Electronic Supplementary Material (ESI) for Dalton Transactions.

On the energetics of P–P bond dissociation of sterically strained tetraamino-diphosphanes

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Contents: Experimental and simulated EPR spectra of **6 - 9**; plot of computed hyperfine couplings vs. skew angles; ^{1}H NMR spectra of mixtures **9**/$\{\mathbf{9}\}_2$; results and evaluation of VT EPR measurements; energies and coordinates of calculated molecular structures of radicals **4** – **9** and diphosphanes $\{\mathbf{4}\}_2$ – $\{\mathbf{9}\}_2$; graphical representation of the structural relaxation.

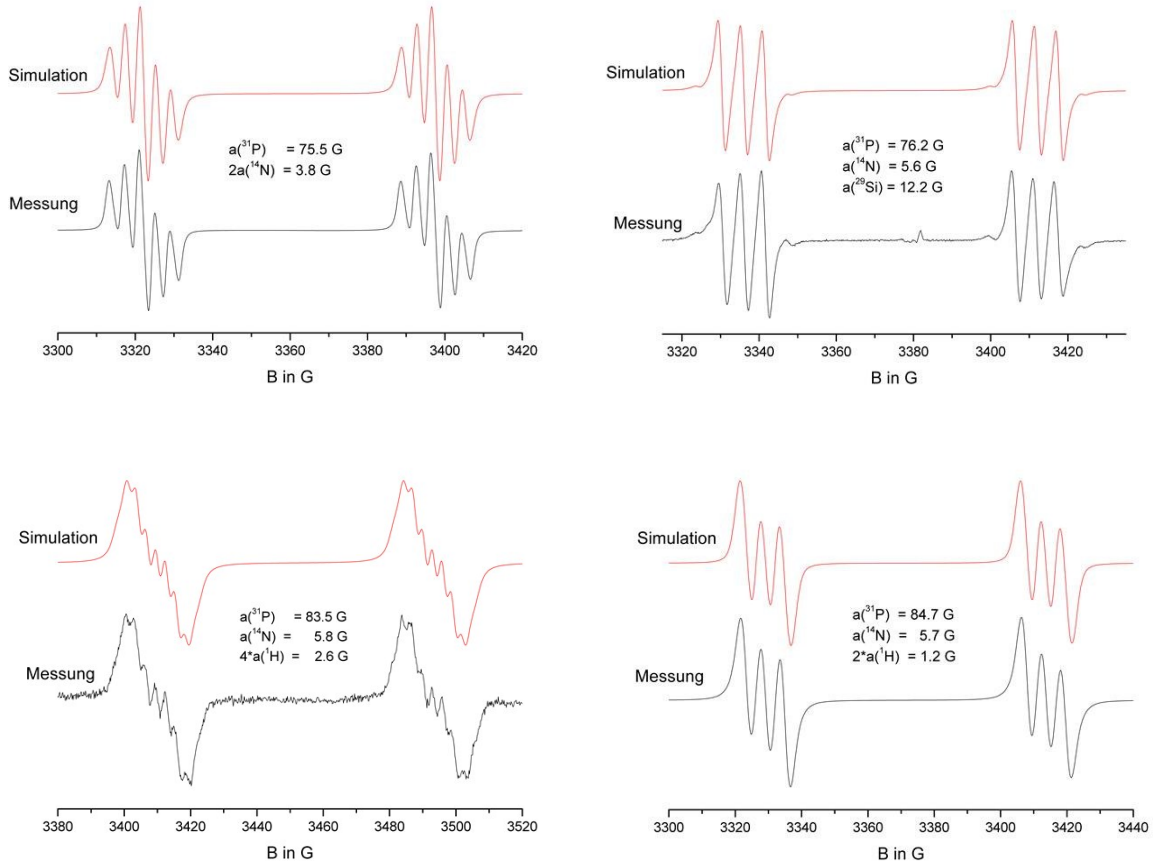

Fig. S1 Experimental (black traces) and simulated (red traces) EPR spectraof **6** (top left), **7** (top right), **8** (bottom left), **9** (bottom right).

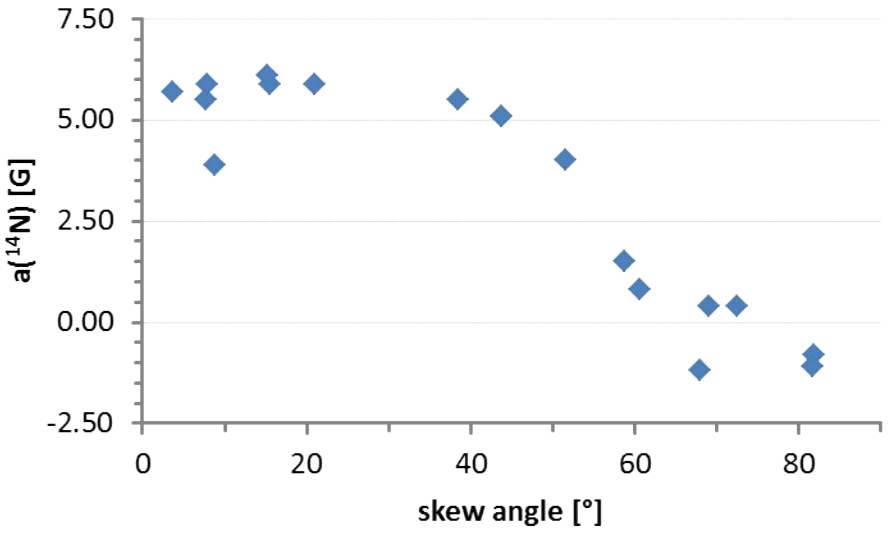

Fig. S2: Plot of calculated (ωB97x-D/cc-pVDZ level) hyperfine couplings a(^{14}N) for **3c** – **6** vs. skew angles.

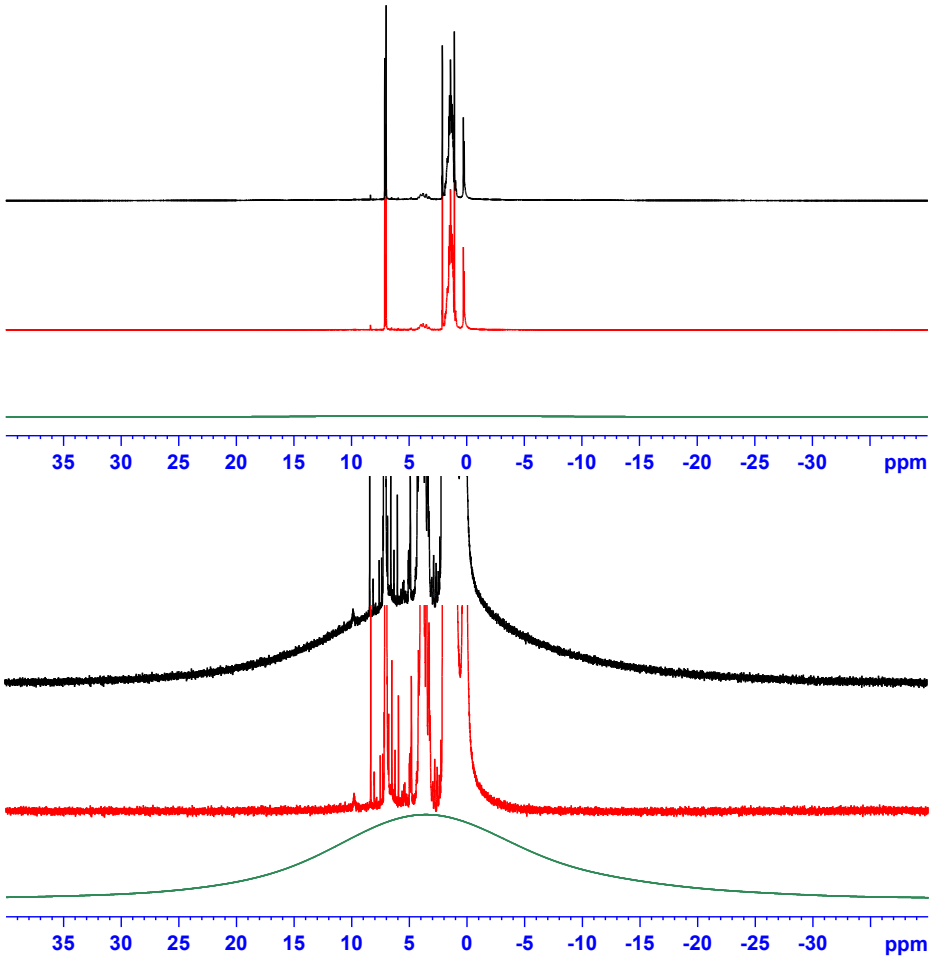

Fig. S3: ^{1}H NMR spectrum of a toluene-d$_8$ solution of {**9**}$_2$ at 298 K (top: spectrum drawn to scale; bottom: 64x vertical expansion). Black traces show the original spectrum, red traces the result of a

deconvolution with suppression of broad lines, and green traces the difference spectrum representing the signal of **9**.

