Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting information

Unprecedented reductive cyclisation of salophen ligands to tetrahydroquinoxalines during metal complex formation

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Contents

General experimental details

All chemicals were provided by Alfa Aesar, Acros Organics, Insight Biotechnology or Sigma-Aldrich and were used without further purification. Chromium(II) chloride (anhydrous, 97%) was purchased from Alfa Aesar. Bis(pentamethylcyclopentadienyl)iron(II) (decamethylferrocene) was purchased from Insight Biotechnology; bis(cyclopentadienyl)titanium dichloride (titanocene dichloride, 99%) was obtained from Alfa Aesar; and bis(cyclopentadienyl)cobalt(III) hexafluorophosphate (98%), bis(pentamethylcyclopentadienyl)cobalt(II) (decamethylcobaltocene) and samarium(II) iodide (0.1 M in THF, stabilised with samarium chips) were sourced from Sigma-Aldrich. A solution of 1 M NaOH was made by dissolving NaOH pellets (40 g) into deionised water (1 L). A 1 M HCl solution was made by adding 42 mL of concentrated HCl (12 M, 37 % w/w, 1.18 g mL^{-1}) first to 125 mL of water, then adding 375 mL of water.

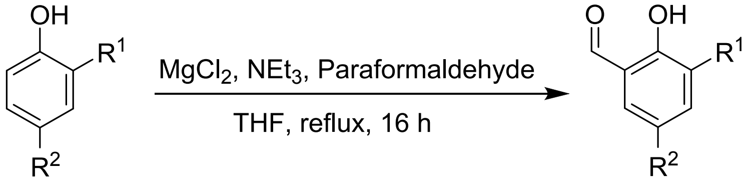
Dry glassware was obtained by leaving glassware in an oven at 60 °C for a minimum of 16 h. Dry solvents were obtained from a Pure Solv MD-7 solvent purification system. Argon was obtained from BOC gases (>99%). For column purification, 40-60 nm silica gel was used (Fluorochem) and monitored using aluminium backed TLC silica gel F_{254} plates (Fisher Scientific) with potassium permanganate ($KMnO_4$) solution as a staining agent. High purity silica gel was used for flash column chromatography purification (pore size 60 Å, 220-550 mesh particle size, 35-75 µm particle size, Sigma-Aldrich). All column and reaction solvents were HPLC grade from Fischer Scientific.

^{1}H, ^{13}C[^{1}H] and ^{19}F NMR 400 MHz spectra were obtained from a Jeol ECS-400 or Jeol ECX-400 NMR spectrometer. When required, further analysis was performed using a Bruker 500 MHz Avance III HD spectrometer, with a 5 mm triple resonance broadband probe and Topspin 3.5pl7 software, or a Bruker 700 MHz Avance Neo spectrometer equipped with a 5 mm triple resonance cryoprobe. Peak assignments were made with the aid of DEPT edited ^{13}C NMR spectra and 2D NMR analyses including COSY, HSQC, HMBC and one bond ^{13}C-^{19}F correlations on one of the three spectrometers using standard pulse sequences. Samples were dissolved and analysed in deuterated $CDCl_3$ (Sigma-Aldrich). Spectra were referenced by assigning the $CHCl_3$ peak to 7.26 ppm for ^{1}H NMR spectra and the middle peak of the triplet $CDCl_3$ peak to 77.16 ppm for ^{13}C[^{1}H] and ^{13}C[^{19}F] NMR spectra.[1,2] All NMR spectra were run at room temperature (298 K) unless otherwise stated. Variable temperature NMR experiments were performed using a Bruker 500 MHz Avance III HD spectrometer, with a Bruker Chiller Unit for temperatures down to -20 °C and a liquid nitrogen evaporator for temperatures lower than -20 °C. Variable temperature NMR analysis was performed from -55 °C to 25 °C in 10 °C increments. NMR spectra were analysed with MestReNova software (Mestrelab).

Mass Spectra were recorded on a Bruker compact time-of-flight mass spectrometer (microTOF) MS, twinned with an Agilent series 1260 LC for Electrospray Ionisation (ESI) and Atmospheric Pressure Chemical Ionisation (APCI) analysis. Samples were dissolved in CH_2Cl_2 prior to analysis. ART-IR spectroscopy was performed using a PerkinElmer Spectrum Two FT-IR Spectrometer and analysed with Spectrum software (PerkinElmer). Samples were prior dissolved in $CDCl_3$ prior to analysis. Melting points were measured with a Stuart SMP20 (25-300 °C) melting point apparatus.

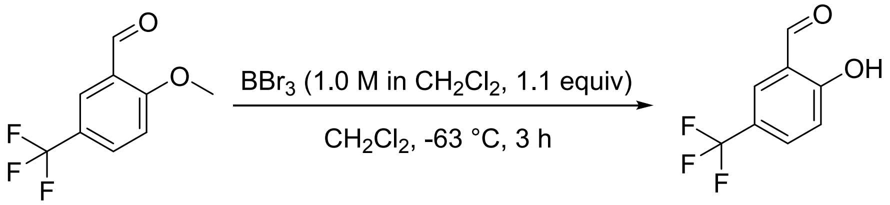
General synthetic procedures

All aldehydes and salophen ligands **1a-h** were synthesised according to methods previously reported in the literature.[3-11] 5-(*Tert*-butyl)-2-hydroxybenzaldehyde[5] and 3-(*tert*-butyl)-2-hydroxy-5-methoxybenzaldehyde[6] were synthesised via a magnesium chloride-triethylamine *ortho*-formylation reaction (Scheme S1).[3,4] 2-Hydroxy-5-(trifluoromethyl)benzaldehyde[9-11] was synthesised by the method of Lynch and Laykea (Scheme S2).[9,10] *N,N′*-Bis(3-*tert*-butyl-5-methoxysalicylidene)-1,2-phenylenediamine (**1a**),[8] *N,N′*-bis(salicylidene)-1,2-phenylenediamine (**1b**),[7] *N,N′*-bis(5-*tert*-butylsalicylidene)-1,2-phenylenediamine (**1c**),[7] *N,N′*-bis(4-methoxy-2-hydroxybenzylidene)-1,2-phenylenediamine (**1d**),[12,13] *N,N′*-bis(2-hydroxy-5-methoxybenzylidene)-1,2-phenylenediamine (**1e**)[13] and *N,N′*-bis(6-methoxysalicylidene)-1,2-phenylenediamine (**1f**)[13-15] were synthesised by condensation of the required salicylaldehyde with 1,2-diaminobenzene in methanol (Scheme S3).[3] All analyses of previously reported aldehydes and salophen ligands matched those reported in the literature.[3-15]

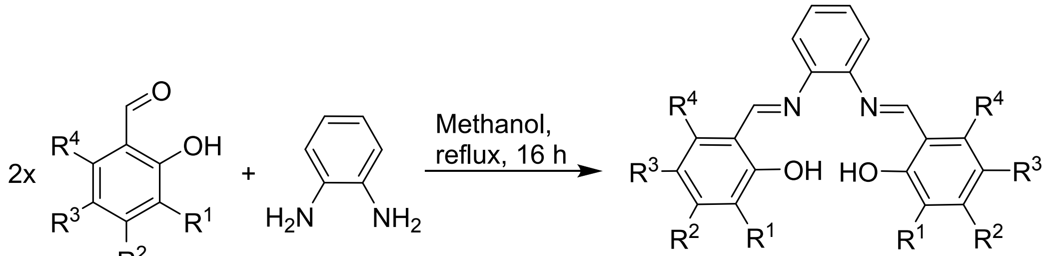


R^1 = H, R^2 = ^{t}Bu;
R^1 = ^{t}Bu, R^2 = OMe

Scheme S1



Scheme S2



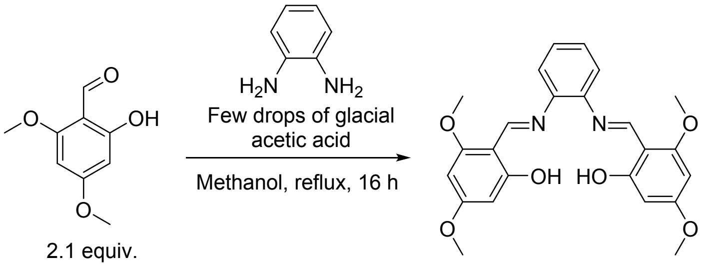
1a-1f

1a: R^1=^{t}Bu, R^2=H, R^3=OMe, R^4=H; **1b**: R^1=H, R^2=H, R^3=H, R^4=H;
1c: R^1=H, R^2=H, R^3=^{t}Bu, R^4=H; **1d**: R^1=H, R^2=OMe, R^3=H, R^4=H;
1e: R^1=H, R^2=H, R^3=OMe, R^4=H; **1f**: R^1=H, R^2=H, R^3=H, R^4=OMe

Scheme S3

Salophen ligand synthesis

2,2'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3,5-dimethoxyphenol) (1g)



2,4-Dimethoxy-6-hydroxybenzaldehyde (0.2515 g, 1.38 mmol, 2.1 equiv.) was dissolved in methanol (12 mL). A solution of 1,2-diaminobenzene (0.0707 g, 0.65 mmol) in methanol (4 mL) was added dropwise to the stirring aldehyde solution. A few drops of acetic acid were added and the reaction mixture was heated at reflux for 16 h. After cooling to room temperature, a precipitate was isolated and purified by washing with methanol (10 mL). The solid was then dried *in vacuo* to afford salophen ligand **1g** as a yellow solid (0.2458 g, 86%).

m.p. 186.7–187.8 ^{o}C.

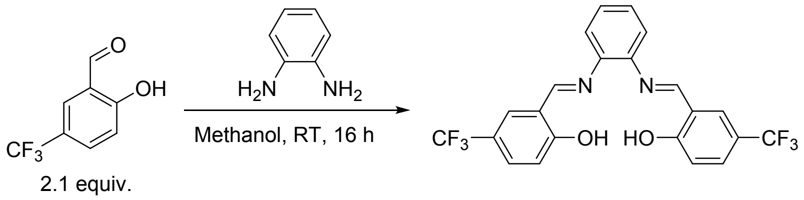
^{1}H NMR (400 MHz): δ_H(CDCl$_3$) 14.55 (2H, s, OH), 14.54 (1H, s, OH), 8.94 (2H, s, HC=N), 8.93 (1H, s, HC=N), 7.27 (4H, s, ArH), 6.13 (2H, d, J = 2.0 H, ArH), 5.84 (2H, d, J = 2.5 Hz, ArH), 3.82 (6H, s, OMe), 3.81 (6H, s, OMe) ppm.

^{13}C NMR (100 MHz): δ_c(CDCl$_3$) 168.74 (C-OH), 166.01 (C=N), 161.24 (ArC), 156.66 (ArC), 141.04 (ArC), 126.81 (ArC), 119.16 (ArC), 104.03(ArC), 94.43 (ArC), 89.81 (ArC), 55.72 (O-CH$_3$), 55.61 (O-CH$_3$) ppm.

Mass Spec ESI: Calc: [$C_{24}H_{25}N_2O_6$]$^+$: 437.1707 (MH$^+$), found: 437.1698. Calc: [$C_{24}H_{24}N_2NaO_6$]$^+$: 459.1527 (M+Na$^+$), found: 459.1519.

IR (CDCl$_3$): 3011, 2938, 2830 (C-H alkyl), 1604 (C=N), 1457 (C=C aromatic) cm^{-1}.

N,N'-Bis(2-hydroxy-5-trifluoromethyl)-1,2-phenylenediamine (1h)



2-Hydroxy-5-(trifluoromethyl)benzaldehyde (0.5002 g, 2.63 mmol, 2.1 equiv.) was dissolved in methanol (4 mL). A solution of 1,2-diaminobenzene (0.1365 g, 1.25 mmol) dissolved in methanol (4 mL) was added dropwise to the stirring aldehyde solution. The reaction was stirred at room temperature for 16 h, during which time a precipitate formed. The precipitate was isolated from the reaction solution and purified by washing with cold methanol (10 mL). The solid was then dried *in vacuo* to afford the salophen ligand **1h** as a yellow solid (0.1561 g, 28% yield).

m.p. 161.7–162.5 ^{o}C.

^{1}H NMR (400 MHz): δ_H($CDCl_3$) 13.51 (2H, s, OH), 8.69 (2H, s, HC=N), 7.69 (2H, d, *J* = 2 Hz, ArH), 7.61 (2H, dd, *J* = 9, 2 Hz, ArH), 7.44–7.40 (2H, m, ArH), 7.30–7.26 (2H, m, ArH), 7.14 (2H, d, *J* = 9 Hz, ArH) ppm.

^{13}C NMR (100 MHz): δ_c($CDCl_3$) 163.94 (s, C-OH), 162.83 (s, C=N), 142.09 (s, ArC), 130.21 (q, $^{3}J_{CF}$ 3.5 Hz, ArCH), 129.77 (q, $^{3}J_{CF}$ 3.5 Hz, ArCH), 128.67 (s, ArC), 124.19 (q, $^{1}J_{CF}$ 270 Hz, CF_3), 121.66 (q, $^{2}J_{CF}$ 33 Hz, Ar$\underline{C}CF_3$) 119.67 (s, ArC), 118.72 (s, ArC), 118.44 (s, ArC) ppm.

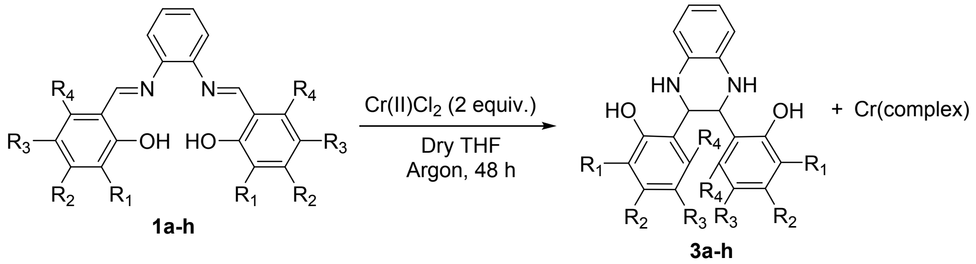
^{19}F NMR (376 MHz): δ_F($CDCl_3$) -61.55 (s, CF_3) ppm.

Mass Spec ESI: Calc: $[C_{22}H_{15}F_6N_2O_2]^+$: 453.1032 (M+H$^+$), found: 453.1030; Calc: $[C_{22}H_{14}F_6N_2NaO_2]^+$: 475.0852 (M+Na$^+$), found: 475.0850; Calc: $[C_{22}H_{14}F_6KN_2O_2]^+$: 491.0591 (M+K$^+$), found: 491.0585.

IR ($CDCl_3$): 1623 (C=N), 1491 (C=C aromatic) cm^{-1}.

Tetrahydroquinoxaline synthesis

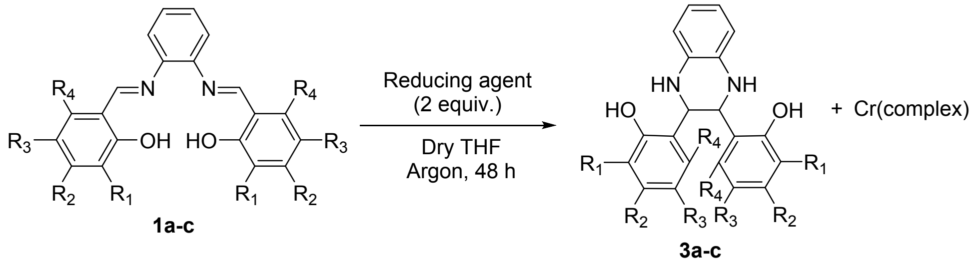
Method A: General procedure with chromium(II) chloride



a: R_1 = ${}^tBu$, $R_2 = R_4 = H$, R_3 = OMe; **b:** $R_1 = R_2 = R_3 = R_4 = H$; **c:** $R_1 = R_2 = R_4 = H$, R_3 = ${}^tBu$; **d:** $R_1 = R_3 = R_4 = H$, R_2 = OMe; **e:** $R_1 = R_2 = R_4 = H$, R_3 = OMe; **f:** $R_1 = R_2 = R_3 = H$, R_4 = OMe; **g:** $R_1 = R_3 = H$, $R_2 = R_4$ = OMe; **h:** $R_1 = R_2 = R_4 = H$, $R_3 = CF_3$

Synthesis of tetrahydroquinoxalines using chromium(II) chloride was performed using conditions for the synthesis of metal(salophen) complexes reported by Darensbourg.[16] Salophen ligand and chromium(II) chloride (2 equiv.) were added to a dry round bottom flask under argon. The flask then placed *in vacuo* for 5 mins. The flask was removed from the vacuum and dry THF (25 mL) was added. The reaction mixture was then left stirring for 2 days under argon. Et_2O was added (25 mL) to the reaction mixture followed by sat. aq. NH_4Cl (25 mL). The organic layer was then separated from the aqueous layer and washed with further with sat aq. NH_4Cl (25 mL) and then sat aq. brine (3 x 25 mL). The catalyst precipitate in the organic phase was separated by filtration from the reaction mixture. The organic phase was then concentrated *in vacuo* and the residue purified by column chromatography (hexane:EtOAc) to isolate the tetrahydroquinoxaline product.

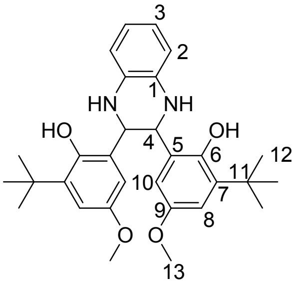
Method B: General procedure with reducing agents



a: R_1 = ${}^tBu$, $R_2 = R_4 = H$, R_3 = OMe; **b:** $R_1 = R_2 = R_3 = R_4 = H$; **c:** $R_1 = R_2 = R_4 = H$, R_3 = ${}^tBu$

Salophen ligand and a reducing agent (2 equiv.) were added to a dry round bottom flask under argon and then placed *in vacuo* for 5 mins. The flask was then removed from the vacuum and dry THF (15 mL) was added. The reaction mixture was then left stirring for 48 h under argon. Et_2O (15 mL) was then added to the reaction mixture followed by sat. aq. NH_4Cl (15 mL). The organic layer was then separated from the aqueous layer and washed further with sat. aq. NH_4Cl (15 mL) and then sat aq. brine (3 x 15 mL). The organic phase was then concentrated *in vacuo* and the residue purified by column chromatography (hexane:EtOAc) to isolate the tetrahydroquinoxaline product.

6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(2-(*tert*-butyl)-4-methoxyphenol) (3a)



Using Method A: Prepared using *N,N'*-bis(3-*tert*-butyl-5-methoxysalicylidene)-1,2-phenylenediamine (**1a**, 0.2558 g, 0.52 mmol) and chromium(**II**) chloride (0.1293 g, 1.05 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3a** as an off white solid (0.0136 g, 5% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **3a** in a 4:1 hexane:EtOAc mixture.

Using Method B: Prepared using *N,N'*-bis(3-*tert*-butyl-5-methoxysalicylidene)-1,2-phenylenediamine (**1a**, 0.1581 g, 0.32 mmol) and decamethylcobaltocene (0.2133 g, 0.64 mmol, 2 equiv.). After workup, the product was purified by column chromatography using first 4:1 hexane:EtOAc then 1:1 hexane:EtOAc, to give compound **3a** as an off white solid (0.0151 g, 10% yield).

***R*$_f$**: 0.65 (4:1 hexane:EtOAc).

^{1}H NMR (400 MHz): $\delta_H(CDCl_3)$ 9.07 (2H, s, OH), 6.83-6.88 (2H, m, ArH, **3**), 6.77-6.89 (2H, m, ArH, **2**), 6.70 (2H, d, *J* = 3 Hz, ArH, **8**), 5.75 (2H, s, ArH, **10**), 4.81 (2H, s, N-C($\underline{H}$)-C, **4**), 4.42 (2H, s, NH), 3.36 (6H, s, 2xOMe, **13**), 1.38 (18H, s, 2x$C(CH_3)_3$, **12**) ppm.

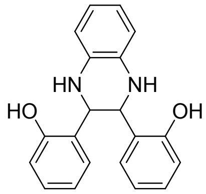
^{13}C NMR (175 MHz): $\delta_c(CDCl_3)$ 152.14 (Ar$\underline{C}$-OMe, **9**), 149.59 ($\underline{C}$-OH, **6**), 138.89 (Ar$\underline{C}$-CMe_3, **7**), 132.20 (Ar$\underline{C}$-NH, **1**), 122.46 (ArC, **5**), 121.94 (ArC, **3**), 117.59 (ArC, **2**), 115.18 (ArC, **8**), 110.93 (ArC, **10**), 59.24 (N-$\underline{C}$(H)-C, **4**), 55.75 (O-$\underline{C}H_3$, **13**), 35.05 ($\underline{C}Me_3$, **11**), 29.66 ($C(\underline{C}H_3)_3$, **12**) ppm.

Mass Spec ESI: Calc: $[C_{30}H_{39}N_2O_4]^+$: 491.2904 (MH^+), found: 491.2916; Calc: $[C_{30}H_{38}N_2NaO_4]^+$: 513.2724 ($M+Na^+$), found: 513.2737; Calc: $[C_{30}H_{38}KN_2O_4]^+$: 529.2463 ($M+K^+$), found: 529.2473.

IR ($CDCl_3$): 3309 (O-H), 2998 (N-H), 2960, 2915, 2869 (C-H alkyl), 1434 (C=C aromatic) cm^{-1}.

Melting Point: 216.5–216.9 °C.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)diphenol (3b)



Using Method A: Prepared using *N,N'*-bis(salicylidene)-1,2-phenylenediamine (**1b**, 0.2530 g, 0.8 mmol) and chromium(II) chloride (0.1944 g, 1.6 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3b** as an off white solid (0.0211 g, 8% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **3b** in a 4:1 hexane:EtOAc mixture.

Using Method B: Prepared using *N,N'*-bis(salicylidene)-1,2-phenylenediamine (**1b**, 0.1594 g, 0.5 mmol) and decamethylcobaltocene (0.3310 g, 1.0 mmol, 2 equiv.). After workup, the product was purified by column chromatography using first 4:1 hexane:EtOAc then 1:1 hexane:EtOAc, to give compound **3b** as an off white solid (0.0243 g, 15% yield).

***R*$_f$**: 0.46 (4:1 hexane:EtOAc).

^{1}H NMR (400 MHz): δ_H($CDCl_3$) 9.00 (2H, s, OH), 7.12–7.08 (2H, m, ArH), 6.90–6.84 (4H, m, ArH), 6.81–6.77 (2H, m, ArH), 6.49 (2H, dd, *J* 7.5, 1.5 Hz, ArH), 6.37 (2H, dd, *J* 7.5 Hz, 1.5 Hz ArH), 4.80 (2H, s, N-C($\underline{H}$)-C), 4.42 (2H, s, NH) ppm.

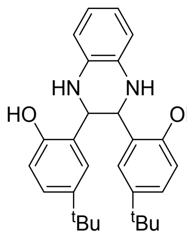
^{13}C NMR (175 MHz δ_c($CDCl_3$) 156.40 ($\underline{C}$-OH), 132.33 (Ar$\underline{C}$-NH), 130.28 (ArC), 129.85 (ArC), 122.18 (ArC), 121.97 (ArC), 119.72 (ArC), 117.65 (ArC), 117.15 (ArC), 59.02 (N-$\underline{C}$(H)-C) ppm.

Mass Spec ESI: Calc: $[C_{20}H_{19}N_2O_2]^+$: 319.1441 (MH^+), found: 319.1436.

IR ($CDCl_3$): 3289 (O-H), 3039 (N-H), 1505 (C=C aromatic) cm^{-1}.

Melting Point: 182.0–183.6°C

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(*tert*-butyl)phenol) (3c)



Using Method A: Prepared using *N,N'*-bis(5-*tert*-butylsalicylidene)-1,2-phenylenediamine (**1c**, 0.2524 g, 0.6 mmol) and chromium(II) chloride (0.1515 g, 1.2 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3c** as an off white solid (0.0306 g, 12% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **3c** in a 4:1 hexane:EtOAc mixture.

***R*$_f$**: 0.55 (4:1 hexane:EtOAc).

^{1}H NMR (400 MHz): 8.83 (2H, s, OH,), 7.06 (2H, dd, *J* 8 Hz, 2.5 Hz, ArH), 6.90–6.86 (2H, m, ArH), 6.80–6.76 (4H, m, ArH), 6.38 (2H, d, *J* 2 Hz, ArH), 4.78 (2H, s, N-C($\underline{H}$)-C), 4.43 (2H, s, NH), 0.99 (18H, s, 2xC(CH_3)$_3$) ppm.

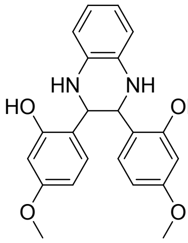
^{13}C NMR (100 MHz): δ_c($CDCl_3$) 153.88 ($\underline{C}$-OH), 142.39 (Ar$\underline{C}$-CMe_3), 132.45 (Ar$\underline{C}$-NH), 127.49 (ArC), 126.25 (ArC), 121.93 (ArC), 121.34 (ArC), 117.60 (ArC), 116.18 (ArC), 59.61 (N-$\underline{C}$(H)-C), 33.81 ($\underline{C}Me_3$), 31.46 (C($\underline{C}H_3$)$_3$) ppm.

Mass Spec ESI: Calc: $[C_{28}H_{35}N_2O_2]^+$: 431.2693 (MH^+), found: 431.2686; Calc: $[C_{28}H_{34}N_2NaO_2]^+$: 453.2512 ($M+Na^+$), found: 453.2511.

IR ($CDCl_3$): 3301 (O-H), 2960 (N-H), 2908, 2867 (C-H alkyl), 1498 (C=C aromatic), cm^{-1}.

Melting Point: 183.1–184.7 °C.

6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3d)



Using Method A: Prepared using *N,N'*-bis(4-methoxy-2-hydroxybenzylidene)-1,2-phenylenediamine (**1d**, 0.2479 g, 0.7 mmol) and chromium(II) chloride (0.1639 g, 1.3 mmol, 2 equiv.) After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3d** as an off white solid (0.0288 g, 12% yield).

***R*$_f$** (0.27) 4:1 hexane:EtOAc.

^{1}H NMR (400 MHz): δ_H(CDCl$_3$) 9.09 (2H, br s, OH), 6.88–6.84 (2H, m, ArH), 6.79–6.74 (2H, m, ArH), 6.41 (2H, d, *J* 2.5 Hz, ArH), 6.27 (2H, d, *J* 8.5 Hz, ArH), 6.08 (2H, dd, *J* = 8.5, 2.5 Hz, ArH), 4.68 (2H, s, N-C($\underline{H}$)-C), 4.37 (2H, br s, NH), 3.72 (6H, s, 2xOMe) ppm.

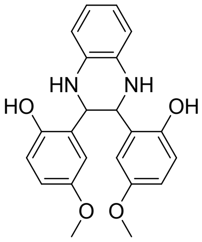
^{13}C NMR (100 MHz): δ_c(CDCl$_3$) 160.99 (Ar$\underline{C}$-OMe), 157.56 ($\underline{C}$-OH), 132.26 (Ar$\underline{C}$-NH), 131.11 (ArC), 121.94 (ArC), 117.47 (ArC), 114.57 (ArC), 105.87 (ArC), 102.39 (ArC), 58.84 (N-$\underline{C}$(H)-C), 55.36 (O-$\underline{C}$H$_3$) ppm.

Mass Spec ESI: Calc: $[C_{22}H_{23}N_2O_4]^+$: 379.1652 (M+H$^+$), found: 379.1652; Calc: $[C_{22}H_{22}N_2NaO_4]^+$: 401.1472 (M+Na$^+$), found: 401.1472.

IR (CDCl$_3$): 3304 (O-H), 2932 (N-H), 2838 (C-H alkyl), 1508 (C=C aromatic), cm^{-1}.

Melting Point: 194.8–195.4 °C.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-methoxyphenol) (3e)



Using Method A: Prepared using *N,N'*-bis(2-hydroxy-5-methoxybenzylidene)-1,2-phenylenediamine (**1e**, 0.2602 g, 0.7 mmol) and chromium(II) chloride (0.1653 g, 1.3 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3e** as an off white solid (0.0137 g, 5% yield).

***R*$_f$** (0.57) 4:1 hexane:EtOAc.

^{1}H NMR (400 MHz): δ_H(CDCl$_3$) 8.50 (2H, br s, OH), 6.91–6.86 (2H, m, ArH), 6.82–6.76 (4H, m, ArH), 6.68 (2H, ddd, *J* 8.5, 3.1 Hz, ArH), 5.95 (2H, d, *J* 2 Hz, ArH), 4.73 (2H, s, N-C($\underline{H}$)-C), 4.28 (2H, br s, NH), 3.61 (6H, s, 2xOMe) ppm.

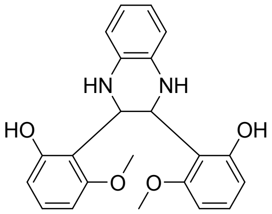
^{13}C NMR (175 MHz): δ_c(CDCl$_3$) 152.94 (Ar$\underline{C}$-OMe), 150.38 ($\underline{C}$-OH), 132.05 (Ar$\underline{C}$-CMe$_3$), 122.26 (Ar$\underline{C}$-NH), 122.14 (ArC), 117.89 (ArC), 117.65 (ArC), 116.66 (ArC), 114.56 (ArC), 59.10 (N-$\underline{C}$(H)-C), 56.02 (O-$\underline{C}$H$_3$) ppm.

Mass Spec ESI: Calc: $[C_{22}H_{23}N_2O_4]^+$: 379.1652 (MH$^+$), found: 379.1651; Calc: $[C_{22}H_{22}N_2NaO_4]^+$: 401.1472 (M+Na$^+$), found: 401.1469.

IR (CDCl$_3$): 3298 (O-H), 2925 (N-H), 1497 (C=C aromatic) cm^{-1}.

Melting Point: 204.5–206.6 °C.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3f)



Using Method A: Prepared using *N,N′*-bis(6-methoxysalicylidene)-1,2-phenylenediamine (**1f**, 0.2508 g, 0.6 mmol) and chromium(II) chloride (0.1478 g,1.2 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc mixture) to give compound **3f** as an off white solid (0.0248 g, 12 % yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **3f** in a 4:1 hexane:EtOAc mixture.

R*f* (0.30) 4:1 hexane:EtOAc

^{1}H NMR (400 MHz): δ_H(CDCl$_3$) 9.67 (2H, s, OH), 6.99 (2H, t, *J* 8.5 Hz, ArH), 6.87–6.83 (2H, m, ArH), 6.79–6.75 (2H, m, ArH), 6.45 (2H, dd, *J* 8.5, 1 Hz, ArH), 6.02 (2H, dd, *J* 8.5, 1 Hz, ArH), 5.48 (2H, s, N-C($\underline{H}$)-C), 4.20 (2H, s, NH), 3.21 (6H, s, 2xOMe) ppm.

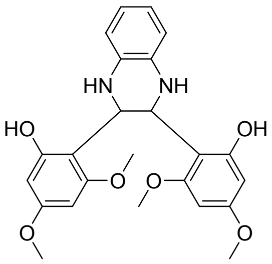
^{13}C NMR (100 MHz): δ_c(CDCl$_3$) 159.04 (Ar$\underline{C}$-OMe), 158.39 ($\underline{C}$-OH), 132.43(Ar$\underline{C}$-NH), 129.50 (ArC), 121.85 (ArC), 117.82 (ArC), 110.64 (ArC), 109.46 (ArC), 101.39 (ArC), 55.31 (N-$\underline{C}$(H)-C), 50.28 (O-$\underline{C}$H$_3$) ppm.

Mass Spec ESI: Calc: $[C_{22}H_{23}N_2O_4]^+$: 379.1652 (MH$^+$), found: 379.1655; Calc: $[C_{22}H_{22}N_2NaO_4]^+$: 401.1472 (M+Na$^+$), found: 401.1475.

IR (CDCl$_3$): 3297 (O-H), 2935 (N-H), 2837 (C-H alkyl), 1466 (C=C aromatic) cm^{-1}.

Melting Point: 207.2–208.7 °C.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3,5-dimethoxyphenol) (3g)



Using Method A: Prepared using *N,N′*-bis(4,6-methoxy-2-hydroxybenzylidene)-1,2-phenylenediamine (**1g**, 0.2508 g, 0.6 mmol) and chromium(II) chloride (0.1478 g, 1.2 mmol, 2 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc then EtOAc) to give compound **3g** as an unstable off white solid (0.0051 g, 2% yield).

R

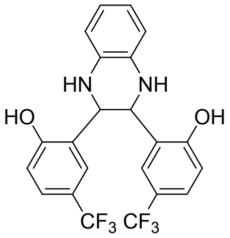
R_f (0.10) 4:1 hexane:EtOAc.

^{1}H NMR (400 MHz): δ_H(CDCl$_3$) 9.71 (2H, br s, OH), 6.86–6.81 (2H, m, ArH), 6.78–6.73 (2H, m, ArH), 6.03 (2H, d, *J* 2.5 Hz, ArH), 5.67 (2H, d, *J* 8.5 Hz, ArH), 6.08 (2H, dd, *J* 8.5, 2.5 Hz, ArH), 5.32 (2H, s, N-C(H)-C), 4.15 (2H, br s, NH), 3.72 (6H, s, 2xOMe) ppm, 3.25 (6H, s, 2xOMe) ppm.

^{13}C NMR (100 MHz): δ_c(CDCl$_3$) 161.15 (ArC-OMe), 159.82 (ArC-OMe), 159.12 (C-OH), 132.60 (ArC-NH), 121.80 (ArC), 117.78 (ArC), 103.41 (ArC), 93.75 (ArC), 89.99 (ArC), 55.50 (N-C(H)-C), 55.35 (O-CH$_3$), 50.42 (O-CH$_3$) ppm.

Mass Spec ESI: Calc: [$C_{24}H_{27}N_2O_6$]$^+$: 439.1864 (MH$^+$), found: 439.1862.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(trifluoromethyl)phenol) (3h)



Using Method A: Prepared using *N,N'*-Bis(2-hydroxy-5-trifluoromethyl)-1,2-phenylenediamine (**1h**, 0.2409 g, 0.5 mmol) and chromium(II) chloride (0.1850 g, 1.5 mmol, 3 equiv.). After workup, the product was purified by column chromatography (4:1 hexane:EtOAc) to give compound **3h** as an off white solid (0.0267 g, 11% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **3h** in a 4:1 hexane:EtOAc mixture.

R_f (0.42) 4:1 hexane:EtOAc.

^{1}H[^{19}F] NMR (400 MHz): δ_H(CDCl$_3$) 9.56 (2H, br s, OH), 7.38 (2H, dd, *J* 8.5, 2 Hz, ArH), 6.97–6.92 (4H, m, ArH), 6.87–6.83 (2H, m, ArH), 6.46 (2H, d, *J* 2.0 Hz, ArH), 4.79 (2H, s, N-C(H)-C), 4.50 (2H, br s, NH) ppm.

^{13}C[^{19}F] NMR (125 MHz): δ_c(CDCl$_3$) 159.33 (C-OH), 131.50 (ArC-NH), 127.31 (ArC), 127.29 (ArC), 123.92 (CF$_3$), 122.81 (ArC), 122.28 (ArC), 121.55 (ArC), 118.06 (ArC), 117.66 (ArC), 59.01 (N-C(H)-C) ppm.

^{19}F NMR (376 MHz): δ_F(CDCl$_3$) -61.95 (s, CF$_3$) ppm.

