Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A New Access to Diazaphospholes *via* Cycloaddition-Cycloreversion Reactions on Triazaphospholes

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1. DFT Calculations

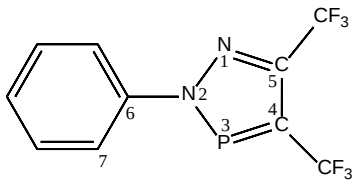
All calculations have been carried out with the Gaussian 09 program package [1]. First the structure of **3** was optimized at different levels of the theory and the structural parameters obtained were compared to the X-ray data (more information can be seen in Table S2). Unless otherwise stated, subsequent calculations were carried out at the ωB97X-D/6-311+G** level of theory [2] (for the W atom, def2TZVP basis set was applied), with the correction of the PCM implicit solvent model (in toluene) [3]. Harmonic vibrational frequency calculations were applied on the fully optimized systems to establish their nature, as characterized by only positive eigenvalues of the Hessian for minima and by a single negative eigenvalue for transition states. The reaction path was checked by IRC calculations starting from the transition structures. Gibbs free energies were obtained at atmospheric pressure utilizing the calculated harmonic frequencies. In accordance with the experimental conditions for the studied cycloaddition reactions 403 K, while for the complex formations (**6** and **7**) 298.15 K was considered. Aromatic properties were investigated by calculating NICS values, which can be accessed by performing NMR calculations on ghost atoms 1 Å above and below the geometric center of the ring in question [4]. Furthermore, Bird indices (aromaticity descriptor based on the standard deviation from the average bond indices) were also calculated [5]. For the visualization of the Kohn-Sham orbitals, the program IQmol [6] was used.

Table S1. NICS(1) and NICS (-1) values in ppm and Bird indexes for **1**, **3**, **6** and **7**.

Compound no.	NICS(1), NICS(-1) (ppm)	Bird indices (-)
1	-12.3,-12.3	66
3	-10.7,-10.7	67
6	-9.6, -8.9	67
7	-11.2,-11.1	64

Both measures indicate significant aromaticity. For comparison, the B3LYP/6-311+G** NICS(1) and BI values for pyrrole are -10.1 ppm and 73, respectively.

Table S2. Comparison of results of optimized geometries obtained by DFT calculations with X-ray data for **3**. As the best match can be seen in case of ωB97X-D/6-311+G** (highlighted in green), unless otherwise stated this level of theory was applied for all calculations.



Funct.		B3LYP	B3LYP	B3LYP	M06-2X	M06-2X	M06-2X	ωB97X-D	ωB97X-D	ωB97X-D
Basis set	X-ray	6-311+G**	cc-pVTZ	def2-TZVP	6-311+G**	cc-pVTZ	def2-TZVP	6-311+G**	cc-pVTZ	def2-TZVP
N1-N2	1.349	1.335	1.333	1.333	1.329	1.328	1.328	1.329	1.327	1.327
N2-P3	1.693	1.724	1.718	1.71	1.707	1.701	1.695	1.700	1.695	1.688
P3-C4	1.712	1.728	1.723	1.718	1.713	1.710	1.706	1.714	1.710	1.705
C4-C5	1.406	1.413	1.408	1.41	1.408	1.404	1.406	1.410	1.406	1.408
C5-N1	1.323	1.321	1.318	1.318	1.314	1.312	1.311	1.315	1.312	1.311
N2-C6	1.436	1.435	1.431	1.431	1.433	1.431	1.43	1.432	1.429	1.429
dihedr1-2-6-7	145.9	149.5	153.9	152.1	151.4	157.3	154.5	146.1	150.2	149.2

Table S3. The comparison of the experimental of computational CO stretching nodes.

$\tilde{\nu}_{(CO)}$ [cm^{-1}]						
6	Experimental	2089	2017	2002	1934	-
	Computational[a]	2085	2014	1989	1985	1977
7	Experimental	2077	2023	1980	1885	-
	Computational[a]	2077	2000	1973	1970	1967

[a]Calculated at the B3LYP/def2TZVP level of theory modified by a scaling factor of 0.968, as suggested by M.K.Assefa, J.L.Devera, A.D.Brathwaite, J.D.Mosley, M.A.Duncan, *Chem. Phys. Lett.* **2015**, *640*, 175-179.

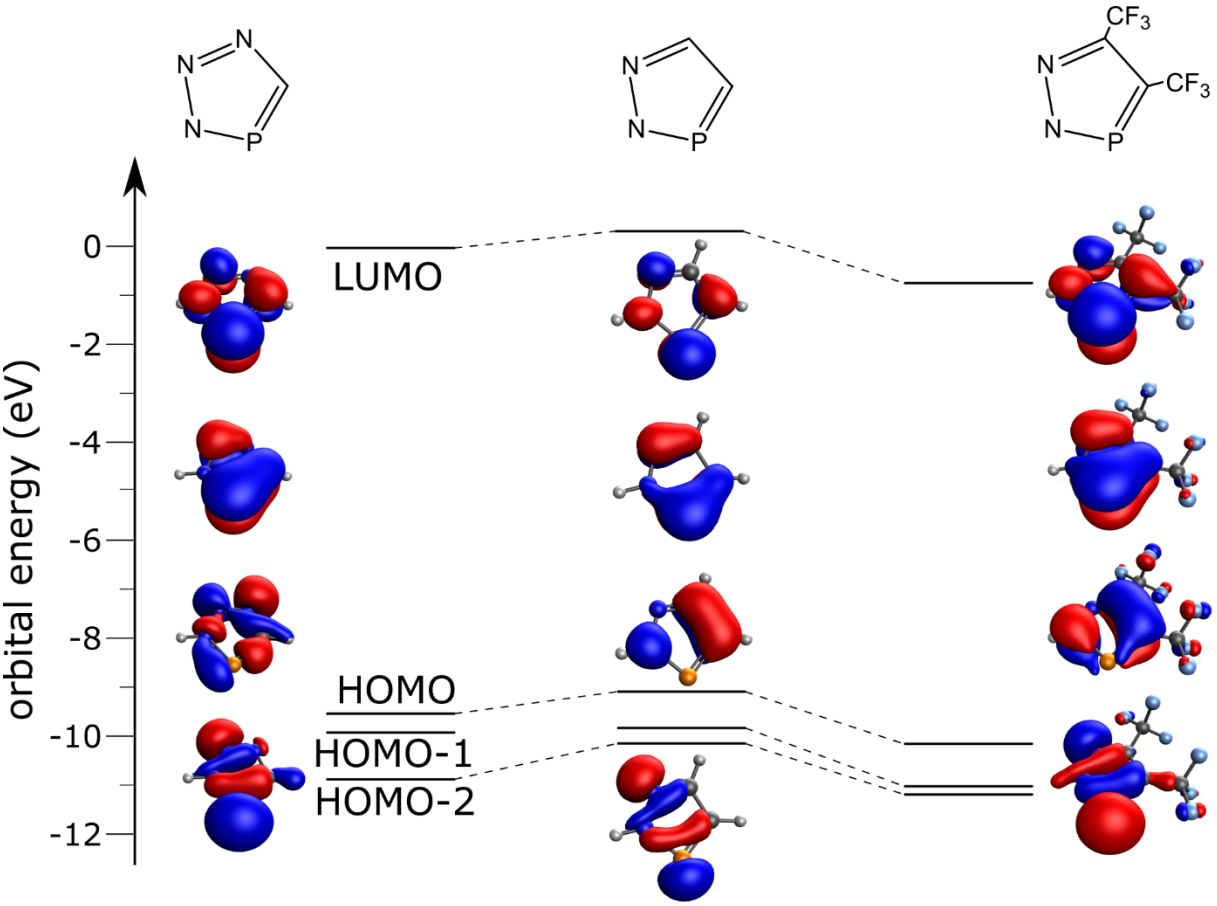


Figure S1. Kohn-Sham orbitals of the 3*H*-1,2,3,4-triazaphosphole, the 2*H*-1,2,3-diazaphosphole and CF_3-substituted diazaphosphole at the ωB97X-D/6-311+G** level of theory.

XYZ coordinates of the investigated systems

XYZ coordinates of the intermediates of the a) reaction on Scheme 1

B intermediate (van der Waals complex of 1 + DMAD)
E(ωB97X-D/6-311+G**) = -1466.21184374
G(403K)= -1465.950793
C 2.97732800 -1.85264800 -1.30033300
C 2.37272300 -0.72039300 -0.76814300
C 3.06839500 0.13669100 0.07713400
C 4.39325000 -0.14663000 0.38109300
C 5.00998300 -1.27885500 -0.14148700
C 4.29943700 -2.13172400 -0.97810100
N 1.00876400 -0.43520600 -1.08429700
P -0.30096200 -1.52807800 -1.03870500
C -1.28534300 -0.17931000 -1.45016600
C -2.78677400 -0.12544900 -1.63201600
C -3.09796400 0.37504600 -3.05194500
N 0.69512800 0.82286700 -1.38512700
N -0.56883000 0.96231600 -1.58924400
C -3.37073700 0.84762400 -0.59327700
C -3.39962800 -1.51520400 -1.42895400
O 1.10512500 2.92201800 0.90860100
C 1.44923800 4.12048700 0.19788700
C -0.18677600 2.73864900 1.14661600
O -1.06076600 3.53713700 0.94080800
C -0.42768700 1.41410600 1.69525200
C -0.70077400 0.31517100 2.09029500
C -0.98982900 -1.02452200 2.56913700
O -2.15616300 -1.45210100 2.09627800
C -2.52365500 -2.79417900 2.44609400
O -0.25833900 -1.64908400 3.29037000
H -3.19394300 -1.89225700 -0.42241400
H -4.48483700 -1.46356500 -1.55129900
H -3.01672500 -2.23578000 -2.15911100
H -2.66260000 1.36236300 -3.21827000
H -4.18053700 0.44438600 -3.19412300
H -2.69559100 -0.31001100 -3.80404700
H -2.91642600 1.83603000 -0.68509700
H -3.19319600 0.48152400 0.42097300
H -4.45043900 0.94429000 -0.74274400
H 2.56796200 1.00555200 0.48701000
H 4.94329400 0.51634500 1.03877600
H 6.04360100 -1.49513600 0.10234400
H 4.77596300 -3.01231700 -1.39255900
H 2.42343300 -2.49968900 -1.97064500
H 2.52740200 4.07732100 0.06879600
H 0.94787500 4.12763900 -0.77018500
H 1.16256500 4.99989800 0.77503100
H -3.48730200 -2.96033200 1.97129000
H -1.78068700 -3.49657200 2.06617600
H -2.60677700 -2.89529500 3.52839000

TS1
E(ωB97X-D/6-311+G**) = -1466.16424154
G(403K)= -1465.899906
C -2.91659400 -0.94995300 -1.81533100
C -2.05527200 0.03718200 -1.34629200
C -2.55304700 1.24251400 -0.86282500
C -3.92490100 1.46453100 -0.86843300
C -4.79269700 0.48507100 -1.33447200
C -4.28498100 -0.72330700 -1.80178700
N -0.65381400 -0.22058300 -1.36198600
P 0.57840800 0.93001300 -1.28713500
C 1.70216200 -0.46588400 -1.23203600
C 3.20281300 -0.39757400 -1.38468700
C 3.53839500 -0.16782800 -2.86903800
N -0.26629300 -1.38116500 -0.76600900
N 1.07012800 -1.55707000 -0.91969700
C 3.72037400 0.78603200 -0.54841600
C 3.85032500 -1.69733200 -0.89865000
C -0.10946300 -0.51732600 1.14466100
C -0.71176200 -1.53223100 1.99443100
O 0.13759300 -2.52556000 2.23646600
C -0.37279300 -3.60790600 3.02410200
C 0.37757500 0.61926600 0.94540000
C 0.80494800 1.80191400 1.69961600
O 0.02996400 2.85208700 1.42256700
C 0.34921600 4.06950200 2.10941300
O 1.74182200 1.82632900 2.45522500
O -1.84304100 -1.47120000 2.40623100
H 3.61839800 -1.88164100 0.15257800
H 3.49797700 -2.55470700 -1.47530900
H 4.93585900 -1.62548800 -1.00976300
H 3.16629100 -0.99107200 -3.48440300
H 4.62283800 -0.10546000 -2.99736700
H 3.09906100 0.76315500 -3.23901000
H 3.47983900 0.66110300 0.51049400
H 4.80659900 0.85969800 -0.64690800
H 3.29882100 1.73847400 -0.88986600
H -1.88240100 1.99509100 -0.46332100
H -4.31371900 2.40261000 -0.48997100
H -5.86231200 0.65952100 -1.32908700
H -4.95722300 -1.49221800 -2.16437600
H -2.50721400 -1.88274200 -2.18220600
H -0.37405100 4.79970200 1.75541100
H 0.25675900 3.93154300 3.18707500
H 1.36432700 4.38618100 1.86689400
H 0.44634300 -4.31791300 3.10364500
H -0.66975300 -3.25283200 4.01173700
H -1.22920100 -4.06474200 2.52677000

F intermediate
E(ωB97X-D/6-311+G**) = -1466.20985218
G(403K)= -1465.938975
C -4.12827200 -1.40480600 0.49209500
C -2.79236300 -1.12083500 0.75556800
C -1.79676900 -1.69479700 -0.03479200
C -2.15287800 -2.54840000 -1.08303000
C -3.48922200 -2.81302900 -1.33955000
C -4.48747300 -2.24389000 -0.55382400
N -0.42671800 -1.46388400 0.21803500
N -0.13836500 -0.49378600 1.23694400
N 1.29147800 -0.71684300 1.54413600
C 1.90886900 -1.02090300 0.47914300
C 3.38553900 -1.29387100 0.39061400
C 3.59014800 -2.73483900 -0.10722300
P 0.72630700 -1.06054500 -1.01373800
C 0.27915500 0.74170100 -0.70987700
C -0.16212200 0.80416500 0.54388600
C -0.53993500 2.03134200 1.29370300
O -1.22405500 1.74836100 2.39457200
C -1.62983700 2.87064500 3.18761100
C 0.51177300 1.83191400 -1.68134000
O -0.60458600 2.46148200 -2.01732000
C -0.45624400 3.56728400 -2.91776300
O 1.60535000 2.06583000 -2.13397500
O -0.25227800 3.14319100 0.92783900
C 3.97133300 -0.30054500 -0.62813700
C 4.05301800 -1.10929700 1.75567800
H 5.12633600 -1.29561700 1.66173800
H 3.90827400 -0.09426100 2.13140500

H 3.64321100 -1.80341000 2.49244600
H 4.66026900 -2.93565200 -0.20584900
H 3.16841100 -3.45689700 0.59673900
H 3.12835600 -2.89428800 -1.08567200
H 5.04614000 -0.47311900 -0.72821500
H 3.52280100 -0.42114600 -1.61920000
H 3.81395400 0.73325600 -0.31169700
H -3.75106400 -3.47664700 -2.15608900
H -5.53107600 -2.45517000 -0.75485500
H -4.89387500 -0.95623800 1.11554600
H -2.51961400 -0.46955900 1.57538000
H -1.38184100 -3.01077400 -1.68973800
H -1.45992300 3.95693900 -3.06604600
H 0.18764800 4.32646700 -2.47291400
H -0.02984400 3.23123800 -3.86368900
H -2.15613300 2.44741600 4.03909800
H -0.75668400 3.43443300 3.51777800
H -2.28849800 3.52084500 2.61061200

