Water-Soluble Ionic Benzoporphyrins

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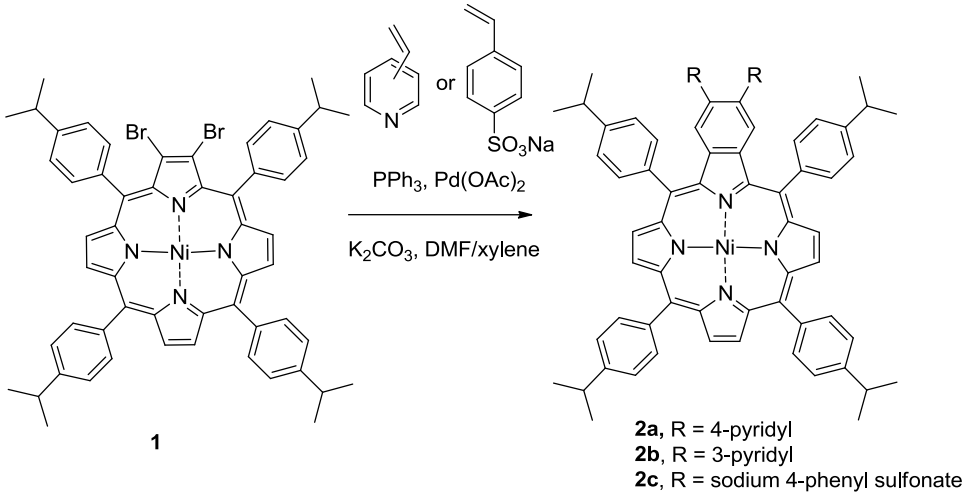
Supporting Information

Contents:

I. General

All solvents were analytical reagent grade unless otherwise stated and were obtained either from Sigma-Aldrich or ACROS. Analytical TLC's were performed on Silicycle UltraPure Silica Gel 60 F254 TLC plates. Preparative column chromatography was performed on silica gel (1000μm), which was purchased from Silicycle. ^{1}H and ^{13}C experiments were conducted on a Bruker Avance 500MHz spectrometer. All samples were prepared in $CDCl_3$ and chemical shifts were referenced to $CDCl_3$ at 7.24ppm for ^{1}H NMR and referenced to $CDCl_3$ at 77 ppm for ^{13}C-NMR unless otherwise stated. UV-Visible spectra were recorded on an Agilent 8453 UV-Visible spectrometer in CH_2Cl_2. Mass spectra were obtained on Bruker MALDI-TOF mass spectrometer and Bruker ESQUIRE~LCMS. M.P.'s were measured on an Electrothermal MEL-TEMP apparatus and were uncorrected.

II. General procedure for the Heck coupling reaction of metalated dibromoporphyrins



1

2a, R = 4-pyridyl
2b, R = 3-pyridyl
2c, R = sodium 4-phenyl sulfonate

3-vinyl pyridine was prepared using literature reported procedure. (A. Gordillo, E. Jesus, C. Lo´pez-Mardomingo; *Chem. Commun.*, 2007, 4056–4058)

Dibromoarylporphyrin **1** (0.045 mmol), palladium acetate (0.012 mmol), triphenylphosphine (0.030 mmol) and K_2CO_3 (0.09 mmol) were added to Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (10 mL) and dry xylene (10 mL) and 4-vinylpyridine or 3-vinylpyridine or sodium 4-phenyl sulfonate (25-fold excess). The mixture was then degassed via four freeze-pump-thaw cycles before the vessel was purged with argon

again. The Schlenk flask was sealed and heated to reflux for 72h. After 72 h, the mixture was diluted with $CHCl_3$ and washed with water. The organic layer was removed under vacuum. The residue was subjected to silica column chromatography. The band containing the desired porphyrin was collected and recrystallized from $CHCl_3$ and methanol. This procedure was used to prepare **2a, 2b**.

For **2c**, after refluxing for 72h, the solvent was removed under vacuum and the compound was redissolved in isopropanol and passed through a short silica gel plug. Solvent was removed again and the mixture was run through a saphadex resin column in methanol to get rid of excess 4-styrenesulfonic acid sodium salt hydrate. The ideal product **2c** was isolated on a silica column (DCM/MeOH). Recrystallization was performed using methanol and DCM, in which DCM served as the poorer solvent. In order to obtain a better ^{1}H NMR, excess of ionic exchange resin (Dowex 50Wx8) was used to convert the product to the acidic form **2c'**.

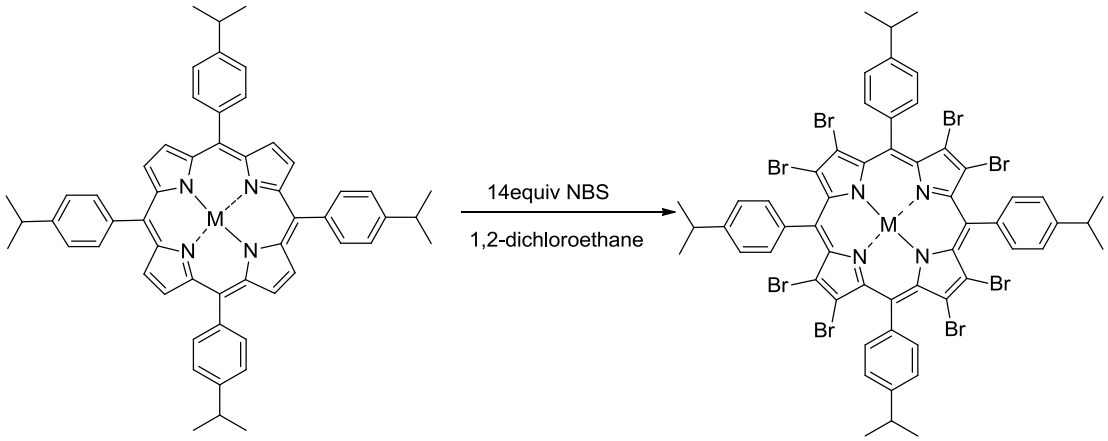
2a: mp > 320^{o}C. Yield: 56%. UV-Vis λmax (CH_2Cl_2)/nm 434 (log ε 5.52), 545 (4.31), 577 (4.12); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.68-8.71 (6 H, m, *β*-H), 8.46-8.48 (4H, m, *o*-pyridine-H), 7.85-7.90 (8H, m, *o*-Ph-H on *meso*-phenyl ring), 7.50-7.56 (8H, m, *m*-Ph-H on *meso*-phenyl ring), 7.21 (2H, s, fused benzene-H), 6.95 (4H, m, *m*-pyridine-H), 3.13-3.19 (4H, m, isopropyl(CH)-H), 1.41-1.47 (24H, m, isopropyl (CH_3)-H) ; ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.21, 24.29, 34.07, 34.15, 115.50, 120.49, 124.88, 125.12, 126.10, 126.47, 131.24, 131.79, 132.77, 132.80, 133.64, 134.44, 137.11, 137.66, 138.15, 140.35, 141.20, 142.14, 143.99, 148.47; Calculated Mass, 1042.42, Found MS (MALDI-TOF), m/z 1042.52.

2b: mp > 320^{o}C. Yield: 50%. UV-Vis λmax (CH_2Cl_2)/nm 433 (log ε 5.51), 538 (4.32), 577 (4.10); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.68-8.70 (6 H, m, *β*-H), 8.43-8.44 (2H, m), 8.26 (2H, m), 7.85-7.91 (8H, m, *o*-Ph-H on *meso*-phenyl ring), 7.50-7.55 (8H, m, *m*-Ph-H on *meso*-phenyl ring), 7.29-7.30 (2H, m), 7.099-7.11 (4H, m), 3.11-3.20 (4H, m, isopropyl(CH)-H), 1.36-1.48 (24H, m, isopropyl (CH_3)-H) ; ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.21, 24.26, 34.08, 34.17, 115.43, 120.38, 122.80, 125.09, 126.12, 126.54, 131.10, 131.62, 132.73, 133.64, 137.09, 137.19, 137.37, 137.75 138.20, 140.17, 141.06, 142.01, 143.96, 147.63, 148.41, 149.54,

150.73; Calculated Mass, 1042.42, Found MS (MALDI-TOF), m/z 1043.18.

2c': mp > 320°C. Yield: 42%. UV-Vis λmax (CH_2Cl_2)/nm 430 (log ε 5.51), 540 (4.60), 575 (4.47); ^{1}H-NMR (500 MHz, $CDCl_3$ with two drops of CD_3OD, Me_4Si) δ 8.56-8.70 (6 H, m, *β*-H), 7.80-8.10 (8H, m), 7.45-7.63 (12H, m), 6.80-7.15 (6H, m), 3.11-3.15 (4H, m, isopropyl(CH)-H), 1.33-1.46 (24H, m, isopropyl (CH_3)-H); Calculated Mass, 1200.35, Found MS (MALDI-TOF), m/z 1200.32. (For **2c'**, five proton NMRs were attached, of which $CDCl_3$ with two drops of CD_3OD gave the best results. Other solvent systems including only $CDCl_3$, only MeOD, and one or three drops of MeOD mixed with $CDCl_3$ gave worse results.)

III. General procedure for the octabromination reactions



3a M = Ni(II)
3b M = Cu(II)
3c M = Zn(II)

Ni-arylporphyrin (1 mmol) or Cu-arylporphyrin (1 mmol) and NBS (14 mmol) were added into a round bottom flask and dissolved in dry 1, 2-dichloroethane. The mixture was then refluxed for 2 hours. The organic layer was removed under vacuum. The residue was subjected to column chromatography. The bands containing the desired porphyrins were collected and recrystallized from $CHCl_3$/MeOH. This procedure was used to prepare **3a** and **3b**. **3c** was prepared by demetalation of **3b** through treatment of concentrated H_2SO_4 and TFA, followed by re-insertion of Zn using $Zn(OAc)_2$.

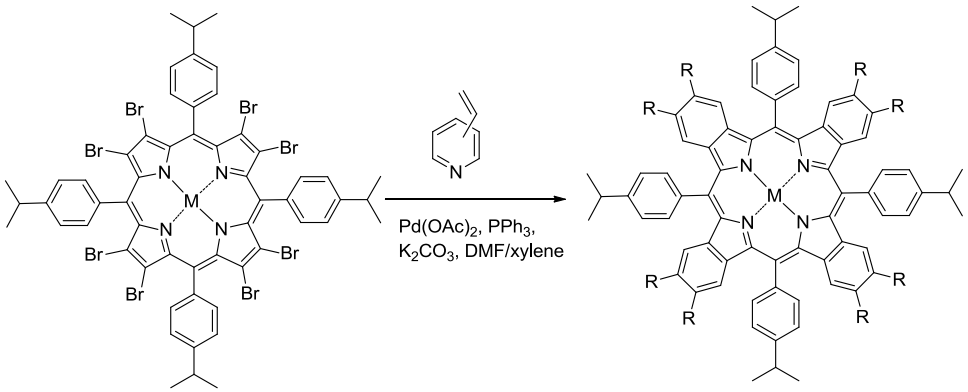
3a: mp > 320°C. yield: 54%. UV-Vis λmax (CH_2Cl_2)/nm 451 (log ε 5.54), 564 (4.96), 598 (4.62); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 7.79 (8H, d, J = 8.0 Hz, *o*-Ph-H),

7.51 (8H, d, J = 8.0 Hz, *m*-Ph-H), 3.13-3.19 (4H, m, isopropyl (CH)-H), 1.44 (24H, d, J = 6.5 Hz, isopropyl (CH_3)-H); ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.33, 24.36, 34.20, 34.25, 120.12, 126.22, 126.29, 126.99, 133.51, 134.97, 143.60, 150.99; Calculated Mass, 1470.90, Found MS (MALDI-TOF), m/z 1470.91.

3b: mp > 320°C. Yield: 55%. UV-Vis λmax (CH_2Cl_2)/nm 461 (log ε 5.56), 579 (4.82), 624 (4.50); Calculated Mass, 1475.75, Found MS (MALDI-TOF), m/z 1475.11.

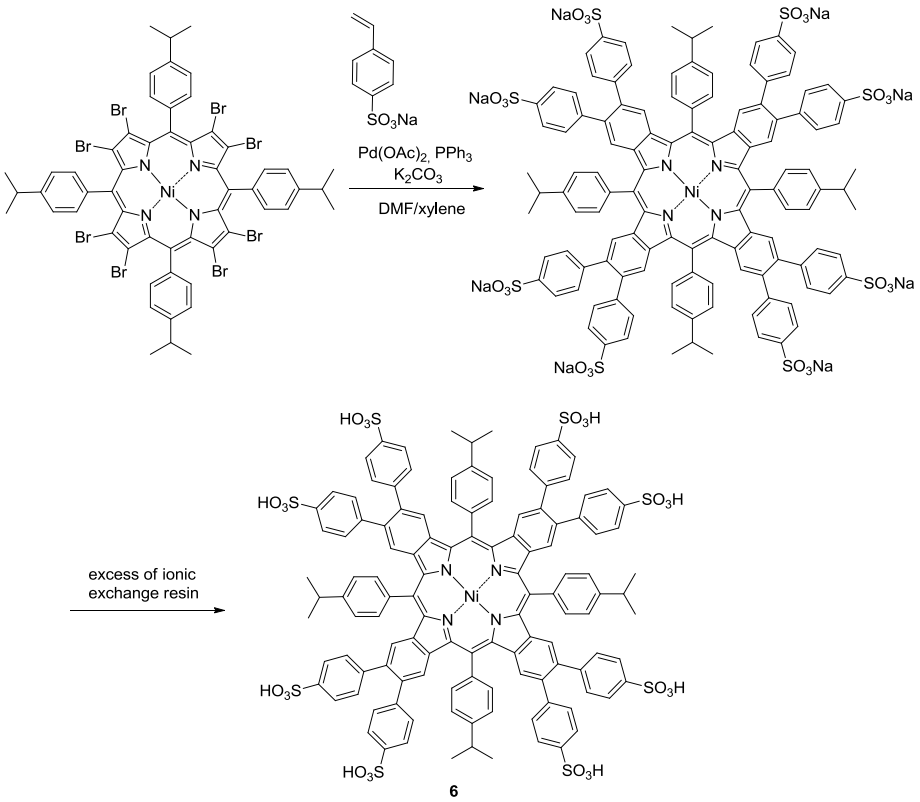
3c: mp > 320°C. Yield: 72% in two steps. UV-Vis λmax (CH_2Cl_2)/nm 463 (log ε 5.55), 597 (4.88), 654 (4.58); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.00 (8H, m, *o*-Ph-H), 7.58 (8H, m, *m*-Ph-H), 3.22 (4H, m, isopropyl (CH)-H), 1.49 (24H, m, isopropyl (CH_3)-H); ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.49, 34.28, 109.88, 111.42, 111.67, 113.33, 113.57, 121.08, 124.62, 126.04, 136.49, 145.51, 150.61; Calculated Mass, 1477.59, Found MS (MALDI-TOF), m/z 1476.70.

IV. General procedure for the Heck coupling reaction of metalated octabromoporphyrins



3a M = Ni(**II**)
3b M = Cu(**II**)
3c M = Zn(**II**)

4a M = Ni, R = 4-pyridyl
4b M = Cu, R = 4-pyridyl
4c M = 2H, R = 4-pyridyl
4d M = Zn, R = 4-pyridyl
4e M = Ni, R = 3-pyridyl



Octabromoarylporphyrins (0.045 mmol), palladium acetate (0.040 mmol), triphenylphosphine (0.120 mmol) and K_2CO_3 (0.36 mmol) were added to Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (10 mL) and dry xylene (10 mL) and relevant alkene (60-fold excess). The mixture was then degassed via four freeze-pump-thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to reflux for 72h. After 72 h, the mixture was diluted with $CHCl_3$ and washed with water. The organic layer was removed under vacuum. The residue was subjected to silica column chromatography. The bands containing the desired porphyrins were collected. This procedure was used to prepare **4a, 4b** and **4e**. **4c** was obtained after demetalation of **4b** by treating with concentrated H_2SO_4 and TFA. **4d** was obtained by re-insertion of Zn using $Zn(OAc)_2$.

Water solubility was tested for **4a**. Porphyrin **4a** (20 mg) was dissolved in methanol and added excess of TFA (0.1 ml). After the mixture was stirred for 30 mins, the solvent was removed. The protonated porphyrin was recrystallized from DCM/MeOH (DCM acts as the bad solvent). The solid porphyrin was tested for

solubility in water.

Both protonation and methylation were performed for **4c**. The protonated **4c** was obtained through the treatment of **4c** in methanol with excess of TFA for 5 hours. The solvent was removed. The desired product was recrystallized from DCM and methanol. The protonated product can be dissolved in methanol and water, but not in chloroform or DCM. A ^{1}HNMR was taken in CD_3OD. Methylation was also performed on **4c**. Excess of MeI was added into the solution of **4c** in methanol, and the resulting mixture was stirred for 1.5 days. The solvent was removed under reduced pressure. The product was recrystallized from DCM and methanol. The methylated product can be dissolved in water (concentration $\geqslant$ 15mM) and methanol, but not in chloroform or DCM. ^{1}HNMR was taken in CD_3OD.

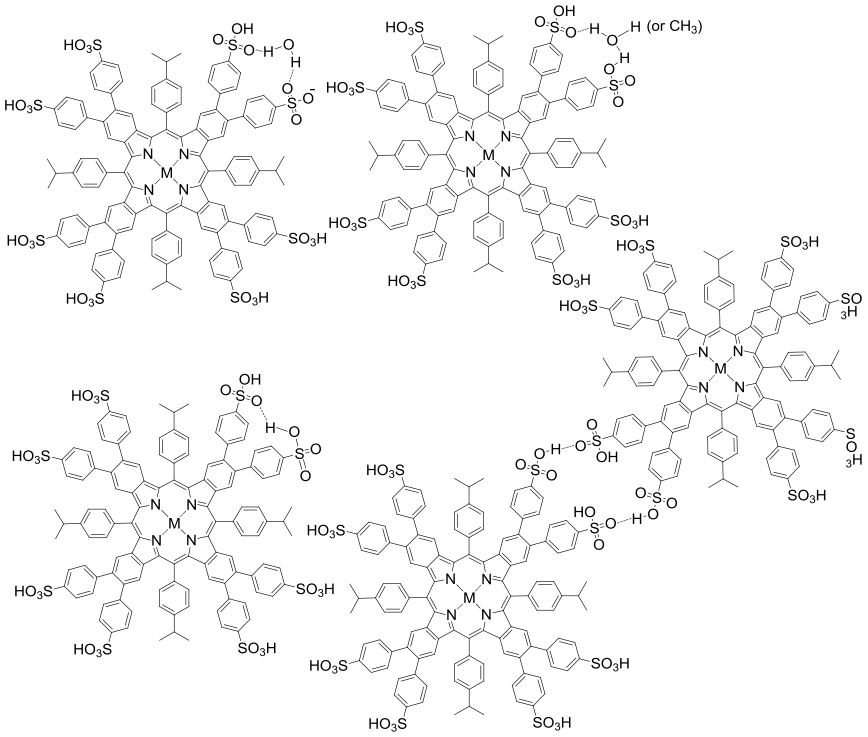
For **6**, after the reaction was completed, the reaction mixture went through a short silica plug using methanol/DCM as the eluent, and was then directly converted to its acidic form **6** using acidic ion exchange resin (Dowex 50Wx8). **6** was then purified by silica column chromatography using MeOH/DCM as the eluent, followed by size-exclusion chromatography (Sephadex LH-20).

Discussion of 6: ESI mass spectrometry revealed the existence of **6**. UV-Vis spectra of **6** showed well defined Soret band at 466 nm, similar to the Soret bands of Ni(II) porphyrin **4a** and **4e**. However, ^{1}H NMR of **6** displayed broadened and undefined proton shifts. This is likely due to the combined effects arising from porphyrin aggregation, intermolecular hydrogen bonding of the sulfonic acid groups, the dynamic ring flipping of the macrocycle owning to the crowding on the porphyrin periphery as well as the hindered ring rotation of phenyl substituents. This phenomenon has been observed for other peripherally crowded porphyrins.[9b] **6** is highly soluble in water, methanol and DMSO, and does not dissolve in DCM, $CHCl_3$, and acetonitrile. ^{1}H NMR measurement of **6** was carried out in deuterated methanol, DMSO and water. All the spectra showed broadened shifts, although the broadening varies to different extent in different solvents. For comparison, we also took a ^{1}H NMR of **4c** (with pyridyl substituents) in deuterated methanol. As expected, the ^{1}H NMR shifts of **4c** were also significantly broadened due to the hydrogen-bonding with

the solvent. In all these solvents, hydrogen bonding can be easily formed between the solvent molecules and the sulfonic groups. For comparison, we also took a ^{1}H NMR of **4c** (with pyridyl substituents) in deuterated methanol. As expected, the ^{1}H NMR shifts of **4c** were also significantly broadened due to the hydrogen-bonding with the solvent. Another factor may make the situation of **6** much more complicated than **4a-e** is that **6** can form "intramolecular" hydrogen bond through a solvent molecule or intermolecular hydrogen bond with itself (see Figure 1), but **4a-e** are less likely to form such kind of hydrogen bonds. We believe that the formation of hydrogen bond restricts the rotation of the aromatic substituents on the fused benzene rings. The restricted rotation will also slow down the dynamic ring flipping of the macrocycle. In addition, **6** is likely to self-assemble leading to more complicated situation to obtain well-defined ^{1}HNMR.

Figure 1.

Possible Hydrogen-bond formation of compound **6** and **2c**.
For clarity, only one set of two sulfonic groups are shown for hydrogen bond formation



Esterification of 6: 20 mg of **6** was treated with 5 mL of thionyl chloride and one drop of dry DMF. The mixture was allowed to stir for four hours and dried under vacuum. Then 10 mL of dry methanol and three drops of dry triethylamine were added and the mixture was stirred overnight. After drying under vacuum, DCM was added and the solution was sonicated for 20 min then passed through a filter to isolate the precipitant. The organic filtrate was then washed with water in order to remove inorganic residues. However, it turned out that

the ester of **6** was hydrolyzed back to sulfonic acid by the acequeous workup.

Amidation of 6 was then performed. A 50 mL round-bottomed flask containing **6** was equipped with a magnetic stirring bar and an addition funnel fitted at the top with an argon balloon. The flask was cooled to 0^{o}C in an ice-water bath and 2 mL of thionyl chloride and one drop of dry DMF were added dropwise through the addition funnel. The reaction mixture was warmed to room temperature and stirred for 1.5 hours after addition of thionyl chloride and DMF. Then the reaction flask is fitted with a distillation head and the excess of thionyl chloride was distilled off at reduced pressure. The flask containing residue was dried for one hour, 5 mL of dry DCM was then added into the flask under argon. Then 1.5 mL of dry hexylamine was added dropwise into the flask. The reaction mixture was stirred for 2 hours. The solvent was removed, and the excess hexylamine was washed off with hexane. The product was isolated and purified through a preparative TLC plate. ^{1}H NMR and MALDI-TOF were done in chloroform.

4a: mp > 320^{o}C. Yield: 54%. UV-Vis λmax (CH_2Cl_2)/nm 465 (log ε 5.93), 608 (4.81), 659 (5.57); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.42 (16 H, d, J = 4.5 Hz, *o*-pyridine-H), 8.01 (8H, d, J = 7.5 Hz, *o*-Ph-H), 7.65 (8H, d, J = 7.5Hz, *m*-Ph-H), 7.22 (8H, s, fused-benzene-H), 6.88 (16H, d, J = 5.0 Hz, *m*-pyridine-H), 3.12-3.18 (4H, m, isopropyl(CH)-H), 1.36 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H) ; ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.32, 34.39, 108.56, 116.27, 124.60, 126.16, 127.39, 133.12, 134.42, 137.69, 138.63, 138.88, 148.87, 149.45, 151.16; Calculated Mass, 1654.63, Found MS (MALDI-TOF), m/z 1654.83.

4b: mp > 320^{o}C. Yield: 51%. UV-Vis λmax (CH_2Cl_2)/nm 473 (log ε 5.82), 612 (4.78), 662 (5.30); Calculated Mass, 1661.49, Found MS (MALDI-TOF), m/z 1661.32.

4c: mp > 320^{o}C. Yield: 90%. UV-Vis λmax (CH_2Cl_2)/nm 484 (log ε 5.80), 605 (4.60), 658 (5.08), 708 (4.49); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.43 (16 H, m, *o*-pyridine-H), 8.30 (8H, d, J = 7.0 Hz, *o*-Ph-H), 7.69 (8H, d, J = 7.0 Hz, *m*-Ph-H), 7.24 (8H, s, fused-benzene-H), 6.90 (16H, m, *m*-pyridine-H), 3.16-3.21 (4H, m, isopropyl(CH)-H), 1.36 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H), -1.01 (2H, s, free base H); ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.32, 34.37, 116.56, 124.58, 127.29,

134.16, 135.56, 139.13, 148.88, 149.52, 149.65, 151.25; Calculated Mass, 1598.71, Found MS (MALDI-TOF), m/z 1598.29. Protonated **4c**: ^{1}H-NMR (500 MHz, CD_3OD) δ 8.68 (16 H, d, J = 5.5 Hz), 8.50 (8 H, d, J = 7.5 Hz), 7.89 (8 H, d, J = 8.0 Hz), 7.56-7.60 (24H, m), 3.34 (4H, m, isopropyl(CH)-H), 1.40 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H). Methylated **4c**: ^{1}H-NMR (500 MHz, CD_3OD) δ 8.82-8.85 (16H, m), 8.52-8.76 (8H, m), 7.89-7.93 (8H, m), 7.75-7.76 (18H, m), 7.50-7.58 (6H, m), 4.40-4.42 (24H, s, -CH_3), 3.34 (4H, m, isopropyl(CH)-H), 1.46 (24H, d, J = 6.5 Hz, isopropyl (CH_3)-H).

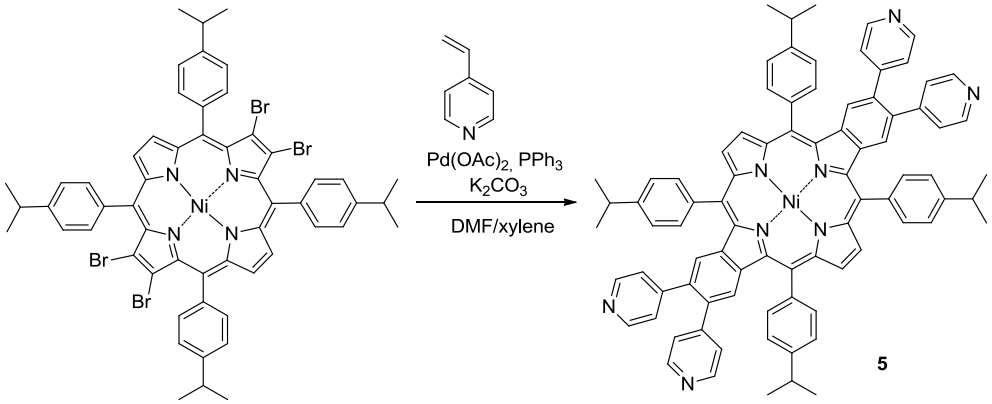
4d: mp > 320^{o}C. Yield: 88%. UV-Vis λmax (CH_2Cl_2)/nm 492 (log ε 5.90), 630 (4.89), 676 (5.19); FL (CH_2Cl_2, excited by 480nm) 707.50 (183.290), 750.0 (202.980); ^{1}H-NMR: No good 1H NMR was got from **3d** by using $CDCl_3$, MeOD or d_5-pyridine. The only interpretable NMR was got from combination of CDCl3 and d_5-pyridine (500 MHz, $CDCl_3$ and d_5-pyridine with a ratio of 2: 1, Me_4Si) δ the singlet peaks at 8.71, 7.83 and 7.33 are from d_5-pyridine solvents with the integration ratio of 2 : 1 : 2. δ 8.61 (16 H, m, *o*-pyridine-H), 8.46 (8H, d, J = 7.5 Hz, *o*-Ph-H), 7.83 (8H, d, J = 7.5 Hz, *m*-Ph-H), 7.55 (8H, s, fused-benzene-H), 7.10 (16H, m, *m*-pyridine-H), 4.32 (water peak from d_5-pyridine), 3.31-3.32 (4H, m, isopropyl(CH)-H), 1.36 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H); Calculated Mass, 1663.33, Found MS (MALDI-TOF), m/z 1662.67.

4e: mp > 320^{o}C. Yield: 49%. UV-Vis λmax (CH_2Cl_2)/nm 463 (log ε 5.95), 605 (4.80), 657 (5.55); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.42 (8 H, m), 8.26 (8H, m), 8.04 (8H, d, J = 8.0 Hz, *o*-Ph-H), 7.64 (8H, d, J = 8.0 Hz, *m*-Ph-H), 7.28-7.29 (8H, m), 7.28 (4H, m), 7.09-7.11 (12H, m), 3.12-3.15 (4H, m, isopropyl(CH)-H), 1.32 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H) ; ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.32, 34.42, 116.08, 122.75, 126.25, 127.37, 128.51, 133.09, 133.74, 136.90, 137.04, 137.91, 138.54, 138.65, 147.81, 150.62, 151.13; Calculated Mass, 1656.64, Found MS (MALDI-TOF), m/z 1656.04.

6: mp > 320^{o}C. Yield: 15%. UV-Vis λmax (MeOH)/nm 466 (log ε 5.68), 630 (5.29), 646 (5.22); No good 1H NMR was got from any solvent. Found MS (ESI) (after treated with excess of triethylamine(TEA)) from negative ion polarity 325.2

([M-7H]$^{7-}$), 380.9 ([M-6H]$^{6-}$), 457.4 ([M-5H]$^{5-}$); from positive ion polarity 102.1 (TEA^{+}).

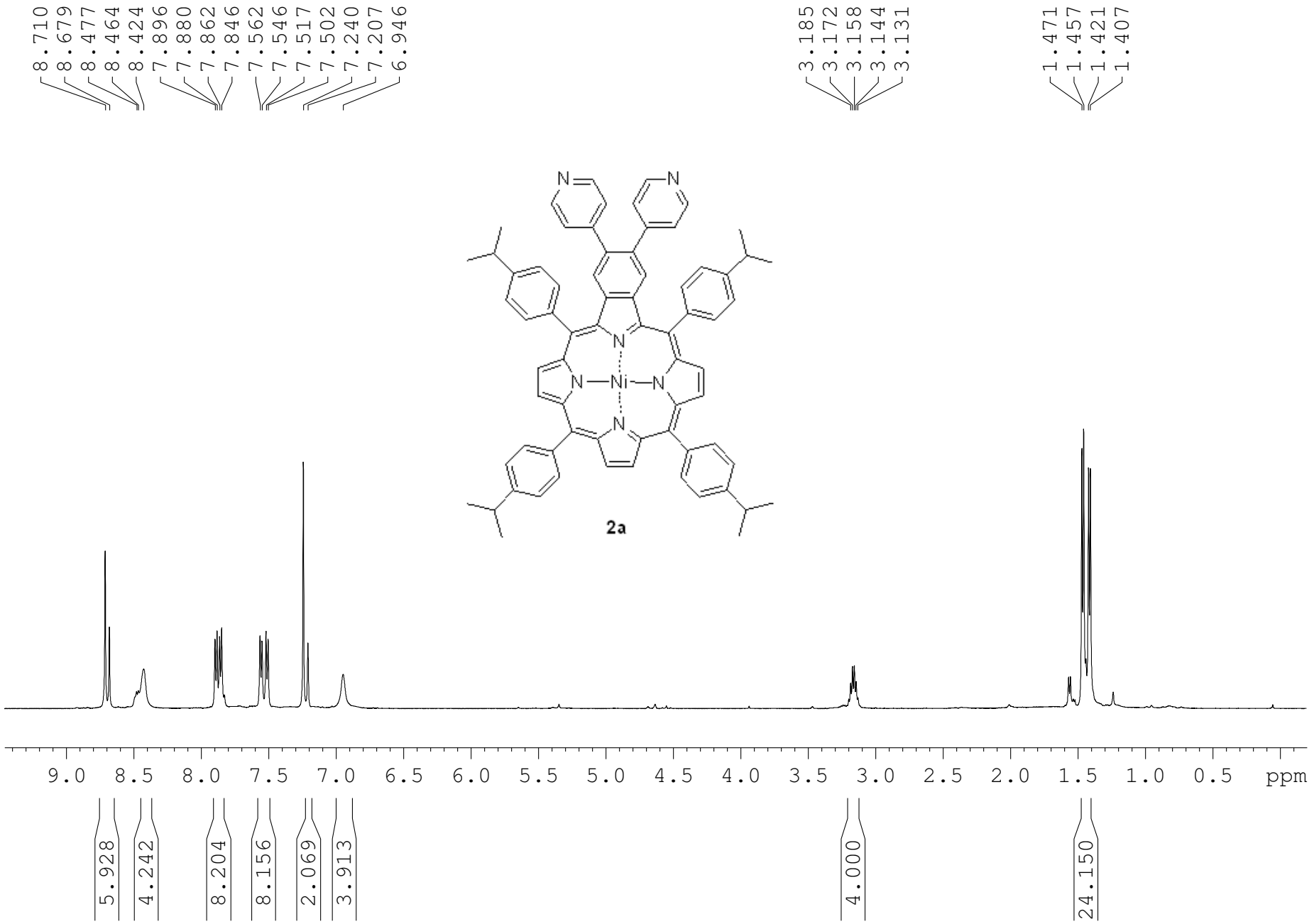
V. General procedure for the Heck coupling reaction of metalated tetrabromoporphyrins



Tetrabromoarylporphyrins (0.045 mmol), palladium acetate (0.023 mmol), triphenylphosphine (0.058 mmol) and K_2CO_3 (0.17 mmol) were added to Schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (10 mL) and dry xylene (10 mL) and 4-vinylpyridine (35-fold excess). The mixture was then degassed via four freeze-pump-thaw cycles before the vessel was purged with argon again. The Schlenk flask was sealed and heated to reflux for 72h. After 72 h, the mixture was diluted with $CHCl_3$ and washed with water. The organic layer was removed under vacuum. The residue was subjected to silica column chromatography. The band containing the desired porphyrin was collected. This procedure was used to prepare **5**.

