

Double axial stabilization of a carbenium ion via convergent P=O→C⁺ tetrel bonding

Elishua D. Litle^a and François P. Gabbaï^{*a}

Department of Chemistry, Texas A&M University, College Station, TX 77843

Supporting Information

Contents

1 Experimental	2
1.1 General experimental	2
1.2 Syntheses	2
2 NMR Spectra	4
2.1 NMR spectra of products	4
3 UV-vis spectra	14
4 pK _R ⁺ measurements.....	16
5 Cyclic voltammetry.....	17
7 Computational studies	20
7.1 General methods	20
7.2 Geometry-optimized structures	20
7.3 Electrostatic potential (ESP) maps	21
7.4 Cartesian coordinates of geometry optimized structures	23
8 X-ray diffraction analysis.....	26
8.1 Experimental details	26
8.2 Table showing the compounds characterized by X-ray diffraction and their corresponding CCDC numbers.....	26
8.3 Solid-state structures.....	27
8.4 X-ray refinement parameters	28
9 References.....	29

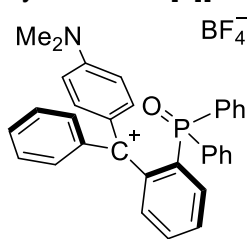
1 Experimental

1.1 General experimental

All reactions and manipulations were carried out under an atmosphere of dry, O₂-free nitrogen using standard double-manifold techniques with a rotary oil pump unless otherwise stated. A nitrogen-filled glove box was used to manipulate solids, store air-sensitive starting materials, carry out room temperature reactions, recover reaction products and prepare samples for analysis. All solvents were dried by refluxing under N₂ over CaH₂ (CH₃CN and CH₂Cl₂) or by refluxing under N₂ over Na/K (Et₂O) and stored under a nitrogen atmosphere over 3Å molecular sieves. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker Avance II 400 and a Bruker Avance 500 cold probe. ¹H and ¹³C chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to CD₃CN (1.94/1.32 ppm) or CD₂Cl₂ (5.32/53.84 ppm) as internal standards. ³¹P NMR chemical shifts are references against H₃PO₄. All coupling constants are absolute values and are expressed in Hertz (Hz). Mass spectrometry analyses were performed in-house at the Center for Mass Spectrometry using a Thermo Scientific Q Exactive Focus instrument. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Compound **1** was prepared according to a literature procedure.¹

1.2 Syntheses

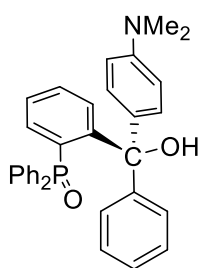
Synthesis of [2][BF₄]



Compound [2][BF₄] was synthesized by treating a CH₃CN (2 mL) solution of **1** (97.5 mg, 0.2 mmol) with 30% H₂O₂ in H₂O (6.8 mg, 0.2 mmol). After stirring at ambient temperature for 3 hours, the resulting mixture was treated with HBF₄ (50% w/w in H₂O, 17.6 mg, 0.2 mmol) and stirred for 15 mins at which point trifluoroacetic anhydride (0.1 mL) was added to scavenge any water. Addition of Et₂O (10 mL) triggered the precipitation of an orange solid that was then filtered and washed with Et₂O (3x1 mL). Subsequent drying under vacuum afforded [2][BF₄]. Orange, needle-like single crystals were obtained by slow evaporation of an acetonitrile and Et₂O solution of [2][BF₄]. Yield: 40 mg, 70 μmol, 35%. ¹H

NMR (500 MHz, CD₃CN, 298 K) δ/ppm: 7.71 (tt, *J* = 7.7, 1.4 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.55 – 7.48 (m, 1H), 7.48 – 7.30 (m, 16H), 7.28 (ddd, *J* = 7.6, 3.6, 1.2 Hz, 1H), 6.79 (d, *J* = 9.6 Hz, 2H), 3.43 (s, 6H). ¹³C **NMR** (126 MHz, CD₃CN, 298 K) δ/ppm: 176.35 (s), 161.42 (s), 144.55 (d, *J* = 6.2 Hz), 143.05 (s), 138.92 (s), 135.40 (s), 135.30 (s), 133.61 (s), 133.05 (d, *J* = 2.9 Hz), 132.99 (s), 132.98 (s), 132.90 (s), 132.71 (s), 132.63 (s), 132.42 (s), 132.34 (s), 131.18 (s), 130.77 (s), 130.68 (s), 129.70 (s), 129.59 (d, *J* = 2.4 Hz), 129.48 (s), 129.21 (s), 43.26 (s). ³¹P **NMR** (162 MHz, CD₃CN, 298 K) δ/ppm: 28.10 (s). **HRMS** (ESI+) *m/z* calculated for [M]⁺ [C₃₃H₂₉NOP]⁺: 486.1981, found: 486.1975.

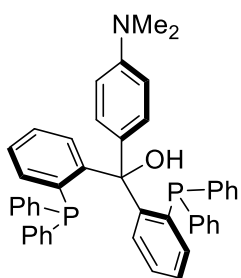
Synthesis of [2]OH



Compound [2]OH was synthesized by treating a CH₃CN (2 mL) solution of **1** (48.4 mg, 0.1 mmol) with an excess of 30% H₂O₂ in H₂O (0.2 mmol). The reaction was stirred for 15 min. and brought to dryness. The residue was dissolved in acetonitrile. The resulting solution was left open to the atmosphere, leading to slow evaporation of the solvent and formation of colorless, block-like single crystals [2]OH. Yield: 5.4 mg, 10 μmol, 10.0%. ¹H **NMR** (500 MHz, CD₂Cl₂, 298 K) δ/ppm: 8.74 (s, 1H), 7.57 – 7.42 (m, 2H), 7.40 – 7.19 (m, 11H), 7.18 – 7.01 (m, 5H), 6.98 – 6.84 (m, 8H), 6.46 – 6.29 (m, 2H), 2.86 (s, 6H). ¹³C **NMR** (126 MHz, CD₂Cl₂, 298 K) δ/ppm: 156.34 (d, *J* = 6.2 Hz), 149.78 (s), 148.04 (s), 136.55 (d, *J* = 13.8 Hz), 134.87 (s), 134.02 (s), 133.21 (d, *J* = 9.3 Hz), 132.39 (s), 132.12 (s), 132.08 (s), 132.04 (s), 132.01 (s),

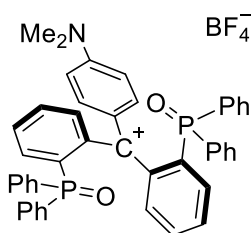
131.97 (s), 131.94 (s), 131.89 (s), 131.19 (d, *J* = 2.8 Hz), 130.28 (s), 129.51 (s), 129.39 (s), 128.83 (s), 128.72 (s), 128.63 (s), 127.59 (s), 127.05 (s), 126.18 (d, *J* = 13.5 Hz), 111.51 (s), 82.50 (d, *J* = 3.2 Hz), 40.58 (s). ³¹P **NMR** (202 MHz, CD₂Cl₂, 298 K) δ/ppm: 36.89 (s). **HRMS** (ESI+) *m/z* calculated for [M]⁺ [C₃₃H₂₉NO₂P]⁺: 502.1930, found: 502.1916.

Synthesis of **3**



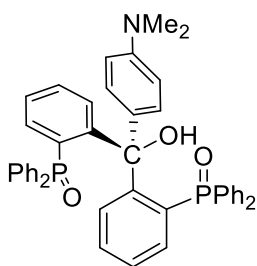
(2-bromophenyl)diphenylphosphane (2.0 g, 5.86 mmol) was placed in a 200 mL Shlenk tube and dissolved in 20 mL of ether under nitrogen while stirring. The flask was cooled to 0 °C and a solution of BuLi in hexanes (2.6 mL, 6.68 mmol) was added dropwise. After stirring for 6 hours at this temperature, a diethylether solution (8 mL) of ethyl 4-(dimethylamino)benzoate (0.51 g, 2.64 mmol) was slowly added. After an additional 2 hours of stirring, distilled H₂O (12 mL) was added to the solution. This addition triggered the formation of a precipitate which was isolated by filtration, washed with hexanes, and then dried under vacuum. This protocol afforded **3** in 94.2% yield (1.67 g). Single crystals of **3** were obtained by slow evaporation of a Benzene/CH₂Cl₂ mixture at low temperature. **¹H NMR** (400 MHz, CD₂Cl₂, 298 K) δ/ppm: 7.34 – 7.13 (m, 21H), 7.10 (td, *J* = 7.9, 1.6 Hz, 4H), 6.98 (s, 2H), 6.79 (ddd, *J* = 7.7, 4.7, 1.4 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 6.26 (t, *J* = 9.7 Hz, 1H), 2.95 (s, 6H), 2.16 (s, 1H). **¹³C NMR** (126 MHz, CDCl₃, 298 K) δ/ppm: 153.90 (d, *J* = 21.7 Hz), 149.34 (s), 138.87 (d, *J* = 11.8 Hz), 137.79 (s), 137.70 (s), 136.72 (d, *J* = 18.2 Hz), 135.96 (s), 133.59 (d, *J* = 20.0 Hz), 133.32 (d, *J* = 18.7 Hz), 129.64 (d, *J* = 7.3 Hz), 129.53 (s), 128.05 (d, *J* = 5.8 Hz), 127.96 (d, *J* = 4.4 Hz), 127.88 (s), 127.73 (d, *J* = 5.1 Hz), 127.06 (s), 111.71 (s), 85.53 (s), 40.63 (s). **³¹P NMR** (162 MHz, CD₂Cl₂, 298 K) δ/ppm: -14.24 (s). **Elemental Analysis** calculated: C: 80.46; H: 5.85; N: 2.09. Found: C: 80.36; H: 5.94; N: 2.11.

Synthesis of [4][BF₄]



Compound [4][BF₄] was synthesized by treating a CH₃CN (2 mL) solution of **3** (134 mg, 0.2 mmol) with 30% H₂O₂ in H₂O (6.8 mg, 0.2 mmol). After stirring at ambient temperature for 15 min, the resulting mixture was treated with HBF₄ (52% w/w in Et₂O, 32 mg, 0.4 mmol) and stirred for 15 min at which point trifluoroacetic anhydride (0.1 mL) was added to scavenge any water. Addition of Et₂O (10 mL) triggered the precipitation of an orange solid that was then filtered and washed with Et₂O (3x1 mL). Subsequent drying under vacuum afforded [4][BF₄]. Yield: 153 mg, 198 μmol, 99%. Orange, block-like single crystals were obtained by slow evaporation of an acetonitrile solution of [4][BF₄]. **¹H NMR** (400 MHz, CD₃CN, 298 K) δ/ppm: 8.42 (ddd, *J* = 7.9, 3.7, 1.2 Hz, 2H), 7.72 (tt, *J* = 7.7, 1.5 Hz, 2H), 7.65 – 7.43 (m, 18H), 7.38 (dddd, *J* = 9.0, 7.8, 4.6, 1.5 Hz, 6H), 6.47 (d, *J* = 9.9 Hz, 2H), 5.76 (d, *J* = 9.9 Hz, 2H), 3.23 (s, 6H). **¹³C NMR** (126 MHz, CD₃CN, 298 K) δ/ppm: 175.48 (t, *J* = 3.5 Hz), 161.06 (s), 143.99 (d, *J* = 5.9 Hz), 140.59 (s), 135.51 (s), 135.27 (d, *J* = 12.1 Hz), 134.67 (s), 134.39 (s), 134.31 (s), 133.91 (s), 133.61 (s), 133.22 (s), 132.80 (d, *J* = 2.8 Hz), 132.51 (d, *J* = 2.8 Hz), 132.41 (s), 132.37 (s), 132.31 (d, *J* = 1.8 Hz), 132.23 (s), 132.21 (s), 130.19 (d, *J* = 12.1 Hz), 129.38 (d, *J* = 12.2 Hz), 129.15 (d, *J* = 12.1 Hz), 115.57 (s), 42.70 (s). **³¹P NMR** (162 MHz, CD₃CN, 298 K) δ/ppm: 28.45 (s). **HRMS** (ESI+) *m/z* calculated for [M]⁺ [C₄₅H₃₈NO₂P₂]⁺: 686.2372, found: 686.2359.

Synthesis of [4]OH



Compound [4]OH was synthesized by treating a CH₃CN (2 mL) solution of **3** (67.9 mg, 0.1 mmol) with an excess of 30% H₂O₂ in H₂O (0.2 mmol). The reaction was stirred for 15 min. and brought to dryness. The residue was dissolved in acetonitrile. The resulting solution was left open to the atmosphere, leading to slow evaporation of the solvent and formation of colorless, needle-like single crystals of [4]OH. Yield: 8.2 mg, 12 μmol, 11.6%. Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of C₆H₆ into a CH₂Cl₂ solution of [4]OH. **¹H NMR** (500 MHz, CD₂Cl₂, 298 K) δ/ppm: 8.83 (s, 1H), 8.32 (s, 1H), 7.68 (s, 2H), 7.59 – 6.98 (m, 23H), 6.96 – 6.73 (m, 2H), 6.56 (s, 1H), 5.83 (s, 1H), 5.52 (s, 1H), 2.78 (s, 6H). **¹³C NMR** (126 MHz, CD₂Cl₂, 298 K) δ/ppm: 149.70 (s), 138.26 (br, s), 137.22 (br, s), 136.32 (br, s), 135.64 (br, s), 134.60 (s), 132.64 (s), 131.36 (s), 130.82 (s), 129.88 (br, s), 128.38 (br, s), 126.96 (br, s), 126.10 (br, s), 112.50 (br, s), 109.59 (br, s), 83.63 (s), 40.34 (s). **³¹P NMR** (162 MHz, CD₂Cl₂, 298 K) δ/ppm: 35.55 (s), 35.54 (s). **HRMS** (ESI+) *m/z* calculated for [M+H]⁺ [C₄₅H₃₉NO₃P₂]⁺: 704.2466, found: 704.2478.

