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

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# Transition Metal Free Sulfenylation and Bis-sulfenylation of Indoles: Persulfate Mediated Synthesis in Methanol

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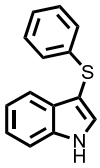
**General Experimental Details**

All NMR experiments were carried out on 400 MHz spectrometer in DMSO or $CDCl_3$ 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) or DMSO (2.50 ppm for $^1H$ and 39.50 ppm for $^{13}C$, respectively). Mass analysis is performed on quadruple-time of flight (Q-TOF) mass spectrometer equipped with an ESI source (+ve/-ve). Phenyl disulfide, 2,2'-dithiodibenzoic acid, and phenyl diselenide were used as received from Aldrich. Substituted aryl disulfides like 4-methylphenyl disulfide, 4-methoxyphenyl disulfide, and 2-aminophenyl disulfide were prepared by the oxidation of respective thiols by using *tert*-butyl hydroperoxide in the presence of catalytic amount of *N*,*N*-dimethylbenzylamine ditelluride. Silica gel (100-200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

**Synthetic procedure for 3-sulfenylation of indoles**:

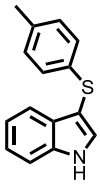
Methanol (5 mL) was added to a single neck flask (10 mL) containing stirrer bar. To this flask, diphenyl disulfide (218 mg, 1.0 mmol) and $(NH_4)_2S_2O_8$ (456 mg, 2.0 mmol) were added and stirred at reflux temperature (70 °C) for 3 hours. After this, reaction mixture was cooled to room temperature, Indole (234 mg, 2.0 mmol) was added and resulted reaction mixture was again refluxed at 70 °C for 3-4 hours. Progress of the reaction was monitored by TLC (10-20% EA: 90-80% Hexane). Upon completion of the reaction, the mixture was cooled to room temperature, poured into water, and extracted four times with 20 mL of ethyl acetate. The combined organic layers were dried over $Na_2SO_4$, and filtered. The solvent was removed *in vacuo* and the residue

was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate) to yield sulfenylated indole as product.



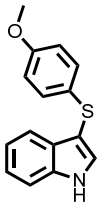
**3-(phenylthio)-1*H*-indole (1).**

White solid. Yield 0.31 g (68%); mp 147-149 $^{o}$C (Lit.[1] 150-152 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.29 (bs, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21-7.17 (m, 1H), 7.11-7.01 (m, 5H), 7.00-6.94 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.2, 136.5, 130.7, 129.1, 128.7, 125.9, 124.8, 123.1, 120.9, 119.7, 111.6, 102.9; GCMS-EI: rt = 10.2 min, *m/z* = 225.0.



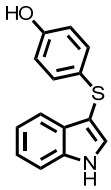
**3-(*p*-tolylthio)-1*H*-indole (2).**

Brown solid. Yield 0.36 g (76%); mp 122-125 $^{o}$C (Lit.[1] 124-126 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.46-7.39 (m, 2H), 7.28-7.22 (m, 1H), 7.18-7.12 (m, 1H), 7.06-6.95 (m, 4H), 2.25 (s, 3H). $^{13}$C NMR (100MHz,$CDCl_3$) δ 136.5, 135.5, 134.7, 130.5, 129.5, 129.1, 126.3, 123.0, 120.9, 119.7, 111.6, 103.5, 20.9; GCMS-EI: rt = 10.2 min, *m/z* = 239.0.



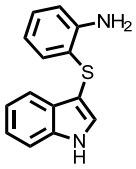
**3-((4-methoxyphenyl)thio)-1*H*-indole (3).**

Pale yellow solid. Yield 0.40 g (78%); mp 120-123 $^{o}$C (Lit.[1] 111-112 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.33 (bs, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.46-7.38 (m, 2H), 7.26-7.21 (m, 1H), 7.17-7.09 (m, 3H), 6.72 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.8, 136.5, 130.0, 129.5, 129.0, 128.6, 122.9, 120.8, 119.7, 114.5, 111.5, 104.7, 55.3. GCMS-EI: rt = 11.2 min, *m/z* = 254.9.



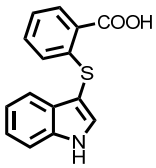
**4-((1*H*-indol-3-yl)thio)phenol (4).**

Light green solid. Yield 0.31 g (64%); mp 169-172 $^{o}$C; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 11.50 (s, 1H), 9.31 (s, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.04-6.95 (m, 3H), 6.61 (d, *J* = 8.6 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 156.1, 137.0, 131.9, 129.4, 129.1, 127.4, 122.4, 120.3, 118.9, 116.4, 112.6, 102.6. HRMS-ESI *m/z*: 240.0495 (Calculated for $C_{14}H_{11}NOS$ - $H^+$: 240.0478).



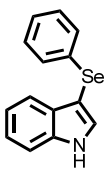
**2-((1*H*-indol-3-yl)thio)aniline (5).**

Yellow solid. Yield 0.28 g (58%); mp 89-92 $^{o}$C; (Lit.[2] 93-94 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.35 (bs, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.25-7.11 (m, 3H), 7.01 (dt, *J* = 7.6, 1.5 Hz, 1H), 6.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 6.61 (dt, *J* = 7.5, 1.0 Hz, 1H), 4.19 (bs, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.6, 136.4, 131.9, 129.2, 128.8, 128.1, 122.9, 120.9, 120.7, 119.4, 119.0, 115.4, 111.6, 104.1. GCMS-EI: rt = 11.8 min, *m/z* = 239.9.



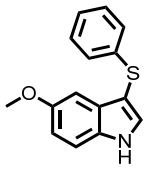
**2-((1*H*-indol-3-yl)thio)benzoic acid (6).**

Green solid. Yield 0.25 g (46%); mp 242-246 $^{o}$C; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 13.05 (bs, 1H), 11.69 (s, 1H), 7.89 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.70 (d, *J* = 2.6 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.20-7.13 (m, 2H), 7.10-6.99 (m, 2H), 6.66 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (100MHz, DMSO-$d_6$) δ 167.9, 144.2, 137.2, 133.1, 132.5, 131.4, 129.2, 127.1, 126.1, 124.2, 122.6, 120.6, 118.8, 112.9, 100.5. HRMS-ESI *m/z*: 270.0560 (Calculated for $C_{15}H_{11}NO_2S$ + $H^+$: 270.0583).



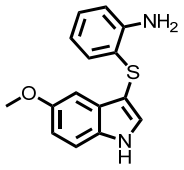
**3-(phenylselanyl)-1*H*-indole (7).**

White solid. Yield 0.44 g (80%); mp 135-138 $^{o}$C; (Lit.[3] 135-137 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.39 (bs, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29-7.21 (m, 3H), 7.20-7.06 (m, 4H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 136.4, 133.8, 131.2, 130.0, 129.0, 128.7, 125.6, 123.0, 120.9, 120.4, 111.4, 98.2. GCMS-EI: rt = 9.9 min, *m/z* = 272.9.




**5-methoxy-3-(phenylthio)-1H-indole (8).**

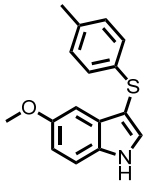
Pale yellow solid. Yield 0.31 g (61%); mp 76-79 $^{o}$C; (Lit.[1] 77-78 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.12-7.10 (m, 2H), 7.08-7.04 (m, 2H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1, 139.4, 131.4, 130.0, 128.8, 125.7, 124.8, 113.6, 112.5, 102.1, 100.8, 55.8. GCMS-EI: rt = 12.2 min, *m/z* = 254.9.




**2-((5-methoxy-1*H*-indol-3-yl)thio)aniline (9).**

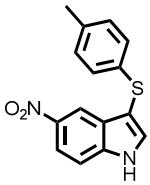
Dark brown oil. Yield 0.40 g (74%); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.27 (bs, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.15 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H),

6.99 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.60 (dt, *J* = 7.6, 1.1 Hz, 1H), 4.22 (bs, 2H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.4, 131.5, 131.3, 129.7, 129.6, 127.9, 121.0, 119.0, 115.4, 113.3, 112.4, 103.5, 100.9, 55.8. LRMS-ESI *m*/*z*: 270.0948 (Calculated for $C_{15}H_{14}N_2OS + H^+$: 270.1125).




**5-methoxy-3-(*p*-tolylthio)-1*H*-indole (10).**

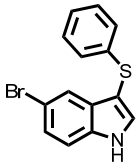
Brown oil. Yield 0.51 g (94%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 2.2 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.1, 135.7, 134.7, 131.4, 130.0, 129.6, 126.1, 113.5, 112.6, 102.6, 100.9, 55.9, 20.9. GCMS-EI: rt = 13.6 min, *m/z* = 268.9.




**5-nitro-3-(p-tolylthio)-1H-indole (11).**

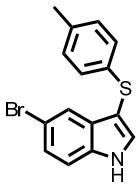
Yellow solid. Yield 0.31 g (55%); mp 204-207 $^o$C; (Lit.[4] 189-193 $^o$C); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.86 (bs, 1H), 8.54 (d, *J* = 2.0 Hz, 1H), 8.14 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 2.24 (s, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.4, 135.6, 134.0, 129.8, 128.8, 127.1, 118.7, 116.9, 111.8, 105.1, 20.9. GCMS-EI: rt = 14.9 min, *m/z* = 318.9. GCMS-EI: rt = 12.8 min, *m/z* = 284.1.



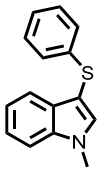

**5-bromo-3-(phenylthio)-1H-indole (12).**

White solid. Yield 0.31 g (52%); mp 120-123 $^{o}$C; (Lit.[1] 120-121 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.44 (bs, 1H), 7.75 (s, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.34 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.30-7.24 (m, 1H), 7.19-7.15 (m, 2H), 7.08-7.05 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.1, 131.9, 131.0, 128.8, 126.1, 125.9, 125.0, 122.3, 114.5, 113.1, 102.8. GCMS-EI: rt = 14.5min, *m/z* = 304.8.



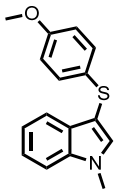

**5-bromo-3-(p-tolylthio)-1H-indole (13).**

Pale yellow solid. Yield 0.44 g (70%); mp 123-125 $^{o}$C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.33 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.28-7.24 (m, 1H), 7.02-6.97 (m, 4H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.1, 135.0, 134.9, 131.6, 131.0, 129.6, 126.4, 126.1, 122.3, 114.4, 113.0, 103.5, 20.9. GCMS-EI: rt = 14.9 min, *m/z* = --318.9.



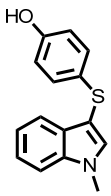
**1-methyl-3-(phenylthio)-1H-indole (14).**

Yellow solid. Yield 0.40 g (84%); mp 86-88 $^{o}$C; (Lit.[1] 84-86 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.33 (s, 1H), 7.29 (dt, *J* = 7.3, 0.7 Hz, 1H), 7.18-7.12 (m, 3H), 7.11-7.06 (m, 2H), 7.06-7.00 (m, 1H), 3.84 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 139.7, 137.6, 135.1, 129.9, 128.7, 125.8, 124.7, 122.6, 120.5, 119.8, 109.7, 33.2. LRMS-ESI *m/z*: 240.0911 (Calculated for $C_{15}H_{13}NS + H^{+}$: 240.0841).



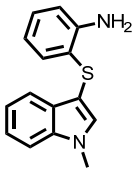
**3-((4-methoxyphenyl)thio)-1-methyl-1H-indole (15).**

Pale Yellow solid. Yield 0.43 g (80%); mp 64-67 $^{o}$C; (Lit.[5] 60-61 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.31-7.26 (m, 2H), 7.20-7.12 (m, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.73 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.8, 137.5, 134.5, 130.0, 129.8, 128.5, 122.5, 120.4, 119.7, 114.5, 109.7, 102.4, 55.4, 33.1. GCMS-EI: rt = 12.1 min, *m/z* = 268.9.



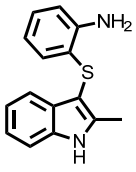
**4-((1-methyl-1H-indol-3-yl)thio)phenol (16).**

Pale yellow solid. Yield 0.35 g (70%); mp 94-97 $^{o}$C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.17 (bs, 1H), 3.78 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 153.6, 137.5, 134.6, 130.0, 129.7, 128.6, 122.5, 120.4, 119.7, 116.0, 109.7, 102.2, 33.1. HRMS-ESI *m*/*z*: 256.0774 (Calculated for $C_{15}H_{13}NOS + H^+$: 256.0791).




**2-((1-methyl-1*H*-indole-3-yl)thio)aniline (17).**

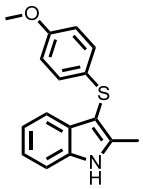
Purple solid. Yield 0.40 g (78%); mp 82-85 $^{o}$C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.35-7.15 (m, 5H), 7.01 (dt, *J* = 7.9, 1.4 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.62 (dt, *J* = 7.6, 1.0 Hz, 1H), 4.27 (bs, 2H), 3.75 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 145.6, 137.4, 133.6, 131.8, 129.6, 127.9, 122.5, 121.2, 120.3, 119.6, 118.9, 115.4, 109.7, 102.1, 33.1. HRMS-ESI *m*/*z*: 256.0963 (Calculated for $C_{15}H_{14}N_2S + H^+$: 256.0950).




**2-((2-methyl-1H-indol-3-yl)thio)aniline (18).**

Greenish yellow solid. Yield 0.36 g (72%); mp 69-72 $^{o}$C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.20 (bs, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.18-7.06 (m, 2H), 6.97-6.91 (m,

2H), 6.67-6.63 (m, 1H), 6.55 (dt, *J* = 7.5, 1.1 Hz, 1H), 4.15 (bs, 2H), 2.50 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 144.7, 140.3, 135.3, 130.2, 130.0, 127.0, 122.1, 121.8, 120.6,118.9, 118.8, 115.4, 110.7, 99.8, 12.3. HRMS-ESI *m*/*z*: 256.0952 (Calculated for $C_{15}H_{14}N_2S + H^+$: 256.0950).



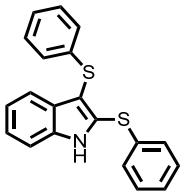
**3-((4-methoxyphenyl)thio)-2-methyl-1H-indole (19).**

Brick red solid. Yield 0.42 g (79%); mp 117-119 $^o$C; (Lit.[6] 119-120 $^o$C); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 (bs, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.19-7.08 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 2.52 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 157.5, 140.6, 135.4, 130.3, 129.9, 127.9, 122.1, 120.6, 119.0, 114.5, 110.6, 100.9, 55.4, 12.2. LRMS-ESI *m*/*z*: 268.0870 (Calculated for $C_{16}H_{15}NOS - H^+$: 268.0791).

**Synthetic procedure for 2,3-bis-sulfenylation of indoles**:

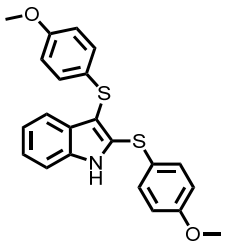
Methanol (5 mL) was added to a single neck flask (10 mL) containing stirrer bar. To this flask, diphenyl disulfide (218 mg, 1.0 mmol) and indole (117 mg, 1.0 mmol) were added. After this, $(NH_4)_2S_2O_8$ (456 mg, 2.0 mmol) and $I_2$ (254 mg, 1.0 mmol) were added one after the other portion wise and resulted reaction mixture was refluxed at 70 °C for 6-7 hours. Progress of the reaction was monitored by TLC (10-20% EA: 90-80% Hexane). Upon completion of the reaction, the mixture was cooled to room temperature, poured into water, and extracted four times with 20 mL of ethyl acetate. The combined organic layers were dried over $Na_2SO_4$, and

filtered. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate) to yield bis-sulfenylated indole as product.



**2,3-bis(phenylthio)-1H-indole (20).**

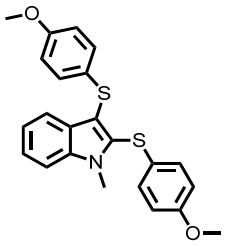
Pale yellow solid. Yield 0.15 g (44%); mp 96-98 $^{o}$C; (Lit.[7] 97-99 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.28-7.19 (m, 6H), 7.17-7.09 (m, 5H), 7.08-7.03 (m, 1H). $^{13}$C NMR (100MHz, $CDCl_3$) δ 138.1, 136.9, 134.3, 133.6, 130.0, 129.8, 129.4, 128.7, 127.3, 126.6, 125.1, 123.9, 121.4, 119.9, 111.1, 109.2. LRMS-ESI *m*/*z*: 333.0629 (Calculated for $C_{20}H_{15}NS_2$ : 333.0646).



**2,3-bis((4-methoxyphenyl)thio)-1H-indole (21).**

Brown solid. Yield 0.24 g (62%); mp 134-137 $^{o}$C; (Lit.[8] 133-135 $^{o}$C); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10 (bs, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.20-7.08 (m, 4H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.72 (s,

3H).[13]C NMR (100 MHz, $CDCl_3$) δ 159.9, 157.9, 136.5, 135.6, 133.7, 130.3, 129.3, 128.7, 127.2, 123.3, 123.2, 121.0, 119.5, 115.2, 114.5, 110.8, 55.4, 55.3. LRMS-ESI *m*/*z*: 393.0655 (Calculated for $C_{22}H_{19}NO_2S_2$ : 393.0857).



**2,3-bis((4-methoxyphenyl)thio)-1-methyl-1*H*-indole (22).**

Gray solid. Yield 0.29 g (71%); mp 92-94 °C; (Lit.[8] 95-96 °C); [1]H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.36-7.26 (m, 2H), 7.19-7.04 (m, 5H), 6.70 (t, *J* = 8.9 Hz, 4H), 3.78 (s, 3H), 3.72 (d, *J* = 4.2 Hz, 6H). [13]C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.0, 138.2, 135.4, 130.5, 129.5, 129.2, 129.1, 126.1, 123.7, 120.9, 120.3, 114.9, 114.4, 112.0, 110.1, 55.33, 55.30, 31.1. LRMS-ESI *m*/*z*: 408.1116 (Calculated for $C_{23}H_{21}NO_2S_2 + H^+$: 408.1087).