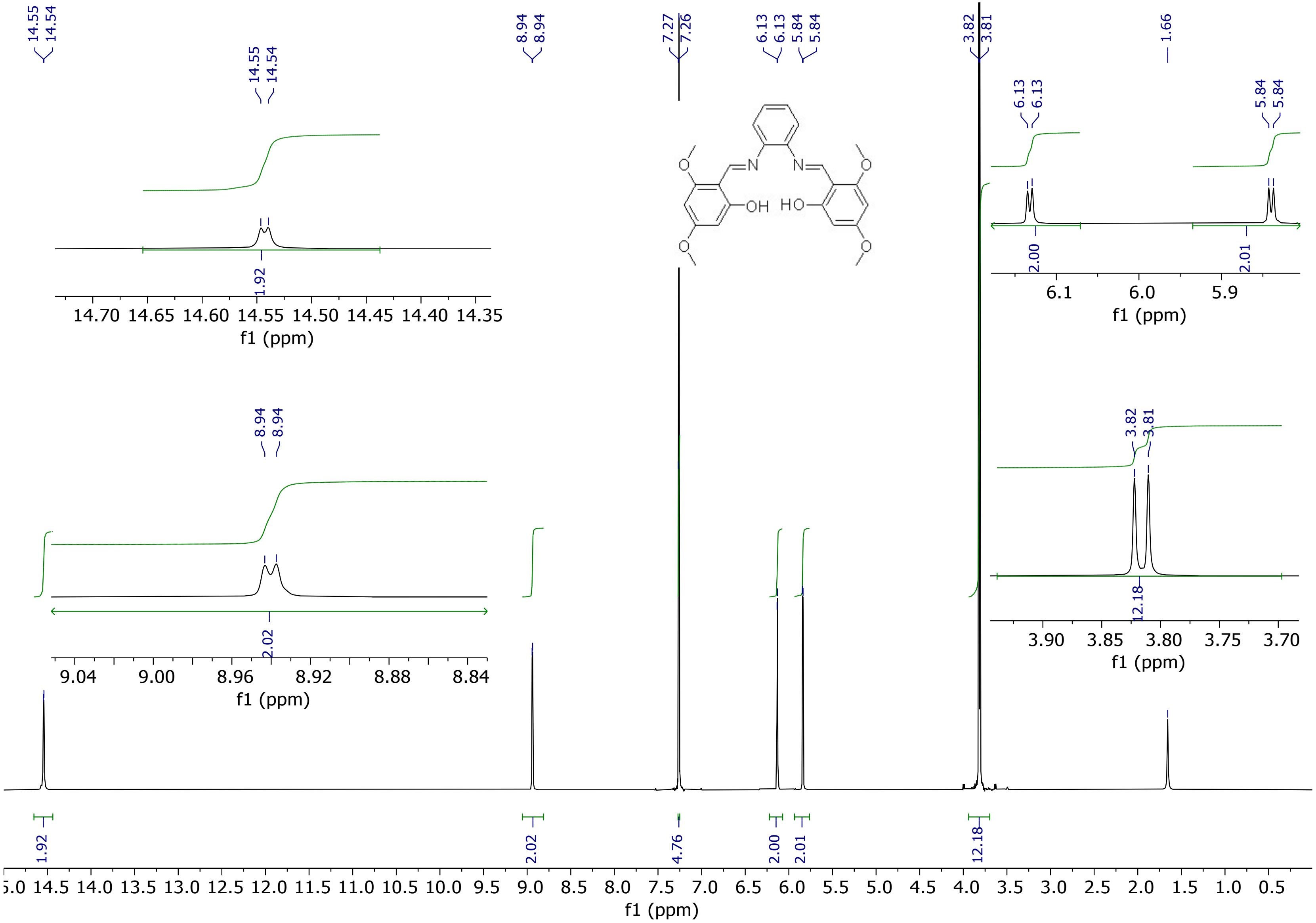
Mass Spec ESI: Calc: [$C_{22}H_{17}F_6N_2O_2$]$^+$: 455.1189 (MH$^+$), found: 455.1184.

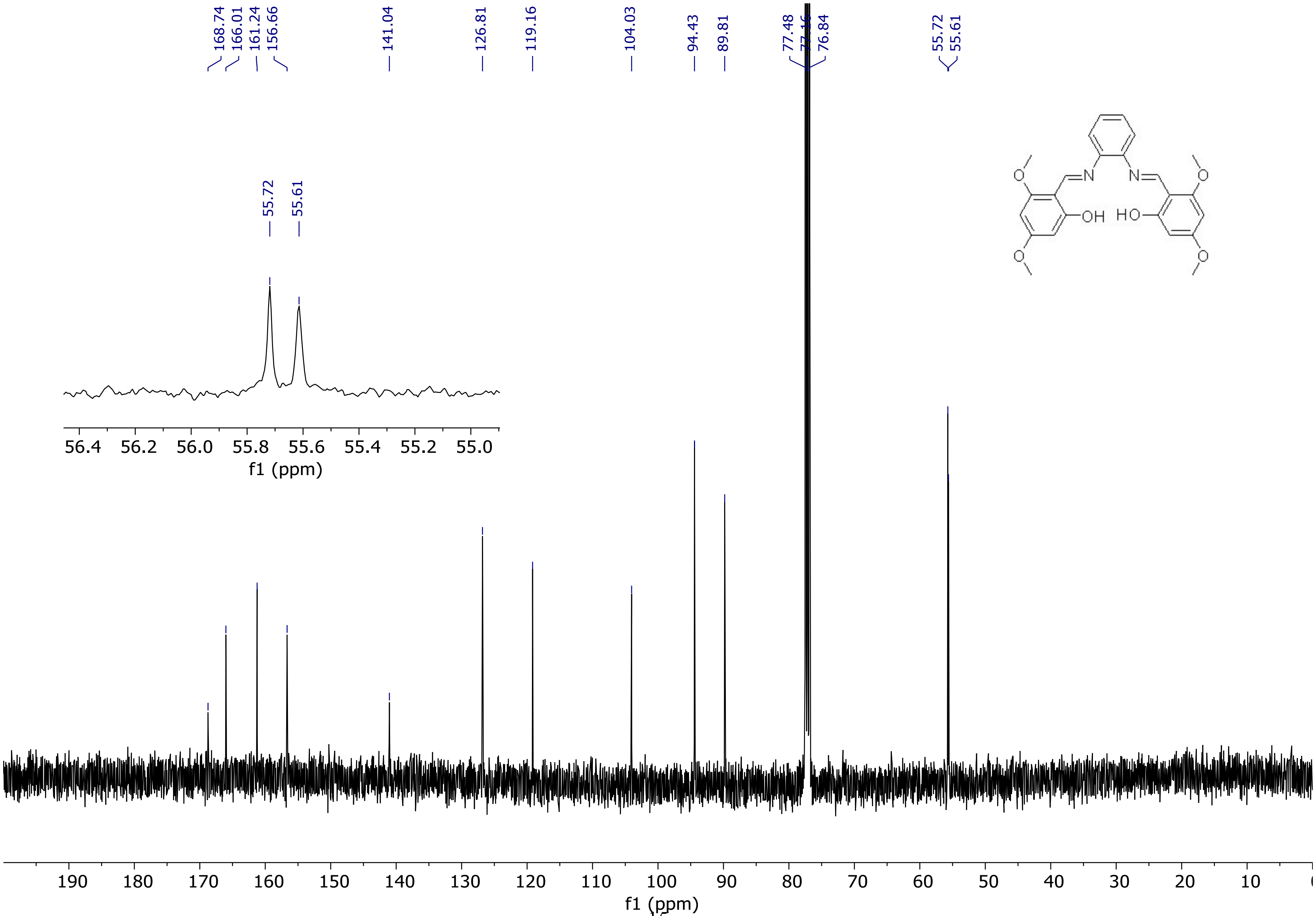
IR (CDCl$_3$): 3299 (O-H), 2925 (N-H), 2835 (C-H alkyl), 1326 (C=C aromatic) cm^{-1}.

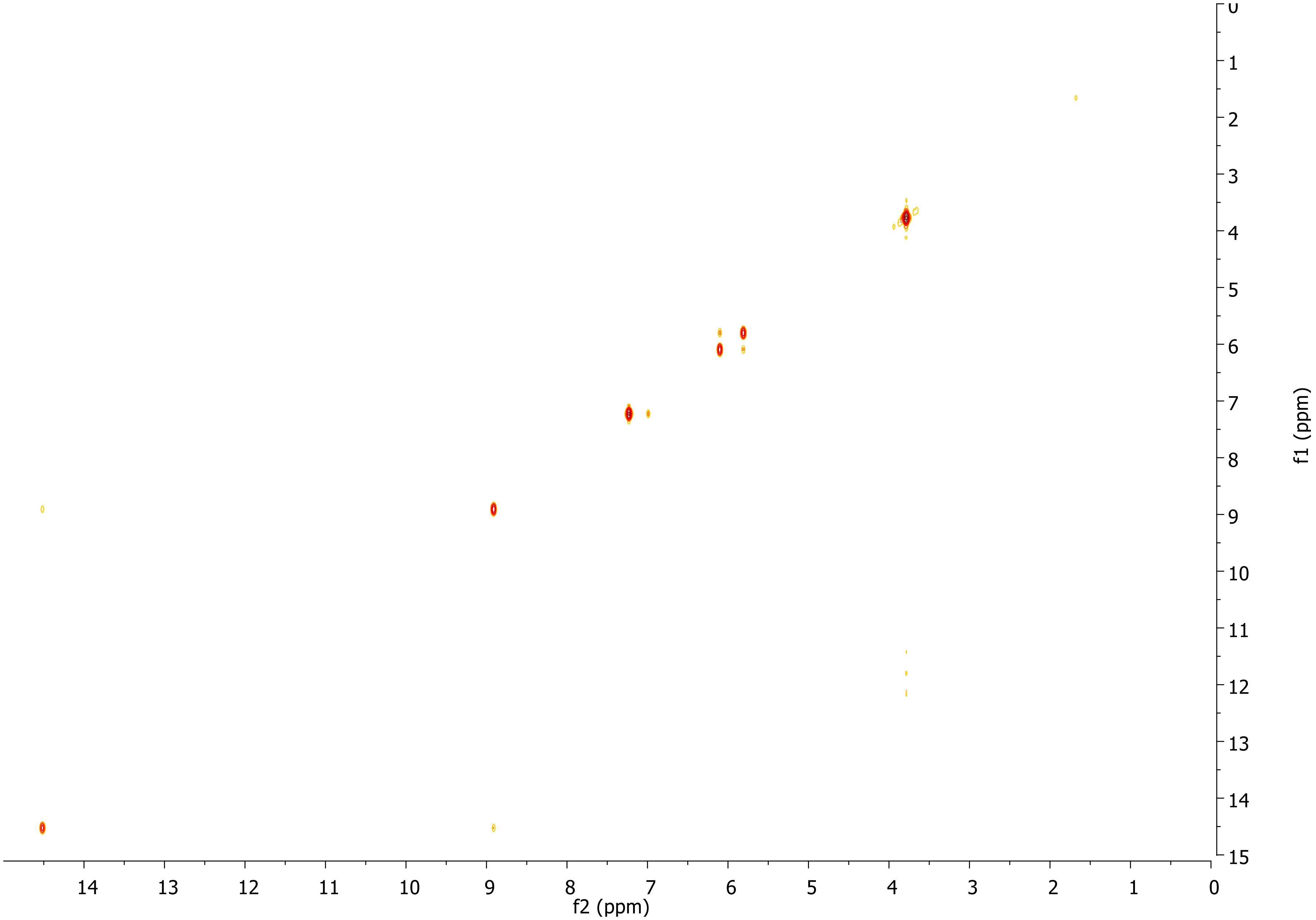
Melting Point: 197.6–198.2 °C.

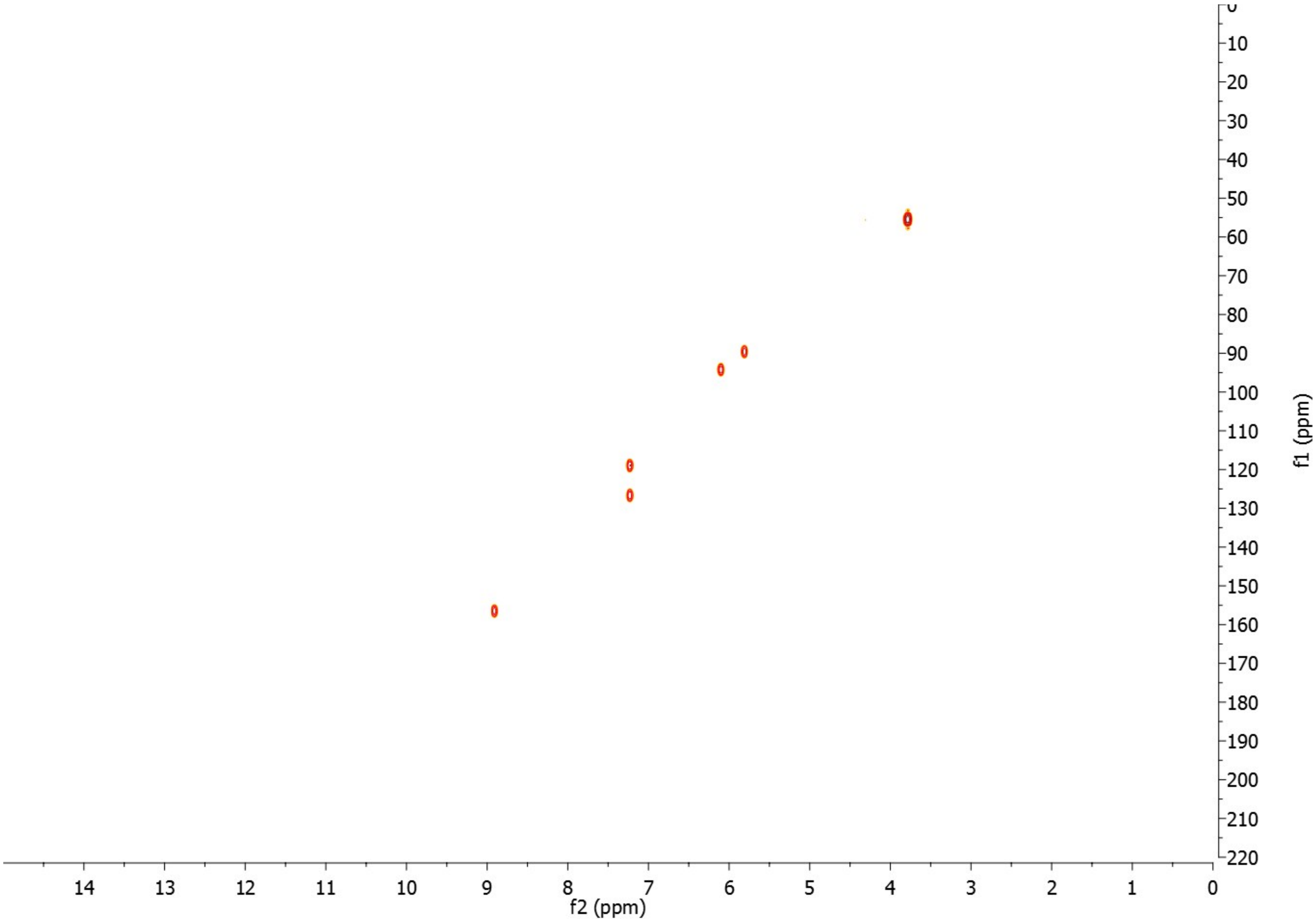
NMR spectra of salophen ligands

2,2'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3,5-dimethoxyphenol) (1g)

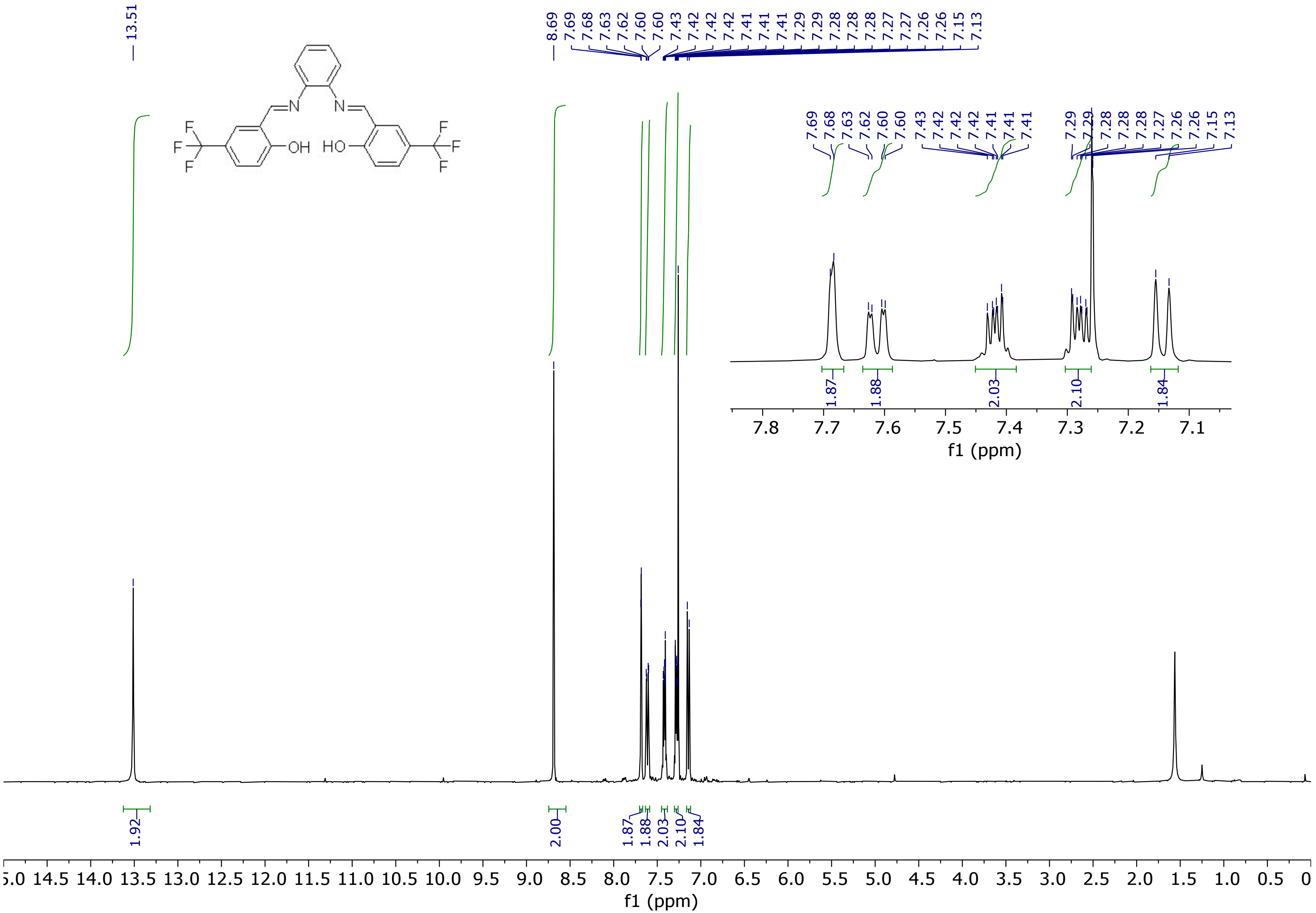


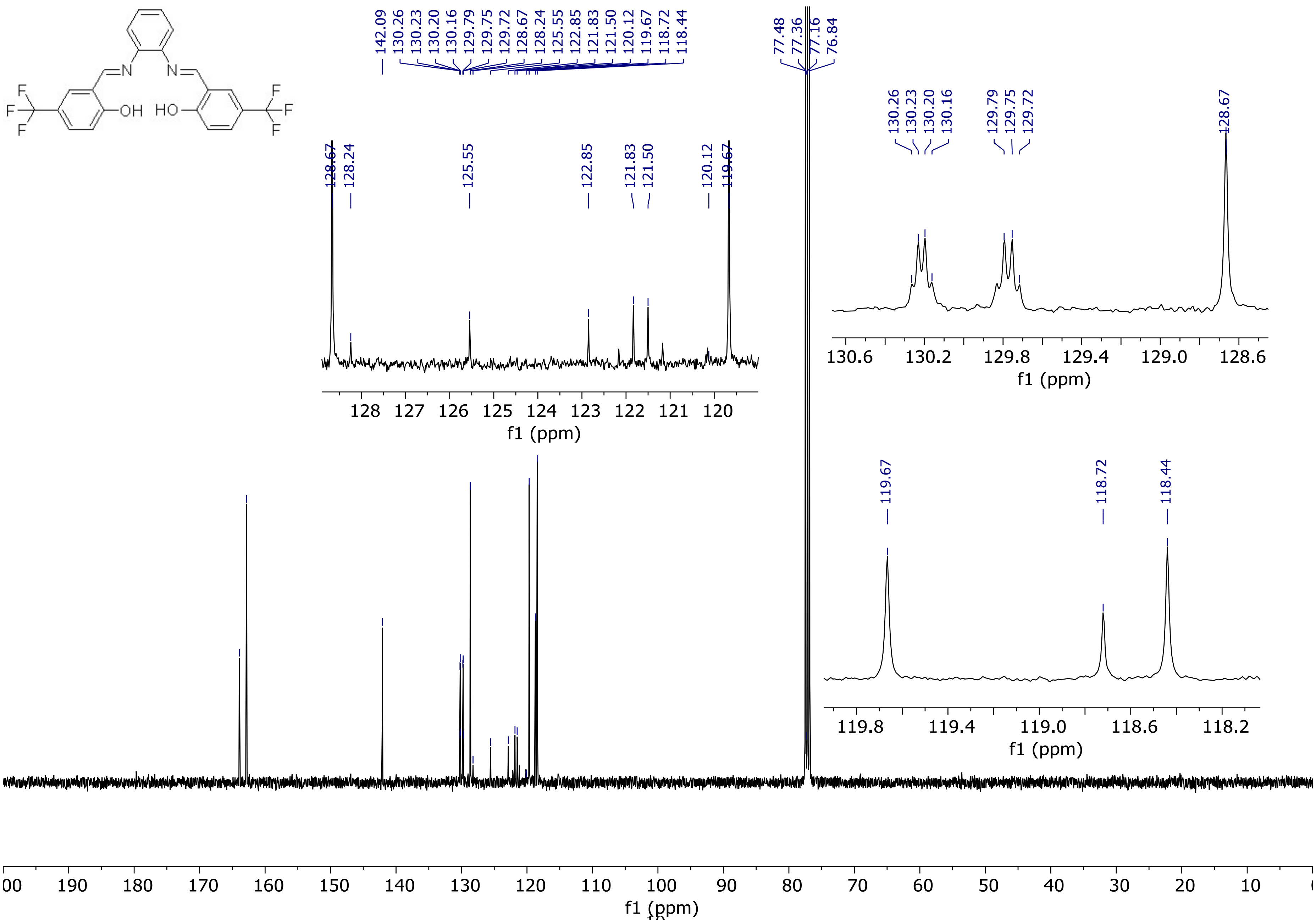

168.74
166.01
161.24
156.66
141.04
126.81
119.16
104.03
94.43
89.81
77.48
77.16
76.84
55.72
55.61
55.72
55.61
56.4 56.2 56.0 55.8 55.6 55.4 55.2 55.0
f1 (ppm)
O
N
N
O
OH
HO
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


f2 (ppm)
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
15

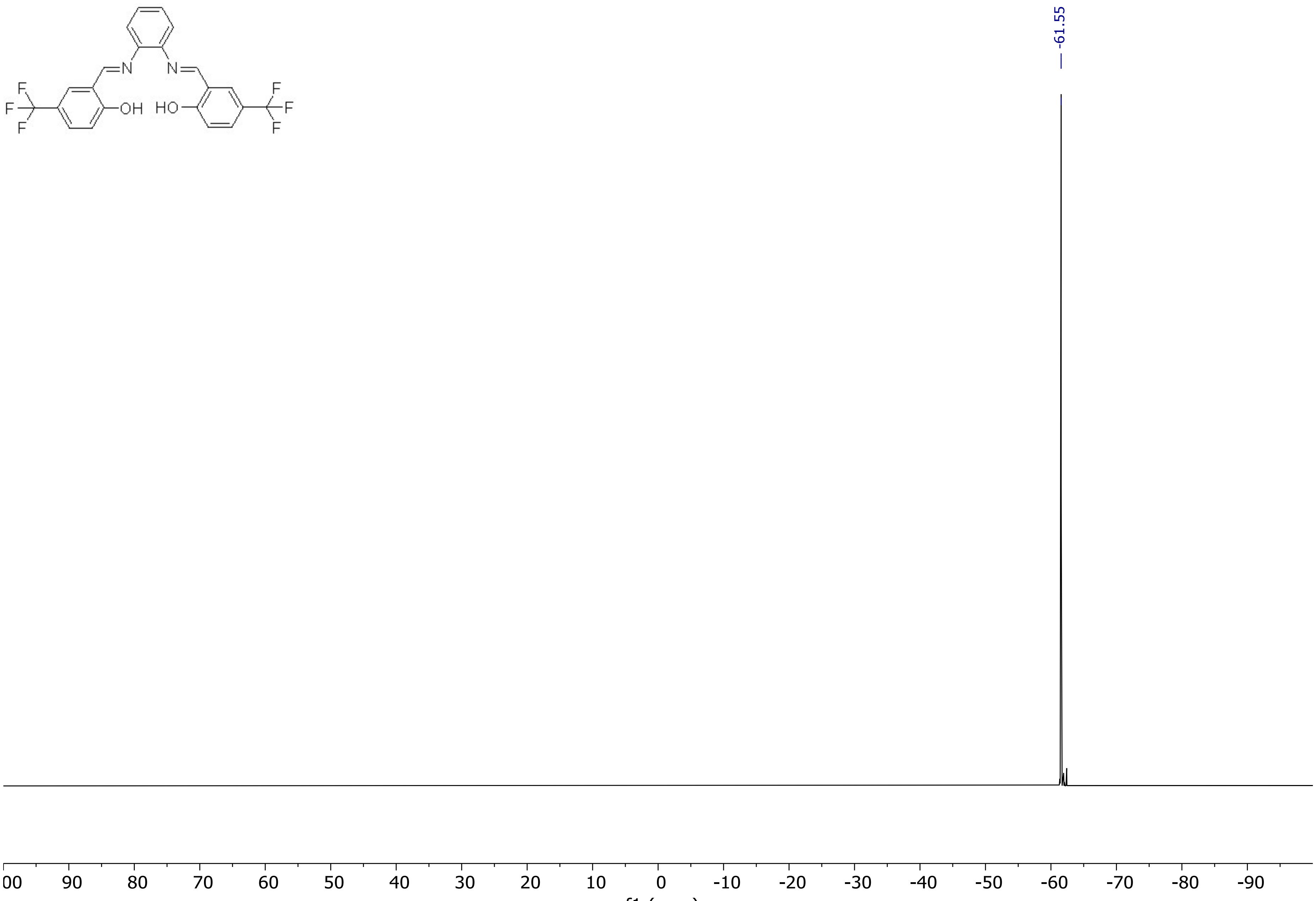

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f2 (ppm)

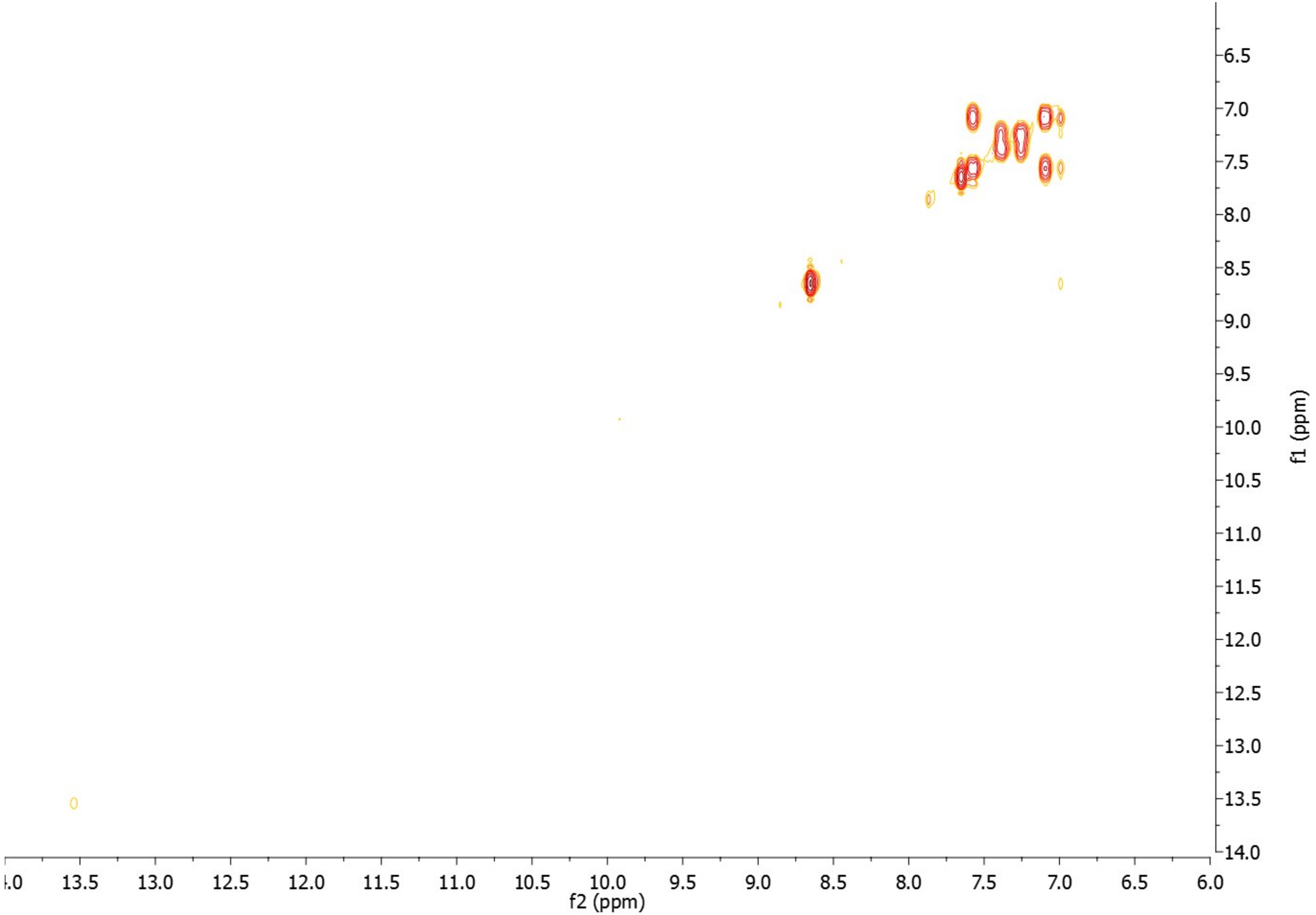
N,N'-Bis(2-hydroxy-5-trifluoromethyl)-1,2-phenylenediamine (1h)



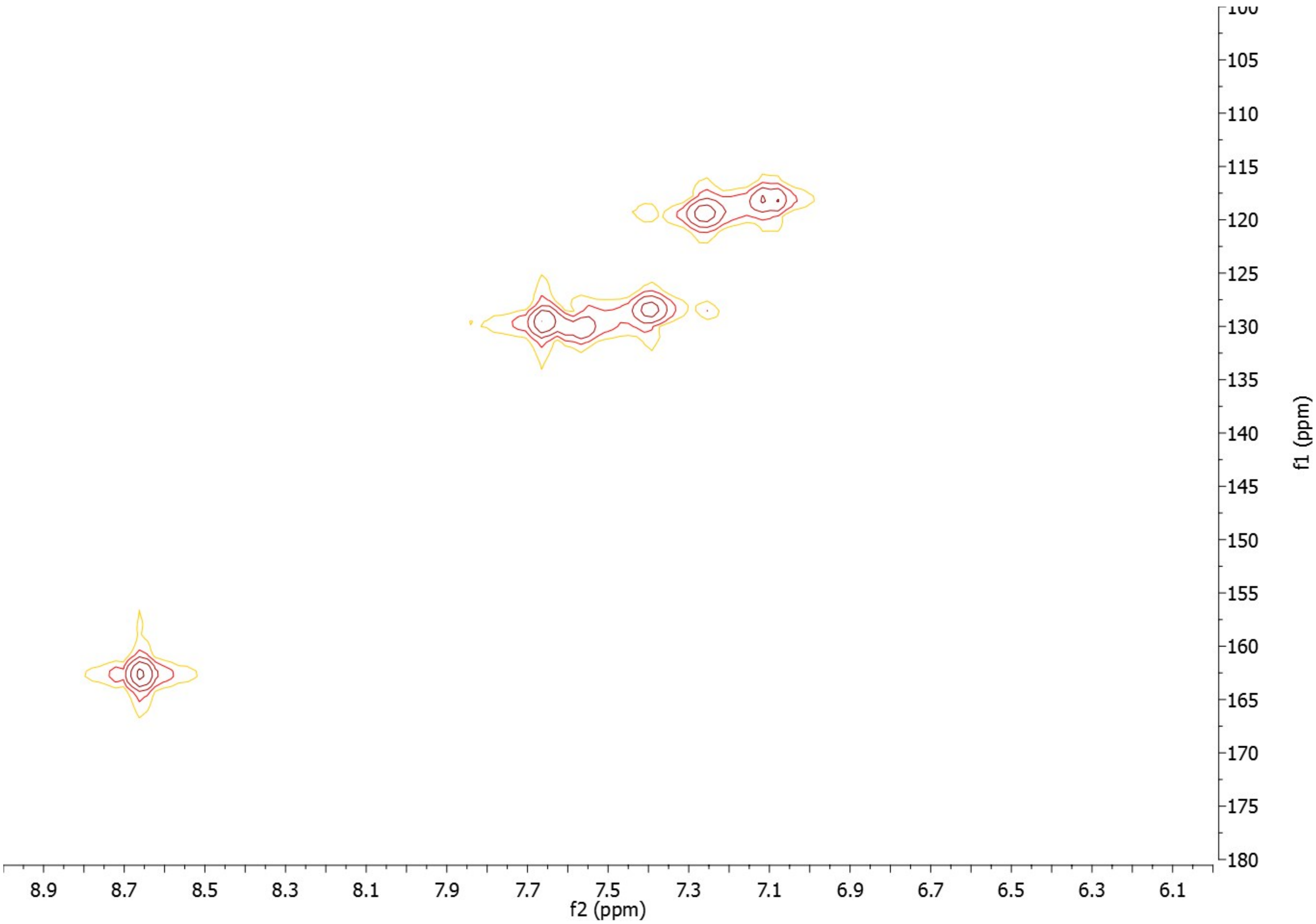


F
F
F
OH
HO
N
N
F
F
F
142.09
130.26
130.23
130.20
130.16
129.79
129.75
129.72
128.67
128.24
125.55
122.85
121.83
121.50
120.12
119.67
118.72
118.44
77.48
77.36
77.16
76.84
128.67
128.24
125.55
122.85
121.83
121.50
120.12
119.67
128 127 126 125 124 123 122 121 120
f1 (ppm)
130.26
130.23
130.20
130.16
129.79
129.75
129.72
128.67
130.6 130.2 129.8 129.4 129.0 128.6
f1 (ppm)
119.67
118.72
118.44
119.8 119.4 119.0 118.6 118.2
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-61.55
F
F
F
OH
HO
N
N
F
F
F
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

