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Phosphaisonitrile Umpolung – Synthesis and Reactivity of Chloroaminophosphino Carbynes.

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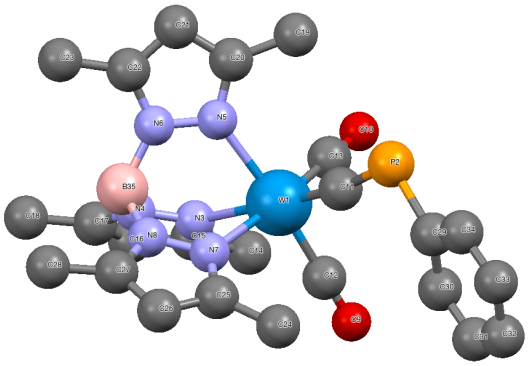
Optimised Geometry and cartesian coordinates for $[Tp^*(CO)_2W(CPPh)]^-$

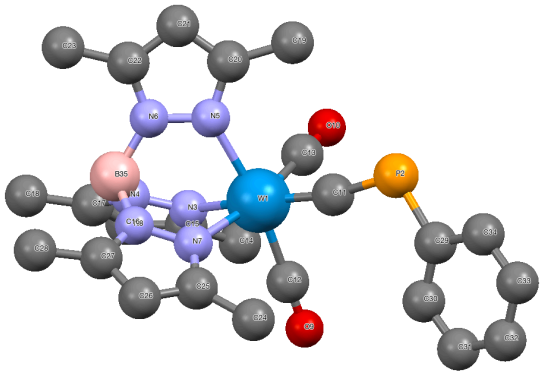
[DFT: B3LYP/6-31G*(LanL2DZ for W), gas phase, H-atoms omitted)



Atom	X	Y	Z
W1	-0.4725	-1.1618	0.2086
P2	-3.1209	-0.1105	2.3923
N3	1.4680	-1.6331	-1.0821
N4	2.4999	-0.7389	-1.1276
N5	1.1704	-0.4501	1.6276
N6	2.2470	0.2648	1.1764
N7	-0.0729	0.8938	-0.7564
N8	1.1970	1.4042	-0.8236
O9	-2.4287	-2.2746	-2.0056
O10	-0.6359	-4.0477	1.4365
C11	-1.9586	-0.6261	1.2420
C12	-1.7048	-1.8470	-1.1837
C13	-0.5811	-2.9608	0.9836
C14	0.9336	-3.8747	-2.0354
C15	1.8189	-2.6806	-1.8434
C16	3.0943	-2.4544	-2.3908
C17	3.4970	-1.2134	-1.9148
C18	4.7795	-0.4807	-2.1656
C19	0.3352	-1.3274	3.8139
C20	1.3166	-0.5937	2.9552
C21	2.5040	0.0398	3.3614
C22	3.0684	0.5720	2.2119
C23	4.3435	1.3445	2.0649
C24	-2.3668	1.5978	-1.4393
C25	-0.8910	1.7999	-1.3148
C26	-0.1388	2.9095	-1.7402
C27	1.1786	2.6265	-1.4147
C28	2.4018	3.4601	-1.6461
C29	-4.6524	0.2610	1.4252
C30	-4.9684	-0.2839	0.1627
C31	-6.1754	0.0118	-0.4702
C32	-7.1158	0.8498	0.1372
C33	-6.8254	1.3906	1.3928
C34	-5.6154	1.1017	2.0224
B35	2.4056	0.5835	-0.3268
H36	1.4446	-4.6242	-2.6494
H37	0.6671	-4.3298	-1.0765
H38	-0.0054	-3.6062	-2.5300
H39	3.6510	-3.1119	-3.0448
H40	5.4105	-1.0706	-2.8377
H41	5.3417	-0.3046	-1.2407
H42	4.6125	0.4985	-2.6294
H43	0.6842	-1.3300	4.8524
H44	-0.6547	-0.8612	3.7761
H45	0.2115	-2.3631	3.4829
H46	2.8925	0.1094	4.3683
H47	4.8147	1.4575	3.0462
H48	4.1756	2.3467	1.6531
H49	5.0590	0.8396	1.4048
H50	-2.8124	2.4339	-1.9889
H51	-2.8451	1.5268	-0.4588
H52	-2.5951	0.6689	-1.9705
H53	-0.5125	3.8033	-2.2210
H54	2.1116	4.4080	-2.1100
H55	2.9288	3.6889	-0.7123
H56	3.1219	2.9659	-2.3093
H57	-4.2601	-0.9496	-0.3207
H58	-6.3862	-0.4262	-1.4445
H59	-8.0583	1.0740	-0.3578
H60	-7.5427	2.0485	1.8820
H61	-5.4005	1.5398	2.9957
H62	3.4108	1.2158	-0.4926

Optimised Geometry and cartesian coordinates for $[Tp^*(CO)_2W(CPPh)]^+$

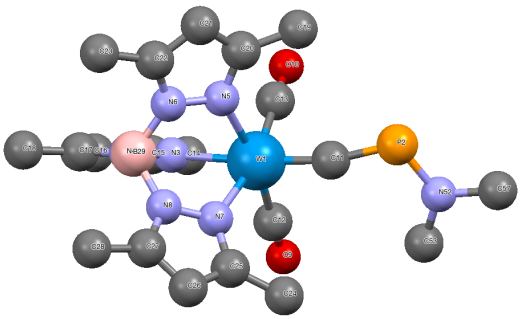
[DFT: B3LYP/6-31G*(LanL2DZ for W), gas phase, H-atoms omitted)



Atom	X	Y	Z
W1	-0.4048	-0.7696	0.2025
P2	-3.2811	-0.4997	2.2729
N3	1.3201	-1.6130	-1.0079
N4	2.4356	-0.8022	-1.0713
N5	1.1438	-0.1590	1.6376
N6	2.3131	0.3819	1.1647
N7	0.0617	1.1138	-0.7568
N8	1.3770	1.4997	-0.8685
O9	-2.2436	-1.5566	-2.2712
O10	-0.3501	-3.7152	1.4652
C11	-2.0199	-0.6512	1.1530
C12	-1.5694	-1.2831	-1.3740
C13	-0.3756	-2.6700	0.9889
C14	0.6193	-3.8537	-1.9204
C15	1.5749	-2.7129	-1.7523
C16	2.8559	-2.6028	-2.2979
C17	3.3723	-1.3908	-1.8548
C18	4.7071	-0.7844	-2.1579
C19	0.1918	-0.7903	3.8791
C20	1.2640	-0.2577	2.9836
C21	2.5157	0.2326	3.3636
C22	3.1593	0.6223	2.1939
C23	4.5262	1.2074	2.0248
C24	-2.1869	2.0429	-1.4107
C25	-0.6941	2.0842	-1.3357
C26	0.1485	3.0916	-1.8000
C27	1.4503	2.6905	-1.5020
C28	2.7341	3.3983	-1.7990
C29	-4.8108	-0.1854	1.3794
C30	-5.0026	-0.3177	-0.0149
C31	-6.2460	-0.0551	-0.5722
C32	-7.3135	0.3454	0.2447
C33	-7.1415	0.4745	1.6257
C34	-5.9007	0.2058	2.1937
B35	2.5089	0.5754	-0.3510
H36	0.9752	-4.5122	-2.7168
H37	0.5395	-4.4557	-1.0086
H38	-0.3858	-3.5192	-2.1912
H39	3.3490	-3.3185	-2.9396
H40	5.2784	-1.4647	-2.7940
H41	5.2888	-0.6001	-1.2488
H42	4.6114	0.1708	-2.6853
H43	0.5421	-0.7829	4.9143
H44	-0.7157	-0.1793	3.8271
H45	-0.0821	-1.8200	3.6274
H46	2.9062	0.2992	4.3688
H47	5.0025	1.3086	3.0028
H48	4.4895	2.1982	1.5598
H49	5.1659	0.5734	1.4011
H50	-2.5514	2.9514	-1.8966
H51	-2.6432	1.9839	-0.4168
H52	-2.5397	1.1853	-1.9922
H53	-0.1472	4.0061	-2.2933
H54	2.5233	4.3370	-2.3168
H55	3.2889	3.6318	-0.8839
H56	3.3901	2.7990	-2.4392
H57	-4.1802	-0.6332	-0.6461
H58	-6.3929	-0.1637	-1.6427
H59	-8.2829	0.5512	-0.2000
H60	-7.9722	0.7788	2.2549
H61	-5.7624	0.3009	3.2679
H62	3.5659	1.0782	-0.5672

Optimised Geometry and cartesian coordinates for $[Tp^*(CO)_2W(CPPNMe_2)]^-$

[DFT: B3LYP/6-31G*(LanL2DZ for W), gas phase, H-atoms omitted)



Atom	X	Y	Z
W1	-0.7683	-0.6842	0.1410
P2	-3.6035	-0.2830	2.2358
N3	1.0209	-1.5299	-1.0214
N4	2.1411	-0.7288	-1.0814
N5	0.7868	-0.0643	1.5881
N6	1.9639	0.4734	1.1330
N7	-0.2431	1.1809	-0.8546
N8	1.0726	1.5667	-0.9374
O9	-2.5648	-1.5530	-2.3367
O10	-0.8056	-3.6272	1.4035
C11	-2.3483	-0.4183	1.0819
C12	-1.8994	-1.2477	-1.4429
C13	-0.7922	-2.5785	0.9307
C14	0.3317	-3.7850	-1.9175
C15	1.2867	-2.6437	-1.7441
C16	2.5770	-2.5488	-2.2689
C17	3.0905	-1.3311	-1.8362
C18	4.4338	-0.7342	-2.1205
C19	-0.1988	-0.6784	3.8210
C20	0.8854	-0.1544	2.9343
C21	2.1316	0.3368	3.3345
C22	2.7932	0.7212	2.1746
C23	4.1636	1.3044	2.0246
C24	-2.4734	2.0982	-1.5794
C25	-0.9825	2.1415	-1.4644
C26	-0.1297	3.1459	-1.9214
C27	1.1625	2.7506	-1.5837
C28	2.4547	3.4537	-1.8570
B29	2.1940	0.6551	-0.3791
H30	0.7239	-4.4741	-2.6699
H31	0.2005	-4.3541	-0.9908
H32	-0.6558	-3.4558	-2.2525
H33	3.0791	-3.2775	-2.8888
H34	5.0145	-1.4233	-2.7384
H35	4.9980	-0.5437	-1.2014
H36	4.3510	0.2150	-2.6606
H37	0.1577	-0.7091	4.8538
H38	-1.0859	-0.0355	3.7919
H39	-0.5103	-1.6906	3.5431
H40	2.5053	0.4048	4.3461
H41	4.6166	1.4271	3.0113
H42	4.1368	2.2852	1.5383
H43	4.8188	0.6584	1.4298
H44	-2.8244	2.9980	-2.0910
H45	-2.9528	2.0568	-0.5948
H46	-2.8106	1.2309	-2.1567
H47	-0.4139	4.0512	-2.4383
H48	2.2579	4.3854	-2.3929
H49	2.9857	3.7015	-0.9314
H50	3.1276	2.8445	-2.4698
H51	3.2541	1.1611	-0.5732
N52	-5.0692	-0.3046	1.4513
C53	-5.3207	-0.4721	0.0175
H54	-4.3854	-0.6207	-0.5167
H55	-5.8288	0.4183	-0.3712
H56	-5.9724	-1.3394	-0.1386
C57	-6.2867	-0.1272	2.2600
H58	-6.0280	-0.0127	3.3147
H59	-6.9371	-1.0004	2.1407
H60	-6.8259	0.7647	1.9222

