Chemical Communications

Supporting Information

Isolable Cyclic (Alkyl)(amino)carbene−Phosphonyl Radical Adducts

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1. General considerations

All preparations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glovebox techniques (Vac.-Atmospheres Nexus II equipped with a −35 °C freezer). Toluene, dichloromethane and hexane were dried using a Vac. Atm. Solvent purification system. DFB and $CDCl_3$ were dried over CaH_2 for several days prior to distillation. All solvents were degassed by freeze−pump−thaw and stored on activated 4 Å molecular sieves prior to use. All glassware was oven dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise.

2. Spectroscopic Analyses

NMR spectra were recorded at room temperature using a Bruker AvanceIII-400 MHz spectrometer and referenced to residual solvent or externally (^{11}B: $BF_3{\cdot}Et_2O$; ^{19}F: $CFCl_3$; ^{31}P: 85% H_3PO_4) in some of the cases the tubes were equipped with DMSO-d_6 capillary as external standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constant (Hz). The EPR spectra were recorded on a Bruker EMX-10/12 X-band (ν = 9.3 GHz) digital EPR spectrometer equipped with a Bruker N_2-temperature controller. The spectra were recorded at a microwave power of 0.1–1.0 mW, 100 kHz magnetic field modulation of 0.05–1.0 G amplitude (unless otherwise specified). Digital field resolution was 2048 points per spectrum. This allowed all hyperfine splittings to be measured directly with accuracy better than 0.1 G. Spectra processing and simulation were performed with the Bruker WIN-EPR and SimFonia Software. When the reactions were carried out under UV irradiation, a high-pressure mercury lamp (100W) (ARC lamp power supply model 69920) was used ($\lambda \approx 280$ nm), with the output being focused onto the sample with a quartz lens.

3. X-ray Crystallography

Data were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.710 73 Å). The crystals were mounted on a cryoloop with Paratone oil, and all data were collected at 100(2) K. Crystal structures were solved by direct methods and refined by full matrix least squares. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXT-2014 and SHELXL-2014.

4. Experimental Details

4.1 Synthesis of [cAAC−P(O)(OPr^i)$_2$]$^\bullet$ (3)

[(^{i}PrO)$_2$(O)P]$_2$Hg (**1**) (0.52 g, 0.99 mmol), was added to a solution of cAAC (**2**) (0.28 g, 0.99 mmol) in benzene. After about 10 minutes, mercury salts precipitated and EPR spectra of **3** was recorded (Figure S1). **3** was crystallized from hexane at –35 °C in 68% yield. The color of **3** is bright yellow. Noteworthy, **3** remained unchanged after a month in hexane solution.

4.2 Synthesis of cAAC−P(O)$_2$(OPr^i) (4).

UV irradiation with light filter, which cuts of wavelengths below (λ = 320 nm), of **3** for 20 minutes led to formation of zwitterion **4**, which was crystallized from hexane/CH_2Cl_2 solution in 87% yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.40 (1H, t, J=7.7 Hz, *p*-H of Dipp), 7.26 (2H, d, J=7.7 Hz, *m*-H of Dipp), 4.56 (1H, sep, J=6.1 Hz, O-C*H*$(CH_3)_2$), 2.70 (2H, sep, J=6.5 Hz, C*H*$(CH_3)_2$ of Dipp), 2.22 (2H, s, 2*H* of cAAC), 1.83 (6H, s, C*H*$_3$ of cAAC), 1.43 (6H, s, C*H*$_3$ of cAAC), 1.39 (6H, d, J=6.5 Hz, CH(C*H*$_3$)$_2$), 1.32 (6H, d, J=6.7 Hz, CH(C*H*$_3$)$_2$), 1.09 (6H, d, J=6.2 Hz, CH(C*H*$_3$)$_2$) ppm; ^{13}C NMR (100 MHz; $CDCl_3$): δ = 205.47 (cAAC *C*-P), 144.88 (*o*-Dipp), 132.26 (*i*-Dipp), 130.41 (*p*-Dipp), 125.34 (*m*-Dipp), 81.84 (O-*C*H(CH_3), 68.69 (C,N-*C*-$(CH_3)_2$), 52.67 (*C*H$(CH_3)_2$), 51.22 (*C*H$_2$ of cAAC), 30.32 (O-CH(*C*H$_3)_2$), 29.97 (*C*H$_3$ of

cAAC), 29.18 (CH_3 of cAAC), 26.49 (CH(CH_3)$_2$), 24.79 (C(CH_3)$_2$), 24.24 (CH(CH_3)$_2$) ppm; ^{31}P NMR (162 MHz; $CDCl_3$): δ = -8.35 ppm. MS (ESI) calc'd for $C_{23}H_{38}NO_3P$ ($M+Na^+$) 430.2484, found 430.2485.

