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# Breaking the symmetry: $C_1$-salans with (N-H) backbones - ESI

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## Contents

## Materials.

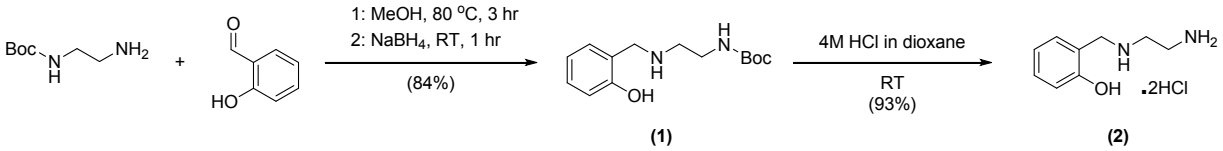
All reagents were purchased from Sigma Aldrich, Fluorochem, Tokyo Chemical Industry, Apollo Scientific, Fischer Scientific or Alfa Aesar and used without further purification. Experiments were performed under aerobic conditions or Argon.

## Instrumentation.

NMR spectra were recorded with a Varian VNMRS 600 at 25 °C, at either 600 MHz or 151 MHz in Chloroform-d or DMSO-$d_6$. Chemical shifts are quoted in parts per million (ppm). Coupling constants (J) are recorded in units of Hz. FT-IR spectra were recorded over the range of 4000–650 $cm^{-1}$ on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a UATR polarisation accessory. HRMS data were obtained with a Bruker Daltonics Fourier Transform (FTMS) Apex II spectrometer with electrospray ionisation (ESI) and methanol as solvent. HR-MS data were obtained on a VG Autospec Fissions instrument (EI at 70 eV). Molecular ions are reported as mass/charge (m/z) ratios. Thermogravimetric analysis was carried out with a Thermogravimetric analyser Q-50 V20.13 using a platinum pan, in a nitrogen atmosphere from 25 – 800 °C, at a scan rate of 5 °C/min. UV–Vis measurements (280-750 nm) were performed at room temperature (15-20˚C) using a Thermo Scientific Evolution 300 UV-Vis spectrophotometer equipped with 5mm path length quartz cells, and the collected data were processed using the Vision Pro software. Purification of compounds with normal-phase silica flash column chromatography was conducted on a Teledyne Isco Combiflash with UV detection at all wavelengths. CHN analysis was carried out by the elemental analysis service at London Metropolitan University.

## Synthesis of Ligands.

### Half units.




***Scheme S1:*** *Synthetic route for the synthesis of salan 'half-unit'*

*tert-butyl (2-((2-hydroxybenzyl)amino)ethyl)carbamate* **(1):**

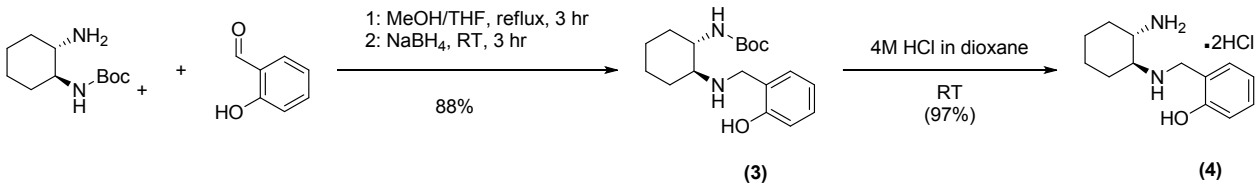
The title compound was synthesised according to the following modified literature procedure[1]:

To a solution of salicylaldehyde (5.04 mL, 48 mmol) in methanol (50 mL) was added N-boc-ethylenediamine (7.68 g, 48 mmol) and the mixture was stirred at reflux for 3 hours. The reaction

mixture was cooled to room temperature and $NaBH_4$ (1.5 g, 39.4 mmol) was added in small portions over 15 minutes. The reaction was further stirred at room temperature for 1 hour before quenching with deionised water (80 mL) and being extracted with ethyl acetate (3 x 50 mL). The combined organic phases were washed with saturated brine (50 mL) and dried over $MgSO_4$. The solvent was evaporated *in vacuo* to give **(1)** as a white solid which was used without further purification (10.75 g, 40.40 mmol, 84%); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 1H), 6.99 (d, J = 7.3 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 4.73 (s, 1H), 4.01 (s, 2H), 3.29 (q, J = 6.0 Hz, 2H), 2.79 (t, J = 5.8 Hz, 2H), 1.44 (s, 9H).; $^{13}$C NMR (151 MHz,$CDCl_3$) $^{13}$C NMR (151 MHz, cdcl3) δ 158.0, 156.2, 128.9, 128.5, 122.1, 119.1, 116.4, 79.7, 52.3, 48.4, 40.0, 28.3; (HRMS + pESI) cald $C_{14}H_{23}N_2O_3$ $[M + H]^+$: 267.1703, observed: 267.1693

*2-(((2-aminoethyl)amino)methyl)phenol hydrochloride* **(2):**

To compound **(1)** (10.75g g, 40.40, mmol) in DCM (150 mL) was added 4M HCl in dioxane (50 mL) and stirred at room temperature until complete by TLC (Hex:EtOAc, 1:1). Hexane (50 mL) was added and the white precipitate was filtered and recrystallized from methanol/ethyl acetate (1:1) to yield **(2)** as a white crystalline solid (8.97 g, 37.53 mmol ); $^1$H NMR (600 MHz, $CD_3OD$) δ 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 (td, *J* = 7.9, 1.7 Hz, 1H), 6.93 – 6.89 (m, 2H), 4.29 (s, 2H), 3.39 – 3.31 (m, 4H), $^{13}$C NMR (151 MHz, $CD_3OD$) δ 157.6, 132.8, 132.7, 121.1, 118.2, 116.4, 48.5, 44.9, 36.7; (HRMS + pESI) cald $C_9H_{15}N_2O_1$ $[M + H]^+$: 167.1179, observed: 167.1182




***Scheme S2:*** *Synthetic route for the synthesis of cyclohexane salan 'half-unit'*

*tert-butyl (2-((2-hydroxybenzyl)amino)cyclohexyl)carbamate* **(3):**

The title compound was synthesised according to the following modified literature procedure[2]:

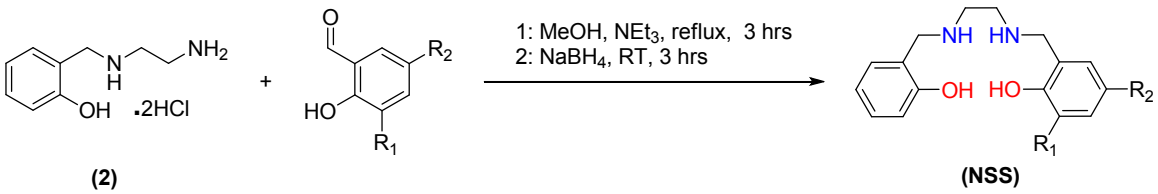
*trans*-N-Boc-1,2-cyclohexanediamine (2.00 g, 9.34 mmol) and salicylaldehyde (9.74 mL, 9.34 mmol) were combined in a mixture of methanol and tetrahydrofuran (1:1, 200 mL). The mixture was heated at reflux for 3 hours then cooled to 0 $^o$C using a ice bath. $NaBH_4$ (1.77 g, 46.7 mmol) was added in portions over 15 minutes then the reaction was then warmed to room temperature and stirred for 3 hours until the yellow solution had turned clear.

Deionised water (200 mL) was added and the mixture was left to stand overnight. The white crystalline precipitate was collected via suction filtration and dried over suction to give **(3)** as a white crystalline solid (2.62 g, 8.18 mmol, 88%); $^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.76 (q, *J* = 6.8, 6.3 Hz, 1H), 4.59 (s, 1H), 4.13 – 3.80 (m, 2H), 3.43 (s, 1H), 2.44 (s, 1H), 2.20 – 2.13 (m, 1H), 2.00 – 1.94 (m, 1H), 1.72 (t, *J* = 15.2 Hz, 2H), 1.44 (d, *J* = 6.1 Hz, 8H), 1.35 – 1.12 (m, 5H); $^{13}$C NMR (151 MHz, DMSO) δ 158.1, 155.9, 128.6, 128.2, 125.2, 118.7, 115.9, 77.9, 60.2, 53.7, 48.5, 32.8, 30.9, 28.7, 25.0, 24.7; (HRMS + pESI) cald $C_{18}H_{29}N_2O_3$ $[M + H]^+$: 321.2178, observed: 321.2183.

*2-(((2-aminocyclohexyl)amino)methyl)phenol hydrochloride* **(4)**:

To compound **(3)** (2.0 g 6.24 mmol) in DCM (40 mL) was added 4M HCl in dioxane (20 mL) and the reaction mixture was stirred until complete by TLC (Hex:EtOAc, 1:1). Hexane (50 mL) was added and the mixture was left to stand for 1 hour then the white precipitate was collected via suction filtration to give **(4)** as a white solid (1.77 g 6.04 mmol, 97%); $^{1}$H NMR (600 MHz, DMSO) δ 10.38 (s, 1H), 9.40 (s, 2H), 8.79 (s, 3H), 7.52 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 4.24 (d, *J* = 12.9 Hz, 1H), 4.10 (d, *J* = 12.9 Hz, 1H), 3.40 (s, 2H), 3.34 – 3.27 (m, 1H), 2.28 – 2.22 (m, 1H), 2.17 – 2.09 (m, 1H), 1.77 – 1.71 (m, 1H), 1.70 – 1.57 (m, 1H), 1.51 – 1.41 (m, 1H), 1.27 – 1.10 (m, 2H); $^{13}$C NMR (151 MHz, DMSO) δ 156.6, 132.4, 130.9, 119.4, 118.2, 115.8, 58.1, 50.5, 43.3, 29.6, 26.4, 23.2, 23.0; (HRMS + pESI) cald $C_{13}H_{21}N_2O$ $[M + H]^+$: 221.1654, observed: 221.1637

Non-Symmetric Salan (NSS) ligands.




***Scheme S3:*** *Synthetic route for the synthesis of Non-Symmetric Salan (NSS) ligands.*

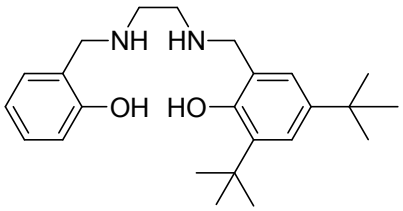
**General procedure for synthesis of NSS ligands.**

Compound (**2**) (600 mg, 2.5 mmol), activated 4Å molecular sieves (~200 mg) and $NEt_3$ (0.70 mL, 5 mmol) were combined in anhydrous methanol (10 mL) and stirred under argon at room temperature for 10 minutes. The salicylaldehyde derivative (2.5 mmol) was then added and the mixture was stirred at reflux for 3 hours. The reaction mixture was then cooled to 0 °C with an ice bath and $NaBH_4$ (284

mg, 7.5 mmol) was added in portions over 15 minutes. The reaction was then allowed to warm to room temperature and stirred for a further 3 hours before being filtered and quenched with deionised water (20 mL). The resulting solution was allowed to stand overnight, the formed precipitate was collected via suction filtration and washed with petroleum ether (3 x 10 mL) to yield non-symmetric salans.

*In the few cases that no precipitate was formed; the aqueous solution was extracted with DCM (3 x 20 mL) and the combined organics were washed with brine (20 mL) and dried over $MgSO_4$ before being concentrated. The crude product was then purified via normal phase column chromatography (DCM:MeOH:$NEt_3$, 90:10:1) to obtain non-symmetric salans.

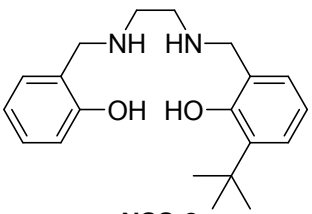
*2,4-di-tert-butyl-6-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol* (**NSS-1**)




**NSS-1**

**NSS-1** was synthesised according to the general procedure using 3,5-di-tert-butylsalicylaldehyde:
Pale yellow solid (846 mg, 2.20 mmol, 88%): $^1$H NMR (600 MHz, DMSO) δ 7.10 – 7.02 (m, 3H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.74 – 6.66 (m, 2H), 3.84 (s, 2H), 3.79 (s, 2H), 2.65 (s, 4H), 1.34 (s, 9H), 1.22 (s, 9H); $^{13}$C NMR (151 MHz, DMSO) δ 157.6, 155.0, 139.7, 134.9, 129.0, 128.2, 124.8, 123.4, 122.9, 121.9, 118.9, 115.7, 52.9, 50.5, 47.7, 40.5, 40.4, 34.8, 32.0, 29.9; FTIR $\nu_{max}$ / $cm^{-1}$: 3272, 2955, 1472, 1244, 757; (HRMS + pESI) cald $C_{24}H_{37}N_2O_2$ $[M + H]^+$: 385.2855, observed: 385.2863

*2-(tert-butyl)-6-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol* (**NSS-2**)

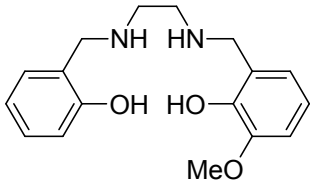



**NSS-2**

**NSS-1** was synthesised according to the general procedure* using 3-tert-butylsalicylaldehyde:
Pale yellow oil (494 mg, 1.50 mmol, 60%); $^1$H NMR (600 MHz, DMSO) δ 7.08 – 6.99 (m, 3H), 6.83 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.71 – 6.64 (m, 2H), 6.60 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 2H), 3.76 (s, 2H), 2.62 (s, 4H), 1.31 (s, 9H); $^{13}$C NMR (151 MHz, dmso) δ 157.6, 157.5, 135.8, 129.0, 128.2, 126.8, 125.4, 124.8, 123.6,

118.9, 118.1, 115.7, 52.4, 50.5, 47.7, 47.6, 34.7, 29.9; FTIR $\nu_{max}$ / $cm^{-1}$: 3313, 2952, 1589, 1435, 1238, 748; (HRMS + pESI) cald $C_{20}H_{29}N_2O_2$ $[M + H]^+$: 329.2224, observed: 329.2234

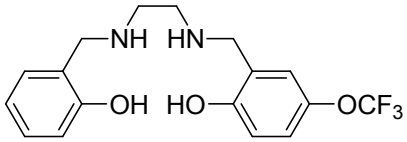
2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)-6-methoxyphenol (**NSS-3**)




**NSS-3**

**NSS-3** was synthesised according to the general procedure using *o*-vanillin:
Pale yellow solid (549 mg, 1.18 mmol, 73%); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 1H), 6.98 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.83 – 6.72 (m, 3H), 6.67 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.98 (d, *J* = 1.8 Hz, 4H), 3.84 (s, 3H), 2.87 (s, 4H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 157.6, 147.7, 146.4, 129.1, 128.9, 121.9, 121.6, 121.2, 119.3, 119.1, 116.4, 111.1, 55.9, 51.8, 50.7, 46.9; FTIR $\nu_{max}$ / $cm^{-1}$: 2923, 1592, 1482, 1240, 755, (HRMS + pESI) cald $C_{17}H_{23}N_2O_3$ $[M + H]^+$: 303.1703, observed: 303.1692

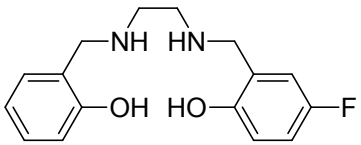
*2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)-4-(trifluoromethoxy)phenol* (**NSS-4**)




**NSS-4**

**NSS-4** was synthesised according to the general procedure using 5-(trifluoromethoxy)salicylaldehyde: Pale yellow solid (722 mg, 2.03 mmol, 81%); $^1$H NMR (600 MHz, DMSO) δ 7.14 (d, *J* = 3.0 Hz, 1H), 7.08 – 7.02 (m, 3H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.73 – 6.67 (m, 2H), 3.79 (d, *J* = 6.7 Hz, 4H), 2.63 (s, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.7, 156.4, 140.6, 129.0, 128.2, 126.9, 124.7, 121.8, 120.9, 118.9, 116.4, 115.7, 50.7, 49.6, 48.0, 47.9; FTIR $\nu_{max}$ / $cm^{-1}$: 3276, 2861, 1590, 1494, 114; (HRMS + pESI) cald $C_{17}H_{20}N_2O_3F_3$ $[M + H]^+$: 357.1421, observed: 357.1414.

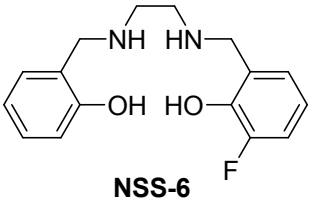
4-fluoro-2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol (**NSS-5**)




**NSS-5**

**NSS-5** was synthesised according to the general procedure using 5-fluorosalicylaldehyde:
Off-white solid (416 mg, 1.43 mmol, 57%); $^{1}$H NMR (600 MHz, DMSO) δ 7.06 (t, *J* = 7.8 Hz, 2H), 6.97 (dd, *J* = 9.4, 3.2 Hz, 1H), 6.87 (td, *J* = 8.7, 3.2 Hz, 1H), 6.73 – 6.66 (m, 3H), 3.79 (s, 2H), 3.75 (s, 2H), 2.62 (s, 4H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 157.9, 156.0 (d, *J* = 236.6 Hz), 153.8, 129.0, 128.5, 122.9 (d, *J* = 6.9 Hz), 122.0, 119.3, 117.0 (d, *J* = 8.0 Hz), 116.4, 115.0 (d, *J* = 22.6 Hz), 114.8 (d, *J* = 23.2 Hz), 52.6, 52.3, 47.8, 47.7; FTIR $\nu_{max}$ / $cm^{-1}$: 3276, 2861, 1589, 1479, 748; (HRMS + pESI) cald $C_{16}H_{20}N_2O_2F_1$ $[M + H]^+$: 291.1503, observed: 291.1511.

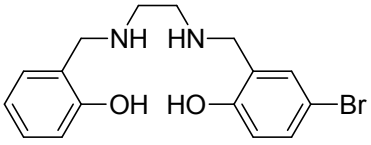
2-fluoro-6-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol (**NSS-6**)




**NSS-6**

**NSS-6** was synthesised according to the general procedure using 3-fluorosalicylaldehyde:
Off-white solid (370 mg, 1.27 mmol, 51%);$^{1}$H NMR (600 MHz, DMSO) δ 7.10 – 7.05 (m, 2H), 7.07 – 6.97 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.75 – 6.64 (m, 3H), 3.88 (s, 2H), 3.79 (s, 2H), 2.64 (s, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.6, 151.3 (d, *J* = 239.6 Hz), 146.1, 129.1, 128.3, 127.0 (d, *J* = 3.2 Hz), 124.8, 124.2 (d, *J* = 2.8 Hz), 118.9, 118.3 (d, *J* = 7.1 Hz), 115.8, 114.8, 50.8 (d, *J* = 2.6 Hz), 50.5, 47.7 (d, *J* = 5.3 Hz); FTIR $\nu_{max}$ / $cm^{-1}$: 3283, 2846, 1588, 1455, 749; (HRMS + pESI) cald $C_{16}H_{20}N_2O_2F_1$ $[M + H]^+$: 291.1509, observed: 291.1495.

4-bromo-2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol (**NSS-7**)

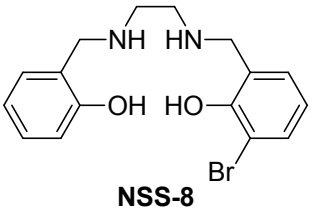



**NSS-7**

**NSS-7** was synthesised according to the general procedure using 5-bromosalicylaldehyde:
Off-white solid (471 mg, 1.34 mmol, 54%); $^{1}$H NMR (600 MHz, DMSO) δ 7.28 (d, *J* = 2.6 Hz, 1H), 7.20 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.74 – 6.65 (m, 3H), 3.79 (s, 2H), 3.76 (s, 2H), 2.62 (s, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.7, 156.8, 131.3, 130.6, 129.0, 128.2, 128.0, 124.7, 118.9, 117.8,

115.7, 110.0, 50.6, 49.5, 47.9 (d, *J* = 2.6 Hz); FTIR $\nu_{max}$ / $cm^{-1}$: 3270, 2861, 1588, 1475, 753; (HRMS + pESI) cald $C_{16}H_{20}N_2O_2Br_1$ $[M + H]^+$: 351.0703, observed: 351.0716.

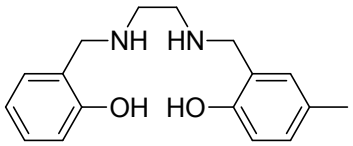
2-bromo-6-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)phenol (**NSS-8**)




**NSS-8**

**NSS-8** was synthesised according to the general procedure using 3-bromosalicylaldehyde:
Pale yellow solid (567 mg, 1.61 mmol, 64%); $^1$H NMR (600 MHz, DMSO) δ 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.10 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.06 (td, *J* = 7.7, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.75 – 6.69 (m, 2H), 6.63 (t, *J* = 7.7 Hz, 1H), 3.91 (s, 2H), 3.79 (s, 2H), 2.66 (s, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.4, 155.9, 131.5, 129.2, 128.3, 128.1, 125.1, 124.9, 119.5, 118.9, 115.7, 110.0, 51.7, 50.3, 47.5 (d, *J* = 4.7 Hz); FTIR $\nu_{max}$ / $cm^{-1}$: 2922, 1587, 1435, 740; (HRMS + pESI) cald $C_{16}H_{20}N_2O_2Br_1$ $[M + H]^+$: 351.0703, observed: 351.0717.

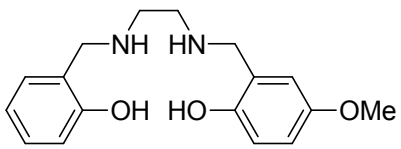
2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)-4-methylphenol (**NSS-9**)




**NSS-9**

**NSS-9** was synthesised according to the general procedure using 5-methylsalicylaldehyde:
Off-white solid (321 mg, 1.12 mmol, 45%): $^1$H NMR (600 MHz, DMSO) δ 7.06 (t, *J* = 7.6 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.74 – 6.67 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 2H), 3.74 (s, 2H), 2.62 (s, 4H), 2.16 (s, 3H); $^{13}$C NMR (151 MHz, DMSO) δ 157.7, 155.3, 129.6, 129.0, 128.5, 128.2, 127.2, 124.8, 124.5, 118.9, 115.7, 115.5, 50.7, 48.0, 20.6; FTIR $\nu_{max}$ / $cm^{-1}$: 2931, 1592, 1455, 1275, 738; (HRMS + pESI) cald $C_{17}H_{23}N_2O_2$ $[M + H]^+$: 287.1754, observed: 287.1762

2-(((2-((2-hydroxybenzyl)amino)ethyl)amino)methyl)-4-methoxyphenol (**NSS-10**)

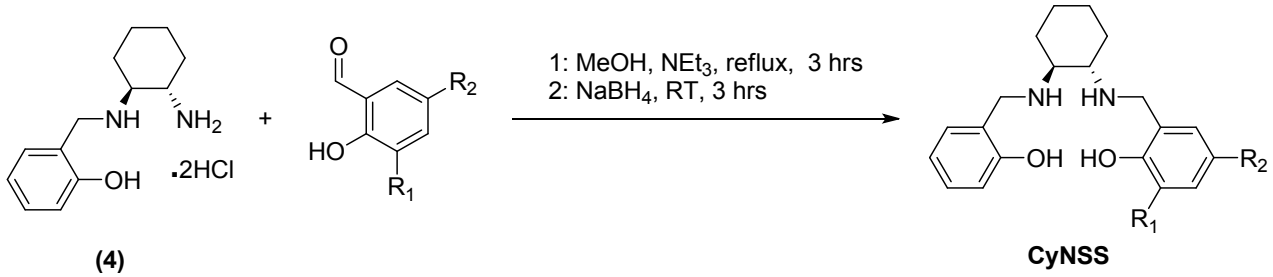



**NSS-10**

**NSS-10** was synthesised according to the general procedure using 5-nitro-3-methoxylsalicylaldehyde:

Off-white solid (451 mg, 1.49 mmol, 60%); $^{1}$H NMR (600 MHz, DMSO) δ 7.06 (t, *J* = 7.4 Hz, 2H), 6.73 – 6.67 (m, 3H), 6.66 – 6.59 (m, 2H), 3.79 (s, 2H), 3.74 (s, 2H), 3.64 (s, 3H), 2.62 (s, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.7, 152.2, 151.1, 129.0, 128.2, 125.7, 124.7, 118.9, 116.0, 115.7, 114.6, 113.1, 55.7, 50.7, 50.5, 48.0; FTIR $\nu_{max}$ / cm$^{-1}$: 3270, 2862, 1590, 1463, 753; (HRMS + pESI) cald $C_{17}H_{23}N_2O_3$ [M + H]$^+$: 303.1703, observed: 303.1708.

## Cyclohexane based Non-Symmetrical Salan (CyNSS) ligands

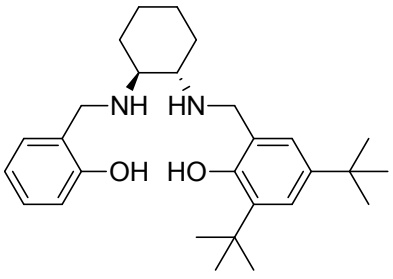



***Scheme S4:*** *Synthetic route for the synthesis of Cyclohexane based Non-Symmetric Salan (CyNSS) ligands.*

General procedure for synthesis of CyNSS ligands:

Compound (**4**) (147 mg, 0.5 mmol), activated 4Å molecular sieves (~50 mg) and $NEt_3$ (135 µL, 1.0 mmol) were combined in anhydrous methanol (5 mL) and stirred under argon at room temperature for 10 minutes. The salicylaldehyde derivative (0.5 mmol) was then added and the mixture was stirred at reflux for 3 hours. The reaction mixture was then cooled to 0 °C with an ice bath and $NaBH_4$ (75 mg, 2.0 mmol) was added in portions over 15 minutes. The reaction was then allowed to warm to room temperature and stirred for a further 3 hours before being filtered and quenched with deionised water (10 mL). The resulting solution was allowed to stand overnight, the formed precipitate was collected via suction filtration and washed with petroleum ether (3 x 10 mL) to yield non-symmetric salans.

2,4-di-tert-butyl-6-(((-2-((2-hydroxybenzyl)amino)cyclohexyl)amino)methyl)phenol (**CyNSS-1**):

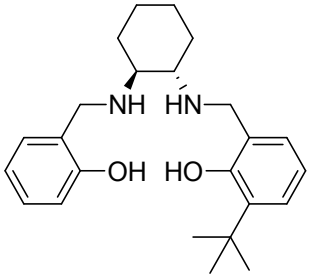



**CyNSS-1**

**CyNSS-1** was synthesised according to the general procedure using 3,5-di-tert-butylsalicylaldehyde:

Off-white solid (150 mg, 0.34 mmol, 68%); $^{1}$H NMR (600 MHz, DMSO) δ 7.11 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.70 – 6.63 (m, 2H), 3.90 – 3.79 (m, 2H), 3.76 – 3.65 (m, 2H), 2.35 (td, *J* = 7.3, 4.7 Hz, 2H), 1.99 (d, *J* = 11.5 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.31 (s, 9H), 1.20 (s, 9H), 1.17 – 1.07 (m, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.0, 154.9, 139.7, 135.0, 129.0, 128.0, 126.1, 123.8, 123.3, 121.8, 118.9, 115.6, 59.8, 59.2, 50.2, 47.0, 34.8, 34.2, 32.0, 30.2, 29.9, 24.3, 24.2; FTIR $\nu_{max}$ / cm$^{-1}$ : 3290, 2944, 1591, 1470, 754; (HRMS + pESI) cald $C_{28}H_{43}N_2O_2$ [M + H]$^+$: 439.3325, observed: 439.3329

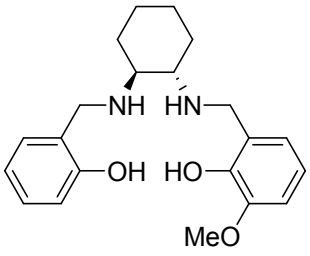
*2-(tert-butyl)-6-(((-2-((2-hydroxybenzyl)amino)cyclohexyl)amino)methyl)phenol* (**CyNSS-2**)




**CyNSS-2**

**CyNSS-2** was synthesised according to the general procedure using 3-tert-butylsalicylaldehyde:
Off-white solid (95 mg, 0.25 mmol, 50%): $^{1}$H NMR (600 MHz, dmso) δ 7.14 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.86 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.75 – 6.66 (m, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 3.95 – 3.67 (m, 4H), 2.36 (d, *J* = 6.1 Hz, 2H), 2.05 – 1.97 (m, 2H), 1.64 – 1.58 (m, 2H), 1.33 (s, 9H), 1.20 (s, 0H), 1.18 – 1.10 (m, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.5, 157.0, 135.9, 129.0, 128.1 (d, *J* = 8.4 Hz), 126.6, 126.0, 125.4, 124.5, 119.0, 118.1, 115.6, 52.3, 49.8, 47.0, 34.8, 34.6, 29.9, 29.7, 8.8.; $\nu_{max}$ / cm$^{-1}$ : 3279, 2941, 1589, 1456, 747; (HRMS + pESI) cald $C_{24}H_{35}N_2O_2$ [M + H]$^+$: 383.2699, observed: 383.2707.

*2-(((-2-((2-hydroxybenzyl)amino)cyclohexyl)amino)methyl)-6-methoxyphenol* (**CyNSS-3**)

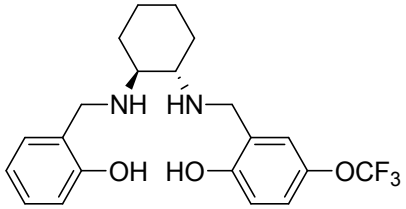



**CyNSS-3**

**CyNSS-3** was synthesised according to the general procedure using *o*-vanillin:

Off-white solid: (111 mg, 0.31 mmol, 62%): $^{1}$H NMR (600 MHz, DMSO) δ 7.09 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.04 (td, *J* = 7.7, 1.7 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.73 – 6.68 (m, 3H), 6.65 (t, *J* = 7.8 Hz, 1H), 3.82 (dd, *J* = 14.0, 2.6 Hz, 2H), 3.73 (s, 3H), 2.32 – 2.28 (m, 2H), 2.00 (d, *J* = 12.4 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.19 – 1.12 (m, 2H), 1.08 (d, *J* = 10.9 Hz, 2H); $^{13}$C NMR (151 MHz, DMSO) δ 157.4, 147.9, 146.6, 128.9, 128.1, 126.2, 125.9, 121.0, 118.9, 118.5, 115.7, 111.3, 60.0, 56.1, 47.5 (d, *J* = 11.3 Hz), 30.4, 24.5; $\nu_{max}$ / cm$^{-1}$ : 3316, 2928, 1593, 1471, 1230, 748; (HRMS + pESI) cald $C_{21}H_{29}N_2O_3$ [M + H]$^+$: 357.2178, observed:357.2167.

2-(((2-((2-hydroxybenzyl)amino)cyclohexyl)amino)methyl)-4-(trifluoromethoxy)phenol (**CyNSS-4**)

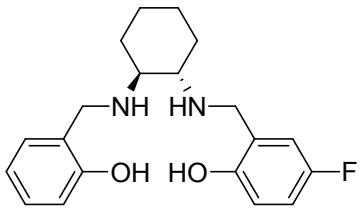



**CyNSS-4**

**CyNSS-4** was synthesised according to the general procedure using 5-(trifluoromethoxy) salicylaldehyde:

Off-white solid (152 mg, 0.37 mmol, 74%); $^{1}$H NMR (600 MHz,DMSO) δ 7.13 (d, *J* = 3.0 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.04 – 6.97 (m, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 2H), 3.80 (dd, *J* = 14.3, 11.1 Hz, 2H), 3.70 (dd, *J* = 14.3, 9.2 Hz, 2H), 2.32 – 2.23 (m, 2H), 2.01 – 1.93 (m, 2H), 1.62 – 1.56 (m, 2H), 1.16 – 1.00 (m, 4H); $^{13}$C NMR (151 MHz, DMSO) δ 157.4, 156.1, 140.6, 128.9, 128.1, 128.0, 125.9, 121.7, 120.7, 118.9, 116.3, 115.7, 60.1, 47.6, 46.4, 40.4 (d, *J* = 17.7 Hz), 30.4, 24.5; $\nu_{max}$ / cm$^{-1}$ : 2930, 1593, 1419, 1207, 755; (HRMS + pESI) cald $C_{21}H_{26}N_2O_3F$ [M + H]$^+$: 411.1896, observed: 411.1904.

4-fluoro-2-(((-2-((2-hydroxybenzyl)amino)cyclohexyl)amino)methyl)phenol (**CyNSS-5**)




**CyNSS-5**

**CyNSS-5** was synthesised according to the general procedure using 5-fluorosalicylaldehyde:

Off-white solid (127 mg, 0.37 mmol, 74%): $^{1}$H NMR (600 MHz, DMSO) δ 7.08 – 7.03 (m, 1H), 7.00 (td, *J* = 7.7, 1.7 Hz, 1H), 6.95 (dd, *J* = 9.5, 3.2 Hz, 1H), 6.80 (td, *J* = 8.6, 3.2 Hz, 1H), 6.72 – 6.61 (m, 3H), 3.78

(dd, *J* = 24.2, 14.2 Hz, 2H), 3.67 (dd, *J* = 30.8, 14.2 Hz, 2H), 2.30 – 2.21 (m, 2H), 1.97 (ddd, *J* = 11.8, 8.2, 4.1 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.18 – 1.05 (m, 2H), 1.08 – 0.98 (m, 2H); $^{13}$C NMR (151 MHz, dmso) δ 157.7, 156.2, 154.7, 153.5, 128.9, 128.1 (d, *J* = 5.0 Hz), 126.0, 118.6, 116.2 (d, *J* = 8.0 Hz), 115.8, 115.1 (d, *J* = 22.9 Hz), 113.8 (d, *J* = 22.5 Hz), 60.2 (d, *J* = 14.6 Hz), 47.7, 46.6, 30.5 (d, *J* = 8.8 Hz), 24.6 (d, *J* = 5.6 Hz); $\nu_{max}$ / $cm^{-1}$ : 2931, 1591, 1493, 1249, 755; (HRMS + pESI) cald $C_{20}H_{26}N_2O_2F$ $[M + H]^+$: 345.1978; observed:345.1960

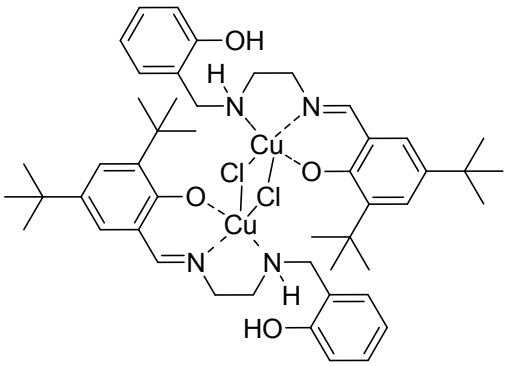
## Synthesis of targeted salan copper (II) complexes.

**General procedure.**

Ligand (50 mg) and $NEt_3$ (2 equiv.) were combined in MeOH (5 mL) and stirred at room temperature for 10 minutes. $CuCl_2$ (1.1 equiv.) was added and the reaction mixture was heated at reflux for 2 hours. The mixture was cooled to room temperature and excess solvent was removed *in vacuo*. The crude product was purified via normal phase column chromatography (DCM:MeOH:$NEt_3$, 90:10:1) to isolate copper complex.

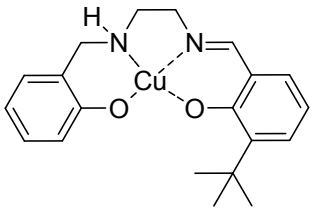
Calculated CHN and HRMS values correspond to the monomeric, tetradentate complexes unless otherwise shown. Variations can be explained as by mixed species from the oxidative dehydrogenation of salan.

**[Cu(II)-NSS-1]:**



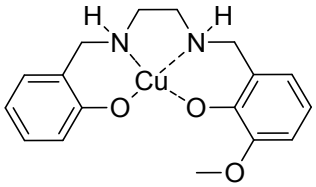

Green solid: (48 mg, 0.11 mmol, 83%): CHN analysis: calculated: %C: 59.99, %H: 7.38, %N: 5.83, observed: %C: 63.50 ,%H 7.38 ,%N 6.18; FTIR $\nu_{max}$ / $cm^{-1}$ : 2949, 2605, 1629, 1478, 1035; (HRMS + pESI) cald $C_{24}H_{33}N_2O_2Cu$ $[M + H]^+$: 444.1838; observed:444.1835

**[Cu(II)-NSS-2]:**



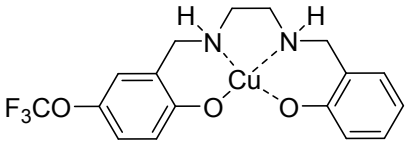
Grey solid: (24 mg, 0.06 mmol, 41%); CHN analysis: calc: %C: 61.60, %H: 6.72, %N: 7.18, observed: %C: 62.35, %H 8.38, %N: 6.90; FTIR $\nu_{max}$ / $cm^{-1}$ : 2911, 1629, 1478, 740; (HRMS + pESI) cald $C_{20}H_{25}N_2O_2Cu$ $[M + H]^+$: 388.1212; observed:388.1202

**[Cu(II)-NSS-3]:**



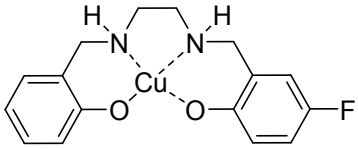
Mixture turned dark brown on addition of $CuCl_2$ and no pure product could be isolated.

