Electronic Supplementary Information for:

Quantum Chemical Calculations of ^{31}P NMR Chemical Shifts: Scopes and Limitations

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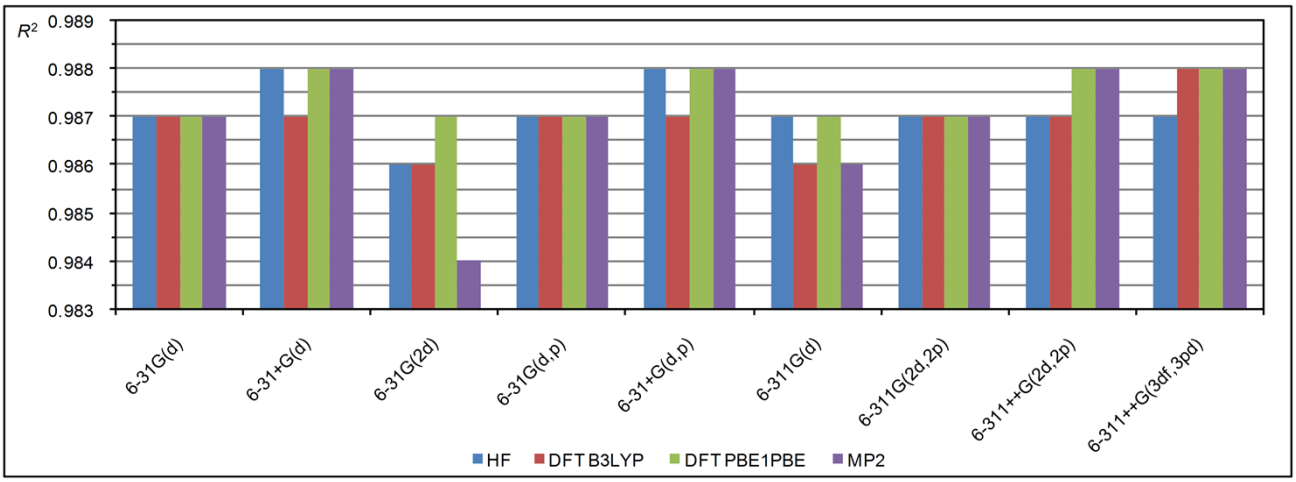

Figure S1. Experimental *versus* calculated ^{31}P CS correlation coefficients R^2 for different (functional/basis set) approaches used at geometry optimization for **2**, **3**, **5-20**, **25**, **29**, **31**, **33** at PBE1PBE/6-31G(d) level for CS calculations.

Table S1. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 and linear regression parameters (slope, intercept) for different (functional/basis set) approaches used at geometry optimization for **1-34** at PBE1PBE/6-31G(d) level for CS calculations.

Geometry Optimization	R^2	R^2 (without low/high field region)	R^2 (without low/high field region and "difficult" cases)	Slope	Intercept
HF/6-31G(d)	0.937	0.897	0.987	0.935	3.0
B3LYP/6-31G(d)	0.920	0.874	0.987	0.961	-2.9
PBE1PBE/6-31G(d)	0.934	0.919	0.987	0.918	-3.0
MP2/6-31G(d)	0.933	0.919	0.987	0.964	-4.7
HF/6-31+G(d)	0.937	0.921	0.988	0.937	4.0
B3LYP/6-31+G(d)	0.921	0.906	0.987	0.969	-0.8
PBE1PBE/6-31+G(d)	0.934	0.920	0.988	0.963	-2.1
MP2/6-31+G(d)	0.934	0.921	0.988	0.980	-4.0
HF/6-31G(2d)	0.933	0.917	0.986	0.923	4.3
B3LYP/6-31G(2d)	0.921	0.907	0.986	0.952	-0.8
PBE1PBE/6-31G(2d)	0.934	0.920	0.987	0.951	-2.4
MP2/6-31G(2d)	0.923	0.912	0.984	0.959	2.8
HF/6-31G(d,p)	0.937	0.921	0.987	0.931	4.4
B3LYP/6-31G(d,p)	0.920	0.905	0.987	0.962	2.8
PBE1PBE/6-31G(d,p)	0.942	0.929	0.987	0.957	-3.5
MP2/6-31G(d,p)	0.933	0.919	0.987	0.978	-6.1
HF/6-31+G(d,p)	0.937	0.921	0.988	0.933	5.3

