Supplementary Material (ESI) for Chemical Communications

Fluorophore-tagged cross coupling catalysts

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1. General

1.1. Equipment and chemicals used

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification unless otherwise noted. KO^{t}Bu (sublimation grade) was purchased from Aldrich. Dansyl chloride was prepared from dansyl acid according to the literature procedure.[1]

The anhydrous solvents were dried by distillation over corresponding agents and were transferred under argon: THF (potassium), dichloromethane and acetonitrile (CaH_2). Dimethylacetamide (DMA), DMF, DMSO and *i*PrOH were degassed by freeze-pump-thaw cycles technique.

Flash column and preparative thin layer chromatographies were performed using silica gel 60 (0.063–0.20 mesh ASTM). TLC was performed by using Fluka silica gel 60 F_{254} (0.2 mm) on alumina plates. NMR spectra were recorded on Bruker DRX500 and Bruker DRX300. The chemical shifts (δ) are given in ppm relative to TMS, coupling constants are (J) in Hz. IR spectra were recorded on a Perkin-Elmer 1600 series. The wavenumbers are given in cm^{-1}. MS spectra were recorded on a Finigan MAT95 spectrometer.

Fluorescence spectra were recorded on a J&M FL3095 spectrometer and fluoresceine was used as a reference standard.

1.2. Fluorescence measurements

A cuvette under argon atmosphere was loaded with 20 μL of 15 mM solution of **9a** in DMA, 50 μL of 2M solution of $PhB(OH)_2$ in DMA and diluted with 0.5 ml of DMA and 2.5 ml of *i*PrOH. Cuvette was placed in special holder which allows the solution to be stirred and heated under temperature control. After temperature stabilised at 40°C 120 μL of 1M solution of KO^{t}Bu in *i*PrOH was added and stirred until the fluorescence decay stopped. After that 14.4 μL of **10** or 13.9 μL **11** was added to start the coupling reaction. (Hint: Before addition of **11**, stirring was slowed down to prevent the formation of suspension. With mild stirring the precipitate remains on the bottom of the cuvette not disturbing the light path.. Fluorescence spectra were recorded at 532 nm using excitation 365 nm.

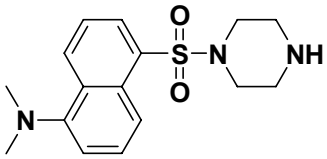
[1] F. Bergmann and W. Pfleiderer. *Helv. Chim. Acta*, **1994**, *77*, 203-215.

2. Experimental section

2.1. Catalysts preparation

N-Dansylpiperazine (1)

To a solution of piperazine (31.00 g, 0.36 mol) in dichloromethane (200 mL) a solution of dansyl chloride (16.18 g, 0.06 mol) in dichloromethane (100 mL) was added over a period of 5 minutes at room temperature. After 15 minutes of stirring the reaction mixture was washed with water (1500 mL) and organic phase was dried over $MgSO_4$. Evaporation of the solvent in vacuo gave the product as a light green solid (17.80 g, 93 %).



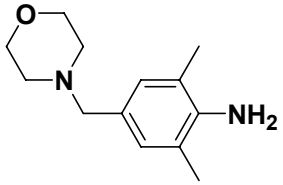
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (dt, *J* = 8.4, 0.9 Hz, 1H), 8.41 (dt, *J* = 8.7, 0.9 Hz, 1H), 8.16 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.53 − 7.47 (m, 2H), 7.14 (dd, *J* = 7.5, 0.6 Hz, 1H), 3.13 − 3.10 (m, 4H), 2.84 (s, 6H), 2.84 − 2.80 (m, 4H), 1.71 (s, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 132.5, 130.5, 130.5, 130.4, 129.9, 127.8, 123.0, 119.7, 115.1, 46.4, 45.4, 45.3.

NMR data are with agreement with those reported in literature.[2]

2,6-Dimethyl-4-(morpholinomethyl)aniline (3a)[3]

To a solution of 2,6-dimethylaniline (24.24 g, 0.20 mol) in EtOH (180 mL) and H_2O (100 mL), morpholine (52.28 g, 0.60 mol) and a solution of CH_2O in H_2O (48.70 g, 40% $^{w}/_{w}$) were added. The mixture was heated under reflux over a period of 10 days. After cooling the mixture to room temperature the product was partitioned between EtOAc (400 mL) and water (500 mL). The aqueous phase was washed with EtOAc (100 mL) and the combined organic phases were dried with saturated NaCl solution (100 mL) and $MgSO_4$. After evaporation of the volatiles the product (40.86 g, 93 %) was obtained as a brown oil.[4]



[2] S. R. Stauffer and J. F. Hartwig. *J. Am. Chem. Soc.*, **2003**, *125*, 6977-6985.
[3] Y. Le Floch, J. M. Morvan, A. Brault, *Bull. Soc. Chim. Fr.* **1980**, 3-4, 157-62.
[4] Intermediates **3-5** were used in further steps without thorough purification for the synthesis of the key compounds **7a** and **7b**.

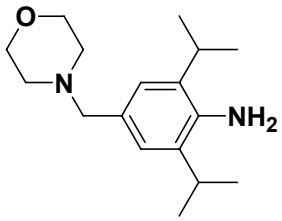
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (s, 2H), 3.72 − 3.65 (m, 4H), 3.52 (s, 2H), 3.34 (s, 2H), 2.51 − 2.41 (m, 4H), 2.16 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.8, 128.9, 126.7, 121.4, 67.0, 63.2, 53.6, 17.6.

NMR data are with agreement with those reported in literature.[3,5]

2,6-Diisopropyl-4-(morpholinomethyl)aniline (3b)

To a solution of 2,6-diisopropylaniline (53.19 g, 0.30 mol) in EtOH (300 mL) and H_2O (150 mL), morpholine (84 mL, 0.90 mol) and a solution of CH_2O in H_2O (79.10 g, 35 % $^w/_w$) were added. The mixture was heated under reflux over a period of 14 days. After cooling the mixture to room temperature the product was partitioned between EtOAc (500 mL) and water (600 mL). The aqueous phase was washed with EtOAc (200 mL) and the combined organic phases were extracted with saturated NaCl solution (100 mL) and dried over $MgSO_4$. Filtration and evaporation of the organic solvent gave the product as a brown oil (79.93 g, 96 %).[4]



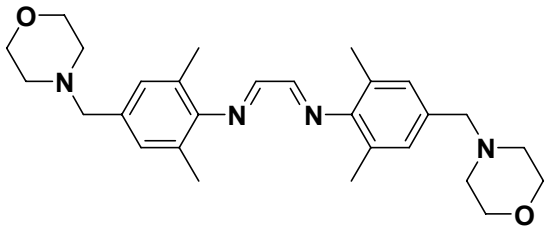
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 2H), 3.73 − 3.69 (m, 6H), 3.43 (s, 2H), 2.3 (pentet, J = 6.9 Hz, 2H), 2.45 − 2.41 (m, 4H), 1.28 (d, J = 6.9 Hz, 12H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 132.2, 127.0, 124.0, 67.1, 63.7, 53.5, 27.9, 22.5.

***N,N'*-Bis(2,6-dimethyl-4-(morpholinomethyl)phenyl)ethylenediimine (4a)**

Aniline **3a** (40.5 g, 184 mmol, 2 eq) was dissolved in MeOH (50 mL). After addition of a 40 % ($^w/_w$) aqueous solution of glyoxal (10.62 mL) and formic acid (5 drops), the mixture was stirred 2 days at room temperature. The solvent was evaporated in vacuo and the resulting dark yellow product was dissolved in $CHCl_3$ (200 mL) and dried over $MgSO_4$. After evaporation of the organic solvent the product (40.43 g, 95 %, 87 mmol) was formed as dark yellow crystals.[4,5]

[5] A. Cooke, A. Anderson, K. Buchanan, A. Byford, D. Gemmell, N. Hamilton, P. McPhail, S. Miller, H. Sundaram, P. Vijn. *Bioorg. Med. Chem. Lett.*, **2001**, *11*, 927-930.

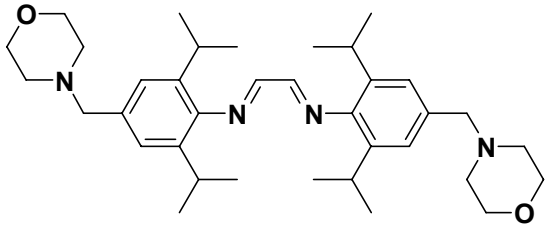


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.05 (s, 4H), 3.76 − 3.68 (m, 8H), 3.44 (s, 4H), 2.49 − 2.45 (m, 8H), 2.17 (s, 12H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5, 148.9, 133.9, 128.9, 126.4, 66.9, 63.1, 53.5, 18.3.

***N,N'*-Bis(2,6-diisopropyl-4-(morpholinomethyl)phenyl)ethylenediimine (4b)**

Aniline **3b** (79.9 g, 0.29 mol) was dissolved in MeOH (80 mL). After addition of a 40 % ($^w/_w$) aqueous solution of glyoxal (22 mL) and formic acid (5 drops), the mixture was stirred for 24 h at room temperature. The formed precipitate was filtered, washed with cold methanol and dried in vacuo affording the product as light-yellow crystals (51.3 g, 61 %).[4]

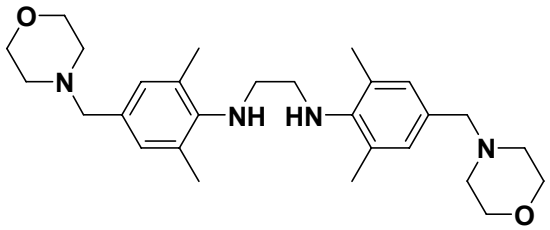


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.11 (s, 4H), 3.75 − 3.72 (m, 8H), 3.50 (s, 4H), 2.93 (pentett, J = 6.9 Hz, 4H), 2.48 − 2.40 (m, 8H), 1.20 (d, J = 6.6 Hz, 24H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 147.0, 136.6, 134.1, 124.0, 67.1, 63.5, 53.6, 28.0, 23.4.

***N,N'*-Bis(2,6-dimethyl-4-(morpholinomethyl)phenyl)ethylenediamine (5a)**

Diimine **4a** (40 g, 86.5 mmol, 1 eq) was suspended in dry THF (120 mL). While the temperature was kept between 0°C and 10°C, $LiAlH_4$ pellets (7 g, 173 mmol, approximately 0.5 g per pellet) were added over a period of 30 minutes. The reaction mixture was then stirred for 20 h at ambient temperature. Afterwards the resulting brown solution was added slowly to an ice/HCl mixture to hydrolyse excess of $LiAlH_4$. The pH was raised to 9-10 with 2N NaOH and the product was extracted from the white suspension with Et_2O. The organic phase was dried with saturated NaCl-solution and $MgSO_4$. Evaporation of the solvent in vacuo led to the product as a bright brownish powder (31.8 g, 68.2 mmol, 79 %).[4]

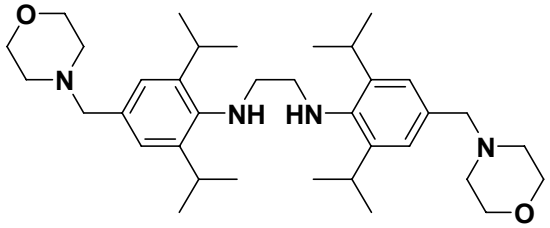


^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 4H), 3.76 − 3.69 (m, 8H), 3.37 (s, 4H), 3.18 (s, 4H), 2.44 − 2.41 (m, 8H), 2.28 (s, 12H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 130.9, 129.3, 128.9, 68.0, 63.2, 53.7, 48.9, 18.4.

***N,N'*-Bis(2,6-diisopropyl-4-(morpholinomethyl)phenyl)ethylenediamine (5b)**

Diimine **4b** (50.0 g, 87.0 mmol) was suspended in dry THF (250 mL). While the temperature was kept between 0°C and 10°C, $LiAlH_4$ pellets (6.6 g, 174.0 mmol, approximately 0.5 g per pellet) were added over a period of 30 minutes. The reaction mixture was left stirring overnight. Afterwards the resulting brown solution was slowly added to an ice/HCl mixture to hydrolyse excess of $LiAlH_4$. The pH was raised to 9-10 with 2N NaOH and the product was extracted from the white suspension with Et_2O. The organic phase was dried with saturated NaCl-solution and $MgSO_4$. Evaporation of the solvent in vacuo led to the product as an orange powder (38.0 g, 76 %).[4]

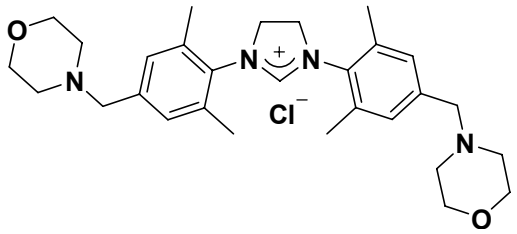


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 4H), 3.77 − 3.69 (m, 8H), 3.47 (s, 4H), 3.36 (heptet, *J* = 6.9 Hz, 4H), 3.15 (4H), 2.46 − 2.44 (m, 8H), 1.26 (d, *J* = 6.9 Hz, 24H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 132.6, 124.5, 67.1, 63.5, 53.5, 52.3, 27.7, 24.2.

1,3-Bis(2,6-dimethyl-4-(morpholinomethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-chloride (6a)

A suspension of the diamine **5a** (20 g, 42.9 mmol, 1 eq) in triethylorthoformiate (60 mL) and NH_4Cl (3.44 g, 64.4 mmol, 1.5 eq) was stirred at 120 °C for 24 h. After cooling to room temperature, the slightly brown suspension was filtered through a D3 glass frit. After washing the resulting solid with Et_2O and drying in vacuo the product (12.8 g, 24.9 mmol, 58 %) was obtained as a colourless powder.

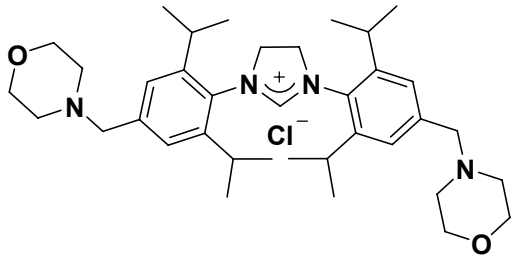


^{1}H NMR (500 MHz , d_6-DMSO): δ 9.12 (s, 1H), 7.21 (s, 4H), 4.48 (s, 4H), 3.57 (bs, 8H), 3.43 (s, 4H), 2.37 (s, 12H), 2.36 (bs, 8H);

^{13}C NMR (125 MHz, d_6-DMSO): δ 160.6, 140.3, 135.9, 132.6, 129.7, 66.5, 62.1, 53.5, 51.3, 17.7.

1,3-Bis(2,6-diisopropyl-4-(morpholinomethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-chloride (6b)

A suspension of diamine **5b** (37.63 g, 65.0 mmol), triethylorthoformiate (90 mL) and ammonium chloride (5.21 g, 97.5 mmol) was stirred at 120°C for 24 h. After cooling to room temperature the resulted viscous solution was treated with 600 mL of Et_2O and the mixture was vigorously stirred causing the salt precipitation. Suspension was filtered and washed with ether to form an off-white solid. The second batch of product was obtained after leaving mother liquid in the fridge at 0°C. Total yield of product is 32.10 g (79 %).



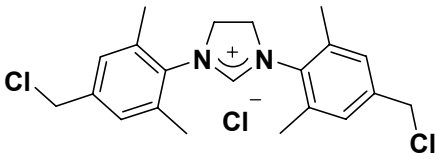
^{1}H NMR (500 MHz, d_6-DMSO) δ 9.54 (s, 1H), 7.41 (bs, 4H), 4.54 (s, 4H), 3.66 (bs, 8H), 3.48 (s, 4H), 3.08 (heptet, *J* = 6.9 Hz, 4H), 2.46 (bs, 8H), 1.36 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H);

^{13}C NMR (125 MHz, d_6-DMSO) δ 160.6, 146.4, 129.4 (m), 125.5 (m), 66.4 (m), 54.1, 53.1 (m), 28.6, 25.3, 23.7.

1,3-Bis(2,6-dimethyl-4-(chloromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-chloride (7a)

To a suspension of **6a** (5.6 g, 10.9 mmol) in dry acetonitrile (50 mL) ethylchloroformiate (7 mL, 73.3 mmol) was added and the reaction mixture was refluxed for 8 h. After that all volatiles were removed under reduced pressure and the residue was dissolved in 200 mL of chloroform. The organic layer was washed with 1N HCl (2x50mL)

and dried over $MgSO_4$. After evaporation of solvent crude product was triturated with ether and the mixture was instantly stirred overnight. Filtration, washing with ether afforded salt as off-white solid (1.23 g). The combined water layers were neutralized with 4N NaOH and extracted with chloroform. Evaporation of solvent gives complex mixture consisting primarily of mono-chloromethyl product and starting material. The residue can be used again for the synthesis of the di-chloromethyl product **7a**. After repeating of whole procedure, a second batch of product was obtained (1.12 g). The combined yield of product is 52 %.



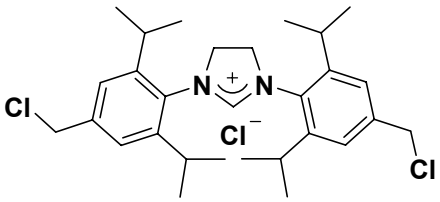
^{1}H NMR (500 MHz, d_6-DMSO) δ 9.16 (s, 1H), 7.36 (s, 4H), 4.76 (s, 4H), 4.52 (s, 4H), 2.42 (s, 12H);

^{13}C NMR (125 MHz, d_6-DMSO) δ 160.7, 139.8, 136.6, 133.6, 129.7, 51.2, 45.5, 17.7.

1,3-Bis(2,6-diisopropyl-4-(chloromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium-chloride (7b)

Salt **6b** (27.5 g, 44 mmol) was dissolved in 250 mL of dry MeCN. To the resulting solution ethylchloroformiate (42 mL, 440 mmol) was added and the mixture was refluxed for 1 h. Next the volatiles were removed under reduced pressure and 500 mL of CH_2Cl_2 was added. The organic layer was washed with 1N HCl (2x300 mL), dried over $MgSO_4$ and the volatiles were evaporated by rotor vapour. The obtained residue was suspended in 300 mL of Et_2O and left stirring overnight. Product was obtained after filtration of the suspension, washing with diethyl ether and drying in vacuo (12.2 g).

