Electronic Supplementary Information

for

P=O-Containing Dibenzopentaarenes: Facile Synthesis, Structures and Optoelectronic Properties

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1. HRMS spectra and thermal properties

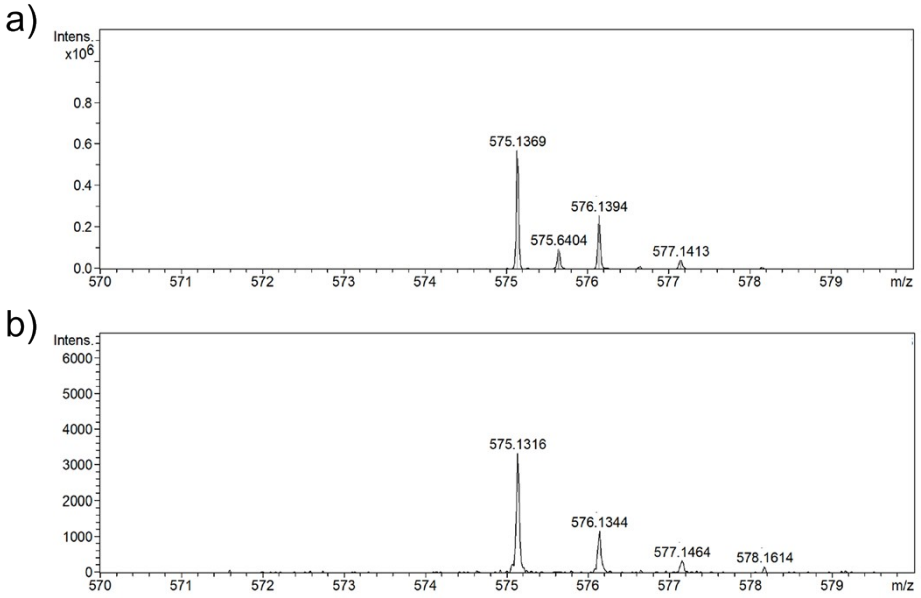

Fig. S1. High-resolution mass spectra of a) **5a** and b) **5b**, $[M+H]^+$ Calcd: 575.1330.

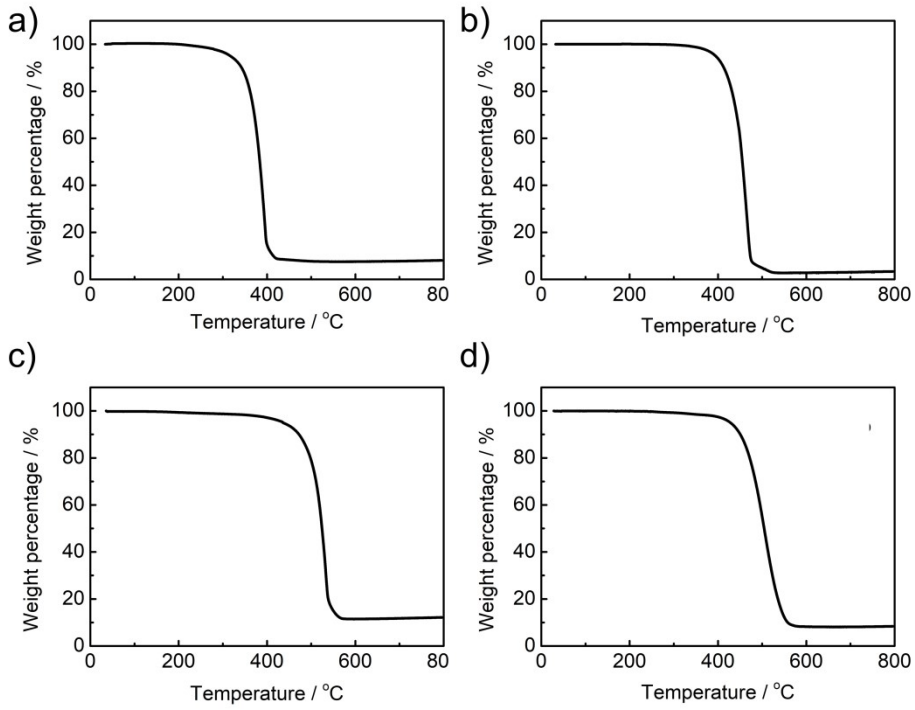

Fig. S2. Thermogravimetric analysis (TGA) curves of a) **3**, b) **4**, c) **5a** and d) **5b**. The decomposition temperature (T_d) at 5% weight loss is 317 °C for **3**, 394 °C for **4**, 428 °C for **5a** and 436 °C for **5b** under N_2.

2. X-ray crystallographic analysis

Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo·Kα radiation. The structure was solved using the SHELXTL-97 and refined by the full-matrix least-squares on F^2 (SHELXL-97). CCDC 2117851 (**3**), 2124936 (**4**) and 2168346 (**5a**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/structures/. The single crystal structure of **4** has been reported in the previous work.[1]

The single crystals of **3** suitable for X-ray diffraction (XRD) analysis were grown by the diffusion of hexane into a solution of **3** in CH_2Cl_2. The crystal data of **3** are as follows: $C_{30}H_{26}Si_2$; FW = 442.69, monoclinic, space group $P2_1/c$, a = 10.925(6) Å, b = 10.856(7) Å, c = 19.250(12) Å, α = 90°, β = 90.827(2)°, γ = 90°, V = 2282.9(2) Å^3, Z = 4, D_{calcd} = 1.288 g cm^{-3}, R_1 = 0.0515 ($I > 2\sigma(I)$), wR_2 = 0.1565 (all data), GOF = 1.092.

The single crystals of **5a** suitable for X-ray diffraction (XRD) analysis were grown by the diffusion of pentane into a solution of **5a** in CH_2Cl_2. The crystal data of **5a** are as follows: $C_{38}H_{24}O_2P_2$; FW = 574.51, monoclinic, space group $P2_1/c$, a = 10.048(5) Å, b = 21.103(13) Å, c = 15.594(10) Å, α = 90°, β = 101.908(2)°, γ = 90°, V = 3235.5(3) Å^3, Z = 4, D_{calcd} = 1.179 g cm^{-3}, R_1 = 0.0498 ($I > 2\sigma(I)$), wR_2 = 0.1488 (all data), GOF = 1.032.

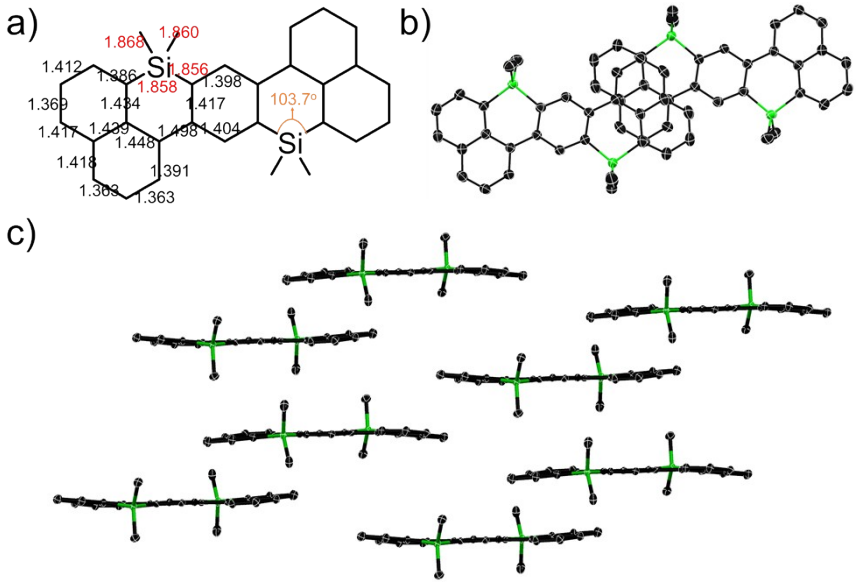

Fig. S3. a) X-ray crystal structure of **3**, along with its bond lengths (Å) and bond angles (°) around the Si atoms. b) The π-π stacking dimer and c) packing structure of **3**. Hydrogen atoms are not shown for clarity.

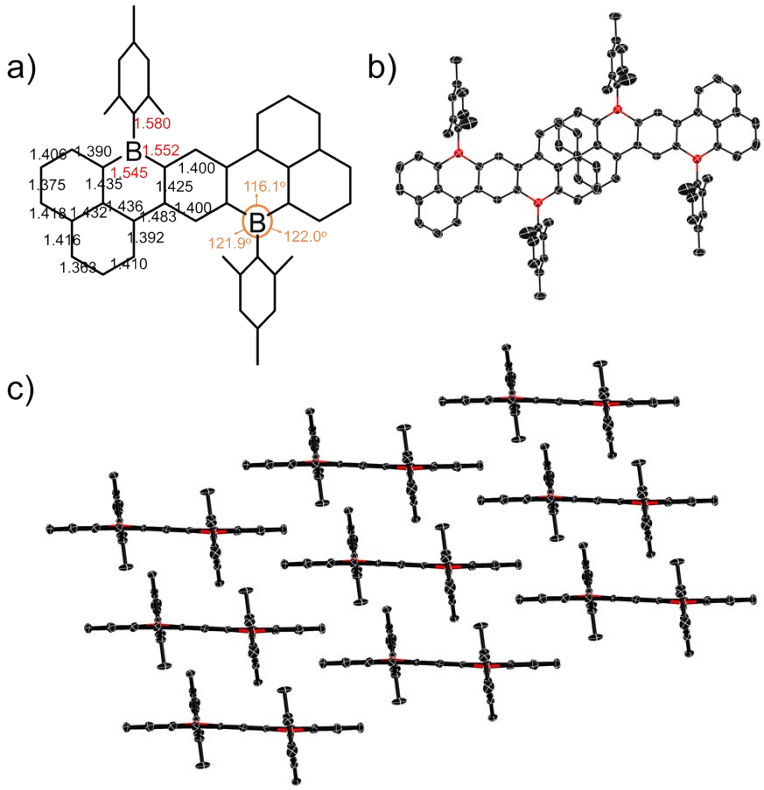

Fig. S4. a) X-ray crystal structure of **4**, along with its bond lengths (Å) and bond angles (°) around the B atoms. b) The π-π stacking and c) packing structure of **4**. Hydrogen atoms and the solvent molecules are not shown for clarity.