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

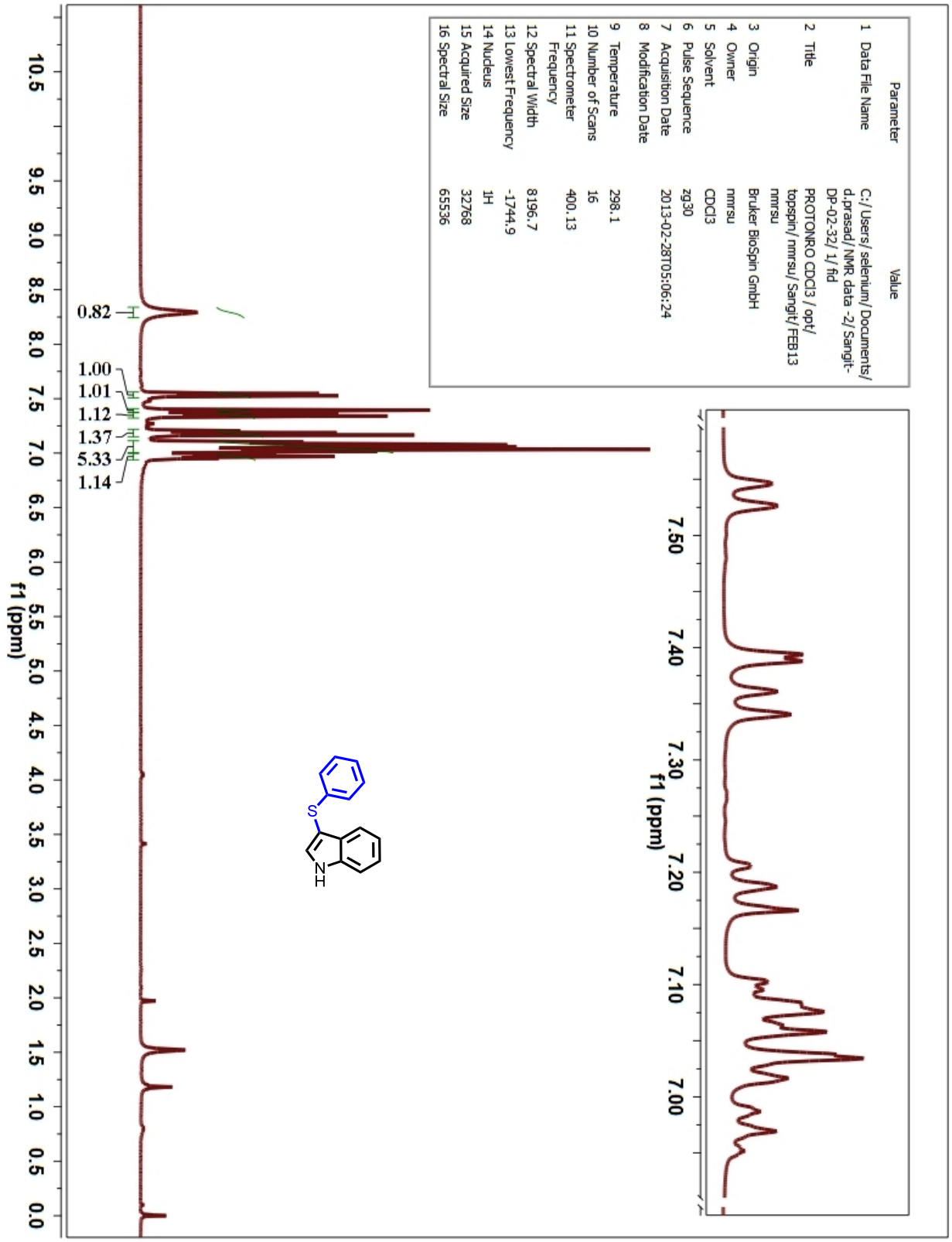


Figure S2 $^{13}$C NMR of **1**

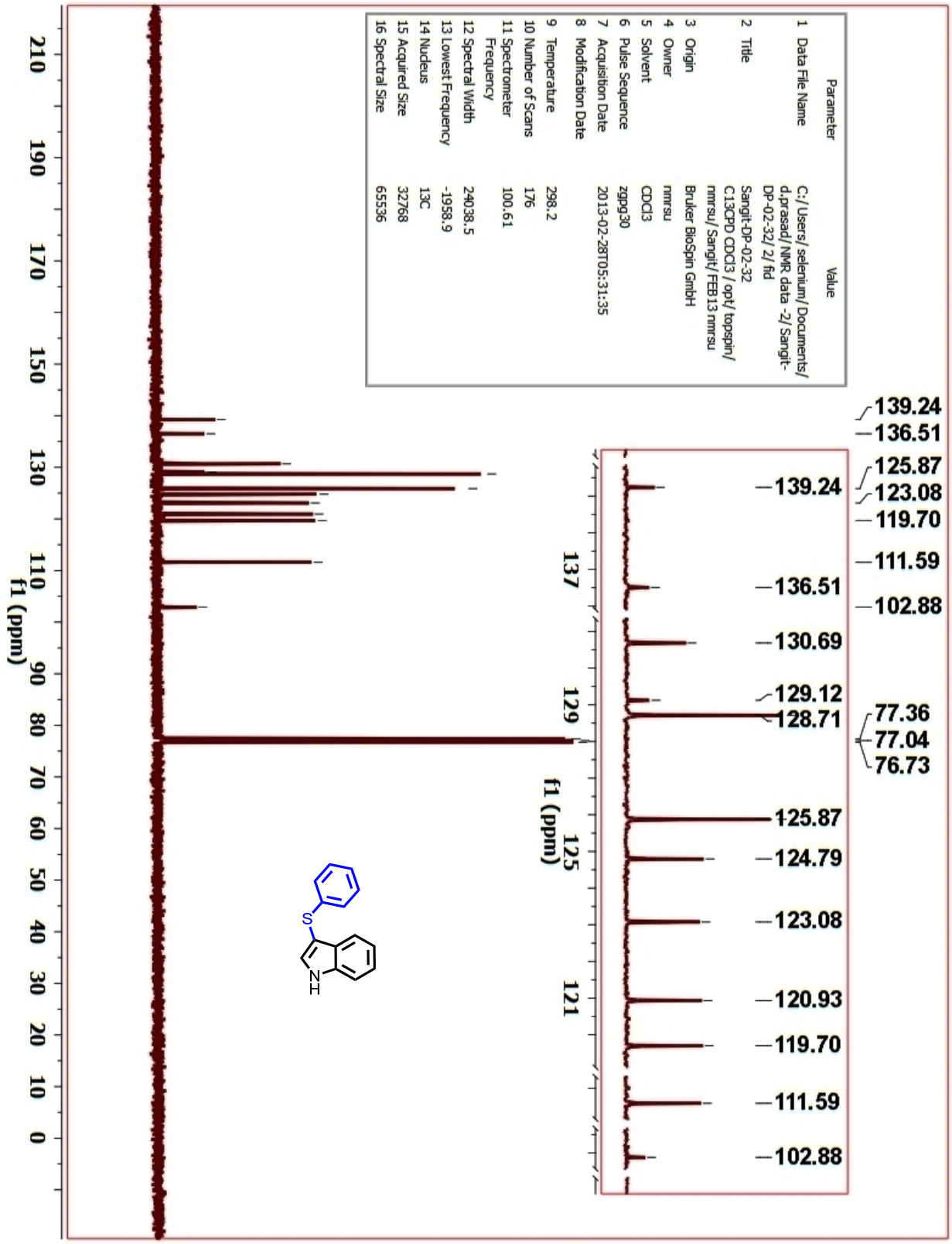


Figure S3 $^{13}$C DEPT-135 NMR of **1**

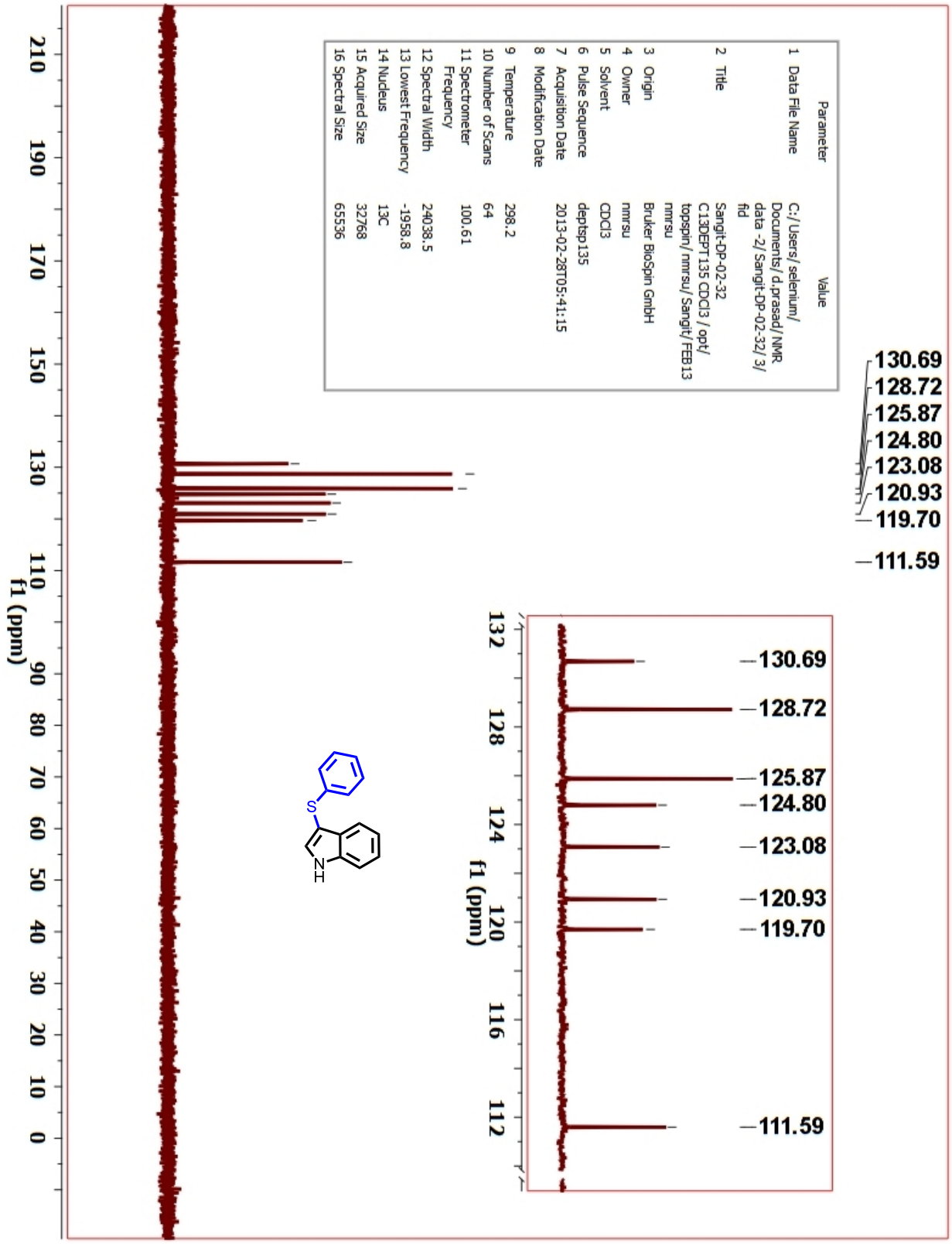


Figure S4 $^{1}$H NMR of **2**

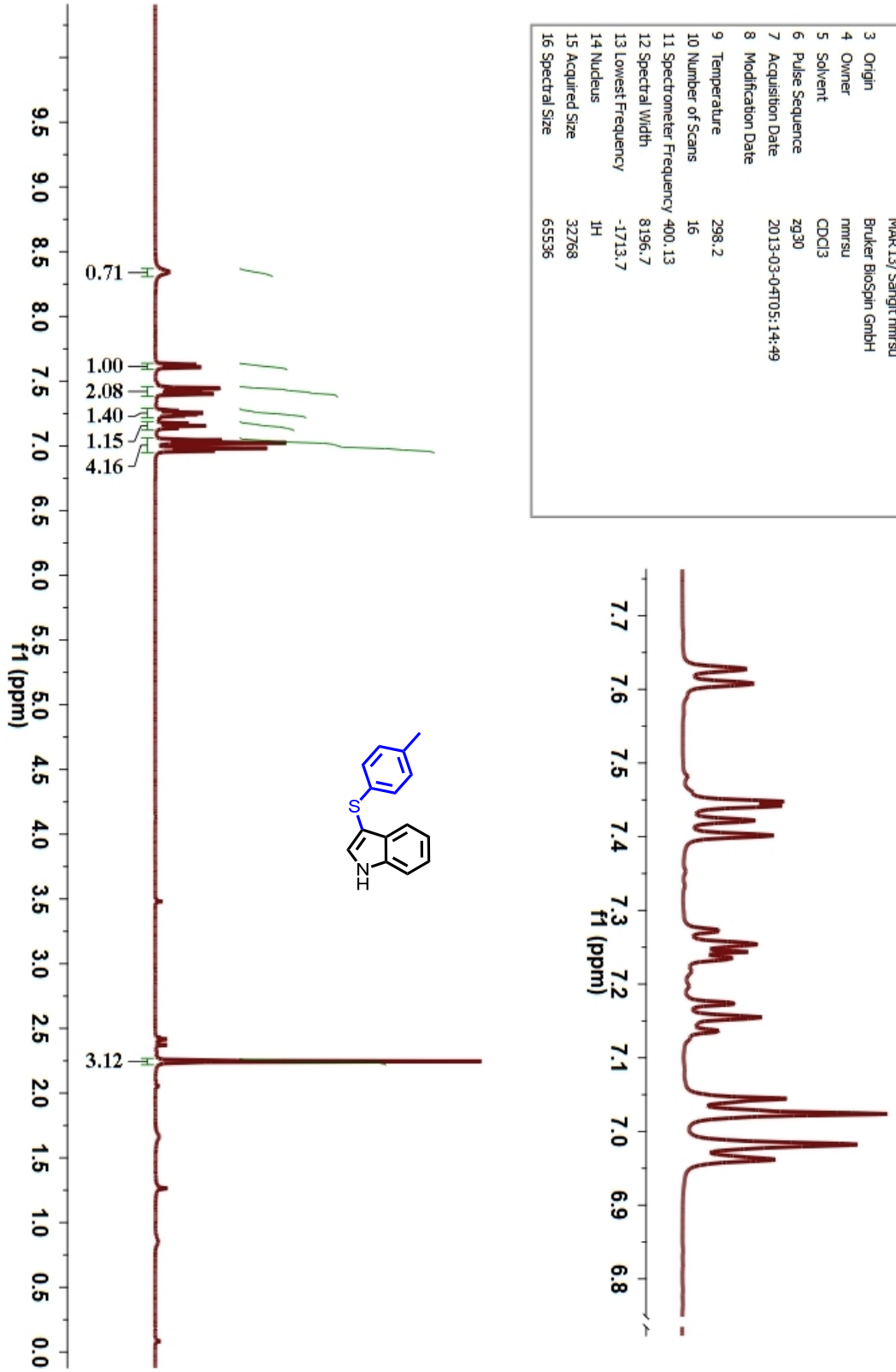


Figure S5 $^{13}$C NMR of **2**

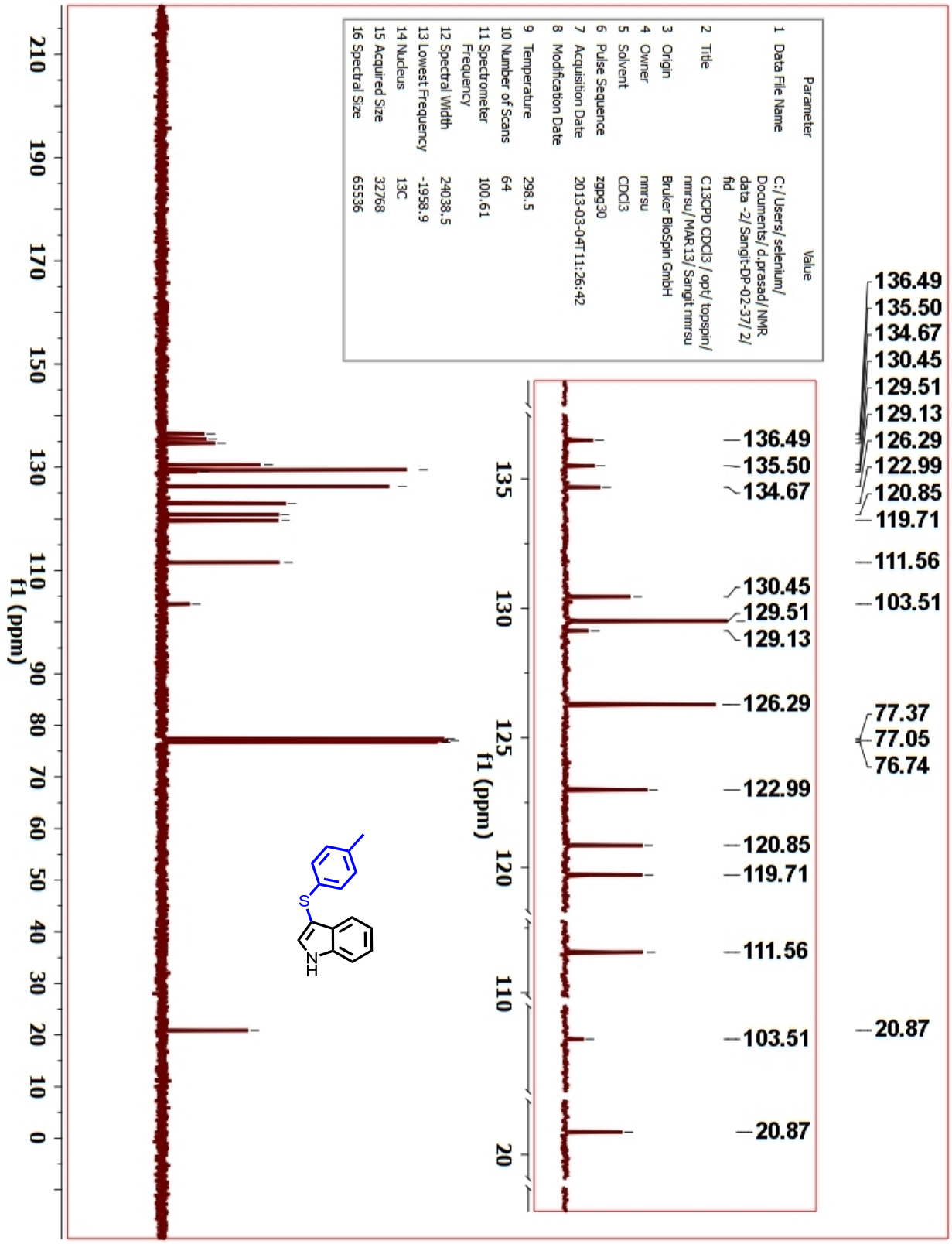


Figure S6 $^{13}$C DEPT-135 NMR of **2**

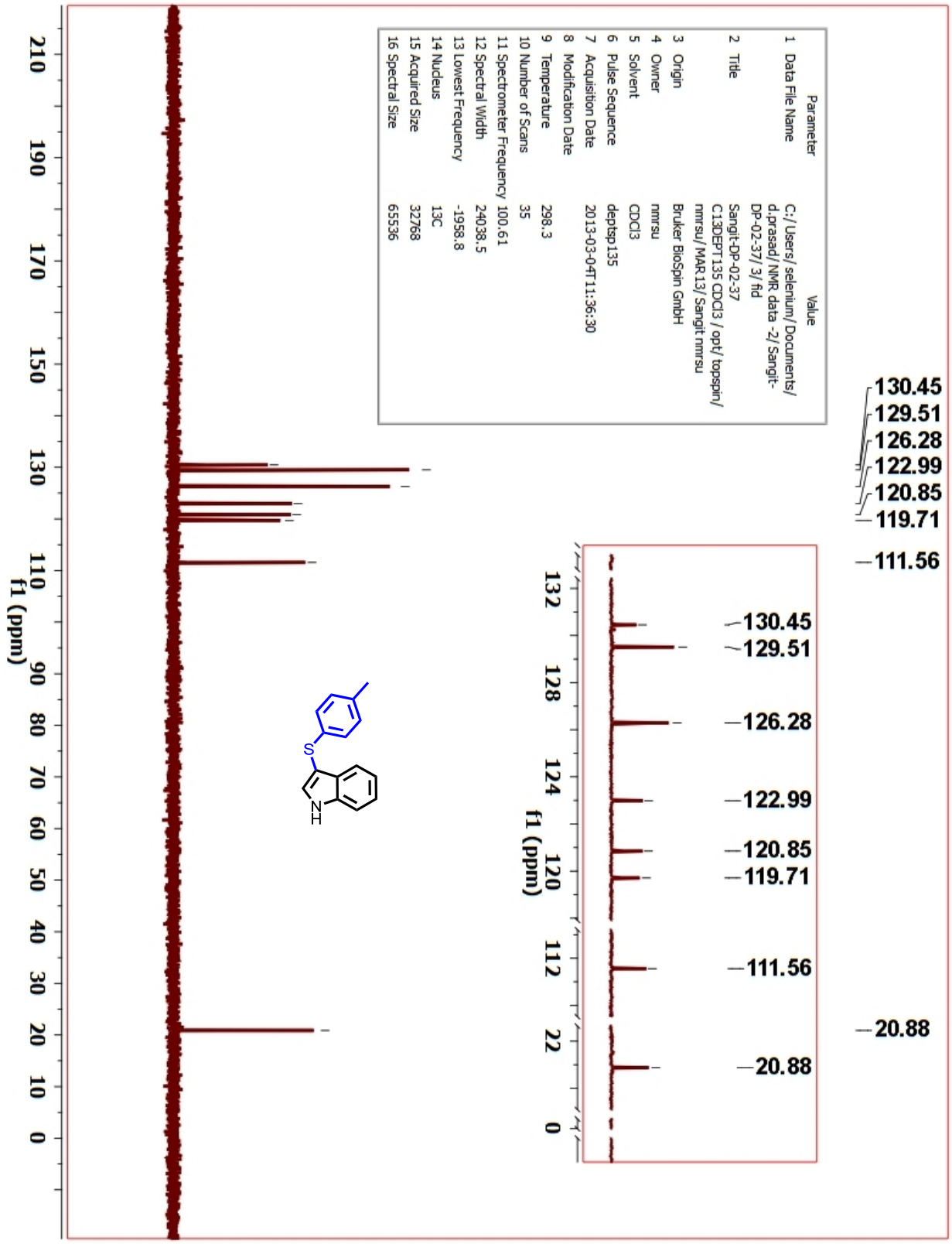


Figure S7 $^{1}$H NMR of **3**

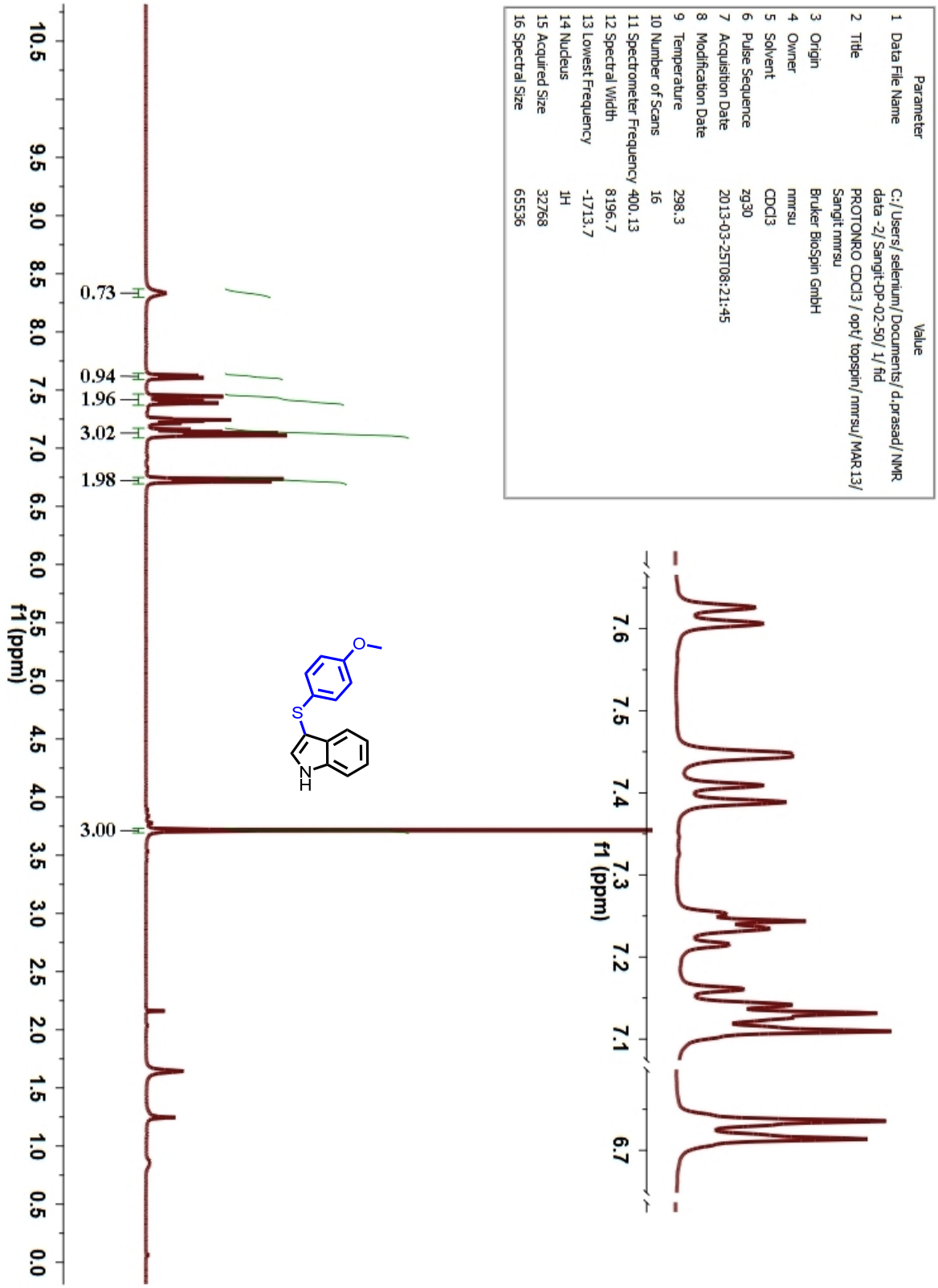


Figure S8 $^{13}$C NMR of **3**

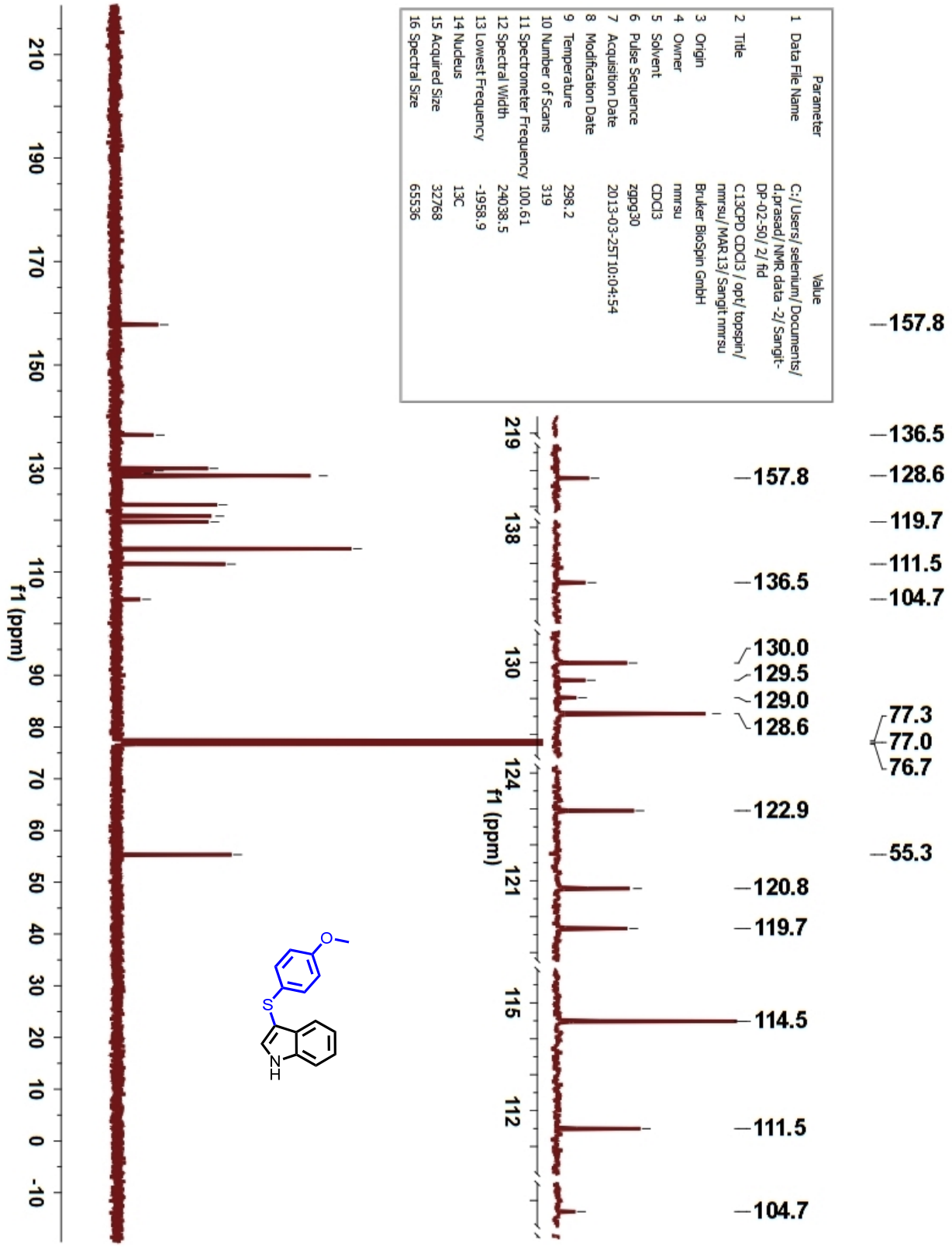


Figure S9 $^{13}$C DEPT-135 NMR of **3**

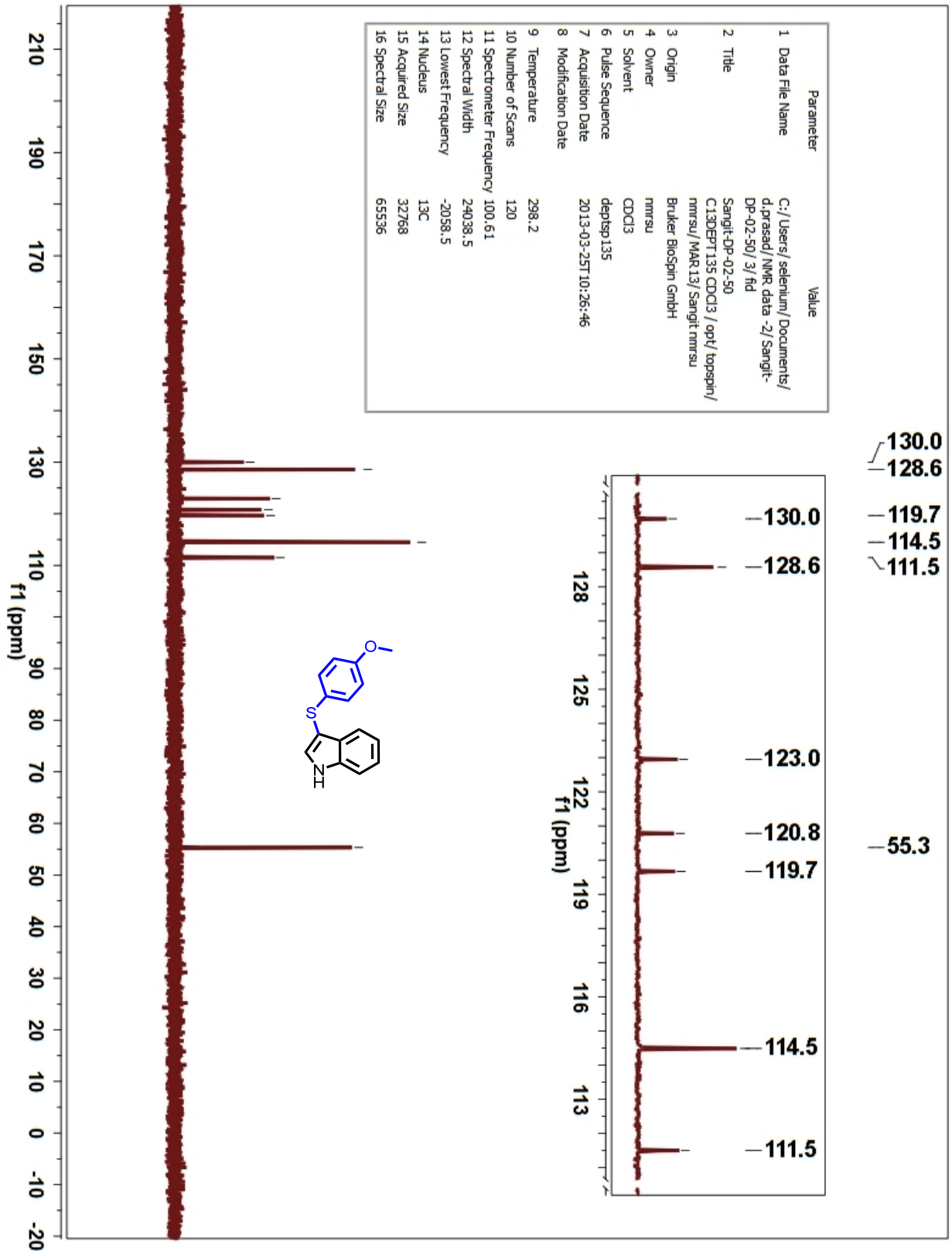


Figure S10 $^{1}$H NMR of **4**