B3LYP/6-31+G(d,p)	0.921	0.906	0.987	0.969	-0.4
PBE1PBE/6-31+G(d,p)	0.934	0.920	0.988	0.963	-1.5
MP2/6-31+G(d,p)	0.934	0.921	0.988	0.982	-4.6
HF/6-311G(d)	0.933	0.916	0.987	0.921	8.9
B3LYP/6-311G(d)	0.914	0.897	0.986	0.958	2.8
PBE1PBE/6-311G(d)	0.929	0.913	0.987	0.951	2.1
MP2/6-311G(d)	0.928	0.913	0.986	0.953	2.1
HF/6-311G(2d,2p)	0.932	0.916	0.987	0.916	5.5
B3LYP/6-311G(2d,2p)	0.921	0.906	0.987	0.958	-0.8
PBE1PBE/6-311G(2d,2p)	0.935	0.921	0.987	0.952	-1.8
MP2/6-311G(2d,2p)	0.924	0.914	0.987	0.968	-4.1
HF/6-311++G(2d,2p)	0.933	0.917	0.987	0.917	6.1
B3LYP/6-311++G(2d,2p)	0.922	0.908	0.987	0.963	0.3
PBE1PBE/6-311++G(2d,2p)	0.936	0.922	0.988	0.956	-0.9
MP2/6-311++G(2d,2p)	0.925	0.915	0.988	0.975	-3.4
HF/6-311++G(3df,3pd)	0.938	0.922	0.987	0.909	5.9
B3LYP/6-311++G(3df,3pd)	0.930	0.915	0.988	0.950	0.9
PBE1PBE/6-311++G(3df,3pd)	0.941	0.927	0.988	0.943	-0.5
MP2/6-311++G(3df,3pd)	0.939	0.926	0.988	0.960	-2.9

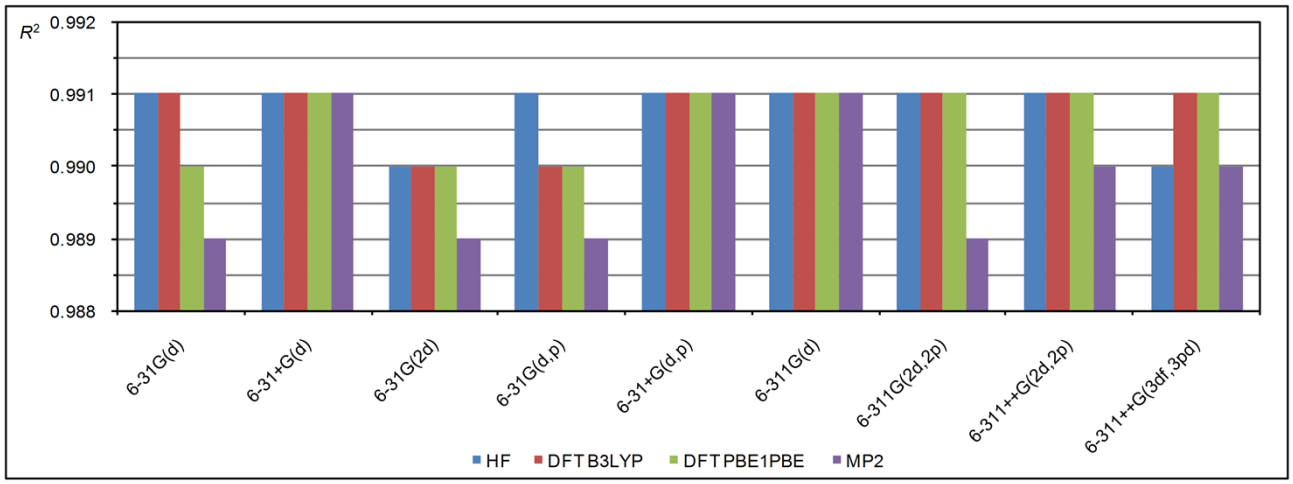

Figure S2. Experimental *versus* calculated ^{31}P CS correlation coefficients R^2 for different (functional/basis set) approaches used at geometry optimization for **2**, **3**, **5-20**, **25**, **29**, **31**, **33** at PBE1PBE/6-311++G(2d,2p) level for CS calculations.

Table S2. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 and linear regression parameters (slope, intercept) for different (functional/basis set) approaches used at geometry optimization for **1-34** at PBE1PBE/6-311++G(2d,2p) level for CS calculations.