**[Cu(II)-NSS-4):**



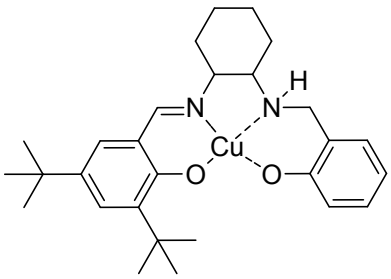
Green solid: (55 mg, 0.13 mmol, 94%); CHN analysis: calc: %C: 48.86, %H: 4.10, %N: 6.70, observed: %C: 46.84, %H 3.73, %N: 5.67; corresponds to [Cu(II)-NSS-4]+1$H_2O$ %C: 46.84, %H 4.39, %N: 6.43; FTIR $\nu_{max}$ / $cm^{-1}$ : 2866, 1597, 1479, 1247; (HRMS + pESI) cald $C_{17}H_{18}N_2O_3F_3Cu$ $[M + H]^+$: 418.0566; observed:418.0457

**[Cu(II)-NSS-5]:**



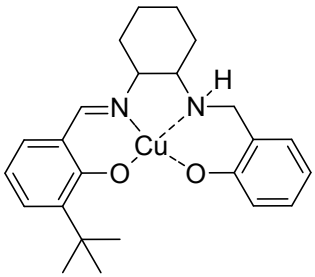
Green viscous oil: (47 mg, 0.13 mmol, 79%); CHN analysis: calc: %C: 54.62, %H: 4.87, %N: 5.40, observed: %C: 51.09 , %H 4.88, %N 7.01: FTIR $\nu_{max}$ / $cm^{-1}$: 3424, 2911, 1595, 1276, 1256, 1035; (HRMS + pESI) cald $C_{16}H_{18}N_2O_2FCu$ $[M + H]^+$: 352.0643; observed:352.0661

**[Cu(II)-CyNSS-1]:**



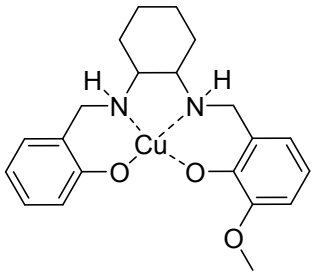
Green solid: (54 mg, 0.11 mmol, 83%); CHN analysis: calc: %C: 67.51, %H: 7.69, %N: 5.62, observed: %C:, %H, %N: FTIR $\nu_{max}$ / $cm^{-1}$: 2946, 2603, 2497, 1623, 1476, 1035; (HRMS + pESI) cald $C_{28}H_{39}N_2O_2Cu$ $[M + H]^+$: 498.2308, observed:498.2296

**[Cu(II)-CyNSS-2]:**



Grey solid: (6 mg, 0.014 mmol, 12%): CHN analysis: not enough sample; FTIR $\nu_{max}$ / $cm^{-1}$: 2937, 1623, 1424, 1287, 753; (HRMS + pESI) cald $C_{24}H_{31}N_2O_2Cu$ $[M + H]^+$:442.1682, observed;442.1695

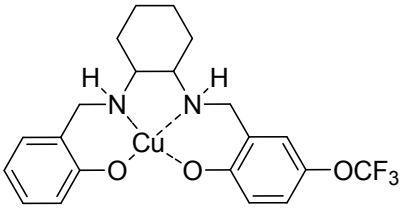
**[Cu(II)-CyNSS-3]:**



Chemical Formula: $C_{21}H_{26}CuN_2O_3$

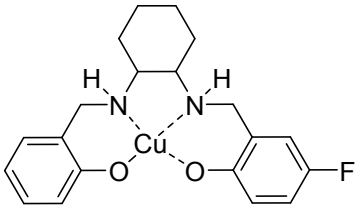
Green solid: (33 mg, 0.08 mmol, 56%); CHN analysis: calc: %C: 60.34, %H: 6.27, %N: 6.70, observed: %C: 53.85 , %H 4.91 , %N 5.92: ; FTIR $\nu_{max}$ / $cm^{-1}$: 3206, 2933, 1594, 1476, 1276, 732; (HRMS + pESI) cald $C_{21}H_{27}N_2O_3Cu$ $[M + H]^+$:418.1335, observed;418.1318

**[Cu(II)-CyNSS-4]:**




Green solid: (47 mg, 0.10 mmol, 83%); CHN analysis: calc: %C: 53.44, %H: 4.91, %N: 5.94, observed: %C: 53.39, %H 4.95, %N: 5.79; FTIR $\nu_{max}$ / $cm^{-1}$: 3204, 2936, 1479, 1246, 757; ; (HRMS + pESI) cald $C_{21}H_{24}N_2O_3F_3Cu$ $[M + H]^+$: 472.1035, observed: 472.1037

**[Cu(II)-CyNSS-5]:**




Green solid: (23 mg, 0. 06 mmol, 38%); CHN analysis: calc: %C: 59.17, %H: 5.71, %N: 6.90, observed: %C: 58.81, %H 5.44, %N: 5.99; FTIR $\nu_{max}$ / $cm^{-1}$: 3206, 2940, 1477, 1294, 752; (HRMS + pESI) cald $C_{20}H_{24}N_2O_2FCu$ $[M + H]^+$: 406.1118, observed: 406.1118

## Characterisation data for ligands.

### Half units.

*tert-butyl (2-((2-hydroxybenzyl)amino)ethyl)carbamate* **(1):**

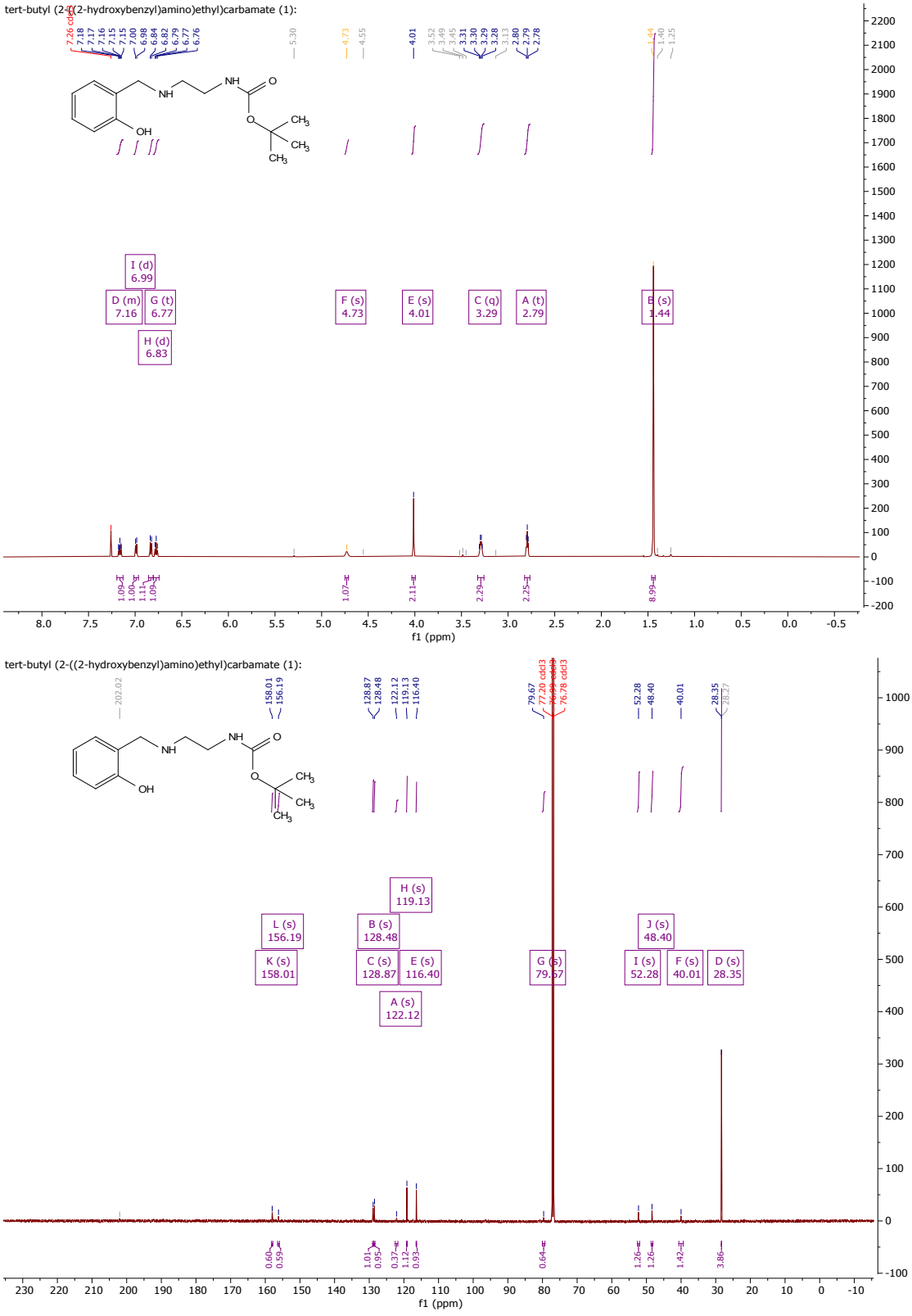
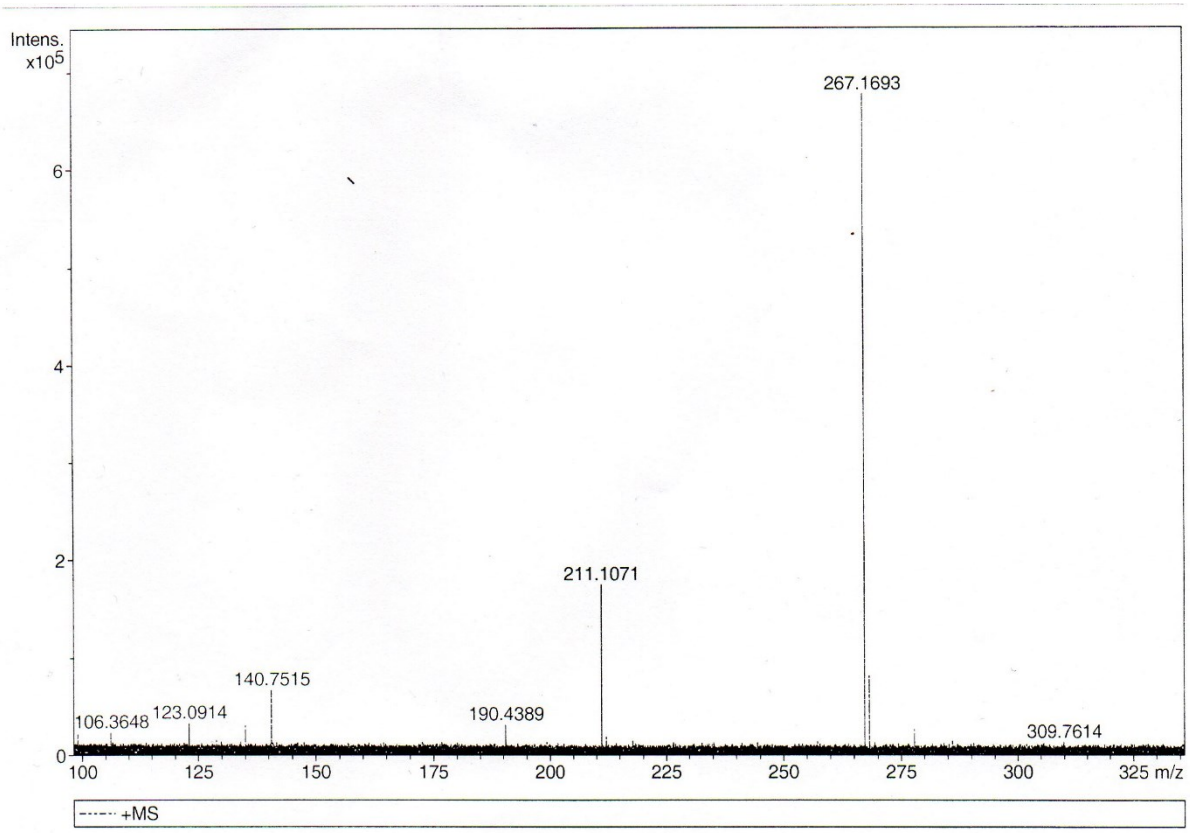



***Figure S1:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***(1).***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 14 H 23 N 2 O 3 | 0.016 | 267.1703 | 3.85 | 8.84 | 2.36 | 4.50 | ok | even |

***Figure S2:*** *HRMS spectra of (**1**).*

*2-(((2-aminoethyl)amino)methyl)phenol hydrochloride* **(2)**

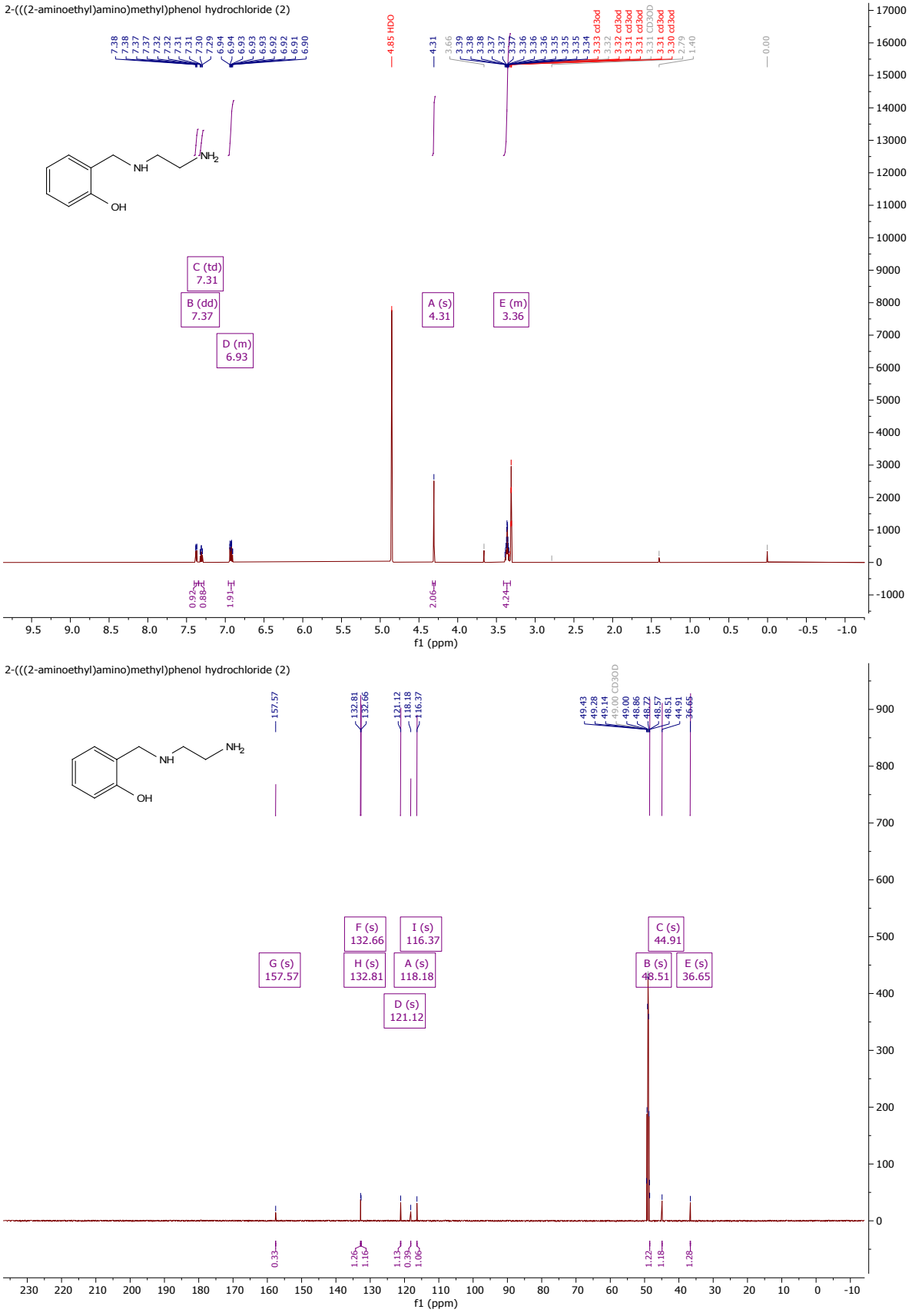
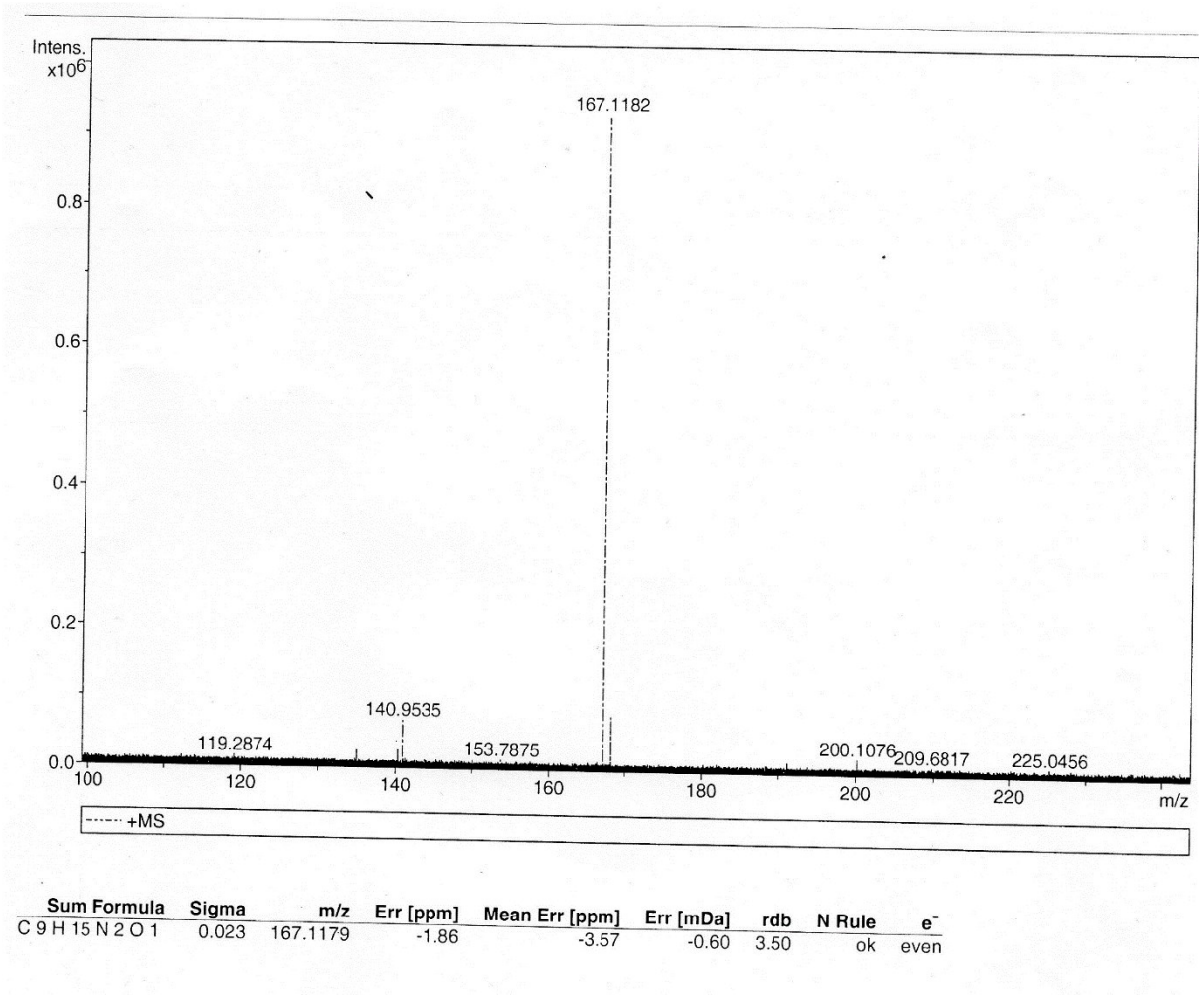


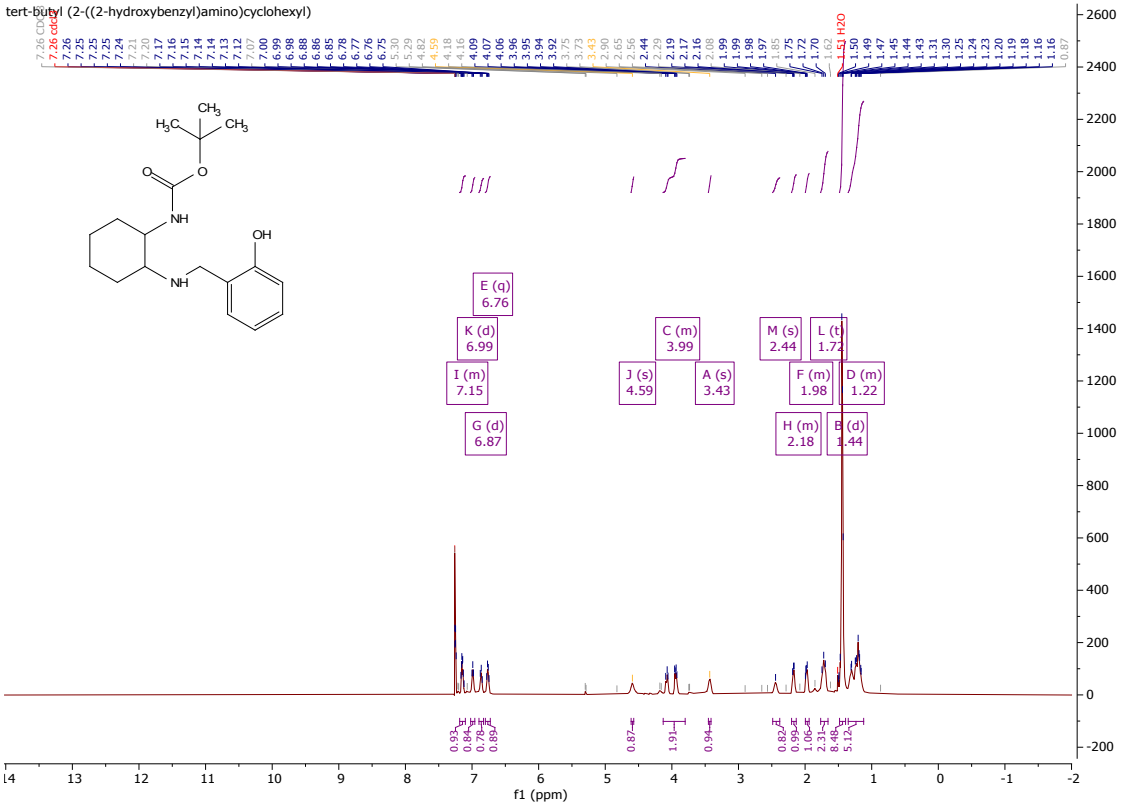

***Figure S3:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***(2).***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 9 H 15 N 2 O 1 | 0.023 | 167.1179 | -1.86 | -3.57 | -0.60 | 3.50 | ok | even |

***Figure S4:*** *HRMS spectra of* ***(1).***

*tert-butyl (2-((2-hydroxybenzyl)amino)cyclohexyl)carbamate* **(3):**



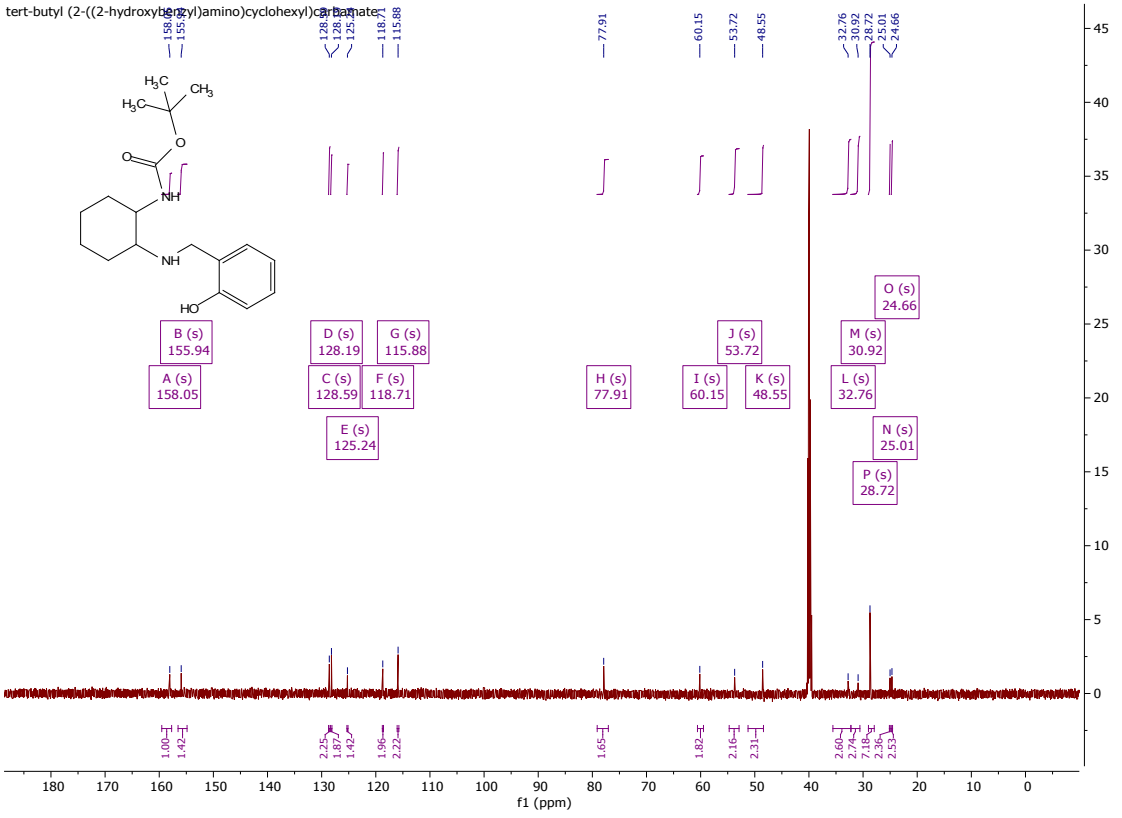




***Figure S5:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***(3).***

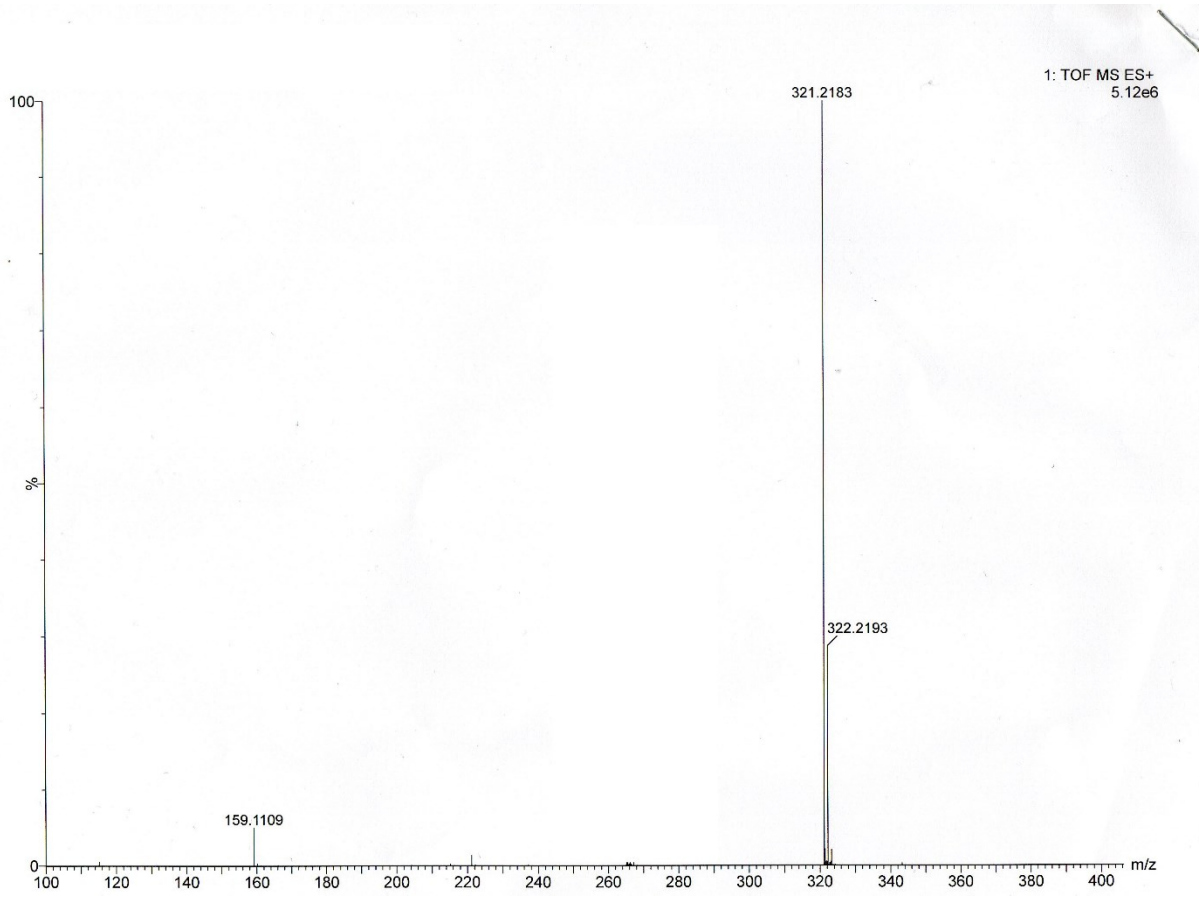



***Figure S6:*** *HRMS spectra of* ***(3).***

2-(((2-aminocyclohexyl)amino)methyl)phenol hydrochloride **(4):**

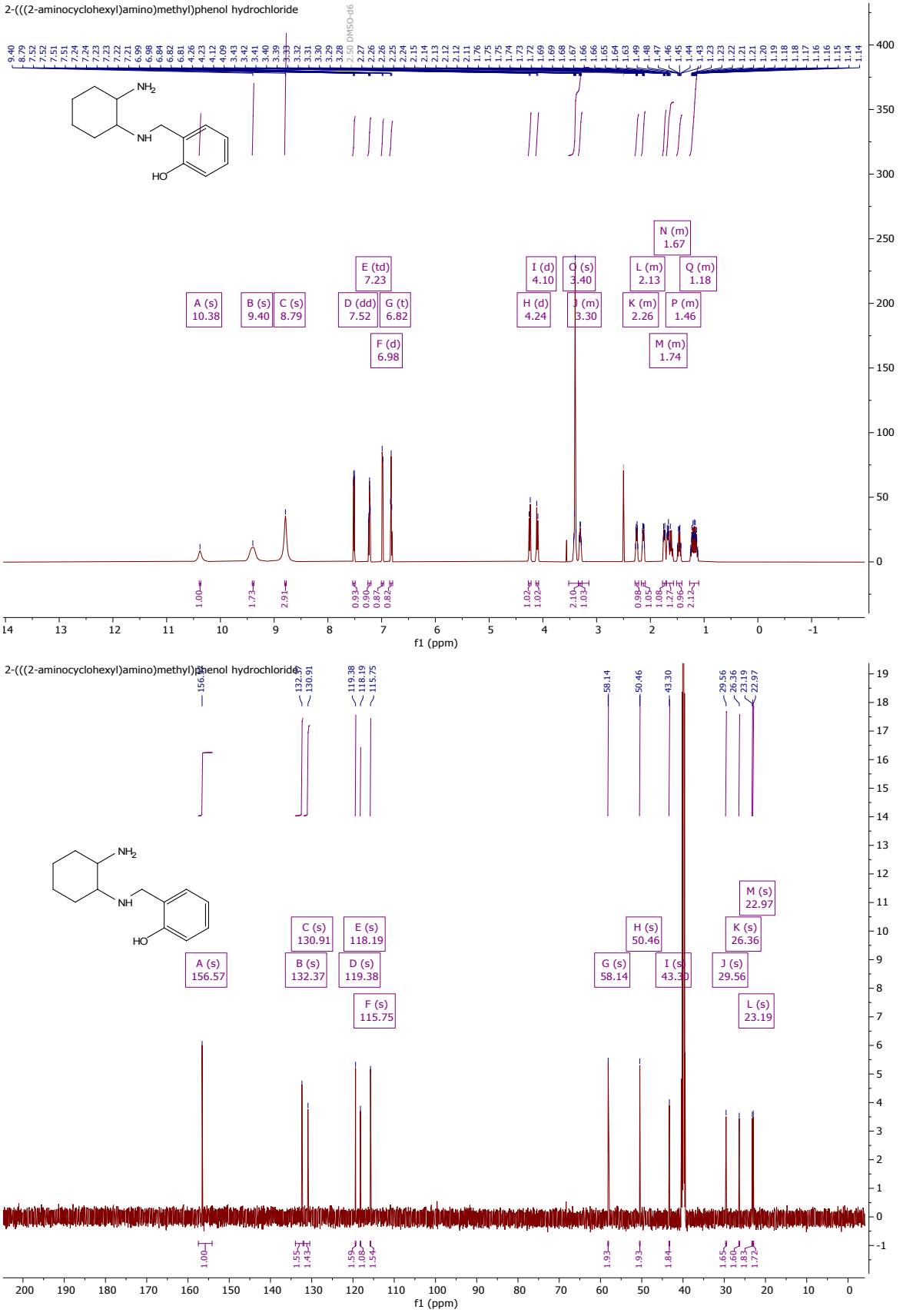



***Figure S7:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***(4).***

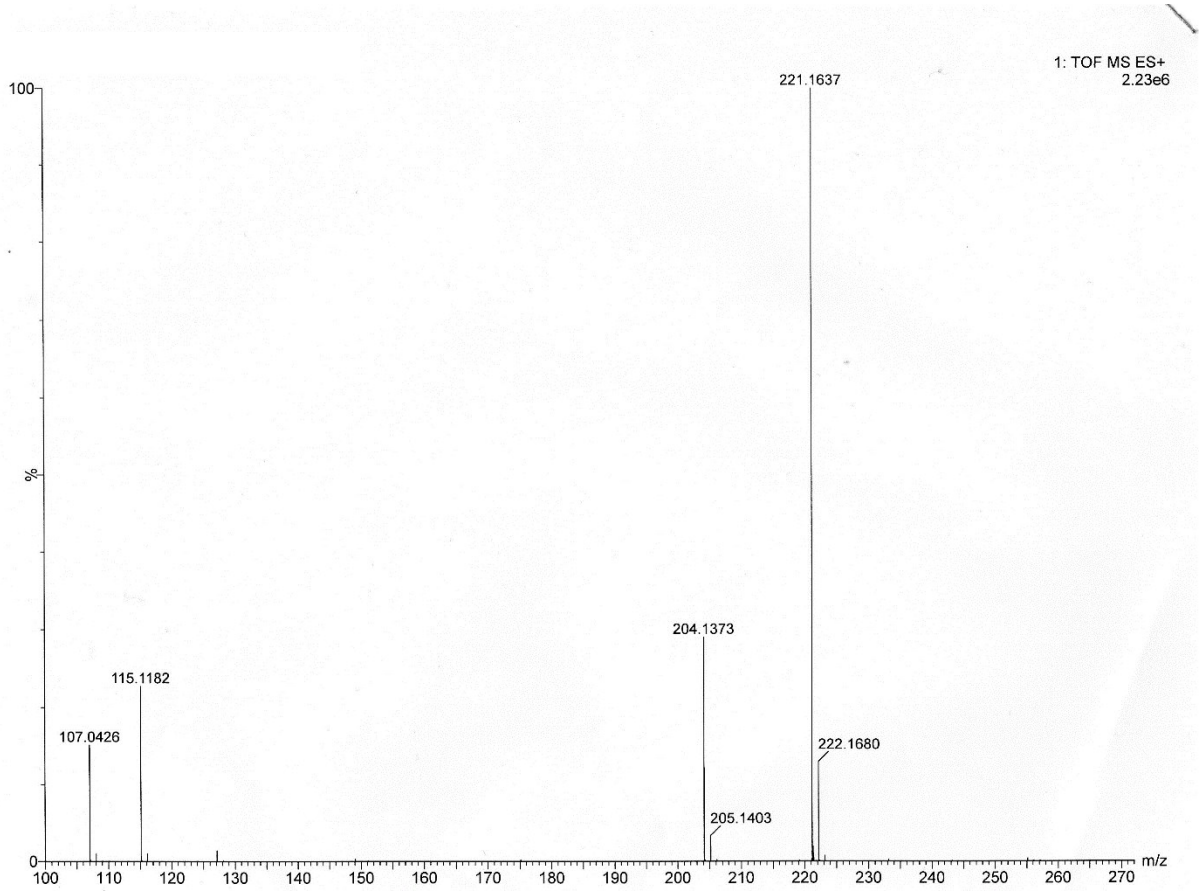



***Figure S8:*** *HRMS spectra of* ***(4).***

Non-Symmetric Salan (NSS) ligands.