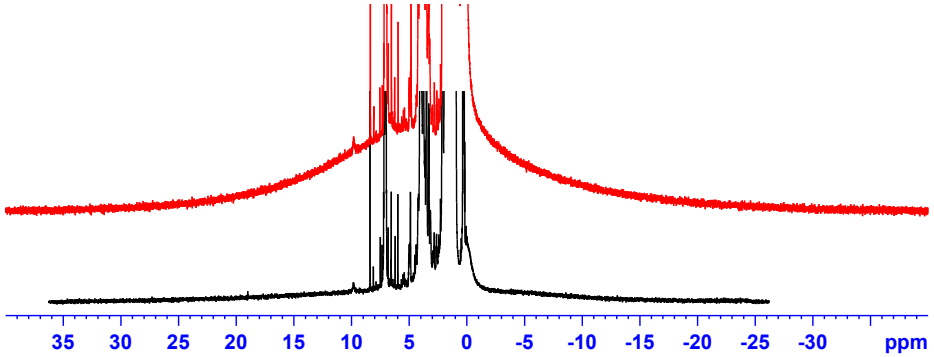

Fig. S4: Vertical expansion of the ^{1}H NMR spectra of a toluene-d_8 solution of $\{\mathbf{9}\}_2$ at 298 K (red trace) and 253 K (black trace). Both spectra are drawn at the same vertical scale. The vertical expansion was adjusted so that the disappearance of the broad line of **9** at lower temperature becomes visible.

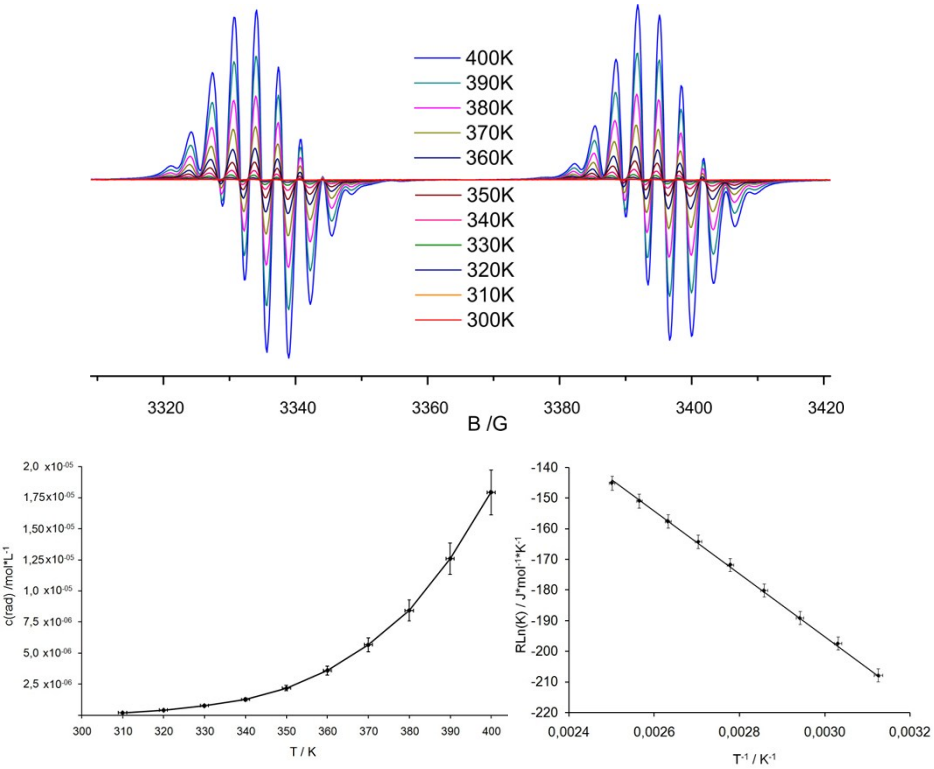

Fig. S5: EPR spectra of **4** (1.22 mM solution in xylene) recorded in the temperature range 300 – 400 K (top), plot of c(**4**) vs. T (bottom left) and van t'Hoff plot of R ln (K_{Diss}) vs. 1/T (bottom right).

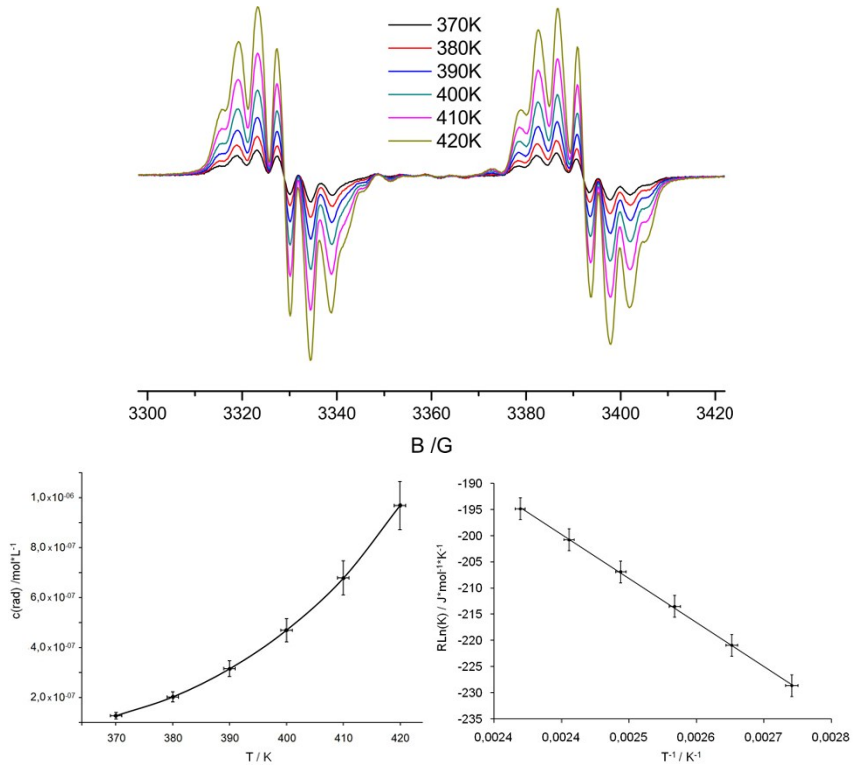

Fig. S6: EPR spectra of **5** (1.42 mM solution in xylene) recorded in the temperature range 370 – 420 K (top), plot of c(**5**) vs. T (bottom left) and van t'Hoff plot of R ln(K_{Diss}) vs. 1/T (bottom right).

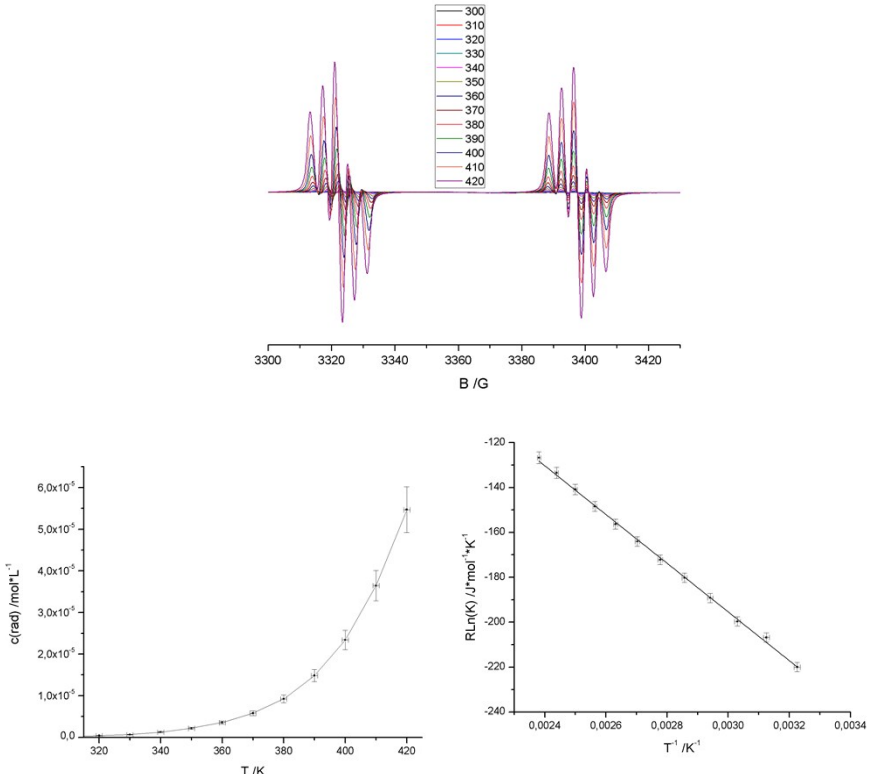

Fig. S7: EPR spectra of **6** (1.25 mM solution in xylene) recorded in the temperature range 300 – 420 K (top), plot of c(**6**) vs. T (bottom left) and van t'Hoff plot of R ln (K_{Diss}) vs. 1/T (bottom right).