Geometry Optimization	R^2	R^2 (without low/high field region)	R^2 (without low/high field region and "difficult" cases)	Slope	Intercept
HF/6-31G(d)	0.958	0.947	0.991	1.090	-9.2
B3LYP/6-31G(d)	0.944	0.932	0.991	1.119	-15.4
PBE1PBE/6-31G(d)	0.955	0.943	0.990	1.115	-16.3
MP2/6-31G(d)	0.952	0.941	0.989	1.120	-16.9
HF/6-31+G(d)	0.958	0.947	0.991	1.092	-8.2
B3LYP/6-31+G(d)	0.945	0.932	0.991	1.128	-13.3
PBE1PBE/6-31+G(d)	0.949	0.935	0.991	1.121	-14.6
MP2/6-31+G(d)	0.953	0.942	0.991	1.127	-15.6
HF/6-31G(2d)	0.957	0.945	0.990	1.078	-7.7
B3LYP/6-31G(2d)	0.941	0.927	0.990	1.111	-13.1
PBE1PBE/6-31G(2d)	0.949	0.937	0.990	1.110	-14.7
MP2/6-31G(2d)	0.947	0.938	0.989	1.114	-15.2
HF/6-31G(d,p)	0.959	0.947	0.991	1.086	-7.7
B3LYP/6-31G(d,p)	0.944	0.932	0.990	1.120	-15.3
PBE1PBE/6-31G(d,p)	0.953	0.941	0.990	1.115	-16.0
MP2/6-31G(d,p)	0.949	0.940	0.989	1.127	-15.8
HF/6-31+G(d,p)	0.958	0.947	0.991	1.088	-6.8

B3LYP/6-31+G(d,p)	0.945	0.932	0.991	1.128	-12.9
PBE1PBE/6-31+G(d,p)	0.955	0.943	0.991	1.121	-14.0
MP2/6-31+G(d,p)	0.953	0.942	0.991	1.141	-16.8
HF/6-311G(d)	0.956	0.944	0.991	1.076	-2.9
B3LYP/6-311G(d)	0.940	0.926	0.991	1.117	-9.6
PBE1PBE/6-311G(d)	0.952	0.939	0.991	1.108	-10.21
MP2/6-311G(d)	0.950	0.938	0.991	1.111	-9.2
HF/6-311G(2d,2p)	0.956	0.945	0.991	1.070	-6.5
B3LYP/6-311G(2d,2p)	0.946	0.934	0.991	1.117	-13.1
PBE1PBE/6-311G(2d,2p)	0.956	0.946	0.991	1.110	-14.1
MP2/6-311G(2d,2p)	0.947	0.938	0.989	1.127	-16.5
HF/6-311++G(2d,2p)	0.957	0.945	0.991	1.073	-6.1
B3LYP/6-311++G(2d,2p)	0.947	0.935	0.991	1.122	-12.1
PBE1PBE/6-311++G(2d,2p)	0.957	0.946	0.991	1.114	-13.3
MP2/6-311++G(2d,2p)	0.948	0.940	0.990	1.134	-15.7
HF/6-311++G(3df,3pd)	0.961	0.949	0.990	1.063	-5.9
B3LYP/6-311++G(3df,3pd)	0.953	0.941	0.991	1.108	-11.3
PBE1PBE/6-311++G(3df,3pd)	0.961	0.950	0.991	1.103	-12.4
MP2/6-311++G(3df,3pd)	0.958	0.948	0.990	1.119	-15.1

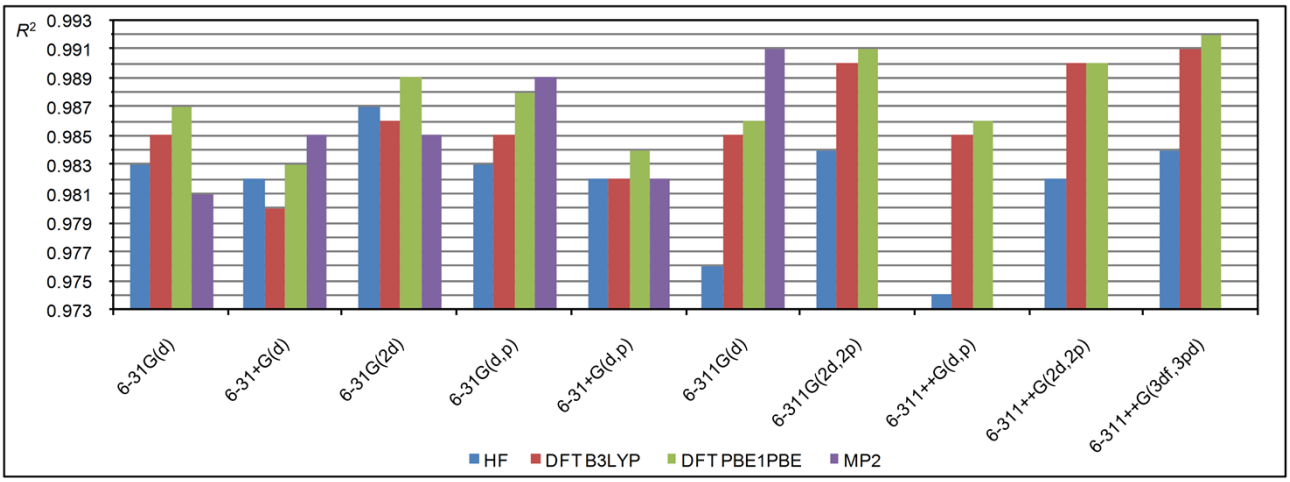

Figure S3. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 for different (functional/basis set) approaches used at CS calculation for **2**, **3**, **5-20**, **25**, **29**, **31**, **33** at PBE1PBE/6-31G(d) level for geometry optimization.