**NSS-1:**

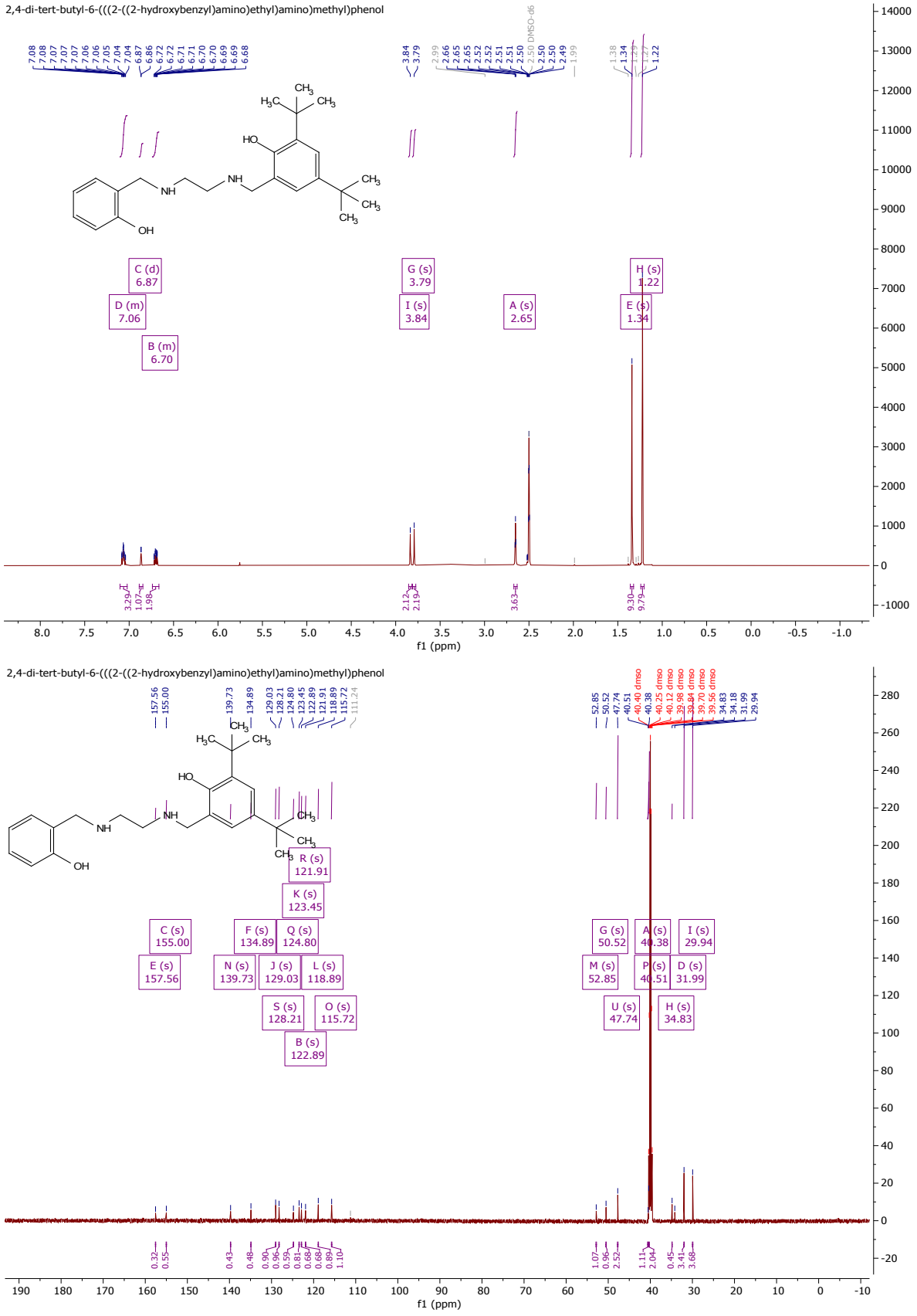



***Figure S9:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-1.***

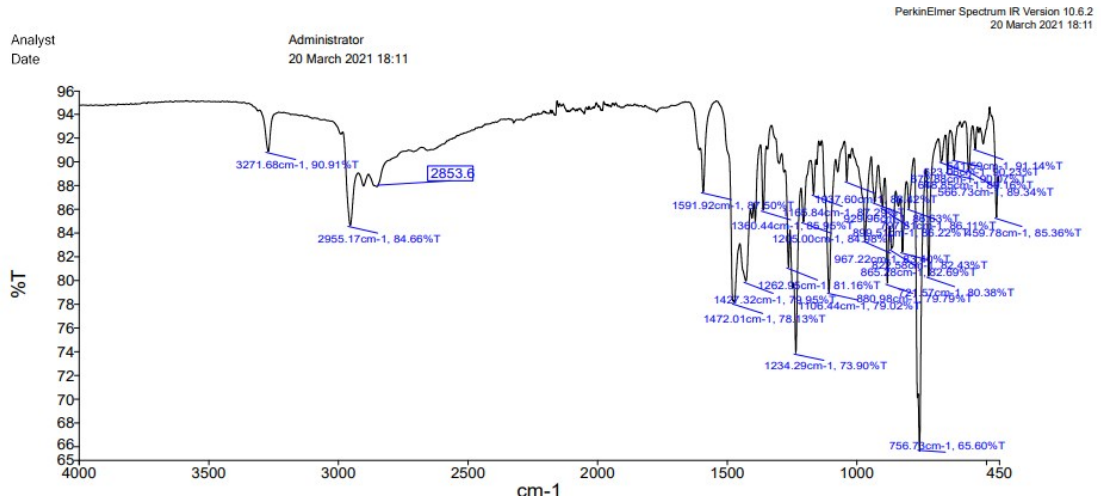



***Figure S10:*** *FTIR spectra of* ***NSS-1.***

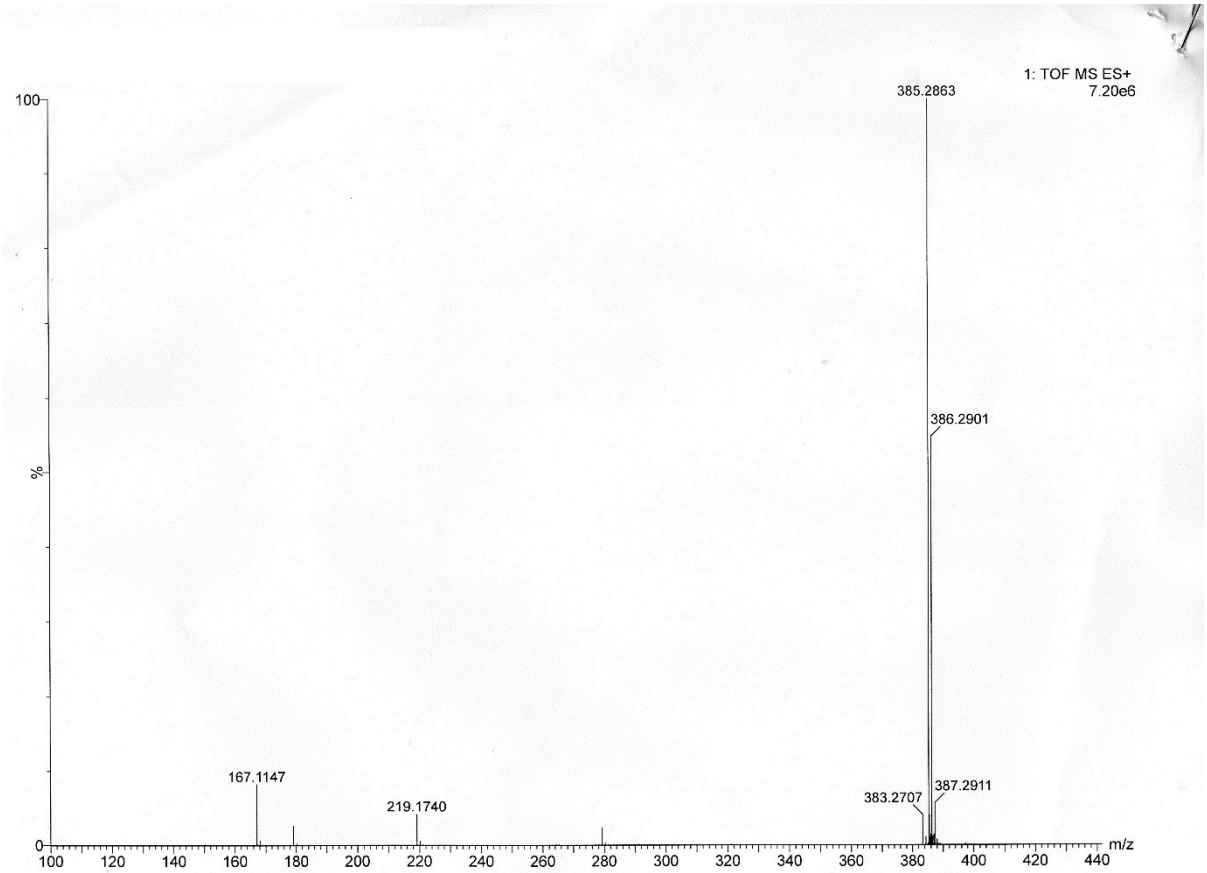



***Figure S11:*** *HRMS spectra of* ***NSS-1.***

**NSS-2:**

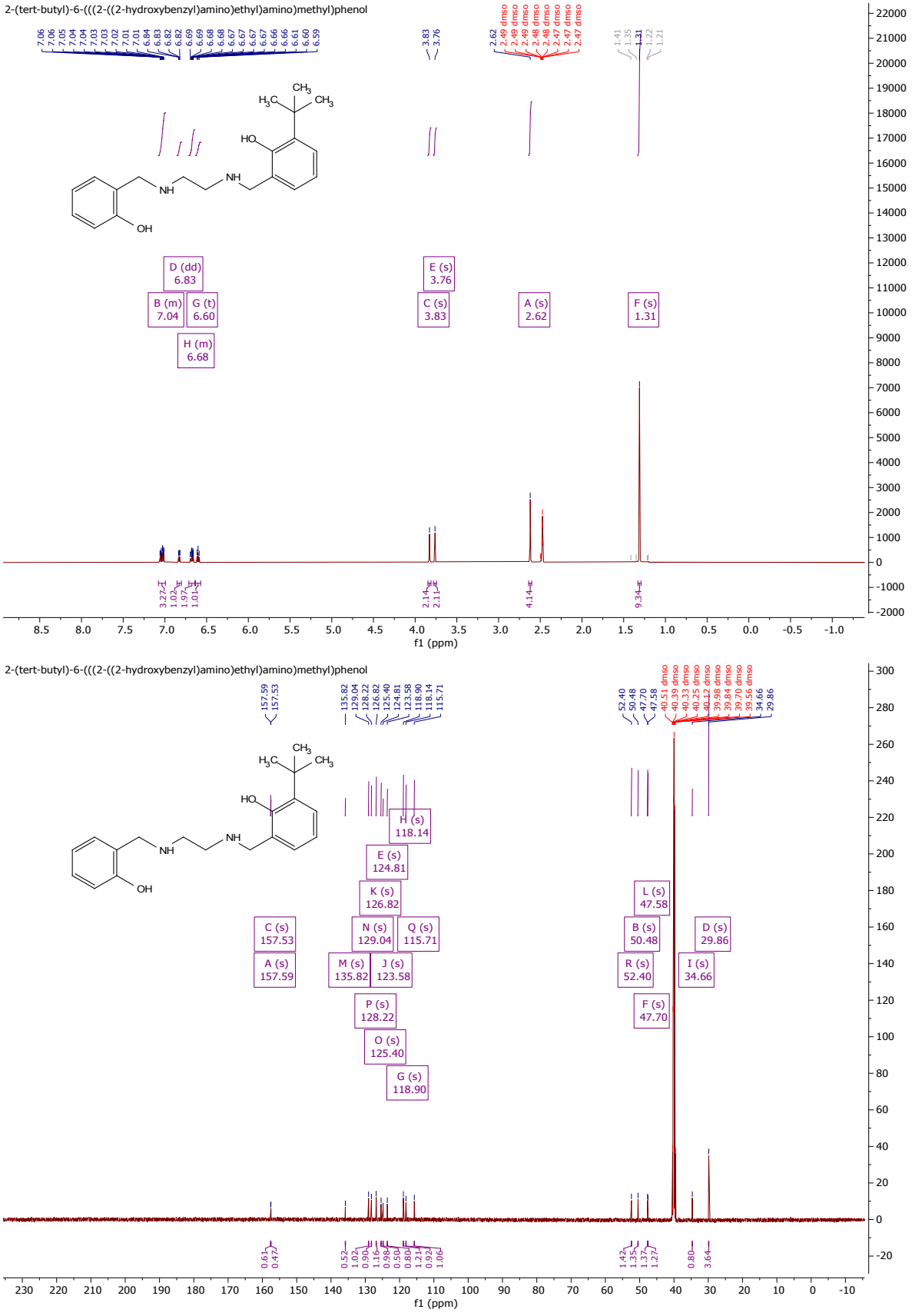



***Figure S12:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-2.***

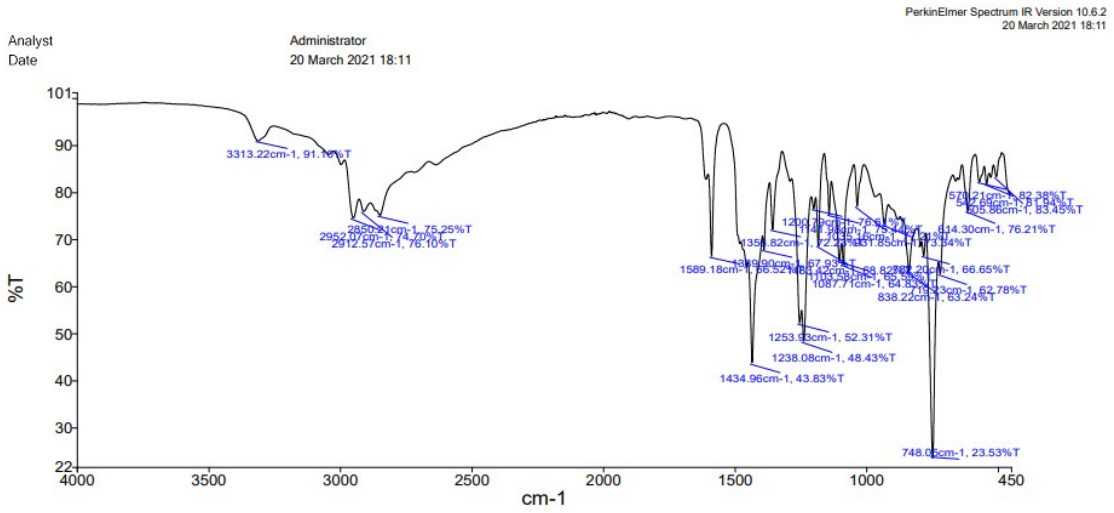
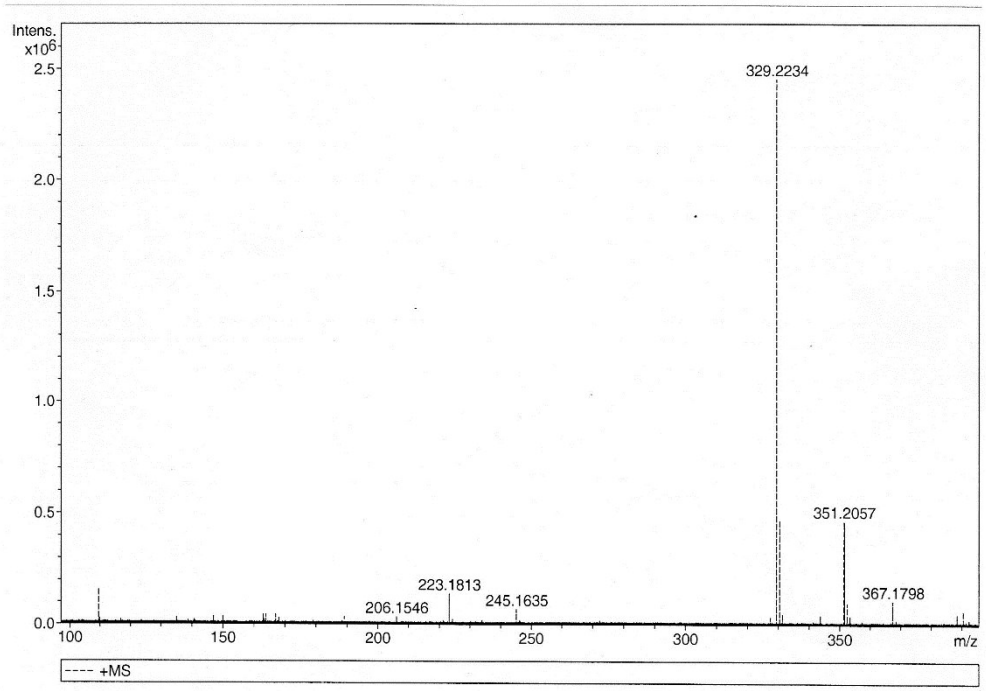



***Figure S13:*** *FTIR spectra of* ***NSS-3.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 20 H 29 N 2 O 2 | 0.043 | 329.2224 | -3.17 | -3.37 | -1.11 | 7.50 | ok | even |

***Figure S14:*** *HRMS spectra of* ***NSS-2.***

**NSS-3**:

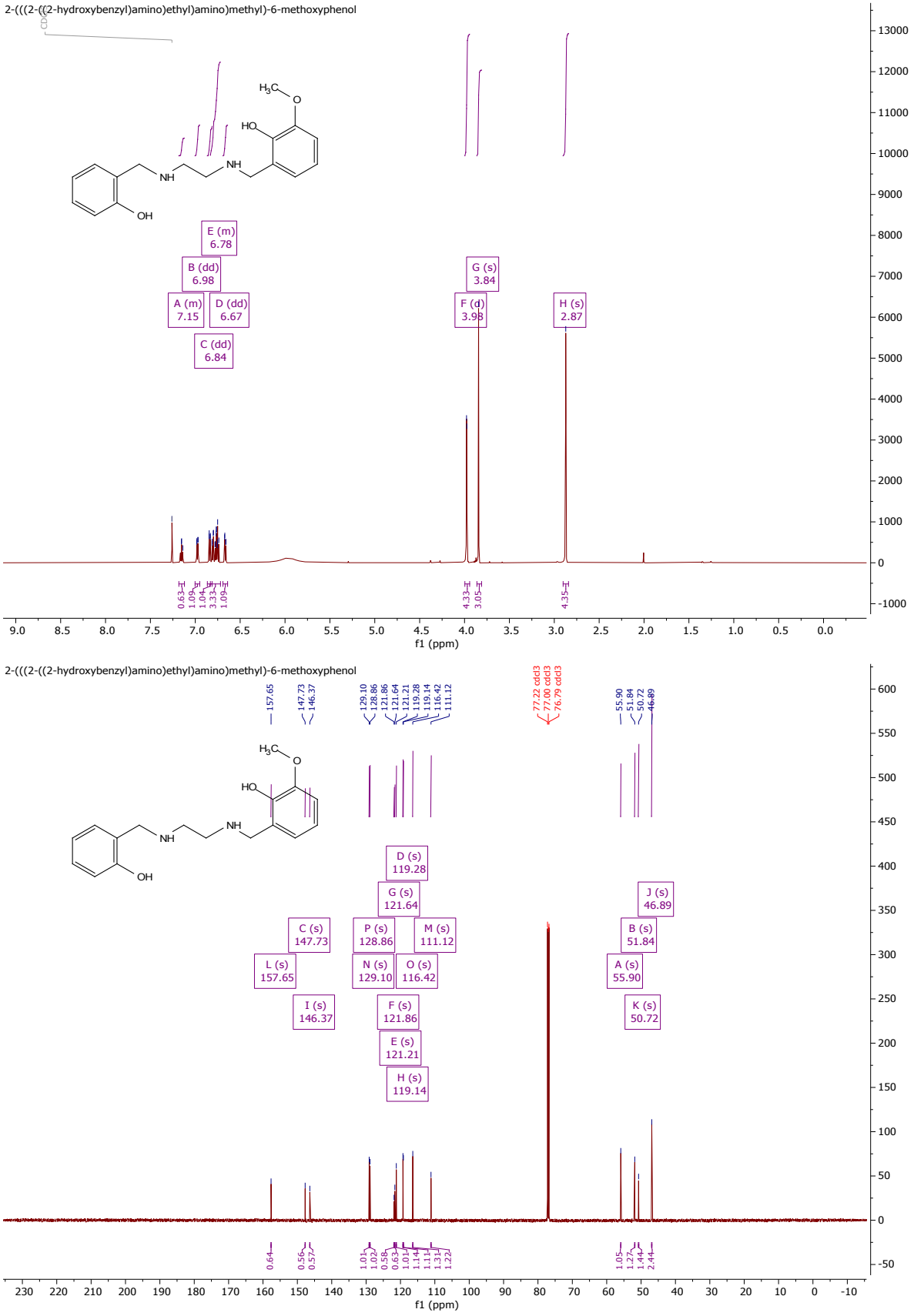



***Figure S15:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-3.***

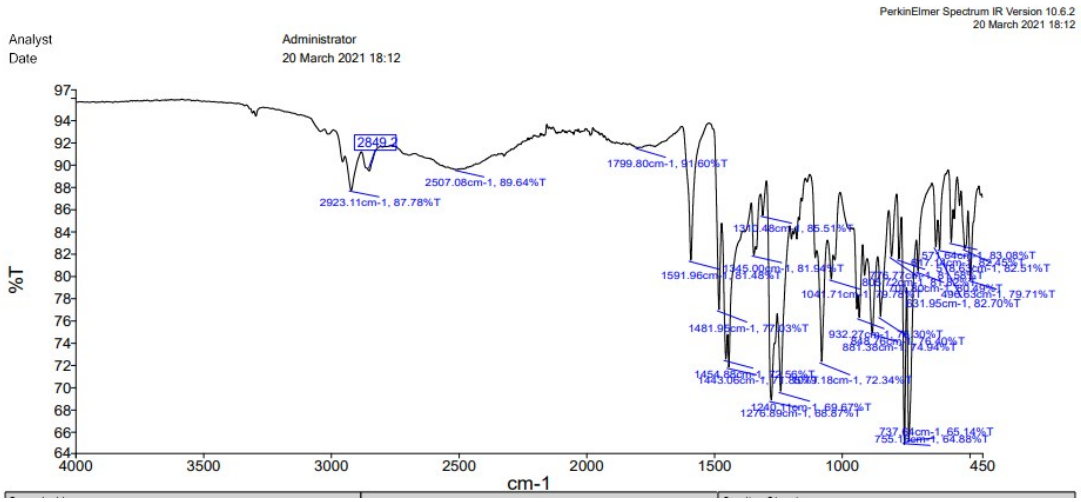
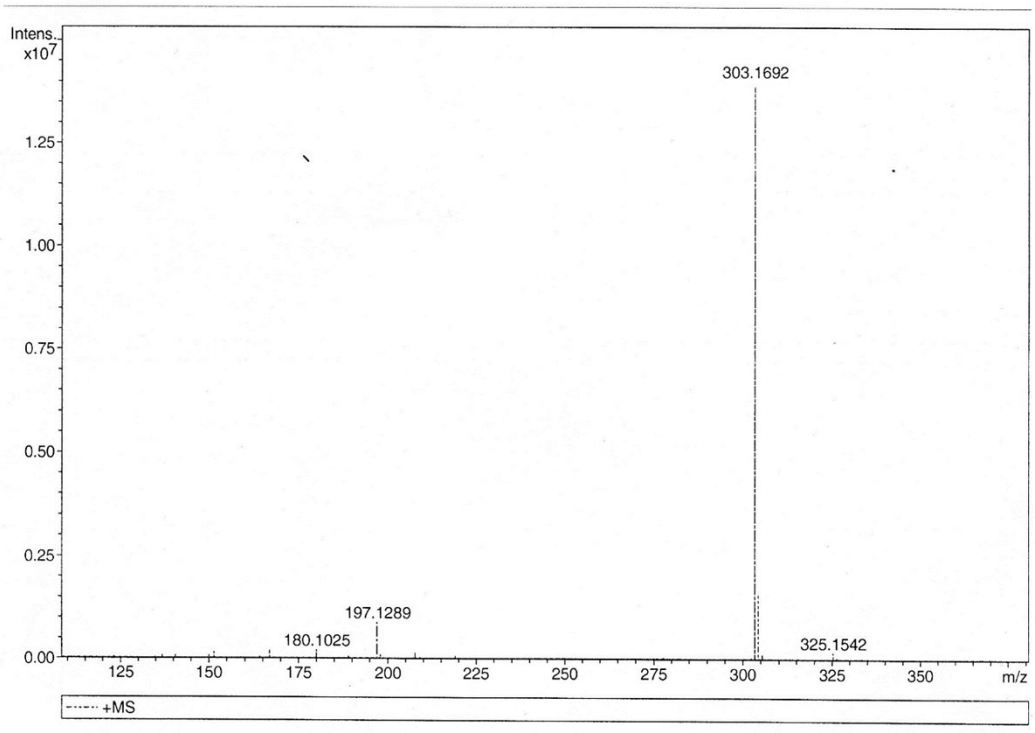



***Figure S16:*** *FTIR spectra of* ***NSS-2.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 17 H 23 N 2 O 3 | 0.034 | 303.1703 | 3.73 | 1.53 | 0.46 | 7.50 | ok | even |

***Figure S17:*** *HRMS spectra of* ***NSS-2.***

**NSS-4**:

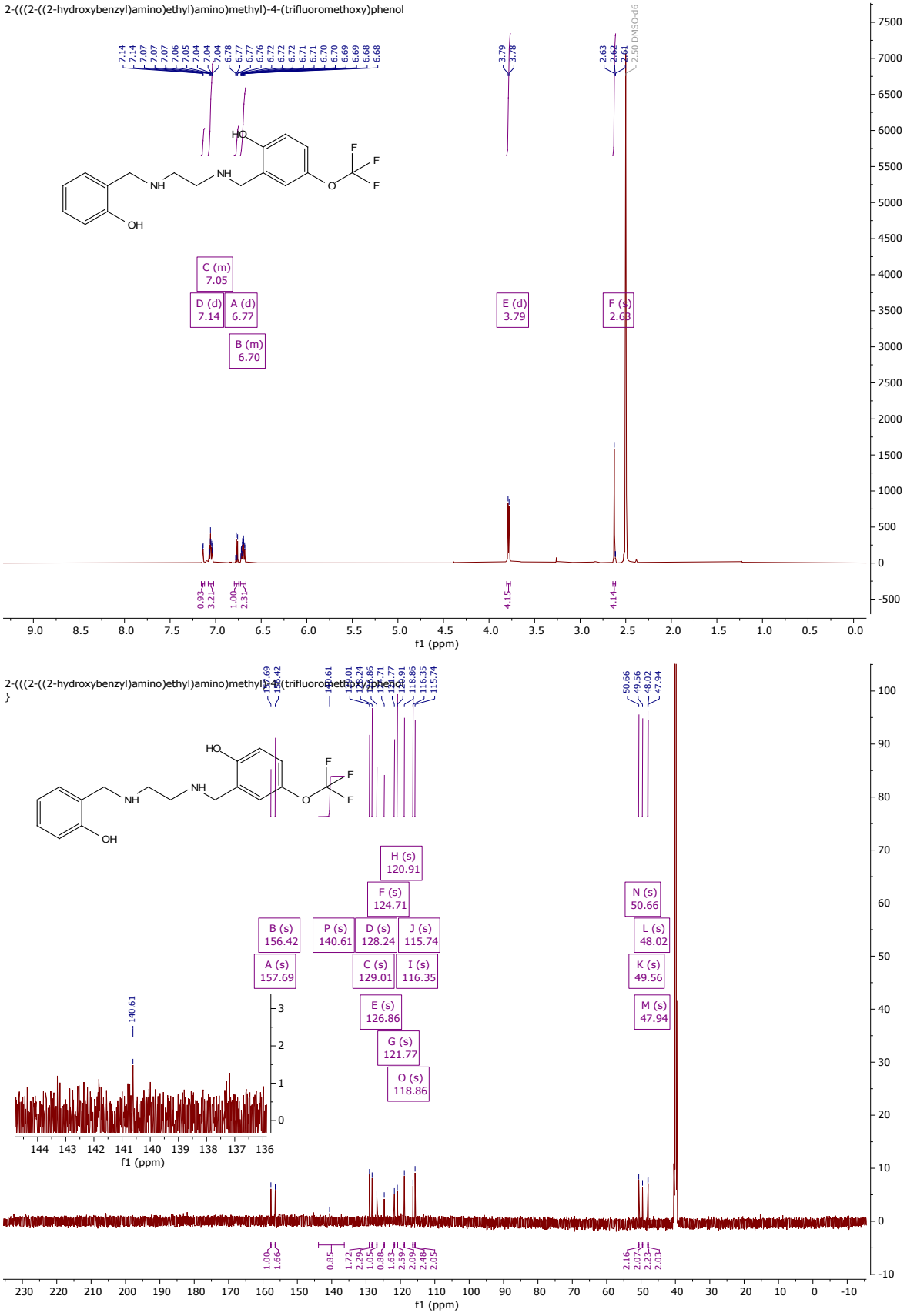



***Figure S18:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-4.***

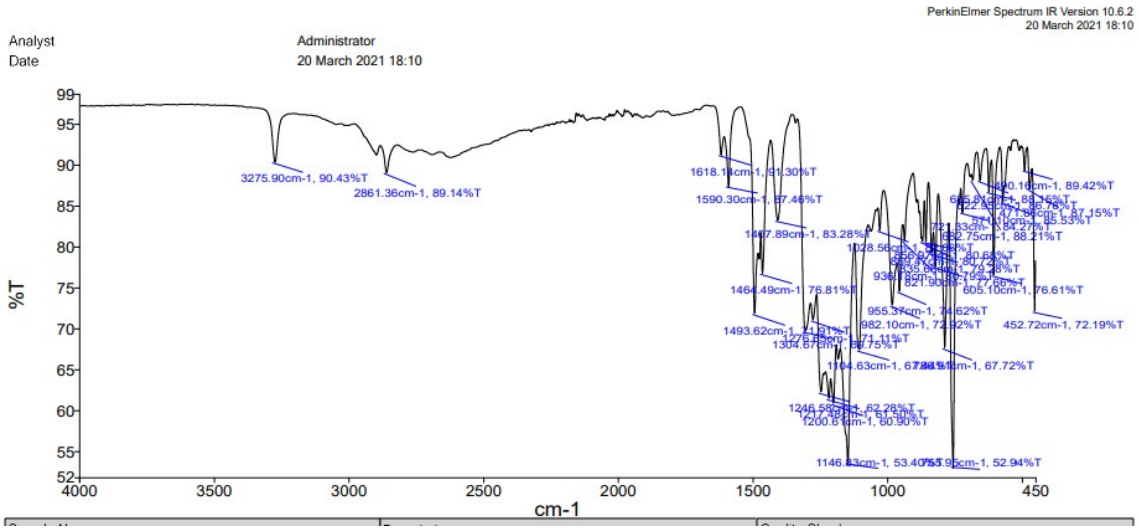
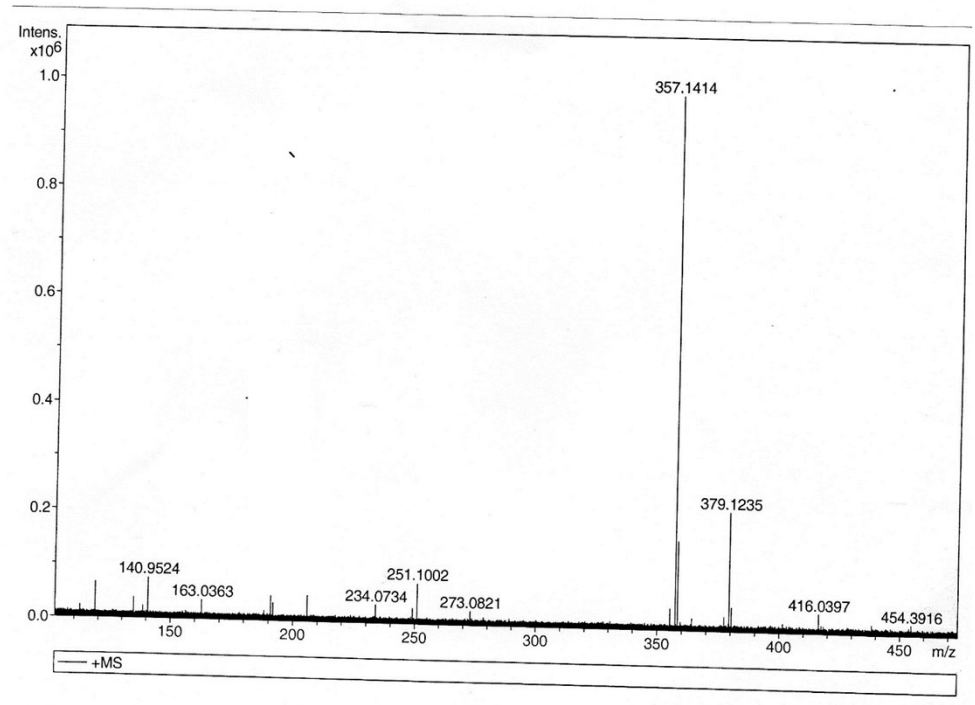



***Figure S19:*** *FTIR spectra of* ***NSS-4.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 17 H 20 F 3 N 2 O 3 | 0.027 | 357.1421 | 1.79 | -1.32 | -0.47 | 7.50 | ok | even |

***Figure S20:*** *HRMS spectra of* ***NSS-4.***

**NSS-5:**

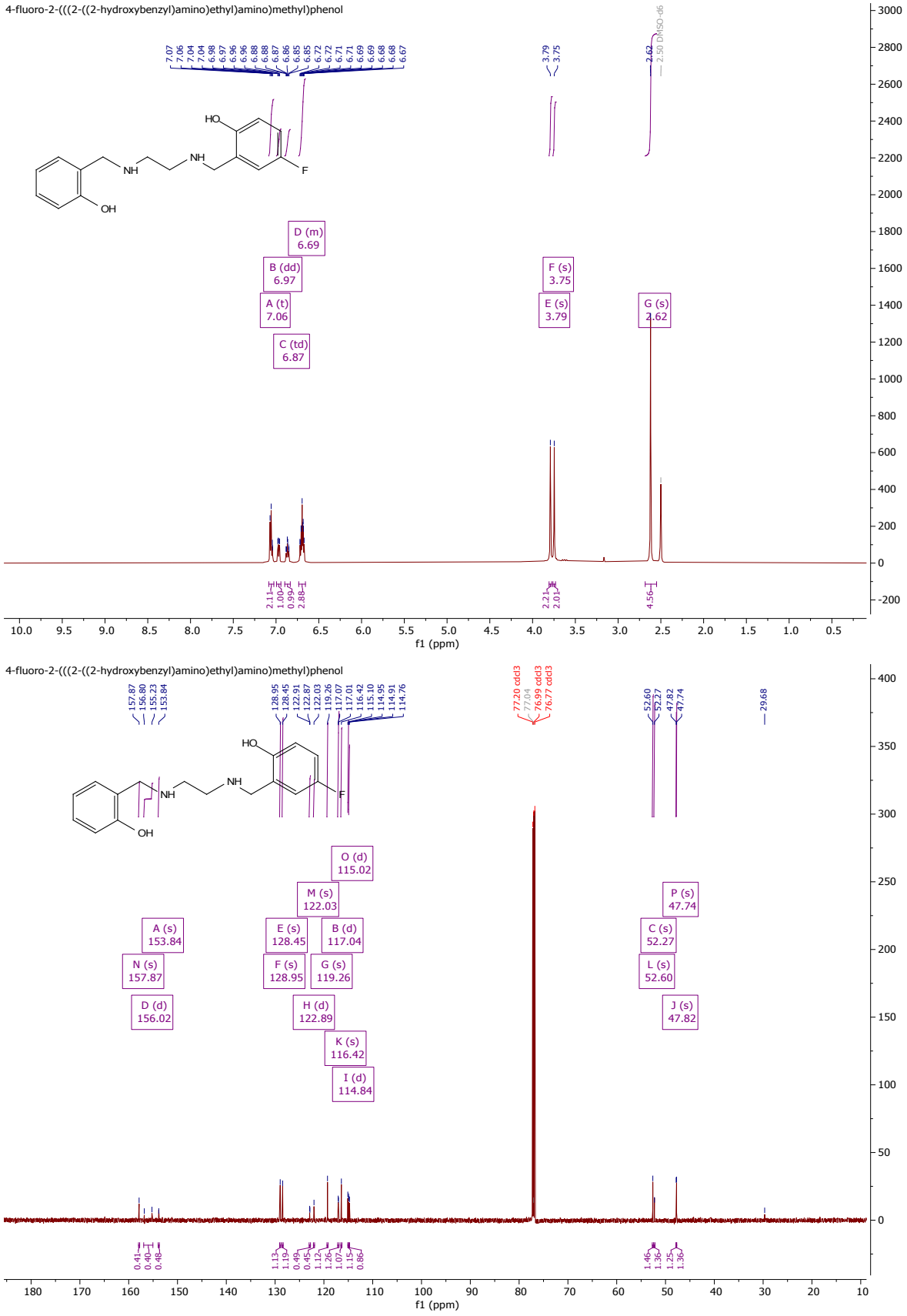



***Figure S21:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-5.***

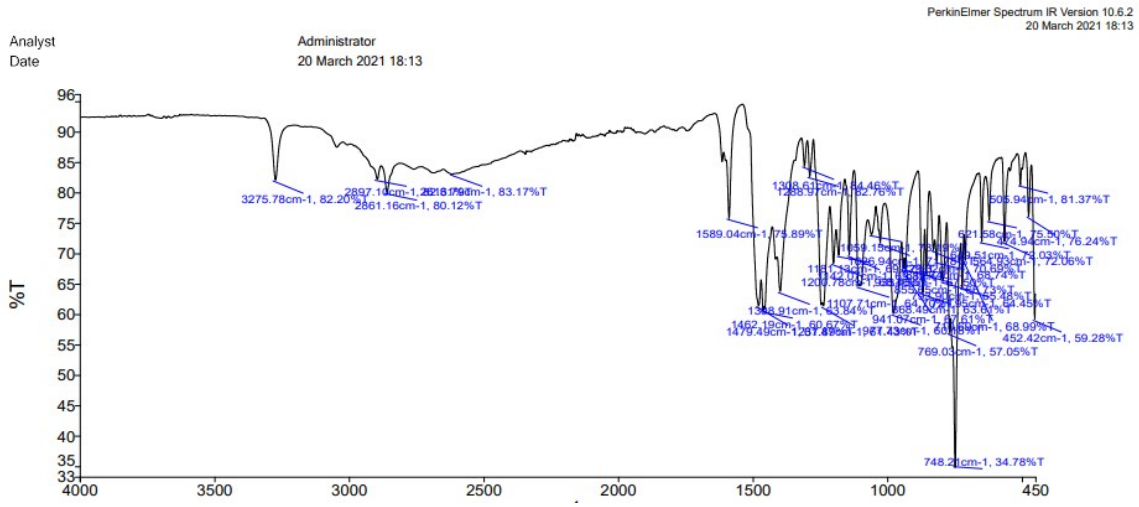
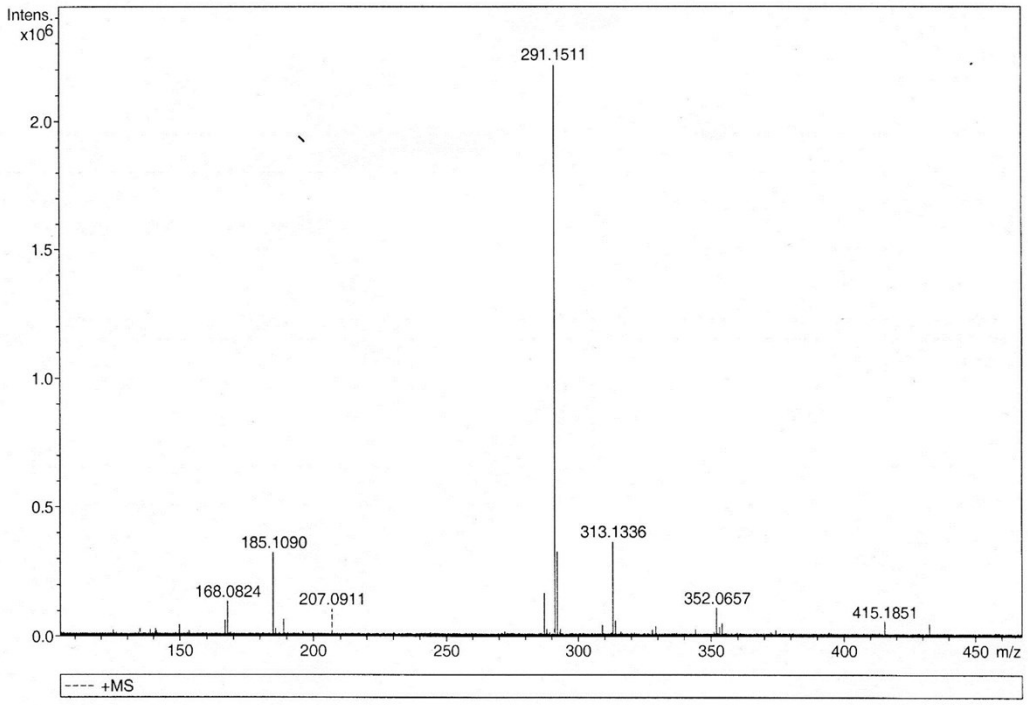



