Instructions for using the Excel file to compute the DP4+ probability

- Despite the DP4+ calculations can be made "by hand", an Excel file is provided from the authors as part of the Supporting Information of this paper that considerably simplifies the procedure.
- The file contains 2 sheets: "Main" and "Detailed Results" (Figure S1).
- The "Main" sheet is divided in 3 different zones: A, B and C.

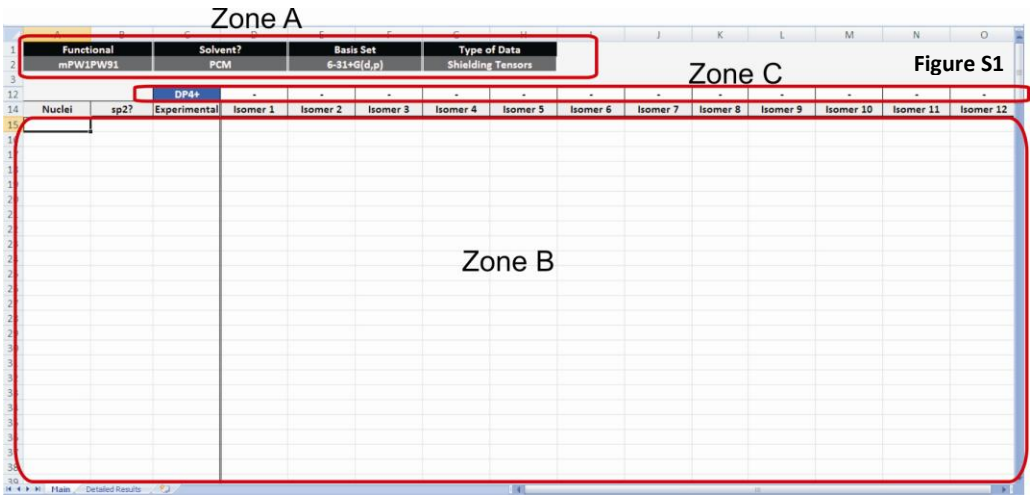


Figure S1

Zone A: user selection (drop down lists):

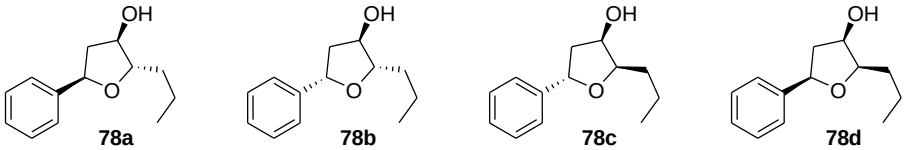
- *Functional:* functional used to perform the GIAO NMR calculations (B3LYP or mPW1PW91).
- *Solvent?:* inclusion of solvent effect in the GIAO NMR calculations (PCM or Gas Phase).
- *Basis Set:* basis set used in the GIAO NMR calculations (6-31G*, 6-31G**, 6-31+G**, 6-311G*, 6-311G** or 6-311+G**)
- *Type of Data:* indicates the type of data entered in Zone B (Shielding Tensors, Unscaled Shifts or Scaled Shifts).

Zone B: enabled cells to enter the data:

- *Nuclei:* enter the letter "C" (without quotes) for ^{13}C data or the letter "H" (without quotes) for ^{1}H data.
- *sp2?:* enter the letter "x" (without quotes) if the carbon is sp-sp^2 hybridized (or if the proton is attached to an sp-sp^2 hybridized carbon).
- *Experimental:* enter the experimental ^{13}C and/or ^{1}H chemical shifts.
- *Isomer 1, Isomer 2, etc:* enter the computed data for the candidate structures.

Zone C: displays the DP4+ probabilities once the data is entered in Zone B.

Tutorial: compounds 78a-d (four candidates). NMR data from: 78b (correct isomer).



Step 1: perform a conformational search using a suitable package (Hyperchem, Spartan, MacroModel, etc).

Step 2: optimize the most significant conformations at the B3LYP/6-31G* level (gas phase).

Step 3: perform the NMR GIAO calculations at the selected level of theory (in this case, at the PCM/mPW1PW91/6-31G**) for all representative conformations.

Step 4: compute all the Boltzmann-averaged shielding tensors values for each compound.

Step 5: open the Excel file.

Step 6: select the correct level of theory that was used to perform the NMR shift calculation (Figure S2). In this particular case, PCM/mPW1PW91/6-31G**.

