Amino acid-derived *N*-Heterocyclic carbene palladium complexes for aqueous phase Suzuki-Miyaura couplings

Supplementary material

New Journal of Chemistry

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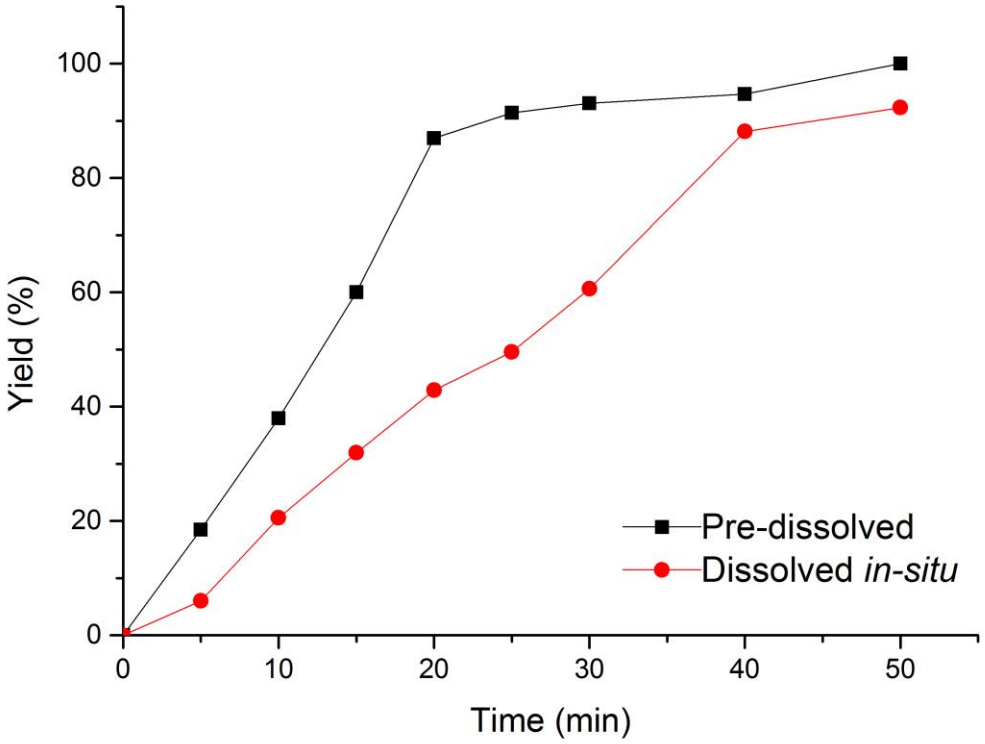
1) Kinetic Line Plot

2) NMR Spectra

15. ^{1}H NMR spectrum of **4a** (*trans*-dichlorido-*bis*(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)palladium(II))
16. ^{13}C NMR spectrum of **4a** (*trans*-dichlorido-*bis*(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)palladium(II))
17. ^{1}H NMR spectrum of **4b** (*trans*-dichlorido-*bis*(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)palladium(II))
18. ^{13}C NMR spectrum of **4b** (*trans*-dichlorido-*bis*(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)palladium(II))
19. ^{1}H NMR spectrum of **5a** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)(pyridine)palladium(II))
20. ^{13}C NMR spectrum of **5a** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxoethyl)-imidazol-2-ylidine)(pyridine)palladium(II))
21. ^{1}H NMR spectrum of **5b** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)(pyridine)palladium(II))
22. ^{13}C NMR spectrum of **5b** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxopropyl)-imidazol-2-ylidine)(pyridine)palladium(II))
23. ^{1}H NMR spectrum of **5c** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl)-imidazol-2-ylidine)(pyridine)palladium(II))
24. ^{13}C NMR spectrum of **5c** (*trans*-dichlorido-(1,3-bis(2-ethoxy-2-oxo(1-((benzyl)ethyl)-imidazol-2-ylidine)(pyridine)palladium(II))

3) Single crystal X-ray structure determinations of 4a, 4b, 5a and 5b

Kinetic Line Plot

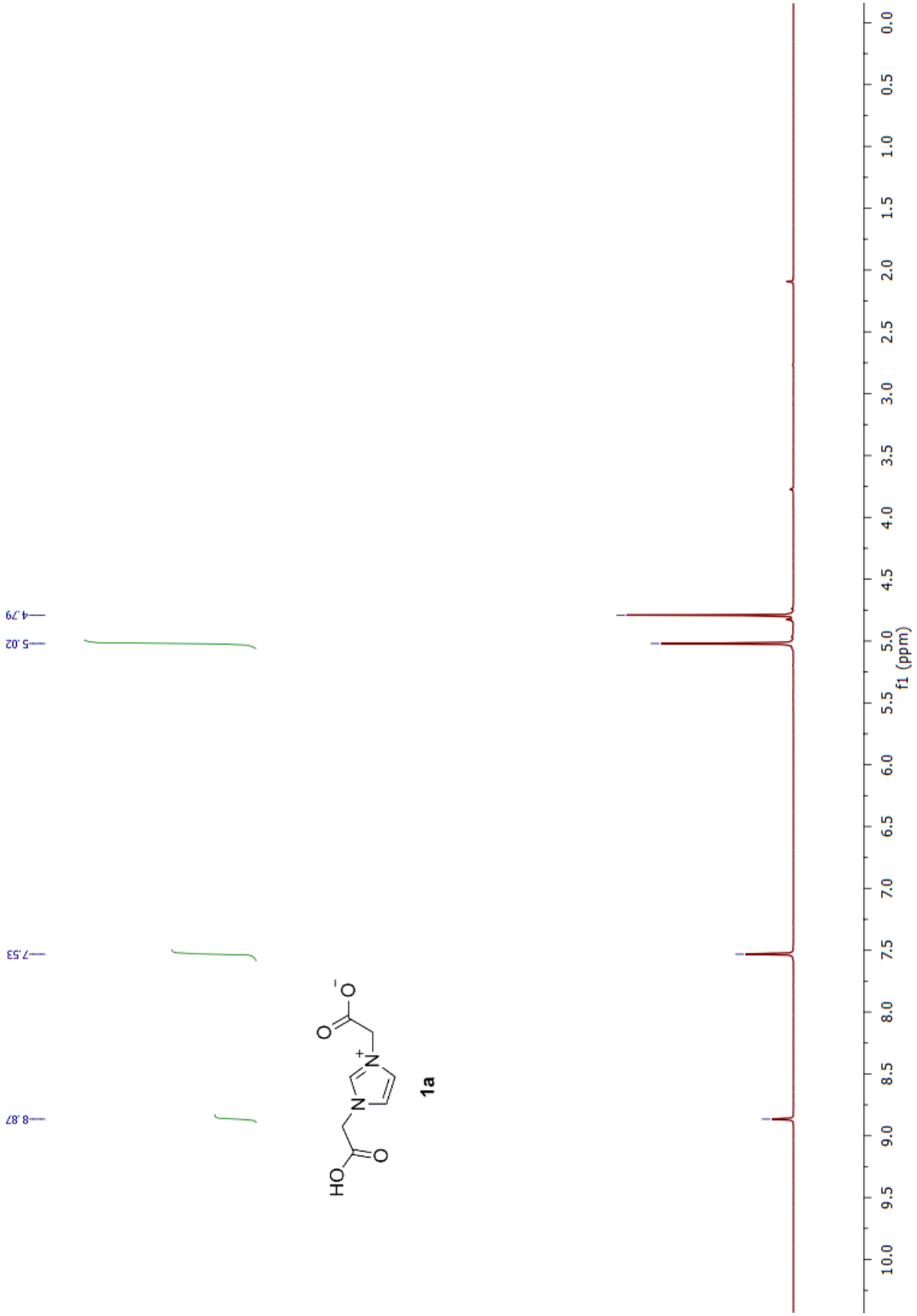


Graph 1 Line plot of the aqueous-phase Suzuki-Miyaura coupling of 4-bromoacetophenone with phenylboronic acid using precatalyst **5b**. The pre-dissolved catalyst reached 100% yield in 50 minutes, whereas the *in situ* catalyst does not reach 100% yield until after 1 hour.

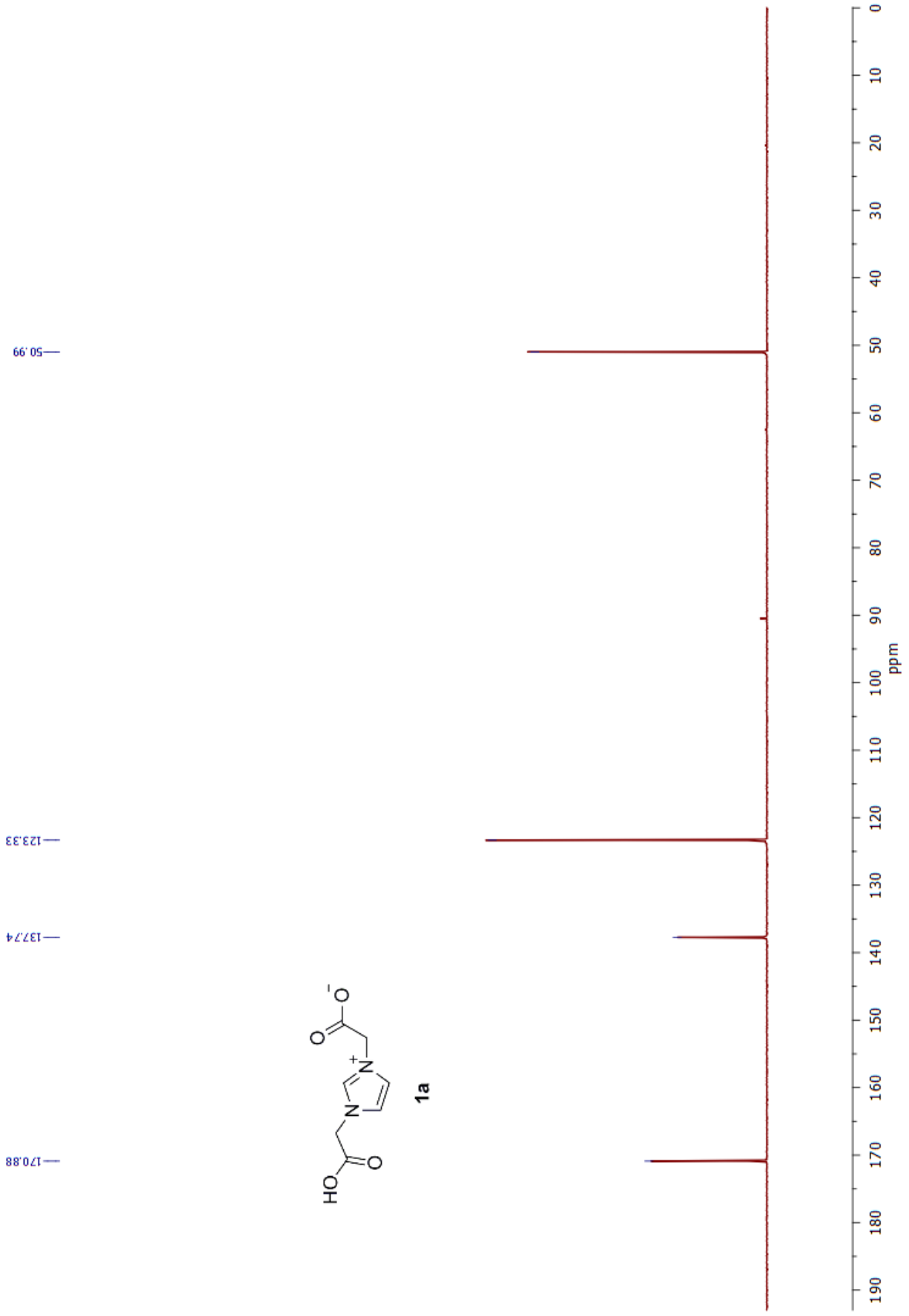
Reaction conditions: bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.0 mmol), **5b** (1 mol%), TBAB (1.0 mmol) in pure H_2O at 60 °C. Yields determined by NMR using trimethoxybenzene as an internal standard.