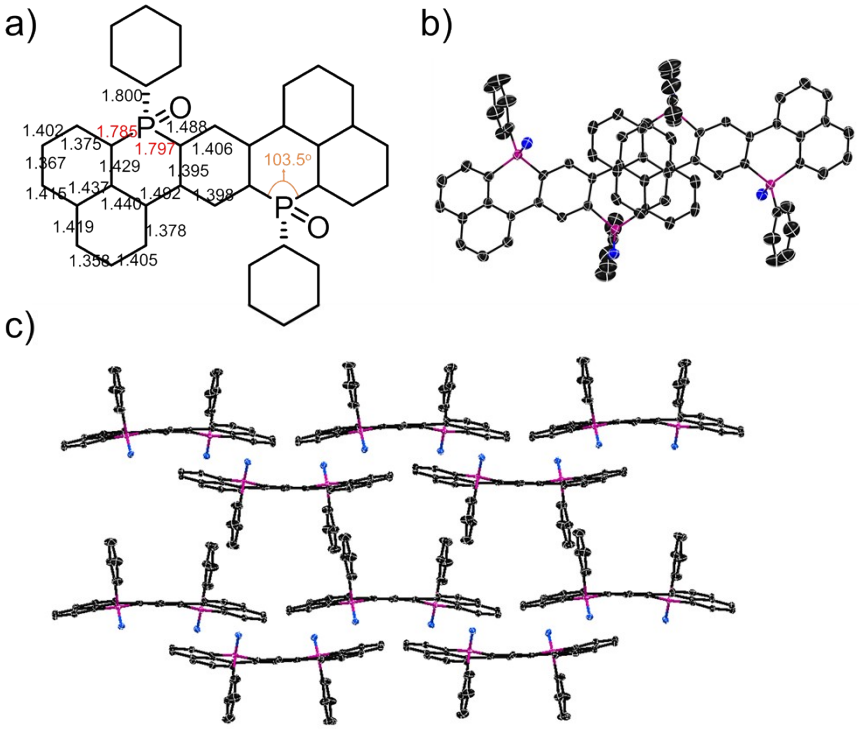

Fig. S5. a) X-ray crystal structure of **5a**, along with its bond lengths (Å) and bond angles (°) around the P atoms. b) The π-π stacking and c) packing structure of **5a**. Hydrogen atoms and the solvent molecules are not shown for clarity.

3. Photophysical and electrochemical properties

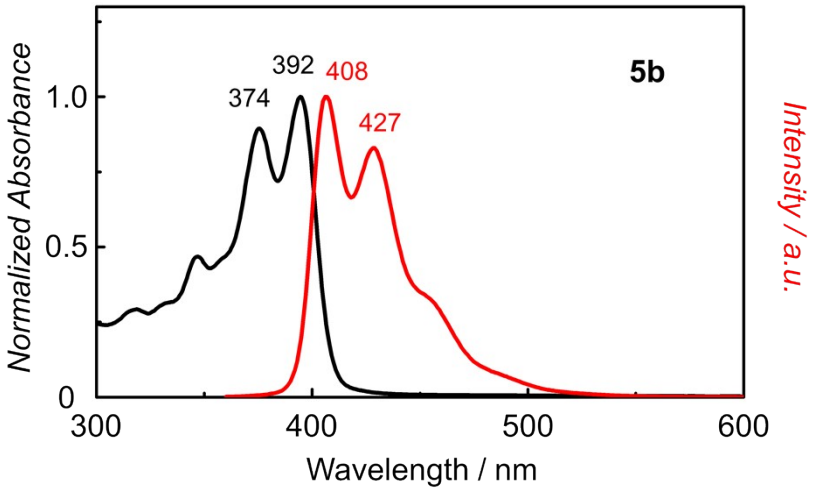

Fig. S6. UV–Vis absorption and fluorescence spectra of **5b** in toluene (1×10^{-5} M^{-1}).

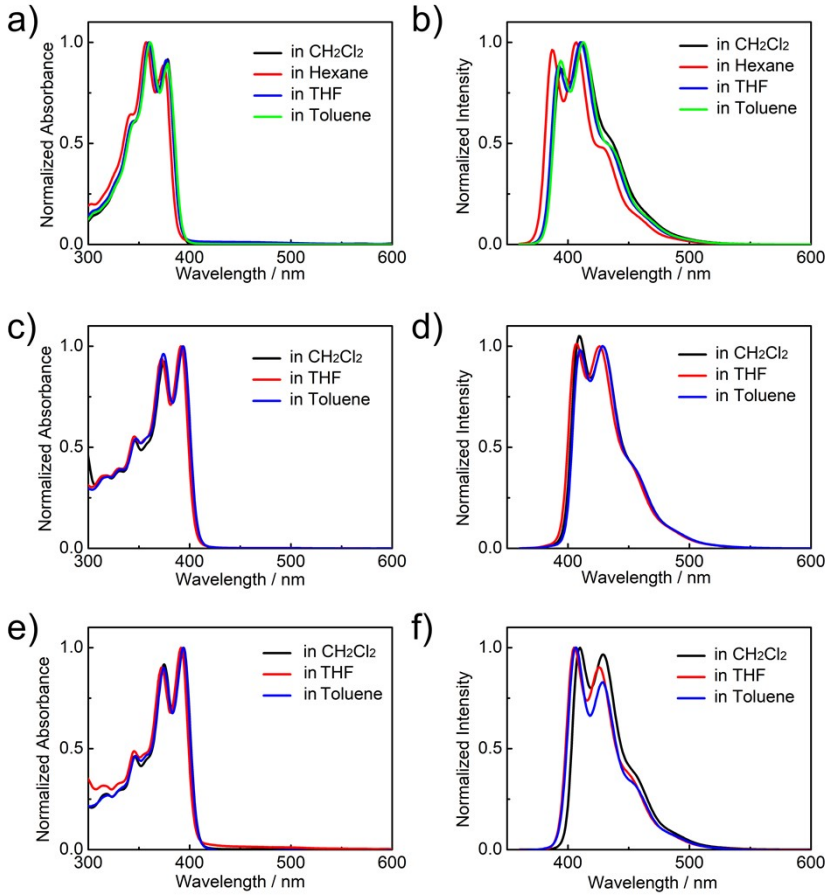

Fig. S7. UV–Vis absorption and fluorescence spectra of a,b) **3**, c,d) **5a** and e,f) **5b** in various solvents, respectively.

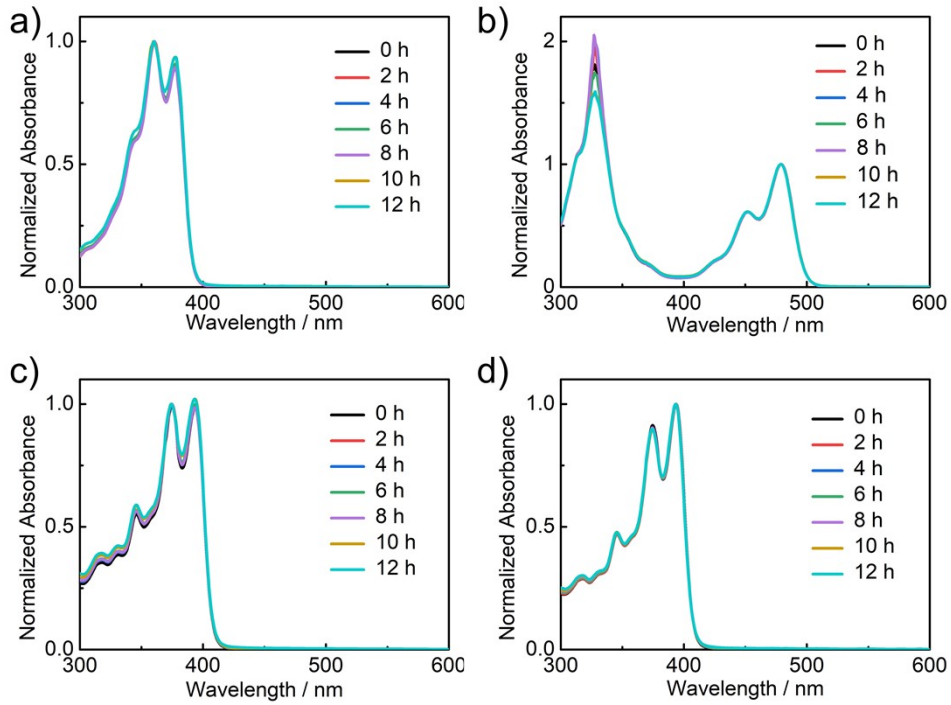

Fig. S8. UV–Vis absorption spectra of a) **3**, b) **4**, c) **5a** and d) **5b** in toluene with the solution left at ambient conditions for 12 h.