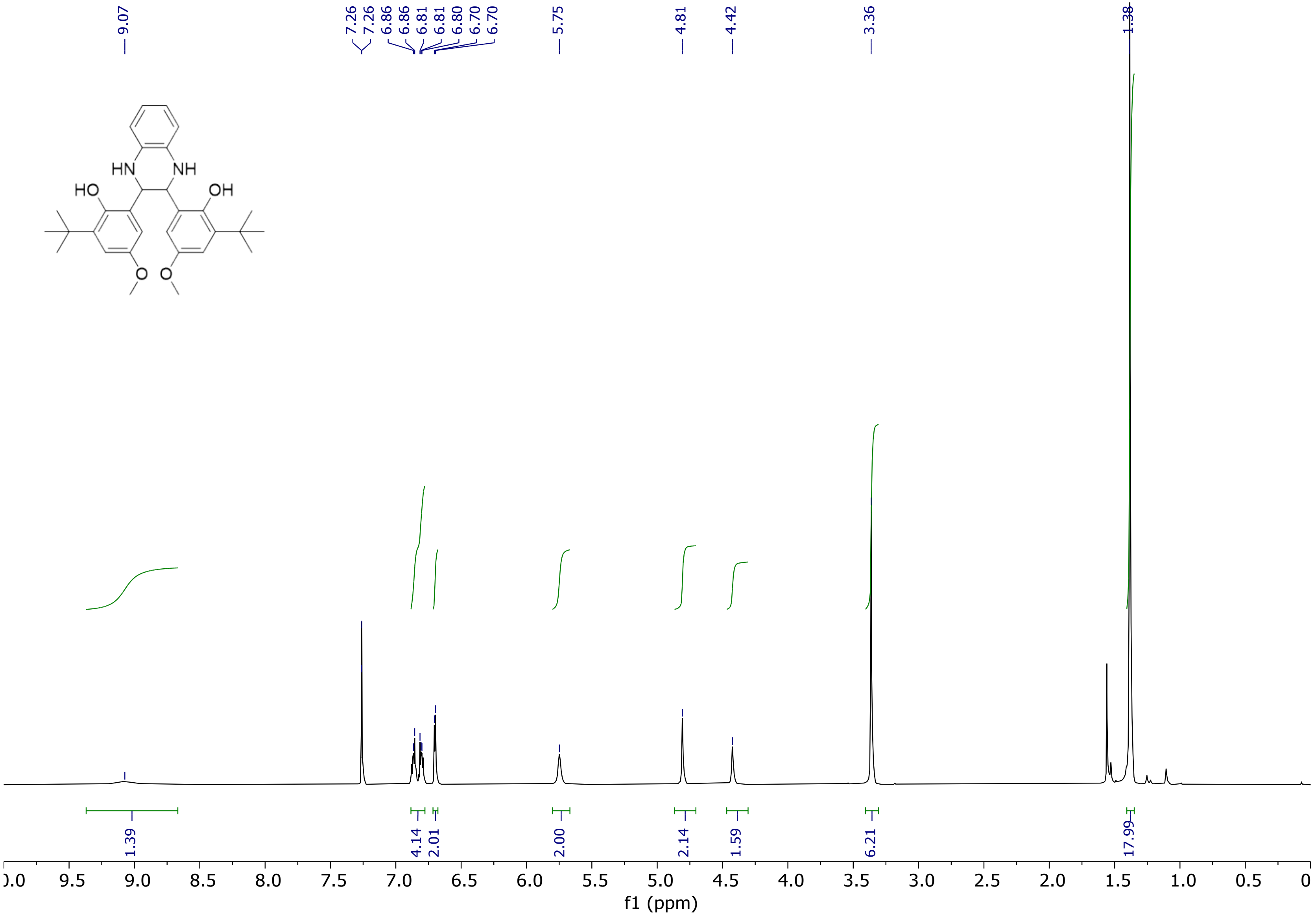


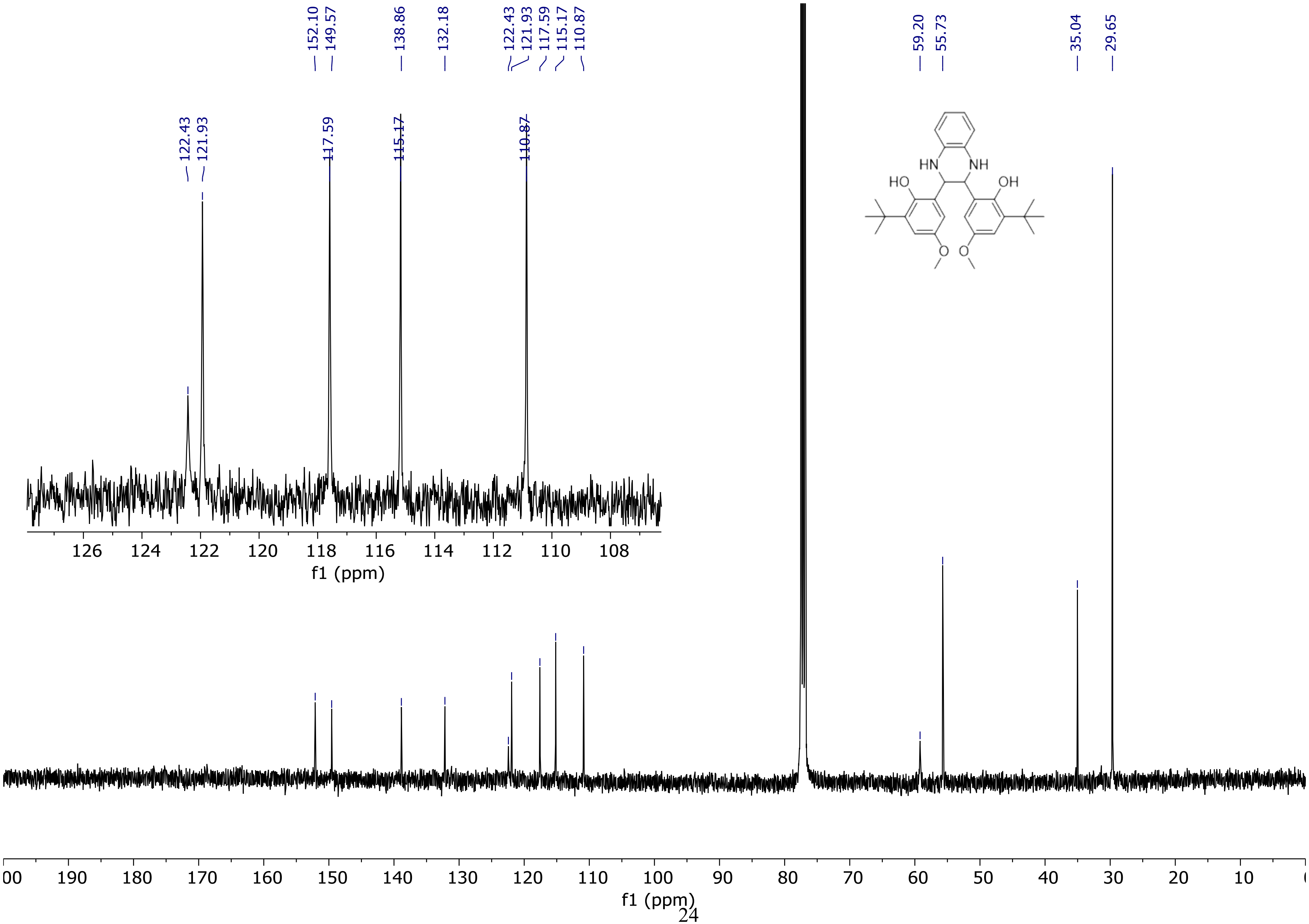
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
14.0
f1 (ppm)
4.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f2 (ppm)

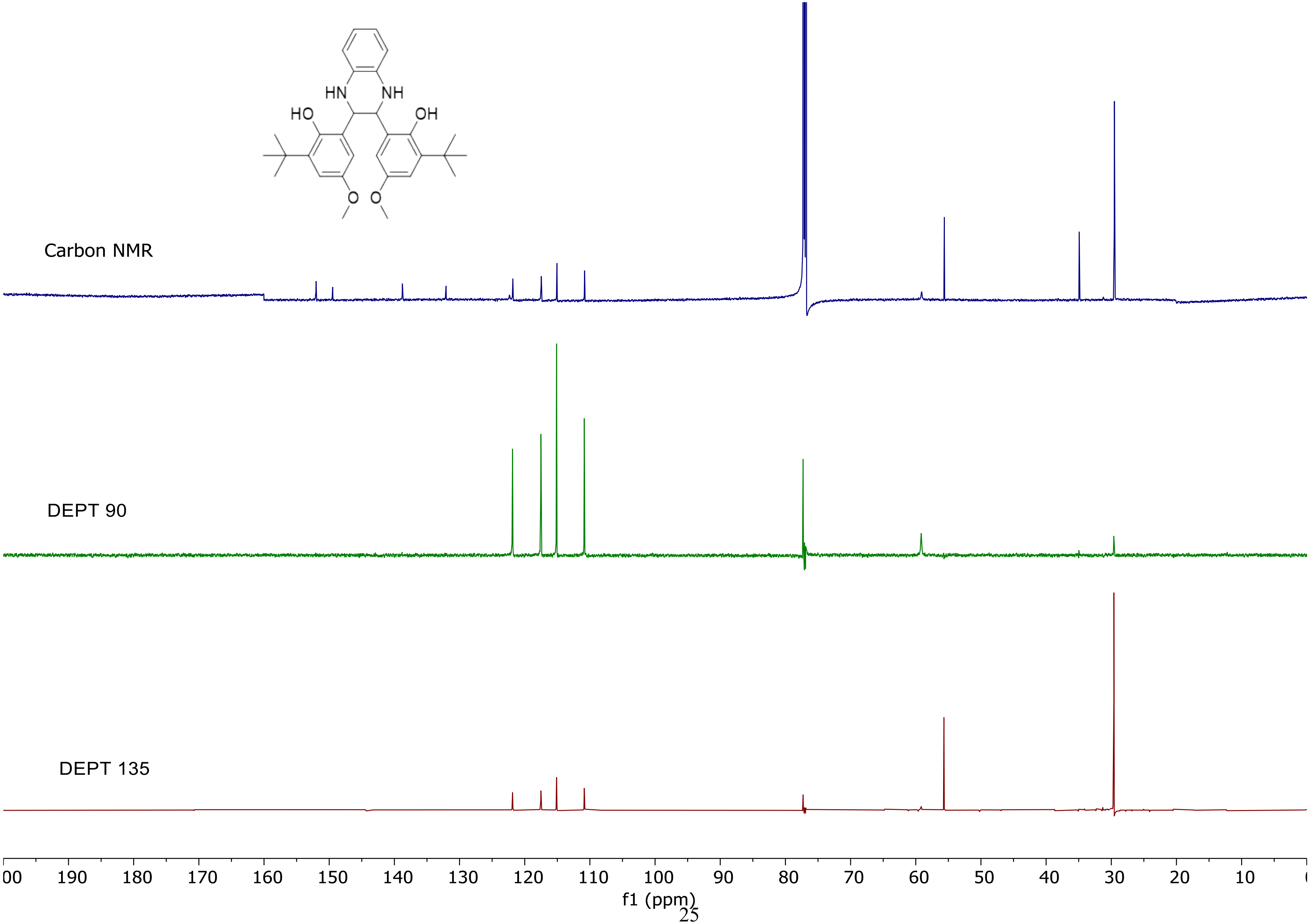

100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
f1 (ppm)
8.9
8.7
8.5
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
f2 (ppm)

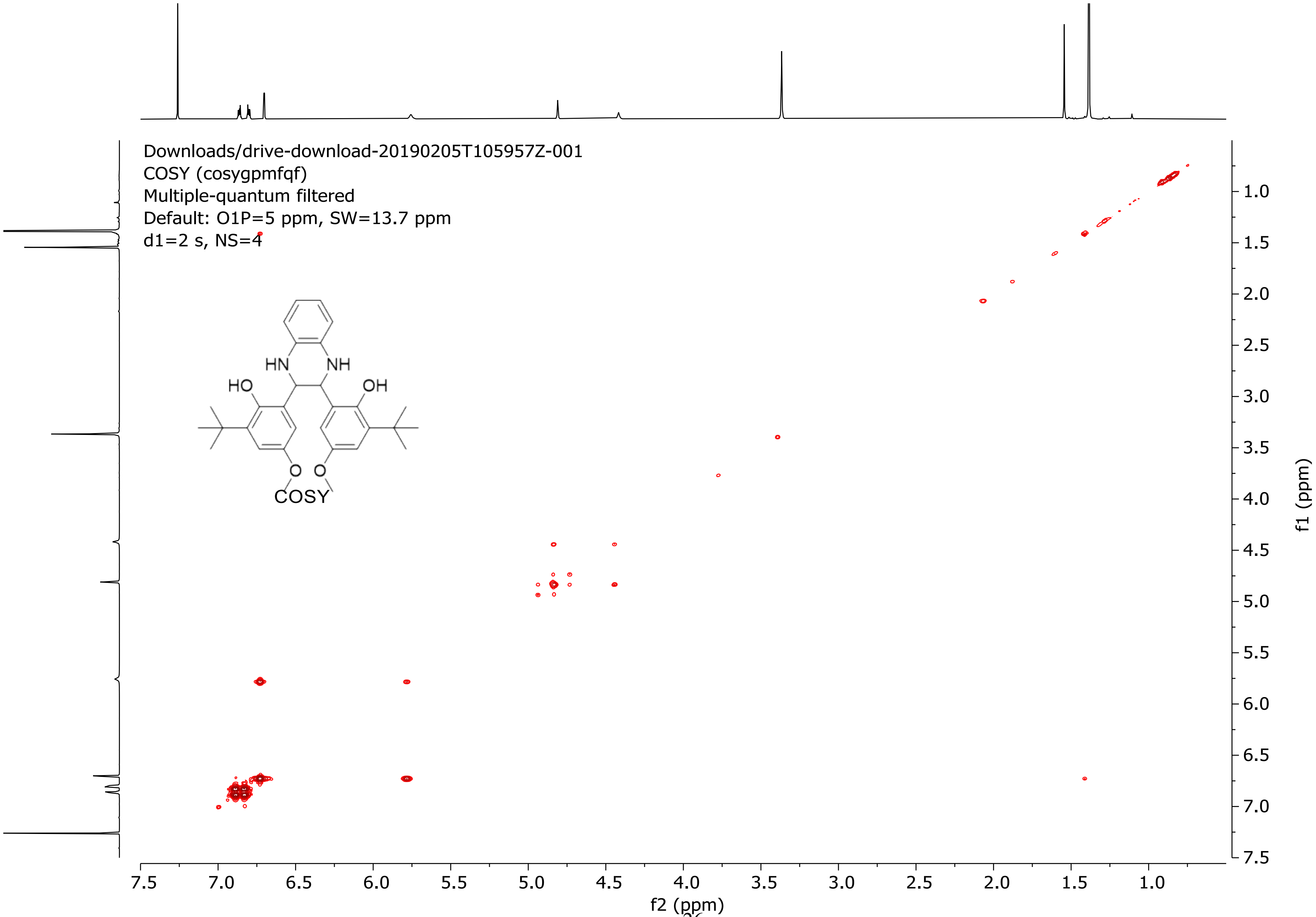
NMR spectra of tetrahydroquinoxalines

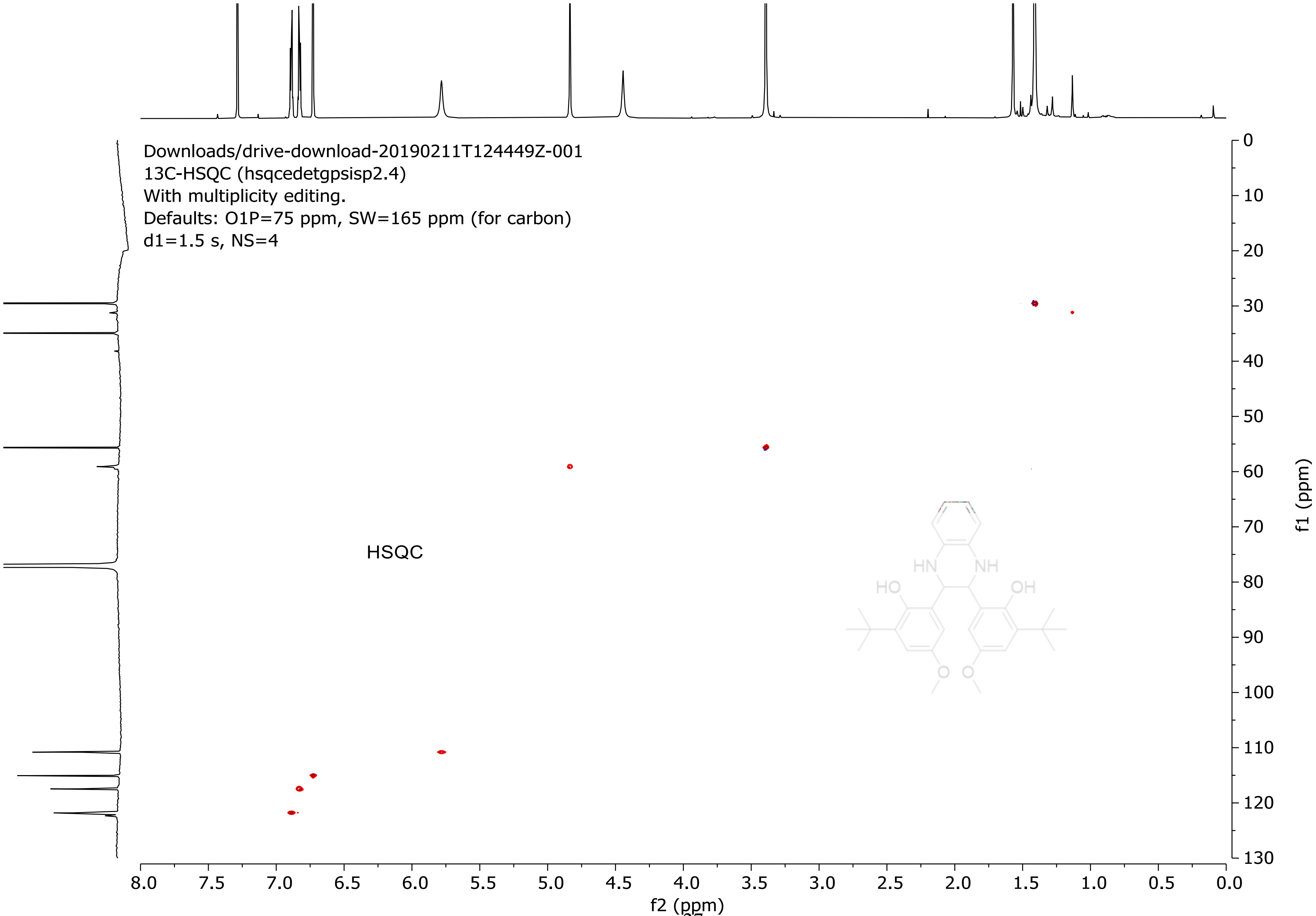
6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(2-(tert-butyl)-4-methoxyphenol) (3a)

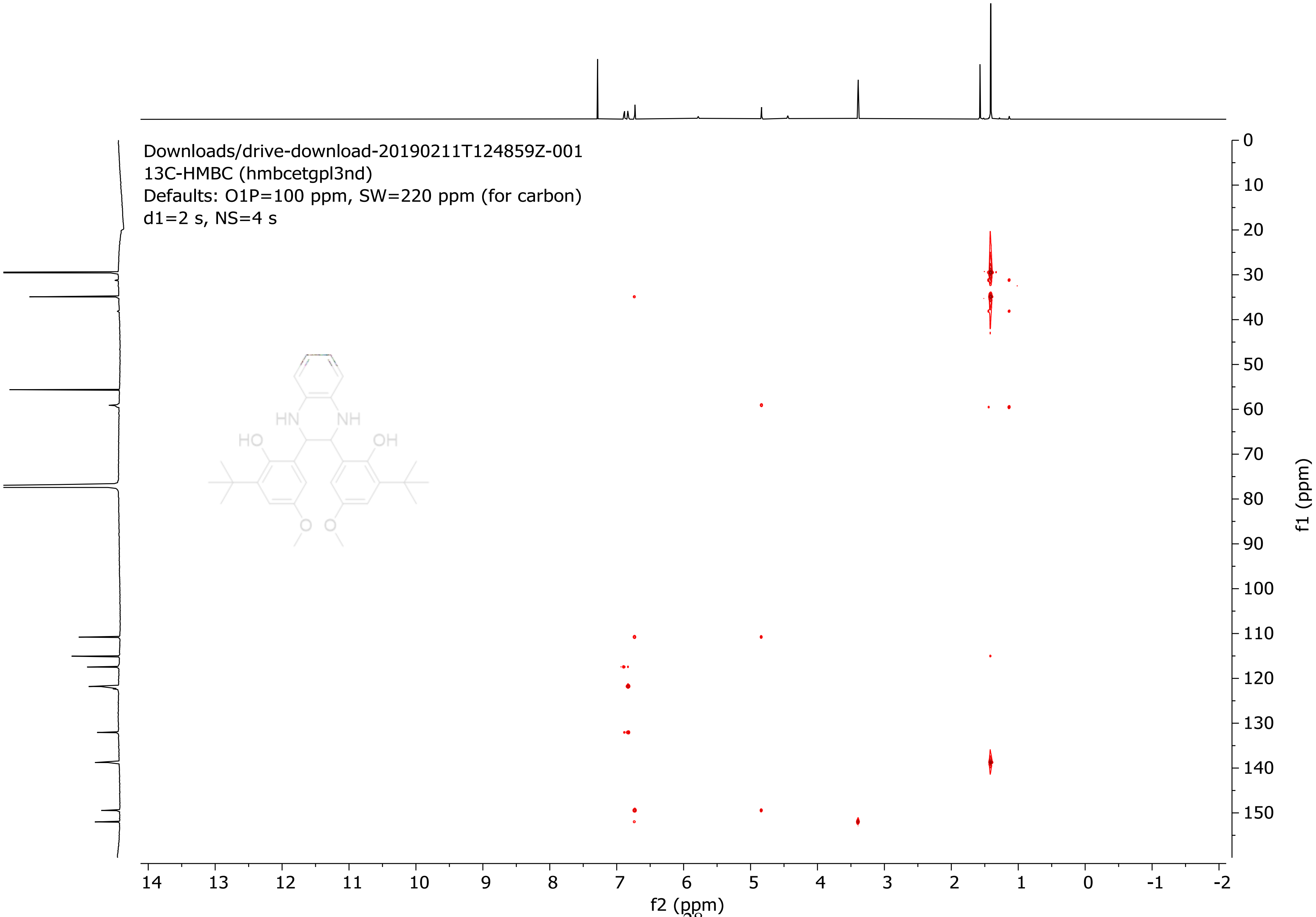


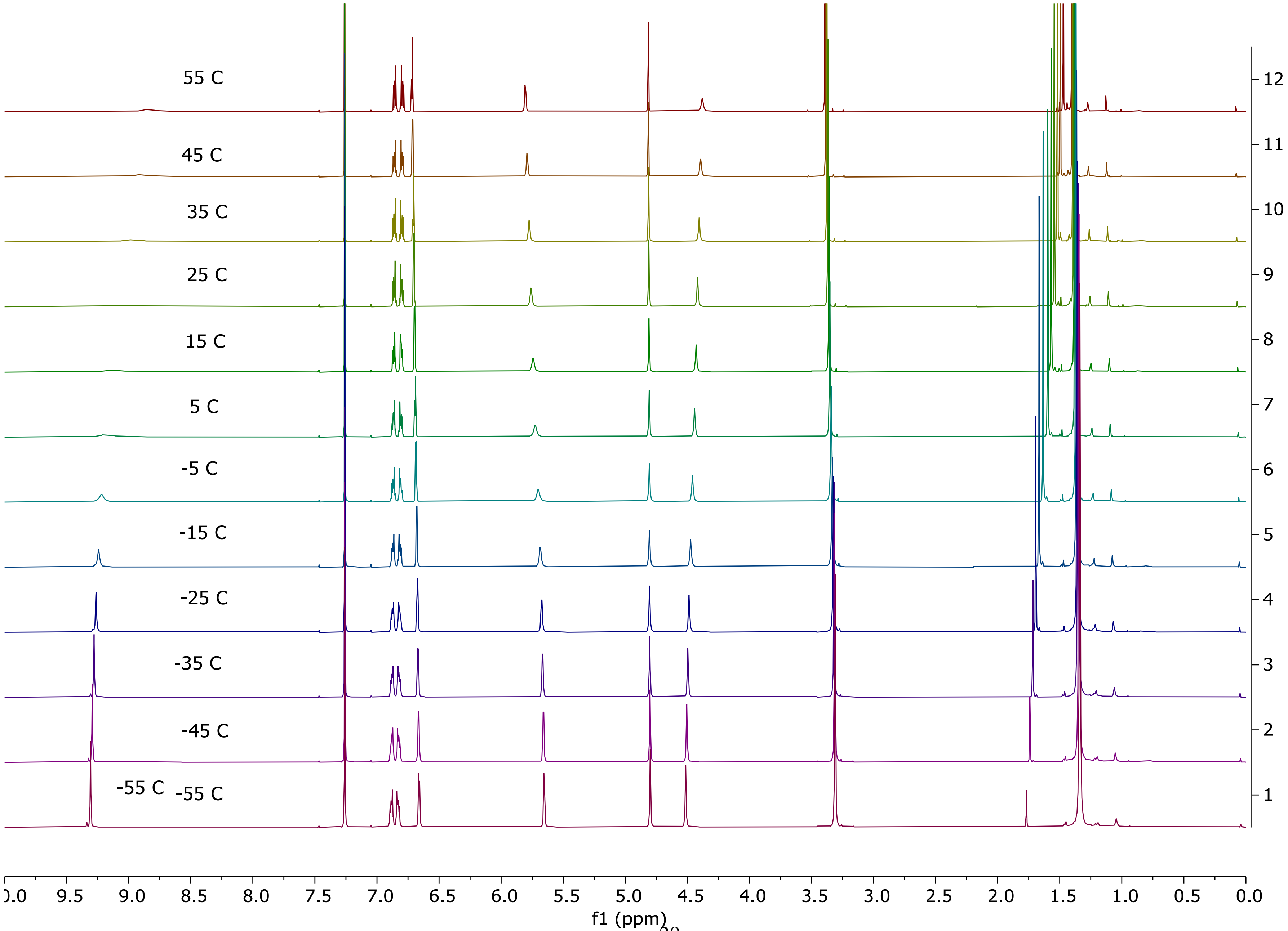

152.10
149.57
138.86
132.18
122.43
121.93
117.59
115.17
110.87
59.20
55.73
35.04
29.65
122.43
121.93
117.59
115.17
110.87
126
124
122
120
118
116
114
112
110
108
f1 (ppm)
HN
NH
HO
OH
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


HN
NH
HO
OH
O
O
Carbon NMR
DEPT 90
DEPT 135
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

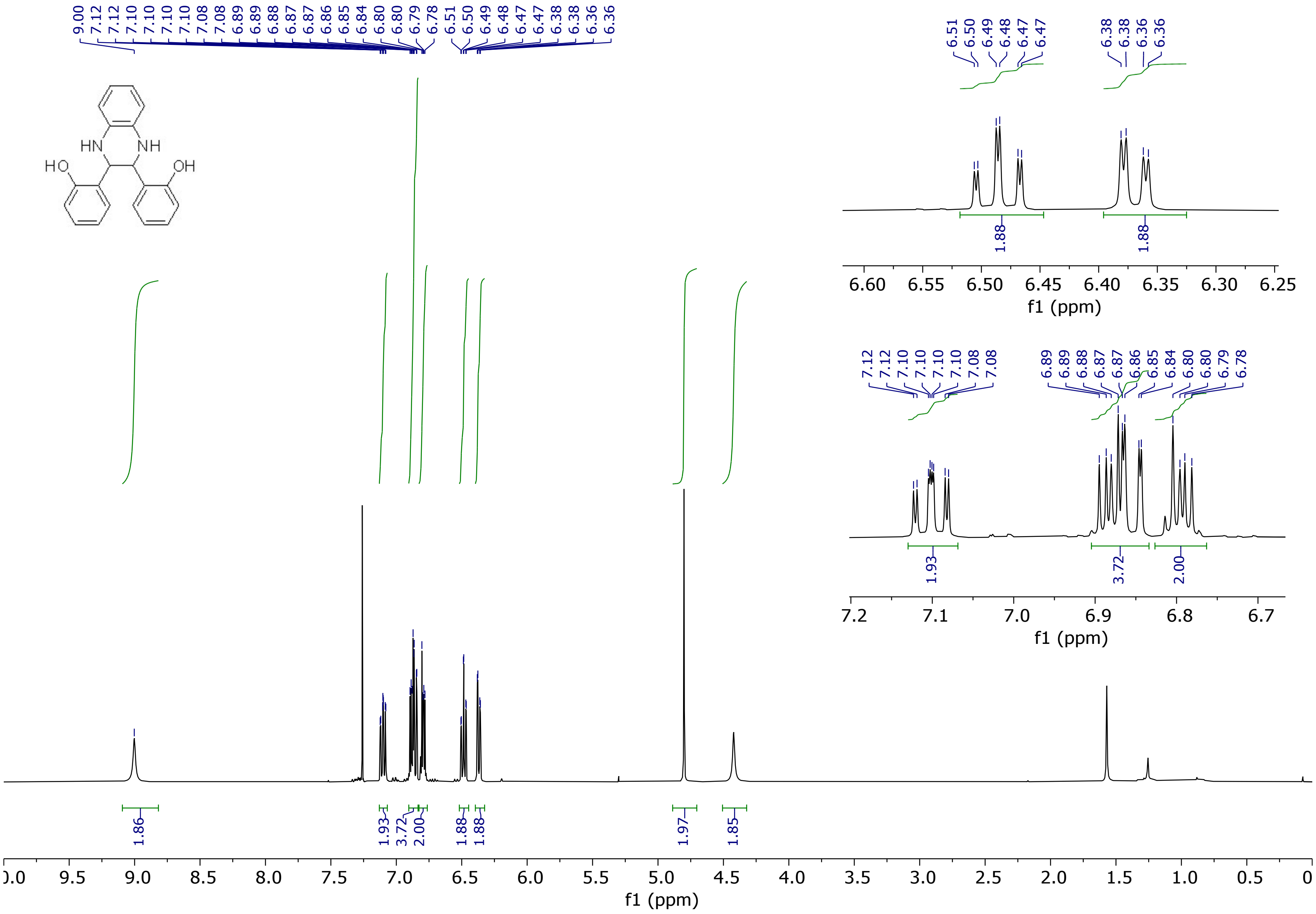

Downloads/drive-download-20190205T105957Z-001
COSY (cosygpmfqf)
Multiple-quantum filtered
Default: O1P=5 ppm, SW=13.7 ppm
d1=2 s, NS=4
HN
NH
HO
OH
O
O
COSY
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

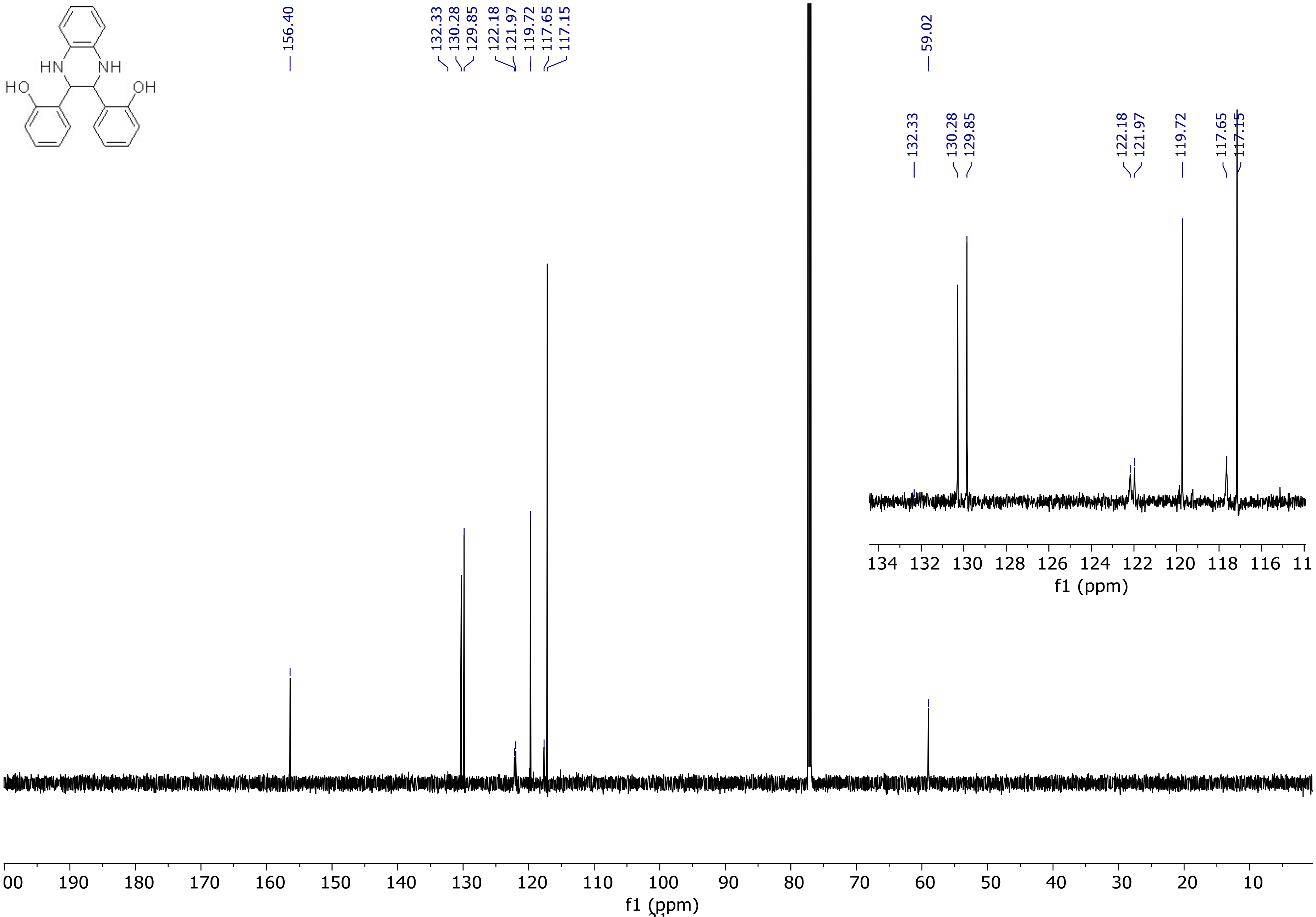

Downloads/drive-download-20190211T124449Z-001
13C-HSQC (hsqcedetgpsisp2.4)
With multiplicity editing.
Defaults: O1P=75 ppm, SW=165 ppm (for carbon)
d1=1.5 s, NS=4
HSQC
HN
NH
HO
OH
O
O
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Downloads/drive-download-20190211T124859Z-001
13C-HMBC (hmbcetgpl3nd)
Defaults: O1P=100 ppm, SW=220 ppm (for carbon)
d1=2 s, NS=4 s
HN
NH
HO
OH
O
O
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

