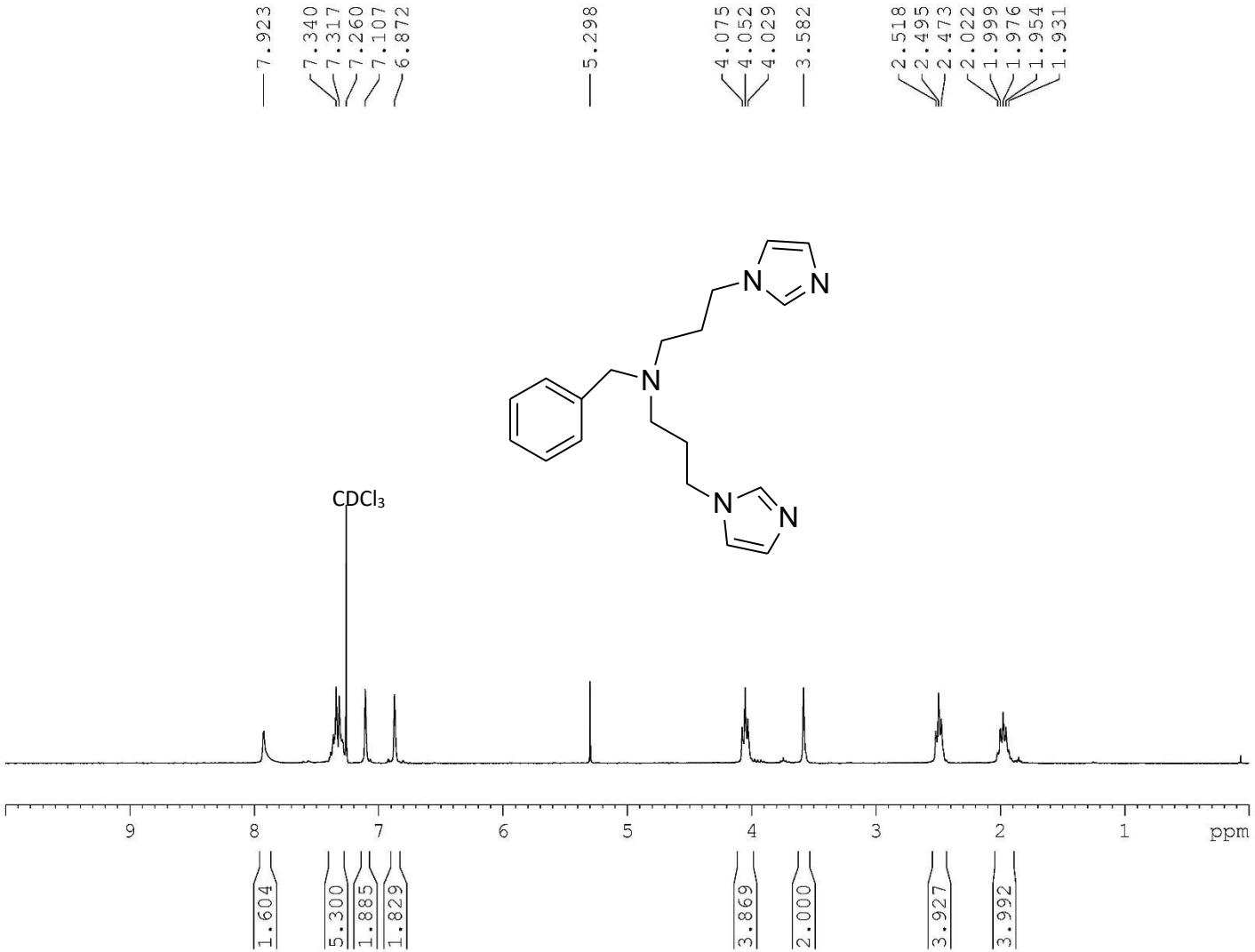
Supporting Information for:

"Synthesis and structural characterization of 20-membered macrocyclic rings bearing *trans*-chelating bis(N-heterocyclic carbene) ligands and the catalytic activity of their palladium(II) complexes "

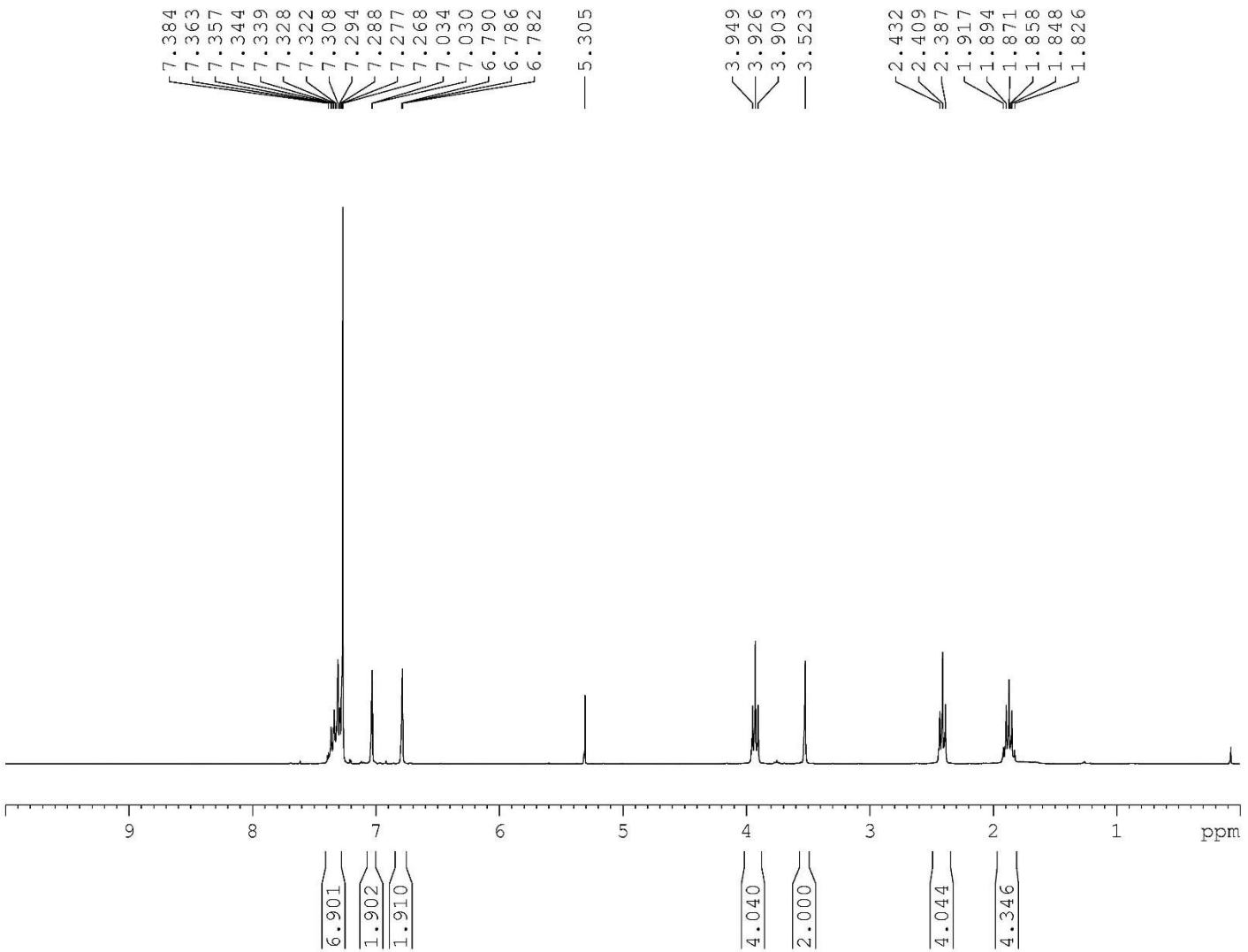
Rajesh Thapa and Stefan M. Kilyanek*

NMR SPECTRA OF INTERMEDIATES AND PRODUCTS

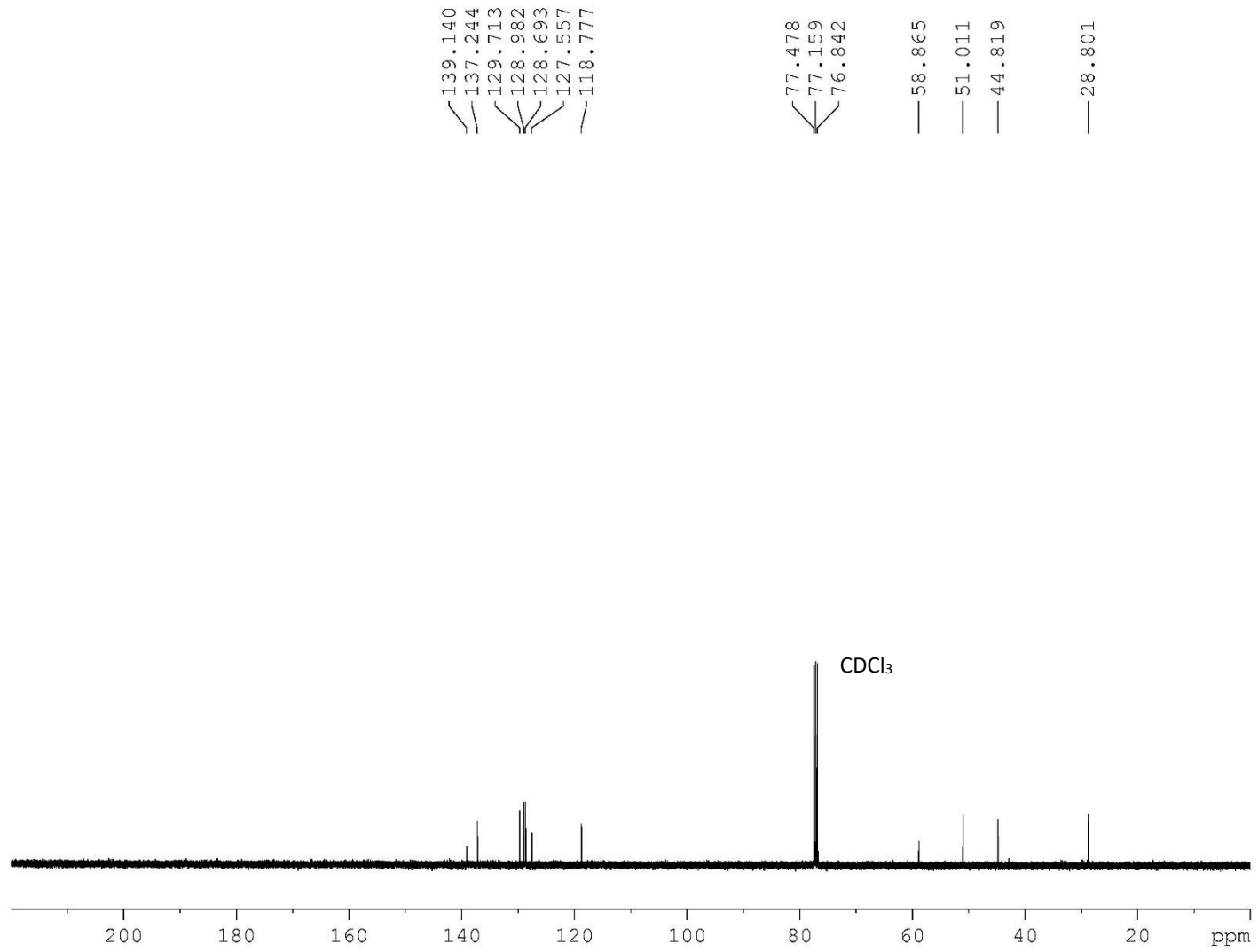
^{1}H NMR ($CDCl_3$, Compound **2a**, 400 MHz)



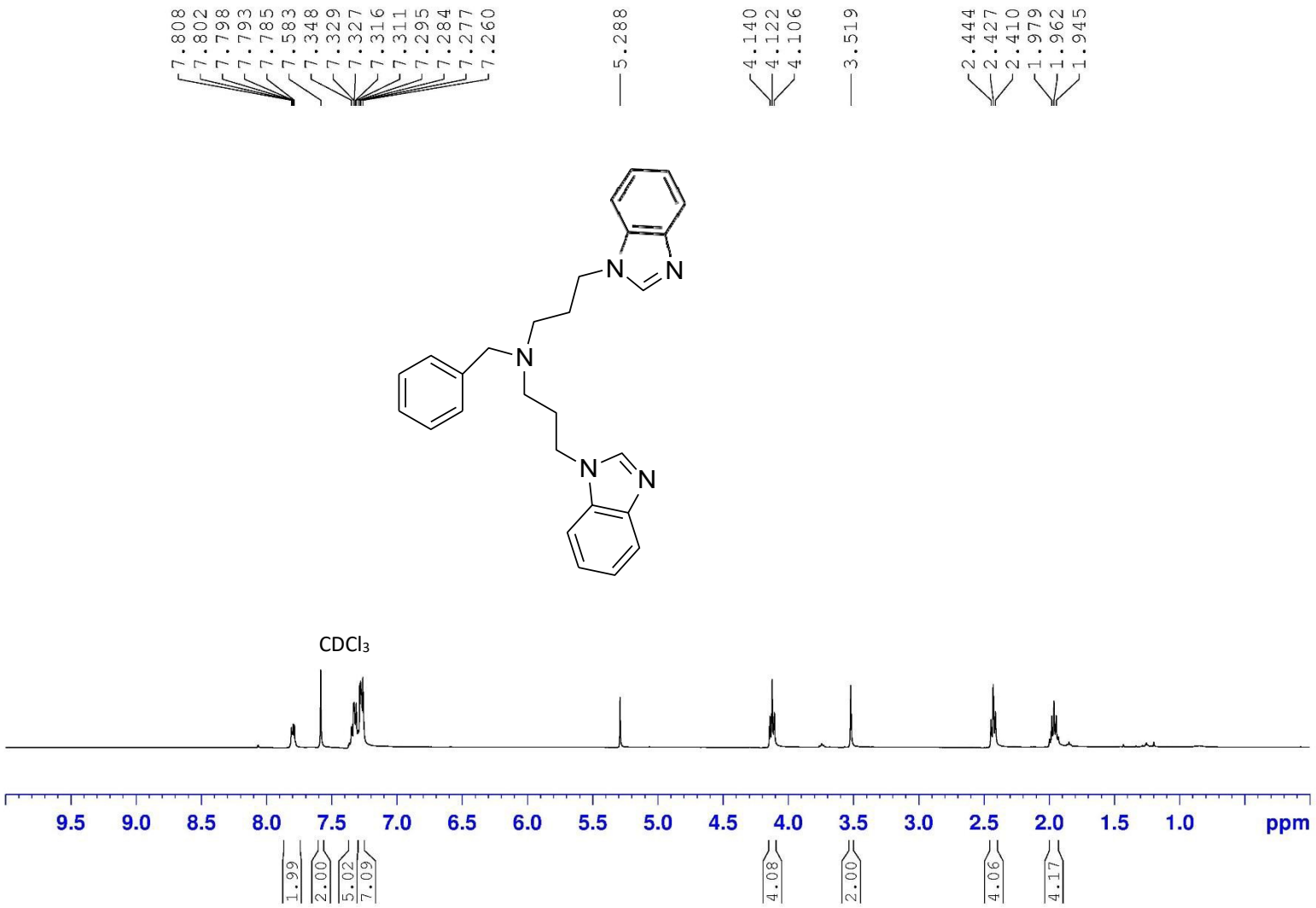
^{1}H NMR (CD_2Cl_2, Compound **2a**, 400 MHz)



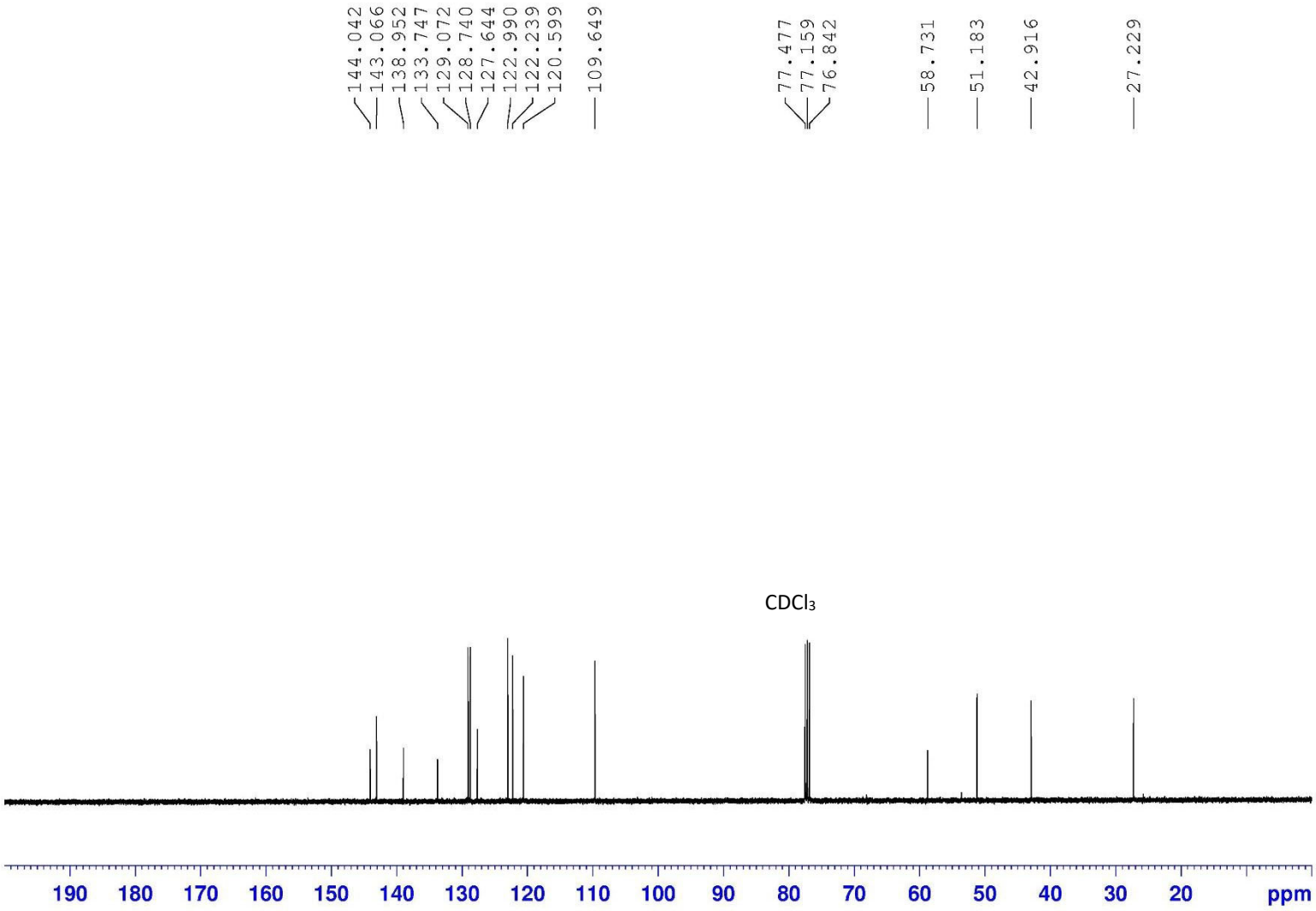
^{13}C NMR ($CDCl_3$, Compound **2a**, 400 MHz)



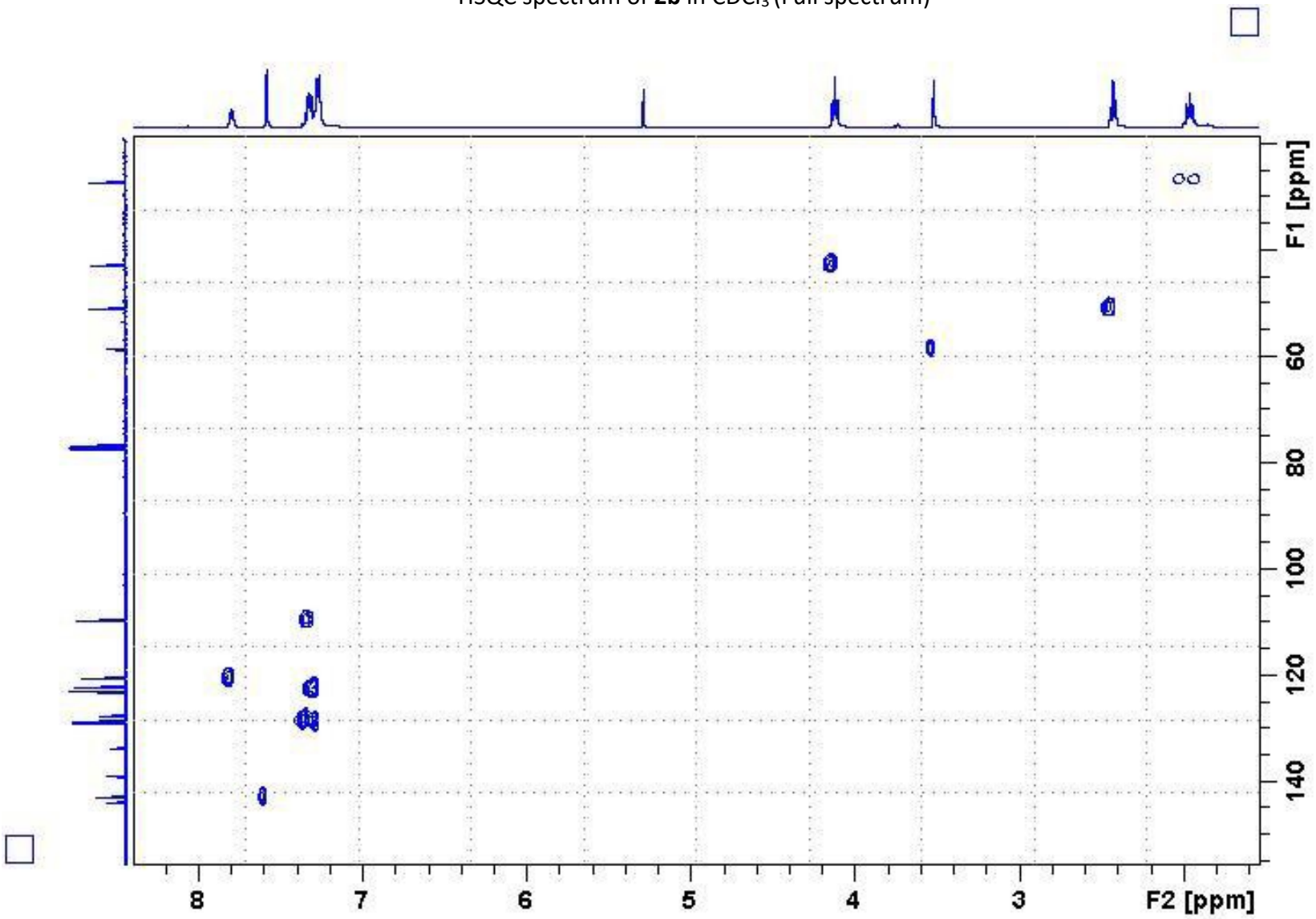
^{1}H NMR ($CDCl_3$, Compound **2b**, 400 MHz)



