Supporting information

for

Synthesis and structure of a phosphinoboronic ester in a fused bicyclic framework

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NMR spectral charts

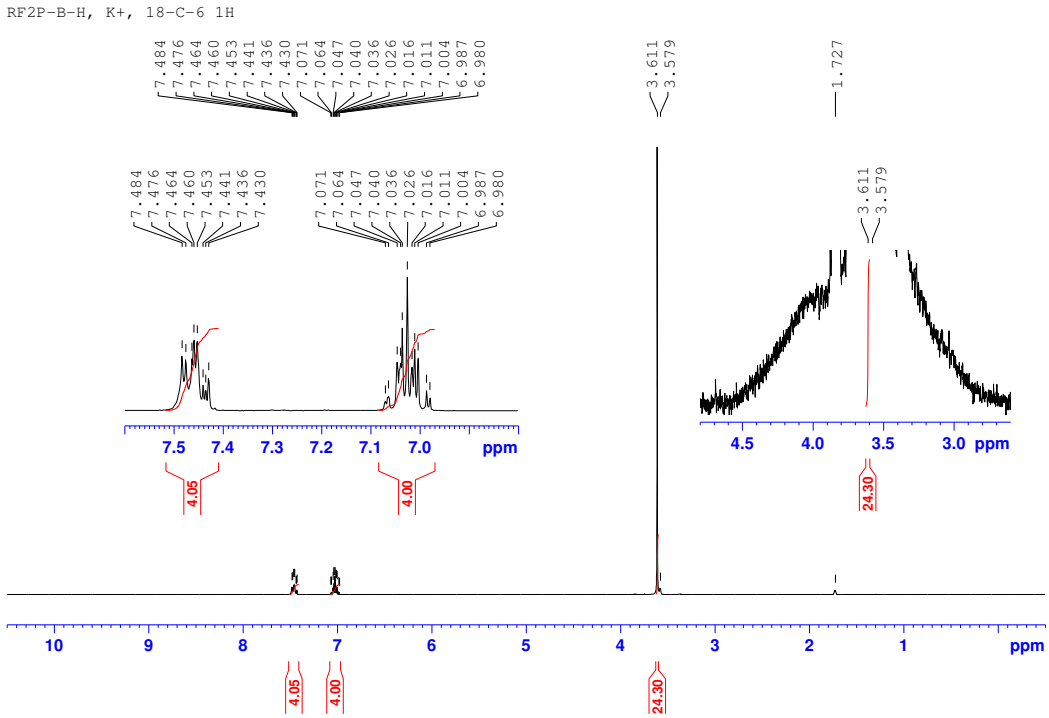

Figure S1. ^{1}H NMR spectrum (300 MHz) of **3** in THF-d_8. The right-hand side insert shows the proton on the boron atom, which is obscured by the aliphatic protons of 18-crown-6 and THF.

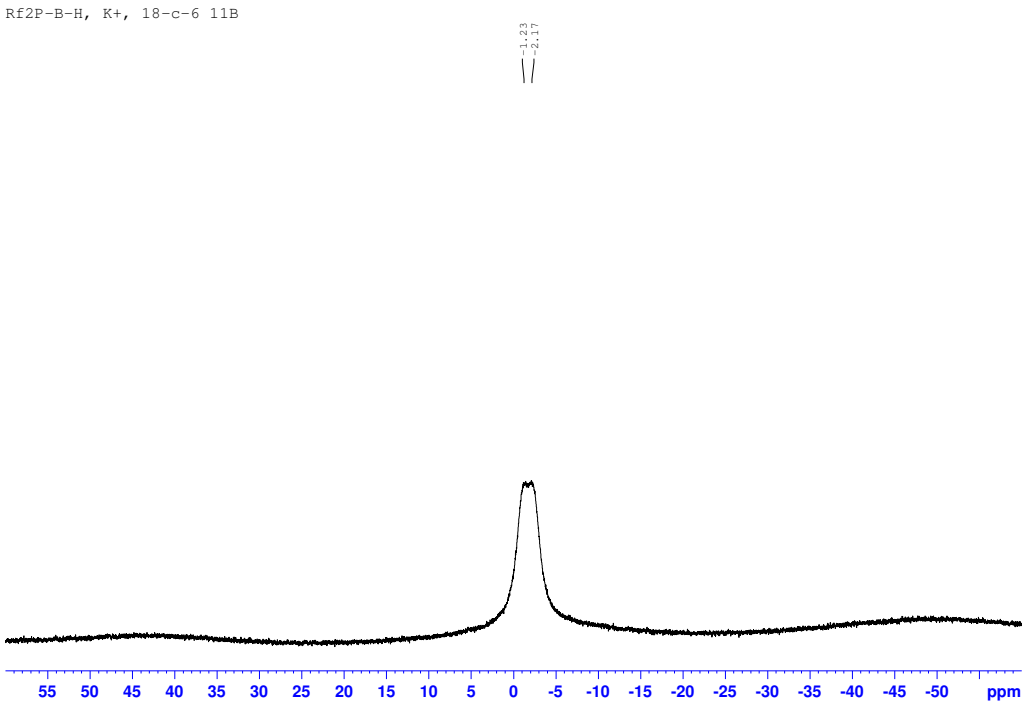

Figure S2. ^{11}B NMR spectrum (96.3 MHz) of **3** in THF-d_8.

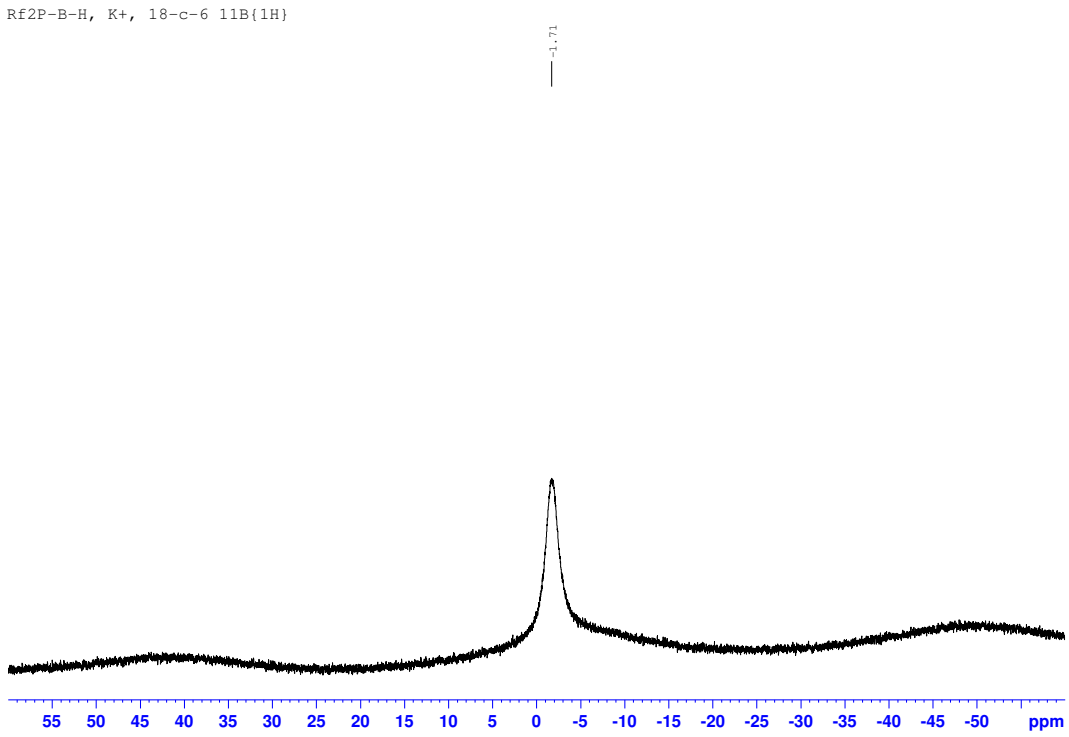

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum (96.3 MHz) of **3** in THF-d_8.

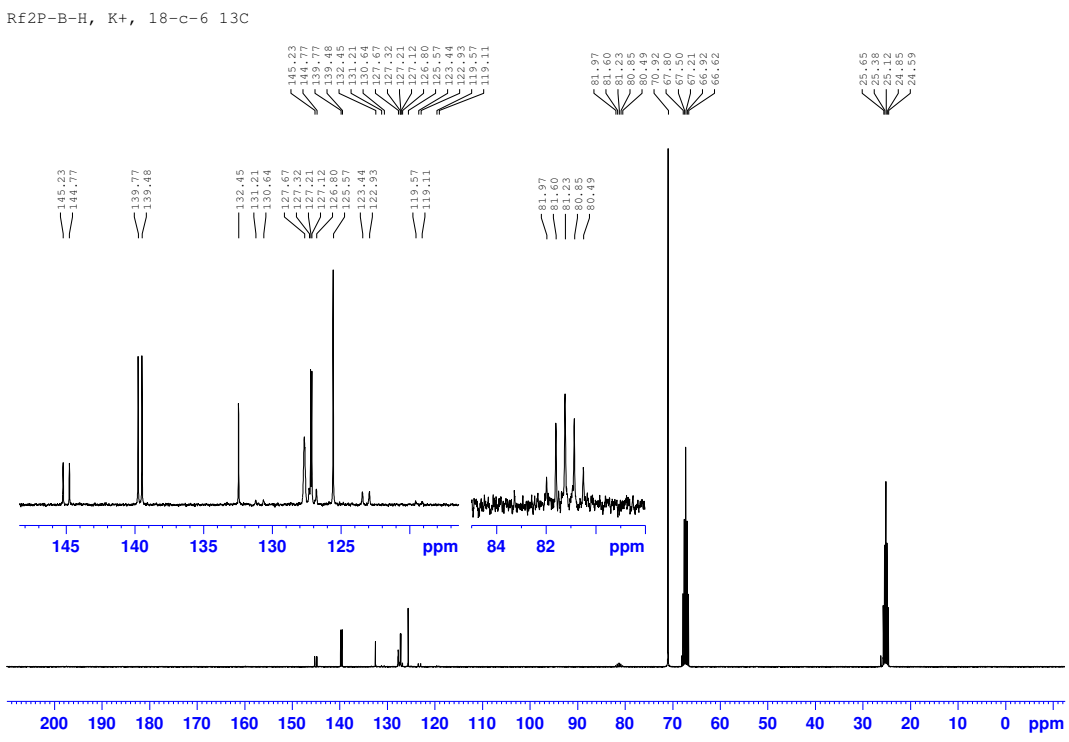

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **3** in THF-d_8.

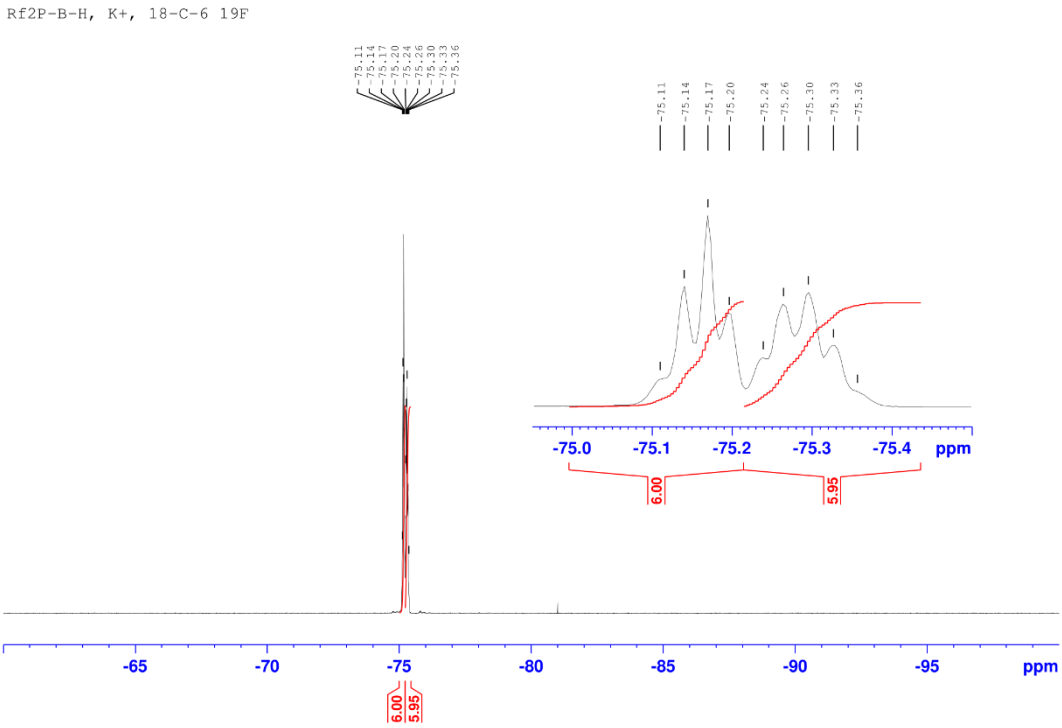

Figure S5. ^{19}F NMR spectrum (282 MHz) of **3** in THF-d_8.

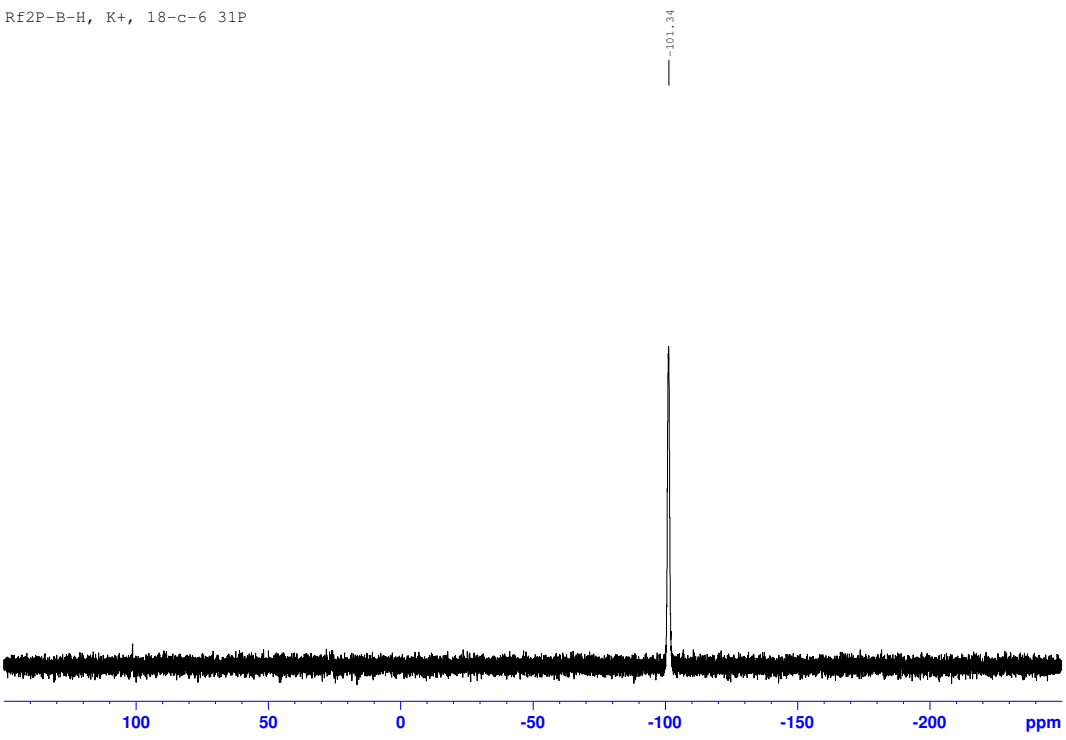

Figure S6. ^{31}P NMR spectrum (121 MHz) of **3** in THF-d_8.

