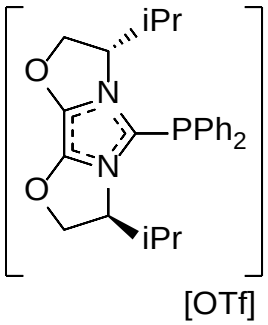
Synthesis and Oxidation of Phosphine Cations†

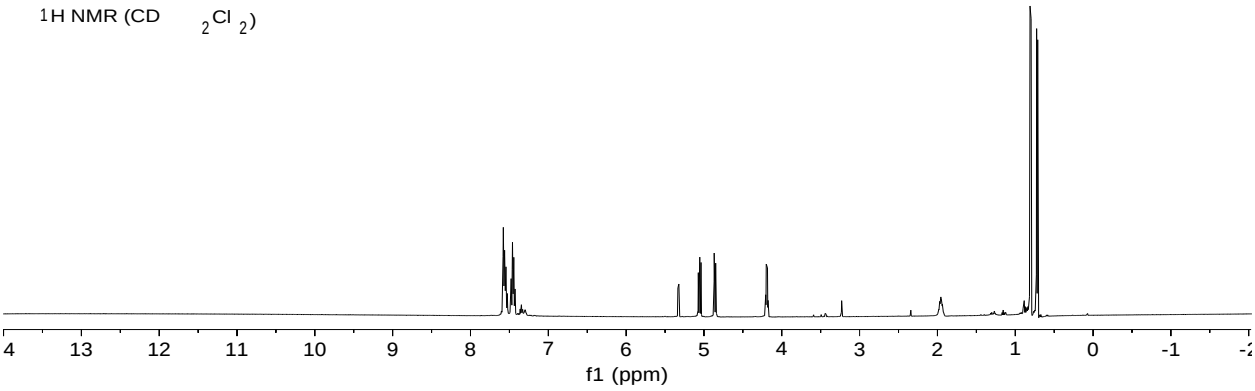
Meera Mehta, Timothy C. Johnstone, Jolie Lam, Bidraha Bagh, André Hermannsdorfer, Matthias Driess* and Douglas W. Stephan*

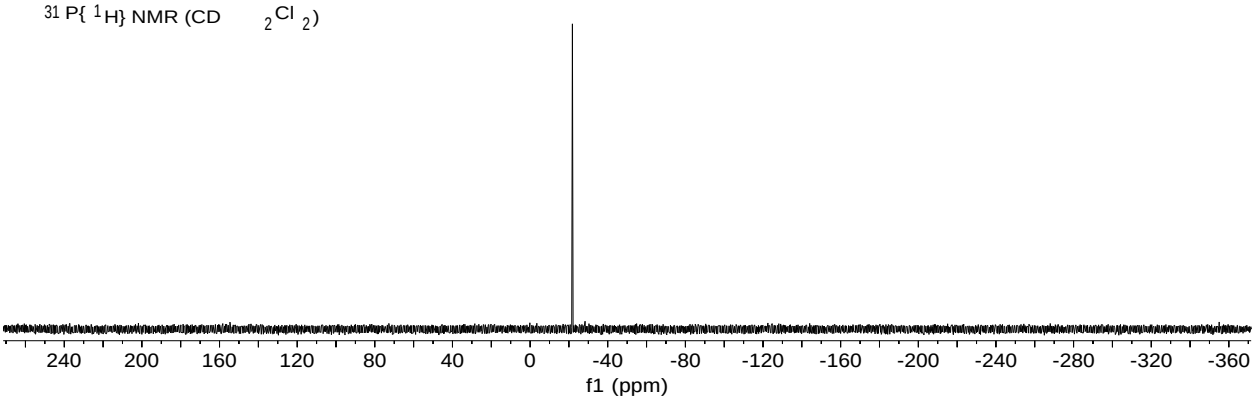
Supporting Information

1. Syntheses and Spectroscopic Data

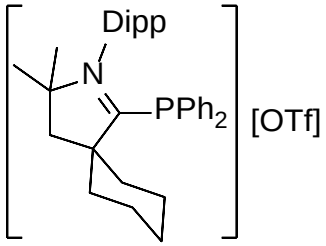
1.1. Preparation of [(IBox-iPr$_2$)PPh$_2$][OTf] (1)

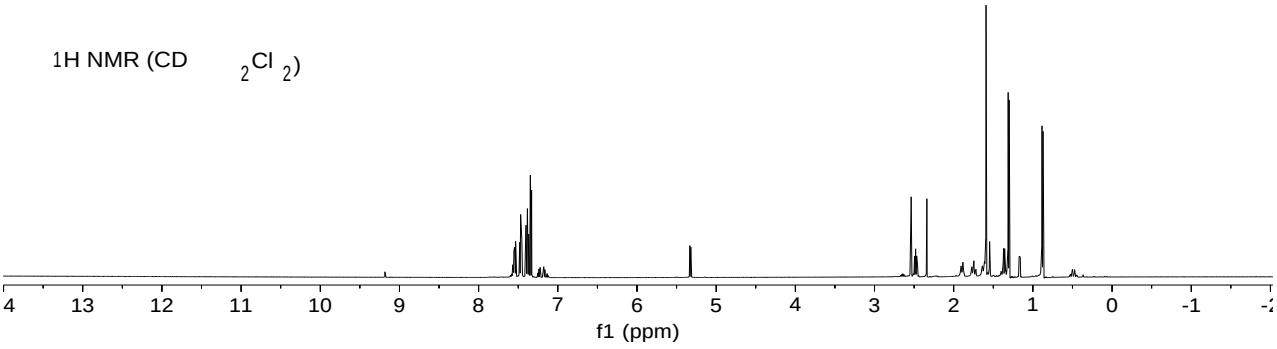


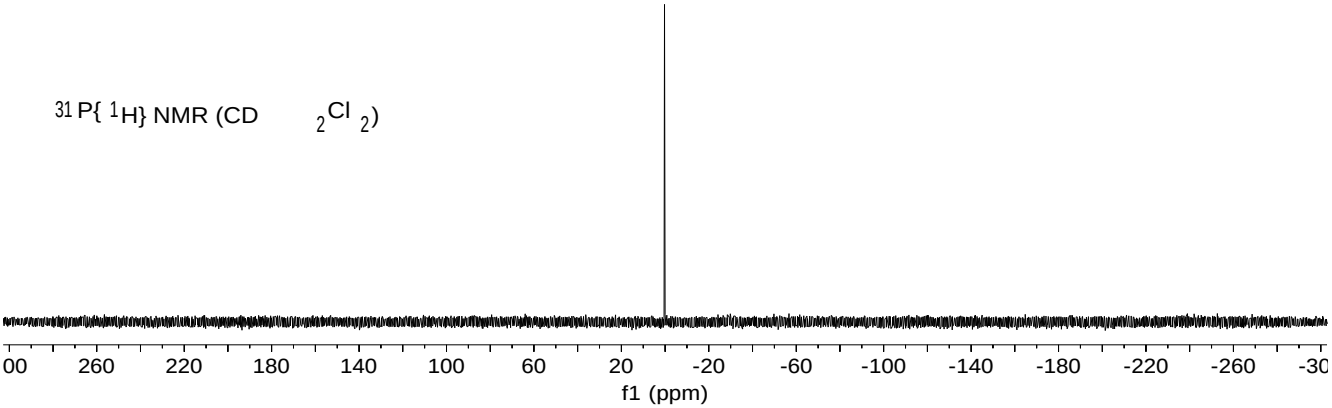




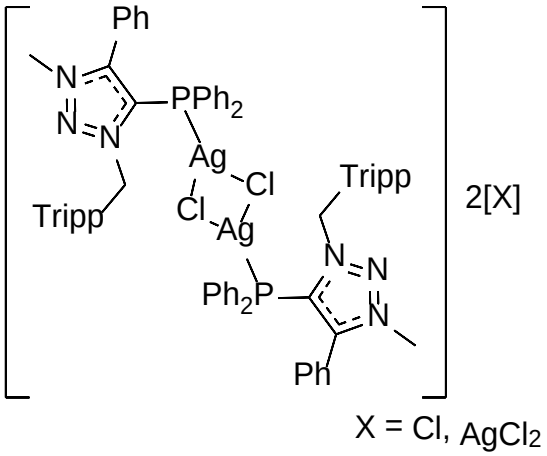
1.2. Preparation of [(cAAC)PPh$_2$][OTf] (2)