TS2
E(ωB97X-D/6-311+G**) = -1466.20721192
G(403K)= -1465.93483
C 3.30270800 0.29070400 -1.45205000
C 2.61077200 -0.10470800 -0.30322200
C 3.26710000 -0.85779300 0.67287500
C 4.60106500 -1.20038300 0.49396300
C 5.29618900 -0.80930900 -0.64457400
C 4.63468700 -0.06252500 -1.61377700
N 1.27424000 0.26143600 -0.13899400
N 0.54631400 -0.15573200 0.99760100
N -0.10264000 1.10055800 1.51942300
C -0.41445300 1.83737900 0.53971600
P 0.10971800 1.02950200 -1.12638800
C -0.99990600 -0.43211900 -0.73310100
C -0.57531000 -0.90938000 0.43666000
C -1.22483400 -1.98147400 1.23336000
C -1.09003700 3.17771800 0.64372800
C -2.33445600 3.14486400 -0.25892100
C -1.49233700 3.46971600 2.09188900
C -0.10762000 4.25034600 0.14171500
C -2.18178900 -0.83144700 -1.53043000
O -2.02580800 -2.01468100 -2.10536400
O -3.14159300 -0.11353700 -1.66426300
O -0.53518000 -2.28205100 2.32450600
O -2.26529400 -2.49945500 0.90993000
H -1.97523400 4.44934100 2.14507700
H -2.19192300 2.71805600 2.46395500
H -0.62114800 3.47563000 2.75008900
H 0.19257200 4.07052900 -0.89457500
H -0.58822300 5.23136300 0.18570600
H 0.79146200 4.27945300 0.76251600
H -2.07043100 2.97925000 -1.30827500
H -3.02672400 2.35535600 0.04275000
H -2.85424500 4.10456700 -0.19682100
H 2.72628300 -1.16221100 1.55885200
H 5.09996800 -1.78395500 1.26001900
H 6.33637200 -1.08233600 -0.77608900
H 5.15816100 0.25184100 -2.50993500
H 2.80074300 0.87413400 -2.21622200
C -1.10588100 -3.28778100 3.17018800
H -0.42111600 -3.38265500 4.00880700
H -2.09320600 -2.97675600 3.51348800
H -1.18738200 -4.23250000 2.63133700
C -3.14737700 -2.50509400 -2.85229200
H -2.83127000 -3.46549800 -3.25092100
H -4.00702000 -2.62823200 -2.19292700
H -3.39695000 -1.81622800 -3.66004900

F' intermediate
E(ωB97X-D/6-311+G**) = -1466.21252337
G(403K)= -1465.942267
C 4.40239500 -1.72245200 0.38161000
C 3.03181900 -1.49884400 0.45902400
C 2.35312100 -0.99989400 -0.65066400
C 3.05270500 -0.72646000 -1.82841100
C 4.42178600 -0.93945000 -1.88612700
C 5.10572700 -1.44052700 -0.78220900
N 0.95357900 -0.77741400 -0.63541300
P 0.26831400 0.76210900 -1.07513100
C 0.52238800 1.19179300 0.79620200
C 0.70232200 2.59694500 1.30571700
C 0.81712300 2.61377900 2.83212300
N 0.30130100 -1.07322900 0.59437600
N 0.52457900 0.15502300 1.51119700
C -1.09623700 -0.96933900 0.23152900
C -2.05370100 -1.80919100 1.01849800
O -2.41220300 -2.88925500 0.34627400
C -1.35575200 -0.01225500 -0.66222300
C -2.70106400 0.38125500 -1.11211800
O -3.71868800 -0.19504600 -0.81648300
O -2.65239700 1.47749700 -1.87306800
C 1.97800200 3.17783900 0.67234000
C -0.52517900 3.40706800 0.85512000
O -2.40282000 -1.52009200 2.13113000
H 0.93884900 3.64392500 3.17847600
H -0.07605700 2.19267000 3.29827100
H 1.67821800 2.03149400 3.16659800
H 2.12276000 4.20364500 1.02202300
H 2.85617300 2.59120300 0.95442600
H 1.91459800 3.19994000 -0.41916700
H -0.42560800 4.44130100 1.19491600
H -0.62340900 3.42442200 -0.23536400
H -1.44513200 2.99486100 1.27854100
H 4.95476800 -0.72276900 -2.80509000
H 6.17446500 -1.61254100 -0.83258800
H 4.92194800 -2.11516700 1.24855700
H 2.48837500 -1.71210800 1.36963000
H 2.52045900 -0.35929300 -2.69911000
C -3.91039000 1.97874100 -2.33982800
H -3.67234900 2.86545400 -2.92179500
H -4.40632300 1.23345400 -2.96259000
H -4.55220100 2.23390300 -1.49584300
C -3.35030600 -3.75619000 1.00132000
H -3.52113800 -4.57406800 0.30657500
H -2.93124200 -4.12658500 1.93729100
H -4.27775700 -3.21778200 1.19783700

TS3
E(ωB97X-D/6-311+G**) = -1466.21011763
G(403K)= -1465.940143
P 0.27736400 0.70356800 -1.09925100
C 0.49790100 1.12364000 0.86942100
N 0.50436600 0.11638700 1.58123800
N 0.28704800 -1.25132200 0.45005400
C -1.07264400 -1.06226900 0.13379100
C -1.32418800 -0.05789000 -0.72767800
C -2.66535900 0.41948900 -1.09436400
O -3.69718500 -0.13595900 -0.80731100
N 0.97999000 -0.81108900 -0.66201200
C 2.38687600 -1.00135800 -0.64201900
C 3.11453000 -0.67786000 -1.78776000
C 4.49207400 -0.84098300 -1.79867200
C 5.15083600 -1.34178600 -0.67984200
C 4.41711500 -1.67515400 0.45172000
C 3.03784400 -1.50217300 0.48221700
C 0.65849300 2.56614000 1.30000600
C 1.94634700 3.11597500 0.66710800
C -0.56186100 3.34493600 0.78617500

C 0.74069500 2.65855400 2.82671100
C -2.06152400 -1.85710400 0.93327700
O -2.38058000 -1.56486100 2.05374200
O -2.49121400 -2.90722700 0.25283900
C -3.47706200 -3.71978100 0.90629000
O -2.59694700 1.56961900 -1.77271400
C -3.84739000 2.15836200 -2.14668200
H 0.84894000 3.70484000 3.12614100
H -0.16065800 2.25464000 3.29251600
H 1.59813300 2.09869000 3.20602200
H 2.08222800 4.15744900 0.97116000
H 2.81825000 2.54494800 0.99617000
H 1.90705100 3.08668000 -0.42509400
H -0.47344800 4.39444800 1.07937800
H -0.63935600 3.31022200 -0.30521300
H -1.48821700 2.94807000 1.21007200
H 5.05087600 -0.58723600 -2.69227200
H 6.22615800 -1.47560400 -0.69381100
H 4.91932900 -2.06829800 1.32847700
H 2.46669200 -1.75094300 1.36608700
H 2.59999100 -0.31335100 -2.67003100
H -3.59185400 3.07409600 -2.67388800
H -4.40303000 1.48367300 -2.79881400
H -4.44207100 2.37953500 -1.25957600
H -3.70901100 -4.51470100 0.20254700
H -3.07388900 -4.13083000 1.83228100
H -4.36509900 -3.12468300 1.12099600

G intermediate (van der Waals complex of **2** + ^{t}BuCN)
E(ωB97X-D/6-311+G**) = -1466.30259288
G(403K)= -1466.038074
C -2.65173400 -1.89305800 0.38348800
C -3.99104000 -2.18760200 0.15797500
C -4.54229200 -2.02292300 -1.10700200
C -3.74614300 -1.57139400 -2.15548300
C -2.40347200 -1.29087200 -1.94665200
C -1.86575100 -1.45228100 -0.67451600
N -0.49247000 -1.13312400 -0.44640100
P 0.56601100 -1.99126200 0.56204400
C 1.77939400 -0.84376500 0.17078500
C 1.25096300 0.11714200 -0.71498900
N -0.00849500 -0.04242700 -1.05615400
C 3.13038200 -0.77967600 0.75416000
O 3.44901500 -1.92586500 1.36770600
O 3.85653900 0.18287000 0.71227900
C 1.98177000 1.28209100 -1.31132900
O 3.00476600 0.87098800 -2.05019500
O 1.66065300 2.43122600 -1.15769900
N -1.05410400 0.35020600 2.42661100
C -1.53942500 1.22265100 1.85248600
C -2.17628100 2.35315300 1.15466200
C -2.81753400 1.84474200 -0.14708700
C -3.24917600 2.93920600 2.08896800
C -1.09438500 3.40069400 0.84291000
H -4.60720300 -2.52737000 0.98215400
H -5.59012300 -2.24217200 -1.27603800
H -4.17064200 -1.44175400 -3.14421900
H -1.77295300 -0.93795700 -2.75270600
H -4.01968800 2.19924600 2.31752600
H -2.80975200 3.28635600 3.02676200
H -3.72325200 3.79030000 1.59336600
H -0.31475600 2.98732000 0.19985700
H -0.63193700 3.77213700 1.76047300
H -1.56039400 4.24410600 0.32609100
H -2.05724200 1.46420300 -0.83062600
H -3.54266700 1.05013700 0.04719200
H -3.33544900 2.67797800 -0.62965200
H -2.23049400 -1.96715600 1.37878000
C 3.84317700 1.89809700 -2.59181300
H 4.62345300 1.37715400 -3.14078400
H 3.27102400 2.54475900 -3.25809300
H 4.27368000 2.48995500 -1.78329300
C 4.71689200 -1.95854800 2.02994200
H 4.78866100 -2.94903900 2.47243800
H 5.52367800 -1.80123200 1.31300300
H 4.76152800 -1.19030200 2.80295600

XYZ coordinates of the intermediates of the b) reaction on Scheme 1

B intermediate (van der Waals complex of 1 + hexafluoro-2-butyne)
E(ωB97X-D/6-311+G**) = -1684.56991593
G(403K)= -1684.382812
C 0.94537200 -1.62787900 -0.77217400
C 1.60927100 -1.07560900 -1.86312100
C 2.94102300 -1.39736200 -2.08186500
C 3.61151400 -2.25204400 -1.21357300
C 2.93982700 -2.79552500 -0.12585000
C 1.60231100 -2.49266900 0.09569600
N -0.42270400 -1.29092800 -0.53464900
N -1.19858400 -1.06756700 -1.59782300
N -2.39873400 -0.76128600 -1.25581900
C -2.60785500 -0.73376400 0.08410300
C -3.98494300 -0.37874200 0.60384500
C -4.33369100 1.04944600 0.15189200
P -1.19210600 -1.11350200 0.98103100
C -5.00597500 -1.37093200 0.02314400
C -4.01428600 -0.45002100 2.13461900
F 0.35940700 2.11936600 -2.27404200
C 0.10603900 2.53110000 -1.02897300
F 0.21787700 3.86302800 -1.00622100
C 1.03551900 1.91730000 -0.07317600
C 1.79701000 1.42410000 0.70112600
C 2.74338900 0.84540400 1.66208500
F 2.17448900 -0.13739900 2.36494300
F 3.16440100 1.77586000 2.52555800
F 3.81273700 0.34702100 1.04041500
F -1.15648800 2.21799400 -0.73695600
H 4.65484900 -2.49065900 -1.38308300
H 3.45830100 -0.96785300 -2.93179600
H 1.08119400 -0.40437000 -2.52678800
H 3.45358200 -3.46488800 0.55396300
H 1.07382400 -2.93232100 0.93341200
H -5.00918100 -1.33002300 -1.06779500
H -6.00943700 -1.12595700 0.38374700
H -4.77235900 -2.39513200 0.32766400
H -5.01035400 -0.18741800 2.50079000
H -3.30208700 0.25096100 2.58209700
H -3.78365300 -1.45779100 2.49449000
H -4.29602500 1.13374300 -0.93607600
H -3.63342900 1.77438100 0.57517100
H -5.34245300 1.30867500 0.48682100

TS1
E(ωB97X-D/6-311+G**) = -1684.53262105
G(403K)= -1684.339296
C -2.46407400 -0.85335700 -1.46744300
C -1.95714500 -1.39185700 -0.28982500
C -2.80607200 -1.95638500 0.65707900
C -4.17211000 -1.97855200 0.41780800
C -4.68915900 -1.45365400 -0.76246300
C -3.83278200 -0.89499500 -1.70269000
N -0.55613800 -1.36802200 -0.02376400
N -0.20143400 -0.95375900 1.21634700
N 1.13513200 -1.06145700 1.38290400
C 1.78960300 -1.19490000 0.26528500
C 3.29278300 -1.34558600 0.21669700

C 3.86234100 -0.39334500 -0.84600000
P 0.68295200 -1.12196600 -1.13655300
C 3.90771200 -1.02551300 1.58267600
C 3.61491000 -2.80157900 -0.16899700
C -0.16230100 1.07670700 0.71109900
C -0.77458700 1.71505700 1.88742200
F -0.80899400 3.05171900 1.74909300
C 0.30649400 1.13241100 -0.43807100
C 0.58559800 2.06401200 -1.54523100
F 1.81181200 1.87794400 -2.06290600
F -2.03586800 1.30247900 2.06005300
F -0.09621100 1.45012500 3.00788400
F -0.29565400 1.88817400 -2.54735000
F 0.50895400 3.34607700 -1.17066300
H 4.99378800 -1.13680800 1.52288700
H 3.67958500 -0.00192100 1.88823000
H 3.53205400 -1.69868000 2.35527800
H 4.69889700 -2.94113800 -0.20751200
H 3.20461400 -3.49971000 0.56523000
H 3.20535600 -3.05489100 -1.15103900
H 4.94438400 -0.52974100 -0.91860400
H 3.44133800 -0.58785200 -1.83804400
H 3.66549800 0.64992100 -0.59005200
H -4.22798700 -0.47479400 -2.61996600
H -5.75681600 -1.47844100 -0.94646700
H -4.83557900 -2.41408300 1.15571500
H -2.39139400 -2.36595300 1.56917000
H -1.80455200 -0.39319000 -2.19402800

F intermediate
E(ωB97X-D/6-311+G**) = -1684.57593715
G(403K)= -1684.377916
C 3.03886900 -0.68724500 -0.97783200
C 2.15941400 -1.27201300 -0.06811600
C 2.66406600 -1.94016300 1.05036800
C 4.03384300 -2.01448400 1.25391600
C 4.91704900 -1.43252800 0.35030500
C 4.40944300 -0.77466800 -0.76211100
N 0.76128200 -1.24621800 -0.27957600
P -0.42072000 -1.09813600 0.97328900
C -0.33779000 0.77062500 0.71211300
C -0.73296000 1.78677400 1.73804000
F -1.71922400 2.58753900 1.30785100
N 0.28372500 -0.32328600 -1.26666100
C 0.08233100 0.93755900 -0.53508800
C 0.29193200 2.17611900 -1.36022800
F 0.16737400 3.29108900 -0.63880500
N -1.09055900 -0.79564000 -1.56528000
C -1.62087900 -1.23318500 -0.50069700
C -3.01685700 -1.78214400 -0.39804100
C -3.74587100 -0.98295000 0.69614500
C -3.75004600 -1.64403000 -1.73463500
C -2.92637000 -3.26323200 0.00824900
F -1.19019800 1.17338700 2.84556000
F 0.29143000 2.56119700 2.11145800
F 1.50994400 2.18472300 -1.91283200
F -0.60441100 2.22486100 -2.35411100
H -4.75960600 -2.05219300 -1.63783600
H -3.82597700 -0.59723000 -2.03635700
H -3.23112200 -2.18663000 -2.52725500
H -3.93421000 -3.67517000 0.10585300
H -2.38944500 -3.84373100 -0.74602800
H -2.41899700 -3.38959300 0.96889500
H -4.76662500 -1.35882800 0.80179300
H -3.25763700 -1.08668700 1.67093300
H -3.79891000 0.07991900 0.44497700
H 4.41133500 -2.53369300 2.12755000
H 5.98648000 -1.49376100 0.51286300
H 5.08383600 -0.31760800 -1.47753400
H 2.65138000 -0.17988700 -1.85015200
H 1.98787500 -2.40862600 1.75716600