***Figure S22:*** *FTIR spectra of* ***NSS-5.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 16 H 20 F 1 N 2 O 2 | 0.037 | 291.1503 | -2.65 | -2.13 | -0.62 | 7.50 | ok | even |

***Figure S23:*** *HRMS spectra of* ***NSS-5.***

**NSS-6:**

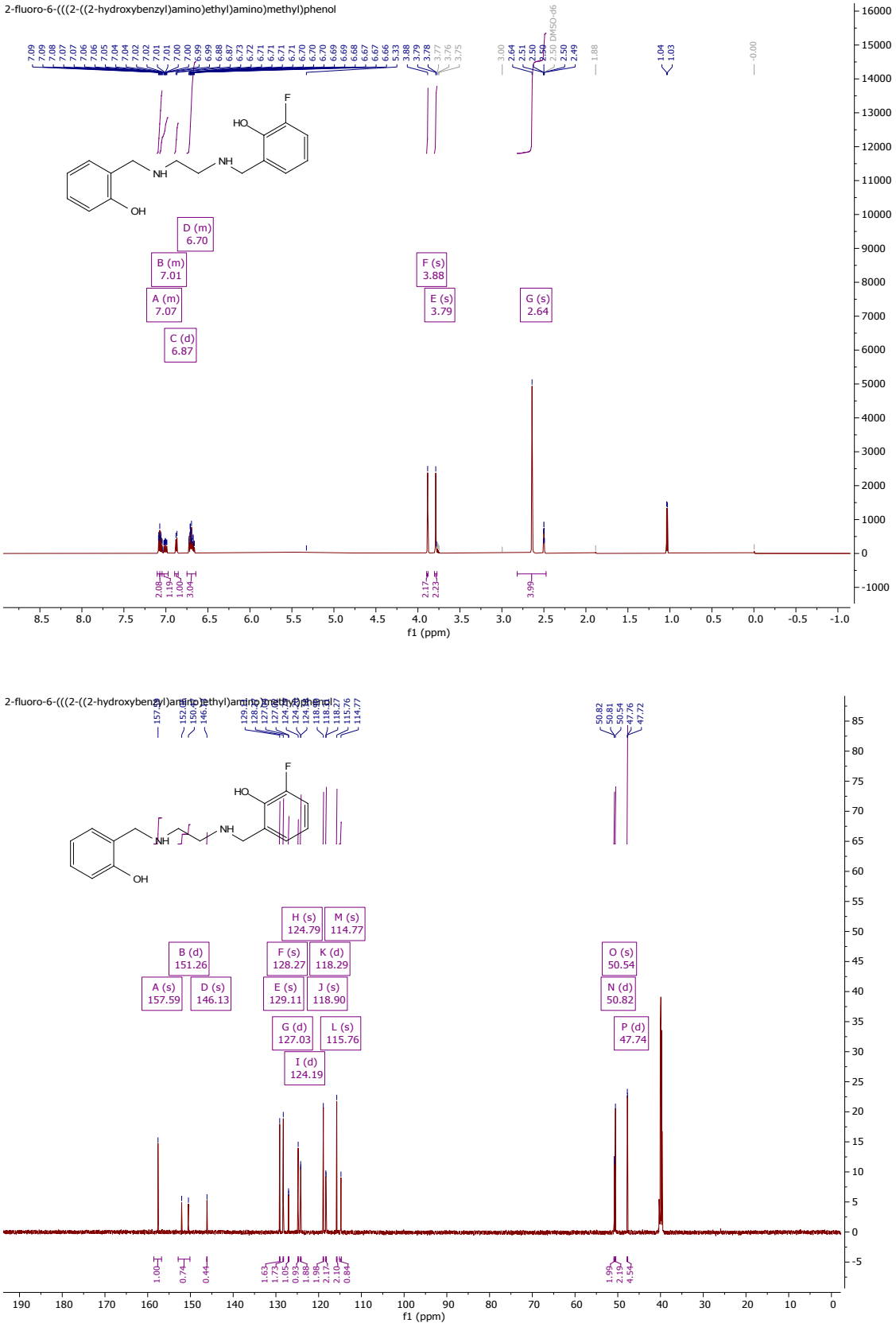



***Figure S24:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-6.***

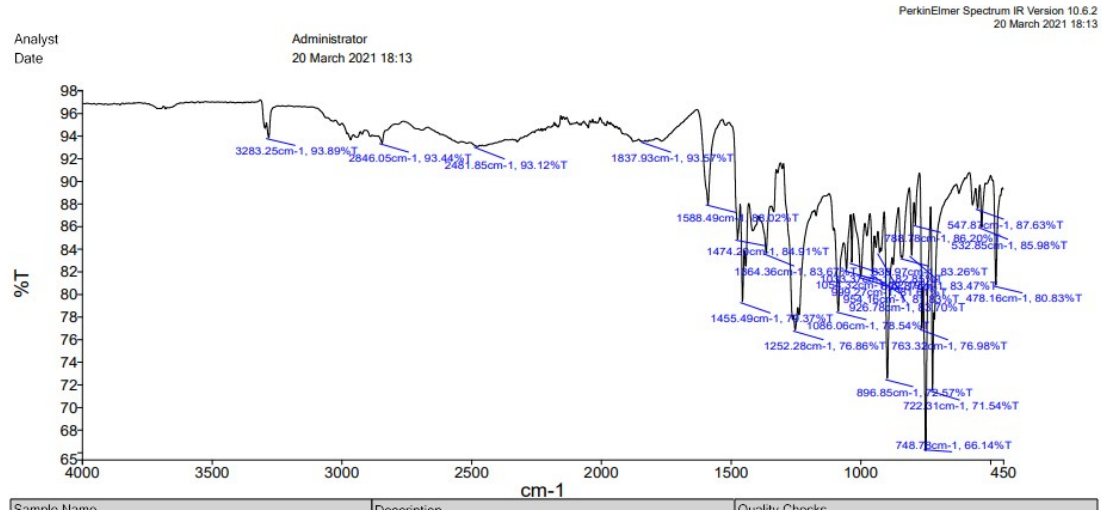



***Figure S25:*** *FTIR spectra of* ***NSS-6.***

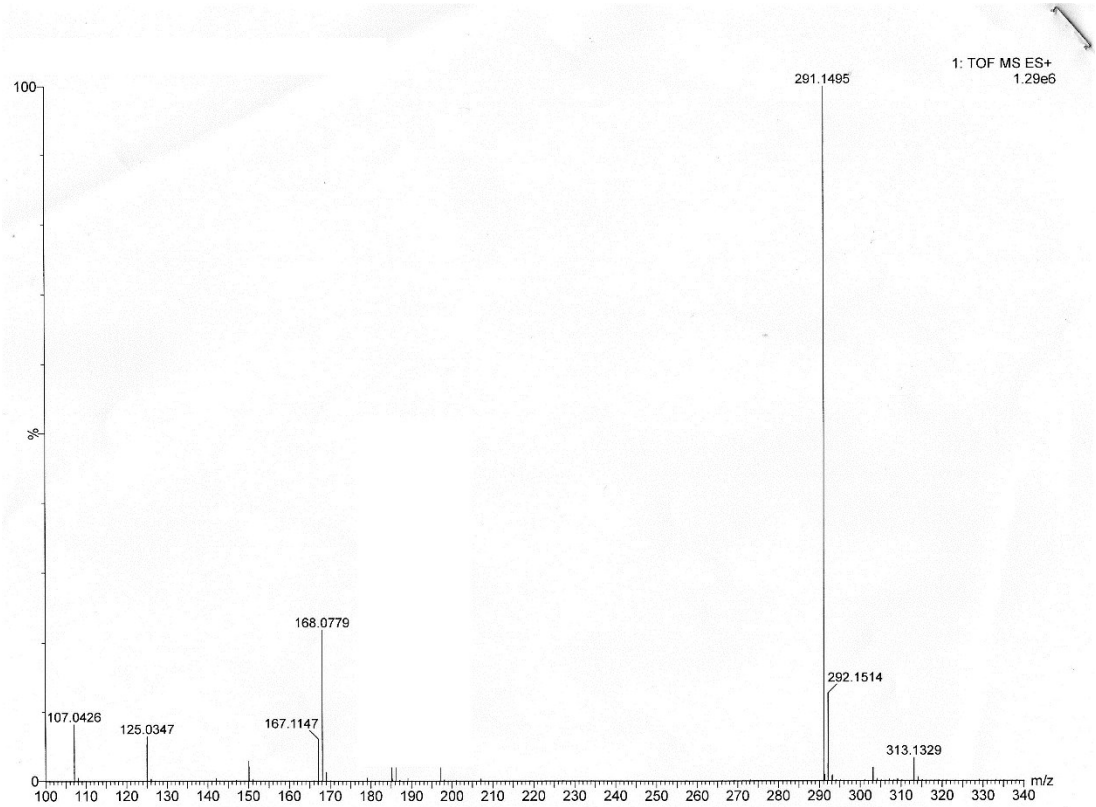



***Figure S26:*** *HRMS spectra of* ***NSS-6.***

**NSS-7:**

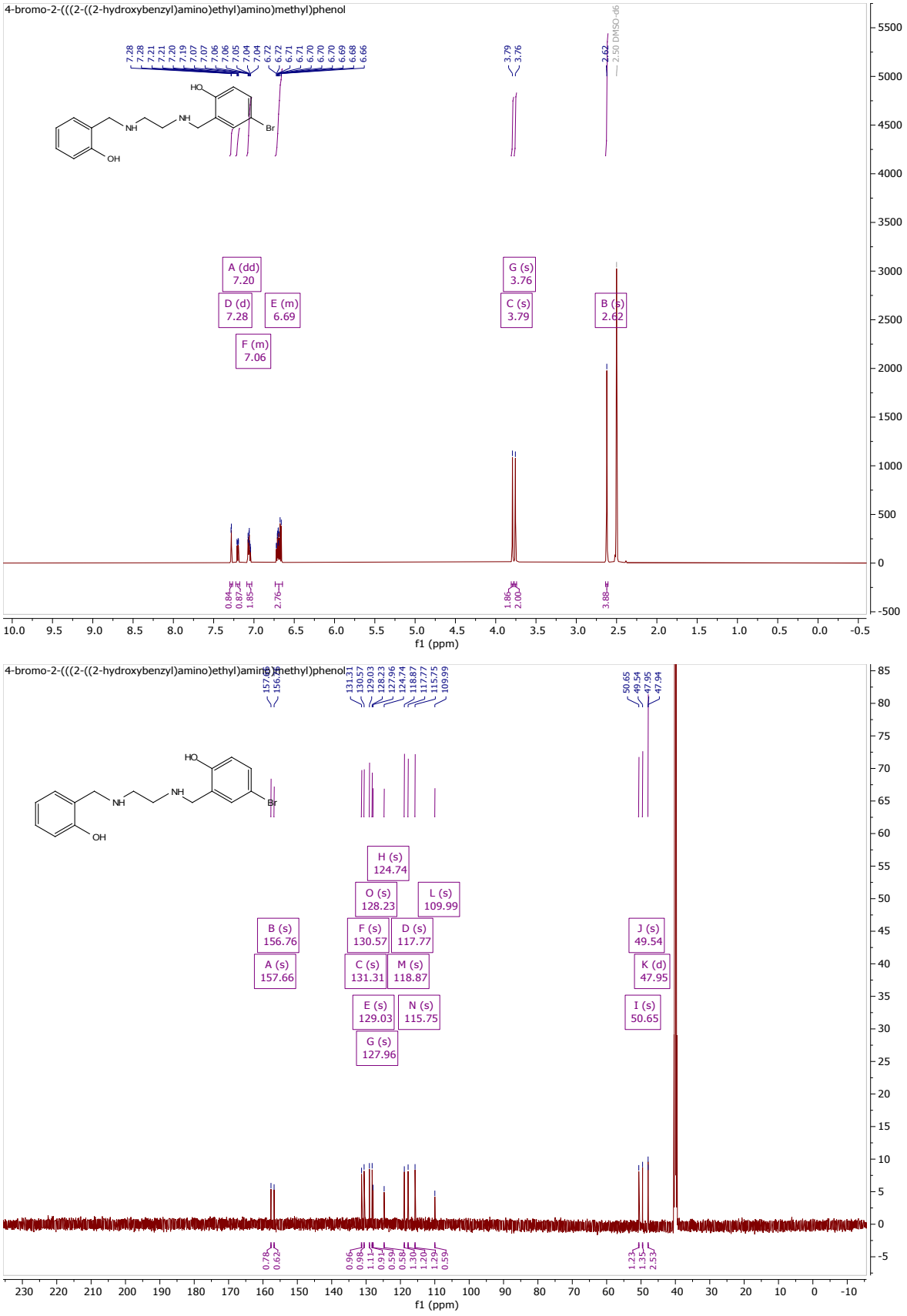



***Figure S27:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-7.***

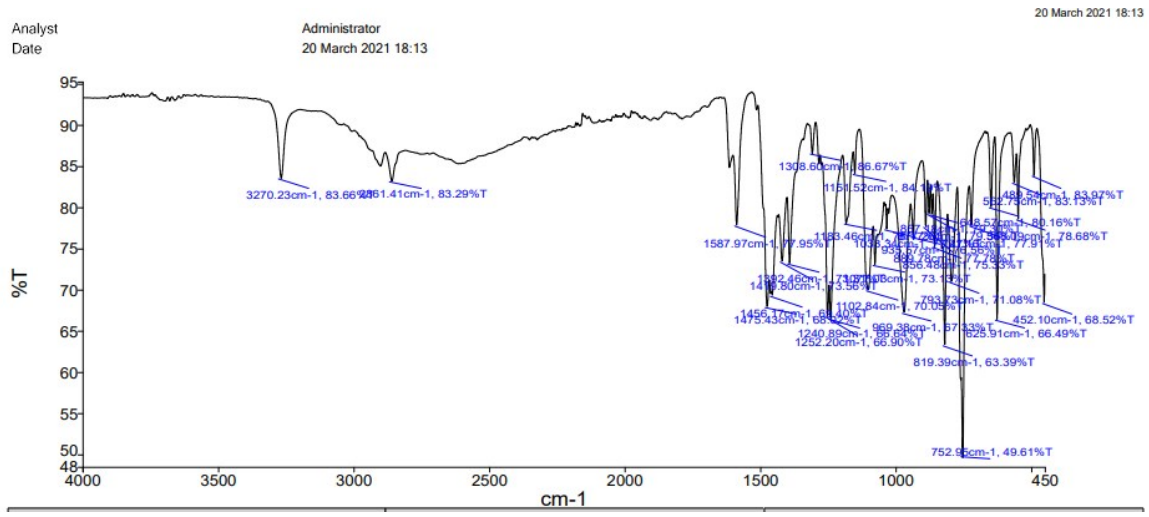
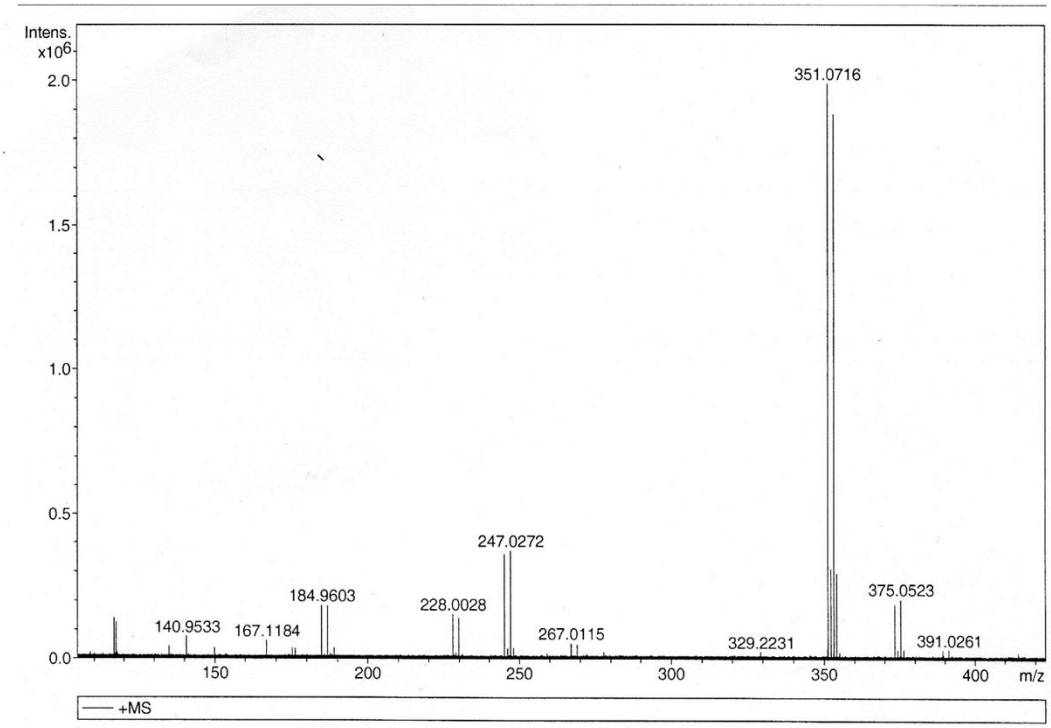



***Figure S28:*** *FTIR spectra of* ***NSS-7.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 16 H 20 Br 1 N 2 O 2 | 0.047 | 351.0703 | -3.72 | -3.74 | -1.32 | 7.50 | ok | even |

***Figure S29:*** *HRMS spectra of* ***NSS-7.***

## NSS-8

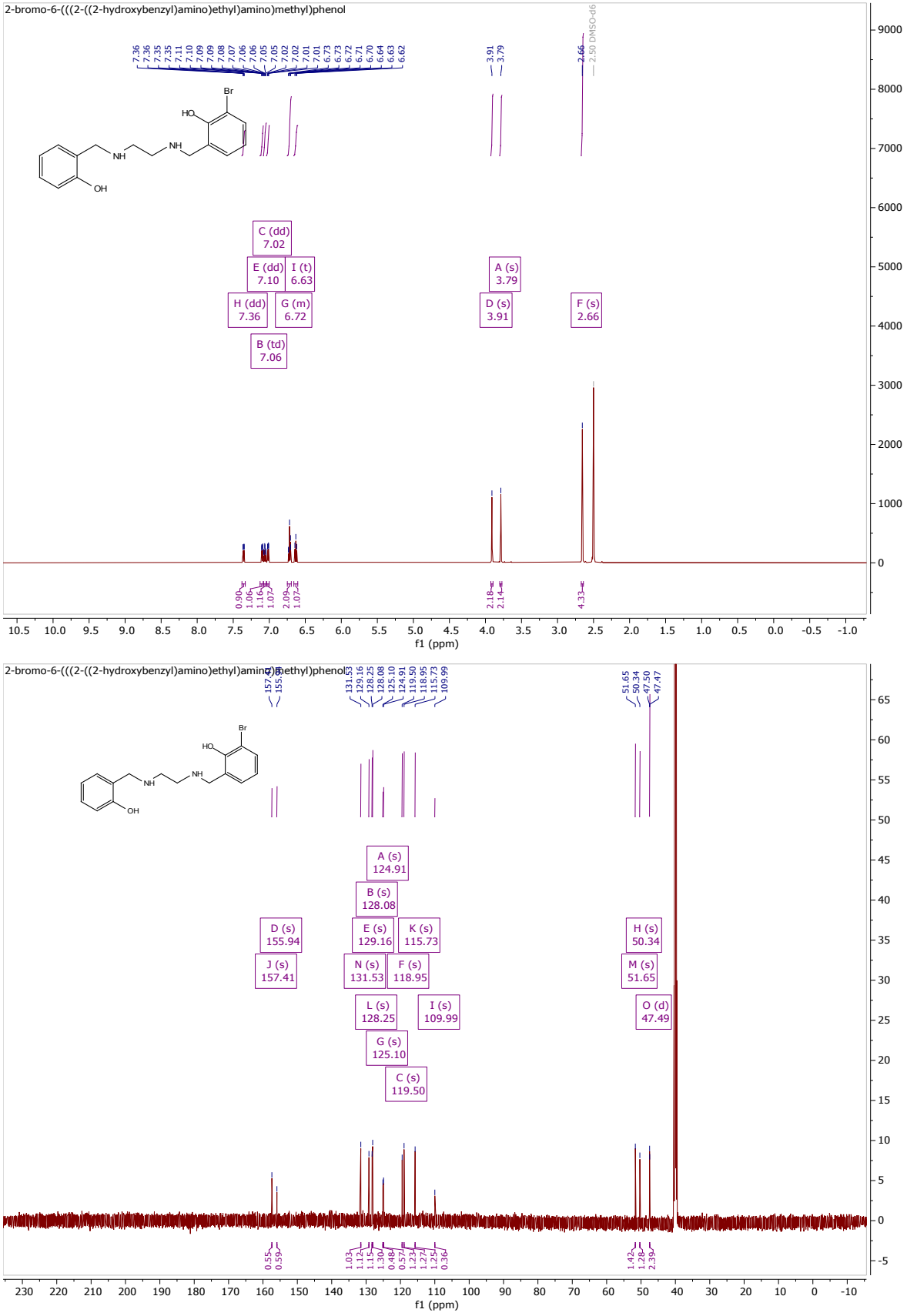



***Figure S30:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-8.***

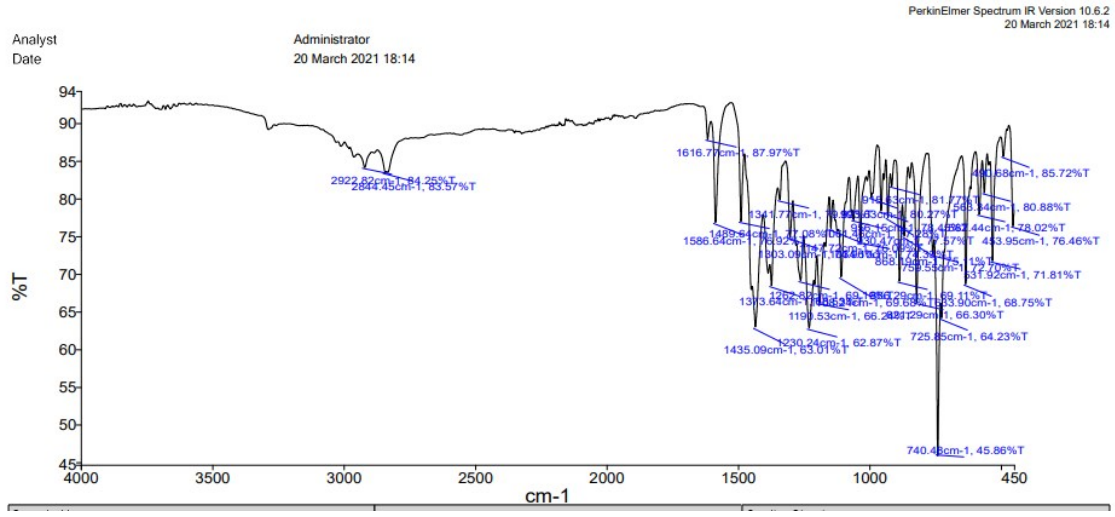
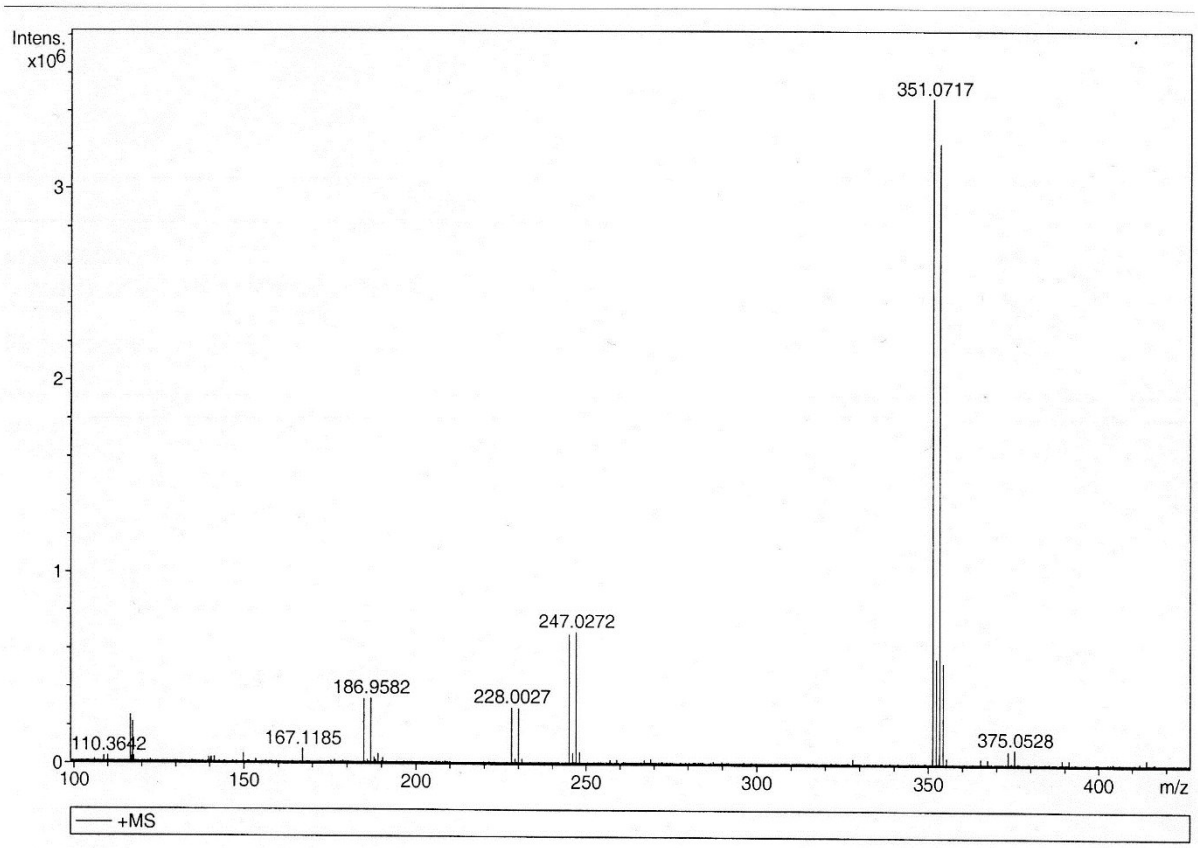



***Figure S31:*** *FTIR spectra of* ***NSS-8.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 16 H 20 Br 1 N 2 O 2 | 0.036 | 351.0703 | -4.18 | -3.86 | -1.36 | 7.50 | ok | even |

***Figure S32:*** *HRMS spectra of* ***NSS-8.***

**NSS-9**

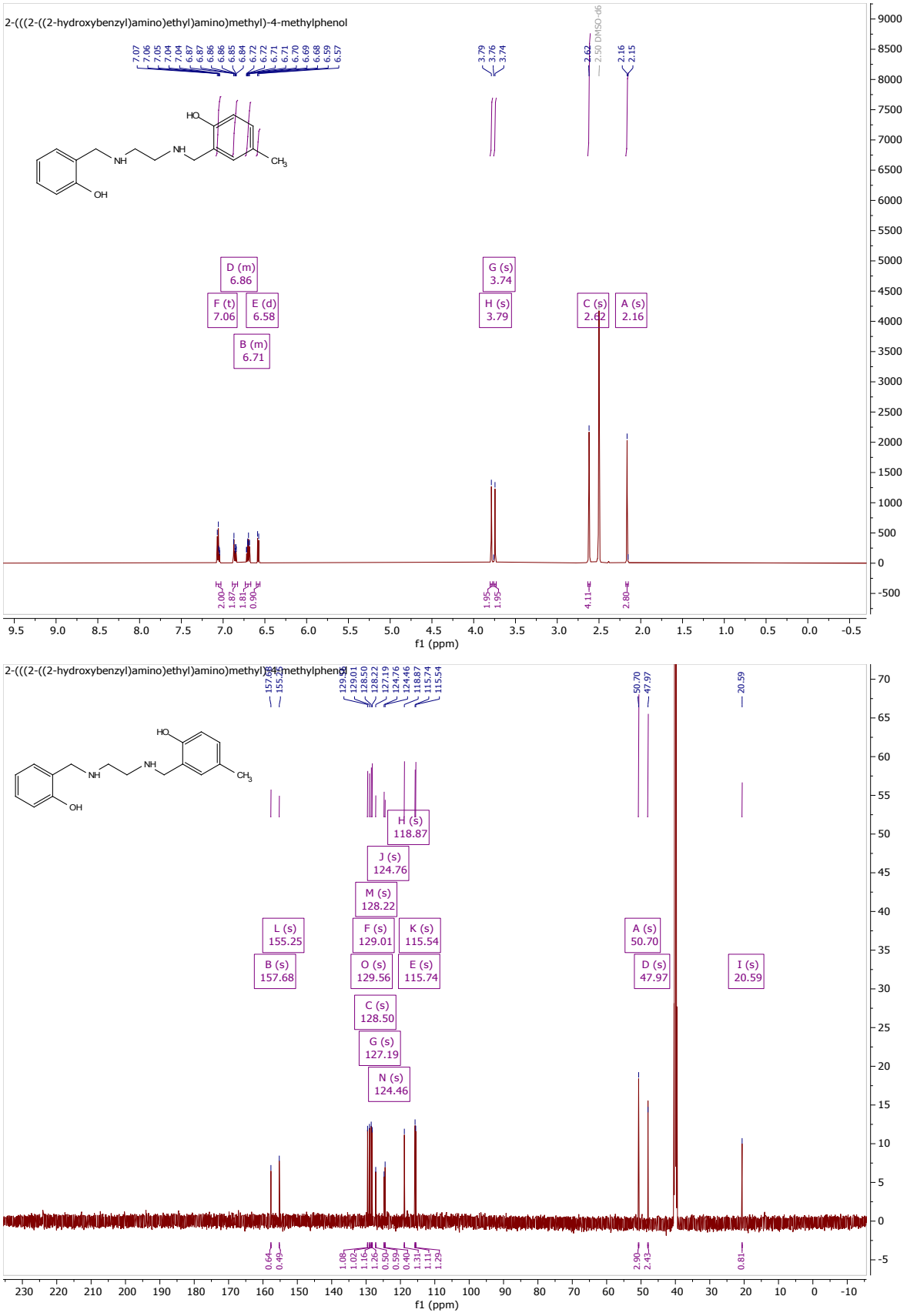



***Figure S33:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-9.***

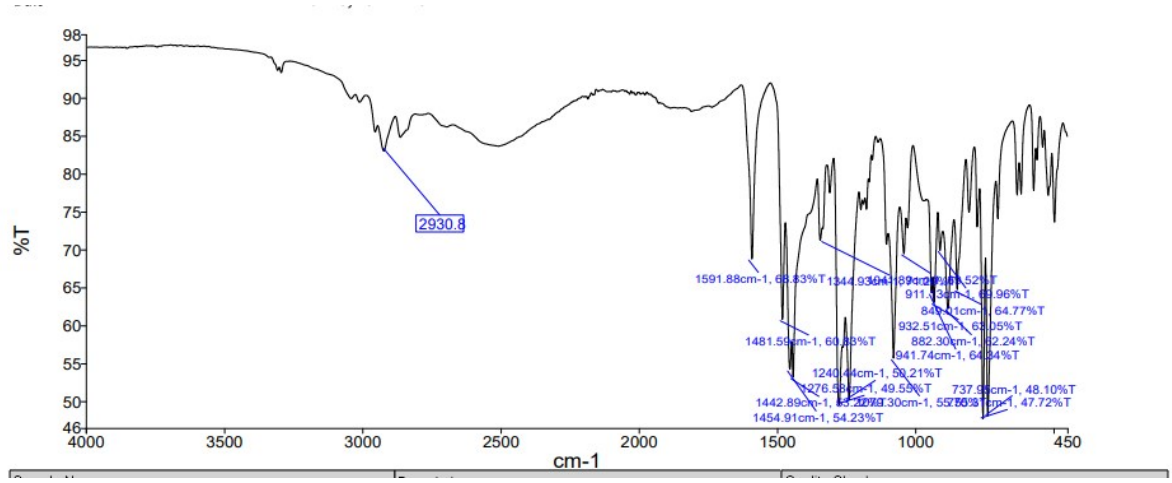
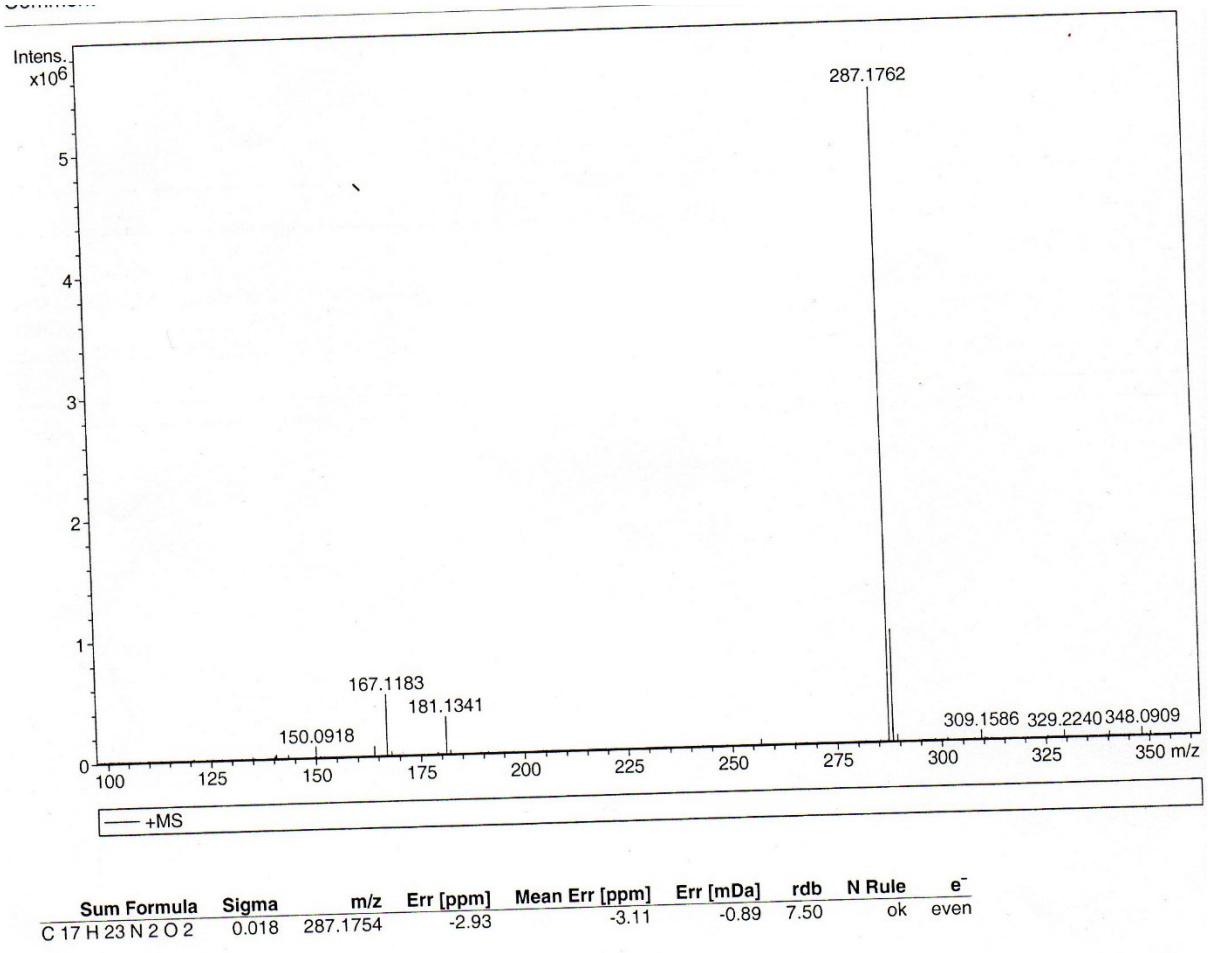



***Figure S34:*** *FTIR spectra of* ***NSS-9.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 17 H 23 N 2 O 2 | 0.018 | 287.1754 | -2.93 | -3.11 | -0.89 | 7.50 | ok | even |