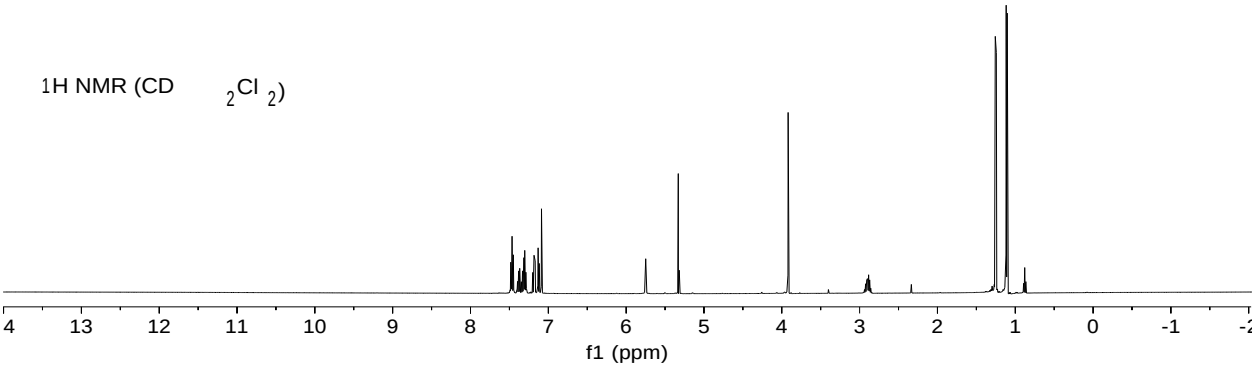


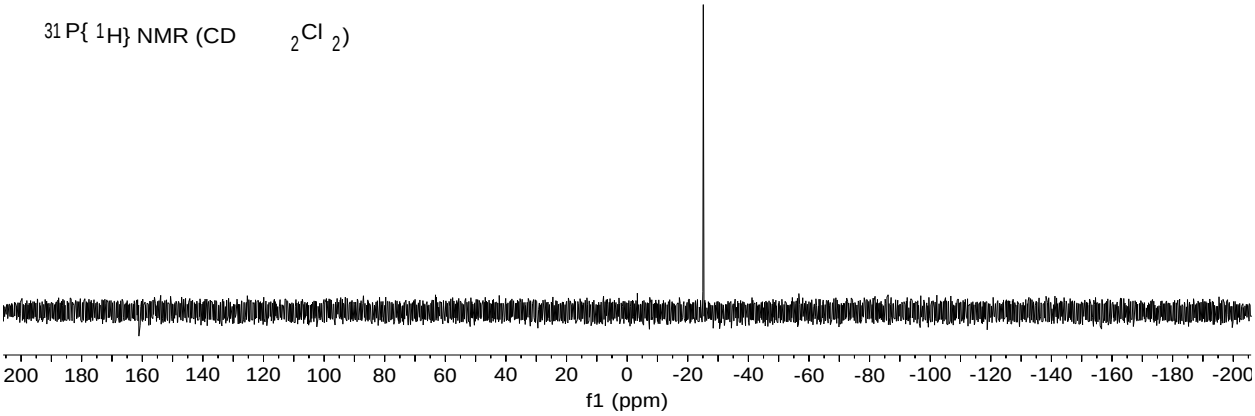




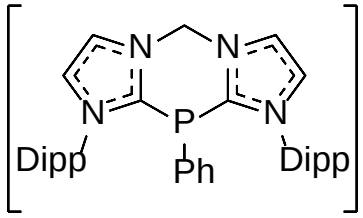
1.3. Preparation of [((TripCH$_2$N$_2$(NMe)C$_2$Ph)PPh$_2$)$_2$(AgCl)$_2$][Cl]$_2$ (3)



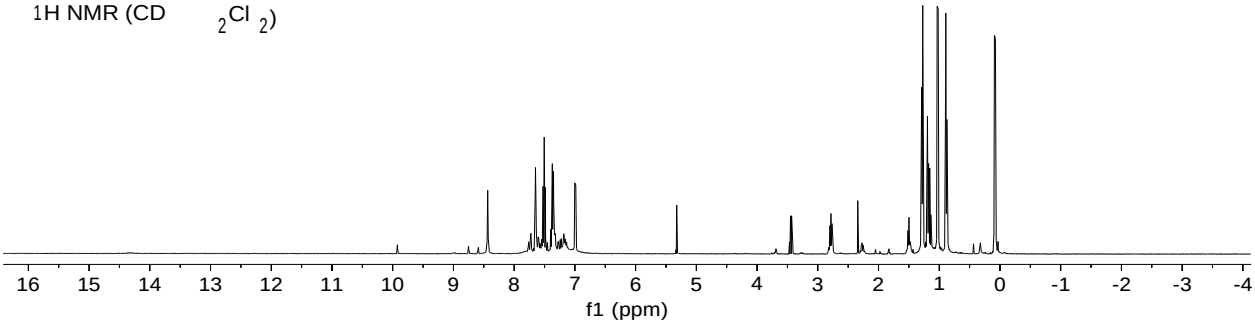


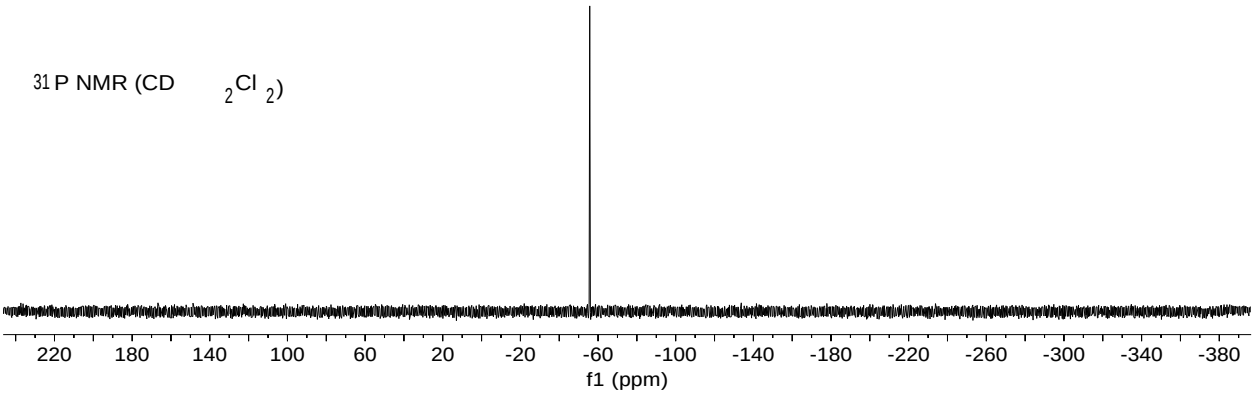


1.4. Preparation of $[CH_2(NC_3H_2NDipp)_2PPh][OTf]_2$ (4a)

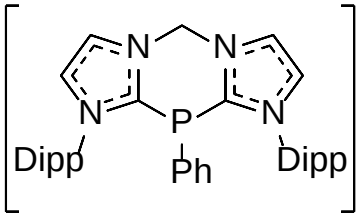


2[OTf]

