Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Nuclear spin-induced optical rotation of functional groups in hydrocarbons

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Supplementary Information

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1 List of molecules

Tables below list the molecules included in the study. The test cases of the contribution model are not included.

Table S 1: Alkane molecules

methane	2-methyl-propane	2,3-dimethyl-butane
ethane	2-methyl-butane	2,2-dimethyl-propane
propane	2-methyl-pentane	2,2-dimethyl-pentane
butane	3-methyl-pentane	2,3-dimethyl-pentane
pentane	2,2-dimethyl-butane	3,3-dimethyl-pentane
hexane		

Table S 2: Alkene molecules

ethene	2,3,3-trimethyl-butene	5-methyl-heptene
propene	2,4-dimethyl-pentene	6-methyl-heptene
trans-but-2-ene	2-methyl-hexene	cis-5,5-dimethyl-hex-2-ene
cis-pent-2-ene	3,3-dimethyl-pentene	cis-6-methyl-hept-2-ene
trans-hex-2-ene	3,4-dimethyl-pentene	trans-5,5-dimethyl-hex-2-ene
trans-pent-2-ene	3-methyl-hexene	trans-6-methyl-hept-2-ene
trans-hex-3-ene	4-methyl-hexene	5,6-dimethyl-heptene
2-methyl-propene	cis-4,4-dimethyl-pent-2-ene	cis-6,6-dimethyl-hepte-2-ene
2-methyl-butene	cis-5-methyl-hex-2-ene	cis-7-methyl-oct-2-ene
2-methyl-pentene	cis-hept-2-ene	trans-6,6-dimethyl-hepte-2-ene
2-methyl-but-2-ene	heptene	trans-7-methyl-oct-2-ene
2-methyl-pent-2-ene	trans-4,4-dimethyl-pent-2-ene	5,6,6-trimethyl-heptene
butene	trans-5-methyl-hex-2-ene	6,6-dimethyl-heptene
3-methyl-butene	trans-hept-2-ene	cis-6-methyl-oct-2-ene
3-methyl-pentene	2-methyl-hex-2-ene	trans-6-methyl-oct-2-ene
3-methyl-pent-2-ene	2,3-dimethyl-pent-2-ene	7-methyl-octene
3,3-dimethyl-butene	4,4-dimethyl-pentene	cis-7,7-dimethyl-oct-2-ene
2,3-dimethyl-butene	5-methyl-hexene	trans-7,7-dimethyl-oct-2-ene
2,3-dimethyl-but-2-ene	cis-2-methyl-hex-3-ene	nonene
pentene	cis-3-methyl-hex-3-ene	2,5,5-trimethyl-hexene
4-methyl-pentene	cis-3,4-dimethyl-pent-2-ene	3,4,4-trimethyl-pentene
trans-4-methyl-pent-2-ene	cis-4-methyl-hex-2-ene	4,4,5-trimethyl-hexene
2-ethyl-butene	trans-2-methyl-hex-3-ene	4,6-dimethyl-heptene
hexene	trans-3-methyl-hex-3-ene	5,5,6,6-tetramethyl-heptene
cis-hex-3-ene	trans-3,4-dimethyl-pent-2-ene	cis-4,5,5-trimethyl-hex-2-ene
cis-3-methyl-pent-2-ene	trans-4-methyl-hex-2-ene	cis-4,7,7-trimethyl-octa-2-ene
cis-4-methyl-pent-2-ene	4,4-dimethyl-hexene	trans-4,5,5-trimethyl-hex-2-ene
cis-hex-2-ene	4,5-dimethyl-hexene	trans-4,7,7-trimethyl-oct-2-ene
cis-but-2-ene	5,5-dimethyl-hexene	octene