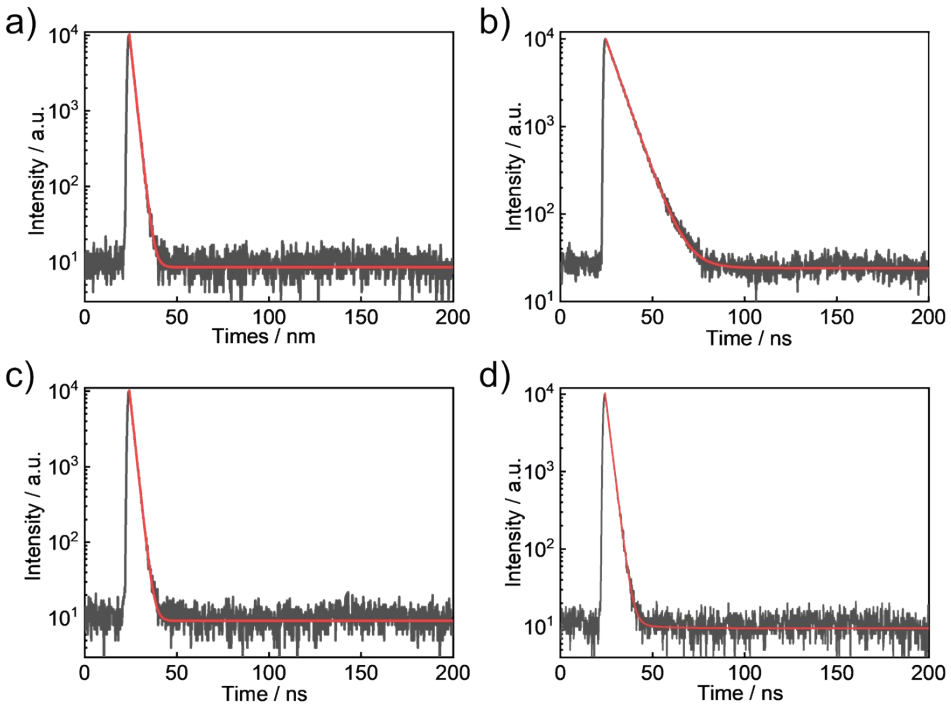

Fig. S9. Transient photoluminescence decay spectra of a) **3**, b) **4**, c) **5a** and d) **5b** in toluene.

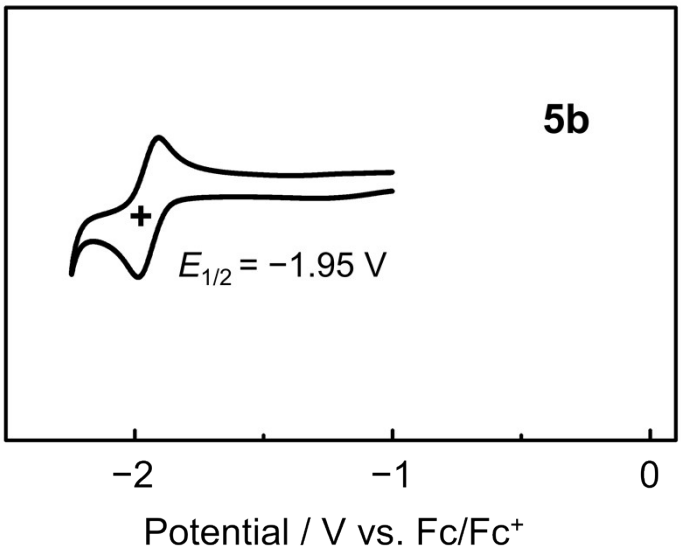

Fig. S10. Cyclic voltammogram of **5b** in CH_2Cl_2 (1.0 mM). Fc/Fc^+ = ferrocene/ferrocenium.

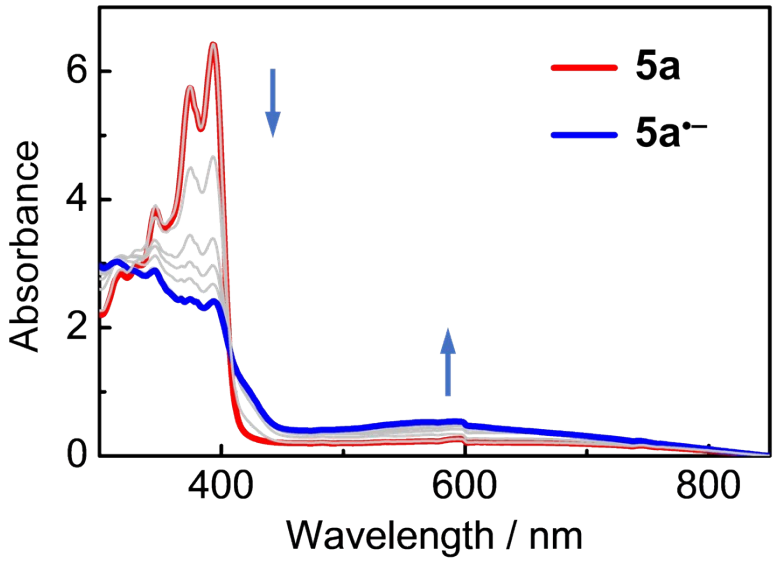

Fig. S11. UV–Vis absorption spectra of **5a** in CH_2Cl_2 (0.10 mM) measured in situ during cyclic voltammetry.

Upon applying a voltage of –2.90 V, the one-electron reduction occurs with the absorption spectrum gradually changing. A long-wavelength absorption band around 600 nm is observed, suggesting the formation of radical anion species **5a**$^{\bullet-}$.

4. Geometry optimizations and time-dependent DFT calculations

All calculations were carried out using the Gaussian 09 program.[2] Density functional theory (DFT) calculations were performed on **3**, **4**, **5a** and **5b**, as well as **1a** and **2a** at the B3LYP/6-311G(d) level of theory to obtain the optimized structures and molecular orbitals. Time-dependent DFT (TD-DFT) calculations were performed on them at the same level of theory to assign the absorption bands observed in the UV–Vis absorption spectra.

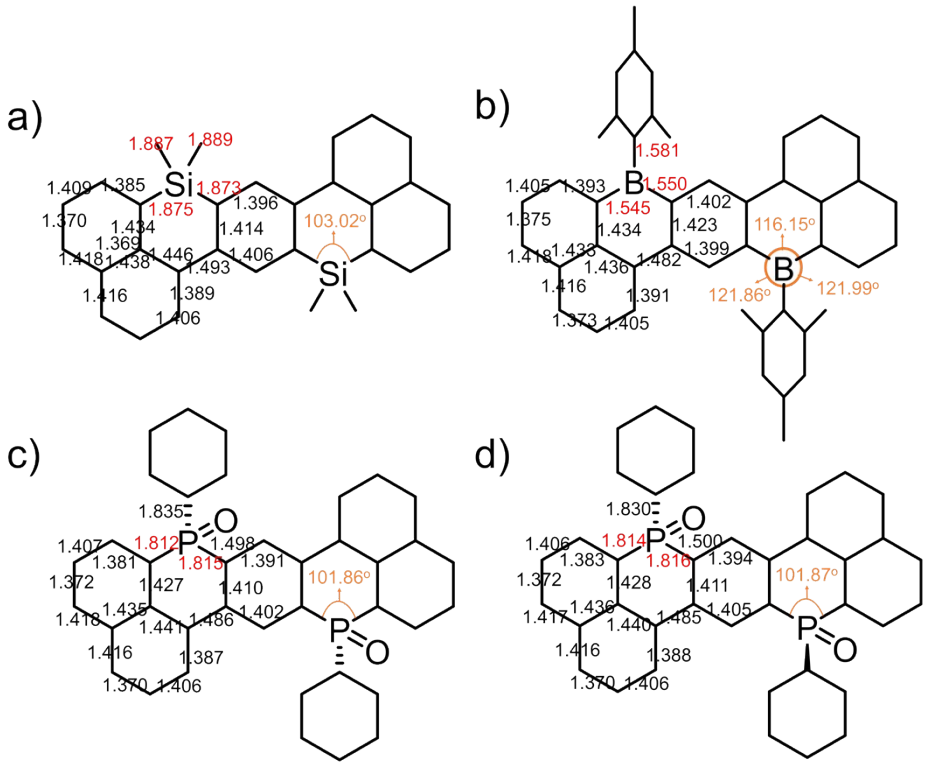

Fig. S12. Optimized structure of a) **3**, b) **4**, c) **5a** and d) **5b**, along with their bond lengths (Å) and bond angles (°) around the heteroatoms.