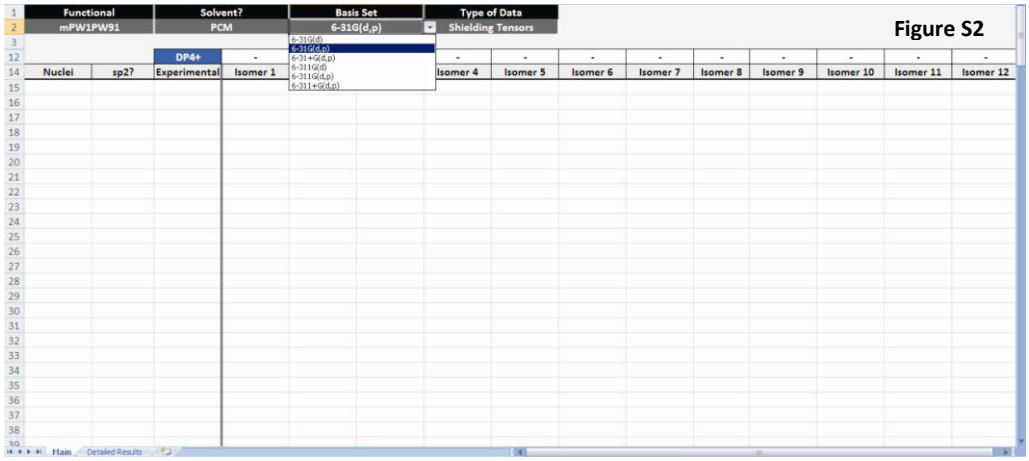


Figure S2

Step 7: Introduce the experimental data (Figure S3). **Important: mark the sp^2 nuclei.**

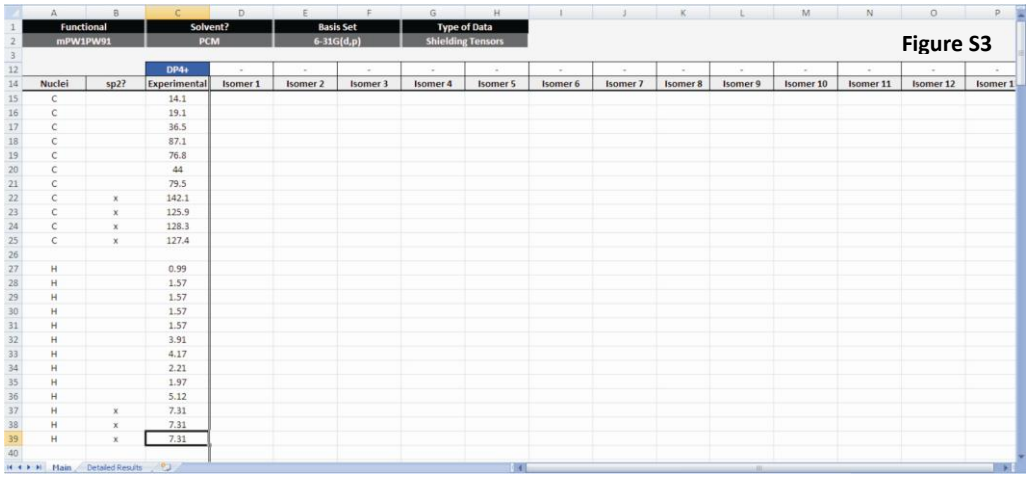


Figure S3

Step 8: Introduce the calculated shielding tensors for each possible candidate structure (4 in this case) (Figure S4). The DP4+ values are automatically calculated and displayed for each isomer above the number of isomer. **Important: the data must be assigned (know which shift corresponds to which nuclei).**

