Ruthenium-Catalysed C-H Silylation of Unprotected Gramines, Tryptamines and Their Congeners

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Supporting Information

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1. General Information

Unless otherwise stated, all reactions were performed under an atmosphere of Argon with magnetic stirring. Thin layer chromatography (TLC) was carried out using aluminium-backed plates coated with Kieselgel 60 (0.20 mm, UV 254) and visualized under ultraviolet light (λ = 254 nm) or with $KMnO_4$ staining solution. Purification by column chromatography was performed using Kiesel gel 60 H silica gel (particle size 0.063-0.100 mm).

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Unity 400 MHz (^{1}H 399.5MHz, ^{13}C 100.6, ^{19}F 376 MHz) or Varian Mercury Plus 300 MHz (^{1}H 300.0 MHz, ^{13}C 75.5 MHz) spectrometer at ambient temperature. NMR data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Chemical shifts are reported in ppm and referenced indirectly to tetramethylsilane *via* the residual solvent signals. ^{1}H: $CDCl_3$ at 7.26, DMSO-d_6 at 2.50, C_6D_6 at 7.16 ppm; ^{13}C: $CDCl_3$ at 77.0, DMSO-d_6 at 39.5, C_6D_6 at 128.1 ppm. ^{19}F spectra were recorded on a Varian Unity 400 MHz spectrometer (376 MHz) and calibrated to an external standard of $CFCl_3$ at 0.00 ppm.

High resolution accurate Electron Ionisation (EI) mass spectrometry was performed on a VG Autospec mass spectrometer or, in the case of Electrospray Ionisation (ESI-MS), on a Bruker Daltonics microOTOF II mass spectrometer.

THF was freshly distilled from Na^0/benzophenone and stored over 4Å molecular sieves under Argon. Toluene and 1,4-dioxane were pre-dried over 4Å molecular sieves and stored under Argon prior to use. Unless otherwise stated, all the other reagents, transition metal salts, silanes and norbornene were obtained commercially and used without further purification. The following known gramine derivatives were synthesized using previously reported literature procedures: 1-(benzo[b]thiophen-3-yl)-*N*,*N*-dimethylmethanamine,[1] *N*,*N*-dimethyl-1-(thiophen-3-yl)methanamine,[2] 1-(6-chloro-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine.[3] 3-(1*H*-Indol-3-yl)propan-1-amine was obtained commercially but found to contain water as an impurity. Prior to its use it was dissolved in CH_2Cl_2 (20 mL/g) and dried over $MgSO_4$. The solution was filtered through a glass frit and concentrated under reduced pressure to give the dry starting material.

2. Procedures for the synthesis of new gramines

2a. Method A:

Based on a modified literature procedure.[4]

In a two necked round bottom flask equipped with a magnetic stirring bar, formaldehyde solution 37% wt. in H_2O (1.1 equiv.) was taken up in a mixture of 1,4-dioxane (2.0 mL) and glacial acetic acid (3.5 mL). The mixture was cooled to 0 °C before dimethylamine solution 40% wt. in H_2O (1.1 equiv.) and the indicated indole (1.0 equiv.) were added. The resulting reaction mixture was stirred at 0 °C for 2 h, allowed to warm up to rt and stirred for 20 h. Water (4.0 mL), charcoal (150 mg) and Celite (150 mg) were added and the mixture was stirred for 10 minutes and filtered through a pad of Celite. The filtrate was adjusted to pH 8-9 by addition of aqueous NaOH solution (2N) and then extracted with CH_2Cl_2 (30 mL × 3). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by column chromatography using CH_2Cl_2/MeOH/NH_3 (28% wt. in H_2O) (100:5:1) as the eluent.

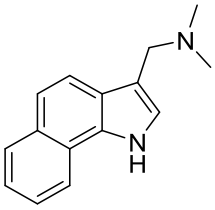
2b. Method B:

Based on a modified literature procedure.[5]

A 20 mL round bottom flask equipped with a magnetic stirring bar under an argon atmosphere, was charged with trimethylamine (2.0 equiv.), EtOH (4.5 mL), dimethylamine hydrochloride (2.0 equiv.), titanium(IV) isopropoxide (2.0 equiv.) and the indicated heteroarene (1.0 equiv.). The reaction was allowed to stir at rt for 10 h. $NaBH_4$ (1.5 equiv.) was added and allowed to stir at rt for 10 h. The reaction was quenched by the addition of aqueous ammonia solution (28% wt. in H_2O, 15 mL) leading to the formation of a thick precipitate. The suspension was filtered through a glass frit and the precipitate was washed with dichloromethane. The filtrate was dried ($MgSO_4$) and concentrated under reduced pressure and purified by column chromatography using CH_2Cl_2/MeOH/NH_3 (28% wt. in H_2O) (100:5:1) as the eluent.

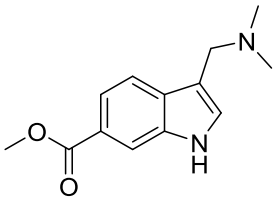
2c. Analytical data for new gramines:

1-(1*H*-benzo[*g*]indol-3-yl)-*N*,*N*-dimethylmethanamine (Method B)



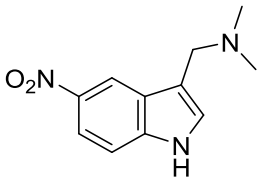
Yield = 0.482 g, 72% (based on 3.0 mmol of 1*H*-benzo-indole-3-carbaldehyde). Colourless solid. R_f = 0.1 (CH_2Cl_2:MeOH:NH_4OH = 10.0:0.5:0.1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.87 (br s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.1, Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.38 (t, J = 8.1Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 3.61 (s, 2H), 2.18 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 130.7, 129.7, 128.3, 125.1, 123.4, 123.3, 122.5, 122.1, 120.6, 119.8, 119.0, 113.6, 54.4, 44.9. HRMS-EI calcd for $C_{15}H_{16}N_2$ $[M]^+$: 224.1313, found 224.1310.

Methyl 3-((dimethylamino)methyl)-1*H*-indole-6-carboxylate (Method A)



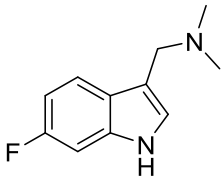
Yield = 0.375 g, 46% (based on 3.5 mmol of methyl 1*H*-indole-6-carboxylate). Colorless solid. R_f = 0.2 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (br s, 1H), 8.08 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 2.1 Hz, 1H), 3.92 (s, 3H), 3.65 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 135.6, 131.4, 127.3, 123.5, 120.5, 118.7, 113.6, 113.3, 54.2, 51.9, 45.2. HRMS-EI calcd for $C_{13}H_{16}N_2O_2$ $[M]^+$: 232.1212, found 232.1216.

***N*,*N*-dimethyl-1-(5-nitro-1*H*-indol-3yl)methanamine (Method A)**



Yield = 0.245 g, 28% (based on 4.0 mmol of 5-nitro-1*H*-indole). Yellow solid. R_f = 0.1 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.66 (br s, 1H), 8.58 (d, J = 1.8 Hz, 1H), 7.98 (dd, J = 9.0, 1.8 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.49 (s, 1H), 3.58 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 140.2, 139.7, 128.1, 126.7, 116.5, 116.4, 114.9, 111.9, 54.2, 44.9. HRMS-ESI calcd for $C_{11}H_{14}N_3O_2$ $[M+H]^+$: 220.1081, found 220.1085.

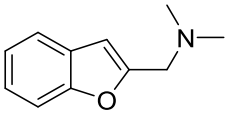
1-(6-fluoro-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (Method A)



Yield = 0.684 g, 59% (based on 6.0 mmol of 6-fluoro-1*H*-indole). Colourless solid. R_f = 0.3 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (br s, 1H), 7.59 (dd, J = 8.6, 5.4 Hz, 1H), 7.05 (d, J = 1.4 Hz, 1H), 6.99 (dd, J = 9.7, 2.1 Hz, 1H), 6.87 (td, J = 9.7, 2.1 Hz, 1H), 3.62 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (d, J_{CF} = 237.3 Hz), 136.1 (d, J_{CF} = 12.4 Hz), 124.4, 124.0 (d, J_{CF} = 3.5 Hz), 119.9 (d, J_{CF} = 10.2 Hz), 113.0, 108.2 (d, J_{CF} = 24.5 Hz), 97.3 (d, J_{CF} =

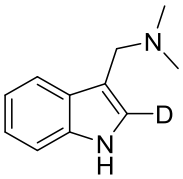
26.0 Hz), 54.4, 45.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –(121.53 – 121.60) (m). HRMS-ESI calcd for $C_{11}H_{14}NO$ $[M+H]^+$: 193.1136, found 193.1135.

1-(benzofuran-2-yl)-*N*,*N*-dimethylmethanamine (Method B)



Yield = 0.046 g, 53% (based on 0.5 mmol benzofuran-2-carbaldehyde). Yellow oil. R_f = 0.8 (CH_2Cl_2:/MeOH = 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.51 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.15 (m, 2H), 6.57 (s, 1H), 3.61 (s, 2H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 155.1, 155.1, 128.3, 123.8, 122.6, 120.6, 111.2, 105.2, 56.4, 45.2. HRMS-EI calcd for $C_{11}H_{13}NO$ $[M]^+$: 175.0997, found 175.0999.

1-(1*H*-indol-3-yl-2-deutero)-*N*,*N*-dimethylmethanamine (Method A)

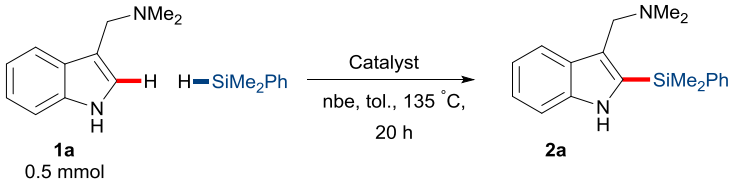


Yield = 0.639 g, 73% (based on 5.0 mmol of 2-deutero-1*H*-indole). Colourless solid. R_f = 0.2 (CH_2Cl_2/MeOH/NH_4OH = 10.0:0.5:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.21 (br s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 3.72 (s, 2H), 2.37 (s, 6H). *δ*. ^{13}C NMR (100 MHz, CDCl3): *δ* 136.1, 127.8, 123.9 (t), 121.6, 119.3, 118.9, 112.2, 111.2, 54.2, 45.1. HRMS-EI calcd for $C_{11}H_{13}DN_2$ $[M]^+$: 175.1220, found 175.1223.

3. Silylation of heteroarenes

3a. Reaction Optimisation

Table S1. Optimisation using gramine.



Entry	Catalyst (mol%)	equiv. silane	equiv. nbe	yield (%)
1[a]	$[Ir(\mu\text{-}OMe)COD]_2$ (5)	3	3	0
2	$RhCl(PPh_3)_3$ (5)	5	5	0 (34)[b]
3	$Ru_3(CO)_{12}$ (5)	5	5	0
4	$RuH_2(PPh_3)_4$ (5)	5	5	56
5	$RuH_2(CO)(PPh_3)_3$ (5)	3	3	62
6	$RuH_2(CO)(PPh_3)_3$ (5)	5	5	85 (83)[c]
7	$RuH_2(CO)(PPh_3)_3$ (2.5)	5	5	71
8[d]	$RuH_2(CO)(PPh_3)_3$ (2.5)	5	5	78
9[e]	$RuH_2(CO)(PPh_3)_3$ (5)	5	0	traces

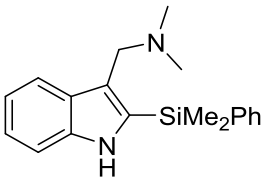
[a] 4,4'-di-*tert*-butylbipyridine ligand (10 mol%), THF, 80 °C, 24 h. [b] 3-Methylindole formed in 34% yield. [c] 3 g (17.2 mmol) scale of **1a**. [d] Reaction time = 16 h. [e] Reaction performed under air in refluent xylene as solvent.

3b. General procedure for silylation reaction

A reaction tube equipped with a Young's tap and a magnetic stirring bar was charged with the appropriate heteroarene substrate (0.5 mmol), $RuH_2(CO)(PPh_3)_3$ (0.023 g, 0.025 mmol) and then evacuated and backfilled with Argon three times. Under a positive flow of Argon, norbornene (0.235 g, 2.5 mmol), toluene (0.25 mL) and hydrosilane (2.5 mmol) were added. Unless indicated otherwise, the reaction mixture was heated for 20 h at 135 °C, cooled to rt and purified directly by silica gel chromatography using the listed solvent system.

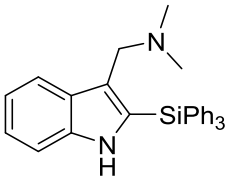
3c. Analytical data for new silylated compounds

1-(2-(dimethyl(phenyl)silyl)-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (2a)



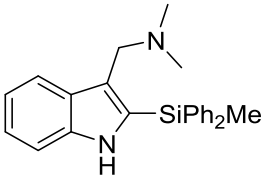
Yield = 0.131 g, 85%. Brown oil, solidifies on standing. R_f = 0.5 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (br s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.53 – 7.43 (m, 3H), 7.32 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.0, 7.5 Hz, 1H), 7.14 (dd, J = 8.0, 7.5 Hz, 1H), 3.65 (s, 2H), 2.23 (s, 6H), 0.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.3, 134.2, 133.2, 129.5, 129.2, 128.1, 123.8, 122.3, 119.7, 119.2, 110.7, 55.2, 45.3, -1.9. HRMS-EI calcd for $C_{19}H_{24}N_2Si$ $[M]^+$: 308.1712, found 308.1709.

***N*,*N*-dimethyl-1-(2-(triphenylsilyl)-1*H*-indol-3-yl)methanamine (2b)**



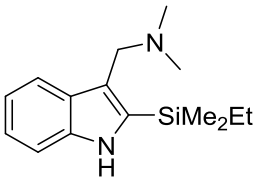
Yield = 0.192 g, 89%. Colourless solid. R_f = 0.5 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.9 Hz, 1H), 7.98 (br s, 1H), 7.66 (d, J = 6.9 Hz, 6H), 7.48 (t, J = 7.2 Hz, 3H), 7.42 (dd, J = 7.2, 6.9 Hz, 6H), 7.30 (d, J = 8.2 Hz, 1H), 7.21 (dd, J = 8.2, 7.5 Hz, 1H), 7.15 (dd, J = 7.9, 7.5 Hz, 1H) 3.56 (s, 2H), 1.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 136.2, 136.0, 133.0, 130.2, 128.9, 128.6, 128.3, 123.2, 120.7, 120.0, 111.0, 54.7, 44.2. HRMS-EI calcd for $C_{29}H_{28}N_2Si$ $[M]^+$: 432.2022, found 432:2025.

***N*,*N*-dimethyl-1-(2-(methyldiphenylsilyl)-1*H*-indol-3-yl)methanamine (2c)**



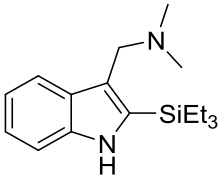
Yield = 0.152 g, 82%. Pale yellow solid. R_f = 0.3 (CH_2Cl_2/MeOH = 20.0:1.0). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (br s, 1H), 7.88 – 7.85 (m, 1H), 7.63 – 7.59 (m, 4H), 7.48 – 7.40 (m, 6H), 7.33 – 7.28 (m, 1H), 7.23 – 7.11 (m, 2H), 3.59 (s, 2H), 2.08 (s, 6H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 135.3, 135.0, 131.7, 129.7, 129.0, 128.1, 128.1, 122.6, 119.9, 119.5, 110.9, 54.9, 44.8, -3.0. HRMS-EI calcd for $C_{24}H_{26}N_2Si$ $[M]^+$: 370.1865, found: 370.1867.

1-(2-(ethyldimethylsilyl)-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (2d)



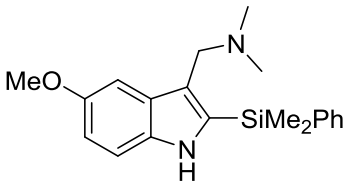
Yield = 0.095 g, 73%. Pale yellow solid. R_f = 0.4 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (br s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.20 (dd, J = 8.1, 7.4 Hz, 1H), 7.13 (dd, J = 7.9, 7.4 Hz, 1H), 3.78 (s, 2H), 2.34 (s, 6H), 1.04 – 1.00 (m, 3H), 0.93 – 0.87 (m, 2H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 135.1, 129.0, 122.2, 121.2, 119.5, 119.3, 110.8, 54.9, 44.9, 7.6, 7.3, -2.9. HRMS-EI calcd for $C_{15}H_{24}N_2Si$ $[M]^+$: 260.1709, found 260.1714.

_N,N_-dimethyl-1-(2-(triethylsilyl)-1_H_-indol-3-yl)methanamine (2e)



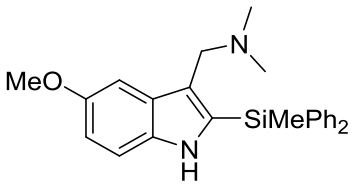
Yield = 0.072 g, 50%. Pale brown solid. R_f = 0.3 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (br s, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.20 (dd, J = 8.1, 7.6 Hz, 1H), 7.12 (dd, J = 7.9, 7.6 Hz, 1H), 3.79 (s, 2H), 2.34 (s, 6H), 1.4 - 1.0 (m, 9H), 0.98 - 0.94 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 133.7, 129.0, 122.2, 121.4, 119.7, 119.3, 110.7, 55.1, 44.8, 7.4, 3.6. HRMS-ESI calcd for $C_{17}H_{29}N_2Si$ $[M+H]^+$: 289.2095, found 289.2084.

1-(2-(dimethyl(phenyl)silyl)-5-methoxy-1_H_-indol-3-yl)-_N,N_-dimethylmethanamine (2j)



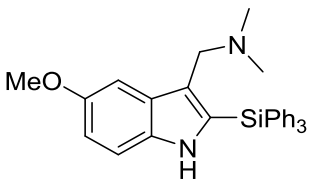
Yield = 0.083 g, 49% Colourless solid. The yield could be improved to 0.101 g (60%) using 6 mol% of $RuH_2(CO)(PPh_3)_3$. R_f = 0.2 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (br s, 1H), 7.60 (d, J = 6.2 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.34 (s, 1H), 7.21 (d, J = 8.8 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 2H), 2.22 (s, 6H), 0.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 136.8, 134.2, 133.4, 129.8, 129.1, 128.2, 113.6, 111.6, 100.9, 76.5, 56.1, 54.4, 44.1, -1.9. HRMS-EI calcd for $C_{20}H_{26}N_2OSi$ $[M]^+$: 338.1814, found 338.1808.

1-(5-methoxy-2-(methyldiphenylsilyl)-1_H_-indol-3-yl)-_N,N_-dimethylmethanamine (2k)



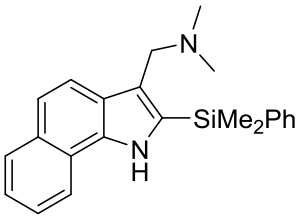
Yield = 0.140 g, 70%. Colourless solid. R_f = 0.3 (CH_2Cl_2/MeOH = 20.0:1.0). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (br s, 1H), 7.60 – 7.58 (m, 4H), 7.47 – 7.39 (m, 6H), 7.28 (s, 1H), 7.17 (d, J = 8.8 Hz, 1H), 6.87 (ddd, J = 8.8, 2.4, 0.7 Hz, 1H), 3.89 (s, 3H), 3.49 (s, 2H), 2.04 (s, 6H), 0.98 – 0.97 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 135.5, 135.0, 134.3, 133.7, 132.1, 129.6, 129.5, 128.1, 113.3, 111.5, 101.2, 55.9, 55.2, 45.0, -3.1. HRMS-EI calcd for $C_{25}H_{28}N_2OSi$ $[M]^+$: 400.1971, found 400.1982.

1-(5-methoxy-2-(triphenylsilyl)-1_H_-indol-3-yl)-_N,N_-dimethylmethanamine (2l)



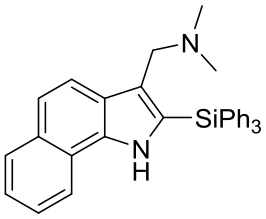
Yield = 0.208 g. 90%. Yellow solid. R_f = 0.4 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (br s, 1H), 7.75 – 7.69 (m, 6H), 7.54 – 7.40 (m, 10H), 7.21 (d, J = 8.8 Hz, 1H), 6.92 (dd, J = 8.8, 2.5 Hz, 1H), 3.91 (s, 3H), 3.44 (s, 2H), 1.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 136.2, 134.0, 133.4, 129.9, 129.6, 128.1, 113.6, 111.5, 101.9, 55.9, 55.5, 44.9. HRMS-EI calcd for $C_{30}H_{31}N_2OSi$ $[M^+]$: 463.2200, found 463.2200.

1-(2-(dimethyl(phenyl)silyl)-1*H*-benzo[*g*]indol-3-yl)-*N*,*N*-dimethylmethanamine (2m)



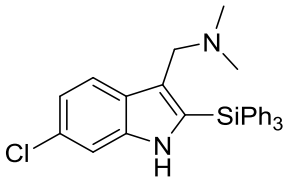
Yield = 0.066 g, 37%. Colourless solid. R_f = 0.4 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (br s, 1H), 7.97 – 7.84 (m, 3H), 7.73 – 7.64 (m, 2H), 7.53 – 7.38 (m, 6H), 3.69 (s, 2H), 2.23 (s, 6H), 0.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 134.2, 132.9, 131.4, 130.7, 129.6, 128.8, 128.1, 127.8, 125.2, 125.2, 124.0, 121.5, 120.3, 119.7, 119.4, 55.2, 45.2, -1.8. HRMS-EI calcd for $C_{23}H_{26}N_2Si$ $[M]^+$: 358.1865, found: 358.1861.

***N*,*N*-dimethyl-1-(2-(triphenylsilyl)-1*H*-benzo[*g*]indol-3-yl)methanamine (2n)**



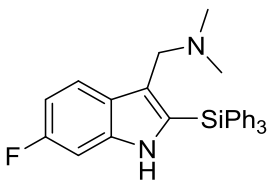
Yield = 0.126 g, 88% (based on 0.3 mmol 1*H*-benzo[*g*]indol-3-yl-*N*,*N*-dimethylmethanamine). Colourless solid. R_f = 0.5 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (br s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.92 (dd, J = 7.5, 1.6 Hz, 1H), 7.75 (dd, 7.5, 1.2 Hz, 1H), 7.72 – 7.70 (m, 6H), 7.54 – 7.41 (m, 12H), 3.57 (s, 2H), 1.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 135.9, 133.9, 133.1, 131.0, 130.2, 128.8, 128.6, 128.3, 125.4, 125.1, 124.5, 121.3, 120.9, 120.3, 119.4, 54.8, 44.2. HRMS-ESI calcd for $C_{33}H_{31}N_2Si$ $[M+H]^+$: 483.2251, found 483.2245.

1-(6-chloro-2-(triphenylsilyl)-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (2o)



Yield = 0.117 g, 50%. Colourless solid. R_f = 0.3 (CH_2Cl_2/MeOH = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.68 (dd, J = 7.8, 1.2 Hz, 6H), 7.52 – 7.42 (m, 9H), 7.29 (d, J = 1.6 Hz, 1H), 7.11 (dd, J = 8.5, 1.6 Hz, 1H), 3.51 (s, 2H), 1.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.2, 135.0, 132.8, 130.2, 129.1, 128.3, 127.8, 127.5, 121.7, 120.5, 110.8, 54.9, 44.4. HRMS-EI calcd for $C_{29}H_{27}N_2SiCl$ $[M]^+$: 466.1632, found: 466.1639.

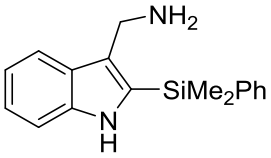
1-(6-fluoro-2-(triphenylsilyl)-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (2p)



Yield = 0.106 g, 47%. Yellow solid. R_f = 0.3 (CH_2Cl_2/MeOH = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.91 (m, 2H), 7.68 (dd, J = 7.9, 1.3 Hz, 6H), 7.52 – 7.41 (m, 9H), 6.97 (dd, J = 9.5, 2.1 Hz, 1H), 6.91 (dt, J = 9.5, 2.1 Hz, 1H), 3.50 (s, 2H), 1.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d,

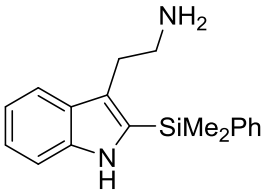
J_{CF} = 239.6 Hz), 138.6 (d, J_{CF} = 12.3 Hz), 136.2, 133.0, 130.1, 128.2, 125.7, 121.8 (d, J_{CF} = 10.2 Hz), 108.7 (d, J_{CF} = 24.5 Hz), 97.0 (d, J_{CF} = 25.8 Hz), 55.1, 44.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.9 (broad). HRMS-EI calcd for $C_{29}H_{27}N_2SiF$ $[M]^+$: 450.1928, found: 450.1934.

(2-(dimethyl(phenyl)silyl)-1*H*-indol-3-yl)methanamine (3)



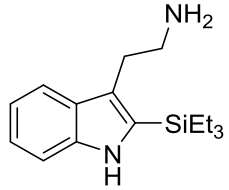
Yield = 0.112 g, 80%. Colourless solid. R_f = 0.5 (CH_2Cl_2:MeOH = 20.0:1.0). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br s, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.48 – 7.37 (m, 3H), 7.32 (d, J = 8.1 Hz, 1H), 7.19 (dd, J = 8.1, 7.6 Hz, 1H), 7.12 (dd, J = 7.9, 7.6 Hz, 1H), 4.02 (s, 2H), 1.49 (s, 2H), 0.68 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 136.8, 134.0, 132.0, 129.8, 128.2, 128.0, 127.6, 122.6, 119.5, 118.6, 111.0, 37.6, -1.7. HRMS-EI calcd for $C_{17}H_{20}N_2Si$ $[M]^+$: 280.1396, found 280.1392.

2-(2-(dimethyl(phenyl)silyl)-1*H*-indol-3-yl)ethan-1-amine (4a)



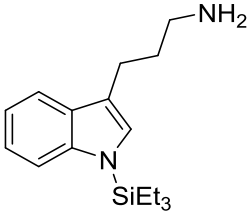
Yield = 0.118 g, 79%. Pale yellow solid. R_f = 0.5 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br s, 1H), 7.66 – 7.56 (m, 3H), 7.48 – 7.36 (m, 3H), 7.30 (d, J = 8.1 Hz, 1H), 7.17 (dd, J = 8.1, 7.5 Hz, 1H), 7.08 (dd, J = 7.9, 7.5 Hz, 1H), 2.94 (s, 4H), 1.79 (s, 2H), 0.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 137.0, 134.2, 132.1, 129.8, 128.9, 128.2, 123.2, 122.5, 119.3, 119.1, 111.0, 43.4, 30.3, -1.6. HRMS-EI calcd for $C_{18}H_{22}N_2Si$ $[M]^+$: 294.1552, found 294.1554.

2-(2-(triethylsilyl)-1*H*-indol-3-yl)ethan-1-amine (4b)



Yield = 0.129 g, 93%. Pale yellow solid. R_f = 0.4 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.17 (dd, J = 8.1, 7.4 Hz, 1H), 7.08 (dd, J = 7.9, 7.4 Hz, 1H), 3.03 (s, 4H), 2.23 (s, 2H), 1.05 – 0.96 (m, 9H), 0.94 – 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 131.6, 128.9, 123.0, 122.2, 119.0, 118.9, 110.8, 43.7, 30.6, 7.4, 3.8. HRMS-EI calcd for $C_{16}H_{26}N_2Si$ $[M]^+$: 274.1865, found: 274:1866.

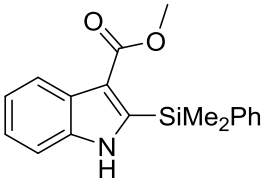
3-(1-(triethylsilyl)-1*H*-indol-3-yl)propan-1-amine (5)



Yield = 0.043 g, 30%. Yellow oil, darkens quickly upon standing. R_f = 0.3 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.20 – 7.07 (m, 2H), 7.02 (s, 1H), 6.85 (s, 2H), 2.96 (s, 2H), 2.85 (t, J = 7.2 Hz, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.03 (t, J = 7.3 Hz, 6H), 1.00 – 0.91 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

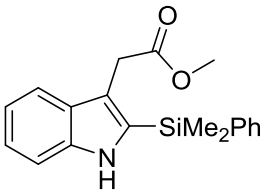
140.9, 130.7, 127.8, 121.4, 119.4, 118.8, 116.1, 112.9, 39.9, 29.1, 22.2, 6.7, 4.3. HRMS-EI calcd for $C_{17}H_{29}N_2Si$ $[M]^+$: 289.2095, found 289.2093.

Methyl 2-(dimethyl(phenyl)silyl)-1*H*-indole-3-carboxylate (6)



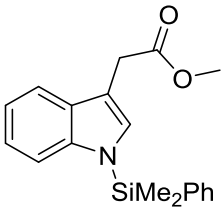
Yield = 0.033 g, 21%. Colourless solid. R_f = 0.5 (petroleum ether/EtOAc = 10:1). ^{1}H NMR (400 MHz, C_6D_6): δ 8.52 (app. d, J = 8.1 Hz, 1H, ^{4}J is not resolved), 7.84 (br s, 1H), 7.53 – 7.45 (m, 2H), 7.28 – 7.18 (m, 4H), 7.09 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 6.61 (app. d, J = 8.2 Hz, 1H, ^{4}J is not resolved), 3.56 (s, 3H), 0.73 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ 166.6, 145.2, 138.4, 137.2, 134.9, 130.1, 128.7, 128.2, 123.5, 122.5, 122.3, 117.2, 111.7, 50.6, -2.9. HRMS-EI calcd for $C_{18}H_{19}NO_2Si$ $[M]^+$: 309.1185, found 309.1196.

Methyl 2-(2-(dimethyl(phenyl)silyl)-1*H*-indol-3-yl)acetate (7)



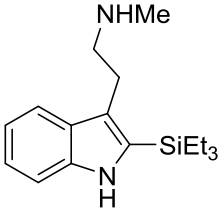
Yield = 0.062 g, 38%. Pale yellow solid. R_f = 0.4 (petroleum ether/EtOAc = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (br s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.49 – 7.39 (m, 3H), 7.31 (d, J = 8.1 Hz, 1H), 7.19 (dd, J = 8.1, 7.4 Hz, 1H), 7.12 (dd, J = 7.9, 7.4 Hz, 1H), 3.78 (s, 2H), 3.61 (s, 3H), 0.67 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 138.1, 136.4, 134.2, 133.1, 129.8, 128.8, 128.2, 122.7, 119.7, 119.1, 117.9, 111.0, 51.8, 31.9, -1.9. HRMS-EI calcd for $C_{19}H_{21}NO_2Si$ $[M]^+$: 323.1342, found 323.1335.

Methyl 2-(1-(dimethyl(phenyl)silyl)-1*H*-indol-3-yl)acetate (7')



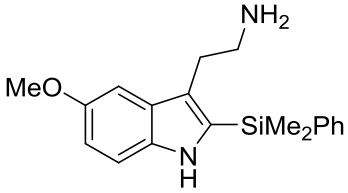
Yield = 0.039 g, 24%. Pale yellow solid. R_f = 0.5 (petroleum ether/EtOAc = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J = 7.8 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.36 (m, 3H), 7.22 (d, J = 8.0 Hz, 1H), 7.17 – 7.03 (m, 3H), 3.77 (s, 2H), 3.71 (s, 3H), 0.79 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 140.6, 135.2, 133.8, 130.9, 130.3, 129.2, 128.2, 121.7, 119.9, 119.0, 113.5, 110.6, 51.9, 31.3, -1.4. HRMS-EI calcd for $C_{19}H_{21}NO_2Si$ $[M]^+$: 323.1342, found 323.1346.

***N*-methyl-2-(2-(triethylsilyl)-1*H*-indol-3-yl)ethan-1-amine (10)**



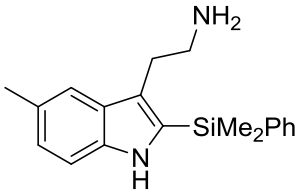
Yield = 0.744 g, 58%. (based on 4.5 mmol of 2-(1*H*-indol-3-yl)-*N*-methylethan-1-amine, 10 equiv. of $HSiEt_3$ used). Brown solid. R_f = 0.4 (CH_2Cl_2:MeOH:NH_4OH = 10.0:1.0:0.1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (br s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.13 – 7.05 (m, 1H), 3.06 (t, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.49 (s, 3H), 1.92 (s, 1H), 1.03 – 0.99 (m, 9H), 0.95 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 131.4, 128.7, 122.8, 122.1, 119.0, 118.8, 110.7, 53.2, 36.0, 26.3, 7.4, 3.7. HRMS-ESI calcd for $C_{17}H_{28}N_2Si$ $[MH]^+$: 289.2100, found 289.2093.

2-(2-(dimethyl(phenyl)silyl)-5-methoxy-1*H*-indol-3-yl)ethan-1-amine (11a)



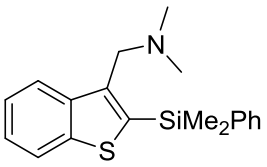
Yield = 0.123 g, 76%. Pale solid. R_f = 0.2 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (br s, 1H), 7.63 – 7.55 (m, 2H), 7.45 – 7.34 (m, 3H), 7.18 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.83 (dd, J = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H), 3.21 (br s, 2H), 3.08 – 2.80 (m, 4H), 0.66 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 136.7, 134.1, 133.6, 133.2, 129.8, 129.1, 128.2, 121.8, 113.3, 111.7, 100.3, 56.0, 42.6, 28.8, -1.7. HRMS-ESI calcd for $C_{19}H_{25}N_2OSi$ $[M+H^+]$: 325.1731, found 325.1718.

2-(2-(dimethyl(phenyl)silyl)-5-methyl-1*H*-indol-3-yl)ethan-1-amine (11b)



Yield = 0.096 g, 62%. Pale solid. R_f = 0.3 (CH_2Cl_2/MeOH/NH_4OH = 10.0:1.0:0.1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (br s, 1H), 7.66 – 7.57 (m, 2H), 7.50 – 7.37 (m, 4H), 7.21 (dd, J = 8.3, 1.0 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 2.93 (s, 4H), 2.46 (s, 3H), 1.45 (br s, 2H), 0.68 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.7, 134.1, 132.0, 129.6, 129.1, 128.4, 128.1, 124.2, 122.8, 118.5, 110.6, 43.5, 30.5, 21.4, -1.6. HRMS-ESI calcd for $C_{19}H_{25}N_2Si$ $[M+H^+]$: 309.1782, found 309.1771.

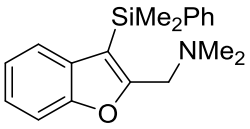
1-(2-(dimethyl(phenyl)silyl)benzo[b]thiophen-3-yl)-*N*,*N*-dimethylmethanamine (12)



Yield = 0.124 g, 76%. Brown oil. R_f = 0.4 (CH_2Cl_2/MeOH = 100:1). ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.02 (m, 1H), 7.96 – 7.82 (m, 1H), 7.69 – 7.57 (m, 2H), 7.46 – 7.31 (m, 5H), 3.57 (s, 2H), 2.05 (s, 6H), 0.78 – 0.68 (m, 6H).

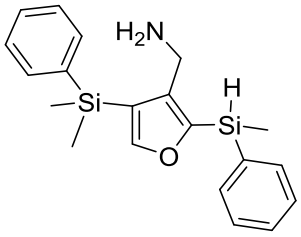
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.9, 141.5, 138.0, 136.4, 134.0, 129.2, 127.7, 124.2, 123.6, 123.1, 122.0, 57.4, 45.0, -0.8. HRMS-ESI calcd for $C_{19}H_{24}NSSi$ $[M+H]^+$: 326.1393, found 326.1394.

1-(3-(dimethyl(phenyl)silyl)benzofuran-2-yl)-*N*,*N*-dimethylmethanamine (13)



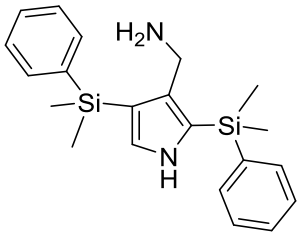
Yield = 0.039 g, 25%. Brown oil. R_f = 0.4 (CH_2Cl_2/MeOH = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.2, 7.3 Hz, 4H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 3.48 (s, 2H), 2.22 (s, 6H), 0.66 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 138.2, 134.2, 134.1, 132.7, 129.5, 128.6, 128.1, 124.0, 122.5, 122.3, 111.2, 56.1, 45.2, -0.5. HRMS-ESI calcd for $C_{19}H_{24}NOSi$ $[M+H]^+$: 310.1622, found 310.1616.

1-(2,4-bis(dimethyl(phenyl)silyl)furan-3-yl)-*N*,*N*-dimethylmethanamine (14a)



Yield = 0.084 g, 46%. Brown oil. R_f = 0.4 (CH_2Cl_2/MeOH = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 4H), 7.50 (s, 1H), 7.38 – 7.35 (m, 6H), 3.41 (s, 2H), 1.62 (s, 2H), 0.59 (s, 6H), 0.54 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 138.3, 133.9, 133.9, 133.8, 129.5, 129.4, 128.1, 128.0, 127.9, 127.9, 117.3, 37.3, -1.7, -2.3. HRMS-EI: calcd for $C_{20}H_{25}NOSi_2$ (17a-CH_3) $[M+H]^+$: 351.1475, found 351.1437

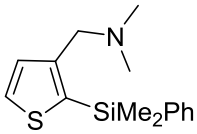
1-(2,4-bis(dimethyl(phenyl)silyl)pyrrol-3-yl)-*N*,*N*-dimethylmethanamine (14b)



Yield = 0.080 g, 43%. Brown solid. R_f = 0.4 (CH_2Cl_2/MeOH = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.59 – 7.55 (m, 4H), 7.43 – 7.36 (m, 3H), 7.36 – 7.32 (m, 3H), 6.85 (d, *J* = 2.5 Hz, 1H), 3.61 (s, 2H), 1.22 (s, 2H), 0.58 (s, 6H), 0.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 139.9, 137.5, 134.0, 133.9, 129.5, 129.3, 128.9, 128.1, 127.8, 127.0, 116.0, 39.6, -1.2, -1.5. HRMS-EI calcd for $C_{21}H_{28}N_2Si_2$ $[M+H]^+$: 365.1791, found 365.1797.

The reaction of *N*,*N*-dimethyl-1-(thiophen-3-yl)methanamine with dimethylphenylsilane gave a separable mixture of mono- and disilylated products, **15a** and **15b**:

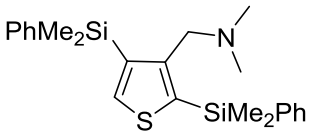
1-(2-(dimethyl(phenyl)silyl)thiophen-3-yl)-*N*,*N*-dimethylmethanamine (15a)



Yield = 0.054 g, 39%. Brown oil. R_f = 0.4 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.49 (m, 3H), 7.41 – 7.28 (m, 4H), 3.35 (s, 2H), 2.03 (s,

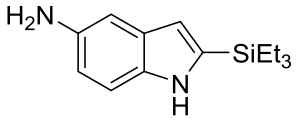
6H), 0.64 – 0.59 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 134.0, 130.8, 130.3, 129.2, 128.8, 127.7, 127.6, 58.7, 44.7, -1.0. HRMS-CI calcd for $C_{15}H_{22}NSSi$ $[M+H]^+$: 276.1242, found 276.1241.

