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An Anionic Phosphenium Complex as an Ambident Nucleophile

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Contents: Representation of the molecular structures of **4** and **6**; details on the computational studies for **2'** – **5'**; graphical representation of NMR spectra of Na[**2**], [PPh_4][**2**], **3a**, **4**, **5**, **7**, and the reaction of Na[**2**] with MeI.

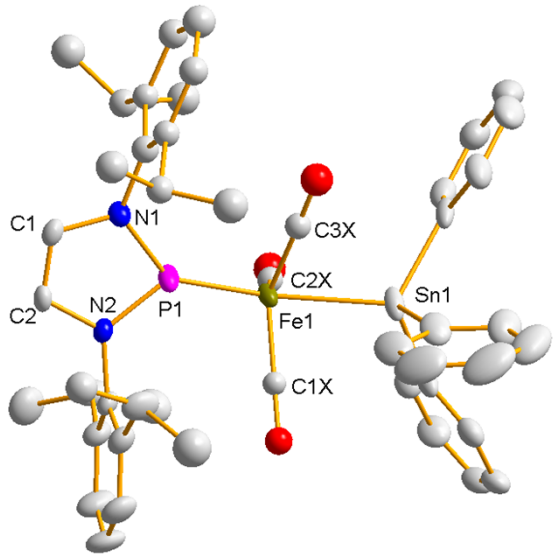


Fig. S1 Representation of the molecular structure of **4** in the crystal. Thermal ellipsoids were drawn at the 50% probability level, and H atoms were omitted for clarity. For all disordered atoms, only one of two split positions with the larger occupancy factor is shown, in order to verify the molecular constitution and conformation. Due to the disorder, no individual bond lengths and angles are given.

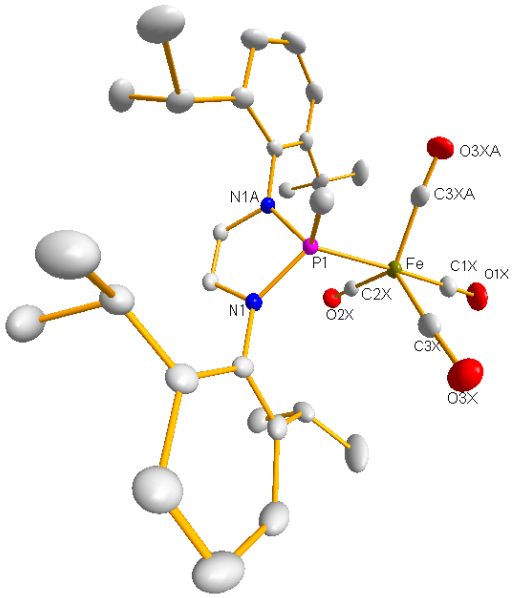


Fig. S2 Representation of the molecular structure of **6** in the crystal. Thermal ellipsoids were drawn at the 50% probability level, and H atoms were omitted for clarity. The molecule has crystallographic mirror symmetry. Selected bond lengths (Å) and angles (°): Fe1-C1X 1.796(2), Fe1-C2X 1.796(2), Fe1-C3X 1.797(2), Fe1-P1 2.2116(6), P1-C14 1.809(2), P1-N1 1.707(1), N1-C1 1.415(2), C1-C1A 1.326(3), C1X-Fe1-C2X 87.5(1), C1X-Fe1-C3X 92.2(1), C2X-Fe1-C3XA 123.6(1), C1X-Fe1-P1 176.2(1).

Table S1 Calculated Fe–P distances and Natural charges and Wiberg Bond Indexes obtained from NBO calculations

	Fe–P	Natural charges from NPA analysis				Wiberg Bond Indexes (WBI)		
	/ Å	Fe [a)]	$Fe(CO)_nX$ [b)]	P [a)]	NHP [b)]	Fe-P	Fe-C	Fe-H
2'	2.006	-2.41	-1.86	+1.52	+0.86	1.41	1.35 1.35 1.36	
$[Li(OMe_2)_3]$[**2'**]	2.012	-2.36	-1.79	+1.54	+0.90	1.37	1.30 1.32 1.43	
3'	2.047	-2.54	-1.19	+1.66	+1.19	1.20	1.20 1.18 1.18	0.68
5'	2.017 2.017	-2.54	-2.02	+1.59 +1.59	+1.01 +1.01	1.33 1.33	1.29 1.29	

[a)] natural charge on given atom; [b)] sum of natural charges of all atoms in the fragment

Table S2 Calculated harmonic vibrational frequencies of νCO modes for **2'**, [Li(OMe$_2$)$_3$][**2'**], **3'**, **5'**. Experimental data for [PPh$_4$][**2**], Na[**2**], **3a**, **5** are given in brackets for comparison.

Compound	ν(CO)			ν(FeH)
2'	1813 [1798]	1828 [1813]	1924 [1894]	
[Li(OMe$_2$)$_3$][**2'**]	1782 [1767]	1853 [1834]	1933 [1912]	
3'	1967 [1933]	1989 [1960]	2052 [2014]	1922 (w)
5'	1887 [1883]	1944 [1930]		

Fig. S3 Correlation plot and regression formula for the comparison of calculated νCO vibrational frequencies of model compounds **2'**, [Li(OMe$_2$)$_3$][**2'**], **3'**, **5'** with the experimental data for [PPh$_4$][**2**], Na[**2**], **3a**, **5**.

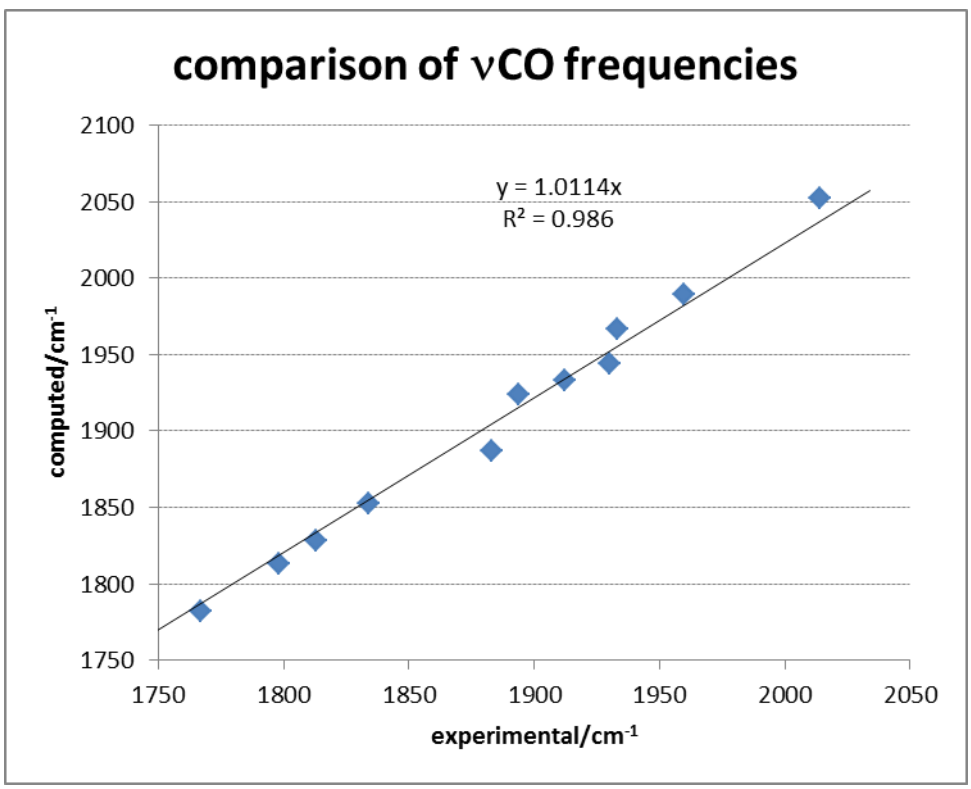
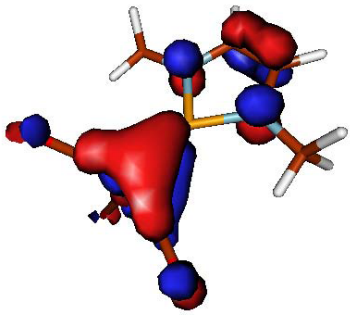
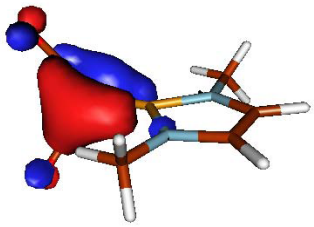


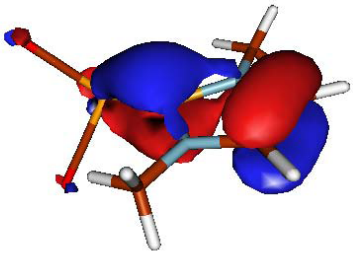
Figure S4 Graphical representation of selected KS-MOs of **2'** with Fe–P bonding contributions



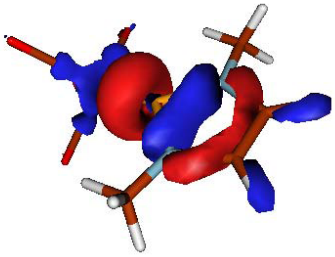
HOMO



HOMO -1



HOMO-5



HOMO-7

Table S3 Ccoordinates of energy optimized geometries and absolute energies for **2'**, $[Li(OMe_2)_3]$[**2'**], **3'**, **5'**.

2' E = -2212.31063732

C	3.8645823057	4.7440919003	14.3041218692
O	4.2440249959	3.8853600868	15.0032374543
Fe	3.2961469399	6.0201705682	13.2438443519
P	4.3607753839	7.7081605655	13.4430992268
N	5.9750031242	8.1788542559	13.1104627543
C	6.9669039907	7.2714143802	12.5644466865
C	1.5955651107	6.3145058495	13.577878347
O	0.4546669859	6.472343062	13.792948475
C	3.5065652139	5.341965991	11.6405446553
O	3.6437423986	4.8743840041	10.5758313368
N	4.0967289063	9.3131180953	13.9893358473
C	2.8197472207	9.7837749959	14.4929219741
C	5.2003582581	10.146762209	13.9037568728
C	6.2710122018	9.5006655193	13.403371018
H	5.1428783822	11.1790784424	14.2189927305
H	7.2599649117	9.901213592	13.2306266834
H	2.4108787447	10.5704699649	13.8531303828
H	2.1196212567	8.9506909765	14.5091171349
H	2.9229271516	10.1740206253	15.5086409166
H	7.3306319197	7.6248540096	11.5960074901
H	7.816915625	7.1674786174	13.2439386204
H	6.505104972	6.2942742888	12.4296751721

[Li(OMe$_2$)$_3$][**2'**] (mixed basis) E = -2684.53635395 a.u.

C	-1.5528261447	2.4892175187	-1.4087594982
Fe	-1.2736116191	1.1812764605	-0.2616674795
P	-2.7590603902	-0.1701052385	-0.1403647795
N	-3.9283056914	-0.6537312397	1.0104333872
C	-4.6804604911	-1.7586717542	0.6439093397
C	-4.3227260036	-2.2195045161	-0.5700253091
N	-3.3016133245	-1.4605552008	-1.1202602526
C	-2.7424349888	-1.7567618556	-2.4273635816
O	-1.7073590828	3.3511266569	-2.1800500842
C	-1.0009654527	1.912728059	1.3154086152
O	-0.7610919254	2.399091273	2.350784137
C	0.1703990998	0.4092744628	-0.798581754
O	1.1895980472	-0.1090496069	-1.1209679161
Li	2.7686649767	-0.4088248617	-0.0354021528
O	3.2105111115	1.2352041132	0.9041245256
C	3.1253349228	2.4605541419	0.1879209835
O	4.2580130437	-0.863889937	-1.1901884934
C	5.596634901	-0.4275804305	-1.0137732799
O	2.4189220455	-1.843419957	1.2322989247
C	3.3918932348	-2.7909504019	1.6408944473
C	4.066021532	-1.6619046206	-2.3492119536
C	-4.1302015434	0.0224892209	2.2799771596
C	1.1159624338	-2.1174398835	1.7338123568
C	3.0437363133	1.3956695077	2.3060428635
H	-5.4474250853	-2.1502829375	1.2972803488
H	-4.7400598622	-3.0615502423	-1.1040381483
H	-3.9288689893	-0.6508169421	3.1169981468
H	-3.447373595	0.8675534741	2.3405118605
H	-5.1548725828	0.3927607523	2.3630487965
H	-3.5160240107	-1.7153999037	-3.1980121362
H	-1.9790579646	-1.0140114845	-2.6540508777
H	-2.2830149997	-2.7484194548	-2.4405576418
H	3.1196398426	-3.8083801668	1.2969488126
H	4.3517310105	-2.5009452082	1.1862315349
H	3.4941718384	-2.7995177816	2.7440078391
H	0.7634744266	-3.1044696992	1.3756014167
H	1.1194611182	-2.1153534361	2.8414943921
H	0.439060559	-1.3300696036	1.3649091741
H	3.8983571001	3.1700403493	0.5427254501
H	3.2972948405	2.2371204326	-0.8765477663
H	2.1228020737	2.9136984207	0.3047818823
H	2.0490971526	1.8227157208	2.5371926933
H	3.1288345408	0.3986791384	2.7637354704
H	3.8324221256	2.0565679344	2.7161959537
H	4.3552802596	-1.1030126342	-3.2604170123
H	4.6654147568	-2.5917402283	-2.2884497736

H	2.9960014518	-1.9145182411	-2.4055450585
H	5.9302539519	0.1744177447	-1.8817567483
H	5.622825276	0.1950405452	-0.1063370786
H	6.279312911	-1.291722433	-0.891198032

3' E = -2212.79288254 a.u.