Table S 3: Alkyne molecules

5,6,6-trimethyl-heptyne	4-methyl-pentyne	hept-2-yne
6,6-dimethyl-heptyne	4-methyl-pent-2-yne	heptyne
6-methyl-oct-2-yne	but-2-yne	4,4-dimethyl-pentyne
7,7-dimethyl-oct-2-yne	butyne	5-methyl-hexyne
7-methyl-octyne	ethyne	2,2,7-trimethyl-oct-4-yne
nonyne	hex-2-yne	3,3,4-trimethyl-pentyne
5,6-dimethyl-heptyne	hex-3-yne	3,5,5-trimethyl-hexyne
6,6-dimethyl-hept-2-yne	hexyne	3,6,6-trimethyl-heptyne
7-methyl-oct-2-yne	pent-2-yne	4,4,5,5-tetramethyl-hexyne
5,5-dimethyl-hex-2-yne	pentyne	4,4,5-trimethyl-hexyne
4,4-dimethyl-hexyne	propyne	4,5,5-trimethyl-hex-2-yne
4,5-dimethyl-hexyne	3-methyl-but-1-yne	4,5,5-trimethyl-hexyne
5,5-dimethyl-hexyne	3,3-dimethyl-pentyne	4,6,6-trimethyl-heptyne
5-methyl-heptyne	3,4-dimethyl-pentyne	5,5,6-trimethyl-heptyne
6-methyl-hept-2-yne	3-methyl-hexyne	octyne
6-methyl-heptyne	4,4-dimethyl-pent-2-yne	4-methyl-hex-2-yne
3-dimethyl-butyne	4-methyl-hexyne	3-methyl-hex-3-yne
3-methyl-pentyne		

Table S 4: Isolated dienes

penta-1,4-diene	cis-3-methyl-hexa-1,4-diene	3,3-dimethyl-hexa-1,5-diene
hexa-1,5-diene	cis-4-methyl-hexa-1,4-diene	3-(tert-butyl)-penta-1,4-diene
2-methyl-penta-1,4-diene	trans-3-methyl-hexa-1,4-diene	3-isopropyl-penta-1,4-diene
3-methyl-penta-1,4-diene	trans-4-methyl-hex-1,4-diene	3-methyl-hepta-1,6-diene
cis-hexa-1,4-diene	5-methyl-hexa-1,4-diene	3-methyl-hexa-1,5-diene
trans-hexa-1,4-diene	3,3,4-trimethyl-hepta-1,6-diene	4,4,5-trimethyl-octa-1,7-diene
2,3-dimethyl-penta-1,4-diene	3,3,4-trimethyl-hexa-1,5-diene	4,4-dimethyl-octa-1,7-diene
2,4-dimethyl-penta-1,4-diene	3,3,5-trimethyl-hepta-1,6-diene	4-methyl-hepta-1,6-diene
2-ethyl-penta-1,4-diene	3,3-dimethyl-hepta-1,6-diene	3,3,4,4-tetramethyl-hepta-1,6-diene
3-ethyl-penta-1,4-diene	trans-3,3-dimethyl-hexa-1,4-diene	cis-3,3-dimethyl-hexa-1,4-diene
3-methyl-3-(tert-butyl)-penta-1,4-diene	3-ethyl-3-methyl-penta-1,4-diene	3-isopropyl-3-methyl-penta-1,4-diene
3,3-dimethyl-hexa-1,4-diene	2,3,3-trimethyl-penta-1,4-diene	

Table S 5: Conjugated dienes

2-methyl-but-1,3-diene	trans-4-methyl-penta-1,3-diene	4-methyl-hexa-1,3-diene
butadiene	trans-hexa-1,3-diene	5-methyl-hepta-1,3-diene
cis-2-methyl-penta-1,3-diene	trans-pent-1,3-diene	6,6,7-trimethyl-octa-2,4-diene
cis-3-methyl-penta-1,3-diene	trans,trans-hexa-2,4-diene	6-methyl-octa-2,4-diene
cis-hexa-1,3-diene	2,6,6,7-tetramethyl-octa-2,4-diene	nona-2,4-diene
cis-pent-1,3-diene	4,5,5,6-tetramethyl-octa-1,3-diene	octa-1,3-diene
cis,cis-hexa-2,4-diene	4,5,6,6-tetramethyl-hepta-1,3-diene	2,3-dimethyl-buta-1,3-diene
cis,trans-hexa-2,4-diene	4,6,6-trimethyl-hepta-1,3-diene	2-ethyl-buta-1,3-diene
trans-2-methyl-penta-1,3-diene	4,6-dimethyl-hepta-1,3-diene	2,3-dimethyl-hexa-1,3-diene
trans-3-methyl-penta-1,3-diene		