1. ^{1}H NMR spectrum of **1a**

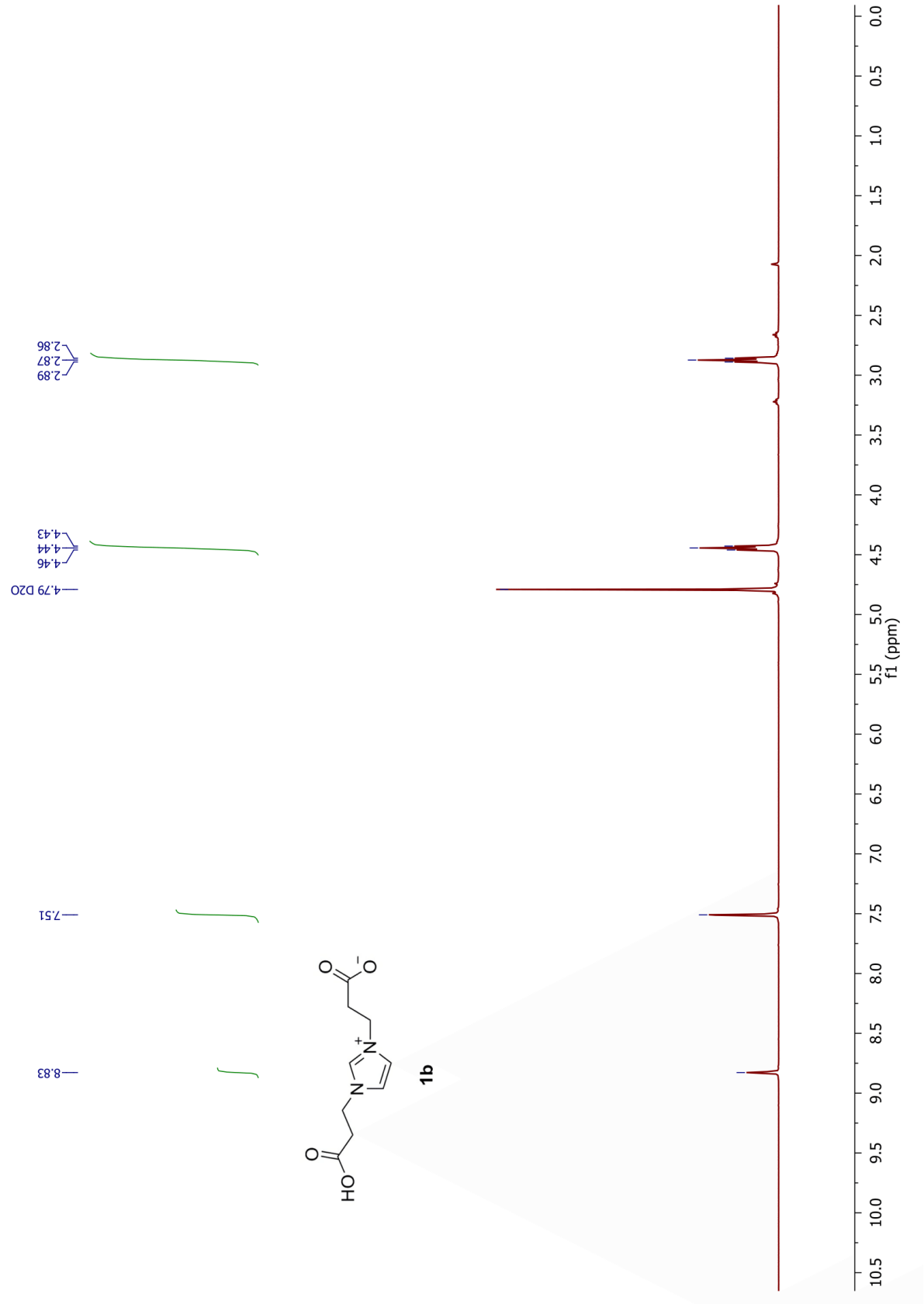
NMR Spectra



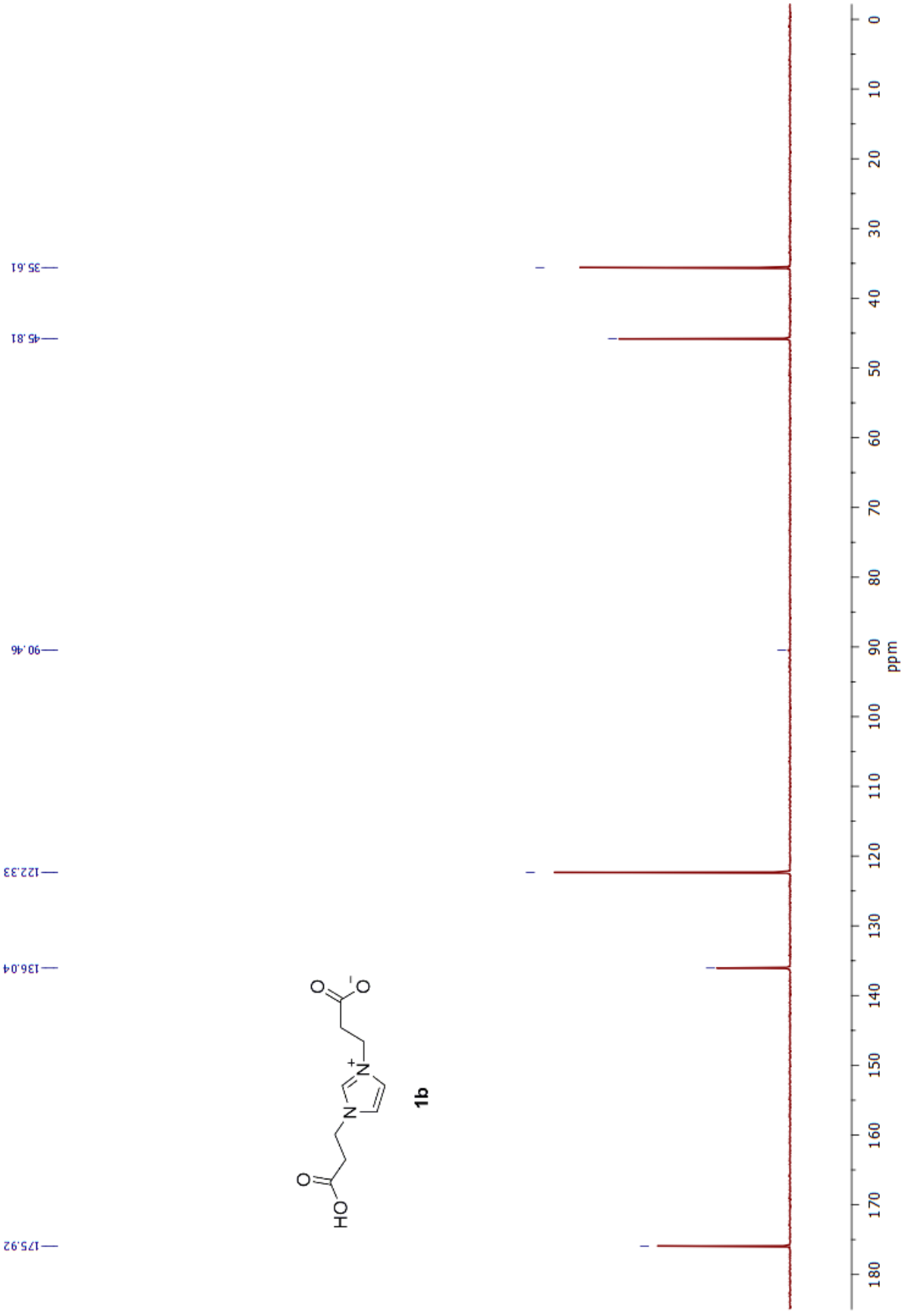
2. ^{13}C NMR spectrum of **1a**



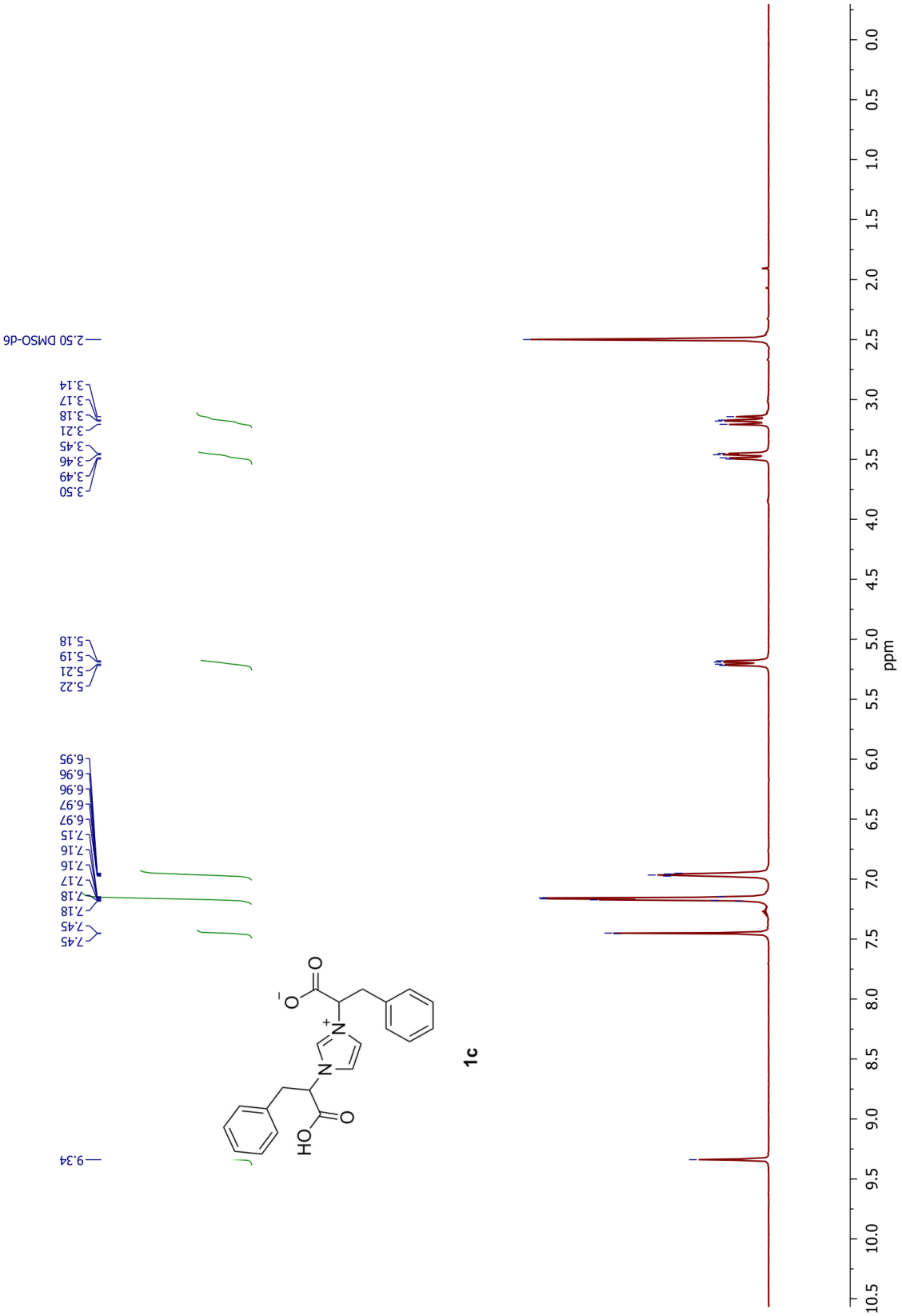
3. ^{1}H NMR spectrum of **1b**



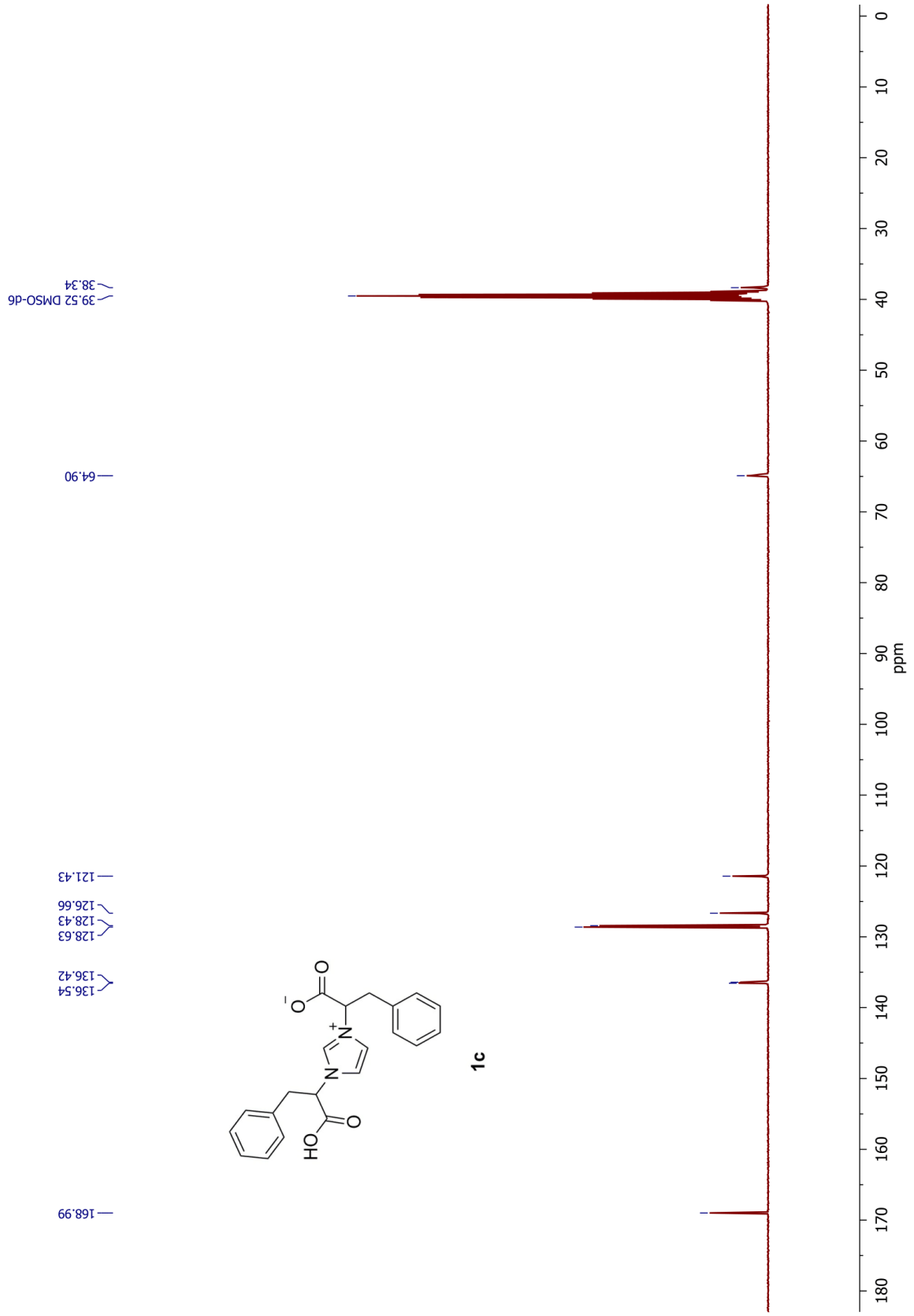
4. ^{13}C NMR spectrum of **1b**



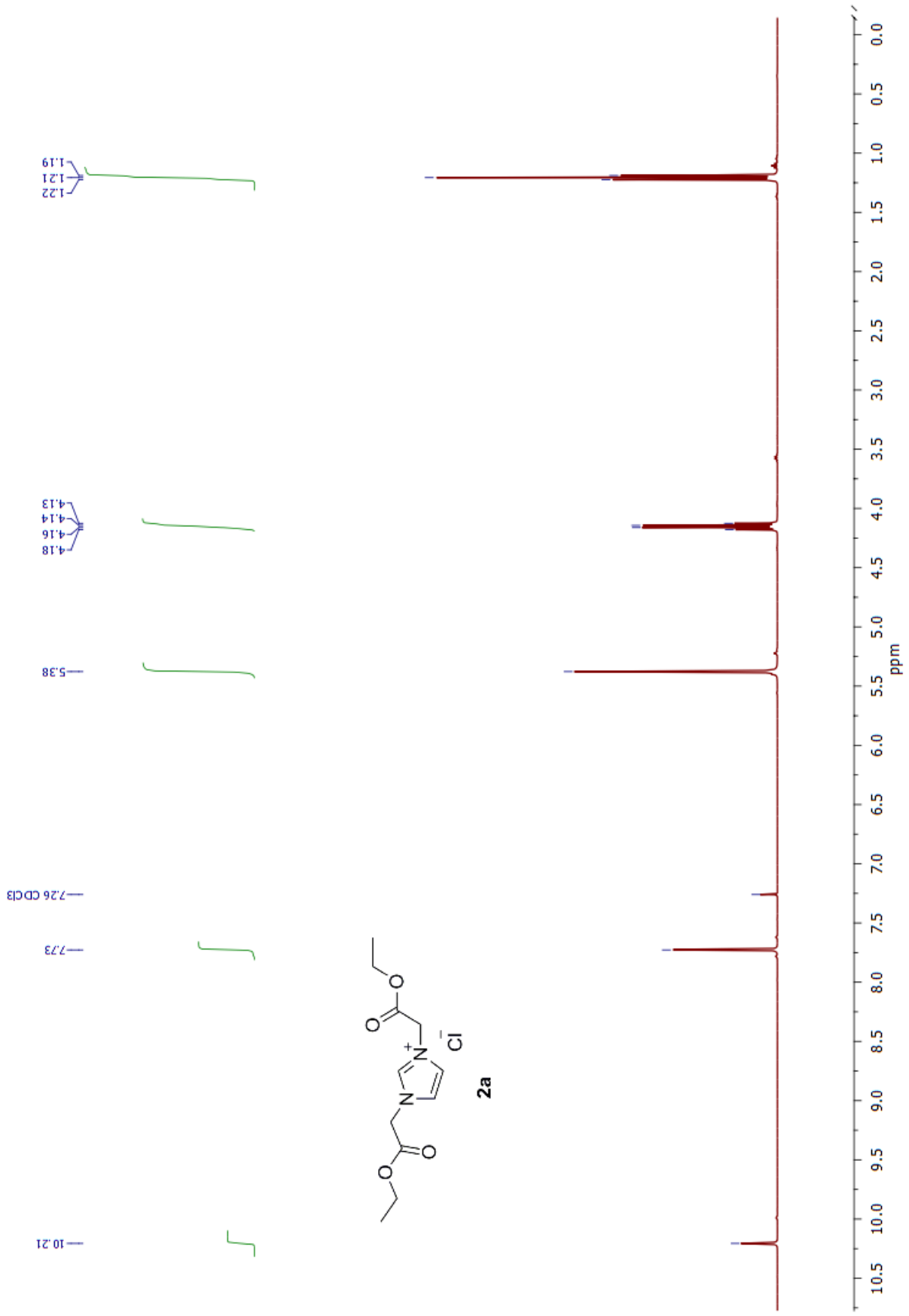
5. ^{1}H NMR spectrum of **1c**



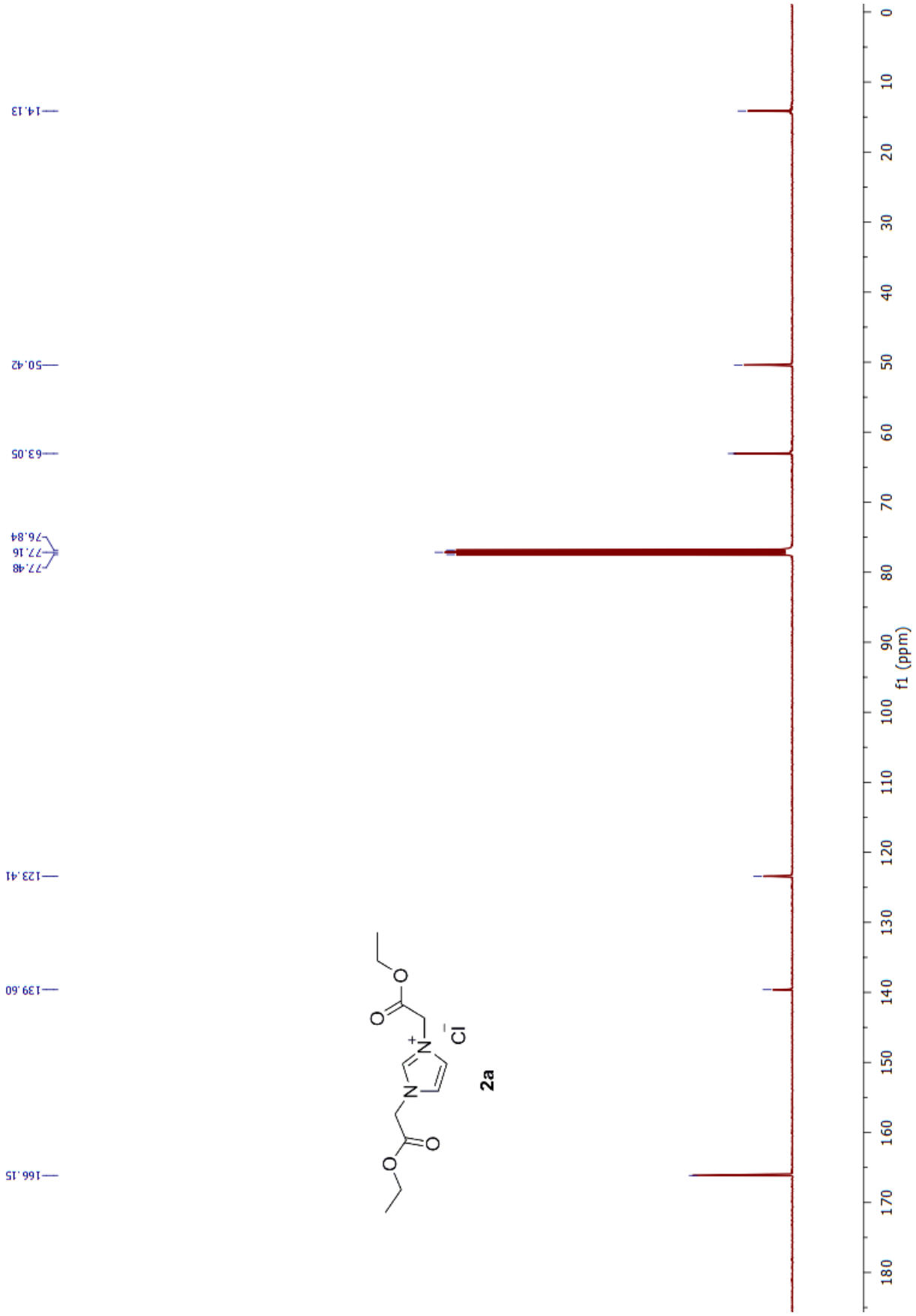
6. ^{13}C NMR spectrum of **1c**



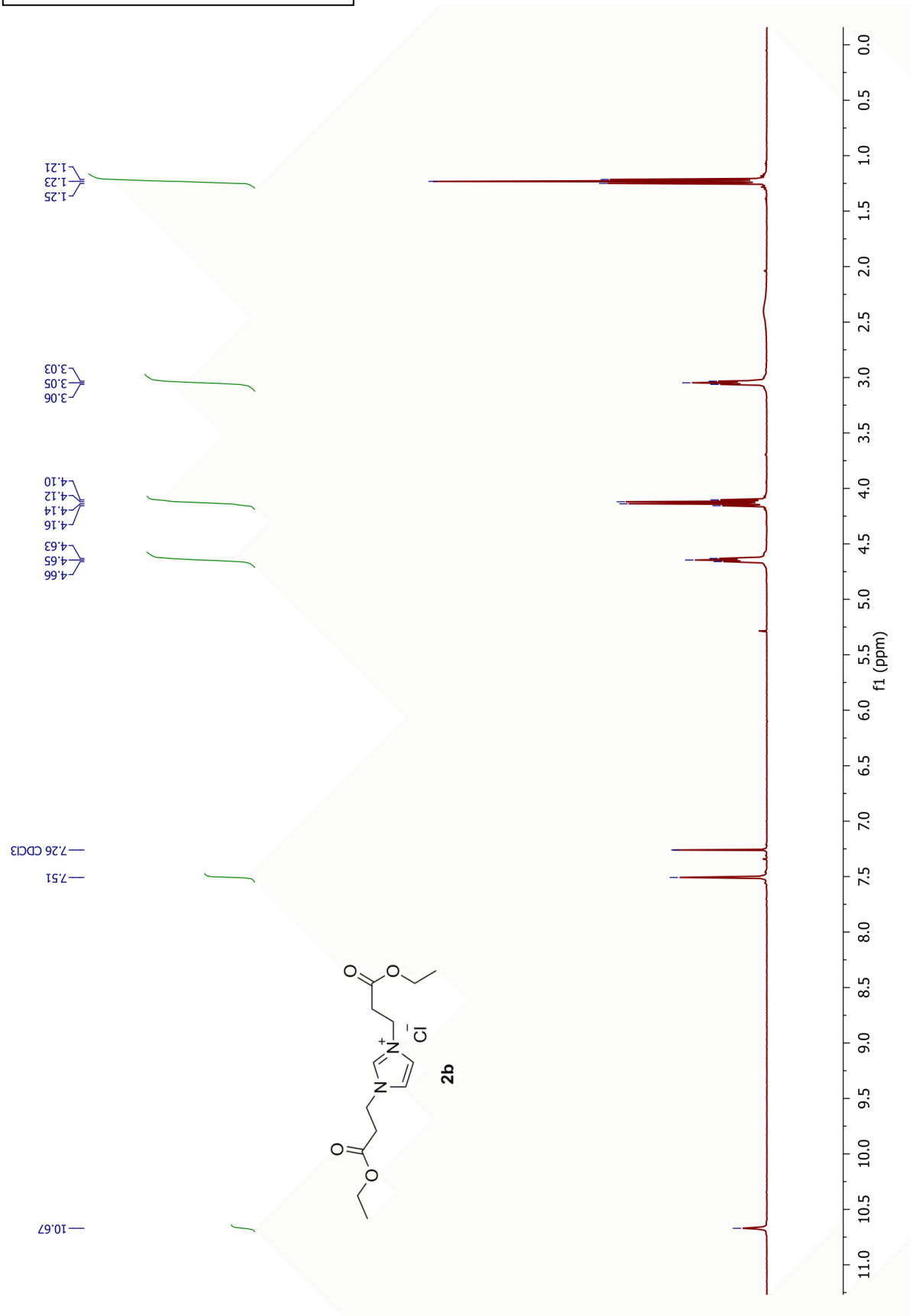
7. ^{1}H NMR spectrum of **2a**



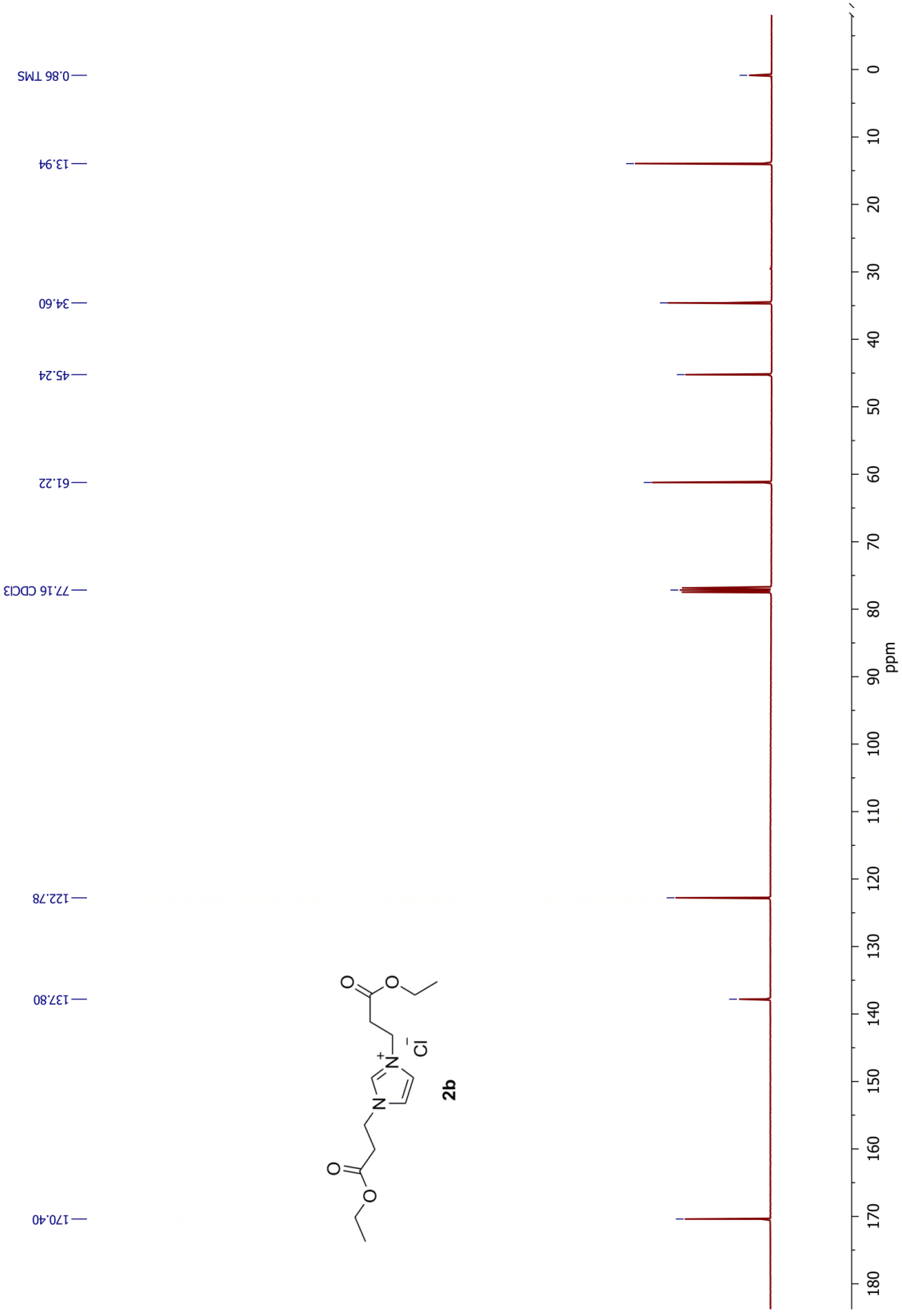
8. ^{13}C NMR spectrum of **2a**



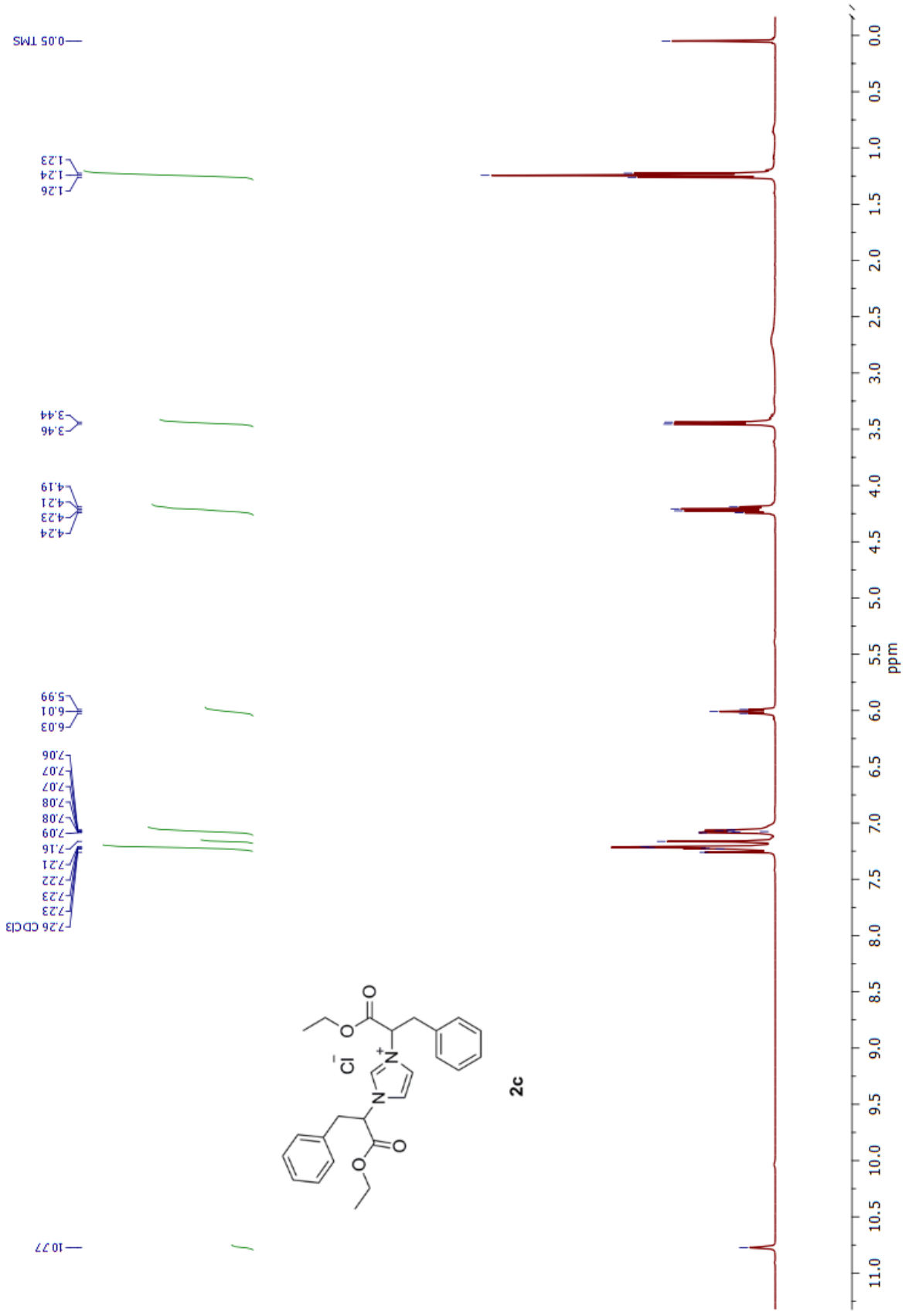
9. ^{1}H NMR spectrum of **2b**



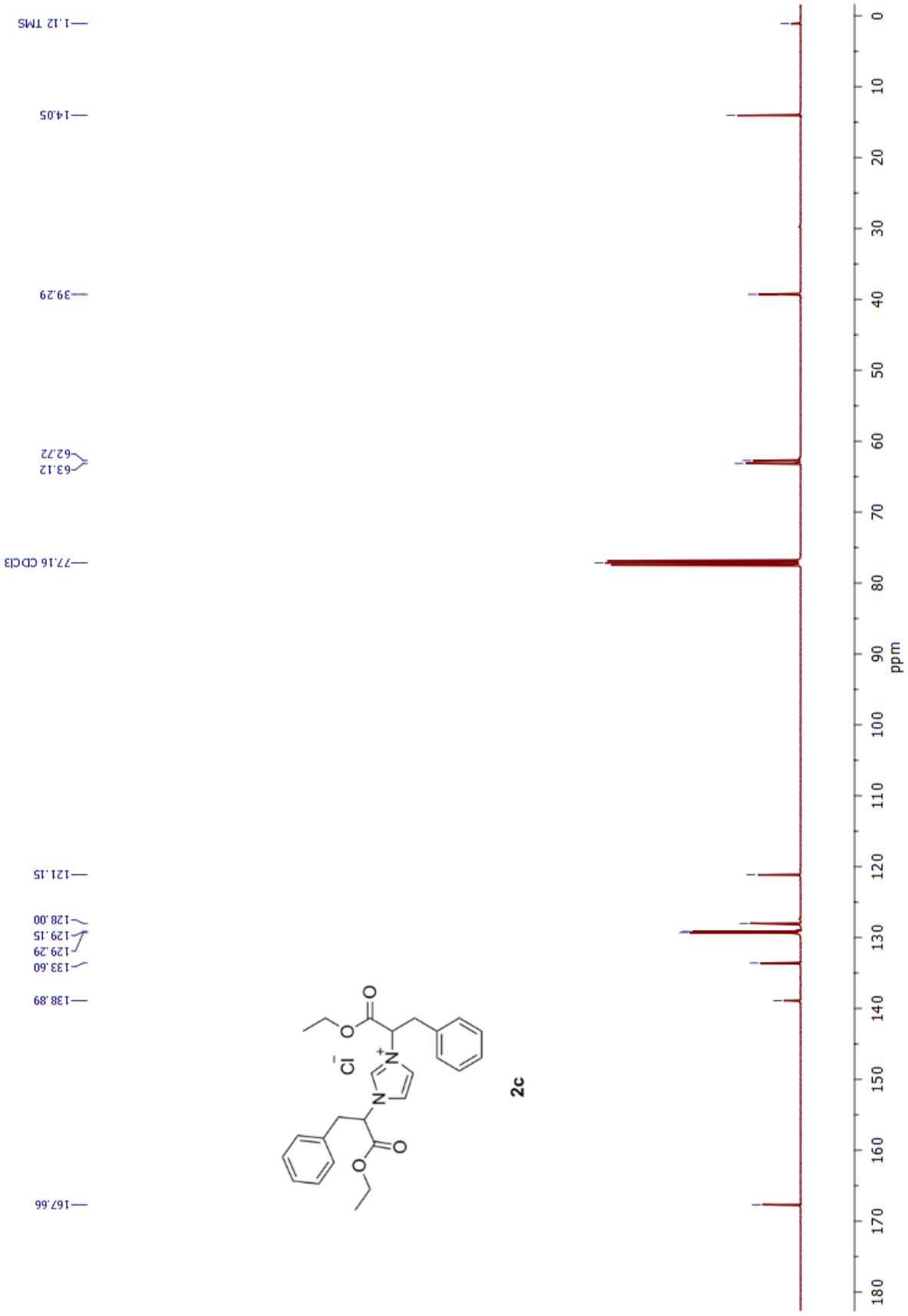
10. ^{13}C NMR spectrum of **2b**



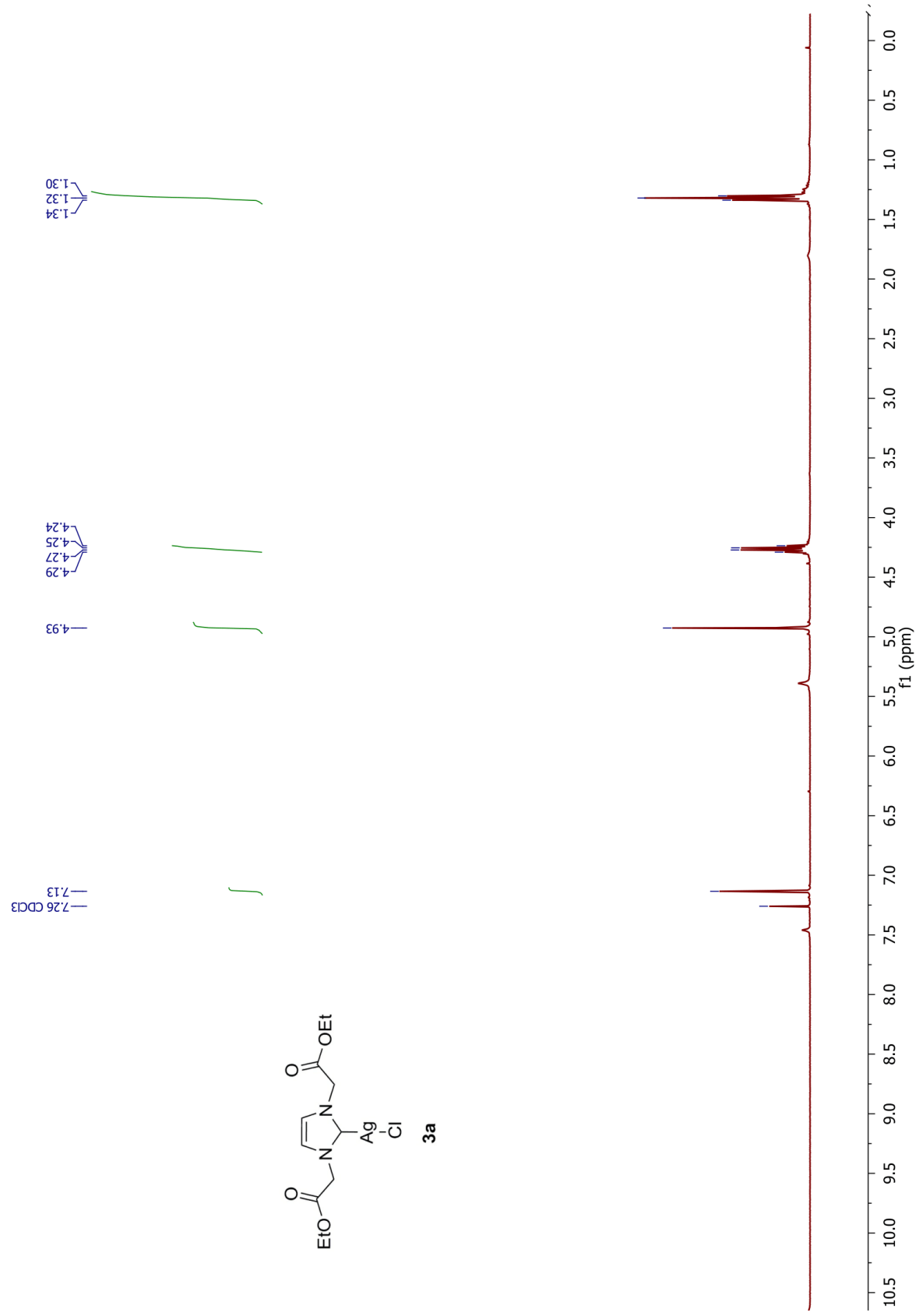