4.3 Syntehsis of [cAAC−P(O)(Ph)$_2$][B(C_6F_5)$_4$] (6)

Excess of (^{t}BuO)$_2$ (0.5 g, 3.41 mmol) was added to a solution of **5** (0.30 g, 0.26 mmol) in *o*-difluorobenzene under ambient conditions. The reaction mixture was exposed to sun light for three days. The pale yellow solid precipitated from the reaction mixture and separated by decanting the solution. The solid was washed with small amount of *o*-difluorobenzene, and dried under vacuum. Product **6** was crystallized from hexane/CH_2Cl_2 solution (1:2). ^{1}H NMR (400 MHz; *o*-difluorobenzene, DMSO-d$_6$ capillary): δ = 6.82-7.06 (m, proper integration could not be obtained due to large *o*-difluorobenzene peak, P*Ph*$_2$, *p*-Dipp, *m*-Dipp), 2.00 (2H, sep, J=6.47 Hz, C*H*(CH_3)$_2$), 1.76 (2H, s, C*H*$_2$ of cAAC), 0.83 (6H, s, C*H*$_3$), 0.69 (6H, d, J-6.47 Hz, CH(C*H*$_3$)$_2$), 0.66 (6H, s, C*H*$_3$), 0.43 (6H, d, J=6.75 Hz, CH(C*H*$_3$)$_2$) ppm; ^{11}B NMR (*o*-difluorobenzene, DMSO-d$_6$ capillary): δ = -16.79 ppm; ^{13}C NMR (100 MHz; *o*-difluorobenzene, DMSO-d$_6$ capillary): δ = 204.03 (*C*-P), 151.47 (*o*-Dipp), 151.07 (*i*-Dipp), 144.42 (P*Ph*$_2$), 135.47 (*p*-Dipp), 133.47 (P*Ph*$_2$), 133.36 (P*Ph*$_2$), 131.85 (*m*-Dipp), 130.04 (P*Ph*$_2$), 129.91, 126.13 (P*Ph*$_2$), 87.99 (N-*C*(CH_3), 55.12 (*C*(CH_3)$_2$), 50.87 (*C*H$_2$ of cAAC), 30.79 (*C*H(CH_3)$_2$), 29.46 (*C*H$_3$), 29.09 (*C*H$_3$), 26.35 (CH(*C*H$_3$)$_2$, 23.73 (CH(*C*H$_3$)$_2$) ppm. The signal-to-noise ratio was too low for properly identifying any C_6F_5 ^{13}C resonance; ^{19}F NMR (376 MHz; *o*-difluorobenzene, DMSO-d$_6$ capillary): δ = -133.07 (*o*-(C_6F_5)), -164.47 (*p*-(C_6F_5)), -168.22 (*m*-(C_6F_5)); ^{31}P NMR (162 MHZ; *o*-difluorobenzene, DMSO-d$_6$ capillary): δ = 22.49 ppm. MS (ESI) calc'd for $C_{32}H_{41}NOP$ (M+) 486.292, found 486.292.

4.4 Synthesis of [cAAC−P(O)(Ph)$_2$]$^\bullet$ (7)

6 (0.035 g, 0.03 mmol) was reduced by addition of Cp^*_2Co(II) (0.01 g, 0.03 mmol) in *o*-difluorobenzene. After 1 h *o*-difluorobenzene was evaporated and the **7** was extracted by hexane. The hexane was then evaporated and replaced by benzene. **7** was isolated by crystallization from benzene solution by slow evaporation in 53% yield. The color of **7** dark orange. EPR spectrum of **7** was recorded both in benzene and in solid state in capillary covered in paraton oil (Figure S13).

5. Spectra of compounds

5.1 Spectra for 3

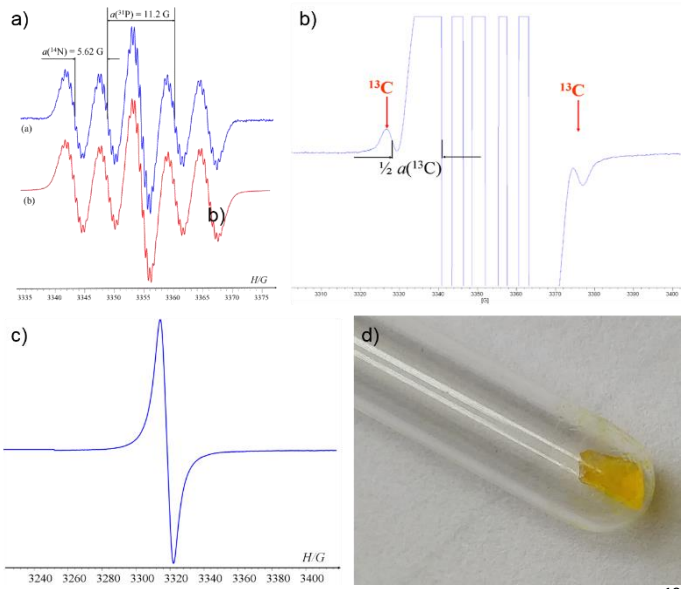

Figure S1. a) EPR spectra of **3** (blue) and its simulation (red); b) Spectra EPR of compound **3** with ^{13}C satellite lines at high gain; c) EPR spectra of the crystal of **3**; Picture of the crystal of **3** inside NMR tube.