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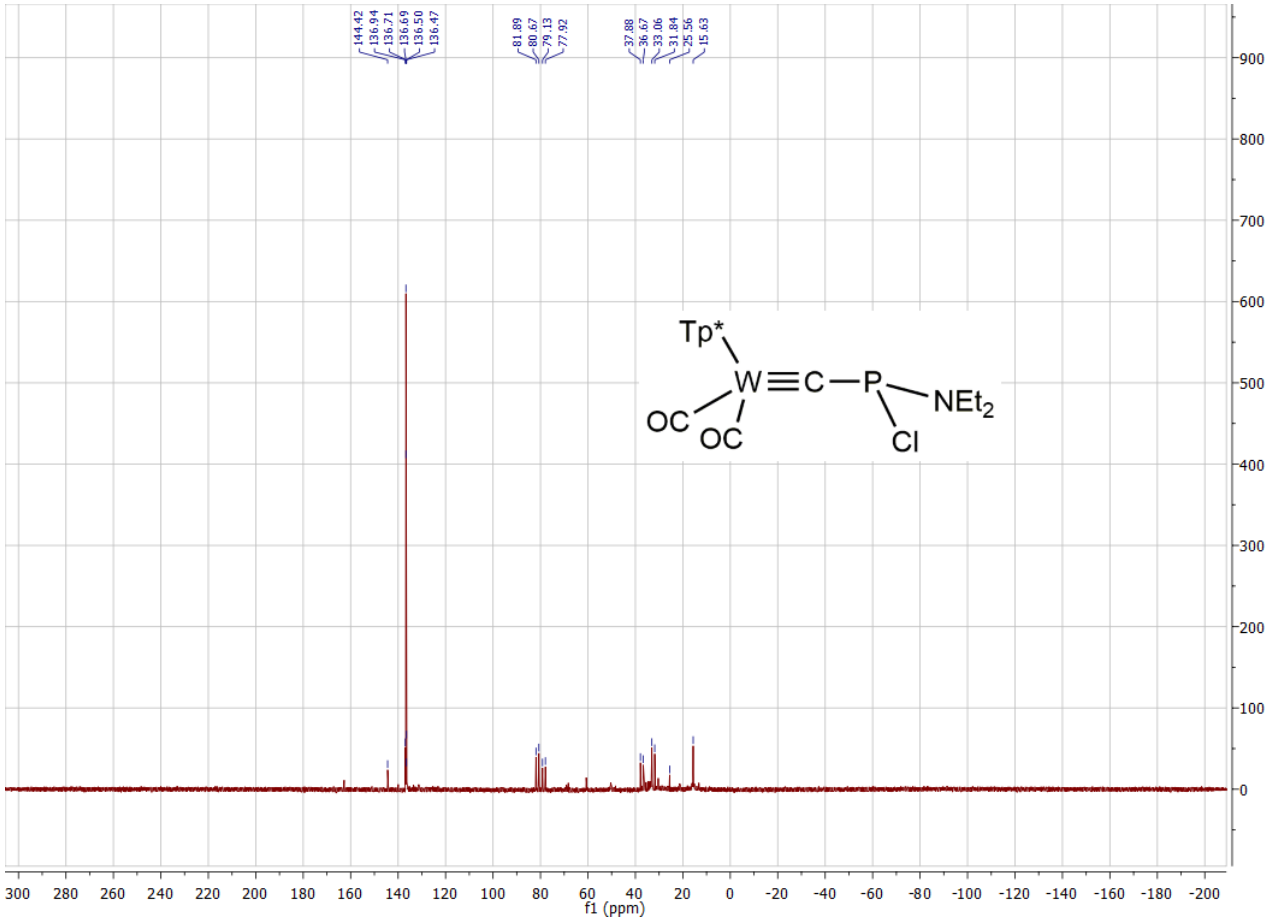

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CPCl(NEt_2)}$(CO)_2$(Tp*)] (**2a**).

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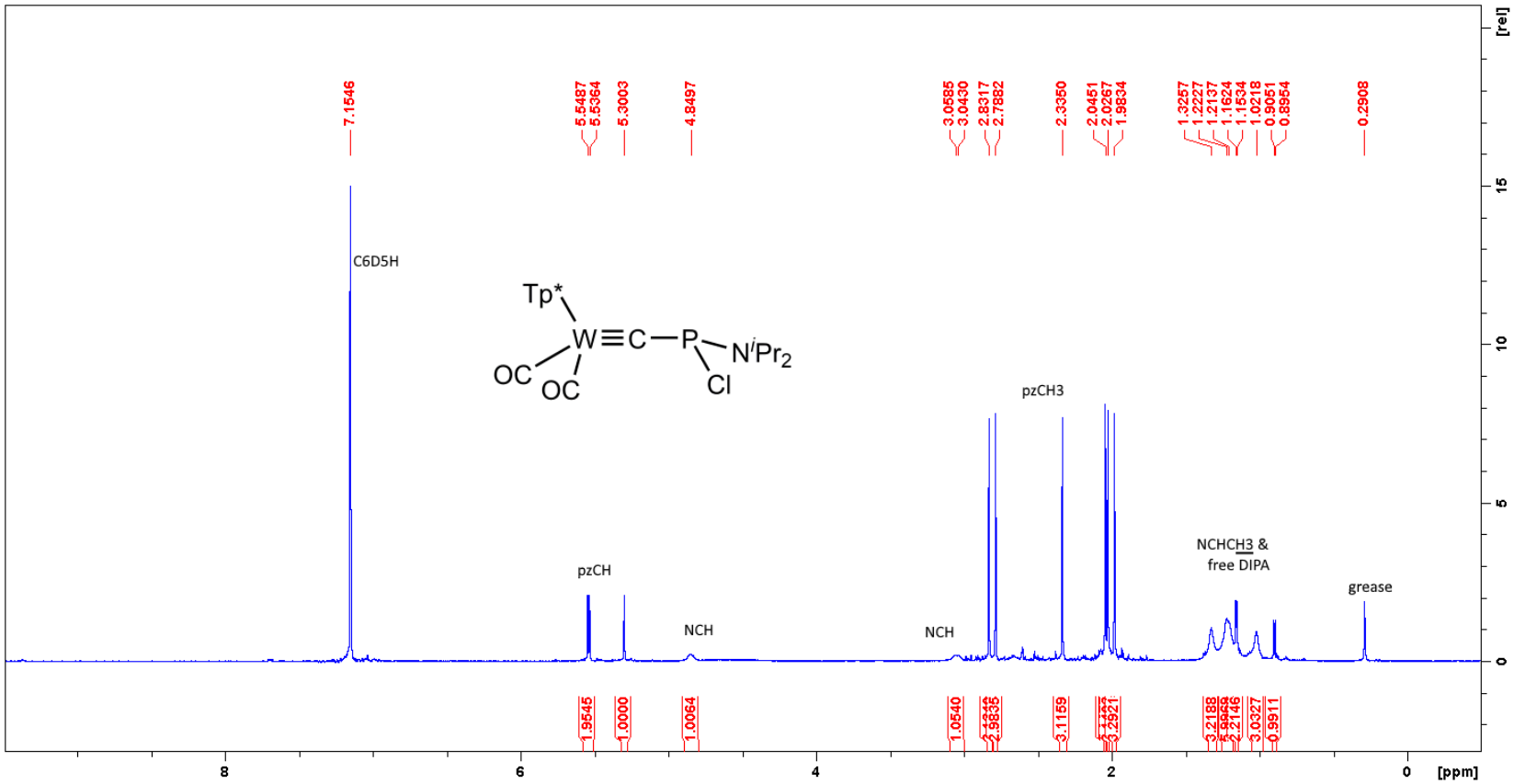

^{1}H NMR (700 MHz, C_6D_6, 25˚C, δ) of [W{≡CPCl(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**2b**).

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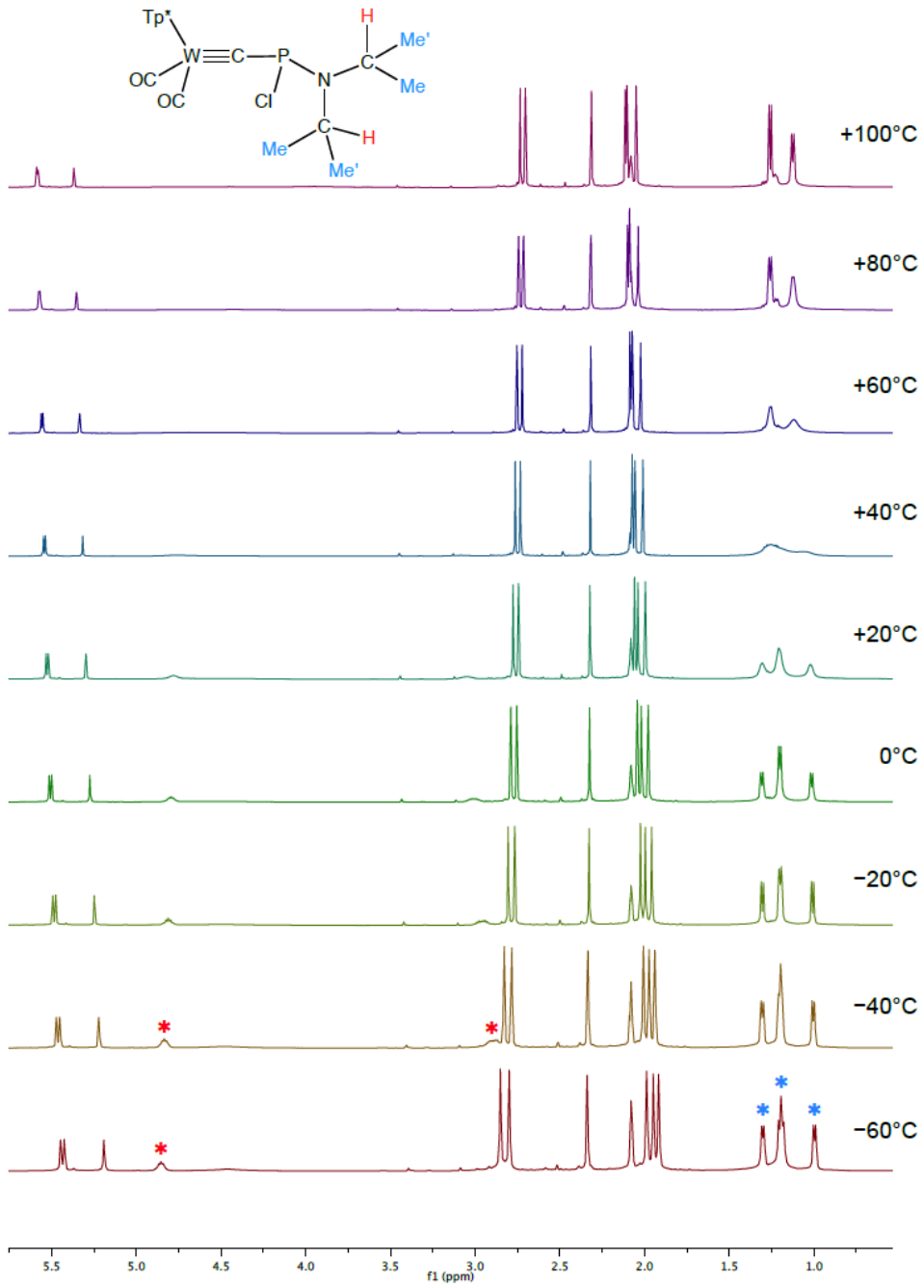

Variable-temperature ^{1}H NMR (500 MHz, C_7D_8, δ) of [W{≡CPCl(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**2b**).