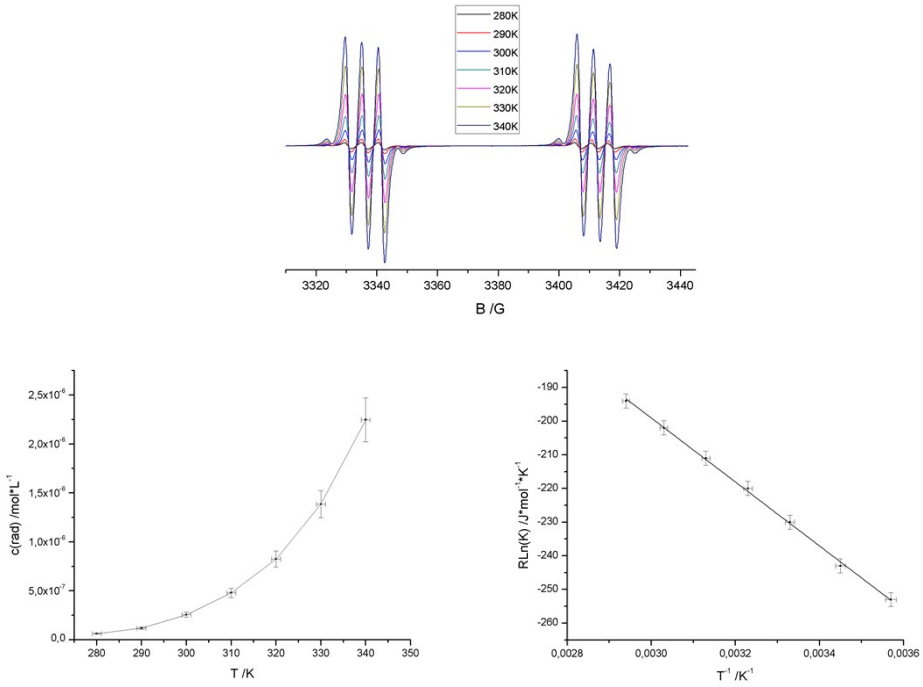

Fig. S8: EPR spectra of **7** (6.75 mM solution in benzene) recorded in the temperature range 200 – 280 K (top), plot of c(**8**) vs. T (bottom left) and van t'Hoff plot of R ln (K_{Diss}) vs. 1/T (bottom right).

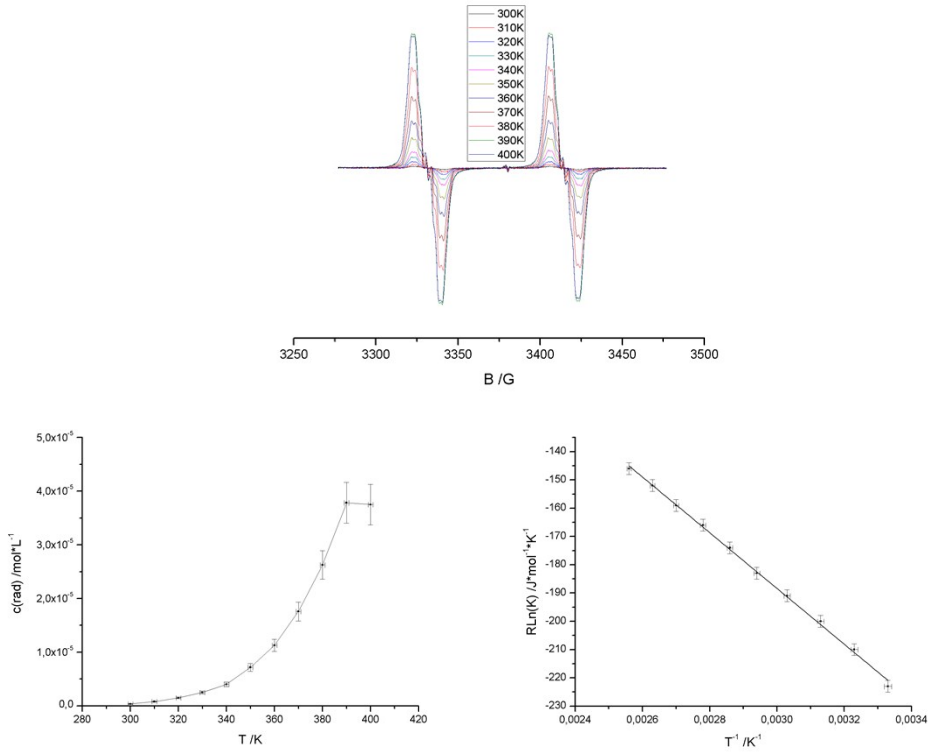

Fig. S9: EPR spectra of **8** (6.03 mM solution in xylene) recorded in the temperature range 300 – 420 K (top), plot of c(**8**) vs. T (bottom left) and van t'Hoff plot of R ln (K_{Diss}) vs. 1/T (bottom right). The spectrum recorded at 400 K was not considered for the further data evaluation as inspection of the solution indicated that partial decomposition of the sample during the measurement had occurred

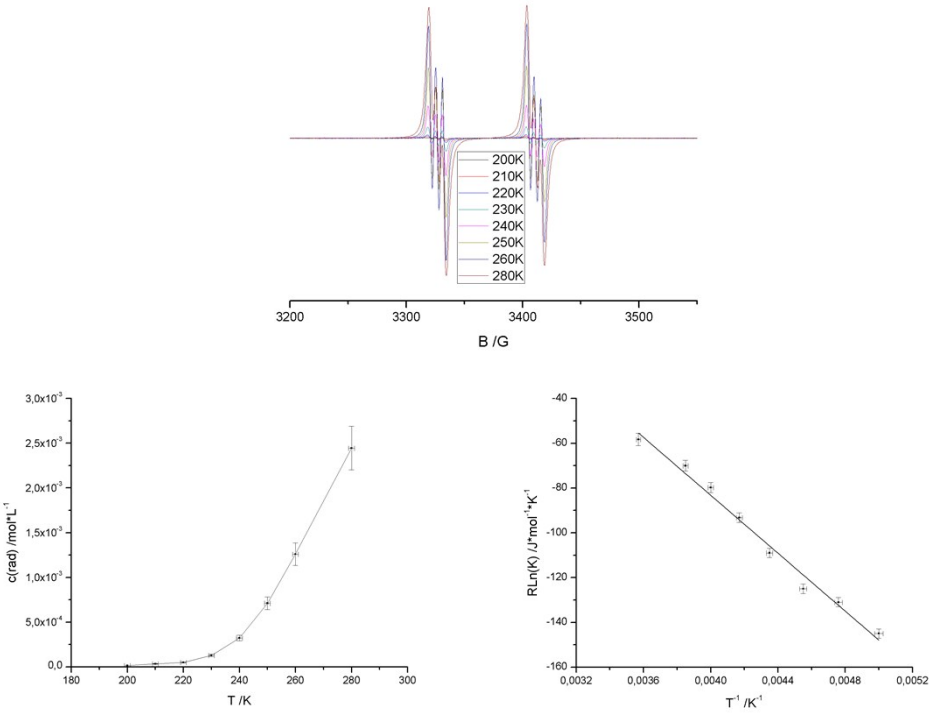

Fig. S10: EPR spectra of **9** (7.85 mM solution in hexane) recorded in the temperature range 200 – 280 K (top), plot of c(**8**) vs. T (bottom left) and van t'Hoff plot of R ln (K_{Diss}) vs. 1/T (bottom right).