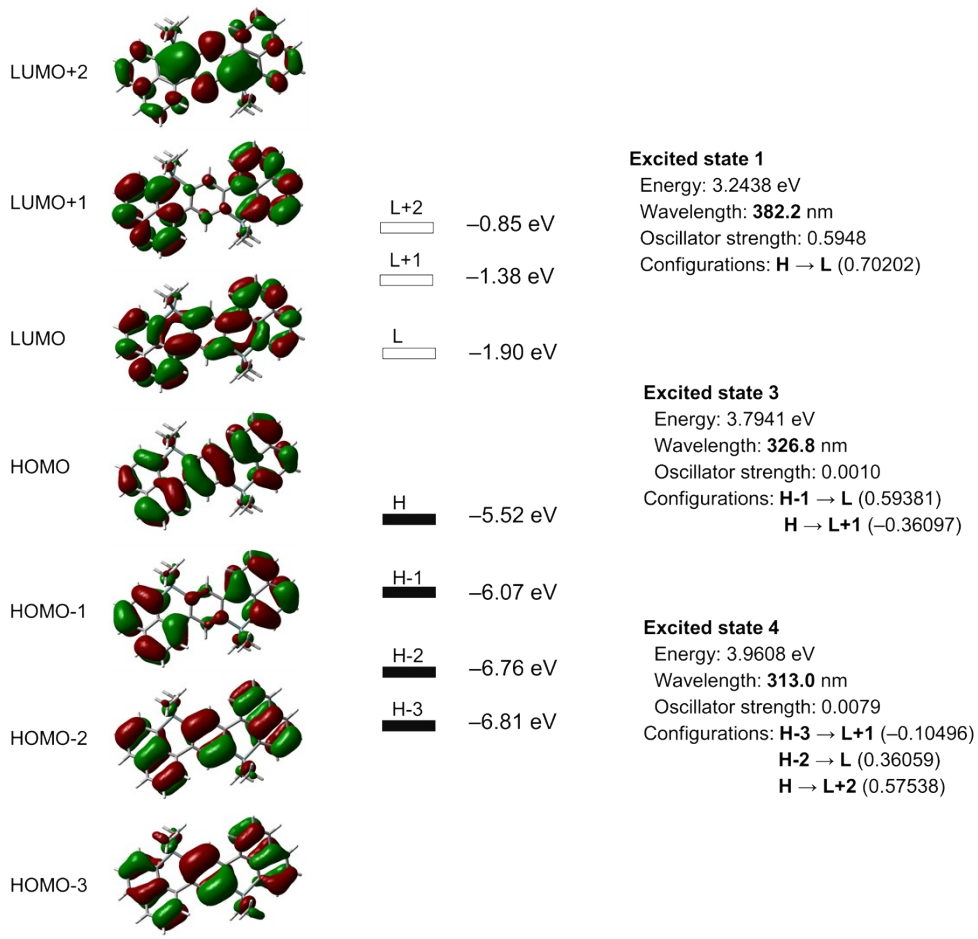

Fig. S13. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **3**, based on the TD-DFT (B3LYP/6-311G(d)) calculation.

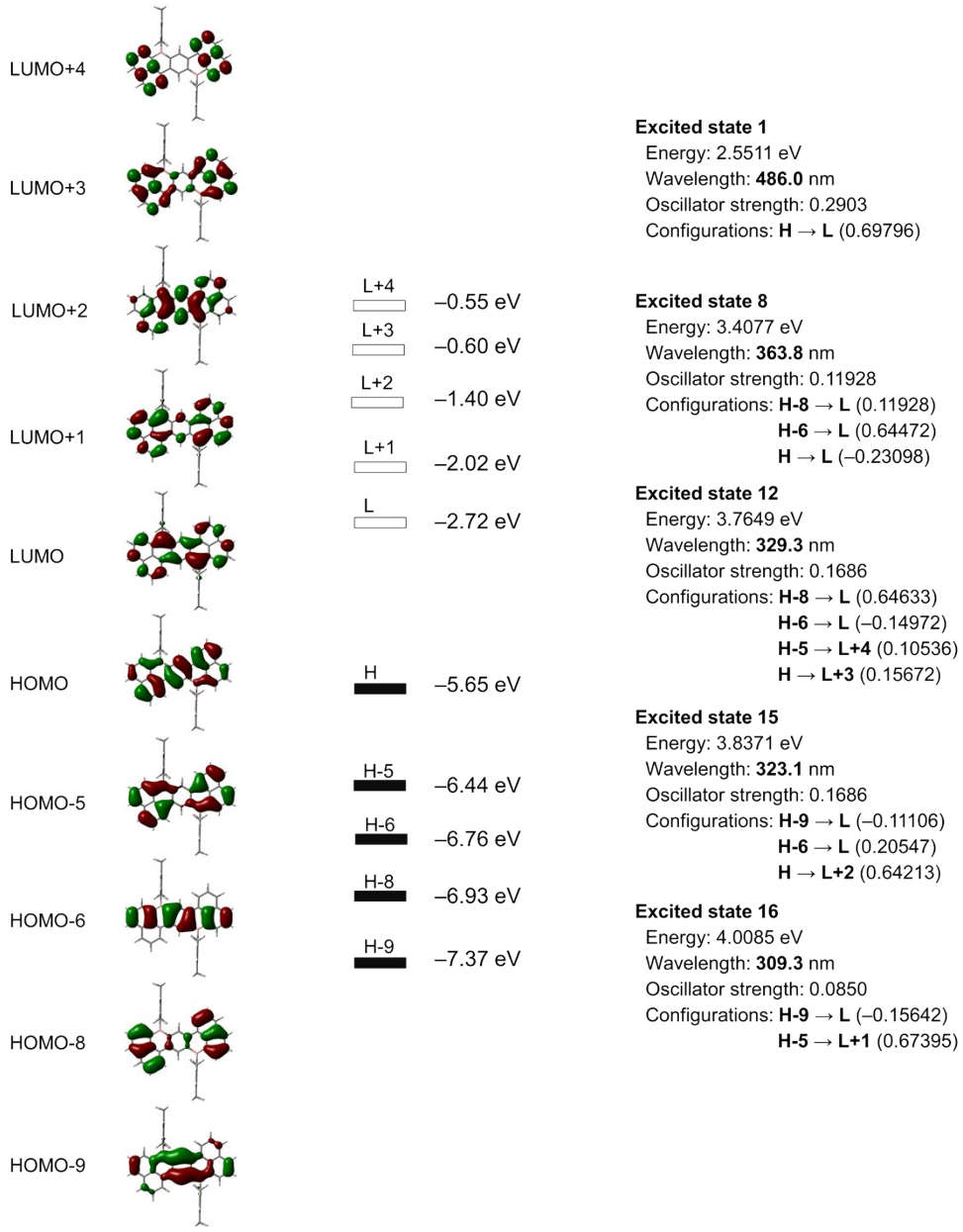

Fig. S14. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **4**, based on the TD-DFT (B3LYP/6-311G(d)) calculation.

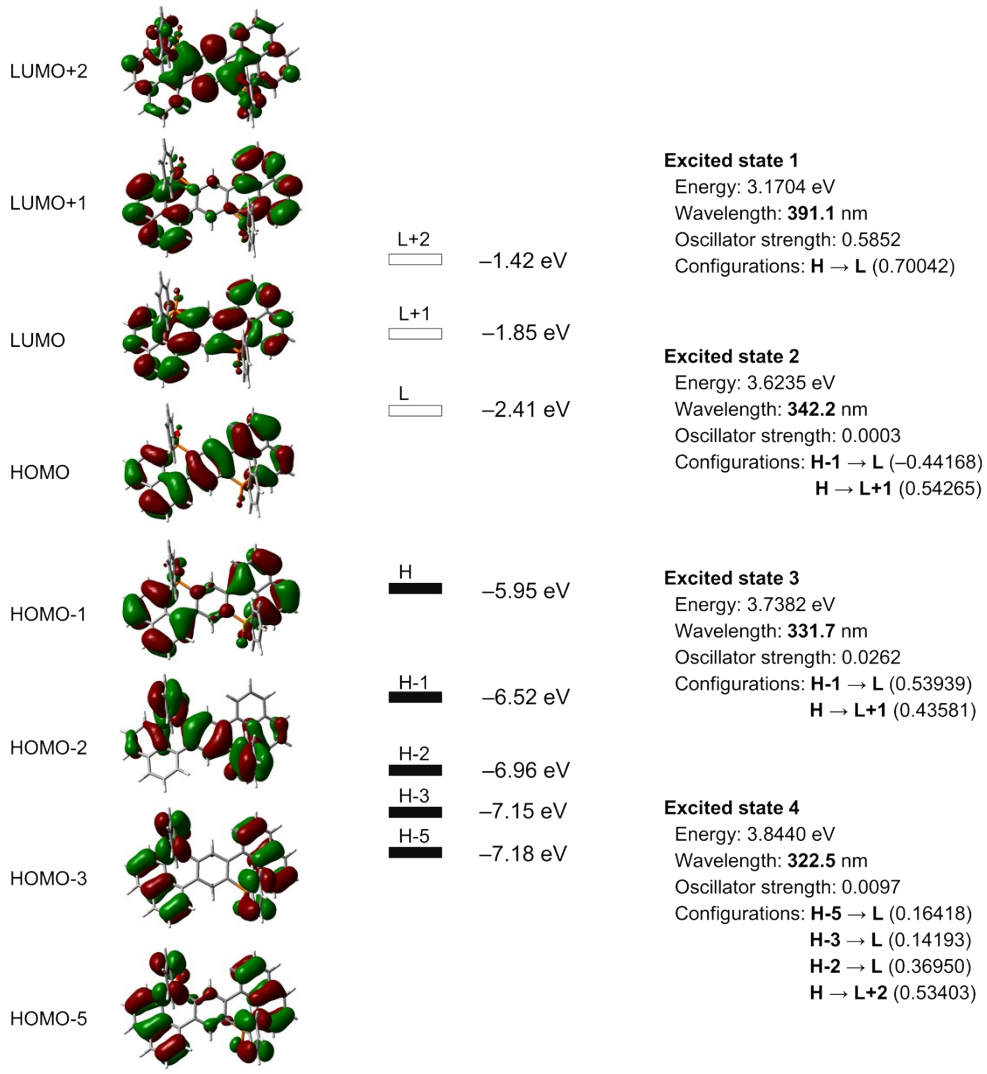

Fig. S15. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **5a**, based on the TD-DFT (B3LYP/6-311G(d)) calculation.