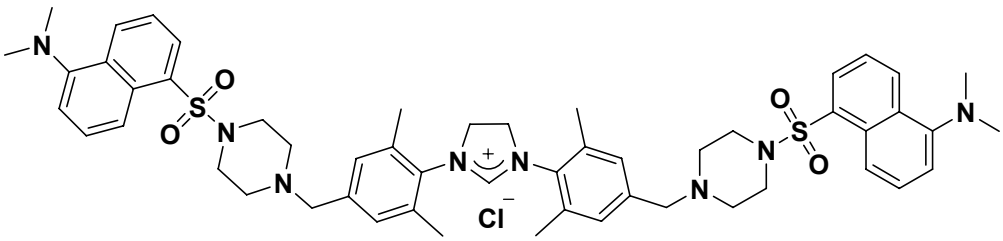
The aqueous layers were neutralized with 4N NaOH to pH = 10, extracted with dichloromethane (2x250 mL), washed with brine and dried over $MgSO_4$. Evaporation of solvent gives residue containing predominantly of monochlorinated product. To this residue 300 mL of dry MeCN was added and 15 mL of ethylchloroformiate and refluxed until TLC (chloroform/methanol = 6:1) showed full conversion to the desired product. The volatiles were distilled off and 400 mL of CH_2Cl_2 was added. The resulting solution was washed with 1N HCl (2x200 mL), dried over $MgSO_4$ and the solvent was evaporated off. Trituration of organic layer with ether gives a second batch of product (3.7 g). The remaining aqueous suspension was filtered. Obtained precipitate was dried in vacuo affording third batch of product as off-white solid (3.4 g). Total yield of product is 19.3 g (84 %).



^{1}H NMR (500 MHz, CD_3OD) δ 9.38 (s, 1H), 7.51 (s, 4H), 4.73 (s, 4H), 4.62 (s, 4H), 3.16 (pentet, *J* = 6.5 Hz, 4H), 1.47 (d, *J* = 6.5 Hz, 12H), 1.33 (d, *J* = 6.5 Hz, 12H);
^{13}C NMR (125 MHz, CD_3OD) δ 161.5, 147.5, 142.1, 130.0, 125.7, 54.3, 45.3, 29.5, 24.6, 23.1.

1,3-Bis[2,6-dimethyl-4-((4-danzylpiperazinyl)methyl)phenyl]-4,5-dihydro-1*H*-imidazol-3-ium-chloride (8a)

To a solution of **7a** (1.24g, 3 mmol) in DMF (technical grade, 30 mL) **1** (3.83 g, 12 mmol) in DMF (10 mL) was added and the mixture was stirred at rt for 24 h. The solvent was evaporated in vacuo and water (300 mL) with small additive of $NaHCO_3$ was added. Extraction with DCM (2x30 mL), drying of combined organic layers over $MgSO_4$ and evaporation of solvent resulted in crude product which was finally purified by flash chromatography (chloroform/methanol = 10:1) affording the product as a yellow solid with green fluorescence (2.31 g, 79 %).

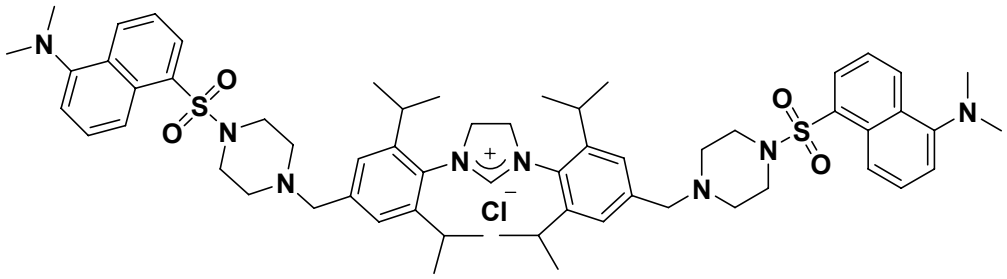


IR (KBr) ν 2941, 2829, 1630, 1455, 1348, 1145, 1066, 949, 794, 720 cm^{-1};
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.54 (d, *J* = 8.5 Hz, 2H), 8.38 (d, *J* = 8.5 Hz, 2H), 8.13 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.51 − 7.48 (m, 4H), 7.14 (d, *J* = 7.5, Hz, 2H), 6.99 (s, 4H), 4.50 (s, 4H), 3.34 (s, 4H), 3.17 (s, 8H), 2.87 (s, 12H), 2.43 (s, 8H), 2.35 (s, 12H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 151.6, 140.2, 135.2, 132.5, 131.6, 130.6, 130.5, 130.4, 130.0, 129.7, 127.9, 123.1, 119.6, 115.2, 61.8, 52.3, 51.6, 45.5, 45.3, 18.0;
MS (ESI) calcd for $C_{53}H_{65}N_8O_4S_2$ ($M^{+\bullet}$-Cl) 941.5, found 941.7.

1,3-Bis[2,6-diisopropyl-4-((4-danzylpiperazinyl)methyl)phenyl]-4,5-dihydro-1*H*-imidazol-3-ium-chlorid (8b)

To a solution of **1** (2.105 g, 6.6 mmol) and triethylamine (1.7 mL, 12 mmol) in DMF (20 mL) a suspension of salt **7b** (1.569 g, 3 mmol) in DMF (10 mL) was added and the

mixture was stirred for 24 h. The volatiles were removed under reduced pressure and the residue was passed through short column filled with silica using chloroform/methanol (10:1) mixture as eluent. Evaporation of solvent and crystallization from EtOAc (20 mL) afforded a yellow precipitate which was filtered, washed with EtOAc and ether. Drying in vacuo gave the desired product (0.893 g, 28 %).[6]



IR (KBr) ν 2963, 2830, 1626, 1456, 1327, 1146, 1071, 944, 794, 719 cm^{-1};

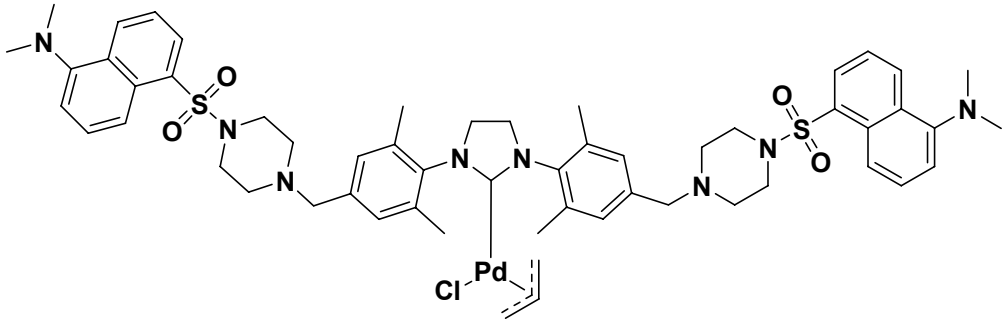
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.54 (d, *J* = 8.7 Hz, 2H), 8.35 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 7.2 Hz, 2H), 7.53 − 7.47 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.09 (s, 4H), 4.62 (s, 4H), 3.42 (s, 4H), 3.20 (bs, 8H), 2.91 − 2.79 (m, 16H), 2.42 (bs, 8H), 1.28 (d, *J* = 7.6 Hz, 12H), 1.17 (d, *J* = 7.6 Hz, 12H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 151.7, 146.0, 141.2, 132.7, 130.7, 130.6, 130.4, 130.0, 128.3, 128.9, 125.2, 123.1, 119.7, 115.2, 62.2, 54.8, 52.4, 45.4, 29.1, 25.3, 23.7;

MS (ESI) calcd for $C_{61}H_{81}N_8O_4S_2$ ($M^{+\bullet}$-Cl) 1053.6, found 1053.8.

1,3-Bis[2,6-dimethyl-4-((4-danzylpiperazinyl)methyl)phenyl]-4,5-dihydro-1*H*-imidazol-3-iumpalladium (II) (η-allyl) chloride (9a)

A Schlenk flask charged with $[Pd(\eta\text{-allyl})Cl]_2$ (73.2 mg, 0.20 mmol), **8a** (430.3 mg, 0.44 mmol), KO^{t}Bu (58.2 mg, 0.52 mmol) was evacuated and backfilled with argon three times. THF (5 mL) was added and the mixture was stirred overnight. The volatiles were evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc/CH_2Cl_2 = 3:2). Evaporation of solvents gave oil-nature substance. Product was precipitated from CH_2Cl_2/pentane as an off-white fluorescent solid (328.0 mg, 73 %).



[6] Conversion is not complete.

IR (KBr) ν 2918, 2829, 1587, 1453, 1348, 1143, 1066, 949, 793, 720 cm^{-1};

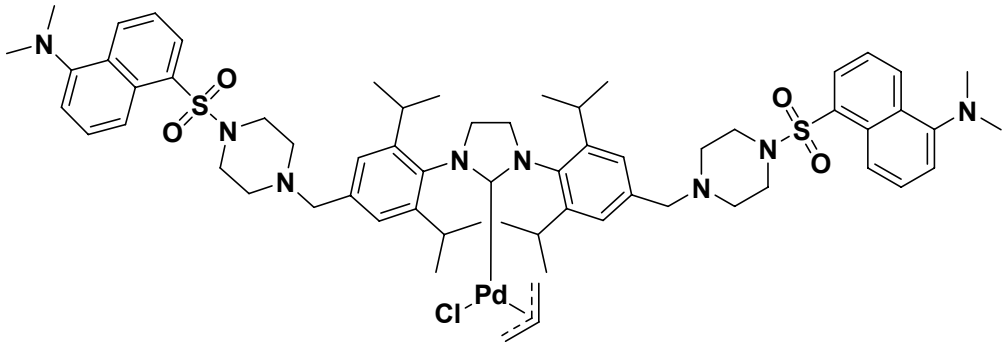
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.5 Hz, 2H), 8.44 (d, *J* = 8.5 Hz, 2H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.17 (d, *J* = 7.5, Hz, 2H), 6.93 (s, 4H), 4.67 (hept., *J* = 6.5 Hz, 1H), 3.96 − 3.90 (m, 4H), 3.73 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.35 (s, 4H), 3.19 (s, 8H), 2.87 (s, 12H), 2.61 (d, *J* = 13.5, Hz, 1H), 2.45 (s, 8H), 2.36 (s, 12H), 1.66 (d, *J* = 12.0, Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 211.0, 151.6, 137.4, 137.2, 136.5, 136.8, 132.6, 130.4, 130.4, 130.0, 129.1, 129.0, 127.9, 123.1, 119.8, 115.2, 114.5, 73.0, 62.2, 52.4, 51.0, 49.3, 45.6, 45.3, 18.4, 18.3;

MS (ESI) calcd for $C_{56}H_{70}N_8O_4S_2Pd$ ($M^{+\bullet}$-Cl) 1088.4, found 1087.6.

1,3-Bis[2,6-diisopropyl-4-((4-danzylpiperazinyl)methyl)phenyl]-4,5-dihydro-1*H*-imidazol-3-iumpalladium (II) (η-allyl) chloride (9b)

A Schlenk flask charged with palladium $[Pd(\eta\text{-allyl})Cl]_2$ (73.2 mg, 0.20 mmol), **9a** (478.7 mg, 0.44 mmol), KO^{t}Bu (58.2 mg, 0.52 mmol) was evacuated and backfilled with argon 3 times. THF (5 mL) was added and the mixture was stirred for 2 h. The volatiles were evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc/CH_2Cl_2 = 2:3). Evaporation of solvents gave an oily residue. Product was precipitated from CH_2Cl_2/pentane as an off-white fluorescent solid (420.0 mg, 85 %).



IR (KBr) ν 2962 2829, 1587, 1458, 1327, 1146, 1070, 945, 792, 719 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 2H), 8.41 (d, *J* = 8.5 Hz, 2H), 8.20 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.55 − 7.51 (m, 4H), 7.18 (d, *J* = 6.5 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 4H), 4.66 (heptet, *J* = 8.0, Hz, 1H), 4.05 − 3.89 (m, 4H), 3.83 (d, *J* = 7.0, Hz, 1H), 3.44 (s, 4H), 3.42 − 3.28 (m, 4H), 3.24 (bs, 8H), 2.93 (d, *J* = 6.0, Hz, 1H), 2.89 (s, 12H), 2.65 d, *J* = 13.5, Hz, 1H), 2.47 (m, 8H), 1.65 (bs, 1H), 1.37 (d, *J* = 6.5, Hz, 6H), 1.27 (d, *J* = 6.5, Hz, 6H), 1.21 (d, *J* = 6.5, Hz, 6H), 1.17 (d, *J* = 6.5, Hz, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 151.7, 147.2, 146.9, 138.0, 135.2, 132.9, 130.6, 130.5, 130.4, 130.0, 127.9, 124.6, 123.1, 119.8, 115.2, 114.5, 73.0, 62.5, 53.9, 52.3, 49.6, 45.5, 45.4, 28.4, 26.5, 26.4, 23.7, 23.5;

MS (ESI) calcd for $C_{64}H_{85}N_8O_4S_2Pd$ ($M^{+\bullet}$-Cl) 1199.5, found 1199.5.

2.2. Pd catalyzed coupling reactions

3-(Trifluoromethyl)-1,1'-biphenyl (12)

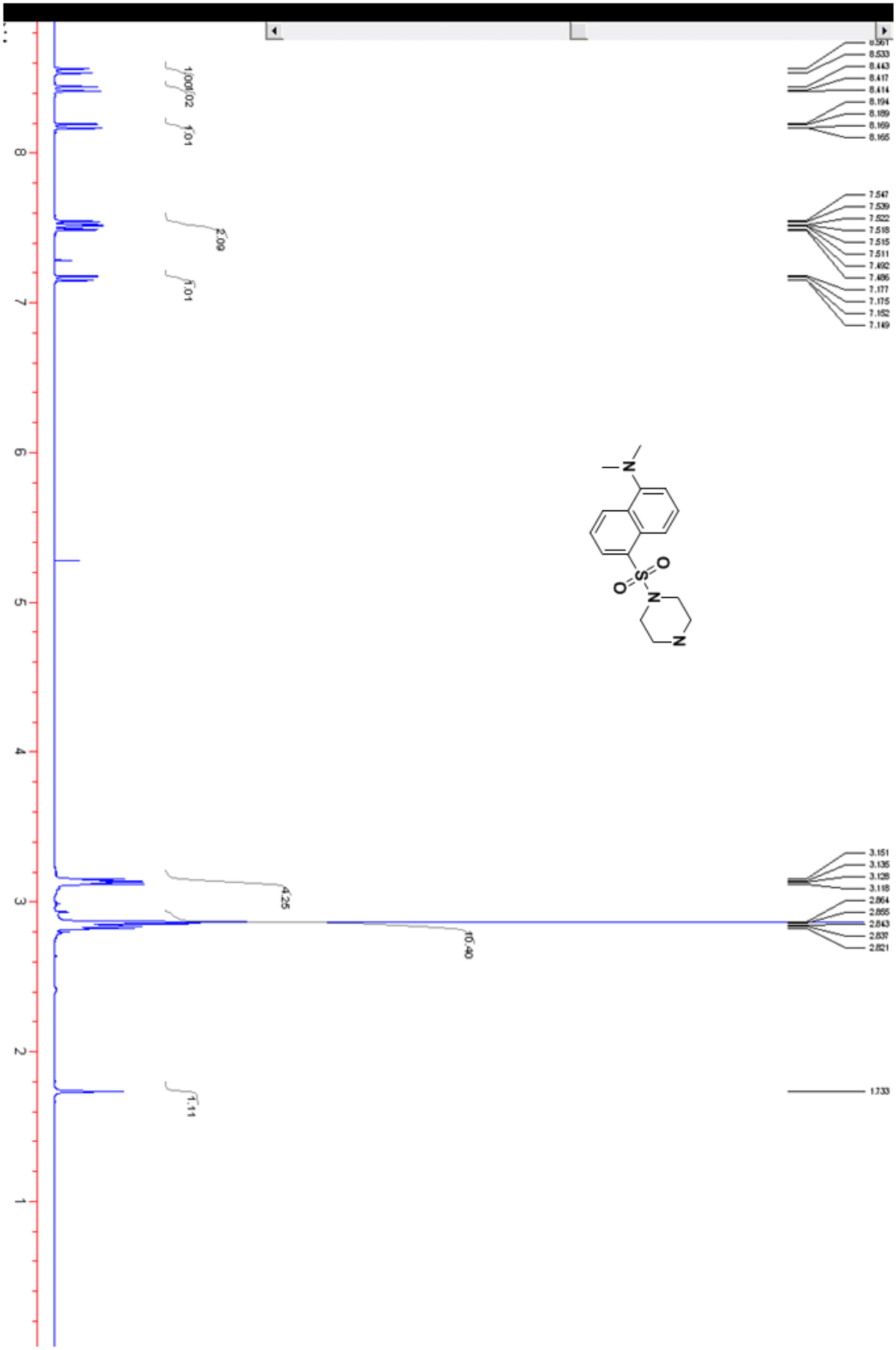
A Schlenk flask under argon atmosphere was charged with 20 μL of 15mM solution of **9a** or **9b** in DMA (0.3% mol), 50 μL of 2M solution of $PhB(OH)_2$ in DMA (0.1 mmol), 120 μL of 1M solution of KO^{t}Bu in *i*PrOH (0.12 mmol), 0.5 ml of DMA and 2.5 ml of *i*PrOH. The mixture was stirred at 40°C for 15 minutes. Next **10** or **11** (0.1 mmol) was added. Aliquots were taken from the reaction mixture after some intervals, quenched with saturated NH_4Cl aqueous solution, extracted with EtOAc and analyzed by GC.

