Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Probing steric influences on electrophilic phosphonium cations: A comparison of $[(3,5\text{-}(CF_3)_2C_6H_3)_3PF]^+$ and $[(C_6F_5)_3PF]^+$

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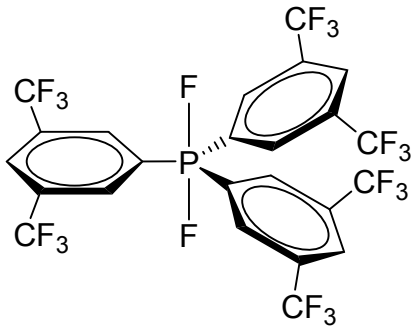
This PDF file includes:

1. Synthesis

2.1 $(3,5\text{-}(CF_3)_2C_6H_3)_3PF_2$ (1)



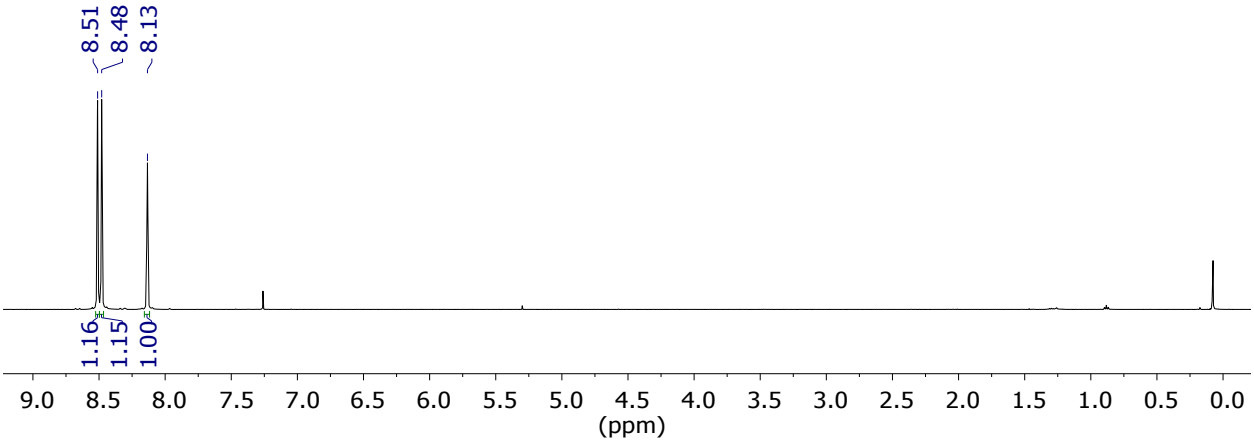


Figure S1. ^1H ($CDCl_3$) NMR spectrum of **1**.

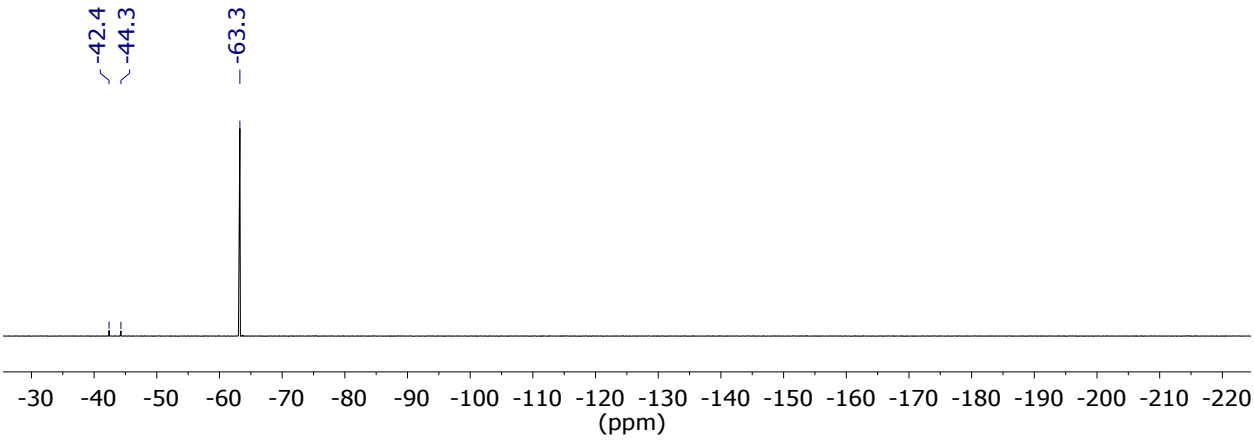


Figure S2. $^{19}F\{^{1}H\}$ ($CDCl_3$) NMR spectrum of **1**.

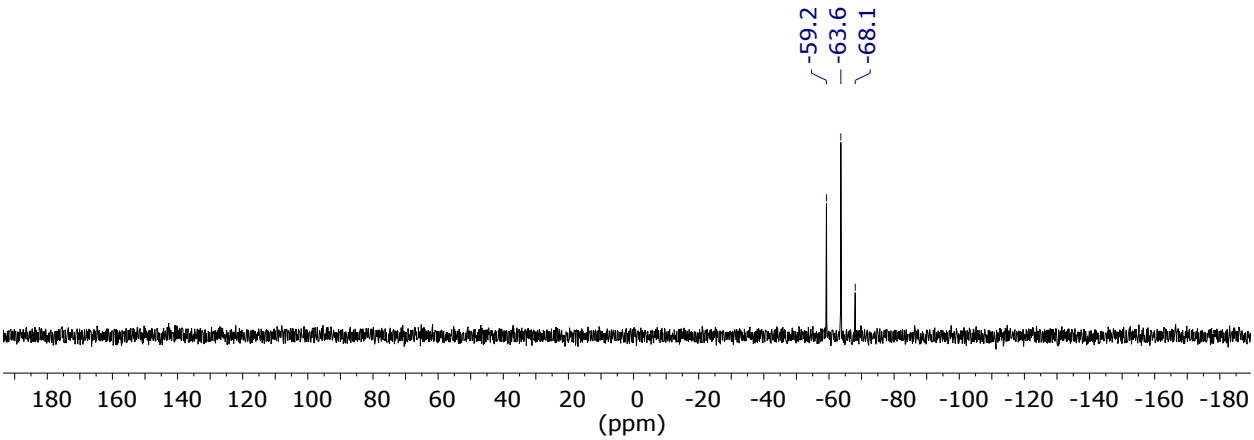


Figure S3. $^{31}P\{^{1}H\}$ ($CDCl_3$) NMR spectrum of **1**.

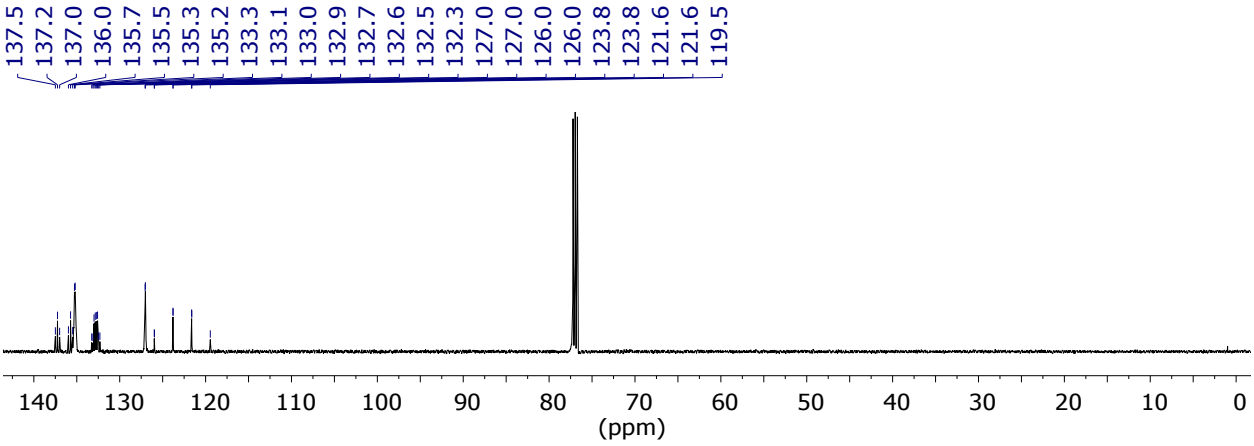


Figure S4. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR spectrum of **1**.

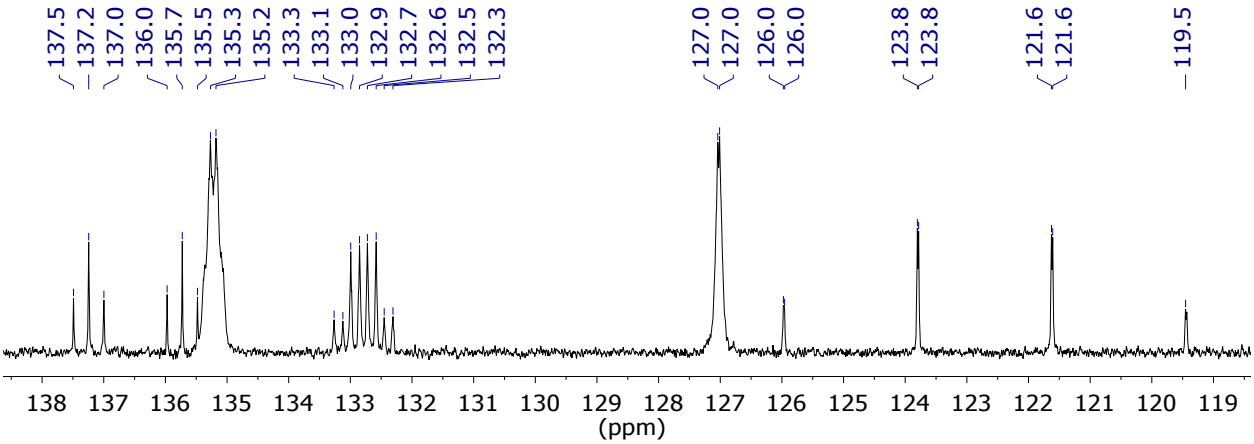
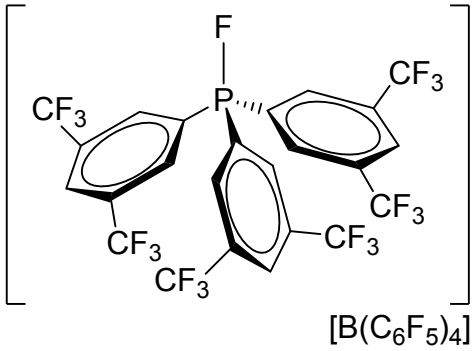


Figure S5. $^{13}C\{^{1}H\}$ ($CDCl_3$) NMR spectrum of **1**, expanded region.

