Electronic Supplementary Information

Synthesis and characterization of a pair of O-fac/O-mer 12-P-6 alkyloxaphosphates with a P-O-C-C four-membered ring

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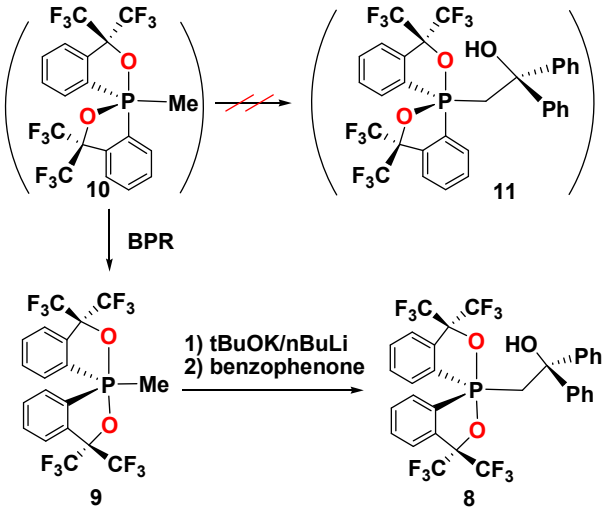
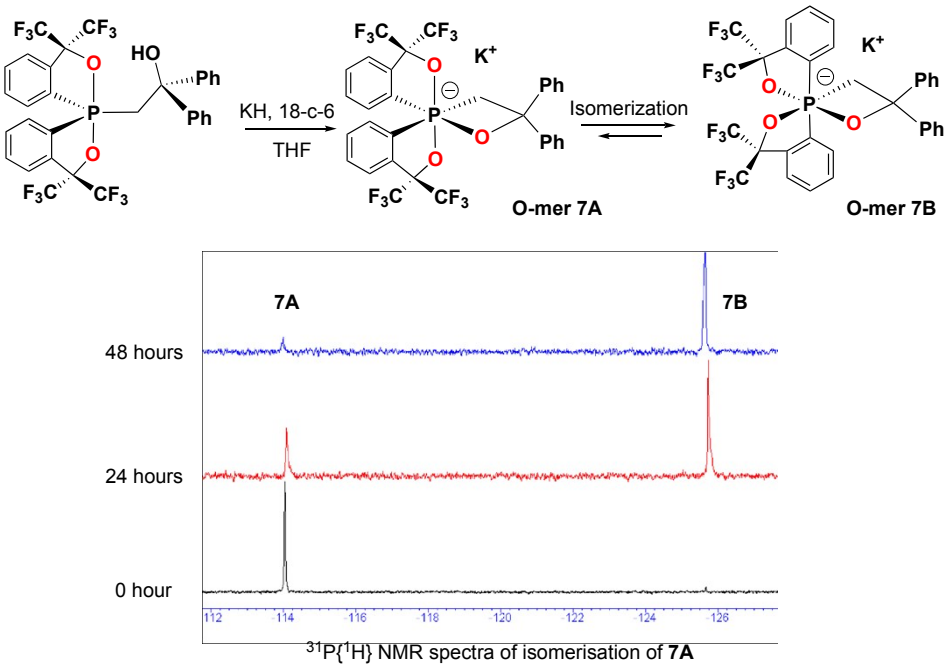
Synthesis of the -CF_3 system

To compare with the properties, the corresponding spirophosphorane **11** with Martin ligand was also investigated (Scheme S1). O-equatorial spirophosphorane **10** with Martin ligand cannot be obtained because of fast Berry pseudorotation which cause isomerization from phosphorane **10** to its stereoisomer **9**, and therefore the corresponding O-equatorial spirophosphorane **11** was not achieved.[1] The spirophosphorane **9** was further treated with benzophenone to provide the stable O-apical phosphorane **8** (Scheme S1), the spectral data of which were consistent with those of the identical compound described by Kawashima et al.[2]



Scheme S1. Synthesis of the pentacoordinate phosphorane bearing Martin ligand **8**. Isomerization of **10** to **9** took place rapidly at ambient condition.

The deprotonation of **8** has also been reported by Kawashima *et al,* although the stereochemistry of isomers were proposed without structural confirmation. Here we include the isolation and structure confirmation of O-mer **7A**, which isomerises to **7B** in solution at room temperature.[2] Upon crystallization, **7B** readily converts back to **7A** in solution and precipitates out of the solution. Consequently, crystals of **7B** could not be obtained in our hands.



Scheme S2. Synthesis of hexacoordinate oxaphosphate **O-mer 7** in $-CF_3$ system.

Isolation of 8 and 7A:

O-apical phosphorane 8: Under Ar, *n*-BuLi (1.67 M *n*-hexane solution, 0.15 mL, 0.25 mmol) was added to an *n*-hexane (5 mL) solution of phosphorane **9** (104 mg, 0.198 mmol) at 0 °C. The mixture was stirred for 5 min at 0 °C. Benzophenone (45.0 mg, 0.247 mmol) was added at 0 °C. The mixture was then stirred for 4 h at room temperature. The resulting solution was treated with aqueous NH_4Cl at 0 °C and the crude products were extracted with Et_2O (10 mL x 3). The combined organic layer was dried over $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by TLC (silica gel, *n*-hexane/CH_2Cl_2 = 2/1) to give compound **8** (84.6 mg, 0.119 mmol, 60%) as white solids. The data of **8** is consistent with that in the reported paper.[2]

O-mer 7A: A THF solution of **8** (84 mg, 0.118 mmol) and 18-crown-6 (31 mg, 0.118 mmol) were added to a THF (5 mL) suspension of KH (75mg, 30% oil dispersion), then the mixture was stirred for 30 min at 0 °C. The supernatent was transfered to a new schrenck. After concentration in vacuo, a white solid of **O-mer 7** was obtained. **O-mer 7** was recrystallized from *n*-hexane/THF to yield colorless crystals (35 mg, 0.030 mmol, 26%). The data of **O-mer 7** is consistent with isomer A paper in the previously reported paper.[2]

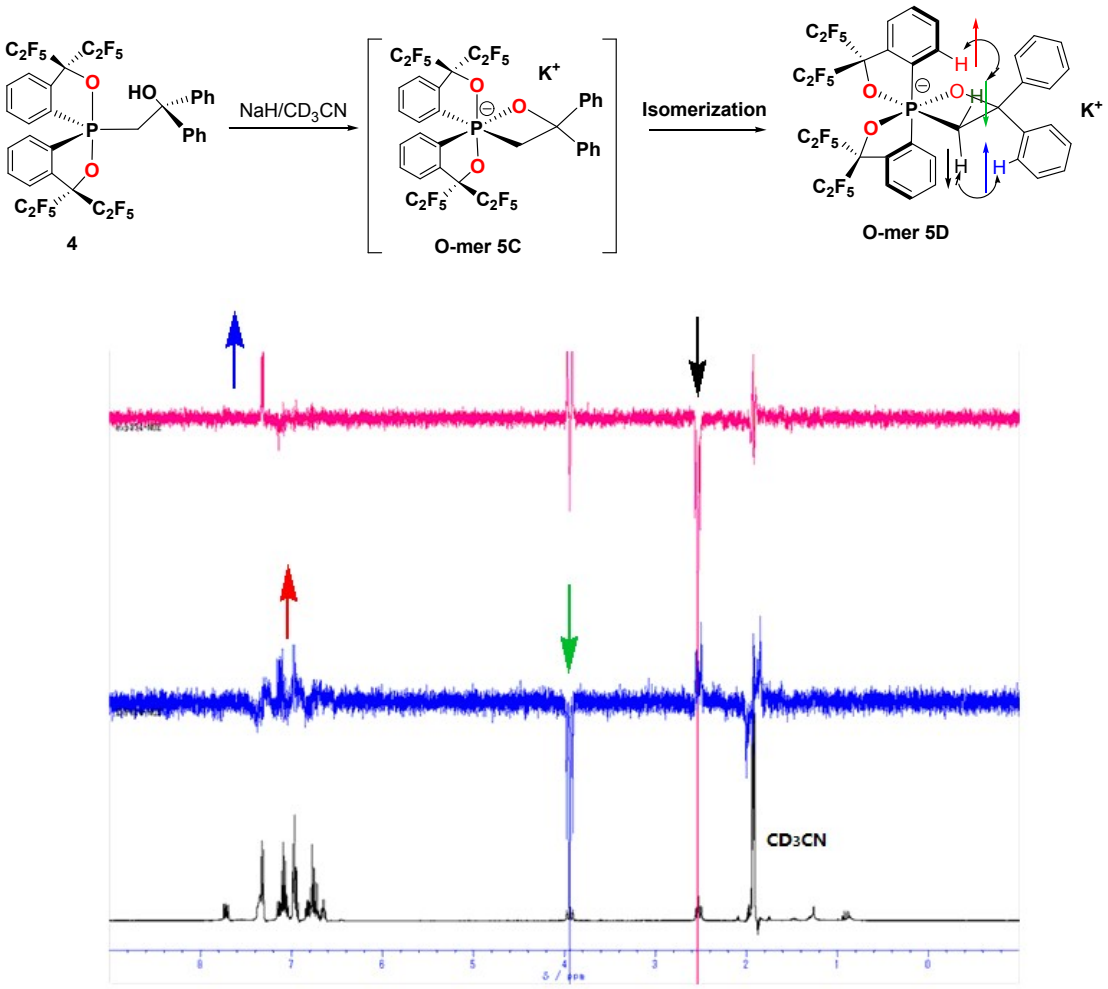


Figure S1. NOE spectra of O-mer **5D**.

X-ray crystal structure determinations

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science).[3] For each data set, the rotation images were collected in 3° increments with a total rotation of 180° about the φ axis. The data were processed using SCALEPACK. The structures were solved by a direct method with the SHELX-97 program.[4] Refinement on F^2 was carried out using the full-matrix least-squares by the SHELX-97 program.[4] All non-hydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters.

CCDC reference number 1856674 for **3**, 1856675 for **4**, 1856676 for **5D,** 1856677 for **5B,** and 1856678 for **7**.

Solid-state structure of 5B with and without 18-crown-6:

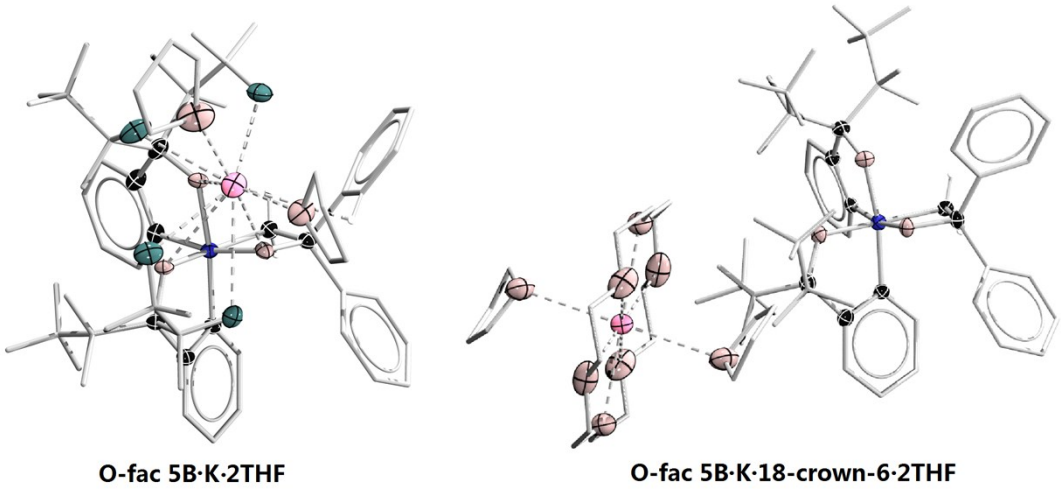


Figure S2. ORTEP diagram of hexacoordinate oxaphosphoranes O-fac **5B•K•2THF** and O-fac **5B(K•18-crown-6)•2THF** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

The crystallographic analysis of O-fac **5B(K•18-crown-6)•2THF** is not publishable due to missing parameters of the old data set. Therefore we attach the cif file as independent supplementary material instead of submission to CCDC.

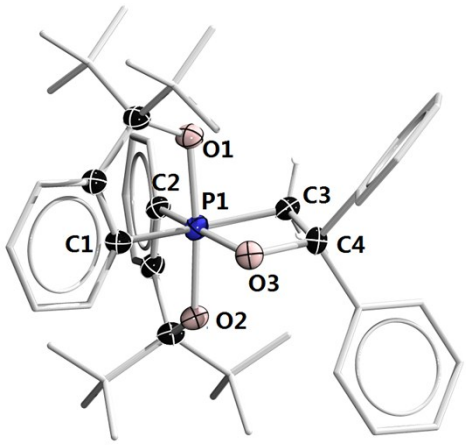


Figure S3. ORTEP diagram of hexacoordinate oxaphosphoranes O-mer **7(K•18-crown-6)•3THF** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

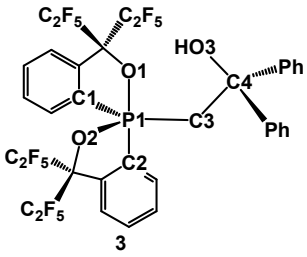
Table S1-1. Crystal and refinement data for 3, 4·CH_2Cl_2 and 5D·K·2THF.

Compound	**3**	**4 · CH_2Cl_2**	**5B·K·2THF**
Formula	$C_{36}H_{21}F_{20}O_3P$	$C_{37}H_{23}Cl_2F_{20}O_3P$	$C_{44}H_{36}F_{20}KO_5P$
Mw	912.50	997.42	1094.80
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P-1*	*C*2/*c*	$P2_1/n$
Color	colorless	colorless	colorless
Habit	plate	plate	plate
Crystal dimensions, [mm]	0.30 × 0.20 × 0.20	0.50 × 0.50 × 0.10	0.20 × 0.10 × 0.10
a, [Å]	9.9730(2)	39.2730(6)	18.972(4)
b, [Å]	10.4830(2)	9.5530(1)	13.493(3)
c, [Å]	19.3940(5)	26.3550(7)	19.631(4)
α, [°]	88.696(1)	90	90
β, [°]	79.354(1)	127.505(5)	111.443(3)
γ, [°]	62.570(1)	90	90
V, [Å^3]	1764.13(7)	7843.9(5)	4677.6(17)
Z	2	8	4
D_{calcd}, [g cm^{-3}]	1.718	1.689	1.555
Abs. coeff., [mm^{-1}]	0.223	0.340	0.272
F(000)	912	3984	2216
Radiation, λ, [Å]	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
T, [K]	200(2)	200(2)	200(2)
Data collected	+*h*, ±*k*, ±*l*	+*h*, +*k*, ±*l*	+*h*, +*k*, ±*l*
Data/restrains/parameters	7683/0/671	8582/0/569	10440/0/639
R_1 ($I > 2\sigma$ (I))	0.0654	0.0645	0.0760
wR_2 (all data)	0.1644	0.1872	0.1995
GOF	1.237	1.101	1.049
CCDC No.	1856674	1856675	1856677

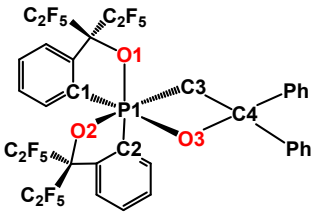
Table S1-2. Crystal and refinement data for **5B(K•18-crown-6)•2THF** and **7(K•18-crown-6)•3THF**.

Compound	**5B(K•18-crown-6)•2THF**	**7(K•18-crown-6)•3THF**
Formula	$C_{56}H_{60}PF_{20}KO_{11}$	$C_{56}H_{68}PF_{12}KO_{12}$
Molecular weight	1359.11	1231.17
Crystal system	Triclinic	monoclinic
Space group	*P*-1	*P*21/c
Color	Colorless	colorless
Habit	Block	Block
a, Å	11.031(2)	15.552(3)
b, Å	12.806(2)	13.580(3)
c, Å	23.283(4)	28.022(6)
α, °	105.457(2)	90
β, °	92.077(3)	95.733(3)
γ, °	96.066(3)	90
V, Å^3	3143.3(10)	5889(2)
Z	1	4
D_{calcd}, g cm^{-3}	1.473	1.389
Abs. coeff., mm^{-1}	0.225	0.214
F(000)	1396	2568
Radiation, λ, Å	Mo Kα, 0.71073	Mo Kα, 0.71073
T, K	173(2)	173(2)
Data, collected	+*h*, ±*k*, ±*l*	+*h*, ±*k*, ±*l*
Data/restrains/parameters	10740/0/838	12833/0/739
$R_1[I > 2\sigma(I)]$	0.0646	0.0744
wR_2 (all data)	0.1660	0.1465
GOF	1.027	1.021
CCDC No.	1856676	1856678

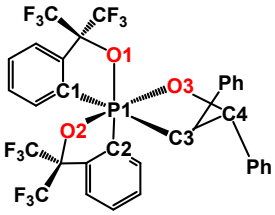
Table S2. Comparison of Bond Distances (Å) and angles (º) for **3**, **5B** and **6**.



3



5B



6

	3	O-fac **5B**	O-mer **6**
P1–O1	1.794	1.835	1.783
P1–O2	1.662	1.806	1.788
P 1–O3		1.741	1.731
P 1–C1	1.827	1.860	1.891
P1–C2	1.876	1.868	1.872
P1–C3	1.857	1.874	1.926
C3–C4	1.794	1.526	1.533
O1-P1-C2		168.04	170.94
O2-P1-C3/O3[a]		164.95	173.77
C1-P1-O3/C3[a]		166.60	164.24
O3/C3[a] -P1-C3/O3[a]		76.24	75.97
P1-C3/O3[a] -C4		88.8	95.90
C3/O3[a] -C4-O3/C3[a]		97.3	98.7
C4-O3/C3[a] -P1		96.8	85.36

[a]: Atoms in compound **6**.

Table S3. Selected bond lengths (Å) and angles (º) for O-mer **7(K•18-crown-6)•3THF**.

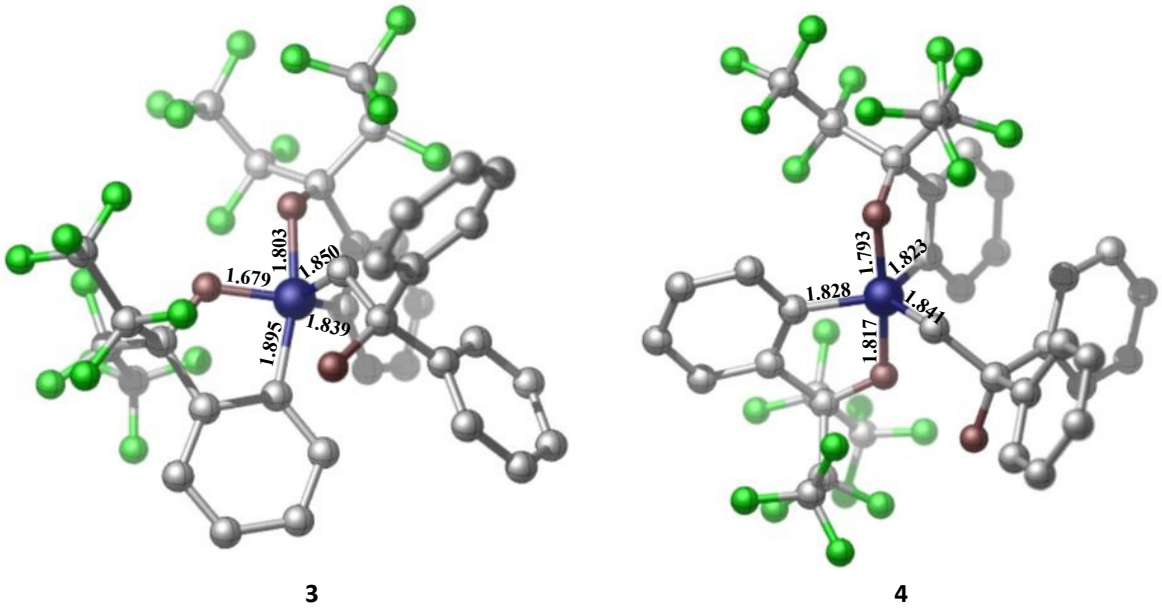
	7(K•18-crown-6)•3THF
P1–O1	1.816(3)
P1–O2	1.795(3)
P1–O3	1.746(3)
P1–C1	1.875(4)
P1–C2	1.884(4)
P1–C3	1.843(4)
O3–C4	1.433(5)
C3–C4	1.514(5)
O1–P1–O2	174.31(14)
O1–P1–O3	97.17(13)
O1–P1–C1	85.33(15)
O1–P1–C2	91.17(14)
O1–P1–C3	87.76(16)
O2–P1–O3	87.31(12)
O2–P1–C1	91.36(15)
O2–P1–C2	85.21(14)
O2–P1–C3	96.80(16)
O3–P1–C1	87.80(15)
O3–P1–C2	165.34(15)
O3–P1–C3	75.31(15)
C1–P1–C2	104.95(17)
C1–P1–C3	160.80(17)
C2–P1–C3	93.07(16)
P1–O3–C4	97.6(2)
P1–C3–C4	90.8(2)
O3–C4–C3	96.2(3)

Computational Methodology

Gas-phase geometry optimizations were carried out by using the Gaussian16 computational package.[5] Our theoretical calculations were performed within the framework of the Density Functional Theory (DFT). We set up the default Berny algorithm in order to proceed to minimize the energy described through the density-functional. We chose the long-range (empirically) corrected hybrid density-functional ω-B97XD,[6] which has a remarkable accuracy for non-covalent interactions present in systems like our studied compounds, in combination with the Weigend-Ahlrichs' basis set def2-svp.[7] Harmonic frequency calculations were also executed for a two-fold reason: 1) to be sure each optimized structure corresponds to a local minimum by verifying the number of negative values (imaginary frequencies) of the Hessian to be zero and only zero and 2) to get the thermal and entropy corrections adjusted to 298.15K and 1 atm as well as the zero-point energy (ZPE) correction that were summed up into the electronic energy in order to express it as enthalpy or Gibbs free-energy.

