Supplementary Material for paper

"New efficient pecS-*n* (*n* = 1, 2) basis sets for quantum chemical calculations of ^{31}P NMR chemical shifts"

by

Yuriy Yu. Rusakov and Irina L. Rusakova

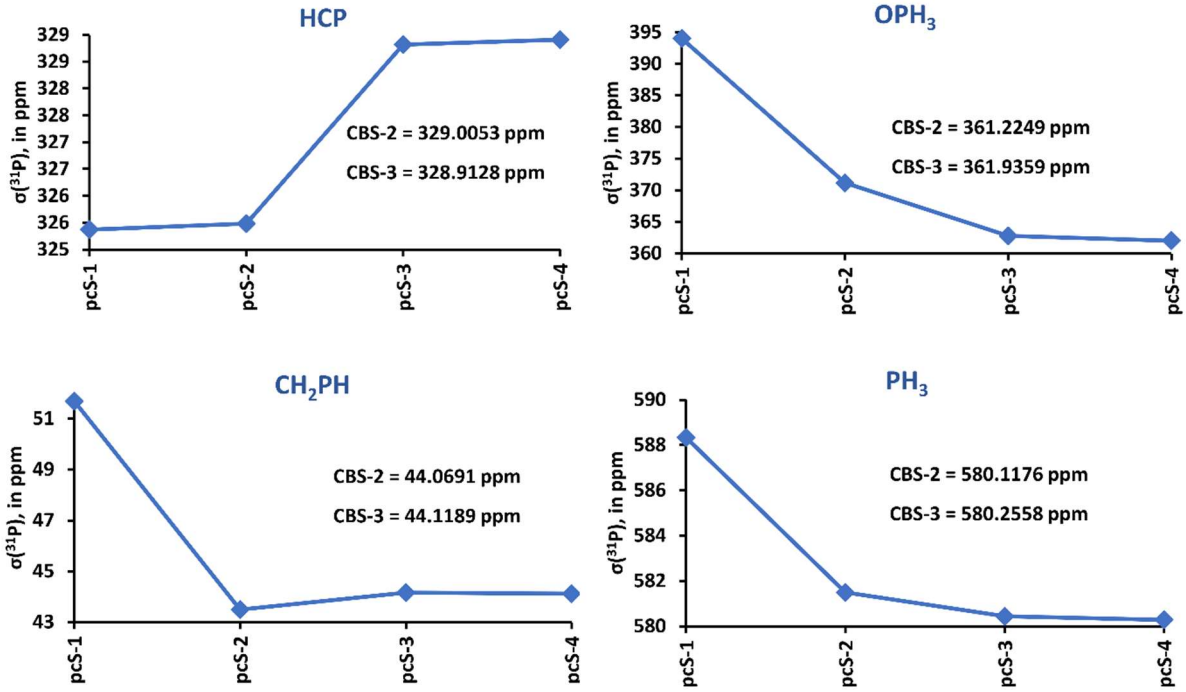
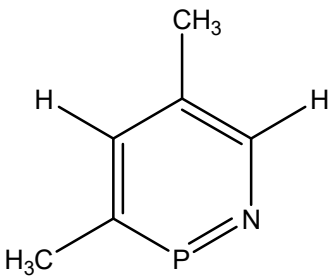
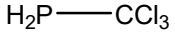
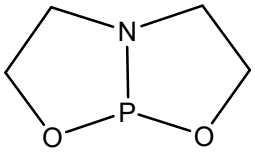
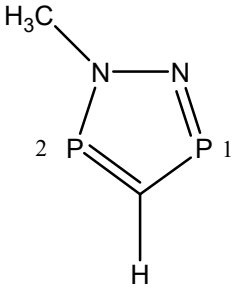
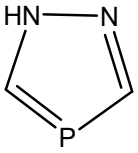
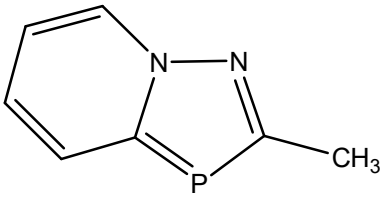
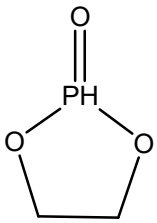
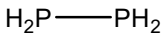
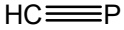
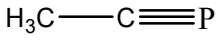
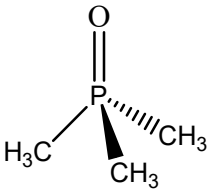
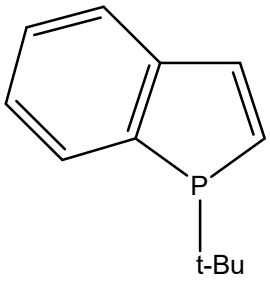


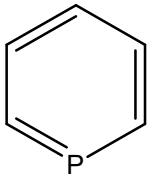
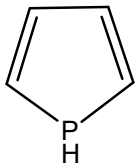
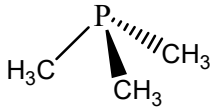
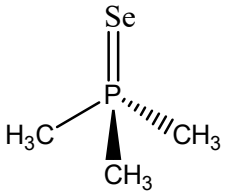
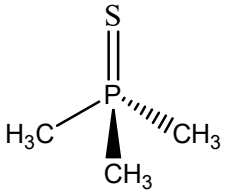
Figure S1. The dependence of the phosphorus shielding constants in the four fitting molecules on the basis set (from pcS-1 to pcS-4), calculated at the GIAO-DFT(PBE0) level of theory.

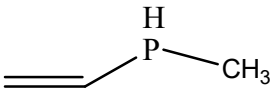
Table S1. Equilibrium geometries of twenty testing compounds obtained at the DFT(M06-2X) level using the pc-3 basis set within the IEF-PCM solvation model with the dielectric constants specified for a particular solvent.[a]

#	Name	Structure	Cartesian Coordinates, Å		
1	3,5-dimethyl-1,2-azaphosphinine		P	-0.015906	0.594800	-0.183640
			C	-2.602226	-1.013340	0.249790
			C	-2.696092	0.371310	0.172534
			C	-1.618786	1.227065	-0.020010
			C	-1.355418	-1.633953	0.130760
			C	-3.837432	-1.840935	0.460703
			C	-1.844463	2.713887	-0.087122
			N	-0.202470	-1.021034	-0.055750
			H	-3.685987	0.811565	0.270424
			H	-1.323484	-2.719465	0.196621
			H	-4.553204	-1.681457	-0.345139
			H	-4.331165	-1.569778	1.393362
			H	-3.599282	-2.901189	0.498404

			H -2.518094 2.964195 -0.906304 H -0.912291 3.254845 -0.240068 H -2.297442 3.076329 0.835337
2	(trichloromethyl) phosphine		P 1.856149 0.138887 0.000000 C -0.017460 -0.006360 0.000000 Cl -0.623721 0.823767 -1.449904 Cl -0.623721 -1.673587 0.000000 Cl -0.623721 0.823767 1.449904 H 2.036157 -0.801126 1.034842 H 2.036157 -0.801126 -1.034842
3	Diaoxazaoctane		P 1.193835 0.185772 0.000000 C -0.752245 0.443926 -1.674079 C -0.752245 -1.019632 -1.249198 C -0.752245 0.443926 1.674079 C -0.752245 -1.019632 1.249198 N 0.017730 -1.103725 0.000000 O 0.551841 0.919079 1.315989 O 0.551841 0.919079 -1.315989 H -0.877392 0.576814 -2.745191 H -1.510450 1.025709 -1.148240 H -0.260148 -1.619335 -2.014511 H -1.755627 -1.411842 -1.103659 H -1.510450 1.025709 1.148240 H -0.877392 0.576814 2.745191 H -1.755627 -1.411842 1.103659 H -0.260148 -1.619335 2.014511
4	1-methyl-1H-1,2,3,5-diazadiphosphole		P 1.161103 -1.304270 0.000000 P -1.410896 -0.013462 0.000000 C -0.565409 -1.482623 0.000000 C -0.008905 2.371329 0.000000 N 0.000000 0.909395 0.000000 N 1.184435 0.331417 0.000000 H -1.069036 -2.437620 0.000000 H 0.503673 2.732190 0.887570 H 0.503673 2.732190 -0.887570 H -1.036573 2.721302 0.000000
5	1H-1,2,4-diazaphosphole		P 1.271190 -0.011651 0.000000 C 0.000000 -1.173075 0.000000 C -0.008718 1.197730 0.000000 N -1.201888 -0.587542 0.000000 N -1.241744 0.742490 0.000000 H 0.046410 -2.249398 0.000000 H -2.083107 -1.076800 0.000000 H 0.126575 2.268391 0.000000
6	2-methyl-[1,2,4]diazaphospholo[1,5-a]pyridine		P 0.826274 -0.019470 -2.535553 C -0.034267 -0.005221 1.269998 C 1.128318 0.002183 1.965770 C 2.361950 0.006578 1.269177 C 2.374046 0.002571 -0.092746 C 1.160969 -0.004561 -0.819377 C -0.877862 -0.021174 -2.087008 C -2.023360 -0.001395 -3.051561 N -0.007386 -0.007161 -0.095195 N -1.152957 -0.017960 -0.799439 H -1.019819 -0.009093 1.705645 H 1.096521 0.004703 3.043364 H 3.289010 0.013020 1.822652 H 3.301715 0.005131 -0.644875 H -1.763103 -0.507248 -3.977887 H -2.894379 -0.483619 -2.614507 H -2.291722 1.025692 -3.297389