1-(2,4-bis(dimethyl(phenyl)silyl)thiophen-3-yl)-*N*,*N*-dimethylmethanamine (15b)



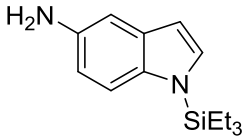
Yield = 0.111 g, 54%. Brown oil. R_f = 0.6 (CH_2Cl_2/MeOH = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.50 (m, 4H), 7.42 – 7.30 (m, 7H), 3.29 (s, 2H), 1.99 (s, 6H), 0.61 (s, 6H), 0.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 139.9, 138.8, 138.2, 138.0, 134.0, 133.9, 130.9, 129.2, 129.1, 127.8, 127.7, 58.9, 45.1, -0.9, -1.2. HRMS-CI calcd for $C_{23}H_{32}NSSi_2$ $[M+H]^+$: 410.1794, found 410.1791.

2-(triethylsilyl)-1*H*-indol-5-amine (16c)



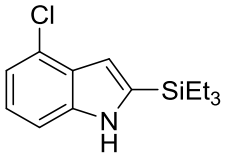
Yield = 0.081 g, 33% (based on 1.0 mmol of 1*H*-indol-5-amine). Pale brown solid. R_f = 0.3 (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (br s, 1H), 7.21 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.69 (dd, J = 8.5, 2.2 Hz, 1H), 6.59 -6.58 (br m, 1H), 3.65 (br s, 2H), 1.08 – 0.98 (m, 9H), 0.92 – 0.77 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.1, 133.8, 129.5, 113.3, 111.2, 111.1, 105.2, 7.4, 3.5. HRMS-EI calcd for $C_{30}H_{31}N_2OSi$ $[M^+]$: 246.1552, found 246.1555.

1-(triethylsilyl)-1*H*-indol-5-amine (16c')



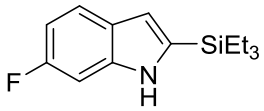
Yield = 0.054 g, 22% (based on 1.0 mmol of 1*H*-indol-5-amine). Pale yellow oil. R_f = 0.5 (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 3.1 Hz, 1H), 7.01 (dd, J = 2.3, 0.9 Hz, 1H), 6.68 (dd, J = 8.6, 2.3 Hz, 1H), 6.45 (dd, J = 3.1, 0.9 Hz, 1H), 3.97 (br s, 2H), 1.07 – 0.95 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 135.3, 132.3, 131.0, 113.2, 112.2, 106.2, 103.7, 6.7, 4.2. HRMS-EI calcd for $C_{30}H_{31}N_2OSi$ $[M^+]$: 246.1552, found 246.1559.

4-chloro-2-(triethylsilyl)-1*H*-indole (16e)



Yield = 0.081 g, 40% (based on 1.0 mmol of 4-chloro-1*H*-indole). Pale brown oil. R_f = 0.5 (petroleum ether/EtOAc = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (br s, 1H), 7.32 –7.30 (m,1H), 7.15 – 7.06 (m, 2H), 6.86- 6.85 (m, 1H), 1.08 – 1.04 (m, 9H), 0.91-0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 136.7, 127.5, 125.7, 122.6, 119.2, 110.6, 109.4, 7.4, 3.5. HRMS-EI calcd for $C_{30}H_{31}N_2OSi$ $[M^+]$: 260.1054, found 260.1060.

6-Fluoro-2-(triethylsilyl)-1*H*-indole (16f)

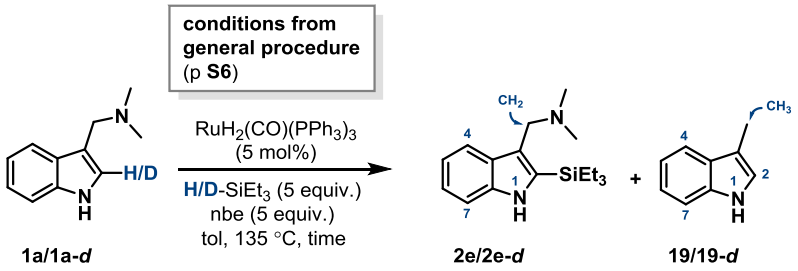


Yield = 0.131 g, 53% (based on 1.0 mmol of 6-fluoro-1*H*-indole). Yellow oil. R_f = 0.5 (petroleum ether/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (br s, 1H), 7.52 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.08 (dd, *J* = 9.6, 2.2 Hz, 2H), 6.87 (ddd, J = 9.6, 8.6, 2.2 Hz, 1H), 6.71 (d, *J* = 2.1), 1.03 (t, *J* = 7.9 Hz, 9H), 0.84 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, J_{CF} = 239.4 Hz), 138.6 (d, J_{CF} = 12.4 Hz), 136.2 (d, J_{CF} = 3.51 Hz), 125.3, 121.0 (d, J_{CF} = 10.3 Hz), 112.3, 108.3 (d, J_{CF} = 24.7 Hz), 96.0 (d, J_{CF} = 25.0 Hz), 7.4, 3.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -121.3. HRMS-EI calcd for $C_{14}H_{20}NFSi$ [M^+]: 249.1349, found 249.1348.

3d. Mechanistic experiments

3d.i. C-H/D exchange using gramines and silanes

The following experiments were performed under the general silylation conditions described on page S6. The extent of deuterium incorporation at the N1-H, C4-H and C7-H positions was determined by ^{1}H NMR spectroscopy ($CDCl_3$) for the silylation product **2e** and skatole. Skatole formation occurs as a result of gramine decomposition in a pathway competing with the silylation reaction. C2-Silylated skatole was not detected under these reaction conditions.

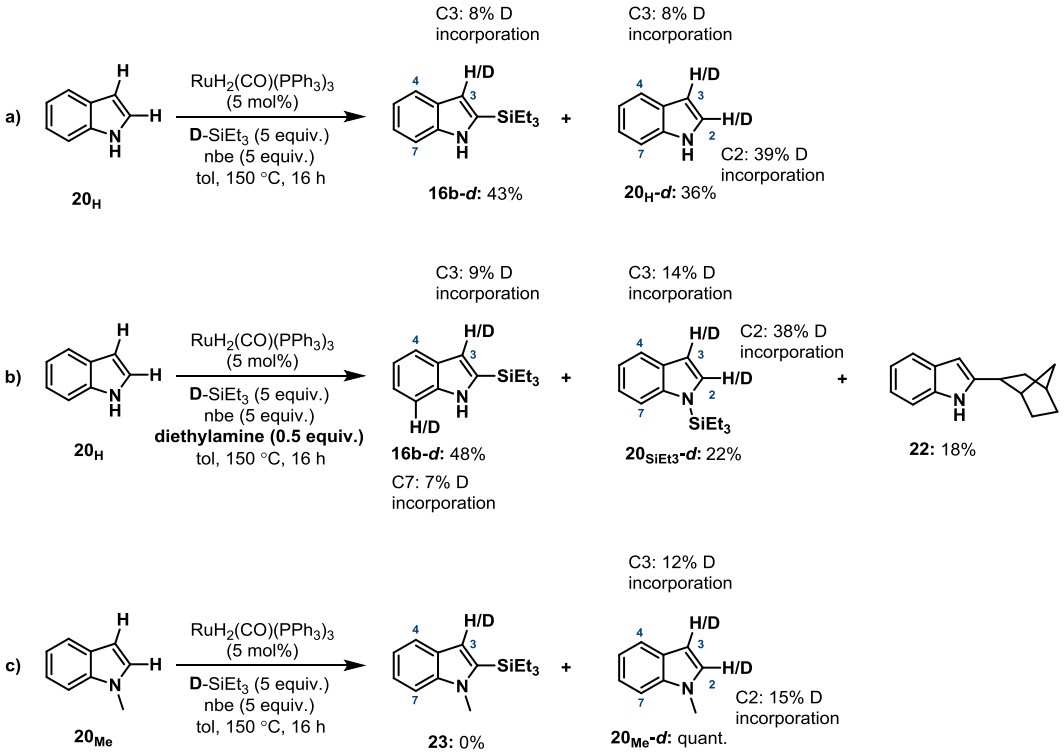


	H/D-Gramine	H/D-$SiEt_3$	Silylation product						Skatole						Other
			yield[a]	*C7-D*	*C4-D*	*N-D*	*CH_2*[b]	*NMe_2*[b]	*yield*[a]	*C7-D*	*C4-D*	*C2-D*	*N-D*	*CH_3*[b]	
1	H	**D**	66%	3%	19%	13%	1.84	6.01	32%	11%	17%	29%	16%	1.95	· *Et_3Si-$SiEt_3$* · *intractable mixture of indole related compounds*
2	**D**	H	22%	5%	15%	20%	1.78	5.73	54%	6%	17%	72%	13%	2.50	· *Et_3Si-$SiEt_3$* · *intractable mixture of indole related compounds*
3	**D**	H	18%	5%	9%	10%	1.60	4.96	55%	9%	16%	69%	15%	2.66	
4	**D**	**D**	17%	8%	40%	13%	1.62	5.44	30%	11%	15%	79%	17%	2.02	· *Et_3Si-$SiEt_3$* · *intractable mixture of indole related compounds*
5[c]	**D**	-	-	-	-	-	-	-	52%	3%	6%	80%	10%	2.97	· *intractable mixture of indole related compounds* · *C2-D-arundine*[6] *detected.*[d]

Table S2: Overview H/D-exchange experiments with Deuterium labelled substrates. The deuterium incorporation at the indicated positions of the reaction products are given in percent. [a]Isolated yield. [b]Integral of resonance corresponding to the indicated group relative to C5-H and C6-H signals. [c]Reaction time 3 h. [d]Detected by ^{1}H NMR[6] and EI-MS.

3d.ii. C-H/D exchange experiments using indoles and silanes

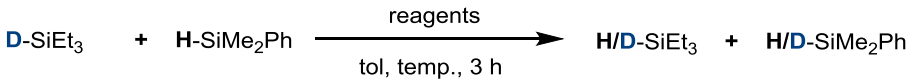
A reaction between the respective indole substrate (0.5 mmol) and D-$SiEt_3$ (0.293 g, 2.5 mmol) was performed in accordance with the general procedure for silylation reactions (p. S6), except that the reaction temperature was 150 °C and the reaction time was 16 h. The crude reaction mixture was purified directly by column chromatography (solvent gradient EtOAc/PE 1:40 to 1:20). The extent of deuterium incorporation in the products was determined by ^{1}H NMR ($CDCl_3$). The reaction mass balance was composed of intractable indole-containing by-products and Et_3Si-$SiEt_3$ (0.150 g). In the case of (b), a C2-alkylation product (**22**) was also isolated in 18% yield.



Scheme S1: C-H/D-exchange experiments using indole substrates and D-$SiEt_3$. The deuterium incorporation at the indicated positions of the reaction products are given in percent relative to the C5-H and C6-H signals. All yields correspond to the isolated products.

3d.iii Si-H/D crossover experiments

The following experiments were performed in pre-dried microwave vials under argon atmosphere. The vial was charged with $RuH_2(CO)(PPh_3)_3$ (0.008 mmol, 7.3 mg) and then evacuated and backfilled with argon three times. Norbornene (if appropriate), deutero-triethylsilane (19 mg, 0.16 mmol) and dimethylphenyl hydrosilane (22 mg, 0.16 mmol) were added. The vial was sealed and the reaction mixture was kept at the indicated temperature (pre-warmed heating bath) for 3 h. The vial was quickly cooled on ice, opened and the crude mixture was diluted with $CDCl_3$ and directly analyzed by NMR. The extent of deuterium incorporation into both silanes was determined by ^{1}H NMR spectroscopy.



	Ru [equiv]	norbornene [equiv]	Temp. [°C]	Deuterium incorporation[a]	
				D-SiMe$_2$Ph	D-SiEt$_3$
1[b]	0.05	0.05	135	58%	42%
2[c]	0.05	-	135	65%	35%
3	-	-	135	0%	100%
4	0.05	-	50	45%	55%
5	0.05	-	rt	19%	81%

Table S3: Deuterium exchange among silanes. [a] The deuterium incorporation into both silanes was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [b] $(Me_2PhSi)_2$ was detected by ^{1}H NMR (9% spectroscopic yield) and by EI-MS. [c] $(Me_2PhSi)_2$ was detected by ^{1}H NMR (12% spectroscopic yield) and by EI-MS. The corresponding $(Et_3Si)_2$ homocoupling product was not detected in any of these experiments.

3d.iv. Additional comments on the mechanism

We summarise selected mechanistic insights on the basis of the experiments in sections **3d.i** and **3d.ii**:

1. Activation of C4-H was observed only in gramine (Table S2) and not indoles (Scheme S1a-c) and therefore requires the directing group at C3.

2. C7-H activation was observed for the reactions with gramines (Table S2). It was also observed for indole (**20$_H$**) only if an amine (in this case specifically diethylamine) was added to the reaction mixture (Scheme S1, reactions (a) vs (b)). This suggests that a strongly donating amine ligand on Ru facilitates C7-H cleavage, and that in the case of gramines, this is obtained from the decomposition of gramine to skatole.

3. The experiments reported in Table S2 show slightly greater levels of C7-H/D exchange in the skatole than in the gramine products. This suggests that the bulk of the C2-silyl substituent in **2e**/**2e-*d*** hinders C7-H activation, presumably by blocking Ru coordination to N1.

4. **20$_{Me}$** also underwent no C7-H/D exchange (Scheme S1c). It seems likely, therefore, that C7-H activation requires insertion of Ru into the N1-H bond, which the methyl group (or steric hindrance – as described above), inhibits.

5. The reaction between N-methylindole (**20$_{Me}$**) and D-SiEt$_3$ gave none of the corresponding C2-silylated product **23** (Scheme S1c). However, 15% C2-D incorporation was observed in the indole (**20$_{Me}$-*d***), indicating that C2-H activation occurs. Presumably, therefore, the N-methyl substituent is sufficiently sterically demanding to prohibit reductive elimination to produce the C2-Si bond.

6. That C2-H activation in **20$_{Me}$** occurs without any coordination available lends credence to the hypothesis that truly intermolecular C-H activation is possible for substrates without directing groups.

7. The presence of amines that do not facilitate the formation of 5- or 6-membered ruthenacycles also gave rise to increased levels of silylation at the pyrrolic nitrogen. For example, product **5** forms presumably because its directing group is too long to favour cycloruthenation at C2. Similarly, the amine groups of **16c'** and **20$_{SiEt3}$-*d*** or the corresponding starting materials (Scheme S1b) cannot effect cycloruthenation, and presumably activate Ru towards intermolecular reactions instead.

8. In all of the presented reactions, C2-H activation/silylation was favoured over other positions (e.g., for silylation: **12** vs **13** or **15a** vs **15b**; for deuterium incorporation: higher levels of C2-H/D over C3-H/D exchange were observed in every reaction in Scheme S1). The origins of this selectivity have not yet been elucidated for Ru-catalysed C-H silylation. However, it is plausible that activation of C2-H benefits from the proximate heteroatom, whose electronegativity lowers the C-H σ* LUMO energy, making oxidative addition to the Ru centre easier. For Rh-catalysed C-H silylation, Hartwig and Chang reported that electron-poor aryls are activated in preference over electron-rich aryls, consistent with transfer of electron-density from the metal to the substrate.[7] Alternatively, as the C-H/D exchange appears to be reversible, C2-ruthenated intermediates/transition states are more stable.

4. References

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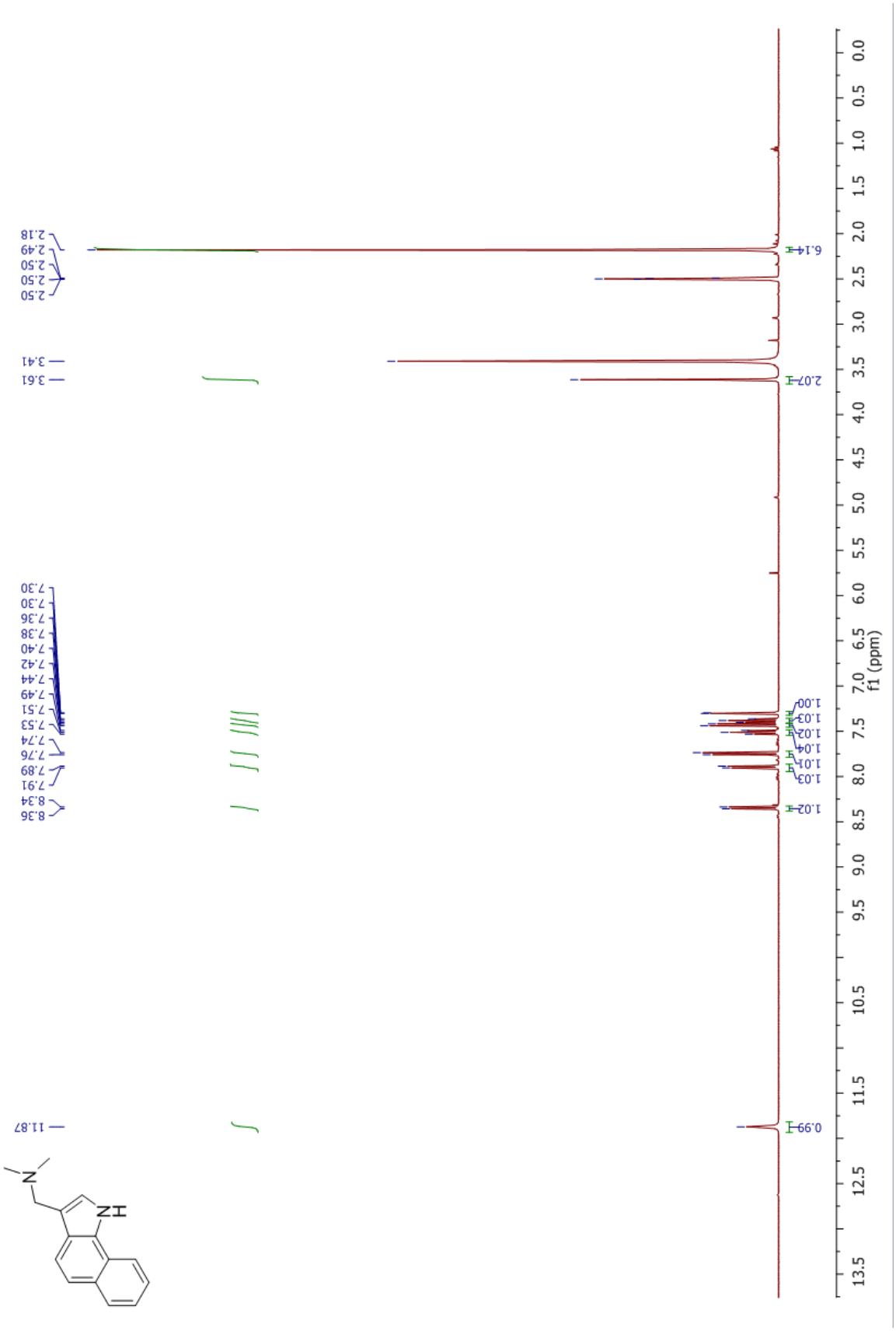
7. C. Cheng and J. F. Hartwig, *J. Am. Chem. Soc*. **2014**, *136*, 12064-12072

5. Spectra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7.36
7.38
7.40
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7.44
7.49
7.51
7.53
7.74
7.76
7.89
7.91
8.34
8.36
11.87
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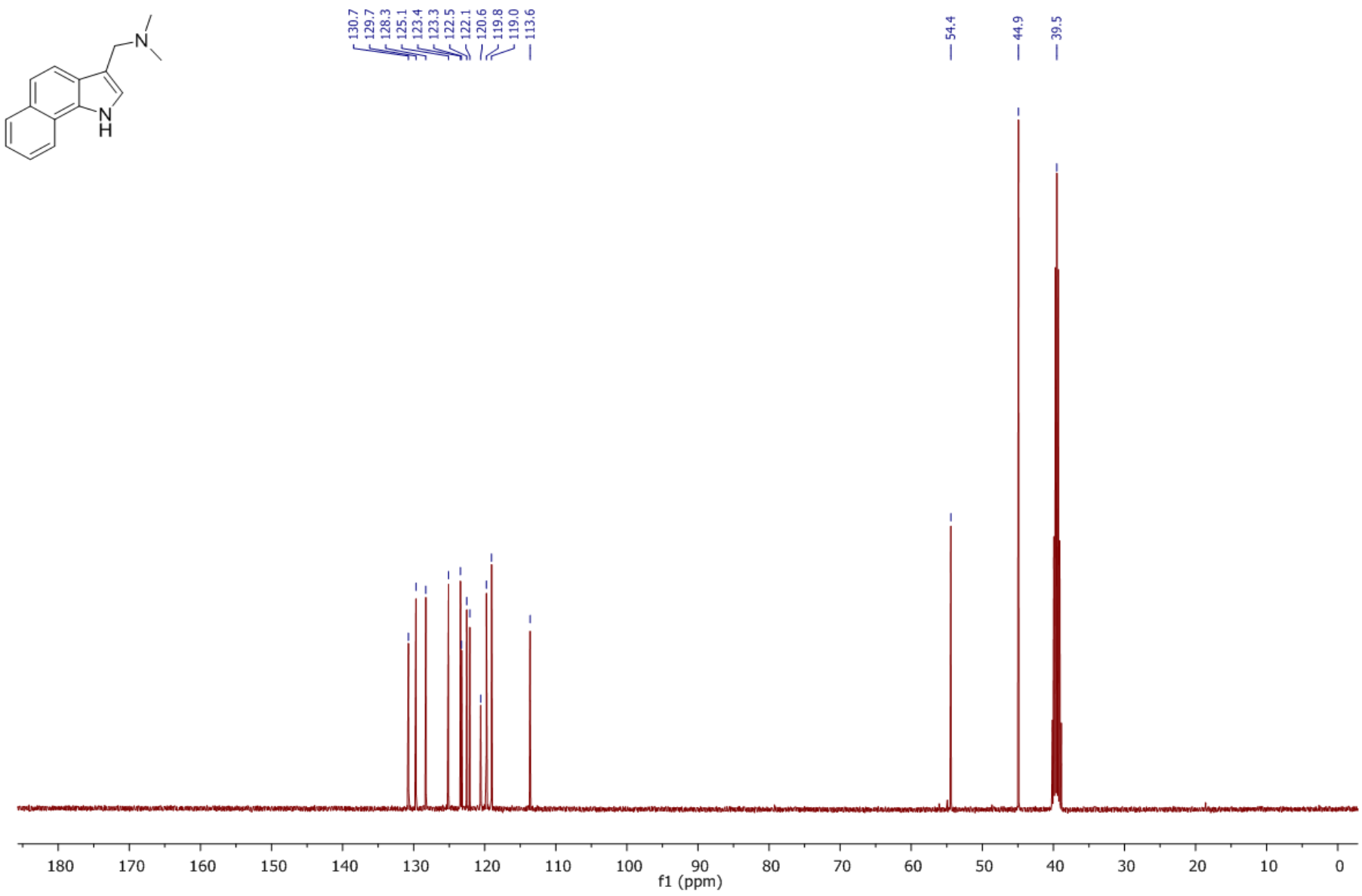
2.07
1.00
1.03
1.02
1.04
1.01
1.03
1.02
0.99
f1 (ppm)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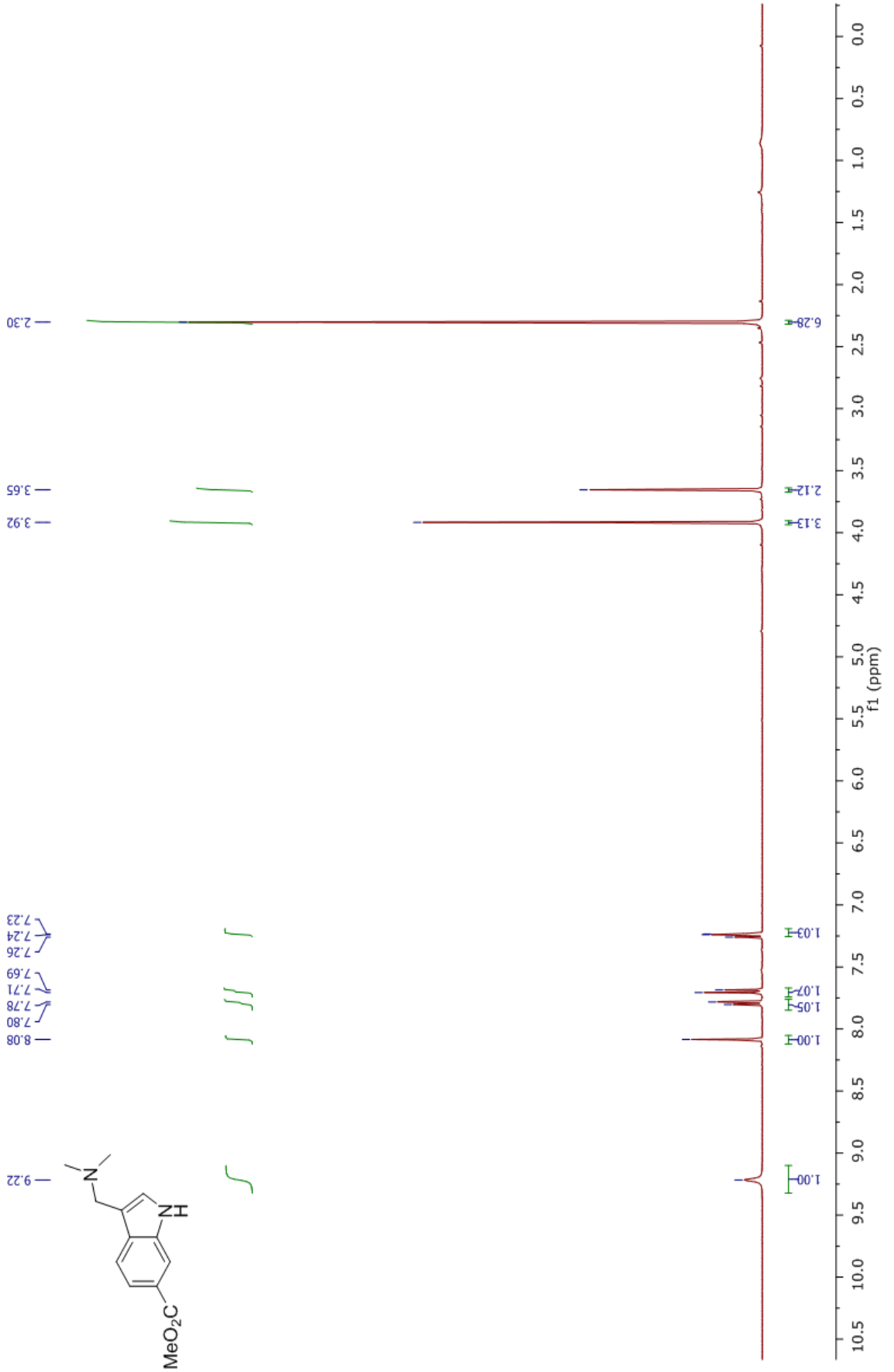
f1 (ppm)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7.80
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3.13
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1.07
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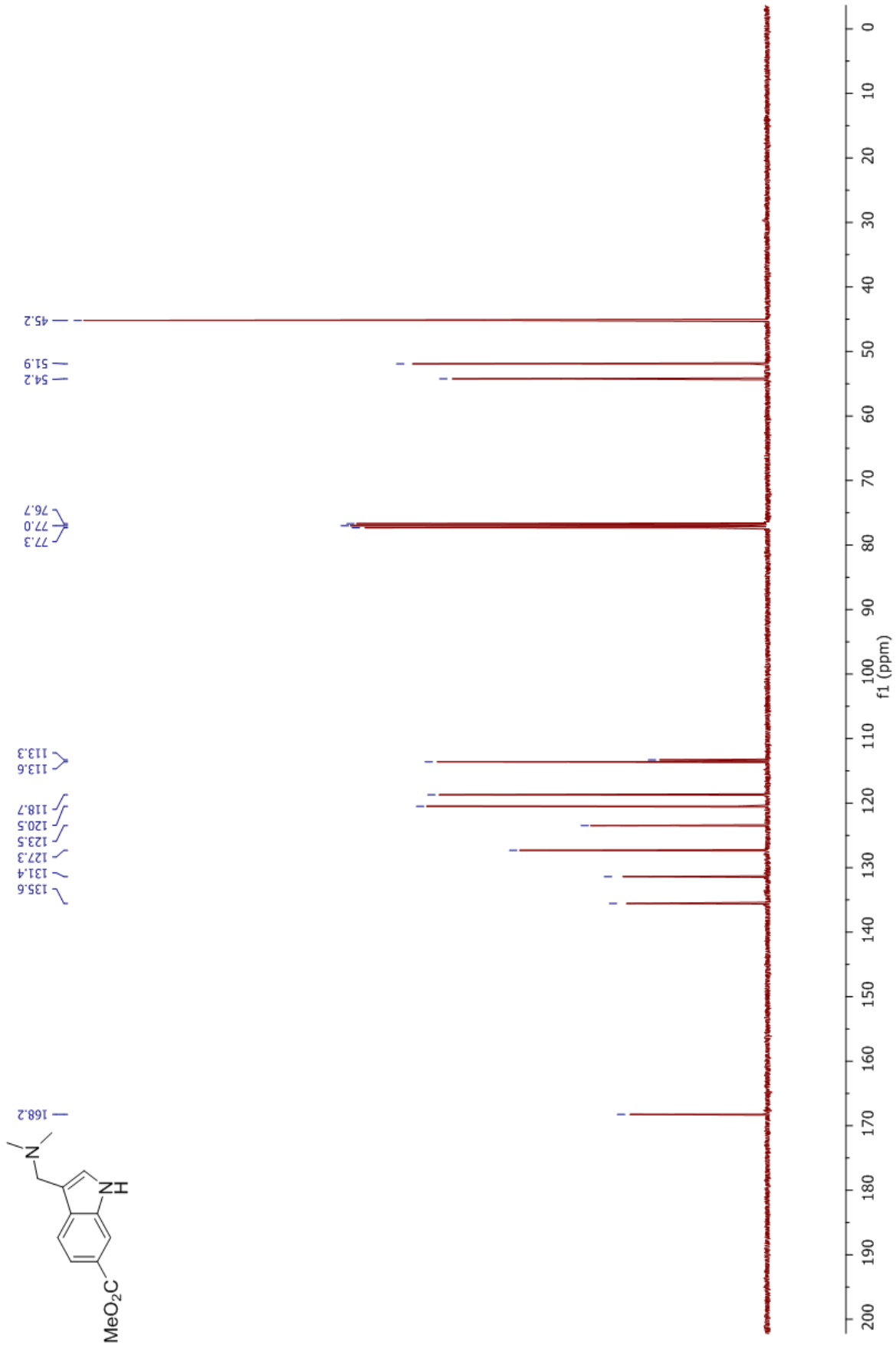
1.00
1.00
f1 (ppm)
MeO2C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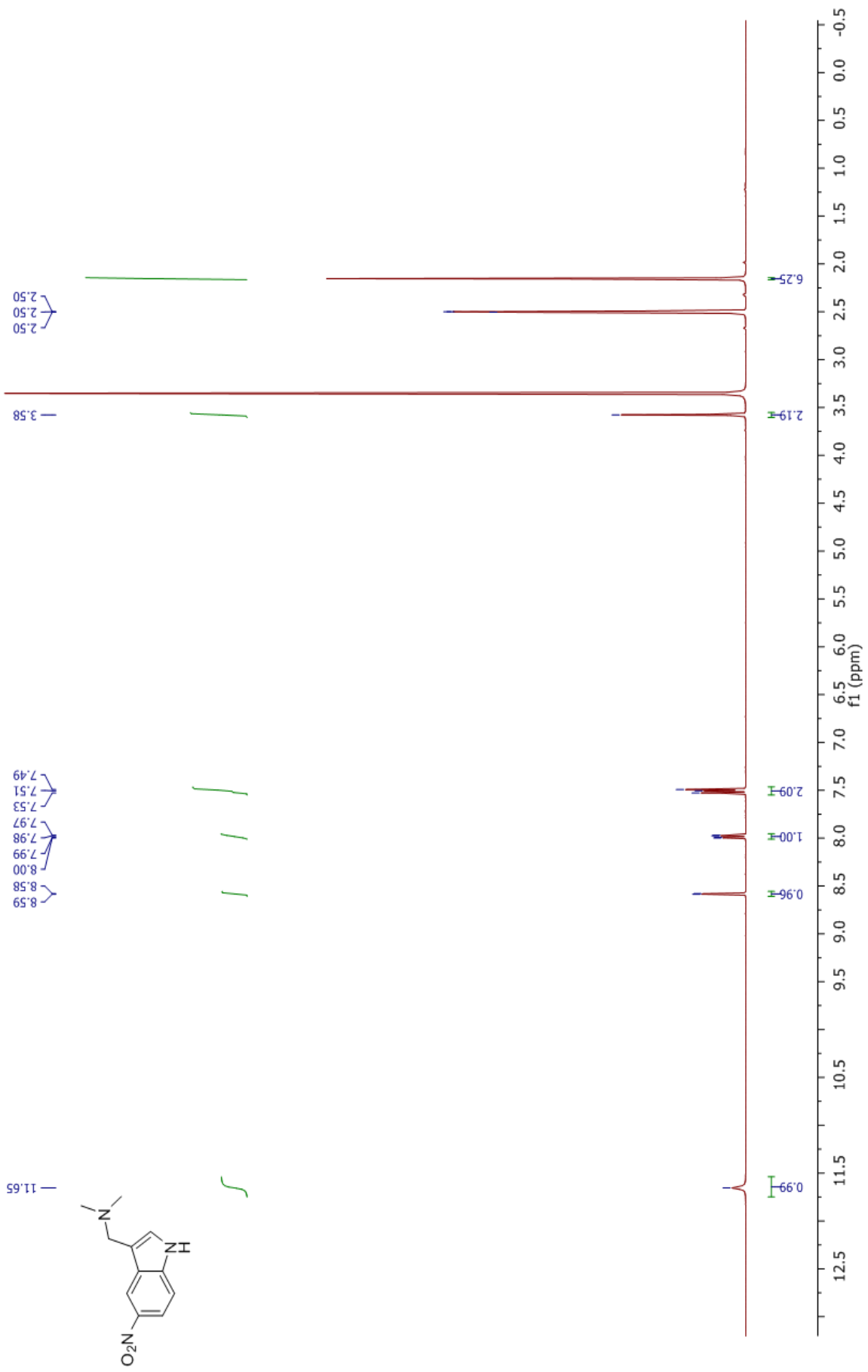
135.6
168.2
f1 (ppm)
MeO2C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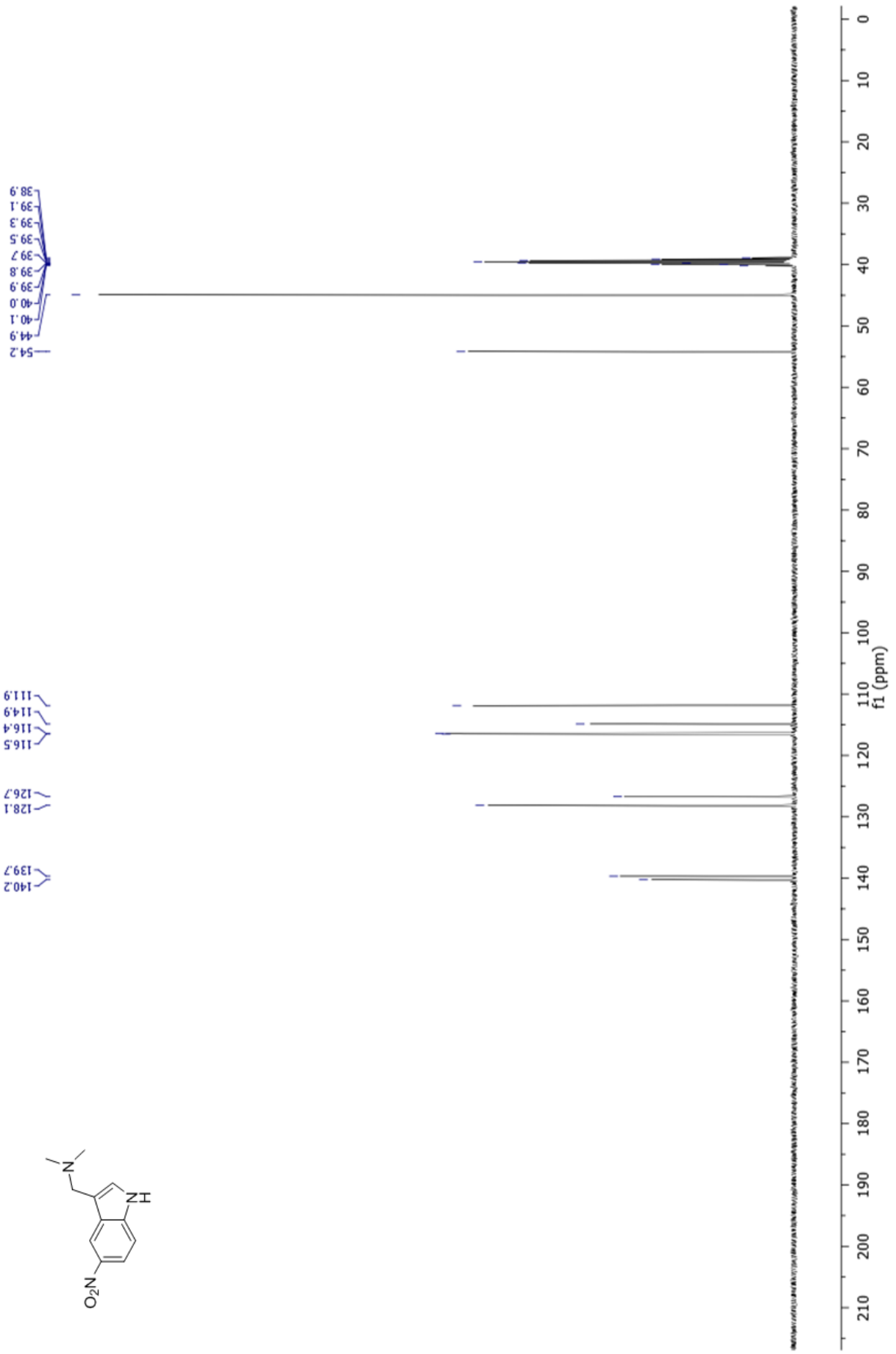
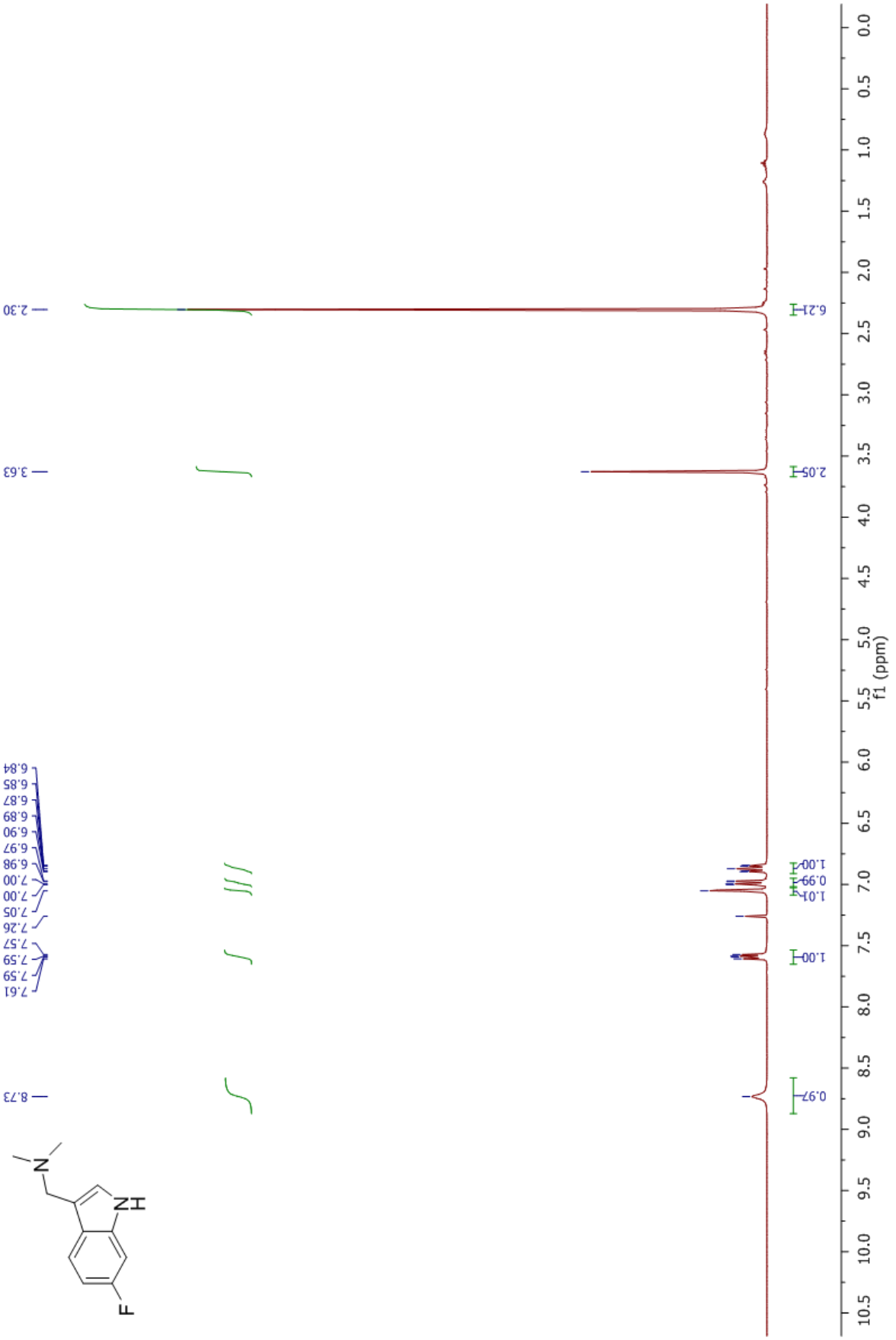
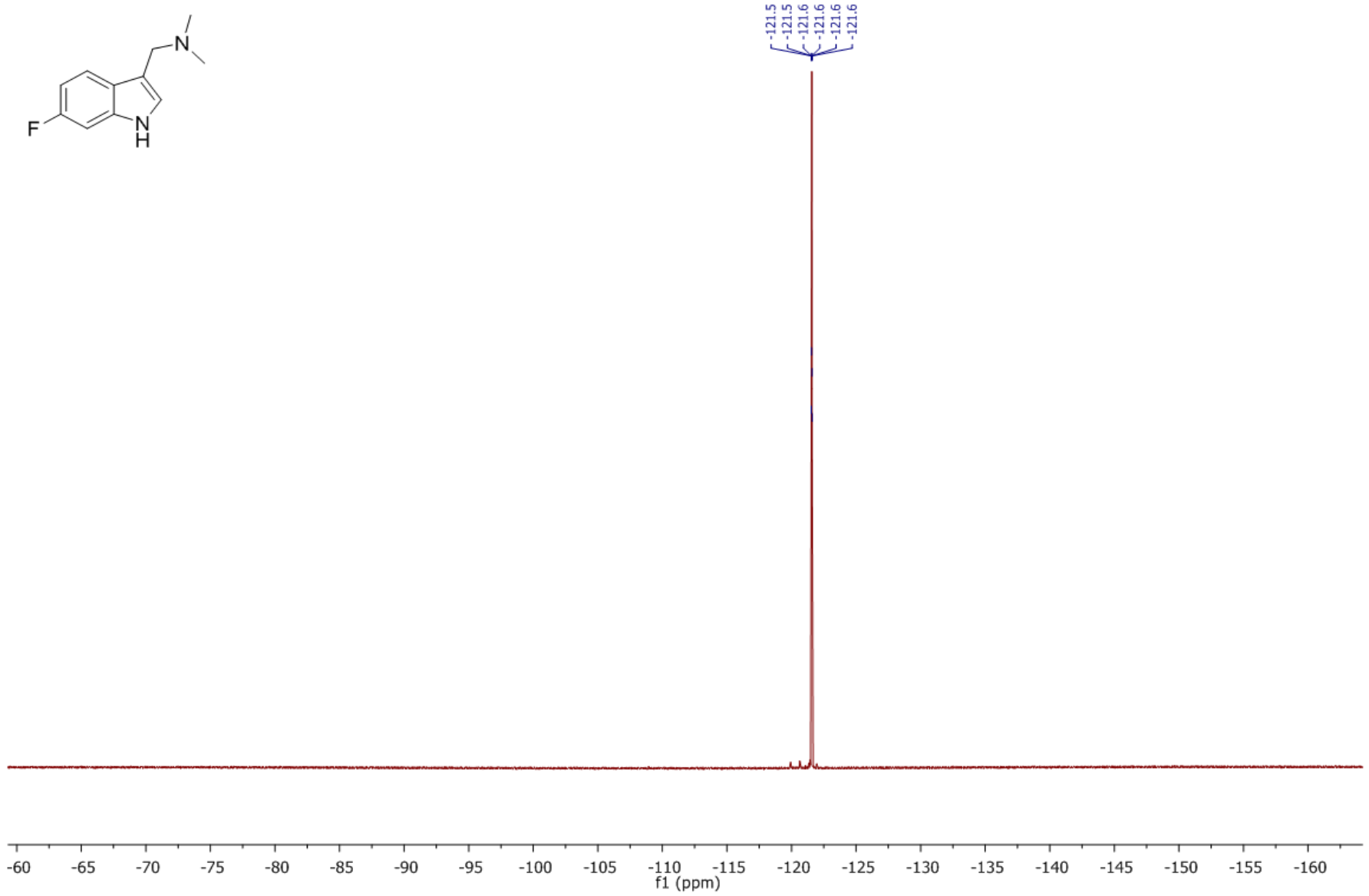
8.59
8.58
8.00
7.99
7.98
7.97
7.53
7.51
7.49
3.58
2.50
2.50
2.50
6.25
2.19
2.09
1.00
0.96
0.99
f1 (ppm)
H
N
N
O2N