C	4.0439472131	4.7633497081	14.3328565906
O	4.4442531523	3.9758249247	15.0698138182
Fe	3.4749809968	5.9417774576	13.125758063
P	4.3205400937	7.8059775852	13.1081198801
N	5.8506589881	8.3684017444	12.6862126761
C	6.9601318297	7.5471969934	12.2118677467
C	1.8596420641	6.2335477768	13.85013831
O	0.8186588961	6.3841543382	14.3130683824
C	2.9066329959	5.2464236387	11.5874809258
O	2.588652539	4.7638592505	10.5928354494
N	3.8636409196	9.3856004998	13.4793016447
C	2.5463381225	9.7790631048	13.9667916457
C	4.8702419497	10.3180298173	13.2856595602
C	5.9975712787	9.7400259974	12.8328339648
H	4.8272340925	5.5882857851	12.5035926054
H	4.6990672874	11.3656055069	13.489751717
H	6.9353711685	10.2194815627	12.5909622663
H	2.137898477	10.5701600933	13.3367094855
H	1.873626706	8.9270108394	13.9320058118
H	2.6100856307	10.1349613201	14.9964775243
H	7.256503275	7.8600535579	11.2094785557
H	7.8117810833	7.6442578325	12.8868829874
H	6.6525522402	6.5057986651	12.1794933889

5' E = -2707.04653598 a.u.

C	0.7663698974	12.8456773323	14.8574309712
O	-0.0361673304	12.1346873714	15.3069920626
Fe	1.9643202656	13.9530092315	14.188490072
P	1.1930865047	15.0886077893	12.7105714466
N	0.8582509567	14.8796664337	11.0559229738
C	1.1214052637	13.6501416319	10.3248627247
C	2.3942759438	15.0153489559	15.5264221341
O	2.6900371266	15.7027869871	16.4158109085
P	3.5452842411	12.8721785076	13.5565011412
N	4.9042700023	13.1558325455	12.5734408845
C	5.1869805258	14.4286115501	11.9286979117
N	4.1252640352	11.2937265379	13.8034707045
C	3.4534076024	10.3006982672	14.6280149769
N	0.5541168058	16.6581733606	12.5828769712

C	0.4556177926	17.589829914	13.6964917505
C	5.3132538232	11.0098358493	13.1485329692
C	5.7552493861	12.068885466	12.4448222741
C	0.105380012	16.9935456776	11.3149513053
C	0.2839922075	15.9832597386	10.4434686316
H	5.7751041606	10.0367922483	13.2375589254
H	6.6502126073	12.1341714551	11.8423454162
H	-0.3257471953	17.9655507758	11.1202006529
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H	2.5459311686	10.7343379466	15.0407501777
H	5.1302848801	14.3377980976	10.8415587809
H	4.4533179164	15.1606856928	12.260768939
H	6.1834249693	14.7798997932	12.203728737

Fig. S5: ^{1}H NMR of Na[**2**] (303 K, in d_8-THF)

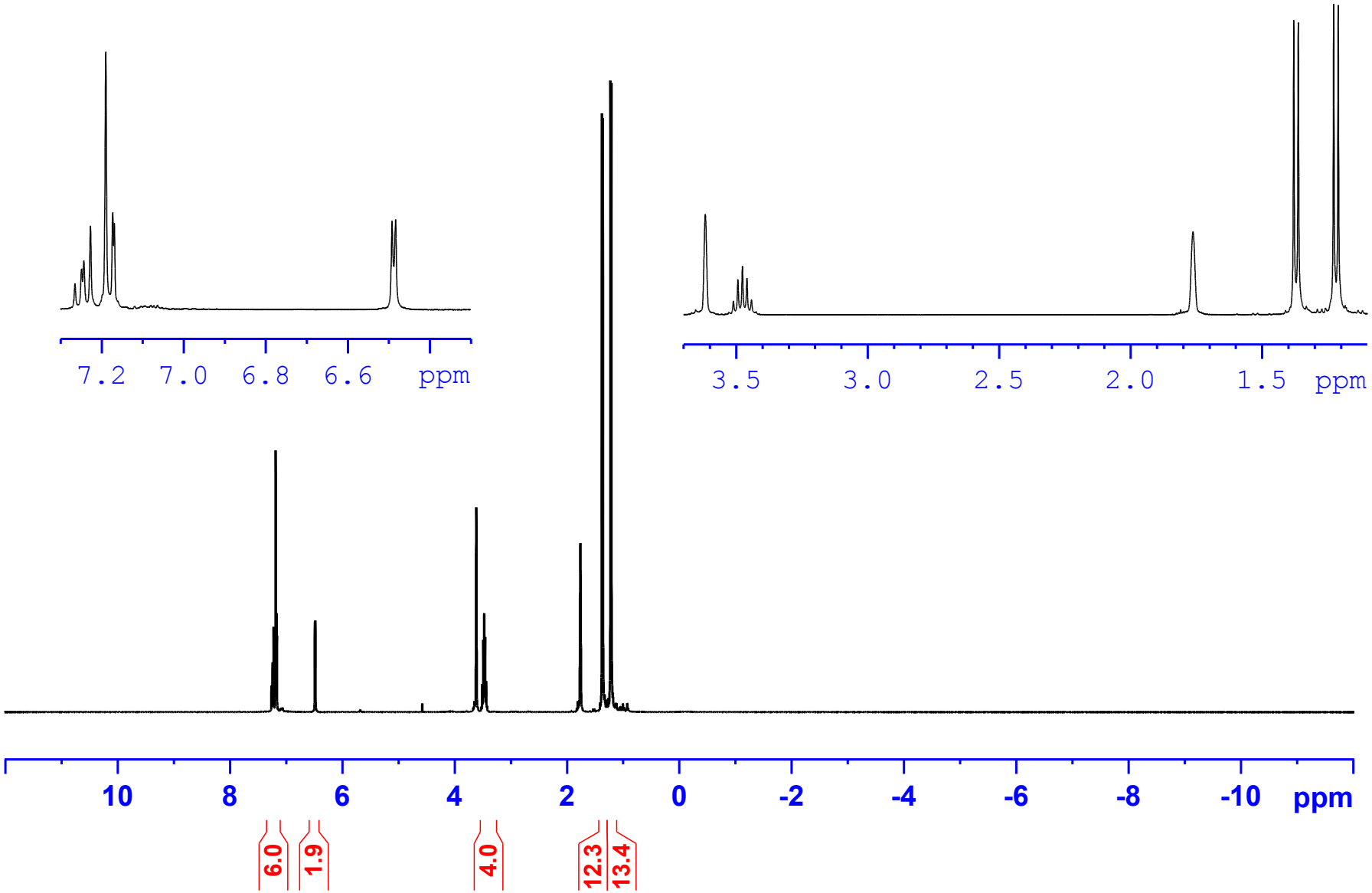

Fig. S6: $^{31}P\{^{1}H\}$ NMR of Na[**2**] (303 K, in d_8-THF)

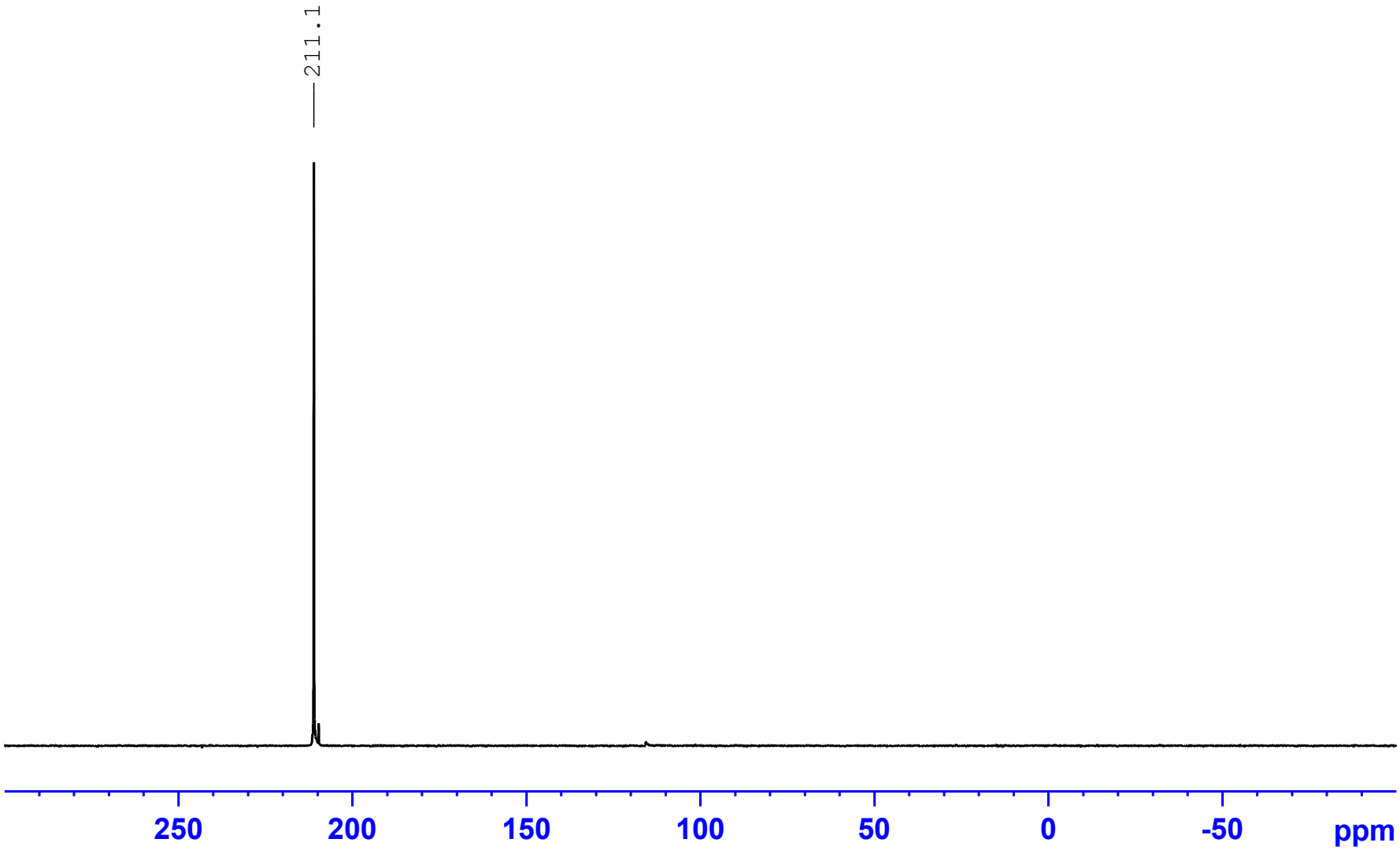

Fig. S7: $^{31}P\{^{1}H\}$ NMR of Na[**2**] (303 K, in d_8-THF)

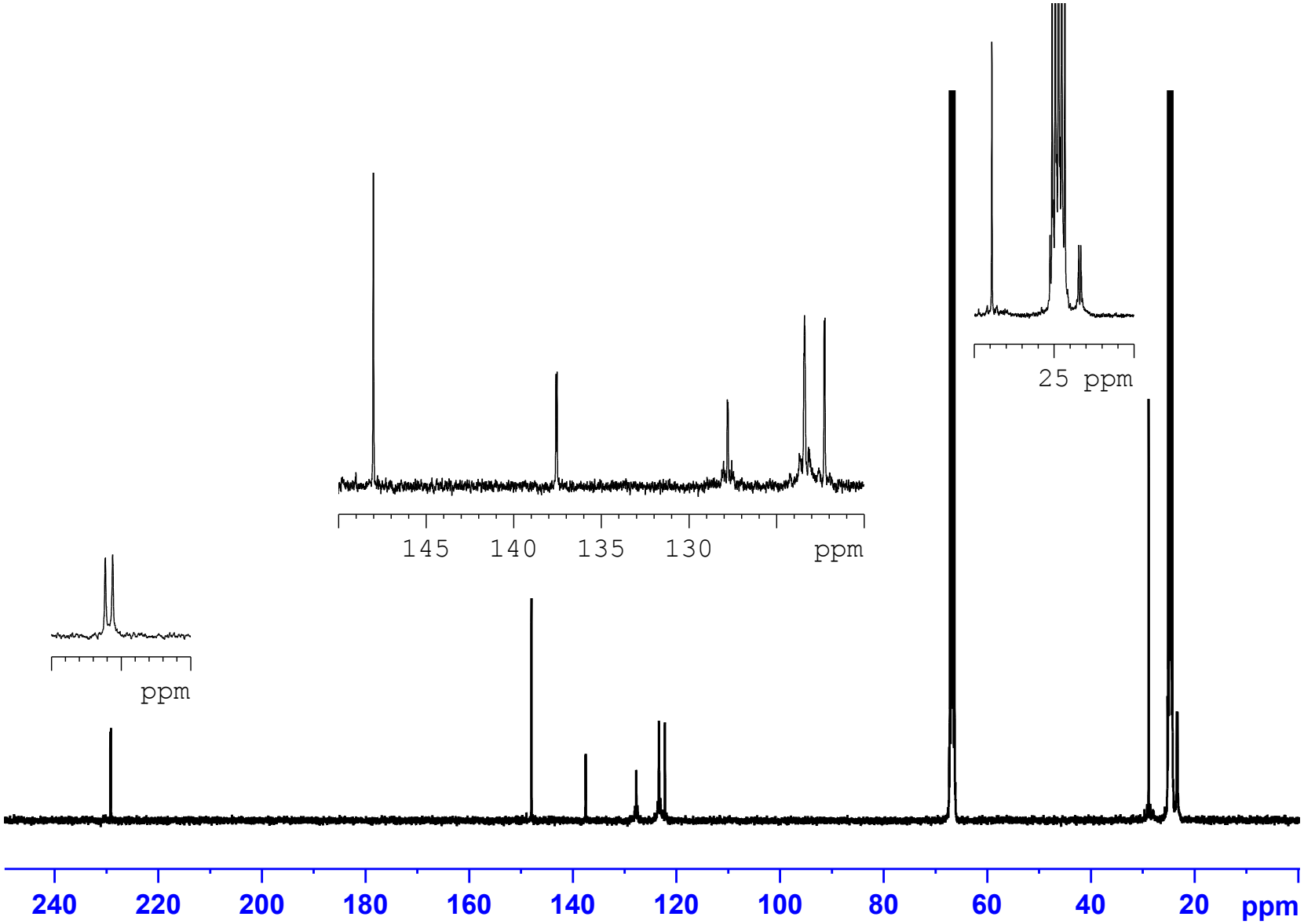

Fig. S8: ^{1}H NMR of $[PPh_4]$[**2**] (303 K, in $CDCl_3$)