Table S1 Ccoordinates of energy optimized geometries and absolute energies for **4** and $\{\mathbf{4}\}_2$.

4 E(ωB97x-D) = -1464.24395752

P	0.014334	-0.333123	-0.850589	C	1.824870	3.098851	-0.374642
N	1.242893	-0.311638	1.174934	C	2.777749	-3.144766	-0.377830
N	-1.188813	-0.161888	1.669002	C	-1.885307	3.050550	-0.102716
C	3.562076	-0.993686	0.913813	C	-3.261183	-3.568818	0.071324
C	2.596026	0.033687	0.836600	H	1.343885	-0.576439	-0.228065
C	2.951830	1.363900	0.832372	H	-1.307055	0.020978	-0.506100
C	4.294165	1.642405	2.467654	H	4.592480	2.665921	-0.485576
C	5.254721	0.639276	2.472488	H	0.945301	2.075489	-0.183017
C	4.889462	-0.669114	0.744103	H	5.653159	-1.448199	-1.718486
C	0.743977	-0.034995	0.024907	H	2.233930	-2.380810	-1.710200
C	-0.706954	-0.499217	0.171368	H	-5.082748	2.206607	-0.103116
C	-2.586276	-0.101321	1.003508	H	-1.521517	2.093480	-0.151469
C	-3.211935	1.163420	0.102715	H	-5.266253	-2.034807	-0.706252
C	-4.577520	1.239714	1.035814	H	-1.594978	-2.511791	-0.126432
C	-5.308440	0.095931	0.004975	H	6.297065	0.877179	-0.436305
C	-4.682280	-1.143285	-0.466751	C	-3.315250	-1.267190	-0.195498
H	1.455453	4.336881	0.706433	C	-2.402453	2.414209	0.793349
H	3.201056	4.070777	0.460302	C	-3.163963	3.436197	0.581317
H	2.305294	3.130042	1.307740	C	-2.661121	-2.639968	-0.229522
H	1.058586	3.889140	1.795098	C	-2.735757	-3.260572	-1.628978
C	1.932432	2.494604	1.690801	H	1.542005	2.329448	-0.264646
C	2.242893	3.566615	2.403062	H	2.778817	3.545857	-0.786285
C	3.147106	-2.428004	1.992031	H	3.784471	-4.195092	0.392081
C	4.196748	-3.220041	1.476780				

H	4.512223	-2.685368	0.614635				
2.083843				H	-2.724245	3.370153	-
H	5.096012	-3.424383	1.476252				
0.571818				H	-1.270315	2.339431	-
H	2.452291	-4.177998	-	1.409152			
0.712762				H	-2.216700	-4.231599	-1.647874
H	3.643926	-3.184567	-	H	-2.260375	-2.604995	-2.373982
1.594644				H	-3.778787	-3.430835	-1.941441
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1.432561				0.840122			
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H	-1.267483	3.935858	-				

$\{\mathbf{4}\}_2$ E(ωB97x-D) = -2928.56093049

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N	0.116895	-1.928670		0.554566			
1.328068				C	-1.504934	2.023820	
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C	2.397257	-0.879767	-	1.791294			
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2.918527				C	-0.832446	-2.927352	
C	2.082459	-1.403787	-	1.730700			
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Table S2 Ccoordinates of energy optimized geometries and absolute energies for **5** and $\{\mathbf{5}\}_2$.

5 E(ωB97x-D) = -1307.00226427

P	0.073684	0.061981	-1.069704	C	-0.700560	0.183908	1.478555
N	1.256007	-0.155963	0.198864	C	5.315986	1.840555	0.375623
N	-1.197118	0.126008	-0.107328	C	3.188406	2.210702	-0.847446
C	-3.500395	2.913138	-0.717088	C	-2.690283	-2.279129	0.037698
C	3.612383	-2.868688	-0.761187	C	-5.009217	-1.927252	-0.708754
C	-2.360281	2.158122	-0.487887	H	-0.542742	1.232781	1.799765
C	-2.428408	0.791285	-0.174699	H	0.430032	-1.667162	1.460705
C	4.882192	-0.865145	-0.339518	H	1.253306	-0.325981	2.307215
C	-4.741502	2.291182	-0.614045	H	-1.421071	-0.279654	2.171557
C	-3.911795	-1.360424	-0.218155	H	1.479535	-2.639207	-0.535730
C	0.613734	-0.574618	1.446720	H	-1.371138	2.618247	-0.542717
C	2.499714	-0.800937	-0.116750	H	3.555233	-3.921736	-1.041261
C	2.456426	-2.153301	-0.476085	H	5.859607	-0.388475	-0.300283
C	4.835664	-2.213193	-0.685275	H	-3.421131	3.973620	-0.961339
C	3.733013	-0.113068	-0.049442	H	-5.800156	0.484636	-0.241207
C	3.848474	1.390574	0.277366	H	3.568728	1.079026	2.429114
C	-4.811231	0.936642	-0.314103	H	3.401327	2.770665	1.899381
C	3.182564	1.726214	1.625412	H	2.093795	1.614166	1.570843
C	-4.389480	-1.461964	1.679588	H	-5.661124	2.857552	-0.771665
C	-3.675085	0.133046	-0.106883	H	-3.023825	-3.324262	0.139746
				H	-2.230308	-2.162917	-0.954110

H	-1.912706	-2.106053	0.789752	H	5.860865	1.304888	1.168619
H	-5.989556	-1.454156	-0.560729	H	5.346927	2.913363	0.618785
H	-4.728871	-1.808387	-1.766637				
H	-5.140241	-3.001925	-0.509459	H	3.666531	1.997917	-1.816446
H	-5.311749	-0.883397	1.843001	H	5.858623	1.706734	-0.572326
H	-4.592426	-2.512020	1.945876	H	3.298775	3.288263	-0.642769
H	-3.625700	-1.076999	2.373290	H	2.116329	1.990308	-0.937541
H	5.763739	-2.745771	-0.900949				

$\{\mathbf{5}\}_2$ E(ωB97x-D) = -2614.07672388

P	-0.055114	1.101523	0.326750	C	-1.831150	4.709454	-0.467288
N	-1.091046	1.813647	-0.880803	C	4.375262	2.544013	-2.642611
N	1.371825	1.684119	-0.539052	C	3.798245	2.248748	-0.213843
C	3.028219	3.692345	2.122698	C	1.016434	2.318732	-1.816517
C	-4.380084	0.433078	-1.905468	C	-4.074964	4.927610	0.545831
C	2.087702	3.048264	1.332512	C	-2.394989	3.507843	1.684175
C	2.435032	2.315522	0.184558	C	3.649355	0.235462	-1.844260
C	-4.757548	2.499103	-0.727838	C	5.847140	1.127404	-1.251595
C	4.363419	3.643722	1.742210	H	1.065083	3.417758	-1.711414
C	4.373844	1.541091	-1.468634	H	-0.376085	0.903902	-2.688330
C	-0.392218	1.876964	-2.161191	H	-0.889879	2.609633	-2.814198
C	-2.514840	1.693145	-0.968225	H	1.703476	2.020812	-2.619762
C	-3.021714	0.592415	-1.668079	H	-2.323573	-0.162051	-2.034344
C	-5.253292	1.402339	-1.428977	H	1.033609	3.103902	-1.608196
C	-3.390137	2.694254	-0.479731	H	-4.741256	-0.446711	-2.439641
C	-2.921308	3.938751	0.303086	H	-5.476143	3.234585	-0.372344
C	4.714474	2.945649	3.011166	H	2.712341	4.241695	

