Aggregation Induced Emission in One Easy Step: Pyridinium AIEgens and Counter Ion Effect

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General considerations

Column chromatography was performed using reversed phase C18-silica gel columns (RP18 25-40 μm) and direct phase silica gel columns.

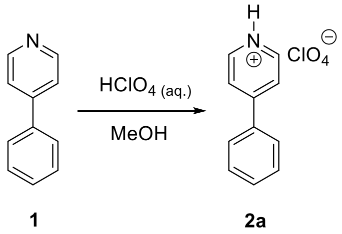
Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies: ^{1}H, 400 MHz; ^{13}C{^{1}H}, 100.6 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS (ESI-TOF)) were recorded on a mass spectrometer with a time-of-flight (TOF) mass analyzer using the ESI technique. Melting points are uncorrected.

Unless otherwise noted, all chemicals were used as received from commercial sources. Anhydrous THF, diethyl ether and CH_2Cl_2 were obtained by passing commercially available solvents through activated alumina columns.

The luminescence data was collected with Edinburgh Instruments *FS5* Spectrofluorometer. Photoluminescence quantum yields (PLQY) were measured using a standard complementary integrating sphere (the measurement module contains a 150 mm inner diameter integrating sphere for the measurement of fluorescence quantum yields by the absolute method and reflection measurements). Single-crystal X-ray diffraction analyses were performed on Rigaku *XtaLAB Synergy S, Dualflex* apparatus with HyPix6000 detector and CuK_α /MoK_α radiation type.

Experimental procedures for synthesis of luminophores

Synthesis of 2a



4-Phenylpyridin-1-ium perchlorate (2a). To a clear solution of 4-phenylpyridine (**1**, 0.30 g, 1.93 mmol, 1.00 equiv) in MeOH (10 mL) was added 60–62% aqueous solution of $HClO_4$ (0.65g, 2.00 equiv) and the resulting clear solution was stirred at ambient temperature for 10 minutes. Afterwards to the clear colorless solution was added H_2O (10 mL) and the resulting clear solution was partially evaporated under reduced pressure to approx. 5 mL volume whereupon a white precipitate was formed. The precipitate was filtered and washed with H_2O to afford the title compound **2a** as white crystals (0.41 g, 1.61 mmol, 83%).

Mp 144–146 °C (recrystallized from MeCN/Et_2O).

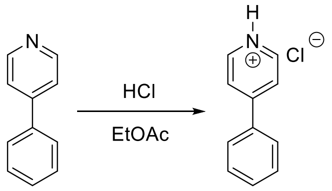
^1H NMR (400 MHz, CD_3OD, δ) 8.86-8.81 (m, 2H), 8.41-8.35 (m, 2H), 8.01-7.95 (m, 2H), 7.67-7.59 (m, 3H) ppm.

^{13}C NMR (100.6 MHz, CD_3OD, δ) 159.6, 142.8, 135.8, 133.2, 130.9, 129.2, 125.6 ppm.

HRMS (ESI-TOF) *m/z*: $[M]^+$ calc for $C_{11}H_{10}N$: 156.0813; Found: 156.0818.

IR (KBr, cm^{-1}) 3453, 3264, 2005, 1638.

Synthesis of 2b



1 2b

4-Phenylpyridin-1-ium chloride (2b). To a clear solution of 4-phenylpyridine (**1**, 0.30 g, 1.93 mmol, 1.00 equiv) in EtOAc (20 mL) was added HCl in dioxane (4M solution in dioxane, 0.97 mL, 3.86 mmol, 2.00 equiv). The formed white suspension was stirred for 5 minutes at ambient temperature, then heated under reflux for 5 minutes, cooled and concentrated to dryness under the reduced pressure. The white material was suspended in Et_2O (20 mL), sonified for 10 minutes, filtered and washed with Et_2O to give the title compound **2b** as white powder (0.36 g, 1.88 mmol, 97%).

Mp 73–75 °C (recrystallized from MeCN/Et_2O).

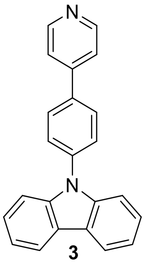
^1H NMR (400 MHz, CD_3OD, δ) 8.90-8.83 (m, 2H), 8.44-8.36 (m, 2H), 8.04-7.97 (m, 2H), 7.70-7.61 (m, 3H) ppm.

^{13}C NMR (100.6 MHz, CD_3OD, δ) 159.6, 142.9, 135.8, 133.3, 130.9, 129.2, 125.6 ppm.

HRMS (ESI-TOF) *m/z*: $[M]^+$ calc for $C_{11}H_{10}N$: 156.0813; Found: 156.0820.

IR (KBr, cm^{-1}) 3393, 2570, 2153, 1635.

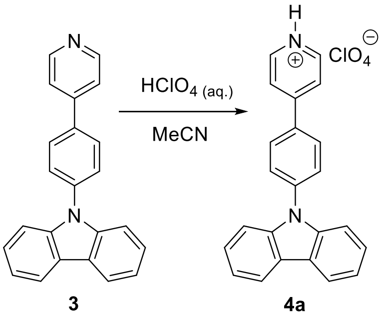
Compound 3


3

9-(4-(Pyridin-4-yl)phenyl)-9*H*-carbazole (3) was synthesized previously.[1] ^{1}H NMR spectrum was consistent with that of the previously reported product.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.76-8.72 (m, 2H), 8.20-8.14 (m, 2H), 7.90-7.85 (m, 2H), 7.74-7.69 (m, 2H), 7.62-7.59 (m, 2H), 7.50-7.41 (m, 4H), 7.35-7.30 (m, 2H) ppm.

Synthesis of 4a



4-(4-(9*H*-Carbazol-9-yl)phenyl)pyridin-1-ium perchlorate (4a). To a suspension of 9-(4-(pyridin-4-yl)phenyl)-9*H*-carbazole (**3**, 0.35 g, 1.09 mmol, 1.00 equiv) in MeCN (40 mL) was added an aqueous HClO$_4$ (60–62% solution in water, 0.36 g, 2.18 mmol, 2.00 equiv) whereupon a clear yellow solution was formed. Shortly, the solution become cloudy and the resulting suspension was heated under reflux for 2 min, followed by hot-filtration through a plug of cotton. The obtained clear solution was concentrated under reduced pressure to approx. 10 mL volume, whereupon crystalline material started to precipitate. The suspension was diluted with Et$_2$O (50 mL) and stirred for 30 minutes, then filtered and washed with Et$_2$O to give the title compound as yellow wool (**4a**, 0.45 g, 1.08 mmol, 99%). ^{1}H and ^{13}C NMR of this salt could not be obtained due to the dynamic equilibrium between the protonated and deprotonated forms in the solution (see Manuscript for further details). Solid state forms **4aA**, **4aB** and **4aC** were obtained as follows:

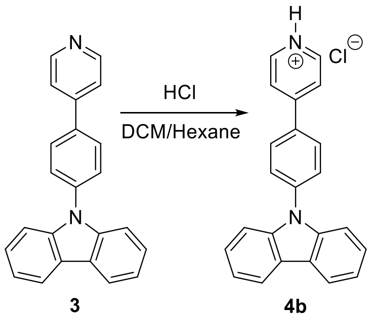
- **4aA** – the partially amorphous solid was obtained by evaporating a solution of **4a** in 10:1 MeCN:H_2O (22 mL total volume) under reduced pressure at 20 °C.
- **4aB** –crystals were obtained by initially dissolving the obtained yellow wool in refluxing MeCN. The hot solution was left to cool and evaporate slowly over time (cotton plug). The formed yellow translucent needles were filtered and washed with cold MeCN.
- **4aC** –crystals were obtained by Et_2O vapour diffusion into MeOH solution of **4a**. The resulting thin yellow rods were filtered and washed with Et_2O.

Mp 275–285 °C (decomposition) (recrystallized from MeCN/Et_2O).

Calculated for: $C_{23}H_{17}ClN_2O_4$: C, 65.64; H, 4.07; N, 6.66. Found: C, 65.65; H, 3.95; N, 6.61;

IR (KBr, cm^{-1}) 3243, 3151, 3090, 1600.

Synthesis of 4b



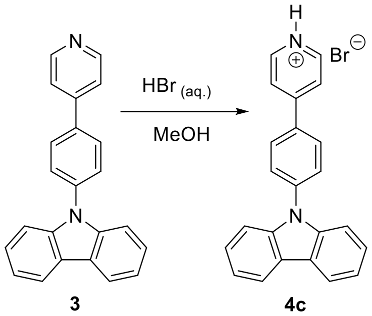
4-(4-(9*H*-Carbazol-9-yl)phenyl)pyridin-1-ium chloride (4b). To a clear solution of 9-(4-(pyridin-4-yl)phenyl)-9*H*-carbazole (**3**, 0.20 g, 0.62 mmol, 1.00 equiv) in 1:2 DCM:Hexane (30 mL) was added HCl in dioxane (4M solution in dioxane, 0.31 mL, 1.25 mmol, 2.00 equiv) whereupon precipitation of a yellow solid was observed. More hexane (20 mL) was added to the formed yellow suspension, and after stirring at ambient temperature for 1h, the yellow suspension was filtered and washed with hexane to give the title product as a yellow powder (**4b**, 0.21 g, 0.59 mmol, 95%).^{1}H and ^{13}C NMR of this salt could not be obtained due to the dynamic equilibrium between the protonated and deprotonated forms in solution (see Manuscript for further details).

Mp 250–260 °C (decomposition) (recrystallized from $CHCl_3$/Et_2O).

Calculated for: $C_{23}H_{17}ClN_2O_4$: C, 77.41; H, 4.80; N, 7.85. Found: C, 77.05; H, 4.73; N, 7.79;

IR (KBr, cm^{-1}) 3430, 3040, 2409, 1601.

Synthesis of 4c



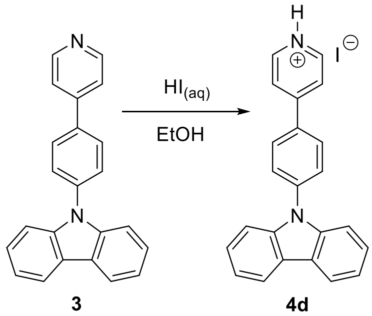
4-(4-(9*H*-Carbazol-9-yl)phenyl)pyridin-1-ium bromide (4c). To a suspension of 9-(4-(pyridin-4-yl)phenyl)-9*H*-carbazole (**3**, 0.20 g, 0.62 mmol, 1.00 equiv) in MeOH (20 mL) was added aqueous HBr (48% solution in water, 0.21 g, 1.25 mmol, 2.00 equiv) whereupon precipitation of a yellow solid was observed. The suspension was stirred at ambient temperature for 1h and then concentrated under reduced pressure. The obtained yellow solid was redissolved in refluxing MeCN (20 mL) and the solution was cooled to room temperature. Et_2O (80 mL) was added, whereupon a yellow precipitate was formed, which was filtered and washed with Et_2O to give the title product as a yellow powder (**4c**, 0.23 g, 0.57 mmol, 92%). ^{1}H and ^{13}C NMR of this salt could not be obtained due to the dynamic equilibrium between the protonated and deprotonated forms in solution (see Manuscript for further details).

Mp 265–275 ^{o}C (decomposition) (recrystallized from MeCN/Et_2O).

Calculated for: $C_{23}H_{17}ClN_2O_4$: C, 68.84; H, 4.27; N, 6.98. Found: C, 68.49; H, 4.14; N, 6.90;

IR (KBr, cm^{-1}) 3452, 3038, 2585, 1600.

Synthesis of 4d



3 **4d**

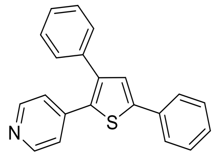
4-(4-(9*H*-Carbazol-9-yl)phenyl)pyridin-1-ium iodide (**4d**). To a suspension of 9-(4-(pyridin-4-yl)phenyl)-9*H*-carbazole (**3**, 0.20 g, 0.62 mmol, 1.00 equiv) in EtOH (15 mL) was added aqueous HI (57% solution in water, 0.28g, 2.00 equiv). The resulting dark suspension was stirred at ambient temperature for 1h, filtered and washed with EtOH and Et_2O to give the title product as dark brown powder (0.17 g, 0.38 mmol, 61%). ^{1}H and ^{13}C NMR of this salt could not be obtained due to the dynamic equilibrium between the protonated and deprotonated forms in solution (see Manuscript for further details).

Mp 226–229 °C (decomposition) (recrystallized from EtOH/Et_2O).

Calculated for: $C_{23}H_{17}IN_2$: C, 61.62; H, 3.82; N, 6.25. Found: C, 61.68; H, 3.59; N, 6.32;

IR (KBr, cm^{-1}) 3420, 3201, 3045, 1598.

Compound 5



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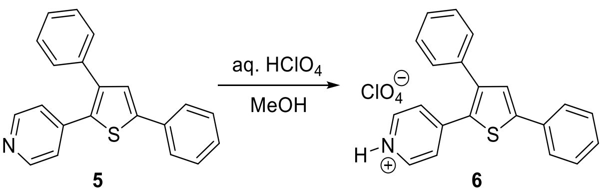
4-(3,5-Diphenylthiophen-2-yl)pyridine (**5**) was synthesized previously.[2] ^{1}H NMR spectrum was consistent with that of the previously reported product.

^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.52-8.46 (m, 2H), 7.79-7.74 (m, 2H), 7.68 (s, 1H), 7.50-7.44 (m, 2H), 7.44-7.32 (m, 6H), 7.25-7.21 (m, 2H) ppm.

Synthesis of 6



4-(3,5-Diphenylthiophen-2-yl)pyridin-1-ium perchlorate (**6**). To a colorless solution of 4-(3,5-diphenylthiophen-2-yl)pyridine (**5**, 0.10 g, 0.32 mmol, 1.00 equiv) in MeCN (15 mL) was added an aqueous $HClO_4$ (60–62% solution in water, 0.10 g, 0.64 mmol, 2.00 equiv) whereupon a yellow solution was formed. After stirring at ambient temperature for 30 minutes, the solution was concentrated to approximately 5 mL volume and diluted with water (20 mL). The formed yellow precipitate filtered and washed with water. The obtained yellow solid material was recrystallized from MeOH, then filtered and washed with Et_2O to give the title product as yellow needles (**6**, 0.04 g, 0.10 mmol, 32%).

^{1}H and ^{13}C NMR of this salt could not be obtained due to the dynamic equilibrium between the protonated and deprotonated forms in solution.

X-Ray suitable crystals were obtained by Et_2O vapor diffusion into MeCN solution of **6**.

Mp 200–202 ^{o}C (recrystallized from MeOH).

Calculated for: $C_{21}H_{16}ClNO_4S$: C, 60.94; H, 3.90; N, 3.38. Found: C, 60.91; H, 3.79; N, 3.36;

IR (KBr, cm^{-1}) 3099, 2506, 2094, 1631.

References:

1) Leduskrasts, K.; Kinens, A.; Suna E. *Chem. Commun.* **2019**, *55*, 12663.

2) Karpaviciene, I.; Jonusis, M.; Leduskrasts, K.; Misiunaite, I.; Suna, E.; Cikotiene, I. *Dyes and Pigments* **2019**, *170*, 107646.