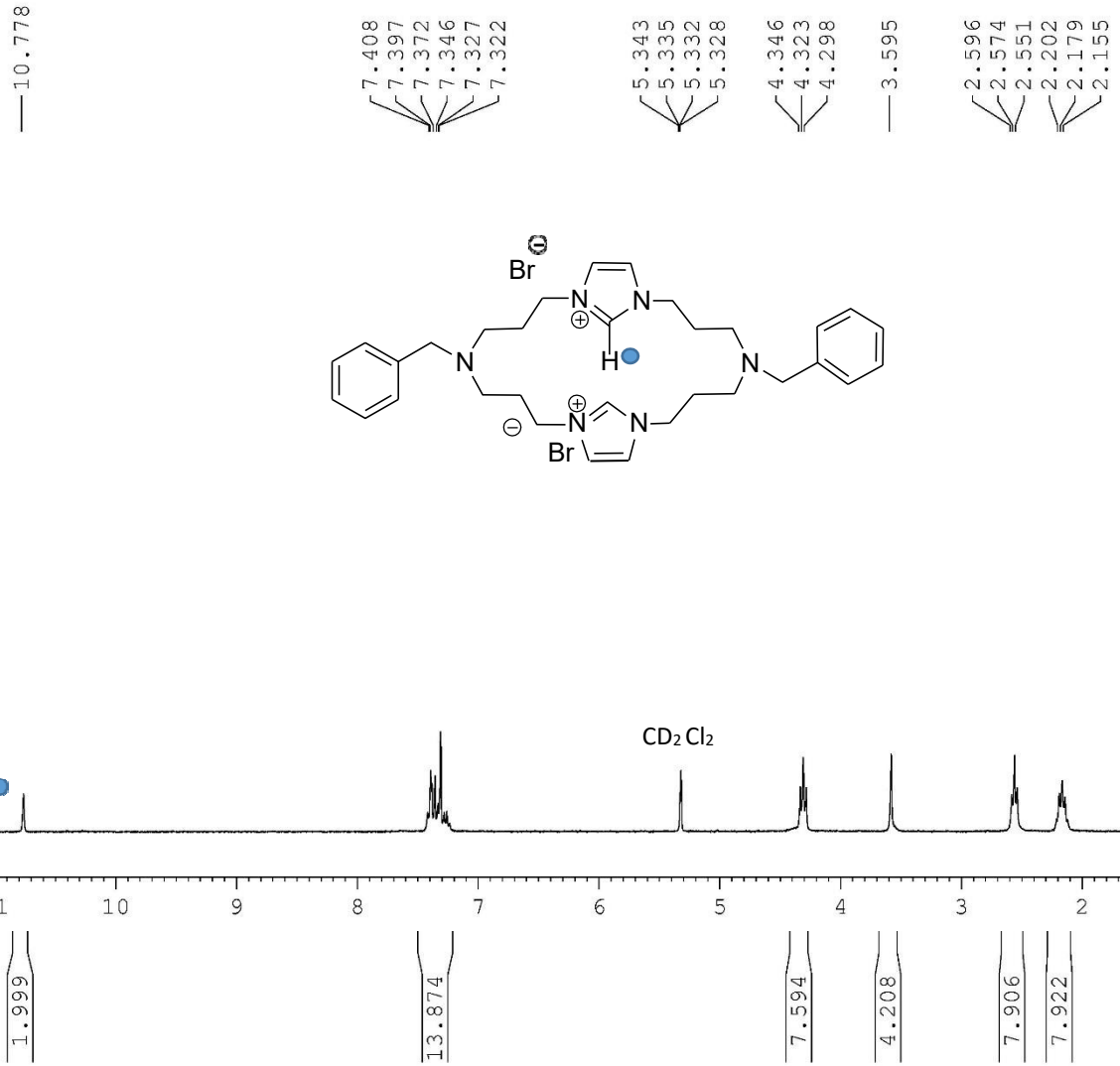
^{13}C NMR ($CDCl_3$, Compound **2b**, 400 MHz)



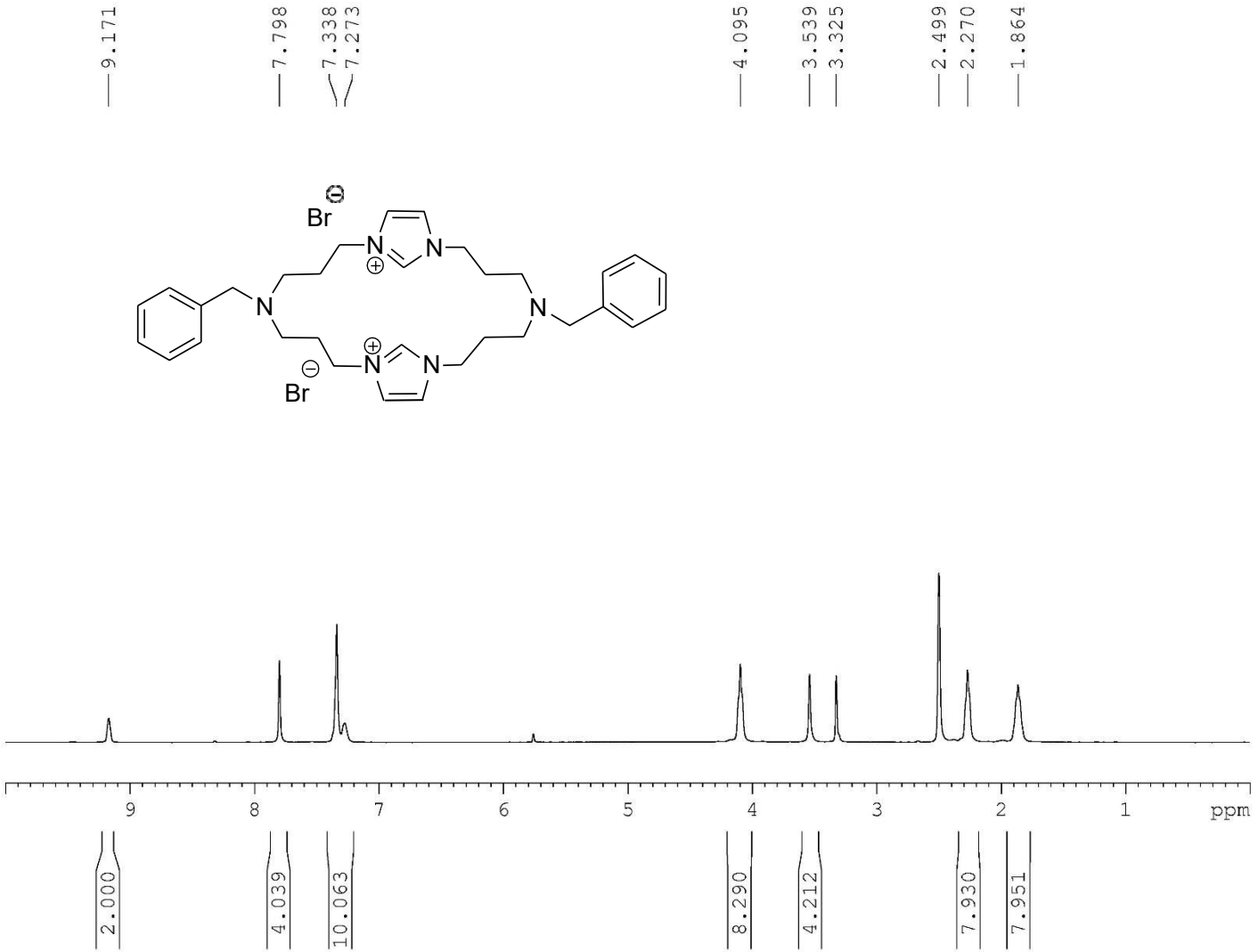
HSQC spectrum of **2b** in $CDCl_3$ (Full spectrum)



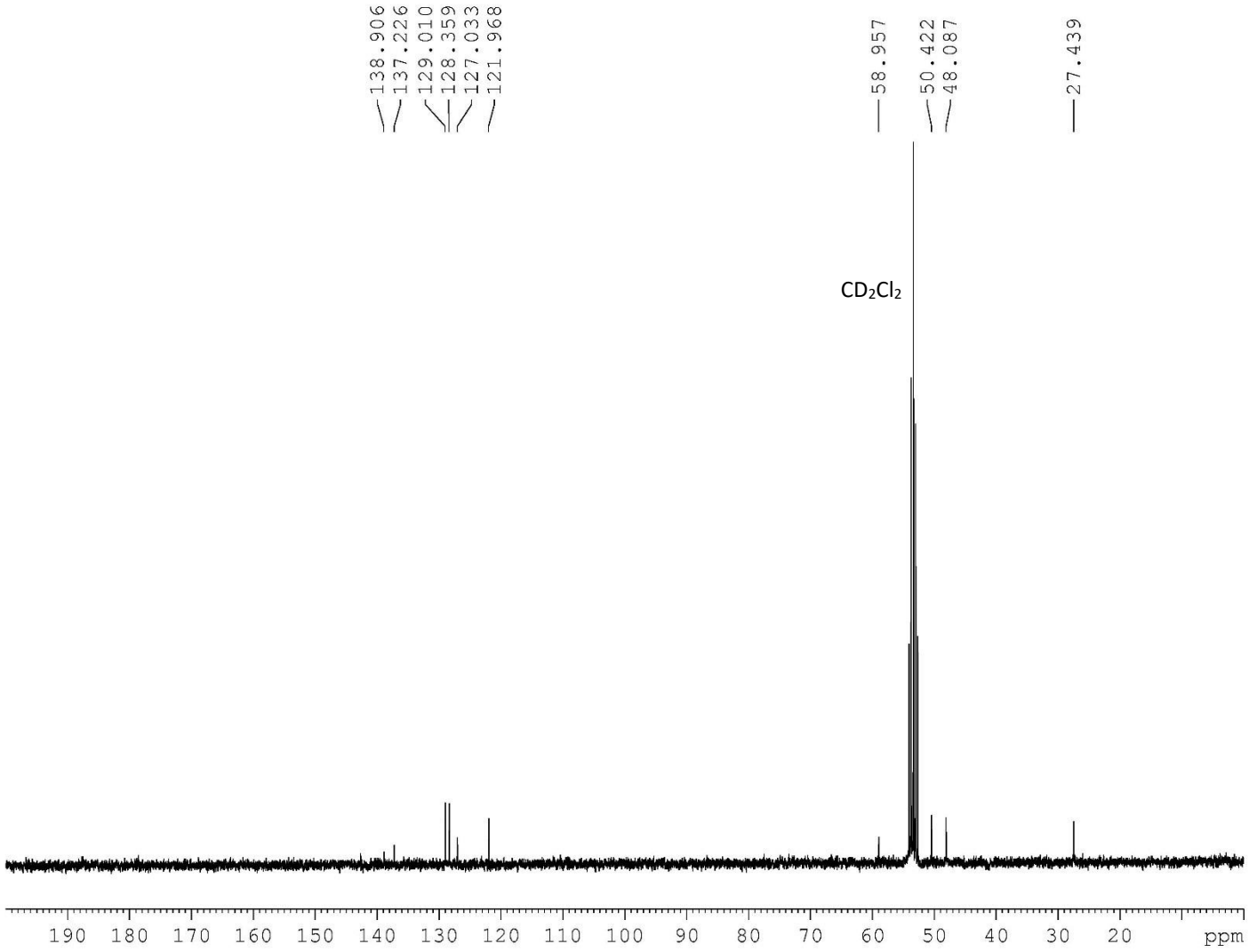
^{1}H NMR (CD_2Cl_2, Compound **3a**, 400 MHz)



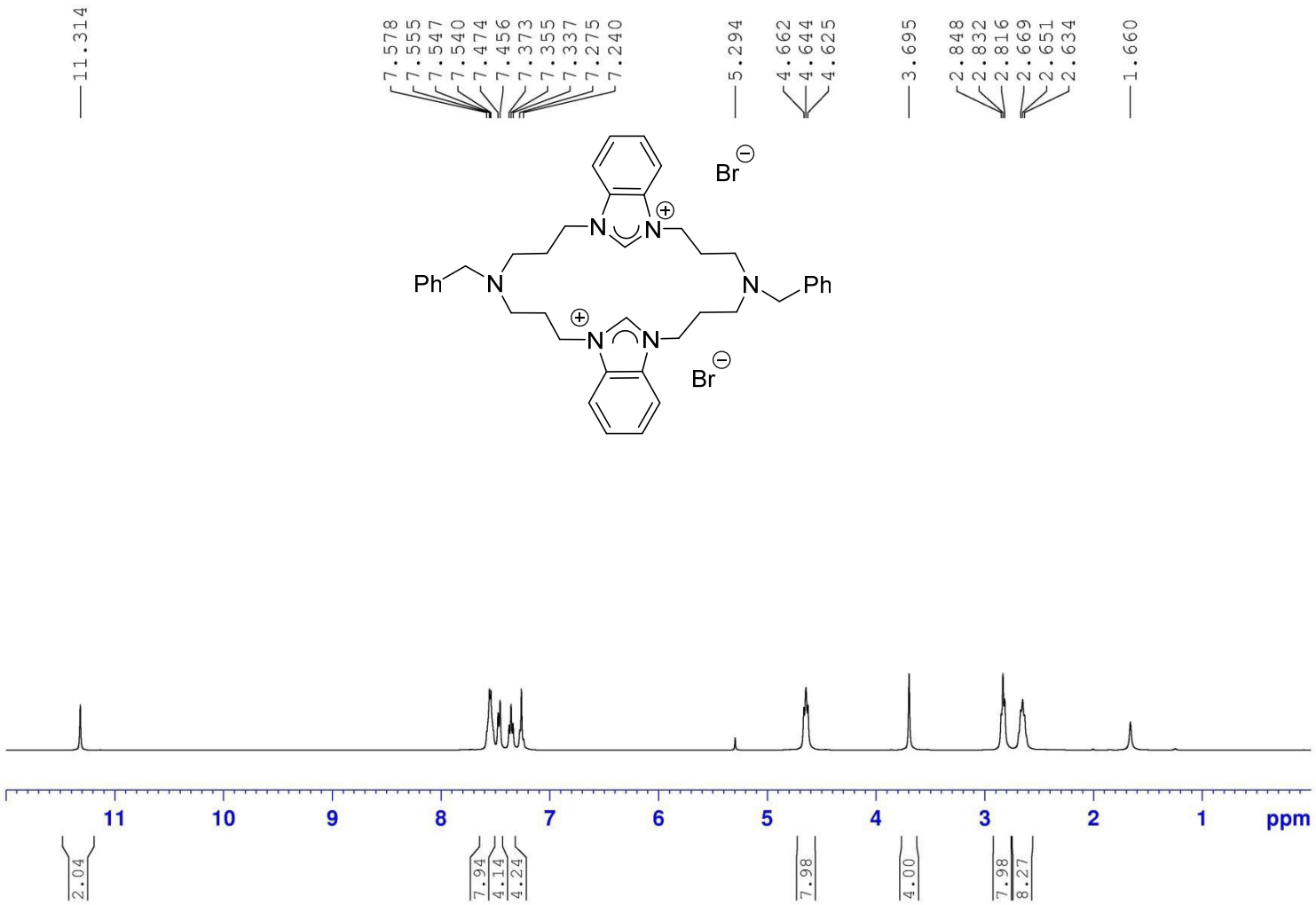
^{1}H NMR (CD_3SOCD_3, Compound **3a**, 400 MHz)



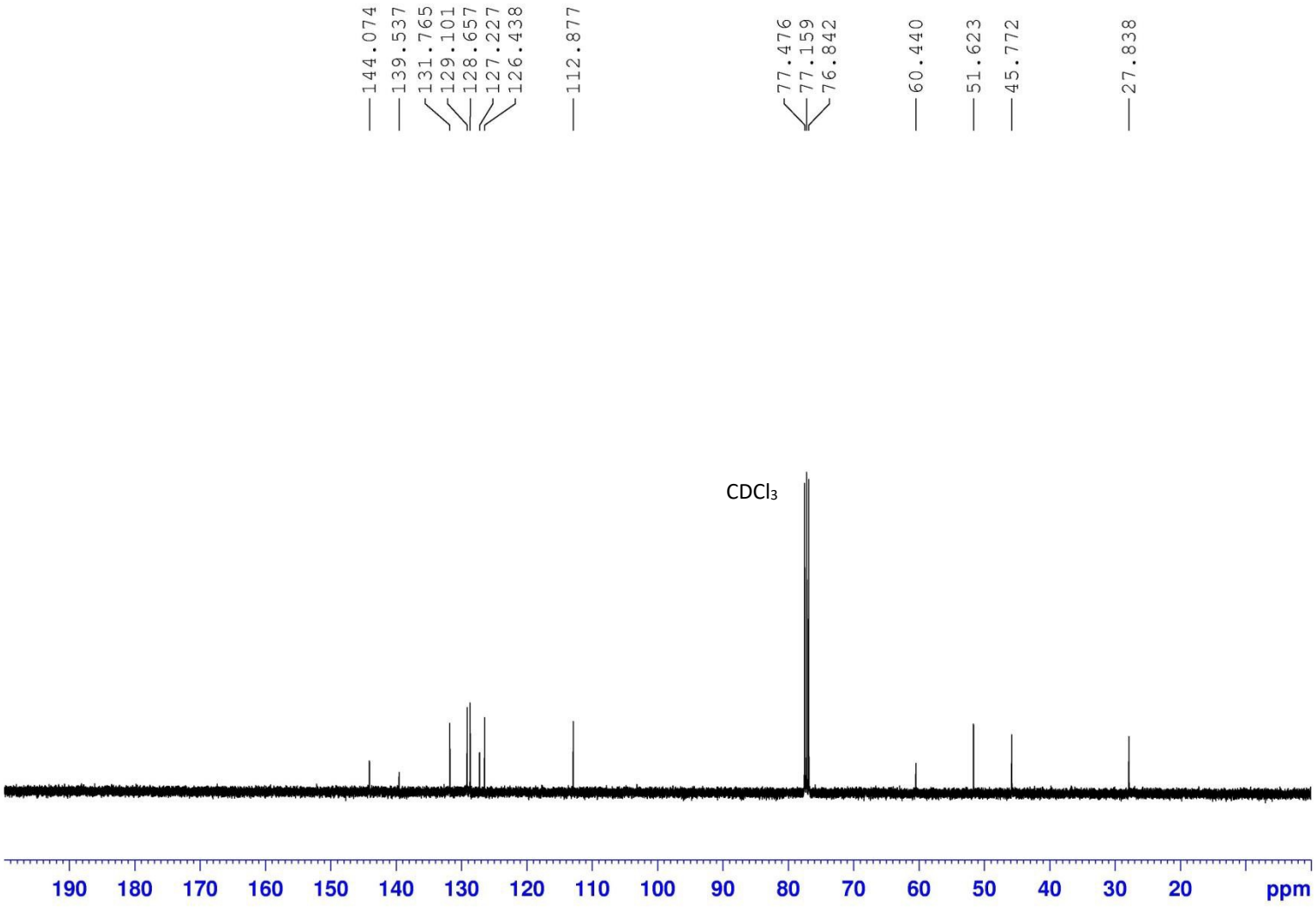
^{13}C NMR (CD_2Cl_2, Compound **3a**, 400 MHz)



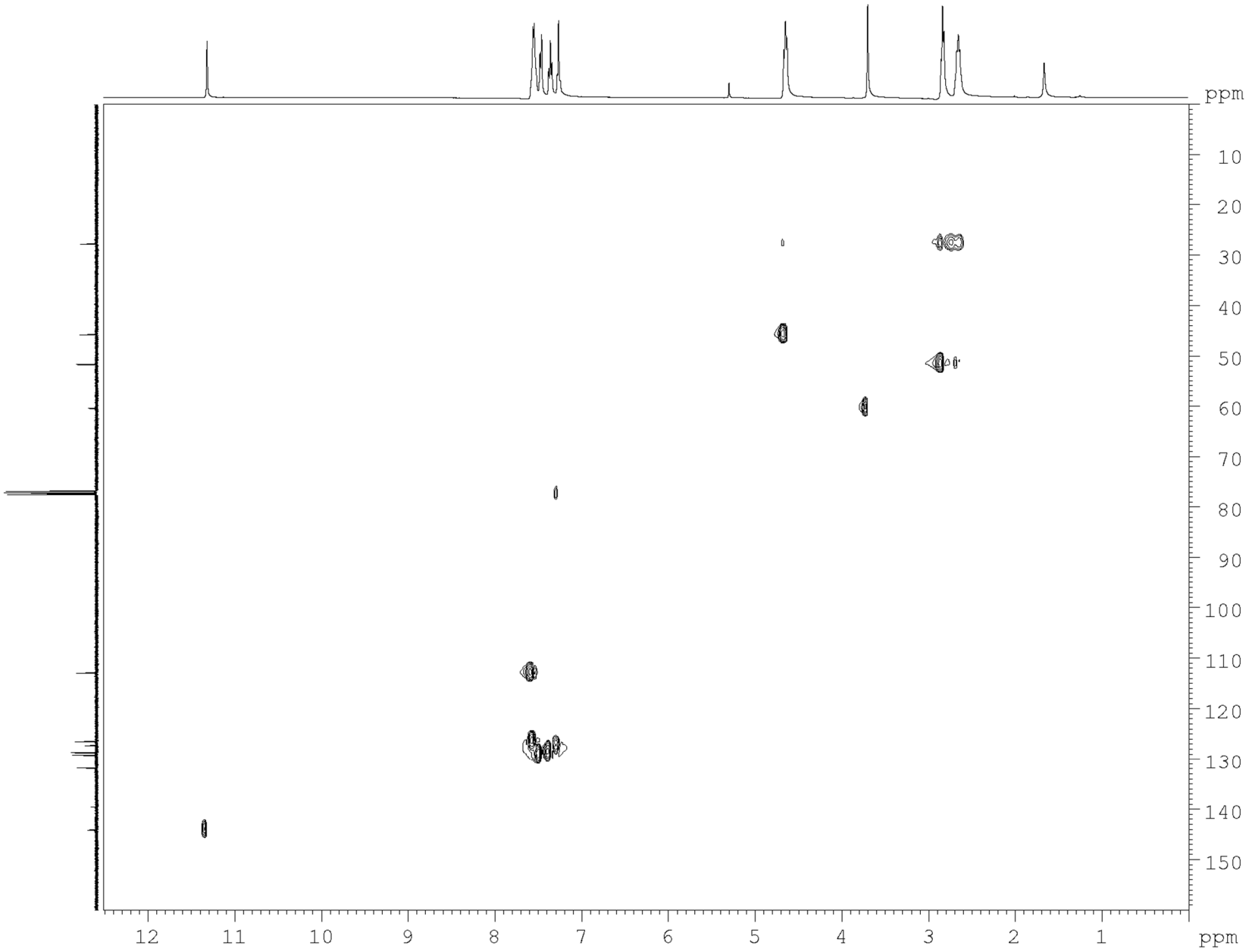
^{1}H NMR ($CDCl_3$, Compound **3b**, 400 MHz)