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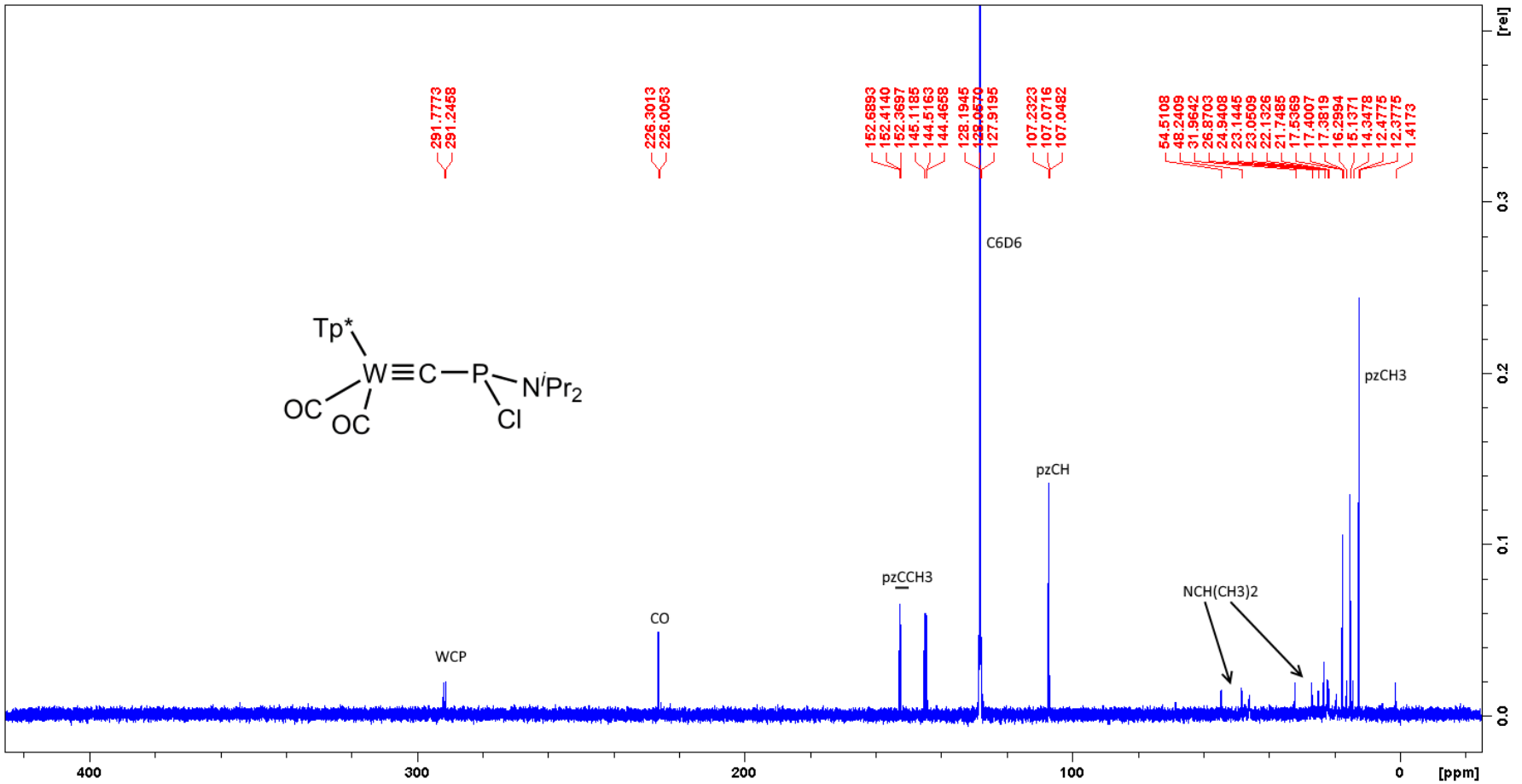
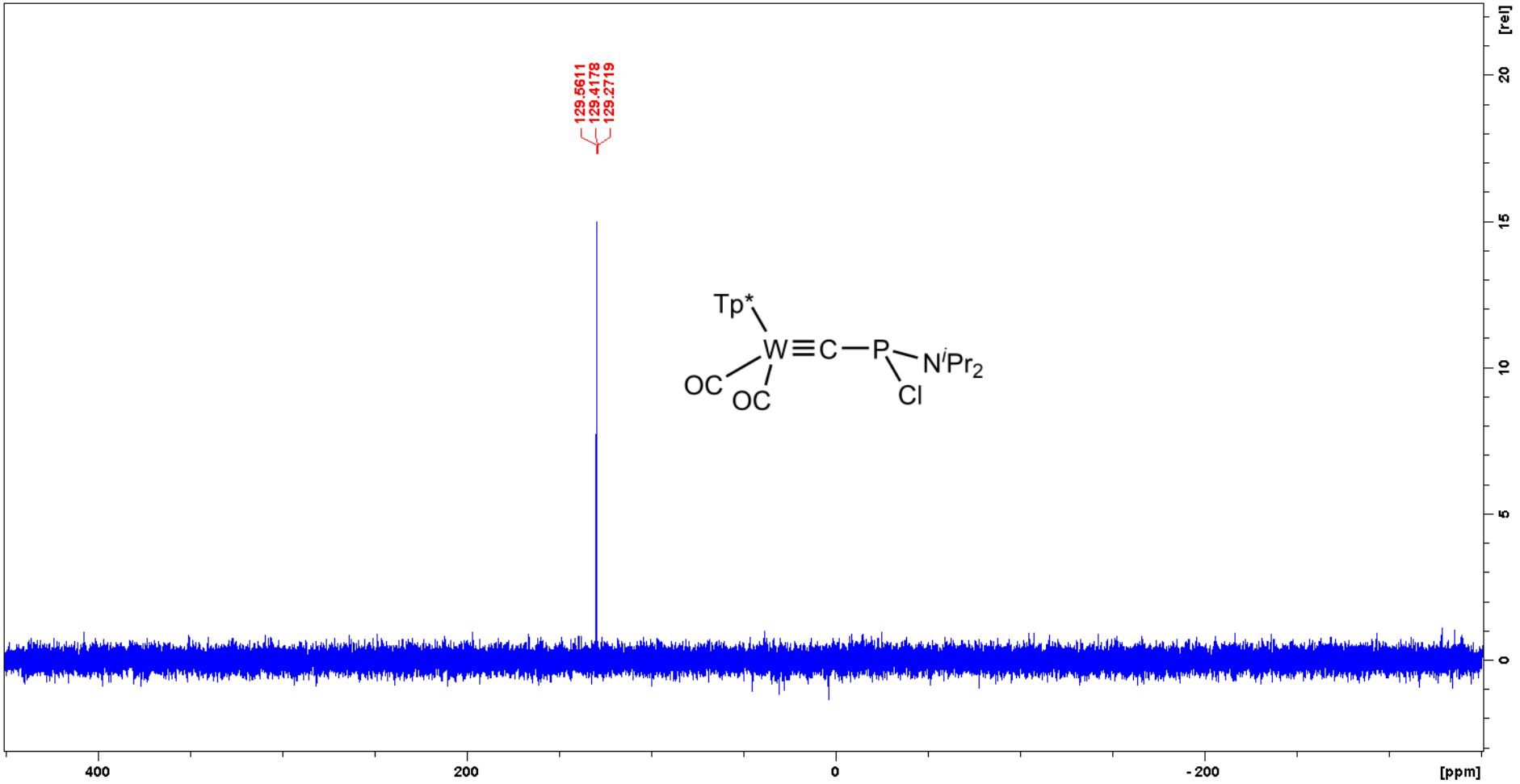
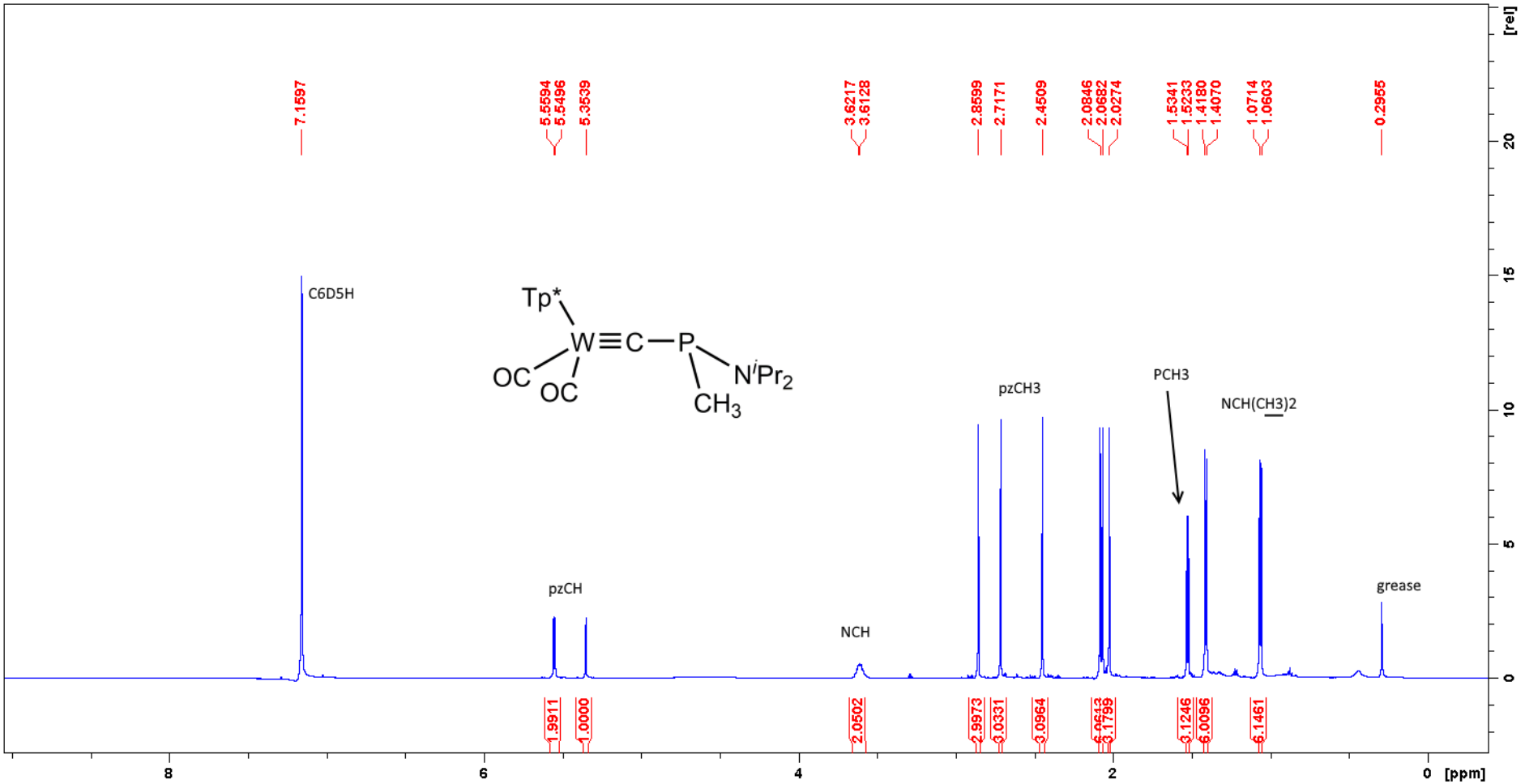


$^{13}C\{^{1}H\}$ NMR (176 MHz, C_6D_6, 25˚C, δ) of [W{≡CPCl(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**2b**).



$^{31}P\{^1H\}$ (283 MHz, C_6D_6, 25˚C, δ) of [W{≡CPCl(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**2b**).



^{1}H NMR (600 MHz, C_6D_6, 25˚C, δ) of [W{≡CPMe(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5a**).

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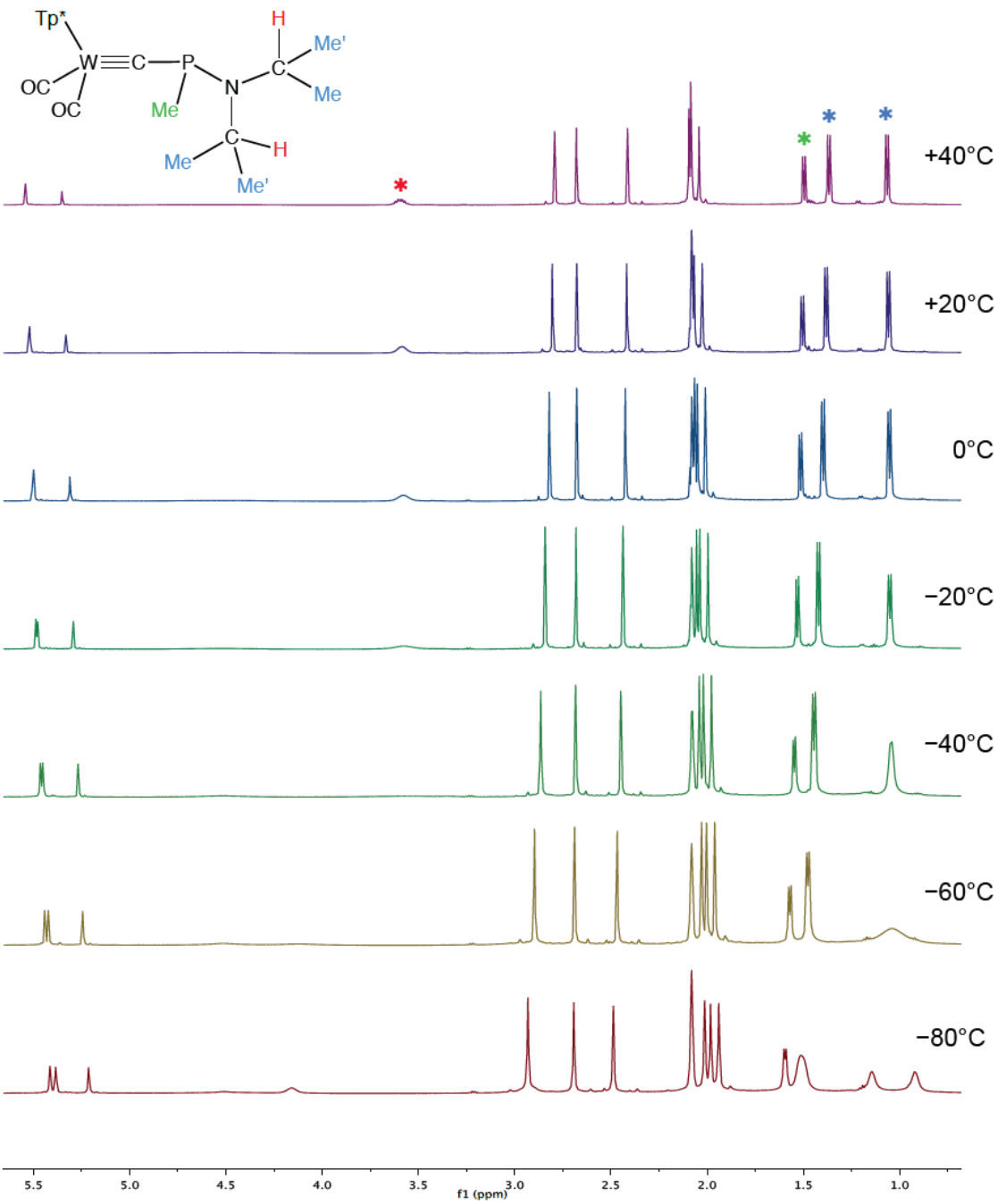

Variable-temperature ^{1}H NMR (500 MHz, C_6D_6, 25˚C, δ) of [W{≡CPMe(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5a**).