7	Dioxaphospholane		P 2.101789 1.146898 0.826458 C 0.010196 0.029415 0.015978 C 0.002281 -0.017996 1.541986 O 1.359302 0.255795 1.922222 O 0.996351 1.015216 -0.315182 O 2.494321 2.499351 1.183144 H -0.941120 0.344261 -0.400255 H 0.303329 -0.927502 -0.413806 H -0.273106 -0.992516 1.931185 H -0.643752 0.748734 1.965147 H 3.169007 0.352641 0.423857
8	Diphosphine (conformer 1)		P 0.010980 0.033753 -0.117395 P 0.020088 0.024996 2.111070 H 1.413199 -0.099607 -0.222485 H -0.190783 -1.360766 -0.211213 H -1.388514 0.072212 2.205613 H 0.135038 1.429416 2.213207
	Diphosphine (conformer 2)		P 0.249138 0.107788 -0.066643 P -0.099970 -0.252934 2.088979 H 1.405016 -0.676041 -0.254618 H -0.633430 -0.902410 -0.497736 H 0.881726 0.661241 2.520057 H 0.720241 -1.383336 2.276658
9	methylidynephosphine		P 0.000000 0.000000 0.534078 C 0.000000 0.000000 -0.991399 H 0.000000 0.000000 -2.062777
10	ethylidynephosphine		P 0.000000 0.000000 1.242663 C 0.000000 0.000000 -0.290806 C 0.000000 0.000000 -1.749185 H 0.000000 1.019508 -2.133332 H 0.882920 -0.509754 -2.133332 H -0.882920 -0.509754 -2.133332
11	phosphine oxide		P -0.059433 0.102899 -0.041439 C 0.004413 -0.008019 1.759252 C 1.659827 -0.009132 -0.582175 C -0.821745 -1.440988 -0.581798 O -0.758470 1.313365 -0.535410 H -1.011951 -0.016586 2.147766 H 0.523677 -0.908238 2.082301 H 0.519829 0.867820 2.148208 H 1.686802 -0.017635 -1.669951 H 2.199158 0.866124 -0.225721 H 2.135478 -0.910371 -0.200094 H -0.828998 -1.468543 -1.669533 H -0.278840 -2.303535 -0.200171 H -1.849062 -1.472087 -0.224411
12	phosphine	PH_3	P 0.000000 0.000000 0.127360 H 0.000000 1.185876 -0.636799 H -1.026999 -0.592938 -0.636799 H 1.026999 -0.592938 -0.636799
13	1-tert-butyl-1H-phosphindole		P -2.502517 0.471689 -1.156671 C 1.092599 -1.371883 0.998391 C 0.310558 -2.242044 0.244459 C -0.805629 -1.773674 -0.438775 C -1.155629 -0.434257 -0.339611 C -0.363924 0.443620 0.420954 C 0.766495 -0.026284 1.081879 C -0.871663 1.813497 0.412799 C -1.999746 1.981455 -0.292058 C -4.050951 -0.064177 -0.228211 C -4.416505 -1.466236 -0.714292 C -3.865427 -0.072520 1.285258 C -5.154051 0.921384 -0.616684 H 1.963786 -1.747008 1.516455 H 0.579241 -3.286929 0.179675 H -1.386431 -2.453391 -1.047913 H 1.381264 0.653435 1.656857

			H -0.358536 2.607932 0.939614 H -2.504749 2.929313 -0.403978 H -3.654641 -2.193538 -0.434403 H -4.543572 -1.495715 -1.796547 H -5.356414 -1.775326 -0.252682 H -4.795460 -0.389815 1.762425 H -3.612910 0.917951 1.660763 H -3.078428 -0.763568 1.585979 H -5.314638 0.937747 -1.694599 H -4.918347 1.933459 -0.287664 H -6.089777 0.623884 -0.139421
14	Phosphinine (Phosphobenzene)		P 0.000000 0.000000 1.473817 C 0.000000 1.326934 0.370616 C 0.000000 1.218161 -1.010531 C 0.000000 0.000000 -1.677915 C 0.000000 -1.218161 -1.010531 C 0.000000 -1.326934 0.370616 H 0.000000 2.320369 0.801414 H 0.000000 2.125019 -1.602462 H 0.000000 0.000000 -2.758696 H 0.000000 -2.125019 -1.602462 H 0.000000 -2.320369 0.801414
15	1H-phosphole		P 0.167401 1.199740 0.000000 C -0.051740 -0.043030 -1.279140 C -0.051740 -1.272182 -0.728075 C -0.051740 -1.272182 0.728075 C -0.051740 -0.043030 1.279140 H -1.085759 1.843910 0.000000 H -0.041047 0.160680 -2.338044 H -0.050704 -2.189407 -1.300802 H -0.050704 -2.189407 1.300802 H -0.041047 0.160680 2.338044
16	trimethylphosphine		P 0.000000 0.000000 0.605003 C 0.000000 1.616549 -0.279671 C -1.399972 -0.808274 -0.279671 C 1.399972 -0.808274 -0.279671 H 0.880185 2.189045 0.007749 H 0.000000 1.484705 -1.362489 H -0.880185 2.189045 0.007749 H -1.455676 -1.856785 0.007749 H -2.335861 -0.332260 0.007749 H -1.285792 -0.742352 -1.362489 H 1.455676 -1.856785 0.007749 H 1.285792 -0.742352 -1.362489 H 2.335861 -0.332260 0.007749
17	Phosphine selenide		P -0.041998 0.073069 -0.029656 C 0.026041 -0.045212 1.775424 C 1.682683 -0.045503 -0.566808 C -0.802137 -1.479623 -0.566947 Se -1.038713 1.799735 -0.735746 H -0.989238 -0.057274 2.164286 H 0.550330 -0.951038 2.076831 H 0.542145 0.829113 2.164380 H 1.710355 -0.056597 -1.653664 H 2.221592 0.828685 -0.209701 H 2.141904 -0.951550 -0.173853 H -0.807378 -1.508676 -1.653808 H -0.246655 -2.330622 -0.175188 H -1.828248 -1.509432 -0.208727
18	Phosphine sulfide		P -0.045412 0.077960 -0.031208 C 0.020952 -0.035585 1.771397 C 1.675610 -0.035497 -0.571391 C -0.806892 -1.470738 -0.571011 S -0.970299 1.682478 -0.685898 H -0.994446 -0.043789 2.160133 H 0.541032 -0.942184 2.076130 H 0.541755 0.836940 2.158919

			H	1.702618	-0.044799	-1.658425
			H	2.214441	0.837005	-0.209607
			H	2.136034	-0.942074	-0.182285
			H	-0.807378	-1.501892	-1.657964
			H	-0.253483	-2.321558	-0.177137
			H	-1.833851	-1.501192	-0.214830
19	Trivinylphosphine oxide (conformer 1)	$(CH_2=CH)_3PO$	P	-0.087941	0.149678	-0.058430
			C	-0.013839	0.027942	1.733393
			C	1.624226	0.027381	-0.591797
			C	-0.839264	-1.394354	-0.588943
			C	-0.559621	0.970643	2.487339
			C	2.149204	0.970799	-1.359295
			C	-1.914149	-1.377659	-1.363033
			O	-0.787059	1.359117	-0.552428
			H	0.485914	-0.829962	2.168934
			H	2.202975	-0.830807	-0.269162
			H	-0.389366	-2.324571	-0.260849
			H	-0.528306	0.922723	3.567501
			H	-1.054189	1.820341	2.034531
			H	3.175906	0.924177	-1.696550
			H	1.554845	1.820232	-1.670400
			H	-2.386601	-2.290371	-1.700110
			H	-2.348857	-0.438332	-1.679905
	Trivinylphosphine oxide (conformer 2)		P	-0.090043	0.151738	-0.029146
			C	-0.044192	0.039563	1.762819
			C	1.621342	0.051651	-0.572265
			C	-0.810907	-1.401911	-0.571955
			C	-0.545499	1.023609	2.494928
			C	2.666519	0.115820	0.240414
			C	-1.859254	-1.401416	-1.382279
			O	-0.808994	1.344397	-0.540074
			H	0.374281	-0.850139	2.218763
			H	1.759713	-0.039019	-1.644165
			H	-0.359937	-2.324362	-0.224099
			H	-0.553683	0.980624	3.575667
			H	-0.966419	1.901540	2.021534
			H	3.678362	0.079667	-0.140762
			H	2.550932	0.214513	1.311904
			H	-2.310938	-2.320948	-1.729552
			H	-2.294264	-0.468560	-1.717395
20	methyl(vinyl)phosphine (conformer 1)		P	1.853362	-0.033502	1.953204
			C	-0.075320	0.175546	-0.009783
			C	0.185891	-0.201765	1.234492
			C	2.052374	-1.714724	2.693555
			H	-1.062447	0.070454	-0.441618
			H	0.692824	0.606975	-0.639822
			H	-0.602147	-0.636541	1.841917
			H	1.460395	0.622182	3.142144
			H	2.906806	-1.706765	3.367068
			H	1.168836	-2.035351	3.240848
			H	2.255202	-2.424947	1.895116
	methyl(vinyl)phosphine (conformer 2)		P	1.675997	-0.113954	2.144652
			C	-0.094992	-0.381026	-0.018138
			C	0.200607	0.205294	1.135140
			C	2.492698	1.542015	2.077253
			H	-1.032795	-0.192197	-0.524021
			H	0.587503	-1.074189	-0.493977
			H	-0.516854	0.888559	1.579701
			H	2.427556	-0.762414	1.142331
			H	3.477641	1.468121	2.533252
			H	2.586766	1.918329	1.062437
			H	1.902298	2.241170	2.666248

[a] The solvents were chosen in accordance with that used in the experimental NMR studies.