Table S 6: Cumulated dienes

2-methyl-penta-2,3-diene	4-methyl-hexa-1,2-diene	5,5-dimethyl-hex-2,3-diene
3-methyl-buta-1,2-diene	4-methyl-hexa-2,3-diene	5-methyl-5-ethyl-hepta-2,3-diene
3-methyl-penta-1,2-diene	5-methyl-hexa-1,2-diene	5,6,6-trimethyl-hepta-2,3-diene
4-methyl-penta-1,2-diene	5-methyl-hexa-2,3-diene	6,6-dimethyl-hepta-2,3-diene
buta-1,2-diene	hepta-1,2-diene	4,6,6-trimethyl-octa-1,2-diene
hexa-2,3-diene	hepta-2,3-diene	4,6-dimethyl-octa-1,2-diene
hexa-1,2-diene	4-methyl-4-ethyl-hepta-1,2-diene	4,7,7-trimethyl-octa-2,3-diene
penta-2,3-diene	2,5,5-trimethyl-hexa-2,3-diene	4,7-dimethyl-octa-2,3-diene
penta-1,2-diene	4,5,5-trimethyl-hepta-12-diene	6,6-dimethyl-octa-1,2-diene
propdiene	4,4,5-trimethyl-hepta-1,2-diene	6-methyl-octa-1,2-diene
2-methyl-hexa-2,3-diene	4,5-dimethyl-hepta-1,2-diene	7,7-dimethyl-octa-2,3-diene
3,4-dimethyl-penta-1,2-diene	4,5-dimethyl-5-ethyl-hepta-1,2-diene	7-methyl-octa-2,3-diene
3-methyl-hexa-1,2-diene	5,5,6-trimethyl-hepta-2,3-diene	

2 Basis set benchmark

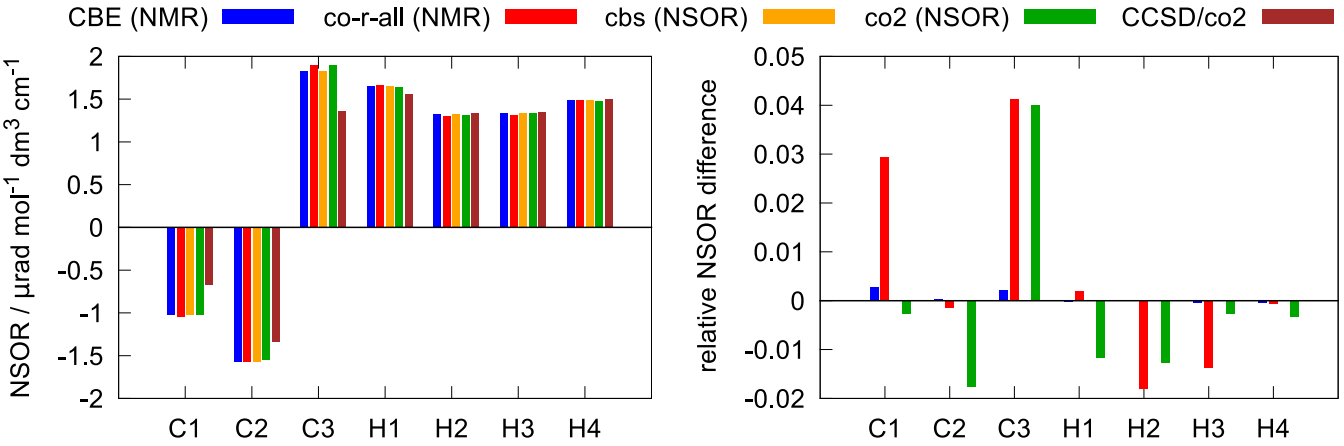

Figure S 1: Comparison of performance of basis set co2[1] ([5s,4p] [12s,7p,3d]) used in the study with larger basis sets co-r-all[2] (H[11s,3p,3d]/C[18s,10p,6d,2f]), cbs[1] (H[10s,7p,6d]/C[16s,15p,7d,4f]) and CBE[2] (H[19s,7p,4d]/C[25s,13p,13d,6f]) for propene using BHandHLYP densityt functional. CBE and co-r-all basis sets were designed for NMR while co2 and cbs for NSOR. CCSD calculation with co2 basis set is included for comparison. The relative errors are with respect to the cbs basis set.