2.2 [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$PF][B(C$_6$F$_5$)$_4$] (2)



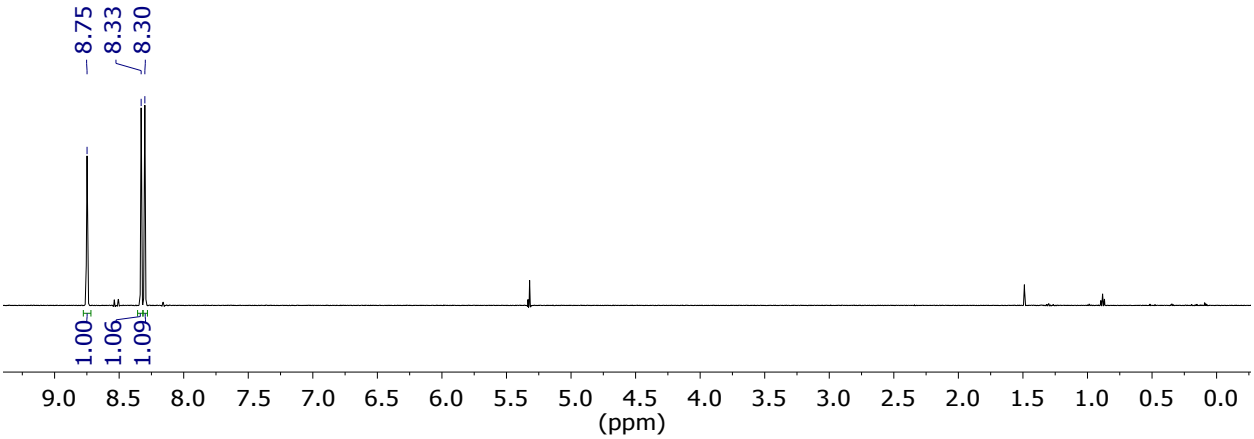


Figure S6. ^{1}H (CD_2Cl_2) NMR spectrum of **2**.

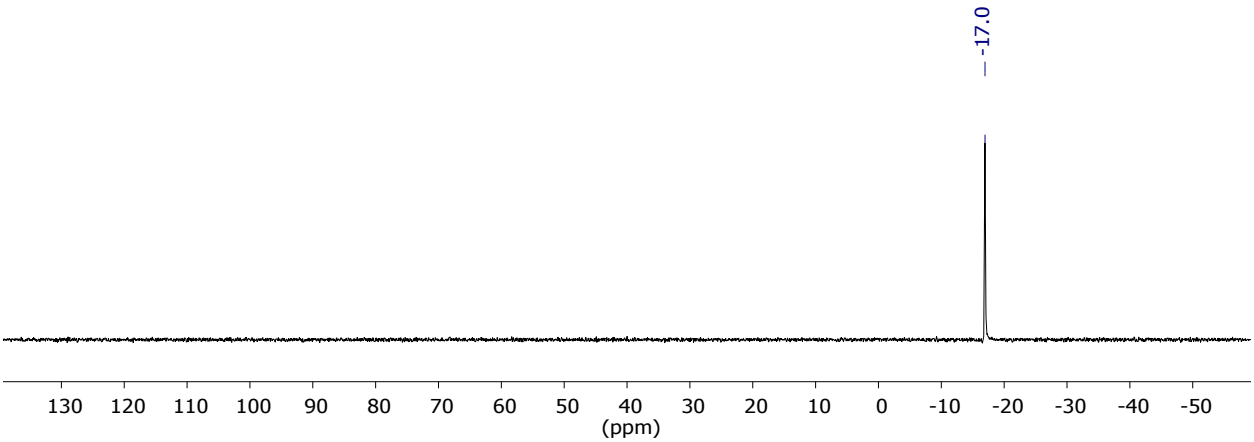


Figure S7. $^{11}B\{^{1}H\}$ (CD_2Cl_2) NMR spectrum of **2**.

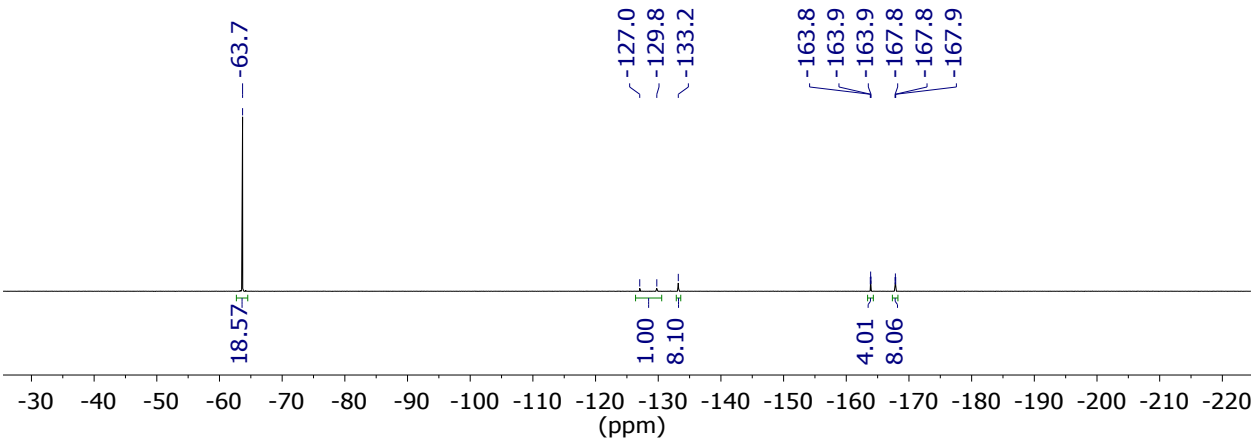


Figure S8. $^{19}F\{^{1}H\}$ (CD_2Cl_2) NMR spectrum of **2**.

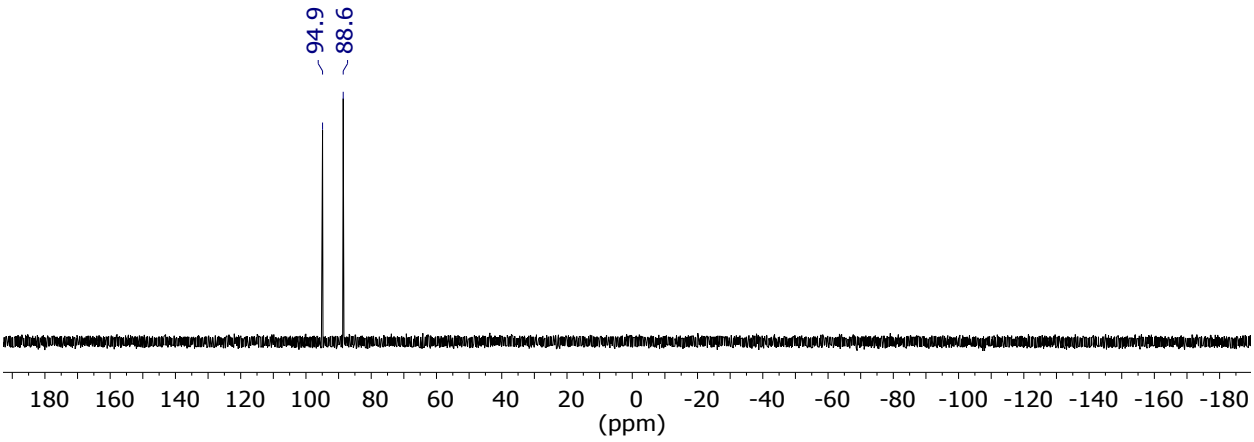


Figure S9. $^{31}P\{^{1}H\}$ (CD_2Cl_2) NMR spectrum of **2**.

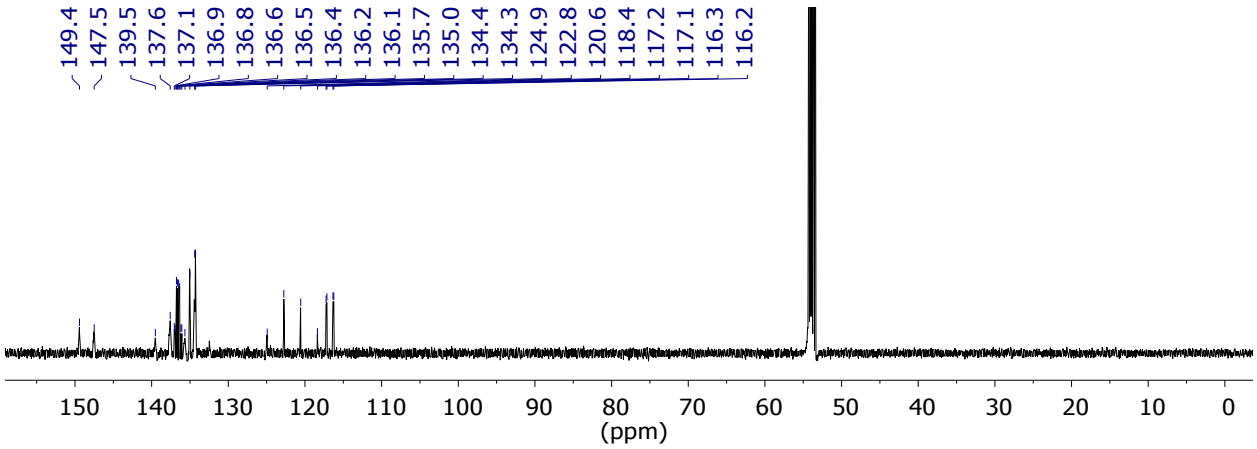


Figure S10. $^{13}C\{^{1}H\}$ (CD_2Cl_2) NMR of **2**.