2 NMR Spectra

2.1 NMR spectra of products

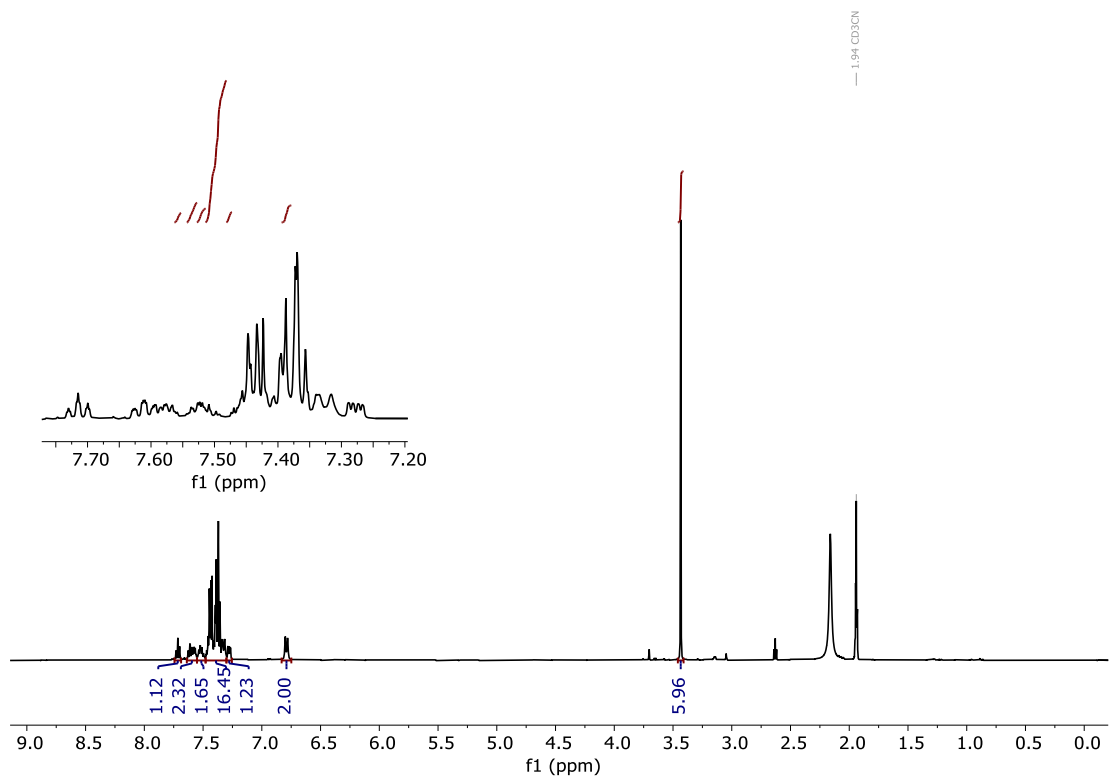


Figure S1. ^1H NMR (500 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{2}][\text{BF}_4]$.

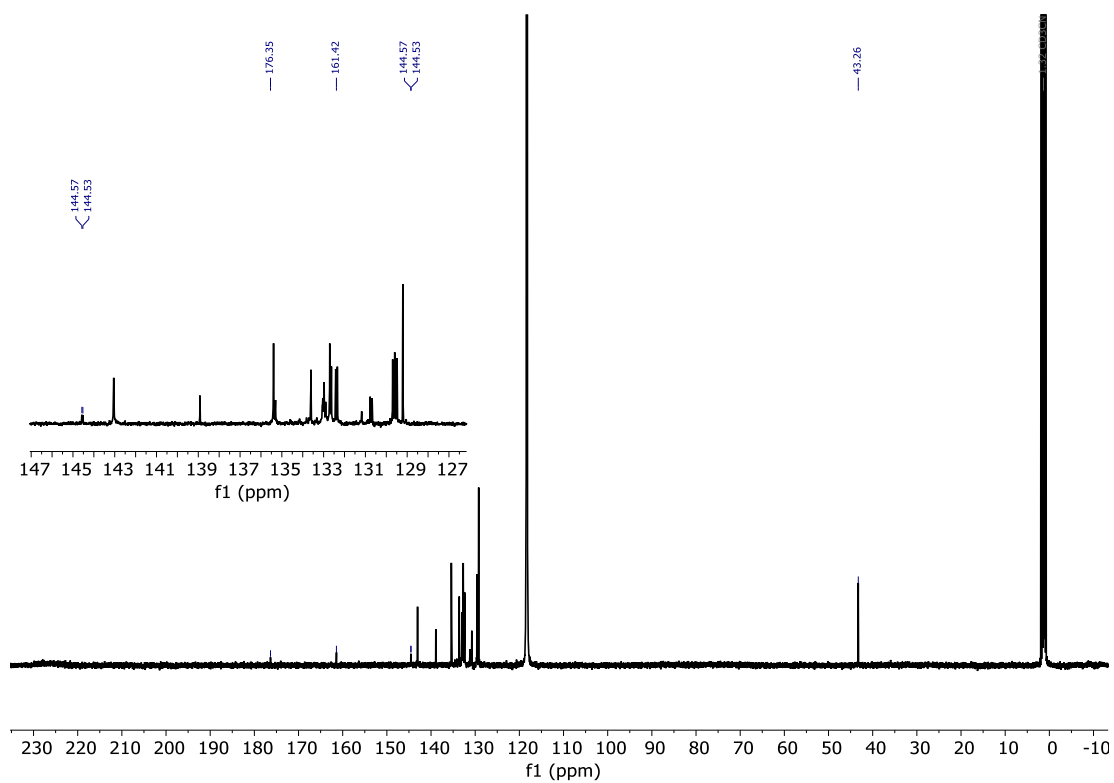


Figure S2. ^{13}C NMR (126 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{2}][\text{BF}_4]$.

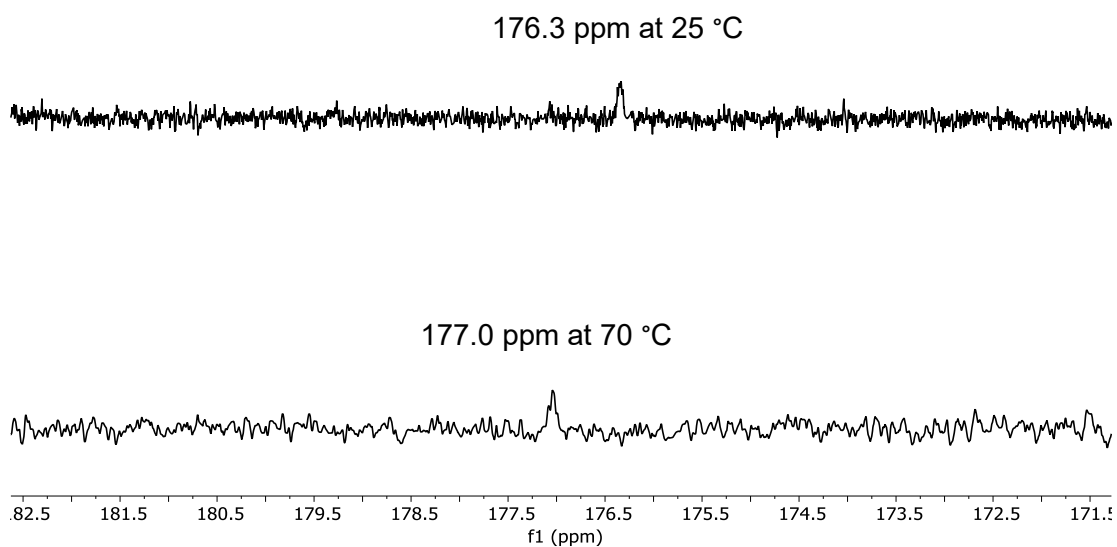


Figure S3. ^{13}C NMR (126 MHz, CD_3CN) spectrum of the $[\mathbf{2}][\text{BF}_4]$ focused on the carbenium signal.

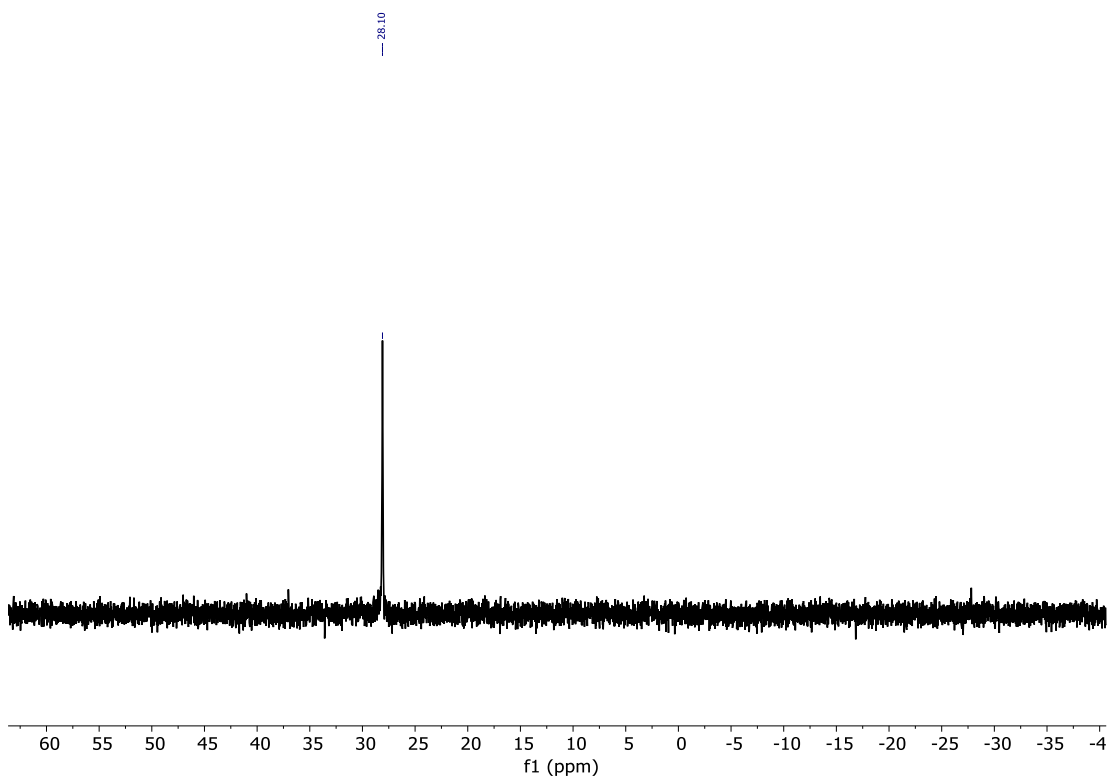
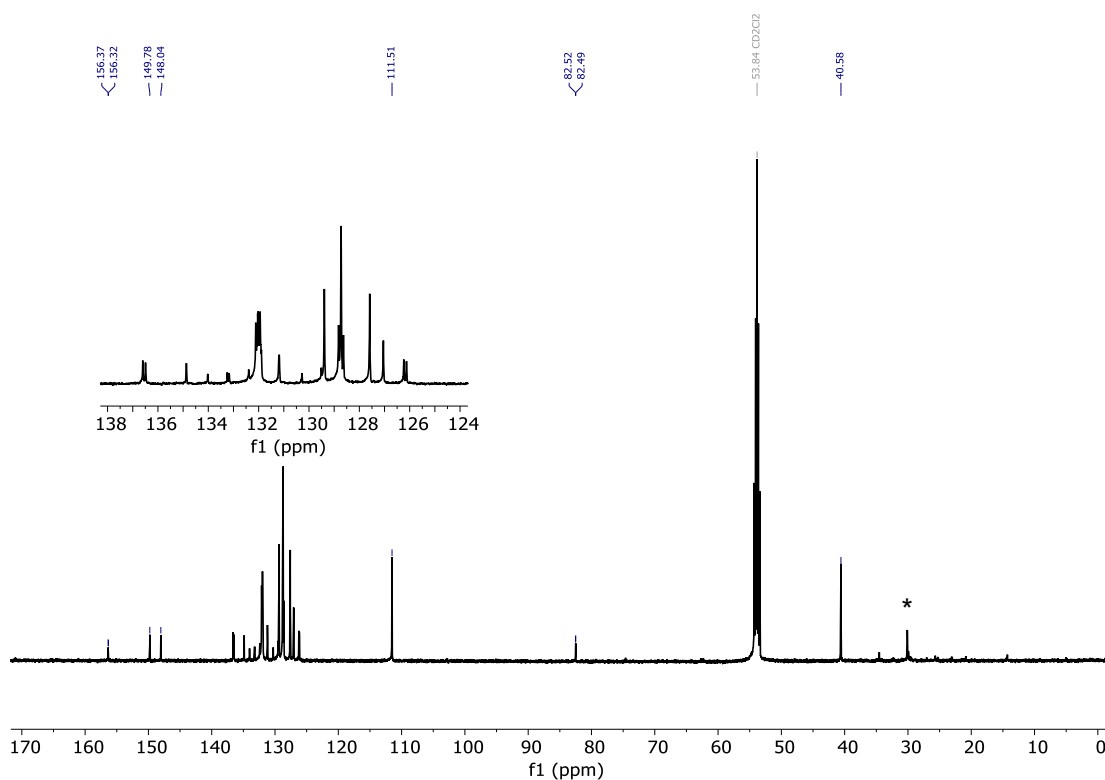
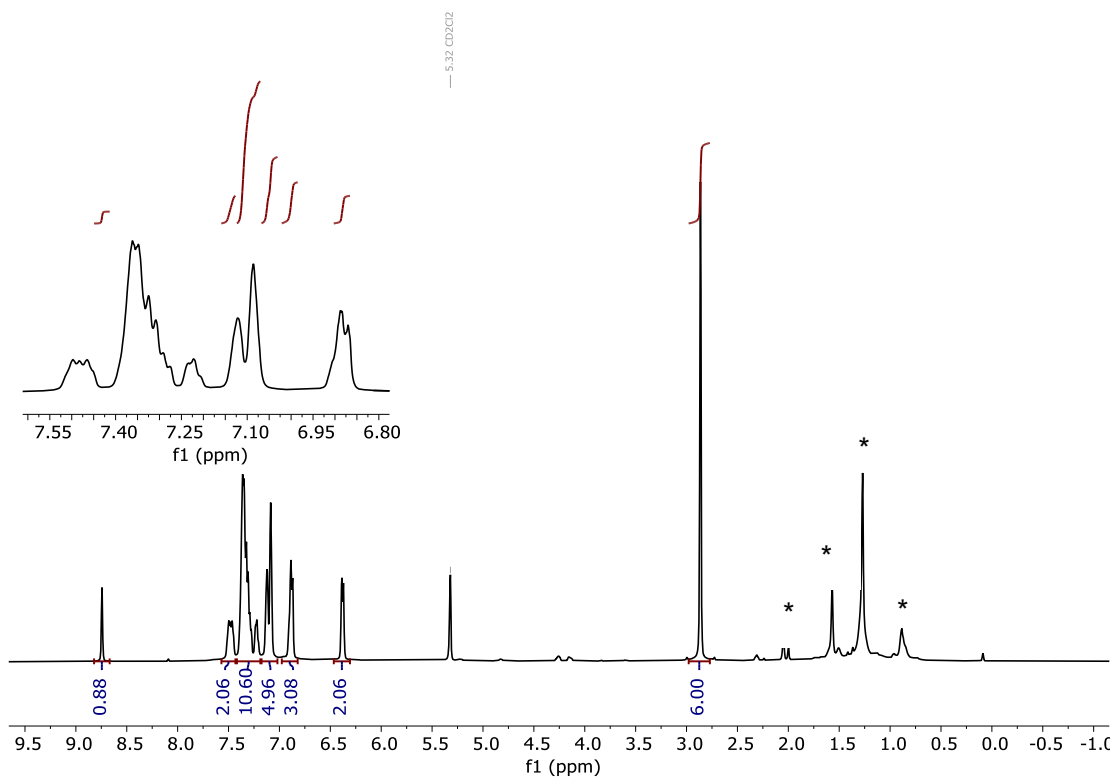


Figure S4. ^{31}P NMR (162 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{2}][\text{BF}_4]$.