H	5.767479	2.932664	0.319834	C	4.380084	-0.433078	1.905468
H	-2.176799	4.963439	-1.482197	C	-2.087702	-3.048264	-1.332512
				C	-2.435032	-2.315522	-0.184558
H	-1.600937	5.651165	0.056032	C	4.757548	-2.499103	0.727838
H	-0.906903	4.128202	-0.549353	C	-4.363419	-3.643722	-1.742210
				C	-4.373844	-1.541091	
H	5.133247	4.148473	2.328479	C	0.392218	-1.876964	
H	4.096156	-0.170157	-2.766184	C	2.514840	-1.693145	
H	3.785244	-0.511817	-1.051292	C	3.021714	-0.592415	
H	2.573684	0.343590	-2.003852	C	5.253292	-1.402339	
H	6.534850	1.984231	-1.210021	C	3.390137	-2.694254	
H	5.966004	0.531786	-0.335949	C	2.921308	-3.938751	-
H	6.169790	0.506505	-2.101185	C	-4.714474	-2.945649	-0.593277
H	4.995681	3.419381	-2.394246	C	1.831150	-4.709454	0.467288
H	4.798377	2.072234	-3.544529	C	-4.375262	-2.544013	2.642611
H	3.374824	2.917151	-2.893280	C	-3.798245	-2.248748	0.213843
H	-6.328325	1.312416	-1.596813	C	-1.016434	-2.318732	1.816517
H	-4.521178	5.281619	-0.396496	C	4.074964	-4.927610	-0.545831
H	-3.685309	5.807203	-1.080161	C	2.394989	-3.507843	-1.684175
H	-3.185975	3.001231	-2.259523	C	-3.649355	-0.235462	1.844260
H	-4.872341	4.497382	-1.170292	C	-5.847140	-1.127404	1.251595
H	-2.066885	4.390519	-2.257469	H	-1.065083	-3.417758	1.711414
H	-1.544753	2.816913	-1.607681	H	0.376085	-0.903902	2.688330
P	0.055114	-1.101523	-0.326750	H	0.889879	-2.609633	
N	1.091046	-1.813647	0.880803	H	-1.703476	-2.020812	2.619762
N	-1.371825	-1.684119	0.539052	H	2.323573	0.162051	
C	-3.028219	-3.692345	-2.122698	2.034344			

H	-1.033609	-3.103902	-1.608196	H	-6.169790	-0.506505	0.335949
H	4.741256	0.446711	2.439641	H	-4.995681	-3.419381	2.101185
H	5.476143	-3.234585	0.372344	H	-4.798377	-2.072234	2.394246
H	-2.712341	-4.241695	-3.011166	H	-5.767479	-2.932664	-0.319834
H	2.176799	-4.963439	3.544529	H	-3.374824	-2.917151	1.482197
H	1.600937	-5.651165	2.893280	H	6.328325	-1.312416	-
H	0.906903	-4.128202	0.056032	H	4.521178	-5.281619	1.596813
H	-5.133247	-4.148473	-2.328479	H	3.685309	-5.807203	0.396496
H	-4.096156	0.170157	0.549353	H	3.185975	-3.001231	-
H	-3.785244	0.511817	1.080161	H	4.872341	-4.497382	-
H	-2.573684	-0.343590	2.766184	H	2.066885	-4.390519	-
H	-6.534850	-1.984231	2.259523	H	1.544753	-2.816913	-
H	-5.966004	-0.531786	1.051292				1.170292
			2.003852				2.257469
			1.210021				1.607681

Table S3 Coordinates of energy optimized geometries and absolute energies for **6** and $\{\mathbf{6}\}_2$.

6	E(ωB97x-D)	= -924.842063177					
P	0.000000	0.000000	1.228183	C	-2.235836	2.351631	0.304116
N	0.000000	1.320566	0.112378	C	-0.377375	3.072091	1.869052
N	0.000000	-1.320566	0.112378	C	0.377375	-3.072091	1.869052
C	-0.415525	-1.819836	-2.292730	H	-1.397298	-0.382252	-1.057113
C	0.415525	1.819836	-2.292730	H	1.397298	0.382252	-1.057113
C	-1.015197	-1.408132	-0.946062	H	0.411904	-3.316695	-0.248630
C	1.015197	1.408132	-0.946062	H	-0.411904	3.316695	-0.248630
C	-2.192744	-2.304909	-0.551360	H	2.783435	-3.279807	0.531661
C	2.192744	2.304909	-0.551360	H	-2.783435	3.279807	0.531661
C	0.727464	-2.545954	0.472372	H	2.473413	-2.050650	-0.727335
C	-0.727464	2.545954	0.472372	H	-2.473413	2.050650	-0.727335
C	2.235836	-2.351631	0.304116				

H	2.597516	-1.562073	0.982379
H	-2.597516	1.562073	0.982379
H	0.875674	-4.036696	2.053415
H	-0.875674	4.036696	2.053415
H	0.704122	-2.370143	2.652607
H	-0.704122	2.370143	2.652607
H	-0.708411	-3.216375	1.970564
H	0.708411	3.216375	1.970564
H	0.421806	-1.162132	-2.567794
H	-0.421806	1.162132	-2.567794
H	-0.044335	-2.857158	-2.280154
H	0.044335	2.857158	-2.280154
H	-1.178122	-1.756074	-3.084564
H	1.178122	1.756074	-3.084564
H	-2.633284	-1.962430	0.397004
H	2.633284	1.962430	0.397004
H	-2.975785	-2.282395	-1.325569
H	2.975785	2.282395	-1.325569
H	-1.879533	-3.354499	-0.426824
H	1.879533	3.354499	-0.426824

$\{\mathbf{6}\}_2$ E(ωB97x-D) -1849.74312649

P	0.313766	1.104406	-0.335836
N	0.669105	1.570034	1.299620
N	1.788968	0.905806	-1.221870
C	1.897880	1.170252	2.000128
C	-0.001948	2.793280	1.790669
H	2.296574	0.317984	1.433980
C	2.978926	2.258769	2.006966
C	1.654389	0.672119	3.426467
H	0.319073	2.902967	2.839358
C	-1.526839	2.659748	1.807907
C	0.377059	4.085324	1.054817
C	2.735393	-0.215753	-1.084376
C	2.098189	1.857941	-2.306425
C	0.942756	2.061207	-3.287474
H	3.152437	2.646734	0.994559
H	3.927267	1.853241	2.393867
H	2.695558	3.102180	2.656808
H	0.980514	-0.191268	3.425730
H	1.216018	1.452306	4.069095
H	2.608483	0.368393	3.885875
H	-1.847598	1.753086	2.335628
H	-1.925505	2.628570	0.781762
H	-1.978208	3.529734	2.310104
H	-0.090055	4.953472	1.546574
H	0.012700	4.052242	0.015880
H	1.462045	4.248736	1.035258
H	2.372042	-0.814063	-0.238654
C	4.163058	0.229717	-0.750829

C	2.735393	-1.142466	-2.305006
H	2.911662	1.392300	-2.883773
C	2.628284	3.198322	-1.794613
H	1.287022	2.623477	-4.169607
H	0.121279	2.627875	-2.824573
H	0.545685	1.091682	-3.624071
H	3.516382	3.055005	-1.161915
H	1.863818	3.718539	-1.200765
H	2.909515	3.853244	-2.634862
H	4.192968	0.851594	0.152884
H	4.612481	0.805913	-1.575401
H	4.801694	-0.651805	-0.583764
H	1.714539	-1.470768	-2.534074
H	3.350601	-2.033996	-2.104002
H	3.154368	-0.651607	-3.197997
P	-0.313766	-1.104406	-0.335836
N	-0.669105	-1.570034	-1.299620
N	-1.788968	-0.905806	-1.221870
C	-1.897880	-1.170252	-2.000128
C	0.001948	-2.793280	-1.790669
H	-2.296574	-0.317984	-1.433980
C	-2.978926	-2.258769	-2.006966
C	-1.654389	-0.672119	-3.426467
H	-0.319073	-2.902967	-2.839358
C	1.526839	-2.659748	-1.807907
C	-0.377059	-4.085324	-1.054817
C	-2.735393	0.215753	-1.084376
C	-2.098189	-1.857941	-2.306425
C	-0.942756	-2.061207	-3.287474
H	-3.152437	-2.646734	-0.994559
H	-3.927267	-1.853241	-2.393867
H	-2.695558	-3.102180	-2.656808
H	-0.980514	0.191268	-3.425730
H	-1.216018	-1.452306	-4.069095
H	-2.608483	-0.368393	-3.885875
H	1.847598	-1.753086	-2.335628
H	1.925505	-2.628570	-0.781762
H	1.978208	-3.529734	-2.310104
H	0.090055	-4.953472	-1.546574
H	-0.012700	-4.052242	-0.015880
H	-1.462045	-4.248736	-1.035258
H	-2.372042	0.814063	-0.238654
C	-4.163058	-0.229717	-0.750829
C	-2.735393	1.142466	-2.305006
H	-2.911662	-1.392300	-2.883773
C	-2.628284	-3.198322	-1.794613
H	-1.287022	-2.623477	-4.169607
H	-0.121279	-2.627875	-2.824573
H	-0.545685	-1.091682	-3.624071
H	-3.516382	-3.055005	-1.161915
H	-1.863818	-3.718539	-1.200765
H	-2.909515	-3.853244	-2.634862
H	-4.192968	-0.851594	0.152884
H	-4.612481	-0.805913	-1.575401
H	-4.801694	0.651805	-0.583764

H -1.714539 1.470768 - 2.104002
2.534074 H -3.154368 0.651607 -
H -3.350601 2.033996 - 3.197997

Table S4 Coordinates of energy optimized geometries and absolute energies for **7** and $\{\mathbf{7}\}_2$.