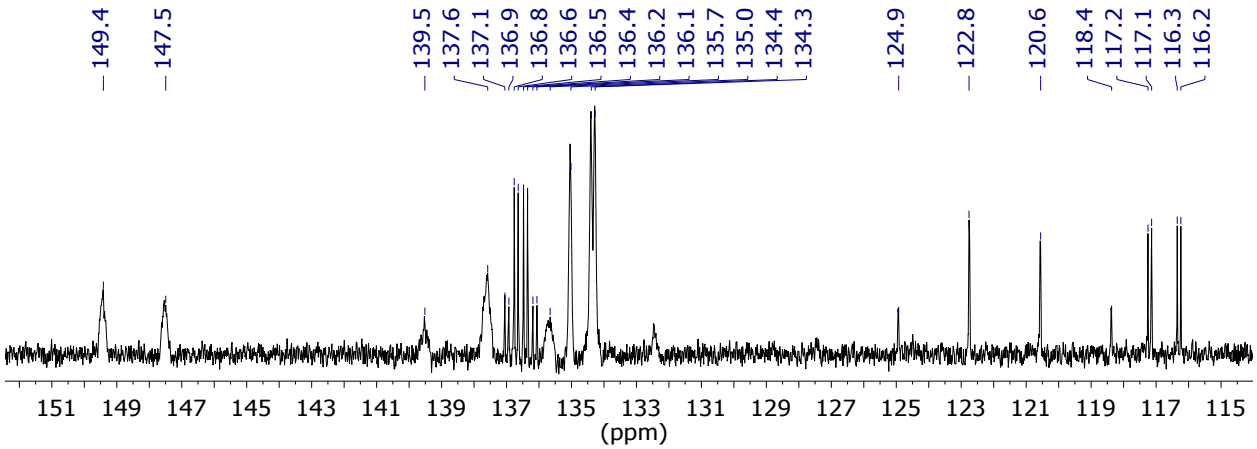


Figure S11. $^{13}C\{^{1}H\}$ (CD_2Cl_2) NMR of **2**, expanded region.

2. Air Stability Test

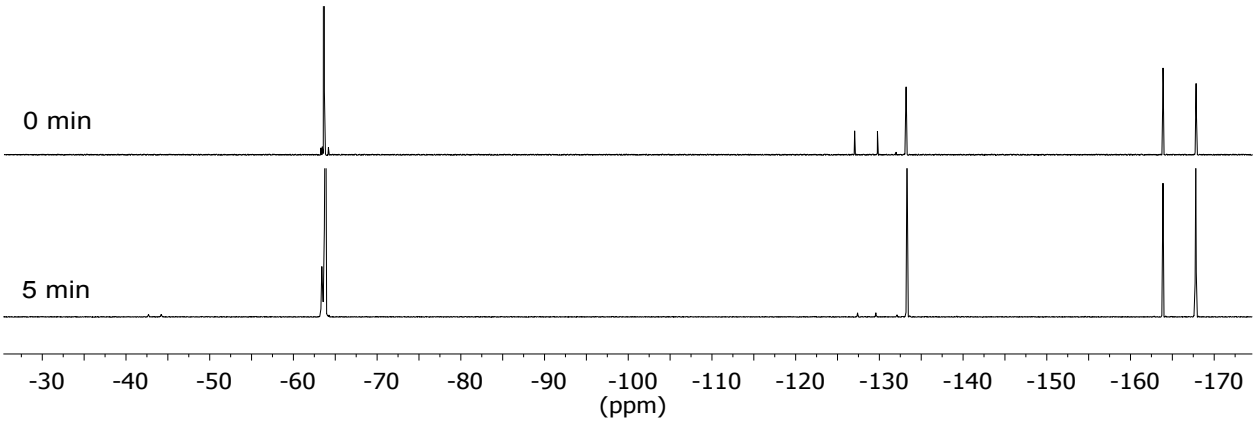


Figure S12. $^{19}F\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of **2** after exposure to air.

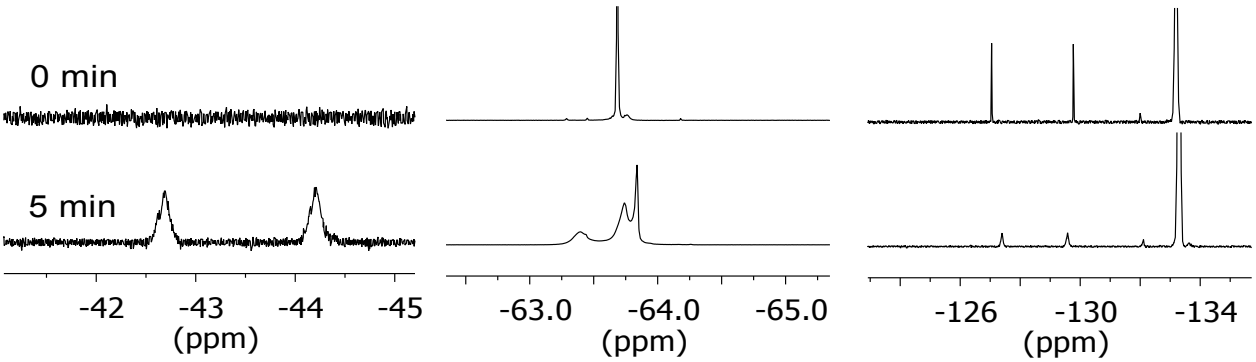


Figure S13. $^{19}F\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of **2** after exposure to air, expanded region.

3. Gutmann-Beckett Method

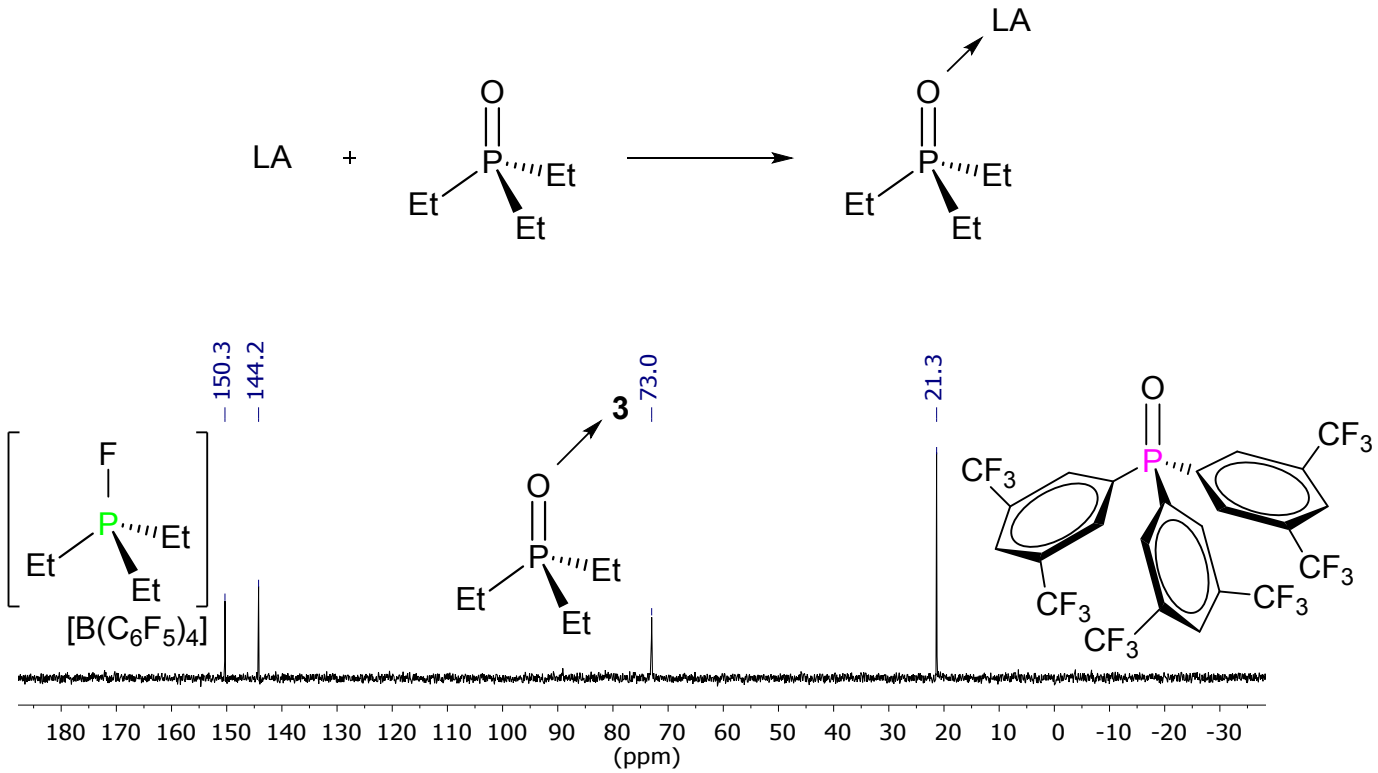


Figure S14. $^{31}P\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of Gutmann-Beckett method with **2**.