Table S2. The pecS-1 basis set for phosphorus atom in Dalton format.

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$ P
a 15
$ s functions
   12    5    0
  9.624103E+04  2.5050E-04  6.9844E-05  2.0156E-05  0.00000000  0.00000000
  1.433680E+04  1.9880E-03  5.3879E-04  1.2087E-04  0.00000000  0.00000000
  3.207817E+03  1.0441E-02  2.8708E-03  6.6397E-04  0.00000000  0.00000000
  9.113076E+02  4.1600E-02  1.1393E-02  2.6610E-03  0.00000000  0.00000000
  2.994035E+02  1.3162E-01  3.9199E-02  9.4376E-03  0.00000000  0.00000000
  1.079598E+02  3.1010E-01  9.9768E-02  2.3077E-02  0.00000000  0.00000000
  4.193807E+01  4.1841E-01  1.9688E-01  4.5304E-02  0.00000000  0.00000000
  1.715217E+01  2.2512E-01  1.1088E-01  2.7232E-02  0.00000000  0.00000000
  4.768204E+00  1.5990E-02 -5.2681E-01 -1.5880E-01  0.00000000  0.00000000
  1.781925E+00 -2.4702E-03 -6.0059E-01 -3.1982E-01  0.00000000  0.00000000
  3.386647E-01  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
  1.326649E-01  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ p functions
   9    4    0
  1.631865E+03  3.7407E-04  6.0339E-05  0.00000000  0.00000000
  2.786509E+02  5.3117E-03  9.0933E-04  0.00000000  0.00000000
  7.645439E+01  3.4379E-02  6.0515E-03  0.00000000  0.00000000
  2.527413E+01  1.3692E-01  2.4440E-02  0.00000000  0.00000000
  9.322672E+00  3.3067E-01  5.9536E-02  0.00000000  0.00000000
  3.567954E+00  4.4178E-01  8.6276E-02  0.00000000  0.00000000
  1.362871E+00  2.1890E-01  3.0239E-03  0.00000000  0.00000000
  3.808971E-01  0.00000000  0.00000000  1.00000000  0.00000000
  1.060116E-01  0.00000000  0.00000000  0.00000000  1.00000000
$ d functions
   3    3    0
  2.584314E+00  1.00000000  0.00000000  0.00000000
  5.760276E-01  0.00000000  1.00000000  0.00000000
  1.632577E-01  0.00000000  0.00000000  1.00000000
```

Table S3. The pecS-2 basis set for phosphorus atom in Dalton format.