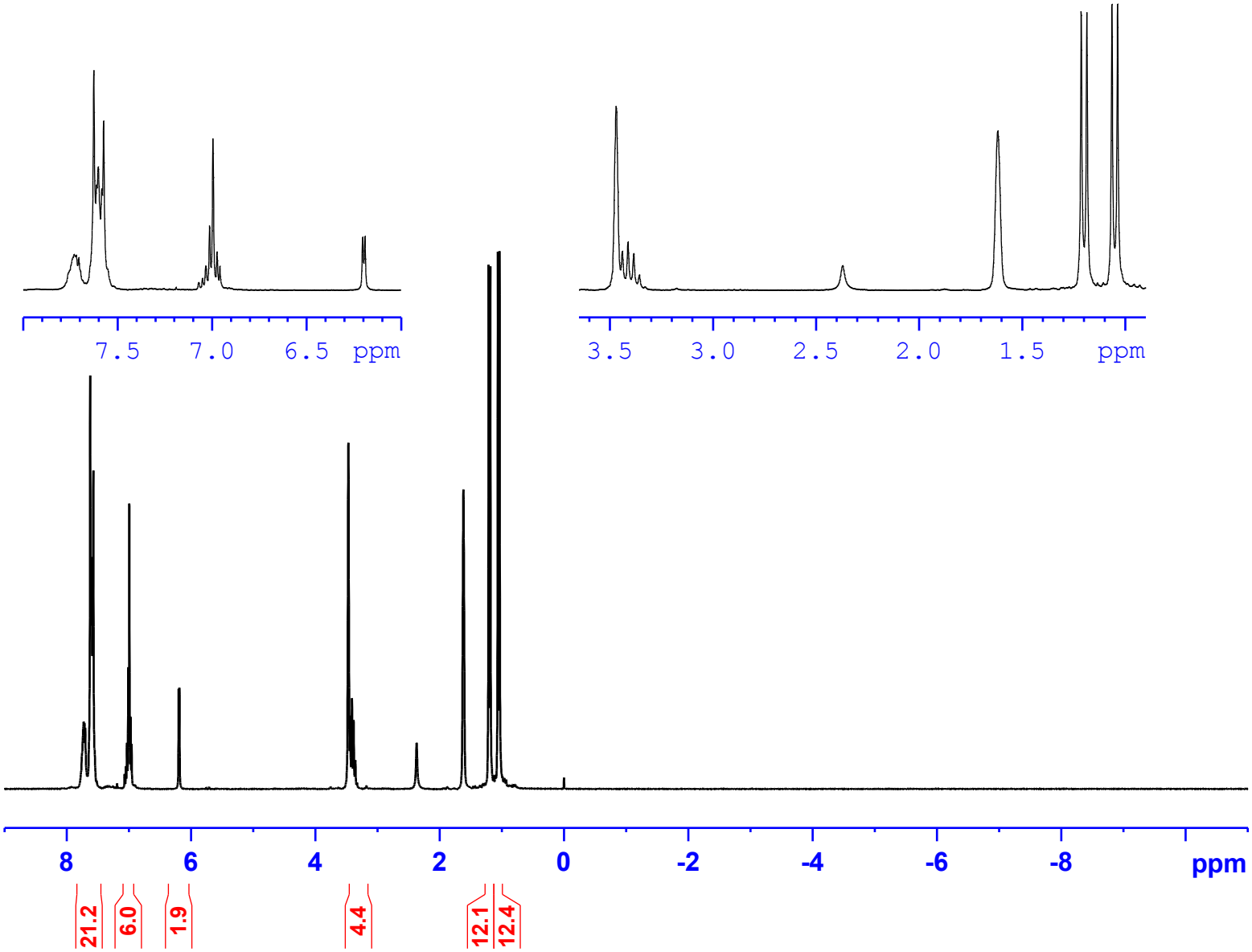

Fig. S9: $^{31}P\{^{1}H\}$ NMR of $[PPh_4]$[**2**] (303 K, in $CDCl_3$)

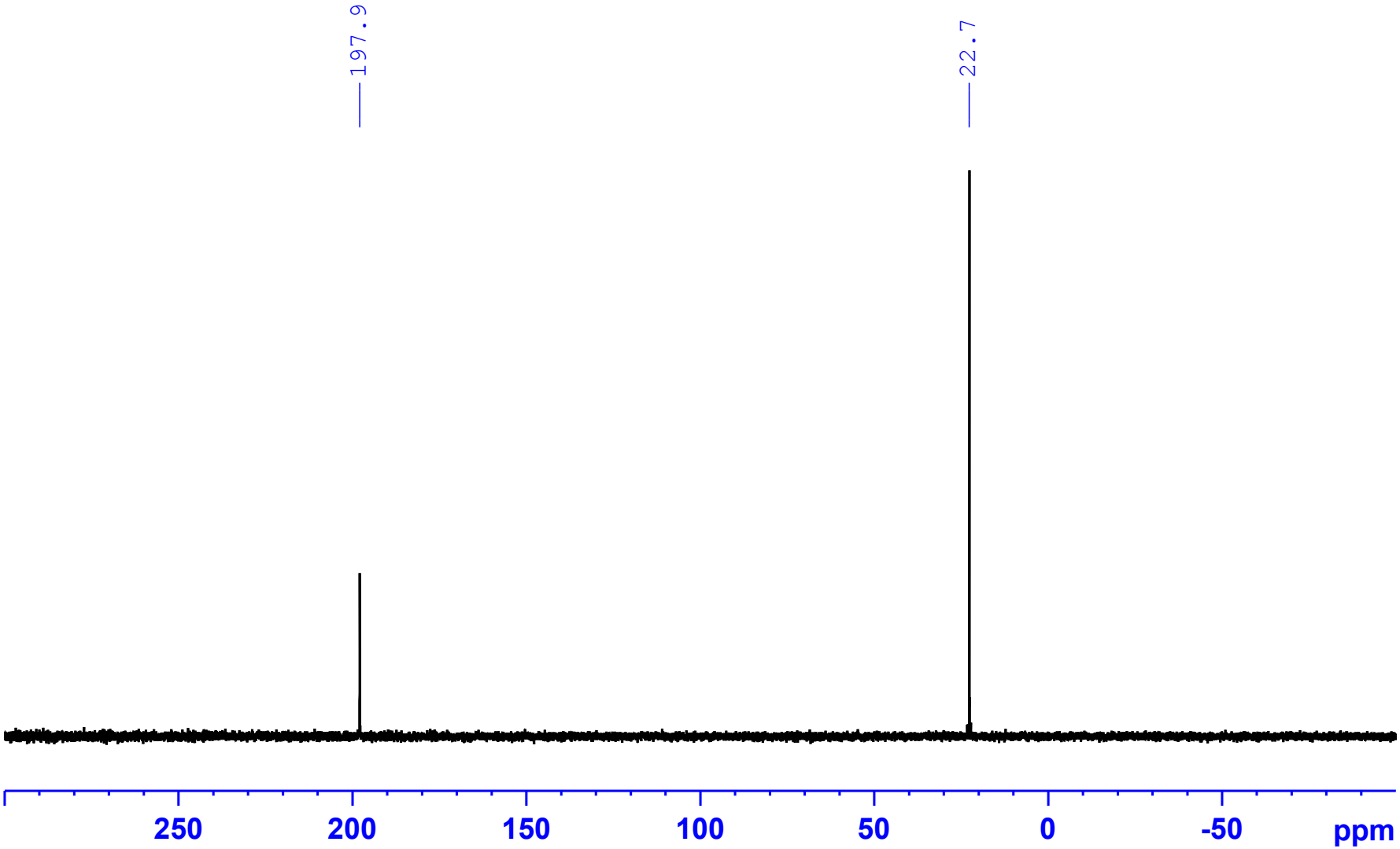

Fig. S10: $^{1}H,^{13}C$ gs-HSQC of [PPh_4][**2**] (303 K, in $CDCl_3$)

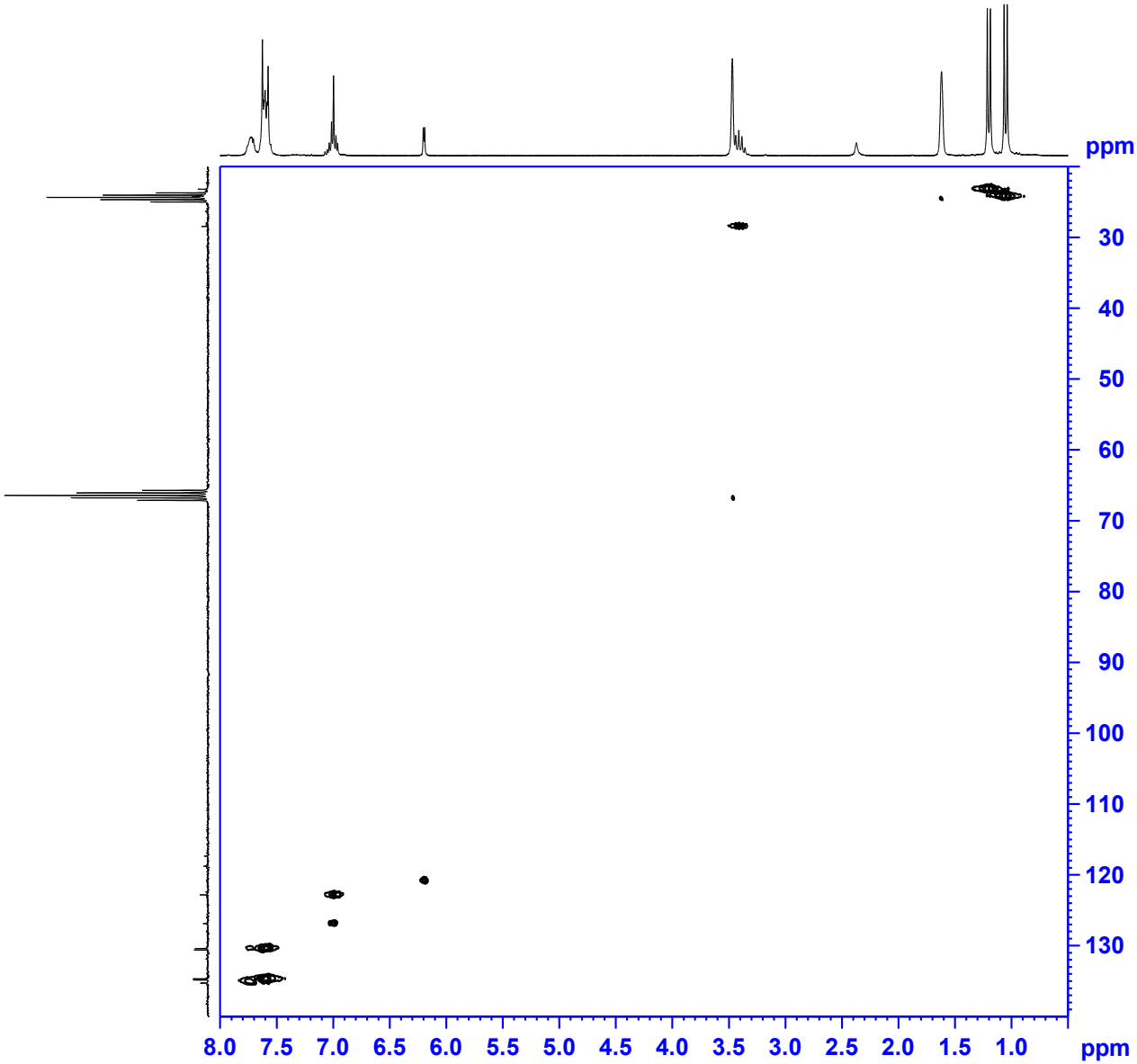

Fig. S11: ^{1}H NMR of **3a** (303 K, in C_6D_6)

