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Supporting Information

Poly- γ -S-perillyl-L-glutamate and Poly- γ -S-perillyl-D-glutamate: Diastereomeric Alignment Media Used for the Investigation of the Alignment Process

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1. Gel permeation chromatography (GPC)

GPC measurements were performed using a PSS SDV THF analytical linear XL column and a PSS SDV 5 μm precolumn. The detector used was a RI-2031 plus from JASCO. The following JASCO devices were used additionally PU-2086 Plus (pump), AS-2055 Plus (sampler) and CO-2060 Plus (oven). The chromatography was done at 25 $^{\circ}\text{C}$ oven temperature and a flow rate of 1 ml/min. Tetrahydrofuran with 0.1 % w/w tetrabutylammonium bromide (TBAB) was used as eluent. The polymer samples were prepared at a concentration of 1 mg/ml in the eluent with 0.1 % w/w toluene as internal standard. Calibration was done using polystyrene standards. All samples were filtered prior to injection, using 0.45 μm PTFE syringe filters.

2. Circular dichroism spectroscopy (CD)

Circular dichroism spectroscopy was performed on a JASCO J-1500 spectrometer. The polymers were dissolved in 1,1,2,2-tetrachloroethane at a concentration of 1 % w/w. A 0.01 mm rectangular quartz glass cuvette in combination with a cell holder for cell type 106 (Hellma Analytics) was used for the measurements in TCE. Additionally, the polymers were dissolved and measured in THF at a concentration of 1 mg/ml. The measurements with THF were performed using a 1 mm rectangular quartz glass cuvette (Hellma Analytics). Ten spectra were recorded for each sample. The resulting curves were averaged and the resulting standard deviation is displayed as error bar. The molar ellipticity ($[\theta]$) was calculated from millidegrees (m°) using the expression $[\theta] = m^{\circ} \cdot M / (10 \cdot d \cdot c)$, where M is the molecular weight of the repeating unit, c is the concentration and d is the path length.

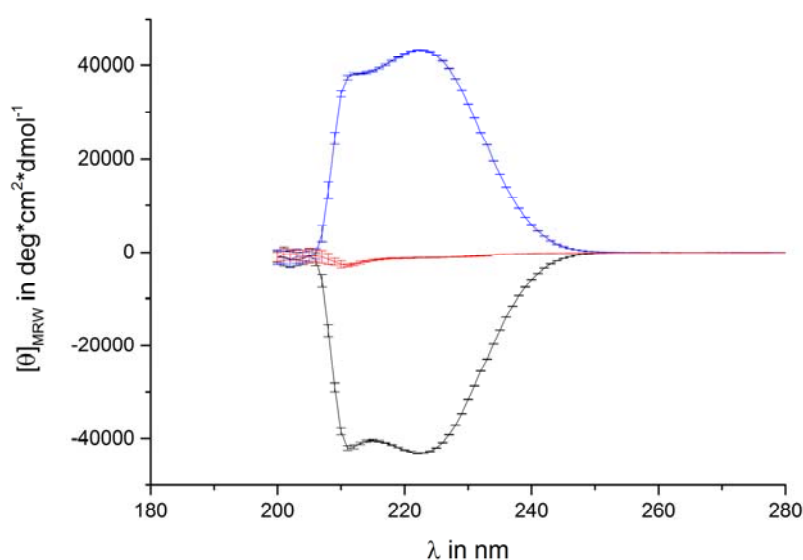


Figure 2.1: CD-spectra of poly- γ -S-perillyl-L-glutamate (black), poly- γ -S-perillyl-D-glutamate (blue) and a 1:1 mixture (red) of them in THF.

3. NMR sample preparation and general NMR information

The analytes (+)- and (-)- β -pinene and (+)- and (-)-IPC were purchased from Sigma Aldrich. (+)- and (-)- β -pinene and (-)-IPC were used as received. (+)-IPC was sublimated prior to use. CDCl_3 was purchased from Sigma Aldrich and distilled over CaH_2 before use.

The anisotropic NMR samples were prepared by weighing the polymers and the appropriate analytes directly into 5 mm NMR tubes. Additionally, the desired amount of solvent was added. Acetone- d_6 capillaries were added to each sample to provide an isotropic lock signal, which was also used for chemical shift referencing. The samples were centrifuged (800 rpm) and turned back and forth to ensure homogeneity. The homogeneity was additionally checked by ^2H -imaging^[1]. Quadrupolar splittings of the solvent signal were determined with ^2H -spectra. The compositions of the different samples used are given below. The β -pinene samples were used for measurements on different days and therefore refilled and homogenized to ensure the same concentration.

All measurements within RDC analysis were performed at 300 K on a 700 MHz spectrometer (Bruker AVANCE III HD with a QCI cryo probe ($^1\text{H}/^{19}\text{F}$ - $^{31}\text{P}/^{13}\text{C}/^{15}\text{N}/^2\text{H}$) with z-gradient and a BCU-II preconditioner).

The scalar coupling constants ($^1J_{\text{CH}}$) as well as the total coupling constants ($^1T_{\text{CH}}$) were extracted from CLIP-HSQC-spectra^[2]. These were recorded with 8192 data points in the direct dimension and 512 data points in the indirect dimension (NS=4, DS=32). The spectral width was set to 10.0 ppm (O2=2.0 ppm) in the direct dimension and 35.0 ppm (O1=32.5 ppm) in the indirect dimension. The INEPT delay was optimized for a coupling constant ($^1J_{\text{CH}}$) of 145 Hz. Zero filling was applied to 16384 data points in the direct dimension and to 1024 data points in the indirect dimension. Multiplication with a squared sine bell function (SSB=2) was done in both dimensions prior to Fourier transformation.

The scalar coupling constants ($^nJ_{\text{HH}}$) as well as the total coupling constants ($^nT_{\text{HH}}$) were extracted from non-pure shift 2D TSE-PSYCHEDELIC spectra^[3,4]. These were recorded with 8192 data points in the direct dimension and 128 or 256 data points (resulting in the same FID resolution of 0.78 Hz) in the indirect dimension (NS=16, DS=16). The spectral width was set to 8.5 ppm (O2=3 ppm) in the direct dimension and to 50 Hz or 100 Hz in the indirect dimension. Selective refocusing was done using *RSnob*^[5] 180° pulses with a duration of 58.3 ms (40Hz bandwidth). The selective offsets were set according to the desired protons (H1, H3a, H3s, H5, H7a and H10s). The bandwidth for the pulse shape used for selective refocusing was calculated with the Bruker Shape Tool of TopSpin 3.5 using the option "calculate bandwidth for refocusing -My". Zero filling was applied to 16384 data points in the direct dimension and to 256 or 512 data points in the indirect dimension. Exponential (LB=0.3 Hz) and Gaussian (LB=-1.5 Hz, GB=0.5) window functions were applied for the direct and indirect dimension, respectively. If the same couplings were accessible in different spectra the corresponding mean is given.

