

# Supplementary Material

***Impact of solvent interactions on  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts investigated using DFT and a reference dataset recorded in  $\text{CDCl}_3$  and  $\text{CCl}_4$***

Thomas Stadelmann, Chantal Balmer, Sereina Riniker\* and Marc-Olivier Ebert\*

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Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1-5, 8093 Zurich, Switzerland

\* [sriniker@ethz.ch](mailto:sriniker@ethz.ch); [marc-olivier.ebert@org.chem.ethz.ch](mailto:marc-olivier.ebert@org.chem.ethz.ch)

## Collection of Chemical Shifts from the Literature

Literature data from different sources (maximum ten per compound) were collected for comparison with our measured chemical shifts in  $\text{CDCl}_3$  (Figure 1 in the main text). In the literature search, only data measured in  $\text{CDCl}_3$  and published in the period between 1980 and 2022 were considered (mostly found via Reaxys). The shifts from the following references were used: **1**<sup>1-6</sup> **2**<sup>2,3,6-8</sup> **3**<sup>3,6-14</sup> **4**<sup>15-20</sup> **5**<sup>3,6,7,21,22</sup> **6**<sup>23</sup> **7**<sup>24-27</sup> **8**<sup>6,28-31</sup> **9**<sup>32-41</sup> **10**<sup>42,43</sup> **11**<sup>44-47</sup> **12**<sup>6,48-50</sup> **13**<sup>1,6,51-53</sup> **14**<sup>54-58</sup> **15**<sup>6,59-68</sup> **16**<sup>69-80</sup> **17**<sup>6,81-89</sup> **18**<sup>90-99</sup> **19**<sup>100-109</sup> **20**<sup>12,110-118</sup> **21**<sup>50,119</sup> **22**<sup>120-122</sup> **23**<sup>6,123-127</sup> **24**<sup>128-138</sup> **25**<sup>136,139,140</sup> **26**<sup>141-151</sup> **27**<sup>152-161</sup> **28**<sup>162-170</sup> **29**<sup>171-179</sup> **30**<sup>180-190</sup> **31**<sup>191-200</sup> **32**<sup>201-207</sup> **33**<sup>208-217</sup> **34**<sup>218-227</sup> **35**<sup>6,228-237</sup>

## Effect of Solute-Solvent Interactions in Experiment: Compounds **26** and **34**

The sites of specific solvent-solute interactions were identified by comparison of the chemical shifts measured in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . For **26**, the  $^{13}\text{C}$  chemical shift of the carbonyl carbon, as well as the shift of the conjugated  $\beta$ -carbon (Figure S1, carbons 1 and 3), move towards higher field when changing the solvent from chloroform-d to tetrachloromethane, whereas the other carbons that are not affected by hydrogen bonding with the solvent, have nearly identical chemical shifts. The shifts of protons close to functional groups involved in hydrogen bonds with chloroform are also affected by the change in solvent (Figure S2, protons at carbon 2 and 6 of **26**,  $\alpha$  to carbonyl group). A similar behavior is observed for the  $^{13}\text{C}$  shifts of **34** (Figure S3).

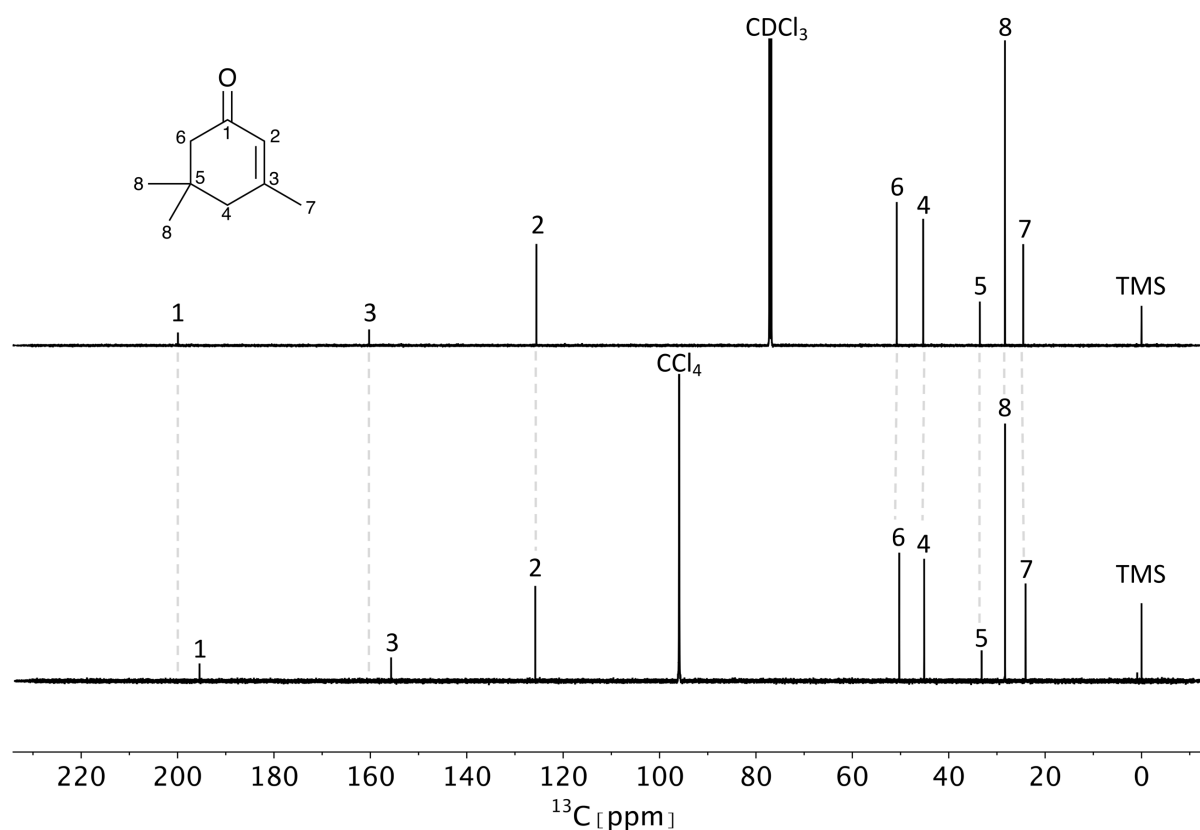


Figure S1:  $^{13}\text{C}$  spectra of **26** in chloroform-d (top) and tetrachloromethane (bottom) referenced to internal TMS. Dashed grey lines help to visualize chemical shift differences between the two solvents.