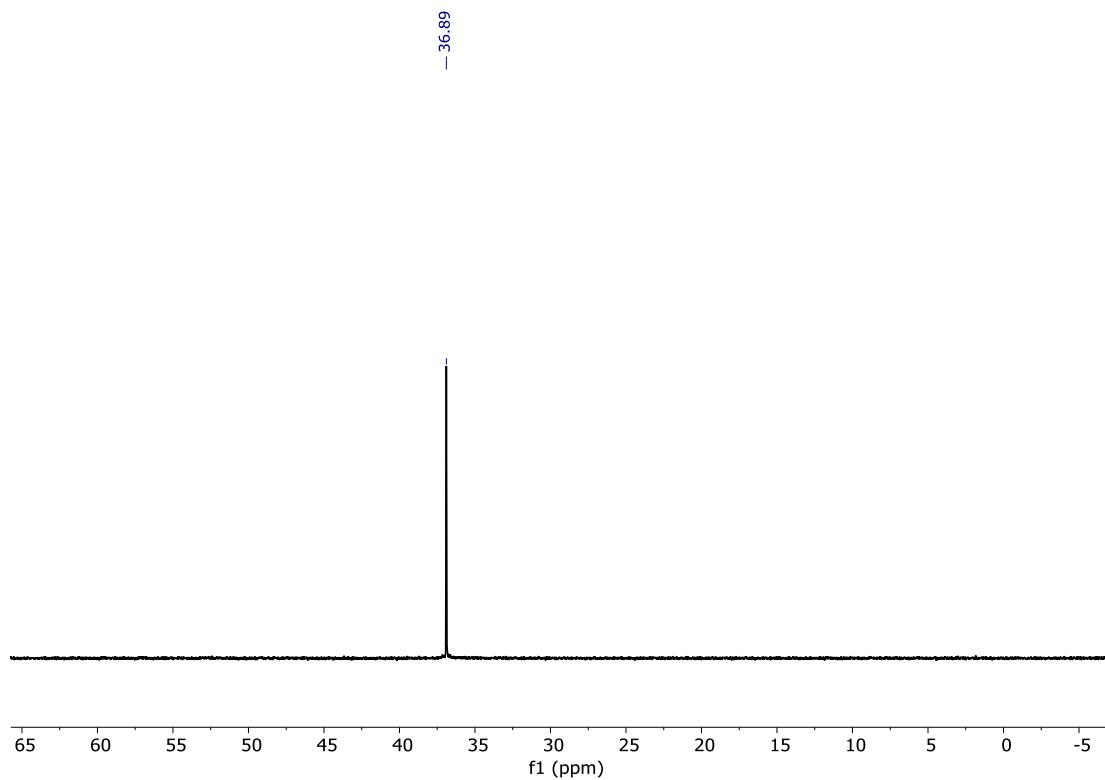


Figure S7. ^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K) spectrum of **[2]OH**.

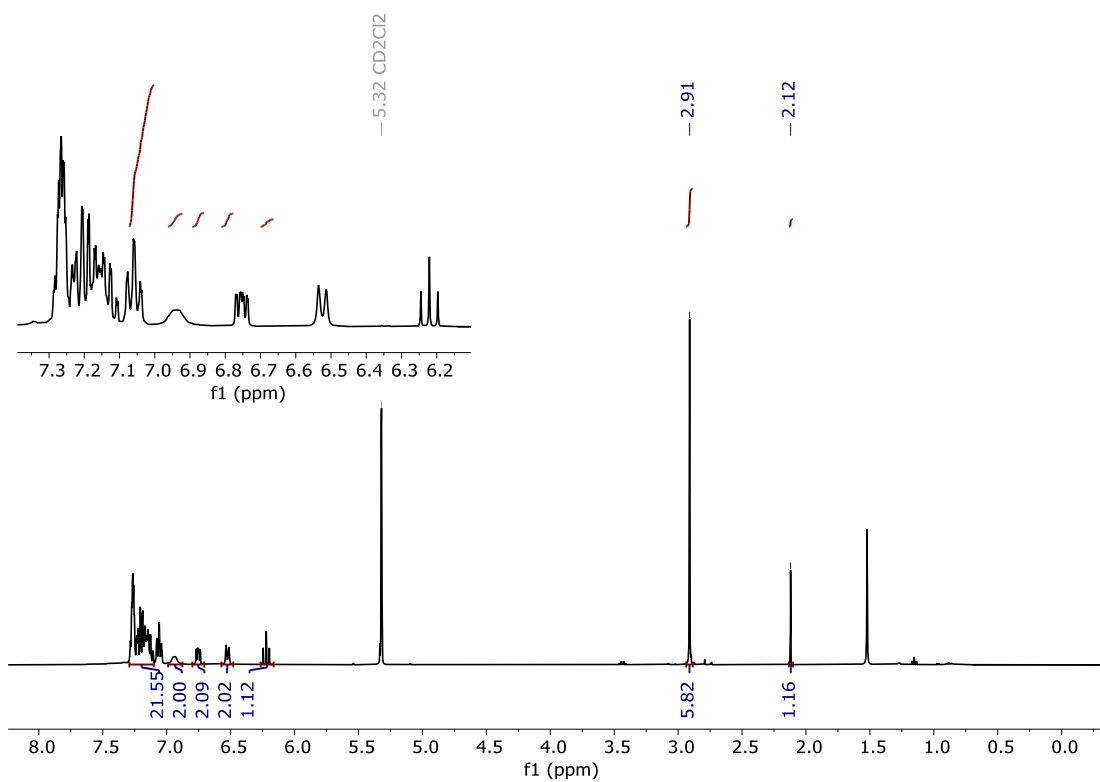


Figure S8. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K) spectrum of **3**.

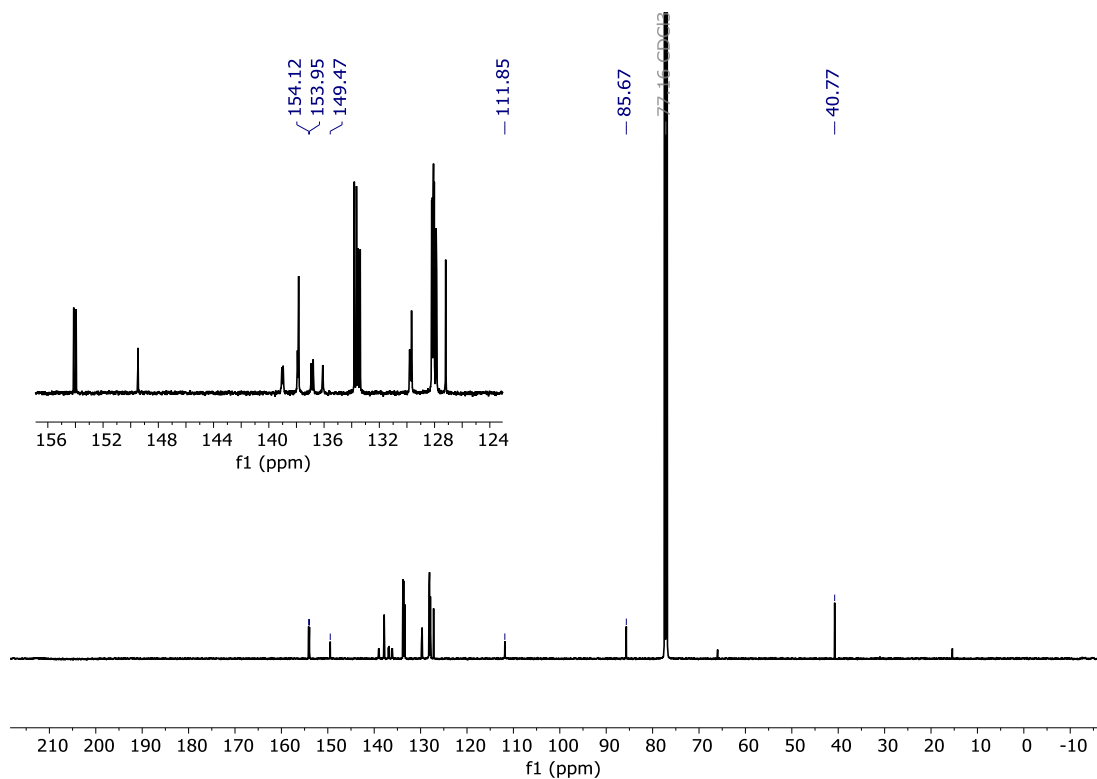


Figure S9. ^{13}C NMR (126 MHz, CDCl_3 , 298 K) spectrum of **3**.

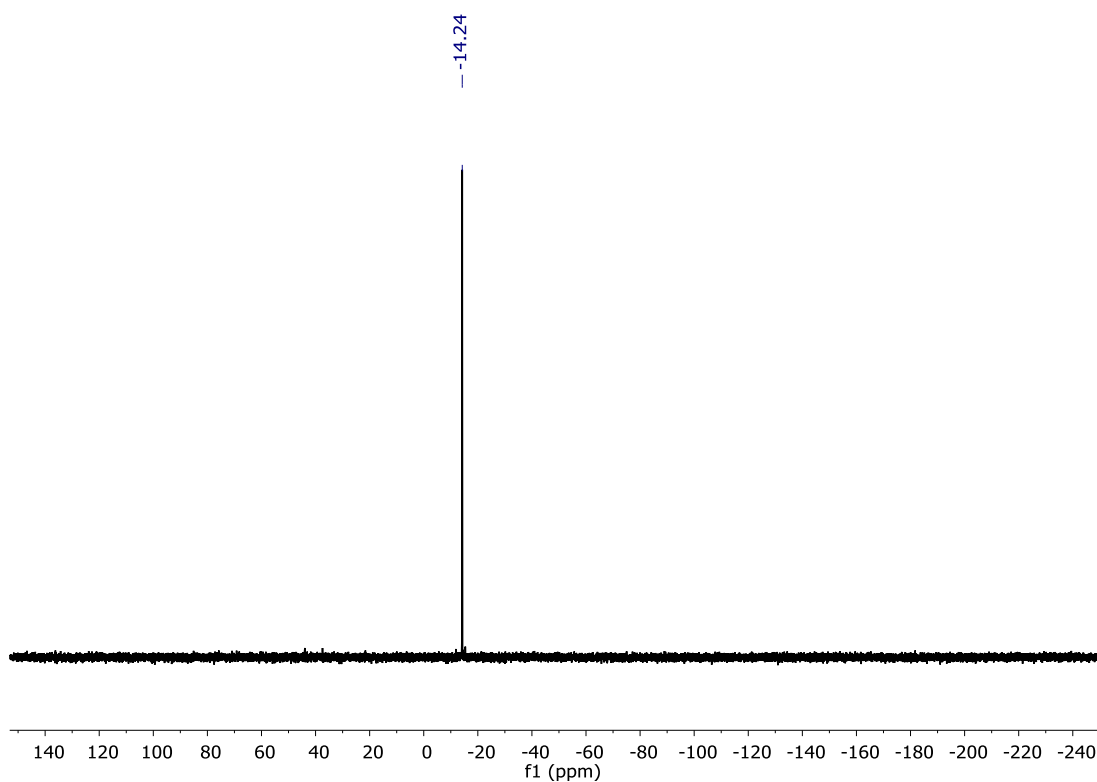


Figure S10. ^{31}P NMR (162 MHz, CD_2Cl_2 , 298 K) spectrum of **3**.

