Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Diferrocenylmercury Diphosphine Diastereomers with Unique Geometries: *trans*-Chelation at Pd(II) with Short Hg(II)···Pd(II) Contacts

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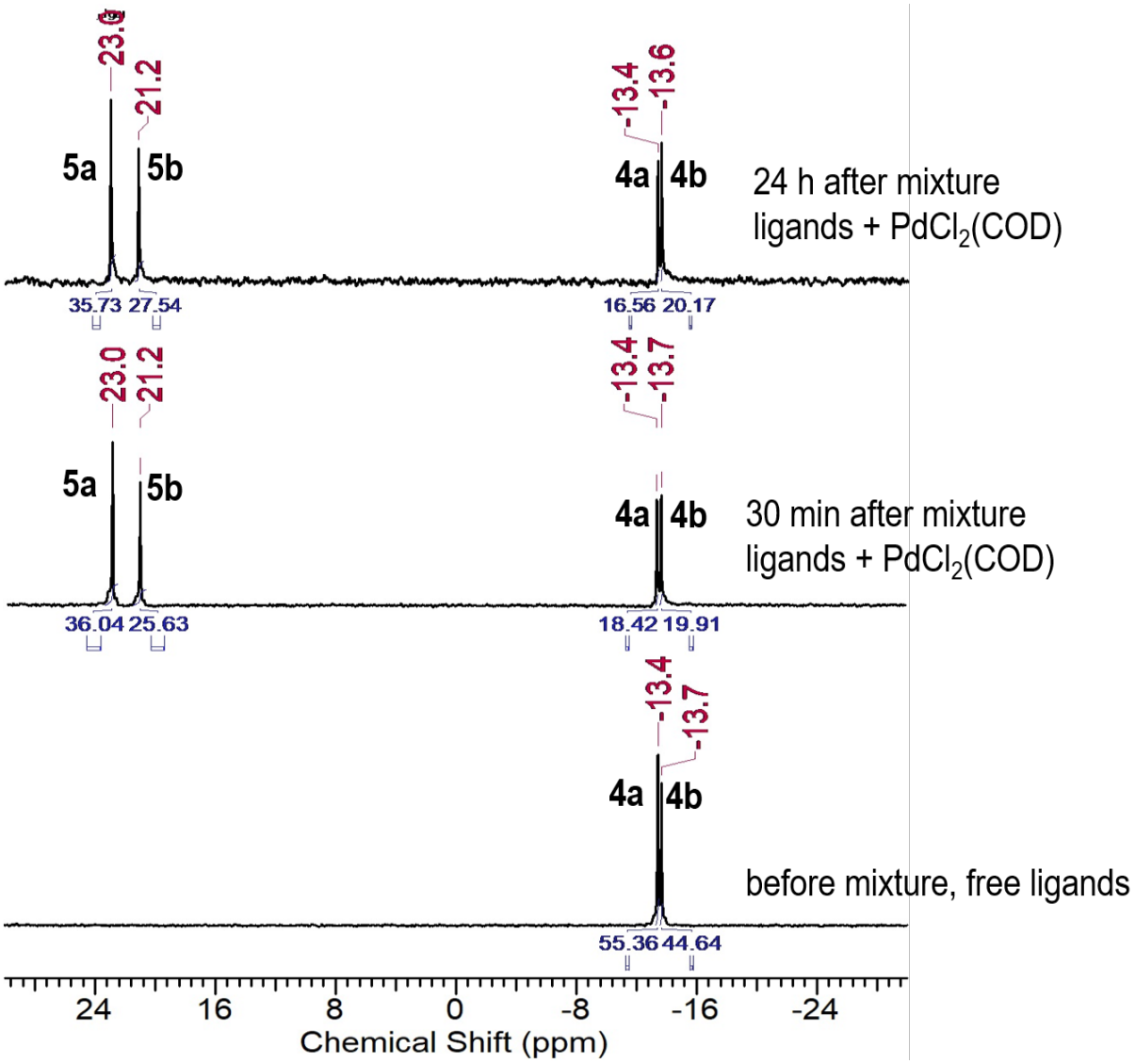
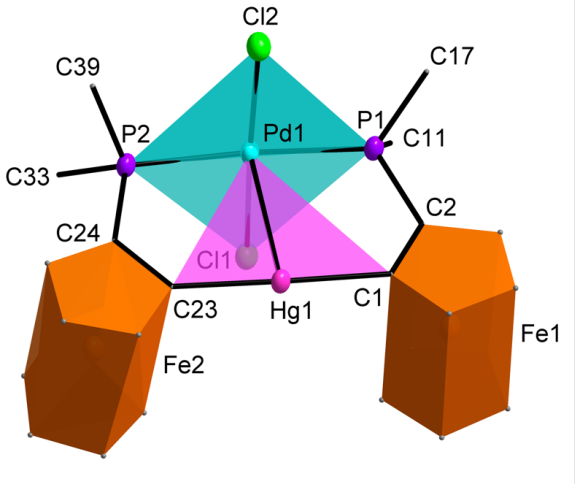
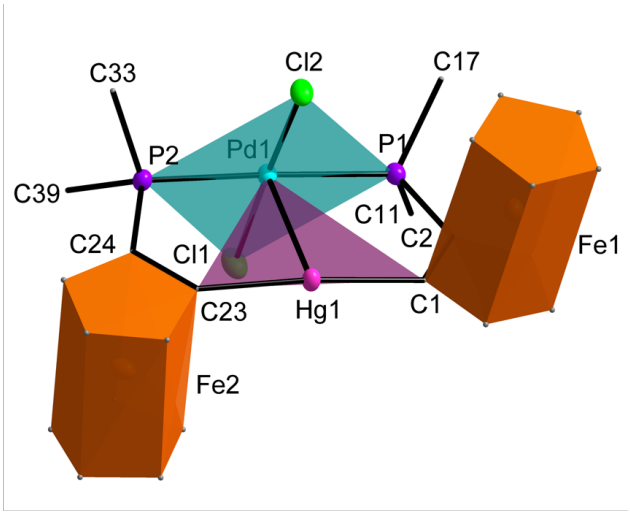


Figure S1. ^{31}P NMR spectra of the competition reaction of **4a**/**4b** and a deficiency of $PdCl_2(COD)$ (50%) in $CDCl_3$.

a)

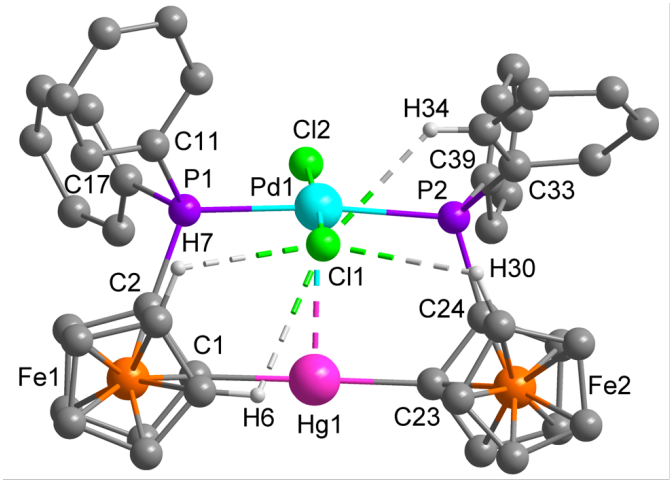


meso-**5a**

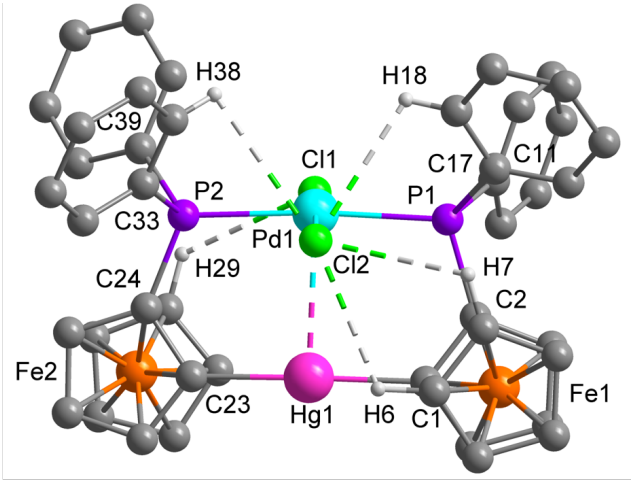


p*S*p*S*-**5b**

b)



meso-**5a**



p*S*p*S*-**5b**

Figure S2. a) Visualization of the 3D structure of *meso*-**5a** and p*S*p*S*-**5b**; b) illustration of the hydrogen bonding interactions in *meso*-**5a** and (p*S*p*S*)-**5b**. Cl–H interatomic distance (Å). For *meso*-**5a**: Cl1···H6 3.189(2), Cl1···H7 3.008(2), Cl1···H30 2.844(2), Cl1···H34 2.711(2). For (p*S*p*S*)-**5b**: Cl1···H29 2.876(2), Cl2···H6 3.041(2), Cl2···H7 2.998(2), Cl2···H18 2.997(2), Cl2···H38 3.173(2).

Table S1. Crystal data and refinement details for **4a**, **4b**, **5a**·CH_2Cl_2, and **5b**·toluene.

Compound	**4a** (*meso*)	**4b** (*rac*)	**5a**·CH_2Cl_2 (*meso*)	**5b**·toluene (p*S*p*S*)
CCDC	**1935847**	**1935848**	**1935849**	**1935850**
empirical formula	$C_{44}H_{36}Fe_2HgP_2$	$C_{44}H_{36}Fe_2HgP_2$	$C_{44}H_{36}Cl_2Fe_2HgP_2Pd$ · CH_2Cl_2	$2C_{44}H_{36}Cl_2Fe_2HgP_2Pd$ · C_7H_8
MW	938.96	938.96	1201.18	2324.65
T, K	100	296	100	100
wavelength, Å	1.54178	1.54178	1.54178	1.54178
crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
space group	$P2_1/n$	*P*-1	*P*-1	*C*2
a, Å	7.2520(1)	11.0312(2)	11.5138(4)	21.669(4)
b, Å	13.2449(2)	12.8295(2)	12.2469(4)	10.733(2)
c, Å	18.3975(2)	15.0553(2)	16.3241(5)	17.663(4)
α, deg	90	114.463(1)	70.183(2)	90
β, deg	92.644(1)	96.008(1)	80.298(2)	99.85(3)
γ, deg	90	101.445(1)	68.115(2)	90
V, Å^3	1765.24(4)	1858.70(5)	2007.12(12)	4047.6(14)
Z	2	2	2	2
ρ_{calc}, g cm^{-3}	1.767	1.678	1.988	1.908
μ (Cu Kα), mm^{-1}	15.24	14.48	19.410	18.040
crystal size, mm	0.21×0.09×0.09	0.24×0.22×0.12	0.13×0.12×0.10	0.14×0.13×0.10
θ range, deg	4.1–69.0	3.3–69.0	2.9–69.0	2.5–68.8
limiting indices	$-7 \leqslant h \leqslant 8$ $-15 \leqslant k \leqslant 15$ $-21 \leqslant l \leqslant 21$	$-13 \leqslant h \leqslant 13$ $-14 \leqslant k \leqslant 15$ $-18 \leqslant l \leqslant 18$	$-13 \leqslant h \leqslant 10$ $-14 \leqslant k \leqslant 11$ $-19 \leqslant l \leqslant 19$	$-26 \leq h \leq 23$ $-12 \leq k \leq 12$ $-20 \leqslant l \leqslant 20$
reflns collected	16200	17538	16676	19025
independent reflns	3172 [*R*(int) = 0.047]	6205 [*R*(int) = 0.041]	6486 [*R*(int) = 0.049]	6757 [*R*(int) = 0.036]
absorption correction	Numerical	Numerical	Numerical	Numerical
data/restraints/parameters	3172/0/224	6205/42/443	6486/0/497	6757/1/502
goodness-of-fit on F^2	1.04	1.03	1.03	0.928
final *R* indices, [I >2σ(I)] [a]	*R1* = 0.025, w*R2* = 0.062	*R1* = 0.026, w*R2* = 0.065	*R1* = 0.043, w*R2* = 0.101	*R1* = 0.028, w*R2* = 0.045
R indices (all data) [a]	*R1* = 0.027	*R1* = 0.028	*R1* = 0.060	*R1* = 0.032
peak$_{max}$/hole$_{min}$ (e Å^{-3})	1.07 / –0.97	0.71 / –0.43	1.52 / –2.33	0.92 / –0.95
Flack parameter				0.010(4)