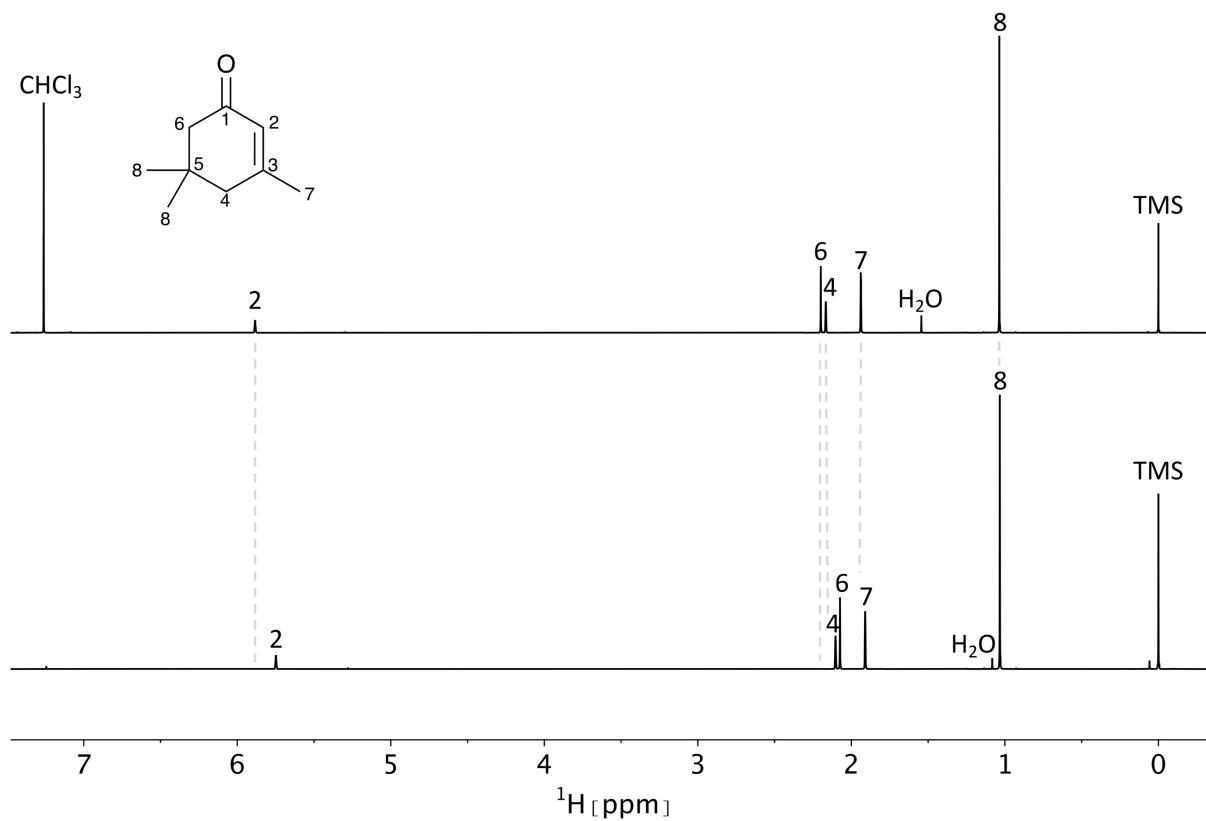


Figure S2:  $^1\text{H}$  spectra of **26** in chloroform- $d$  (top) and tetrachloromethane (bottom) referenced to internal TMS. Dashed grey lines help to visualize the chemical shift differences between the two solvents.

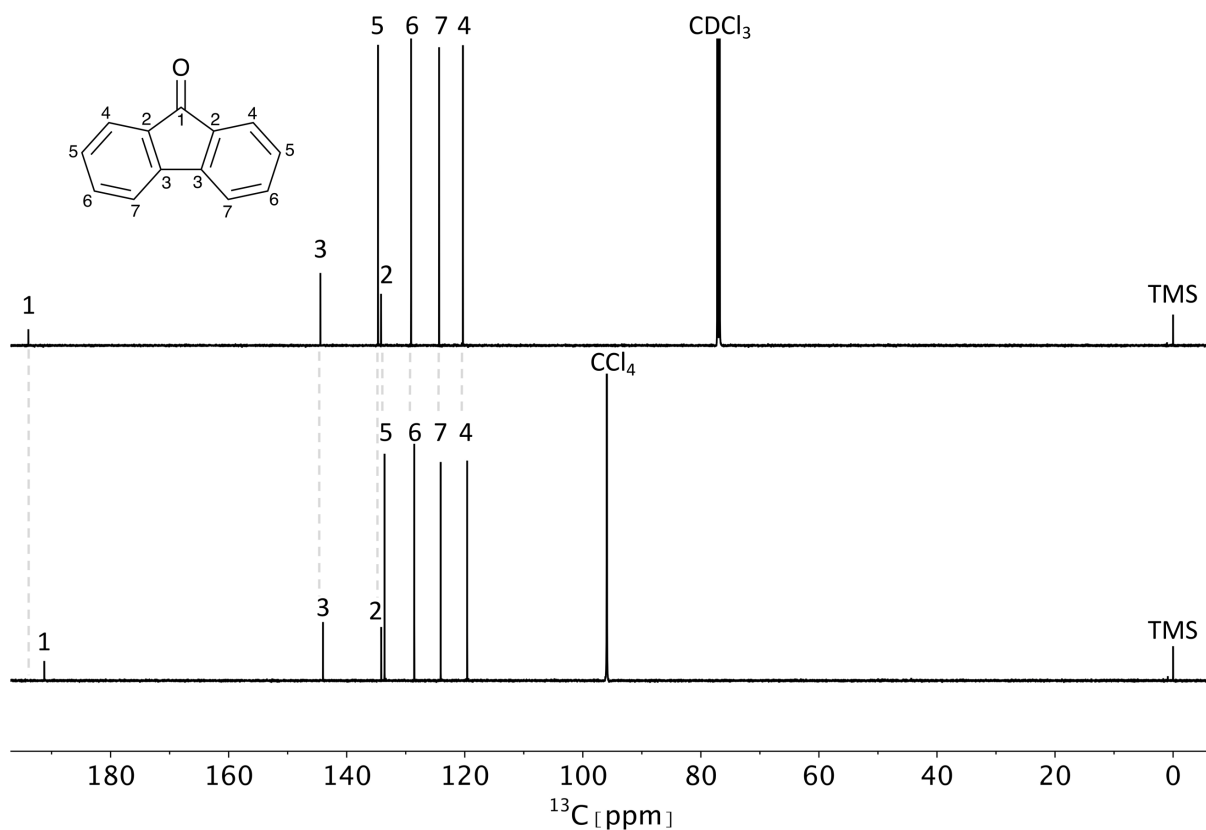


Figure S3:  $^{13}\text{C}$  spectra of **34** in chloroform- $d$  (top) and tetrachloromethane (bottom) referenced to internal TMS. Dashed grey lines help to visualize the chemical shift differences between the two solvents. The largest change is observed for carbonyl carbon 1.

## Additional Figures and Tables:

### Comparison of experimental data

Table S1: Root-mean-square deviation (RMSD), mean absolute deviation (MAD), maximum absolute deviation (Max. AD) when comparing the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts measured under standardized conditions to values collected from multiple literature sources in  $\text{CDCl}_3$ . (a) methyl protons of **11**, (b) carbons of the pyrimidine ring next to amine of **20**.

	$^1\text{H}$	$^{13}\text{C}$
RMSD [ppm]	0.05	0.26
MAD [ppm]	0.09	0.15
Max. AD [ppm]	0.40 <sup>a</sup>	3.00 <sup>b</sup>

Table S2: RMSD, MAD and max. AD when comparing the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts measured in  $\text{CCl}_4$  and  $\text{CDCl}_3$ .