TS2
E(ωB97X-D/6-311+G**) = -1684.57396709
G(403K)= -1684.374221
C -3.25234500 0.82385500 1.28904300
C -2.60570000 0.29683300 0.16857100
C -3.34985600 -0.32738100 -0.83301400
C -4.73007300 -0.41653600 -0.70464900
C -5.38186200 0.10391300 0.40695100
C -4.63172800 0.72360800 1.40052600
N -1.21425700 0.40364400 0.06137900
N -0.53135500 -0.12825900 -1.05109500
N 0.35825300 0.99158800 -1.53471300
C 0.76203000 1.65049000 -0.53390200
P 0.02974600 0.94329100 1.09792000
C 0.88861900 -0.69143500 0.71968700
C 0.40661400 -1.08048800 -0.45516900
C 0.69551600 -2.28103400 -1.31046600
F -0.43234500 -2.95304000 -1.57039800
C 1.70289500 2.82267800 -0.59166100
C 2.93299800 2.45205300 0.25565900
C 2.12094300 3.11007000 -2.03607800
C 1.00102200 4.05031500 0.01261500
C 1.91401400 -1.33143100 1.60333100
F 1.50566000 -2.51012300 2.08748600
F 2.17395000 -0.53760200 2.65897900
F 3.08161500 -1.52880500 0.97456600
F 1.22445100 -1.90506000 -2.48081200
F 1.54603300 -3.12639500 -0.72633000
H 2.82294100 3.94799400 -2.05163400
H 2.60648600 2.24162600 -2.48580300
H 1.25680400 3.36940800 -2.65121500
H 0.72103300 3.88420300 1.05656600
H 1.67975600 4.90656500 -0.01908500
H 0.10059300 4.30600100 -0.55174100
H 2.66739500 2.25910100 1.30051400
H 3.43623800 1.56791100 -0.14435800
H 3.64443800 3.28159900 0.24786100
H -2.84457500 -0.73483900 -1.69823100
H -5.29866300 -0.90421000 -1.48873800
H -6.45831300 0.02553100 0.50057500
H -5.12095100 1.13629100 2.27570500
H -2.68064100 1.31078400 2.07168800

F' intermediate
E(ωB97X-D/6-311+G**) = -1684.58003252
G(403K)= -1684.381027
C 4.42983400 -1.11301500 -1.63388000
C 3.05369500 -0.94045300 -1.64629600
C 2.33514400 -1.00564300 -0.45141500
C 2.99637200 -1.25681800 0.74765200
C 4.37461800 -1.44329300 0.74250600
C 5.09843300 -1.36692400 -0.44003200
N 0.92683500 -0.83214400 -0.50645600
P 0.21811300 0.58386600 -1.22119100
C -1.40847100 -0.16049100 -0.70722800
C -2.71771200 0.12839700 -1.37681900
F -3.57721700 0.75081500 -0.55679400
N 0.25085200 -0.92027700 0.74036900
C -1.13736600 -0.94089800 0.33635300
C -2.01998800 -1.79791200 1.20132700
F -3.31434500 -1.63751800 0.91933300
N 0.41256300 0.44963700 1.42989800
C 0.39961900 1.34785700 0.54742100
C 0.53413700 2.82466500 0.80214900
C 1.82823200 3.30787100 0.12477800
F -1.72280600 -3.09229400 1.03694100

F -1.84011800 -1.49794800 2.49164100
C -0.68445400 3.51641300 0.16818700
C 0.58629700 3.11237900 2.30491000
F -3.31588200 -0.97740600 -1.83366900
F -2.53070500 0.94248700 -2.43116900
H 0.68502800 4.18901300 2.46719600
H -0.32179700 2.76687600 2.80341300
H 1.43818900 2.61265300 2.77045000
H 1.81178000 3.13268800 -0.95463800
H 1.94367700 4.38252500 0.28850200
H 2.70140600 2.80101000 0.54345600
H -0.73486000 3.34726500 -0.91258200
H -1.61681700 3.16493600 0.61809800
H -0.61448200 4.59536100 0.32741000
H 2.43545400 -1.31202700 1.67100200
H 4.88238900 -1.64365000 1.67920900
H 6.17261100 -1.50967300 -0.43489300
H 4.97948400 -1.06102300 -2.56681500
H 2.53380600 -0.77048700 -2.58285300

TS3
E(ωB97X-D/6-311+G**) = -1684.57718424
G(403K)= -1684.378819
C 2.97975500 -1.29640800 0.72511200
C 2.33848500 -1.01786900 -0.47778000
C 3.07282200 -0.88664900 -1.65579600
C 4.45352000 -1.01907400 -1.62228300
C 5.10465700 -1.29785400 -0.42474500
C 4.36242200 -1.44122100 0.74074700
N 0.92607500 -0.86273100 -0.54480800
N 0.22471900 -1.13095300 0.60993300
C -1.13342600 -1.02862400 0.25086600
C -1.39426300 -0.16847400 -0.74709900
C -2.70783100 0.25427400 -1.32757500
F -3.49179700 0.86766800 -0.42771900
N 0.40378600 0.39490500 1.51860400
C 0.39514300 1.28278100 0.66375500
C 0.56415900 2.77452300 0.85629600
C 1.89593700 3.18369900 0.20653800
P 0.21203700 0.55071900 -1.22069800
C -2.05730300 -1.84769400 1.11414800
F -1.84932200 -3.15592200 0.91674500
F -1.84107400 -1.59182200 2.40750800
F -3.34336000 -1.60035100 0.85577300
C -0.60685100 3.48380900 0.16189100
C 0.57974800 3.11398700 2.34996800
F -2.51010600 1.13509500 -2.32709700
F -3.39950100 -0.77126300 -1.83736800
H 0.70657900 4.19221500 2.47963600
H -0.35438200 2.81430100 2.82979800
H 1.40168200 2.60510200 2.85759100
H 2.04393300 4.25892800 0.33729700
H 2.73568900 2.66168900 0.67187700
H 1.90852600 2.97166400 -0.86609900
H -0.50640100 4.56392700 0.29484000
H -0.62407700 3.28723900 -0.91513800
H -1.56538900 3.17649900 0.58793900
H 5.01946200 -0.91748500 -2.54111600
H 6.18229800 -1.41002400 -0.40301100
H 4.85970100 -1.66131600 1.67850900
H 2.40017800 -1.39862400 1.63251800
H 2.56420100 -0.69933700 -2.59512600

G intermediate (van der Waals complex of **3** + ^{t}BuCN)
E(ωB97X-D/6-311+G**) = -1684.67113362
G(403K)= --1684.478090
C 2.51461600 -1.85688800 -0.75737100
C 3.85615900 -2.18777800 -0.60823200
C 4.42953200 -2.23545200 0.65654600
C 3.65576300 -1.96204800 1.78084700
C 2.31117700 -1.64818600 1.64632700
C 1.75349300 -1.59524000 0.37464600
N 0.37634000 -1.23693400 0.22727900
P -0.71768900 -1.97338200 -0.83647100
C -1.90307000 -0.86279100 -0.29194700
C -1.33746400 -0.00628800 0.67346000
N -0.07099400 -0.21709900 0.95528900
C -3.31658300 -0.86892800 -0.77274900
F -3.44256400 -1.64616000 -1.86564100
F -3.75692600 0.35316500 -1.10365400
F -4.16806500 -1.35729000 0.14617000
C -2.00383900 1.15648400 1.36453200
F -3.22896100 0.83360700 1.80139500
F -1.29681900 1.57661000 2.41634000
F -2.14149000 2.20401100 0.53454000
N 0.83322200 0.76231500 -2.21167400
C 1.41577100 1.49547600 -1.54158300
C 2.17272800 2.45076000 -0.71366000
C 2.89256600 1.68614300 0.40910500
C 3.19193200 3.15956100 -1.62230300
C 1.18322000 3.46419400 -0.11515600
H 4.45565600 -2.38922900 -1.48811300
H 5.47920400 -2.48071100 0.76834900
H 4.09974300 -2.00003800 2.76860200
H 1.69661700 -1.43245500 2.51137400
H 3.89927300 2.44534400 -2.04979100
H 2.69448400 3.68844000 -2.43815200
H 3.75167600 3.88619600 -1.02794500
H 0.45770500 2.96661000 0.52984400
H 0.64427100 4.00217300 -0.89787400
H 1.73941100 4.18831000 0.48555900
H 2.17346300 1.21219500 1.07853800
H 3.55583900 0.91529400 0.00868200
H 3.49205400 2.39438900 0.98705000
H 2.07338300 -1.76337100 -1.74245400

XYZ coordinates of the intermediates of the c) reaction on Scheme 1

B intermediate (van der Waals complex of 4 + hexafluoro-2-butyne)
E(ωB97X-D/6-311+G**) = -1381.92254491
G(403K)= -1381.714429
C 2.73347900 0.21234200 -1.03649100
H 2.17068000 1.08323500 -1.34575000
C 4.11067200 0.26664200 -0.87155100
H 4.63178200 1.19892600 -1.05501200
C 4.81635400 -0.86014400 -0.46327100
H 5.89033000 -0.80886000 -0.32813800
C 4.14093800 -2.05256600 -0.23065500
H 4.68574500 -2.93707200 0.07785100
C 2.76495100 -2.12433100 -0.40655000
H 2.24012400 -3.05957900 -0.25140800
C 2.07149300 -0.98663300 -0.80014700
N 0.65886200 -1.03845300 -0.94720500
N -1.23750900 -0.49192900 -1.73621100
C -0.69589300 2.95706200 -0.70832600
N 0.03437100 -0.28837600 -1.86326800
F -0.78705900 4.19644500 -0.20447700
F -1.84414600 2.67919600 -1.31746000
F 0.27847200 2.96170500 -1.61982100
C -0.16490500 1.28722100 1.29501900
C -0.24335400 -1.73852300 -0.21506500
H 0.04642500 -2.39018900 0.59046400
C 0.14489100 0.46760400 2.46971100
F -0.86621800 -0.35698100 2.76586500
F 0.36784300 1.23867000 3.53802000
F 1.23562500 -0.27826600 2.26953700

C -1.46348000 -1.37880700 -0.72847500
C -2.85763300 -1.78317300 -0.32329800
C -0.40909600 2.00117800 0.37063200
C -3.57943900 -2.38724000 -1.53803200
C -2.79586500 -2.81537600 0.80734700
C -3.61353800 -0.53268700 0.15587900
H -4.60356800 -2.66217900 -1.26806300
H -3.61932800 -1.66925900 -2.35991000
H -3.06446200 -3.28479200 -1.89213100
H -4.63896100 -0.79509600 0.43332600
H -3.12482400 -0.09174400 1.02925100
H -3.65064800 0.22188600 -0.63274700
H -3.80836000 -3.10890900 1.09715000
H -2.26313600 -3.71824000 0.49338600
H -2.29996900 -2.40915800 1.69319400

TS1
E(ωB97X-D/6-311+G**) = -1381.86788451
G(403K)= -1381.655577
N 0.14914400 -0.57803000 -1.55479100
C 0.17457200 1.09896400 -0.53342800
C -0.29532500 0.80315100 0.58642800
C -0.65772700 -1.24999500 0.34296300
N -1.21583000 -0.63440700 -1.71463700
C -1.73479400 -1.05785200 -0.59849500
N 0.43058300 -1.35565500 -0.46578100
C 1.78538800 -1.46539900 -0.06096700
C 2.75600700 -1.64254100 -1.04200000
C 4.08730900 -1.74290500 -0.66799700
C 4.44891100 -1.68056000 0.67446900
C 3.47111400 -1.50677100 1.64499200
C 2.13425300 -1.38991700 1.28274000
C -3.20556400 -1.24570100 -0.34824800
C -3.60555100 -0.43642200 0.89617400
C -0.56484200 1.37977000 1.91209100
F -0.77324700 0.43083000 2.85155400
C 0.78716200 2.11962800 -1.39853600
F 0.78287100 3.32731500 -0.80823500
C -4.01328600 -0.77230700 -1.55929600
C -3.46606200 -2.74219100 -0.09818600
F -1.65810200 2.15868000 1.90240600
F 0.45892400 2.12725500 2.34981800
F 2.06264400 1.81753500 -1.67713700
F 0.13470900 2.24348300 -2.55995100
H 4.84592900 -1.87534700 -1.43034300
H 3.74434900 -1.44690600 2.69184400
H 5.49055700 -1.76504000 0.96087200
H 2.46161600 -1.69156100 -2.08243500
H 1.38261500 -1.23007100 2.04596900
H -0.71227300 -1.75227400 1.29731100
H -4.53208800 -2.90496000 0.08207800
H -3.16997400 -3.34089300 -0.96354800
H -2.91898600 -3.10678900 0.77598200
H -4.66904000 -0.58485800 1.10016300
H -3.05032000 -0.75204200 1.78397300
H -3.43437300 0.63132600 0.74354300
H -5.07809700 -0.93007600 -1.36826700
H -3.84892200 0.28996600 -1.75210100
H -3.73784900 -1.32342600 -2.46088000

F intermediate
E(ωB97X-D/6-311+G**) = -1381.91312973
G(403K)= -1381.695442
H 4.83996300 -1.38519100 -1.63954000
C 4.08542100 -1.48562700 -0.86767200
C 4.46225700 -1.76114900 0.44428800
H 5.50893200 -1.87767500 0.69914600
C 3.48460900 -1.88282100 1.42100900
H 3.76125100 -2.09155800 2.44813200
C 2.14004600 -1.72514800 1.09923200
H 1.39458500 -1.81911600 1.87961500
C 1.76940200 -1.45820500 -0.21643700
C 2.74882400 -1.33911900 -1.20361600
H 2.45379900 -1.12451500 -2.22274300
N 0.40490700 -1.35778100 -0.58890500
N 0.12488400 -0.26588100 -1.51853800
N -1.33603900 -0.48582700 -1.73685200
C -1.76535500 -0.92744600 -0.62441400
C -0.59942300 -0.96263700 0.38759400
C 0.17588500 0.89504100 -0.60922100
C -0.23821400 0.52429500 0.59446900
C -3.18045000 -1.31325100 -0.31482300
C 0.62385600 2.19701500 -1.18801000
F 1.89750700 2.12831400 -1.59153000
C -0.40525300 1.28550400 1.86955300
F -0.75296300 0.44971400 2.86624700
F 0.72027200 1.90034800 2.24282500
F -1.36969300 2.21393100 1.78552600
F -0.12179100 2.51716100 -2.25267700
F 0.52708700 3.19431600 -0.30382800
H -0.71594100 -1.58629100 1.26597000
C -4.08789200 -1.01355400 -1.51003300
C -3.21431000 -2.81677800 0.01276300
C -3.62850800 -0.49799700 0.91107000
H -4.66648700 -0.74308000 1.14913200
H -3.02533300 -0.72240500 1.79531100
H -3.57165800 0.57611700 0.71559600
H -5.11398400 -1.30427700 -1.27000000
H -4.07804200 0.05100300 -1.75361500
H -3.76881800 -1.56535400 -2.39640600
H -4.23934400 -3.10994800 0.25394300
H -2.87844200 -3.41030900 -0.84083500
H -2.58589600 -3.06376400 0.87277700