```
$ P
a 15
$ s functions
   15    6    0
   3.047447E+05  5.9741E-05  1.9953E-05  3.0035E-06  0.00000000  0.00000000  0.00000000
   4.452317E+04  4.7390E-04  1.2845E-04  3.0031E-05  0.00000000  0.00000000  0.00000000
   1.024494E+04  2.4057E-03  6.4622E-04  1.5120E-04  0.00000000  0.00000000  0.00000000
   2.995194E+03  9.5460E-03  2.6595E-03  6.1263E-04  0.00000000  0.00000000  0.00000000
   9.979339E+02  3.3268E-02  9.2826E-03  2.1449E-03  0.00000000  0.00000000  0.00000000
   3.613183E+02  9.8679E-02  2.8877E-02  6.7375E-03  0.00000000  0.00000000  0.00000000
   1.398529E+02  2.3513E-01  7.5834E-02  1.7466E-02  0.00000000  0.00000000  0.00000000
   5.749685E+01  3.7565E-01  1.4910E-01  3.5729E-02  0.00000000  0.00000000  0.00000000
   2.462460E+01  3.1592E-01  1.9192E-01  4.5430E-02  0.00000000  0.00000000  0.00000000
   1.051605E+01  7.0672E-02 -3.4788E-02 -7.6765E-03  0.00000000  0.00000000  0.00000000
   4.293991E+00  1.8235E-03 -5.3547E-01 -1.7029E-01  0.00000000  0.00000000  0.00000000
   1.800446E+00  6.3013E-04 -5.1834E-01 -2.6849E-01  0.00000000  0.00000000  0.00000000
   6.456697E-01  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
   3.085029E-01  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
   1.259483E-01  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ p functions
   10    5    0
   2.501047E+03  1.7954E-04  3.0118E-05  0.00000000  0.00000000  0.00000000
   4.125818E+02  2.7706E-03  4.8392E-04  0.00000000  0.00000000  0.00000000
   1.085274E+02  1.9980E-02  3.3721E-03  0.00000000  0.00000000  0.00000000
   3.560937E+01  8.7359E-02  1.5145E-02  0.00000000  0.00000000  0.00000000
   1.326035E+01  2.5192E-01  4.4984E-02  0.00000000  0.00000000  0.00000000
   5.157181E+00  4.3614E-01  7.9740E-02  0.00000000  0.00000000  0.00000000
   2.023144E+00  3.6101E-01  6.7662E-02  0.00000000  0.00000000  0.00000000
   6.701044E-01  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
   2.568871E-01  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
   8.404583E-02  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ d functions
    4    4    0
   4.501459E+00  1.00000000  0.00000000  0.00000000  0.00000000
   1.126071E+00  0.00000000  1.00000000  0.00000000  0.00000000
   3.989444E-01  0.00000000  0.00000000  1.00000000  0.00000000
   1.545745E-01  0.00000000  0.00000000  0.00000000  1.00000000
$ f functions
    1    1    0
   5.004978E-01  1.00000000
```

Table S4. Shielding constants calculated within GIAO-DFT(B97-2)/pecS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	46.5415	6.7124	10.5639	63.8178	258.3734	263.3	[63]
2	343.1765	1.9705	11.5824	356.7294	-23.7004	-12	[64]
3	177.4508	-7.0040	12.6304	183.0772	143.5266	139	[65]
4	49.9473	-1.2837	9.9063	58.5699	263.4272	265.1	[66]
	29.2087	2.7341	10.0887	42.0315	279.3537	279.5	
5	228.8470	1.0903	12.0950	242.0323	86.7529	82.8	[67]
6	244.1158	11.2691	12.3738	267.7587	61.9784	63	[68]
7	304.4077	-3.6598	14.4231	315.1710	16.3203	21.3	[69]
8[a]	538.3327	0.7015	15.0480	554.0821	-213.7511	-203.2	[70]
9	344.2081	-2.6298	13.3471	354.9254	-21.9632	-32	[71]
10	364.1169	4.3823	12.7239	381.2231	-47.2878	-61	[64]
11	299.1040	-6.0644	14.8160	307.8556	23.3651	31.5	[72]
12	581.3677	-	14.3551	595.7228	-253.8511	-266.1	[73]
13	288.2899	0.8313	13.2638	302.3850	28.6332	23.5	[74]
14	93.0040	-4.0202	11.1085	100.0923	223.4411	211	[75]
15	363.2812	-3.1574	13.5291	373.6529	-39.9977	-49.2	[76, 77]
16	387.8544	-	14.3417	402.1961	-67.4848	-63.36	[73]
17	279.7940	-2.8829	61.1792	338.0903	-5.7510	5.74	[78]
18	287.9865	-5.5704	21.3094	303.7255	27.3423	30.57	[79]
19[a]	315.8578	-3.8793	14.1829	326.1614	5.7366	17.7	[80]
20[a]	397.9792	1.0797	14.0426	413.1016	-77.9868	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.963, B = 319.83; [c] For references, see the original article.

Table S5. Shielding constants calculated within GIAO-DFT(B97-2)/pecS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	42.0953	7.5647	10.5639	60.2239	259.8397	263.3	[63]
2	335.3417	-0.1201	11.5824	346.804	-16.9680	-12	[64]
3	175.0887	-3.7822	12.6304	183.9369	140.3453	139	[65]
4	39.5021	2.9776	9.9063	52.386	267.4104	265.1	[66]
	22.3439	-0.1195	10.0887	32.3131	286.7988	279.5	
5	222.4714	8.5331	12.0950	243.0995	83.2002	82.8	[67]
6	241.5663	11.671	12.3738	265.6111	61.4562	63	[68]
7	299.1151	-3.56	14.4231	309.9782	18.6021	21.3	[69]
8[a]	535.6006	0.4499	15.0480	551.0986	-214.2961	-203.2	[70]
9	343.4074	-1.156	13.3471	355.5985	-25.4626	-32	[71]
10	364.06	9.9423	12.7239	386.7262	-55.5288	-61	[64]
11	291.2926	-5.9434	14.8160	300.1652	28.0804	31.5	[72]
12	578.9579	-	14.3551	593.313	-255.0710	-266.1	[73]

13	285.2994	0.7646	13.2638	299.3278	28.8893	23.5	[74]
14	93.1394	9.4773	11.1085	113.7252	208.1628	211	[75]
15	365.8414	-0.7348	13.5291	378.6357	-47.7142	-49.2	[76, 77]
16	379.9235	-	14.3417	394.2652	-62.8108	-63.36	[73]
17	272.5472	-2.7562	61.1792	330.9702	-1.6741	5.74	[78]
18	282.1538	-5.2056	21.3094	298.2576	29.9230	30.57	[79]
19[a]	309.0625	-3.6826	14.1829	319.5627	9.3443	17.7	[80]
20[a]	392.8997	0.9335	14.0426	407.8758	-75.9573	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9659, B = 318.01; [c] For references, see the original article.

Table S6. Shielding constants calculated within GIAO-DFT(B97-2)/pcS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	62.9288	7.6577	9.6765	80.2630	260.1123	263.3	[63]
2	353.1045	3.8253	10.4897	367.4195	-16.9363	-12	[64]
3	200.7152	-6.4738	11.8594	206.1008	138.7039	139	[65]
4	64.6757	-1.9811	9.1412	71.8358	268.2428	265.1	[66]
	44.4551	2.7054	9.3077	56.4682	283.0695	279.5	
5	239.2723	4.1346	11.1562	254.5631	91.9475	82.8	[67]
6	257.1133	11.6867	11.5186	280.3186	67.0986	63	[68]
7	328.3295	-3.4332	13.5321	338.4284	11.0343	21.3	[69]
8[a]	548.8960	1.5332	14.4035	564.8326	-207.4005	-203.2	[70]
9	344.2336	-4.4419	12.2344	352.0261	-2.0848	-32	[71]
10	363.1188	1.2001	11.6816	376.0005	-25.2153	-61	[64]
11	328.9647	-5.4308	13.7868	337.3207	12.1030	31.5	[72]
12	592.8267	-	14.0566	606.8833	-247.9710	-266.1	[73]
13	312.2851	1.3517	12.2510	325.8878	23.1335	23.5	[74]
14	111.7772	0.7435	10.1145	122.6352	219.2316	211	[75]
15	389.2228	-1.1957	12.6025	400.6296	-48.9774	-49.2	[76, 77]
16	412.7016	-	13.2083	425.9099	-73.3679	-63.36	[73]
17	311.2617	-2.7783	60.3884	368.8718	-18.3375	5.74	[78]
18	319.9669	-5.4889	20.2116	334.6896	14.6415	30.57	[79]
19[a]	342.7104	-3.5364	13.0466	352.2206	-2.2725	17.7	[80]
20[a]	417.9369	2.2575	12.8660	433.0604	-80.2667	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9648, B = 337.55; [c] For references, see the original article.

Table S7. Shielding constants calculated within GIAO-DFT(B97-2)/pcS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	41.4357	7.9579	9.6765	59.0701	258.8604	263.3	[63]
2	336.5525	3.8545	10.4897	350.8967	-20.5636	-12	[64]
3	177.1615	-10.7715	11.8594	178.2494	144.7462	139	[65]
4	41.3158	-3.3907	9.1412	47.0663	270.3540	265.1	[66]
	26.0179	4.2436	9.3077	39.5692	277.5325	279.5	
5	223.3145	3.3815	11.1562	237.8522	87.6765	82.8	[67]

6	241.5281	12.2658	11.5186	265.3125	61.3833	63	[68]
7	302.7666	-3.6045	13.5321	312.6942	16.0153	21.3	[69]
8[a]	534.5916	1.0804	14.4035	550.0755	-211.2773	-203.2	[70]
9	338.041	-2.5343	12.2344	347.7411	-17.5421	-32	[71]
10	360.1485	8.7534	11.6816	380.5835	-48.9887	-61	[64]
11	298.1572	-5.9643	13.7868	305.9797	22.4444	31.5	[72]
12	580.0163	-	14.0566	594.0729	-253.4048	-266.1	[73]
13	287.4716	0.9651	12.2510	300.6877	27.5115	23.5	[74]
14	92.6741	-2.7455	10.1145	100.0431	219.6287	211	[75]