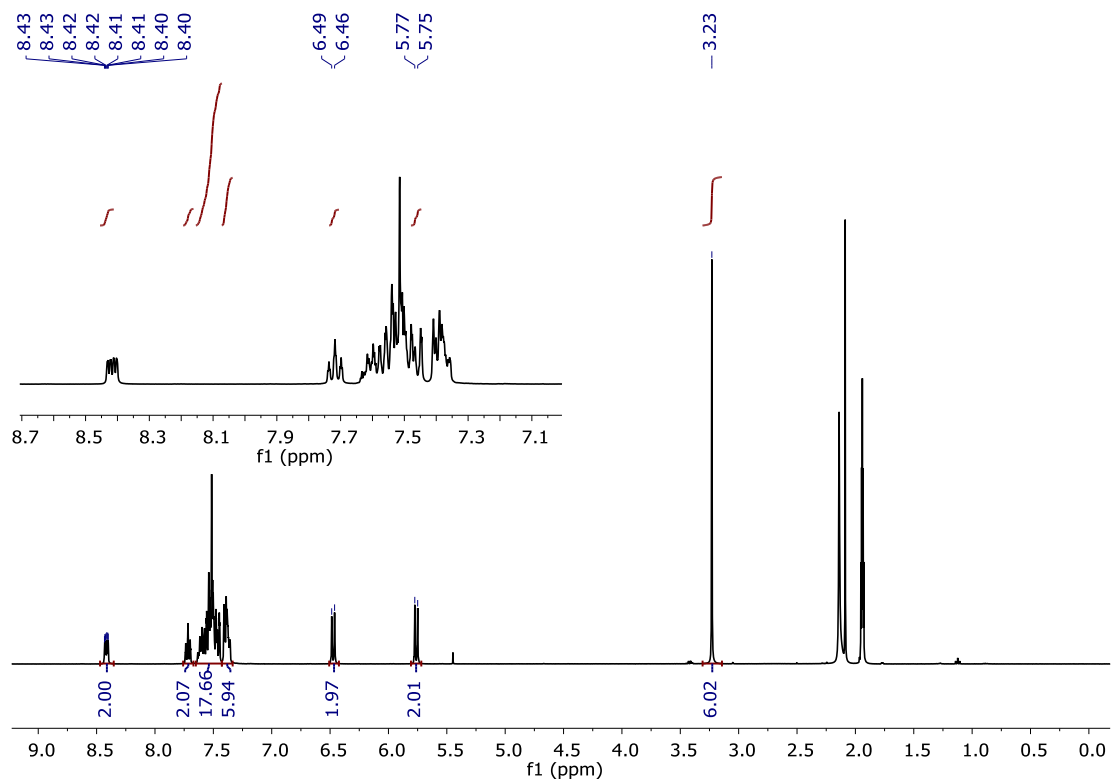


Figure S11. ^1H NMR (400 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{4}][\text{BF}_4]$.

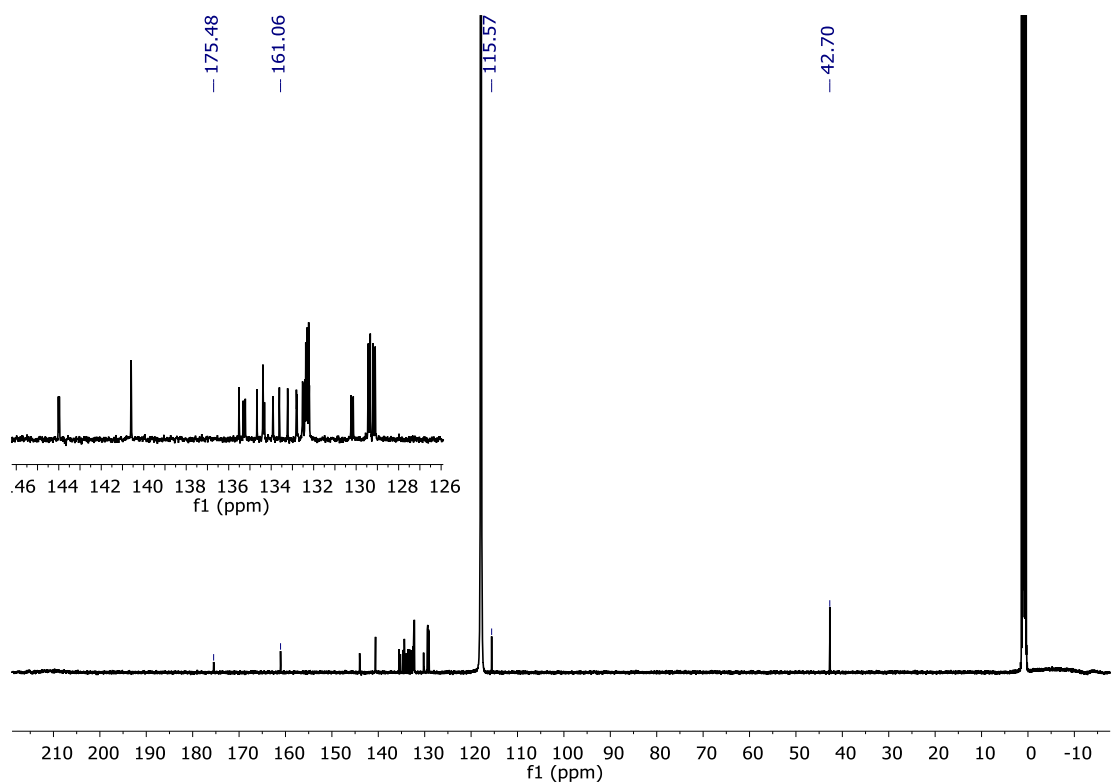


Figure S12. ^{13}C NMR (126 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{4}][\text{BF}_4]$.

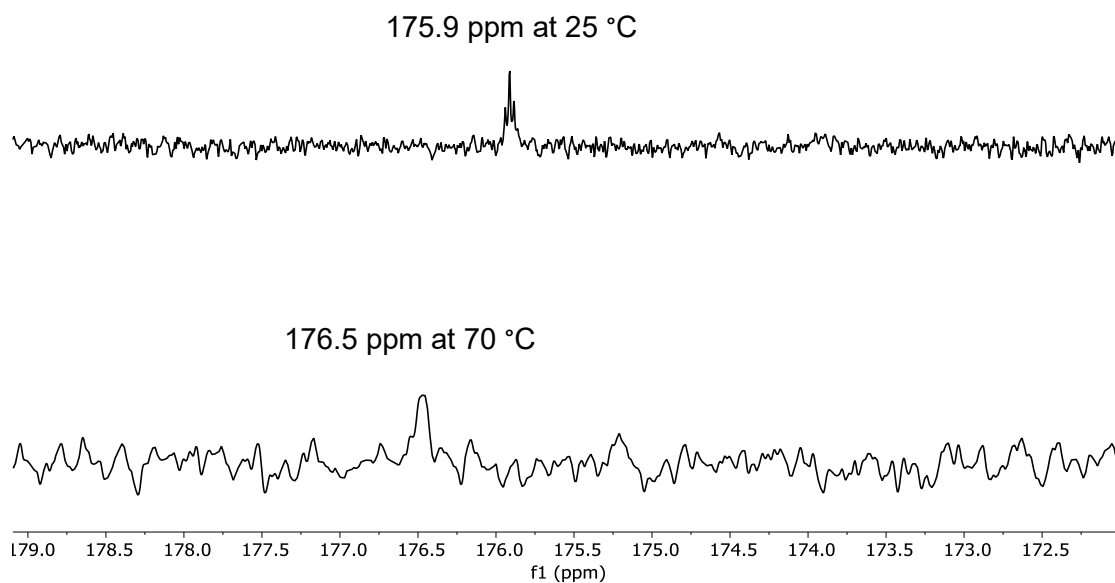


Figure S13. ^{13}C NMR (126 MHz, CD_3CN) spectrum of the $[\mathbf{4}][\text{BF}_4]$ focused on the carbenium signal.

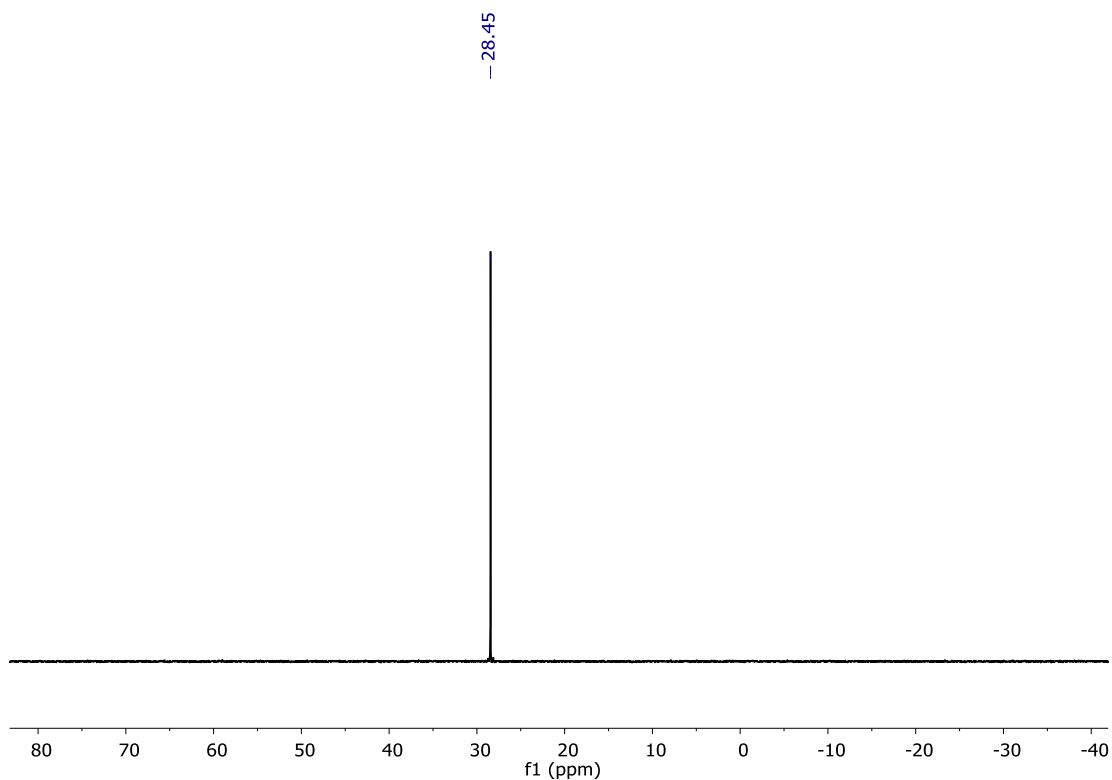


Figure S14. ^{31}P NMR (162 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{4}][\text{BF}_4]$.

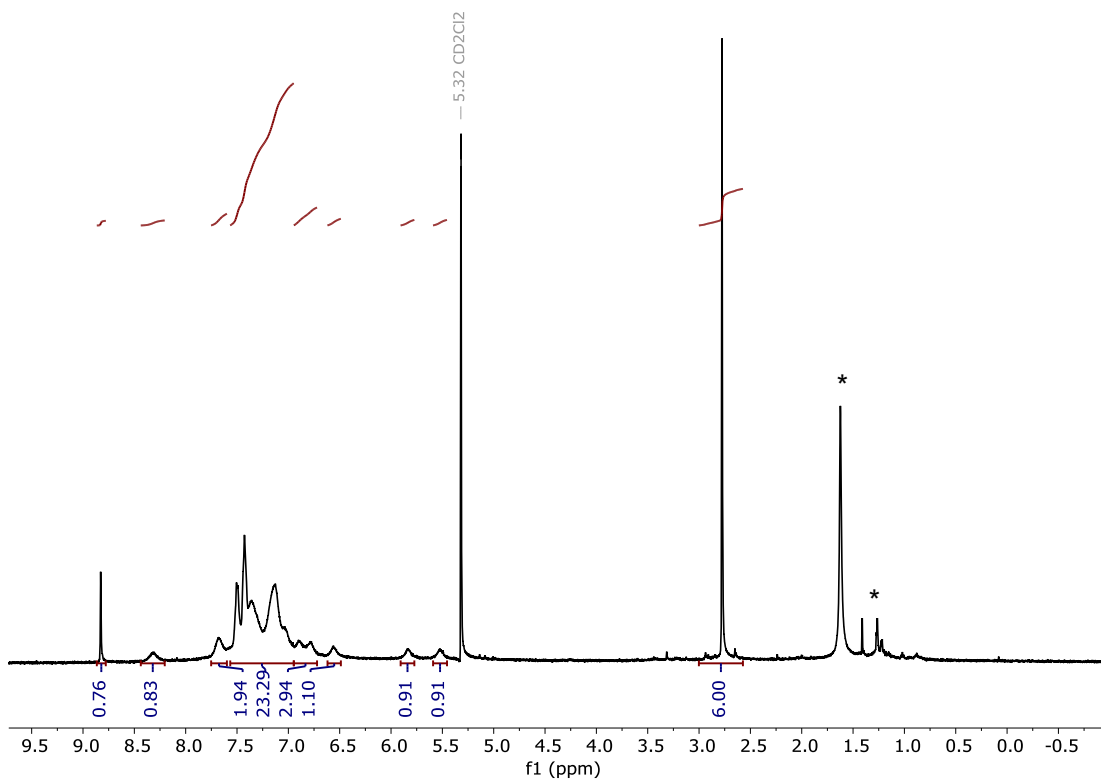


Figure S15. ^1H NMR (500 MHz, CD_2Cl_2 , 298 K) spectrum of [4]OH. * solvent impurities.

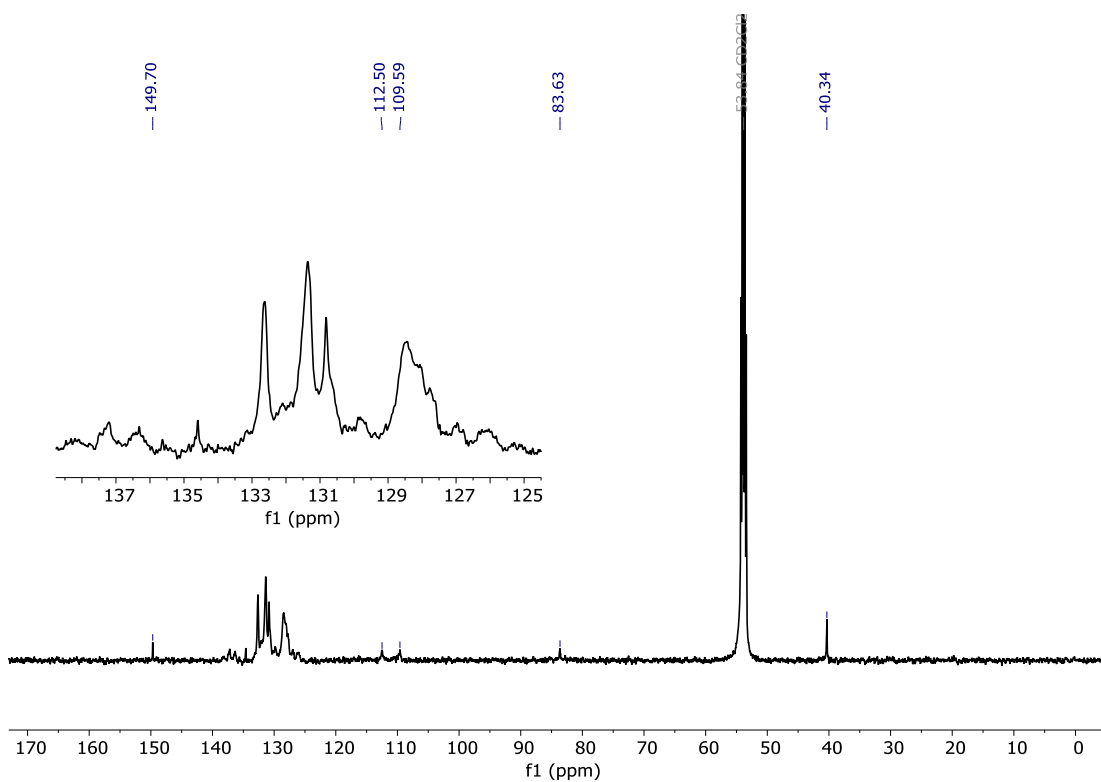


Figure S16. ^{13}C NMR (126 MHz, CD_2Cl_2 , 298 K) spectrum of [4]OH.