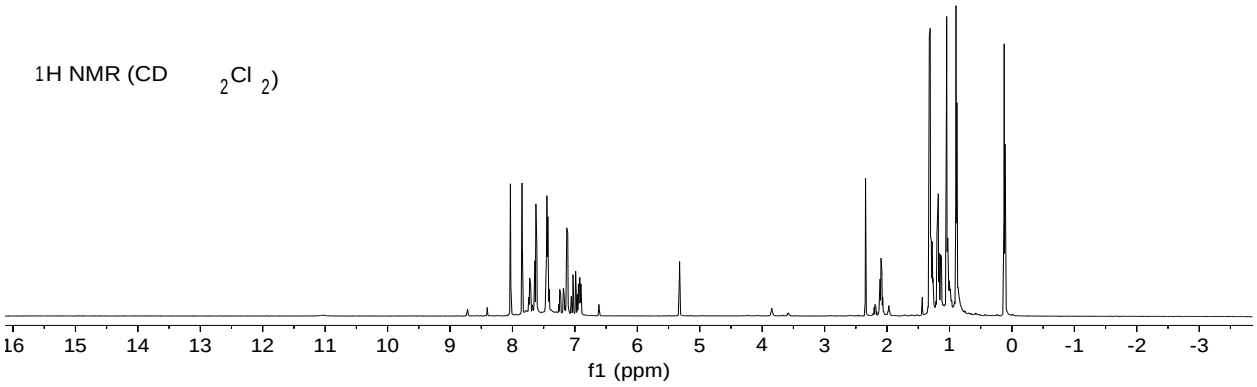


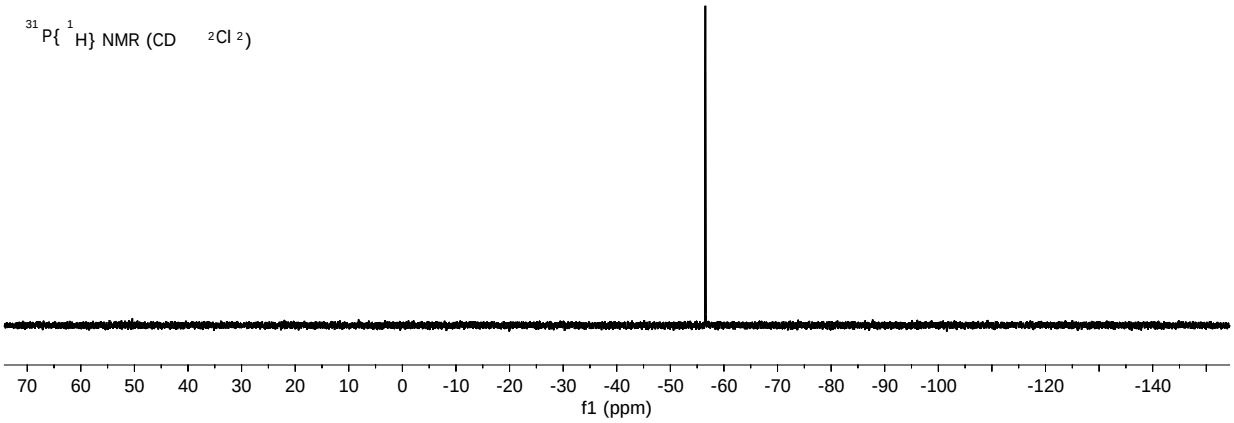


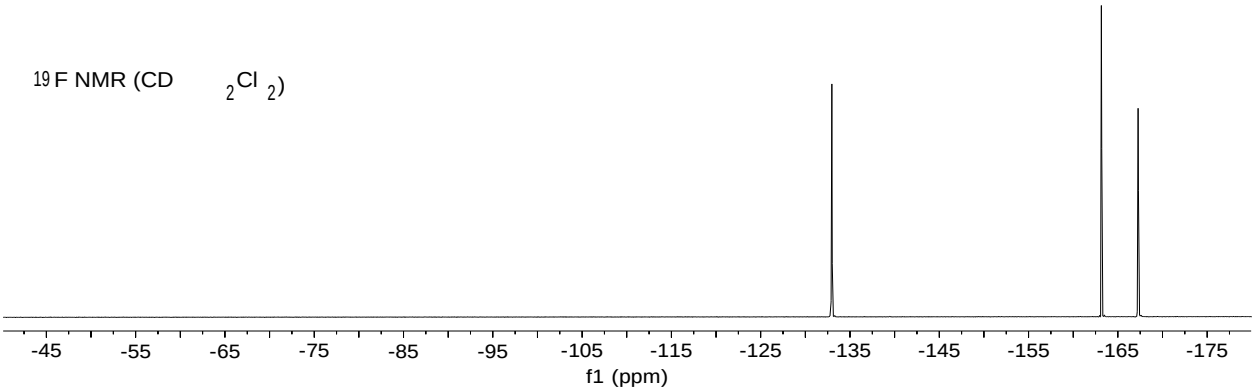
1.5. Preparation of $[CH_2(NC_3H_2NDipp)_2PPh][B(C_6F_5)_4]_2$ (4b)