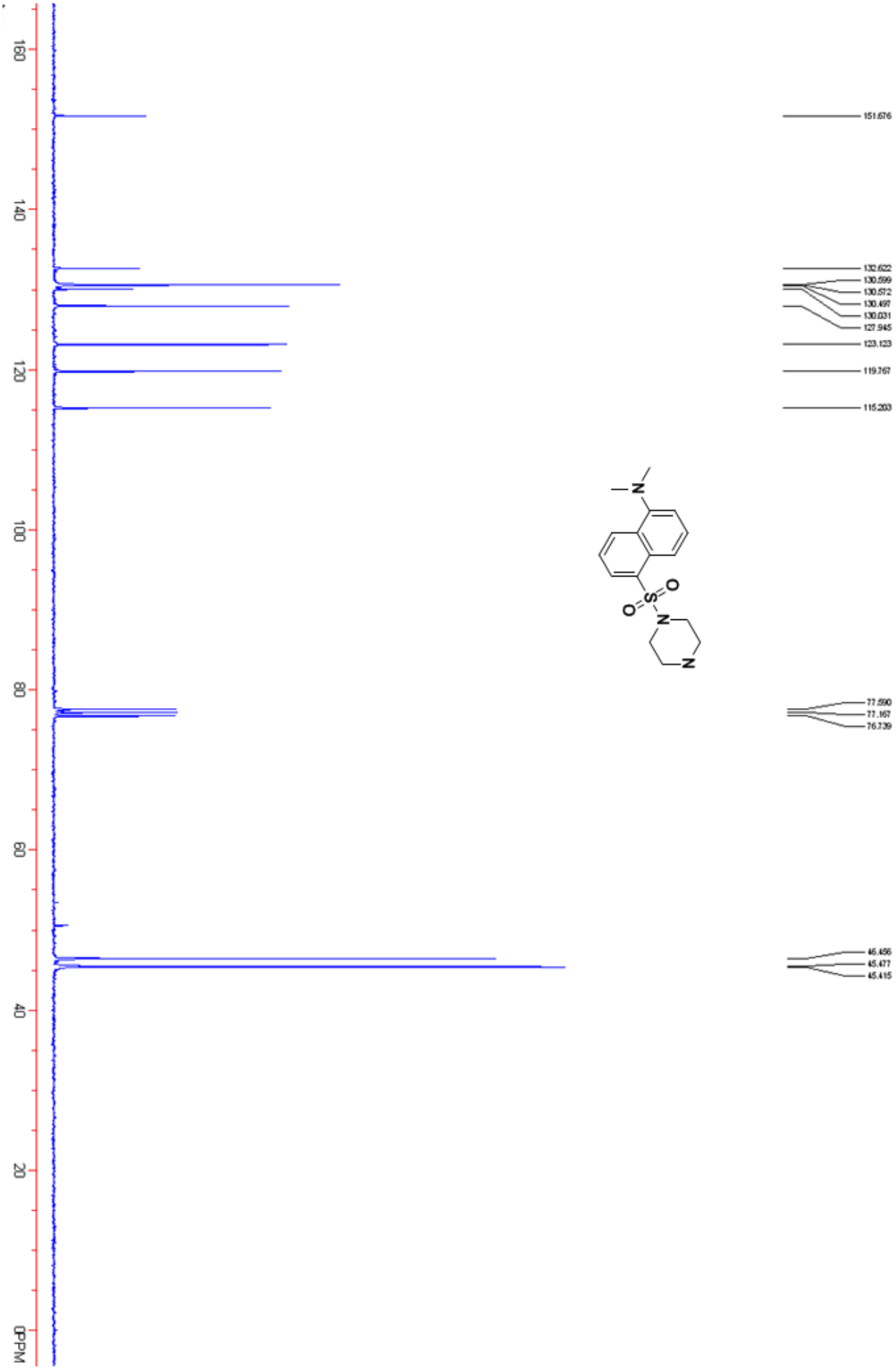
2,6-Dimethyl-1,1'-biphenyl (13)

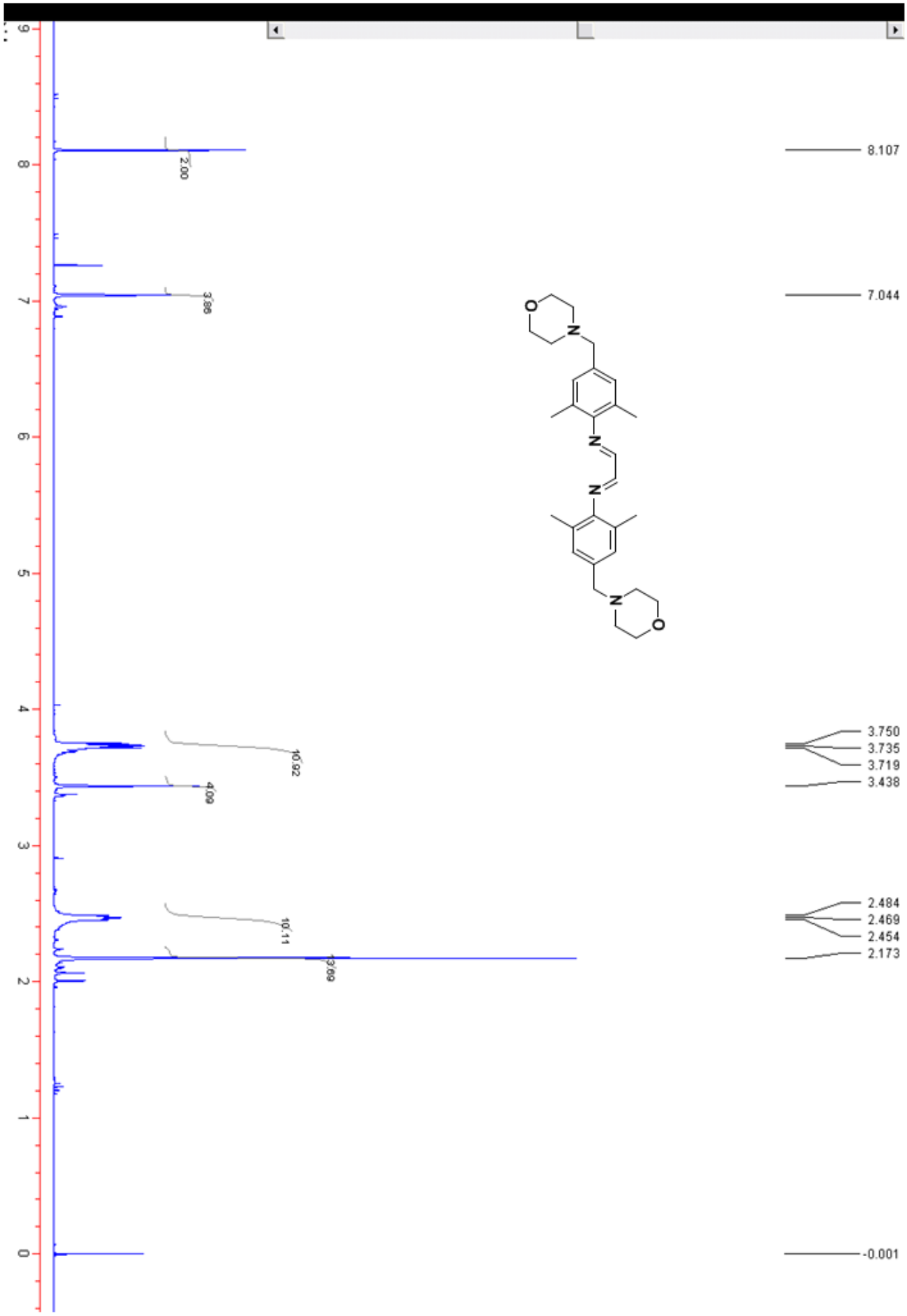
A Schlenk flask under argon atmosphere was charged with **9b** (0.1% mol), phenylboronic acid (256 mg, 2.1 mmol), KO^{t}Bu (246 mg, 2.2 mmol) and filled with technical grade *i*PrOH (3 ml). The reaction mixture was stirred at 40°C for 15 minutes and 2-chloro-1,3-dimethylbenzene (265 μL, 2.0 mmol) was added. After 2h GC analysis shows no further changes in conversion. Fractions **a-c** (see figure) were obtained:

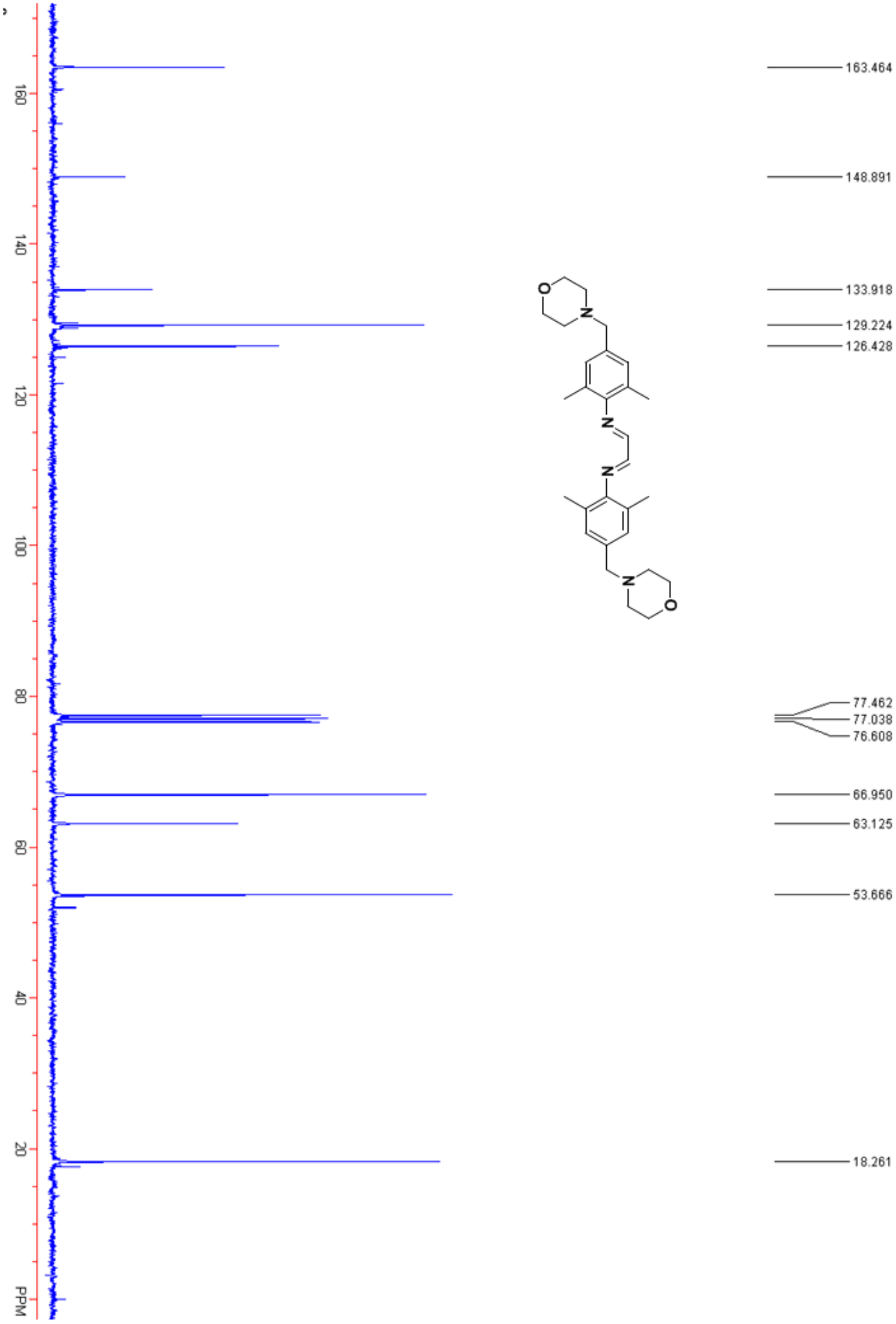
a) Simple filtration of reaction mixture through a short pad of silica gel;
b) Flash chromatography of fraction **a** using EtOAc as eluent;
c) Flash chromatography of fraction **b** using *c*-hexane as eluent.