***Figure S35:*** *HRMS spectra of* ***NSS-9.***

**NSS-10:**

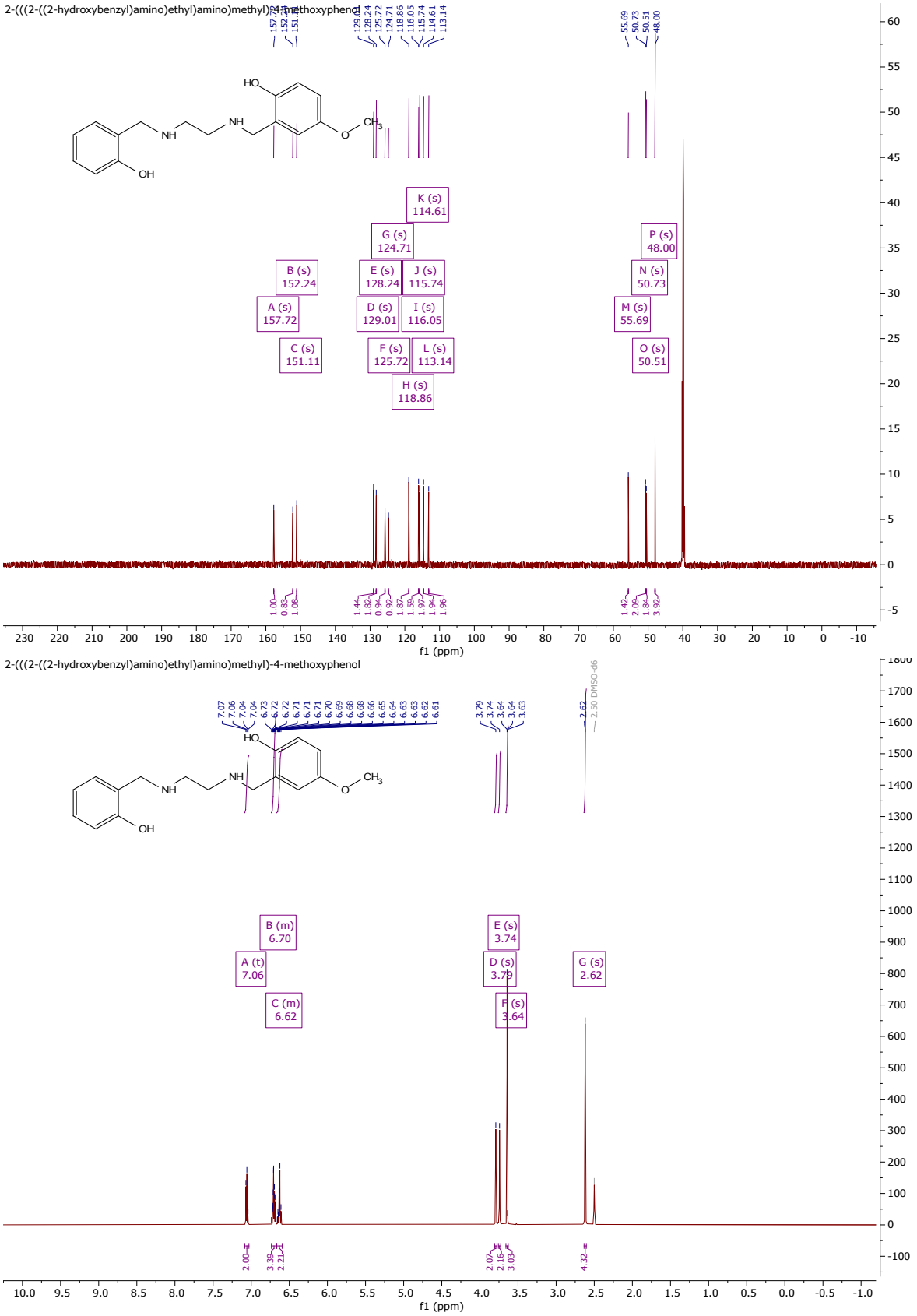



***Figure S36:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***NSS-10.***

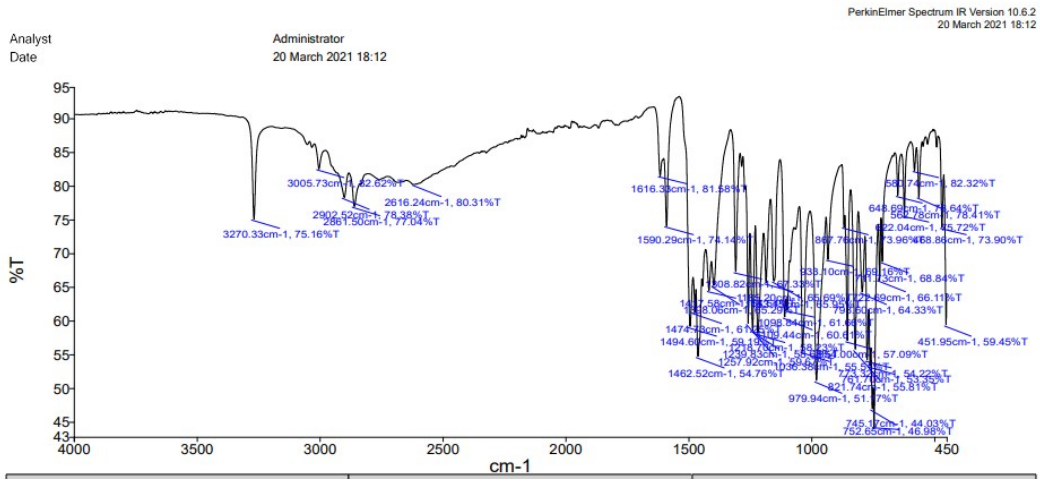
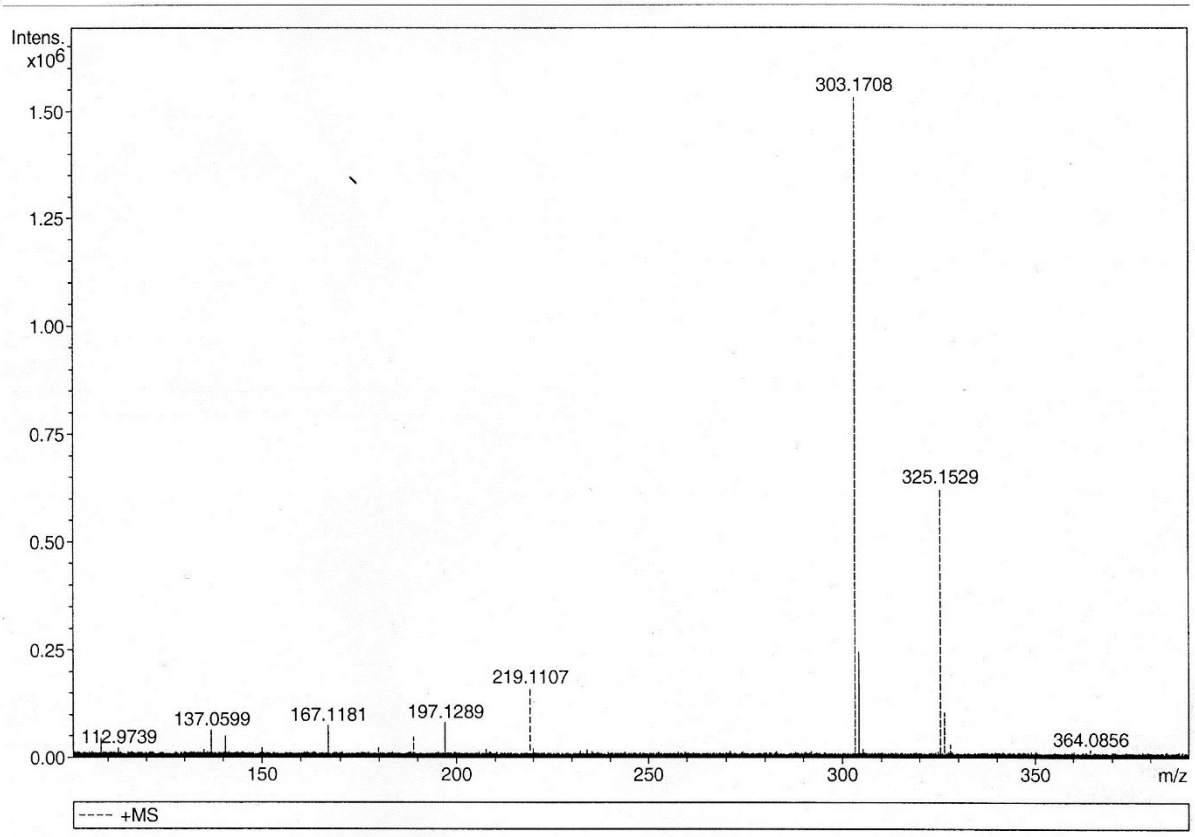



***Figure S37:*** *FTIR spectra of* ***NSS-10.***




| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e⁻ |
|---|---|---|---|---|---|---|---|---|
| C 17 H 23 N 2 O 3 | 0.043 | 303.1703 | -1.74 | -2.52 | -0.76 | 7.50 | ok | even |