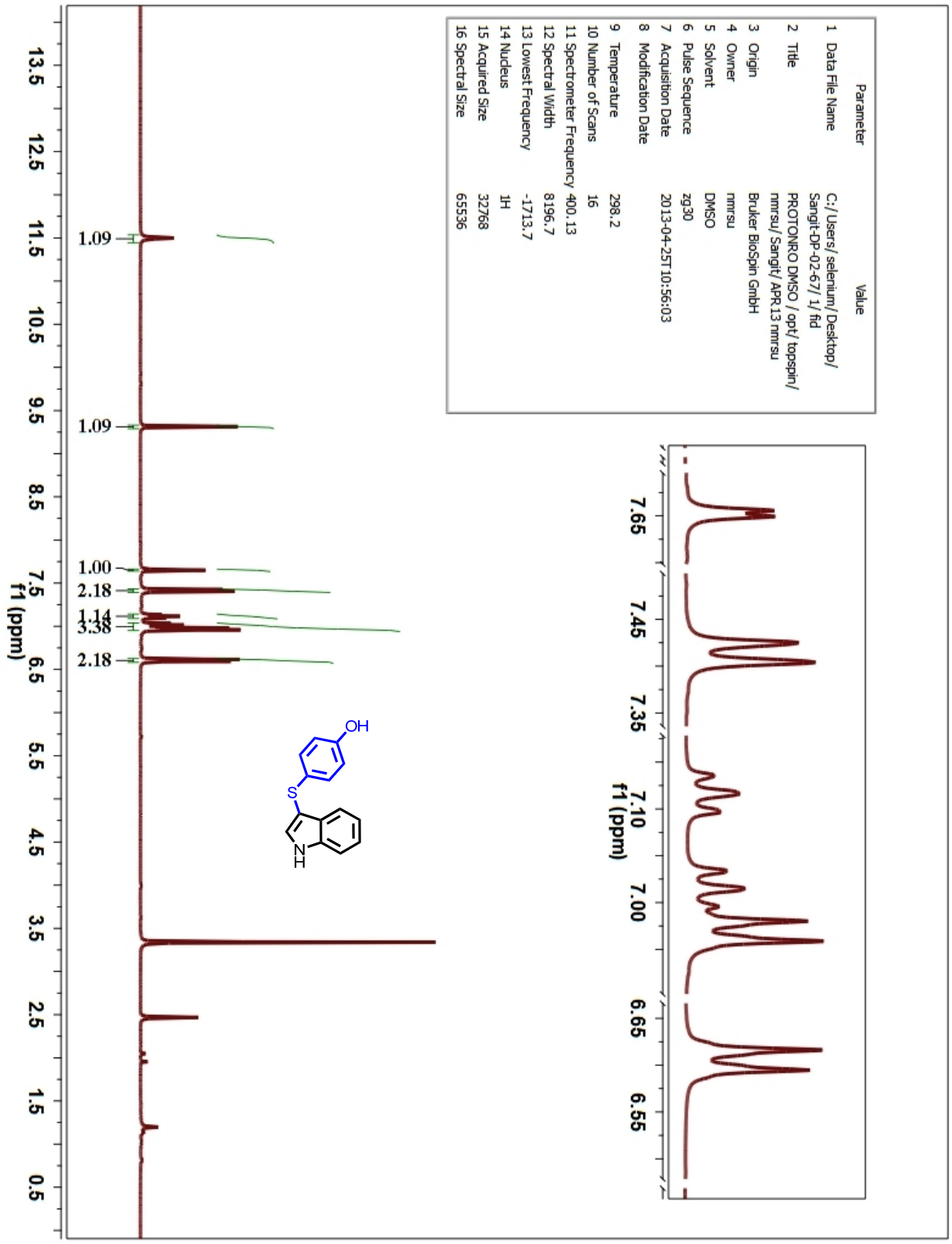


Figure S11 $^{13}$C NMR of **4**

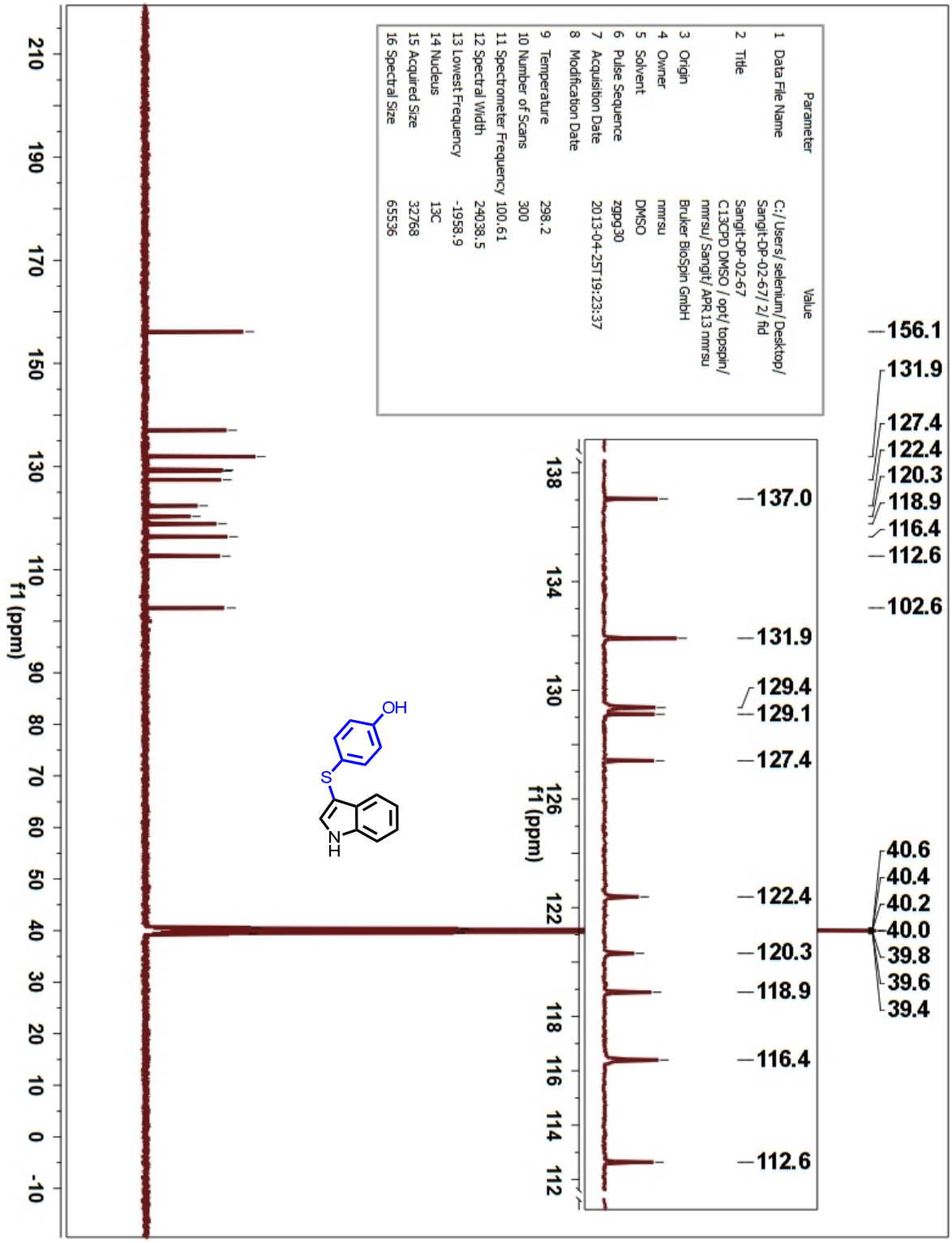


Figure S12 $^{13}$C DEPT-135 NMR of **4**

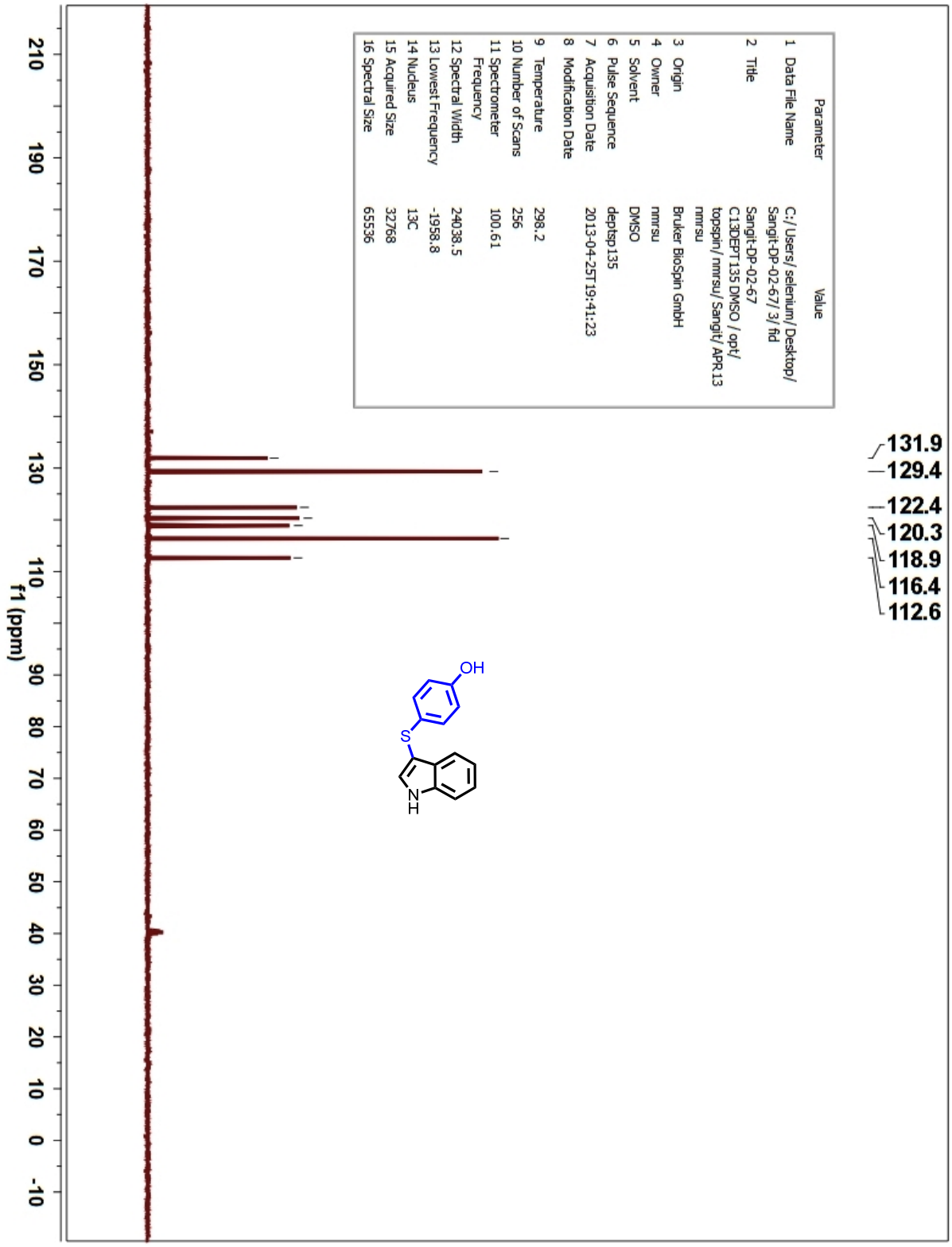


Figure S13 $^{1}$H NMR of **5**

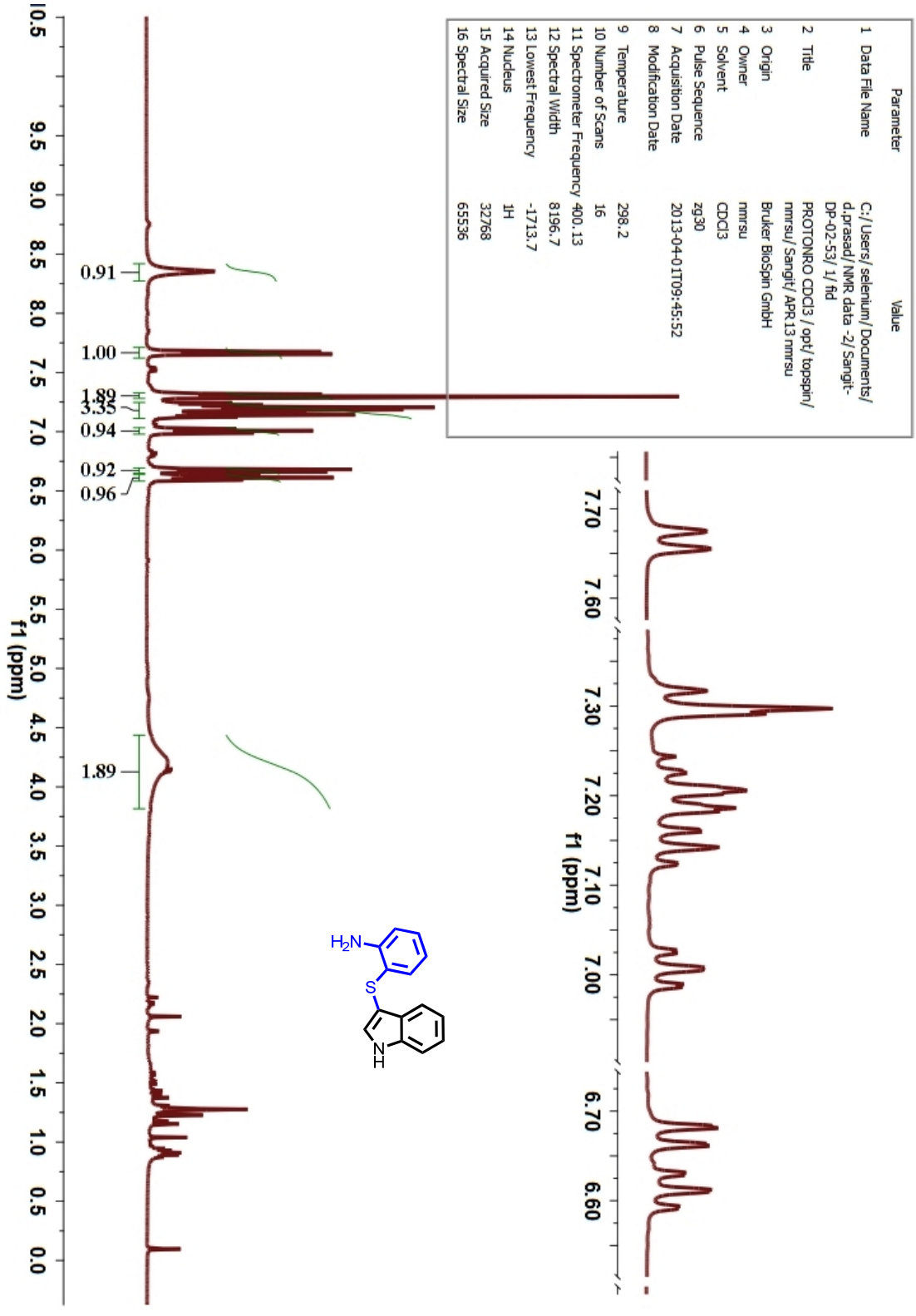


Figure S14 $^{13}$C NMR of **5**

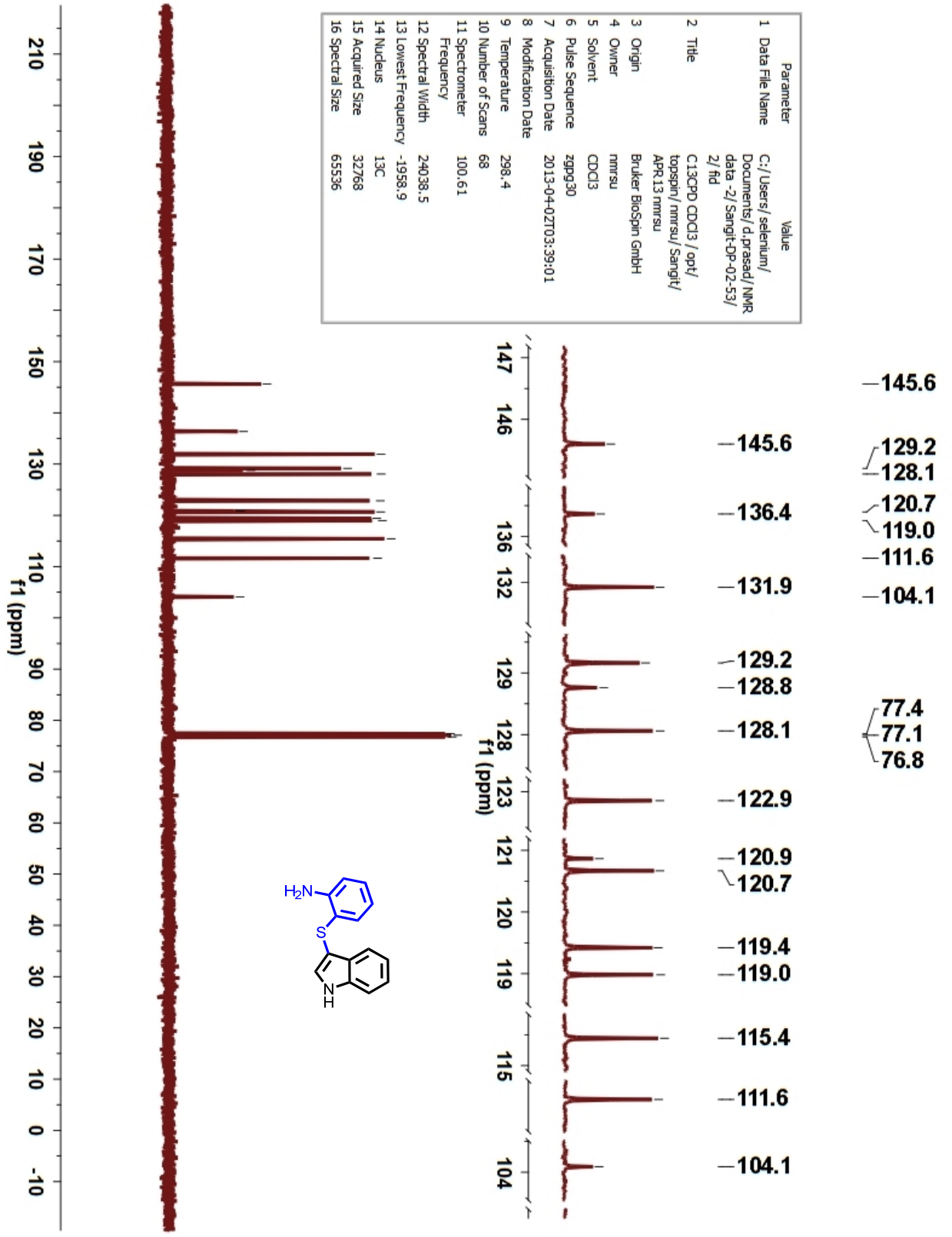


Figure S15 $^{13}$C DEPT-135 NMR of **5**

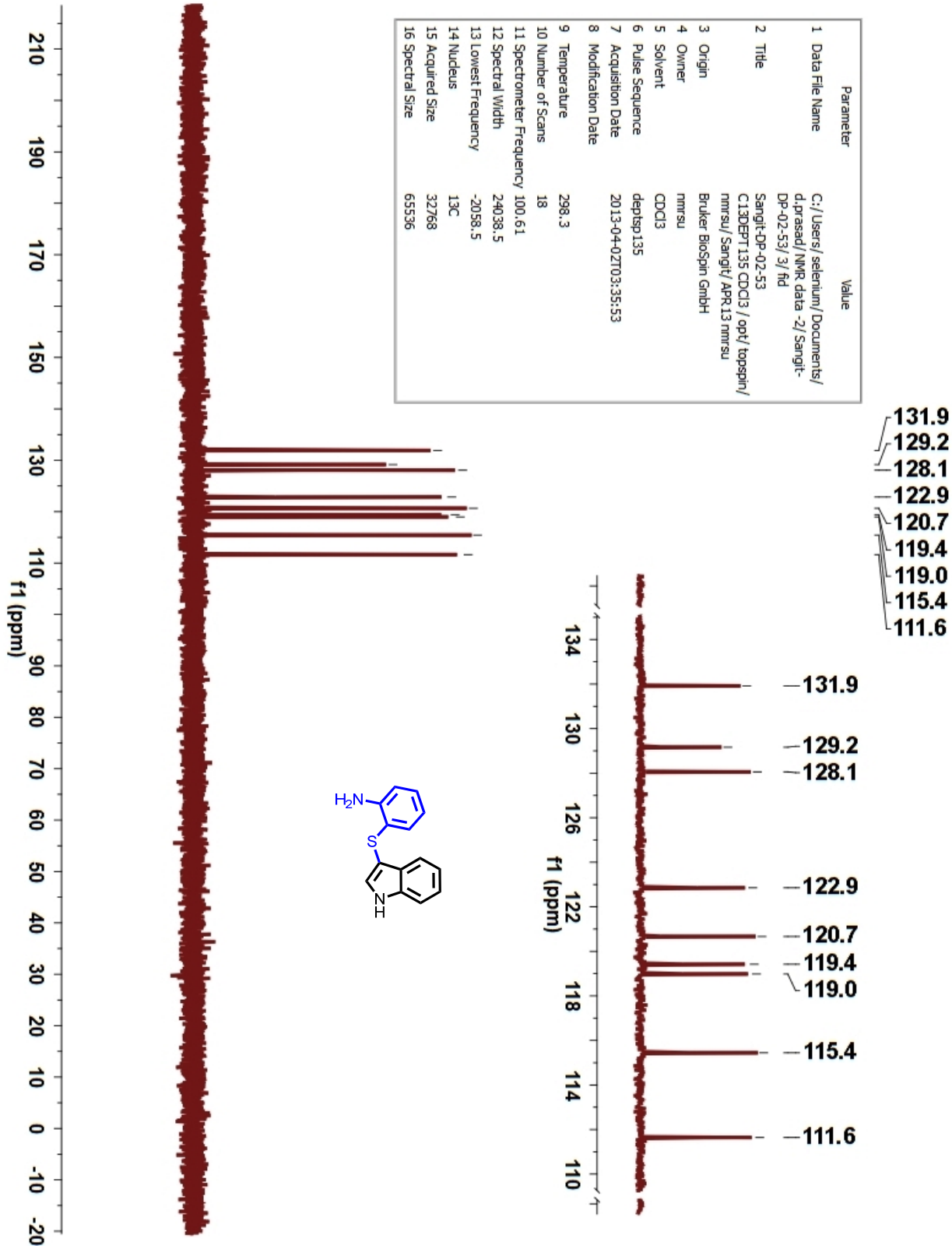


Figure S16 $^{1}$H NMR of **6**

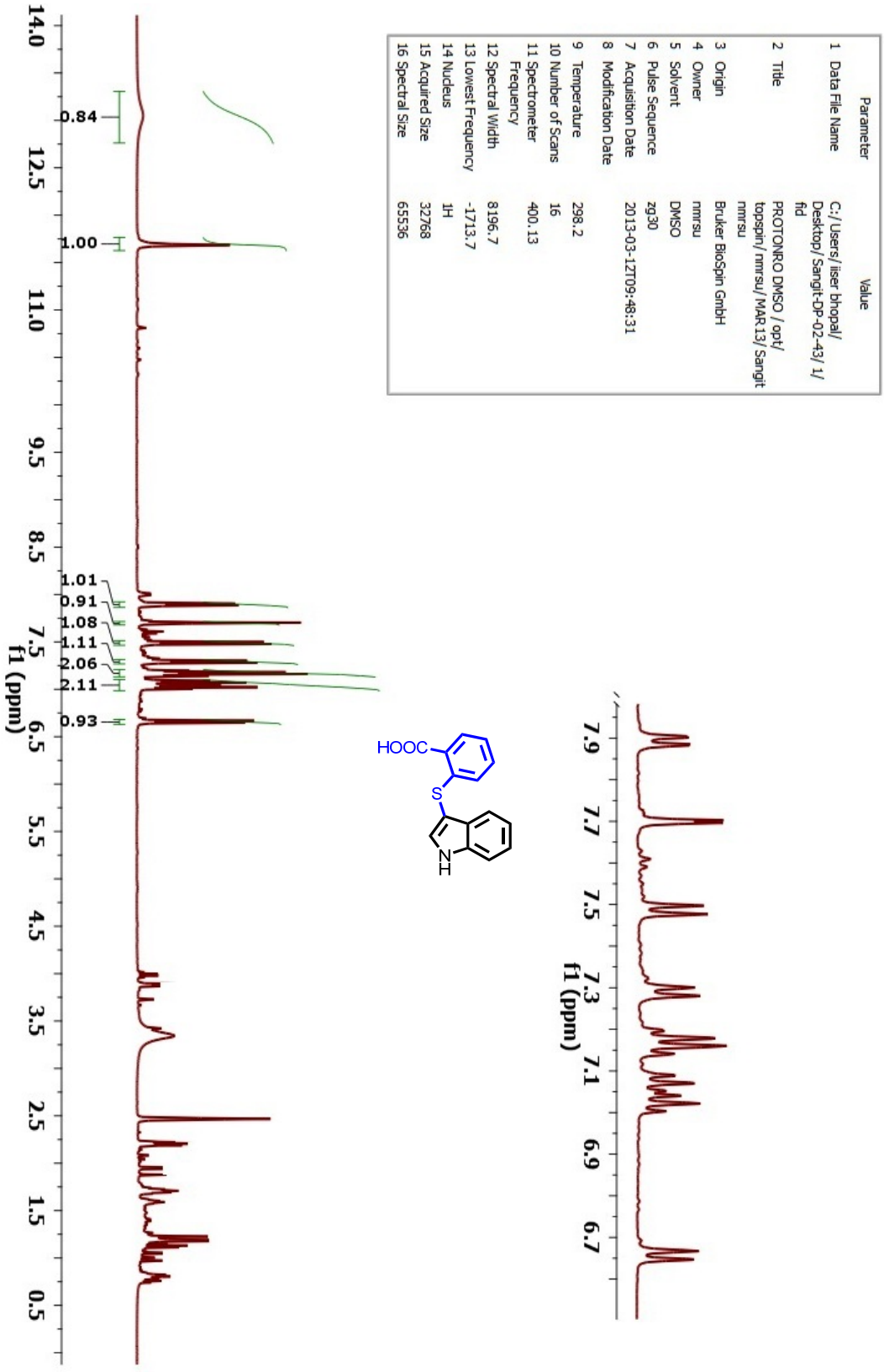


Figure S17 $^{13}$C NMR of **6**

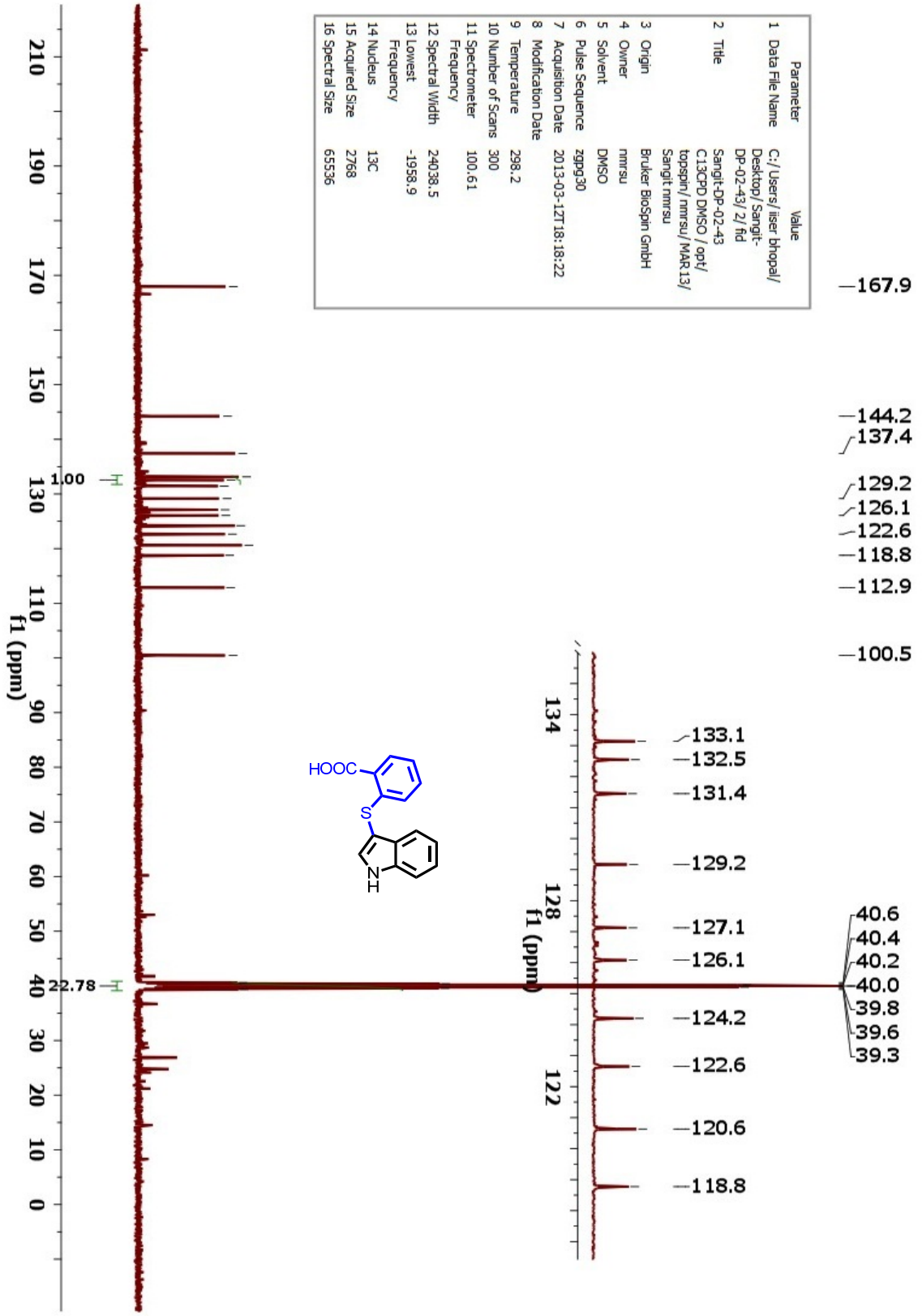


Figure S18 $^{13}$C DEPT-135 NMR of **6**

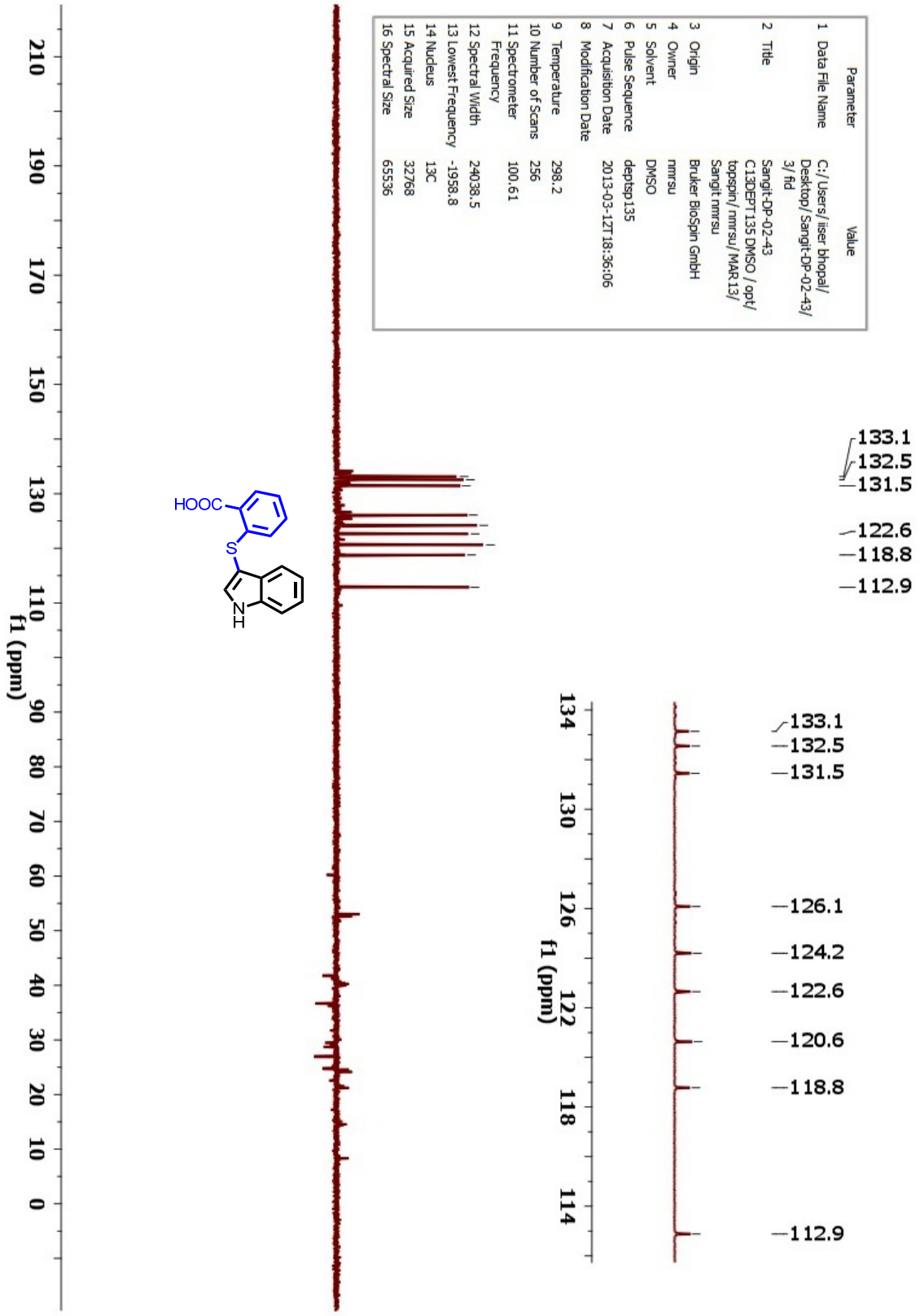


Figure S19 $^{1}$H NMR of **7**

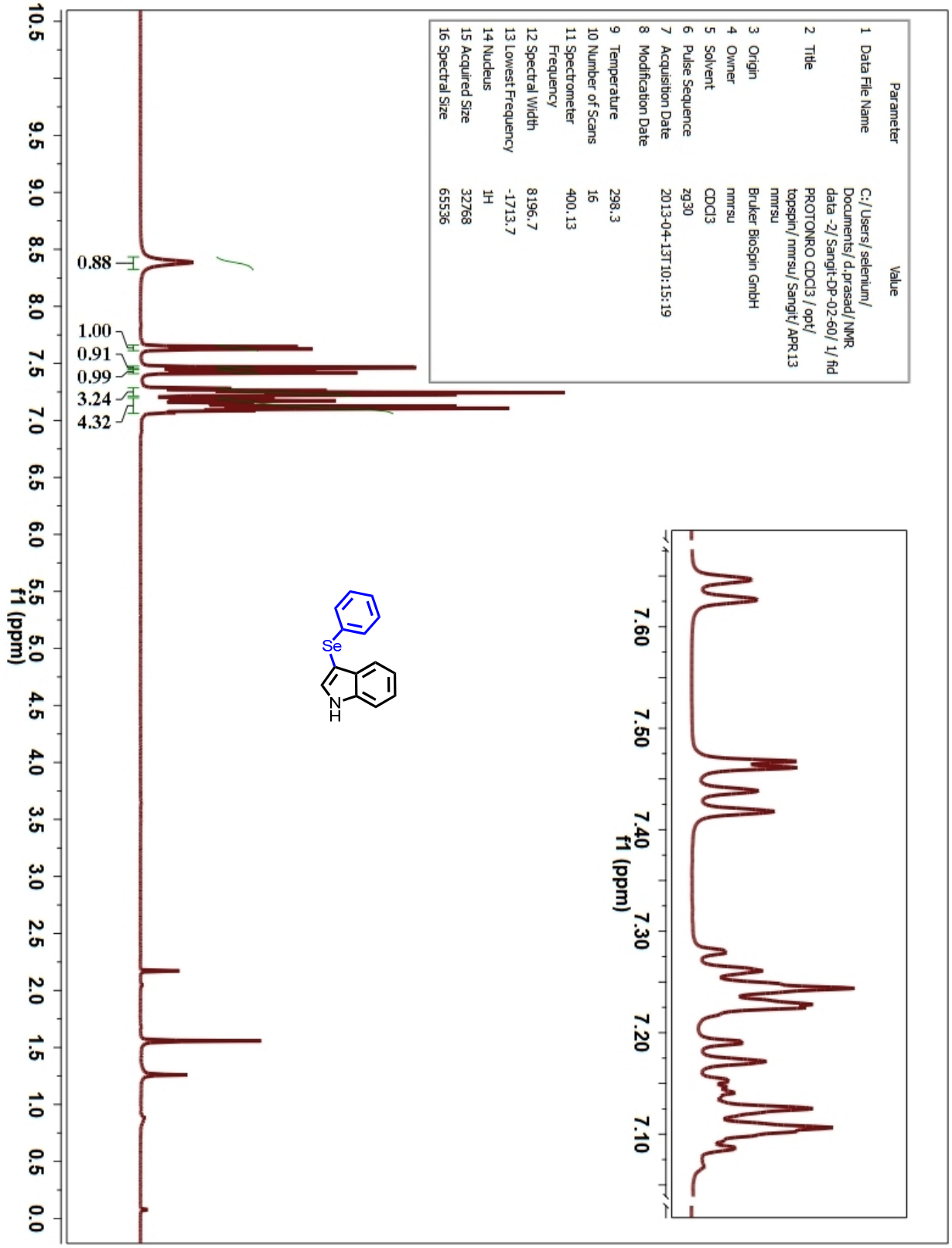