#	Sample ID	Comments
2	radical (1)	402.80 nm, 0.846 Abs

#	Sample ID	Comments
5	radical (2)	299.17 nm, 0.808 Abs

#	Sample ID	Comments
7	radical (3)	299.13 nm, 0.494 Abs

#	Sample ID	Comments
8	radical (4)	298.37 nm, 0.283 Abs

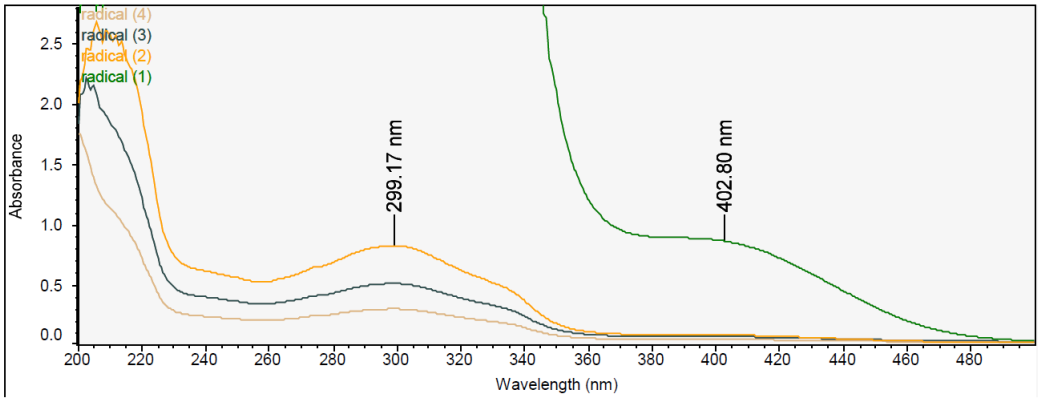

Figure S2. UV-vis spectra of **3**

5.2 Spectra for 4

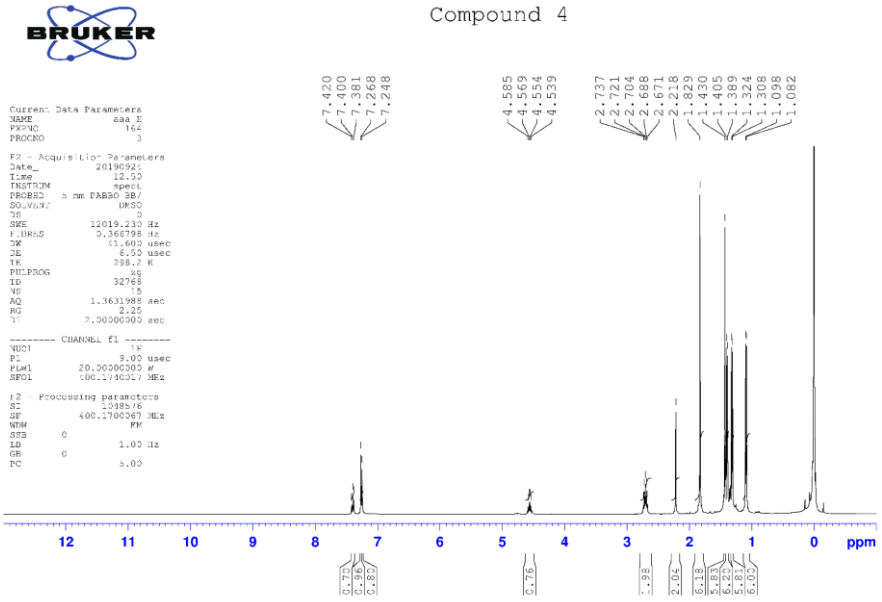

Figure S3. ^{1}H NMR of compound **4**, $CDCl_3$

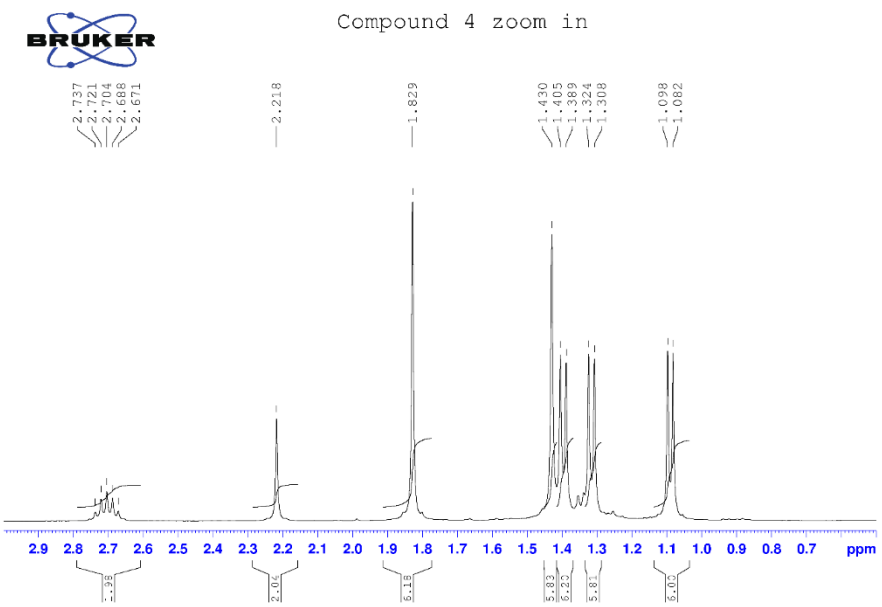

Figure S4. ^{1}H NMR of compound **4**, zoom in, $CDCl_3$

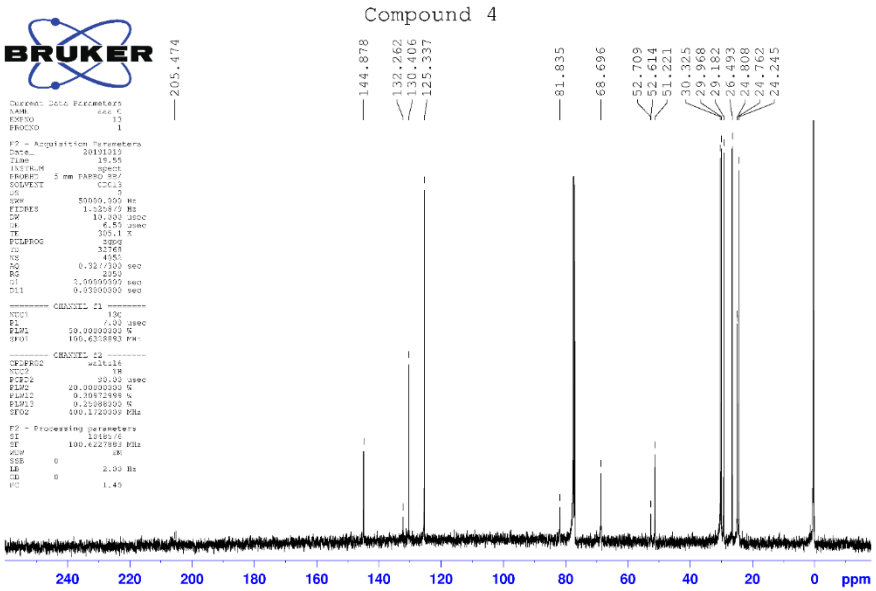