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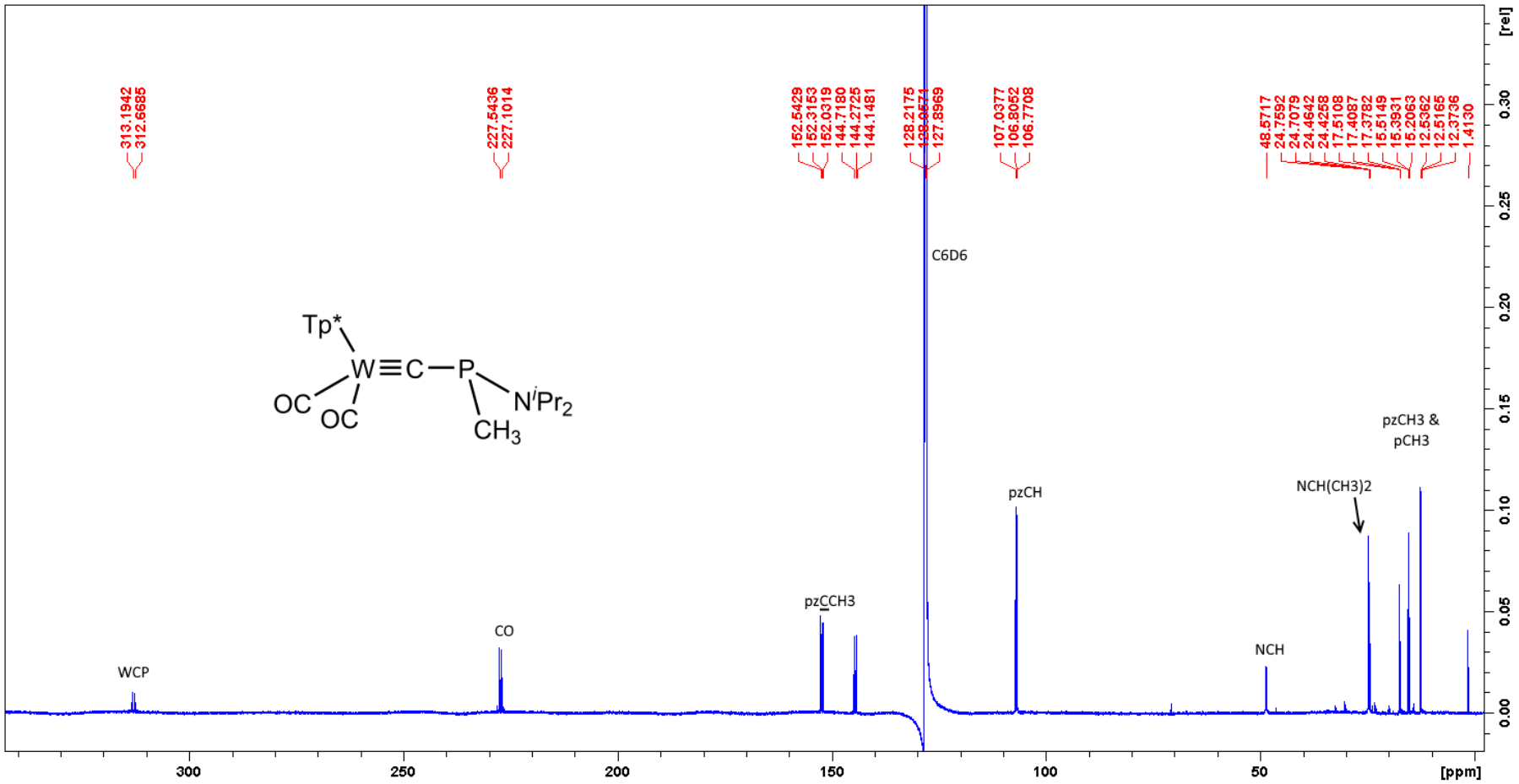
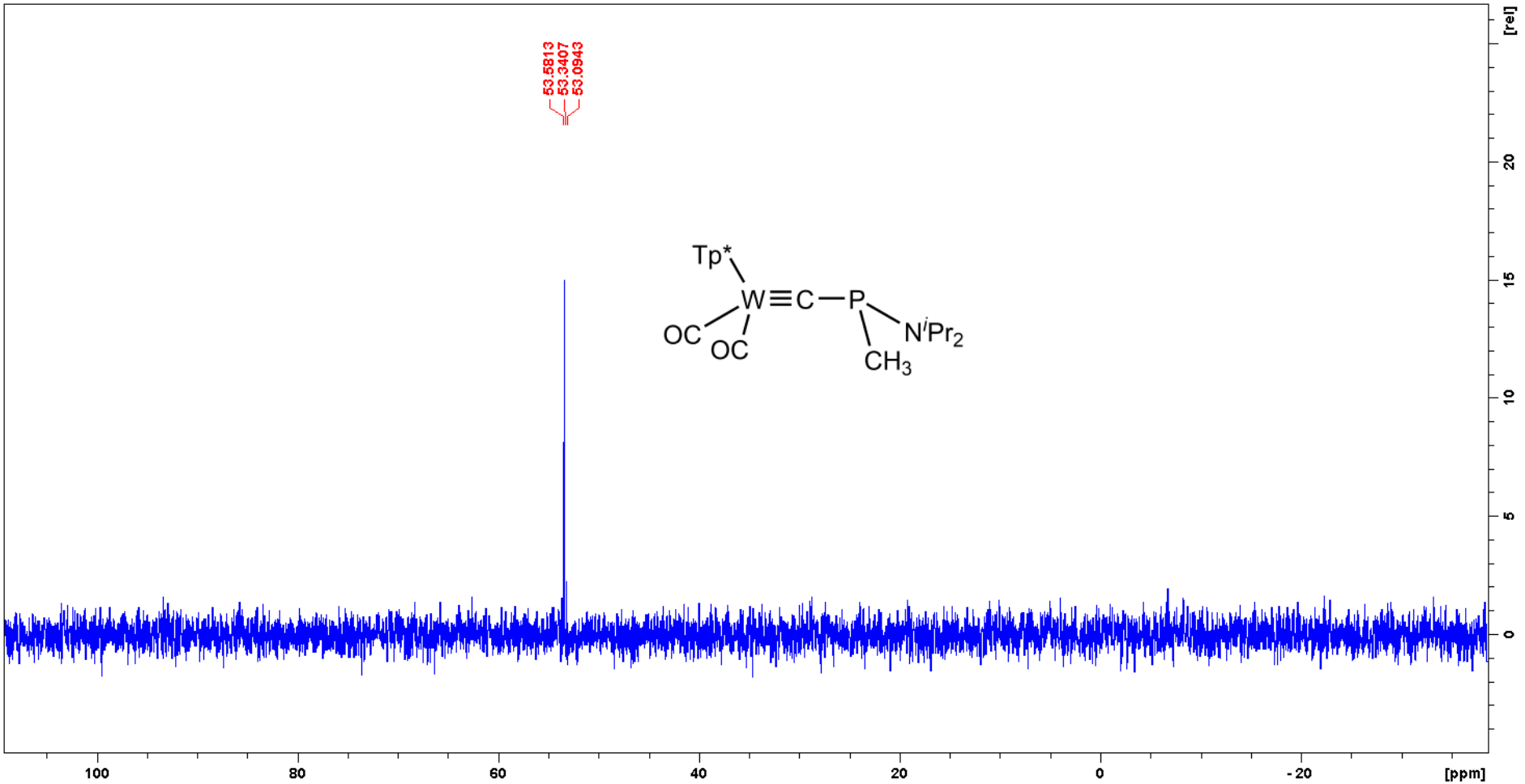
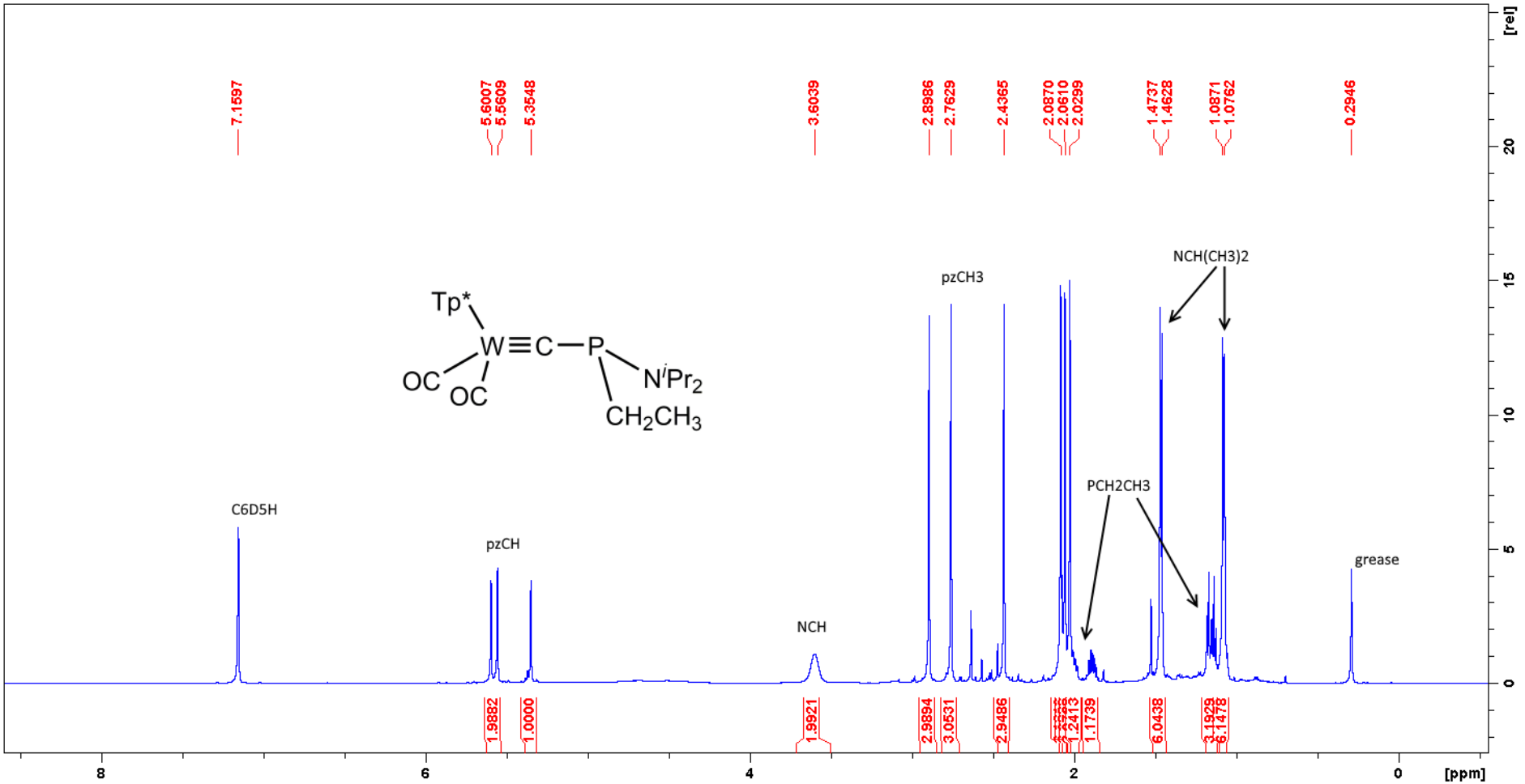


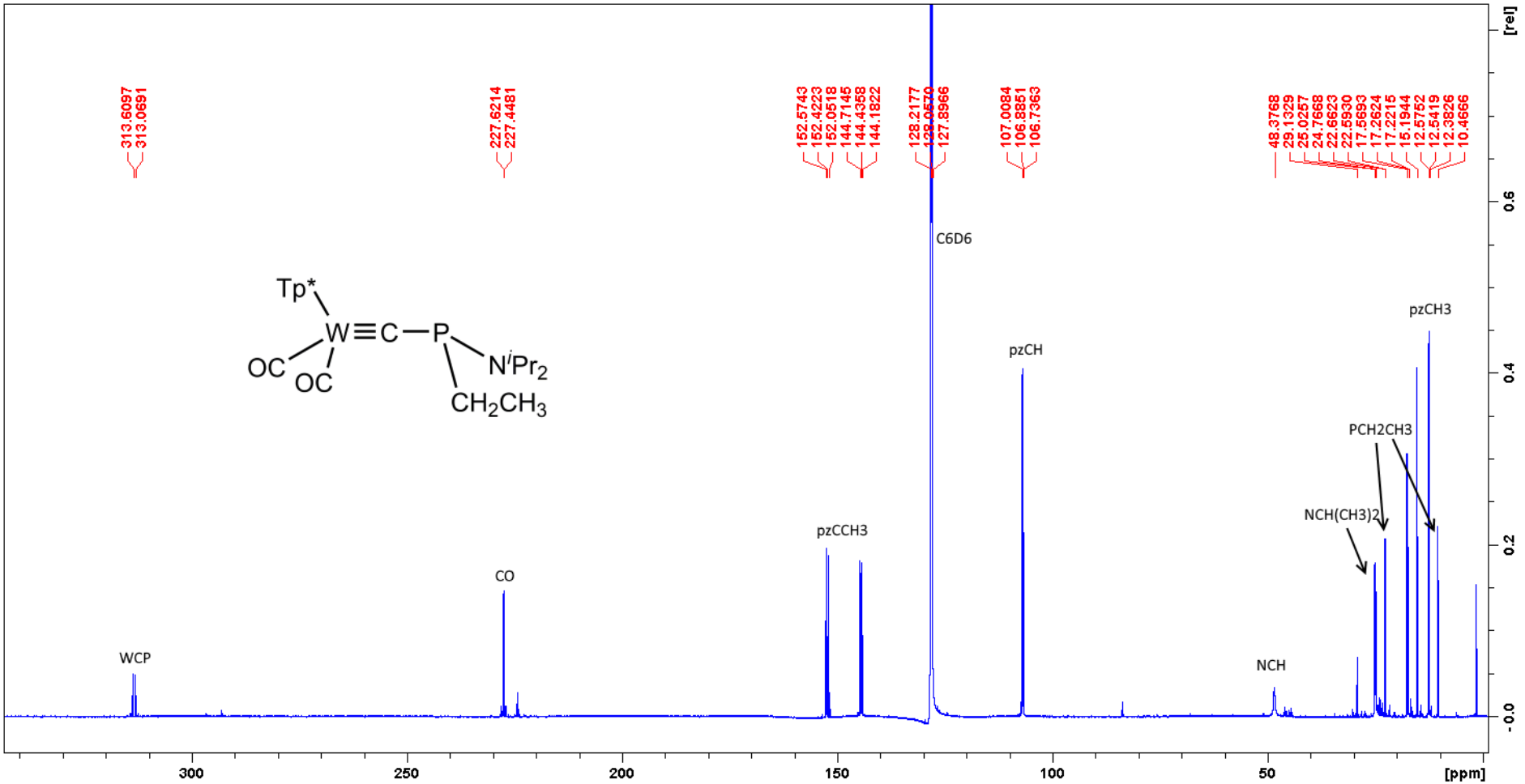
$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 25˚C, δ) of [W{≡CPMe(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5a**).