Figure S20 $^{13}$C NMR of **7**

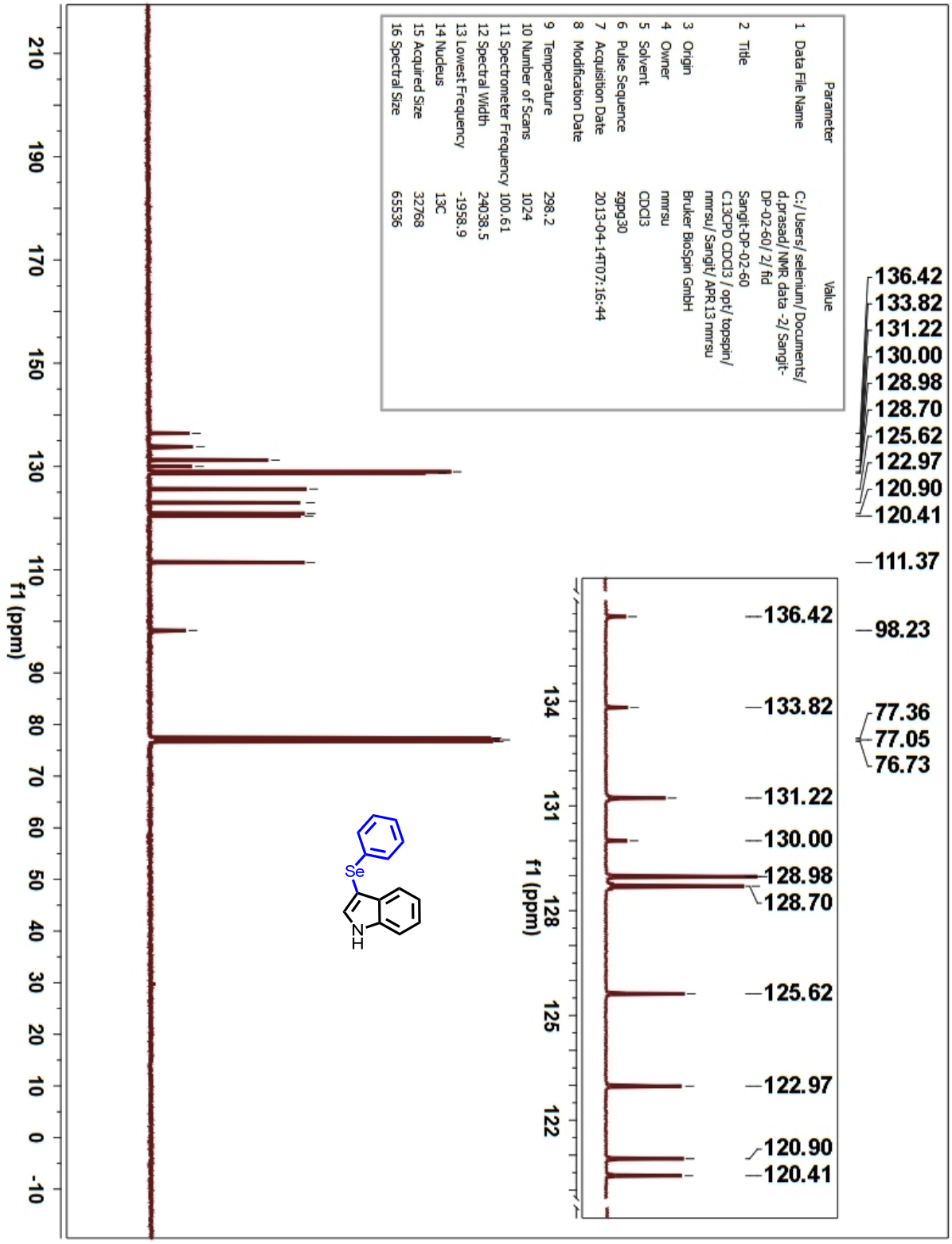


Figure S21 $^{13}$C DEPT-135 NMR of **7**

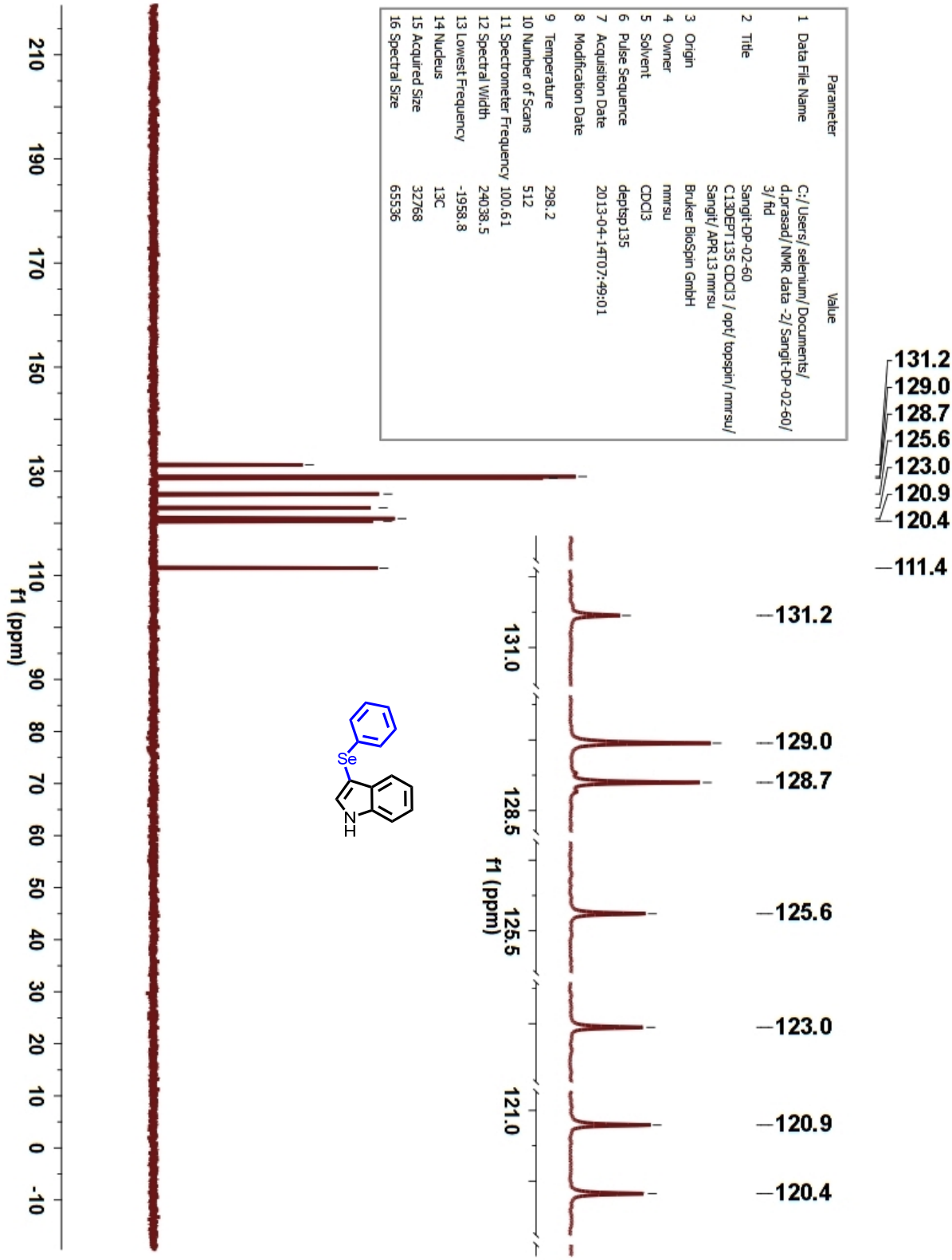


Figure S22 $^{1}$H NMR of **8**

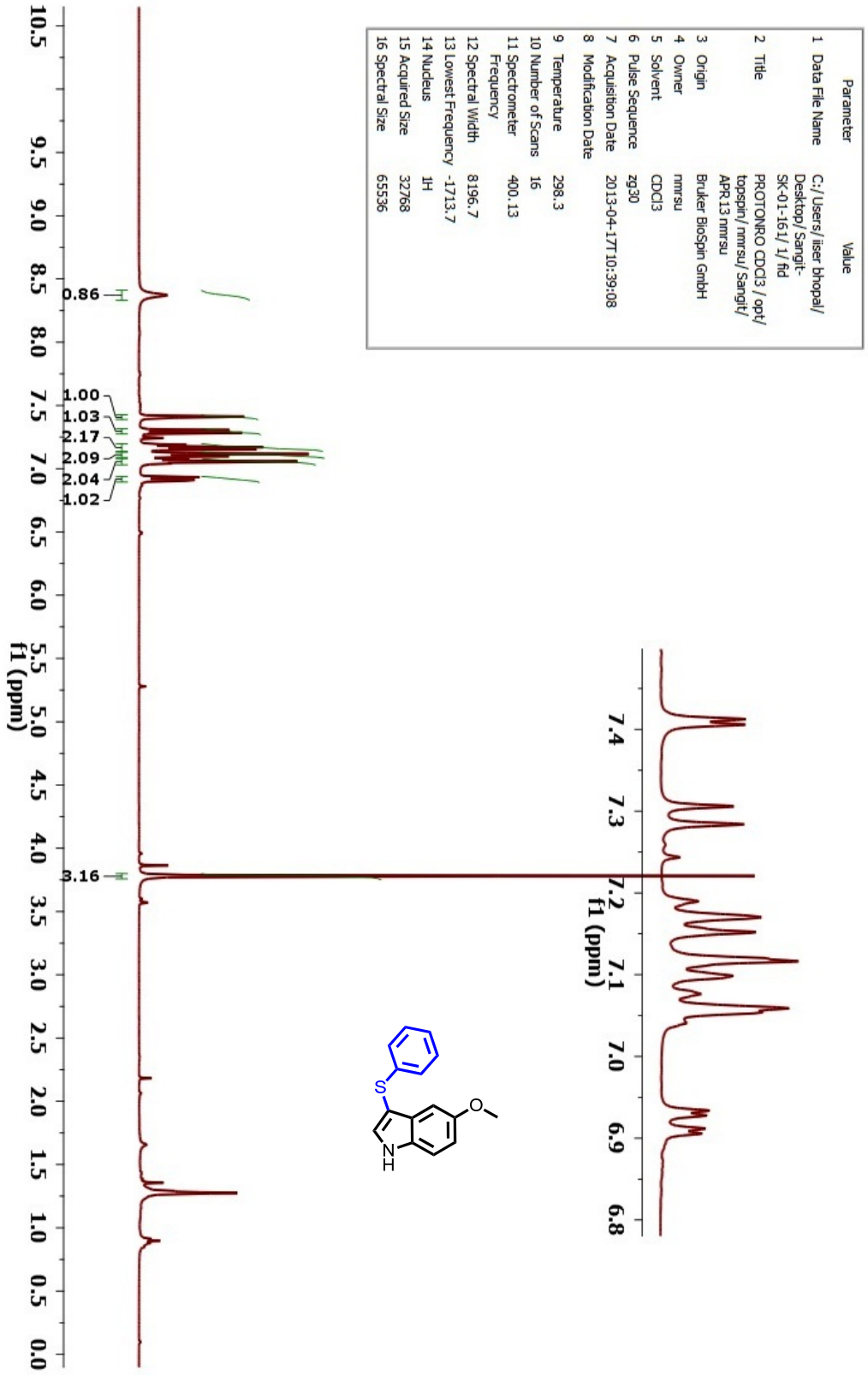


Figure S23 $^{13}$C NMR of **8**

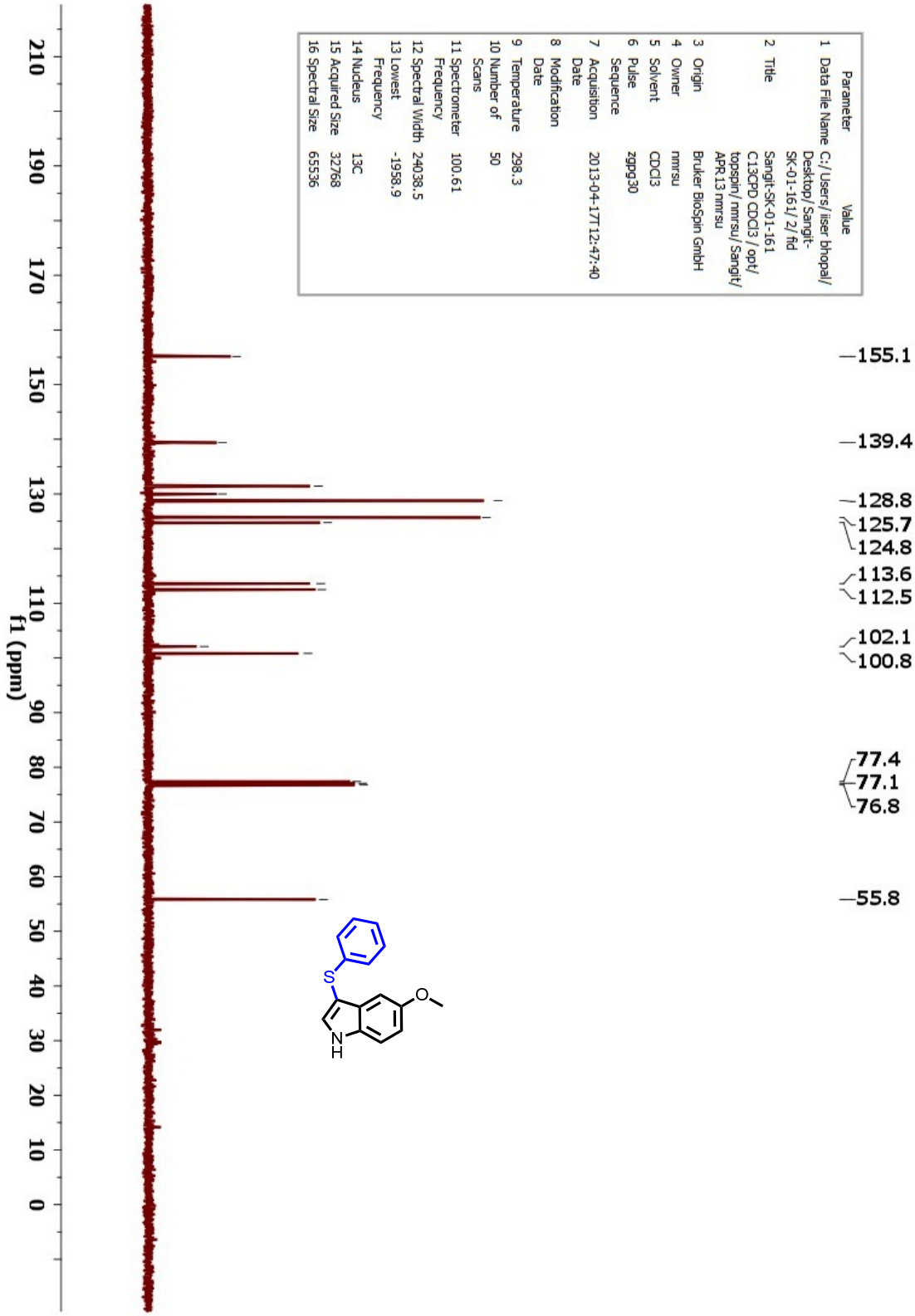


Figure S24 $^{13}$C DEPT-135 NMR of **8**

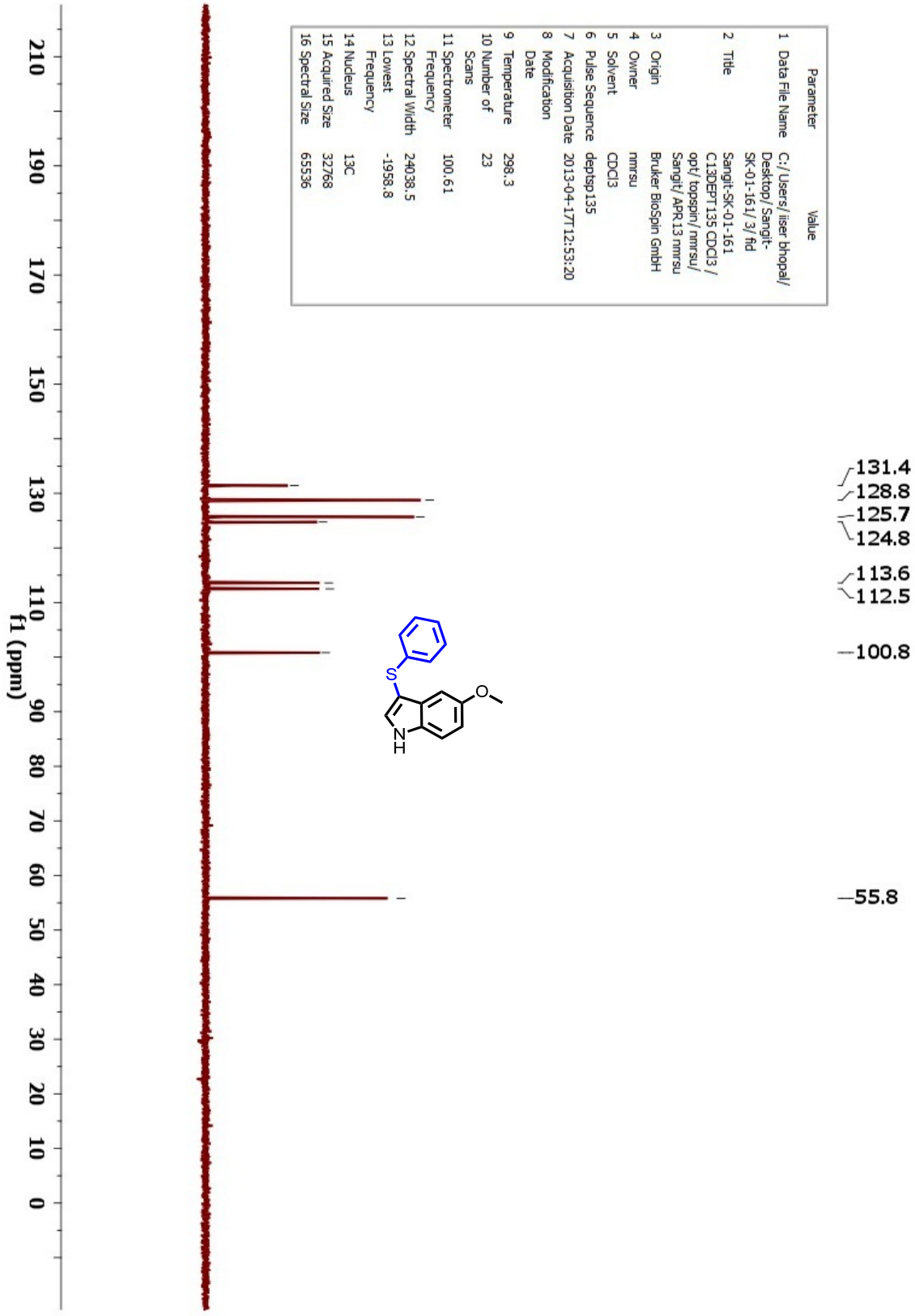


Figure S25 $^{1}$H NMR of **9**

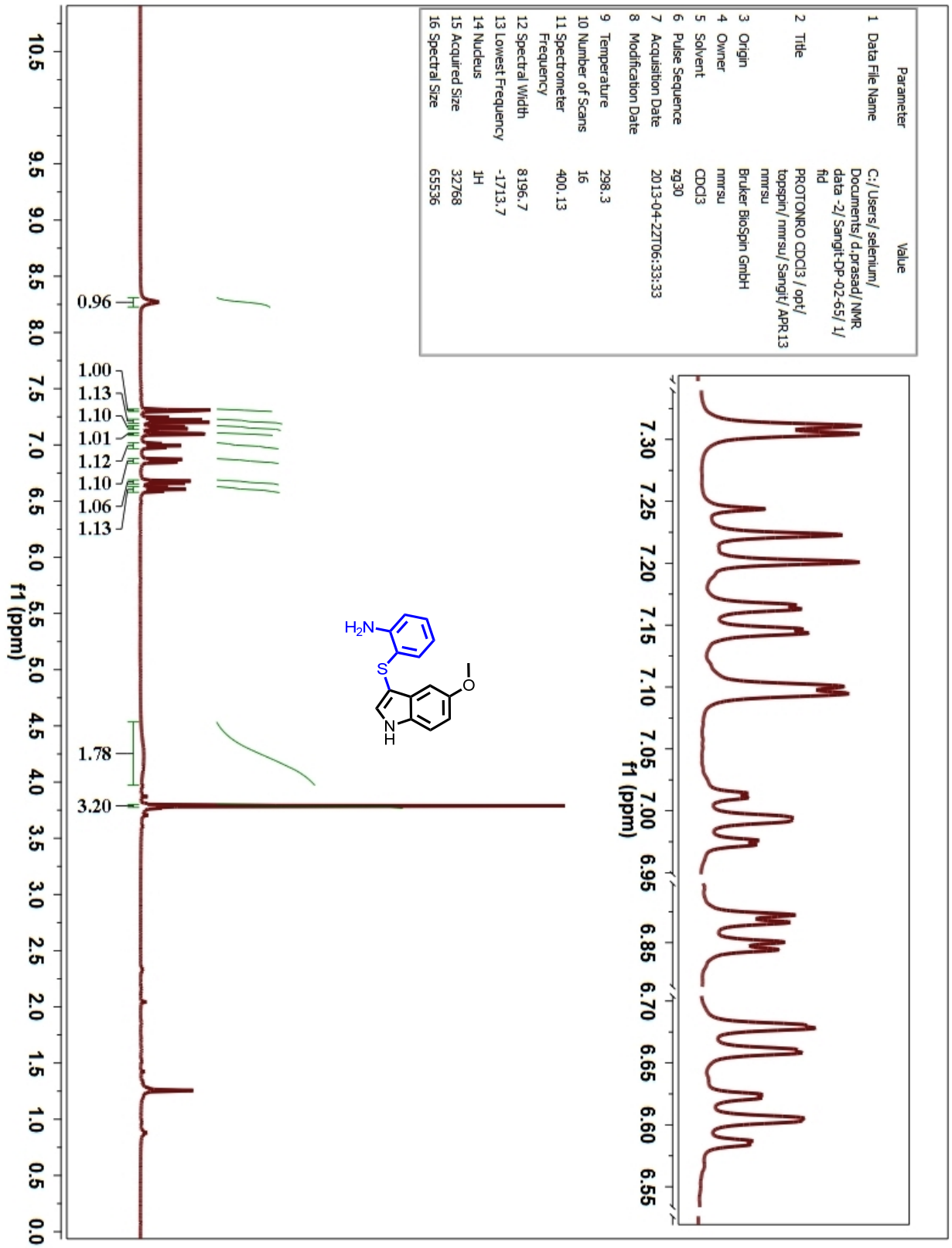


Figure S26 $^{13}$C NMR of **9**

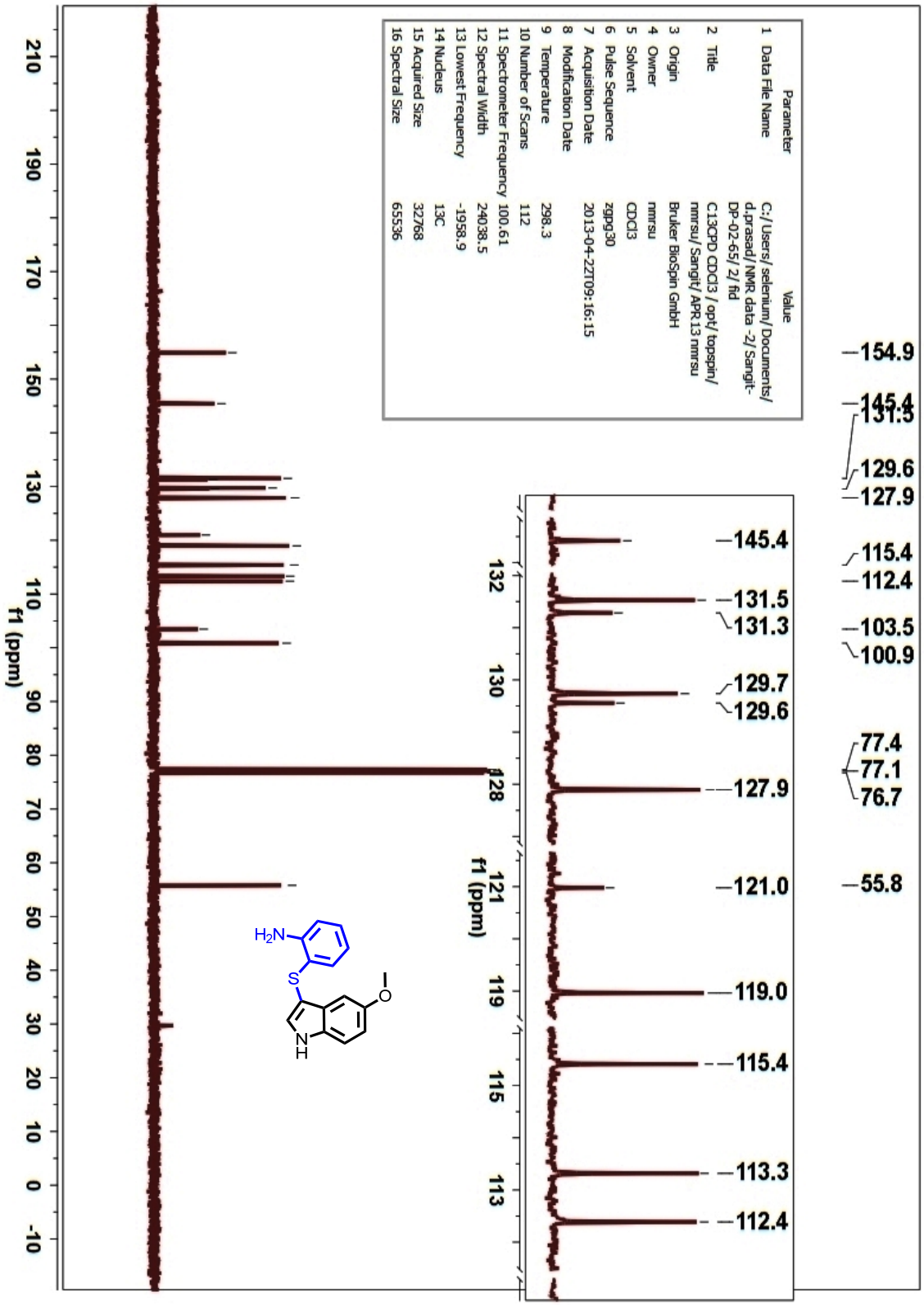


Figure S27 $^{13}$C DEPT-135 NMR of **9**

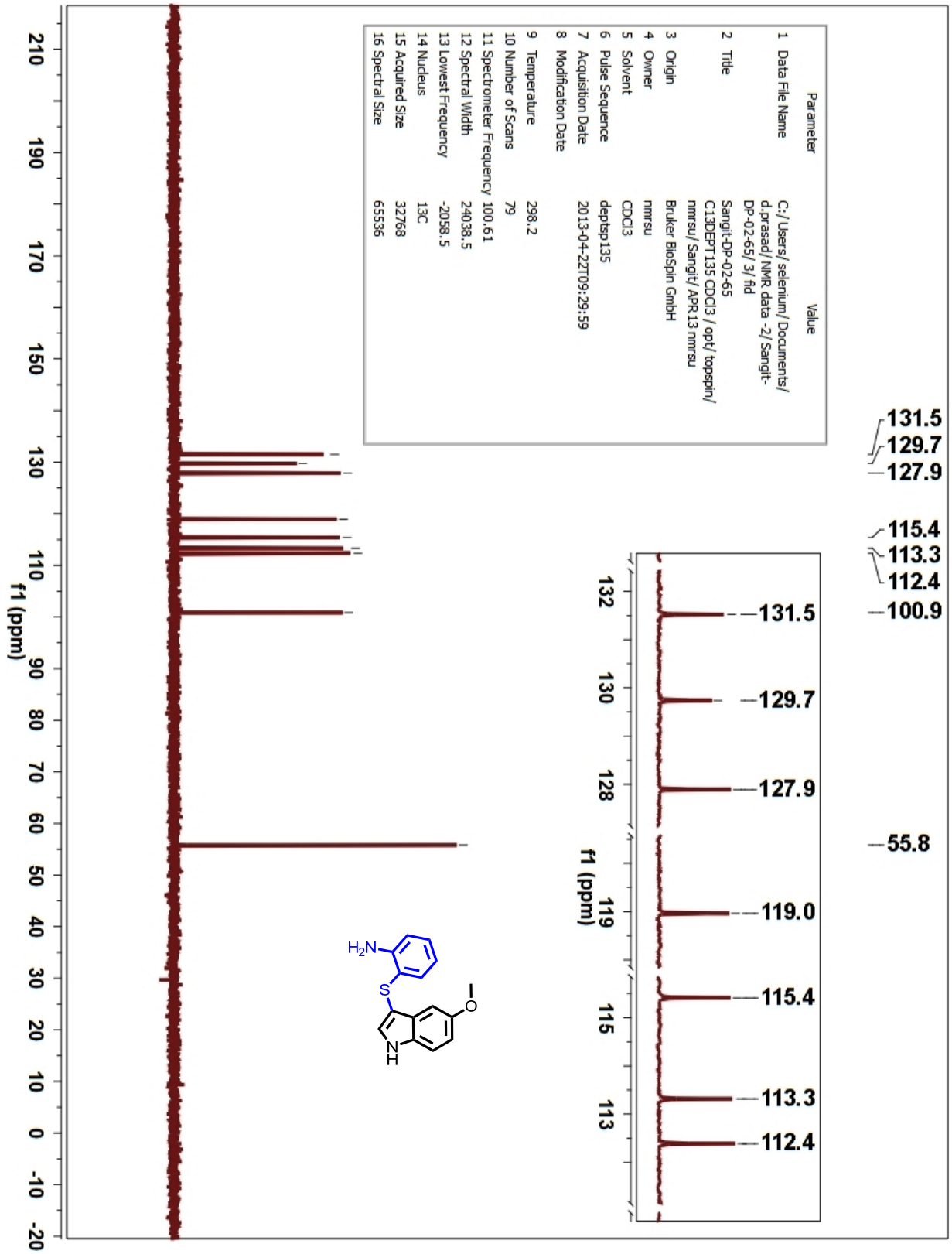


Figure S28 $^{1}$H NMR of **10**

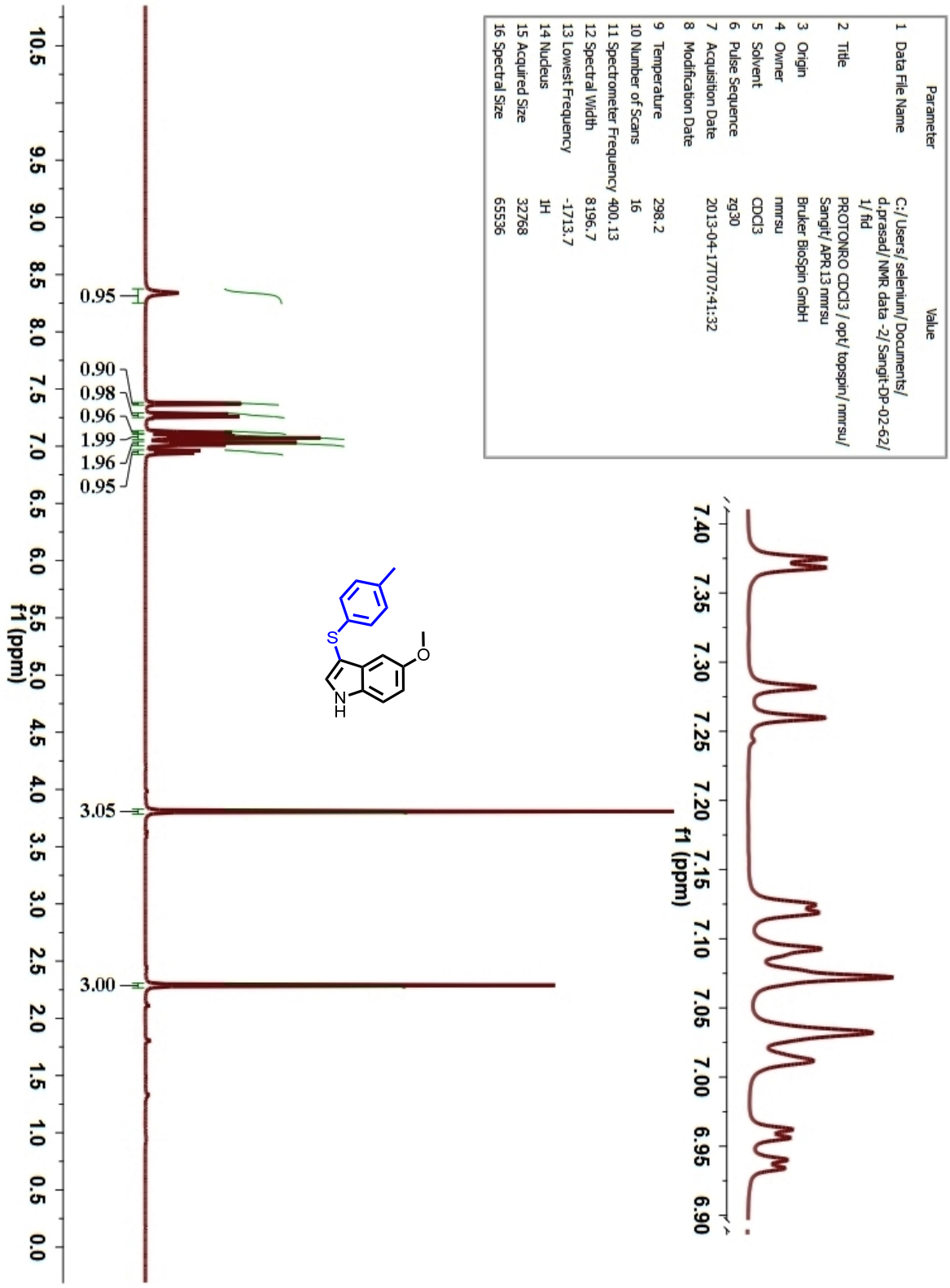


Figure S29 $^{13}$C NMR of **10**