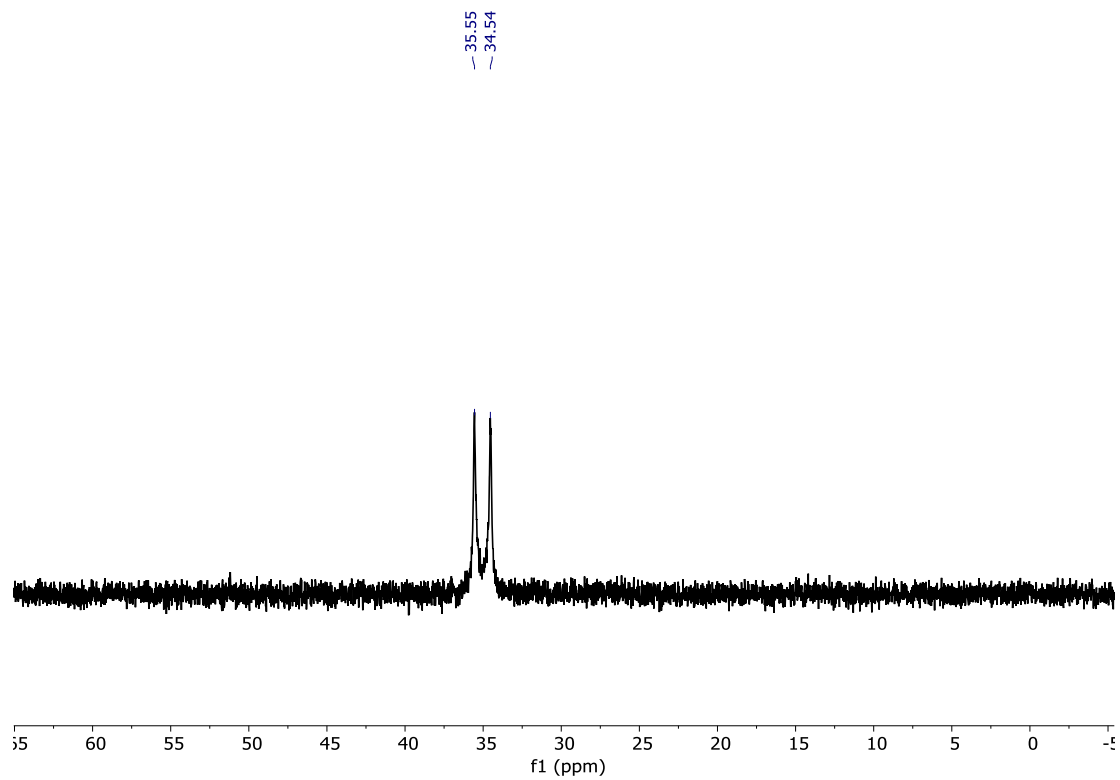


Figure S17. ^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K) spectrum of **[4]OH**.

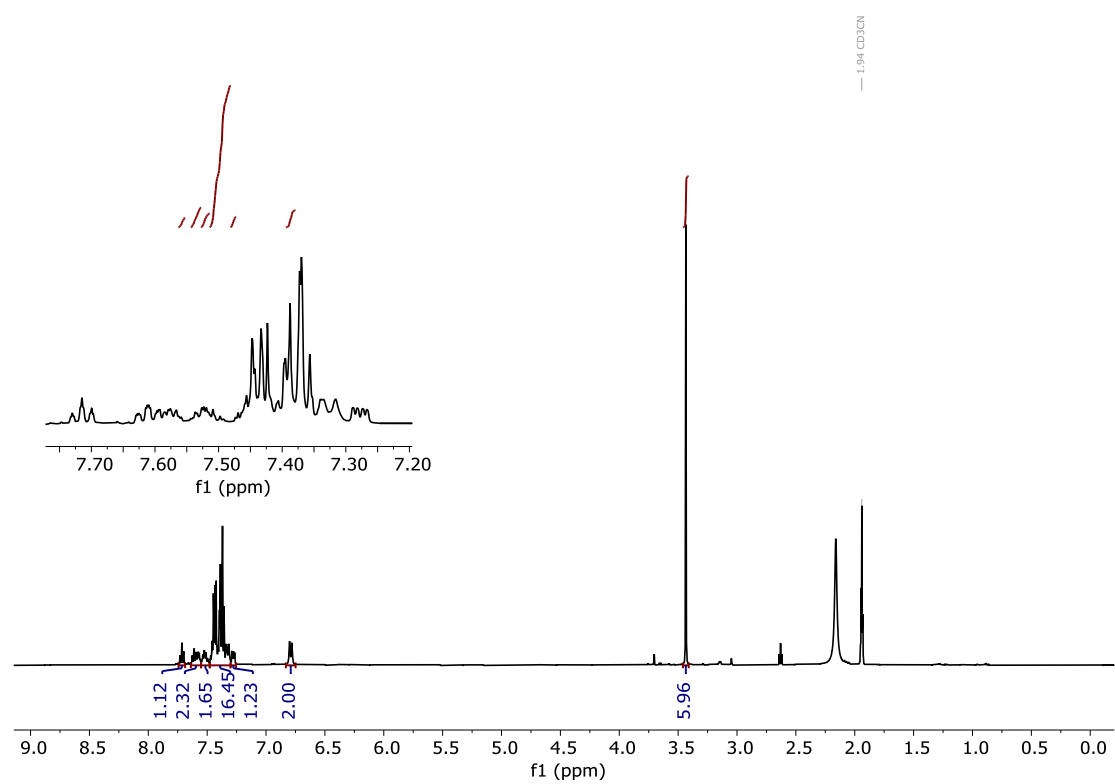


Figure S18. ^1H NMR (500 MHz, CD_3CN , 298 K) spectrum of **[5][BF₄]**.

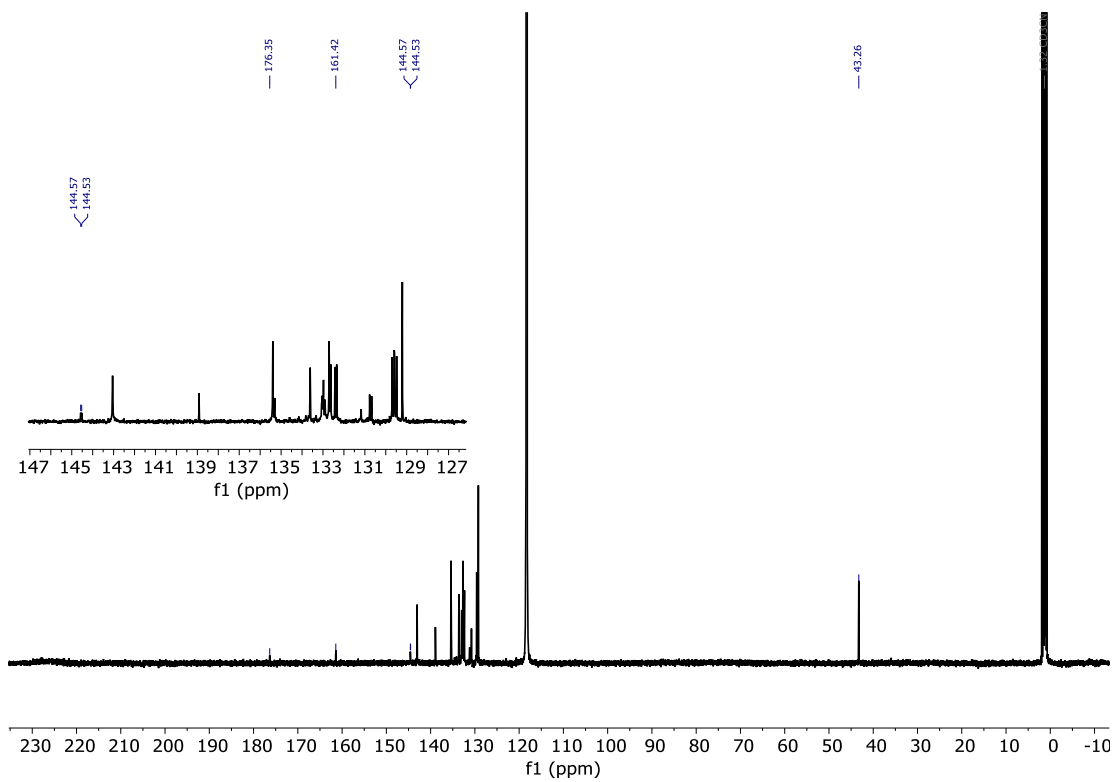


Figure S19. ^{13}C NMR (126 MHz, CD_3CN , 298 K) spectrum of $[\mathbf{5}][\text{BF}_4]$.

3 UV-vis spectra

UV-Vis absorbance spectra were recorded on a Shimadzu UV-2502PC UV-Vis spectrophotometer. Spectra were collected at a concentration of 5×10^{-5} M in acetonitrile using a 1cm quartz cuvette.

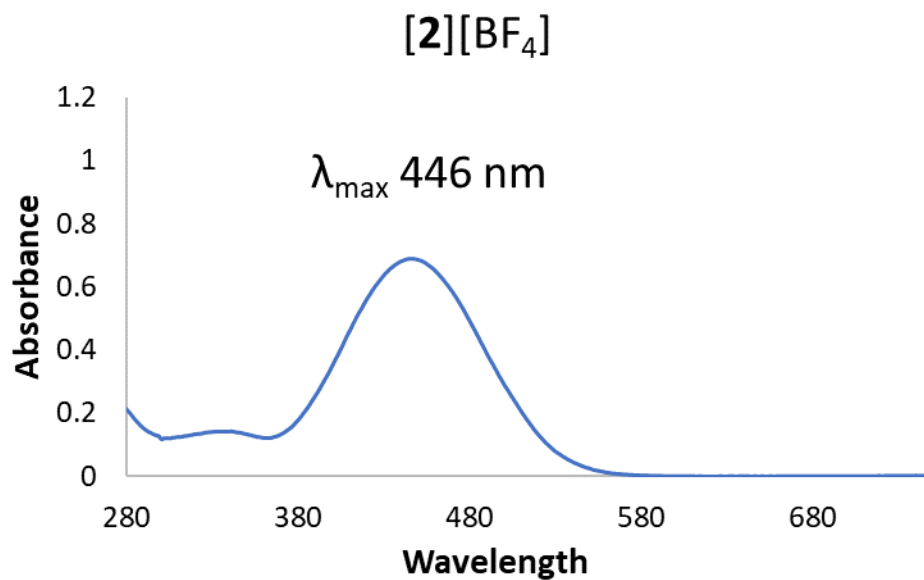


Figure S20. UV-vis spectrum of [2][BF₄].

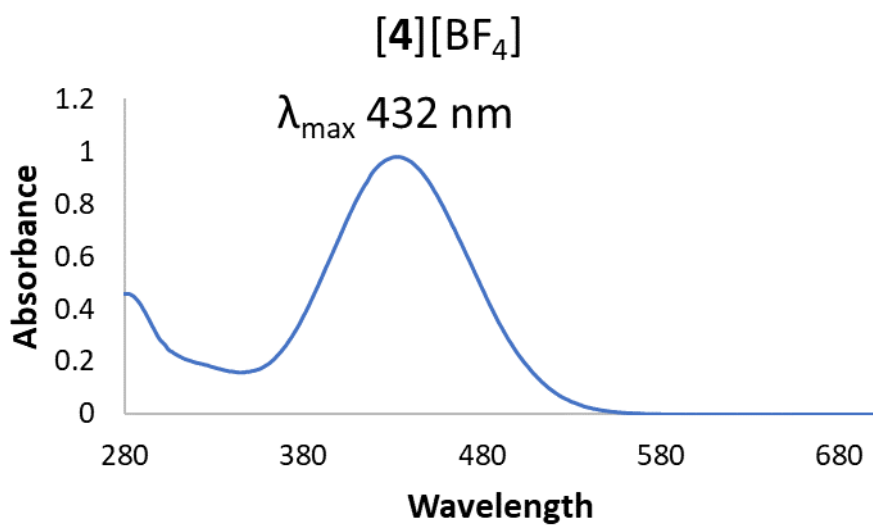


Figure S21. UV-vis spectrum of [4][BF₄].

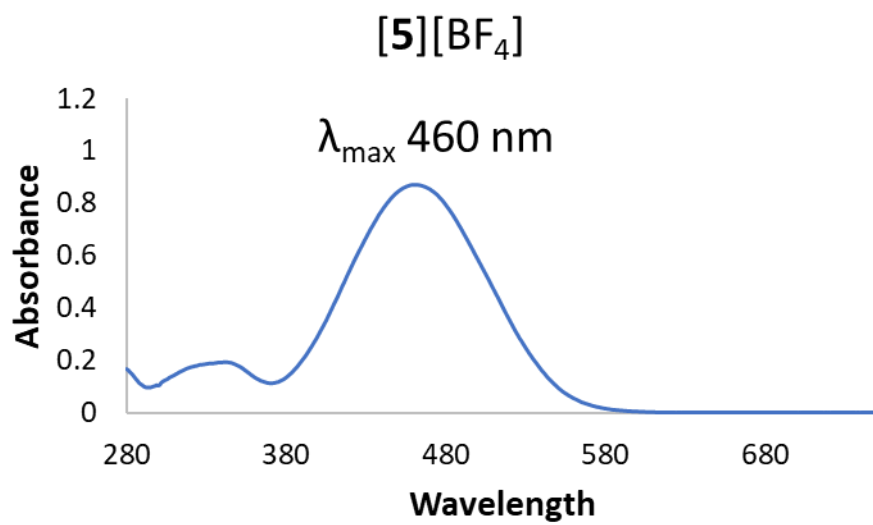


Figure S22. UV-vis spectrum of [5][BF₄].