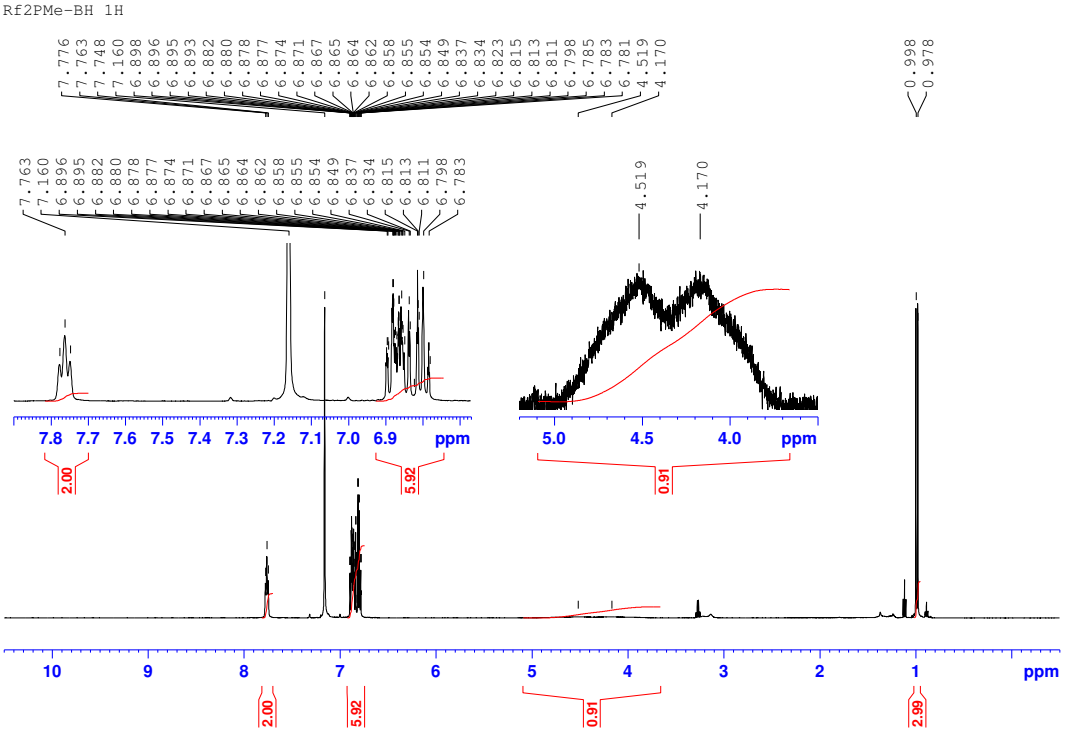

Figure S7. ^{1}H NMR spectrum (500 MHz) of **4** in C_6D_6.

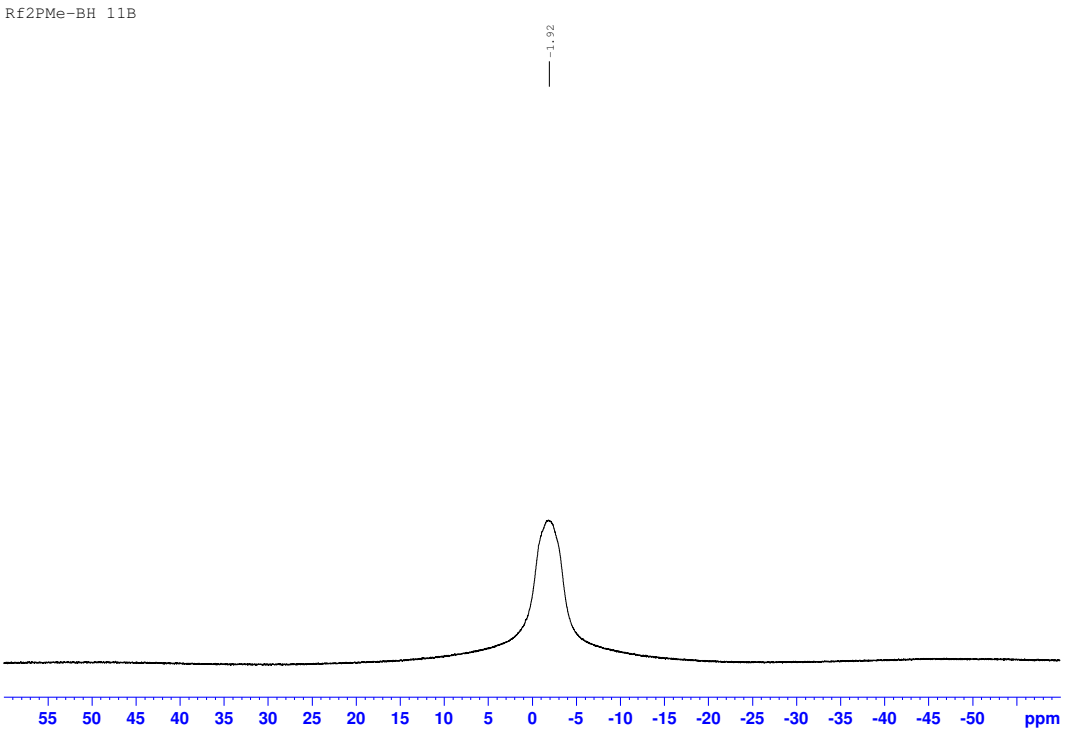

Figure S8. ^{11}B NMR spectrum (96.3 MHz) of **4** in C_6D_6.

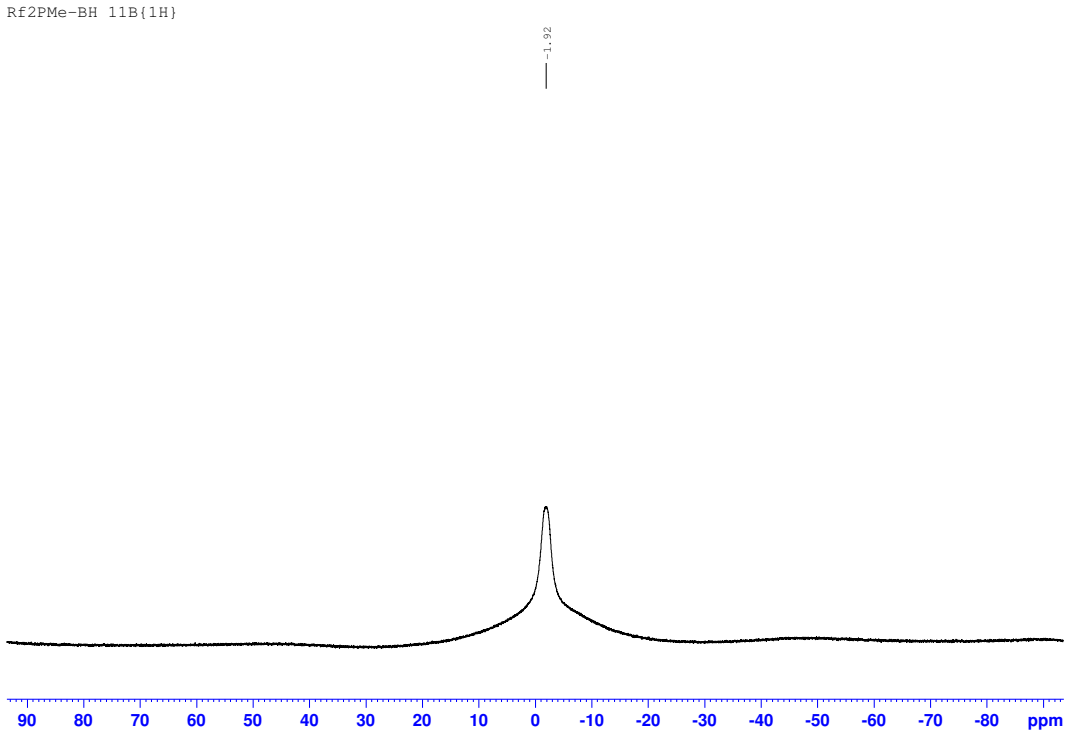

Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum (96.3 MHz) of **4** in C_6D_6.

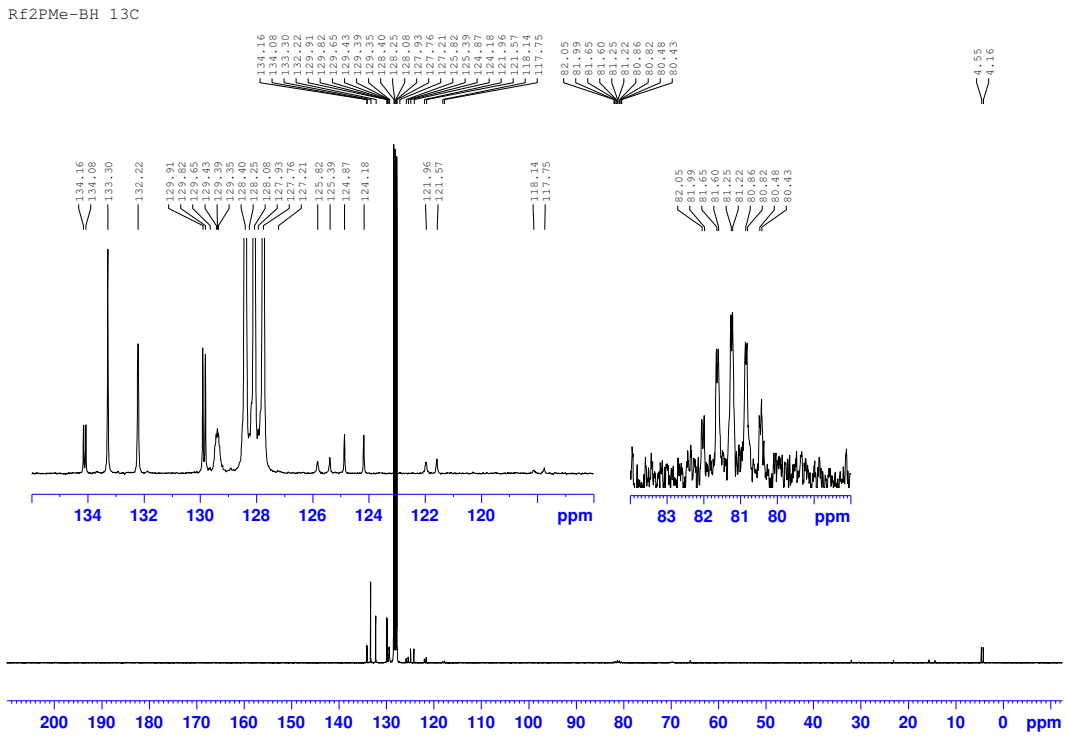

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz) of **4** in C_6D_6.

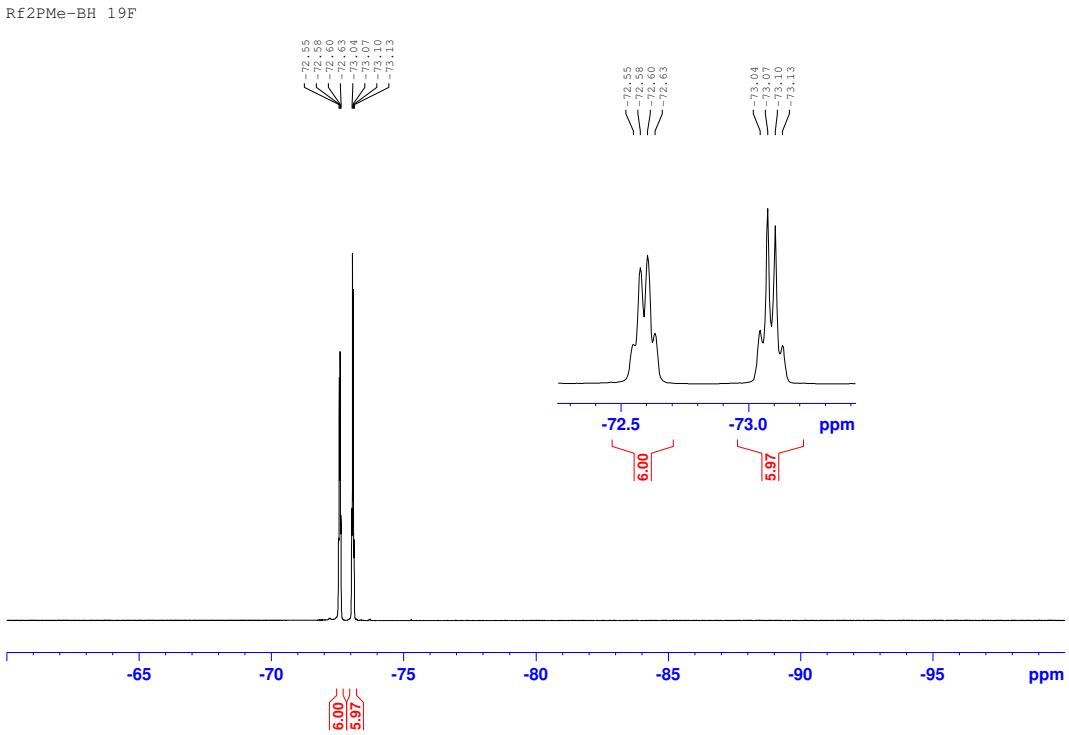

Figure S11. ^{19}F NMR spectrum (282 MHz) of **4** in C_6D_6.