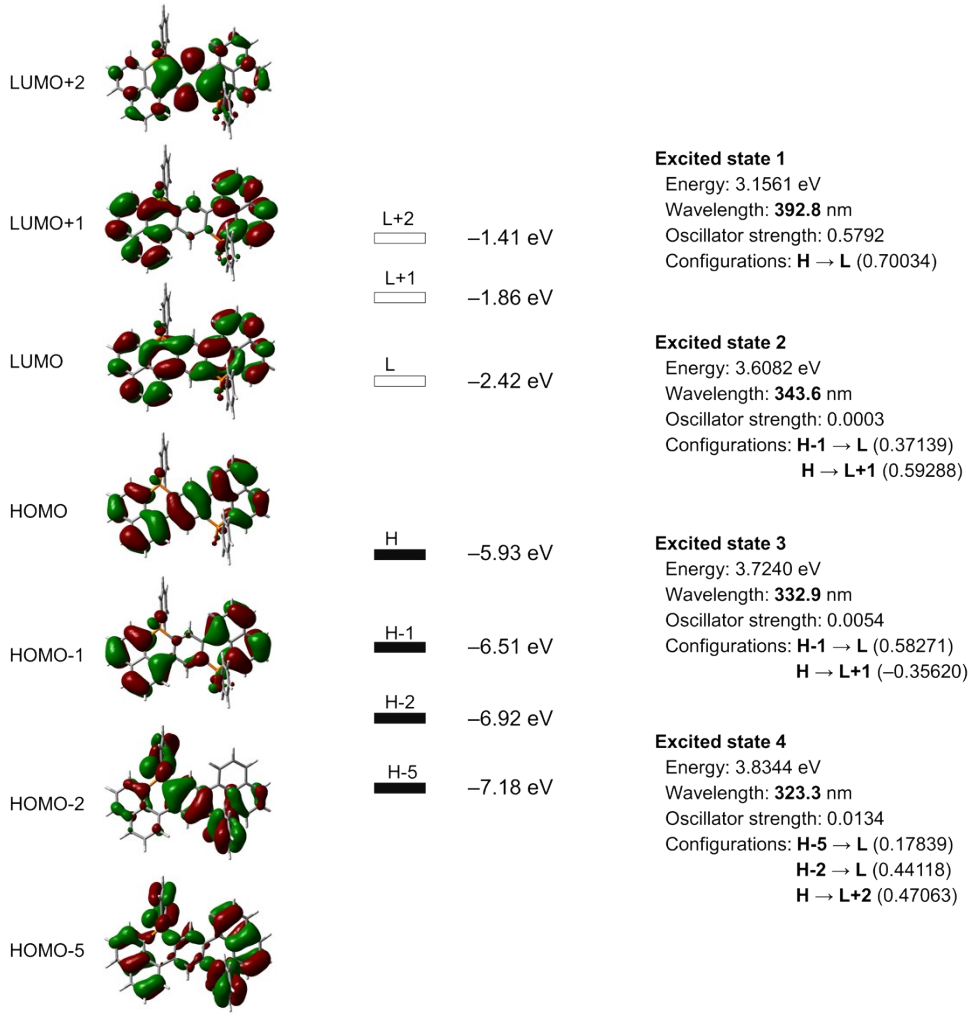

Fig. S16. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **5b**, based on the TD-DFT (B3LYP/6-311G(d)) calculation.

Table S1. Coordinates of the optimized structure for **3** at the B3LYP/6-311G(d) level.

Atom	x	y	z
Si	-2.528975	2.07214	-0.003310
Si	2.528783	-2.072097	-0.003973
C	-3.911145	-0.451341	-0.074534
C	-3.967593	0.941171	-0.412684
C	-5.150934	1.477301	-0.893022
H	-5.198312	2.533181	-1.148565
C	-6.318168	0.70329	-1.045961
H	-7.223954	1.155442	-1.437621
C	-6.305321	-0.612383	-0.661001
H	-7.205941	-1.21574	-0.730720
C	-5.126659	-1.215839	-0.152592
C	-5.158054	-2.559485	0.295800
H	-6.091656	-3.111306	0.239192
C	-4.030795	-3.135286	0.819256
H	-4.055794	-4.149434	1.204930
C	-2.821013	-2.418408	0.839690
H	-1.951015	-2.911587	1.254591
C	-2.704114	-1.120167	0.359175
C	-1.342149	-0.513325	0.282104
C	-0.212954	-1.347939	0.215427
H	-0.365904	-2.417692	0.120886
C	1.101955	-0.878127	0.213384
C	3.967827	-0.941255	-0.412065
C	5.151393	-1.477697	-0.891536
H	5.1988	-2.533693	-1.146614
C	6.318756	-0.70386	-1.044236
H	7.224717	-1.156252	-1.435218
C	6.305773	0.612015	-0.659967
H	7.20644	1.215307	-0.729610
C	5.126917	1.215768	-0.152381
C	5.158234	2.559632	0.295360

H	6.091886	3.111372	0.238793
C	4.030827	3.135744	0.818126
H	4.055736	4.150085	1.203300
C	2.821023	2.418903	0.838571
H	1.950956	2.912324	1.253028
C	2.704185	1.120415	0.358689
C	3.911316	0.451372	-0.074443
C	1.342204	0.513549	0.281747
C	0.212975	1.348153	0.215081
H	0.365874	2.417887	0.120284
C	-1.101923	0.878342	0.213462
C	-2.179136	3.298287	-1.395419
H	-1.953959	2.784242	-2.333169
H	-1.328396	3.944983	-1.159680
H	-3.036189	3.95515	-1.574256
C	-2.888482	3.027832	1.587052
H	-3.101015	2.350338	2.418286
H	-2.037552	3.651865	1.878692
H	-3.754443	3.686834	1.468727
C	2.887218	-3.029519	1.585593
H	3.098628	-2.352905	2.417840
H	3.753557	-3.688063	1.467435
H	2.036225	-3.654203	1.875636
C	2.1789	-3.296965	-1.397216
H	3.035334	-3.954767	-1.575579
H	1.955084	-2.782251	-2.334908
H	1.32719	-3.942782	-1.162482

Table S2. Coordinates of the optimized structure for **4** at the B3LYP/6-311G(d) level.

Atom	x	y	z
B	-2.904589	0.590389	0.000038
C	-3.309212	2.081619	0.000039
C	-4.648301	2.465562	0.000062
H	-5.410853	1.692806	0.000082
C	-5.040169	3.814967	0.000058
H	-6.093154	4.077772	0.000087
C	-4.077687	4.797339	0.000024
H	-4.36456	5.845346	0.000018
C	-2.697171	4.474834	-0.000005
C	-1.719488	5.499045	-0.000049
H	-2.038956	6.536942	-0.000065
C	-0.386236	5.173174	-0.000077
H	0.37095	5.950398	-0.000116
C	0.012433	3.82558	-0.000055
H	1.075361	3.622033	-0.000079
C	-0.899348	2.775113	-0.000007
C	-2.298241	3.098788	0.000011
C	-0.443963	1.365235	0.000015
C	-1.382482	0.295364	0.000016
C	-0.913719	-1.025958	0.000022
H	-1.670809	-1.80012	0.000014
C	-3.979287	-0.568973	0.000004
C	-4.465174	-1.102243	1.213331
C	-5.406796	-2.133941	1.194600
H	-5.767644	-2.535085	2.139202
C	-5.894355	-2.664071	-0.000085
C	-5.406633	-2.13398	-1.194733
H	-5.767362	-2.535172	-2.139359
C	-4.465021	-1.102289	-1.213382
C	-3.971252	-0.568157	2.540782
H	-2.885614	-0.668829	2.639675
H	-4.427994	-1.098228	3.379383
H	-4.201018	0.495648	2.659408

C	-6.936693	-3.756451	-0.000131
H	-6.85121	-4.394859	0.882914
H	-6.851645	-4.394363	-0.883574
H	-7.950163	-3.339362	0.000242
C	-3.970939	-0.568212	-2.540774
H	-4.200901	0.49554	-2.659523
H	-4.42741	-1.098434	-3.379424
H	-2.885262	-0.668665	-2.639448
B	2.90459	-0.590389	0.000027
C	3.309212	-2.081619	-0.000007
C	4.648301	-2.465563	-0.000047
H	5.410853	-1.692807	-0.000061
C	5.040169	-3.814967	-0.000064
H	6.093154	-4.077773	-0.000106
C	4.077687	-4.797339	-0.000031
H	4.36456	-5.845347	-0.000040
C	2.697171	-4.474834	0.000015
C	1.719488	-5.499045	0.000059
H	2.038956	-6.536943	0.000062
C	0.386236	-5.173175	0.000103
H	-0.37095	-5.950399	0.000142
C	-0.012432	-3.825581	0.000097
H	-1.075361	-3.622033	0.000132
C	0.899349	-2.775113	0.000052
C	2.298242	-3.098788	0.000018
C	0.443963	-1.365235	0.000039
C	1.382483	-0.295364	0.000040
C	0.913719	1.025958	0.000031
H	1.670809	1.800121	0.000039
C	3.979287	0.568973	0.000005
C	4.465093	1.102263	-1.213346
C	5.406715	2.133961	-1.194661
H	5.767498	2.535122	-2.139281
C	5.894354	2.664073	-0.000001
C	5.406713	2.133961	1.194672

H	5.767506	2.535137	2.139279
C	4.465102	1.10227	1.213368
C	3.971077	0.568202	-2.540772
H	2.885432	0.668878	-2.639587
H	4.42776	1.098288	-3.379395
H	4.200833	-0.4956	-2.659435
C	6.936691	3.756453	-0.000007
H	6.851144	4.394879	-0.883033
H	6.851707	4.394347	0.883455
H	7.950161	3.339364	-0.000462
C	3.971115	0.568168	2.540784
H	4.201087	-0.495586	2.659497
H	4.427645	1.098374	3.379412
H	2.885445	0.668618	2.639538

Table S3. Coordinates of the optimized structure for **5a** at the B3LYP/6-311G(d) level.