4 pK_{R^+} measurements

The carbenium salts (4.55 μmol of **[2]** $[\text{BF}_4]$, **[4]** $[\text{BF}_4]$ and **[5]** $[\text{BF}_4]$) were dissolved in acetonitrile (2 mL). 30 μL of the resulting acetonitrile solution was added to a solution consisting of water and a citric acid buffer solution (9 mM, 2.7 mL) affording a final concentration of 25 μM for the carbenium ions. The solution was titrated by incremental addition of a solution of NaOH in water. The solutions were buffered in order to obtain a better control of the pH near the equivalence point.

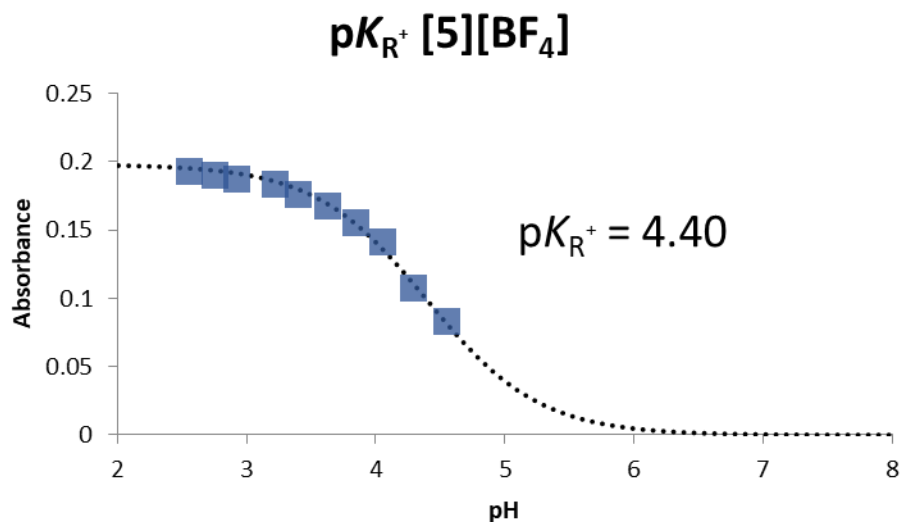


Figure S23. Spectrophotometric titration curve of **[5]** $[\text{BF}_4]$ in $\text{H}_2\text{O}/\text{MeCN}$ 9:1 (v/v) upon incremental additions of NaOH dissolved in H_2O . The absorbance was measured at 460 nm.

5 Cyclic voltammetry

Cyclic voltammetry measurements were recorded with a Pine instruments WaveNow potentiostat, using a glassy carbon working electrode, an Ag pseudo reference electrode and a platinum wire as the auxiliary electrode. Solutions of the concentration 5×10^{-4} M were prepared in dried and degassed solutions of dichloromethane with 100 mM TBAPF₆ as the supporting electrolyte. The voltammograms were collected at a scan rate of 500 mV/s. All potentials were referenced against Fc/Fc⁺ in the same solvent. All CV measurements were carried out inside a glove box. Differential Pulse Voltammetry (DPV) was performed with the same samples on a CH Instruments (Model 660 D) electrochemical analyzer. Using the parameters: Amplitude (V) = 0.05; Pulse Width (sec) = 0.05; Sample Width (sec) = 0.0167; Pulse Period (sec) = 0.2; Quiet Time (sec) = 2; Sensitivity (A/V) = 1e-6.

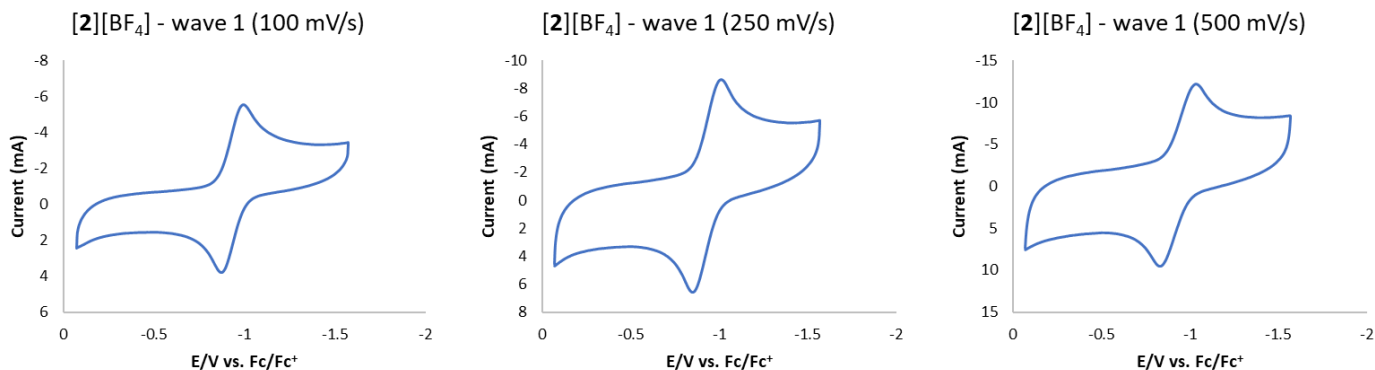


Figure S24. Cyclic voltammogram of the first reduction wave of [2][BF₄].

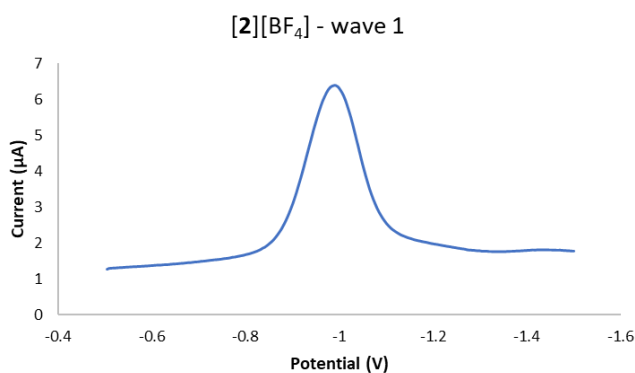


Figure S25. Differential Pulse Voltammetry of the first reduction wave of [2][BF₄].

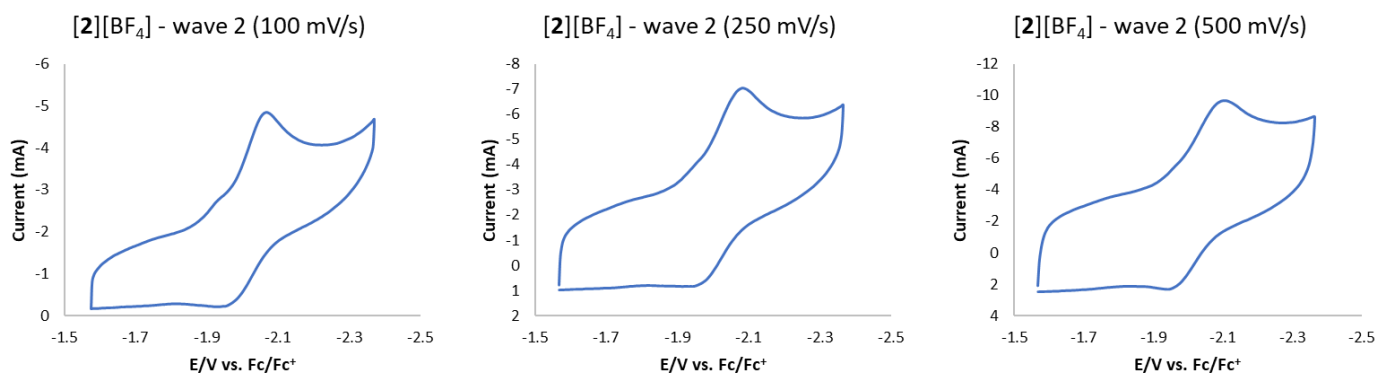


Figure S26. Cyclic voltammogram of the second reduction wave of [2][BF₄].

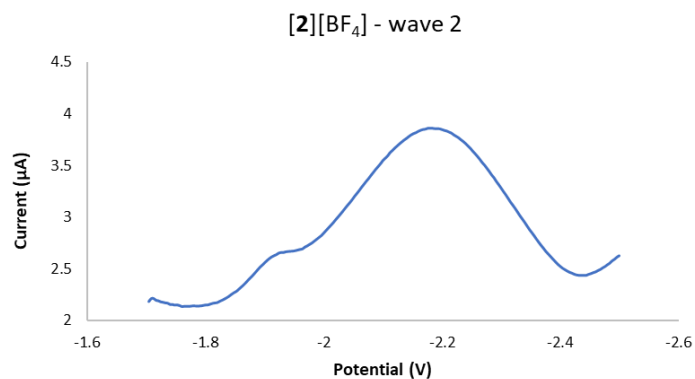


Figure S27. Differential Pulse Voltammetry of the second reduction wave of $[2][BF_4]$. We are not sure that the small shoulder around -2 V can be assigned to conformational switching.

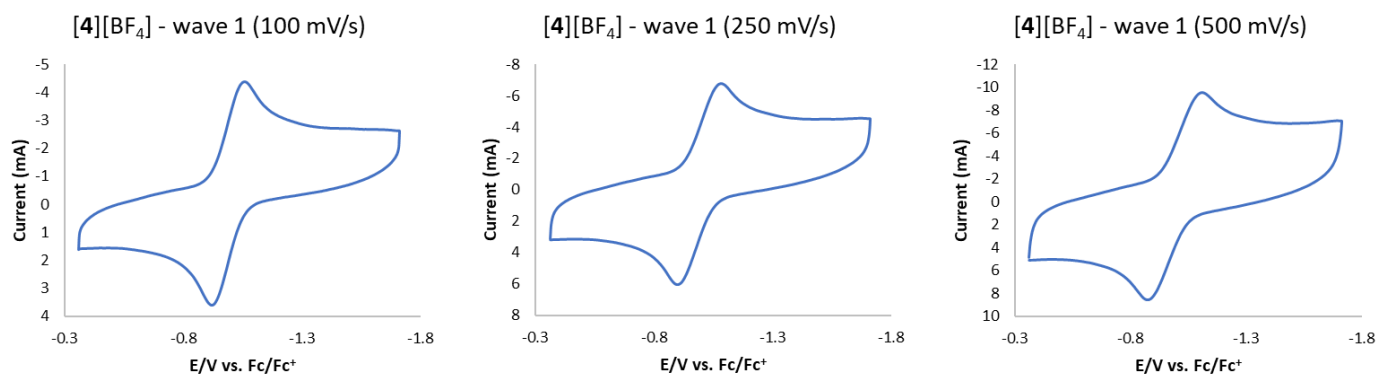


Figure S28. Cyclic voltammogram of the first reduction wave of $[4][BF_4]$.

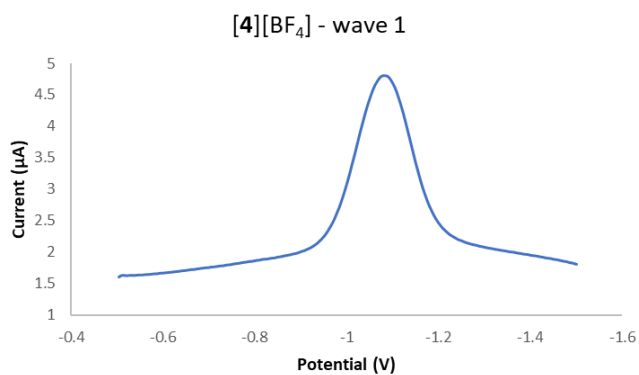


Figure S29. Differential Pulse Voltammetry of the first reduction wave of $[4][BF_4]$.

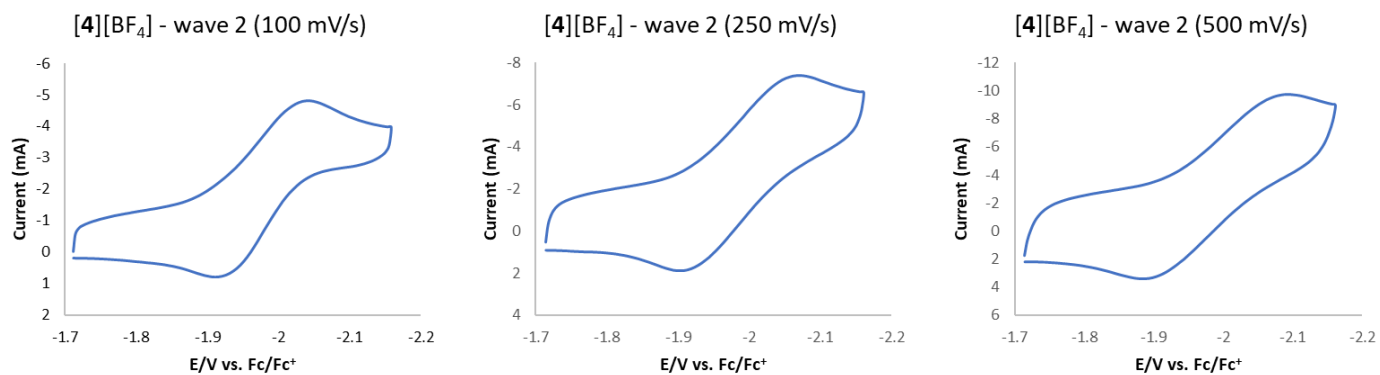


Figure S30. Cyclic voltammogram of the second reduction wave of $[4][BF_4]$.