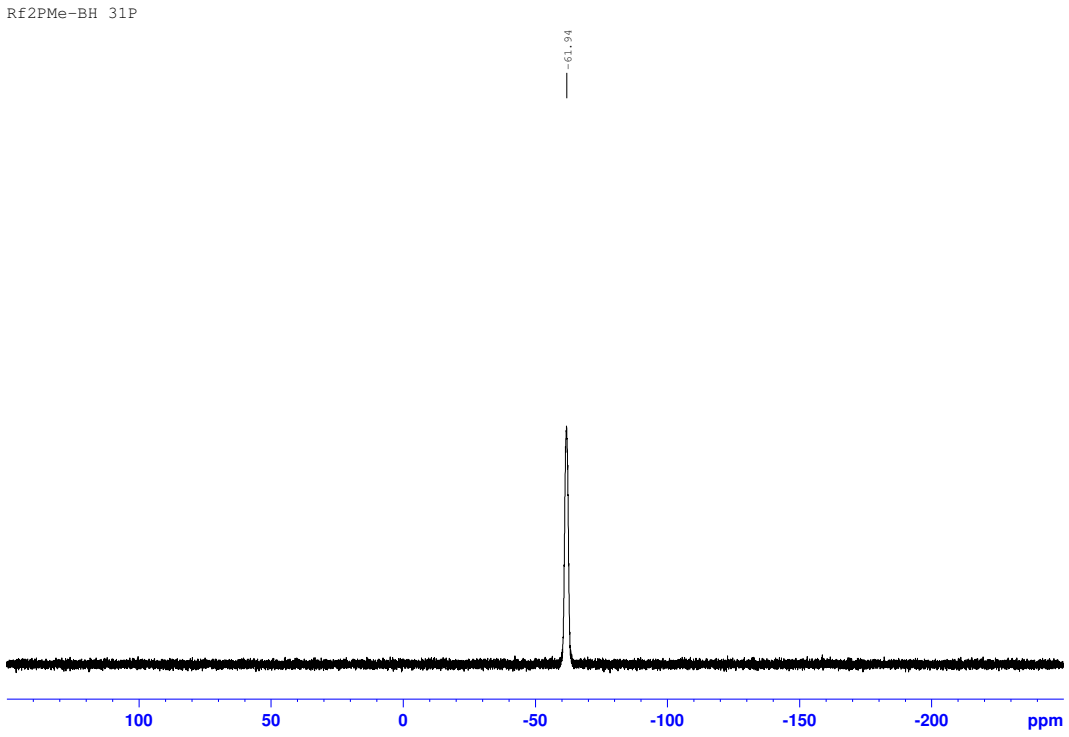

Figure S12. ^{31}P NMR spectrum (121 MHz) of **4** in C_6D_6.

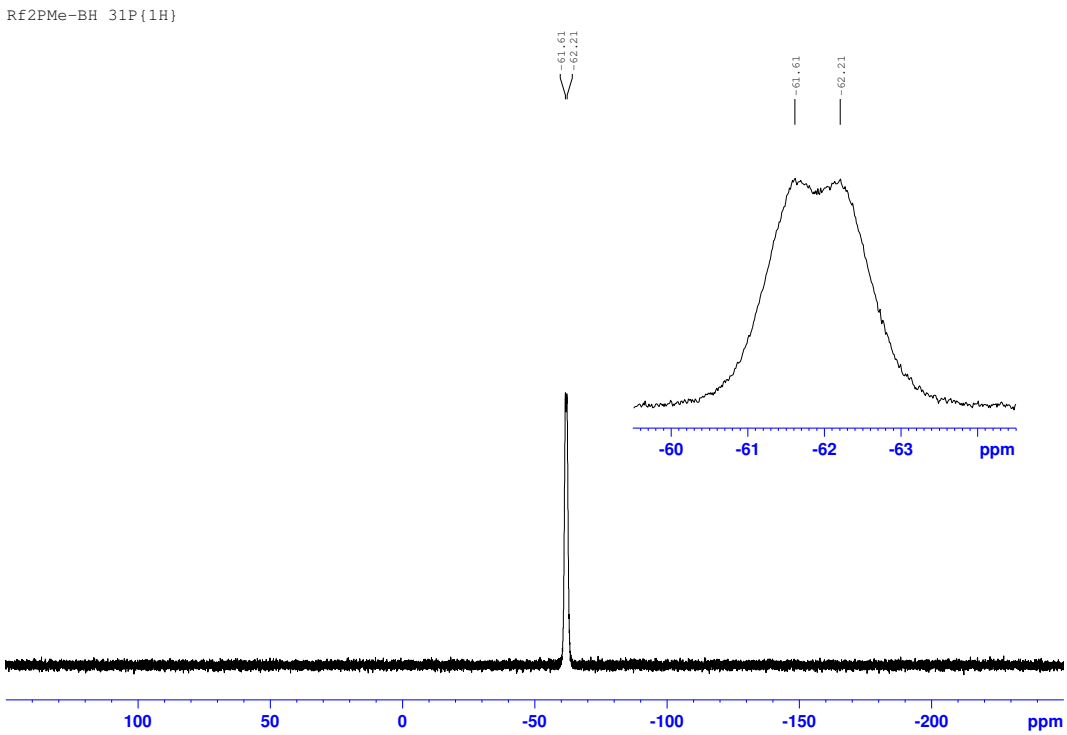

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz) of **4** in C_6D_6.

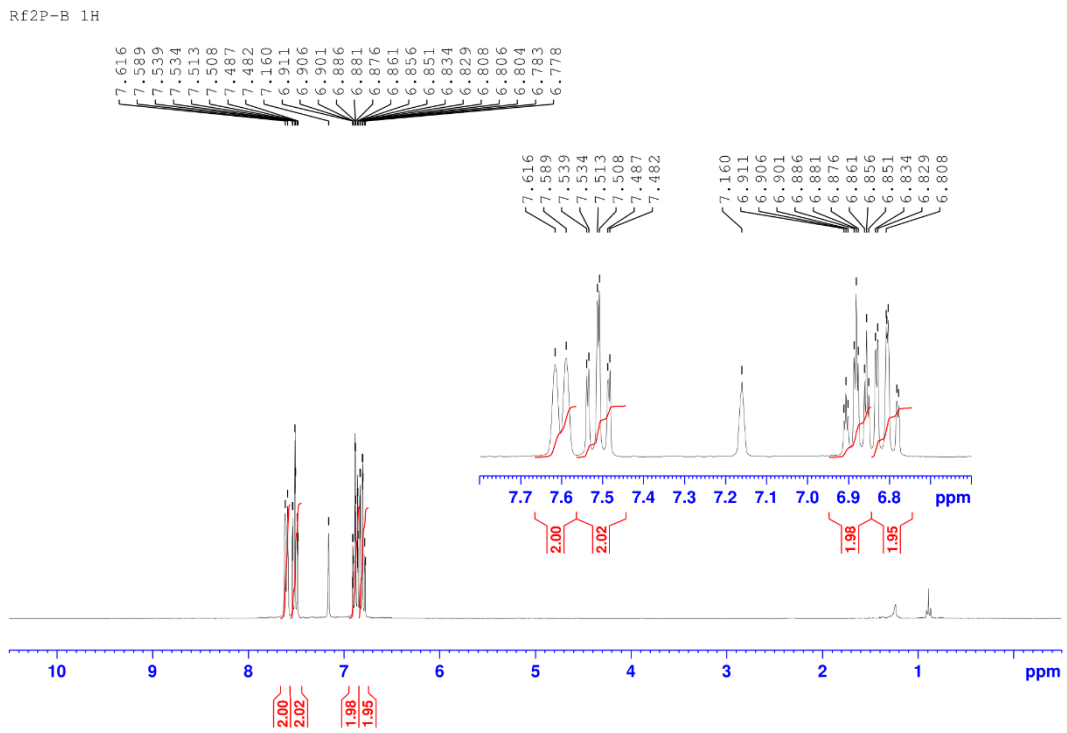

Figure S14. ^{1}H NMR spectrum of **5** (300 MHz) in C_6D_6.

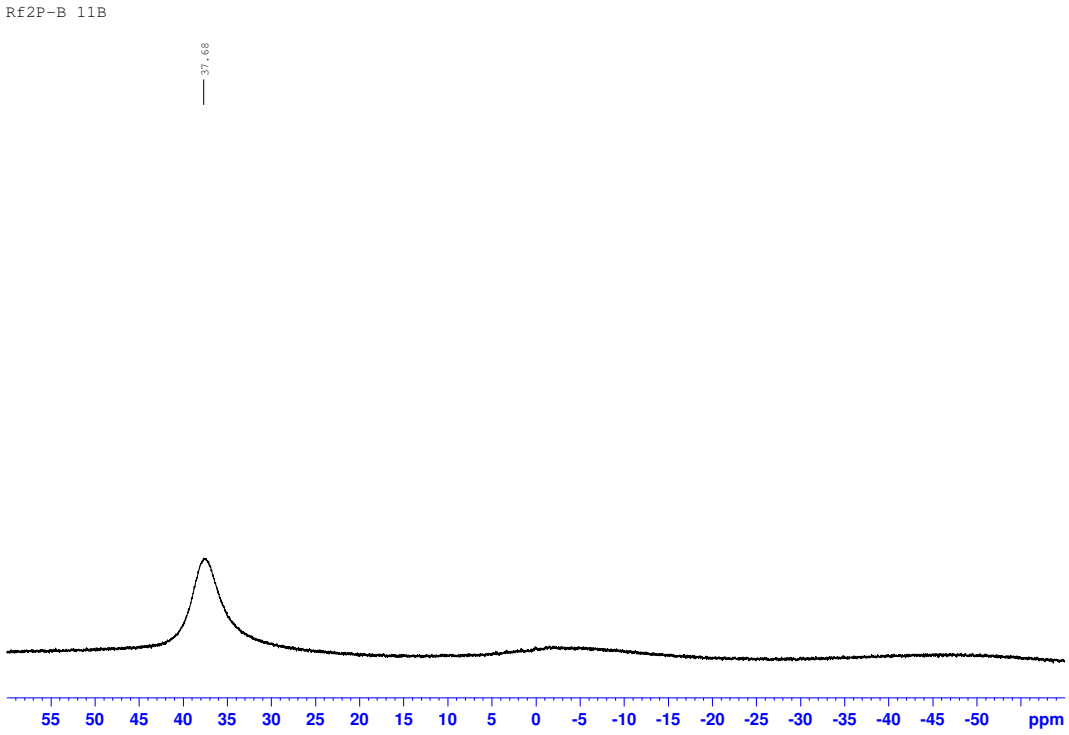

Figure S15. ^{11}B NMR spectrum (96.3 MHz) of **5** in C_6D_6.

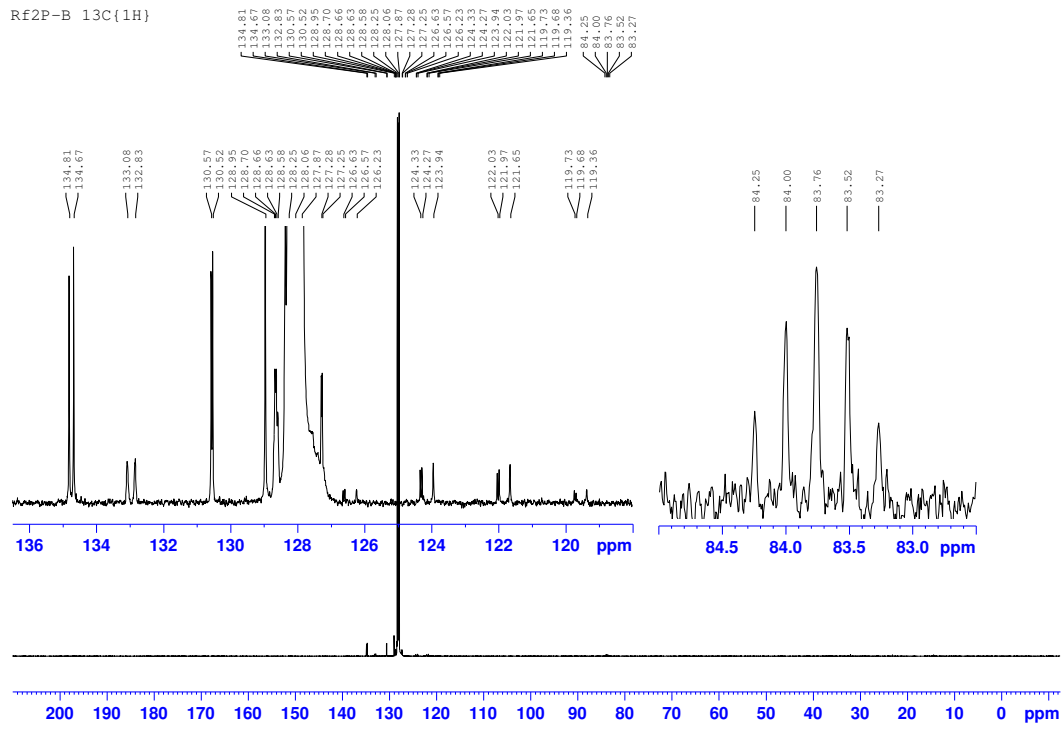

Figure S16. $^{13}C\{^1H\}$ NMR (125 MHz) spectrum of **5** in C_6D_6.

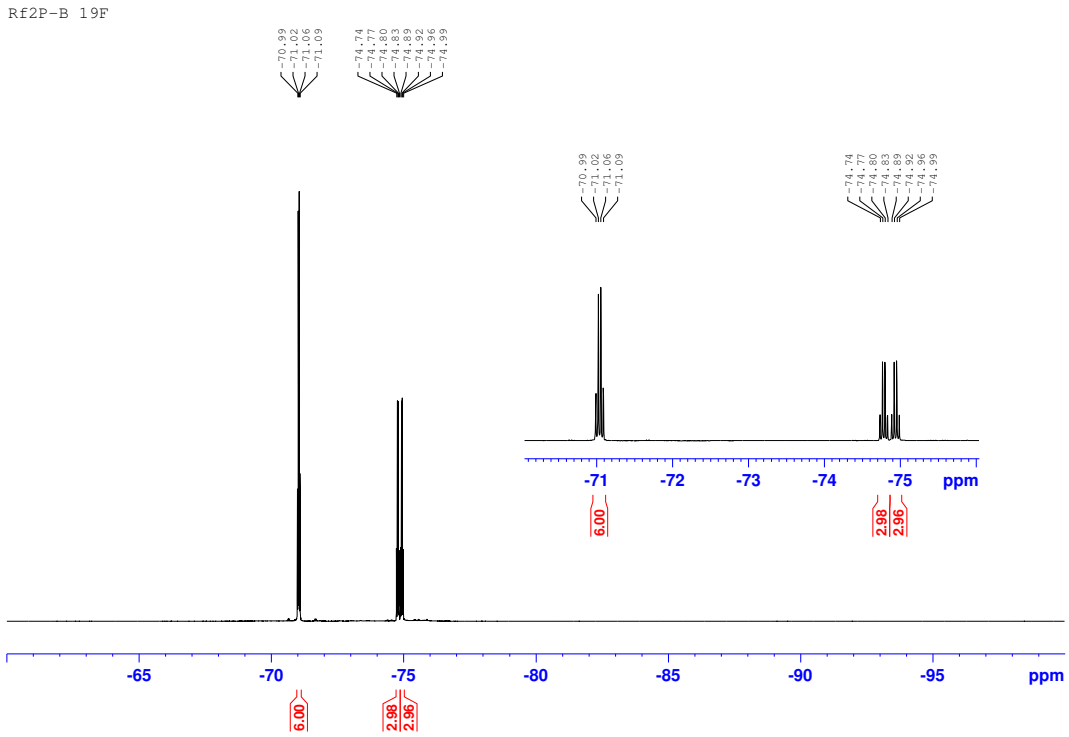

Figure S17. ^{19}F NMR spectrum (282 MHz) of **5** in C_6D_6.