***Figure S38:*** *HRMS spectra of* ***NSS-10***

Cyclohexane base Non-Symmetric Salan (CyNSS) ligands

**CyNSS-1:**

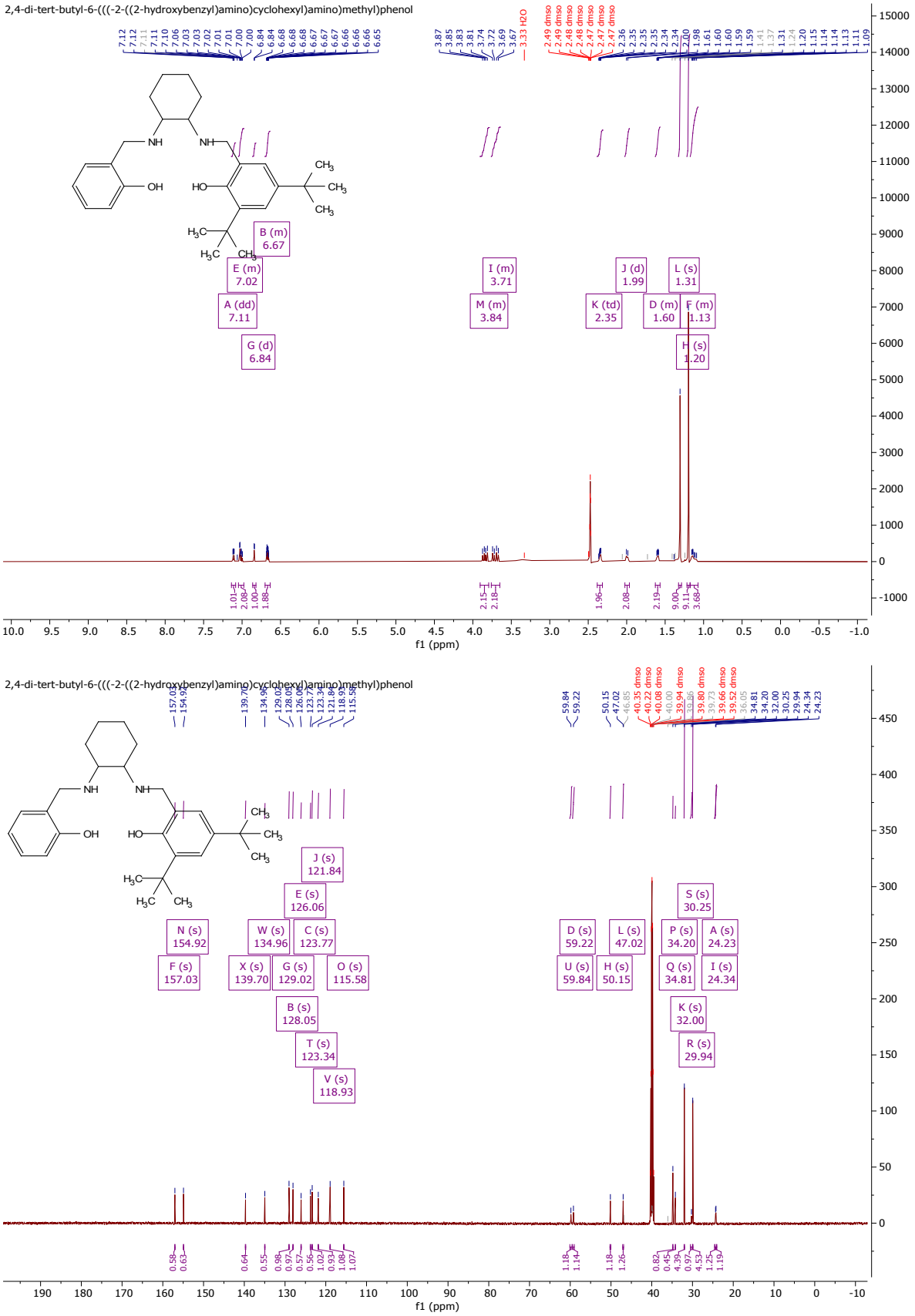



***Figure S39:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***CyNSS-1.***

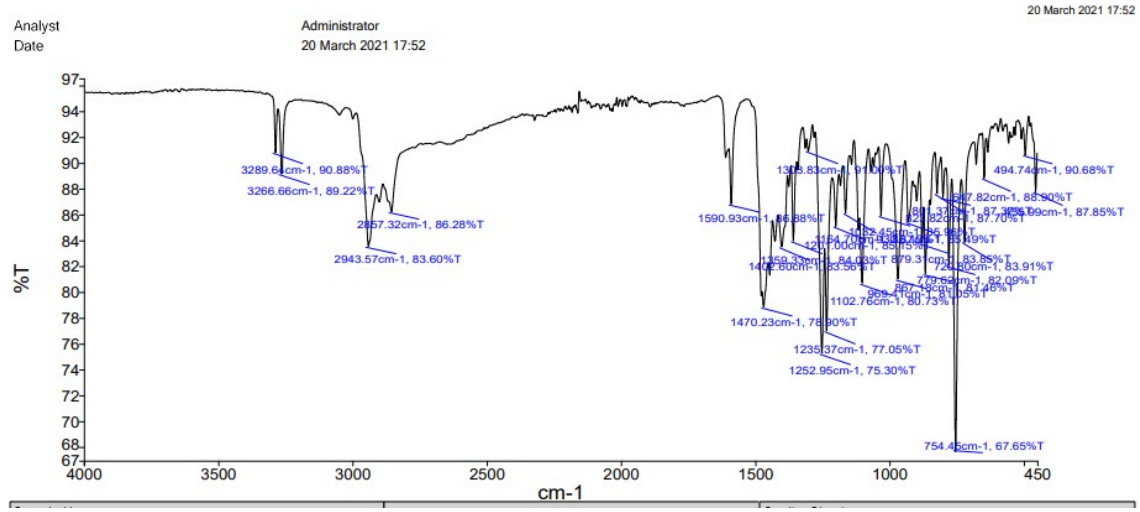



***Figure S40:*** *FTIR spectra of* ***CyNSS-1.***

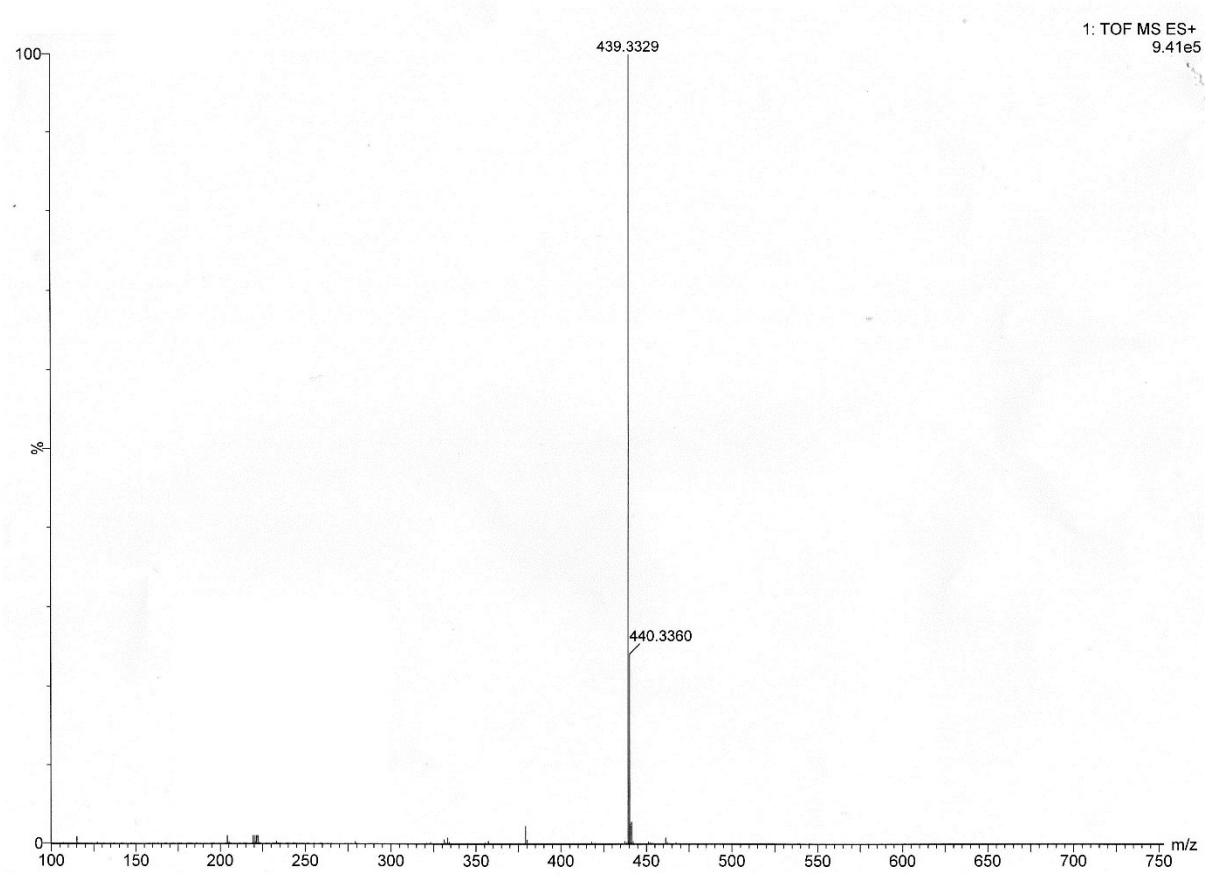



***Figure S41:*** *HRMS spectra of* ***CyNSS-1.***

**CyNSS-2:**

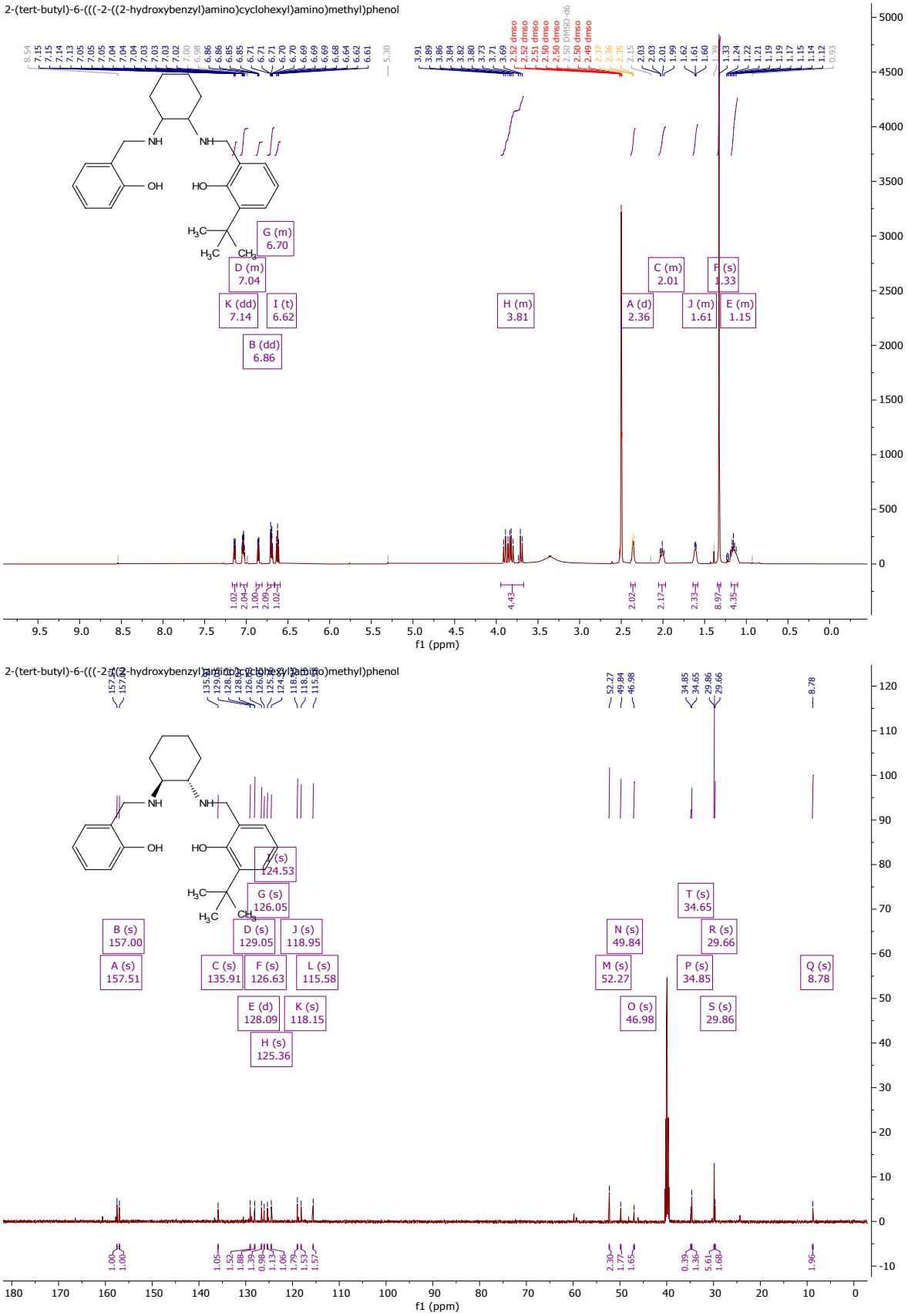



***Figure S42:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***CyNSS-2.***

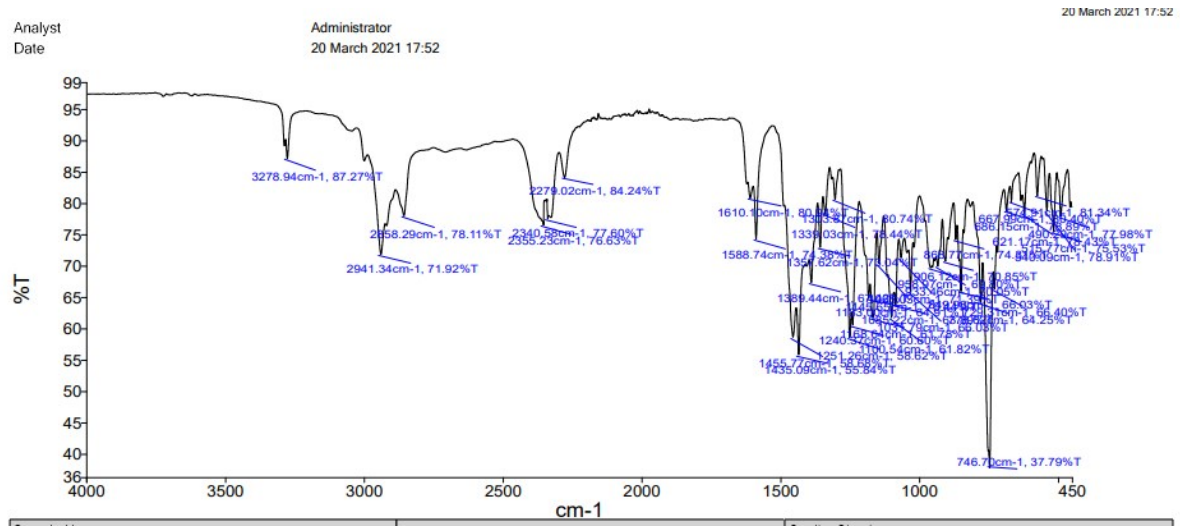



***Figure S43:*** *FTIR spectra of* ***CyNSS-2.***

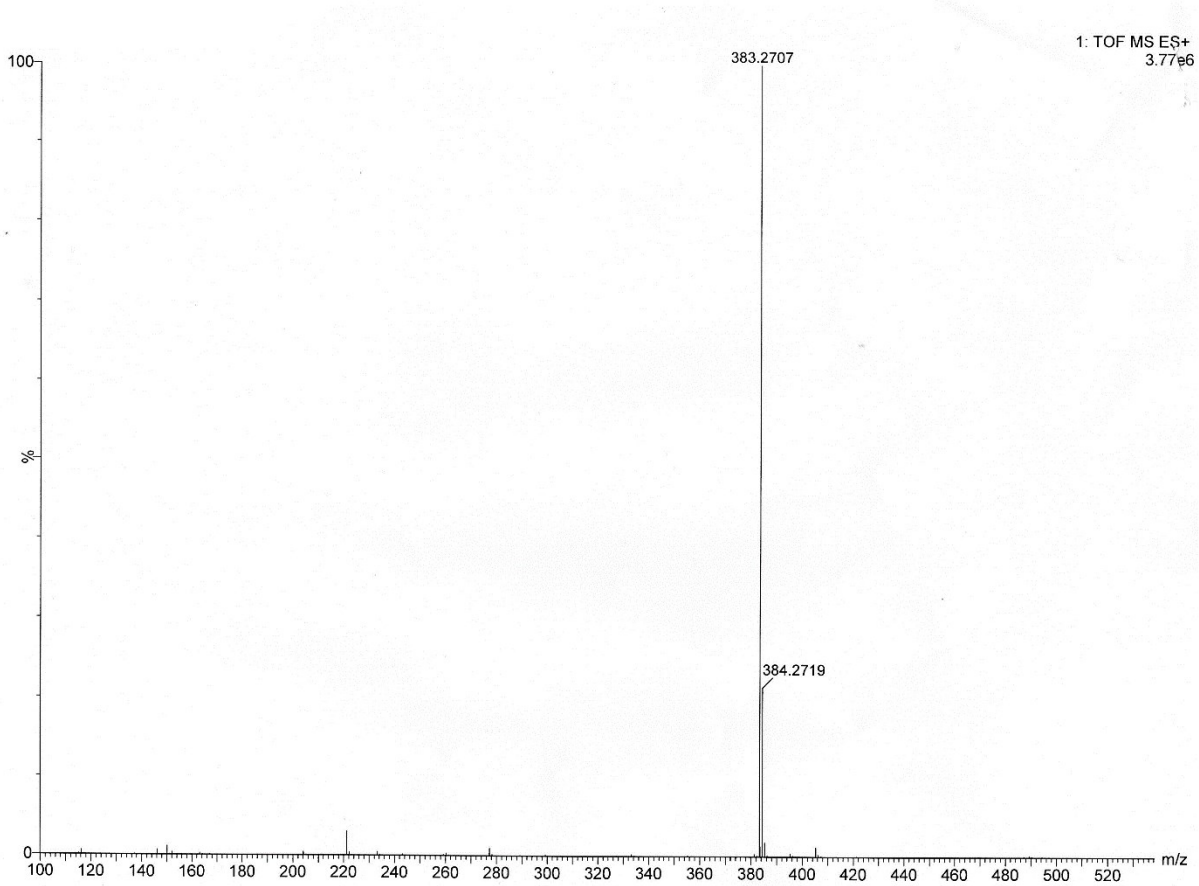



***Figure S44:*** *HRMS spectra of* ***CyNSS-2.***

**CyNSS-3:**

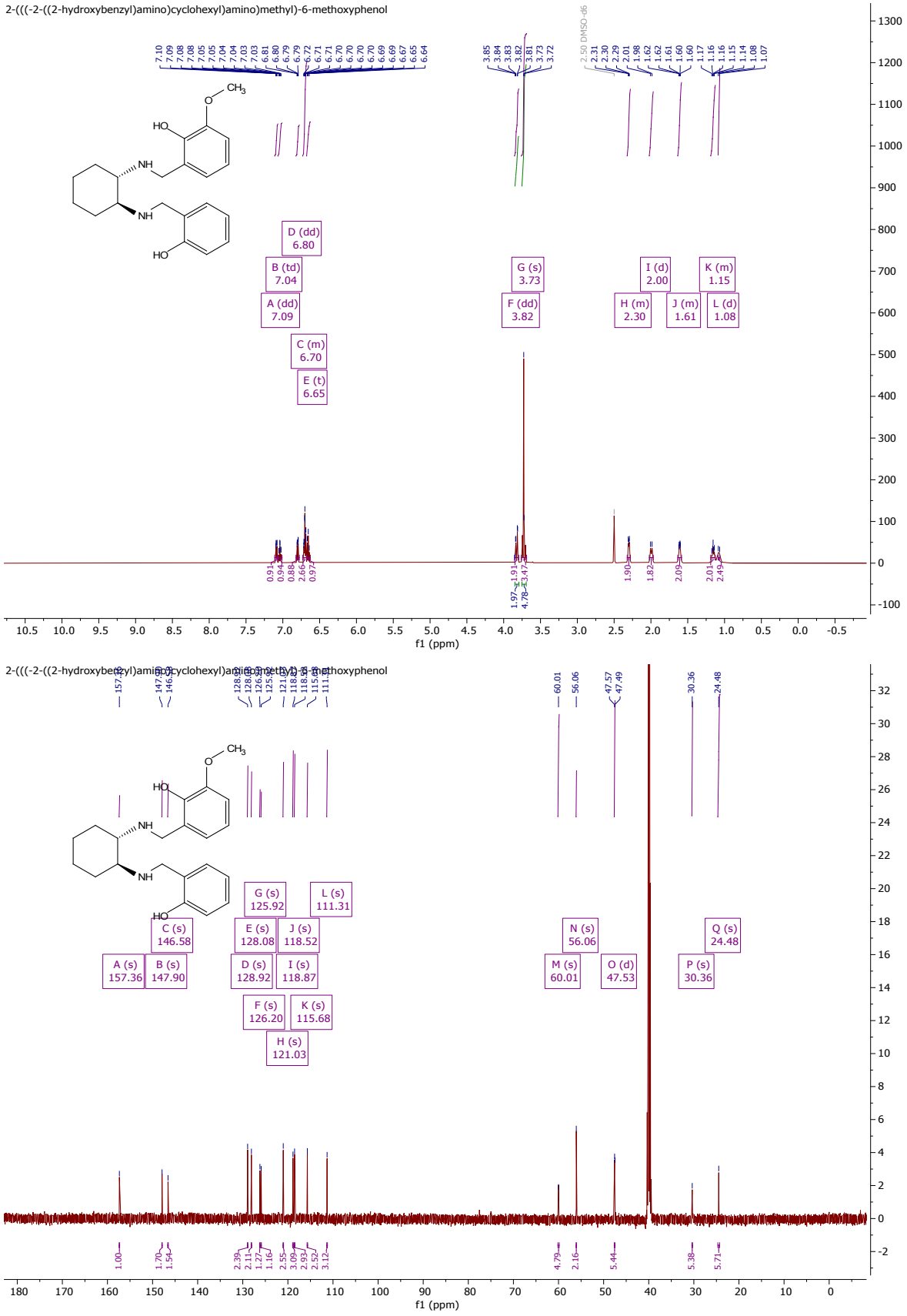



***Figure S45:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***CyNSS-3.***

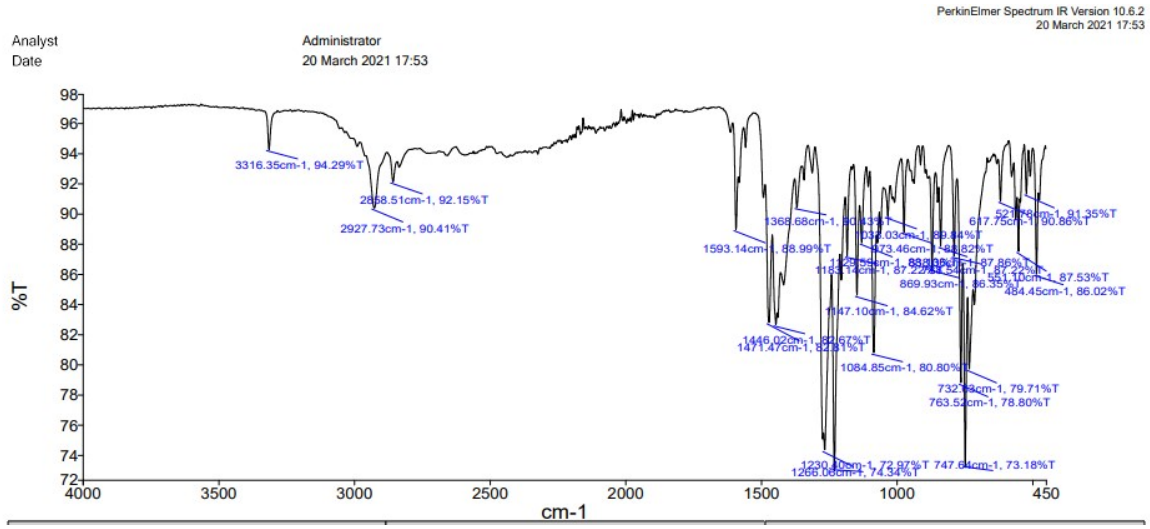



***Figure S46:*** *FTIR spectra of* ***CyNSS-3.***

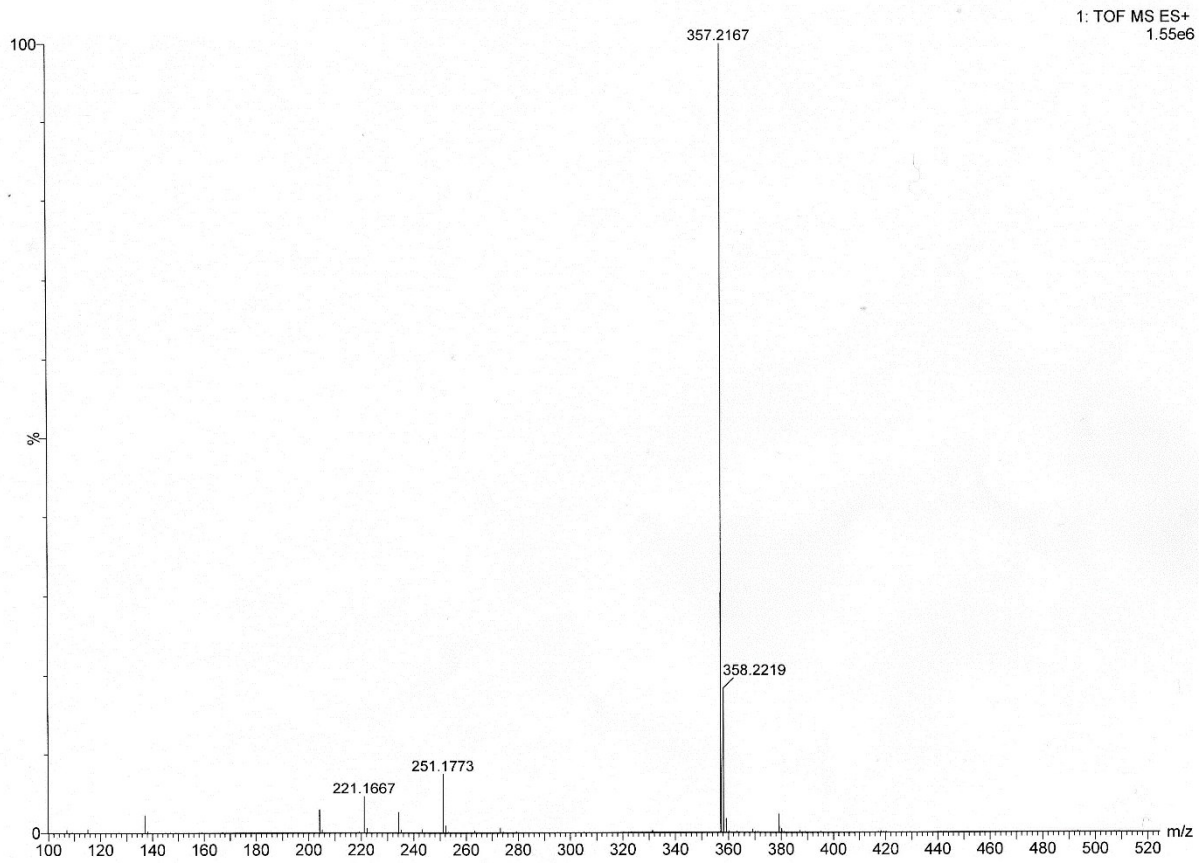



***Figure S47:*** *HRMS spectra of* ***CyNSS-3.***

**CyNSS-4**

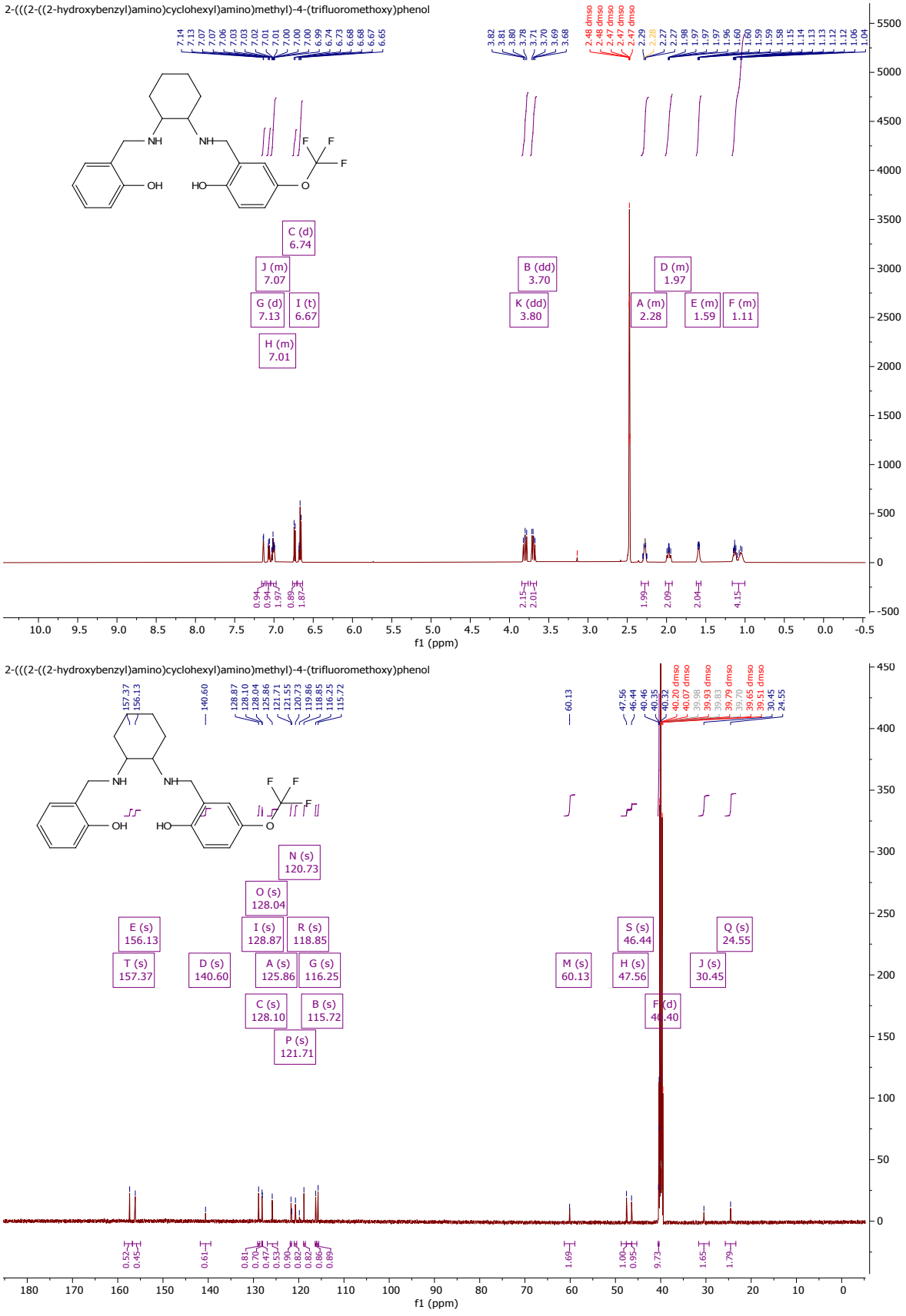



***Figure S48:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***CyNSS-4.***

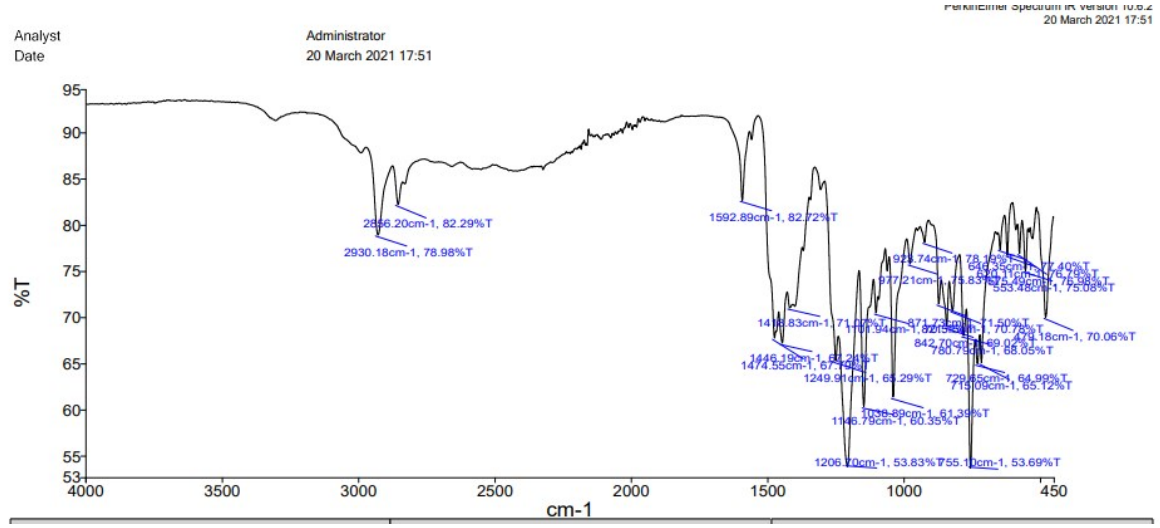



***Figure S49:*** *FTIR spectra of* ***CyNSS-4.***

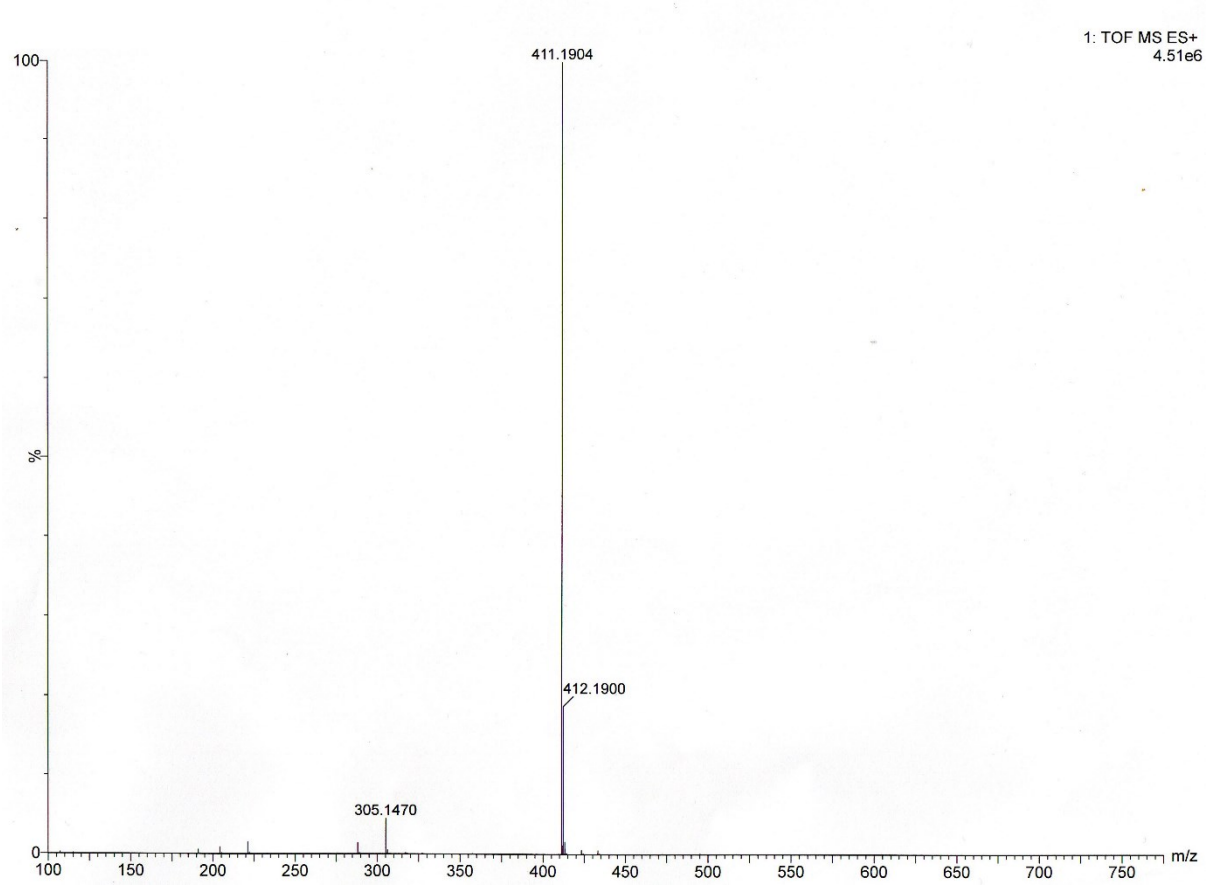



***Figure S50:*** *HRMS spectra of* ***CyNSS-4.***

**CyNSS-5**

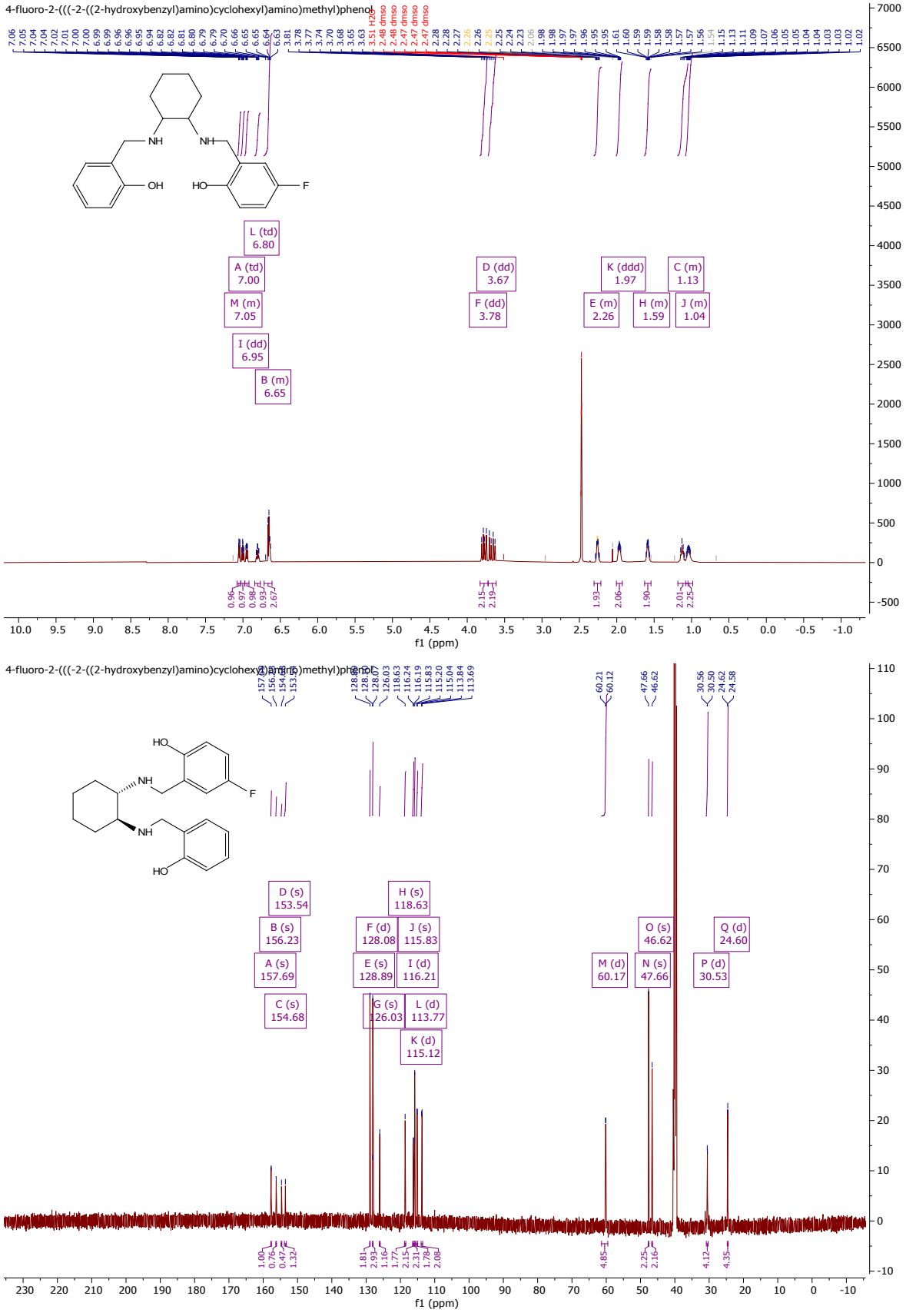



***Figure S51:*** *$^{1}$H-NMR (top) and $^{13}$C spectra (bottom) of* ***CyNSS-5.***

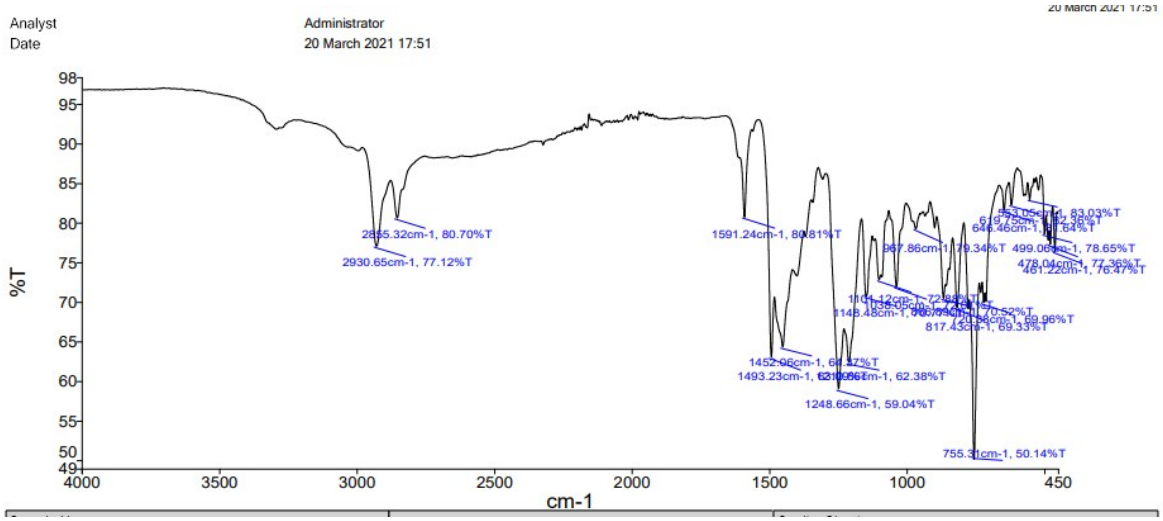



***Figure S52:*** *FTIR spectra of* ***CyNSS-5.***

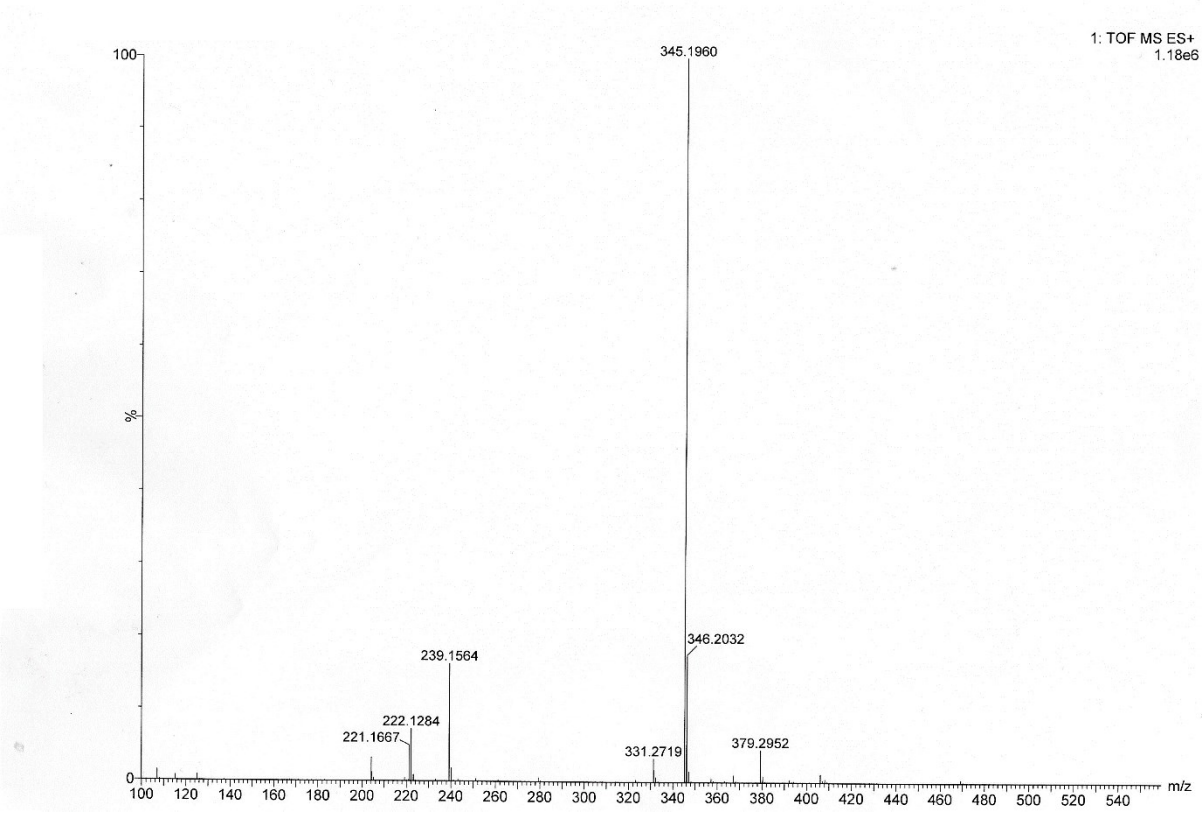



***Figure S53:*** *HRMS spectra of* ***CyNSS-5.***

Characterisation data for copper complexes

FTIR spectra.

**[Cu(II)-NSS-1]:**

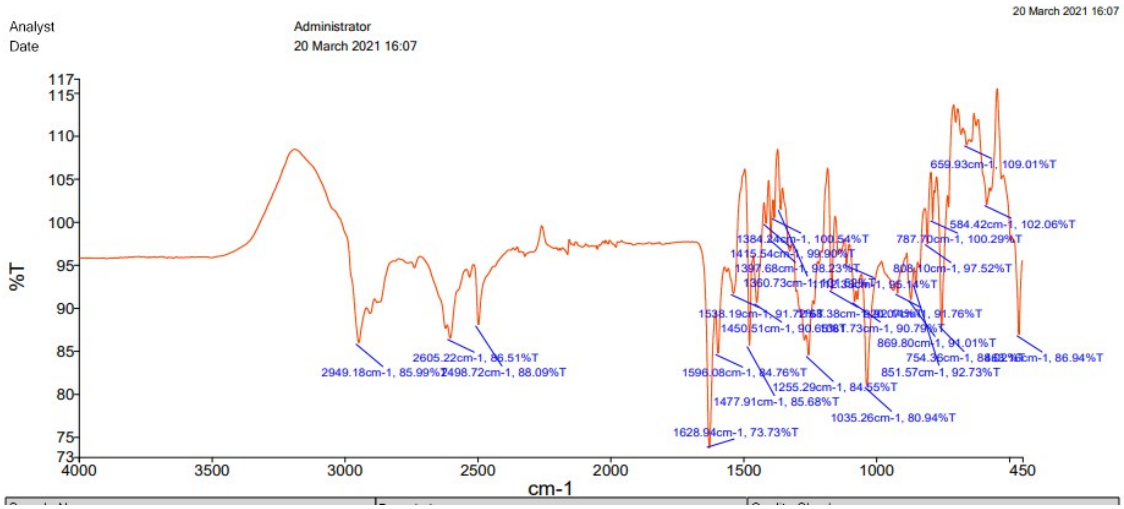



***Figure S54:*** *FTIR spectra of* ***[Cu(II)-NSS-1]:***

**[Cu(II)-NSS-2]:**

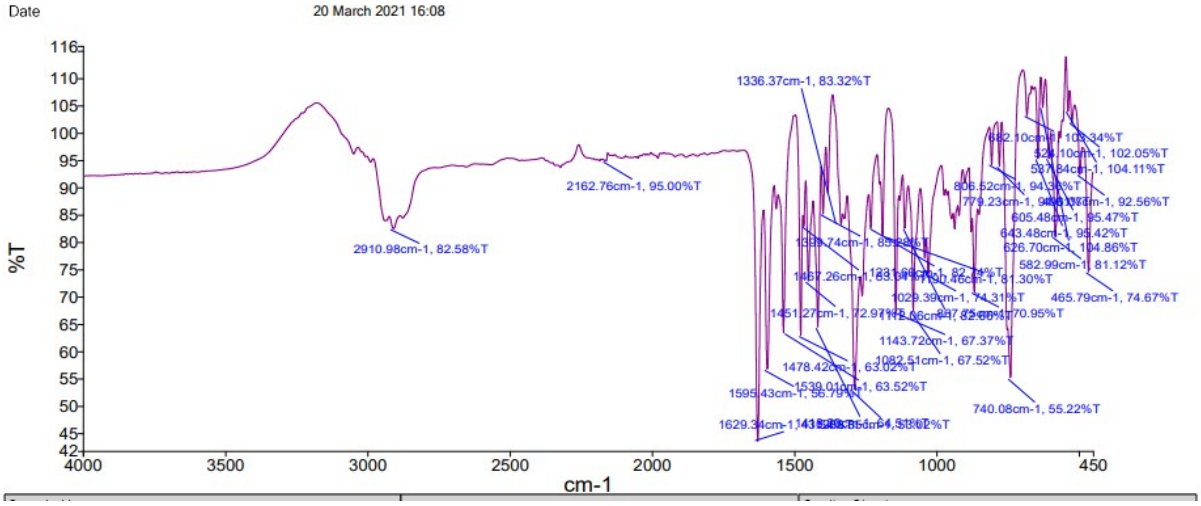



***Figure S55:*** *FTIR spectra of* ***[Cu(II)-NSS-2]:***

**[Cu(II)-NSS-4]:**

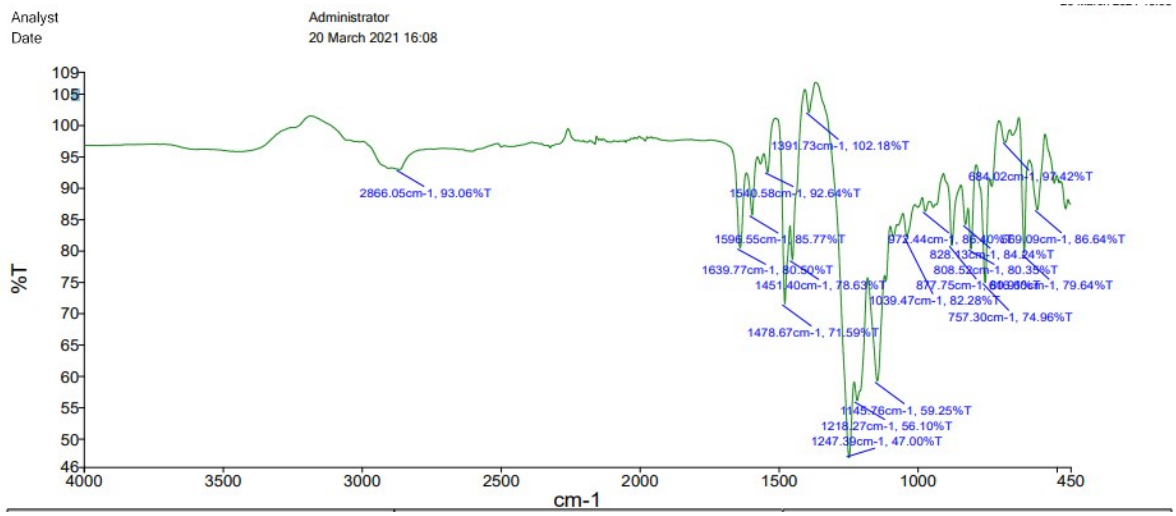



***Figure S56:*** *FTIR spectra of* ***[Cu(II)-NSS-4]:***

**[Cu(II)-NSS-5]:**

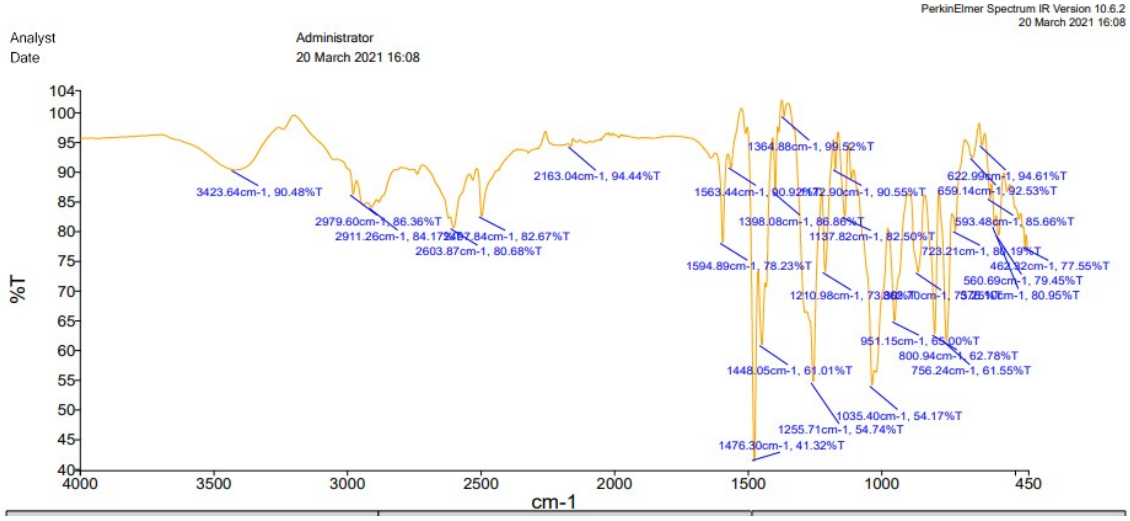



***Figure S57:*** *FTIR spectra of* ***[Cu(II)-NSS-5]:***

**[Cu(II)-CyNSS-1]:**

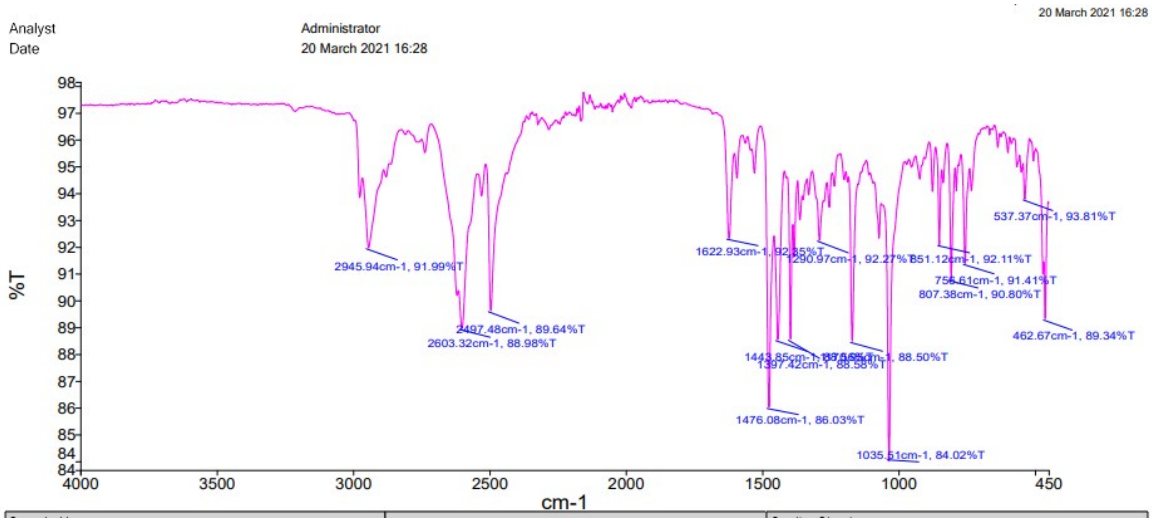



***Figure S58:*** *FTIR spectra of* ***[Cu(II)-CyNSS-1]:***

**[Cu(II)-CyNSS-2]:**

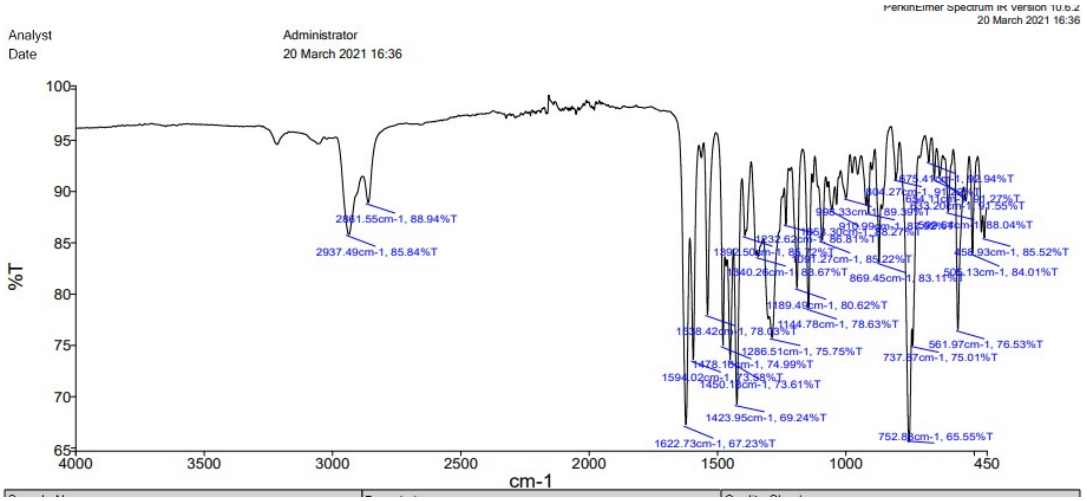



***Figure S59:*** *FTIR spectra of* ***[Cu(II)-CyNSS-2]:***

**[Cu(II)-CyNSS-3]:**

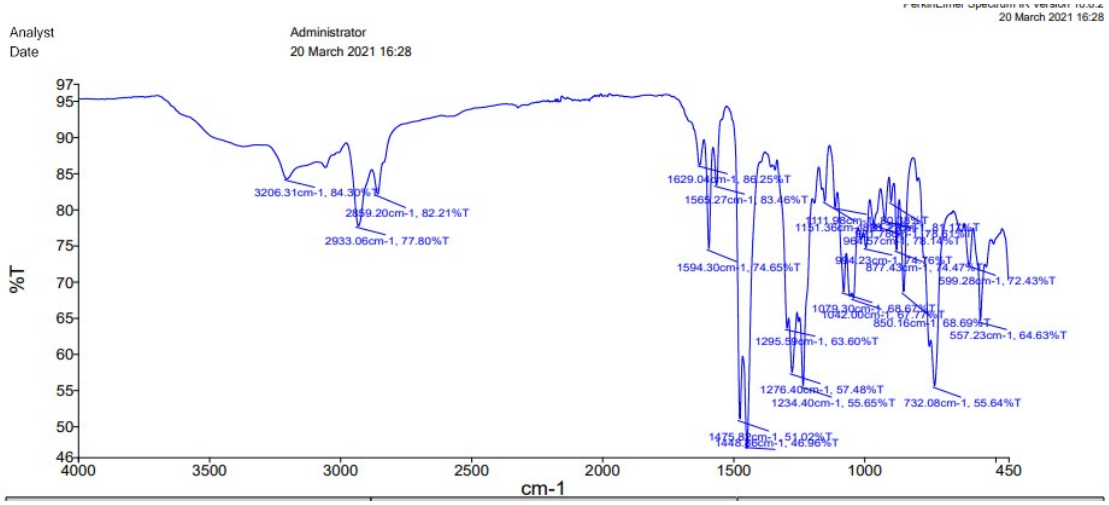



***Figure S60:*** *FTIR spectra of* ***[Cu(II)-CyNSS-3]:***

**[Cu(II)-CyNSS-4]:**

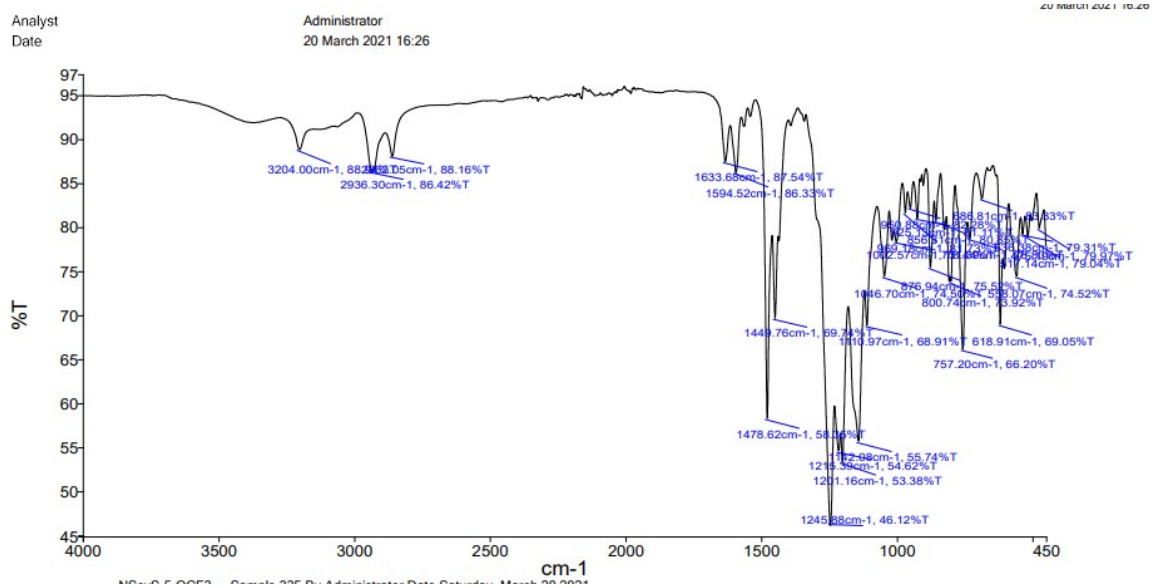



***Figure S61:*** *FTIR spectra of* ***[Cu(II)-CyNSS-4]:***

**[Cu(CyNSS-5)]:**

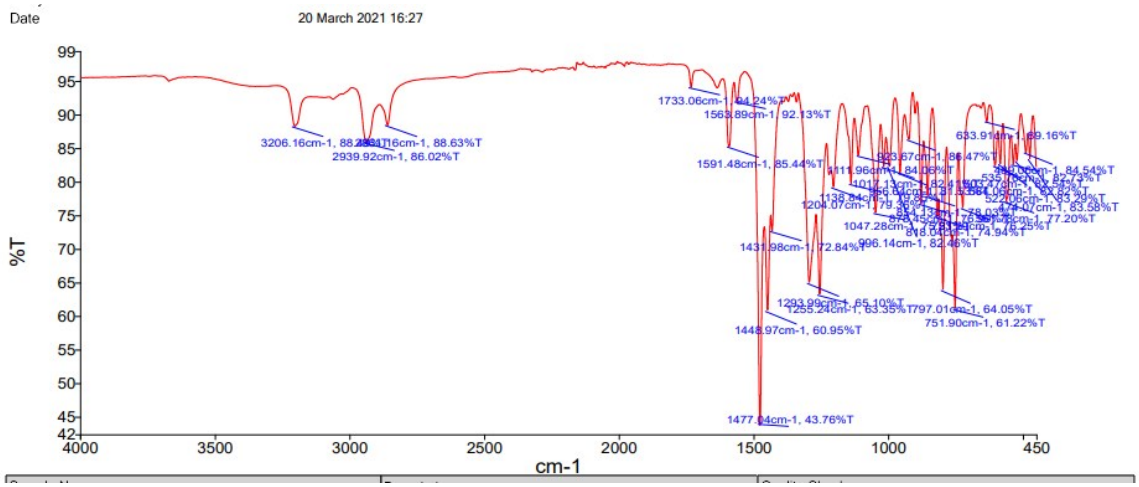



***Figure S62:*** *FTIR spectra of* ***[Cu(II)-CyNSS-5]:***

HRMS spectra.

