Electronic Supporting Information

Chemically cross-linked PDMS as versatile alignment medium for organic compounds

Yulia E. Moskalenko, Viktor Bagutski, Christina M. Thiele

Technische Universität Darmstadt, Clemens Schöpf Institut für Organische Chemie und Biochemie, Alarich-Weiss-Str. 16, 64287 Darmstadt, Germany
Materials and Methods

General. All reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on Macherey Nagel aluminum plates coated with silica gel containing green fluorescence indicator for short wave UV (254nm). Visualization was achieved by UV light (254 nm), saturated aqueous potassium permanganate or 5% ethanolic solution of phosphomolybdic acid and subsequent heating.

NMR experiments. All NMR experiments were obtained on Bruker DRX-400, Avance-III HD-400 and Avance-III-600 spectrometers. Chemical shifts (δ) are referenced from TMS (0 ppm in "H, 13C and 29Si NMR) or residual CDCl3 signal (7.27 ppm in "H NMR and 77.3 in 13C NMR spectra). Assignment of NMR spectra of (+)-isopinocampheol and β-(-)-cariophyllene was performed using standard 1D- and 2D-NMR techniques (including H2BC)[1]. Diastereotopic protons of β-(-)-cariophyllene were assigned using 3J-couplings analysis obtained from DQF-COSY experiment. The PDMS was analyzed using 1D and 2D 29Si NMR (1D-inept, 1D-ig, "H-29Si HMBC). Decomposition of PDMS in the presence of (+)-isopinocampheol was investigated by "H DOSY experiment (stimulated echo with bipolar gradients, Bruker pulse sequence library stebpgp1s)[2] performed on Avance-III HD-400 NMR spectrometer equipped with either 5 mm inverse probe with Z-gradient or 5 mm microimaging probe equipped with Diff30L Z-gradient with lock channel and 60 A GREAT amplifier. The RDC data (D_{C-H}) were extracted from CLIP-HSQC,[3] scaled F1-coupled BIRD-HSQC[4] and scaled F1-coupled BIRD-HSQC spectra with MQ-evolution[5]. These were recorded for isotropic and anisotropic samples and RDCs are calculated according to the formula:

\[ D_{C-H} = (1 T_{C-H}^{aniso} J_{C,H}^{iso})/2 \]

For the methyl groups the D_{C-C} rather than D_{C-H} was used for the spatial structure elucidation. The following equation was applied [6]:

\[ D_{C-C} = D_{CH3} (-3\gamma_C/\gamma_H)(r^3_{CH}/r^3_{CC}) \]
Preparation of PDMS-sticks.

1. Cross-linker (Bis-D_4).

To moderately stirred neat octamethyltetrasiloxane [D_4 (17.3 g)] at 120 °C freshly re-crystallized (ethanol-water) dry benzoyl peroxide (450 mg) was gradually added (CAUTION! avoid an addition of big chunks/ portions; in total it may take about 1 h; the smoother the addition is, the higher is the yield). After completion, the reaction mixture was heated for an additional 30 min, cooled to room temperature and passed through a plug of activated alumina (2.5×3 cm) and washed with petrol ether. After removing of solvents under reduced pressure, D_4 was recovered by distillation in a vacuum of water-jet pump (b.p. 62–64°C/∼10 Torr). The residue was purified by multiple Kugelrohr distillations collecting a middle fraction boiling between 100–120 °C/0.01 mbar until the product is free of aromatic contaminations and crystallizes as colorless needles (m.p. 55 °C). Yield: 353 mg. \(^{1}H\) NMR (600 MHz, CDCl_3, 300 K) δ = 0.47 (s, 2 H, CH_2), 0.1–0.08 (m, 18 H, 6 CH_3), 0.08 (s, 3 H, CH_3) ppm. \(^{13}C\) NMR (150 MHz, CDCl_3, 300 K) δ = 8.2 (2 CH_2), 0.8 (6 CH_3), −1.6 (CH_3) ppm. \(^{29}Si\) NMR (119.3MHz, CDCl_3, 300 K) δ = −19.15, −19.24, −19.37 ppm.