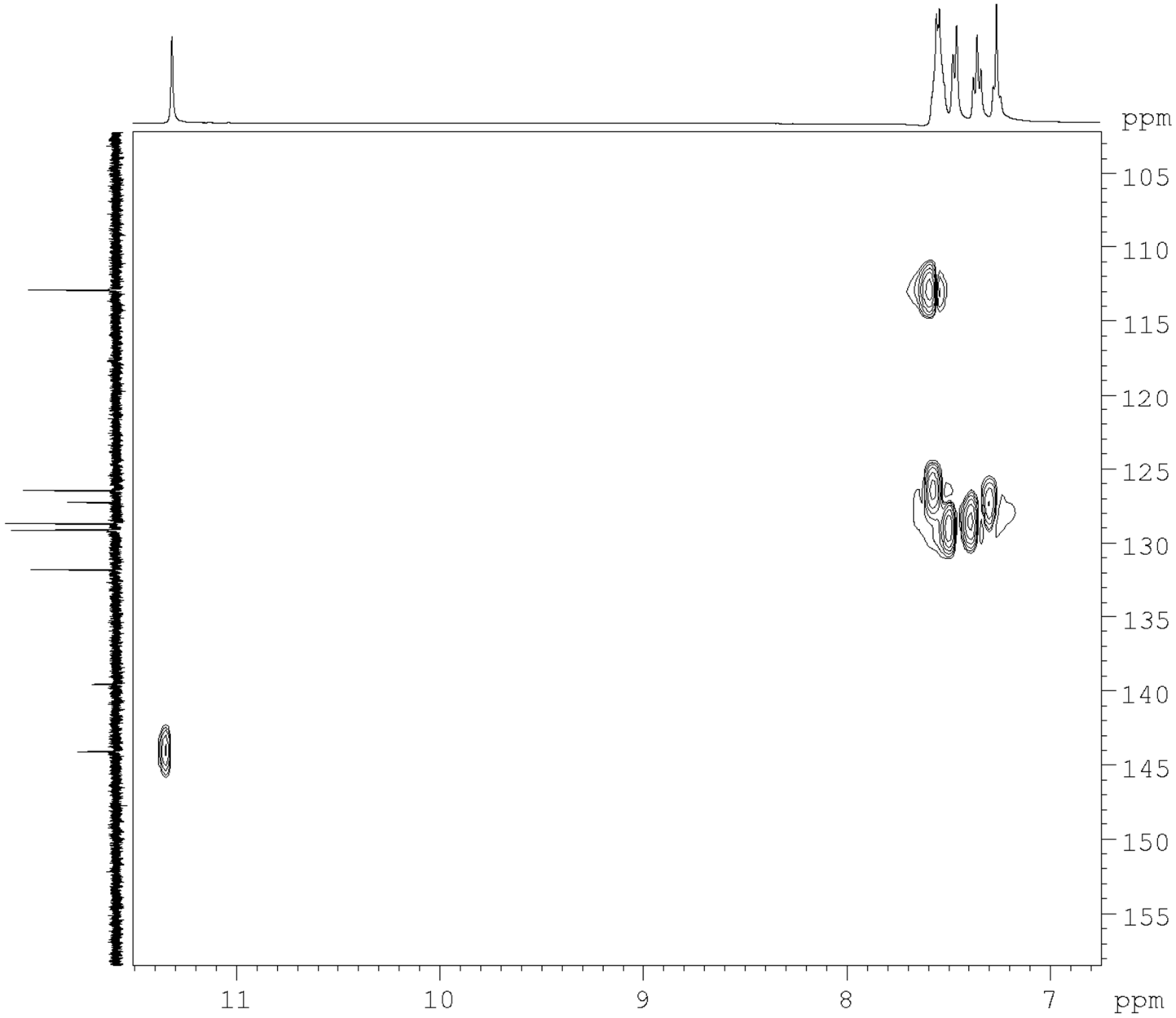
^{13}C NMR ($CDCl_3$, Compound **3b**, 400 MHz)



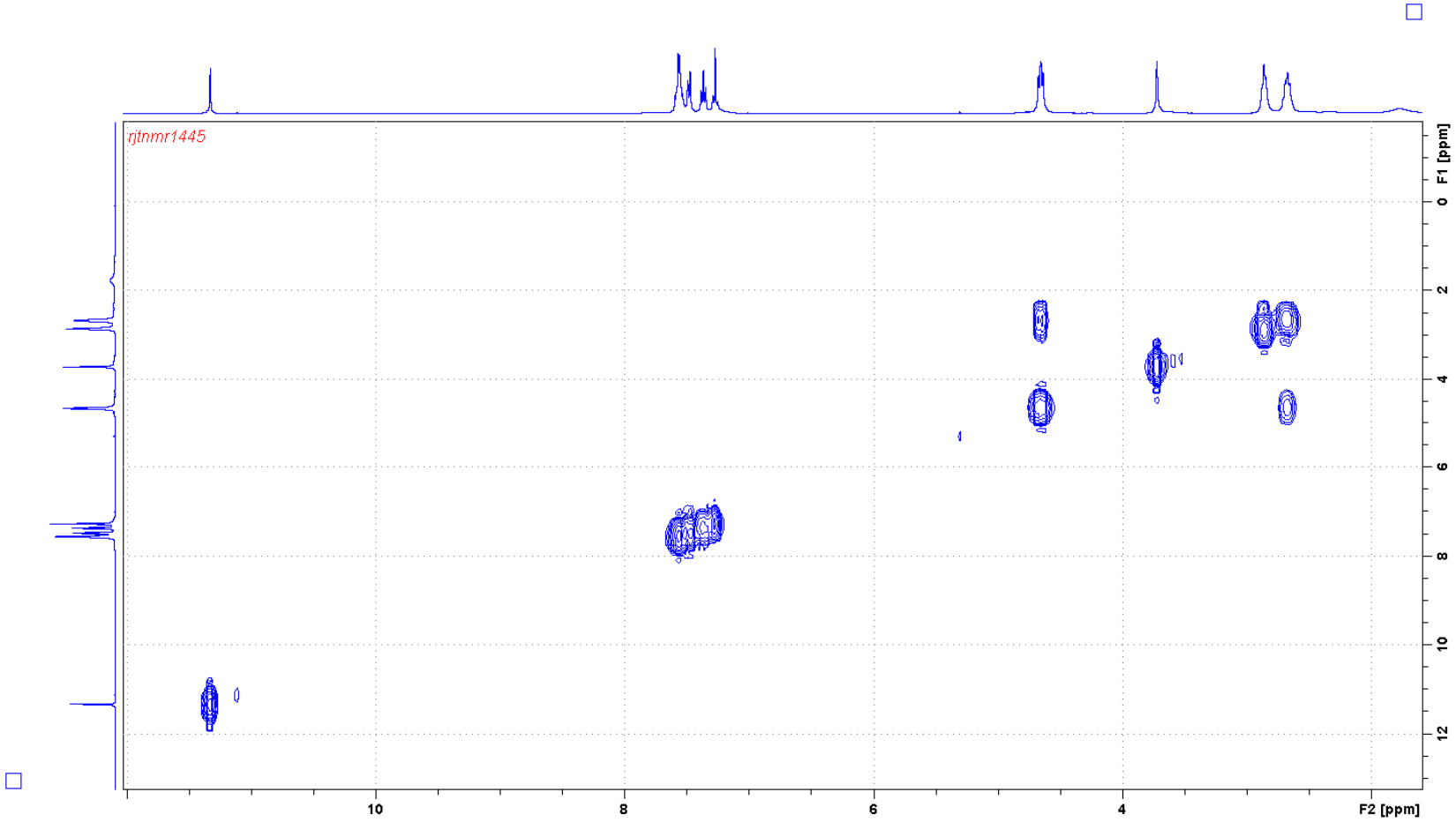
HSQC spectrum of **3b** in $CDCl_3$ (full spectrum)



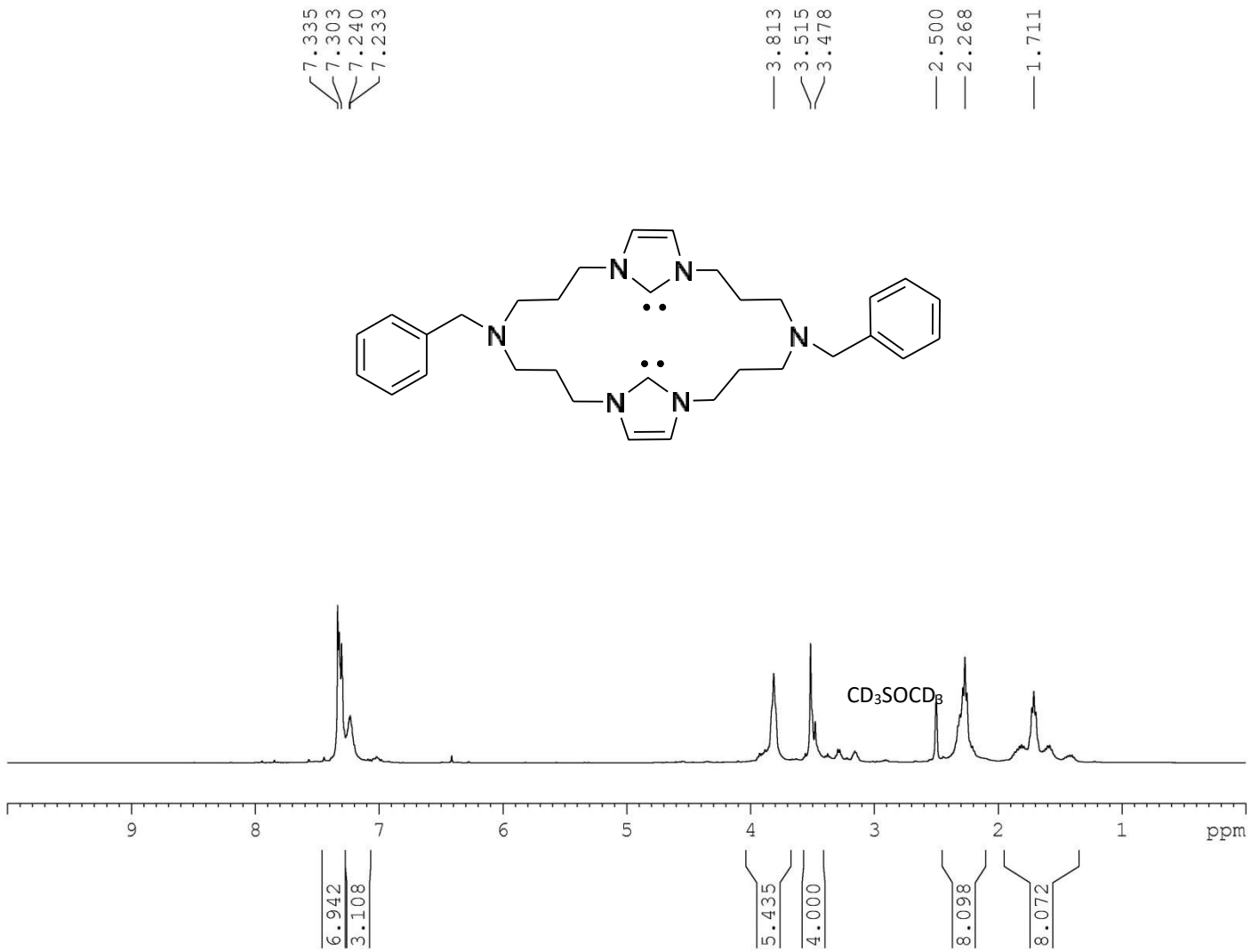
HSQC spectrum of **3b** in $CDCl_3$ (aromatic region)



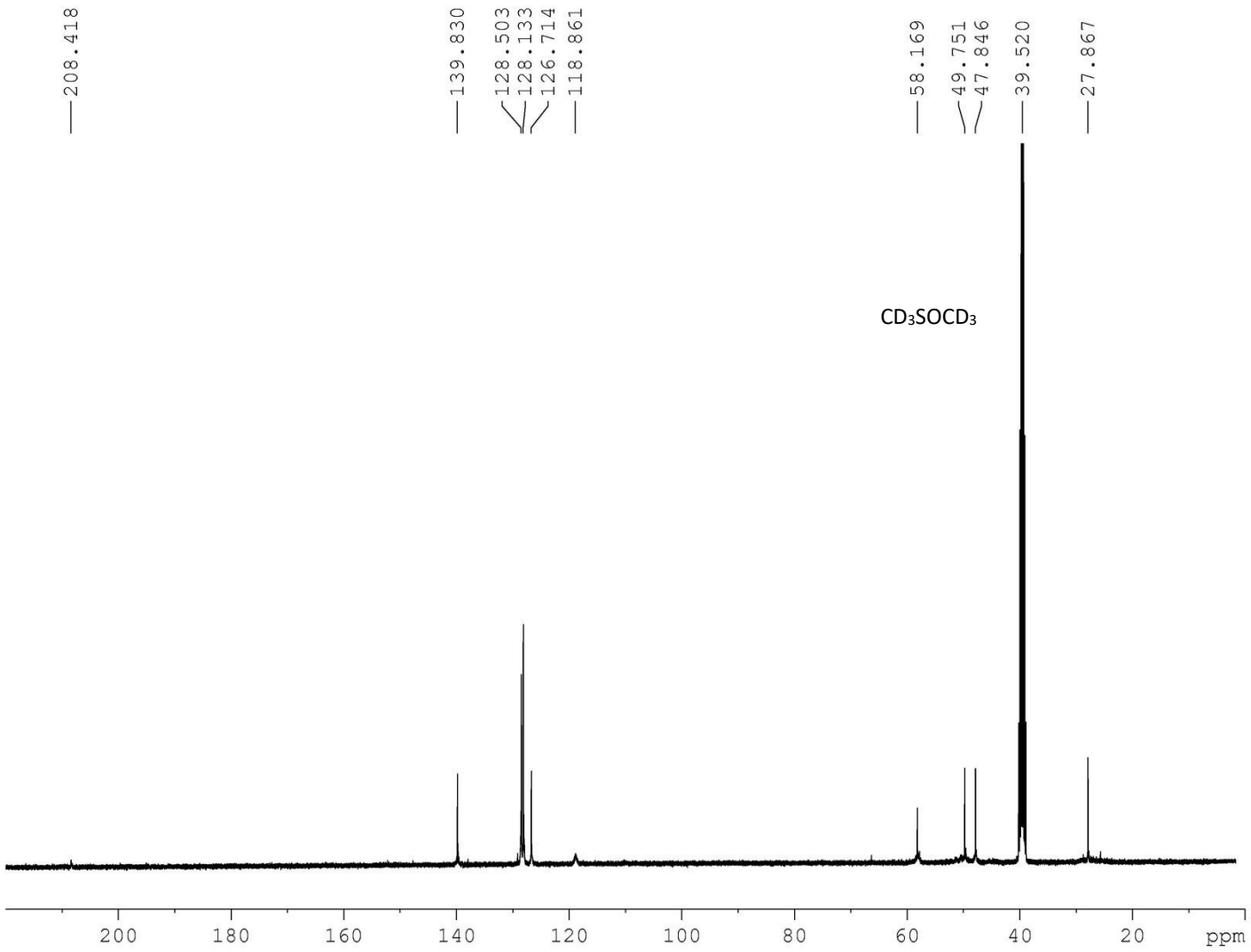
COSY spectrum of **3b** in $CDCl_3$ (full spectrum)



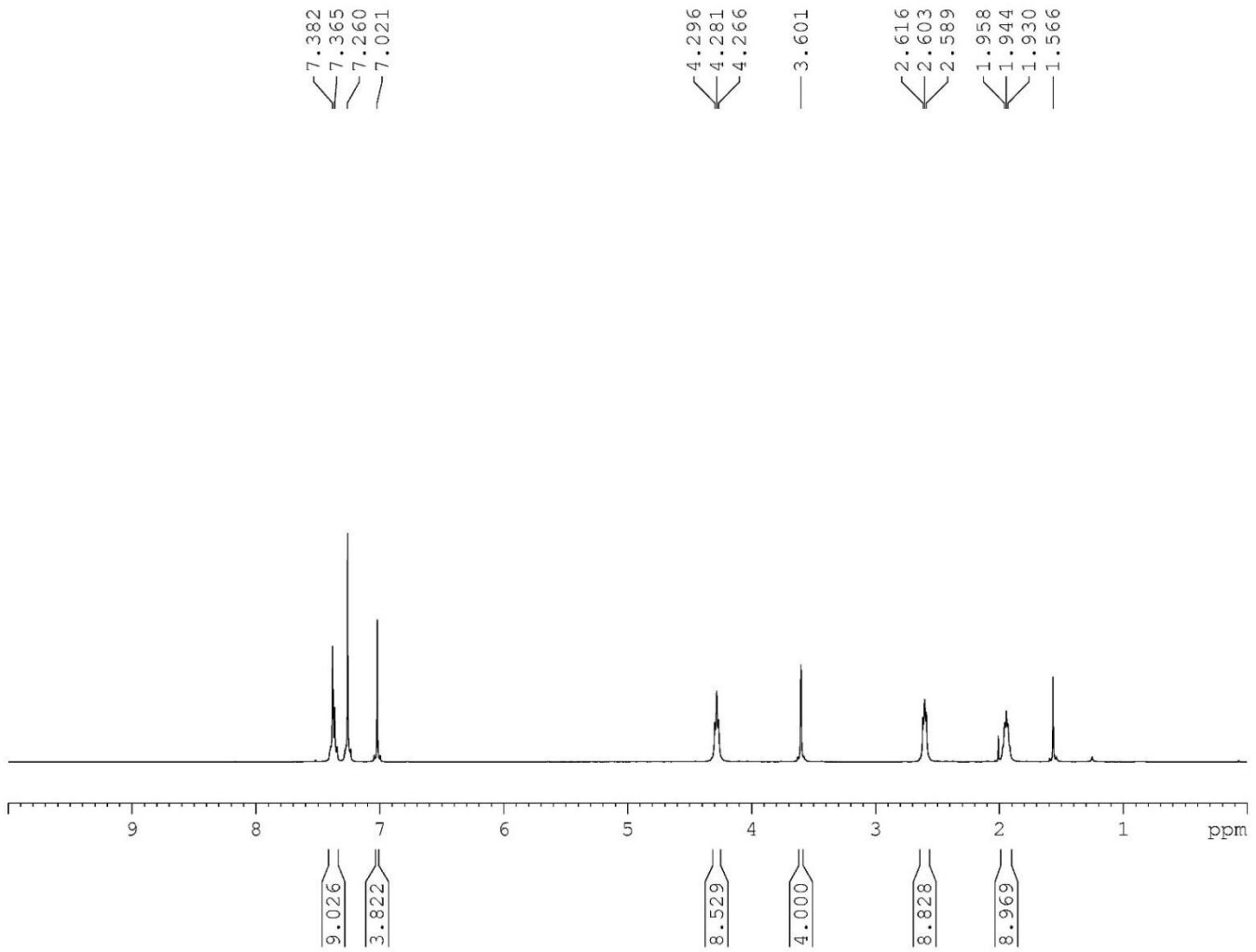
^{1}H NMR (CD_3SOCD_3, Compound **3c in situ**, 400 MHz)



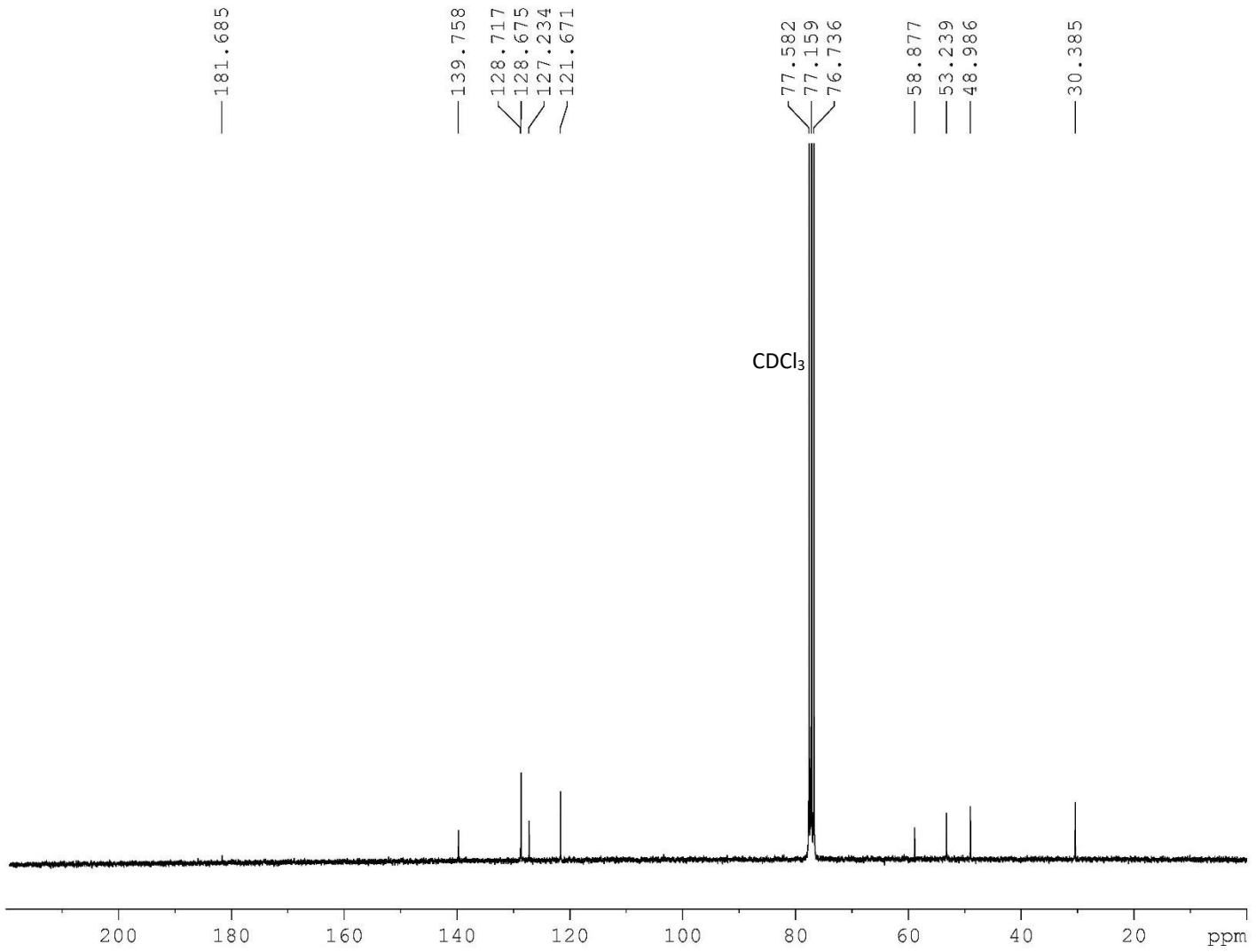
^{13}C NMR (CD_3SOCD_3, Compound **3c in situ**, 400 MHz)