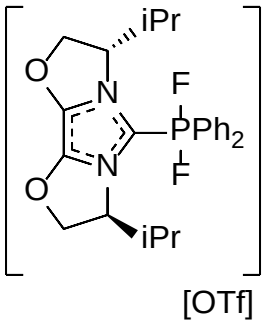
$2[B(C_6F_5)_4]$

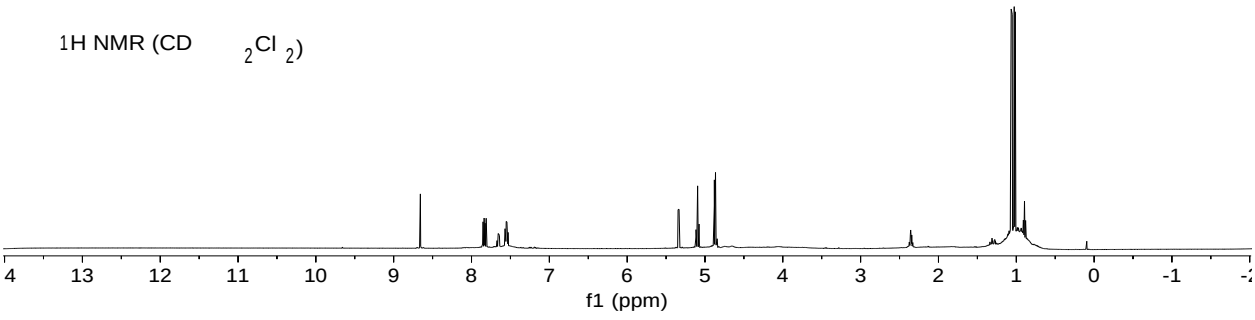


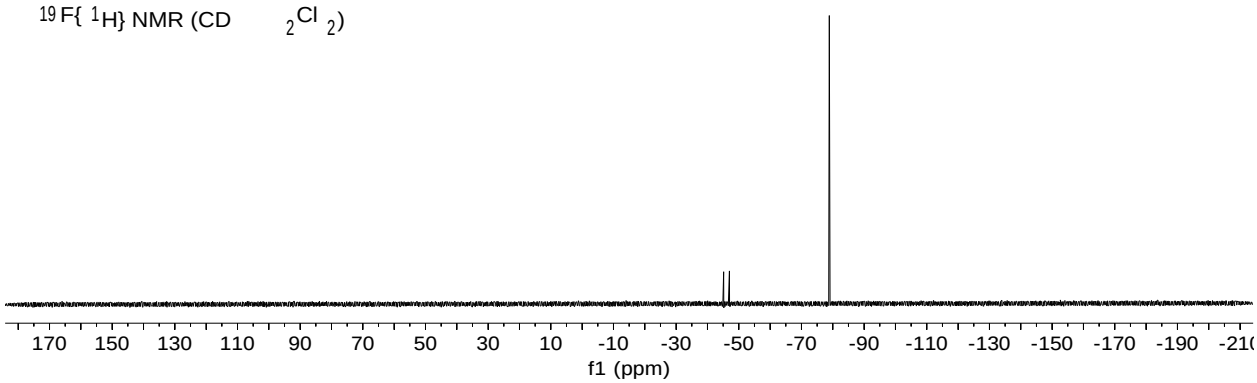


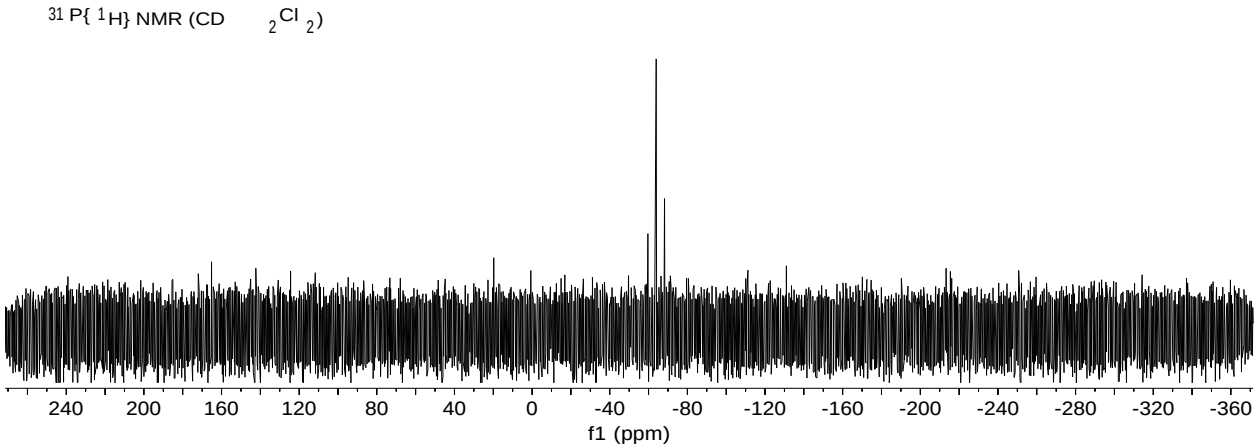


1.6. Preparation of [(IBox-iPr$_2$)PF$_2$Ph$_2$][OTf] (5)

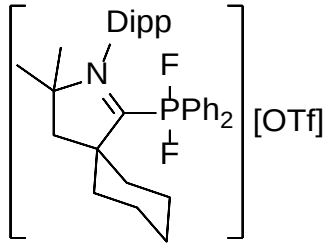


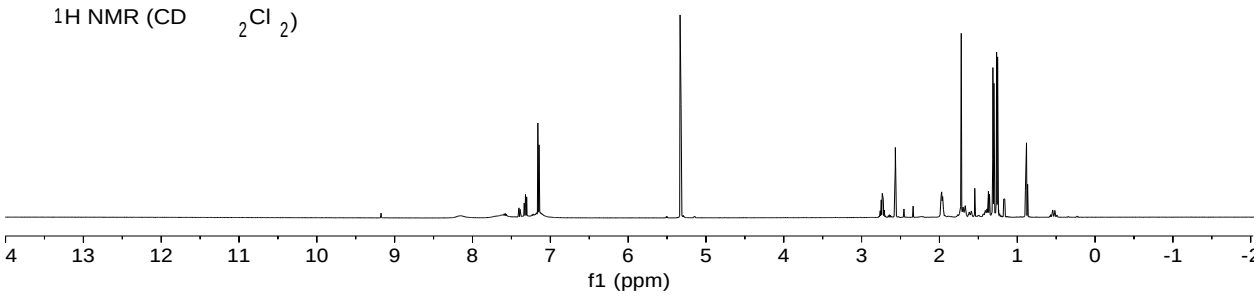


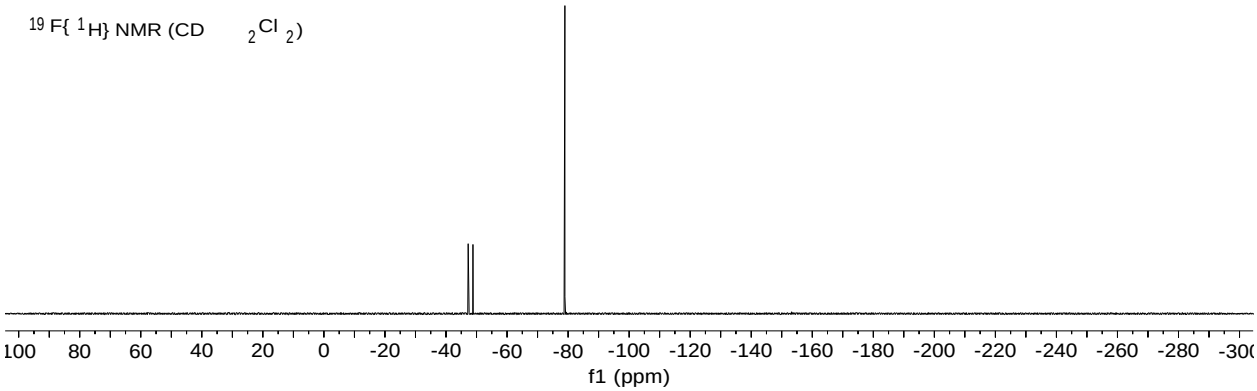


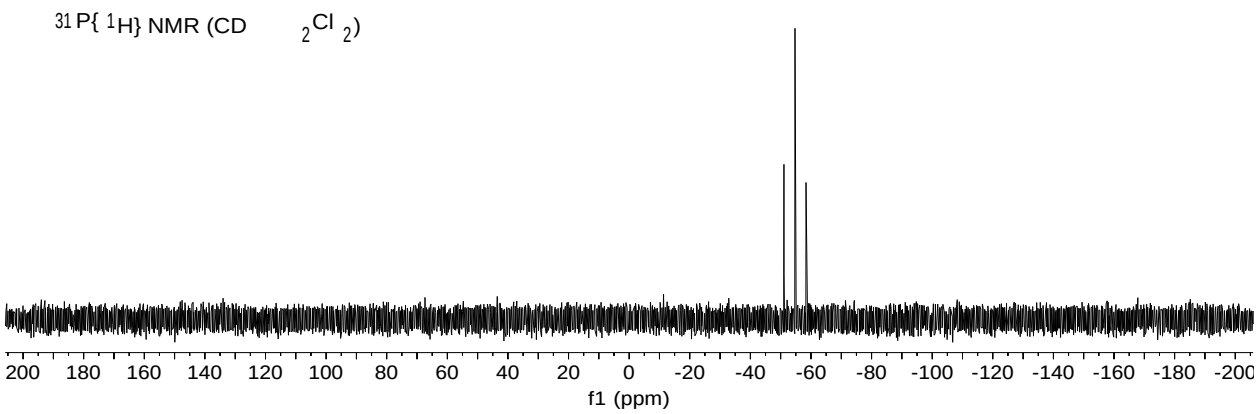


1.7. Preparation of [(cAAC)PF_2Ph_2][OTf] (6)

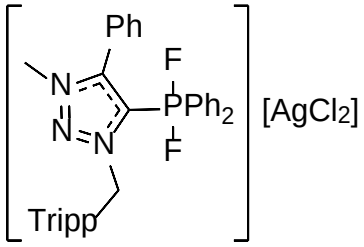


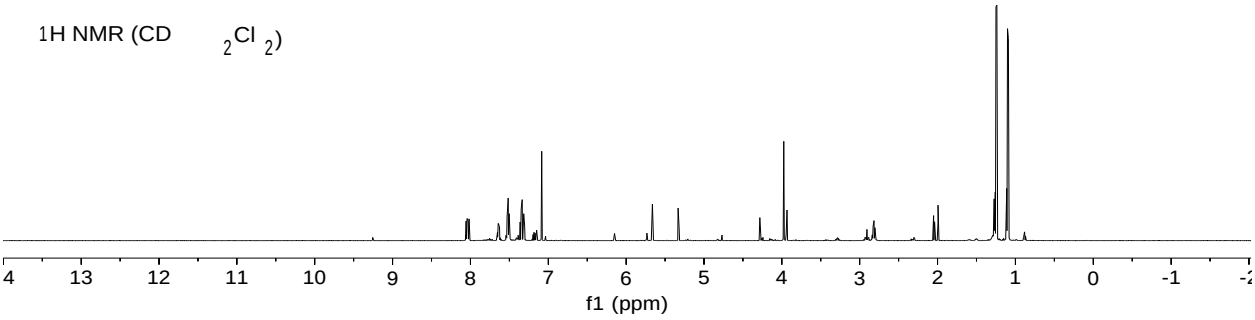

1H NMR (CD 2Cl 2)
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

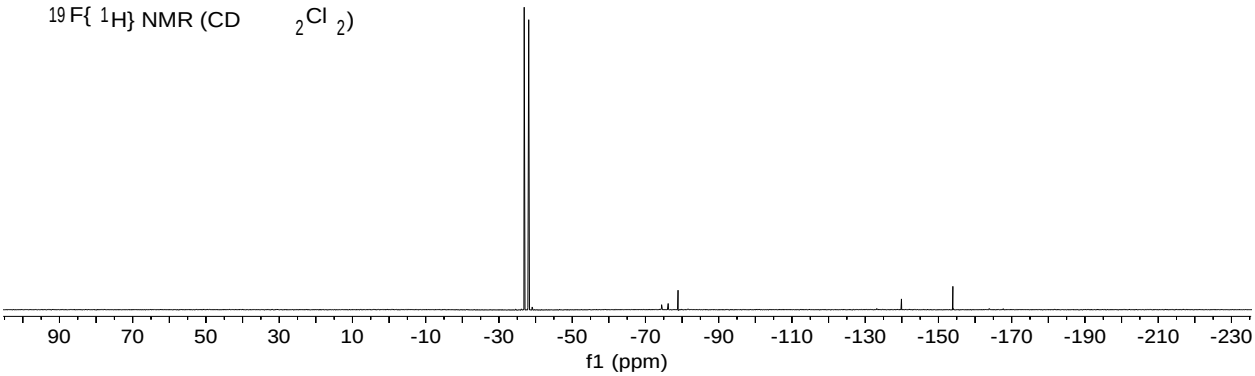

19 F{ 1H} NMR (CD 2Cl 2)
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

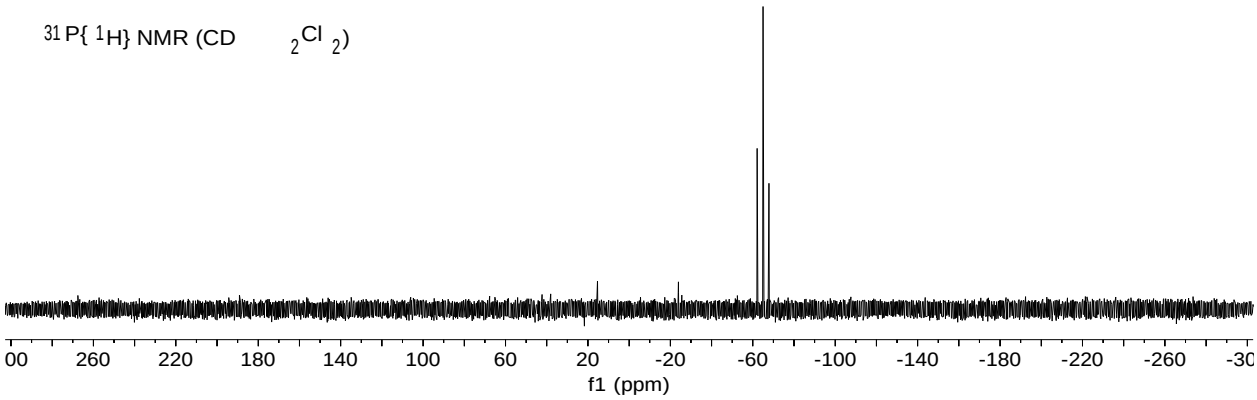

31 P{ 1H} NMR (CD 2Cl 2)
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

1.8. Preparation of [(TripCH$_2$N$_2$(NMe)C$_2$Ph)PF$_2$Ph$_2$][Cl] (7)








31P{1H} NMR (CD2Cl2)
00
260
220
180
140
100
60
20
-20
-60
-100
-140
-180
-220
-260
-30
f1 (ppm)

2. Crystallographic Details

Table S1. Crystallographic refinement parameters

	1	**3**	**4b**	**7**
formula	$C_{26}H_{30}F_3N_2O_5PS$	$C_{81}H_{103}Ag_3Cl_5N_6O_{0.50}P_2$	$C_{109}H_{66}B_2F_{47}N_4P$	$C_{39}H_{46}AgCl_6F_2N_3P$