TS2
E(ωB97X-D/6-311+G**) = -1381.90276101
G(403K) =-1381.684548
C 4.46514300 -0.51466600 1.41066600
C 3.09908100 -0.64408700 1.19848200
C 2.51027200 -0.04159900 0.08153300
C 3.30212300 0.69102000 -0.80944800
C 4.66442000 0.80709600 -0.57706500
C 5.25969400 0.20880400 0.52934200
N 1.15471800 -0.17173300 -0.14036400
C 0.05786500 -0.78160800 0.54643600
C -0.86655400 0.44920000 0.66439200
C -1.85102500 0.68899600 1.76327000
F -3.11983300 0.55691800 1.34805000
N 0.43935900 0.40785100 -1.20605500
C -0.59408900 1.12665700 -0.44513700
C -1.15768500 2.36538400 -1.06138100
F -2.16936500 2.86173900 -0.34378000
N -0.31859400 -0.81508500 -1.73699700
C -0.51700600 -1.52570100 -0.70490400
C -1.21027700 -2.85441000 -0.65909200
C -0.21293000 -3.90111000 -0.13065200
F -0.22113100 3.31651200 -1.16318300
F -1.61167900 2.11023800 -2.29380800
C -2.39993500 -2.72867100 0.30851700
C -1.69999100 -3.25205300 -2.05337200
F -1.72373100 1.90647000 2.29825600
F -1.66829900 -0.20467400 2.75283200
H -2.20400200 -4.22061500 -1.99943100
H -2.40355700 -2.51632700 -2.44826100
H -0.86715300 -3.33326100 -2.75486300
H 0.12915600 -3.66633200 0.88102900
H -0.70008100 -4.87887900 -0.09684700
H 0.66056700 -3.97578300 -0.78300300

H -2.07962100 -2.46653100 1.32095600
H -3.11249100 -1.97495700 -0.03602200
H -2.92165700 -3.68712200 0.36664200
H 2.84094200 1.15777100 -1.67005200
H 5.26782900 1.37721200 -1.27486100
H 6.32455300 0.30657400 0.70206700
H 4.90857800 -0.98718900 2.28016400
H 2.49782200 -1.21174700 1.89907300
H 0.26243600 -1.35440700 1.44250300

F' intermediate
E(ωB97X-D/6-311+G**) = -1381.91630651
G(403K)= -1381.698815
C 2.81231900 -1.66914900 0.46328600
C 2.15236200 -1.02188200 -0.57656400
H 2.24720300 -2.05672300 1.30036100
C 4.19511400 -1.80676100 0.41515900
H 4.70342600 -2.31245200 1.22836800
C 4.92406900 -1.29532800 -0.65083800
H 6.00207900 -1.40223900 -0.67850800
C 4.25640900 -0.65120100 -1.68775100
H 4.81058200 -0.25627300 -2.53162700
C 2.87570800 -0.52088400 -1.65890000
H 2.35929900 -0.04457100 -2.48501300
N 0.73788300 -0.88372100 -0.60342100
N 0.06645300 -1.21432100 0.62760700
N 0.39633400 -0.00552100 1.53177100
C -1.29808400 -0.95317500 0.19574600
C -2.38035500 -1.78448400 0.80567600
F -2.30700400 -1.73946000 2.14106100
F -3.59436300 -1.35806000 0.44560000
F -2.26830100 -3.06551700 0.43663000
H 0.49651300 1.06435400 -1.55993900
F -3.19297500 -0.06210400 -2.04347200
C -2.41147600 0.77820000 -1.35994600
F -1.91247400 1.66560700 -2.23910100
C 0.17187700 0.46151700 -0.71953900
C 0.48939400 0.96466400 0.72539700
C -1.30008600 0.07165600 -0.65075900
C 0.86230000 2.37591500 1.06721500
F -3.19284800 1.46436800 -0.51271100
C 0.98864000 2.54764200 2.58253800
C 2.21302800 2.67177600 0.38802600
C -0.22542100 3.30974900 0.51186200
H 1.27089400 3.57913300 2.80965500
H 0.04283500 2.32911400 3.08305200
H 1.74990400 1.88034400 2.99152800
H 0.03759900 4.34743800 0.73170000
H -0.32974500 3.21862400 -0.57299900
H -1.19567300 3.10275300 0.97098100
H 2.51848400 3.69514200 0.62100200
H 2.98751700 1.98757100 0.74369200
H 2.15129800 2.57969500 -0.69965400

TS3
E(ωB97X-D/6-311+G**) = -1381.91070937
G(403K)= -1381.693164
C 4.18652900 -1.78234300 0.46605800
C 2.80122800 -1.66562100 0.47924100
C 2.16334200 -1.03471600 -0.58275800
C 2.89988900 -0.53158200 -1.65315100
C 4.28265600 -0.64065700 -1.64646300
C 4.93188500 -1.26673200 -0.58687800
N 0.75003000 -0.89222500 -0.62248800
C 0.15881700 0.40486200 -0.74756700
C 0.46948600 0.93207400 0.81207100
C 0.86250600 2.37592100 1.03574600
C 0.99259200 2.65003000 2.53694900
N 0.03458200 -1.40328400 0.43634100
N 0.38744300 0.01191900 1.62688100
C -1.28220400 -1.03976500 0.10476000
C -2.39078900 -1.81809100 0.74637100
F -3.57237700 -1.21075600 0.59485500
C -1.28244200 0.04699400 -0.68606800
C -2.40061100 0.83937400 -1.27727000
F -3.28459200 0.06291400 -1.91206500
F -3.07403000 1.54869100 -0.35747600
F -1.92451200 1.72137000 -2.17596900
C 2.21912200 2.59898000 0.34392700
C -0.20689300 3.29016400 0.42365000
F -2.49278600 -3.04222500 0.20967400
F -2.16930900 -1.96766000 2.05469900
H 1.28212600 3.69243100 2.69560800
H 0.04475100 2.47255800 3.04959800
H 1.74958800 2.00554600 2.98818800
H 2.55224200 3.62343400 0.52961400
H 2.97530900 1.91182000 0.73164400
H 2.15654800 2.46015000 -0.73851300
H 0.07498800 4.33372300 0.58532000
H -0.31274000 3.14140300 -0.65406600
H -1.18058500 3.12710600 0.89180300
H 4.85287400 -0.24623500 -2.47957500
H 6.01175000 -1.35789000 -0.58700300
H 4.68352100 -2.27362600 1.29470500
H 2.21706700 -2.05070400 1.30392600
H 2.39375800 -0.07102400 -2.49424000
H 0.52219500 1.05205100 -1.53731600

G intermediate (van der Waals complex of **5** + ^{t}BuCN)
E(ωB97X-D/6-311+G**) = -1382.02236899
G(403K)= -1381.815373
C 2.48645700 -0.13645100 -1.62514400
C 0.03896700 0.48438800 -1.31207000
C -4.78838000 1.92945400 -0.31595600
N 0.07630200 1.42513200 0.71308700
F 2.08095800 2.14882300 2.32290700
C 2.40236200 1.24302600 1.39934700
F 2.68647000 0.09613300 2.04354000
F 3.53311700 1.64678800 0.80180300
C -2.08017300 1.36606300 -0.33381400
C -2.94576100 0.56990500 -1.07331800
C -4.30339400 0.86421300 -1.06503700
H -2.57828100 -0.28543300 -1.62679500
H -4.98201400 0.24531500 -1.63987900
C -3.90873100 2.70919400 0.42730600
H -1.85302800 3.03757300 0.99066800
C -2.54769000 2.43591500 0.41959500
F 3.30608400 0.81097800 -2.11332200
H -0.40181000 0.14037800 -2.23248600
F 2.05742000 -0.85980800 -2.67063100
H -5.84944500 2.14949300 -0.30824100
F 3.23938300 -0.94351800 -0.85894000
C 1.29982800 1.04960300 0.40109200
C 1.33938000 0.43560900 -0.87080700
N -0.68058100 1.07867100 -0.33566800
N -1.43200600 -2.48977000 -1.65935600
C -1.26234600 -2.66486400 -0.53393300
C -1.04436500 -2.87303500 0.90746100
H -4.27989800 3.54166400 1.01335500
C -1.95170500 -1.90313200 1.68385600
C -1.39589200 -4.33076600 1.24825700
C 0.43341600 -2.58357000 1.21681200
H -1.79944500 -2.06118800 2.75432000
H -1.71133100 -0.86240100 1.45642400
H -3.00545500 -2.07510100 1.45416200
H -1.22729900 -4.49447400 2.31551100
H -2.44351400 -4.54575700 1.02685700
H -0.76956400 -5.02786800 0.68777000

H 0.61606000 -2.74412500 2.28193800
H 1.09598300 -3.23685500 0.64571500
H 0.68030400 -1.54731300 0.98415900

XYZ coordinates of other investigated systems

6
E(ωB97X-D/6-311+G**) = -2067.85434537
G(298K)= -2067.729907
C 1.04597800 5.06123200 -0.03183100
C 0.14242800 4.78304200 0.98885100
C -0.62009500 3.62461600 0.95184000
C -0.47545600 2.75926000 -0.12418000
C 0.40143000 3.03783300 -1.16228000
C 1.17343400 4.19084600 -1.10717400
N -1.22376800 1.53874000 -0.14748300
P -0.56106800 -0.00893800 -0.18485600
W 1.80039500 -0.66135500 0.03890800
C 1.53626800 -2.35873300 -1.13136300
O 1.43943800 -3.28653600 -1.78155400
N -2.55556300 1.60546500 -0.07042300
C -3.05566200 0.39259000 -0.05220400
C -2.12832400 -0.67365400 -0.11637800
C -2.42623700 -2.13788200 -0.06866800
F -2.73345300 -2.54945600 1.16955500
C -4.56361400 0.28106500 -0.01956500
F -5.04960600 -0.02033000 -1.23214200
F -4.95752100 -0.68241300 0.82386200
F -5.12806700 1.42056500 0.37132400
F -1.35246200 -2.85338500 -0.45820400
F -3.43998600 -2.48009000 -0.86994400
C 2.40414900 0.35786300 -1.65426400
O 2.76440300 0.90635700 -2.58727700
C 2.17242300 1.03113400 1.17808100
O 2.41874300 1.95031200 1.80363700
H 1.86602200 4.41092800 -1.91072300
H 1.64673100 5.96218700 0.00936700
H 0.03933100 5.46550800 1.82404000
H -1.32002300 3.38454000 1.74283900
H 0.46701100 2.36688200 -2.00985300
C 1.25829800 -1.73523800 1.73606300
O 0.98053300 -2.33038000 2.66481300
C 3.73037900 -1.22362300 0.35239400
O 4.81194500 -1.53741400 0.53630300

6 (in case of coordination to the nitrogen atom)
E(ωB97X-D/6-311+G**) = -2067.83736022
G(298K) = -2067.711662
C 0.25169000 2.56100100 -0.22266000
C 0.57198500 3.43631100 0.80460900
C 1.59517800 4.35494200 0.61169600
C 2.29072300 4.38174600 -0.58974200
C 1.95432900 3.50075900 -1.61314300
C 0.91922800 2.59530100 -1.44046200
N -0.85526000 1.66433800 -0.05357600
N -0.73423400 0.35346700 -0.32722700
C -1.94906700 -0.19488600 -0.30078400
C -2.11770000 -1.64449300 -0.71461900
F -1.76153100 -2.49317500 0.25352300
P -2.39468700 2.25071400 0.30620200
C -2.99587300 0.66392800 0.06831300
C -4.45386800 0.35343000 0.25619000
F -5.09579900 0.14585100 -0.89679900
F -5.05400600 1.40848400 0.84852600
F -4.65647900 -0.70507700 1.04455300
F -3.39036900 -1.89798500 -1.01930800
F -1.39362500 -1.91306800 -1.80403800
H 1.86378100 5.03255400 1.41269800
H 3.09831700 5.09018800 -0.73046000
H 2.49249700 3.52240000 -2.55297400
H 0.62893800 1.91773100 -2.23367200
H 0.05280800 3.37625700 1.75403700
W 1.47463100 -0.79806400 0.14377100
C 2.34473600 -0.24623400 -1.64079600
O 2.86181200 0.03970200 -2.61927700
C 2.37029400 0.79490300 1.08673300
O 3.02200800 1.55336300 1.64365000
C 1.03633000 -2.63427500 -0.69977200
O 0.96163800 -3.69322500 -1.11743000
C 0.58832600 -1.34730700 1.93622500
O 0.13092100 -1.65151200 2.93555400
C 3.13732500 -1.70596100 0.67377500
O 4.11014300 -2.23432500 0.98906000

7
E(ωB97X-D/6-311+G**) = -1567.02813923
G(298K)= -1566.808566
C 2.24627300 3.04835700 0.96396200
C 3.63166000 3.11382400 1.00697100
C 4.39023400 2.57833400 -0.02823100
C 3.76303900 1.99229800 -1.12120100
C 2.37683500 1.93675400 -1.18083100
C 1.63195100 2.45379600 -0.13002900
N 0.20690300 2.35135900 -0.15634700
P -0.71553100 0.93536600 -0.20353300
W 0.20437200 -1.39869400 0.03859900
C 0.94153600 -3.25539000 0.33245500
O 1.35967000 -4.30652700 0.50325700
N -0.51356300 3.47575300 -0.07210800
N -1.77289100 3.22920600 -0.05168300
C -2.11201300 1.91637500 -0.11096300
C -3.58035300 1.54826800 -0.07402300
C -4.30962500 2.31302100 -1.19073700
C -3.77939600 0.04458000 -0.27427100
C -4.14204900 1.96537300 1.29621400
C -0.89425200 -1.57605500 1.78681000
O -1.49822800 -1.68760500 2.74722700
C 1.29884000 -1.26360900 -1.70936700
O 1.90714900 -1.21993100 -2.67404300
C 1.82842500 -0.67747200 1.11403800
O 2.73953800 -0.34621200 1.71183000
C -1.33407600 -2.25268100 -1.04459300
O -2.15308200 -2.77116100 -1.64567900
H 5.47220600 2.62094700 0.01662000
H 4.11948500 3.57273600 1.85867000
H 1.63851800 3.44586400 1.76749000
H 4.35006800 1.58381700 -1.93518800
H 1.87594300 1.50661600 -2.03924800
H -4.17530800 3.38966700 -1.07475700
H -5.37933900 2.08717700 -1.15644700
H -3.92866300 2.02301900 -2.17404900
H -4.84544500 -0.19396100 -0.23920000
H -3.28764000 -0.53781300 0.51006000
H -3.39917900 -0.28369200 -1.24541800
H -4.00212500 3.03536000 1.46205100
H -3.64284800 1.42322800 2.10462900
H -5.21195600 1.74256300 1.34448100

7 (in case of coordination to the nitrogen atom closer to the Ph substituent)
E(ωB97X-D/6-311+G**) = -1567.02904162
G(298K)= -1566.811500
C 1.71099900 3.62781200 1.23628500
C 0.66262900 2.71964300 1.21980100
C -0.01938000 2.49937100 0.03074900
C 0.30841200 3.18357700 -1.13064700
C 1.35131400 4.09978300 -1.10046500

C 2.05397300 4.31723100 0.07815200
N -1.10603800 1.56328700 0.01076500
N -0.85821000 0.24883600 0.05418000
N -1.94717900 -0.44623100 0.06468900
C -3.07189200 0.29148400 0.02645400
C -4.40578100 -0.42421100 0.04399000
C -4.51920200 -1.21254200 1.35981000
P -2.75191700 1.98378500 -0.02035600
C -5.55192000 0.58798400 -0.05466900
C -4.46411900 -1.39213500 -1.14909500
H 2.87457000 5.02465200 0.09394700
H 1.62450800 4.63069600 -2.00425100
H -0.23575600 2.98386100 -2.04626000
H 2.25730200 3.79718800 2.15627500
H 0.37548100 2.18041700 2.11405200
H -3.71020400 -1.94050900 1.44782900
H -5.47230200 -1.74815000 1.39070100
H -4.47550500 -0.54202300 2.22284000
H -6.51212200 0.06685400 -0.02818000
H -5.50907200 1.15339400 -0.99120000
H -5.53909400 1.29594000 0.78064700
H -3.65815800 -2.12630700 -1.09403900
H -4.37371600 -0.85367200 -2.09670000
H -5.41945400 -1.92462400 -1.14778500
W 1.16034700 -0.94249400 -0.01982300
C 2.36022100 0.53059000 -0.80594800
O 3.11529800 1.27461000 -1.23755600
C 1.73244600 -0.36505500 1.87031300
O 2.09059100 -0.05925600 2.91377000
C 0.63143800 -1.53337000 -1.93656200
O 0.37002700 -1.87389600 -2.99409200
C 0.09978300 -2.54144800 0.77769400
O -0.42771300 -3.45388700 1.21303500
C 2.76333000 -2.11165800 -0.10609900
O 3.69093200 -2.79176200 -0.15660800