4. Silane Stability Test

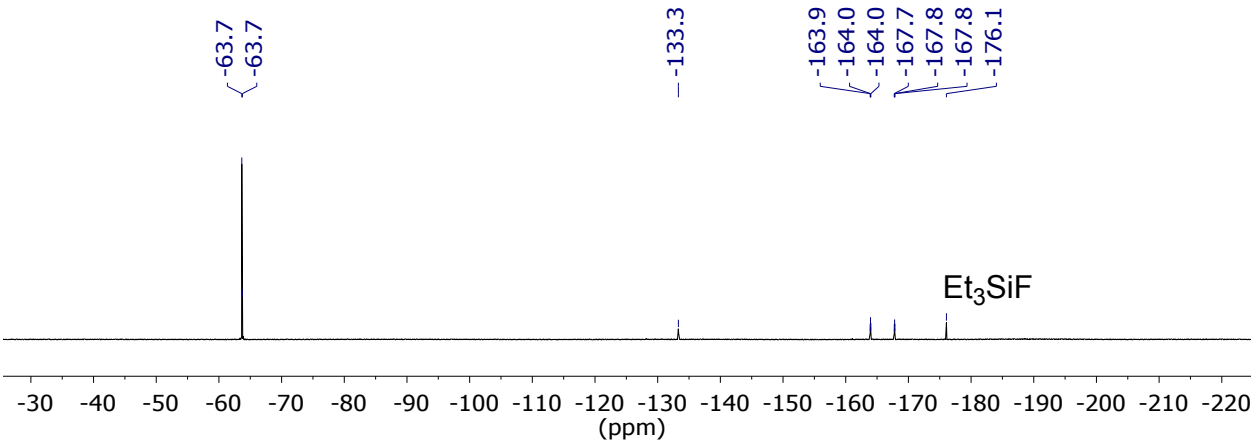


Figure S15. $^{19}F\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of **2** after exposure to Et_3SiH for 16 hours.

5. Lewis Acid Catalysis

5.1 Dimerization of 1,1-diphenylethylene

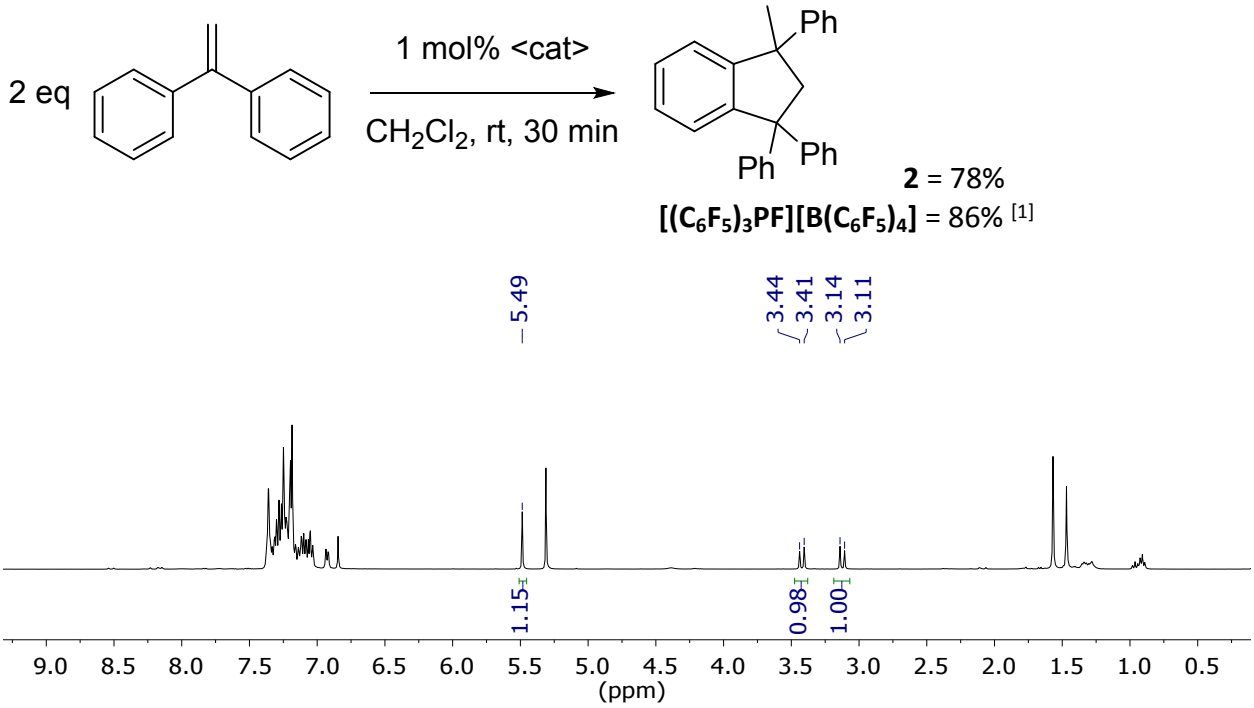
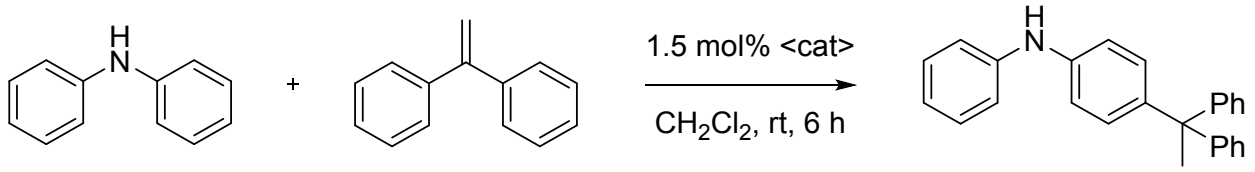


Figure S16. ^1H ($CDCl_3$) NMR spectrum from the catalytic dimerization of 1,1-diphenylethylene by **2**.

5.2 Hydroarylation of diphenylamine with 1,1'-diphenylethylene



2 = 84%
$[(C_6F_5)_3PF][B(C_6F_5)_4]$ = >99% [2]

MS (EI ionization), [m/z]: 349.2 (M-H).

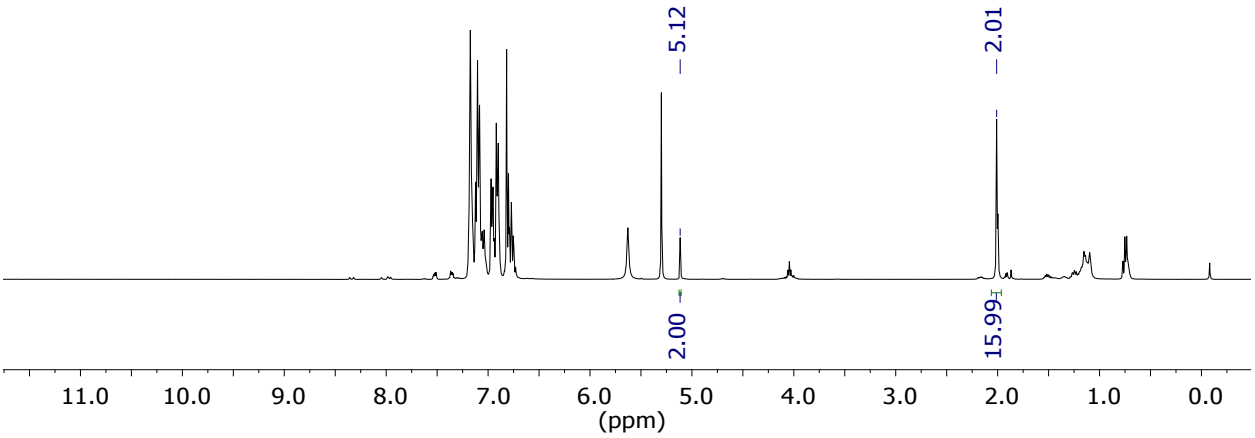
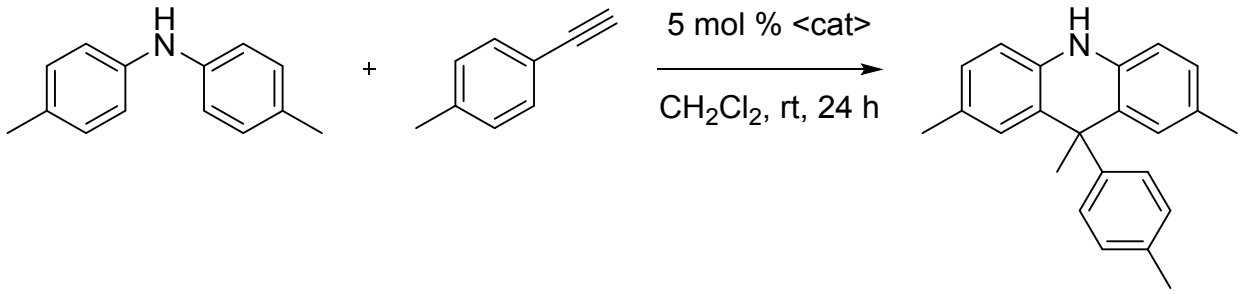


Figure S17. ^1H ($CDCl_3$) NMR spectrum from the catalytic hydroarylation of diphenylamine with 1,1'-diphenylethylene by **2**.

5.3 Double hydroarylation of di-para-tolylamine with para-tolylacetylene



2 = 91%
$[(C_6F_5)_3PF][B(C_6F_5)_4]$ = 74%

MS (EI ionization), [m/z]: 298.1 (M-H).