The signs of the scalar coupling constants ($^nJ_{\text{HH}}$) and the signs of the total coupling constants ($^nT_{\text{HH}}$) were determined with COSY based spectra^[4] and P.E.HSQMBC spectra^[6]. The results from the P.E.HSQMBC spectra were used as starting point for the relative results from the the COSY based spectra. P.E.HSQMBC spectra were recorded with 4096 data points in the direct dimension and 256 data points in the indirect dimension (NS=16 (isotropic sample) or 32 (anisotropic samples), DS=32). The spectral width was set to 6.0 ppm (O2=2 ppm) in the direct dimension and to 165 ppm (O2=80 ppm) in the indirect dimension. The INEPT delay

was optimized for a long range coupling constant (${}^nJ_{\text{CH}}$) of 8 Hz. The delay in the G-BIRD element was optimized for a coupling constant (${}^1J_{\text{CH}}$) of 145 Hz. A k-factor of 4 was used for ${}^1J_{\text{CH}}$ -scaling. Selective refocusing during INEPT was done using *RSnob*^[5] 180° pulses with a duration of 58.3 ms (40Hz bandwidth). The selective offsets were set according to the desired protons (H1, H3a, H3s, H5, H7a, H7s, H10a and H10s). The bandwidth for the pulse shape used for selective refocusing was calculated with the Bruker Shape Tool of TopSpin 3.5 using the option “calculate bandwidth for refocusing –My”. Zero filling was applied to 8192 data points in the direct dimension and to 512 data points in the indirect dimension. Multiplication with a squared sine bell function (SSB=2) was done in both dimensions prior to Fourier transformation. The COSY based spectra^[4] were recorded with 4096 or 8192 data points (resulting both in a FID resolution of about 0.8 Hz) in the direct and 256 or 512 data points (resulting both in a FID resolution of about 13 Hz) in the indirect dimension (NS=8 or 16, DS=32). The spectral width was set to 2.5 ppm (O2=0.8 ppm) or 4.6 ppm (O2=1.7 ppm) in the direct dimension and to 2.5 ppm (O2=0.8 ppm) or 4.6 ppm (O1=1.7 ppm) in the indirect dimension. A *J* scaling factor of 2 was applied. Selective refocusing was done using *RSnob*^[5] 180° pulses with a duration of 58.3 ms (40Hz bandwidth). The bandwidth for the pulse shape used for selective refocusing was calculated with the Bruker Shape Tool of TopSpin 3.5 using the option “calculate bandwidth for refocusing –My”. The selective offsets were set according to the desired protons (H1, H3a, H5, H7a and H7s (anisotropic); H1, H3a and H7s (isotropic)). Zero filling was applied to 8192 or 16384 data points in the direct dimension and to 512 or 1024 data points in the indirect dimension. Gaussian (LB=-1.0Hz, GB0.35) and squared sine bell (SSB=2) window functions were applied to the direct and indirect dimension, respectively.

In the case of the methyl groups, ${}^1D_{\text{CC}}$ RDCs were calculated from ${}^1D_{\text{CH}}$ RDCs according to the literature^[7]. The descriptors a (antiperiplanar) and s (synperiplanar) describe the orientation of the diastereotopic protons relative to the dimethyl bridges.

Calculations were done using the software RDC@hotFCHT^[8,9]. The same structural models of the analytes as before were used^[10]. The quality of the correlation of experimental and back-calculated RDCs is given by the RMSD (root-mean-square deviation), the Q-factor^[11], the Q-Da^[12] and the q-Baltzar^[13]. Calculations for IPC as solute were done with error weighting of RDCs. Calculations for β -pinene as solute were done without error weighting of RDCs to avoid overestimation of HH RDCs.

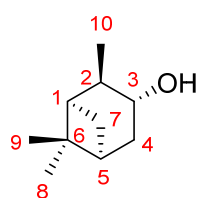
The signal assignment of the synthesized compounds was done using HSQC, HMBC and COSY experiments.

4. IPC data

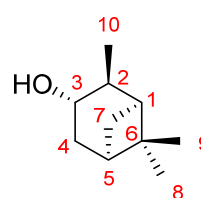
Table 4.1: Data of the IPC samples.

polymer	m(polymer) [g]	w(polymer) [%w/w]	analyte	m(analyte) [g]	solvent
PSPLG ^[a]	0.0593	10.5	(+)-IPC	0.0149	CDCl ₃
PSPLG ^[a]	0.0597	10.6	(-)-IPC	0.0148	CDCl ₃
PSPDG ^[a]	0.0580	10.6	(+)-IPC	0.0148	CDCl ₃
PSPDG ^[a]	0.0579	10.5	(-)-IPC	0.0148	CDCl ₃
PSPDG ^[b] / PSPLG ^[b] (1:1)	0.0295+0.0295	10.3	(+)-IPC	0.0143	CDCl ₃
PSPDG ^[b] / PSPLG ^[b] (1:1)	0.0296+0.0296	10.3	(-)-IPC	0.0147	CDCl ₃

[a] batch 1 [b] batch 2



(-)-IPC



(+)-IPC

Table 4.2: Extracted isotropic coupling constants ($^1J_{CH}$) for (-)-IPC in CDCl₃.

coupling pair	$^1J_{CH}$ [Hz]	error [Hz]
C10-H10	124.82	0.11
C9-H9	123.67	0.10
C8-H8	124.69	0.12
C7-H7s	135.27	0.36
C7-H7a	136.95	0.26
C3-H3	142.02	0.18
C4-H4s	126.73	0.40
C4-H4a	126.94	0.30
C5-H5	141.61	0.34
C2-H2	126.64	0.40
C1-H1	141.35	0.31