5: mp > 320^{o}C. Yield: 48%. UV-Vis λmax (CH_2Cl_2)/nm 454 (log ε 5.67), 579 (4.68), 618 (4.60); ^{1}H-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 8.74 (4H, s, *β*-H), 8.42 (8H, m, *o*-pyridine), 7.86 (8H, d, J = 8.0 Hz, *o*-Ph-H), 7.56 (8H, d, J = 8.0 Hz, *m*-Ph-H), 7.17 (4H, s, fused-benzene-H), 6.91(8H, m, *m*-pyridine-H), 3.13-3.18 (4H, m, isopropyl(CH)-H), 1.41 (24H, d, J = 7.0 Hz, isopropyl (CH_3)-H); ^{13}C-NMR (500 MHz, $CDCl_3$, Me_4Si) δ 24.28, 29.70, 34.17, 113.78, 116.91, 118.08, 120.15, 124.81, 126.18, 131.61, 132.66, 134.39, 136.52, 137.59, 139.96, 142.38, 149.05, 149.46, 149.66; Calculated Mass, 1246.49, Found MS (MALDI-TOF), m/z 1246.09.

VI. Spectroscopy data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7.546
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7.240
7.207
6.946
3.185
3.172
3.158
3.144
3.131
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1.421
1.407
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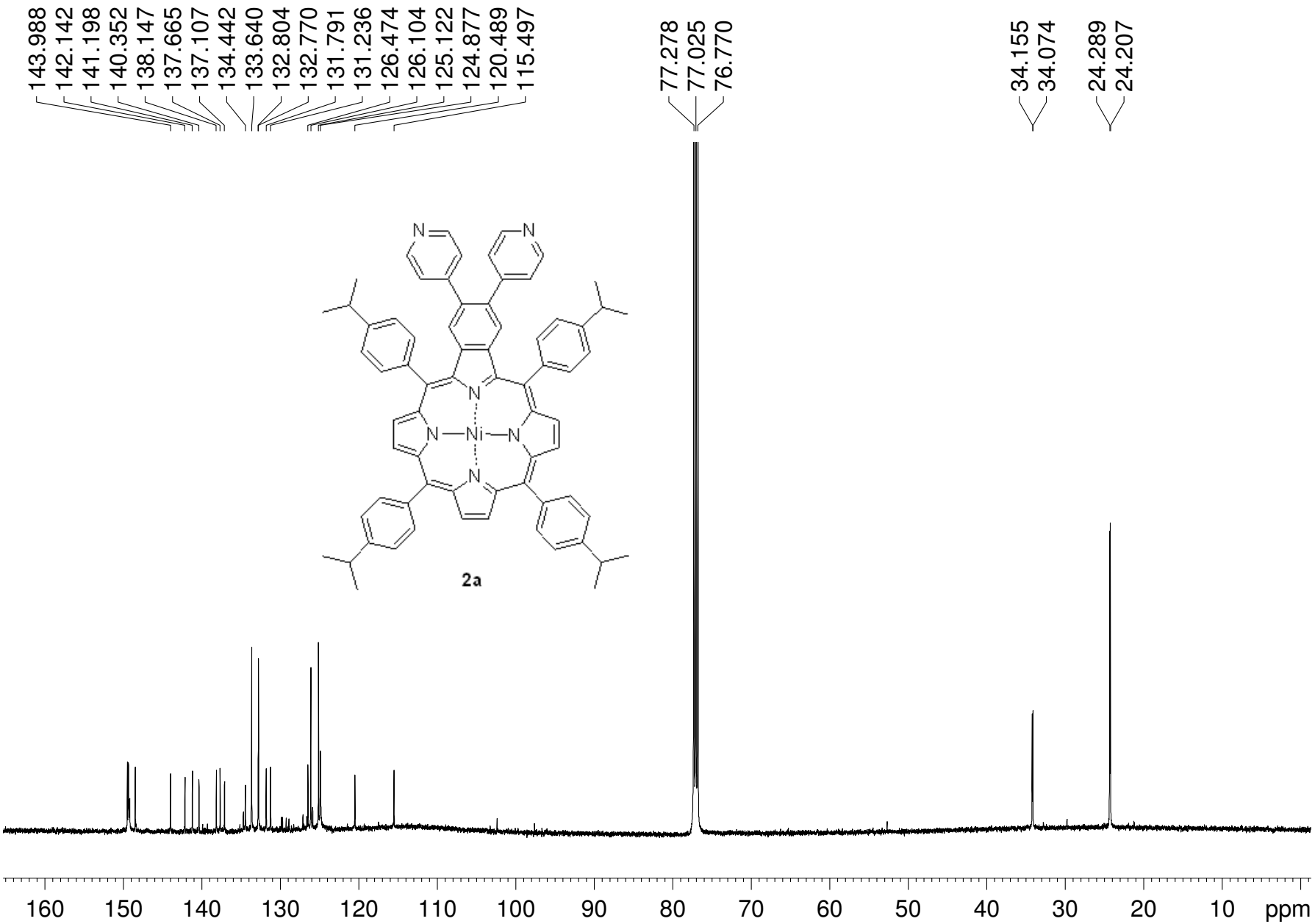
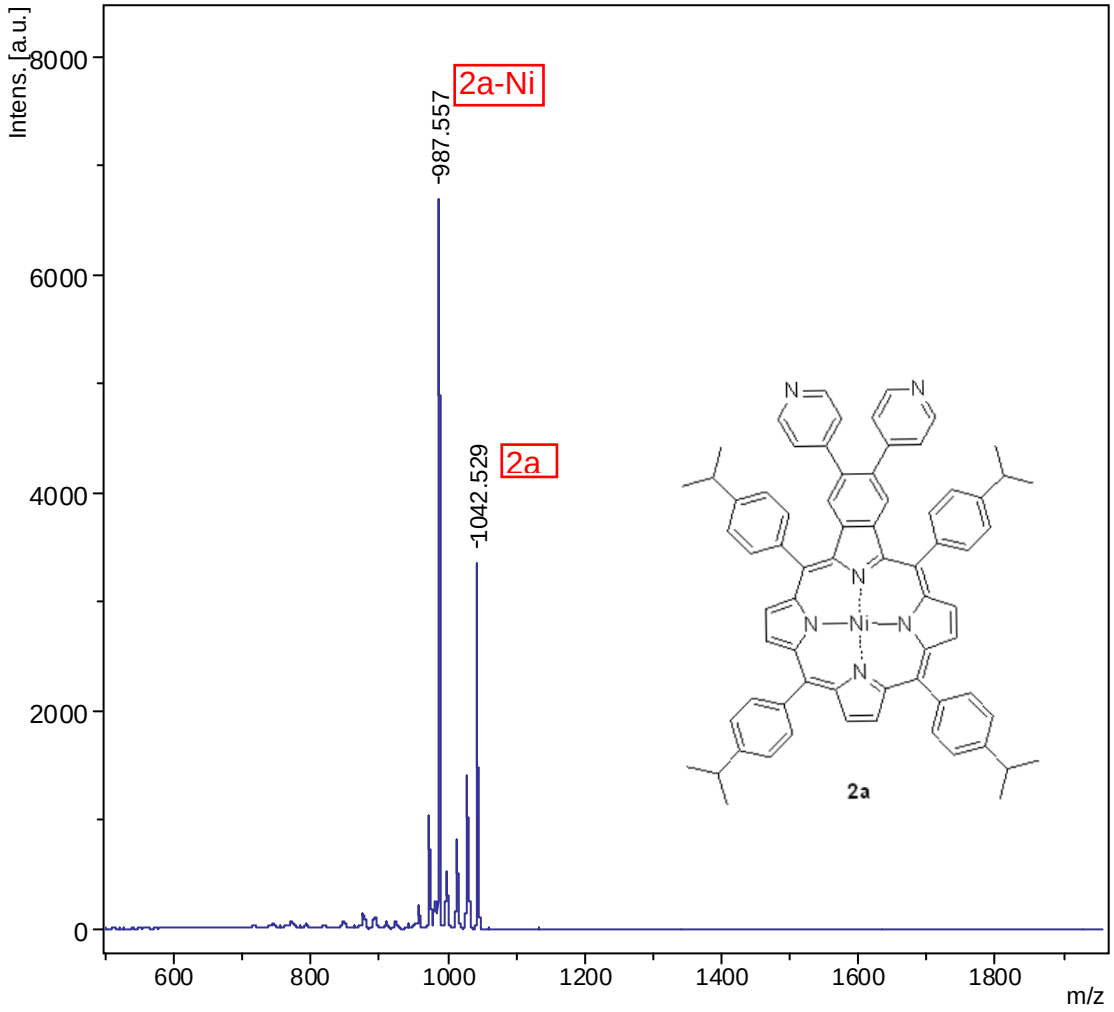
2.069
3.913
4.000
24.150

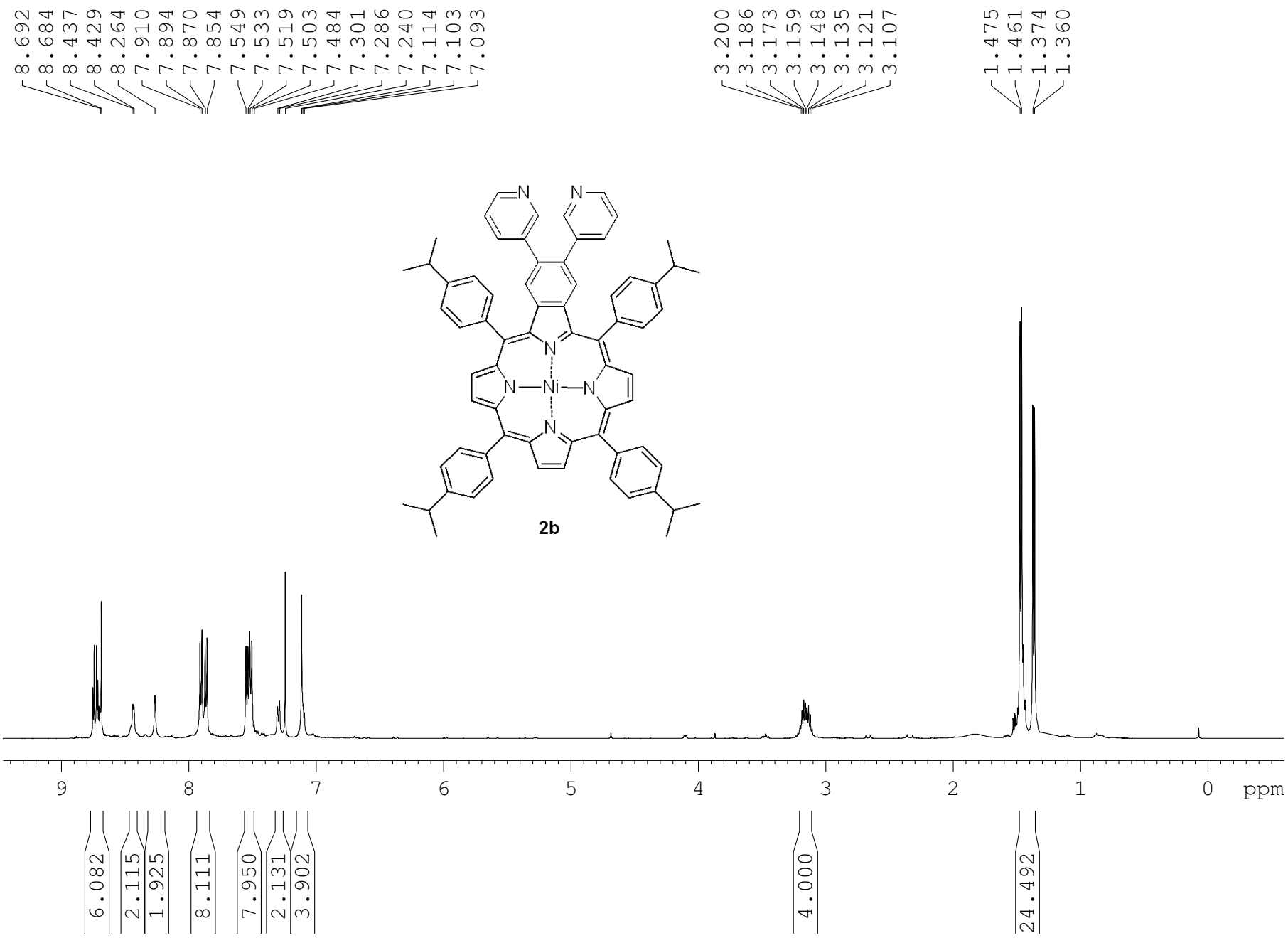

143.988
142.142
141.198
140.352
138.147
137.665
137.107
134.442
133.640
132.804
132.770
131.791
131.236
126.474
126.104
125.122
124.877
120.489
115.497
77.278
77.025
76.770
34.155
34.074
24.289
24.207
N
N
N
N
Ni
N
N
2a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

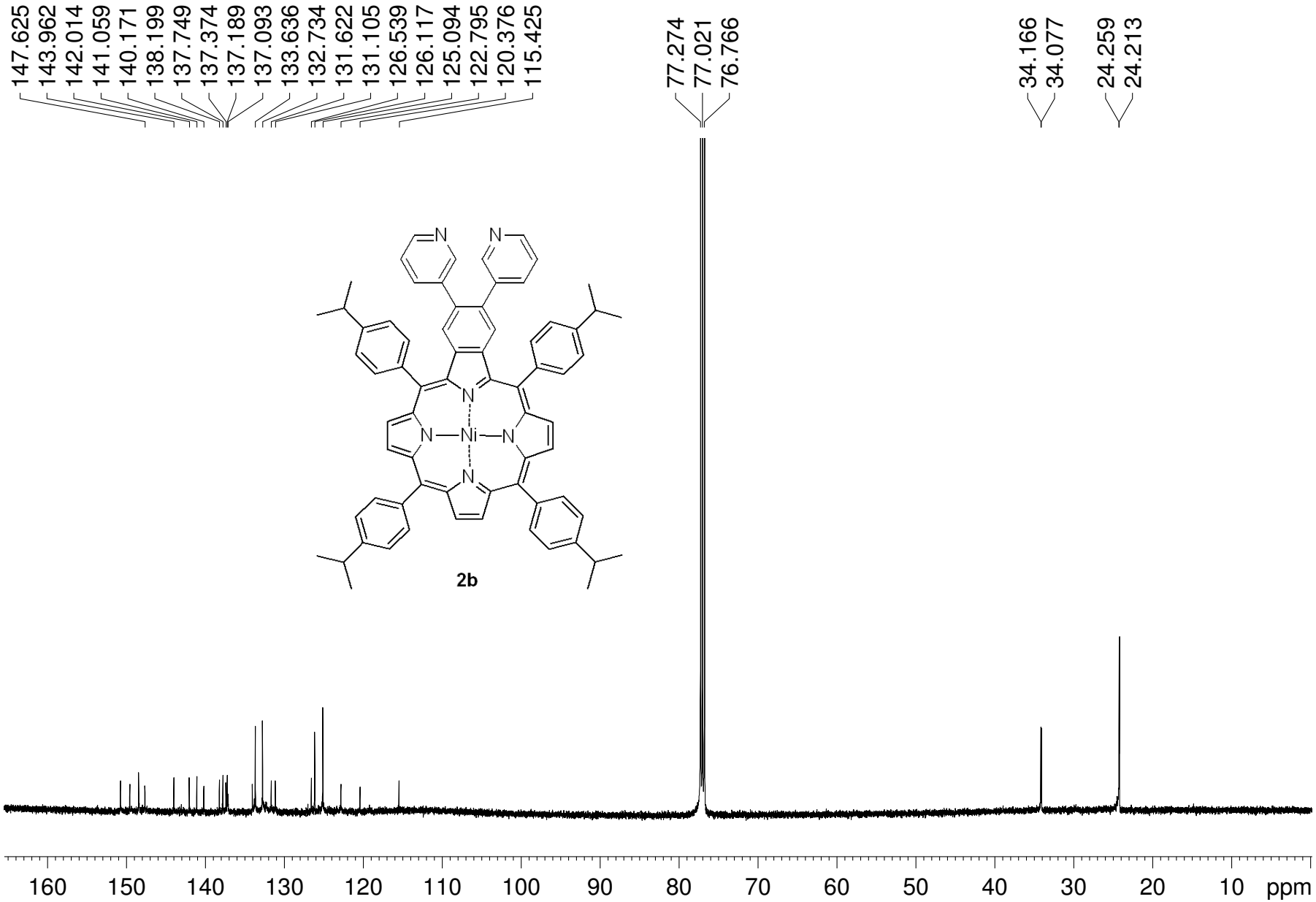
Comment 1

Comment 2



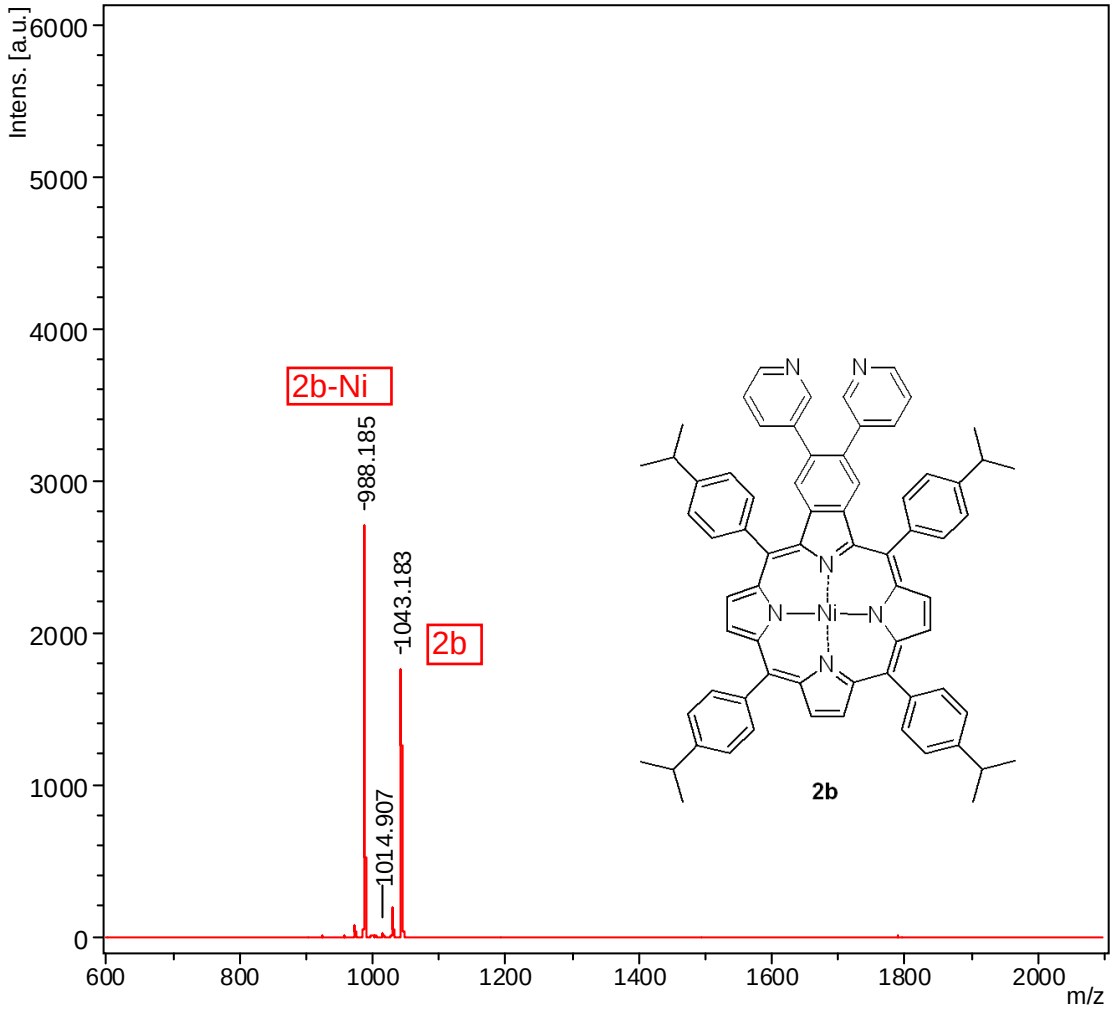
m/z	Res.	Intens.
987.557		6691.92
1042.529		3349.23
1044.522		2515.85


8.692
8.684
8.437
8.429
8.264
7.910
7.894
7.870
7.854
7.549
7.533
7.519
7.503
7.484
7.301
7.286
7.240
7.114
7.103
7.093
3.200
3.186
3.173
3.159
3.148
3.135
3.121
3.107
1.475
1.461
1.374
1.360
N
N
N
Ni
N
N
2b
9
8
7
6
5
4
3
2
1
0
ppm
6.082
2.115
1.925
8.111
7.950
2.131
3.902
4.000
24.492


147.625
143.962
142.014
141.059
140.171
138.199
137.749
137.374
137.189
137.093
133.636
132.734
131.622
131.105
126.539
126.117
125.094
122.795
120.376
115.425
77.274
77.021
76.766
34.166
34.077
24.259
24.213
N
N
N
Ni
N
N
2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

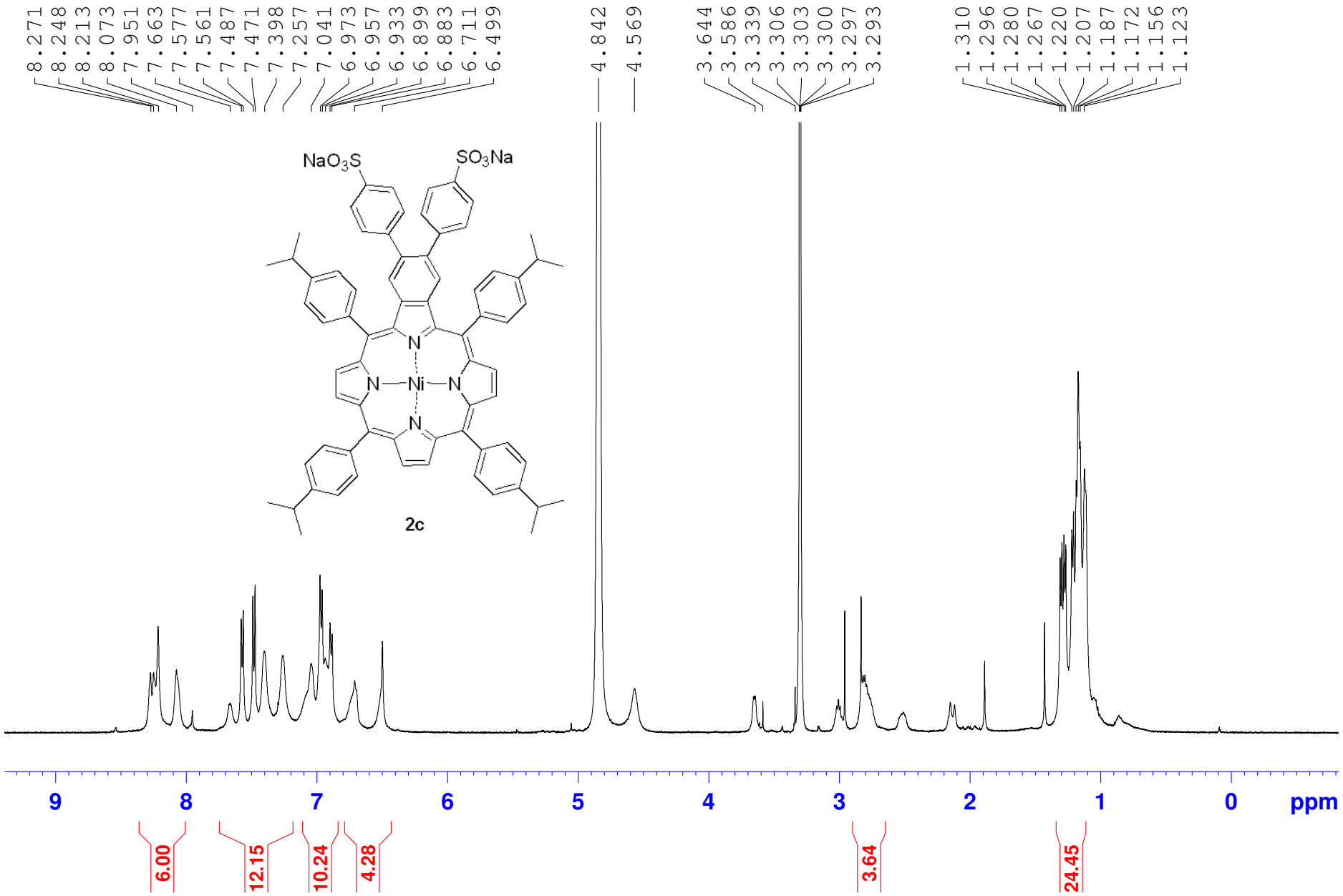
Comment 1

Comment 2



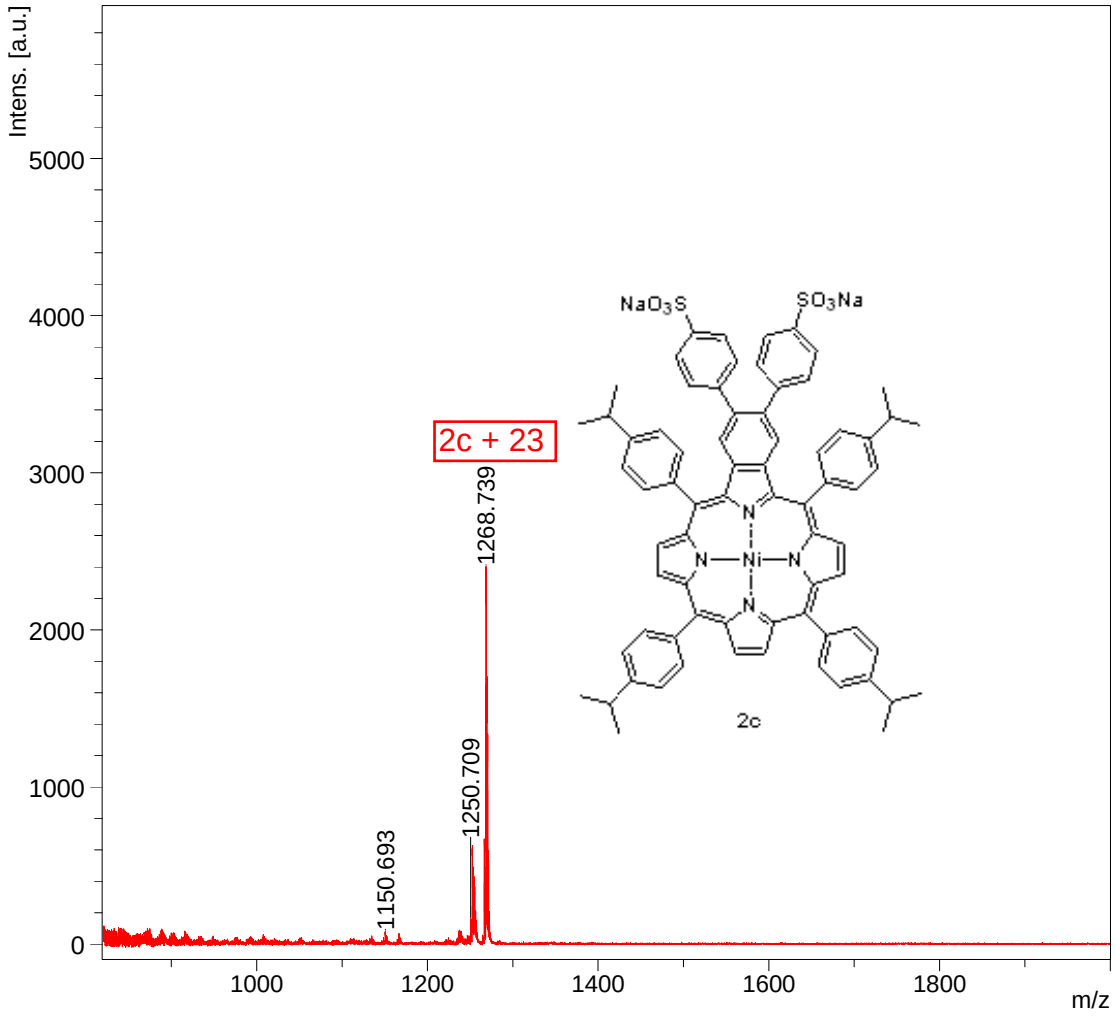
m/z	Res.	Intens.
974.941	3999	69.75
988.185	4225	2827.55
1014.907	2279	24.48
1029.951	3421	120.74
1030.879	2975	146.74
1043.183	4329	1817.25
1045.183	4512	651.64

2c in MeOD


8.271
8.248
8.213
8.073
7.951
7.663
7.577
7.561
7.487
7.471
7.398
7.257
7.041
6.973
6.957
6.933
6.899
6.883
6.711
6.499
4.842
4.569
3.644
3.586
3.339
3.306
3.303
3.300
3.297
3.293
1.310
1.296
1.280
1.267
1.220
1.207
1.187
1.172
1.156
1.123
NaO3S
SO3Na
N
N
Ni
N
N
2c
9
8
7
6
5
4
3
2
1
0
ppm
6.00
12.15
10.24
4.28
3.64
24.45