38.9
39.1
39.3
39.5
39.7
39.8
39.9
40.0
40.1
44.9
54.2
111.9
114.9
116.4
116.5
126.7
128.1
139.7
140.2
f1 (ppm)


8.73
7.61
7.59
7.59
7.57
7.26
7.05
7.00
7.00
6.98
6.97
6.90
6.89
6.87
6.85
6.84
3.63
2.30
0.97
1.00
1.01
0.99
1.00
2.05
6.21
f1 (ppm)

45.2
54.4
76.7
77.0
77.3
97.2
97.5
108.1
108.3
113.0
119.8
119.9
124.0
124.0
124.4
136.0
136.2
158.7
161.1
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
N
NH
F


F
N
H
N
-121.5
-121.5
-121.6
-121.6
-121.6
-121.6
-60
-65
-70
-75
-80
-85
-90
-95
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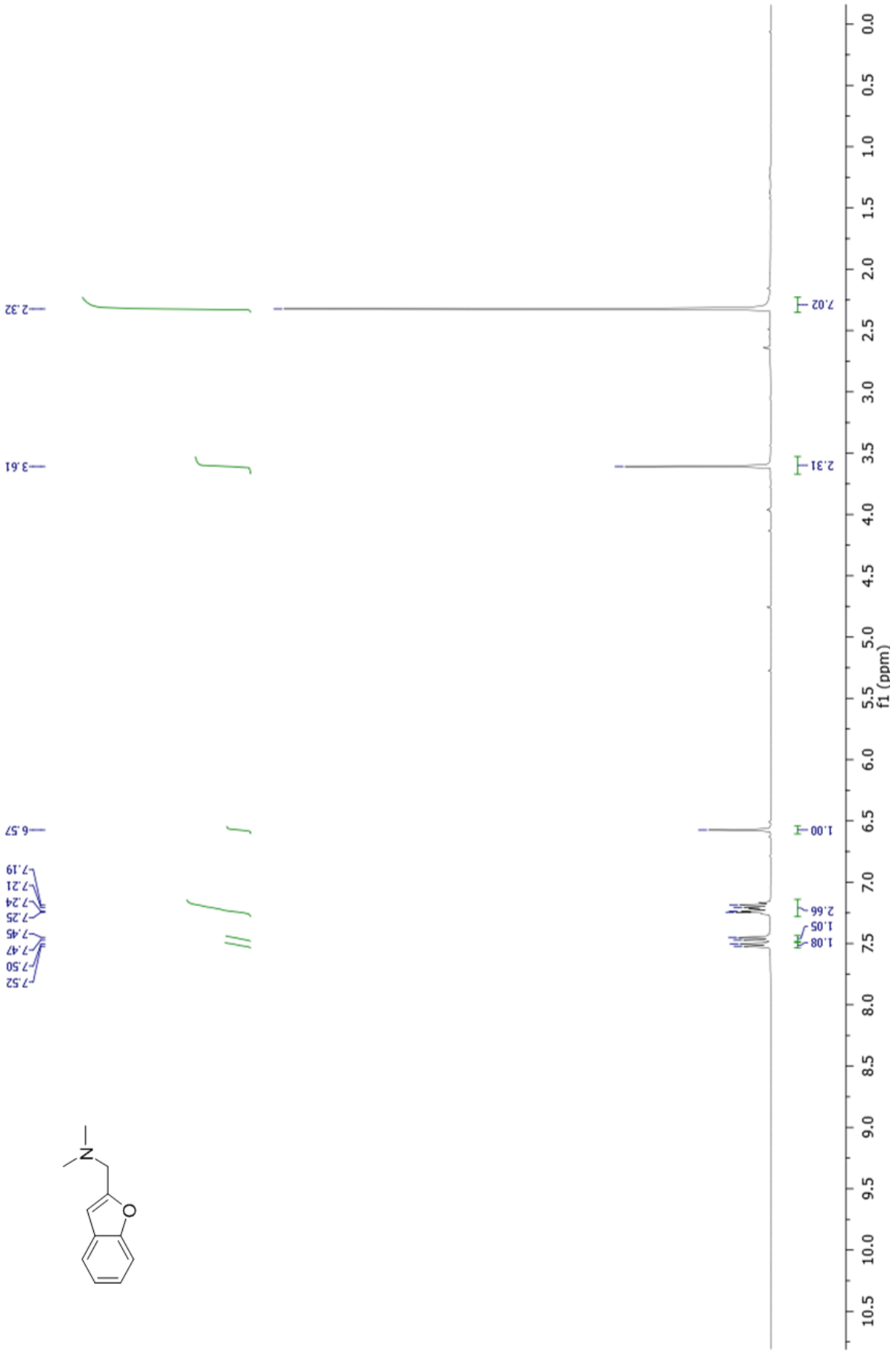
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)


2.32
3.61
6.57
7.19
7.21
7.24
7.25
7.45
7.47
7.50
7.52
7.02
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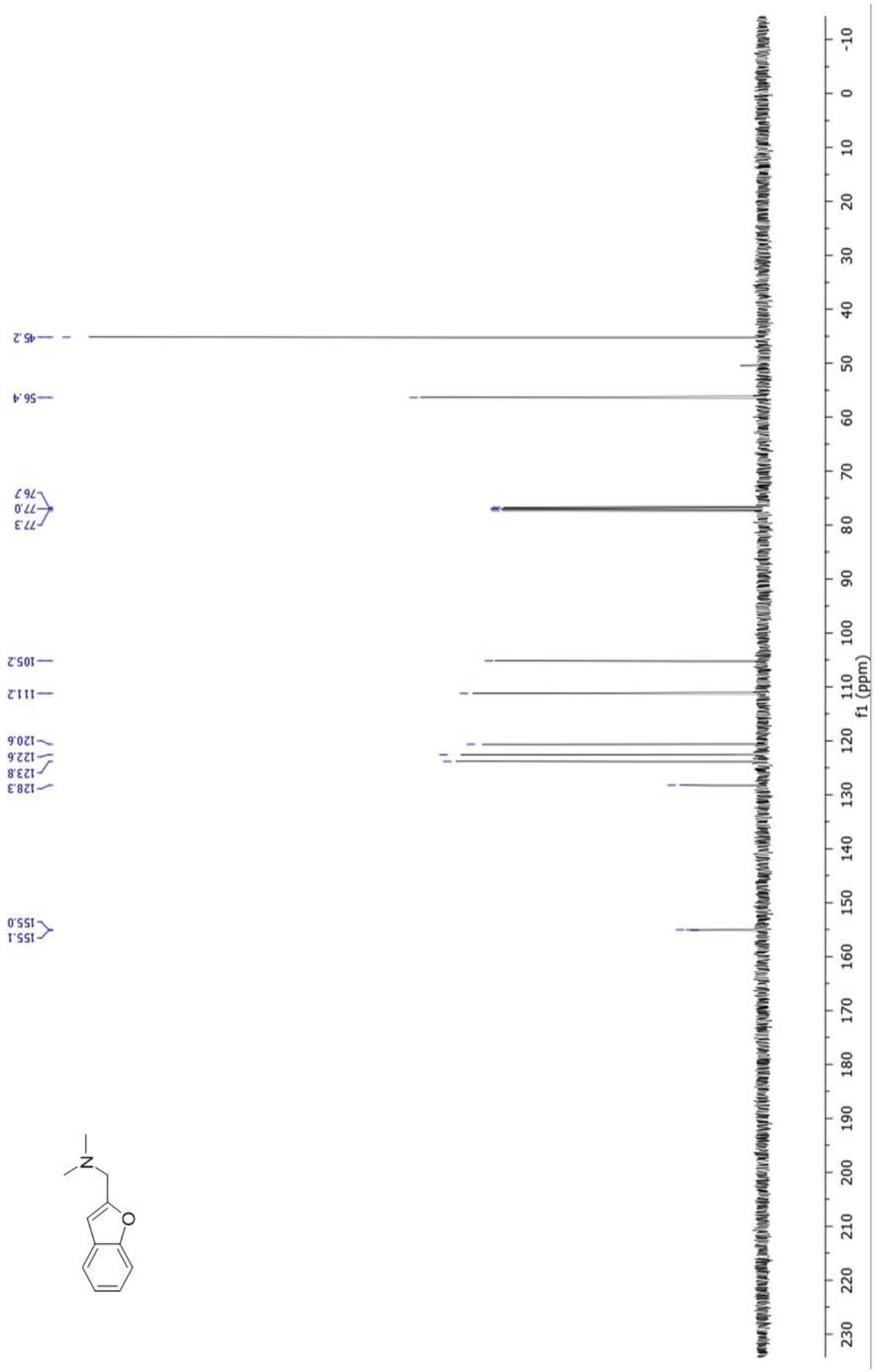
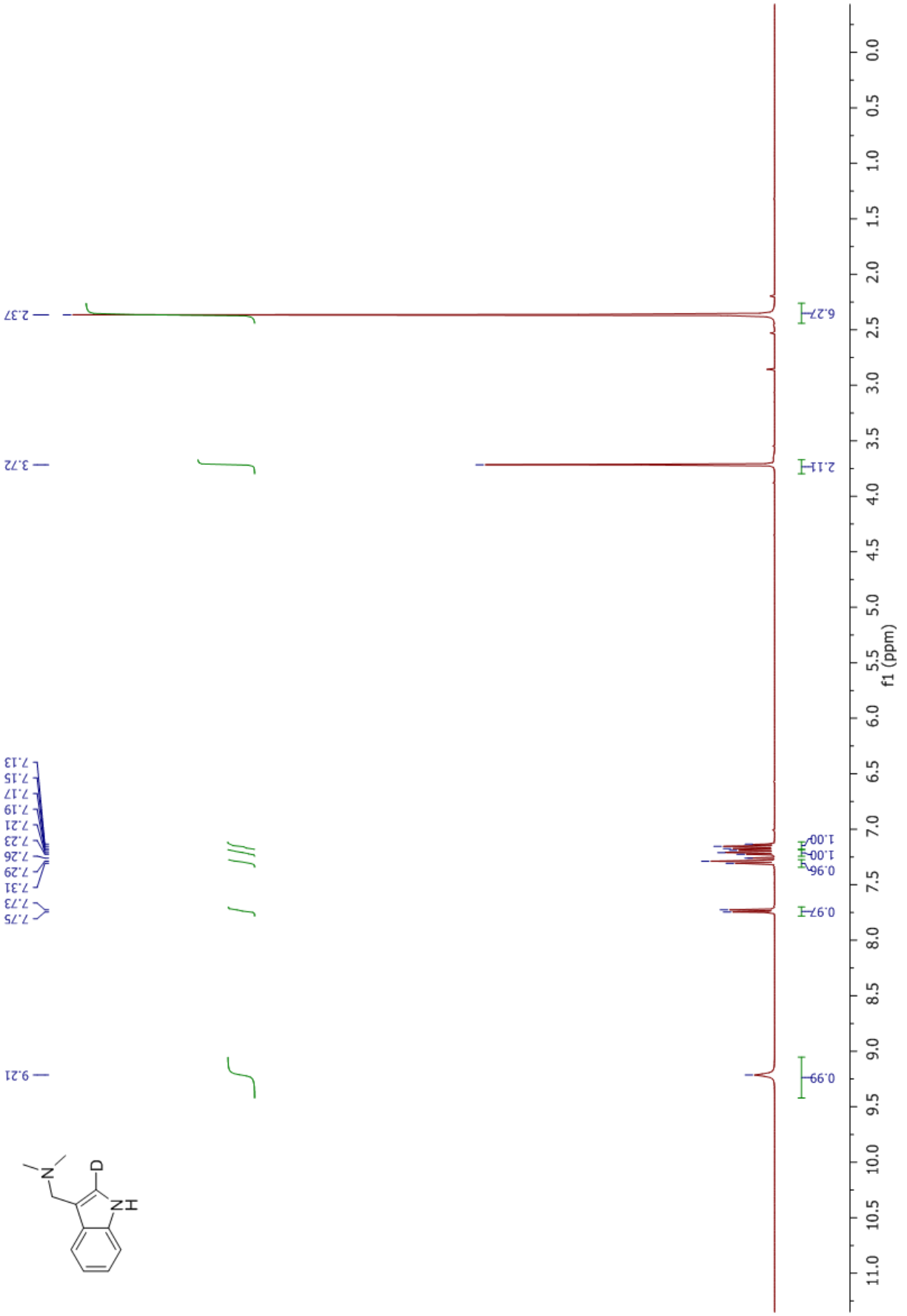
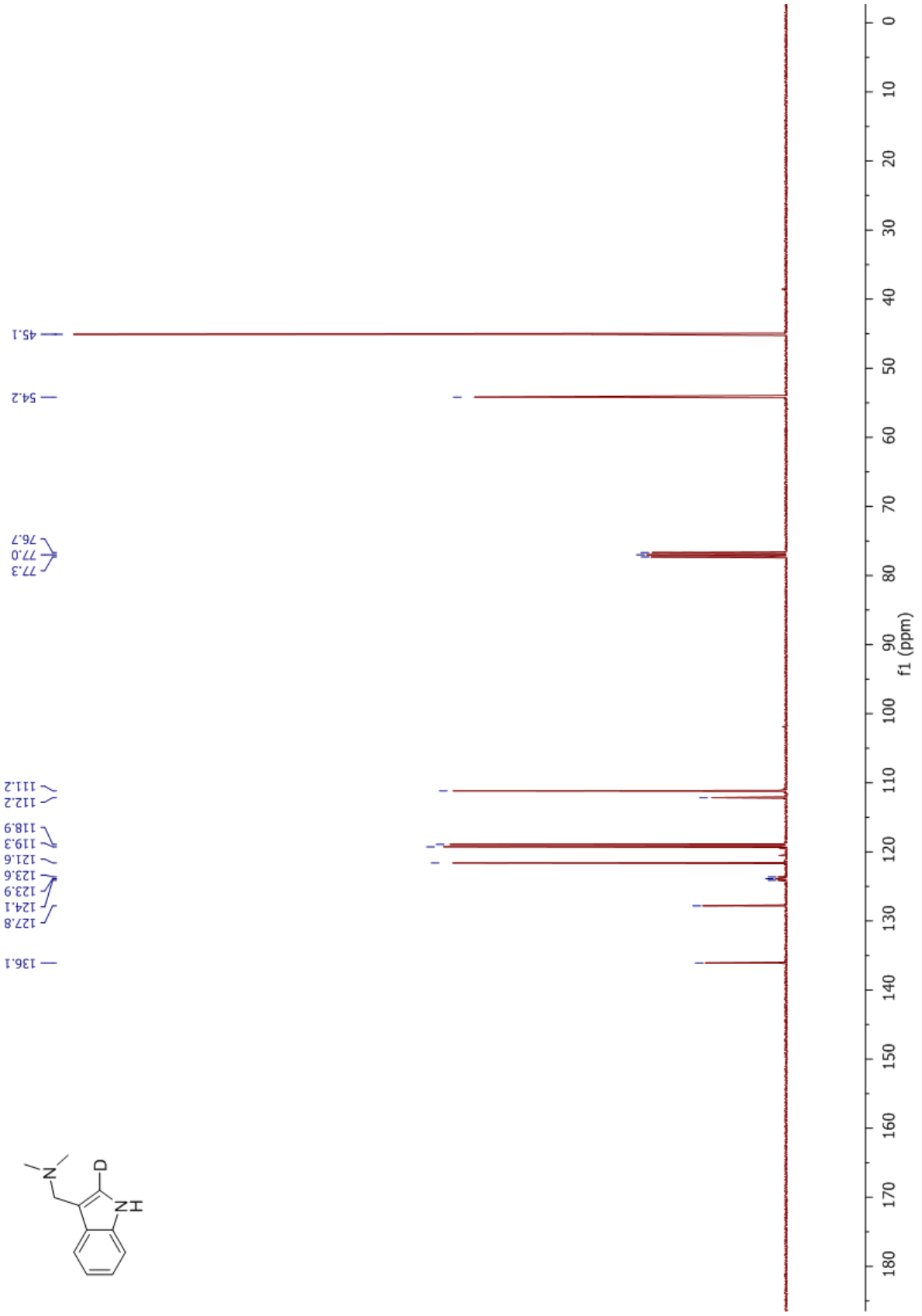
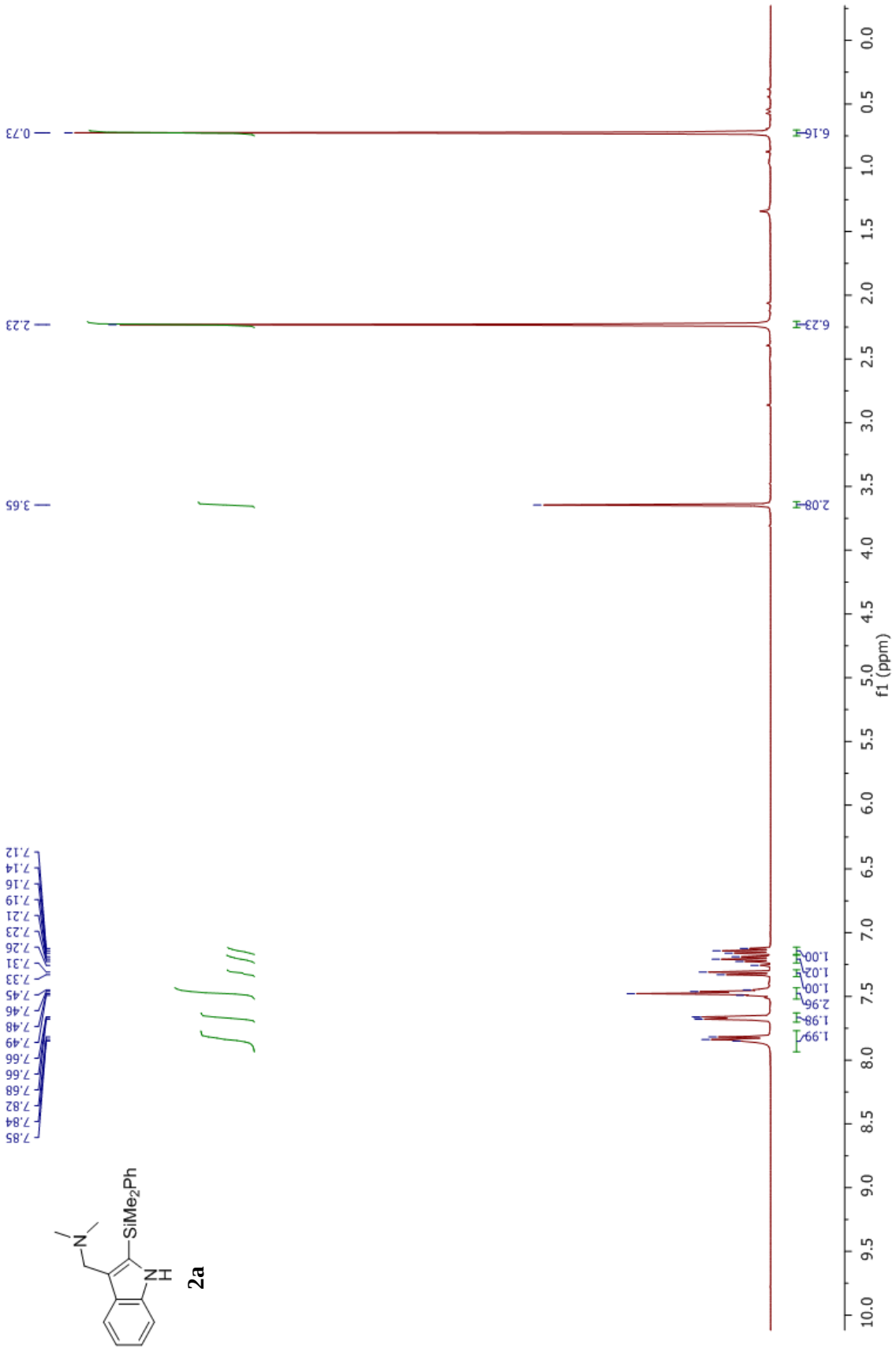
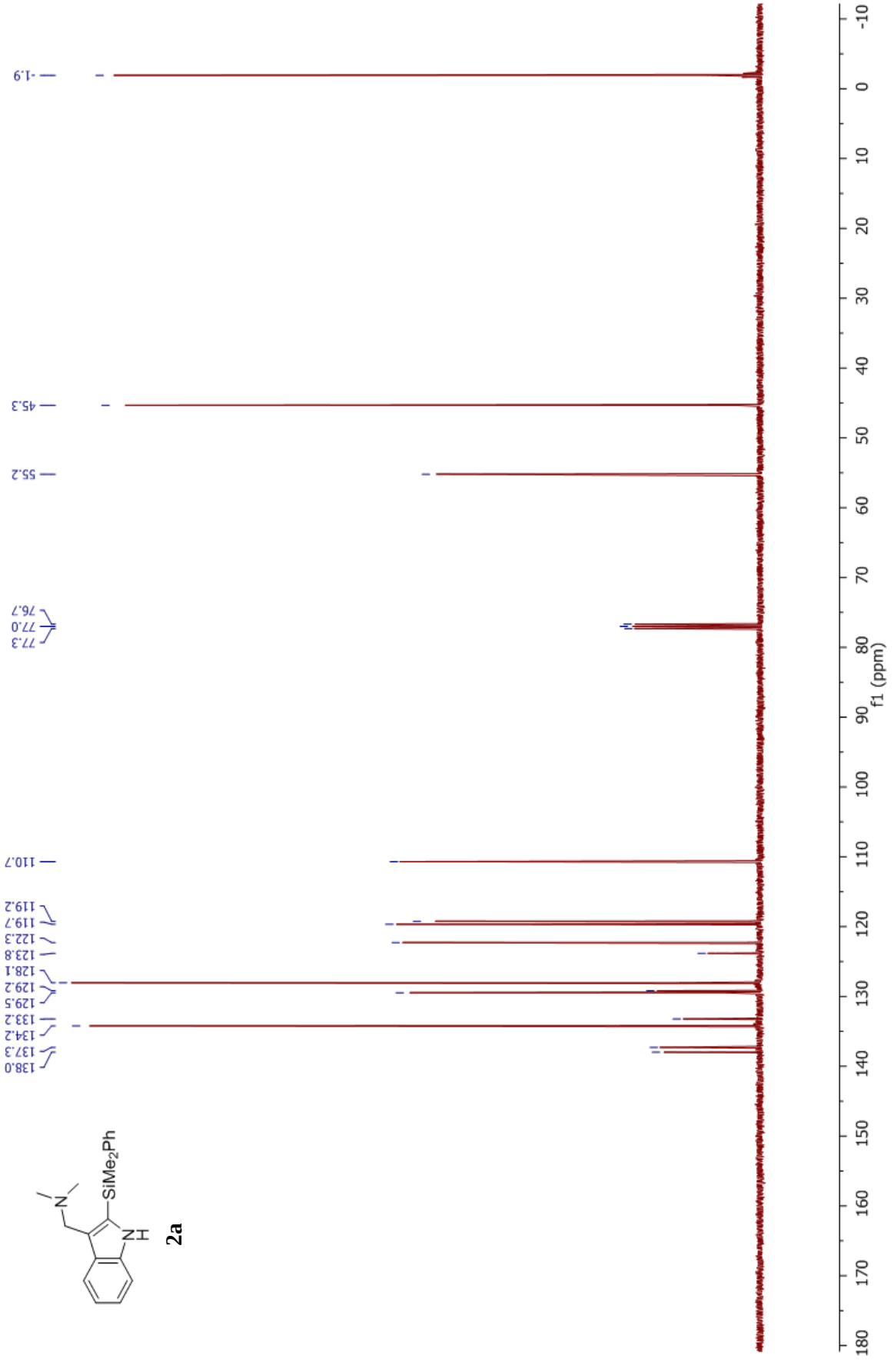
1.00
2.66
1.05
1.08
f1 (ppm)

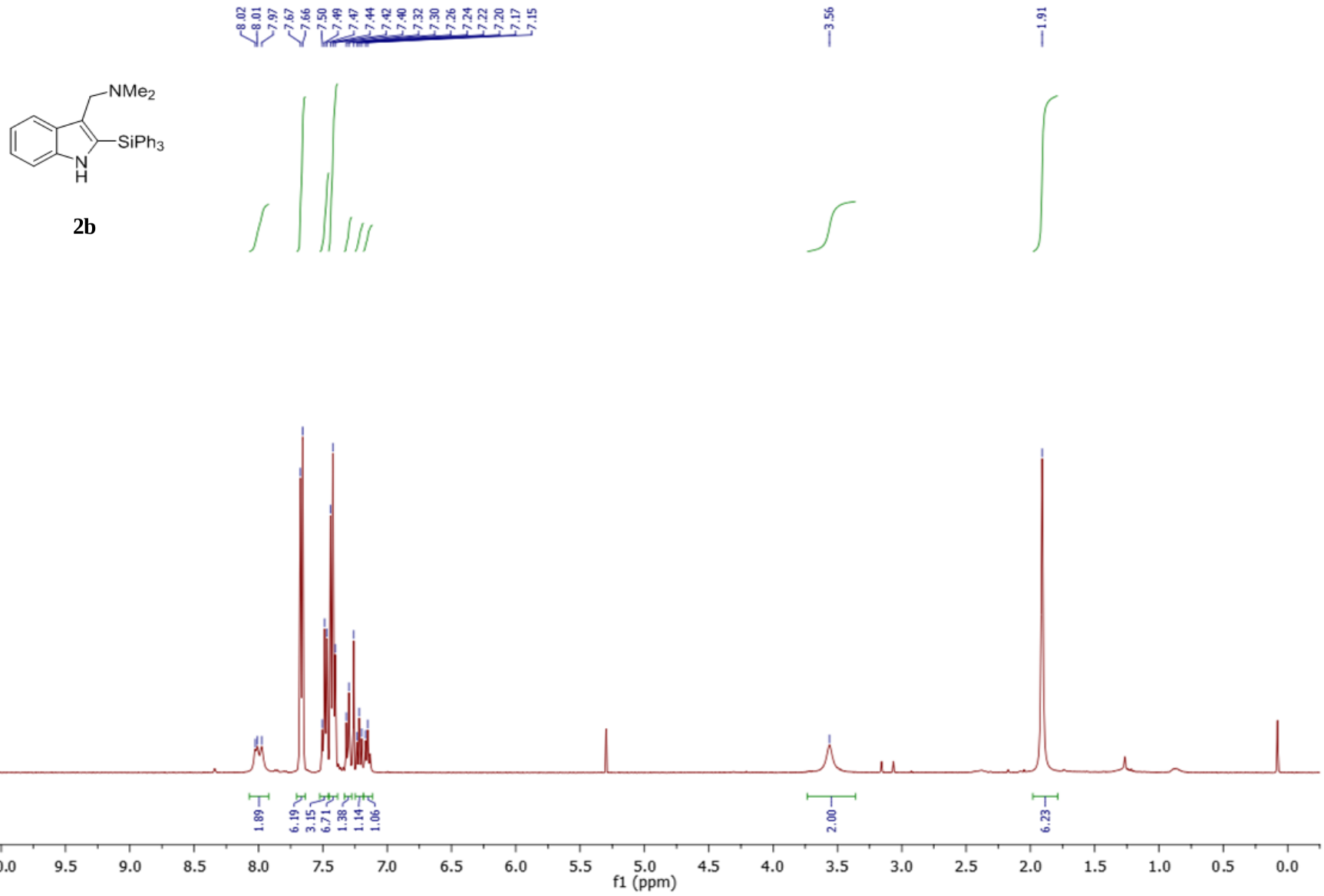

45.2
56.4
77.3
77.0
76.7
105.2
111.2
120.6
122.6
123.8
128.3
155.1
155.0
f1 (ppm)

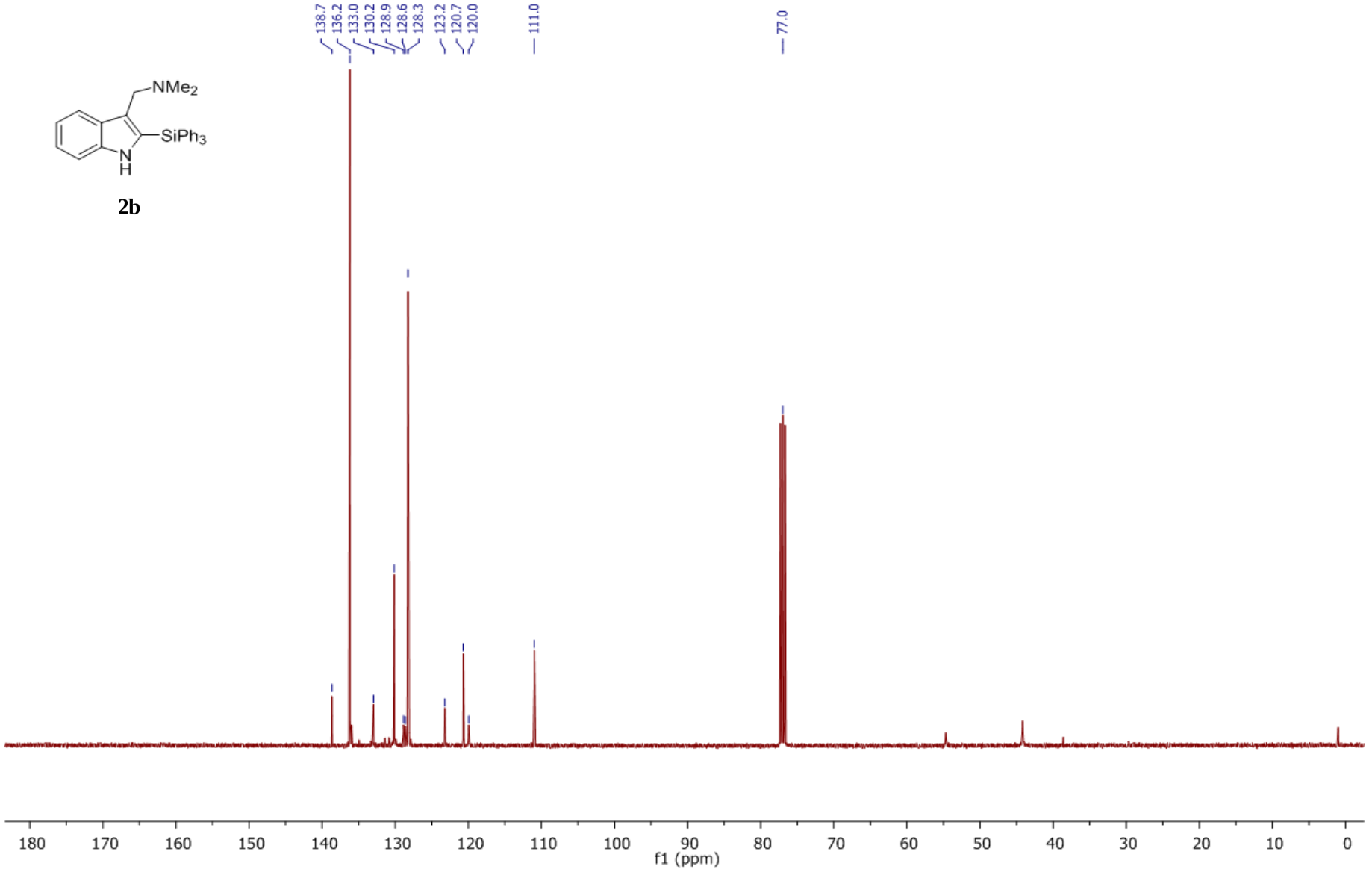

2.37
3.72
9.21
7.13
7.15
7.17
7.19
7.21
7.23
7.26
7.29
7.31
7.73
7.75
6.27
2.11
1.00
1.00
0.96
0.97
0.99
O
N
H
N
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
f1 (ppm)


45.1
54.2
77.3
77.0
76.7
136.1
127.8
124.1
123.9
123.6
121.6
119.3
118.9
112.2
111.2
f1 (ppm)