11. ^{1}H NMR spectrum of **2c**



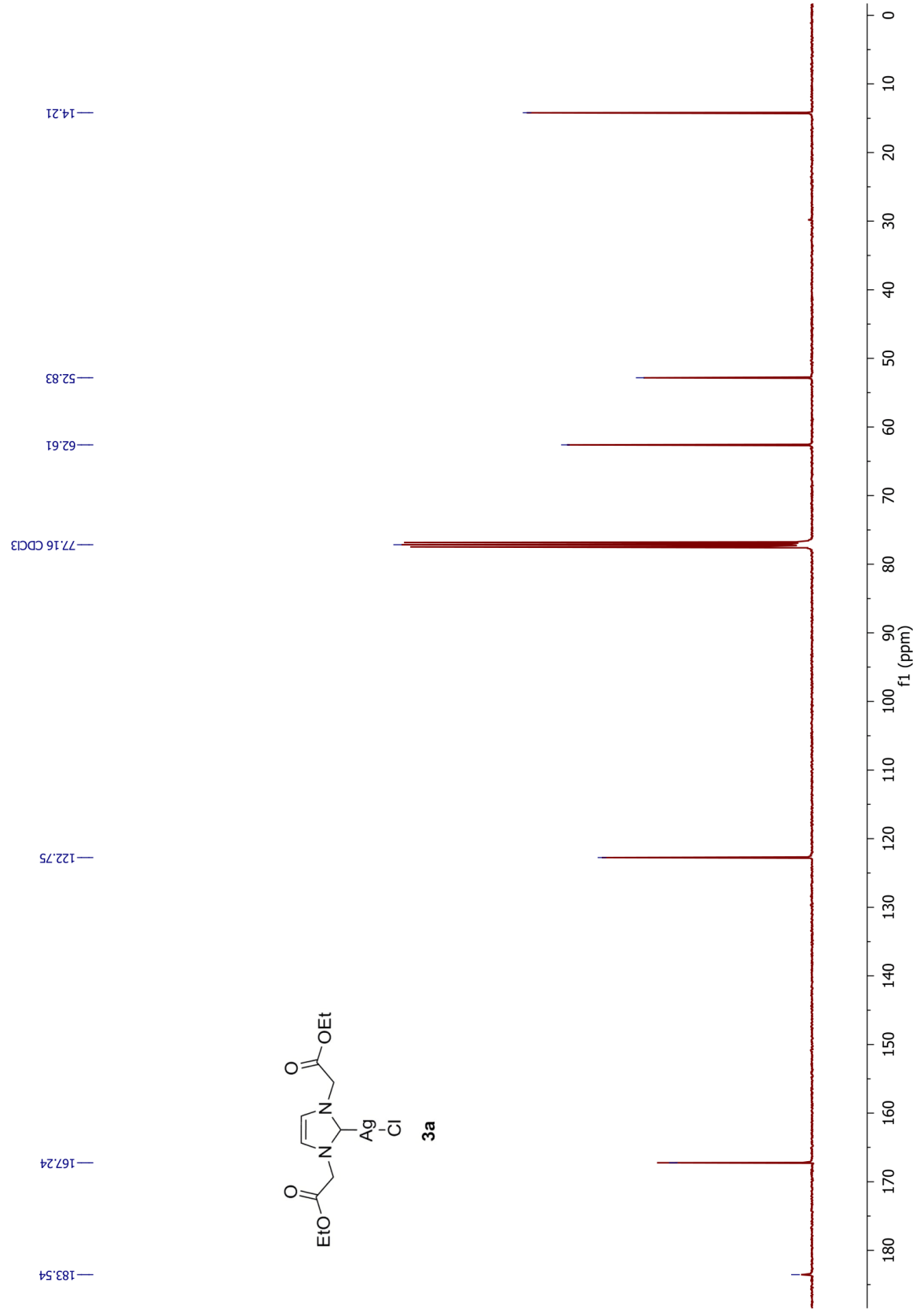
12. ^{13}C NMR spectrum of **2c**



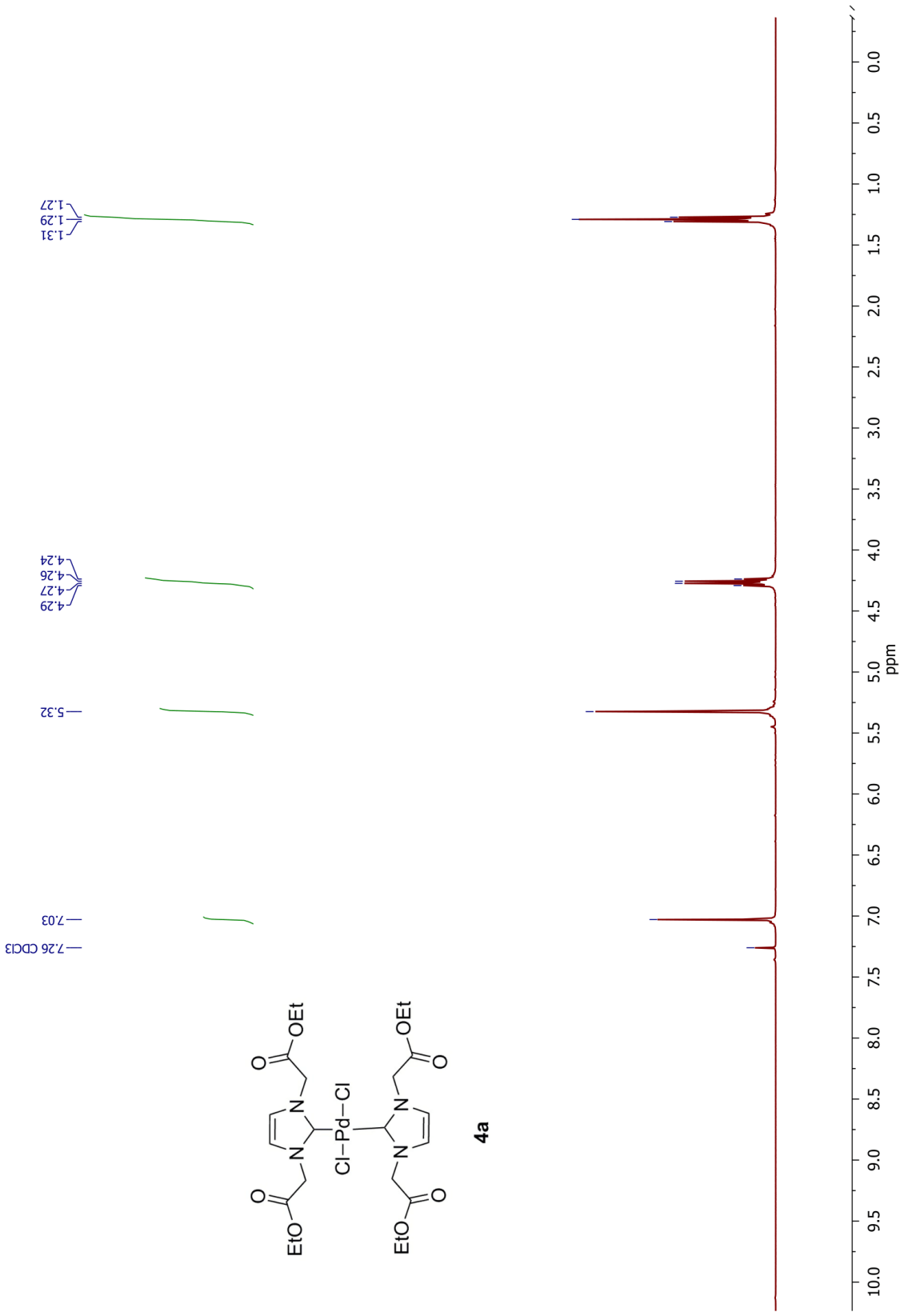
13. ^{1}H NMR spectrum of **3a**



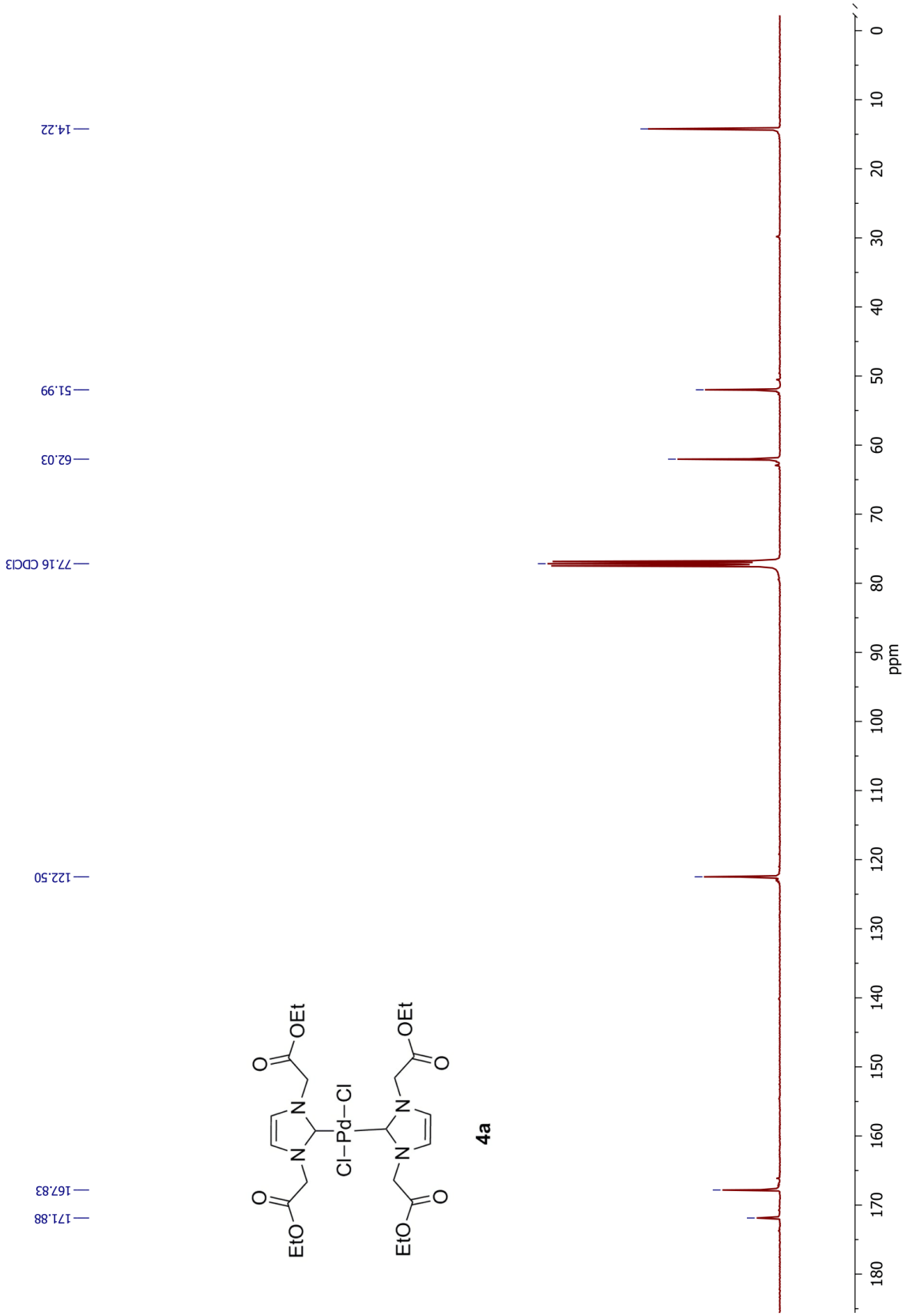
14. ^{13}C NMR spectrum of **3a**



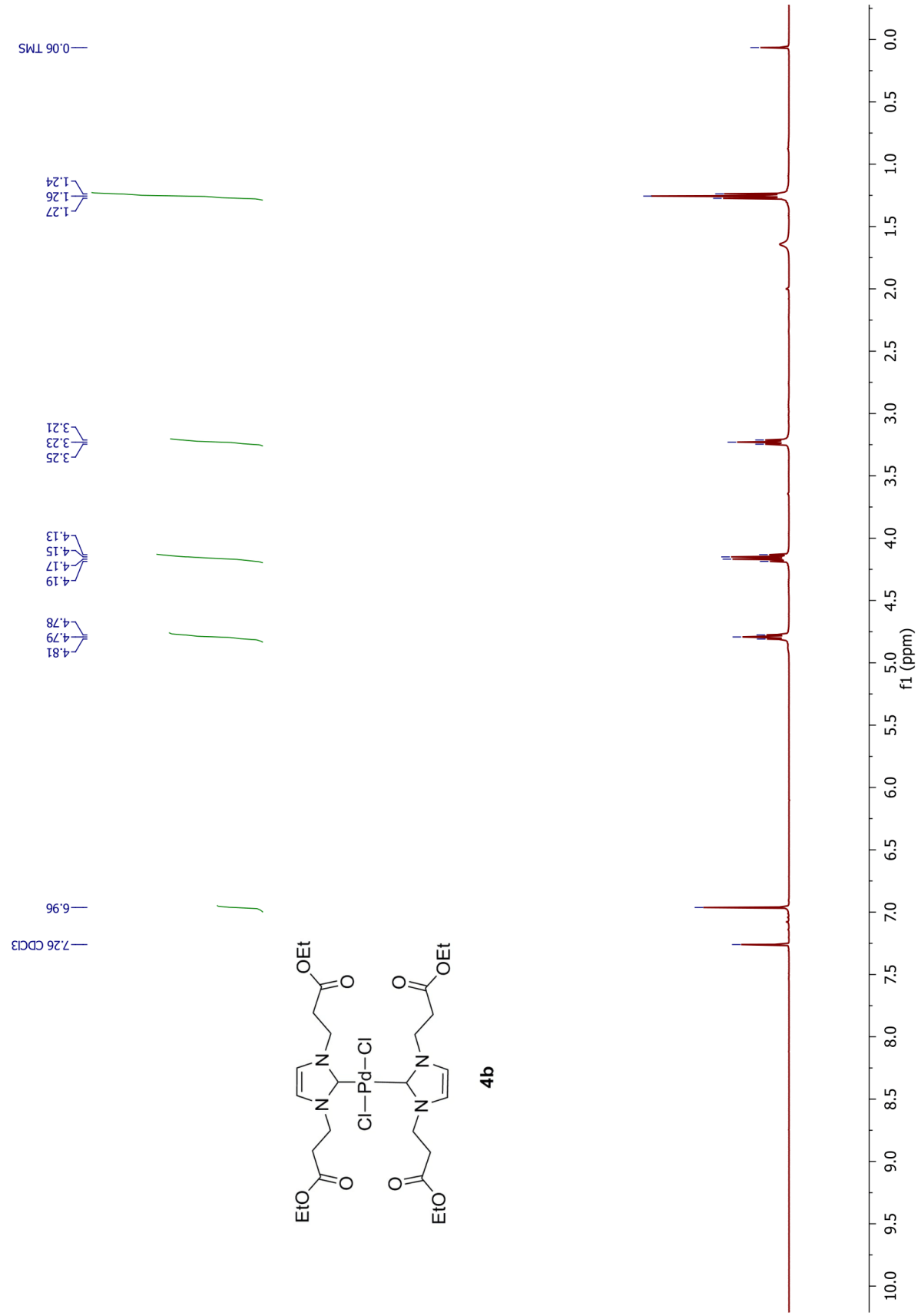
15. ^{1}H NMR spectrum of **4a**



16. ^{13}C NMR spectrum of **4a**

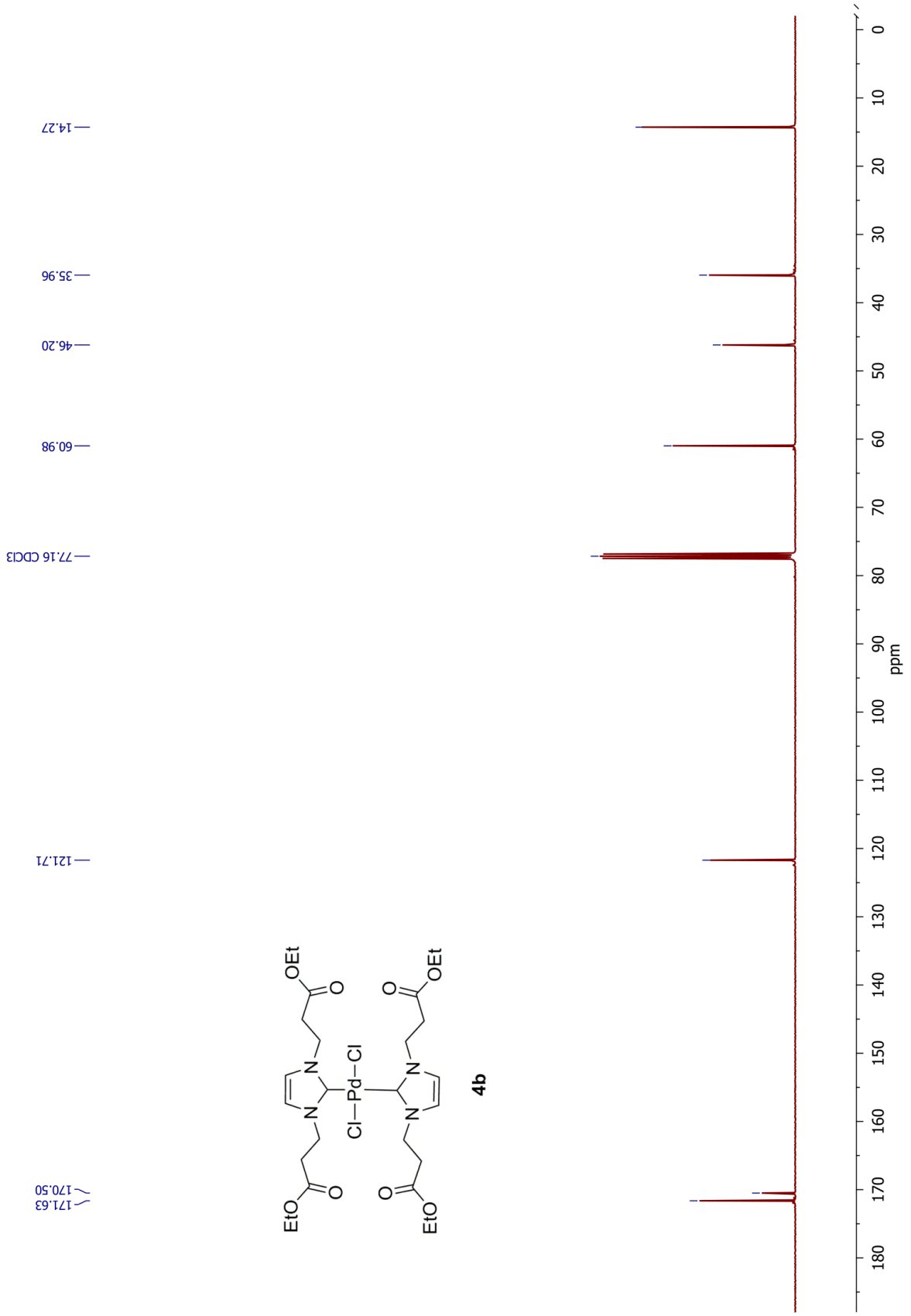


17. ^{1}H NMR spectrum of **4b**

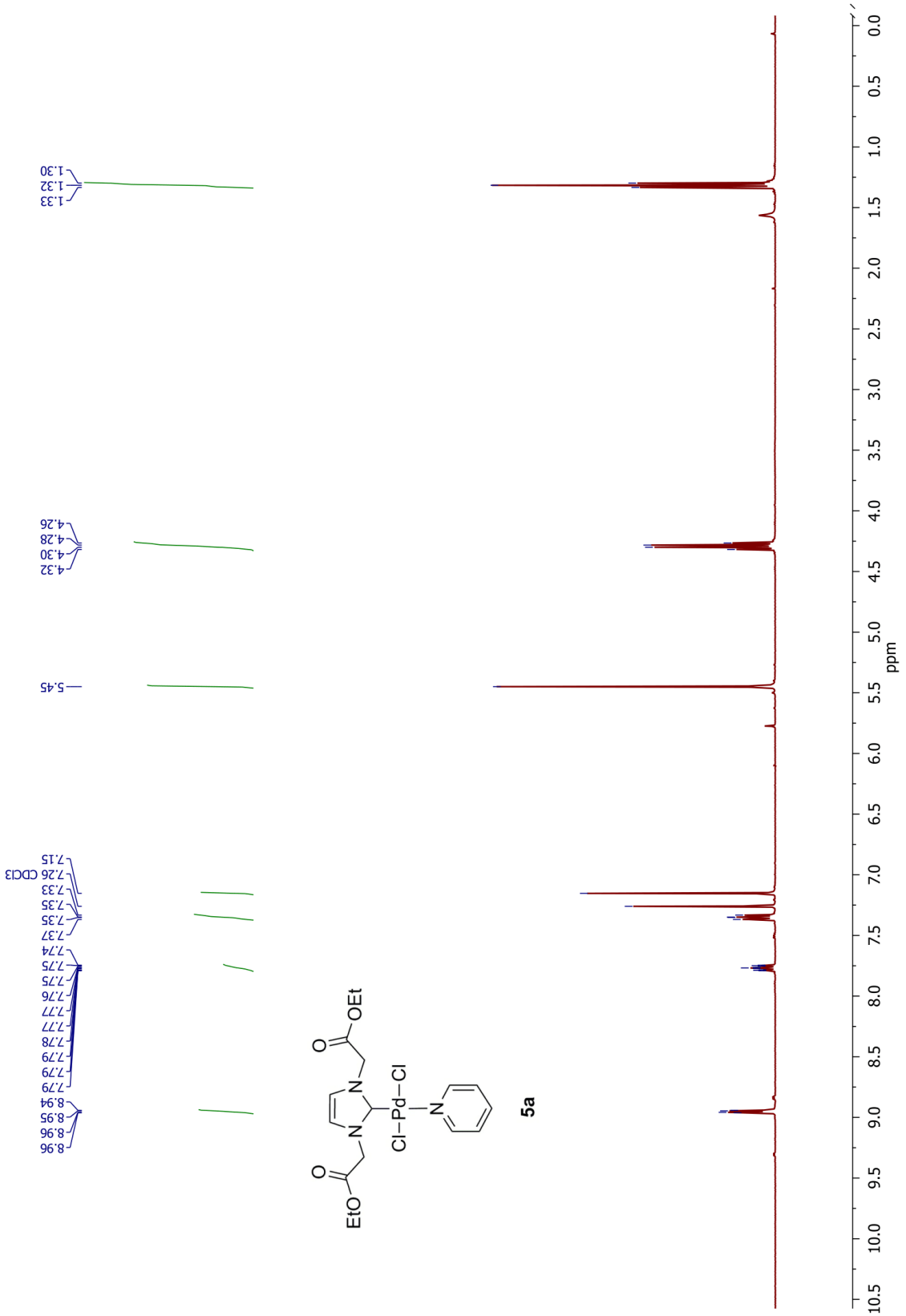


4b

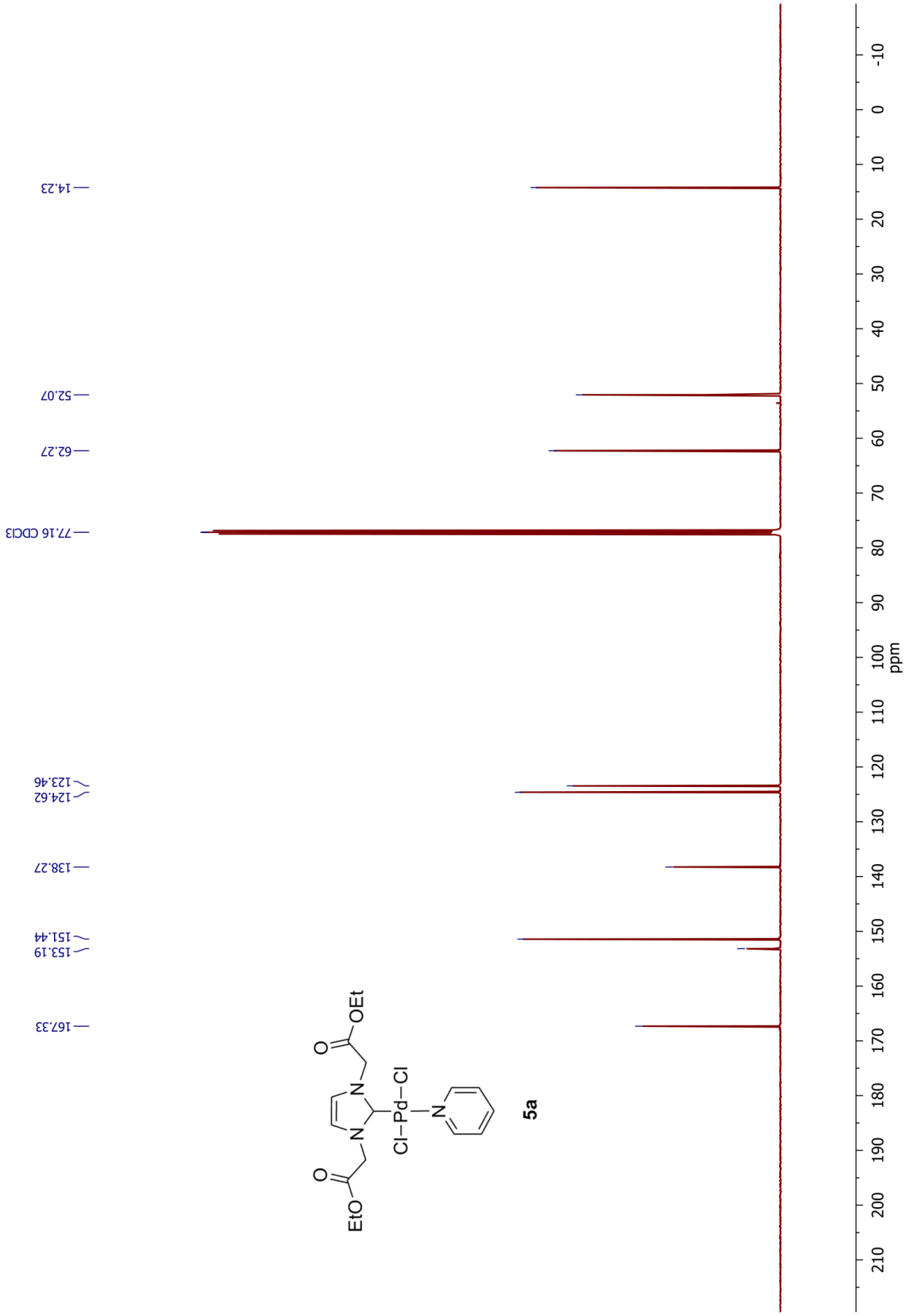
18. ^{13}C NMR spectrum of **4b**



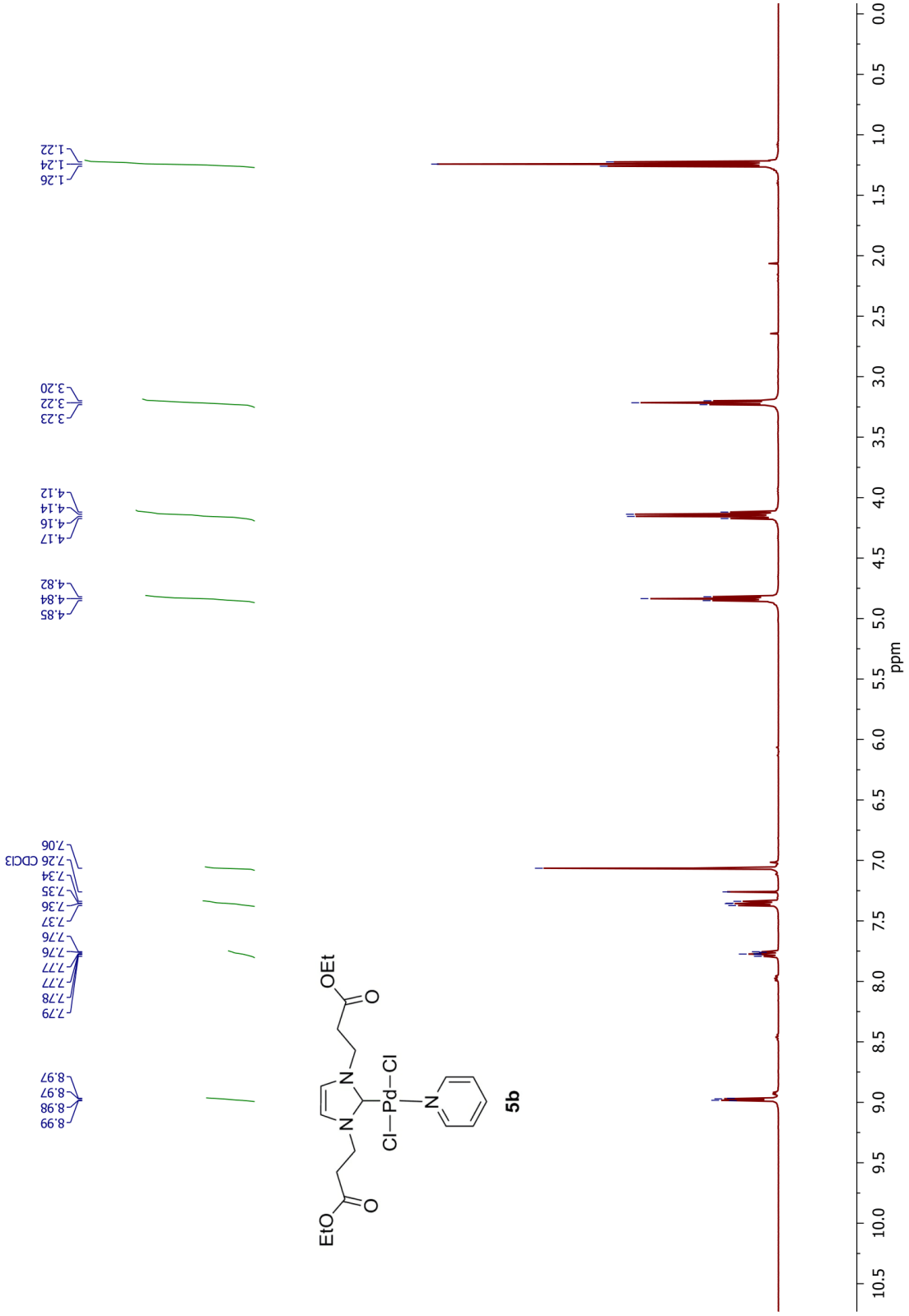
19. ^{1}H NMR spectrum of **5a**



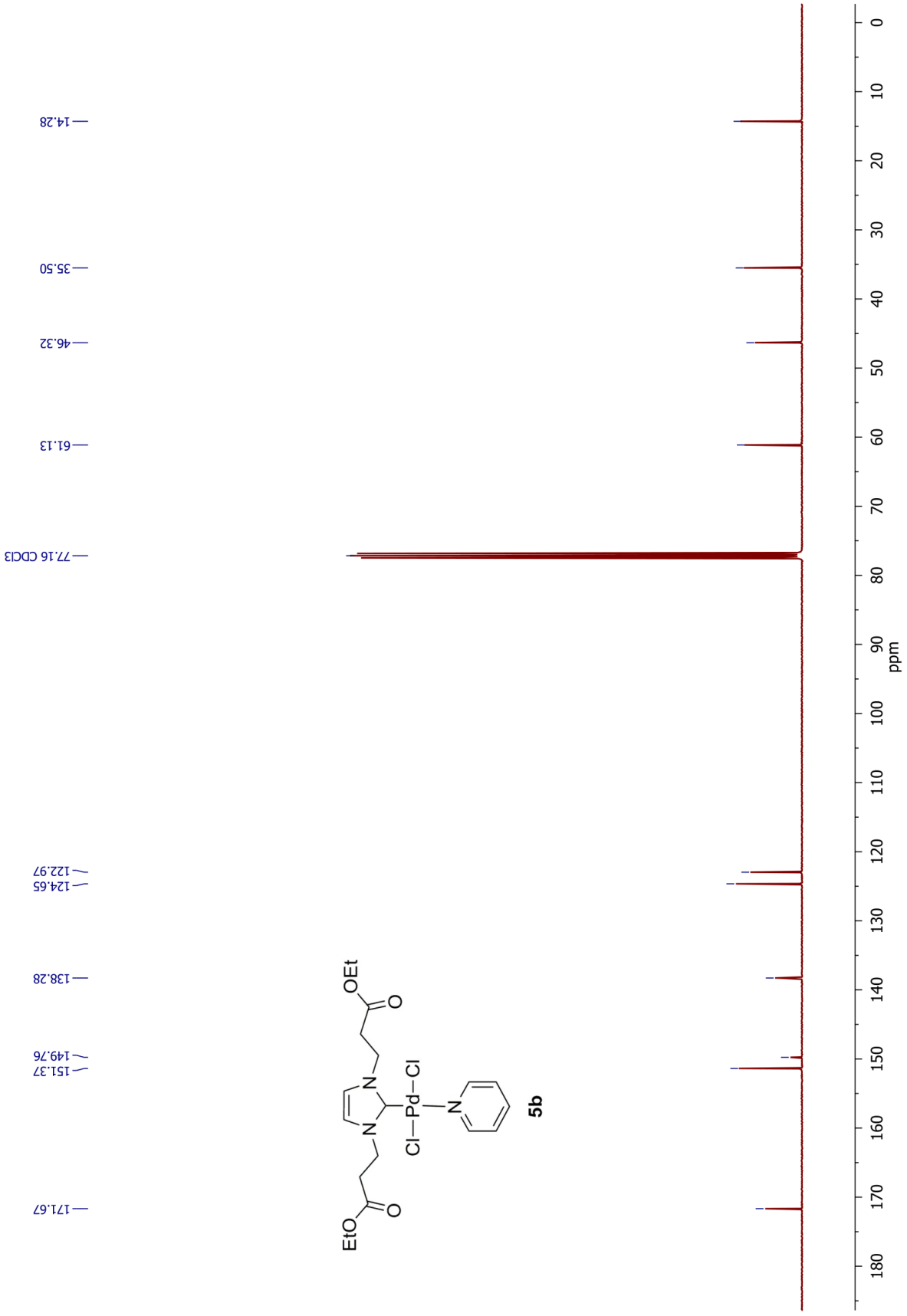
20. ^{13}C NMR spectrum of **5a**



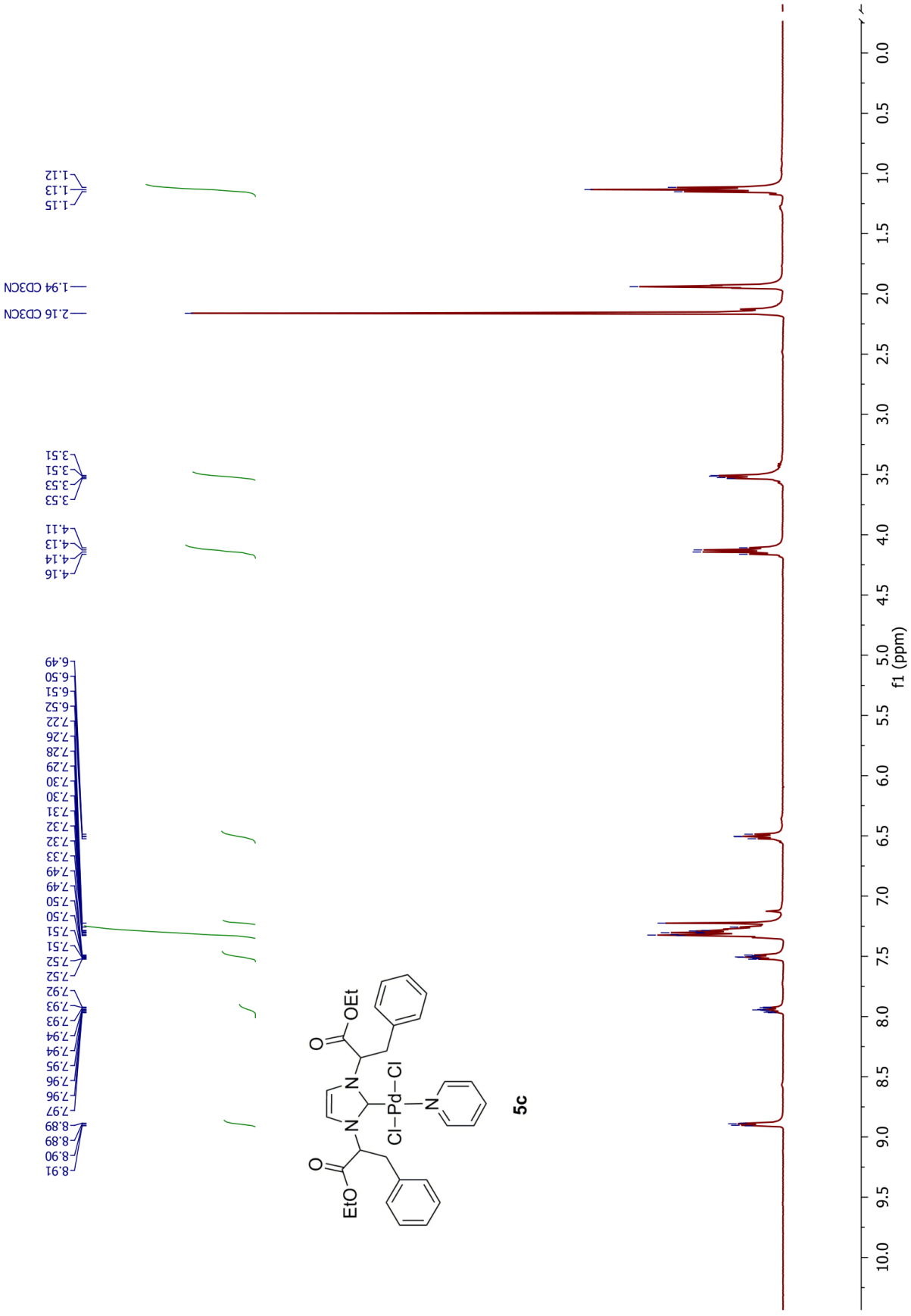
21. ^{1}H NMR spectrum of **5b**