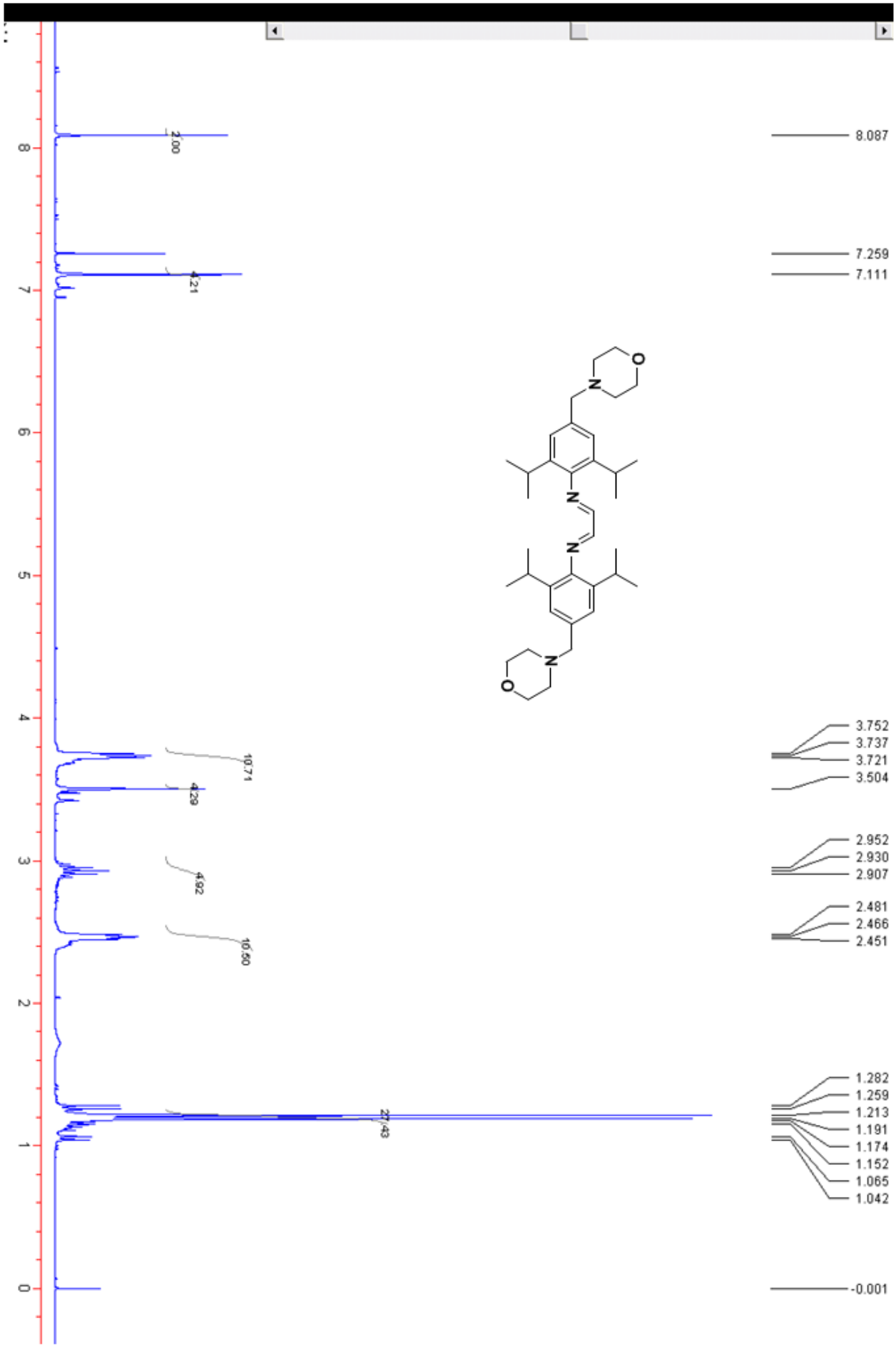
3. Copies of ^{1}H and ^{13}C spectra

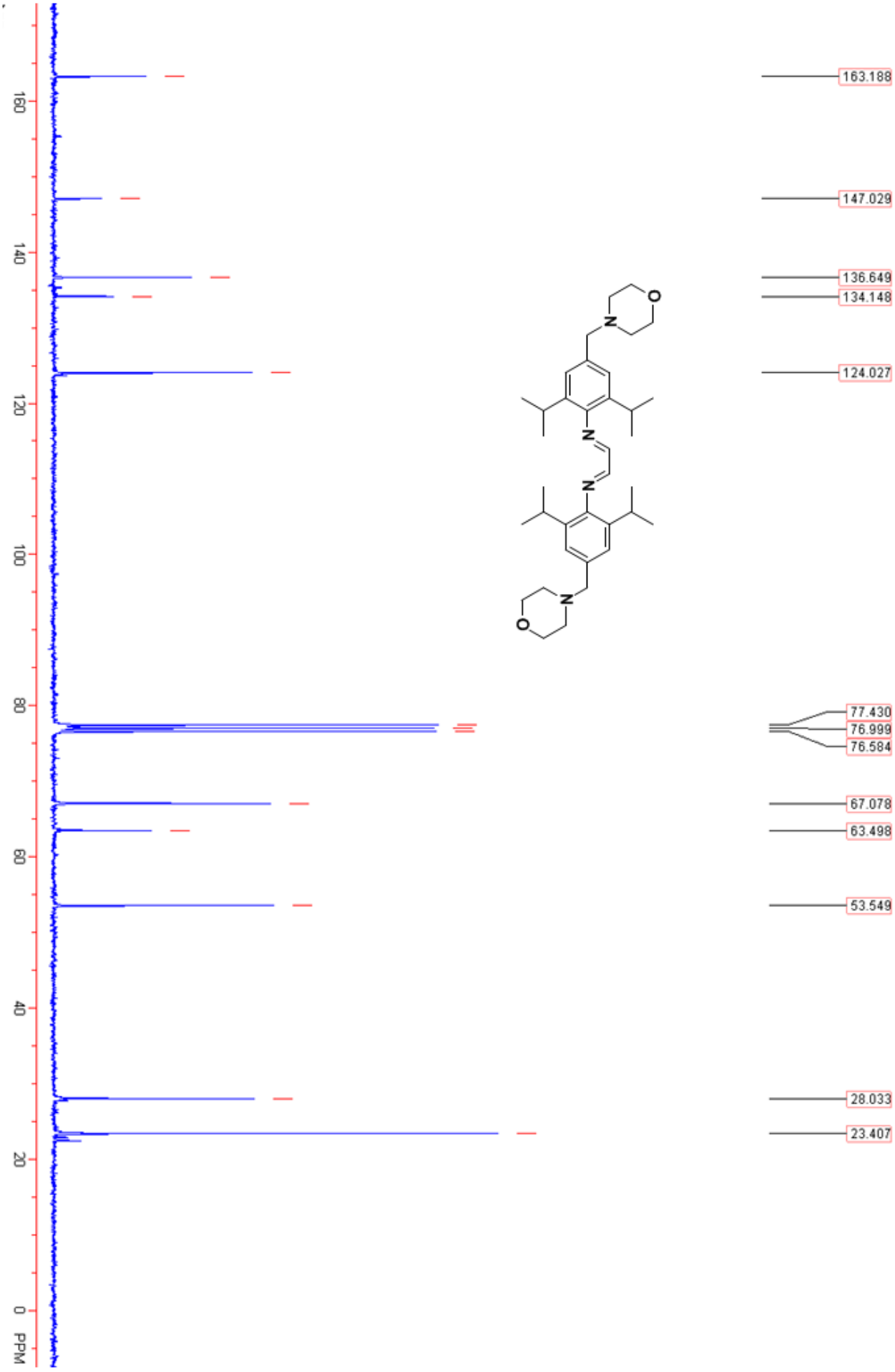


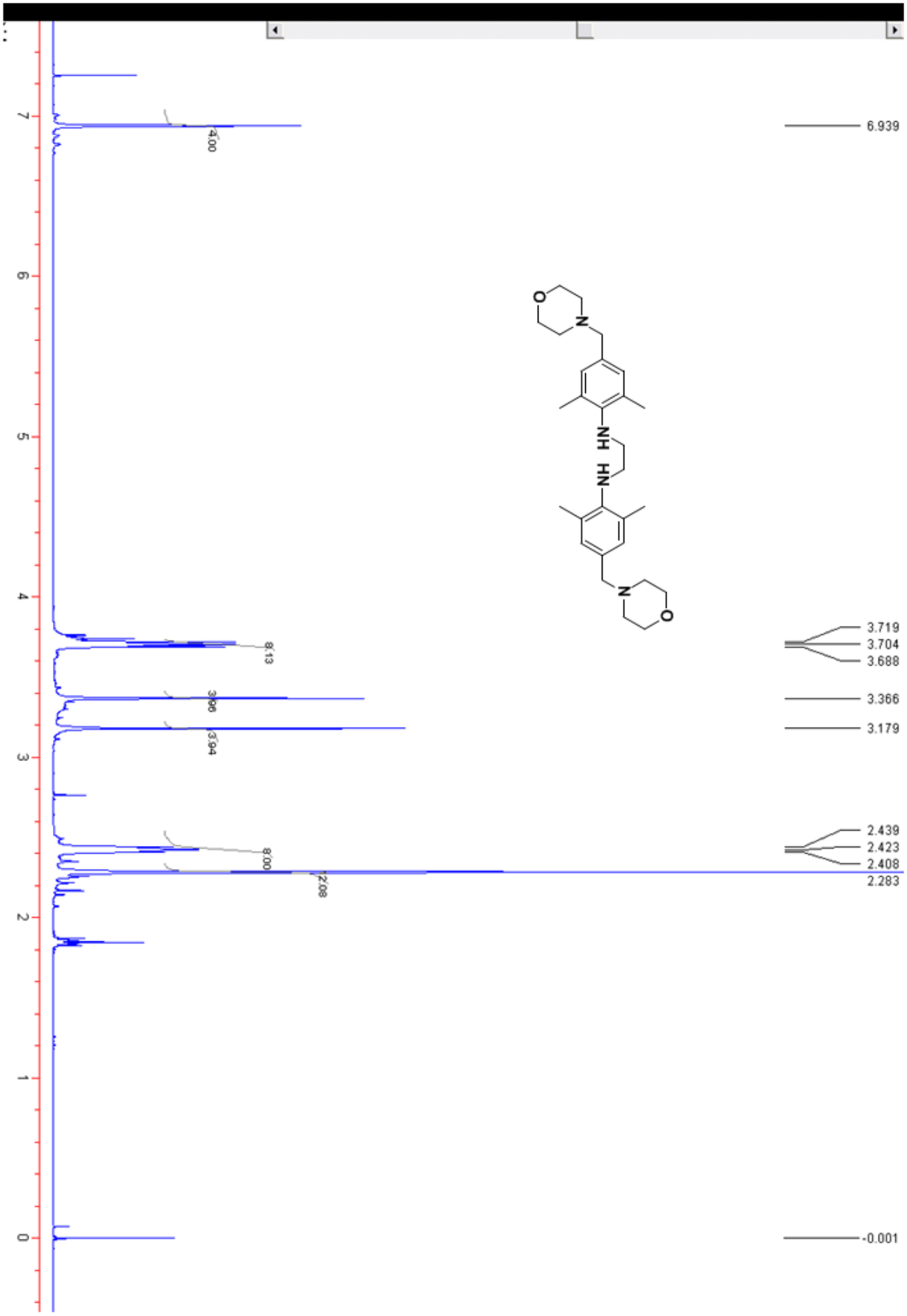


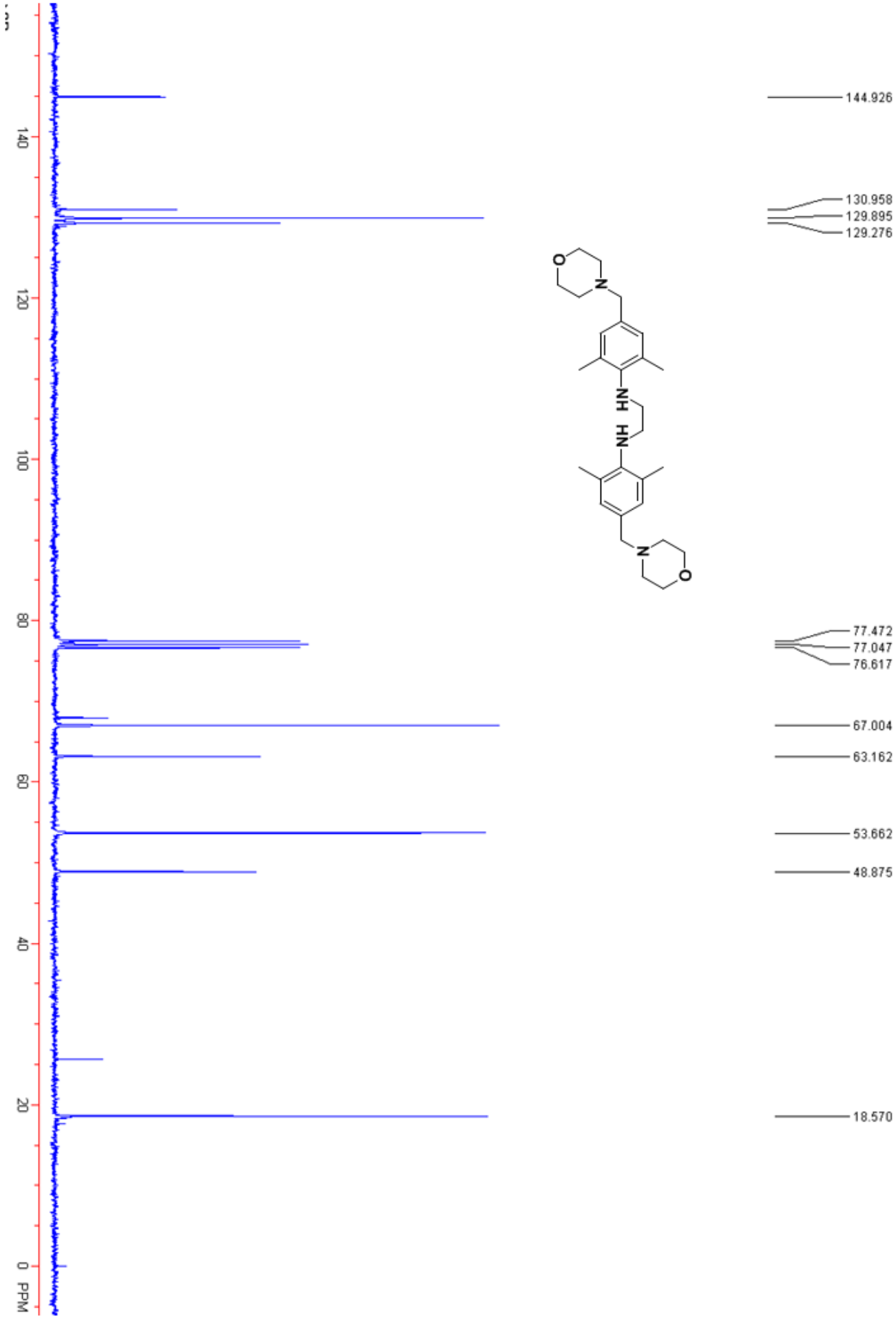


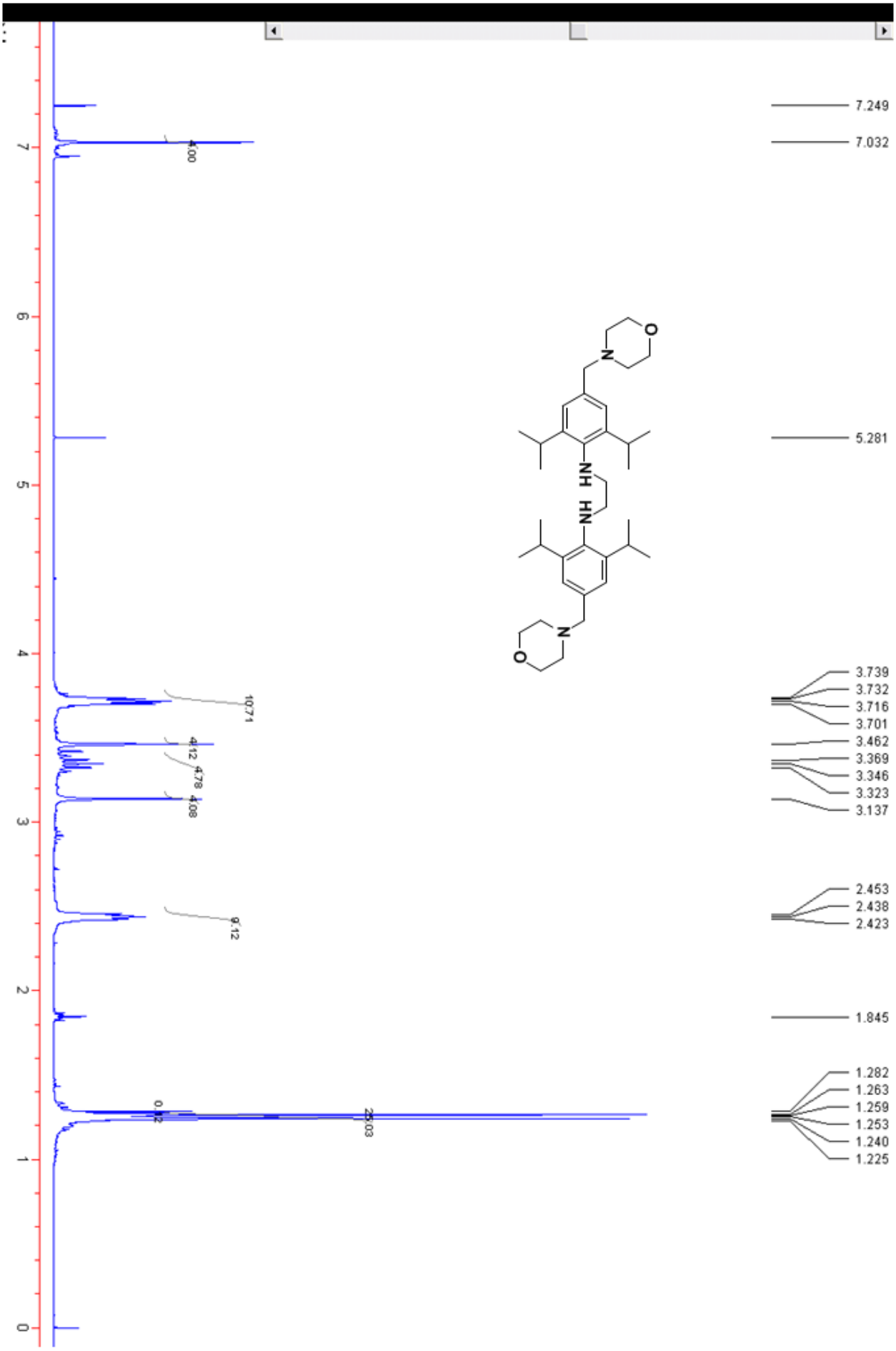


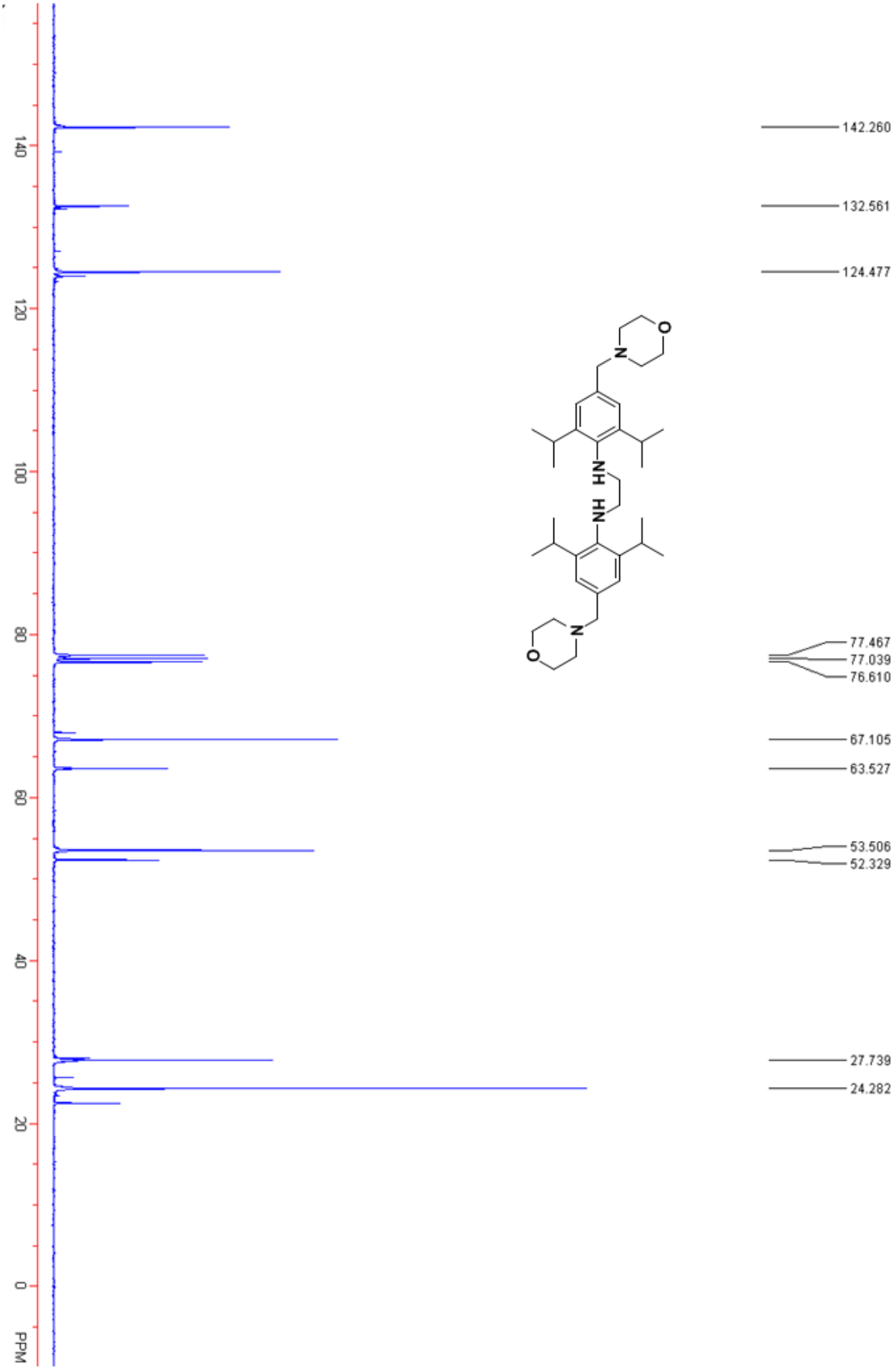


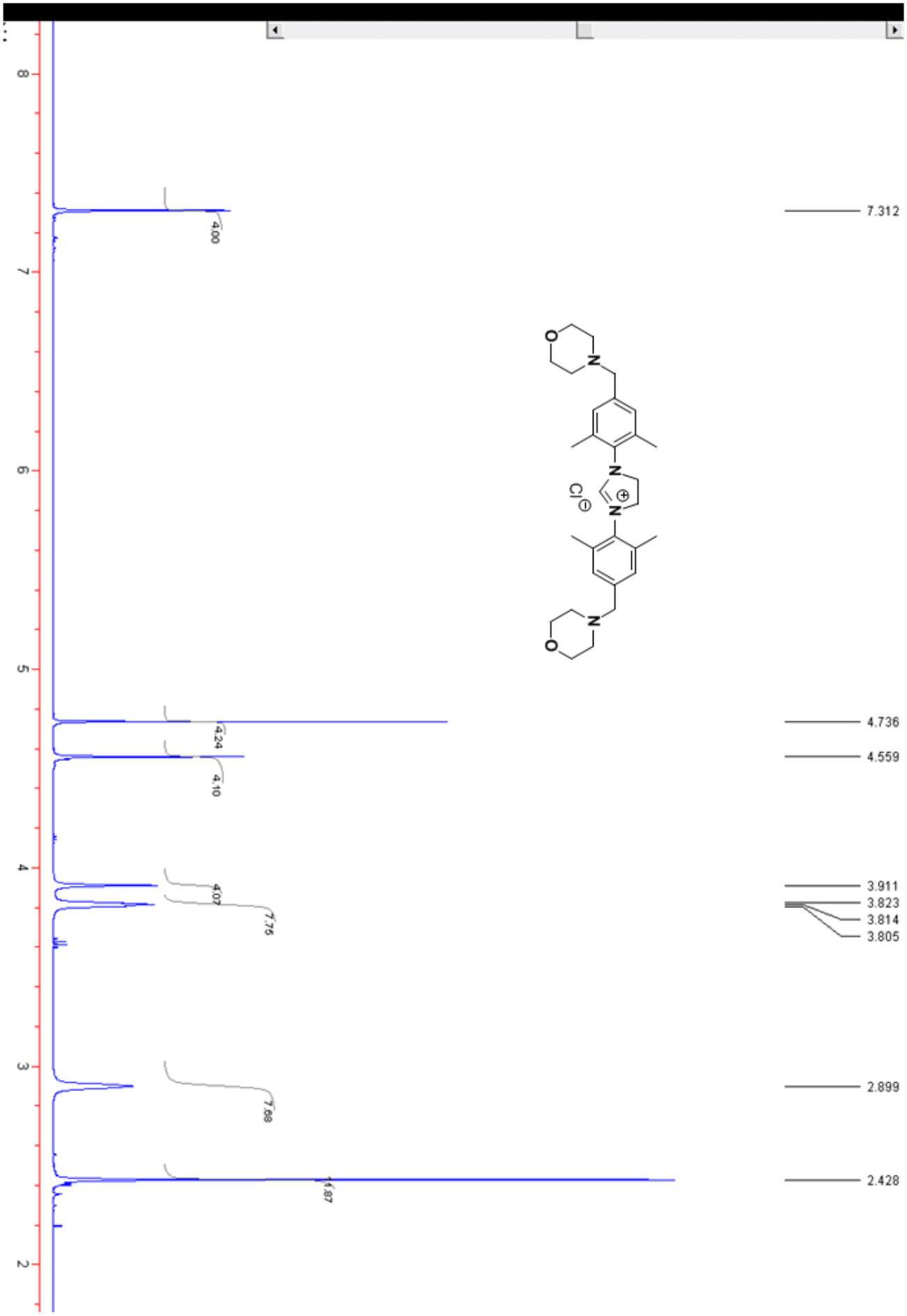