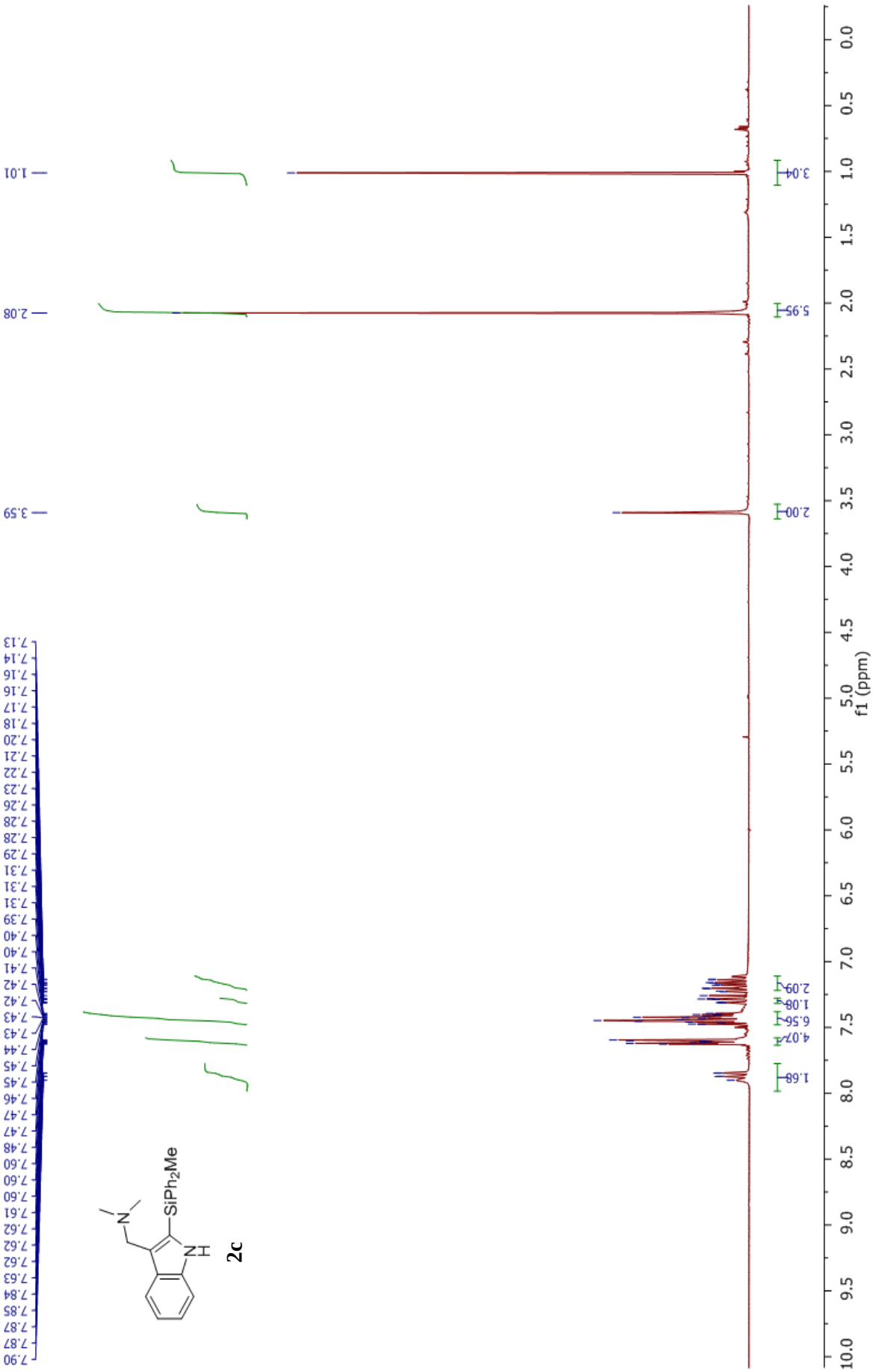

0.73
2.23
3.65
7.12
7.14
7.16
7.19
7.21
7.23
7.26
7.31
7.33
7.45
7.46
7.48
7.49
7.66
7.66
7.68
7.82
7.84
7.85
6.16
6.23
2.08
1.00
1.02
1.00
2.96
1.98
1.99
f1 (ppm)
SiMe2Ph
N
H
2a

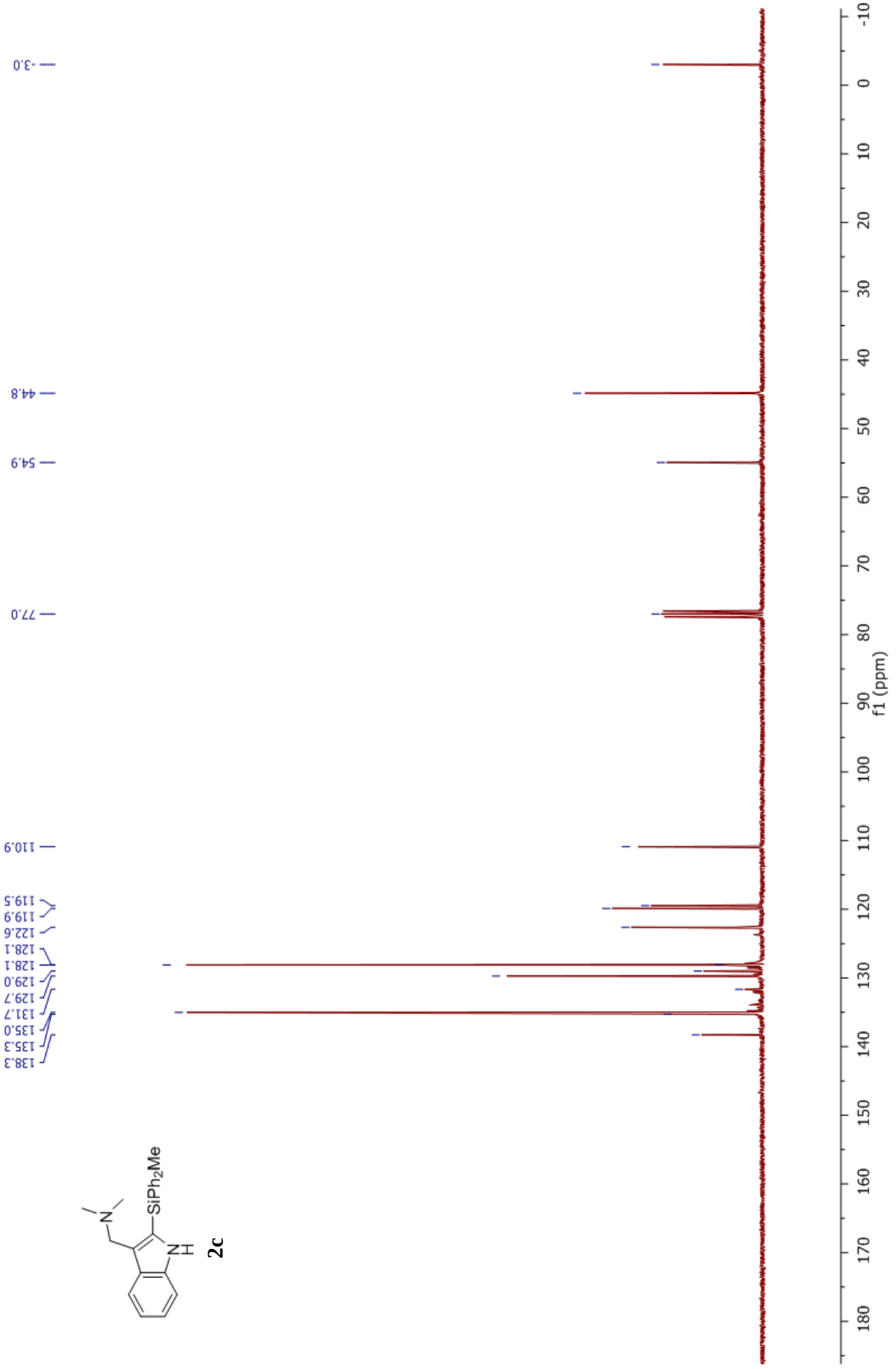

-1.9
45.3
55.2
76.7
77.0
77.3
110.7
119.2
119.7
122.3
123.8
128.1
129.2
129.5
133.2
134.2
137.3
138.0
SiMe2Ph
N
H
2a
f1 (ppm)

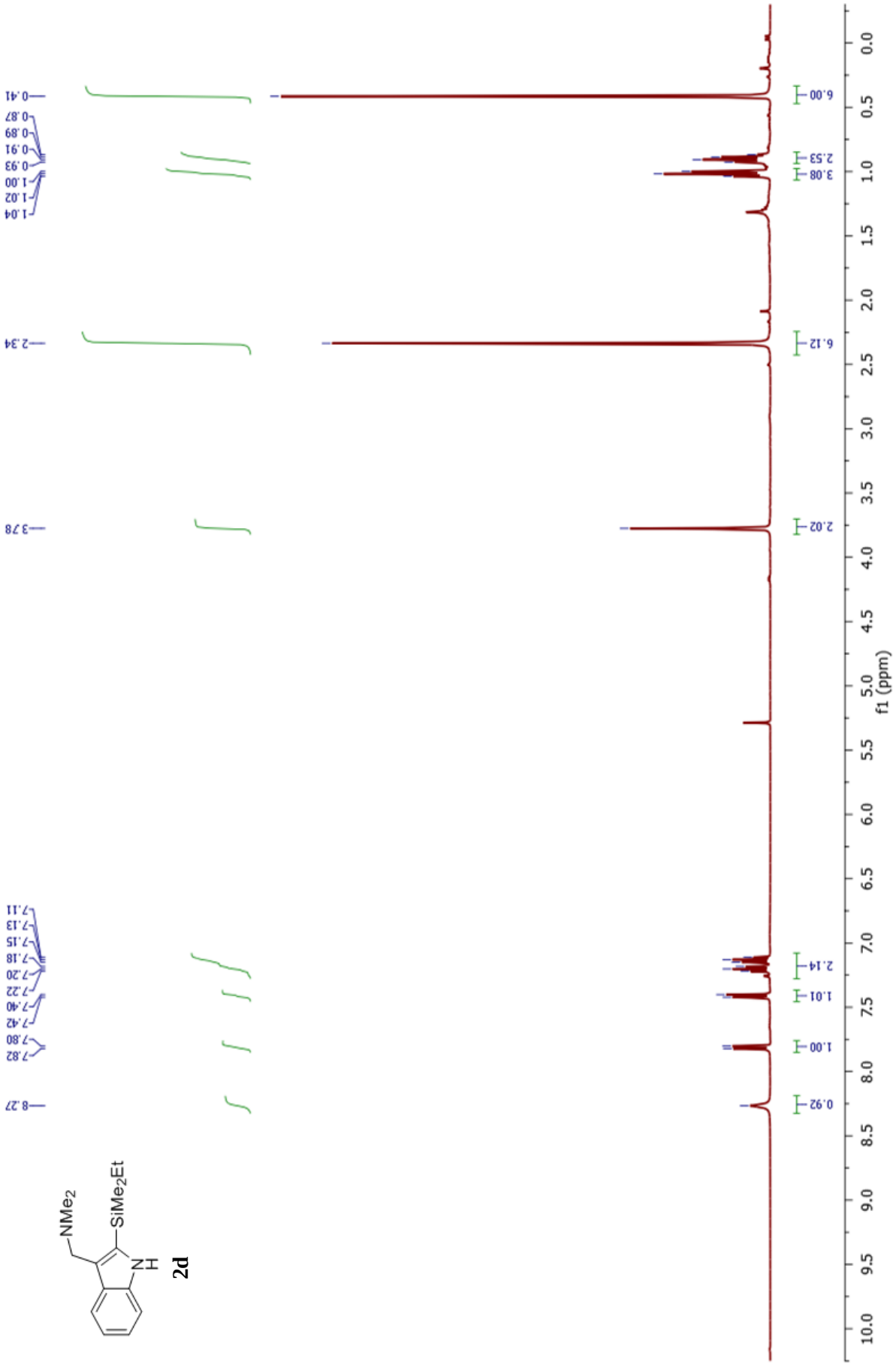

NMe2
SiPh3
N
H
2b
8.02
8.01
7.97
7.67
7.66
7.50
7.49
7.47
7.44
7.42
7.40
7.32
7.30
7.26
7.24
7.22
7.20
7.17
7.15
3.56
1.91
1.89
6.19
3.15
6.71
1.38
1.14
1.06
2.00
6.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

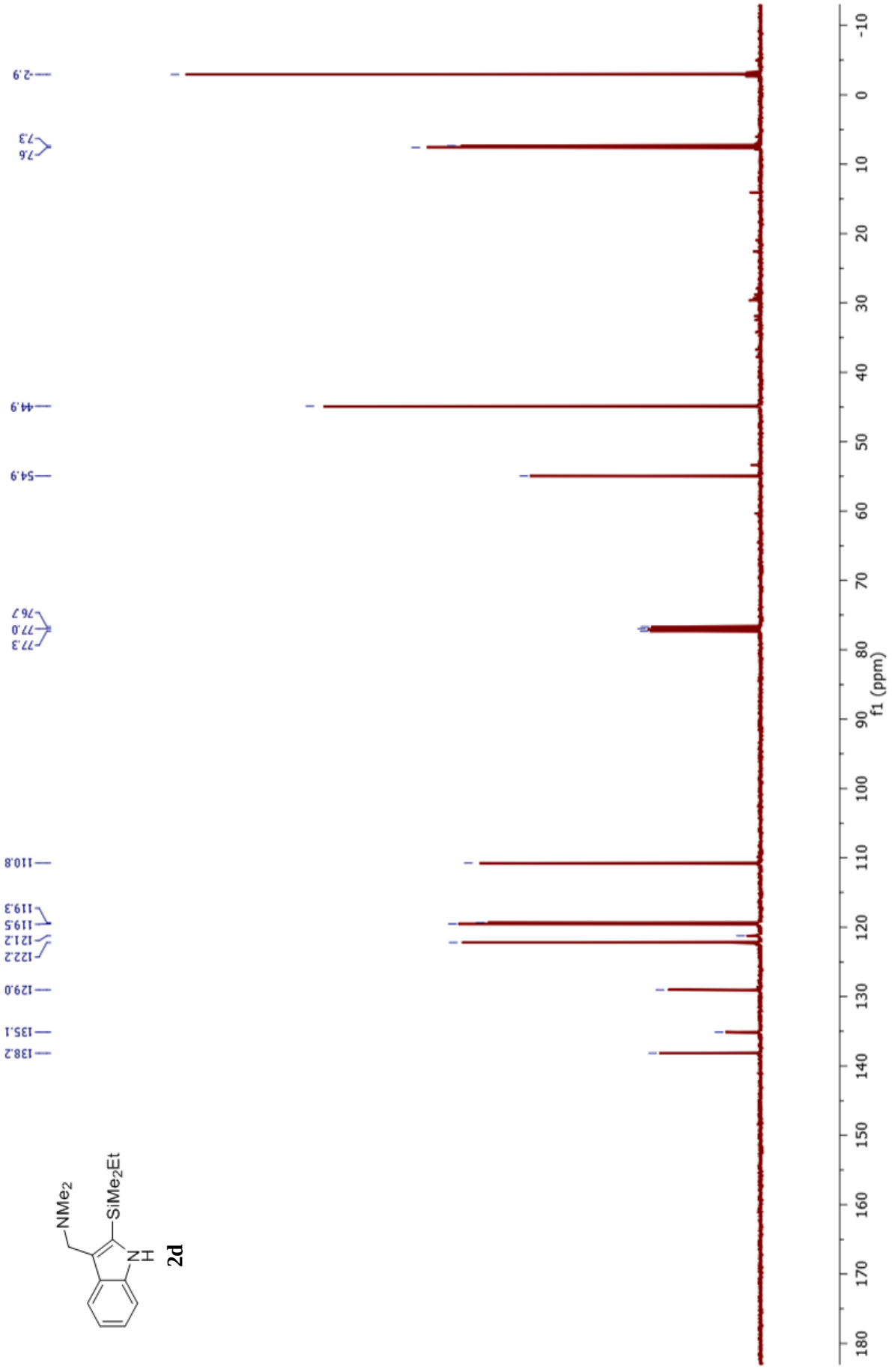

138.7
136.2
133.0
130.2
128.9
128.6
128.3
123.2
120.7
120.0
111.0
77.0
NMe2
SiPh3
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

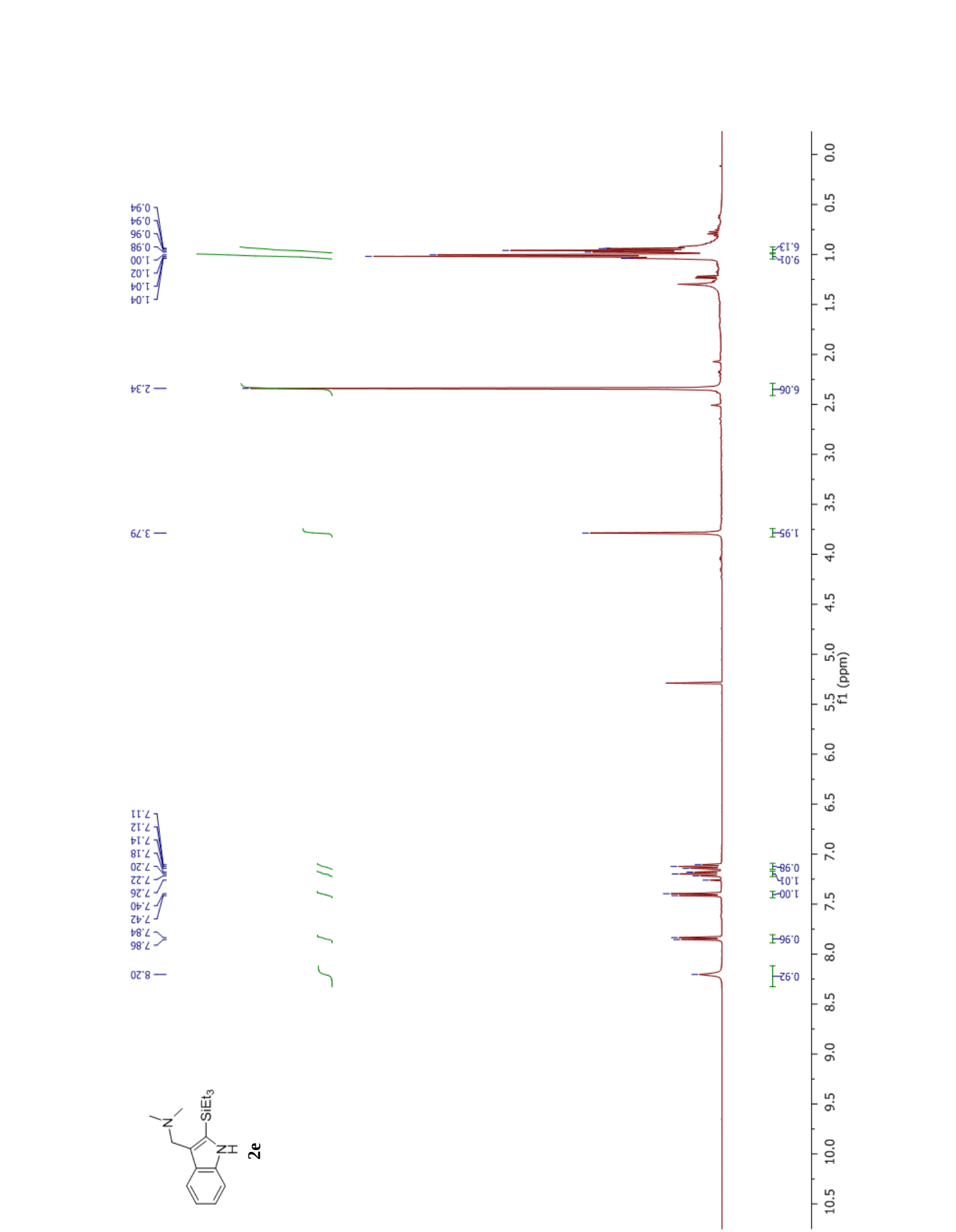
2b

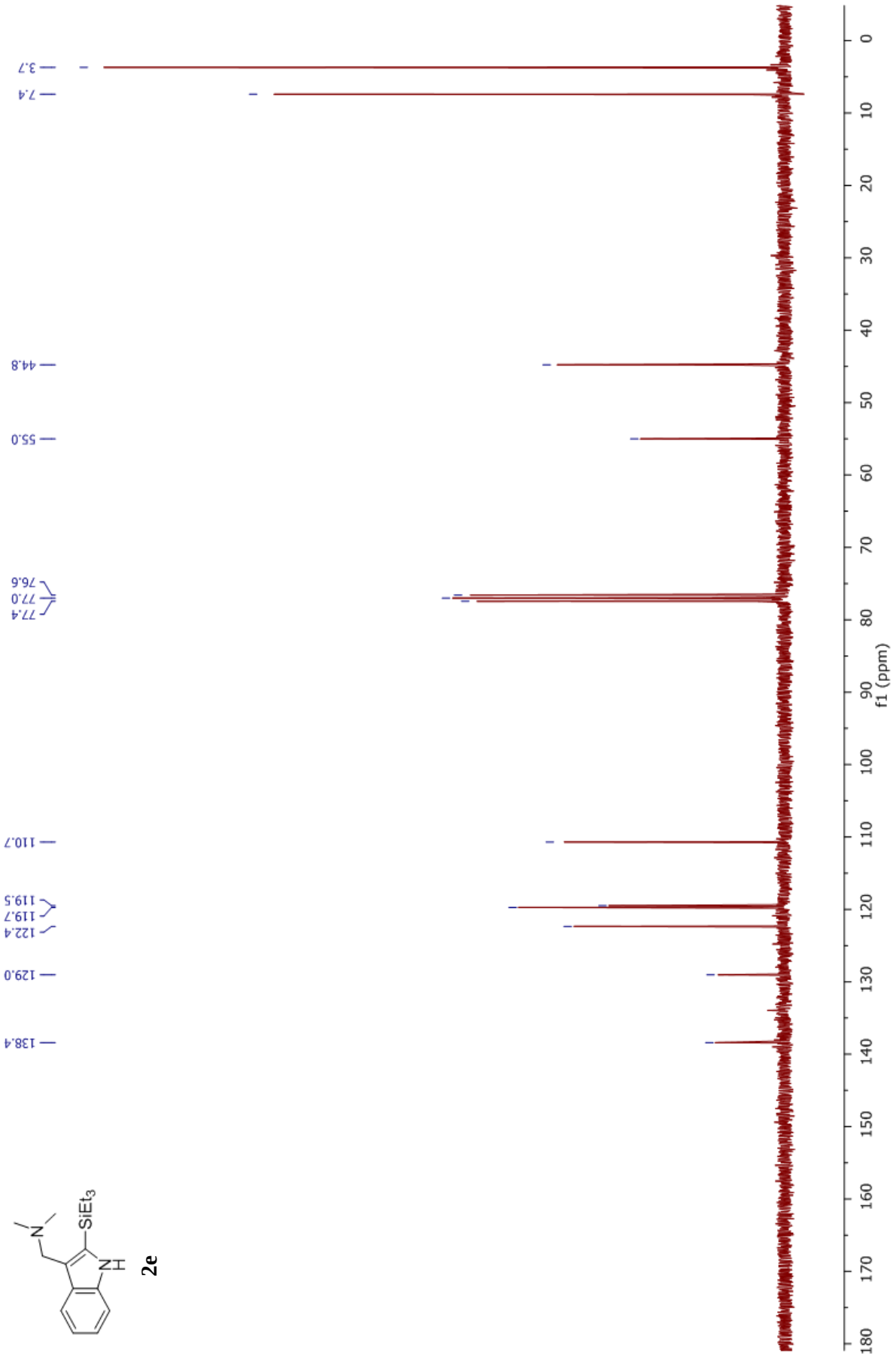

SiPh2Me
N
H
2c
f1 (ppm)

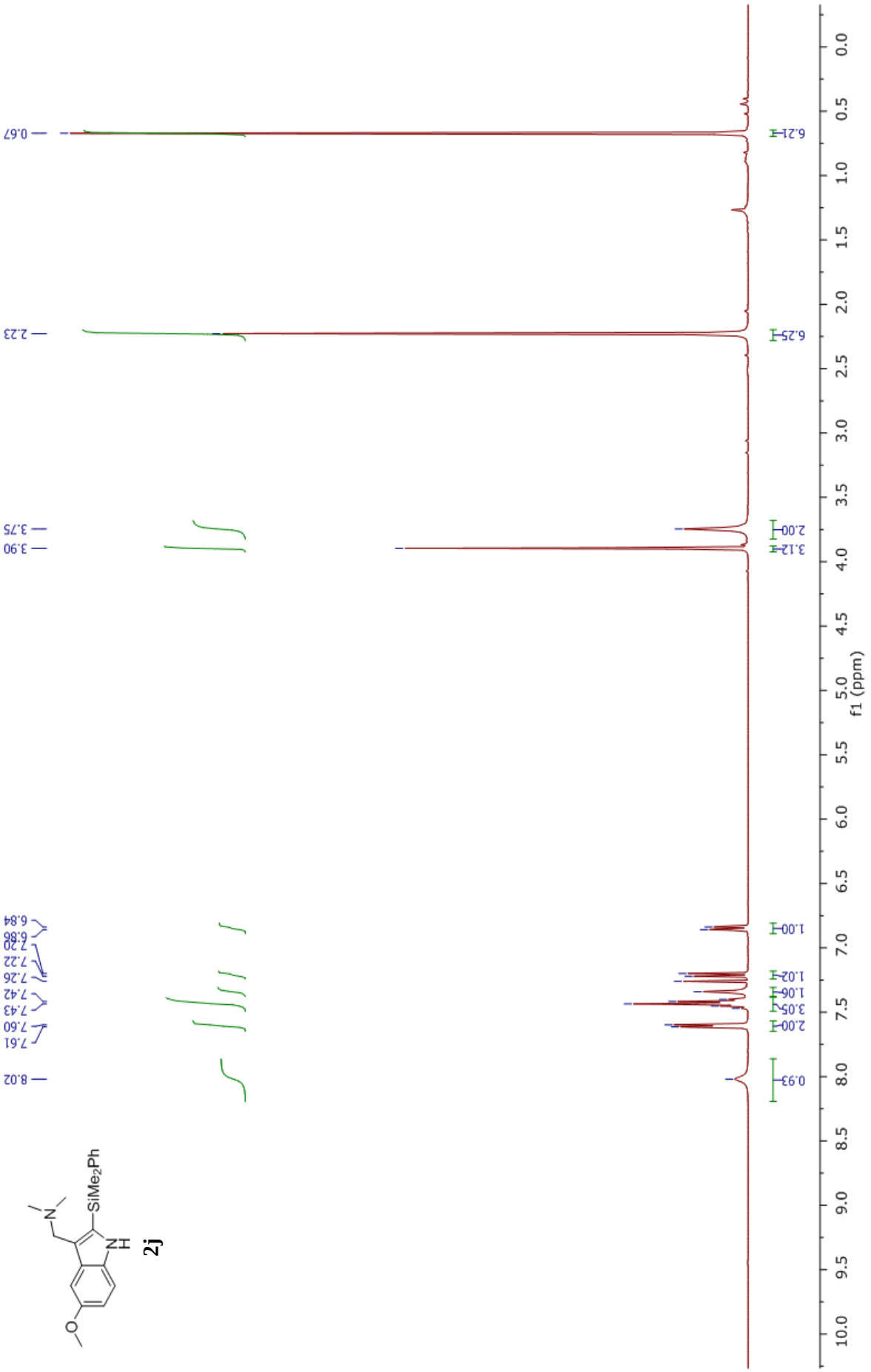

-3.0
44.8
54.9
77.0
110.9
119.5
119.9
122.6
128.1
128.1
129.0
129.7
131.7
135.0
135.3
138.3
f1 (ppm)
SiPh2Me
2c


NMe2
SiMe2Et
N
H
2d
f1 (ppm)

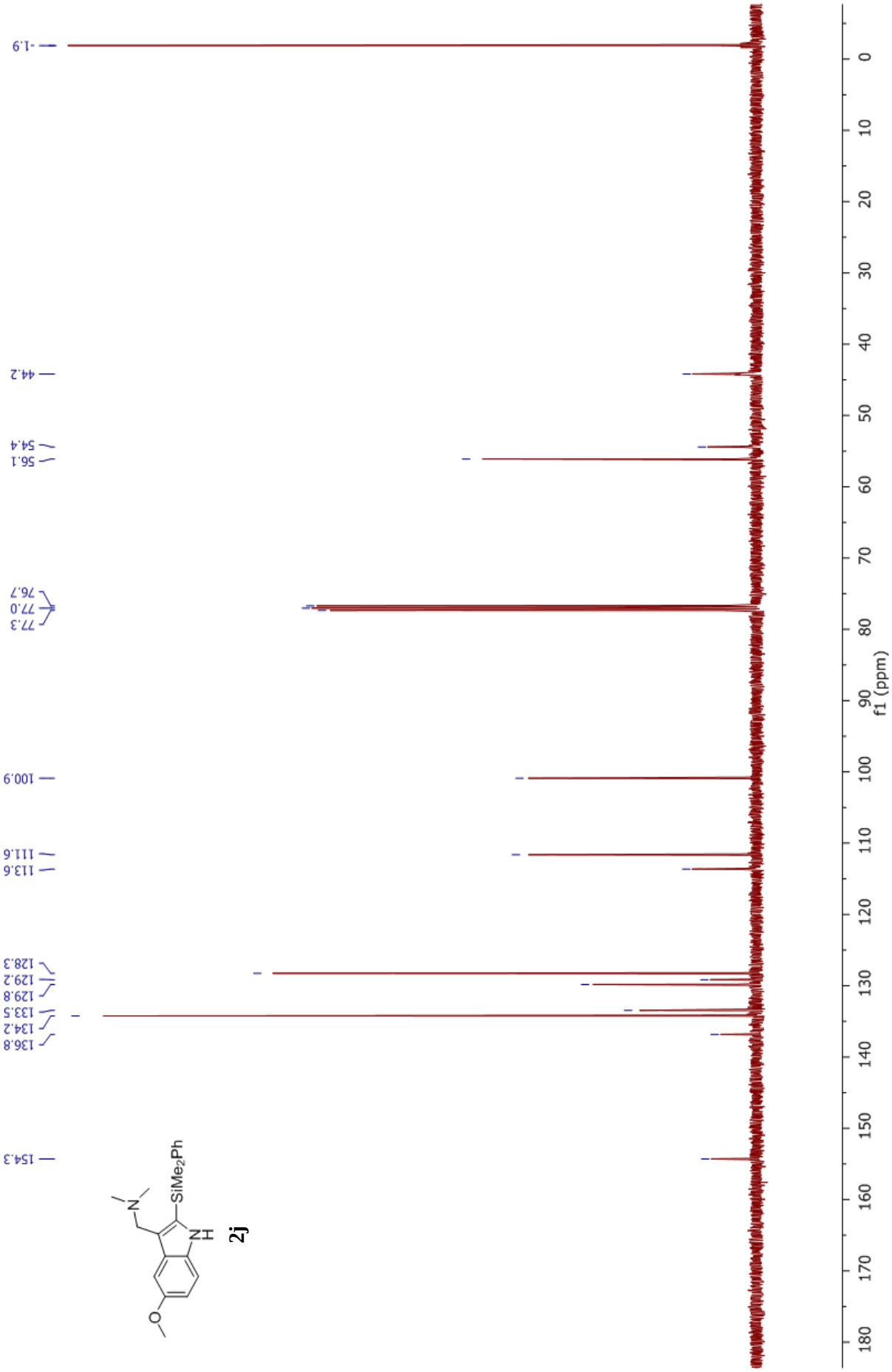

-2.9
7.3
7.6
44.9
54.9
76.7
77.0
77.3
110.8
119.3
119.5
121.2
122.2
129.0
135.1
138.2
f1 (ppm)
NMe2
SiMe2Et
H
N
2d

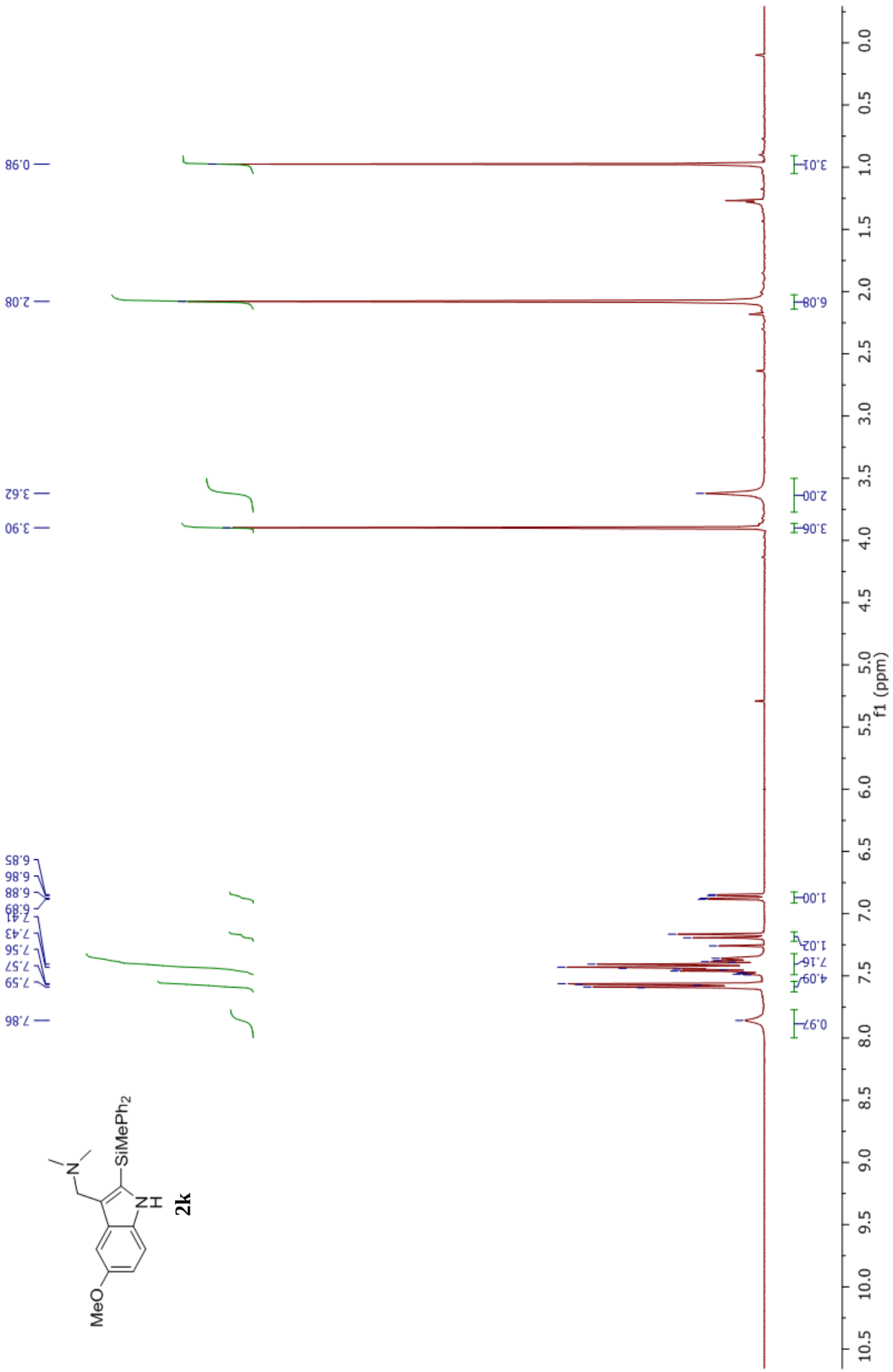

SiEt3
N
H
2e
f1 (ppm)

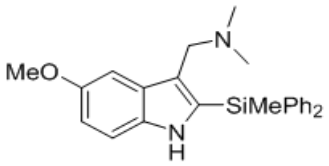

3.7
7.4
44.8
55.0
76.6
77.0
77.4
110.7
119.5
119.7
122.4
129.0
138.4
SiEt3
N
H
2e
f1 (ppm)


0.67
2.23
3.75
3.90
6.84
6.86
7.20
7.22
7.26
7.42
7.43
7.60
7.61
8.02
6.21
6.25
2.00
3.12
1.00
1.02
1.06
3.05
2.00
0.93
f1 (ppm)
SiMe2Ph
N
H
N
O

2j

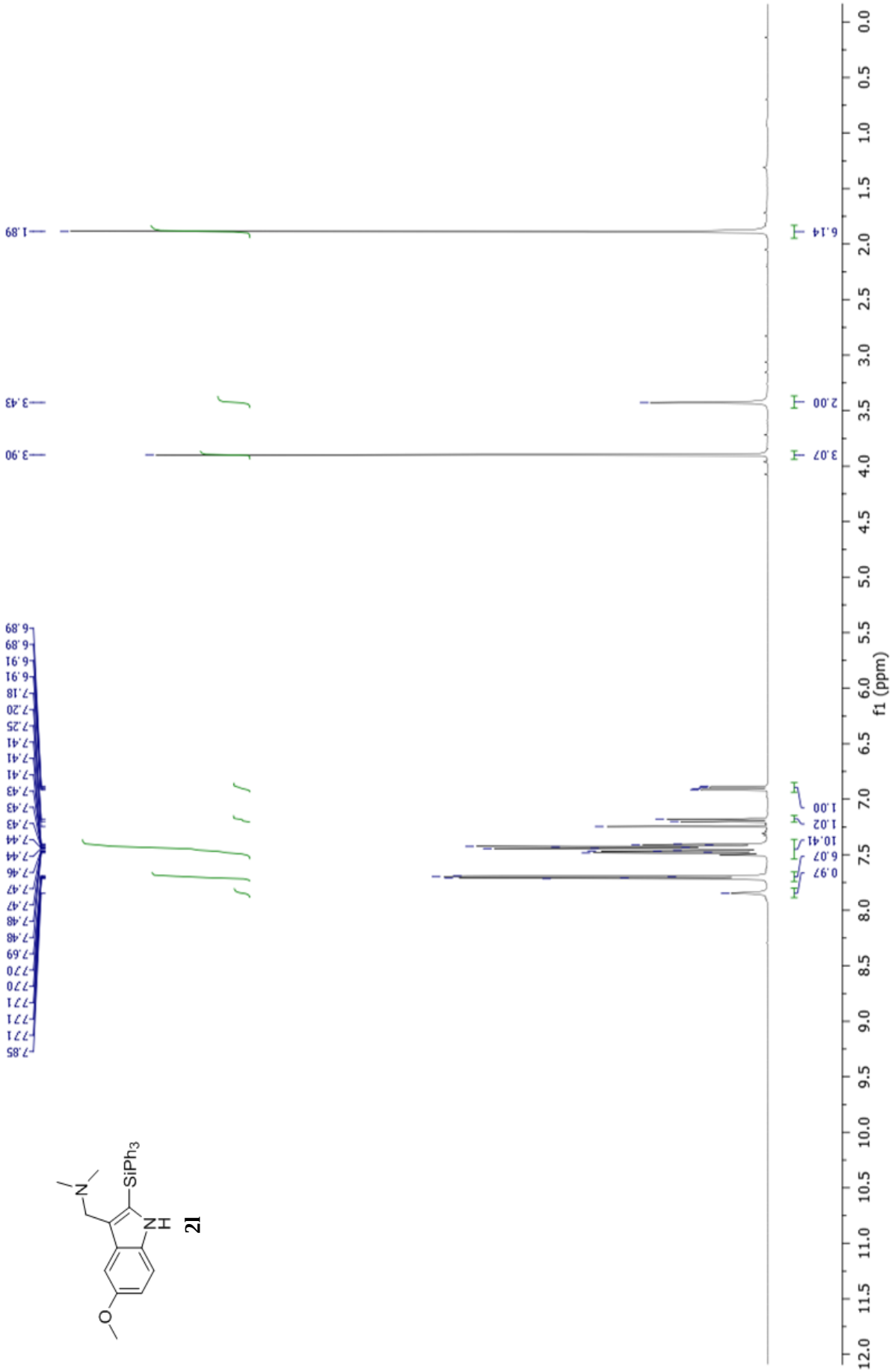

-1.9
44.2
54.4
56.1
76.7
77.0
77.3
100.9
111.6
113.6
128.3
129.2
129.8
133.5
134.2
136.8
154.3
SiMe2Ph
N
H
O
2j
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