7 E(ωB97x-D) = -1506.34812435
H 3.884263 0.284304 H 2.454555 -2.868445
0.529874 0.159014
C 3.178772 0.462288 - H 0.957398 -2.082684
0.298924 2.826036
C 3.053904 1.976828 - H 4.044240 2.426426 -
0.462341 0.635069
C 3.785287 -0.162450 - H 0.070294 -0.693952
1.563476 2.142014
N 1.901994 -0.151134 H 2.612837 2.439128
0.134824 0.432463
C 2.055295 -1.056656 H 0.210444 -2.208906
1.293478 1.221856
C 0.740067 -1.525700 H 2.419596 2.220261 -
1.902022 1.328447
P 0.672118 -0.267573 -1.088505 C -0.130576 1.988571
N -0.838938 0.055068 - 1.964234
0.270016 H -3.393186 1.296412
Si -1.096320 1.709607 0.369493 1.391151
C -0.590823 2.987823 - H 0.492046 3.006754 -
0.919119 1.099849
Si -2.139493 -1.162737 -0.429821 H -0.895916 3.991517 -
C -1.472731 -2.725736 -1.247338 0.579370
C -2.828780 -1.645899 H -2.966925 3.014450
1.261059 1.265533
C 2.920901 -2.282392 H -0.620530 -3.162477 -0.704695
0.967744 H -2.086681 -2.209944
H 2.579131 -0.464997 1.845975
2.068433 H -1.153359 -2.543088 -2.284766
C -2.917871 2.045216 H -3.137378 -0.775449
0.741309 1.858557
H 3.880419 -1.253228 - H -3.512348 2.137987 -
1.471359 0.179758
H 3.936613 -2.006369 H -1.094367 2.782516 -
0.651064 1.877267
H 3.015419 -2.929743 C -3.549153 -0.532326 -1.515511
1.853490 H -2.283010 -3.474242 -1.266288
H 4.785557 0.258080 - H -3.714061 -2.289405
1.752035 1.126200
H 3.160925 0.049750 - H -4.196952 -1.376869 -1.803208
2.445325 H -4.178954 0.211132 -
1.006321

H	-3.154395	-0.077939	-2.438289	H	-0.571333	1.423678	2.232971
H	-0.147281	3.057593	2.801450	H	0.915396	1.670231	1.845672

$\{\mathbf{7}\}_2$ E(ωB97x-D) = -3012.75116781

C	1.804558	-0.411312	3.048439	C	-1.059888	-3.187416	1.060051
Si	2.894765	-0.737443	1.533497	C	-2.586216	-3.329458	1.095106
C	3.212782	-2.600856	1.545500	C	-1.729615	-0.133555	-3.074594
N	2.288236	-0.153972	-0.065588	C	-4.238323	-1.379068	-1.811833
Si	-3.402536	0.805219	1.249976	P	0.779214	0.591452	-0.582676
C	-5.139907	0.076013	1.074786	P	-0.808729	-0.493922	0.638518
C	-2.846667	0.340096	2.991791	N	-2.303315	0.175641	-0.032467
C	-3.564455	2.685706	1.194861	Si	-2.999995	0.054910	-1.687287
C	-0.521284	-3.042081	2.483951	C	-4.018195	1.592623	-2.116974
C	1.162188	-3.315944	-1.183691	C	4.542419	0.107113	-1.921531
H	0.726319	-0.397388	2.839851	Si	3.468896	-0.156798	-1.435699
H	2.082751	0.530974	3.545214	C	4.675771	-1.610906	-1.362116
H	2.001012	-1.227160	3.763303	C	2.599338	-0.322914	-3.101195
H	4.884119	-0.237188	2.911953	C	4.517576	1.409935	-1.438112
H	4.423926	1.200518	1.968528	N	0.686350	2.167475	0.112368
H	5.339501	-0.121247	1.198902	C	0.423679	3.318268	-0.772780
H	3.918712	-2.937907	0.776133	C	-0.931152	3.214177	-1.464836
H	2.283322	-3.173934	1.425120	C	1.151046	2.478715	1.464817
H	3.641222	-2.855269	2.529747	C	0.074042	3.126965	2.335138
H	2.048713	0.581293	-3.394850	N	-0.589331	-2.131672	0.136990
H	1.889309	-1.164341	-3.098143	C	-0.179692	-2.582025	-1.207131
H	3.365510	-0.526809	-3.868260	C	-1.219819	-3.436938	-1.938645
				C	2.451665	3.288547	1.478518
				C	1.532037	3.600817	-1.789113

H	5.239741	1.372951	-2.270396
H	5.084911	1.516726	-0.501377
H	3.898953	2.307613	-1.567904
H	5.346958	-1.503504	-2.230807
H	4.164329	-2.580660	-1.456324
H	5.307280	-1.632405	-0.462647
H	1.373012	1.513721	1.922651
H	0.366677	4.190975	-0.102936
H	2.299864	4.318191	1.116501
H	3.208887	2.808091	0.842285
H	2.849079	3.357505	2.503686
H	0.451528	3.286741	3.357560
H	-0.808672	2.476824	2.393089
H	-0.243813	4.107258	1.944366
H	1.669349	2.740354	-2.462681
H	2.488437	3.810074	-1.290842
H	1.272523	4.474737	-2.407146
H	-1.189640	4.164092	-1.959431
H	-1.711061	2.965363	-0.736132
H	-0.920407	2.428646	-2.235146
H	-3.586431	0.760765	3.694507
H	-1.854809	0.730302	3.258407
H	-2.827184	-0.750916	3.135943
H	-4.252576	3.007246	1.994361
H	-3.967182	3.047535	0.238268
H	-2.597450	3.180538	1.365777
H	-5.114137	-1.024842	1.062278
H	-5.672941	0.414149	0.174324
H	-5.734661	0.391014	1.948206
H	-0.647128	-4.130587	0.666122
H	-0.033116	-1.665947	-1.795543
H	-2.148923	0.361629	-3.966040
H	-1.558321	-1.186283	-3.338197
H	-0.759351	0.328525	-2.847237
H	-5.262910	-1.028148	-1.617233
H	-4.023830	-2.180981	-1.092467
H	-4.221179	-1.811121	-2.825935
H	-4.452273	1.414485	-3.115736
H	-3.419047	2.512130	-2.170124
H	-4.857745	1.762692	-1.427231
H	-0.942121	-2.160052	2.988324
H	0.571083	-2.944658	2.491042
H	-0.792905	-3.931222	3.073857
H	-2.884254	-4.135614	1.783852
H	-2.995393	-3.564110	0.104164
H	-3.053446	-2.395371	1.443113
H	1.112807	-4.241124	-0.586749
H	1.936701	-2.670565	-0.759109
H	1.460163	-3.600092	-2.205688
H	-0.886958	-3.617629	-2.972872
H	-2.201159	-2.951060	-1.978739
H	-1.343687	-4.422209	-1.461912

Table S5 Coordinates of energy optimized geometries and absolute energies for **8** and $\{\mathbf{8}\}_2$.