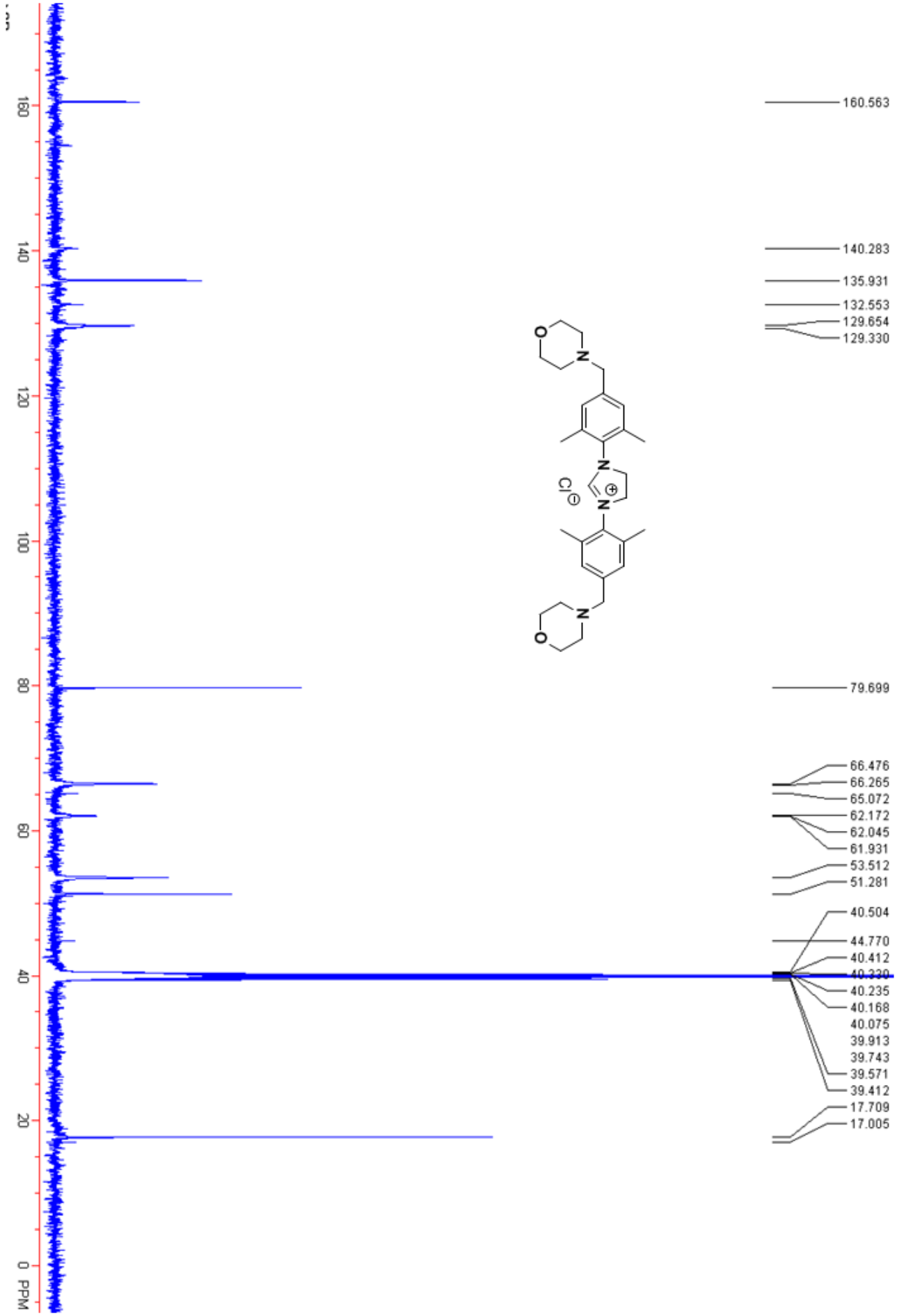


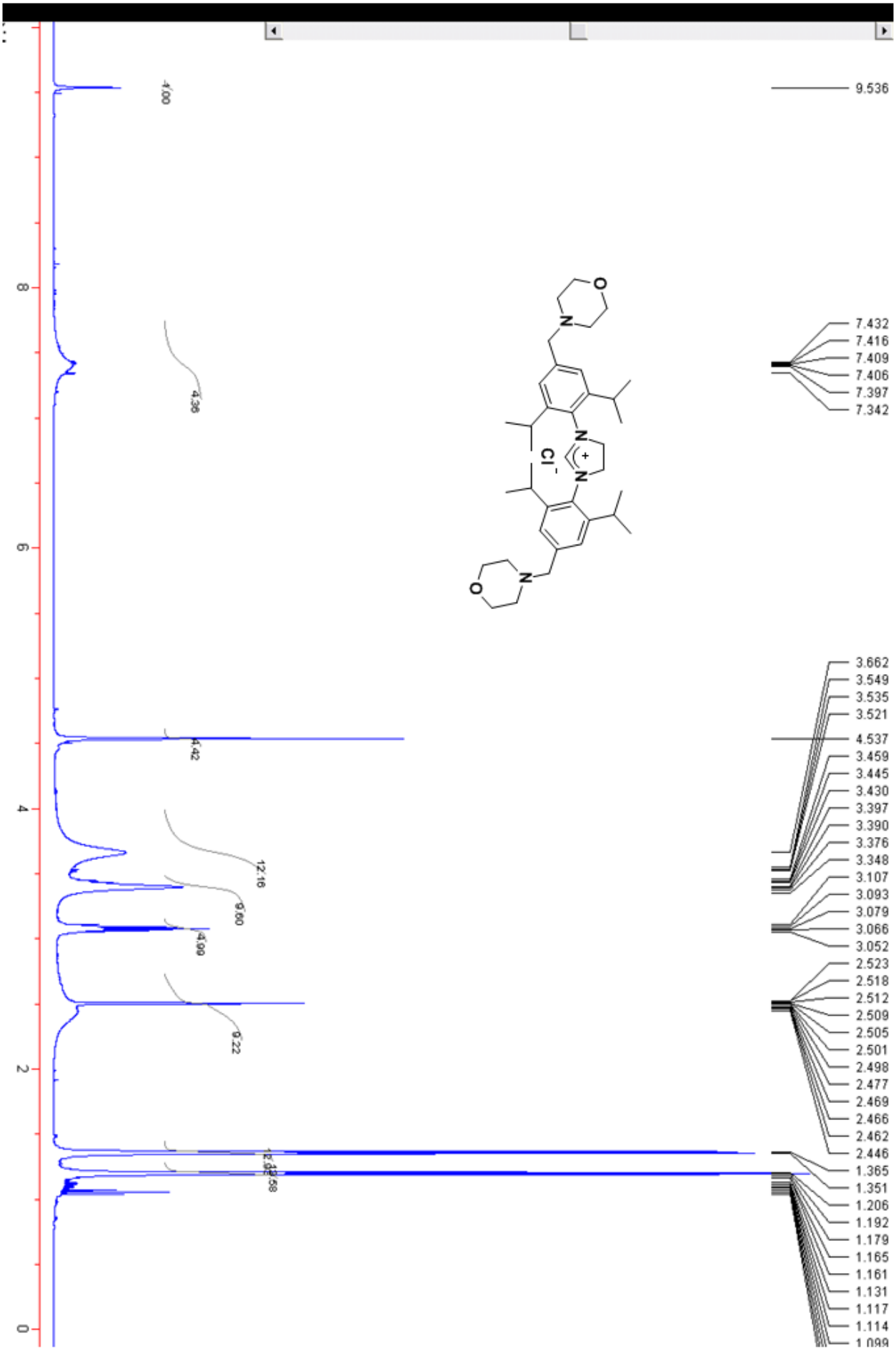


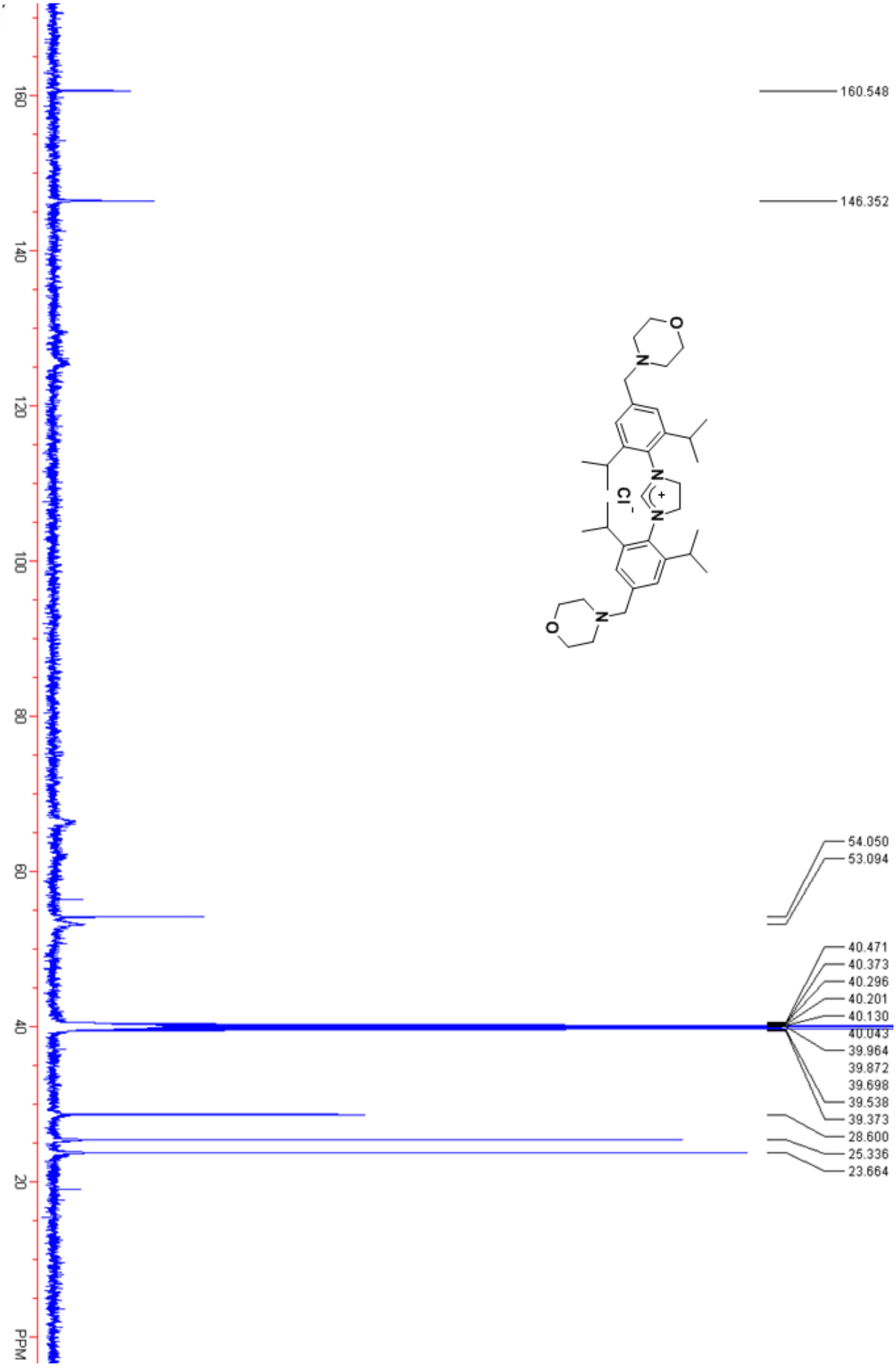


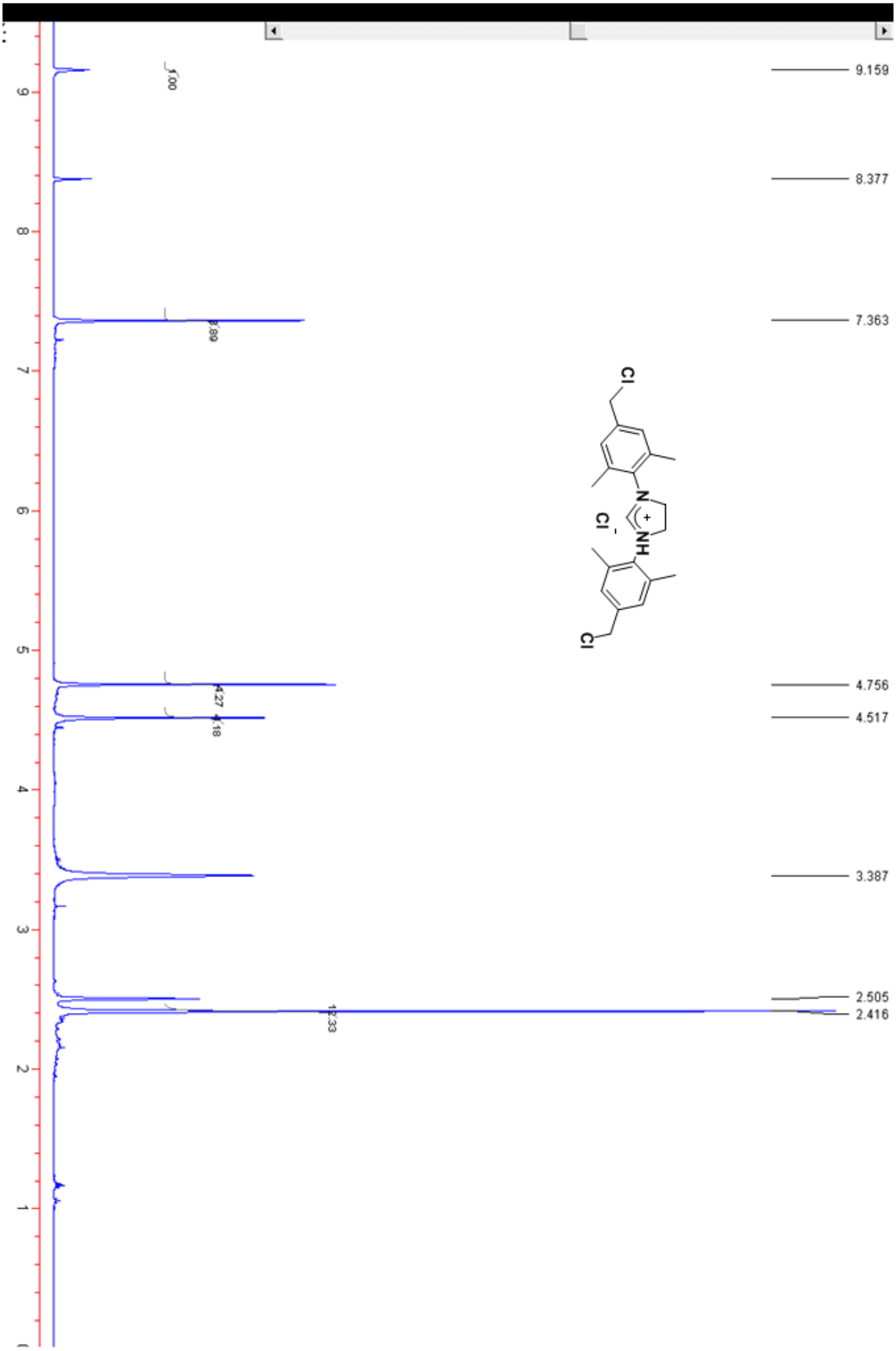


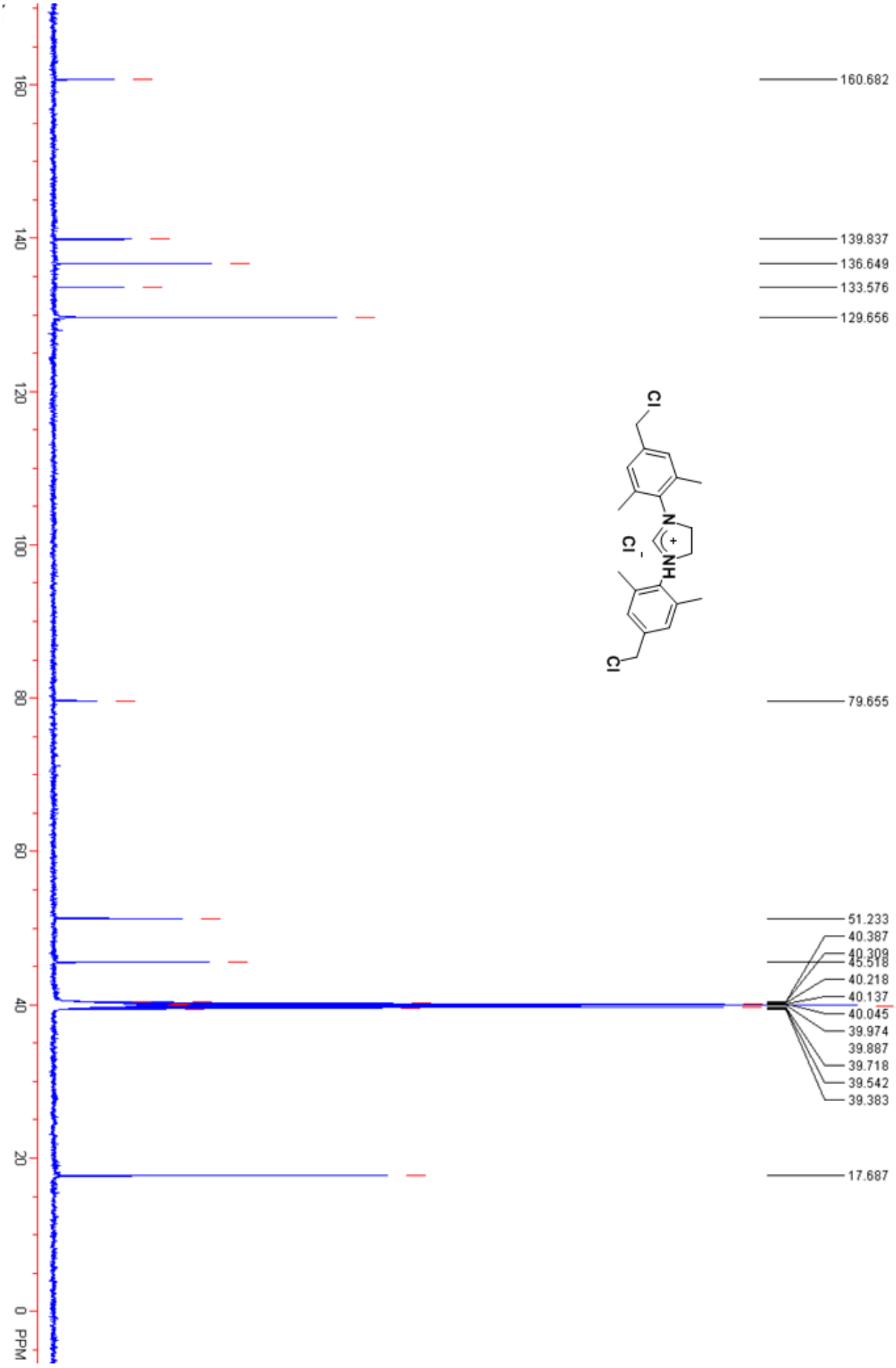


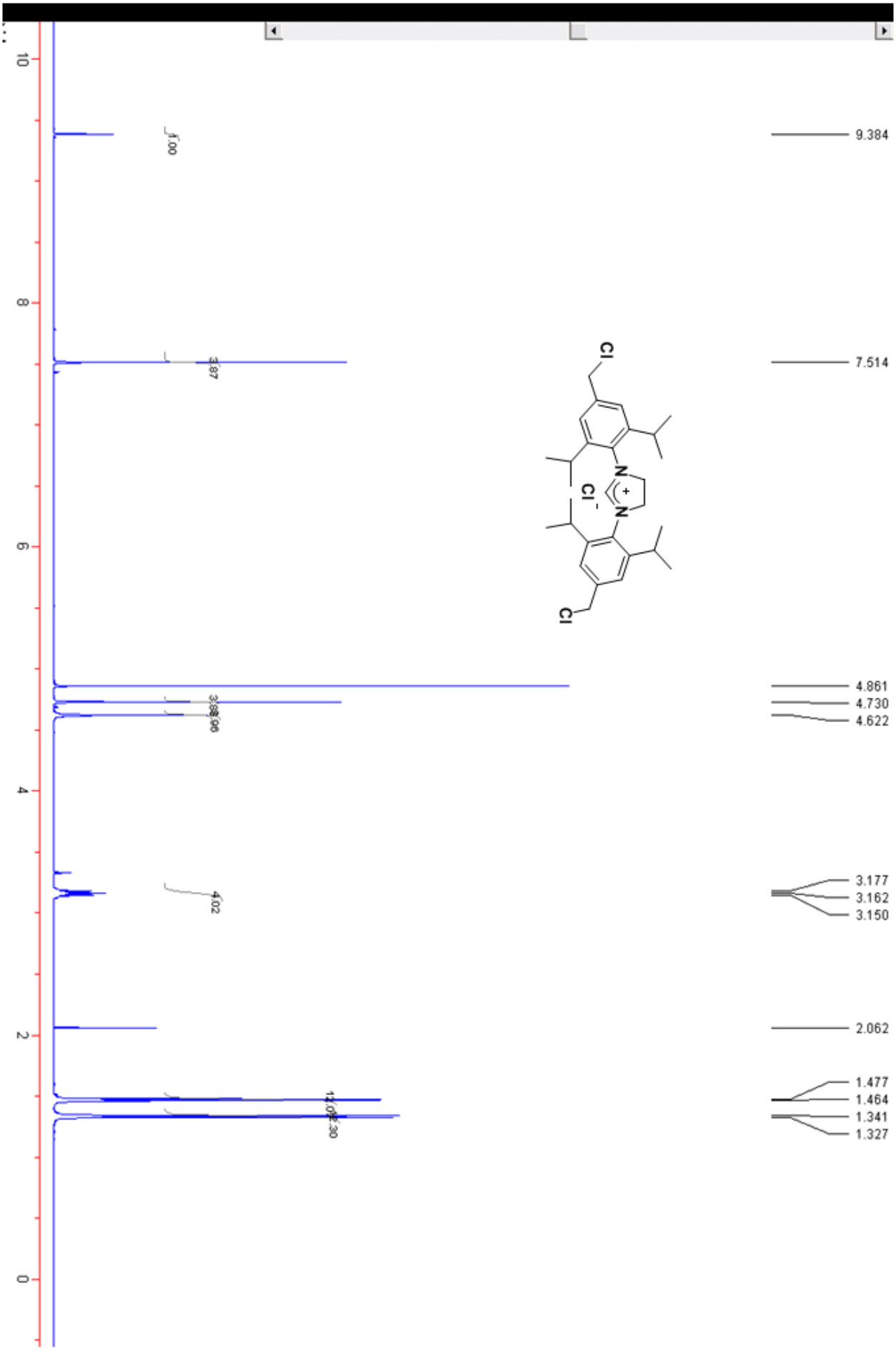


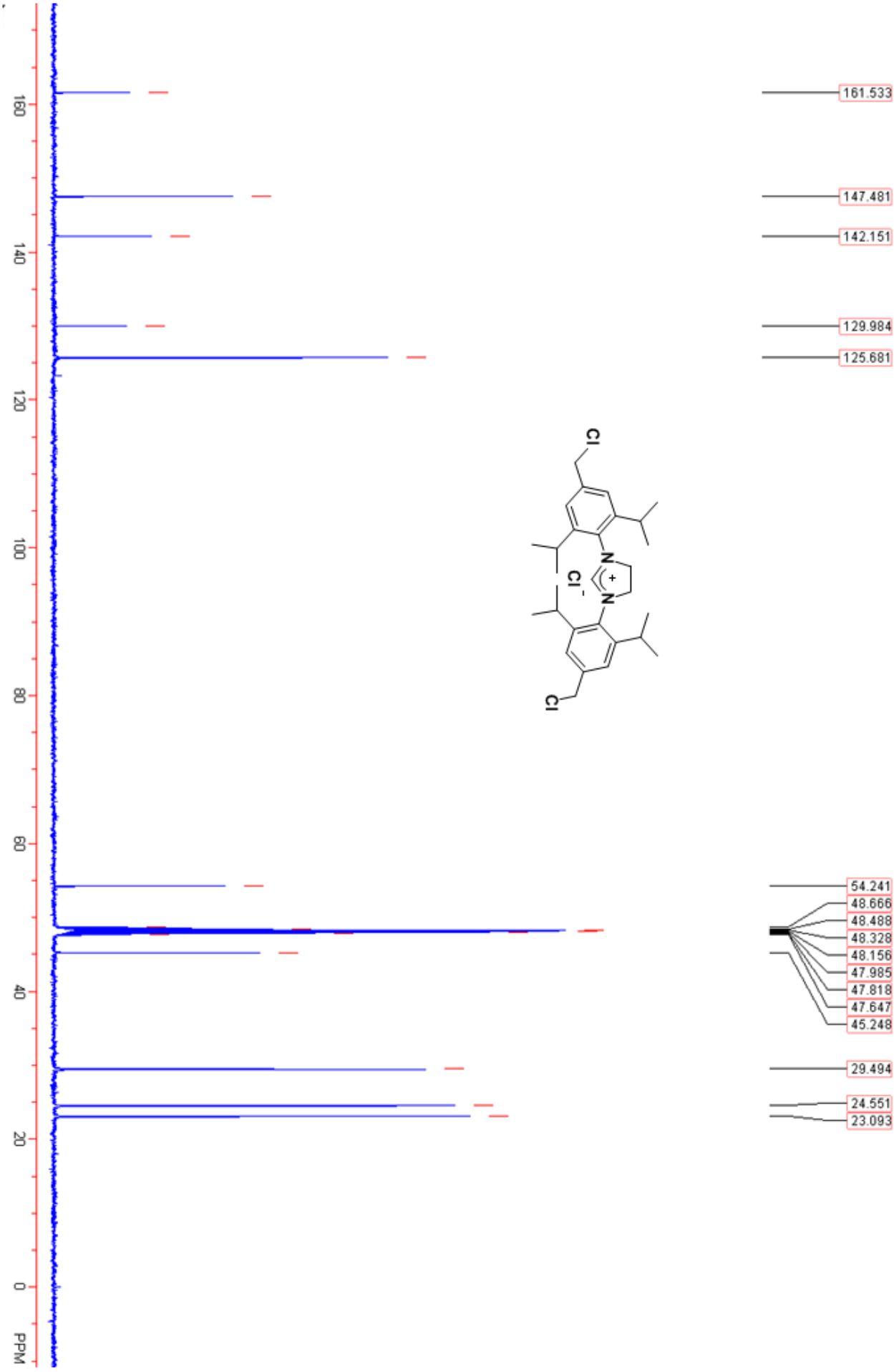


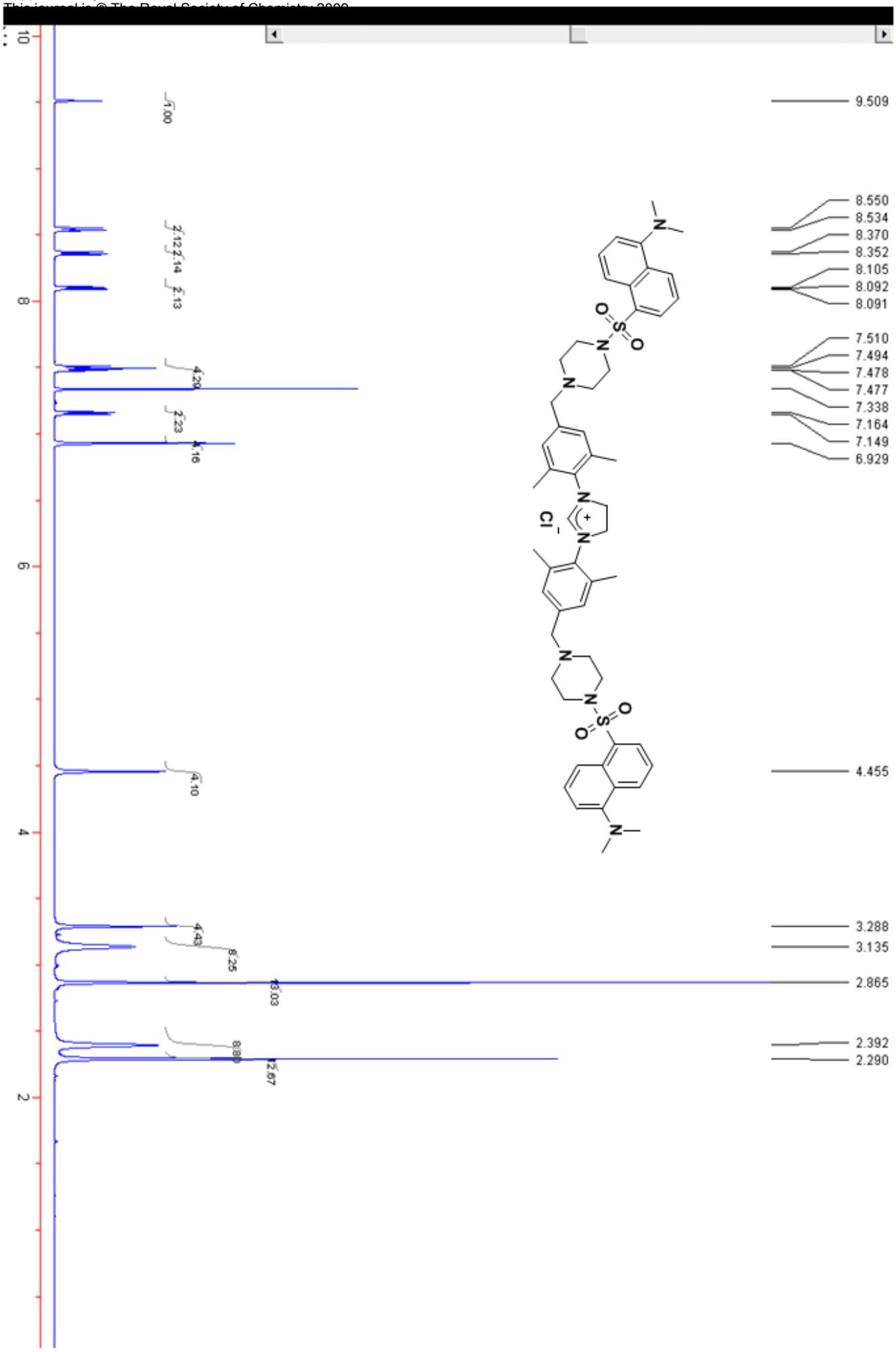