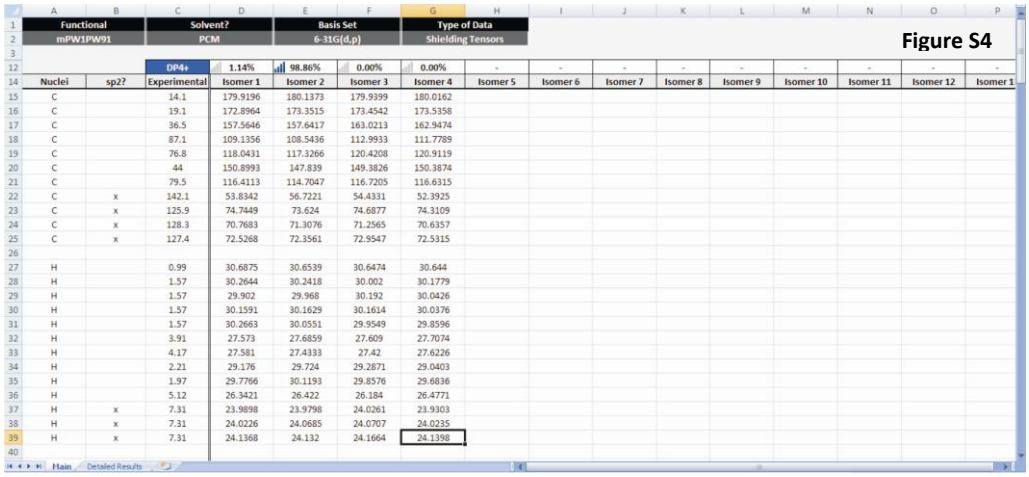
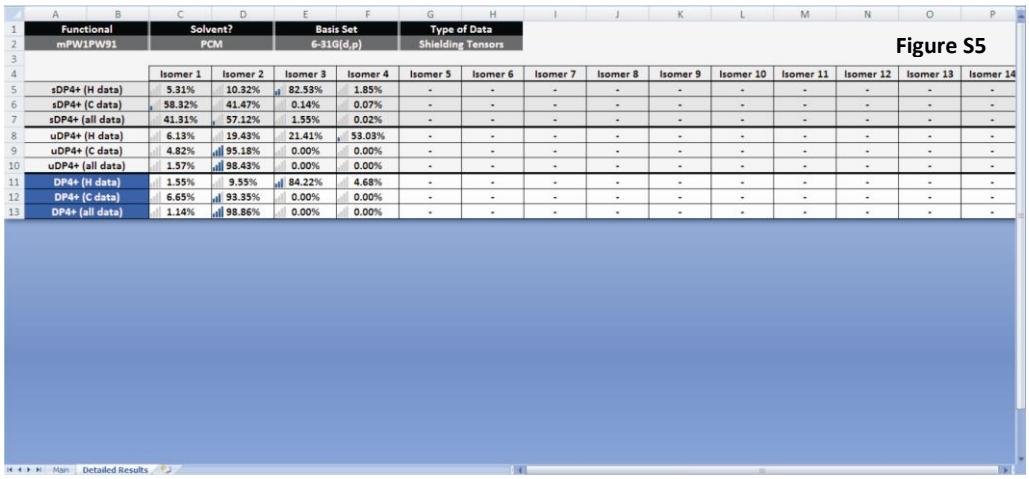


Figure S4

Step 9: The probabilities computed using unscaled (*u*DP4+) and scaled (*s*DP4+), as well as using carbon and/or proton data, is shown in the sheet "Detailed Results" (Figure S5)