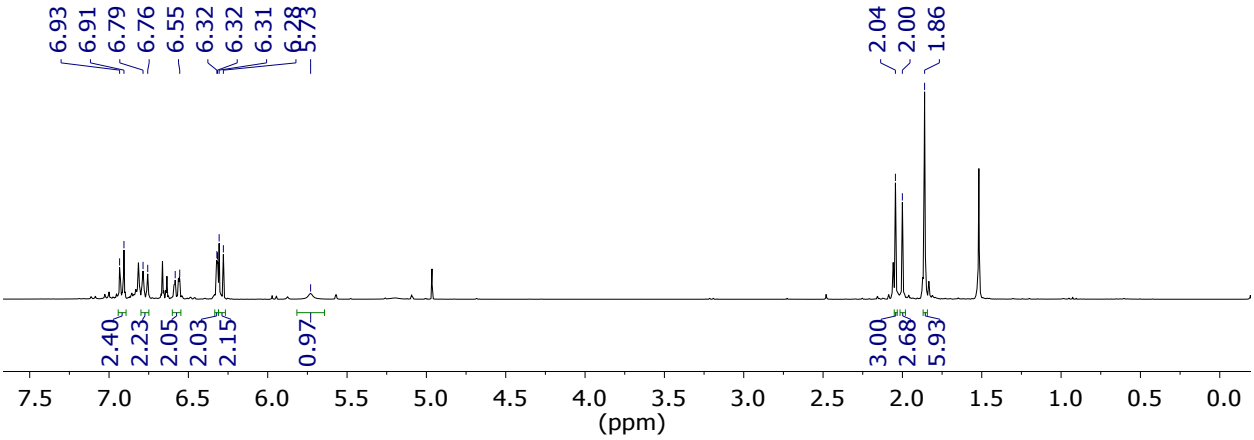


Figure S18. ^{1}H NMR spectrum for the catalytic double hydroarylation of di-*para*-tolylamine with *para*-tolylacetylene by **2**.

6. Phosphorane/Phosphonium Exchange Experiments

5.1 Competition between 2 and $(C_6F_5)_3PF_2$

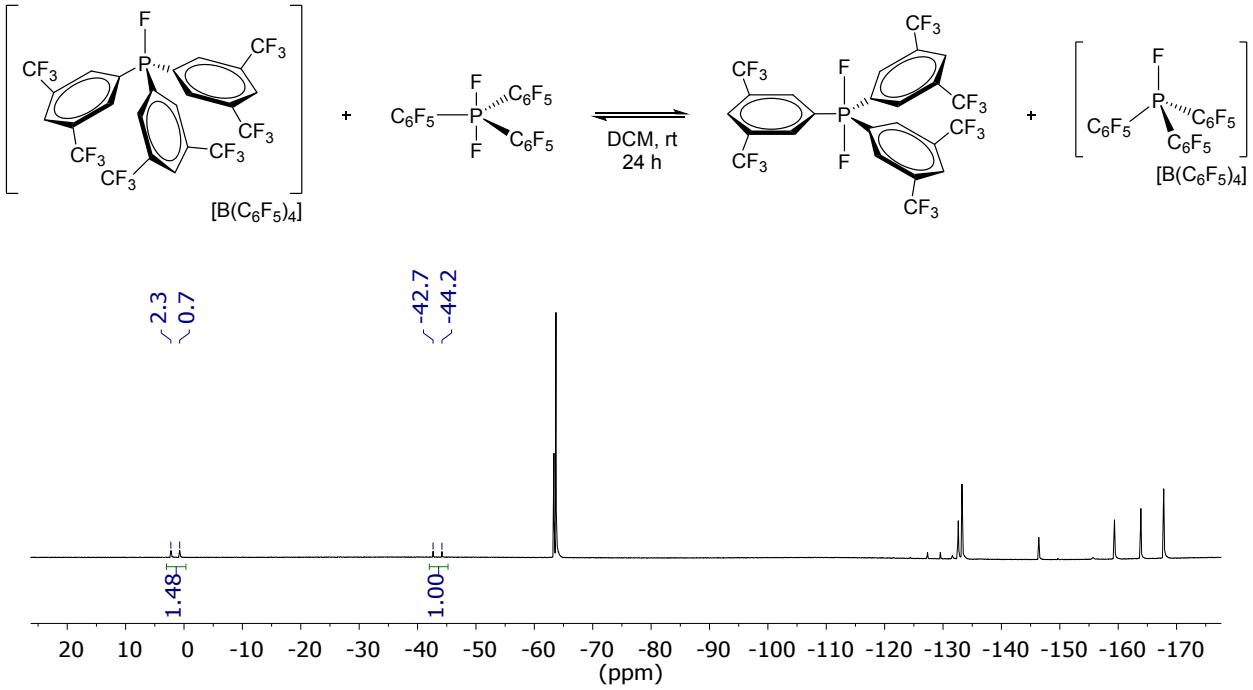


Figure S19. $^{19}F\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of **2** and $(C_6F_5)_3PF_2$.

5.1 Competition between 1 and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$]

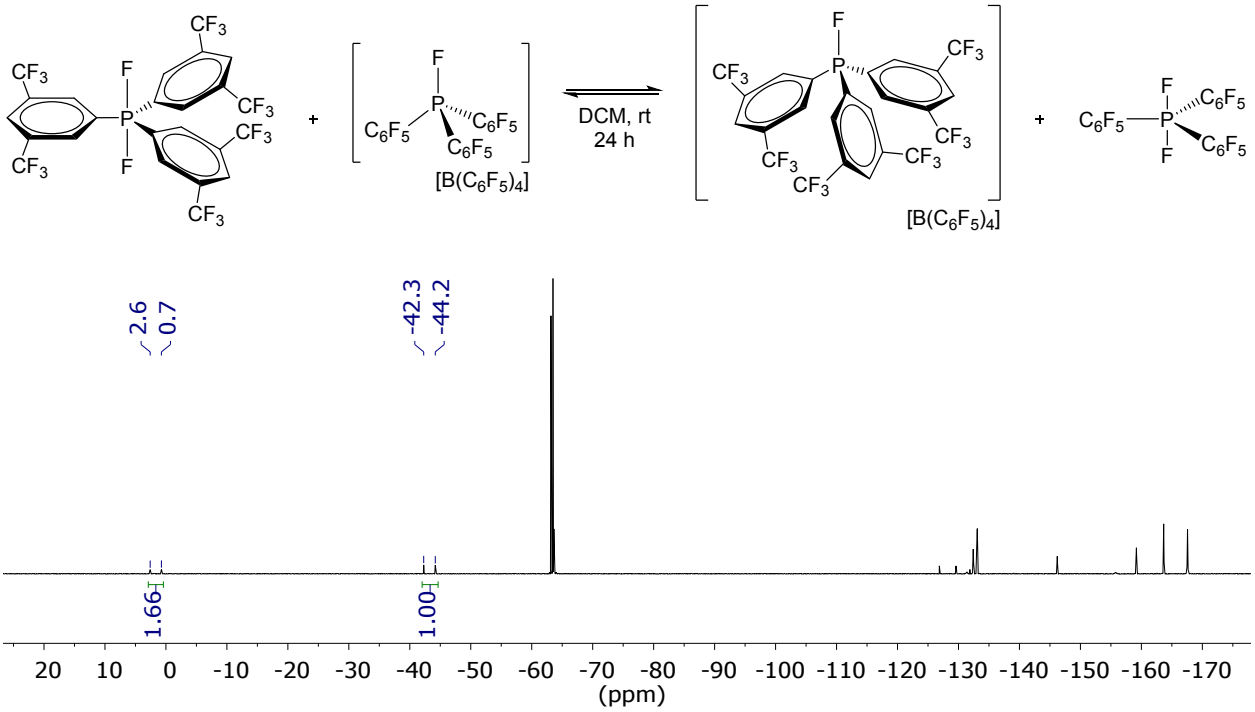


Figure S20. $^{19}F\{^{1}H\}$ (CH_2Cl_2) NMR spectrum of **1** and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$].

7. Phosphorane/Phosphonium Self-Exchange Experiments

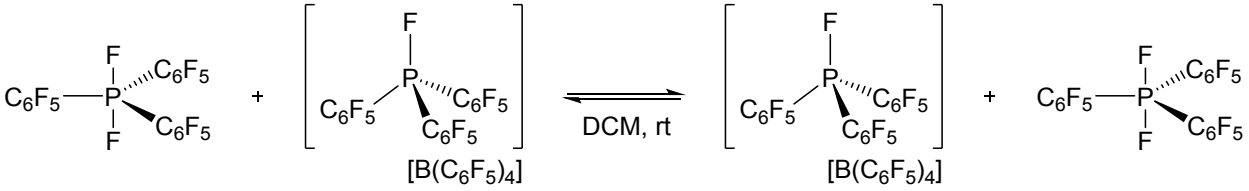
$$\frac{[AA]}{[AB]} = \frac{\left(1 - 2k^2\right)\left(1 - e^{-2k\tau}\right)}{2k^2 + \left(1 - 2k^2\right)\left(e^{-2k\tau}\right)}$$