Table S3. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 and linear regression parameters (slope, intercept) for different (functional/basis set) approaches used at CS calculation for **1-34** at PBE1PBE/6-31G(d) level for geometry optimization.

CS calculations	R^2	R^2 (without low/high field region)	R^2 (without low/high field region and "difficult" cases)	Slope	Intercept
HF/6-31G(d)	0.933	0.916	0.983	0.897	-5.0
B3LYP/6-31G(d)	0.923	0.905	0.985	0.926	1.6
PBE1PBE/6-31G(d)	0.934	0.919	0.987	0.918	-3.0
MP2/6-31G(d)	0.927	0.910	0.981	0.923	-12.2
HF/6-31+G(d)	0.933	0.916	0.982	0.899	-9.6
B3LYP/6-31+G(d)	0.929	0.912	0.980	0.927	-3.8
PBE1PBE/6-31+G(d)	0.938	0.924	0.983	0.958	-9.5
MP2/6-31+G(d)	0.924	0.904	0.985	0.926	-14.4
HF/6-31G(2d)	0.952	0.938	0.987	0.935	-25.2
B3LYP/6-31G(2d)	0.941	0.925	0.986	0.991	-26.6
PBE1PBE/6-31G(2d)	0.949	0.935	0.989	0.971	-29.8
MP2/6-31G(2d)	0.928	0.907	0.985	0.986	-31.8
HF/6-31G(d,p)	0.933	0.917	0.983	0.905	-6.9
B3LYP/6-31G(d,p)	0.923	0.906	0.985	0.941	1.0
PBE1PBE/6-31G(d,p)	0.934	0.919	0.988	0.971	-6.3
MP2/6-31G(d,p)	0.926	0.905	0.989	0.923	-9.0
HF/6-31+G(d,p)	0.934	0.917	0.982	0.908	-11.2

B3LYP/6-31+G(d,p)	0.930	0.913	0.982	0.943	-6.1
PBE1PBE/6-31+G(d,p)	0.941	0.927	0.984	0.974	-11.6
MP2/6-31+G(d,p)	0.925	0.905	0.982	0.917	-11.8
HF/6-311G(d)	0.935	0.919	0.976	0.998	-12.2
B3LYP/6-311G(d)	0.944	0.930	0.985	1.062	-12.8
PBE1PBE/6-311G(d)	0.948	0.936	0.986	1.080	-19.9
MP2/6-311G(d)	0.959	0.947	0.991	1.086	-23.7
HF/6-311G(2d,2p)	0.951	0.938	0.984	1.008	-7.1
B3LYP/6-311G(2d,2p)	0.948	0.935	0.990	1.094	9.4
PBE1PBE/6-311G(2d,2p)	0.955	0.944	0.991	1.111	-16.0
MP2/6-311G(2d,2p)	–[a]	–	–	–	–
HF/6-311++G(d,p)	0.937	0.922	0.974	1.009	-10.5
B3LYP/6-311++G(d,p)	0.942	0.927	0.985	1.083	-11.6
PBE1PBE /6-311++G(d,p)	0.948	0.936	0.986	1.100	-18.7
MP2/6-311++G(d,p)	–	–	–	–	–
HF/6-311++G(2d,2p)	0.952	0.938	0.982	1.010	-6.4
B3LYP/6-311++G(2d,2p)	0.947	0.934	0.990	1.096	-8.8
PBE1PBE/6-311++G(2d,2p)	0.955	0.943	0.990	1.115	-16.3
MP2/6-311++G(2d,2p)	–	–	–	–	–
HF/6-311++G(3df,3pd)	0.949	0.936	0.984	1.007	-3.9
B3LYP/6-311++G(3df,3pd)	0.946	0.932	0.991	1.099	-7.5
PBE1PBE/6-311++G(3df,3pd)	0.953	0.941	0.992	1.120	-15.4
MP2/6-311++G(3df,3pd)	–	–	–	–	–

[a] Not affordable for computational reasons.