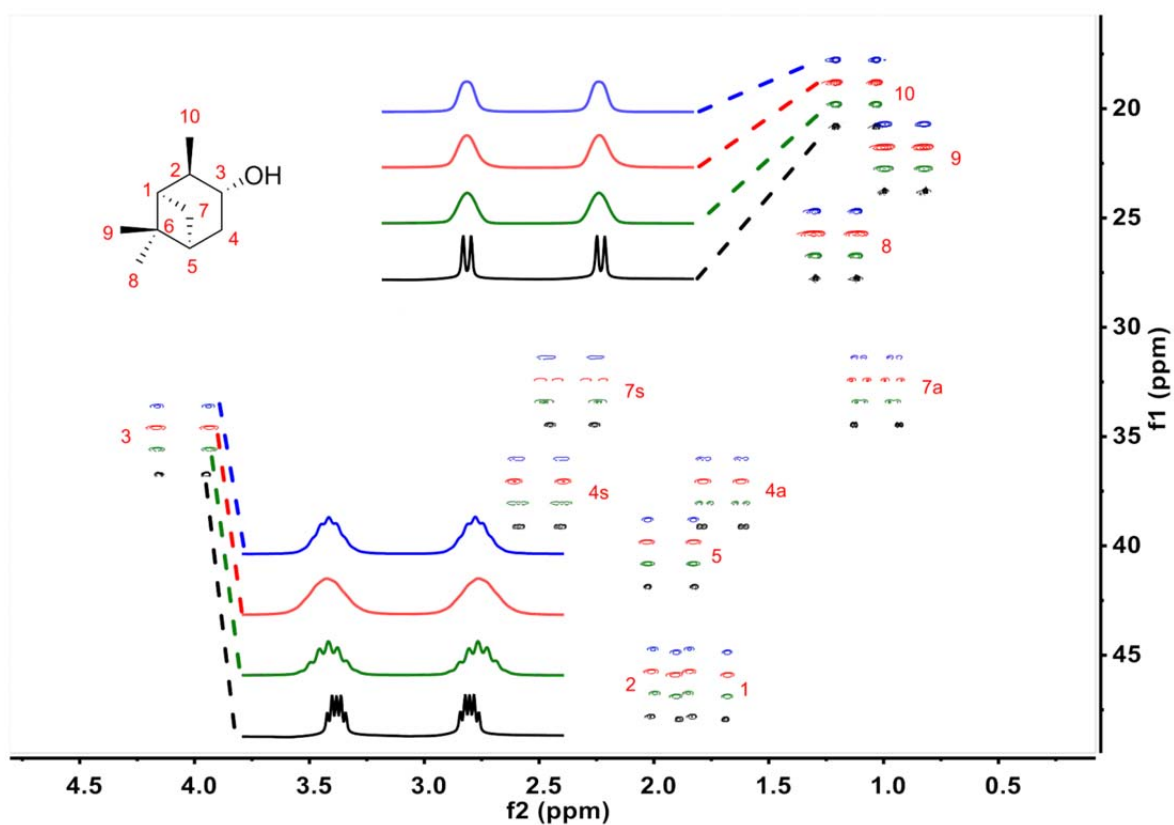


Figure 4.1: CLIP-HSQC^[2] spectra (700M Hz, 300 K) of (-)-IPC in an anisotropic phases of PSPLG/CDCl₃ (green, 10.6 % w/w), PSPDG/CDCl₃ (red, 10.5 % w/w), PSPLG/PSPDG(1:1)/CDCl₃ (blue, 10.3 % w/w) and (-)-IPC in CDCl₃ (black). The descriptors a (antiperiplanar) and s (synperiplanar) describe the orientation of the diastereotopic protons relative to the dimethyl bridge. Chemical shift referencing was done with respect to the isotropic measurement. The spectra from anisotropic measurements are shifted in order to obtain the stacked plot

Table 4.3: Extracted coupling constants (${}^1T_{\text{CH}}$) for (+)-IPC in PSPLG/ CDCl_3 (10.5% w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C10-H10	123.25	0.32	-0.79	0.22
C9-H9	118.83	0.31	-2.42	0.21
C8-H8	131.37	0.75	3.34	0.44
C7-H7s	139.29	1.85	2.01	1.11
C7-H7a	103.21	0.45	-16.87	0.35
C3-H3	161.54	0.31	9.76	0.25
C4-H4s	147.44	0.49	10.35	0.45
C4-H4a	115.64	0.45	-5.65	0.37
C5-H5	141.44	0.56	-0.09	0.45
C2-H2	114.80	4.00	-5.92	2.20
C1-H1	162.56	4.31	10.61	2.31
C2-C10			0.22	0.06
C6-C8			-0.91	0.12
C6-C9			0.66	0.06

Table 4.4: Extracted coupling constants (${}^1T_{\text{CH}}$) for (-)-IPC in PSPLG/ CDCl_3 (10.6% w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C10-H10	123.00	0.20	-0.91	0.16
C9-H9	119.73	0.26	-1.97	0.18
C8-H8	125.87	0.74	0.59	0.43
C7-H7s	163.33	1.36	14.03	0.86
C7-H7a	100.90	0.47	-18.03	0.36
C3-H3	159.55	0.28	8.77	0.23
C4-H4s	132.04	0.56	2.66	0.48
C4-H4a	110.29	0.34	-8.33	0.32
C5-H5	138.21	0.62	-1.70	0.48
C2-H2	101.70	0.79	-12.47	0.60
C1-H1	156.53	4.00	7.59	2.16
C2-C10			0.25	0.04
C6-C8			-0.16	0.12
C6-C9			0.54	0.05

Table 4.5: Extracted coupling constants ($^1T_{CH}$) for (+)-IPC in PSPDG/ $CDCl_3$ (10.6% w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C10-H10	122.66	0.33	-1.08	0.22
C9-H9	120.16	0.77	-1.75	0.44
C8-H8	126.73	0.38	1.02	0.25
C7-H7s	163.52	1.10	14.13	0.73
C7-H7a	96.66	0.51	-20.14	0.38
C3-H3	163.14	0.51	10.56	0.34
C4-H4s	134.63	0.69	3.95	0.55
C4-H4a	109.16	0.58	-8.89	0.44
C5-H5	138.37	0.43	-1.62	0.38
C2-H2	101.51	0.81	-12.56	0.61
C1-H1	157.21	4.00	7.93	2.16
C2-C10			0.30	0.06
C6-C8			-0.28	0.07
C6-C9			0.48	0.12

Table 4.6: Extracted coupling constants ($^1T_{CH}$) for (-)-IPC in PSPDG/ $CDCl_3$ (10.5% w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C10-H10	123.69	0.17	-0.57	0.14
C9-H9	119.43	1.16	-2.12	0.63
C8-H8	132.02	0.53	3.66	0.33
C7-H7s	138.62	1.30	1.67	0.83
C7-H7a	102.50	0.67	-17.23	0.47
C3-H3	161.99	0.44	9.99	0.31
C4-H4s	149.85	0.43	11.56	0.41
C4-H4a	115.51	0.38	-5.72	0.34
C5-H5	141.91	0.40	0.15	0.37
C2-H2	116.77	1.91	-4.94	1.16
C1-H1	161.94	4.00	10.30	2.16
C2-C10			0.16	0.04
C6-C8			-1.00	0.09
C6-C9			0.58	0.17

Table 4.7: Extracted coupling constants (${}^1T_{\text{CH}}$) for (+)-IPC in PSPLG/PSPDG(1:1)/CDCl₃ (10.3% w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C10-H10	123.11	0.51	-0.86	0.31
C9-H9	119.69	0.54	-1.99	0.32
C8-H8	127.23	0.38	1.27	0.25
C7-H7s	151.10	1.32	7.91	0.84
C7-H7a	107.45	0.47	-14.75	0.37
C3-H3	157.12	0.53	7.55	0.36
C4-H4s	137.07	0.80	5.17	0.60
C4-H4a	114.79	0.44	-6.07	0.37
C5-H5	139.18	1.00	-1.21	0.67
C2-H2	110.18	1.31	-8.23	0.85
C1-H1	157.02	1.19	7.83	0.75
C2-C10			0.23	0.08
C6-C8			-0.35	0.07
C6-C9			0.55	0.09

Table 4.8: Extracted coupling constants (${}^1T_{\text{CH}}$) for (-)-IPC in PSPLG/PSPDG(1:1)/CDCl₃ (10.3% w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C10-H10	123.34	0.44	-0.7	0.3
C9-H9	120.86	0.42	-1.4	0.3
C8-H8	126.67	0.45	1.0	0.3
C7-H7s	150.21	1.18	7.47	0.77
C7-H7a	108.44	0.58	-14.26	0.42
C3-H3	156.43	0.38	7.21	0.28
C4-H4s	137.23	0.87	5.25	0.64
C4-H4a	114.84	0.46	-6.05	0.38
C5-H5	139.20	0.88	-1.20	0.61
C2-H2	111.15	1.26	-7.74	0.83
C1-H1	157.46	1.91	8.05	1.11
C2-C10			0.20	0.08
C6-C8			-0.27	0.08
C6-C9			0.39	0.07

Table 4.9: Orientational properties of IPC in PSPLG/ CDCl_3 .