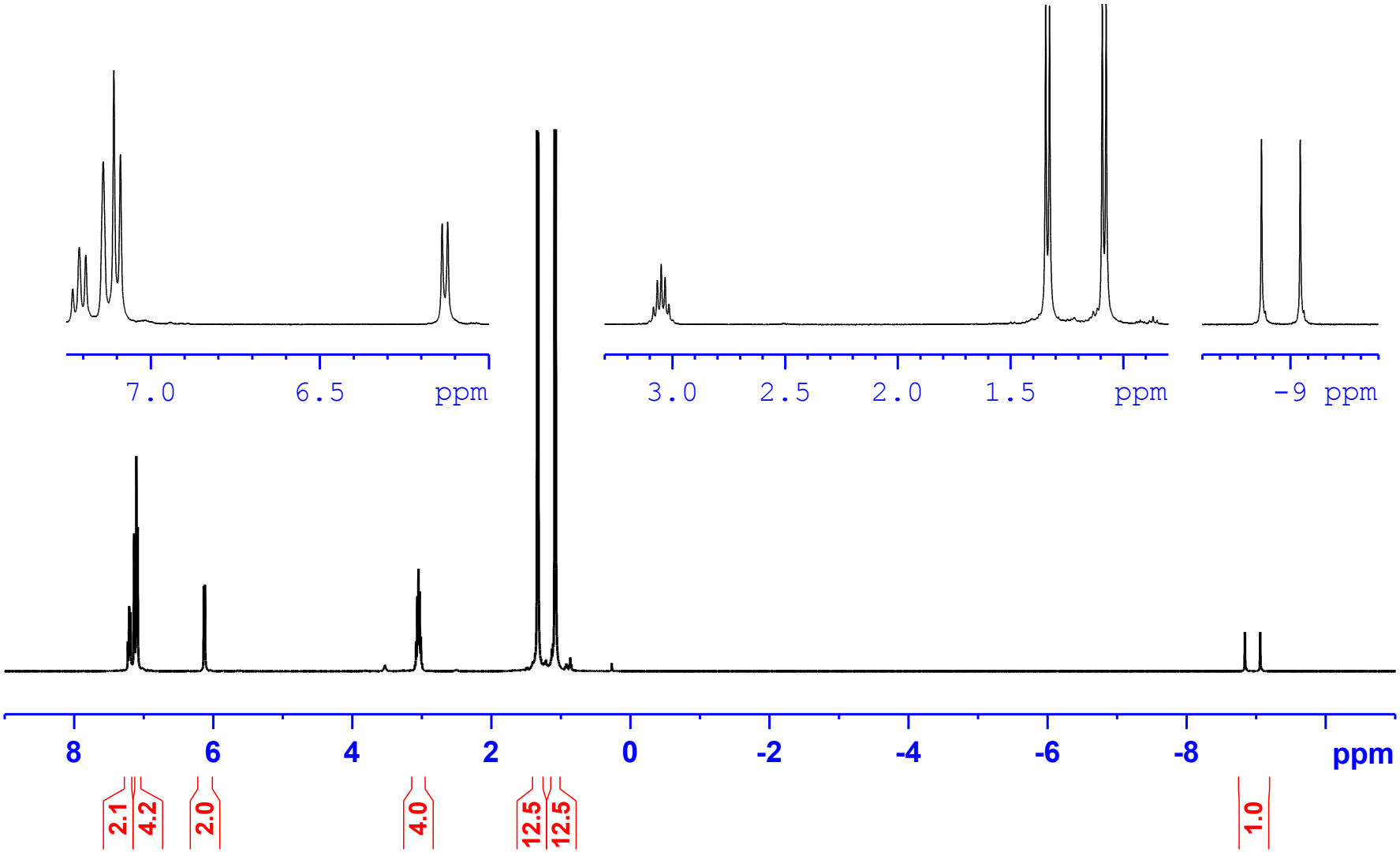

Fig. S12: $^{31}P\{^{1}H\}$ NMR of **3a** (303 K, in C_6D_6)

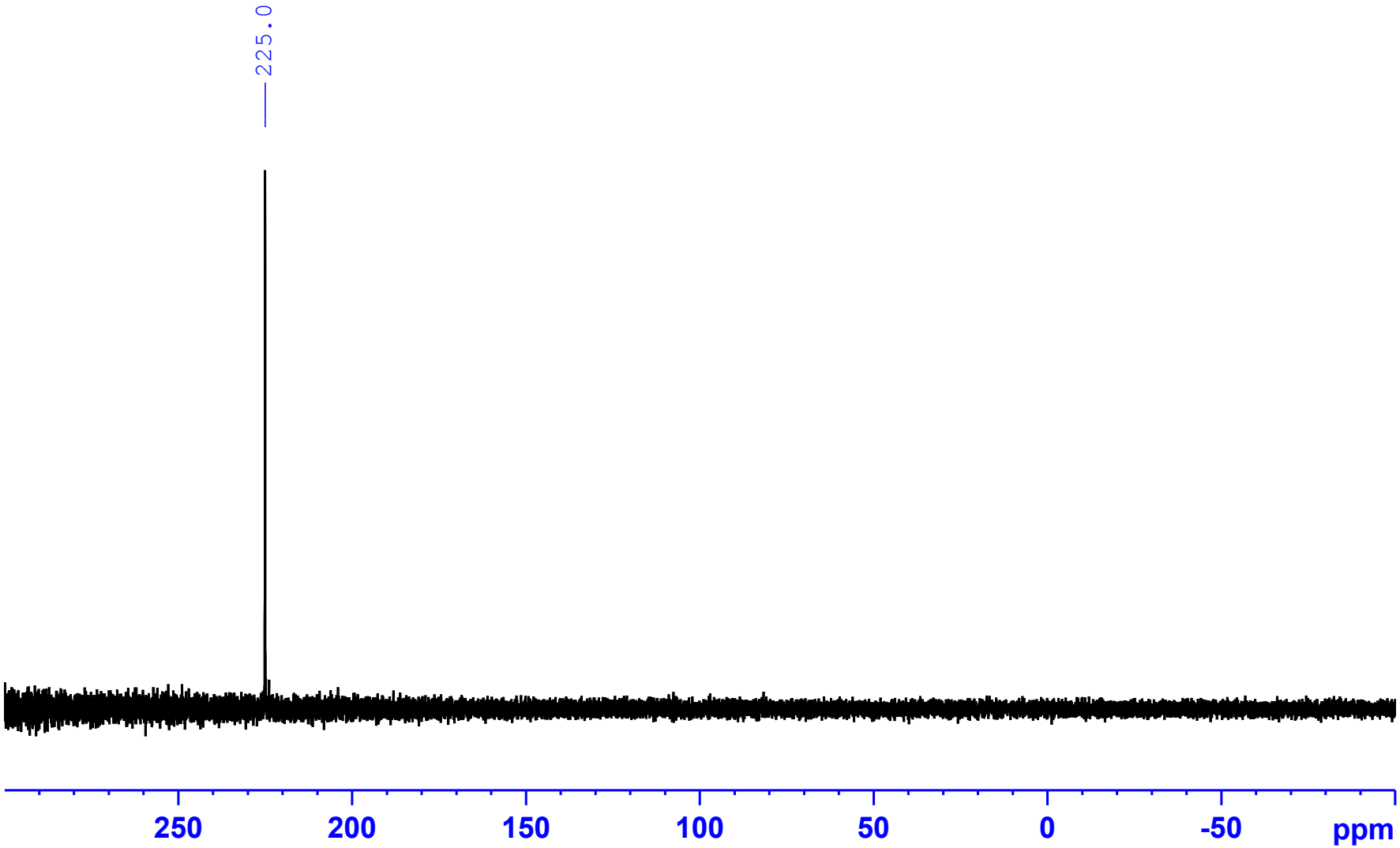

Fig. S13: $^{13}C\{^{1}H\}$ NMR of **3a** (303 K, in C_6D_6)

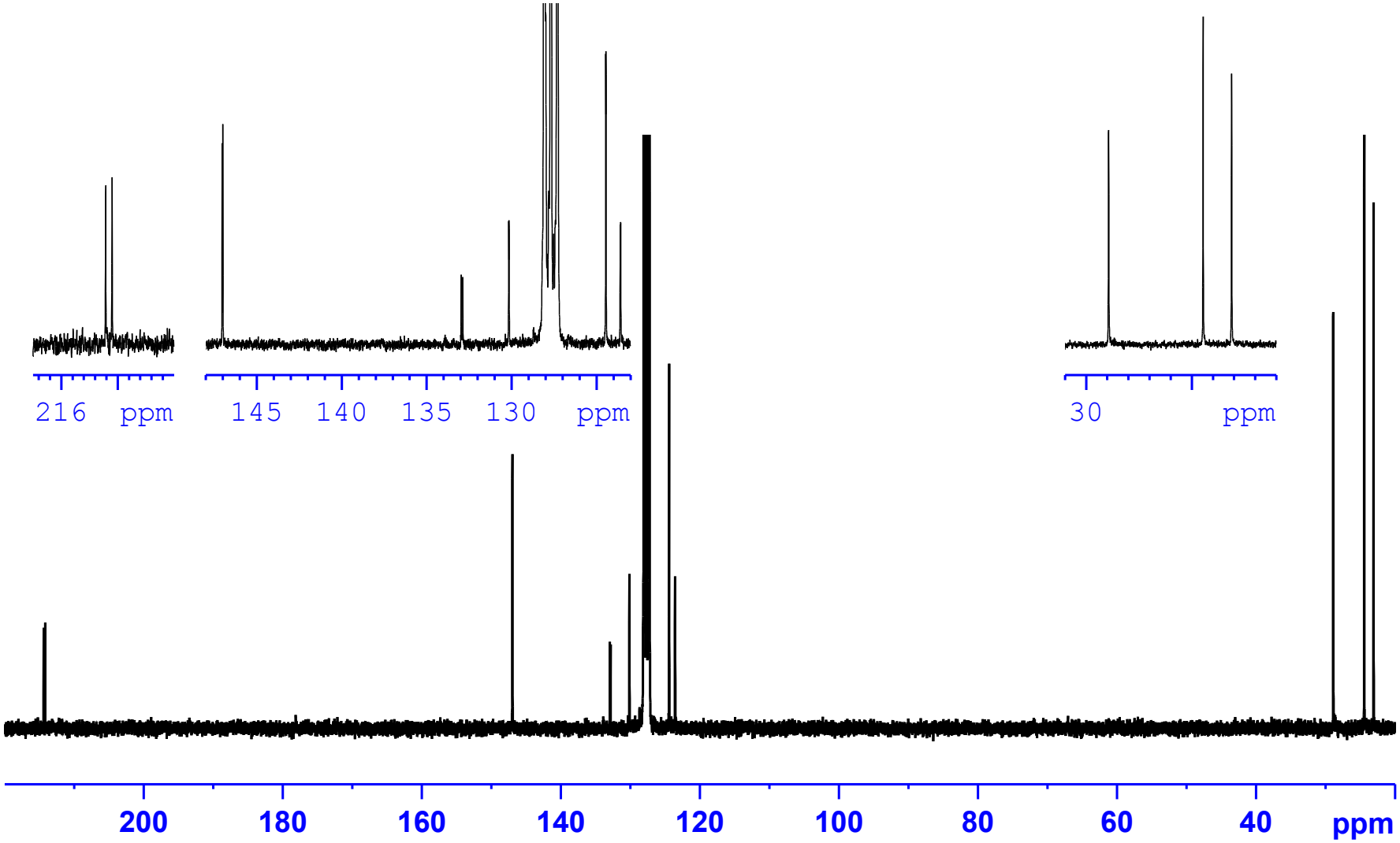

Fig. S14: ^{1}H NMR of **5** (303 K, in C_6D_6)

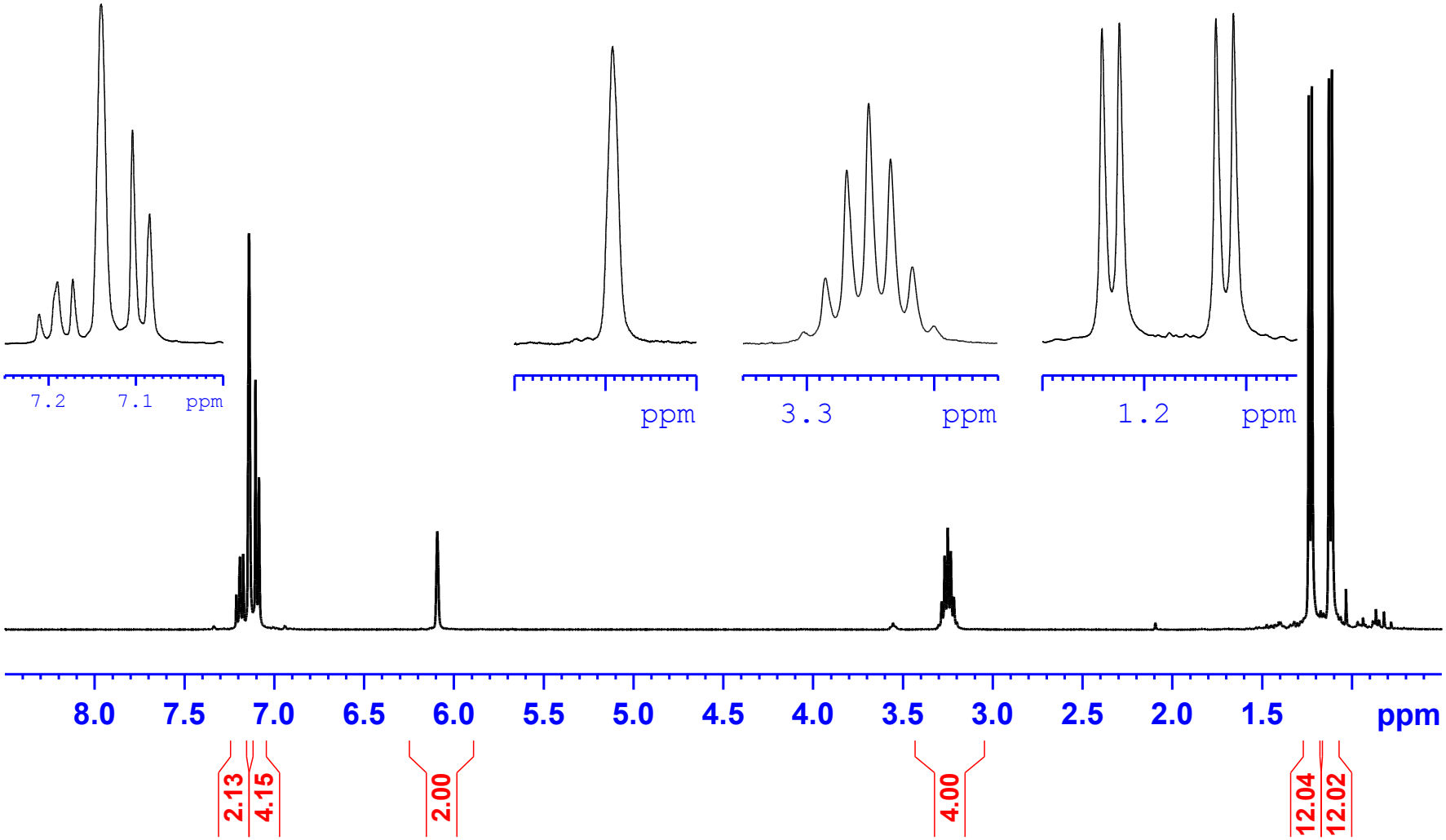

Fig. S15: $^{31}P\{^{1}H\}$ NMR of **5** (303 K, in C_6D_6)