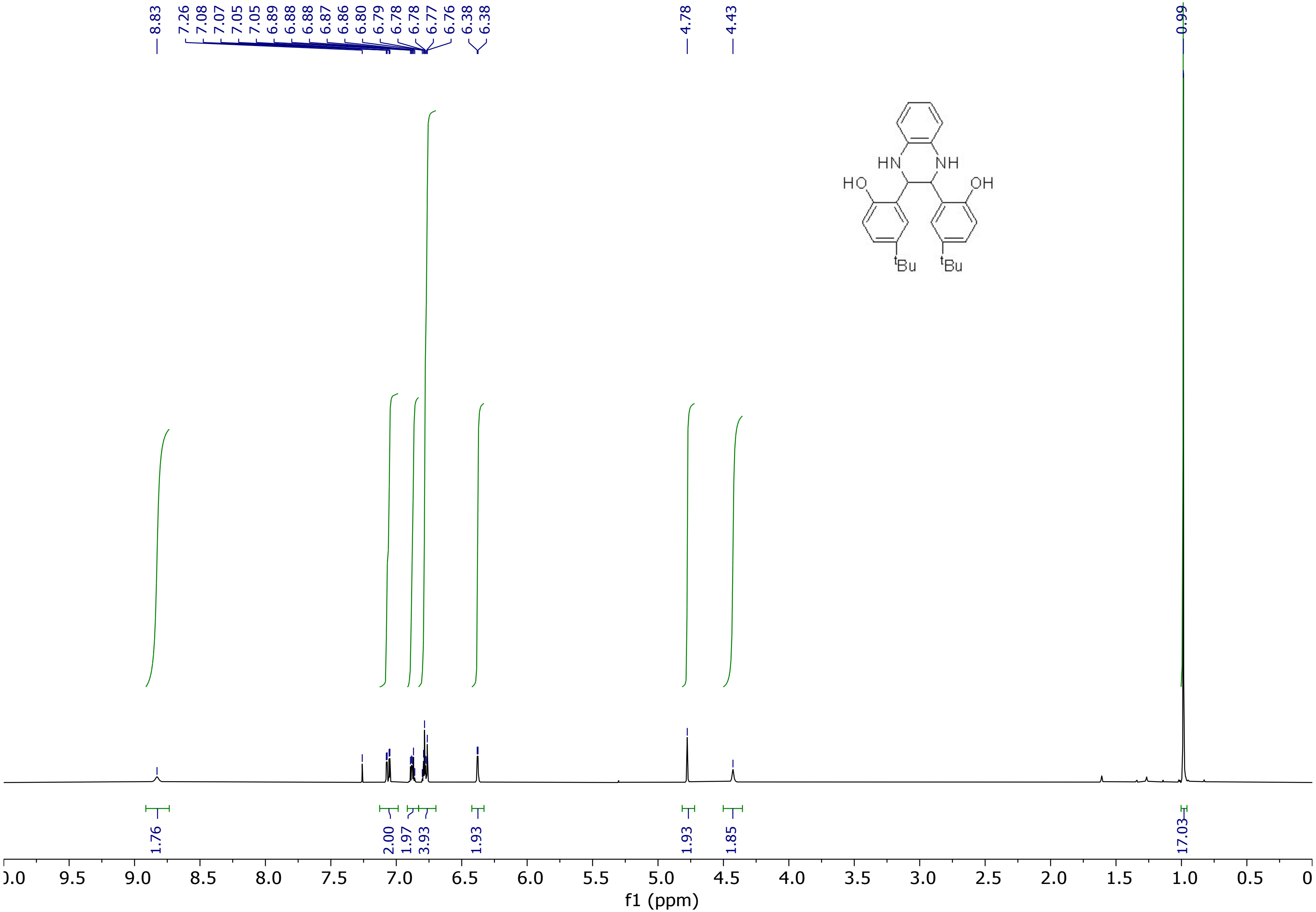

55 C
45 C
35 C
25 C
15 C
5 C
-5 C
-15 C
-25 C
-35 C
-45 C
-55 C
-55 C
12
11
10
9
8
7
6
5
4
3
2
1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

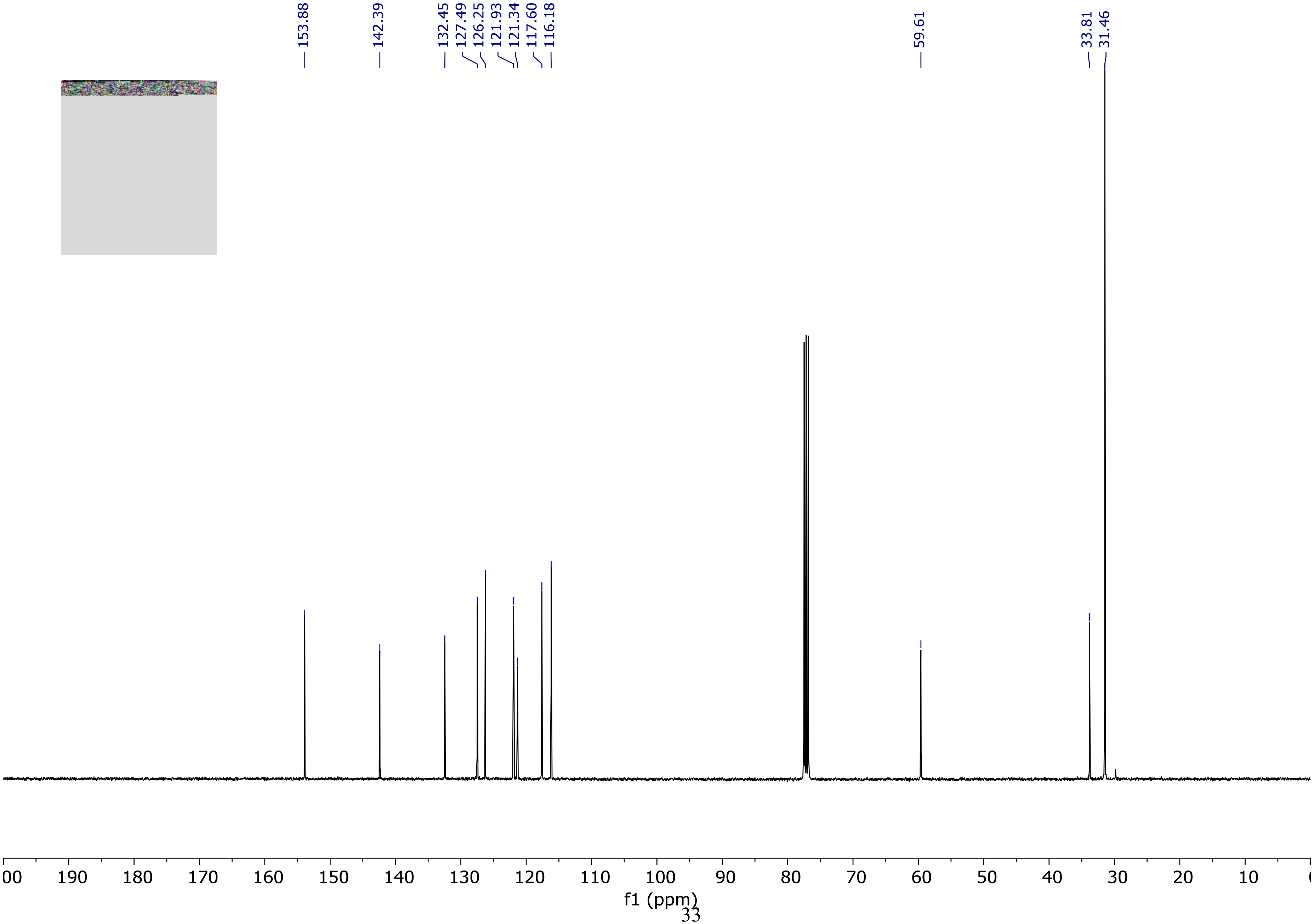
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)diphenol (3b)



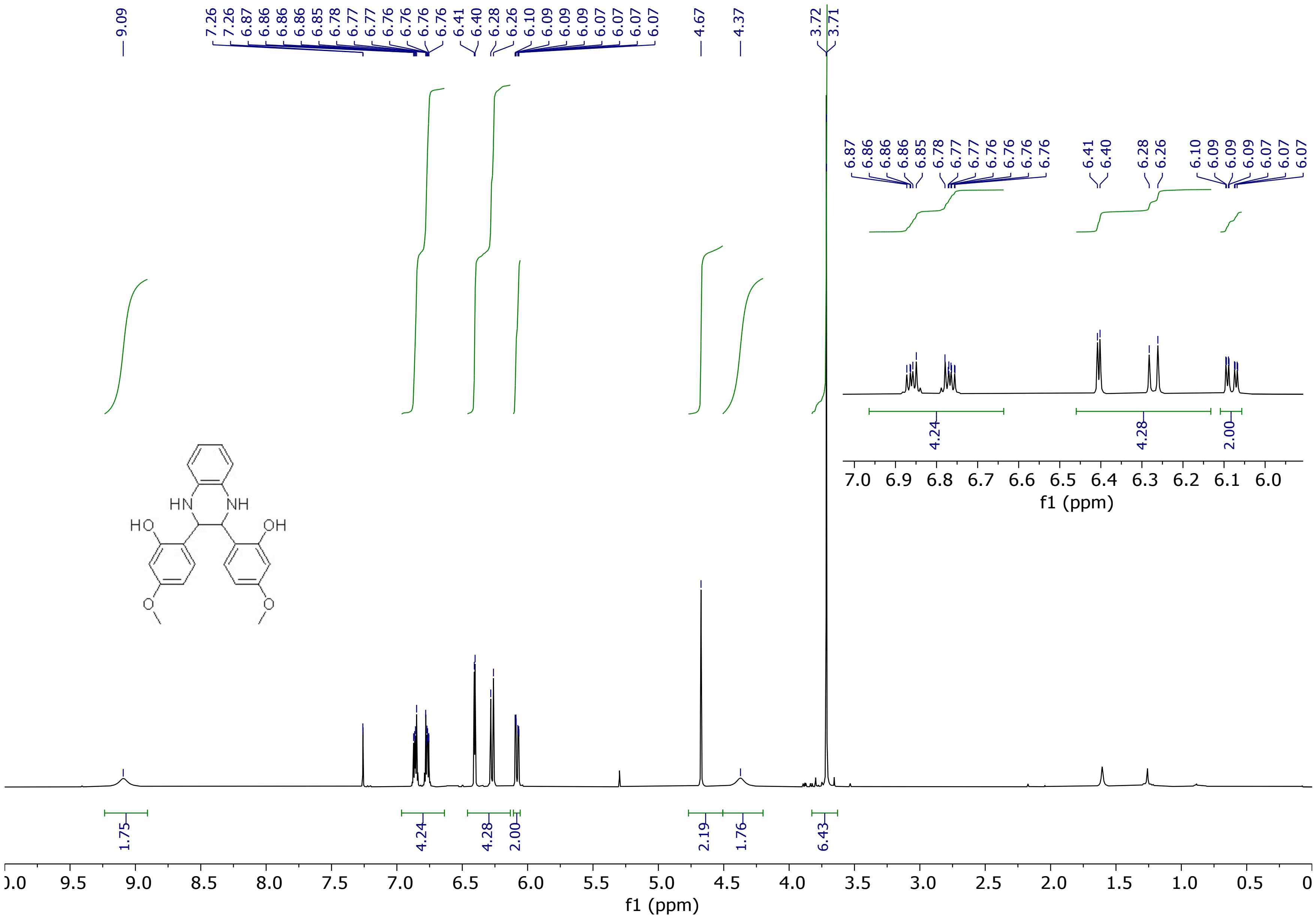

HN
NH
HO
OH
156.40
132.33
130.28
129.85
122.18
121.97
119.72
117.65
117.15
59.02
132.33
130.28
129.85
122.18
121.97
119.72
117.65
117.15
134 132 130 128 126 124 122 120 118 116 11
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

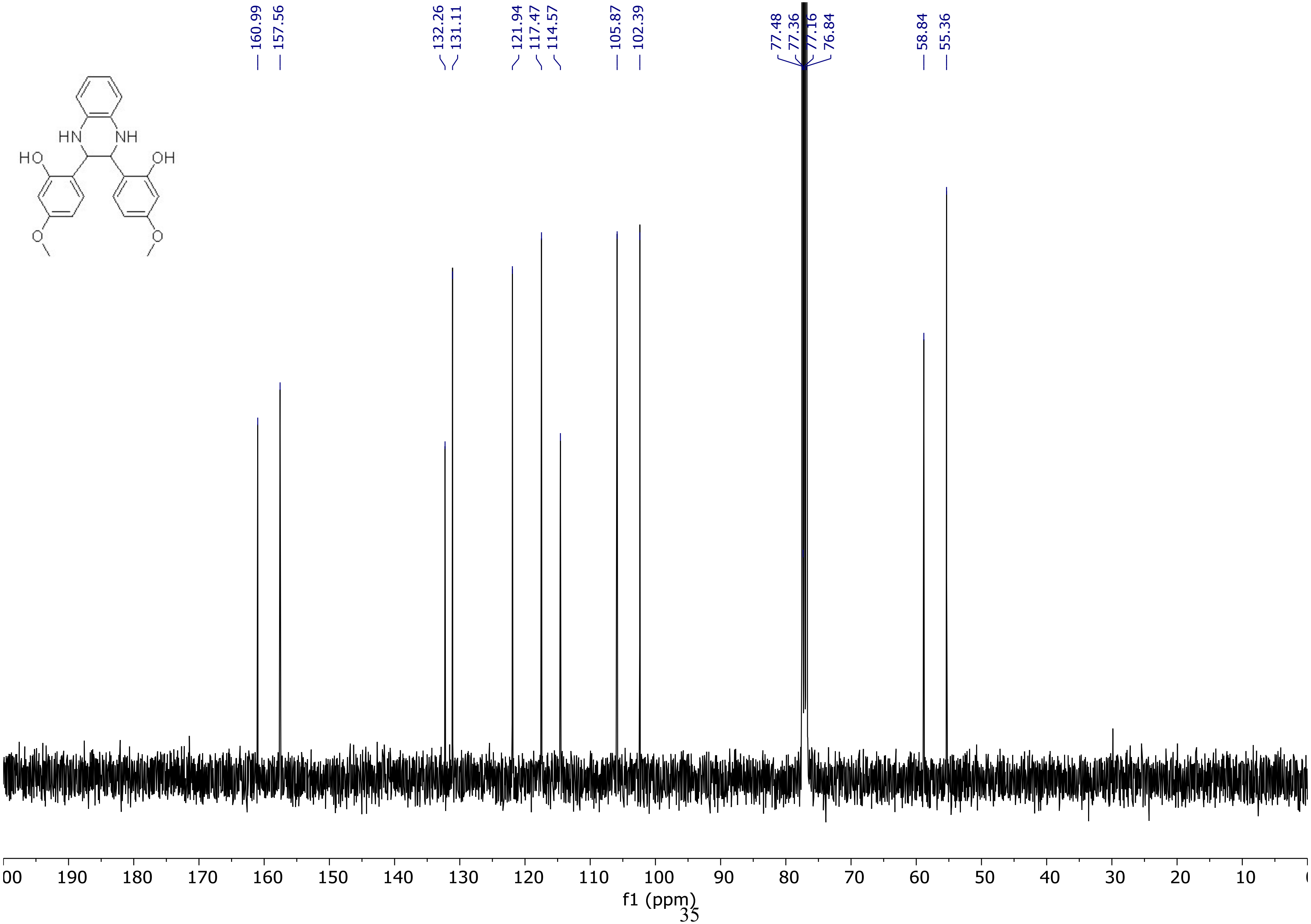
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(*tert*-butyl)phenol) (3c)



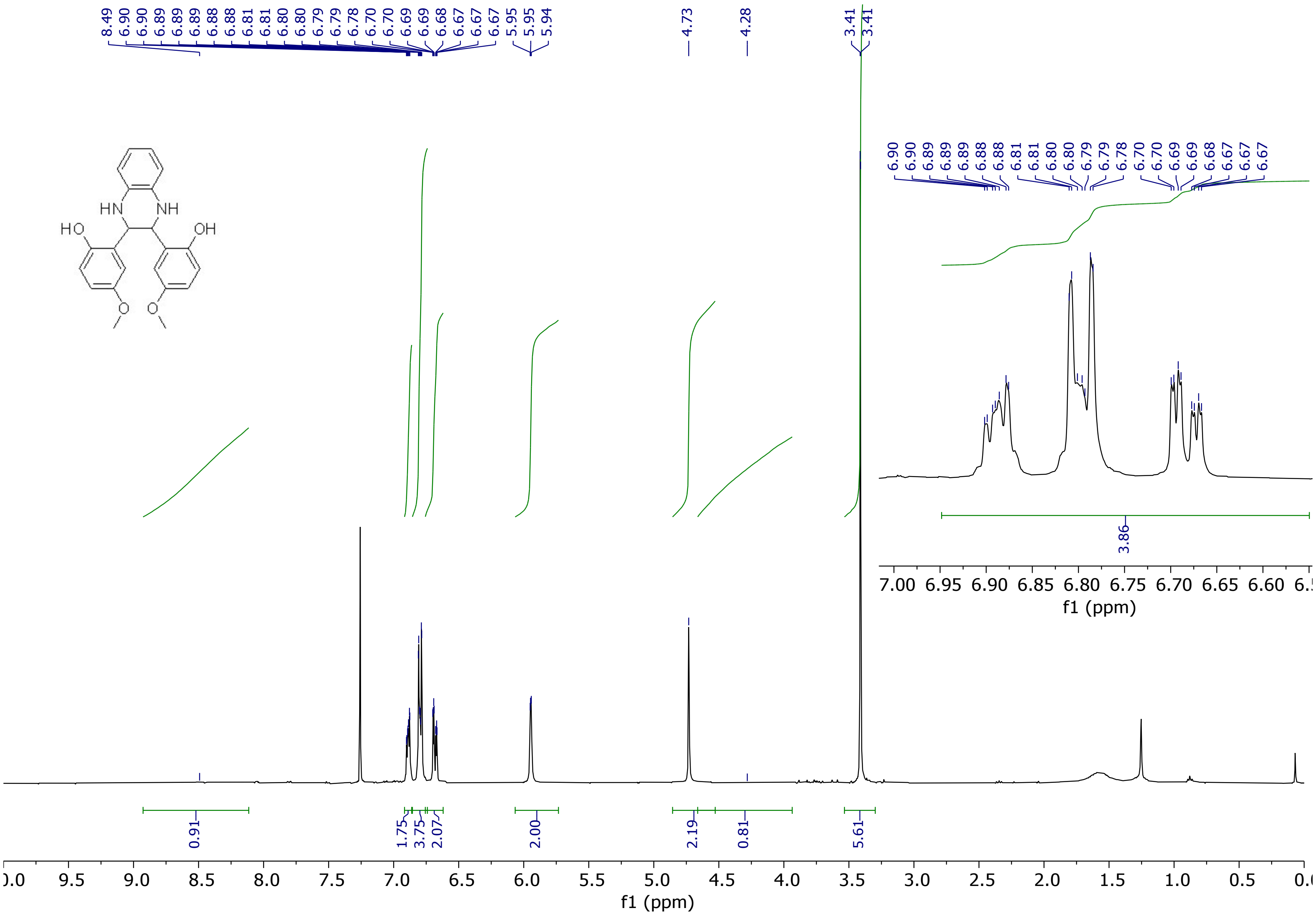

153.88
142.39
132.45
127.49
126.25
121.93
121.34
117.60
116.18
59.61
33.81
31.46
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

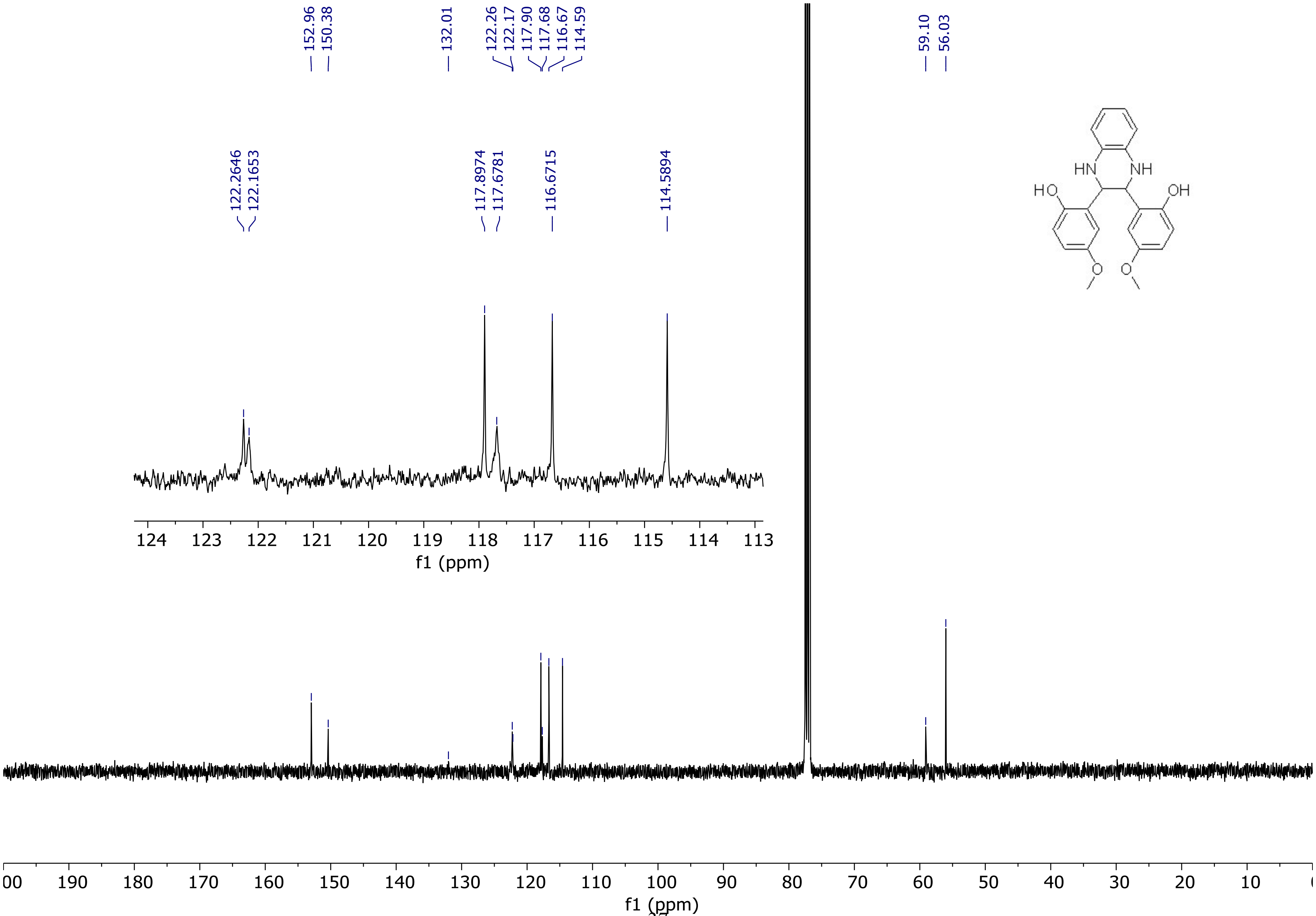
6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3d)




160.99
157.56
132.26
131.11
121.94
117.47
114.57
105.87
102.39
77.48
77.36
77.16
76.84
58.84
55.36
HN
NH
HO
OH
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

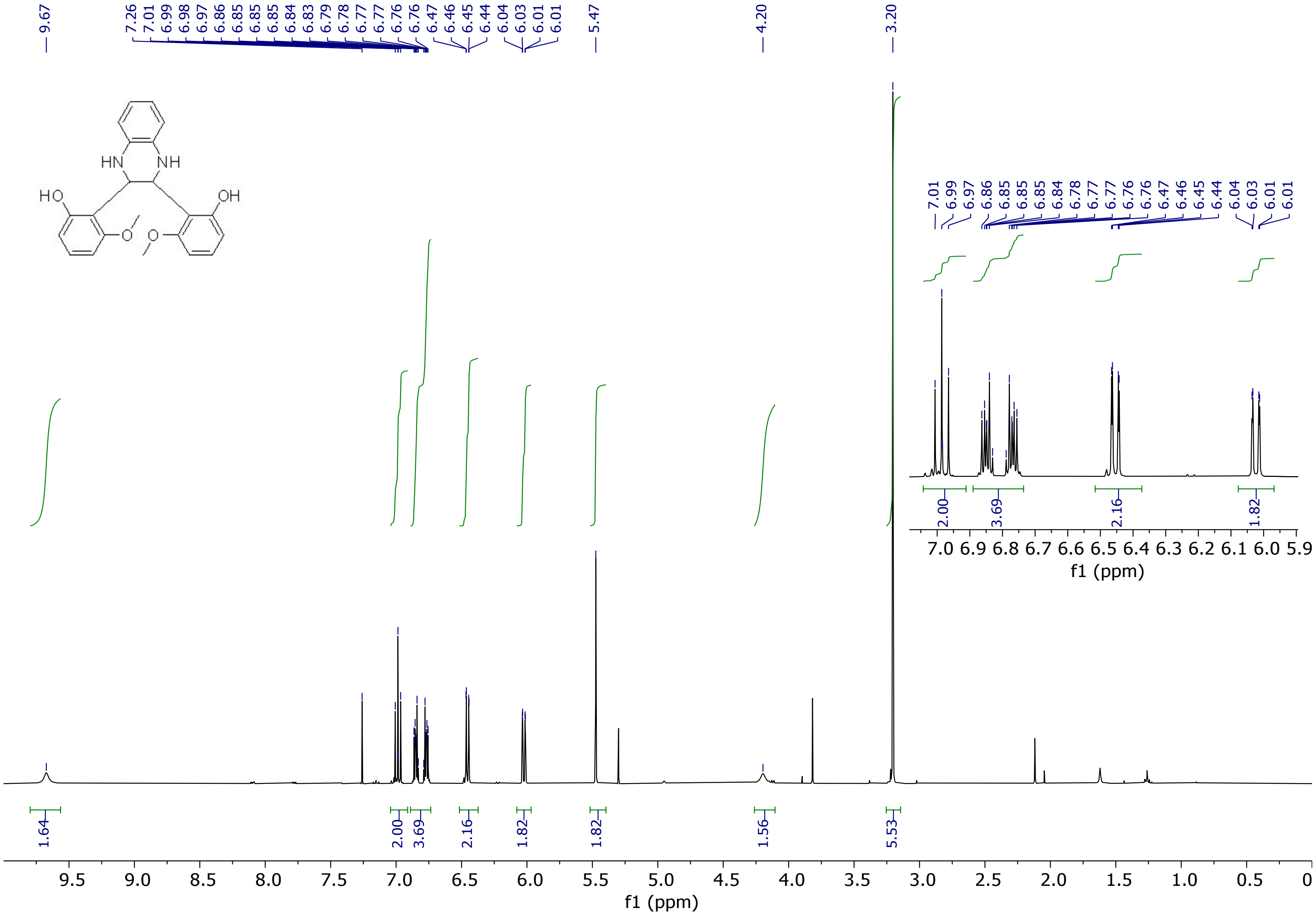
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-methoxyphenol) (3e)

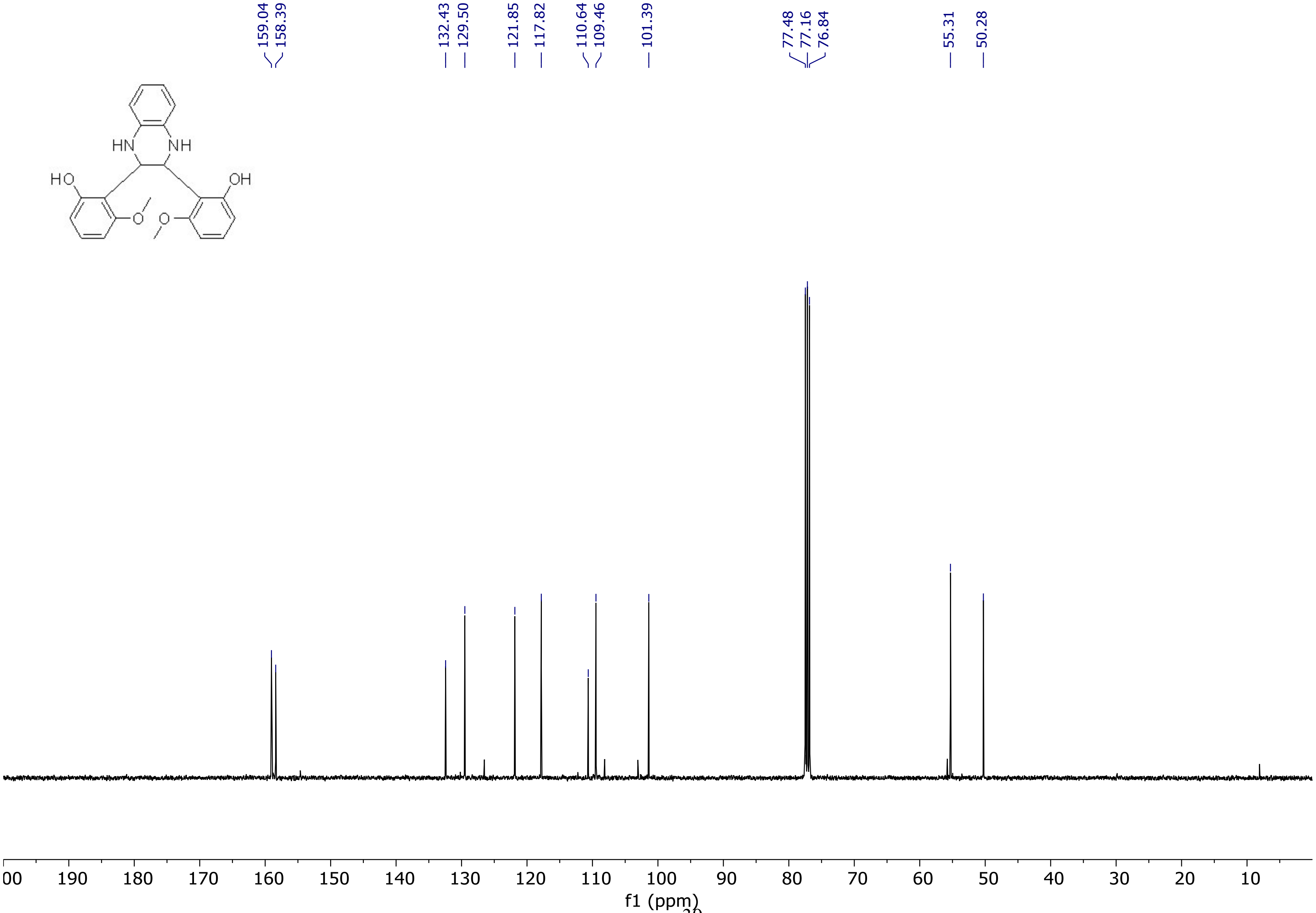




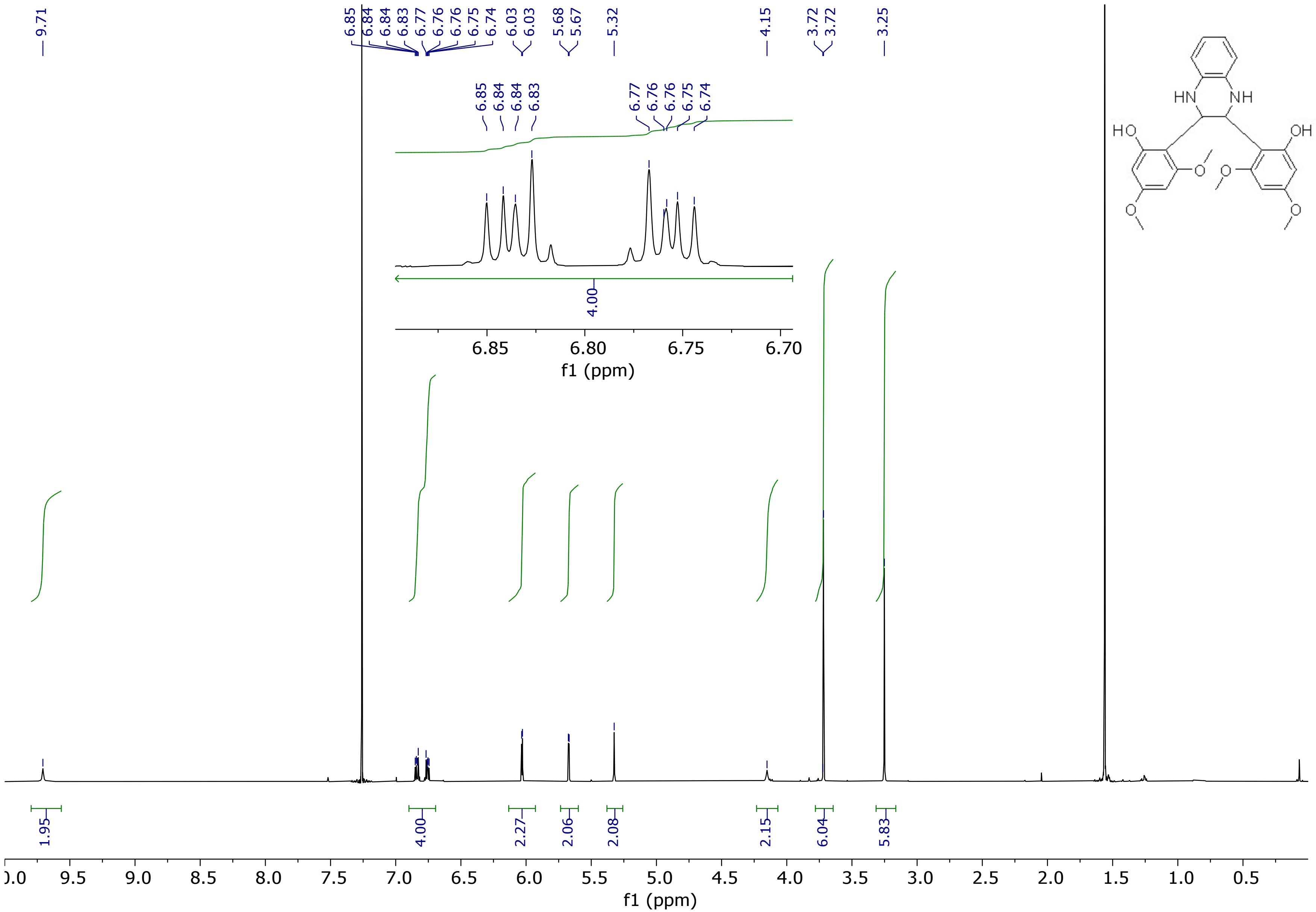
152.96
150.38
132.01
122.26
122.17
117.90
117.68
116.67
114.59
59.10
56.03
122.2646
122.1653
117.8974
117.6781
116.6715
114.5894
124 123 122 121 120 119 118 117 116 115 114 113
f1 (ppm)
HN
NH
HO
OH
O
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