Eq'n 1

$$2\tau = \frac{1}{k} ln\left(1 + \left(\frac{[AB]}{[AA]}\right)\right)$$

Eq'n 2

6.1 Self-Exchange of $(C_6F_5)_3PF_2$ and $[(C_6F_5)_3PF][B(C_6F_5)_4]$



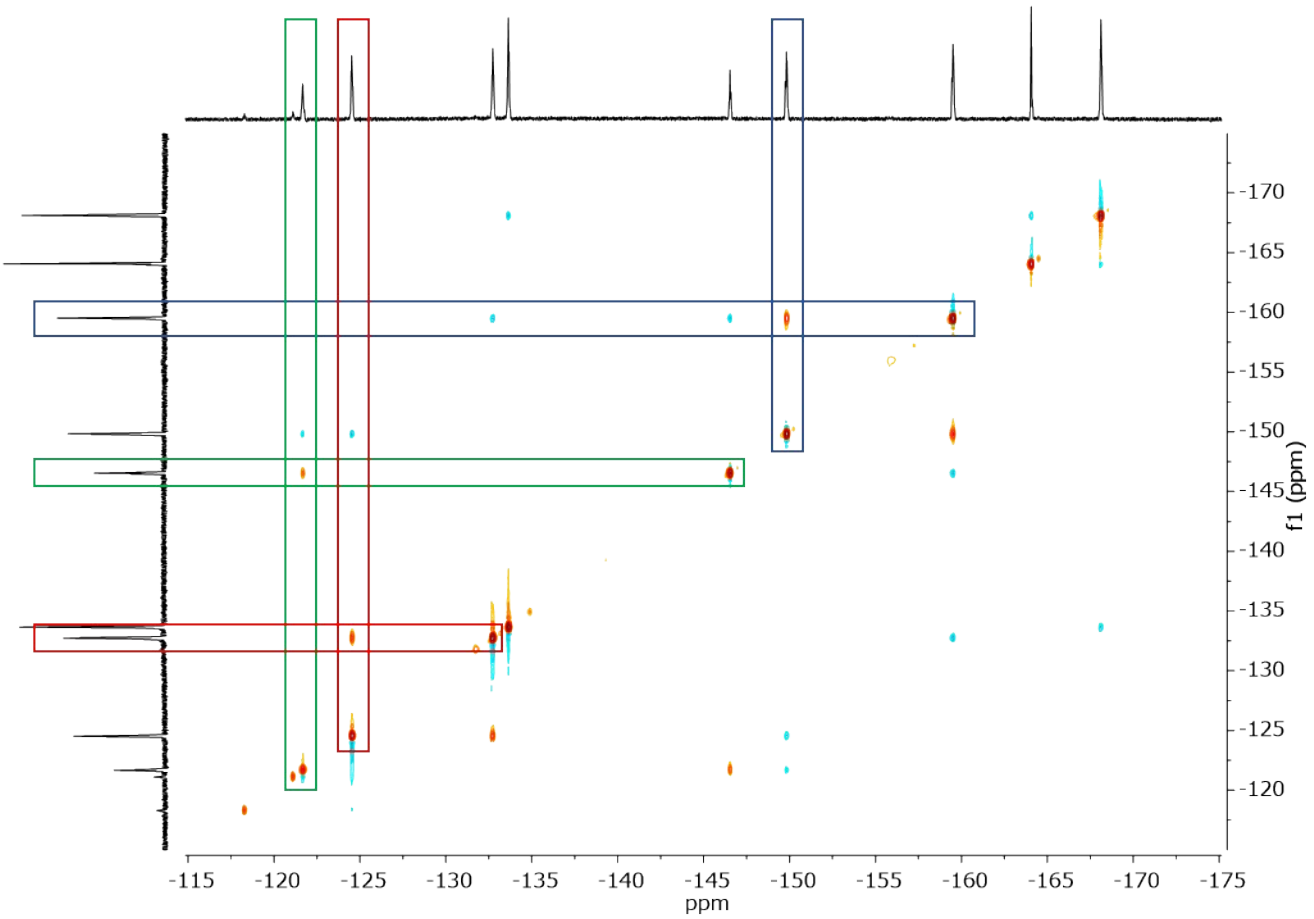


Figure S21. 2D ^{19}F-^{19}F NOSY/EXSY of $(C_6F_5)_3PF_2$ and $[(C_6F_5)_3PF][B(C_6F_5)_4]$.

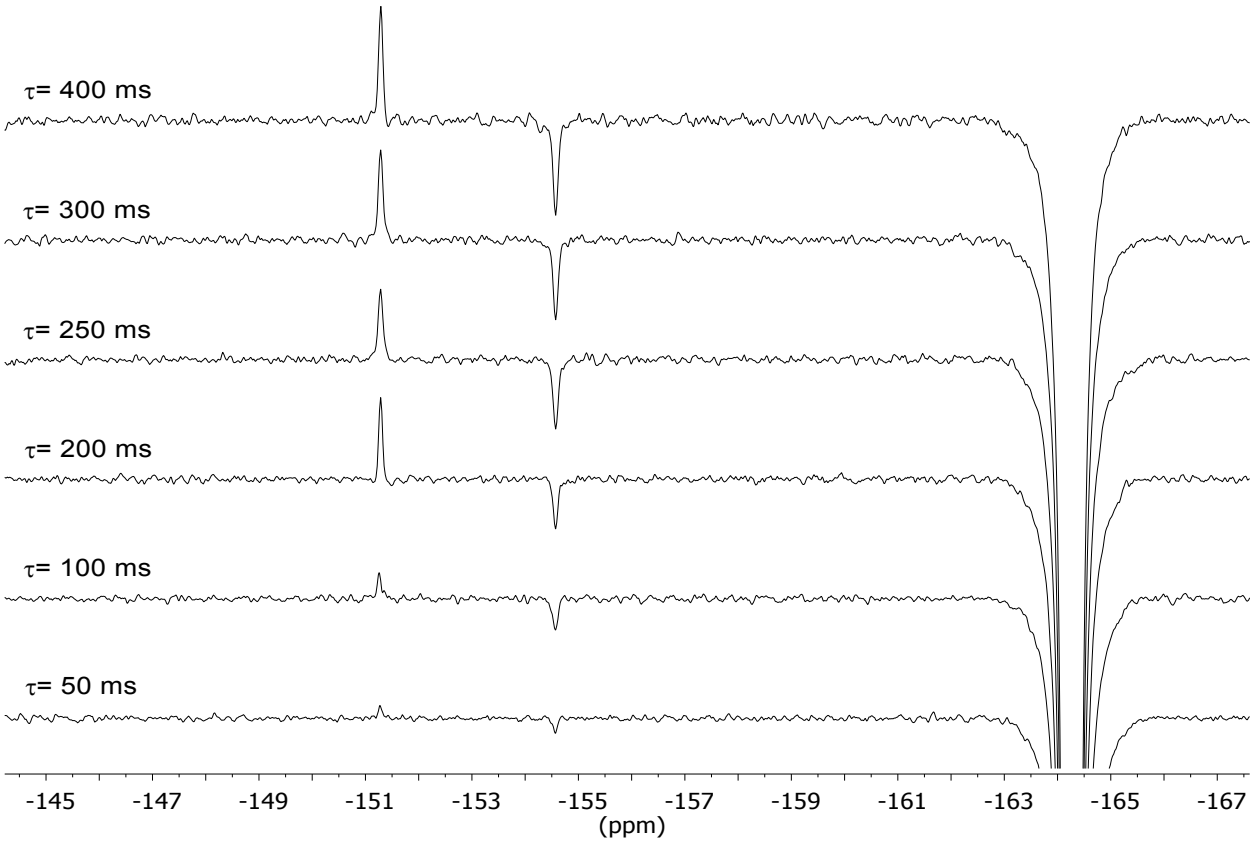


Figure S22. Selective 1D ^{19}F NMR exchange spectroscopy (SEXY) for phosphorus-substituted *meta*-C-F $[(C_6F_5)_3PF][B(C_6F_5)_4]$ exchanging with $(C_6F_5)_3PF_2$.

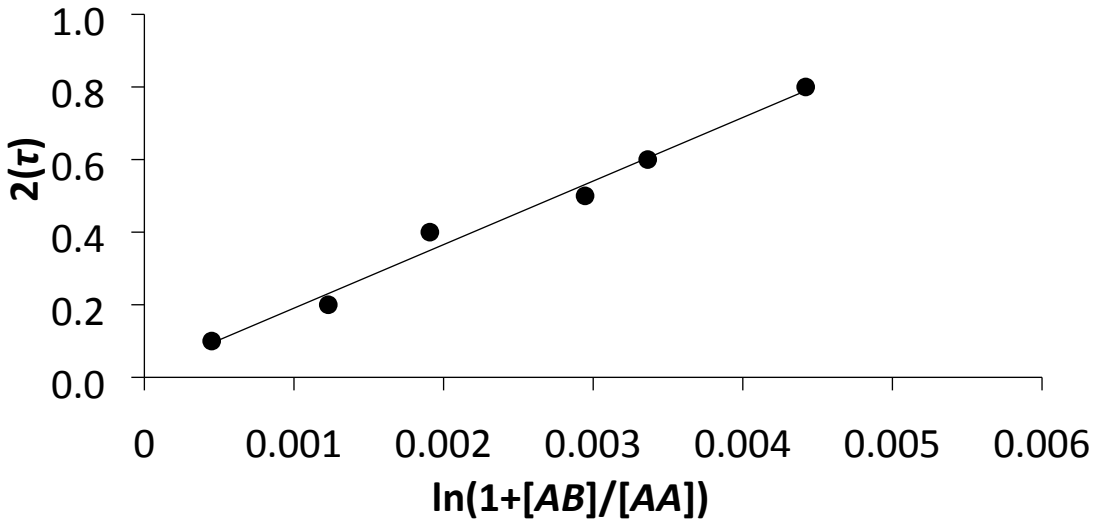
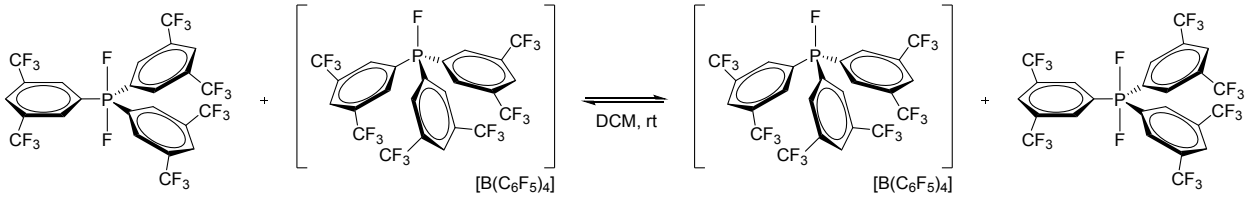


Figure S23. Graph of 2τ vs ln (1+([*AB*]/[*AA*])) for phosphorus-substituted *meta*-C-F of $[(C_6F_5)_3PF][B(C_6F_5)_4]$ exchanging with $(C_6F_5)_3PF_2$. k = 0.0057 s^{-1}.