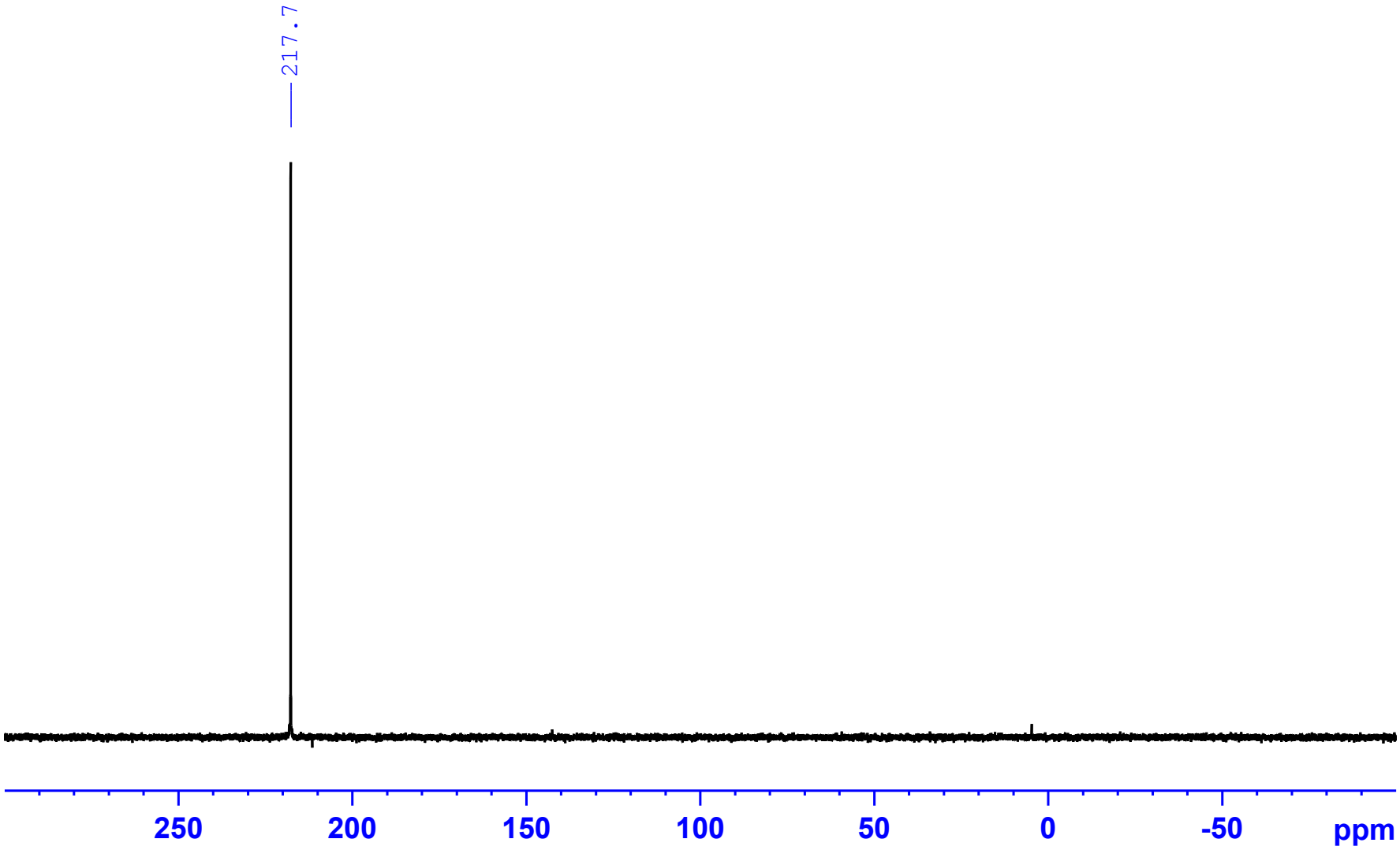

Fig. S16: $^{13}C\{^{1}H\}$ NMR of **5** (303 K, in C_6D_6)

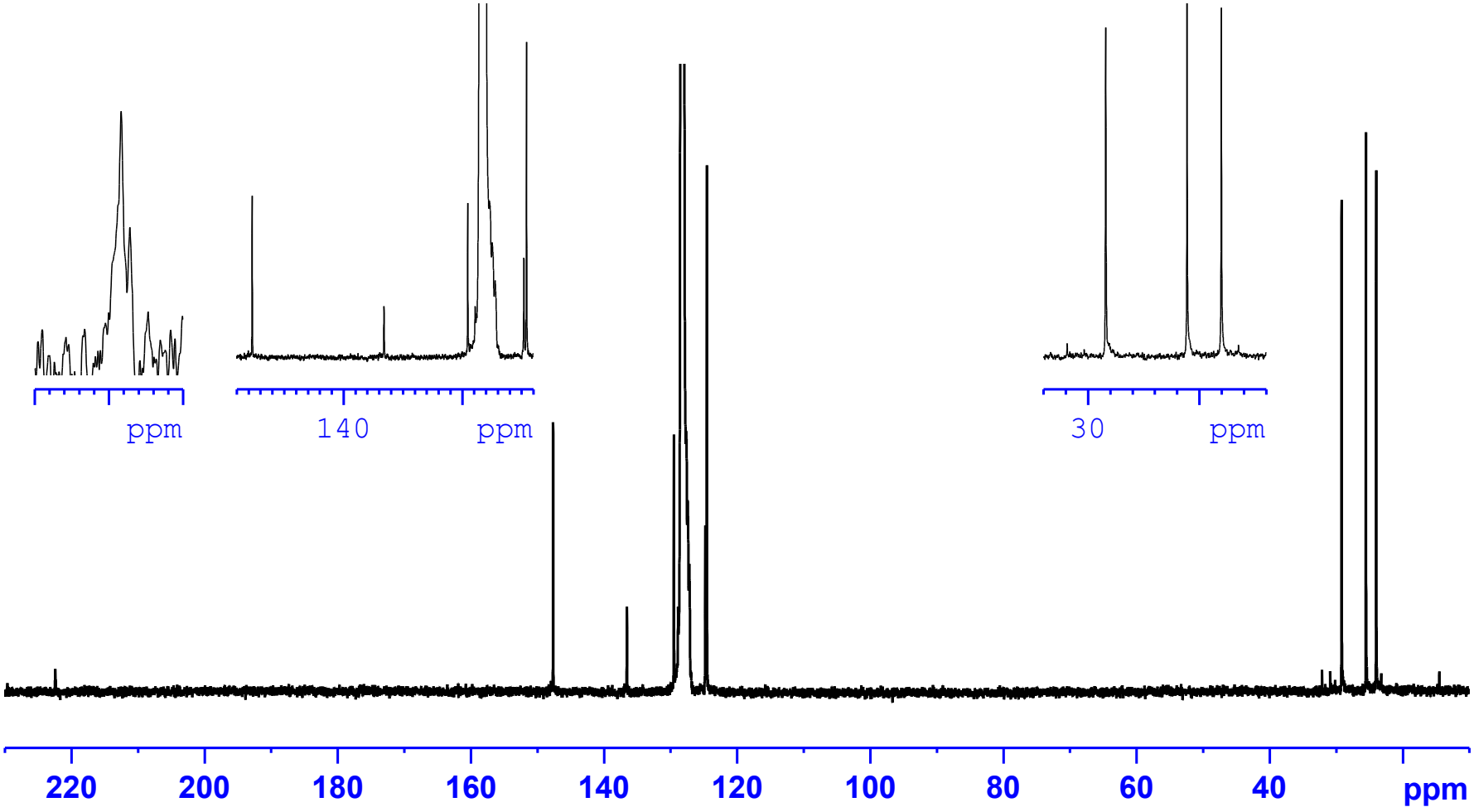

Fig. S17: ^{1}H NMR of **7** (303 K, in C_6D_6)

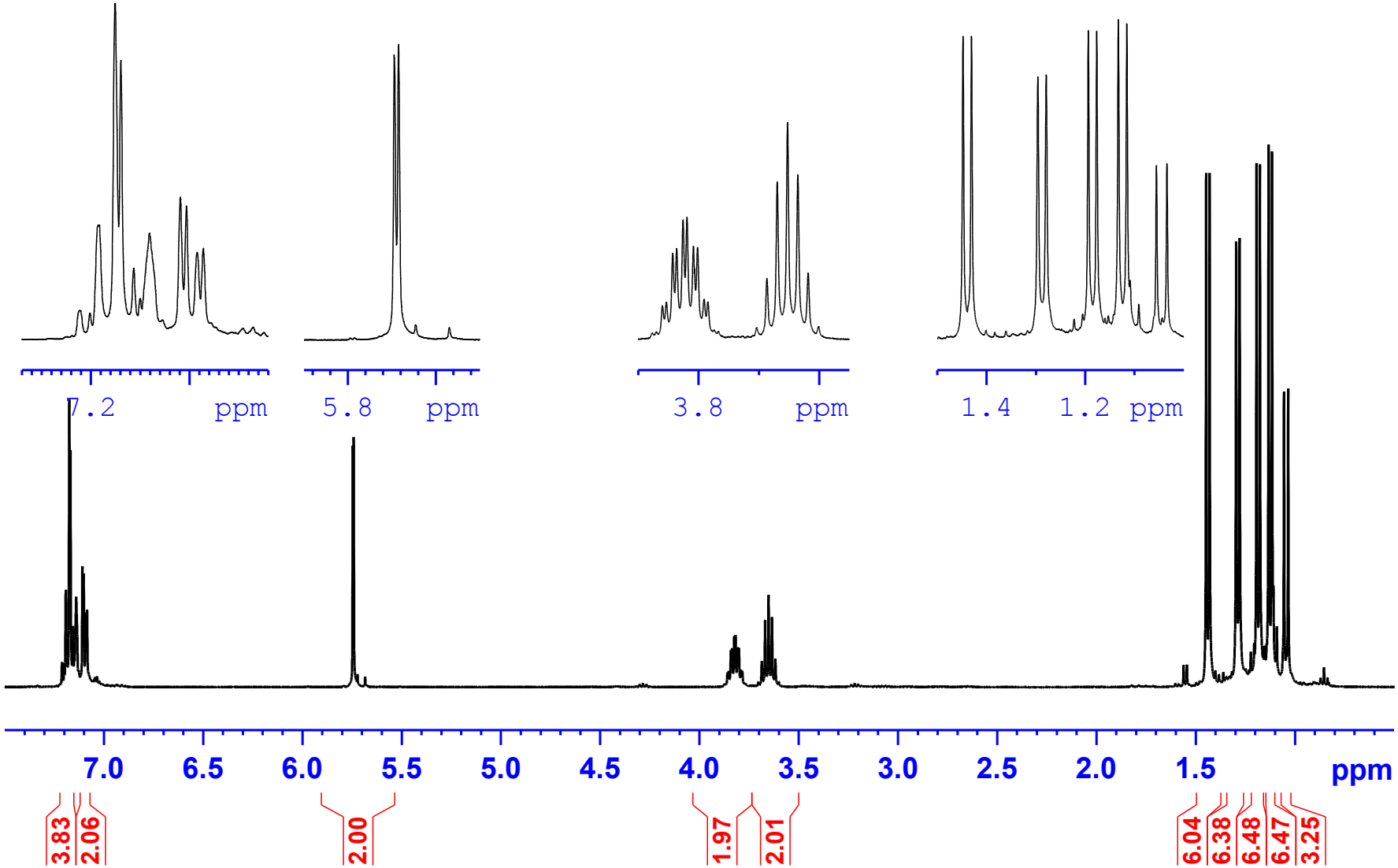

Fig. S18: $^{31}P\{^{1}H\}$ NMR of **7** (303 K, in C_6D_6)