15	368.5608	-3.3479	12.6025	377.8154	-46.3382	-49.2	[76, 77]
16	384.5311	-	13.2083	397.7394	-65.4155	-63.36	[73]
17	279.8574	-2.6541	60.3884	337.5917	-7.8241	5.74	[78]
18	289.5204	-5.1023	20.2116	304.6297	23.7371	30.57	[79]
19[a]	315.2815	-3.6636	13.0466	324.6646	4.5537	17.7	[80]
20[a]	394.6743	1.5370	12.8660	409.0773	-76.2715	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9575, B = 315.42; [c] For references, see the original article.

Table S8. Shielding constants calculated within GIAO-DFT(B97-2)/pcS-3 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	39.6332	7.7148	9.6765	57.0245	257.2863	263.3	[63]
2	332.0392	3.4276	10.4897	345.9565	-19.6839	-12	[64]
3	174.0166	-9.0987	11.8594	176.7773	142.4913	139	[65]
4	36.9461	-2.2304	9.1412	43.8569	269.9088	265.1	[66]
	21.1496	3.2088	9.3077	33.6661	279.6777	279.5	
5	220.598	3.8466	11.1562	235.6008	86.1031	82.8	[67]
6	240.2356	12.1560	11.5186	263.9102	58.9657	63	[68]
7	297.6557	-3.5917	13.5321	307.5961	17.0884	21.3	[69]
8[a]	533.1891	0.5465	14.4035	548.1390	-213.4961	-203.2	[70]
9	341.8616	-4.3406	12.2344	349.7554	-23.3255	-32	[71]
10	362.2833	2.1344	11.6816	376.0993	-48.5788	-61	[64]
11	290.2143	-5.9377	13.7868	298.0634	26.2264	31.5	[72]
12	578.371	-	14.0566	592.4276	-255.9511	-266.1	[73]
13	284.359	0.8358	12.2510	297.4458	26.8185	23.5	[74]
14	90.1063	-1.9716	10.1145	98.2492	217.7683	211	[75]
15	364.3005	-2.8617	12.6025	374.0413	-46.6060	-49.2	[76, 77]
16	378.5736	-	13.2083	391.7819	-63.6121	-63.36	[73]
17	272.4769	-2.6879	60.3884	330.1774	-4.5581	5.74	[78]
18	281.8461	-5.0908	20.2116	296.9669	27.2775	30.57	[79]
19[a]	308.07191	-3.6931	13.0466	317.4254	7.6660	17.7	[80]
20[a]	389.7433	1.1461	12.8660	403.7554	-75.0900	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9586, B = 311.95; [c] For references, see the original article.

Table S9. Shielding constants calculated within GIAO-DFT(PBE0)/pecS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	35.9367	6.7565	10.5639	53.2571	257.4816	263.3	[63]
2	341.0777	2.0816	11.5824	354.7417	-25.6125	-12	[64]
3	171.6166	-7.1892	12.6304	177.0578	141.2327	139	[65]
4	40.169	-1.3987	9.9063	48.6766	261.7827	265.1	[66]
	19.07	2.7903	10.0887	31.9490	277.4899	279.5	
5	220.6968	0.9696	12.0950	233.7614	87.9880	82.8	[67]
6	237.2938	11.4677	12.3738	261.1353	62.2840	63	[68]
7	297.5184	-3.7322	14.4231	308.2093	18.0815	21.3	[69]
8[a]	542.4993	0.7828	15.0480	558.3301	-216.7819	-203.2	[70]
9	331.4684	-2.7602	13.3471	342.0553	-13.6999	-32	[71]
10	353.6658	4.4533	12.7239	370.8430	-40.7316	-61	[64]
11	293.6873	-6.1926	14.8160	302.3107	23.6203	31.5	[72]
12	585.5154	0.0000	14.3551	599.8705	-255.7884	-266.1	[73]
13	284.0688	0.8210	13.2638	298.1536	27.5238	23.5	[74]
14	82.2773	-4.3259	11.1085	89.0599	223.8628	211	[75]
15	359.6192	-3.2188	13.5291	369.9295	-39.8738	-49.2	[76, 77]
16	386.9944	0.0000	14.3417	401.3361	-69.3646	-63.36	[73]
17	275.5323	-2.8213	61.1792	333.8902	-6.0329	5.74	[78]
18	283.3215	-5.5458	21.3094	299.0851	26.6491	30.57	[79]
19[a]	310.7647	-3.9681	14.1829	320.9795	6.0903	17.7	[80]
20[a]	397.2563	1.0827	14.0426	412.3817	-79.7364	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.939, B = 307.49; [c] For references, see the original article.

Table S10. Shielding constants calculated within GIAO-DFT(PBE0)/pecS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	32.1513	7.6315	10.5639	50.3467	259.1982	263.3	[63]
2	334.0361	-0.0381	11.5824	345.5804	-19.0595	-12	[64]
3	169.6702	-3.8938	12.6304	178.4068	138.5016	139	[65]
4	30.4986	2.9777	9.9063	43.3826	265.7619	265.1	[66]
	13.1725	-0.1597	10.0887	23.1015	284.8768	279.5	
5	215.1077	8.6227	12.0950	235.8254	84.3846	82.8	[67]
6	235.7036	11.8181	12.3738	259.8955	61.6985	63	[68]
7	292.4369	-3.6337	14.4231	303.2263	20.8592	21.3	[69]
8[a]	540.4447	0.5120	15.0480	556.0047	-217.3844	-203.2	[70]
9	330.9273	-1.2485	13.3471	343.0259	-16.6519	-32	[71]
10	354.1615	10.1601	12.7239	377.0455	-48.7154	-61	[64]
11	286.6339	-6.0767	14.8160	295.3732	28.2608	31.5	[72]
12	583.9220	0.0000	14.3551	598.2771	-257.2262	-266.1	[73]
13	281.8583	0.7703	13.2638	295.8924	27.7714	23.5	[74]
14	83.1144	9.5379	11.1085	103.7608	208.8554	211	[75]
15	362.9929	-0.7841	13.5291	375.7379	-47.4830	-49.2	[76, 77]
16	380.0209	0.0000	14.3417	394.3626	-65.0368	-63.36	[73]

17	269.4901	-2.6813	61.1792	327.9880	-2.4787	5.74	[78]
18	278.6979	-5.1522	21.3094	294.8551	28.7491	30.57	[79]
19[a]	304.6612	-3.7732	14.1829	315.0709	9.6957	17.7	[80]
20[a]	392.9316	0.9422	14.0426	407.9165	-77.8113	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9425, B = 306.65; [c] For references, see the original article.

Table S11. Shielding constants calculated within GIAO-DFT(PBE0)/pcS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	52.4421	7.7024	9.6765	69.8210	258.8770	263.3	[63]
2	351.2419	3.9872	10.4897	365.7188	-18.7640	-12	[64]
3	195.0188	-6.6429	11.8594	200.2353	136.5092	139	[65]
4	55.2142	-2.1635	9.1412	62.1919	266.0353	265.1	[66]
	34.2799	2.7178	9.3077	46.3054	280.9416	279.5	
5	231.3756	4.0501	11.1562	246.5819	93.0222	82.8	[67]
6	250.7758	11.8099	11.5186	274.1043	67.1979	63	[68]
7	321.5859	-3.4933	13.5321	331.6247	13.2265	21.3	[69]
8[a]	553.5335	1.6147	14.4035	569.5517	-210.0203	-203.2	[70]
9	331.0008	-4.7325	12.2344	338.5027	6.7729	-32	[71]
10	352.4558	1.1186	11.6816	365.2560	-18.3297	-61	[64]
11	324.5679	-5.5453	13.7868	332.8094	12.1149	31.5	[72]
12	597.6455	0.0000	14.0566	611.7021	-249.5701	-266.1	[73]
13	308.4427	1.3564	12.2510	322.0501	22.2104	23.5	[74]
14	101.4432	0.5174	10.1145	112.0751	219.2299	211	[75]
15	386.1252	-1.3155	12.6025	397.4122	-48.5019	-49.2	[76, 77]
16	412.6854	0.0000	13.2083	425.8937	-75.2261	-63.36	[73]
17	308.4363	-2.7137	60.3884	366.1110	-19.1320	5.74	[78]
18	316.7045	-5.4655	20.2116	331.4506	13.3899	30.57	[79]
19[a]	338.1526	-3.6181	13.0466	347.5810	-1.7453	17.7	[80]
20[a]	417.8886	2.3126	12.8660	433.0672	-81.9569	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9383, B = 324.39; [c] For references, see the original article.

Table S12. Shielding constants calculated within GIAO-DFT(PBE0)/pcS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	29.8909	8.0132	9.6765	47.5806	258.0363	263.3	[63]
2	333.9888	4.0549	10.4897	348.5334	-22.6322	-12	[64]
3	170.4640	-11.1252	11.8594	171.1982	142.7506	139	[65]
4	30.6857	-3.6121	9.1412	36.2148	268.6361	265.1	[66]
	15.1047	4.3002	9.3077	28.7126	275.6326	279.5	
5	214.4670	3.2675	11.1562	228.8907	88.9465	82.8	[67]
6	234.2260	12.3938	11.5186	258.1384	61.6701	63	[68]
7	295.3715	-3.6811	13.5321	305.2225	17.7595	21.3	[69]
8[a]	538.2854	1.1226	14.4035	553.8114	-214.0745	-203.2	[70]
9	324.3048	-2.7274	12.2344	333.8118	-8.9029	-32	[71]
10	349.1424	8.8666	11.6816	369.6906	-42.3635	-61	[64]

11	292.5673	-6.1087	13.7868	300.2454	22.4011	31.5	[72]
12	583.9631	0.0000	14.0566	598.0197	-255.3032	-266.1	[73]
13	282.6042	0.9611	12.2510	295.8163	26.5317	23.5	[74]
14	81.0483	-2.9899	10.1145	88.1729	220.1800	211	[75]
15	364.4445	-3.4882	12.6025	373.5588	-45.9709	-49.2	[76, 77]
16	383.2766	0.0000	13.2083	396.4849	-67.3518	-63.36	[73]
17	275.5048	-2.5856	60.3884	333.3076	-8.4327	5.74	[78]
18	284.8002	-5.0814	20.2116	299.9304	22.6949	30.57	[79]
19[a]	309.9536	-3.7649	13.0466	319.2353	4.6912	17.7	[80]
20[a]	393.5244	1.5535	12.8660	407.9439	-78.0385	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9326, B = 302.41; [c] For references, see the original article.

Table S13. Shielding constants calculated within GIAO-DFT(PBE0)/pcS-3 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	29.5420	7.7720	9.6765	46.9905	256.4521	263.3	[63]