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Computational Details

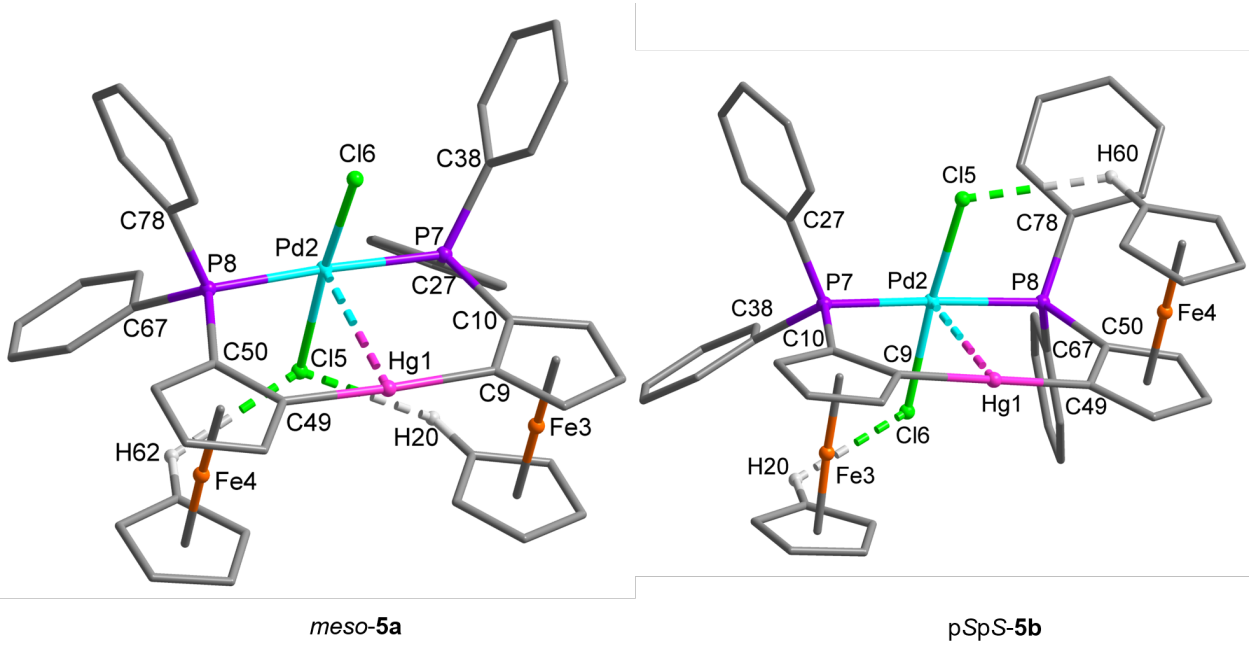


Figure S3. DFT-optimized structures for *meso*-**5a** and (p*S*p*S*)-**5b**. Selected distances (Å) for *meso*-**5a**: Pd2–P7 2.3658, Pd2–P8 2.3658, Pd2–Cl5 2.3874, Pd2–Cl6 2.3559, Pd2···Hg1 2.9775, Cl5···H20 2.8834, Cl5···H62 2.8835, P7–C10 1.8157, P8–C50 1.8156, Hg1−C9 2.1171, Hg1–C49 2.1171, C9−Hg1−C49 178.9, P7–Pd2−P8 176.1, Cl5–Pd2–Cl6 172.7, dihedral angle for substituted Cp//Cp 0.75; for (p*S*p*S*)-**5b**: Pd2–P7 2.3643, Pd2–P8 2.3641, Pd2–Cl5 2.3711, Pd2–Cl6 2.3713, Pd2···Hg1 2.9721, Cl5···H20 2.8775, Cl5···H60 2.8768, P7–C10 1.8147, P8–C50 1.8148, Hg1−C9 2.1146, Hg1–C49 2.1147, C9−Hg1−C49 179.7, P7–Pd2−P8 176.1, Cl5–Pd2–Cl6 172.3, dihedral angle for substituted Cp//Cp 10.2;

Table S2. Total energy, enthalpy, Gibb-free energy, ionization energy for *meso*- and (p*S*p*S*)-**5b**.

Compound	**E_{0K} [hartee]**	**E_{298K} [Hartee]**	**H_{298K} [Hartee]**	**G_{298K} [Hartee]**	**E_{EI} [Hartee]**	
meso-**5a**	-3830.2294	-3830.1800	-3830.1790	-3830.3152	-3830.8812	
(p*S*p*S*)-**5b**	-3830.2313	-3830.1820	-3830.1811	-3830.3166	-3830.8833	**GZ**
	1.2	1.3	1.3	0.8	1.3	kcal/mol

Table S3. Internal coordinates for *meso*-**5a.**

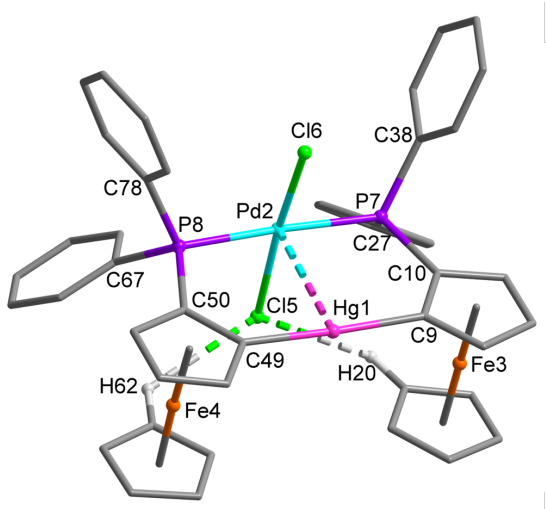
1 Hg1	0.0001	-1.3094	-1.4690 Hg	45 C45	-3.9609	3.5362	-2.8069 C
2 Pd2	0.0001	1.1809	0.1631 Pd	46 H46	-4.0939	3.4869	-3.8867 H
3 Fe3	-3.3554	-2.2116	-0.1907 Fe	47 C47	-3.3703	2.4621	-2.1346 C
4 Fe4	3.3553	-2.2117	-0.1907 Fe	48 H48	-3.0431	1.5844	-2.6866 H
5 Cl5	0.0000	-0.3633	1.9838 Cl	49 C49	2.1164	-1.2733	-1.5141 C
6 Cl6	0.0001	2.4629	-1.8135 Cl	50 C50	2.9669	-0.3319	-0.7975 C
7 P7	-2.3644	1.1182	0.1140 P	51 C51	4.3484	-0.6640	-1.0709 C
8 P8	2.3646	1.1182	0.1141 P	52 H52	5.2187	-0.1322	-0.7042 H
9 C9	-2.1162	-1.2734	-1.5140 C	53 C53	4.3641	-1.8056	-1.9299 C
10 C10	-2.9668	-0.3319	-0.7976 C	54 H54	5.2512	-2.3251	-2.2779 H
11 C11	-4.3482	-0.6638	-1.0711 C	55 C55	3.0052	-2.1732	-2.1994 C
12 H12	-5.2185	-0.1320	-0.7045 H	56 H56	2.6924	-3.0308	-2.7863 H
13 C13	-4.3639	-1.8055	-1.9300 C	57 C57	2.9365	-4.1301	0.3457 C
14 H14	-5.2510	-2.3249	-2.2782 H	58 H58	2.5943	-4.8942	-0.3443 H
15 C15	-3.0050	-2.1733	-2.1994 C	59 C59	2.1062	-3.2145	1.0738 C
16 H16	-2.6922	-3.0309	-2.7862 H	60 H60	1.0277	-3.1472	1.0343 H
17 C17	-2.1068	-3.2147	1.0740 C	61 C61	2.9552	-2.3325	1.8164 C
18 H18	-1.0282	-3.1478	1.0347 H	62 H62	2.6143	-1.4997	2.4171 H
19 C19	-2.9556	-2.3324	1.8164 C	63 C63	4.3144	-2.7029	1.5521 C
20 H20	-2.6145	-1.4996	2.4172 H	64 H64	5.1960	-2.2083	1.9435 H
21 C21	-4.3149	-2.7024	1.5520 C	65 C65	4.3059	-3.8135	0.6422 C
22 H22	-5.1964	-2.2075	1.9432 H	66 H66	5.1785	-4.3005	0.2198 H
23 C23	-4.3065	-3.8131	0.6422 C	67 C67	3.0835	1.1841	1.8020 C
24 H24	-5.1792	-4.2998	0.2198 H	68 C68	2.3604	1.8718	2.7915 C
25 C25	-2.9372	-4.1301	0.3459 C	69 H69	1.3715	2.2604	2.5569 H
26 H26	-2.5951	-4.8944	-0.3439 H	70 C70	2.8931	2.0249	4.0767 C
27 C27	-3.0834	1.1842	1.8019 C	71 H71	2.3217	2.5528	4.8387 H
28 C28	-2.3603	1.8717	2.7915 C	72 C72	4.1466	1.4816	4.3854 C
29 H29	-1.3713	2.2601	2.5571 H	73 H73	4.5568	1.5895	5.3886 H
30 C30	-2.8931	2.0248	4.0767 C	74 C74	4.8684	0.7908	3.4024 C
31 H31	-2.3216	2.5526	4.8388 H	75 H75	5.8405	0.3601	3.6394 H
32 C32	-4.1468	1.4817	4.3852 C	76 C76	4.3438	0.6487	2.1129 C
33 H33	-4.5570	1.5897	5.3884 H	77 H77	4.8972	0.0926	1.3642 H
34 C34	-4.8685	0.7911	3.4021 C	78 C78	3.1948	2.5173	-0.7394 C
35 H35	-5.8408	0.3606	3.6390 H	79 C79	3.3706	2.4621	-2.1345 C
36 C36	-4.3439	0.6491	2.1127 C	80 H80	3.0436	1.5844	-2.6865 H
37 H37	-4.8974	0.0932	1.3638 H	81 C81	3.9611	3.5363	-2.8067 C
38 C38	-3.1947	2.5173	-0.7395 C	82 H82	4.0943	3.4870	-3.8865 H
39 C39	-3.6019	3.6604	-0.0302 C	83 C83	4.3698	4.6742	-2.0978 C
40 H40	-3.4725	3.7073	1.0493 H	84 H84	4.8262	5.5110	-2.6251 H
41 C41	-4.1881	4.7343	-0.7103 C	85 C85	4.1880	4.7345	-0.7101 C
42 H42	-4.5057	5.6154	-0.1540 H	86 H86	4.5053	5.6156	-0.1538 H
43 C43	-4.3698	4.6741	-2.0980 C	87 C87	3.6018	3.6605	-0.0300 C
44 H44	-4.8263	5.5108	-2.6253 H	88 H88	3.4723	3.7074	1.0494 H