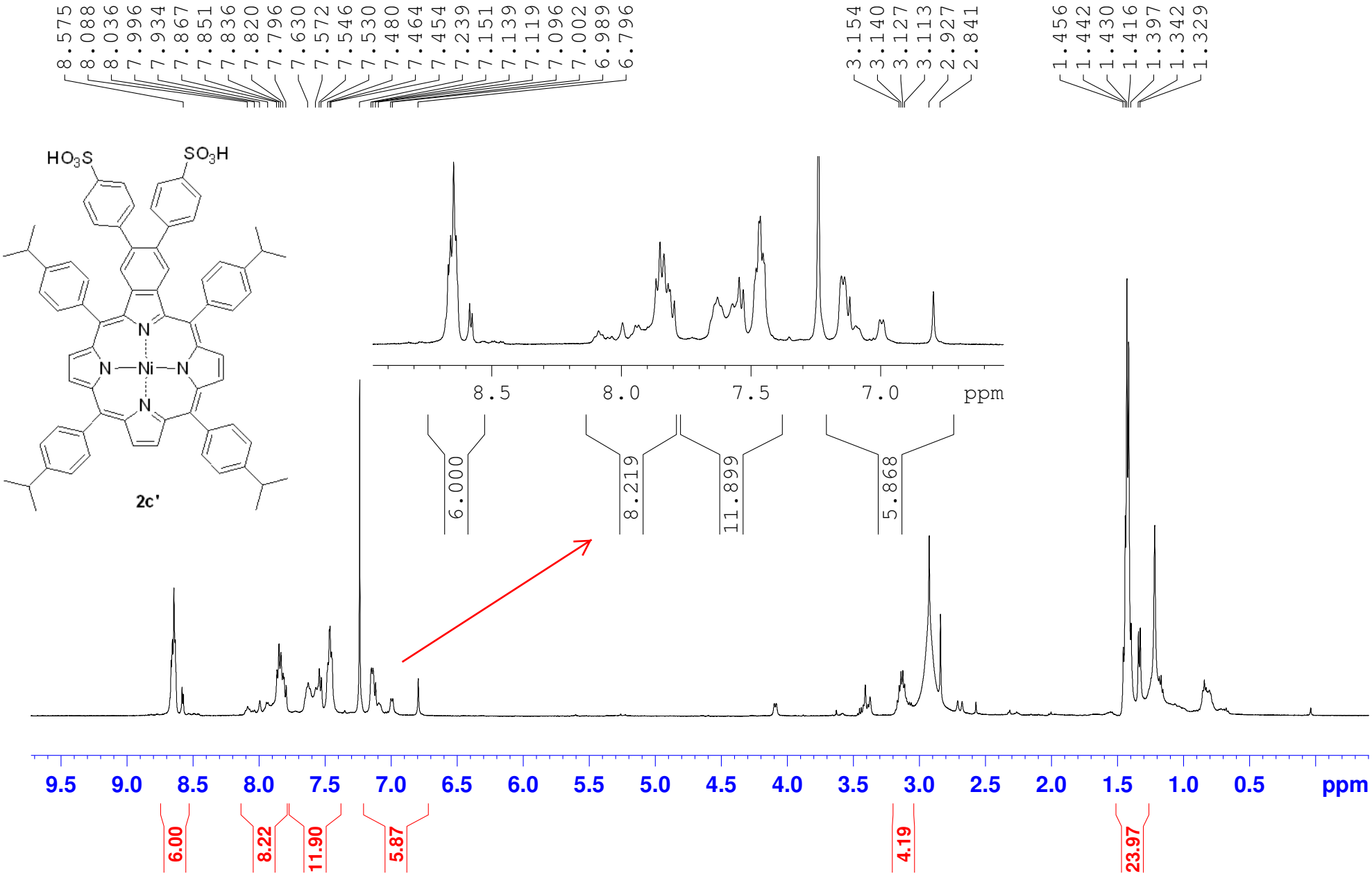
Comment 1

Comment 2

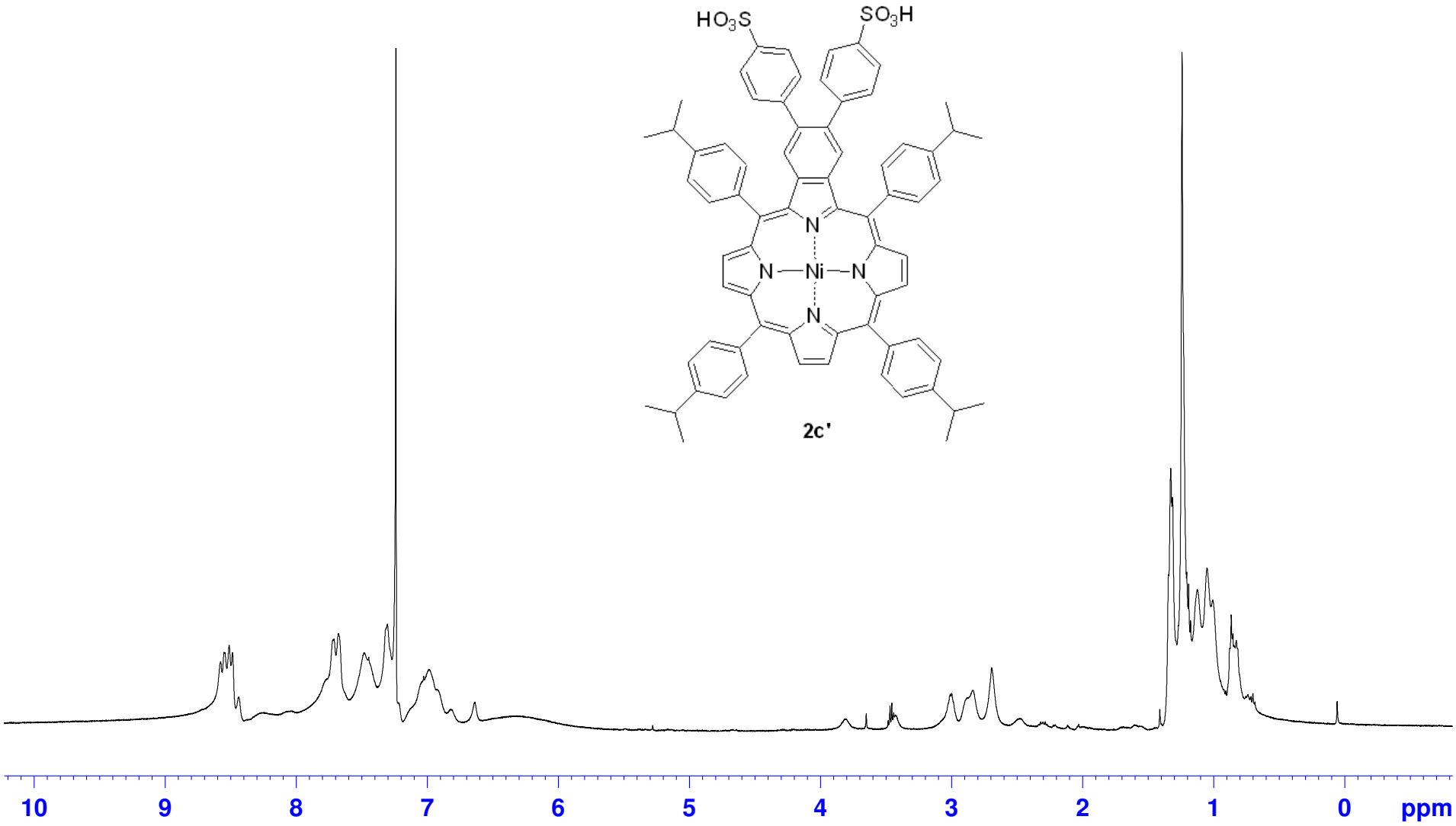


m/z	Res.	Intens.
1150.693	2941	79.35
1236.555	2690	91.49
1250.709	3072	150.81
1252.659	2731	577.97
1255.441	1430	207.84
1266.723	3418	658.79
1268.739	3395	2275.69
1270.704	3119	615.65

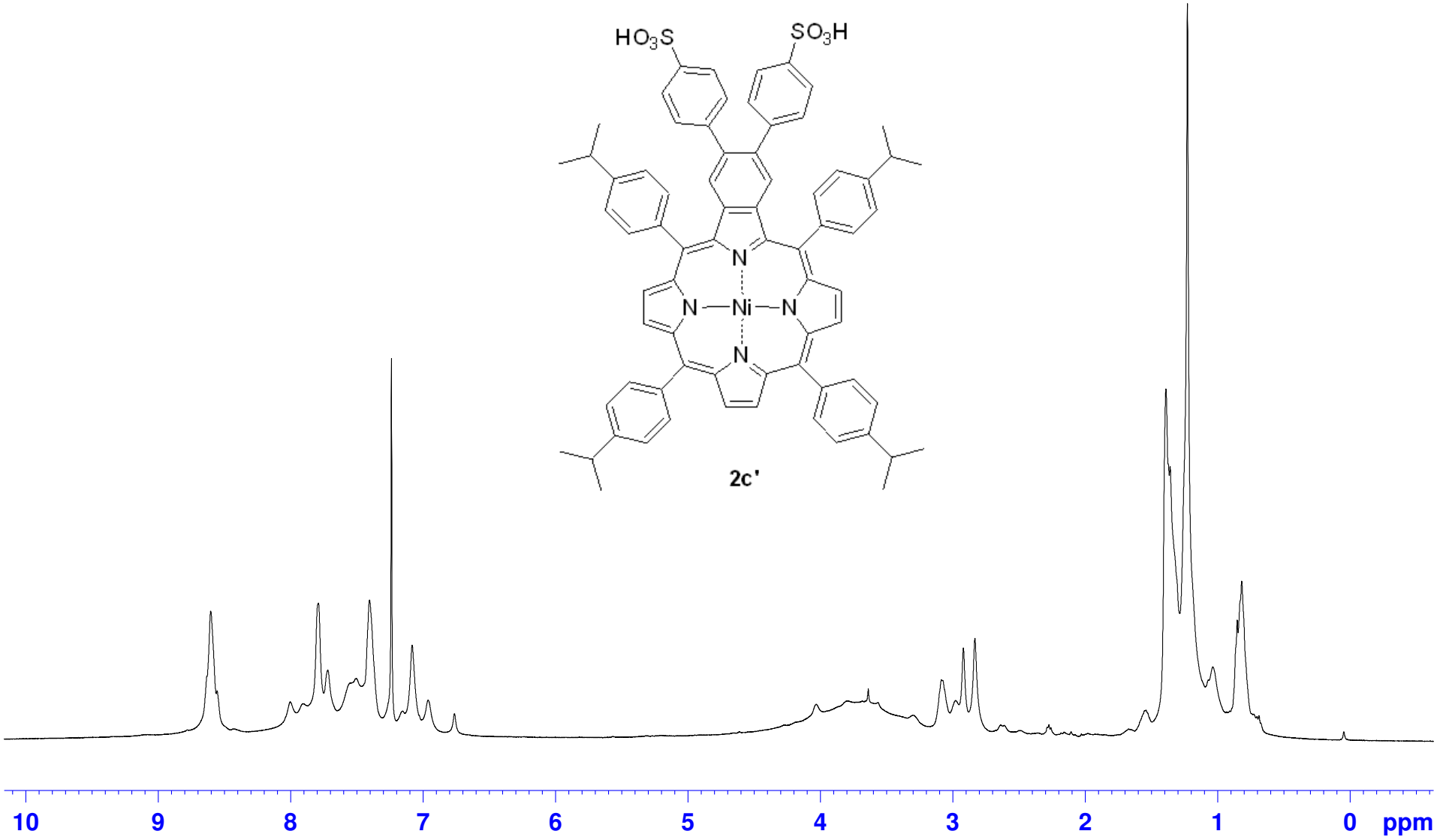
2c' in CDCl3 and two drops of MeOD



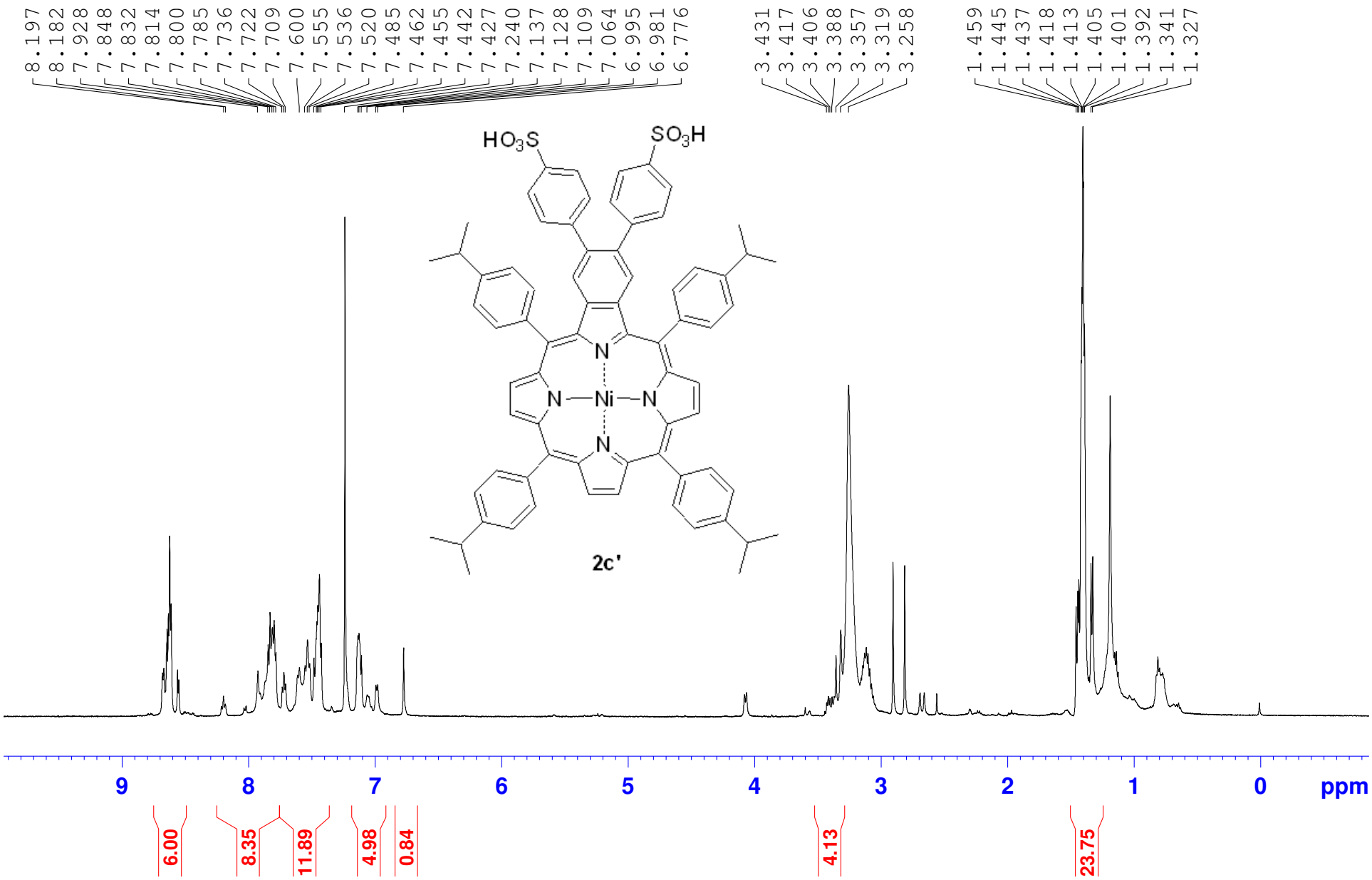
2c' in CDCl3 only



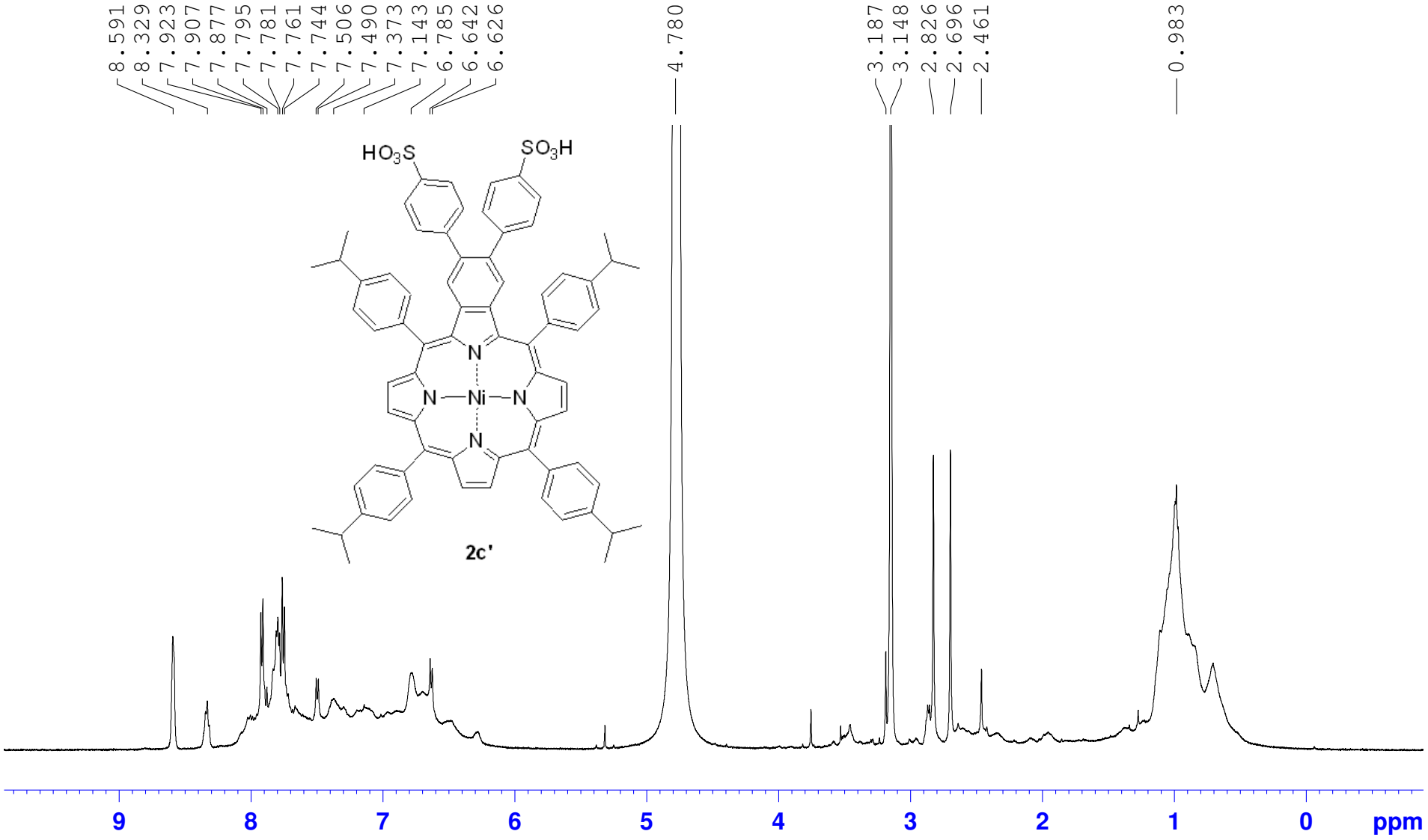
2c' in CDCl3 and one drop of MeOD



2c' in CDCl3 and three drops of MeOD

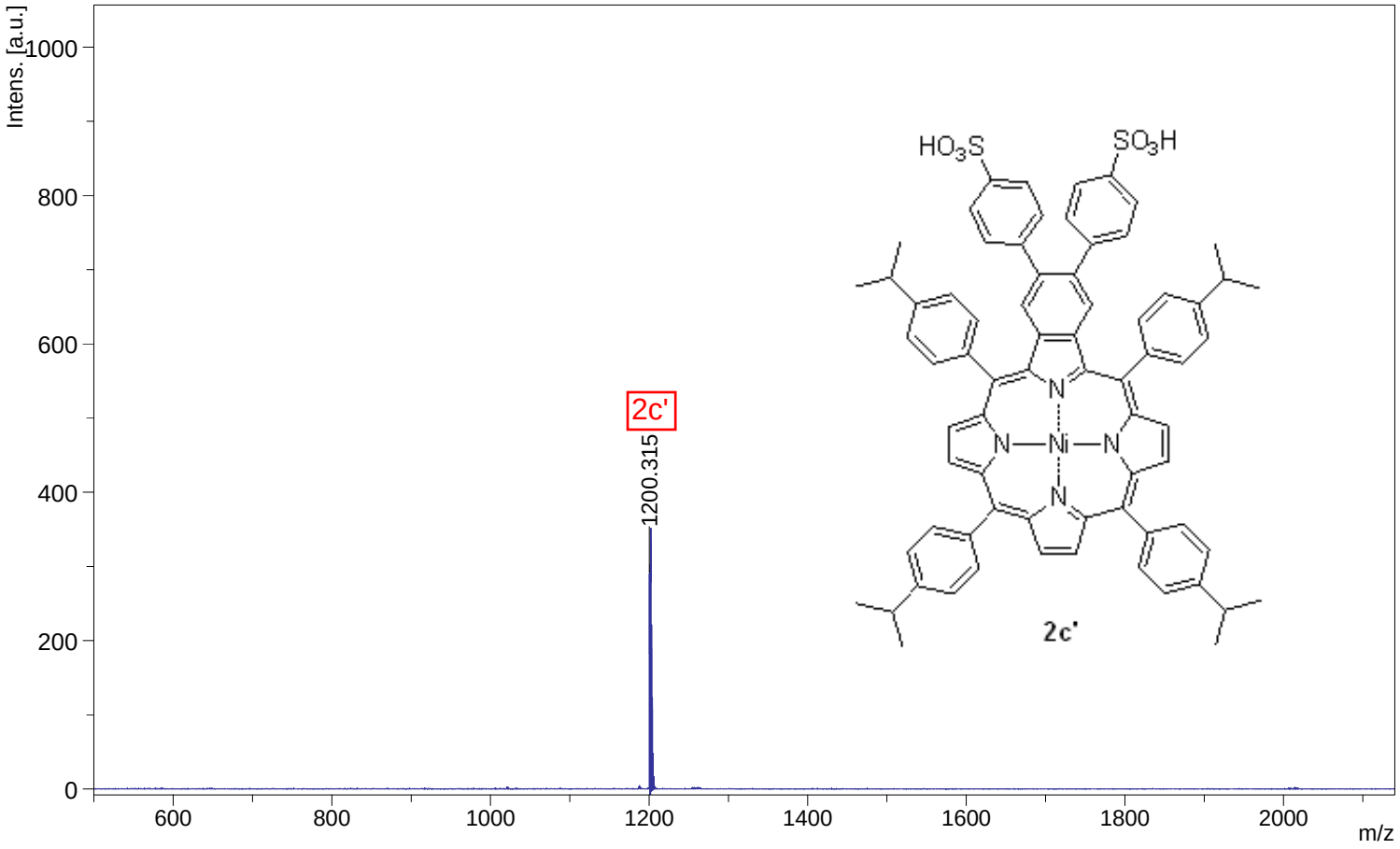


2c' in MeOD only



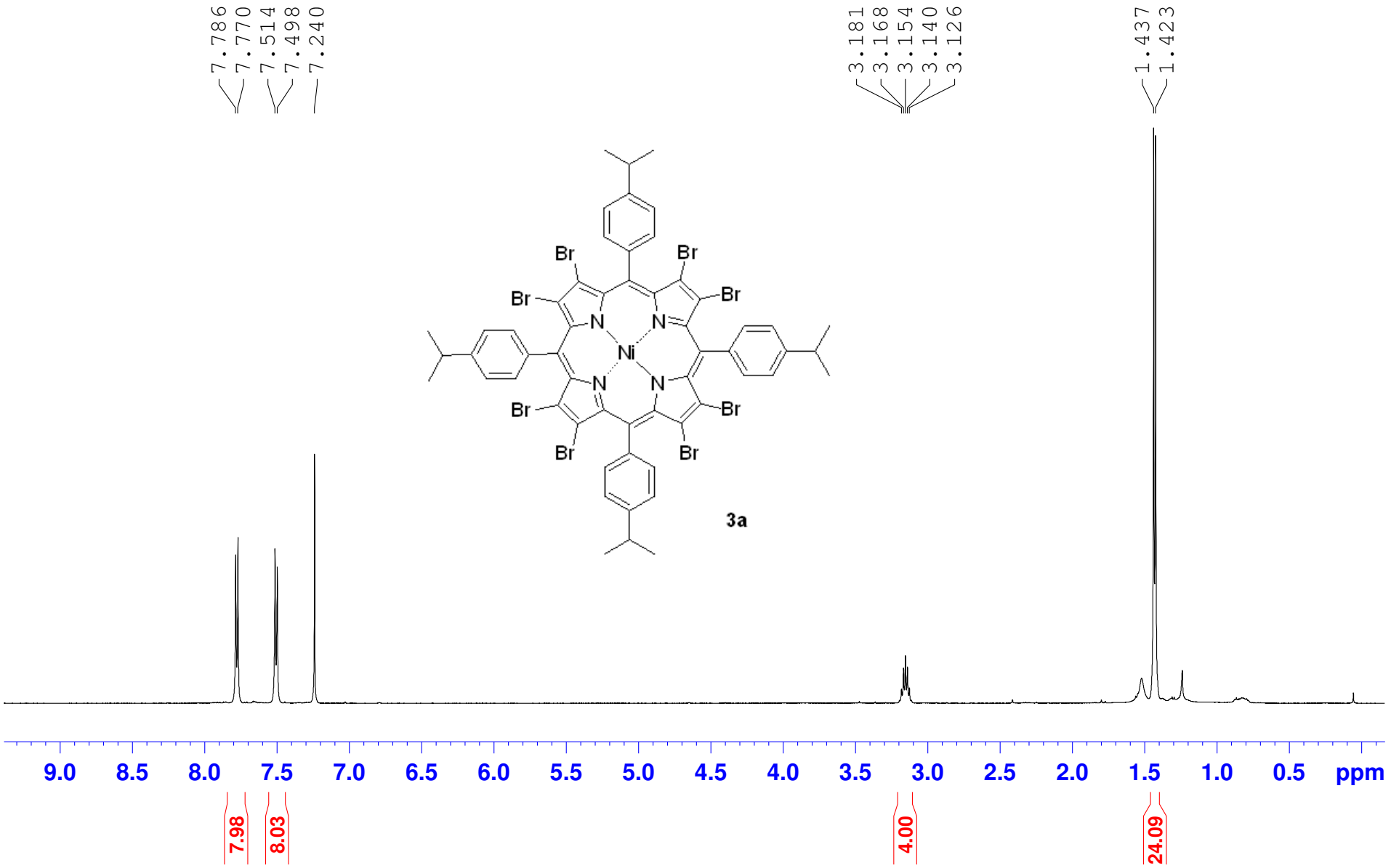
Comment 1

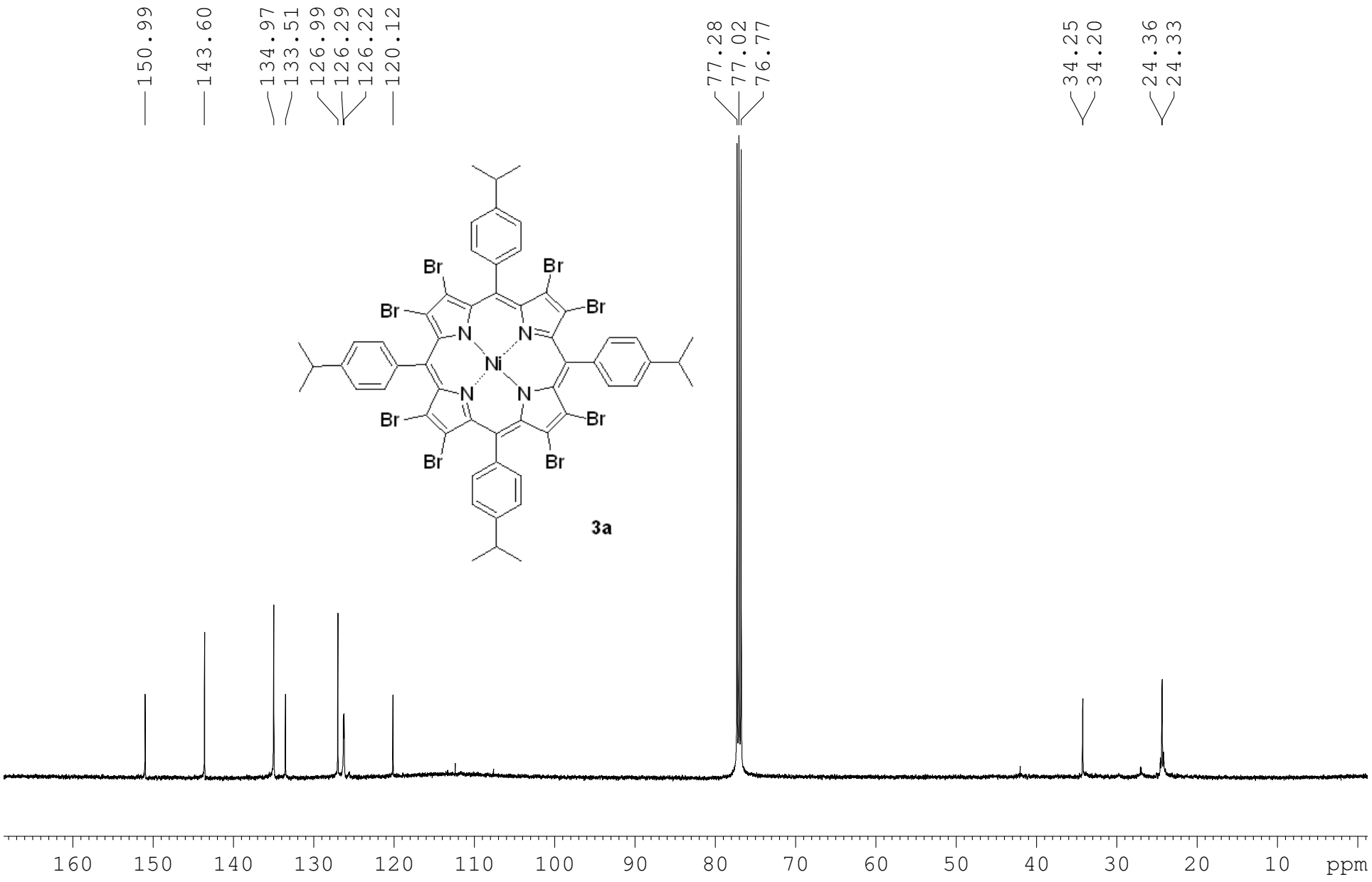
Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1200.315	181.5	418	5678	364.61	163
1202.334	144.7	4648	5505	290.29	134
1204.343	23.6	312	5461	47.01	22

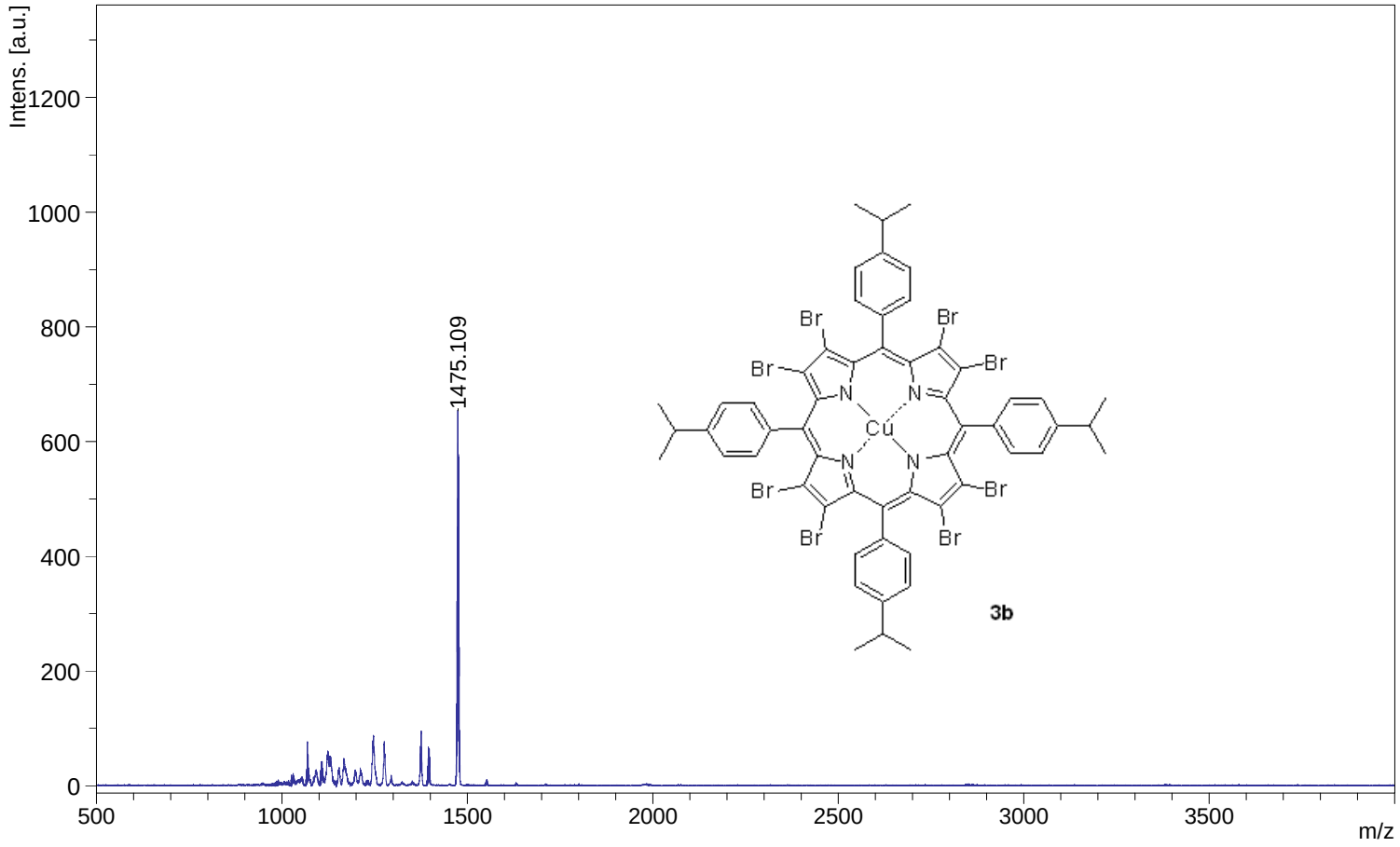
printed: 10/3/2011 1:12:34 PM


7.786
7.770
7.514
7.498
7.240
3.181
3.168
3.154
3.140
3.126
1.437
1.423
Br
Br
Br
Br
N
N
Ni
N
N
Br
Br
Br
Br
3a
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
ppm
7.98
8.03
4.00
24.09


150.99
143.60
134.97
133.51
126.99
126.29
126.22
120.12
77.28
77.02
76.77
34.25
34.20
24.36
24.33
Br
Br
Br
Br
N
N
Ni
N
N
Br
Br
Br
Br
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1475.109				597.56	