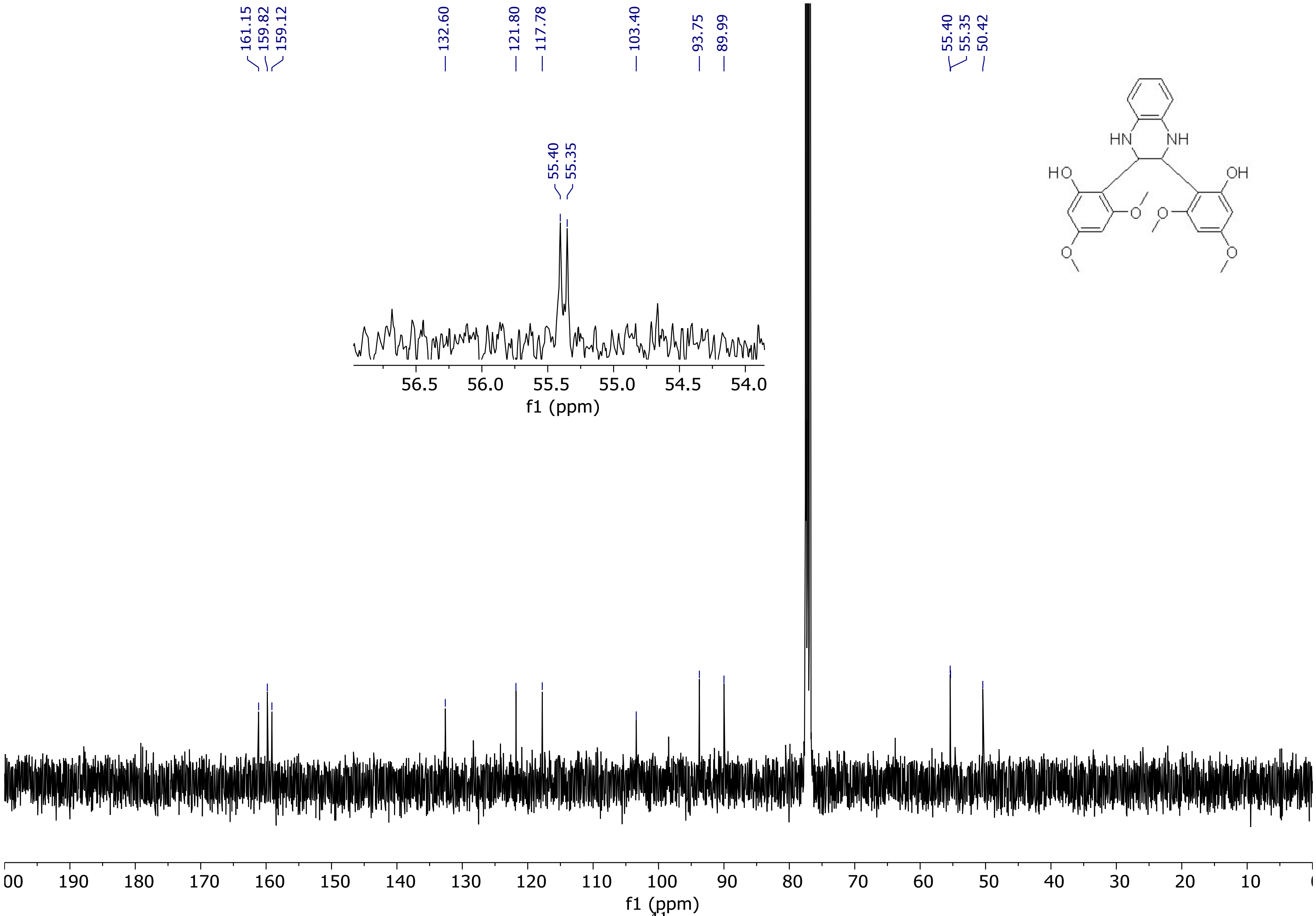
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3f)



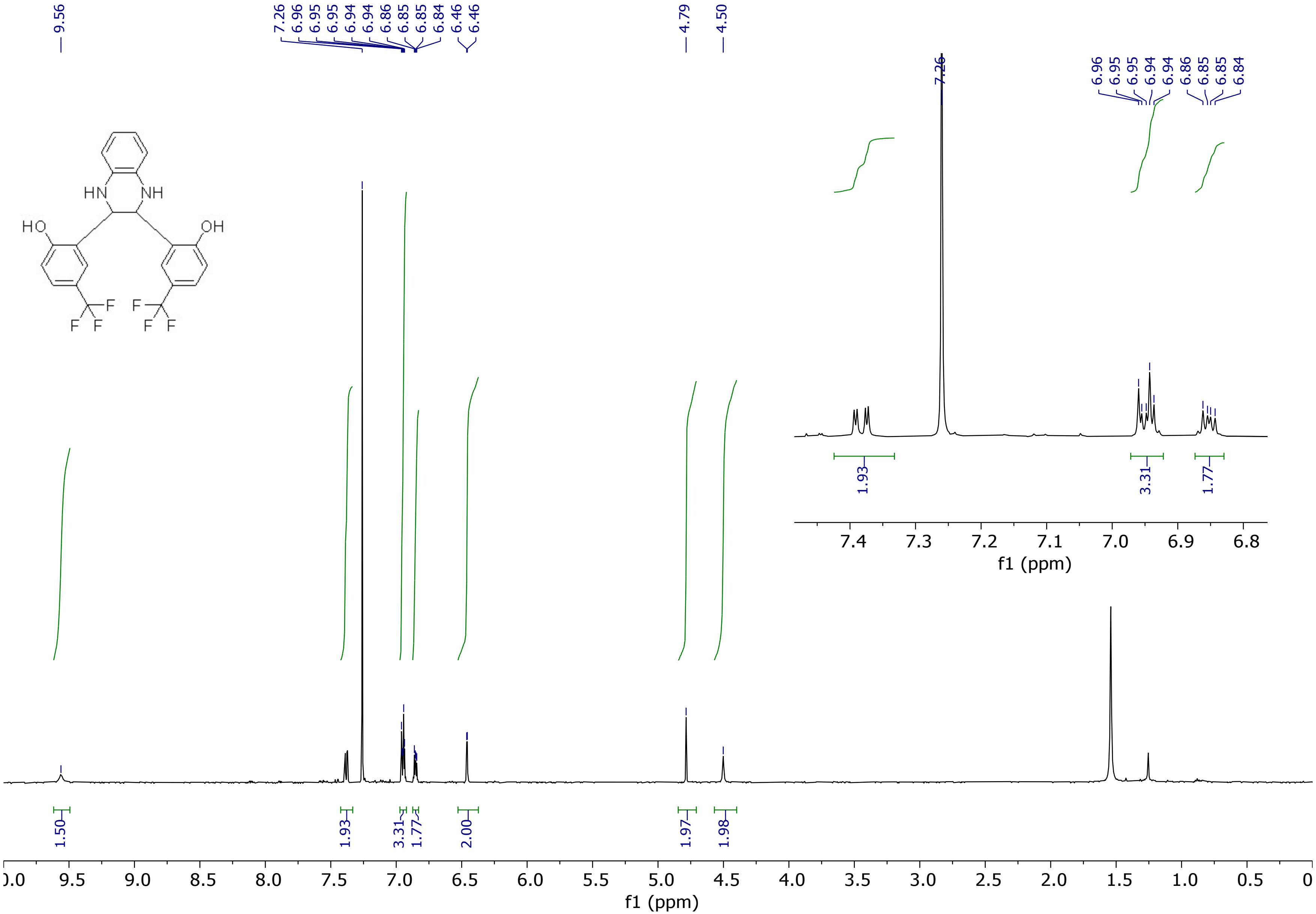

159.04
158.39
132.43
129.50
121.85
117.82
110.64
109.46
101.39
77.48
77.16
76.84
55.31
50.28
HN
NH
HO
OH
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

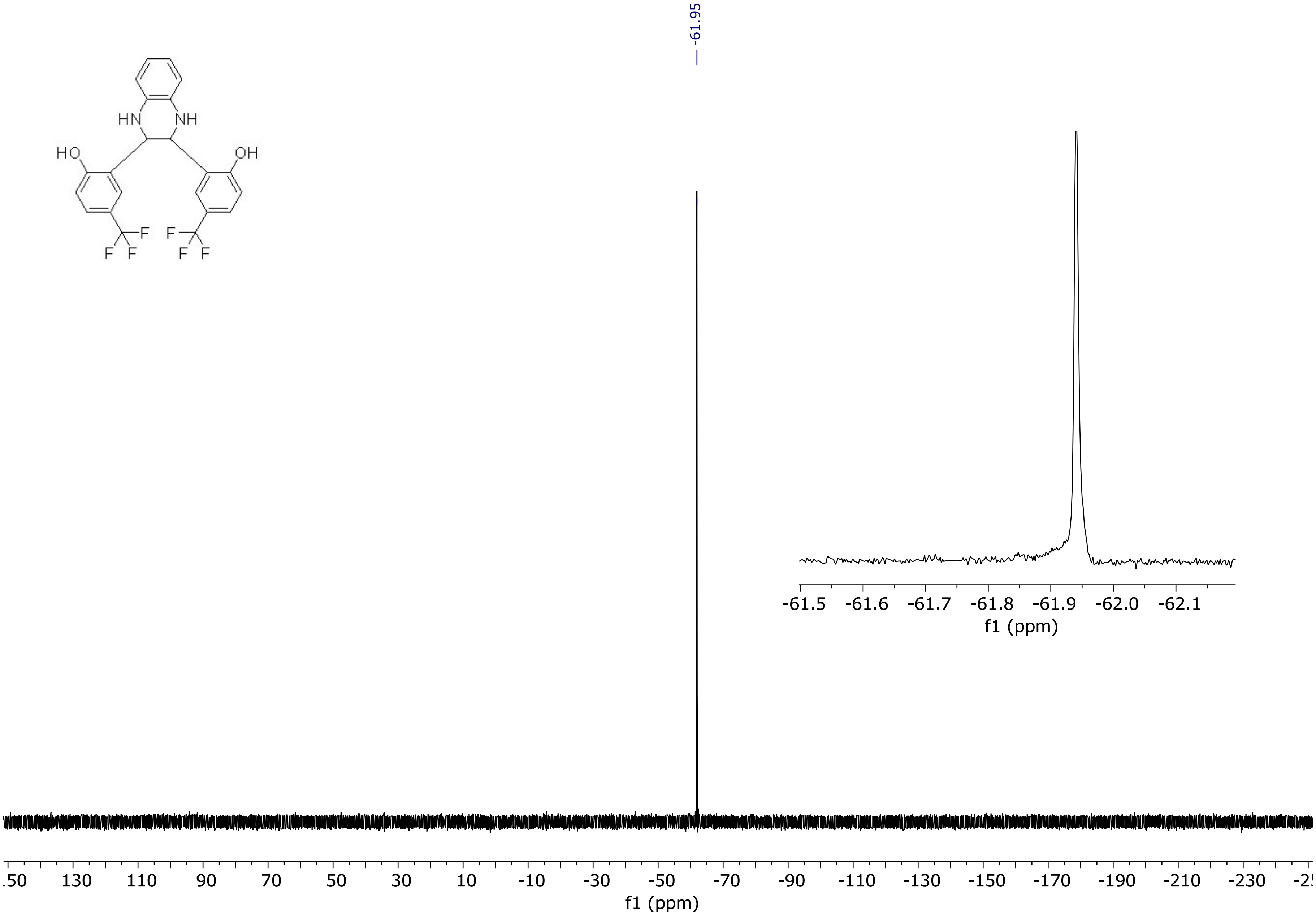
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3,5-dimethoxyphenol) (3g)

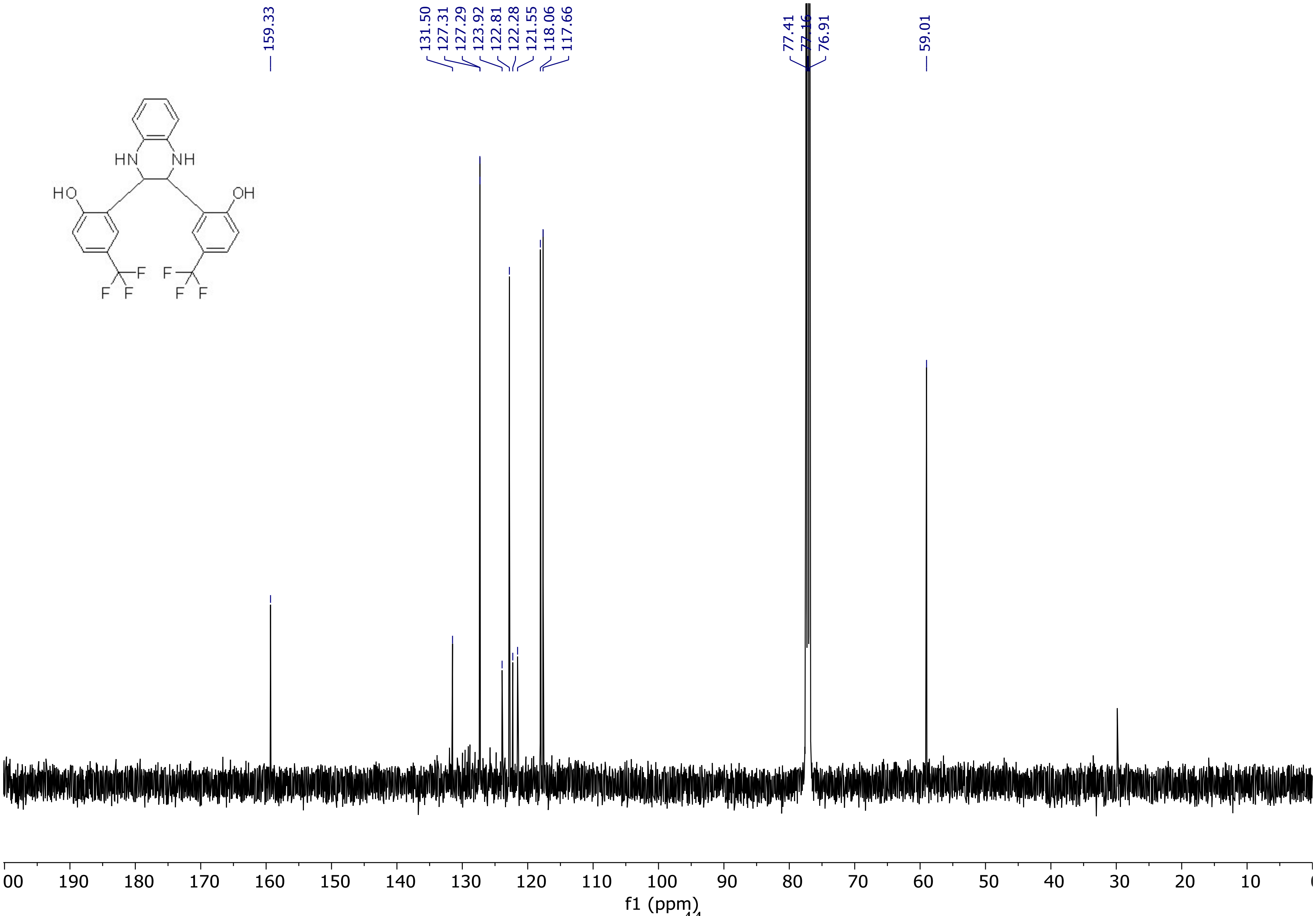


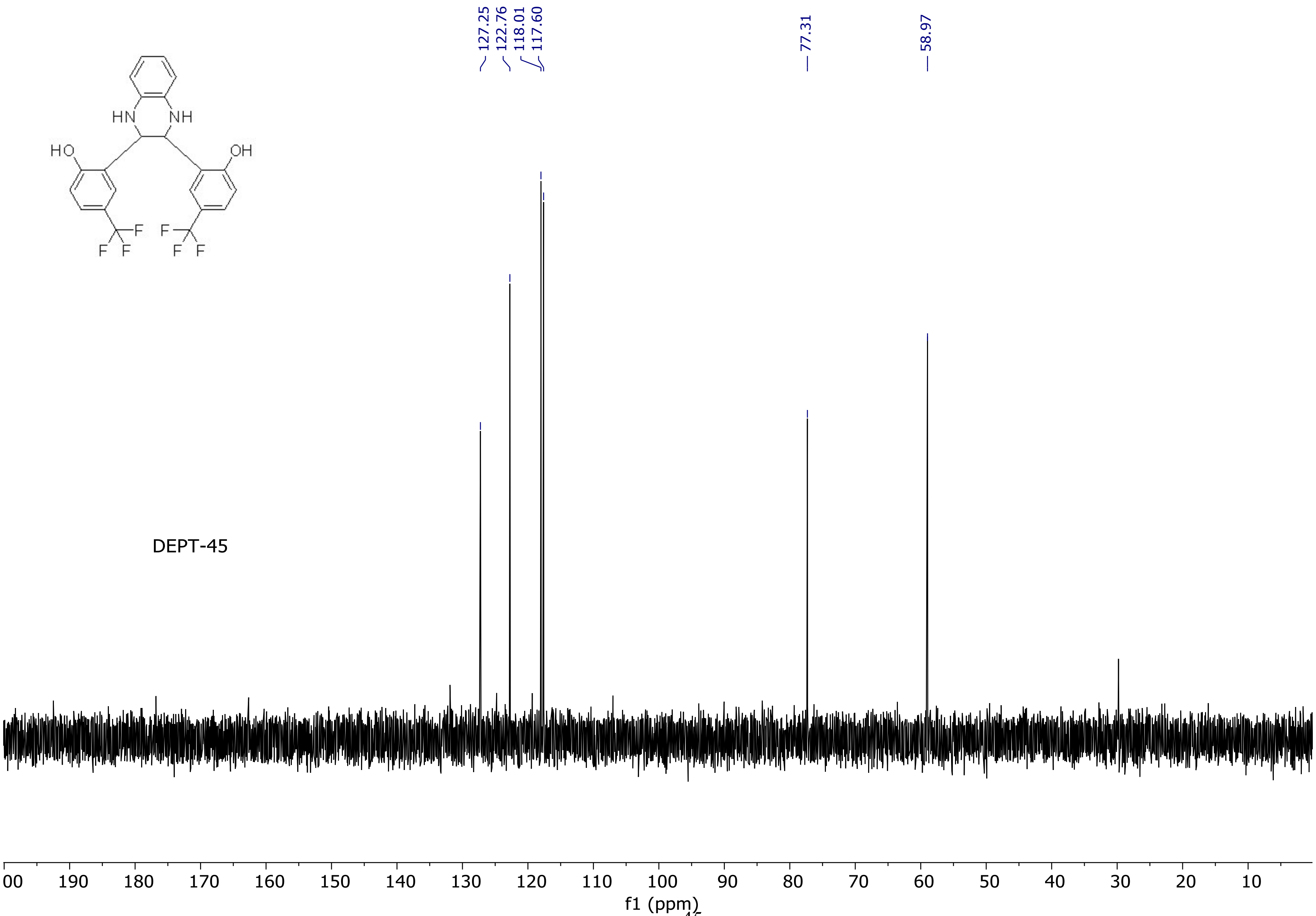

161.15
159.82
159.12
132.60
121.80
117.78
103.40
93.75
89.99
55.40
55.35
50.42
55.40
55.35
56.5
56.0
55.5
55.0
54.5
54.0
f1 (ppm)
HN
NH
HO
OH
O
O
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(trifluoromethyl)phenol) (3h)

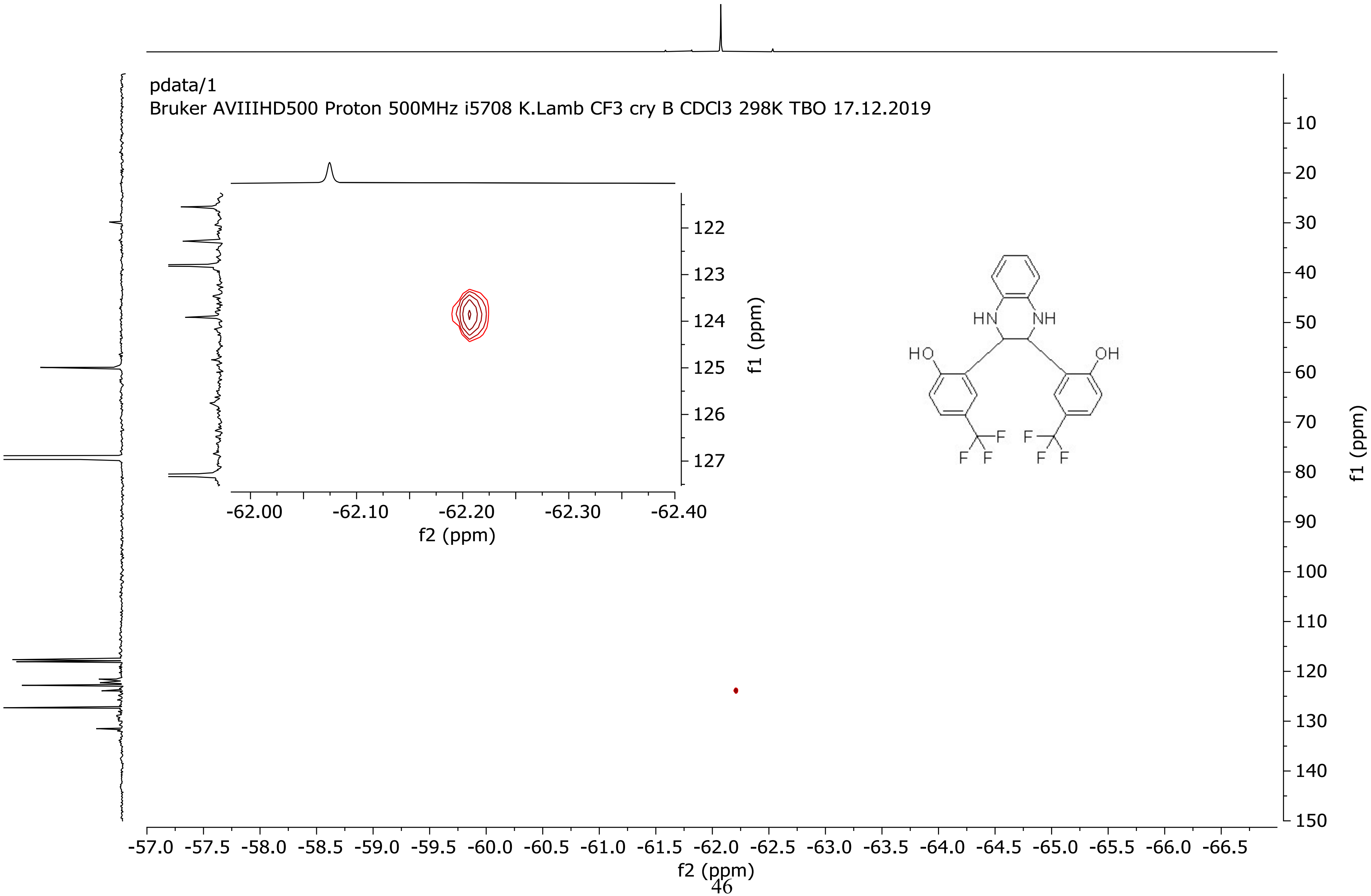



HN
NH
HO
OH
F
F F
F
F F
-61.95
-61.5
-61.6
-61.7
-61.8
-61.9
-62.0
-62.1
f1 (ppm)
.50
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-2
f1 (ppm)


159.33
131.50
127.31
127.29
123.92
122.81
122.28
121.55
118.06
117.66
77.41
77.16
76.91
59.01
HN
NH
HO
OH
F
F
F
F
F
F
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

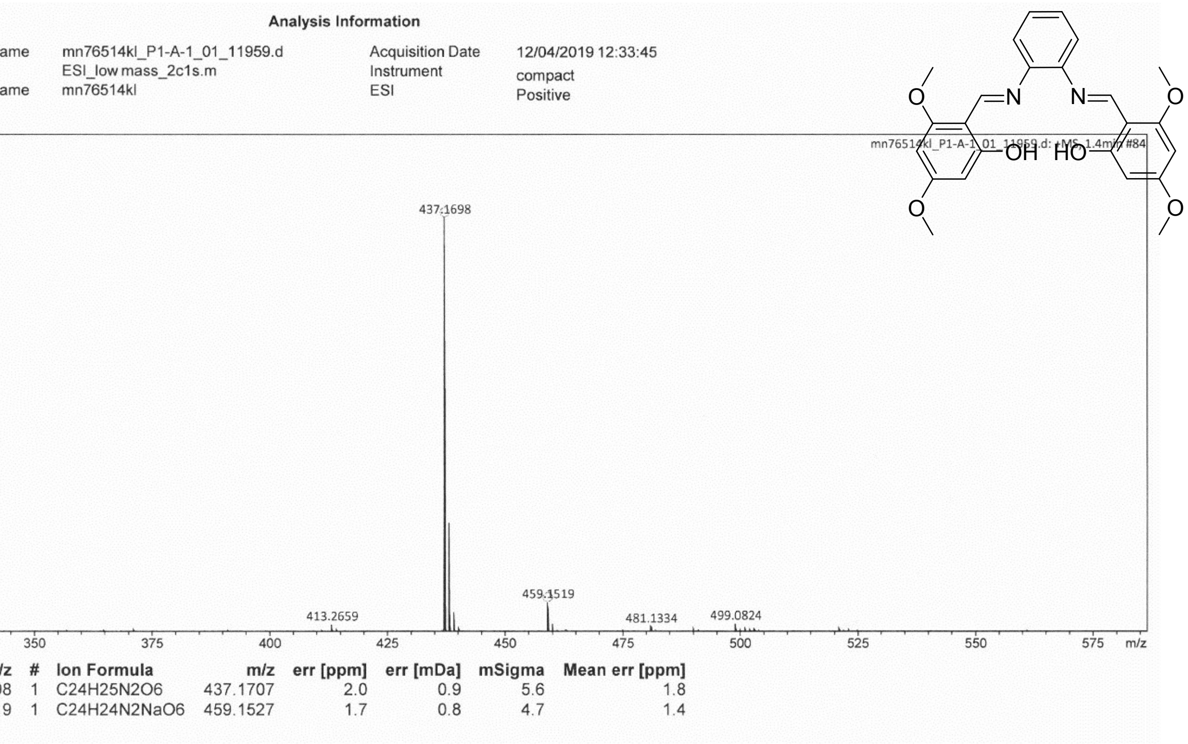

127.25
122.76
118.01
117.60
77.31
58.97
HN
NH
HO
OH
F
F F
F
F F
DEPT-45
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

One Bond 13C-19F correlation



Mass spectra of salophen ligands

2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3,5-dimethoxyphenol) (1g)



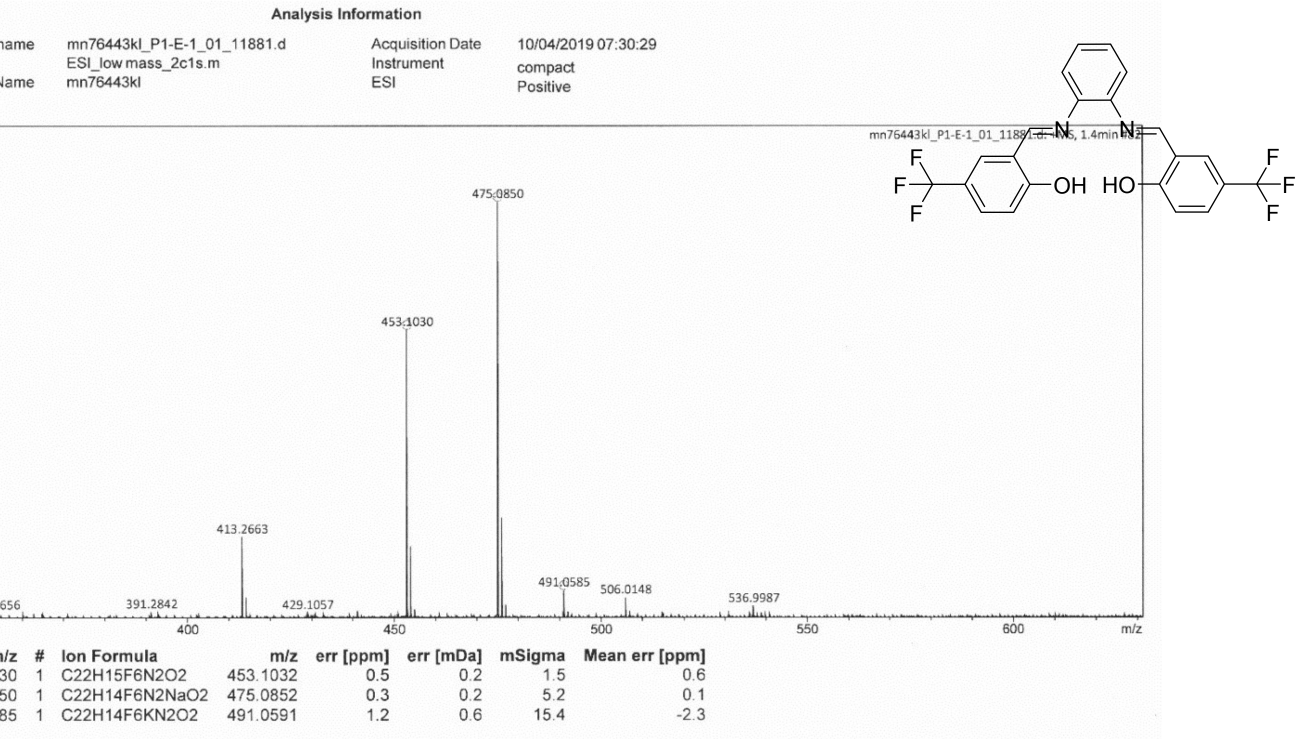
Analysis Information

ame mn76514kl_P1-A-1_01_11959.d
ESI_low mass_2c1s.m
ame mn76514kl

Acquisition Date 12/04/2019 12:33:45
Instrument compact
ESI Positive

/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
08	1	C24H25N2O6	437.1707	2.0	0.9	5.6	1.8
9	1	C24H24N2NaO6	459.1527	1.7	0.8	4.7	1.4

N,N'-Bis(2-hydroxy-5-trifluoromethyl)-1,2-phenylenediamine (1h)



Analysis Information

ame mn76443kl_P1-E-1_01_11881.d
ESI_low mass_2c1s.m
ame mn76443kl

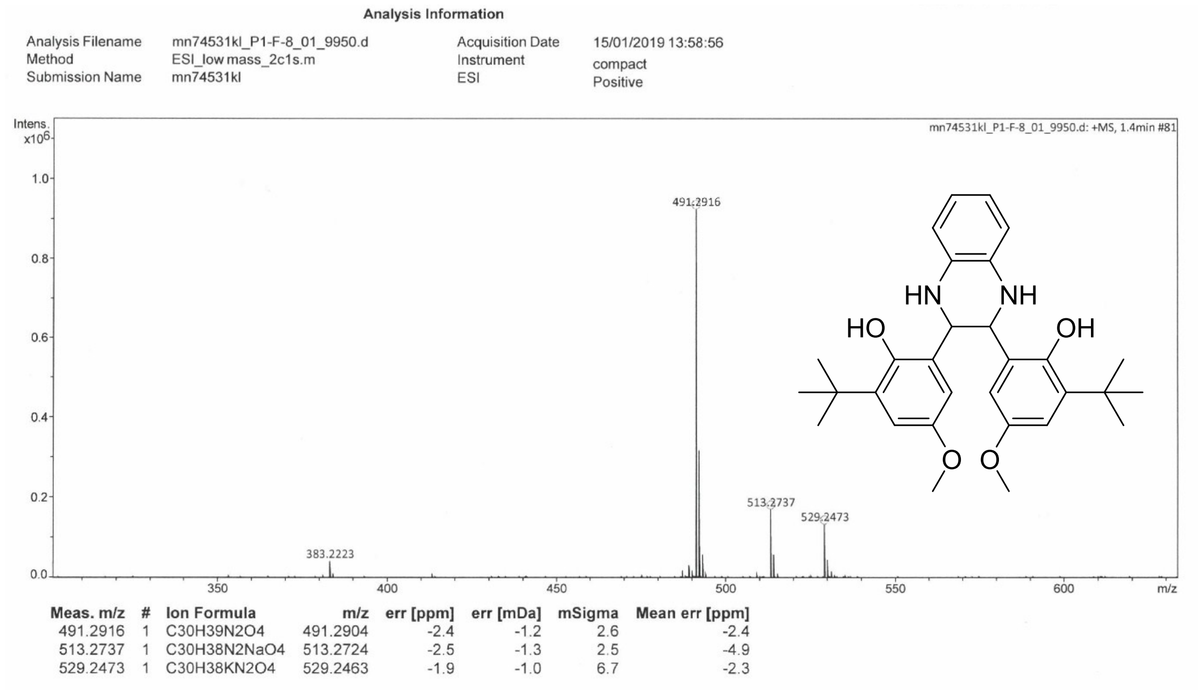
Acquisition Date 10/04/2019 07:30:29
Instrument compact
ESI Positive

/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
30	1	C22H15F6N2O2	453.1032	0.5	0.2	1.5	0.6
50	1	C22H14F6N2NaO2	475.0852	0.3	0.2	5.2	0.1
85	1	C22H14F6KN2O2	491.0591	1.2	0.6	15.4	-2.3

Mass spectra of tetrahydroquinoxalines

6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(2-(*tert*-butyl)-4-methoxyphenol) (3a)

<u>Purified product</u>

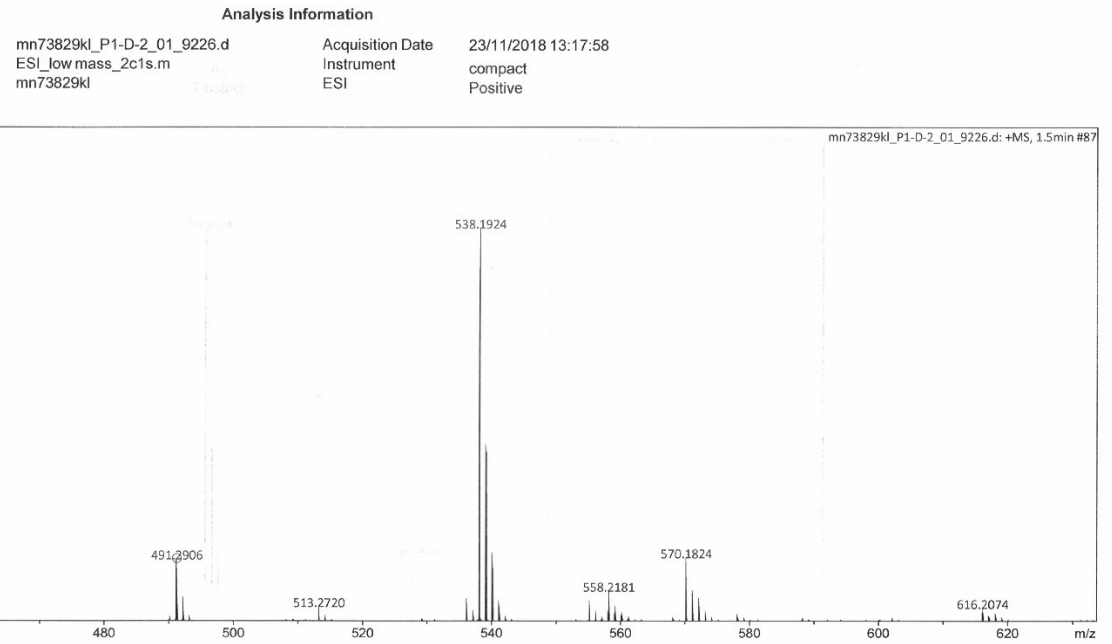


Analysis Information

Analysis Filename	mn74531kl_P1-F-8_01_9950.d	Acquisition Date	15/01/2019 13:58:56
Method	ESI_low mass_2c1s.m	Instrument	compact
Submission Name	mn74531kl	ESI	Positive

Meas. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
491.2916	1	C30H39N2O4	491.2904	-2.4	-1.2	2.6	-2.4
513.2737	1	C30H38N2NaO4	513.2724	-2.5	-1.3	2.5	-4.9
529.2473	1	C30H38KN2O4	529.2463	-1.9	-1.0	6.7	-2.3

Unpurified reaction mixture



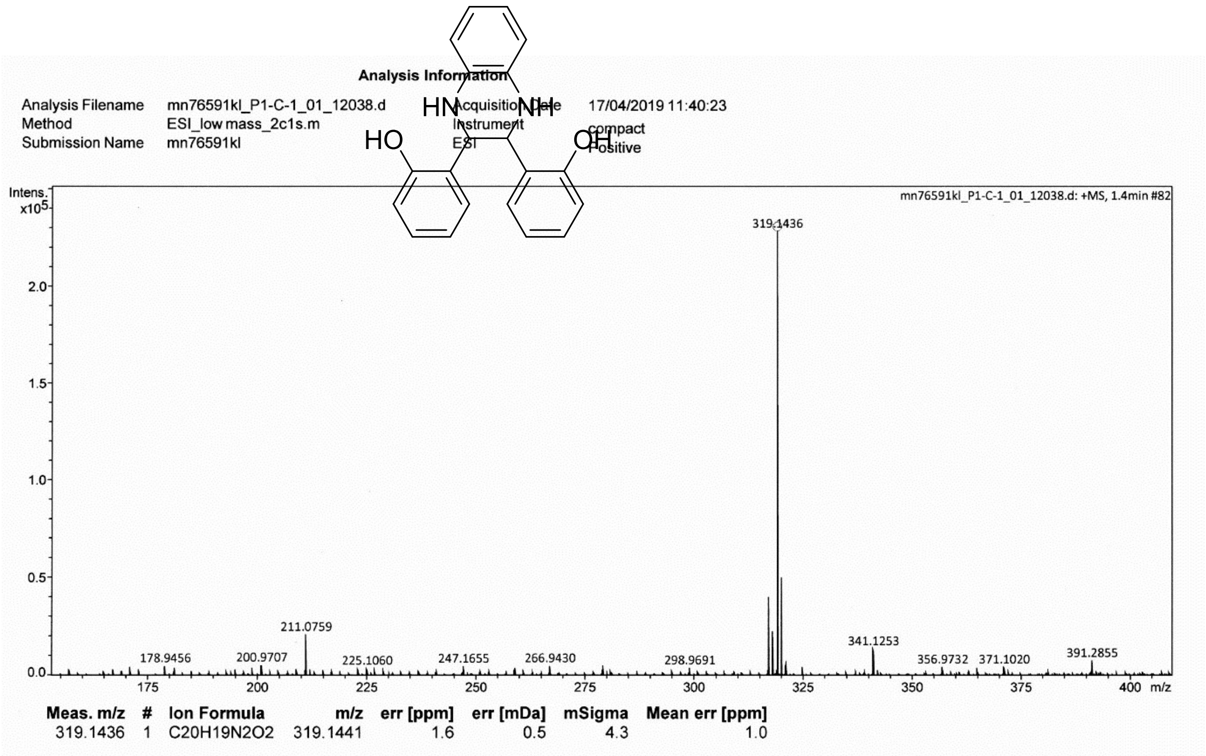
Analysis Information

mn73829kl_P1-D-2_01_9226.d
ESI_low mass_2c1s.m
mn73829kl

Acquisition Date 23/11/2018 13:17:58
Instrument compact
ESI Positive

491.2906 corresponds to [**3a**+H]$^+$ (1 ppm error between the measured mass and the theoretical mass of 491.2904).
538.1924 corresponds to [**2a**-Cl]$^+$ (3 ppm error between the measured mass and the theoretical mass of 538.1918).