M_r [g mol^{-1}]	570.55	1731.49	2377.25	946.33
colour, habit	colourless, needle	colourless, block	colouless, needle	colourless, block
crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$P2_1/c$
a [Å]	10.4215(11)	20.2421(7)	15.5736(4)	22.377(4)
b [Å]	10.4310(13)	25.5536(9)	17.4980(5)	10.6024(18)
c [Å]	24.812(3)	31.5604(11)	18.9275(4)	18.089(3)
α [°]	90	90	83.610(2)	90
β [°]	90	94.9190(10)	89.0867(19)	91.717(7)
γ [°]	90	90	73.915(3)	90
V [Å^3]	2697.2(6)	16264.8(10)	4924.5(2)	4289.6(12)
Z	4	8	2	4
T [K]	150(2)	150(2)	150(2)	150(2)
Crystal size [mm]	0.48 x 0.08 x 0.08	0.07 x 0.06 x 0.04	0.54 x 0.08 x 0.08	0.27 x 0.12 x 0.06
ρ_c [g cm^{-3}]	1.405	1.414	1.603	1.465
F(000)	1192	7128	2392	1932
Wavelength (Å)	0.71073	0.71073	1.54184	0.71073
θ_{min} [°]	1.641	2.57	2.35	2.42
θ_{max} [°]	27.608	27.46	67.49	27.56
μ [mm^{-1}]	0.240	0.965	1.539	0.921
reflections collected	24768	73113	34478	36624
reflections unique	6250	18666	17749	9846
R_{int}	0.0346	0.0340	0.0244	0.0386
reflection obs. [F>2σ(F)]	5640	14516	14663	7811
residual density [e Å^{-3}]	0.212, –0.298	5.526, –1.192	0.756, –0.792	1.734, –1.253
parameters	347	951	1465	486
GOF	1.030	1.027	1.062	1.045
R_1 [I>2σ(I)]	0.0297	0.0512	0.0746	0.0624
wR_2 (all data)	0.0690	0.1465	0.1941	0.1637

Table S2. Selected bond lengths and angles of cationic phosphines.