Figure S5. ^{13}C NMR of compound **4**, $CDCl_3$

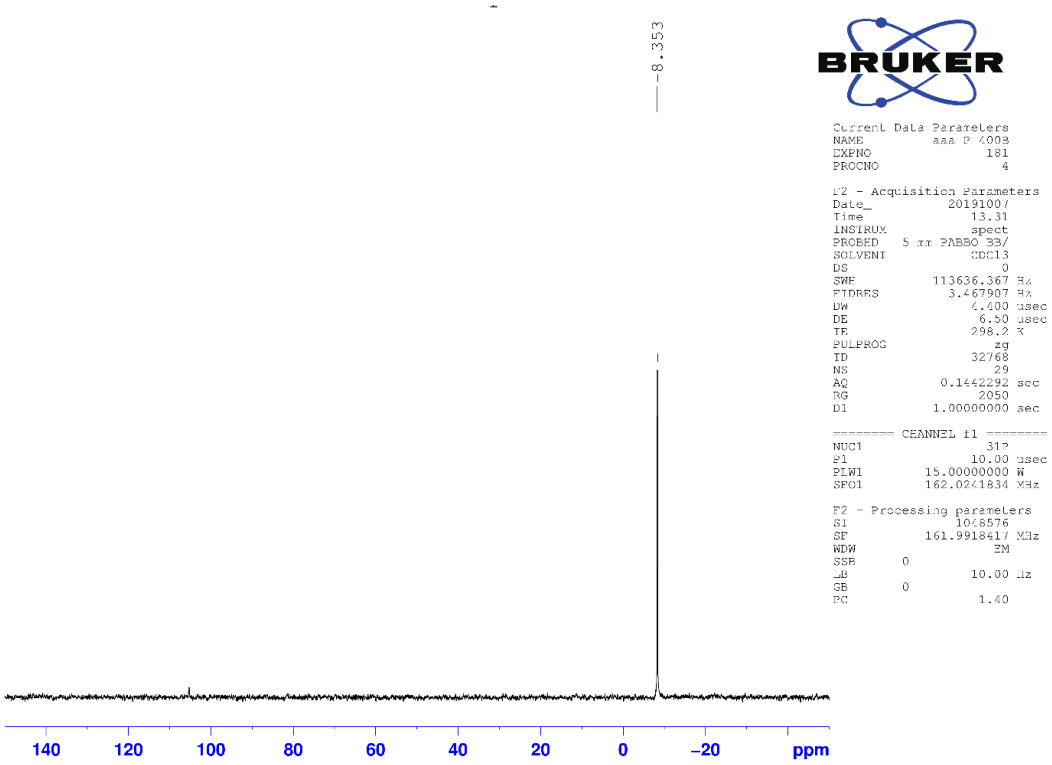

Figure S6. ^{31}P NMR of compound **4**, $CDCl_3$

5.3 Mass Spectra of cAAC-Pr^{i} cation and trap experiment with C_{60}

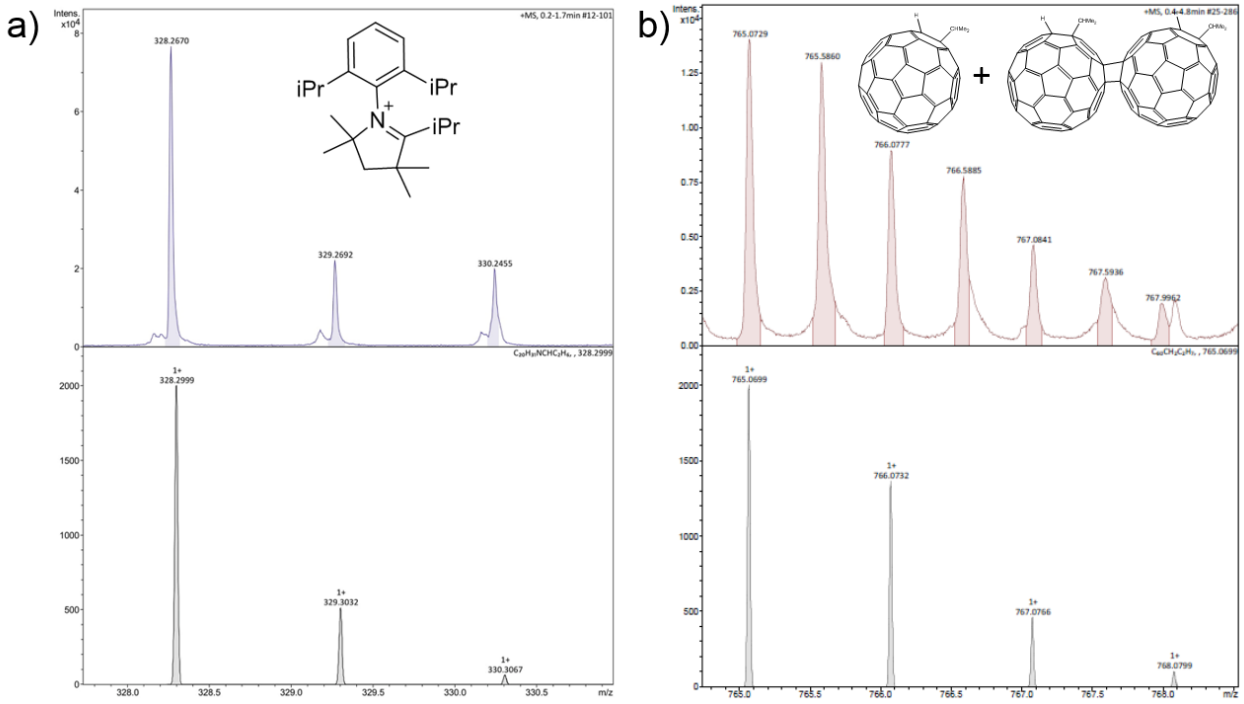

Figure S7. a) APCI mass spectrum (in the positive mode) of [cAAC-Pr^{i}]$^{+}$, at the bottom simulation; b) APCI mass spectrum (in the positive mode) of trap with C_{60}, superposition of two species $[C_{63}H_9]^{+}$ and its dimer $[C_{126}H_{17}]^{2+}$, at the bottom simulation of $[C_{63}H_9]^{+}$.