	(+)-IPC	(-)-IPC
number of RDCs	11	11
$ \Delta\nu_Q $ [Hz]	134	139
RMSD [Hz]	0.7097	0.4032
Q-factor	0.0908	0.0448
Q-Da	0.0282	0.0159
q-Baltzar	0.0789	0.0802
Euler α	69.97	48.63
Euler β	84.52	70.76
Euler γ	148.93	157.65
Da [10^{-4}]	4.087	4.054
Dr [10^{-4}]	1.481	2.364
condition number	2.93	3.07

Table 4.10: Orientational properties of IPC in PSPDG/ CDCl_3 .

	(+)-IPC	(-)-IPC
number of RDCs	11	11
$ \Delta\nu_Q $ [Hz]	194	184
RMSD [Hz]	0.4821	0.7820
Q-factor	0.0497	0.0982
Q-Da	0.0171	0.0310
q-Baltzar	0.0831	0.1047
Euler α	48.14	71.66
Euler β	73.70	86.51
Euler γ	156.67	148.76
Da [10^{-4}]	4.52	4.08
Dr [10^{-4}]	2.36	1.70
condition number	2.33	2.62

Table 4.11: Orientational properties of IPC in PSPLG/PSPDG(1:1)/ CDCl_3 .

	(+)-IPC	(-)-IPC
number of RDCs	11	11
$ \Delta\nu_Q $ [Hz]	140	139
RMSD [Hz]	0.3140	0.3685
Q-factor	0.0452	0.0546
Q-Da	0.0148	0.0182
q-Baltzar	0.0475	0.0798
Euler α	58.66	59.09
Euler β	75.84	75.93
Euler γ	153.40	154.10
Da [10^{-4}]	3.42	3.27
Dr [10^{-4}]	1.50	1.49
condition number	2.18	2.67

5. Pinene data

Table 5.1: Data of the β -pinene samples.

polymer	m(polymer) [g]	w(polymer) [%w/w]	analyte	m(analyte) [g]	solvent
PSPLG ^[b]	0.0595	10.4	(+)- β -pinene	0.0161	CDCl ₃
PSPLG ^[b]	0.0588	10.5	(-)- β -pinene	0.0160	CDCl ₃
PSPDG ^[b]	0.0592	10.3	(+)- β -pinene	0.0163	CDCl ₃
PSPDG ^[b]	0.0603	10.8	(-)- β -pinene	0.0162	CDCl ₃
PSPDG ^[b] / PSPLG ^[b] (1:1)	0.0300+0.0300	10.3	(+)- β -pinene	0.0163	CDCl ₃
PSPDG ^[b] / PSPLG ^[b] (1:1)	0.0293+0.0293	10.4	(-)- β -pinene	0.0161	CDCl ₃

[a] batch 1 [b] batch 2

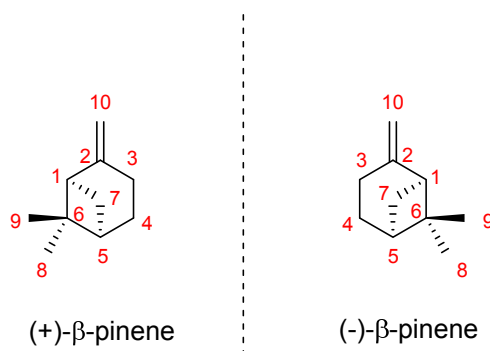


Table 5.2 Extracted isotropic coupling constants ($^1J_{CH}$) for (-)- β -pinene in CDCl₃.

coupling pair	$^1J_{CH}$ [Hz]	error [Hz]
C1-H1	142.99	0.27
C9-H9	124.25	0.11
C3-H3a	125.86	0.38
C3-H3s	129.08	0.29
C8-H8	124.79	0.17
C7-H7a	137.61	0.26
C10-H10a	153.76	0.15
C10-H10s	155.71	0.17
C5-H5	141.39	0.41

Table 5.3: Extracted coupling constants ($^1T_{CH}$) for (+)- β -pinene in PSPLG/ $CDCl_3$ (10.4 % w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C1-H1	155.71	0.69	6.36	0.48
C9-H9	125.03	0.31	0.39	0.21
C3-H3a	120.25	0.41	-2.81	0.40
C3-H3s	132.59	0.36	1.76	0.32
C8-H8	123.32	0.40	-0.73	0.29
C7-H7a	134.44	0.48	-1.58	0.37
C10-H10a	159.49	0.53	2.87	0.34
C10-H10s	171.74	0.46	8.01	0.31
C5-H5	132.85	0.49	-4.27	0.45
C6-C8			0.20	0.08
C6-C9			-0.11	0.06

Table 5.4: Extracted coupling constants ($^1T_{CH}$) for (-)- β -pinene in PSPLG/ $CDCl_3$ (10.5 % w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C1-H1	156.70	0.65	6.85	0.46
C9-H9	124.00	0.27	-0.13	0.19
C3-H3a	117.46	0.74	-4.20	0.56
C3-H3s	135.62	0.36	3.27	0.32
C8-H8	123.97	0.53	-0.41	0.35
C7-H7a	129.99	0.59	-3.81	0.42
C10-H10a	158.34	0.53	2.29	0.34
C10-H10s	170.52	0.54	7.41	0.36
C5-H5	132.67	0.62	-4.36	0.52
C6-C8			0.11	0.10
C6-C9			0.03	0.05

Table 5.5: Extracted coupling constants (${}^1T_{\text{CH}}$) for (+)- β -pinene in PSPDG/ CDCl_3 (10.3 % w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C1-H1	155.71	0.45	6.36	0.36
C9-H9	123.27	0.34	-0.49	0.22
C3-H3a	119.09	0.52	-3.39	0.45
C3-H3s	135.78	0.42	3.35	0.35
C8-H8	124.73	0.45	-0.03	0.31
C7-H7a	129.58	0.54	-4.01	0.40
C10-H10a	156.34	0.53	1.29	0.34
C10-H10s	168.92	0.36	6.61	0.26
C5-H5	132.53	0.65	-4.43	0.53
C6-C8			0.01	0.08
C6-C9			0.14	0.06