0.98
2.08
3.62
3.90
6.85
6.86
6.88
6.89
7.41
7.43
7.56
7.57
7.59
7.86
3.01
6.08
2.00
3.06
1.00
1.02
7.16
4.09
0.97
f1 (ppm)
SiMePh2
N
H
MeO
2k

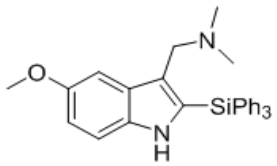

MeO
N
SiMePh2
N
H

2k

153.9
135.5
135.0
134.3
133.7
132.1
129.7
129.5
128.1
113.3
111.5
101.2
77.3
77.0
76.7
55.9
55.2
45.1
-3.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

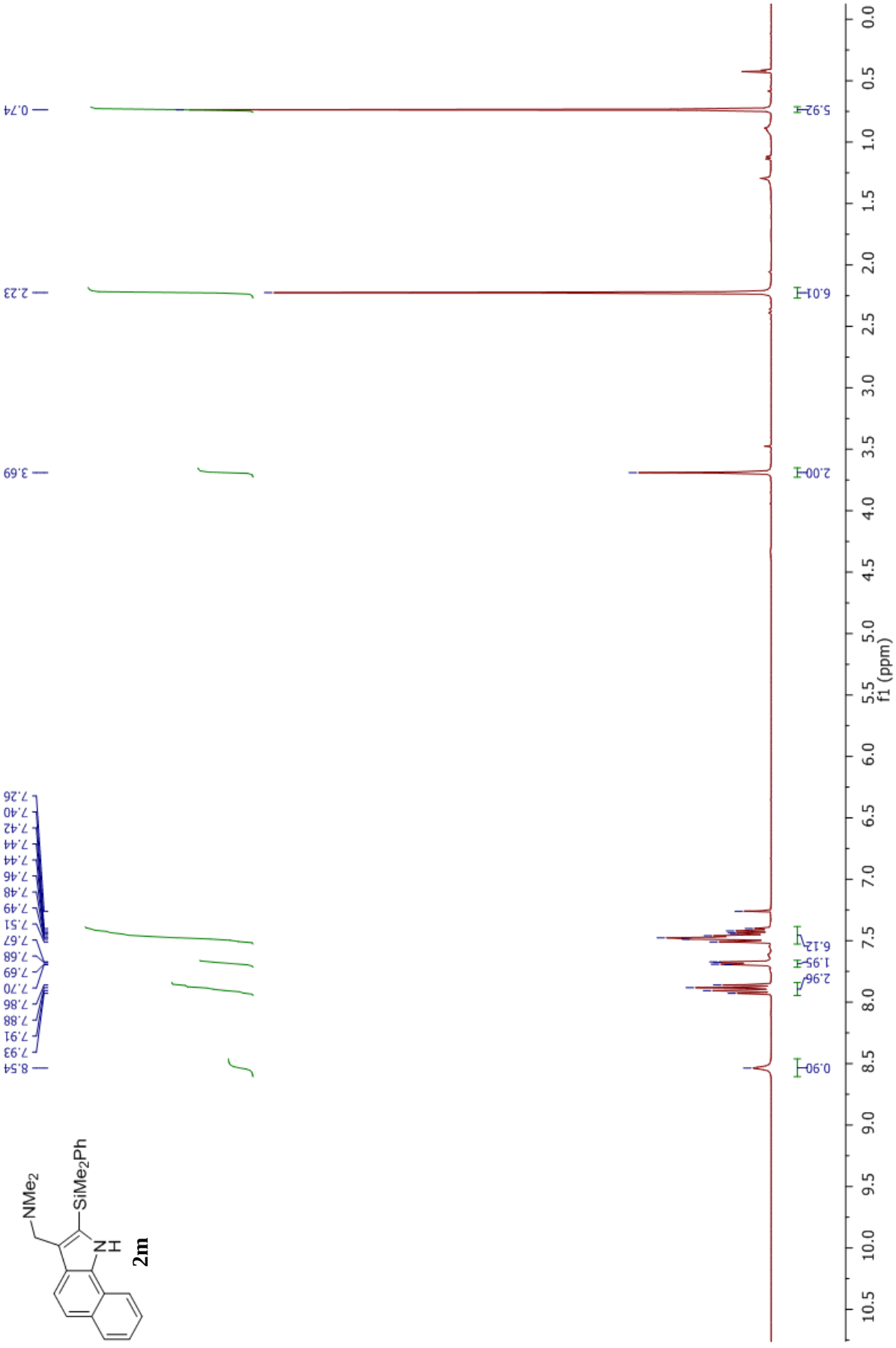


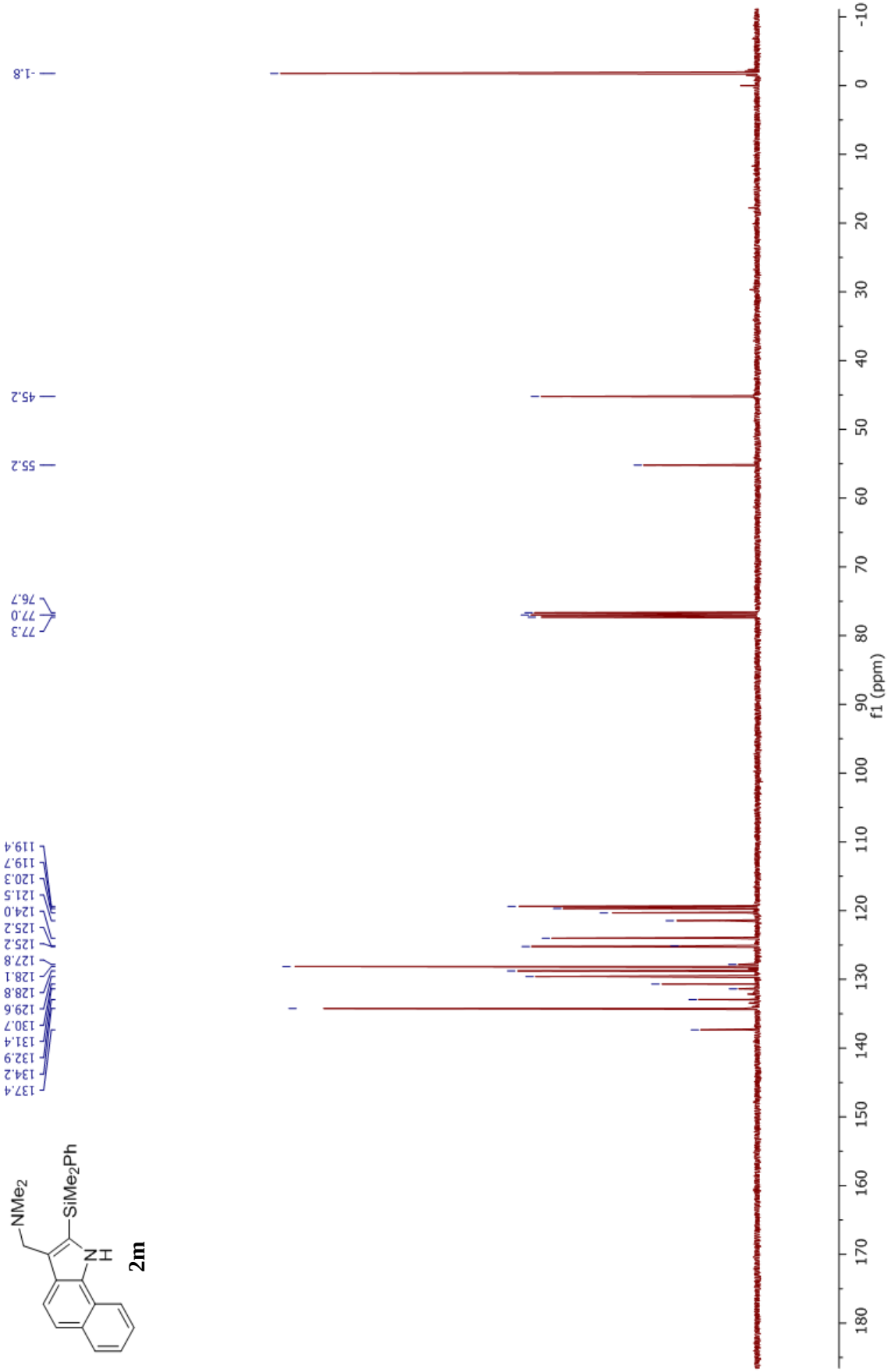
2l

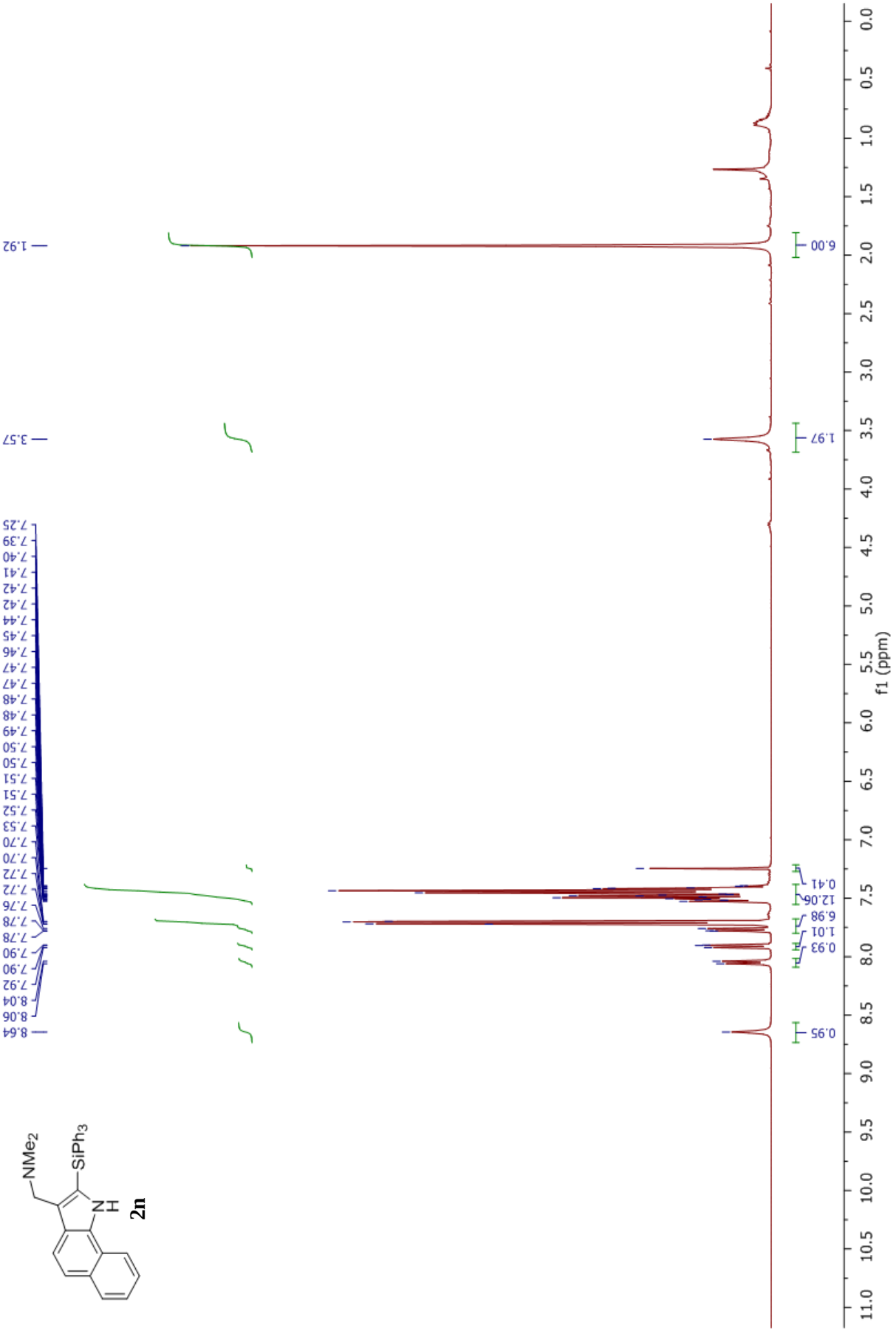

O
N
SiPh3
N
H

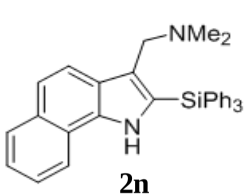
2l

153.9
136.3
134.1
133.5
129.9
129.6
128.1
113.7
111.6
102.0
77.4
77.1
76.8
56.0
55.6
45.0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


0.74
2.23
3.69
7.26
7.40
7.42
7.44
7.44
7.46
7.48
7.49
7.51
7.67
7.68
7.69
7.70
7.86
7.88
7.91
7.93
8.54
5.92
6.01
2.00
6.12
1.95
2.96
0.90
f1 (ppm)
NMe2
SiMe2Ph
H
N
2m


NMe2
SiMe2Ph
N
H
2m
-1.8
45.2
55.2
76.7
77.0
77.3
119.4
119.7
120.3
121.5
124.0
125.2
125.2
127.8
128.1
128.8
129.6
130.7
131.4
132.9
134.2
137.4
f1 (ppm)


1.92
3.57
8.64
8.06
8.04
7.92
7.90
7.90
7.78
7.78
7.76
7.72
7.72
7.70
7.70
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.42
7.42
7.41
7.40
7.39
7.25
6.00
1.97
0.41
12.06
6.98
1.01
0.93
0.95
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
f1 (ppm)
NMe2
SiPh3
H
N
2n



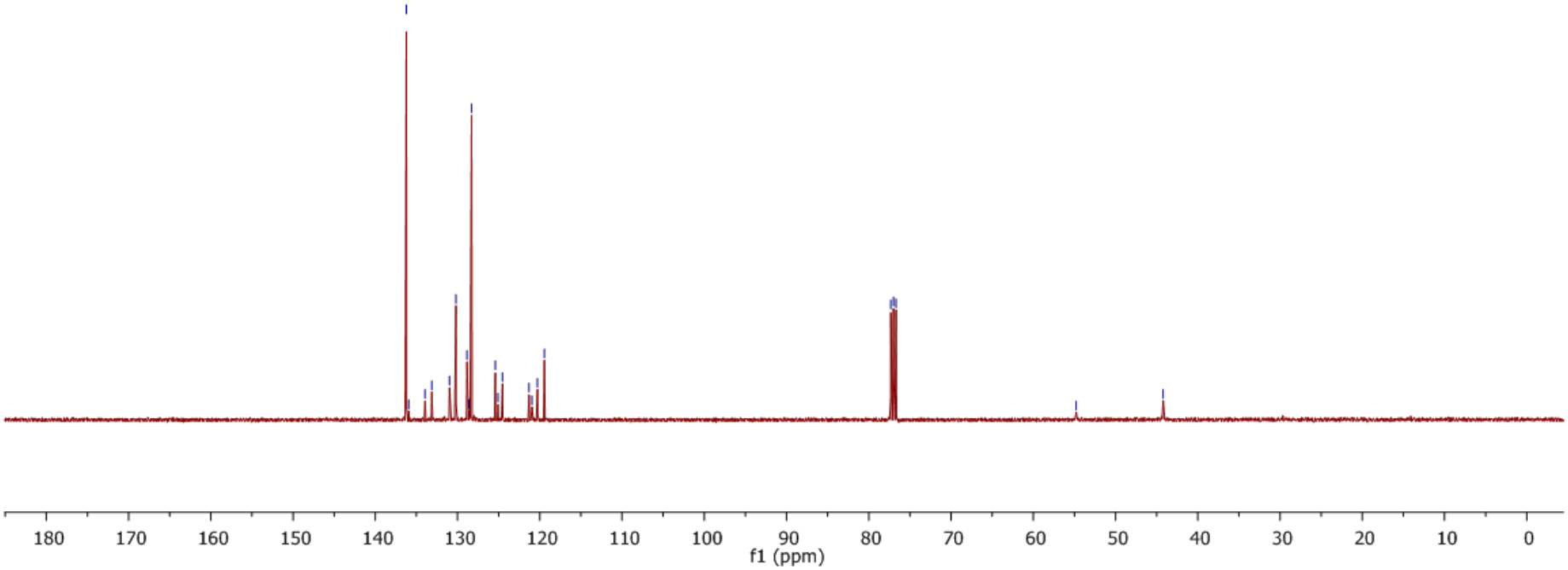
2n

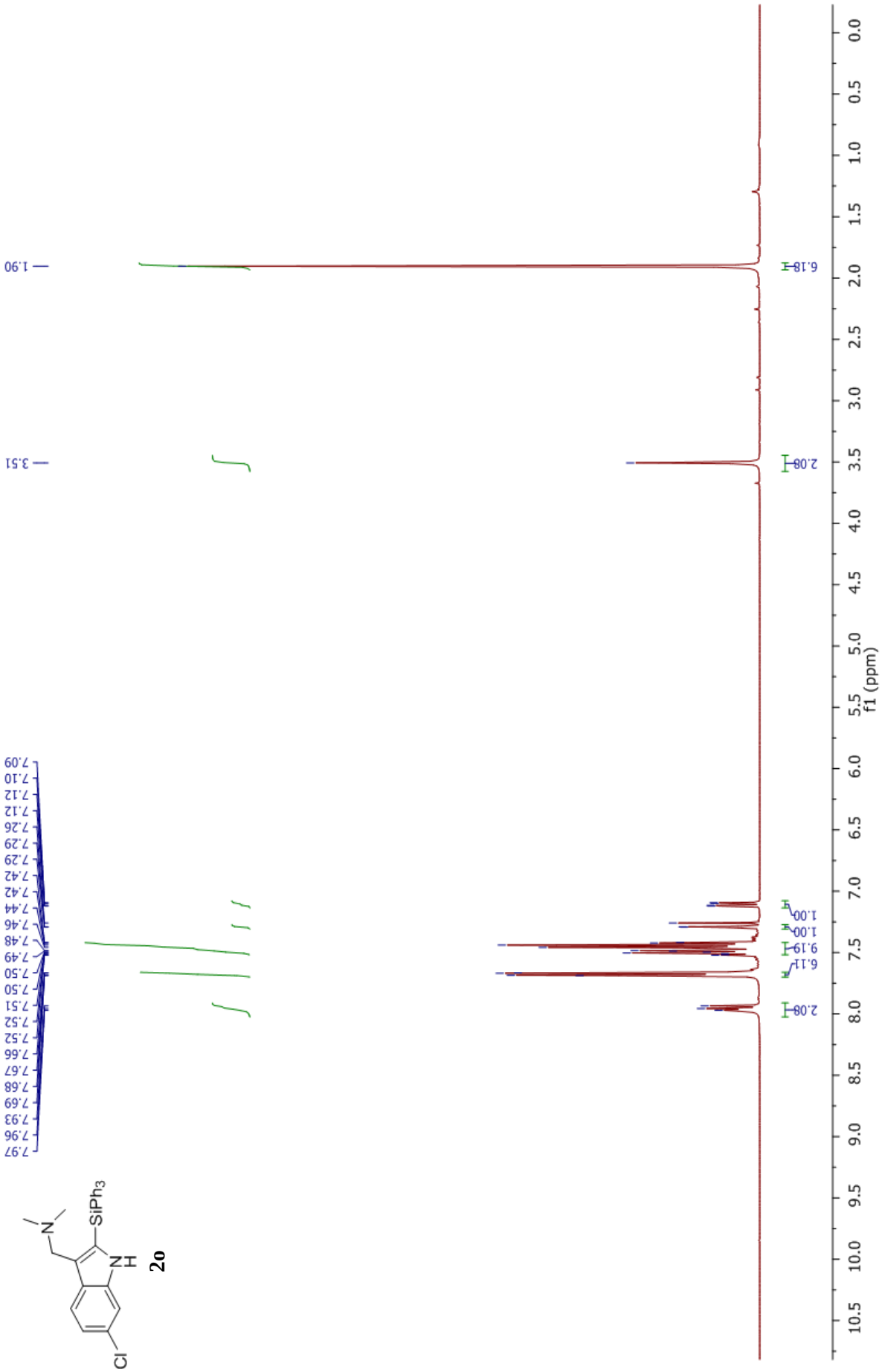
136.2
135.9
133.9
133.1
131.0
130.2
128.8
128.6
128.3
125.4
125.1
124.5
121.3
120.9
120.3
119.4

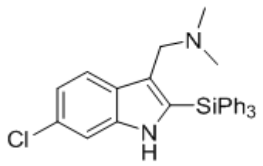
77.3
77.0
76.7

54.8

44.2

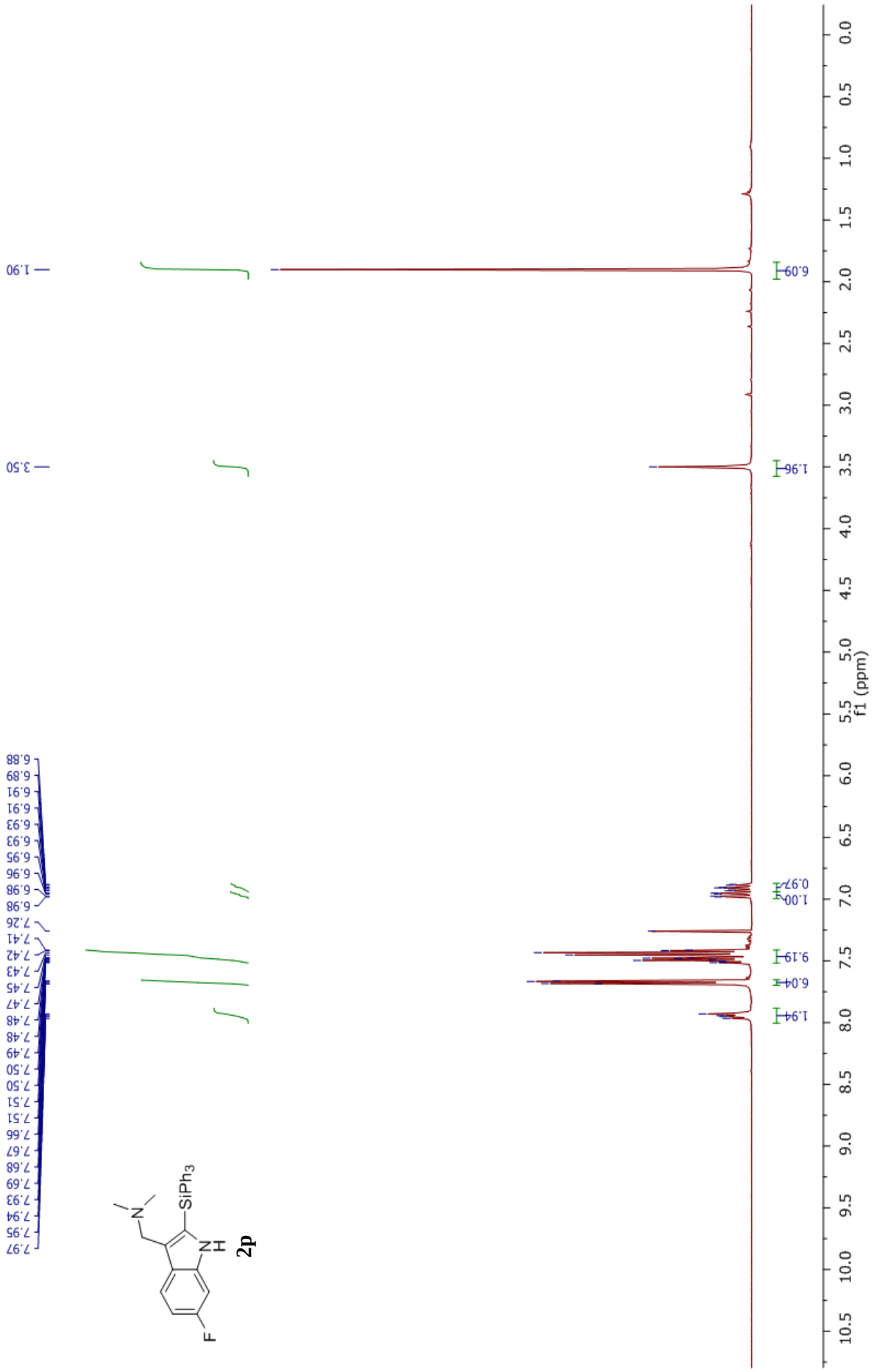


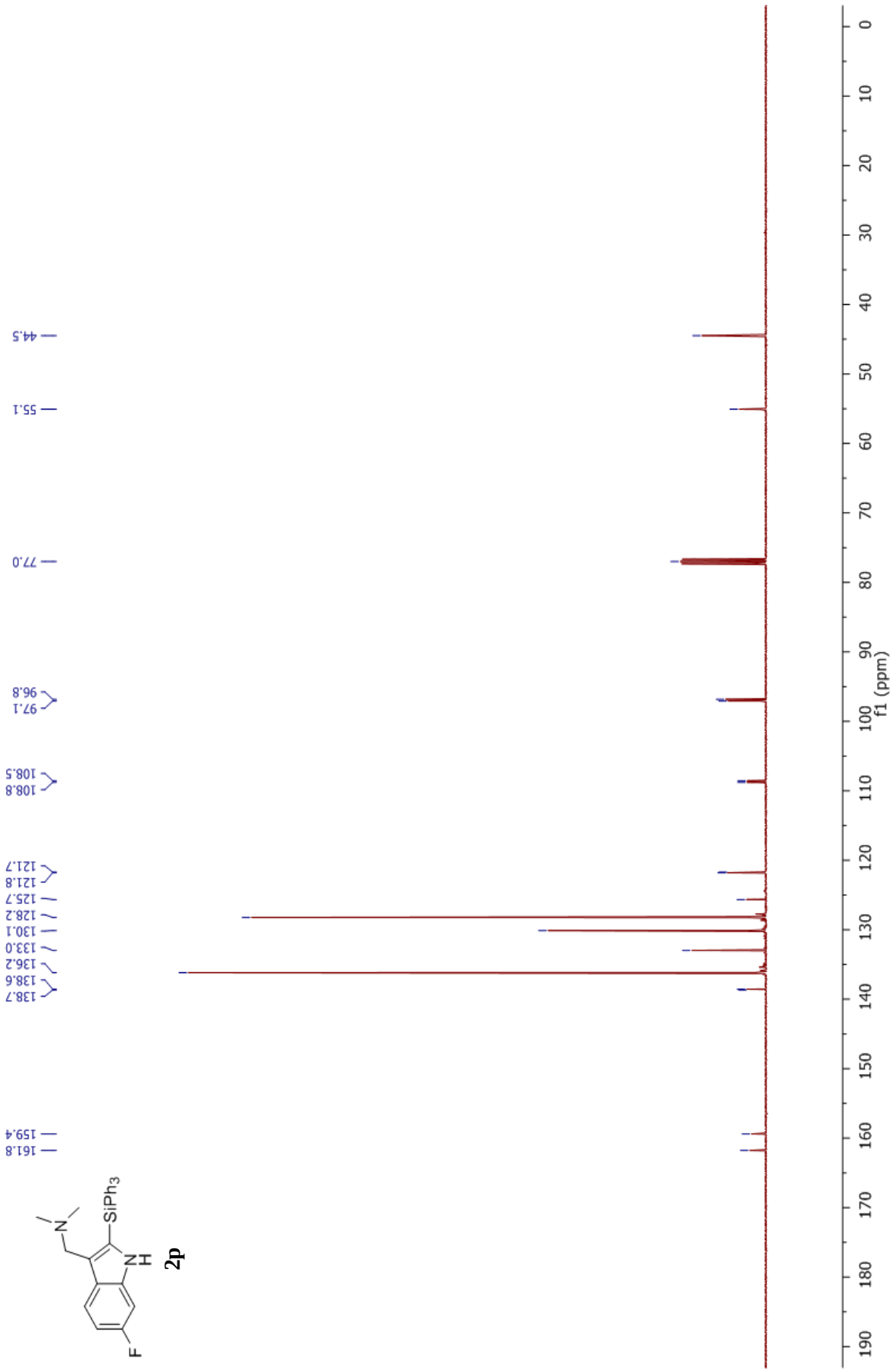

1.90
3.51
7.97
7.96
7.93
7.69
7.68
7.67
7.66
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.46
7.44
7.42
7.42
7.29
7.29
7.26
7.12
7.12
7.10
7.09
6.18
2.08
1.00
1.00
9.19
6.11
2.08
f1 (ppm)
SiPh3
N
H
N
Cl
2o

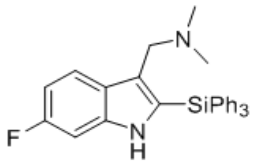

N
SiPh3
Cl
N
H

2o

138.9
136.2
135.0
132.8
130.2
129.1
128.3
127.8
127.5
121.7
120.5
110.8
77.3
77.0
76.7
54.9
44.4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

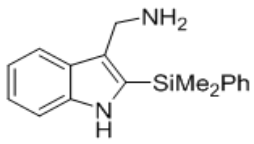

1.90
3.50
7.97
7.95
7.94
7.93
7.69
7.68
7.67
7.66
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.45
7.43
7.42
7.41
7.26
6.98
6.98
6.96
6.95
6.93
6.93
6.91
6.91
6.89
6.88
6.09
1.96
1.00
0.97
9.19
6.04
1.94
SiPh3
N
H
N
F
2p
f1 (ppm)


f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
44.5
55.1
77.0
96.8
97.1
108.5
108.8
121.7
121.8
125.7
128.2
130.1
133.0
136.2
138.6
138.7
159.4
161.8
SiPh3
N
H
F
2p


N
SiPh3
F
N
H

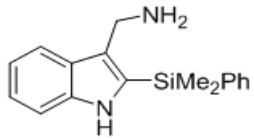
2p

-119.9
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
f1 (ppm)


NH2
SiMe2Ph
N
H

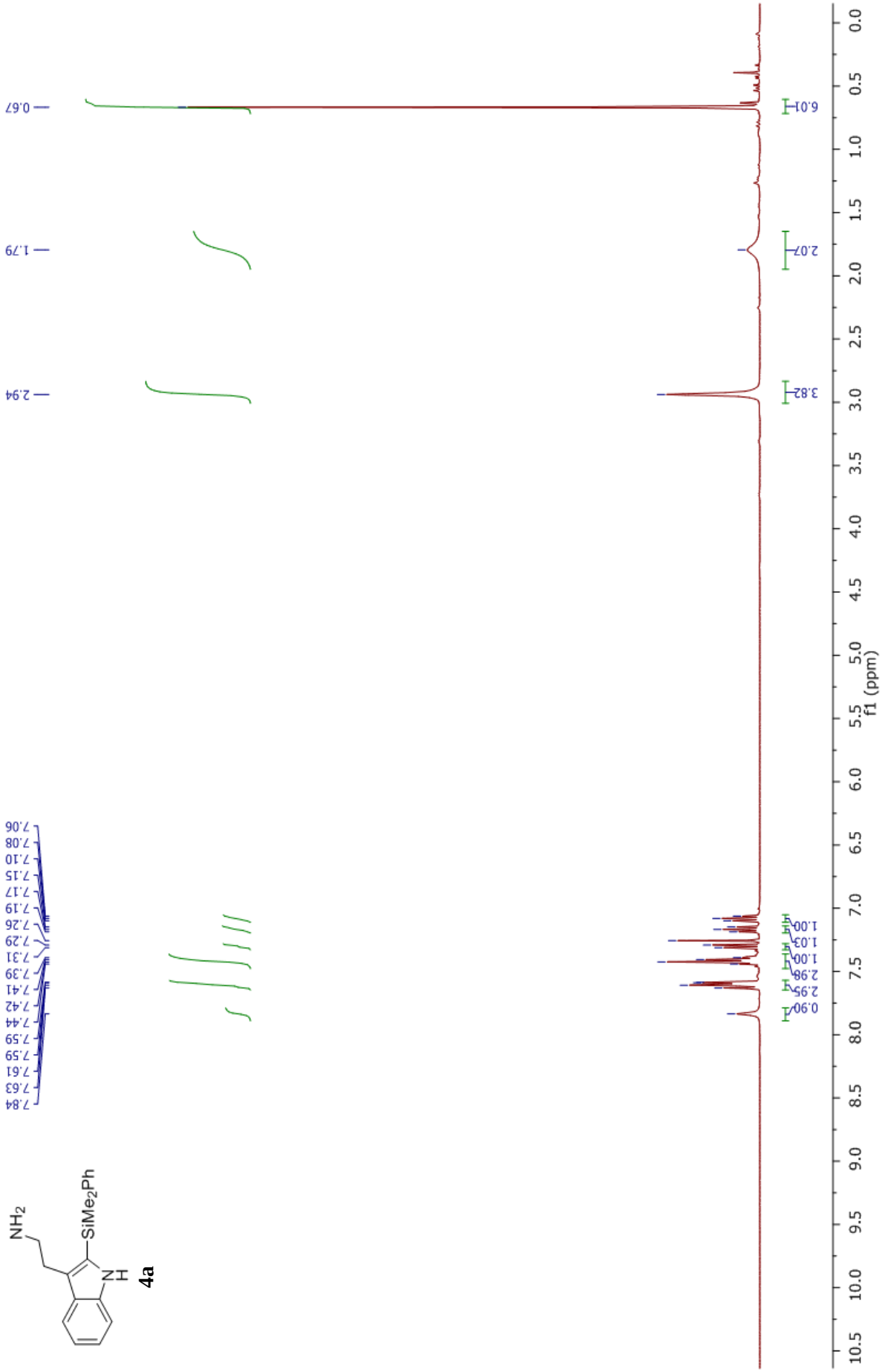
3

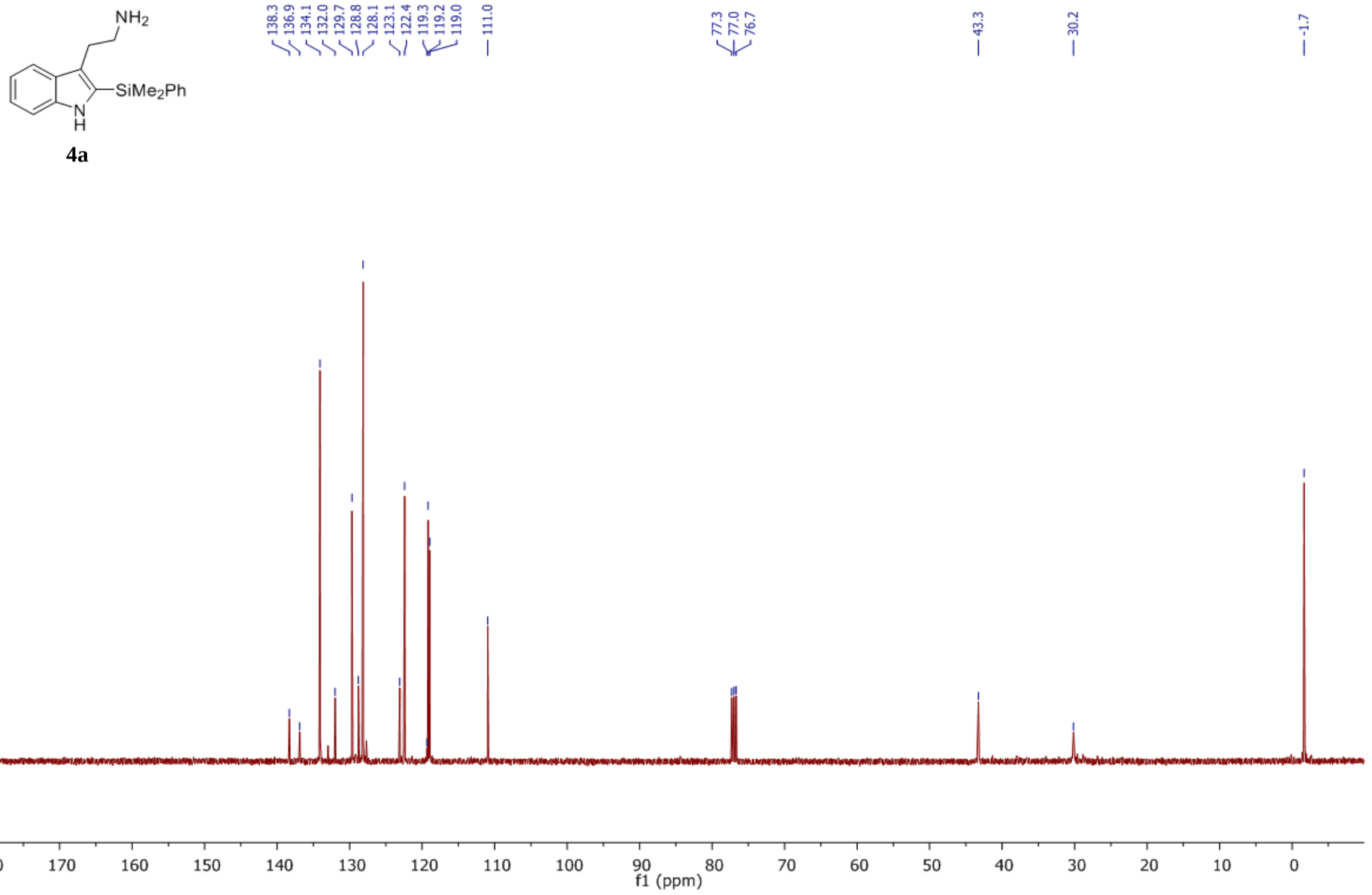
7.84
7.70
7.68
7.61
7.60
7.59
7.45
7.43
7.42
7.40
7.33
7.31
7.26
7.21
7.19
7.17
7.14
7.12
7.10
4.02
1.49
0.68
0.91
0.98
1.96
2.89
1.00
1.02
1.02
1.98
2.23
5.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