Table S4. Wiberg Bond Indices, NBO and Mulliken charges of *meso*-**5a**

Charges			**NBO analysis**	
Atom	Mulliken	NBO	Bond	WBI
Hg1	1.12	1.02	Hg1-Pd2	0.15
Pd2	-0.32	-0.29	Pd2-Cl5	0.59
Cl5	-0.49	-0.41	Pd2-Cl6	0.65
Cl6	-0.44	-0.35	Pd2-P7	0.54
P7	0.82	1.20	Pd2-P8	0.54
P8	0.82	1.20		

Table S5. Electron density and Laplacian of the electron density from AIM analysis of *meso*-**5a**.

	e ¯ density	**Laplacian**	**G(r)**	**V(r)**	**H(r)**
bcp Hg-Pd	0.0285	0.0716	0.0206	-0.0233	-0.0027
bcp Pd-Cl5	0.0710	0.2025	0.0632	-0.0758	-0.0126
bcp Pd-Cl6	0.0764	0.2090	0.0671	-0.0819	-0.0148
bcp Cl5–H20	0.0052	0.0172	0.0034	-0.0024	0.0009
bcp Cl5–H60	0.0052	0.0172	0.0034	-0.0024	0.0009
bcp H18–H60	0.0076	0.0213	0.0044	-0.0035	0.0009



meso-**5a**

Table S6. Internal coordinates for (p*S*p*S*)-**5b.**

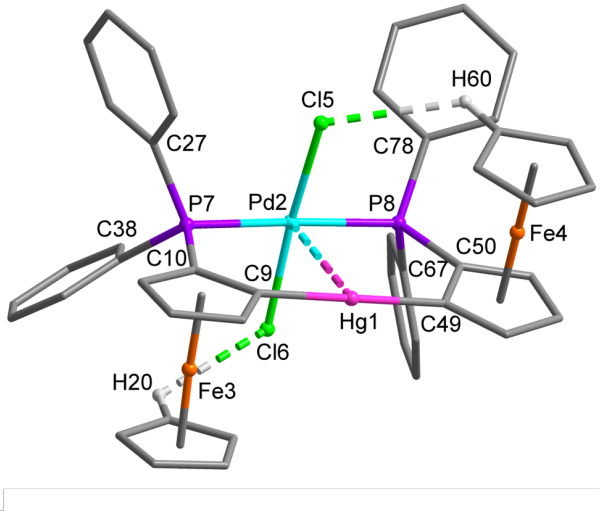
1 Hg1	-0.0004	-1.8857	-0.0005 Hg	45 C45	-5.4981	2.4861	-1.4212 C
2 Pd2	0.0003	1.0864	0.0004 Pd	46 H46	-6.5380	2.2180	-1.6043 H
3 Fe3	-3.5721	-1.9763	-0.5064 Fe	47 C47	-4.7000	1.6576	-0.6239 C
4 Fe4	3.5717	-1.9768	0.5049 Fe	48 H48	-5.1128	0.7412	-0.2170 H
5 Cl5	0.6910	0.9256	2.2630 Cl	49 C49	1.9743	-1.8794	-0.7571 C
6 Cl6	-0.6905	0.9271	-2.2625 Cl	50 C50	2.8330	-0.7062	-0.8642 C
7 P7	-2.2559	1.0065	0.7026 P	51 C51	4.1536	-1.1426	-1.2626 C
8 P8	2.2562	1.0068	-0.7021 P	52 H52	5.0069	-0.5041	-1.4582 H
9 C9	-1.9750	-1.8797	0.7562 C	53 C53	4.1293	-2.5661	-1.3801 C
10 C10	-2.8335	-0.7063	0.8633 C	54 H54	4.9798	-3.1969	-1.6184 H
11 C11	-4.1543	-1.1425	1.2612 C	55 C55	2.8024	-3.0118	-1.0741 C
12 H12	-5.0075	-0.5038	1.4567 H	56 H56	2.4842	-4.0484	-1.0290 H
13 C13	-4.1304	-2.5660	1.3784 C	57 C57	2.7449	-2.0786	2.3738 C
14 H14	-4.9811	-3.1967	1.6162 H	58 H58	1.6871	-1.9743	2.5856 H
15 C15	-2.8035	-3.0120	1.0725 C	59 C59	3.6761	-0.9932	2.3009 C
16 H16	-2.4856	-4.0487	1.0272 H	60 H60	3.4266	0.0507	2.4392 H
17 C17	-2.7450	-2.0774	-2.3752 C	61 C61	4.9560	-1.5294	1.9424 C
18 H18	-1.6871	-1.9735	-2.5869 H	62 H62	5.8623	-0.9567	1.7791 H
19 C19	-3.6756	-0.9914	-2.3018 C	63 C63	4.8170	-2.9502	1.7887 C
20 H20	-3.4254	0.0524	-2.4391 H	64 H64	5.5968	-3.6403	1.4844 H
21 C21	-4.9558	-1.5271	-1.9438 C	65 C65	3.4461	-3.2890	2.0540 C
22 H22	-5.8619	-0.9541	-1.7803 H	66 H66	3.0096	-4.2794	1.9784 H
23 C23	-4.8177	-2.9481	-1.7911 C	67 C67	2.5909	1.7198	-2.3636 C
24 H24	-5.5981	-3.6380	-1.4874 H	68 C68	2.4482	0.9033	-3.5008 C
25 C25	-3.4470	-3.2875	-2.0563 C	69 H69	2.1843	-0.1448	-3.3840 H
26 H26	-3.0111	-4.2783	-1.9815 H	70 C70	2.6418	1.4419	-4.7767 C
27 C27	-2.5908	1.7180	2.3648 C	71 H71	2.5296	0.8038	-5.6521 H
28 C28	-2.4467	0.9005	3.5012 C	72 C72	2.9685	2.7962	-4.9293 C
29 H29	-2.1813	-0.1471	3.3834 H	73 H73	3.1154	3.2136	-5.9247 H
30 C30	-2.6406	1.4376	4.7776 C	74 C74	3.1059	3.6120	-3.7986 C
31 H31	-2.5272	0.7987	5.6524 H	75 H75	3.3647	4.6643	-3.9108 H
32 C32	-2.9692	2.7912	4.9318 C	76 C76	2.9180	3.0783	-2.5183 C
33 H33	-3.1165	3.2074	5.9276 H	77 H77	3.0382	3.7139	-1.6433 H
34 C34	-3.1081	3.6080	3.8019 C	78 C78	3.3544	1.9826	0.3983 C
35 H35	-3.3684	4.6597	3.9152 H	79 C79	2.8163	3.1450	0.9787 C
36 C36	-2.9197	3.0758	2.5210 C	80 H80	1.7610	3.3740	0.8421 H
37 H37	-3.0410	3.7121	1.6467 H	81 C81	3.6213	3.9777	1.7638 C
38 C38	-3.3534	1.9838	-0.3972 C	82 H82	3.1927	4.8705	2.2165 H
39 C39	-2.8148	3.1467	-0.9758 C	83 C83	4.9642	3.6480	1.9876 C
40 H40	-1.7595	3.3753	-0.8384 H	84 H84	5.5876	4.2892	2.6094 H
41 C41	-3.6192	3.9805	-1.7604 C	85 C85	5.4998	2.4834	1.4216 C
42 H42	-3.1902	4.8738	-2.2118 H	86 H86	6.5398	2.2149	1.6038 H
43 C43	-4.9621	3.6513	-1.9853 C	87 C87	4.7010	1.6560	0.6238 C
44 H44	-5.5850	4.2934	-2.6067 H	88 H88	5.1135	0.7401	0.2155 H

Table S7. Wiberg Bond Indices, NBO and Mulliken charges of (p*S*p*S*)-**5b.**

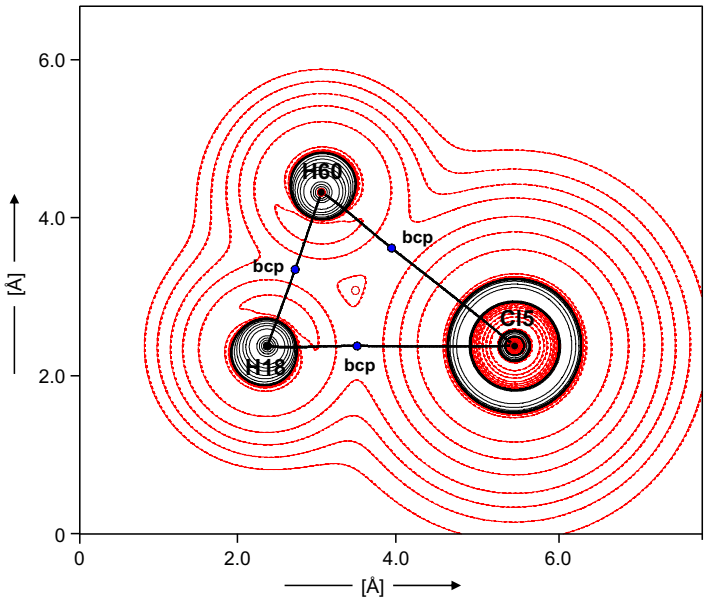
Charges			NBO analysis	
Atom	Mulliken	NBO	Bond	WBI
Hg1	1.12	1.01	Hg1-Pd2	0.16
Pd2	-0.33	-0.28	Pd2-Cl5	0.61
Cl5	-0.46	-0.38	Pd2-Cl6	0.61
Cl6	-0.46	-0.38	Pd2-P7	0.53
P7	0.80	1.20	Pd2-P8	0.53
P8	0.80	1.20		

Table S8. Electron density and Laplacian of the electron density from AIM analysis of (p*S*p*S*)-**5b**.

	e^- density	Laplacian	G(r)	V(r)	H(r)
bcp Hg-Pd	0.0288	0.0724	0.0209	-0.0236	-0.0028
bcp Pd-Cl5	0.0737	0.2064	0.0653	-0.0790	-0.0137
bcp Pd-Cl6	0.0737	0.2063	0.0653	-0.0790	-0.0137
bcp Cl5–H60	0.0075	0.0245	0.0048	-0.0036	0.0013
bcp Cl6–H20	0.0075	0.0245	0.0048	-0.0036	0.0013



p*S*p*S*-**5b**



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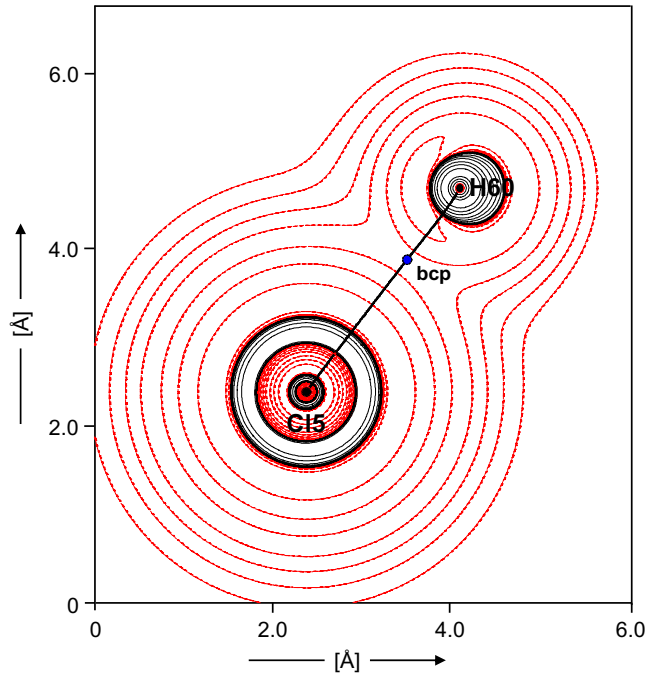

Figure S4. AIM contour plot of the Laplacian for *meso*-**5a** (top) *and* (p*S*p*S*)-**5b** (bottom) showing the bond paths (black line) and the BCPs (blue circle) between Cl and H.