2	330.7460	3.6425	10.4897	344.8782	-21.8942	-12	[64]
3	168.3889	-9.3964	11.8594	170.8519	140.7160	139	[65]
4	27.7320	-2.4683	9.1412	34.4049	268.2121	265.1	[66]
	11.7922	3.2587	9.3077	24.3586	277.5993	279.5	
5	213.1223	3.7040	11.1562	227.9825	87.3332	82.8	[67]
6	234.3925	12.2814	11.5186	258.1925	59.1049	63	[68]
7	290.9603	-3.6624	13.5321	300.8300	19.2644	21.3	[69]
8[a]	538.1049	0.6071	14.4035	553.1155	-216.4711	-203.2	[70]
9	329.4017	-4.6941	12.2344	336.9420	-14.4786	-32	[71]
10	352.4122	1.9370	11.6816	366.0308	-41.6592	-61	[64]
11	285.5293	-6.0743	13.7868	293.2418	26.3549	31.5	[72]
12	583.4222	0.0000	14.0566	597.4788	-257.9242	-266.1	[73]
13	280.8881	0.8279	12.2510	293.9670	25.6772	23.5	[74]
14	79.9226	-2.3362	10.1145	87.7009	218.4123	211	[75]
15	361.4141	-2.9828	12.6025	371.0338	-46.3340	-49.2	[76, 77]
16	378.4943	0.0000	13.2083	391.7026	-65.6469	-63.36	[73]
17	269.2249	-2.6260	60.3884	326.9873	-5.1769	5.74	[78]
18	278.1828	-5.0760	20.2116	293.3184	26.2833	30.57	[79]
19[a]	303.6433	-3.7836	13.0466	312.9062	7.9804	17.7	[80]
20[a]	389.7703	1.1603	12.8660	403.7967	-76.9476	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9344, B = 300.36; [c] For references, see the original article.

Table S14. Shielding constants calculated within GIAO-DFT(B3LYP)/pecS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	19.9966	6.4064	10.5639	36.9669	257.3617	263.3	[63]
2	316.3883	2.3355	11.5824	330.3062	-20.7533	-12	[64]
3	154.2623	-7.2767	12.6304	159.6160	141.0781	139	[65]

4	21.5309	-1.2907	9.9063	30.1465	263.8281	265.1	[66]
	1.3897	3.0537	10.0887	14.5321	278.6321	279.5	
5	201.9066	1.0309	12.0950	215.0325	88.5377	82.8	[67]
6	216.8101	11.1024	12.3738	240.2863	64.5946	63	[68]
7	288.6754	-3.8396	14.4231	299.2589	8.6826	21.3	[69]
8[a]	515.322	0.5655	15.0480	530.9355	-210.9700	-203.2	[70]
9	327.5695	-2.6149	13.3471	338.3017	-28.3338	-32	[71]
10	350.26	4.5196	12.7239	367.5035	-56.0201	-61	[64]
11	277.8998	-6.3246	14.8160	286.3912	20.8825	31.5	[72]
12	565.0259	0.0000	14.3551	579.3810	-256.9011	-266.1	[73]
13	259.1682	0.8255	13.2638	273.2575	33.3346	23.5	[74]
14	64.041	-4.2074	11.1085	70.9421	225.1498	211	[75]
15	338.7429	-2.7799	13.5291	349.4921	-38.9435	-49.2	[76, 77]
16	359.4592	0.0000	14.3417	373.8009	-61.9906	-63.36	[73]
17	250.8511	-2.9979	61.1792	309.0324	-0.5836	5.74	[78]
18	261.0056	-5.8498	21.3094	276.4652	30.2933	30.57	[79]
19[a]	296.0029	-4.0332	14.1829	306.1526	2.1467	17.7	[80]
20[a]	370.4929	0.9984	14.0426	385.5340	-73.1148	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9481, B = 292.41; [c] For references, see the original article.

Table S15. Shielding constants calculated within GIAO-DFT(B3LYP)/pecS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	13.8344	7.2068	10.5639	31.6051	258.3626	263.3	[63]
2	306.1254	-0.1418	11.5824	317.5660	-12.8714	-12	[64]
3	151.2068	-3.7043	12.6304	160.1329	136.4539	139	[65]
4	9.5298	3.0163	9.9063	22.4524	267.0439	265.1	[66]
	-6.7351	-0.7081	10.0887	2.6455	285.8307	279.5	
5	193.5690	8.1245	12.0950	213.7885	85.5616	82.8	[67]
6	212.5045	11.4583	12.3738	236.3366	64.1747	63	[68]
7	282.2482	-3.7920	14.4231	292.8793	10.5440	21.3	[69]
8[a]	512.3086	0.2984	15.0480	527.6551	-212.1408	-203.2	[70]
9	324.9382	-1.3269	13.3471	336.9584	-31.2650	-32	[71]
10	348.7374	9.9915	12.7239	371.4528	-63.9830	-61	[64]
11	268.2663	-6.2774	14.8160	276.8049	25.7906	31.5	[72]
12	562.8833	0.0000	14.3551	577.2384	-259.1706	-266.1	[73]
13	254.2906	0.7356	13.2638	268.2900	33.8669	23.5	[74]
14	61.8994	9.4478	11.1085	82.4557	210.1308	211	[75]
15	340.0481	-0.7707	13.5291	352.8065	-46.2970	-49.2	[76, 77]
16	349.4778	0.0000	14.3417	363.8195	-56.7428	-63.36	[73]
17	241.7323	-2.8571	61.1792	300.0544	3.7384	5.74	[78]
18	253.6185	-5.4570	21.3094	269.4709	32.7469	30.57	[79]
19[a]	287.8825	-3.8793	14.1829	298.1860	5.5106	17.7	[80]
20[a]	363.5121	0.8561	14.0426	378.4109	-70.5827	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9485, B = 288.34; [c] For references, see the original article.

Table S16. Shielding constants calculated within GIAO-DFT(B3LYP)/pcS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	37.4027	7.3650	9.6765	54.4442	259.0915	263.3	[63]
2	328.0375	4.1738	10.4897	342.7010	-14.2048	-12	[64]
3	179.2604	-6.5484	11.8594	184.5714	135.7179	139	[65]
4	37.7968	-1.8605	9.1412	45.0775	267.9720	265.1	[66]
	17.7825	3.0276	9.3077	30.1178	282.1553	279.5	
5	212.0529	4.1847	11.1562	227.3938	95.1179	82.8	[67]
6	229.6621	11.4164	11.5186	252.5971	71.2227	63	[68]
7	313.7862	-3.5960	13.5321	323.7223	3.7889	21.3	[69]
8[a]	528.8293	1.3049	14.4035	544.5376	-205.5661	-203.2	[70]
9	326.0055	-4.4420	12.2344	333.7979	-5.7638	-32	[71]
10	347.6120	1.5274	11.6816	360.8210	-31.3844	-61	[64]
11	310.5410	-5.6093	13.7868	318.7185	8.5330	31.5	[72]
12	579.8018	0.0000	14.0566	593.8584	-252.3271	-266.1	[73]
13	284.9464	1.2838	12.2510	298.4812	27.7200	23.5	[74]
14	83.0317	1.1060	10.1145	94.2522	221.3495	211	[75]
15	366.9029	-0.7682	12.6025	378.7372	-48.3707	-49.2	[76, 77]
16	386.8441	0.0000	13.2083	400.0524	-68.5797	-63.36	[73]
17	285.1606	-2.8156	60.3884	342.7334	-14.2355	5.74	[78]
18	295.8301	-5.6704	20.2116	310.3713	16.4470	30.57	[79]
19[a]	325.1561	-3.6522	13.0466	334.5505	-6.4773	17.7	[80]
20[a]	392.3997	2.1150	12.8660	407.3807	-75.5277	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9481, B = 310.71; [c] For references, see the original article.

Table S17. Shielding constants calculated within GIAO-DFT(B3LYP)/pcS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	9.3506	7.5874	9.6765	26.6145	257.7962	263.3	[63]
2	304.4793	4.4444	10.4897	319.4134	-16.7320	-12	[64]
3	149.7359	-11.0414	11.8594	150.5539	141.5907	139	[65]
4	7.3767	-3.3728	9.1412	13.1451	270.4252	265.1	[66]
	-6.9942	4.7793	9.3077	7.0928	276.0998	279.5	
5	191.4383	3.6228	11.1562	206.2173	89.4007	82.8	[67]
6	209.4162	12.0689	11.5186	233.0037	64.2857	63	[68]
7	283.4109	-3.8601	13.5321	293.0829	7.9555	21.3	[69]
8[a]	509.4859	0.8441	14.4035	524.7334	-209.2401	-203.2	[70]
9	316.6576	-2.7036	12.2344	326.1884	-23.0842	-32	[71]
10	342.1592	8.8662	11.6816	362.7070	-57.3241	-61	[64]
11	272.8429	-6.3194	13.7868	280.3103	19.9311	31.5	[72]
12	562.8068	0.0000	14.0566	576.8634	-258.1171	-266.1	[73]
13	253.3454	0.9068	12.2510	266.5032	32.8766	23.5	[74]
14	57.7225	-2.1721	10.1145	65.6649	221.1826	211	[75]
15	340.1934	-2.8036	12.6025	349.9923	-45.4028	-49.2	[76, 77]
16	351.7117	0.0000	13.2083	364.9200	-59.3990	-63.36	[73]

17	246.5557	-2.7682	60.3884	304.1759	-2.4453	5.74	[78]
18	258.4300	-5.4021	20.2116	273.2395	26.5606	30.57	[79]
19[a]	291.7252	-3.8797	13.0466	300.8920	0.6336	17.7	[80]
20[a]	362.5963	1.4065	12.8660	376.8689	-70.6023	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9376, B = 282.75; [c] For references, see the original article.

Table S18. Shielding constants calculated within GIAO-DFT(B3LYP)/pcS-3 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	11.6373	7.3646	9.6765	28.6784	256.1734	263.3	[63]
2	304.2917	4.1378	10.4897	318.9192	-17.5527	-12	[64]
3	149.5214	-9.6011	11.8594	151.7797	140.0766	139	[65]
4	7.2738	-2.4376	9.1412	13.9774	270.0379	265.1	[66]
	-8.3022	3.7887	9.3077	4.7942	278.6986	279.5	
5	193.5140	3.9342	11.1562	208.6044	86.4852	82.8	[67]
6	212.4982	11.9766	11.5186	235.9934	60.6546	63	[68]
7	280.0931	-3.8308	13.5321	289.7944	9.9149	21.3	[69]
8[a]	509.1259	0.3803	14.4035	523.9096	-210.8792	-203.2	[70]
9	322.8467	-4.4547	12.2344	330.6264	-28.5938	-32	[71]