	$^1\text{H}$	$^{13}\text{C}$
RMSD [ppm]	0.08	1.40
MAD [ppm]	0.07	0.85
Max. AD [ppm]	0.20	5.90

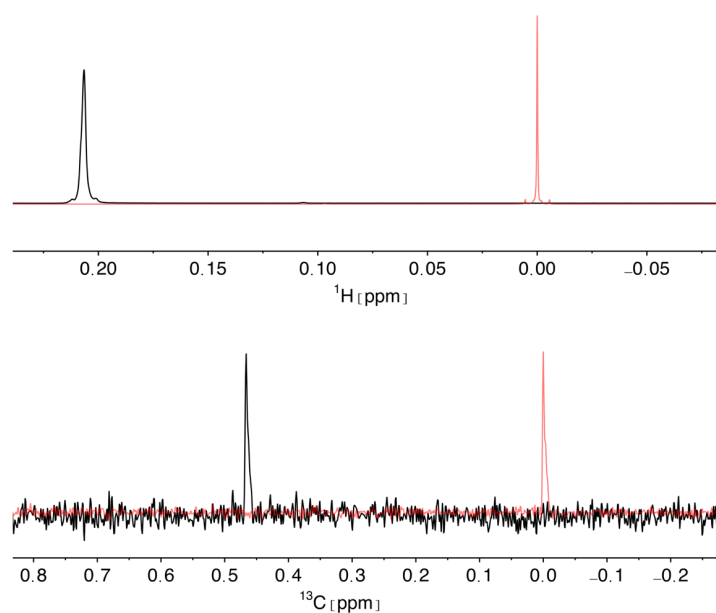


Figure S4: Overlay of  $^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) spectra of TMS in  $\text{CDCl}_3$  (red) and  $\text{CCl}_4$  (black) recorded with the same FIELD value. The TMS signal in the  $\text{CDCl}_3$  spectra was referenced to 0 ppm. The same SR value was set in the  $\text{CCl}_4$  spectra.

### Comparison of experimental data to vacuum calculations (PBE0 & PBEP86)

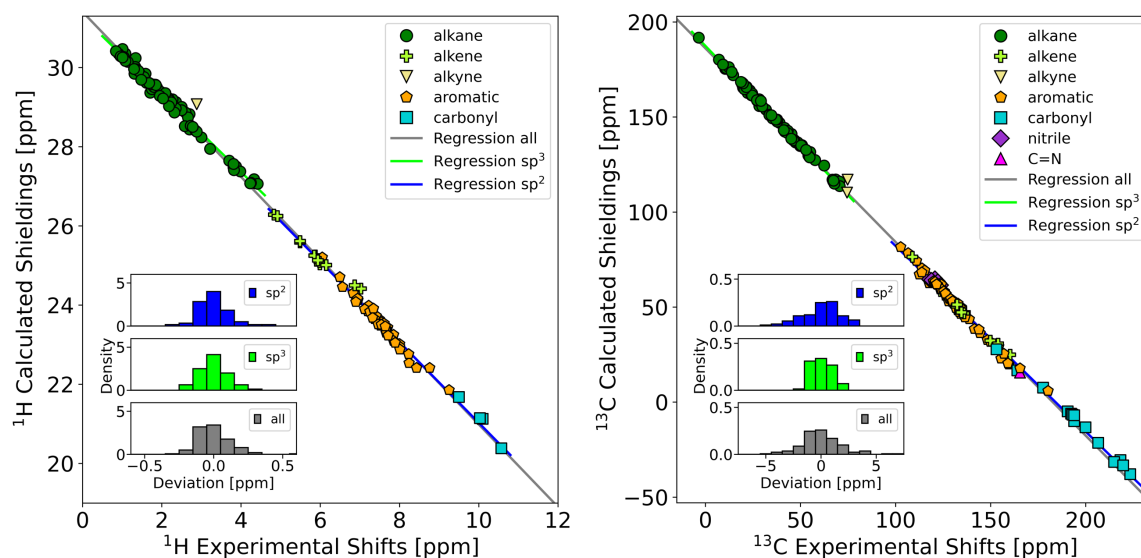


Figure S5: Regression of the calculated chemical shieldings (PBE0, in vacuum) versus the experimental chemical shifts measured in  $\text{CDCl}_3$ . (Left):  $^1\text{H}$ . (Right):  $^{13}\text{C}$ . The histograms show the deviations after conversion of the shieldings into chemical shifts using the parameters from the regression.

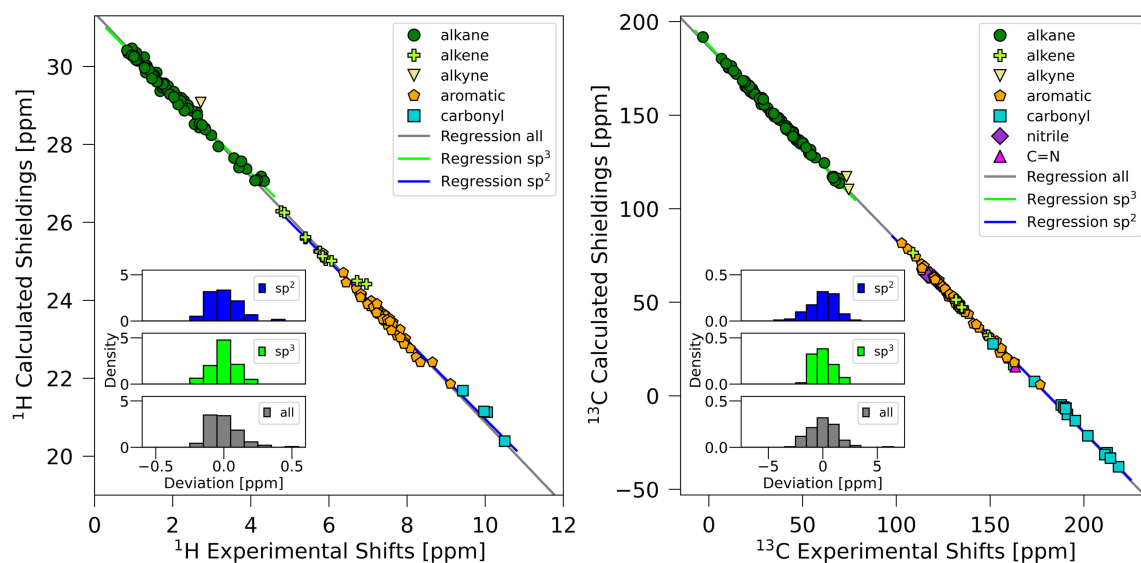


Figure S6: Regression of the calculated chemical shieldings (PBEP86, in vacuum) versus the experimental chemical shifts measured in  $\text{CCl}_4$ . (Left):  $^1\text{H}$ . (Right):  $^{13}\text{C}$ . The histograms show the deviations after conversion of the shieldings into chemical shifts using the parameters from the regression.

Table S3: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.09	0.08	0.07	1.05	1.08	0.83
PBEP86	$\text{CCl}_4$	0.09	0.08	0.07	0.98	0.99	0.73
PBE0	$\text{CDCl}_3$	0.09	0.08	0.08	1.14	1.32	0.88
PBEP86	$\text{CDCl}_3$	0.09	0.08	0.08	1.32	1.40	0.80

Table S4: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	0.32	0.34	0.23	5.10	5.04	2.56
PBEP86	$\text{CCl}_4$	0.53	0.38	0.23	6.10	3.52	2.27
PBE0	$\text{CDCl}_3$	0.43	0.31	0.26	5.17	4.65	2.82
PBEP86	$\text{CDCl}_3$	0.64	0.36	0.28	7.00	5.22	2.40

Table S5: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	31.476	31.176	31.371	185.47	187.75	185.79
		-1.062	-1.024	-1.006	-1.033	-1.048	-1.047
PBEP86	$\text{CCl}_4$	31.374	31.067	31.285	186.51	187.56	185.41
		-1.051	-1.011	-1.004	-1.031	-1.062	-1.023
PBE0	$\text{CDCl}_3$	31.508	31.316	31.368	185.14	182.17	185.67
		-1.053	-1.030	-0.983	-1.021	-1.001	-1.032
PBEP86	$\text{CDCl}_3$	31.405	31.209	31.281	186.17	179.88	187.43
		-1.042	-1.018	-0.980	-1.019	0.977	-1.047