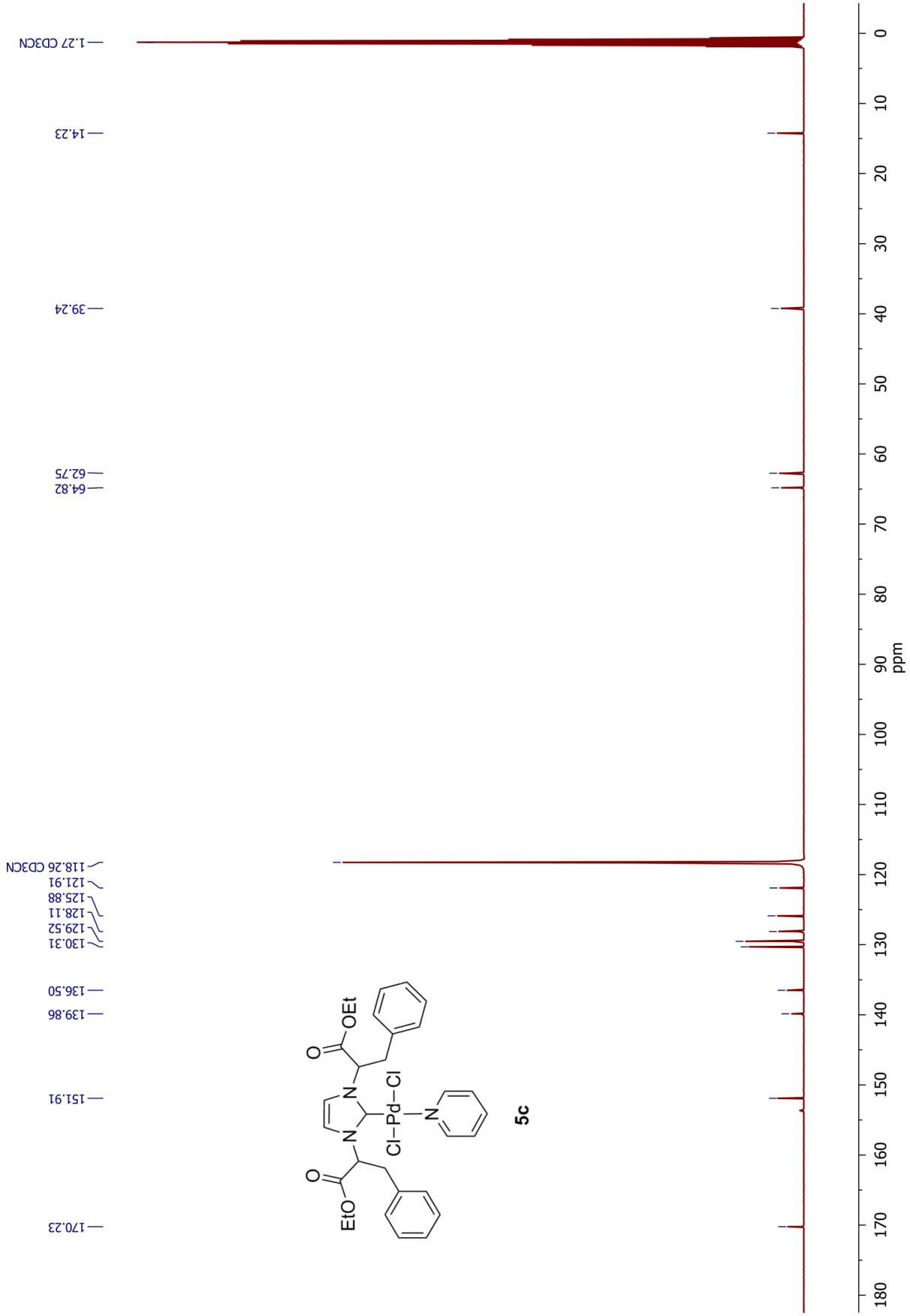
22. ^{13}C NMR spectrum of **5b**



23. ^{13}C NMR spectrum of **5b**



24. ^{13}C NMR spectrum of **5c**



Single crystal X-ray structure determinations of 4a, 4b, 5a and 5b

The crystals were mounted on a glass fibre. Intensity data were collected at 210 K using a STOE Imaging Plate Diffraction System IPDS-2 with graphite monochromatized MoKα radiation (λ = 0.71073 Å) at 50 kV and 40 mA. **4a**: 360 frames, Δω=1°, 1 min; **4b**: 180 frames, Δω=1°, 1 min; **5a**: 180 frames (then decay), Δω=1°, 4 min; **5b**: 360 frames, Δω=1°, 0.7 min. The data were corrected for Lorentz and polarisation effects using the program X-Area1 (Stoe, 2004). Numerical absorption corrections was applied using optimized shape.