8 E(ωB97x-D) =

C	-3.248938	-0.152888	1.046122	H	-2.669262	-1.750824	-1.265245
C	-2.164730	-1.160189	1.391243	H	-2.980816	0.167887	-1.821451
C	-1.128279	-1.353974	0.270258	H	-2.880500	1.934960	-1.947772
N	-0.610759	-0.022040	-0.184314	H	-1.970065	-3.204100	-0.526995
C	-1.563210	1.110273	-0.412061	H	-2.064433	1.528297	-1.643751
C	-2.586902	1.179033	0.736133	H	-1.635978	-0.811929	-2.295703
P	0.770708	-0.073718	-1.253799	H	-1.026445	-2.266372	-1.711265
N	2.082761	0.208990	-0.164840	H	-1.565277	0.921229	-2.589301
C	1.988892	0.714670	1.191615	H	-1.485044	3.276926	-0.472343
H	2.496541	0.019467	1.886498	H	-0.370375	-3.096154	-1.309507
C	-0.783466	2.433193	-0.381356	H	-0.239631	2.542190	-0.568025
C	-2.292132	1.021099	-1.768393	H	0.538234	-1.604521	-1.665298
C	0.028084	-2.167972	0.871308	H	-0.059987	2.503353	-1.206863
C	-1.739127	-2.185197	-0.876309	H	0.771663	-2.447002	0.111642
C	3.402592	-0.138163	-0.668856	H	0.922916	0.707342	-1.459746
C	3.917204	-1.480308	-0.150259	H	2.072043	2.825037	-0.673489
H	3.349519	-0.168949	-1.770283	H	2.400669	2.473119	-2.393387
C	2.562183	2.121037	-1.362579	H	3.244813	-2.294418	-0.460390
H	-3.948688	-0.042302	1.889005	H	3.983022	-1.491221	-0.948630
H	-3.849410	-0.501365	0.189703	H	3.645136	2.155176	-1.168404
H	-3.336840	1.946003	-0.484297	H	4.118122	0.664403	-0.420681
H	-2.599675	-2.143249	-1.633125	H	4.922090	-1.689550	-0.548715

$\{\mathbf{8}\}_2$ E(ωB97x-D) =

C	-5.093954	1.045417	0.641737	C	2.839342	-0.622226	2.441448
C	-3.964883	1.134721	1.648722	C	4.044572	1.212202	1.316456
C	-2.837275	0.105120	1.427084	C	0.050095	2.626361	-1.210393
N	-2.347926	0.159073	0.008870	C	-1.197466	3.492670	-1.055587
C	-3.404733	0.170430	-1.080650	C	-0.050085	-2.626364	1.210364
C	-4.501634	1.201196	-0.744464	C	1.197480	-3.492665	1.055545
P	-0.836283	-0.524708	-0.586102	H	-0.197909	1.751313	-1.824708
N	-0.578806	-2.149961	-0.060071				
C	-0.849241	-3.187010	-1.054035	H	0.820580	3.187750	-1.775023
C	-1.857927	-4.241526	-0.602745				
C	-3.325933	-1.296855	1.854805	H	1.219807	2.683759	1.959680
C	-1.730182	0.523477	2.398674	H	-0.089707	3.690959	1.354242
C	-2.839360	0.622226	-2.441436	H	0.197915	-1.751323	1.824690
C	-4.044579	-1.212202	-1.316434	H	-0.820566	-3.187765	1.774990
P	0.836284	0.524721	0.586097	H	-1.219813	-2.683731	-1.959703
N	0.578810	2.149970	0.060050	H	0.089685	-3.690954	-1.354272
C	0.849228	3.187027	1.054009	H	4.332087	1.530914	-1.483583
C	1.857898	4.241557	0.602716	H	2.642491	2.071868	-1.487750
N	2.347927	-0.159073	-0.008861	H	3.366209	1.360211	-2.953608
C	2.837284	-0.105135	-1.427073	H	0.939183	0.227543	-2.495868
C	3.964890	-1.134740	-1.648696	H	1.273444	-1.471815	-2.084411
C	5.093958	-1.045425	-0.641708	H	2.171052	-0.666085	-3.397196
C	4.501631	-1.201195	0.744492	H	3.521528	-2.144531	-1.594889
C	3.404727	-0.170429	1.080667	H	4.342415	-1.005470	-2.676026
C	3.325951	1.296833	-1.854804	H	5.284725	-1.125494	1.515513
C	1.730194	-0.523496	-2.398664	H	4.065139	-2.210530	0.833800

H	2.189627	0.127445	2.906819	H	-3.521522	2.144512	1.594924
H	3.687453	-0.806529	3.119617	H	-4.342404	1.005439	2.676052
H	2.276656	-1.558047	2.349116	H	-5.284731	1.125503	-1.515482
H	3.272446	1.951332	1.569440	H	-4.065139	2.210530	-0.833767
H	4.601202	1.589042	0.450897	H	-2.189651	-0.127447	-2.906813
H	4.745593	1.159855	2.164632	H	-3.687475	0.806534	-3.119596
H	-1.625912	3.724533	-2.042960	H	-2.276667	1.558044	-2.349108
H	-0.981331	4.451676	-0.561267	H	-3.272454	-1.951328	-1.569435
H	-1.948348	2.950776	-0.461124	H	-4.601192	-1.589049	-0.450868
H	2.061481	4.946222	1.423705	H	-4.745615	-1.159853	-2.164598
H	1.483363	4.829076	-0.249806	H	1.625926	-3.724545	2.042914
H	2.808981	3.777588	0.300621	H	0.981349	-4.451663	0.561208
H	-4.332078	-1.530930	1.483601	H	1.948360	-2.950756	0.461093
H	-2.642483	-2.071885	1.487725	H	-2.061515	-4.946189	-1.423735
H	-3.366169	-1.360250	2.953608	H	-1.483403	-4.829051	0.249778
H	-0.939166	-0.227559	2.495867	H	-2.809006	-3.777545	-0.300656
H	-1.273438	1.471802	2.084428	H	5.839407	-1.833540	-0.830892
H	-2.171036	0.666055	3.397209	H	5.629407	-0.086007	-0.733097
				H	-5.839401	1.833533	0.830931
				H	-5.629408	0.086000	0.733120

Table S6 Coordinates of energy optimized geometries and absolute energies for **9** and $\{\mathbf{9}\}_2$.

9 E(ωB97x-D) = -1041.552954

N	1.784271	-0.032955	0.012393	C	3.356491	1.713344	-0.784724
P	0.506149	0.059965	-1.153670	C	3.532772	-0.658977	-1.669746
N	-0.936542	0.004115	-0.157473	C	3.147159	0.227179	-0.480174

C	2.243609	0.413840	-2.420137	H	-1.309720	2.084687	-1.925314
C	2.226276	-1.948464	1.529659	H	-1.016991	3.219139	1.020661
C	1.645485	-0.538067	1.379645	H	-1.608997	-3.354587	-0.264900
C	-0.968149	-2.465694	-0.158446	H	-0.137165	1.812244	1.670688
C	-0.539043	2.263945	0.753487	H	-0.537029	-2.474699	0.852707
C	-1.576662	1.334839	0.110033	H	0.299162	2.481231	0.076214
C	-1.804401	-1.197782	-0.381424	H	-0.149035	-2.548681	-0.888293
C	-2.395180	-1.266105	-1.805275	H	0.560100	-0.584828	1.551246
C	-2.103407	2.024851	-1.165167	H	1.853658	1.433584	2.296424
C	-2.937688	-1.232252	0.660086	H	1.796019	-2.630051	0.782480
C	-2.718119	1.175298	1.130412	H	2.009971	-2.350378	2.532214
C	-3.702847	0.075293	0.772547	H	1.991419	0.067369	3.434403
H	-4.482410	-0.005199	1.545959	H	2.931199	-0.422886	-2.560928
H	-4.225081	0.307111	-0.170243	H	2.699470	2.038475	-1.606467
H	-3.227506	2.147033	1.232234	H	3.379539	-1.720907	-1.426988
H	-3.611744	-2.066659	0.408110	H	3.124011	2.324822	0.099638
H	-3.118043	-0.463839	-2.001434	H	3.342555	0.460733	2.356028
H	-2.959136	1.499294	-1.608400	H	3.321298	-1.950374	1.402348
H	-2.429336	3.051276	-0.933928	H	3.827430	-0.037038	0.343933
H	-2.915176	-2.225364	-1.956211	H	4.592693	-0.508898	-1.927842
H	-2.273652	0.941432	2.113441	H	4.399652	1.908395	-1.644586
H	-2.495236	-1.463710	1.079173				

$\{\mathbf{9}\}_2$ E(ωB97x-D) = -2083.142606

C	-3.191306	3.463412	-1.110857	N	-1.888072	0.891900	-0.477577
C	-2.702980	2.526520	-2.196464	C	-2.206744	1.859628	0.621476
C	-2.641947	1.040109	-1.782695	C	-2.274678	3.304053	0.086008