6.2 Self-Exchange of 1 and 2



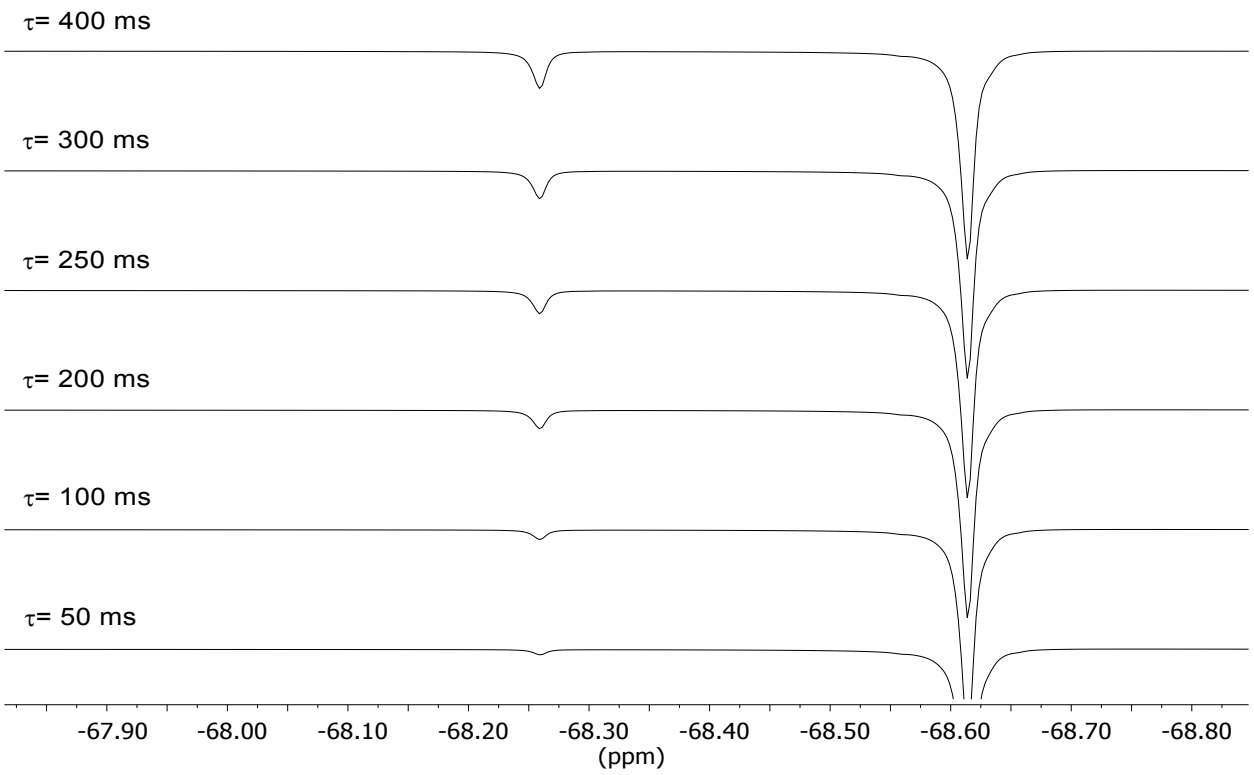


Figure S24. Selective 1D ^{19}F NMR exchange spectroscopy (SEXY) for CF_3 of **2** exchanging with **1**.

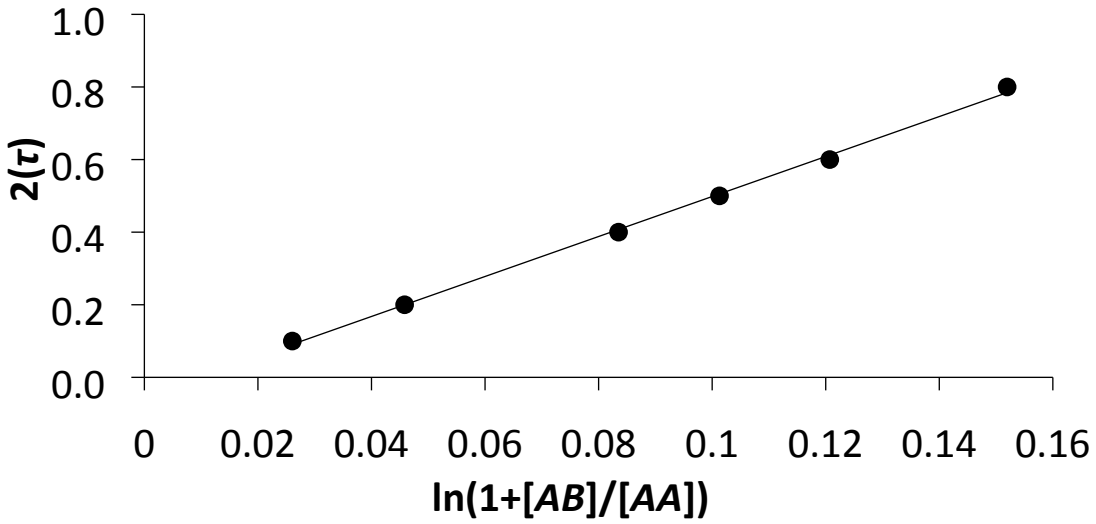


Figure S25. Graph of 2τ vs ln (1+([*AB*]/[*AA*])) for CF_3 of **2** exchanging with **1**. k = 0.18.

8. Computational Details

Table S1. Cartesian coordinates (Å) of $[(3,5\text{-}(CF_3)_2C_6H_3)_3PF]^+$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.635604	0.526982	-0.535622
2	15	0	0.001519	-0.000581	-1.022988
3	6	0	-0.360081	-1.680660	-0.540738
4	6	0	-1.273900	1.151894	-0.542039
5	6	0	-1.319723	-1.941663	0.450197
6	6	0	-1.578548	-3.265118	0.818544
7	6	0	-0.893863	-4.314429	0.202424
8	6	0	0.060962	-4.046357	-0.789276
9	6	0	0.339159	-2.734809	-1.164618
10	6	0	2.202290	1.657163	-1.160959
11	6	0	3.475817	2.072424	-0.781586
12	6	0	4.180661	1.382591	0.215693
13	6	0	3.610972	0.267486	0.833133
14	6	0	2.336748	-0.170678	0.460597
15	6	0	-1.022307	2.111851	0.451098
16	6	0	-2.039310	2.998104	0.817518
17	6	0	-3.288585	2.931936	0.197299
18	6	0	-3.531685	1.972560	-0.796281
19	6	0	-2.534491	1.075430	-1.169852
20	9	0	-3.595587	-2.640054	1.903772
21	9	0	-3.121654	-4.778427	1.807991
22	6	0	0.770712	-5.213464	-1.463508
23	9	0	1.273353	-6.065060	-0.539723
24	9	0	-0.093905	-5.906939	-2.241980
25	9	0	1.791629	-4.789995	-2.245761
26	6	0	-1.782199	4.009313	1.926479
27	9	0	-0.491147	4.427520	1.911591
28	9	0	-2.577949	5.091286	1.806776
29	9	0	-2.016390	3.446403	3.139487
30	9	0	-5.888630	1.980325	-0.562267
31	9	0	-5.037169	3.018401	-2.291361
32	6	0	4.135259	3.268829	-1.455518
33	9	0	3.267644	3.928079	-2.259236
34	9	0	4.598974	4.141686	-0.530993
35	9	0	5.184650	2.867074	-2.211578
36	6	0	4.352497	-0.461528	1.945366
37	9	0	5.687312	-0.302666	1.840558
38	9	0	3.965631	0.012545	3.157320
39	9	0	4.079261	-1.790724	1.919657
40	6	0	-4.893557	1.944530	-1.478240
41	9	0	-5.050771	0.827925	-2.228120
42	6	0	-2.585824	-3.546626	1.925145
43	9	0	-1.985398	-3.462273	3.139853
44	9	0	0.005160	0.000065	-2.600599
45	1	0	-1.869660	-1.130935	0.929572
46	1	0	-1.106107	-5.345449	0.490027
47	1	0	1.080811	-2.542936	-1.941274
48	1	0	1.668901	2.200982	-1.941841
49	1	0	5.178705	1.714556	0.506357
50	1	0	1.907196	-1.050709	0.940773
51	1	0	-0.046583	2.181115	0.933443
52	1	0	-4.075813	3.631202	0.483652
53	1	0	-2.737565	0.337976	-1.947689

Table S2. Cartesian coordinates (Å) of $(3,5(CF_3)_2C_6H_3)_3PF_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.002178	-0.009529	0.000545
2	6	0	0.200218	-1.842618	-0.003913
3	6	0	-0.336362	-2.615840	1.036747
4	6	0	0.888157	-2.478461	-1.047935
5	6	0	-0.200112	-4.006725	1.018340
6	1	0	-0.864368	-2.137574	1.859619
7	6	0	1.050320	-3.867088	-1.037329
8	1	0	1.302153	-1.894382	-1.867877
9	6	0	0.500538	-4.639343	-0.011662
10	1	0	0.616643	-5.722837	-0.014883
11	6	0	-1.684098	0.736179	-0.015198
12	6	0	-2.562210	0.479149	-1.078228
13	6	0	-2.103904	1.562984	1.038284
14	6	0	-3.848126	1.028518	-1.074226
15	1	0	-2.250737	-0.155401	-1.906076
16	6	0	-3.379314	2.133704	1.015575
17	1	0	-1.442758	1.756389	1.880900
18	6	0	-4.260050	1.866372	-0.035936
19	1	0	-5.261519	2.295703	-0.038721
20	6	0	1.488834	1.080872	0.020633
21	6	0	1.715478	1.989781	-1.023971
22	6	0	2.407079	1.006921	1.078480
23	6	0	2.838512	2.821538	-0.997913
24	1	0	1.024087	2.045373	-1.862758
25	6	0	3.544607	1.819689	1.077392
26	1	0	2.243459	0.311014	1.899336
27	6	0	3.761325	2.738213	0.047755
28	1	0	4.647163	3.372718	0.052718
29	6	0	-0.765823	-4.826971	2.158937
30	6	0	1.778404	-4.538151	-2.183340
31	6	0	4.518122	1.735187	2.234581
32	6	0	3.034161	3.845028	-2.097067
33	6	0	-4.775525	0.746722	-2.238048
34	6	0	-3.795538	3.078489	2.123783
35	9	0	-3.215917	2.757924	3.309457
36	9	0	-5.140683	3.077677	2.312680
37	9	0	-3.433307	4.362053	1.837175
38	9	0	-6.079148	0.934435	-1.908725
39	9	0	-4.506170	1.567522	-3.293155
40	9	0	-4.646888	-0.529968	-2.686805
41	9	0	0.020972	-0.003839	-1.690479
42	9	0	-0.014870	-0.016042	1.691618
43	9	0	0.127430	-4.928671	3.184407
44	9	0	-1.895587	-4.271771	2.669942
45	9	0	-1.071646	-6.092300	1.770900
46	9	0	2.299051	-5.739105	-1.821655
47	9	0	0.940587	-4.765601	-3.234992
48	9	0	2.800417	-3.772906	-2.648863
49	9	0	4.111628	2.512639	3.278652
50	9	0	5.761482	2.154851	1.885509
51	9	0	4.632512	0.465907	2.706568
52	9	0	2.378369	5.006135	-1.809647
53	9	0	4.343767	4.160079	-2.270888
54	9	0	2.557396	3.405410	-3.290619

