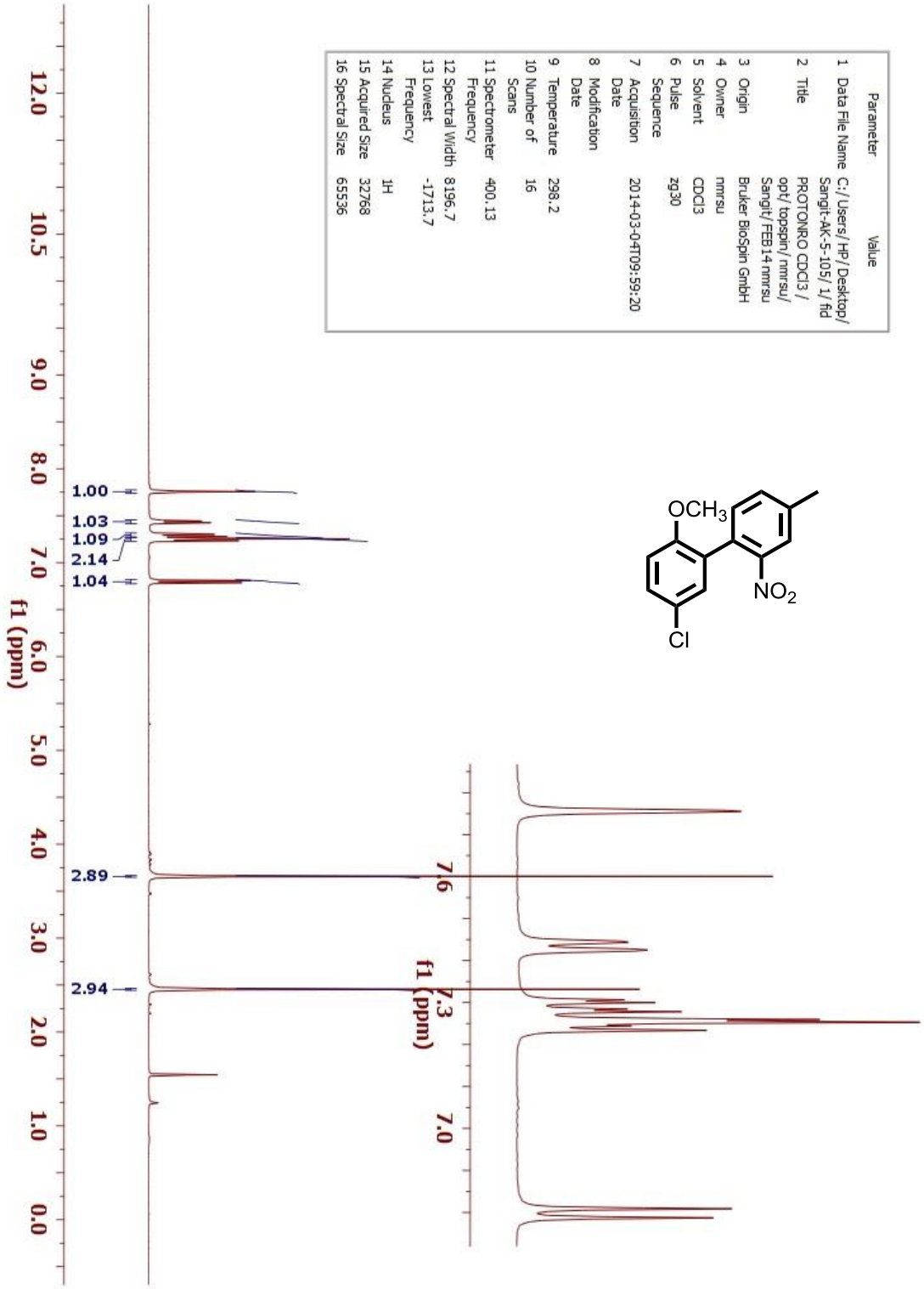


Figure S4 ^{13}C NMR spectrum of 5'-chloro-2'-methoxy-4-methyl-2-nitro-1,1'-biphenyl **(substrate for 52)**