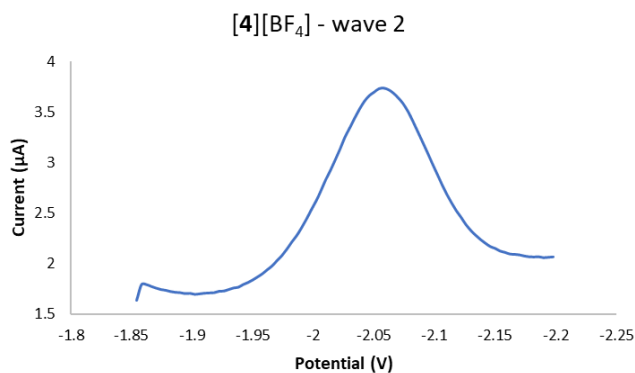


Figure S31. Differential Pulse Voltammetry of the second reduction wave of $[4][BF_4]$.

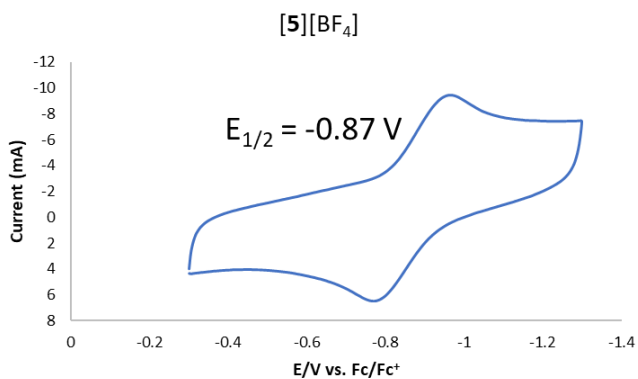


Figure S32. Cyclic voltammogram of the first reduction wave of $[5][BF_4]$ at 500 mV/s.

7 Computational studies

7.1 General methods

The structures of **[2]⁺**, **[4]⁺** and **[5]⁺** were optimized using DFT methods as implemented in Gaussian 09 using the MPW1PW91 functional and a 6-311G(d,p) basis set with SMD solvation (solvent = dichloromethane). ESP maps were generated and visualized in GaussView 6.1.1.² Frequency calculations, performed using the same level of theory on the optimized geometries, found no imaginary frequencies. NBO analysis was performed using the same functional and basis set using the NBO 6.0 program.³ The resulting NBOs were visualized using the Avogadro program.⁴ QTAIM calculations were carried out on the wave functions derived from the optimized structures using the AIMAll program.⁵

7.2 Geometry-optimized structures

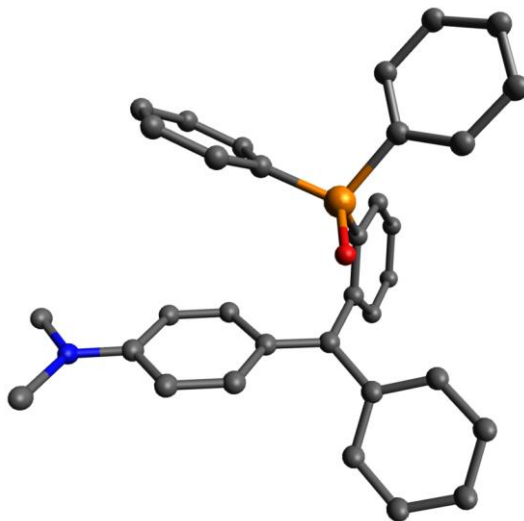


Figure S33. Optimized structure of **[2]⁺**. Hydrogen atoms were omitted for clarity.

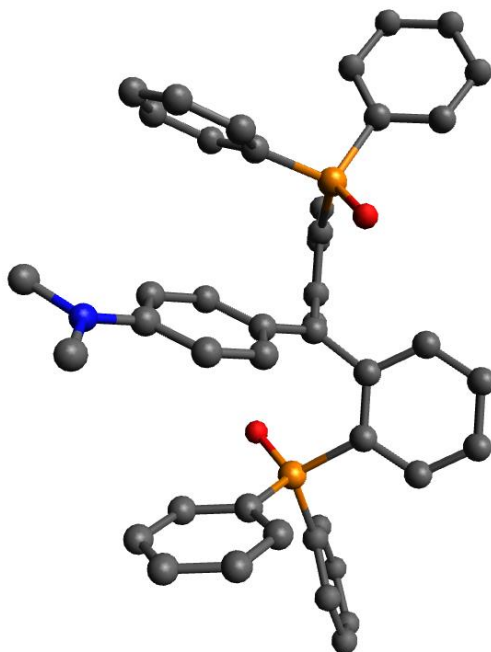


Figure S34. Optimized structure of **[4]⁺**. Hydrogen atoms were omitted for clarity.

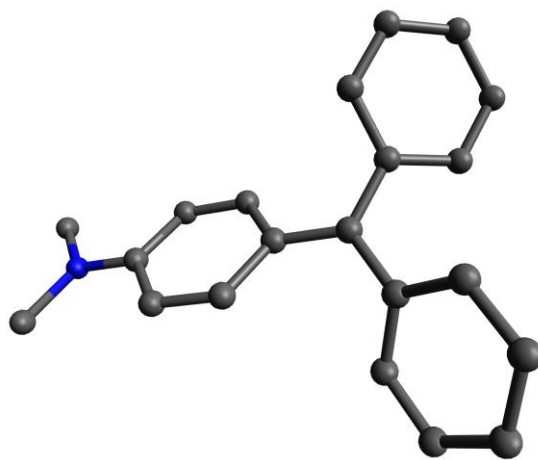


Figure S35. Optimized structure of [5]⁺. Hydrogen atoms were omitted for clarity.

7.3 Electrostatic potential (ESP) maps

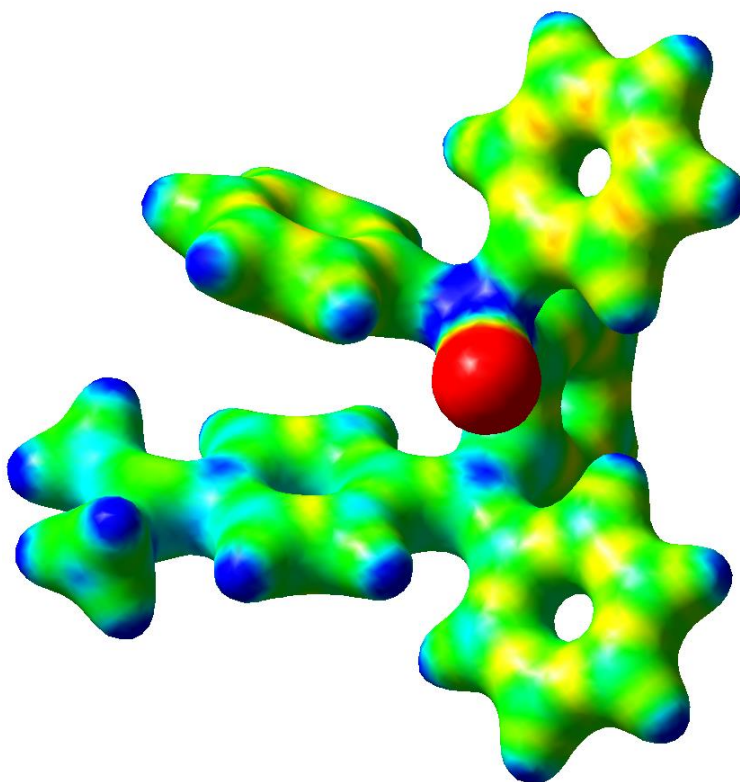


Figure S36. ESP map for compound [2]⁺. ESP maps are computed with an isovalue of 0.06 a.u., between a range of 0.12 to 0.46 a.u.

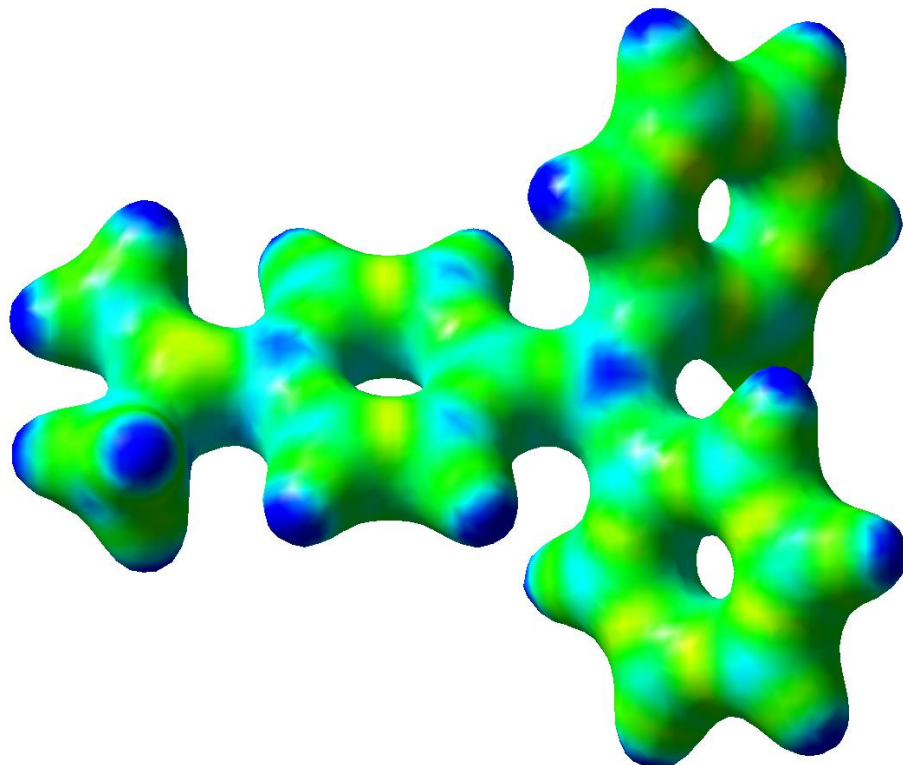


Figure S37. ESP map for compound [5]⁺. ESP maps are computed with an isovalue of 0.06 a.u., between a range of 0.12 to 0.46 a.u.

7.4 Cartesian coordinates of geometry optimized structures

Table S 1. Cartesian coordinates for compound [2]⁺.

Atom Number	Coordinates			Atom Number	Coordinates		
	X	Y	Z		X	Y	Z
P1	1.39353	-0.61789	-0.41176	C34	-6.05715	-1.03608	-1.38353
O2	0.81841	0.28807	-1.47549	C35	1.1407	4.83531	-1.08332
N3	-5.17124	-1.2587	-0.23488	C36	0.03899	5.67461	-1.29207
C4	-1.66185	1.02872	0.25706	H37	-2.19144	1.84526	-1.68767
C5	-0.5007	1.80689	0.43996	H38	0.85218	-2.48323	1.91113
C6	-2.50316	1.17705	-0.89413	H39	-4.20339	0.54105	-1.98042
C7	0.46341	-2.17847	-0.19919	H40	0.05265	3.01504	2.72097
C8	0.38445	-2.87895	1.01422	H41	3.0324	-0.87776	2.04386
C9	-3.63513	0.42564	-1.06689	H42	-0.11296	-2.15334	-2.27798
C10	0.68394	2.14229	2.58376	H43	-6.43723	-2.79976	0.39589
C11	1.3986	0.2588	1.21562	H44	-5.74315	-1.85547	1.72281
C12	0.5492	1.37573	1.41218	H45	-4.74138	-3.03746	0.83876
C13	2.33566	-0.06164	2.208	H46	1.66854	2.37934	4.48151
C14	-0.16369	-2.70124	-1.3417	H47	3.11855	-2.99587	0.27436
C15	3.12519	-1.08628	-0.75095	H48	3.15321	0.40324	4.14571
C16	-5.53744	-2.29296	0.73956	H49	-1.324	-4.31886	-2.1607
C17	1.59523	1.78378	3.577	H50	-0.35329	-4.63382	2.0221
C18	3.70505	-2.28005	-0.29377	H51	3.42614	0.70538	-1.91469
C19	2.42287	0.6763	3.39049	H52	-1.44156	-5.56421	-0.01074
C20	-4.04064	-0.5357	-0.08342	H53	5.48074	-3.49611	-0.23818
C21	-0.84975	-3.9154	-1.27087	H54	5.80179	0.19473	-2.42887
C22	-0.3031	-4.0937	1.08119	H55	6.8324	-1.90415	-1.58521
C23	3.88733	-0.19762	-1.52678	H56	-1.43731	-0.12381	2.08814
C24	-0.9173	-4.61436	-0.06153	H57	-3.455	-1.42553	1.82706
C25	5.03901	-2.56898	-0.59064	H58	1.81486	2.92616	-0.36733
C26	5.21915	-0.49244	-1.82288	H59	-2.09383	5.9129	-1.06084
C27	5.79734	-1.67453	-1.3509	H60	-6.9547	-1.63925	-1.26007
C28	-2.04481	0.02394	1.20242	H61	-5.5721	-1.32644	-2.32238
C29	-3.192	-0.71135	1.05828	H62	-6.35821	0.01391	-1.44717
C30	0.96388	3.5808	-0.51303	H63	2.13566	5.16421	-1.36564
C31	-1.43057	3.9858	-0.38025	H64	0.18242	6.66023	-1.72428
C32	-0.32962	3.12022	-0.17159	H65	-2.42061	3.68356	-0.05677
C33	-1.24357	5.25133	-0.9288				

Table S 2. Cartesian coordinates for compound [4]⁺.