2. Polymerization Catalyst.

A mixture of 3.3 mL (11 mmol, 1.1 equivalents) of D_4 and tetramethylammonium hydroxide pentahydrate (1.8 g, 10 mmol) was refluxed in benzene (60 mL) with Dean-Stark trap until the water doesn’t separated any more (typically overnight). At this point, the solution should be completely homogeneous. Then, the majority of benzene was distilled off at atmospheric pressure and the rest of volatile material was removed in high vacuum to result in a colorless waxy semisolid. It was transferred in a glove-box and used there without additional purification. The purity is estimated to be ∼75% from its crude \(^{1}H\) NMR spectra.

\(^{1}H\) NMR (400 MHz, CDCl_3, 300 K) δ = 2.79 (s, 24 H, 2 NMe_4), 0.44 (s, 12 H, 4 CH_3), 0.36 (s, 24 H, 8 CH_3) ppm.
3. Polymerization.

A 5-mL round-bottom flask was weighed in a glove-box and a little crumble of the polymerisation catalyst (see above) was stuck to the internal surface of the flask with spatula tip. A PTFE-coated stirring bar followed, the flask was closed with a septum and removed from the glove-box. 4 wt%-stock solution (4 wt%=2mol %) of bis-D₄ in D₄ was diluted with D₄ to reach the required cross-linker concentration (see above 0.5-2 mol%) and added by stirring to the polymerisation catalyst in such amount to adjust the catalysts concentration exactly to 0.12 mol %. After complete homogenization (about 30 min; don't wait any longer if you see it's dissolved, otherwise it might become too viscous for subsequent sampling with the syringe), the polymerizing mixture was withdrawn with syringe and evenly distributed within the array of semi-closed pieces of PTFE tube (ID 3 or 3.2 mm, l~25-30 mm) packed in the Schlenk tube under argon. The Schlenk was carefully (CAUTION! DO IT SLOWLY!) evacuated, purged with argon and placed in an oven pre-heated to 90 °C. To equalize the pressure in the reaction flask one can pierce the septum with a thin needle, or, more correctly, use any kind of "CaCl₂-tube" packed with activated molecular sieves. After the time required (typically, 5 h), the temperature was raised to 150 °C and polymerization was terminated (decatalysed, removal of NMe₃) by heating for at least 3 h. Then, the reaction vessel was cooled to room temperature under argon, the tipped ends of the PTFE-tubes were cut with a razor blade and thus prepared PDMS-sticks were pushed out by 2.5-3 mm rod. To protect the surface of the stick, a piece of finger-rolled cotton was placed between rod and stick. The freshly prepared PDMS sticks were dried at ambient temperature in vacuo (0.002 mbar) over night.
### Data for swelling of PDMS sticks in THF-$d_8$.

#### 1.2 mol% bis-D$_4$ in THF-$d_8$, at 300K. Start: 10/04/2013, 15:00.

<table>
<thead>
<tr>
<th>time, h</th>
<th>42h</th>
<th>+72h</th>
<th>+2h</th>
<th>+6h</th>
<th>+18h</th>
<th>+23h</th>
<th>+47h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta v_O$, Hz</td>
<td>4.4/3.6</td>
<td>7.0/5.6</td>
<td>7.1/5.7</td>
<td>7.2/5.8</td>
<td>7.5/5.9</td>
<td>7.8/6.2</td>
<td>8.1/6.4</td>
</tr>
</tbody>
</table>

Swelling has been performed at room temperature, measurement performed at 300K at an Avance-III-600 spectrometer.

#### 1.5 mol% bis-D$_4$ in THF-$d_8$, at 263K. Start: 23/05/2013, 18:00.

<table>
<thead>
<tr>
<th>time, h</th>
<th>161h</th>
<th>+25h</th>
<th>+26h</th>
<th>+34h</th>
<th>+8h</th>
</tr>
</thead>
<tbody>
<tr>
<td>date</td>
<td>30/05, 11:20</td>
<td>31/05, 12:27</td>
<td>01/06, 14:27</td>
<td>03/06, 00:48</td>
<td>03/06, 9:05</td>
</tr>
<tr>
<td>$\Delta v_O$, Hz</td>
<td>6.0/4.5</td>
<td>6.5/4.9</td>
<td>6.8/5.2</td>
<td>7.1/5.4</td>
<td>7.2/5.4</td>
</tr>
</tbody>
</table>