Atom	x	y	z
P	2.856258	-1.436036	-0.559075
P	-2.856142	1.436374	-0.558545
O	-2.869302	2.725366	-1.322529
O	2.869412	-2.724621	-1.323739
C	4.025863	-2.27996	3.837575
H	4.302826	-2.498211	4.864152
C	3.689577	-0.977268	3.468843
H	3.704022	-0.181706	4.206924
C	3.334249	-0.693722	2.153699
H	3.075316	0.323766	1.879904
C	3.313122	-1.715063	1.1963
C	1.261243	-0.569546	-0.529189
C	1.174317	0.838582	-0.531928
C	-0.12338	1.370645	-0.55845
H	-0.276612	2.438281	-0.654319
C	-1.261086	0.569956	-0.528924
C	-3.313344	1.714425	1.196899
C	-3.333696	0.692775	2.153983
H	-3.073825	-0.324399	1.879916
C	-3.689427	0.975611	3.469172
H	-3.703259	0.179812	4.207009
C	-4.02689	2.277896	3.838264
H	-4.304158	2.495591	4.864877
C	4.005382	-3.299131	2.888674
H	4.266204	-4.313583	3.17321
C	3.649603	-3.019904	1.57023
H	3.626992	-3.803511	0.821039
C	0.123534	-1.370224	-0.55891
H	0.276718	-2.437837	-0.655165
C	-1.174156	-0.838163	-0.532133

C	-2.363432	-1.726569	-0.599231
C	-3.658034	-1.241846	-1.006286
C	-4.699731	-2.189257	-1.282991
C	-5.943967	-1.733996	-1.78916
H	-6.712616	-2.469611	-2.006768
C	-6.181917	-0.39902	-2.002418
H	-7.132726	-0.065426	-2.404169
C	-5.193772	0.544582	-1.664157
H	-5.389755	1.60429	-1.79125
C	-3.971898	0.141776	-1.161353
C	2.363602	1.727007	-0.598772
C	3.658286	1.242372	-1.005698
C	4.700051	2.189844	-1.281969
C	4.481776	3.56831	-1.038161
H	5.284979	4.271161	-1.236847
C	3.277984	3.999324	-0.543474
H	3.114197	5.049965	-0.328793
C	2.229087	3.084083	-0.340938
H	1.284994	3.471676	0.019995
C	5.94442	1.734705	-1.78791
H	6.713109	2.470378	-2.005175
C	6.18245	0.399775	-2.001369
H	7.133375	0.066271	-2.402923
C	5.194215	-0.543895	-1.663591
H	5.390226	-1.603571	-1.790902
C	3.972198	-0.141206	-1.16102
C	-3.650982	3.018865	1.571196
H	-3.628885	3.802737	0.822268
C	-4.007163	3.297378	2.889681
H	-4.268873	4.311522	3.174501
C	-4.481507	-3.567766	-1.039389
H	-5.284659	-4.270584	-1.238395
C	-3.277824	-3.99888	-0.544509

H	-3.114103	-5.049561	-0.329976
C	-2.228955	-3.083689	-0.341606
H	-1.284913	-3.47132	0.019431

Table S4. Coordinates of the optimized structure for **5b** at the B3LYP/6-311G(d) level.

Atom	x	y	z
C	3.303053	1.680718	-0.37123
C	3.695629	0.553219	-1.153247
C	4.821766	0.597601	-1.951855
H	5.079557	-0.269502	-2.551217
C	5.637447	1.744414	-1.987294
H	6.51348	1.764591	-2.626777
C	5.335371	2.815461	-1.183567
H	5.980494	3.688918	-1.16836
C	4.184105	2.813167	-0.355132
C	3.903917	3.911299	0.495235
H	4.589206	4.75321	0.510024
C	2.793502	3.895718	1.299488
H	2.591551	4.718899	1.976573
C	1.886753	2.822118	1.231451
H	1.008671	2.861103	1.863867
C	2.07977	1.73762	0.387299
C	1.008719	0.720492	0.229761
C	-0.313086	1.006646	0.594868
H	-0.559827	1.989344	0.977133
C	-1.354811	0.091974	0.447345
C	-4.084656	-0.606572	0.255157
C	-5.441644	-0.338086	0.270967
H	-5.790807	0.633692	0.605426
C	-6.382362	-1.307781	-0.118434
H	-7.440809	-1.070712	-0.106183
C	-5.94953	-2.558419	-0.482043
H	-6.664698	-3.328913	-0.754312
C	-4.56973	-2.881351	-0.50629
C	-4.149032	-4.188833	-0.851389
H	-4.898651	-4.934934	-1.096309

C	-2.815423	-4.504445	-0.855762
H	-2.486633	-5.511201	-1.090344
C	-1.856563	-3.516174	-0.573199
H	-0.815406	-3.809667	-0.595168
C	-2.198394	-2.204812	-0.270919
C	-3.597228	-1.880128	-0.167581
C	-1.129081	-1.18942	-0.098977
C	0.180669	-1.446462	-0.536526
H	0.409549	-2.361652	-1.067473
C	1.221176	-0.541136	-0.365355
C	3.68035	-1.934965	0.355669
C	4.231067	-3.185915	0.059783
C	3.781741	-1.423461	1.654974
C	4.879459	-3.916213	1.054194
H	4.14077	-3.57503	-0.948321
C	4.429282	-2.156582	2.64457
H	3.356015	-0.456413	1.901769
C	4.979326	-3.40305	2.345044
H	5.304633	-4.886896	0.819523
H	4.502721	-1.756659	3.650741
H	5.482789	-3.973188	3.119378
C	-3.337731	2.214302	0.228444
C	-3.677636	3.298748	1.042681
C	-3.276632	2.381596	-1.160321
C	-3.954378	4.540468	0.471593
H	-3.722676	3.154177	2.116746
C	-3.551507	3.622192	-1.726287
H	-3.0139	1.544919	-1.800226
C	-3.890979	4.702366	-0.910187
H	-4.219572	5.379664	1.10669
H	-3.501276	3.74821	-2.802977
H	-4.105795	5.66927	-1.354149
O	2.806672	-1.877012	-2.253163

O	-3.122859	0.713648	2.53008
P	2.843546	-1.041284	-1.009818
P	-2.991952	0.610469	1.03922

5. Aromaticity

Theoretical calculations were performed on **3**, **4**, **5a** and **5b** to investigate their aromaticity. Nucleus-independent chemical shift (NICS) and anisotropy of the induced current density (ACID) were employed to study the aromaticity. The $NICS(1)_{ZZ}$ calculations were performed with the nmr=GIAO key word based on the B3LYP/6-311+G(d) level of theory. The ACID calculations were performed with the nmr=CSGT iop(10/93=2) key word based on the B3LYP/6-311G(d) level of theory.