3 Effect of *cis*/*trans* isomerism on ^{1}H NSOR of T_1 atom type in alkenes

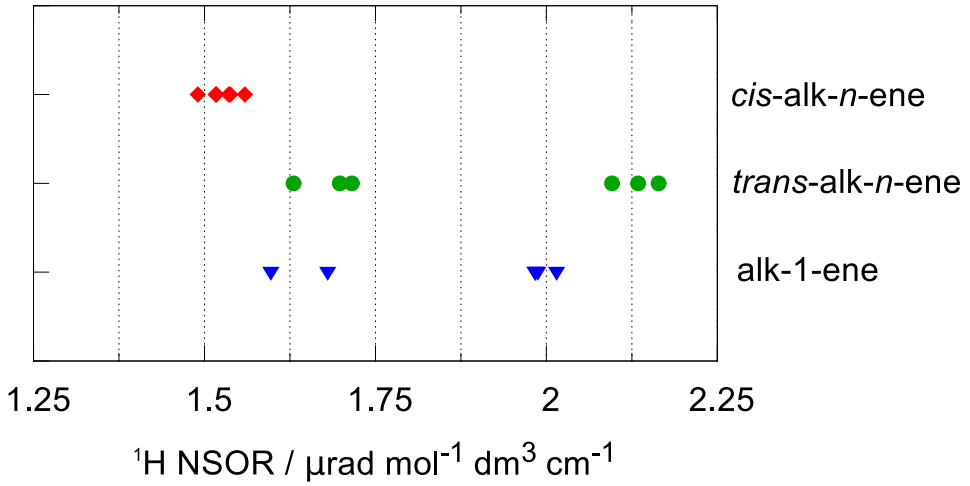

Figure S 2: Effect of *cis*/*trans* isomerism on ^{1}H NSOR for atom type $\mathbf{T}_1$ in alkenes. The NSOR values in *cis*- alkenes are lower than NSOR of either *trans*-alkenes or alk-1-enes.