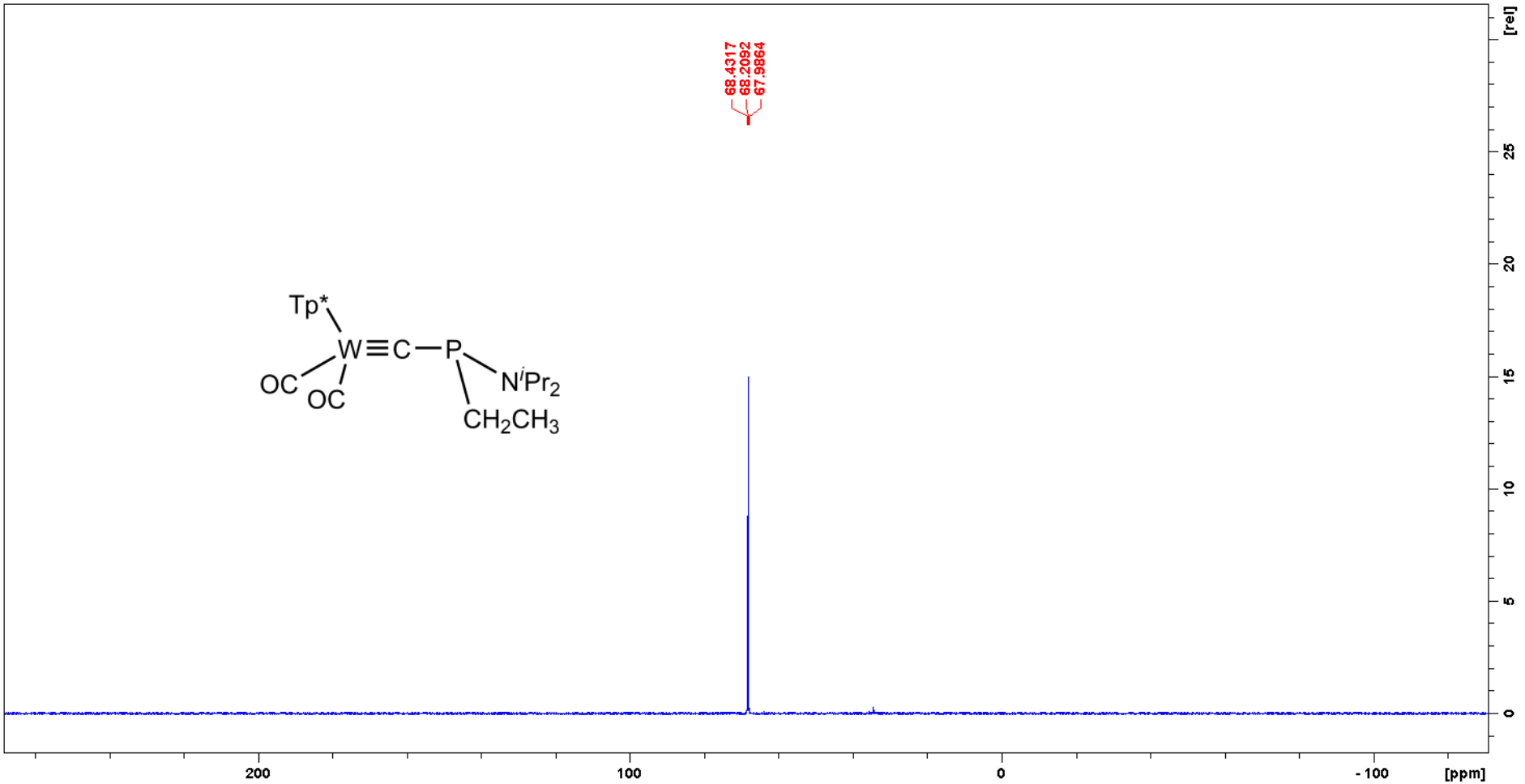
$^{31}P\{^{1}H\}$ (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CPMe(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5a**).



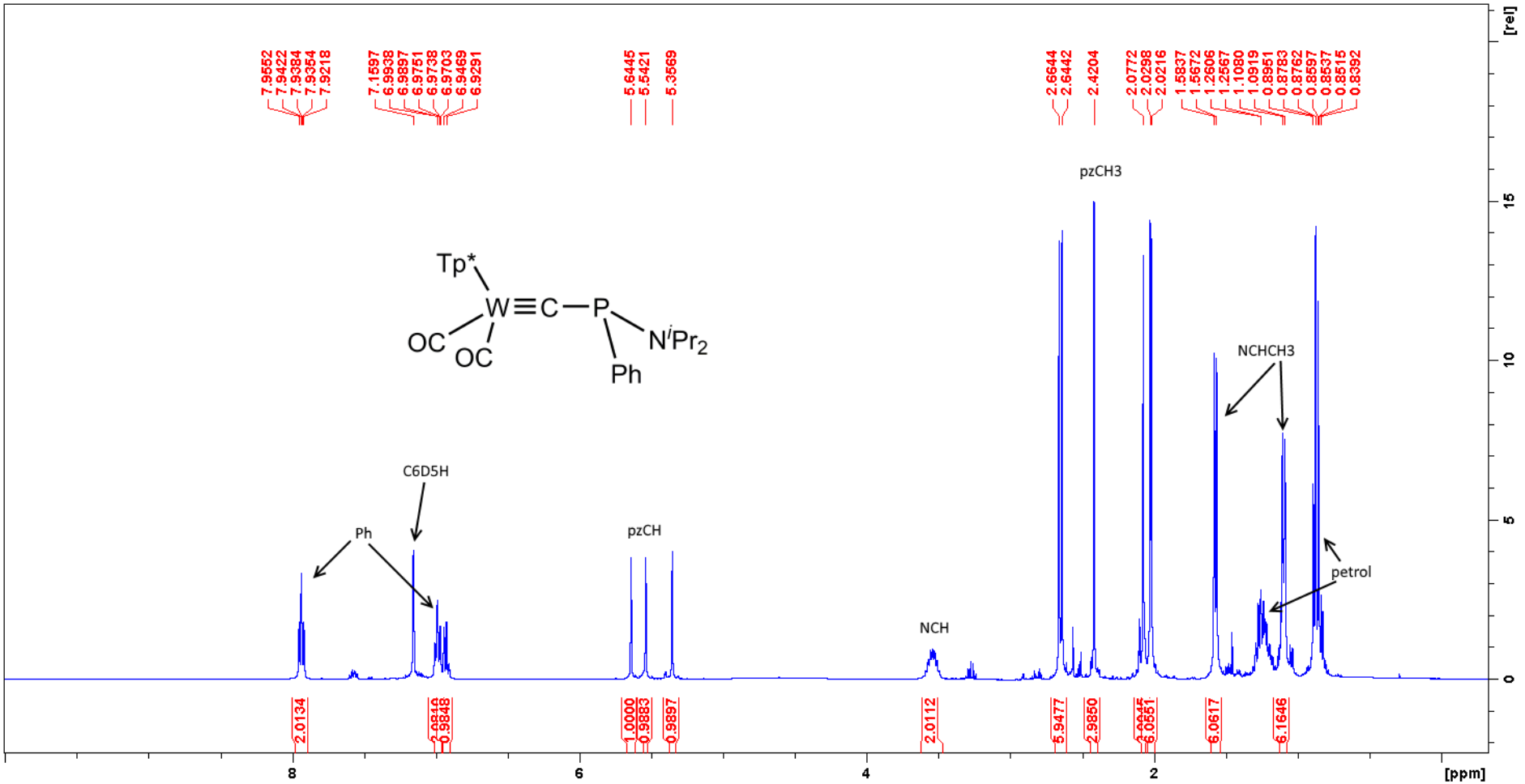
^{1}H NMR (600 MHz, C_6D_6, 25˚C, δ) of [W{≡CPEt(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5b**).



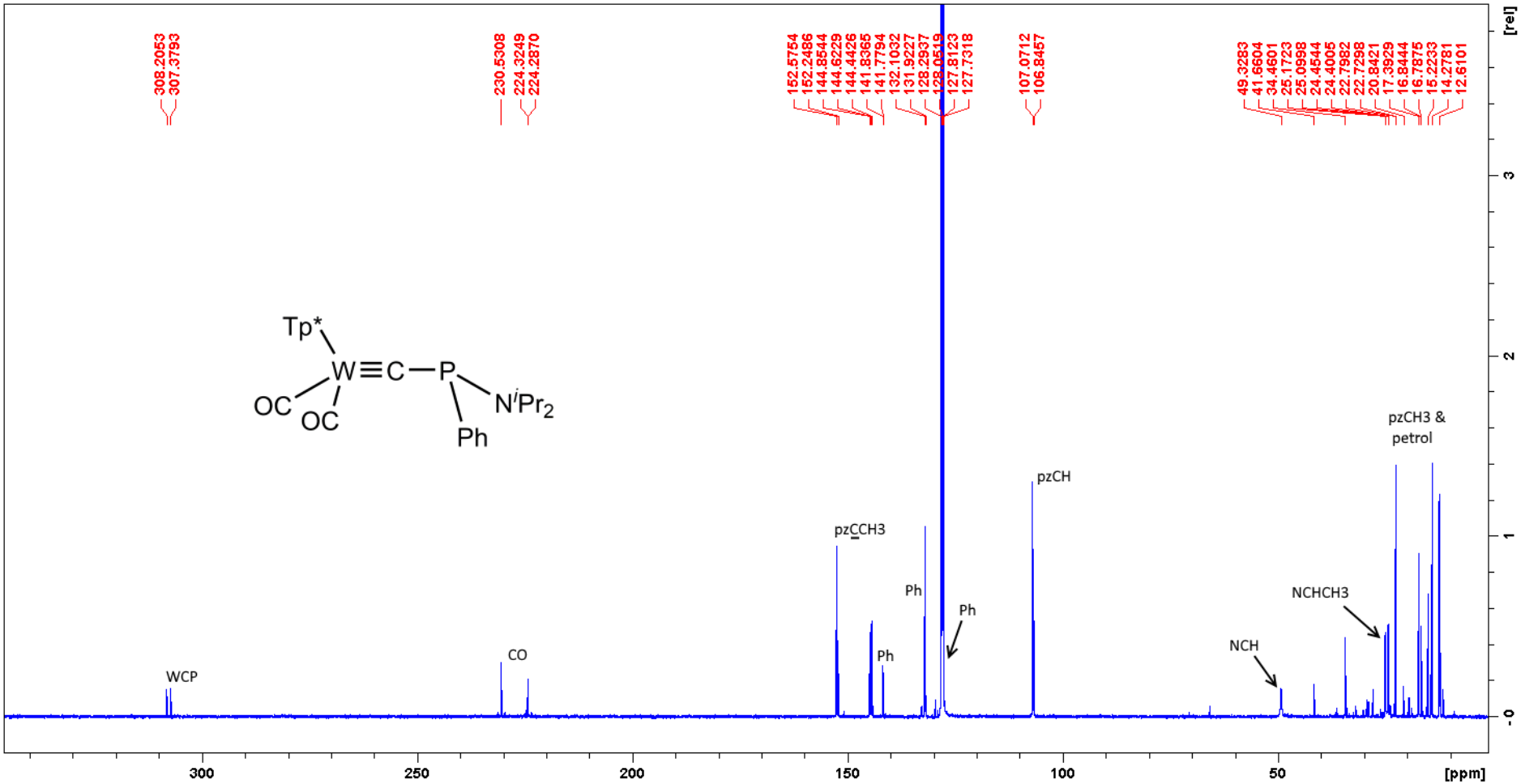
$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 25˚C, δ) of [W{≡CPEt(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5b**).