7 (in case of coordination to the nitrogen atom closer to the ^{t}Bu substituent)
E(ωB97X-D/6-311+G**) = -1567.02378855
G(298K)= -1566.804627
C 6.05346700 -0.61106400 0.63831200
C 4.90353800 0.16732900 0.65811600
C 3.76798700 -0.28581200 -0.00075500
C 3.75900300 -1.50608900 -0.66587800
C 4.91038300 -2.28025000 -0.66543000
C 6.05871800 -1.83440200 -0.02031700
N 2.58444700 0.52211400 0.00082100
N 1.43281500 -0.10879900 0.04235200
N 0.42364200 0.71082100 0.00223500
C 0.78863700 2.02395800 -0.06601100
C -0.20704900 3.16664400 -0.10980600
C -1.05445900 3.15461300 1.17341400
P 2.49750300 2.22174800 -0.10046900
C 0.54315500 4.50661700 -0.17256200
C -1.07307700 3.04950700 -1.37497900
H 6.95608100 -2.44182400 -0.02792200
H 4.90903800 -3.23496900 -1.17763700
H 2.86027000 -1.84078800 -1.16726800
H 6.94223300 -0.26269400 1.15073800
H 4.88706600 1.10958500 1.19372600
H -1.55220800 2.19876900 1.32453500
H -1.81987200 3.93305800 1.12037200
H -0.42576200 3.34888000 2.04686800
H -0.18136000 5.32392900 -0.20304800
H 1.16323500 4.58496200 -1.07136500
H 1.17558100 4.66204200 0.70727800
H -1.58295900 2.09013600 -1.43395700
H -0.45602600 3.15865900 -2.27116900
H -1.83001400 3.83789500 -1.38001400
W -1.57748400 -0.66292400 0.03835800
C -1.55974700 -0.67661600 -2.02649300
O -1.56044200 -0.69119500 -3.16916000
C -0.32711800 -2.32161900 0.05545200
O 0.26473000 -3.29757000 0.05646200
C -3.08511700 0.72500500 0.01871600
O -4.01302800 1.39790900 0.00793600
C -1.53497100 -0.59140700 2.10586000
O -1.52364300 -0.55613800 3.24721000
C -3.06725400 -1.96149300 0.06965200
O -3.93223700 -2.72250100 0.08702900

2. Experimental Procedures

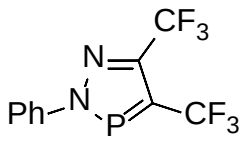
2.1 General Information

All reactions involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques or in an MBraun glovebox under an argon atmosphere. All common chemicals and solvents were commercially available. 2,5-diisopropylphenyl azide [7], *tert*-butylphosphaalkyne [8] and 5-(*tert*-butyl)-3-phenyl-3*H*-1,2,3,4-triazaphosphole (**1**)[9] were prepared by methods described in the literature. Hexafluoro-2-butyne was purchased at 99% purity from ABCR. Commercially available chemicals were used without further purification. Toluene and *n*-pentane were prepared using an MBraun Solvent Purification System MB-SPS 800. THF was dried over K/benzophenone under argon. The deuterated dry solvents DCM-d_2 were dried over CaH_2 and THF-d_8 and benzene-d_6 over a sodium-potassium alloy. ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectra were recorded by using a JEOL ECS400 spectrometer (400 MHz), or a JEOL ECZ600 spectrometer (600 Hz). All chemical shifts are reported relative to the residual resonance in the deuterated solvents. IR spectra were recorded on a 5 SXC Nicolet FT-IR spectrometer with a DTGS detector (**6**) and on a Bruker Alpha FTIR spectrometer equipped with a diamond ATR in the solid state (pure powder) under an argon atmosphere (**7**, **9**). Characteristic absorption bands are given in wavenumbers (in cm^{-1}). ESI-MS spectra were recorded on an Agilent 6210 ESI-TOF (4 kV) from Agilent Technologies. EI measurements were conducted with a modified device of a MAT 711 from Varian MAT. CHN-Analysis was performed on an ELEMENTAR VARIO EL.

Caution: Azides are potentially hazardous compounds and adequate safety measures should be taken when weighing, heating and working up.

2.2 Synthesis and Characterization

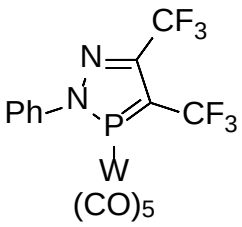
2-phenyl-4,5-bis(trifluoromethyl)-2*H*-1,2,3-diazaphosphole (3)



1 (500 mg, 2.28 mmol, 1 eq.) was placed in a pressure tube, and dissolved in dry toluene (10 mL). The solution was frozen at *T* = -160°C and hexafluoro-2-butyne was condensed in excess (11 mmol, 5 eq.). The reaction mixture was warmed overnight and heated at *T* = 60 °C for eight weeks. The excess hexafluoro-2-butyne was removed with the solvent in vacuo, and the compound was crystallized from DCM. **3** was obtained as a light brown crystalline material (590 mg, 87%).

^{1}H-NMR (400 MHz, THF-d_8): δ = 7.93 – 7.85 (m, 2H, H_{Ar}), 7.60 – 7.51 (m, 2H, H_{Ar}), 7.51 – 7.44 (m, 1H, H_{Ar}) ppm. $^{13}C\{^{1}H\}$-NMR (176 MHz, THF-d_8): δ = 146.4 - 145.6 (m, P*C*CF_3), 144.5 - 143.6 (m, N*C*CF_3), 143.5 (d, *J* = 11.5 Hz, C_{Ar}), 130.9 (C_{Ar}), 130.2 (d, *J* = 1.7 Hz, C_{Ar}), 124.6 (q, *J* = 269.2 Hz, *C*F_3), 124.5 (q, *J* = 269.4 Hz, *C*F_3), 122.1 (d, *J* = 9.6 Hz, C_{Ar}) ppm. $^{31}P\{^{1}H\}$-NMR (162 MHz, THF-d_8): δ = 233.9 (q, $^{3}J_{P\text{-}F}$ = 22.9 Hz) ppm. ^{19}F-NMR (377 MHz, THF-d_8): δ = -53.3 (dq, *J* = 25.7, 7.2 Hz, PCCF_3), -61.8 (qd, *J* = 7.3, 1.2 Hz, NCCF_3) ppm. EI (m/z): 298.0097 g/mol (calc.: 298.0095 g/mol) $[M]^+$. ESI-TOF (m/z): 299.1622 g/mol (calc.: 299.0167 g/mol) $[M+H]^+$.

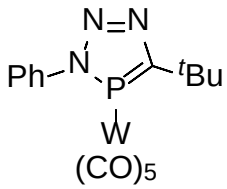
2-Benzyl-4,5-bis(trifluoromethyl)-2*H*-1,2,3-diazaphosphole-*P*-pentacarbonyl-tungsten(0) (6)



In a J-Young NMR tube, **3** (15.0 mg, 0.05 mmol) was placed together with $W(CO)_6$ (17.7 mg, 0.05 mmol) and dissolved in dry deuterated THF (0.5 mL). The reaction mixture was irradiated with a UV lamp (100 W, 365 nm) for 68 h at room temperature. The reaction solution was filtered over Celite and the solvent was removed in vacuo. According to NMR spectroscopy, **6** was quantitatively obtained as a dark brown solid. Single Crystals of were obtained by evaporation of the solvent of a saturated *n*-pentane solution of **6**.

^{1}H-NMR (400 MHz, THF-d_8): δ = 7.70 - 7.65 (m, 2H, H_{Ar}), 7.61 - 7.54 (m, 3H, H_{Ar}) ppm. ^{13}C{^{1}H}-NMR (101 MHz, THF-d_8): δ = 196.0 (d, J = 43.3 Hz, CO_{trans}), 192.8 (d, J = 9.0 Hz, CO_{cis}), 140.9 (m, CCF$_3$), 131.4 (C_{Ar}), 130.9 (C_{Ar}), 130.6 (C_{Ar}), 128.3 (d, J = 4.0 Hz, C_{Ar}), 124.6 (q, J = 268.6 Hz, CCF$_3$), 120.9 (q, J = 222.2 Hz. CCF$_3$) ppm. ^{31}P{^{1}H}-NMR (162 MHz, THF-d_8): δ = 217.3 (q, $^1J_{P\text{-}W}$ = 326.5 Hz, $^3J_{P\text{-}F}$ = 16.1 Hz) ppm. ^{19}F-NMR (377 MHz, THF-d_8): δ = -51.3 (dq, J = 16.2, 8.1 Hz), -62.9 (qd, J = 8.1, 0.3 Hz) ppm. IR (solid): $\tilde{\nu}$ = 2089, 2017, 2002, 1934 cm^{-1}. EI (m/z): 621.9389 g/mol (calc.: 621.9350 g/mol) [M]$^+$.

5-(*tert*-butyl)-3-phenyl-3*H*-1,2,3,4-triazaphosphole-*P*-pentacarbonyl-tungsten(0) (7)

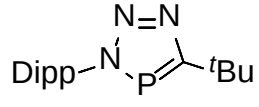


1 (30.0 mg, 0.14 mmol) and tungsten hexacarbonyl (40.9 mg, 0.14 mmol) were placed in a *J*-Young NMR tube and dissolved in THF-d$_8$ (0.7 mL). The reaction mixture was irradiated with a UV lamp (100 W, 365 nm) for 5 days at room temperature, with overpressure released from the J-Young NMR tube twice a day. After removing the solvent under high vacuum, **7** was obtained as a brown solid.

^{31}P{^{1}H}-NMR (162 MHz, THF-d_8): δ = 136.1 ($^1J_{P\text{-}W}$ = 260 Hz) ppm, ^{1}H-NMR (400 MHz, DCM-d_2): δ = 7.58 (dd, J = 5.1, 1.8 Hz, 2H, H_{Ar}), 7.51 (td, J = 7.3, 2.0 Hz, 3H, H_{Ar}), 1.61 (d, J = 0.9 Hz, 9H, C(CH_3)$_3$) ppm.^{13}C{^{1}H}-NMR (101 MHz, THF-d_8): δ = 197.53(CO_{trans}), 196.08 (d, J = 8.8 Hz, CO_{cis}), 162.56 (C=P), 124.47 (d, J = 6.6 Hz, C_{Ar}), 121.9 (C_{Ar}), 121.36 (d, J = 14.9 Hz, C_{Ar}), 120.84 (d, J = 2.5 Hz, C_{Ar}), 36.35 (d, J = 13.7 Hz, C(CH$_3$)$_3$), 32.84 (d, J = 11.1 Hz, C(CH_3)$_3$) ppm. EI (m/z): 543.0168 g/mol (calc.: 543.0180 g/mol) [M]$^+$. IR (solid): $\tilde{\nu}$ = 2077, 2023, 1980, 1885 cm^{-1}.

5-(*tert*-butyl)-3-(2,6-diisopropylphenyl)-3*H*-1,2,3,4-triazaphosphole (8)

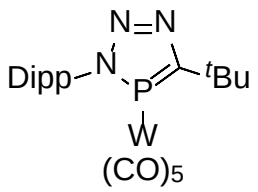
2,6-Diisopropylphenyl azide (0.46 g, 2.27 mmol) was added to a 100 mL Normag flask with a stir bar, the azide was



frozen at T = -160°C, and the flask was evacuated. Subsequently, an excess of *tert*-butylphosphaalkyne in 50 mL dry toluene was condensed into the reaction flask. The reaction solution was warmed to r.t. and stirred for 24 h. The reaction was stopped and the solvent and excess alkyne were removed in vacuo. The resulting solid was recrystallized from a hot saturated n-pentane solution. Triazaphosphole **8** was obtained as an off white solid (0.69 g, 64%).

^{1}H-NMR (400 MHz, DCM-d_2): δ = 7.49 (t, J = 7.8 Hz, 1H, H_{Ar}), 7.32 (d, J = 7.8 Hz, 2H, H_{Ar}), 2.18 (hept, J = 6.8 Hz, 2H, $H_{i\text{-}Propyl}$), 1.55 (d, J = 1.3 Hz, 9H, C(CH$_3$)$_3$), 1.13 (dd, J = 6.8, 4.7 Hz, 12H, $H_{i\text{-}Propyl}$) ppm. ^{13}C{^{1}H}-NMR (101 MHz, DCM-d_2): δ = 199.9 (d, J = 57.9 Hz, C=P), 149.6 (C_2), 136.0 (d, J = 7.8 Hz, C_4), 130.6 (C_1), 124.3 (C_1), 35.9 (d, J = 14.9 Hz, C(CH$_3$)$_3$), 32.03 (d, J = 7.5 Hz, C(CH_3)$_3$), 28.86 ($H_{i\text{-}Propyl}$), 24.66 (d, J = 20.7 Hz, $H_{i\text{-}Propyl}$) ppm. ^{31}P{^{1}H}-NMR (162 MHz, DCM-d_2): δ = 179.5 ppm.

5-(*tert*-butyl)-3-(2,6-diisopropylphenyl)-3*H*-1,2,3,4-triazaphosphole *P*-pentacarbonyl-tungsten(0) (9)



8 (50.0 mg, 0.16 mmol) and tungsten hexacarbonyl (58.0 mg, 0.16 mmol) were placed in a *J*-Young NMR tube and dissolved in THF-d_8 (0.7 mL). The reaction mixture was irradiated with a UV lamp (100 W, 365 nm) for 5 days at room temperature, with overpressure released from the J-Young NMR tube twice a day. The crude product was sublimed at *T* = 60°C for 2 hours. **9** stayed behind during sublimation and was obtained as a green solid. Single Crystals of were obtained by evaporation of the solvent of a saturated THF solution of **9**.

^{1}H-NMR (400 MHz, DCM-d_2): δ = 7.54 (t, *J* = 7.8 Hz, 1H, H_{Ar}), 7.35 (d, *J* = 7.8 Hz, 2H, H_{Ar}), 2.24 (hept, *J* = 6.8 Hz, 2H, $H_{i\text{-}Propyl}$), 1.65 (s, 9H, $C(CH_3)_3$), 1.24 (d, *J* = 6.8 Hz, 6H, $H_{i\text{-}Propyl}$), 1.06 (d, *J* = 6.8 Hz, 6H, $H_{i\text{-}Propyl}$) ppm. $^{31}P\{^1H\}$-NMR (162 MHz, DCM-d_2): δ = 160.6 ($^1J_{P\text{-}W}$ = 285.6 Hz) ppm. IR (solid): $\tilde{\nu}$ =2081, 2000, 1954, 1934 cm^{-1}. EI (m/z): 627.1133 g/mol (calc.: 627.1119 g/mol) $[M]^+$. C-H-N-Analysis: N: 6.85; C: 42.92; H: 5.85, (Calc.: N: 6.70; C: 42.13; H: 4.18).

2. Crystallographic Details

X-ray studies were carried out on a D8 Venture, Bruker Photon CMOS diffractometer[10] (MoKα radiation; λ = 0.71073 Å) up to a resolution of $(\sin\Theta/\lambda)_{max}$ = 0.58 Å (**6**) 0.60 Å (**3**, **9**) at 100(2) K. The structures of **3** and **6** were solved with SHELXS-2014[10] using direct methods and refined with SHELXL-2014[11] on F^2 for all reflections. The structure of **9** was solved with SHELXT-2014/5[12a] by using direct methods and refined with SHELXL-2017/1[12b] on F^2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[13] Crystal data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Database Center: CCDC number: 2163856 (**3**), CCDC number: 2163857 (**6**) and CCDC number: 2163858 (**9**). Details of the X-ray structure determinations and refinements are provided in Table S4.