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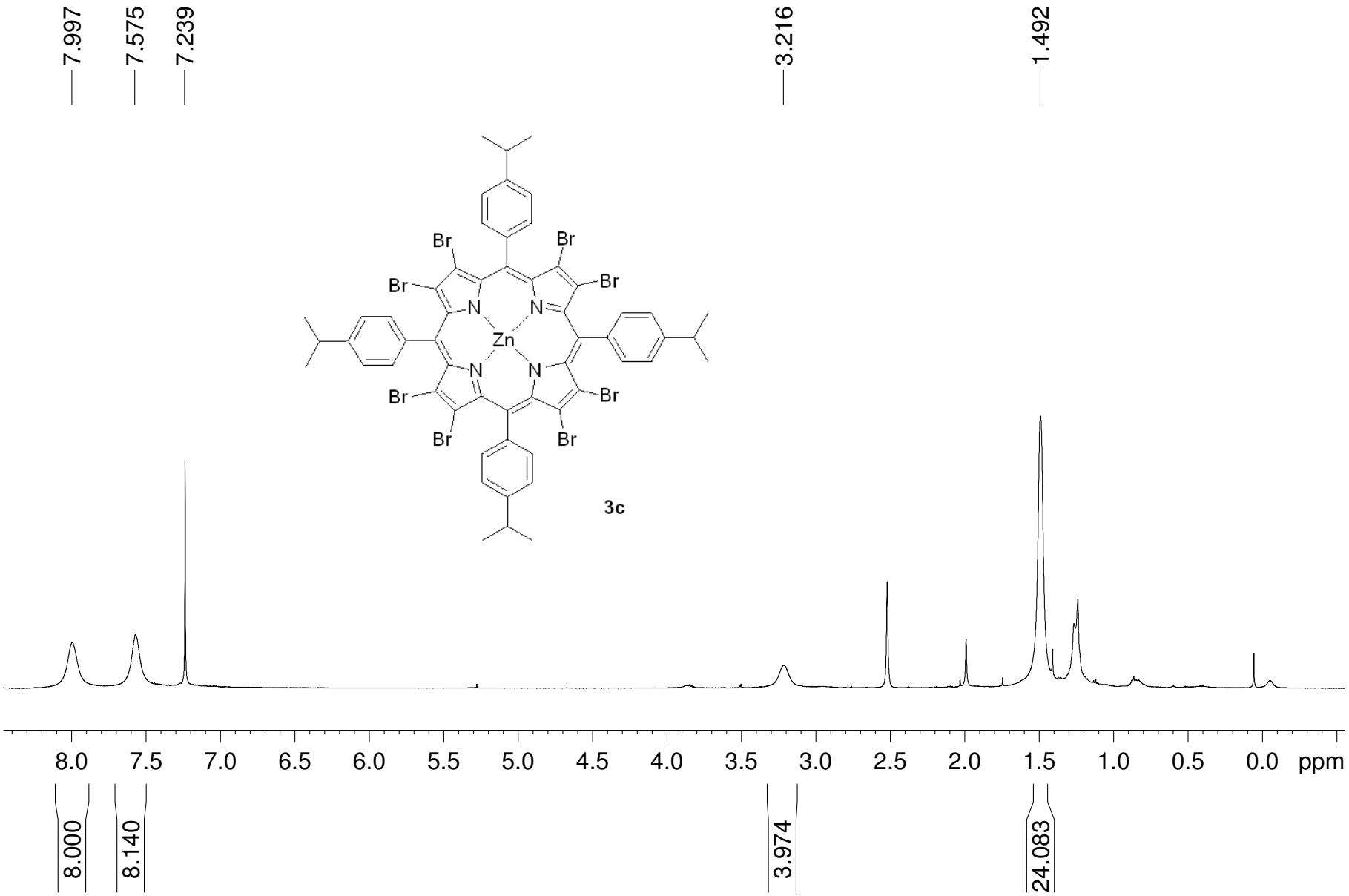
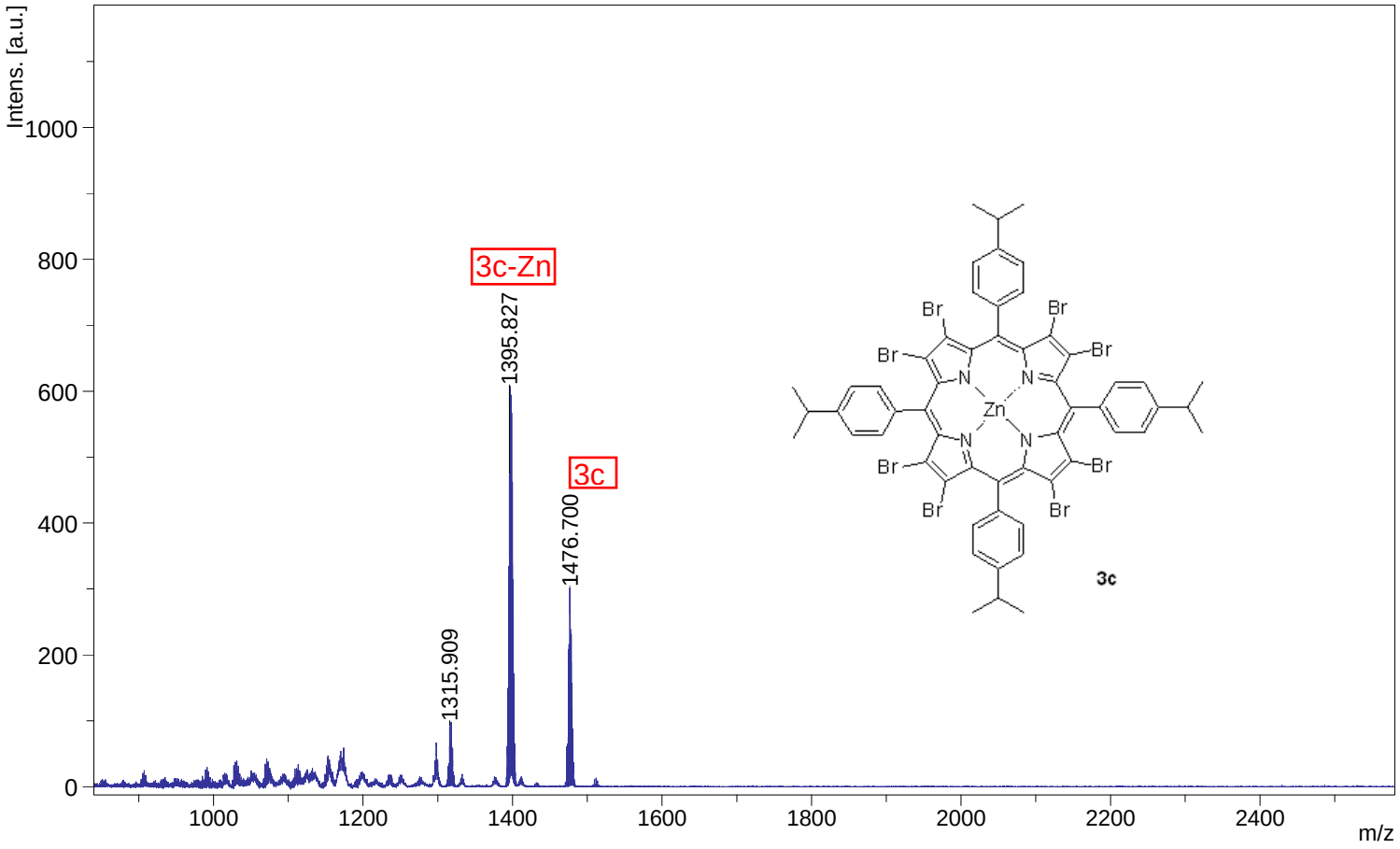

7.997
7.575
7.239
3.216
1.492
Br
Br
Br
Br
N
N
Zn
N
N
Br
Br
Br
Br
3c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
8.000
8.140
3.974
24.083

Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1313.894	6.6	534	3675	27.19	26
1315.909	19.0	11678	4727	77.78	52
1317.922	16.3	4722	4575	66.92	45
1393.832	32.8	163	4622	111.39	81
1394.830	53.2	300	4439	179.66	139
1395.827	130.3	2511	4362	440.79	340
1397.822	116.7	8983	4170	393.02	317
1398.820	83.0	5692	4352	279.49	215
1400.820	51.3	11639	5475	173.35	106
1474.711	69.0	11247	5040	196.14	144
1476.700	81.9	44167	4923	233.71	176
1478.690	51.6	17440	5186	146.35	104

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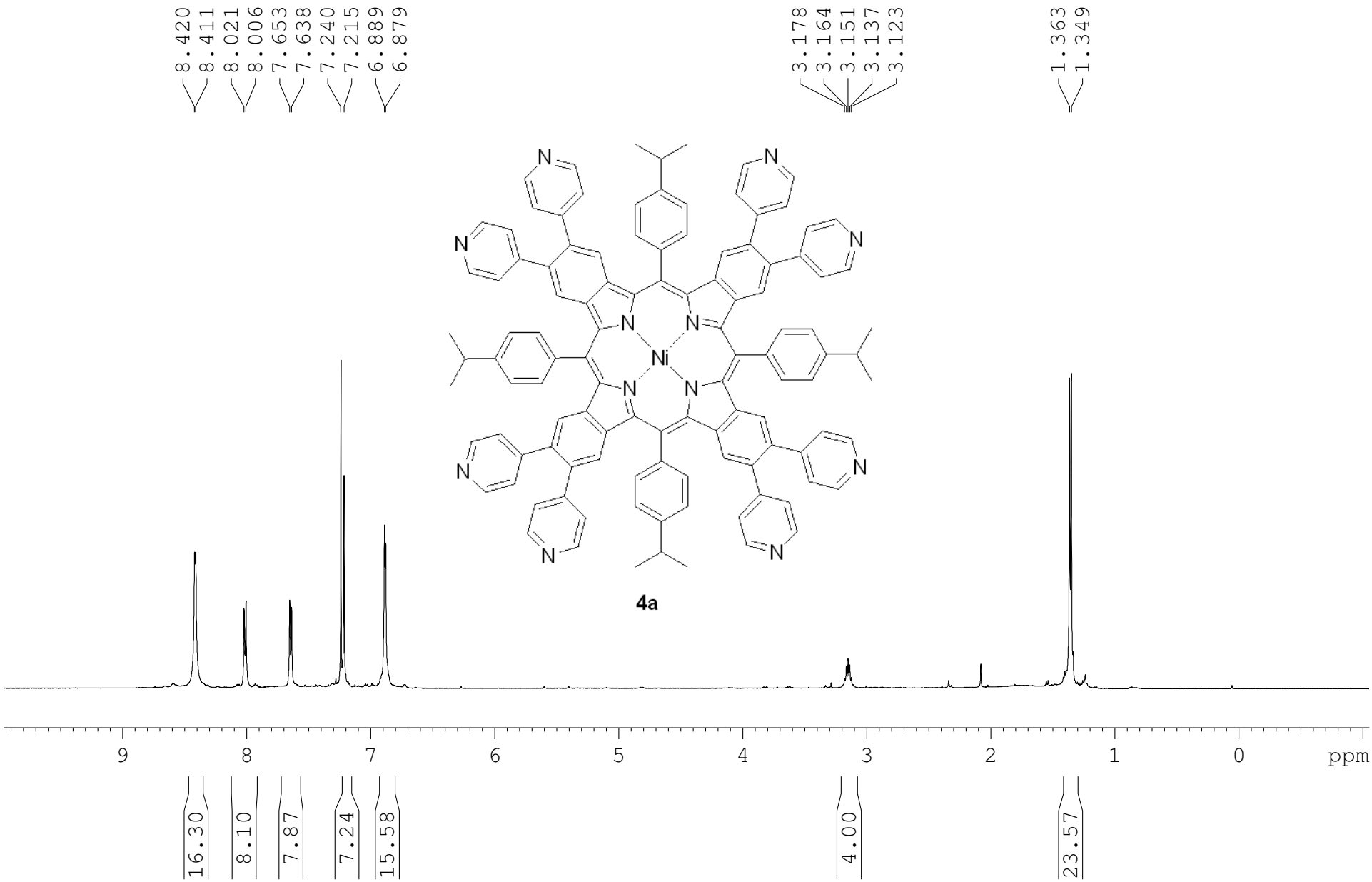
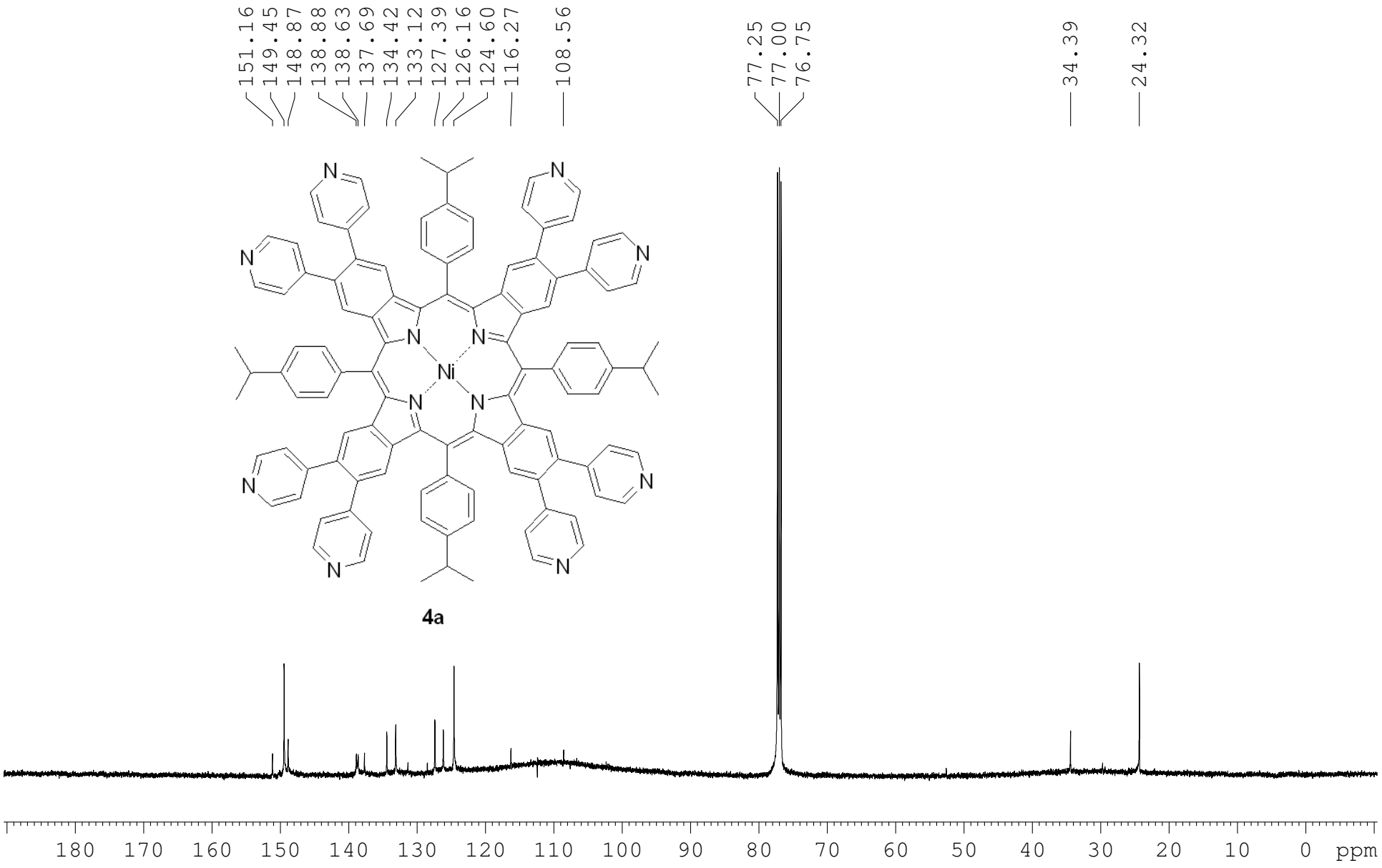

8.420
8.411
8.021
8.006
7.653
7.638
7.240
7.215
6.889
6.879
3.178
3.164
3.151
3.137
3.123
1.363
1.349
N
Ni
9
8
7
6
5
4
3
2
1
0
ppm
16.30
8.10
7.87
7.24
15.58
4.00
23.57

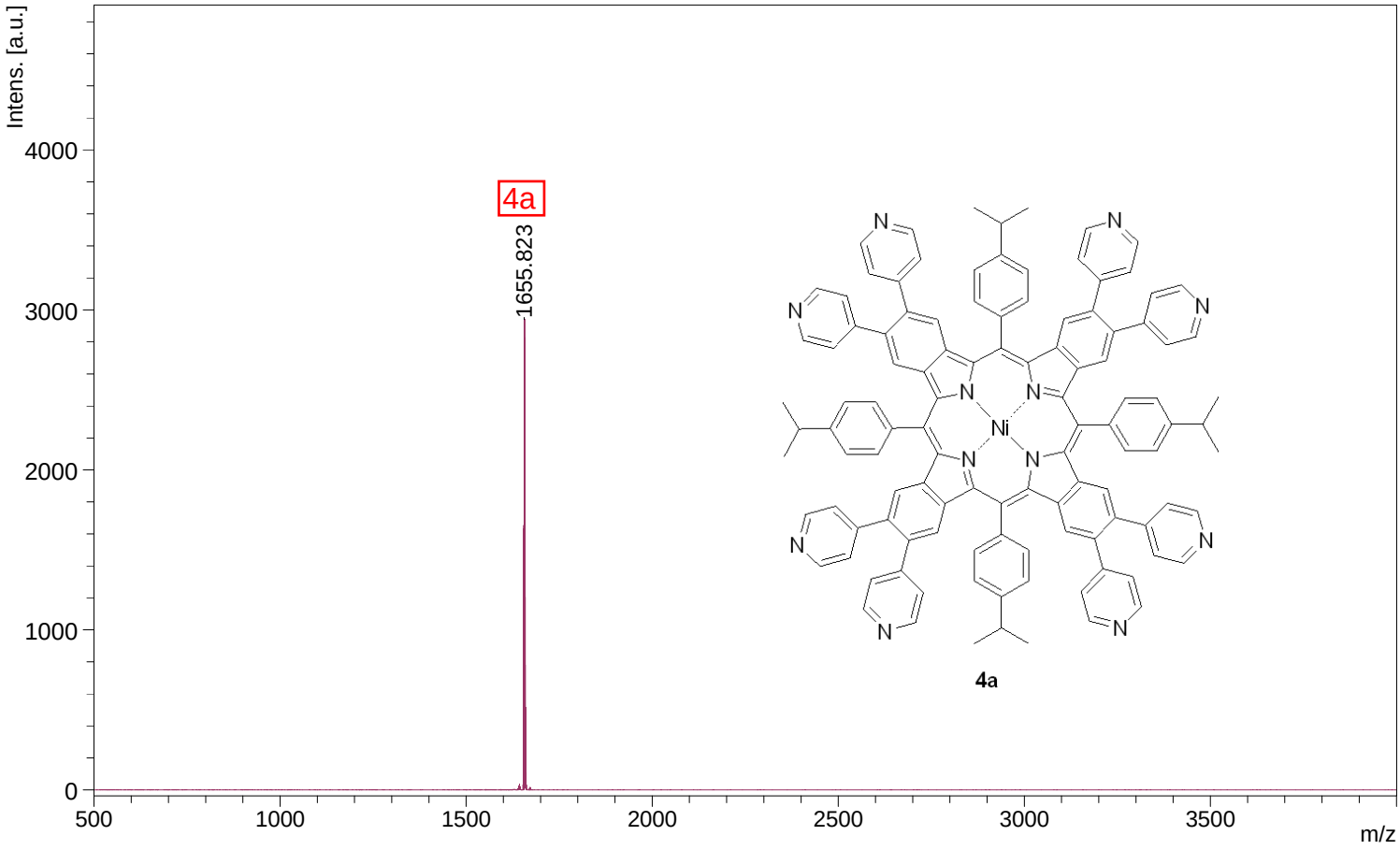
4a



4a

Comment 1 unknown 1 in CCA anchorchip

Comment 2 RP

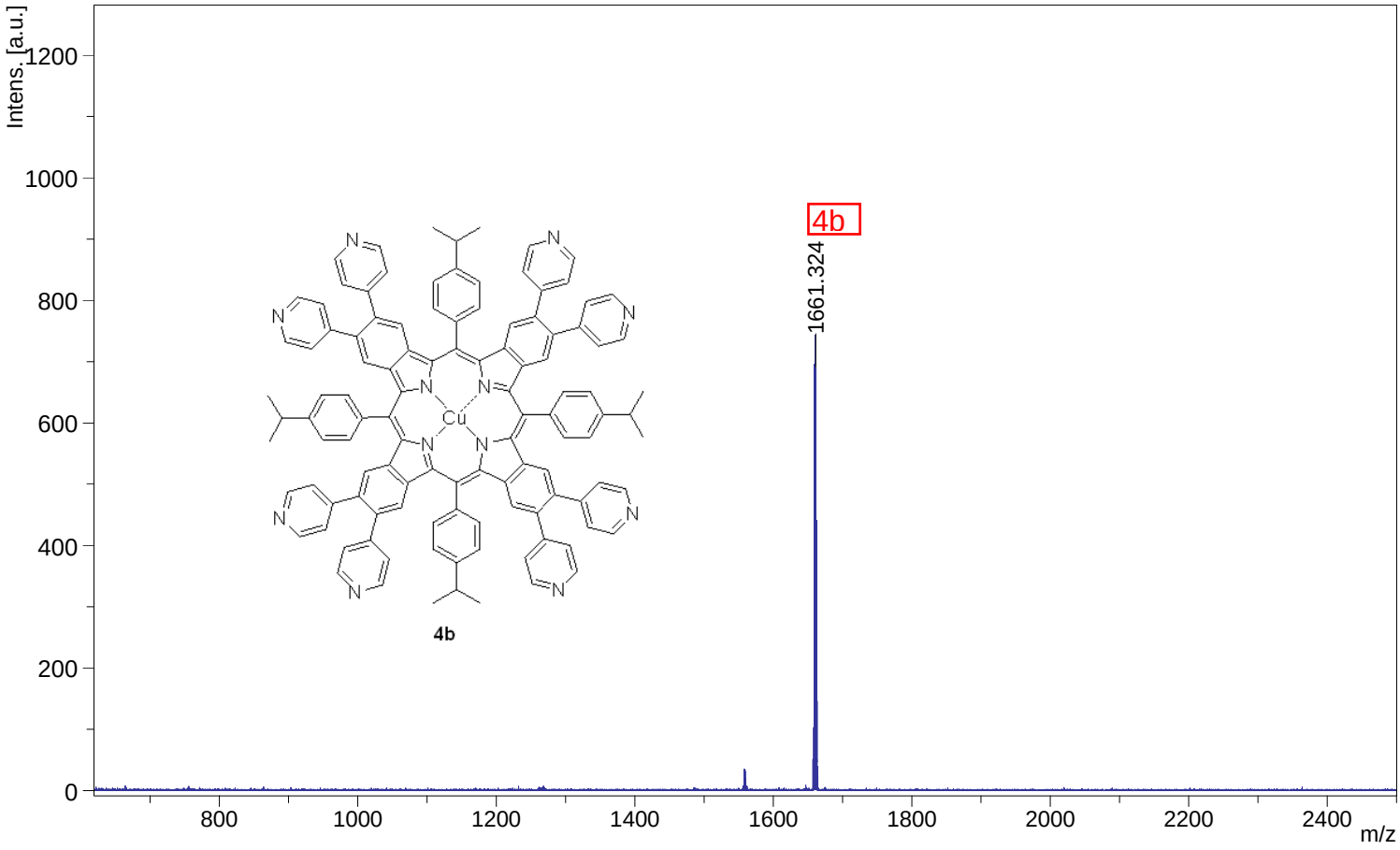


m/z	SN	Quality Fac.	Res.	Intens.	Area
1642.201	15.9	64	743	7.00	43
1654.826	2280.7	2860	6766	1359.75	940
1655.823	3816.0	9407	6232	2258.66	1685
1657.728	1212.6	646	7190	724.21	463
1658.800	232.2	101	7801	137.18	81
1670.831	26.4	1692	8248	15.51	9

printed: 9/28/2011 10:27:48 AM

Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1661.324				688.00	

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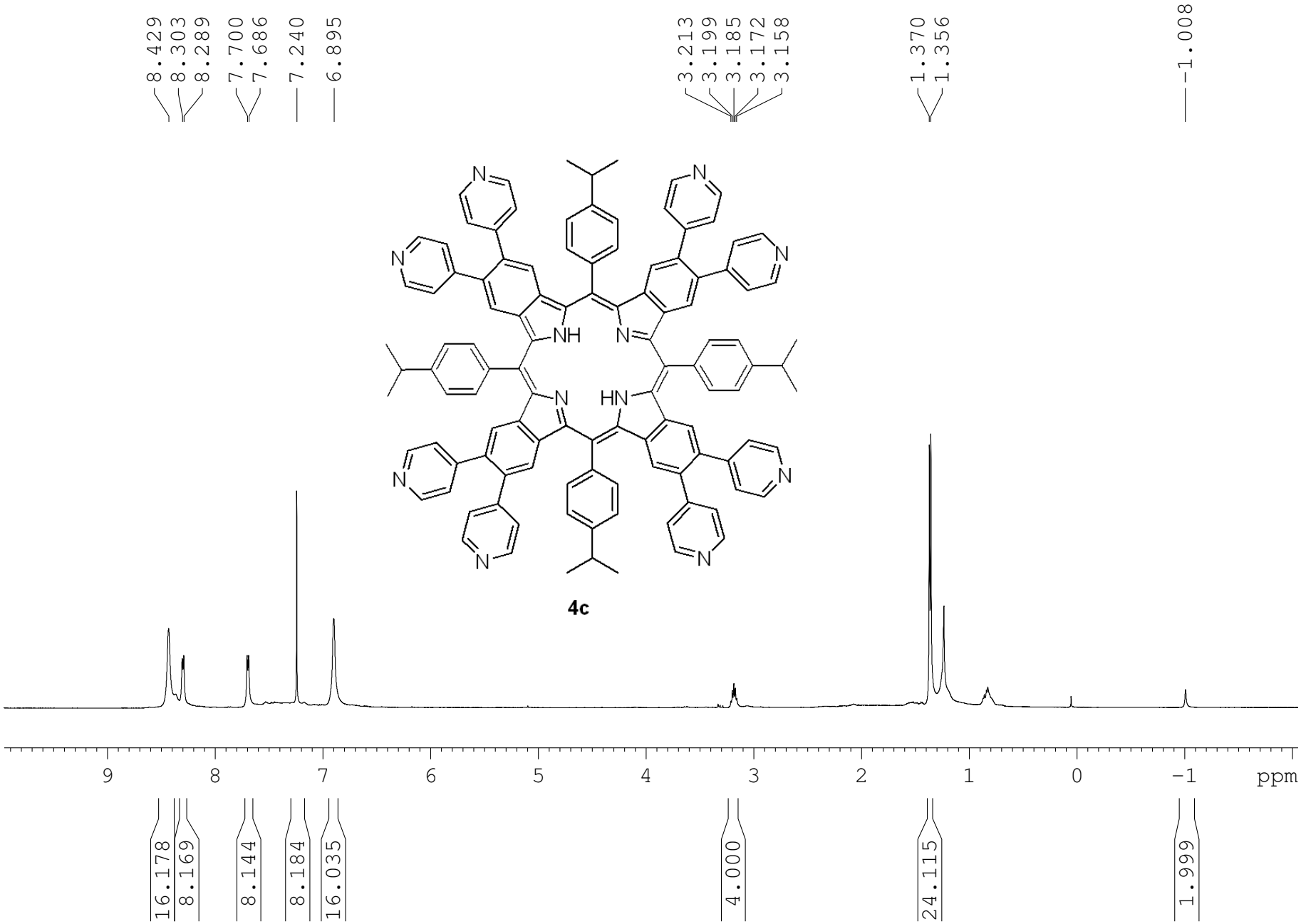
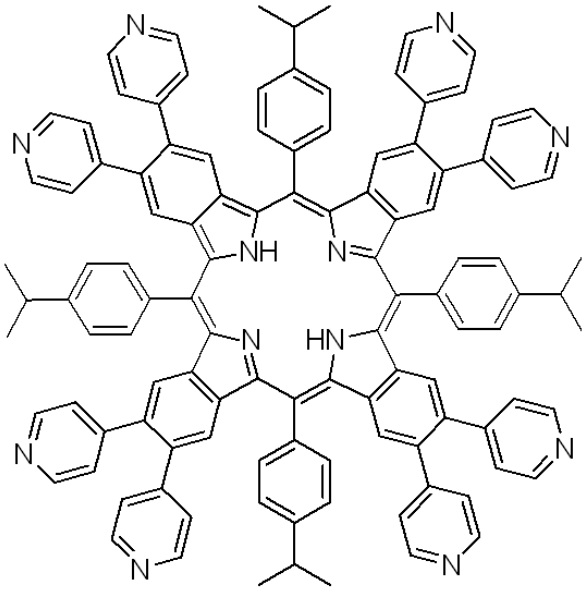
in CDCl3


8.429
8.303
8.289
7.700
7.686
7.240
6.895
3.213
3.199
3.185
3.172
3.158
1.370
1.356
-1.008
NH
N
N
HN
9
8
7
6
5
4
3
2
1
0
-1
ppm
16.178
8.169
8.144
8.184
16.035
4.000
24.115
1.999

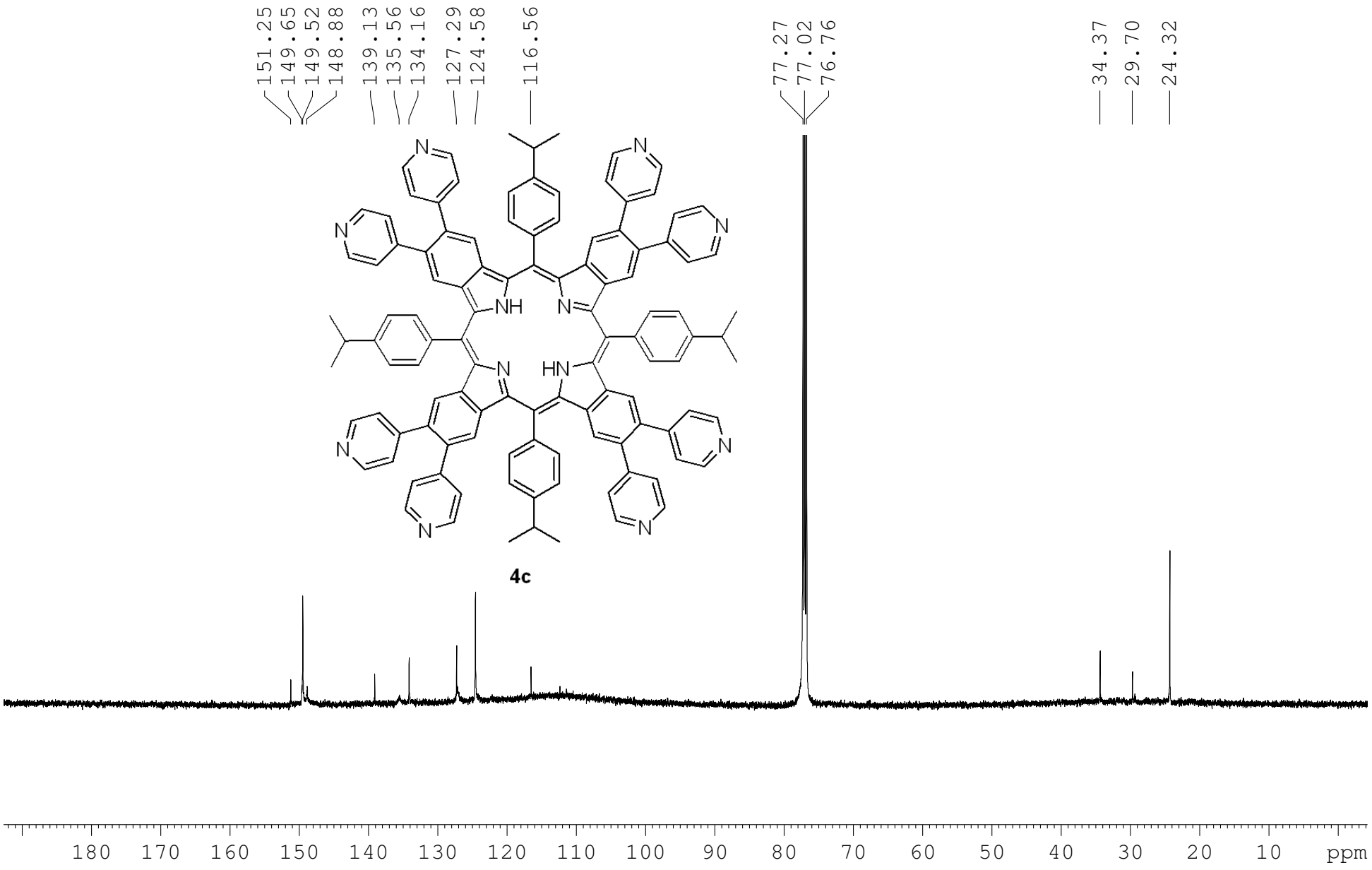
4c

in MeOD

For comparison, 1HNMR was also done in CD3OD, please refer to 1HNMR done in CD3Cl in previous page. Broadened shifts in protonic solvent suggest the presence of hydrogen bonding.