Luminescence spectra

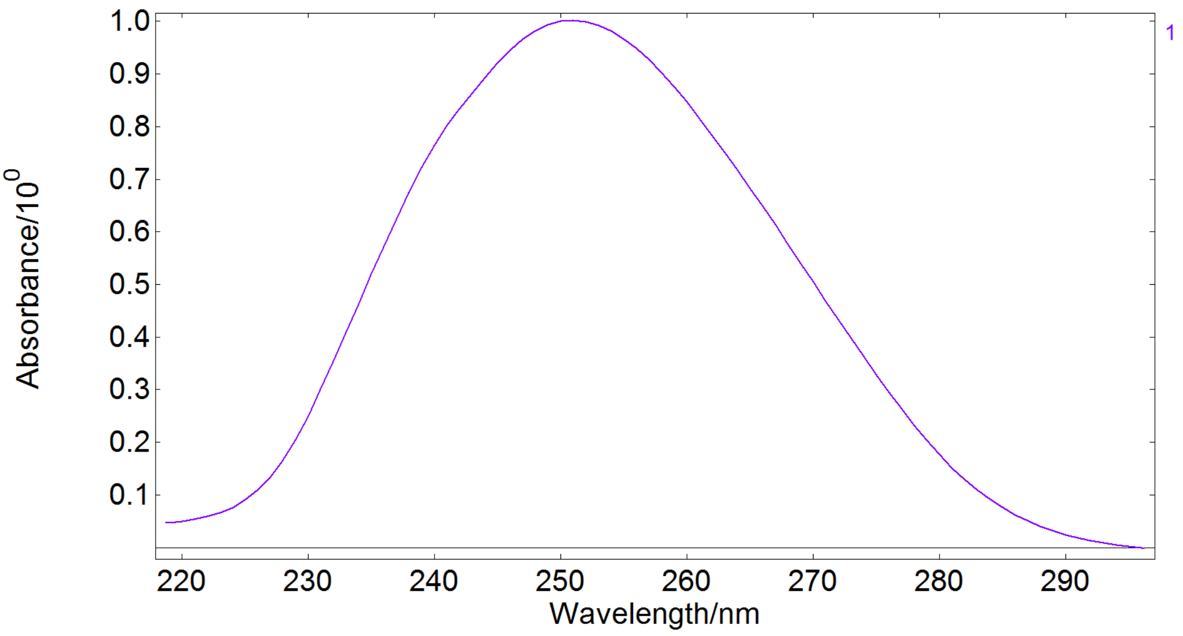


Fig. S1. Absorption of **1** in MeCN solution (at 10^{-5} mol/L)

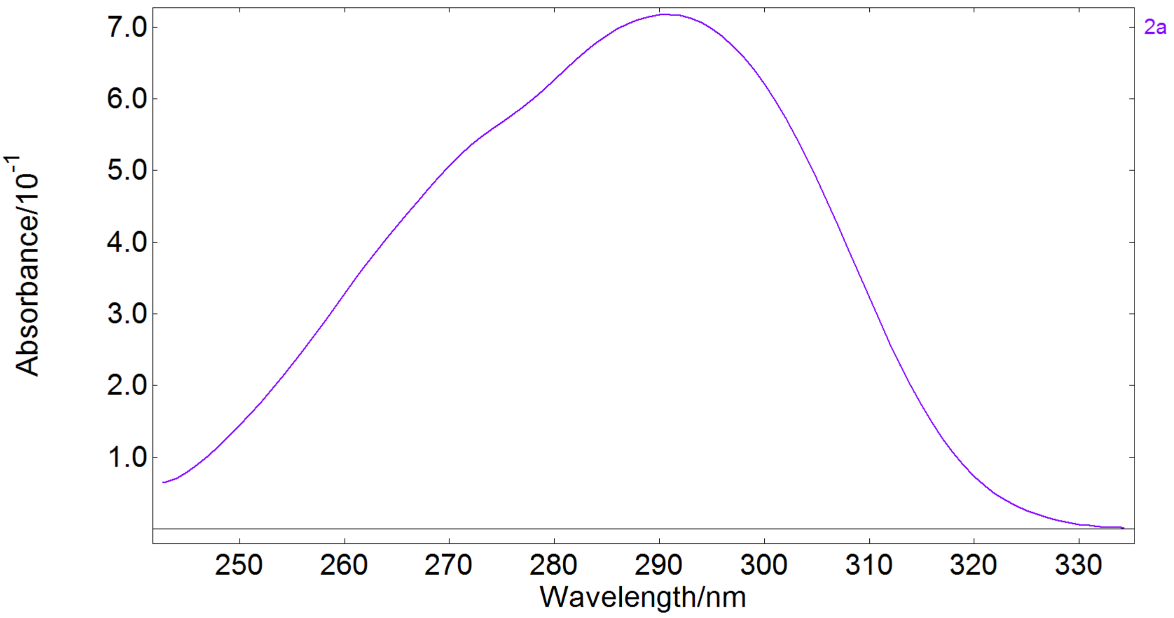


Fig. S2. Absorption of **2a** in MeCN solution (at 10^{-5} mol/L)

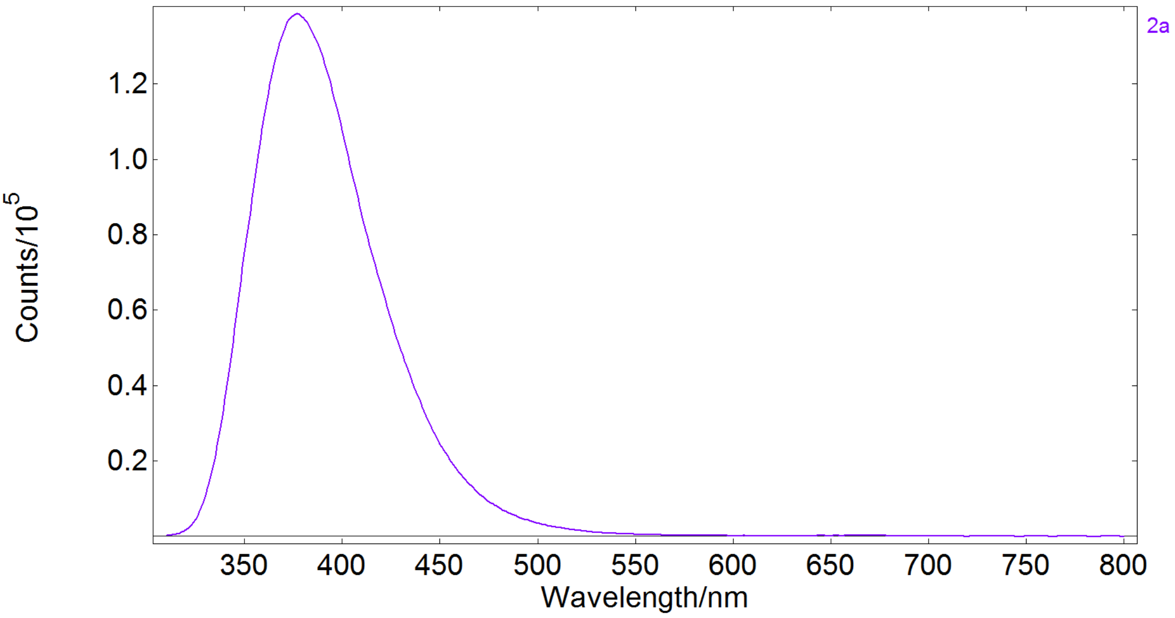


Fig. S3. Emission of **2a** in MeCN solution (at 10^{-5} mol/L)

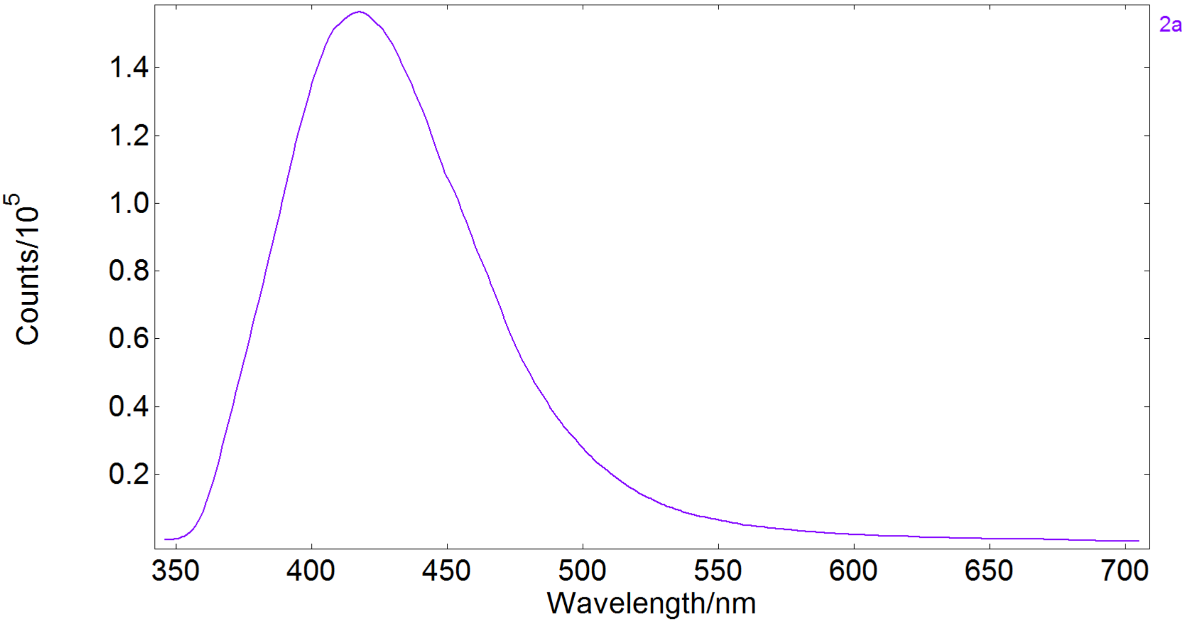


Fig. S4. Emission of **2a** in the solid state

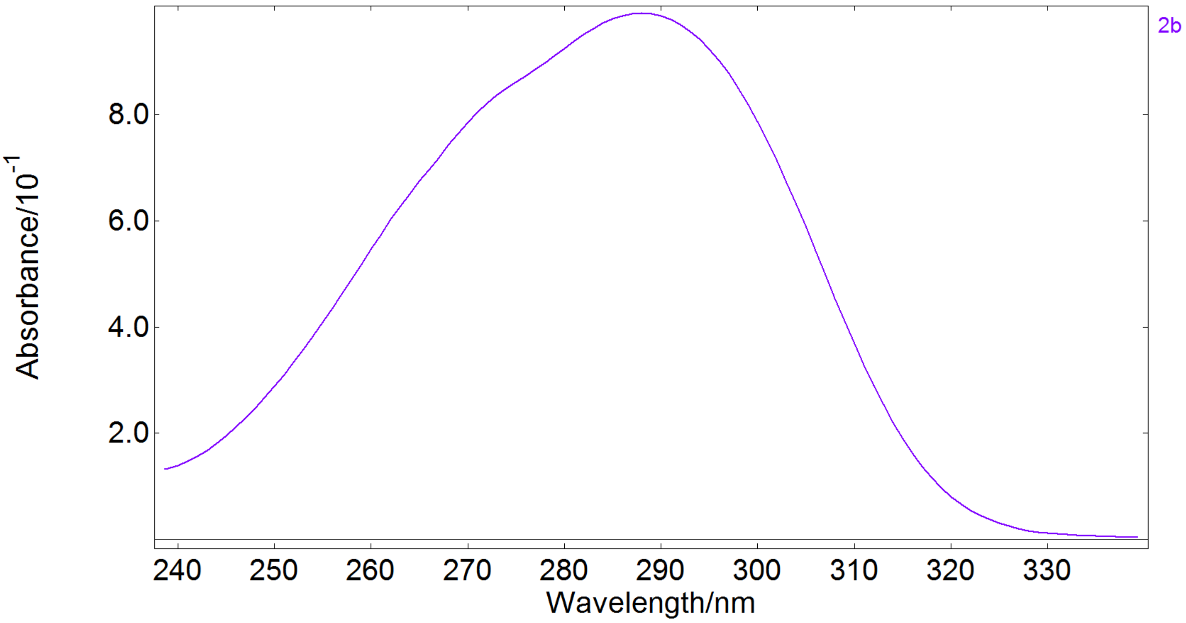


Fig. S5. Absorption of **2b** in MeCN solution (at 10^{-5} mol/L)

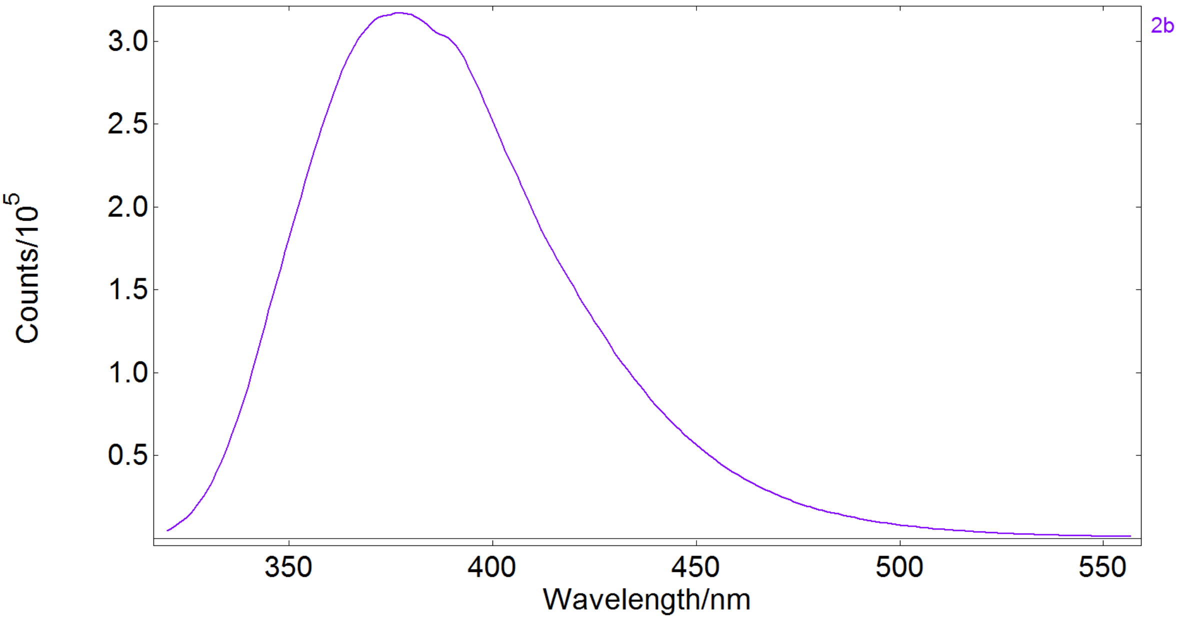


Fig. S6. Emission of **2b** in MeCN solution (at 10^{-5} mol/L)