We also performed single-point calculations over the optimized structures (in gas phase) in order to incorporate solvation effects with the same level of theory as defined above. The SMD variant model of IEFPCM of Truhlar and coworkers[8] was used as implemented in Gaussian16 program. Tetrahydrofuran (ε = 7.4257) was the solvent chosen as employed in our experiments. We have used the solvation free energy for K+ (–66.2 kcal/mol) as reported by Ziegler and co-workers[9] in our calculations. And finally, we also carried out single-point calculations over the optimized structures with the same functional but a different, larger basis set, namely def2-tzvpp in order to improve the numerical accuracy in our final energies reported. Thus, we can define the enthalpy and Gibbs free energy values reported were calculated at the (SMD:thf)ω-B97XD/def2-tzvpp//ω-B97XD/def2-svp level.

Color code: P – dark blue, O – Palid Red, F – Green, C – Gray, K – magenta.



3 4

Figure S4. Selected bond distances (in Å) of the optimized geometries of **3 (O-equatorial)** and **4 (O-apical)** compounds calculated at the ω-B97XD/def2-svp level. Hydrogens were omitted for clarity.

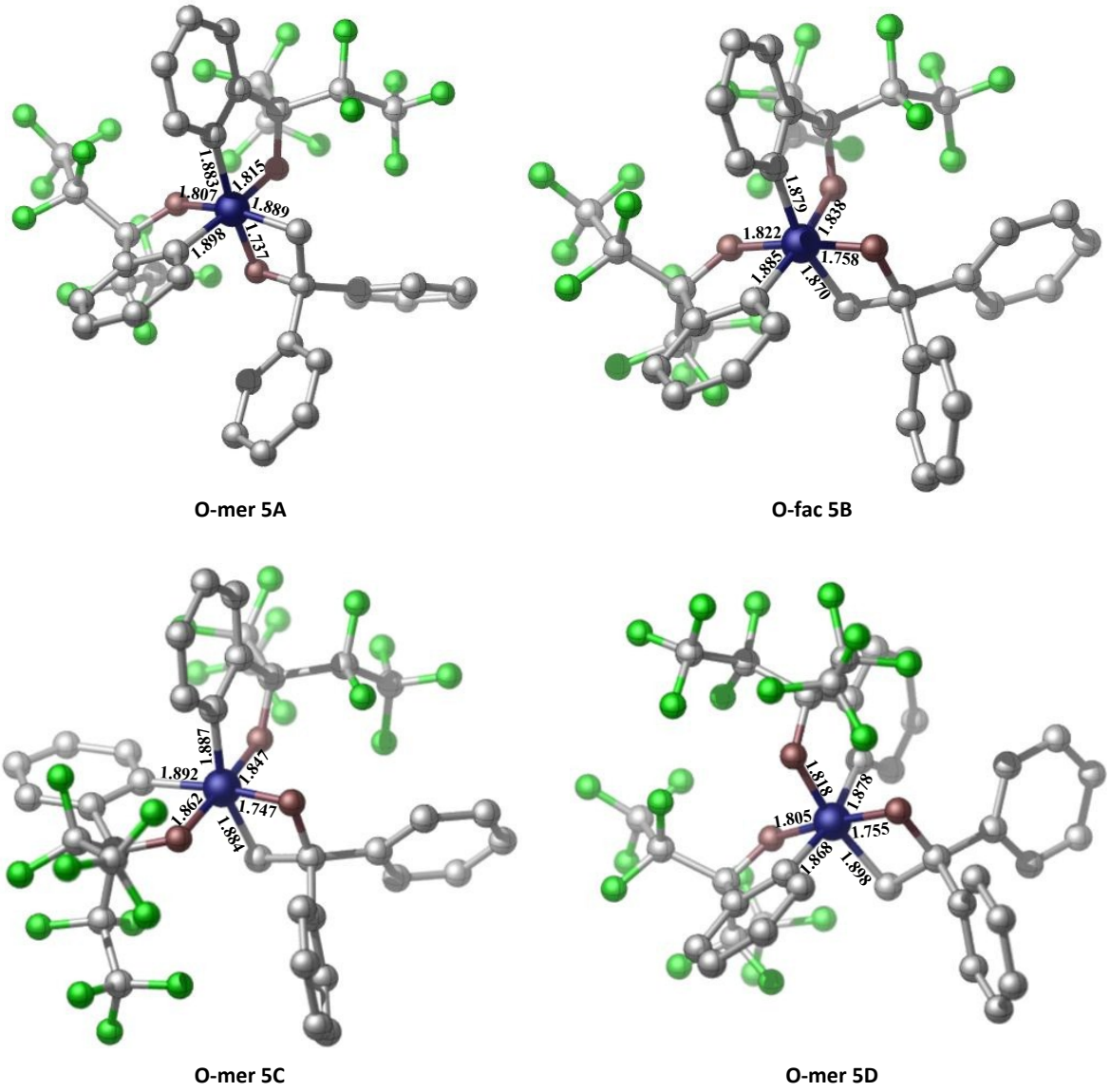


Figure S5. Selected bond distances (in Å) of the optimized geometries of isomers of **5** in its anionic form calculated at the ω-B97XD/def2-svp level. Hydrogens were omitted for clarity.

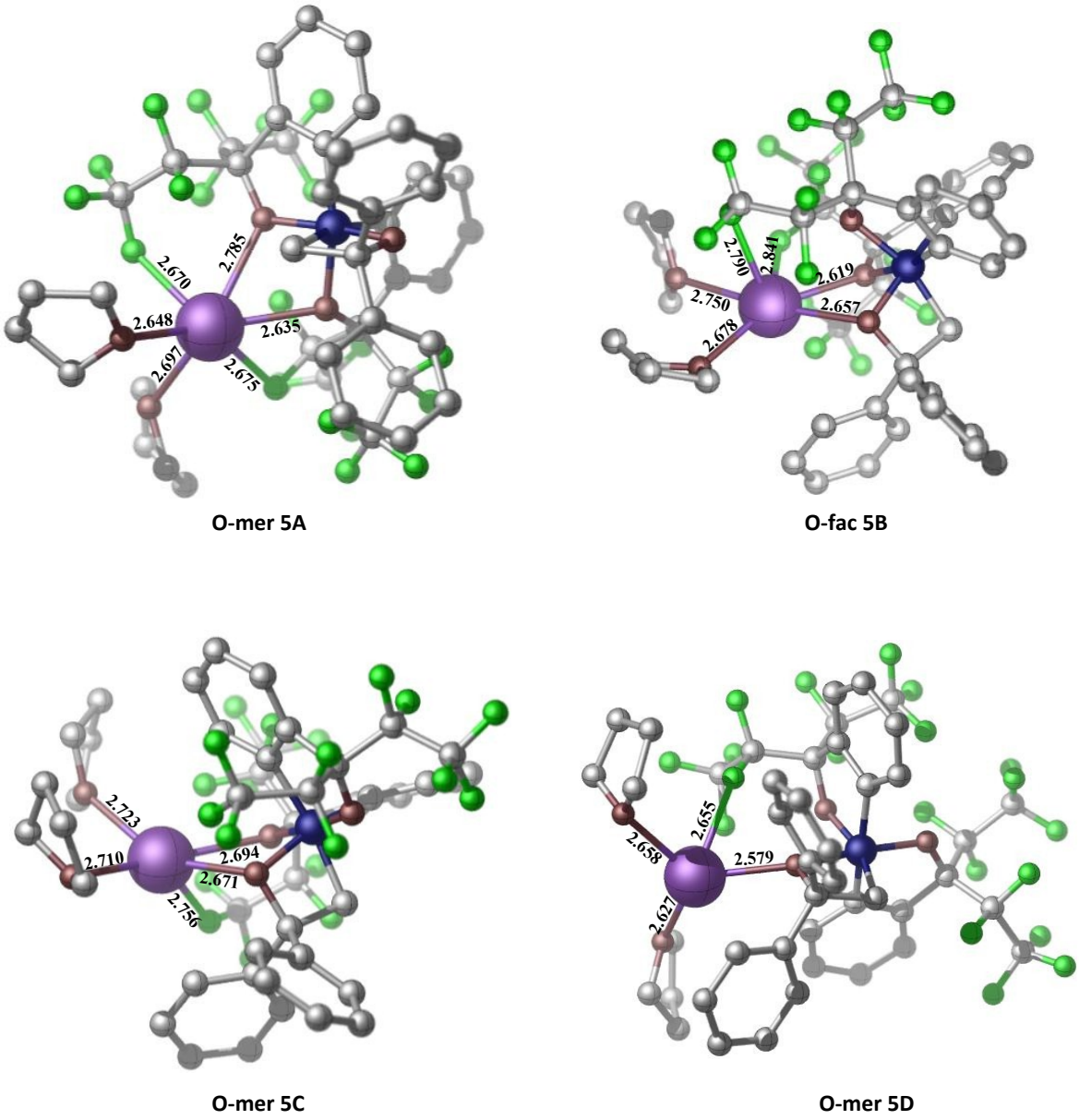


Figure S6. Selected bond distances (in Å) of the optimized geometries of isomers of **5**, including the potassium cation (solvated with two THF solvent molecules as it was obtained in our crystals), calculated at the ω-B97XD/def2-svp level. Hydrogens were omitted for clarity.

References

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Appendix 1 Cartesian coordinates (x-y-z format) of all the optimized structures calculated at the ω-B97XD/def2-svp level.

Benzophenone

E(scf) = –576.022866595 a.u.

O	0.000026	-2.313949	0.000267
C	0.000031	-1.101264	0.000180
C	-1.299427	-0.347941	0.027592
C	-2.428664	-0.971305	-0.518541
H	-2.312567	-1.959034	-0.968755
C	-3.667584	-0.340520	-0.481463
H	-4.540431	-0.827033	-0.921881
C	-3.795908	0.909632	0.126444
H	-4.769931	1.402788	0.161600
C	-2.682730	1.525014	0.696701
H	-2.784488	2.494507	1.188829
C	-1.436875	0.902305	0.643430
H	-0.571090	1.383278	1.103183
H	0.570677	1.383648	-1.102169
C	1.436654	0.902516	-0.642938
C	2.428906	-0.971387	0.518179
C	1.299458	-0.347892	-0.027422
H	2.312946	-1.959241	0.968148
C	3.667774	-0.340558	0.480852
H	4.540802	-0.827130	0.920850
C	3.795864	0.909775	-0.126779
H	4.769879	1.402938	-0.162101
H	2.784027	2.494918	-1.188375
C	2.682497	1.525285	-0.696476

1,1-diphenylethylene

E(scf) = –540.134207189 a.u.

H	-2.667412	-2.323497	-1.563485
C	-2.593906	-1.441081	-0.923932
C	-3.699962	-1.017770	-0.186899
H	-4.640717	-1.569921	-0.241463
C	-3.594079	0.109045	0.626613
H	-4.450620	0.440074	1.218138
H	-2.308037	1.680245	1.354251
C	-2.392311	0.810777	0.698284
C	-1.276354	0.401720	-0.044191
C	-1.392350	-0.741797	-0.848687
H	-0.529358	-1.079795	-1.427151
C	0.000135	1.170898	-0.000310
H	0.528548	-1.080577	1.425751
C	1.391878	-0.742391	0.847909
C	1.276299	0.401401	0.043709
C	2.392718	0.810905	-0.697829
H	2.308775	1.680733	-1.353355
C	3.594490	0.109159	-0.625726
H	4.451421	0.440595	-1.216460
H	4.640595	-1.570188	0.242210
C	3.699864	-1.018032	0.187268
C	2.593340	-1.441732	0.923450
H	2.666546	-2.324455	1.562612
H	-0.929998	3.080644	-0.078334
C	0.000204	2.513148	0.000177
H	0.930454	3.080644	0.078280

KOH_2thf

E(scf) = –1140.06815436 a.u.

H	2.793984	2.218343	-1.604718
O	2.148612	1.972633	-0.939108
K	0.563096	1.763852	0.689488
O	-1.905564	0.699491	0.385724
C	-2.617204	0.801152	-0.843623
H	-1.909141	0.680031	-1.683528
H	-3.064607	1.804114	-0.919982
H	-3.913799	-0.675206	-1.826300
H	-4.581636	0.025565	-0.333866

K^+_2thf

E(scf) = –1064.17368812 a.u.

K	-0.006522	2.513167	-0.042733
O	1.693000	0.559624	0.101764
C	1.486956	-0.364703	1.180993
H	0.426316	-0.668818	1.171874
H	1.694485	0.140309	2.137445
H	2.002632	-2.496766	1.260925
H	3.382357	-1.395338	1.441734
C	2.424773	-1.542261	0.920239
C	2.629308	-1.472400	-0.593268

C	-3.655066	-0.318353	-0.820069
C	-2.961186	-1.371951	0.043748
H	-2.232924	-1.942405	-0.553603
H	-3.655302	-2.087566	0.505296
H	-2.899106	-0.269213	1.926006
C	-2.239958	-0.505619	1.070563
H	-1.311937	-0.959065	1.450393
O	1.051752	-0.958397	0.791846
C	0.815724	-1.395214	-0.538658
H	-0.061589	-0.848143	-0.914897
H	0.573111	-2.476496	-0.533220
C	2.101365	-1.097895	-1.321516
H	2.004136	-0.125870	-1.827842
H	2.334404	-1.900682	-2.035850
C	3.166551	-0.915483	-0.219268
H	3.438304	0.151511	-0.229168
H	4.057223	-1.546438	-0.350108
C	2.412760	-1.248572	1.069414
H	2.717721	-0.642762	1.935705
H	2.516017	-2.317126	1.344177
H	1.783670	-1.936845	-1.125572
H	3.550756	-1.963980	-0.931568
H	3.641551	0.459189	-0.622884
C	2.645352	0.029849	-0.827357
H	2.341955	0.324912	-1.843085
O	-1.647618	0.506149	-0.111136
C	-1.383714	-0.504683	-1.091321
H	-0.295821	-0.548507	-1.254180
H	-1.873480	-0.231930	-2.042640
C	-1.967890	-1.785811	-0.515966
H	-1.256201	-2.255614	0.181943
H	-2.216912	-2.522524	-1.290936
C	-3.189529	-1.253687	0.233074
H	-3.550047	-1.929749	1.019234
H	-4.020503	-1.078438	-0.466872
C	-2.673619	0.068100	0.793450
H	-2.227745	-0.061670	1.794813
H	-3.451985	0.842979	0.857617

Water

E(scf) = –76.3370011263 a.u.

O	0.000000	0.000000	0.119092
H	0.000000	0.754852	-0.476366
H	0.000000	-0.754852	-0.476366

2 (O-apical)

E(scf) = –3368.52408819 a.u.

P	0.065749	1.174652	-0.715451
F	2.118352	0.817789	1.982291
F	4.126572	0.149411	1.468168
F	2.900677	-1.258952	3.354507
F	3.319155	-2.423448	1.598339
F	1.294736	-1.796634	2.031546
F	4.284481	-1.345422	-0.756645
F	3.246128	-0.349198	-2.378837
F	1.796276	-2.867997	-0.472913
F	3.037959	-3.076078	-2.214052
F	1.224422	-1.925100	-2.324967
F	-3.148208	1.798240	-1.280841
F	-4.542916	1.127249	0.247920
F	-5.133717	0.472979	-2.272259
F	-4.821907	-1.234867	-1.010171

3 (O-equatorial)

E(scf) = –3944.56853079 a.u.

C	-0.152399	0.551902	2.100756
C	-0.274664	-0.051900	3.356308
H	-0.299463	-1.133675	3.458358
C	-0.348546	0.735709	4.500238
H	-0.449776	0.258003	5.476483
C	-0.289361	2.126529	4.404642
H	-0.356174	2.740588	5.304890
C	-0.118466	2.734690	3.165703
H	-0.039546	3.818574	3.085122
C	-0.037405	1.937193	2.027263
C	0.237398	2.431174	0.610722
C	0.000117	-2.081365	1.038077
C	-0.835049	-2.810792	1.896884
H	-1.695992	-2.343128	2.372783
C	-0.584915	-4.159892	2.139219

F	-3.331361	-0.678773	-2.479435
F	-3.805477	-1.035074	1.600948
F	-1.753007	-0.861969	2.281108
F	-2.668376	-3.311300	1.357926
F	-0.840602	-2.524320	0.548454
F	-2.625996	-2.532081	-0.645304
O	1.039846	-0.122425	-0.285578
O	-1.264699	-0.008129	-0.584276
C	-0.326013	1.392501	-2.487512
H	0.529170	0.974588	-3.038641
H	-1.248773	0.883071	-2.772690
H	-0.383761	2.465135	-2.715120
C	1.631847	2.204877	-0.840852
C	1.766131	3.534918	-1.252851
H	0.883124	4.143254	-1.469837
C	3.034238	4.093970	-1.380746
H	3.141373	5.133757	-1.696824
C	4.173368	3.326536	-1.116689
H	5.165545	3.767680	-1.229292
C	4.050632	1.999335	-0.721606
H	4.935601	1.392049	-0.531002
C	2.769979	1.462098	-0.587457
C	2.420056	0.034259	-0.189140
C	2.818671	-0.121113	1.318544
C	2.564085	-1.446635	2.082746
C	3.074023	-0.968870	-1.193491
C	2.246596	-2.244165	-1.545384
C	-0.742816	2.078874	0.654168
C	-0.237109	3.192049	1.332275
H	0.700742	3.653467	1.025312
C	-0.927693	3.699097	2.428890
H	-0.533875	4.567350	2.960466
C	-2.107643	3.091933	2.861667
H	-2.637914	3.488228	3.729880
C	-2.605913	1.971729	2.203249
H	-3.516615	1.483058	2.549387
C	-1.911311	1.474239	1.105016
C	-2.300077	0.261790	0.264932
C	-3.554283	0.723529	-0.568179
C	-4.215341	-0.220448	-1.606206
C	-2.526378	-0.978916	1.186237
C	-2.147845	-2.366103	0.578542
H	-1.248809	-4.715551	2.804369
C	0.499298	-4.800263	1.537163
H	0.690355	-5.856829	1.733450
C	1.340788	-4.091998	0.686477
H	2.195400	-4.579034	0.217864
C	1.072720	-2.744451	0.450598
C	1.868749	-1.824473	-0.455114
C	3.355818	-1.676343	-0.025012
C	3.600618	-1.501889	1.506476
C	1.698412	-2.316397	-1.933476
C	2.362998	-1.503360	-3.080590
C	-1.655517	-0.312560	-0.563000
H	-2.089563	0.681050	-0.433277
H	-1.237078	-0.303842	-1.581456
C	-2.779486	-1.366978	-0.522042
C	-3.484277	-1.440148	0.838330
C	-3.457413	-0.396962	1.768182
H	-2.938753	0.537538	1.549629
C	-4.077221	-0.535623	3.011444
H	-4.028984	0.286037	3.729262
C	-4.745052	-1.713600	3.334358
H	-5.226561	-1.824263	4.308309
C	-4.802915	-2.748479	2.398444
H	-5.336112	-3.671679	2.636533
C	-4.180909	-2.610379	1.161795
H	-4.207142	-3.422505	0.433509
C	-3.790880	-0.924763	-1.593672
C	-4.605491	0.194195	-1.391354
H	-4.561448	0.742441	-0.447519
C	-5.483397	0.620891	-2.383548
H	-6.111107	1.497346	-2.208905
C	-5.562888	-0.069533	-3.592701
H	-6.253162	0.262879	-4.371048
C	-4.755429	-1.185184	-3.798995
H	-4.809230	-1.732791	-4.742681
C	-3.871074	-1.610202	-2.807290
H	-3.234537	-2.479838	-2.966823
O	0.116709	1.368753	-0.231868
O	1.303770	-0.561938	-0.390667
O	-2.322160	-2.636771	-0.914551
H	-1.653993	-2.936377	-0.290234
P	-0.114887	-0.279849	0.461339
F	3.883020	-0.604188	-0.623769
F	4.054163	-2.764907	-0.398715

F	3.535869	-2.673502	2.127692
F	2.710352	-0.686982	2.058359
F	4.809099	-0.997909	1.695156
F	0.375616	-2.299759	-2.180717
F	2.125416	-3.582692	-2.061939
F	3.679897	-1.657378	-3.059810
F	2.068329	-0.220260	-3.006455
F	1.910423	-1.977783	-4.236452
C	-0.833215	3.498951	0.217431
C	-1.239627	3.581752	-1.292943
F	-0.460420	4.722814	0.620731
F	-1.991204	3.202537	0.854445
F	-2.112477	2.627234	-1.590007
F	-0.213287	3.480035	-2.114784
F	-1.829939	4.754224	-1.498034
C	2.392150	3.437597	-0.689356
F	1.854827	4.596406	-1.058177
F	2.285019	2.564887	-1.670759
F	3.682905	3.645692	-0.448886
C	1.731810	2.927905	0.616931
F	2.470436	1.874942	1.008893
F	1.901596	3.908451	1.525218

4 (O-apical)

E(scf) = –3944.59911096 a.u.