4 Effect of conformation on NSOR

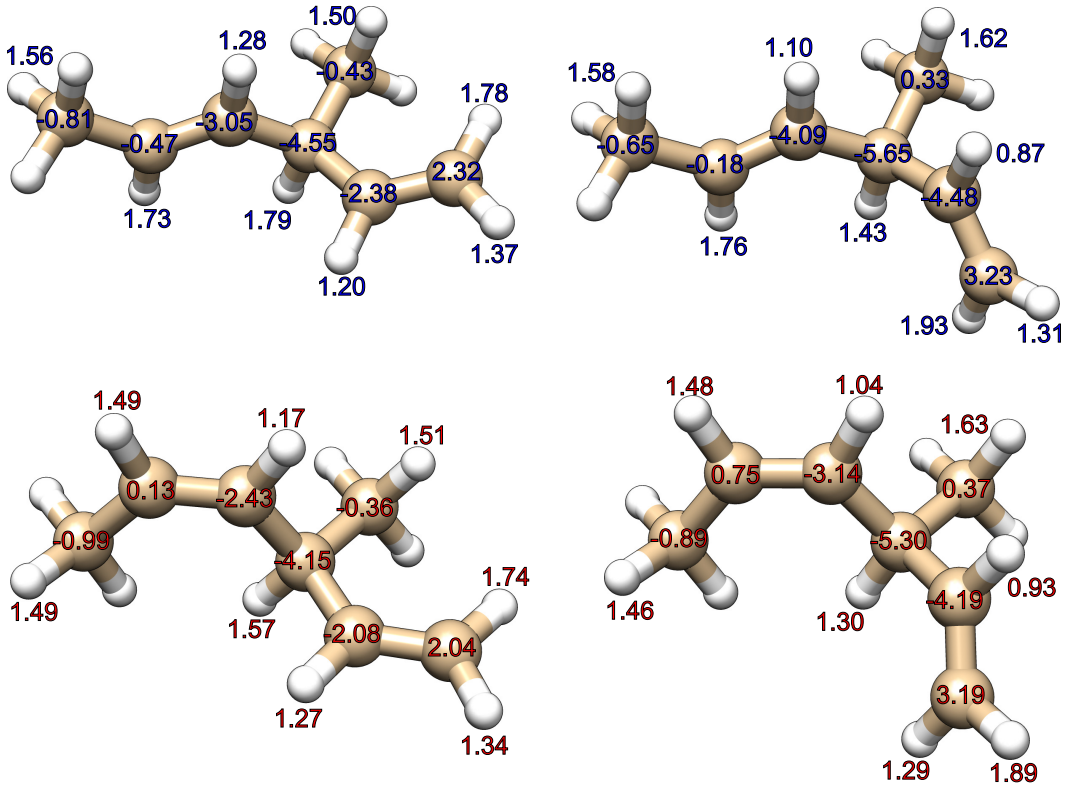

Figure S 3: Effect of conformation on NSOR of *trans*- (top) and *cis*- (bottom) 3-methyl-hexa-1,4-diene. Each structure represents a local energy minimum.