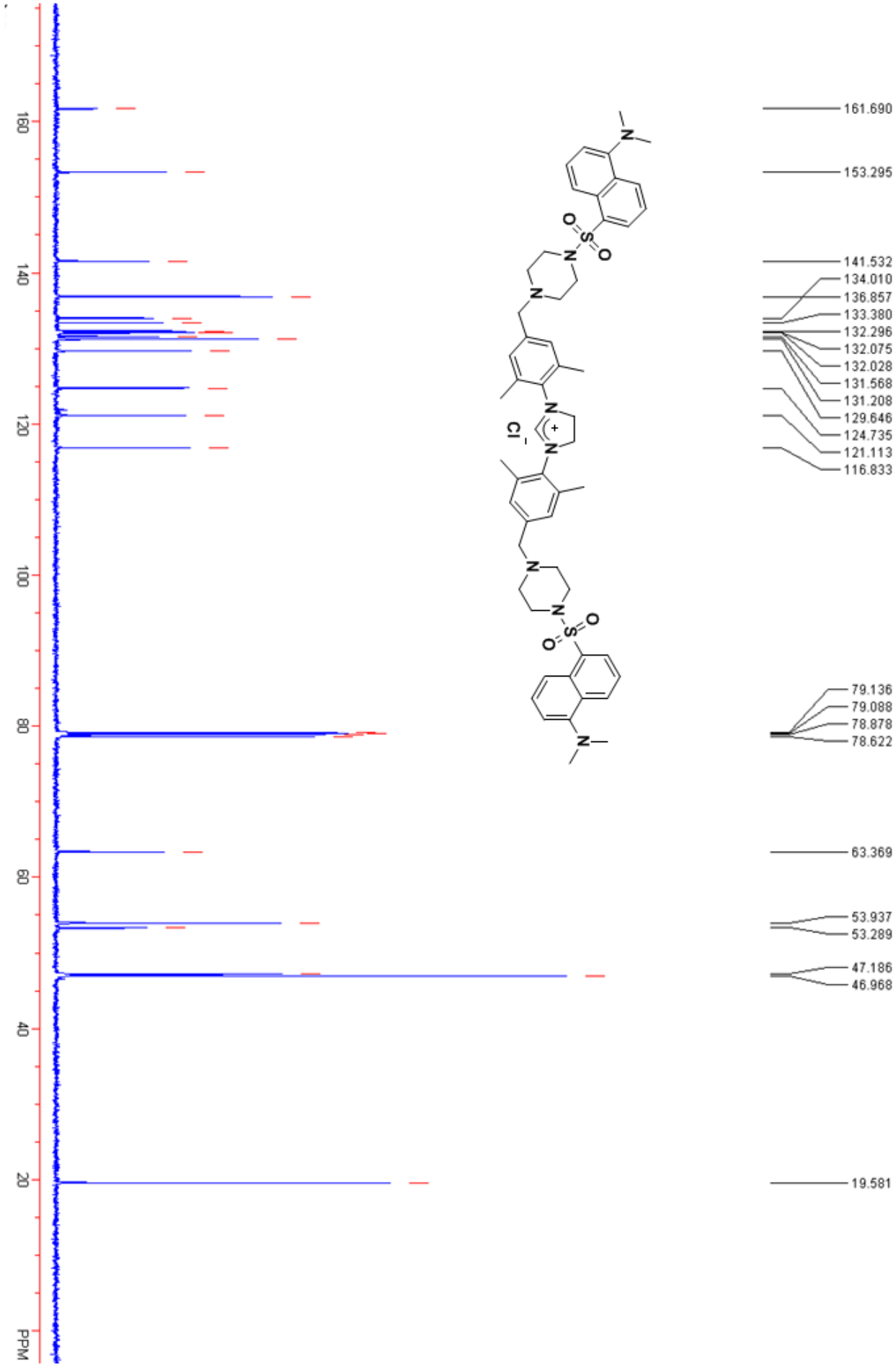


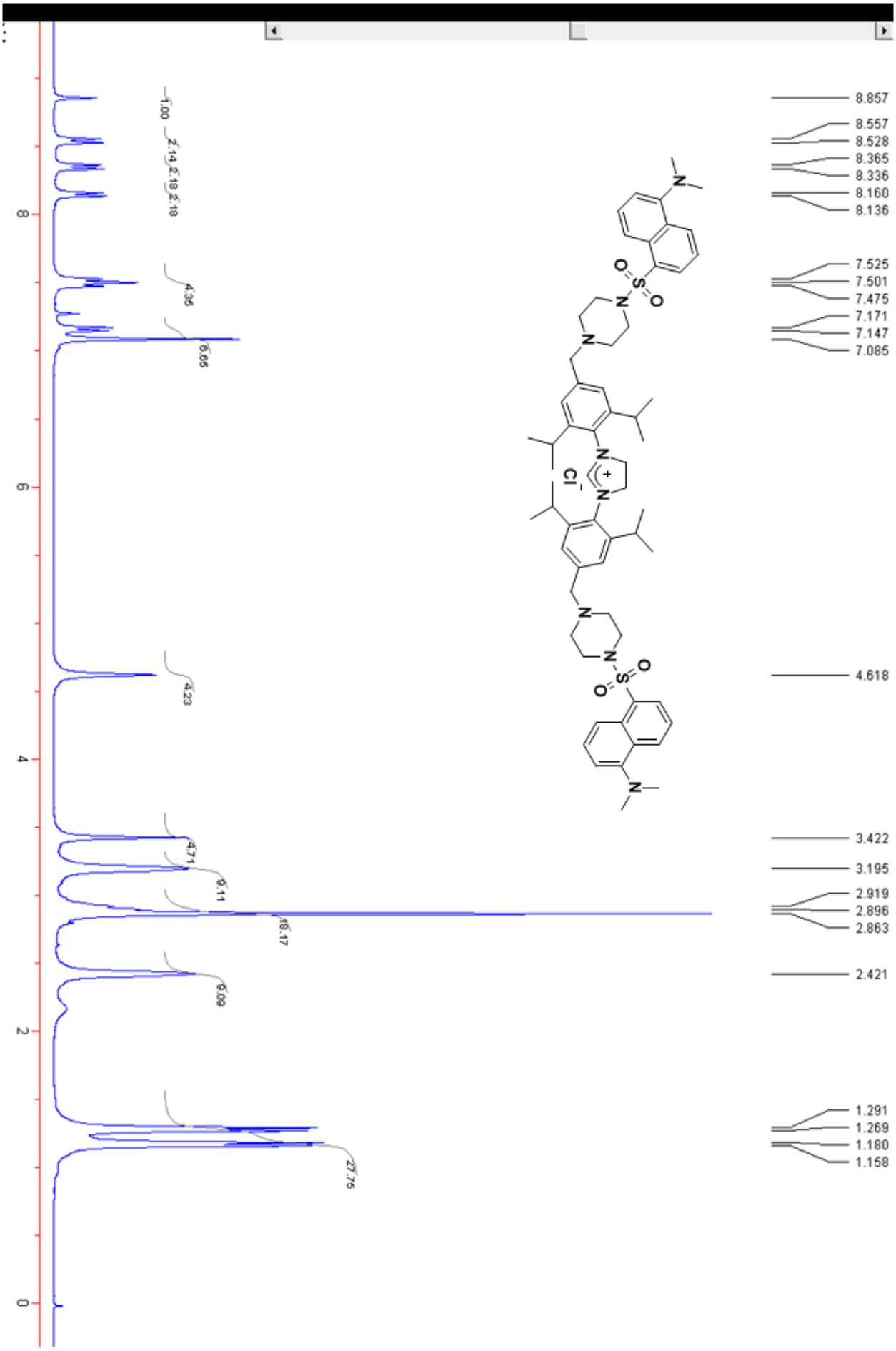


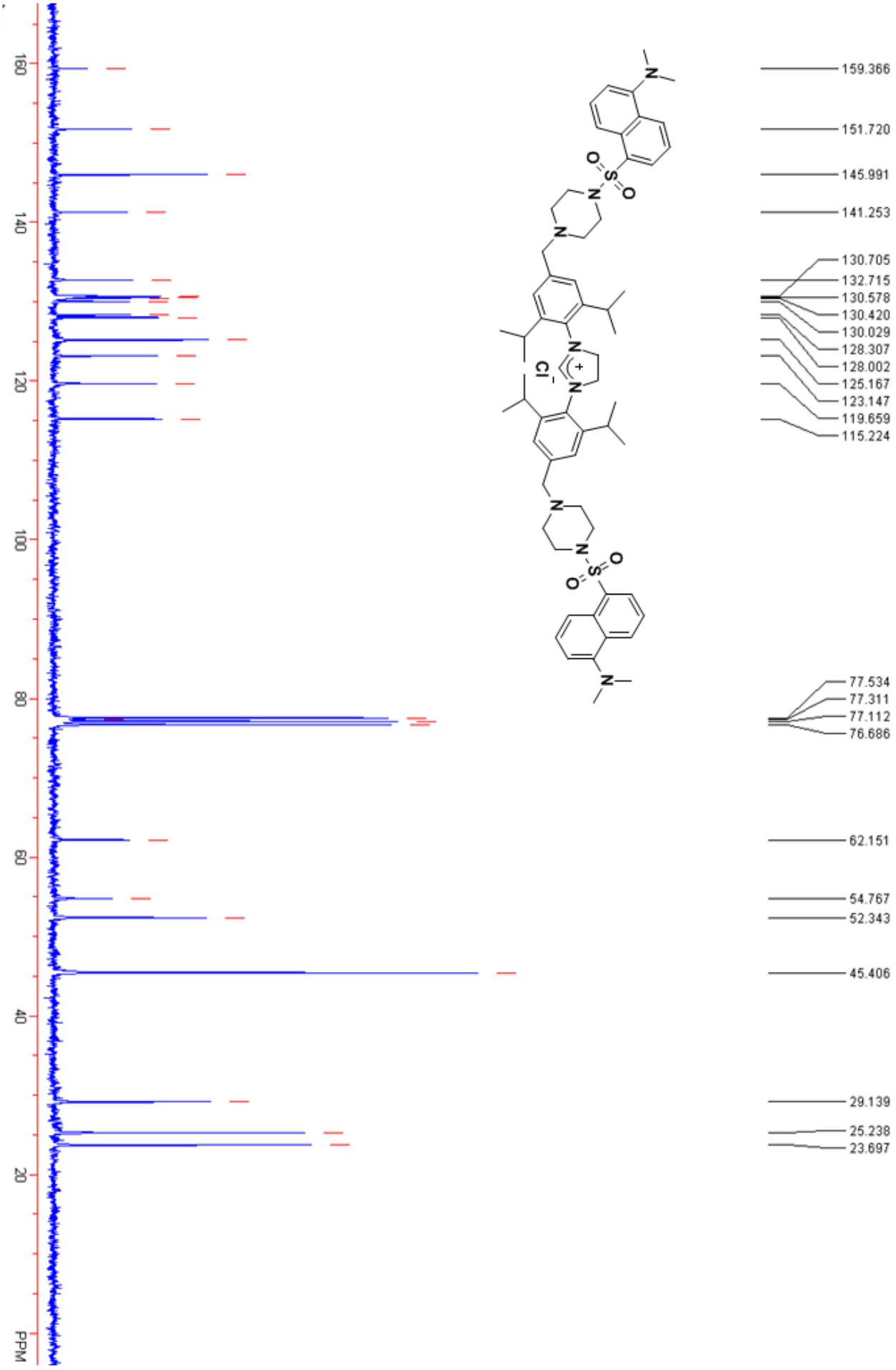


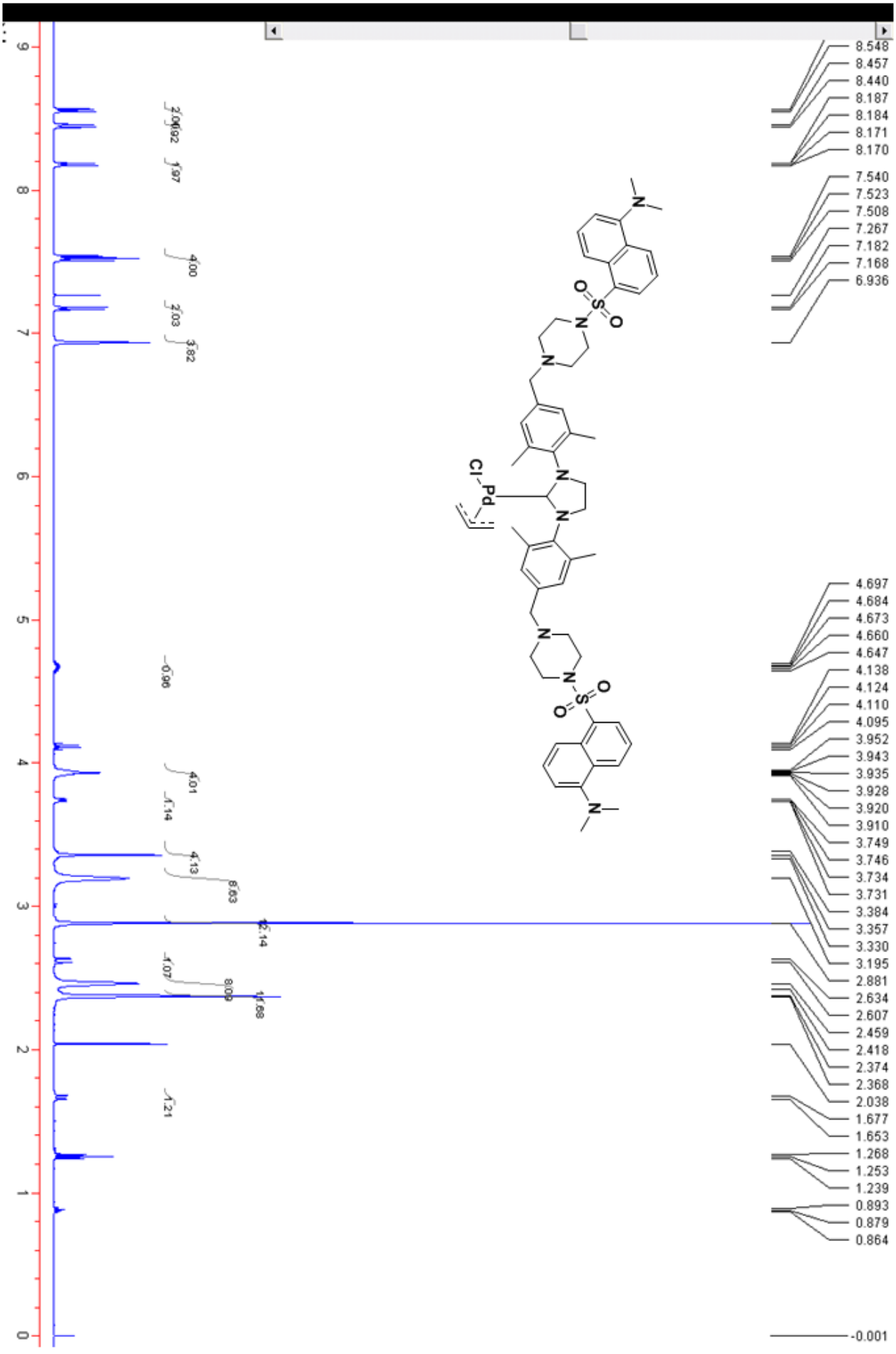


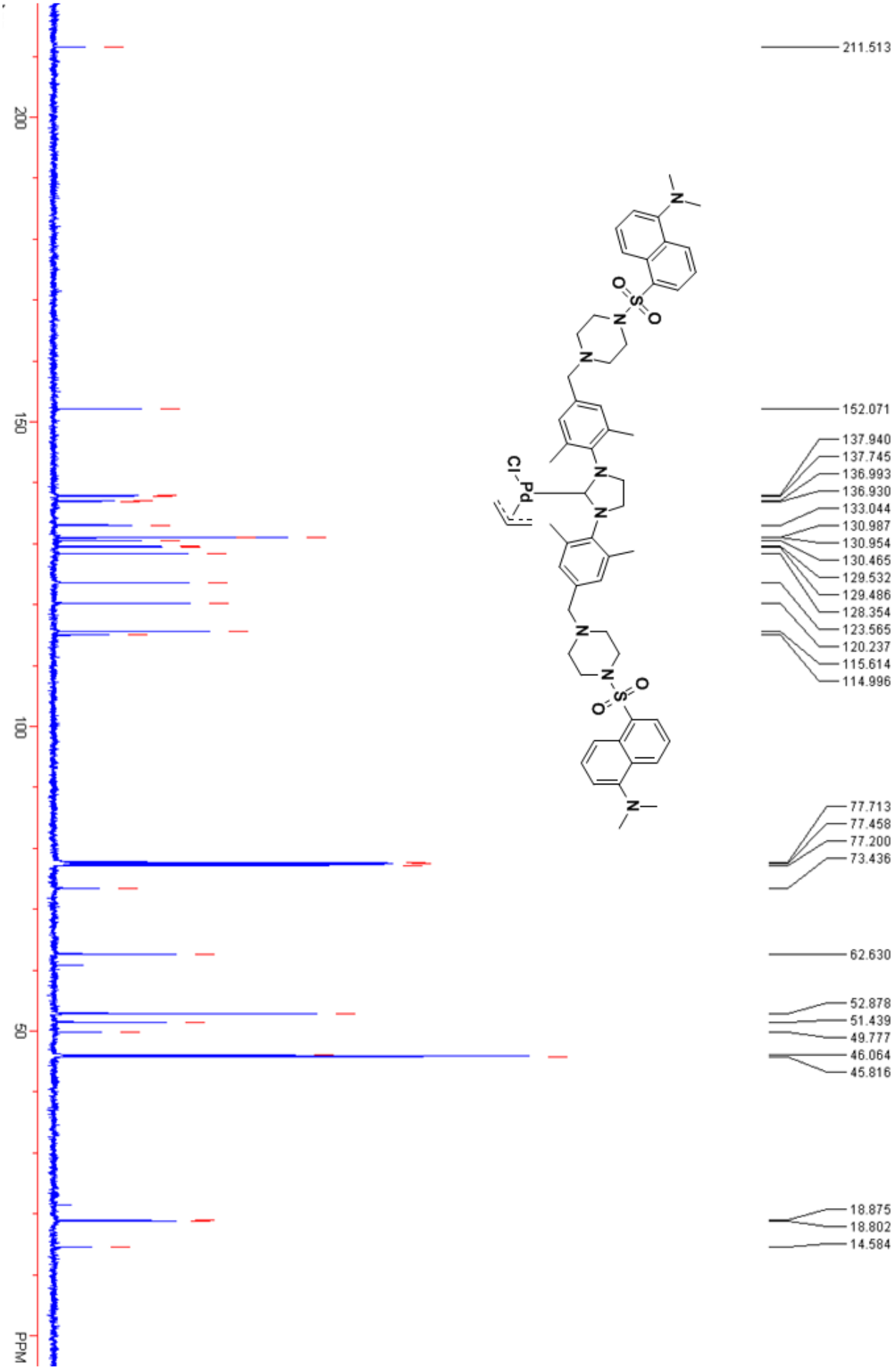


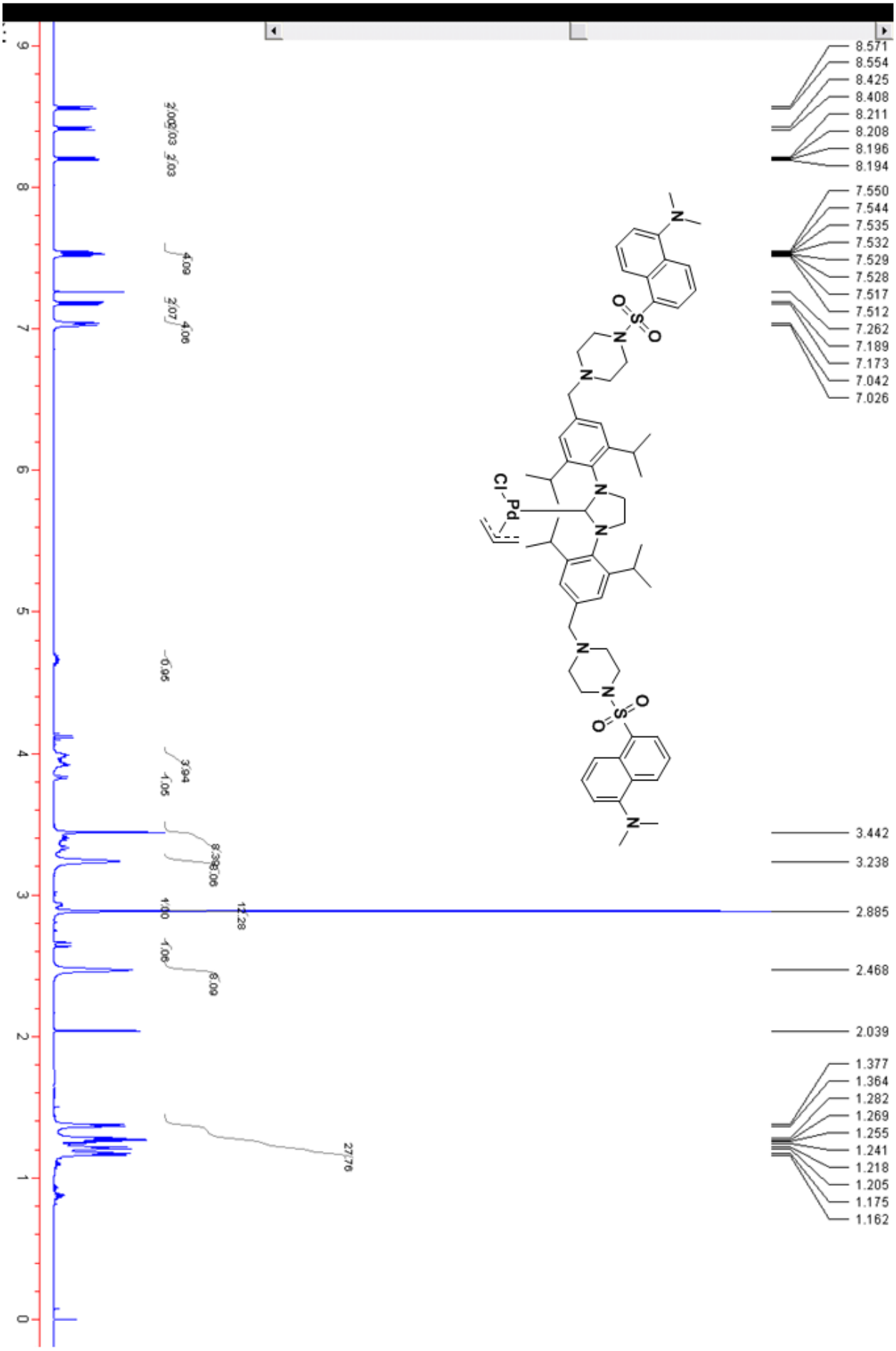


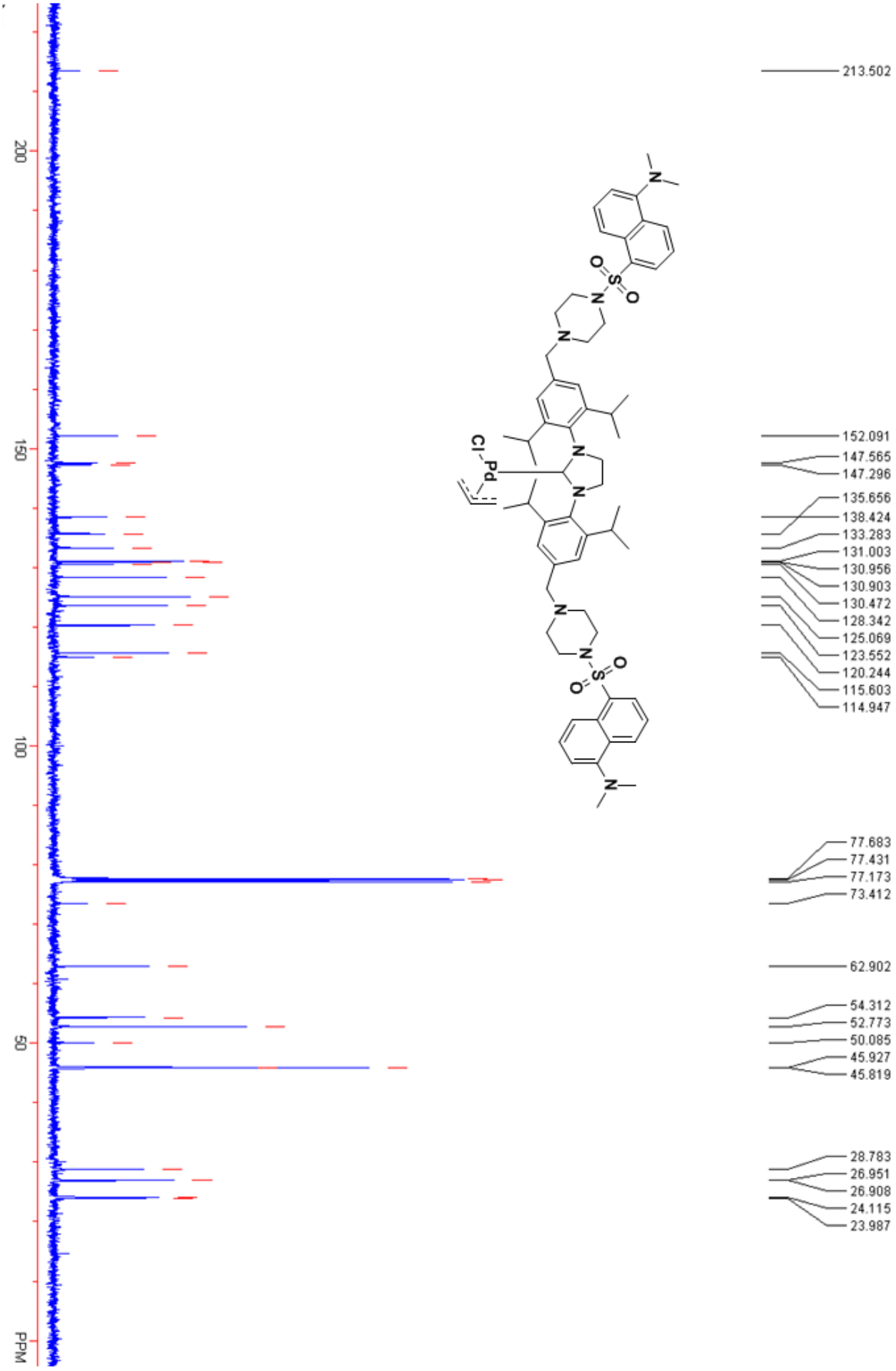