C	0.608708	-0.395577	1.534341
C	-0.178050	-0.238049	2.675815
H	-1.240567	-0.040850	2.581120
C	0.418265	-0.298931	3.928612
H	-0.193412	-0.158277	4.821218
C	1.790988	-0.522041	4.046956
H	2.254104	-0.566456	5.034605
C	2.579559	-0.674200	2.911901
H	3.653945	-0.832990	3.001702
C	1.978093	-0.598207	1.657768
C	2.688570	-0.677979	0.311783
C	-0.402377	-1.516498	-1.379187
C	0.412555	-1.984481	-2.408126
H	1.403311	-1.563231	-2.543293
C	-0.056559	-2.988960	-3.249671
H	0.581482	-3.355641	-4.055871
C	-1.328735	-3.528519	-3.063000
H	-1.687463	-4.323929	-3.719034

O-mer 5A (anion)

E(scf) = –3944.04573106 a.u.

P	0.093069	0.463689	0.852306
F	2.647844	-2.037511	1.576488
F	4.485954	-1.644487	0.497904
F	3.454936	-4.123139	0.340470
F	3.709263	-3.119213	-1.539712
F	1.728393	-3.396959	-0.715195
F	4.210535	-0.447987	-1.812715
F	2.980974	1.323427	-1.663435
F	1.905937	-1.756508	-2.861593
F	2.785653	-0.110873	-3.916075
F	0.938787	0.166382	-2.856235
F	-3.264630	-0.022112	2.084501
F	-3.991200	-2.035431	1.824778
F	-5.482774	-0.053207	0.815751
F	-4.830219	-1.483062	-0.644905
F	-3.945617	0.489914	-0.586881
F	-2.989813	-3.453591	-0.015190
F	-0.832056	-3.437007	0.051147

C	-2.157840	-3.043881	-2.054684	F	-2.120168	-3.523405	-2.387085
H	-3.164482	-3.440156	-1.927792	F	-0.625719	-2.019393	-2.102456
C	-1.689469	-2.024229	-1.230327	F	-2.708483	-1.475410	-2.138012
C	-2.486076	-1.295250	-0.163143	O	0.097486	1.547800	-0.505241
C	-3.812392	-0.708609	-0.740541	O	1.110105	-0.665127	-0.125695
C	-3.729483	-0.006985	-2.141750	O	-1.326759	-0.362528	0.080095
C	-2.770054	-2.294565	1.017319	C	-0.991293	1.902289	1.420933
C	-3.662559	-1.826443	2.207546	H	-2.045304	1.634781	1.507259
C	-0.086955	1.514327	-0.839729	H	-0.689650	2.444658	2.322631
H	0.943426	1.849420	-0.984659	C	-0.652585	2.583873	0.079561
H	-0.522498	1.404550	-1.841476	C	-1.874481	2.901470	-0.783577
C	-0.907957	2.611334	-0.095568	C	-1.892899	2.485518	-2.127255
C	-0.397253	2.852171	1.334136	H	-1.030894	1.927618	-2.514746
C	0.957651	2.782998	1.669778	C	-2.999947	2.755716	-2.927887
H	1.701632	2.534493	0.915078	H	-3.005022	2.412901	-3.972460
C	1.384684	2.994265	2.977953	C	-4.098802	3.447261	-2.403054
H	2.447759	2.916790	3.214208	H	-4.972104	3.652309	-3.025669
C	0.457847	3.284391	3.977042	C	-4.084217	3.872002	-1.064457
H	0.788867	3.445604	5.005349	H	-4.945695	4.399053	-0.633267
C	-0.895109	3.363558	3.652498	C	-2.975772	3.589044	-0.259587
H	-1.631338	3.593364	4.426207	H	-2.989209	3.900996	0.791795
C	-1.318556	3.151557	2.341563	C	0.211523	3.846948	0.226092
H	-2.376636	3.210411	2.084927	C	1.380988	3.963601	-0.529718
C	-0.767708	3.884458	-0.949443	H	1.643265	3.140077	-1.193432
C	0.430780	4.603593	-1.007657	C	2.201832	5.082472	-0.396749
H	1.288202	4.297168	-0.406546	H	3.120013	5.142754	-0.985326
C	0.548565	5.724794	-1.825189	C	1.863926	6.100391	0.498528
H	1.492322	6.273791	-1.854471	H	2.518389	6.968755	0.609229
C	-0.532947	6.147495	-2.596856	C	0.694047	5.988719	1.251651
H	-0.442474	7.029083	-3.235244	H	0.421472	6.778678	1.957927
C	-1.729131	5.436115	-2.544266	C	-0.123544	4.872665	1.111753
H	-2.584235	5.757760	-3.143282	H	-1.027109	4.793902	1.721887
C	-1.846174	4.310615	-1.729143	C	1.740412	1.160228	1.488450
H	-2.779375	3.750487	-1.686692	C	1.953254	2.173523	2.428025
O	1.773824	-0.323157	-0.651812	H	1.121664	2.611457	2.970513
O	-1.702720	-0.261844	0.303588	C	3.234733	2.650216	2.678860
O	-2.270298	2.301866	-0.068701	H	3.384428	3.452900	3.406592
H	-2.354094	1.415015	0.310705	C	4.328607	2.129376	1.980438
P	0.045904	-0.203051	-0.188689	H	5.332535	2.521495	2.159427
F	-4.291262	0.196623	0.127448	C	4.136990	1.115127	1.055634
F	-4.730843	-1.683149	-0.868949	H	4.977255	0.699395	0.504780
F	-3.944734	-0.893468	-3.105877	C	2.847088	0.632326	0.839004
F	-2.550307	0.557217	-2.361205	C	2.460463	-0.470577	-0.154388
F	-4.663284	0.925831	-2.217006	C	3.148775	-1.793639	0.354862

F	-1.573282	-2.618081	1.532816	C	2.981376	-3.131662	-0.421190
F	-3.333121	-3.426578	0.561226	C	2.944631	-0.021602	-1.582124
F	-4.941671	-1.842400	1.869141	C	2.096020	-0.448137	-2.816408
F	-3.350550	-0.602281	2.619942	C	-0.138561	-0.788371	2.239641
F	-3.487331	-2.662982	3.221597	C	0.601080	-0.885740	3.420181
C	3.880283	0.338251	0.280101	H	1.410860	-0.182972	3.620778
C	4.161579	1.013421	-1.098388	C	0.334941	-1.905388	4.332226
F	5.011806	-0.241055	0.709656	H	0.923999	-1.979774	5.249962
F	3.636544	1.369085	1.114143	C	-0.662136	-2.844505	4.068203
F	3.264547	1.964739	-1.337814	H	-0.855548	-3.655956	4.774837
F	4.141897	0.150538	-2.100651	C	-1.412939	-2.745551	2.900939
F	5.359724	1.579642	-1.055428	H	-2.196572	-3.471833	2.686978
C	3.973788	-2.671792	-1.081532	C	-1.149308	-1.704141	2.011223
F	5.181613	-2.129291	-1.086946	C	-1.920968	-1.416208	0.723468
F	3.384800	-2.409730	-2.240626	C	-3.377435	-1.013836	1.184645
F	4.110378	-3.987652	-0.980412	C	-4.412034	-0.497419	0.150218
C	3.131060	-2.184201	0.134860	C	-1.903908	-2.676217	-0.215411
F	1.993361	-2.900561	0.095177	C	-1.832830	-2.388358	-1.746312
F	3.830708	-2.578586	1.214695				

O-fac 5B (anion)

E(scf) = –3944.05057075 a.u.

P	-0.097033	0.602115	0.525404
F	3.188350	-0.296010	1.864157
F	4.782601	0.788425	0.867977
F	5.049650	-1.871062	1.077654
F	5.075134	-1.112480	-0.930057
F	3.360594	-2.205872	-0.205160
F	4.324782	1.449608	-1.639085
F	2.377931	2.363764	-1.900787
F	3.067569	-0.976648	-2.577809
F	3.261377	0.733976	-3.858032
F	1.350865	0.251402	-3.008668
F	-3.002667	-1.218939	1.574949
F	-2.684919	-3.346349	1.803673
F	-4.718051	-2.553113	0.215765
F	-3.251852	-3.809793	-0.721745
F	-3.348506	-1.713035	-1.212166
F	-0.813022	-4.414069	0.401144
F	1.034342	-3.306207	0.574622
F	0.395954	-4.447503	-1.838158
F	0.870918	-2.355736	-1.841638
F	-1.163230	-2.995467	-2.113191

O-mer 5C (anion)

E(scf) = –3944.03473957 a.u.

P	-0.022939	-0.249198	-0.050620
F	2.519091	-0.235075	-2.462599
F	4.114305	-1.650989	-2.114242
F	4.817395	0.834777	-2.729409
F	5.552322	0.160704	-0.831163
F	3.950227	1.610251	-0.927122
F	4.701697	-2.237209	0.277280
F	2.996821	-2.694240	1.519325
F	4.394083	0.498135	1.420146
F	5.184861	-1.190756	2.486445
F	3.193003	-0.507833	2.879061
F	-2.755670	1.076207	1.743711
F	-4.425385	-0.262506	2.020283
F	-5.013718	2.090822	0.918555
F	-5.461587	0.392400	-0.321773
F	-3.803329	1.682068	-0.808614
F	-4.654591	-2.292247	0.548869
F	-2.852420	-3.167084	-0.237284
F	-5.420342	-1.995742	-1.723406
F	-3.569823	-2.733040	-2.505187
F	-3.833316	-0.630963	-2.195870

O	-1.629026	1.317405	1.006180	O	-0.149404	1.228039	0.872767
O	1.462835	-0.024468	-0.177958	O	1.808791	-0.202262	0.282443
O	-0.856025	-0.942349	-0.119939	O	-1.818800	-0.372306	-0.462876
C	-0.716021	1.406554	-1.045828	C	0.085702	1.114017	-1.346137
H	-0.049698	2.186110	-1.430860	H	0.996850	1.146978	-1.944878
H	-0.944801	0.679843	-1.830643	H	-0.802198	1.115193	-1.988868
C	-1.937817	1.900758	-0.254692	C	0.027160	2.137153	-0.197419
C	-2.070283	3.422645	-0.126272	C	1.308070	2.954660	0.000578
C	-2.668802	3.956414	1.020999	C	2.016014	2.859763	1.198644
H	-2.983673	3.270808	1.810534	H	1.669710	2.141341	1.941567
C	-2.833702	5.329705	1.168200	C	3.149570	3.641816	1.414093
H	-3.293854	5.726667	2.076818	H	3.700098	3.545596	2.353418
C	-2.409028	6.199846	0.162059	C	3.592535	4.527584	0.433957
H	-2.532444	7.279545	0.277430	H	4.484920	5.136126	0.601609
C	-1.826601	5.677798	-0.989817	C	2.892403	4.623143	-0.769092
H	-1.488753	6.346981	-1.785123	H	3.233867	5.307763	-1.549915
C	-1.661353	4.299098	-1.131914	C	1.758259	3.843601	-0.980325
H	-1.197071	3.904895	-2.038273	H	1.212629	3.929635	-1.923512
C	-3.286347	1.405079	-0.773522	C	-1.123345	3.139426	-0.261581
C	-4.274407	1.008958	0.129373	C	-1.684205	3.607782	0.929643
H	-4.027076	0.984947	1.190434	H	-1.322676	3.193485	1.871501
C	-5.529673	0.611153	-0.323270	C	-2.701097	4.557084	0.911362
H	-6.284134	0.282340	0.395447	H	-3.142551	4.895518	1.852034
C	-5.816980	0.608556	-1.687548	C	-3.165626	5.067792	-0.301404
H	-6.798383	0.285747	-2.043900	H	-3.968939	5.808663	-0.316143
C	-4.837896	1.011346	-2.594454	C	-2.600453	4.620202	-1.492815
H	-5.048785	1.007516	-3.666933	H	-2.958577	5.007752	-2.450050
C	-3.582677	1.408803	-2.138221	C	-1.588062	3.661151	-1.470321
H	-2.818115	1.717911	-2.855505	H	-1.166786	3.301677	-2.412202
C	0.940995	2.069879	1.092519	C	0.418136	-1.813603	-1.019990
C	0.504494	3.160441	1.847622	C	-0.436135	-2.589579	-1.799056
H	-0.523667	3.174435	2.207304	H	-1.434600	-2.227173	-2.012246
C	1.372442	4.210166	2.134849	C	-0.019141	-3.816398	-2.310440
H	1.018889	5.062832	2.720198	H	-0.712682	-4.414301	-2.907003
C	2.687046	4.181593	1.663481	C	1.268240	-4.285013	-2.048738
H	3.364729	5.013027	1.872533	H	1.588930	-5.259908	-2.423862
C	3.138735	3.091935	0.925091	C	2.160551	-3.487123	-1.337319
H	4.162288	3.067567	0.551445	H	3.187911	-3.816860	-1.178122
C	2.259677	2.038358	0.665492	C	1.731180	-2.251223	-0.856369
C	2.574897	0.765934	-0.129728	C	2.618204	-1.154650	-0.269355
C	3.701315	-0.000248	0.660277	C	3.424787	-0.633237	-1.550281
C	4.287689	-1.332100	0.121586	C	4.450277	0.528460	-1.481366
C	2.997569	1.205874	-1.578348	C	3.591165	-1.701919	0.829019
C	2.648073	0.262143	-2.764448	C	4.086557	-0.685403	1.916493

C	0.070325	-0.367716	2.125865	C	-0.517225	-1.212770	1.494243
C	0.602608	0.094986	3.331696	C	0.315648	-1.635525	2.527058
H	0.965802	1.119684	3.415406	H	1.366904	-1.388221	2.498443
C	0.696114	-0.753535	4.431917	C	-0.189606	-2.364075	3.600968
H	1.117628	-0.379907	5.368639	H	0.486211	-2.688982	4.396240
C	0.271232	-2.079621	4.338278	C	-1.546767	-2.677081	3.662612
H	0.361968	-2.749800	5.196590	H	-1.945387	-3.256240	4.499125
C	-0.267412	-2.549210	3.145033	C	-2.398639	-2.235919	2.655368
H	-0.600424	-3.583873	3.057764	H	-3.464552	-2.458376	2.699668
C	-0.372670	-1.679001	2.060358	C	-1.875589	-1.502067	1.590064
C	-0.979976	-2.021675	0.698712	C	-2.691483	-0.896123	0.447823
C	-2.507072	-2.301169	0.959254	C	-3.572405	0.243868	1.095737
C	-3.460063	-2.587010	-0.234708	C	-4.462892	1.125554	0.184061
C	-0.214243	-3.243327	0.081242	C	-3.568455	-2.030550	-0.208717
C	-0.031459	-3.233031	-1.464072	C	-4.102055	-1.820563	-1.690869

O-mer 5D (anion)

E(scf) = –3944.05327915 a.u.

P	-0.372088	-0.392689	0.014563
F	3.048506	0.440728	-1.022615
F	4.182355	-1.333484	-1.541276
F	5.273244	0.318059	0.270712
F	4.939040	-1.688222	0.961725
F	3.700667	-0.073254	1.679530
F	3.440024	-3.566998	-0.425231
F	1.297880	-3.856840	-0.535944
F	2.856114	-2.545122	2.286720
F	2.655125	-4.612797	1.746531
F	0.906894	-3.386726	1.951932
F	2.155919	2.083165	1.015600
F	1.262237	4.006984	1.462023
F	3.285745	3.981561	-0.299915
F	1.440960	4.772386	-1.063857
F	2.139713	2.839505	-1.711756
F	-0.941741	4.562895	0.205367
F	-2.389501	2.975546	0.404312
F	-2.243731	4.362067	-1.962467
F	-2.156020	2.222015	-2.068496
F	-0.383257	3.389167	-2.414890
O	-2.041046	-0.011012	-0.370449
O	1.272783	-0.957397	0.498494
O	0.086976	1.283807	-0.517812
C	-1.313976	-2.003328	0.360913

O-mer 5A (K^+_2thf)

E(scf) = –5008.38270062 a.u.