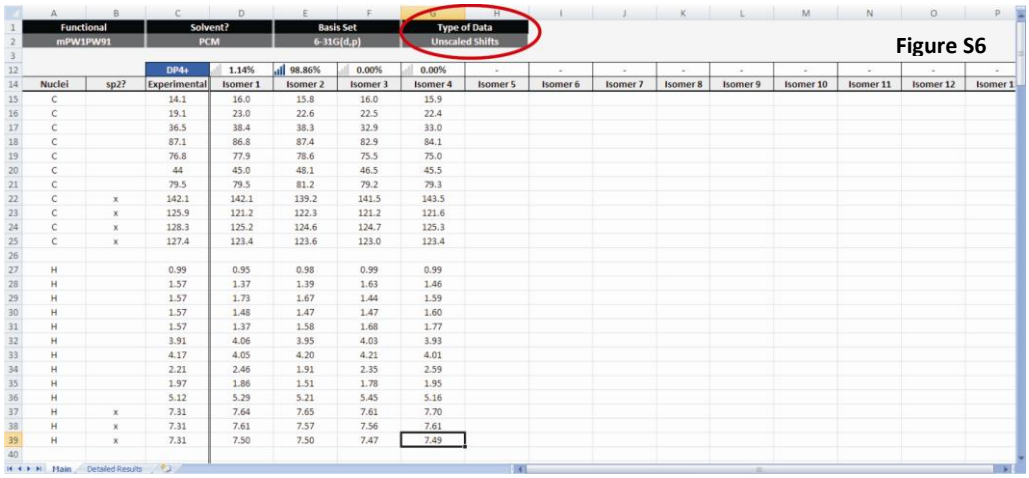


Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8	Isomer 9	Isomer 10	Isomer 11	Isomer 12	Isomer 13	Isomer 14
sDP4+ (H data)	5.31%	10.32%	82.53%	1.85%	-	-	-	-	-	-	-	-	-	-
sDP4+ (C data)	58.32%	41.47%	0.14%	0.07%	-	-	-	-	-	-	-	-	-	-
sDP4+ (all data)	41.31%	57.12%	1.55%	0.02%	-	-	-	-	-	-	-	-	-	-
uDP4+ (H data)	6.13%	19.43%	21.41%	53.03%	-	-	-	-	-	-	-	-	-	-
uDP4+ (C data)	4.82%	95.18%	0.00%	0.00%	-	-	-	-	-	-	-	-	-	-
uDP4+ (all data)	1.57%	98.43%	0.00%	0.00%	-	-	-	-	-	-	-	-	-	-
DP4+ (H data)	1.55%	9.55%	84.22%	4.68%	-	-	-	-	-	-	-	-	-	-
DP4+ (C data)	6.65%	93.35%	0.00%	0.00%	-	-	-	-	-	-	-	-	-	-
DP4+ (all data)	1.14%	98.86%	0.00%	0.00%	-	-	-	-	-	-	-	-	-	-

Figure S5

Note 1: the same results are obtained using unscaled shifts (Figure S6).

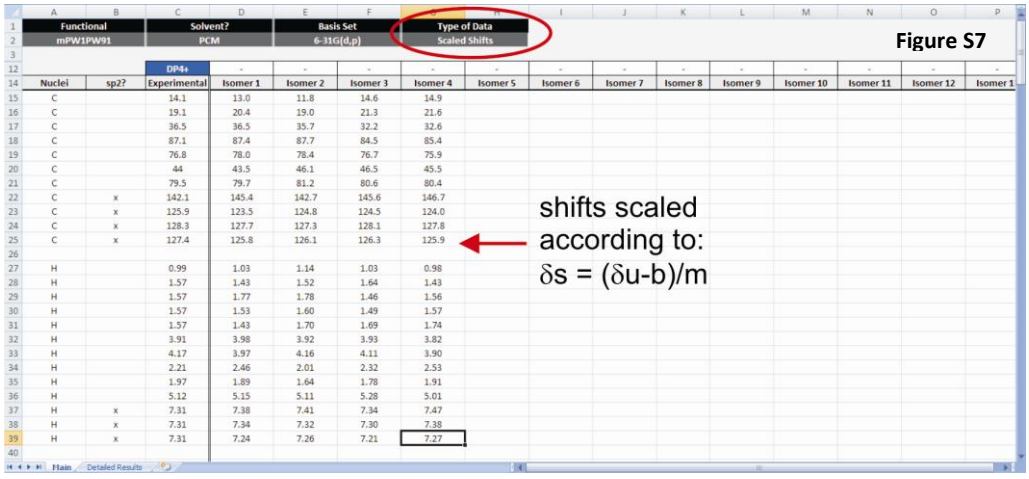


Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Unscaled Shifts

		DP4+	1.14%	98.86%	0.00%	0.00%									
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8	Isomer 9	Isomer 10	Isomer 11	Isomer 12	Isomer 1
C		14.1	16.0	15.8	16.0	15.9									
C		19.1	23.0	22.6	22.5	22.4									
C		36.5	38.4	38.3	32.9	33.0									
C		87.1	86.8	87.4	82.9	84.1									
C		76.8	77.9	78.6	75.5	75.0									
C		44	45.0	48.1	46.5	45.5									
C		79.5	79.5	81.2	79.2	79.3									
C	x	142.1	142.1	139.2	141.5	143.5									
C	x	125.9	121.2	122.3	121.2	121.6									
C	x	128.3	125.2	124.6	124.7	125.3									
C	x	127.4	123.4	123.6	123.0	123.4									
H		0.99	0.95	0.98	0.99	0.99									
H		1.57	1.37	1.39	1.63	1.46									
H		1.57	1.73	1.67	1.44	1.59									
H		1.57	1.48	1.47	1.47	1.60									
H		1.57	1.37	1.58	1.68	1.77									
H		3.91	4.06	3.95	4.03	3.93									
H		4.17	4.05	4.20	4.21	4.01									
H		2.21	2.46	1.91	2.35	2.59									
H		1.97	1.86	1.51	1.78	1.95									
H		5.12	5.29	5.21	5.45	5.16									
H	x	7.31	7.64	7.65	7.61	7.70									
H	x	7.31	7.61	7.57	7.56	7.61									
H	x	7.31	7.50	7.50	7.47	7.49									