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)diphenol (3b)



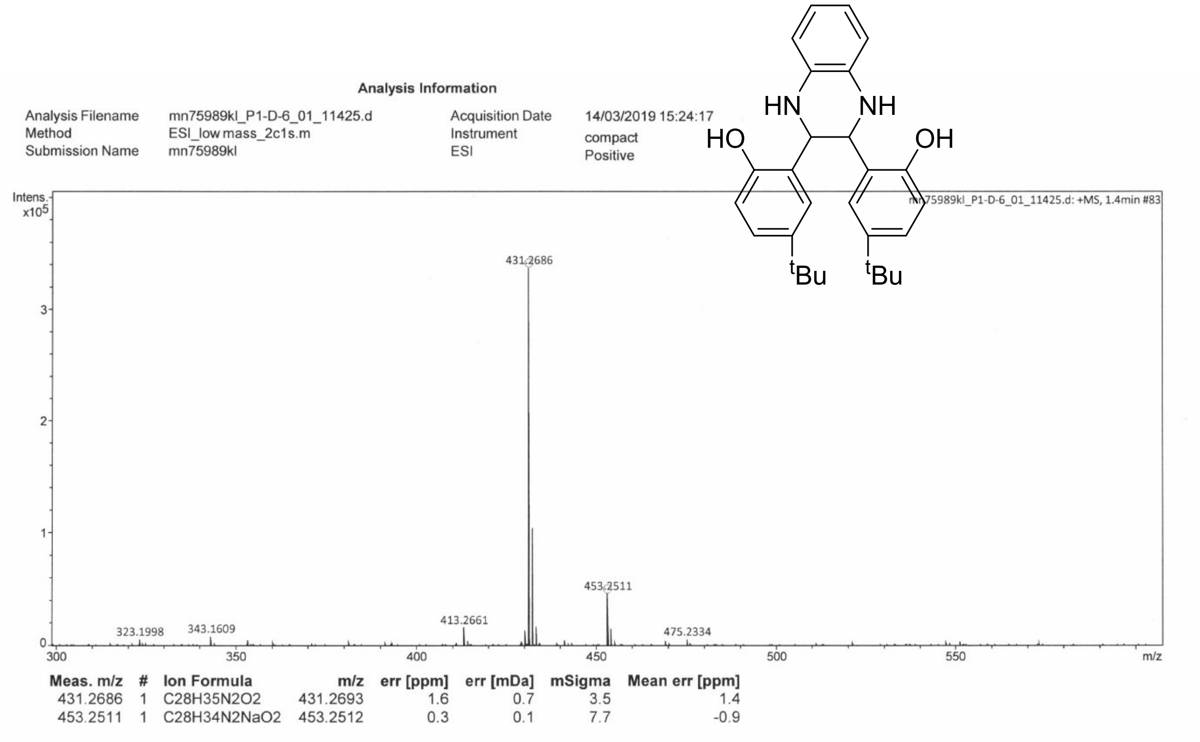
Analysis Information

Analysis Filename mn76591kl_P1-C-1_01_12038.d Acquisition Date 17/04/2019 11:40:23
Method ESI_low mass_2c1s.m Instrument compact
Submission Name mn76591kl ESI Positive

Meas. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
319.1436	1	$C_{20}H_{19}N_2O_2$	319.1441	1.6	0.5	4.3	1.0

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(*tert*-butyl)phenol) (3c)

Purified product

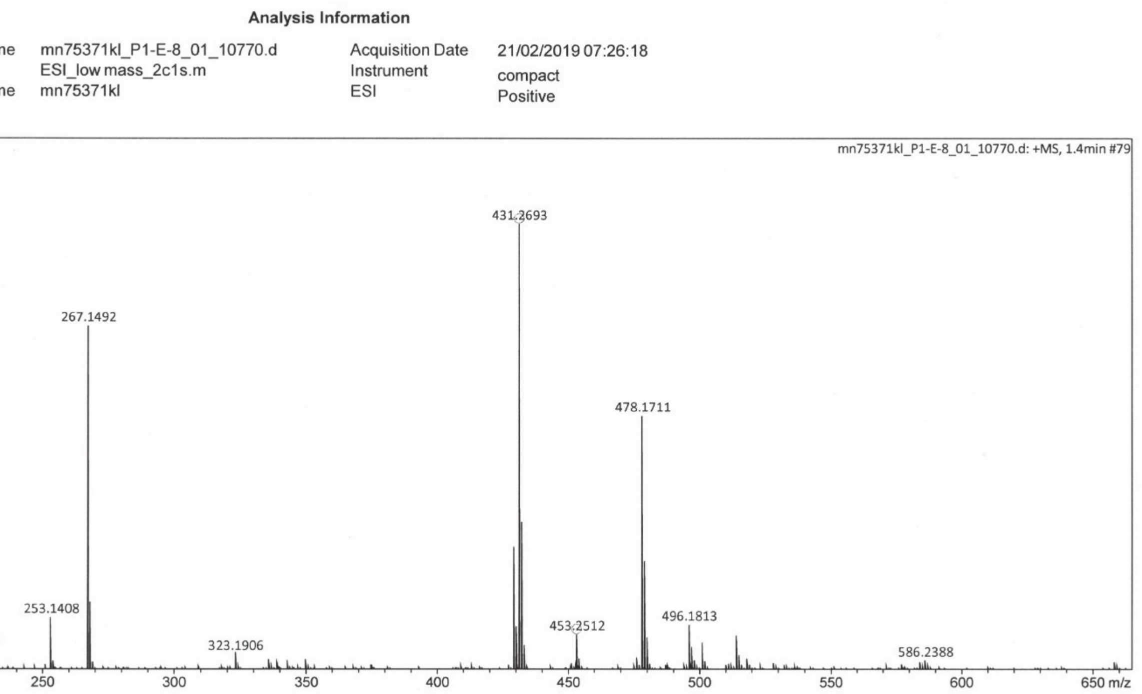


Analysis Information

Analysis Filename mn75989kl_P1-D-6_01_11425.d
Method ESI_low mass_2c1s.m
Submission Name mn75989kl
Acquisition Date 14/03/2019 15:24:17
Instrument compact
ESI Positive

Meas. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
431.2686	1	C28H35N2O2	431.2693	1.6	0.7	3.5	1.4
453.2511	1	C28H34N2NaO2	453.2512	0.3	0.1	7.7	-0.9

Unpurified reaction mixture



Analysis Information

ne mn75371kl_P1-E-8_01_10770.d
ESI_low mass_2c1s.m
ne mn75371kl

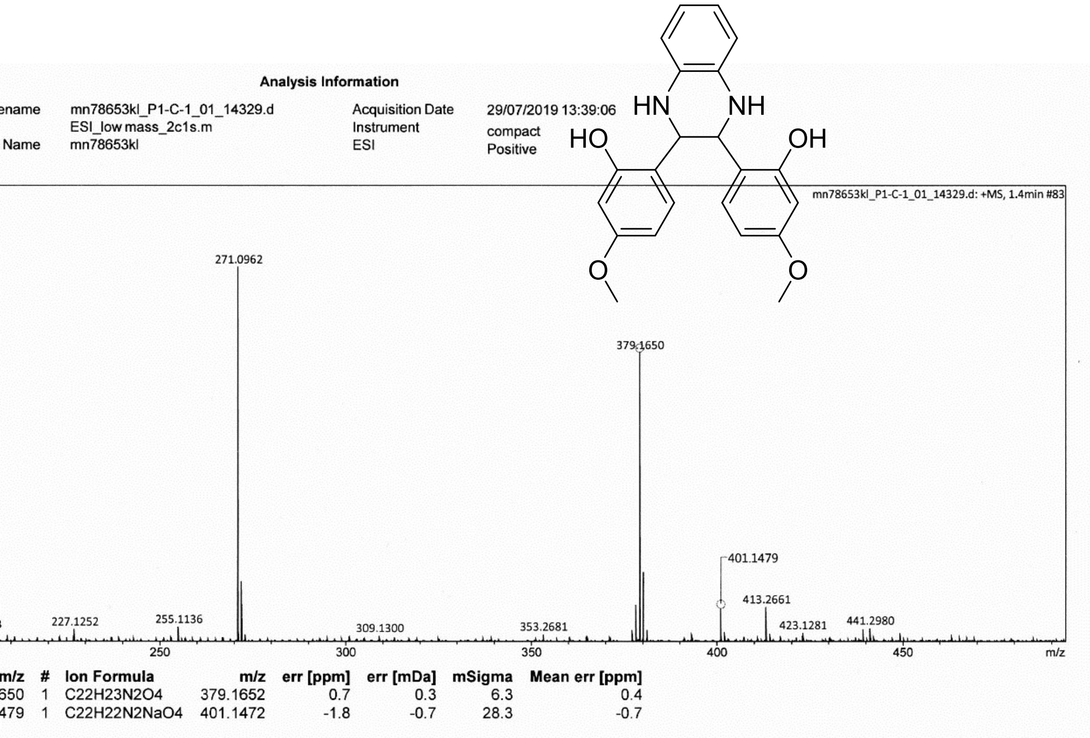
Acquisition Date 21/02/2019 07:26:18
Instrument compact
ESI Positive

431.2693 corresponds to [**3c**+H]$^+$ (0 ppm error between the measured mass and the theoretical mass of 431.2693).

453.2512 corresponds to [**3c**+Na]$^+$ (0 ppm error between the measured mass and the theoretical mass of 453.2512).

478.1711 corresponds to [**2c**-Cl]$^+$ (1 ppm error between the measured mass and the theoretical mass of 478.1707).

6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3d)

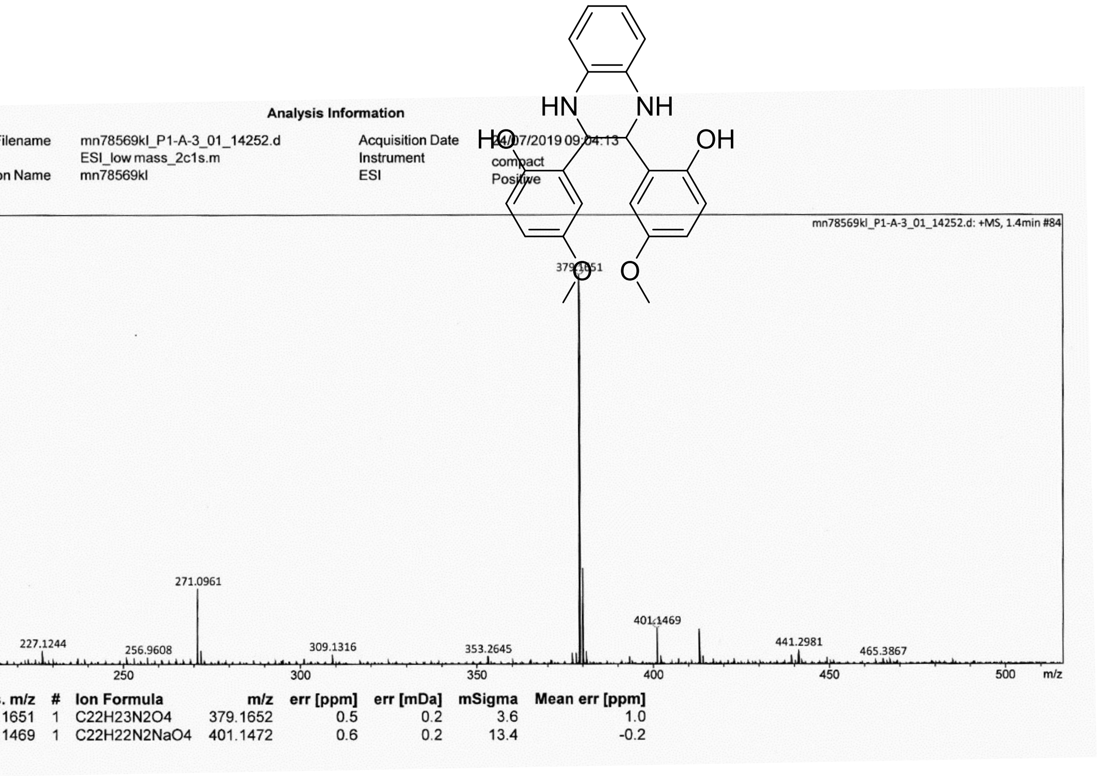


Analysis Information

ename mn78653kl_P1-C-1_01_14329.d Acquisition Date 29/07/2019 13:39:06
ESI_low mass_2c1s.m Instrument compact
Name mn78653kl ESI Positive

m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
650	1	C22H23N2O4	379.1652	0.7	0.3	6.3	0.4
479	1	C22H22N2NaO4	401.1472	-1.8	-0.7	28.3	-0.7

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-methoxyphenol) (3e)



Analysis Information

ilename mn78569kl_P1-A-3_01_14252.d
ESI_low mass_2c1s.m
on Name mn78569kl

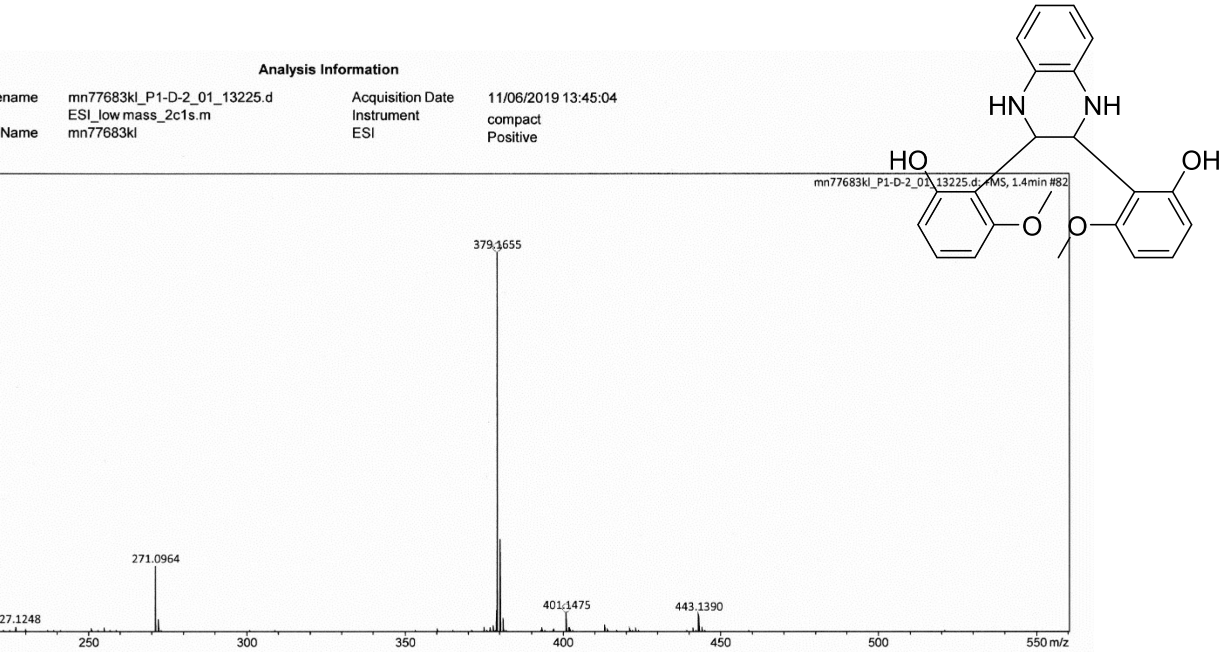
Acquisition Date 24/07/2019 09:04:13
Instrument compact
ESI Positive

. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
1651	1	C22H23N2O4	379.1652	0.5	0.2	3.6	1.0
1469	1	C22H22N2NaO4	401.1472	0.6	0.2	13.4	-0.2

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3f)

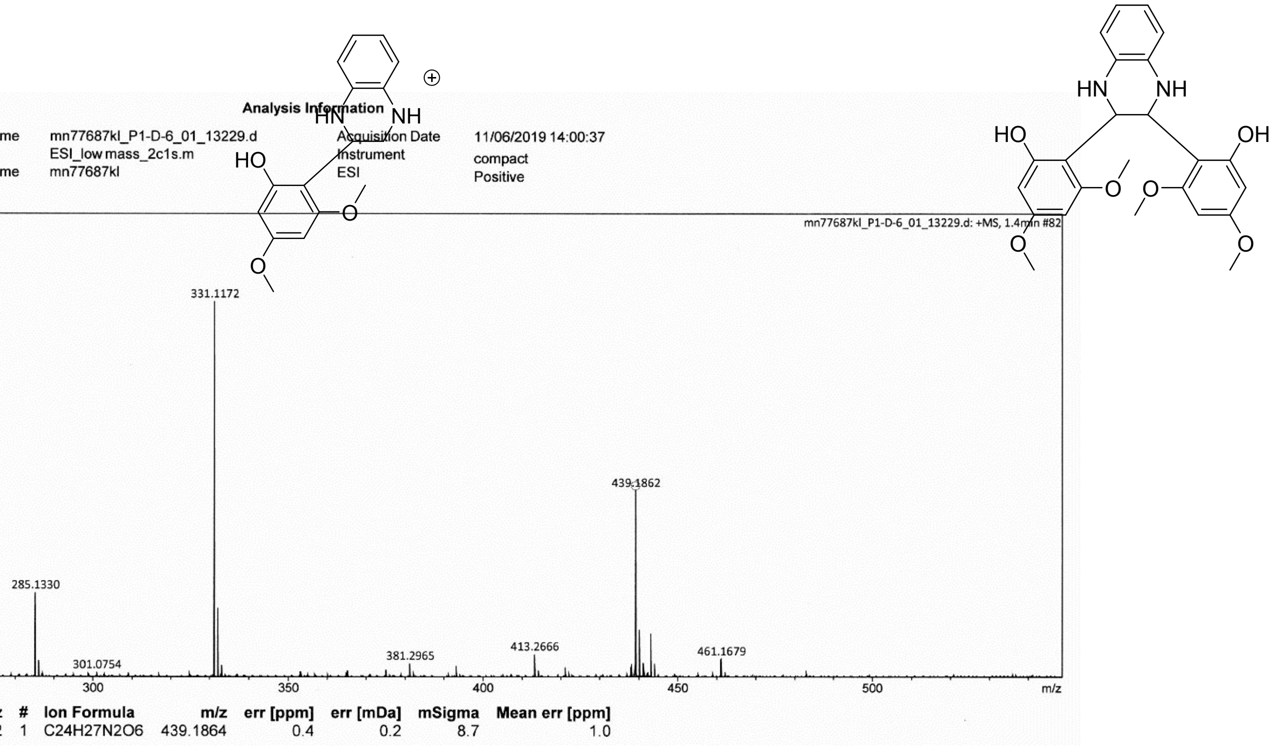
Analysis Information

ename	mn77683kl_P1-D-2_01_13225.d	Acquisition Date	11/06/2019 13:45:04
	ESI_low mass_2c1s.m	Instrument	compact
Name	mn77683kl	ESI	Positive



m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
655	1	C22H23N2O4	379.1652	-0.6	-0.2	4.3	-0.9
475	1	C22H22N2NaO4	401.1472	-0.8	-0.3	8.0	-0.8

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3,5-dimethoxyphenol) (3g)



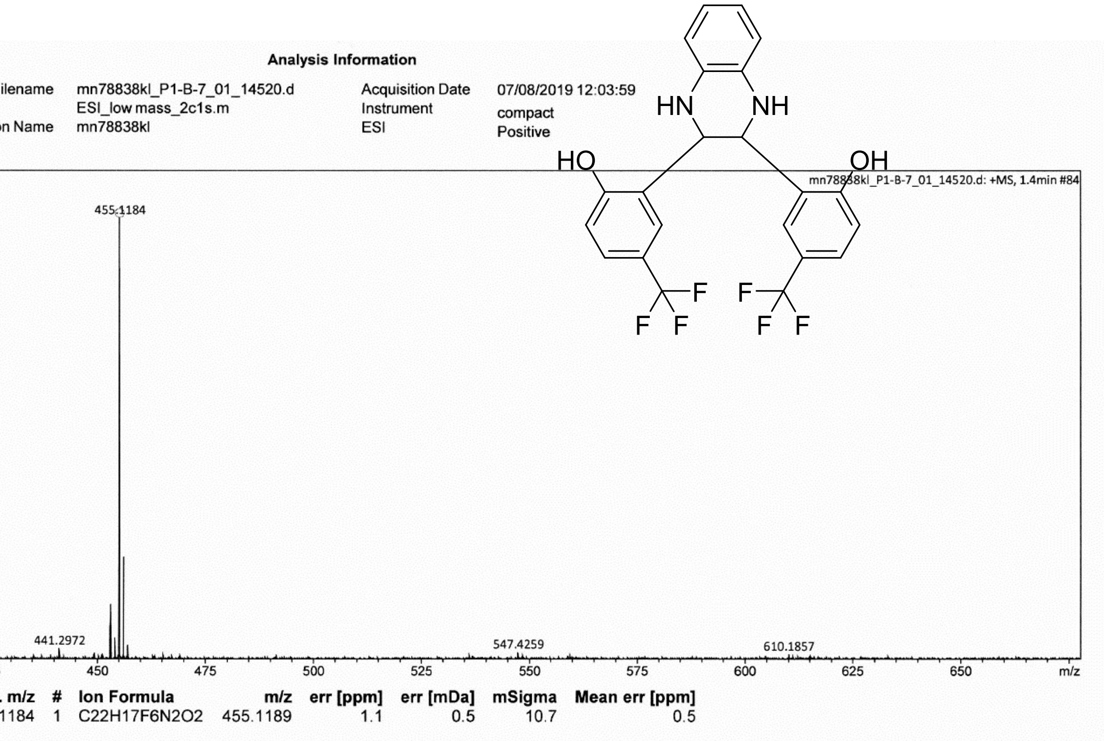
Analysis Information

me mn77687kl_P1-D-6_01_13229.d
ESI_low mass_2c1s.m
me mn77687kl

Acquisition Date 11/06/2019 14:00:37
Instrument compact
ESI Positive

#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
1	C24H27N2O6	439.1864	0.4	0.2	8.7	1.0

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(trifluoromethyl)phenol) (3h)



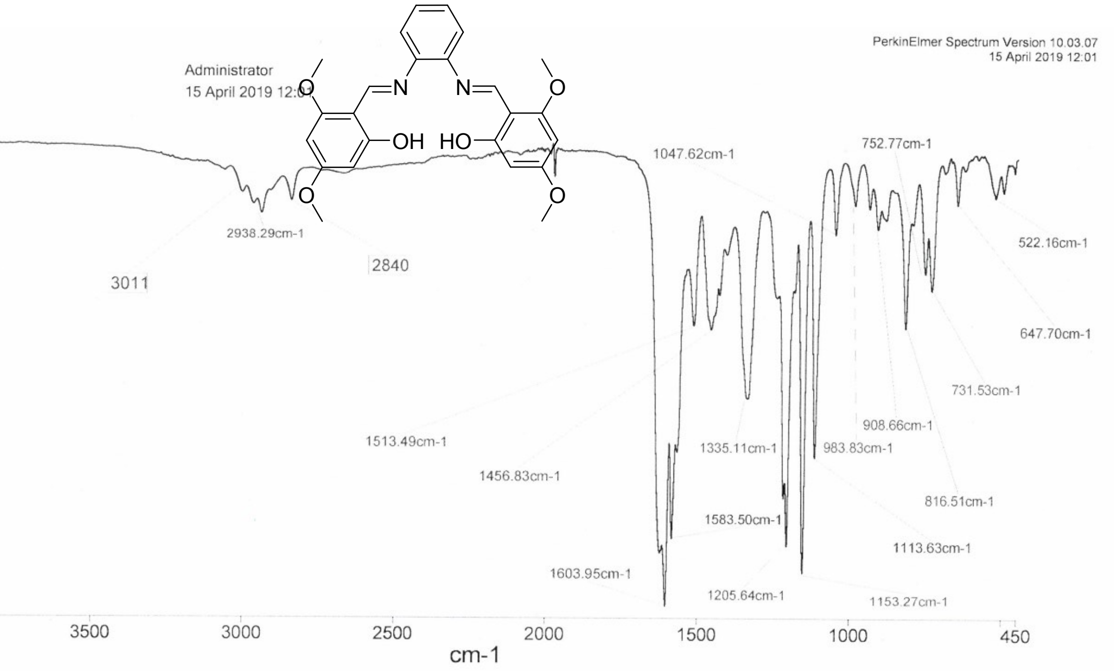
Analysis Information

ilename	mn78838kl_P1-B-7_01_14520.d	Acquisition Date	07/08/2019 12:03:59
	ESI_low mass_2c1s.m	Instrument	compact
on Name	mn78838kl	ESI	Positive

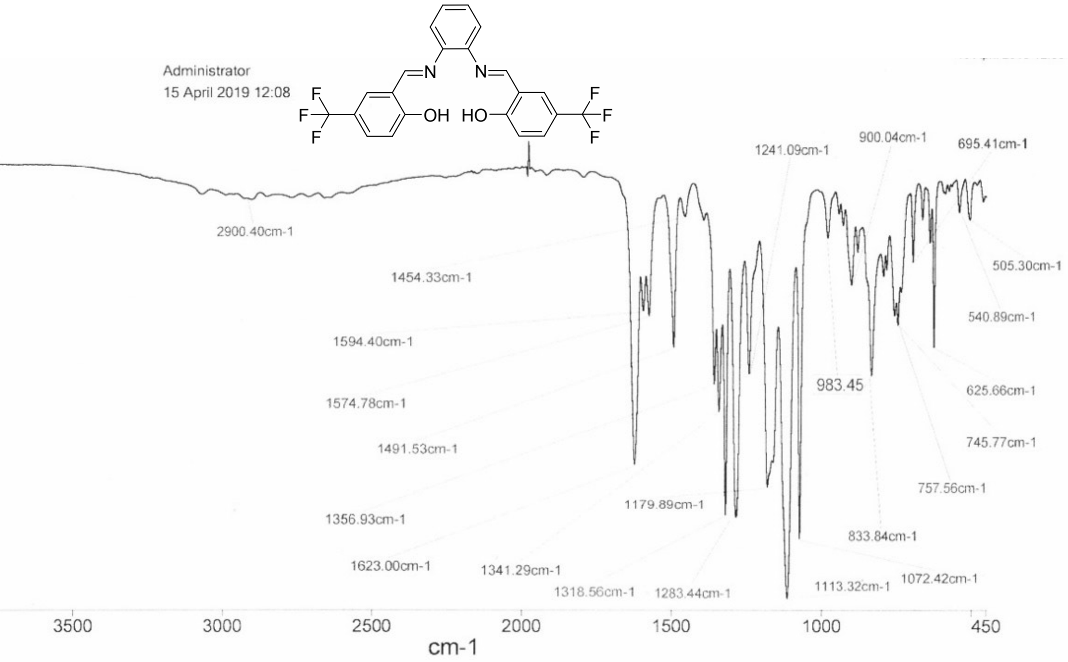
. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
1184	1	C22H17F6N2O2	455.1189	1.1	0.5	10.7	0.5

IR spectra of salophen ligands

2,2'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3,5-dimethoxyphenol) (1g)

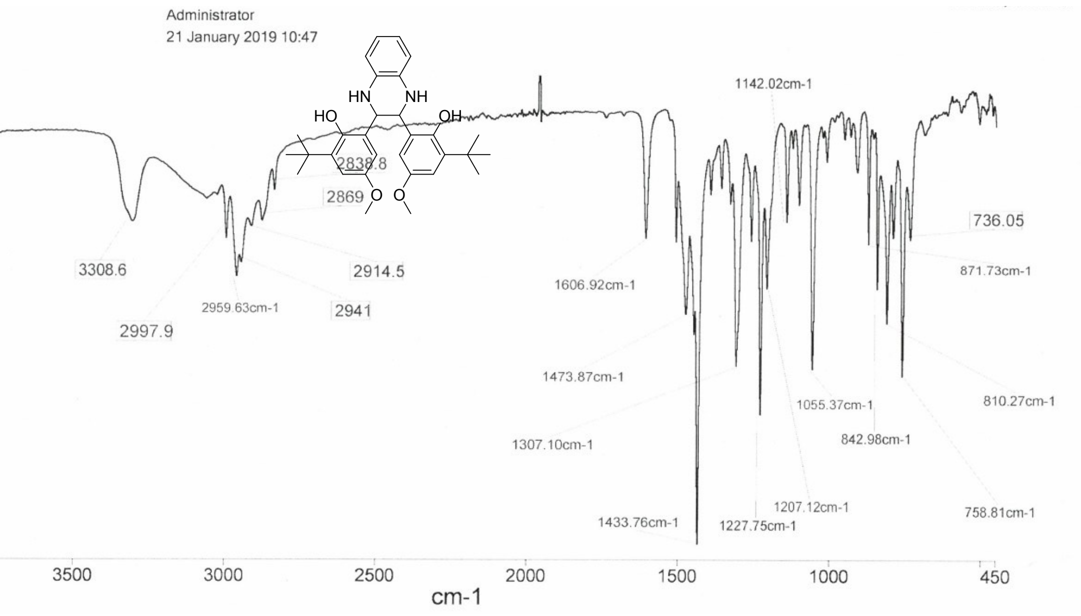


N,*N*'-Bis(2-hydroxy-5-trifluoromethyl)-1,2-phenylenediamine (1h)

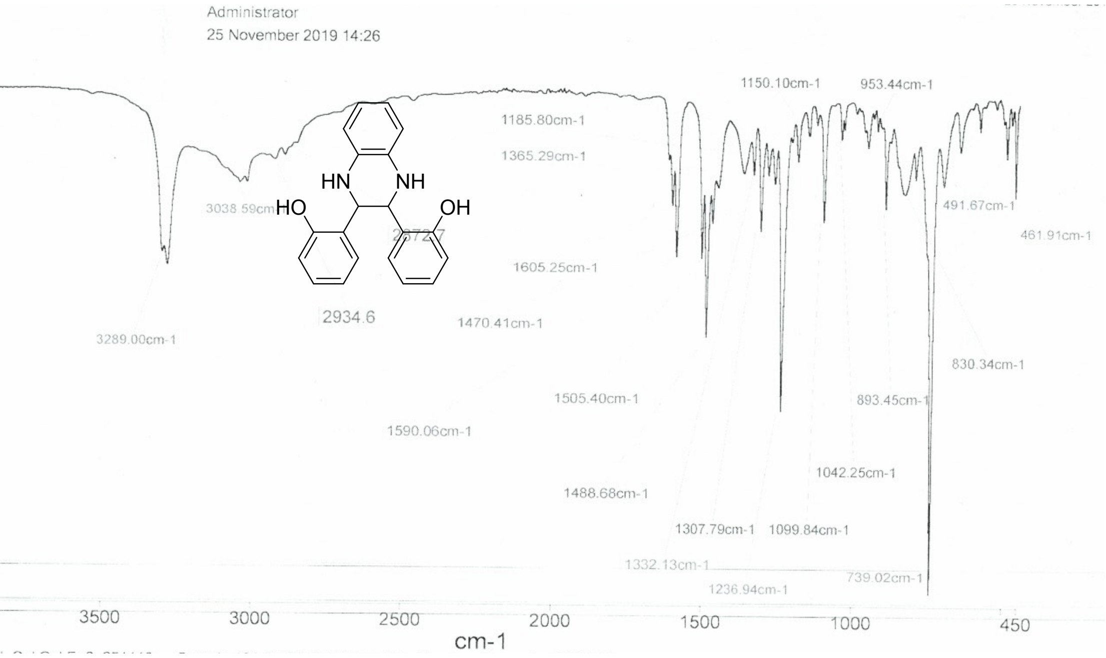

Administrator
15 April 2019 12:08
F
F
F
OH
HO
N
N
F
F
F
2900.40cm-1
1454.33cm-1
1594.40cm-1
1574.78cm-1
1491.53cm-1
1356.93cm-1
1623.00cm-1
1341.29cm-1
1318.56cm-1
1283.44cm-1
1179.89cm-1
1241.09cm-1
900.04cm-1
695.41cm-1
983.45
833.84cm-1
1113.32cm-1
1072.42cm-1
757.56cm-1
745.77cm-1
625.66cm-1
540.89cm-1
505.30cm-1
3500
3000
2500
2000
1500
1000
450
cm-1