K	-1.328836	-0.388786	-1.562549
P	1.378987	0.264619	0.650814
O	2.341669	1.702990	0.550023
O	-0.270806	1.135828	0.308724
O	0.323649	-1.272249	0.497840
C	1.751521	0.429117	-1.190002
H	2.358230	-0.406770	-1.549837
H	0.929512	0.607468	-1.888709
C	2.545058	1.700177	-0.862392
C	1.995350	2.969575	-1.508740
C	1.987329	4.165449	-0.790306
H	2.311374	4.153029	0.250227
C	1.540979	5.343862	-1.382498
H	1.523061	6.267713	-0.800247
C	1.103306	5.344345	-2.706109
H	0.746490	6.267778	-3.167541
C	1.126275	4.157741	-3.436423
H	0.792663	4.147133	-4.476799
C	1.573176	2.979842	-2.840673
H	1.594439	2.057930	-3.428305
C	4.036958	1.645888	-1.192769
C	4.943769	2.320137	-0.368323
H	4.567377	2.831908	0.519750
C	6.304679	2.319319	-0.659860
H	7.000452	2.844014	-0.000911

H	-1.061604	-2.781473	-0.369585	C	6.780863	1.650432	-1.788380
H	-1.263627	-2.438576	1.362824	H	7.848923	1.647105	-2.016835
C	-2.610298	-1.238811	0.041307	C	5.882809	0.989088	-2.622412
C	-3.470126	-1.812208	-1.082324	H	6.243796	0.464000	-3.509763
C	-4.150407	-0.930550	-1.929299	C	4.519654	0.989288	-2.325653
H	-4.008801	0.141866	-1.782838	H	3.826738	0.466277	-2.989241
C	-4.965003	-1.413906	-2.949347	F	-2.894446	1.012535	0.093678
H	-5.483501	-0.711656	-3.607211	F	-2.114773	-0.424754	1.515367
C	-5.115833	-2.788903	-3.137980	F	-4.523151	0.269199	2.008689
H	-5.751750	-3.168839	-3.941488	F	-4.098450	2.369084	2.076567
C	-4.441964	-3.672970	-2.298268	F	-3.263664	1.047525	3.563110
H	-4.544162	-4.751620	-2.442047	C	-0.984434	1.639615	1.360105
C	-3.623040	-3.185761	-1.278969	C	-0.201851	1.374667	2.648216
H	-3.084258	-3.887035	-0.637075	C	-0.537404	1.834506	3.921954
C	-3.501200	-1.037291	1.273200	H	-1.426391	2.439965	4.083949
C	-3.846743	0.251393	1.680071	C	0.287926	1.530816	4.999977
H	-3.459654	1.093539	1.108488	H	0.026663	1.886851	5.998583
C	-4.625860	0.448510	2.818846	C	1.445084	0.782858	4.798143
H	-4.869369	1.466286	3.133510	H	2.097182	0.542478	5.640670
C	-5.074347	-0.640838	3.563418	C	1.783306	0.349920	3.519294
H	-5.677546	-0.485775	4.461623	H	2.698077	-0.224332	3.379922
C	-4.740842	-1.933188	3.155767	C	0.958216	0.641219	2.431797
H	-5.084523	-2.796143	3.732183	C	-2.366862	0.880359	1.349537
C	-3.961204	-2.127405	2.017926	C	-3.576916	1.172836	2.285541
H	-3.695595	-3.142821	1.711607	C	-1.129556	3.181566	1.162913
C	0.124945	-0.896992	-1.714047	F	-1.895824	3.716520	2.145451
C	-0.641212	-0.750803	-2.869815	F	0.086156	3.717581	1.274383
H	-1.595456	-0.227491	-2.812941	C	-1.739548	3.720364	-0.171005
C	-0.184039	-1.281065	-4.073492	F	-3.066780	3.595401	-0.162300
H	-0.786307	-1.169192	-4.978763	F	-1.459260	5.012169	-0.273816
C	1.033918	-1.964008	-4.127404	F	-1.278062	3.102555	-1.248872
H	1.383488	-2.389765	-5.071223	F	1.285293	-2.434770	-1.647537
C	1.807615	-2.103249	-2.978587	F	1.740738	-4.328978	-0.690242
H	2.758962	-2.635009	-3.014067	F	-1.452369	-3.038187	-1.255903
C	1.344077	-1.551459	-1.783803	F	-0.226616	-4.260083	-2.526872
C	2.055233	-1.588955	-0.426536	F	-0.813129	-4.992870	-0.600462
C	3.389419	-0.778422	-0.592778	F	-1.179716	-3.340480	1.413634
C	4.325494	-0.552505	0.624714	F	0.579790	-4.580806	1.761599
C	2.259555	-3.080515	0.009478	F	-0.525908	-1.709212	3.386508
C	2.165688	-3.385030	1.537509	F	1.373706	-2.688636	3.696664
C	-0.494878	0.367682	1.726968	F	-0.461081	-3.774218	3.962846
C	-0.722432	-0.294387	2.933409	C	0.912157	-2.493219	0.681933
H	-0.717181	-1.383666	2.973194	C	2.384888	-2.285485	1.041138
C	-0.972203	0.430322	4.095824	C	3.303697	-3.286265	1.367544

H	-1.164380	-0.098163	5.032705
C	-0.996876	1.825425	4.063563
H	-1.215213	2.393210	4.971228
C	-0.727761	2.496195	2.873840
H	-0.725089	3.586365	2.842416
C	-0.458663	1.753270	1.725332
C	-0.075975	2.318415	0.353479
C	1.321434	3.016163	0.540009
C	2.048350	3.650047	-0.678780
C	-1.202163	3.286117	-0.155022
C	-1.484414	3.291909	-1.688275
H	2.998910	-4.331009	1.411031
C	4.620057	-2.933637	1.646151
H	5.344816	-3.709736	1.900955
C	5.011224	-1.594364	1.601786
H	6.045948	-1.318859	1.817442
C	4.082398	-0.604601	1.293990
H	4.374687	0.444727	1.285365
C	2.758228	-0.946122	1.012398
C	0.878721	-3.300387	-0.691681
C	-0.440507	-3.914855	-1.256649
C	0.126341	-3.306801	1.752312
C	0.140786	-2.836591	3.232834
C	-4.705137	0.533496	-2.358614
C	-4.646587	-1.411129	-1.039510
C	-5.768790	0.668080	-1.274734
H	-5.156046	0.419219	-3.360788
H	-4.013380	1.389888	-2.388214
C	-6.034972	-0.792994	-0.910307
H	-4.089278	-1.339063	-0.090406
H	-4.661960	-2.465708	-1.352038
H	-5.361956	1.212302	-0.411408
H	-6.662610	1.201070	-1.626014
H	-6.455355	-0.918643	0.096222
H	-6.730316	-1.250458	-1.631632
O	-3.971184	-0.646557	-2.039069
C	-2.125252	-1.444307	-4.798084
C	0.194778	-1.588466	-4.716589
C	-1.783818	-2.853107	-5.258982
H	-2.329477	-0.779765	-5.659929
H	-2.972349	-1.386674	-4.099492
C	-0.310802	-2.700155	-5.653609
H	0.837001	-1.975922	-3.913895
H	0.755236	-0.811632	-5.263209
H	-1.890875	-3.554700	-4.418781
H	-2.419606	-3.202901	-6.083893
H	0.259471	-3.631338	-5.536780
H	-0.226689	-2.387870	-6.705364
O	-0.960370	-1.012070	-4.110003

O-fac 5B (K^+_2thf)

E(scf) = –5008.40235734 a.u.

K	-0.752112	1.649745	-0.694033
P	1.017906	-0.735824	1.159110

O-mer 5C (K^+_2thf)

E(scf) = –5008.37330790 a.u.

K	-1.485825	2.067416	-0.116269
P	0.519565	-0.904265	0.372004

O	1.299199	0.975555	0.854387	O	0.713976	0.849897	0.784123
O	-0.784701	-0.275666	1.080982	O	-1.329587	-0.570172	0.410681
O	0.798622	-0.941935	-0.640046	O	2.274309	-1.221229	0.212610
C	1.195555	0.011285	2.871394	C	0.746533	-0.857468	2.227253
H	0.257210	-0.040073	3.424731	H	-0.117839	-1.241209	2.771119
H	1.998499	-0.374153	3.509038	H	1.647012	-1.407329	2.521826
C	1.475634	1.372877	2.210960	C	0.898629	0.663346	2.192934
C	2.899774	1.873834	2.448386	C	2.256349	1.170971	2.675363
C	3.807722	1.973275	1.394272	C	2.859279	2.271483	2.066890
H	3.484868	1.678241	0.396166	H	2.385991	2.708288	1.190039
C	5.112391	2.409935	1.626474	C	4.060903	2.786706	2.544427
H	5.815767	2.473795	0.792906	H	4.525032	3.635589	2.037805
C	5.522010	2.751288	2.913161	C	4.677041	2.210098	3.653011
H	6.544822	3.089151	3.094839	H	5.622954	2.607490	4.027375
C	4.615721	2.657692	3.971001	C	4.076863	1.118342	4.278143
H	4.926052	2.924963	4.983840	H	4.549563	0.657213	5.148315
C	3.313501	2.224595	3.737755	C	2.874986	0.606265	3.793856
H	2.606183	2.158317	4.569292	H	2.414079	-0.246724	4.297509
C	0.489633	2.494423	2.532145	C	-0.153069	1.453744	2.981276
C	0.368922	3.544666	1.613304	C	-0.407331	2.787649	2.633222
H	1.003242	3.548678	0.723984	H	0.162299	3.247982	1.822629
C	-0.543856	4.574376	1.817037	C	-1.353972	3.546027	3.316168
H	-0.633805	5.369252	1.072925	H	-1.536601	4.580569	3.015369
C	-1.333944	4.588146	2.968465	C	-2.050855	2.989871	4.389898
H	-2.052077	5.394121	3.134676	H	-2.794578	3.579264	4.930288
C	-1.193297	3.569714	3.906636	C	-1.772102	1.682409	4.776882
H	-1.803988	3.571448	4.812048	H	-2.298070	1.238898	5.625049
C	-0.289720	2.527960	3.687899	C	-0.830153	0.924045	4.080537
H	-0.210620	1.726449	4.424512	H	-0.630135	-0.098539	4.402369
F	-2.911376	-0.177896	-0.432291	F	-3.436194	-0.314667	-1.062640
F	-1.687013	-1.898267	-0.923500	F	-2.297823	-2.012577	-1.823569
F	-4.173099	-2.242423	-1.452669	F	-4.757432	-2.247025	-2.315340
F	-4.829560	-1.843918	0.548640	F	-5.409841	-1.976756	-0.295259
F	-3.582517	-3.555078	0.145301	F	-4.239926	-3.706814	-0.825031
C	-1.736399	-1.221601	1.338729	C	-2.210327	-1.619993	0.498691
C	-1.025168	-2.501200	1.784178	C	-1.398849	-2.912475	0.577003
C	-1.632386	-3.650640	2.289415	C	-1.912886	-4.177185	0.867566
H	-2.713459	-3.712341	2.399292	H	-2.976033	-4.322444	1.044671
C	-0.841189	-4.731178	2.669834	C	-1.049619	-5.264509	0.956103
H	-1.312173	-5.634118	3.063583	H	-1.447747	-6.255593	1.183084
C	0.544806	-4.655003	2.550783	C	0.318570	-5.073982	0.782177
H	1.166889	-5.502350	2.847550	H	1.007203	-5.916379	0.878635
C	1.142774	-3.497974	2.057604	C	0.820741	-3.803672	0.512208
H	2.228807	-3.453342	1.968883	H	1.891470	-3.660386	0.442906

C	0.361046	-2.409593	1.666651	C	-0.031765	-2.707349	0.374709
C	-2.531093	-1.419352	-0.009896	C	-3.086126	-1.608364	-0.816861
C	-3.811309	-2.290029	-0.169589	C	-4.407184	-2.412333	-1.038036
C	-2.628535	-0.668391	2.497819	C	-3.068576	-1.437828	1.792874
F	-3.605266	-1.543839	2.820408	F	-4.019744	-2.396609	1.868568
F	-1.850116	-0.532405	3.583332	F	-2.269871	-1.589560	2.859084
C	-3.347285	0.712002	2.313346	C	-3.829784	-0.094386	2.029707
F	-4.466925	0.573243	1.611133	F	-4.863845	0.030295	1.205031
F	-3.673951	1.180970	3.510509	F	-4.289771	-0.083425	3.270899
F	-2.596411	1.623729	1.705671	F	-3.059807	0.978603	1.866418
F	2.367825	0.997195	-1.620752	F	2.704970	-3.279668	-1.610716
F	3.410548	-0.303292	-3.005956	F	4.341711	-2.221049	-2.526492
F	-0.003536	0.423151	-3.086111	F	4.025432	-3.307006	0.787816
F	1.622828	1.513117	-3.971433	F	5.130390	-4.096862	-0.877542
F	1.284109	-0.524042	-4.538713	F	5.639501	-2.173578	-0.062373
F	0.371374	-2.326809	-2.926973	F	4.331763	0.244861	0.455418
F	2.489376	-2.785405	-3.156643	F	5.101081	-0.091656	-1.539344
F	0.159900	-3.908450	-0.832177	F	2.326773	1.927464	-1.054873
F	2.290015	-4.242228	-0.734051	F	3.774340	1.718500	-2.620863
F	1.175073	-4.860081	-2.463649	F	4.371103	2.486749	-0.710438
C	1.874690	-1.300206	-1.403302	C	2.918675	-1.017906	-0.979385
C	3.080235	-1.518221	-0.489974	C	1.867548	-0.691159	-2.029236
C	4.348590	-1.934748	-0.898172	C	2.127880	-0.504320	-3.385614
H	4.548480	-2.165392	-1.943569	H	3.130436	-0.661533	-3.781559
C	5.358944	-2.059371	0.049204	C	1.099612	-0.093660	-4.226187
H	6.355376	-2.382334	-0.259115	H	1.287058	0.047096	-5.292374
C	5.095927	-1.770941	1.388013	C	-0.162867	0.147711	-3.691447
H	5.889432	-1.858405	2.133184	H	-0.976249	0.469907	-4.345711
C	3.822369	-1.369579	1.781425	C	-0.406531	-0.050222	-2.332466
H	3.644586	-1.152519	2.834804	H	-1.411284	0.124954	-1.960344
C	2.793915	-1.243212	0.843786	C	0.599405	-0.508136	-1.479079
C	2.235344	-0.104775	-2.382623	C	3.648751	-2.350998	-1.378317
C	1.253588	0.311708	-3.520434	C	4.632190	-2.983393	-0.346152
C	1.512856	-2.558529	-2.249895	C	3.980504	0.159270	-0.825705
C	1.279276	-3.916684	-1.529584	C	3.583609	1.598183	-1.308426
C	-4.156575	2.418030	-1.631311	C	-4.763537	2.258872	-1.820673
C	-3.239846	0.994895	-3.259352	C	-3.106811	2.357900	-3.402108
C	-5.209397	1.374636	-1.987494	C	-5.202412	1.313122	-2.958815
H	-4.443520	3.423125	-1.990660	H	-5.323355	3.210049	-1.847926
H	-3.963653	2.482343	-0.549857	H	-4.881241	1.817490	-0.822009
C	-4.759833	0.940024	-3.382926	C	-3.931600	1.144026	-3.809519
H	-2.833959	0.034128	-2.902887	H	-2.021542	2.235931	-3.523363
H	-2.732983	1.256462	-4.200202	H	-3.418321	3.261591	-3.962711
H	-5.157798	0.530734	-1.285984	H	-5.563610	0.350458	-2.576783

H	-6.230119	1.779741	-1.962488
H	-5.119326	-0.059391	-3.662396
H	-5.113471	1.655445	-4.142140
O	-2.962805	2.006789	-2.291209
C	-0.767930	4.539483	-2.814480
C	1.412251	4.282435	-2.055379
C	0.099189	4.524588	-4.065058
H	-1.034122	5.575111	-2.525133
H	-1.687784	3.943143	-2.893481
C	1.484111	4.842364	-3.488571
H	2.010527	3.369888	-1.925434
H	1.748440	5.021918	-1.308624
H	0.086231	3.519961	-4.512403
H	-0.228988	5.245570	-4.826577
H	2.298575	4.389361	-4.069278
H	1.652879	5.929529	-3.471113
O	0.048051	3.944290	-1.819791

H	-6.015780	1.764853	-3.544417
H	-3.401977	0.221554	-3.531961
H	-4.134785	1.110819	-4.888398
O	-3.378517	2.518600	-2.021992
C	-0.946692	4.937854	-1.991388
C	0.907139	4.772756	-0.641442
C	0.178099	4.520002	-2.929007
H	-1.090350	6.036035	-2.007822
H	-1.917330	4.459532	-2.179262
C	1.416016	4.876500	-2.094482
H	1.368534	3.942198	-0.091435
H	1.085458	5.703402	-0.076538
H	0.133748	3.432864	-3.108271
H	0.148314	5.029019	-3.902264
H	2.260596	4.204295	-2.288748
H	1.748287	5.901414	-2.315515
O	-0.492294	4.515976	-0.717999

O-mer 5D (K^+_2thf)

E(scf) = –5008.36719136 a.u.

K	3.388737	0.893198	-0.509521
P	-0.601485	0.144978	0.628230
O	1.163550	0.533498	0.743617
O	-2.361679	-0.099036	0.718295
O	-0.231273	-0.828980	-0.891393
C	-0.413461	1.273222	2.138004
H	-0.831484	2.263093	1.942879
H	-0.821120	0.929724	3.094121
C	1.112608	1.202004	2.001829
C	1.746877	0.362633	3.110909
C	2.436685	-0.814643	2.827005
H	2.483789	-1.157561	1.793723
C	2.995076	-1.577895	3.852842
H	3.511474	-2.510261	3.611721
C	2.871827	-1.168964	5.177861
H	3.300139	-1.769698	5.983162
C	2.185167	0.011153	5.470555
H	2.078538	0.339401	6.506977
C	1.629118	0.769332	4.444226
H	1.090134	1.691106	4.680517
C	1.867174	2.539436	1.859867
C	3.224814	2.632927	2.202667

Compound analogue to the reported one by *Matsukawa et. al. (JACS, 2002)* (anion)

E(scf) = –3403.88327256 a.u.

P	0.286717	0.825234	-1.394454
O	0.171297	0.733824	-2.887800
O	-1.213916	-0.180606	-1.096317
O	0.967759	-0.361406	-0.318301
F	-1.771195	-1.925037	0.673857
F	-1.054797	-0.220926	1.809608
F	-2.825943	-1.541389	3.107188
F	-4.271928	-1.509753	1.524666
F	-3.701720	0.324271	2.508303
C	-2.153125	0.255786	-0.232936
C	-1.826844	1.706980	0.140305
C	-2.624808	2.583401	0.873042
H	-3.596106	2.265871	1.248029
C	-2.171938	3.877620	1.114819
H	-2.793267	4.571297	1.686593
C	-0.928020	4.282765	0.632642
H	-0.565828	5.294481	0.831586
C	-0.142225	3.399160	-0.103488
H	0.835729	3.722935	-0.459559
C	-0.594759	2.104814	-0.370791

H	3.720104	1.781335	2.675458
C	3.953560	3.802261	1.976984
H	5.006879	3.846334	2.263767
C	3.333617	4.913867	1.409416
H	3.895356	5.835920	1.243952
C	1.984338	4.837844	1.064663
H	1.480860	5.701637	0.624445
C	1.263629	3.665506	1.284861
H	0.213530	3.634881	0.994938
F	-4.637190	0.630056	1.973360
F	-3.080726	2.131977	2.007410
F	-5.667605	2.951447	2.033300
F	-5.911720	2.314777	-0.004276
F	-4.400866	3.763065	0.501530
C	-3.207415	0.774422	0.077426
C	-2.357096	1.722881	-0.771935
C	-2.829473	2.694423	-1.657875
H	-3.896558	2.853513	-1.800482
C	-1.919863	3.456378	-2.382134
H	-2.281311	4.215855	-3.078280
C	-0.551101	3.241770	-2.222326
H	0.159207	3.839449	-2.796847
C	-0.091159	2.267045	-1.341053
H	0.979714	2.108662	-1.222229
C	-0.995049	1.501960	-0.604737
C	-3.991085	1.529652	1.215421
C	-5.019440	2.659680	0.911454
C	-4.110043	-0.082599	-0.876802
F	-4.832777	0.703864	-1.705684
F	-3.280771	-0.794762	-1.645996
C	-5.147261	-1.075106	-0.260649
F	-6.243929	-0.413350	0.102525
F	-5.494589	-1.951388	-1.199081
F	-4.692956	-1.737515	0.783271
F	2.448515	-1.589556	-0.455638
F	2.078384	-3.530043	-1.303636
F	1.829953	-0.336674	-2.696733
F	3.253968	-1.917971	-2.967896
F	1.239565	-2.166900	-3.673458
F	-1.248267	-2.259385	-2.700793
F	-0.139067	-4.059820	-2.240639
F	-2.586125	-2.881238	-0.092056
F	-1.712295	-4.813064	-0.436502
F	-2.963563	-3.920206	-1.936528
C	-2.075006	-0.677928	1.053823
C	-3.252824	-0.844981	2.053723
C	-3.504387	0.244664	-1.002188
F	-4.548613	0.479253	-0.165120
F	-3.494251	1.242500	-1.901365
C	-3.854477	-1.033303	-1.812624
F	-3.775091	-2.129057	-1.066765
F	-5.124550	-0.925742	-2.230546
F	-3.091871	-1.175954	-2.873692
F	2.583025	-1.483260	-2.132162
F	4.237534	-1.702502	-0.743544
F	1.067540	-3.126802	-0.368189
F	2.793467	-3.923856	-1.371799
F	2.905236	-3.441455	0.717400
F	1.713437	-1.425754	1.967109
F	3.802625	-0.859325	1.736150
F	1.174685	1.427993	1.922687
F	3.301813	1.648800	2.155295
F	2.184882	0.478284	3.566647
C	2.320055	-0.390669	-0.079787
C	2.957081	0.855755	-0.684410
C	4.309017	1.208478	-0.653476
H	5.032917	0.600828	-0.109463
C	4.712588	2.350890	-1.334444
H	5.763228	2.650768	-1.319040
C	3.778056	3.102338	-2.058138
H	4.107785	3.982621	-2.616836
C	2.439844	2.723692	-2.085639
H	1.718374	3.284596	-2.685613
C	2.009662	1.607009	-1.359435
C	2.889825	-1.641170	-0.838791
C	2.378471	-3.055799	-0.444281
C	2.529161	-0.493734	1.454898
C	2.280771	0.804401	2.276992