5 Extended Figure for NSOR of dienes

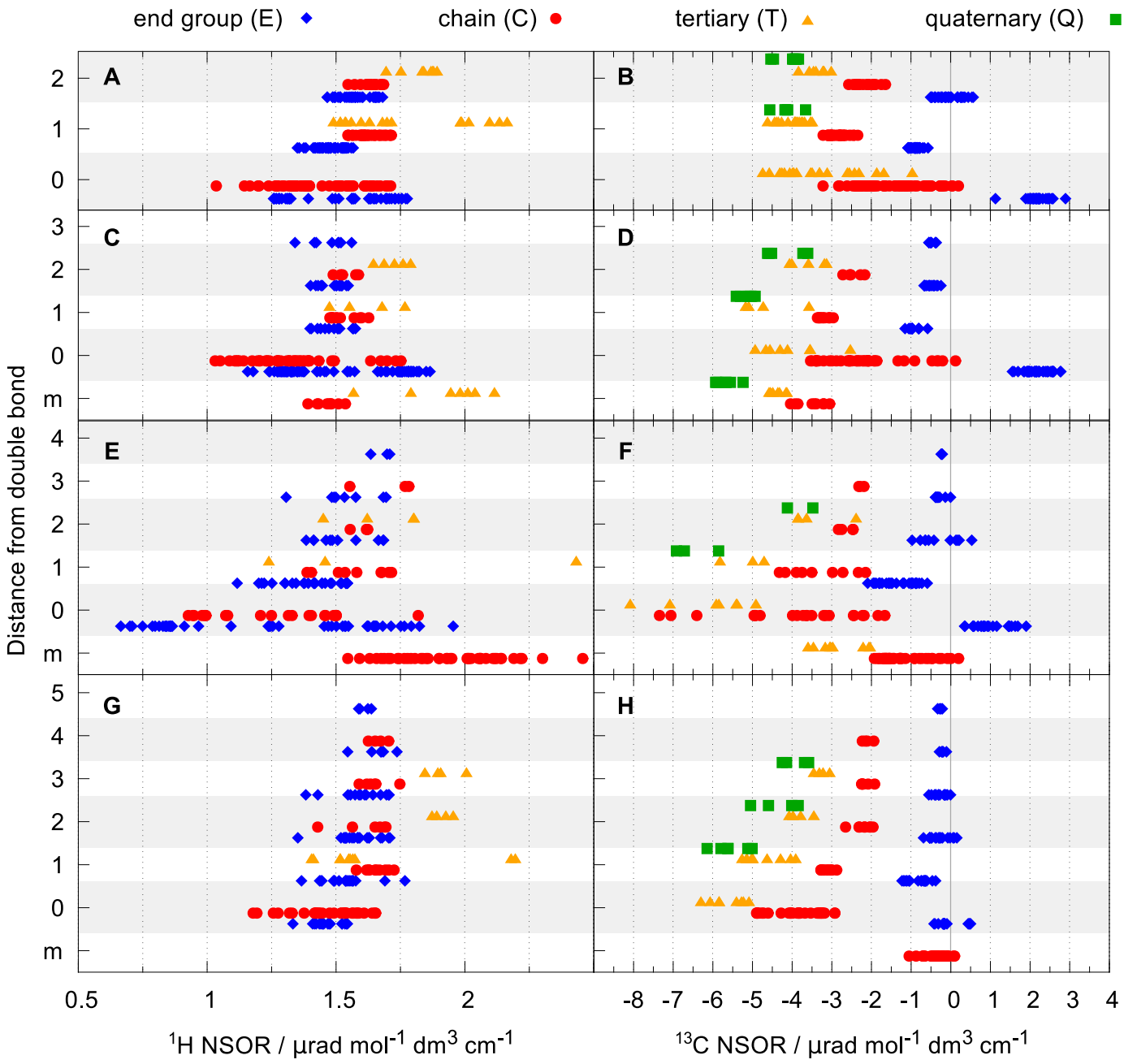

Figure S 4: Figure 5 from the main text extended with data points for nuclei further from the unsaturated bond. Comparison of ^{1}H (left) and ^{13}C (right) NSOR signals for alkenes (top row, panels A and B), isolated dienes (second row, panels C and D), conjugated dienes (third row, panels E and F) and cumulated dienes (bottom row, panels G and H). The different distances are alternatively shaded for easier readability. Signals labelled *m* correspond to atoms between two double bonds (see Methods section for details). The chart distinguishes atoms corresponding to the end of chain (blue diamonds), atoms in a chain bonded to two carbon atoms (red circles), carbons with three carbon neighbours (orange triangles) and quaternary carbons (green squares).

6 Effect of *cis*/*trans* isomerism in dienes

The comparison of effects of *cis*/*trans* isomerism in NSOR of isolated and conjugated dienes for ^{1}H are shown in Fig. S5, where the same convention for labeling the nuclei has been used as in the case of alkenes in the main text. The ^{13}C is not discussed here as it does not appear to be significantly differentiated.

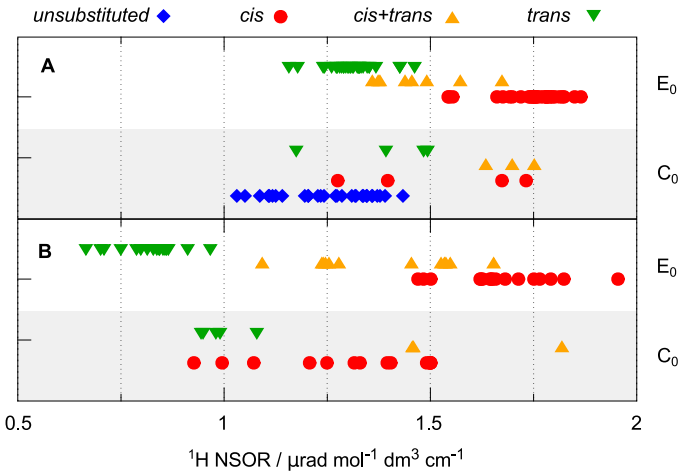

Figure S 5: Comparison of effect of *cis*/*trans* isomerism on ^{1}H NSOR signals in isolated dienes (top panel A) and in conjugated dienes (bottom panel B). On the x-axis is the normalized optical rotation, the y-axis distinguishes positions of the atoms around the double bond. Nuclei of atoms inside the chain (**C**) and at the end of the chain (**E**) are plotted separately.

7 Supporting data for solvent and geometry effects

Table S 7: Molecules used for testing the effect of implicit solvent in NSOR response calculation (left column) and of including dispersion correction in the geometry optimization (right column)

Solvent effect in response calculation (IEF-PCM)	Optimization with DFT-D3
2,2-dimethyl-butane	2,5,5-trimethyl-hexa-2,3-diene
2,3-dimethyl-pentane	4,6,6-trimethyl-hepta-1,3-diene
2-ethyl-butene	2,3,3-trimethyl-butene
2,3-dimethyl-but-2-ene	2-ethyl-penta-1,4-diene
3,4-dimethyl-pentyne	2-ethyl-buta-1,3-diene
4-methyl-pent-2-yne	3-isopropyl-penta-1,4-diene
2-ethyl-penta-1,4-diene	3-tert-butyl-penta-1,4-diene
5-methyl-hexa-1,4-diene	4,5-dimethyl-5-ethyl-hepta-1,2-diene
2-ethyl-buta-1,3-diene	
trans,trans-hexa-2,4-diene	
3,4-dimethyl-penta-1,2-diene	
2-methyl-penta-2,3-diene	