IR spectra of tetrahydroquinoxalines

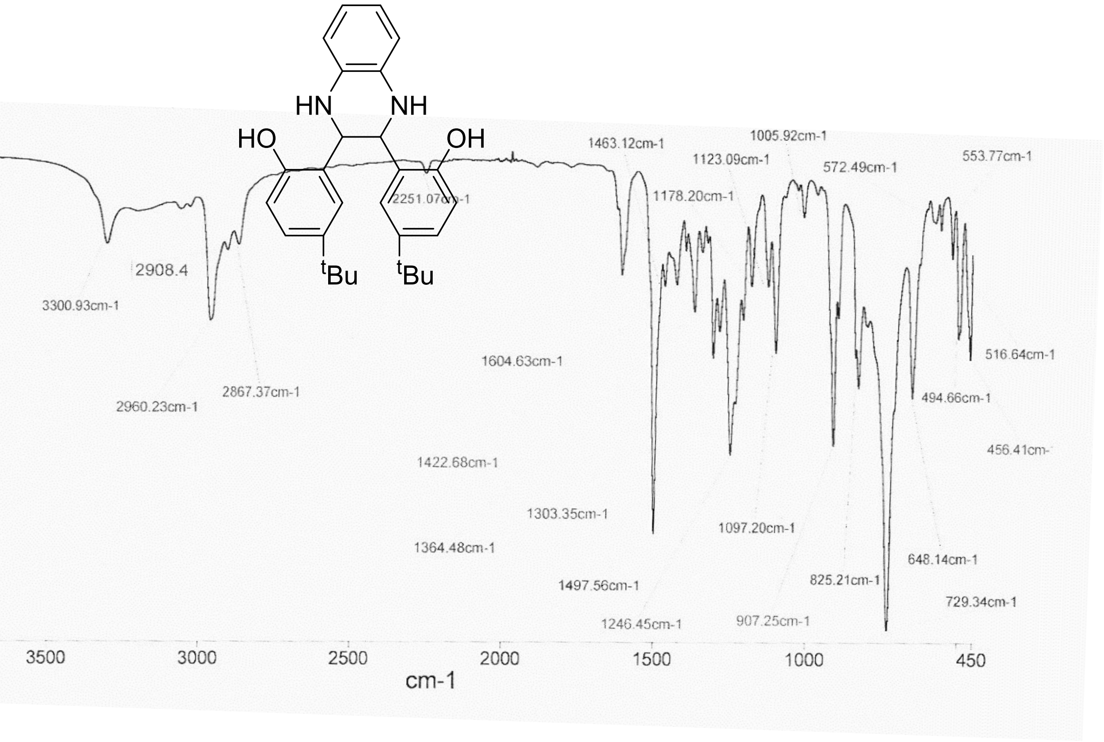
6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(2-(*tert*-butyl)-4-methoxyphenol) (3a)



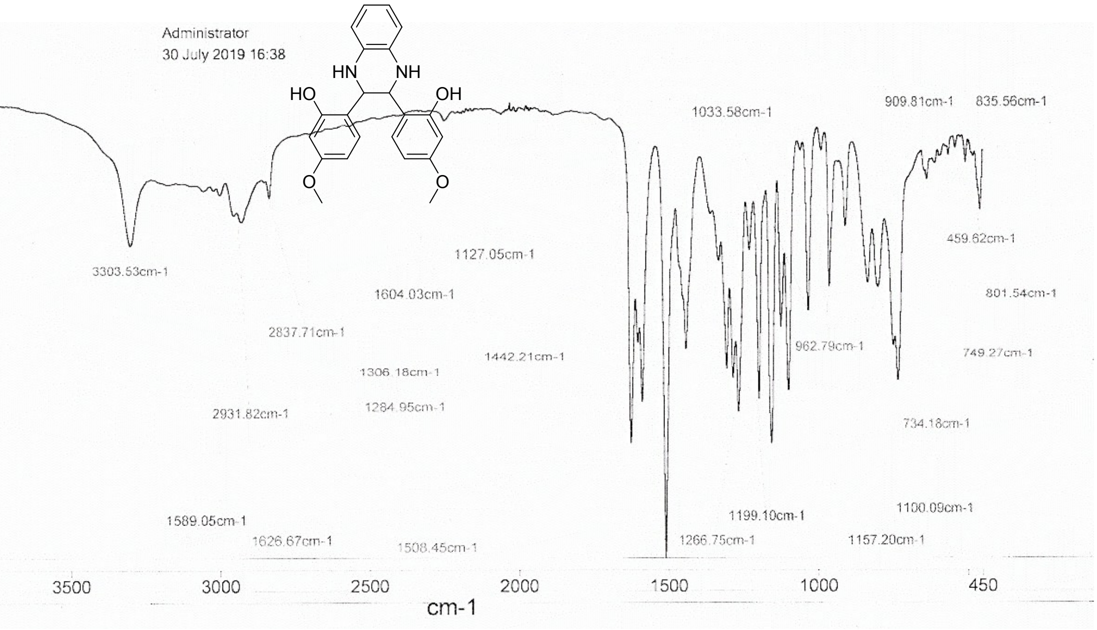
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)diphenol (3b)


Administrator
25 November 2019 14:26
HN
NH
HO
OH
3289.00cm-1
3038.59cm
2934.6
2727
1185.80cm-1
1365.29cm-1
1605.25cm-1
1470.41cm-1
1505.40cm-1
1590.06cm-1
1488.68cm-1
1150.10cm-1
953.44cm-1
491.67cm-1
461.91cm-1
830.34cm-1
893.45cm-1
1042.25cm-1
1307.79cm-1
1099.84cm-1
1332.13cm-1
1236.94cm-1
739.02cm-1
3500
3000
2500
2000
1500
1000
450
cm-1

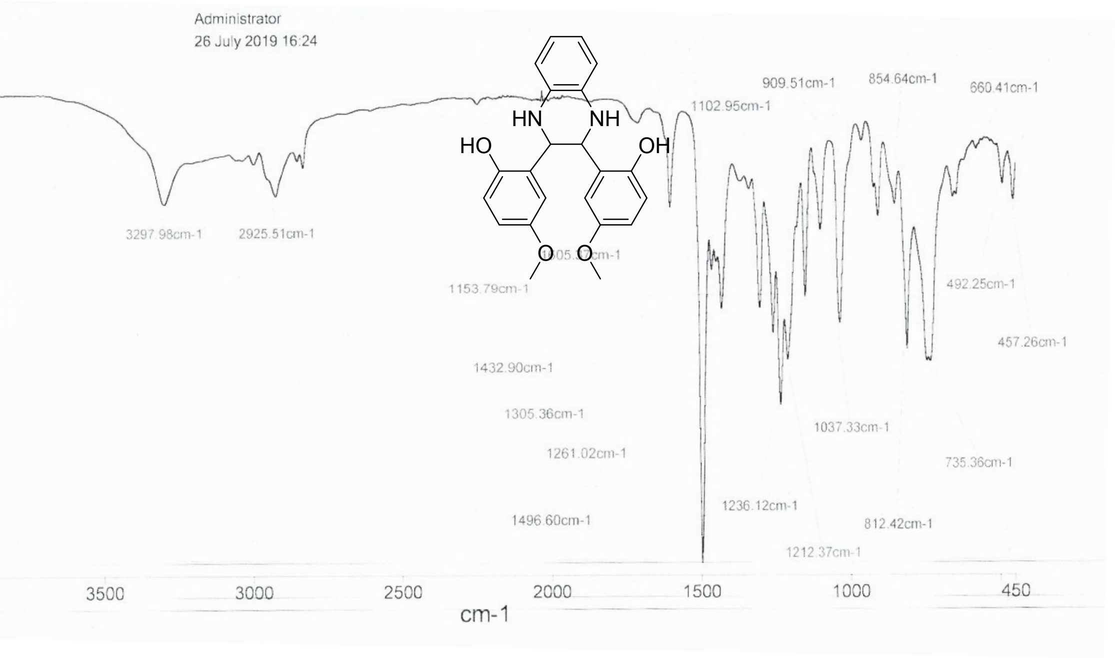
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(*tert*-butyl)phenol) (3c)



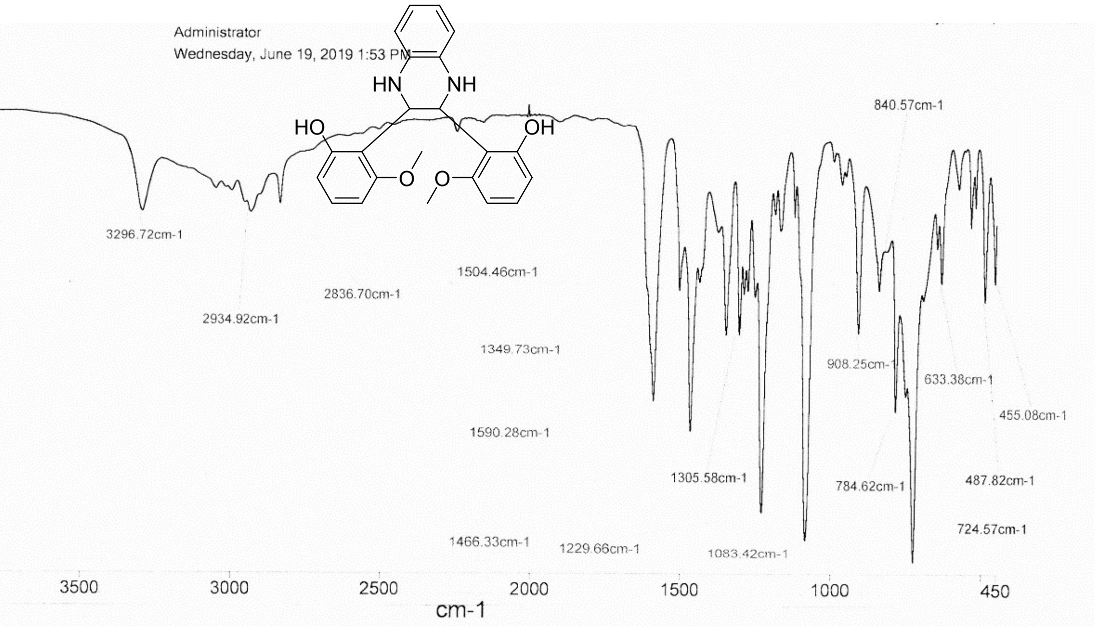
6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3d)



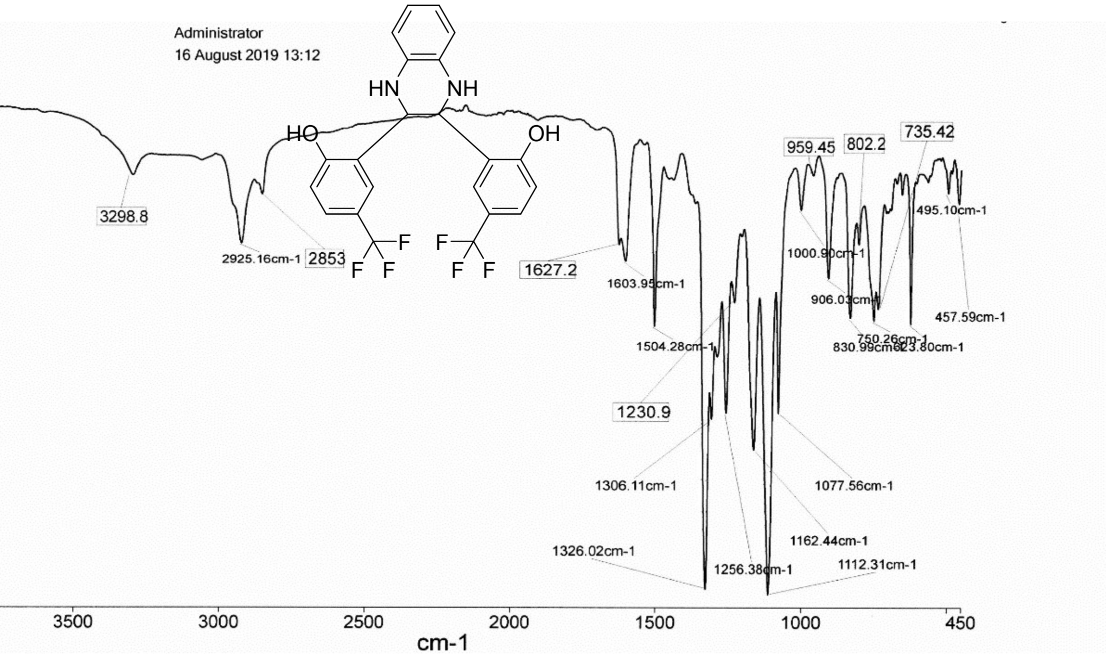
2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-methoxyphenol) (3e)



2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3f)


Administrator
Wednesday, June 19, 2019 1:53 PM
HN
NH
HO
OH
O
O
3296.72cm-1
2934.92cm-1
2836.70cm-1
1504.46cm-1
1349.73cm-1
1590.28cm-1
1466.33cm-1
1229.66cm-1
1305.58cm-1
1083.42cm-1
840.57cm-1
908.25cm-1
633.38cm-1
784.62cm-1
455.08cm-1
487.82cm-1
724.57cm-1
3500
3000
2500
2000
1500
1000
450
cm-1

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(trifluoromethyl)phenol) (3h)



Cyclic voltammetry

General

Cyclic voltammetry analysis was performed using an EmStat3 potentiostat and PSTrace5.7 software (PalmSens). Cyclic voltammetry experiments were performed using two separate Pt wires as a counter and a reference electrode, and a glassy carbon electrode as the working electrode. The experiments were performed in a specially designed glass electrochemical chamber/reaction vessel designed in-house at the University of York (Figure 1). Glassy carbon electrodes were prepared by polishing with an aluminium-water slurry paste, using aluminium oxide (1-5 micron powder, 99+%, Strem Chemicals) and de-ionised water on a polishing pad. The electrode was then washed with water before polishing with an alumina solution (alumina suspension, 0.3 microns, MetPrep). The carbon electrode was then placed in a centrifuge tube of de-ionised water and sonicated (3 x 5 mins). The water was discarded from the centrifuge tube and replenished for each sonication. This process was repeated prior to analysing every solution.[17]

Figure 1: Electrochemical cell used to perform cyclic voltammetry experiments.

All electrochemical solutions contained 1 mM of analyte, 1 mM of ferrocene and 100 mM of tetrabutylammonium hexafluorophosphate in dry THF. Control reference experiments were performed with a reference solution of 1 mM of ferrocene and 100 mM of tetrabutylammonium hexafluorophosphate in dry THF. Analysis was performed under ambient conditions and solutions were pre-purged with N_2(g) for 2-3 min. prior to analysis.

All cyclic voltammograms reported were performed under $N_2(g)$. The glass reaction vessel was washed with THF in-between runs. The ferrocene control solution was analysed from -2.0 V to +2.0 V versus Pt and from -1.0 V to +2.0 V versus Pt, with a scan rate of 100 mV s^{-1} over 4-5 scans. Reducing agents and complex **2a** were analysed from a starting potential of 0.0 V versus Pt to a potential of -2.0 V versus Pt, in increasing 0.5 V increments, before then analysing from 0.0 V to +2.0 V versus Pt, also in increasing 0.5 V increments, with a scan rate of 100 mV s^{-1} over 5-10 scans. All analysis was performed with an E step of 0.005 V, current range of 100 mA to 10 nA and equilibration time of 2 s. All reported $E_{1/2}$ values are quoted versus Pt (Table S1) and are average values of 3-10 runs.

Table S1: $E_{1/2}$ values of reducing agents and chromium(salophen) complex **2a**

Complex	**$E_{1/2}$ (V vs Pt)**[a]	**STD**[b]	**$E_{1/2}$ (V vs SHE)**[c]	**$E_{1/2}$ (V vs SHE) lit**[d]	**Redox process**
Decamethylcobaltocene	-1.23	0.028	-1.50	-1.54[18]	$[Co(\eta^5\text{-}C_5Me_5)_2]^+ + e^- \leftrightarrow Co(\eta^5\text{-}C_5Me_5)_2$
Samarium(II) iodide	-1.04	0.060	-1.31	-1.55[19]	$Sm^{3+} + e^- \leftrightarrow Sm^{2+}$
Titanocene dichloride	-0.67	0.006	-0.94	-0.81[20]	$[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]^+ + e^- \leftrightarrow Ti(\eta^5\text{-}C_5H_5)_2Cl_2$
Titanocene dichloride	-0.67	0.006	-0.94	-0.90[19]	$Ti^{3+} + e^- \leftrightarrow Ti^{2+}$
Chromium(II) chloride	-0.13	N/A	-0.40	-0.41[19]	$Cr^{3+} + e^- \leftrightarrow Cr^{2+}$
Decamethylferrocene	+0.11	0.007	-0.16	-0.19[18]	$Me_{10}Fc^+ + e^- \leftrightarrow Me_{10}Fc$
Chromium salophen complex **2a** (peak 1)[e]	+0.92	0.016	+0.65	+0.78[21]	Metal phenoxyl oxidation[22,23]
Chromium salophen complex **2a** (peak 2)[e]	+1.19	0.007	+0.92	+0.89[21]	Metal bis-phenoxyl oxidation[22,23]

a) Experimental reduction potentials recorded in THF vs Pt. All experimental $E_{1/2}$ results are average results from a minimum of 3 runs.

b) Standard deviation of $E_{1/2}$ results.

c) Experimental $E_{1/2}$ converted to vs SHE.

d) Literature $E_{1/2}$ values under standard electrochemical conditions in aqueous solution vs SHE.

e) Reported $E_{1/2}$ values for a copper non-halide version of **2a** for comparison. Salen and salophen complexes undergo two reversible one-electron redox processes, due to the oxidation of both phenolic moieties.

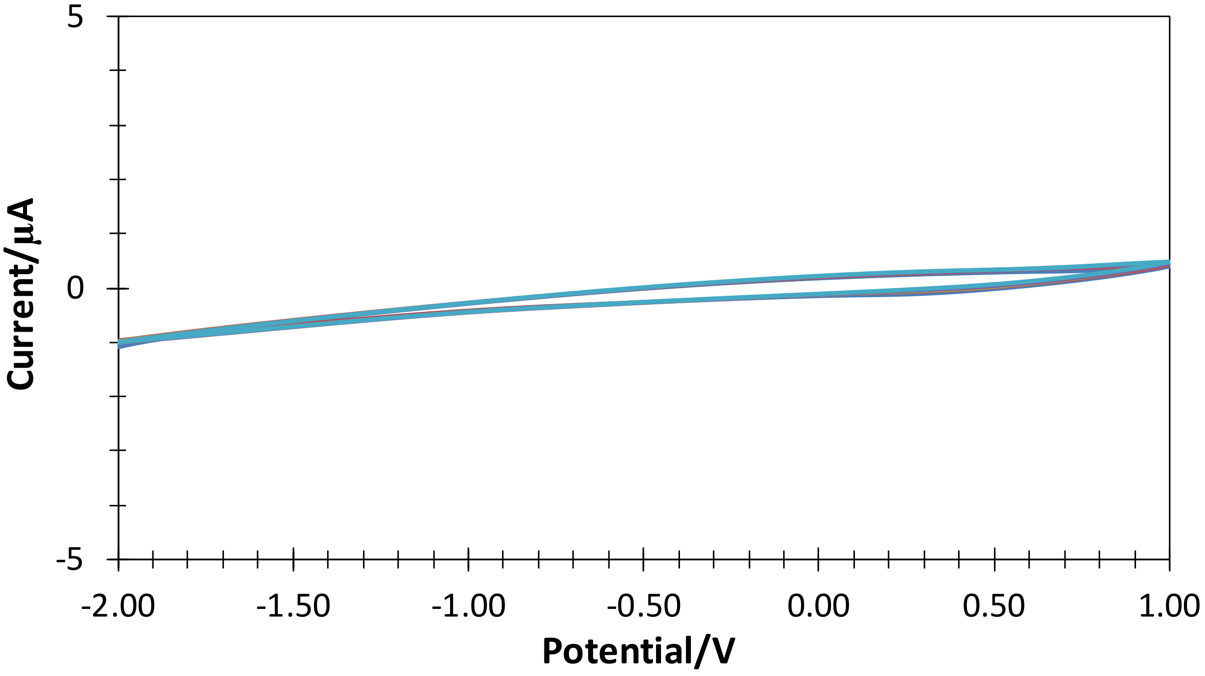
Comparing to SHE values

By analysing the ferrocene standard solution, it was found that the reduction potential ($E_{1/2}$) for ferrocene was +0.589 V (± 0.012 V) versus Pt in THF with tetrabutylammonium hexafluorophosphate. The reported value of $E_{1/2}$ for ferrocene in THF with tetrabutylammonium hexafluorophosphate is +0.560 V versus SCE,[18] which correlates to +0.319 V versus SHE (0.560-0.241 V).[19] The difference between the $E_{1/2}$ versus Pt and $E_{1/2}$ versus SHE was therefore 0.270 V (0.589-0.319 V). To compare the reported experimental $E_{1/2}$ values to those quoted in the literature versus SHE, all values were therefore changed by 0.270 V to report them versus SHE (Table S1).

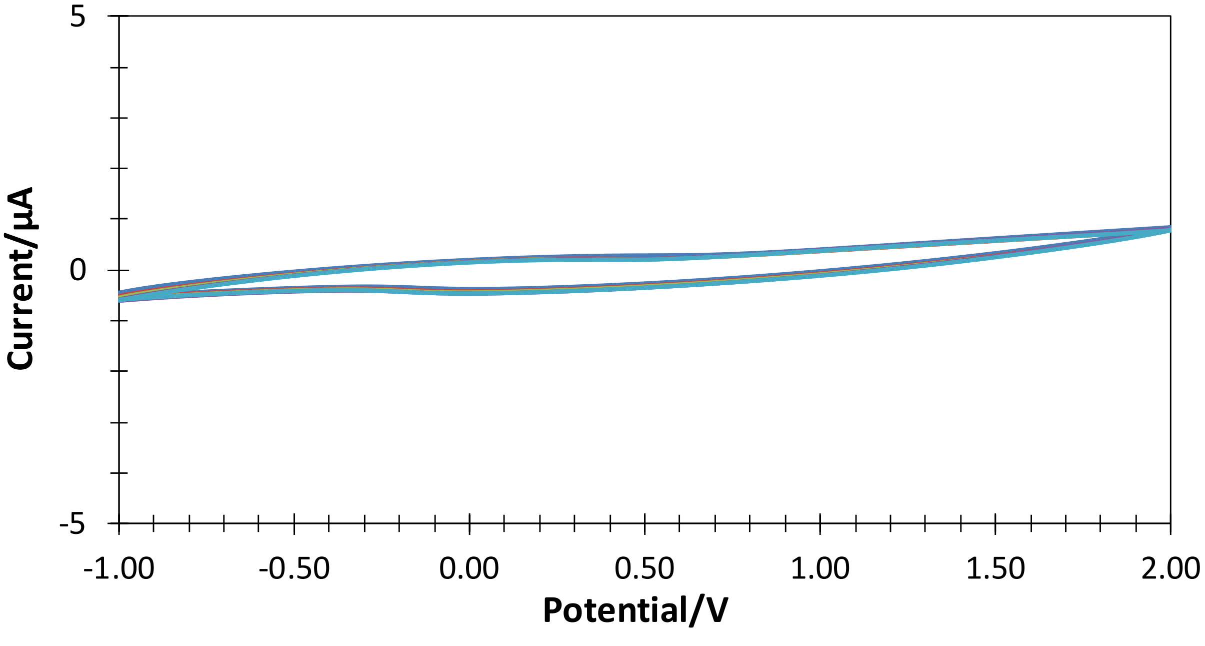
Cyclic voltammograms

Where inserts are shown, these are the results of separate experiments with a narrower scan range rather than expansions of the main plot.

Bare electrodes

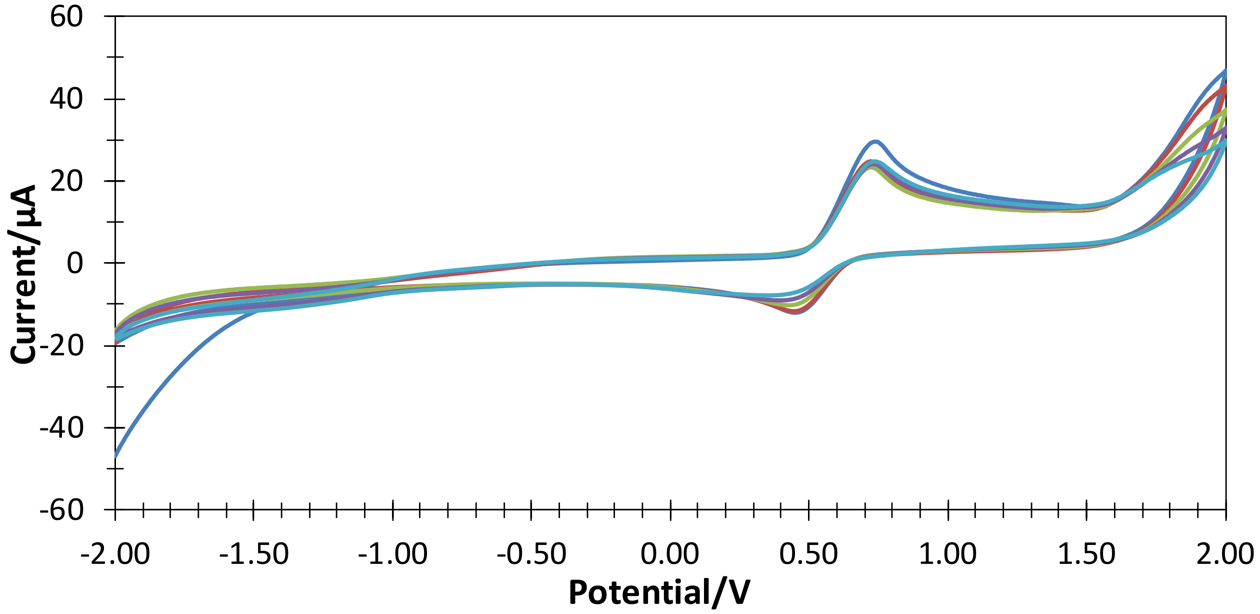


Cyclic voltammogram of bare electrodes in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-2.0 V to +1.0 V vs Pt.**

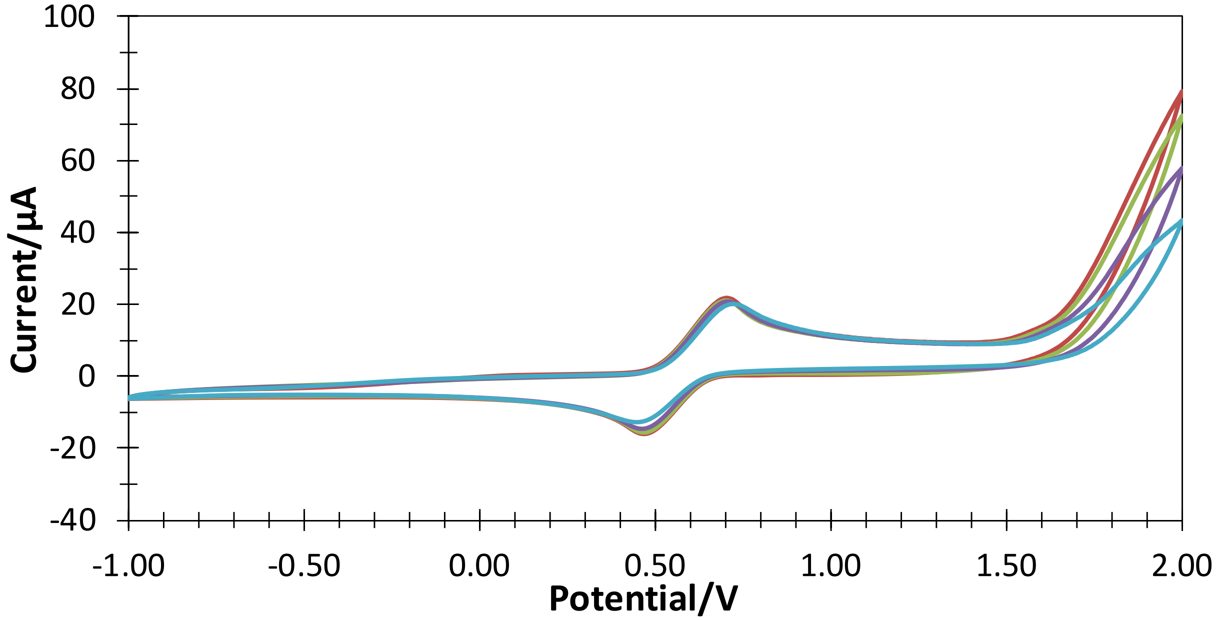


Cyclic voltammogram of bare electrodes in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-1.0 V to +2.0 V vs Pt.**

Ferrocene control

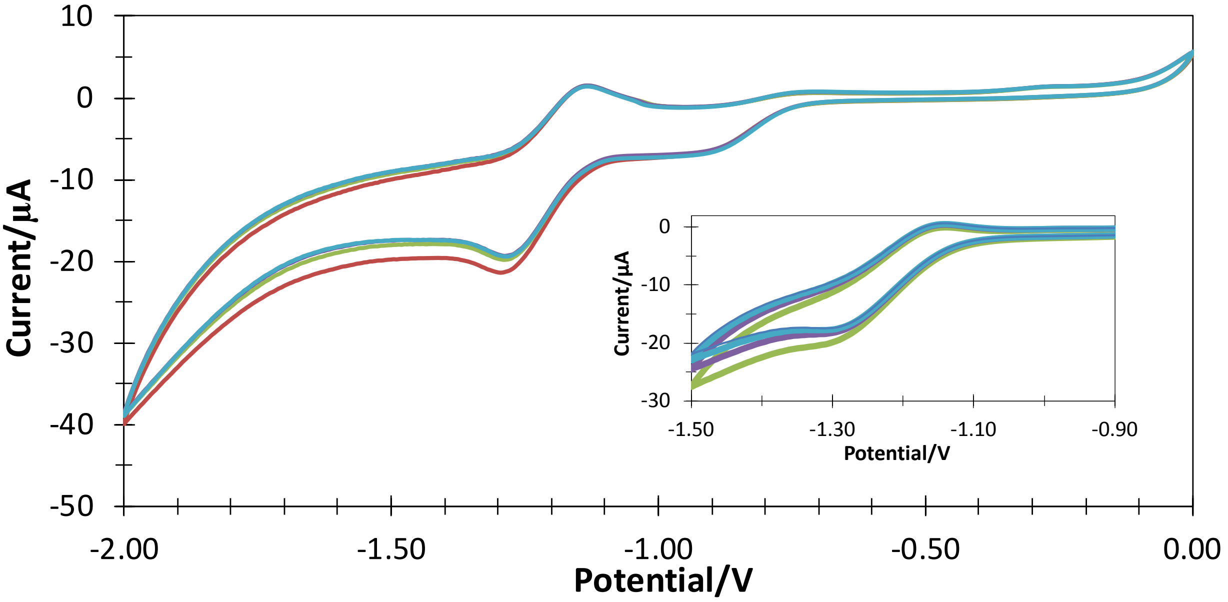


Cyclic voltammogram of 1 mM of ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-2.0 V to +2.0 V vs Pt.**

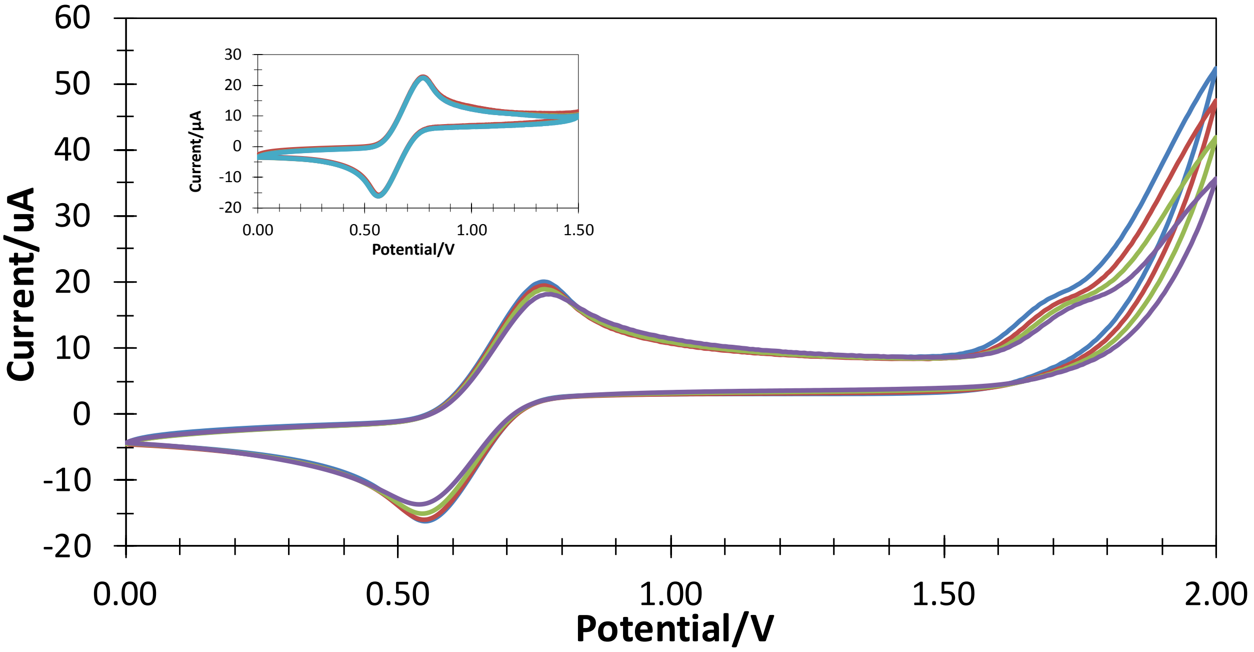


Cyclic voltammogram of 1 mM of ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-1.0 V to +2.0 V vs Pt.**

Decamethylcobaltocene

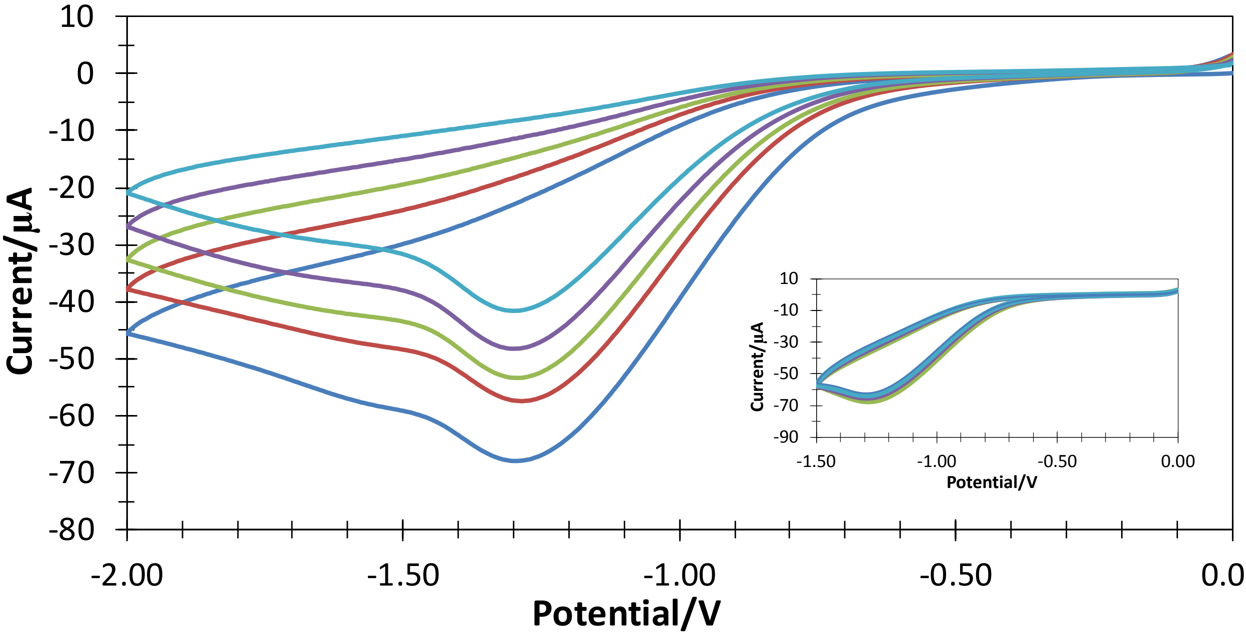


Cyclic voltammogram of 1 mM of decamethylcobaltocene, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-2.0 V to 0.0 V vs Pt.**