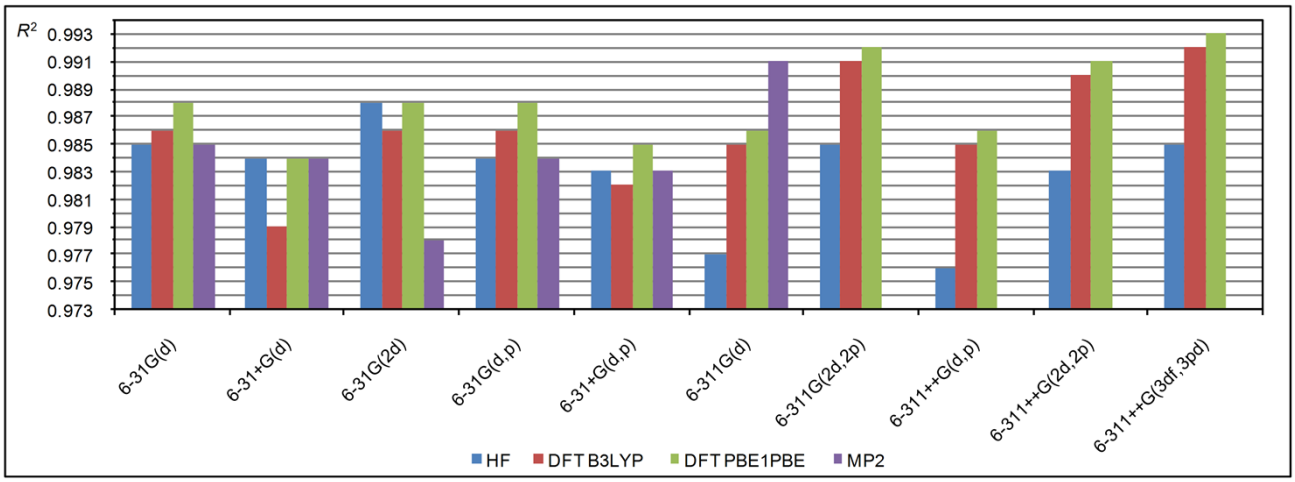

Figure S4. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 for different (functional/basis set) approaches used at CS calculation for **2**, **3**, **5-20**, **25**, **29**, **31**, **33** at PBE1PBE/6-31+G(d,p) level for geometry optimization.

Table S4. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 and linear regression parameters (slope, intercept) for different (functional/basis set) approaches used at CS calculation for **1-34** at PBE1PBE/6-31+G(d,p) level for geometry optimization.

CS calculations	R^2	R^2 (without low/high field region)	R^2 (without low/high field region and "difficult" cases)	Slope	Intercept
HF/6-31G(d)	0.934	0.918	0.985	0.902	-3.3
B3LYP/6-31G(d)	0.924	0.907	0.986	0.938	3.5
PBE1PBE/6-31G(d)	0.934	0.920	0.988	0.963	-1.5
MP2/6-31G(d)	0.921	0.899	0.985	0.902	-3.3
HF/6-31+G(d)	0.935	0.918	0.984	0.904	-8.0
B3LYP/6-31+G(d)	0.929	0.911	0.979	0.928	-2.7
PBE1PBE/6-31+G(d)	0.939	0.925	0.984	0.965	-7.3
MP2/6-31+G(d)	0.924	0.904	0.984	0.926	-11.9
HF/6-31G(2d)	0.953	0.939	0.988	0.939	-23.9
B3LYP/6-31G(2d)	0.942	0.925	0.986	0.997	-24.9
PBE1PBE/6-31G(2d)	0.949	0.935	0.988	1.018	-28.8
MP2/6-31G(2d)	0.952	0.938	0.978	0.989	-24.5
HF/6-31G(d,p)	0.935	0.919	0.984	0.910	-5.1
B3LYP/6-31G(d,p)	0.924	0.907	0.986	0.947	1.3
PBE1PBE/6-31G(d,p)	0.935	0.920	0.988	0.977	-4.0
MP2/6-31G(d,p)	0.933	0.916	0.984	0.910	-5.1
HF/6-31+G(d,p)	0.935	0.919	0.983	0.913	-9.6