[1] The structures were solved by direct methods (SHELXS-2013/1), and refined with full-matrix least-squares on F^2 using the program SHELXL-2014/72b (Sheldrick, 2014). [2,3] Non-hydrogen atoms were refined with anisotropic temperature factors. In **4a**, C11 is disordered over two sites with occupancies of 0.75/0.25; C22 is disordered over two sides with occupancies of 0.6788/0.3213; O12; C32 and C33 were refined as disordered over two sides (occupancies 0.5627/0.4373). O15, C43 and C44 were refined as disordered over two sides (occupancies 0.5627/0.4373); The Hirshfeld test violations (Alert_B in PLATON) are caused by vibrations of the ethyl substituents. The maximal crystal size of **5a** was 1.3 mm, but it was not possible to cut the crystal into pieces without bursting. All hydrogen atoms connected to carbon atoms were calculated in their expected positions and refined as riding with C—H = 0.97 Å (CH3), 0.98 Å (CH2), 0.94 Å (Carom) and with Uiso(H) = 1.2Ueq(C) with the exception of methyl hydrogen atoms, which were refined with Uiso(H) = 1.5Ueq(C). The hydrogen atoms within the imidazole rings were located from the difference Fourier map and refined with Uiso(H) = 1.2Ueq(C). For the visualization the program DIAMOND3 (Brandenburg, 2015) was used.[4]

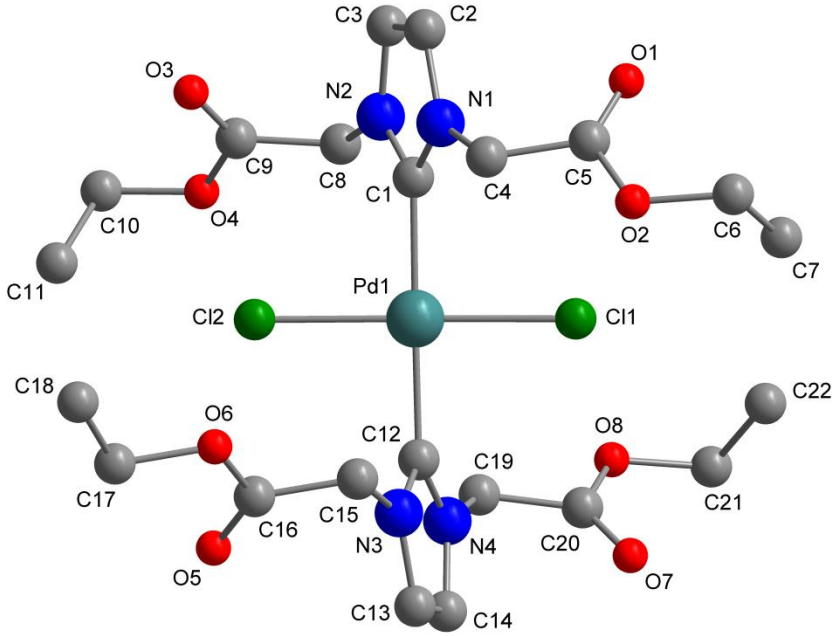
For further details of the refinement – see crystallographic information files (deposited cifs).

CCDC-1438609 (**4a**), 1438610 (**4b**), 1438611 (**5a**) and 1438612 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

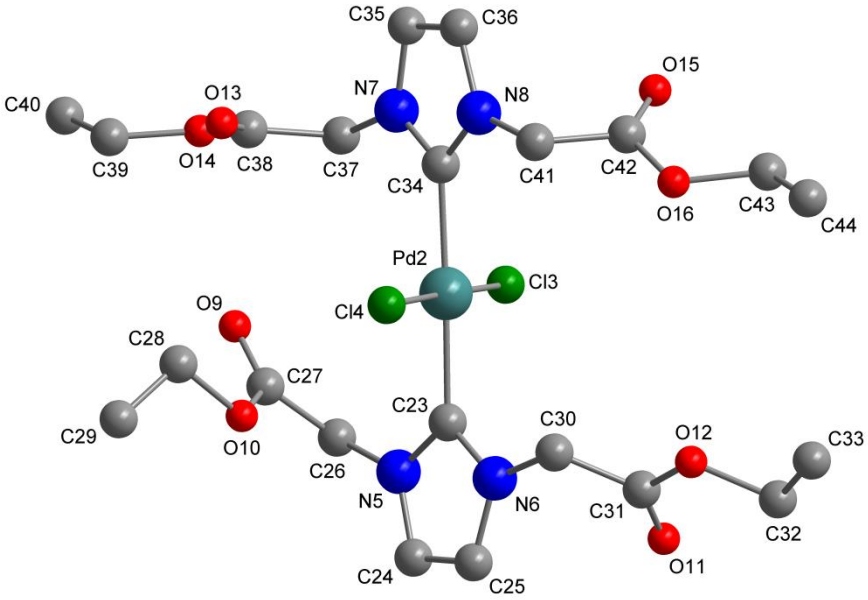
Table S1 Crystal Data, Details of Intensity Measurements, and Structure Refinement for 4a and 4b.