Table 5.6: Extracted coupling constants (${}^1T_{\text{CH}}$) for (-)- β -pinene in PSPDG/ CDCl_3 (10.8 % w/w).

coupling pair	${}^1T_{\text{CH}}$ [Hz]	error [Hz]	${}^1D_{\text{CH}}/{}^1D_{\text{CC}}$ [Hz]	error [Hz]
C1-H1	157.16	0.69	7.08	0.48
C9-H9	124.34	0.45	0.05	0.28
C3-H3a	120.63	0.47	-2.61	0.42
C3-H3s	133.32	0.55	2.12	0.42
C8-H8	123.51	0.40	-0.64	0.29
C7-H7a	133.86	0.61	-1.88	0.44
C10-H10a	158.10	0.56	2.17	0.35
C10-H10s	172.62	0.45	8.46	0.31
C5-H5	130.81	0.70	-5.29	0.55
C6-C8			0.18	0.08
C6-C9			-0.01	0.08

Table 5.7 Extracted coupling constants ($^1T_{CH}$) for (+)- β -pinene in PSPLG/PSPDG(1:1)/CDCl₃ (10.3 % w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C1-H1	155.62	0.45	6.31	0.36
C9-H9	124.32	0.34	0.04	0.22
C3-H3a	120.03	0.50	-2.92	0.44
C3-H3s	134.46	0.55	2.69	0.42
C8-H8	124.23	0.31	-0.28	0.24
C7-H7a	132.16	0.52	-2.73	0.39
C10-H10a	157.67	0.32	1.95	0.24
C10-H10s	170.01	0.54	7.15	0.35
C5-H5	132.79	0.54	-4.30	0.48
C6-C8			0.08	0.07
C6-C9			-0.01	0.06

Table 5.8: Extracted coupling constants ($^1T_{CH}$) for (-)- β -pinene in PSPLG/PSPDG(1:1)/CDCl₃ (10.4 % w/w).

coupling pair	$^1T_{CH}$ [Hz]	error [Hz]	$^1D_{CH}/^1D_{CC}$ [Hz]	error [Hz]
C1-H1	155.57	0.51	6.29	0.39
C9-H9	124.11	0.18	-0.07	0.14
C3-H3a	119.42	0.44	-3.22	0.41
C3-H3s	134.12	0.35	2.52	0.32
C8-H8	123.77	0.41	-0.51	0.29
C7-H7a	132.26	0.36	-2.67	0.31
C10-H10a	157.76	0.43	2.00	0.29
C10-H10s	170.20	0.60	7.24	0.39
C5-H5	132.47	0.50	-4.46	0.45
C6-C8			0.14	0.08
C6-C9			0.02	0.04

Table 5.9 Extracted isotropic coupling constants ($|^nJ_{\text{HH}}|$) for (-)- β -pinene in CDCl_3 .

coupling pair	$ ^nJ_{\text{HH}} $ [Hz]	error [Hz]
H1-H10s	n.o. ^[a]	
H1-H7s	5.57	0.06
H1-H3s	n.o. ^[a]	
H1-H5	5.32	0.08
H1-H7a	n.o. ^[a]	
H3s-H10a	1.25	0.04
H3s-H10s	1.14	0.03
H3a-H10a	2.51	0.06
H3a-H10s	3.01	0.04
H3a-H3s	17.45	0.11
H3a-H5	n.o. ^[a]	
H3a-H7a	n.o. ^[a]	
H5-H7s	6.07	0.05
H5-H7a	n.o. ^[a]	
H7a-H7s	9.89	0.07
H10s-H10a	2.04	0.04

[a] not observed, assumed to be 0 Hz

Table 5.10 Extracted coupling constants ($|^nT_{\text{HH}}|$) for (+)- β -pinene in PSPLG/ CDCl_3 (10.4 % w/w).

coupling pair	$ ^nT_{\text{HH}} $ [Hz]	error [Hz]	$^nD_{\text{HH}}$ [Hz]	error [Hz]
H1-H10s	1.65	0.06	-0.83	0.10
H1-H7s	6.56	0.03	0.50	0.10
H1-H3s	1.17	0.05	0.59	0.10
H1-H5	5.23	0.06	-0.05	0.10
H1-H7a	3.21	0.04	1.61	0.10
H3a-H10a	1.25	0.02	0.63	0.10
H3a-H10s	1.57	0.06	0.72	0.10
H3a-H3s	21.37	0.17	-1.96	0.14
H3a-H5	1.27	0.04	-0.64	0.10
H3a-H7a	2.58	0.05	1.29	0.10
H5-H7s	4.34	0.05	-0.87	0.10
H5-H7a	3.70	0.05	-1.85	0.10
H7a-H7s	5.50	0.06	2.20	0.10

Table 5.11 Extracted coupling constants ($|{}^nT_{HH}|$) for (-)- β -pinene in PSPLG/ $CDCl_3$ (10.5 % w/w).

coupling pair	$ {}^nT_{HH} $ [Hz]	error [Hz]	${}^nD_{HH}$ [Hz]	error [Hz]
H1-H10s	2.26	0.06	-1.13	0.10
H1-H7s	5.02	0.05	-0.28	0.10
H1-H3s	1.25	0.04	0.63	0.10
H1-H5	5.35	0.08	0.02	0.10
H1-H7a	1.35	0.03	0.68	0.10
H3a-H10a	2.43	0.03	0.04	0.10
H3a-H10s	2.19	0.05	0.41	0.10
H3a-H3s	18.92	0.11	-0.74	0.11
H3a-H5	1.30	0.04	-0.65	0.10
H3a-H7a	3.12	0.05	1.56	0.10
H5-H7s	7.42	0.07	0.68	0.10
H5-H7a	2.51	0.07	-1.26	0.10
H7a-H7s	9.43	0.11	0.23	0.10

Table 5.12 Extracted coupling constants ($|{}^nT_{HH}|$) for (+)- β -pinene in PSPDG/ $CDCl_3$ (10.3 % w/w).

coupling pair	$ {}^nT_{HH} $ [Hz]	error [Hz]	${}^nD_{HH}$ [Hz]	error [Hz]
H1-H10s	2.63	0.07	-1.32	0.10
H1-H7s	4.96	0.12	-0.31	0.10
H1-H3s	1.22	0.06	0.61	0.10
H1-H5	5.35	0.06	0.02	0.10
H1-H7a	1.20	0.02	0.60	0.10
H3a-H10a	2.54	0.08	-0.02	0.10
H3a-H10s	2.29	0.07	0.36	0.10
H3a-H3s	16.67	0.09	0.39	0.10
H3a-H5	1.44	0.08	-0.72	0.10
H3a-H7a	2.54	0.04	1.27	0.10
H5-H7s	7.81	0.14	0.87	0.10
H5-H7a	2.04	0.04	-1.02	0.10
H7a-H7s	11.59	0.13	-0.85	0.10