**[Cu(II)-NSS-1]:**

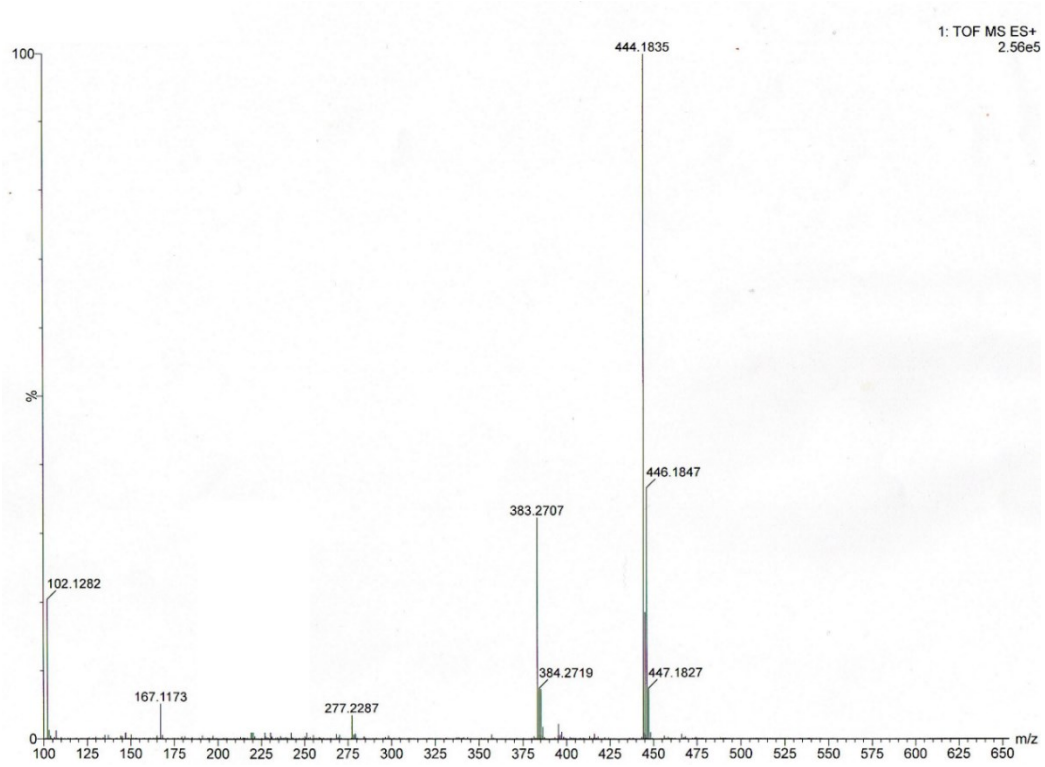



***Figure S63:*** *HRMS spectra of* ***[Cu(II)-NSS-1]:***

**[Cu(II)-NSS-2]:**

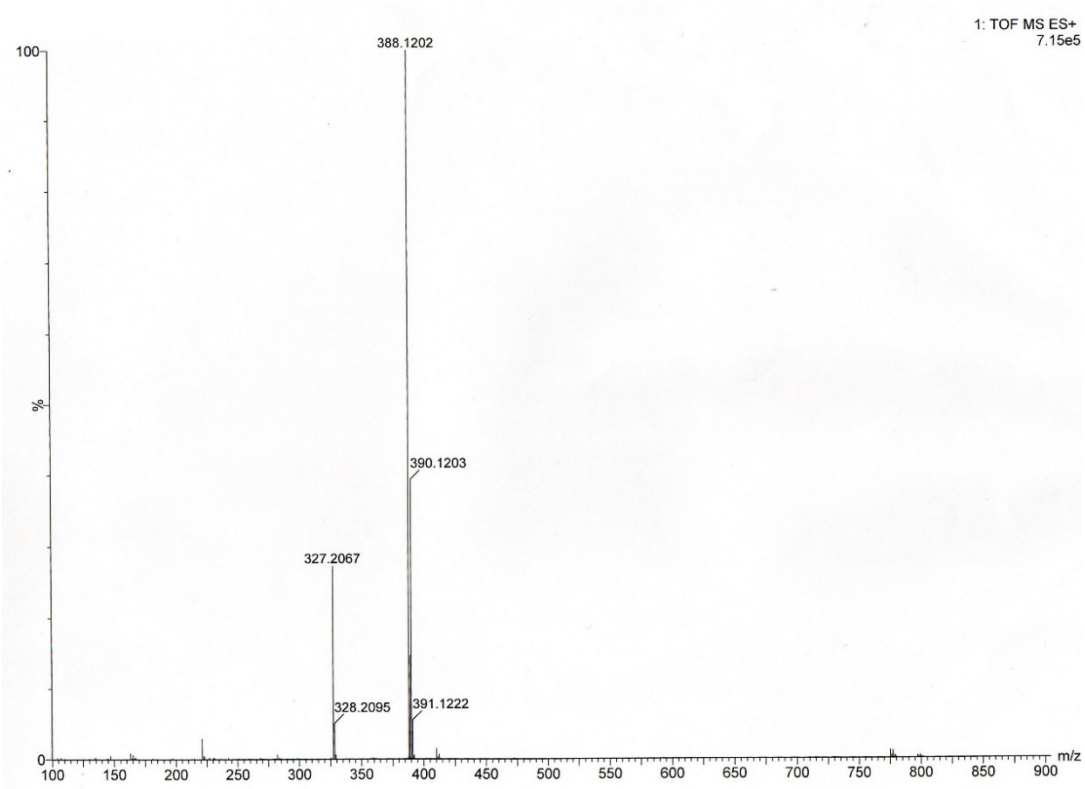



***Figure S64:*** *HRMS spectra of* ***[Cu(II)-NSS-2]:***

**[Cu(II)-NSS-4]:**

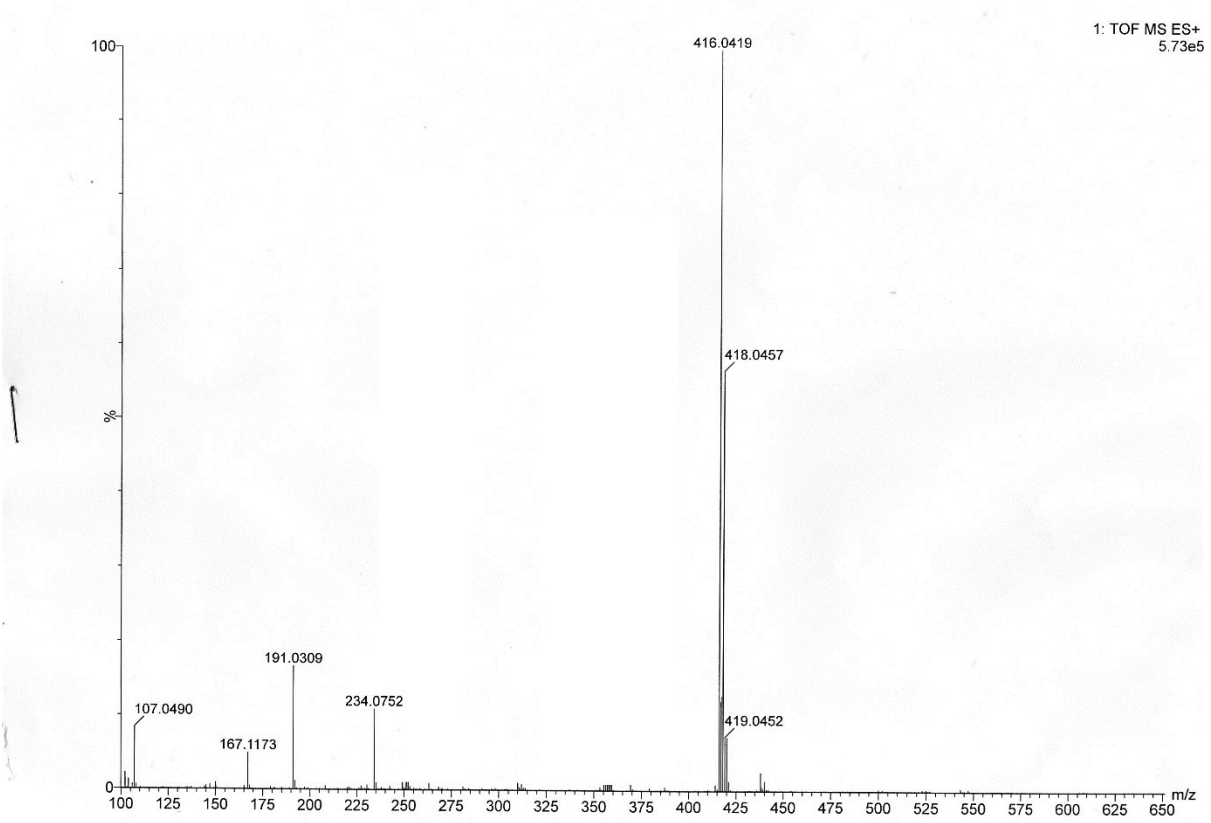



***Figure S65:*** *HRMS spectra of* ***[Cu(II)-NSS-4]:***

**[Cu(II)-NSS-5]:**

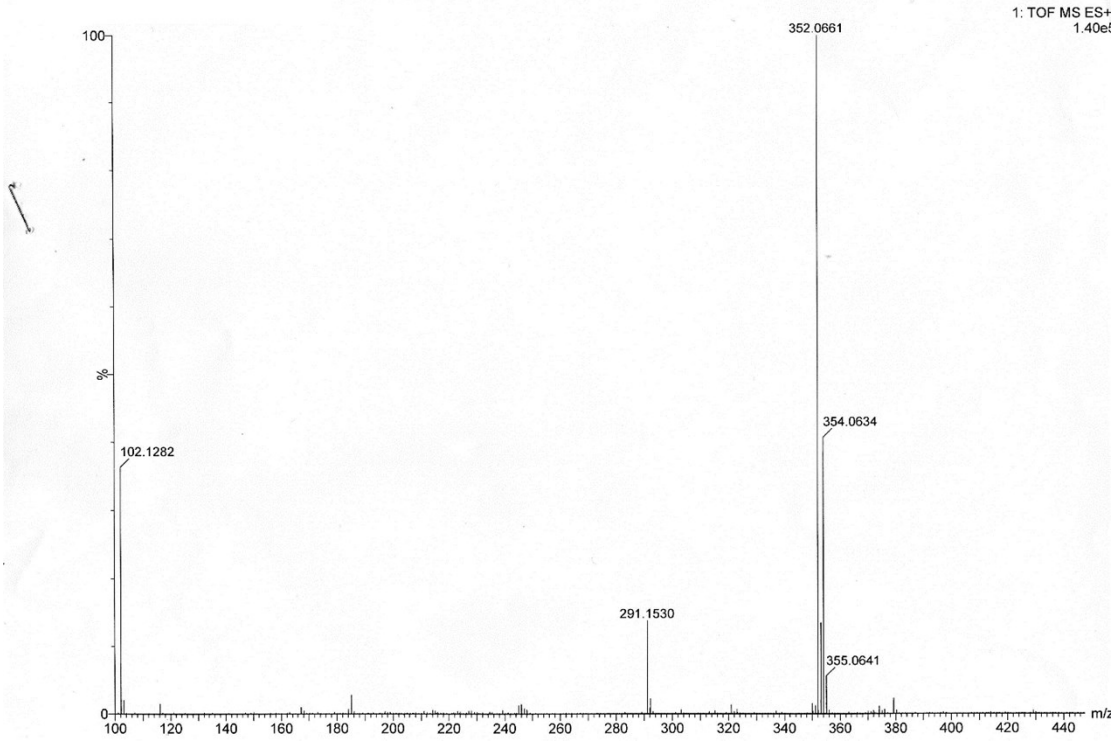



***Figure S66:*** *HRMS spectra of* ***[Cu(II)-NSS-5]:***

**[Cu(II)-CyNSS-1]:**

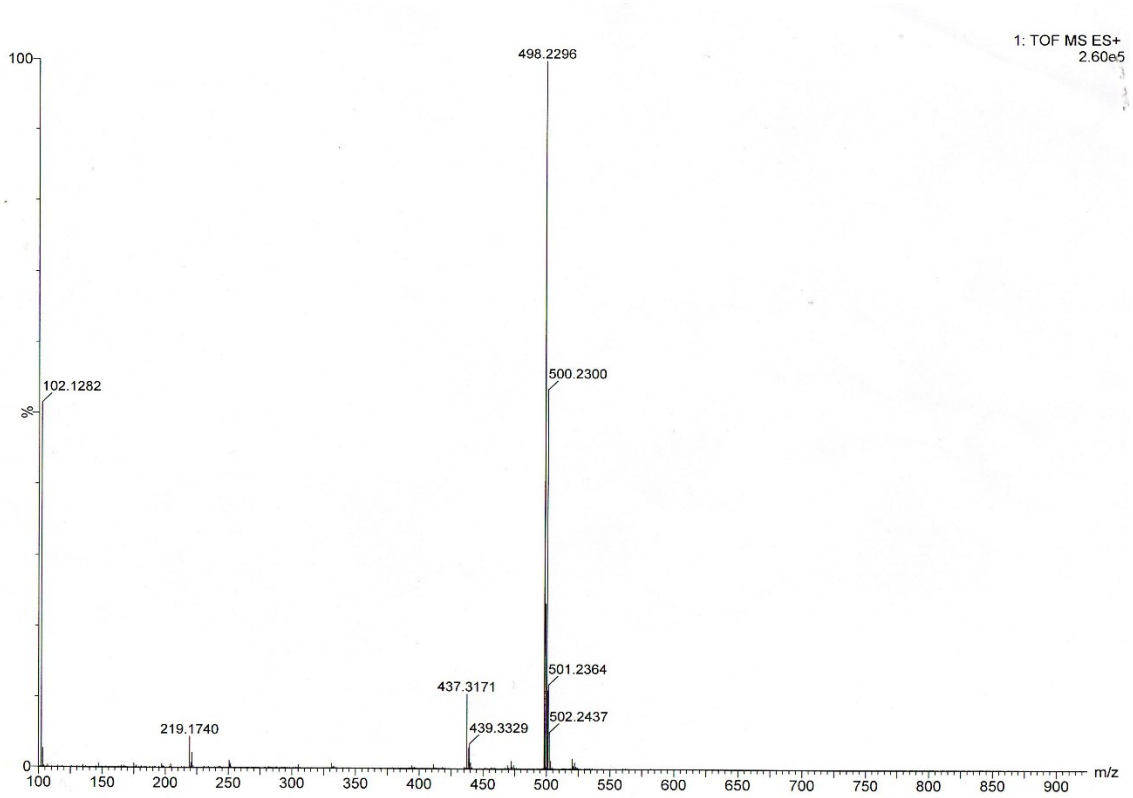



***Figure S67:*** *HRMS spectra of* ***[Cu(II)-CyNSS-1]:***

**[Cu(II)-CyNSS-2]:**

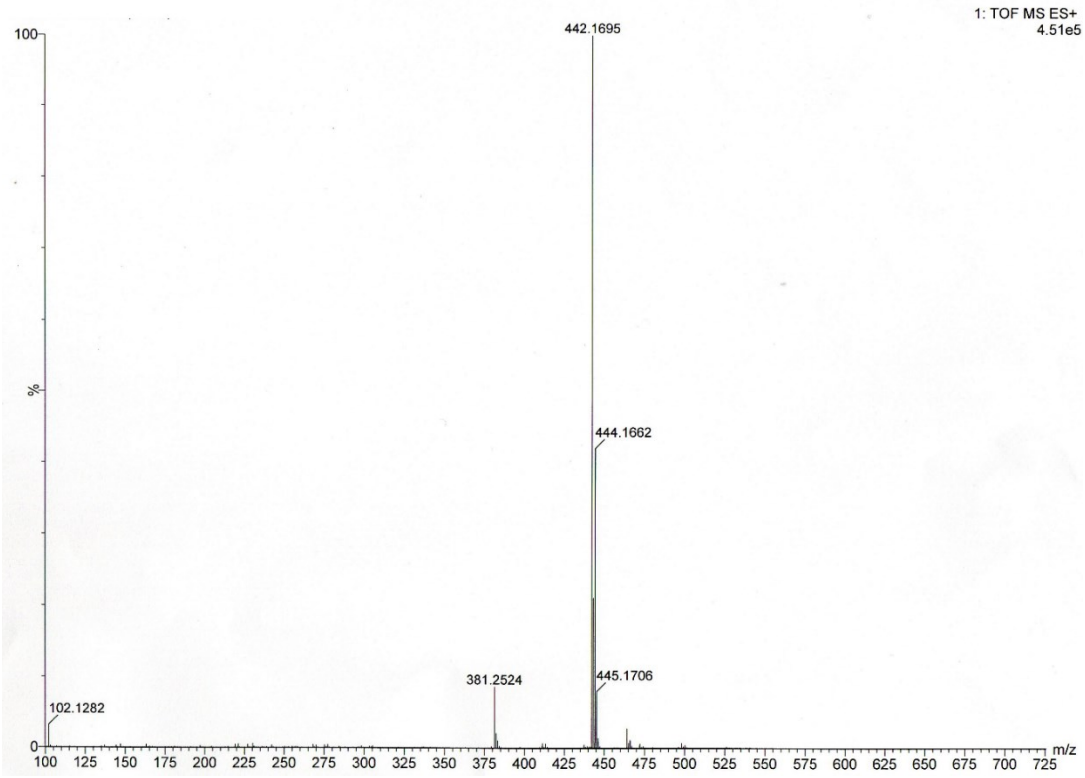



***Figure S68:*** *HRMS spectra of* ***[Cu(II)-CyNSS-2]:***

**[Cu(II)-CyNSS-3]:**

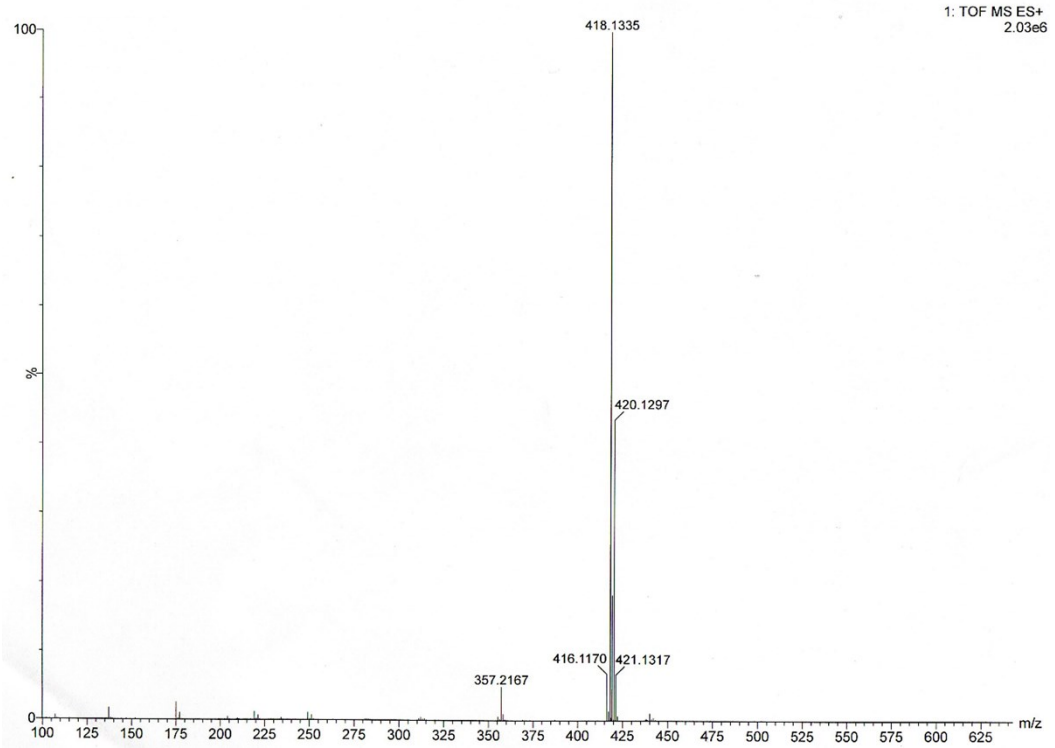



***Figure S69:*** *HRMS spectra of* ***[Cu(II)-CyNSS-3]:***

**[Cu(CyNSS-4)]:**

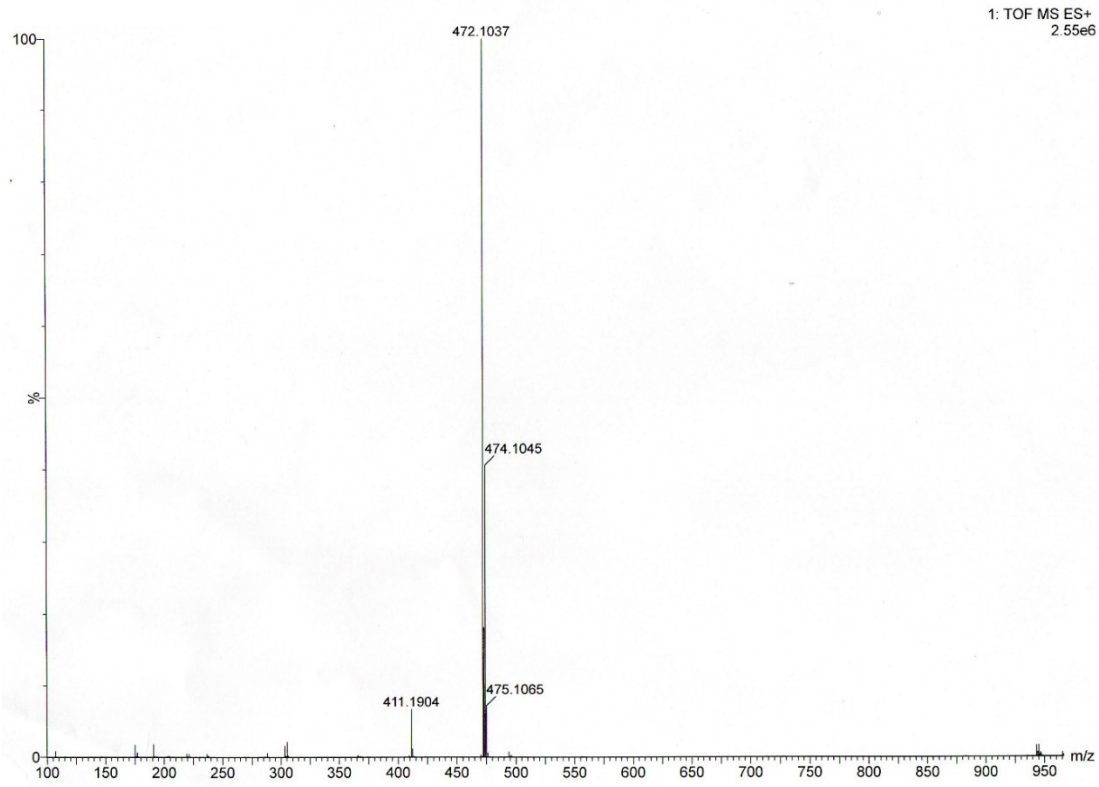



***Figure S70:*** *HRMS spectra of* ***[Cu(II)-CyNSS-4]:***

**[Cu(CyNSS-5)]:**

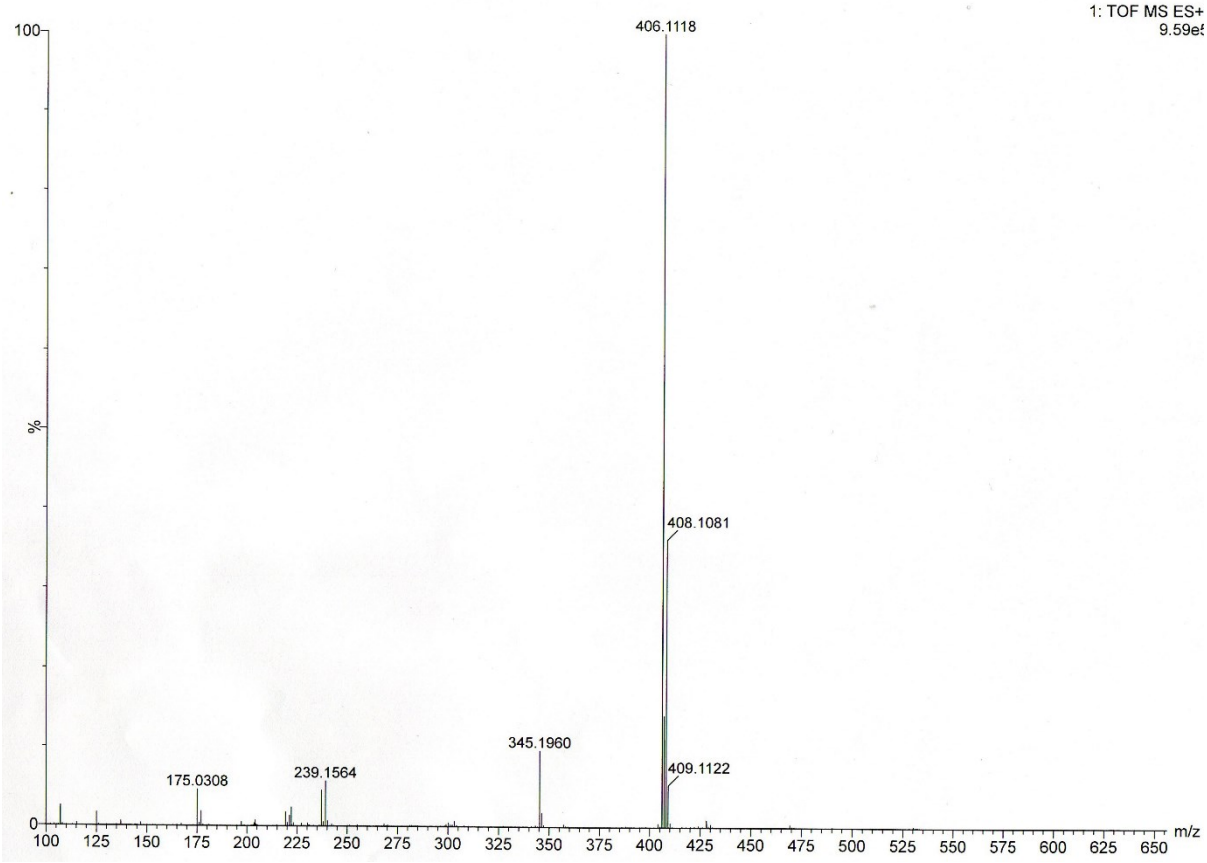



***Figure S71:*** *HRMS spectra of* ***[Cu(II)-CyNSS-5]:***

UV-Vis spectra.

UV-Vis spectra were obtained using prepared $10^{-4}$ M dichloromethane solutions of the Cu(II) complexes.

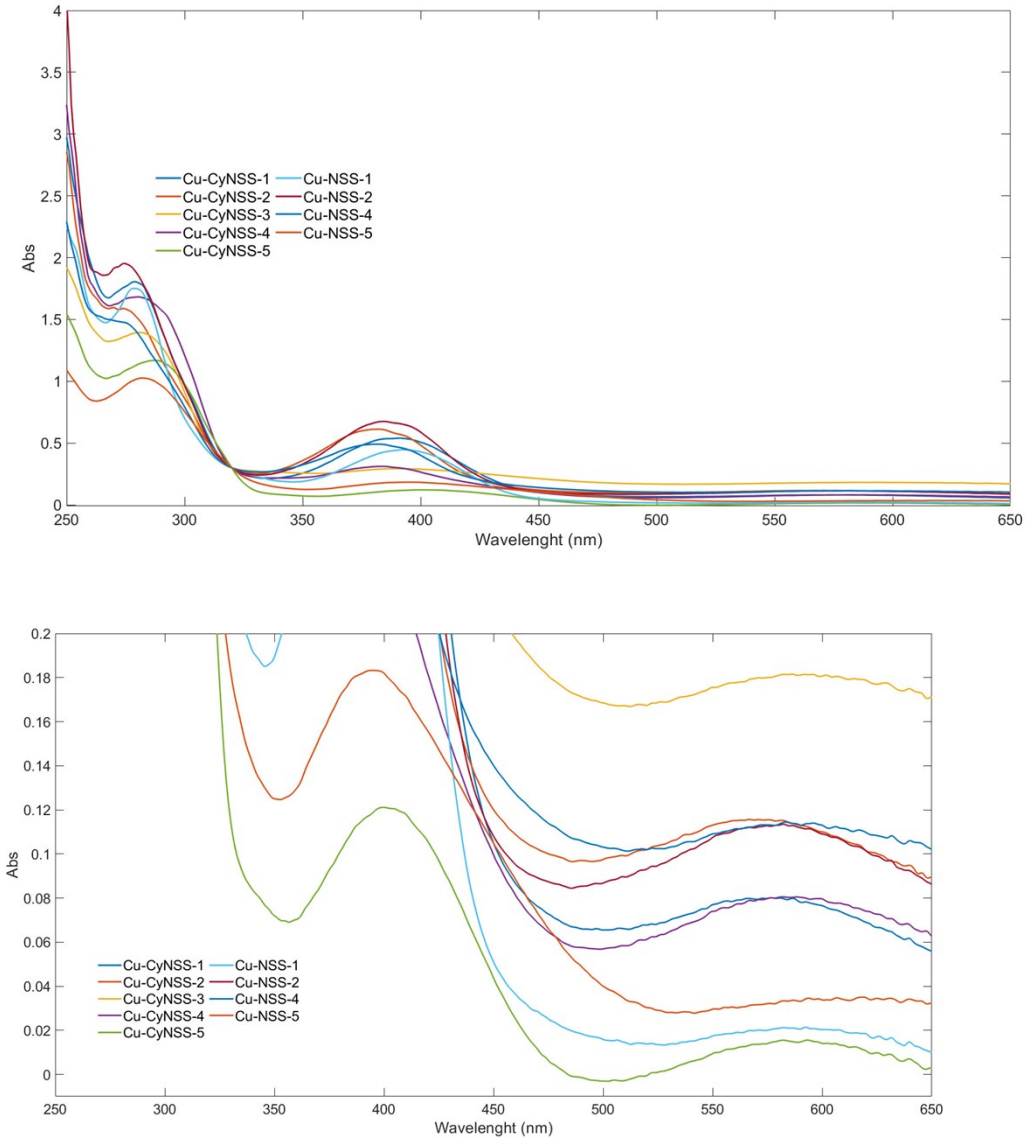



***Figure S72:*** *Overlayed UV-Vis spectra of non-symmetric salan Cu(II) complexes showing the full spectra (top) and weaker d-d transition at ~550 nm (bottom).*

Thermogravimetric analysis.

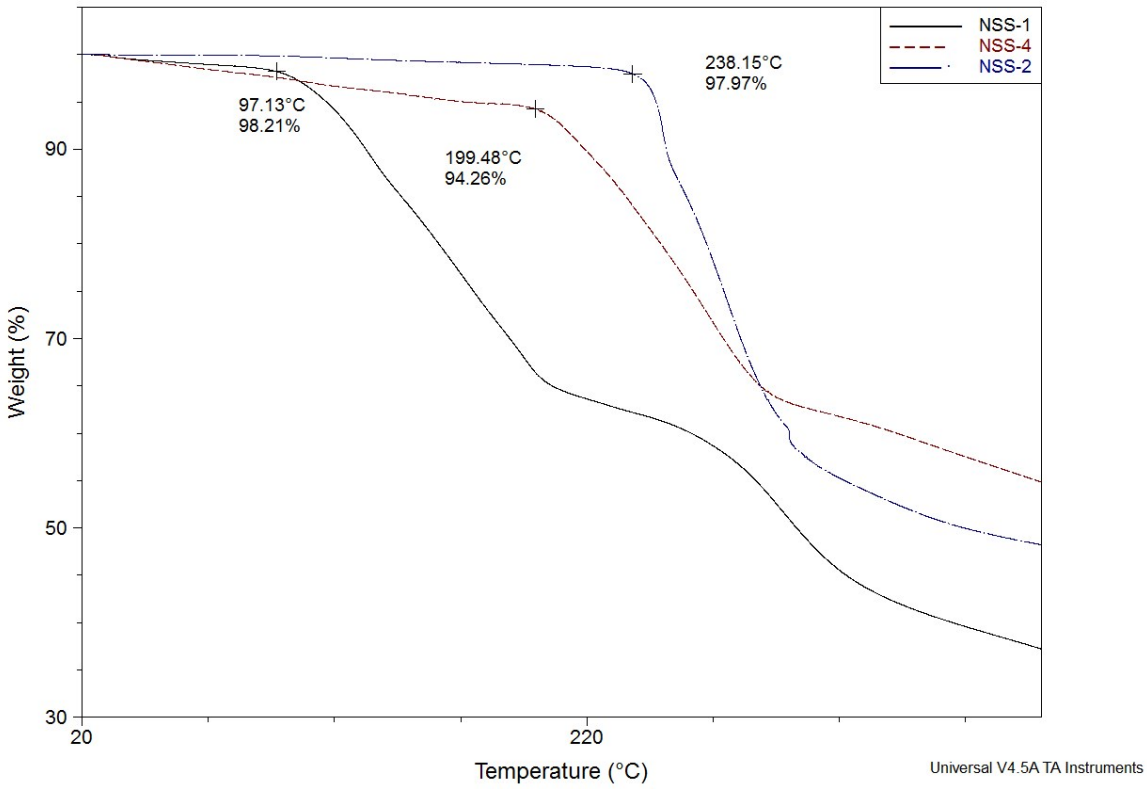



***Figure S73:*** *TGA analysis of Cu(II)-NSS complexes in the range 20-400 ºC*

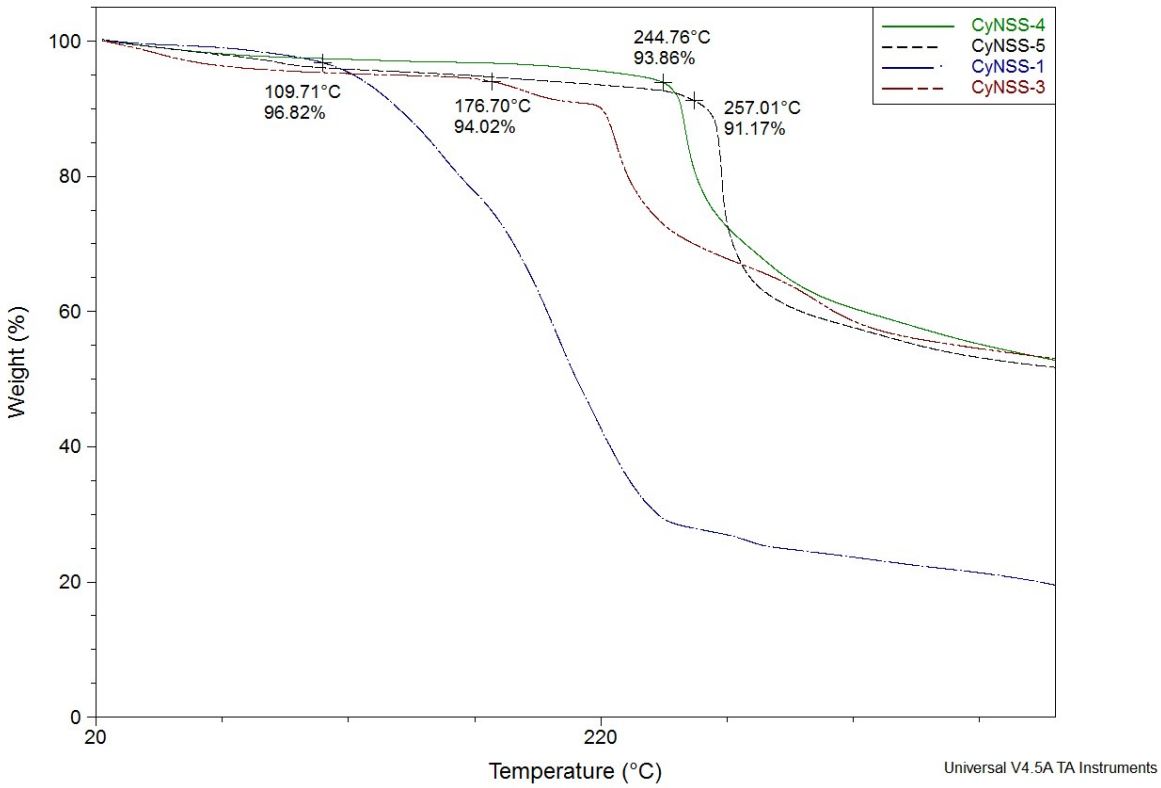



***Figure S74:*** *TGA analysis of Cu(II)-CyNSS complexes in the range 20-400 ºC*

## Anaerobic studies.

Anaerobic studies using NSS-1 and CyNSS-1 were carried out according to the following procedure: Under argon, the ligand (50 mg) was suspended in anhydrous methanol (5 mL) and triethylamine (2 equiv.) was added. The solution was stirred at room temperature for 10 minutes. $CuCl_2$ (1.1 equiv.) was added, and the reaction mixture was heated at reflux for 2 hours under an argon atmosphere. The mixture was cooled to room temperature and excess solvent was removed *in vacuo*. The crude product was purified via normal phase column chromatography (DCM:MeOH:$NEt_3$, 90:10:1) to isolate the copper complex.

[Cu(NSS-1)]: Green solid (36 mg, 62%); FTIR $\nu_{max}$ / $cm^{-1}$: 3242, 2958 2606, 1640, 1481, 1274; (HRMS + pESI) cald $C_{24}H_{33}N_2O_2Cu$ $[M + H]^+$: 446.1995; observed: 446.1933.

[Cu(CyNSS-1)]: Dark green solid (11 mg, 20%); FTIR $\nu_{max}$ / $cm^{-1}$: 3206., 2947, 1593, 1442, 1278, 1001; (HRMS + pESI) cald $C_{24}H_{33}N_2O_2Cu$ $[M + H]^+$:500.2464, observed: 500.2438

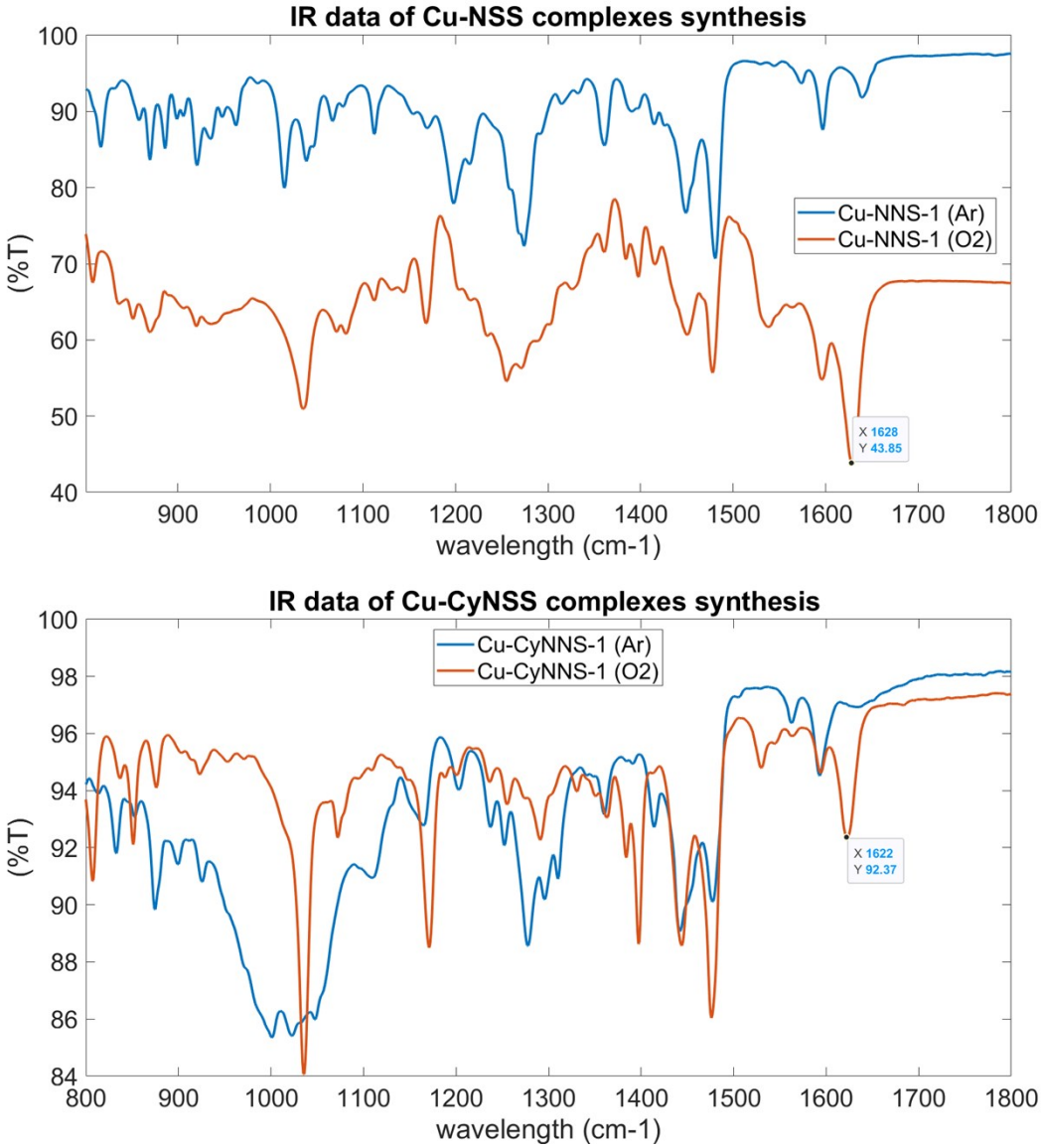



**Figure S75.** IR of the two different protocols (Ar or O2) for **Cu-NSS**-1 and **Cu-CyNSS-1**.

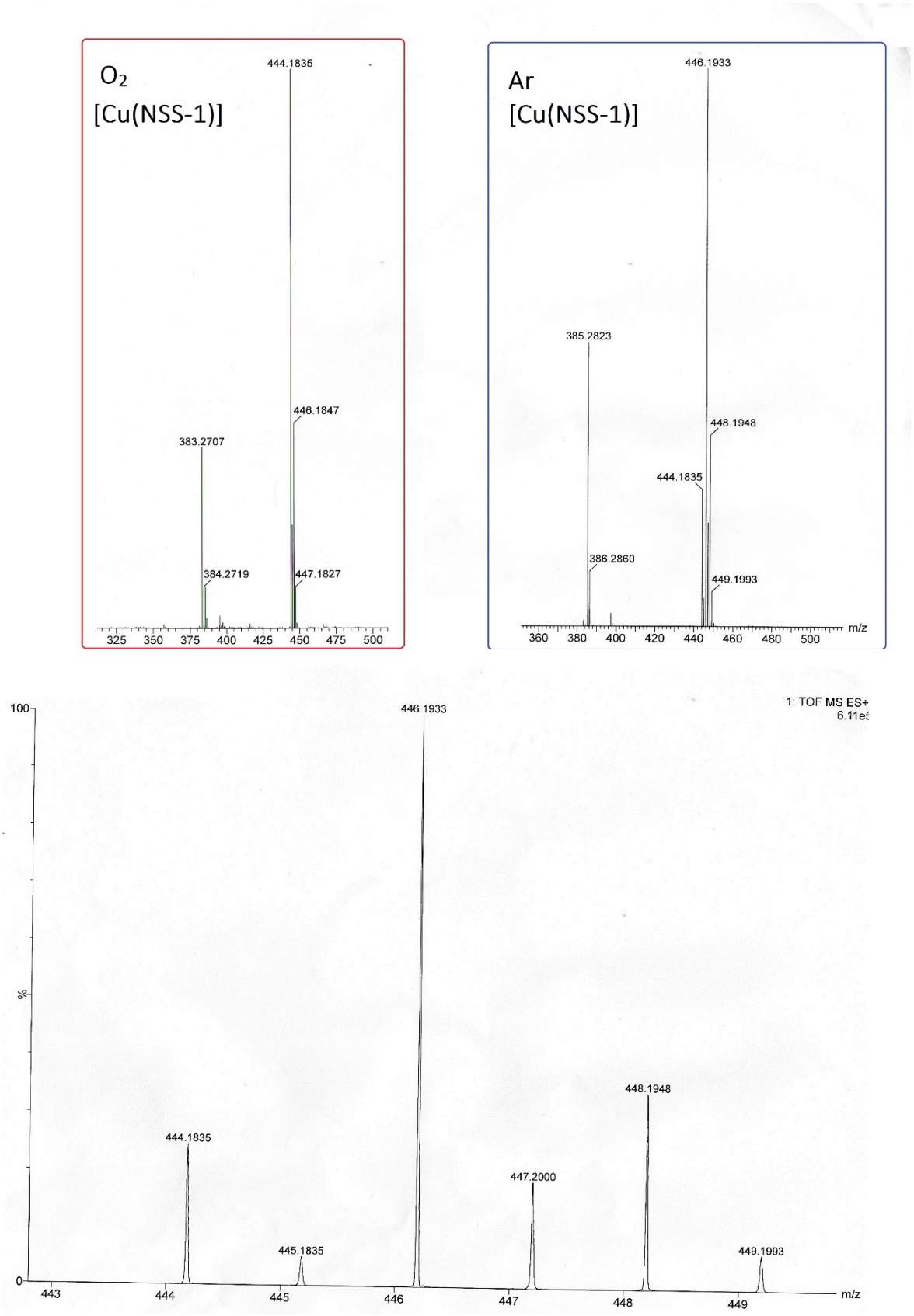



**Figure S76** HRMS for synthesis of Cu-NSS-1 under Ar (upper left) and $O_2$ atmosphere (upper right) and the zoom in of the peak at 446.1933.