NH2
SiMe2Ph
N
H

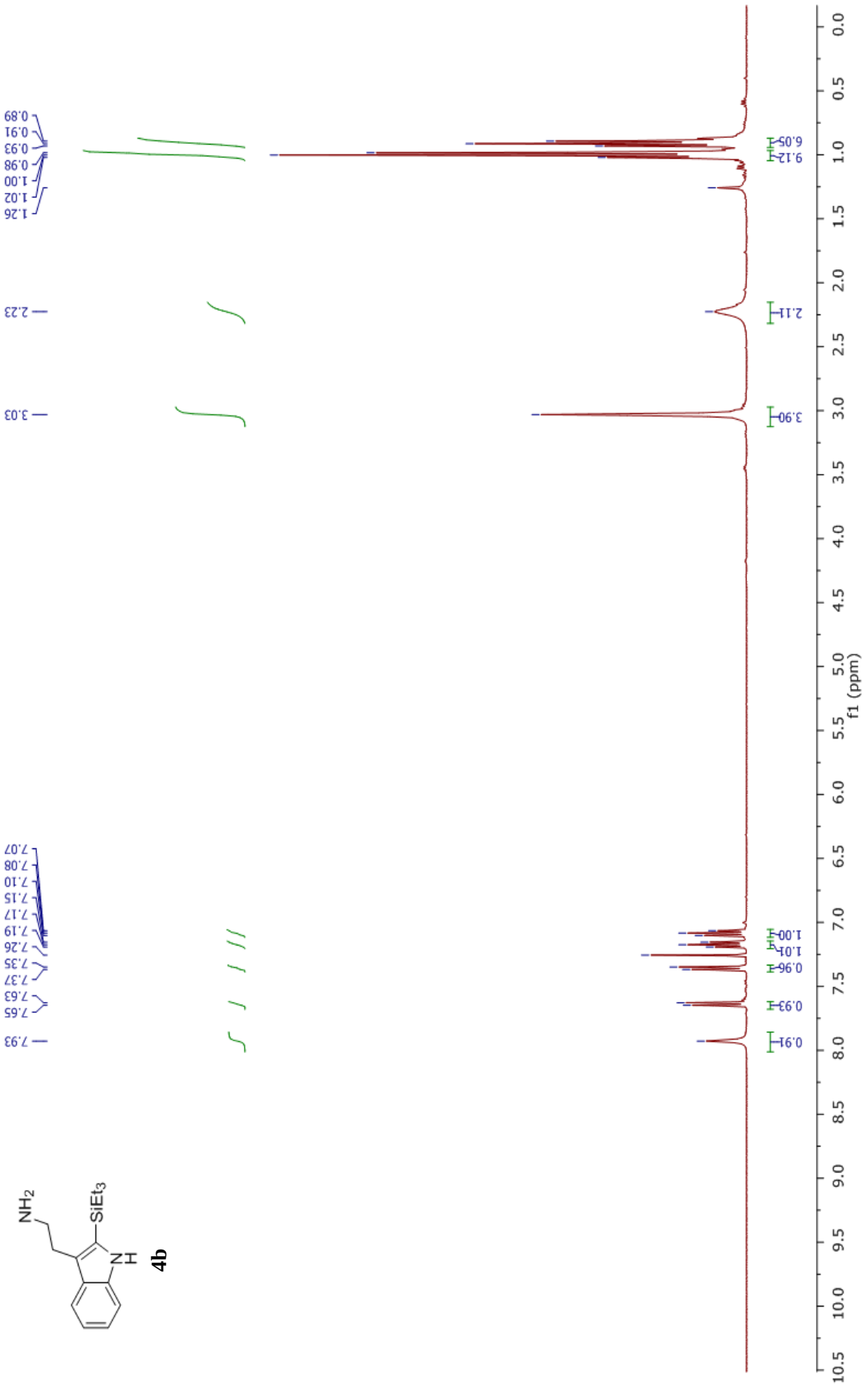
3

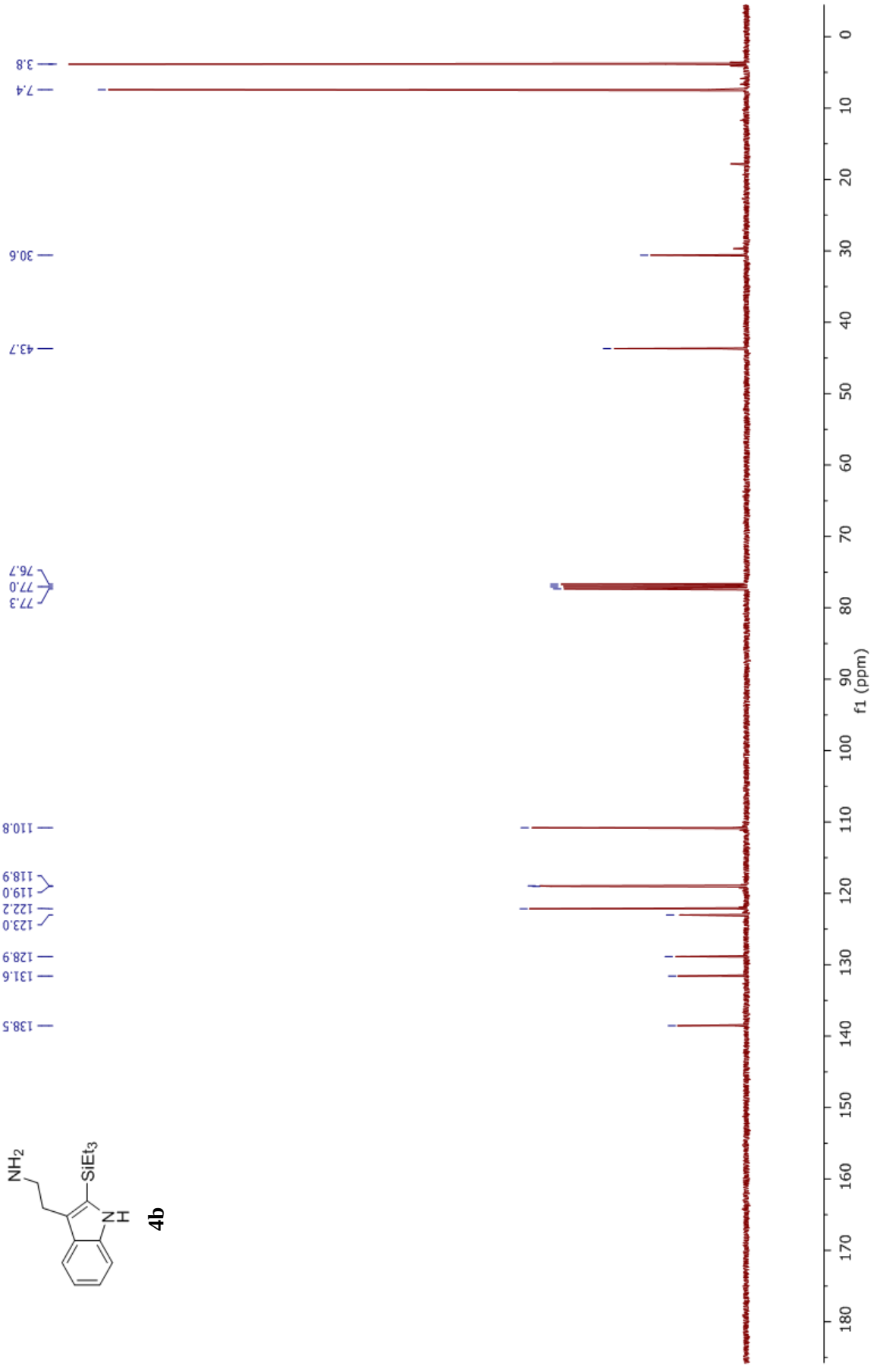
138.3
136.8
134.0
132.0
129.8
128.2
128.0
127.6
122.6
119.5
118.6
111.0
77.3
77.0
76.7
37.6
-1.7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

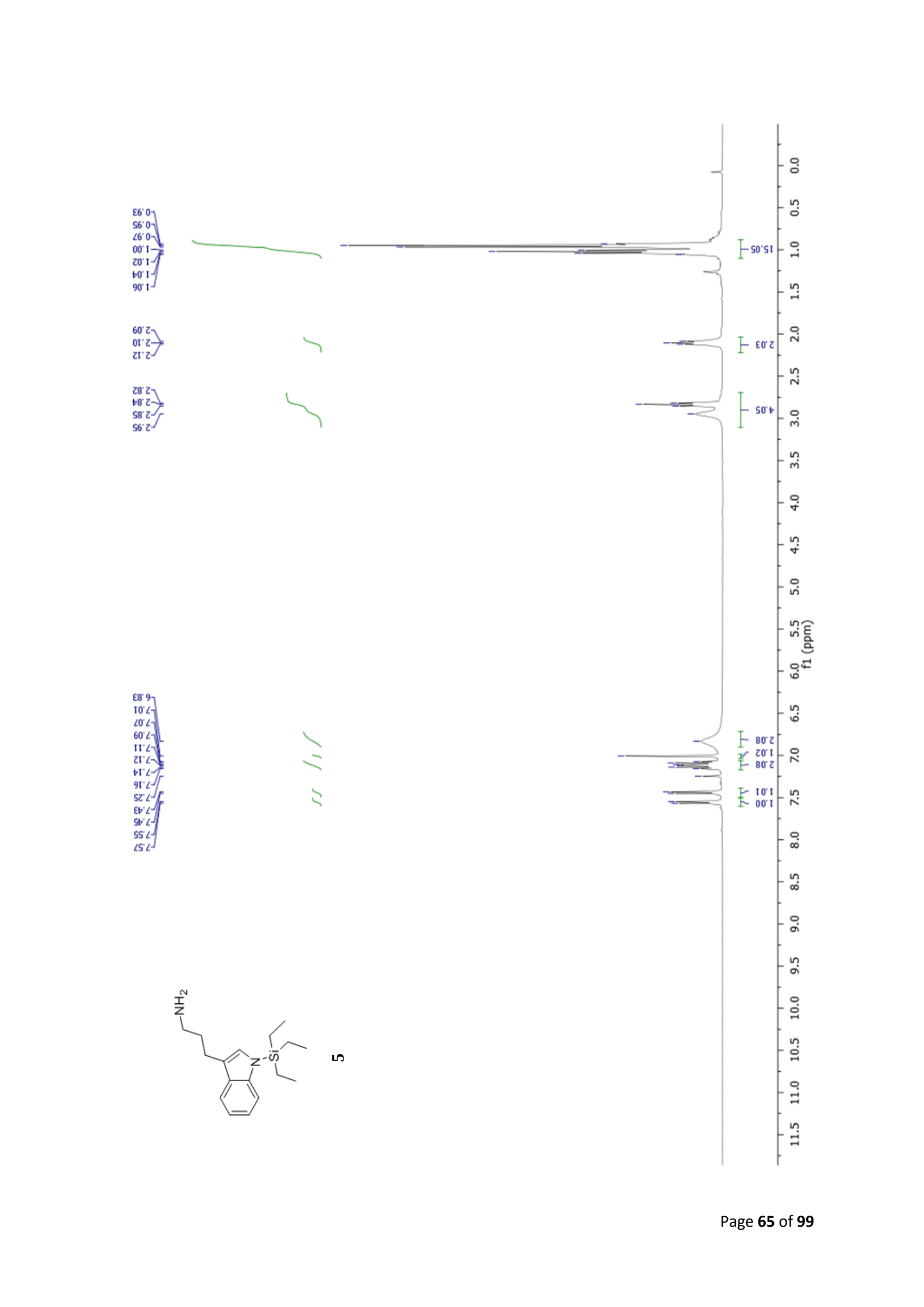

NH2
SiMe2Ph
H
N
4a
f1 (ppm)

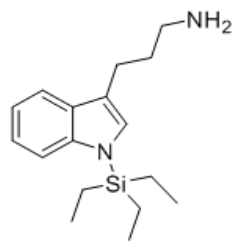

NH2
SiMe2Ph
N
H
138.3
136.9
134.1
132.0
129.7
128.8
128.1
123.1
122.4
119.3
119.2
119.0
111.0
77.3
77.0
76.7
43.3
30.2
-1.7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4a


NH2
SiEt3
H
N
4b
f1 (ppm)

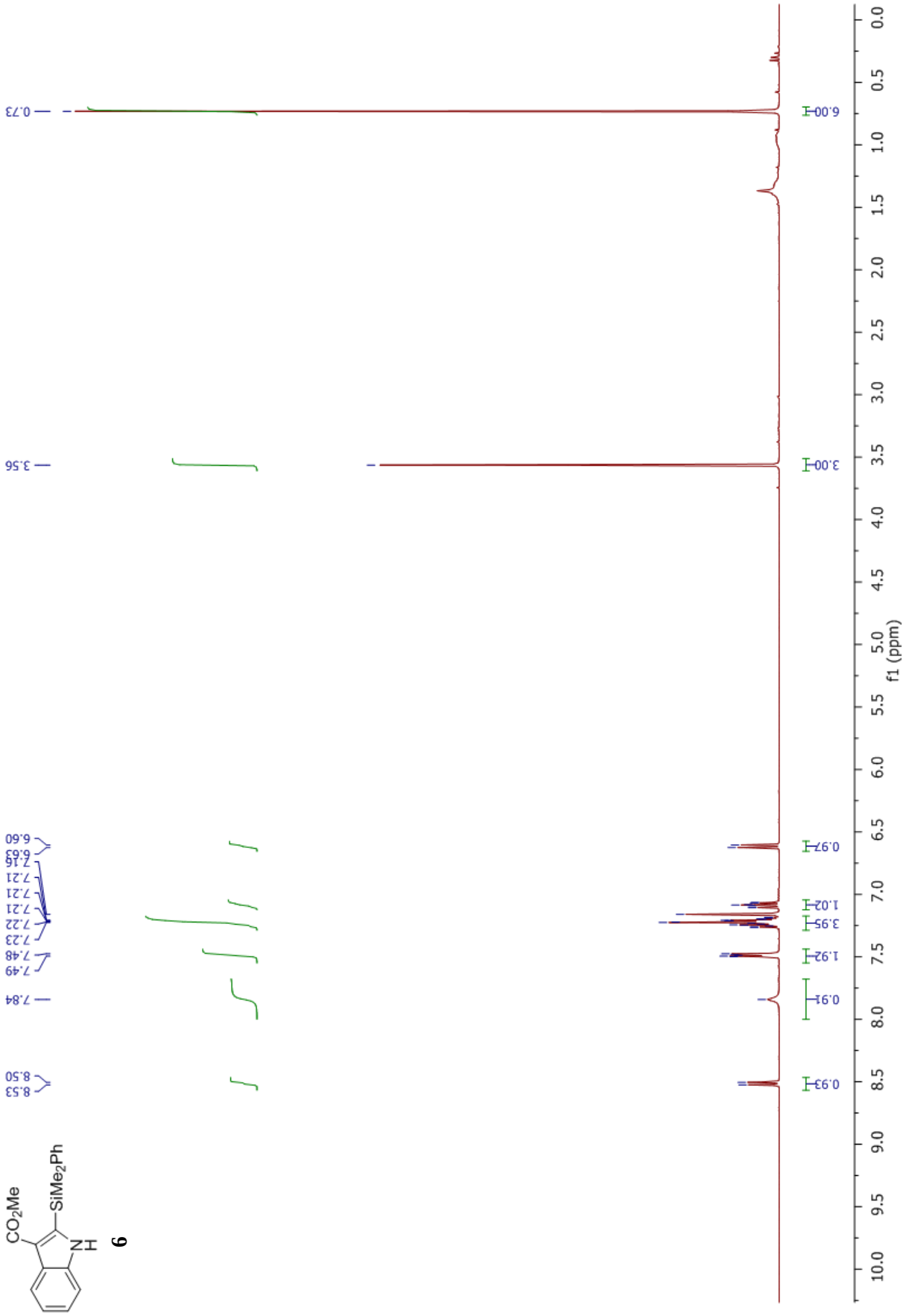

3.8
7.4
30.6
43.7
76.7
77.0
77.3
110.8
118.9
119.0
122.2
123.0
128.9
131.6
138.5
f1 (ppm)
NH2
SiEt3
H
N
4b

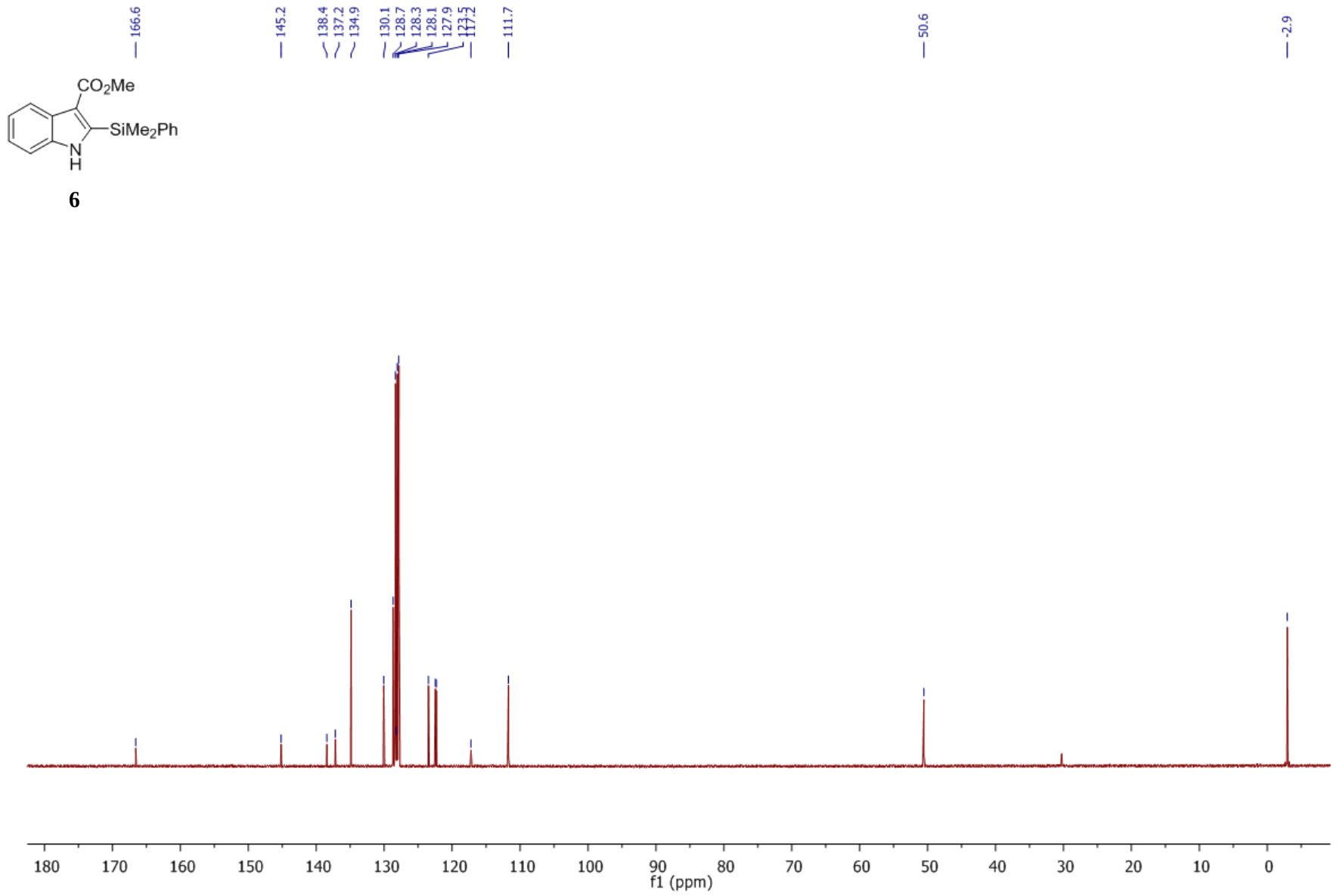

NH2
Si
N
5
f1 (ppm)


NH2
N
Si

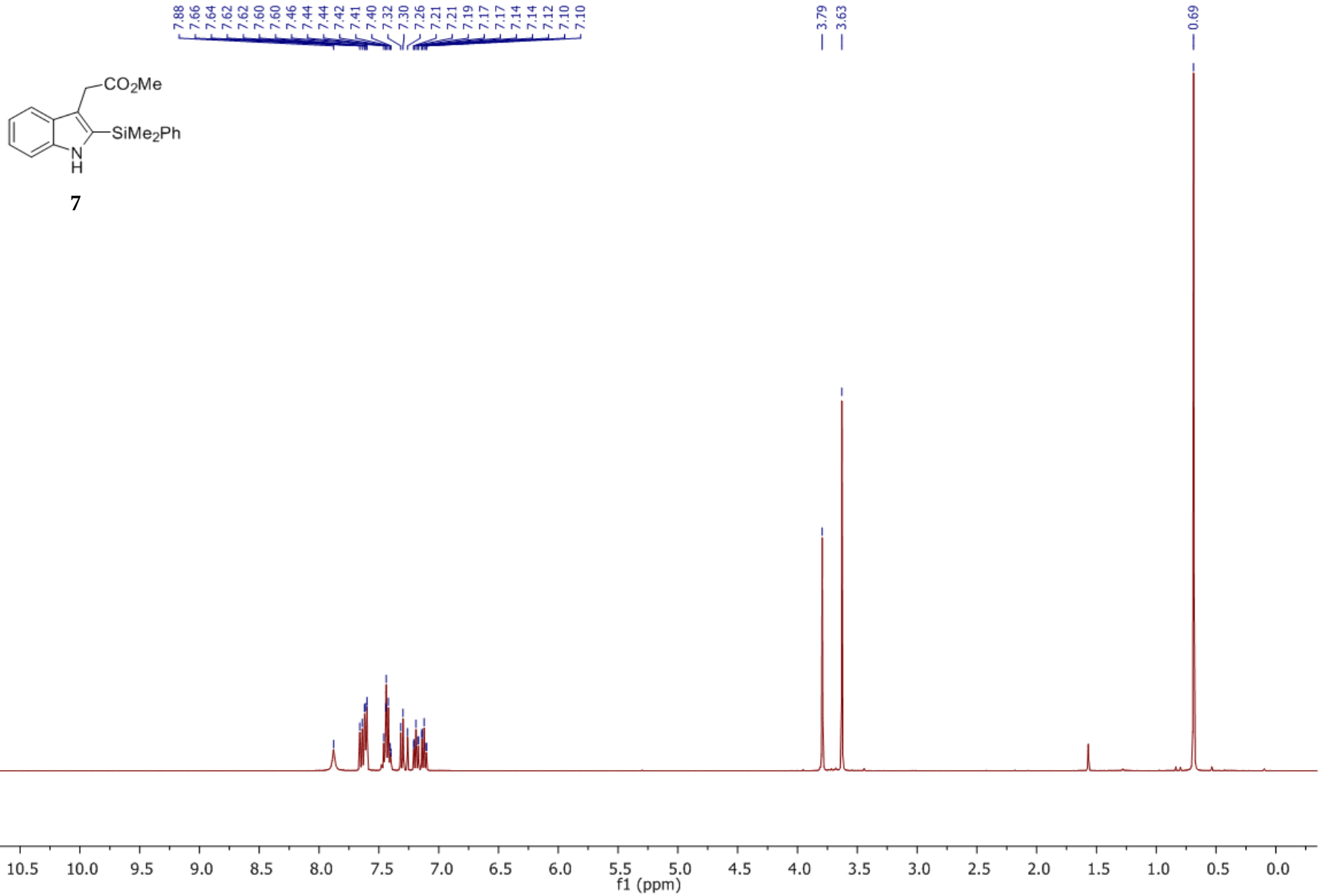
5

140.9
130.7
127.8
121.4
119.4
118.8
116.1
112.9
77.3
77.0
76.7
39.9
29.1
22.2
6.7
4.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

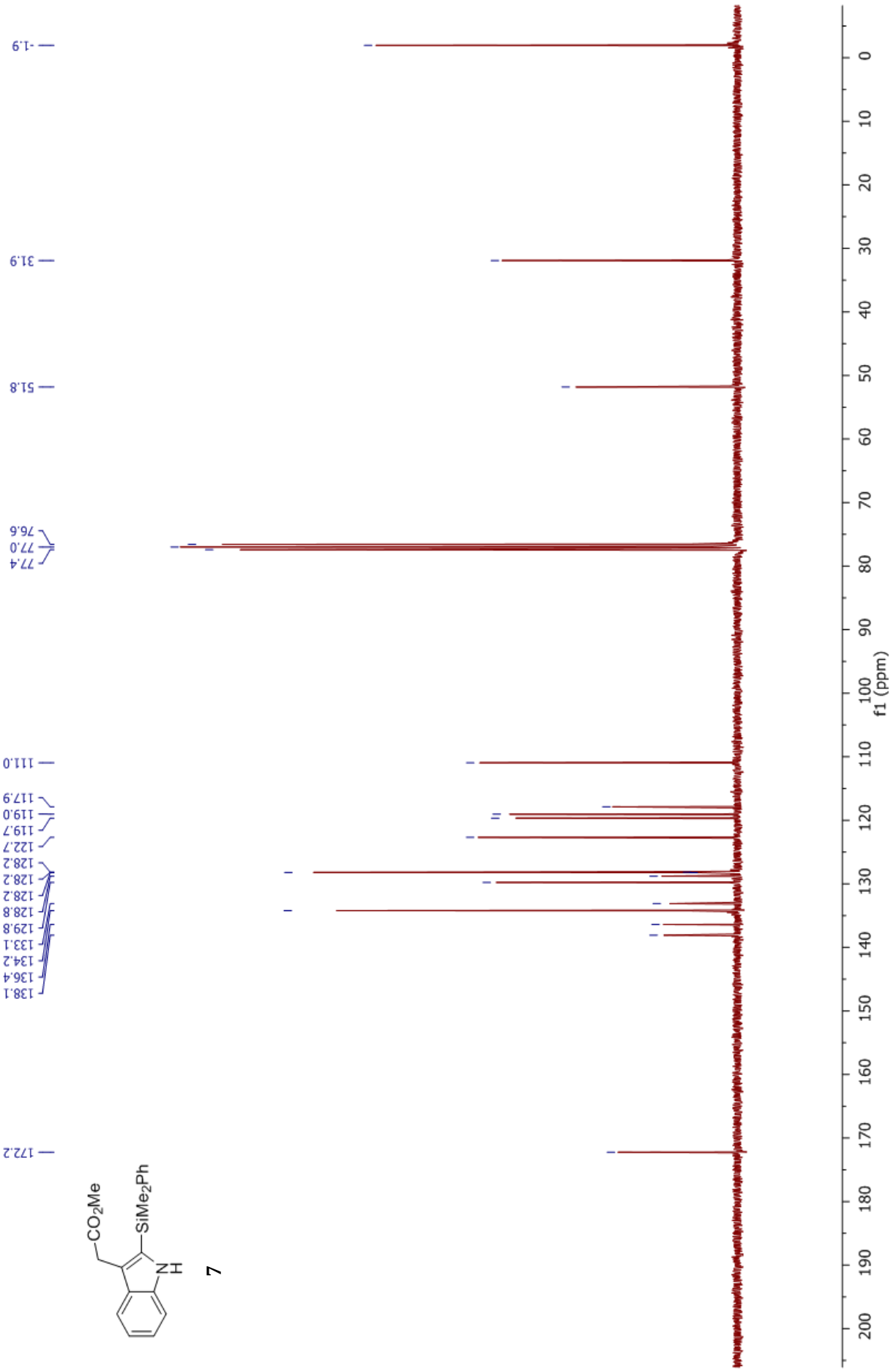

0.73
3.56
8.53
8.50
7.84
7.49
7.48
7.23
7.22
7.21
7.21
7.16
6.63
6.60
6.00
3.00
0.97
1.02
3.95
1.92
0.91
0.93
f1 (ppm)
CO2Me
SiMe2Ph
N
H
9

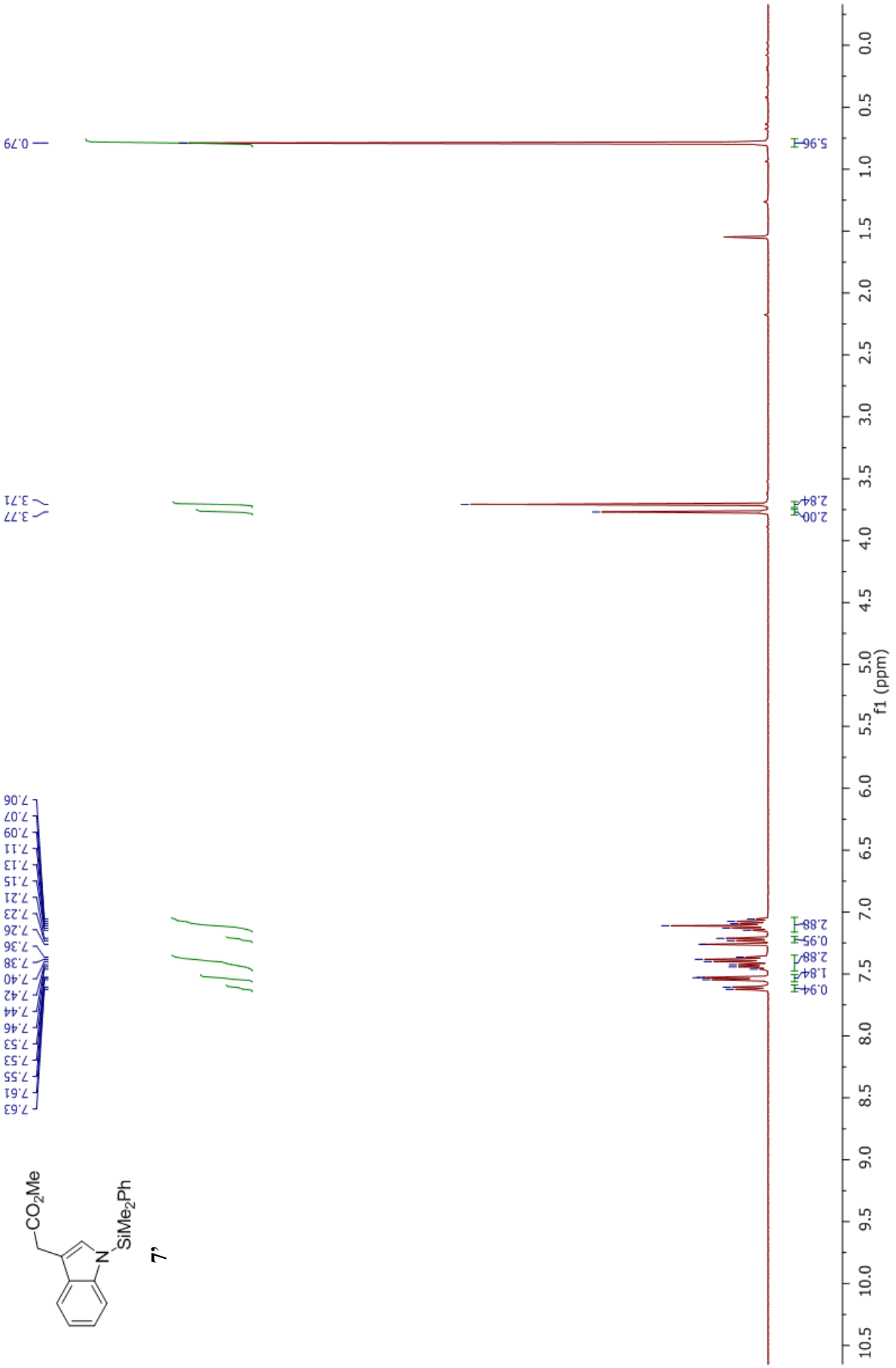

166.6
145.2
138.4
137.2
134.9
130.1
128.7
128.3
128.1
127.9
123.5
117.2
111.7
50.6
-2.9
CO2Me
SiMe2Ph
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

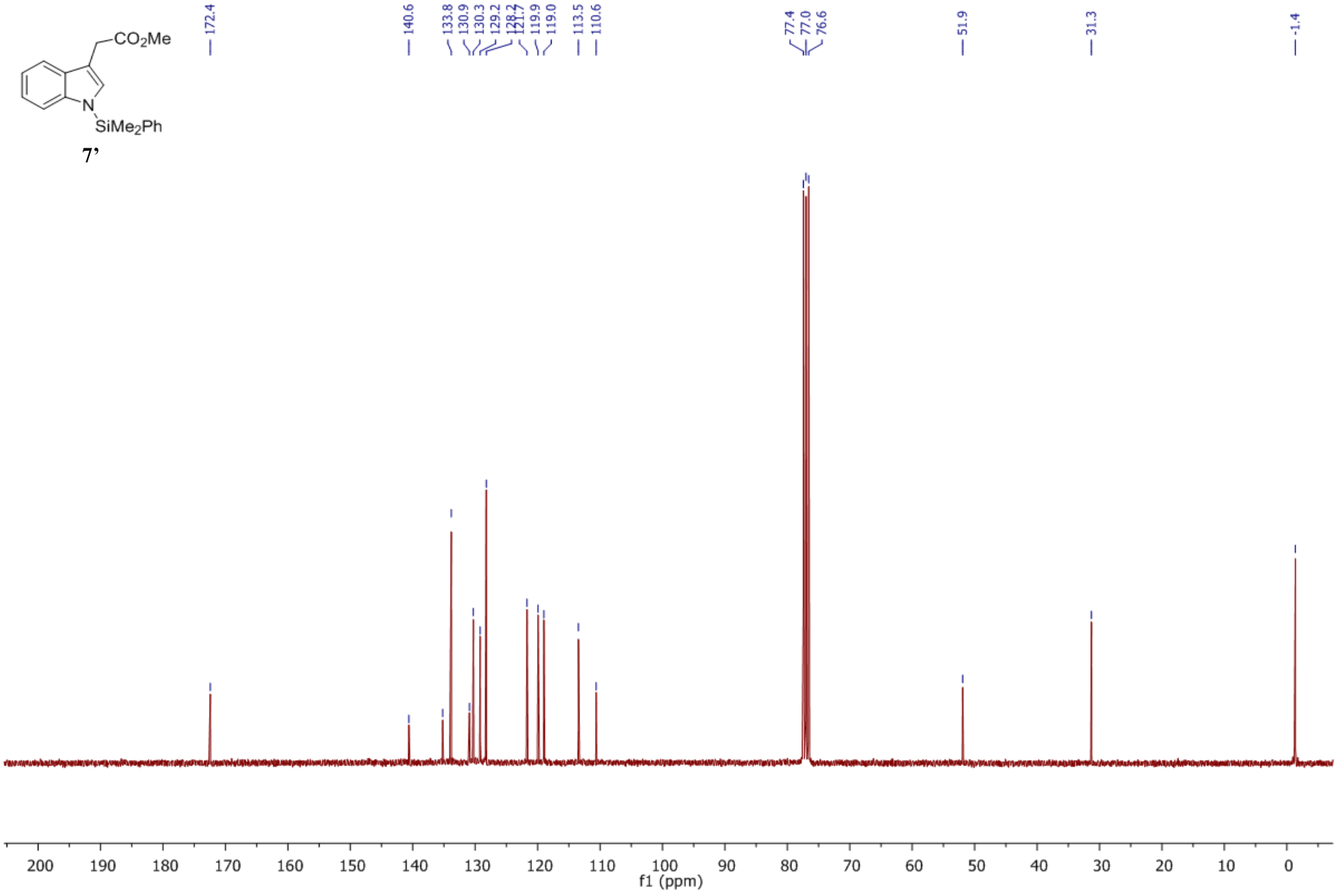
6


7.88
7.66
7.64
7.62
7.62
7.60
7.60
7.46
7.44
7.44
7.42
7.41
7.40
7.32
7.30
7.26
7.21
7.21
7.19
7.17
7.17
7.14
7.14
7.12
7.10
7.10
3.79
3.63
0.69
CO2Me
SiMe2Ph
N
H
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

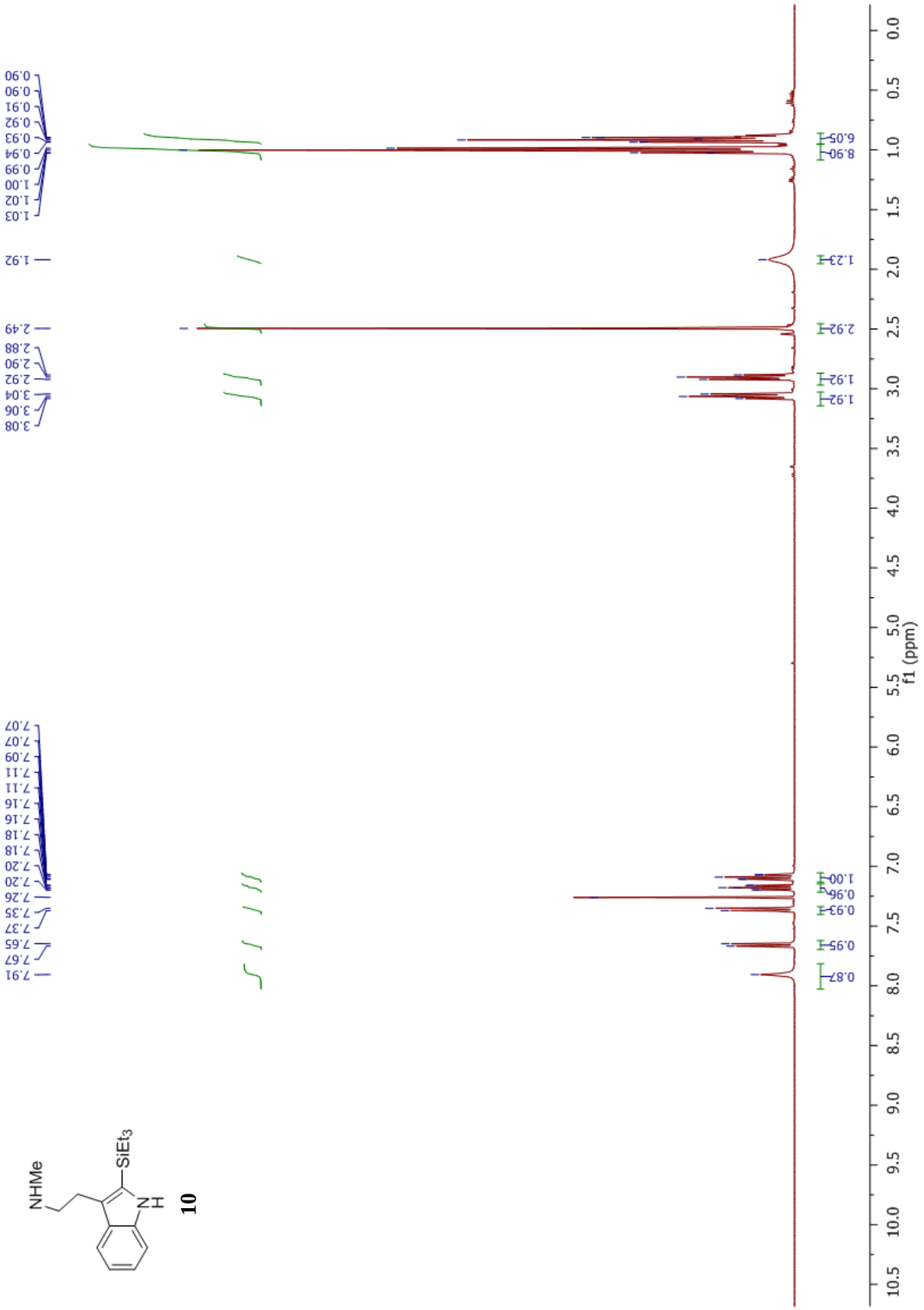
7

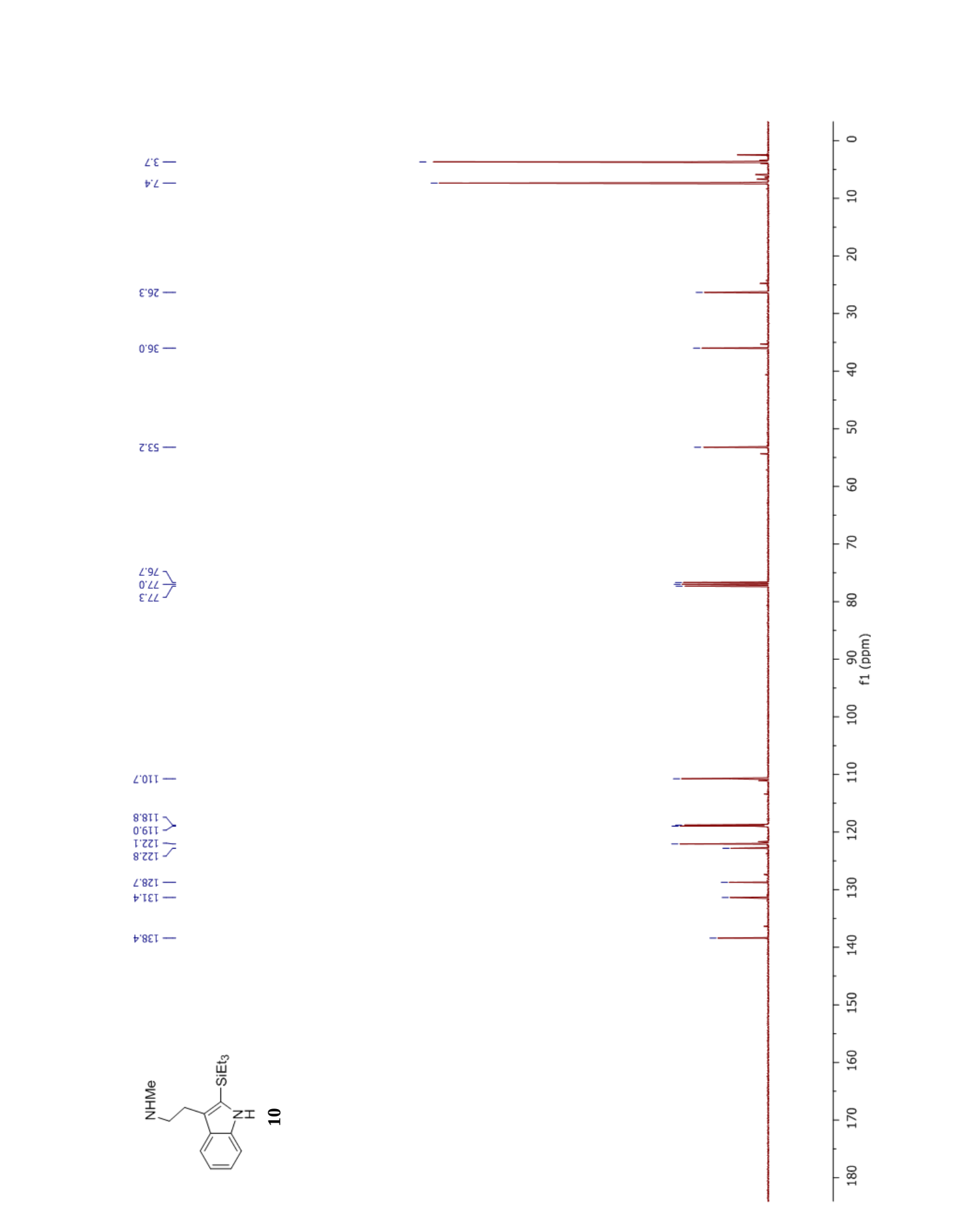

-1.9
31.9
51.8
76.6
77.0
77.4
111.0
117.9
119.0
119.7
122.7
128.2
128.2
128.2
128.8
129.8
133.1
134.2
136.4
138.1
172.2
CO2Me
SiMe2Ph
H
N
7
f1 (ppm)