B3LYP/6-31+G(d,p)	0.930	0.914	0.982	0.943	-6.1
PBE1PBE/6-31+G(d,p)	0.940	0.926	0.985	0.980	-9.4
MP2/6-31+G(d,p)	0.941	0.924	0.983	0.920	-10.0
HF/6-311G(d)	0.937	0.921	0.977	1.003	-10.4
B3LYP/6-311G(d)	0.942	0.928	0.985	1.070	-10.2
PBE1PBE/6-311G(d)	0.949	0.937	0.986	1.086	-17.4
MP2/6-311G(d)	0.958	0.946	0.991	1.100	-21.2
HF/6-311G(2d,2p)	0.953	0.940	0.985	1.013	-5.3
B3LYP/6-311G(2d,2p)	0.949	0.935	0.991	1.100	-7.0
PBE1PBE/6-311G(2d,2p)	0.956	0.944	0.992	1.118	-14.3
MP2/6-311G(2d,2p)	–[a]	–	–	–	–
HF/6-311++G(d,p)	0.939	0.923	0.976	1.015	-8.8
B3LYP/6-311++G(d,p)	0.942	0.928	0.985	1.090	-9.2
PBE1PBE/6-311++G(d,p)	0.949	0.937	0.986	1.106	-16.4
MP2/6-311++G(d,p)	–	–	–	–	–
HF/6-311++G(2d,2p)	0.953	0.940	0.983	1.015	-4.6
B3LYP/6-311++G(2d,2p)	0.946	0.932	0.990	1.103	-6.4
PBE1PBE/6-311++G(2d,2p)	0.955	0.943	0.991	1.121	-14.0
MP2/6-311++G(2d,2p)	–	–	–	–	–
HF/6-311++G(3df,3pd)	0.951	0.937	0.985	1.012	-2.1
B3LYP/6-311++G(3df,3pd)	0.947	0.933	0.992	1.105	-5.1
PBE1PBE/6-311++G(3df,3pd)	0.954	0.942	0.993	1.126	-13.0
MP2/6-311++G(3df,3pd)	–	–	–	–	–

[a] Not affordable for computational reasons.

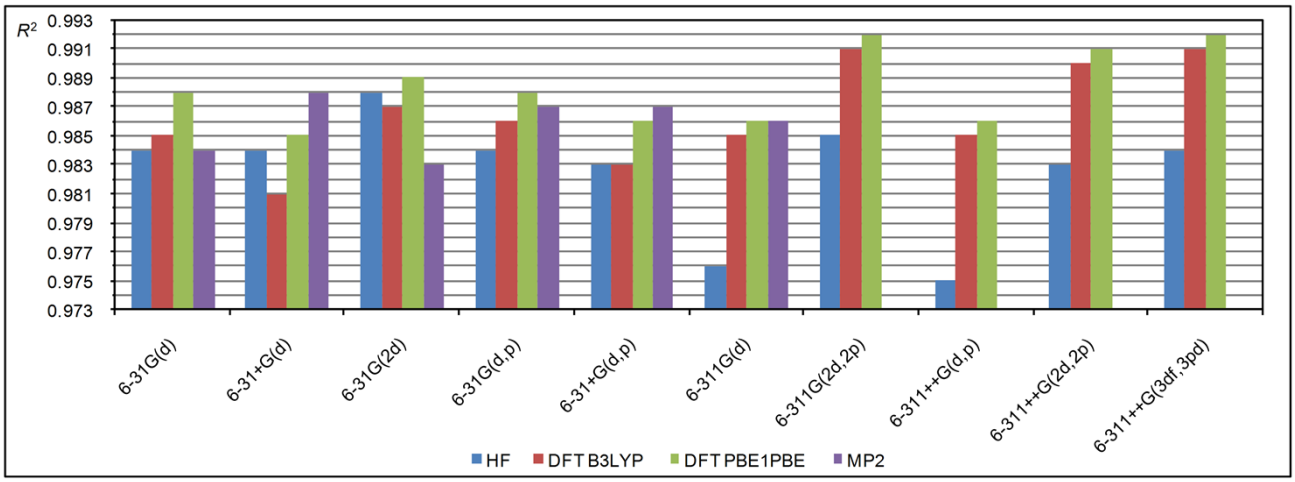

Figure S5. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 for different (functional/basis set) approaches used at CS calculation for **2**, **3**, **5-20**, **25**, **29**, **31**, **33** at PBE1PBE/6-311++G(2d,2p) level for geometry optimization.

Table S5. Experimental *versus* calculated ^{31}P CS correlation coefficient R^2 and linear regression parameters (slope, intercept) for different (functional/basis set) approaches used at CS calculation for **1-34** at PBE1PBE/6-311++G(2d,2p) level for geometry optimization.

CS calculations	R^2	R^2 (without low/high field region)	R^2 (without low/high field region and "difficult" cases)	Slope	Intercept
HF/6-31G(d)	0.937	0.922	0.984	0.897	-2.6
B3LYP/6-31G(d)	0.925	0.909	0.985	0.925	4.5
PBE1PBE/6-31G(d)	0.936	0.922	0.988	0.956	-0.9
MP2/6-31G(d)	0.938	0.923	0.984	0.898	-2.3
HF/6-31+G(d)	0.938	0.922	0.984	0.898	-7.2
B3LYP/6-31+G(d)	0.932	0.916	0.981	0.926	-1.2
PBE1PBE/6-31+G(d)	0.941	0.928	0.985	0.957	-6.9
MP2/6-31+G(d)	0.927	0.909	0.988	0.898	-20.8
HF/6-31G(2d)	0.955	0.943	0.988	0.937	-23.7
B3LYP/6-31G(2d)	0.944	0.928	0.987	0.992	-24.5
PBE1PBE/6-31G(2d)	0.952	0.938	0.989	1.014	-28.4
MP2/6-31G(2d)	0.928	0.907	0.983	1.064	-39.8
HF/6-31G(d,p)	0.938	0.923	0.984	0.905	-4.4
B3LYP/6-31G(d,p)	0.925	0.909	0.986	0.939	2.0
PBE1PBE/6-31G(d,p)	0.936	0.923	0.988	0.970	-3.4
MP2/6-31G(d,p)	0.935	0.917	0.987	0.954	-15.0
HF/6-31+G(d,p)	0.939	0.924	0.983	0.908	-8.8