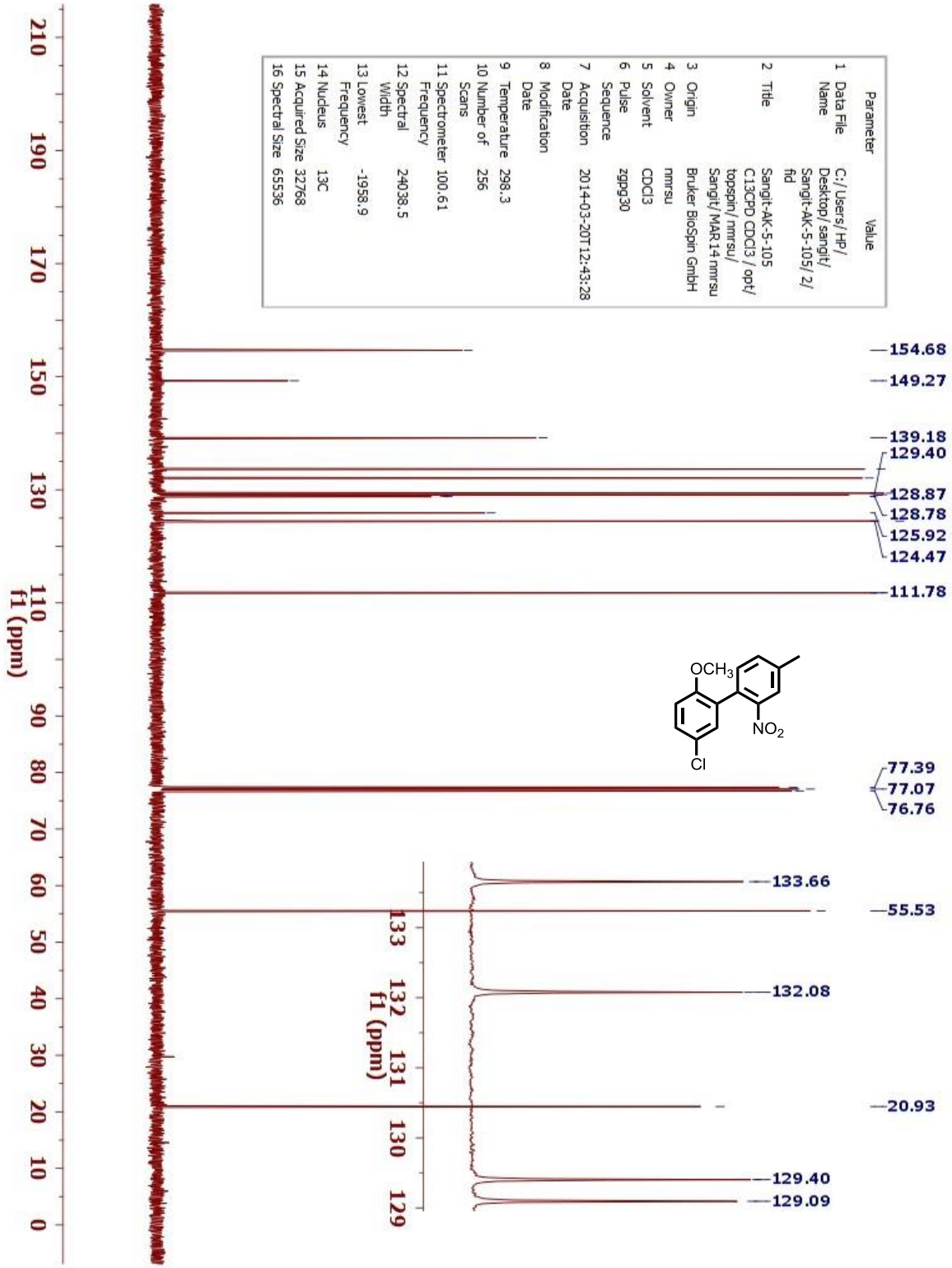


Figure S103 ^{1}H NMR spectrum of **52**

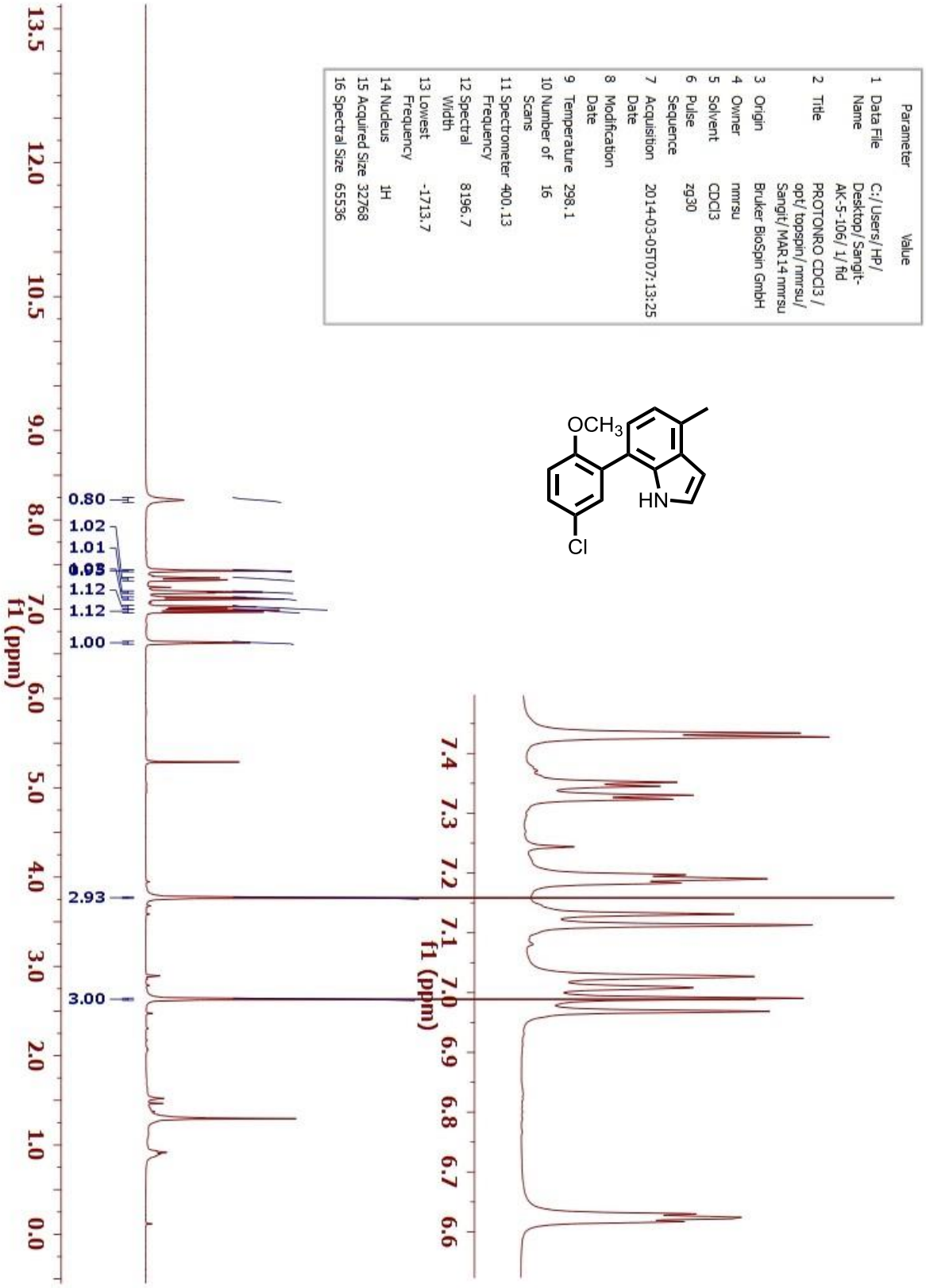


Figure S104 ^{13}C NMR spectrum of **52**

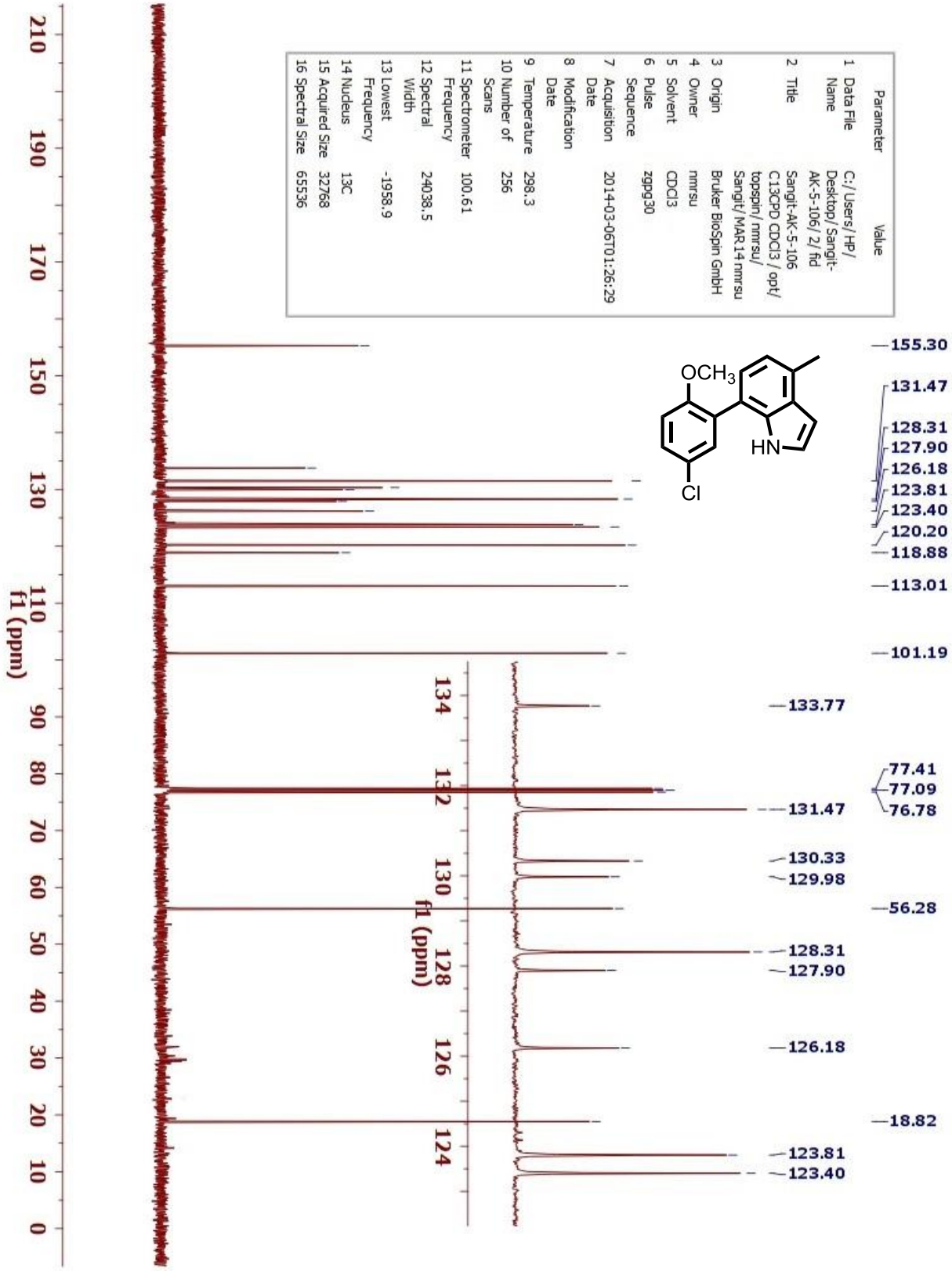


Figure S105 ^{1}H NMR spectrum of **53**

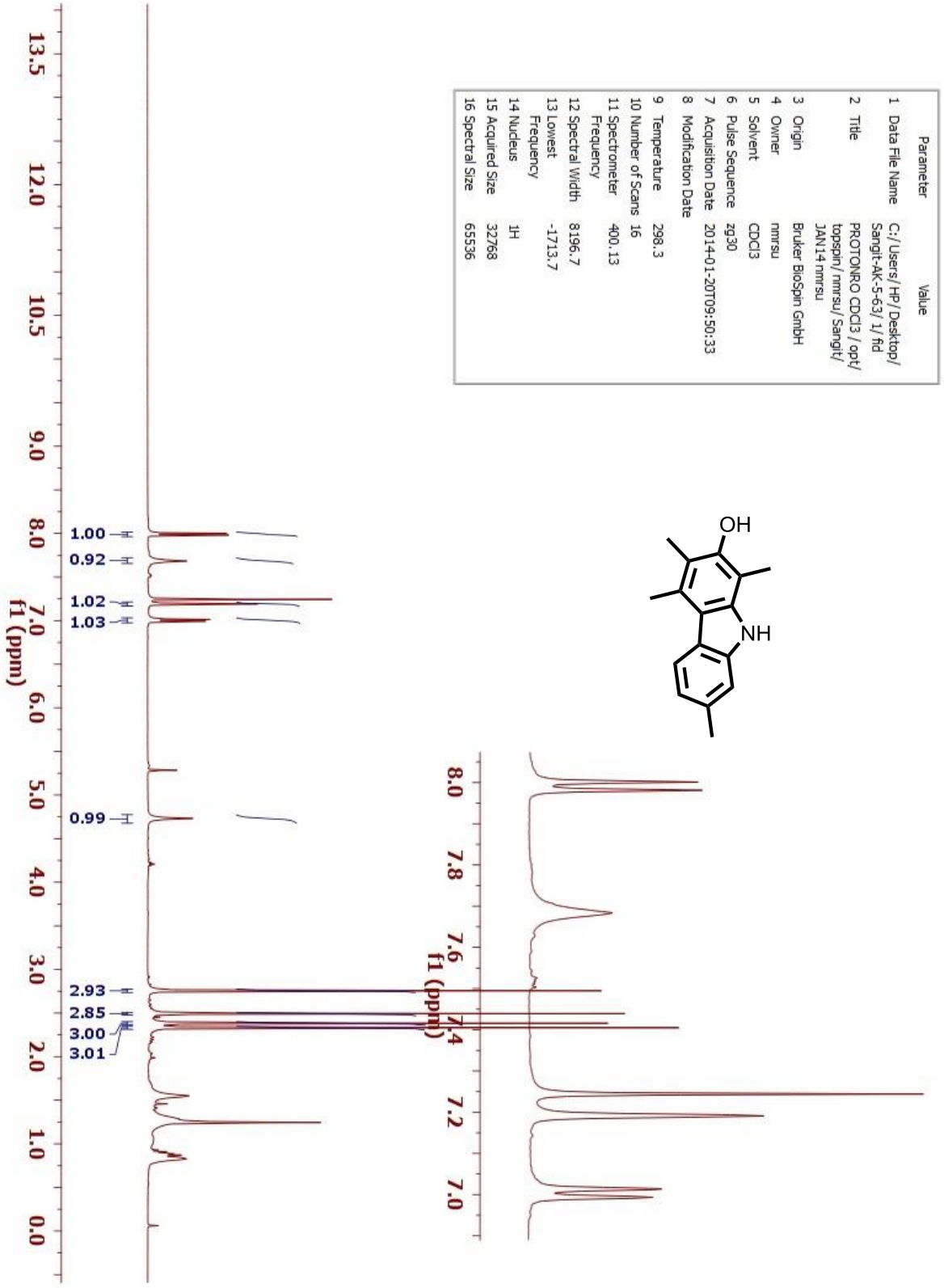