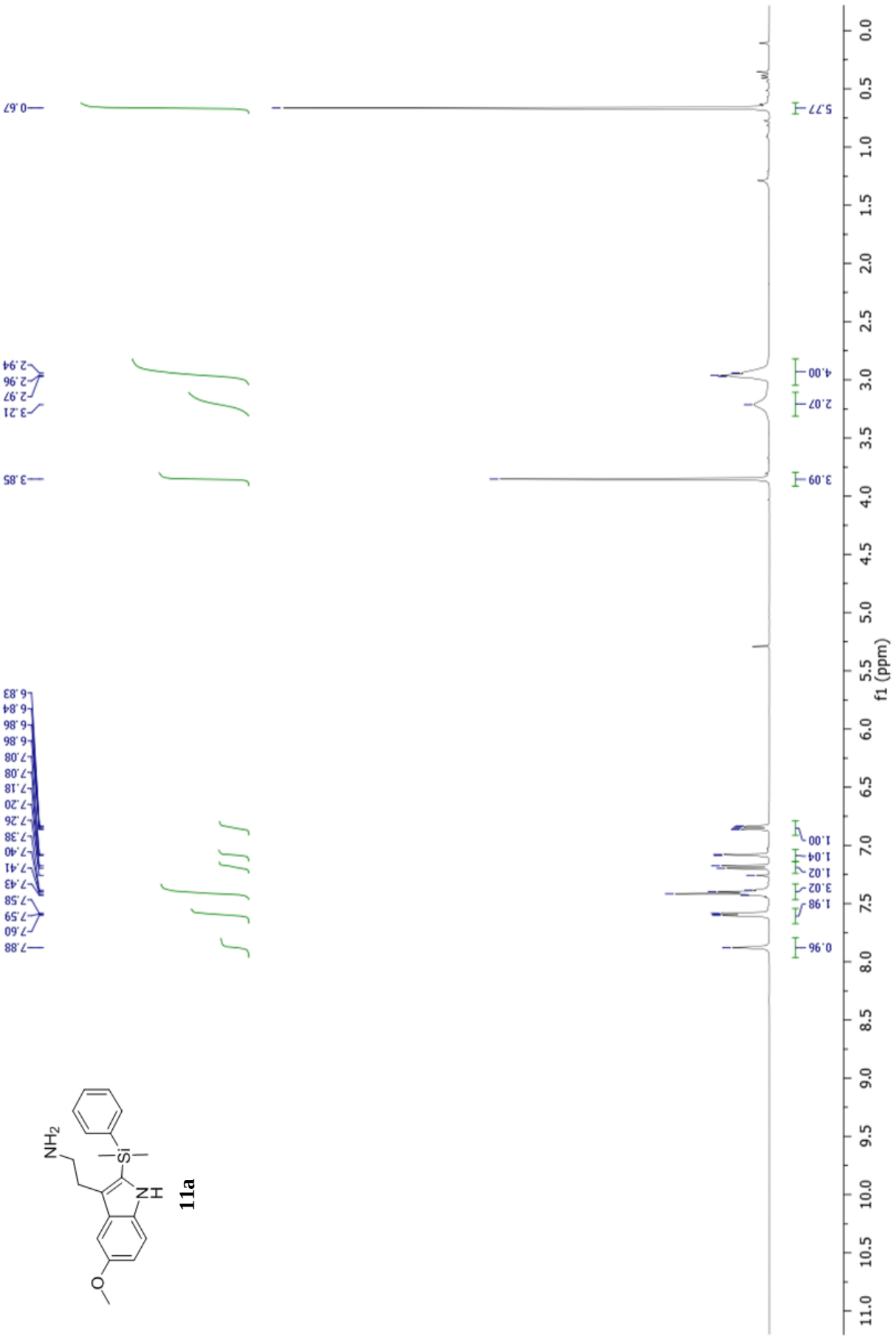

0.79
3.77
3.71
7.63
7.61
7.55
7.53
7.53
7.46
7.44
7.42
7.40
7.38
7.36
7.26
7.23
7.21
7.15
7.13
7.11
7.09
7.07
7.06
5.96
2.84
2.00
2.88
0.95
2.88
1.84
0.94
f1 (ppm)
CO2Me
SiMe2Ph
N
7'


CO2Me
N
SiMe2Ph
172.4
140.6
133.8
130.9
130.3
129.2
128.2
121.7
119.9
119.0
113.5
110.6
77.4
77.0
76.6
51.9
31.3
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

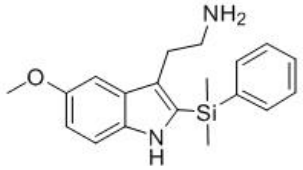
7’


NHMe
SiEt3
H
N
10
f1 (ppm)


3.7
7.4
26.3
36.0
53.2
76.7
77.0
77.3
110.7
118.8
119.0
122.1
122.8
128.7
131.4
138.4
f1 (ppm)
NHMe
SiEt3
H
N
10

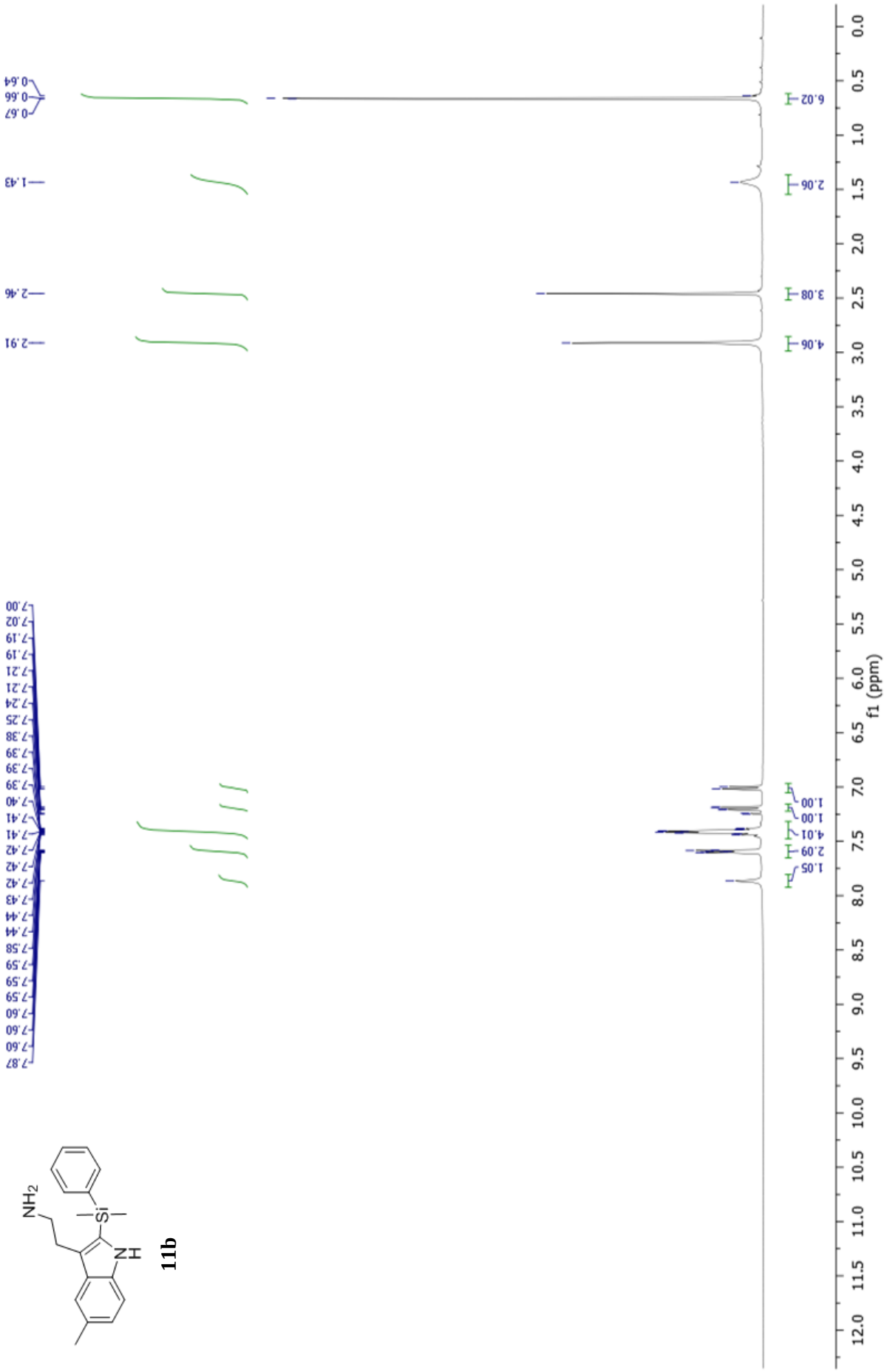

0.67
2.94
2.96
2.97
3.21
3.85
6.83
6.84
6.86
6.86
7.08
7.08
7.18
7.20
7.26
7.38
7.40
7.41
7.43
7.58
7.59
7.60
7.88
5.77
4.00
2.07
3.09
1.00
1.04
1.02
3.02
1.98
0.96
f1 (ppm)
NH2
Si
N
H
O

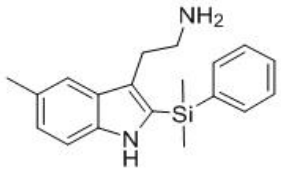
11a


NH2
O
Si
N
H

11a

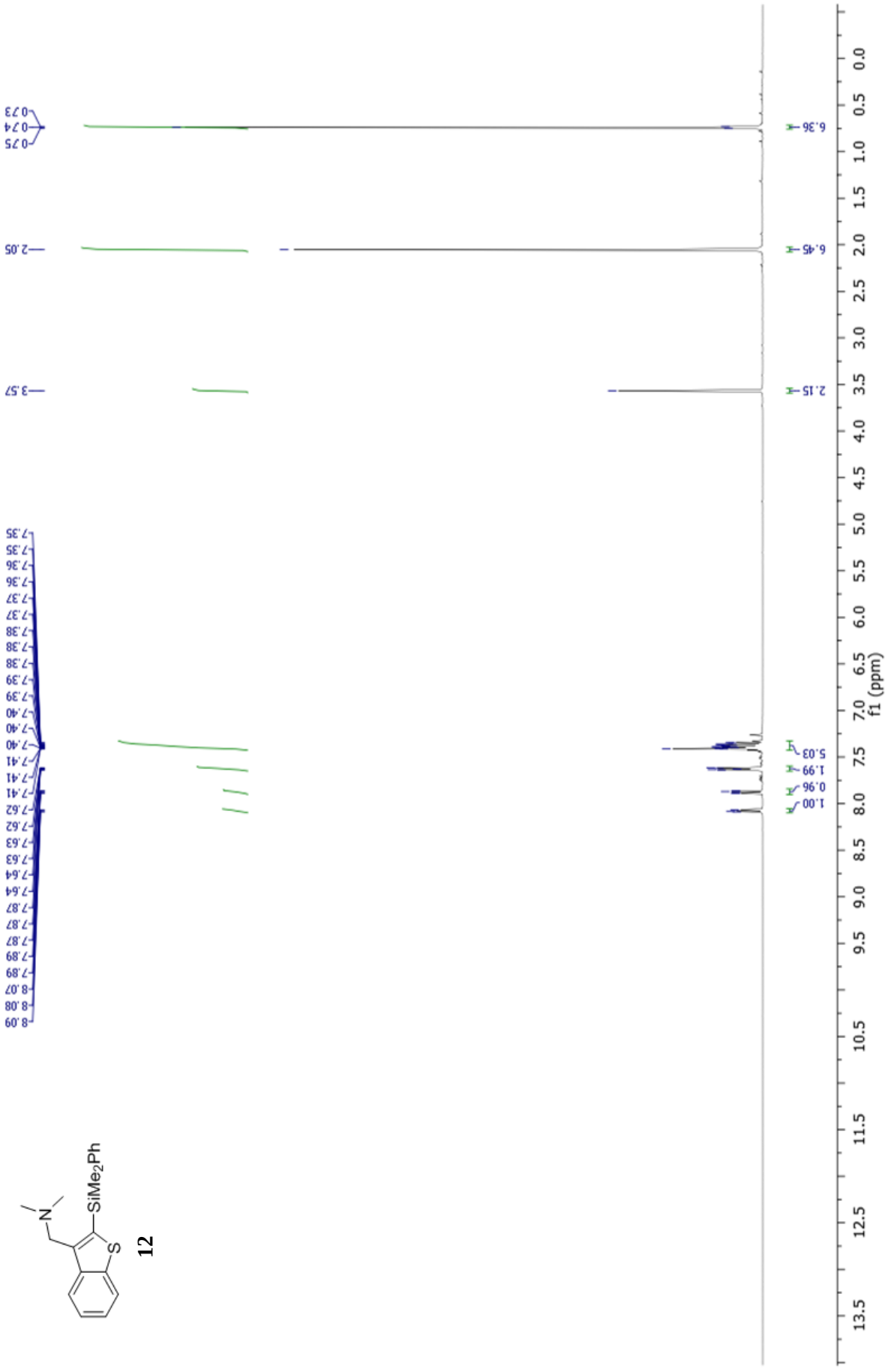
154.0
136.7
134.1
133.6
133.2
129.8
129.1
128.2
121.8
113.3
111.7
100.3
77.3
77.0
76.7
56.0
42.6
28.8
-1.7
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NH2
Si
NH
11b
f1 (ppm)


NH2
Si
N
H

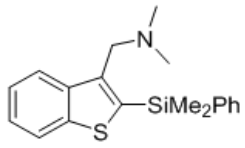
11b

137.1
136.7
134.1
132.0
129.6
129.1
128.4
128.1
124.2
122.8
118.5
110.6
77.3
77.0
76.7
43.5
30.5
21.4
-1.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


0.73
0.74
0.75
2.05
3.57
7.35
7.35
7.36
7.36
7.37
7.37
7.38
7.38
7.38
7.39
7.39
7.40
7.40
7.40
7.41
7.41
7.41
7.62
7.62
7.63
7.63
7.64
7.64
7.87
7.87
7.87
7.89
7.89
8.07
8.08
8.09
6.36
6.45
2.15
5.03
1.99
0.96
1.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.5
11.5
12.5
13.5
f1 (ppm)

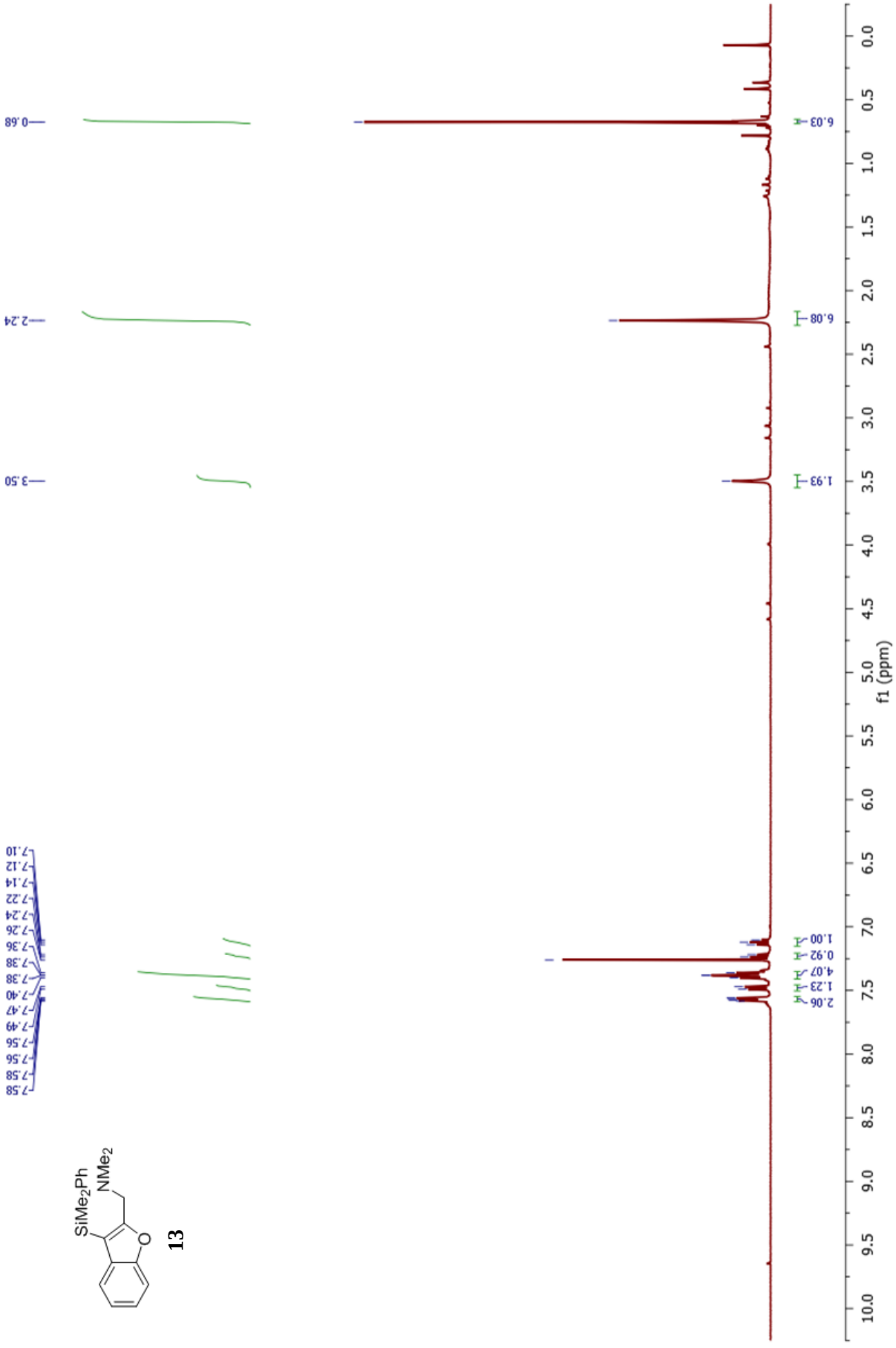
SiMe2Ph
N
S

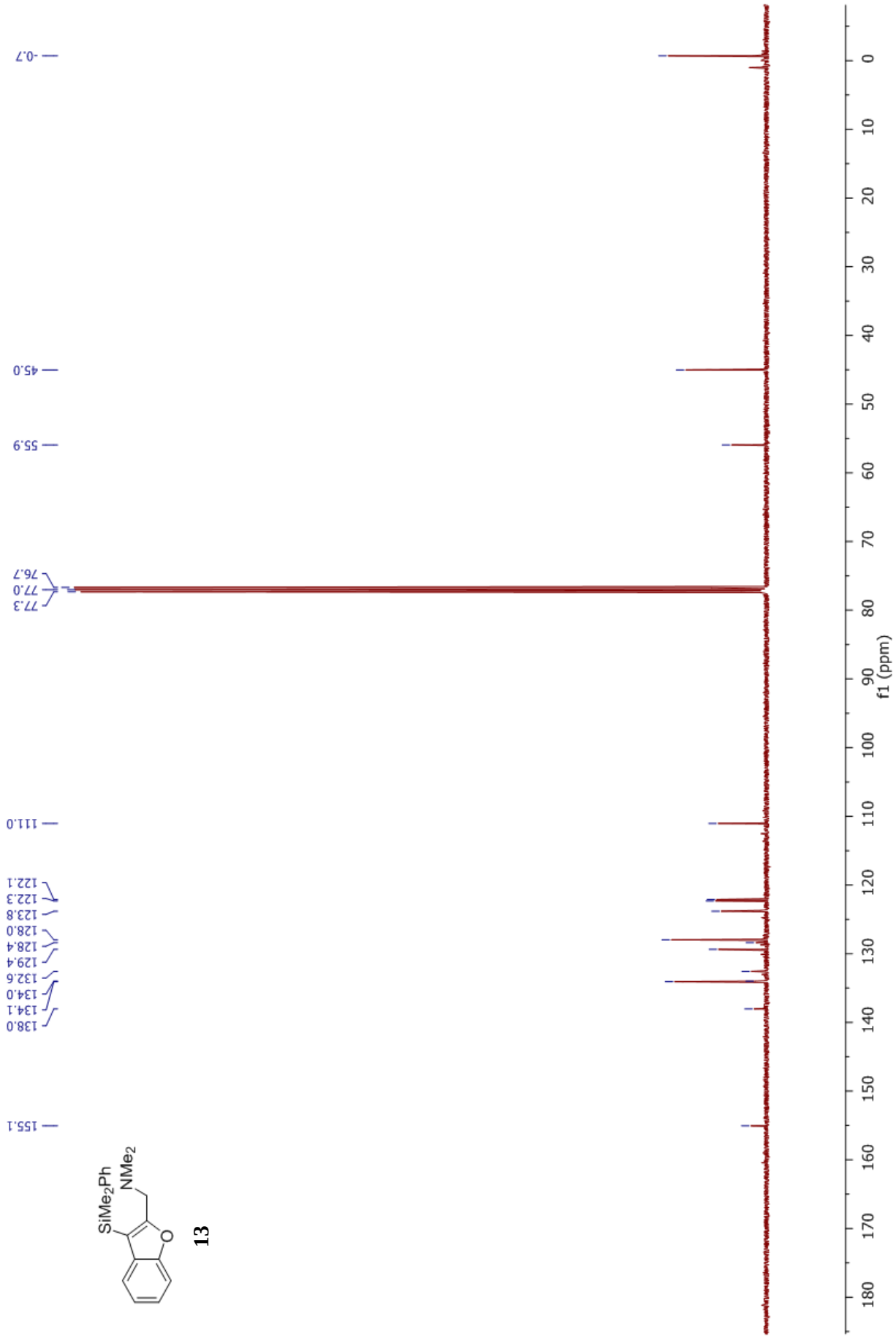
12


N
SiMe2Ph
S

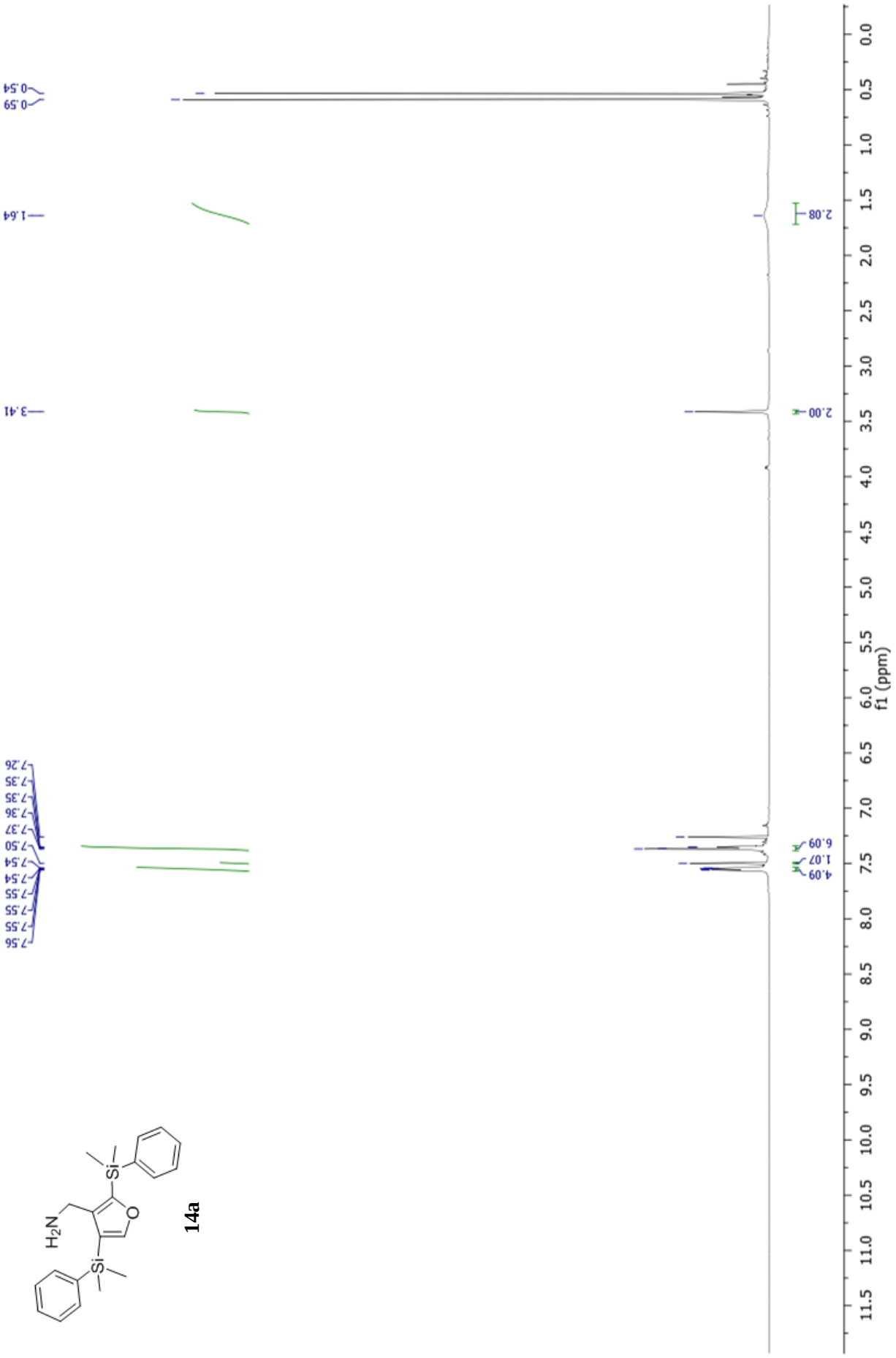
12

143.3
141.9
141.5
138.0
136.4
134.0
129.2
127.7
124.2
123.6
123.1
122.0
77.3
77.0
76.7
57.4
45.0
-0.8
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SiMe2Ph
NMe2
O
13
f1 (ppm)

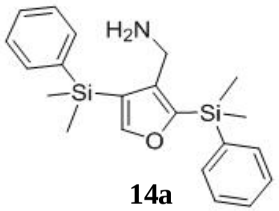

-0.7
45.0
55.9
76.7
77.0
77.3
111.0
122.1
122.3
123.8
128.0
128.4
129.4
132.6
134.0
134.1
138.0
155.1
f1 (ppm)
SiMe2Ph
NMe2
O

13


0.54
0.59
1.64
3.41
7.26
7.35
7.35
7.36
7.37
7.50
7.54
7.54
7.55
7.55
7.55
7.56
2.08
2.00
6.09
1.07
4.09
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)

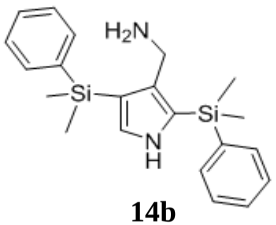
Si
O
H2N
Si

14a


H2N
Si
Si
O

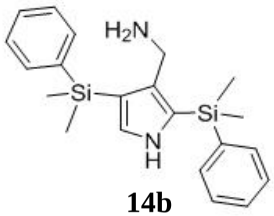
14a

153.5
138.3
133.9
133.9
133.8
129.5
129.4
128.1
128.0
127.9
127.9
117.3
77.3
77.0
76.7
37.3
-1.7
-2.3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H2N
Si
Si
N
H

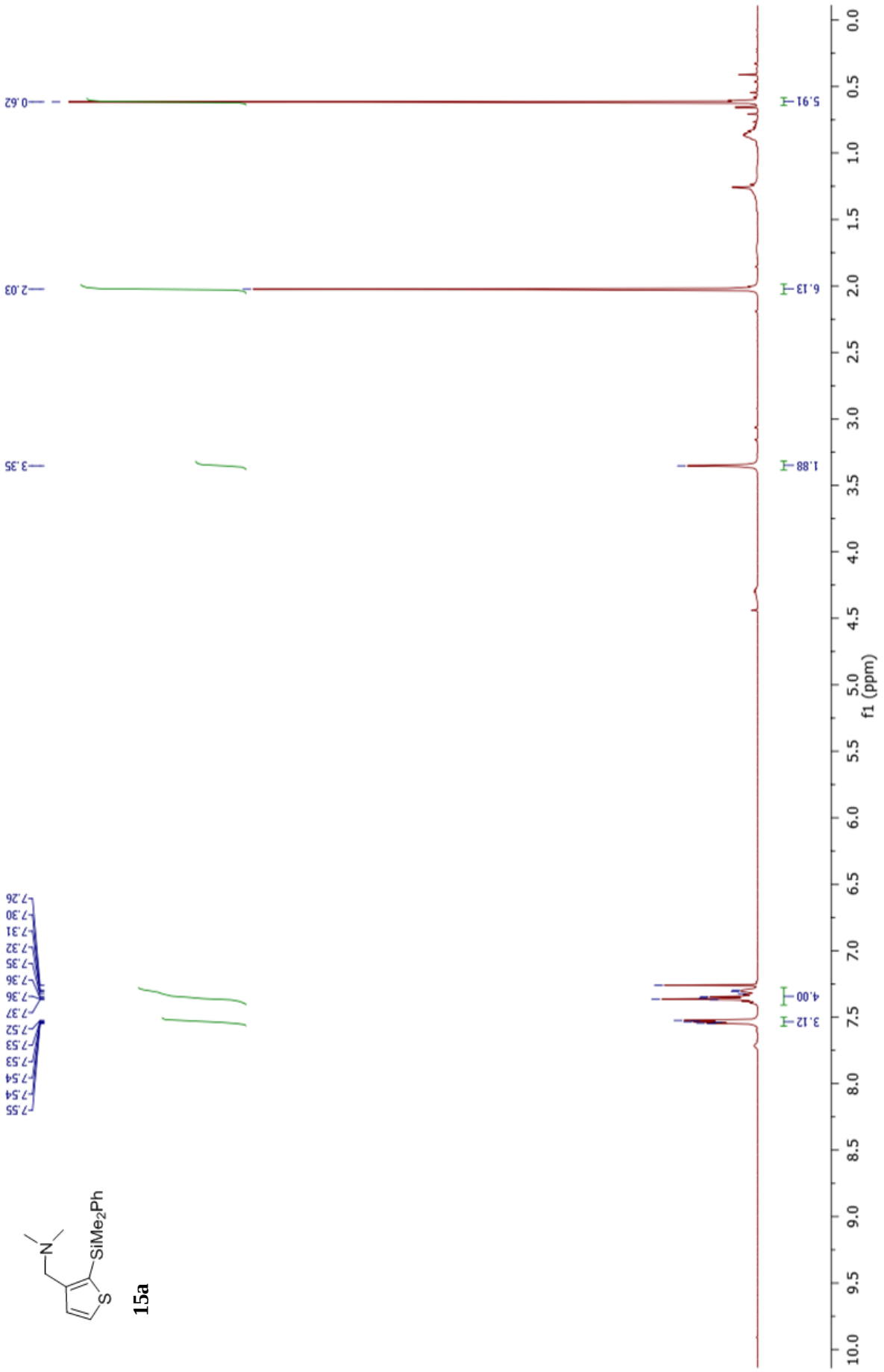
14b

8.17
7.58
7.56
7.56
7.40
7.39
7.34
7.34
6.85
6.85
3.61
1.22
0.58
0.58
0.57
0.54
0.53
0.53
0.52
0.48
0.98
4.09
3.23
3.15
1.00
2.11
2.08
6.18
6.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

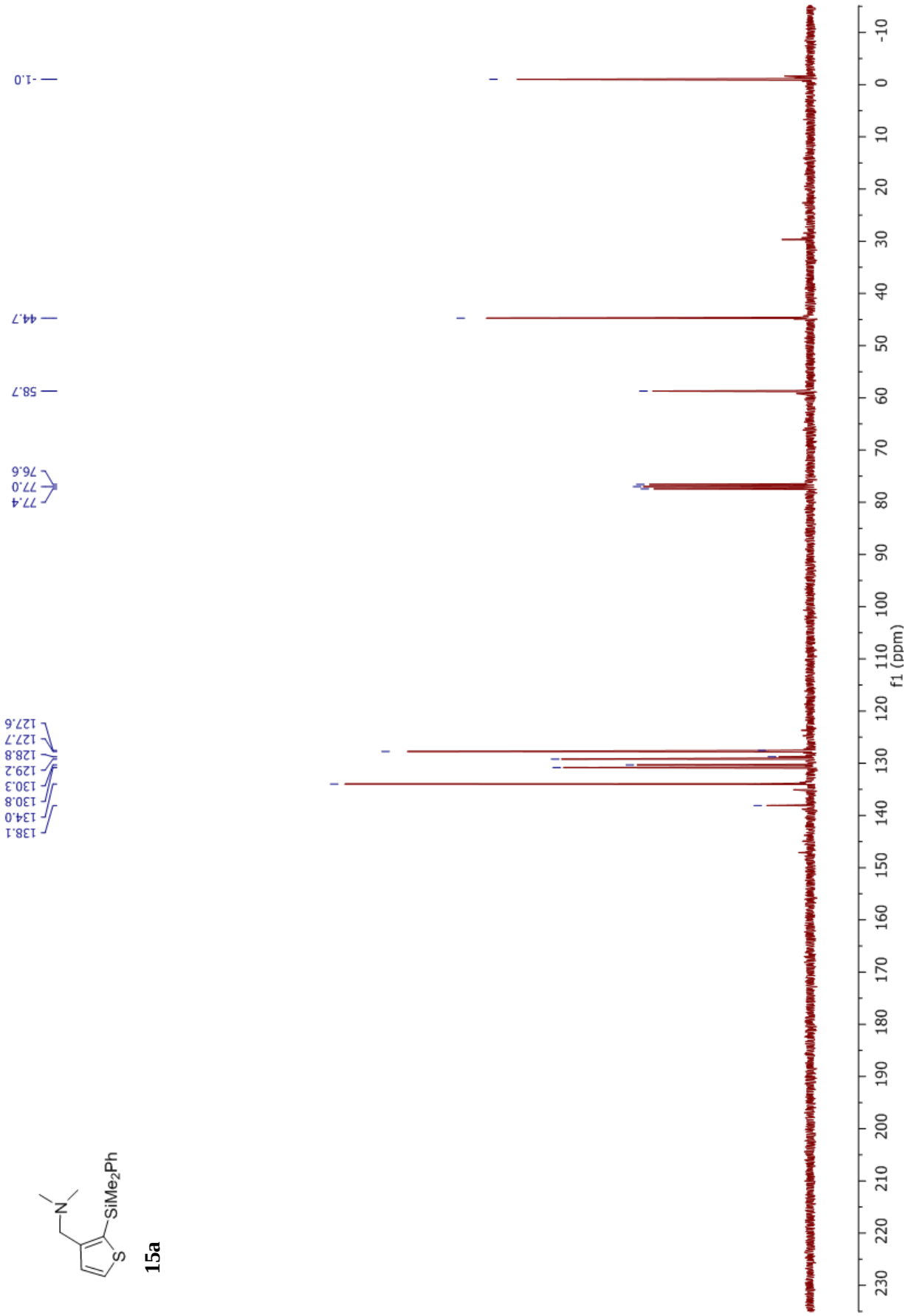

H2N
Si
Si
N
H

14b

141.3
139.9
137.5
134.0
133.9
129.5
129.3
128.9
128.1
127.8
127.0
116.0
77.3
77.0
76.7
39.6
-1.2
-1.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