B3LYP/6-31+G(d,p)	0.933	0.917	0.983	0.942	-3.5
PBE1PBE/6-31+G(d,p)	0.942	0.929	0.986	0.972	-9.0
MP2/6-31+G(d,p)	0.933	0.914	0.987	0.956	-19.0
HF/6-311G(d)	0.939	0.924	0.976	0.987	-8.3
B3LYP/6-311G(d)	0.944	0.931	0.985	1.060	-8.9
PBE1PBE/6-311G(d)	0.951	0.940	0.986	1.078	-16.3
MP2/6-311G(d)	0.931	0.915	0.986	0.999	-11.2
HF/6-311G(2d,2p)	0.956	0.944	0.985	1.009	-4.3
B3LYP/6-311G(2d,2p)	0.951	0.938	0.991	1.093	-6.1
PBE1PBE/6-311G(2d,2p)	0.958	0.947	0.992	1.112	-13.6
MP2/6-311G(2d,2p)	–[a]	–	–	–	–
HF/6-311++G(d,p)	0.942	0.928	0.975	1.008	-7.3
B3LYP/6-311++G(d,p)	0.944	0.931	0.985	1.080	-7.9
PBE1PBE/6-311++G(d,p)	0.951	0.940	0.986	1.098	-15.2
MP2/6-311++G(d,p)	–	–	–	–	–
HF/6-311++G(2d,2p)	0.956	0.944	0.983	1.010	-3.7
B3LYP/6-311++G(2d,2p)	0.950	0.937	0.990	1.095	-5.6
PBE1PBE/6-311++G(2d,2p)	0.957	0.946	0.991	1.114	-13.3
MP2/6-311++G(2d,2p)	–	–	–	–	–
HF/6-311++G(3df,3pd)	0.954	0.941	0.984	1.008	-1.3
B3LYP/6-311++G(3df,3pd)	0.949	0.936	0.991	1.098	-4.5
PBE1PBE/6-311++G(3df,3pd)	0.956	0.945	0.992	1.120	-12.6
MP2/6-311++G(3df,3pd)	–	–	–	–	–

[a] Not affordable for computational reasons.

Table S6. CPU time (t) dependence on the indicated basis set used at geometry optimization and ^{31}P CS calculation for **35**.

Basis set[a]	Geometry optimization		CS calculation	
	t[b]	$t_{relative}$	t[b]	$t_{relative}$
6-31G(d)	6.5	1.0	0.6	1.0
6-31G(d,p)	8.2	1.3	0.8	1.4
6-31G(2d)			1.3	2.2
6-311G(d)			1.3	2.3
6-31+G(d)	31.0	4.8	2.6	4.6
6-31+G(d,p)			3.9	6.9
6-311G(2d,2p)	98.1	15.2	4.9	8.7
6-311++G(d,p)			6.6	11.7
6-311++G(2d,2p)			22.7	40.1
6-311++G(3df,3pd)			103.8	183.1

[a] At DFT PBE1PBE level of theory; [b] In hours.

Table S7. CPU time dependence on level of theory for **5**.

Level of theory[a]	Geometry optimization		CS calculation	
	t[b]	$t_{relative}$	t[b]	$t_{relative}$
HF	0.3	1.0	0.018	1.0
DFT PBE1PBE	0.4	1.3	0.021	1.2
MP2	1.5	5.4	0.579	31.1

[a] With 6-31G(d) basis set; [b] In hours.

Table S8. Calculated dipole moments (μ, D), ^{31}P shielding constants[a] (σ_{iso}, ppm) and experimental ^{31}P CSs (δ, ppm) for **4**, **7**, **36-38**.

Molecules	μ	σ_{iso}, gas phase	σ_{iso}, PCM, C_6H_6	σ_{iso}, PCM, $CHCl_3$	δ_{exp} C_6H_6	δ_{exp} $CHCl_3$
H_3PO_4 (**4**)	0.02	374.8	375.3	375.5		
$(CH_3)_3PO$ (**7**)	4.32	369.6	362.7	359.0		
$P(OEt)_3$ (**36**)	1.50	228.5	228.6	229.3	139.2	139.5
$HP(O)(OEt)_2$ (**37**)	4.45	369.2	365.6	363.1	7.7	8.1
$ClP(O)(OEt)_2$ (**38**)	2.86	351.4	350.7	351.0	3.8	4.6

[a] At PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d)

Table S9. Experimental (δ_{exp}) and calculated ^{31}P CSs (δ, ppm) and relative energies (kcal/mol) for **1**, **2**, **3**, **39**.