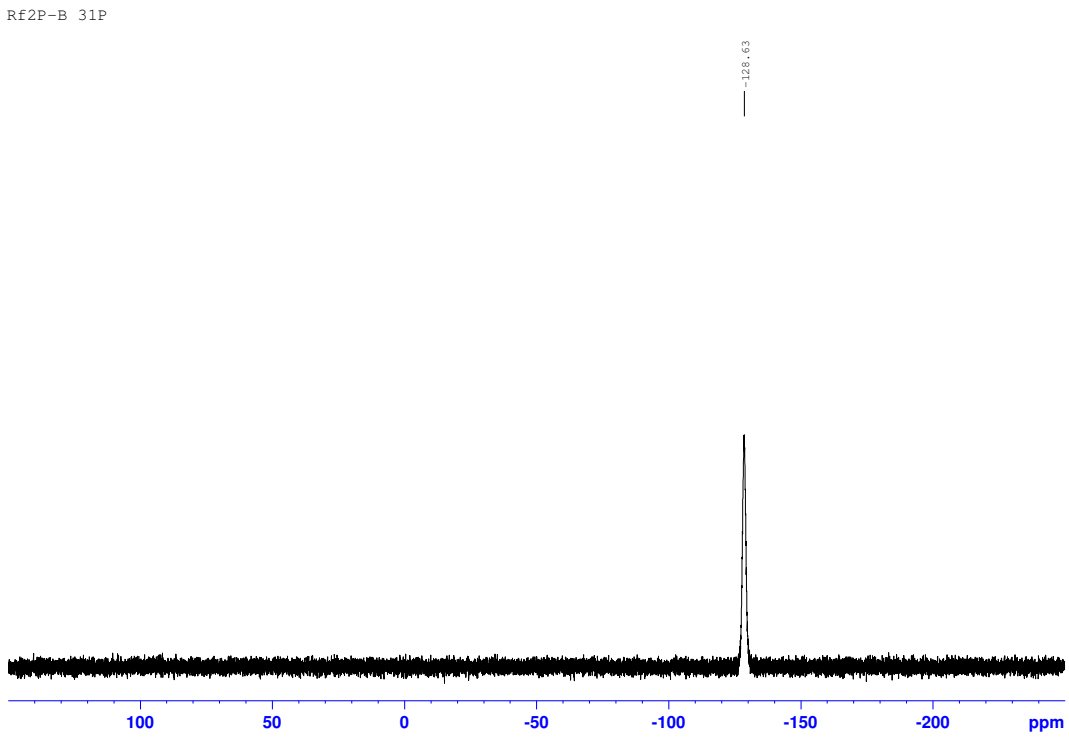

Figure S18. ^{31}P NMR spectrum (121 MHz) of **5** in C_6D_6.

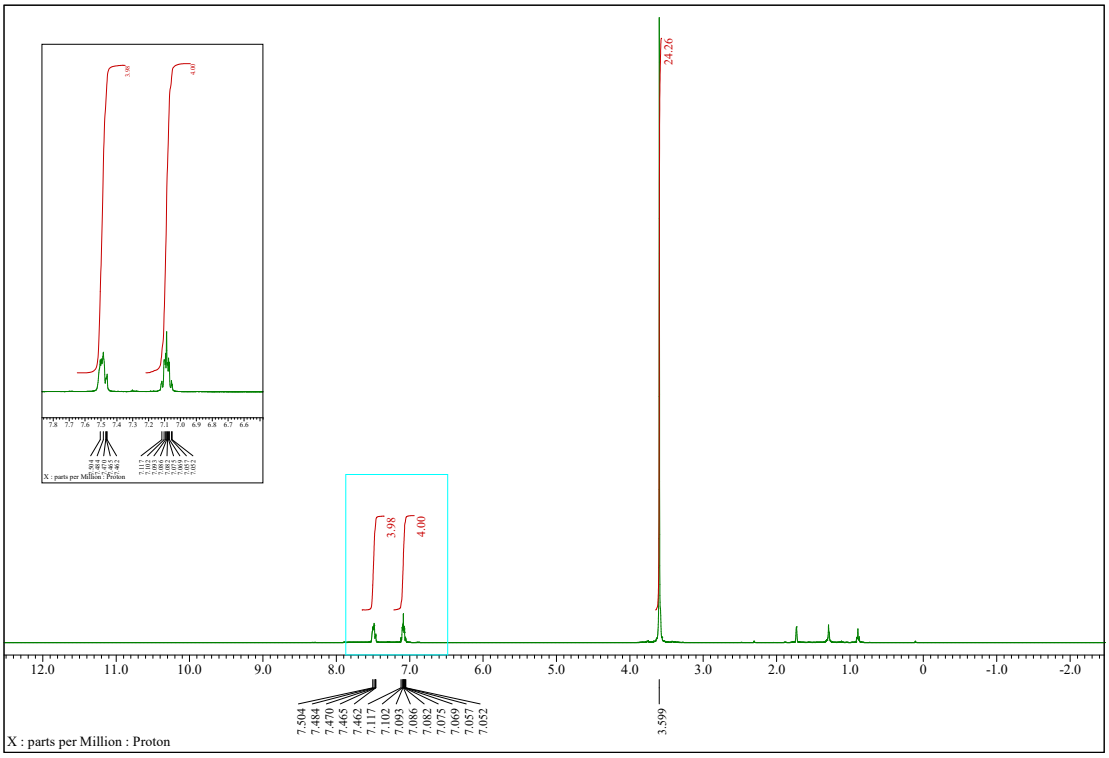

Figure S19. ^{1}H NMR (400 MHz) spectrum of **6** in THF-d_8.

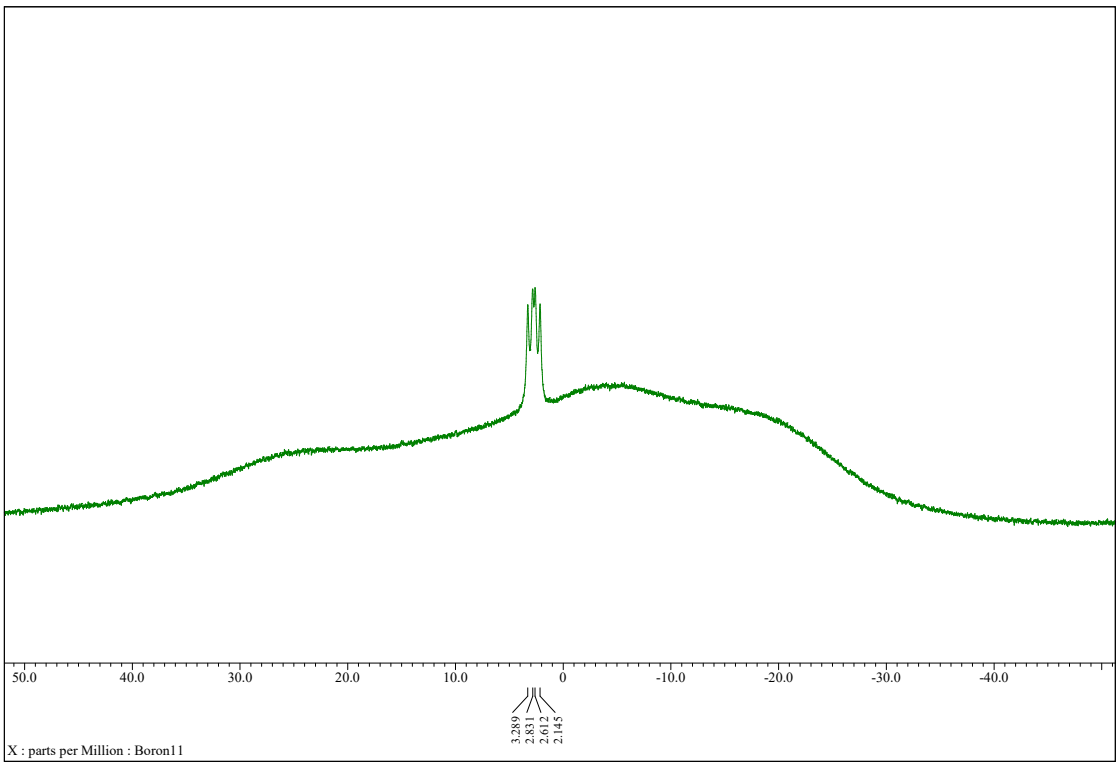

Figure S20. ^{11}B{^{1}H} NMR (128 MHz) spectrum of **6** in THF-d_8.

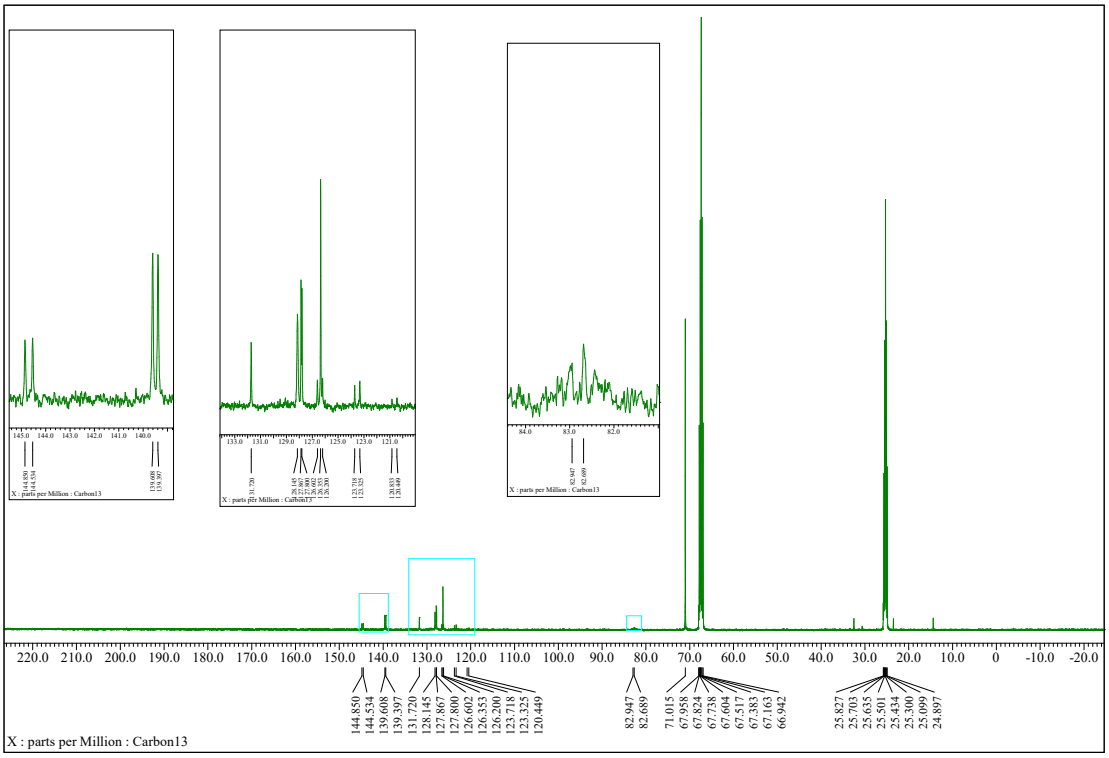

Figure S21. $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **6** in THF-d_8.

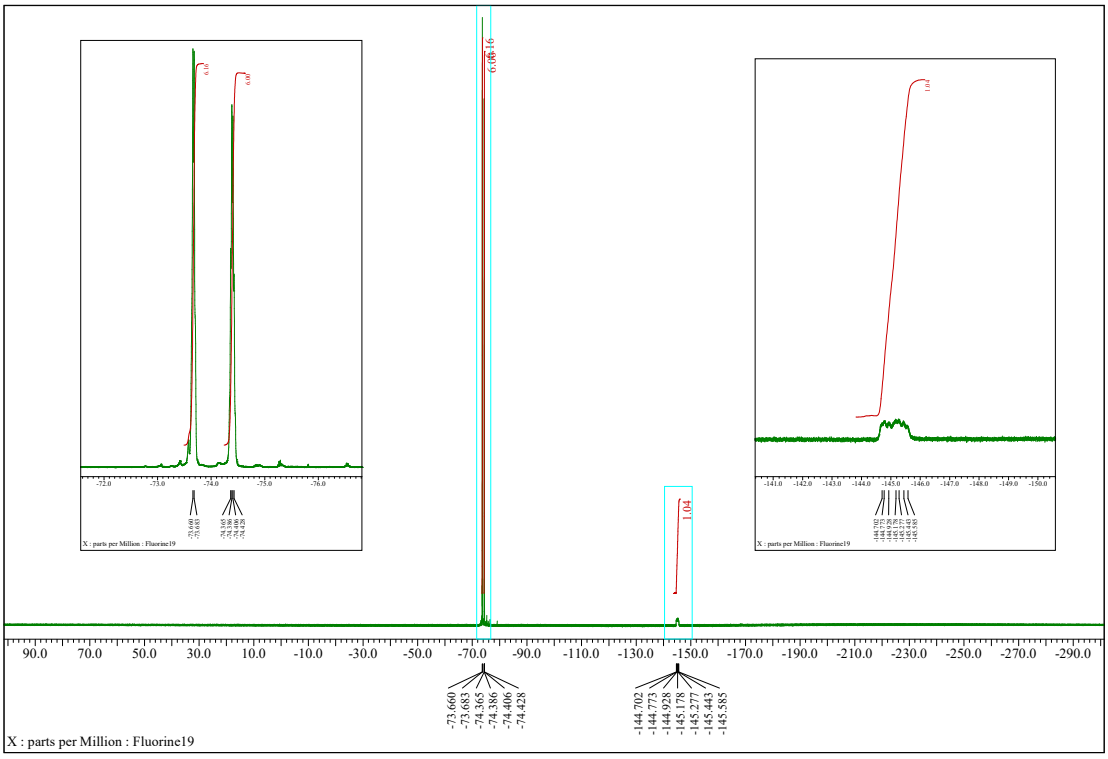

Figure S22. ^{19}F NMR (376 MHz) spectrum of **6** in THF-d_8.

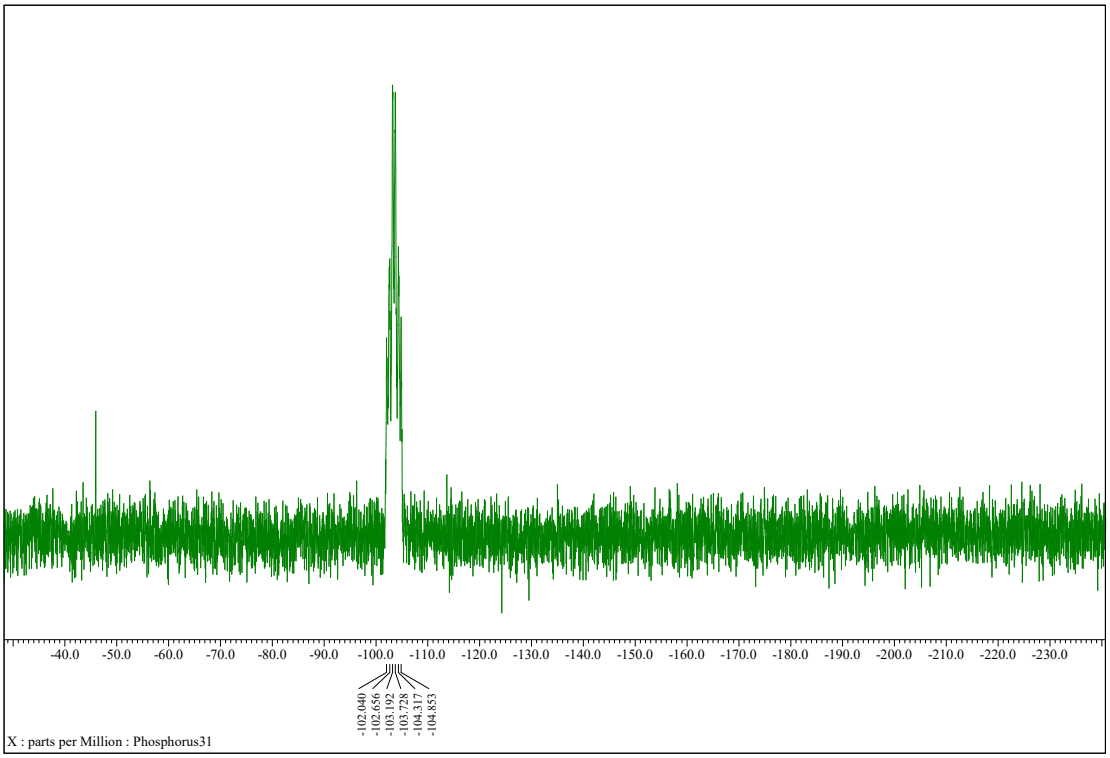

Figure S23. $^{31}P\{^{1}H\}$ NMR (161 MHz) spectrum of **6** in THF-d_8.