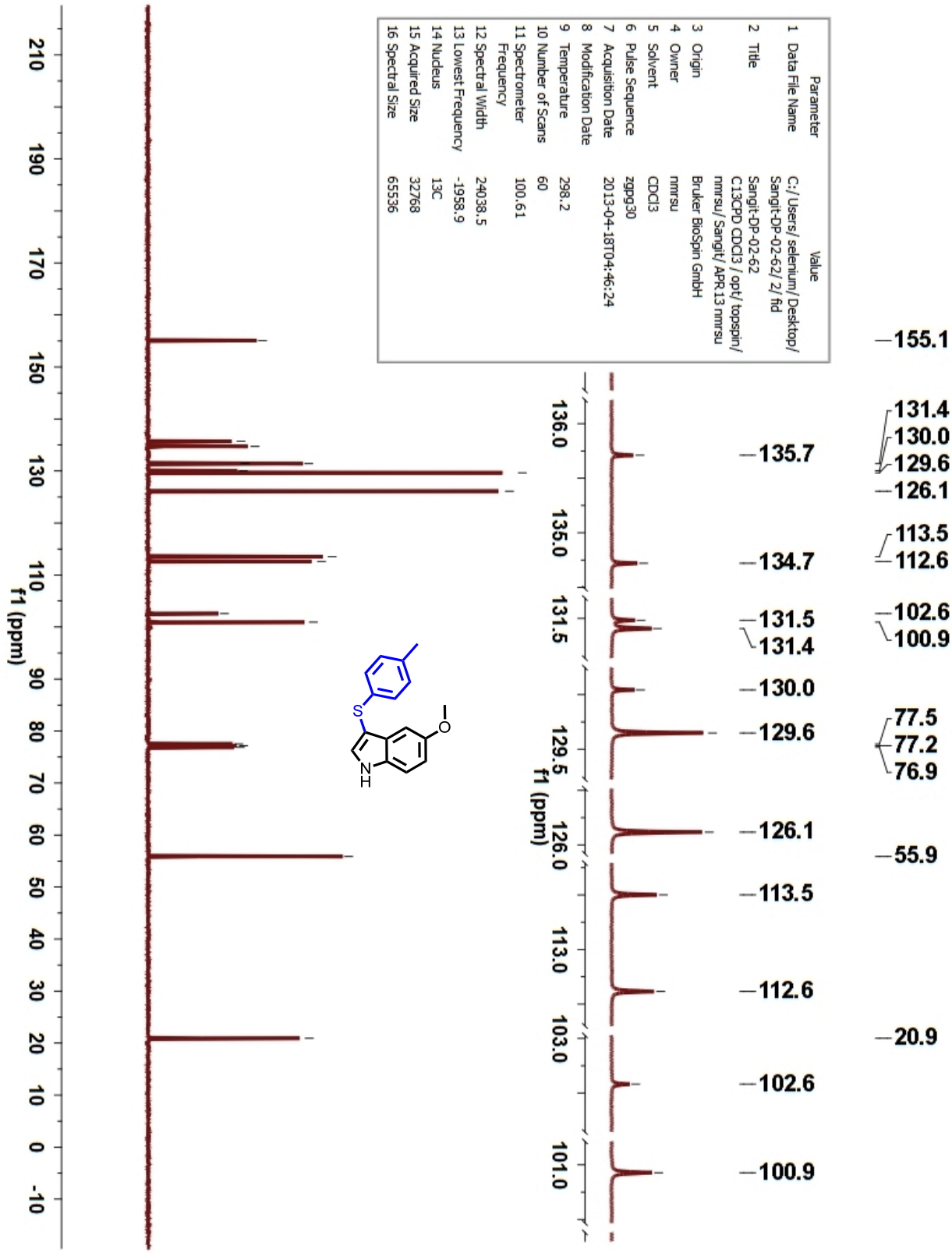


Figure S30 $^{13}$C DEPT-135 NMR of **10**

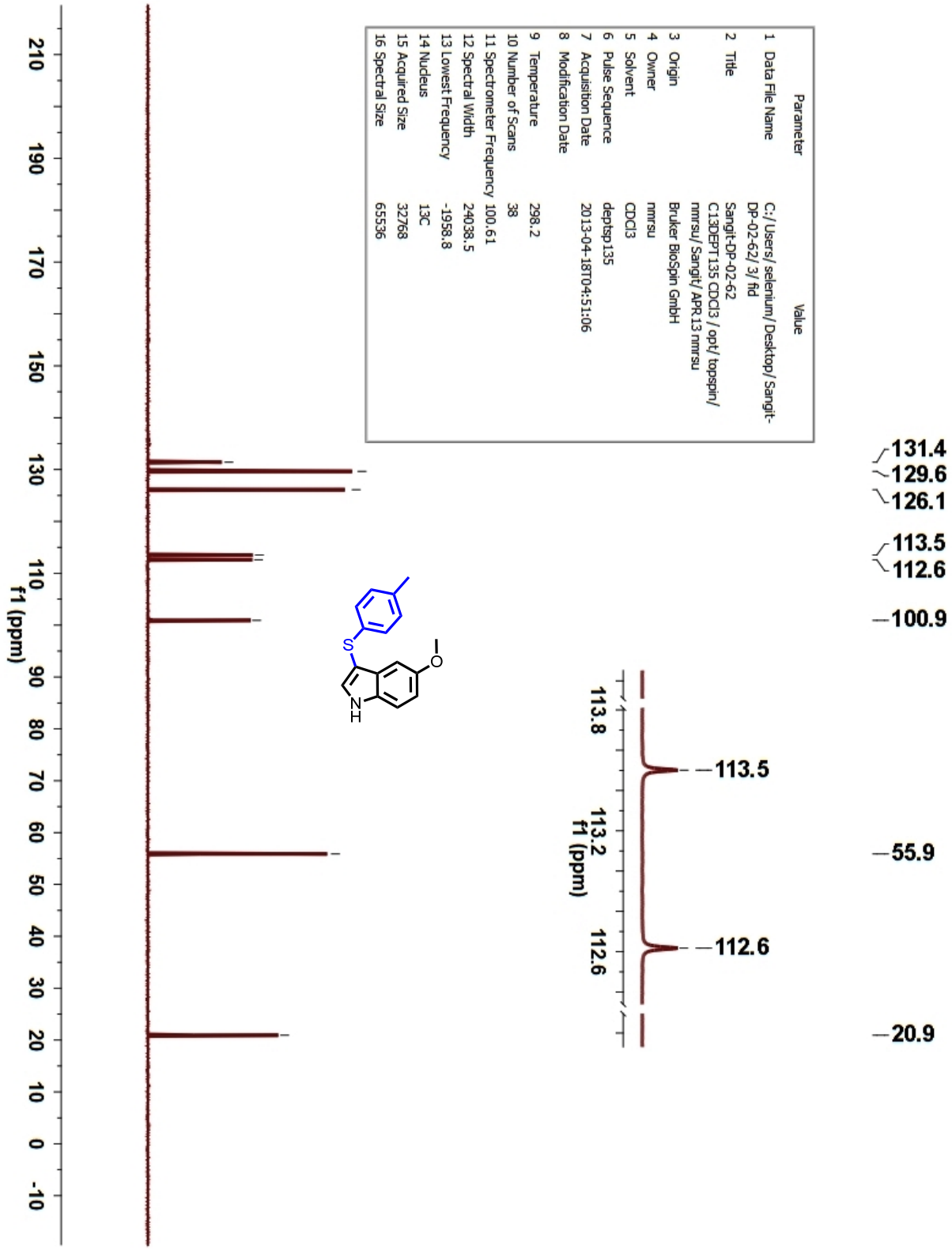


Figure S31 $^{1}$H NMR of **11**

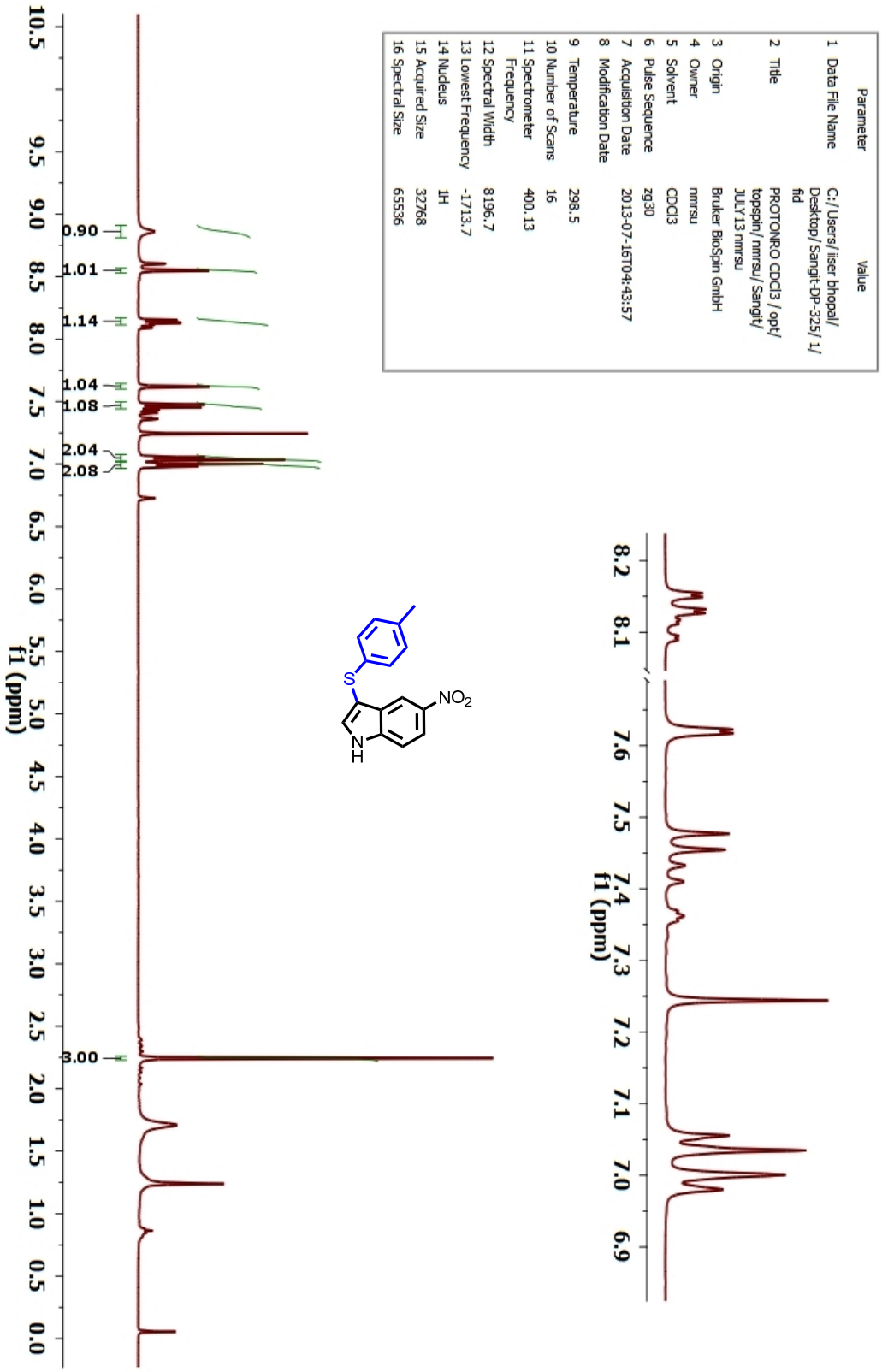


Figure S32 $^{13}$C NMR of **11**

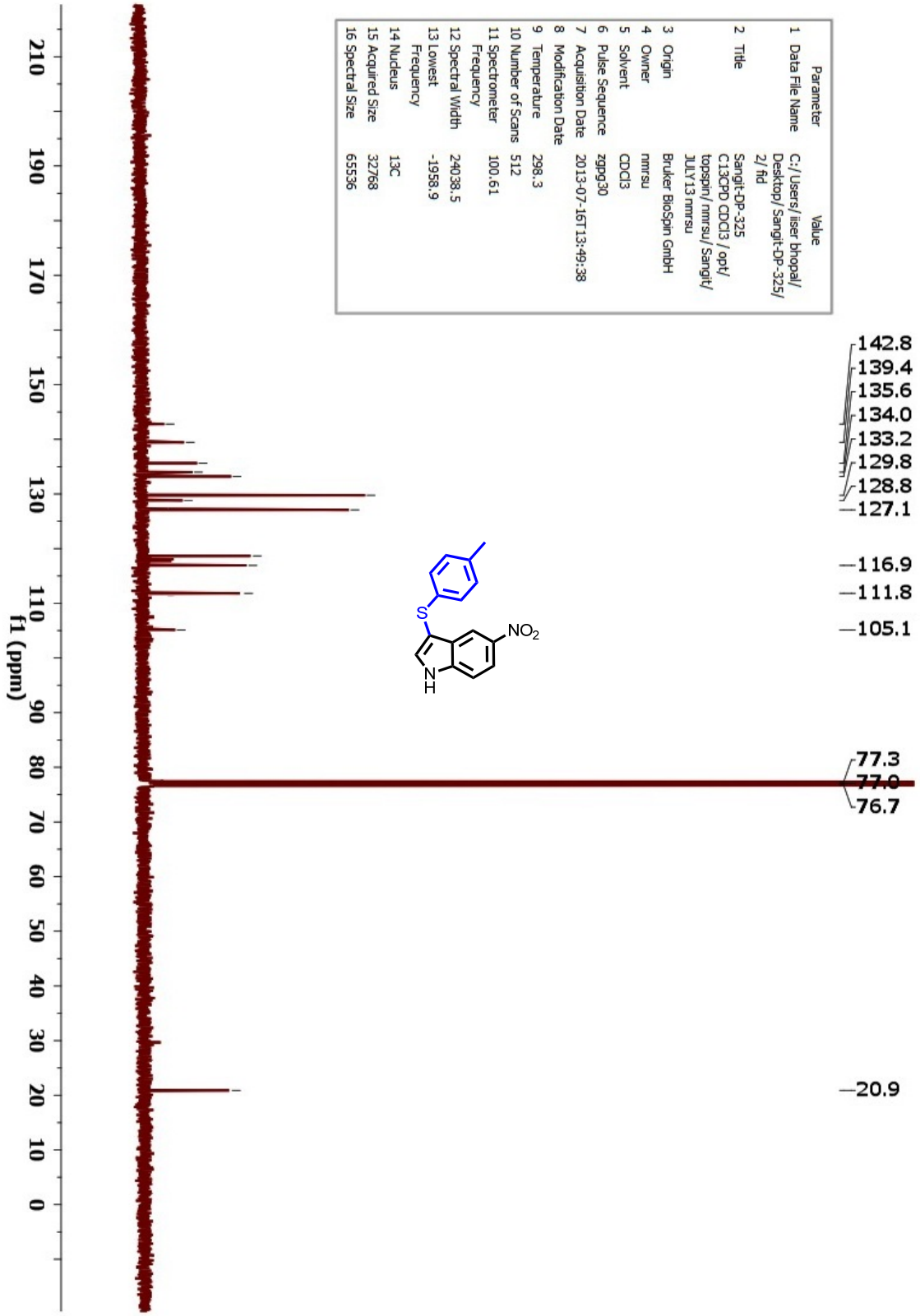


Figure S33 $^{1}$H NMR of **12**

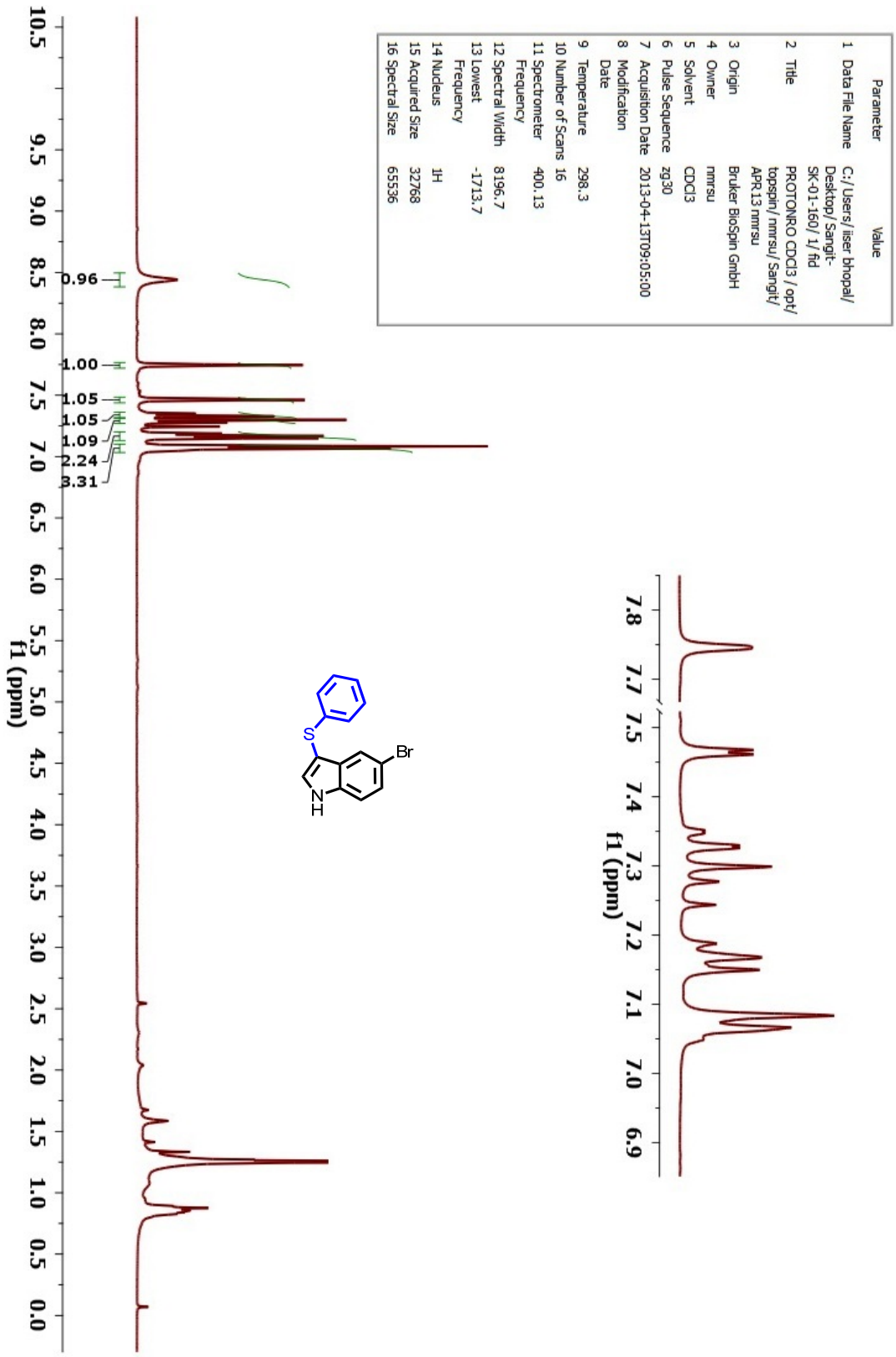


Figure S34 $^{13}$C NMR of **12**

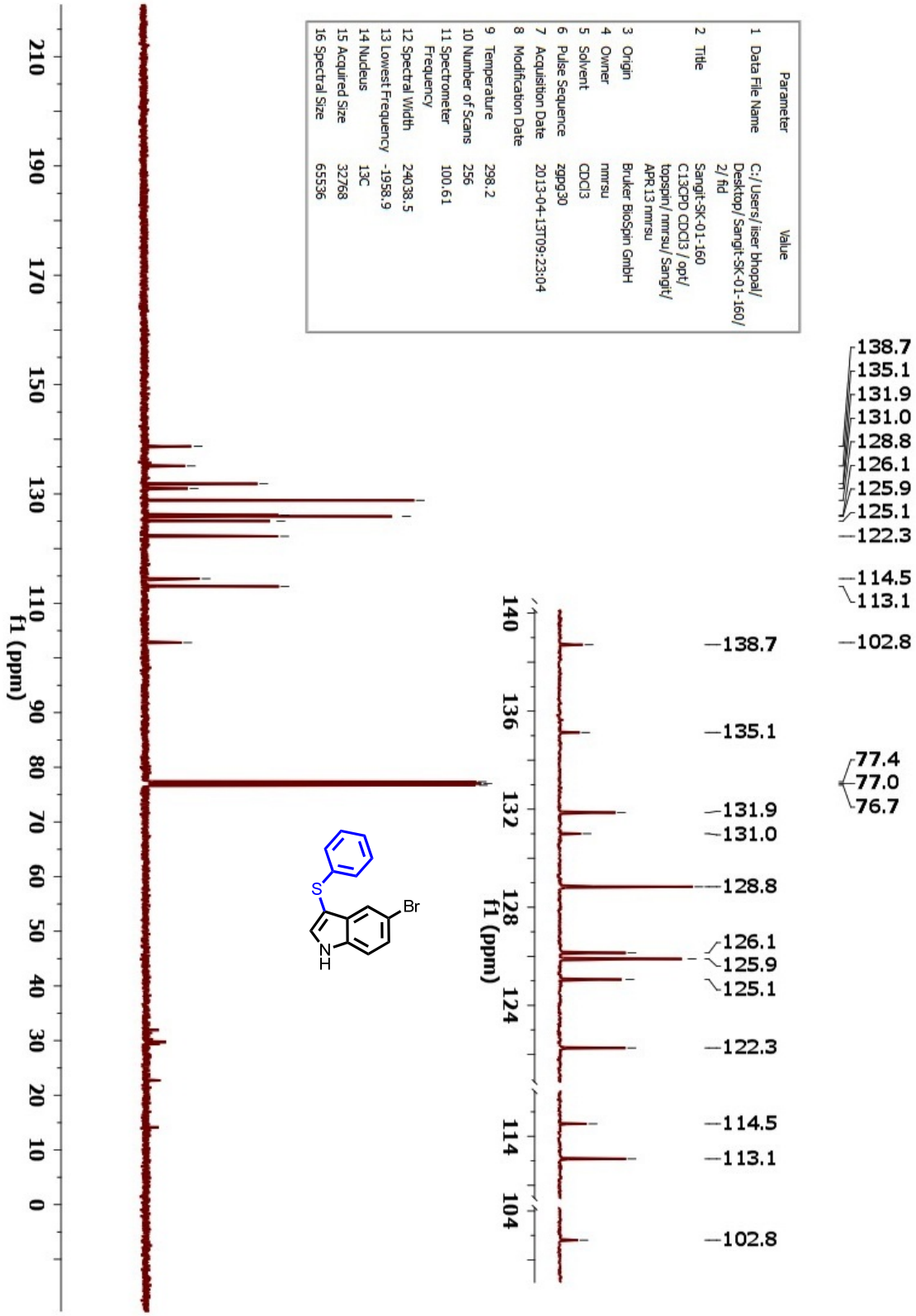


Figure S35 $^{13}$C DEPT-135 NMR of **12**

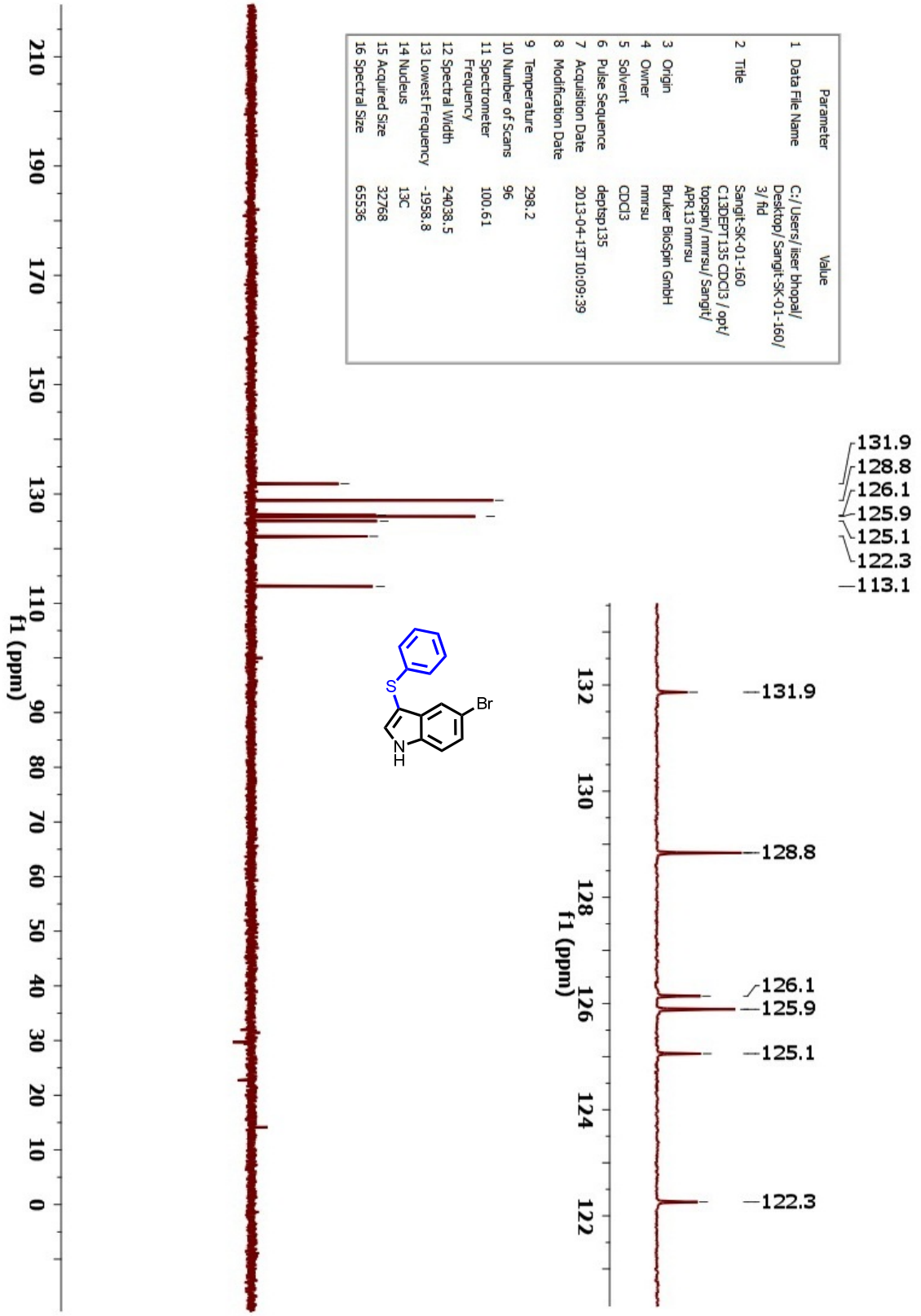


Figure S36 $^{1}$H NMR of **13**

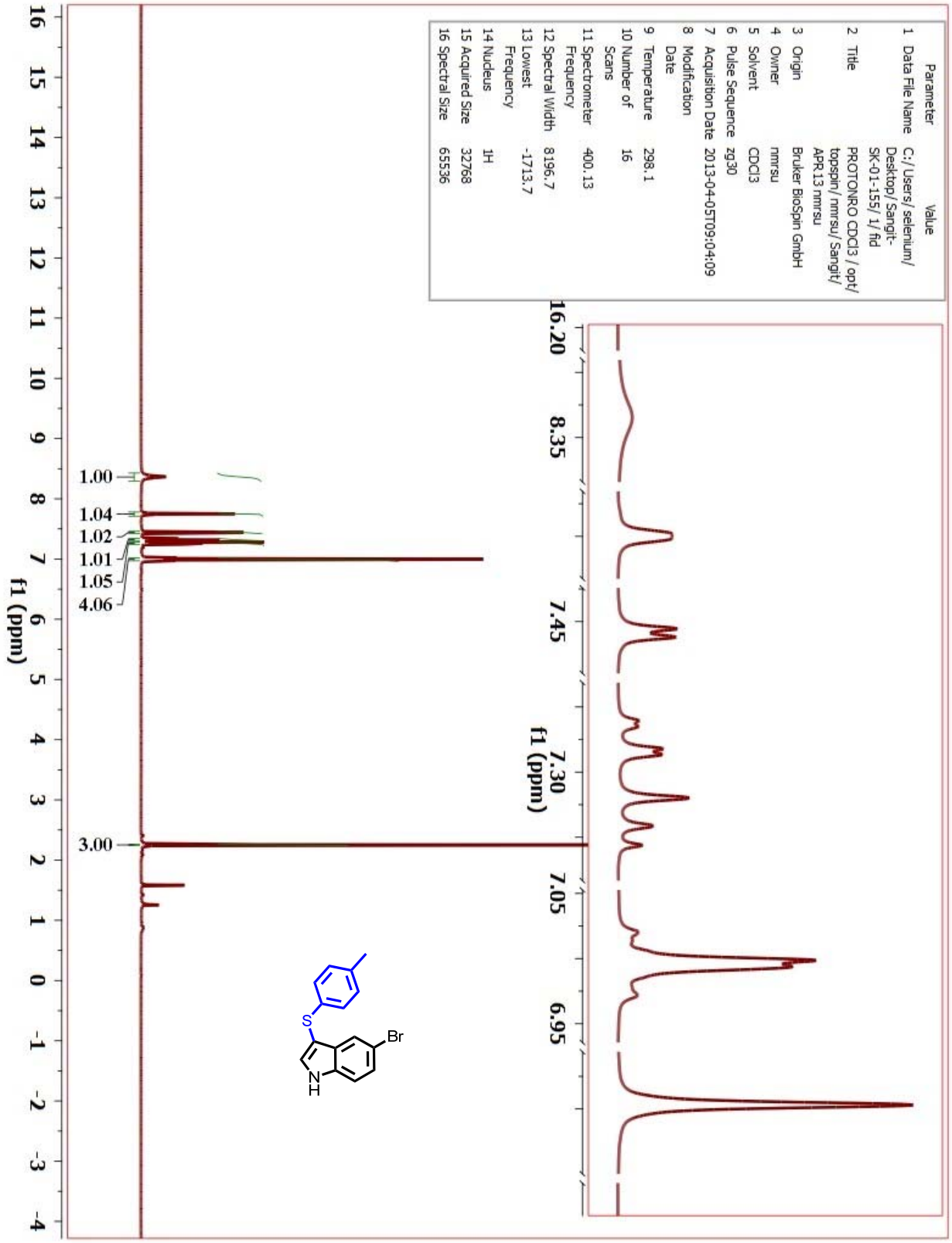


Figure S37 $^{13}$C NMR of **13**

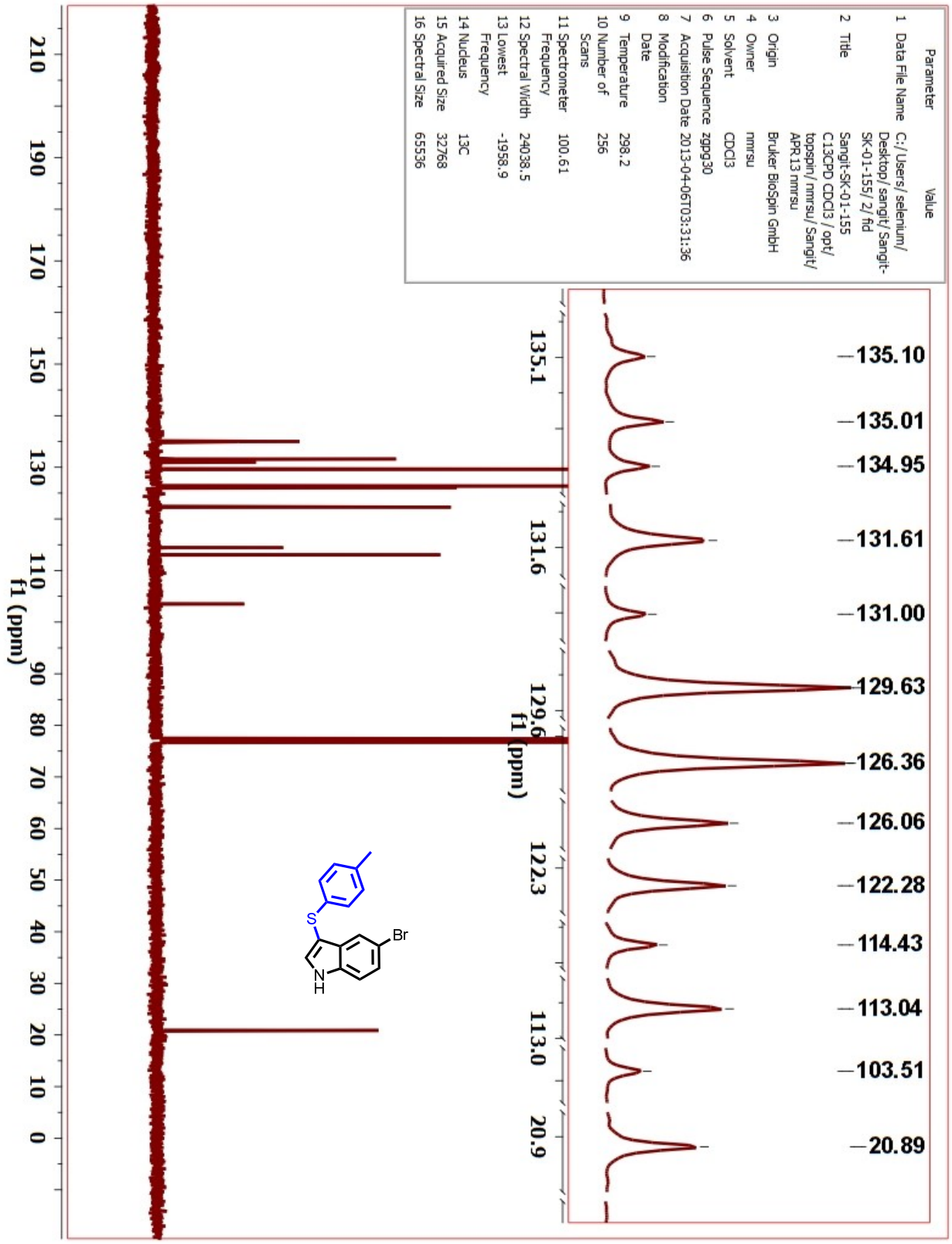


Figure S38 $^{13}$C DEPT-135 NMR of **13**

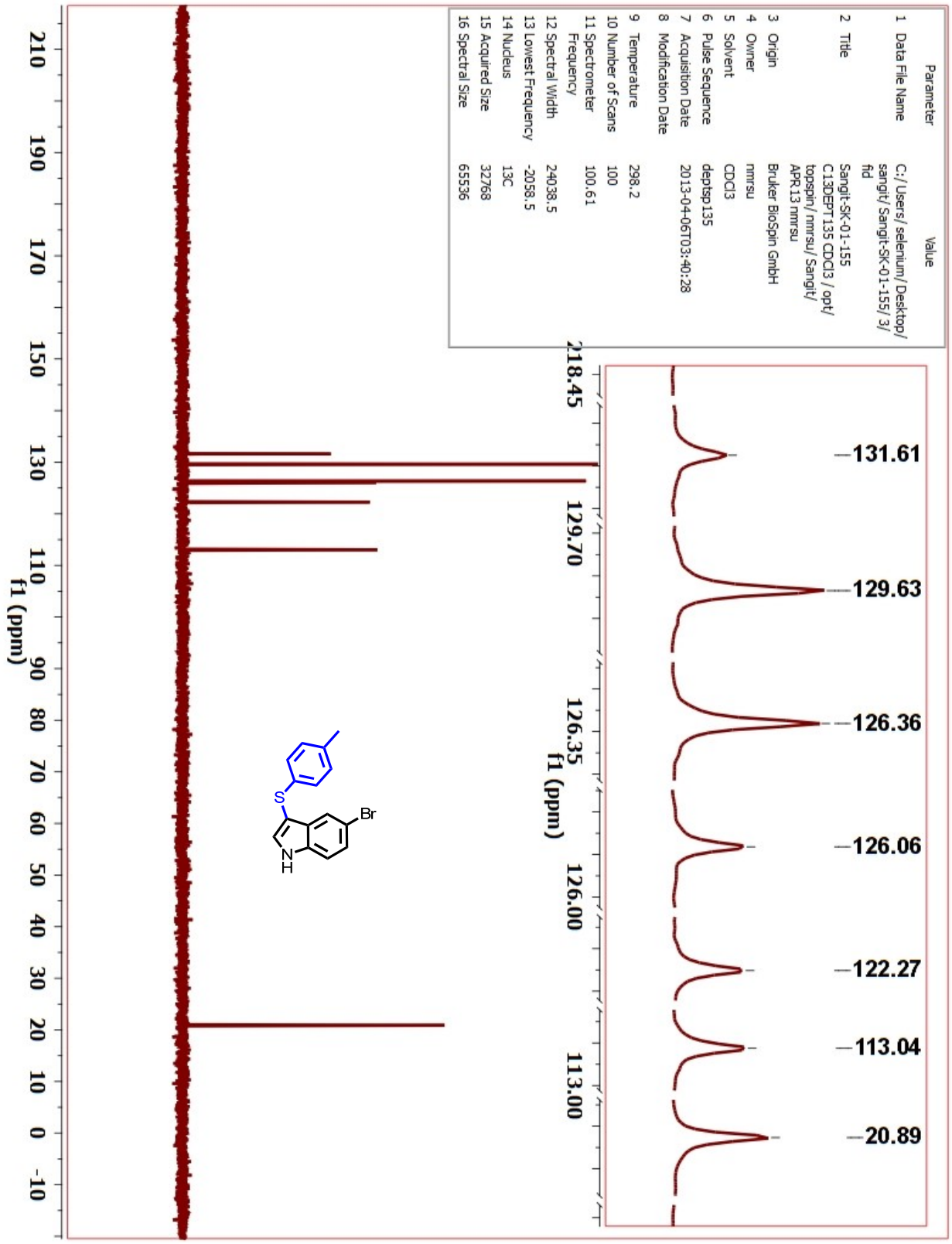