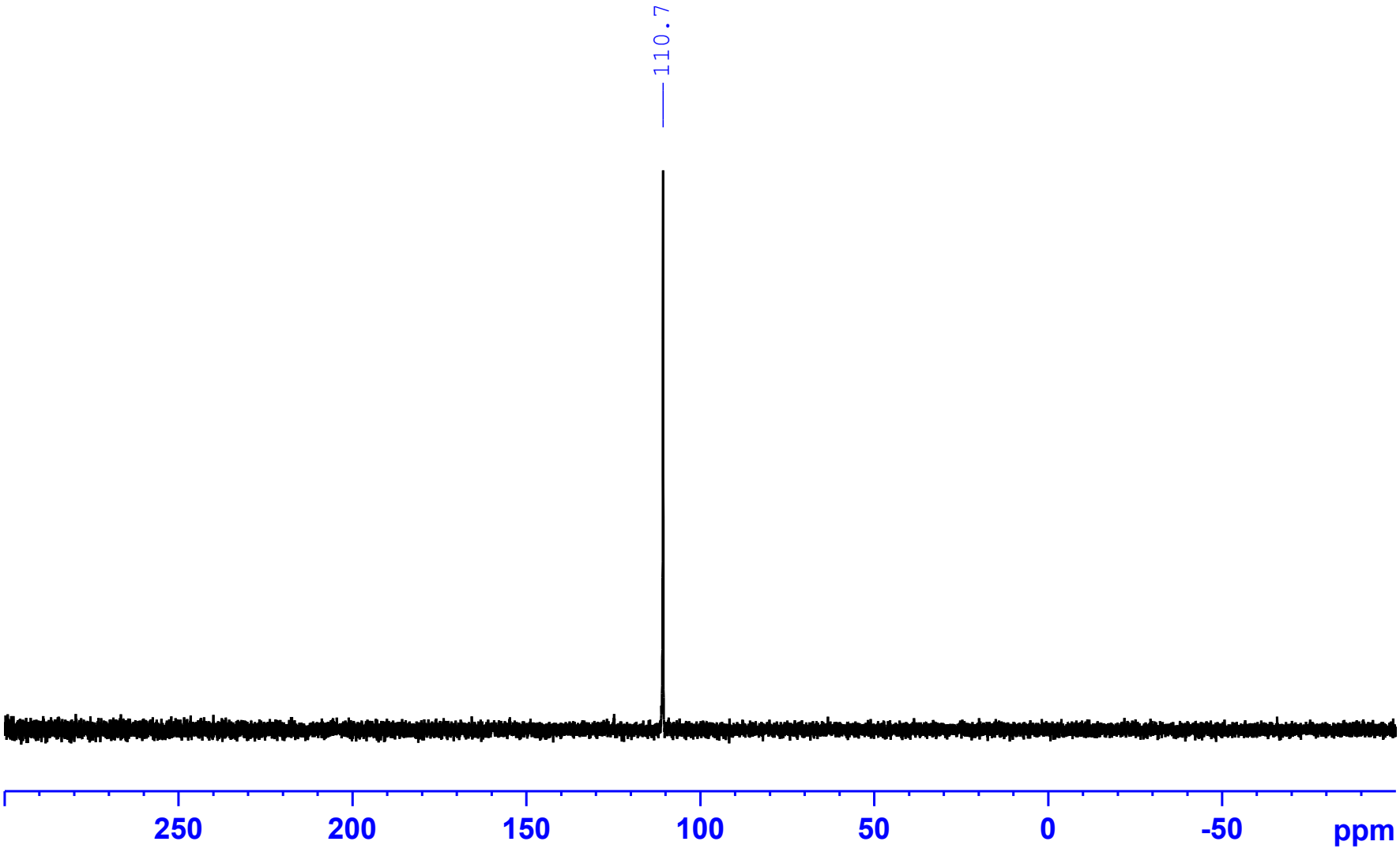

Fig. S19: $^{13}C\{^{1}H\}$ NMR of **7** (303 K, in C_6D_6)

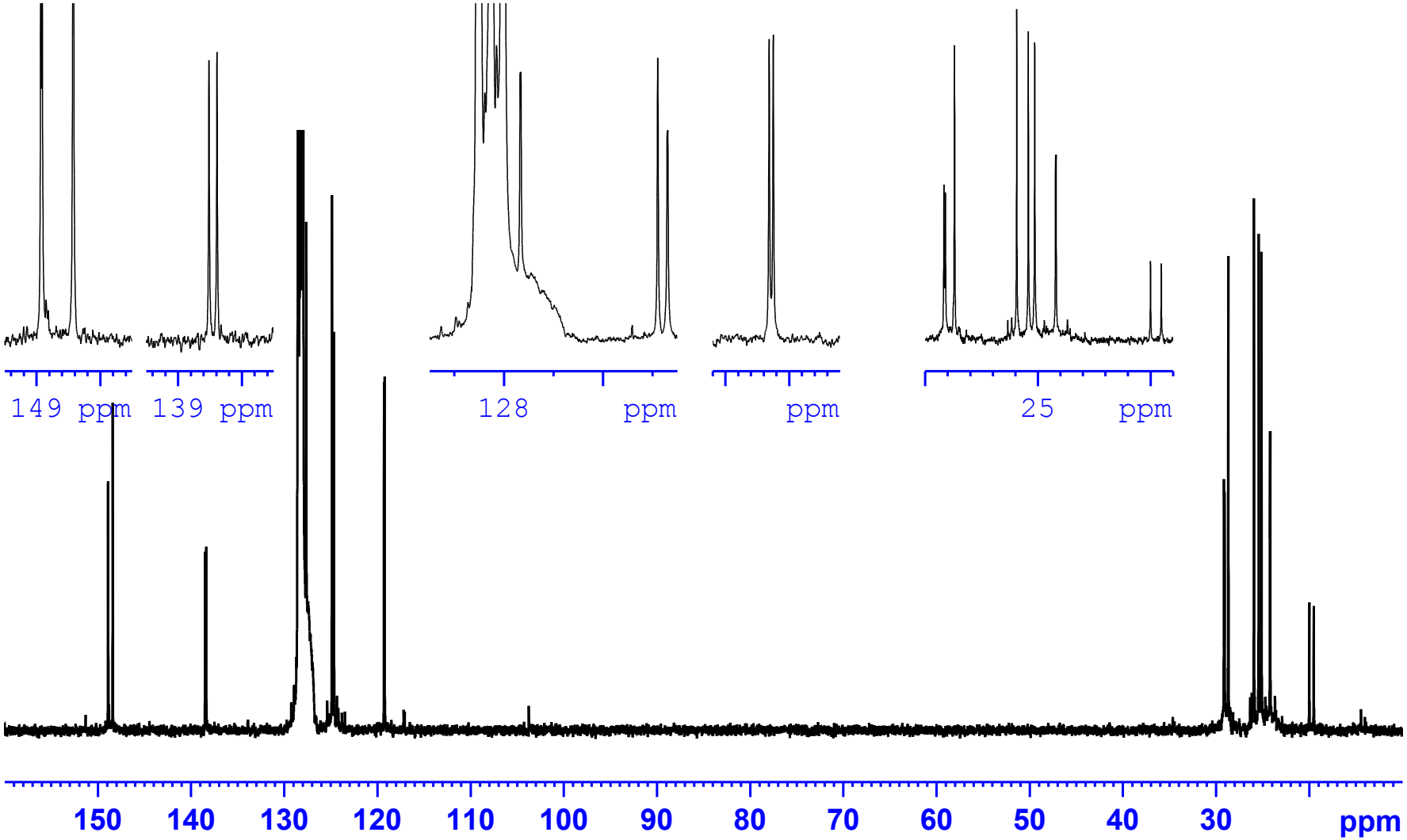

Fig. S20: ^{1}H NMR of the reaction of Na[**2**] and MeI (203 K, in d_8-THF)

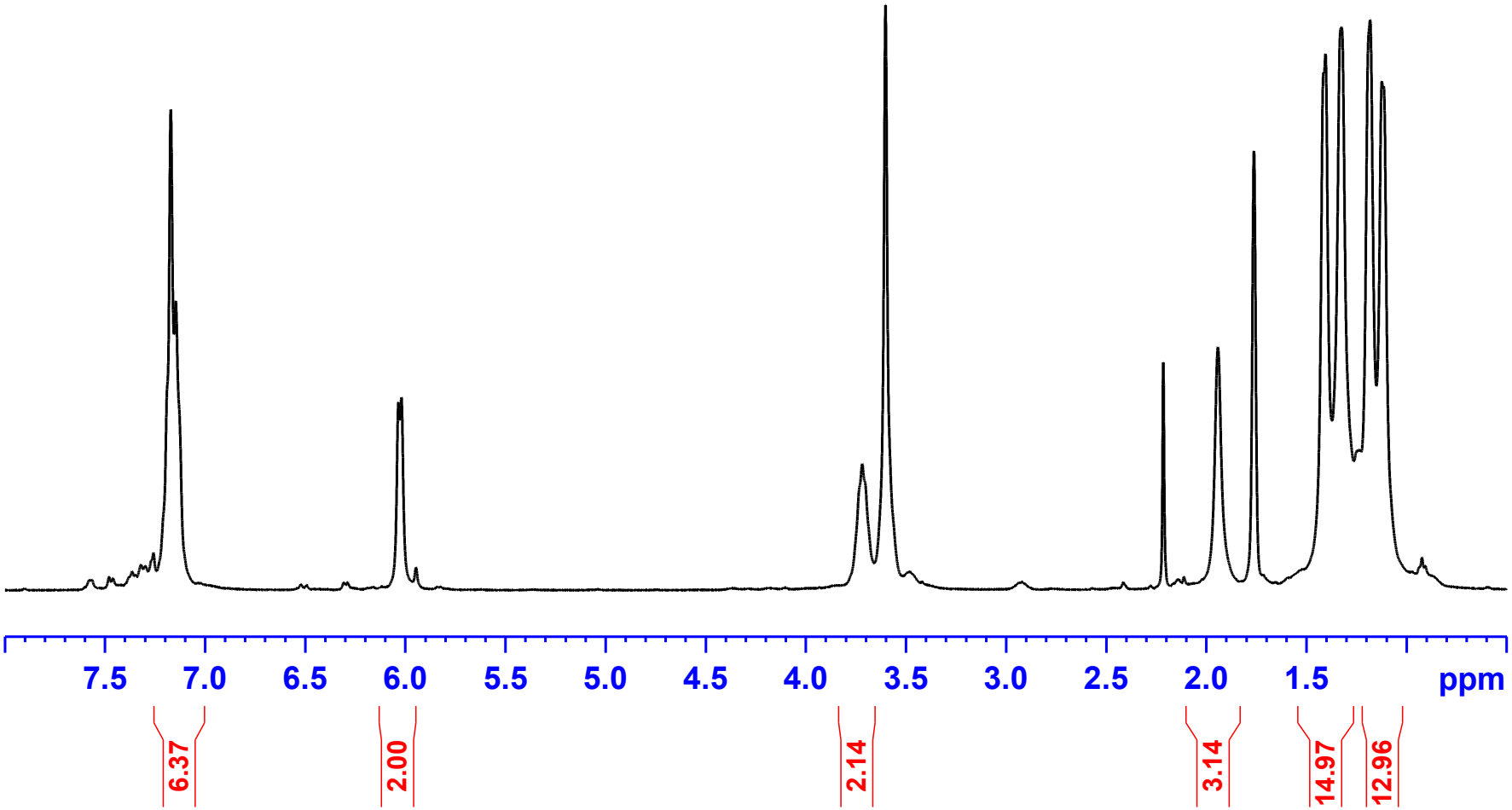

Fig. S21: ^{1}H NOESY of the reaction of Na[**2**] and MeI (203 K, in d_8-THF, mixing time 100 ms)

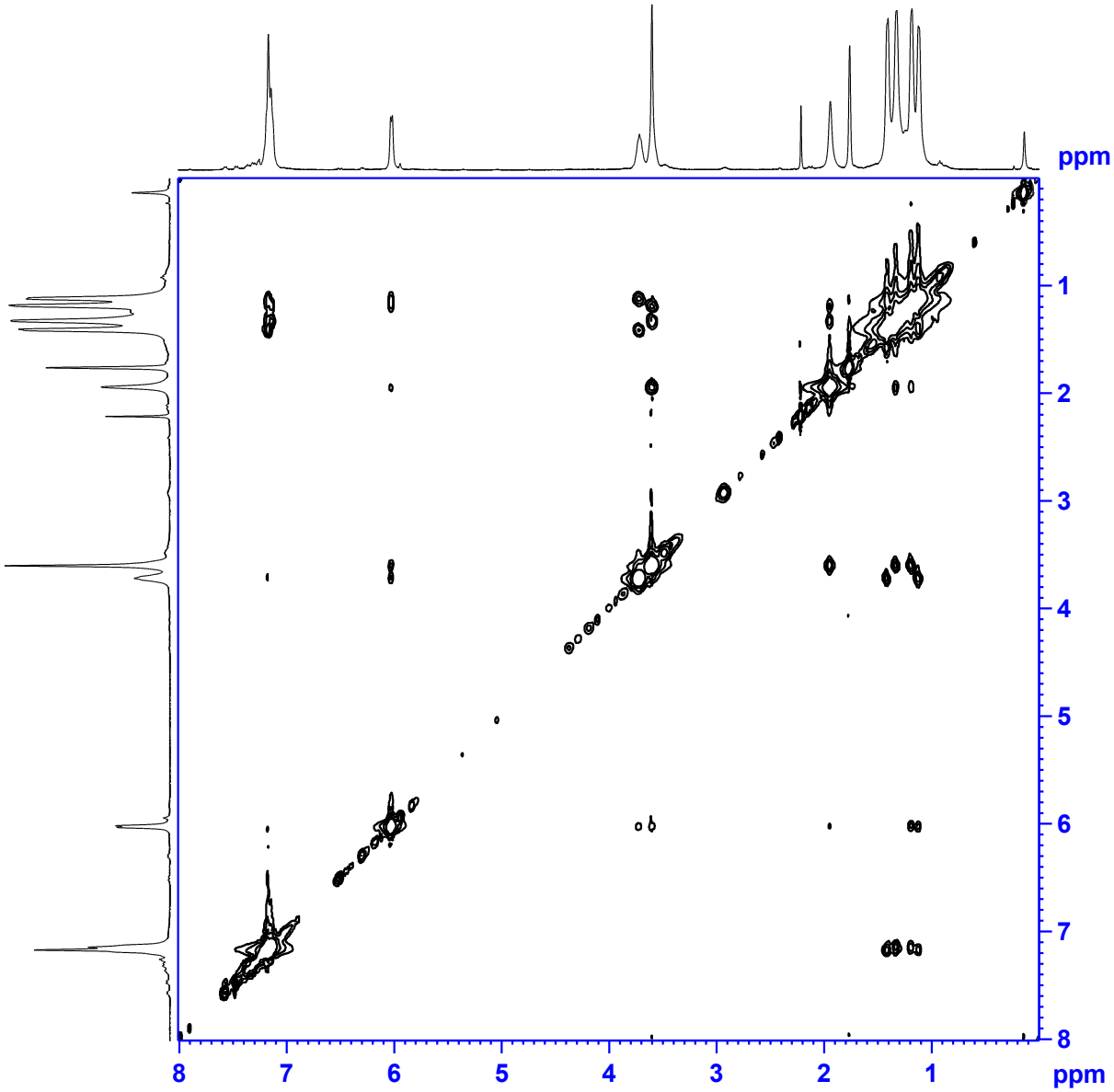

Fig. S22: $^{1}H,^{13}C$ HSQC of the reaction of Na[**2**] and MeI (203 K, in d_8-THF)