Table S6: Cf. Table 3 in the main text: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3) using the calculated  $^1\text{H}$  and  $^{13}\text{C}$  shieldings of TMS as reference. Values are given for the complete set (all), for  $sp^2$  carbons and attached protons ( $sp^2$ ), and for  $sp^3$  carbons and attached protons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	0.24	0.35	0.10	5.79	6.95	3.73
PBEP86	$\text{CCl}_4$	0.19	0.26	0.10	6.46	7.63	4.52
PBE0	$\text{CDCl}_3$	0.20	0.27	0.12	4.89	5.85	3.31
PBEP86	$\text{CDCl}_3$	0.17	0.18	0.14	5.68	6.69	4.10

Table S7: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	0.19	0.25	0.08	5.29	8.62	3.45
PBEP86	$\text{CCl}_4$	0.15	0.18	0.08	6.09	9.71	4.28
PBE0	$\text{CDCl}_3$	0.17	0.18	0.10	4.49	7.26	3.06
PBEP86	$\text{CDCl}_3$	0.14	0.12	0.12	5.30	8.35	3.89

Table S8: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$  (ppm). But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.64	0.64	0.24	12.4	12.4	6.24
PBEP86	$\text{CCl}_4$	0.57	0.47	0.29	11.4	11.4	7.31
PBE0	$\text{CDCl}_3$	0.57	0.57	0.31	9.41	9.41	5.98
PBEP86	$\text{CDCl}_3$	0.73	0.44	0.36	11.2	11.2	6.80

Table S9: Cf. Table 3 in the main text: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively.

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.31/0.38	0.45/0.15	0.13/0.47	2.38/2.44	2.71/2.11	1.94/2.86
PBEP86	$\text{CCl}_4$	0.29/0.44	0.41/0.26	0.13/0.53	2.20/2.25	2.19/1.70	2.12/2.72
PBE0	$\text{CDCl}_3$	0.26/0.35	0.37/0.16	0.11/0.43	1.95/2.26	2.03/1.69	1.91/2.88
PBEP86	$\text{CDCl}_3$	0.23/0.42	0.32/0.26	0.11/0.49	2.12/2.32	2.06/1.83	2.06/2.70

Table S10: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively.

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.25/0.32	0.44/0.12	0.32/0.68	1.89/1.97	2.12/1.61	1.58/2.53
PBEP86	$\text{CCl}_4$	0.23/0.40	0.39/0.23	0.11/0.52	1.78/1.75	1.78/1.28	1.75/2.33
PBE0	$\text{CDCl}_3$	0.20/0.30	0.35/0.13	0.08/0.42	1.59/1.85	1.64/1.32	1.59/2.59
PBEP86	$\text{CDCl}_3$	0.19/0.38	0.30/0.23	0.09/0.48	1.70/1.86	1.64/1.41	1.71/2.38

Table S11: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum with PBE0 or PBEP86 from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively.

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.75/0.76	0.75/0.46	0.32/0.68	7.54/6.40	7.54/6.40	4.85/5.99
PBEP86	$\text{CCl}_4$	0.62/1.04	0.62/0.62	0.33/0.75	6.75/7.50	5.60/4.84	4.95/5.70
PBE0	$\text{CDCl}_3$	0.68/0.83	0.68/0.44	0.28/0.66	4.93/5.92	4.93/4.64	4.76/5.92
PBEP86	$\text{CDCl}_3$	0.60/1.11	0.60/0.60	0.30/0.73	7.76/8.53	5.76/4.99	4.47/5.24

**Comparison of experimental data to shielding calculations using CPCM and geometries reoptimized with the corresponding implicit solvent (PBE0 & PBEP86)**

Table S12: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.08	0.07	0.06	1.59	1.19	0.90
PBEP86	$\text{CCl}_4$	0.07	0.08	0.05	1.22	0.83	0.82
PBE0	$\text{CDCl}_3$	0.08	0.08	0.06	1.42	1.26	0.89
PBEP86	$\text{CDCl}_3$	0.08	0.09	0.05	1.07	0.89	0.78

Table S13: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.27	0.22	0.18	9.63	9.12	2.42
PBEP86	$\text{CCl}_4$	0.42	0.29	0.18	5.46	5.30	2.52
PBE0	$\text{CDCl}_3$	0.27	0.21	0.17	9.16	8.81	2.42
PBEP86	$\text{CDCl}_3$	0.41	0.31	0.16	4.73	4.76	2.20

Table S14: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	31.407	30.902	31.344	186.47	195.35	186.45
		-1.072	-1.006	-1.033	-1.052	-1.112	-1.065
PBEP86	$\text{CCl}_4$	31.307	30.801	31.261	187.55	193.57	188.23
		-1.061	-0.995	-1.032	-1.051	-1.091	-1.082
PBE0	$\text{CDCl}_3$	31.409	30.934	31.332	186.55	192.35	186.62
		-1.068	-1.006	-1.023	-1.048	-1.085	-1.058
PBEP86	$\text{CDCl}_3$	31.310	30.842	31.250	187.67	191.03	188.41
		-1.057	-0.997	-1.022	-1.047	-1.069	-1.076



Table S15: Cf. Table 5 in the main text: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.30	0.45	0.09	7.52	9.15	4.26
PBEP86	$\text{CCl}_4$	0.25	0.37	0.07	8.09	9.71	5.11
PBE0	$\text{CDCl}_3$	0.25	0.42	0.08	7.18	8.69	4.14
PBEP86	$\text{CDCl}_3$	0.23	0.34	0.07	7.81	9.35	4.97

Table S16: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.23	0.33	0.07	6.58	10.9	3.94
PBEP86	$\text{CCl}_4$	0.18	0.27	0.18	7.40	12.1	8.71
PBE0	$\text{CDCl}_3$	0.21	0.31	0.07	6.36	10.5	3.83
PBEP86	$\text{CDCl}_3$	0.17	0.24	0.06	7.21	11.8	4.68

Table S17: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.63	0.63	0.23	19.5	19.5	6.68
PBEP86	$\text{CCl}_4$	0.64	0.64	0.18	16.6	16.6	8.71
PBE0	$\text{CDCl}_3$	0.61	0.61	0.21	18.7	13.6	6.64
PBEP86	$\text{CDCl}_3$	0.63	0.63	0.14	15.6	9.48	7.75

Table S18: Cf. Table 5 in the main text: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.40/0.46	0.58/0.19	0.18/0.59	3.89/3.65	4.79/3.91	2.07/3.31
PBEP86	$\text{CCl}_4$	0.38/0.53	0.54/0.30	0.19/0.64	3.48/3.28	4.11/3.32	2.30/3.18
PBE0	$\text{CDCl}_3$	0.38/0.48	0.55/0.22	0.17/0.60	3.56/3.36	4.32/3.33	2.00/3.41
PBEP86	$\text{CDCl}_3$	0.36/0.54	0.51/0.33	0.17/0.65	3.20/3.02	3.74/2.80	2.20/3.24