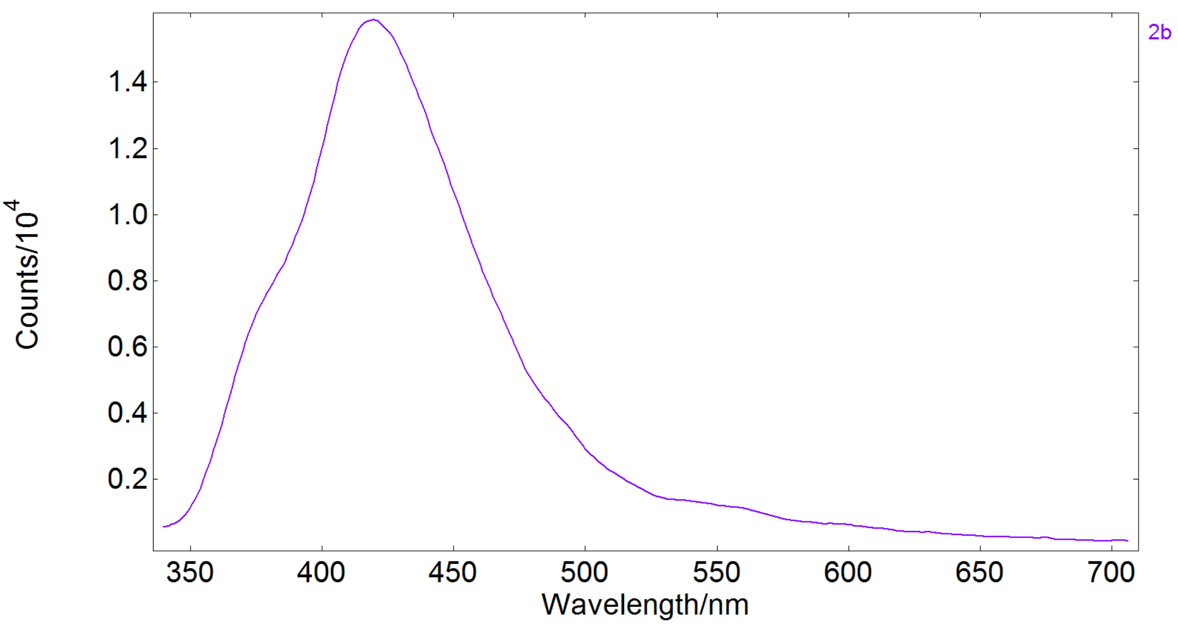


Fig. S7. Emission of **2b** in the solid state

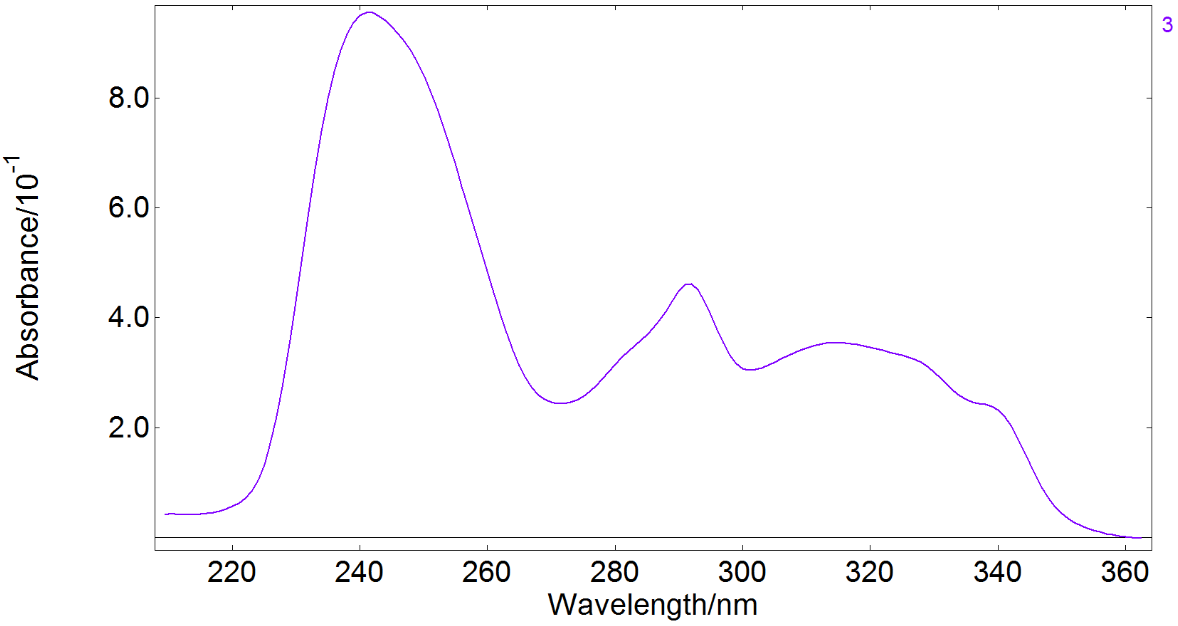


Fig. S8. Absorption of **3** in MeCN solution (at 10^{-5} mol/L)

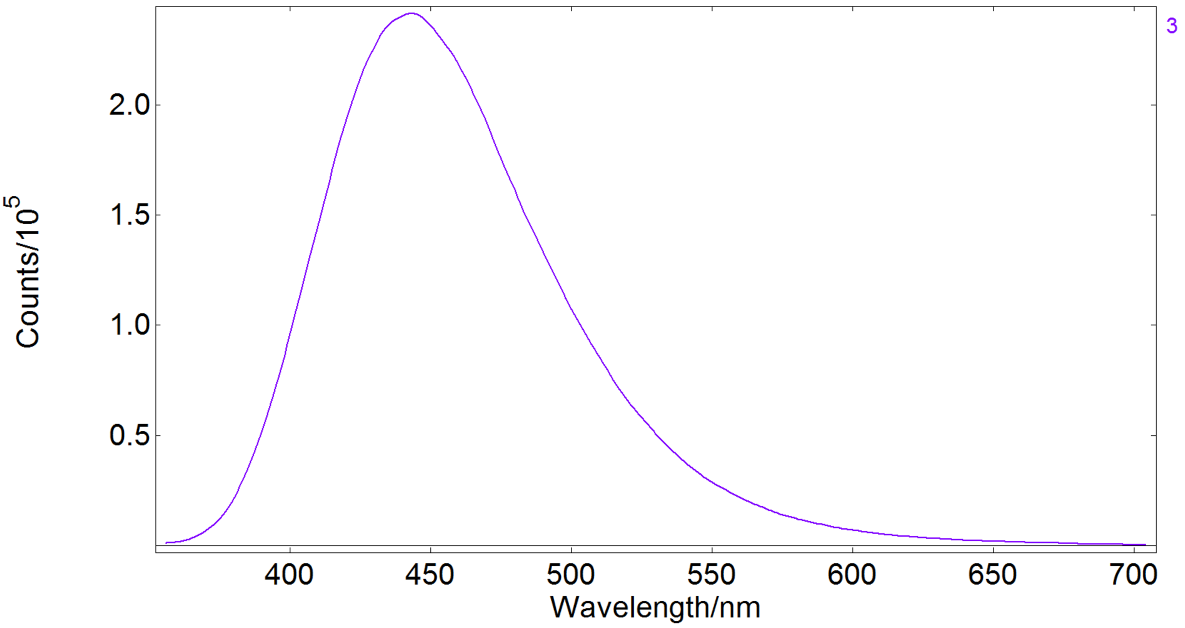


Fig. S9. Emission of **3** in MeCN solution (at 10^{-5} mol/L)

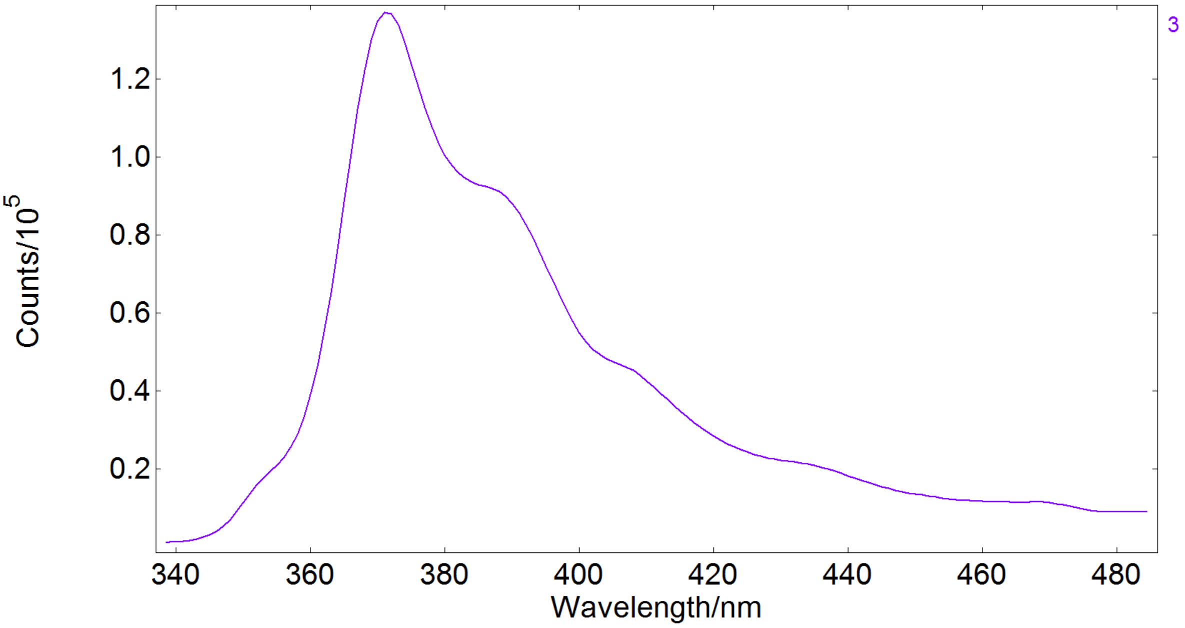


Fig. S10. Emission of **3** in the solid state

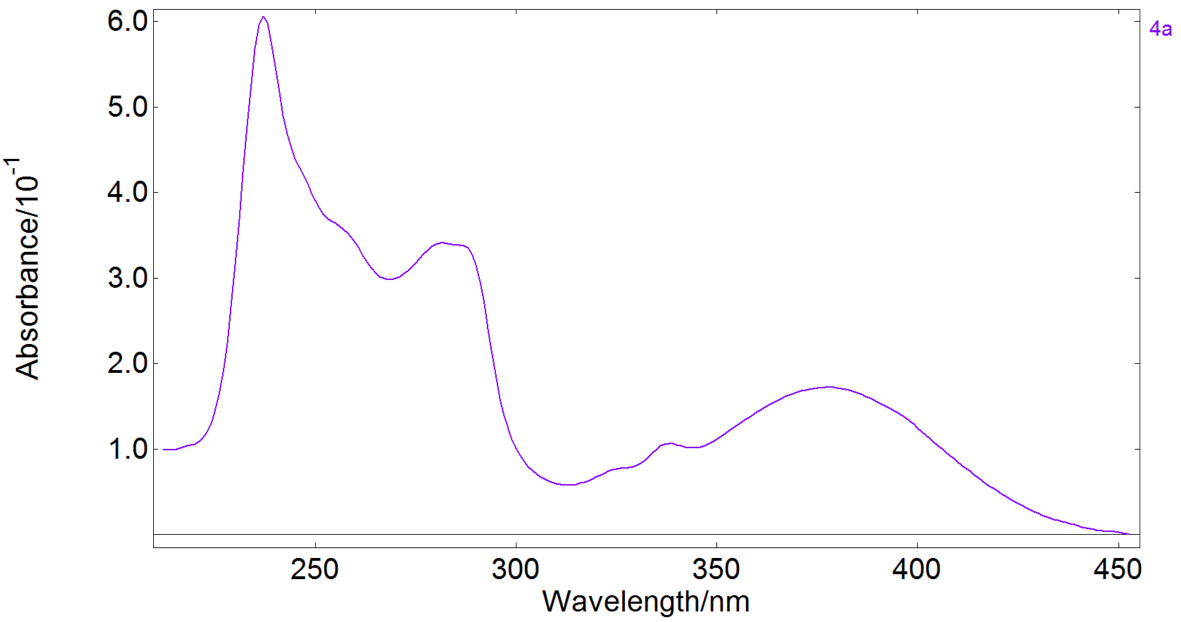


Fig. S11. Absorption of **4a** in MeCN solution (at 10^{-5} mol/L)

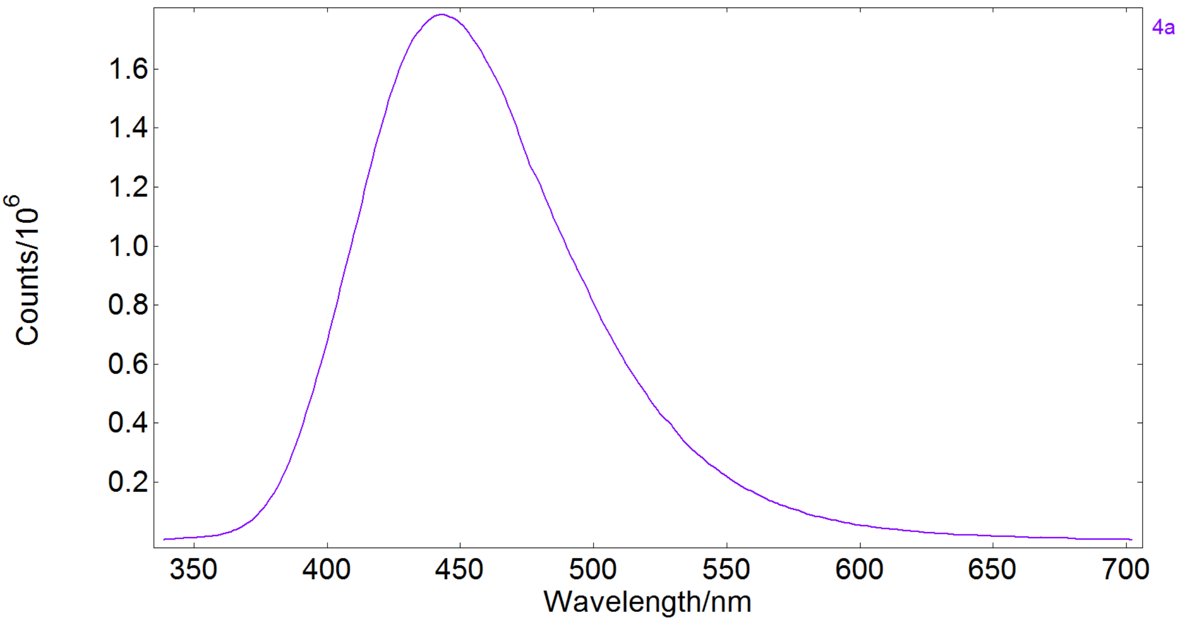


Fig. S12. Emission of **4a** in MeCN solution (at 10^{-5} mol/L)