5.4 EPR spectra of the decay of compound 3 under UV-irradiation

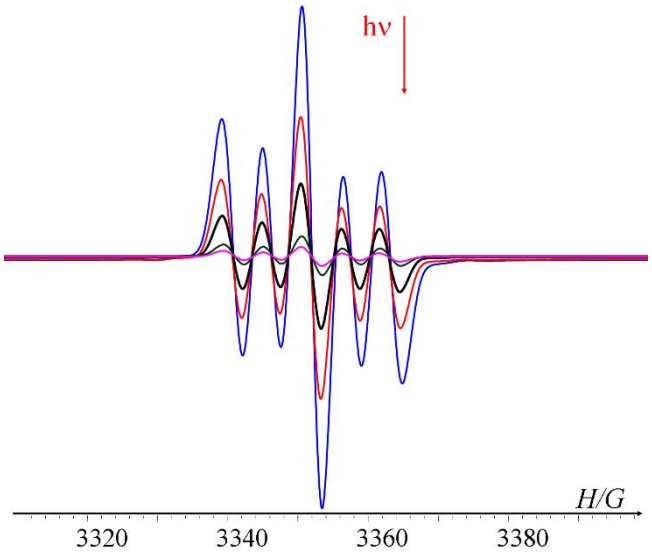

Figure S8. EPR spectra of compound **3** decay under UV-irradiation recorded at intervals of 100 sec.