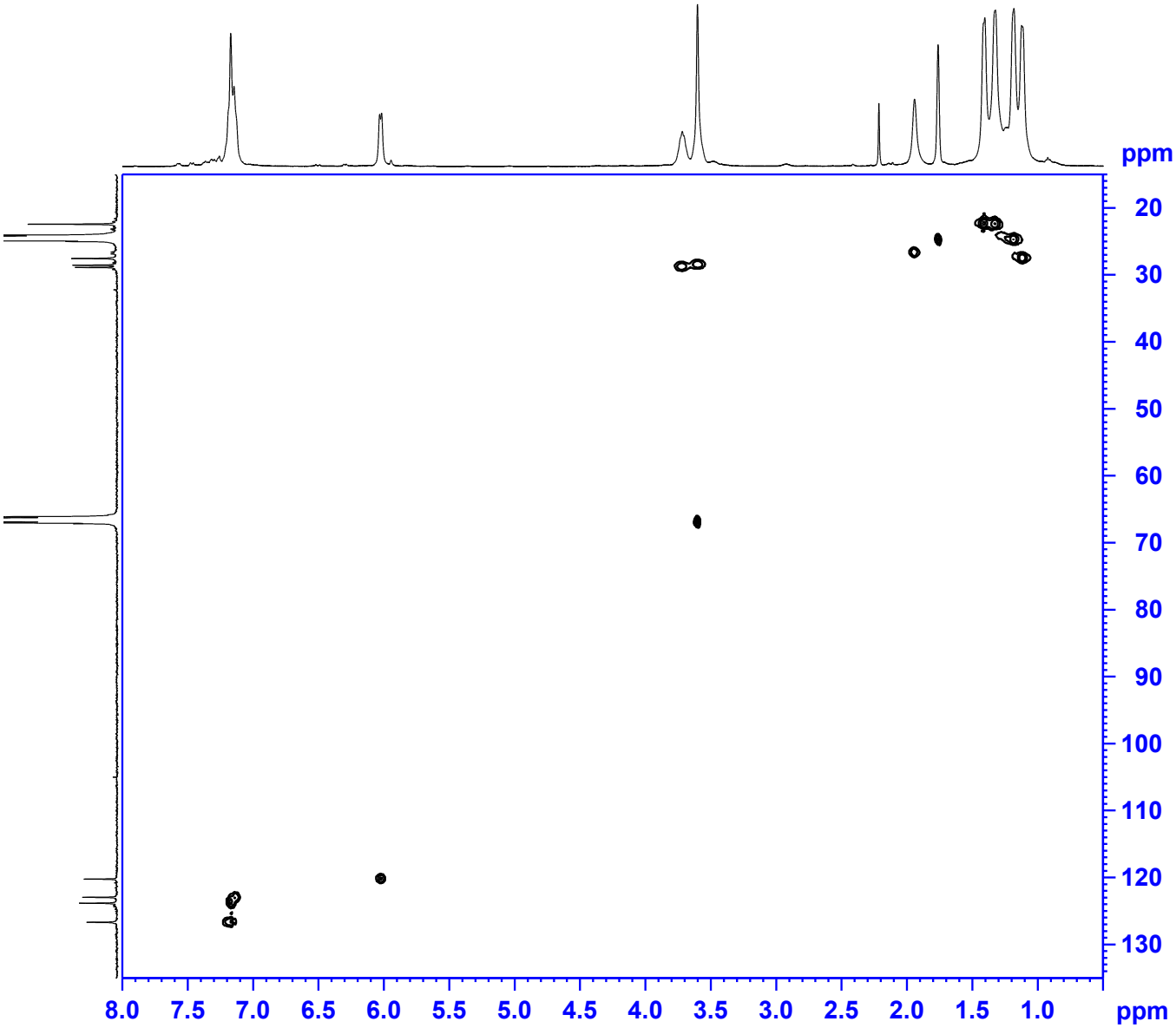

Fig. S23: $^{31}P\{^{1}H\}$ NMR of the reaction of Na[**2**] and MeI (203 K, in d_8-THF)

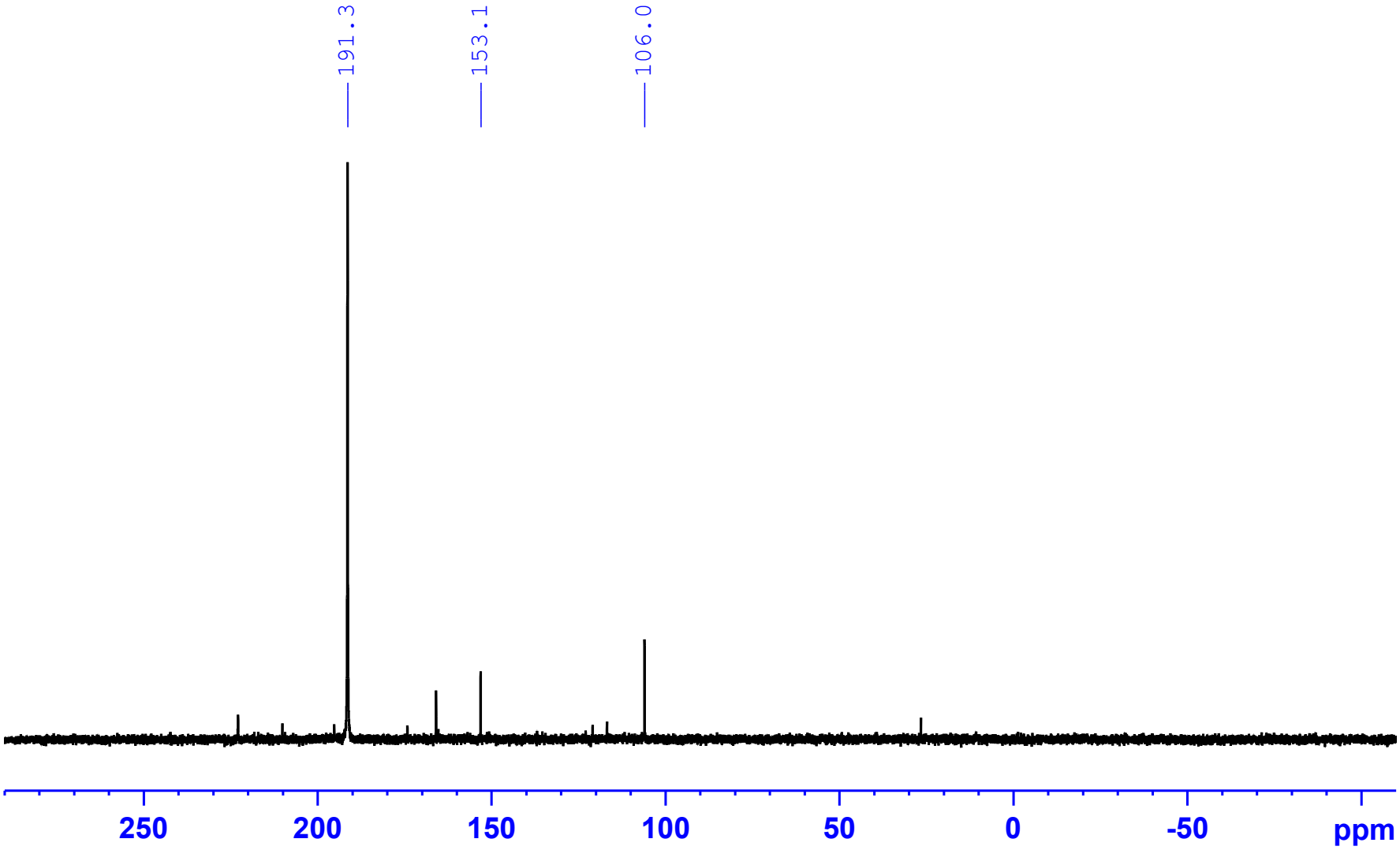

Fig. S24: $^{13}C\{^{1}H\}$ NMR of the reaction of Na[**2**] and MeI (203 K, in d_8-THF)

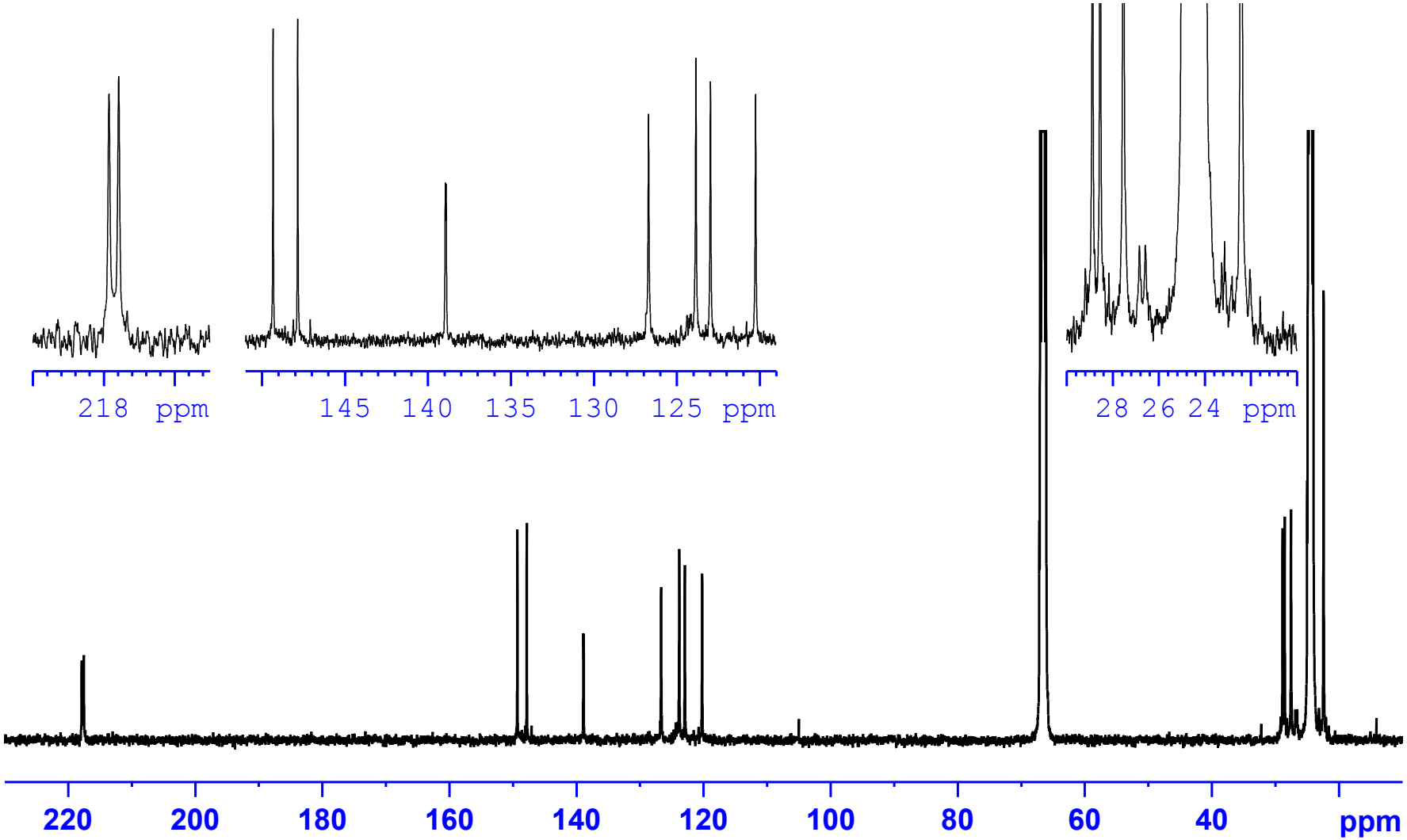

Fig. S25: $^{31}P\{^{1}H\}$ NMR monitoring of the reaction of Na[**2**] and MeI (203 K, in d_8-THF). Spectra were recorded (from bottom to top) at 233 K, 253 K, 253 K (+33 min delay), 263 K, 263 K (+18 min delay), 283 K, 293 K, 303 K, 303 K (+ 60 min delay).