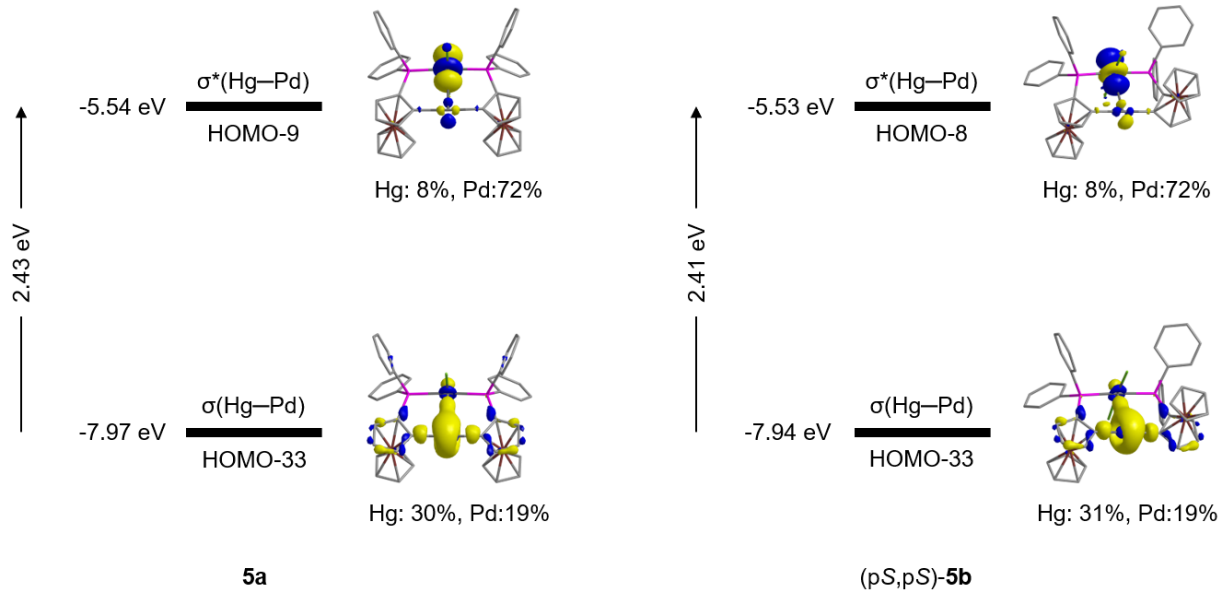

Figure S5. Contour plots and eigenvalues (in eV) for the bonding σ(Hg-Pd) and antibonding σ*(Hg-Pd) molecular orbitals (MOs) in **5a** (left) and (p*S*,p*S*)-**5b** (right). Since all orbitals are doubly occupied MOs the overall contributions of this metal-metal interaction to a covalent mercury-palladium bond in both complexes **5a**,**b** is zero.

The program GaussSum 3.0 has been applied for the bonding analysis of the canonical molecular orbitals. For more details, please visit the website http://gausssum.sourceforge.net/.

Spectral Data for Isolated Compounds

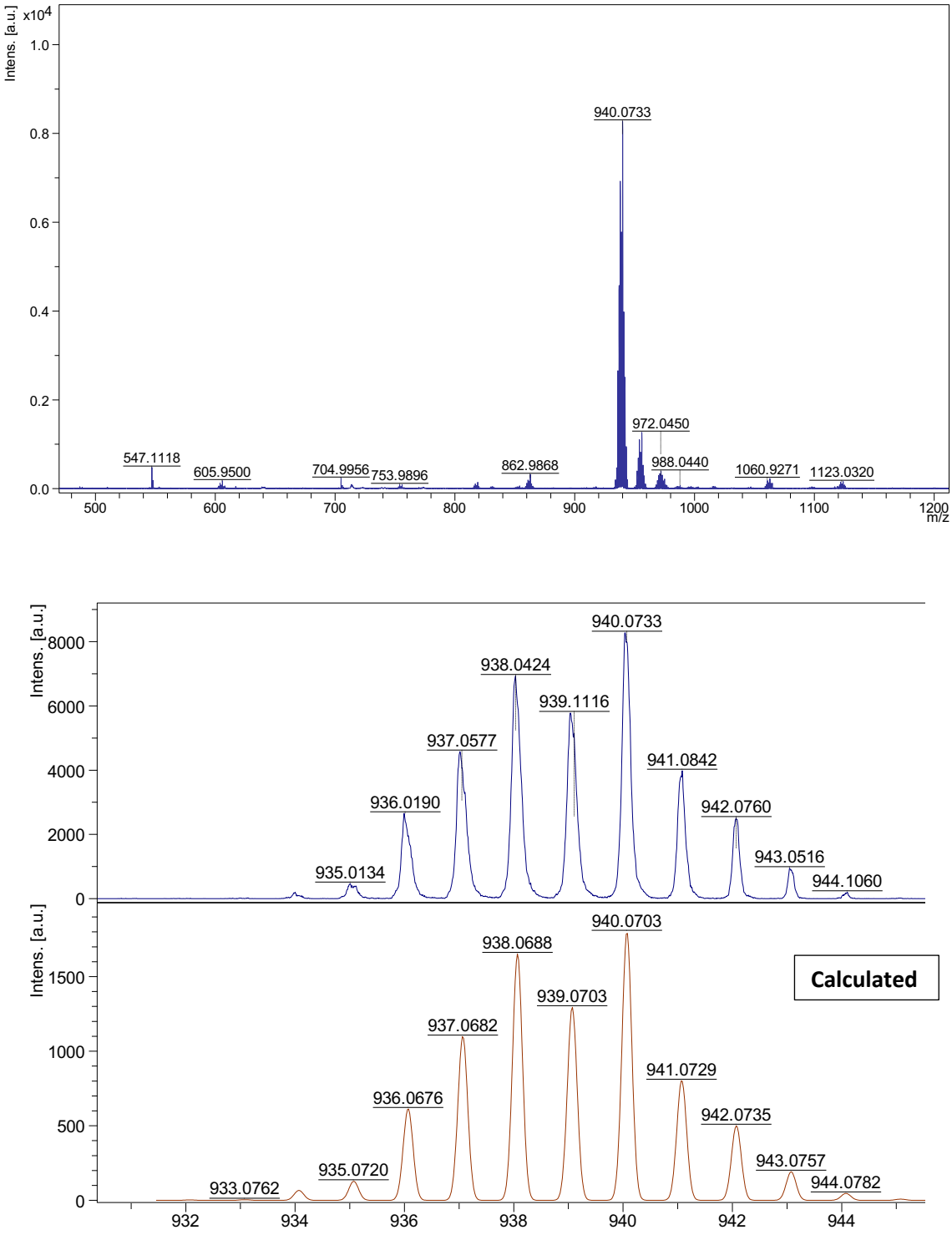

Figure S6. Maldi-TOF MS spectrum of the diastereoisomer mixture *meso*-**4a**/*rac*-**4b.**

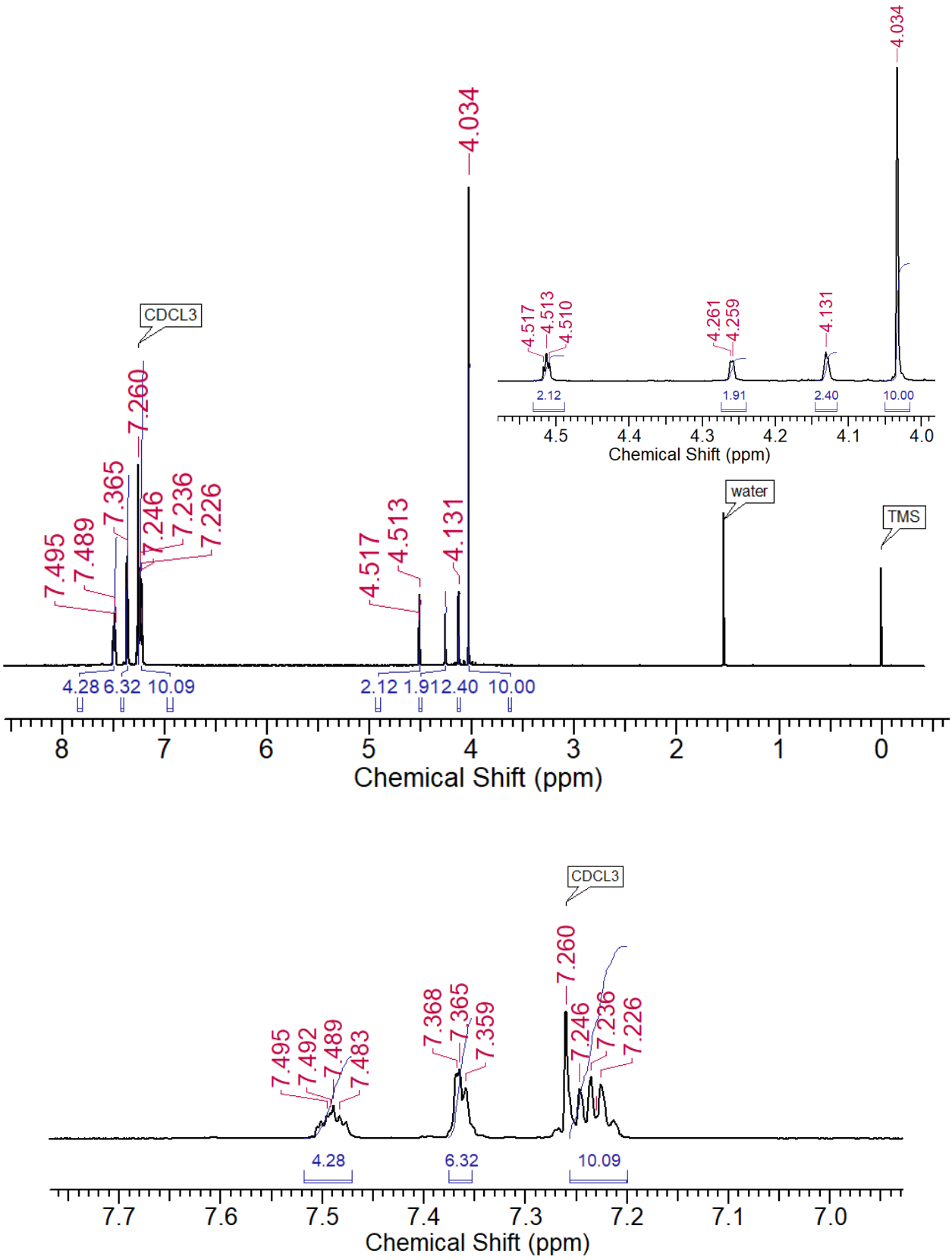

Figure S7. ^{1}H NMR spectrum and expansions of *meso*-**4a** in $CDCl_3$.