Figure S39 $^{1}$H NMR of **14**

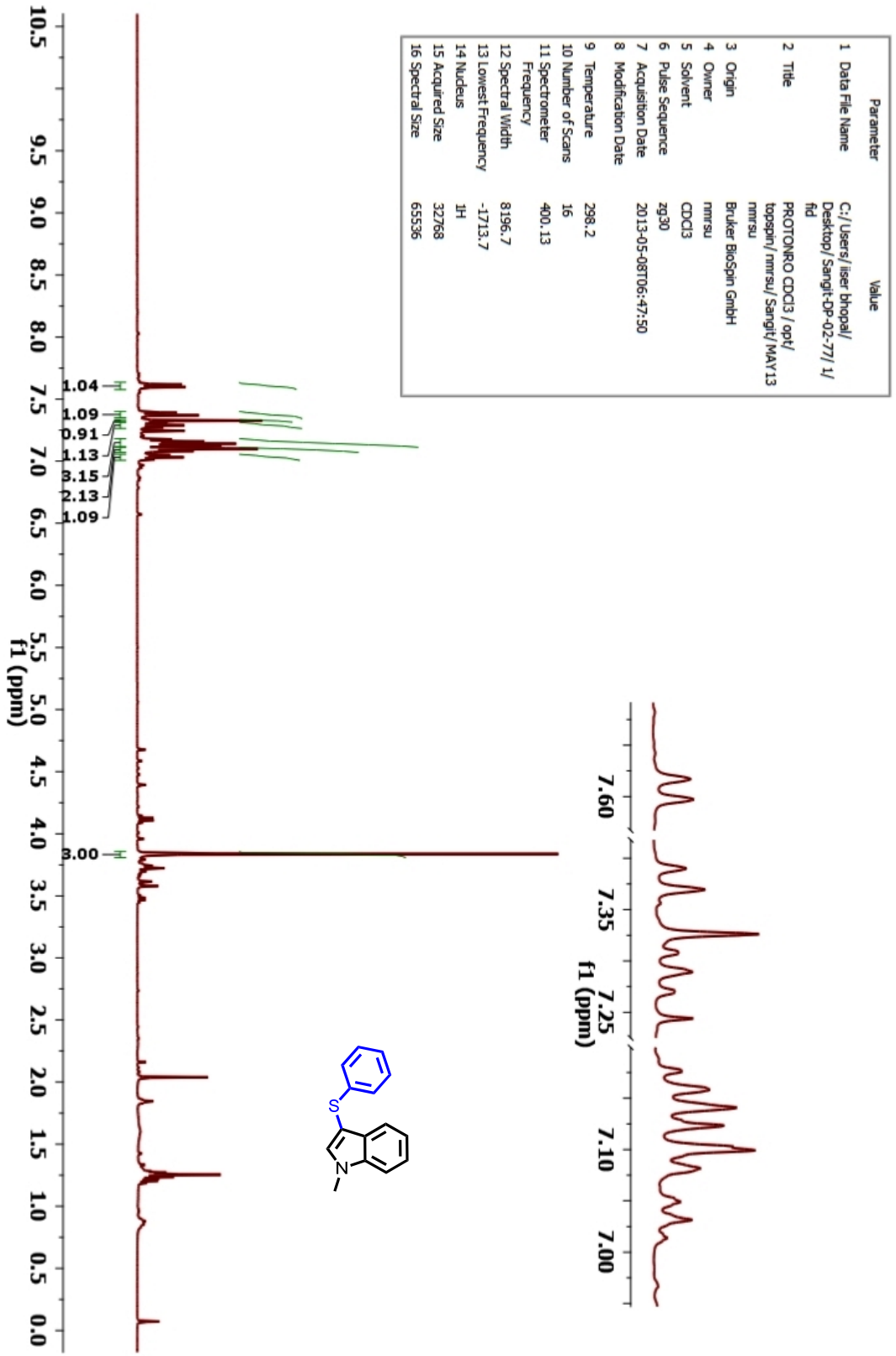


Figure S40 $^{13}$C NMR of **14**

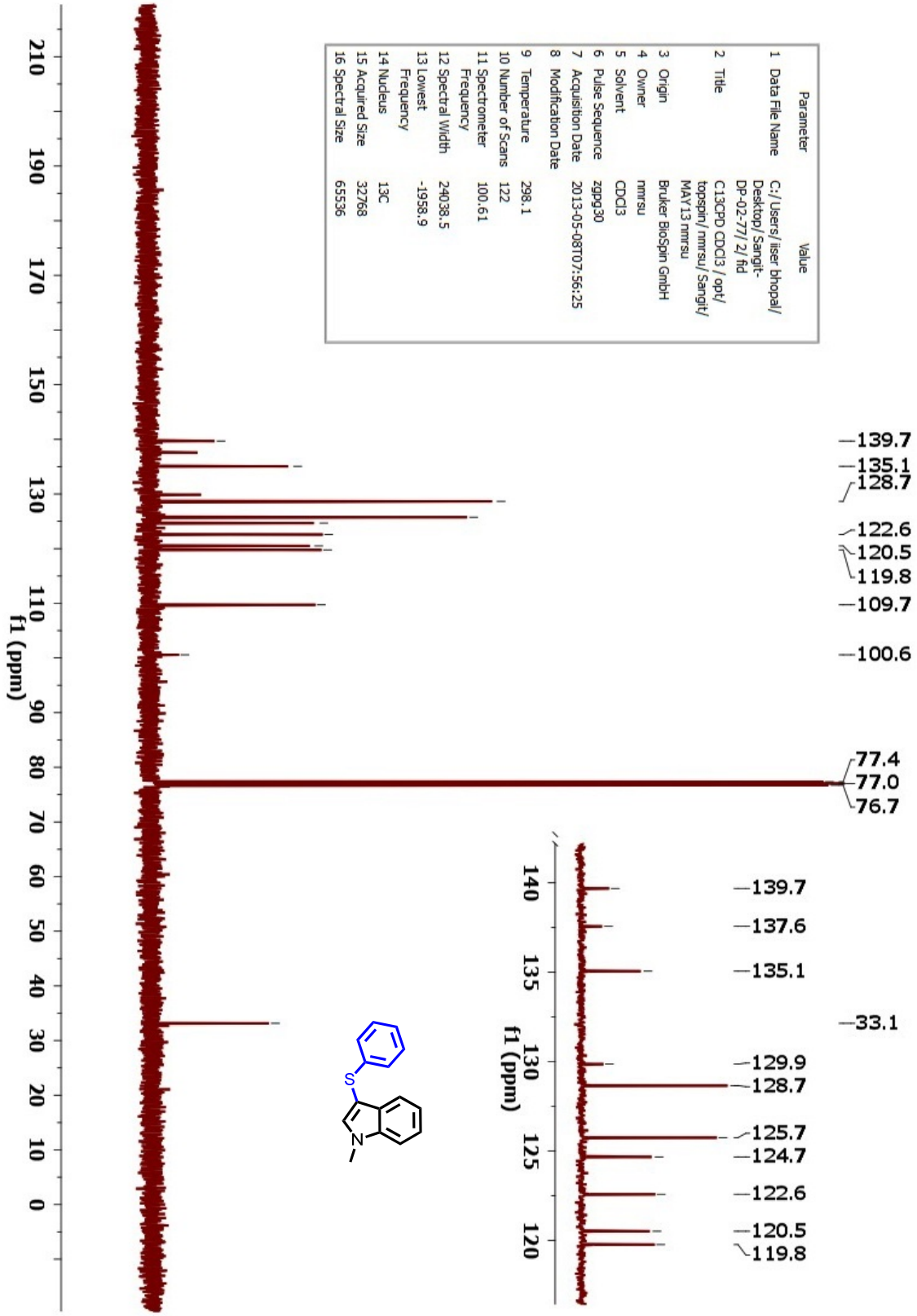


Figure S41 $^{13}$C DEPT-135 NMR of **14**

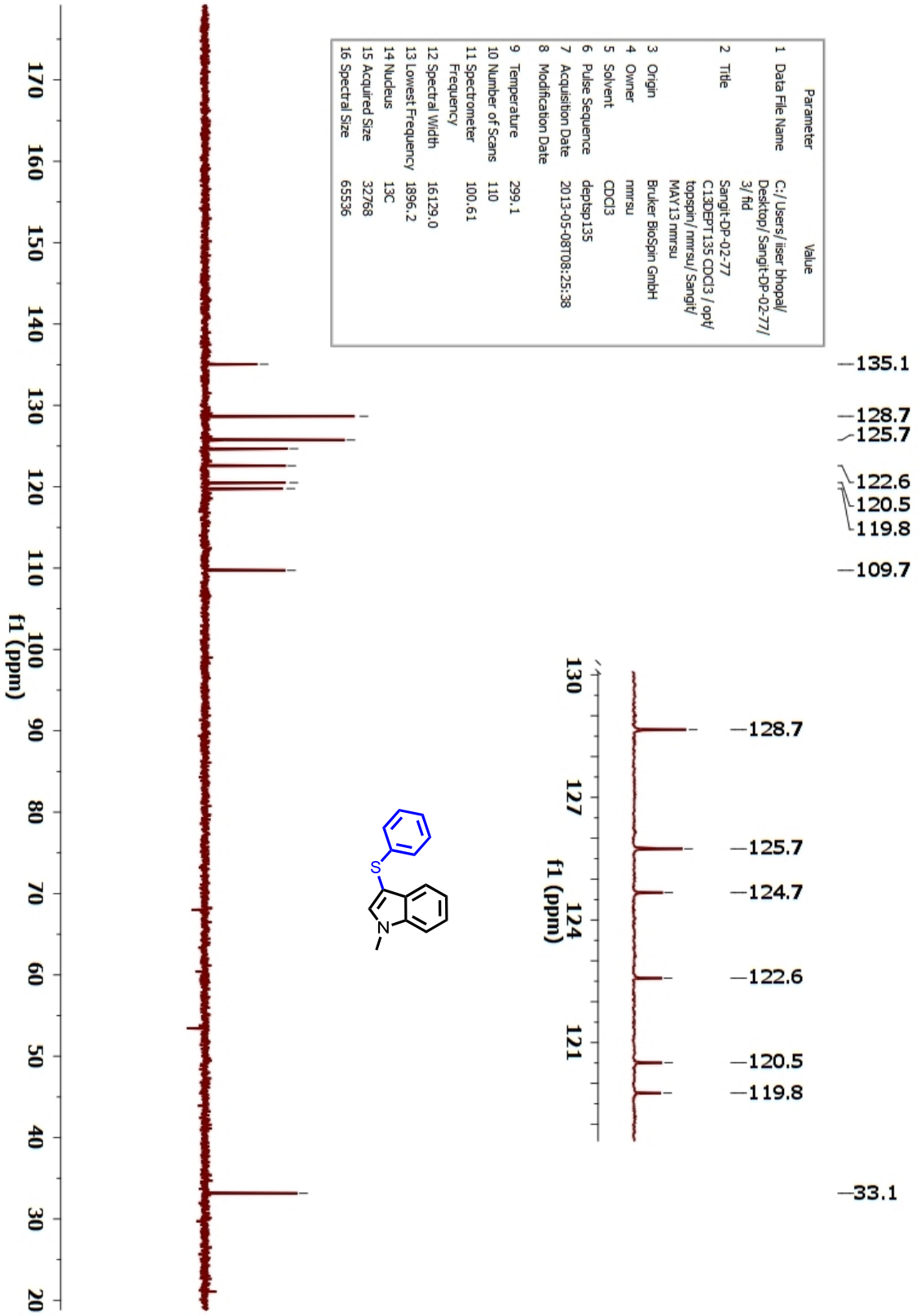
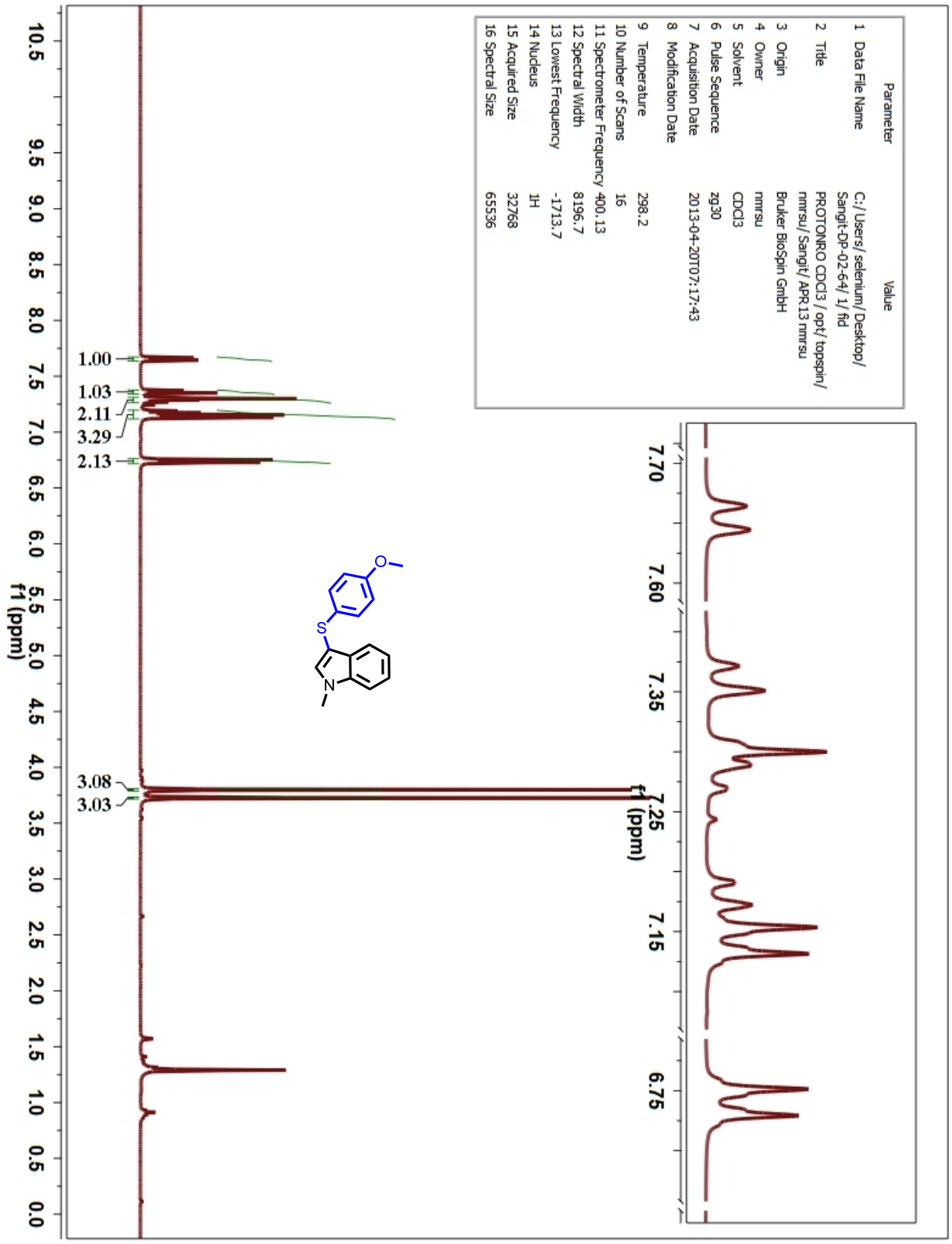


Figure S42 $^{1}$H NMR of **15**



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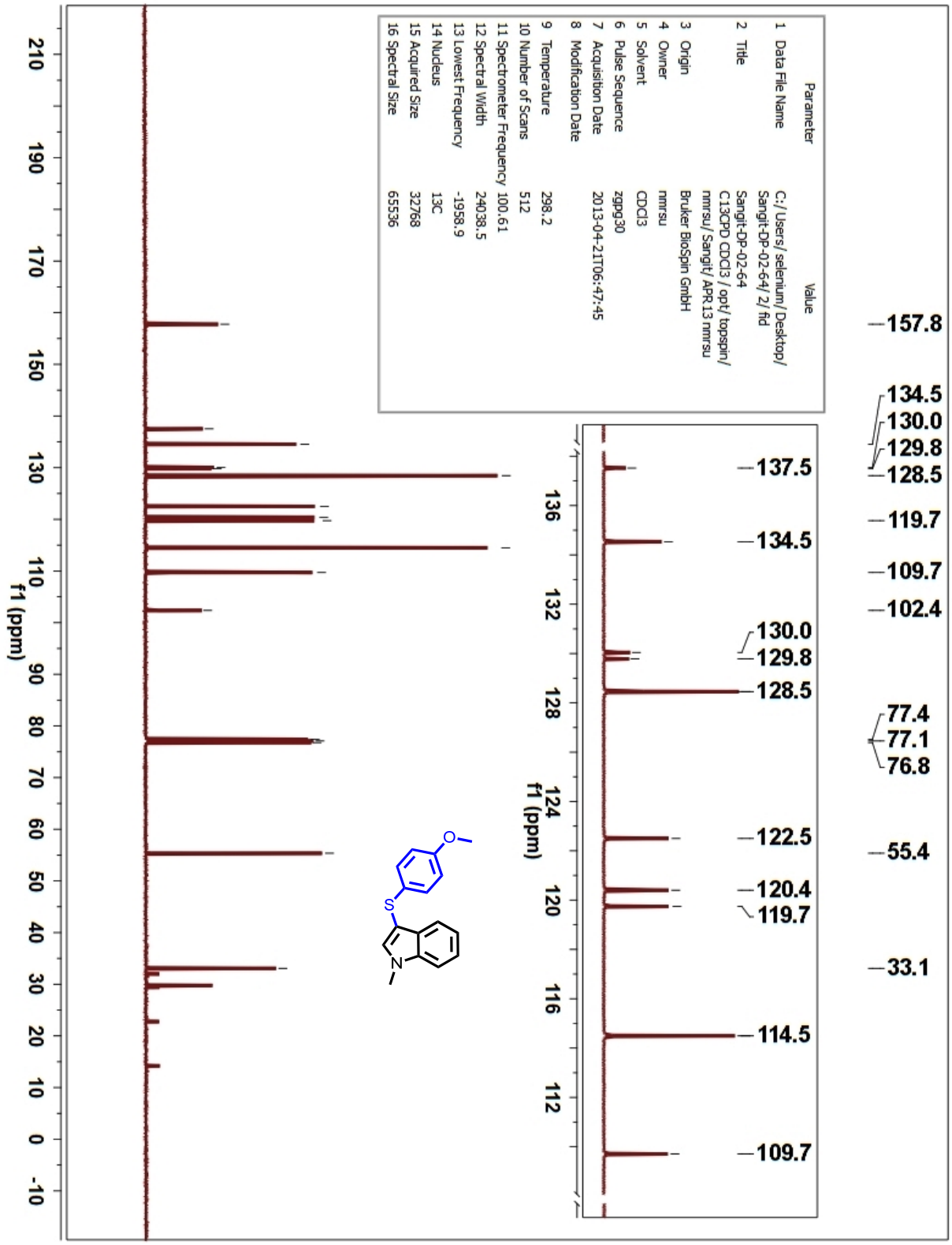

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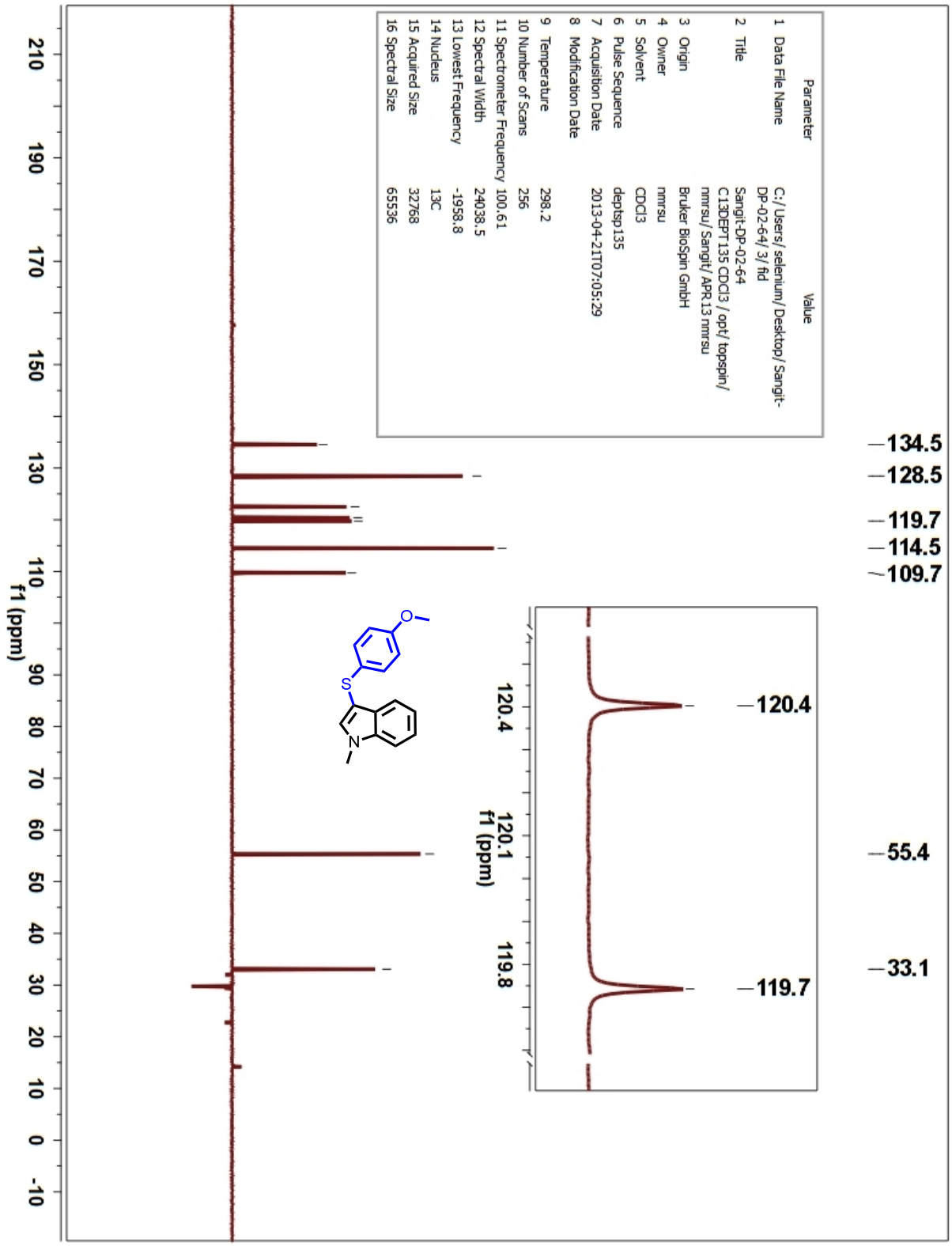
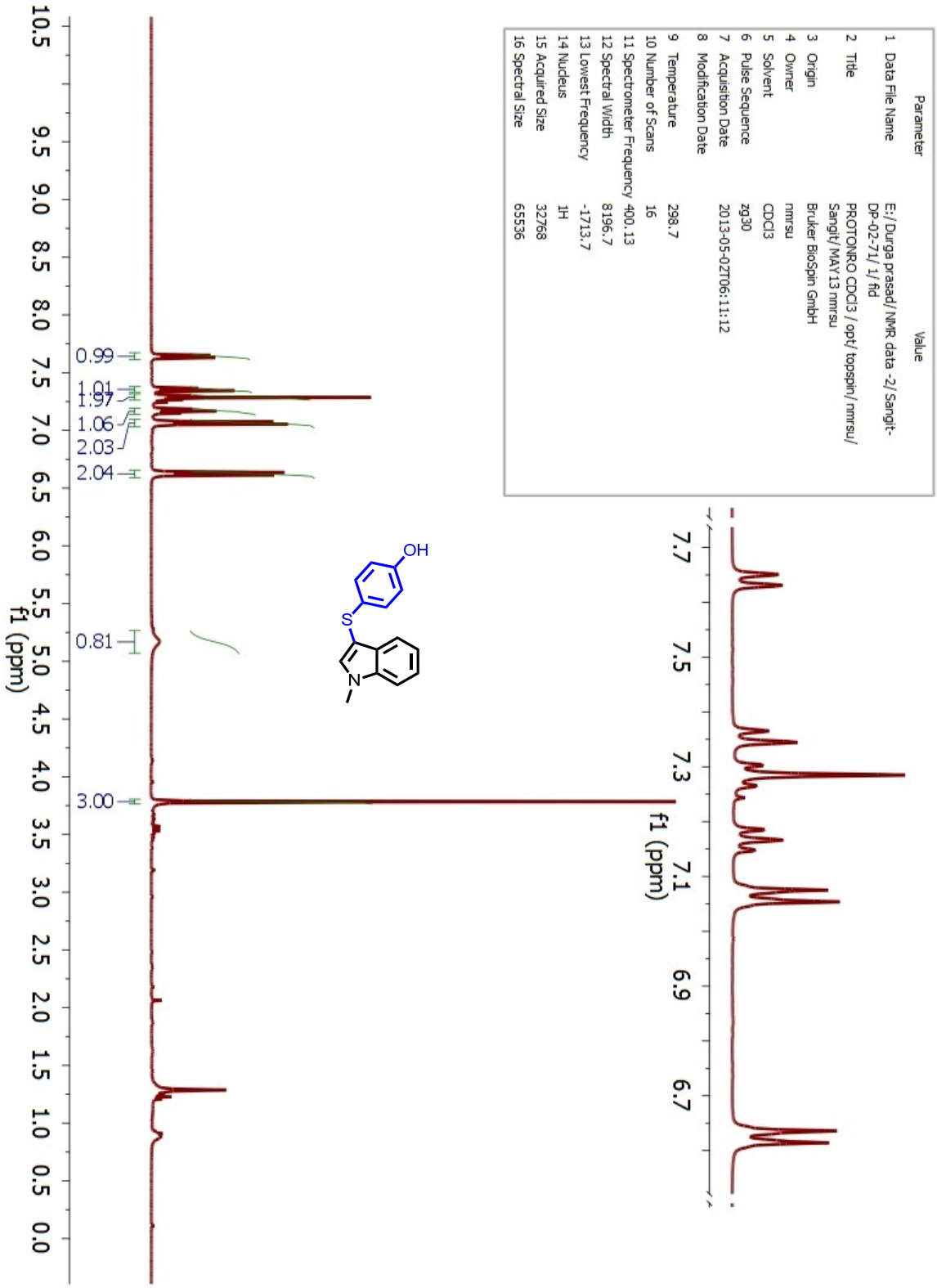


Figure S45 $^{1}$H NMR of **16**



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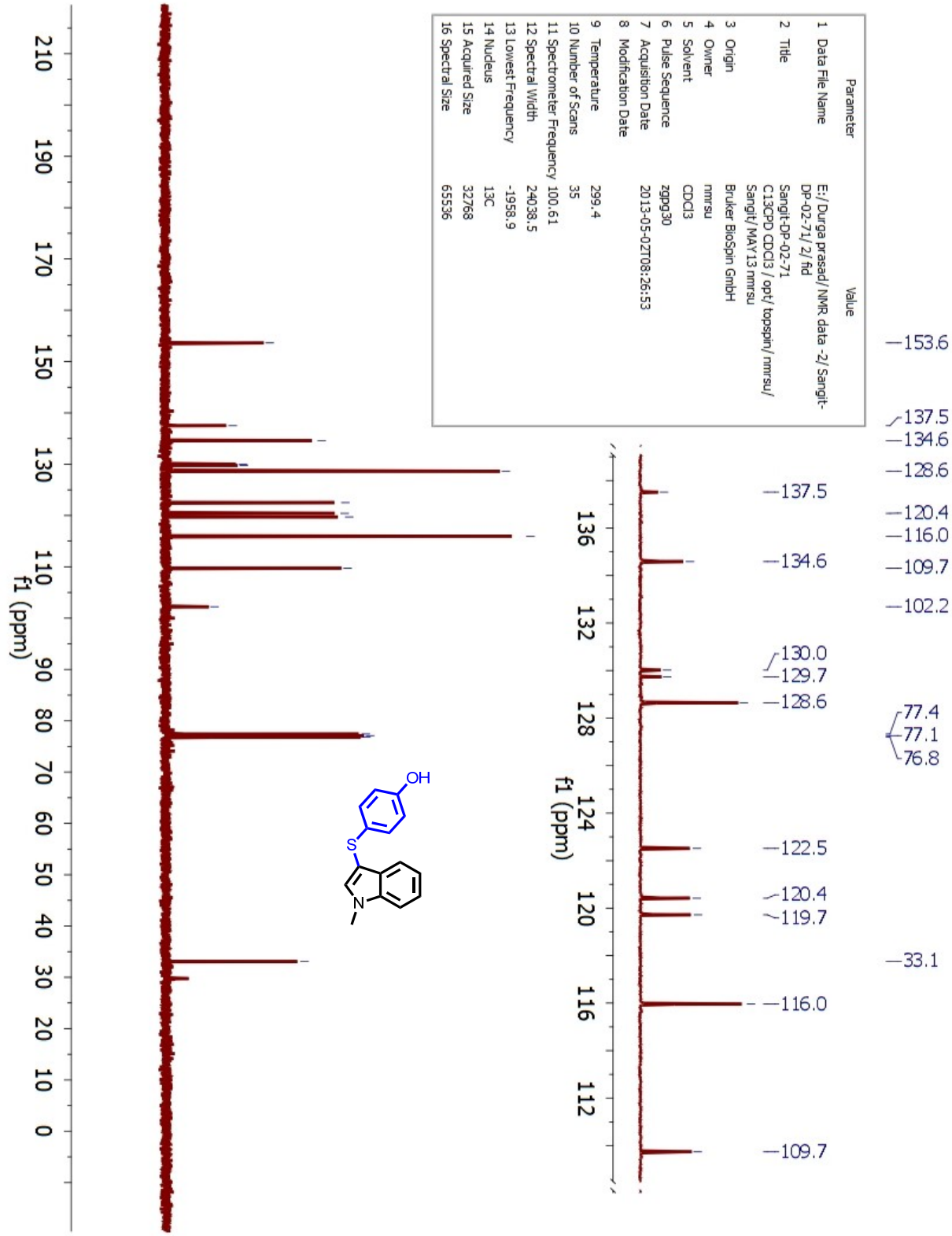

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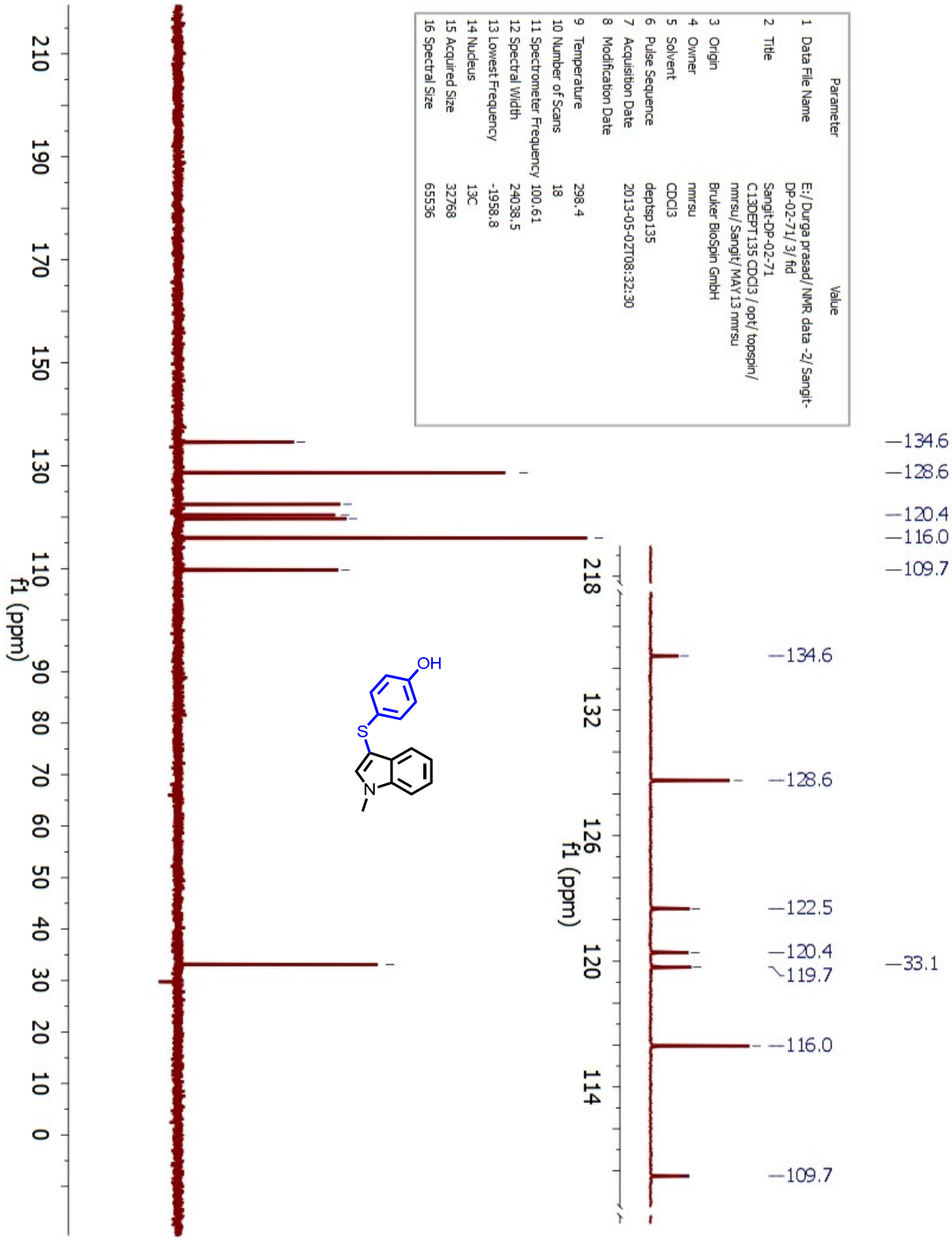