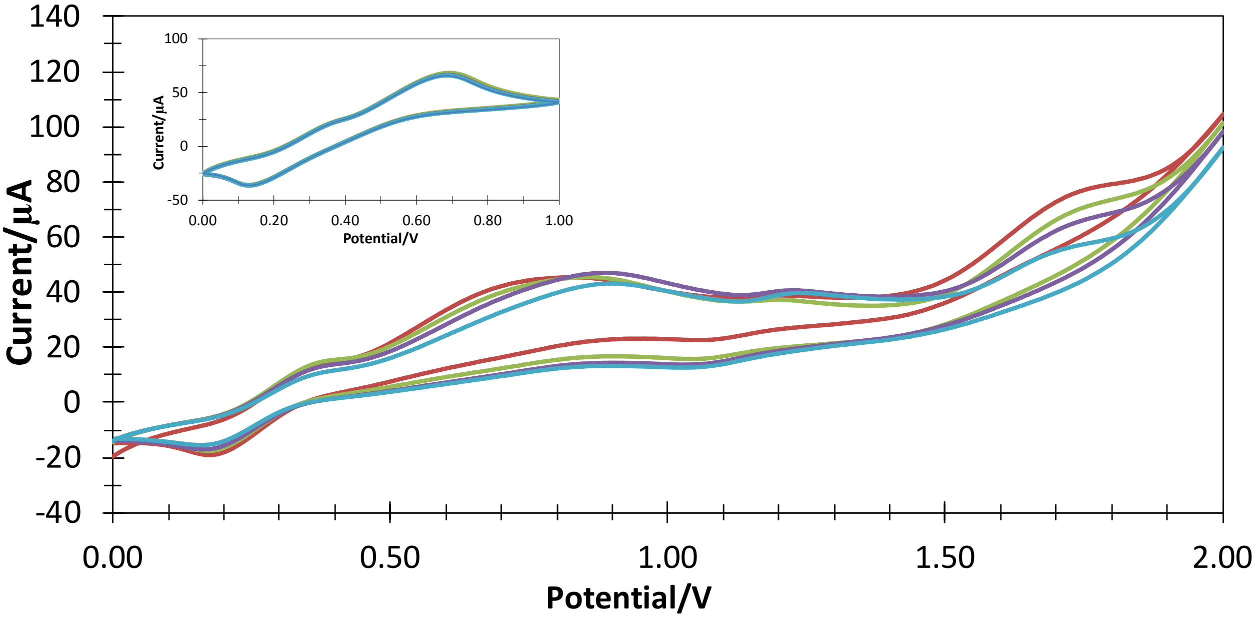


Cyclic voltammogram of 1 mM of decamethylcobaltocene, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **0.0 V to +2.0 V vs Pt.**

Samarium(II) iodide

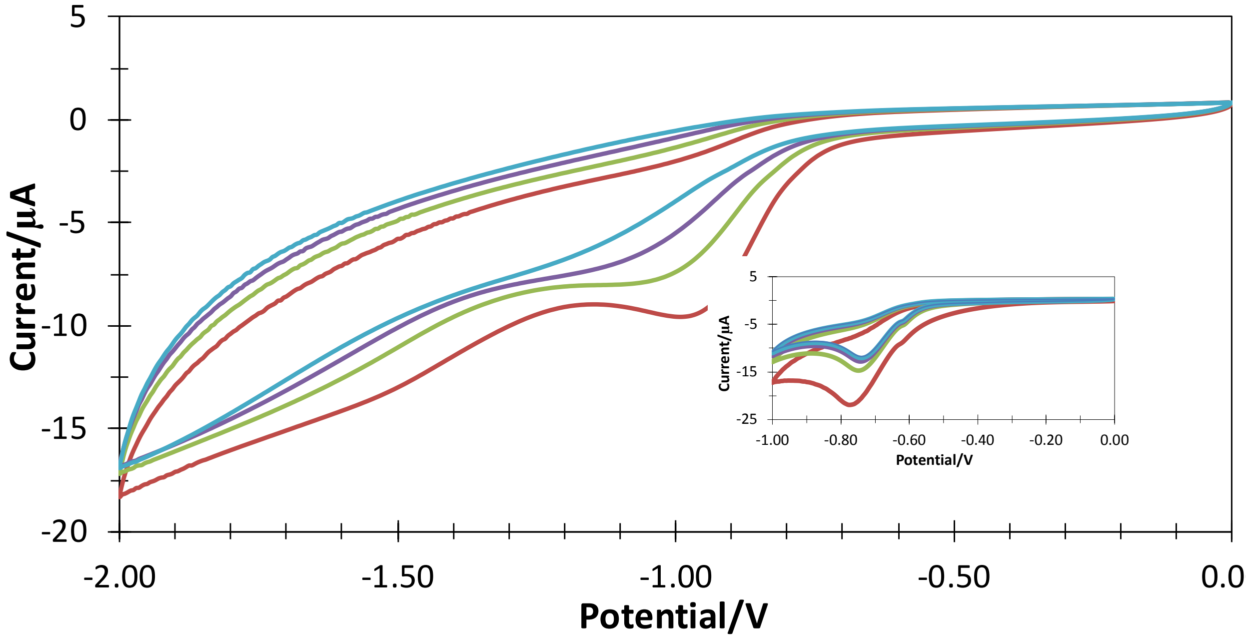


Cyclic voltammogram of 1 mM of samarium(II) iodide, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-2.0 V to 0.0 V vs Pt.**

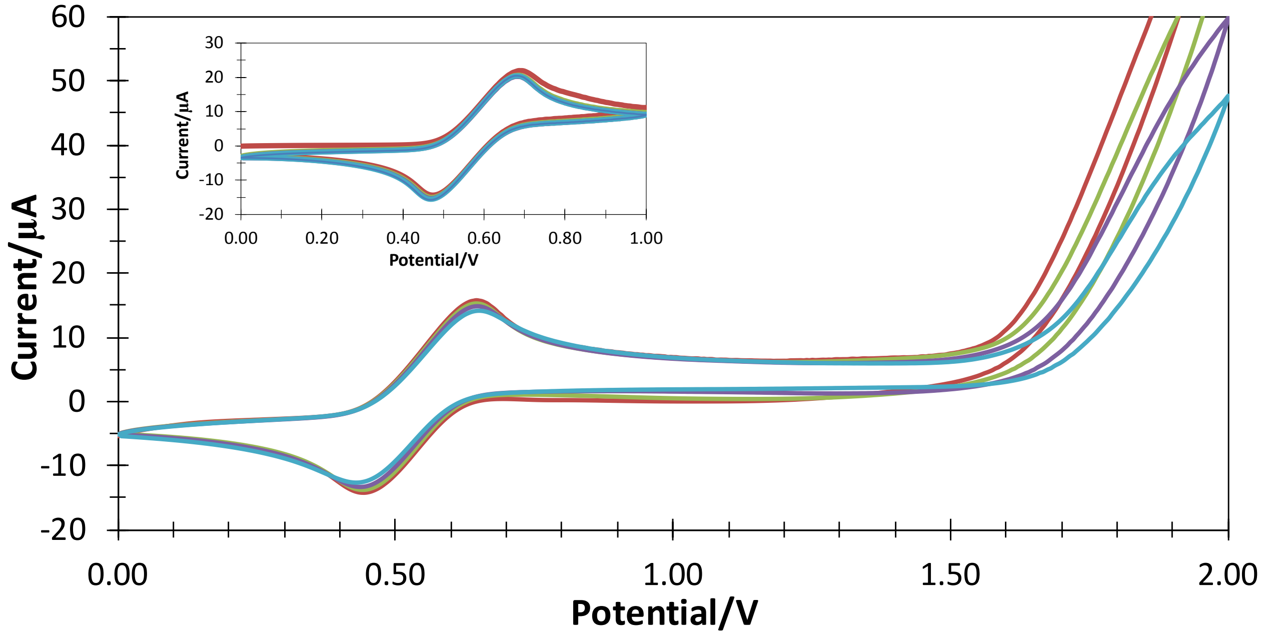


Cyclic voltammogram of 1 mM of samarium(II) iodide, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **0.0 V to +2.0 V vs Pt.**

Titanocene dichloride

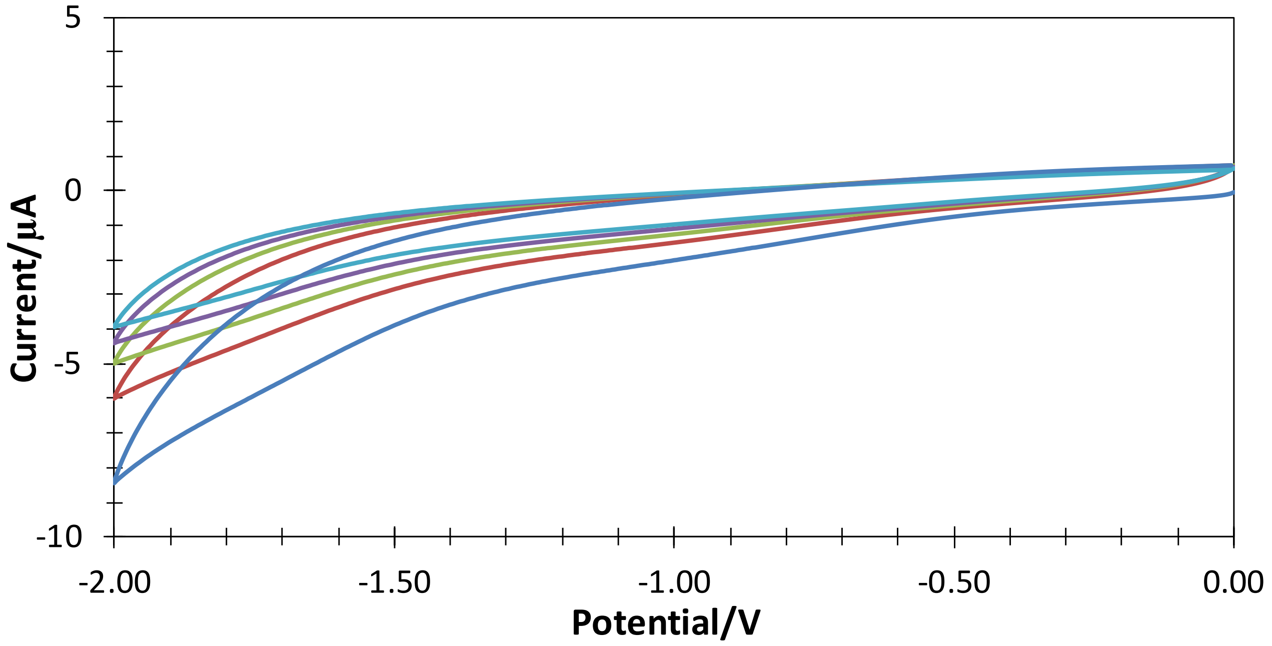


Cyclic voltammogram of 1 mM of titanocene dichloride, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from **-2.0 V to 0.0 V vs Pt.**

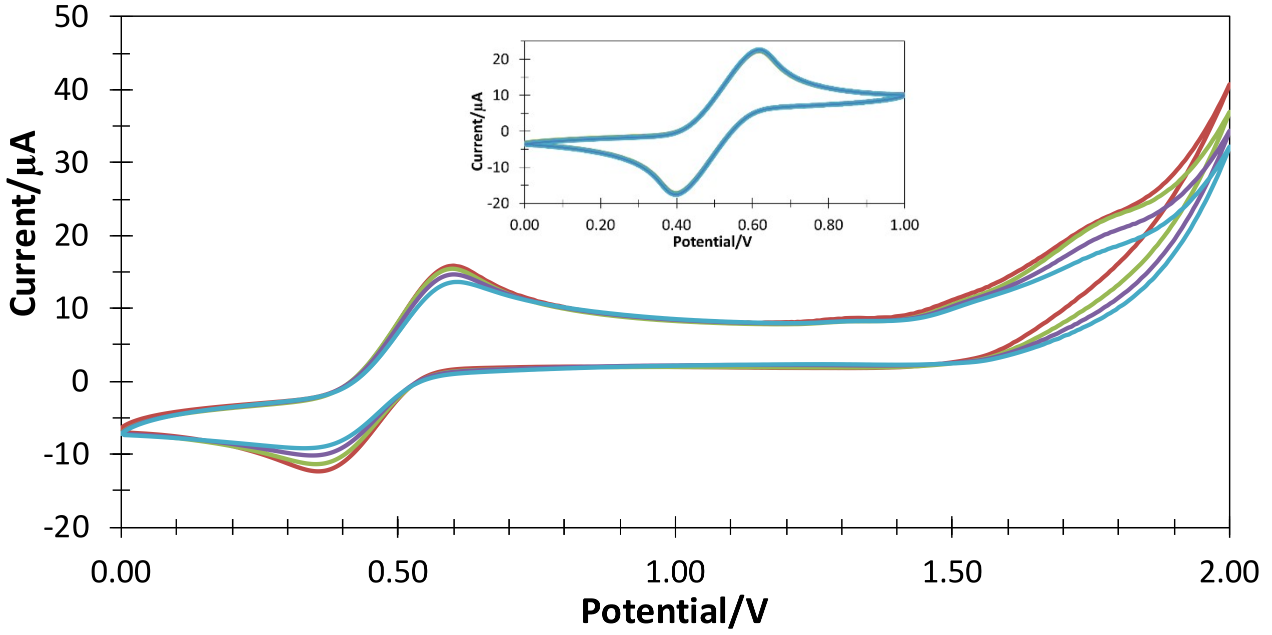


Cyclic voltammogram of 1 mM of titanocene dichloride, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from 0**.0 V to +2.0 V vs Pt.**

Chromium(II) chloride

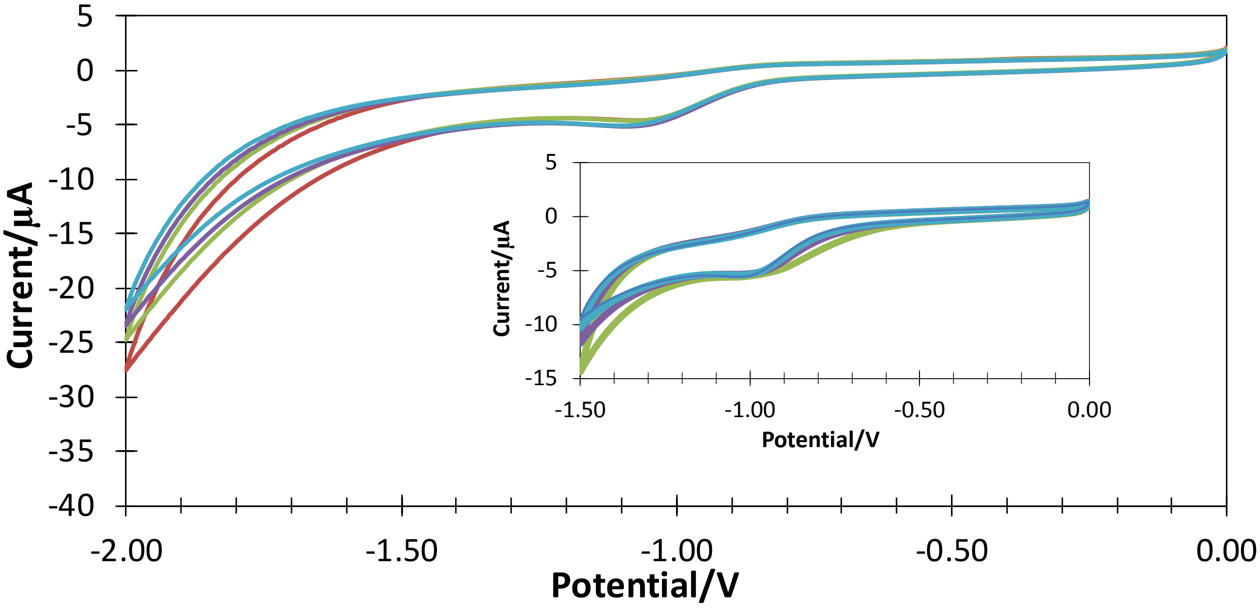


Cyclic voltammogram of 1 mM of chromium(II) chloride, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from -2**.0 V to 0.0 V vs Pt.**

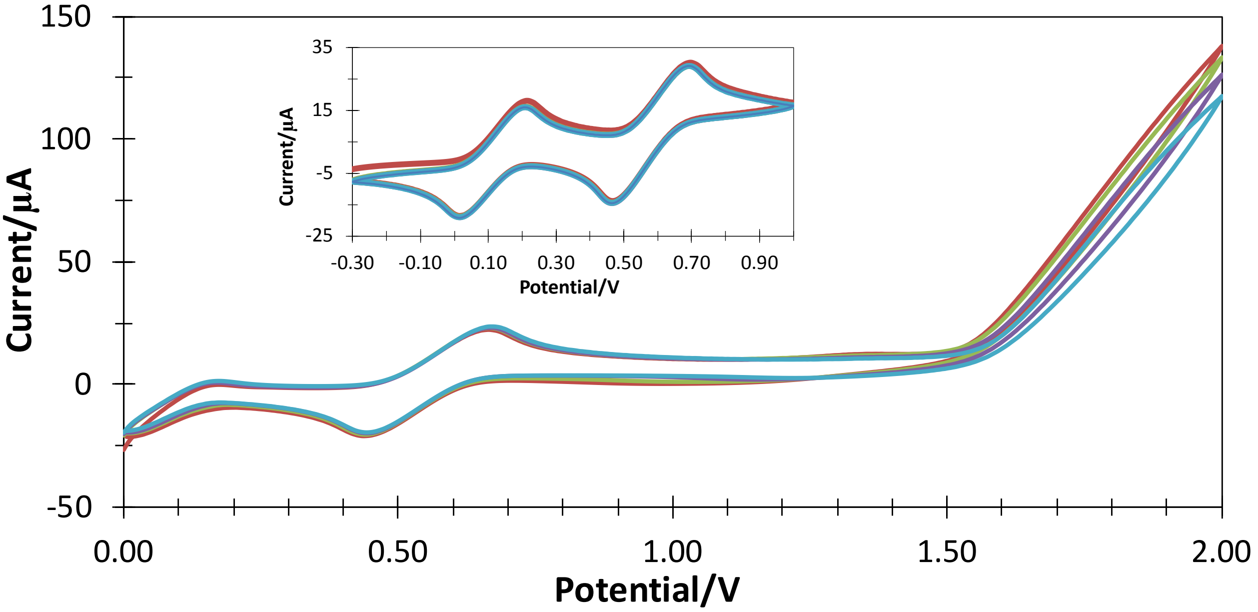


Cyclic voltammogram of 1 mM of chromium(II) chloride, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from 0**.0 V to +2.0 V vs Pt.**

Decamethylferrocene

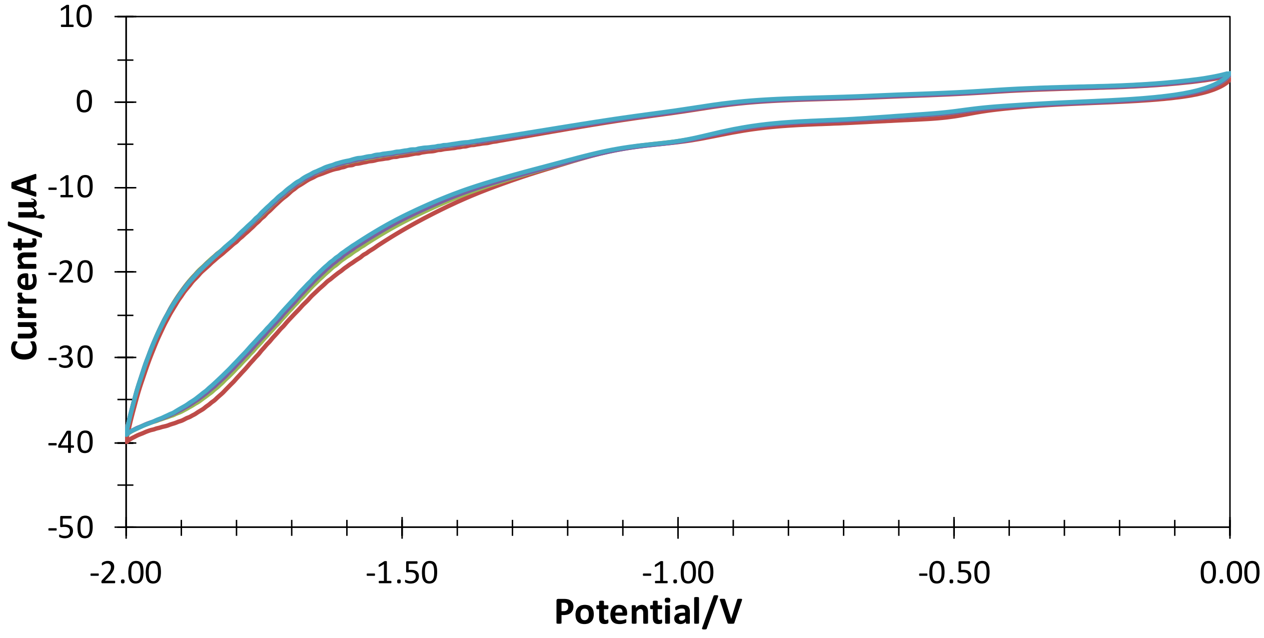


Cyclic voltammogram of 1 mM of decamethylferrocene, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from -2**.0 V to 0.0 V vs Pt.**

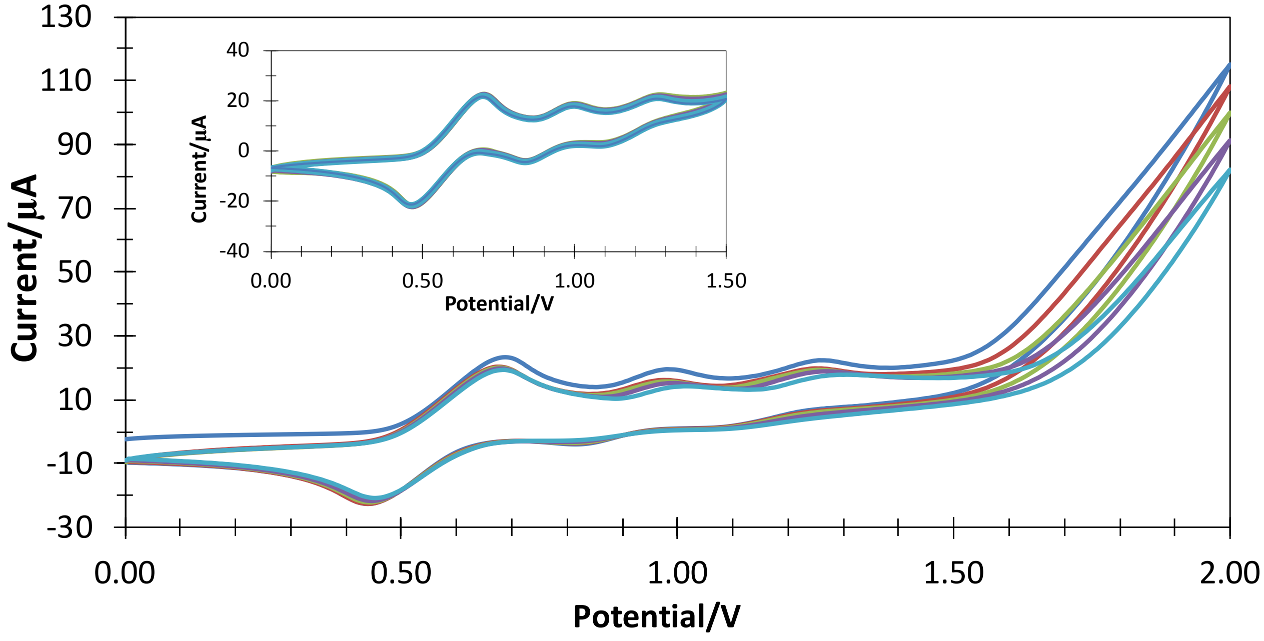


Cyclic voltammogram of 1 mM of decamethylferrocene, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from 0**.0 V to +2.0 V vs Pt.**

Chromium(III) salophen complex (2a)



Cyclic voltammogram of 1 mM of **2a**, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from -2.**0 V to +0.0 V vs Pt.**



Cyclic voltammogram of 1 mM of **2a**, with 1 mM ferrocene in THF and 100 mM tetrabutylammonium hexafluorophosphate, from 0.**0 V to +2.0 V vs Pt.**

X-ray crystallography

Experimental procedures

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-K_α radiation (λ = 1.54184 Å) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis".[24] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[25] OLEX2[26] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution was "ShelXT dual-space"[27] . Refinement by full-matrix least-squares used the SHELXL[28] algorithm within OLEX2.[26] All non-hydrogen atoms were refined anisotropically.

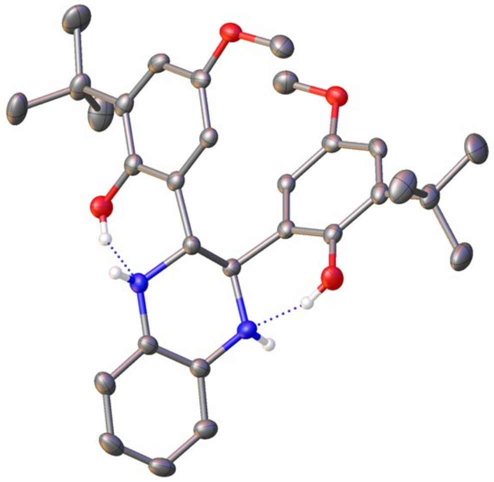
X-ray data for compounds 3a-c,f,h

Compound	3a	3b	3c	3f	3h
ID	mn1601	mn1904	mn1909	mn1908	mn2001
CCDC	1983173	1983171	1983172	1983170	1983169
Empirical formula	$C_{30}H_{38}N_2O_4$	$C_{20}H_{18}N_2O_2$	$C_{28}H_{34}N_2O_2$	$C_{22}H_{22}N_2O_4$	$C_{22}H_{16}F_6N_2O_2$
Formula weight	490.62	318.36	430.57	378.41	454.37
Temperature/K	110.05(10)	110.00(14)	110.00(10)	110.00(10)	110.05(10)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	C2/c	$P2_1/n$	$P2_1/c$	P-1	Pbcn
a/Å	17.8343(6)	7.16584(13)	16.29085(17)	7.3701(5)	28.1272(4)
b/Å	12.4405(4)	10.4417(2)	20.8151(2)	10.2836(7)	9.04947(13)
c/Å	13.0921(5)	21.8016(4)	23.2057(3)	12.5573(7)	14.7304(2)
α/°	90	90	90	97.383(5)	90
β/°	107.301(4)	96.8756(17)	105.2865(12)	104.649(6)	90
γ/°	90	90	90	99.610(6)	90
Volume/Å^3	2773.29(17)	1619.54(6)	7590.57(15)	893.21(10)	3749.43(9)
Z	4	4	12	2	8
ρ_{calc}g/cm^3	1.175	1.306	1.130	1.407	1.610
μ/mm^{-1}	0.618	0.683	0.552	0.796	1.265
F(000)	1056.0	672.0	2784.0	400.0	1856.0
Crystal size/mm^3	0.2008 × 0.1607 × 0.1298	0.258 × 0.098 × 0.048	0.166 × 0.092 × 0.044	0.218 × 0.176 × 0.113	0.267 × 0.163 × 0.141
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.804 to 142.972	8.17 to 134.09	7.048 to 134.154	7.396 to 134.072	10.268 to 134.104
Index ranges	-21 ≤ h ≤ 13, -15 ≤ k ≤ 14, -13 ≤ l ≤ 15	-8 ≤ h ≤ 5, -12 ≤ k ≤ 12, -25 ≤ l ≤ 26	-19 ≤ h ≤ 19, -24 ≤ k ≤ 13, -25 ≤ l ≤ 27	-8 ≤ h ≤ 6, -12 ≤ k ≤ 11, -14 ≤ l ≤ 14	-26 ≤ h ≤ 33, -10 ≤ k ≤ 5, -9 ≤ l ≤ 17
Reflections collected	4991	5918	29179	5380	8178
Independent reflections	2640 [R_{int} = 0.0124, R_{sigma} = 0.0171]	2901 [R_{int} = 0.0178, R_{sigma} = 0.0236]	13536 [R_{int} = 0.0228, R_{sigma} = 0.0304]	3183 [R_{int} = 0.0160, R_{sigma} = 0.0247]	3350 [R_{int} = 0.0154, R_{sigma} = 0.0180]
Data/restraints/parameters	2640/0/168	2901/0/290	13536/0/926	3183/0/342	3350/0/354
Goodness-of-fit on F^2	1.062	1.040	1.047	1.032	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 =0.0966	R_1 = 0.0322, wR_2 = 0.0752	R_1 = 0.0504, wR_2 = 0.1290	R_1 = 0.0329, wR_2 = 0.0829	R_1 = 0.0343, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0414, wR_2 = 0.1008	R_1 = 0.0381, wR_2 = 0.0789	R_1 = 0.0646, wR_2 = 0.1379	R_1 = 0.0393, wR_2 = 0.0875	R_1 = 0.0389, wR_2 = 0.0942
Largest diff. peak/hole / e Å^{-3}	0.23/-0.22	0.24/-0.14	0.44/-0.19	0.23/-0.22	0.42/-0.37

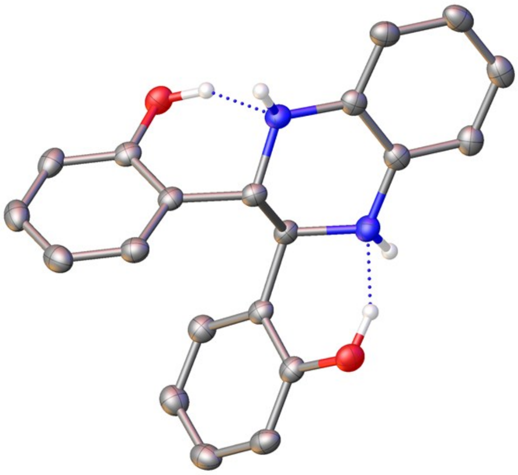
Hydrogen bond data

Phenolic H to N Hydrogen Bonds							
Compound	**D**	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
3a	O2	H2	N1	0.82	1.97	2.6977(13)	147.6
3b	O1	H1A	N1	0.923(19)	1.926(19)	2.7308(15)	144.5(15)
	O2	H2B	N2	0.94(2)	1.85(2)	2.6844(14)	146.4(17)
3c	O1	H1A	N1	0.82(3)	2.04(3)	2.771(2)	148(3)
	O2	H2B	N2	0.85(3)	1.93(3)	2.689(2)	149(3)
	O3	H3B	N3	0.82	2.02	2.726(2)	144.3
	O4	H4A	N4	0.82	2.08	2.783(3)	144.1
	O5	H5B	N5	0.84(3)	1.93(3)	2.696(2)	151(3)
	O6	H6A	N6	0.86(3)	1.93(3)	2.695(2)	148(2)
3f	O1	H1A	N1	0.93(2)	1.84(2)	2.6731(15)	148.3(18)
	O4	H4A	N2	0.94(2)	1.80(2)	2.6583(15)	150.9(19)
3h	O1	H1A	N1	0.85(3)	1.87(3)	2.6490(17)	152(2)
	O2	H2B	N2	0.87(2)	1.87(2)	2.6718(17)	152(2)

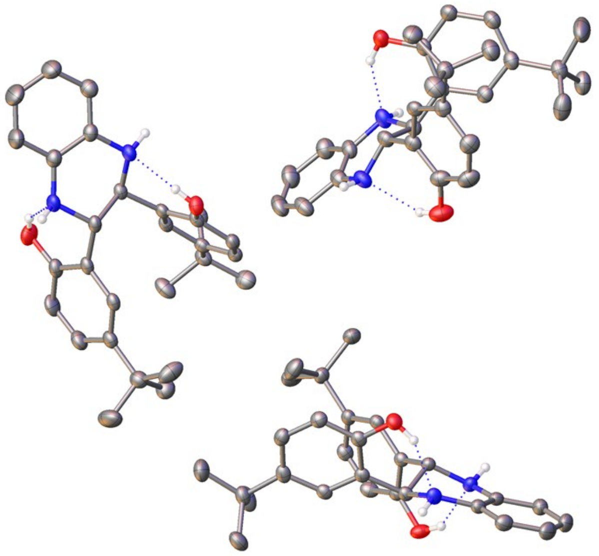
6,6'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(2-(*tert*-butyl)-4-methoxyphenol) (3a)



2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)diphenol (3b)

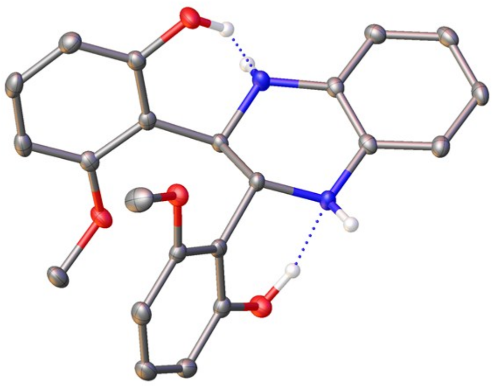


2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(*tert*-butyl)phenol) (3c)

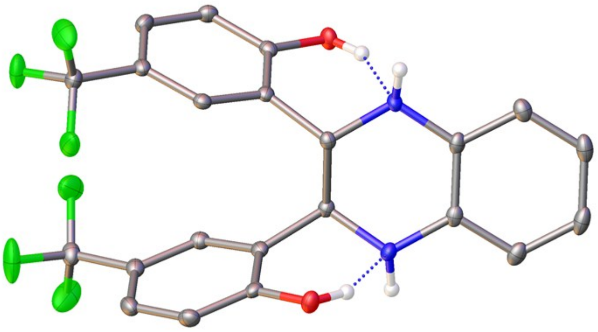


For **3c**, the crystal contained highly disordered solvents of crystallisation for which a satisfactory discrete atom model could not be obtained. Therefore a solvent mask was used which revealed two solvent voids per unit cell with a predicted electron count of 38 which corresponds approximately to one dichloromethane. The asymmetric unit contained 3 molecules of the phenol. Acidic hydrogens were located by difference map and allowed to refine apart from H3b and H4b. For these two hydrogens, refinement gave unrealistic O-H bond lengths so hydrogens on O3 and O4 were placed using a riding model.

2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(3-methoxyphenol) (3f)



2,2'-(1,2,3,4-tetrahydroquinoxaline-2,3-diyl)bis(4-(trifluoromethyl)phenol) (3h)



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