10	346.5666	1.9962	11.6816	360.2444	-56.5265	-61	[64]
11	267.2474	-6.2721	13.7868	274.7621	24.0919	31.5	[72]
12	562.0656	0.0000	14.0566	576.1222	-260.1208	-266.1	[73]
13	253.5399	0.7918	12.2510	266.5827	31.8059	23.5	[74]
14	59.0696	-1.9381	10.1145	67.2460	219.8003	211	[75]
15	338.4128	-2.4742	12.6025	348.5411	-45.4891	-49.2	[76, 77]
16	348.0608	0.0000	13.2083	361.2691	-57.4929	-63.36	[73]
17	241.7743	-2.7834	60.3884	299.3793	0.8754	5.74	[78]
18	253.2383	-5.3631	20.2116	268.0868	30.3873	30.57	[79]
19[a]	286.9762	-3.8830	13.0466	296.1398	3.9305	17.7	[80]
20[a]	360.3823	1.0614	12.8660	374.3098	-69.7915	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9431, B = 283.22; [c] For references, see the original article.

Table S19. Shielding constants calculated within GIAO-DFT(B3PW91)/pecS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	33.7659	7.2553	10.5639	51.5851	256.1064	263.3	[63]
2	336.1156	2.0625	11.5824	349.7605	-23.9101	-12	[64]
3	165.8695	-7.3320	12.6304	171.1679	143.8062	139	[65]
4	37.3288	-1.0980	9.9063	46.1371	261.2226	265.1	[66]
	17.3474	2.8710	10.0887	30.3071	276.0886	279.5	
5	217.4449	1.1886	12.0950	230.7285	87.8729	82.8	[67]

6	233.6798	11.7667	12.3738	257.8203	62.4310	63	[68]
7	293.6373	-3.8378	14.4231	304.2226	18.8546	21.3	[69]
8[a]	540.2228	0.8210	15.0480	556.0918	-217.6758	-203.2	[70]
9	330.3883	-2.5516	13.3471	341.1838	-15.8557	-32	[71]
10	353.1838	4.8490	12.7239	370.7567	-43.6276	-61	[64]
11	289.6351	-6.3940	14.8160	298.0571	24.6446	31.5	[72]
12	584.5810	0.0000	14.3551	598.9361	-257.9109	-266.1	[73]
13	278.7932	0.8800	13.2638	292.9370	29.4529	23.5	[74]
14	80.0124	-3.8995	11.1085	87.2214	222.6404	211	[75]
15	355.4402	-3.2885	13.5291	365.6808	-38.8608	-49.2	[76, 77]
16	383.5192	0.0000	14.3417	397.8609	-69.0812	-63.36	[73]
17	271.2768	-3.0758	61.1792	329.3802	-4.7709	5.74	[78]
18	279.3465	-5.8900	21.3094	294.7659	27.7353	30.57	[79]
19[a]	306.1648	-4.0623	14.1829	316.2853	7.5264	17.7	[80]
20[a]	394.0698	1.1240	14.0426	409.2364	-79.7639	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9391, B = 304.55; [c] For references, see the original article.

Table S20. Shielding constants calculated within GIAO-DFT(B3PW91)/pecS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	28.8127	7.9933	10.5639	47.3699	258.0976	263.3	[63]
2	328.6830	-0.0960	11.5824	340.1694	-17.7196	-12	[64]
3	163.3143	-3.7303	12.6304	172.2144	140.4940	139	[65]
4	26.9986	3.3044	9.9063	40.2093	264.8428	265.1	[66]
	10.3555	-0.0827	10.0887	20.3615	283.5395	279.5	
5	210.6712	8.9060	12.0950	231.6722	84.4848	82.8	[67]
6	231.0302	12.0334	12.3738	255.4374	62.0980	63	[68]
7	288.0140	-3.7399	14.4231	298.6972	21.3472	21.3	[69]
8[a]	537.4892	0.5110	15.0480	553.0482	-218.2514	-203.2	[70]
9	328.7868	-1.2592	13.3471	340.8747	-18.3840	-32	[71]
10	352.7460	10.3669	12.7239	375.8368	-51.3183	-61	[64]
11	282.3070	-6.2767	14.8160	290.8463	28.7428	31.5	[72]
12	582.0446	0.0000	14.3551	596.3997	-259.0885	-266.1	[73]
13	275.6732	0.7897	13.2638	289.7267	29.7974	23.5	[74]
14	79.4360	9.9751	11.1085	100.5196	208.0305	211	[75]
15	357.8838	-0.7286	13.5291	370.6843	-46.4646	-49.2	[76, 77]
16	375.7788	0.0000	14.3417	390.1205	-64.7735	-63.36	[73]
17	264.5887	-2.9480	61.1792	322.8199	-1.3763	5.74	[78]
18	274.1511	-5.5027	21.3094	289.9578	29.5798	30.57	[79]
19[a]	299.6692	-3.8569	14.1829	309.9952	10.7046	17.7	[80]
20[a]	388.9550	0.9206	14.0426	403.9182	-77.7709	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.942, B = 302.72; [c] For references, see the original article.

Table S21. Shielding constants calculated within GIAO-DFT(B3PW91)/pcS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	50.6688	8.0124	9.6765	68.3577	258.0859	263.3	[63]
2	346.4606	3.9969	10.4897	360.9472	-17.1530	-12	[64]
3	189.4532	-6.7244	11.8594	194.5882	139.3409	139	[65]
4	53.1768	-1.9425	9.1412	60.3755	265.5948	265.1	[66]
	33.3151	2.7902	9.3077	45.4130	279.6700	279.5	
5	228.8563	4.1595	11.1562	244.1720	92.6974	82.8	[67]
6	247.8908	11.9483	11.5186	271.3577	67.1238	63	[68]
7	317.8178	-3.5997	13.5321	327.7502	14.0754	21.3	[69]
8[a]	551.0218	1.6986	14.4035	567.1239	-211.1034	-203.2	[70]
9	329.9097	-4.5667	12.2344	337.5774	4.8309	-32	[71]
10	352.1899	1.4062	11.6816	365.2777	-21.2267	-61	[64]
11	321.1236	-5.7166	13.7868	329.1938	12.7174	31.5	[72]
12	595.8713	0.0000	14.0566	609.9279	-251.3692	-266.1	[73]
13	303.2665	1.3870	12.2510	316.9045	24.2779	23.5	[74]
14	99.4084	0.6723	10.1145	110.1952	218.7294	211	[75]
15	381.9292	-1.2959	12.6025	393.2358	-47.5269	-49.2	[76, 77]
16	409.4373	0.0000	13.2083	422.6456	-75.1927	-63.36	[73]
17	304.7654	-2.9772	60.3884	362.1766	-18.3095	5.74	[78]
18	313.3136	-5.8256	20.2116	327.6996	14.1230	30.57	[79]
19[a]	334.2418	-3.6899	13.0466	343.5985	-0.8331	17.7	[80]
20[a]	414.8678	2.3730	12.8660	430.1068	-82.2115	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9407, B = 322.39; [c] For references, see the original article.

Table S22. Shielding constants calculated within GIAO-DFT(B3PW91)/pcS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}P)$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	25.8413	8.3781	9.6765	43.8959	257.0066	263.3	[63]
2	328.3584	4.0202	10.4897	342.8683	-21.5161	-12	[64]
3	163.4118	-11.2778	11.8594	163.9934	145.1237	139	[65]
4	26.4468	-3.4086	9.1412	32.1794	267.9217	265.1	[66]
	11.7405	4.3669	9.3077	25.4151	274.2233	279.5	
5	209.4728	3.4274	11.1562	224.0564	89.1691	82.8	[67]
6	229.0894	12.5837	11.5186	253.1917	62.0266	63	[68]
7	290.4577	-3.7970	13.5321	300.1928	18.2404	21.3	[69]
8[a]	534.6781	1.1833	14.4035	550.2648	-214.7267	-203.2	[70]
9	321.8021	-2.6384	12.2344	331.3981	-10.8305	-32	[71]
10	347.3250	9.1924	11.6816	368.1990	-45.1142	-61	[64]
11	287.9009	-6.3212	13.7868	295.3665	22.7366	31.5	[72]
12	581.3781	0.0000	14.0566	595.4347	-256.8070	-266.1	[73]
13	276.0616	0.9758	12.2510	289.2884	28.3989	23.5	[74]

14	76.6583	-2.8728	10.1145	83.9000	219.7388	211	[75]
15	358.9806	-3.4344	12.6025	368.1487	-45.0673	-49.2	[76, 77]
16	378.7610	0.0000	13.2083	391.9693	-67.2586	-63.36	[73]
17	270.3029	-2.8559	60.3884	327.8354	-7.5115	5.74	[78]
18	279.9527	-5.4536	20.2116	294.7107	23.3475	30.57	[79]
19[a]	304.6273	-3.8558	13.0466	313.8181	5.5471	17.7	[80]
20[a]	389.3622	1.5472	12.8660	403.7754	-78.2571	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9316, B = 297.9; [c] For references, see the original article.

Table S23. Shielding constants calculated within GIAO-DFT(B3PW91)/pcS-3 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	27.0531	8.1634	9.6765	44.8930	255.3526	263.3	[63]
2	327.4748	3.5661	10.4897	341.5306	-22.1519	-12	[64]
3	162.0092	-9.5505	11.8594	164.3181	143.6304	139	[65]
4	25.0831	-2.2069	9.1412	32.0174	267.3977	265.1	[66]
	9.1224	3.3071	9.3077	21.7372	277.0148	279.5	
5	210.7863	3.9009	11.1562	225.8434	86.0735	82.8	[67]
6	231.1608	12.5167	11.5186	255.1961	58.6140	63	[68]
7	286.1815	-3.7749	13.5321	295.9387	20.4993	21.3	[69]
8[a]	534.5066	0.6538	14.4035	549.5639	-216.7670	-203.2	[70]
9	327.2172	-4.3831	12.2344	335.0685	-16.1066	-32	[71]
10	350.9514	2.4800	11.6816	365.1130	-44.2132	-61	[64]
11	281.3759	-6.2723	13.7868	288.8904	27.0930	31.5	[72]
12	580.9457	0.0000	14.0566	595.0023	-259.2747	-266.1	[73]
13	275.1968	0.8563	12.2510	288.3041	27.6415	23.5	[74]
14	77.2921	-2.1500	10.1145	85.2566	217.5925	211	[75]
15	356.6356	-2.9904	12.6025	366.2477	-45.2747	-49.2	[76, 77]
16	374.6018	0.0000	13.2083	387.8101	-65.4463	-63.36	[73]
17	264.5713	-2.8941	60.3884	322.0656	-3.9424	5.74	[78]
18	273.8035	-5.4289	20.2116	288.5862	27.3776	30.57	[79]