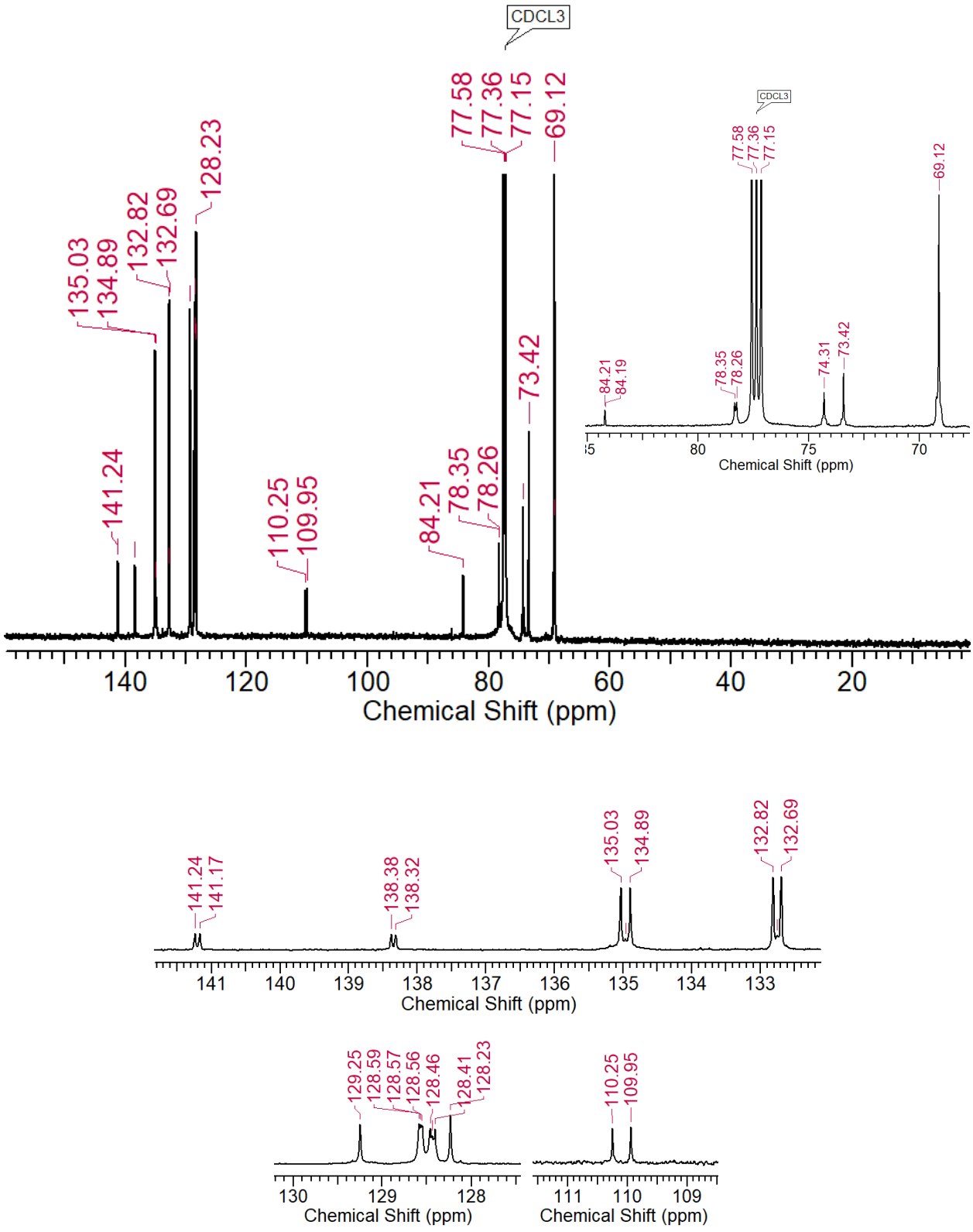

Figure S8. ^{13}C NMR spectrum and expansions of *meso*-**4a** in $CDCl_3$.

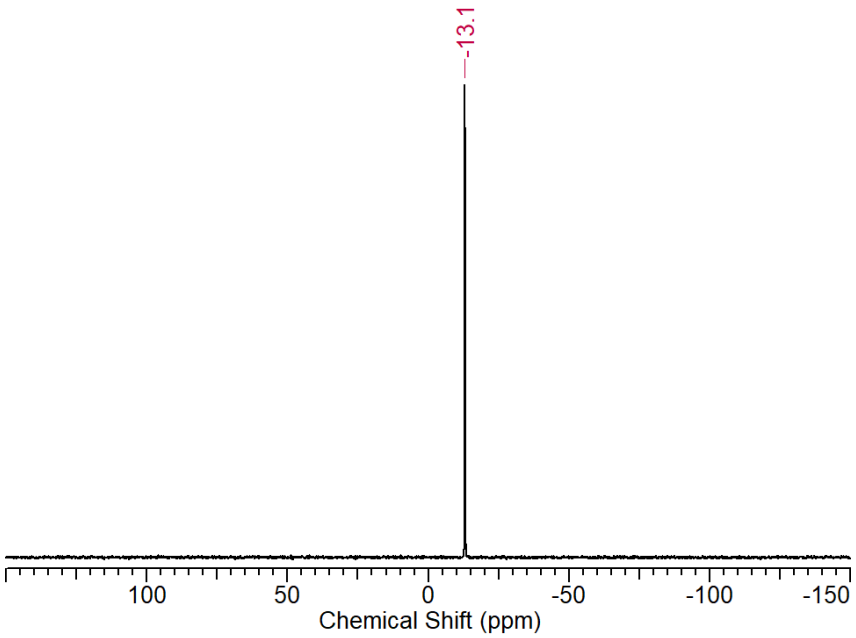

Figure S9. ^{31}P NMR spectrum of *meso*-**4a** in $CDCl_3$.

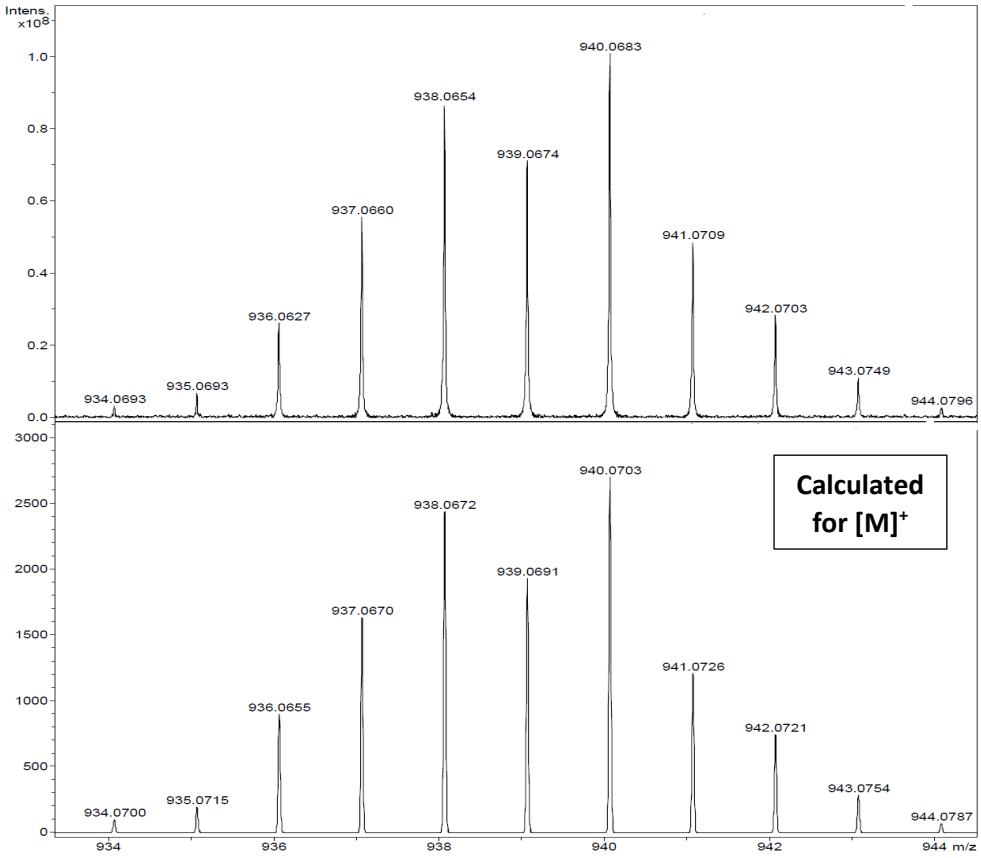

Figure S10. Expansion of the ESI-MS spectrum of **4a** (*meso*) in CH_2Cl_2/CH_3CN