C	0.151863	-2.130958	-0.786895
C	0.106313	-2.529765	0.688345
C	0.449513	-3.774653	1.212122
H	0.845638	-4.560289	0.567604
C	0.241105	-4.016959	2.568022
H	0.502033	-4.988503	2.992850
C	-0.334659	-3.031489	3.368990
H	-0.528735	-3.230832	4.425004
C	-0.655488	-1.786924	2.831517
H	-1.097805	-1.026966	3.475861
C	-0.399741	-1.512653	1.489722
C	1.626933	-2.264035	-1.306215
C	1.964357	-1.663590	-2.701428
C	-0.804730	-3.014514	-1.693563
C	-2.050381	-3.658966	-1.009209
C	3.955004	3.931070	-2.105088
C	2.792837	2.698527	-3.712277
C	2.935431	4.878453	-2.714062
H	4.967387	4.111663	-2.514012
H	4.005747	3.985768	-1.007693
C	2.650445	4.189469	-4.051707
H	1.820013	2.202715	-3.575089
H	3.352096	2.145103	-4.483426
H	2.035538	4.906703	-2.079356
H	3.311411	5.904762	-2.823559
H	1.660791	4.430171	-4.463991
H	3.400145	4.490311	-4.799126
O	3.500119	2.636239	-2.471348
C	5.943455	-1.570856	-0.984008
C	5.641486	-1.307364	1.248668
C	5.498581	-2.961826	-0.499522
H	7.044401	-1.507435	-1.064554
H	5.510582	-1.280780	-1.950944
C	5.178761	-2.743482	0.995675
H	5.044441	-0.770627	1.998392
H	6.703590	-1.275816	1.558340
H	4.610829	-3.304084	-1.045000
H	6.291889	-3.705963	-0.654347
H	4.097593	-2.831933	1.173016
H	5.686727	-3.460978	1.654266
O	5.489593	-0.654679	-0.000711

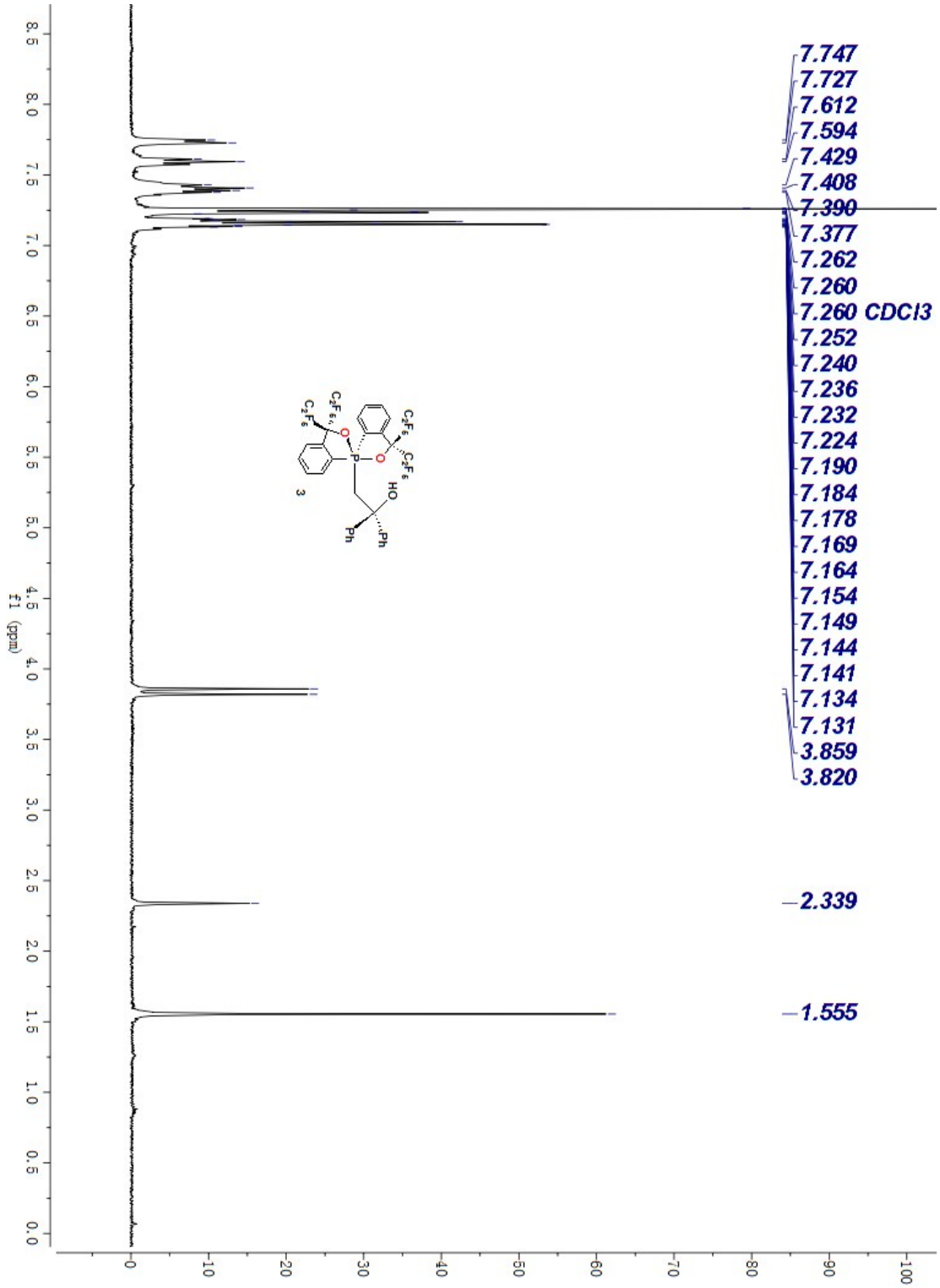
Compound analogue to the reported one by *Matsukawa et. al. (JACS, 2002)*

(K^+_2thf)
E(scf) = –4468.23668582 a.u.

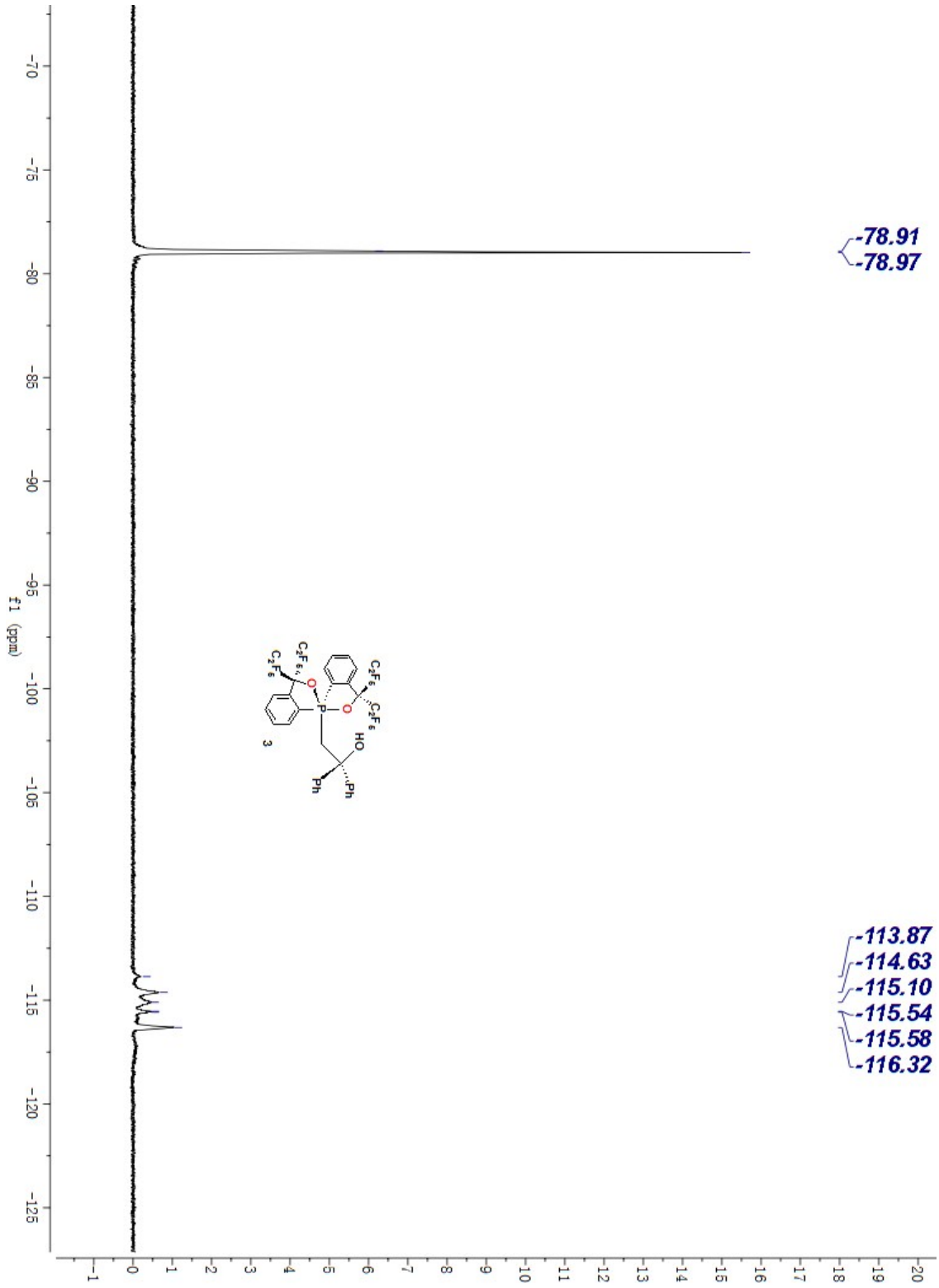
K	0.117274	1.997049	-1.399936
P	-0.496609	-1.199499	-1.446013
O	-0.512759	-0.280024	-2.647799
O	1.085202	-0.339962	-0.831747
O	-1.087878	-0.607135	0.065140
F	2.276395	0.627398	1.197518
F	1.305726	-1.238189	1.748091
F	3.401658	-0.714855	3.174562
F	4.697453	-0.508890	1.476625
F	3.806179	-2.419085	1.931069
C	2.141747	-1.084315	-0.437152
C	1.783613	-2.559408	-0.654289
C	2.614986	-3.655182	-0.431269
H	3.622940	-3.520413	-0.046716
C	2.153662	-4.937678	-0.715104
H	2.804243	-5.796515	-0.537781
C	0.868997	-5.122130	-1.219203
H	0.501319	-6.127668	-1.433481
C	0.047356	-4.022736	-1.450877
H	-0.961059	-4.185605	-1.827795
C	0.505150	-2.729122	-1.185524
C	2.349386	-0.721777	1.084172
C	3.600681	-1.107590	1.920002
C	3.341931	-0.774438	-1.389171
F	4.450243	-1.444616	-0.996450
F	3.010062	-1.209914	-2.613170
C	3.799500	0.694520	-1.601546
F	4.257338	1.241373	-0.483267
F	4.778565	0.710882	-2.495486
F	2.817064	1.469492	-2.067546
F	-2.940146	1.026036	-0.907266
F	-4.476570	0.403619	0.500677
F	-1.430270	1.938084	1.230499
F	-3.365983	2.813083	0.896425
F	-3.082844	1.467193	2.540226
F	-1.628048	-0.695054	2.640332
F	-3.679823	-1.371470	2.344524
F	-0.775234	-3.100928	1.459593
F	-2.831143	-3.742420	1.466137
F	-1.877660	-3.171192	3.305323
C	-2.407554	-0.836734	0.410882

C	-3.045270	-1.740954	-0.636843
C	-4.360206	-2.213591	-0.647611
H	-5.033767	-2.019875	0.187171
C	-4.794624	-2.937547	-1.751204
H	-5.816319	-3.321687	-1.778769
C	-3.934718	-3.157087	-2.833809
H	-4.295440	-3.701410	-3.709629
C	-2.628716	-2.679817	-2.803668
H	-1.963994	-2.835653	-3.656934
C	-2.165748	-1.993977	-1.676174
C	-3.153235	0.546587	0.337531
C	-2.738321	1.702621	1.289288
C	-2.426349	-1.425799	1.846259
C	-1.960325	-2.900144	2.007354
C	2.771083	4.112784	0.218916
C	1.146135	3.533058	1.801843
C	3.495613	3.799617	1.519359
H	2.751794	5.202138	0.023656
H	3.203033	3.612841	-0.657995
C	2.385189	4.037060	2.542900
H	0.932602	2.480333	2.037348
H	0.244636	4.127167	2.020924
H	3.810478	2.746546	1.528534
H	4.381333	4.429974	1.677436
H	2.545906	3.505910	3.490702
H	2.295317	5.111486	2.768048
O	1.445389	3.633228	0.406749
C	-0.983475	5.403203	-1.032244
C	-2.764877	4.283362	-1.999242
C	-2.193164	5.774007	-0.186725
H	-0.757555	6.195656	-1.772852
H	-0.073724	5.182592	-0.457105
C	-3.351354	5.408537	-1.123576
H	-3.207552	3.301428	-1.784419
H	-2.897261	4.492280	-3.074367
H	-2.215947	5.151235	0.719650
H	-2.199515	6.829337	0.119272
H	-4.248542	5.085307	-0.579246
H	-3.632750	6.273349	-1.742802
O	-1.376013	4.210503	-1.689746

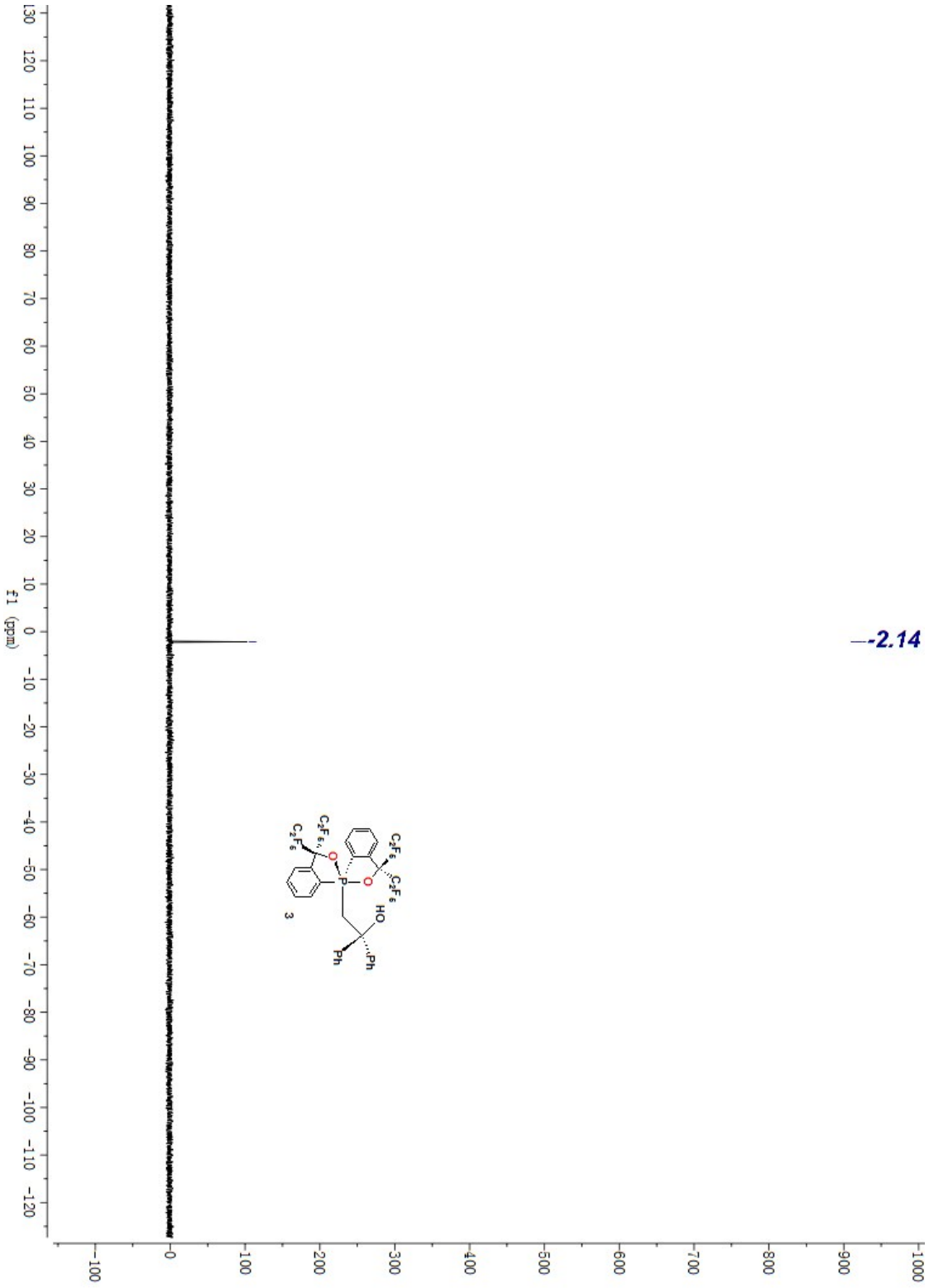
Appendixes 2: NMR Spectra



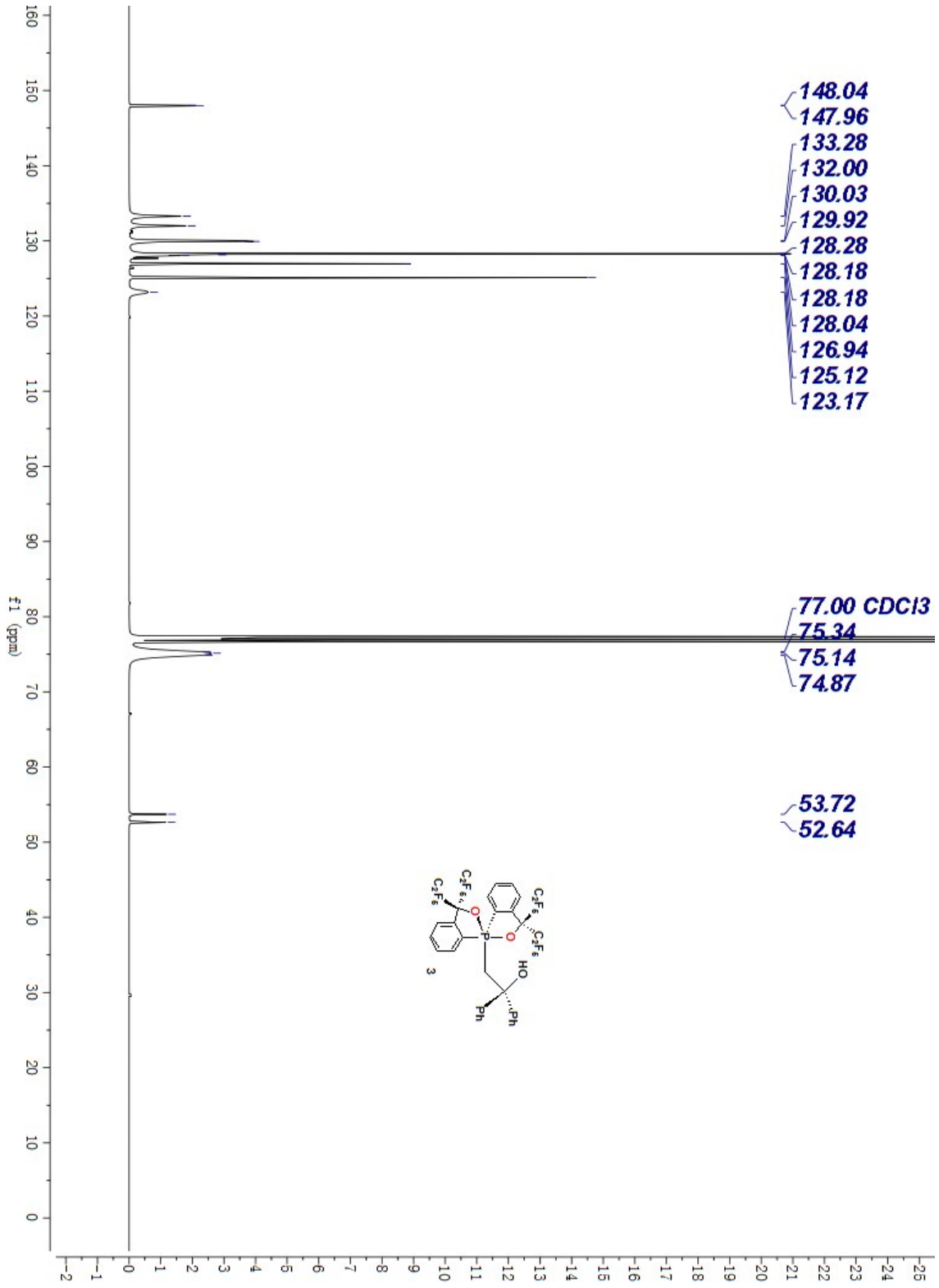
^{1}H NMR ($CDCl_3$) of O-equatorial phosphorane **3**