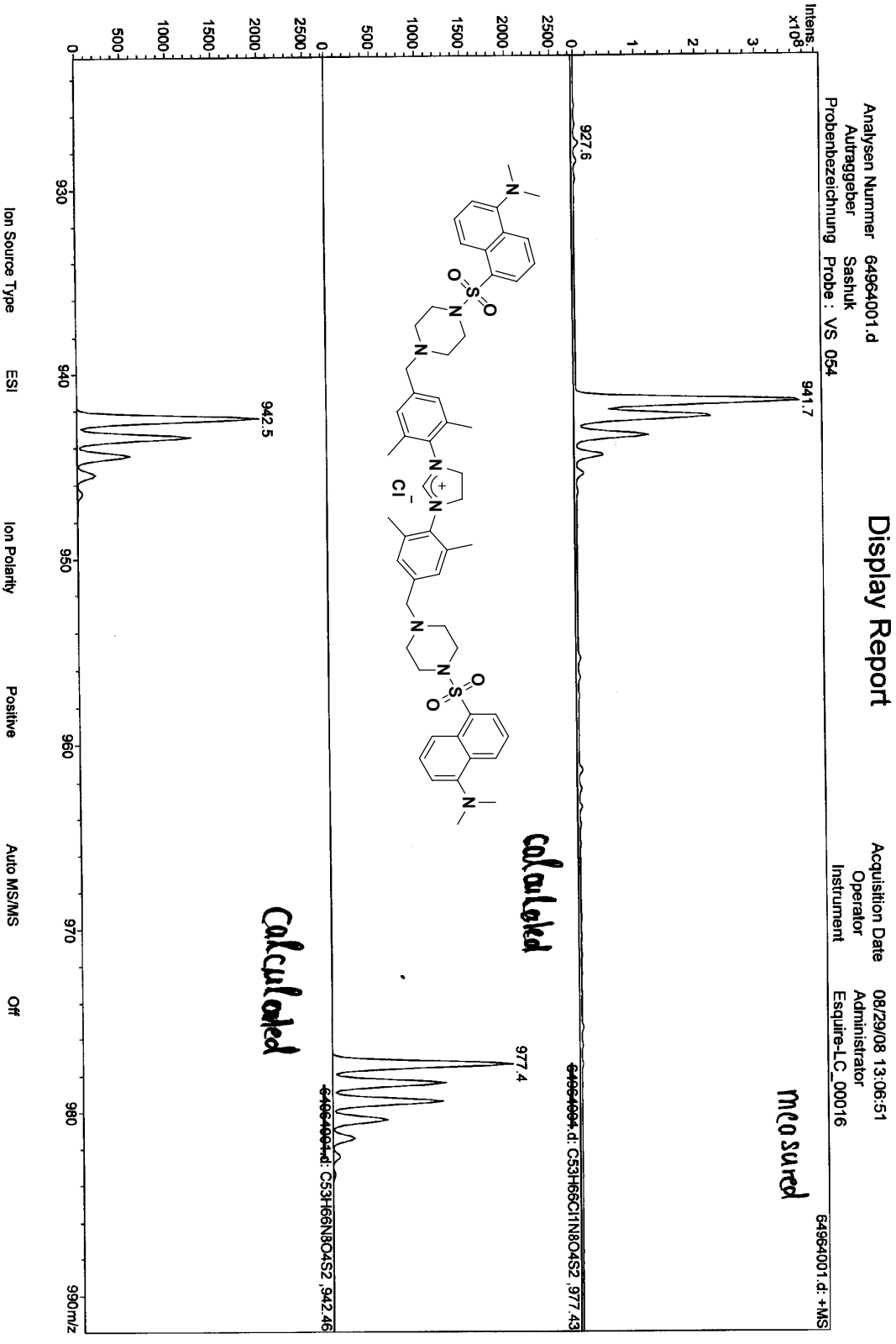


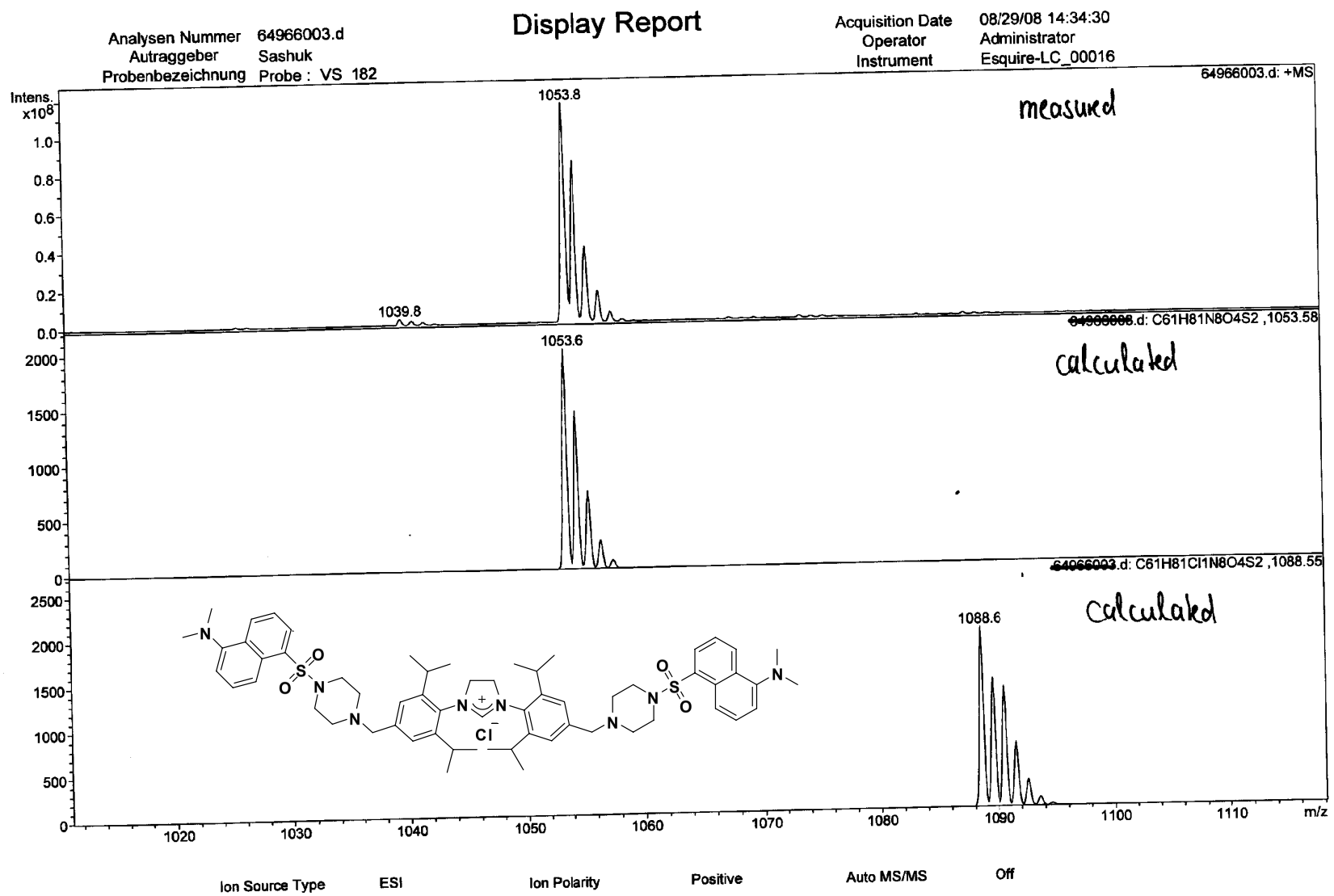


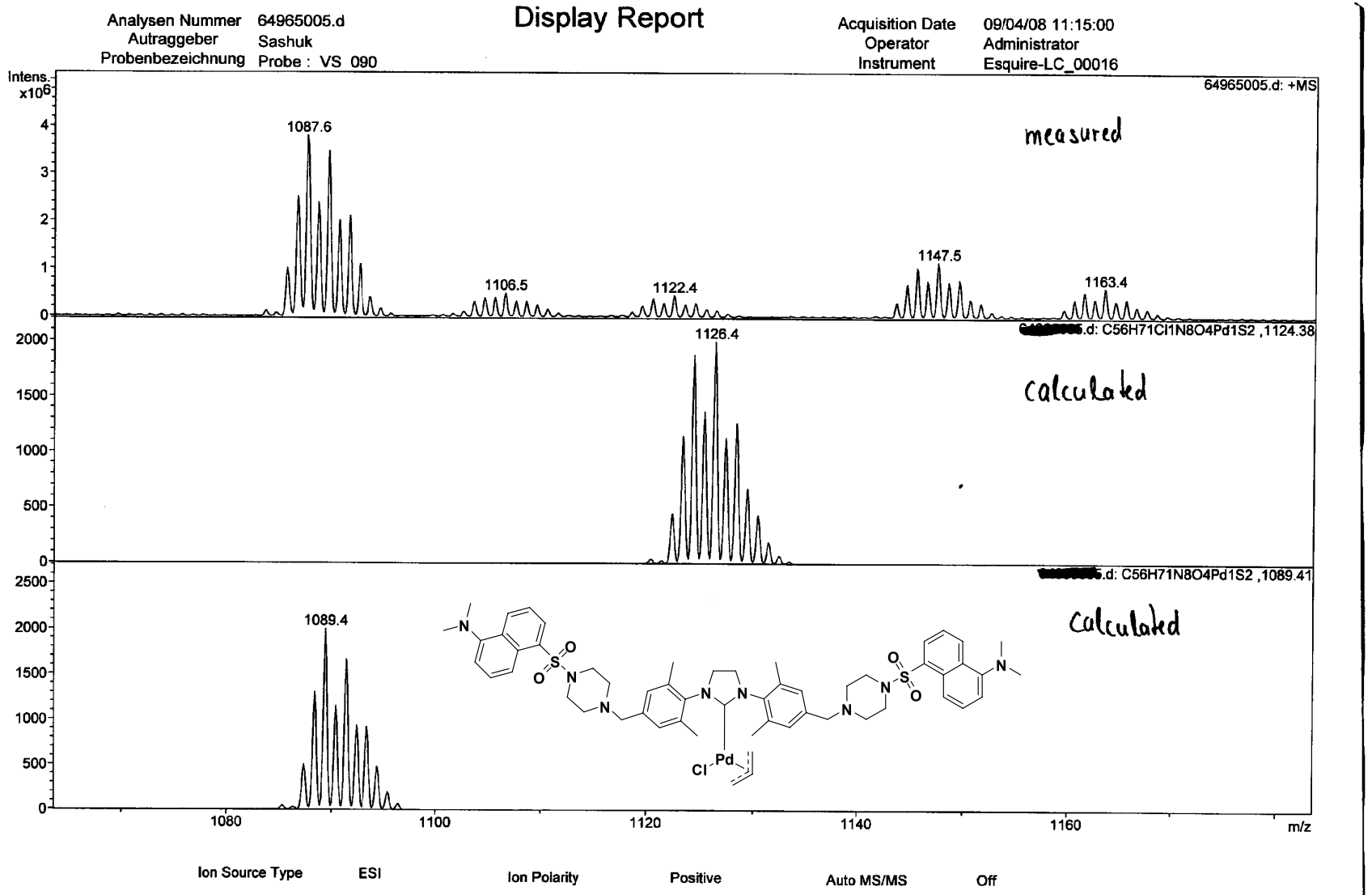


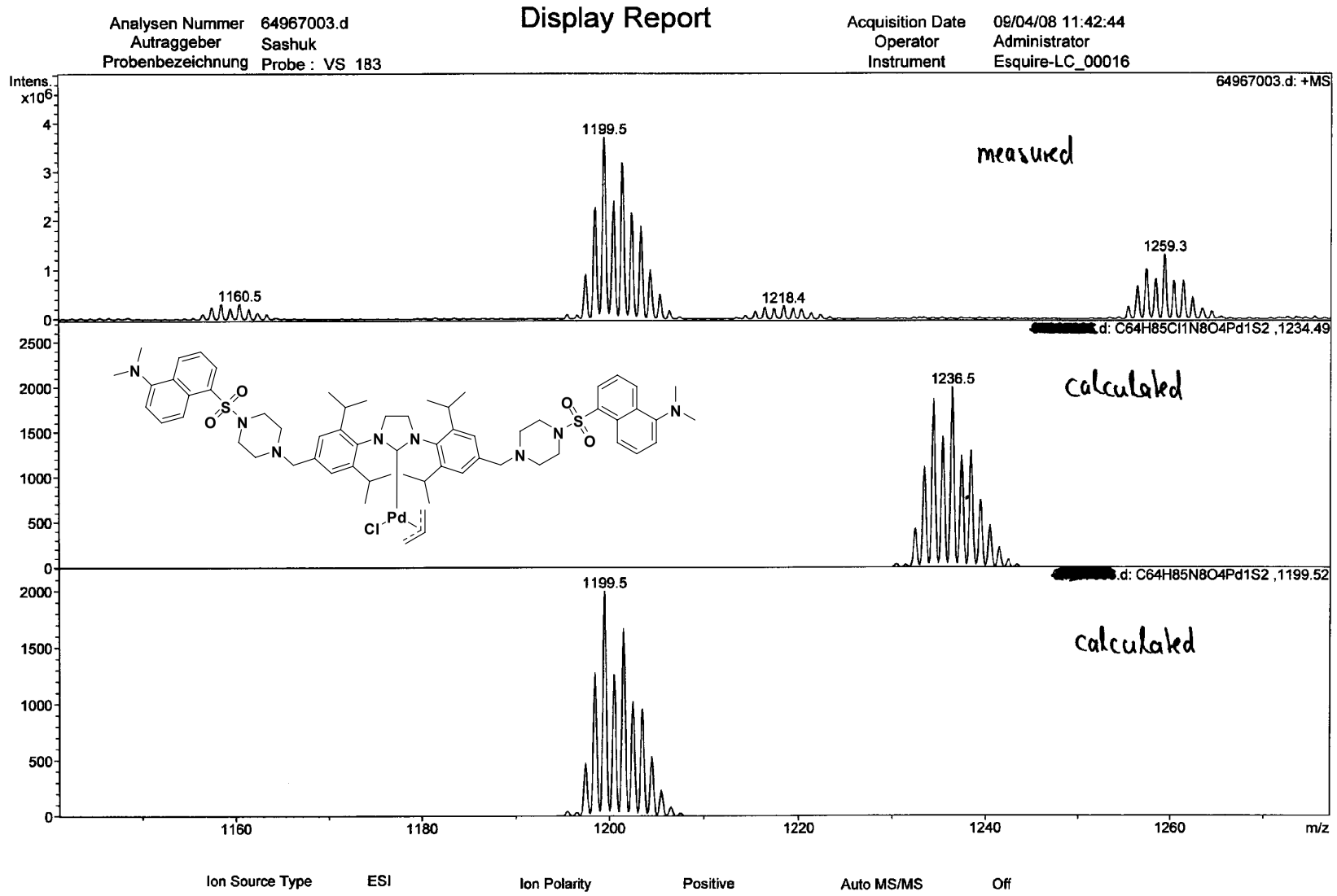


4. Copies of MS spectra









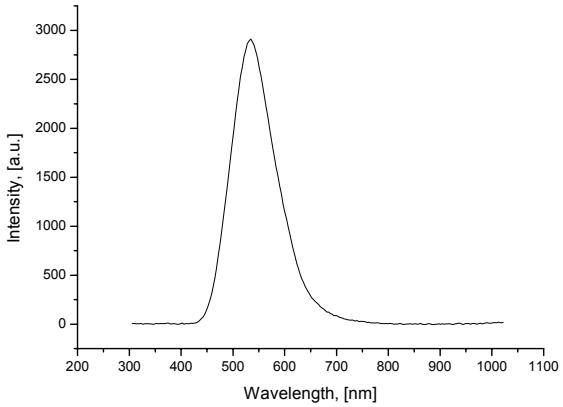


Fig 1. Emission spectrum of **8a**
(max λ_{em} = 535 nm with λ_{ex} = 350 nm)

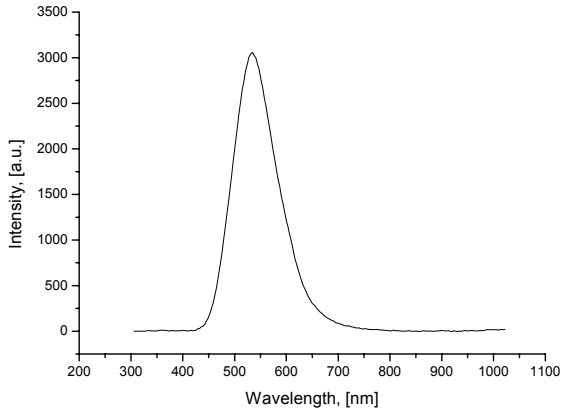