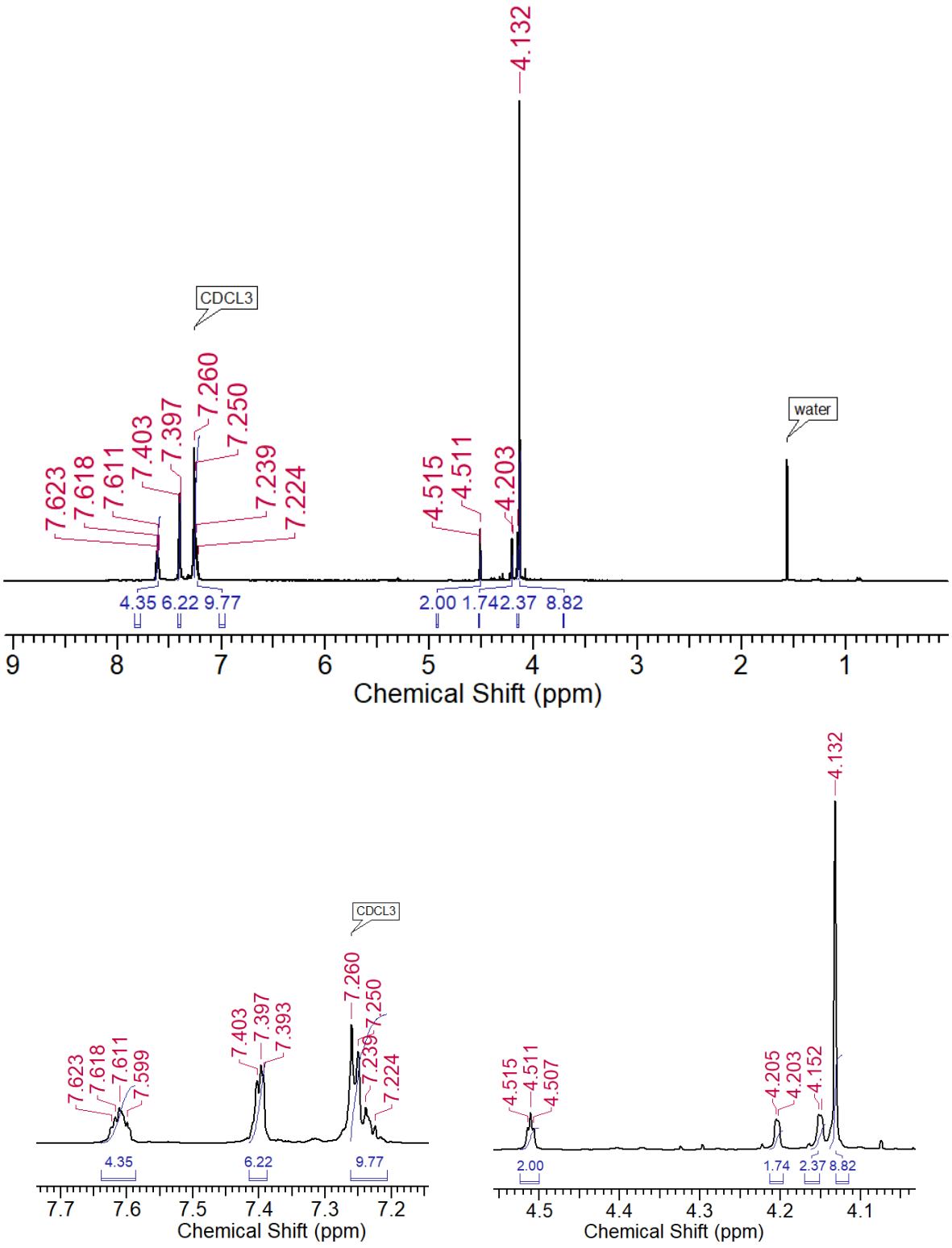

Figure S11. ^{1}H NMR spectrum and expansions of **4b** (p*S*p*S*) in $CDCl_3$.

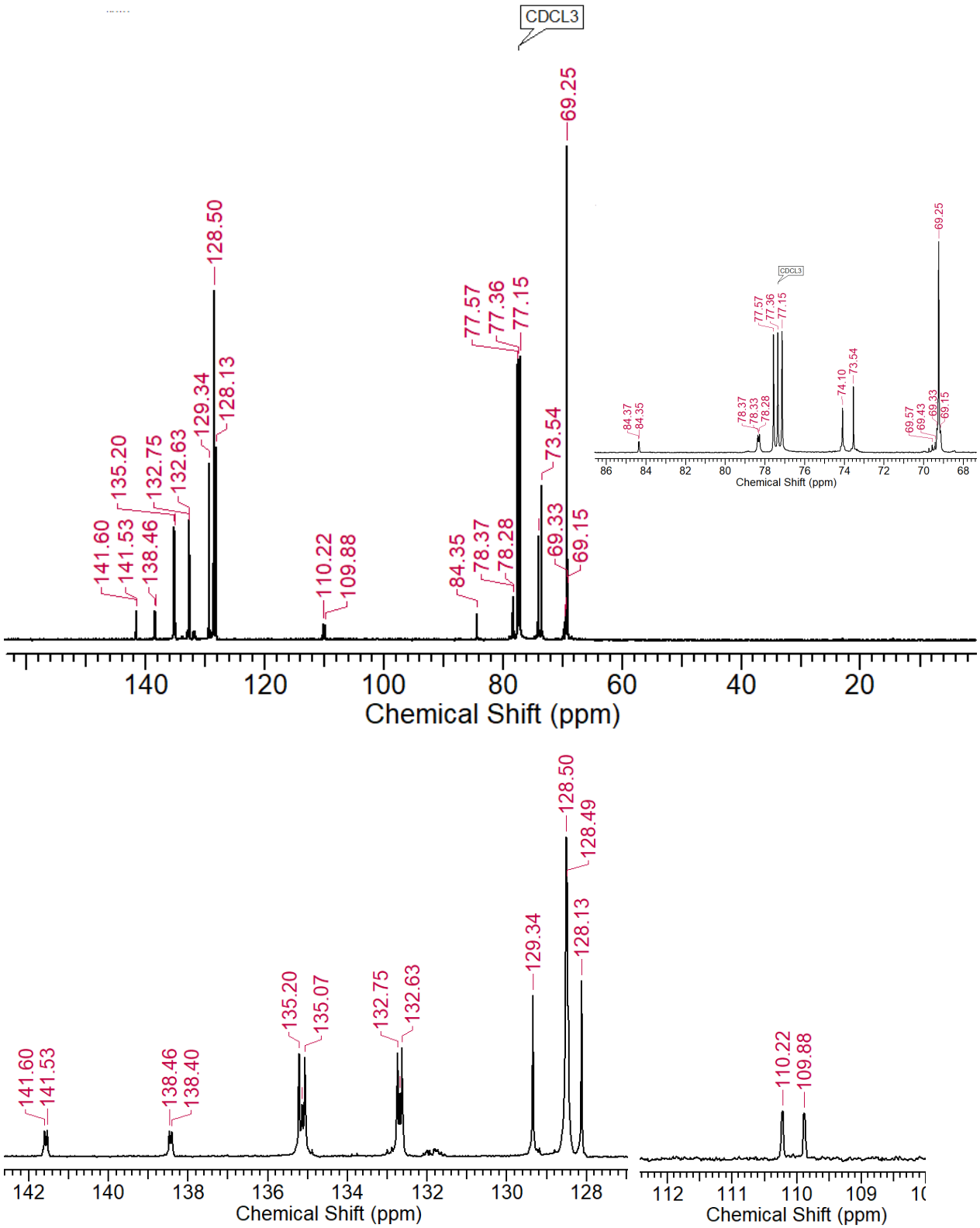

Figure S12. ^{13}C NMR spectra of **4b** (p*S*p*S*) in $CDCl_3$.

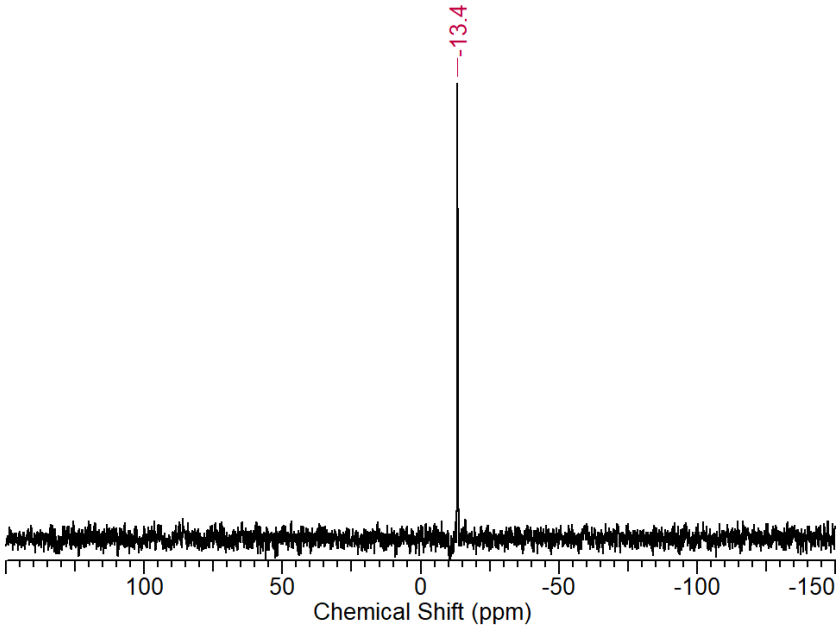

Figure S13. ^{31}P NMR spectrum of **4b** (p*S*p*S*) in $CDCl_3$.

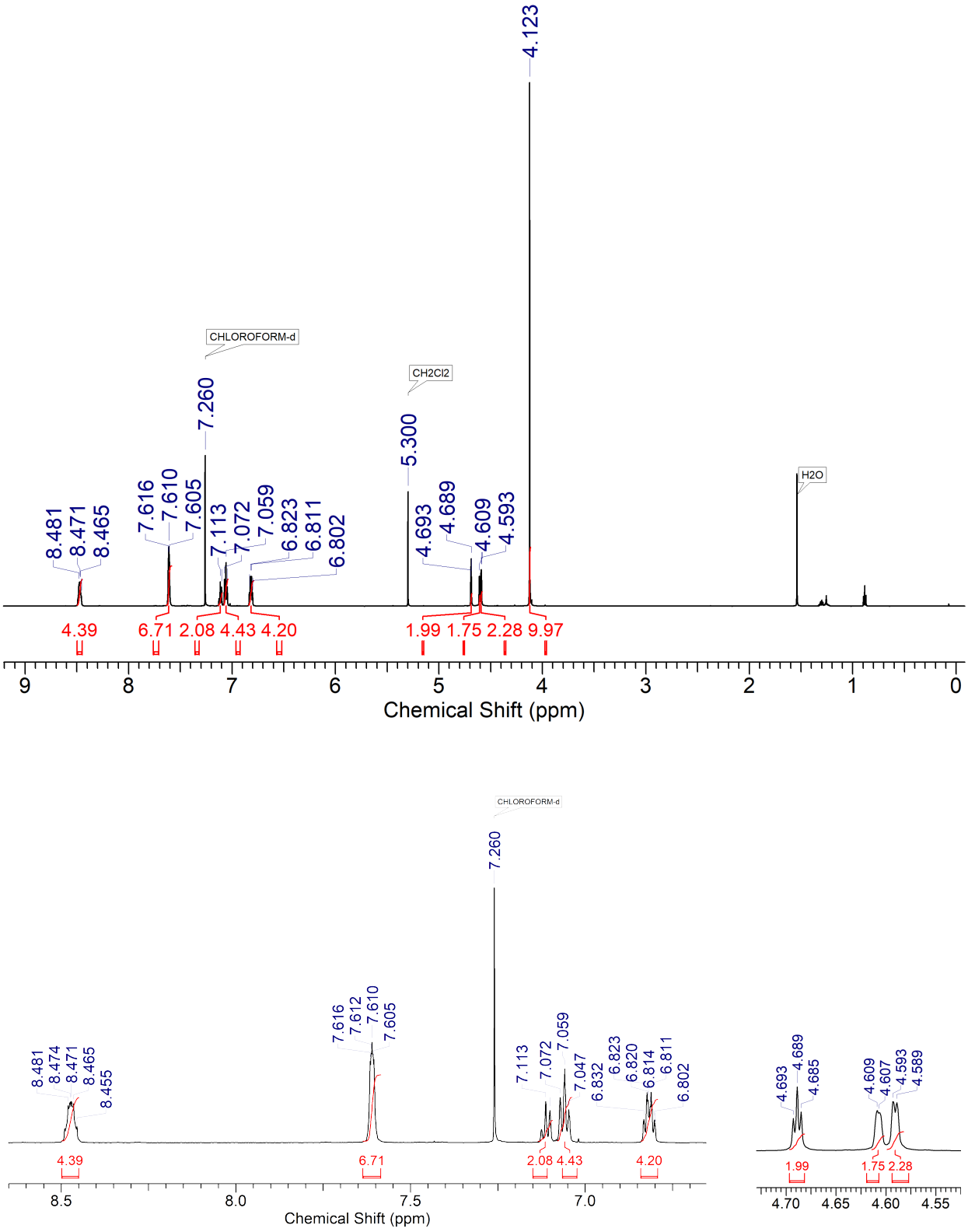

Figure S14. ^{1}H NMR spectrum and expansions of **5a** (*meso*) in $CDCl_3$.