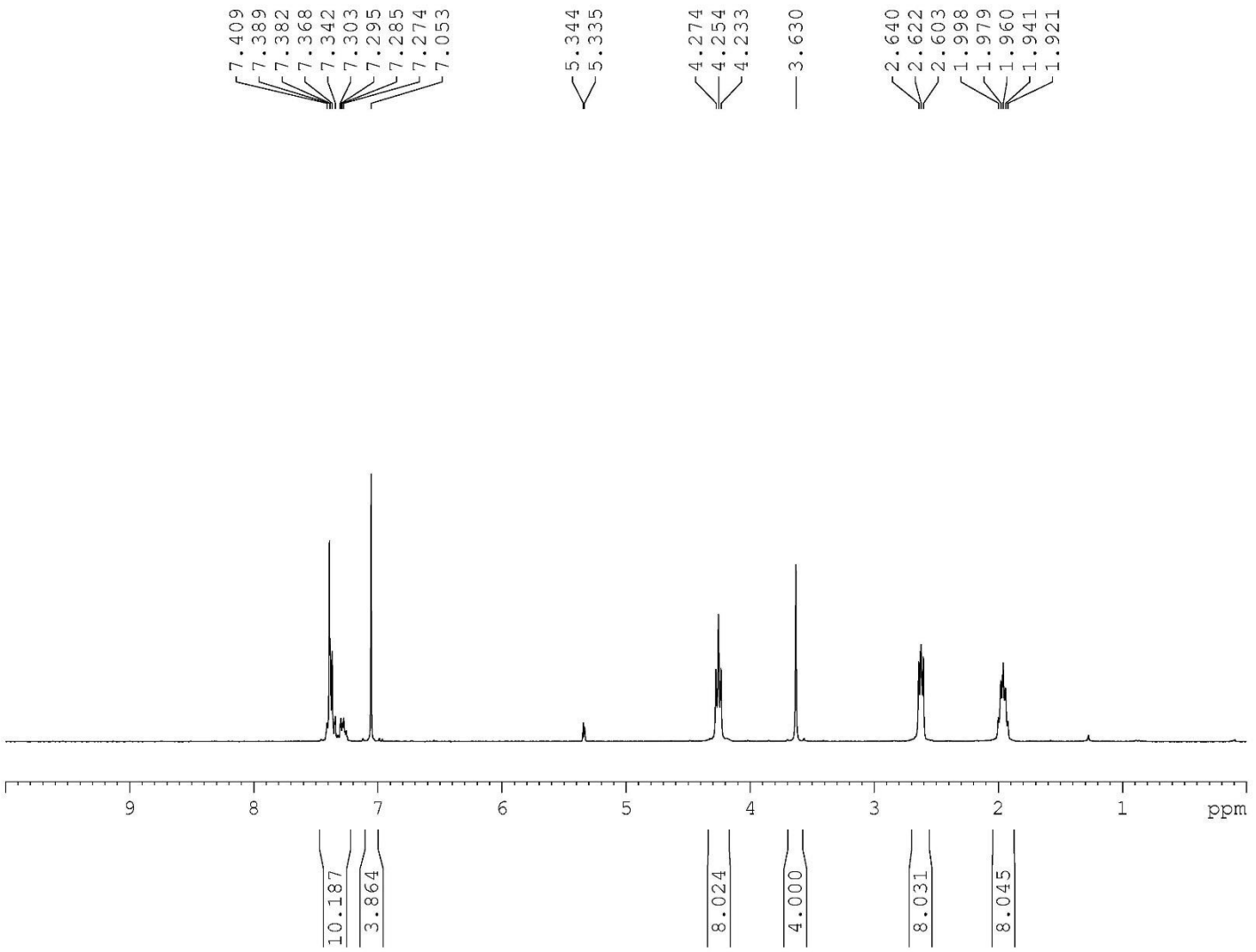
^{1}H NMR ($CDCl_3$, Compound **4a**, 400 MHz)



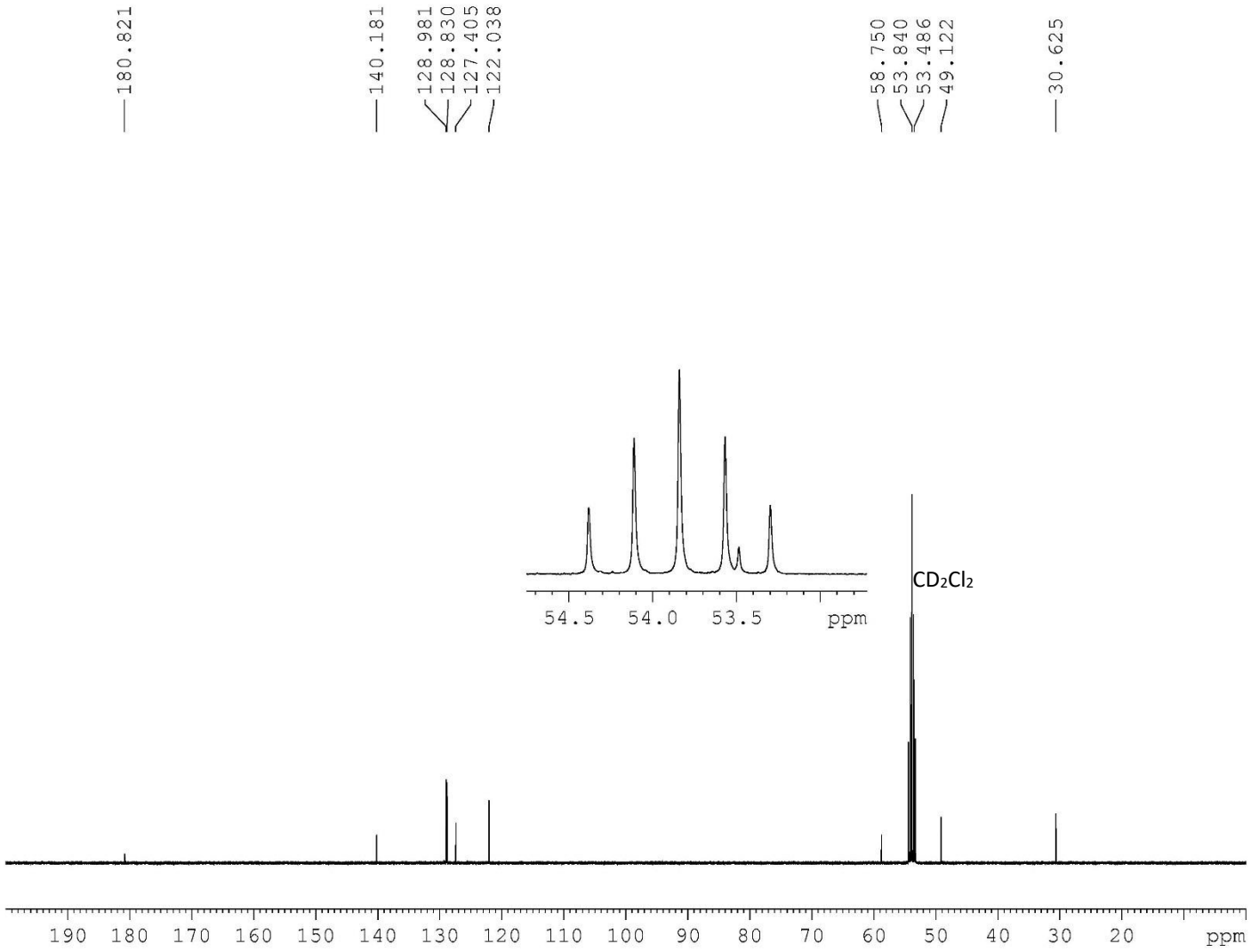
^{13}C NMR ($CDCl_3$, Compound **4a**, 400 MHz)



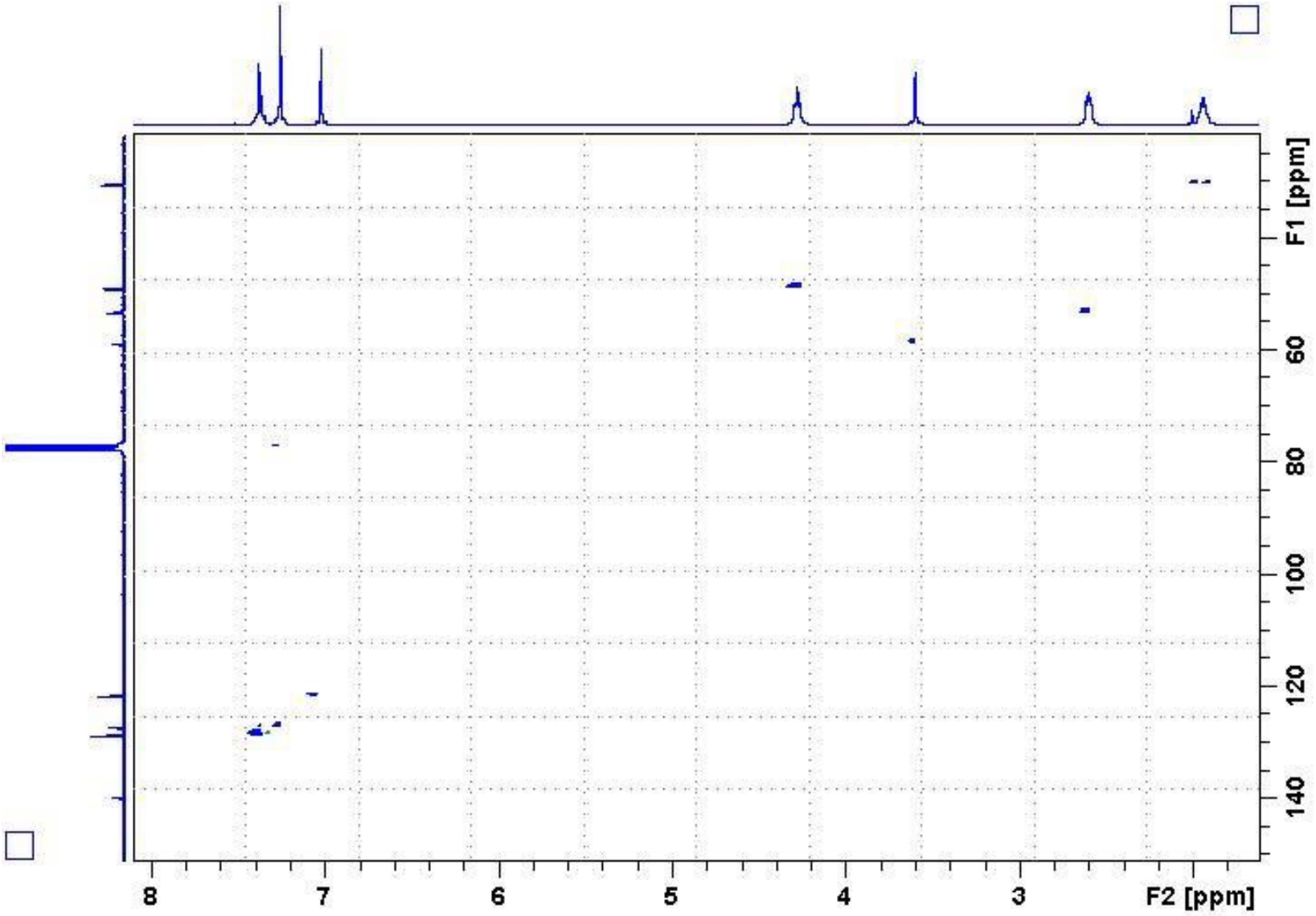
^{1}H NMR (CD_2Cl_2, Compound **4a**, 400 MHz)



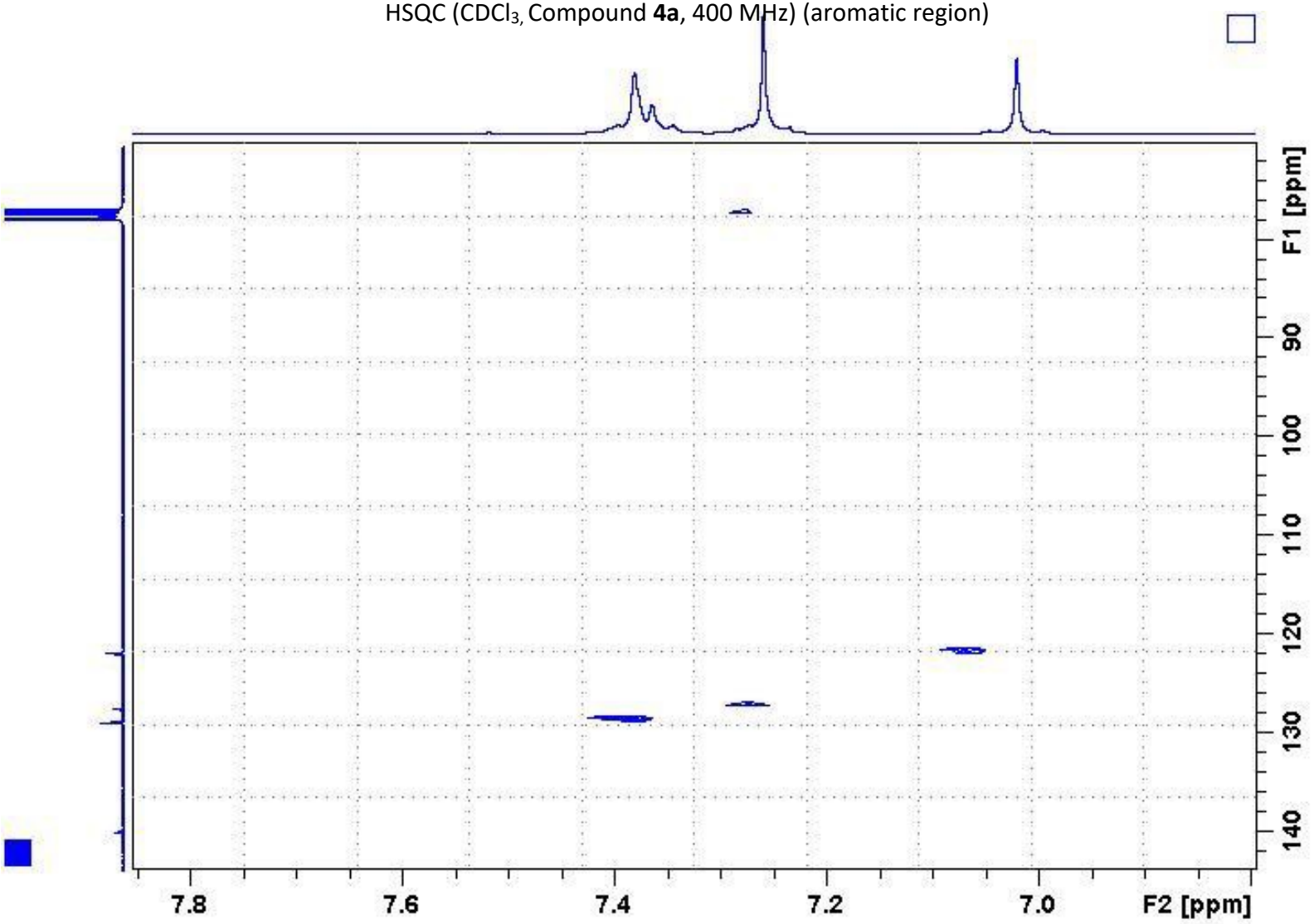
^{13}C NMR (CD_2Cl_2, Compound **4a**, 400 MHz)



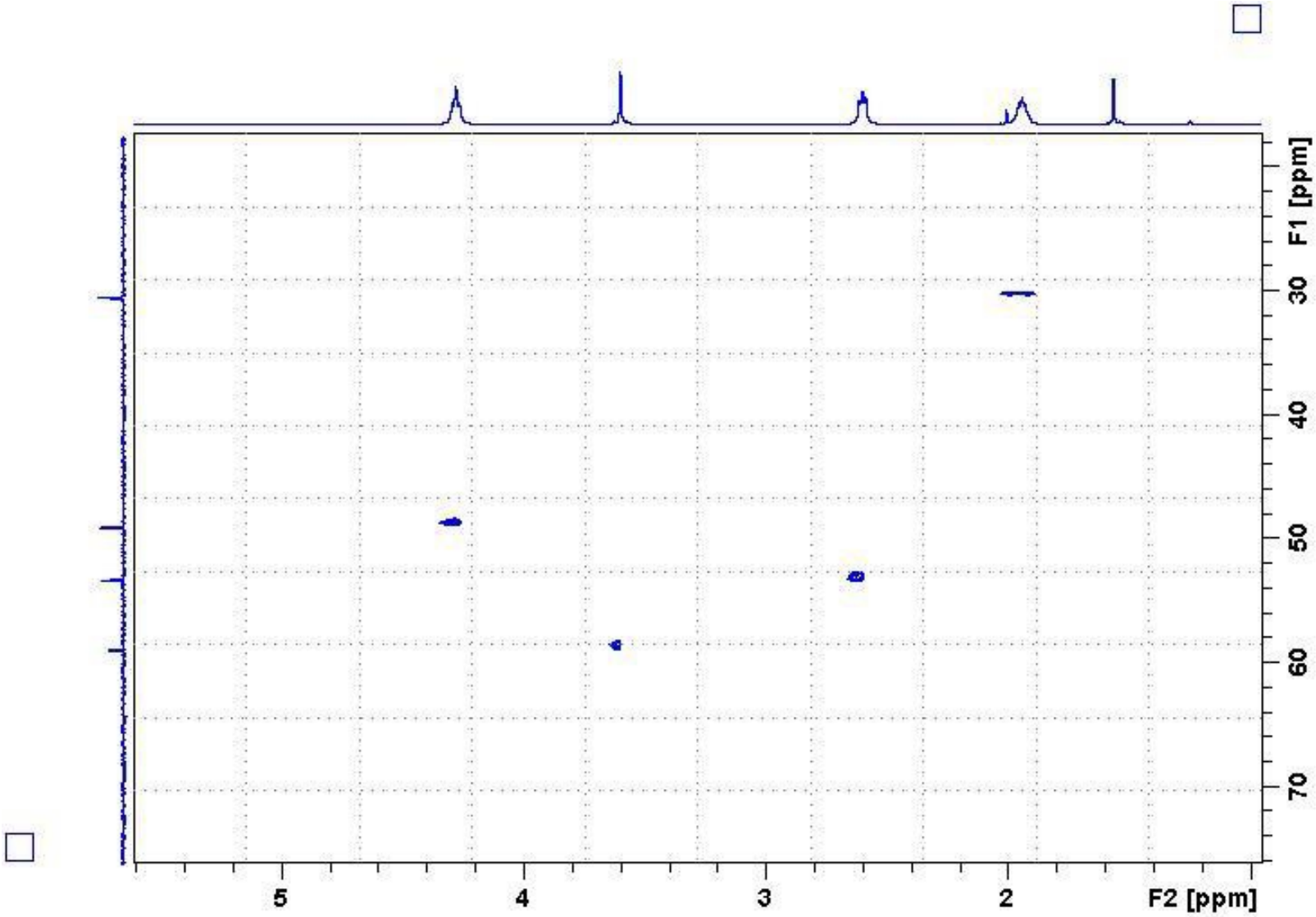
HSQC ($CDCl_3$, Compound **4a**, 400 MHz) (Full spectrum)



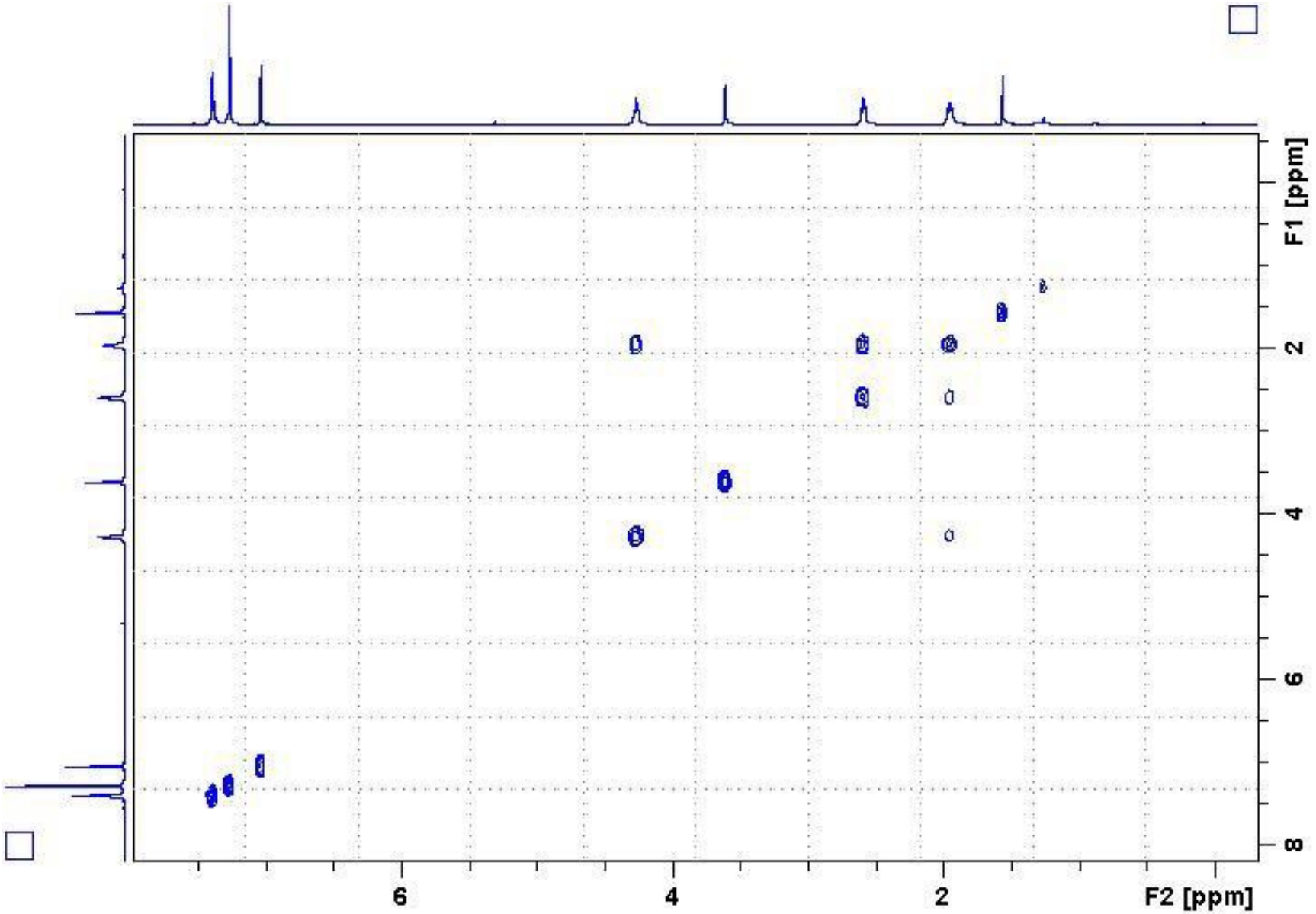
HSQC ($CDCl_3$, Compound **4a**, 400 MHz) (aromatic region)