Figure S106 ^{13}C NMR spectrum of **53**

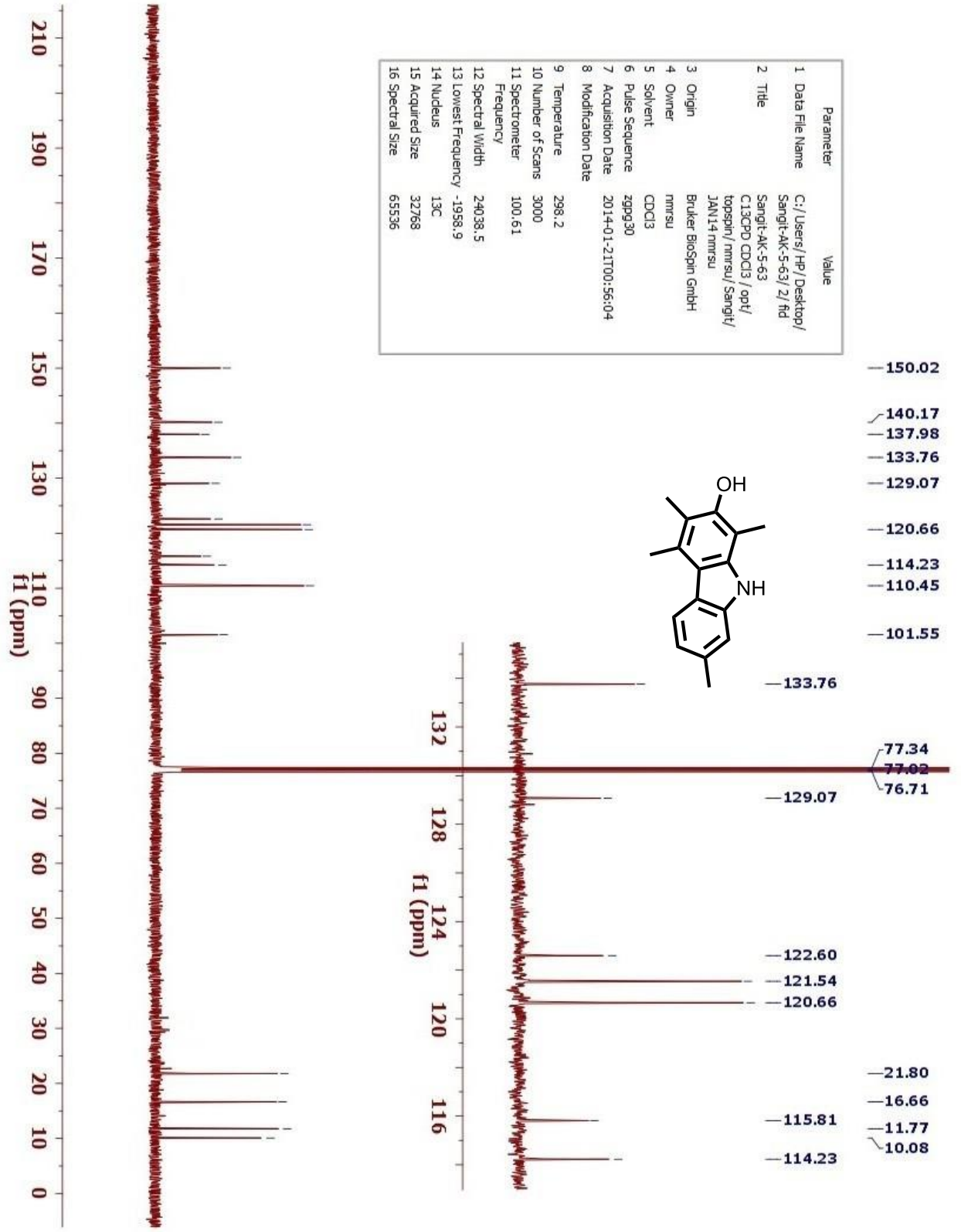


Figure S107 ^{1}H NMR spectrum of **54**

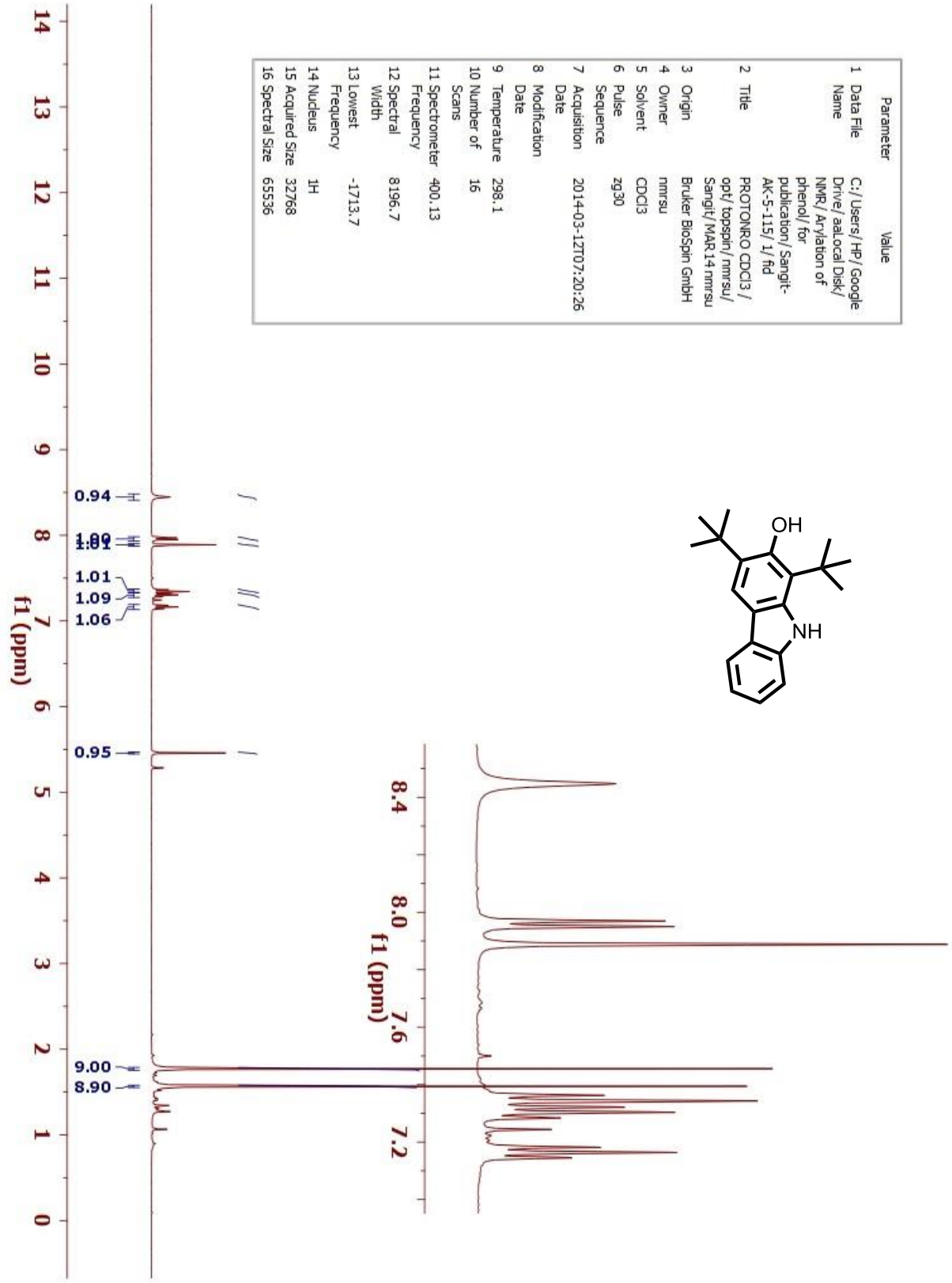


Figure S108 ^{13}C NMR spectrum of **54**

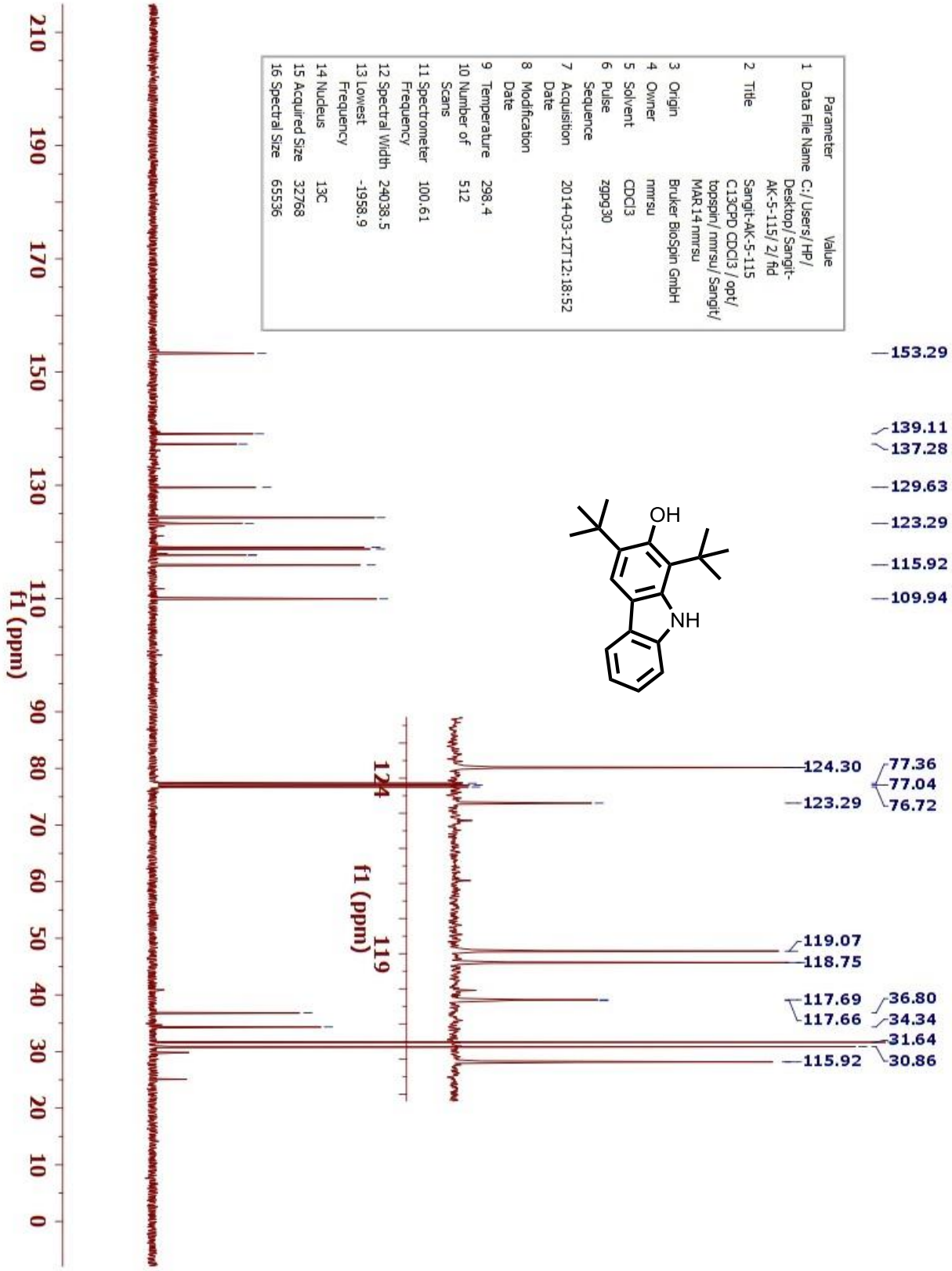


Figure S109 ^{1}H NMR spectrum of **55**