Compound	**4a**	**4b**
Chemical formula	$C_{22}H_{32}Cl_2N_4O_8Pd$	$C_{26}H_{40}Cl_2N_4O_8Pd$
Molecular weight / g mol^{-1}	657.81	713.92
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
a / Å	12.2261(3)	10.3920(5)
b / Å	27.7257(6)	12.0677(7)
c / Å	17.0282(4)	25.5618(10)
β / °	99.793(2)	98.377(3)
Unit cell volume / Å3	5688.1(2)	3171.4(3)
Temperature / K	210(2)	210(2)
Z	8	4
Density (calculated) / g cm^{-1}	1.536	1.495
Radiation type	MoKα	MoKα
μ / mm-1	0.890	0.804
Reflections collected	69663	10088
Independent reflections	9541	2804
R_{int}	0.0616	0.0178
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0297 / 0.0823	0.0234 / 0.0601
R_1 / wR_2 (all data)	0.0362 / 0.0846	0.0251 / 0.0610
Goodness of fit on F^2	1.093	1.052

Fig. S1 Molecular structures of 4a with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.



Molecule 1



Molecule 2

Table S2 Selected bond lengths [Å] for 4a.

C1—N2	1.351 (4)	C12—N3	1.351 (4)
C1—N1	1.354 (4)	C12—N4	1.354 (4)
C1—Pd1	2.033 (3)	C12—Pd1	2.029 (3)
C2—C3	1.335 (5)	C13—C14	1.327 (5)
C2—N1	1.388 (4)	C13—N3	1.388 (4)
C3—N2	1.381 (4)	C14—N4	1.387 (4)
C4—N1	1.451 (4)	C15—N3	1.448 (4)
C4—C5	1.498 (5)	C15—C16	1.505 (4)
C5—O1	1.186 (5)	C16—O5	1.204 (4)
C5—O2	1.336 (4)	C16—O6	1.329 (4)
C6—C7	1.453 (8)	C17—C18	1.390 (7)
C6—O2	1.457 (6)	C19—N4	1.449 (4)
C8—N2	1.455 (4)	C19—C20	1.503 (4)
C8—C9	1.502 (4)	C20—O7	1.197 (4)
C9—O3	1.197 (4)	C20—O8	1.332 (4)
C9—O4	1.331 (4)	C21—O8	1.468 (4)
C10—O4	1.455 (4)		

Table S3 Selected bond angles [°] for 4a.

N2—C1—N1	104.0 (2)	O13—C38—O14	124.5 (3)
N2—C1—Pd1	129.6 (2)	O13—C38—C37	125.1 (3)
N1—C1—Pd1	126.3 (2)	O14—C38—C37	110.4 (3)
C3—C2—N1	106.6 (3)	O16—C42—C41	110.5 (4)
C2—C3—N2	106.8 (3)	N8—C41—C42	112.5 (3)
N1—C4—C5	111.6 (3)	O15—C42—O16	118.8 (13)
O1—C5—O2	124.9 (4)	O15—C42—C41	126.9 (14)
O1—C5—C4	125.4 (3)	C1—N2—C3	111.4 (2)
O2—C5—C4	109.7 (3)	C2—N1—C4	124.3 (2)
O3—C9—C8	125.4 (3)	C1—N1—C2	111.1 (2)
N2—C8—C9	111.8 (3)	C1—N1—C4	124.5 (2)
O3—C9—O4	125.2 (3)	O4—C9—C8	109.4 (3)
N3—C12—N4	104.0 (3)	C1—N2—C8	123.5 (2)
N3—C12—Pd1	125.8 (2)	C3—N2—C8	125.0 (2)
N4—C12—Pd1	130.0 (2)	C12—N3—C13	111.0 (2)
C14—C13—N3	107.0 (3)	C12—N3—C15	124.5 (2)
C13—C14—N4	106.7 (3)	C13—N3—C15	124.2 (2)
N3—C15—C16	111.2 (2)	C12—N4—C14	111.2 (2)
O5—C16—O6	124.7 (3)	C12—N4—C19	124.0 (2)
O5—C16—C15	125.2 (3)	C14—N4—C19	124.8 (2)
O6—C16—C15	110.1 (3)	C23—N5—C24	111.4 (3)
N4—C19—C20	111.9 (2)	C23—N5—C26	123.5 (3)

O7—C20—O8	125.4 (3)	C24—N5—C26	125.1 (3)
O7—C20—C19	125.5 (3)	C23—N6—C25	111.0 (3)
O8—C20—C19	109.1 (3)	C23—N6—C30	123.1 (3)
N5—C23—N6	104.4 (2)	C25—N6—C30	125.8 (3)
N5—C23—Pd2	127.5 (3)	C34—N7—C35	111.2 (3)
N6—C23—Pd2	128.0 (2)	C34—N7—C37	125.2 (2)
C25—C24—N5	106.7 (3)	C35—N7—C37	123.4 (3)
C24—C25—N6	106.4 (3)	C34—N8—C36	111.1 (3)
N5—C26—C27	114.5 (3)	C34—N8—C41	124.6 (3)
O9—C27—O10	126.0 (4)	C36—N8—C41	124.3 (3)
O9—C27—C26	121.3 (4)	C5—O2—C6	117.3 (3)
O10—C27—C26	112.8 (3)	C9—O4—C10	117.5 (3)
N6—C30—C31	114.3 (3)	C16—O6—C17	115.2 (3)
O11—C31—O12	123.0 (7)	C20—O8—C21	115.9 (3)
O12—C31—C30	110.9 (7)	C27—O10—C28	116.3 (4)
O12—C32—C33	106.4 (12)	C31—O12—C32	120.9 (12)
N8—C34—N7	104.2 (2)	C38—O14—C39	115.5 (3)
N8—C34—Pd2	129.0 (2)	C42—O16—C43	115.8 (5)
N7—C34—Pd2	126.9 (2)	C12—Pd1—C1	177.02 (11)
C36—C35—N7	106.4 (3)	C12—Pd1—Cl1	88.53 (8)
C35—C36—N8	107.1 (3)	C1—Pd1—Cl1	90.81 (8)
N7—C37—C38	112.0 (2)	C12—Pd1—Cl2	91.04 (8)
C23—Pd2—Cl4	89.62 (8)	C1—Pd1—Cl2	89.56 (8)

C34—Pd2—Cl4	89.65 (8)	Cl1—Pd1—Cl2	178.73 (3)
C23—Pd2—Cl3	89.34 (8)	C23—Pd2—C34	178.41 (12)
C34—Pd2—Cl3	91.40 (8)	Cl4—Pd2—Cl3	178.95 (3)

Table S4 Selected torsion angles [°] for 4a.

N1—C2—C3—N2	-0.1 (3)	N6—C23—N5—C26	−179.4 (3)
N1—C4—C5—O1	26.4 (5)	Pd2—C23—N5—C26	3.5 (4)
N1—C4—C5—O2	−155.7 (3)	C25—C24—N5—C23	−0.6 (4)
N2—C8—C9—O3	21.6 (4)	C25—C24—N5—C26	180.0 (3)
N2—C8—C9—O4	−159.6 (2)	C27—C26—N5—C23	−62.8 (4)
N3—C13—C14—N4	−0.6 (3)	C27—C26—N5—C24	116.5 (3)
N3—C15—C16—O5	14.4 (5)	N5—C23—N6—C25	−1.3 (3)
N3—C15—C16—O6	−165.6 (3)	Pd2—C23—N6—C25	175.8 (2)
N4—C19—C20—O7	19.1 (4)	N5—C23—N6—C30	−177.2 (3)
N4—C19—C20—O8	−163.0 (2)	Pd2—C23—N6—C30	−0.1 (4)
N5—C24—C25—N6	−0.2 (4)	C24—C25—N6—C23	1.0 (4)
N5—C26—C27—O9	146.1 (4)	C24—C25—N6—C30	176.7 (3)
N5—C26—C27—O10	−34.0 (4)	C31—C30—N6—C23	−128.7 (3)
N6—C30—C31—O11	−2.3 (6)	C31—C30—N6—C25	56.0 (5)
N6—C30—C31—O12	−177.1 (10)	N8—C34—N7—C35	−0.2 (3)
N7—C35—C36—N8	−1.2 (4)	Pd2—C34—N7—C35	179.1 (2)
N7—C37—C38—O13	−16.2 (5)	N8—C34—N7—C37	−176.5 (3)

N7—C37—C38—O14	163.7 (3)	Pd2—C34—N7—C37	2.8 (4)
N8—C41—C42—O15	39.1 (11)	C36—C35—N7—C34	1.0 (4)
N8—C41—C42—O16	−163.3 (4)	C36—C35—N7—C37	177.3 (3)
N2—C1—N1—C2	-0.1 (3)	C38—C37—N7—C34	103.6 (3)
Pd1—C1—N1—C2	−176.3 (2)	C38—C37—N7—C35	−72.3 (4)
N2—C1—N1—C4	−175.5 (3)	N7—C34—N8—C36	−0.6 (4)
Pd1—C1—N1—C4	8.3 (4)	Pd2—C34—N8—C36	−179.9 (2)
C3—C2—N1—C1	0.1 (4)	N7—C34—N8—C41	−178.8 (3)
C3—C2—N1—C4	175.5 (3)	Pd2—C34—N8—C41	1.9 (4)
C5—C4—N1—C1	100.3 (3)	C35—C36—N8—C34	1.2 (4)
C5—C4—N1—C2	−74.6 (4)	C35—C36—N8—C41	179.4 (3)
N1—C1—N2—C3	0.0 (3)	C42—C41—N8—C34	96.8 (4)
Pd1—C1—N2—C3	176.1 (2)	C42—C41—N8—C36	−81.1 (4)
N1—C1—N2—C8	−177.5 (2)	O1—C5—O2—C6	−0.1 (6)
Pd1—C1—N2—C8	−1.4 (4)	C4—C5—O2—C6	−177.8 (3)
C2—C3—N2—C1	0.0 (3)	C7—C6—O2—C5	−81.2 (5)
C2—C3—N2—C8	177.5 (3)	O3—C9—O4—C10	2.5 (5)
C9—C8—N2—C1	102.6 (3)	C8—C9—O4—C10	−176.2 (3)
C9—C8—N2—C3	−74.6 (4)	C11—C10—O4—C9	−87.0 (4)
N4—C12—N3—C13	0.2 (3)	O5—C16—O6—C17	4.4 (5)
Pd1—C12—N3—C13	−175.2 (2)	C15—C16—O6—C17	−175.5 (4)
N4—C12—N3—C15	−174.2 (2)	C18—C17—O6—C16	−174.7 (4)
Pd1—C12—N3—C15	10.3 (4)	O7—C20—O8—C21	−0.8 (5)

C14—C13—N3—C12	0.2 (3)	C19—C20—O8—C21	−178.8 (3)
C14—C13—N3—C15	174.7 (3)	C22—C21—O8—C20	−74.7 (5)
C16—C15—N3—C12	98.3 (3)	O9—C27—O10—C28	−6.3 (6)
C16—C15—N3—C13	−75.4 (4)	C26—C27—O10—C28	173.8 (4)
N3—C12—N4—C14	−0.6 (3)	C29—C28—O10—C27	136.8 (5)
Pd1—C12—N4—C14	174.6 (2)	O11—C31—O12—C32	−1.5 (2)
N3—C12—N4—C19	−177.8 (2)	C30—C31—O12—C32	165.6 (13)
Pd1—C12—N4—C19	−2.6 (4)	O13—C38—O14—C39	−8.5 (5)
C13—C14—N4—C12	0.8 (3)	C37—C38—O14—C39	171.6 (3)
C13—C14—N4—C19	177.9 (3)	C40—C39—O14—C38	165.7 (4)
C20—C19—N4—C12	108.2 (3)	O15—C42—O16—C43	-0.4 (15)
C20—C19—N4—C14	−68.6 (3)	C41—C42—O16—C43	−160.0 (7)
N6—C23—N5—C24	1.2 (3)	C44—C43—O16—C42	165.0 (9)
Pd2—C23—N5—C24	−175.9 (2)		

Table S5 Selected dihedral angles [°] for 4a.

$Pd/Cl_2/C_2$ // N1/N2/C1-C3	68.60(7)	$Pd/Cl_2/C_2$ // N3/N4/C12-C14	69.12(7)
$Pd/Cl_2/C_2$ // N7/N8/C34-C36	62.29(9)	$Pd/Cl_2/C_2$ // N5/N6/C23-C25	69.05(7)

Fig. S2 Molecular structure of 4b with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

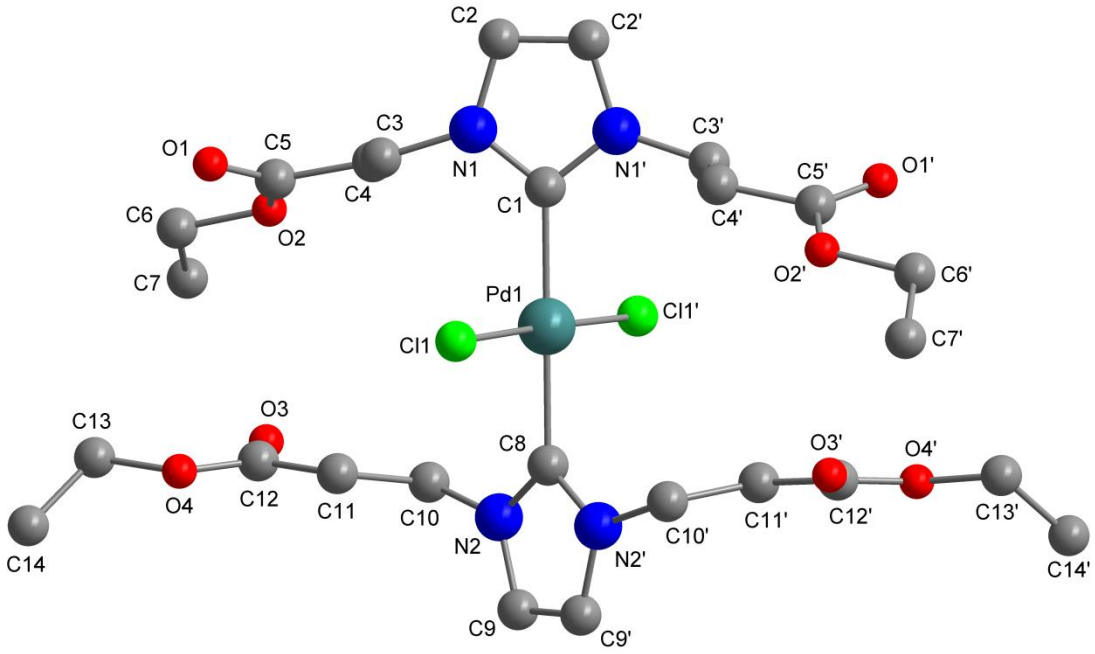


Table S6 Selected bond lengths [Å] for 4b.

C1—N1‘	1.352 (2)	C8—N2‘	1.345 (2)
C1—N1	1.352 (2)	C8—Pd1	2.021 (3)
C1—Pd1	2.029 (3)	C9—C9‘	1.333 (5)
C2—C2‘	1.336 (5)	C9—N2	1.382 (3)
C2—N1	1.380 (3)	C10—N2	1.460 (3)
C3—N1	1.461 (3)	C10—C11	1.511 (3)
C3—C4	1.511 (3)	C11—C12	1.488 (3)
C4—C5	1.500 (3)	C12—O3	1.158 (3)

C5—O1	1.186 (3)	C12—O4	1.292 (3)
C5—O2	1.311 (3)	C13—C14	1.455 (5)
C6—O2	1.458 (3)	C13—O4	1.446 (3)
C6—C7	1.492 (4)	Cl1—Pd1	2.3124 (5)
C8—N2	1.345 (2)	Pd1—Cl1i	2.3124 (5)

Symmetry code: ‘ –x, y, -z-0.5

Table S7 Selected bond angles [°] for 4b.