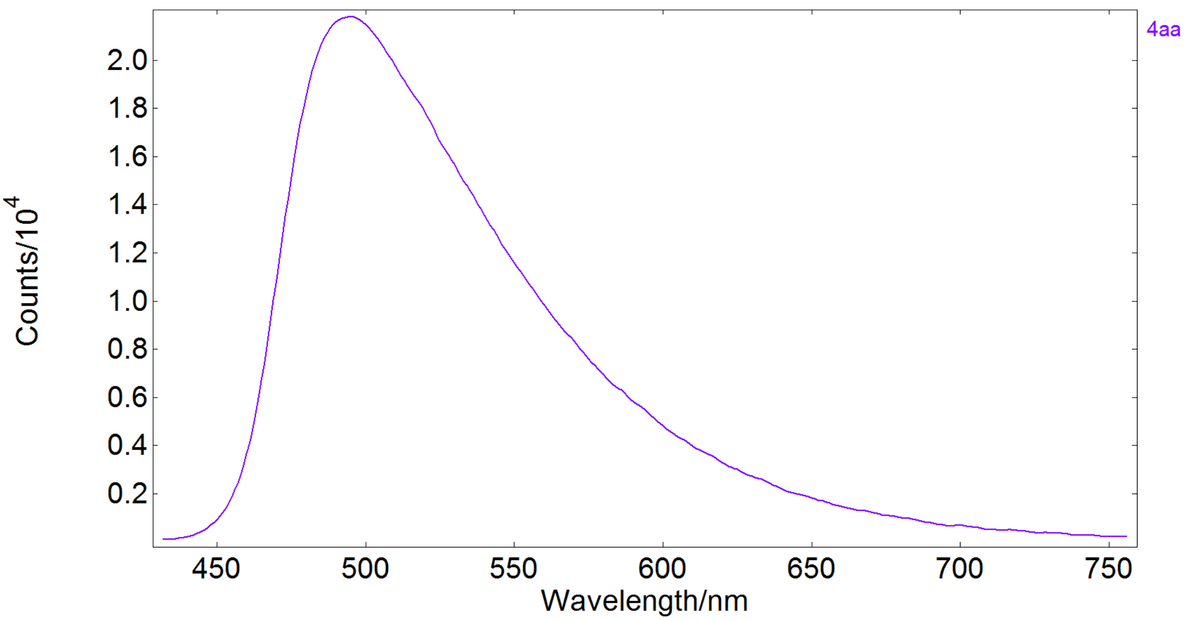


Fig. S13. Emission of **4aA** in the solid state

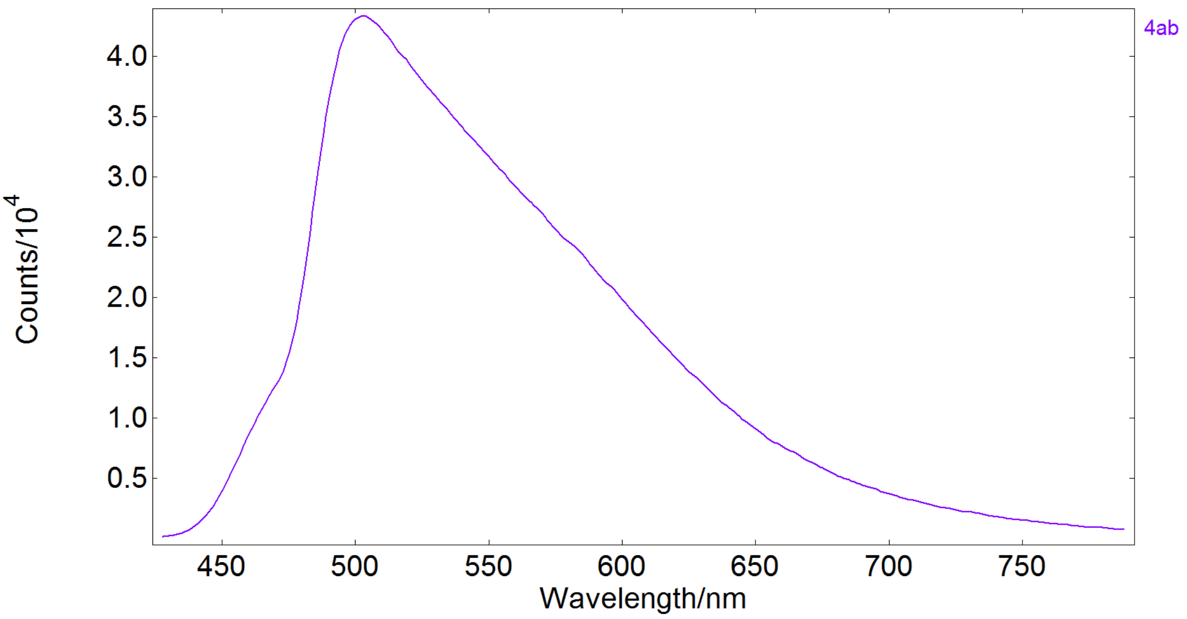


Fig. S14. Emission of **4aB** in the solid state

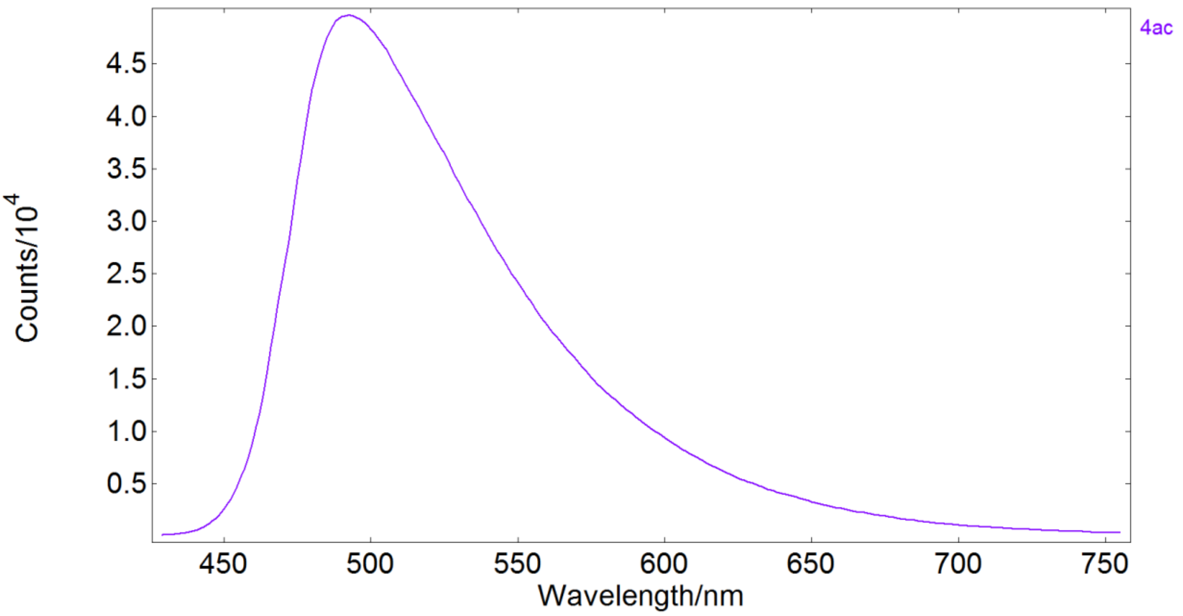


Fig. S15. Emission of **4aC** in the solid state

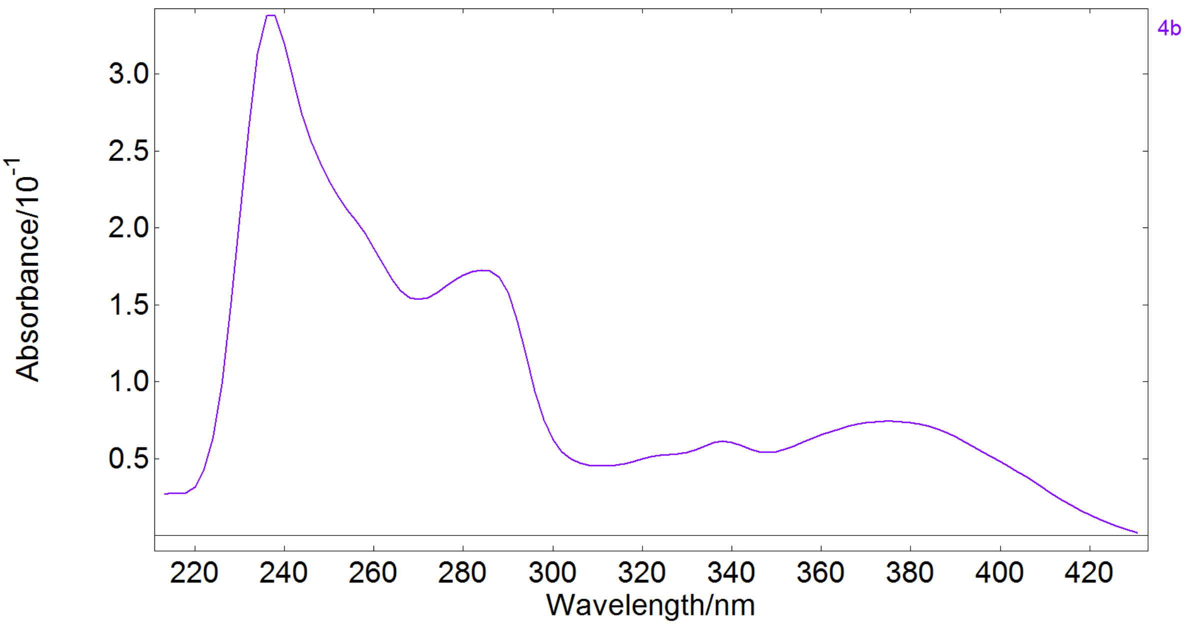


Fig. S16. Absorption of **4b** in MeCN solution (at 10^{-5} mol/L)

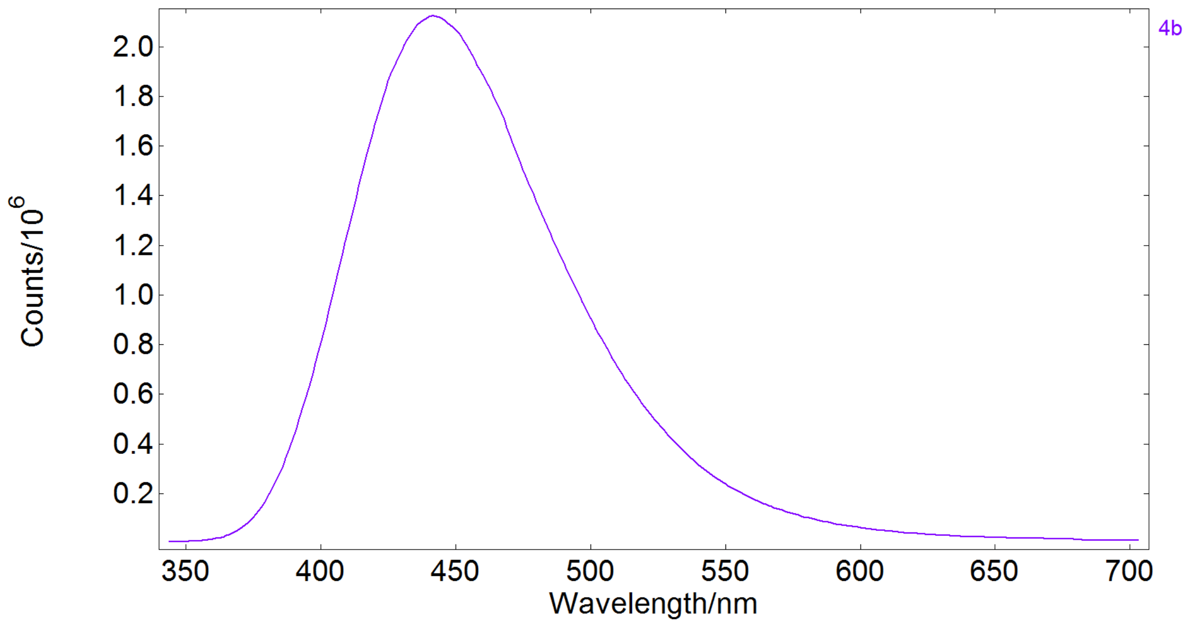


Fig. S17. Emission of **4b** in MeCN solution (at 10^{-5} mol/L)

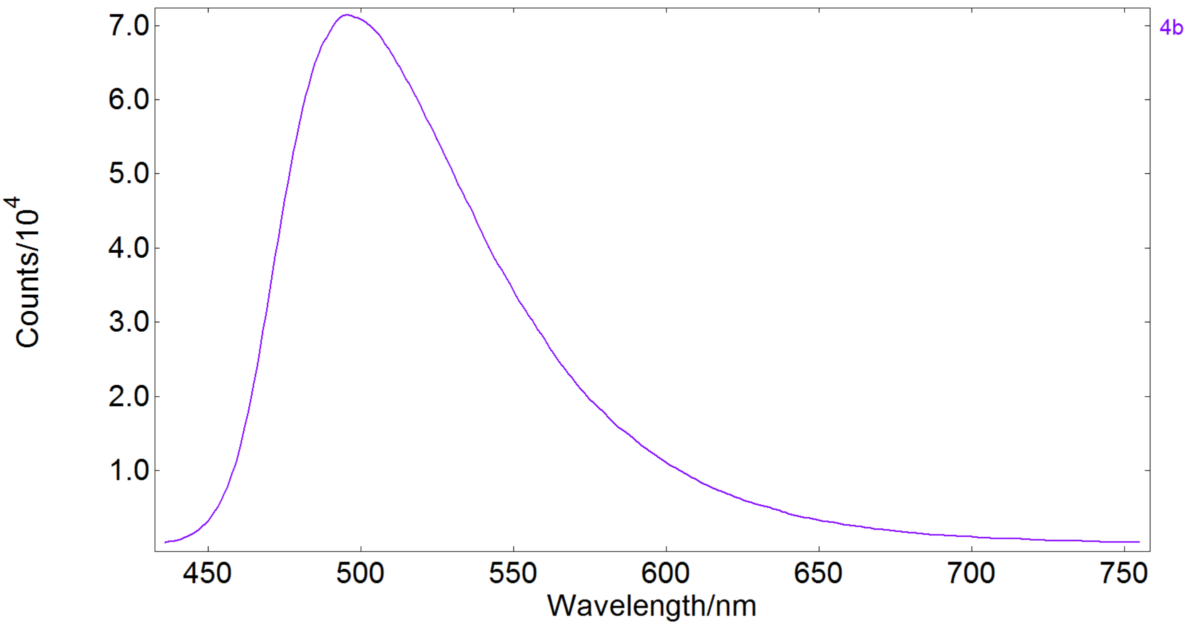


Fig. S18. Emission of **4b** in the solid state

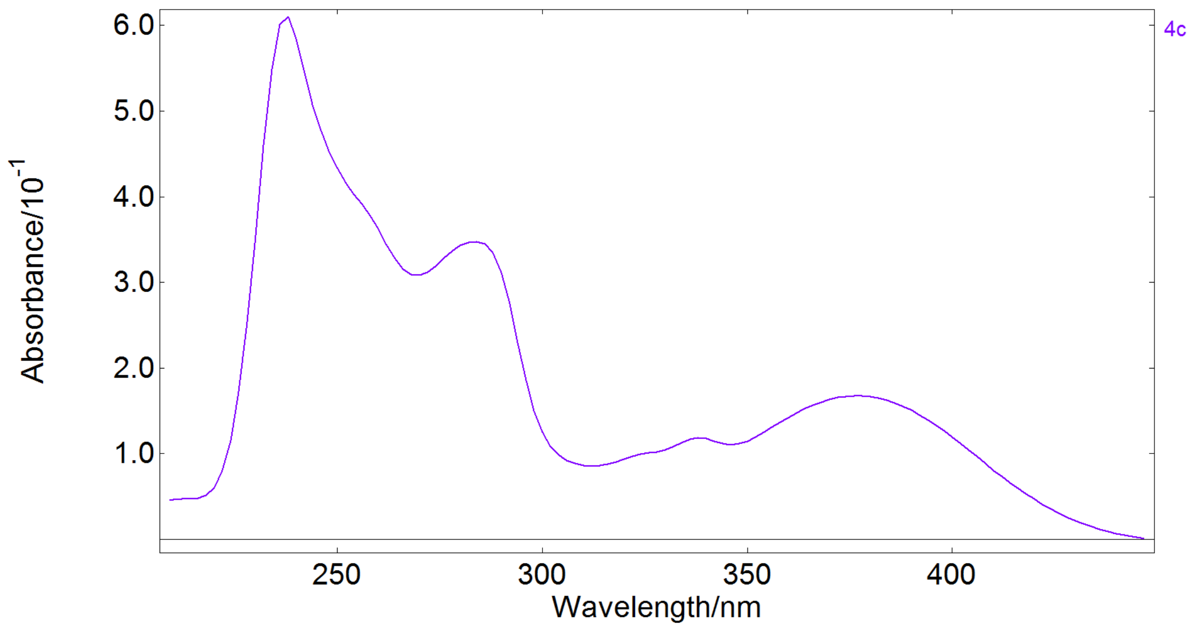


Fig. S19. Absorption of **4c** in MeCN solution (at 10^{-5} mol/L)

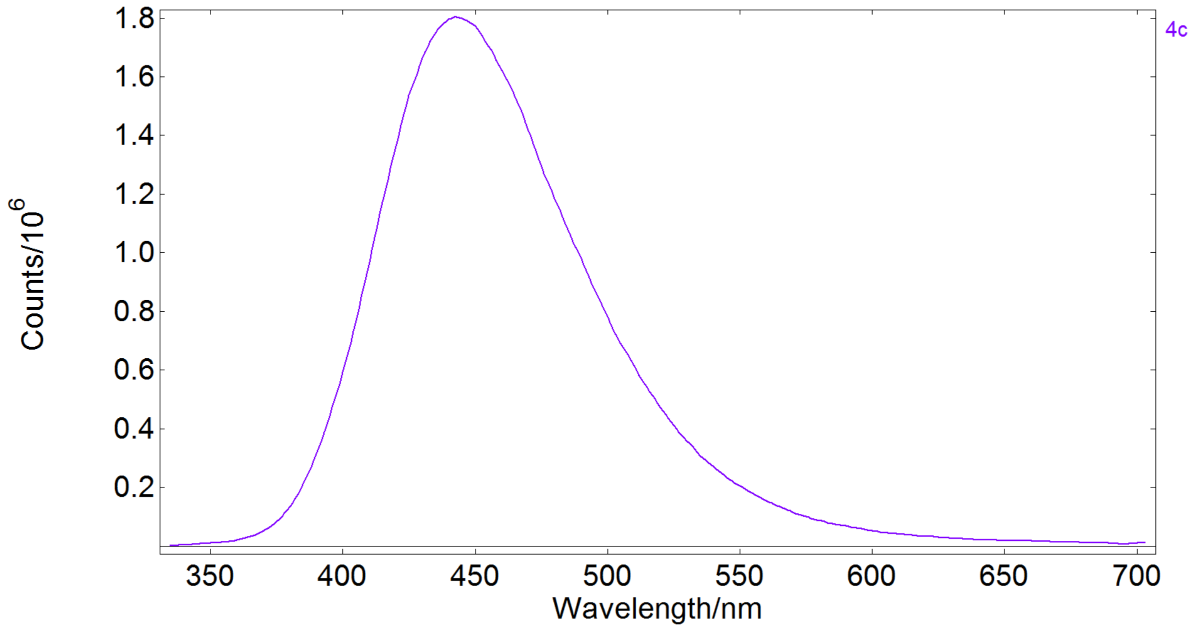


Fig. S20. Emission of **4c** in MeCN solution (at 10^{-5} mol/L)