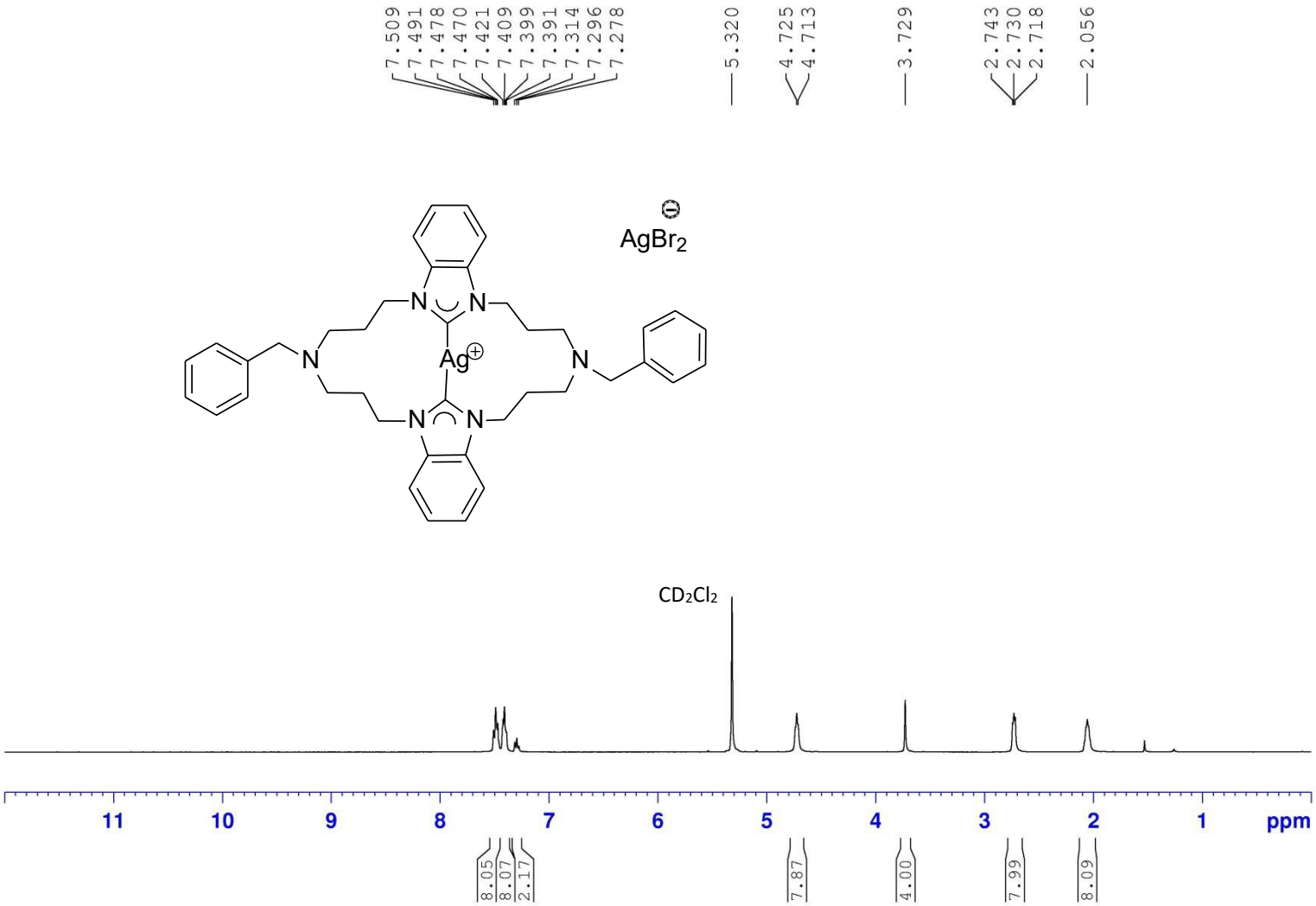
HSQC ($CDCl_3$, Compound **4a**, 400 MHz) (aliphatic region)



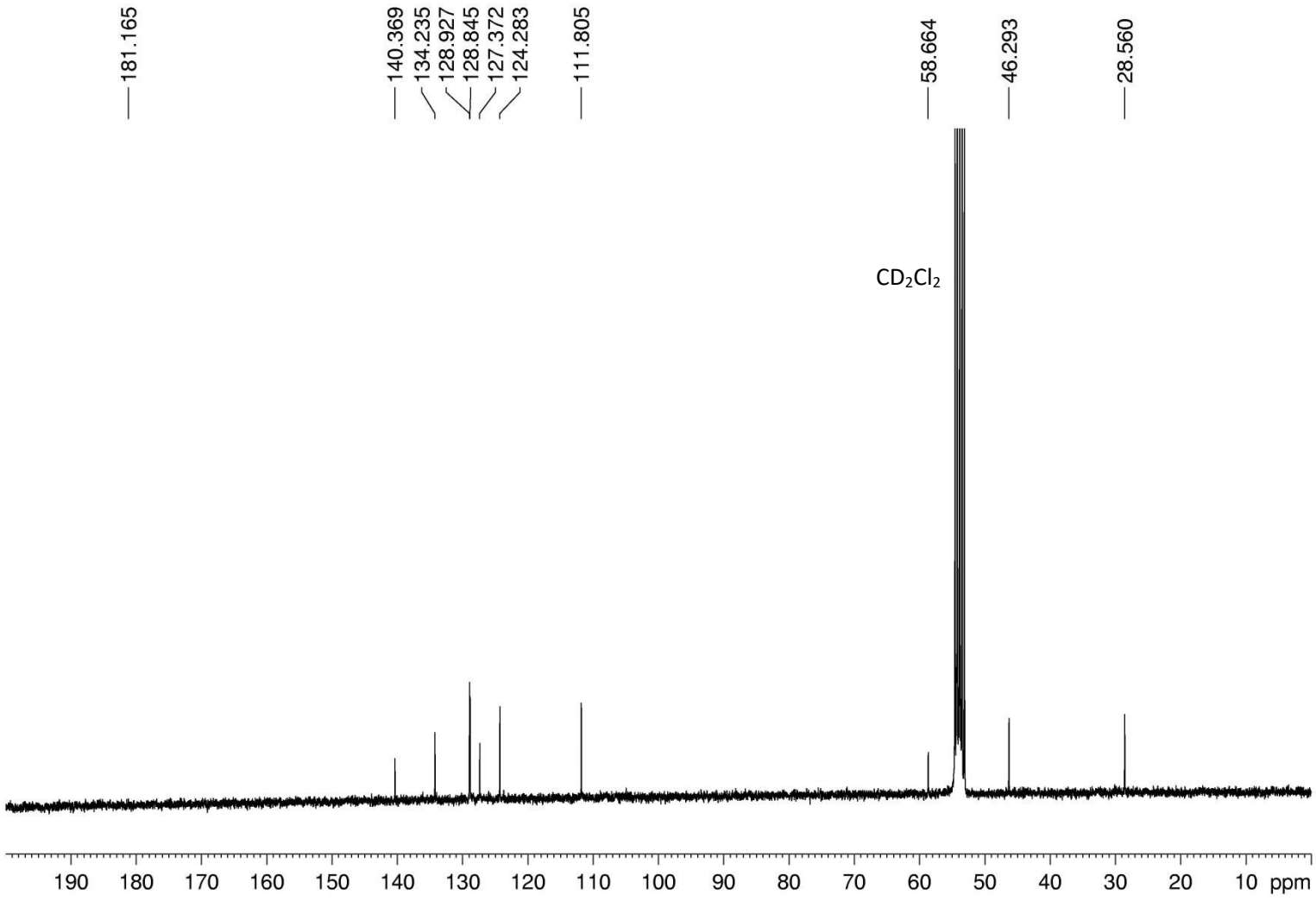
COSY ($CDCl_3$, Compound **4a**, 400 MHz)



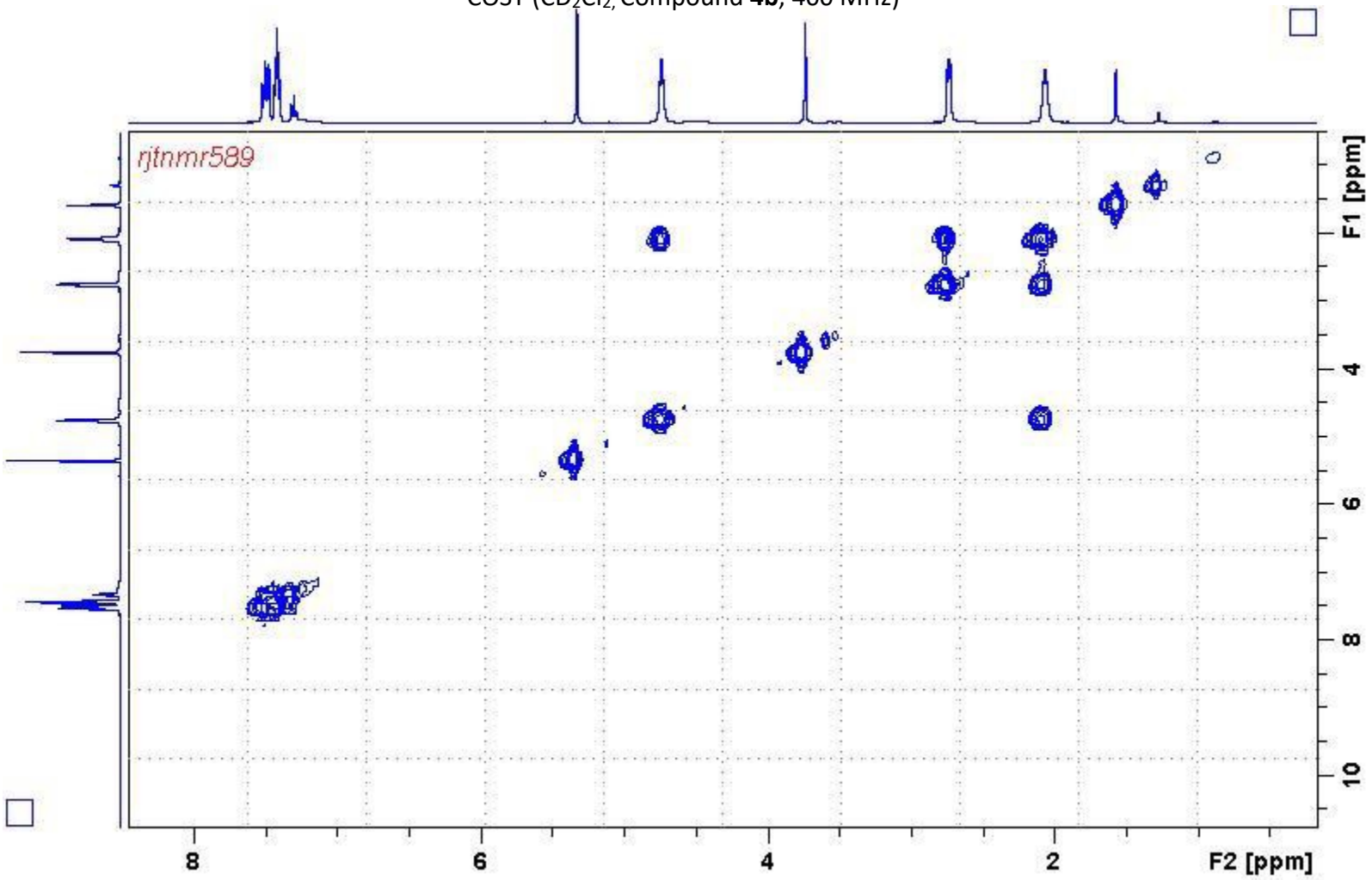
^{1}H NMR (CD_2Cl_2, Compound **4b**, 400 MHz)



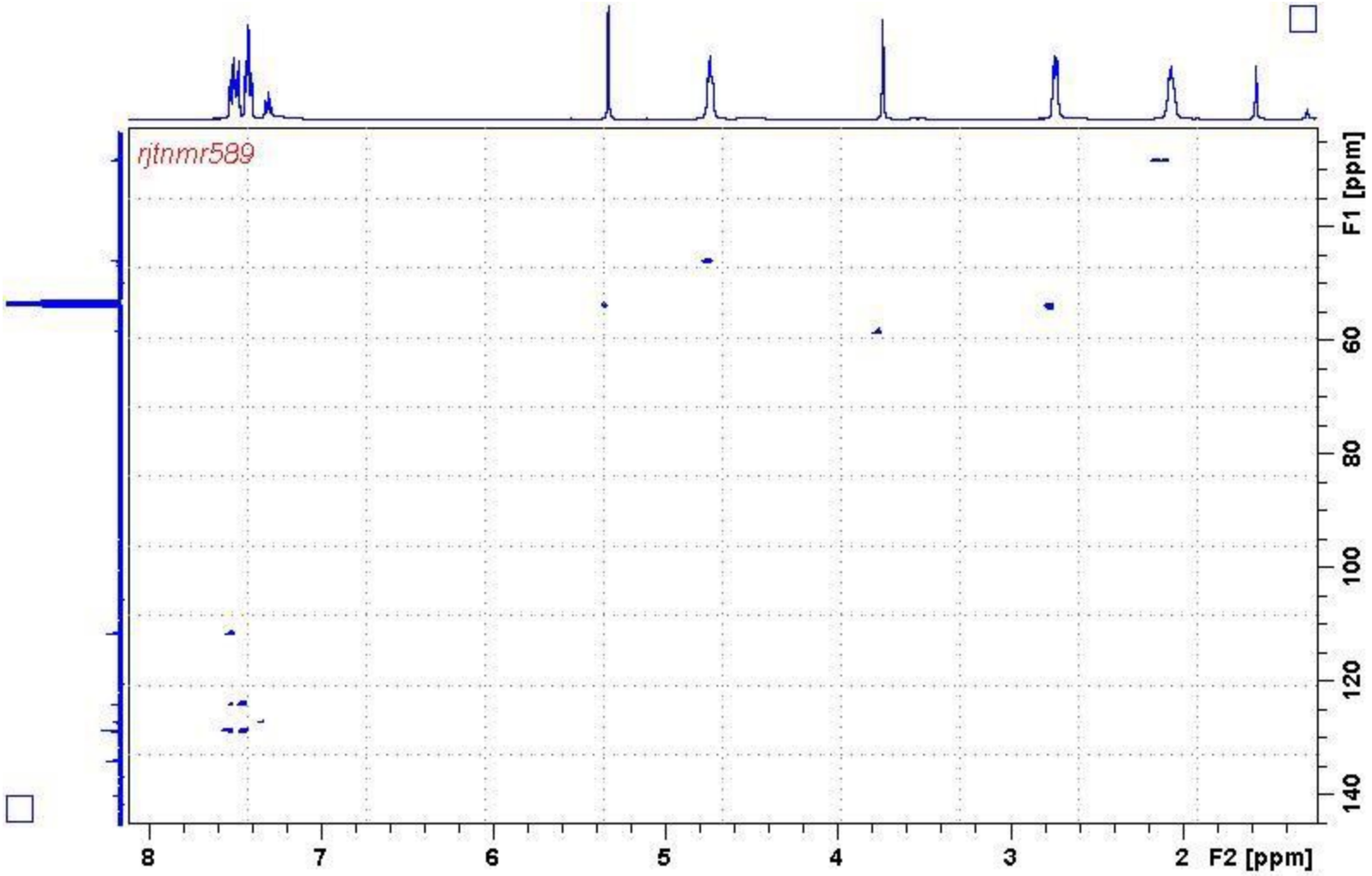
^{13}C NMR (CD_2Cl_2, Compound **4b**, 400 MHz)



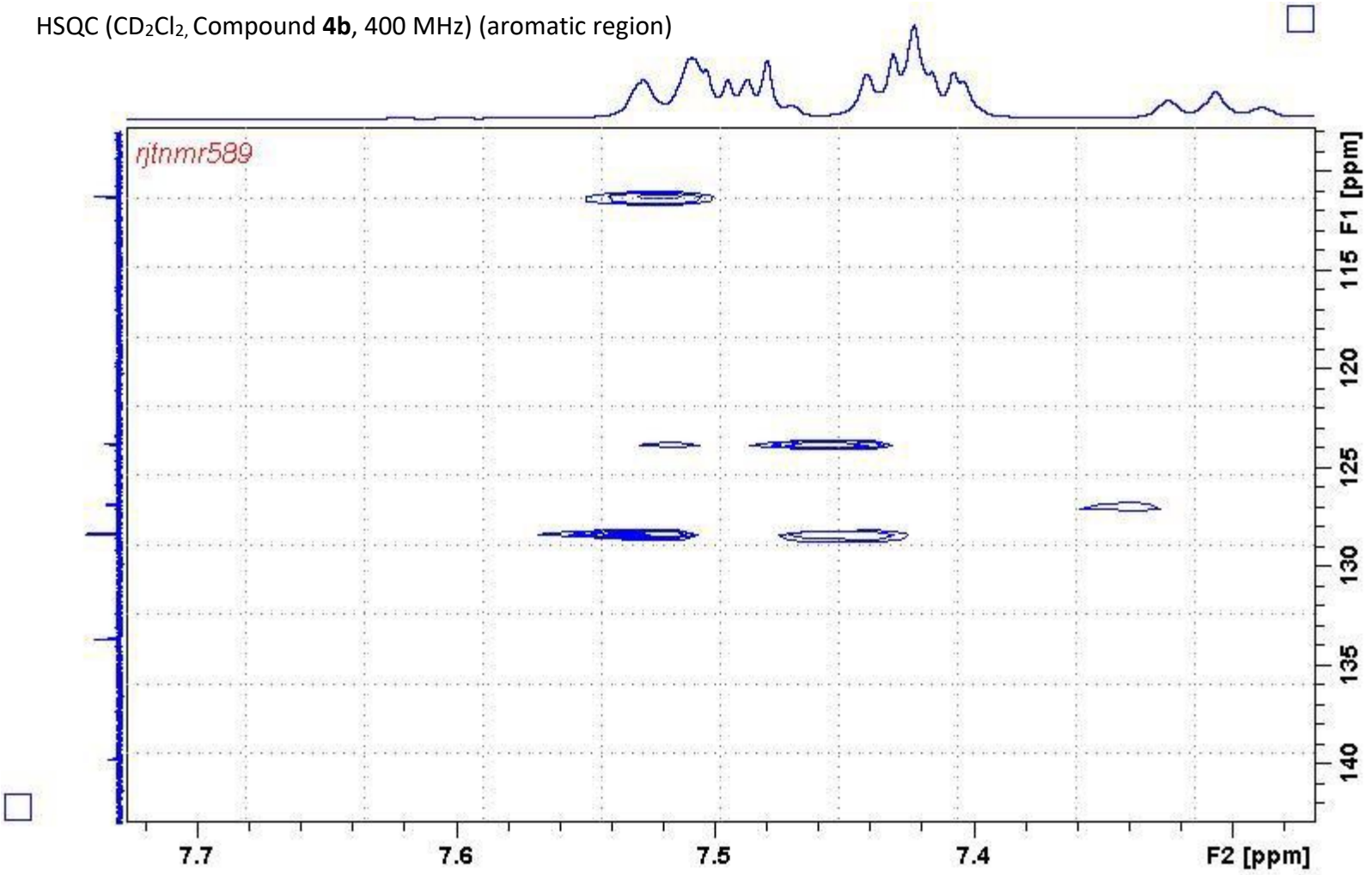
COSY (CD_2Cl_2, Compound **4b**, 400 MHz)



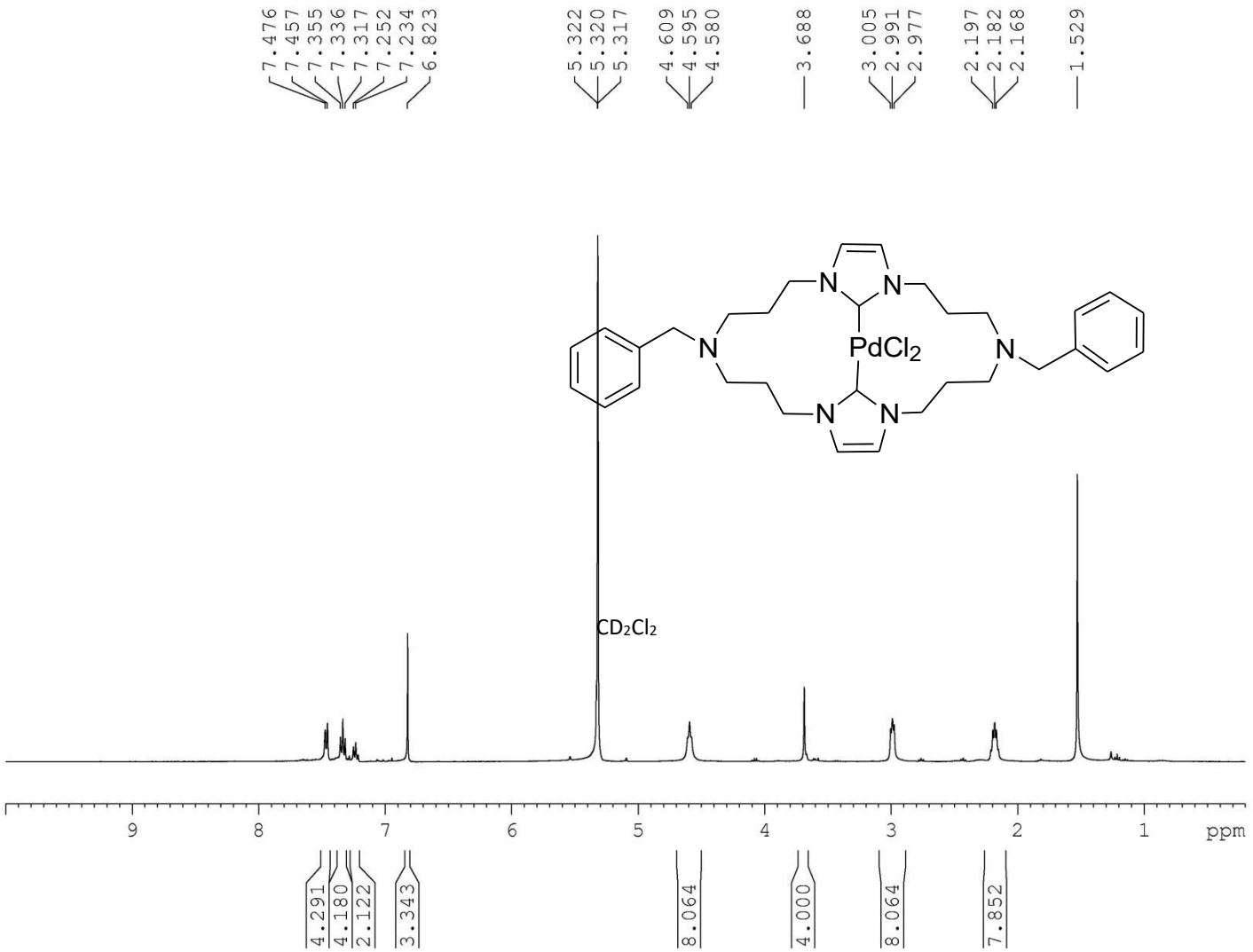
HSQC (CD_2Cl_2, Compound **4b**, 400 MHz) (full spectrum)