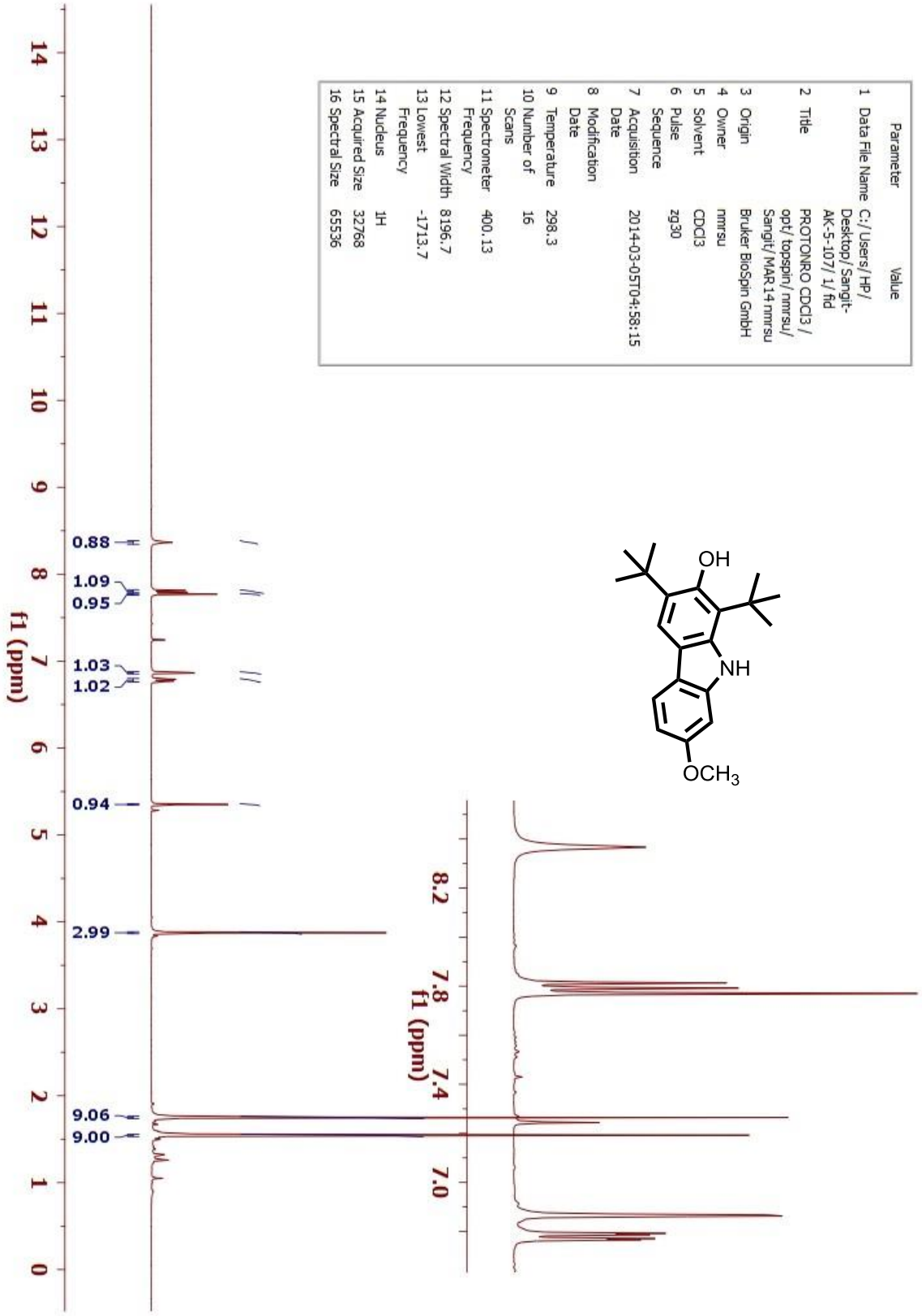


Figure S110 ^{13}C NMR spectrum of **55**

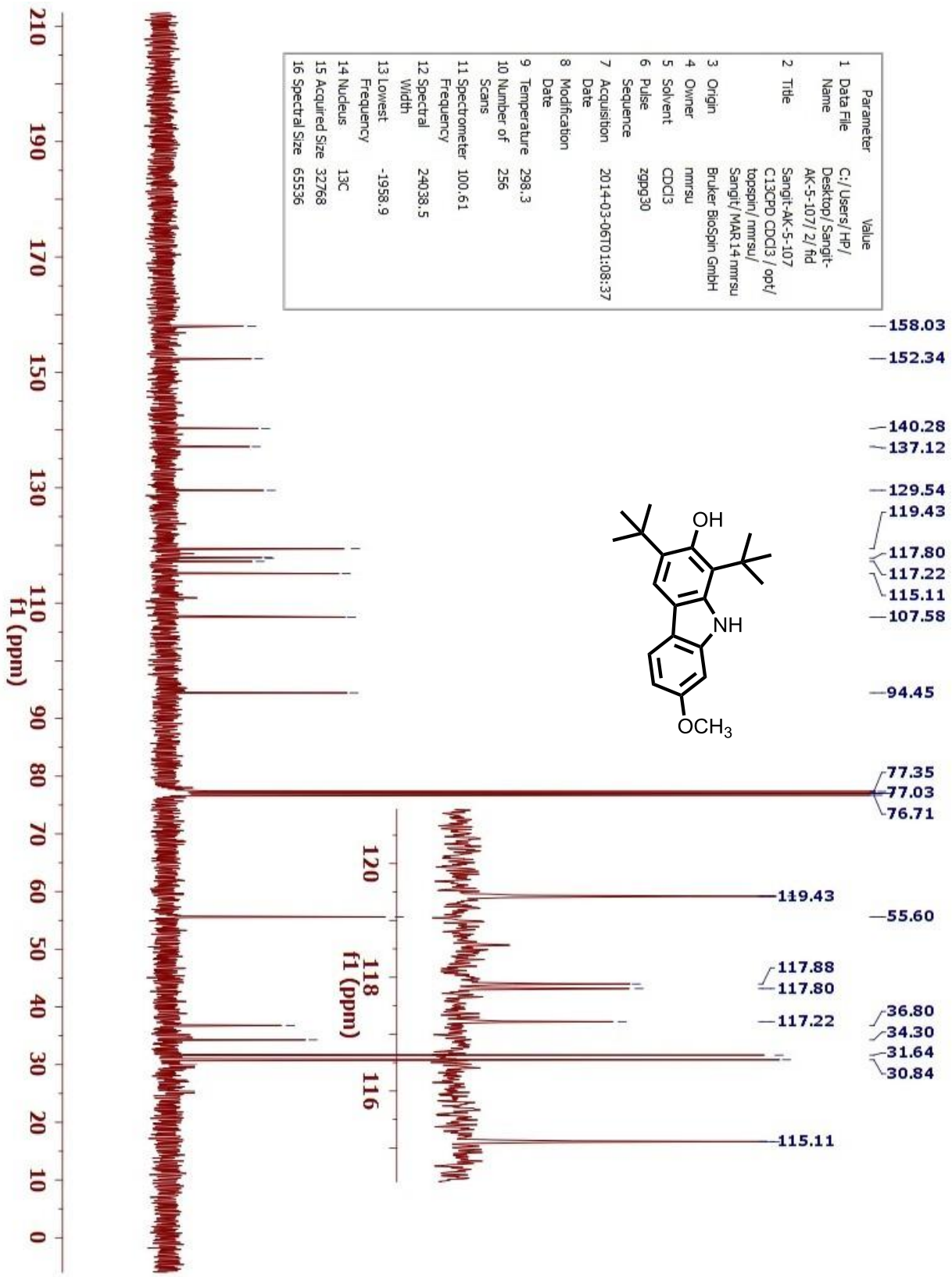


Figure Sxxx ^{1}H NMR spectrum of **substrate**

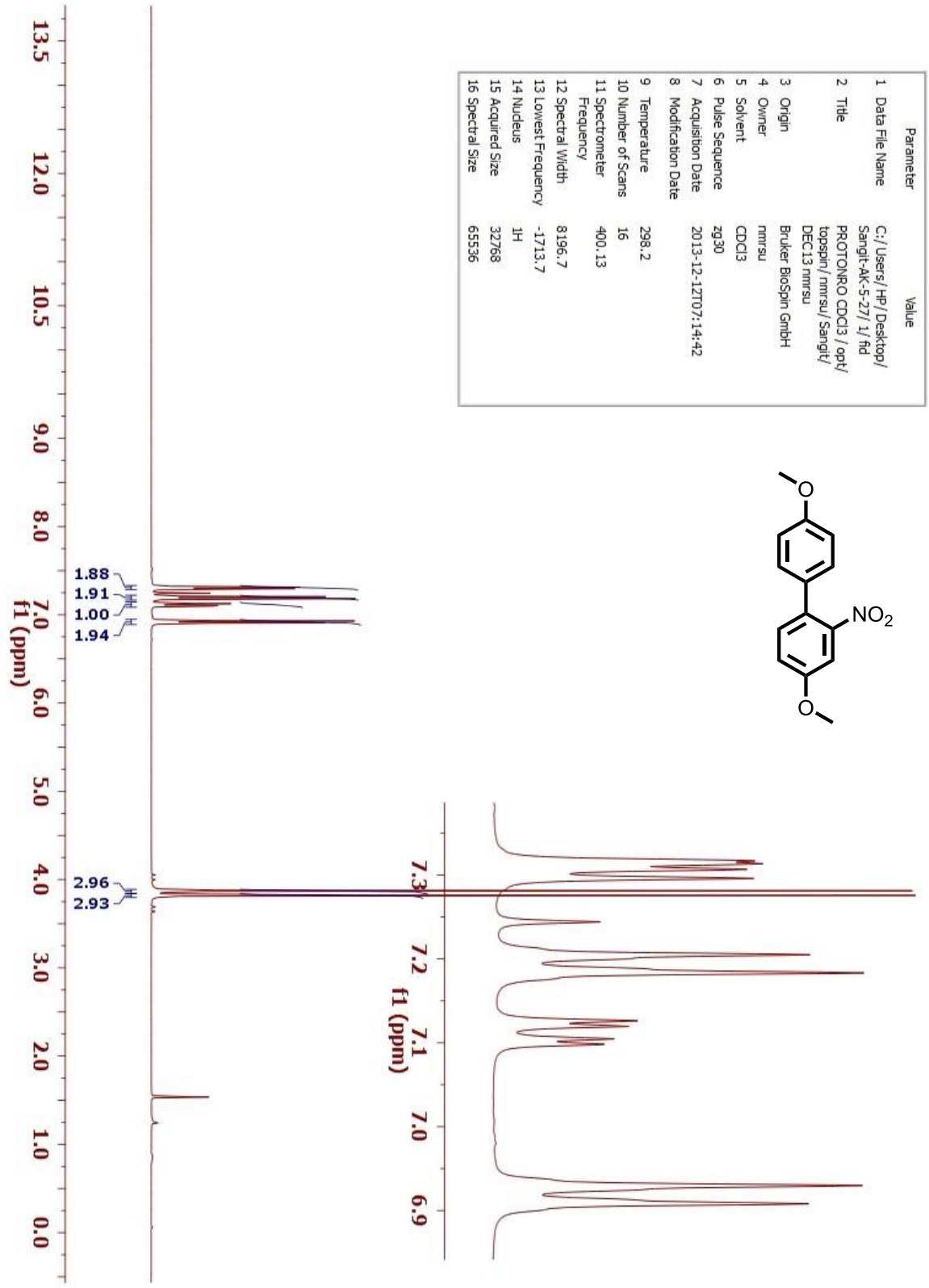


Figure S112 ^{13}C NMR spectrum of 4,4'-dimethoxy-2-nitro-1,1'-biphenylfor **56**