Fig 2. Emission spectrum of **8b**
(max λ_{em} = 535 nm with λ_{ex} = 355 nm)

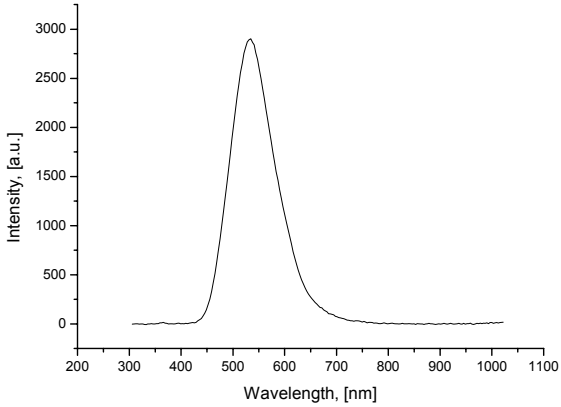


Fig 3. Emission spectrum of **9a**
(max λ_{em} = 535 nm with λ_{ex} = 360 nm)

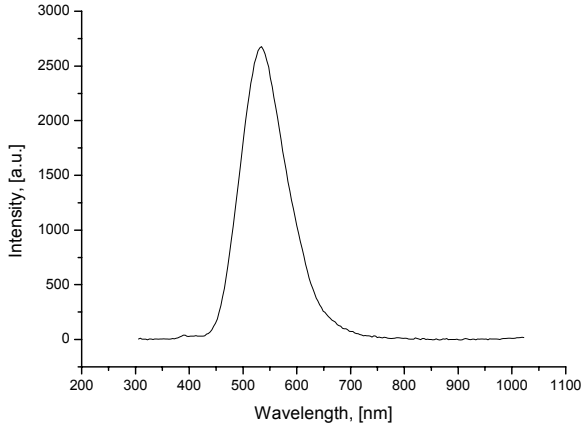


Fig 4. Emission spectrum of **9b**
(max λ_{em} = 535 nm with λ_{ex} = 340 nm)