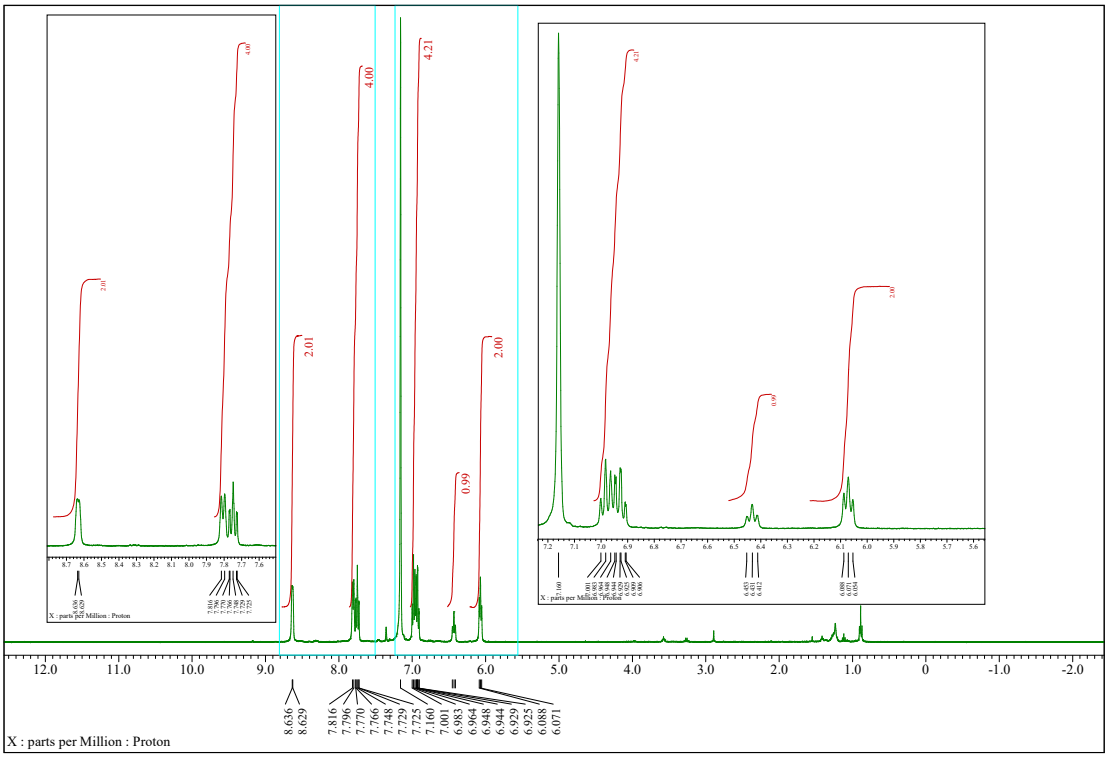

Figure S24. ^{1}H NMR (400 MHz) spectrum of **7** in C_6D_6.

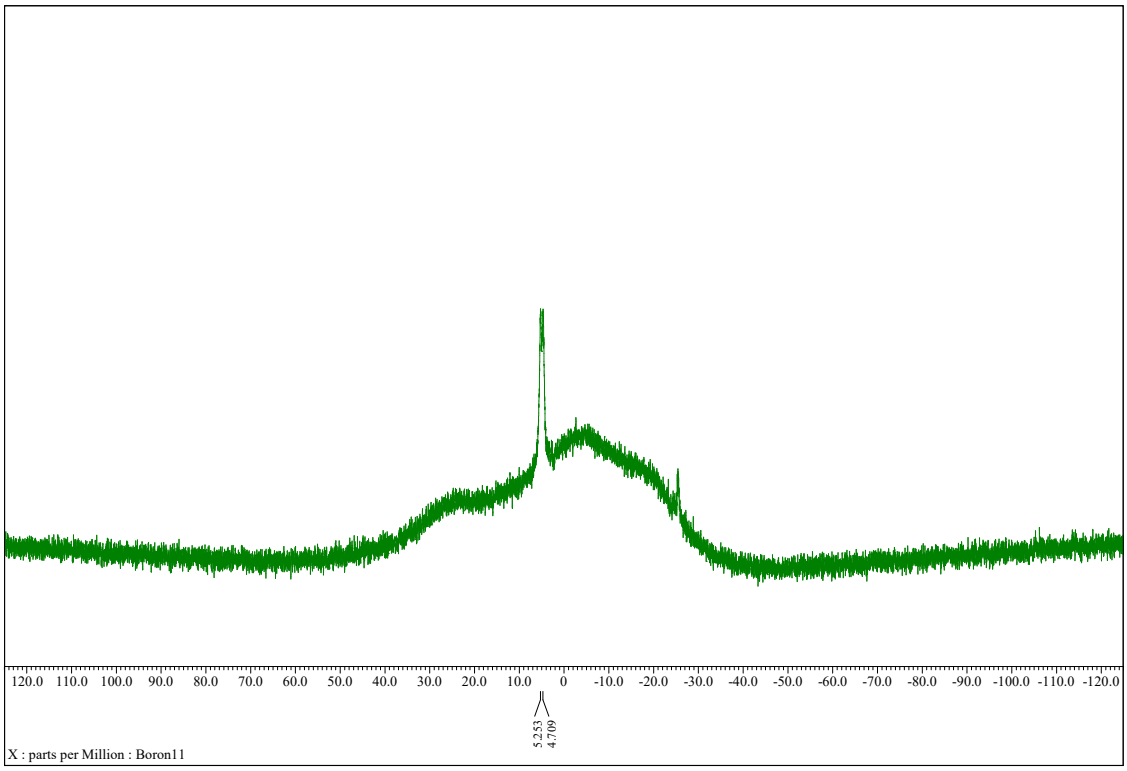

Figure S25. $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **7** in C_6D_6.

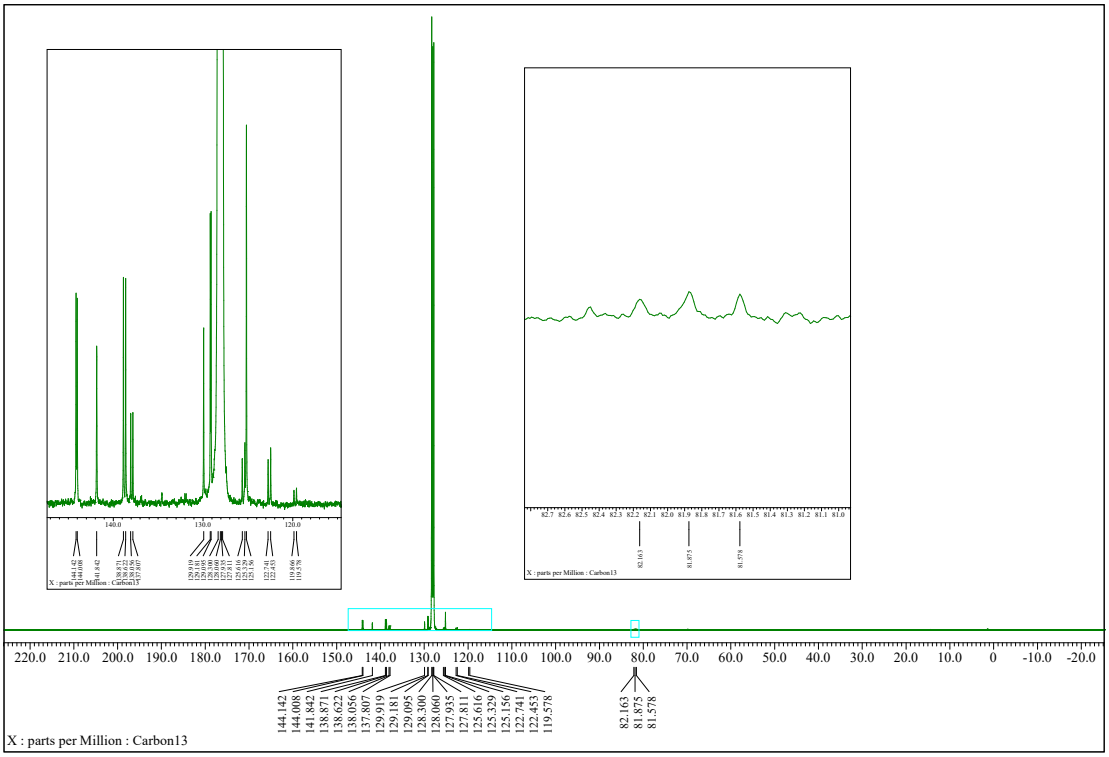

Figure S26. ^{13}C NMR (100 MHz) spectrum of **7** in C_6D_6.

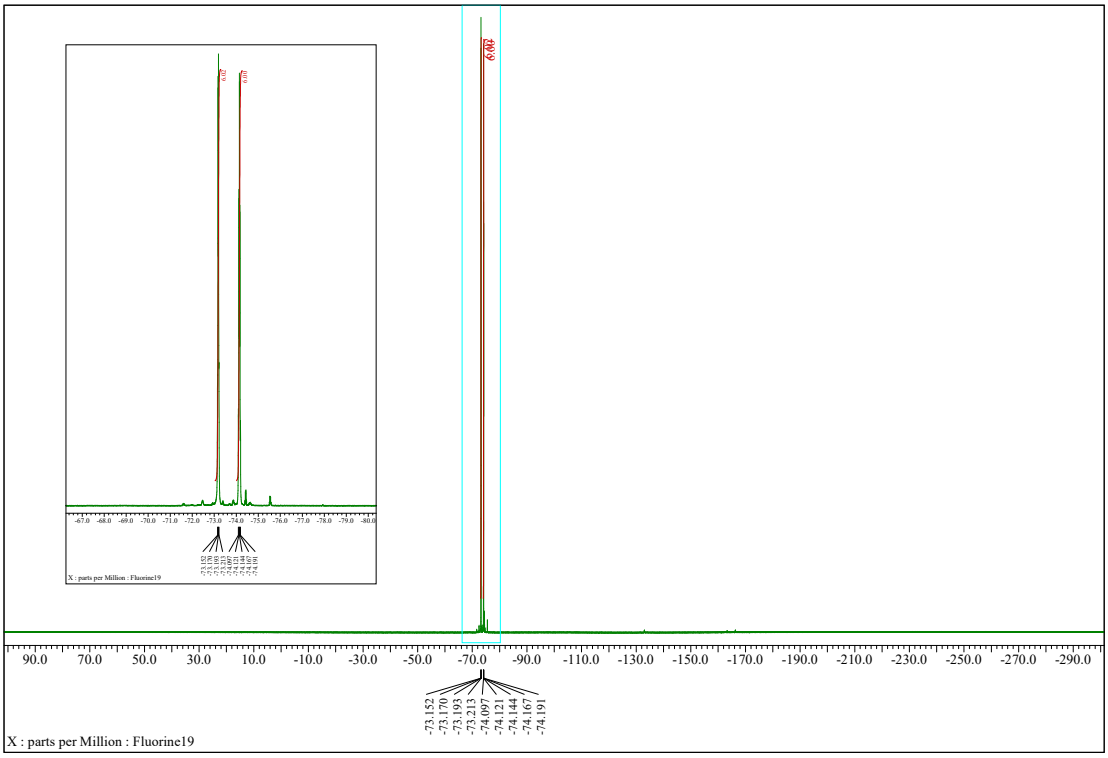

Figure S27 ^{19}F NMR (376 MHz) spectrum of **7** in C_6D_6.

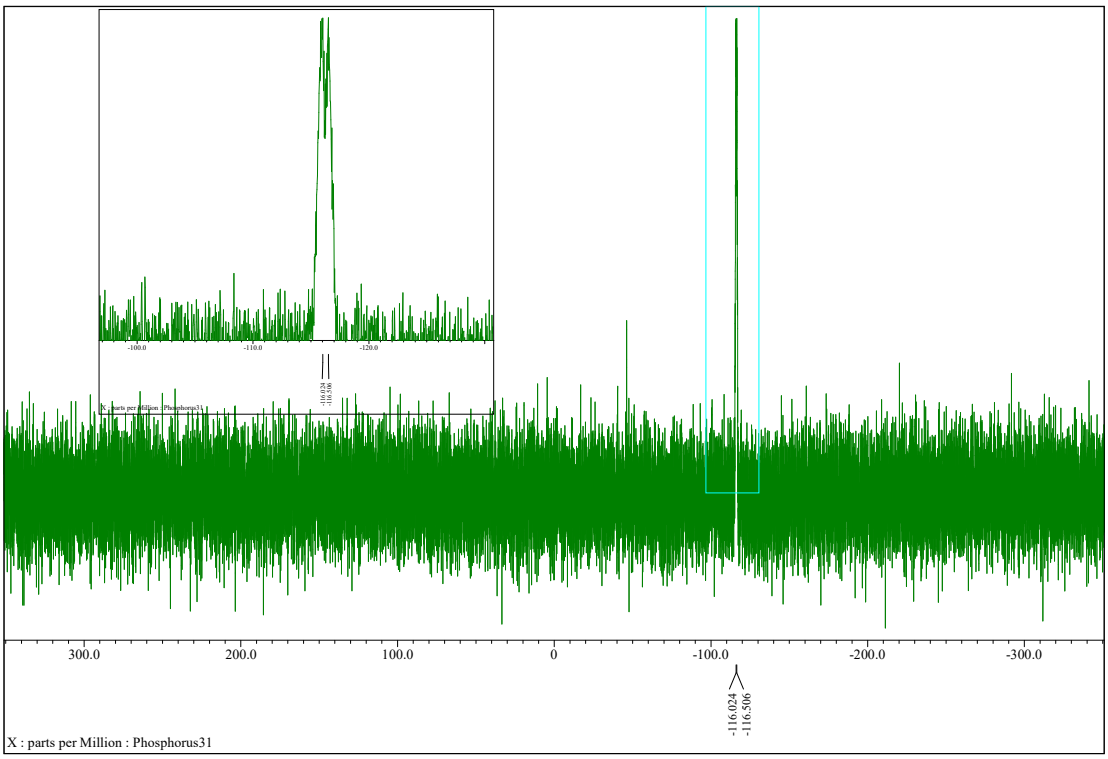

Figure S28. $^{31}P\{^{1}H\}$ NMR (161 MHz) spectrum of **7** in C_6D_6.