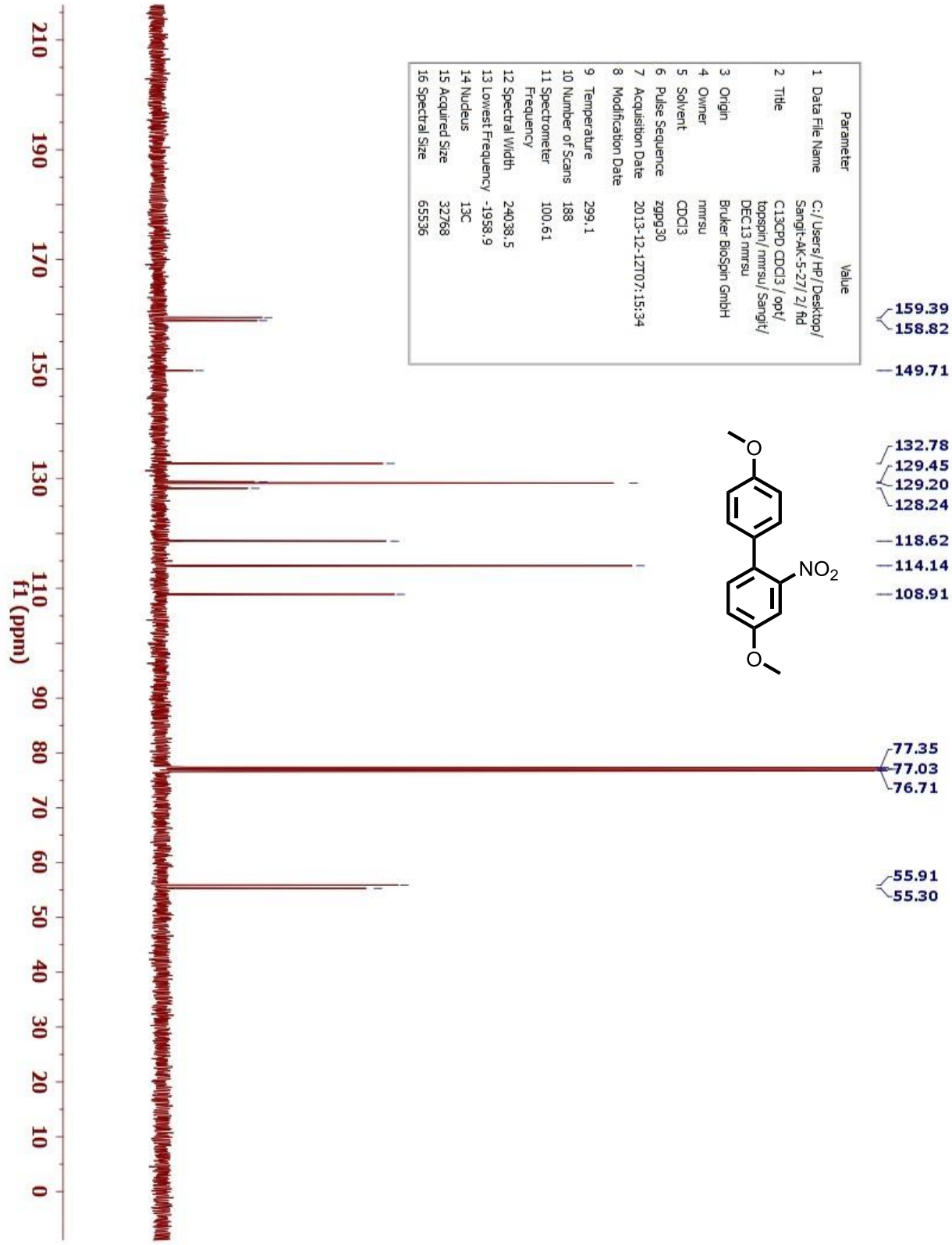


Figure S111 ^{1}H NMR spectrum of **56**

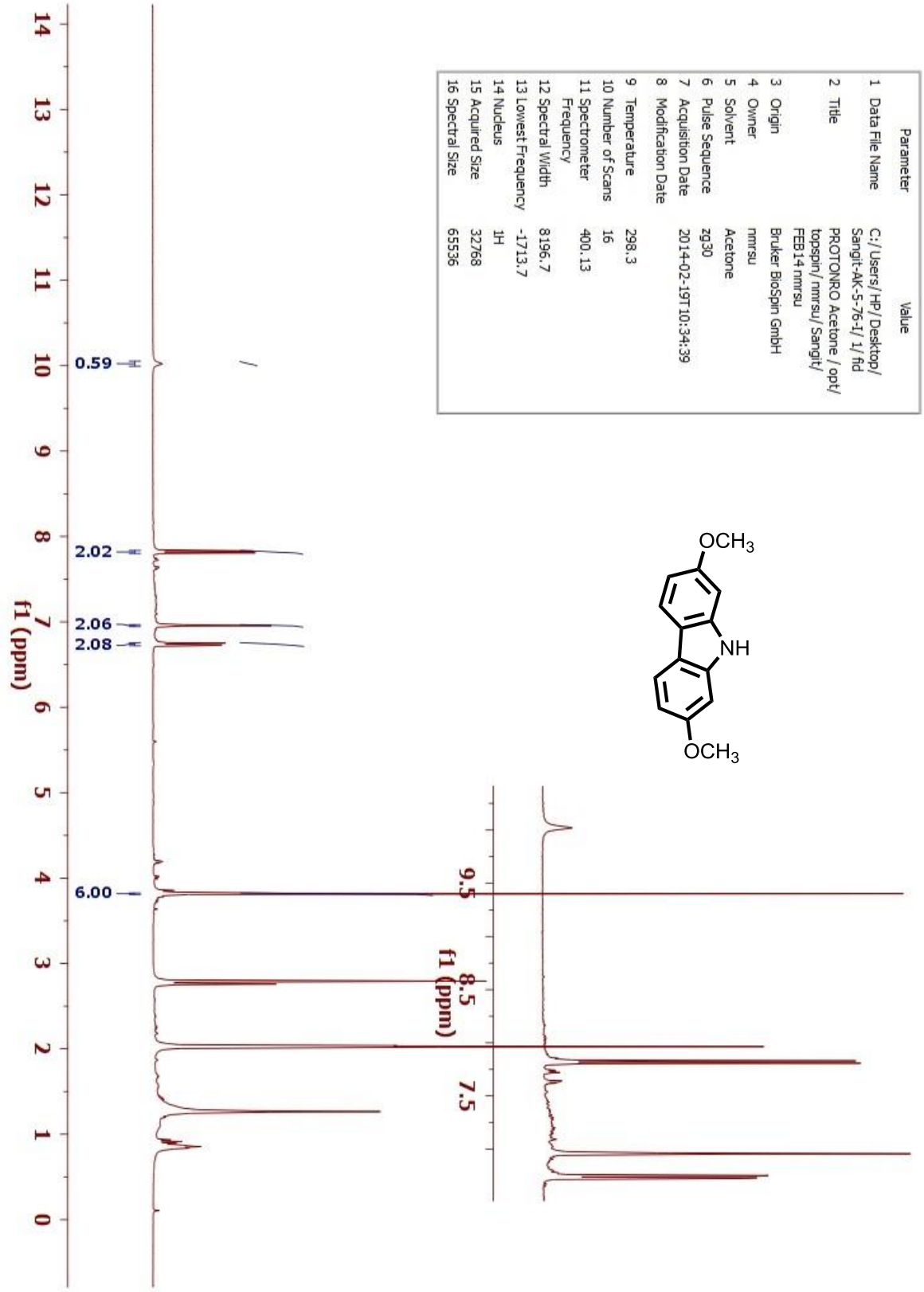


Figure S112 ^{13}C NMR spectrum of **56**

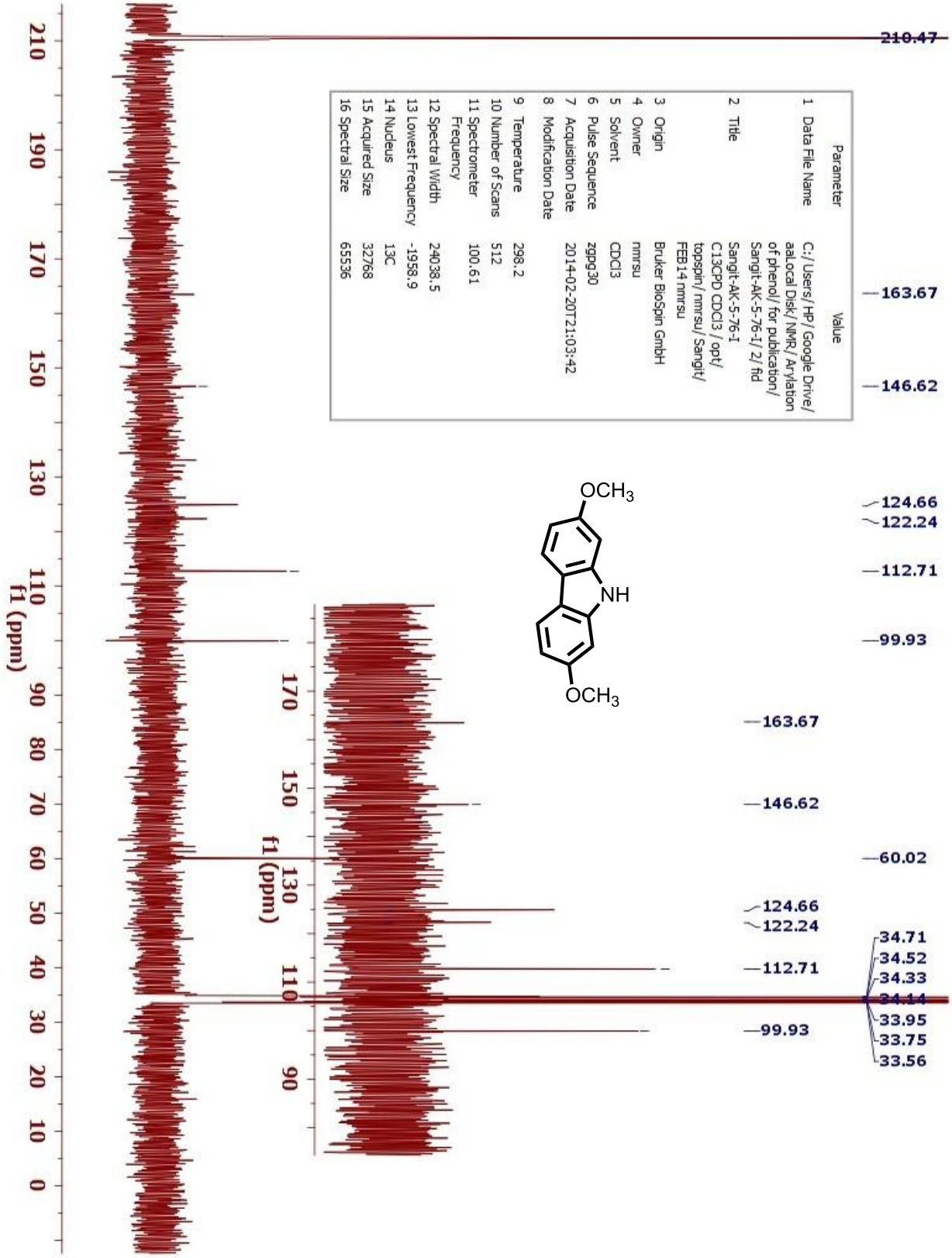


Figure S113. ORTEP views of **10**

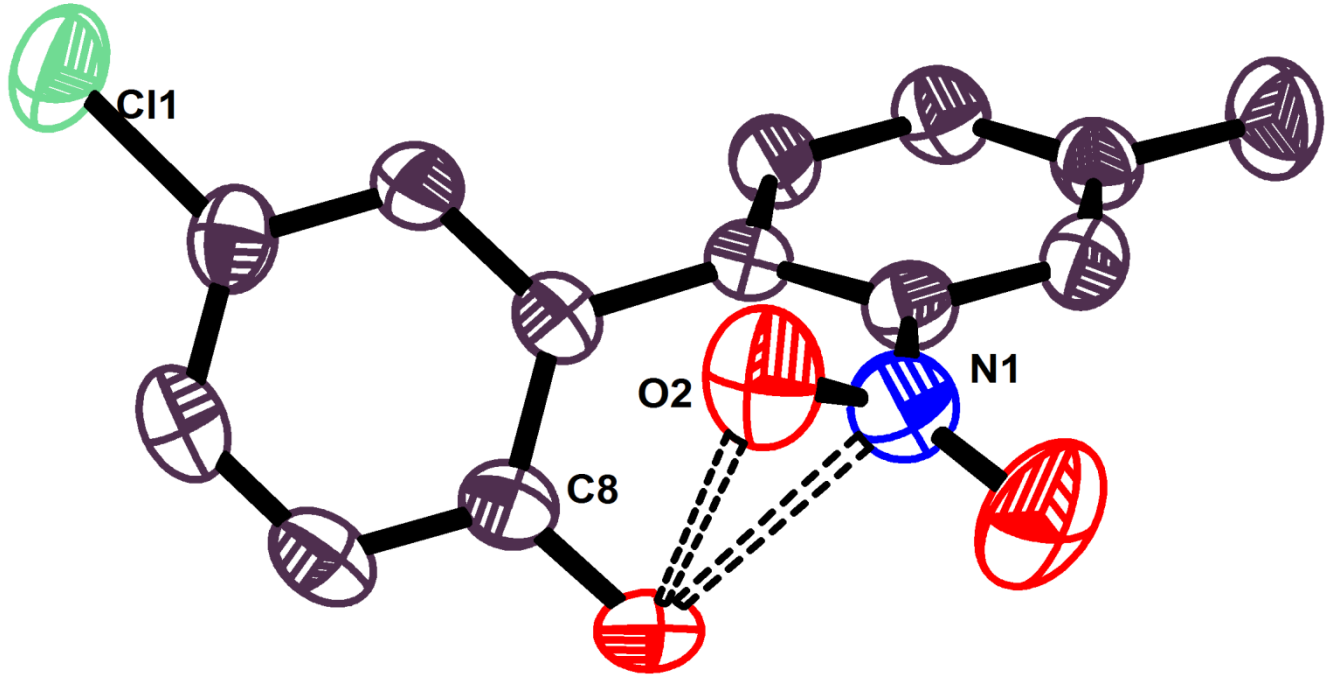


Figure S114. Packing diagram of **10**

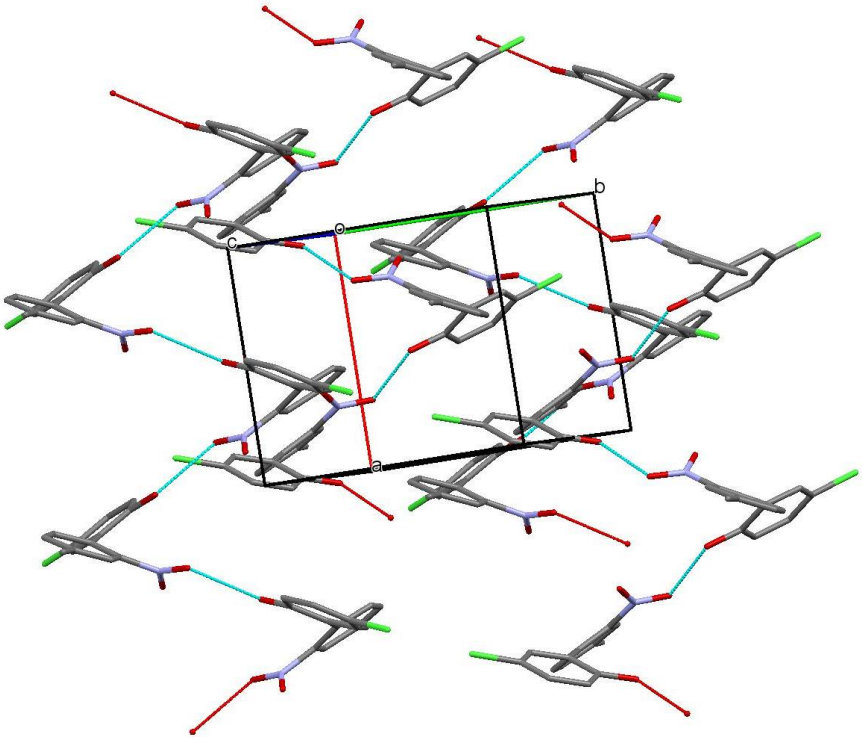


Table S2. Crystal data and structure refinement for 5-chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **10**

Identification code	5-chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol	
Empirical formula	C13 H8 Cl N O3	
Formula weight	261.65	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.9194(3) Å	α = 90°.
	b = 8.8519(3) Å	β = 90°.
	c = 17.3430(6) Å	γ = 90°.
Volume	1215.77(7) $Å^3$	
Z	4	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.312 mm^{-1}	
F(000)	536	
Theta range for data collection	3.647 to 28.064°.	
Index ranges	-10<=h<=7, -11<=k<=10, -22<=l<=22	
Reflections collected	8652	
Independent reflections	2912 [R(int) = 0.0795]	
Completeness to theta = 25.242°	99.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2912 / 0 / 167	
Goodness-of-fit on F^2	0.801	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1082	
R indices (all data)	R1 = 0.0452, wR2 = 0.1145	
Absolute structure parameter	-0.08(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.204 and -0.291 $e.Å^{-3}$	

Table S3. Bond lengths [Å] for 5-chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **10**

Cl1—C11	1.737 (3)	C7—C8	1.394 (3)
O1—N1	1.226 (3)	C8—C9	1.392 (3)
O2—N1	1.215 (3)	C9—C10	1.375 (4)