	P–C$_{cation}$ (Å)	**P–C$_{phenyl}$ (Å)**	**∠C–P–C (°)**
1	1.826(2)	1.824(2) 1.819(2)	100.89(7) 104.26(7) 103.14(7)
3†	1.831(4)/1.825(4)	1.822(4)/1.819(4) 1.825(4)/1.823(4)	100.9(2)/100.9(2) 106.1(2)/104.1(2) 102.8(2)/103.7(2)
4b	1.824(3) 1.830(3)	1.821(3)	91.9(2) 105.7(2) 101.0(2)

† Values are given for both half-dimers in the asymmetric unit

3. Computations Studies

Table S3. Optimized Cartesian coordinates (Å) of the cation of **1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	7.837053	4.402054	4.618361
2	6	0	7.950339	8.270728	6.725901
3	1	0	8.504904	8.197292	7.682257
4	1	0	8.682274	8.083327	5.913471
5	1	0	7.586060	9.314879	6.627077
6	6	0	7.619161	2.619010	2.488939
7	1	0	6.537148	2.724764	2.671997
8	6	0	6.031871	7.251077	5.356633
9	1	0	5.256716	6.457952	5.369883
10	6	0	8.735848	5.448216	0.556632
11	1	0	8.364709	4.521461	1.039062
12	6	0	10.379288	2.315717	2.041853
13	1	0	11.460274	2.182934	1.878021
14	8	0	6.386710	9.233168	3.996614
15	8	0	8.792254	8.587864	1.619089
16	6	0	9.454859	1.646379	1.218474
17	1	0	9.812629	0.995092	0.406021
18	6	0	8.074760	1.791828	1.447880
19	1	0	7.349220	1.251728	0.820075
20	6	0	8.544443	3.322089	3.295314
21	6	0	7.760194	6.034302	3.765395
22	7	0	6.929175	7.029293	4.201122
23	6	0	6.799439	7.254856	6.703203
24	1	0	7.238046	6.236148	6.799415
25	6	0	5.816893	7.450190	7.868918
26	1	0	4.999022	6.700136	7.852094
27	1	0	6.347866	7.347028	8.836070
28	1	0	5.356514	8.461148	7.858555
29	6	0	7.535904	6.181968	-0.061621
30	1	0	7.051163	5.541108	-0.824836
31	1	0	6.764011	6.429016	0.697176
32	1	0	7.833441	7.127349	-0.561421
33	6	0	9.776867	5.031548	-0.494695
34	1	0	10.627140	4.487427	-0.034103
35	1	0	9.312803	4.352234	-1.237219

36	1	0	10.179572	5.901445	-1.056413
37	6	0	9.424367	6.255910	1.684011
38	1	0	10.257987	5.665894	2.112155
39	7	0	8.485157	6.637113	2.769858
40	6	0	9.929444	3.146145	3.082388
41	1	0	10.658107	3.653680	3.734740
42	6	0	9.268762	4.706814	5.753652
43	6	0	9.329639	3.885431	6.903324
44	1	0	8.554374	3.120414	7.075411
45	6	0	10.373083	4.041305	7.831045
46	1	0	10.414097	3.393708	8.720608
47	6	0	11.354549	5.028241	7.629987
48	1	0	12.166360	5.156111	8.362718
49	6	0	11.296114	5.855152	6.493861
50	1	0	12.062170	6.630378	6.335528
51	6	0	10.260837	5.694910	5.557253
52	1	0	10.228998	6.350590	4.672927
53	6	0	5.419686	8.619422	4.912447
54	1	0	4.464592	8.482244	4.363204
55	1	0	5.264703	9.320502	5.752743
56	6	0	7.133788	8.224259	3.533072
57	6	0	8.124578	7.970261	2.600864
58	6	0	9.897260	7.686100	1.283652
59	1	0	10.101025	7.792534	0.202930
60	1	0	10.790750	8.003128	1.863427

Table S4. Optimized Cartesian coordinates (Å) of the cation of **2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	16.405374	5.287958	-3.665473
2	6	0	17.222907	5.647506	-5.273654
3	6	0	16.874114	6.854716	-5.919457
4	1	0	16.169016	7.552955	-5.440412
5	6	0	17.432643	7.171089	-7.169427
6	1	0	17.155857	8.113022	-7.667721
7	6	0	18.345900	6.291806	-7.777812
8	1	0	18.787372	6.545461	-8.754048
9	6	0	18.692177	5.085304	-7.141795
10	1	0	19.401696	4.391799	-7.619398
11	6	0	18.129320	4.759563	-5.897975
12	1	0	18.389778	3.806393	-5.412682
13	6	0	17.756897	4.536776	-2.677725
14	6	0	16.670592	2.399338	-1.939712
15	6	0	15.779857	2.436323	-0.835263
16	6	0	14.784097	1.440702	-0.778909
17	1	0	14.074104	1.436826	0.061903
18	6	0	14.676345	0.466822	-1.778139
19	1	0	13.880945	-0.292161	-1.722352
20	6	0	15.582636	0.448420	-2.848443
21	1	0	15.489476	-0.327765	-3.621277
22	6	0	16.614340	1.400711	-2.949517
23	6	0	15.098598	4.065697	-4.096512
24	6	0	14.991991	3.495881	-5.384743
25	1	0	15.755760	3.697949	-6.149593
26	6	0	13.900758	2.667329	-5.696637
27	1	0	13.824449	2.228553	-6.703740
28	6	0	12.915154	2.396608	-4.732531
29	1	0	12.065416	1.741961	-4.980672
30	6	0	13.004745	2.983019	-3.457223
31	1	0	12.229000	2.790370	-2.700595
32	6	0	14.075426	3.833566	-3.150151
33	1	0	14.121804	4.315232	-2.163197

34	6	0	15.888643	3.465857	0.291024
35	6	0	16.491134	2.805650	1.553030
36	6	0	14.551190	4.151648	0.633946
37	1	0	16.577068	4.271068	-0.042877
38	1	0	17.450785	2.291406	1.340043
39	1	0	16.668140	3.559633	2.347666
40	1	0	15.797607	2.040646	1.960285
41	1	0	14.113883	4.676680	-0.239022
42	1	0	13.797847	3.428354	1.007377
43	1	0	14.703699	4.905236	1.433156
44	6	0	17.662798	1.305833	-4.054972
45	6	0	17.133304	0.722974	-5.376368
46	6	0	18.879966	0.482803	-3.572662
47	1	0	18.010278	2.340003	-4.264216
48	1	0	16.193903	1.212801	-5.692441
49	1	0	17.886596	0.857026	-6.179282
50	1	0	16.941888	-0.367125	-5.294737
51	1	0	19.322084	0.882092	-2.639719
52	1	0	18.577739	-0.566060	-3.372713
53	1	0	19.676800	0.470257	-4.344675
54	7	0	17.722200	3.401246	-1.992203
55	6	0	19.944130	4.221203	-1.704447
56	6	0	20.695573	3.573832	-2.887923
57	1	0	21.462571	4.259480	-3.297640
58	1	0	21.218744	2.655742	-2.552562
59	1	0	20.015486	3.290592	-3.716557
60	6	0	20.960409	4.573843	-0.605195
61	1	0	21.507726	3.654676	-0.308173
62	1	0	21.712652	5.304522	-0.956588
63	1	0	20.477311	4.977344	0.305206
64	6	0	18.915372	3.229420	-1.132099
65	1	0	19.232904	2.169252	-1.161389
66	1	0	18.637393	3.467018	-0.084044
67	6	0	18.978829	5.378990	-2.223866
68	6	0	18.425641	6.304651	-1.067574
69	6	0	19.563664	6.299319	-3.324118
70	6	0	19.386443	7.416117	-0.594261
71	1	0	18.101324	5.687318	-0.202416
72	1	0	17.504176	6.787140	-1.457969
73	6	0	20.603288	7.304119	-2.808418
74	1	0	19.957255	5.703047	-4.168282
75	1	0	18.728152	6.891851	-3.752326
76	6	0	19.974216	8.228471	-1.756411
77	1	0	20.213031	6.992185	0.009270
78	1	0	18.819624	8.078103	0.094638
79	1	0	20.982504	7.896107	-3.667368
80	1	0	21.487044	6.779424	-2.385400
81	1	0	20.716344	8.959689	-1.373997
82	1	0	19.166974	8.823875	-2.240967