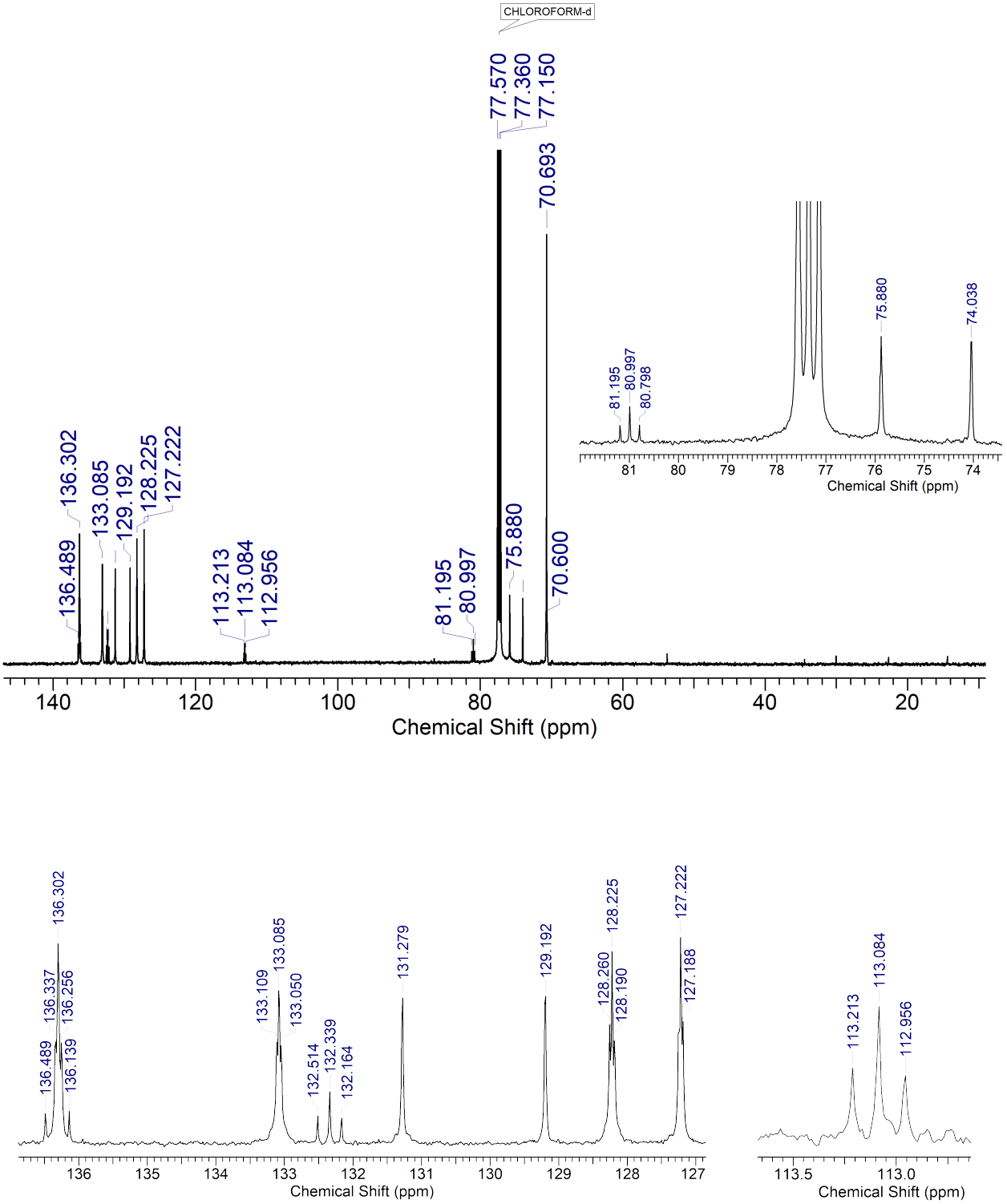

Figure S15. ^{13}C NMR spectrum and expansions of **5a** (*meso*) in $CDCl_3$.

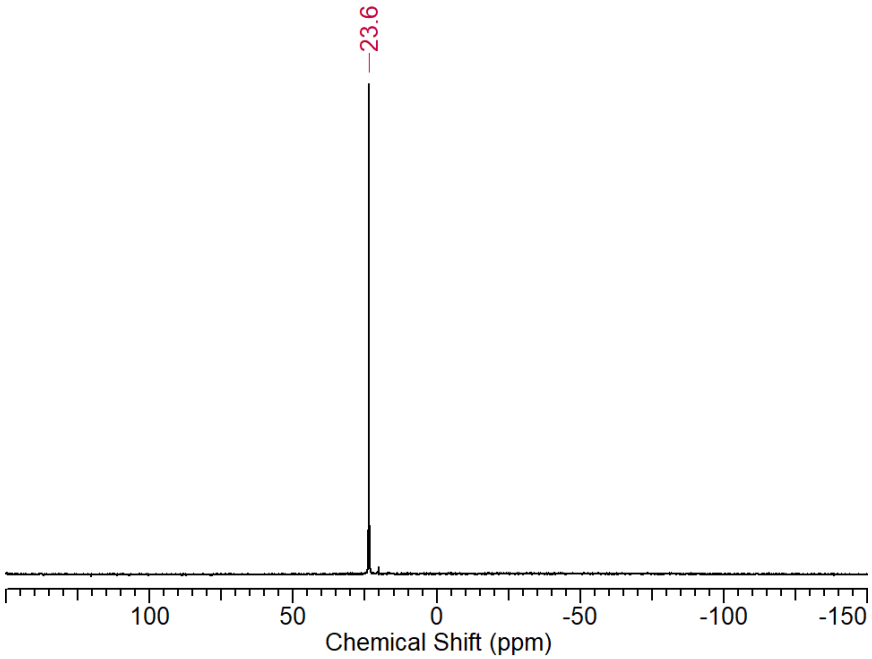

Figure S16. ^{31}P NMR spectra of **5a** (meso) in $CDCl_3$.

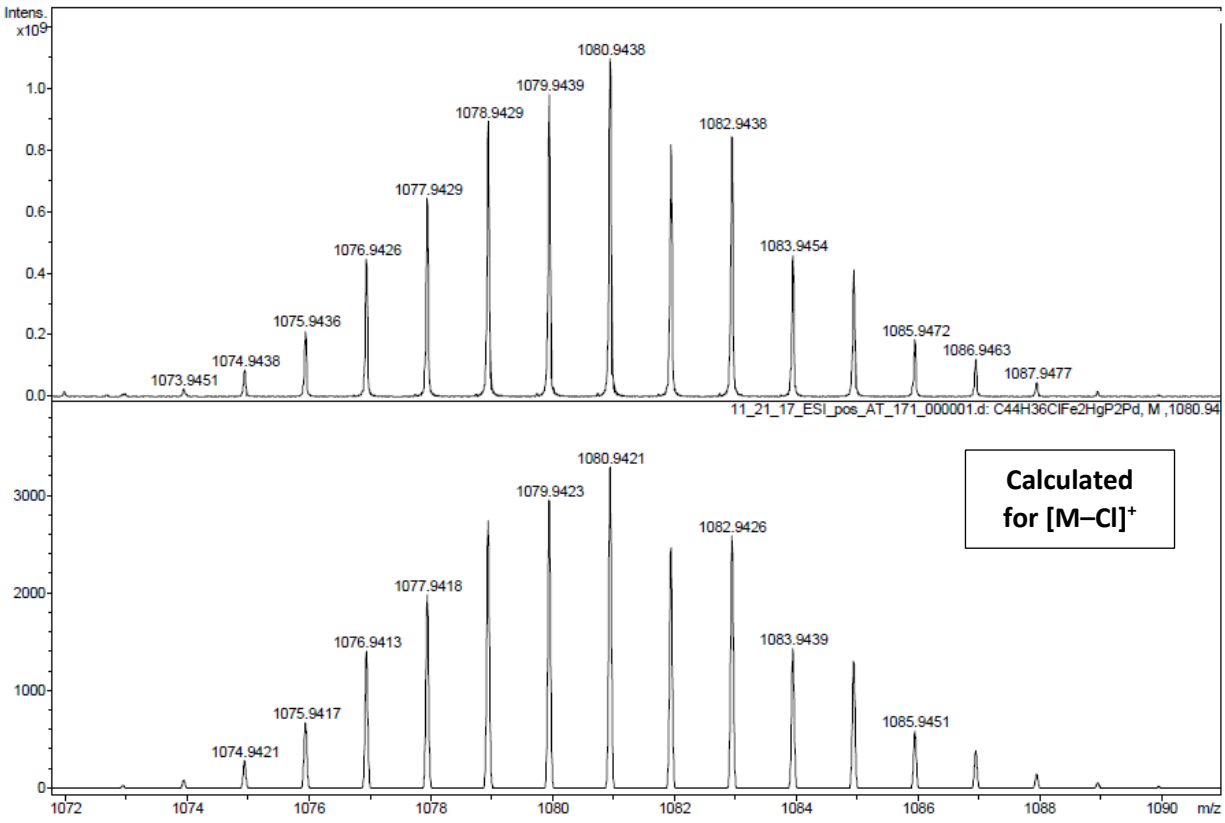

Figure S17. Expansion of the ESI-MS spectrum of **5a** (*meso*) in CH_2Cl_2/CH_3CN.