Table S19: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.33/0.41	0.57/0.17	0.16/0.58	2.74/2.80	3.42/2.67	1.67/2.89
PBEP86	$\text{CCl}_4$	0.32/0.49	0.53/0.28	0.34/0.64	2.67/2.50	10.4/9.18	5.90/7.08
PBE0	$\text{CDCl}_3$	0.31/0.42	0.54/0.20	0.14/0.60	2.58/2.68	3.19/2.36	1.60/3.04
PBEP86	$\text{CDCl}_3$	0.30/0.50	0.50/0.31	0.16/0.65	2.55/2.37	3.03/1.99	1.80/2.78

Table S20: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.75/0.79	0.75/0.39	0.36/0.79	14.3/12.7	14.3/12.7	5.13/6.74
PBEP86	$\text{CCl}_4$	0.81/0.82	0.81/0.58	0.34/0.82	10.4/9.18	10.4/9.18	5.90/7.08
PBE0	$\text{CDCl}_3$	0.75/0.76	0.75/0.37	0.34/0.76	13.6/11.8	13.6/11.8	5.08/6.86
PBEP86	$\text{CDCl}_3$	0.81/0.81	0.81/0.61	0.33/0.81	9.48/8.14	9.48/8.14	5.31/6.65

## Comparison of experimental data to shielding calculations using CPCM and geometries optimized in vacuum (PBE0 & PBEP86)

Table S21: RMSD (ppm) of the  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.09	0.08	0.08	1.87	1.73	1.09
PBEP86	$\text{CCl}_4$	0.10	0.11	0.07	1.37	1.17	0.92
PBE0	$\text{CDCl}_3$	0.10	0.10	0.08	1.73	1.77	1.14
PBEP86	$\text{CDCl}_3$	0.10	0.12	0.07	1.27	1.22	0.92

Table S22: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.07	0.07	0.06	1.45	1.17	0.87
PBEP86	$\text{CCl}_4$	0.07	0.08	0.05	1.11	0.84	0.74
PBE0	$\text{CDCl}_3$	0.08	0.08	0.06	1.34	1.25	0.92
PBEP86	$\text{CDCl}_3$	0.09	0.10	0.05	1.01	0.93	0.75

Table S23: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.32	0.34	0.23	8.30	7.99	2.58
PBEP86	$\text{CCl}_4$	0.40	0.28	0.19	4.35	4.17	2.13
PBE0	$\text{CDCl}_3$	0.25	0.21	0.20	7.72	7.57	2.86
PBEP86	$\text{CDCl}_3$	0.38	0.30	0.19	4.18	3.46	2.11

Table S24: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 using the structures optimized in vacuum versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	31.417	30.948	31.350	186.27	193.20	186.41
		-1.071	-1.010	-1.031	-1.047	-1.093	-1.062
PBEP86	$\text{CCl}_4$	31.317	30.853	31.267	187.37	191.54	188.19
		-1.061	-1.000	-1.030	-1.046	-1.074	-1.078
PBE0	$\text{CDCl}_3$	31.419	30.984	31.338	186.35	190.28	186.057
		-1.020	-1.011	-1.021	-1.042	-1.068	-1.054
PBEP86	$\text{CDCl}_3$	31.320	30.897	31.256	187.48	189.05	188.36
		-1.057	-1.002	-1.020	-1.042	-1.052	-1.072

Table S25: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.24	0.35	0.10	6.03	7.33	3.67
PBEP86	$\text{CCl}_4$	0.19	0.26	0.11	6.63	7.90	4.49
PBE0	$\text{CDCl}_3$	0.20	0.27	0.13	5.06	6.13	3.26
PBEP86	$\text{CDCl}_3$	0.17	0.18	0.15	5.78	6.86	4.07

Table S26: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.19	0.25	0.08	5.42	8.98	3.39
PBEP86	$\text{CCl}_4$	0.15	0.18	0.08	6.20	10.0	4.21
PBE0	$\text{CDCl}_3$	0.17	0.18	0.11	4.61	7.61	3.00
PBEP86	$\text{CDCl}_3$	0.14	0.12	0.12	5.41	8.66	3.82

Table S27: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.63	0.63	0.28	14.0	14.0	6.18
PBEP86	$\text{CCl}_4$	0.50	0.47	0.33	11.5	11.5	7.33
PBE0	$\text{CDCl}_3$	0.56	0.56	0.35	10.0	10.0	5.92
PBEP86	$\text{CDCl}_3$	0.66	0.43	0.40	11.3	11.3	6.82

Table S28: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0	$\text{CCl}_4$	0.32/0.38	0.47/0.16	0.13/0.48	2.73/2.72	2.55/2.55	1.97/3.01
PBEP86	$\text{CCl}_4$	0.29/0.45	0.42/0.26	0.14/0.54	2.43/2.44	2.55/1.94	2.19/2.89
PBE0	$\text{CDCl}_3$	0.26/0.35	0.38/0.16	0.11/0.44	2.10/2.36	2.29/1.75	1.92/3.02
PBEP86	$\text{CDCl}_3$	0.24/0.42	0.33/0.26	0.12/0.50	2.12/2.31	2.02/1.60	2.11/2.86

Table S29: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$  (ppm). But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	0.25/0.32	0.45/0.12	0.11/0.47	2.10/2.17	2.49/1.88	1.60/2.66
PBEP86	$\text{CCl}_4$	0.24/0.41	0.40/0.23	0.12/0.53	1.99/1.92	2.10/1.47	1.81/2.50
PBE0	$\text{CDCl}_3$	0.20/0.30	0.36/0.13	0.09/0.43	1.71/1.93	1.87/1.36	1.57/2.72
PBEP86	$\text{CDCl}_3$	0.19/0.38	0.31/0.23	0.09/0.49	1.66/1.82	1.56/1.23	1.73/2.51

Table S30: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with PBE0 or PBEP86 with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$  (ppm). But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0	$\text{CCl}_4$	0.76/0.73	0.76/0.45	0.32/0.73	9.27/7.97	9.27/7.97	4.99/6.29
PBEP86	$\text{CCl}_4$	0.64/0.97	0.64/0.61	0.33/0.80	6.90/7.79	5.75/4.85	5.46/6.36
PBE0	$\text{CDCl}_3$	0.69/0.76	0.69/0.43	0.28/0.71	5.61/6.22	5.61/4.29	4.90/6.22
PBEP86	$\text{CDCl}_3$	0.60/1.04	0.60/0.59	0.30/0.78	7.91/8.82	5.91/5.00	4.68/5.60

**Comparison of experimental data to vacuum calculations with PBE0/pcSseg-3 and PBEP86/cc-pVTZ (cross-validation)**

Table S31: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.10	0.10	0.09	1.36	1.49	1.03
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.12	0.11	0.10	1.33	1.36	0.93
PBE0/pcSseg-3	$\text{CDCl}_3$	0.11	0.10	0.09	1.47	1.66	1.08
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.13	0.12	0.12	1.89	1.88	1.02

Table S32: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.08	0.08	0.07	1.05	1.09	0.83
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.09	0.09	0.08	1.00	1.02	0.74
PBE0/pcSseg-3	$\text{CDCl}_3$	0.09	0.08	0.07	1.12	1.32	0.87
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.10	0.09	0.09	1.41	1.44	0.84

Table S33: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.32	0.29	0.22	5.73	5.67	2.54
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.52	0.43	0.28	5.49	4.19	2.81
PBE0/pcSseg-3	$\text{CDCl}_3$	0.43	0.32	0.24	5.35	4.82	2.80
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.63	0.40	0.33	6.68	5.92	2.98