Table 5.13 Extracted coupling constants ($|{}^nT_{HH}|$) for (-)- β -pinene in PSPDG/ CDCl_3 (10.8 % w/w).

coupling pair	$ {}^nT_{HH} $ [Hz]	error [Hz]	${}^nD_{HH}$ [Hz]	error [Hz]
H1-H10s	2.47	0.09	-1.24	0.10
H1-H7s	6.65	0.10	0.54	0.10
H1-H3s	1.26	0.04	0.63	0.10
H1-H5	5.26	0.09	-0.03	0.10
H1-H7a	3.51	0.09	1.76	0.10
H3a-H10a	1.21	0.03	0.65	0.10
H3a-H10s	1.54	0.03	0.74	0.10
H3a-H3s	19.23	0.10	-0.89	0.11
H3a-H5	1.60	0.03	-0.80	0.10
H3a-H7a	2.51	0.05	1.26	0.10
H5-H7s	4.71	0.11	-0.68	0.10
H5-H7a	4.10	0.09	-2.05	0.10
H7a-H7s	7.17	0.12	1.36	0.10

Table 5.14 Extracted coupling constants ($|{}^nT_{HH}|$) for (+)- β -pinene in PSPLG/PSPDG(1:1)/ CDCl_3 (10.3 % w/w).

coupling pair	$ {}^nT_{HH} $ [Hz]	error [Hz]	${}^nD_{HH}$ [Hz]	error [Hz]
H1-H10s	2.12	0.05	-1.06	0.10
H1-H7s	5.75	0.02	0.09	0.10
H1-H3s	1.09	0.03	0.55	0.10
H1-H5	5.31	0.02	-0.01	0.10
H1-H7a	2.15	0.03	1.08	0.10
H3a-H10a	1.91	0.05	0.30	0.10
H3a-H10s	1.95	0.03	0.53	0.10
H3a-H3s	18.97	0.06	-0.76	0.10
H3a-H5	1.32	0.04	-0.66	0.10
H3a-H7a	2.55	0.04	1.28	0.10
H5-H7s	6.10	0.03	0.02	0.10
H5-H7a	2.81	0.02	-1.41	0.10
H7a-H7s	8.60	0.02	0.65	0.10

Table 5.15 Extracted coupling constants ($|^nT_{HH}|$) for (-)- β -pinene in PSPLG/PSPDG(1:1)/CDCl₃ (10.4 % w/w).

coupling pair	$ ^nT_{HH} $ [Hz]	error [Hz]	$^nD_{HH}$ [Hz]	error [Hz]
H1-H10s	2.19	0.02	-1.10	0.10
H1-H7s	5.76	0.02	0.10	0.10
H1-H3s	1.15	0.06	0.58	0.10
H1-H5	5.33	0.02	0.01	0.10
H1-H7a	2.23	0.05	1.12	0.10
H3a-H10a	1.95	0.01	0.28	0.10
H3a-H10s	1.98	0.02	0.52	0.10
H3a-H3s	19.01	0.10	-0.78	0.11
H3a-H5	1.27	0.12	-0.64	0.10
H3a-H7a	2.58	0.04	1.29	0.10
H5-H7s	6.07	0.02	0.00	0.10
H5-H7a	2.87	0.03	-1.44	0.10
H7a-H7s	8.50	0.03	0.70	0.10

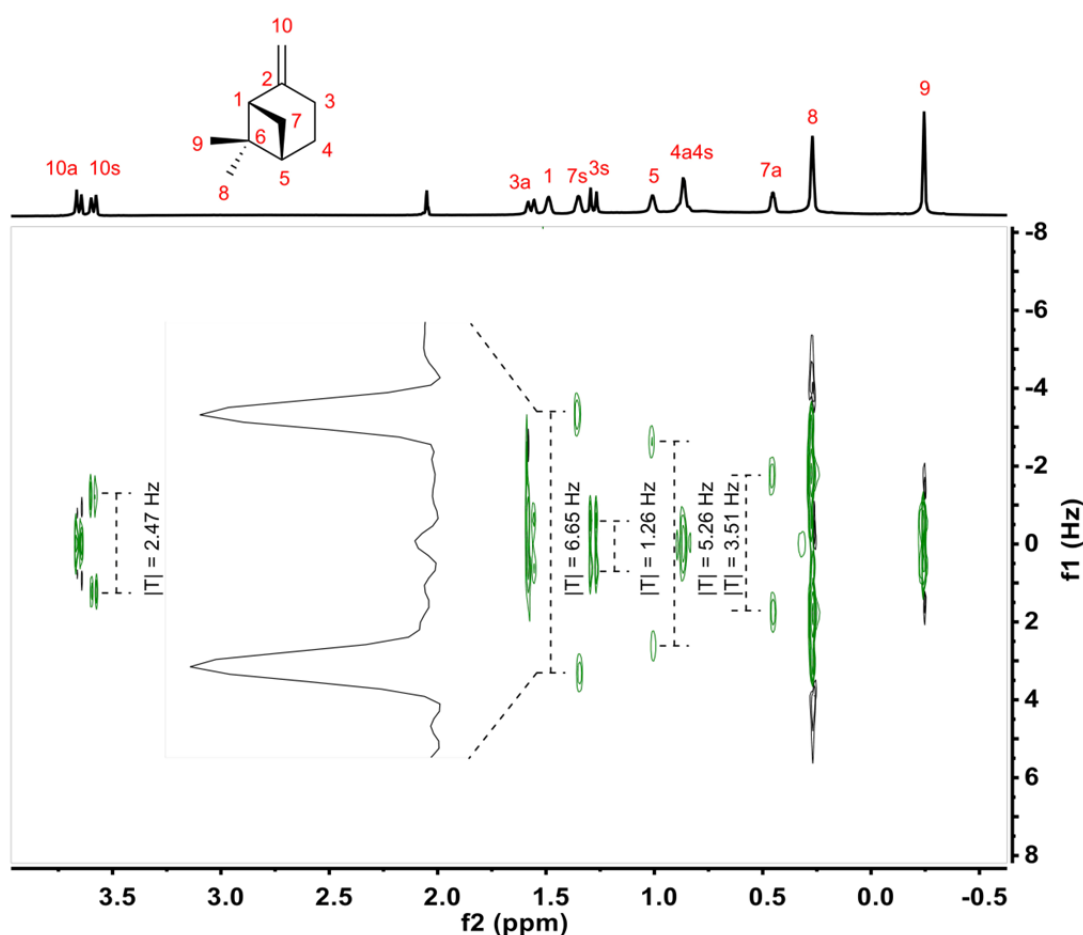


Figure 5.1: Non-pure shift 2D TSE-PSYCHEDELIC^[3,4] spectrum (700 MHz, 300 K) of (-)- β -pinene in PSPDG/CDCl₃ (10.8 % w/w) with excitation of H1. The descriptors a (antiperiplanar) and s (synperiplanar) describe the orientation of the diastereotopic protons relative to the dimethyl bridge.