Figure S6

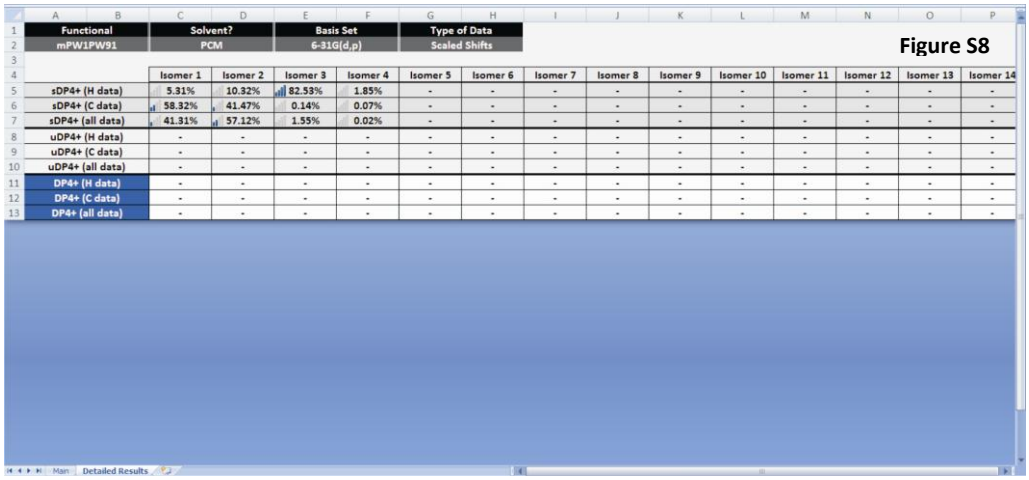
Note 2: if scaled shifts are introduced, the Excel file cannot compute the DP4+ probability (Figure S7), but instead the *s*DP4+ values can be seen in the "Detailed Results" sheet (Figure S8).



Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Scaled Shifts

		DP4+	-	-	-	-									
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8	Isomer 9	Isomer 10	Isomer 11	Isomer 12	Isomer 1
C		14.1	13.0	11.8	14.6	14.9									
C		19.1	20.4	19.0	21.3	21.6									
C		36.5	36.5	35.7	32.2	32.6									
C		87.1	87.4	87.7	84.5	85.4									
C		76.8	78.0	78.4	76.7	75.9									
C		44	43.5	46.1	46.5	45.5									
C		79.5	79.7	81.2	80.6	80.4									
C	x	142.1	145.4	142.7	145.6	146.7									
C	x	125.9	123.5	124.8	124.5	124.0									
C	x	128.3	127.7	127.3	128.1	127.8									
C	x	127.4	125.8	126.1	126.3	125.9									
H		0.99	1.03	1.14	1.03	0.98									
H		1.57	1.43	1.52	1.64	1.43									
H		1.57	1.77	1.78	1.46	1.56									
H		1.57	1.53	1.60	1.49	1.57									
H		1.57	1.43	1.70	1.69	1.74									
H		3.91	3.98	3.92	3.93	3.82									
H		4.17	3.97	4.16	4.11	3.90									
H		2.21	2.46	2.01	2.32	2.53									
H		1.97	1.89	1.64	1.78	1.91									
H		5.12	5.15	5.11	5.28	5.01									
H	x	7.31	7.38	7.41	7.34	7.47									
H	x	7.31	7.34	7.32	7.30	7.38									
H	x	7.31	7.24	7.26	7.21	7.27									

Figure S7



Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31G(d,p)	Scaled Shifts

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8	Isomer 9	Isomer 10	Isomer 11	Isomer 12	Isomer 13	Isomer 14
sDP4+ (H data)	5.31%	10.32%	82.53%	1.85%	-	-	-	-	-	-	-	-	-	-
sDP4+ (C data)	58.32%	41.47%	0.14%	0.07%	-	-	-	-	-	-	-	-	-	-
sDP4+ (all data)	41.31%	57.12%	1.55%	0.02%	-	-	-	-	-	-	-	-	-	-
uDP4+ (H data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
uDP4+ (C data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
uDP4+ (all data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DP4+ (H data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DP4+ (C data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DP4+ (all data)	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Figure S8