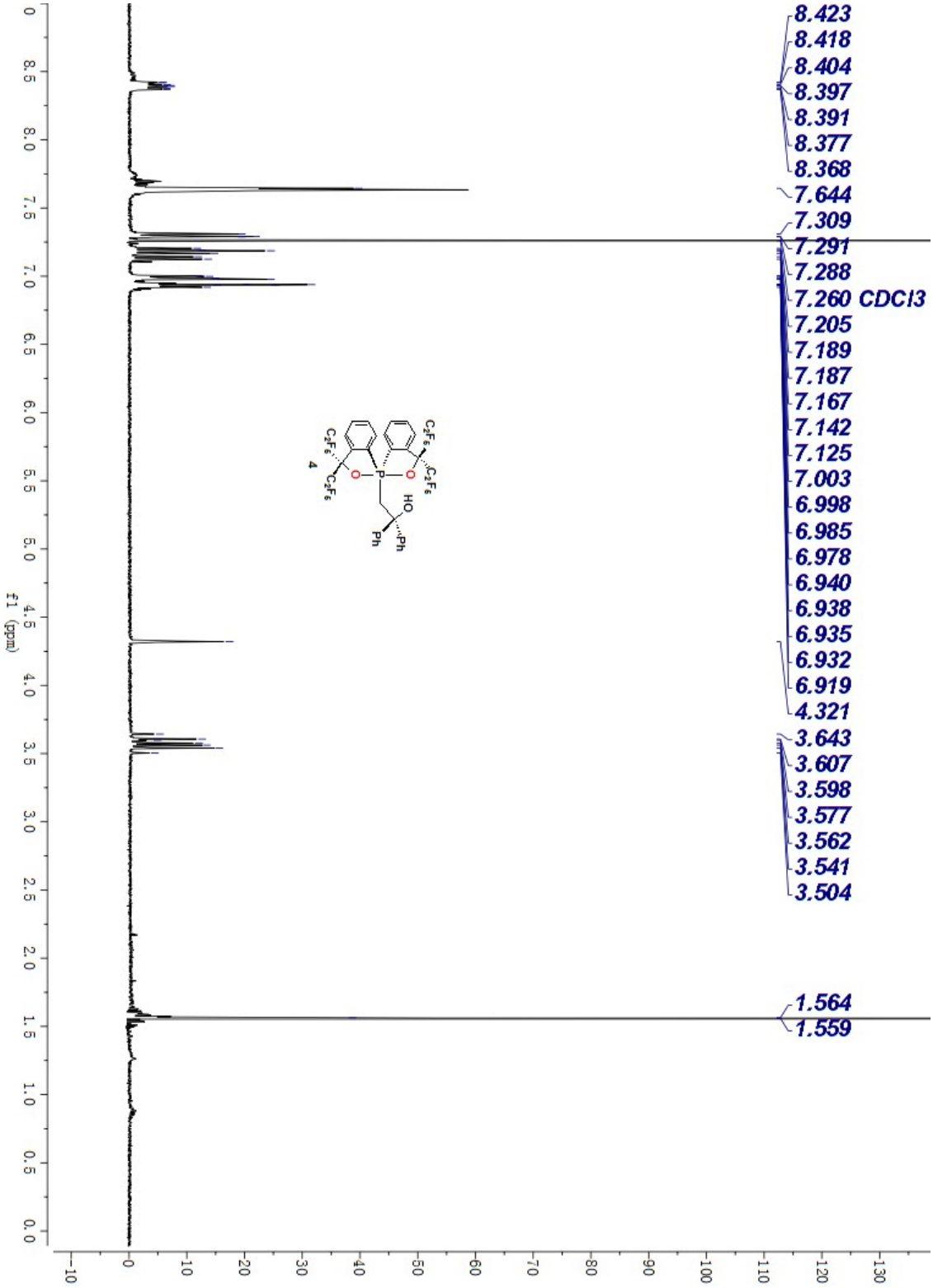
^{19}F NMR ($CDCl_3$) of O-equatorial phosphorane **3**



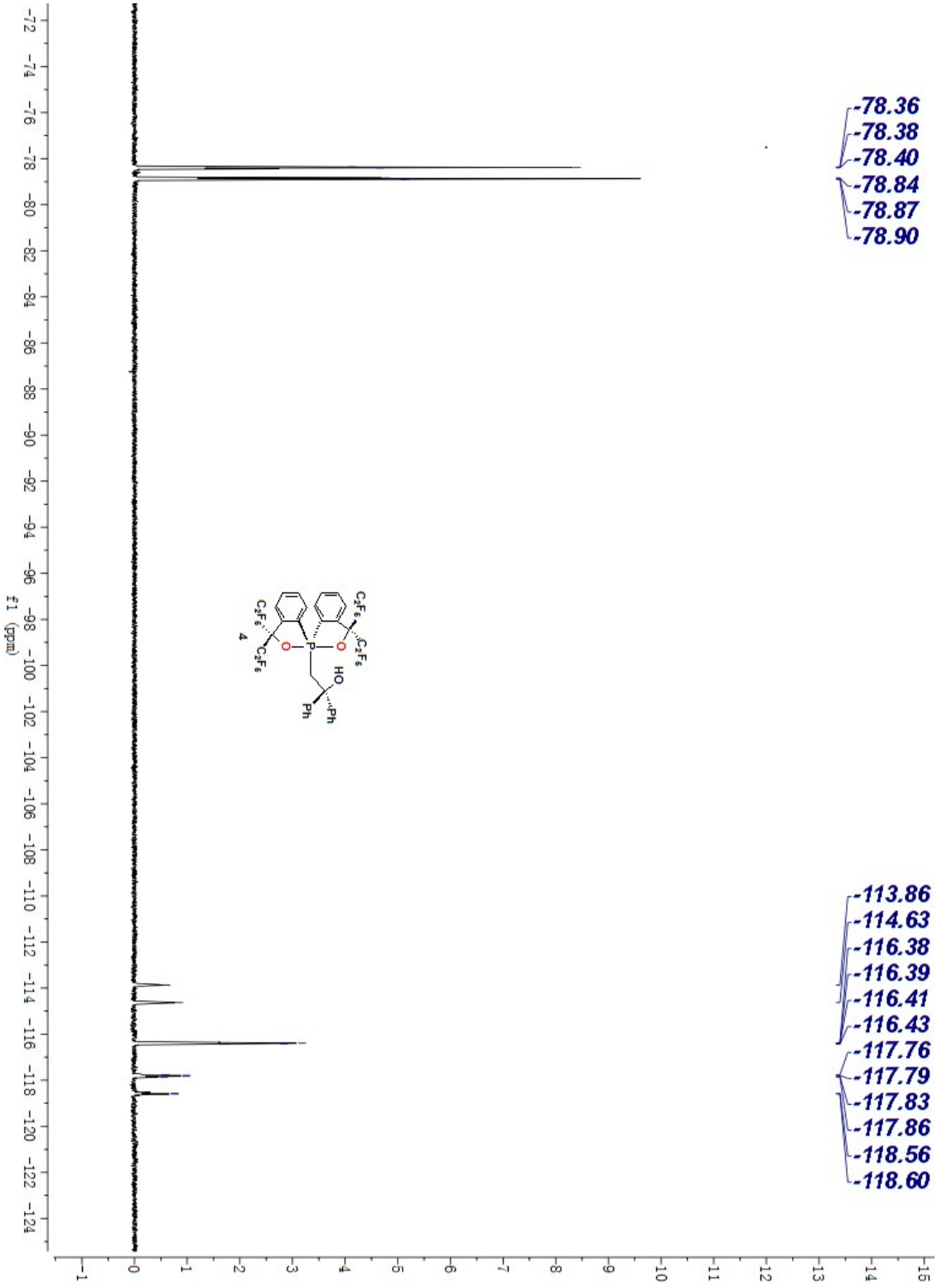
^{31}P NMR ($CDCl_3$) of O-equatorial phosphorane **3**



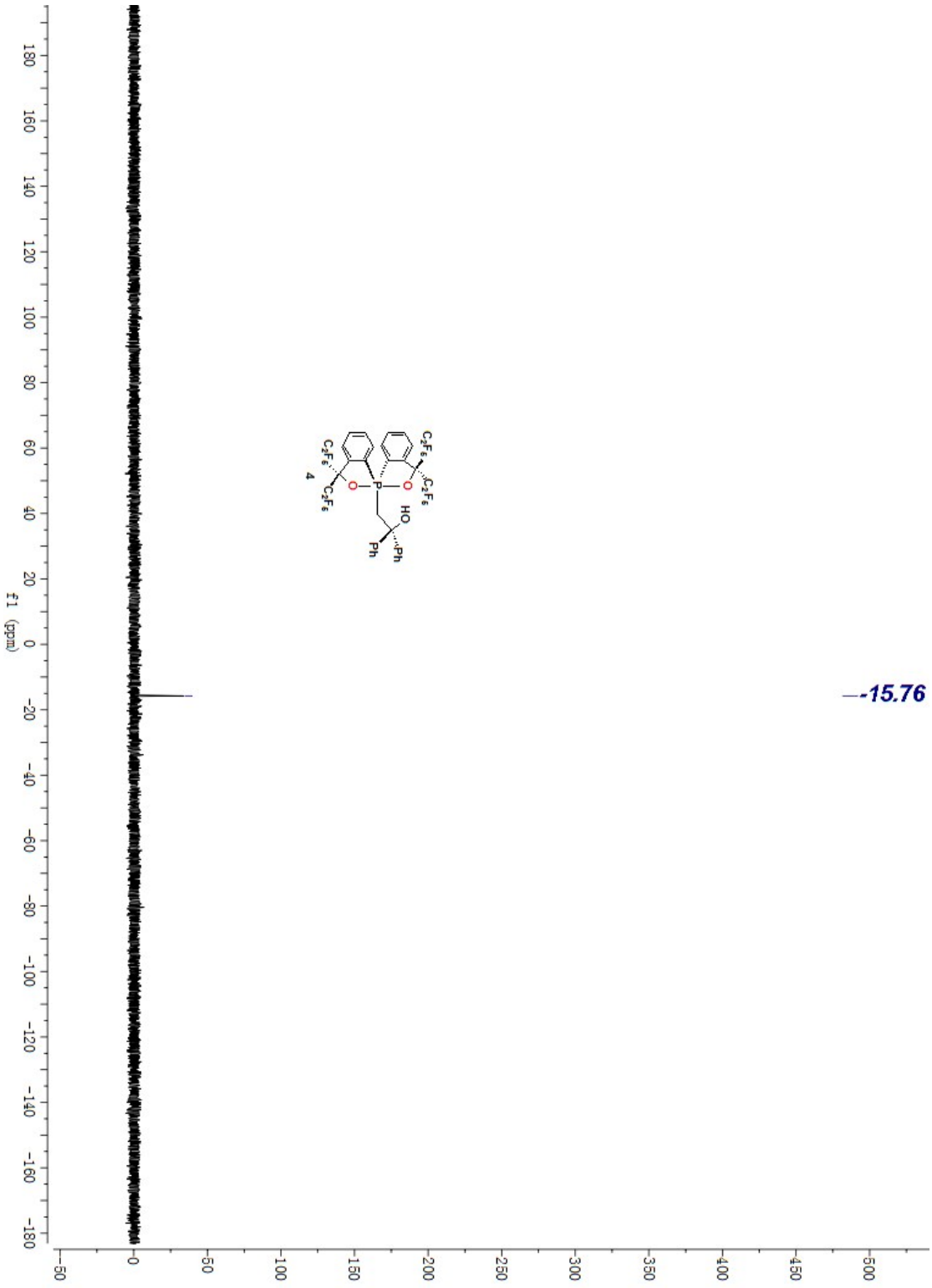
^{13}C NMR ($CDCl_3$) of O-equatorial phosphorane **3**



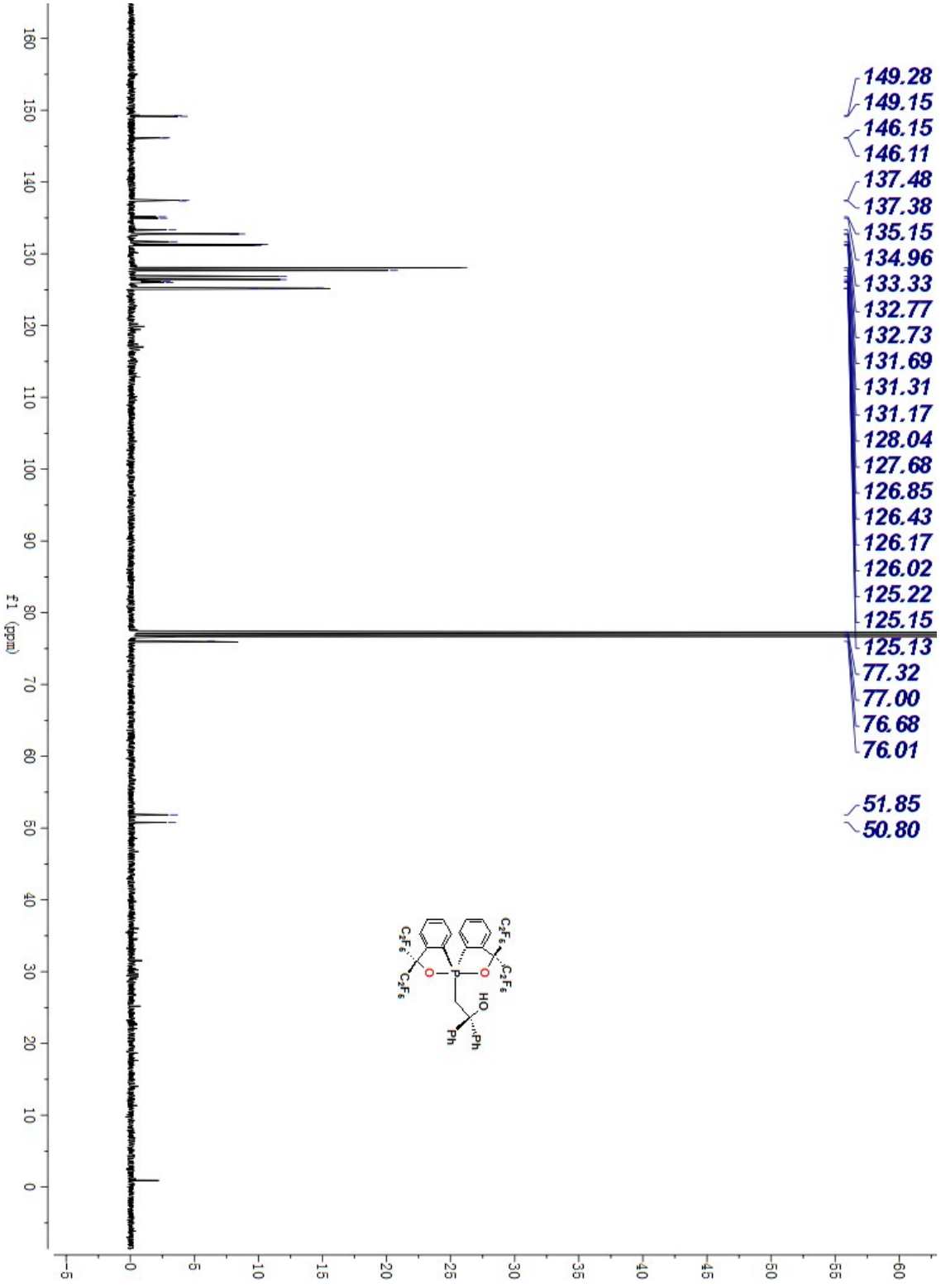
^{1}H NMR ($CDCl_3$) of O-apical phosphorane **4**



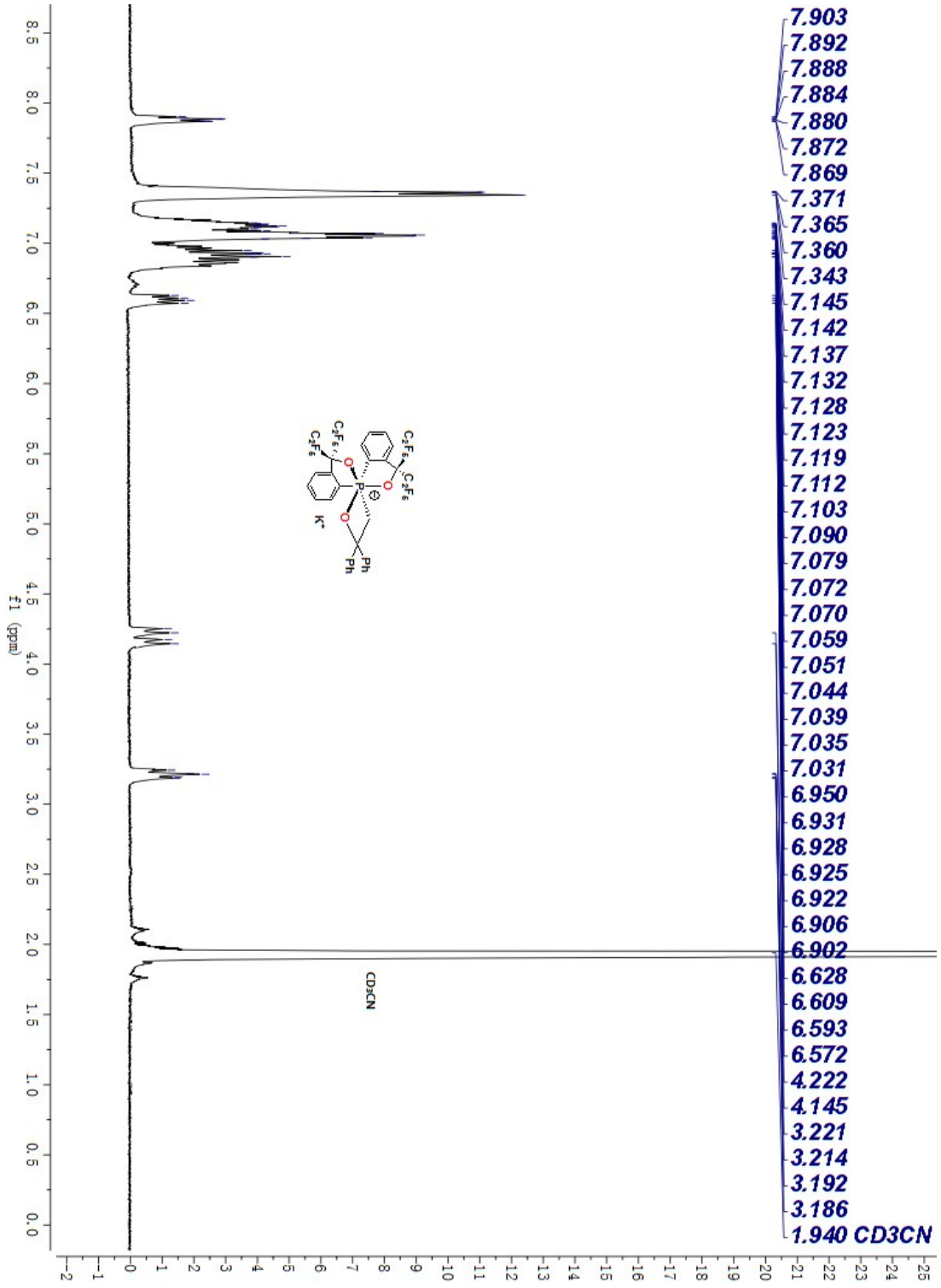
^{19}F NMR ($CDCl_3$) of O-apical phosphorane **4**