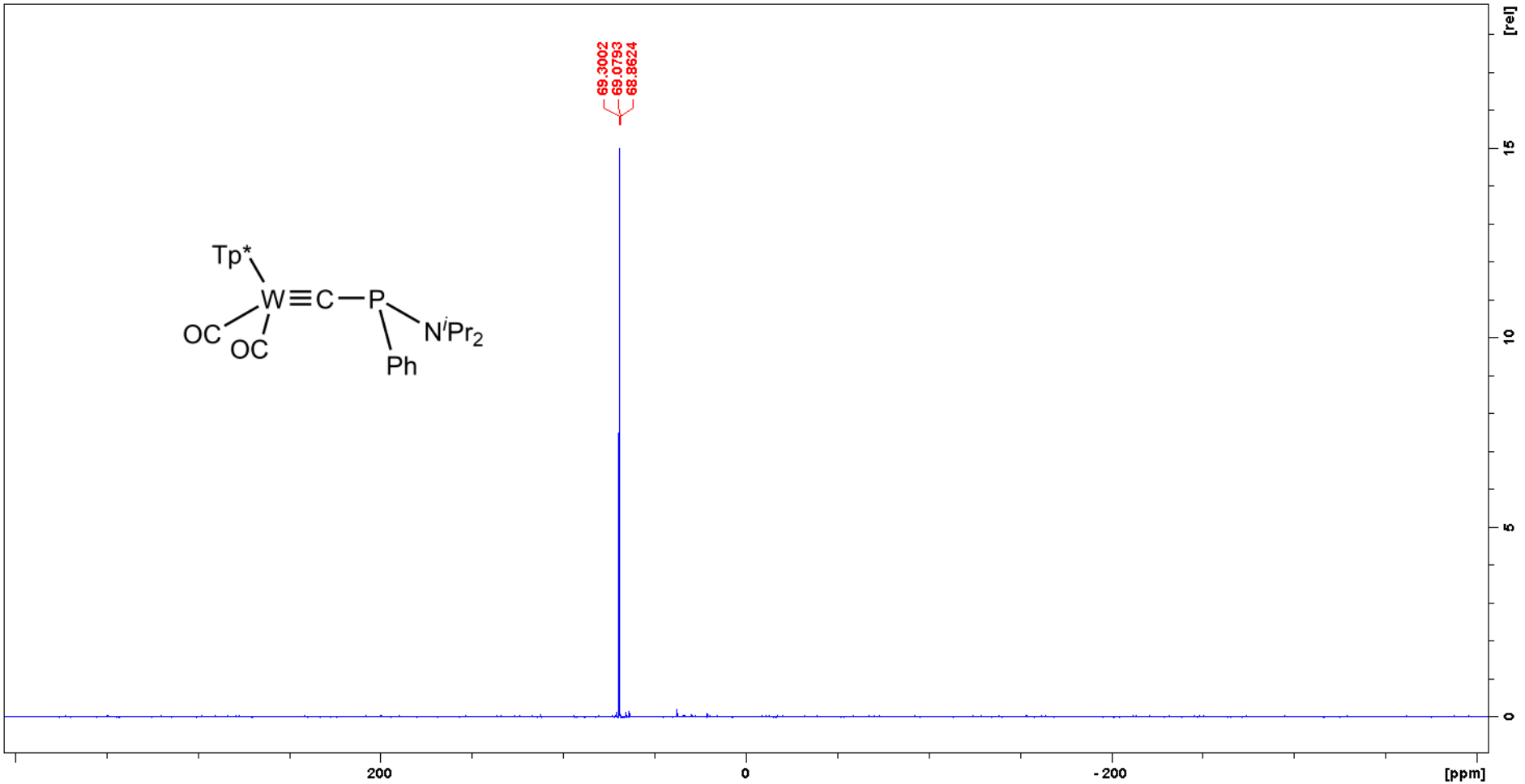
$^{31}P\{^{1}H\}$ (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CPEt(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5b**).



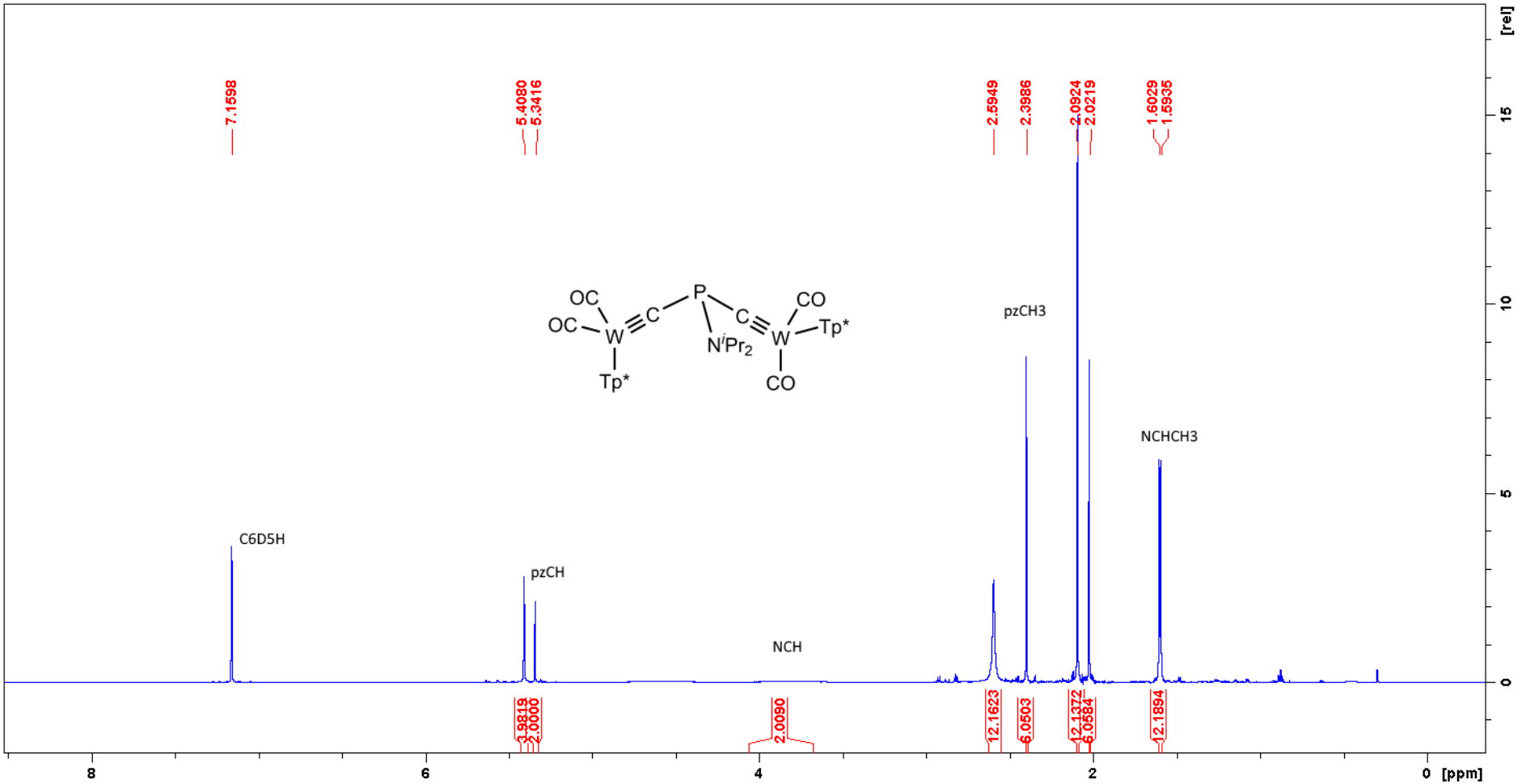
^{1}H NMR (400 MHz, C_6D_6, 25˚C, δ) of [W{≡CPPh(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5c**).



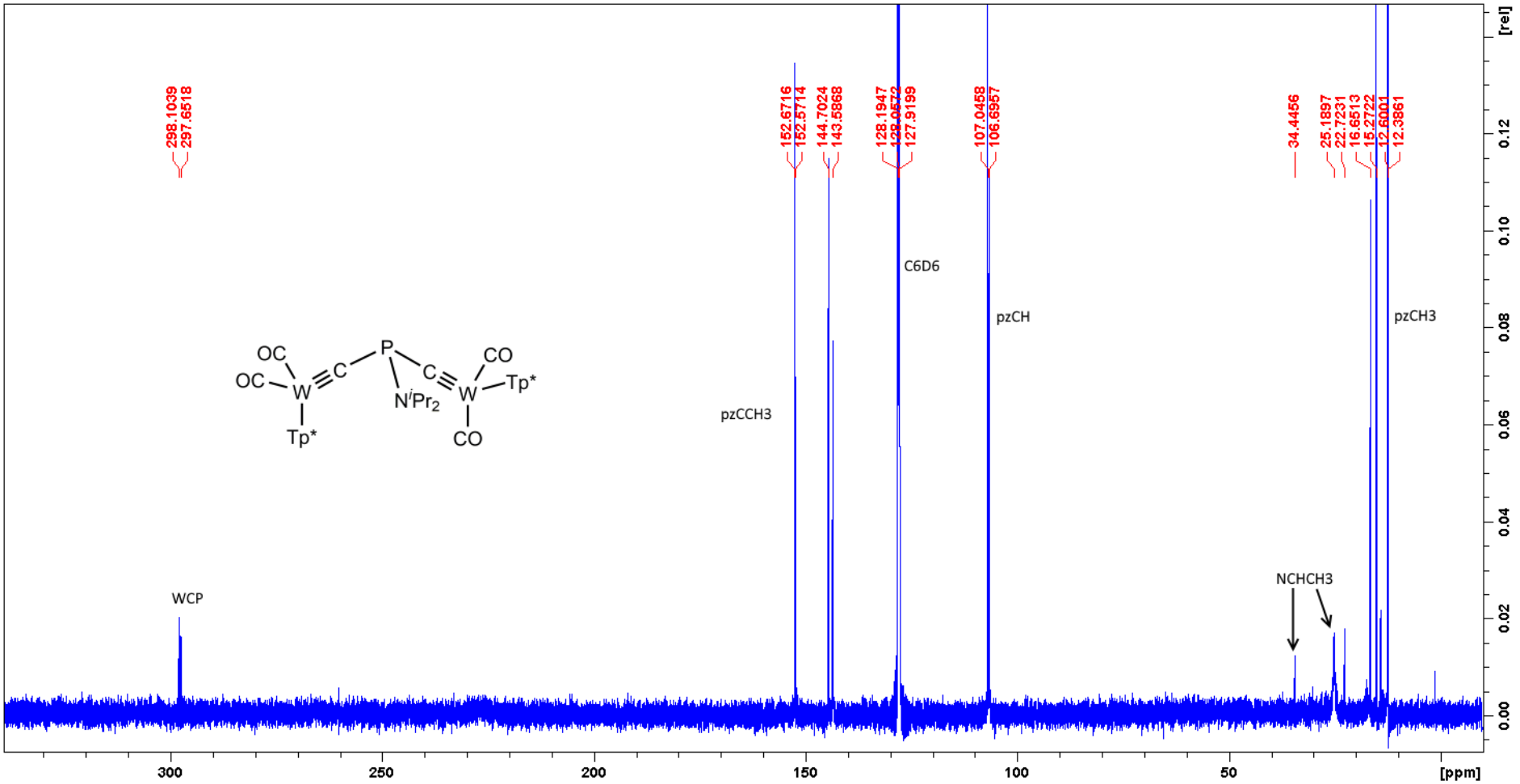
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 25˚C, δ) of [W{≡CPPh(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5c**).