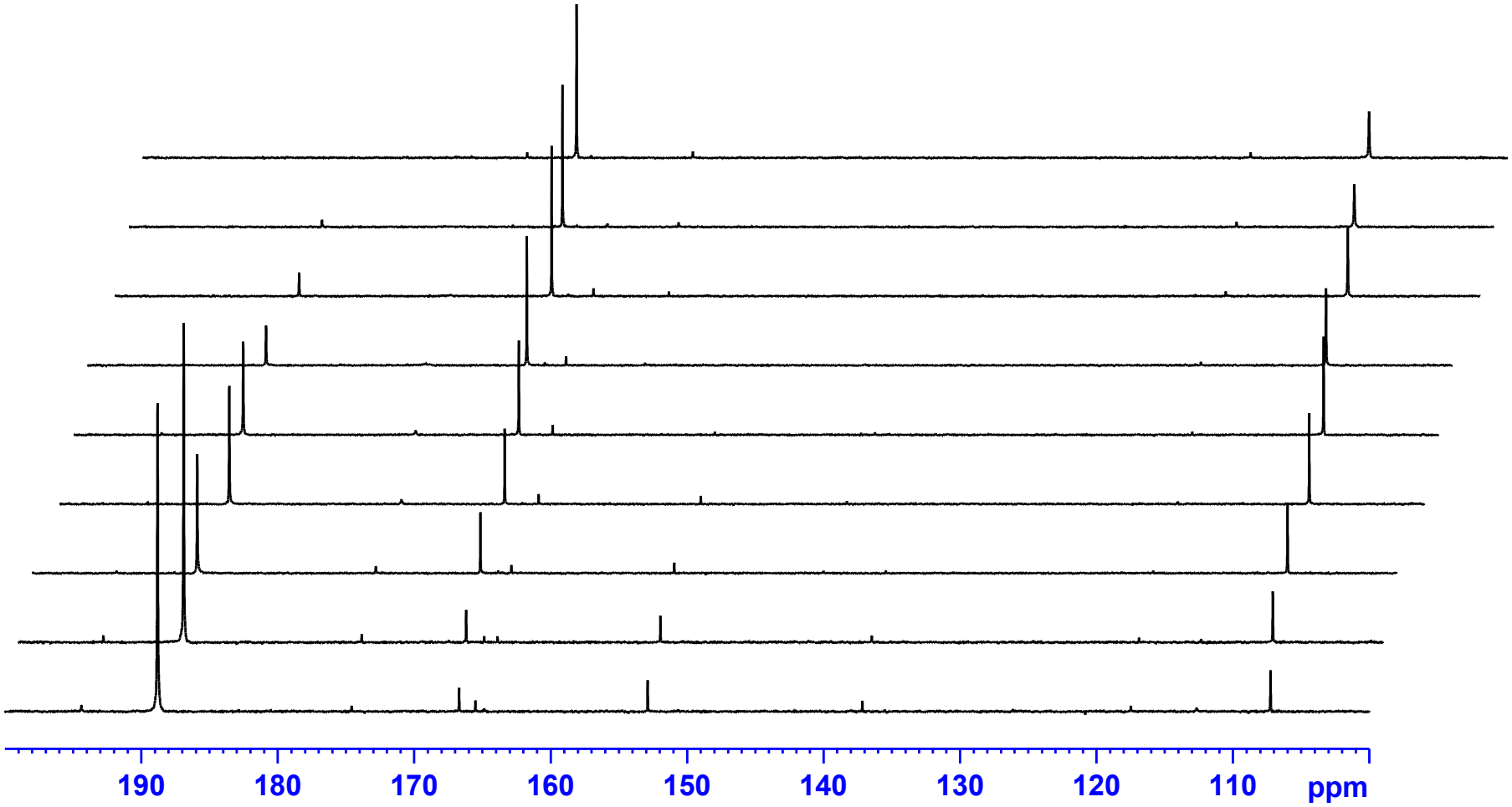

Fig. S26: ^{1}H NMR of **4** (303 K, in C_6D_6)

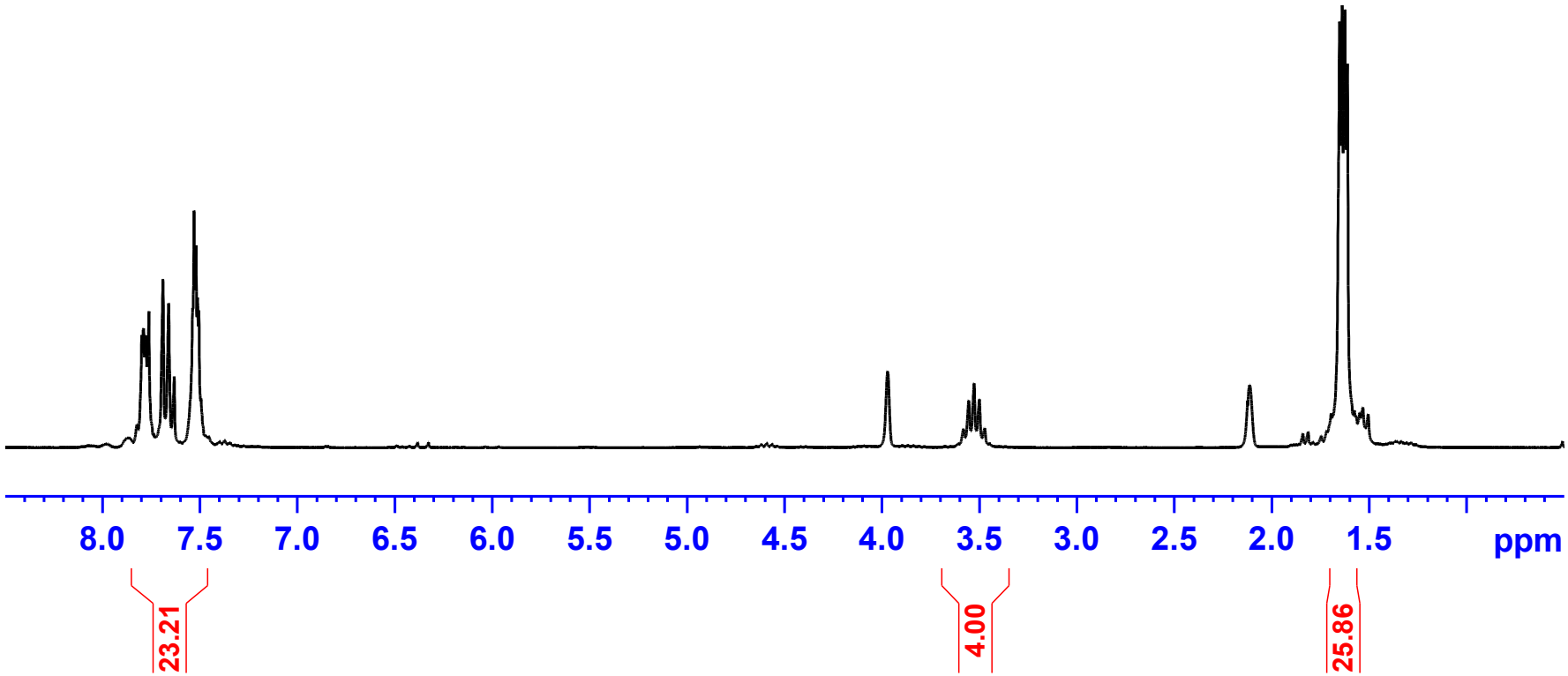

Fig. S27: $^{13}C\{^{1}H\}$ NMR of **4** (303 K, in C_6D_6)

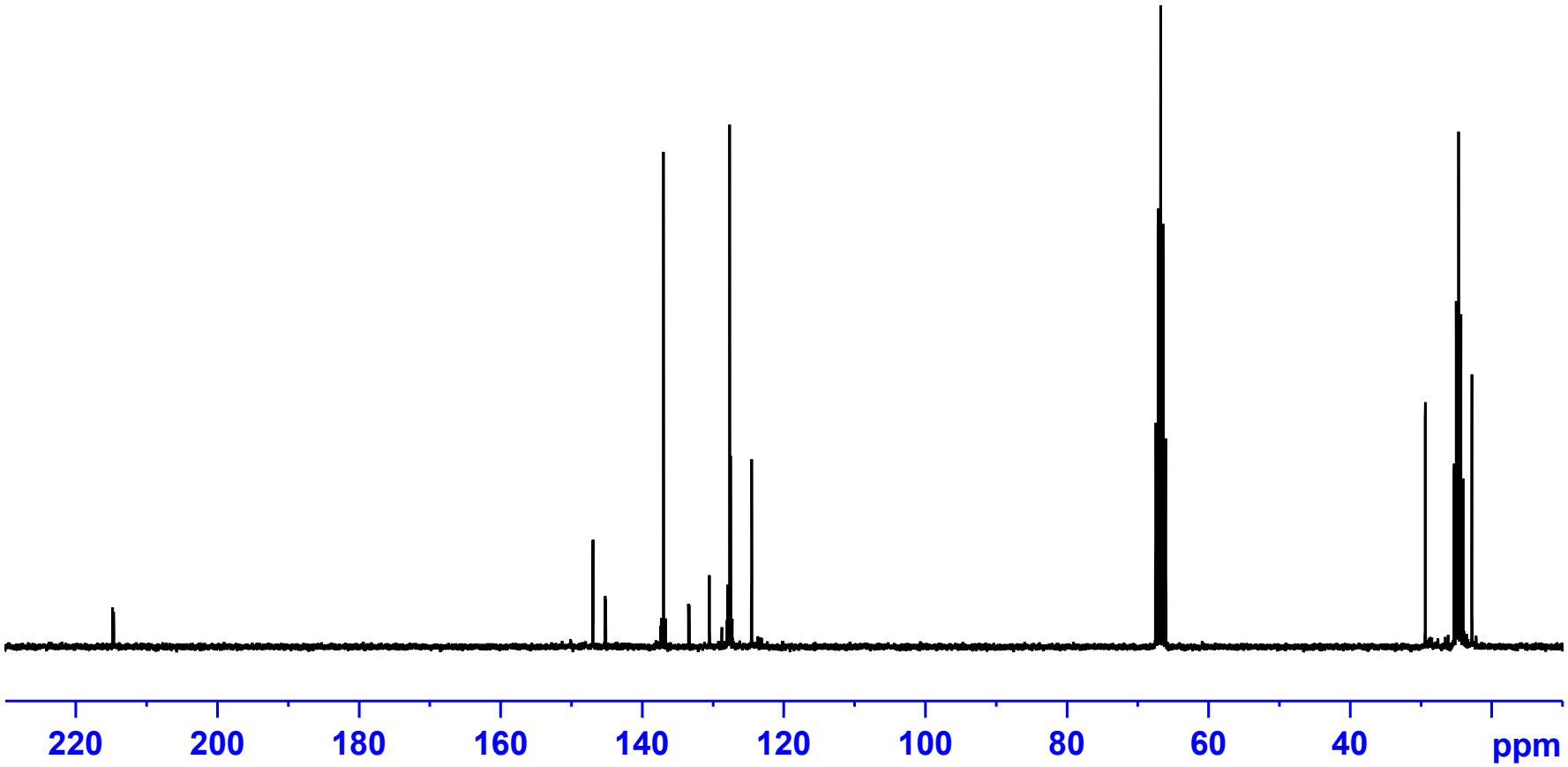
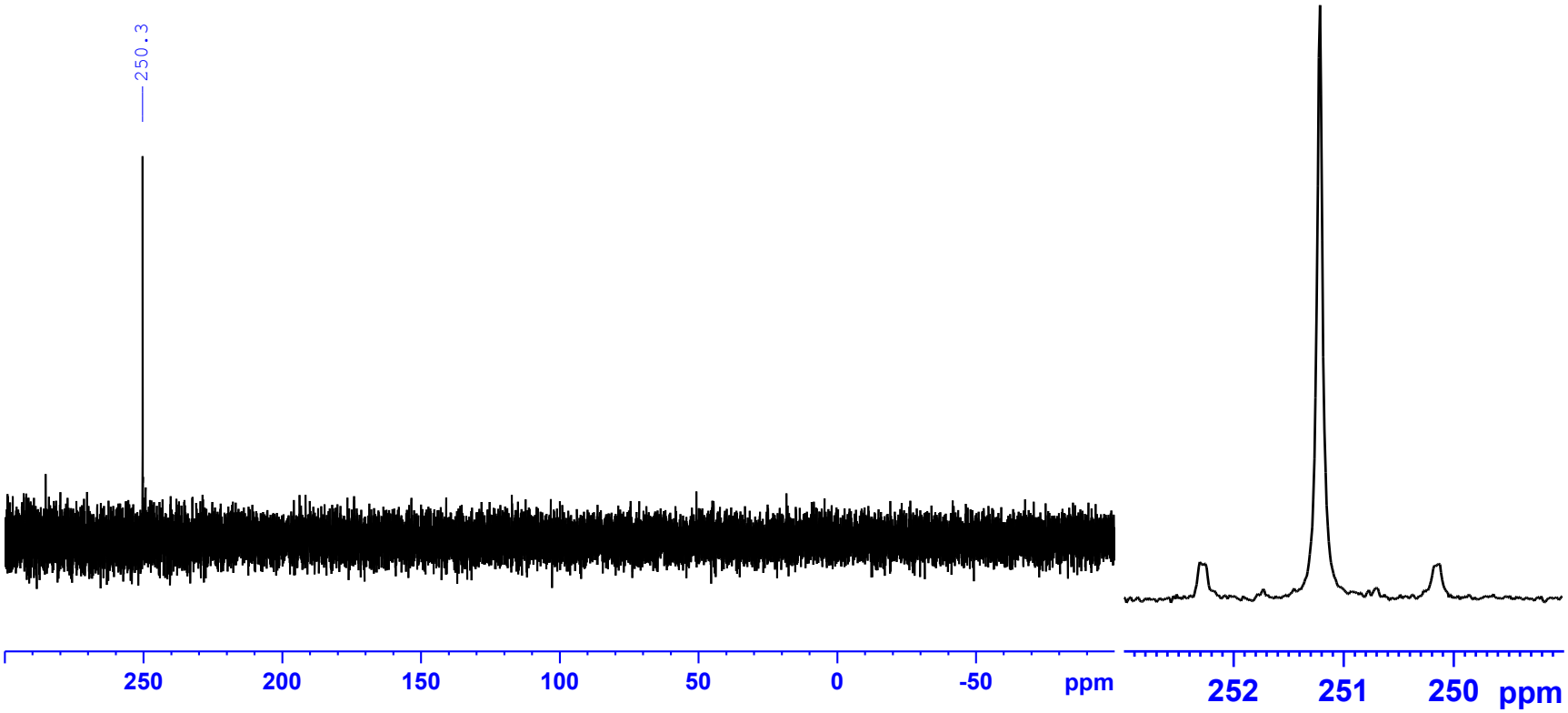
Fig. S28: $^{31}P\{^{1}H\}$ NMR of **4** (303 K, in C_6D_6); left: dilute solution; right: concentrated solution (expansion)