5.5 Spectra for 6

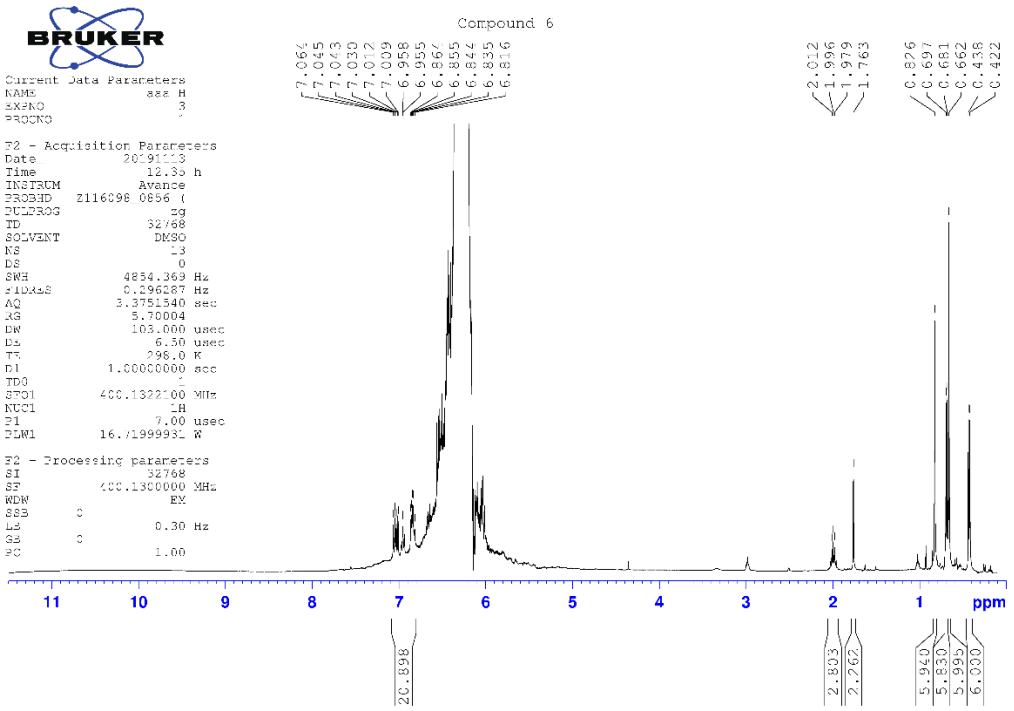

Figure S9. ^{1}H NMR of compound **6**, *o*-difluorobenzene, d_6-DMSO capillary

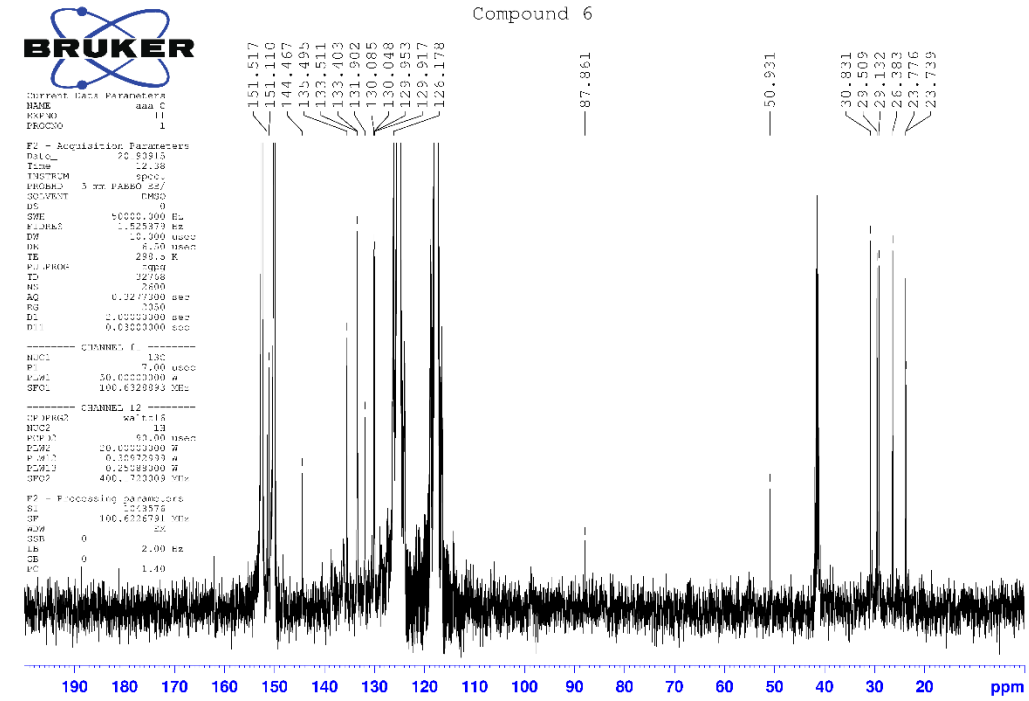

Figure S10. ^{13}C NMR of compound **6**, *o*-difluorobenzene, d_6-DMSO capillary

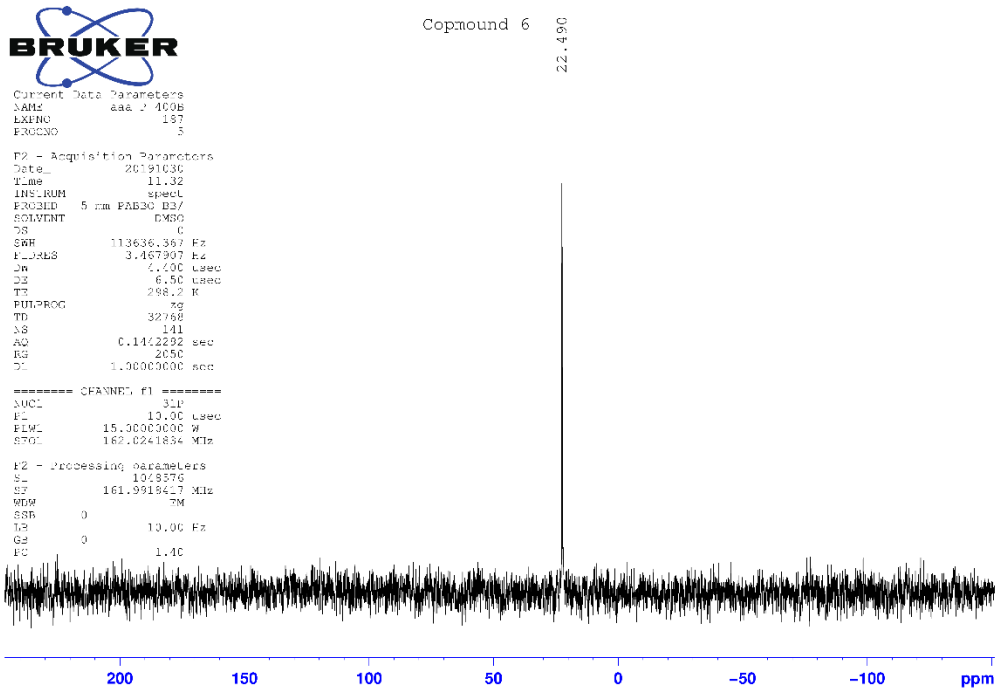

Figure S11. ^{31}P NMR of compound **6**, *o*-difluorobenzene, d_6-DMSO capillary

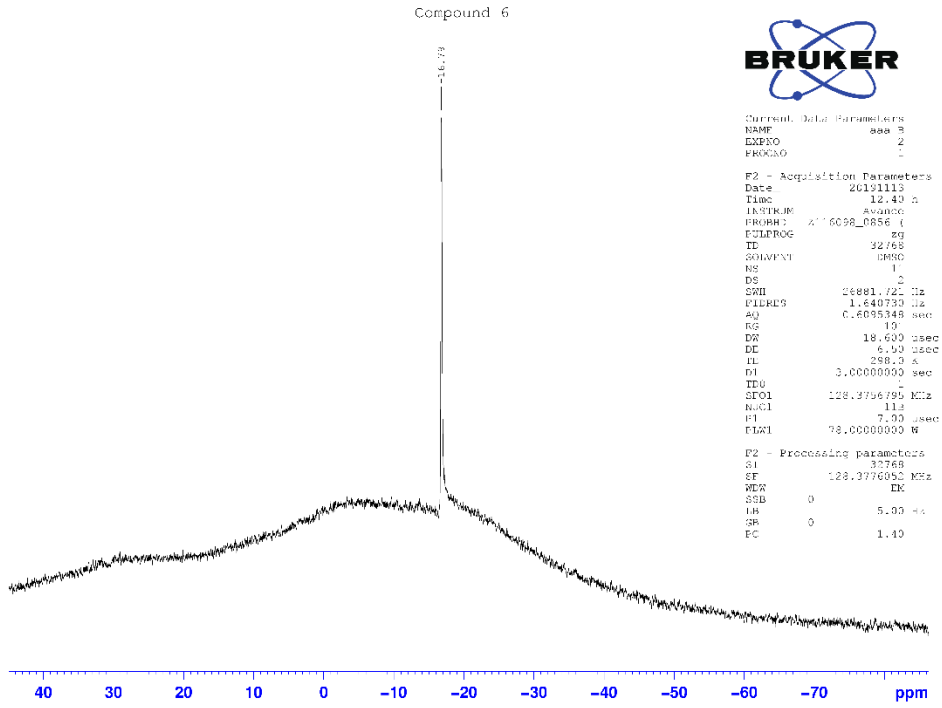

Figure S12. ^{11}B NMR of compound **6**, *o*-difluorobenzene, d_6-DMSO capillary