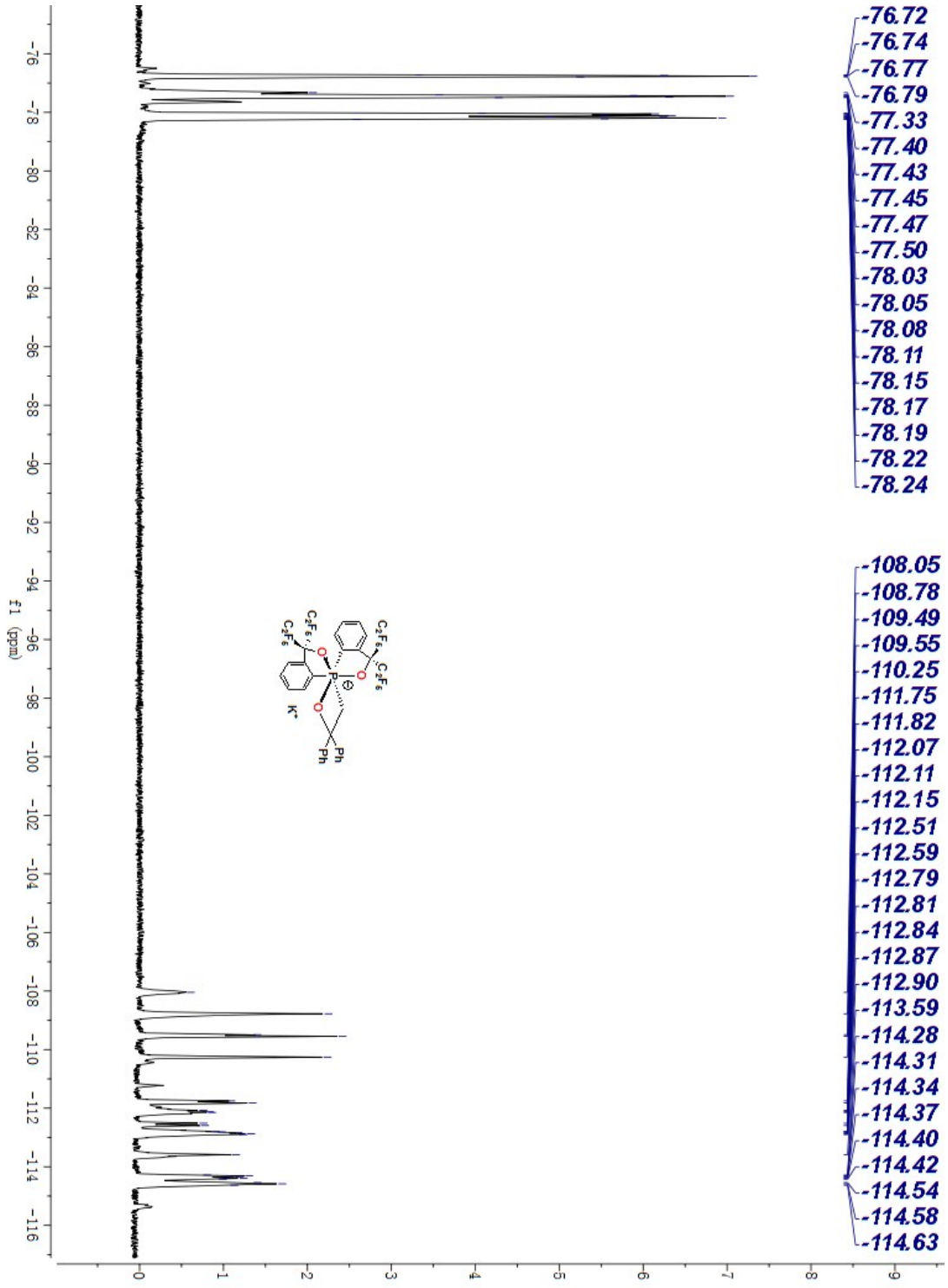
^{31}P NMR ($CDCl_3$) of O-apical phosphorane **4**



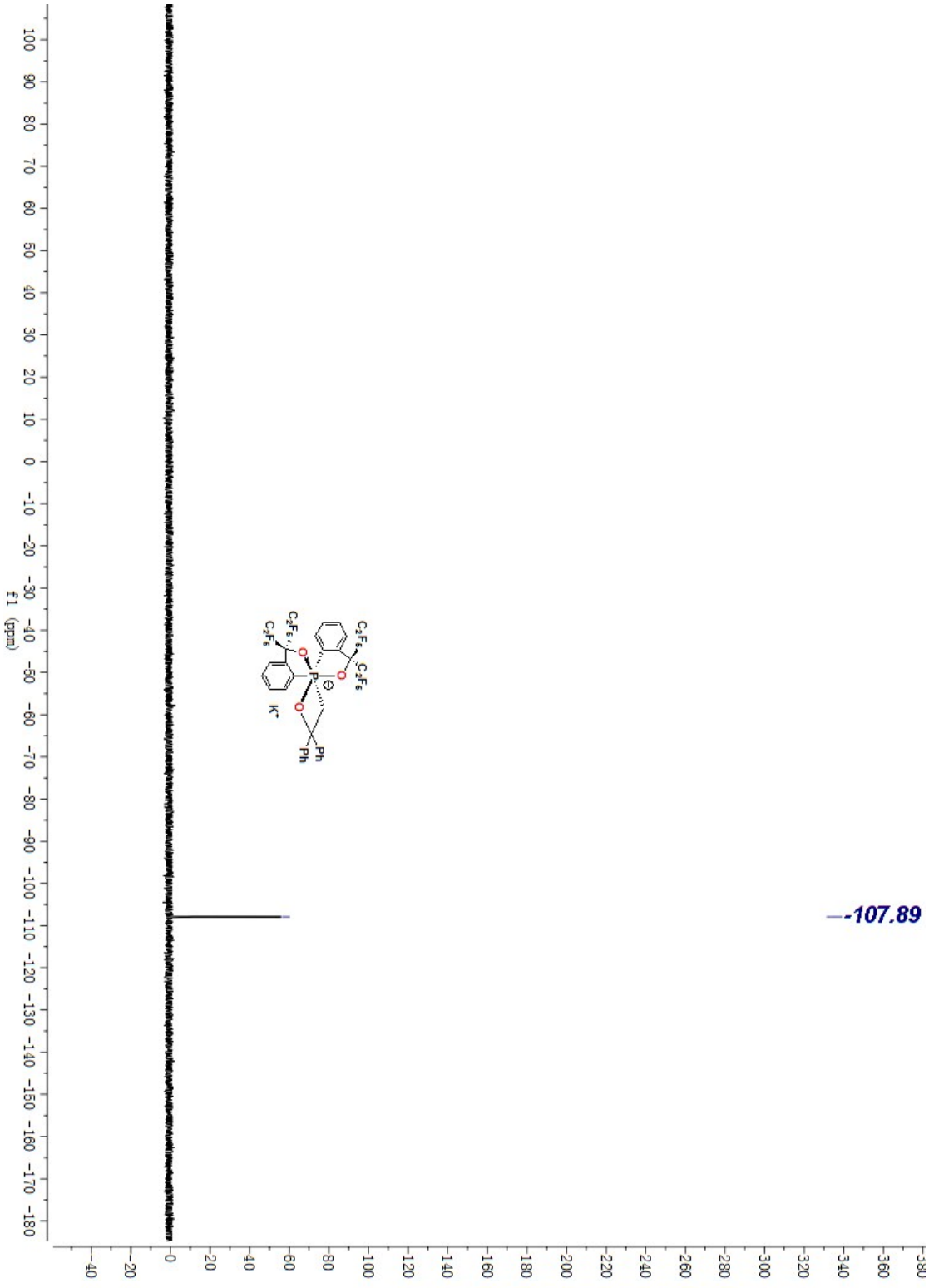
^{13}C NMR ($CDCl_3$) of O-apical phosphorane **4**