Table S34: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	31.363	31.068	31.276	181.63	183.89	181.95
		-0.999	-0.993	-0.992	-0.999	-0.997	-0.996
PBEP86/cc-pVTZ	$\text{CCl}_4$	31.545	31.239	31.434	189.70	187.98	190.72
		-1.042	-1.004	-0.984	-0.995	-0.983	-1.024
PBE0/pcSseg-3	$\text{CDCl}_3$	31.396	31.210	31.274	181.29	178.10	181.83
		-1.062	-1.040	-1.001	-1.063	-1.041	-1.073
PBEP86/cc-pVTZ	$\text{CDCl}_3$	31.577	31.379	31.429	189.37	182.66	190.60
		-1.034	-1.010	-0.960	-0.984	-0.939	-1.010

Table S35: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.27	0.41	0.09	10.4	13.0	5.42
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.18	0.22	0.12	2.99	2.84	3.14
PBE0/pcSseg-3	$\text{CDCl}_3$	0.23	0.32	0.11	9.46	11.8	4.99
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.17	0.15	0.17	2.79	2.82	2.77

Table S36: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.21	0.29	0.07	9.43	16.5	5.08
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.14	0.15	0.09	2.72	3.27	2.96
PBE0/pcSseg-3	$\text{CDCl}_3$	0.18	0.22	0.09	8.63	15.1	4.68
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.13	0.10	0.13	2.50	3.21	2.57

Table S37: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.71	0.71	0.23	20.8	20.8	8.57
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.57	0.39	0.34	6.36	6.36	5.02
PBE0/pcSseg-3	$\text{CDCl}_3$	0.66	0.66	0.27	17.0	17.0	8.06
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.73	0.32	0.41	6.71	6.71	4.51

Table S38: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.36/0.42	0.53/0.14	0.15/0.53	5.46/4.82	7.04/3.20	2.24/6.47
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.24/0.39	0.34/0.23	0.12/0.47	2.41/1.36	2.60/1.41	1.99/1.14
PBE0/pcSseg-3	$\text{CDCl}_3$	0.30/0.39	0.44/0.17	0.12/0.49	4.74/4.51	6.10/2.19	2.12/6.48
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.19/0.37	0.23/0.23	0.12/0.43	3.20/2.10	3.77/2.54	2.02/1.13

Table S39: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.29/0.36	0.52/0.14	0.12/0.52	4.42/3.89	6.43/2.30	1.82/6.19
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.19/0.35	0.32/0.20	0.10/0.46	2.06/1.02	2.29/1.03	1.71/0.94
PBE0/pcSseg-3	$\text{CDCl}_3$	0.23/0.34	0.43/0.14	0.09/0.48	3.95/3.62	5.73/1.72	1.72/6.25
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.16/0.33	0.23/0.20	0.10/0.41	2.50/1.40	2.99/1.68	1.74/0.94

Table S40: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively.

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.84/0.81	0.84/0.44	0.36/0.71	14.5/10.6	14.5/9.55	5.57/10.6
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.52/0.95	0.52/0.63	0.31/0.72	7.36/5.19	5.53/3.86	3.97/2.53
PBE0/pcSseg-3	$\text{CDCl}_3$	0.79/0.88	0.79/0.42	0.31/0.69	11.1/10.5	11.1/6.12	5.48/10.5
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.60/1.02	0.43/0.61	0.28/0.70	11.0/8.87	11.0/8.87	4.41/2.36



**Comparison of experimental data to shielding calculations using CPCM and geometries reoptimized with the corresponding implicit solvent with PBE0/pcSseg-3 and PBEP86/cc-pVTZ (cross-validation)**

Table S41: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.09	0.08	0.07	2.12	1.92	1.11
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.11	0.11	0.07	1.44	1.20	0.98
PBE0/pcSseg-3	$\text{CDCl}_3$	0.09	0.09	0.07	1.93	1.93	1.11
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.11	0.13	0.07	1.29	1.23	0.95

Table S42: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.07	0.07	0.06	1.61	1.22	0.91
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.08	0.08	0.06	1.14	0.85	0.78
PBE0/pcSseg-3	$\text{CDCl}_3$	0.07	0.08	0.06	1.46	1.26	0.90
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.08	0.06	0.10	1.01	1.23	0.77

Table S43: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.26	0.19	0.17	10.4	9.86	2.48
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.42	0.32	0.19	4.62	4.54	2.91
PBE0/pcSseg-3	$\text{CDCl}_3$	0.28	0.25	0.18	10.0	9.64	2.48
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.41	0.33	0.18	3.86	3.87	2.59

Table S44: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $sp^2$  carbons ( $sp^2$ ) and for only  $sp^3$  carbons ( $sp^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$sp^2$	$sp^3$	all	$sp^2$	$sp^3$
PBE0/pcSseg-3	$\text{CCl}_4$	31.292	30.787	31.249	182.66	192.04	182.64
		-1.081	-1.015	-1.052	-1.095	-1.158	-1.109
PBEP86/cc-pVTZ	$\text{CCl}_4$	31.482	30.981	31.410	190.71	195.55	191.36
		-1.053	-0.986	-1.011	-1.014	-1.046	-1.042
PBE0/pcSseg-3	$\text{CDCl}_3$	31.293	30.817	31.237	182.75	189.10	182.83
		-1.077	-1.015	-1.042	-1.091	-1.132	-1.103
PBEP86/cc-pVTZ	$\text{CDCl}_3$	31.486	31.023	31.399	190.81	192.92	191.52
		-1.049	-0.989	-1.000	-1.010	-1.023	-1.035

Table S45: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.34	0.51	0.10	12.3	15.3	6.07
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.22	0.32	0.08	4.22	4.53	3.63
PBE0/pcSseg-3	$\text{CDCl}_3$	0.32	0.48	0.09	12.0	14.9	5.97
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.20	0.29	0.08	3.91	4.12	3.47

Table S46: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.26	0.38	0.09	10.8	18.9	5.63
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.16	0.22	0.06	3.89	5.42	3.41
PBE0/pcSseg-3	$\text{CDCl}_3$	0.24	0.35	0.07	10.6	18.6	6.56
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.15	0.20	0.07	3.65	5.01	3.27

Table S47: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.71	0.71	0.25	27.7	27.7	9.70
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.55	0.55	0.21	9.33	9.33	6.13
PBE0/pcSseg-3	$\text{CDCl}_3$	0.72	0.72	0.23	26.8	26.8	9.27
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.55	0.55	0.20	8.10	8.10	5.21

Table S48: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.46/0.51	0.65/0.20	0.21/0.65	7.12/5.96	9.18/5.29	2.49/6.89
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.32/0.48	0.46/0.28	0.15/0.58	2.02/1.75	1.94/1.94	2.06/1.25
PBE0/pcSseg-3	$\text{CDCl}_3$	0.43/0.52	0.63/0.23	0.20/0.65	6.88/5.75	8.84/4.74	2.40/6.98
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.30/0.49	0.43/0.31	0.14/0.59	1.89/1.44	1.74/1.51	2.00/1.16

Table S49: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.39/0.44	0.65/0.18	0.19/0.64	5.42/4.73	7.89/3.45	2.03/6.51
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.26/0.44	0.45/0.26	0.13/0.57	1.71/1.27	1.69/1.34	1.71/1.02
PBE0/pcSseg-3	$\text{CDCl}_3$	0.37/0.46	0.62/0.21	0.18/0.65	5.32/4.62	7.76/3.17	1.96/6.63
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.24/0.46	0.42/0.28	0.12/0.58	1.59/1.08	1.52/1.06	1.65/0.97