N1‘—C1—N1	104.5 (2)	O2—C5—C4	112.7 (2)
N1‘—C1—Pd1	127.77 (12)	N2—C8—N2‘	104.7 (2)
N1—C1—Pd1	127.77 (12)	N2—C8—Pd1	127.66 (12)
C2‘—C2—N1	106.86 (12)	N2‘—C8—Pd1	127.66 (12)
N1—C3—C4	111.33 (17)	C9‘—C9—N2	106.77 (13)
C5—C4—C3	111.43 (18)	N2—C10—C11	110.40 (19)
O1—C5—O2	123.4 (2)	C12—C11—C10	113.6 (2)
O1—C5—C4	123.8 (2)		

Table S8 Selected torsion angles [°] for 4b.

N1—C3—C4—C5	−172.8 (2)	N2‘—C8—N2—C9	0.32 (11)
C3—C4—C5—O1	21.4 (4)	Pd1—C8—N2—C9	−179.68 (11)
C3—C4—C5—O2	−161.4 (2)	N2‘—C8—N2—C10	175.5 (2)

N2—C10—C11—C12	−165.7 (2)	Pd1—C8—N2—C10	−4.5 (2)
C10—C11—C12—O3	−14.2 (5)	C9‘—C9—N2—C8	−0.8 (3)
C10—C11—C12—O4	167.4 (3)	C9‘—C9—N2—C10	−176.1 (2)
N1‘—C1—N1—C2	0.13 (12)	C11—C10—N2—C8	−84.4 (2)
Pd1—C1—N1—C2	−179.87 (12)	C11—C10—N2—C9	90.2 (3)
N1‘—C1—N1—C3	177.4 (2)	O1—C5—O2—C6	−2.7 (5)
Pd1—C1—N1—C3	−2.7 (2)	C4—C5—O2—C6	−179.9 (2)
C2‘—C2—N1—C1	−0.4 (3)	C7—C6—O2—C5	−169.1 (3)
C2‘—C2—N1—C3	−177.6 (2)	O3—C12—O4—C13	−1.1 (6)
C4—C3—N1—C1	−86.6 (2)	C11—C12—O4—C13	177.2 (3)
C4—C3—N1—C2	90.2 (3)	C14—C13—O4—C12	142.7 (3)

Table S9 Selected dihedral angles [°] for 4b.

Pd/Cl2/C2 // N1/N1‘/C1/C2/C2‘	68.44(7)	Pd/Cl2/C2 // N3/N4/C12-C14	69.0(1)

Table S10 Crystal Data, Details of Intensity Measurements, and Structure Refinement for 5a and 5b.

Compound	**5a**·$CHCl_3$	**5b**
Chemical formula	$C_{17}H_{22}Cl_5N_3O_4Pd$	$C_{18}H_{25}Cl_2N_3O_4Pd$
Molecular weight / g mol^{-1}	616.02	524.71
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\ -1$ (no. 15)
a / Å	11.7256(4)	9.4985(8)
b / Å	23.0938(8)	9.7104(7)
c / Å	9.0944(6)	12.2951(10)
α / °	90	93.265(6)
β / °	99.520(4)	95.848(6)
γ / °	90	98.828(6)
Unit cell volume / Å3	2428.7(2)	1111.72(15)
Temperature / K	210(2)	210(2)
Z	4	2
Density (calculated) / g cm^{-1}	1.685	1.567
Radiation type	MoKα	MoKα
μ / mm^{-1}	1.342	1.102
Reflections collected	15567	14413
Independent reflections	4269	3924
R_{int}	0.0364	0.0243
R_1 / wR_2 $[I > 2\sigma(I)]$	0.0241 / 0.0581	0.0194 / 0.0525
R_1 / $wR2$ (all data)	0.0327 / 0.0613	0.0213 / 0.0533
Goodness of fit on F^2	1.015	1.059

Fig. S3 Molecular structure of 5a with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

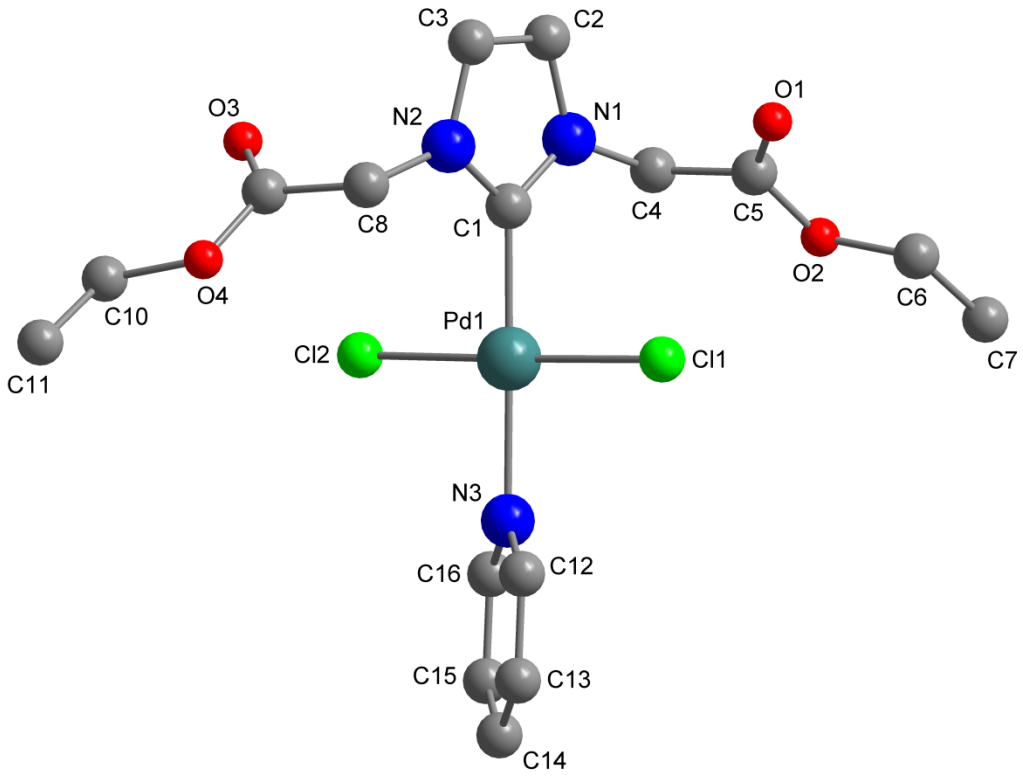


Table S11 Selected bond lengths [Å] for 5a.

C1—N1	1.347 (3)	C9—O4	1.324 (3)
C1—N2	1.350 (3)	C10—O4	1.453 (3)
C1—Pd1	1.969 (2)	C10—C11	1.480 (5)
C2—C3	1.339 (4)	C12—N3	1.342 (3)
C2—N1	1.387 (3)	C12—C13	1.377 (4)
C3—N2	1.384 (3)	C13—C14	1.376 (4)
C4—N1	1.451 (3)	C14—C15	1.379 (4)
C4—C5	1.510 (3)	C15—C16	1.379 (4)
C5—O1	1.200 (3)	C16—N3	1.336 (3)

C5—O2	1.332 (3)	Cl1—Pd1	2.3046 (6)
C6—O2	1.461 (3)	Cl2—Pd1	2.3014 (6)
C6—C7	1.484 (4)	N3—Pd1	2.091 (2)
C8—N2	1.450 (3)	Cl3—C17	1.734 (4)
C8—C9	1.510 (3)	Cl4—C17	1.762 (4)
C9—O3	1.200 (3)	Cl5—C17	1.756 (4)

Table S12 Selected bond angles [°] for 5a.

N1—C1—N2	105.0 (2)	C1—N2—C3	110.7 (2)
N1—C1—Pd1	128.09 (17)	C1—N2—C8	124.4 (2)
N2—C1—Pd1	126.92 (17)	C3—N2—C8	124.7 (2)
C3—C2—N1	106.8 (2)	C16—N3—C12	118.2 (2)
C2—C3—N2	106.8 (2)	C16—N3—Pd1	121.76 (17)
N1—C4—C5	110.50 (19)	C12—N3—Pd1	120.05 (17)
O1—C5—O2	125.4 (2)	C5—O2—C6	115.2 (2)
O1—C5—C4	124.5 (2)	C9—O4—C10	115.6 (2)
O2—C5—C4	110.1 (2)	C1—Pd1—N3	178.00 (9)
N2—C8—C9	111.4 (2)	C1—Pd1—Cl2	90.09 (7)
O3—C9—O4	125.5 (2)	N3—Pd1—Cl2	90.38 (6)
O3—C9—C8	125.0 (2)	C1—Pd1—Cl1	89.12 (6)
O4—C9—C8	109.4 (2)	N3—Pd1—Cl1	90.49 (6)
N3—C12—C13	122.3 (2)	Cl2—Pd1—Cl1	177.58 (3)
N3—C16—C15	122.5 (3)	Cl3—C17—Cl5	110.7 (2)

C1—N1—C2	110.7 (2)	Cl3—C17—Cl4	111.1 (2)
C1—N1—C4	124.0 (2)	Cl5—C17—Cl4	109.7 (2)
C2—N1—C4	124.9 (2)		

Table S13 Selected torsion angles [°] for 5a.

N1—C4—C5—O1	−25.8 (3)	N1—C1—N2—C8	175.9 (2)
N1—C4—C5—O2	155.3 (2)	Pd1—C1—N2—C8	−5.7 (3)
N2—C8—C9—O3	−23.8 (4)	C2—C3—N2—C8	−176.3 (2)
N2—C8—C9—O4	157.2 (2)	C9—C8—N2—C1	−87.9 (3)
Pd1—C1—N1—C2	−178.16 (17)	C9—C8—N2—C3	87.1 (3)
N2—C1—N1—C4	173.9 (2)	C15—C16—N3—Pd1	−178.0 (2)
Pd1—C1—N1—C4	−4.6 (3)	C13—C12—N3—C16	−0.7 (4)
C3—C2—N1—C4	−174.2 (2)	C13—C12—N3—Pd1	177.4 (2)
C5—C4—N1—C1	−93.0 (3)	O1—C5—O2—C6	8.6 (4)
C5—C4—N1—C2	79.7 (3)	C4—C5—O2—C6	−172.6 (2)
N1—C1—N2—C3	0.2 (2)	C7—C6—O2—C5	−173.6 (2)
Pd1—C1—N2—C3	178.68 (16)	O3—C9—O4—C10	4.7 (4)
C11—C10—O4—C9	−170.8 (3)	C8—C9—O4—C10	−176.4 (2)

Table S14 Selected dihedral angles [°] for 5a.

Pd/Cl2/C2 // N1/N2/C1-C3	75.46(5)	Pd/Cl2/C2 // N3/C12-C16	47.79(7)

Fig. S4 Molecular structure of 5b with the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

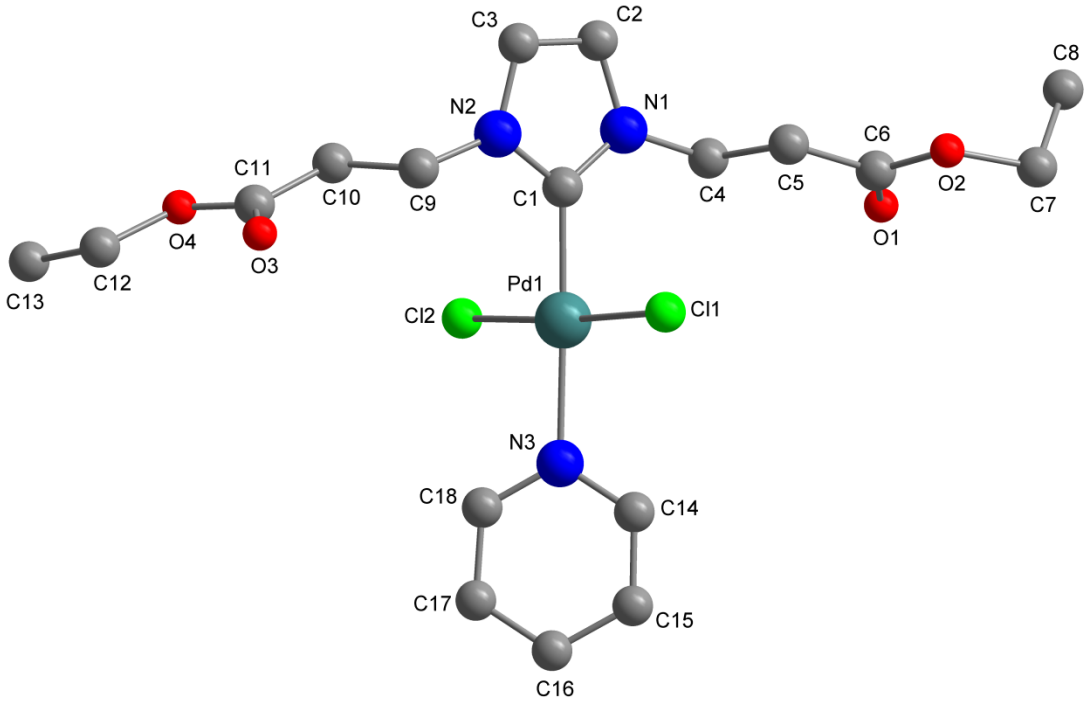


Table S15 Selected bond lengths [Å] for 5b.

C1—N1	1.343 (2)	C11—O3	1.201 (3)
C1—N2	1.348 (2)	C11—O4	1.323 (3)
C1—Pd1	1.9578 (17)	C12—O4	1.466 (3)
C2—C3	1.343 (3)	C14—N3	1.330 (3)
C2—N1	1.387 (2)	C18—N3	1.328 (3)
C3—N2	1.382 (2)	Cl1—Pd1	2.2988 (5)
C4—N1	1.465 (2)	Cl2—Pd1	2.3167 (5)
C5—C6	1.505 (2)	N3—Pd1	2.1102 (15)
C6—O1	1.202 (2)	C9—N2	1.465 (2)
C6—O2	1.335 (2)	C10—C11	1.505 (3)
C7—O2	1.463 (2)		

Table S16 Selected bond angles [°] for 5b.

N1—C1—N2	105.71 (15)	C1—N1—C2	110.38 (15)
N1—C1—Pd1	128.72 (13)	C1—N1—C4	124.80 (15)
N2—C1—Pd1	125.57 (13)	C2—N1—C4	124.76 (15)
C3—C2—N1	106.67 (16)	C1—N2—C3	110.22 (15)
C2—C3—N2	107.02 (16)	C1—N2—C9	124.11 (15)
N1—C4—C5	111.21 (14)	C3—N2—C9	125.63 (15)
C6—C5—C4	111.15 (15)	C18—N3—C14	117.99 (18)
O1—C6—O2	124.30 (16)	C18—N3—Pd1	120.12 (15)

O1—C6—C5	124.87 (17)	C14—N3—Pd1	121.87 (14)
O2—C6—C5	110.83 (15)	C6—O2—C7	116.48 (14)
N2—C9—C10	112.65 (15)	C11—O4—C12	115.81 (18)
C11—C10—C9	110.76 (17)	C1—Pd1—N3	177.50 (6)
O3—C11—O4	123.87 (19)	C1—Pd1—Cl1	87.60 (5)
O3—C11—C10	124.2 (2)	N3—Pd1—Cl1	91.87 (5)
O4—C11—C10	111.91 (18)	C1—Pd1—Cl2	88.76 (5)
N3—C14—C15	122.5 (2)	N3—Pd1—Cl2	91.81 (5)
N3—C18—C17	122.5 (2)	Cl1—Pd1—Cl2	176.213 (17)

Table S17 Selected torsion angles [°] for 5b.

N1—C4—C5—C6	−178.29 (15)	N1—C1—N2—C9	−177.92 (16)
C4—C5—C6—O1	−5.8 (3)	Pd1—C1—N2—C9	2.4 (3)
C4—C5—C6—O2	174.20 (16)	C2—C3—N2—C9	177.76 (17)
N2—C9—C10—C11	176.20 (17)	C10—C9—N2—C1	−105.0 (2)
C9—C10—C11—O3	4.1 (3)	C10—C9—N2—C3	77.4 (2)
C9—C10—C11—O4	−175.28 (19)	C17—C18—N3—Pd1	−177.5 (2)
Pd1—C1—N1—C2	179.75 (13)	C15—C14—N3—Pd1	177.83 (18)
N2—C1—N1—C4	177.20 (15)	O1—C6—O2—C7	3.9 (3)
Pd1—C1—N1—C4	−3.2 (3)	C5—C6—O2—C7	−176.13 (16)
C3—C2—N1—C4	−177.28 (16)	C8—C7—O2—C6	81.3 (2)
C5—C4—N1—C1	−102.2 (2)	O3—C11—O4—C12	0.3 (4)
C5—C4—N1—C2	74.5 (2)	C10—C11—O4—C12	179.7 (2)
Pd1—C1—N2—C3	−179.65 (13)	C13—C12—O4—C11	−168.5 (3)

Table S18 Selected dihedral angles [°] for 5b.

Pd/Cl2/C2 // C1/N1/C2/C3/N2	79.49(6)	Pd/Cl2/C2 // N3/C14-C18	39.31(6)

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