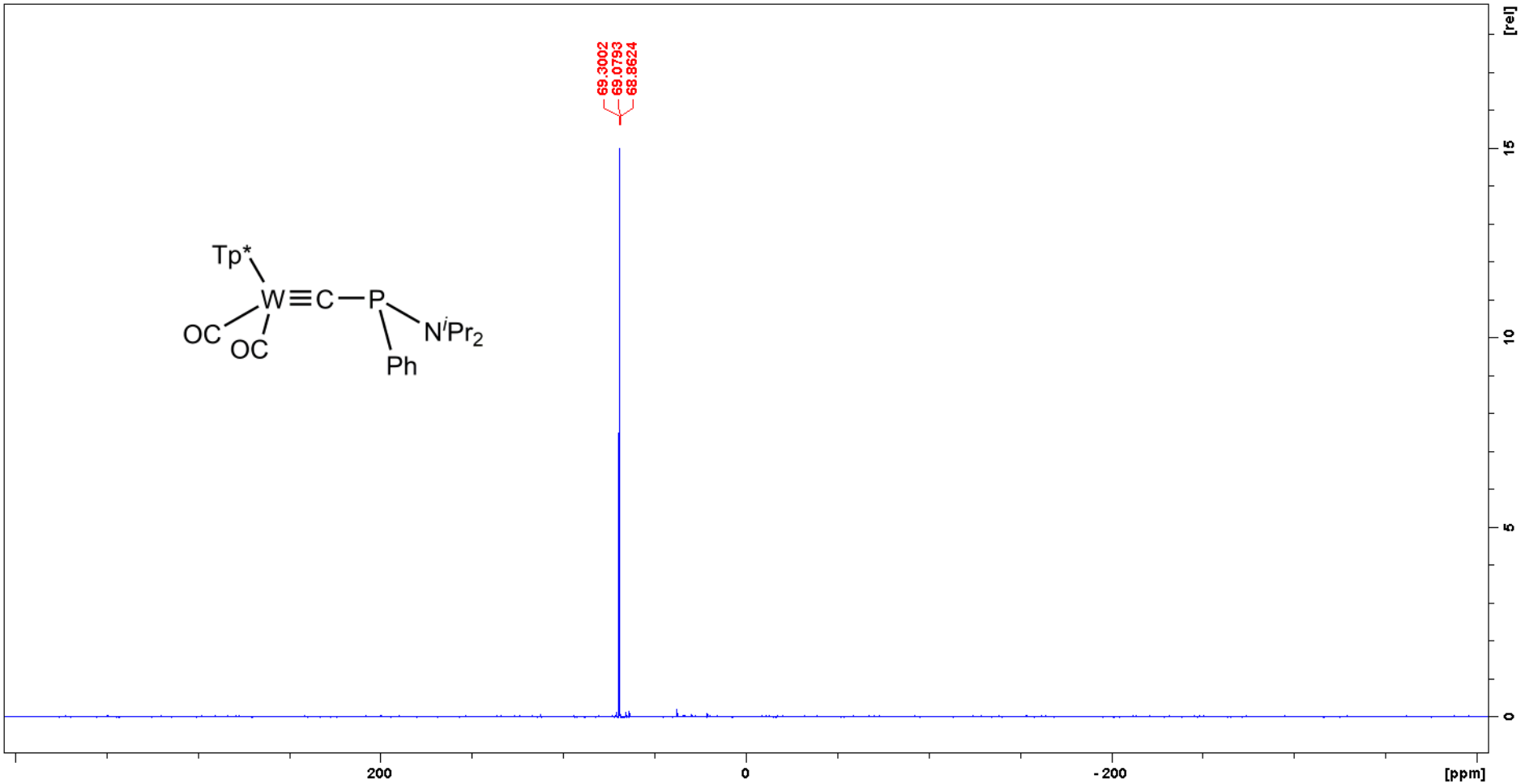
$^{31}P\{^{1}H\}$ (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CPPh(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**5c**).



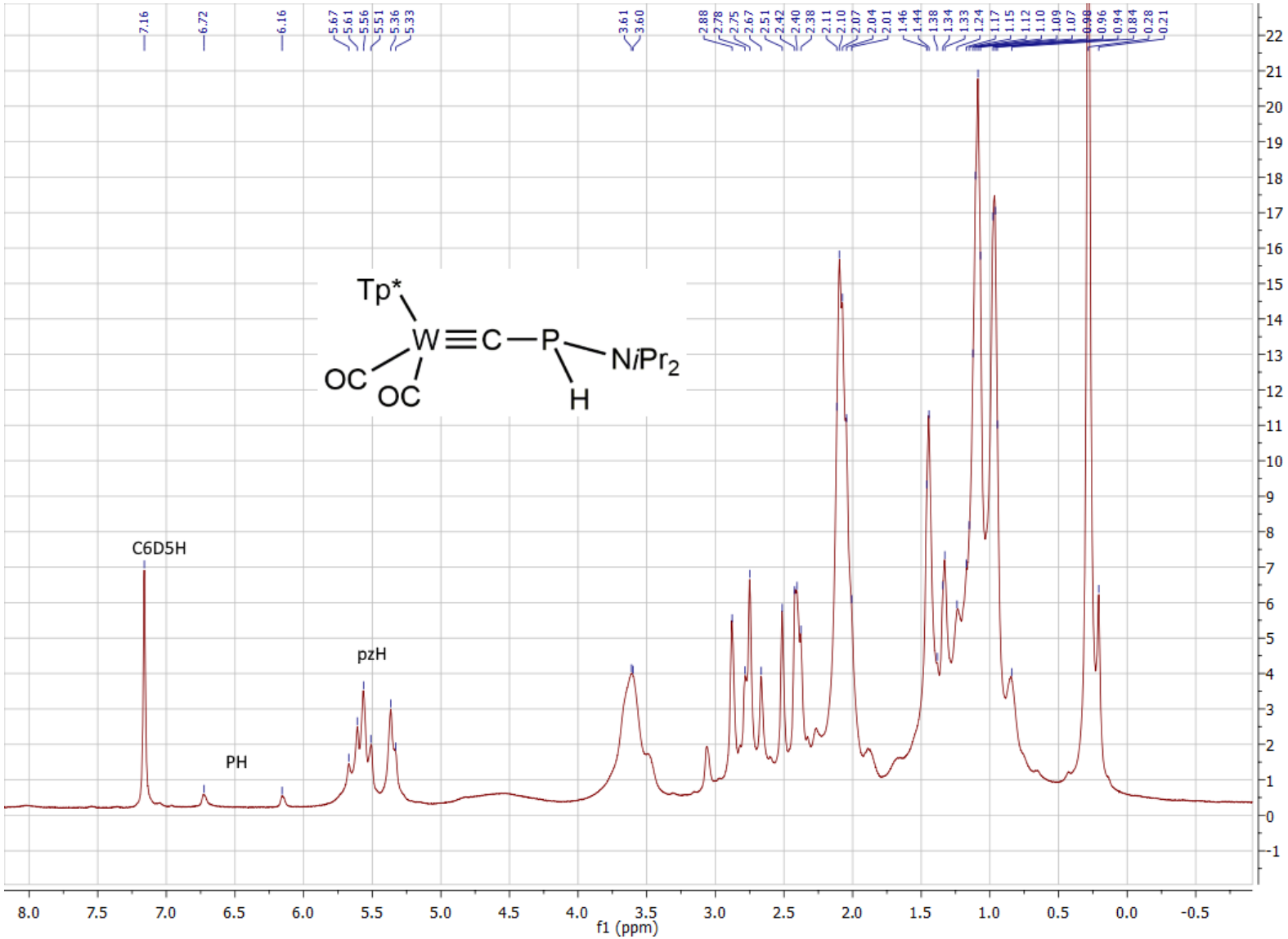
^{1}H NMR (700 MHz, C_6D_6, 25˚C, δ) of [^{i}Pr$_2$NP{C≡W(CO)$_2$(Tp*)}$_2$] (**6**).



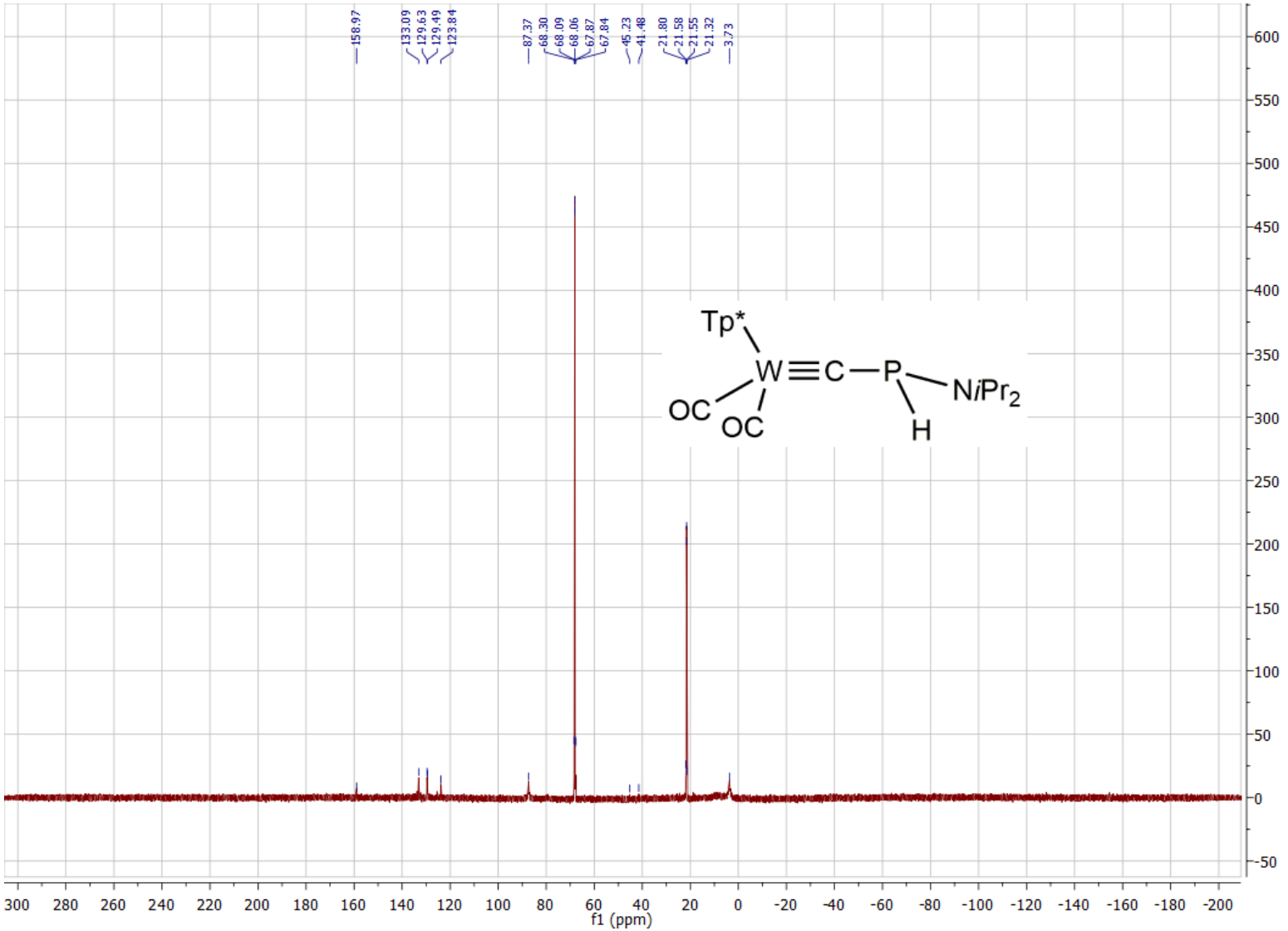
$^{13}C\{^1H\}$ NMR (176 MHz, C_6D_6, 25˚C, δ) of [^{i}Pr$_2$NP{C≡W(CO)$_2$(Tp*)}$_2$] (**6**).



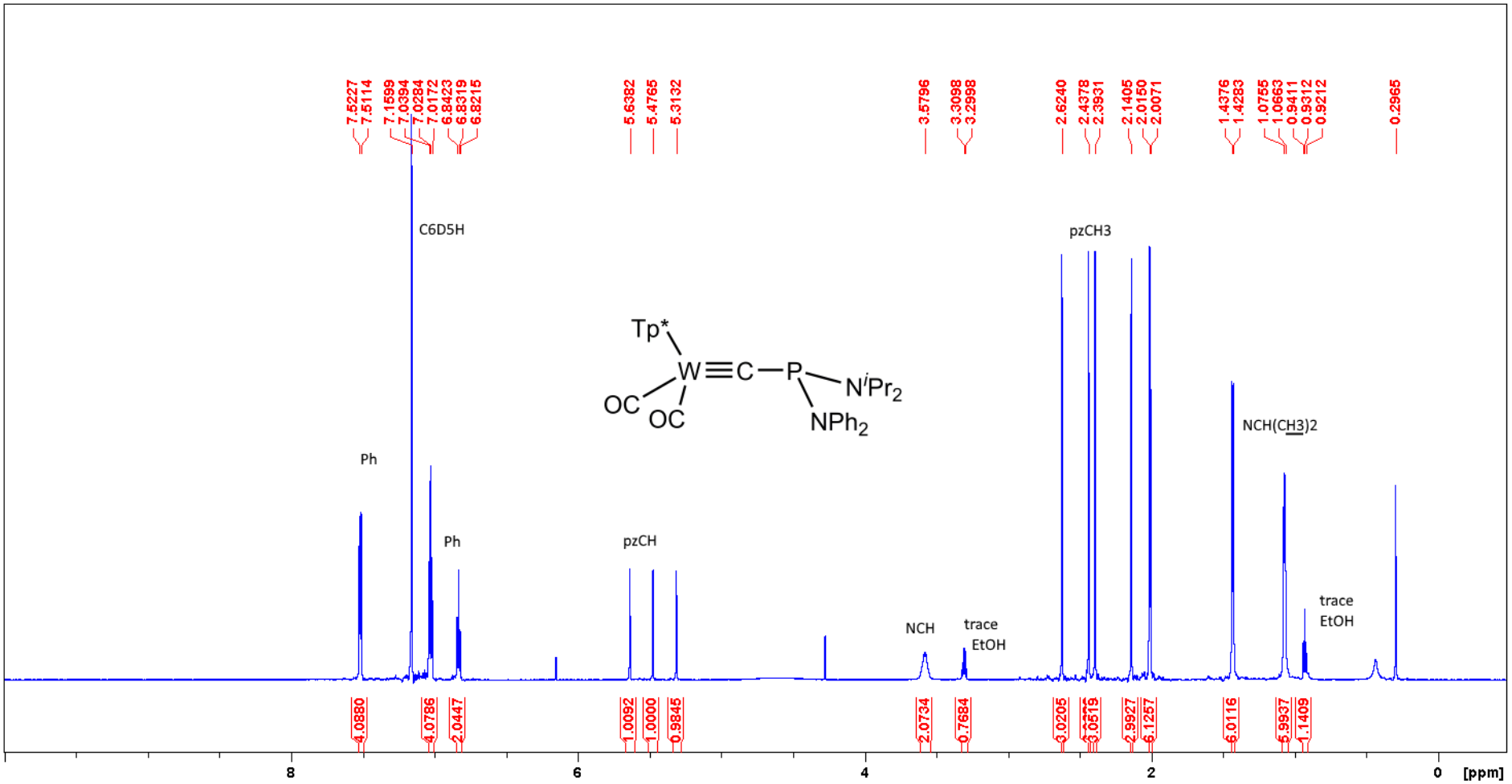
$^{31}P\{^{1}H\}$ (283 MHz, C_6D_6, 25˚C, δ) of [$^{i}Pr_2NP\{C{\equiv}W(CO)_2(Tp^*)\}_2$] (**6**).