Figure S48 $^{1}$H NMR of **17**

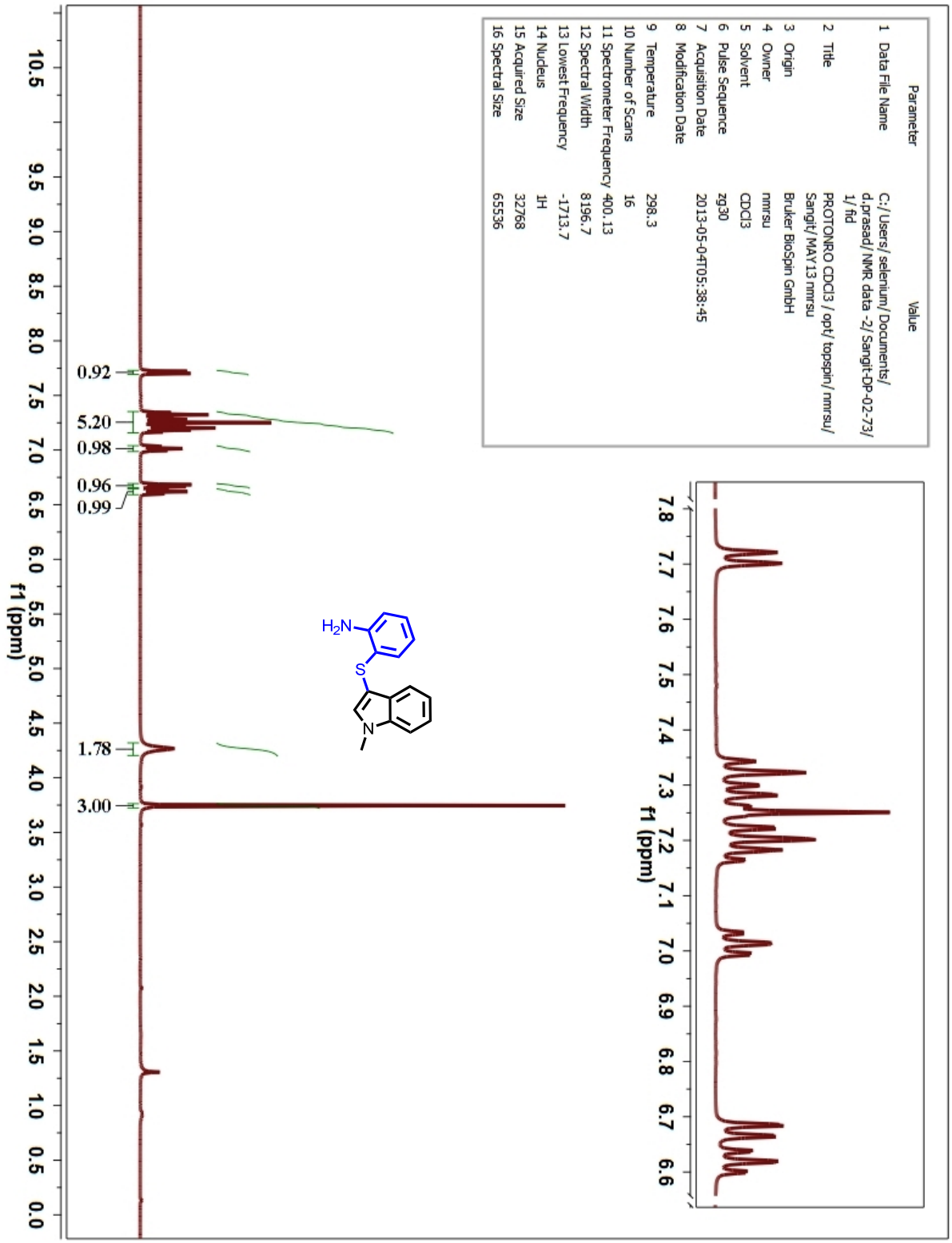


Figure S49 $^{13}$C NMR of **17**

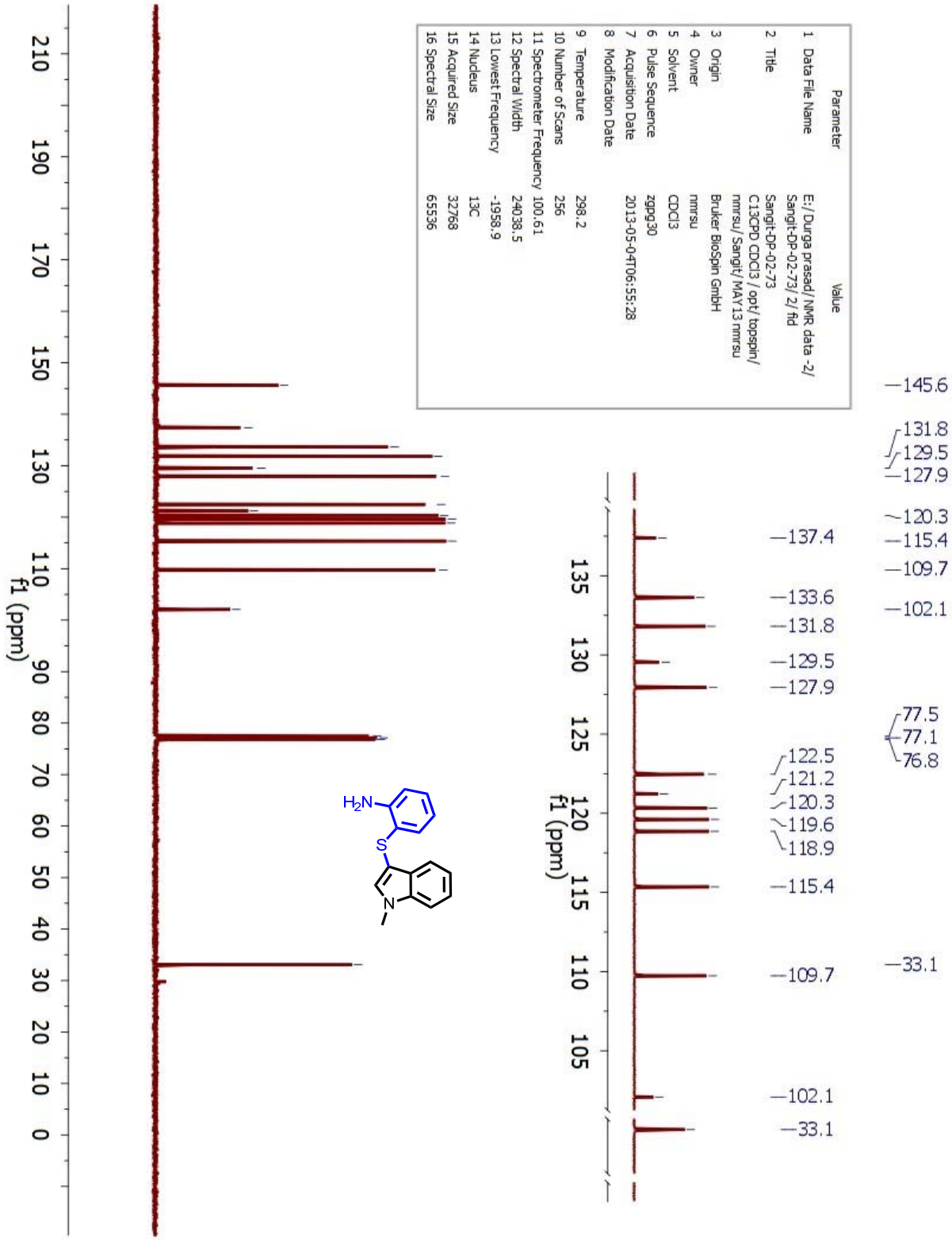


Figure S50 $^{13}$C DEPT-135 NMR of **17**

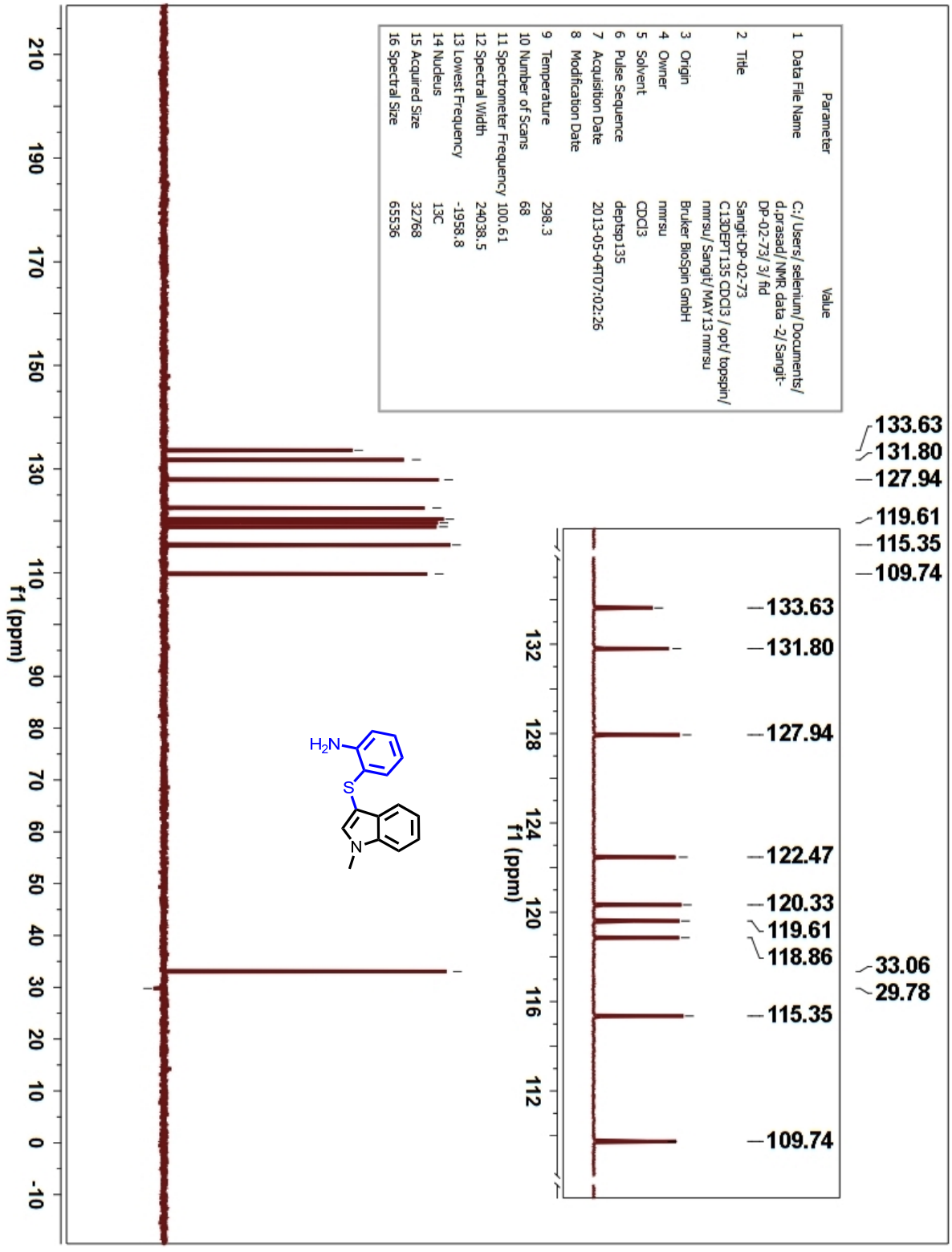


Figure S51 $^{1}$H NMR of **18**

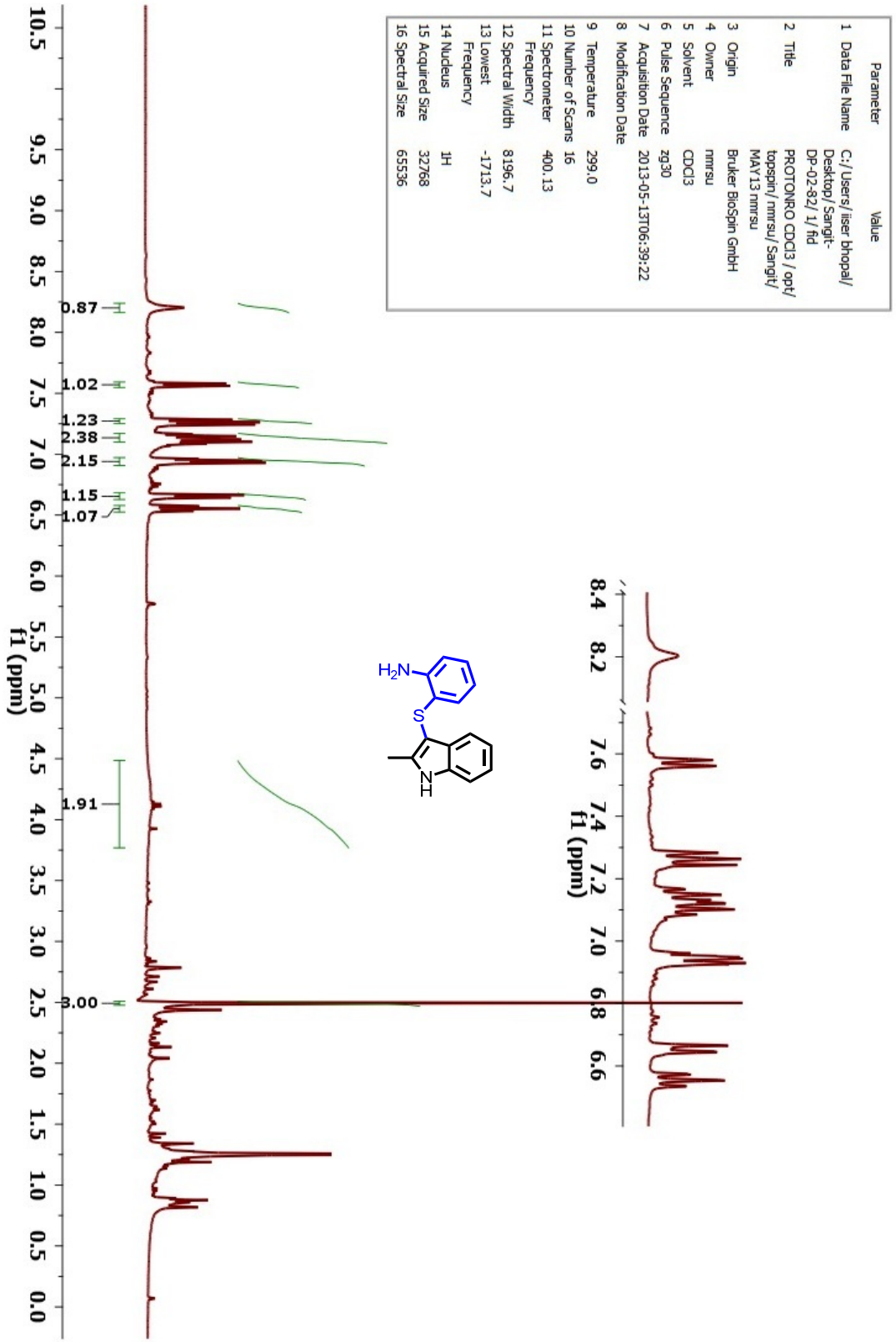


Figure S52 $^{13}$C NMR of **18**

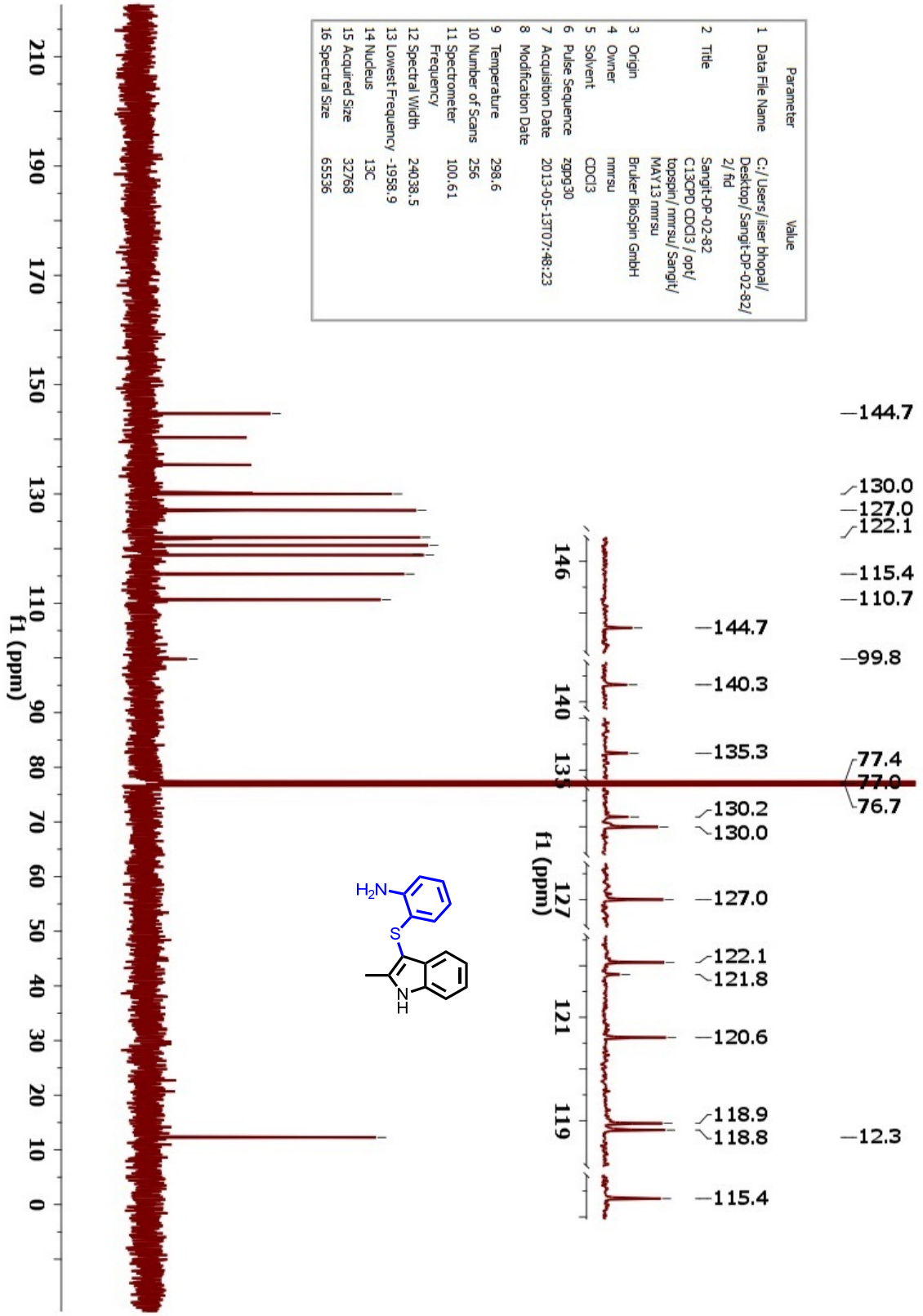


Figure S53 $^{13}$C DEPT-135 NMR of **18**

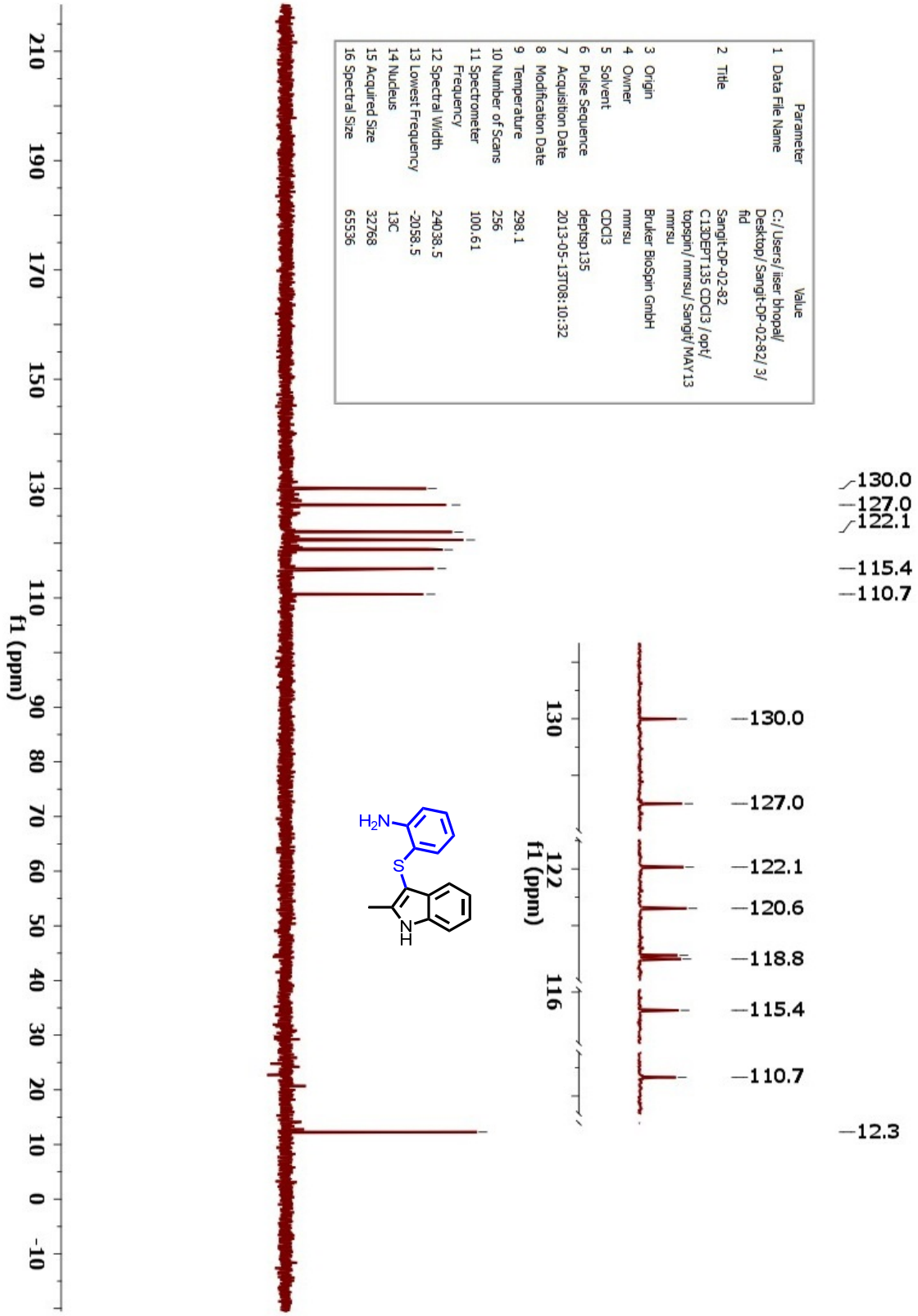


Figure S54 $^{1}$H NMR of **19**

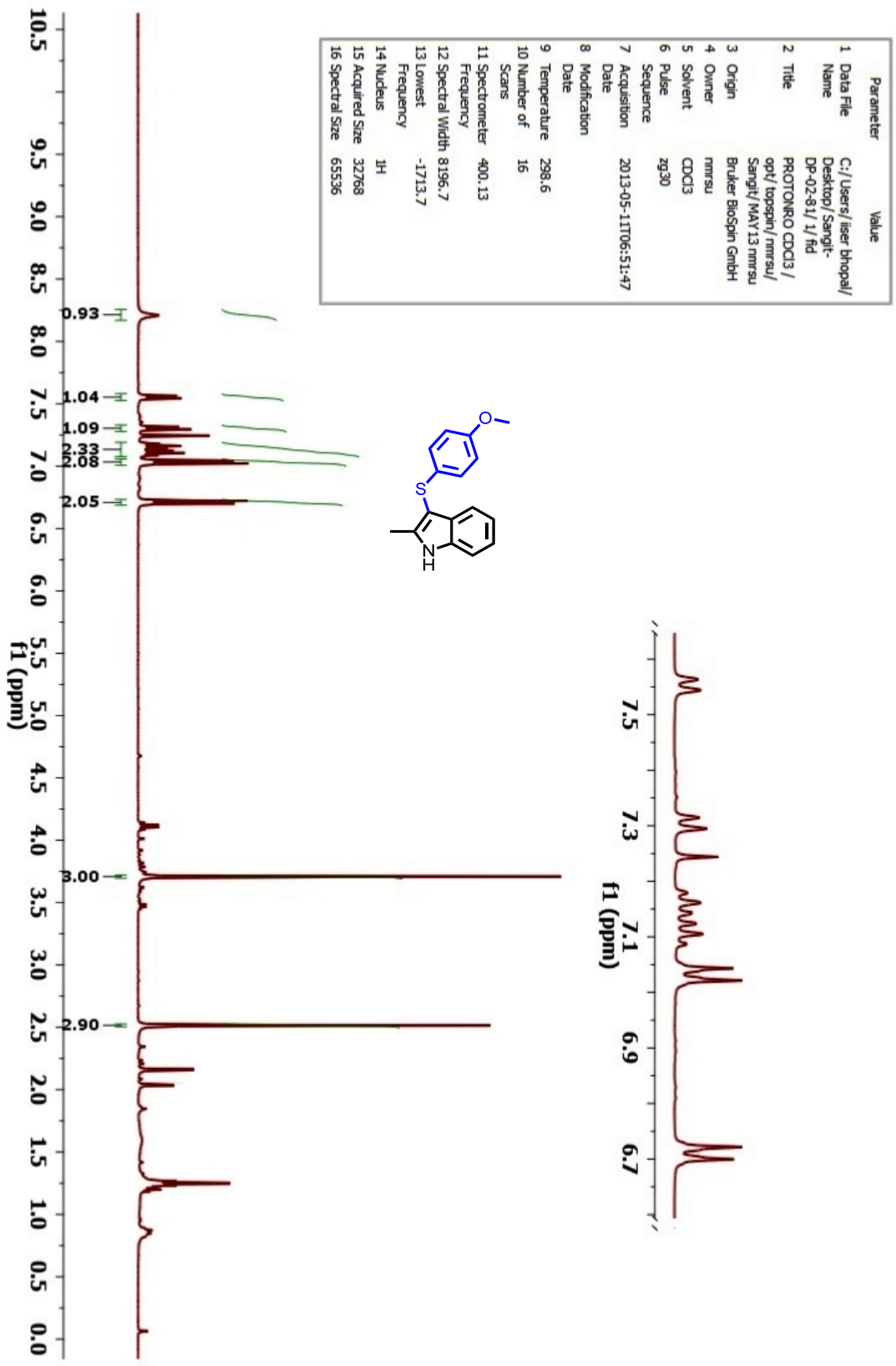


Figure S55 $^{13}$C NMR of 1**9**

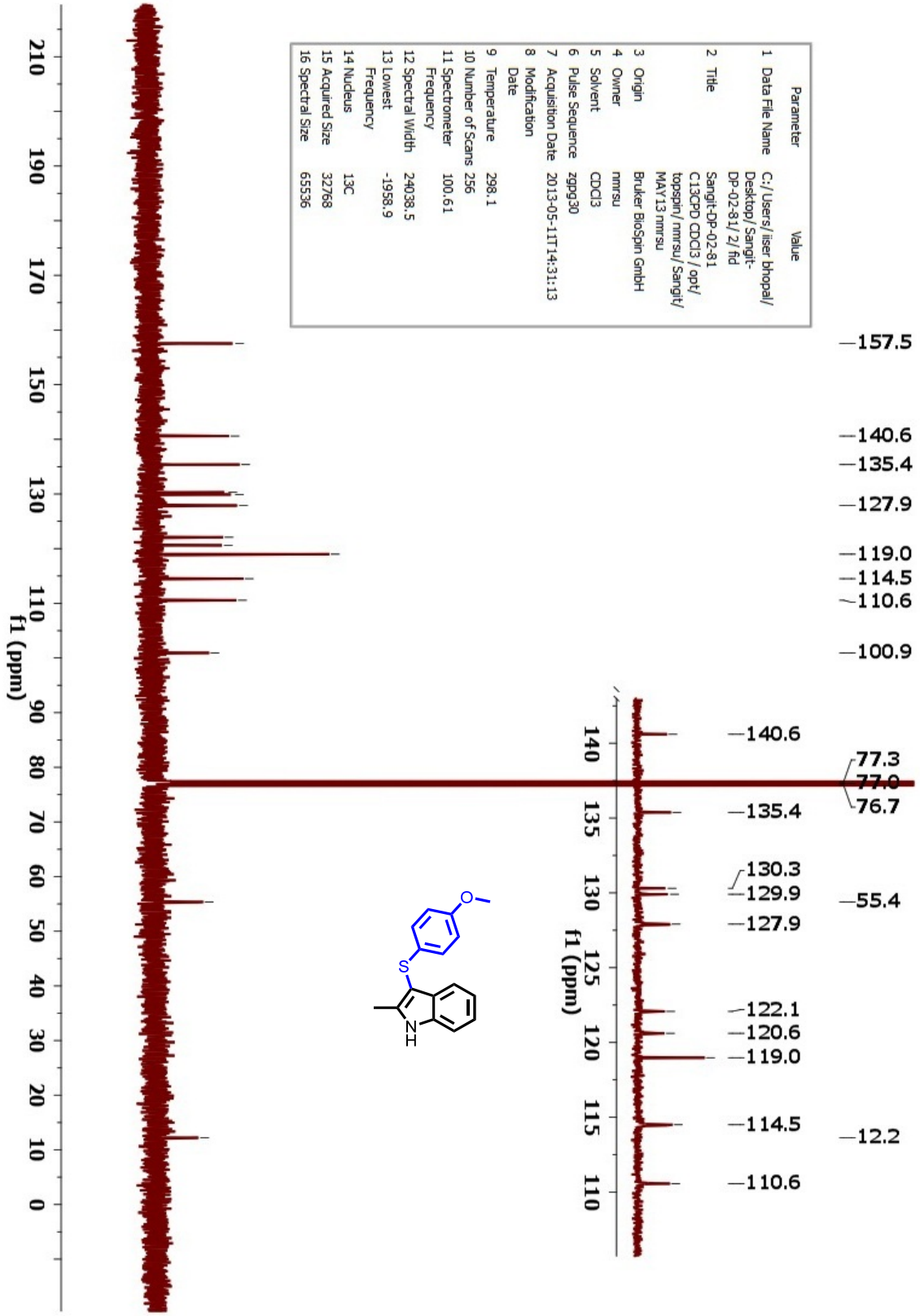


Figure S56 $^{1}$H NMR of **20**

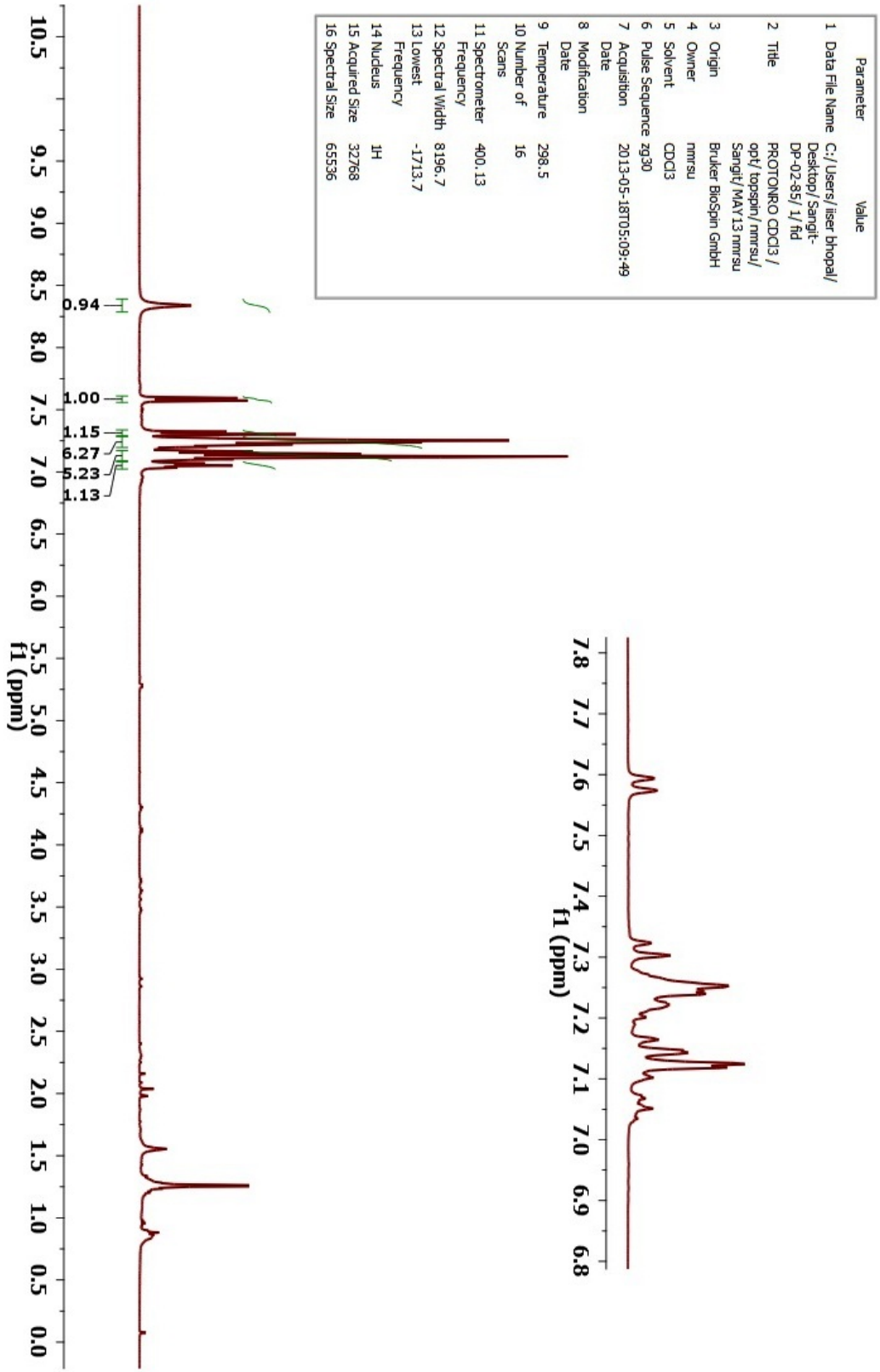
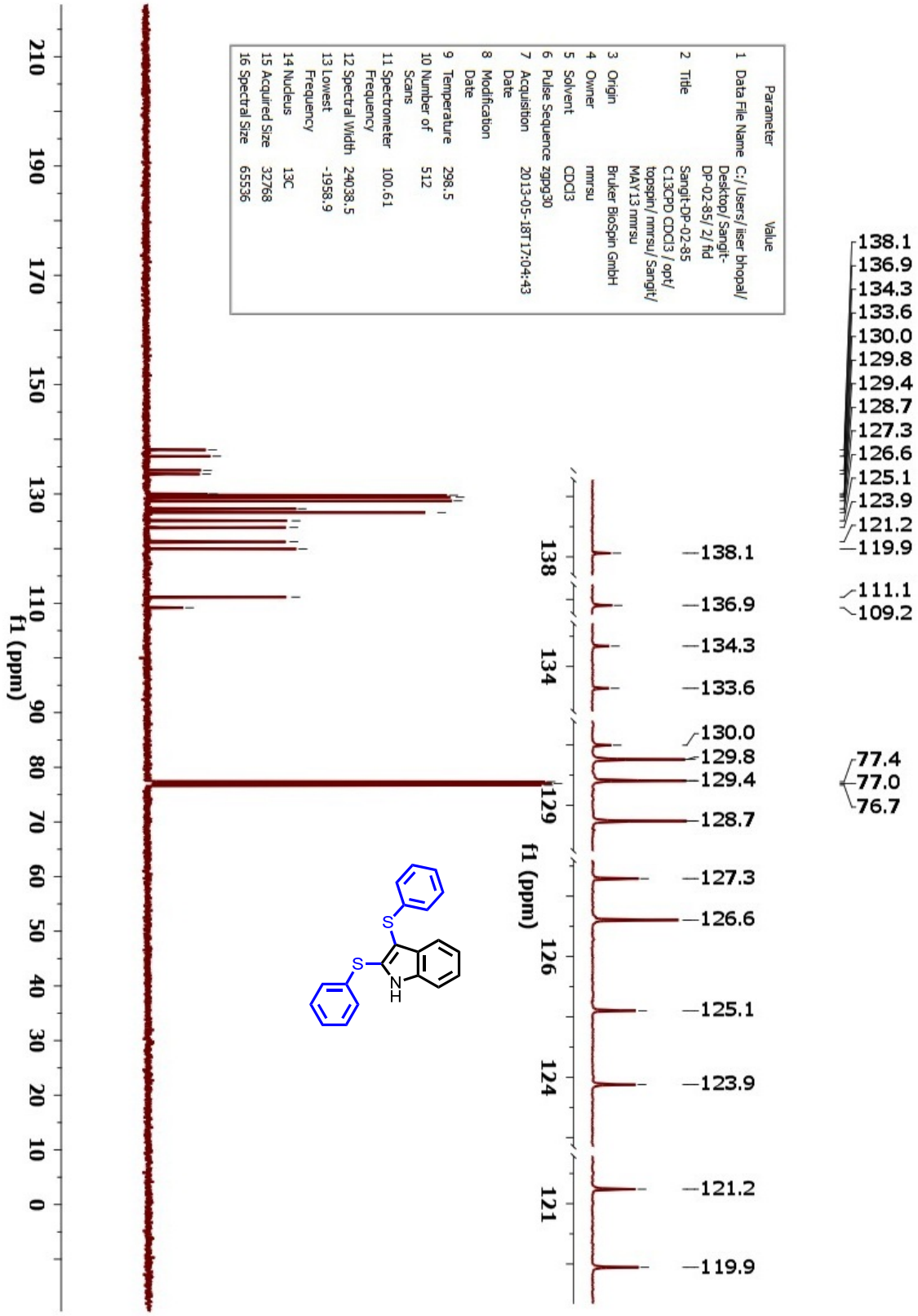