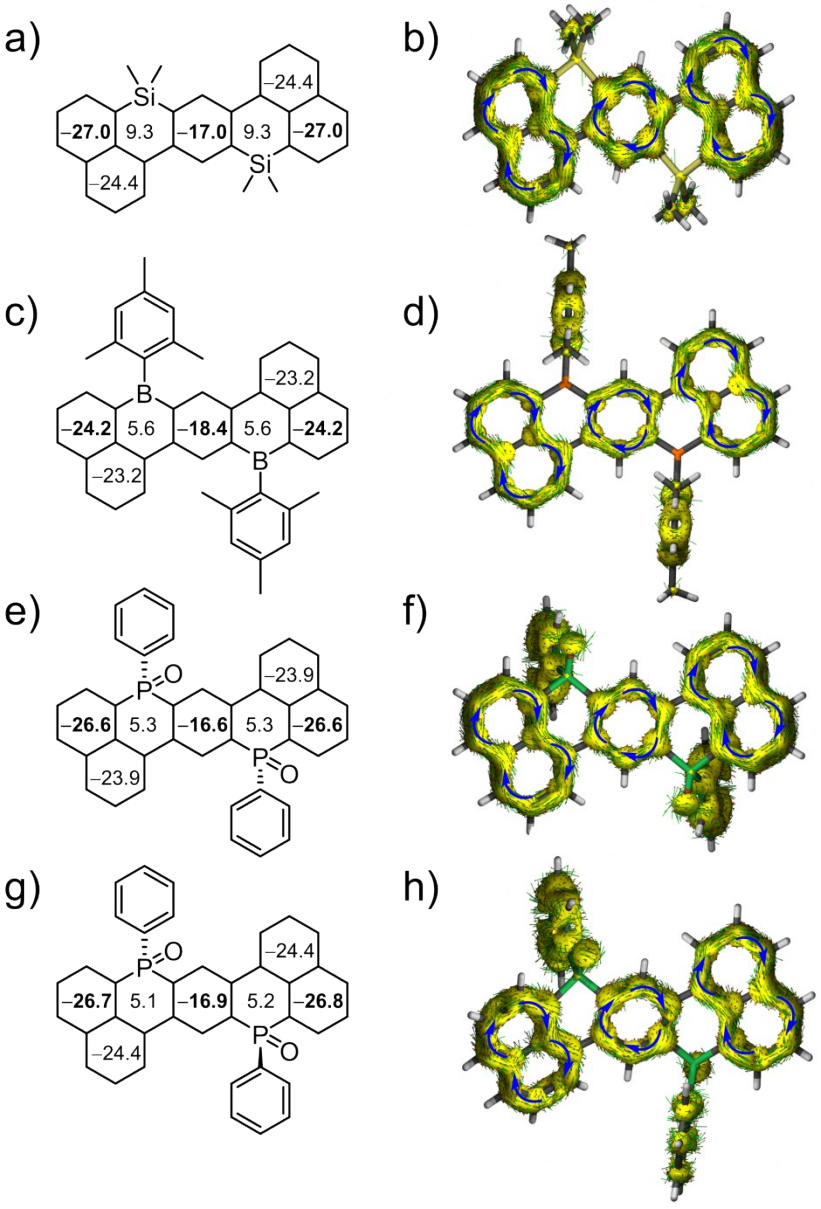

Fig. S17. $NICS(1)_{ZZ}$ values and ACID plots of a,b) **3**, c,d) **4**, e,f) **5a** and g,h) **5b** (contribution from π electrons only).

6. ^{1}H NMR and ^{13}C NMR spectra

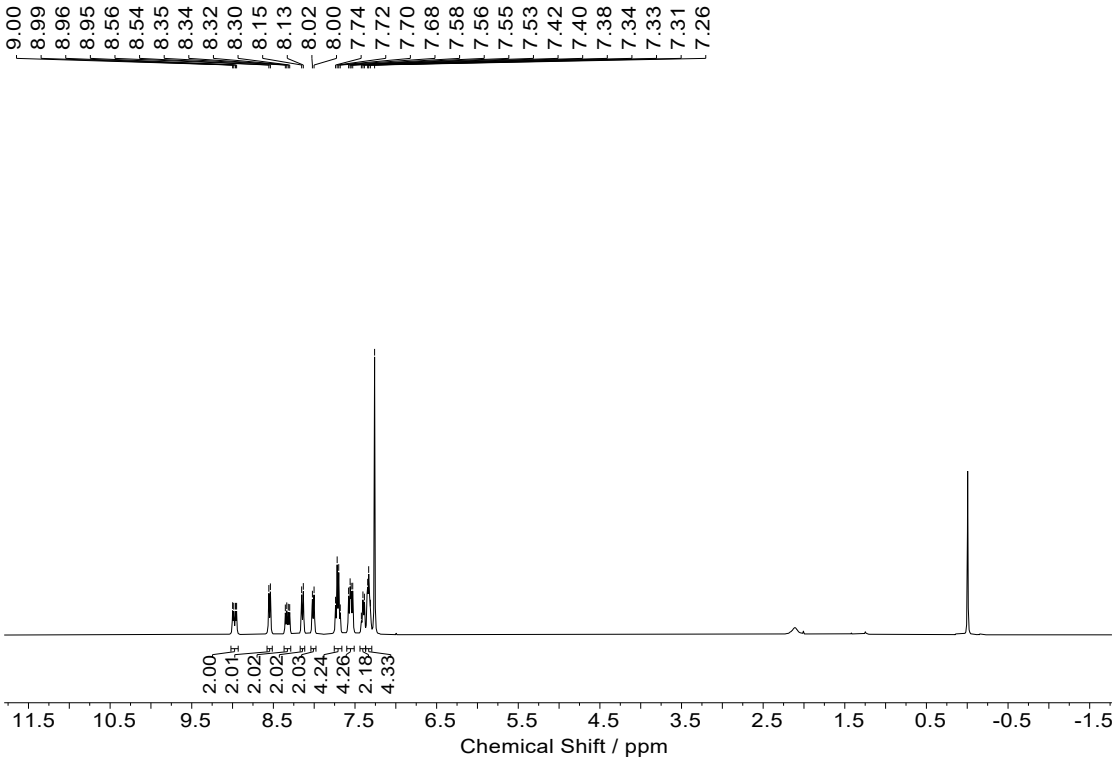

Fig. S18. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

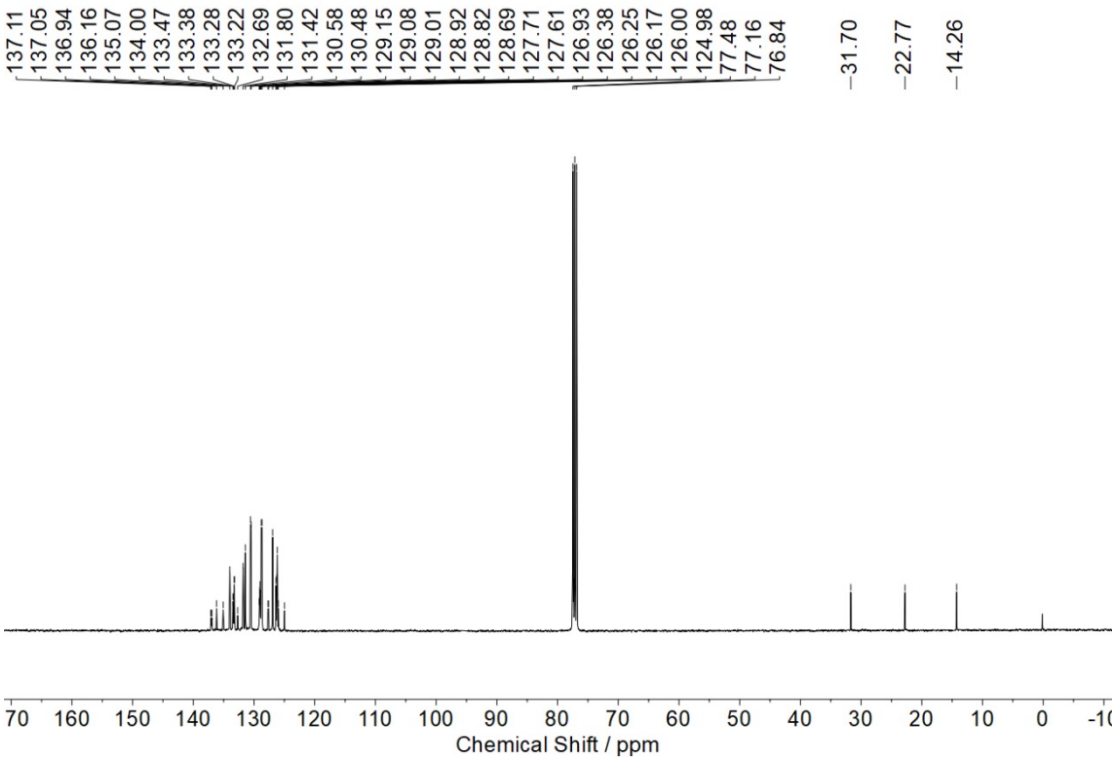

Fig. S19. ^{13}C NMR spectrum of **5a** in $CDCl_3$.

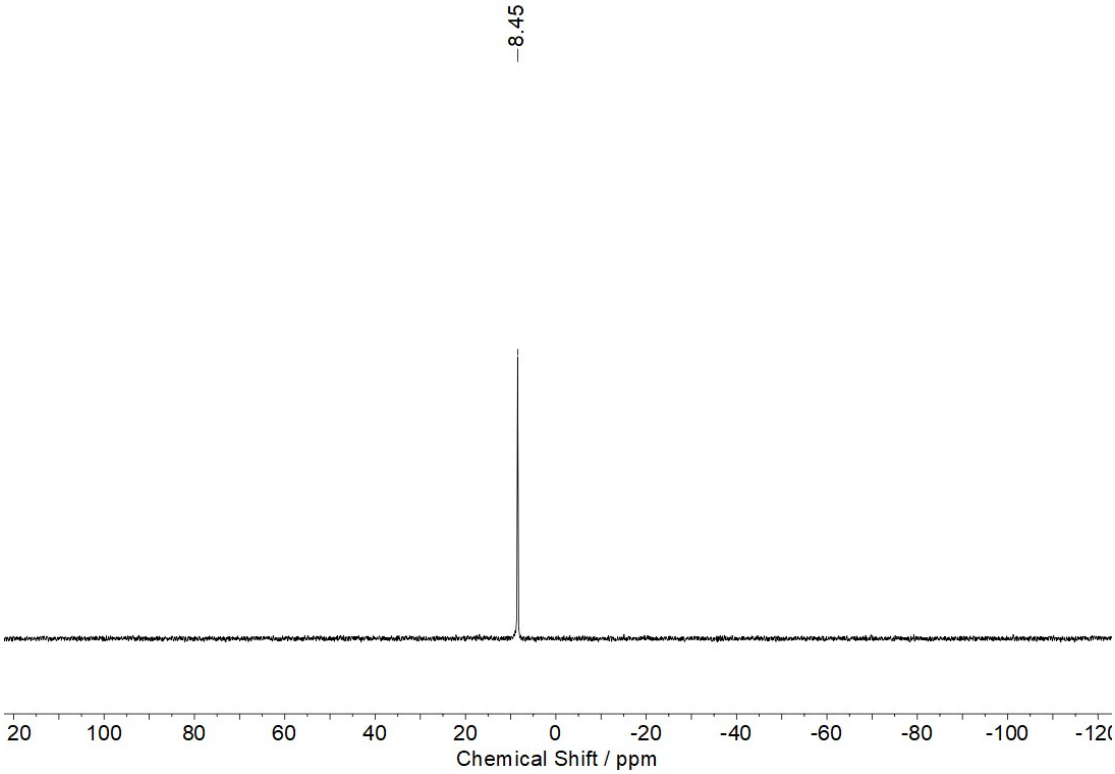

Fig. S20. ^{31}P NMR spectrum of **5a** in $CDCl_3$.