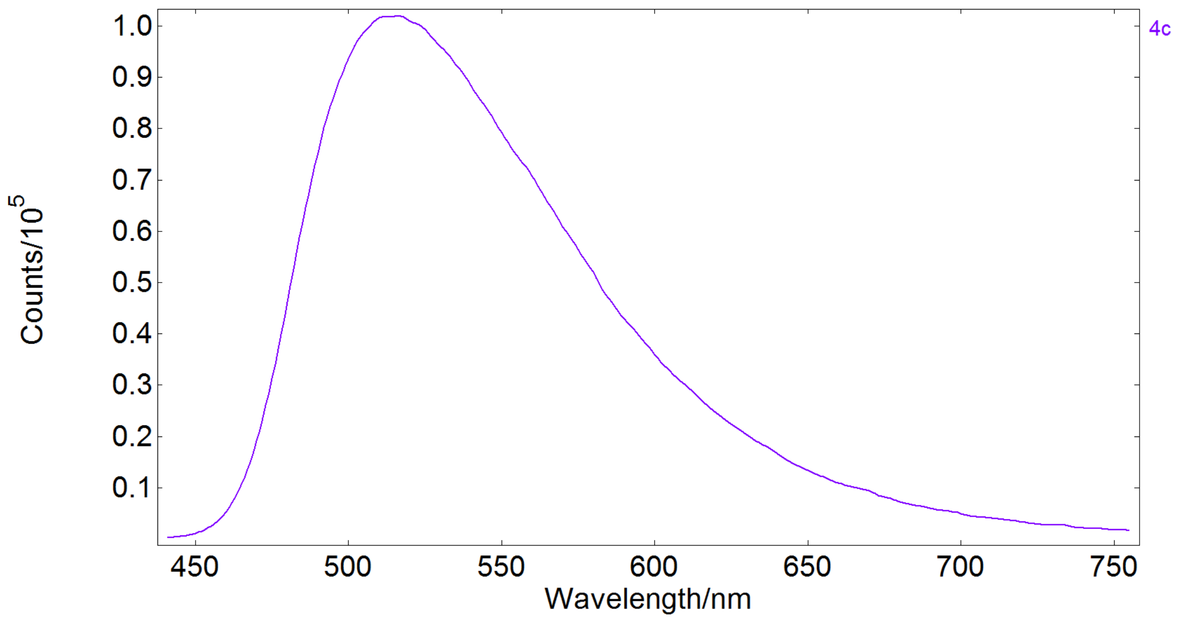


Fig. S21. Emission of **4c** in the solid state

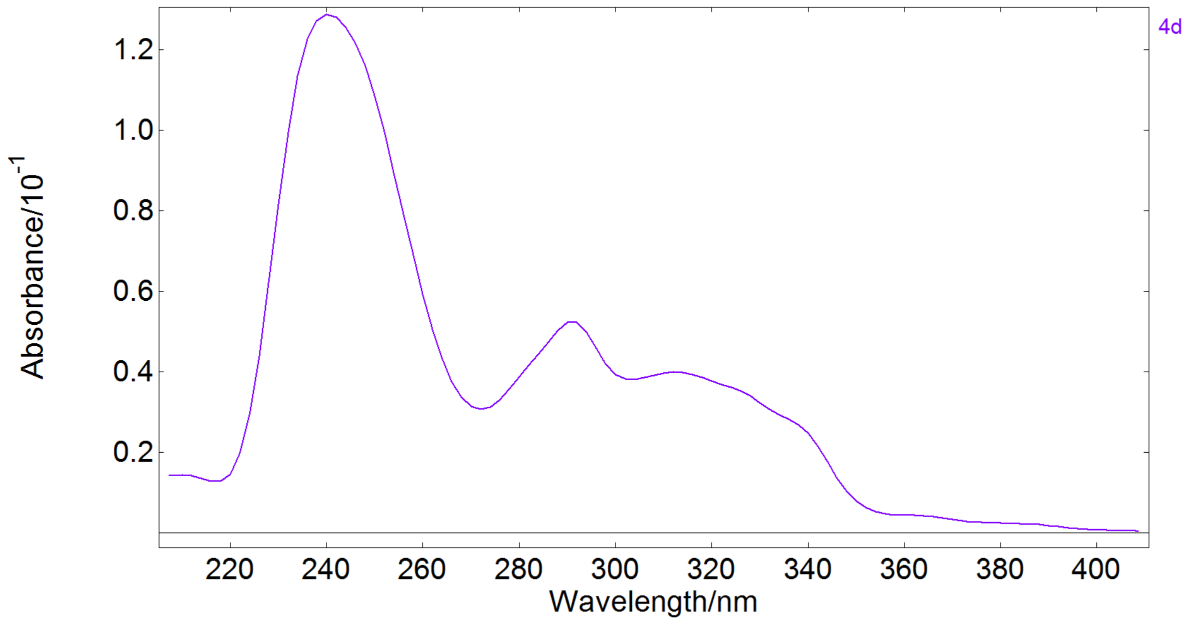


Fig. S22. Absorption of **4d** in MeCN solution (at 10^{-5} mol/L)

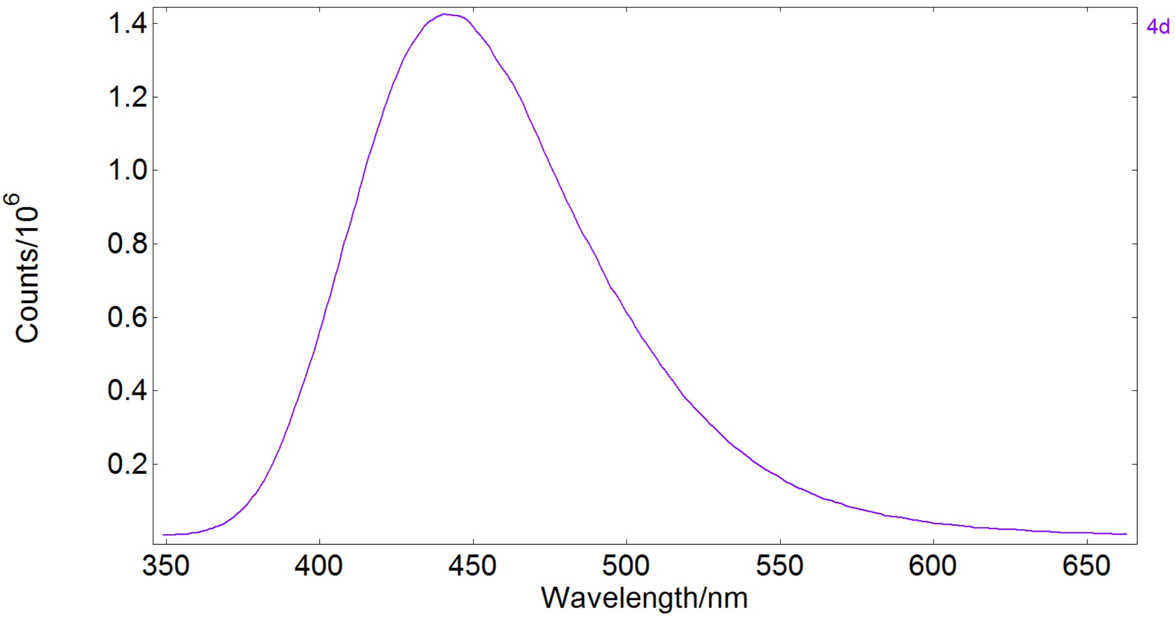


Fig. S23. Emission of **4d** in MeCN solution (at 10^{-5} mol/L)

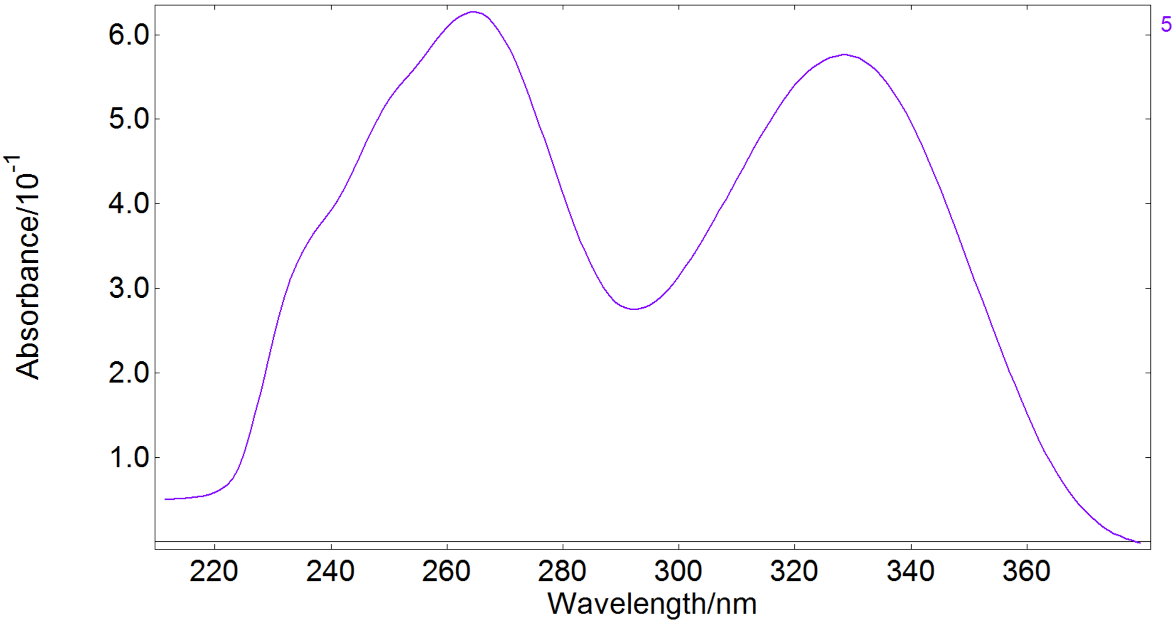


Fig. S24. Absorption of **5** in MeCN solution (at 10^{-5} mol/L)

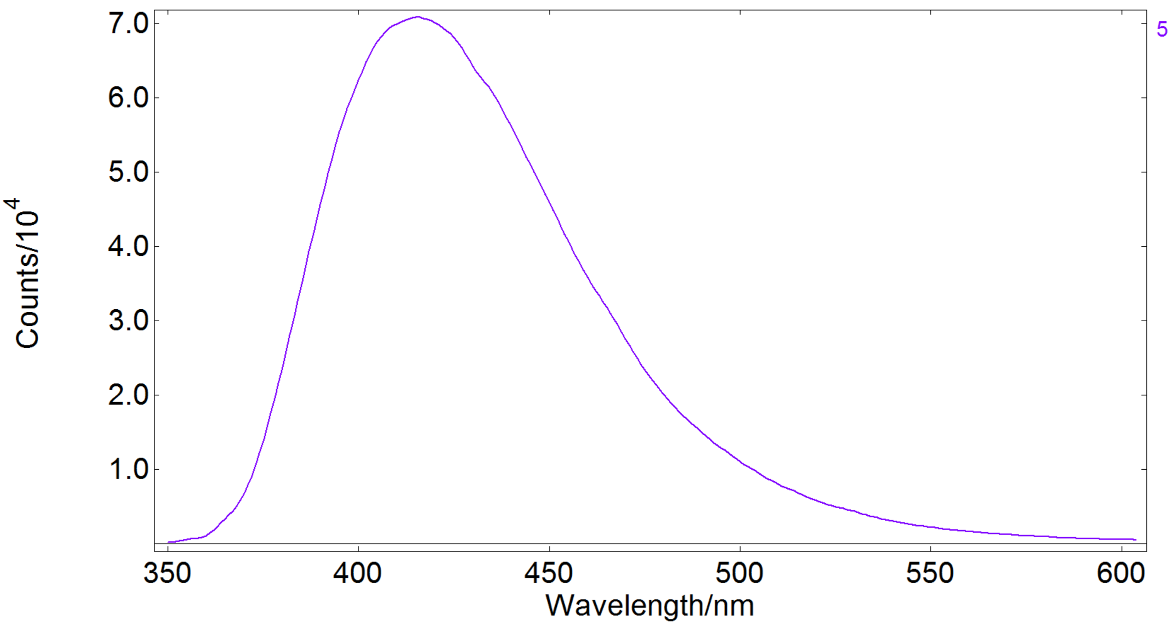


Fig. S25. Emission of **5** in MeCN solution (at 10^{-5} mol/L)

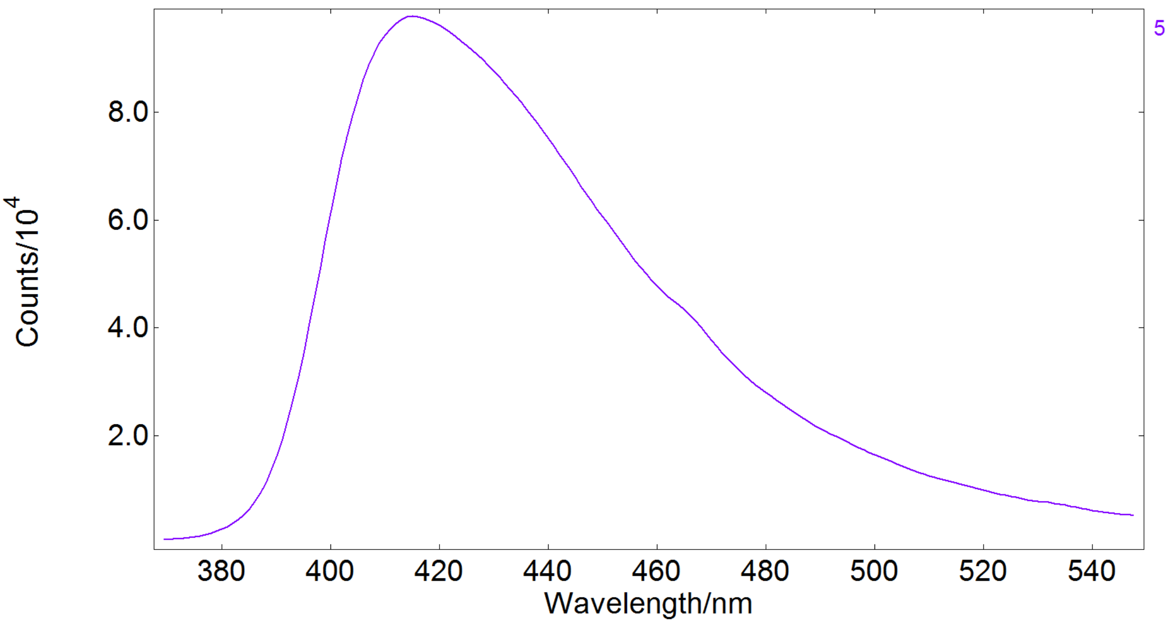


Fig. S26. Emission of **5** in the solid state

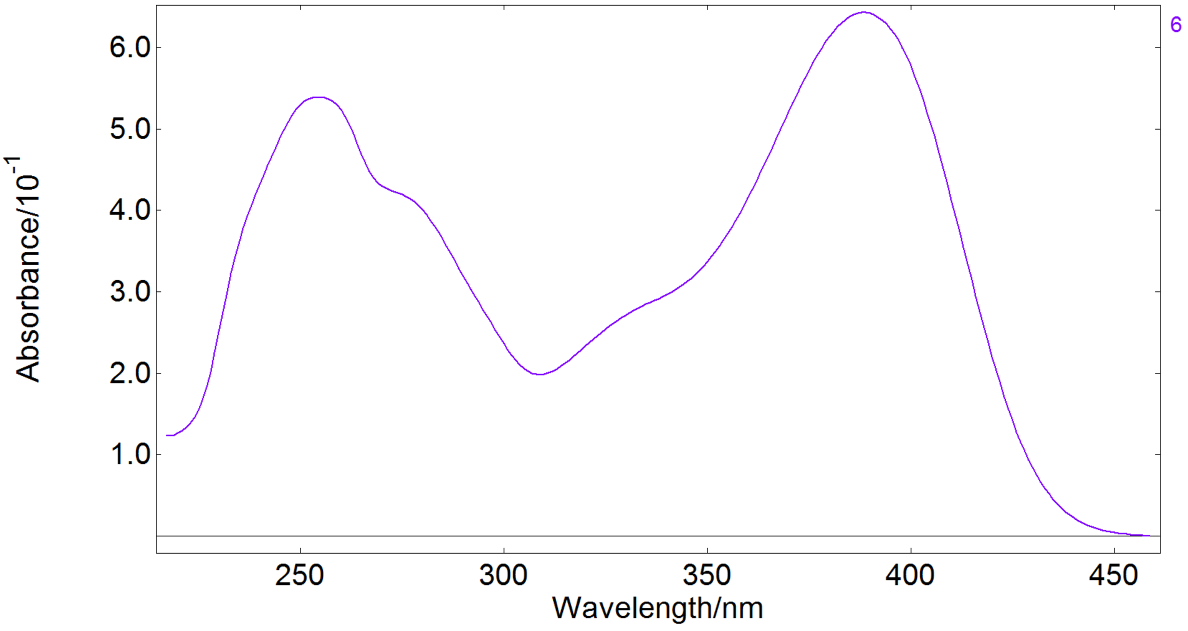


Fig. S27. Absorption of **6** in MeCN solution (at 10^{-5} mol/L)