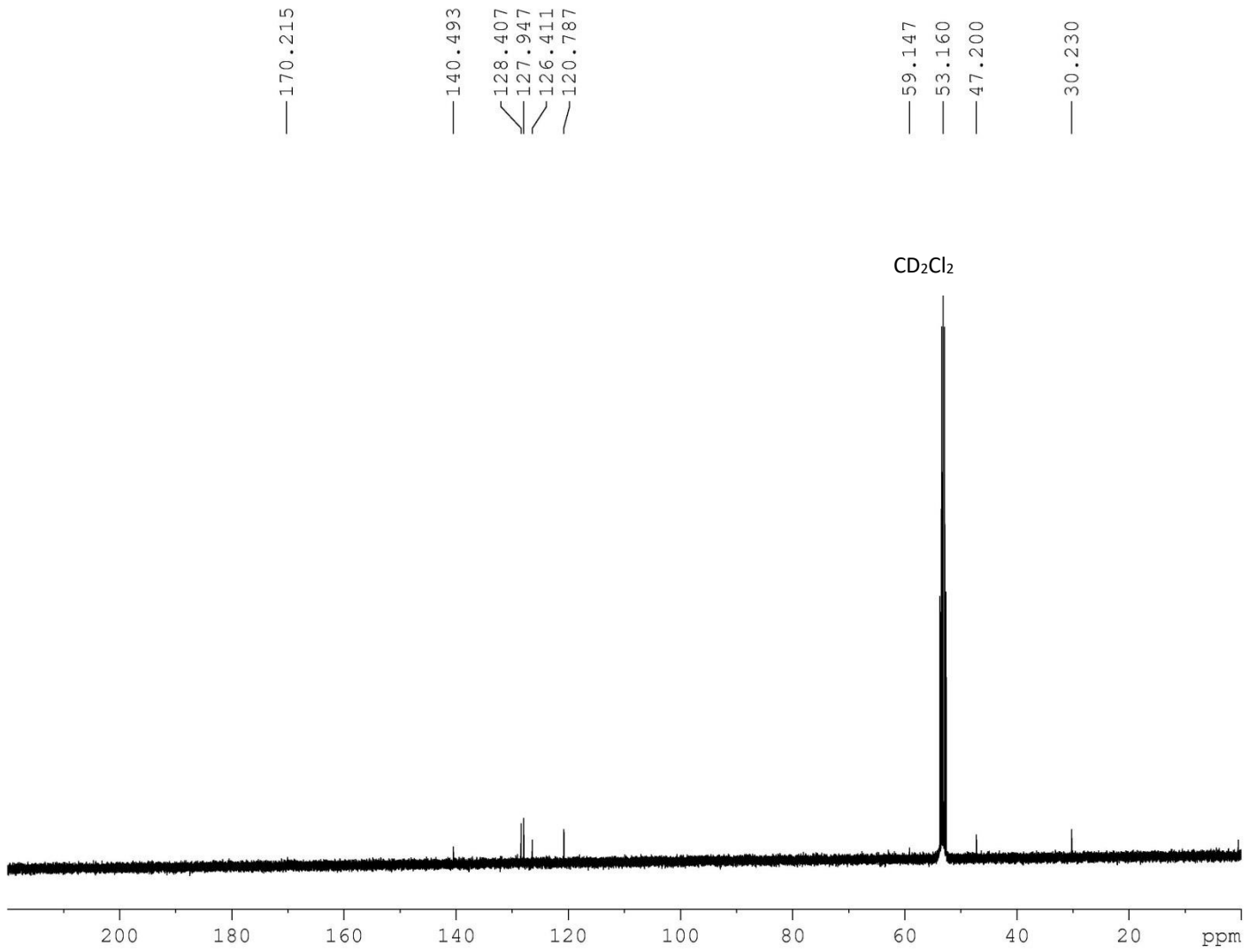
HSQC (CD_2Cl_2, Compound **4b**, 400 MHz) (aromatic region)



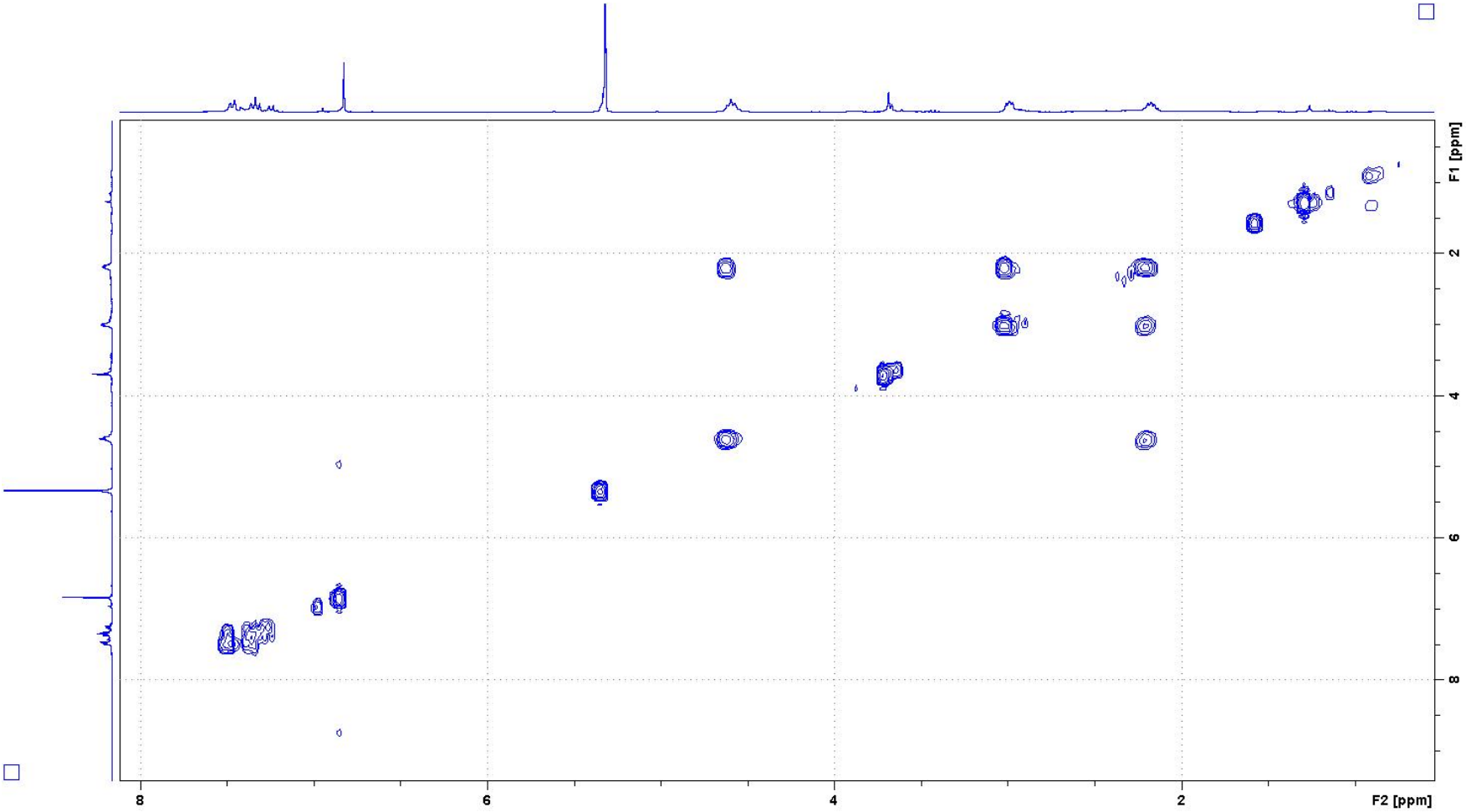
^{1}H NMR (CD_2Cl_2, Compound **5a**, 400 MHz)



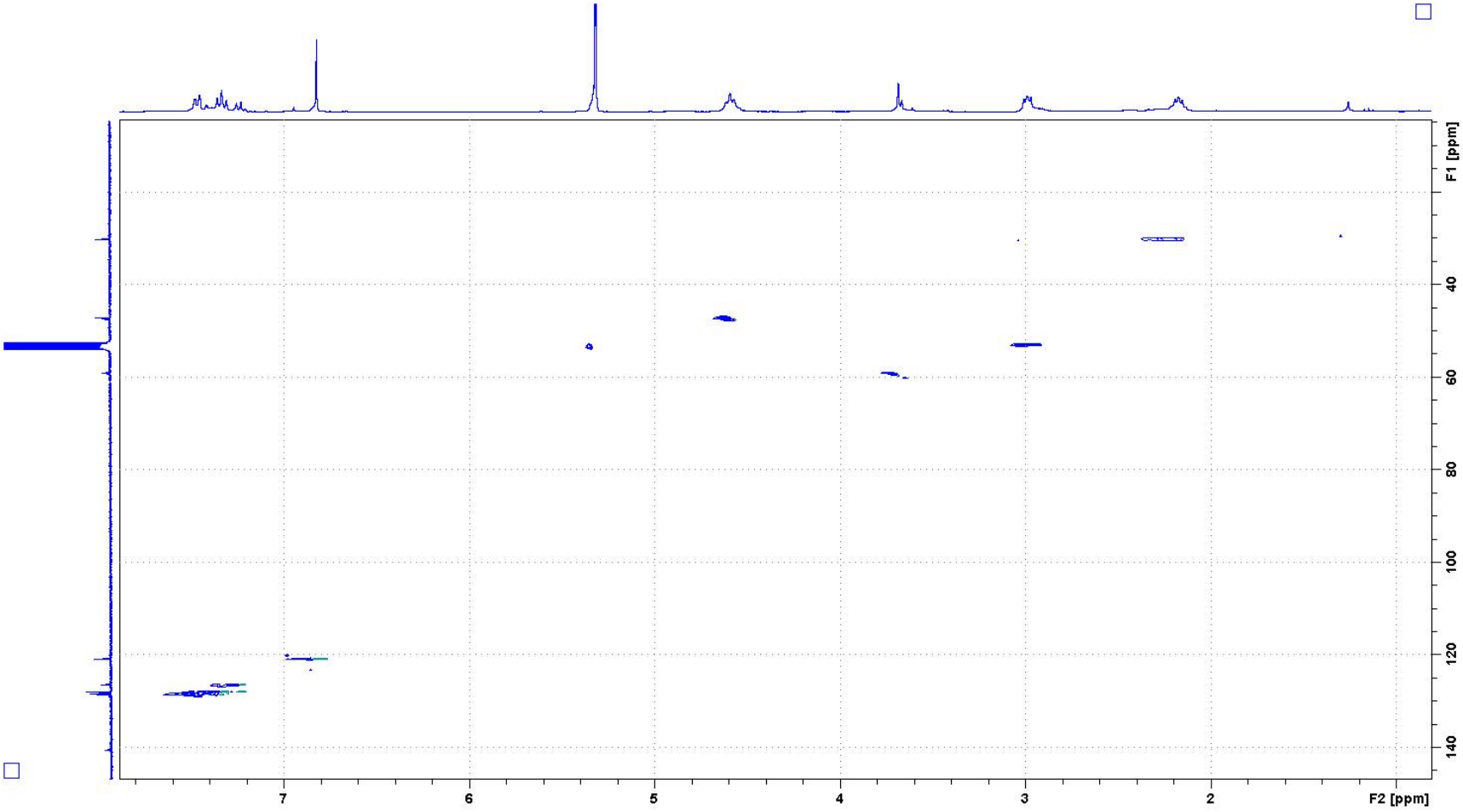
^{13}C NMR (CD_2Cl_2, Compound **5a**, 300 MHz)



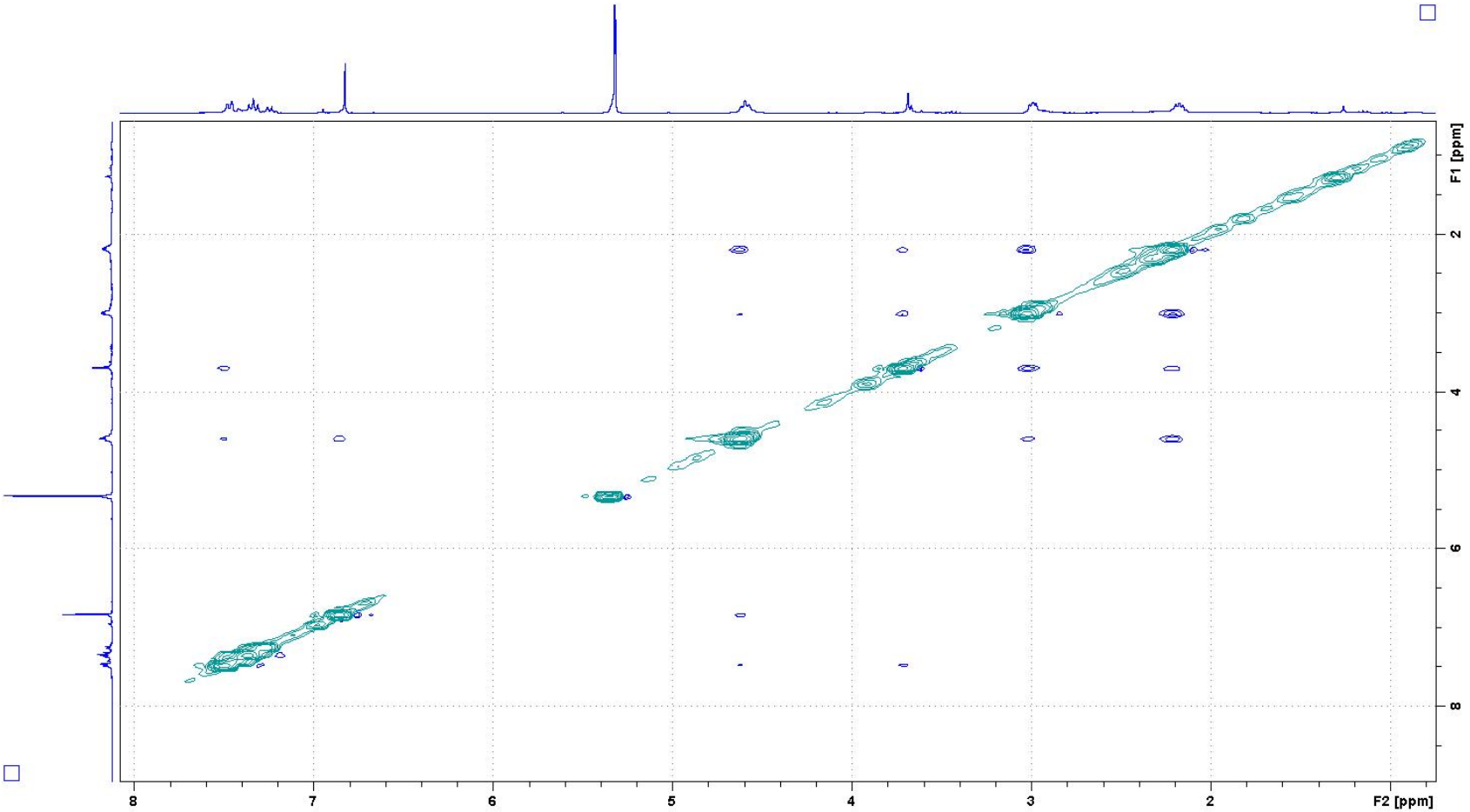
COSY spectrum of **5a** in CD_2Cl_2



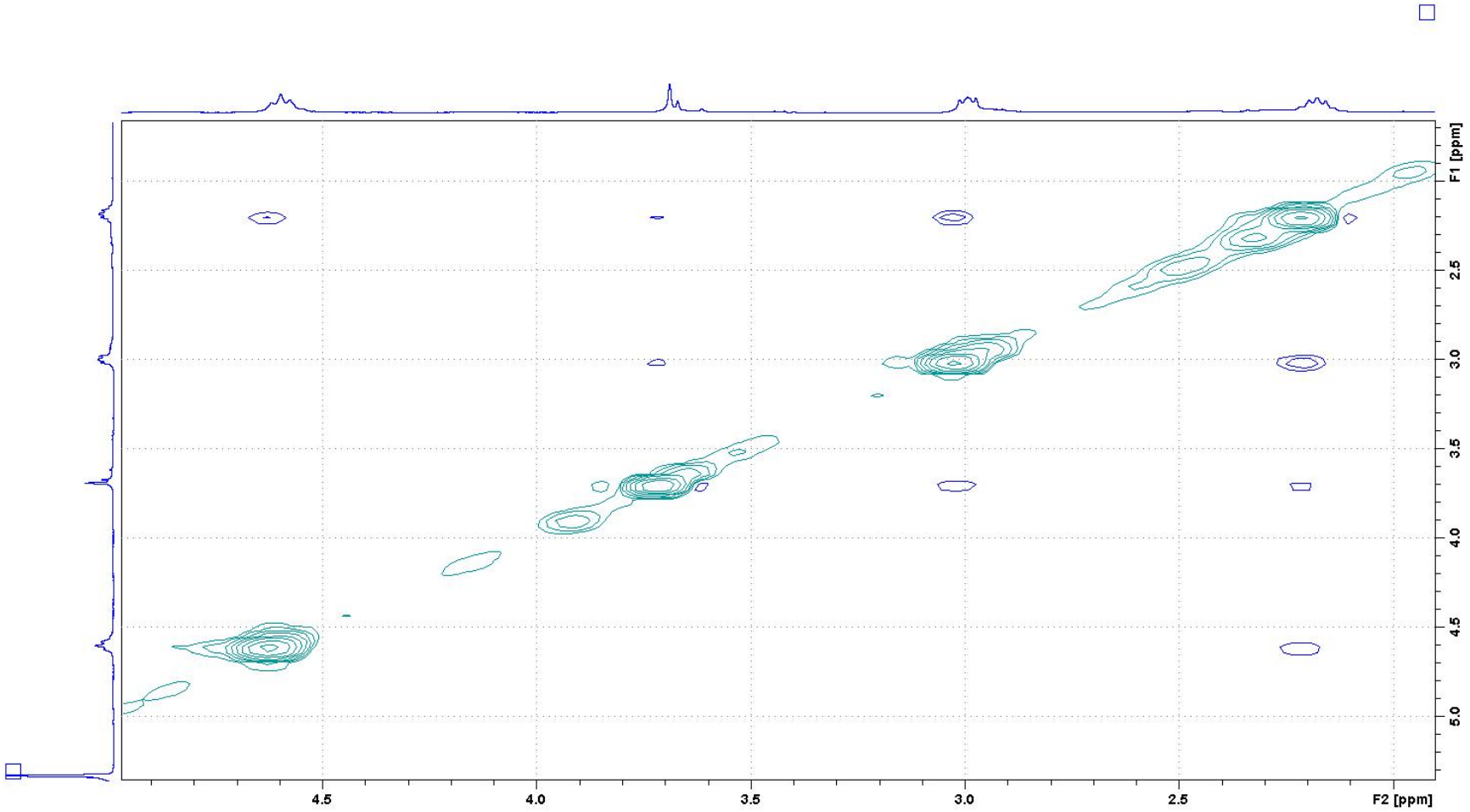
HSQC spectrum of **5a** in CD_2Cl_2



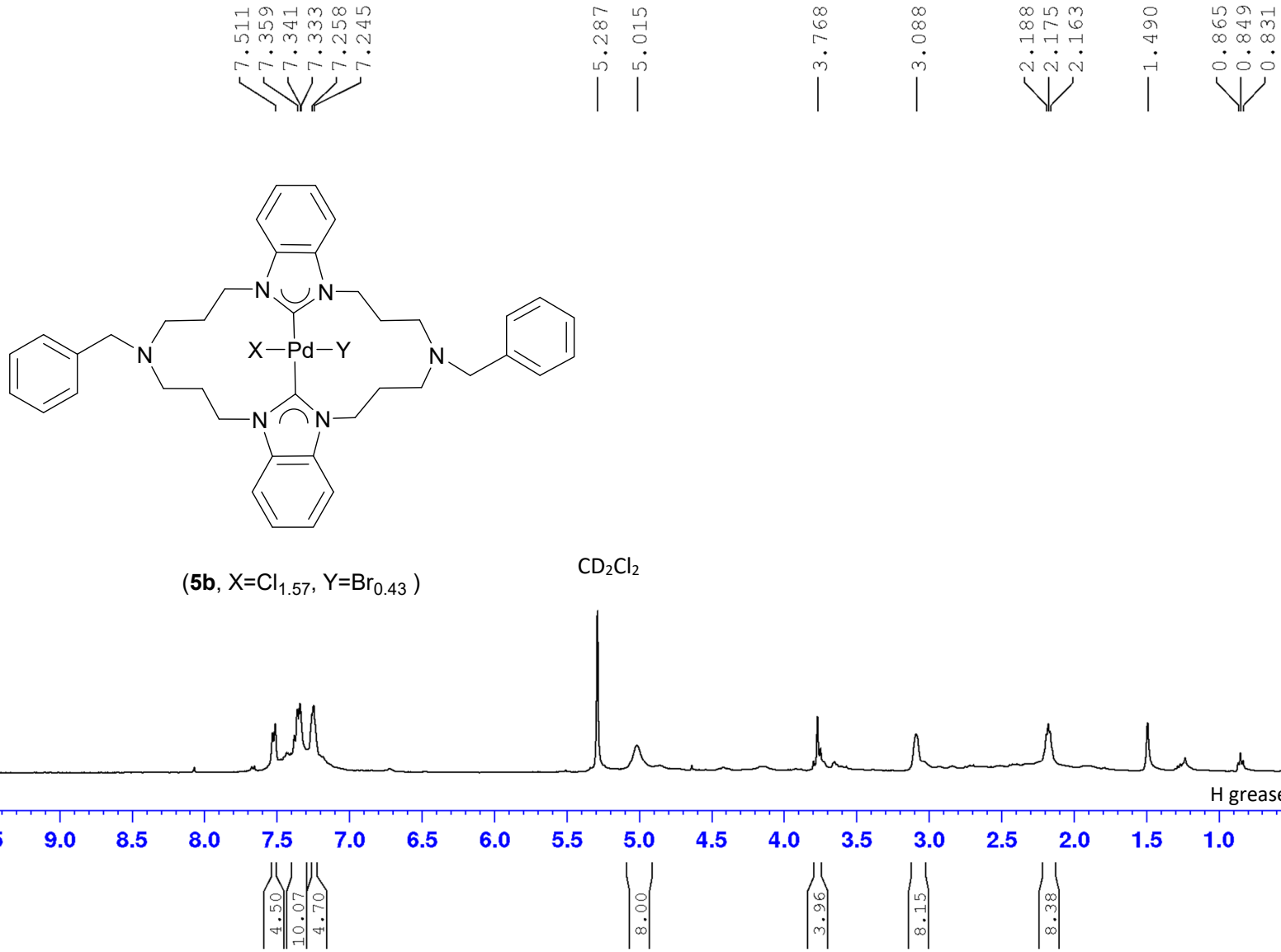
NOESY spectrum of **5a** in CD_2Cl_2 (Full spectrum)