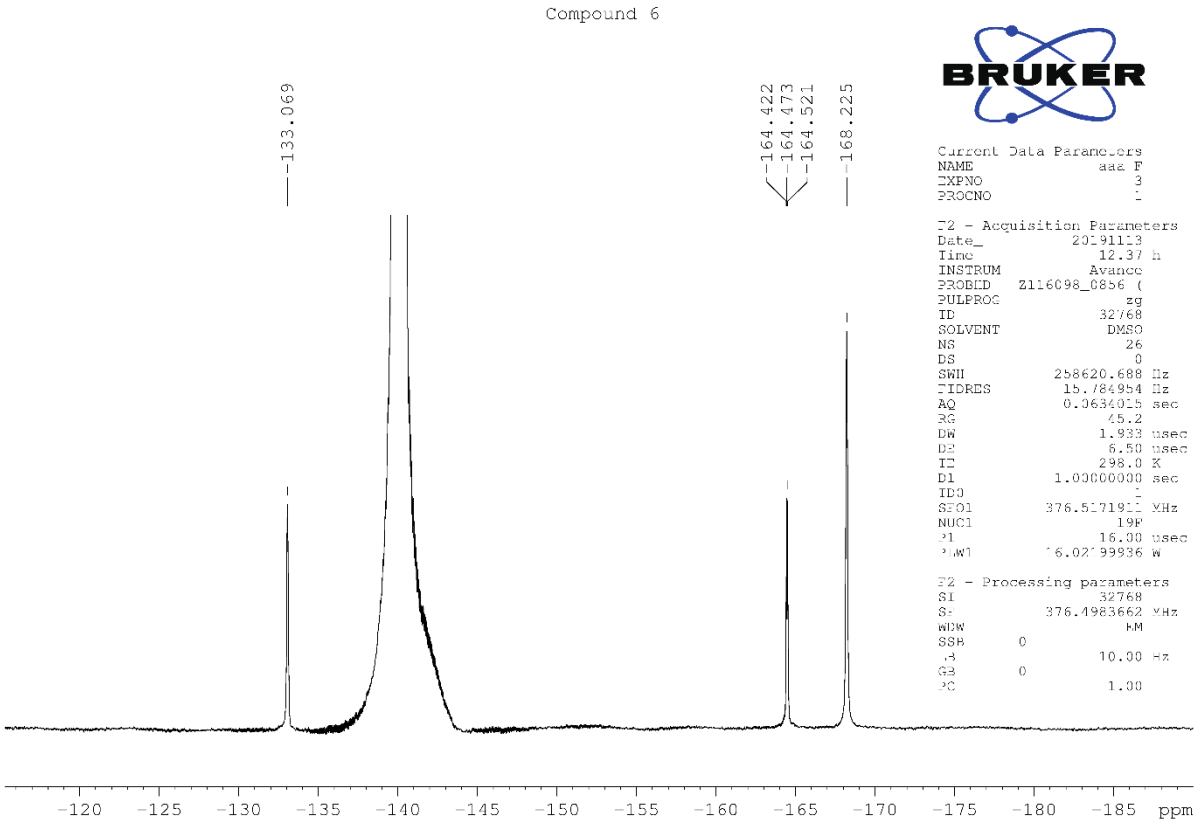

Figure S13. ^{19}F NMR of compound **6**, *o*-difluorobenzene, d_6-DMSO capillary

5.6 Spectra of 7

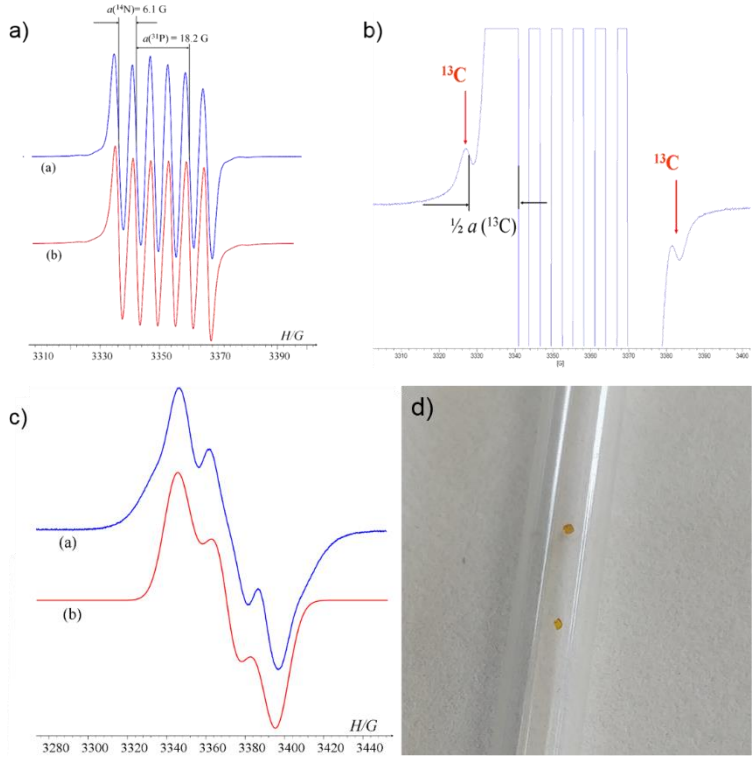

Figure S14. a) EPR spectra of **7** (blue) and its simulation (red); b) Spectra EPR of compound **7** with ^{13}C satellite lines at high gain. c) EPR spectra of the crystal of **7** (blue) and its simulation (red) ($a(^{31}P)$ = 23.0 G; $a(^{14}N)$ = 9.5 G); d) Picture of the crystal of **7** inside NMR tube.