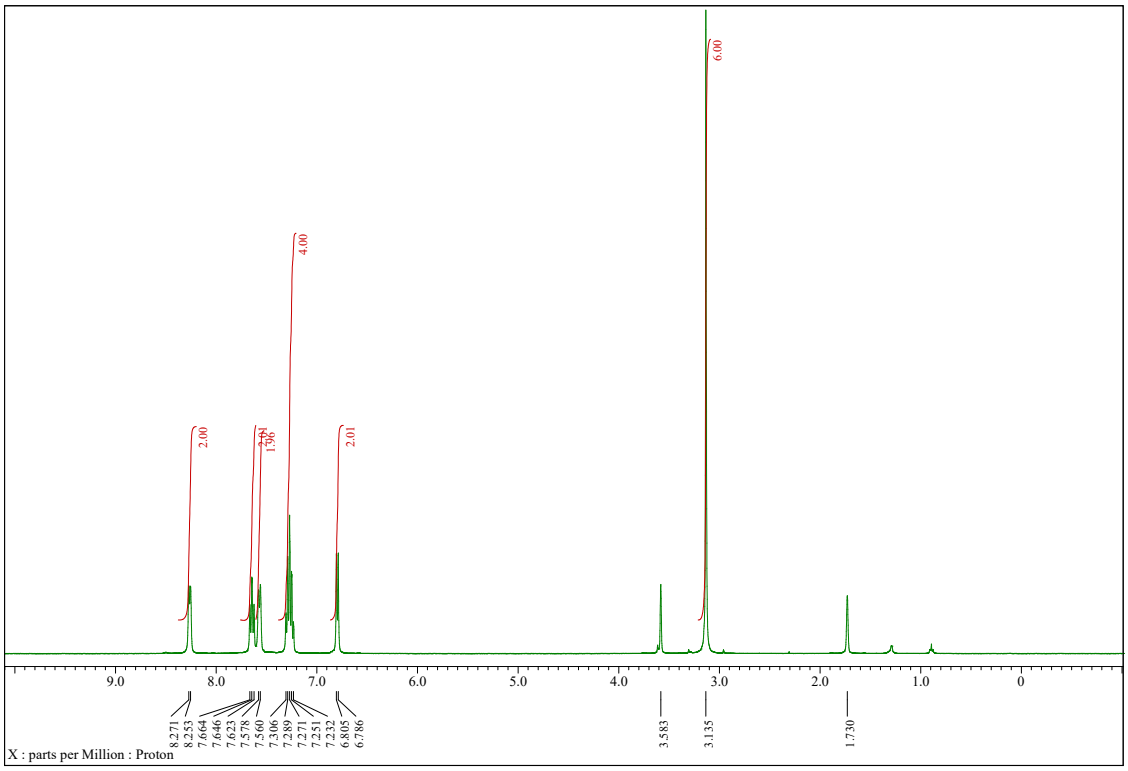

Figure S29. ^{1}H NMR (400 MHz) spectrum of **8** in THF-d_8.

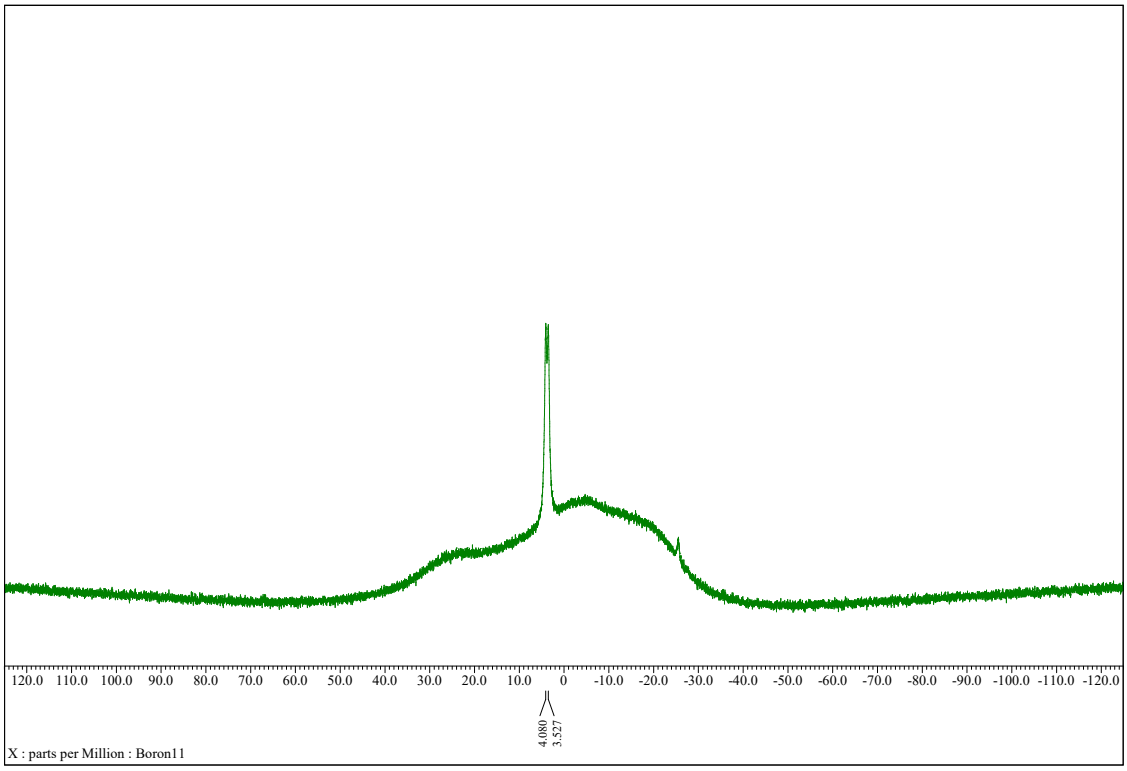

Figure S30. ^{11}B{^{1}H} NMR (128 MHz) spectrum of **8** in C_6D_6.

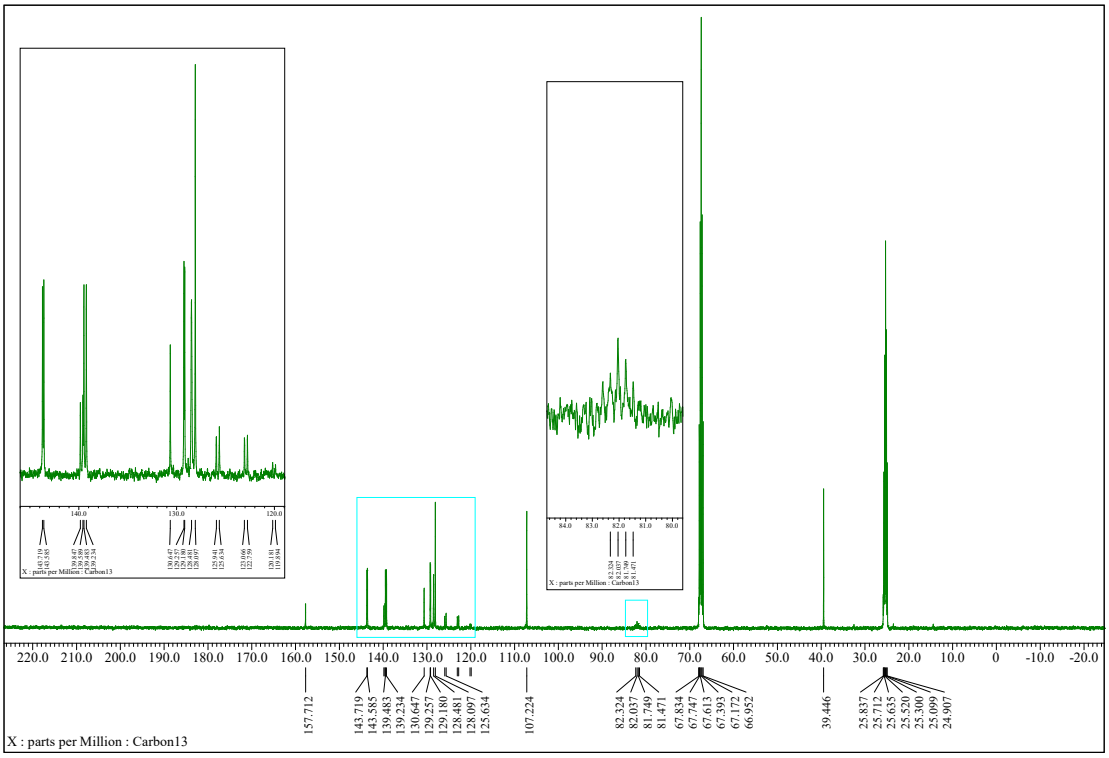

Figure S31. ^{13}C NMR (100 MHz) spectrum of **8** in C_6D_6.

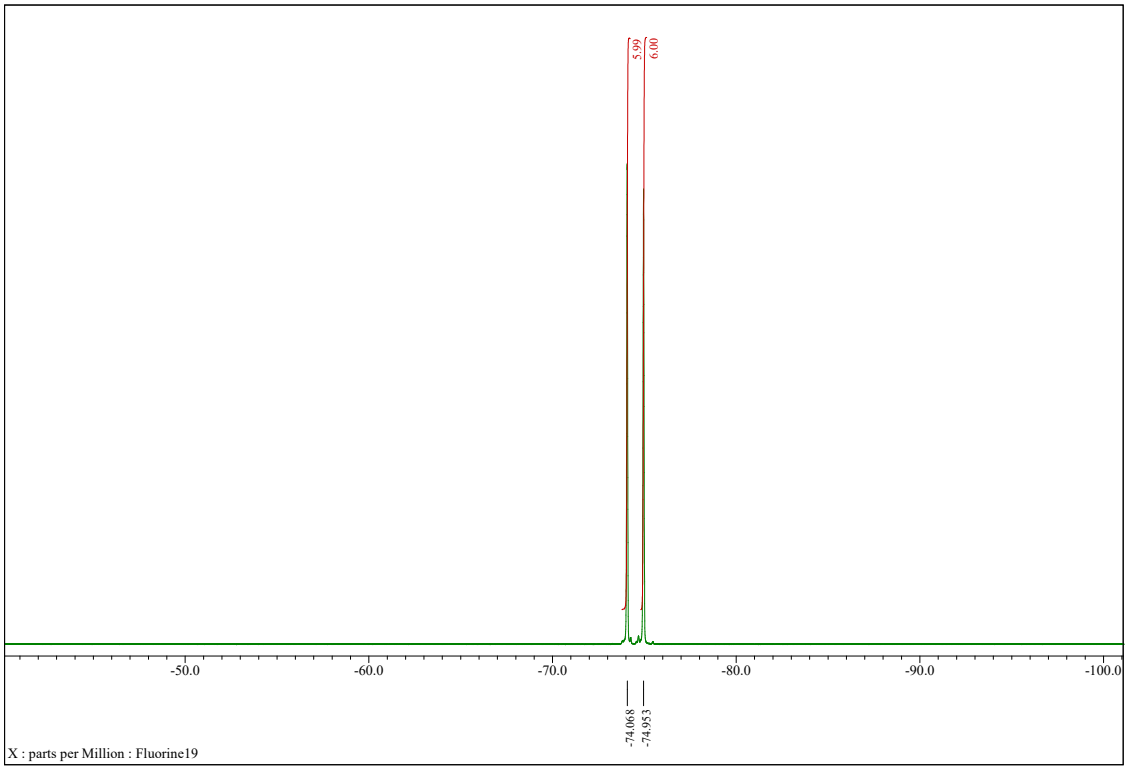

Figure S32. ^{19}F NMR (376 MHz) spectrum of **8** in C_6D_6.

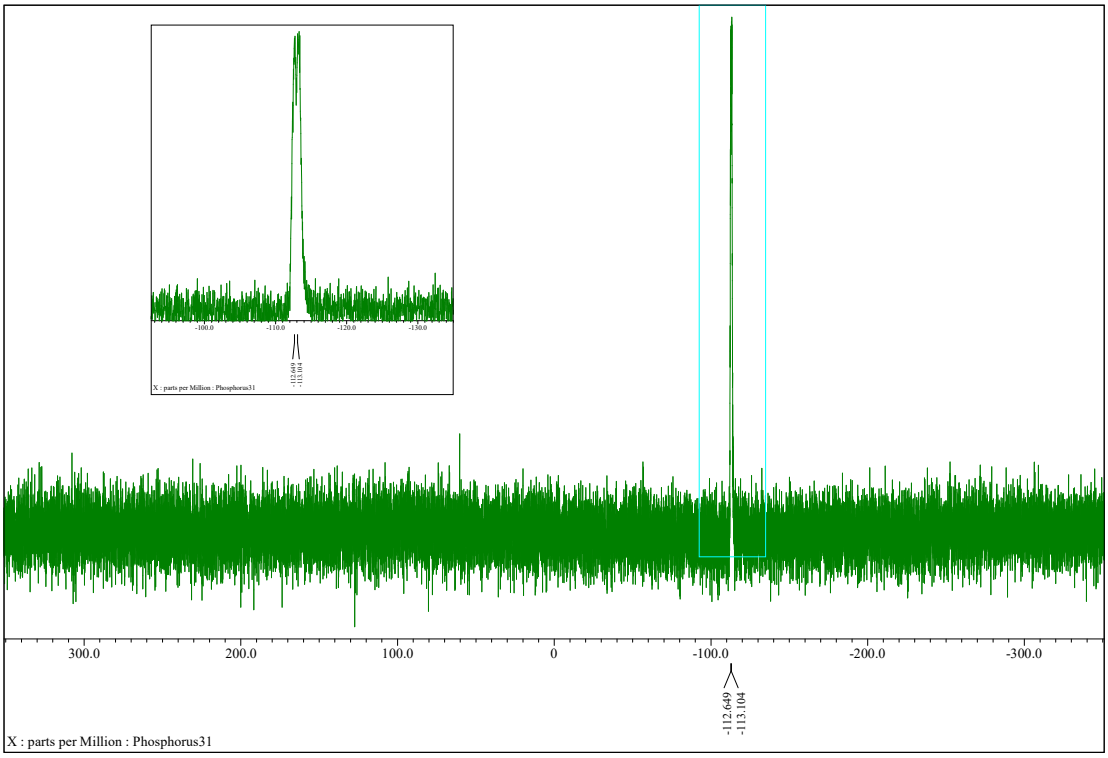

Figure S33. $^{31}P\{^{1}H\}$ NMR (161 MHz) spectrum of **8** in C_6D_6.