19[a]	298.8459	-3.8682	13.0466	308.0243	9.1933	17.7	[80]
20[a]	386.5405	1.1652	12.8660	400.5718	-77.3849	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9355, B = 297.35; [c] For references, see the original article.

Table S24. Shielding constants calculated within GIAO-DFT(OLYP)/pecS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	55.941	5.9749	10.5639	72.4798	257.9149	263.3	[63]
2	339.4907	2.0823	11.5824	353.1554	-21.8906	-12	[64]
3	177.3952	-6.6751	12.6304	183.3505	147.3879	139	[65]

4	61.3919	-0.6858	9.9063	70.6124	259.7765	265.1	[66]
	43.2864	2.8058	10.0887	56.1809	274.1633	279.5	
5	232.7881	-0.1383	12.0950	244.7448	86.1839	82.8	[67]
6	241.4724	10.0168	12.3738	263.8630	67.1250	63	[68]
7	304.3452	-3.8229	14.4231	314.9454	16.2009	21.3	[69]
8[a]	527.7959	0.6883	15.0480	543.5322	-211.6773	-203.2	[70]
9	354.8862	-2.8075	13.3471	365.4258	-34.1230	-32	[71]
10	376.8819	3.7192	12.7239	393.3250	-61.9357	-61	[64]
11	299.8134	-6.3517	14.8160	308.2777	22.8480	31.5	[72]
12	576.2332	0.0000	14.3551	590.5883	-258.5875	-266.1	[73]
13	280.7117	0.5431	13.2638	294.5186	36.5644	23.5	[74]
14	98.6126	-5.0512	11.1085	104.6699	225.8246	211	[75]
15	356.4139	-2.3368	13.5291	367.6062	-36.2966	-49.2	[76, 77]
16	377.9738	0.0000	14.3417	392.3155	-60.9293	-63.36	[73]
17	279.0281	-3.9975	61.1792	336.2098	-4.9975	5.74	[78]
18	287.979	-7.0464	21.3094	302.2420	28.8650	30.57	[79]
19[a]	314.964	-3.8655	14.1829	325.2815	5.8969	17.7	[80]
20[a]	388.1038	1.0356	14.0426	403.1821	-71.7622	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9969, B = 330.17; [c] For references, see the original article.

Table S25. Shielding constants calculated within GIAO-DFT(OLYP)/pecS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	54.6080	7.4532	10.5639	72.6251	257.5728	263.3	[63]
2	332.3153	-0.0675	11.5824	343.8302	-12.8187	-12	[64]
3	175.3382	-4.4629	12.6304	183.5057	147.0248	139	[65]
4	53.1610	3.2470	9.9063	66.3143	263.8646	265.1	[66]
	40.2158	0.0841	10.0887	50.3886	279.7426	279.5	
5	230.4250	7.6621	12.0950	250.1821	80.5484	82.8	[67]
6	241.9006	10.9632	12.3738	265.2376	65.5381	63	[68]
7	298.5780	-3.7956	14.4231	309.2055	21.7021	21.3	[69]
8[a]	529.2636	0.5190	15.0480	544.8305	-213.2160	-203.2	[70]
9	358.8724	-0.9095	13.3471	371.3100	-40.2161	-32	[71]
10	380.7573	10.6020	12.7239	404.0832	-72.8910	-61	[64]
11	290.9953	-6.2263	14.8160	299.5850	31.2938	31.5	[72]
12	579.9084	0.0000	14.3551	594.2635	-262.5007	-266.1	[73]
13	280.2978	0.6595	13.2638	294.2211	36.6416	23.5	[74]
14	104.2787	8.6244	11.1085	124.0116	206.3404	211	[75]
15	362.8659	-0.7814	13.5291	375.6136	-44.5068	-49.2	[76, 77]
16	372.2725	0.0000	14.3417	386.6142	-55.4744	-63.36	[73]
17	272.0847	-3.7799	61.1792	329.4840	1.4845	5.74	[78]
18	282.3178	-6.5038	21.3094	297.1234	33.7480	30.57	[79]
19[a]	307.8456	-3.6599	14.1829	318.3686	12.5665	17.7	[80]
20[a]	385.9133	1.0771	14.0426	401.0330	-69.8499	-80.5	[81]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.997, B = 329.98; [c] For references, see the original article.

Table S26. Shielding constants calculated within GIAO-DFT(OLYP)/pcS-1 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	72.0384	7.6855	9.6765	89.4004	259.4265	263.3	[55]
2	345.6464	3.6542	10.4897	359.7903	-13.1806	-12	[56]
3	198.0928	-6.3147	11.8594	203.6375	144.2527	139	[57]
4	73.8913	-1.0630	9.1412	81.9695	266.9184	265.1	[58]
	57.4842	2.8405	9.3077	69.6324	279.3566	279.5	[58]
5	240.7035	3.7947	11.1562	255.6544	91.8092	82.8	[59]
6	251.6185	11.2172	11.5186	274.3543	72.9560	63	[60]
7	327.6890	-3.6725	13.5321	337.5486	9.2435	21.3	[61]
8[a]	534.0953	1.4729	14.4035	549.9717	-204.9214	-203.2	[62]
9	355.7999	-3.5312	12.2344	364.5031	-17.9320	-32	[63]
10	375.5365	1.9401	11.6816	389.1582	-42.7893	-61	[56]
11	326.4328	-5.6645	13.7868	334.5551	12.2615	31.5	[64]
12	587.3665	0.0000	14.0566	601.4231	-256.7948	-266.1	[65]
13	302.7153	1.2037	12.2510	316.1700	30.7974	23.5	[66]
14	117.2245	1.6889	10.1145	129.0279	219.4741	211	[67]
15	380.6925	-0.5713	12.6025	392.7237	-46.3840	-49.2	[68, 69]
16	398.3368	0.0000	13.2083	411.5451	-65.3598	-63.36	[65]
17	306.1093	-3.8255	60.3884	362.6722	-16.0861	5.74	[70]
18	315.5366	-6.9396	20.2116	328.8086	18.0552	30.57	[71]
19[a]	339.6016	-3.5567	13.0466	349.0914	-2.3940	17.7	[72]
20[a]	403.1144	2.2743	12.8660	418.2548	-72.1244	-80.5	[73]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -1.0082, B = 349.56; [c] For references, see the original article.

Table S27. Shielding constants calculated within GIAO-DFT(OLYP)/pcS-2 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	54.6707	7.9901	9.6765	72.3373	257.0291	263.3	[55]
2	332.1064	3.8645	10.4897	346.4606	-15.1754	-12	[56]
3	178.4614	-10.6898	11.8594	179.6310	150.4864	139	[57]
4	55.5391	-2.1724	9.1412	62.5079	266.7897	265.1	[58]
	44.5954	4.2455	9.3077	58.1486	271.1184	279.5	[58]
5	231.3854	3.1386	11.1562	245.6802	84.8996	82.8	[59]
6	240.7573	11.7223	11.5186	263.9982	66.7098	63	[60]
7	303.7987	-3.8486	13.5321	313.4822	17.5722	21.3	[61]
8[a]	527.5029	1.0289	14.4035	542.9353	-210.2747	-203.2	[62]
9	353.6079	-2.1596	12.2344	363.6827	-32.2769	-32	[63]
10	376.8895	9.1962	11.6816	397.7673	-66.1229	-61	[56]
11	298.8863	-6.1758	13.7868	306.4973	24.5082	31.5	[64]
12	582.1130	0.0000	14.0566	596.1696	-263.1364	-266.1	[65]

13	281.2750	0.8784	12.2510	294.4044	36.5164	23.5	[66]
14	103.2507	-1.6031	10.1145	111.7621	217.8802	211	[67]
15	364.7515	-2.5945	12.6025	374.7595	-43.2762	-49.2	[68, 69]
16	375.5964	0.0000	13.2083	388.8047	-57.2231	-63.36	[65]
17	279.5883	-3.6815	60.3884	336.2952	-5.0811	5.74	[70]
18	289.9774	-6.4374	20.2116	303.7516	27.2347	30.57	[71]
19[a]	315.0952	-3.5855	13.0466	324.5562	6.5757	17.7	[72]
20[a]	384.9026	1.7770	12.8660	399.5457	-67.8888	-80.5	[73]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.993, B = 328.86; [c] For references, see the original article.

Table S28. Shielding constants calculated within GIAO-DFT(OLYP)/pcS-3 approach taking into account solvent and relativistic corrections, together with scaled $\delta(^{31}\text{P})$ against experiment.

Molecule	Basic σ_{calc}	$\Delta_{solv}\sigma$	$\Delta_{rel}\sigma$	σ_{calc}(total)	δ_{scaled}[b]	δ_{exp}	*Ref.*[c]
1	52.4071	7.5884	9.6765	69.6720	255.9351	263.3	[55]
2	329.3193	3.5362	10.4897	343.3452	-16.1781	-12	[56]
3	173.6816	-8.8832	11.8594	176.6578	149.5591	139	[57]
4	51.3130	-0.9946	9.1412	59.4596	266.0893	265.1	[58]
	39.3983	3.2622	9.3077	51.9682	273.5380	279.5	[58]
5	230.4731	3.7520	11.1562	245.3813	81.2274	82.8	[59]
6	241.3356	11.5072	11.5186	264.3614	62.3555	63	[60]
7	296.5465	-3.8478	13.5321	306.2308	20.7247	21.3	[61]
8[a]	525.7664	0.4553	14.4035	540.6251	-212.3336	-203.2	[62]
9	356.1479	-3.4742	12.2344	364.9081	-37.6181	-32	[63]
10	378.3104	2.6183	11.6816	392.6103	-65.1624	-61	[56]
11	289.6853	-6.2023	13.7868	297.2698	29.6346	31.5	[64]
12	579.3670	0.0000	14.0566	593.4236	-264.8311	-266.1	[65]
13	278.6282	0.7235	12.2510	291.6027	35.2694	23.5	[66]
14	100.8938	-0.3534	10.1145	110.6549	215.1858	211	[67]
15	360.9068	-1.9093	12.6025	371.6000	-44.2719	-49.2	[68, 69]
16	369.9954	0.0000	13.2083	383.2037	-55.8094	-63.36	[65]
17	271.5753	-3.6647	60.3884	328.2990	-1.2177	5.74	[70]
18	281.5207	-6.2993	20.2116	295.4330	31.4610	30.57	[71]
19[a]	307.1315	-3.6506	13.0466	316.5275	10.4867	17.7	[72]
20[a]	380.6366	1.2882	12.8660	394.7908	-67.3305	-80.5	[73]

[a] Conformational averaging; [b] Parameters of linear model $\delta_{scaled} = A\sigma_{calc}(\text{total}) + B$: A = -0.9943, B = 325.21; [c] For references, see the original article.