Thermo Scientific

#	Sample ID	User Name	Date and Time	Comments
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Peaks:

nm	Abs
218.230	1.402
210.884	1.087
207.985	1.086
205.204	0.907
201.990	0.780
280.637	0.645
355.917	0.337

#	Sample ID	User Name	Date and Time	Comments
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Peaks:

nm	Abs
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305.784	1.147
355.977	0.684

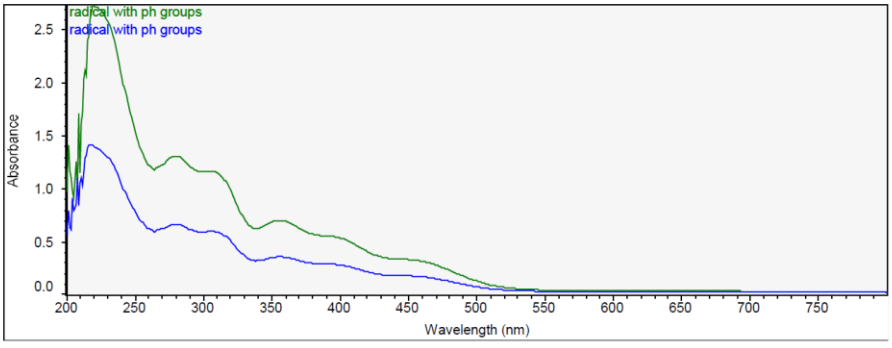
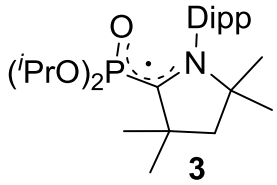


Figure S15. UV-vis spectra of **7**

6. DFT calculations

DFT calculations were performed using Gaussian 09.2.1 Geometry optimization of all the molecules were carried out using the UB3LYP-D3/def2-TZVP basis sets2 implemented in the Gaussian 09 software. Frequency analysis at the same level of theory of all the molecules contained no imaginary frequency showing that these are energy minima.



3

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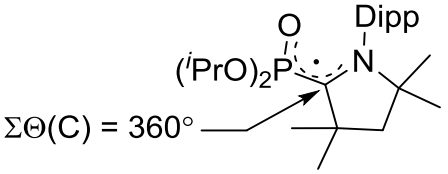
Sum of electronic and thermal Free Energies= -1639.748972



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H	-0.92905700	0.17394400	-2.74743500
C	-4.25032800	0.73346700	-1.89715800
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H	-0.98504400	2.96208500	3.27326000
C	0.02517300	3.18715200	-1.76570500
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H	-0.09104100	4.27296900	-1.83330300
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C	-0.84409300	-1.50004100	3.82866000
H	0.26960300	-0.44432300	2.32923200
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H	1.61749000	-2.37999500	2.99805700
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O	2.54386600	0.22028900	0.48524700
O	1.05830900	-1.23502600	-0.88620000
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H	-0.03612400	-3.65884700	-2.90486300
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H	2.82903500	-3.06348800	-1.69243900
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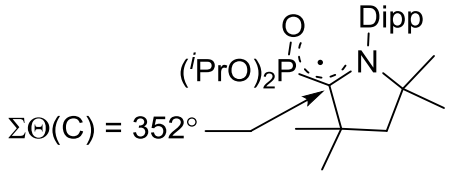

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H	-4.89569000	0.83831600	-0.27012800
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H	-0.31436800	3.28597300	2.89622600
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H	-1.49685300	-3.28152400	2.41261500
C	-0.25056000	-1.08550800	3.95566100
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H	0.79124100	-3.26386300	2.58326100
H	2.07754600	-2.09439500	2.87400900
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C	2.05081400	-2.59856000	-2.81248200
H	2.55816500	-3.26930100	-2.11564200
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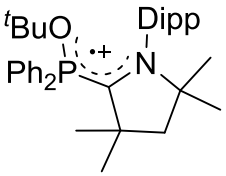

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H	1.67913200	-0.94186300	-4.17042900
H	2.55521400	-1.09758100	-2.66019600
C	-0.81863700	-0.65938900	-3.33715100
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C	-2.99774100	-1.65546700	-2.44876000
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H	-1.72803000	2.21378600	-0.97438400
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H	-4.12462200	3.51589400	0.39562400
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C	3.78209200	-2.99180600	0.31299700
H	3.74414300	-4.03138600	0.61086800
C	4.98486500	-2.42433400	-0.09759500
H	5.88593600	-3.02337700	-0.11899200
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H	2.33530300	5.49295600	-1.18129600
C	2.73337900	3.85582200	0.15150500
H	3.44219300	4.41061700	0.75211900
C	2.44915700	2.53601300	0.46852900
H	2.95383200	2.08244000	1.30831900
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C	0.91590800	0.15912700	2.92440500
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H	0.22172500	-0.63059100	4.78724200
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H	0.38198000	-1.85369700	3.52525200
C	2.39905100	-0.10068600	3.13730400
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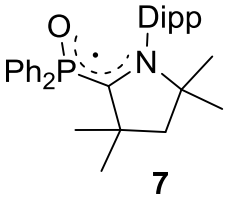

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C	2.11154600	-0.06243300	-0.28991800
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7. Bibliography

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