Table S3. Cartesian coordinates (Å) of $[(C_6F_5)_3PF]^+$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.000241	-0.000265	0.700889
2	6	0	-1.221522	-1.210246	0.241603
3	6	0	-2.485078	-1.163650	0.874634
4	6	0	-1.001287	-2.229370	-0.711070
5	6	0	-3.475996	-2.102546	0.603448
6	6	0	-1.984420	-3.175767	-0.997849
7	6	0	-3.220537	-3.113485	-0.337233
8	6	0	1.658847	-0.452992	0.240641
9	6	0	2.251028	-1.570484	0.873051
10	6	0	2.430752	0.248601	-0.711516
11	6	0	3.559753	-1.958285	0.601366
12	6	0	3.742063	-0.128740	-0.998832
13	6	0	4.306863	-1.230569	-0.339080
14	6	0	-0.437282	1.662495	0.240910
15	6	0	0.233073	2.734219	0.874568
16	6	0	-1.428753	1.980097	-0.713410
17	6	0	-0.084969	4.061473	0.602062
18	6	0	-1.757123	3.304335	-1.001540
19	6	0	-1.086762	4.344503	-0.340527
20	9	0	0.000674	-0.000118	2.269402
21	9	0	1.537408	-2.287364	1.751585
22	9	0	4.097760	-3.008203	1.212633
23	9	0	5.549343	-1.591314	-0.610288
24	9	0	4.454679	0.546190	-1.895906
25	9	0	1.921868	1.292635	-1.378420
26	9	0	1.209046	2.474916	1.755068
27	9	0	0.553996	5.052451	1.214539
28	9	0	-1.395022	5.600849	-0.612608
29	9	0	-2.695967	3.583833	-1.900742
30	9	0	-2.076721	1.017327	-1.381942
31	9	0	-2.748264	-0.187131	1.753342
32	9	0	-4.653860	-2.042810	1.215420
33	9	0	-4.154879	-4.008548	-0.607988
34	9	0	-1.757387	-4.130216	-1.895392
35	9	0	0.156465	-2.310899	-1.379390

Table S4. Cartesian coordinates (Å) of $(C_6F_5)_3PF_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.000271	-0.001799	-0.000476
2	9	0	0.002514	-0.002241	1.666664
3	9	0	-0.001597	-0.002271	-1.667463
4	6	0	0.031221	1.834428	-0.000377
5	6	0	-0.913578	2.581026	-0.719322
6	6	0	1.000333	2.548781	0.718968
7	6	0	-0.906026	3.977543	-0.718137
8	6	0	1.039091	3.944772	0.718767
9	6	0	0.078133	4.661334	0.000582
10	6	0	1.575450	-0.946119	-0.002112
11	6	0	1.710999	-2.142163	0.717623
12	6	0	2.693708	-0.500146	-0.721452
13	6	0	2.901332	-2.872454	0.717363
14	6	0	3.900203	-1.203530	-0.720096
15	6	0	4.001778	-2.397392	-0.001039
16	6	0	-1.606225	-0.891782	0.001339
17	6	0	-1.782718	-2.082420	-0.718491
18	6	0	-2.708341	-0.408204	0.721323
19	6	0	-2.997145	-2.771924	-0.717568
20	6	0	-3.937979	-1.070279	0.720677
21	6	0	-4.080391	-2.259960	0.001599
22	9	0	-0.765283	-2.628801	-1.406365
23	9	0	-3.126750	-3.922517	-1.393197
24	9	0	-5.250467	-2.906970	0.001657
25	9	0	-4.981352	-0.568198	1.396269
26	9	0	-2.630341	0.744424	1.408644
27	9	0	-1.895212	1.971502	-1.406240
28	9	0	-1.839485	4.663506	-1.392860
29	9	0	0.100308	5.998193	0.001041
30	9	0	1.994809	4.598935	1.393907
31	9	0	1.961242	1.906557	1.405369
32	9	0	0.675133	-2.653762	1.404786
33	9	0	2.991459	-4.026858	1.392906
34	9	0	5.149262	-3.083683	-0.000434
35	9	0	4.960386	-0.737069	-1.395056
36	9	0	2.655258	0.654441	-1.408838

Table S5. Cartesian coordinates (Å) of $B(C_6F_5)_3$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.094953	2.489641	-0.656690
2	6	0	0.515293	1.487129	-1.433171
3	6	0	1.611722	1.905108	-2.210128
4	6	0	2.069444	3.221994	-2.234028
5	6	0	1.436055	4.179230	-1.434702
6	6	0	0.349688	3.810999	-0.634289
7	5	0	0.006554	0.001806	-1.434001
8	9	0	2.248187	1.026002	-3.012134
9	9	0	3.103895	3.580476	-3.009614
10	9	0	-0.248120	4.728704	0.140651
11	9	0	-1.135786	2.185124	0.146397
12	6	0	-1.534094	-0.299791	-1.440231
13	6	0	-2.443158	0.451045	-2.209290
14	6	0	-3.812186	0.188026	-2.241266
15	6	0	-4.326049	-0.850980	-1.458539
16	6	0	-3.465811	-1.618242	-0.666235
17	6	0	-2.099458	-1.340984	-0.680003
18	9	0	-1.999981	1.452779	-2.997326
19	9	0	-1.318258	-2.101370	0.115191
20	9	0	-3.963347	-2.605858	0.093382
21	9	0	-4.637892	0.914306	-3.009819
22	6	0	1.037863	-1.181754	-1.430635
23	6	0	0.844706	-2.347137	-2.196280
24	6	0	1.752099	-3.405460	-2.214062
25	6	0	2.901219	-3.332630	-1.419856
26	6	0	3.133662	-2.200729	-0.631809
27	6	0	2.215542	-1.151582	-0.660104
28	9	0	-0.238813	-2.463587	-2.992212
29	9	0	1.537974	-4.487284	-2.978070
30	9	0	4.230462	-2.139114	0.138400
31	9	0	2.480872	-0.091899	0.131896
32	9	0	3.775507	-4.343456	-1.413798
33	9	0	-5.637113	-1.110209	-1.467543
34	9	0	1.868432	5.443945	-1.435570

Table S6. Cartesian coordinates (Å) of $[FB(C_6F_5)_3]^-$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.125172	2.589072	-0.607718
2	6	0	0.550241	1.713780	-1.617001
3	6	0	1.450908	2.276476	-2.525841
4	6	0	1.931976	3.586852	-2.438268
5	6	0	1.495770	4.408471	-1.400931
6	6	0	0.579141	3.904818	-0.478797
7	9	0	1.907043	1.563351	-3.590586
8	9	0	2.810983	4.071141	-3.348529
9	9	0	0.133179	4.703928	0.520273
10	9	0	-0.799139	2.198028	0.302263
11	6	0	-1.558038	0.001975	-2.151554
12	6	0	-2.280662	0.972430	-2.850875
13	6	0	-3.631257	0.843013	-3.192817
14	6	0	-4.319975	-0.314903	-2.838493
15	6	0	-3.641069	-1.324700	-2.157038
16	6	0	-2.291911	-1.150834	-1.837734
17	9	0	-1.689441	2.125606	-3.264131
18	9	0	-1.698016	-2.196815	-1.214112
19	9	0	-4.298208	-2.462371	-1.826627
20	9	0	-4.278929	1.825155	-3.864822
21	6	0	1.057013	-0.867034	-2.453887
22	6	0	0.808433	-1.487096	-3.681125
23	6	0	1.690533	-2.382622	-4.295192
24	6	0	2.901965	-2.684220	-3.676389
25	6	0	3.210119	-2.076730	-2.459674
26	6	0	2.297159	-1.188723	-1.884341
27	9	0	-0.332302	-1.231653	-4.376376
28	9	0	1.387206	-2.957752	-5.483889
29	9	0	4.394720	-2.348474	-1.861092
30	9	0	2.693558	-0.611718	-0.724043
31	9	0	3.770117	-3.546936	-4.251617
32	9	0	-5.625843	-0.461476	-3.157757
33	9	0	1.947171	5.678906	-1.295800
34	5	0	0.016489	0.133319	-1.617410
35	9	0	0.025449	-0.313482	-0.257156

Table S7. Cartesian coordinates (Å) of CF_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.392343	-0.881189	0.000024
2	8	0	1.574231	-0.881188	-0.000009
3	9	0	-0.396439	0.193561	-0.000006
4	9	0	-0.396439	-1.955938	0.000039

Table S8. Cartesian coordinates (Å) of $[CF_3O]^-$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.922255	-0.027060	-0.141732
2	9	0	-0.535423	0.520074	1.151943
3	9	0	-0.535528	-1.420909	0.031214
4	9	0	-2.365460	-0.126958	0.031190
5	8	0	-0.515657	0.548010	-1.137934

9. References

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[2] M. Perez, T. Mahdi, L. J. Hounjet, D. W. Stephan, *Chem. Commun.,* **2015**, *51*, 11301-11304.