Molecules	δ_{exp}	Calculations[a]			
		Gas phase		In H_2O (in frame of PCM)	
		δ	ΔE	δ	ΔE
H_3PO (**1a**)	-13.9	-49.7	3.2	-45.1	0
H_2POH (**1b**)		33.7	0	34.7	0.5
$H_2P(O)OH$ (**2a**)	12.5	-0.2	0	-1.1	0
$HP(OH)_2$ (**2b**)		153.9	5.3	155.0	7.1
$HP(O)(OH)_2$ (**3a**)	3.0	6.0	0	-3.2	0
$P(OH)_3$ (**3b**)		94.1	14.3	85.4	10.2
$C_6F_5(C_2F_5)POH$ (**39a**)	80.6	71.4	0	65.8	0
$C_6F_5(C_2F_5)P(O)H$ (**39b**)	-1.9	-10.8	3.6	-4.8	1.0

[a] At PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d).

Table S10. Calculated (unscaled and scaled) and experimental ^{31}P CSs (δ_{exp}, ppm) for **35**, **40**-**48**.

№	PBE1PBE/6-31G(d)// PBE1PBE/6-31G(d)[a]		PBE1PBE/6-31G(2d)// PBE1PBE /6-31G(d)[a]		PBE1PBE/6-311G(2d,2p)// HF/6-31G(d)[a]		PBE1PBE/6-311G(2d,2p)// PBE1PBE/6-31G(d)[a]		δ_{exp}	Solvent	Ref.
	Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled			
35	34.6 291.3	41.0 320.6	24.0 258.8	55.4 297.2	78.6 350.6	80.5 333.7	32.1 309.6	43.3 302.0	54.8 322.9	C_6H_6	97
40	-160.1 67.7	-171.1 77.0	-194.2 48.5	-169.3 80.6	-146.4 74.8	-129.0 76.9	-172.4 63.9	-147.3 72.9	-157.7 76.7	na[b]	98
41	-108.6	-115.0	-131.0	-104.2	-133.3	-116.8	-129.3	-107.2	-110.0	na	99
42	-62.0	-64.2	-71.9	-43.3	-66.2	-54.4	-68.6	-50.5	-54.5	na	100
43	-24.1 95.1 7.7 73.3	-23.0 106.8 11.7 83.1	-29.7 100.5 -10.6 75.7	-25.6 99.9 2.4 77.7	-6.7 61.8 -51.1 56.5	1.1 64.8 -40.3 59.8	-41.9 84.1 -7.1 58.7	-25.7 91.7 6.7 68.1	-29.7 100.5 -10.6 75.7	$CHCl_3$	101
44	27.6	33.3	15.0	46.1	22.7	28.4	22.5	34.3	24.0	C_6H_6	102
45	88.7 -19.0	99.9 -22.6	51.8 -50.7	84.0 -21.6	88.6 -27.6	89.8 -18.5	74.3 -36.5	82.6 -20.6	84.1 -22.6	$CHCl_3$	103
46	21.2 12.4	26.4 16.8	15.4 3.5	46.5 34.3	15.8 6.5	21.9 13.3	15.0 5.8	27.4 18. 8	27.6 18.3	$CHCl_3$	104
47	-13.9	-11.9	-36.1	-6.5	-1.7	5.7	-23.1	-8.1	-10.2	$CHCl_3$	105
48	34.1	40.4	10.3	41.2	50.4	54.2	36.8	47.7	38.7	$CHCl_3$	106
R^2	0.992	0.992	0.989	0.989	0.967	0.967	0.996	0.996			
RMSE, ppm	11.1	9.4	29.3	11.6	19.9	18.2	13.6	9.0			

[a] First row – level of theory used for CS calculation, second row – for geometry optimization; [b] not available.

Table S11. Experimental (δ_{exp}) and calculated (δ_{scaled})[a] ^{31}P CSs, $\Delta\delta = \delta_{scaled} - \delta_{exp}$ for isomers of **45**.

Isomers	δ_{exp}		δ_{scaled}		$\Delta\delta$	
	P_1	P_2	P_1	P_2	P_1	P_2
A	-22.6	84.1	-20.6	82.6	2.0	-1.5
B			-8.6	34.3	14.0	-49.8
C			-18.2	132.6	4.4	48.5
D			-5.9	91.7	16.7	7.6

[a] PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d).