Table 5.16: Signs (m = minus, p = plus) of ${}^nJ_{\text{HH}}$ determined for (-)- β -pinene in CDCl_3 .

coupling pair	sign
H1H5	p ^[a]
H3s-H10a	m ^[a]
H3s-H10s	m ^[a]
H3aH10a	m ^[a]
H3aH10s	m ^[a]
H3aH3s	m ^[b]
H1H7s	p ^[b]
H5H7s	p ^[a]
H7sH7a	m ^[b]

[a] determined by P.E.HSQMBC [b] determined by a COSY based experiment

Table 5.17: Signs (m = minus, p = plus) of ${}^nT_{\text{HH}}$ determined for (-)- β -pinene (left) and (+)- β -pinene (right) in PSPDG/ CDCl_3 .

coupling pair	sign	coupling pair	sign
H1H5	p ^[a]	H1H5	p ^[a]
H1H3s	p ^[a]	H1H3s	p ^[a]
H1H10s	m ^[a]	H1H10s	m ^[a]
H3aH10a	m ^[a]	H3aH10a	m ^[a]
H3aH10s	m ^[a]	H3aH10s	m ^[a]
H3aH3s	m ^[a]	H3aH3s	m ^[a]
H1H7s	p ^[b]	H1H7s	p ^[b]
H3aH7a	p ^[b]	H3aH7a	p ^[b]
H5H7a	m ^[b]	H5H7a	m ^[b]
H5H7s	p ^[b]	H5H7s	p ^[b]
H3aH5	m ^[b]	H3aH5	m ^[b]
H7sH7a	m ^[b]	H7sH7a	m ^[b]
H1H7a	p ^[b]	H1H7a	p ^[b]

[a] determined by P.E.HSQMBC [b] determined by a COSY based experiment

As carried out above for isopinocampheol, results of the CH-RDC fits for the β -pinene enantiomers are given in the Tables 5.18 to 5.20. The observed condition number of 10.24 indicates sub-optimal sampling of orientations and is strongly improved to a value of 3.80, when using the full CH and HH RDC dataset (see Tables 5.21 to 5.23) or the HH RDC dataset alone (4.61, see Tables 5.24 to 5.26).

The tables also report the orientational properties derived from Eigen decomposition of the best-fit alignment tensor. Surprisingly, the sign of the tensor components D_a and D_r are inconsistent over the entire dataset, as are the Euler angles. While this would at first glance suggest an enormous enantiodifferentiation, this is merely a result of numerical instability of the Eigen decomposition and subsequent sorting of eigenvalues according to their magnitude. For this particular system, two eigenvalues are fairly close in magnitude, and even slight changes in the tensor parameters may result in the conventional eigenvalue sorting to assign the value with larger magnitude to the 'zz' component - whether it is the positive value or the negative one. The eigenvectors are sorted accordingly and when used to calculate the Euler angles, again result in apparently different values.

The full 3-by-3 Saupe order matrix (or the scaled equivalent full second rank alignment tensor) however show a much more consistent behavior. Here, the 'zz'-value is always positive while the 'yz'-value is very sensitive to the actual RDC dataset and is sometimes orders of magnitude smaller compared to other tensor components, indicating the high similarity in alignment along these directions.

Comparisons based on the generalized scalar product (or the corresponding generalized angle β) are not affected, as the calculation of this parameter involves the full tensor(s), and does not employ Eigen decomposition.

Thus, while the reported parameters are mathematically correct, they are inconvenient for quick cross-comparisons of orientational properties. Higher consistency of the reported values may be achieved by careful weighting of the individual RDCs. The most commonly suggested weighting scheme is weighting with the relative distances and gyromagnetic ratios (combined in the maximum dipolar coupling constant D_{\max})^[12]. This weighting scheme may be automatically applied by RDC@hotFCHT before the SVD fit.

The results of the fits of the CH RDC set with automated D_{\max} scaling are reported exemplarily in Tables 5.27 to 5.29 and contrary to the corresponding values in Tables 5.18 to 5.20 all show positive D_a and D_r values. This shows exemplarily the sensitivity discussed above.

The effects of D_{\max} weighting on the Saupe order matrix, the Eigen decomposition as well as the error estimation by Monte-Carlo bootstrapping^[14] are summarized exemplarily for the CH RDC dataset of (+)- β -pinene in PSPLG/ CDCl_3 in Tables 5.30 and 5.31.

Table 5.18: Orientational properties (using CH RDCs) of β -pinene in PSPLG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta v_Q $ [Hz]	130	134
RMSD [Hz]	0.2846	0.1476
Q-factor	0.0710	0.0341
Q-Da	0.0236	0.0129
q-Baltzar	0.0970	0.0660
Euler α	147.98	152.23
Euler β	90.35	74.81
Euler γ	77.83	75.67
Da [10^{-4}]	-1.94	-1.84
Dr [10^{-4}]	-0.98	-0.82
condition number	10.24	10.24

Table 5.19: Orientational properties (using CH RDCs) of β -pinene in PSPDG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta v_Q $ [Hz]	170	190
RMSD [Hz]	0.1854	0.2759
Q-factor	0.0463	0.0636
Q-Da	0.0178	0.0221
q-Baltzar	0.0591	0.0805
Euler α	158.26	157.19
Euler β	70.33	86.82
Euler γ	73.56	76.48
Da [10^{-4}]	-1.67	-2.00
Dr [10^{-4}]	-0.91	-0.99
condition number	10.24	10.24

Table 5.20: Orientational properties (using CH RDCs) of β -pinene in PSPLG/PSPDG(1:1)/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta v_Q $ [Hz]	149	149
RMSD [Hz]	0.2574	0.1602
Q-factor	0.0661	0.0406
Q-Da	0.0244	0.0149
q-Baltzar	0.0898	0.0868
Euler α	155.50	154.95
Euler β	81.03	81.41
Euler γ	75.84	76.01
Da [10^{-4}]	-1.69	-1.73
Dr [10^{-4}]	-0.93	-0.91
condition number	10.24	10.24

Table 5.21: Orientational properties (using CH + HH RDCs) of β -pinene in PSPLG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	22	22
RMSD [Hz]	0.2371	0.1616
Q-factor	0.0868	0.0570
Q-Da	0.0181	0.0143
q-Baltzar	0.1062	0.1300
Euler α	8.23	153.06
Euler β	122.30	75.27
Euler γ	169.34	75.09
Da [10^{-4}]	2.09	-1.81
Dr [10^{-4}]	1.27	-0.97
condition number	3.80	3.80

Table 5.22: Orientational properties (using CH + HH RDCs) of β -pinene in PSPDG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	22	22
RMSD [Hz]	0.1707	0.2582
Q-factor	0.0650	0.0890
Q-Da	0.0164	0.0182
q-Baltzar	0.1248	0.1204
Euler α	158.45	7.63
Euler β	70.38	116.88
Euler γ	73.13	166.76
Da [10^{-4}]	-1.66	2.27
Dr [10^{-4}]	-1.00	1.26
condition number	3.80	3.80