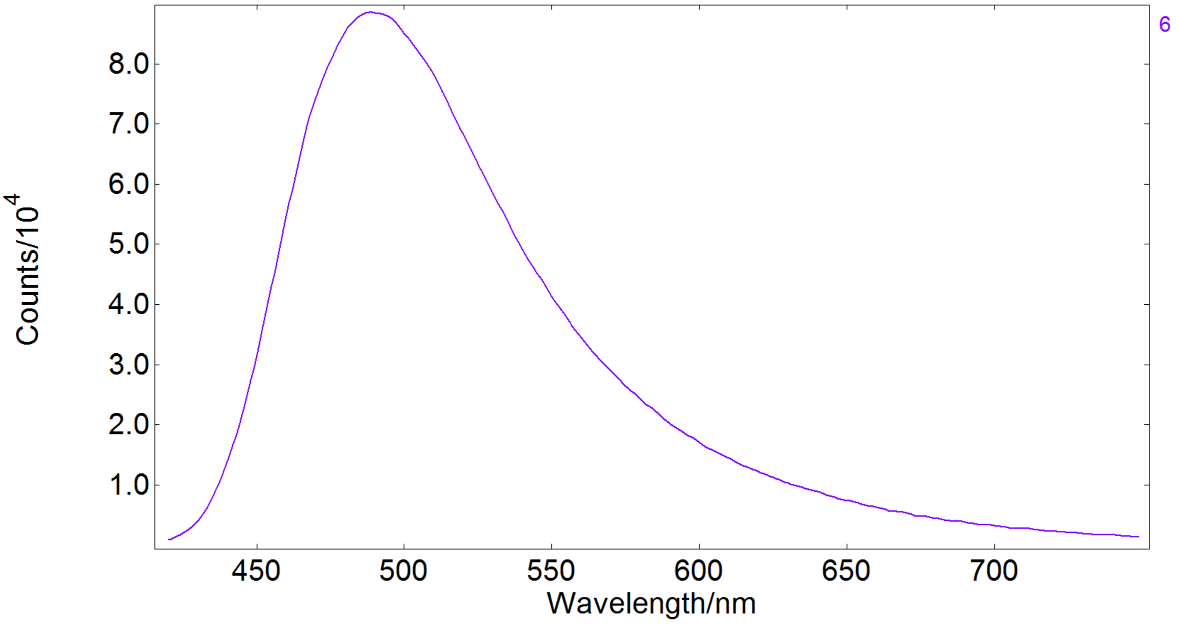


Fig. S28. Emission of **6** in MeCN solution (at 10^{-5} mol/L)

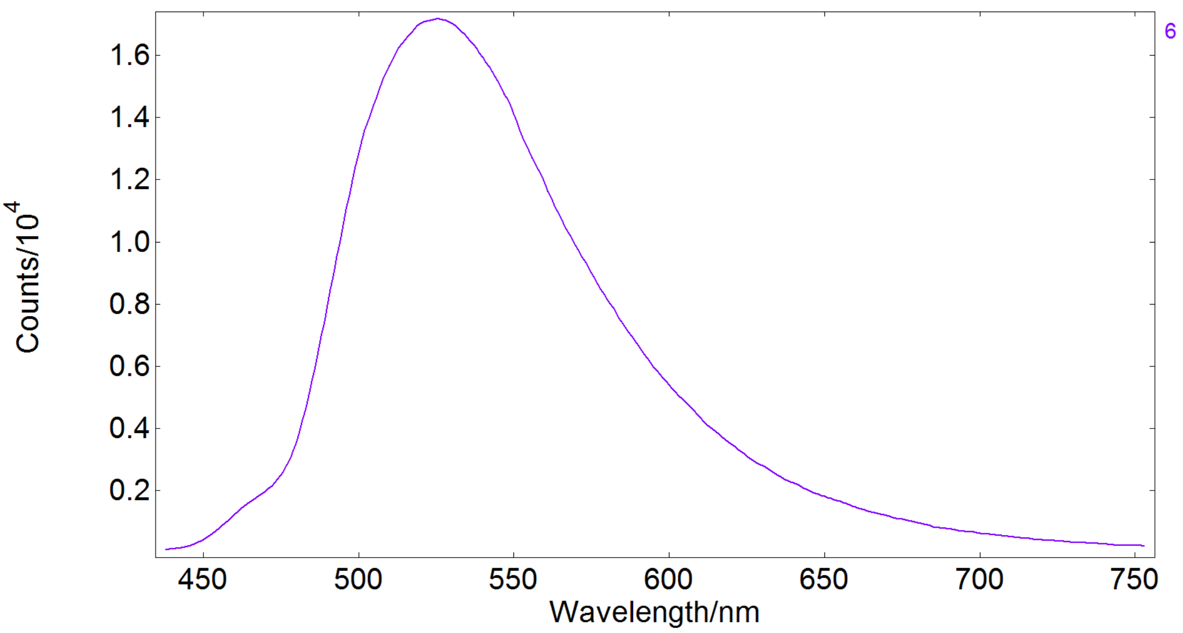
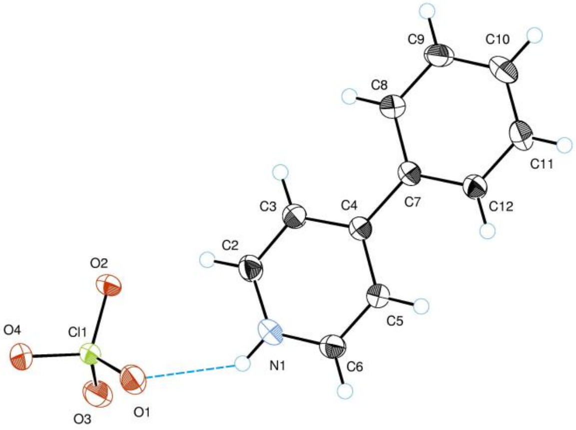


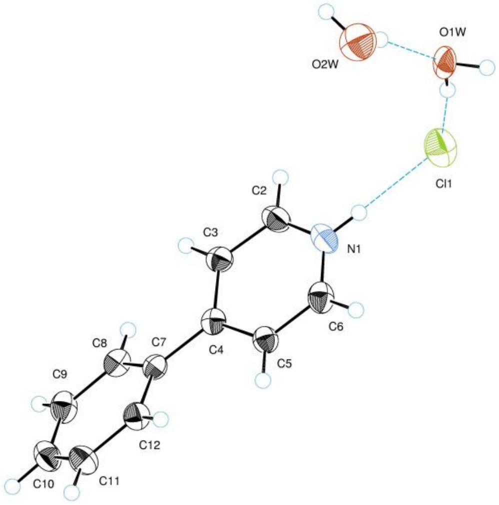
Fig. S29. Emission of **6** in the solid state

X-Ray Structure, crystal data and structure refinements for 2a



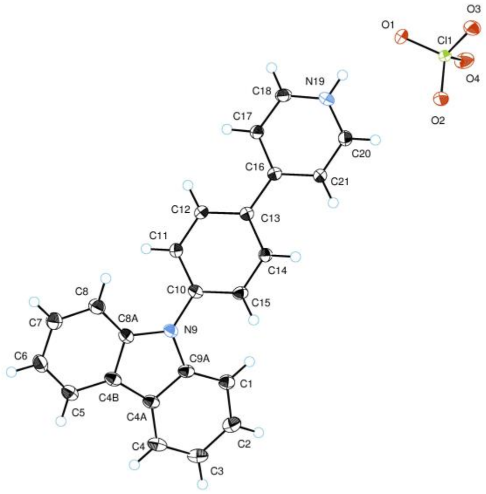
Identification code	KL-1248
Empirical formula	$C_{11}H_{10}ClNO_4$
Formula weight	255.66
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.8571(1)
b/Å	18.2247(2)
c/Å	9.2749(1)
α/°	90
β/°	109.383(2)
γ/°	90
Volume/Å^3	1093.38(3)
Z	4
ρ_{calc}g/cm^3	1.5530
μ/mm^{-1}	3.155
F(000)	528
Crystal size/mm^3	0.17 × 0.16 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ max. for data collection/°	155.0
Index ranges	$-8 \le h \le 8$, $-23 \le k \le 22$, $-11 \le l \le 10$
Reflections collected	10027
Independent reflections	2308 [R_{int} = 0.0304, R_{sigma} = 0.0211]
Data/restraints/parameters	2308/0/158
Goodness-of-fit on F^2	1.024
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0414, wR_2 = 0.1144
Largest diff. peak/hole / e Å^{-3}	0.34/-0.60

X-Ray Structure, crystal data and structure refinements for 2b



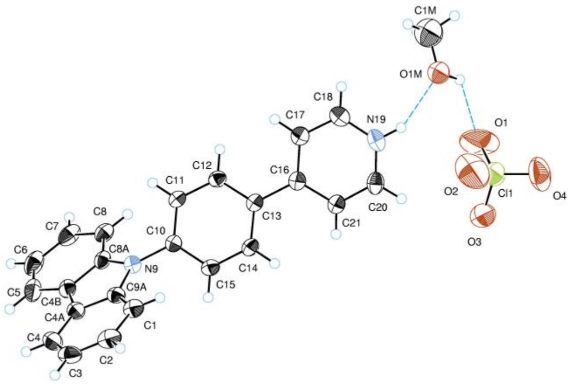
Identification code	KL-1302
Empirical formula	$C_{11}H_{14}ClNO_2$
Formula weight	227.65
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.0110(1)
b/Å	9.8156(1)
c/Å	17.0473(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1173.15(2)
Z	4
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	2.734
F(000)	480.0
Crystal size/mm^3	0.18 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ max. for data collection/°	155.0
Index ranges	$-8 \leq h \leq 6$, $-12 \leq k \leq 12$, $-21 \leq l \leq 19$
Reflections collected	6367
Independent reflections	2351 [R_{int} = 0.0272, R_{sigma} = 0.0296]
Data/restraints/parameters	2351/0/136
Goodness-of-fit on F^2	1.101
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0678, wR_2 = 0.1990
Final R indexes [all data]	R_1 = 0.0693, wR_2 = 0.2025
Largest diff. peak/hole / e Å^{-3}	0.90/-0.75

X-Ray Structure, crystal data and structure refinements for 4aB



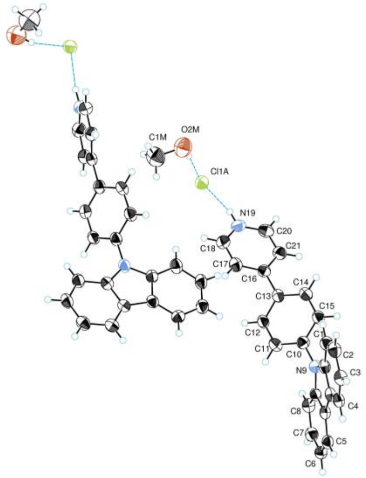
Identification code	KL_PyClO4
Empirical formula	$C_{23}H_{17}ClN_2O_4$
Formula weight	420.84
Temperature/K	120.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.14553(5)
b/Å	8.93108(11)
c/Å	40.8075(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1875.31(4)
Z	4
ρ_{calc}g/cm^3	1.483
μ/mm^{-1}	2.090
F(000)	868.0
Crystal size/mm^3	0.25× 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ max. for data/°	155.0
Index ranges	$-5 \leq h \leq 6$, $-11 \leq k \leq 11$, $-51 \leq l \leq 51$
Reflections collected	17540
Independent reflections	3970 [R_{int} = 0.0370, R_{sigma} = 0.0258]
Data/restraints/parameters	3970/0/276
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0849
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.0851
Largest diff. peak/hole / e Å^{-3}	0.21/-0.26

X-Ray Structure, crystal data and structure refinements for 4aC



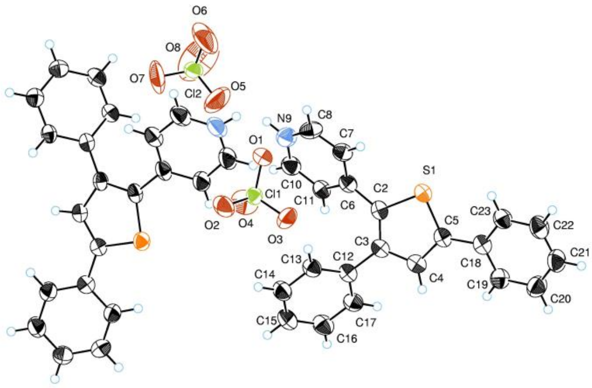
Identification code	kl-1301
Empirical formula	$C_{24}H_{21}ClN_2O_5$
Formula weight	452.89
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7838(1)
b/Å	7.8328(1)
c/Å	23.3380(2)
α/°	90
β/°	103.889(1)
γ/°	90
Volume/Å^3	2091.12(4)
Z	4
ρ_{calc}g/cm^3	1.4384
μ/mm^{-1}	1.966
F(000)	944
Crystal size/mm^3	0.18 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ max. for data collection/°	155.0
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-29 \leq l \leq 29$
Reflections collected	24797
Independent reflections	4427 [R_{int} = 0.0343, R_{sigma} = 0.0273]
Data/restraints/parameters	4427/0/283
Goodness-of-fit on F^2	1.052
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0836, wR_2 = 0.2264
Final R indexes [all data]	R_1 = 0.0888, wR_2 = 0.2318
Largest diff. peak/hole / e Å^{-3}	1.54/-1.12