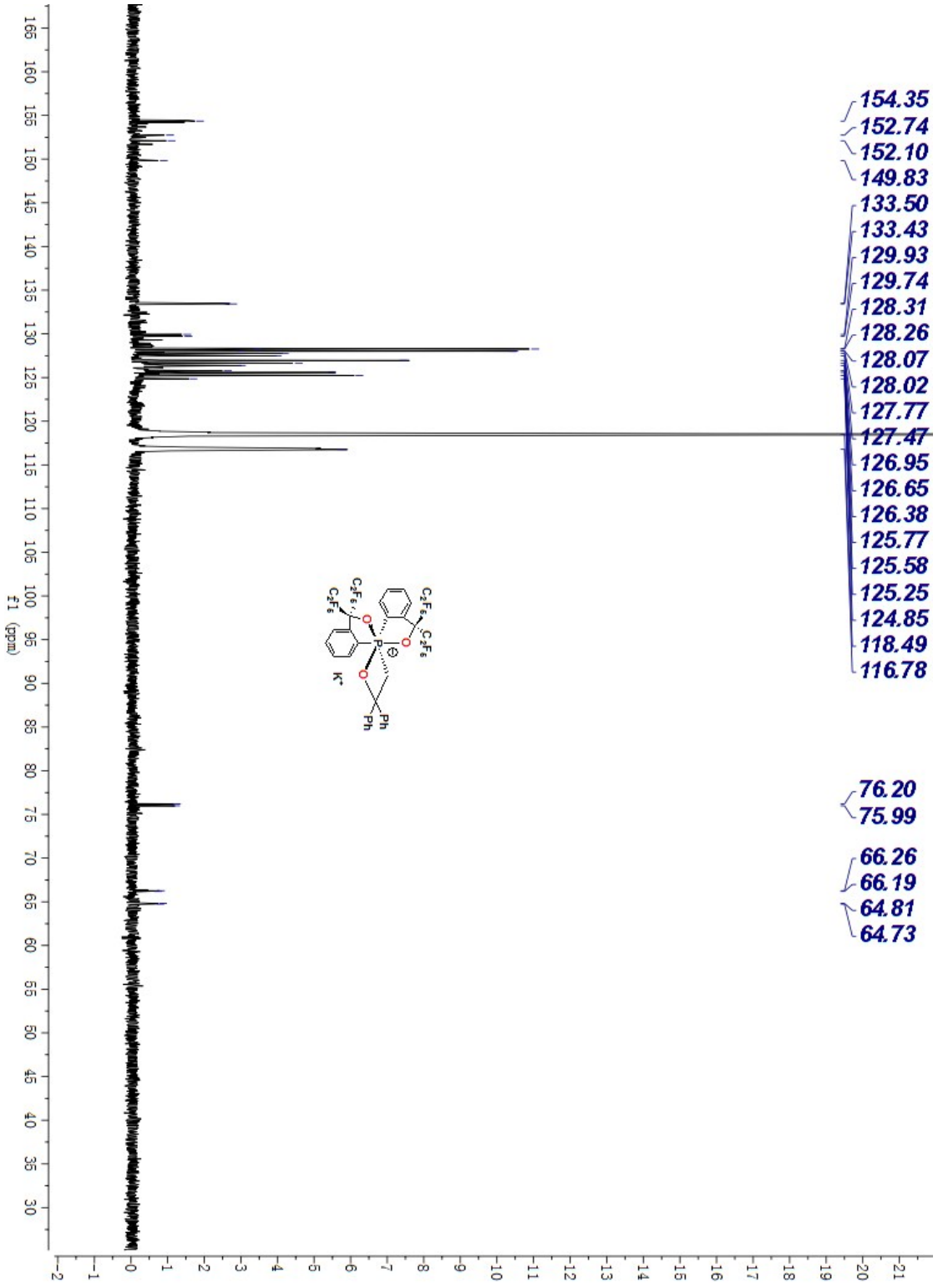
^{1}H NMR (CD_3CN) of O-fac **5B**



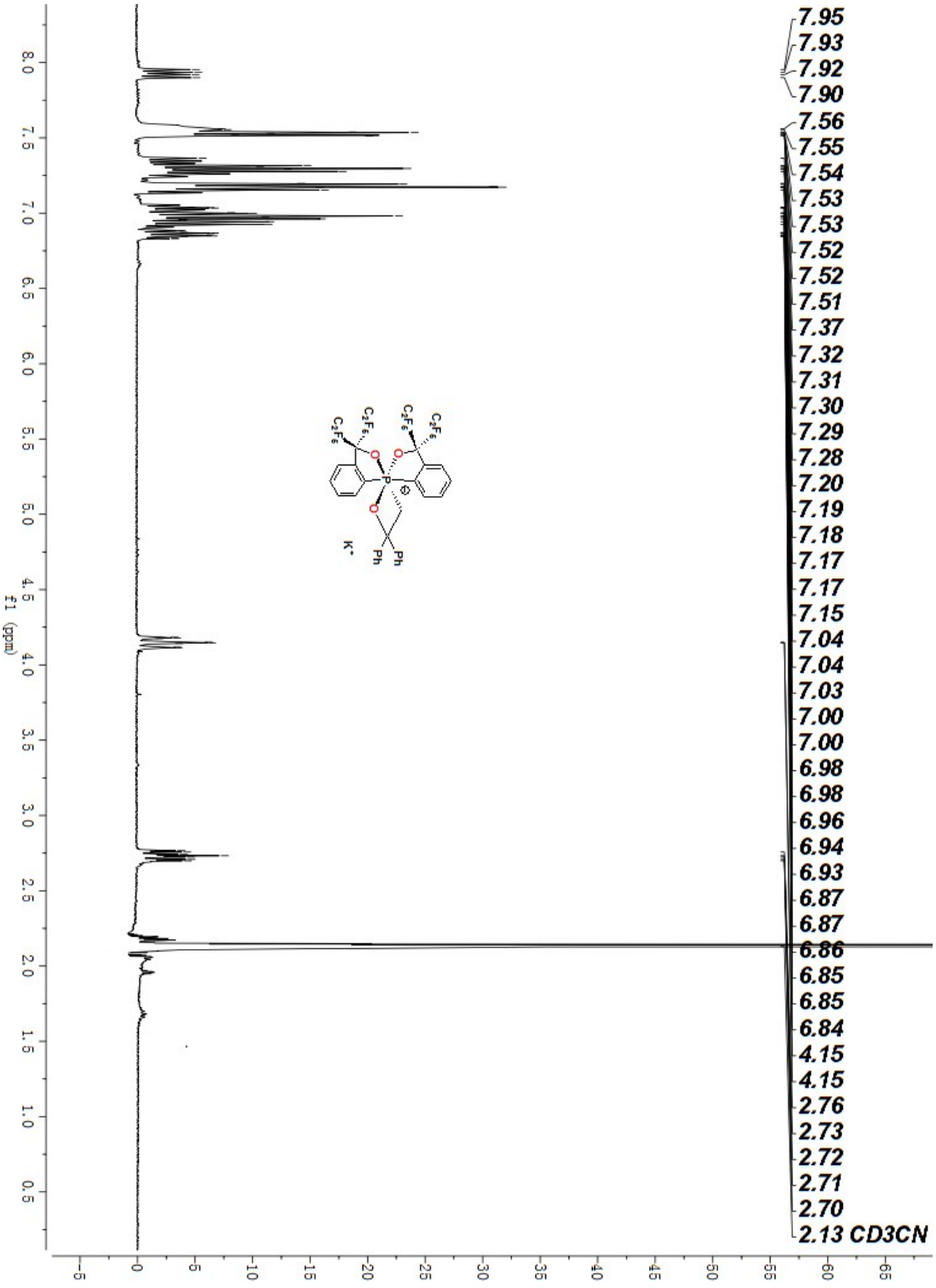
^{19}F NMR (CD_3CN) of O-fac **5B**



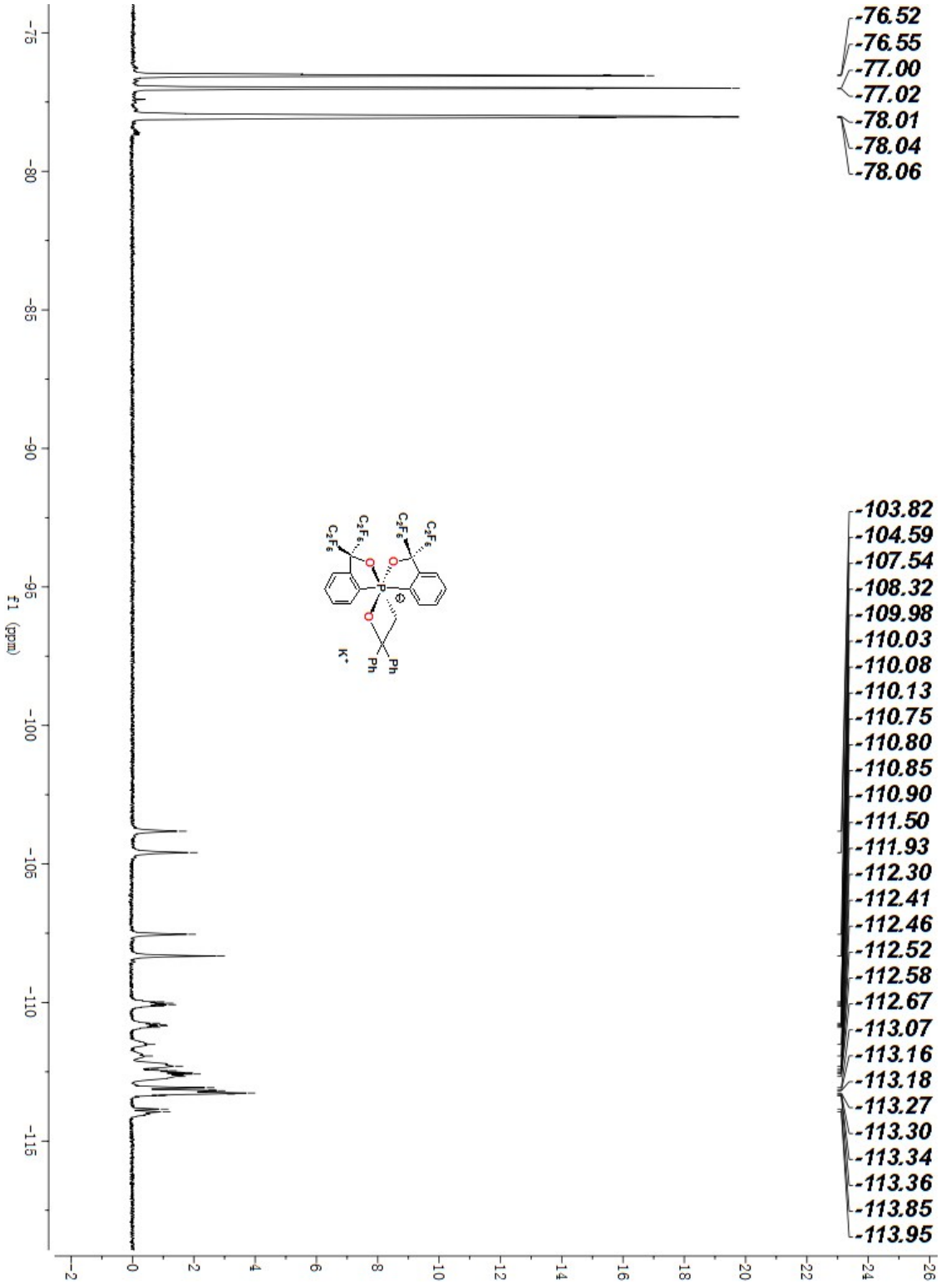
^{31}P NMR (CD_3CN) of O-fac **5B**



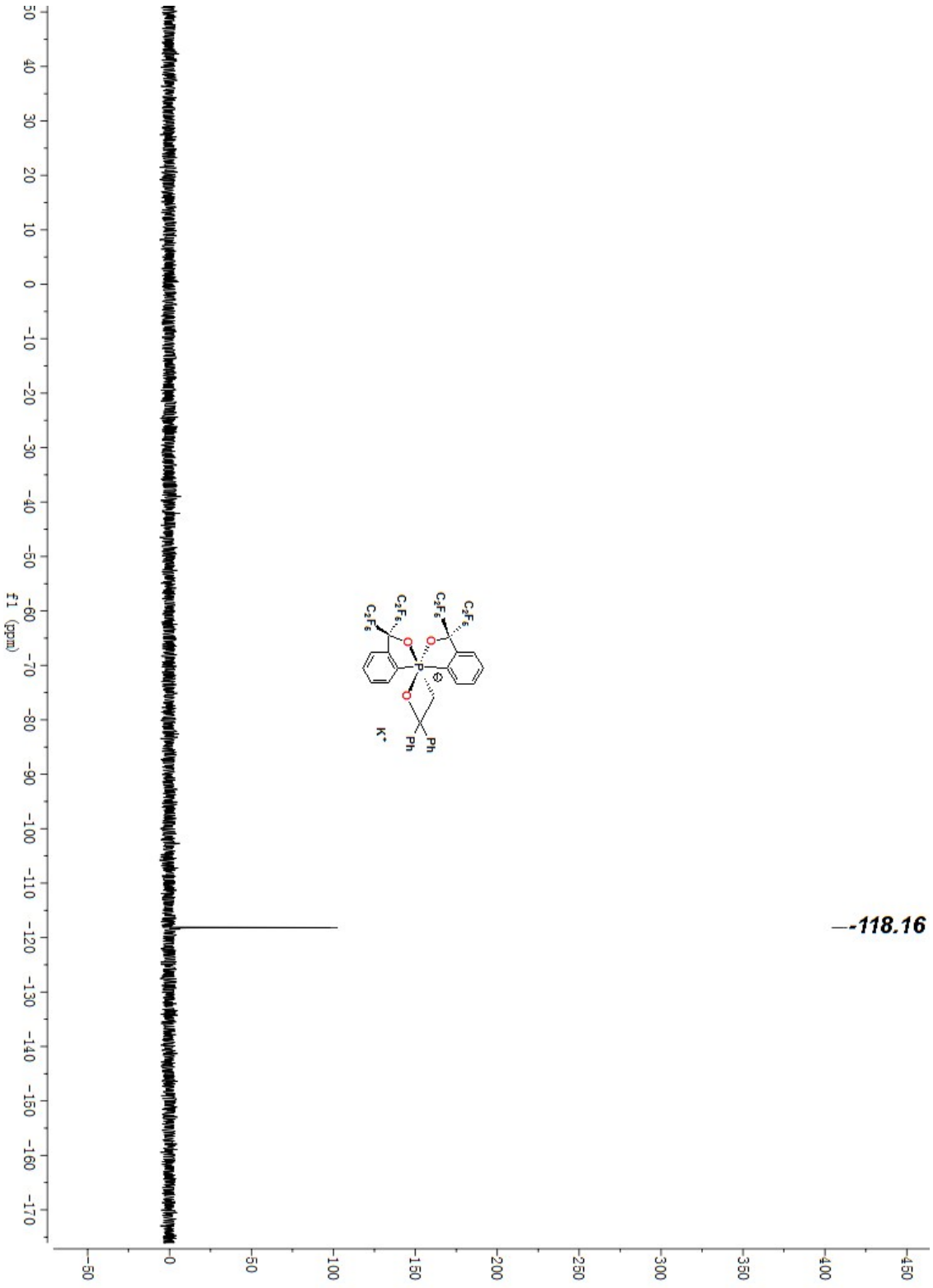
^{13}C NMR (CD_3CN) of O-fac **5B**



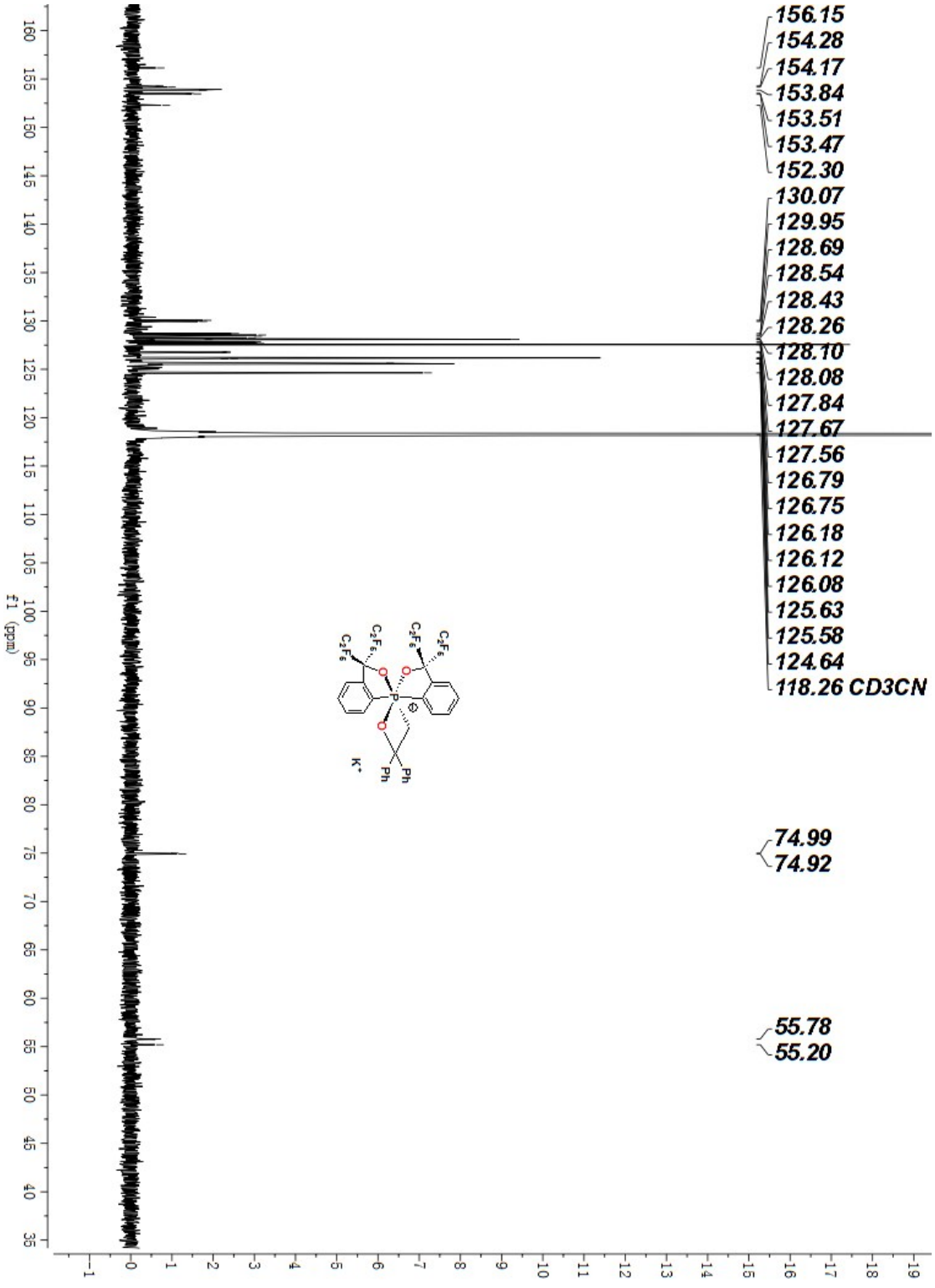
^{1}H NMR (CD_3CN) of O-mer **5D**



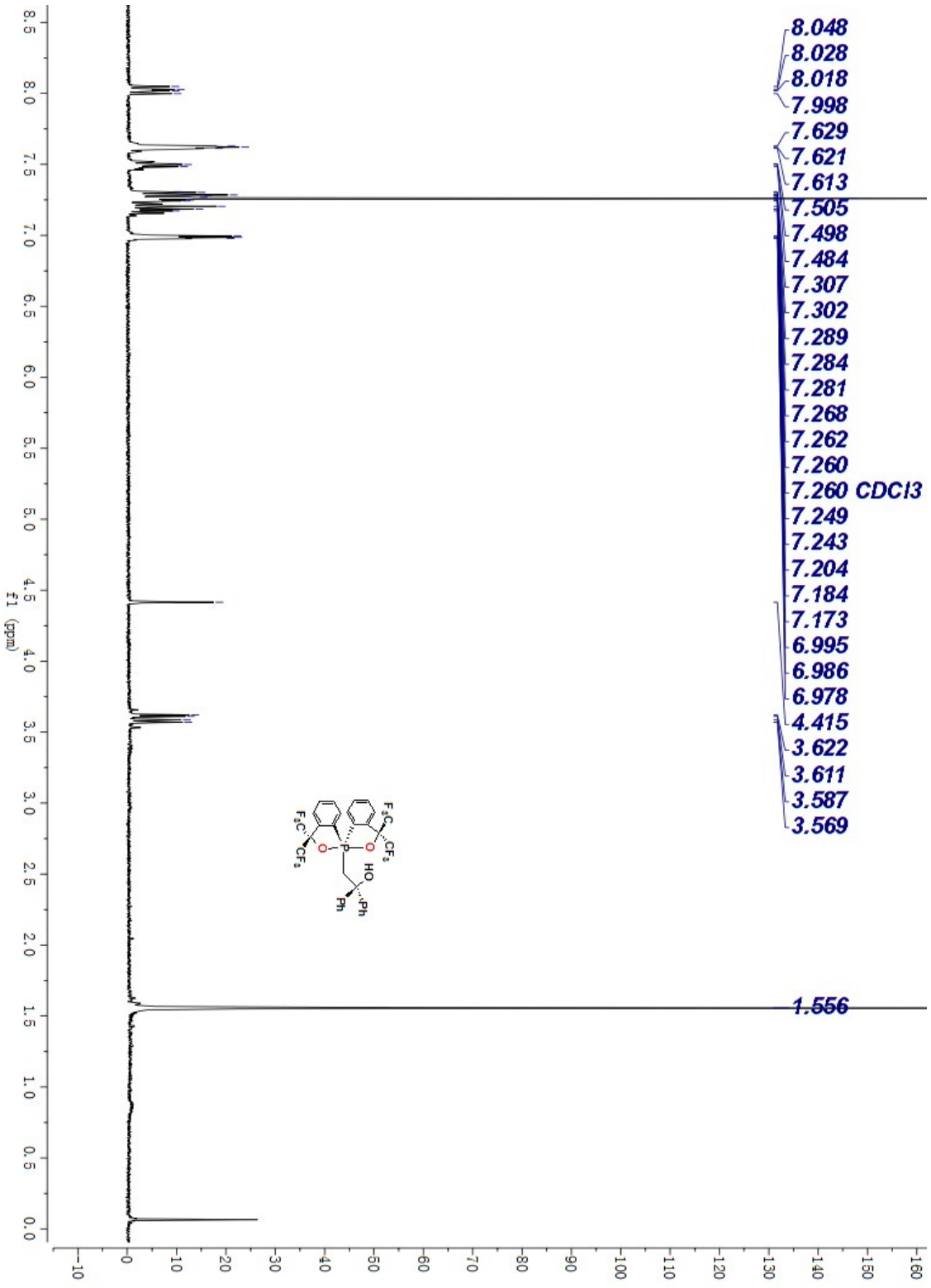
^{19}F NMR (CD_3CN) of O-mer **5D**



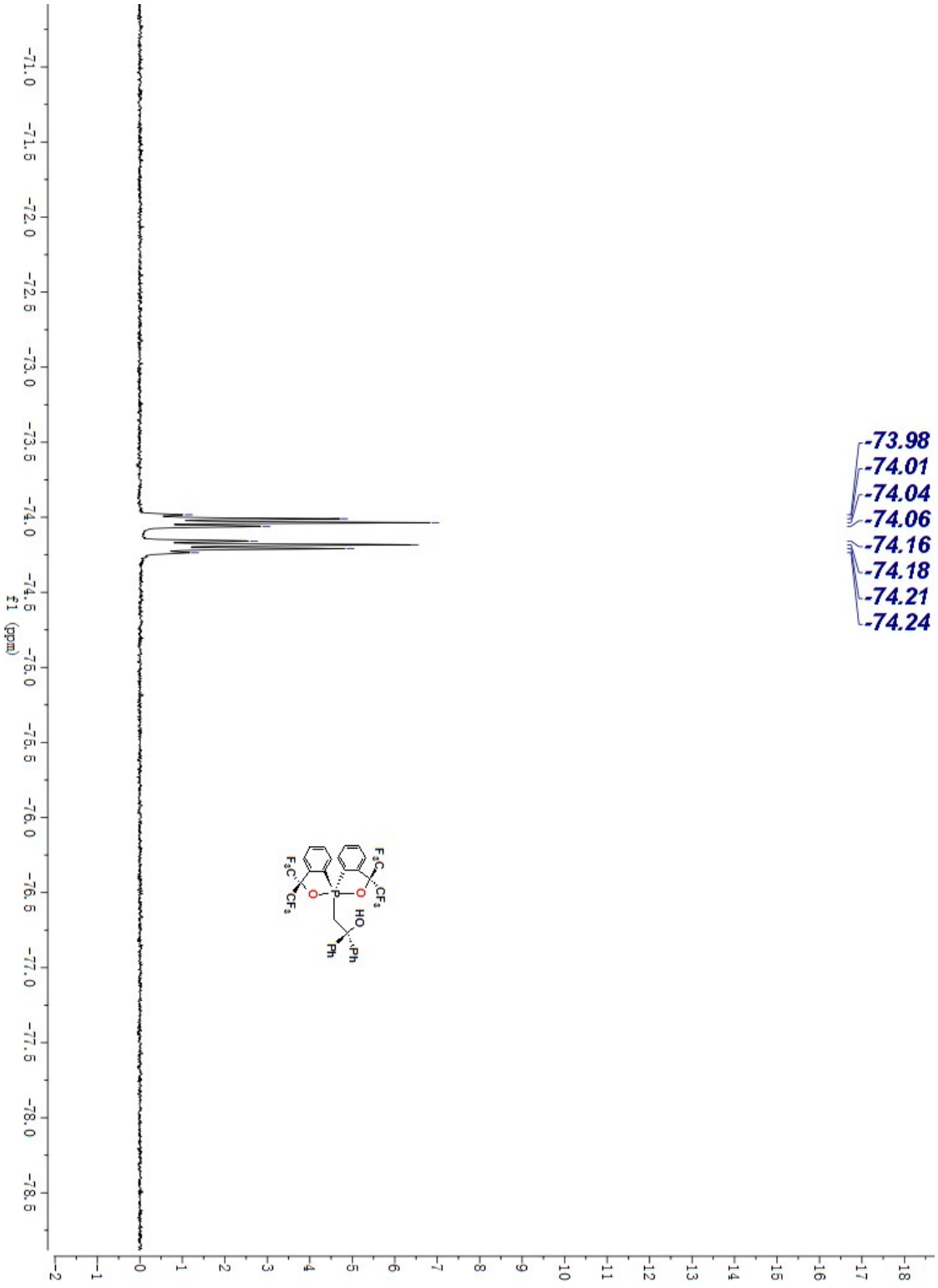
^{31}P NMR (CD_3CN) of O-mer **5D**



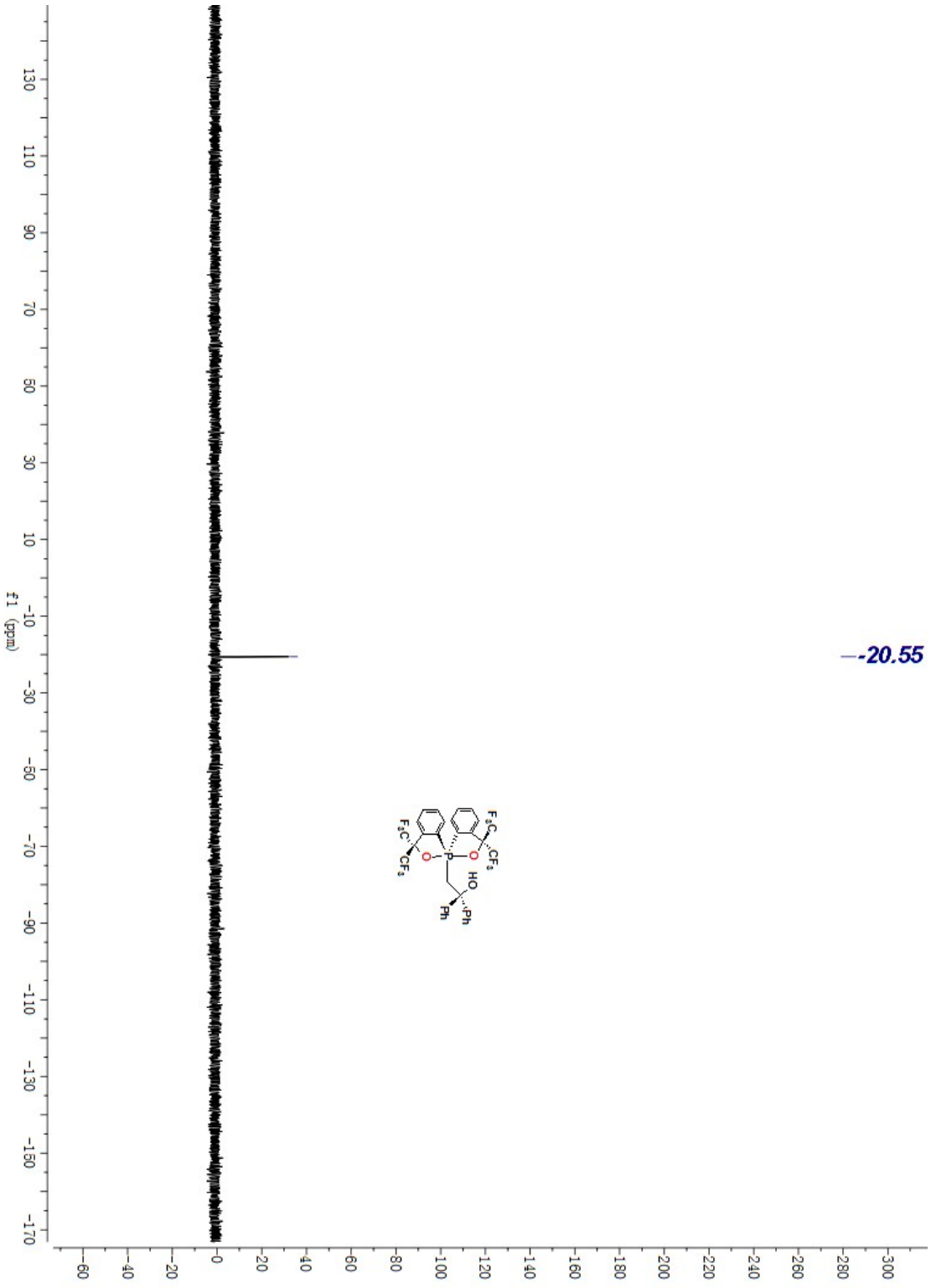
^{13}C NMR (CD_3CN) of O-mer **5D**



^{1}H NMR ($CDCl_3$) of phosphorane **8**



^{19}F NMR ($CDCl_3$) of phosphorane **8**



^{31}P NMR ($CDCl_3$) of phosphorane **8**