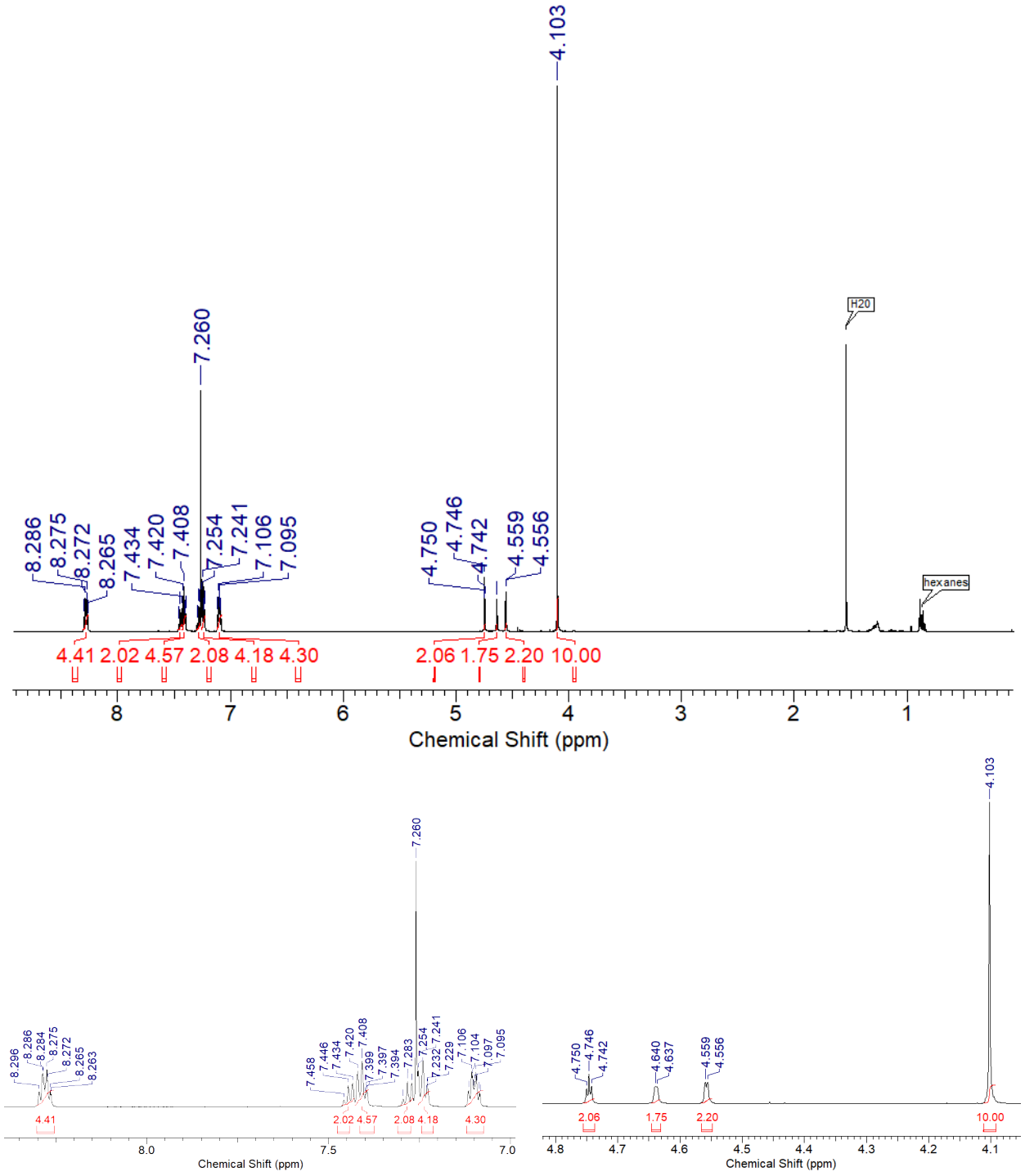

Figure S18. ^{1}H NMR spectrum and expansions of **5b** (p*S*p*S*) in $CDCl_3$.

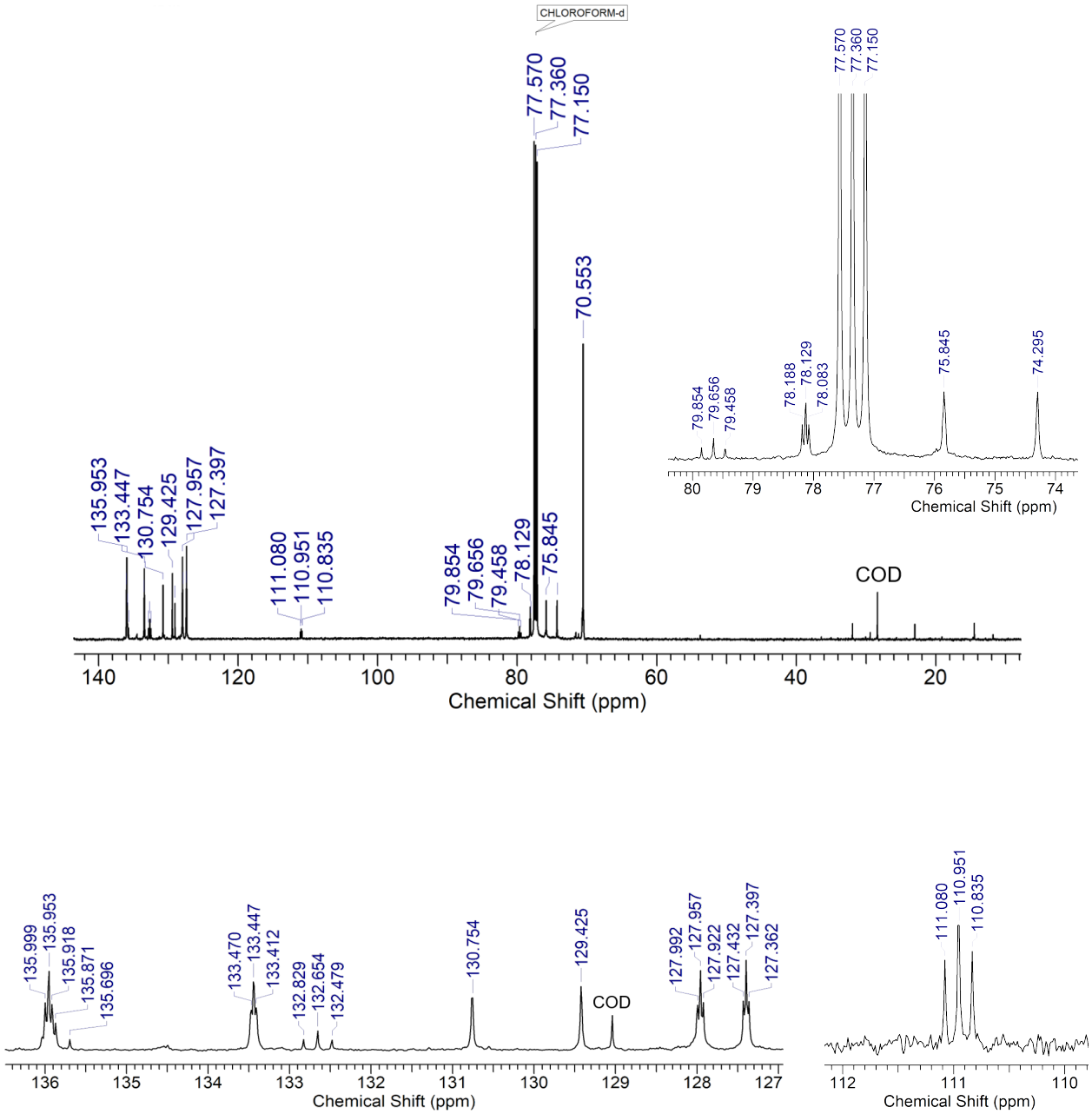

Figure S19. ^{13}C NMR spectra of **5b** (p*S*p*S*) in $CDCl_3$.

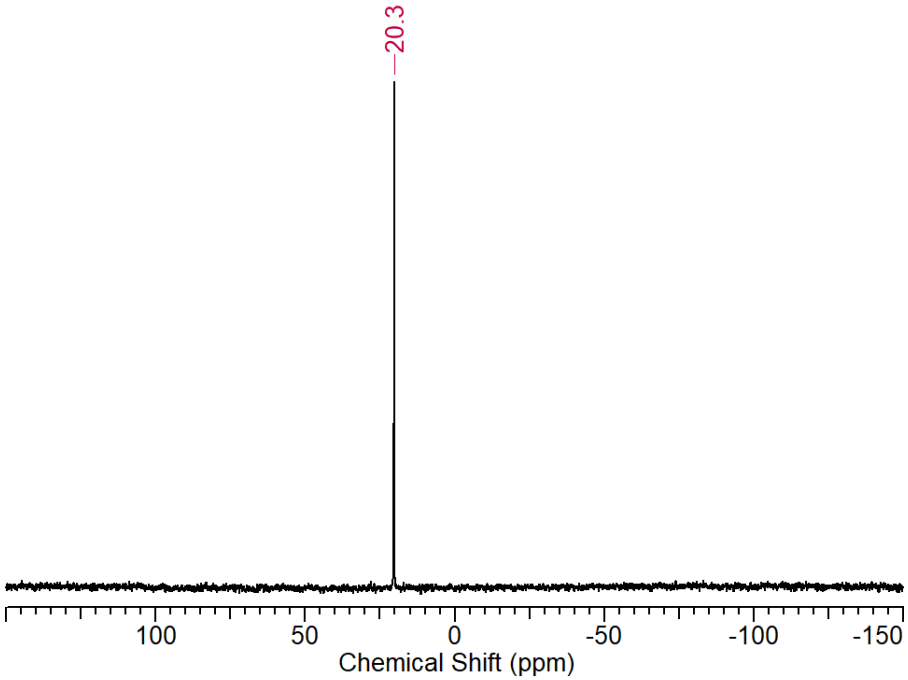

Figure S20. ^{31}P NMR spectrum of **5b** (p*S*p*S*) in $CDCl_3$.

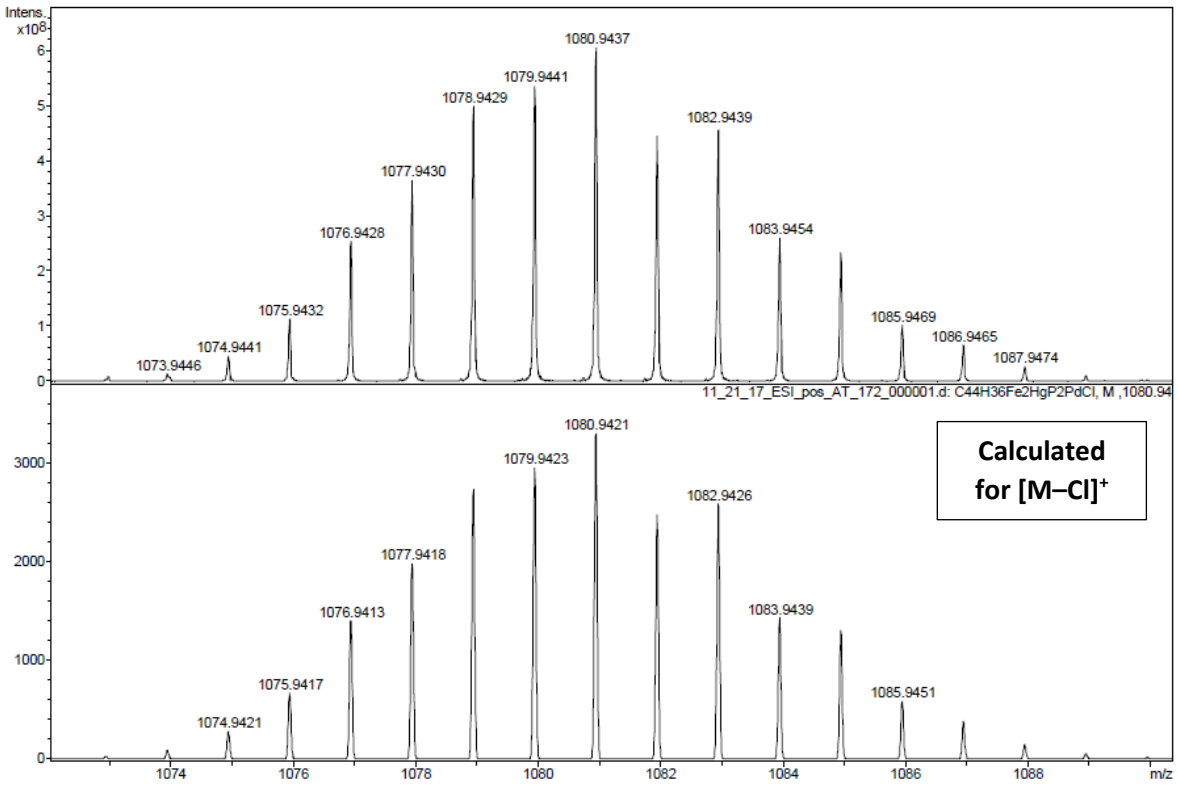

Figure S21. Expansion of the ESI-MS spectrum of **5b** (p*S*p*S*) in CH_2Cl_2/CH_3CN.