X-Ray Structure, crystal data and structure refinements for 4b



Identification code	KL1223
Empirical formula	$C_{24}H_{21}ClN_2O$
Formula weight	388.88
Temperature/K	150(2) K
Crystal system	Monoclinic, P 21/c
Space group	*P*2$_1$/*n*
a/Å	9.2977(7)
b/Å	18.190(1) A
c/Å	23.399(2) A
α/°	90
β/°	100.702(7)
γ/°	90
Volume/Å^3	3888.7(5) A^3
Z	8
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	1.864
F(000)	1632
Crystal size/mm^3	0.19 x 0.16 x 0.01 mm
Radiation	Cu Kα (λ = 1.54184)
2Θ max. for data collection/°	155.0
Index ranges	-11<=h<=11, 0<=k<=22, 0<=l<=29
Reflections collected / unique	8211 / 8200 [R(int) = 0.0048]
Completeness to theta = 77.84	98.8 %
Data/restraints/parameters	8200 / 0 / 511
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0897, wR2 = 0.2275
Final R indexes [all data]	R1 = 0.1212, wR2 = 0.2553
Largest diff. peak/hole / e Å^{-3}	0.974 and -0.902

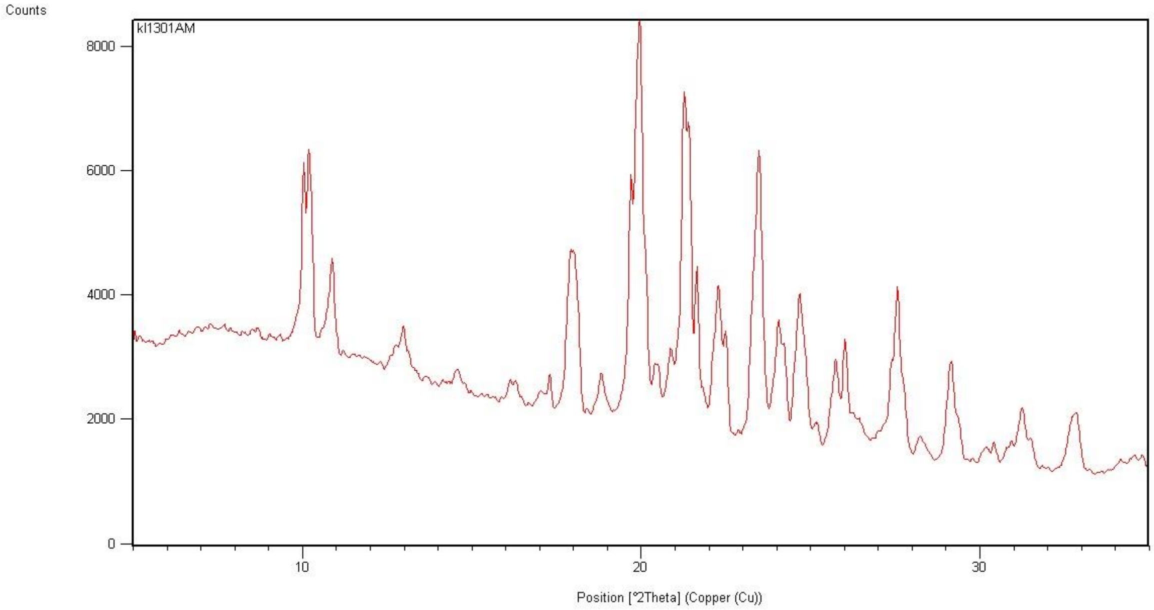
X-Ray Structure, crystal data and structure refinements for 6



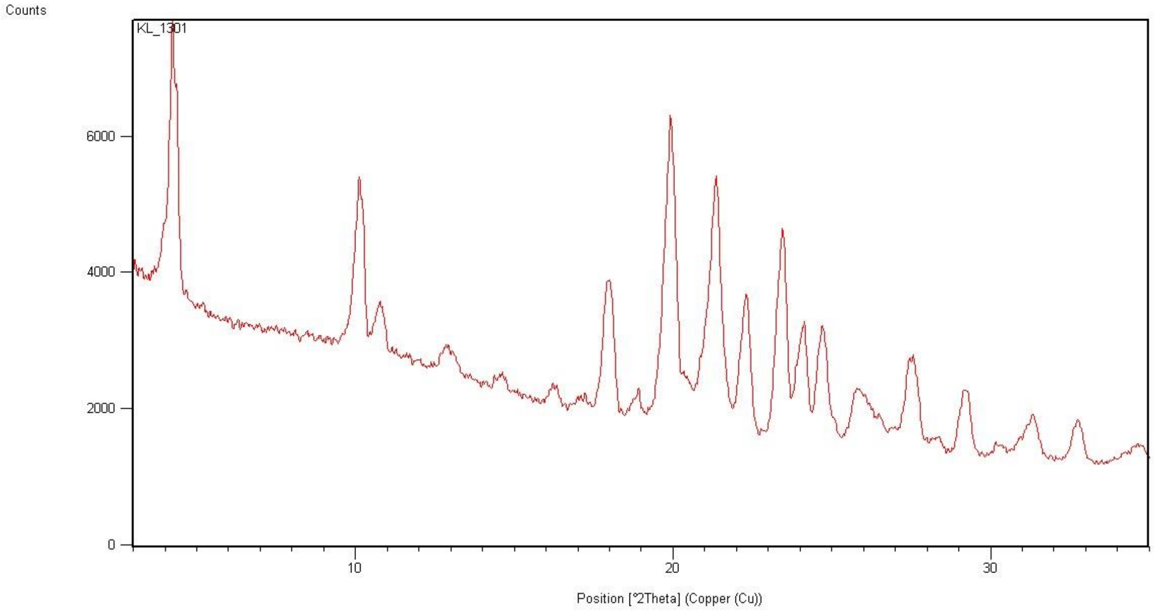
Identification code	LT-4-AiE1
Empirical formula	$C_{21}H_{16}ClNO_4S$
Formula weight	413.86
Temperature/K	140.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.7267(2)
b/Å	13.0423(3)
c/Å	36.8750(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3716.0(2)
Z	4
ρ_{calc}g/cm^3	1.480
μ/mm^{-1}	3.121
F(000)	1712.0
Crystal size/mm^3	0.25 × 0.24 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ max. for data collection/°	160.0
Index ranges	$-9 \leq h \leq 9$, $-16 \leq k \leq 16$, $-46 \leq l \leq 46$
Reflections collected	53801
Independent reflections	7836 [R_{int} = 0.1173, R_{sigma} = 0.0533]
Data/restraints/parameters	7836/0/514
Goodness-of-fit on F^2	1.056
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0649, wR_2 = 0.1724
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1832
Largest diff. peak/hole / e Å^{-3}	0.87/-0.60