Figure S57 $^{13}$C NMR of **20**



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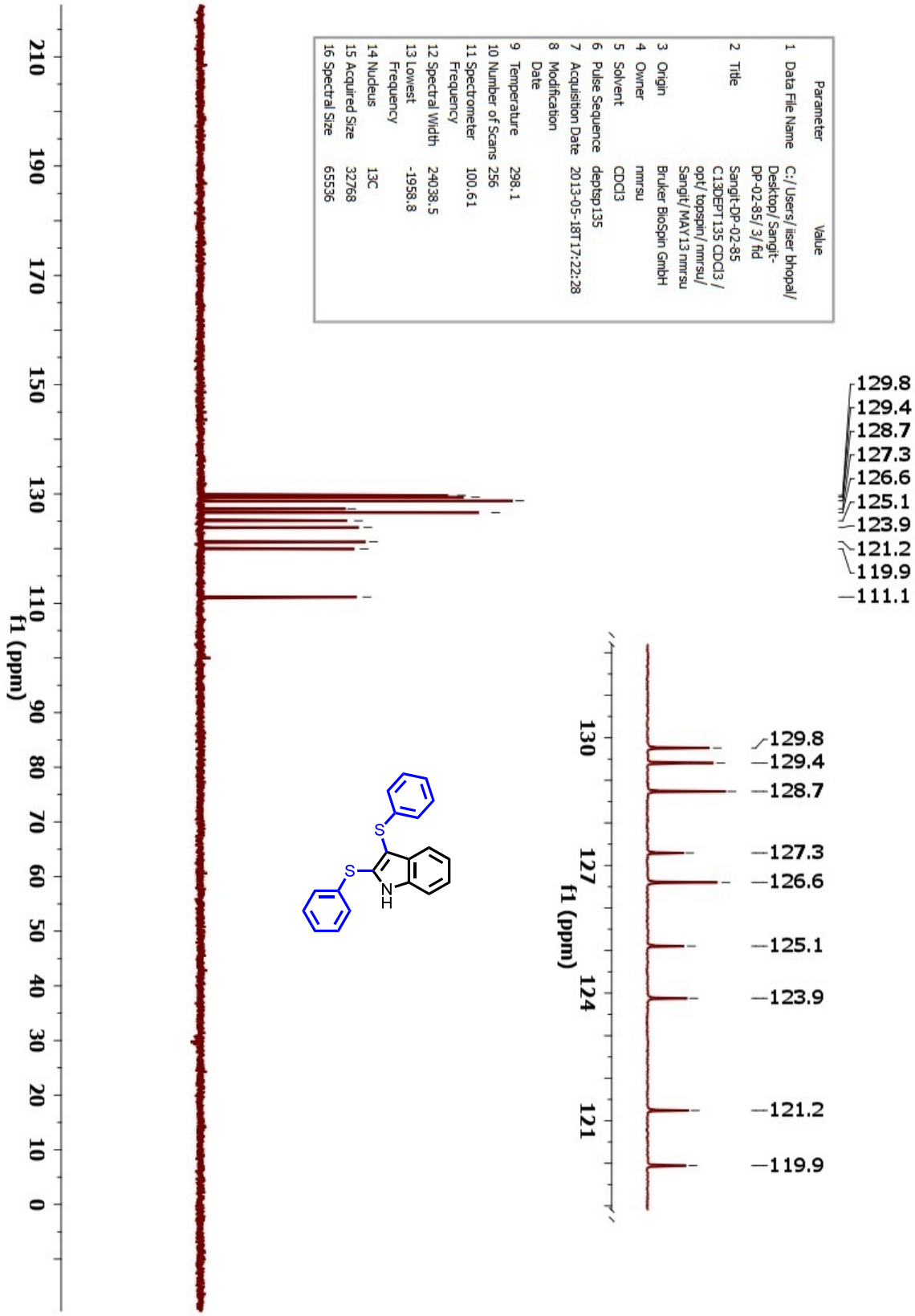
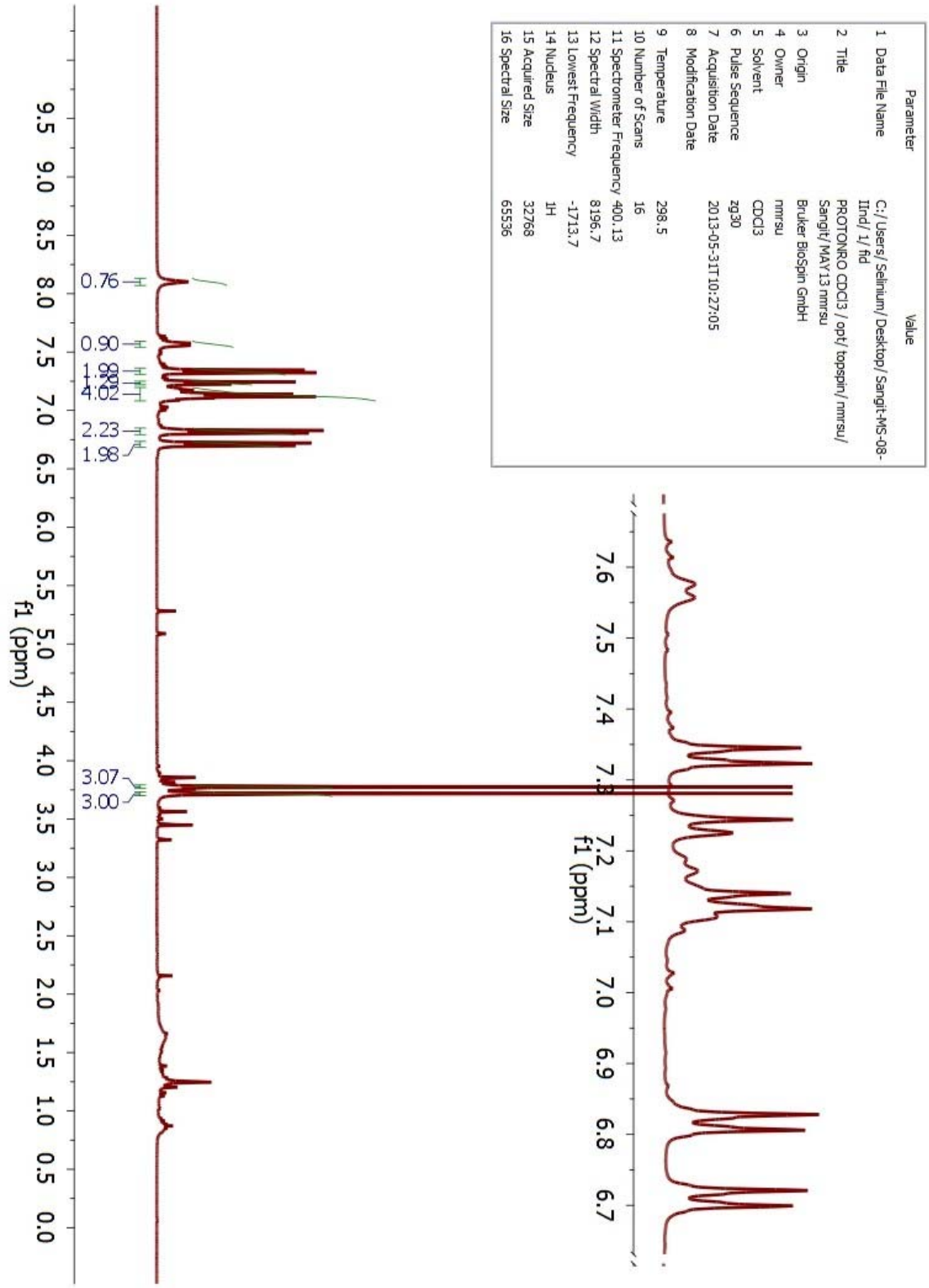



Figure

S59 $^{1}$H NMR of **21**



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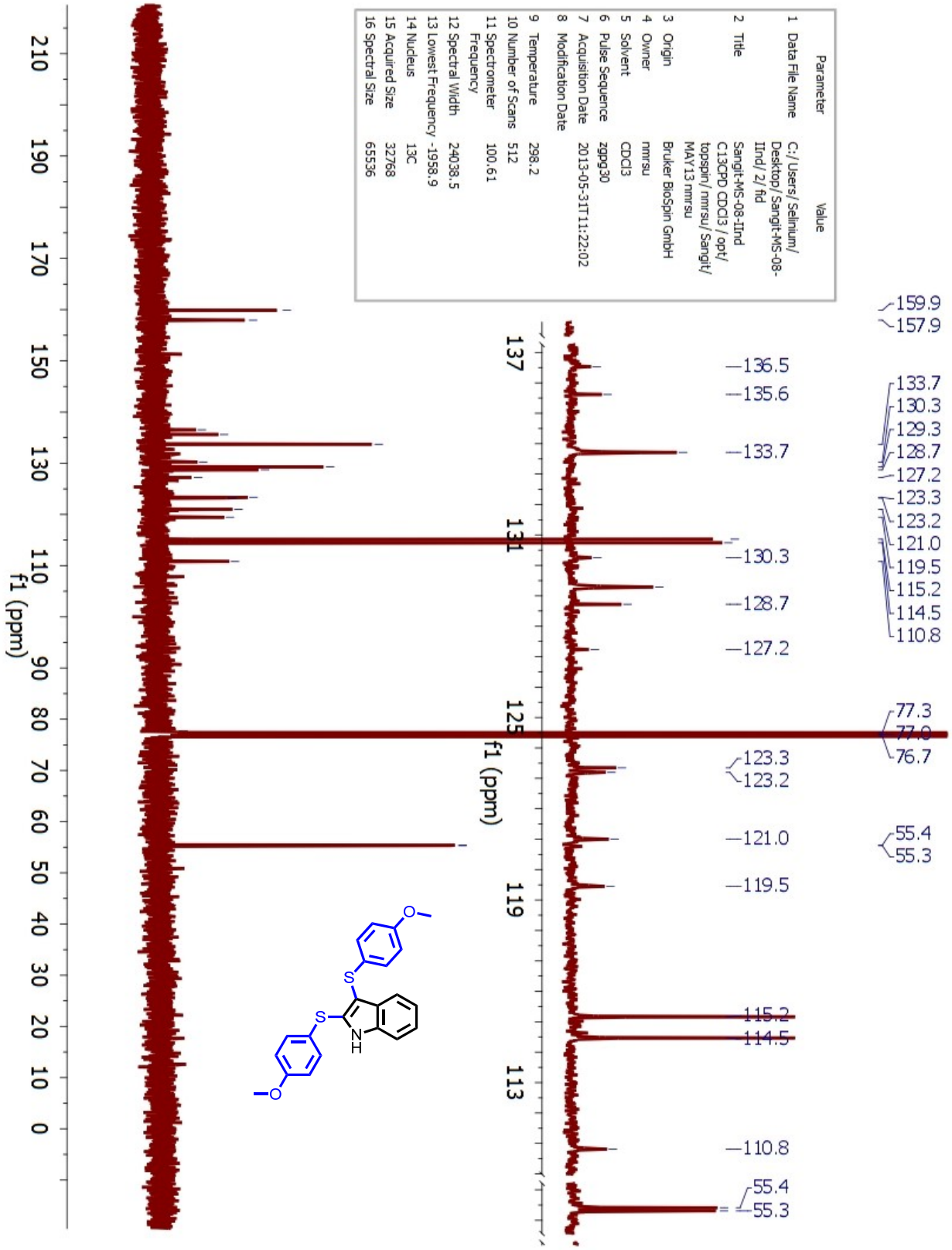


Figure S61 $^{1}$H NMR of **22**

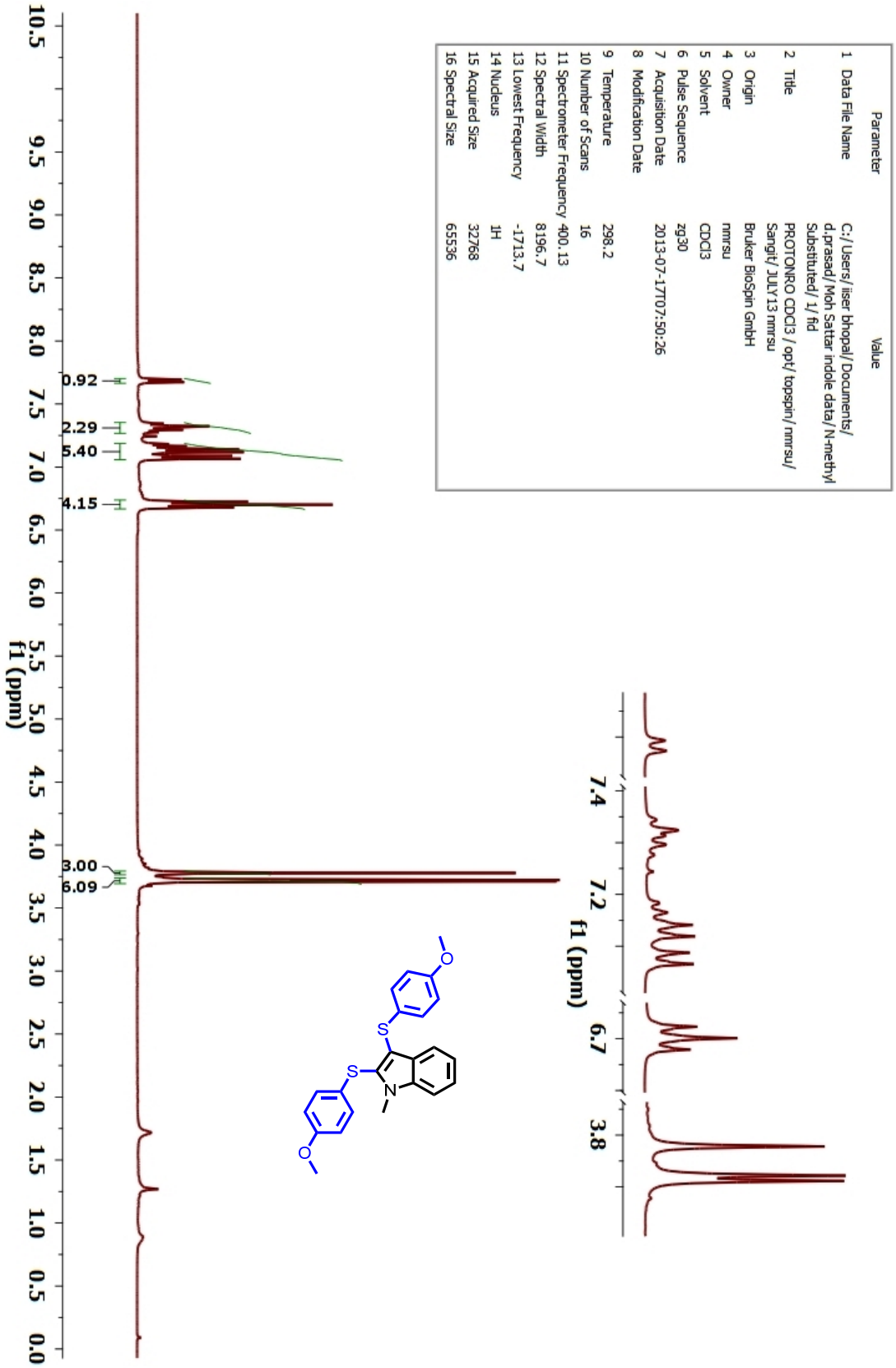
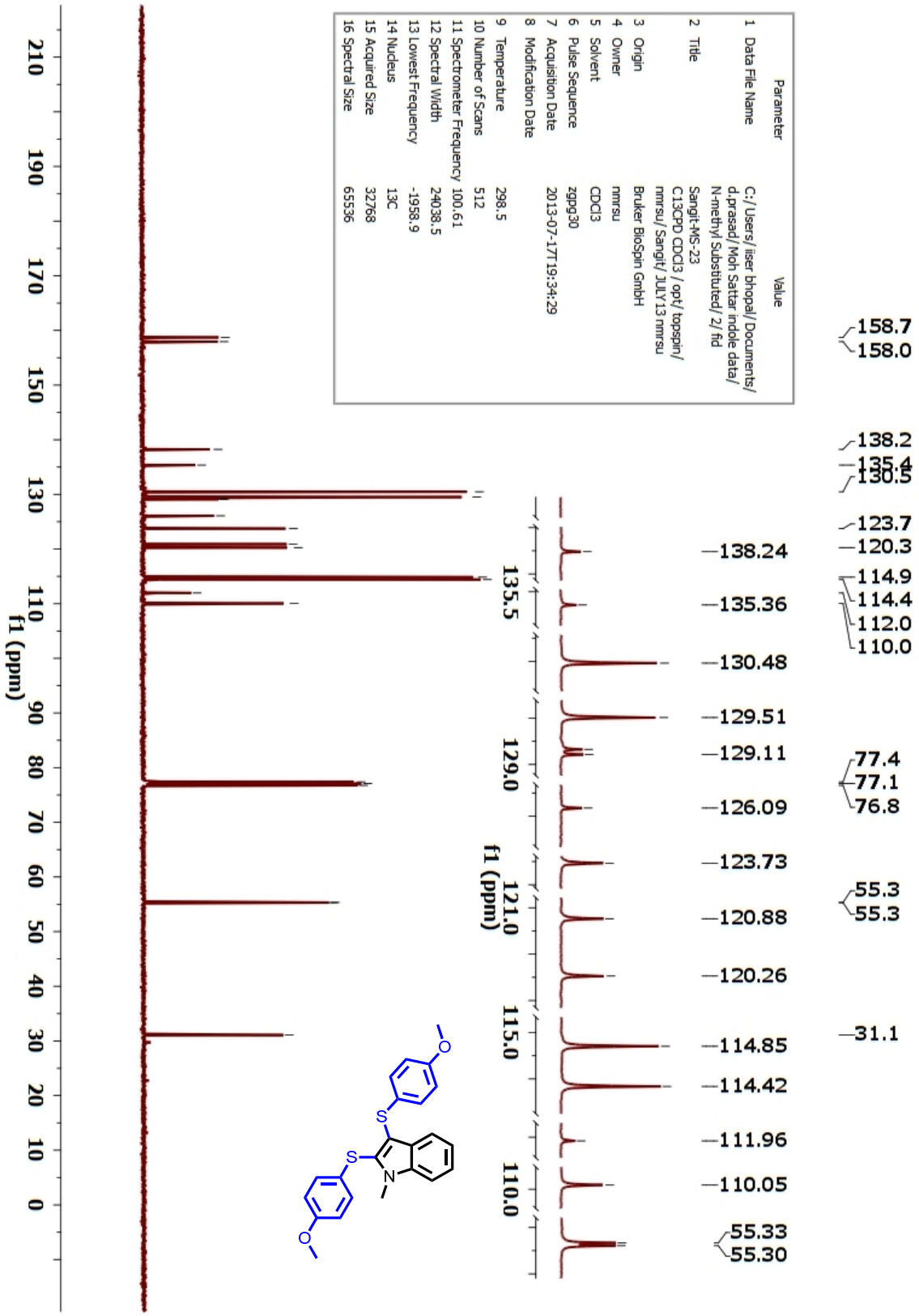


Figure S62 $^{13}$C NMR of **22**



# **Crystal Structure data of sulfide** 11 (CCDC No. 953902)

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C118 0.042(4) 0.131(6) 0.066(6) -0.024(7) 0.026(4) -0.020(4)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken

```
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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S1 C1 1.750(7) . ?
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N121 H121 0.8600 . ?
O18 N92 1.221(7) . ?
O81 N92 1.257(8) . ?
C123 C112 1.373(12) . ?
C123 H123 0.9300 . ?
N92 C107 1.438(10) . ?
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C1# H1 0.9803 . ?
C107 C108 1.374(8) . ?
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C108 H108 0.9300 . ?
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C110 C111 1.357(11) . ?
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C111 H111 0.9300 . ?
C113 C117 1.386(12) . ?
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C115 H115 0.9300 . ?
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N121 C123 H123 124.3 . . ?
C112 C123 H123 124.3 . . ?
O18 N92 O81 123.8(8) . . ?
O18 N92 C107 118.5(8) . . ?
O81 N92 C107 117.7(7) . . ?
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C115 C1# H1 92.8 . . ?
C116 C1# H1 90.0 . . ?
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C107 C108 C109 117.8(6) . . ?
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C108 C109 C112 130.9(7) . . ?
C118 C109 C112 108.1(7) . . ?
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C1# C115 H115 119.2 . . ?
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H11A C116 H11B 109.5 . . ?
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C113 C117 H117 118.3 . . ?
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C110 C107 C108 C109 -1.3(8) . . . . ?
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C107 C108 C109 C112 -178.7(6) . . . . ?
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C118 C109 C112 S1 -175.5(5) . . . . ?
C1 S1 C112 C123 117.2(7) . . . . ?
C1 S1 C112 C109 -68.7(7) . . . . ?
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C1 C113 C117 C1# -1.4(14) . . . . ?
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# **Crystal Structure data of sulfide** 21 (CCDC No. 952234)

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_cell_length_c                  24.4275(12)
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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S2 S 0.39422(7) 0.00199(4) 0.069275(19) 0.0554(2) Uani 1 1 d . . .
O2 O 0.98152(19) 0.73658(14) 0.05839(7) 0.0761(5) Uani 1 1 d . . .
O1 O 0.71061(16) -0.44153(11) 0.19141(5) 0.0575(4) Uani 1 1 d . . .
C1 C 0.8897(3) 0.8276(2) 0.02244(11) 0.0806(7) Uani 1 1 d . . .
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H1 H 0.9456 0.9082 0.0290 0.121 Uiso 1 1 calc R . .
H19 H 0.7678 0.8327 0.0293 0.121 Uiso 1 1 calc R . .
C2 C 0.9175(2) 0.61650(18) 0.05685(8) 0.0538(5) Uani 1 1 d . . .
C3 C 0.7777(2) 0.57398(19) 0.02050(8) 0.0571(5) Uani 1 1 d . . .
H4 H 0.7196 0.6279 -0.0059 0.069 Uiso 1 1 calc R . .
C4 C 0.7236(3) 0.45045(19) 0.02320(8) 0.0587(5) Uani 1 1 d . . .
H5 H 0.6289 0.4216 -0.0017 0.070 Uiso 1 1 calc R . .
C5 C 0.8072(3) 0.36895(17) 0.06215(8) 0.0539(5) Uani 1 1 d . . .
C6 C 0.5713(2) 0.22003(15) 0.10748(7) 0.0450(4) Uani 1 1 d . . .
C7 C 0.4401(2) 0.13278(15) 0.11185(7) 0.0434(4) Uani 1 1 d . . .
C8 C 0.4964(2) -0.12435(15) 0.10909(7) 0.0424(4) Uani 1 1 d . . .
C9 C 0.4144(2) -0.24043(17) 0.10308(8) 0.0506(5) Uani 1 1 d . . .
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C10 C 0.4917(2) -0.34369(16) 0.13037(9) 0.0525(5) Uani 1 1 d . . .
H9 H 0.4371 -0.4219 0.1251 0.063 Uiso 1 1 calc R . .
C11 C 0.6474(2) -0.33308(15) 0.16508(7) 0.0440(4) Uani 1 1 d . . .
C12 C 0.8637(3) -0.4330(2) 0.23129(10) 0.0749(6) Uani 1 1 d . . .
H6 H 0.9606 -0.3979 0.2145 0.112 Uiso 1 1 calc R . .
H7 H 0.8959 -0.5154 0.2452 0.112 Uiso 1 1 calc R . .
H2 H 0.8383 -0.3800 0.2611 0.112 Uiso 1 1 calc R . .
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C15 C 0.3419(2) 0.17603(15) 0.15473(7) 0.0431(4) Uani 1 1 d . . .
C16 C 0.6546(3) -0.11490(16) 0.14317(8) 0.0558(5) Uani 1 1 d . . .
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C18 C 0.1971(3) 0.12831(18) 0.17822(9) 0.0572(5) Uani 1 1 d . . .
H15 H 0.1420 0.0540 0.1653 0.069 Uiso 1 1 calc R . .
C19 C 0.1378(3) 0.1937(2) 0.22085(10) 0.0681(6) Uani 1 1 d . . .

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C20 C 0.2178(3) 0.3057(2) 0.24040(9) 0.0698(6) Uani 1 1 d . . .
H12 H 0.1746 0.3474 0.2694 0.084 Uiso 1 1 calc R . .
C21 C 0.3594(3) 0.35590(18) 0.21764(8) 0.0563(5) Uani 1 1 d . . .
H13 H 0.4121 0.4312 0.2303 0.068 Uiso 1 1 calc R . .
C22 C 0.9514(3) 0.4127(2) 0.09840(9) 0.0617(5) Uani 1 1 d . . .
H18 H 1.0114 0.3588 0.1244 0.074 Uiso 1 1 calc R . .
C23 C 1.0044(3) 0.5358(2) 0.09552(9) 0.0648(6) Uani 1 1 d . . .
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O2 0.0605(9) 0.0582(9) 0.1072(12) 0.0230(8) 0.0021(9) -0.0142(7)
O1 0.0602(8) 0.0366(7) 0.0712(9) 0.0014(6) -0.0085(7) 0.0013(6)
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C3 0.0507(11) 0.0604(12) 0.0600(12) 0.0143(10) 0.0062(9) 0.0031(9)
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C5 0.0520(11) 0.0520(11) 0.0615(12) 0.0056(9) 0.0222(10) -0.0019(9)
C6 0.0554(11) 0.0318(9) 0.0486(10) 0.0024(7) 0.0092(8) 0.0007(7)
C7 0.0525(10) 0.0322(8) 0.0447(10) 0.0035(7) 0.0033(8) -0.0008(7)
C8 0.0516(10) 0.0337(8) 0.0417(9) -0.0035(7) 0.0053(8) -0.0024(7)
C9 0.0459(10) 0.0420(10) 0.0602(11) -0.0033(8) -0.0072(8) -0.0057(8)
C10 0.0516(10) 0.0332(9) 0.0704(12) -0.0035(8) -0.0017(9) -0.0079(7)
C11 0.0487(10) 0.0333(8) 0.0502(10) -0.0022(7) 0.0070(8) -0.0002(7)
C12 0.0784(14) 0.0573(13) 0.0805(15) 0.0087(11) -0.0219(12) 0.0054(11)
N1 0.0561(9) 0.0308(7) 0.0629(10) -0.0030(6) 0.0137(8) -0.0059(6)
C14 0.0524(10) 0.0344(9) 0.0478(10) 0.0056(7) 0.0058(8) 0.0057(7)
C15 0.0501(10) 0.0332(8) 0.0454(9) 0.0080(7) 0.0035(8) 0.0034(7)
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C21 0.0704(13) 0.0423(10) 0.0562(12) -0.0025(8) 0.0082(10) 0.0121(9)
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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
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 and torsion angles; correlations between esds in cell parameters are only
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C6 N1 1.376(2) . ?
C7 C15 1.435(2) . ?
C8 C16 1.372(2) . ?
C8 C9 1.381(2) . ?
C9 C10 1.376(3) . ?
C9 H8 0.9300 . ?
C10 C11 1.366(3) . ?
C10 H9 0.9300 . ?
C11 C17 1.385(2) . ?
C12 H6 0.9600 . ?
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O2 C1 H19 109.5 . . ?
H3 C1 H19 109.5 . . ?
H1 C1 H19 109.5 . . ?
O2 C2 C3 124.72(17) . . ?
O2 C2 C23 115.28(18) . . ?
C3 C2 C23 120.00(18) . . ?
C2 C3 C4 119.56(18) . . ?
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C4 C3 H4 120.2 . . ?
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C5 C4 H5 119.4 . . ?
C3 C4 H5 119.4 . . ?

C4 C5 C22 118.76(18) . . ?
C4 C5 S1 120.07(16) . . ?
C22 C5 S1 121.13(15) . . ?
C7 C6 N1 109.32(15) . . ?
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N1 C6 S1 124.60(13) . . ?
C6 C7 C15 106.68(15) . . ?
C6 C7 S2 125.68(13) . . ?
C15 C7 S2 127.47(13) . . ?
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C16 C8 S2 124.17(13) . . ?
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C14 N1 H16 125.5 . . ?
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C18 C19 C20 121.54(19) . . ?

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C5 C22 C23 C2 -0.5(3) . . . . ?
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