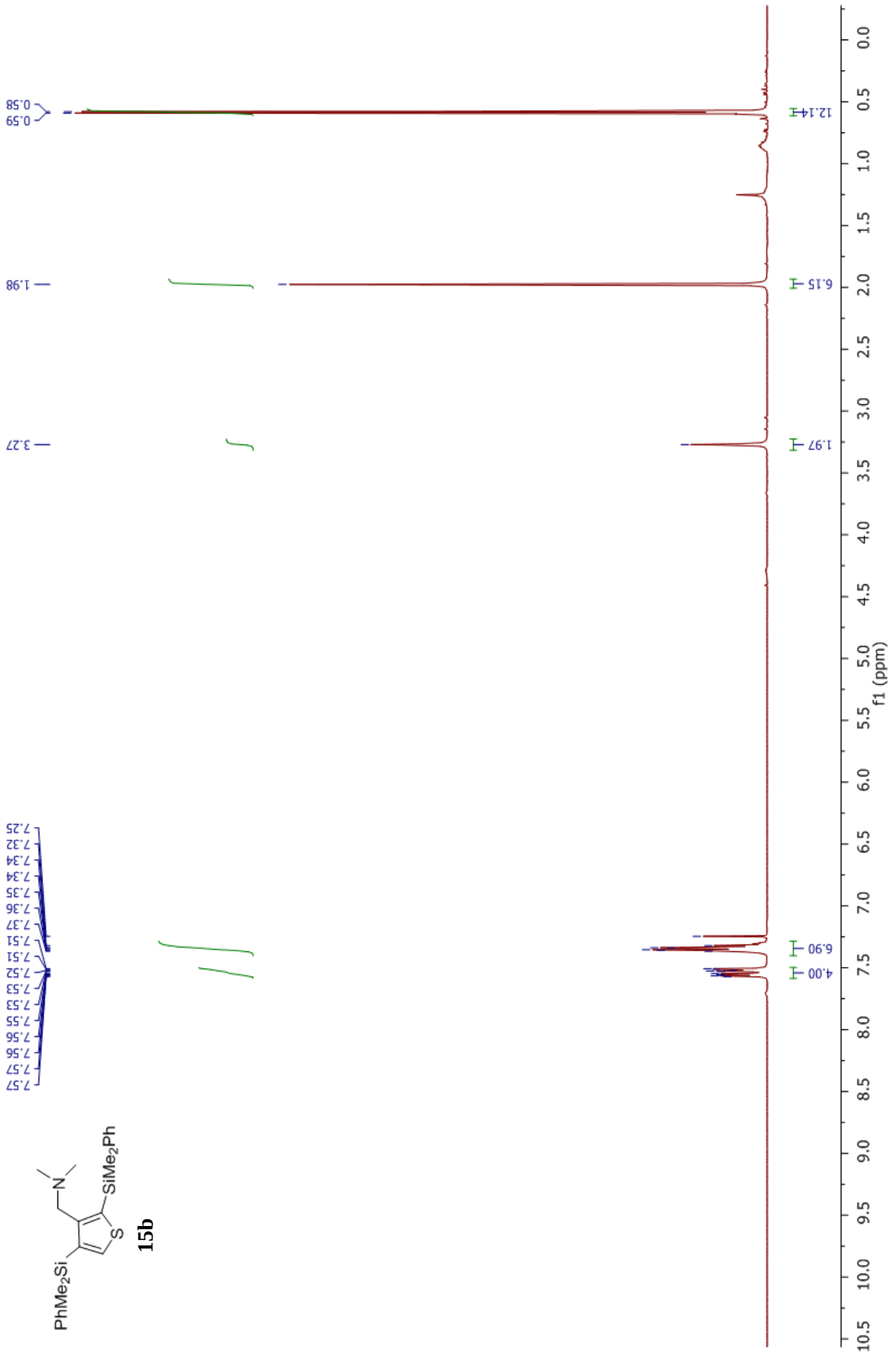

0.62
2.03
3.35
5.91
6.13
1.88
4.00
3.12
7.55
7.54
7.54
7.53
7.53
7.52
7.37
7.36
7.36
7.35
7.32
7.31
7.30
7.26
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
N
S
SiMe2Ph

15a

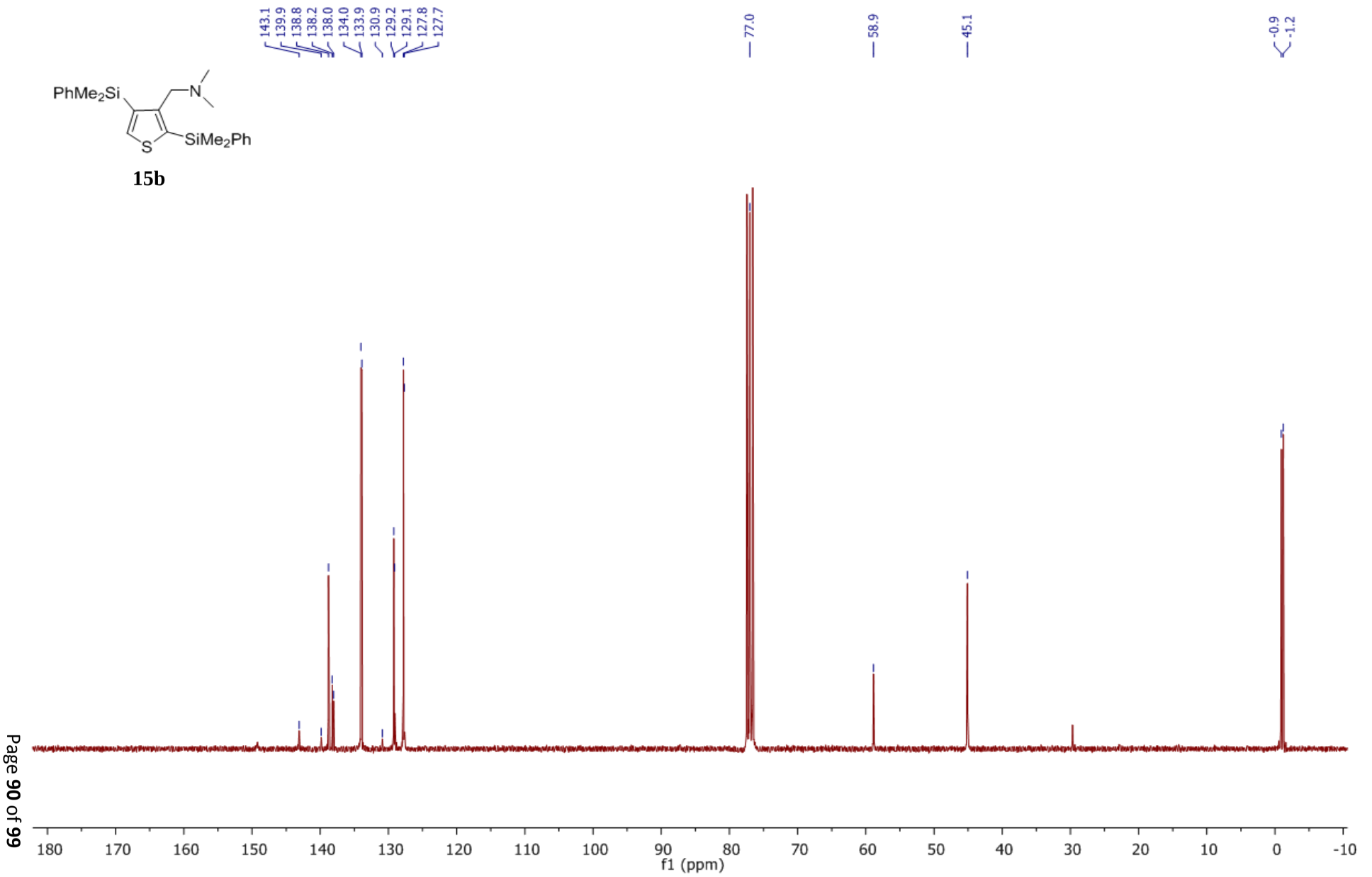

-1.0
44.7
58.7
76.6
77.0
77.4
127.6
127.7
128.8
129.2
130.3
130.8
134.0
138.1
f1 (ppm)

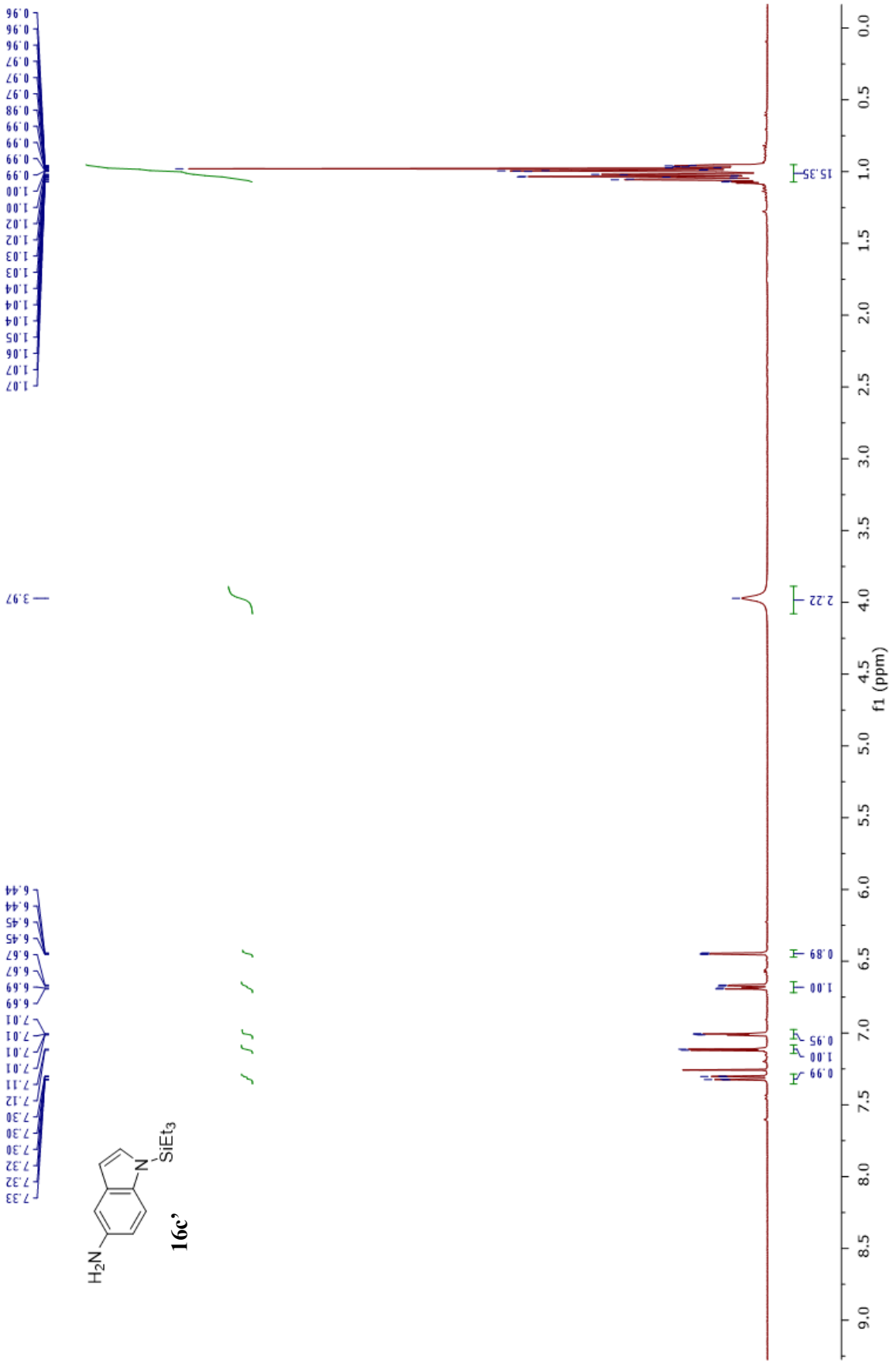
N
SiMe2Ph
S

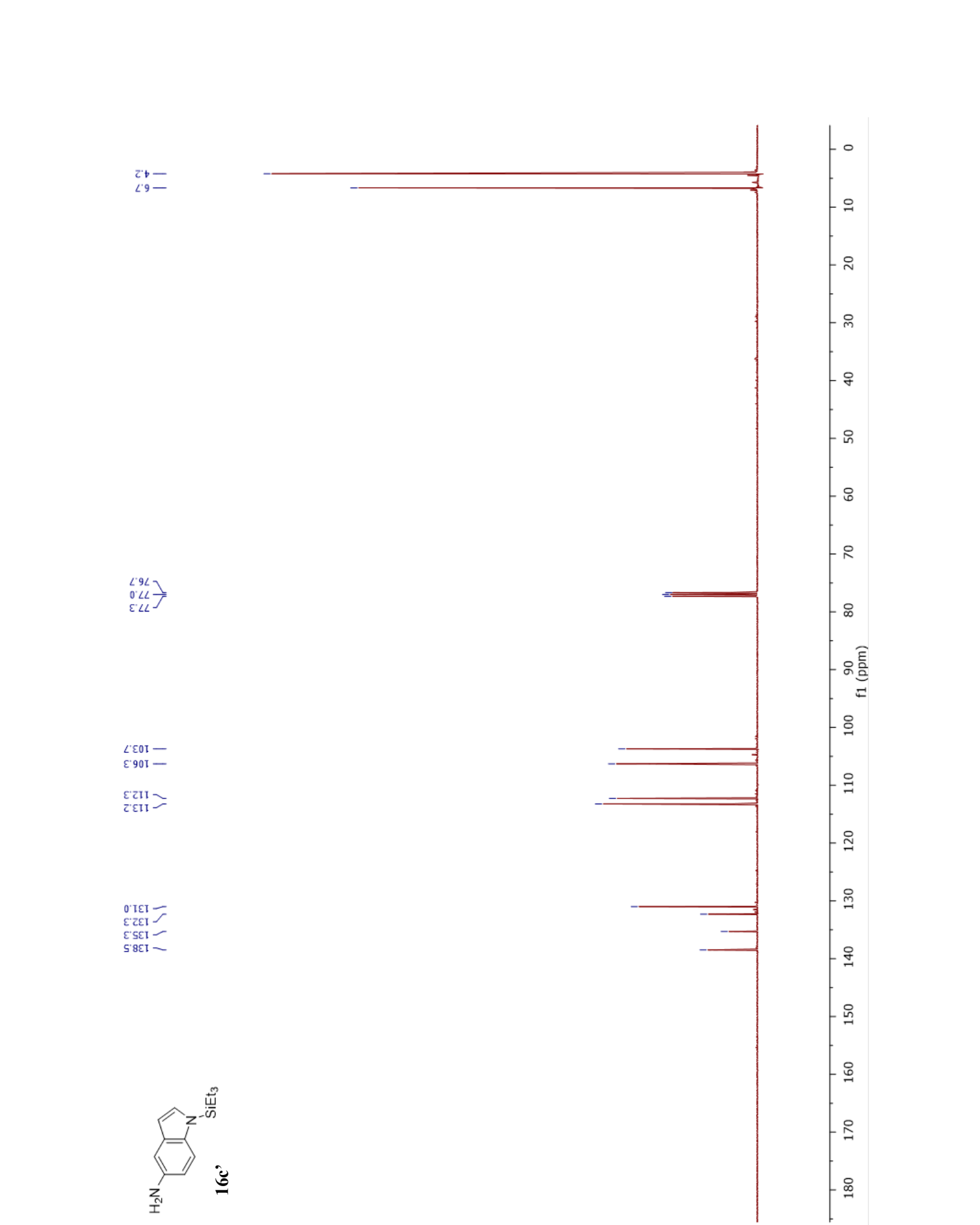
15a

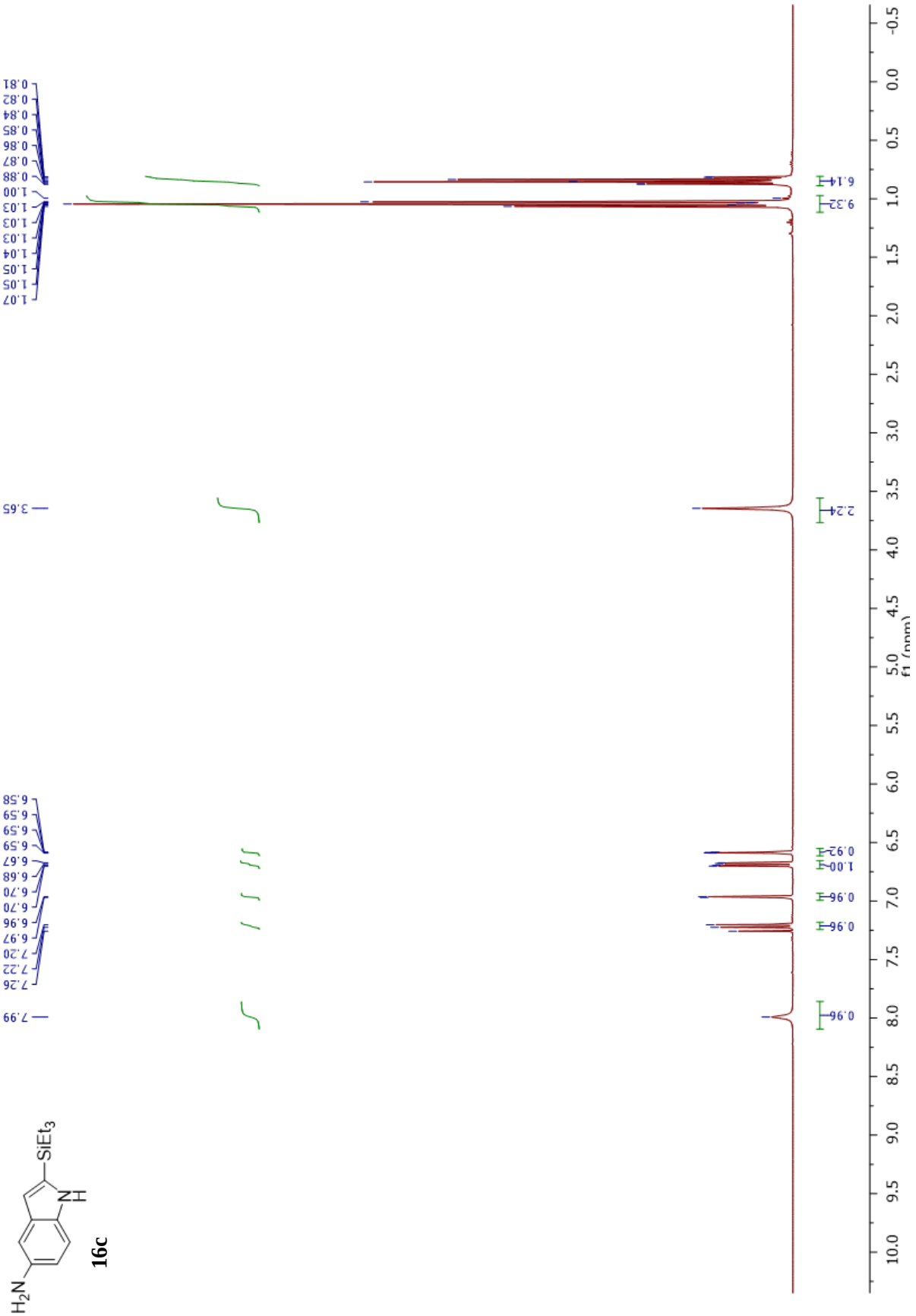

0.59
0.58
1.98
3.27
7.57
7.57
7.56
7.56
7.55
7.53
7.53
7.52
7.51
7.51
7.37
7.36
7.35
7.34
7.34
7.32
7.25
12.14
6.15
1.97
6.90
4.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
PhMe2Si
SiMe2Ph
N
S

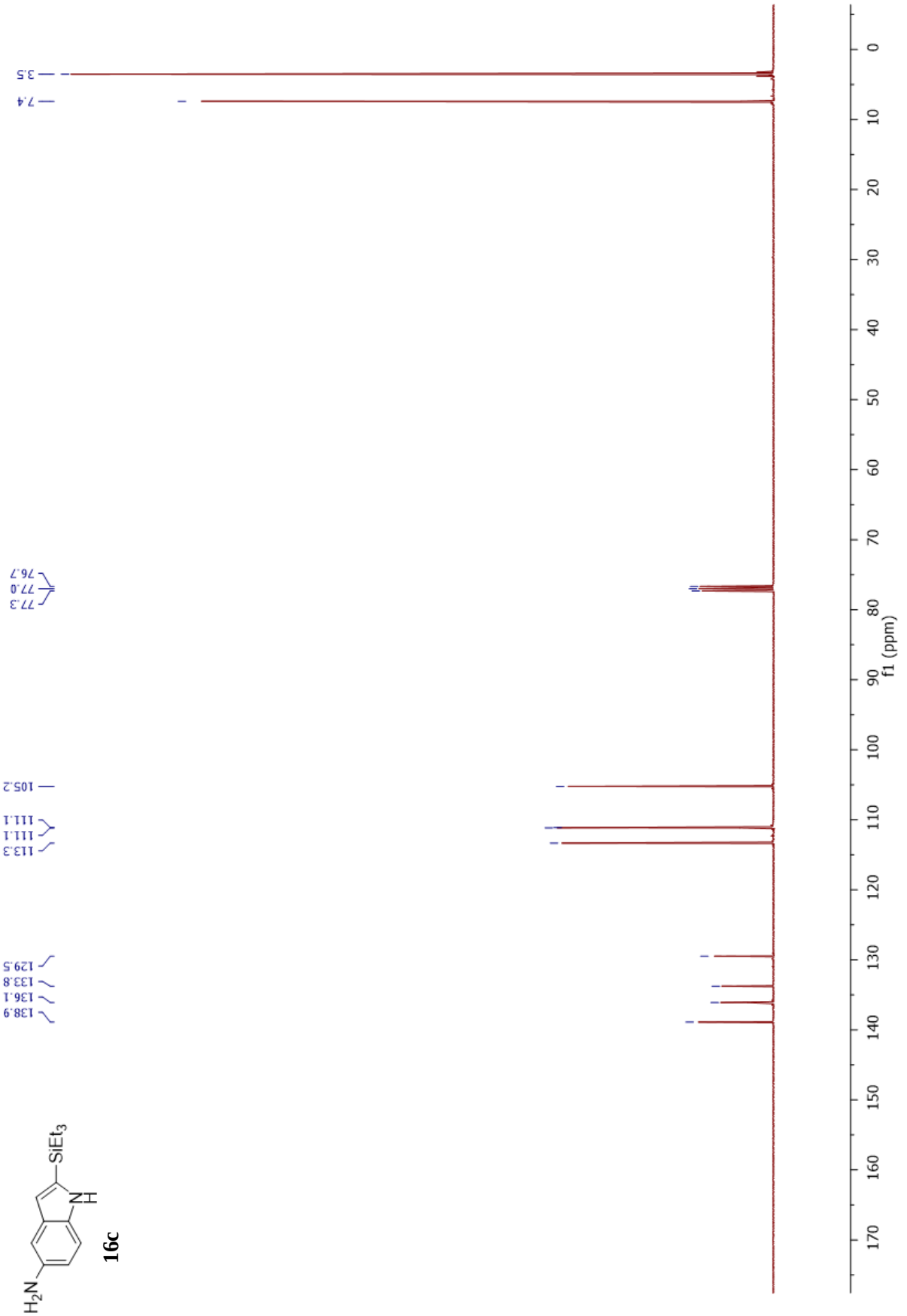
15b


143.1
139.9
138.8
138.2
138.0
134.0
133.9
130.9
129.2
129.1
127.8
127.7
77.0
58.9
45.1
-0.9
-1.2
PhMe2Si
N
SiMe2Ph
S
15b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

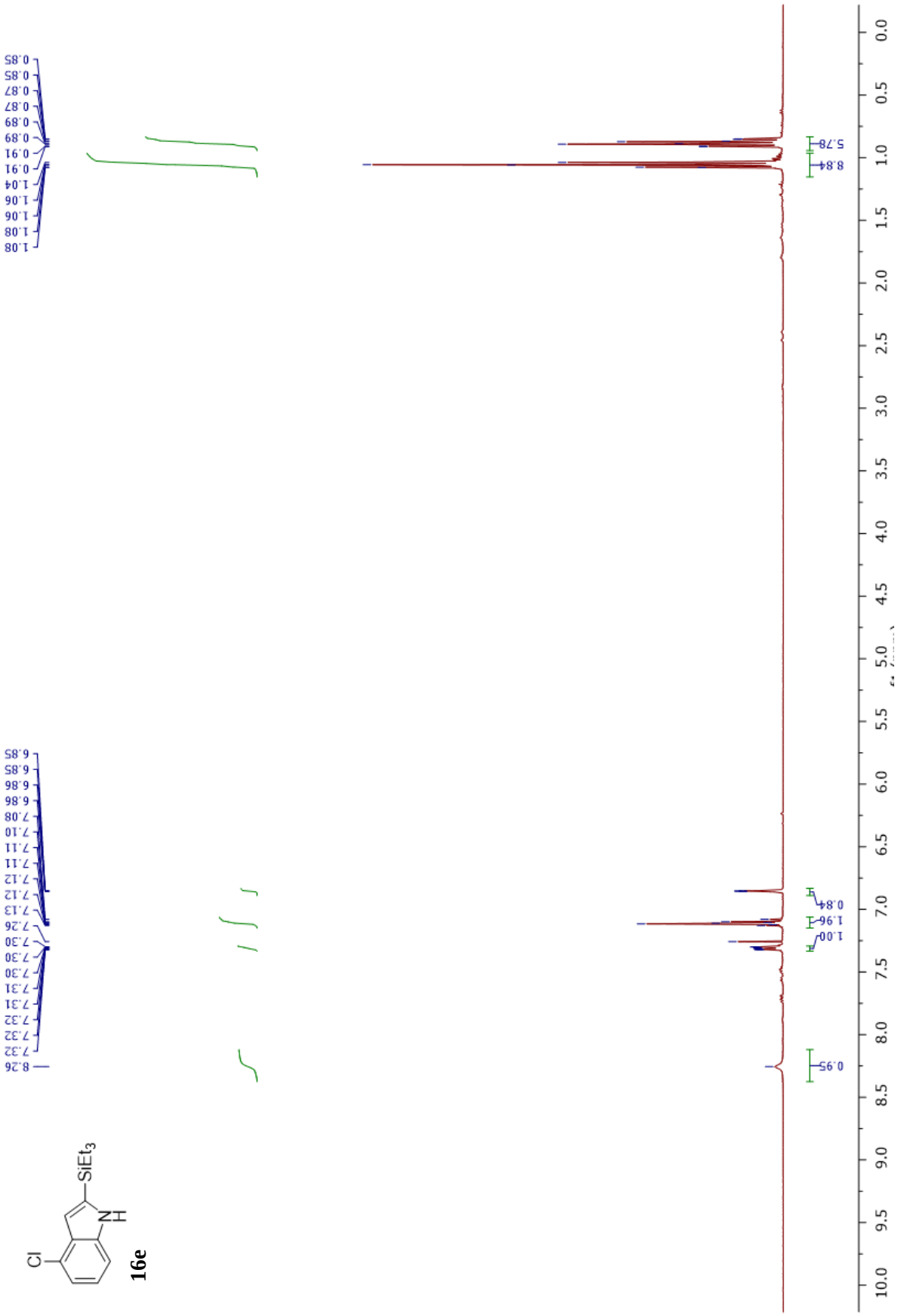

H2N
N
SiEt3
16c'
f1 (ppm)

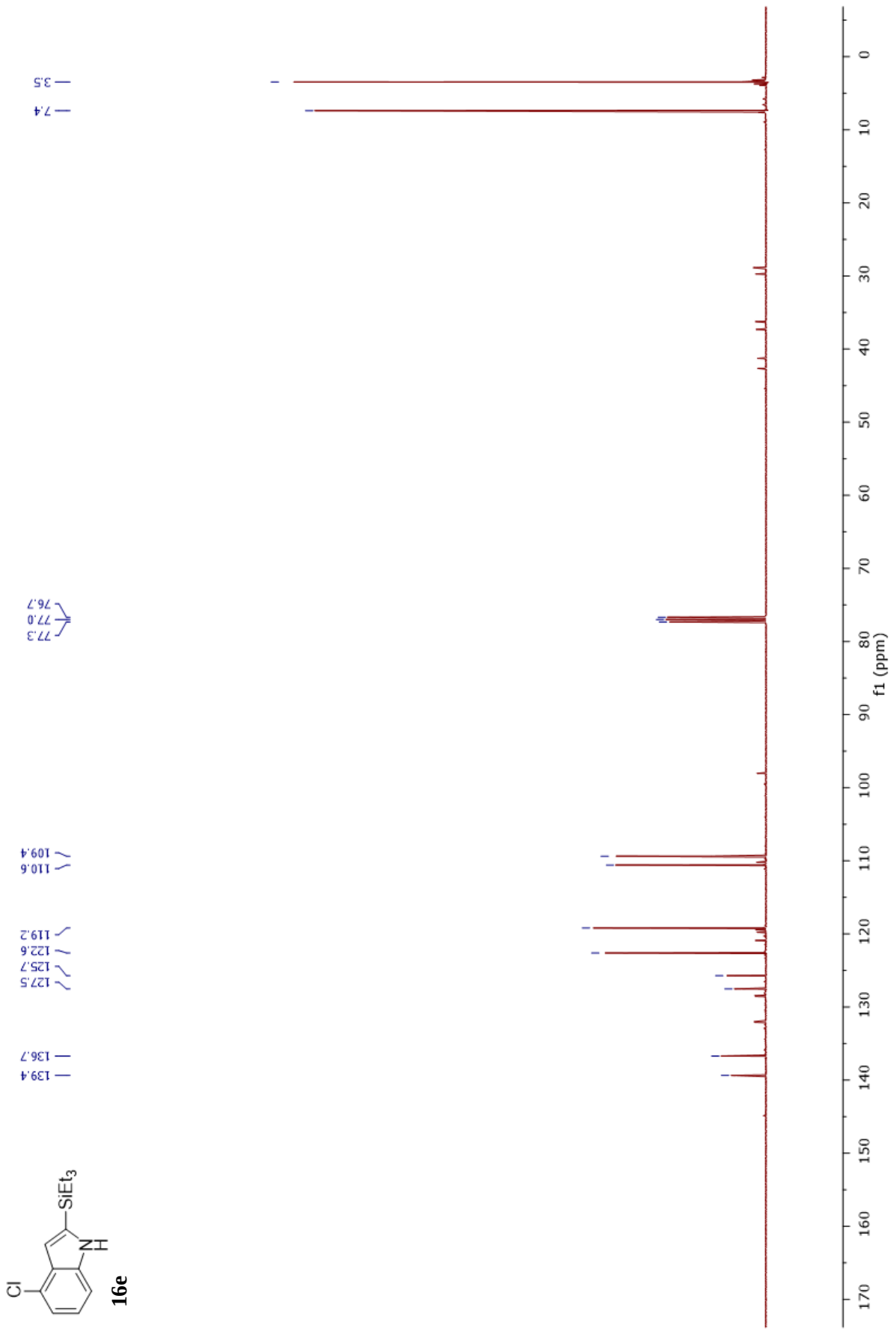

4.2
6.7
76.7
77.0
77.3
103.7
106.3
112.3
113.2
131.0
132.3
135.3
138.5
f1 (ppm)
SiEt3
H2N
16c'


SiEt3
NH
H2N
16c

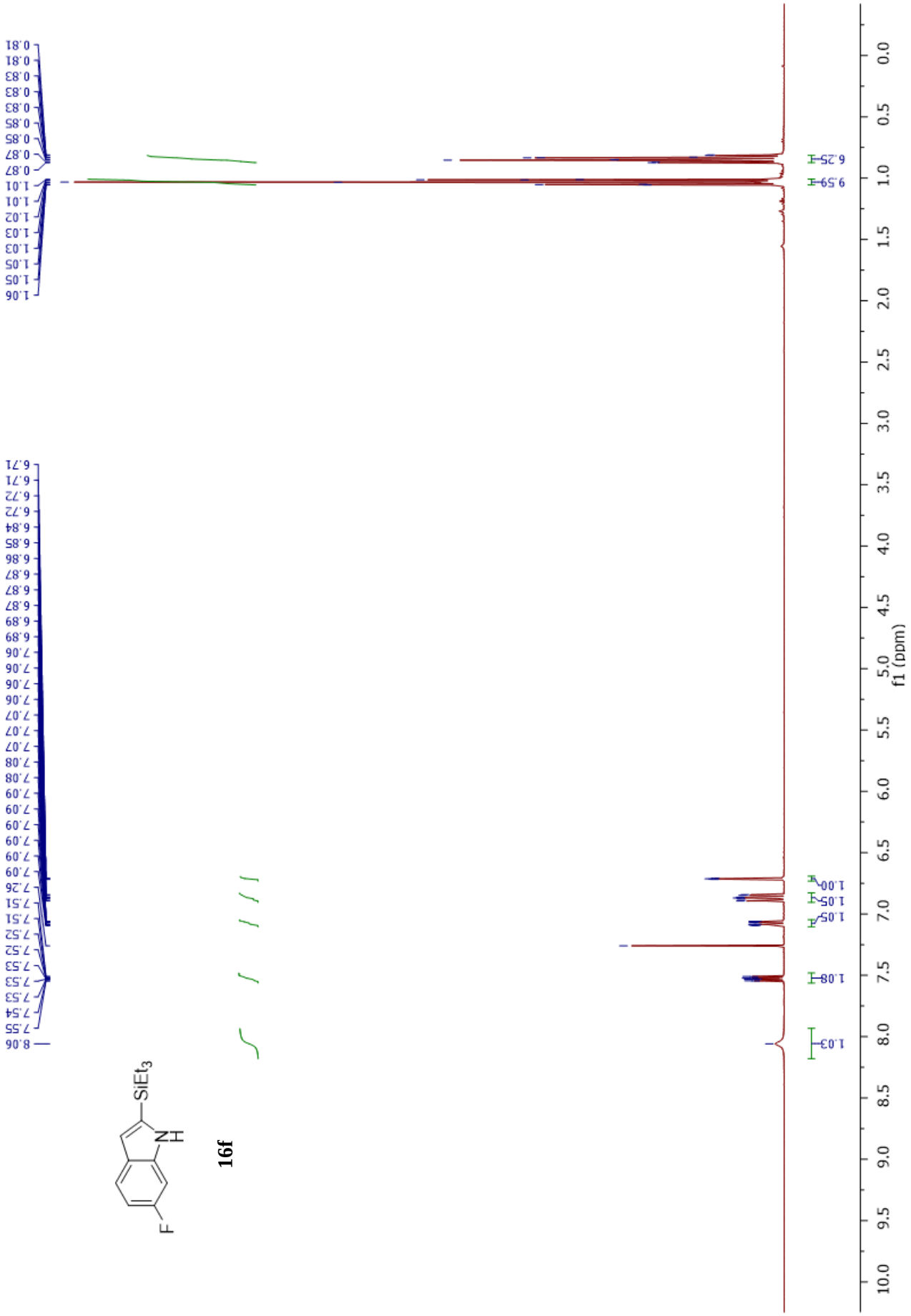

3.5
7.4
76.7
77.0
77.3
105.2
111.1
111.1
113.3
129.5
133.8
136.1
138.9
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
SiEt3
N
H
H2N

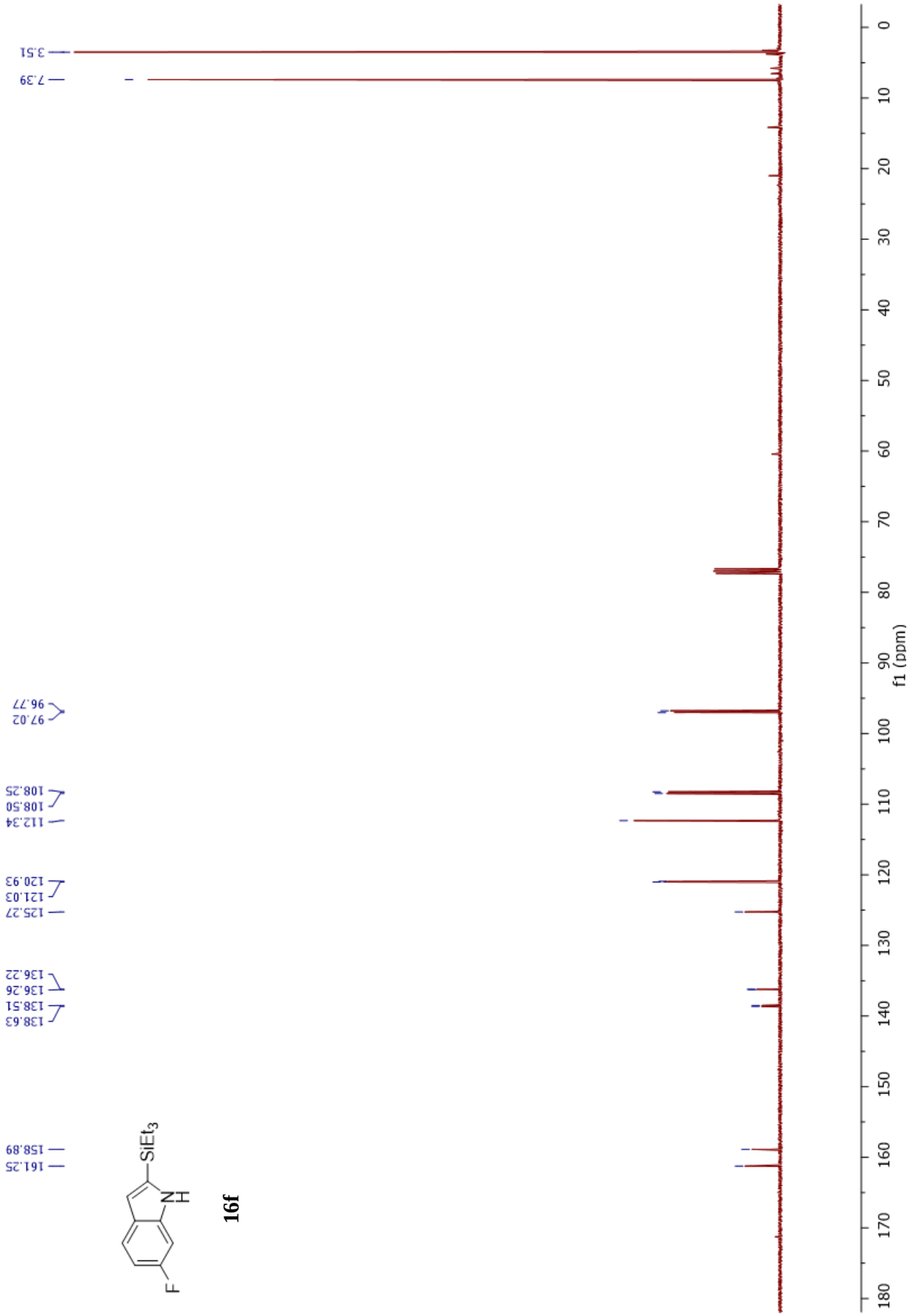
16c


SiEt3
Cl
N
H
16e

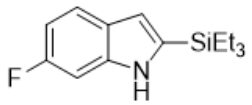

3.5
7.4
77.3
77.0
76.7
109.4
110.6
119.2
122.6
125.7
127.5
136.7
139.4
f1 (ppm)
SiEt3
Cl
N
H

16e

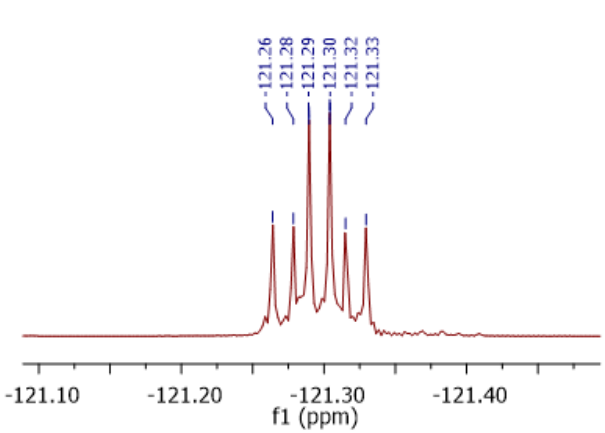

SiEt3
N
H
F
16f
f1 (ppm)

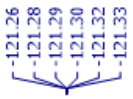

3.51
7.39
96.77
97.02
108.25
108.50
112.34
120.93
121.03
125.27
136.22
136.26
138.51
138.63
158.89
161.25
SiEt3
N
H
F
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

16f


F
N
H
SiEt3

16f


-121.26
-121.28
-121.29
-121.30
-121.32
-121.33
-121.10
-121.20
-121.30
-121.40
f1 (ppm)


-121.26
-121.28
-121.29
-121.30
-121.32
-121.33

30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)