X-Ray Powder Diffraction (XRPD) data

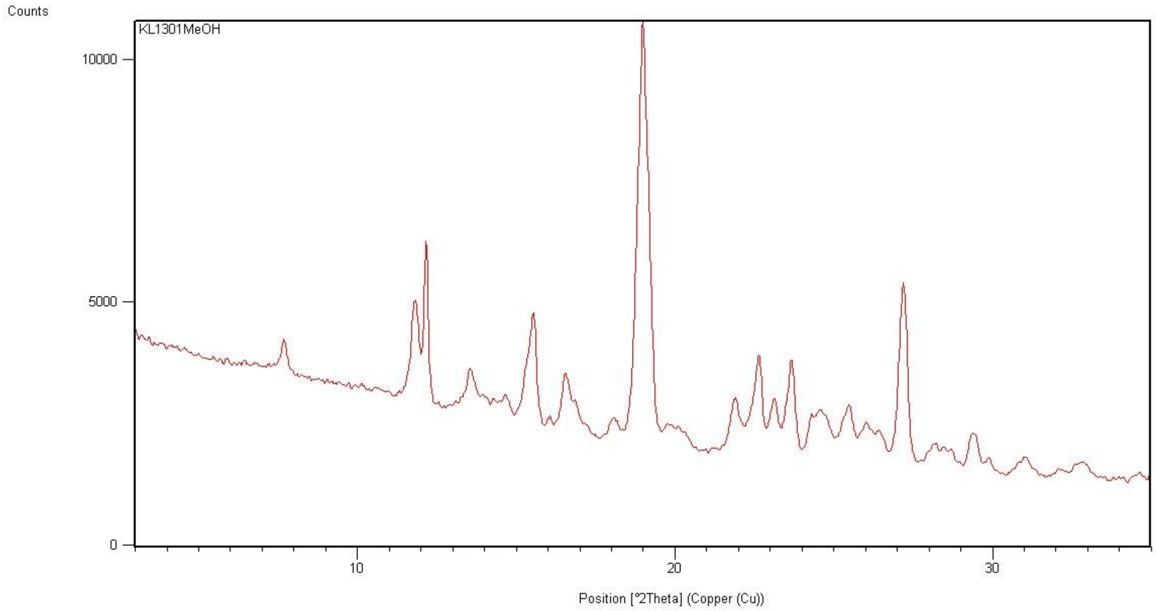
XRPD data for 4aA



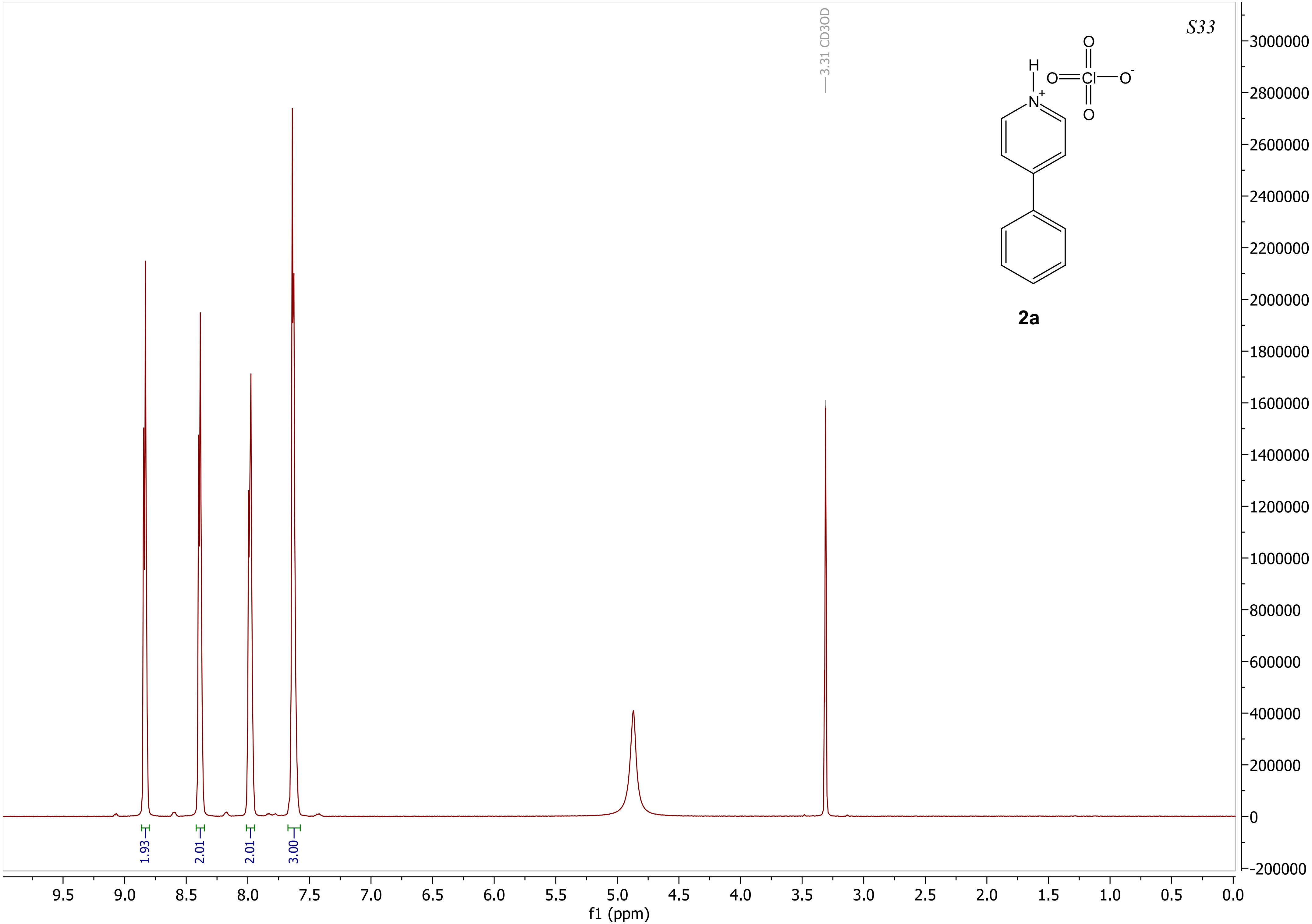
XRPD data for 4aB



XRPD data for 4aC



^{1}H and ^{13}C NMR data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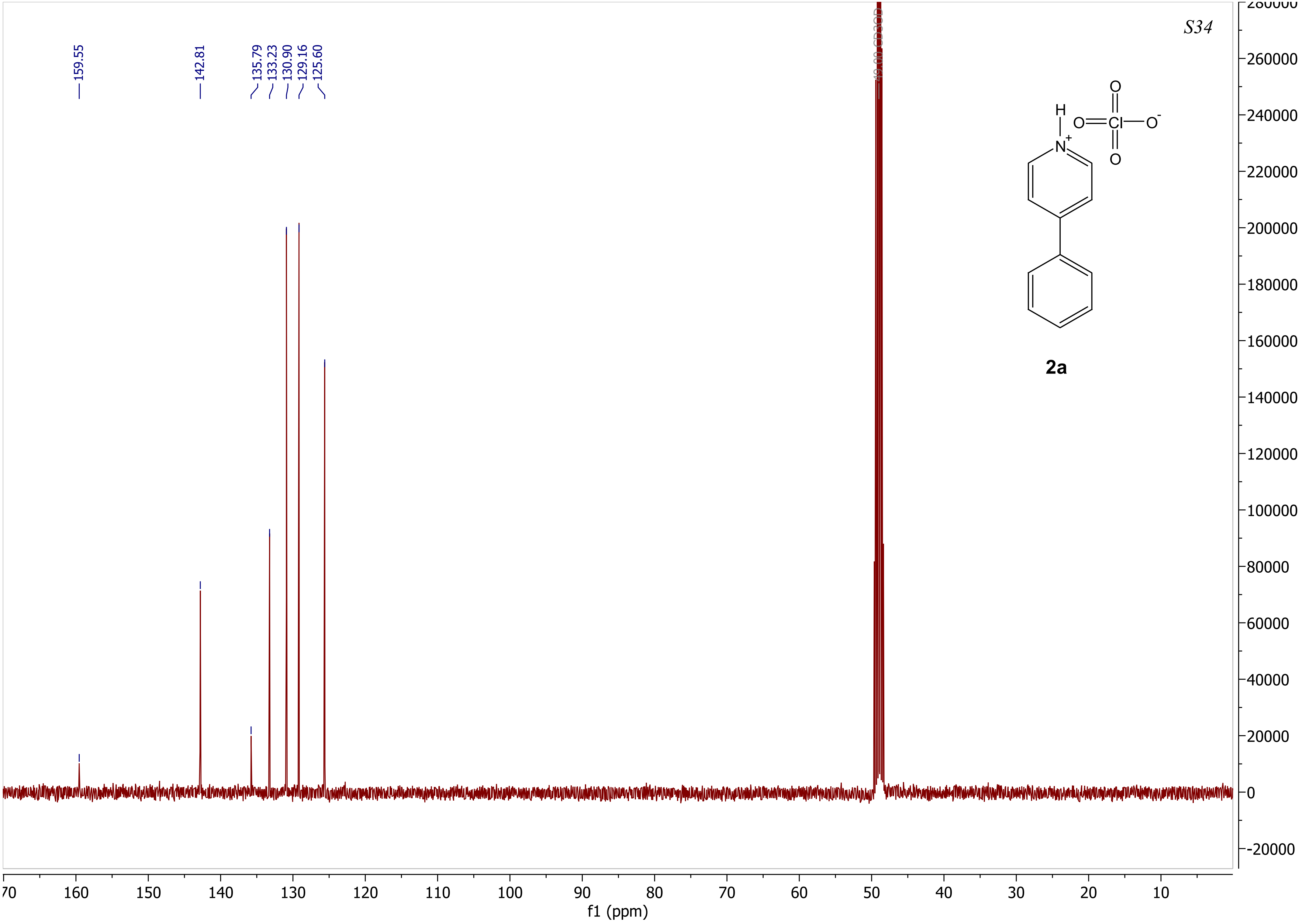
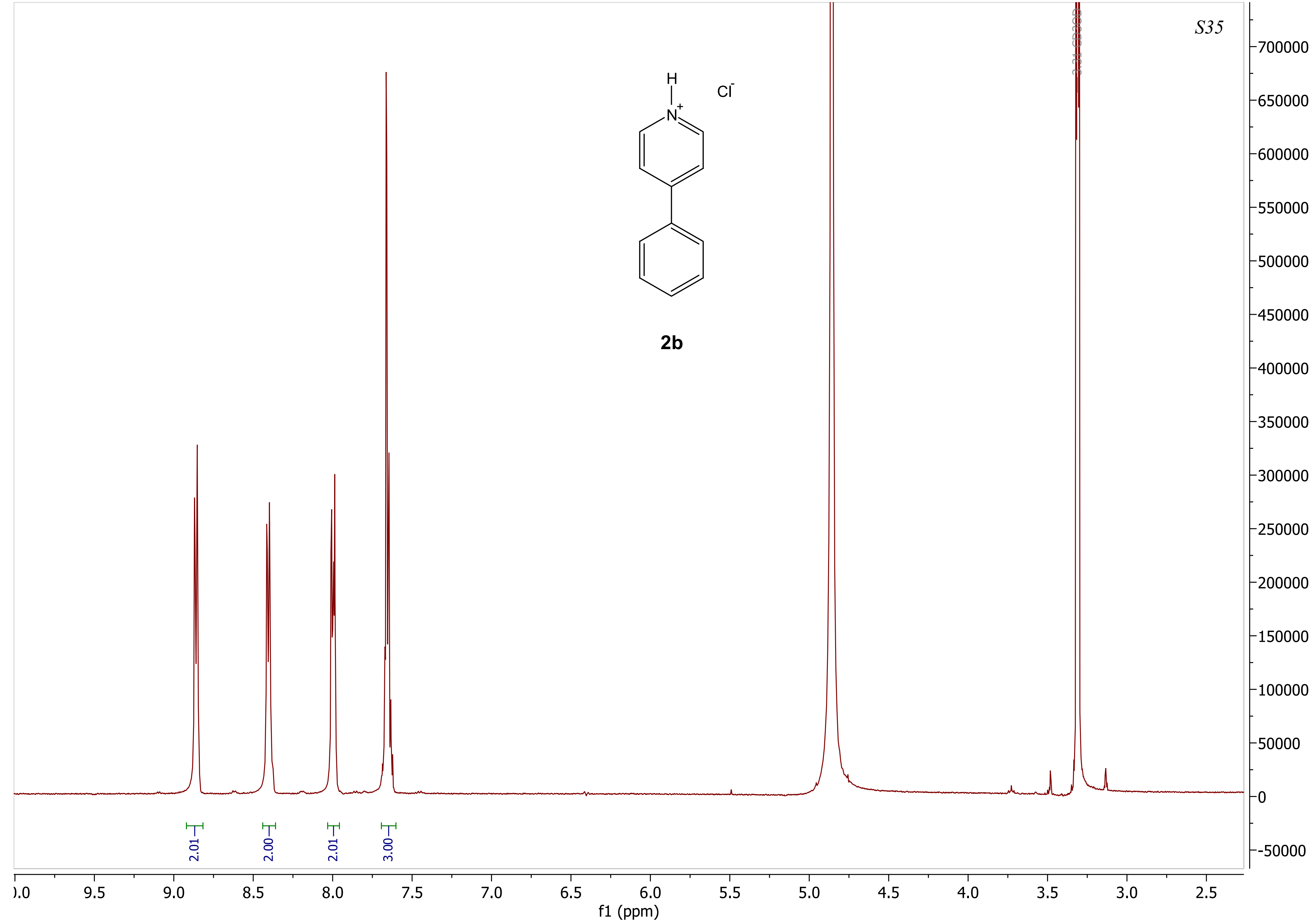
2.01
2.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
H
N+
O
O
Cl
O-
O

2a


159.55
142.81
135.79
133.23
130.90
129.16
125.60
49.00 CD3OD
H
N+
O
O
Cl
O-
O
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2a


H
N+
Cl-
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2.00
2.01
3.00
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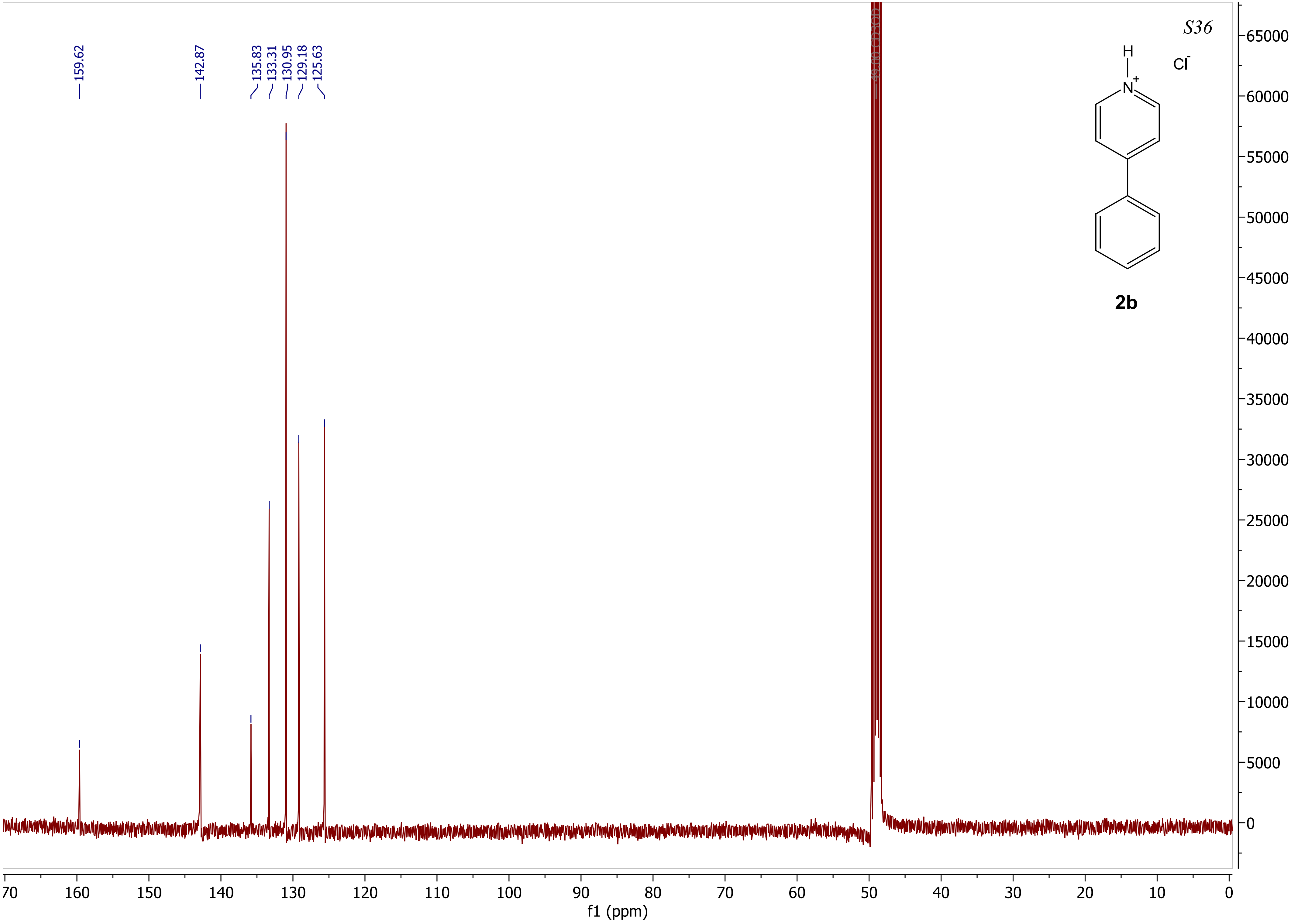
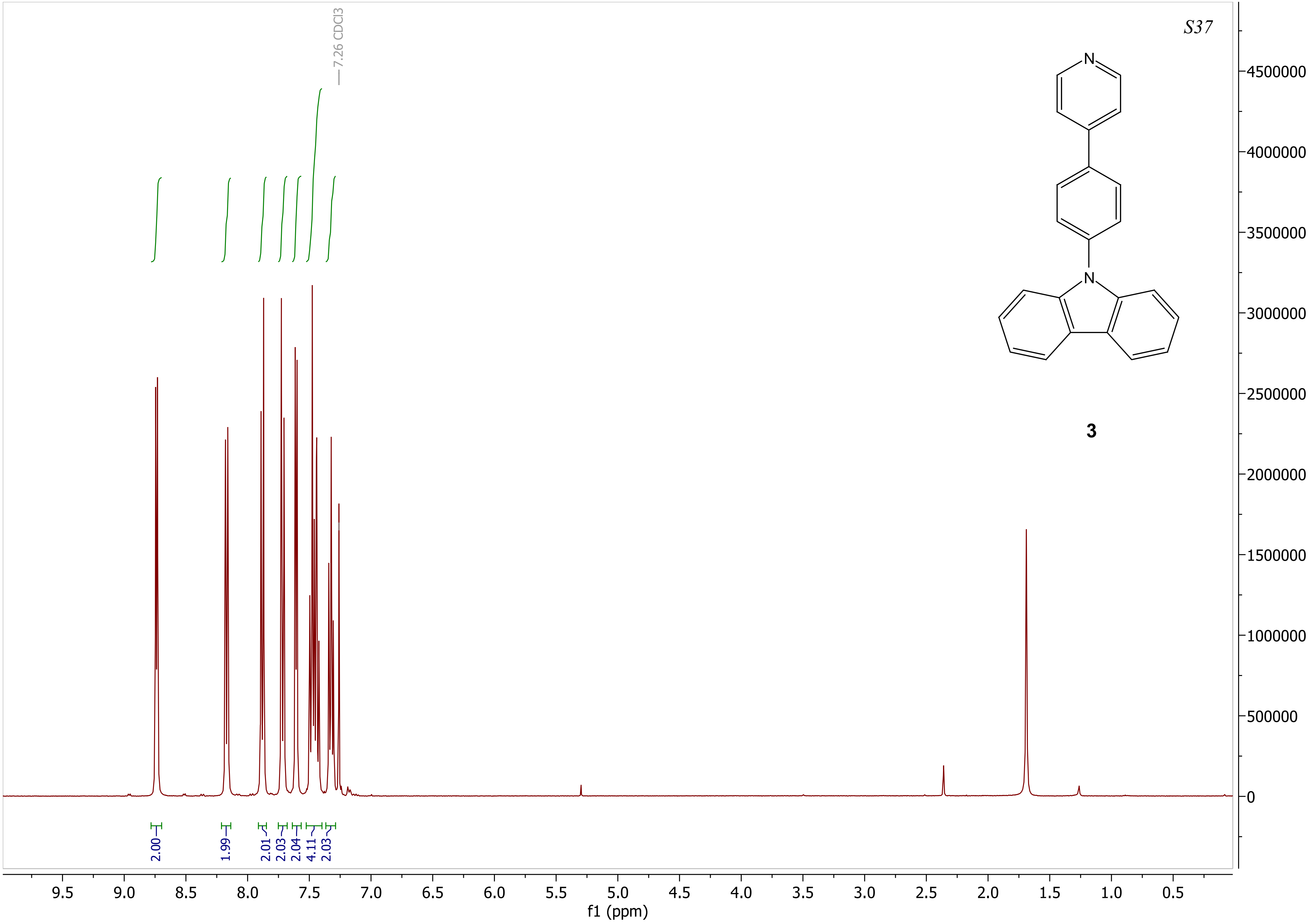
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

2b


159.62
142.87
135.83
133.31
130.95
129.18
125.63
49.00 CD3OD
H
N+
Cl-
2b
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
N
N
3
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1.99
2.01
2.03
2.04
4.11
2.03
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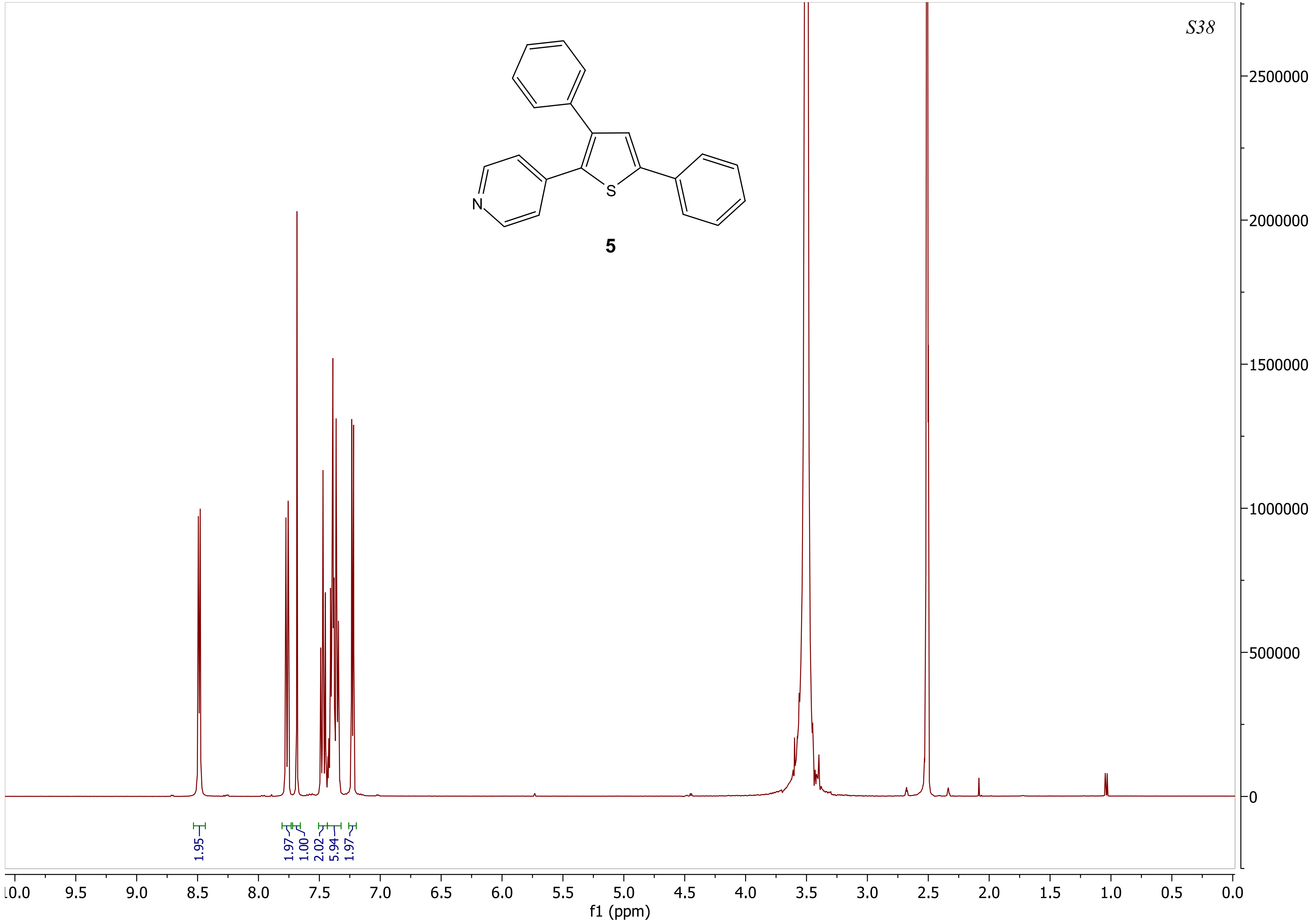
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


N
S
5
2500000
2000000
1500000
1000000
500000
0
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1.97
1.00
2.02
5.94
1.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)