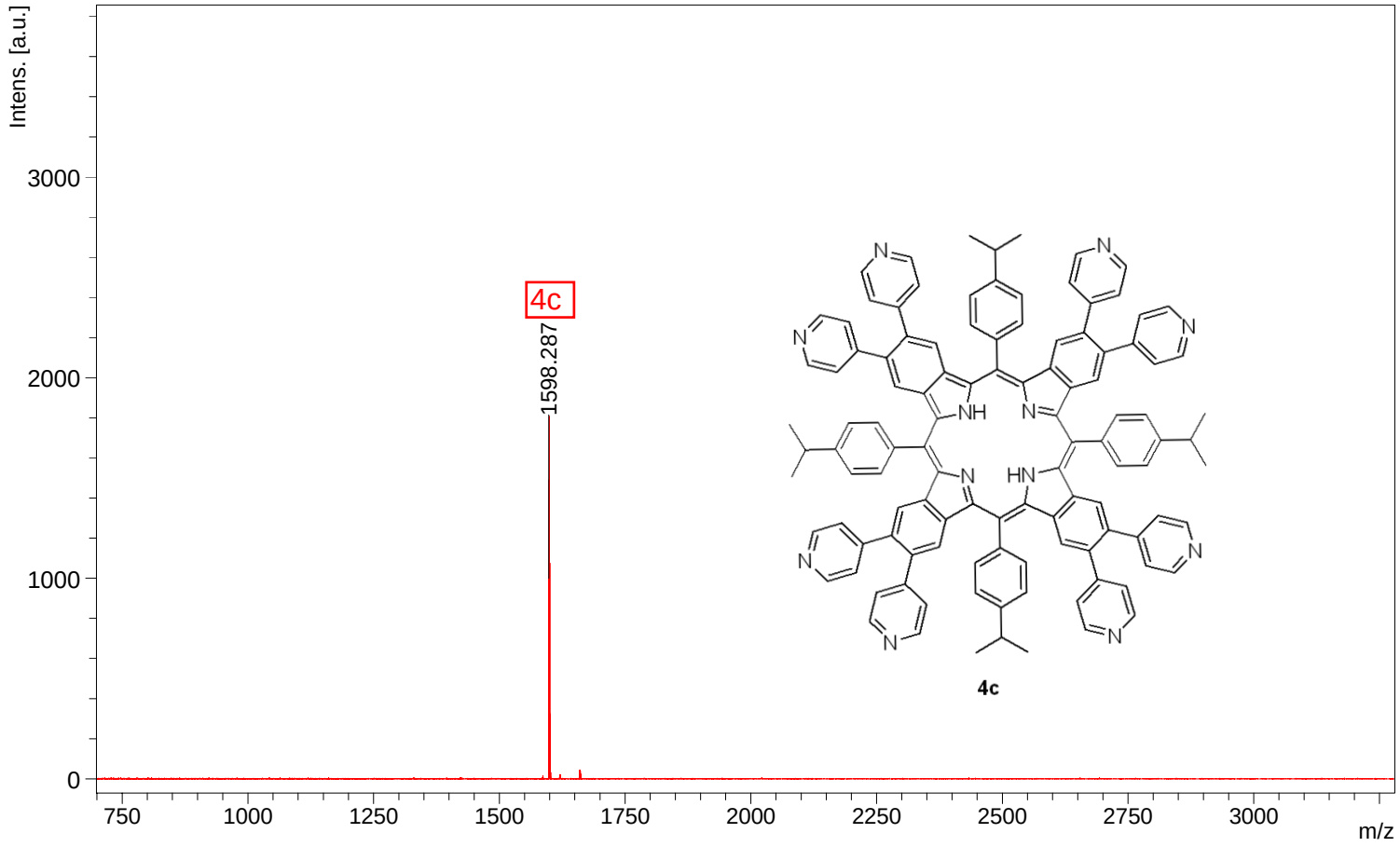
4c


151.25
149.65
149.52
148.88
139.13
135.56
134.16
127.29
124.58
116.56
77.27
77.02
76.76
34.37
29.70
24.32
NH
N
HN
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4c

Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1598.287				993.00	

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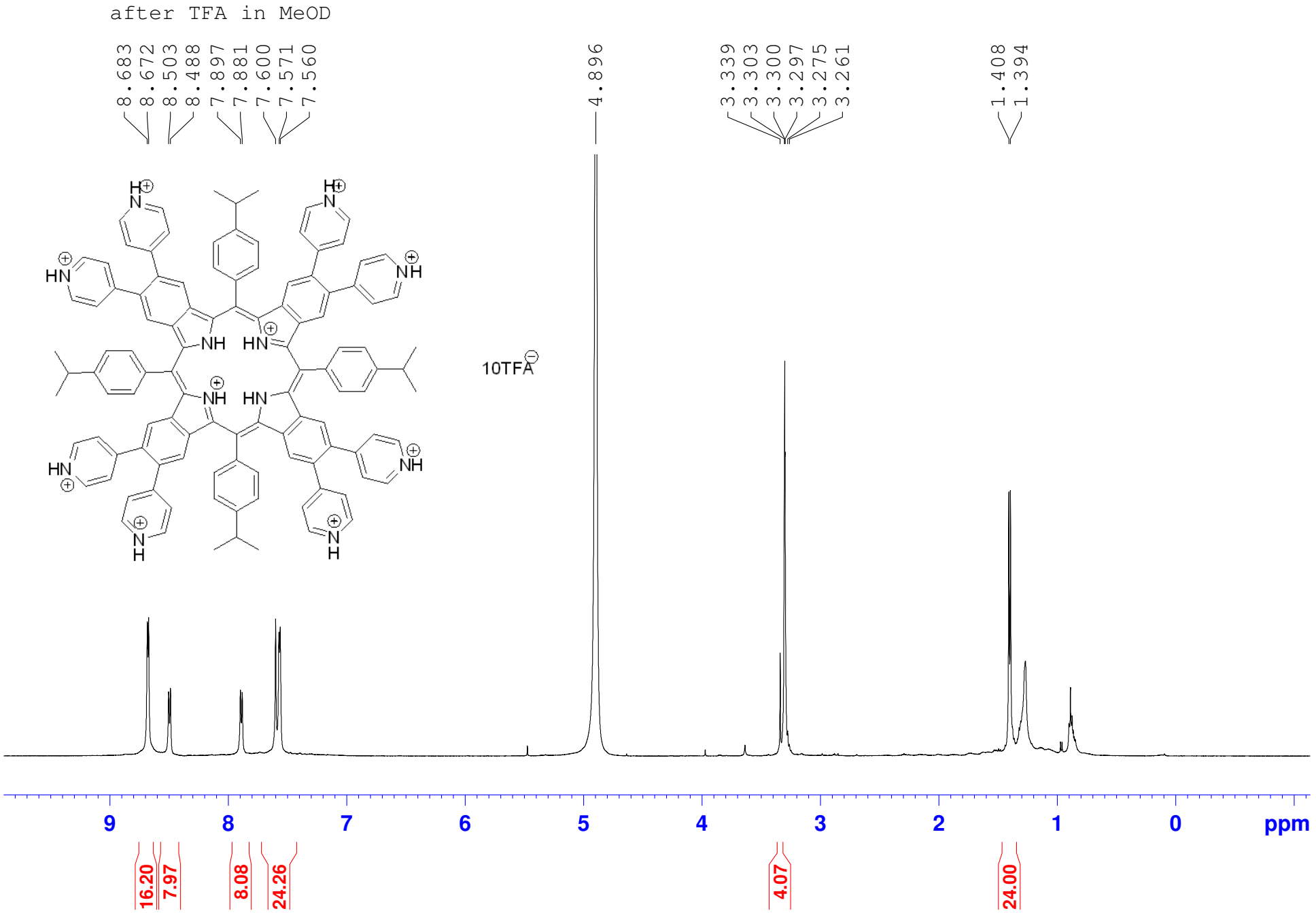
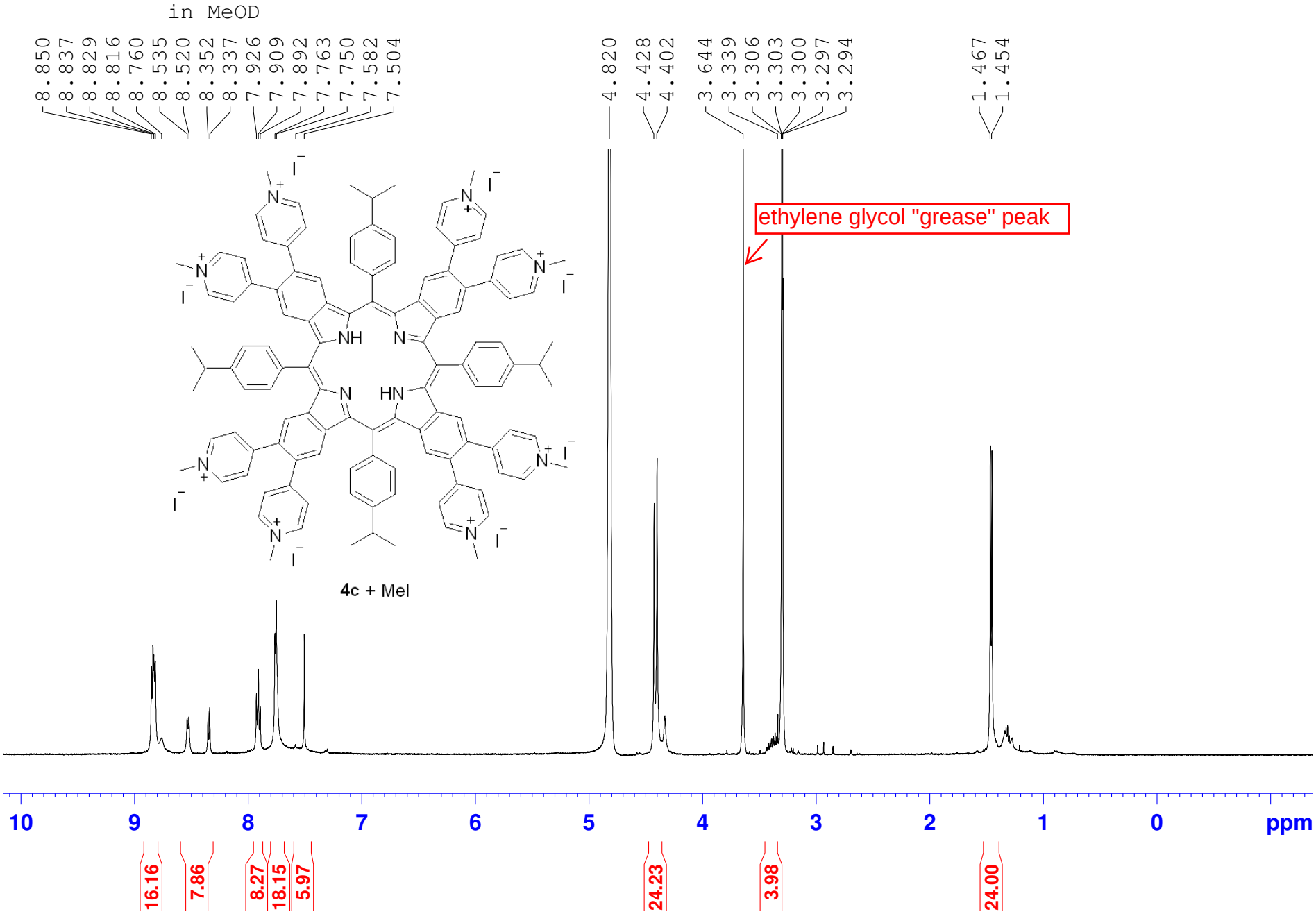
1 PM


after TFA in MeOD
8.683
8.672
8.503
8.488
7.897
7.881
7.600
7.571
7.560
4.896
3.339
3.303
3.300
3.297
3.275
3.261
1.408
1.394
10TFA
9
8
7
6
5
4
3
2
1
0
ppm
16.20
7.97
8.08
24.26
4.07
24.00

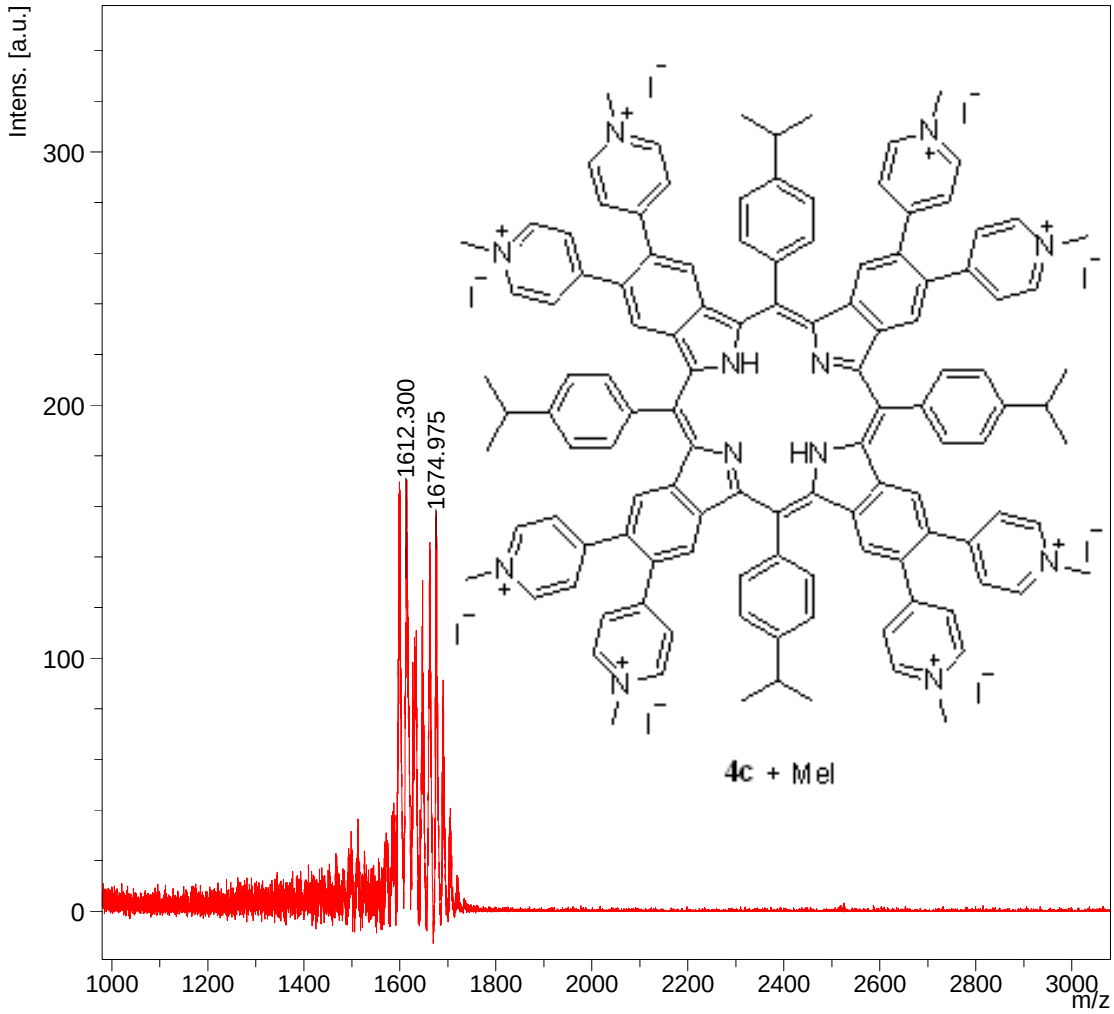

in MeOD
8.850
8.837
8.829
8.816
8.760
8.535
8.520
8.352
8.337
7.926
7.909
7.892
7.763
7.750
7.582
7.504
4.820
4.428
4.402
3.644
3.339
3.306
3.303
3.300
3.297
3.294
1.467
1.454
ethylene glycol "grease" peak
4c + MeI
10
9
8
7
6
5
4
3
2
1
0
ppm
16.16
7.86
8.27
18.15
5.97
24.23
3.98
24.00

D:\Data\hong wang\031612\4c + MeI\0_L8\1

Comment 1 casein in CCA 1:1

Comment 2

details in next page

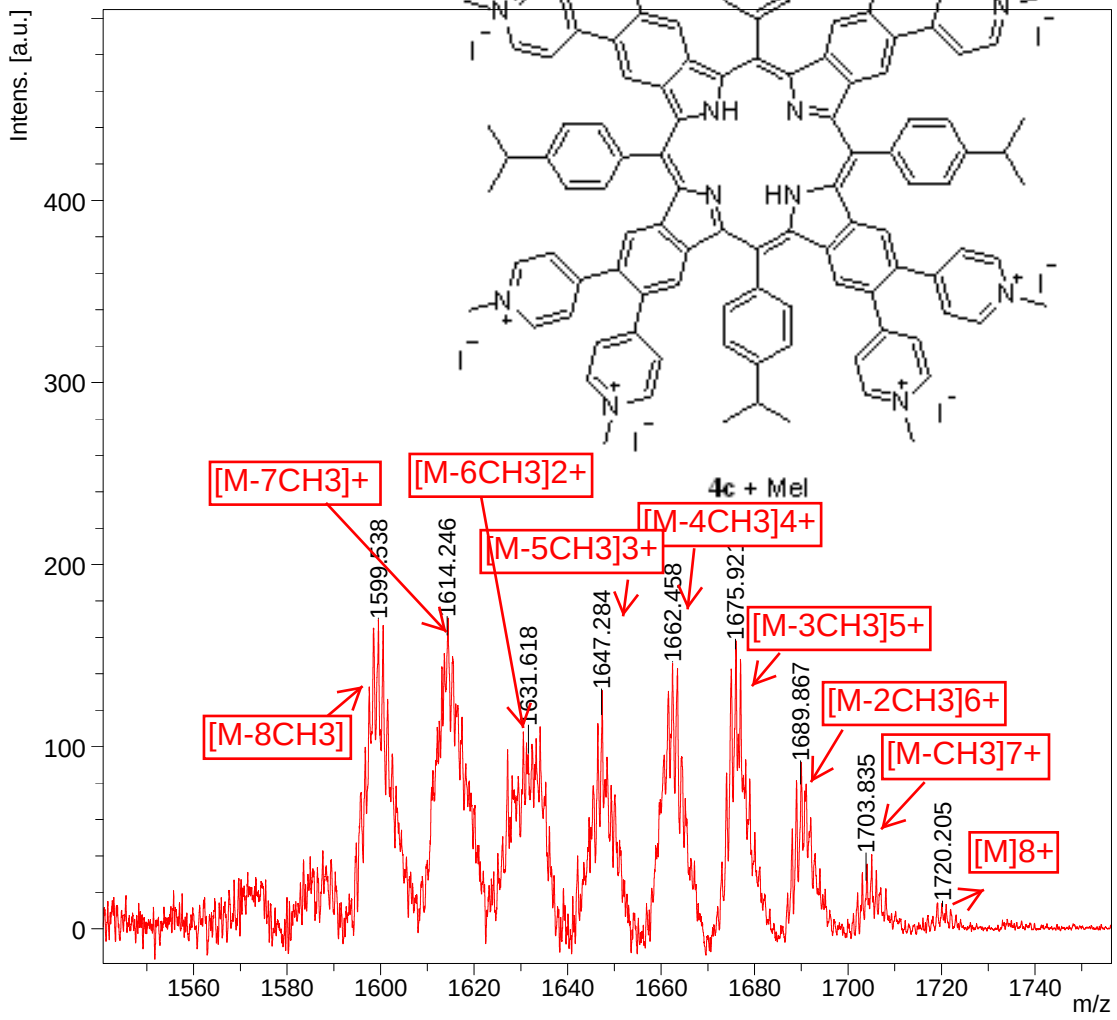


m/z	Res.	Intens.
1598.221	314	61.09
1612.300	444	66.78
1628.545	594	46.76
1633.016	715	44.23
1660.314	694	63.39
1663.433	1784	55.91
1674.975	496	57.25

D:\Data\hong wang\031612\4c + MeI\0_L8\1

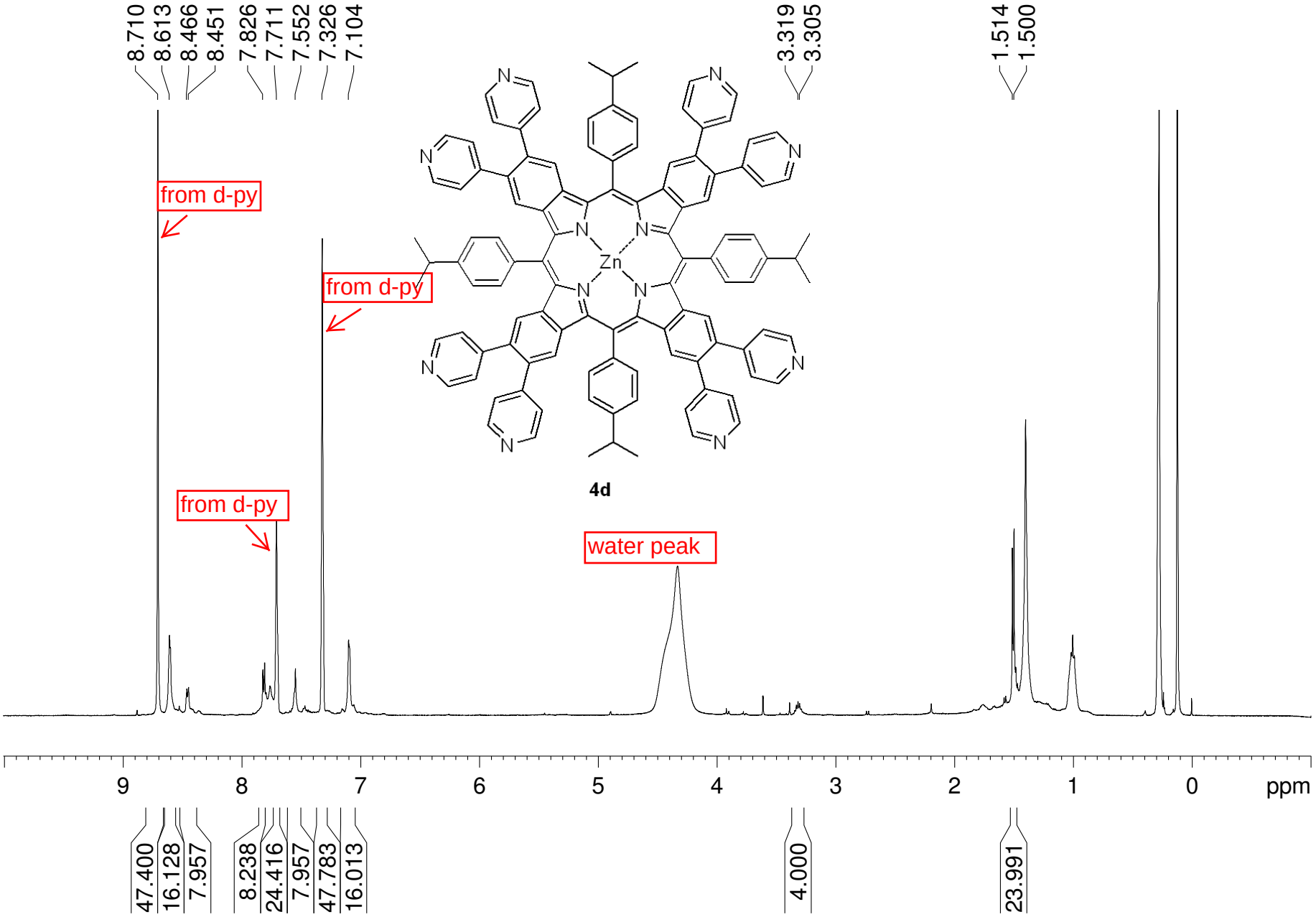
Comment 1 casein in CCA 1:1

Comment 2



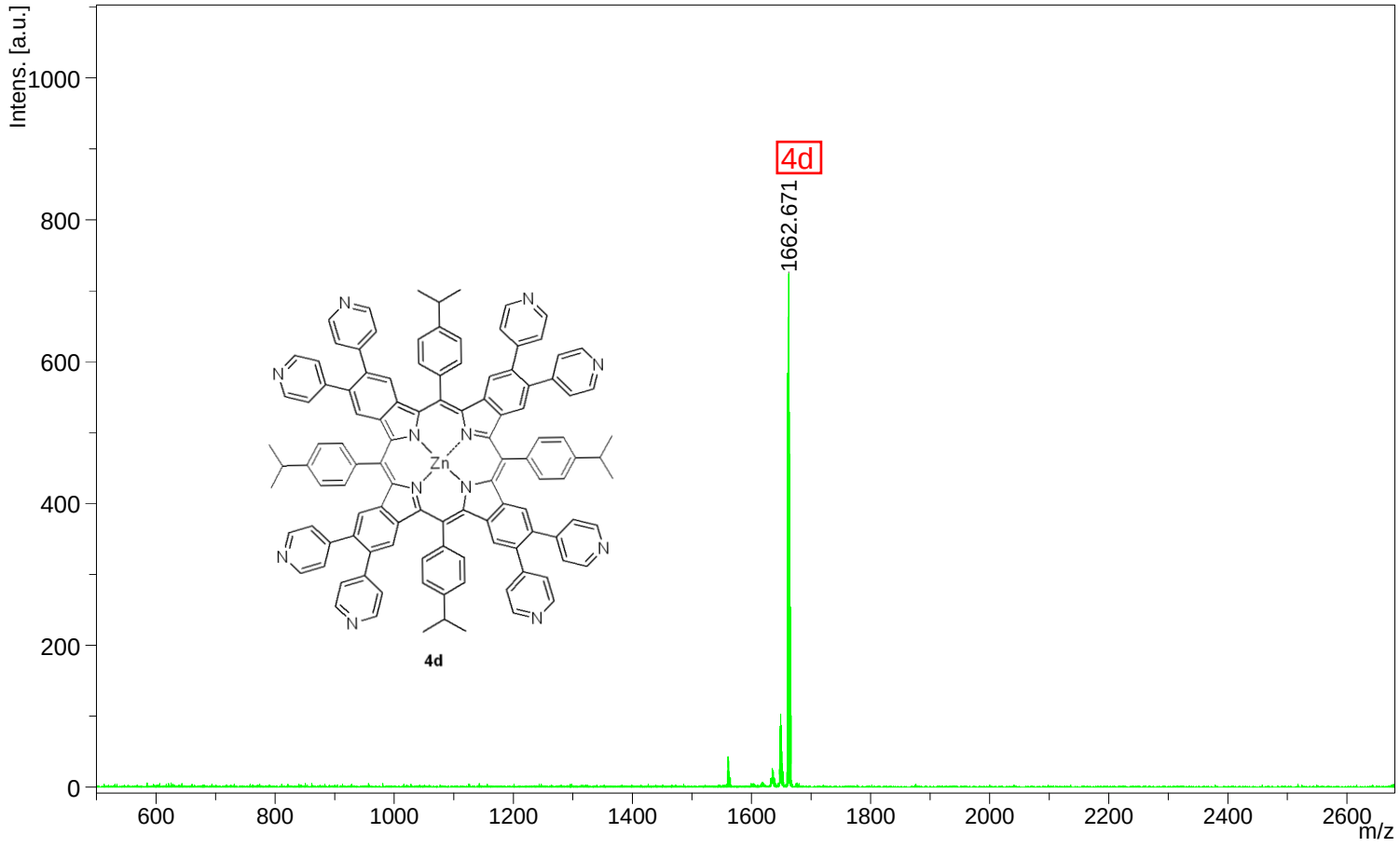
m/z	Res.	Intens.
1599.538		169.61
1614.246		153.80
1631.618		92.70
1647.284		107.01
1662.458		145.73
1675.921		143.15
1689.867		69.81
1703.835		18.58
1720.205		8.88

CDCl3 and Pyridine in 2:1 ratio



Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
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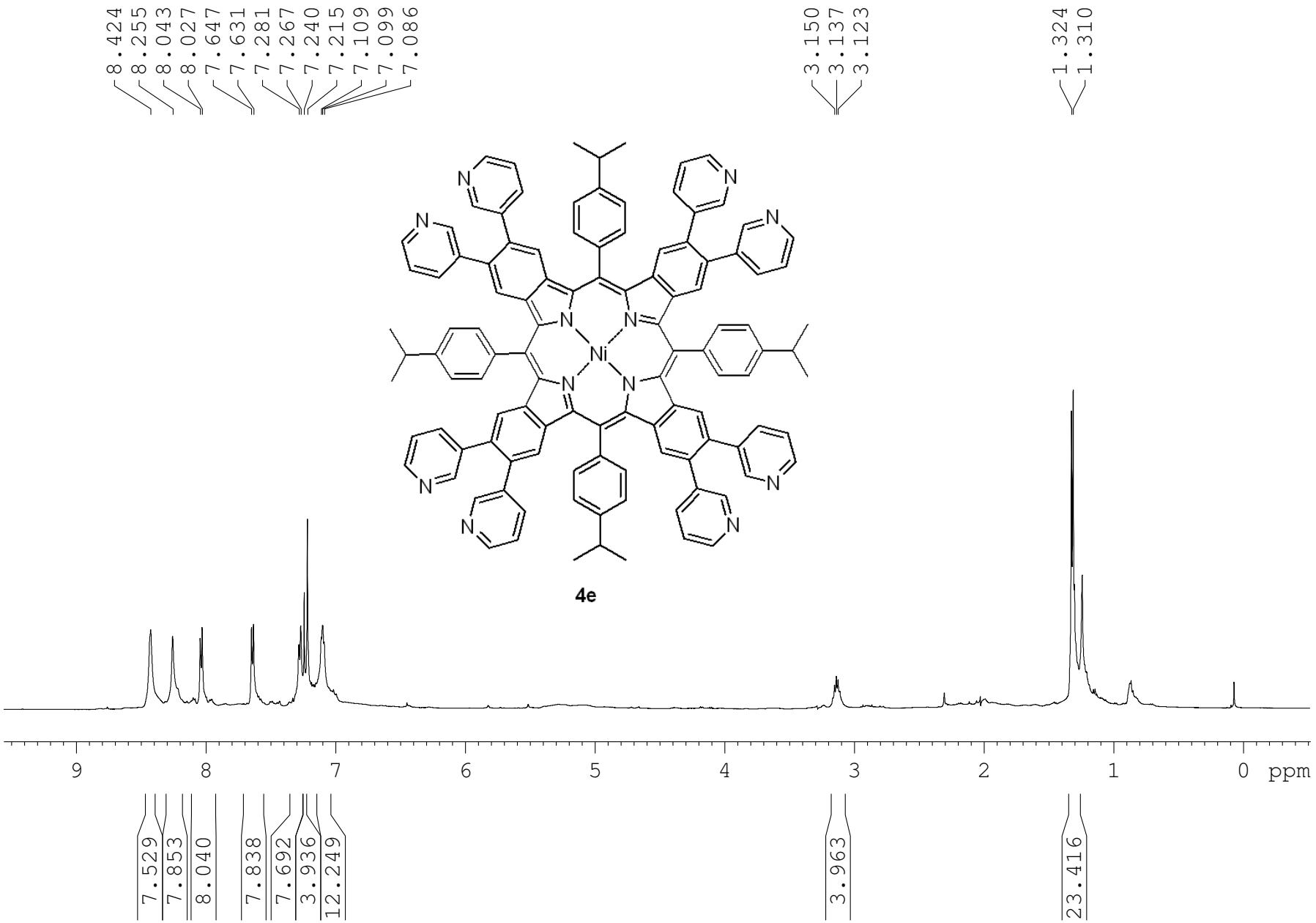
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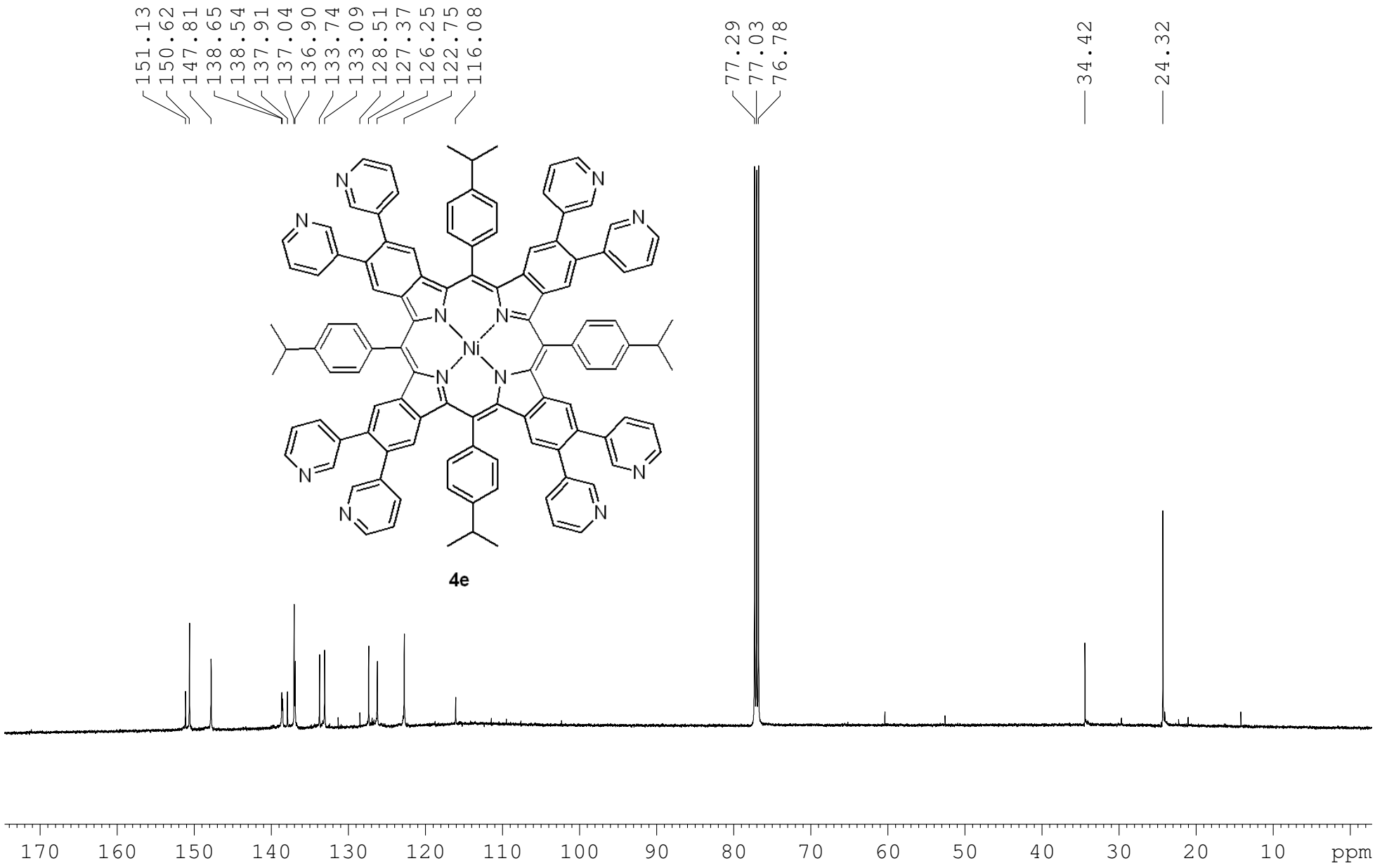
8.255
8.043
8.027
7.647
7.631
7.281
7.267
7.240
7.215
7.109
7.099
7.086
3.150
3.137
3.123
1.324
1.310
Ni
N
4e
9
8
7
6
5
4
3
2
1
0
ppm
7.529
7.853
8.040
7.838
7.692
3.936
12.249
3.963
23.416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150.62
147.81
138.65
138.54
137.91
137.04
136.90
133.74
133.09
128.51
127.37
126.25
122.75
116.08
77.29
77.03
76.78
34.42
24.32
Ni
N
4e
170
160
150
140
130
120
110
100
90
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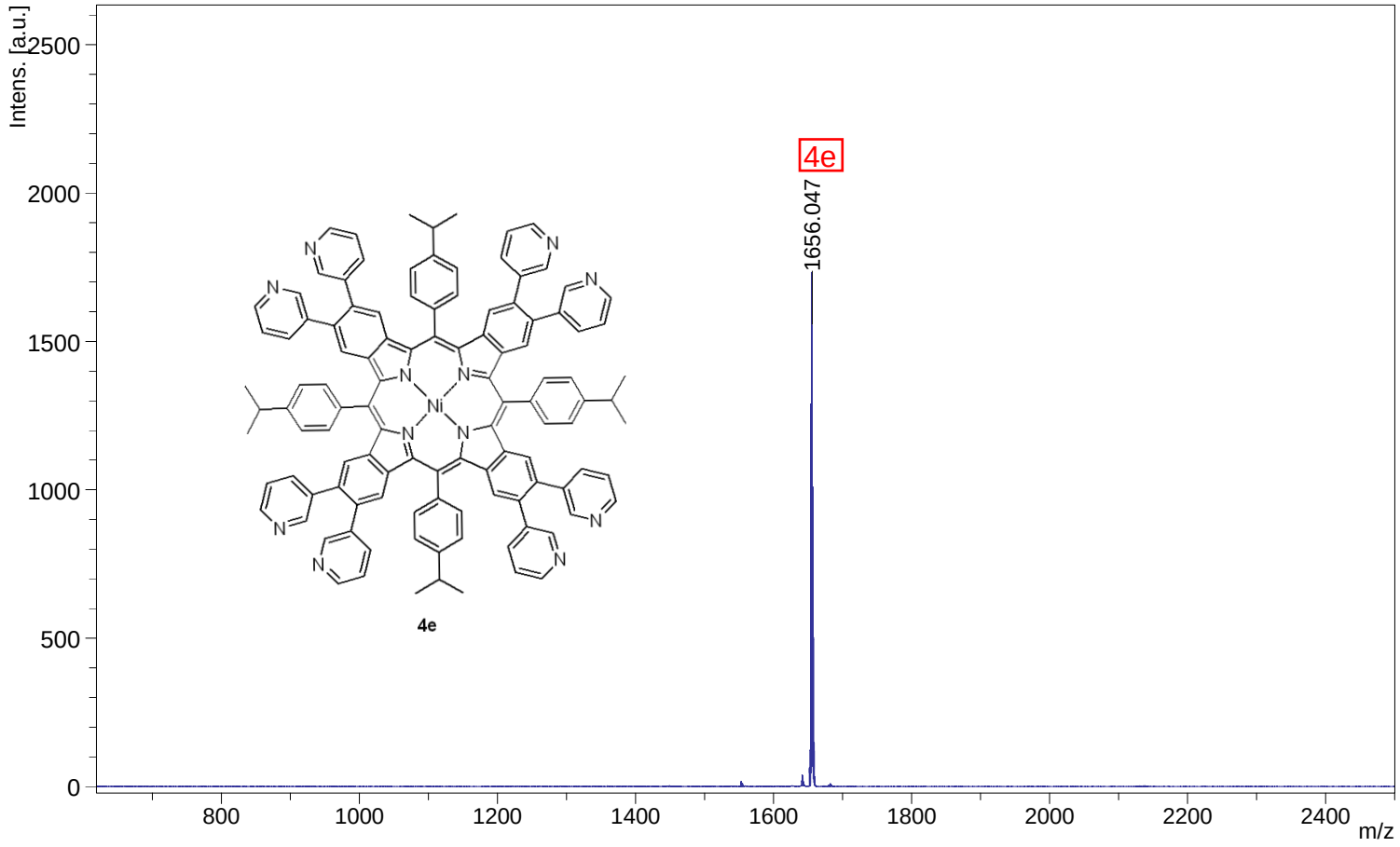
50
40
30
20
10
ppm