Table S5. Optimized Cartesian coordinates (Å) of the cation of **3**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	16.213894	5.678240	-3.324080
2	7	0	18.738404	5.337032	-2.131594
3	7	0	19.568014	4.544637	-1.477431
4	7	0	18.991434	3.353869	-1.509390
5	6	0	16.976162	6.103551	-4.954862
6	6	0	16.763119	7.411069	-5.446620
7	1	0	16.165654	8.127403	-4.859251
8	6	0	17.315868	7.802480	-6.678891
9	1	0	17.148394	8.824117	-7.053465

10	6	0	18.078702	6.891176	-7.429203
11	1	0	18.510882	7.198272	-8.394130
12	6	0	18.295533	5.587456	-6.945211
13	1	0	18.897714	4.875025	-7.530209
14	6	0	17.754416	5.196133	-5.710943
15	1	0	17.951155	4.183264	-5.325614
16	6	0	17.610063	4.688639	-2.601816
17	6	0	19.065025	6.787560	-2.272525
18	1	0	18.689566	7.076893	-3.271799
19	1	0	18.441270	7.316200	-1.525291
20	6	0	20.537792	7.078814	-2.123896
21	6	0	21.393340	6.980497	-3.259480
22	6	0	20.898359	6.469297	-4.613895
23	1	0	19.802516	6.636251	-4.681609
24	6	0	21.515738	7.201331	-5.818851
25	1	0	22.594301	6.970184	-5.941456
26	1	0	21.006881	6.886449	-6.752891
27	1	0	21.410039	8.300873	-5.723043
28	6	0	21.130554	4.944897	-4.720197
29	1	0	20.625537	4.393747	-3.900677
30	1	0	20.751852	4.552077	-5.686471
31	1	0	22.214153	4.711757	-4.655752
32	6	0	22.754573	7.295195	-3.099929
33	1	0	23.423597	7.221682	-3.970605
34	6	0	23.292002	7.699221	-1.862696
35	6	0	22.427661	7.760609	-0.754805
36	1	0	22.844704	8.062761	0.218375
37	6	0	21.059535	7.444488	-0.852451
38	6	0	20.166910	7.538273	0.388037
39	1	0	19.311340	6.840924	0.246522
40	6	0	20.866803	7.086021	1.683351
41	1	0	21.658819	7.796983	1.997328
42	1	0	20.135187	7.033522	2.515710
43	1	0	21.333910	6.086951	1.565136
44	6	0	19.599709	8.967842	0.536024
45	1	0	19.046214	9.292203	-0.370140
46	1	0	18.913518	9.039558	1.405564
47	1	0	20.426103	9.692901	0.689611
48	6	0	24.769944	8.046973	-1.726704
49	1	0	24.938992	8.342952	-0.667394
50	6	0	25.665052	6.824477	-2.018186
51	1	0	25.562762	6.492600	-3.073440
52	1	0	26.733670	7.072151	-1.850109
53	1	0	25.402859	5.966089	-1.366089
54	6	0	25.151310	9.249527	-2.614688
55	1	0	24.518446	10.133233	-2.393708
56	1	0	26.211453	9.534839	-2.452921
57	1	0	25.032249	9.009319	-3.692678
58	6	0	19.675437	2.220806	-0.882543
59	1	0	20.762314	2.413822	-0.922385
60	1	0	19.351104	2.114922	0.170751
61	1	0	19.420088	1.302135	-1.441537
62	6	0	17.784360	3.354534	-2.187184
63	6	0	16.968278	2.142231	-2.366102
64	6	0	16.502608	1.426733	-1.238009
65	1	0	16.750244	1.776484	-0.223438
66	6	0	15.690068	0.296004	-1.410210
67	1	0	15.321785	-0.252000	-0.529448
68	6	0	15.335261	-0.124372	-2.704158
69	1	0	14.689533	-1.006035	-2.837250
70	6	0	15.801198	0.580429	-3.828602
71	1	0	15.520181	0.256333	-4.841610
72	6	0	16.619650	1.705981	-3.664070
73	1	0	16.977821	2.262247	-4.541800
74	6	0	14.968143	4.375275	-3.712318
75	6	0	14.625402	4.007182	-5.031090
76	1	0	15.148255	4.457275	-5.888672
77	6	0	13.611017	3.059668	-5.254026
78	1	0	13.344272	2.782091	-6.285811
79	6	0	12.943413	2.466743	-4.169177

80	1	0	12.155155	1.719131	-4.348005
81	6	0	13.273678	2.840151	-2.853150
82	1	0	12.748387	2.384880	-1.999638
83	6	0	14.265146	3.805105	-2.624898
84	1	0	14.503544	4.105760	-1.591190

Table S6. Optimized Cartesian coordinates (Å) of the cation of **4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	14.420703	5.931659	14.252389
2	7	0	14.039217	8.516744	15.338838
3	7	0	14.043856	8.606445	13.157712
4	7	0	13.957163	6.836387	11.525580
5	7	0	13.974261	4.665378	11.769870
6	6	0	14.224701	7.770220	14.223642
7	6	0	13.758189	9.827218	14.988231
8	1	0	13.558752	10.594672	15.743342
9	6	0	13.756167	9.890758	13.613213
10	1	0	13.573889	10.730970	12.933257
11	6	0	14.050981	7.951211	16.681042
12	6	0	15.292253	7.890373	17.367923
13	6	0	15.268526	7.282728	18.638113
14	1	0	16.198360	7.209371	19.220127
15	6	0	14.073900	6.781386	19.180498
16	1	0	14.084104	6.313176	20.176899
17	6	0	12.865842	6.886998	18.476620
18	1	0	11.938467	6.503688	18.928671
19	6	0	12.817373	7.484838	17.200760
20	6	0	16.557295	8.534327	16.806248
21	1	0	16.501815	8.478382	15.694957
22	6	0	16.609362	10.027768	17.205830
23	1	0	15.719281	10.591303	16.859124
24	1	0	17.509224	10.515963	16.779112
25	1	0	16.655051	10.131130	18.309418
26	6	0	17.846835	7.813286	17.230640
27	1	0	18.070301	7.969893	18.305911
28	1	0	18.711003	8.210667	16.661754
29	1	0	17.784266	6.723851	17.045210
30	6	0	11.493579	7.609705	16.448658
31	1	0	11.675126	8.177322	15.509196
32	6	0	10.458774	8.412641	17.264876
33	1	0	9.533317	8.563447	16.672711
34	1	0	10.850952	9.408434	17.555397
35	1	0	10.172456	7.879748	18.194642
36	6	0	10.952090	6.223968	16.042111
37	1	0	11.687493	5.669106	15.425019
38	1	0	10.013181	6.325554	15.460190
39	1	0	10.727682	5.600252	16.931698
40	6	0	14.186640	5.833208	12.423030
41	6	0	13.603784	6.288939	10.293690
42	1	0	13.380591	6.905601	9.415485
43	6	0	13.618255	4.922079	10.455321
44	1	0	13.404532	4.115482	9.747030
45	6	0	14.192337	3.363852	12.389521
46	6	0	15.485519	2.794090	12.253082
47	6	0	15.685591	1.547166	12.877513
48	1	0	16.665632	1.054572	12.800179
49	6	0	14.652525	0.920879	13.590394
50	1	0	14.833332	-0.056216	14.064571
51	6	0	13.388990	1.521039	13.701826
52	1	0	12.596172	1.005456	14.262182
53	6	0	13.118226	2.766696	13.100352
54	6	0	16.584651	3.449555	11.419217
55	1	0	16.402337	4.549244	11.416655
56	6	0	17.993316	3.231006	11.997884