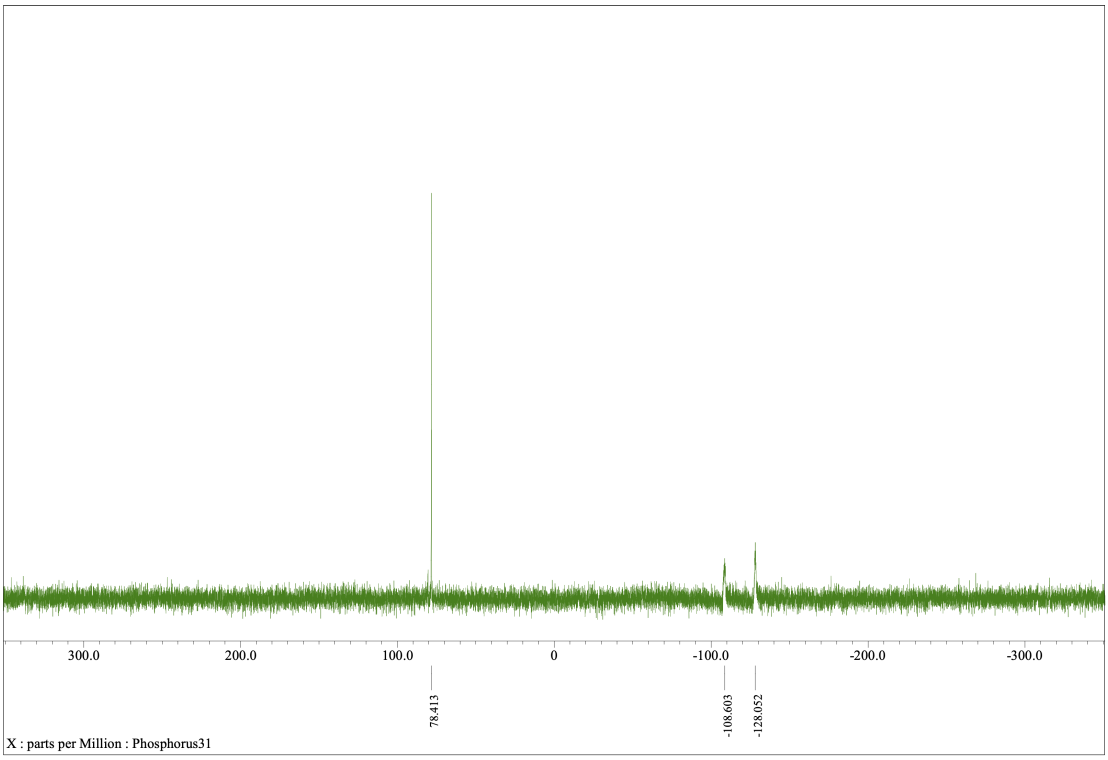

Figure S34. $^{31}P\{^{1}H\}$ NMR (161 MHz) spectrum after mixing **5** and Et_3PO in C_6D_6.

Computational results

Optimised structures of compounds **5**, **9**, **10**, **11** and **5**·F^- (Chart S1) are shown in Figures S35-S39, respectively. LUMO is shown in Figure S40. Cartesian coordinates in the optimised geometry of **5**, **9**, **10**, **11**, **5**·F^-, CF_2O and CF_3O^- are shown in Tables S1-S7.

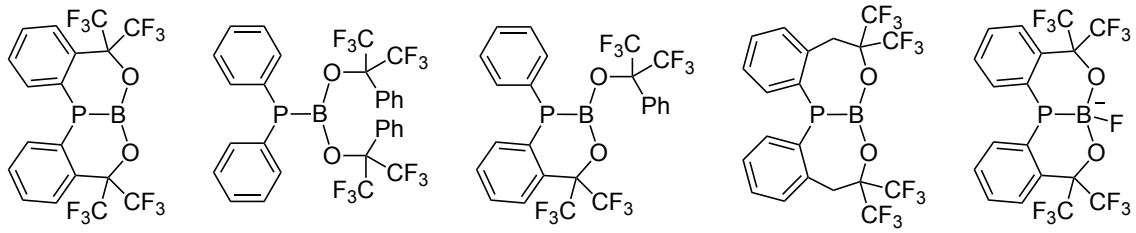

Chart S1.

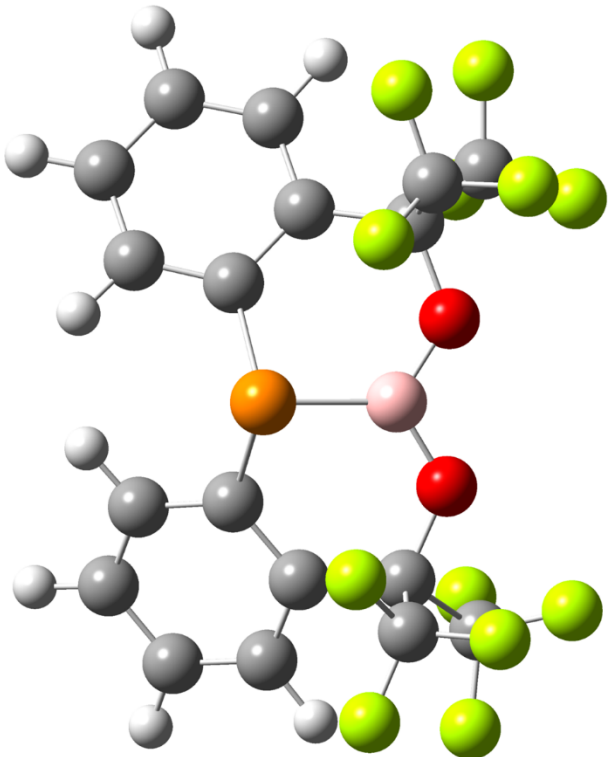

Figure S35. Optimised structure of compound **5** at B3PW91/6–31G(d,p) level of theory.

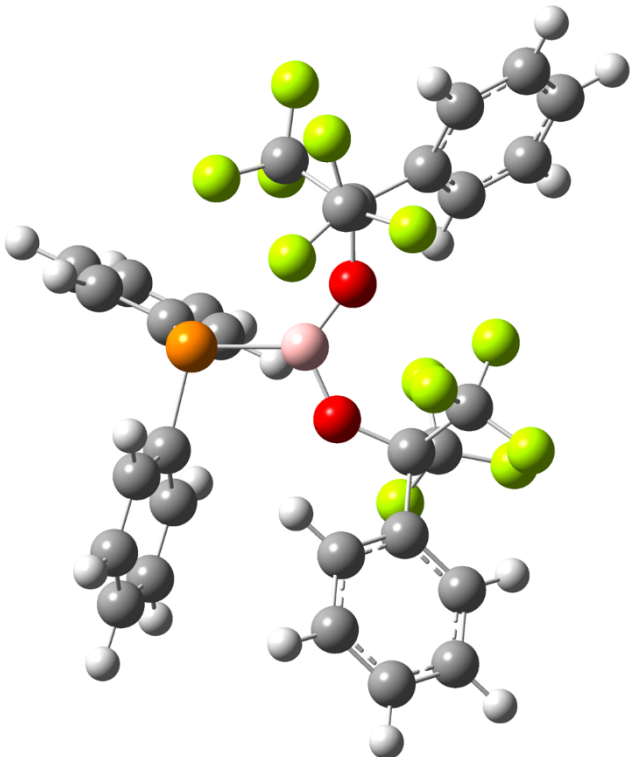

Figure S36. Optimised structure of compound **9** at B3PW91/6–31G(d,p) level of theory.

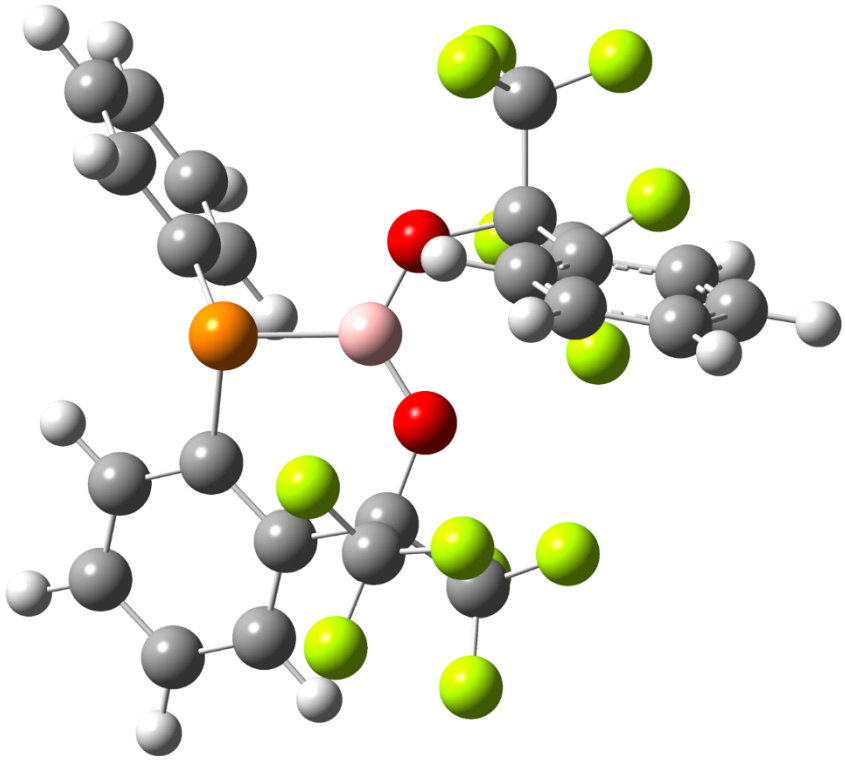

Figure S37. Optimised structure of compound **10** at B3PW91/6–31G(d,p) level of theory.

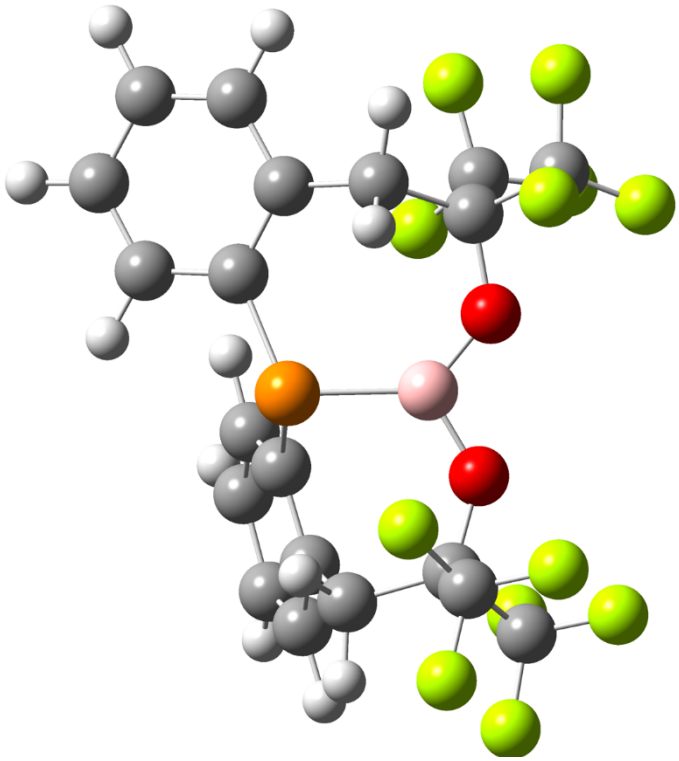

Figure S38. Optimised structure of compound **11** at B3PW91/6–31G(d,p) level of theory.

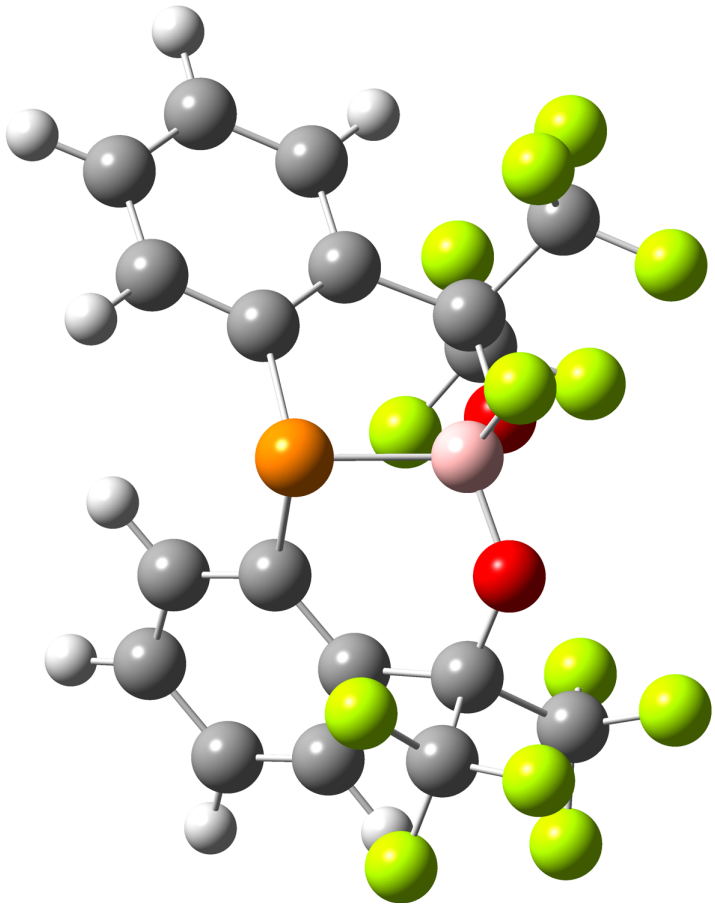

Figure S39. Optimised structure of compound **5**·$\mathbf{F}^-$ at B3PW91/6–31G(d,p) level of theory.

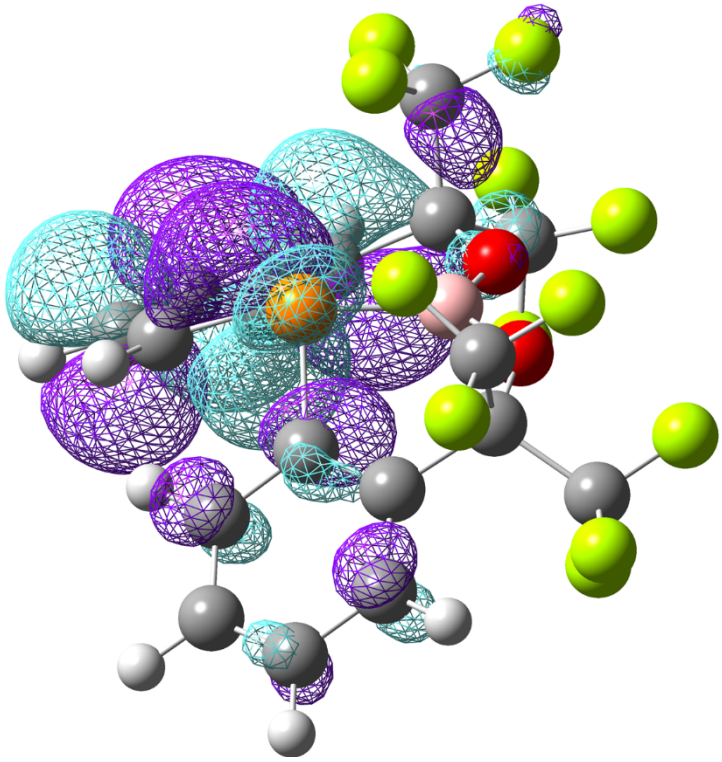

Figure S40. LUMO of compound **5** at B3PW91/6–31G(d,p) level of theory.