Swelling has been performed at 253K, measurement performed at 263K at an Avance-III-600 spectrometer.
RDC structure elucidation for β(-)-cariophyllene (BCP) in PDMS gel

NMR spectral assignment (CDCl₃ at 279 K) and RDC data

Previously, NMR experimental data [7] in Me₂O-d₆ or DFT calculated chemical shifts [8] were published. Here we provide the full NMR attribution of BCP in CDCl₃, including assignment of diastereotopic protons. For the spatial structure representation one can use the Cartesian coordinates for the three naturally populated conformers provided here below.

For the isotropic sample 50 µL of BCP was dissolved in 0.5 mL of CDCl₃. Anisotropic measurements were performed for a PDMS gel sample containing 1.3 mol% of cross-linker and solution of 5 µL of BCP in 1 mL of CDCl₃. About half of the BCP solution was placed at the bottom of an 5 mm OD NMR tube, then a PDMS stick (length 14 mm) was pushed inside using a rod such that the gel would be in the coil of NMR spectrometer. The rest of BCP/CDCl₃ solution was added to the top of the PDMS stick (the stick floats in CDCl₃ and needs to be hold covered by the solution by putting a rod on the top of the stick until the stick swells – usually a matter of 1-2 minutes). The anisotropic gel was then equilibrated at 279 K. All NMR measurements for both isotropic and anisotropic samples were performed at 279 K on Avance-III-600 spectrometer.
Table SI-1. Assignment and RDCs for αα/βα conformers (isochronous NMR signals) of BCP.

<table>
<thead>
<tr>
<th>C</th>
<th>δ_C, ppm</th>
<th>H</th>
<th>δ_H, ppm</th>
<th>NMR attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>53.3</td>
<td>H1</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>29.3</td>
<td>H2A</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2B</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>39.9</td>
<td>H3A</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H3B</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>135.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>124.2</td>
<td>H5</td>
<td>5.31</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>28.4</td>
<td>H6A</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H6B</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>34.7</td>
<td>H7A</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H7B</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>154.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>48.4</td>
<td>H9</td>
<td>2.32</td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>40.2</td>
<td>H10A</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H10B</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>16.3</td>
<td>H12</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>33.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>111.7</td>
<td>H13A</td>
<td>4.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H13B</td>
<td>4.94</td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>22.6</td>
<td>H14</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>C15</td>
<td>30.0</td>
<td>H15</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling nuclei</th>
<th>1Dexp, Hz</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CLIP HSQC</td>
<td>F1-cpd HSQC (MQ evol.)</td>
</tr>
<tr>
<td>C1</td>
<td>H1</td>
<td>3.37±0.10</td>
</tr>
<tr>
<td>C2</td>
<td>H2A</td>
<td>-0.50±0.30</td>
</tr>
<tr>
<td>C2</td>
<td>H2B</td>
<td>3.63±0.20</td>
</tr>
<tr>
<td>H2A</td>
<td>H2B</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>H3A</td>
<td>3.80±0.20</td>
</tr>
<tr>
<td>C3</td>
<td>H3B</td>
<td>-0.04±0.10</td>
</tr>
<tr>
<td>C5</td>
<td>H5</td>
<td>2.91±0.10</td>
</tr>
<tr>
<td>C6</td>
<td>H6A</td>
<td>1.79±0.30</td>
</tr>
<tr>
<td>C6</td>
<td>H6B</td>
<td>0.18±0.30</td>
</tr>
<tr>
<td>H6A</td>
<td>H6B</td>
<td>-</td>
</tr>
<tr>
<td>C7</td>
<td>H7A</td>
<td>1.45±0.50</td>
</tr>
<tr>
<td>C7</td>
<td>H7B</td>
<td>-0.01±0.30</td>
</tr>
<tr>
<td>C9</td>
<td>H9</td>
<td>3.61±0.10</td>
</tr>
<tr>
<td>C10</td>
<td>H10A</td>
<td>Str. Coupl. 8.47±0.10</td>
</tr>
<tr>
<td>C10</td>
<td>H10B</td>
<td>Str. Coupl. -4.78±0.10</td>
</tr>
<tr>
<td>H10A</td>
<td>H10B</td>
<td>-</td>
</tr>
<tr>
<td>C12</td>
<td>C4</td>
<td>0.28±0.10</td>
</tr>
<tr>
<td>C13</td>
<td>H13A</td>
<td>-1.23±0.10</td>
</tr>
<tr>
<td>C13</td>
<td>H13B</td>
<td>0.27±0.10</td>
</tr>
<tr>
<td>C14</td>
<td>C11</td>
<td>0.14±0.10</td>
</tr>
<tr>
<td>C15</td>
<td>C11</td>
<td>0.16±0.10</td>
</tr>
</tbody>
</table>
### Table SI-2. NMR signals assignment and RDCs of $\beta\beta$-conformer of BCP.