Table S50: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries reoptimized using CPCM from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.86/0.83	0.86/0.37	0.40/0.83	21.0/15.5	21.0/15.5	5.84/11.3
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.70/0.76	0.70/0.57	0.32/0.76	5.41/6.02	4.29/6.02	4.76/3.04
PBE0/pcSseg-3	$\text{CDCl}_3$	0.86/0.83	0.86/0.36	0.38/0.83	20.2/14.6	20.2/14.6	5.77/11.4
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.70/0.75	0.70/0.63	0.30/0.75	5.28/4.76	4.14/4.76	4.23/2.67

**Comparison of experimental data to shielding calculations using CPCM and geometries optimized in vacuum with with PBE0/pcSseg-3 and PBEP86/cc-pVTZ (cross-validation)**

Table S51: RMSD (ppm) of the  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only the  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.09	0.08	0.07	1.92	1.79	1.11
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.11	0.12	0.07	1.31	1.20	0.87
PBE0/pcSseg-3	$\text{CDCl}_3$	0.09	0.10	0.07	1.79	1.83	1.16
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.11	0.13	0.08	1.26	1.29	0.89

Table S52: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.07	0.07	0.06	1.47	1.19	0.90
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.08	0.08	0.06	1.03	0.88	0.71
PBE0/pcSseg-3	$\text{CDCl}_3$	0.07	0.08	0.06	1.38	1.25	0.95
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.09	0.10	0.06	0.98	0.98	0.73

Table S53: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent using the structures optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.24	0.19	0.17	9.04	8.70	2.57
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.39	0.33	0.20	3.66	3.44	1.89
PBE0/pcSseg-3	$\text{CDCl}_3$	0.26	0.23	0.17	8.56	8.37	2.84
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.40	0.33	0.21	3.58	3.68	1.84

Table S54: Intercept (ppm) and slope of the linear regression of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent using the structures optimized in vacuum versus the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	31.302	30.833	31.255	182.46	189.84	182.60
		-1.080	-1.050	-1.019	-1.090	-1.105	-1.139
PBEP86/cc-pVTZ	$\text{CCl}_4$	31.491	31.033	31.417	190.53	193.56	191.32
		-1.052	-0.993	-1.010	-1.009	-1.029	-1.039
PBE0/pcSseg-3	$\text{CDCl}_3$	31.303	30.867	31.243	182.55	186.99	182.78
		-1.076	-1.020	-1.040	-1.086	-1.114	-1.098
PBEP86/cc-pVTZ	$\text{CDCl}_3$	31.496	31.079	31.405	190.62	190.97	191.47
		-1.048	-0.995	-0.999	-1.005	-1.006	-1.031

Table S55: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.34	0.51	0.10	12.0	14.9	6.10
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.22	0.32	0.06	4.03	4.19	3.64
PBE0/pcSseg-3	$\text{CDCl}_3$	0.32	0.48	0.09	11.7	14.5	6.01
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.20	0.29	0.08	3.76	3.84	3.48

Table S56: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.26	0.38	0.08	10.7	18.5	5.69
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.16	0.22	0.06	3.77	5.09	3.46
PBE0/pcSseg-3	$\text{CDCl}_3$	0.24	0.35	0.08	10.51	18.2	5.61
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.15	0.20	0.07	3.53	4.68	3.32

Table S57: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (1) instead of Eq. (3). Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvent	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.72	0.72	0.27	26.2	26.2	9.53
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.55	0.55	0.20	7.89	7.89	5.47
PBE0/pcSseg-3	$\text{CDCl}_3$	0.72	0.72	0.25	25.1	25.1	9.80
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.54	0.54	0.24	7.46	7.46	5.19

Table S58: RMSD (ppm) between  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum and experimental values in  $\text{CDCl}_3$  or  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.44/0.50	0.64/0.20	0.20/0.44	6.70/5.62	8.59/4.73	2.45/6.74
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.31/0.47	0.45/0.28	0.15/0.57	1.95/1.52	1.87/1.60	2.00/1.15
PBE0/pcSseg-3	$\text{CDCl}_3$	0.42/0.51	0.61/0.23	0.19/0.65	6.47/5.44	8.27/4.20	2.38/6.83
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.29/0.49	0.42/0.31	0.13/0.58	1.94/1.32	1.89/1.32	1.96/1.06

Table S59: MAD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.37/0.44	0.63/0.18	0.18/0.63	5.19/4.50	7.51/3.13	2.00/6.37
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.26/0.43	0.43/0.25	0.13/0.56	1.68/1.10	1.67/1.11	1.66/0.94
PBE0/pcSseg-3	$\text{CDCl}_3$	0.35/0.46	0.60/0.21	0.17/0.64	5.10/4.39	7.38/2.86	1.95/6.49
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.24/0.45	0.40/0.28	0.11/0.58	1.66/1.00	1.67/0.98	1.66/0.88

Table S60: Max. AD (ppm) of  $^1\text{H}$  and  $^{13}\text{C}$  shifts calculated in the corresponding implicit solvent with geometries optimized in vacuum from the experimental values in  $\text{CDCl}_3$  and  $\text{CCl}_4$ . But conversion to chemical shifts was done using Eq. (2) instead of Eq. (3). Two variants are given for each entry: conversion based on shifts of bridgehead CH of adamantane (left) or the innermost CH pairs of anthracene, respectively. Values are given for the complete carbon set (all), for only  $\text{sp}^2$  carbons ( $\text{sp}^2$ ) and for only  $\text{sp}^3$  carbons ( $\text{sp}^3$ ).

DFT Method	Exp. Solvt.	$^1\text{H}$			$^{13}\text{C}$		
		all	$\text{sp}^2$	$\text{sp}^3$	all	$\text{sp}^2$	$\text{sp}^3$
PBE0/pcSseg-3	$\text{CCl}_4$	0.85/0.83	0.85/0.38	0.40/0.83	19.4/14.1	19.4/14.1	5.67/11.0
PBEP86/cc-pVTZ	$\text{CCl}_4$	0.69/0.76	0.69/0.58	0.32/0.76	5.25/4.65	4.22/4.65	4.23/2.36
PBE0/pcSseg-3	$\text{CDCl}_3$	0.86/0.81	0.86/0.41	0.38/0.81	18.5/13.0	18.5/13.0	5.60/11.0
PBEP86/cc-pVTZ	$\text{CDCl}_3$	0.68/0.78	0.68/0.62	0.30/0.78	5.12/4.20	4.23/4.20	4.08/2.37