Table S1. Cartesian coordinates in the optimised geometry of compound **5**.
Energy: –2404.779876 a.u.

Symbol	X	Y	Z
P	-0.0074922	1.1324076	1.1799025
B	-0.0249510	-0.5121502	0.2556427
C	-1.4414854	1.7851666	0.1887260
C	-1.5551341	3.1641058	-0.0406742
H	-0.7493030	3.8231323	0.2593837
C	-2.6786218	3.7202022	-0.6398902
H	-2.7262570	4.7920441	-0.8094412
C	-3.7426667	2.8974036	-0.9948718
H	-4.6405997	3.3117105	-1.4428129
C	-3.6545766	1.5284762	-0.7732994
H	-4.4955578	0.9090865	-1.0559452
C	-2.5115986	0.9469687	-0.2050443
O	-1.1848891	-1.1405739	-0.0823364
C	-3.0897425	-0.9677076	1.3670971
F	-2.3274742	-0.4678540	2.3569824
F	-4.3262295	-0.4687454	1.5129226
F	-3.1537725	-2.2940976	1.5385829
C	-3.2118687	-1.3516719	-1.1653789
F	-4.5539752	-1.2523168	-1.0799428
F	-2.9136003	-2.6520537	-1.1412556
F	-2.8359129	-0.8681971	-2.3592002
C	1.5630249	1.7418561	0.4146957
C	1.8468296	3.1137484	0.5073034
H	1.1326499	3.7708477	0.9929677
C	3.0358555	3.6541929	0.0331805
H	3.2171298	4.7222135	0.1116990
C	3.9969447	2.8085471	-0.5108037
H	4.9400924	3.2026781	-0.8766938
C	3.7625724	1.4390014	-0.5577891
H	4.5451344	0.80095130	-0.9465743
C	2.5567225	0.8816702	-0.1073394
C	3.0364332	-1.2317198	1.2018949
F	2.3188756	-0.8035070	2.2577131
F	4.3033396	-0.8305669	1.3787758
F	3.0188174	-2.5701183	1.2165102
C	3.0739145	-1.3187652	-1.3678563
F	4.4211996	-1.3208742	-1.3081654
F	2.6867631	-2.5881994	-1.5010710
F	2.7100235	-0.6600707	-2.4794083
O	1.0995610	-1.1416124	-0.1795365
C	-2.4700807	-0.5794608	-0.0146548
C	2.4108088	-0.6505351	-0.1096861

Table S2. Cartesian coordinates in the optimised geometry of compound **9**.
Energy: –2869.104216 a.u.

Symbol	X	Y	Z
P	0.4556798	2.2201332	-0.8828964

B	0.0330600	0.3922216	-0.2943117
C	2.3031377	2.2533425	-0.8705657
C	3.0995653	2.3168041	0.2799166
H	2.6329518	2.3176374	1.2601434
C	4.4862566	2.3907013	0.1788306
H	5.0897936	2.4411847	1.0810606
C	5.1015798	2.3969870	-1.0730579
H	6.1838125	2.4585737	-1.1479832
C	4.3218177	2.3348015	-2.2258795
H	4.7914536	2.3530598	-3.2058398
O	1.1356836	-0.3638141	0.0251300
C	0.4896547	-2.7397147	-0.1715652
F	0.3874775	-2.4750264	-1.4804761
F	1.0100935	-3.9677945	-0.0366976
F	-0.7396637	-2.7834026	0.3541164
C	1.1928423	-1.6296257	2.0301848
F	1.1465357	-2.8649673	2.5569443
F	0.0405476	-1.0145526	2.3520432
F	2.1765108	-0.9530782	2.6303367
C	0.0180796	3.1928261	0.6261501
C	-0.0022593	2.6771509	1.9306862
H	0.2416718	1.6342370	2.1116583
C	-0.3341360	3.4899091	3.0133646
H	-0.3483103	3.0713283	4.0160742
C	-0.6438970	4.8333862	2.8120117
H	-0.9010853	5.4662533	3.6568234
C	-0.6268420	5.3599613	1.5218028
H	-0.8717452	6.4054879	1.3559836
C	-3.0582908	1.3873204	-0.6133038
F	-2.8902212	1.8103753	0.6439374
F	-4.3675136	1.4136346	-0.8934152
F	-2.4608225	2.2616994	-1.4353469
C	-2.3505728	-0.4468878	-2.2524066
F	-3.4277522	-0.0654784	-2.9620594
F	-1.2776937	0.1365582	-2.8039020
F	-2.2086913	-1.7673835	-2.3922605
O	-1.2111335	-0.1739873	-0.1769474
C	-0.3060860	4.5444532	0.4391589
C	2.9321366	2.2720468	-2.1237602
C	-2.4867412	-0.0577146	-0.7504517
C	1.4073640	-1.6636747	0.4913269
H	-0.3097562	4.9556464	-0.5667761
H	2.3241027	2.2516493	-3.0251665
C	2.8665026	-1.9913476	0.1451468
C	3.4976879	-1.2778196	-0.8740581
C	3.5640600	-3.0172565	0.7943776
C	4.8084059	-1.5811164	-1.2365246
H	2.9742825	-0.4715404	-1.3717033
C	4.8748438	-3.3110117	0.4332022
H	3.0937238	-3.5926049	1.5822165

C	5.5020107	-2.5964075	-0.5855003
H	5.2844668	-1.0094866	-2.0272010
H	5.4046013	-4.1055549	0.9506873
H	6.5250349	-2.8296768	-0.8668464
C	-3.4403791	-0.9928677	0.002735
C	-3.1972625	-1.2503971	1.3531317
C	-4.5858927	-1.5245450	-0.5982215
C	-4.0736467	-2.0453292	2.0868237
H	-2.3129422	-0.8427200	1.8238521
C	-5.4557566	-2.3239503	0.1377181
H	-4.8096982	-1.3230334	-1.6385177
C	-5.2042816	-2.5875975	1.4819441
H	-3.8666846	-2.2413143	3.1348836
H	-6.3354917	-2.7385781	-0.3456883
H	-5.8857493	-3.2110597	2.0535944

Table S3. Cartesian coordinates in the optimised geometry of compound **10**.
Energy: -2636.954430 a.u.

Symbol	X	Y	Z
P	1.6036340	1.1308987	-1.3938864
B	0.1374202	0.3342845	-0.4573763
C	2.9119709	0.2447749	-0.4481598
C	4.1801054	0.8434446	-0.3856984
H	4.3157379	1.8276527	-0.8252310
C	5.2542952	0.2098753	0.2217703
H	6.2236247	0.6987360	0.2575372
C	5.0803160	-1.0582513	0.7697785
H	5.9112210	-1.5779599	1.2369414
C	3.8339946	-1.6679258	0.7174905
H	3.7235900	-2.6542977	1.1474155
C	2.7320688	-1.0277012	0.1305523
O	0.2470637	-0.9120471	0.0782237
C	1.2932060	-2.6324536	-1.1922117
F	1.2782129	-1.8407749	-2.2789919
F	2.3446134	-3.4531195	-1.2929561
F	0.1802653	-3.3728452	-1.2155853
C	1.1272183	-2.6334341	1.3517657
F	1.8770349	-3.7535223	1.3448805
F	-0.1467593	-3.0152465	1.4234756
F	1.4172711	-1.9445717	2.4616224
C	1.6552912	2.8429150	-0.7107677
C	1.5811090	3.9010529	-1.6245758
H	1.5136988	3.6857678	-2.6877907
C	1.5934121	5.2237493	-1.1823018
H	1.5325004	6.0346102	-1.9027396
C	1.6897186	5.5016042	0.1784349
H	1.7021478	6.5312062	0.5249340
C	1.7707764	4.4545096	1.0975087
H	1.8426759	4.6673449	2.1605307
C	-2.0819775	0.6200476	1.7490203

F	-1.5907993	-0.5541999	2.1577478
F	-3.2480679	0.8155853	2.3925782
F	-1.2328902	1.5755999	2.1452282
C	-3.1939736	1.8631141	-0.1737932
F	-4.4598210	1.6420052	0.2021254
F	-2.7803567	3.0001106	0.3996120
F	-3.1816539	2.0402413	-1.5000829
O	-1.0407983	1.0194305	-0.3901717
C	1.3800409	-1.7500467	0.0870664
C	-2.2716011	0.6619669	0.2007389
C	1.7505906	3.1345518	0.6578406
H	1.8128879	2.3263479	1.3810350
C	-2.8719738	-0.6168794	-0.3740733
C	-2.5577288	-0.9766634	-1.6872910
C	-3.7930115	-1.3873019	0.3423658
C	-3.1284005	-2.1072064	-2.2644010
H	-1.8698691	-0.3683921	-2.2644018
C	-4.3613270	-2.5175366	-0.2384802
H	-4.0721557	-1.1155031	1.3531927
C	-4.0296600	-2.8837024	-1.5406189
H	-2.8673450	-2.3776140	-3.2832034
H	-5.0673025	-3.1125975	0.3333317
H	-4.4733517	-3.7676516	-1.9894352

Table S4. Cartesian coordinates in the optimised geometry of compound **11**.
Energy: –2483.389478 a.u.

Symbol	X	Y	Z
P	-0.0669707	1.1912904	-1.2196469
B	0.1729884	-0.4272802	-0.1844704
C	0.8486477	2.2250689	0.0173722
C	0.2552923	3.1639592	0.8684822
H	-0.8215577	3.2930822	0.8656559
C	1.0347643	3.9358383	1.7259927
H	0.5559884	4.6626978	2.3761651
C	2.4175944	3.7733227	1.7532709
H	3.0299955	4.3791118	2.4144801
C	3.0108691	2.8166615	0.9363079
H	4.0866772	2.6660308	0.9705677
O	1.4403626	-0.8416387	0.1378620
C	3.0327533	-1.4170148	-1.5185210
F	2.1375323	-1.2057991	-2.5020695
F	4.2546280	-1.1640013	-2.0133746
F	2.9705819	-2.7082978	-1.1928659
C	3.6517952	-0.7806430	0.8725076
F	4.9288774	-0.4978715	0.5535703
F	3.5957212	-2.0598704	1.2492868
F	3.3133286	-0.0301237	1.9271452
C	-1.8118949	1.7385640	-1.1479706
C	-2.0657862	3.1052505	-1.3437846
H	-1.2319548	3.7923673	-1.4582094

C	-3.3649603	3.5992719	-1.3969939
H	-3.5323560	4.6629417	-1.5394420
C	-4.4407345	2.7239438	-1.2797931
H	-5.4608527	3.0938861	-1.3193609
C	-4.1995800	1.3618850	-1.1344565
H	-5.0379035	0.6734226	-1.0682095
C	-2.4997545	-2.8272127	0.1619630
F	-2.1174500	-3.3291456	-1.0244344
F	-3.8283081	-3.0057722	0.2747849
F	-1.8992293	-3.5341019	1.1157880
C	-2.6960175	-0.6864117	1.5277204
F	-4.0288733	-0.5421507	1.4609358
F	-2.4140232	-1.4287764	2.6033042
F	-2.1511552	0.5238289	1.7201096
O	-0.7458490	-1.3065234	0.3104342
C	2.7106583	-0.4782154	-0.3243518
C	-2.8992887	0.8493423	-1.0769068
C	2.2431479	2.0308210	0.0740666
C	-2.1414799	-1.3150077	0.2243360
C	-2.7250910	-0.6506703	-1.0394076
H	-3.7030849	-1.1063515	-1.2114308
H	-2.0887554	-0.9811996	-1.8685441
C	2.8891903	0.9869912	-0.7975692
H	2.4689382	1.0532441	-1.8085226
H	3.9629506	1.1673730	-0.8856733

Table S5. Cartesian coordinates in the optimised geometry of compound **5**·F^-.
Energy: –2504.710103 a.u.

Symbol		X	Y	Z
B	0.0900807	-0.4741916	-1.3836209	
C	1.9176578	0.9773774	0.5037082	
C	2.6186146	1.3285872	1.6676148	
H	3.4432823	0.7124184	2.0019721	
C	2.2758179	2.4462185	2.4177309	
H	2.8364274	2.6837737	3.3182535	
C	1.2161325	3.2500745	2.0045519	
H	0.9293015	4.1272978	2.5802316	
C	0.5292275	2.9243702	0.8442013	
H	-0.2961153	3.5526154	0.5188254	
C	0.8541115	1.7967315	0.0716884	
C	2.3698367	-0.2655560	-0.2906829	
C	3.6458212	0.1186684	-1.1001818	
C	2.7047848	-1.4629211	0.6635932	
C	-2.5585324	0.6196286	-0.2684963	
C	-3.9186545	0.8275151	0.0062450	
H	-4.4958402	0.0417026	0.4757161	
C	-4.5548611	2.0232248	-0.3109312	
H	-5.6098827	2.1471414	-0.0788112	
C	-3.8393704	3.0431206	-0.9286055	
H	-4.3229365	3.9816032	-1.1898511	

C	-2.4966018	2.8378968	-1.2256692
H	-1.9317433	3.6106462	-1.7422564
C	-1.8266923	1.6468934	-0.9016518
C	-1.9217839	-0.7283627	0.1442112
C	-1.9380941	-0.8475771	1.7013490
C	-2.7366899	-1.9154573	-0.4789445
F	3.8853893	-1.3099730	1.3266714
F	2.8136642	-2.6067041	-0.0199616
F	1.7556749	-1.6274426	1.5905059
F	4.6392622	0.6215989	-0.3363629
F	3.3391594	1.0542498	-2.0111977
F	4.1565532	-0.9367384	-1.7564738
F	-3.0172853	-1.6881650	-1.7681612
F	-2.0588486	-3.0631826	-0.3991140
F	-3.9276519	-2.1302099	0.1455704
F	-1.4432059	-2.0289715	2.1012000
F	-3.1684338	-0.7394533	2.2541732
F	-1.1863554	0.1198644	2.2375236
F	-0.3676376	-1.1249793	-2.5192429
O	-0.5986076	-0.9207049	-0.1600295
O	1.5111016	-0.7751102	-1.2360729
P	-0.0753170	1.4999094	-1.5014476

Table S6. Cartesian coordinates in the optimised geometry of CF_2O.
Energy: –312.893533 a.u.

Symbol	X	Y	Z
C	0.0000000	0.1417450	0.0000000
F	1.0650470	-0.6341860	0.0000000
F	-1.0649370	-0.6344390	0.0000000
O	-0.0001230	1.3208950	0.0000000

Table S7. Cartesian coordinates in the optimised geometry of CF_3O^-.
Energy: –412.756950 a.u.

Symbol	X	Y	Z
C	-0.1889031	-0.0006200	0.0016691
O	-1.4121065	-0.0047509	0.0123322
F	0.4601296	1.1966207	0.4271801
F	0.4501608	-0.2225476	-1.2544694
F	0.4708507	-0.9694366	0.8152147