<table>
<thead>
<tr>
<th>NMR attribution</th>
<th>Coupling nuclei</th>
<th>$^{1}J_{Dexp},\ Hz$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CLIP HSQC</td>
</tr>
<tr>
<td>C</td>
<td>$\delta_C,\ ppm$</td>
<td>H</td>
</tr>
<tr>
<td>C1</td>
<td>55.7</td>
<td>H1</td>
</tr>
<tr>
<td>C2</td>
<td>31.3</td>
<td>H2A</td>
</tr>
<tr>
<td></td>
<td>H2B</td>
<td>1.55</td>
</tr>
<tr>
<td>C3</td>
<td>34.7</td>
<td>H3A</td>
</tr>
<tr>
<td></td>
<td>H3B</td>
<td>2.51</td>
</tr>
<tr>
<td>C4</td>
<td>135.1</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>124.4</td>
<td>H5</td>
</tr>
<tr>
<td>C6</td>
<td>29.3</td>
<td>H6A</td>
</tr>
<tr>
<td></td>
<td>H6B</td>
<td>2.11</td>
</tr>
<tr>
<td>C7</td>
<td>40.2</td>
<td>H7A</td>
</tr>
<tr>
<td></td>
<td>H7B</td>
<td>2.42</td>
</tr>
<tr>
<td>C8</td>
<td>155.0</td>
<td>-</td>
</tr>
<tr>
<td>C9</td>
<td>49.3</td>
<td>H9</td>
</tr>
<tr>
<td>C10</td>
<td>42.5</td>
<td>H10A</td>
</tr>
<tr>
<td></td>
<td>H10B</td>
<td>1.56</td>
</tr>
<tr>
<td>C11</td>
<td>32.6</td>
<td>-</td>
</tr>
<tr>
<td>C12</td>
<td>22.1</td>
<td>H12</td>
</tr>
<tr>
<td>C13</td>
<td>110.8</td>
<td>H13A</td>
</tr>
<tr>
<td></td>
<td>H13B</td>
<td>4.95</td>
</tr>
<tr>
<td>C14</td>
<td>21.9</td>
<td>H14</td>
</tr>
<tr>
<td>C15</td>
<td>29.7</td>
<td>H15</td>
</tr>
</tbody>
</table>
Cartesian coordinates for β-Caryophyllene conformers

Structural models for the RDC fits were generated computationally by geometry optimization using density functional theory as implemented in ORCA v3.0.1.9 While the previously published studies by Alagona et al.[8] give some torsion angles, electronic energies and predicted NMR chemical shifts, no Cartesian coordinates of the conformers are reported. Starting from a geometry used by Krupp et al.,[10] bonds were rotated manually into geometries resembling the αα, βα, ββ and αβ conformers reported by Alagona et al. These starting geometries were subsequently re-optimized at the B3LYP/def2-TZVP[11] level of theory. Numerical frequency analysis was performed to confirm the local minimum nature of the respective geometries. Table SI-3 compares the relevant torsion angles and relative conformer populations (derived from Boltzmann weighting) to those reported previously by Alagona et al. The αβ geometry is not expected to be populated significantly at room temperature and is not observed in the NMR measurements.