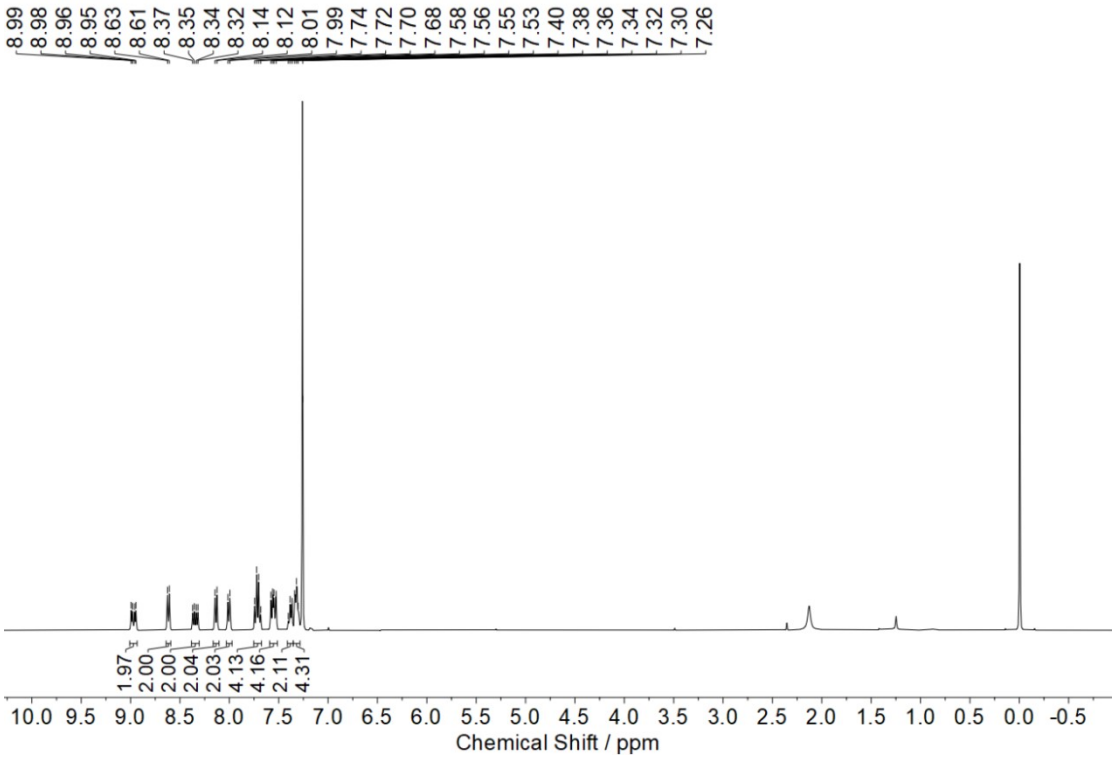

Fig. S21. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

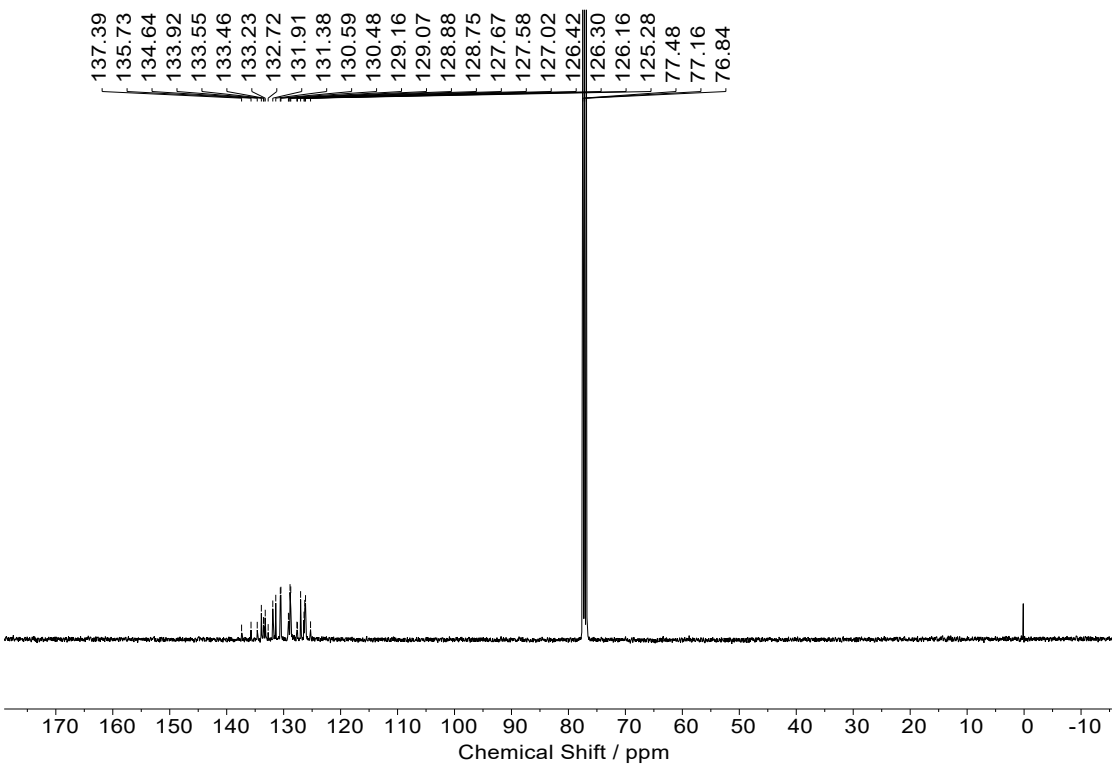

Fig. S22. ^{13}C NMR spectrum of **5b** in $CDCl_3$.

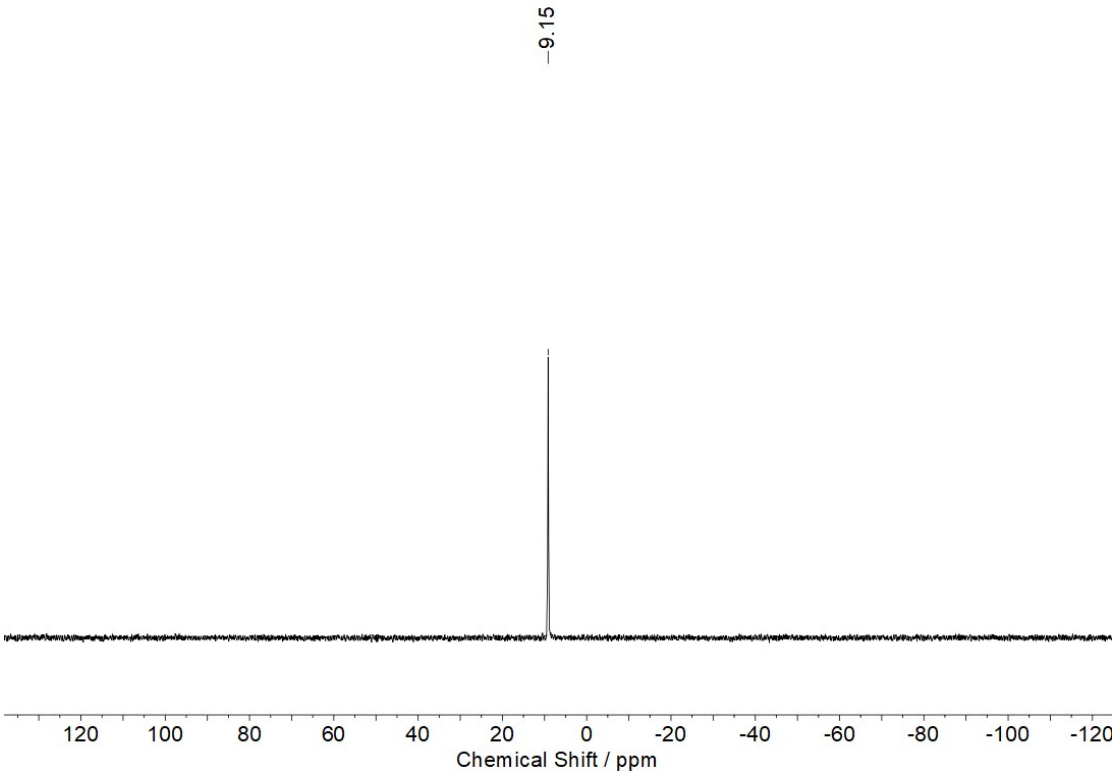

Fig. S23. ^{31}P NMR spectrum of **5b** in $CDCl_3$.

7. Reference

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