47

Comment 1

Comment 2



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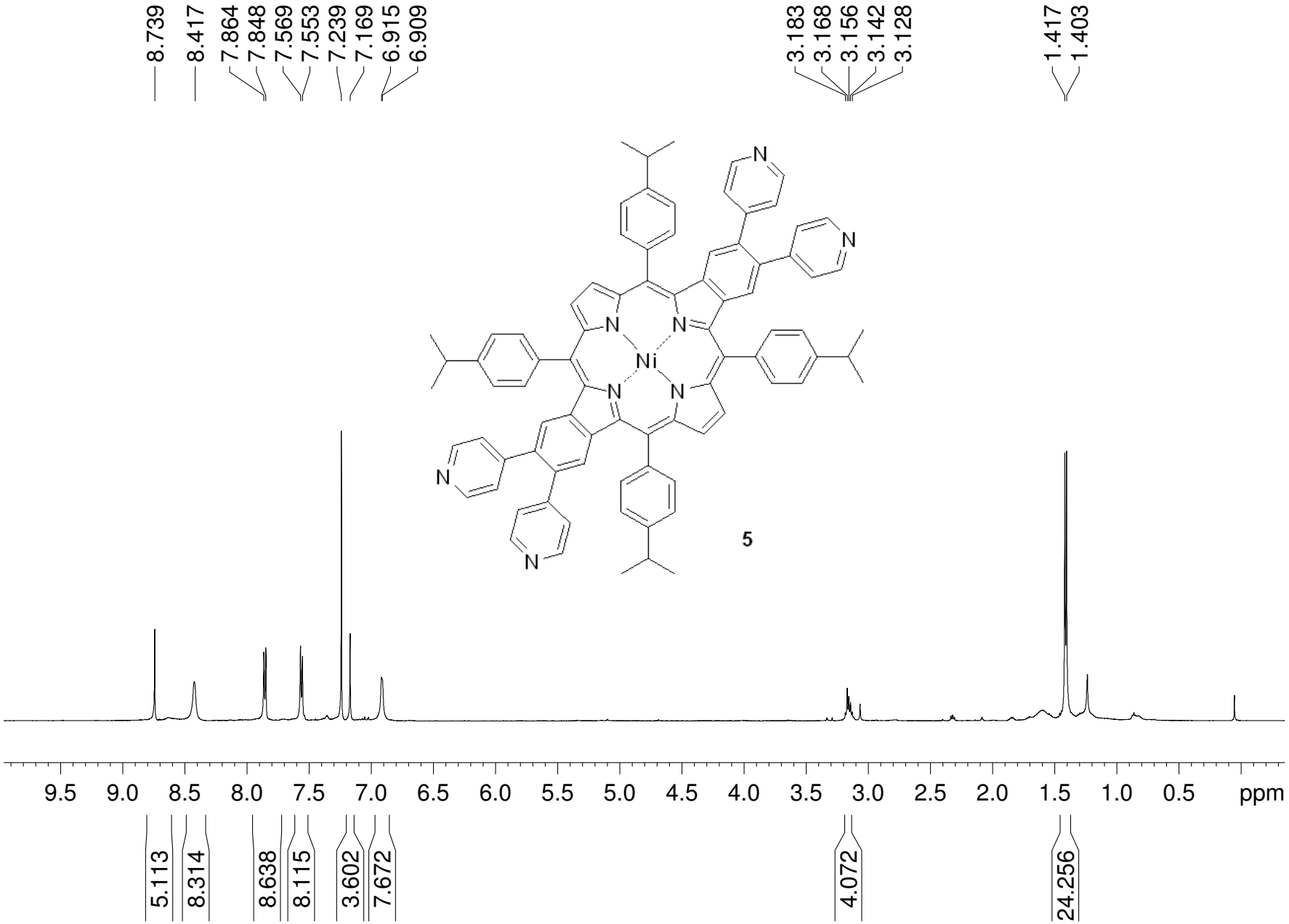
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8.417
7.864
7.848
7.569
7.553
7.239
7.169
6.915
6.909
3.183
3.168
3.156
3.142
3.128
1.417
1.403
N
N
N
Ni
N
N
N
N
N
5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
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8.115
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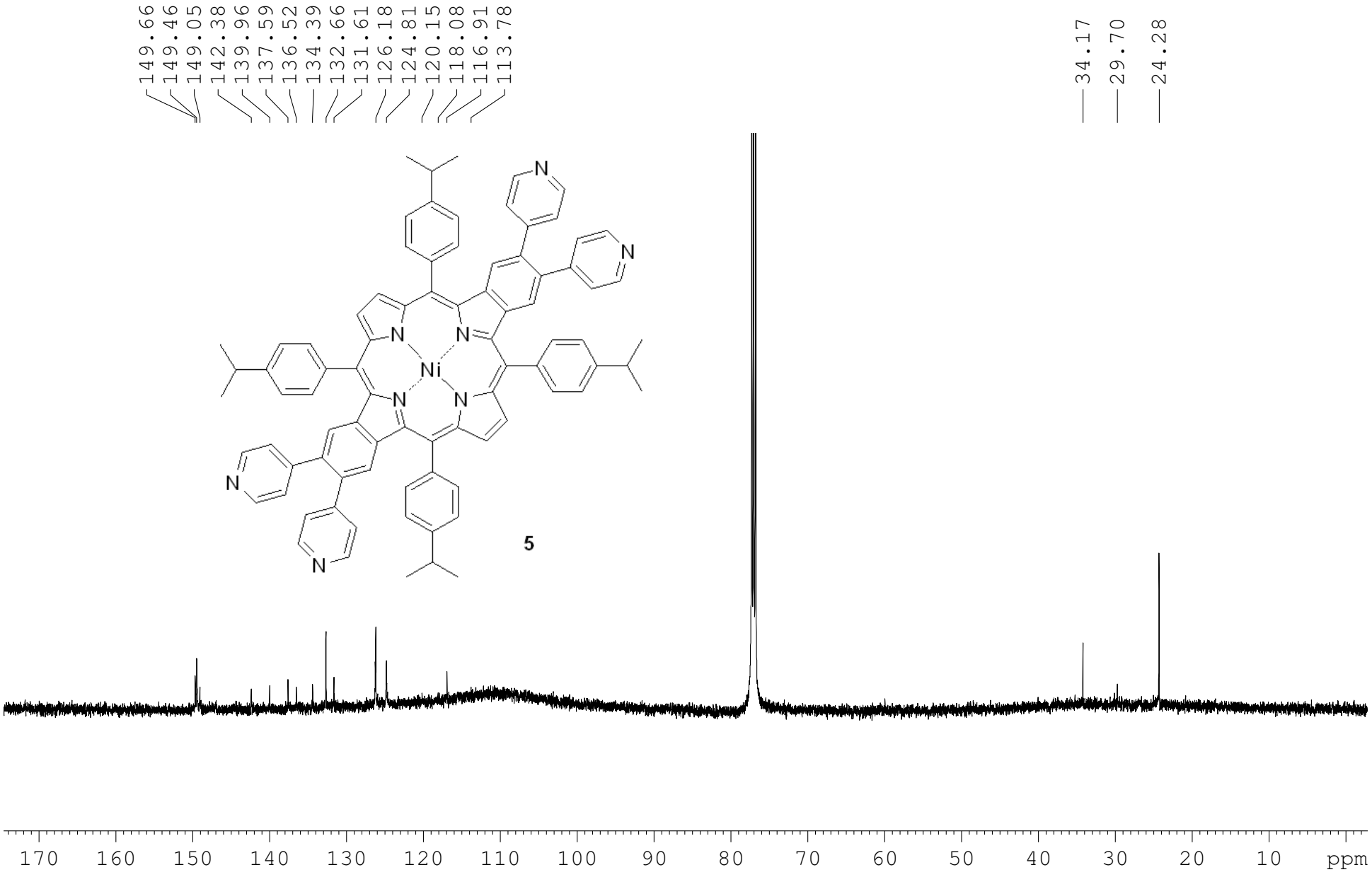
7.672
4.072
24.256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149.46
149.05
142.38
139.96
137.59
136.52
134.39
132.66
131.61
126.18
124.81
120.15
118.08
116.91
113.78
34.17
29.70
24.28
N
N
N
N
Ni
N
N
N
N
5
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110
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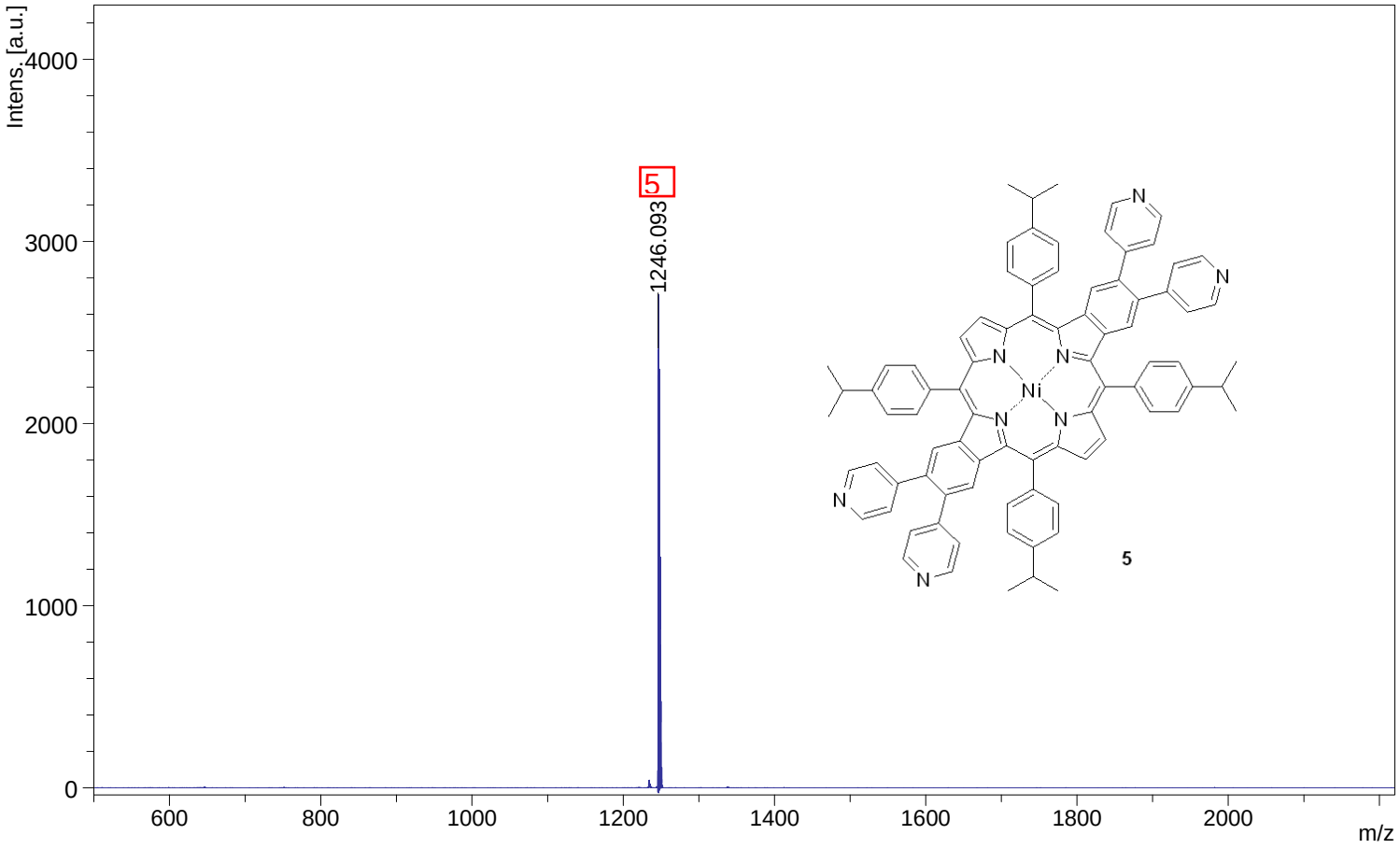
50
40
30
20
10
ppm

Comment 1

Comment 2



m/z	SN	Quality Fac.	Res.	Intens.	Area
1233.678	12.1	854	4313	50.04	32
1246.093	615.8	2145	4985	2595.90	1412
1248.095	273.2	1655	4994	1142.05	621

printed: 12/5/2011 10:51:49 AM

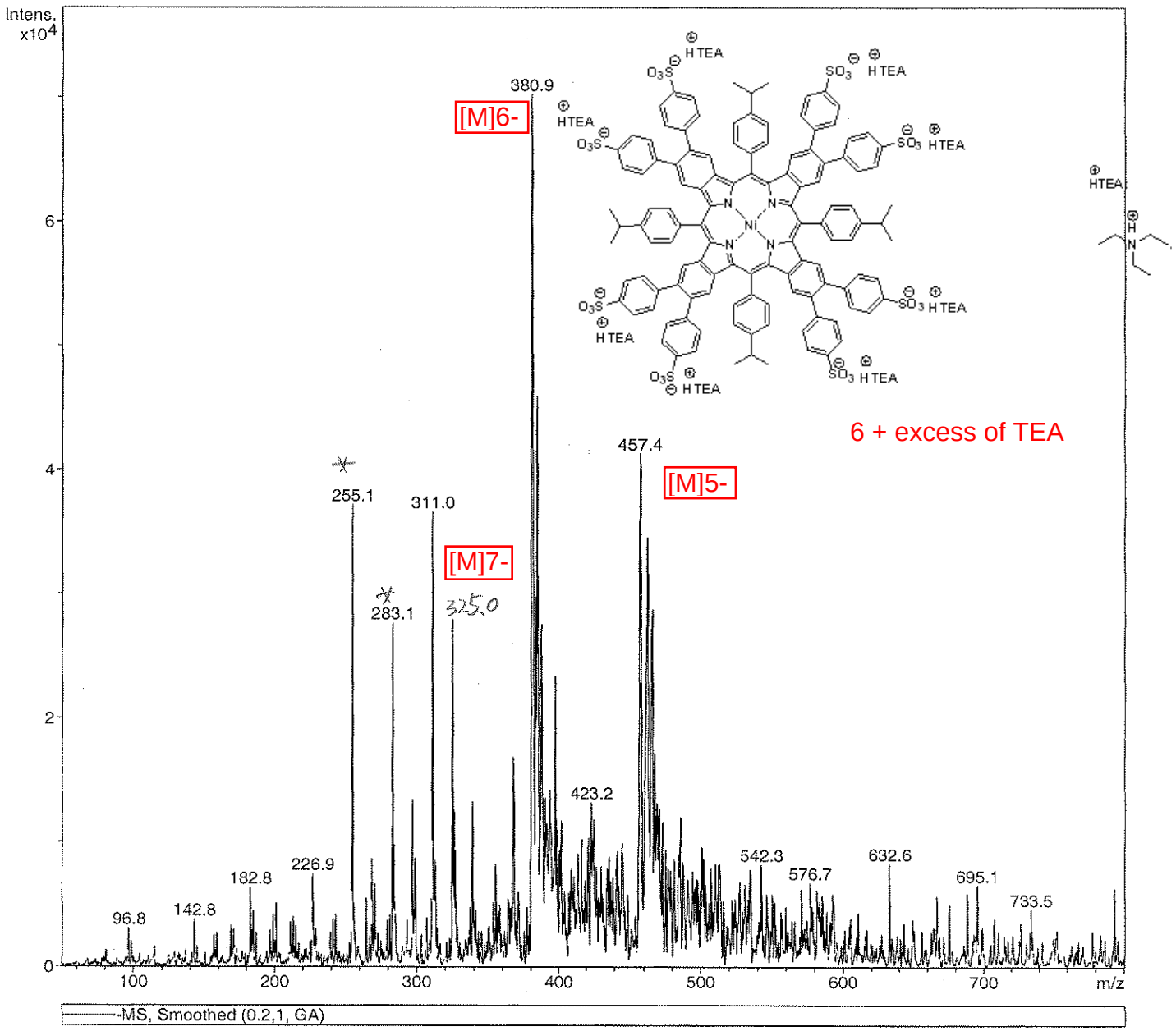
Display Report

Analysis Info

Analysis Name	79_3_204.d	Acquisition Date	01/18/12 10:32:25
Method	CAFFEINE.M	Operator	Administrator
Sample Name	lin4_79_3_2	Instrument	Esquire-LC_00137
Comment	Dissolved in MeOH/0.1%AceticAcid		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	800.00 m/z
Capillary Exit	-102.8 Volt	Skim 1	-31.1 Volt	Trap Drive	42.5
Accumulation Time	1052 µs	Averages	20 Spectra	Auto MS/MS	Off



* — background.

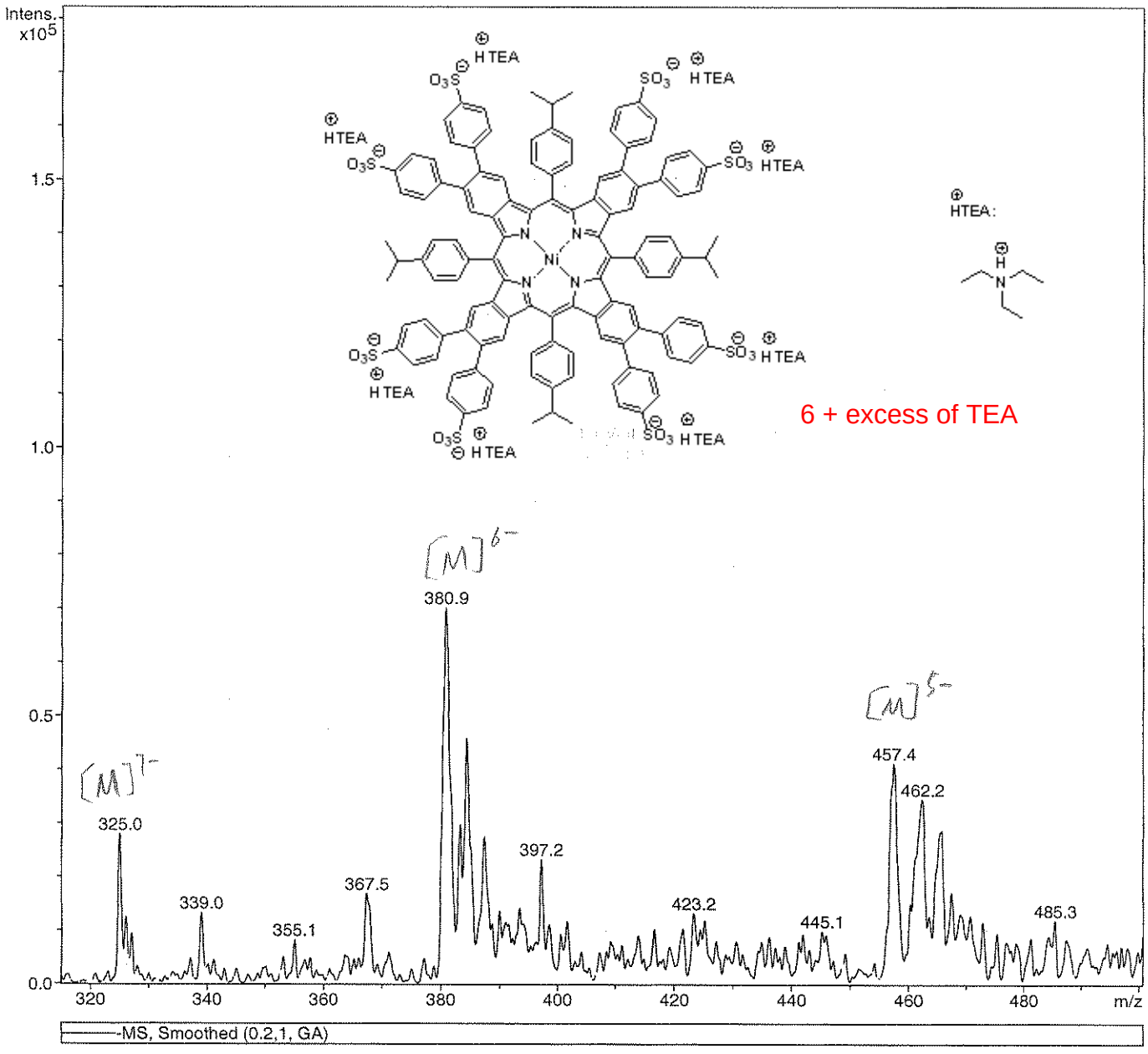
Display Report

Analysis Info

Analysis Name	79_3_204.d	Acquisition Date	01/18/12 10:32:25
Method	CAFFEINE.M	Operator	Administrator
Sample Name	lin4_79_3_2	Instrument	Esquire-LC_00137
Comment	Dissolved in MeOH/0.1%AceticAcid		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	800.00 m/z
Capillary Exit	-102.8 Volt	Skim 1	-31.1 Volt	Trap Drive	42.5
Accumulation Time	1052 µs	Averages	20 Spectra	Auto MS/MS	Off



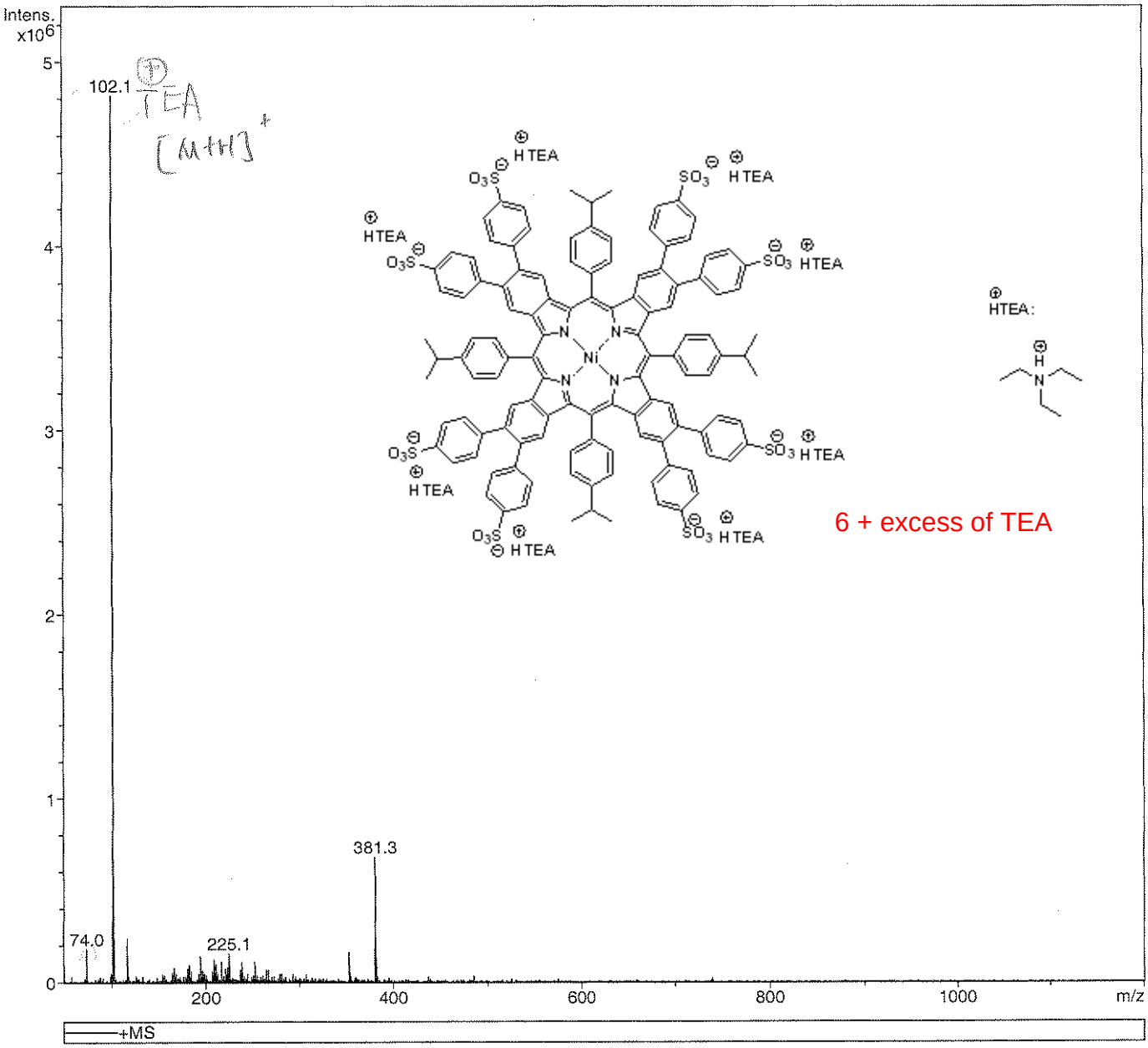
Display Report

Analysis Info

Analysis Name	79_30004.d	Acquisition Date	12/07/11 11:35:52
Method	XQ Default.ms	Operator	Administrator
Sample Name	lin_79_3	Instrument	Esquire-LC_00137
Comment	dissolved in MEOH/0.1% acetic acid		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	1200.00 m/z
Capillary Exit	85.2 Volt	Skim 1	17.6 Volt	Trap Drive	29.2
Accumulation Time	414 µs	Averages	20 Spectra	Auto MS/MS	Off



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Analysis Info

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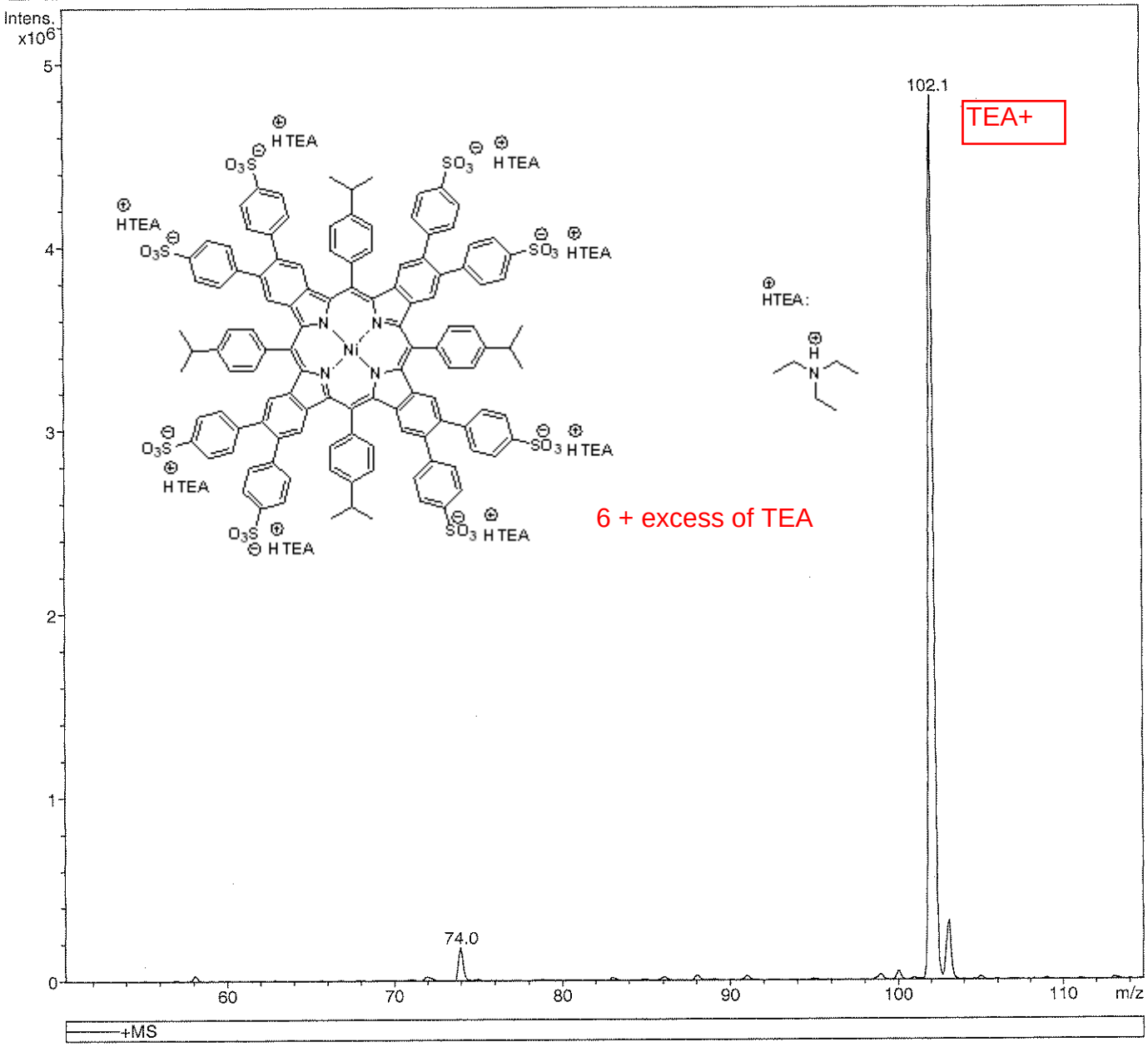
Method	XQ Default.ms	Operator	Administrator
Sample Name	lin_79_3	Instrument	Esquire-LC_00137
Comment	dissolved in MEOH/0.1% acetic acid		