Table S4. Crystal data and structure refinement for **3**, **6** and **9** (CCDC: 2163856 (**3**), 2163857 (**6**) 2163858 (**9**)).

Identification code	**3**	**6**	**9**
Empirical formula	$C_{10}H_5F_6N_2P$	$C_{15}H_5F_6N_2O_5PW$	$C_{22}H_{26}N_3O_5PW$
Formula weight	298.13	622.03	627.28
Temperature/K	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	triclinic
Space group	P b c a	$P2_1/c$	P-1
a/Å	7.5247(5)	6.6629(3)	11.1075(2)
b/Å	12.9354(9)	18.3901(8),	14.6470(2)
c/Å	22.6658(15)	15.6561(7)	16.9008(3)
α/°	90	90	112.5214(6)
β/°	90	100.123(2)	102.9855(5)
γ/°	90	90	91.3575(5)
Volume/Å^3	2206.2(3)	1888.50(15)	2456.50(7)
Z	8	4	4
ρ_{calc}g/cm^3	1.795	2.188	1.696
μ/mm^{-1}	0.318	6.290	4.804
F(000)	1184	1168.0	1232.0
Crystal size/mm^3	0.2 x 0.15 x 0.06	0.24x0.11x0.02	0.40 × 0.34 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα(λ = 0.71073)
2Θ range for data collection/°	6.5 to 54.336	5.158 to 61.114	3.792 to 56.564
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -29 ≤ l ≤ 28	-9 ≤ h ≤ 9, -25 ≤ k ≤ 25, -22 ≤ l ≤ 21	-13 ≤ h ≤ 14, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected	18484	30420	68480
Independent reflections	2444 [R_{int} = 0.0329, R_{sigma} = 0.0229]	5650 [R_{int} = 0.0282, R_{sigma} = 0.0210]	12174 [R_{int} = 0.0425, R_{sigma} = 0.0292]
Data/restraints/parameters	2444/0/172	5650/0/271	12174/0/591
Goodness-of-fit on F^2	1.171	1.178	1.040
Completeness to θ	99.4%	97.3%	99.8%
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1017	R_1 = 0.0192 wR_2 = 0.0413	R_1 = 0.0192, wR_2 = 0.0440
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1047	R_1 = 0.0223 wR_2 = 0.0422	R_1 = 0.0220, wR_2 = 0.0452
Largest diff. peak/hole/e Å^{-3}	0.52/-0.37	0.57/-1.70	1.15/-1.22

3. NMR Spectroscopic Data

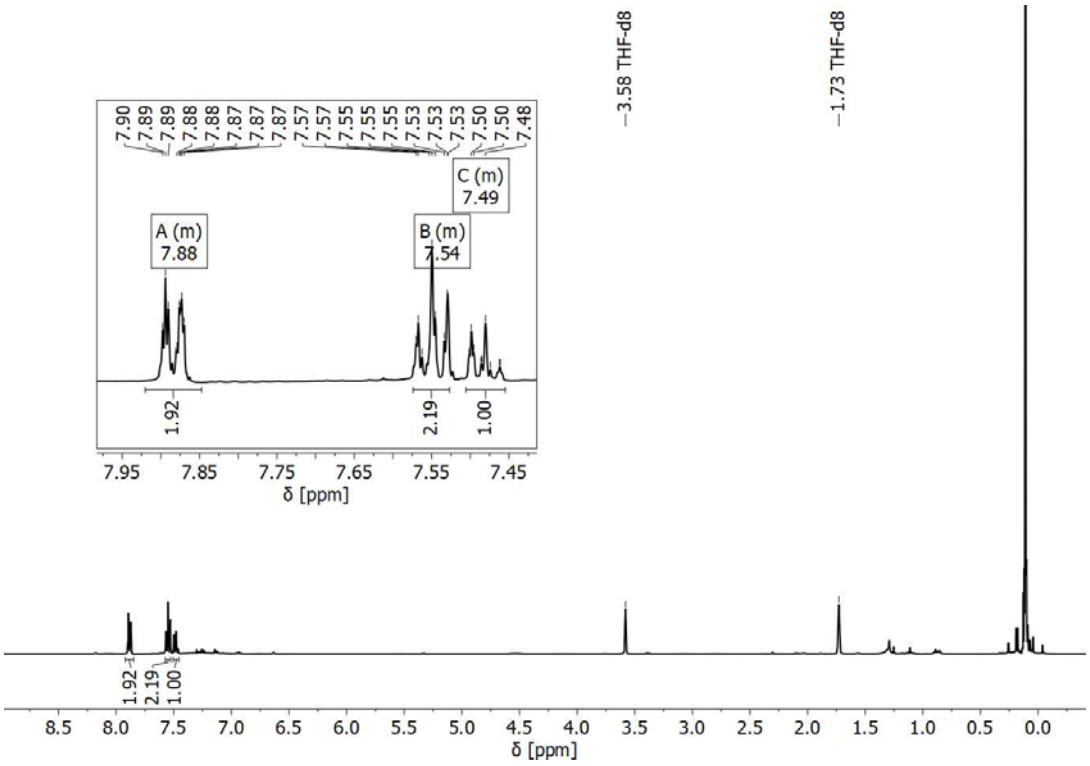


Figure S2. ^{1}H NMR spectrum of **3** in THF-d_8.

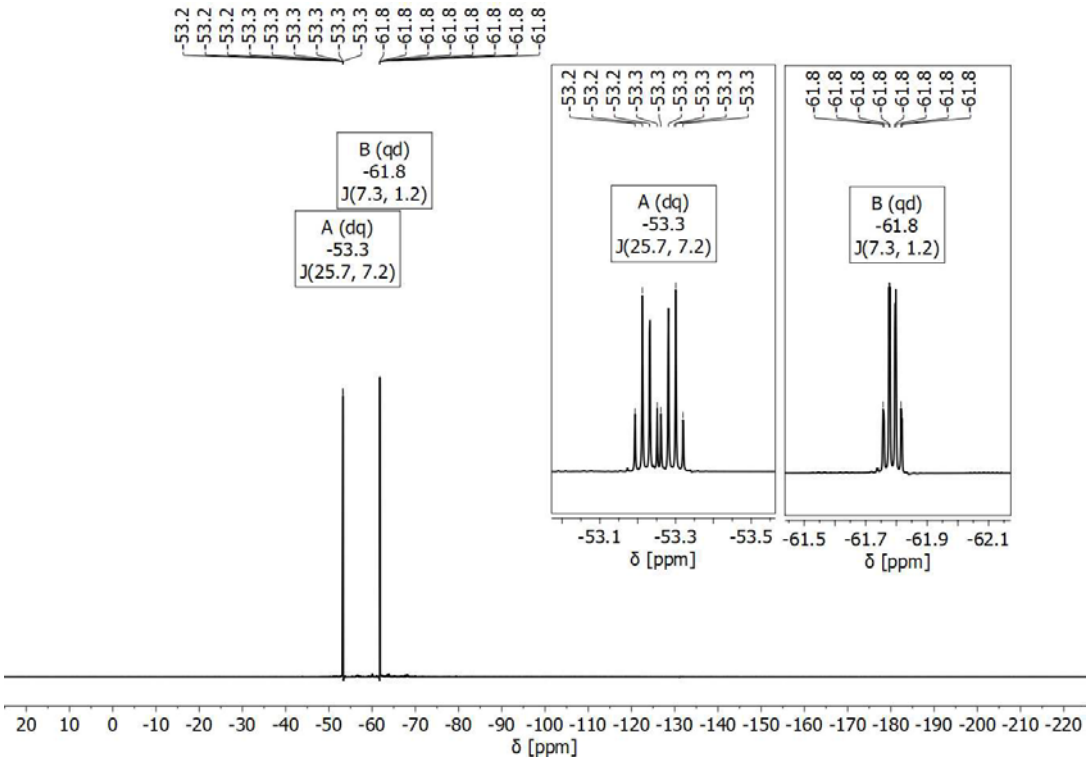


Figure S3. ^{19}F NMR spectrum of **3** in THF-d_8.

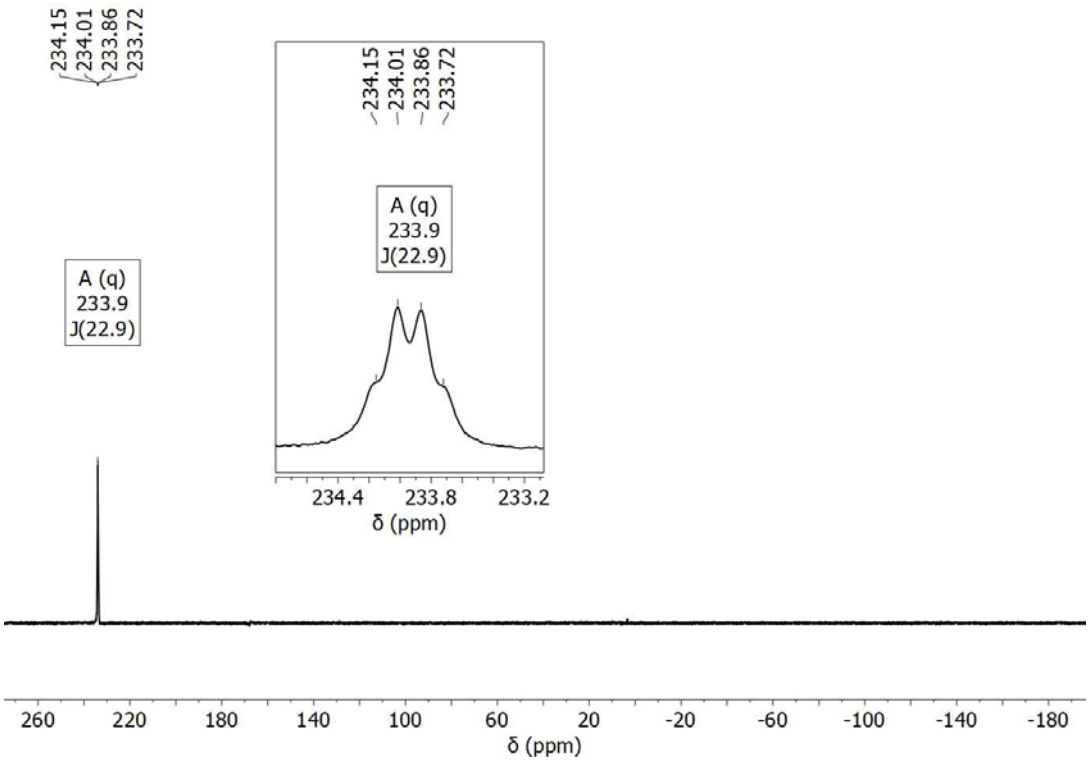


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in THF-d_8.

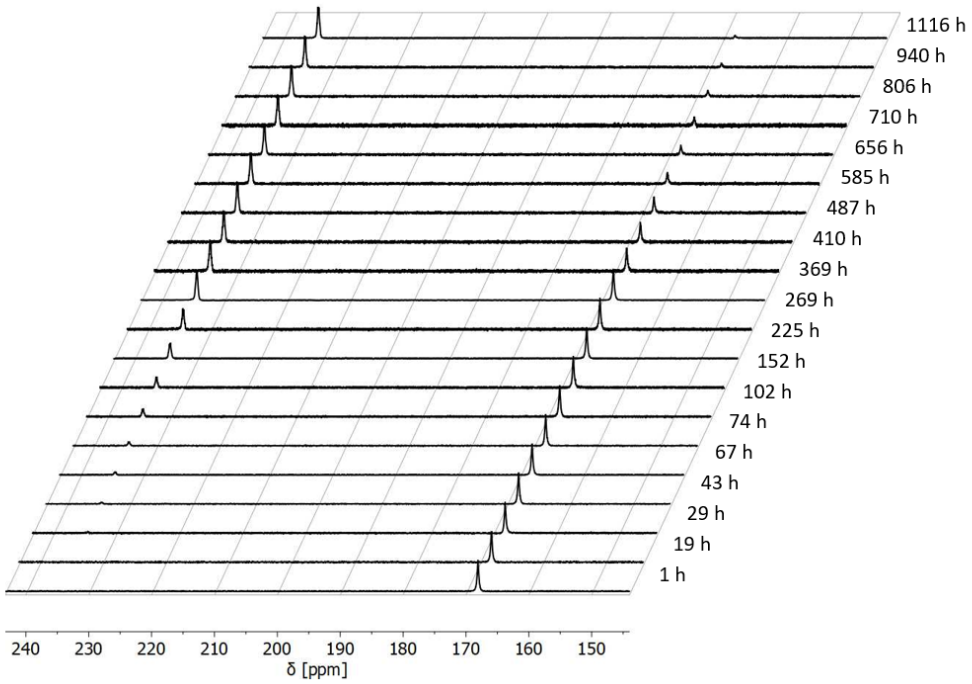


Figure S5. Advance of the [4+2]-cycloaddition reaction of **1** (δ = 169.3 ppm) with Hexafluoro-2-butyne according to $^{31}P\{^{1}H\}$ NMR spectroscopy over t = 1116 h.

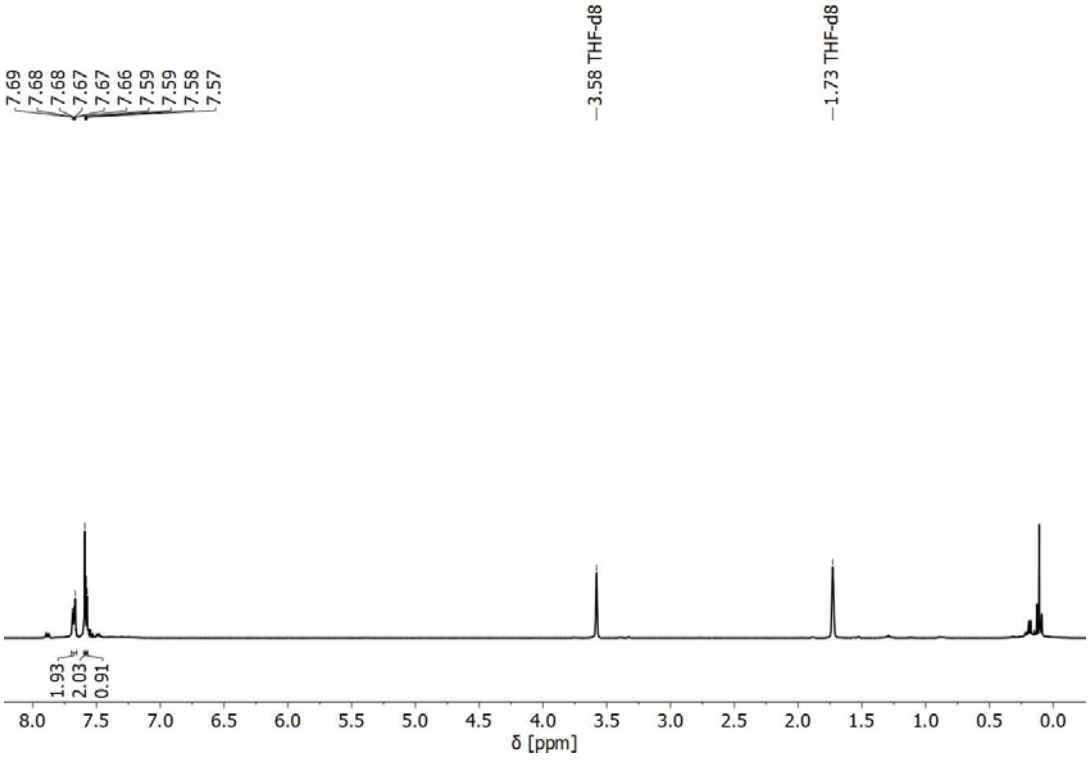


Figure S6. ^{1}H NMR spectrum of **6** in THF-d_8.