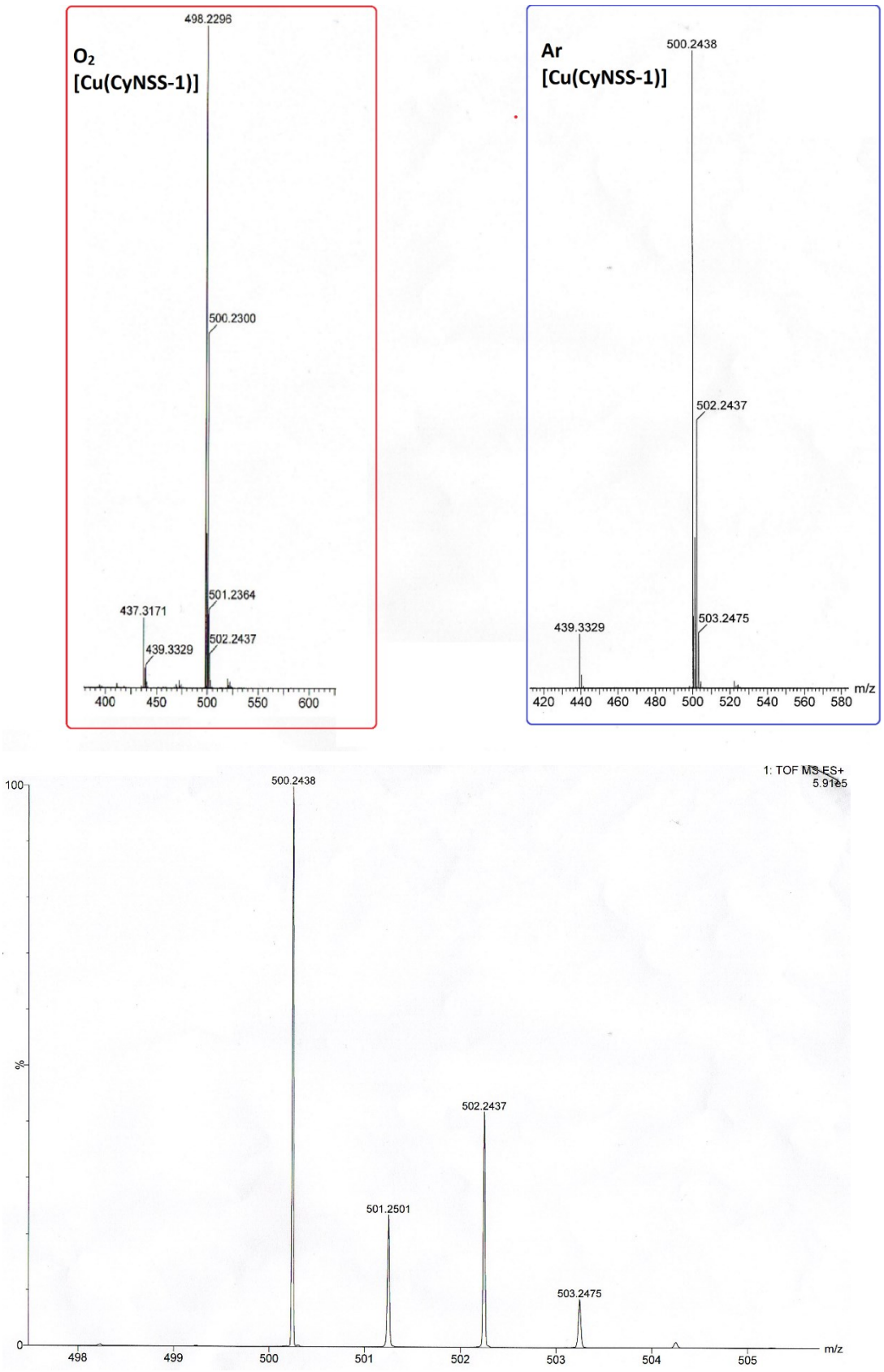



**Figure S77** HRMS for synthesis of Cu-CyNSS-1 under Ar (upper left) and $O_2$ atmosphere (upper right) and the zoom in of the peak at 500.2438

## Crystallographic Data.

X-ray quality crystals were obtained by suspending the isolated copper complexes in organic solventsl (~5 mL) and allowing the solvent to slowly evaporate over 48 hours at room temperature. Due to the lack of isolated complex for **NSS-2**, **NSS-3** and **CyNSS-2** the complexation reaction was repeated, and the crude material was crystallised using the same procedure. Small x-ray quality crystals (<3 mg) formed from these crude solutions. Crystallographic data for **Cu(II)-NSS-1** and **Cu(II)-NSS-3** were collected at the National Crystallography Service, University of Southampton.[3] In both cases, a suitable green block-shaped crystal $mm^3$ was selected and mounted on a MITIGEN holder in perfluoro ether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000HE detector and data were collected at *T* = 100(2)K. The data were processed with CrysAlisPro and solved by intrinsic phasing methods with SHELXT.[4] Crystallographic data for **Cu(II)-CyNSS-1**, **Cu(II)-CyNSS-1$^{solv}$**, **Cu(II)-CyNSS-2**, **Cu(II)-CyNSS-3**, **Cu(II)-CyNSS-4** and **Cu(II)-CyNSS-5** were collected (ω scans) at the University of Sussex using an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 100(2) K of 173(2)K and Cu Kα radiation (λ =1.54184 Å). CRYSALIS CCD and RED software were used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multiscan method. All crystal structures were then refined on $Fo^2$ by full-matrix least-squares refinements using SHELXL.[4] Geometric/crystallographic calculations were performed using PLATON,[5]Olex2,[6] and WINGX[7] packages; graphics were prepared with Crystal Maker.[8] Structures **Cu(II)-NSS-1**, **Cu(II)-NSS-3**, **Cu(II)-CyNSS-1**, **Cu(II)-CyNSSL-1$^{EtOAc}$**, **Cu(II)-CyNSS-2**, **Cu(II)-CyNSS-2**, **Cu(II)-CyNSS-4** and **Cu(II)-CyNSS-5** have been given CCDC deposition numbers 2086033- 2086040.

| Identification code | **Cu(II)-NSS-1** | **Cu(II)-NSS-3** | **Cu(II)-CyNSS-1** | **Cu(II)-CyNSSL-1$^{EtOAc}$** | **Cu(II)-CyNSS-2** | **Cu(II)-CyNSS-3** | **Cu(II)-CyNSS-4** | **Cu(II)-CyNSS-5** |
|---|---|---|---|---|---|---|---|---|
| Empirical formula | $C_{24}H_{33}ClCuN_2O_2$ | $C_{17}H_{22}CuN_2O_4$ | $C_{28}H_{36}CuN_2O_2$ | $C_{28}H_{38}CuN_2O_2$ | $C_{24}H_{32}CuN_2O_2$ | $C_{86}H_{122}Cu_4N_8O_{21}$ | $C_{40}H_{46}Cu_2F_2N_4O_4$ | $C_{131}H_{158}Cu_6F_{18}N_{12}O_{23}$ |
| Formula weight | 480.51 | 381.90 | 496.13 | 498.14 | 444.05 | 1858.07 | 811.89 | 2991.92 |
| Temperature/K | 100(2) | 100.00(10) | 100.0(3) | 100.0(3) | 100(1) | 173.0 | 100(2) | 100.0 |
| Crystal system | orthorhombic | orthorhombic | triclinic | monoclinic | orthorhombic | monoclinic | triclinic | triclinic |
| Space group | Pbca | Iba2 | P-1 | $P2_1/n$ | $P2_12_12_1$ | C2/c | P-1 | P-1 |
| a/Å | 11.2264(2) | 25.4875(6) | 9.4670(5) | 15.1367(3) | 7.6031(4) | 24.19436(19) | 9.0899(5) | 12.0183(9) |
| b/Å | 11.5091(3) | 14.8482(3) | 10.0851(7) | 12.1270(3) | 16.8736(6) | 14.08347(11) | 9.3275(6) | 14.9866(16) |
| c/Å | 35.7717(8) | 8.4815(2) | 13.7290(9) | 28.2251(8) | 18.7628(8) | 25.8393(3) | 10.9768(5) | 20.1854(14) |
| α/° | 90 | 90 | 86.427(6) | 90 | 90 | 90 | 79.623(5) | 104.492(8) |
| β/° | 90 | 90 | 78.259(5) | 95.326(2) | 90 | 96.7456(8) | 89.276(4) | 103.593(6) |
| γ/° | 90 | 90 | 76.948(5) | 90 | 90 | 90 | 67.850(5) | 102.304(8) |
| Volume/Å$^3$ | 4621.91(18) | 3209.77(13) | 1250.02(14) | 5158.7(2) | 2407.10(17) | 8743.56(13) | 846.33(9) | 3275.5(5) |
| Z | 8 | 8 | 2 | 8 | 4 | 4 | 1 | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.381 | 1.581 | 1.318 | 1.283 | 1.225 | 1.412 | 1.593 | 1.517 |
| μ/mm$^{-1}$ | 1.083 | 2.137 | 1.434 | 1.390 | 1.430 | 1.714 | 2.064 | 1.915 |
| F(000) | 2024.0 | 1592.0 | 526.0 | 2120.0 | 940.0 | 3912.0 | 422.0 | 1548.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.02 | 0.5 × 0.3 × 0.01 | 0.1 × 0.08 × 0.04 | 0.08 × 0.04 × 0.02 | 0.1 × 0.08 × 0.04 | 0.05 × 0.03 × 0.01 | 0.02 × 0.02 × 0.01 | 0.14 × 0.1 × 0.03 |
| Radiation | Mo Kα (λ = 0.71075) | CuKα (λ = 1.54178) | Cu Kα (λ = 1.54184) | CuKα (λ = 1.54184) | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 4.284 to 62 | 11.92 to 140.222 | 9.002 to 143.786 | 9.36 to 143.662 | 7.06 to 143.52 | 9.724 to 136.018 | 10.428 to 136.108 | 9.068 to 143.04 |
| Index ranges | -16 ≤ h ≤ 15, -16 ≤ k ≤ | -30 ≤ h ≤ 29, -17 ≤ k ≤ | -11 ≤ h ≤ 8, -12 ≤ k ≤ | -18 ≤ h ≤ 18, -8 ≤ k ≤ | -8 ≤ h ≤ 9, -20 ≤ k ≤ | -29 ≤ h ≤ 27, -16 ≤ k ≤ | -10 ≤ h ≤ 10, -11 ≤ k ≤ | -14 ≤ h ≤ 8, -16 ≤ k ≤ |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 16, -50 ≤ l ≤ 51 | 17, -9 ≤ l ≤ 9 | 12, -16 ≤ l ≤ 16 | 14, -34 ≤ l ≤ 32 | 17, -18 ≤ l ≤ 22 | 16, -30 ≤ l ≤ 30 | 11, -12 ≤ l ≤ 13 | 18, -22 ≤ l ≤ 24 |
| Reflections collected | 50406 | 14210 | 8028 | 17558 | 6887 | 54226 | 17272 | 18274 |
| Independent reflections | 7359 [$R_{int}$ = 0.0583, $R_{sigma}$ = 0.0396] | 2673 [$R_{int}$ = 0.0445, $R_{sigma}$ = 0.0340] | 4696 [$R_{int}$ = 0.0320, $R_{sigma}$ = 0.0508] | 9608 [$R_{int}$ = 0.0424, $R_{sigma}$ = 0.0598] | 4518 [$R_{int}$ = 0.0225, $R_{sigma}$ = 0.0370] | 7901 [$R_{int}$ = 0.0283, $R_{sigma}$ = 0.0141] | 3029 [$R_{int}$ = 0.1099, $R_{sigma}$ = 0.0659] | 12116 [$R_{int}$ = 0.1030, $R_{sigma}$ = 0.1332] |
| Data/restraints/parameters | 7359/1/288 | 2673/3/224 | 4696/0/304 | 9608/0/603 | 4518/1/269 | 7901/0/551 | 3029/0/235 | 12116/3/871 |
| Goodness-of-fit on $F^2$ | 1.146 | 1.106 | 1.059 | 1.031 | 1.032 | 1.092 | 1.061 | 1.089 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0508, $wR_2$ = 0.0909 | $R_1$ = 0.0476, $wR_2$ = 0.1232 | $R_1$ = 0.0441, $wR_2$ = 0.1076 | $R_1$ = 0.0678, $wR_2$ = 0.1787 | $R_1$ = 0.0351, $wR_2$ = 0.0915 | $R_1$ = 0.0697, $wR_2$ = 0.1919 | $R_1$ = 0.0811, $wR_2$ = 0.1877 | $R_1$ = 0.0892, $wR_2$ = 0.2133 |
| Final R indexes [all data] | $R_1$ = 0.0740, $wR_2$ = 0.0978 | $R_1$ = 0.0497, $wR_2$ = 0.1246 | $R_1$ = 0.0571, $wR_2$ = 0.1182 | $R_1$ = 0.0986, $wR_2$ = 0.2071 | $R_1$ = 0.0386, $wR_2$ = 0.0937 | $R_1$ = 0.0714, $wR_2$ = 0.1934 | $R_1$ = 0.0933, $wR_2$ = 0.1933 | $R_1$ = 0.1596, $wR_2$ = 0.2543 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.47/-0.45 | 0.42/-1.06 | 1.27/-0.38 | 1.24/-0.86 | 0.35/-0.41 | 1.67/-0.75 | 1.89/-0.67 | 0.95/-0.73 |
| Flack parameter | | -0.03(5) | | | 0.32(2) | | | |

**[Cu(II)-NSS-1]:** Crystallisation solvent: Methanol

Table S1 Bond Lengths for Cu(II)-NSS-1.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | Cl1 | 2.2786(5) | O3 | C24 | 1.221(5) |
| Cu1 | O1 | 1.8763(16) | **N1** | **C15** | **1.288(3)** |
| Cu1 | N1 | 1.9235(17) | N1 | C16 | 1.467(2) |
| Cu1 | N2 | 2.0283(17) | **N2** | **C17** | **1.491(2)** |
| O1 | C1 | 1.307(3) | N2 | C18 | 1.497(2) |
| O2 | C20 | 1.314(3) | | | |

Table S2 Bond Angles for Cu(II)-NSS-1.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | Cl1 | 89.79(5) | N1 | Cu1 | Cl1 | 175.87(6) |
| O1 | Cu1 | N1 | 92.70(7) | N1 | Cu1 | N2 | 85.27(7) |
| O1 | Cu1 | N2 | 174.24(8) | N2 | Cu1 | Cl1 | 91.93(5) |
| C8 | C7 | C2 | 113.37(17) | | | | |

**[Cu(II)-NSS-2]:** Crystallisation solvent: Methanol –
Low-quality crystallographic data were collected for this compound. A picture that confirms connectivity is shown below; however, better quality data are required to determine if dehydrogentation occurs upon crystallisation. The C-N bond length values are indicative of a single bond (left part), but the values (right part) are on the borderline of a single and double bond.

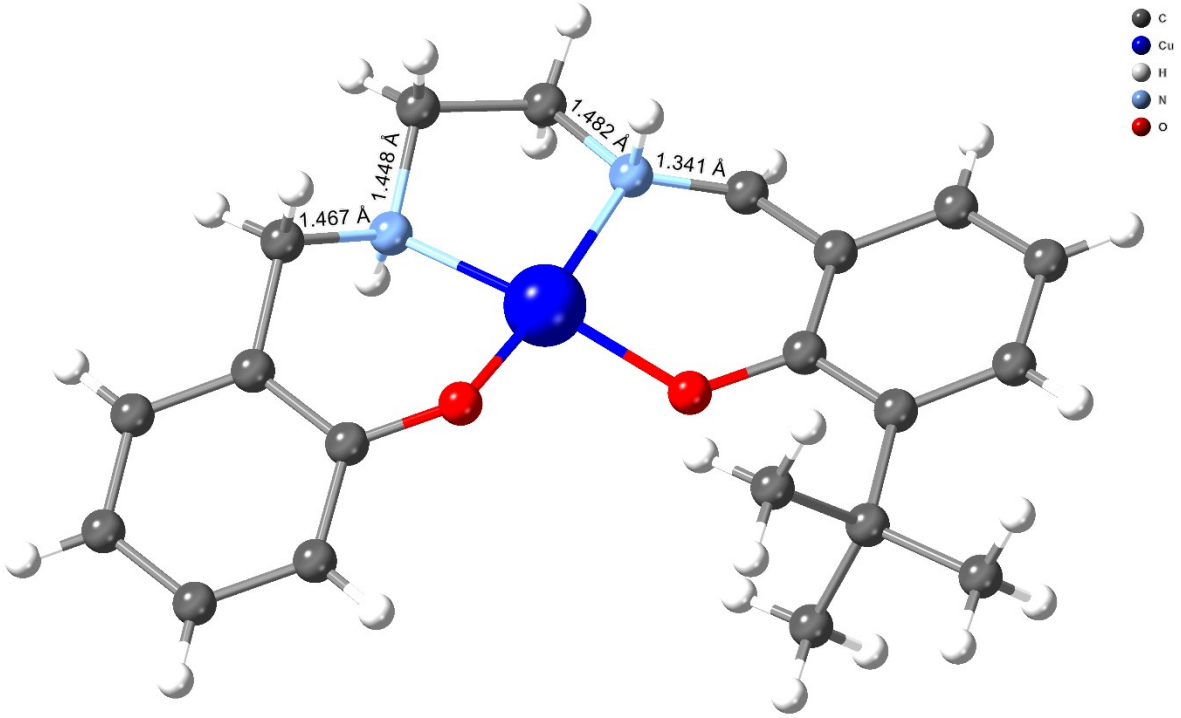



**Figure S78 [Cu(II)-NSS-3]:** Crystallisation solvent: Methanol

Table S3 Bond Lengths for Cu(II)-NSS-3.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O1 | 1.961(5) | O3 | C17 | 1.431(8) |

Table S3 Bond Lengths for Cu(II)-NSS-3.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O2 | 1.925(4) | O3 | C15 | 1.384(8) |
| Cu1 | O4 | 2.312(4) | **N1** | **C7** | **1.475(8)** |
| Cu1 | N1 | 2.024(5) | N1 | C8 | 1.472(8) |
| Cu1 | N2 | 2.037(6) | **N2** | **C9** | **1.498(8)** |
| O1 | C1 | 1.334(7) | N2 | C10 | 1.463(8) |
| O2 | C16 | 1.332(7) | | | |

Table S4 Bond Angles for Cu(II)-NSS-3.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | O4 | 97.74(17) | O2 | Cu1 | N1 | 170.60(18) |
| O1 | Cu1 | N1 | 89.6(2) | O2 | Cu1 | N2 | 93.4(2) |
| O1 | Cu1 | N2 | 168.9(2) | N1 | Cu1 | O4 | 89.61(17) |
| O2 | Cu1 | O1 | 89.70(18) | N1 | Cu1 | N2 | 85.6(2) |
| O2 | Cu1 | O4 | 99.77(16) | N2 | Cu1 | O4 | 92.3(2) |

**[Cu(II)-NSS-4]: – No single crystals could be isolated**
**[Cu(II)-NSS-5]: – No single crystals could be isolated**

**[Cu(CyNSS-1)]:** Crystallisation solvent: Ethyl acetate

Table S5 Bond Lengths for Cu(II)-CyNSS-1.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O1 | 1.8913(18) | O2 | C20 | 1.311(3) |
| Cu1 | O2 | 1.9022(18) | **N1** | **C7** | **1.291(3)** |
| Cu1 | N1 | 1.931(2) | N1 | C8 | 1.482(3) |
| Cu1 | N2 | 1.934(2) | N2 | C13 | 1.479(3) |
| O1 | C1 | 1.316(3) | **N2** | **C14** | **1.287(3)** |

Table S6 Bond Angles for Cu(II)-CyNSS-1.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | O2 | 90.46(8) | O2 | Cu1 | N1 | 165.21(9) |
| O1 | Cu1 | N1 | 93.75(8) | O2 | Cu1 | N2 | 94.49(8) |
| O1 | Cu1 | N2 | 167.64(9) | N1 | Cu1 | N2 | 84.30(9) |

**[Cu(CyNSS-2)]:** Crystallisation solvent: Ethanol

Table S7 Bond Lengths for Cu(II)-CyNSS-2.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O1 | 1.893(2) | O2 | C24 | 1.327(4) |
| Cu1 | O2 | 1.927(2) | **N1** | **C11** | **1.448(5)** |
| Cu1 | N1 | 1.997(3) | N1 | C12 | 1.488(5) |

Table S7 Bond Lengths for Cu(II)-CyNSS-2.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| Cu1 | N2 | 2.018(3) | N2 | C17 | 1.494(4) |
| O1 | C6 | 1.326(4) | **N2** | **C18** | **1.485(4)** |

Table S8 Bond Angles for Cu(II)-CyNSS-2.

| **Atom** | **Atom** | **Atom** | **Angle/˚** | **Atom** | **Atom** | **Atom** | **Angle/˚** |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | O2 | 90.17(10) | O2 | Cu1 | N1 | 163.87(15) |
| O1 | Cu1 | N1 | 94.19(11) | O2 | Cu1 | N2 | 94.65(10) |
| O1 | Cu1 | N2 | 162.46(12) | N1 | Cu1 | N2 | 85.82(12) |

**[Cu(CyNSS-3)]:** Crystallisation solvent: Methanol

Table S9 Bond Lengths for Cu(II)-CyNSS-3.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| Cu1 | O1 | 1.902(3) | O3 | C19 | 1.394(5) |
| Cu1 | O2 | 1.891(3) | O3 | C21 | 1.426(5) |
| Cu1 | N1 | 2.009(3) | **N1** | **C7** | 1.495(5) |
| Cu1 | N2 | 1.996(4) | N1 | C8 | 1.483(5) |
| O1 | C1 | 1.350(5) | N2 | C13 | 1.500(5) |
| O2 | C20 | 1.333(5) | **N2** | **C14** | 1.487(5) |

Table S10 Bond Angles for Cu(II)-CyNSS-3.

| **Atom** | **Atom** | **Atom** | **Angle/˚** | **Atom** | **Atom** | **Atom** | **Angle/˚** |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | N1 | 93.09(13) | O2 | Cu1 | N1 | 172.54(14) |
| O1 | Cu1 | N2 | 173.93(14) | O2 | Cu1 | N2 | 94.80(13) |
| O2 | Cu1 | O1 | 86.56(12) | N2 | Cu1 | N1 | 86.32(13) |

**[Cu(CyNSS-4)]:** Crystallisation solvent: Ethanol

Table S11 Bond Lengths for Cu(II)-CyNSS-4.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O1[1] | 2.359(3) | O1 | C1 | 1.350(6) |
| Cu1 | O1 | 1.944(3) | O2 | C20 | 1.340(6) |
| Cu1 | O2 | 1.905(3) | **N1** | **C7** | **1.493(6)** |
| Cu1 | N1 | 2.028(4) | N1 | C8 | 1.486(6) |
| Cu1 | N2 | 2.016(4) | **N2** | **C13** | **1.486(6)** |
| F1 | C4 | 1.368(6) | N2 | C14 | 1.487(6) |

[1]-X,1-Y,1-Z

Table S12 Bond Angles for Cu(II)-CyNSS-4.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | O1[1] | 84.52(14) | O2 | Cu1 | N2 | 94.06(15) |
| O1 | Cu1 | N1 | 93.11(15) | N1 | Cu1 | O1[1] | 98.78(15) |
| O1 | Cu1 | N2 | 169.97(16) | N2 | Cu1 | O1[1] | 86.13(14) |
| O2 | Cu1 | O1[1] | 104.51(14) | N2 | Cu1 | N1 | 84.73(17) |
| O2 | Cu1 | O1 | 91.79(14) | Cu1 | O1 | Cu1[1] | 95.48(14) |
| O2 | Cu1 | N1 | 156.55(17) | | | | |

**[Cu(CyNSS-5)]:** Crystallisation solvent: Methanol

Table S13 Bond Lengths for Cu(II)-CyNSS-5.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | O1 | 1.925(5) | Cu2 | O4 | 1.909(5) |
| Cu1 | O2 | 1.903(5) | Cu2 | O5 | 1.934(5) |
| Cu1 | N1 | 2.000(6) | Cu2 | N3 | 2.000(6) |
| Cu1 | N2 | 1.999(6) | Cu2 | N4 | 2.009(6) |
| **N1** | **C10** | **1.484(9)** | **N3** | **C39** | **1.499(9)** |
| N1 | C17 | 1.499(10) | N3 | C41 | 1.483(9) |
| **N2** | **C12** | **1.499(10)** | **N4** | **C46** | **1.467(9)** |
| N2 | C19 | 1.473(9) | N4 | C48 | 1.495(9) |
| **N5** | **C70** | **1.508(9)** | **N6** | **C68** | **1.475(9)** |
| N5 | C77 | 1.491(8) | N6 | C75 | 1.487(10) |

Table S14 Bond Angles for Cu(II)-CyNSS-5.

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| O1 | Cu1 | N1 | 94.9(2) | O4 | Cu2 | O5 | 88.1(2) |
| O1 | Cu1 | N2 | 158.3(2) | O4 | Cu2 | N3 | 174.6(2) |
| O2 | Cu1 | O1 | 87.6(2) | O4 | Cu2 | N4 | 94.7(2) |
| O2 | Cu1 | N1 | 167.7(3) | O5 | Cu2 | N3 | 92.9(2) |
| O2 | Cu1 | N2 | 95.5(2) | O5 | Cu2 | N4 | 169.7(2) |
| N2 | Cu1 | N1 | 86.7(3) | N3 | Cu2 | N4 | 85.3(2) |

Elemental analysis data

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## Elemental Analysis Sample Results

**Name** Jack Devonport

**Organisation Name** University of Sussex

**Purchase order number** 8256824/CHEM

| [Cu(NSSL-5)] | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **Repeated** | 48.93 | 49.91 |
| **Hydrogen** | **-** | 6.19 | 6.34 |
| **Nitrogen** | **-** | 6.87 | 6.96 |

| [Cu(CyNSSL-1)] | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **Repeated** | 44.84 | 41.62 |
| **Hydrogen** | **-** | 7.98 | 7.36 |
| **Nitrogen** | **-** | 6.15 | 5.56 |

| [Cu(CyNSSL-4) | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **53.44** | 53.39 | 53.52 |
| **Hydrogen** | **4.91** | 4.95 | 4.96 |
| **Nitrogen** | **5.94** | 5.79 | 5.83 |

| [Cu(CyNSSL-5)] | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **57.59** | 58.81 | 56.69 |
| **Hydrogen** | **6.21** | 5.44 | 5.23 |
| **Nitrogen** | **6.40** | 5.99 | 5.96 |

| Separate Study | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | | 58.43 | 58.13 |
| **Hydrogen** | | 7.50 | 7.58 |
| **Nitrogen** | | 6.35 | 6.32 |

| [Cu(NSSL-4)] | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **45.66** | 44.77 | 45.84 |
| **Hydrogen** | **3.94** | 3.73 | 3.72 |
| **Nitrogen** | **6.08** | 5.67 | 5.83 |

| [Cu(NSSL-2)] | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **Repeated** | 62.35 | 66.72 |
| **Hydrogen** | **-** | 5.86 | 6.12 |
| **Nitrogen** | **-** | 6.70 | 7.10 |

| [Cu(NSS-1)]1DCM 1NEt3 | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **58.99** | 57.77 | 59.33 |
| **Hydrogen** | **7.98** | 8.38 | 8.17 |
| **Nitrogen** | **6.66** | 6.90 | 6.93 |

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# Elemental Analysis Sample Results

| | |
|---|---|
| **Name** | Jack Devonport |
| **Organisation Name** | University of Sussex |
| **Purchase order number** | 8257425/CHEM |

| **Standard – Acetanilide** | | |
|---|---|---|
| **Element** | **Expected %** | **Found** |
| **Carbon** | 71.06 (+/- 0.26) | 71.02 |
| **Hydrogen** | 6.70 (+/- 0.09) | 6.76 |
| **Nitrogen** | 10.36 (+/- 0.18) | 10.35 |

| **[Cu(NSSL-2)]** | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **61.92** | 63.50 | 62.97 |
| **Hydrogen** | **6.24** | 7.38 | 7.33 |
| **Nitrogen** | **7.22** | 6.18 | 6.13 |

| **[Cu(CyNSS-1)]2DCM 2NEt3** | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **58.09** | 57.80 | 57.18 |
| **Hydrogen** | **8.12** | 8.89 | 8.75 |
| **Nitrogen** | **6.45** | 7.24 | 7.10 |

| **[Cu(CyNSS-3)]DCM** | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **52.54** | 53.85 | 53.13 |

| | | | |
|---|---|---|---|
| **Hydrogen** | **5.61** | 4.91 | 4.85 |
| **Nitrogen** | **5.57** | 5.92 | 5.87 |

| **[Cu2(NSS-5)2]DCM** | | | |
|---|---|---|---|
| **Element** | **Expected %** | **Found (1)** | **Found (2)** |
| **Carbon** | **50.26** | 51.09 | 50.30 |
| **Hydrogen** | **4.60** | 4.88 | 4.79 |
| **Nitrogen** | **7.10** | 7.01 | 6.89 |

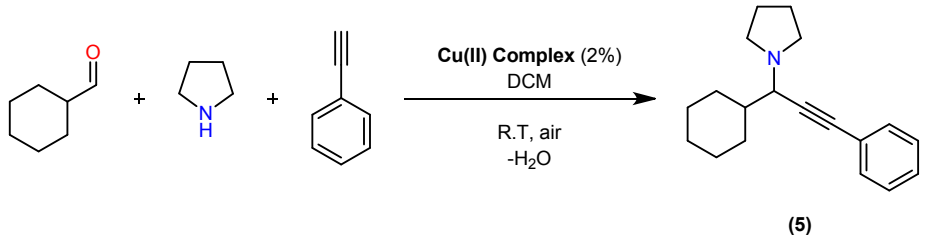
**Date completed** 10.05.2021

**Signature** O. McCullough

**Comments**

## Catalytic Screens.

Condition used in the catalytic screens are similar to those described in previous work on a state-of-the-art symmetrical copper-salen complex.[9]




***Scheme S5:*** *A[3]-coupling reaction used to screen catalytic activity of non-symmetric salan complexes.*

Cyclohexanecarboxaldehyde (121 µL, 1 mmol) Pyrrolidine (92 µL, 1.1 mmol), alkyne (132 µL, 1.2 mmol), copper complex (2 mol%) and activated, crushed, 4Å molecular sieves (100 mg) were combined in dry dichloromethane (2 mL) and stirred for 24 hours. The reaction mixture was filtered, then passed over a silica plug, the silica plug was washed with dichloromethane (3x 5 mL) and the filtrate was concentrated. The sample was dissolved in $CDCl_3$ and durene (ca. 10 mg) was added. NMR yields were then based comparing the integrals arising from the signals corresponding to the known product and durene.

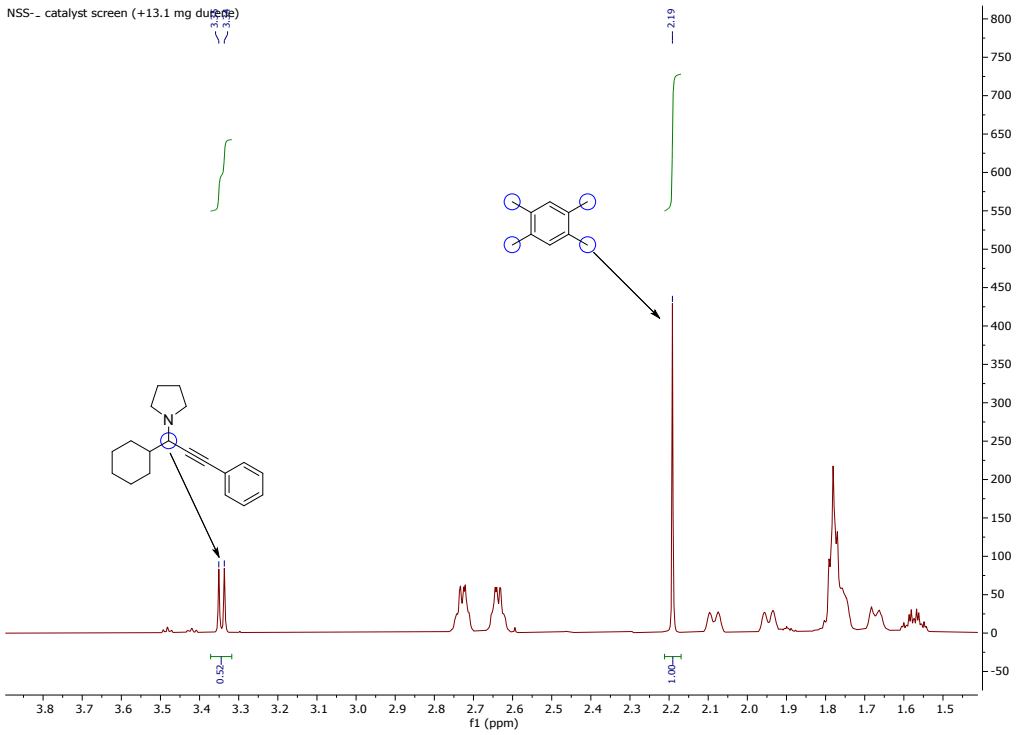
**Table S15***: Synthesis of propargylamine* ***2.4*** *using various non-symmetric salan Cu(II) complexes [a]: Yield giving as [1]H-NMR conversions achieved by comparing to durene internal standard*

| Entry | Catalyst | NMR Yield[a] (%) |
|---|---|---|
| ***1*** | *[Cu(II)-NSS-1]* | *42* |
| ***2*** | *[Cu(II)-NSS-2]* | *44* |
| ***3*** | *[Cu(II)-NSS-4]* | *27* |
| ***4*** | *[Cu(II)-NSS-5]* | *32* |
| ***5*** | *[Cu(II)-CyNSS-1]* | *49* |
| ***6*** | *[Cu(II)-CyNSS-3]* | *53* |
| ***7*** | *[Cu(II)-CyNSS-4]* | *55* |
| ***8*** | *[Cu(II)-CyNSS-5]* | *33* |

**Example calculation of NMR conversions:**

**NSS-5**:

$Exact\ mass\ of\ durene\ added\ =\ 6.8\ mg\ (0.05067\ mmol)$:




$Ration\ of\ Integrals\ =\ 0.52/(1/12)\ =\ 6.24$

$NMR\ yield$: $(6.24\ X\ 0.05067)\ x\ 100\ =\ 32\%$

***Figure S79:*** *Example calculation for entry 4 (table S15) of* $^{1}$*H-NMR conversion using durene internal standard.*

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