Atom Number	Coordinates			Atom Number	Coordinates		
	X	Y	Z		X	Y	Z
P1	-3.22376	-0.62661	-0.41056	C45	4.49079	2.49133	-2.00672
P2	3.2239	-0.62649	0.41063	C46	4.72715	-2.55968	1.68548
O3	-2.40585	-0.51297	-1.67343	C47	4.64047	3.52024	-1.07348
O4	2.40606	-0.51302	1.67355	C48	7.03795	-2.21441	0.15317
N5	-0.0004	4.91846	-0.00014	C49	5.85387	-3.34158	1.93588
C6	-0.00001	0.7148	0.00002	C50	7.00713	-3.17362	1.16715
C7	0.00006	-0.67966	0.00006	H51	0.9165	0.92996	-1.95824
C8	0.54317	1.46519	-1.09408	H52	-3.92745	0.44176	2.32844
C9	-3.7604	0.99581	0.24202	H53	0.91738	3.35146	-1.97233
C10	-4.05143	1.23244	1.59399	H54	0.91043	-2.20319	1.92773
C11	0.53411	2.83045	-1.10574	H55	-4.03308	-2.30543	1.83468
C12	-0.17197	-2.24426	1.90186	H56	-3.66445	1.85039	-1.73139
C13	-2.26832	-1.46948	0.92716	H57	-0.71302	6.721	0.78363
C14	-0.84693	-1.46388	0.94594	H58	-0.12261	5.5914	2.01501
C15	-2.95044	-2.24823	1.87238	H59	-1.68931	5.31051	1.21174
C16	-3.90584	2.03436	-0.68913	H60	-0.33031	-3.55286	3.59612
C17	-4.74587	-1.60461	-0.65791	H61	-5.9587	-0.66631	0.87184
C18	-0.66723	5.67084	1.06734	H62	-2.82365	-3.57279	3.56358
C19	-0.87521	-2.97951	2.85285	H63	-4.46658	4.0887	-0.99967
C20	-5.91421	-1.42743	0.09897	H64	-4.72093	2.66636	3.05361
C21	-2.26772	-2.98471	2.84021	H65	-3.83677	-2.66832	-2.29677
C22	-0.00024	3.56992	-0.0001	H66	-4.99692	4.49459	1.39461
C23	-4.34516	3.29117	-0.2726	H67	-7.93943	-2.07163	0.43382
C24	-4.49113	2.49091	2.00692	H68	-5.83358	-4.07669	-2.73499
C25	-4.72673	-2.55992	-1.68557	H69	-7.88416	-3.78207	-1.36517
C26	-4.64074	3.51991	1.07377	H70	-0.91655	0.92999	1.95826
C27	-7.03769	-2.21487	-0.15346	H71	3.92714	0.44219	-2.32837
C28	-5.85336	-3.34192	-1.93608	H72	-0.91786	3.3515	1.97212
C29	-7.00669	-3.17406	-1.16745	H73	-0.91028	-2.20321	-1.9276
C30	-0.54329	1.46521	1.09407	H74	4.03323	-2.30518	-1.83471
C31	3.76035	0.99602	-0.24187	H75	3.66459	1.85041	1.73163
C32	4.05119	1.2328	-1.59386	H76	0.71173	6.72118	-0.78392
C33	-0.53445	2.83047	1.10561	H77	0.12159	5.59145	-2.0153
C34	0.17212	-2.24423	-1.90175	H78	1.68839	5.31096	-1.21207
C35	2.26845	-1.46936	-0.9271	H79	0.33047	-3.55276	-3.59606
C36	0.84706	-1.46384	-0.94583	H80	5.95874	-0.66594	-0.87202
C37	2.95058	-2.24803	-1.87237	H81	2.82381	-3.57254	-3.56361
C38	3.90584	2.0345	0.68935	H82	4.46653	4.08883	1.00003
C39	4.74612	-1.60436	0.65782	H83	4.72044	2.66689	-3.05342
C40	0.66621	5.67102	-1.06764	H84	3.83726	-2.66816	2.29676
C41	0.87537	-2.97941	-2.85279	H85	4.99657	4.49497	-1.39428
C42	5.91438	-1.42707	-0.09915	H86	7.93963	-2.07109	-0.43419
C43	2.26787	-2.98452	-2.8402	H87	5.83423	-4.07636	2.73479
C44	4.34506	3.29136	0.27289	H88	7.88466	-3.78156	1.36478

Table S 3. Cartesian coordinates for compound [5]⁺.

Atom Number	Coordinates			Atom Number	Coordinates		
	X	Y	Z		X	Y	Z
N1	-4.69231	0.00002	-0.00003	H23	-0.11995	0.00116	0.00162
C2	-0.46846	0.00004	0.00008	H24	-0.72265	1.93824	-0.85441
C3	0.95005	0.00003	0.00009	H25	-3.09958	1.92149	-0.90878
C4	-1.226	1.11079	-0.49805	H26	3.23422	-0.58593	1.30364
C5	-2.59669	1.1101	-0.51666	H27	0.40954	-2.28505	-1.34405
C6	2.8912	-1.38619	0.7496	H28	1.69419	-4.33391	-1.38537
C7	1.27342	-2.35939	-0.78441	H29	-4.76025	-1.93209	0.78118
C8	1.70258	-1.25719	-0.00748	H30	-6.05996	-1.54127	-0.31931
C9	2.00588	-3.54276	-0.8006	H31	-6.06009	-0.88629	1.30059
C10	-5.44413	-1.16919	0.47266	H32	4.45156	-2.67518	1.331
C11	3.60135	-2.58262	0.75342	H33	3.69777	-4.54452	-0.02646
C12	3.16454	-3.66095	-0.0248	H34	-0.72265	-1.93814	0.85463
C13	-3.34289	0	0.00001	H35	-3.09958	-1.9214	0.909
C14	-1.226	-1.11071	0.49823	H36	3.23413	0.58578	-1.30363
C15	-2.59669	-1.11003	0.51681	H37	0.40977	2.28513	1.34428
C16	2.8912	1.38608	-0.74959	H38	1.69445	4.33399	1.38522
C17	1.27359	2.35941	0.78452	H39	-6.4932	0.97442	-0.3941
C18	1.70265	1.25714	0.00762	H40	-5.19335	1.36518	-1.49444
C19	2.00608	3.54278	0.8005	H41	-5.19339	2.02021	0.12543
C20	-5.44404	1.16924	-0.47285	H42	4.45158	2.67494	-1.33118
C21	3.60139	2.58247	-0.75356	H43	3.69787	4.54447	0.02612
C22	3.16464	3.6609	0.0246				

8 X-ray diffraction analysis

8.1 Experimental details

The crystallographic measurements were performed at 110(2) K using a three circle (Quest; Mo K α radiation, λ = 0.71073 Å) and kappa (Venture; Cu K α radiation, λ = 1.54178 Å) Bruker-AXS with I μ S source and a Photon III area detector diffractometer. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop and cooled to 110(2) K in a cold nitrogen stream (OXFORD Cryosystems). The structure data was collected and reduced using Bruker AXS APEX 3 software⁶ and solved by direct methods. Semiempirical absorption corrections were applied using SADABS.⁷ Subsequent refinement using a difference map on F² using the SHELXTL/PC package (version 6.1 & OLEX²).^{8, 9} Thermal parameters were refined anisotropically for all non-hydrogen atoms to convergence. H atoms were added at idealized positions using a riding model. The results of these X-ray measurements are provided as CIF files. CCDC 2296317-2296321 contain the supplementary crystallographic data for this paper. Crystal structure of **1** has been previously published¹ and structures [**2**][BF₄] and [**4**][BF₄] are presented in the text.

8.2 Table showing the compounds characterized by X-ray diffraction and their corresponding CCDC numbers.

Compound	CCDC
[2][BF ₄]	2296317
[2]OH	2296318
3	2296319
[4][BF ₄]	2296320
[4]OH	2296321

8.3 Solid-state structures

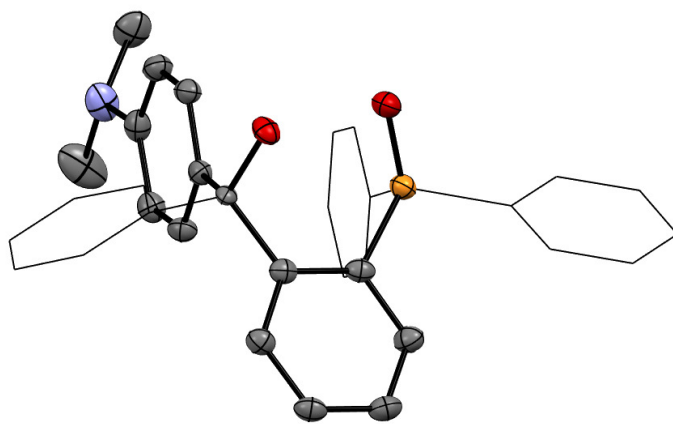


Figure S38. Solid-state structure of [2]OH. Hydrogens atoms were omitted for clarity.

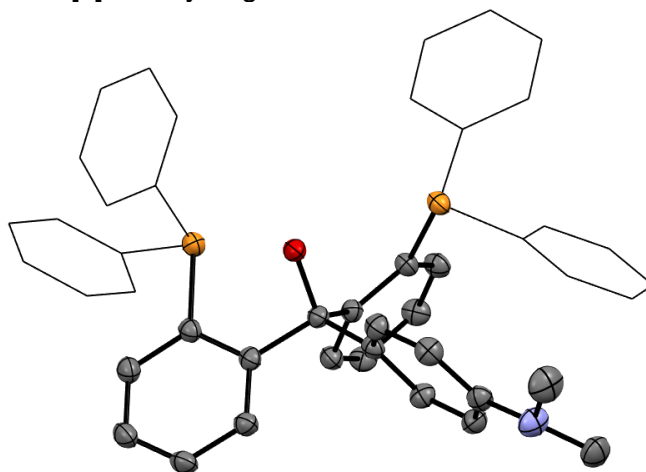


Figure S39. Solid-state structure of **3**. Hydrogens atoms and solvent were omitted for clarity.

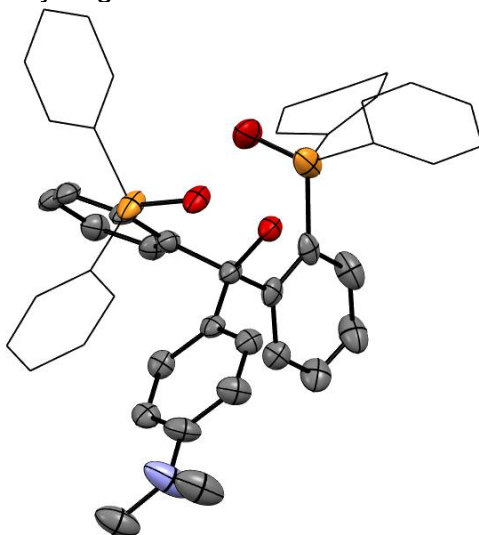


Figure S40. Solid-state structure of [4]OH. Hydrogens atoms and solvent were omitted for clarity.

8.4 X-ray refinement parameters

Compound	[2][BF ₄]	[2]OH	3
Empirical formula	C ₄₅ H ₃₈ NO ₂ P ₂ ·BF ₄	C ₄₅ H ₃₉ NOP ₂ ·2.5(C ₆ H ₆)·CH ₂ Cl ₂	C ₄₅ H ₃₉ NO ₃ P ₂ ·0.5(H ₂ O)
Formula weight	773.51	951.90	712.72
Temperature/K	110.0	110.01	109.99
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/m	P-1	P-1
a/Å	12.224(2)	13.849(3)	12.0136(17)
b/Å	25.959(5)	13.924(3)	12.8997(18)
c/Å	12.870(2)	14.623(3)	13.4490(19)
α/°	90	115.720(5)	71.834(3)
β/°	91.755(5)	90.378(5)	71.445(3)
γ/°	90	96.195(5)	67.410(3)
Volume/Å ³	4082.1(13)	2520.9(9)	1781.0(4)
Z	4	2	2
ρ _{calc} /cm ³	1.259	1.254	1.329
μ/mm ⁻¹	1.435	0.235	0.168
F(000)	1608.0	1002.0	750.0
Crystal size/mm ³	0.21 × 0.177 × 0.082	0.275 × 0.24 × 0.15	0.169 × 0.149 × 0.053
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	7.998 to 136.482	4.638 to 61.316	4.244 to 54.97
Index ranges	-14 ≤ h ≤ 14, -31 ≤ k ≤ 29, -15 ≤ l ≤ 15	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	26069	57558	40080
Independent reflections	3817 [R _{int} = 0.0535, R _{sigma} = 0.0348]	15420 [R _{int} = 0.0632, R _{sigma} = 0.0629]	8168 [R _{int} = 0.1538, R _{sigma} = 0.1395]
Data/restraints/parameters	3817/0/256	15420/0/607	8168/36/526
Goodness-of-fit on F ²	1.112	1.023	1.180
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0453, wR ₂ = 0.1249	R ₁ = 0.0562, wR ₂ = 0.1206	R ₁ = 0.1369, wR ₂ = 0.2074
Final R indexes [all data]	R ₁ = 0.0485, wR ₂ = 0.1288	R ₁ = 0.0946, wR ₂ = 0.1465	R ₁ = 0.2190, wR ₂ = 0.2382
Largest diff. peak/hole / e Å ⁻³	0.54/-0.48	0.70/-0.90	0.38/-0.34
CCDC identifier	2296317	2296318	2296319

Compound	[4][BF ₄]	[4]OH
Empirical formula	2(C ₃₃ H ₂₉ NOP)·2(BF ₄)·C ₄ H ₁₀ O	C ₃₃ H ₃₀ NO ₂ P
Formula weight	1220.82	503.55
Temperature/K	110.0	293(2)
Crystal system	monoclinic	monoclinic
Space group	Pc	P2 ₁ /c
a/Å	8.3585(6)	15.3105(10)
b/Å	14.7884(10)	10.7158(8)
c/Å	25.0191(17)	15.7073(11)
α/°	90	90
β/°	90.077(4)	92.104(2)
γ/°	90	90
Volume/Å ³	3092.6(4)	2575.3(3)
Z	2	4
ρ _{calc} /cm ³	1.311	1.299
μ/mm ⁻¹	1.256	0.139
F(000)	1276.0	1064.0
Crystal size/mm ³	0.257 × 0.027 × 0.02	0.326 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.976 to 136.522	4.602 to 54.972
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -30 ≤ l ≤ 29	-19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	52504	40373
Independent reflections	10607 [R _{int} = 0.1138, R _{sigma} = 0.0885]	5895 [R _{int} = 0.0426, R _{sigma} = 0.0256]
Data/restraints/parameters	10607/2/790	5895/0/337
Goodness-of-fit on F ²	1.028	1.121
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0579, wR ₂ = 0.1402	R ₁ = 0.0544, wR ₂ = 0.1326
Final R indexes [all data]	R ₁ = 0.0681, wR ₂ = 0.1481	R ₁ = 0.0631, wR ₂ = 0.1371
Largest diff. peak/hole / e Å ⁻³	0.36/-0.48	0.56/-0.54
CCDC identifier	2296320	2296321

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