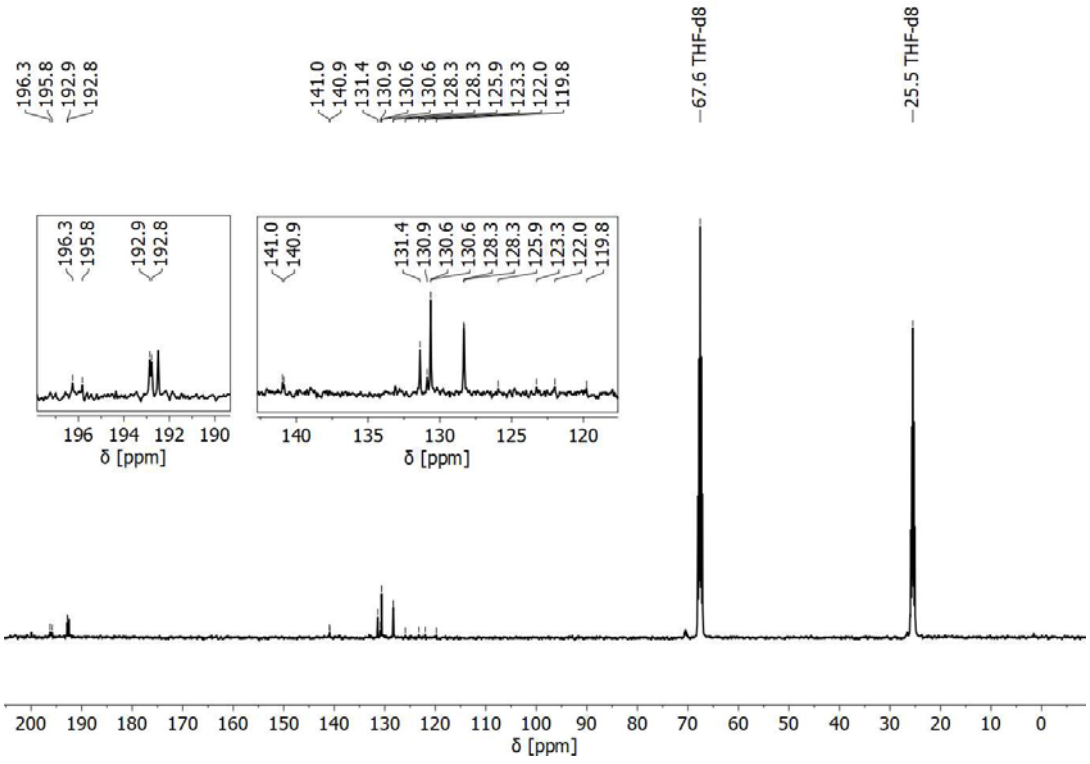


Figure S7. ^{13}C{^{1}H} NMR spectrum of **6** in THF-d_8.

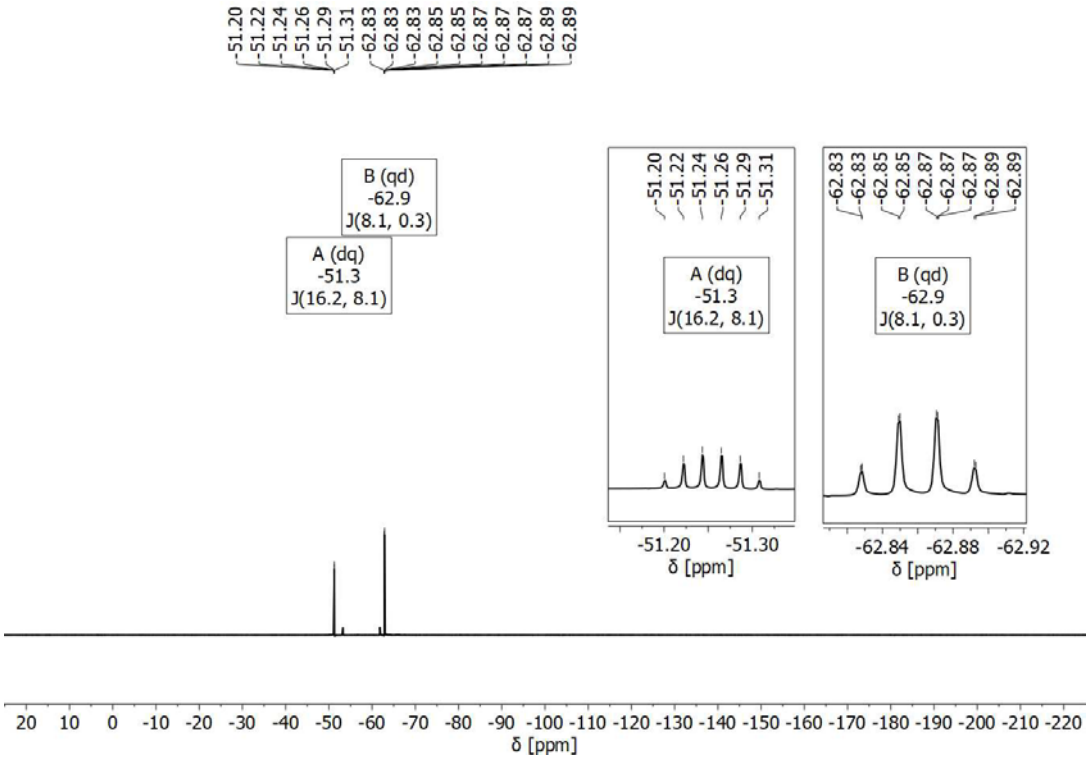


Figure S8. ^{19}F NMR spectrum of **6** in THF-d_8.

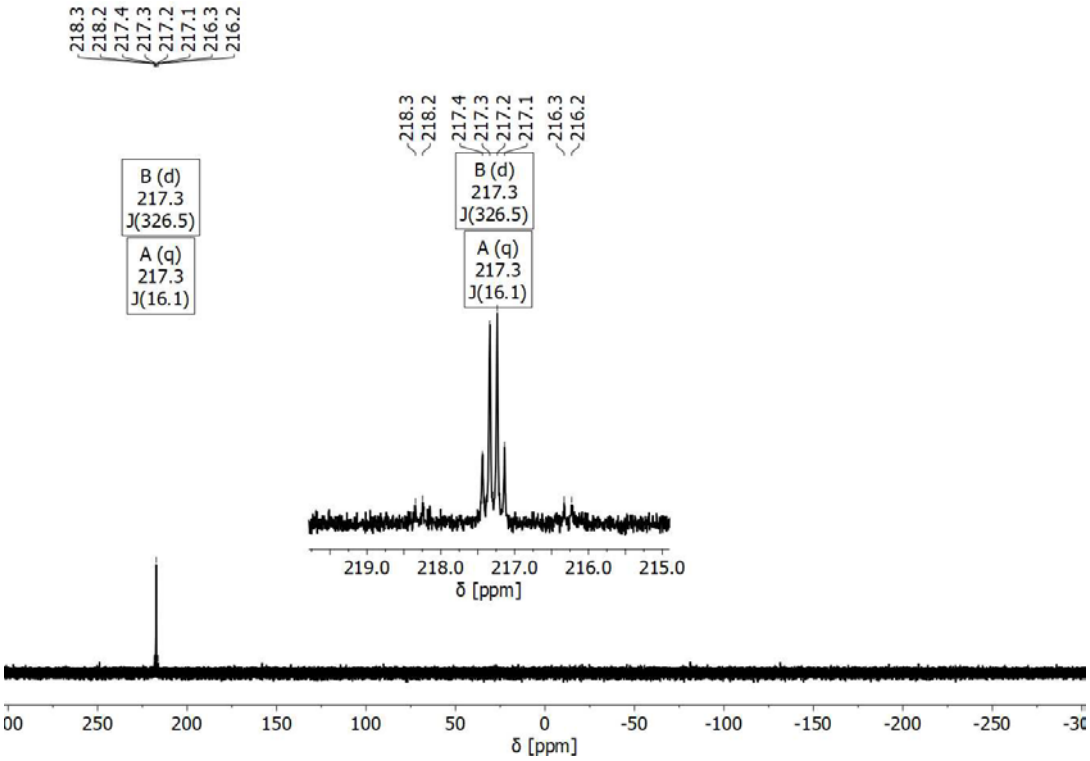


Figure S9. $^{31}P\{^1H\}$ NMR spectrum of **6** in THF-d_8.

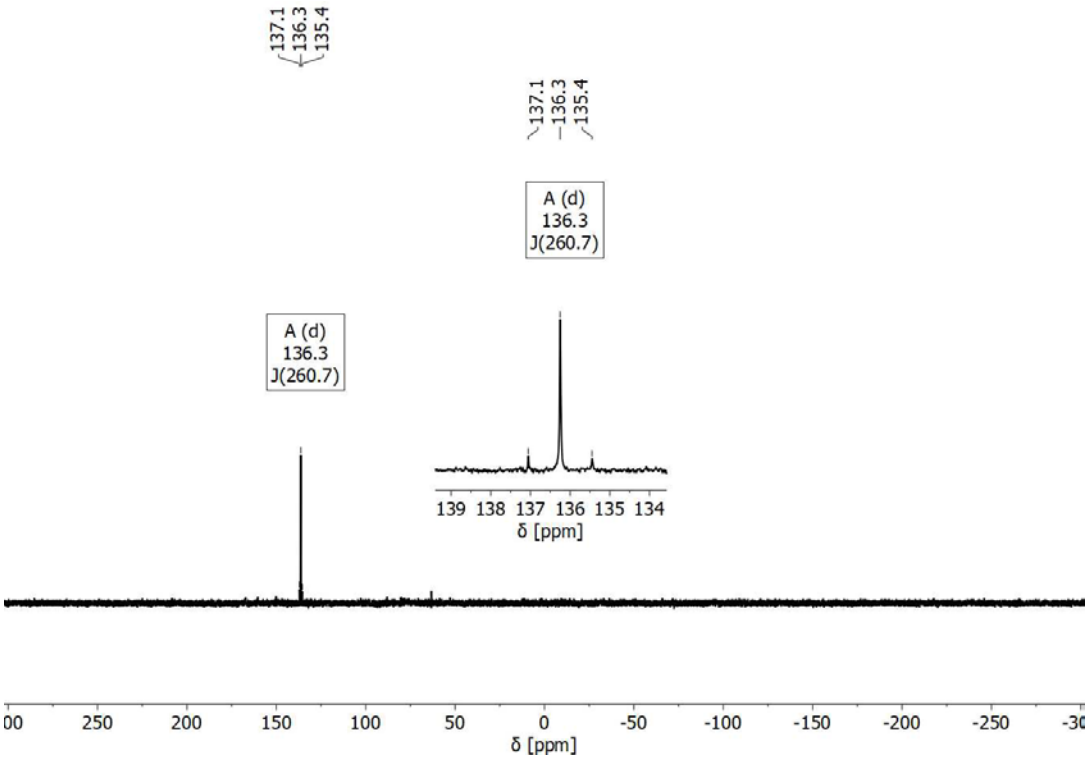


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in THF-d_8.

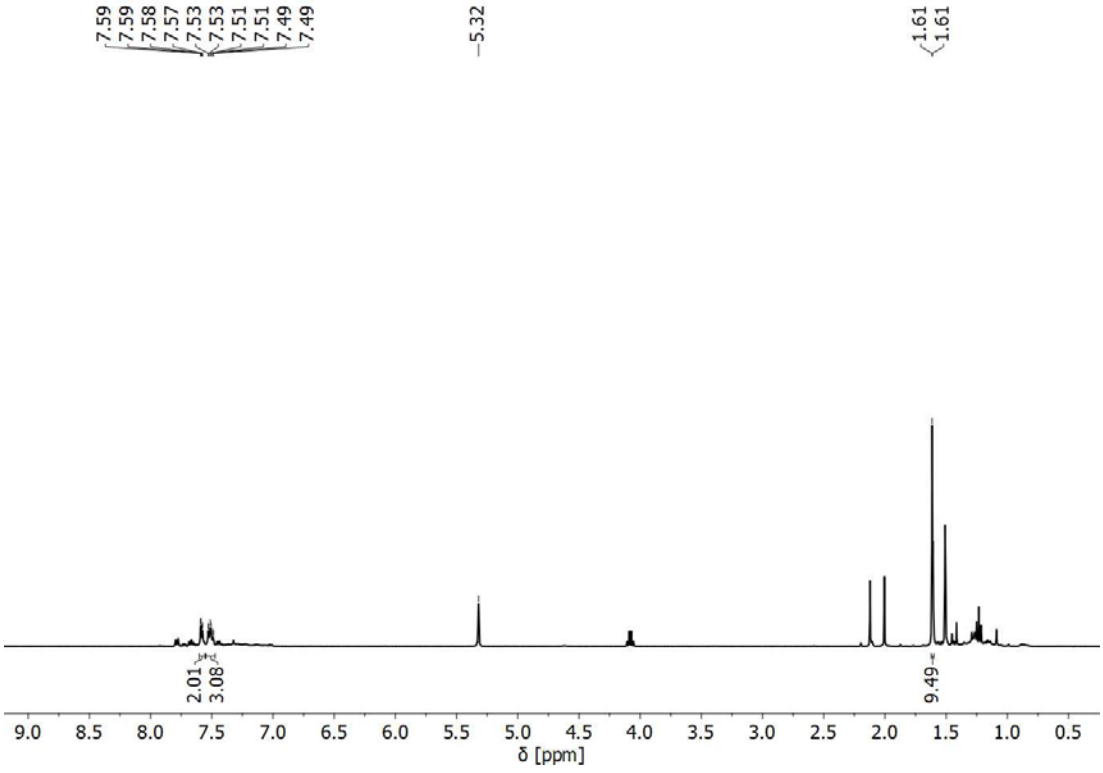


Figure S11. ^{1}H NMR spectrum of **7** in DCM-d_2.

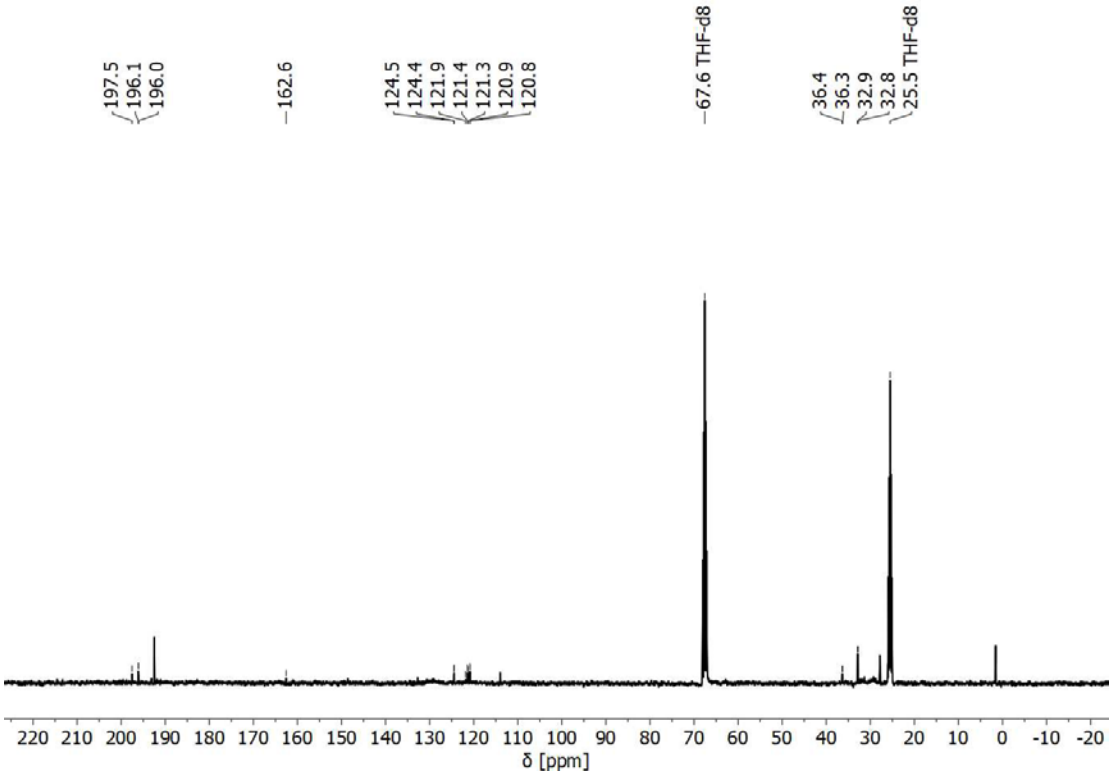


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in THF-d_8.