O3—C8	1.363 (3)	C9—H9	0.9300
O3—H10	0.84 (4)	C10—C11	1.374 (4)
C13—C3	1.509 (3)	C10—H8	0.9300
C13—H12	0.9600	C11—C12	1.387 (3)
C13—H11	0.9600	C12—H7	0.9300
C13—H13	0.9600	C5—C4	1.391 (3)
N1—C1	1.472 (3)	C5—H6	0.9300
C1—C2	1.384 (3)	C4—C3	1.385 (3)
C1—C6	1.389 (3)	C4—H5	0.9300
C6—C5	1.387 (3)	C3—C2	1.387 (3)
C6—C7	1.486 (3)	C2—H4	0.9300
C7—C12	1.390 (3)		

Table S4. Bond angles [°] for 5-chloro-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **10**

C8—O3—H10	111 (3)	C10—C9—H9	119.7
C3—C13—H12	109.5	C8—C9—H9	119.7
C3—C13—H11	109.5	C11—C10—C9	119.12 (19)
H12—C13—H11	109.5	C11—C10—H8	120.4
C3—C13—H13	109.5	C9—C10—H8	120.4
H12—C13—H13	109.5	C10—C11—C12	121.3 (2)
H11—C13—H13	109.5	C10—C11—Cl1	119.79 (16)
O2—N1—O1	122.9 (2)	C12—C11—Cl1	118.9 (2)

O2—N1—C1	119.0 (2)	C11—C12—C7	120.1 (2)
O1—N1—C1	118.1 (2)	C11—C12—H7	120.0
C2—C1—C6	123.4 (2)	C7—C12—H7	120.0
C2—C1—N1	116.4 (2)	C6—C5—C4	122.1 (2)
C6—C1—N1	120.15 (17)	C6—C5—H6	118.9
C5—C6—C1	115.38 (17)	C4—C5—H6	118.9
C5—C6—C7	118.18 (19)	C3—C4—C5	121.3 (2)
C1—C6—C7	126.37 (18)	C3—C4—H5	119.3
C12—C7—C8	118.60 (18)	C5—C4—H5	119.3
C12—C7—C6	119.33 (19)	C4—C3—C2	117.42 (18)
C8—C7—C6	121.82 (19)	C4—C3—C13	121.2 (2)
O3—C8—C9	122.5 (2)	C2—C3—C13	121.4 (2)
O3—C8—C7	117.10 (18)	C1—C2—C3	120.3 (2)
C9—C8—C7	120.3 (2)	C1—C2—H4	119.9
C10—C9—C8	120.6 (2)	C3—C2—H4	119.9

Figure S115. ORTEP views of **11**

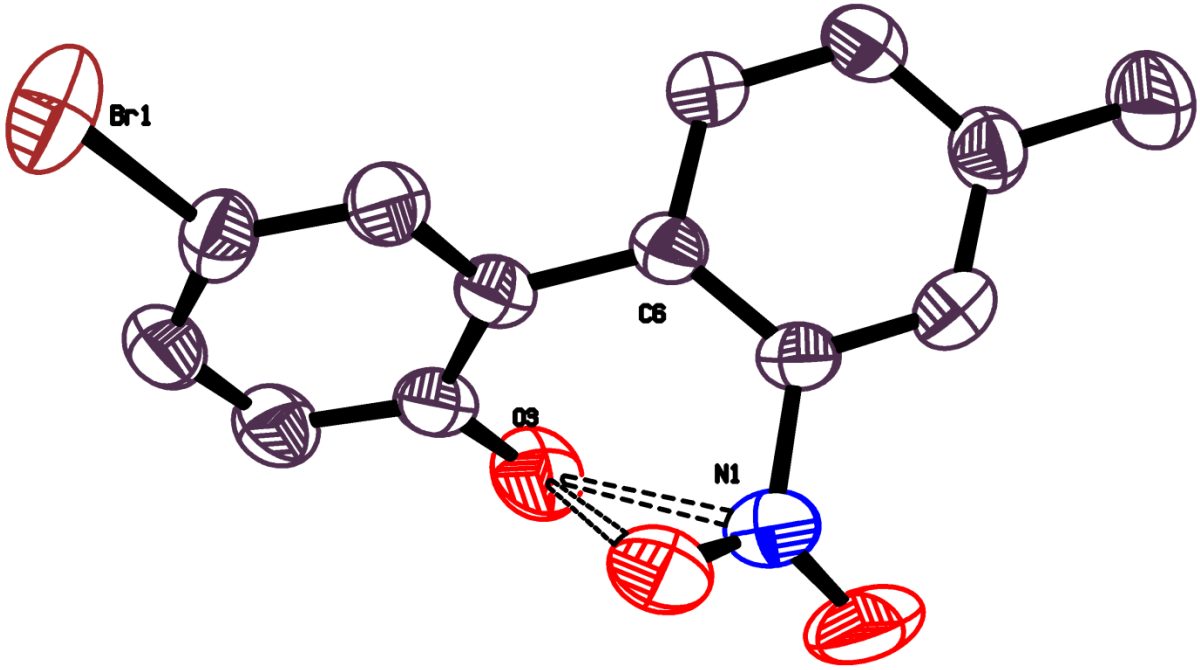


Figure S116. Packing diagram of **11**

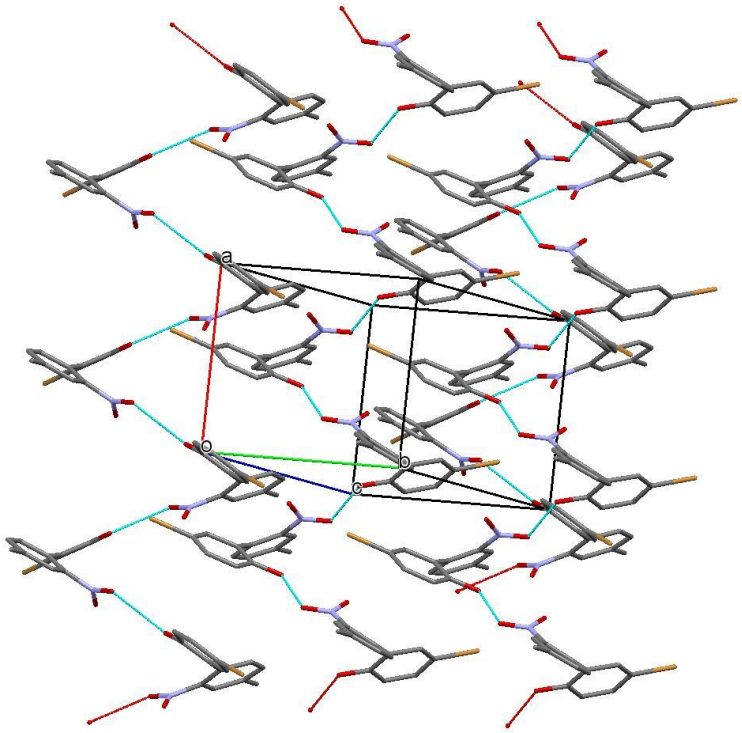


Table S5. Crystal data and structure refinement for 5-bromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **11**