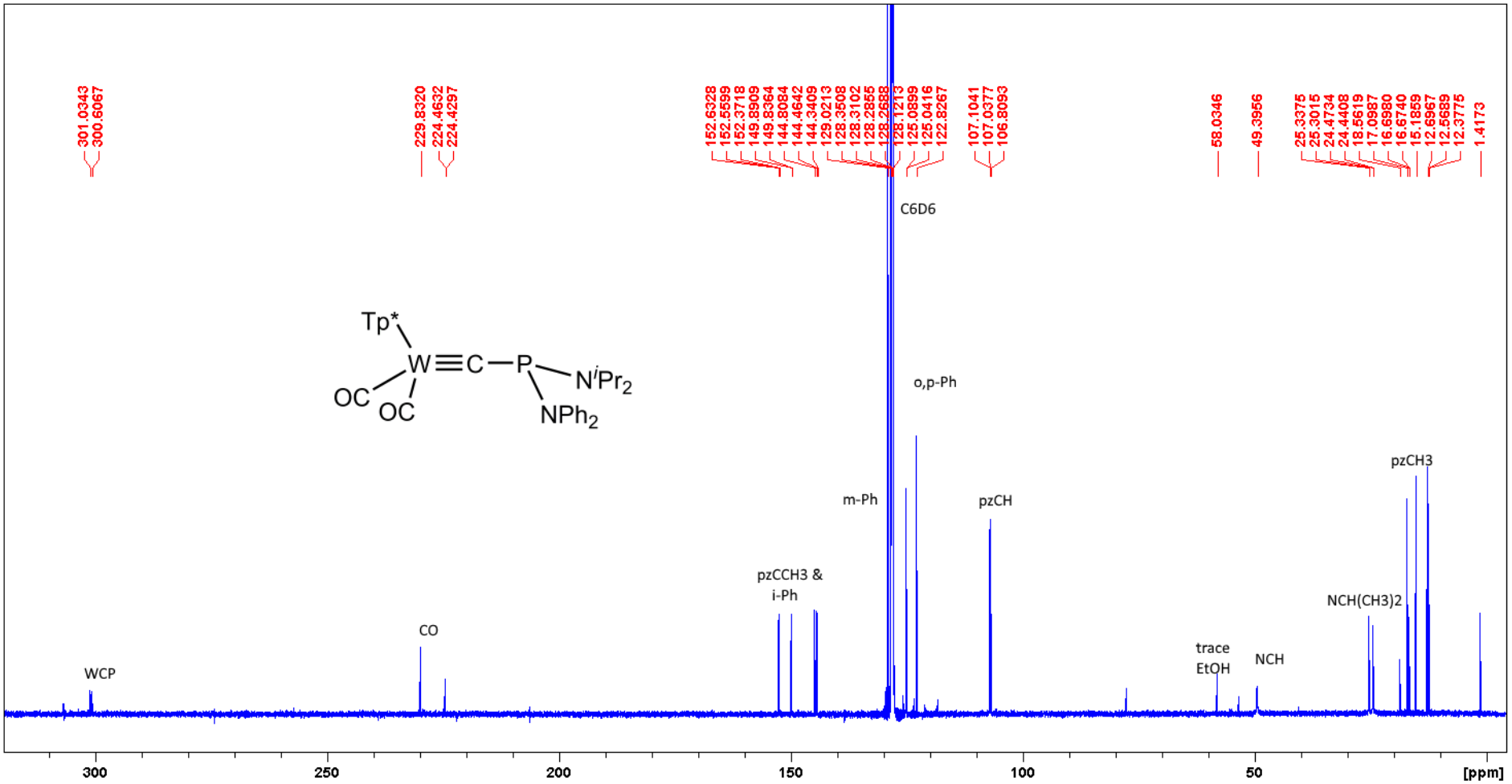
^{1}H (400 MHz, C_6D_6, 25˚C, δ) of [W{≡CPH(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**7**) in a mixture with **5b**.



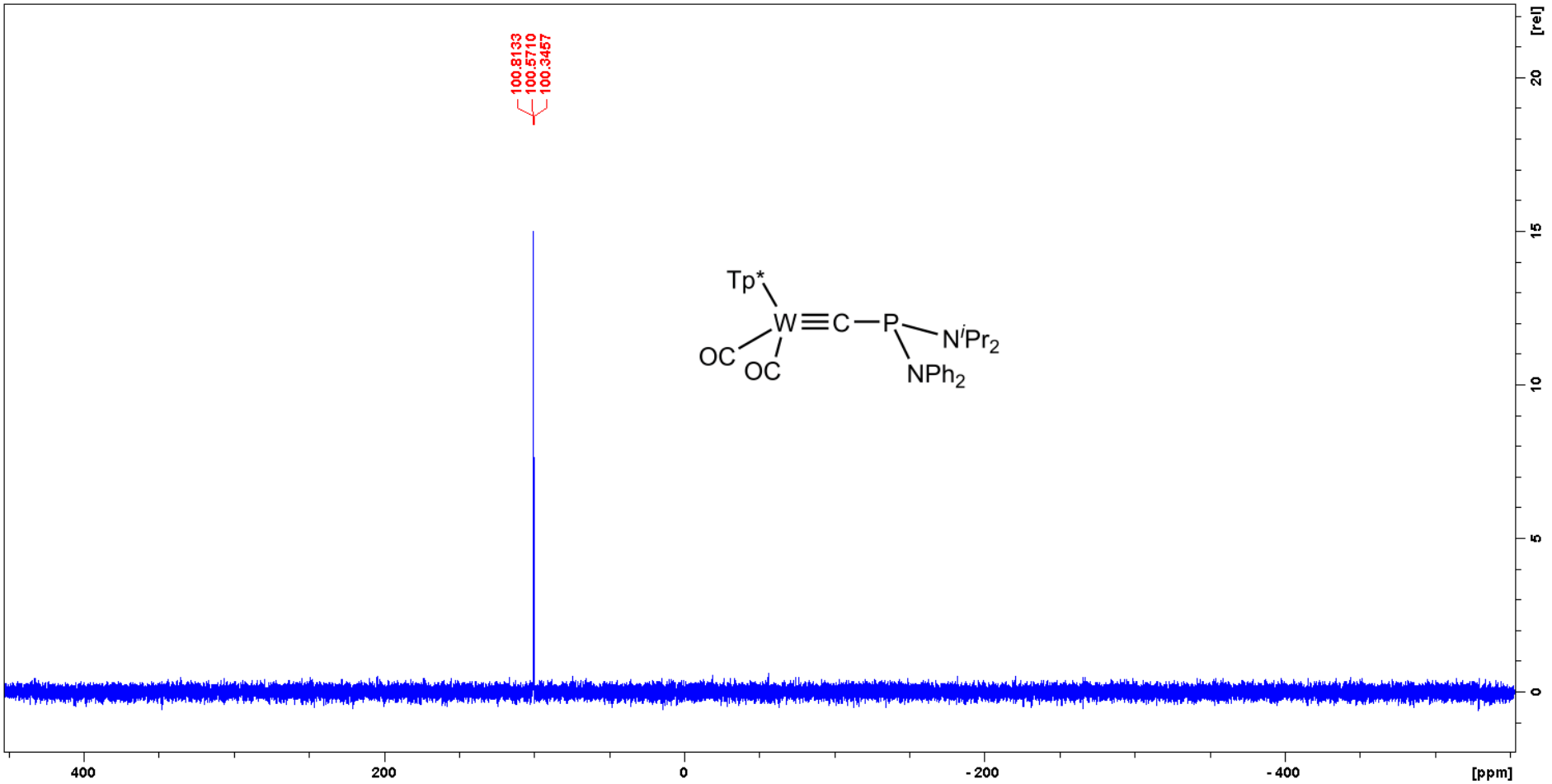
$^{31}P\{^{1}H\}$ (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CPH(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**7**) in a mixture with **5b**.



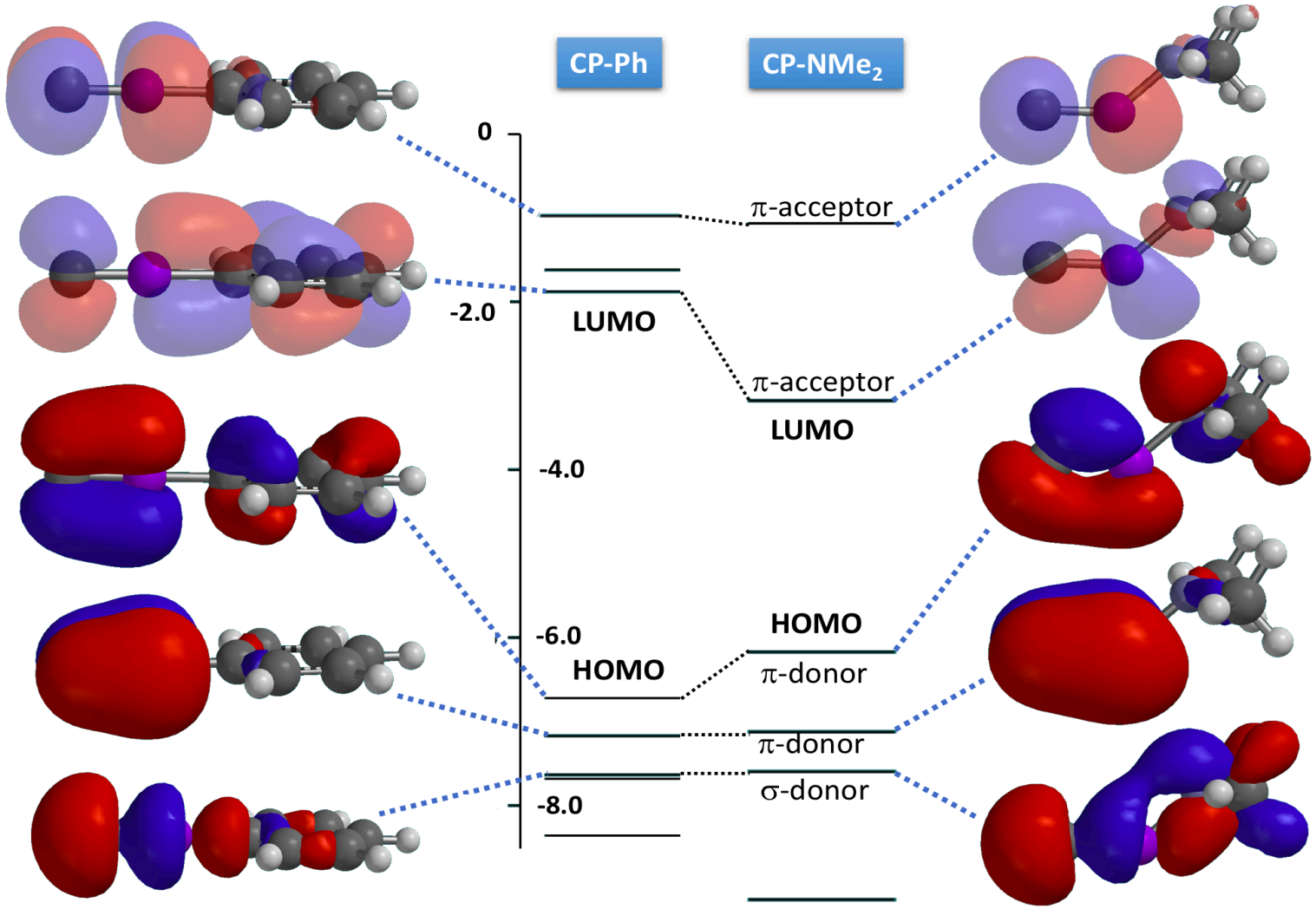
^{1}H NMR (700 MHz, C_6D_6, 25˚C, δ) of [W{≡CP(NPh$_2$)(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**10**).



$^{13}C\{^{1}H\}$ NMR (176 MHz, C_6D_6, 25˚C, δ) of [W{≡CP(NPh$_2$)(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**10**).



$^{31}P\{^{1}H\}$ (162 MHz, C_6D_6, 25˚C, δ) of [W{≡CP(NPh$_2$)(N^{i}Pr$_2$)}(CO)$_2$(Tp*)] (**10**).



Frontier Orbitals of Interest and optimised (unconstrained) geometry for the hypothetical phospha-isonitriles CPPh and $CPNMe_2$ (DFT: B3LYP-6-31G*).