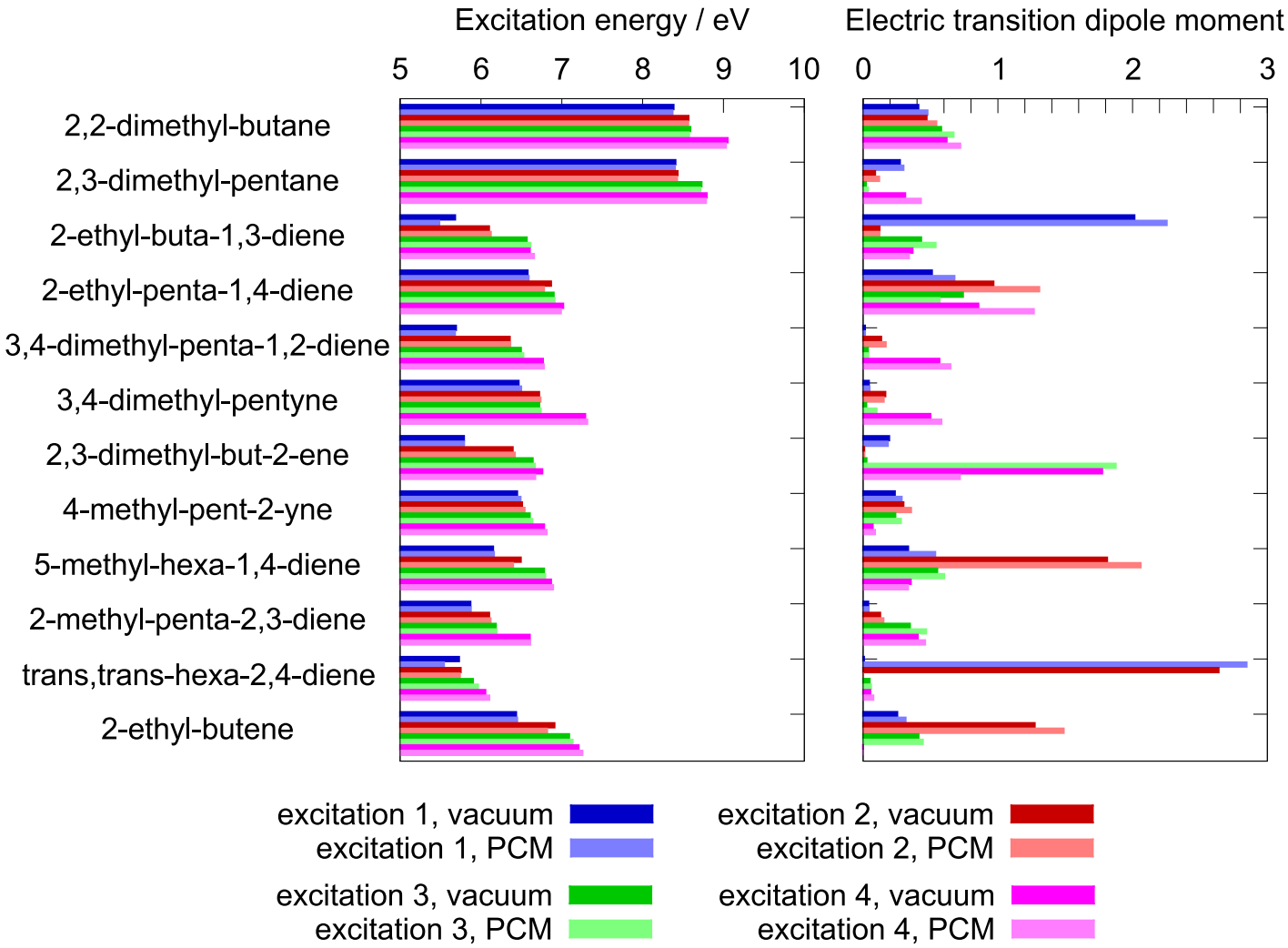

Figure S 6: Comparison of excitation energies (left) and electric transition dipole moments (right) for first four excited states for the twelve selected molecules, calculated in vacuum and with PCM. The values were calculated with identical geometries using BHandHLYP/co2 for both vacuum and PCM case.