P	-1.141794	-0.691708	-0.272815	C	2.121331	-1.179416	-3.605542
N	-1.704792	-1.530700	1.146749	C	2.471693	-3.488369	0.262055
C	-2.705682	-2.607537	0.965619	C	-1.112245	-1.492460	2.495452
C	-4.153831	-2.112818	1.021560	C	-0.317512	-2.756728	2.844140
C	-1.935929	0.346971	-2.962487	C	-2.121331	-1.179414	3.605542
C	-4.059422	0.441683	-1.725537	C	-2.471702	-3.488362	-0.262059
C	-1.089589	1.857129	-1.663837	H	0.380887	-0.682828	-2.473139
C	-3.525049	1.526646	-1.349833	H	2.574108	-3.272568	-1.832818
P	1.141795	-0.691709	0.272815	H	2.591200	3.956045	-0.916096
N	1.704792	-1.530700	-1.146749	H	1.255690	3.619569	0.198997
C	2.705680	-2.607540	-0.965619	H	0.100100	1.872964	-1.191597
C	4.153830	-2.112823	-1.021553	H	1.150797	0.983091	-2.318080
N	1.888074	0.891898	0.477577	H	1.190402	2.744271	-2.308104
C	2.206747	1.859626	-0.621477	H	4.418577	1.803336	-0.775243
C	2.274682	3.304051	-0.086010	H	3.572372	2.076217	-2.303838
C	3.191309	3.463410	1.110856	H	3.574624	0.453602	-1.563790
C	2.702981	2.526520	2.196463	H	1.688359	2.839407	2.496798
C	2.641947	1.040109	1.782695	H	3.335615	2.600245	3.095092
C	1.089593	1.857127	-1.663839	H	0.914067	0.725598	3.093534
C	3.525053	1.526642	-1.349833	H	2.494240	0.586245	3.880874
C	1.935928	0.346972	2.962488	H	1.903140	-0.743778	2.860766
C	4.059422	0.441681	1.725540	H	4.677621	0.859672	0.923174
C	1.112244	-1.492460	-2.495452	H	3.994804	-0.645736	1.577517
C	0.317509	-2.756727	-2.844139	H	4.582978	0.613912	2.679260

H	2.683181	-0.258289	-3.399002	H	-4.582978	0.613911	-2.679258
H	1.592553	-1.050468	-4.563187	H	-2.591195	3.956048	0.916094
H	2.845727	-1.998153	-3.741491	H	-1.255687	3.619570	-0.199000
H	-0.423918	-2.967311	-2.064299	H	-0.100097	1.872967	1.191594
H	0.960200	-3.642234	-2.970090	H	-1.150792	0.983092	2.318077
H	-0.216698	-2.608060	-3.796217	H	-1.190398	2.744272	0.284517
H	1.433025	-3.850766	2.308103	H	-4.418574	1.803341	1.201917
H	2.666125	-2.951106	0.775244	H	-3.572367	2.076221	0.222988
H	3.142489	-4.360830	2.303838	H	-3.574621	0.453606	1.563792
H	4.360454	-1.590799	-1.966305	H	-2.683179	-0.258285	3.399002
H	4.852038	-2.961820	-0.945027	H	-1.592554	-1.050469	4.563187
H	4.372328	-1.418881	-0.200037	H	-2.845731	-1.998149	3.741488
H	-0.380887	-0.682829	2.473139	H	0.423911	-2.967317	2.064297
H	-2.574108	-3.272569	1.832815	H	-0.960205	-3.642233	2.970096
H	3.179753	4.504215	1.470113	H	0.216699	-2.608060	3.796215
H	4.236454	3.239543	0.840425	H	-1.433035	-3.850764	-0.284524
H	-1.688358	2.839407	-2.496800	H	-2.666133	-2.951094	-1.201919
H	-3.335615	2.600244	-3.095093	H	-3.142501	-4.360821	-0.222994
H	-0.914069	0.725596	-3.093535	H	-4.360450	-1.590794	1.966313
H	-2.494242	0.586244	-3.880873	H	-4.852041	-2.961814	0.945037
H	-1.903142	-0.743779	-2.860764	H	-4.372332	-1.418875	0.200045
H	-4.677620	0.859677	-0.923172	H	-4.236451	3.239546	-0.840425
H	-3.994805	-0.645734	-1.577510	H	-3.179749	4.504216	-1.470116

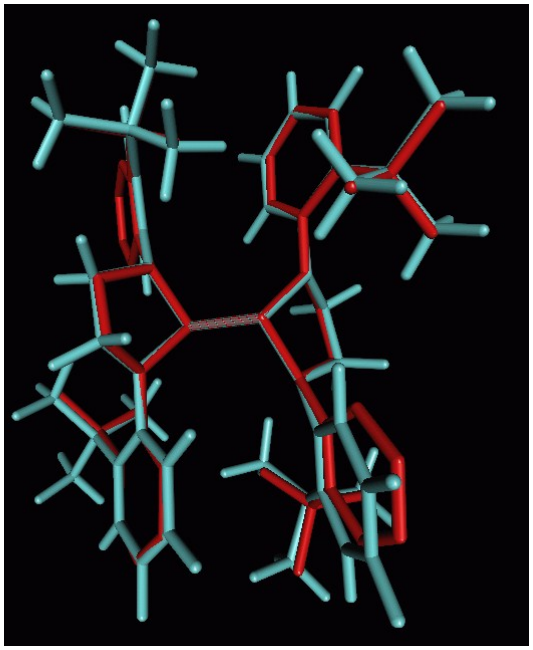

Fig. S11: Overlay of the experimental (red, H-atoms omitted) and calculated (blue) geometries (ωB97x-D) of **5.**

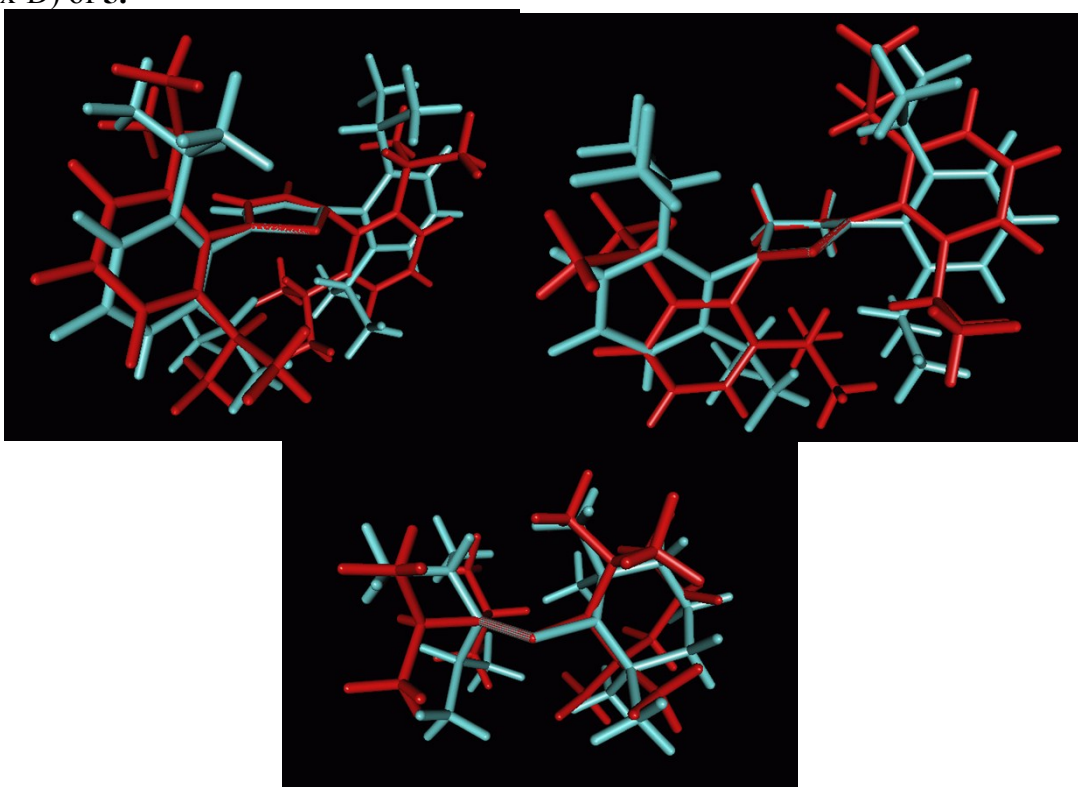

Fig. S12: Overlay of the calculated geometries (ωB97x-D) of selected radicals (blue; top left – **3c**; top right – **4**; bottom – **9**) and half the molecule of the corresponding diphosphanes (red) showing the geometrical distortion during structural relaxation of the radicals.