57	1	0	18.035161	3.484464	13.073625
58	1	0	18.728134	3.865507	11.463014
59	1	0	18.328700	2.180728	11.876919
60	6	0	16.517036	2.946903	9.958196
61	1	0	16.695811	1.852612	9.919763
62	1	0	17.292260	3.441025	9.337758
63	1	0	15.531206	3.134173	9.486855
64	6	0	11.729443	3.399629	13.161694
65	1	0	11.857276	4.507315	13.135353
66	6	0	10.902908	2.992037	11.919421
67	1	0	11.394091	3.285540	10.969392
68	1	0	9.899909	3.464734	11.943940
69	1	0	10.762234	1.891958	11.893421
70	6	0	10.967505	3.061928	14.455237
71	1	0	10.046601	3.674069	14.525256
72	1	0	11.580305	3.254506	15.358692
73	1	0	10.648371	1.999931	14.476412
74	6	0	14.239423	8.252549	11.753130
75	1	0	13.550954	8.859336	11.133184
76	1	0	15.286203	8.475783	11.451281
77	6	0	16.229403	5.689776	14.477160
78	6	0	16.590888	4.657251	15.371374
79	1	0	15.815456	4.053837	15.869254
80	6	0	17.951434	4.403384	15.621047
81	1	0	18.237597	3.599423	16.316075
82	6	0	18.940274	5.177361	14.989101
83	1	0	20.004103	4.979817	15.191364
84	6	0	18.577798	6.205599	14.096187
85	1	0	19.356229	6.807682	13.603124
86	6	0	17.224404	6.462984	13.835285
87	1	0	16.947667	7.271544	13.139129

Table S7. Optimized Cartesian coordinates (Å) of the cation of $[(SIMes)PPh_2]^+$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.230630	0.994199	11.927730
2	7	0	-1.673595	-0.345190	14.515871
3	7	0	-2.387047	-1.384393	12.693289
4	6	0	0.535438	3.713480	17.945328
5	1	0	-0.224560	4.220239	18.571409
6	1	0	1.001414	4.480841	17.288571
7	1	0	1.336794	3.332659	18.611461
8	6	0	-0.059005	2.609248	17.107150
9	6	0	-1.450102	2.452425	16.975641
10	1	0	-2.124367	3.122104	17.534528
11	6	0	-2.014404	1.472664	16.134148
12	6	0	-1.130514	0.642088	15.409243
13	6	0	-1.820524	-0.264196	13.181968
14	6	0	-2.560847	-1.687349	11.295964
15	6	0	-3.819404	-1.484885	10.686856
16	6	0	-3.932554	-1.776833	9.311965
17	1	0	-4.903492	-1.611234	8.817134
18	6	0	-2.850039	-2.267248	8.559256
19	6	0	-2.988661	-2.577965	7.087791
20	1	0	-2.239226	-2.018438	6.489159
21	1	0	-3.995310	-2.325103	6.701791
22	1	0	-2.810857	-3.657093	6.893558
23	6	0	-5.318289	2.761980	10.546163
24	6	0	-5.078537	2.624014	11.925794
25	1	0	-5.844654	2.932454	12.654141
26	6	0	-3.864410	2.081908	12.376386
27	1	0	-3.693785	1.955136	13.454749

28	6	0	-2.872990	1.686366	11.449825
29	6	0	-3.125729	1.812794	10.065817
30	1	0	-2.370955	1.475665	9.337772
31	6	0	-4.344659	2.350252	9.618341
32	1	0	-4.534890	2.446148	8.538141
33	6	0	-2.063891	-1.693354	15.009514
34	1	0	-2.736563	-1.591484	15.883191
35	1	0	-1.150293	-2.234653	15.336303
36	6	0	-2.742913	-2.329349	13.777505
37	1	0	-2.359888	-3.340039	13.533979
38	1	0	-3.848416	-2.393967	13.868909
39	6	0	-1.445993	-2.206437	10.582052
40	6	0	-1.616193	-2.479371	9.216273
41	1	0	-0.761637	-2.874684	8.642855
42	6	0	-5.017768	-0.976222	11.449821
43	1	0	-4.758865	-0.621444	12.465204
44	1	0	-5.790095	-1.769044	11.544941
45	1	0	-5.484794	-0.122913	10.917393
46	6	0	-0.115792	-2.416391	11.264790
47	1	0	0.383535	-1.439535	11.454081
48	1	0	0.566159	-3.024656	10.640560
49	1	0	-0.220810	-2.922675	12.247137
50	6	0	0.785074	1.725816	16.400164
51	1	0	1.877452	1.830604	16.500280
52	6	0	0.277975	0.725234	15.557522
53	6	0	1.204810	-0.235175	14.850664
54	1	0	0.855809	-0.497888	13.832010
55	1	0	1.299111	-1.186173	15.420081
56	1	0	2.220994	0.192441	14.755022
57	6	0	-3.517678	1.335096	16.046894
58	1	0	-4.000265	2.319620	15.876901
59	1	0	-3.931544	0.941687	17.000054
60	1	0	-3.841462	0.653500	15.236745
61	6	0	-0.344669	2.309339	12.866758
62	6	0	1.062226	2.282331	12.714520
63	1	0	1.530361	1.494436	12.102298
64	6	0	1.864981	3.253650	13.334650
65	1	0	2.958594	3.221466	13.211221
66	6	0	1.266882	4.272938	14.094048
67	6	0	-0.133569	4.321464	14.227100
68	1	0	-0.603818	5.122754	14.817648
69	6	0	-0.938596	3.351826	13.612482
70	1	0	-2.030582	3.410760	13.719469
71	1	0	1.891964	5.041811	14.574554
72	1	0	-6.271116	3.186165	10.193034

Table S8. Selected NBO and AIM parameters for cationic phosphines.

	1	**2**	**3**	**4**[†]	**[(SIMes)PPh$_2$]$^+$** [‡]
P–C_{cation} bond polarization	33% P	35% P	33% P	33% P	33% P / 39% P
	67% C	65% C	67% C	67% C	67% C / 61% C
ρ at P–C_{cation} BCP (a.u.)	0.147	0.153	0.146	0.149 / 0.149	0.143 / 0.161
$\nabla^2\rho$ at P–C_{cation} BCP (a.u.)	-0.013	-0.049	-0.055	-0.048 / -0.049	-0.066 / -0.233
Lone pair (NBO) energy (meV)	-500.28	-468.98	-492.43	-645.03	-483.26
I(r) at VSCC (meV)	623.76	620.08	613.91	760.87	614.75

[†] Multiplicity of values corresponds to those for the different P–C_{cation} bonds.

[‡] Multiplicity of values corresponds to comparison between the P–C_{cation} and P–C_{phenyl} bonds.

BCP = bond critical point

VSCC = valence shell charge concentration