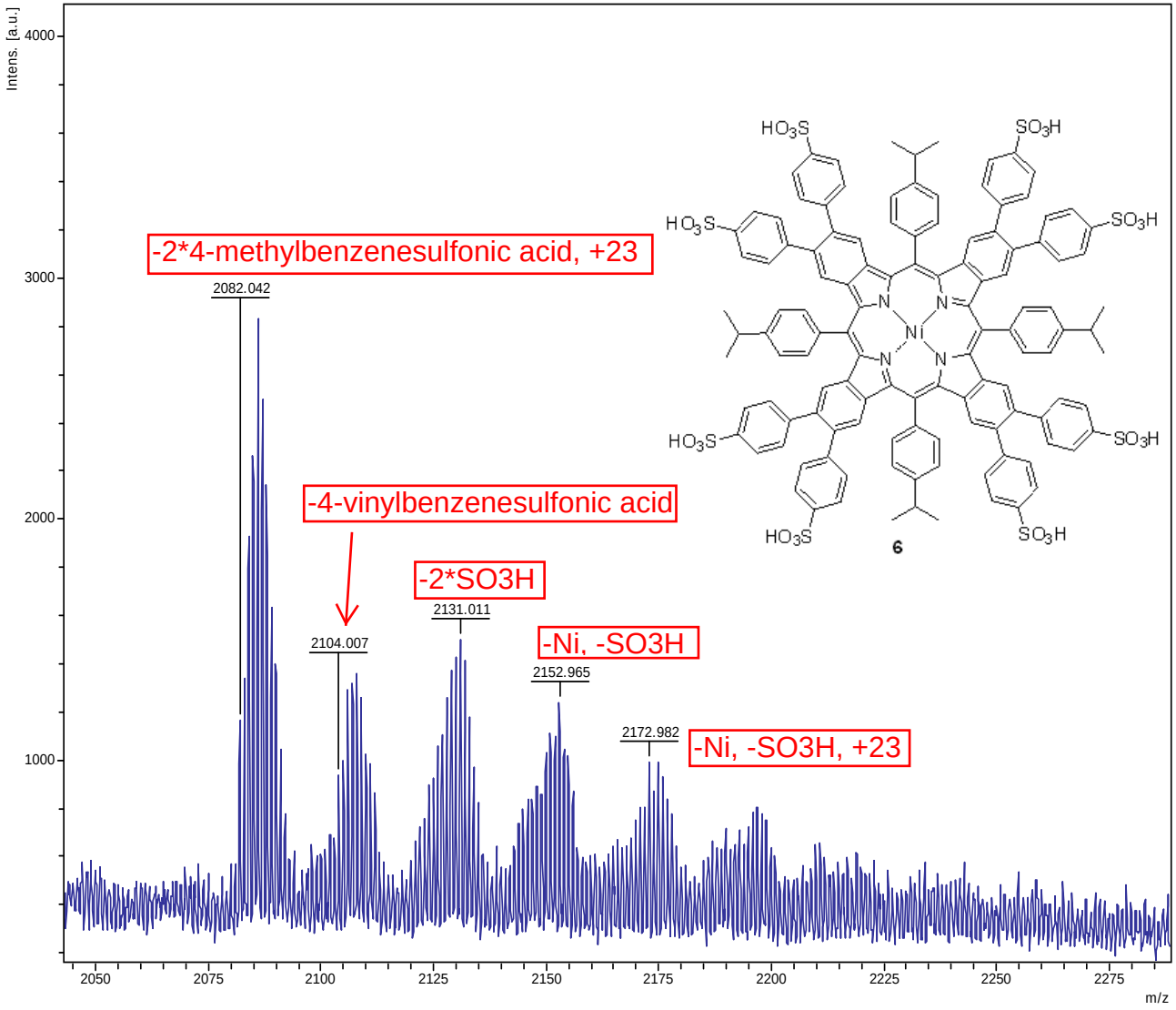
Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Mass Range Mode	Std/Normal	Scan Begin	50.00 m/z	Scan End	1200.00 m/z
Capillary Exit	85.2 Volt	Skim 1	17.6 Volt	Trap Drive	29.2
Accumulation Time	414 µs	Averages	20 Spectra	Auto MS/MS	Off



D:\Data\2012\02_February_2012\M022412\16956 Lin 4-67\0_J17\1

HRMASS

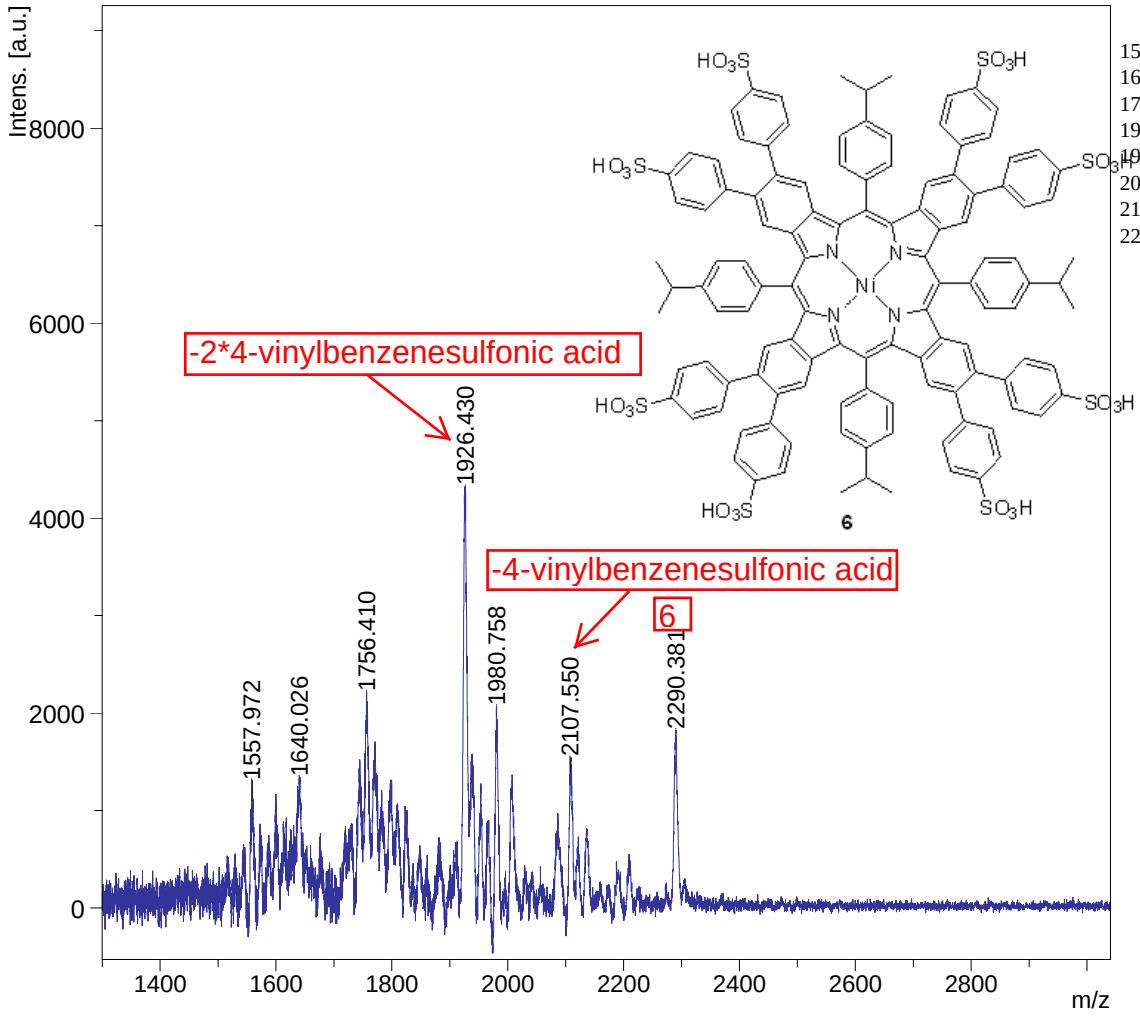


m/z	S/N	Quality Fac.	Res.	Intens.	Area
1875.856	2.8		10282	598.00	87
1899.851	2.8		5215	598.00	110
1920.818	4.7		10873	866.00	154
1942.799	4.1		8799	812.00	141
1964.832	3.2		7348	689.00	110
2024.891	3.3		6755	732.00	152
2082.042	6.6		12646	1167.00	198
2104.007	5.0		10626	935.00	140
2131.011	9.2		11502	1501.00	300
2152.965	7.4		11721	1236.00	211
2172.982	5.7		13245	991.00	177

MALDI-TOF

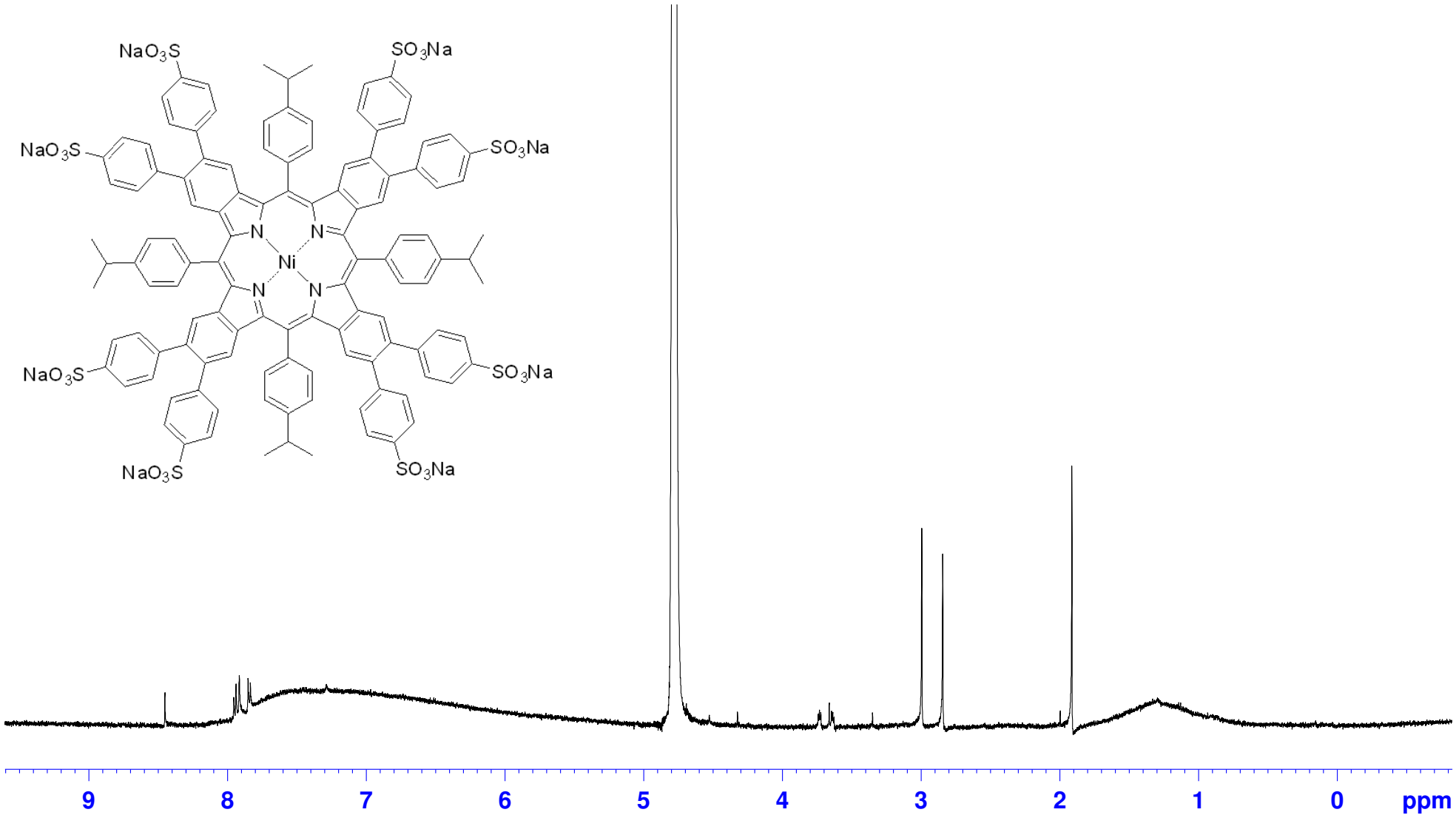
Comment 1

Comment 2

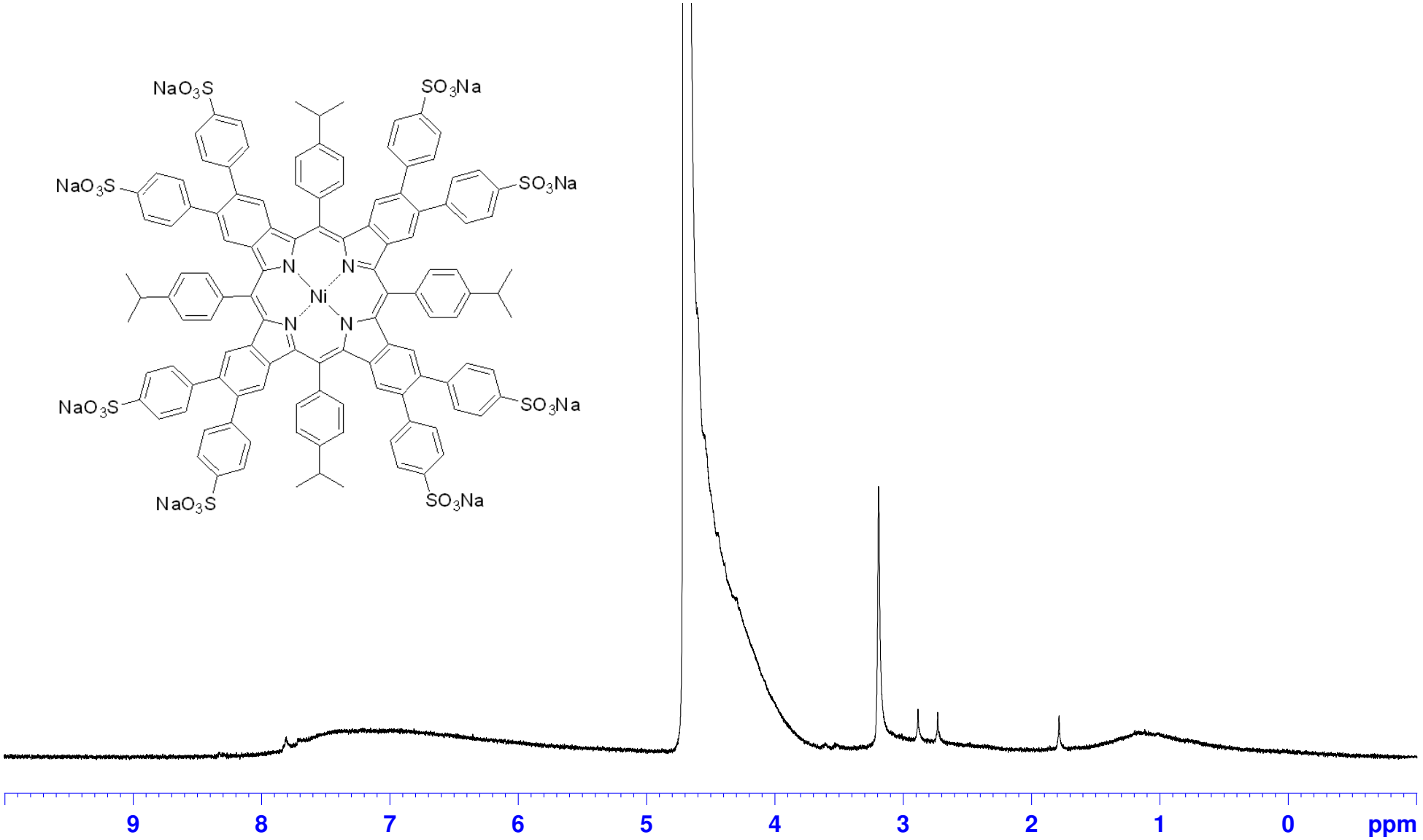


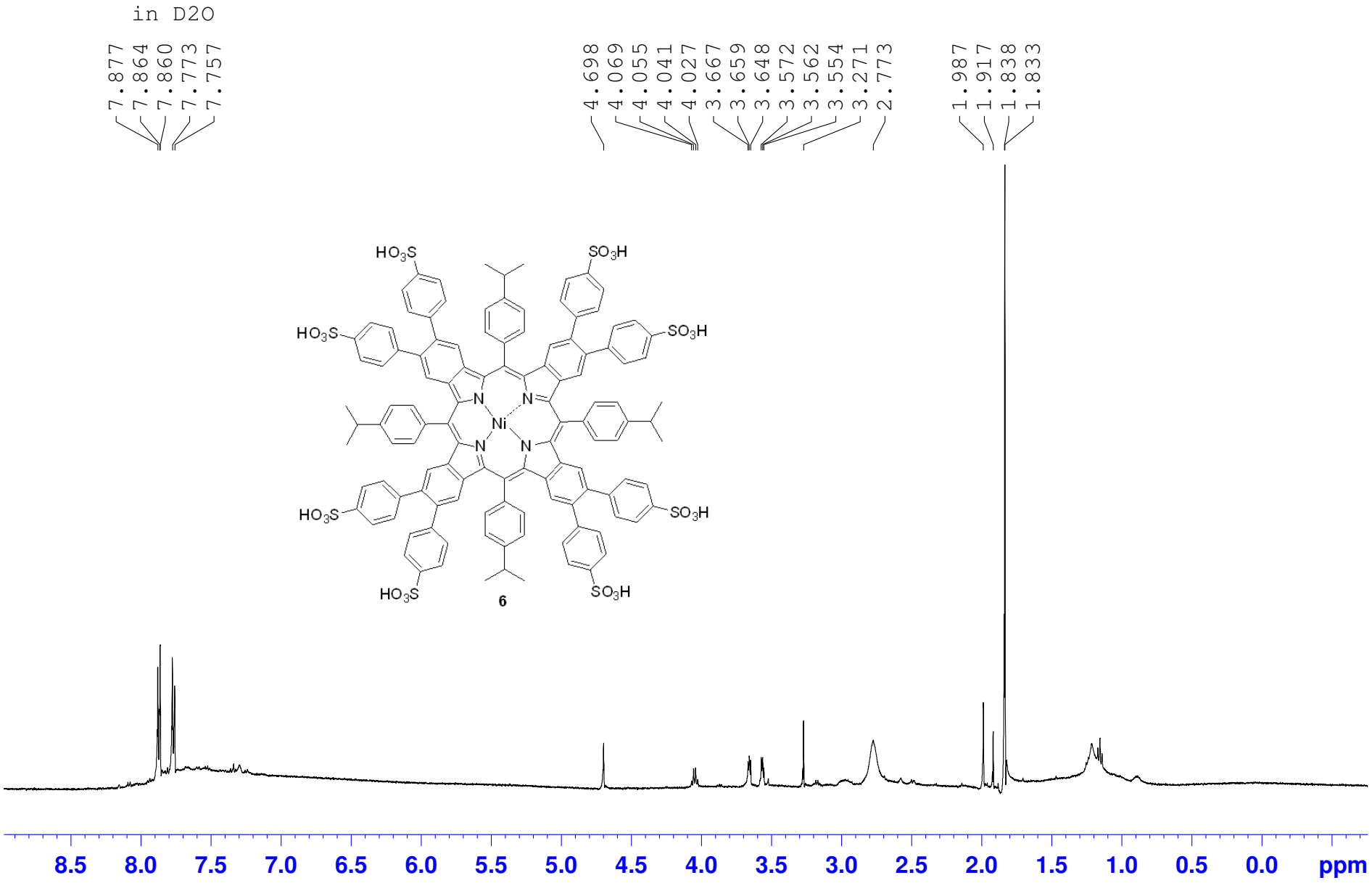
m/z	Res.	Intens.
1557.972		1071.19
1640.026		1334.95
1756.410		2217.29
1926.430		4323.79
1980.758		2067.37
2007.527		1364.21
2107.550		1376.60
2290.381		1824.67

in D2O

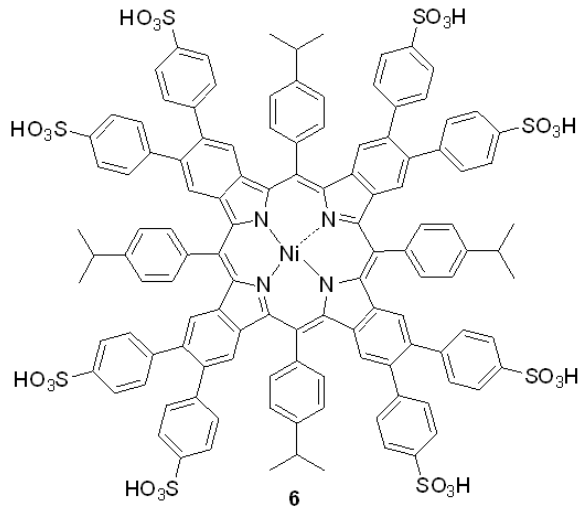

NaO3S
SO3Na
NaO3S
SO3Na
N
N
Ni
N
N
NaO3S
SO3Na
NaO3S
SO3Na
9
8
7
6
5
4
3
2
1
0
ppm

in D2O and MeOD




in D2O
7.877
7.864
7.860
7.773
7.757
4.698
4.069
4.055
4.041
4.027
3.667
3.659
3.648
3.572
3.562
3.554
3.271
2.773
1.987
1.917
1.838
1.833
HO3S
SO3H
Ni
N
6
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
ppm

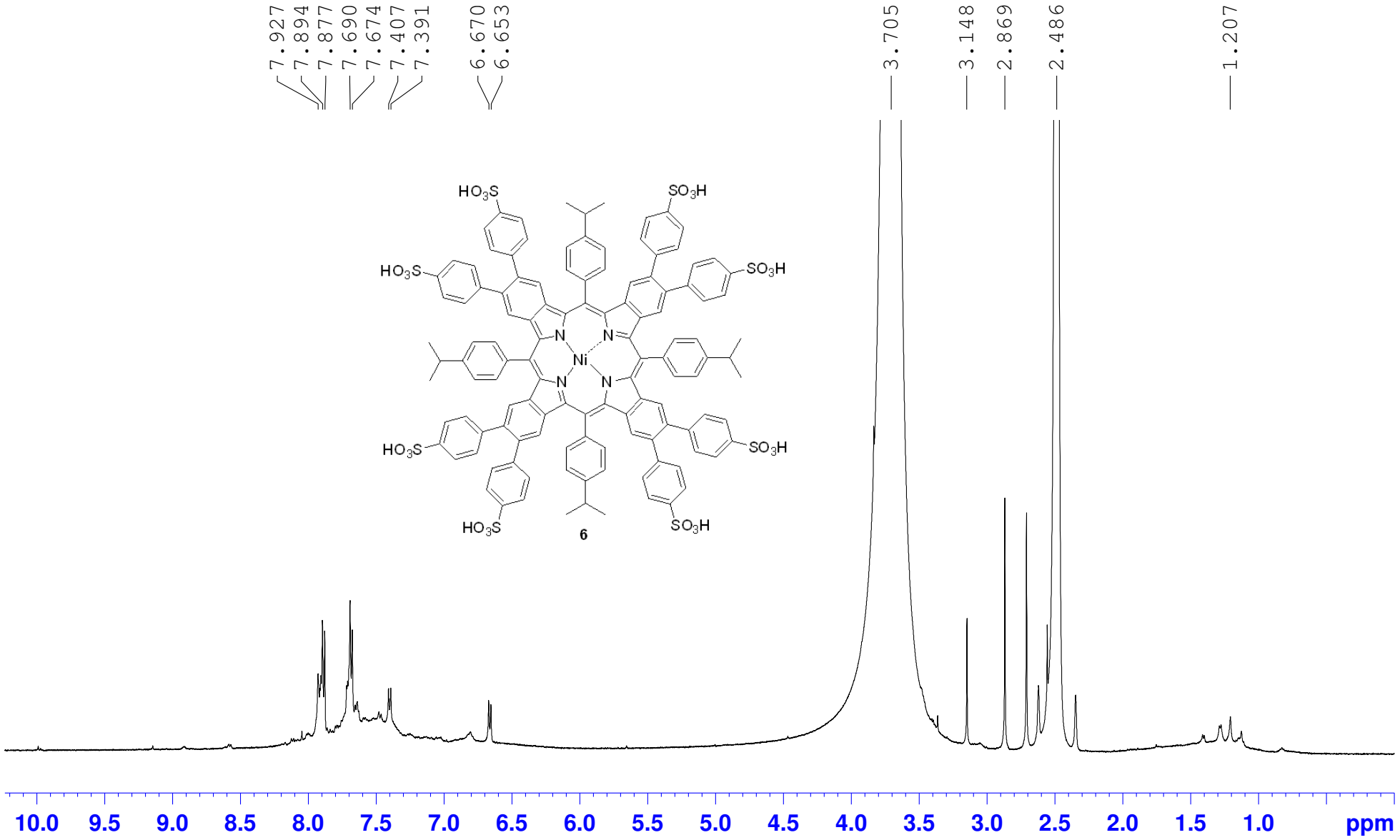
in MeOD


HO3S
SO3H
HO3S
SO3H
N
N
Ni
N
N
HO3S
SO3H
HO3S
SO3H

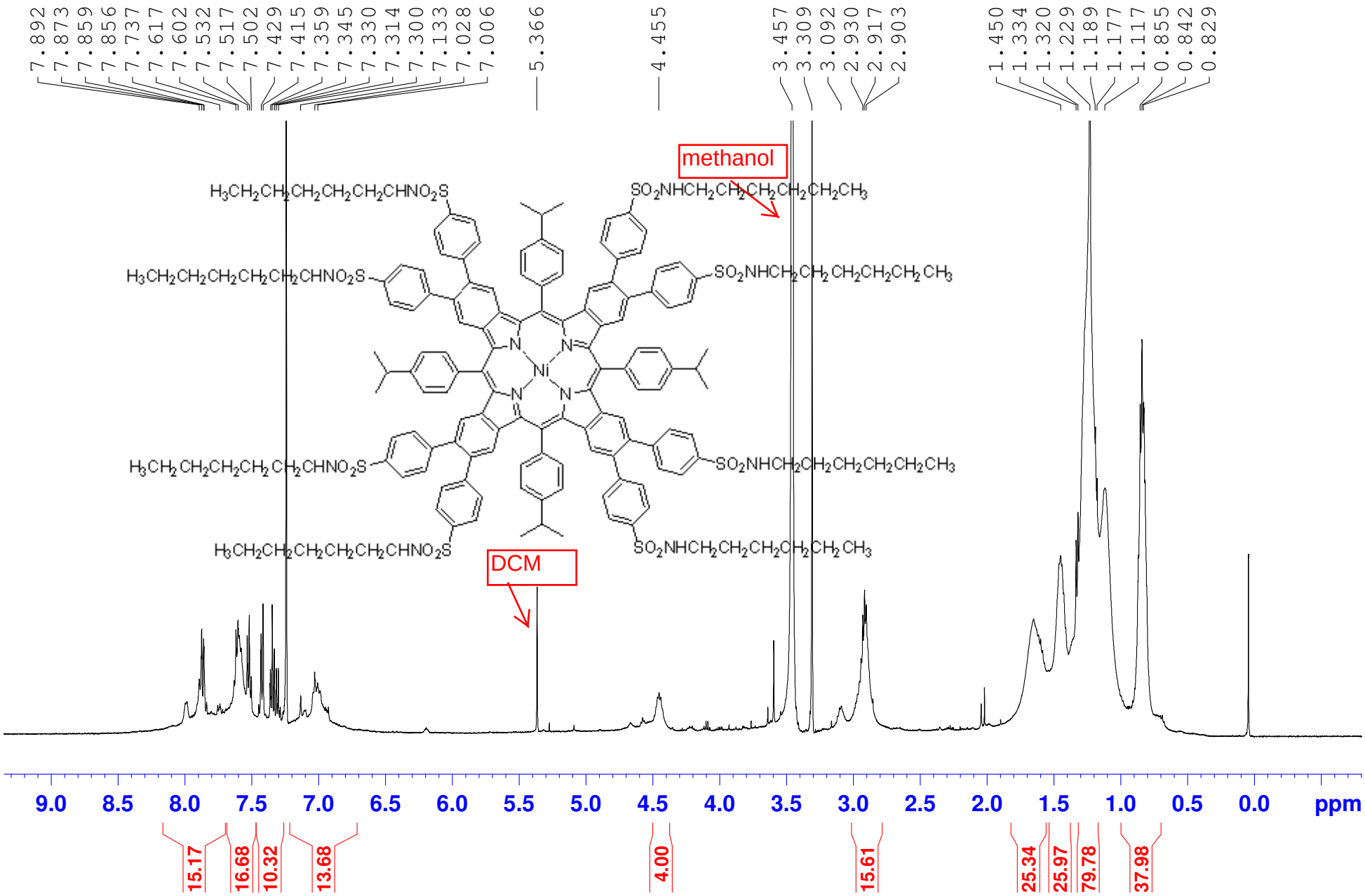
6

10
9
8
7
6
5
4
3
2
1
ppm

in DMSO

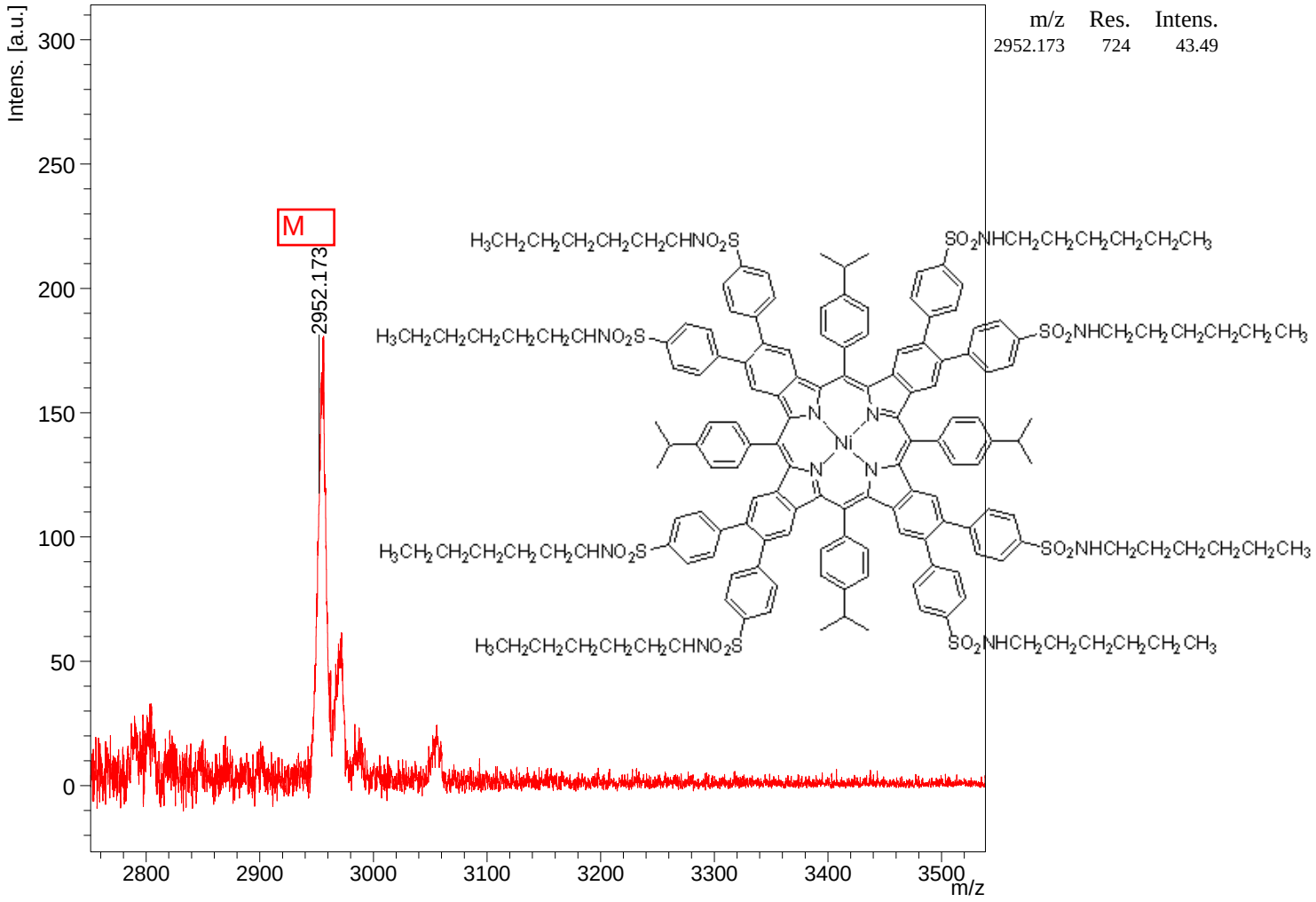

7.927
7.894
7.877
7.690
7.674
7.407
7.391
6.670
6.653
3.705
3.148
2.869
2.486
1.207
HO3S
SO3H
N
Ni
6
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

in CDCl3


7.892
7.873
7.859
7.856
7.737
7.617
7.602
7.532
7.517
7.502
7.429
7.415
7.359
7.345
7.330
7.314
7.300
7.133
7.028
7.006
5.366
4.455
3.457
3.309
3.092
2.930
2.917
2.903
1.450
1.334
1.320
1.229
1.189
1.177
1.117
0.855
0.842
0.829
methanol
DCM
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
ppm
15.17
16.68
10.32
13.68
4.00
15.61
25.34
25.97
79.78
37.98