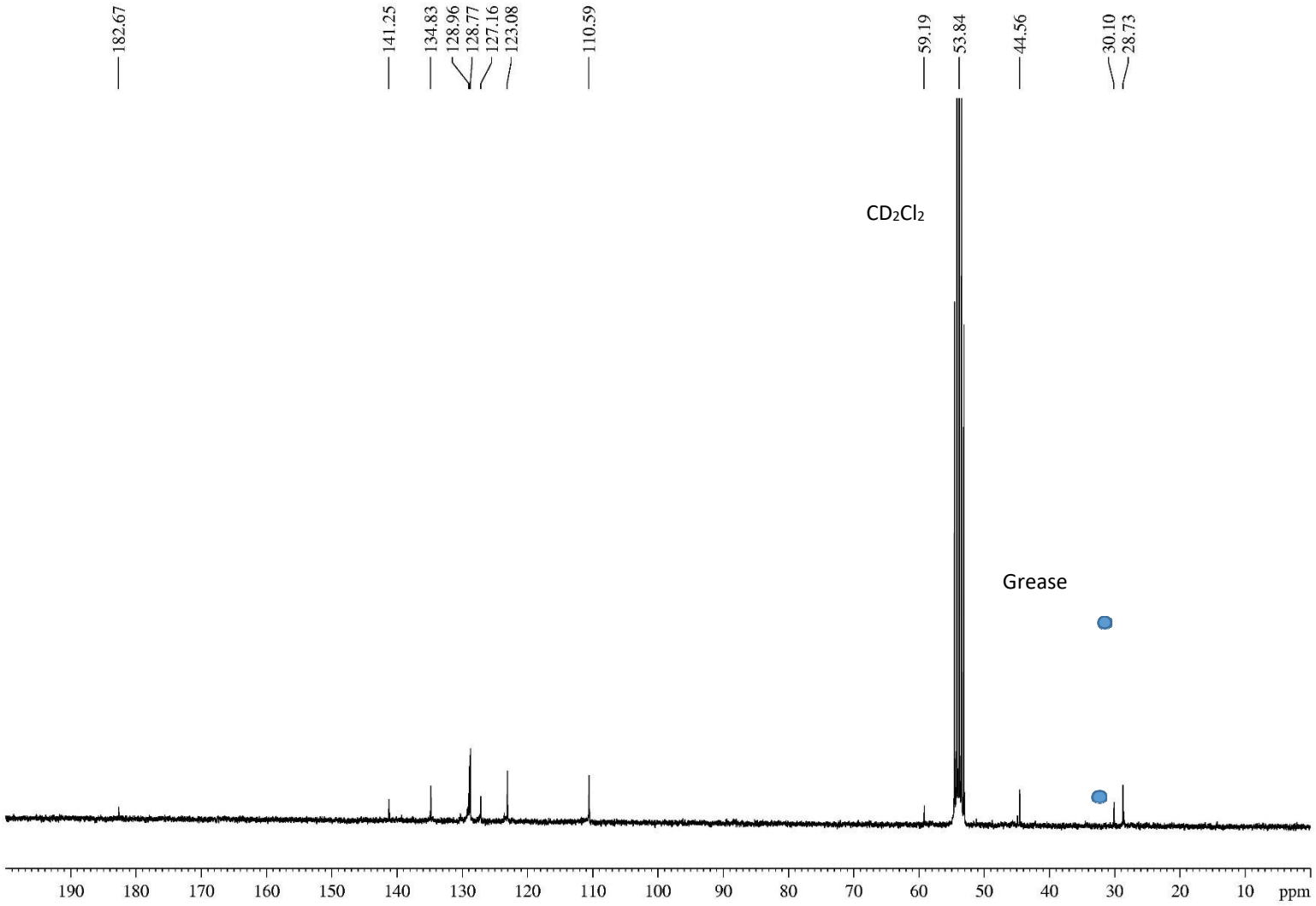
NOESY spectrum of **5a** in CD_2Cl_2 (aliphatic region)



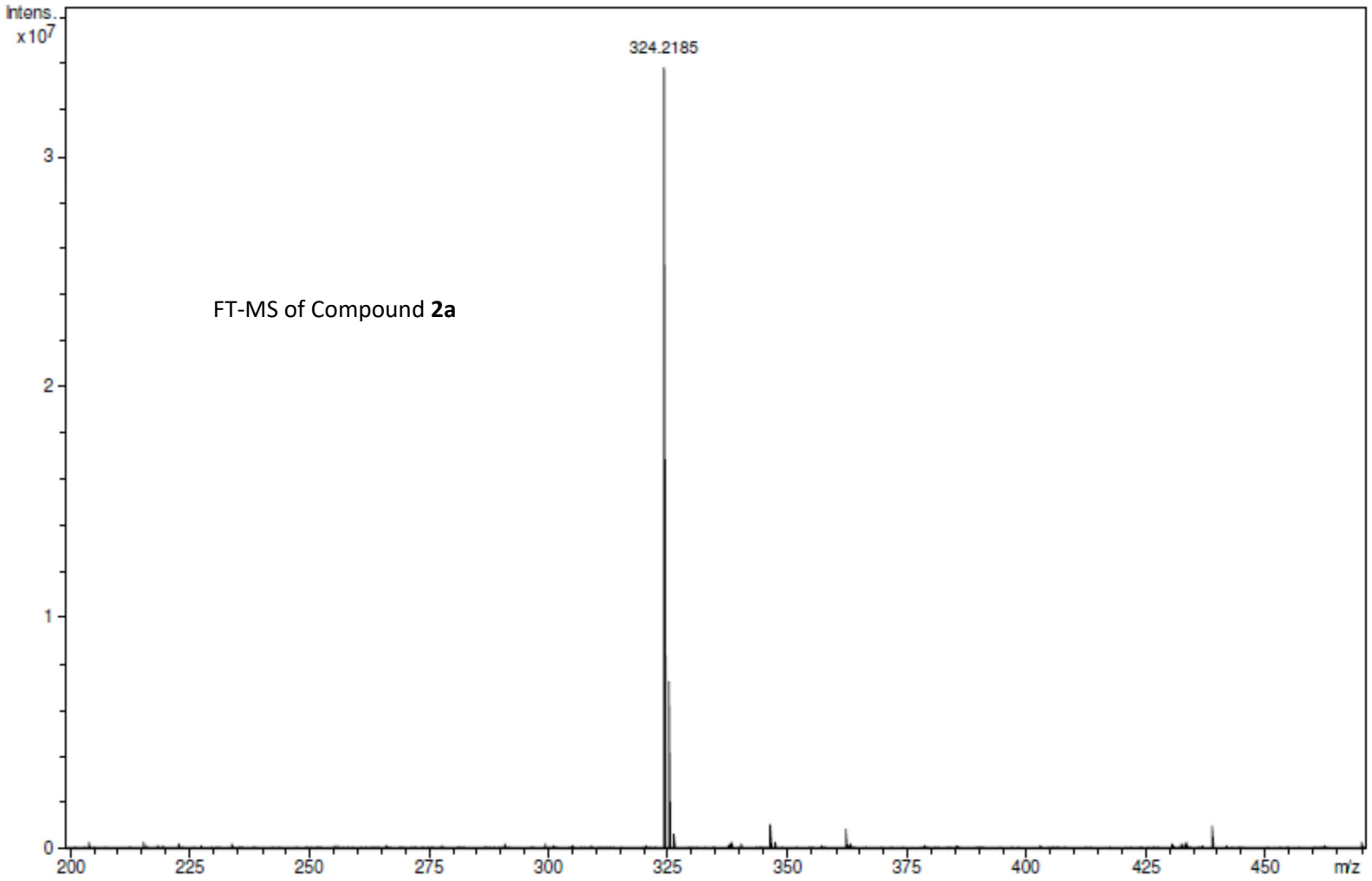
^{1}H NMR (CD_2Cl_2, Compound **5b**, 400 MHz)



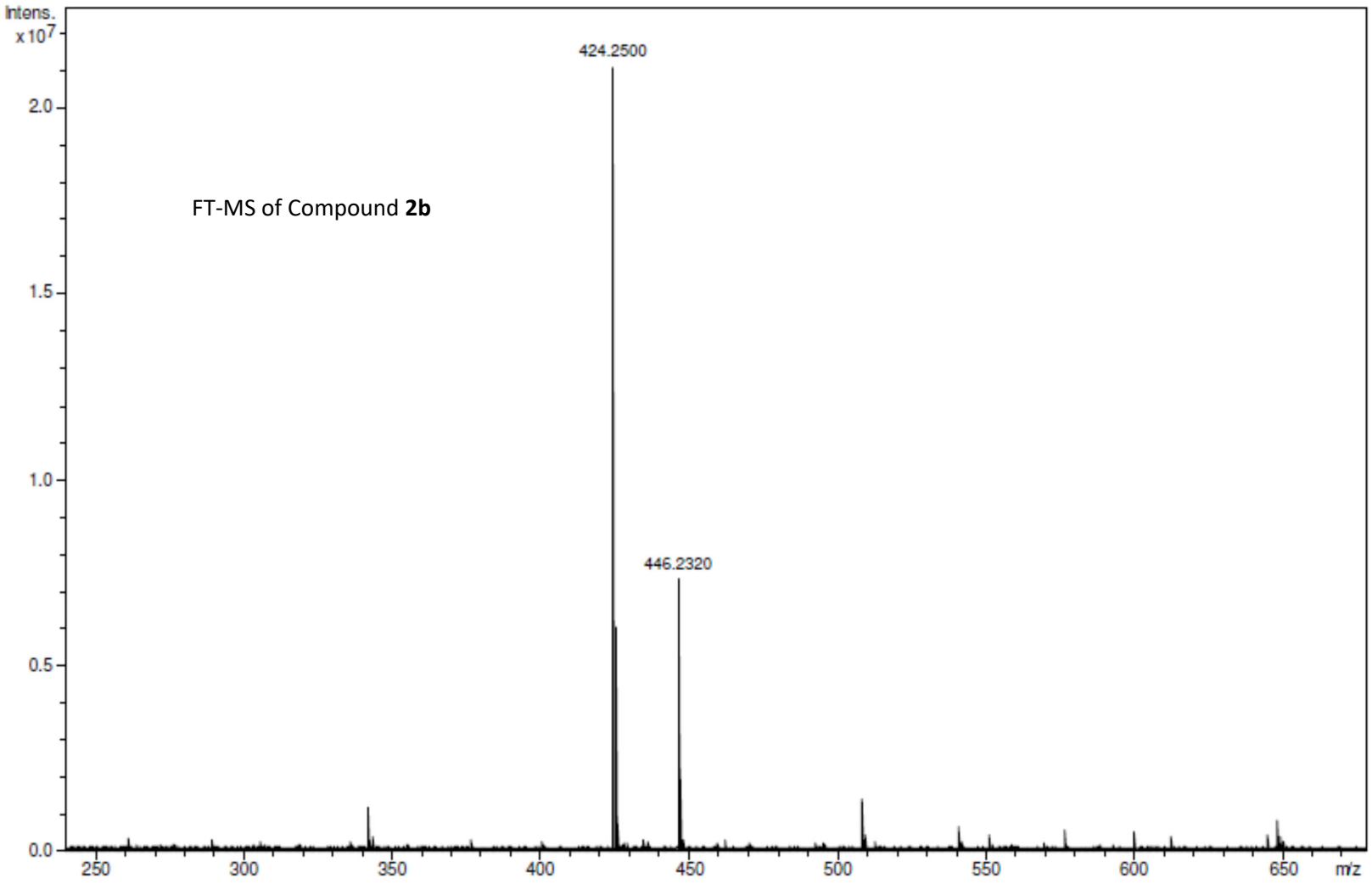
^{13}C NMR (CD_2Cl_2, Compound **5b**, 300 MHz)



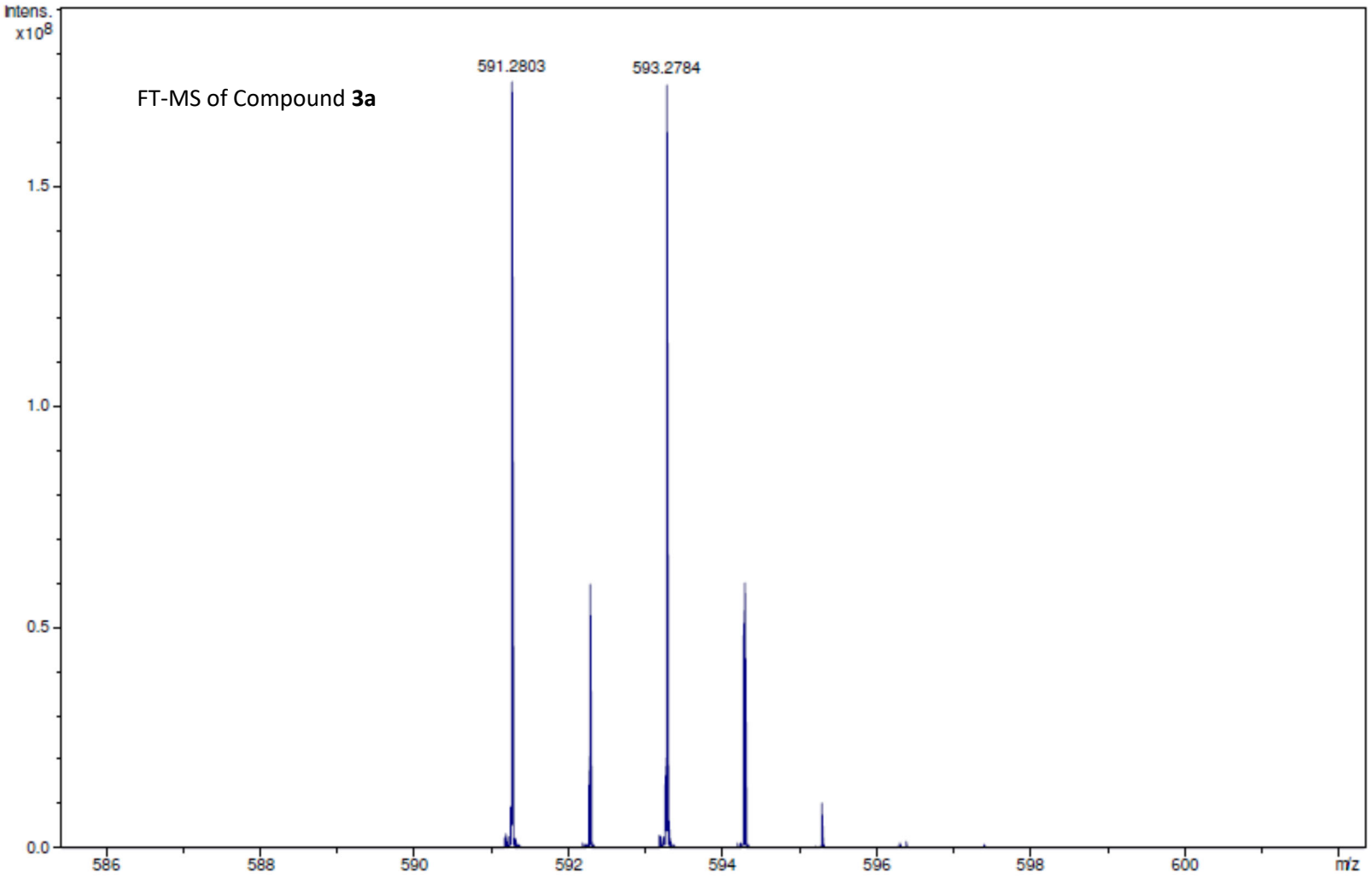
ESI-FTMS Mass Spectrum:



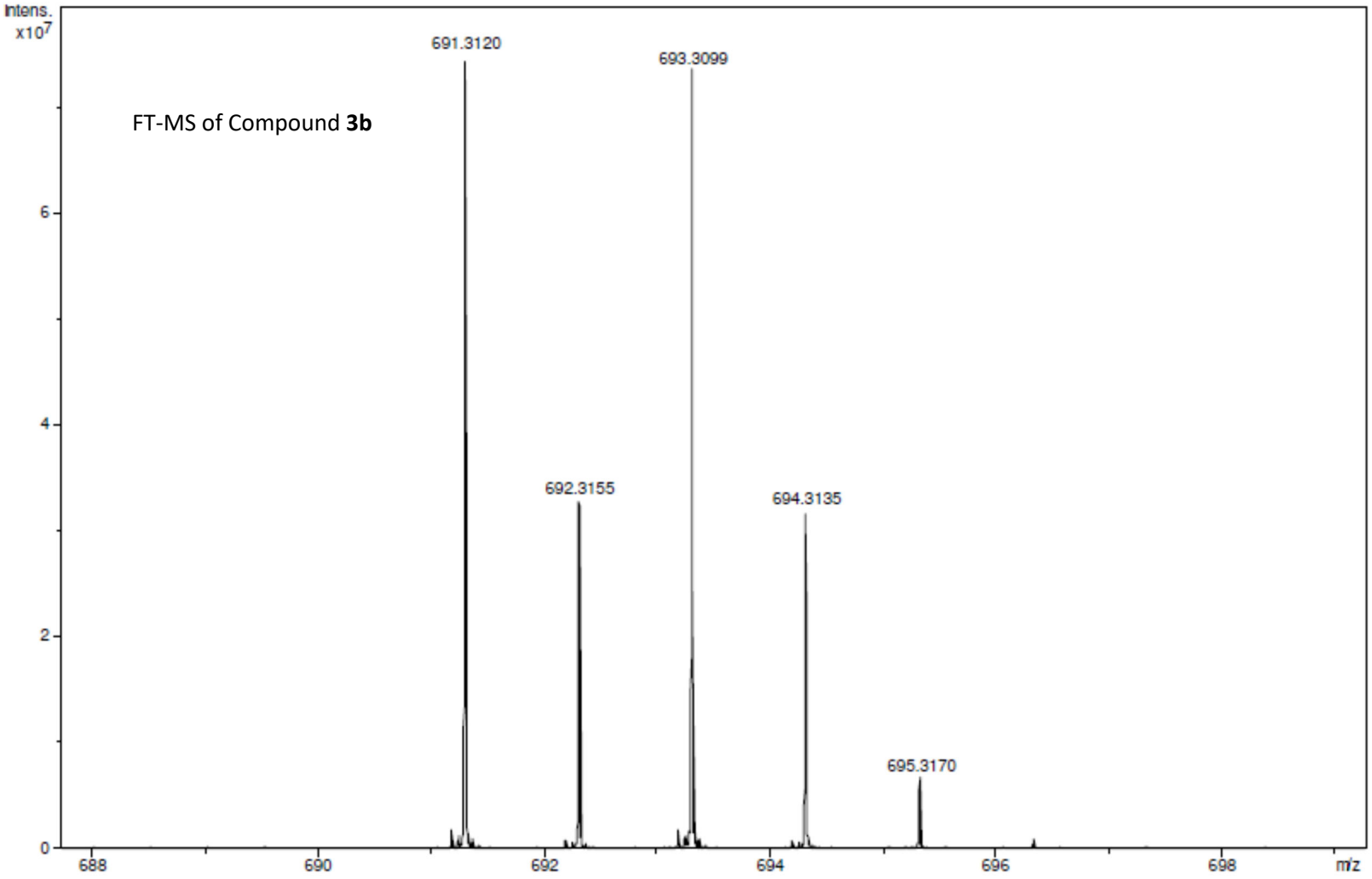
FT-MS of Compound **2a**



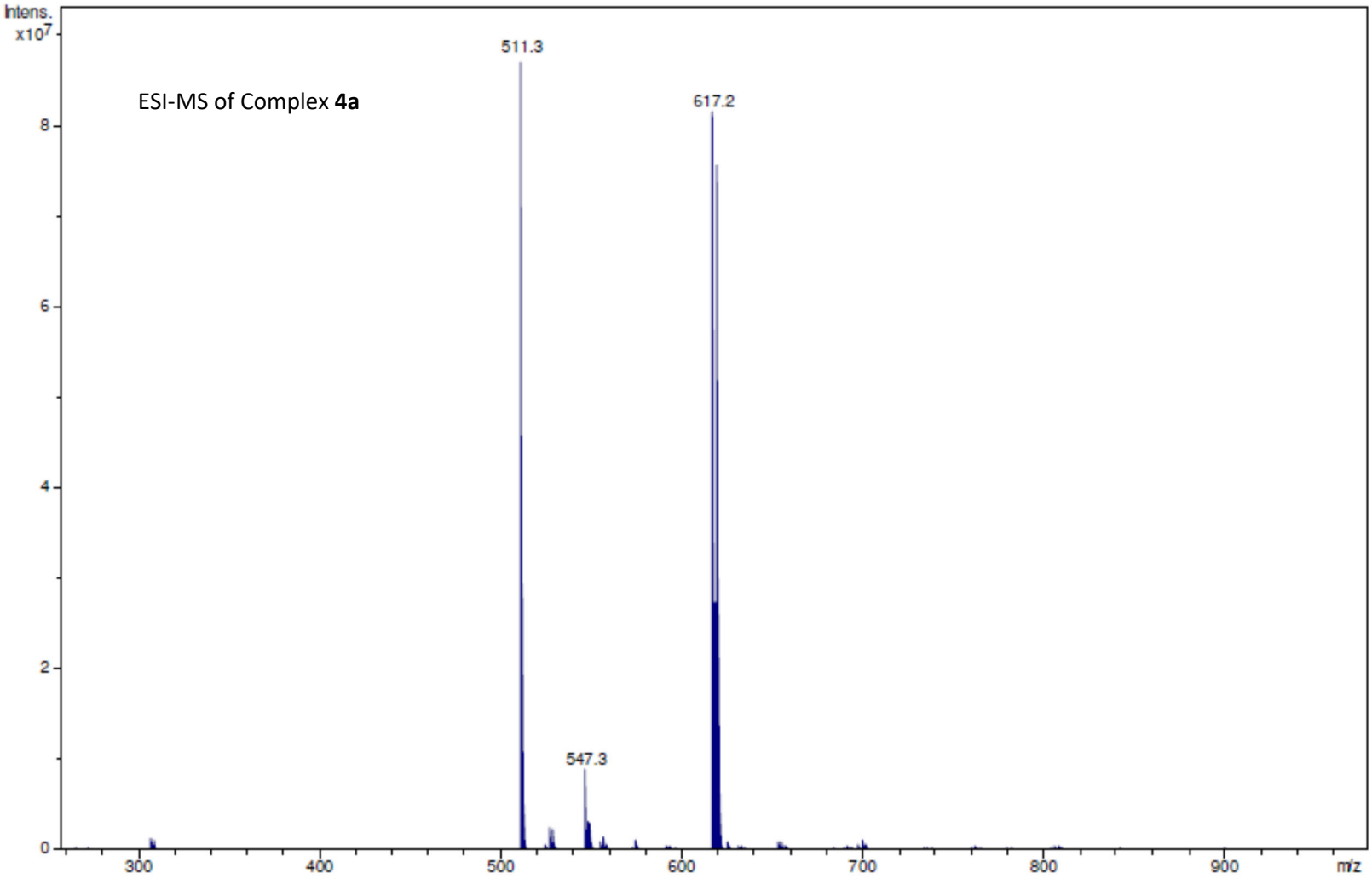
FT-MS of Compound **2b**

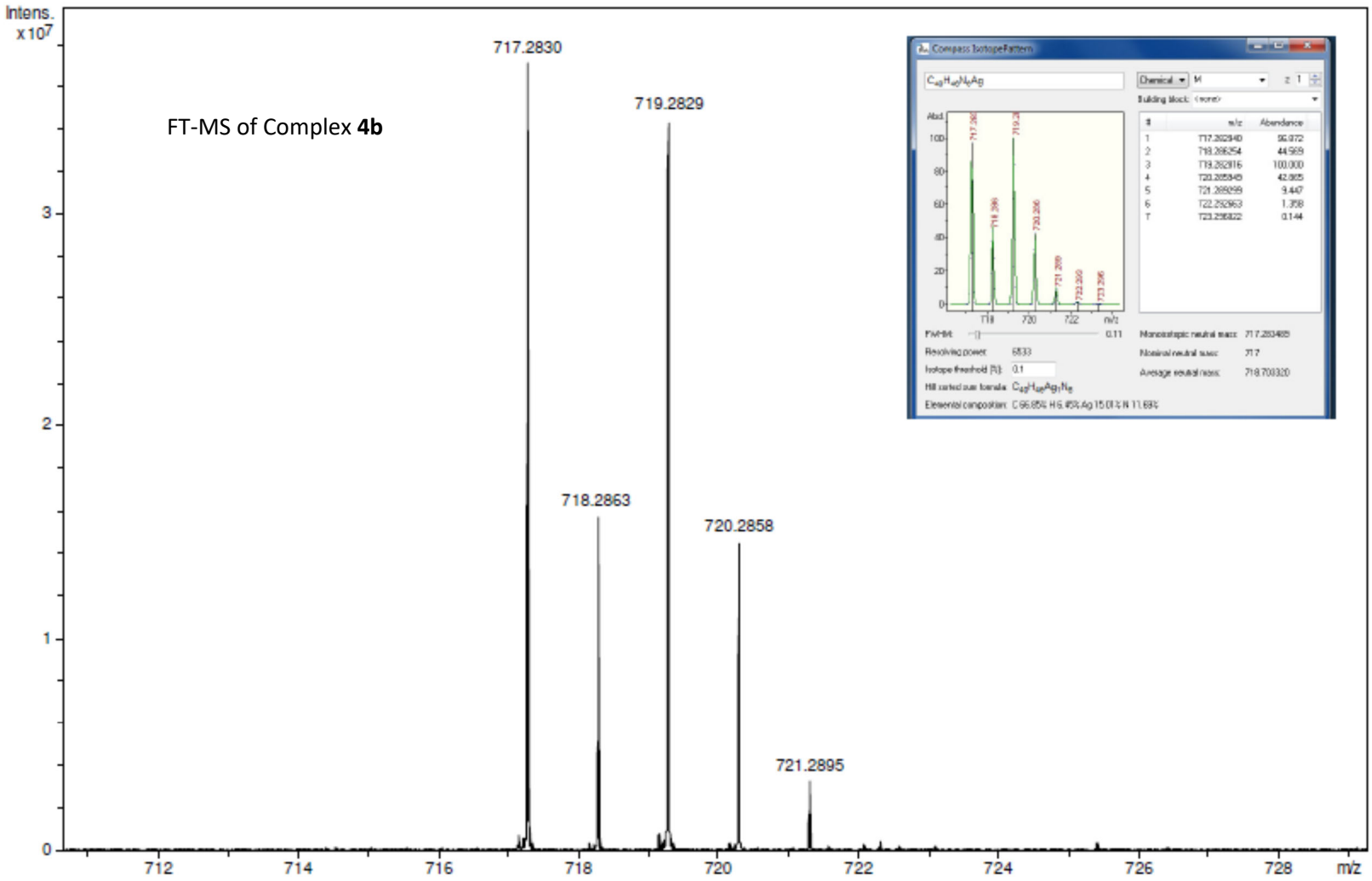


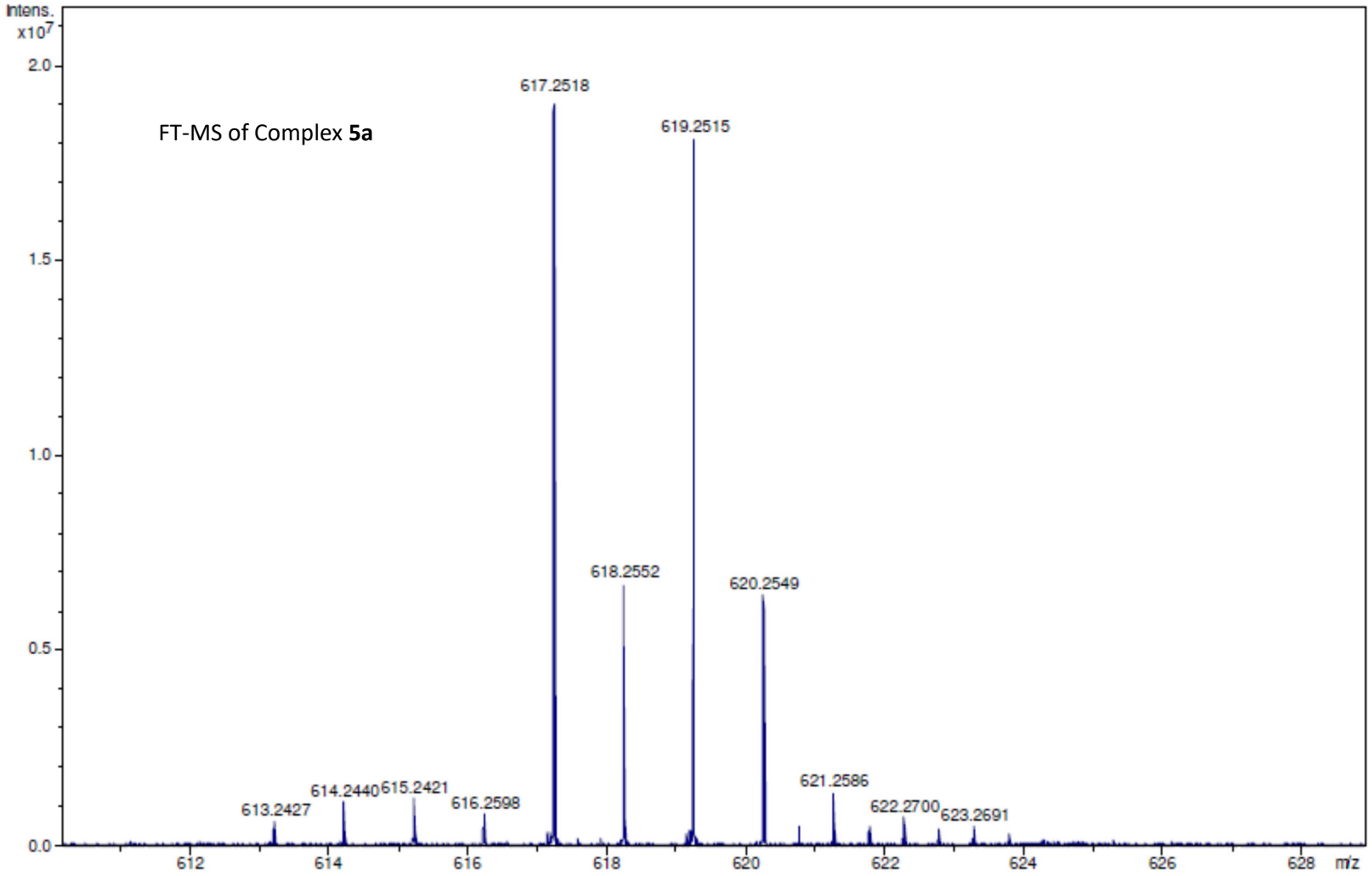
FT-MS of Compound **3a**



FT-MS of Compound **3b**


ESI-MS of Complex **4a**
Intens.
x10^7
8
6
4
2
0
511.3
617.2
547.3
300
400
500
600
700
800
900
m/z


Intens.
x 10^7
FT-MS of Complex **4b**
717.2830
719.2829
718.2863
720.2858
721.2895
0
1
2
3
712
714
716
718
720
722
724
726
728
m/z


FT-MS of Complex **5a**
Intens.
x10^7
2.0
1.5
1.0
0.5
0.0
617.2518
619.2515
618.2552
620.2549
613.2427
614.2440
615.2421
616.2598
621.2586
622.2700
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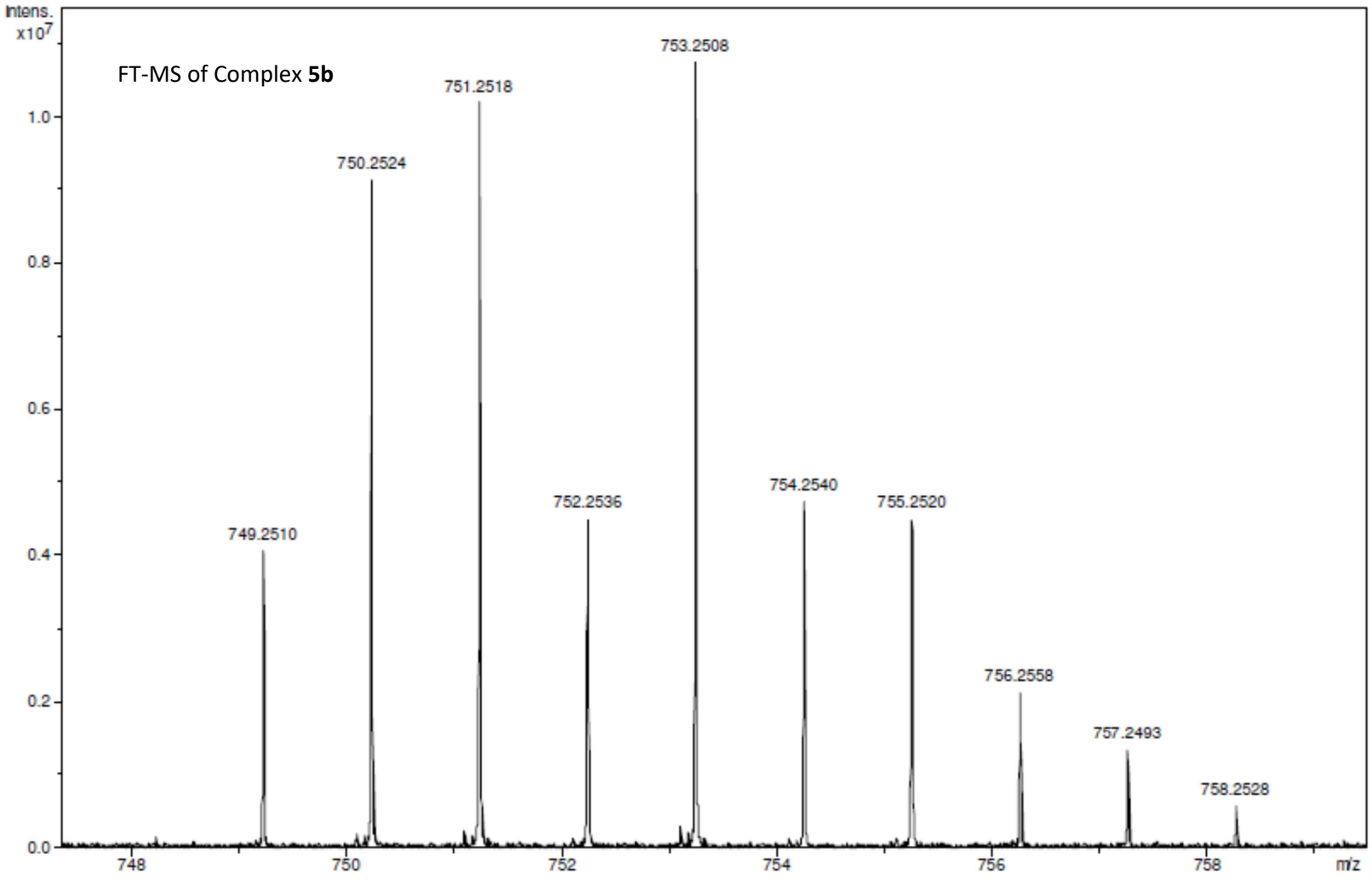
614
616
618
620
622
624
626
628
m/z


FT-MS of Complex **5b**
Intens.
x10^7
1.0
0.8
0.6
0.4
0.2
0.0
749.2510
750.2524
751.2518
752.2536
753.2508
754.2540
755.2520
756.2558
757.2493
758.2528
748
750
752
754
756
758
m/z

X-Ray Crystallography Details for 5a

Comments and Additional Details

In the case of complex **5a** the crystal was determined to be a 3-component twin by non-merohedry during data collection. The individual reflections from each component were integrated using SAINT (1b). Absorption correction was applied using TWINABS (1c,1d) in the semi-empirical method (2) Initial structure solution was solution was determined using reflections from the primary component and the final refinement was performed against reflections from all components to give the refined twin ratios of 0.1076(11) and 0.0212(5). Details of the twin laws can be found in the cif file. The molecule was located on an inversion center, thus only ½ of the atoms are unique. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A yellow, block-shaped crystal of dimensions 0.28 x 0.30 x 0.38 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 diffractometer with a Bruker APEX ccd area detector (1) and a sealed-tube Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 9819 peaks in the range 2.51 < θ < 27.45°. A total of 81927 data were measured in the range 1.760 < θ < 27.581° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.757 and 0.812. The data were merged to form a set of 14455 independent data with R(int) = 0.0474 and a coverage of 100.0 %.

The monoclinic space group $P2_1/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 189 parameters were refined against 14455 data to give wR(F^2) = 0.2326 and S = 1.004 for weights of w = 1/[σ^2 (F^2) + (0.0950 P)^2 + 6.8000 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0751 for the 9254 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 3.153 and -1.415 e/Å^3, respectively.

Table S1. Crystal data and structure refinement for **5a.**

Empirical formula	C_{32} H_{42} Cl_2 N_6 Pd	
Formula weight	688.01	
Crystal system	monoclinic	
Space group	*P*2$_1$/*c*	
Unit cell dimensions	*a* = 11.612(4) Å	α= 90°
	b = 8.505(2) Å	β= 94.685(4)°
	c = 16.280(5) Å	γ= 90°
Volume	1602.4(8) Å^3	
Z, Z'	2, 0.5	
Density (calculated)	1.426 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	712	
Absorption coefficient	0.777 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.812 and 0.757	
Theta range for data collection	1.760 to 27.581°	
Reflections collected	81927	
Independent reflections	14455 [R(int) = 0.0474]	
Data / restraints / parameters	14455 / 0 / 189	
wR(*F*^{2} all data)	*wR*2 = 0.2326	
R(*F* obsd data)	*R*1 = 0.0751	
Goodness-of-fit on *F*^{2}	1.004	
Observed data [I > 2σ(I)]	9254	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	3.153 and -1.415 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

X-Ray Crystallography Details for 5b

Comments and Additional Details

The intensity data were truncated to 0.920 Å because data in higher resolution shells all had $<F^2> < 2.0$. The compound was located on an inversion center, thus one half of the atoms were unique. The Cl was slightly disordered with Br. The occupancies for the Cl and Br refined to 0.786(11) and 0.214(11). The atoms N3 and C11-C20 were disordered. The occupancies of N3, C11-C20 refined to 0.590(15) and 0.410(15) for the unprimed and primed atoms. Restraints on the positional of the disordered atoms and displacement parameters of all atoms were required. A RIGU restraint of modest strength is used in this case to account for issues resulting from parameter correlation that are common with lower resolution structures. Disorder in the benzylamine fragment of the ligand was modeled over two positions with similarity restraints placed on C-C and C-N bond lengths for the disordered atoms. The atoms of the disordered phenyl groups are restrained to fall on a plane using a FLAT instruction. Thermal ellipsoids of disordered atoms are refined with additional similarity restraints. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colourless, block-shaped crystal of dimensions 0.09 x 0.24 x 0.41 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 diffractometer with a Bruker APEX ccd area detector (1) and a sealed-tube Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 2452 peaks in the range $2.39 < \theta < 19.24°$. A total of 14735 data were measured in the range $1.950 < \theta < 22.722°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.2597 and 0.3782. The data were merged to form a set of 2508 independent data with R(int) = 0.1061 and a coverage of 99.8 %.

The monoclinic space group $P2_1/n$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 333 parameters were refined against 667 restraints and 2508 data to give $wR(F^2) = 0.2636$ and S = 1.007 for weights of $w = 1/[\sigma^2 (F^2) + (0.1400\ P)^2 + 20.3000\ P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final R(*F*) was 0.0879 for the 1897 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.035 in the final refinement cycle. The final difference map had maxima and minima of 0.779 and -0.853 e/Å^3, respectively.

Table S2. Crystal data and structure refinement for **5b**.

Empirical formula	0.57(C_{40} H_{46} Cl_2 N_6 Pd) 0.43(C_{40} H_{46} Br Cl N_6 Pd)	
	C_{40} H_{46} $Br_{0.43}$ $Cl_{1.57}$ N_6 Pd	
Formula weight	807.24	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.462(17) Å	α= 90°
	b = 10.751(15) Å	β= 103.665(19)°
	c = 14.335(19) Å	γ= 90°
Volume	1866(4) Å^3	
Z, Z'	2, 0.5	
Density (calculated)	1.437 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	831	
Absorption coefficient	1.107 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.3782 and 0.2597	
Theta range for data collection	1.950 to 22.722°	
Reflections collected	14735	
Independent reflections	2508 [R(int) = 0.1061]	
Data / restraints / parameters	2508 / 667 / 333	
$wR(F^2$ all data)	$wR2$ = 0.2636	
R(F obsd data)	$R1$ = 0.0879	
Goodness-of-fit on F^2	1.007	
Observed data [I > 2σ(I)]	1897	
Largest and mean shift / s.u.	0.035 and 0.003	
Largest diff. peak and hole	0.779 and -0.853 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

X-Ray Crystallography Details for 4a

Comments and Additional Details

In the case of complex **4a** the crystal was determined to be a 2 component twin by non-merohedry during data collection and was twinned by non-merohedry with a 2-fold rotation about the [1 0 0] axis. The individual reflections from each component were integrated using SAINT (1b). Absorption correction was applied using TWINABS (1c,1d) in the semi-empirical method (2) Initial structure solution was determined using reflections from the primary component and the final refinement was performed against reflections from all components to give a refined twin ratio of 0.4134(10). Details of the twin laws can be found in the cif file. A dichloromethane was severely disordered and was best modeled using SQUEEZE (4). The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colourless, needle-shaped crystal of dimensions 0.04 x 0.05 x 0.34 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 diffractometer with a Bruker APEX ccd area detector (1) and a sealed tube Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 5253 peaks in the range 2.26 < θ < 22.38°. A total of 49788 data were measured in the range 1.581 < θ < 27.723° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.386 and 0.874. The data were merged to form a set of 11151 independent data with R(int) = 0.0427 and a coverage of 99.9 %.

The monoclinic space group $P2_1/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 380 parameters were refined against 321 restraints and 11151 data to give wR(F^2) = 0.1415 and S = 1.007 for weights of w = 1/[σ^2 (F^2) + (0.0750 P)^2 + 4.2000 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0579 for the 7804 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 2.592 and -0.912 e/Å^3, respectively.

Table S3. Crystal data and structure refinement for **4a**

Empirical formula	$C_{65}H_{86}Ag_4Br_4Cl_2N_{12}$	
Formula weight	1857.47	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.840(4) Å	α= 90°
	b = 22.482(8) Å	β= 93.172(5)°
	c = 15.732(6) Å	γ= 90°
Volume	3475(2) Å^3	
Z, Z'	2, 0.5	
Density (calculated)	1.775 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1844	
Absorption coefficient	3.536 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.869 and 0.373	
Theta range for data collection	1.581 to 27.723°	
Reflections collected	49788	
Independent reflections	11151 [R(int) = 0.0427]	
Data / restraints / parameters	11151 / 321 / 380	
$wR(F^2$ all data)	$wR2$ = 0.1415	
R(F obsd data)	$R1$ = 0.0579	
Goodness-of-fit on F^2	1.007	
Observed data [I > 2σ(I)]	7804	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	2.592 and -0.912 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

X-Ray Crystallography Details for 4b

Comments and Additional Details

The intensity data were truncated to 0.92 Å resolution because data in higher resolution shells all had $<F^2/\sigma> < 2$. Both the metal complex and the anion were located on inversion centers. There were three regions of disorder in the structure. The occupancies of atoms C21-C23 refined to 0.50(3) and 0.50(3) for the unprimed and primed atoms. The occupancies of atoms C24-C26 refined to 0.57(3) and 0.43(3) for the unprimed and primed atoms. The occupancies of the DCM solvent atoms refined to 0.646(10) and 0.354(10) for the A and primed atoms. Restraints on the positional parameters of the disordered atoms and the displacement parameters of all atoms were required. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colourless, rod-shaped crystal of dimensions 0.06 x 0.06 x 0.23 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 diffractometer with a Bruker APEX ccd area detector (1) and a sealed-tube Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 1874 peaks in the range $2.40 < \theta < 21.20°$. A total of 17622 data were measured in the range $1.333 < \theta < 22.721°$ using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.2313 and 0.3766. The data were merged to form a set of 5545 independent data with R(int) = 0.0990 and a coverage of 99.9 %.

The monoclinic space group *C*2/*c* was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 529 parameters were refined against 588 restraints and 5545 data to give $wR(F^2) = 0.2256$ and S = 1.009 for weights of $w = 1/[\sigma^2 (F^2) + (0.1000 P)^2 + 238.0000 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final R(*F*) was 0.0835 for the 3917 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 1.485 and -1.066 e/Å^3, respectively.

Table S4. Crystal data and structure refinement for **4b.**

Empirical formula	$(C_{80}\ H_{92}\ Ag_3\ Br_2\ N_{12})^+\ (Ag\ Br_2)^-\cdot 2(C\ H_2\ Cl_2)$	
	$C_{82}\ H_{96}\ Ag_4\ Br_4\ Cl_4\ N_{12}$	
Formula weight	2142.62	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 31.67(4) Å	α= 90°
	b = 10.719(17) Å	β= 105.24(2)°
	c = 25.17(4) Å	γ= 90°
Volume	8244(21) Å^3	
Z, Z'	4, 0.5	
Density (calculated)	1.726 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	4272	
Absorption coefficient	3.056 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.3766 and 0.2313	
Theta range for data collection	1.333 to 22.721°	
Reflections collected	17622	
Independent reflections	5545 [R(int) = 0.0990]	
Data / restraints / parameters	5545 / 588 / 529	
wR(*F*^{2} all data)	*wR*2 = 0.2256	
R(*F* obsd data)	*R*1 = 0.0835	
Goodness-of-fit on *F*^{2}	1.009	
Observed data [I > 2σ(I)]	3917	
Extinction coefficient	0.00174(15)	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	1.485 and -1.066 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

X-Ray Crystallography Details for 3a

Comments and Additional Details

In the case of compound **3a** the crystal was determined to be a 2-component twin by non-merohedry during data collection. The individual reflections from each component were integrated using SAINT (1b). Absorption correction was applied using TWINABS (1c,1d) in the semi-empirical method (2) Initial structure solution was determined using reflections from the primary component and the final refinement was performed against reflections from all components to give a refined twin ratio of 0.1578(8). Details of the twin laws can be found in the cif file. The molecule was located on an inversion center, thus only ½ of the atoms are unique. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colourless, block-shaped crystal of dimensions 0.11 x 0.12 x 0.32 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 diffractometer with a Bruker APEX ccd area detector (1) and a sealed-tube Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 2245 peaks in the range 2.43 < θ < 26.32°. A total of 149026 data were measured in the range 1.588 < θ < 27.569° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method (2) giving minimum and maximum transmission factors of 0.509 and 0.775. The data were merged to form a set of 11335 independent data with R(int) = 0.0759 and a coverage of 100.0 %.

The orthorhombic space group *Pbca* was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). The positions of hydrogens were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the isotropic equivalent displacement parameters of the bonded atoms. A total of 218 parameters were refined against 11335 data to give wR(F^2) = 0.1750 and S = 1.006 for weights of w = 1/[σ^2 (F^2) + (0.1150 P)^2], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0597 for the 7787 observed, [$F > 4\sigma(F)$], data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 3.282 and -0.783 e/Å^3, respectively.

Table S5. Crystal data and structure refinement for **3a.**

Empirical formula	$(C_{32}\ H_{44}\ N_6)^{2+}\ 2Br^- \cdot 2(C\ H\ Cl_3)$	
	$C_{34}\ H_{46}\ Br_2\ Cl_6\ N_6$	
Formula weight	911.29	
Crystal system	orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	*a* = 9.350(3) Å	α= 90°
	b = 16.797(6) Å	β= 90°
	c = 25.649(8) Å	γ= 90°
Volume	4028(2) $Å^3$	
Z, Z'	4, 0.5	
Density (calculated)	1.503 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1856	
Absorption coefficient	2.443 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.775 and 0.509	
Theta range for data collection	1.588 to 27.569°	
Reflections collected	149026	
Independent reflections	11335 [R(int) = 0.0759]	
Data / restraints / parameters	11335 / 0 / 218	
wR(F^2 all data)	*wR*2 = 0.1750	
R(*F* obsd data)	*R*1 = 0.0597	
Goodness-of-fit on F^2	1.006	
Observed data [I > 2σ(I)]	7787	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	3.282 and -0.783 $e/Å^3$	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

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