Identification code	5-bromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol	
Empirical formula	C13 H10 Br N O3	
Formula weight	308.12	
Temperature	305(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.9842(14) Å	α= 90°.
	b = 8.9505(15) Å	β= 90°.
	c = 17.463(3) Å	γ = 90°.
Volume	1248.0(4) $Å^3$	
Z	4	
Density (calculated)	1.635 Mg/m^3	
Absorption coefficient	3.292 mm^{-1}	
F (000)	612	
Theta range for data collection	2.557 to 30.100°.	
Index ranges	0<=h<=11, 0<=k<=12, 0<=l<=24	
Reflections collected	2091	
Independent reflections	2091 [R(int) = 0.0000]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2091 / 0 / 165	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1223	
R indices (all data)	R1 = 0.0764, wR2 = 0.1396	
Absolute structure parameter	0.415(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.676 and -0.273 $e.Å^{-3}$	

Table S6. Bond lengths [Å] for 5-bromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **11**

Br1—C9	1.897 (5)	C7—C6	1.488 (6)
O3—C12	1.349 (6)	C6—C5	1.391 (6)
O3—H7	0.8200	C6—C1	1.406 (6)
O2—N1	1.214 (6)	C5—C4	1.389 (6)
O1—N1	1.221 (6)	C5—H3	0.9300
C3—C4	1.377 (7)	C4—H2	0.9300
C3—C2	1.392 (6)	C13—H8	0.9600
C3—C13	1.493 (7)	C13—H10	0.9600
C10—C9	1.370 (7)	C13—H9	0.9600
C10—C11	1.389 (7)	C11—C12	1.390 (6)
C10—H5	0.9300	C11—H6	0.9300
C9—C8	1.382 (6)	C1—C2	1.381 (6)
C8—C7	1.387 (6)	C1—N1	1.463 (6)
C8—H4	0.9300	C2—H1	0.9300
C7—C12	1.405 (6)		

Table S7. Bond angles [°] for 5-bromo-4'-methyl-2'-nitro-[1,1'-biphenyl]-2-ol **11**

C12—O3—H7	109.5	C3—C4—H2	118.9
C4—C3—C2	117.5 (4)	C5—C4—H2	118.9
C4—C3—C13	121.5 (4)	C3—C13—H8	109.5
C2—C3—C13	120.9 (4)	C3—C13—H10	109.5
C9—C10—C11	118.4 (4)	H8—C13—H10	109.5
C9—C10—H5	120.8	C3—C13—H9	109.5
C11—C10—H5	120.8	H8—C13—H9	109.5
C10—C9—C8	121.9 (4)	H10—C13—H9	109.5
C10—C9—Br1	119.2 (3)	C10—C11—C12	121.0 (4)
C8—C9—Br1	118.8 (4)	C10—C11—H6	119.5

C9—C8—C7	120.0 (4)	C12—C11—H6	119.5
C9—C8—H4	120.0	O3—C12—C11	122.9 (4)
C7—C8—H4	120.0	O3—C12—C7	117.6 (4)
C8—C7—C12	119.0 (4)	C11—C12—C7	119.5 (4)
C8—C7—C6	119.3 (4)	C2—C1—C6	122.4 (4)
C12—C7—C6	121.4 (4)	C2—C1—N1	117.2 (4)
C5—C6—C1	116.3 (4)	C6—C1—N1	120.3 (4)
C5—C6—C7	117.8 (4)	O2—N1—O1	123.1 (4)
C1—C6—C7	125.9 (4)	O2—N1—C1	119.2 (4)
C4—C5—C6	121.0 (4)	O1—N1—C1	117.6 (4)
C4—C5—H3	119.5	C1—C2—C3	120.4 (4)
C6—C5—H3	119.5	C1—C2—H1	119.8
C3—C4—C5	122.2 (4)	C3—C2—H1	119.8

Figure S117. ORTEP views of **27**

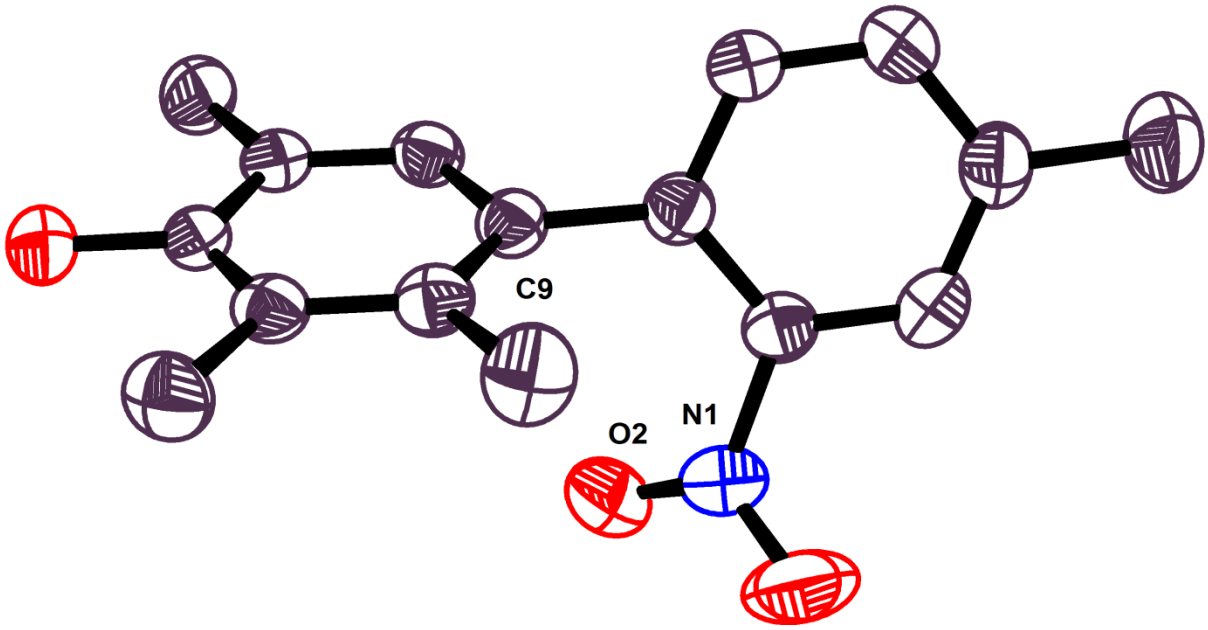


Figure S118. Packing diagram of **27**

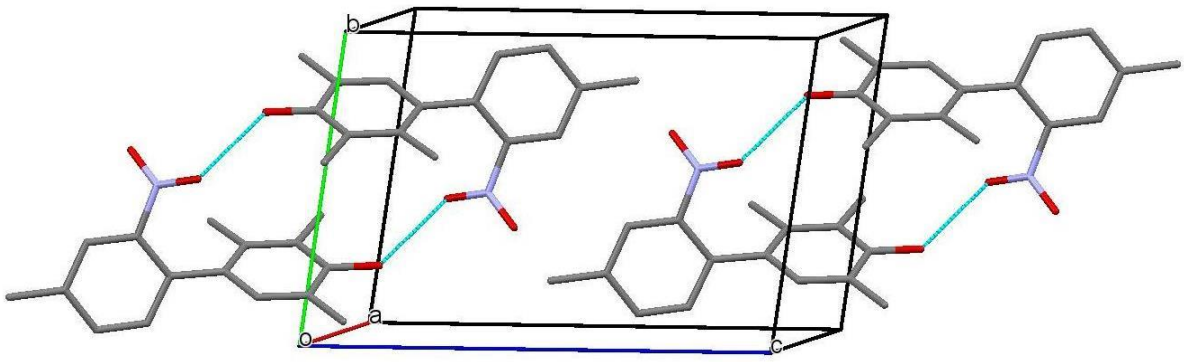


Table S8 Crystal data and structure refinement for 2,3,4',5-tetramethyl-2'-nitro-[1,1'-biphenyl]-4-ol **27**

Identification code	2,3,4',5-tetramethyl-2'-nitro-[1,1'-biphenyl]-4-ol	
Empirical formula	C16 H17 N O3	
Formula weight	271.31	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.8419(3) Å	α= 82.195(3)°.
	b = 8.4340(3) Å	β= 79.847(3)°.
	c = 12.6395(5) Å	γ= 85.040(2)°.
Volume	709.82(5) $Å^3$	
Z	2	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	288	
Theta range for data collection	1.65 to 25.242°.	
Index ranges	-7<=h<=8, -10<=k<=10, 0<=l<=14	
Reflections collected	2208	
Independent reflections	2208 [R(int) = 0.0000]	
Completeness to theta = 26.63°	86.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2208 / 0 / 188	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1340	
R indices (all data)	R1 = 0.0552, wR2 = 0.1404	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.199 and -0.184 e.$Å^{-3}$	

Table S9. Bond lengths [Å] for 2,3,4',5-tetramethyl-2'-nitro-[1,1'-biphenyl]-4-ol **27**

O1—C1	1.377 (2)	C13—C12	1.388 (3)
O1—H1	0.85 (3)	C13—C14	1.508 (3)
O3—N1	1.220 (2)	C14—H15	0.9600

O2—N1	1.219 (2)	C14—H14	0.9600
N1—C11	1.470 (2)	C14—H13	0.9600
C1—C6	1.391 (3)	C9—H6	0.9600
C1—C2	1.393 (3)	C9—H7	0.9600
C2—C3	1.397 (3)	C9—H5	0.9600
C2—C8	1.511 (3)	C5—C6	1.375 (3)
C3—C4	1.407 (3)	C5—H8	0.9300
C3—C9	1.512 (3)	C6—C7	1.508 (3)
C4—C5	1.393 (2)	C7—H9	0.9600
C4—C10	1.487 (3)	C7—H11	0.9600
C10—C16	1.392 (3)	C7—H10	0.9600
C10—C11	1.399 (3)	C12—C11	1.374 (3)
C16—C15	1.380 (3)	C12—H12	0.9300
C16—H17	0.9300	C8—H2	0.9600
C15—C13	1.383 (3)	C8—H4	0.9600
C15—H16	0.9300	C8—H3	0.9600

Table S10. Bond angels [^{o}] for 2,3,4',5-tetramethyl-2'-nitro-[1,1'-biphenyl]-4-ol **27**