**Residual plots of experimental shifts and calculated shifts in vacuum using Eq. (3) with  $m = -1$  for conversion**

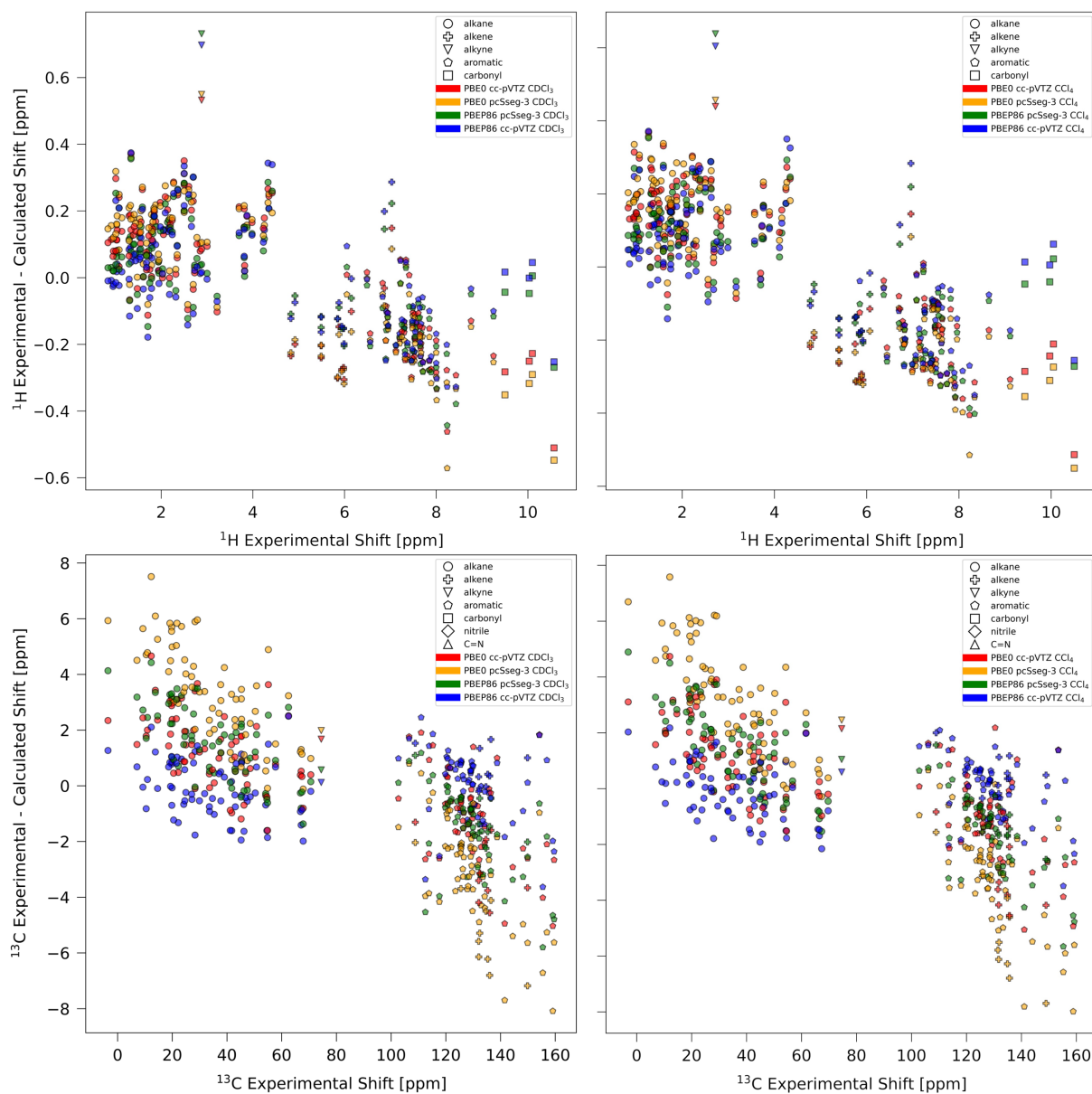


Figure S7: Residual plots between experimental and calculated chemical shifts in vacuum using Eq. (3) with  $m = -1$  for conversion. Top  $^1\text{H}$ . Bottom  $^{13}\text{C}$ .

**Residual plots of experimental shifts and calculated shifts in implicit solvent using Eq. (3) with  $m = -1$  for conversion**

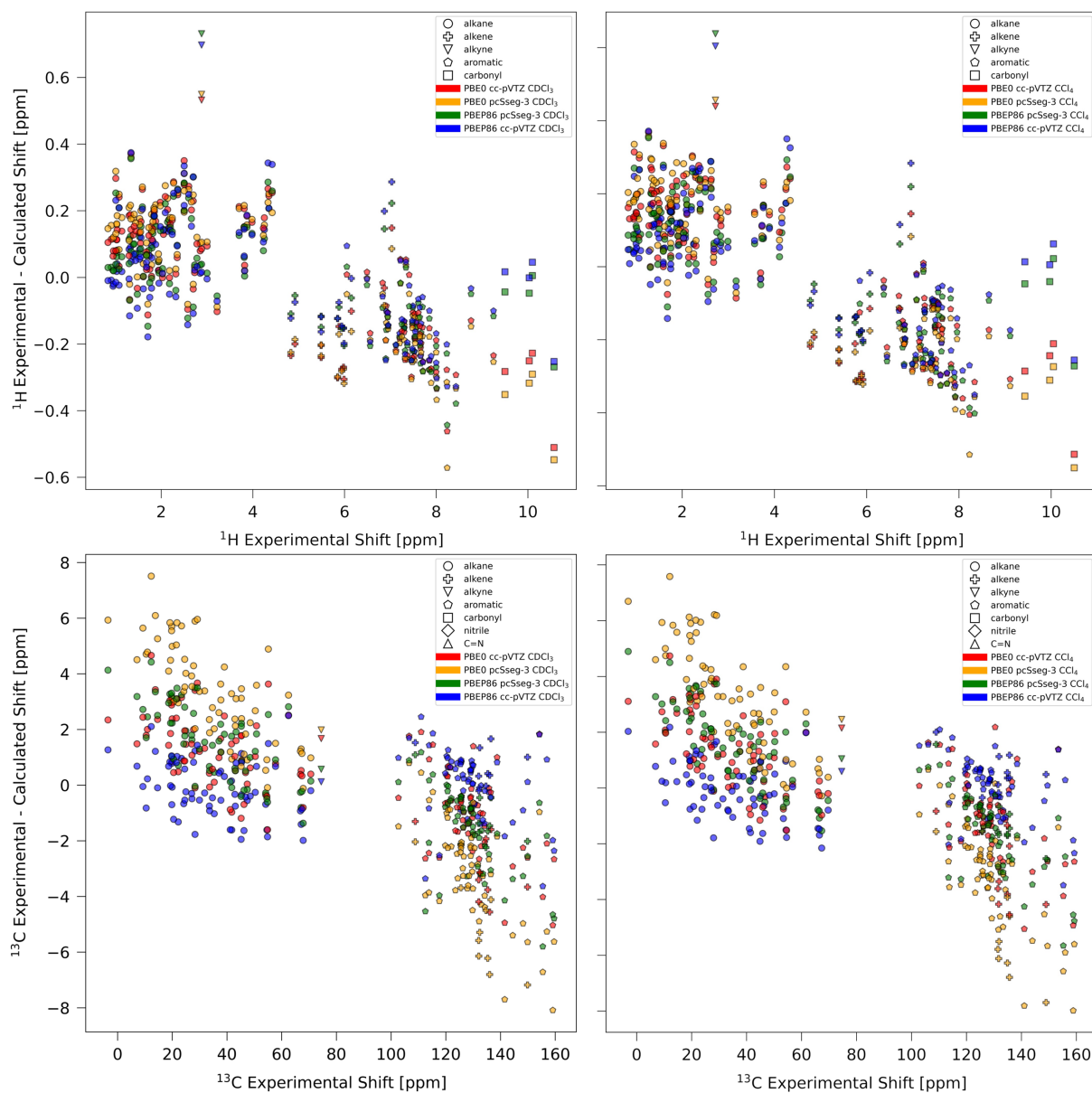


Figure S8: Residual plots between experimental and calculated chemical shifts in implicit solvent using Eq. (3) with  $m = -1$  for conversion. Top  $^1\text{H}$ . Bottom  $^{13}\text{C}$ .



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