Table 5.23: Orientational properties (using CH + HH RDCs) of β -pinene in PSPLG/PSPDG(1:1)/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	22	22
RMSD [Hz]	0.2015	0.1642
Q-factor	0.0786	0.0633
Q-Da	0.0185	0.0149
q-Baltzar	0.1296	0.1275
Euler α	174.53	174.91
Euler β	115.62	115.87
Euler γ	162.41	162.58
Da [10^{-4}]	1.74	1.76
Dr [10^{-4}]	1.08	1.10
condition number	3.80	3.80

Table 5.24: Orientational properties (using HH RDCs only) of β -pinene in PSPLG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	13	13
$ \Delta v_Q $ [Hz]	132	135
RMSD [Hz]	0.1039	0.0967
Q-factor	0.0845	0.1244
Q-Da	0.0073	0.0077
q-Baltzar	0.0889	0.1251
Euler α	7.71	153.88
Euler β	120.76	75.23
Euler γ	168.43	74.23
Da [10^{-4}]	2.26	-2.02
Dr [10^{-4}]	1.34	-1.12
condition number	4.61	4.61

Table 5.25: Orientational properties (using HH RDCs only) of β -pinene in PSPDG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	13	13
$ \Delta v_Q $ [Hz]	171	195
RMSD [Hz]	0.1100	0.1010
Q-factor	0.1449	0.0917
Q-Da	0.0095	0.0064
q-Baltzar	0.1449	0.0921
Euler α	159.69	7.36
Euler β	71.80	115.59
Euler γ	72.13	166.15
Da [10^{-4}]	-1.84	2.53
Dr [10^{-4}]	-1.12	1.36
condition number	4.61	4.61

Table 5.26: Orientational properties (using HH RDCs only) of β -pinene in PSPLG/PSPDG(1:1)/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	13	13
$ \Delta v_Q $ [Hz]	150	151
RMSD [Hz]	0.1031	0.1034
Q-factor	0.1315	0.1290
Q-Da	0.0086	0.0085
q-Baltzar	0.1315	0.1299
Euler α	174.82	175.11
Euler β	114.90	114.73
Euler γ	161.80	162.01
Da [10^{-4}]	1.91	1.94
Dr [10^{-4}]	1.18	1.20
condition number	4.61	4.61

Table 5.27: Orientational properties (using CH RDCs with D_{\max} scaling) of β -pinene in PSPLG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta v_Q $ [Hz]	130	134
RMSD [Hz]	0.4089	0.2775
Q-factor	0.1020	0.0640
Q-Da	0.0328	0.0249
q-Baltzar	0.1052	0.0760
Euler α	7.43	166.14
Euler β	120.83	116.16
Euler γ	167.58	157.85
Da [10^{-4}]	1.99	1.77
Dr [10^{-4}]	1.22	1.14
condition number	9.67	9.67

Table 5.28: Orientational properties (using CH RDCs with D_{\max} scaling) of β -pinene in PSPDG/ CDCl_3 .

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta v_Q $ [Hz]	170	190
RMSD [Hz]	0.2727	0.3790
Q-factor	0.0681	0.0874
Q-Da	0.0253	0.0292
q-Baltzar	0.0658	0.0870
Euler α	161.25	2.99
Euler β	111.21	114.41
Euler γ	155.57	164.97
Da [10^{-4}]	1.72	2.07
Dr [10^{-4}]	0.95	1.25
condition number	9.67	9.67

Table 5.29: Orientational properties (using CH RDCs with D_{\max} scaling) of β -pinene in PSPLG/PSPDG(1:1)/CDCl₃.

	(+)- β -pinene	(-)- β -pinene
number of RDCs	9	9
$ \Delta\nu_Q $ [Hz]	149	149
RMSD [Hz]	0.3525	0.2600
Q-factor	0.0905	0.0660
Q-Da	0.0333	0.0232
q-Baltzar	0.1266	0.0835
Euler α	173.57	175.51
Euler β	114.21	115.31
Euler γ	160.64	162.00
Da [10^{-4}]	1.68	1.79
Dr [10^{-4}]	1.03	1.03
condition number	9.67	9.67

Table 5.30: Tensor parameters (using CH RDCs) of (+)- β -pinene in PSPLG/CDCl₃.

Averages and errors of saupe vector (Losonczi method)					
	zz	xx-yy	xy	xz	yz
average	$1.29 \cdot 10^{-4}$	$5.91 \cdot 10^{-4}$	$1.32 \cdot 10^{-4}$	$-1.33 \cdot 10^{-4}$	$-2.32 \cdot 10^{-5}$
error	$2.36 \cdot 10^{-5}$	$3.69 \cdot 10^{-5}$	$1.43 \cdot 10^{-5}$	$7.93 \cdot 10^{-5}$	$4.04 \cdot 10^{-5}$
% error	18.25	6.25	10.80	59.79	173.83
saupe order	$2.30 \cdot 10^{-4}$	$1.32 \cdot 10^{-4}$	$-1.30 \cdot 10^{-4}$		
matrix	$1.32 \cdot 10^{-4}$	$-3.60 \cdot 10^{-4}$	$-2.47 \cdot 10^{-5}$		
	$-1.30 \cdot 10^{-4}$	$-2.47 \cdot 10^{-5}$	$1.30 \cdot 10^{-4}$		
eigenvalues	xx	yy	zz		
of saupe	$4.71 \cdot 10^{-5}$	$3.41 \cdot 10^{-4}$	$-3.88 \cdot 10^{-4}$		
matrix					

Table 5.31: Tensor parameters (using CH RDCs with D_{\max} scaling) of (+)- β -pinene in PSPLG/CDCl₃.

Averages and errors of saupe vector (Losonczi method)					
	zz	xx-yy	xy	xz	yz
average	$8.87 \cdot 10^{-5}$	$5.83 \cdot 10^{-4}$	$1.61 \cdot 10^{-4}$	$-1.88 \cdot 10^{-4}$	$-1.06 \cdot 10^{-6}$
error	$2.01 \cdot 10^{-5}$	$3.88 \cdot 10^{-5}$	$1.48 \cdot 10^{-5}$	$7.46 \cdot 10^{-5}$	$3.91 \cdot 10^{-5}$
% error	22.67	6.66	9.21	39.77	3702.80
saupe order	$2.46 \cdot 10^{-4}$	$1.61 \cdot 10^{-4}$	$-1.89 \cdot 10^{-4}$		
matrix	$1.61 \cdot 10^{-4}$	$-3.35 \cdot 10^{-4}$	$-2.34 \cdot 10^{-7}$		
	$-1.89 \cdot 10^{-4}$	$-2.34 \cdot 10^{-7}$	$8.85 \cdot 10^{-5}$		
eigenvalues	xx	yy	zz		
of saupe	$-1.54 \cdot 10^{-5}$	$-3.82 \cdot 10^{-4}$	$3.97 \cdot 10^{-4}$		
matrix					

6. References

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