Comment 1

Comment 2



VII. X-ray crystal structure of compound 4a

Crystal of compound **4a** suitable for X-ray diffraction analysis was obtained by slow evaporation from $CHCl_3$/pyridine in a ratio of 1:30. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 865552). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. Crystal data for **4a**:

Bond precision: C-C = 0.0065 A Wavelength=1.54178

Cell: a=12.6976(4) b=21.9195(5) c=22.0585(5)
alpha=97.683(2) beta=101.995(2) gamma=96.078(2)
Temperature: 100 K

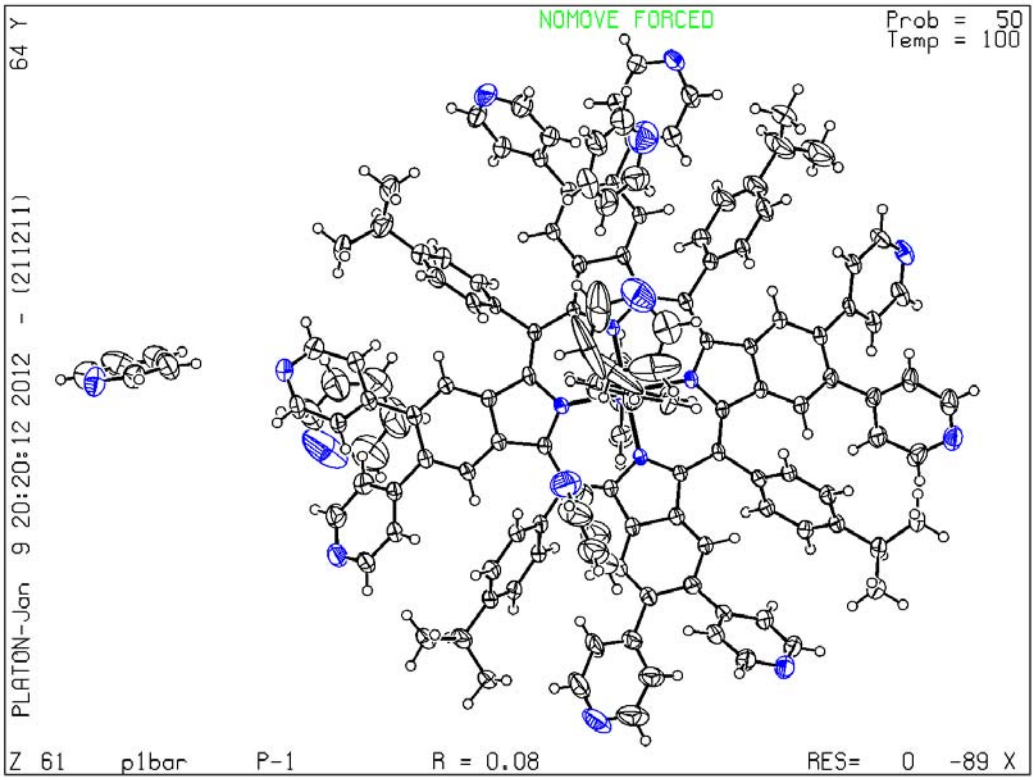
	Calculated	Reported
Volume	5894.6(3)	5894.6(3)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C122 H94 N14 Ni, 5(C5 H5 N)	?
Sum formula	C147 H119 N19 Ni	C147 H119 N19 Ni
Mr	2210.31	2210.32
Dx,g cm-3	1.245	1.245
Z	2	2
Mu (mm-1)	0.724	0.724
F000	2324.0	2324.0
F000'	2324.02	
h,k,lmax	14,24,25	14,24,25
Nref	18025	17351
Tmin,Tmax	0.893,0.910	0.818,0.912
Tmin'	0.811	

Correction method= MULTI-SCAN

Data completeness= 0.963 Theta(max)= 61.000

R(reflections)= 0.0785(12877) wR2(reflections)= 0.2717(17351)

S = 1.122 Npar= 1512



NSD data for **4a**:

Normal-Coordinate Structure Decomposition (NSD) Analysis of **4a**

Summary of the NSD (in Å):

basis	Dip	dip	B2g (m-str)	B1g (n-str)	Eu(x) (trn)	Eu(y) (trn)	A1g (bre)	A2g (rot)
min.	0.0936	0.0345	-0.0304	0.0152	-0.0136	-0.0173	0.0841	0.0062
ext.	0.1363	0.0271	-0.0302	0.0150	-0.0132	-0.0171	0.0915	0.0048
			-0.0122	-0.0116	0.0152	0.0102	-0.0592	-0.0749
			0.0121	-0.0050	0.0019	0.0000	0.1428	-0.0037
			0.0043	-0.0036	0.0103	0.0086	0.0570	-0.0012
			0.0033	0.0110	0.0074	0.0032	0.0146	-0.0182
			0.0010	0.0146	-0.0072	0.0047	-0.0173	
					0.0014	-0.0018		
					0.0060	0.0008		
					-0.0014	-0.0010		
					-0.0052	0.0000		
					-0.0016	-0.0057		
comp.	0.2092	0.0000	0.0354	0.0272	0.0266	0.0233	0.1859	0.0772
basis	Doop	doop	B2u (*sad*)	B1u (*ruf*)	A2u (*dom*)	Eg(x) (*wav*)	Eg(y) (*wav*)	A1u (*pro*)
min.	2.0650	0.0278	-2.0109	0.4647	-0.0214	-0.0452	0.0072	-0.0449
ext.	2.0713	0.0051	-2.0079	0.4647	-0.0205	-0.0463	0.0075	-0.0449
			0.1542	-0.0346	0.0219	-0.0225	0.0039	0.0079
			0.0017	0.0041	-0.0012	-0.0274	-0.0048	
						0.0078	-0.0029	
						0.0030	0.0101	
comp.	2.0715	0.0000	2.0168	0.4660	0.0306	0.0579	0.0142	0.0456

VIII. DFT calculations: Gaussian 03 (Rev. D.02) calculations were carried out on Miami University's Redhawk computer cluster. Following geometry optimizations, vibrational frequency analysis was used to ensure that all stationary points were energy minima. Geometry optimization and electronic structure calculations of the porphyrins were performed by using the B3LYP functional and 6-31G(d,p) basis set. Molecular orbitals were visualized using Molekel 5.4.0. [Ref: Ugo Varetto, Molekel 5.4.0.8; Swiss National Supercomputing Centre: Manno (Switzerland)]

Density functional calculations (B3LYP/6-31G(d,p)) were conducted for **4a-e**. Similar to the crystal structure of **4a**, the calculated structure of **4a** also adopts a saddle conformation. All the other tetrabenzoporphyrins **4b**-**4c** assume a similar conformation (**Fig.1**).

The electronic absorption of porphyrins including both Soret band and Q bands arises from π-π* transitions. The frontier orbitals responsible for the transitions in the parent porphin are two π orbitals (a_{1u} and a_{2u}) and two degenerate π* orbitals (eg_x and eg_y) in the Gouterman four-orbital model. (Ref: A. Ceulemans, W. Oldenhof, C. Gorllerwalrand and L. G. Vanquickenborne, *Journal of the American Chemical Society* **1986**, *108*, 1155-1163; Gouterman, M. ***J. Chem.*** *Phys.* **1959,** *30*, 1139.) **Fig. 2** illustrates the calculated HOMOs and LUMOs for compounds **4a**-**4d**, and protonated **4a**. It is interesting to note that, while all the HOMOs and LUMOs of **4a**-**4d** do not clearly involve the participation of the pyridyl substitutes on the fused benzene rings, the HOMOs and LUMOs of protonated **4a** heavily involve those substitutes.

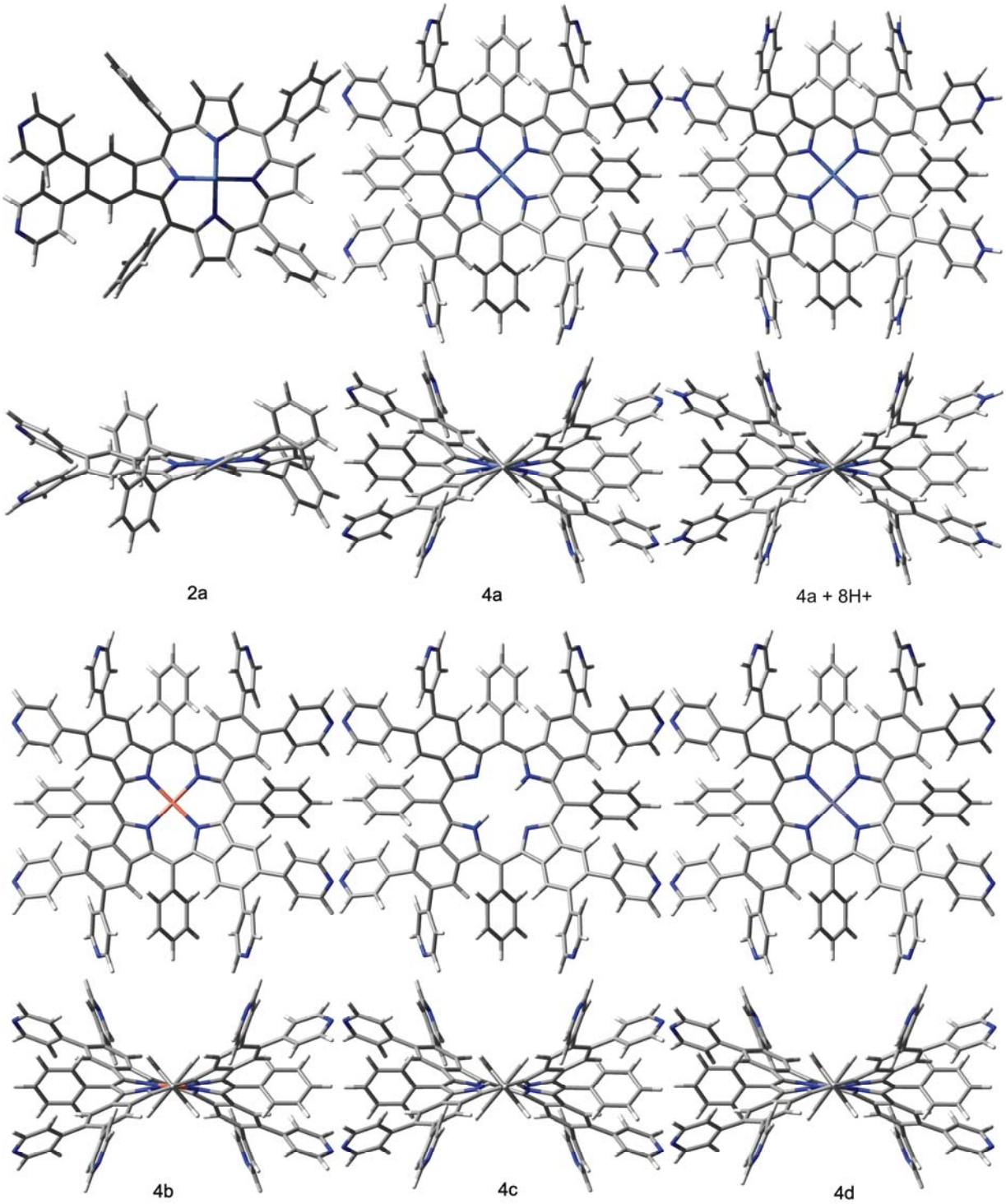


Fig. 1 Optimized molecular structure of **4a**-**4d**, protonated **4a** and **2a**.

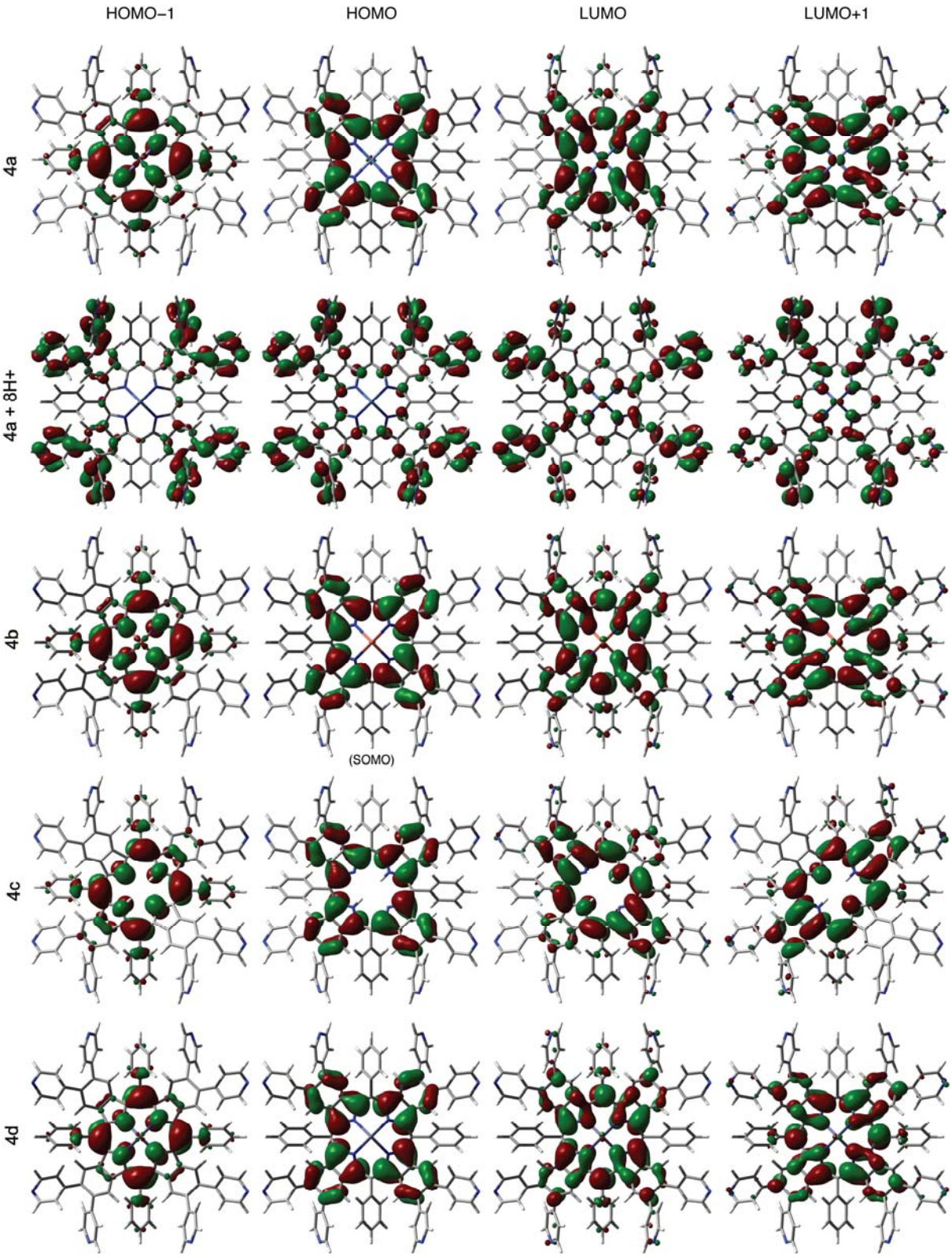
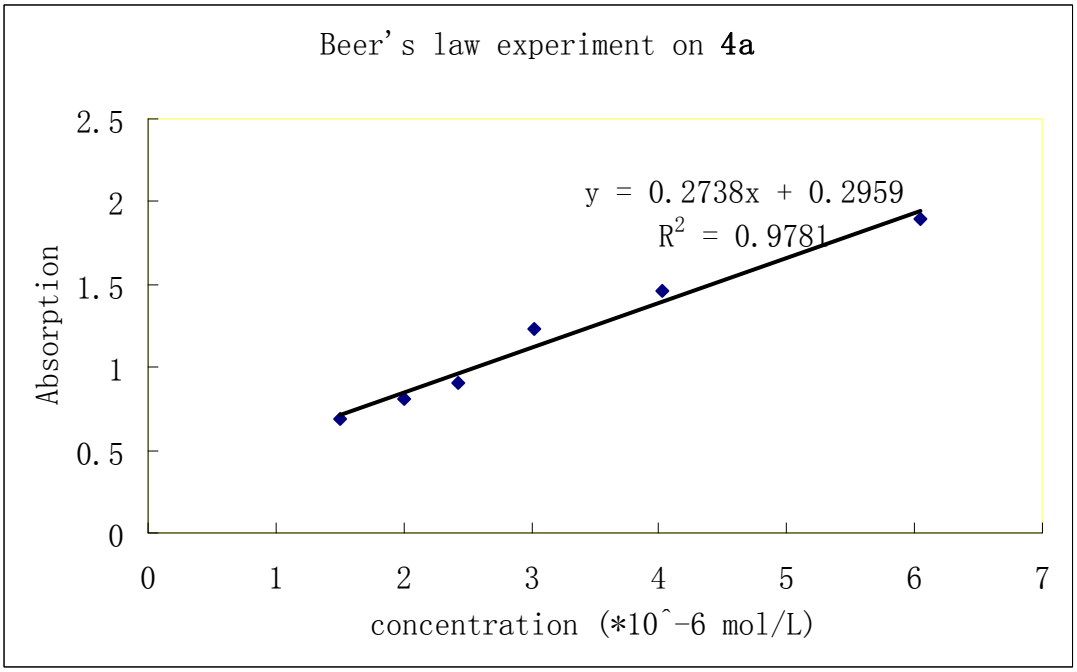


Fig.2 The calculated HOMOs and LUMOs of **4a**-**4d** and protonated **4a**

IX. Beer's law experiment and selected UV-vis spectra

Beer's law experiment:

Compound **4a** was chosen to perform the Beer's law experiment. 1mg of **4a** was dissolved in 10 mL of DCM. 0.1 mL of this solution was dissolved in 1 mL, 1.5 mL, 2 mL, 2.5 mL, 3 mL and 4 mL respectively. The absorption was measured for these solutions using a UV-vis spectrophotometer. Graph **1** displays the absorption vs. the concentration. The trendline equation is y = 0.2738x + 0.2959 with an R^2 value equal to 0.9781. So the porphyrin is monomeric.

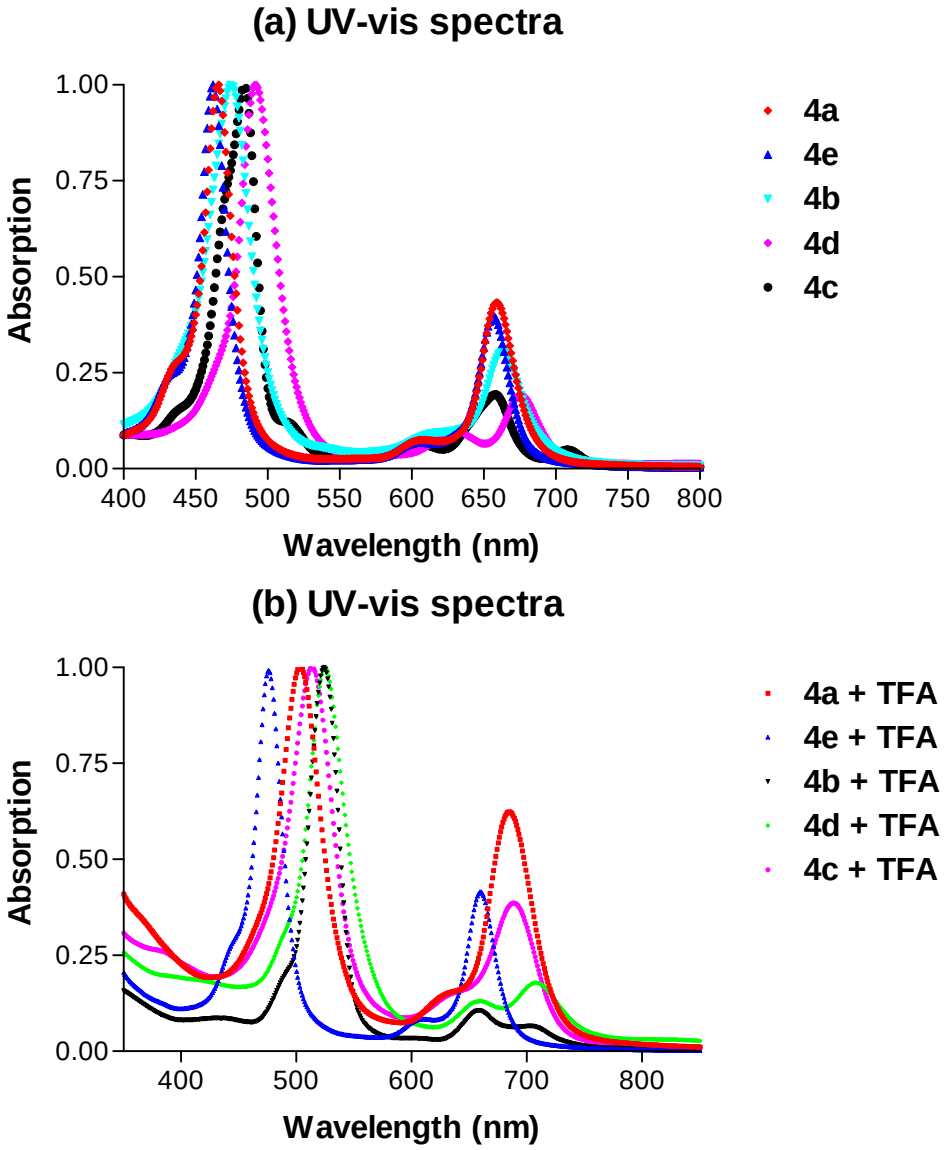


Graph **1**. Beer's law experiment on **4a**.

Selected UV-vis spectra:

UV-Visible spectra were recorded on an Agilent 8453 UV-Visible spectrometer in CH_2Cl_2, calculated log ε numbers are displayed with each characterized compound. One drop of TFA was added into the cuvettes of **2a**, **4a-e** and **5**, after testing the UV-vis spectra in DCM and UV-vis were collected again to get the protonated spectra. The absorption spectra of **4a-e** were shown in **Fig. 2**. (larger scale than in manuscript) Original and protonated absorption spectra of monobenzoporphyrin **2a** an *opp*-dibenzoporphyrin 5 are shown in **Fig. 3** and **Fig. 4**. Methylation was also done for **4c**. **4c** was dissolved in methanol and 100 equivalent of MeI was added and the

mixture was stirred for 1.5 days. The methylated compound can dissolve in methanol and water, but not chloroform. UV-vis spectra of both compounds are got from methanol and shown in **Fig. 5**. UV-vis spectra of **4a** and **6** were also shown in **Fig. 6**. for comparative purpose. **Fig. 7.** shows the comparative UV-vis of **4a** and amidation product of **6** in DCM.



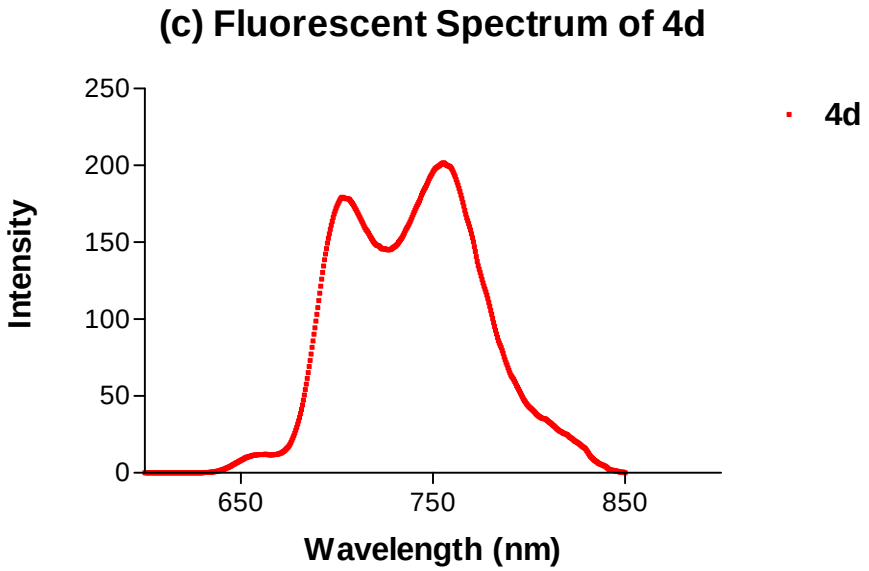


Fig. 2. (a) Normalized absorption spectra of porphyrins **4a-e** in CH_2Cl_2 solution; (b) normalized absorption spectra of porphyrins **4a-e** upon treatment with TFA in CH_2Cl_2 solution; (c) fluorescent spectrum of **4d** (excitation wavelength: 480 nm).

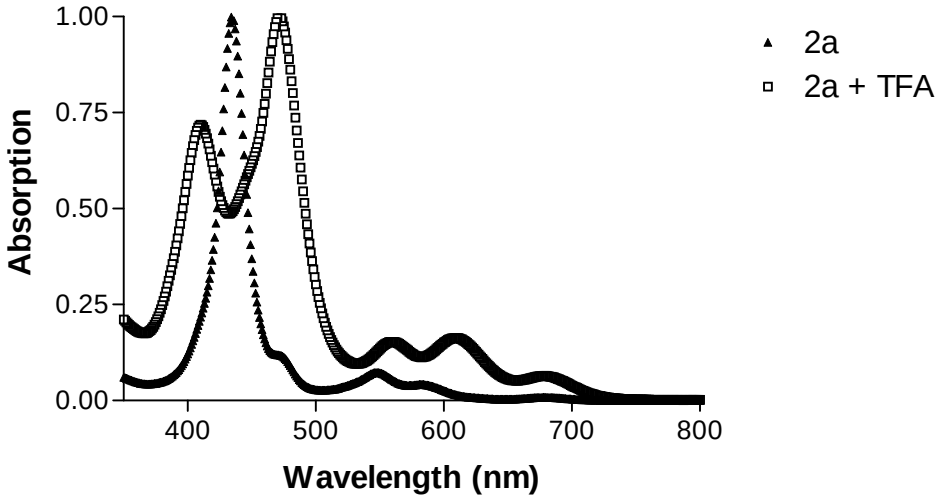


Fig. 3. Normalized absorption spectra of **2a** and protonated **2a** in DCM.

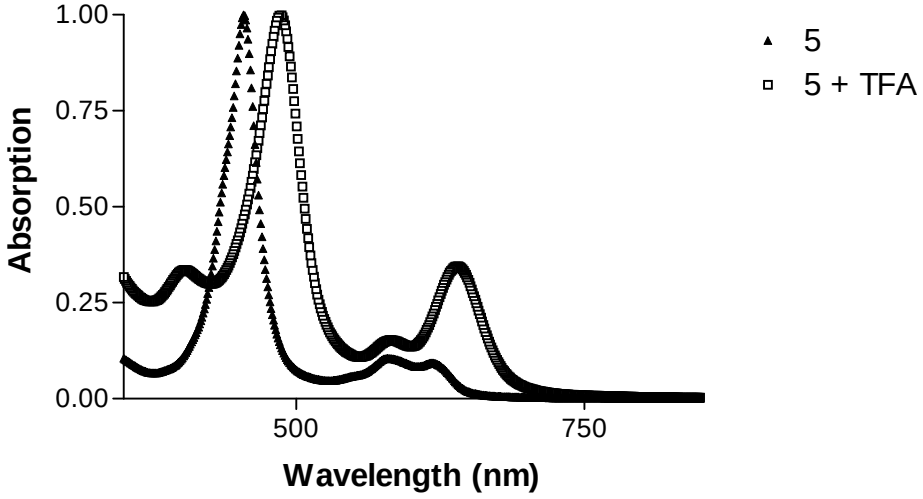


Fig. 4. Normalized absorption spectra of **5** and protonated **5** in DCM.

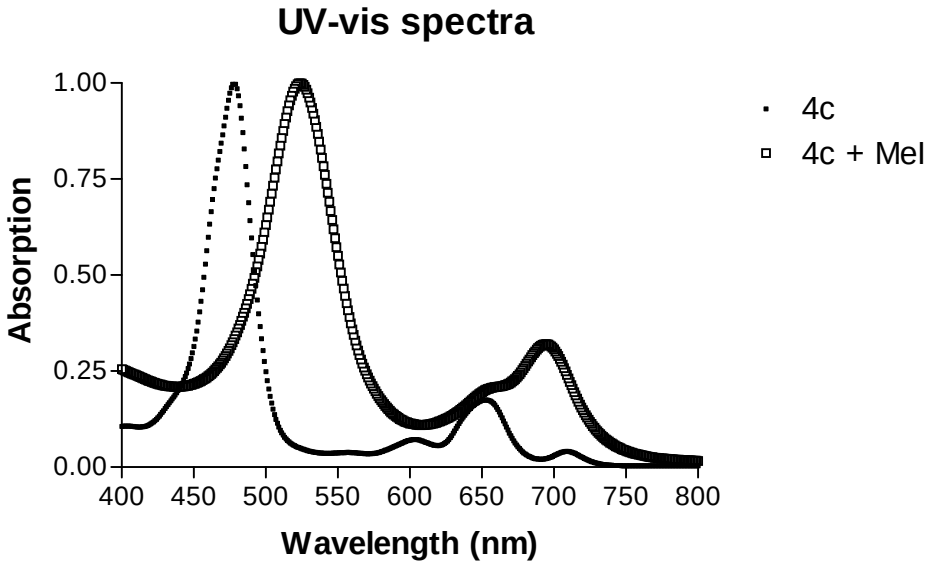


Fig. 5. Normalized absorption spectra of **4c** and methylated **4c** in methanol.

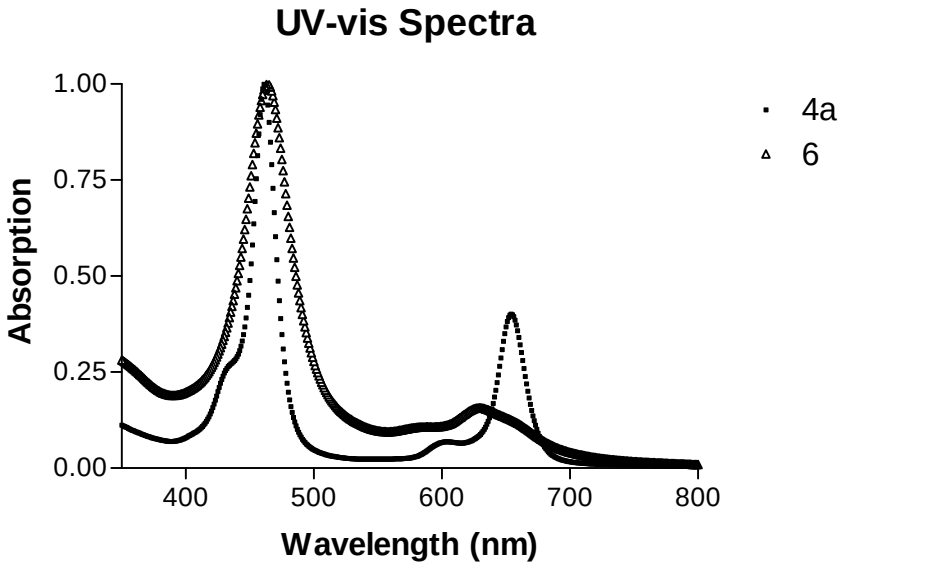


Fig. 6. Normalized UV-vis spectra for **4a** and **6** in methanol.

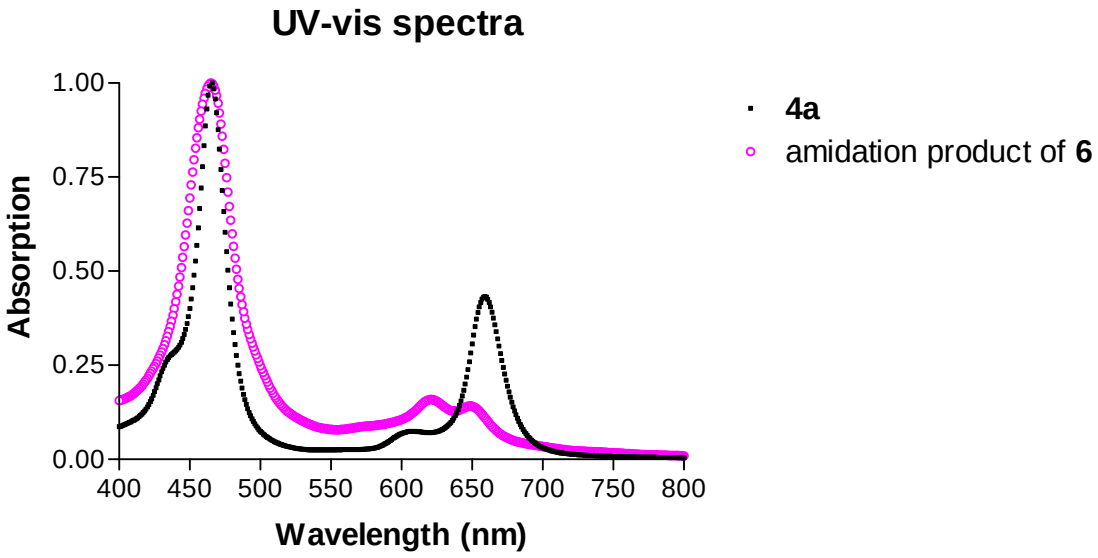


Fig. 7. Normalized UV-vis spectra of **4a** and amidation product of **6** in DCM.