C1—O1—H1	111.7 (18)	H15—C14—H13	109.5
O2—N1—O3	123.03 (18)	H14—C14—H13	109.5
O2—N1—C11	119.25 (16)	C3—C9—H6	109.5
O3—N1—C11	117.7 (2)	C3—C9—H7	109.5
O1—C1—C6	115.72 (17)	H6—C9—H7	109.5
O1—C1—C2	122.02 (16)	C3—C9—H5	109.5
C6—C1—C2	122.27 (18)	H6—C9—H5	109.5
C1—C2—C3	119.20 (16)	H7—C9—H5	109.5
C1—C2—C8	118.94 (18)	C6—C5—C4	123.04 (17)
C3—C2—C8	121.86 (17)	C6—C5—H8	118.5
C2—C3—C4	119.57 (16)	C4—C5—H8	118.5
C2—C3—C9	120.63 (17)	C5—C6—C1	117.23 (17)
C4—C3—C9	119.77 (19)	C5—C6—C7	122.06 (17)

C5—C4—C3	118.57 (18)	C1—C6—C7	120.70 (18)
C5—C4—C10	117.78 (16)	C6—C7—H9	109.5
C3—C4—C10	123.56 (16)	C6—C7—H11	109.5
C16—C10—C11	114.46 (18)	H9—C7—H11	109.5
C16—C10—C4	119.65 (16)	C6—C7—H10	109.5
C11—C10—C4	125.89 (16)	H9—C7—H10	109.5
C15—C16—C10	122.68 (18)	H11—C7—H10	109.5
C15—C16—H17	118.7	C11—C12—C13	120.69 (18)
C10—C16—H17	118.7	C11—C12—H12	119.7
C13—C15—C16	121.55 (19)	C13—C12—H12	119.7
C13—C15—H16	119.2	C12—C11—C10	123.55 (17)
C16—C15—H16	119.2	C12—C11—N1	116.45 (16)
C15—C13—C12	117.0 (2)	C10—C11—N1	119.98 (18)
C15—C13—C14	121.6 (2)	C2—C8—H2	109.5
C12—C13—C14	121.3 (2)	C2—C8—H4	109.5
C13—C14—H15	109.5	H2—C8—H4	109.5
C13—C14—H14	109.5	C2—C8—H3	109.5
H15—C14—H14	109.5	H2—C8—H3	109.5
C13—C14—H13	109.5	H4—C8—H3	109.5

Figure S119. ORTEP views of **33**

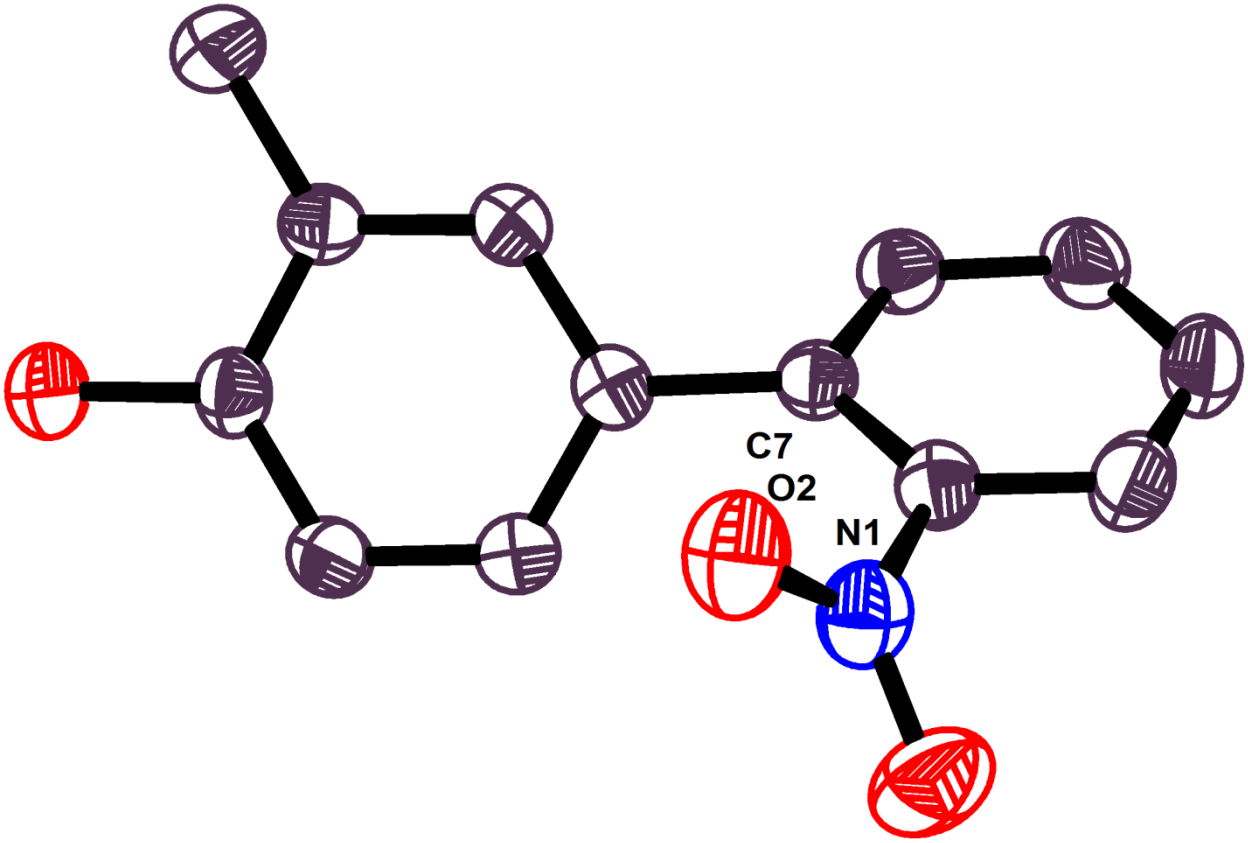


Figure S120. Packing diagram of Nitrobiarylol **33**

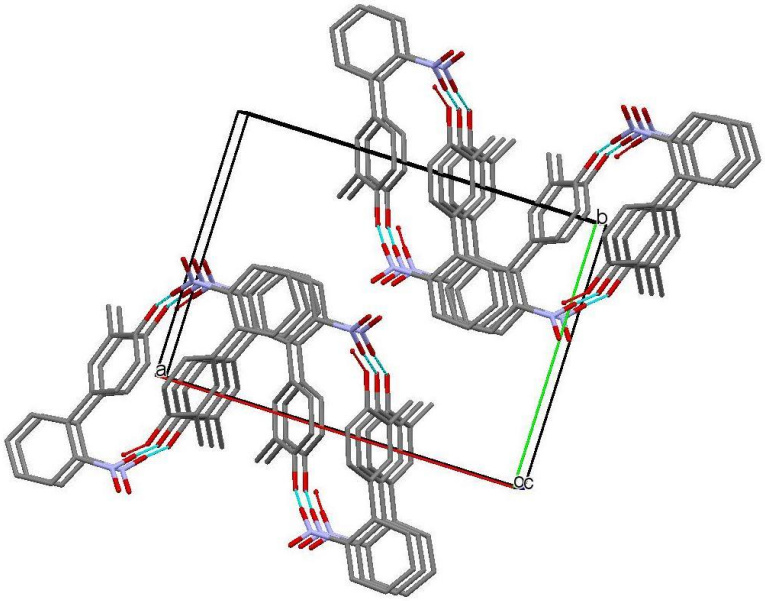


Table S11. Crystal data and structure refinement for 3-methyl-2'-nitro-[1,1'-biphenyl]-4-ol **33**

Identification code	3-methyl-2'-nitro-[1,1'-biphenyl]-4-ol	
Empirical formula	C13 H11N O3	
Formula weight	229.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 14.4397(11) Å	α= 90°.
	b = 10.6268(9) Å	β= 90°.
	c = 7.2172(5) Å	γ = 90°.
Volume	1107.46(15)Å^3	
Z	4	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F (000)	480	
Theta range for data collection	1.92 to 26.83°.	
Index ranges	0<=h<=18, -13<=k<=0, -9<=l<=9	
Reflections collected	2244	
Independent reflections	2244 [R(int) = 0.0000]	
Completeness to theta = 25.242°	94.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2244 / 1 / 159	
Goodness-of-fit on F^2	1.150	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.0904	
R indices (all data)	R1 = 0.0554, wR2 = 0.1087	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.197 and -0.193 e.Å^{-3}	

Table S12. Bond lengths [Å] for 3-methyl-2'-nitro-[1,1'-biphenyl]-4-ol **33**

O1—C1	1.375 (3)	C12—C11	1.382 (3)
O1—H1	0.81 (4)	C12—H7	0.9300
O2—N1	1.229 (3)	C11—C10	1.378 (4)
O3—N1	1.228 (3)	C11—H6	0.9300
N1—C8	1.467 (3)	C10—C9	1.380 (4)
C1—C2	1.392 (3)	C10—H5	0.9300
C1—C6	1.393 (4)	C9—C8	1.385 (3)
C2—C3	1.389 (3)	C9—H4	0.9300
C2—C13	1.496 (3)	C5—C6	1.379 (3)
C3—C4	1.398 (3)	C5—H3	0.9300
C3—H8	0.9300	C6—H2	0.9300
C4—C5	1.393 (3)	C13—H11	0.9600
C4—C7	1.486 (3)	C13—H9	0.9600
C7—C8	1.390 (3)	C13—H10	0.9600
C7—C12	1.398 (3)		

Table S13. Bond angels [^{o}] for 3-methyl-2'-nitro-[1,1'-biphenyl]-4-ol **33**

C1—O1—H1	107 (2)	C10—C11—H6	119.9
O3—N1—O2	122.9 (2)	C12—C11—H6	119.9
O3—N1—C8	117.7 (2)	C11—C10—C9	119.8 (2)
O2—N1—C8	119.4 (2)	C11—C10—H5	120.1
O1—C1—C2	117.2 (2)	C9—C10—H5	120.1
O1—C1—C6	121.4 (2)	C10—C9—C8	118.8 (2)
C2—C1—C6	121.3 (2)	C10—C9—H4	120.6

C3—C2—C1	117.4 (2)	C8—C9—H4	120.6
C3—C2—C13	121.3 (2)	C9—C8—C7	123.7 (2)
C1—C2—C13	121.4 (2)	C9—C8—N1	115.3 (2)
C2—C3—C4	122.7 (2)	C7—C8—N1	121.00 (19)
C2—C3—H8	118.7	C6—C5—C4	120.7 (2)
C4—C3—H8	118.7	C6—C5—H3	119.7
C5—C4—C3	118.1 (2)	C4—C5—H3	119.7
C5—C4—C7	121.7 (2)	C5—C6—C1	119.9 (2)
C3—C4—C7	120.1 (2)	C5—C6—H2	120.1
C8—C7—C12	115.3 (2)	C1—C6—H2	120.1
C8—C7—C4	125.74 (19)	C2—C13—H11	109.5
C12—C7—C4	118.85 (19)	C2—C13—H9	109.5
C11—C12—C7	122.2 (2)	H11—C13—H9	109.5
C11—C12—H7	118.9	C2—C13—H10	109.5
C7—C12—H7	118.9	H11—C13—H10	109.5
C10—C11—C12	120.2 (2)	H9—C13—H10	109.5

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