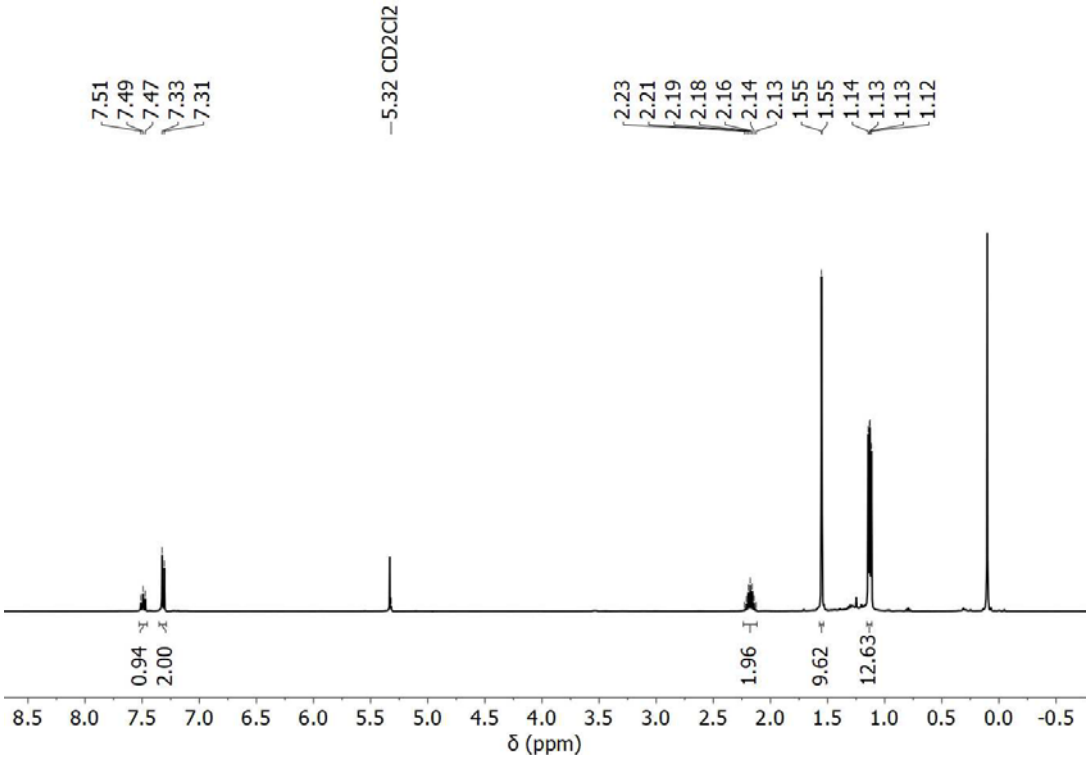


Figure S13. ^{1}H NMR spectrum of **8** in DCM-d_2.

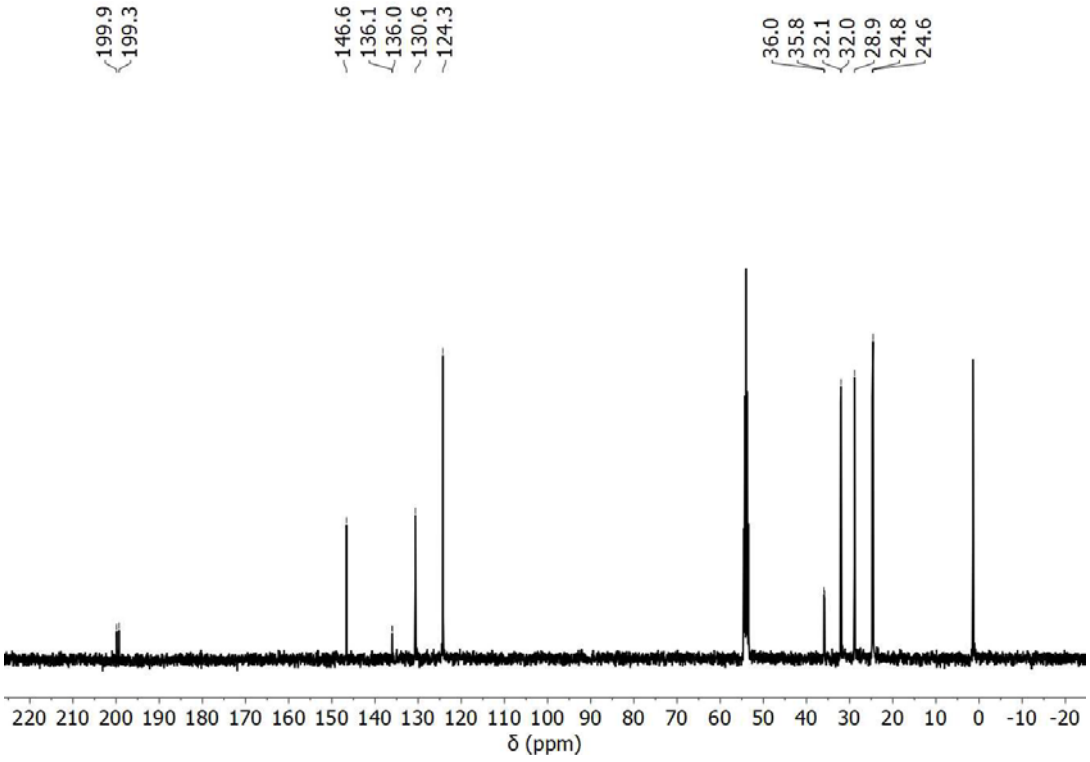


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in DCM-d_2.

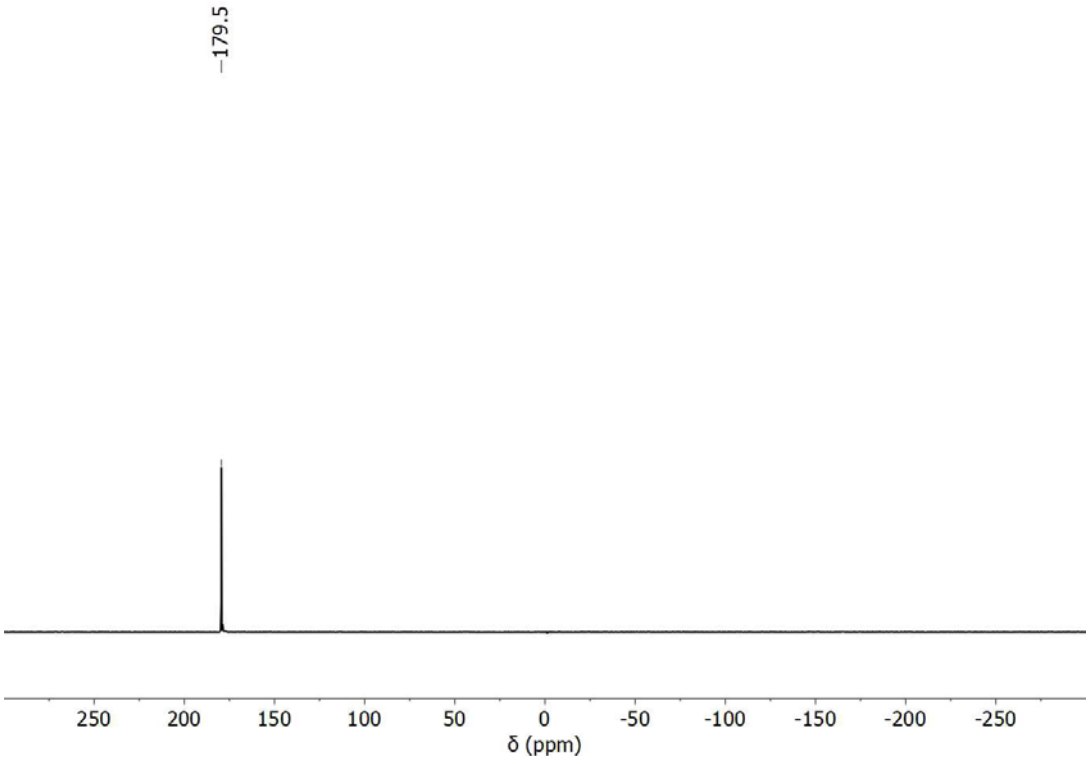


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in DCM-d_2

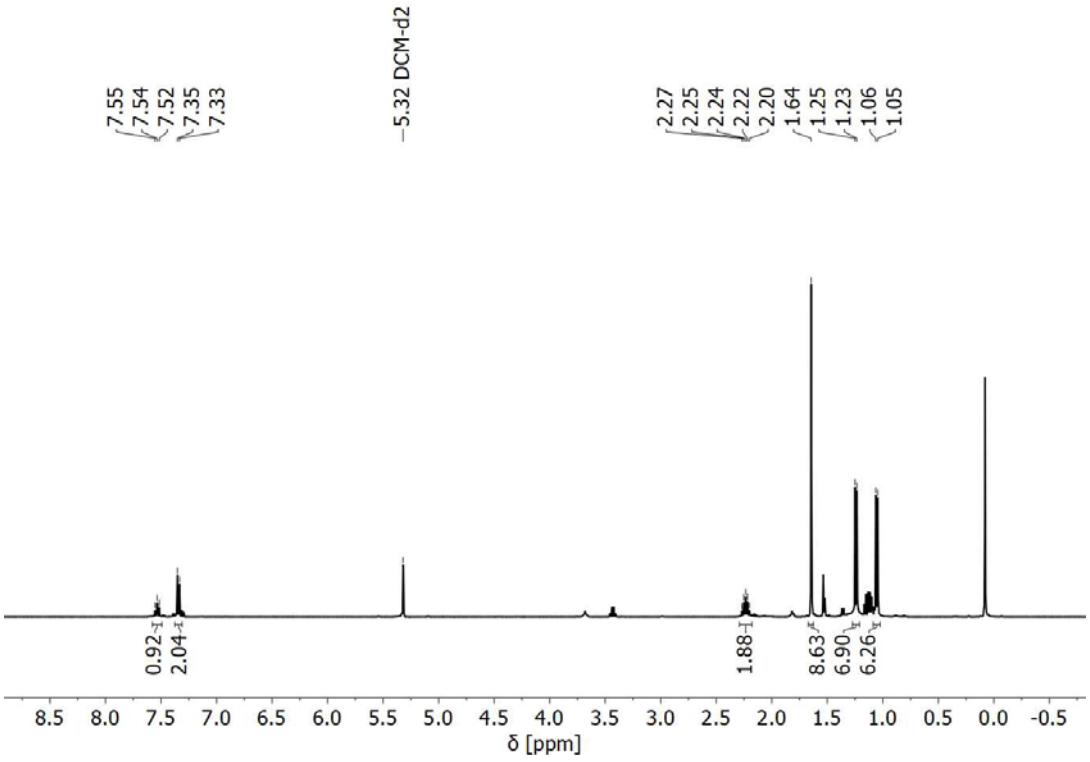


Figure S16. ^{1}H NMR spectrum of **9** in DCM-d_2.

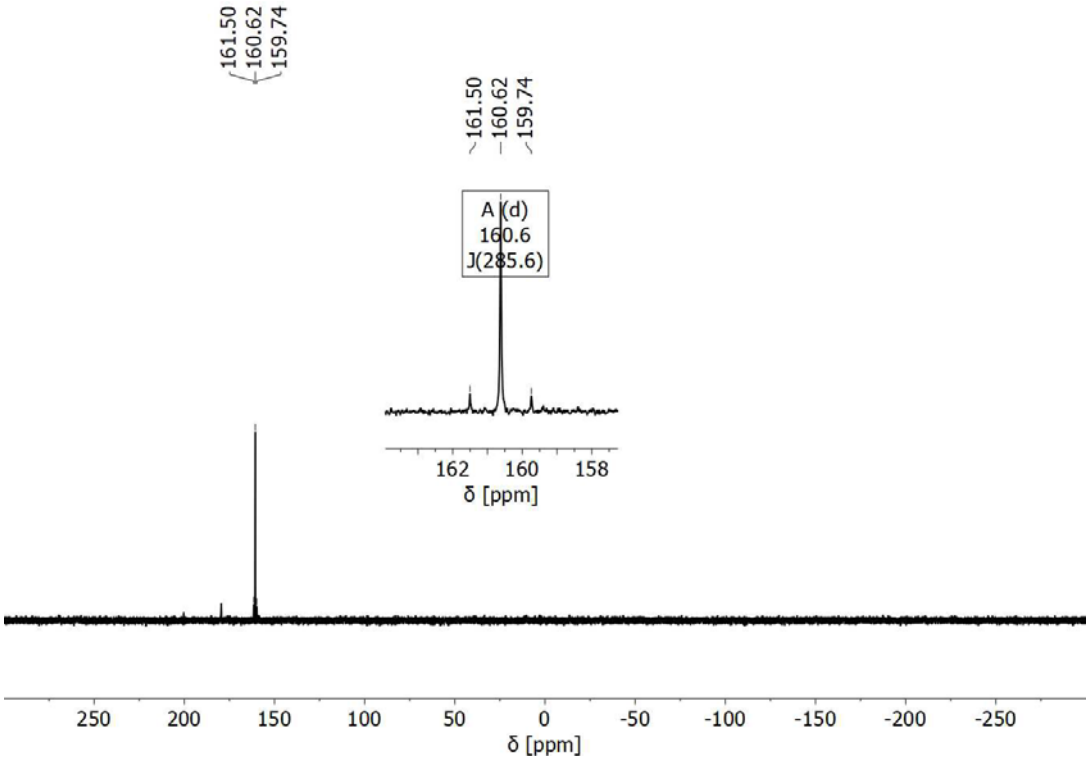


Figure S17. ^{31}P{^{1}H} NMR spectrum of **9** in DCM-d_2

5. References

[1] M. J. Frisch, G.; Trucks, W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision E.01. *Gaussian, Inc.: Wallingford, CT*. 2009.

[2] J.-D. Chai, M. Head-Gordon. *Phys. Chem. Chem. Phys.* **2008**, *10* (44), 6615–6620.

[3] S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys*. **1981**, *55* (1), 117–129.

[4] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. V. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118* (26), 6317–6318. b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105* (10), 3842–3888.

[5] a) C. W. Bird, *Tetrahedron* **1985**, *41* (7), 1409–1414. b) C. W. Bird, *Tetrahedron* **1986**, *42* (1), 89–92.

[6] A. T. B. Gilbert, IQmol molecular viewer. Available at: http://iqmol.org (Accessed October, 2012).

[7] G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G.Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 4759-4762.

[8] G. Becker, H. Schmidt, G. Uhl, W. Uhl, M. Regitz, W. Rösch, U.-J. Vogelbacher, *Inorg. Synth.* **1990**, *27*, 249–253.

[9] Y. Y. C. Yeung Lam Ko, R. Carrié, A. Muench, G. Becker, *J. Chem. Soc. Chem. Commun*.**1984**, 1634-1635.

[10] Bruker (**2010**). APEX2, SAINT, SADABS and XSHELL. Bruker AXS Inc., Madison, Wisconsin, USA.

[11] G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112.

[12] a) G. M. Sheldrick, *Acta Cryst*. **2015**, *C71*, 3; b) G. M. Sheldrick, *Acta Cryst*. **2015**, *A71*, 3.

[13] Spek, A. L. *Acta Cryst.* **2009**, *D65* (2), 148.