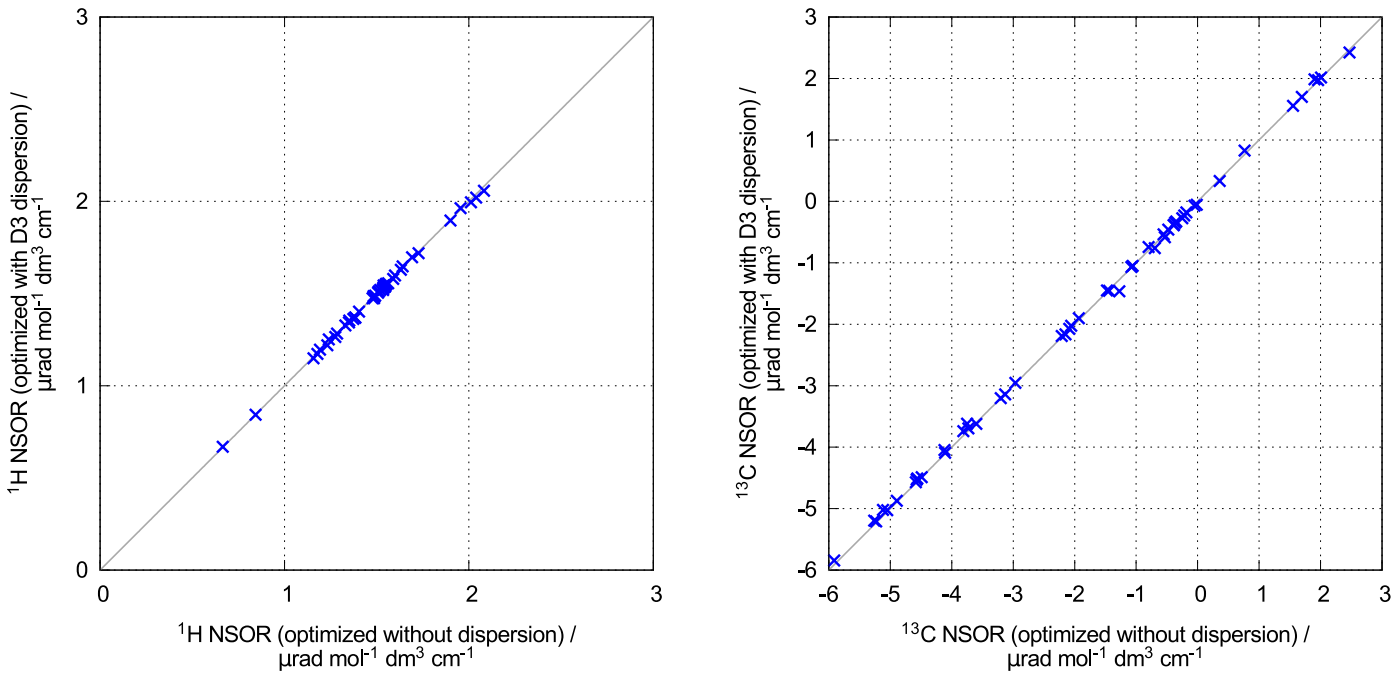

Figure S 7: Effect of geometry on ^{1}H NSOR (left) and ^{13}C NSOR (right). On the x-axis is the NSOR calculated for structures optimized in vacuum (RI-B3LYP/def-TZVP), on the y-axis is the NSOR for structures optimized with addition of DFT-D3 dispersion correction.

References

[1] J. Vähäkangas, P. Lantto and J. Vaara, *Journal of Physical Chemistry C*, 2014, **118**, 23996–24005.

[2] J. Vähäkangas, S. Ikäläinen, P. Lantto and J. Vaara, *Physical Chemistry Chemical Physics*, 2013, **15**, 4634–4641.