### Table SI-3. Comparison of DFT-optimized geometries calculated in this work with those reported previously by Alagona et al. (values given in parentheses).

<table>
<thead>
<tr>
<th>Conformer</th>
<th>C6-C7-C8-C13 torsion (deg.)</th>
<th>C2-C3-C4-C12 torsion (deg.)</th>
<th>ΔE (kJ/mol)*</th>
<th>Boltzmann population (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>αα</td>
<td>87.8 (84.5)</td>
<td>81.9 (82.6)</td>
<td>0.000 (0.000)</td>
<td>47.53 (54.12)</td>
</tr>
<tr>
<td>βα</td>
<td>-82.2 (-81.3)</td>
<td>83.2 (81.1)</td>
<td>0.847 (1.849)</td>
<td>33.77 (25.67)</td>
</tr>
<tr>
<td>ββ</td>
<td>-97.0 (-91.5)</td>
<td>-128.6 (-126.0)</td>
<td>2.313 (2.443)</td>
<td>18.69 (20.20)</td>
</tr>
<tr>
<td>αβ</td>
<td>83.4 (86.4)</td>
<td>-102.2 (-129.5)</td>
<td>21.543 (20.815)</td>
<td>0.01 (0.01)</td>
</tr>
</tbody>
</table>

* relative electronic energies. Values given by Alagona et al. in kcal/mol were converted to kJ/mol for comparison.
RDC cross-fits:

\( \beta \beta \)-BCP RDCs fitted to Cartesian coordinates of either \( \alpha \alpha \) conformer or \( \beta \alpha \) conformer

The results show that the RDC data of the \( \beta \beta \) conformer are described the best with the Cartesian coordinates of \( \beta \beta \) conformer (as judged from the lowest quality factor, see the main manuscript text). The cross fitting to the coordinates of other conformers give worse quality factors \( Q \).

**Fig. SI-1.** Correlation fit for 15 experimental and calculated RDCs for \( \beta \beta \) conformer of BCP and different Cartesian coordinates. Counterclockwise: \( \alpha \alpha \) conformer coordinates (Q-Factor 0.319), \( \beta \beta \) coordinates (Q-factor 0.074), \( \beta \alpha \) conformer coordinates (Q-Factor 0.319).
Anisotropic alignment study of (+)-isopinocampheol and its acetyl ester

Isopinocampheol (IPC) has been traditionally used as a test small molecule for the performance of new alignment media in our and other groups developing RDC methods for small organic molecules. Technically, one can prepare an aligned sample in two ways. First, the gel can be pre-swollen in pure solvent up to its equilibration point, when neither length nor ΔνQ of the gel changes anymore. The solution of a small molecule is then applied on the top of a pre-swollen gel and allowed to diffuse. The second option is to achieve simultaneous gel equilibration and analyte diffusion. The latter approach implies that the degree of alignment of a gel in the pure solvent is known.

We prepared samples either by simultaneous gel swelling and diffusion of the small molecule or diffusion of (+)-IPC into pre-swollen PDMS gel being applied in solution on the top of the gel. In both cases degradation of ΔνQ was observed, seen in 2H NMR spectra and images (Fig. SI-2).[12] For the sample, in which (+)-IPC diffused from the top of the gel, 2H NMR images indicate a ΔνQ reduction at the analyte location, propagating together with (+)-IPC diffusion (Fig. SI-3).

![Fig. SI-2](image.png)

**Fig. SI-2.** 2H NMR spectra (400 MHz): simultaneous swelling-diffusion of a 1.3 mol% PDMS gel in 8 mg (+)-IPC/1 mL CDCl₃ solution. The analyte diffusion in course of gel swelling is characterized by ΔνQ reduction (the value of ΔνQ in pure solvent is ca. 23 Hz).

![Fig. SI-3](image.png)

**Fig. SI-3.** 2H NMR image (400 MHz) of a gel when (+)-IPC/CDCl₃ was added on the top of a pre-swollen gel. We observed ΔνQ degradation for 1 and 1.3 mol% PDMS gels, commencing with the analyte diffusion (top of the graph corresponds to the top of the NMR tube).
We observed an elongation of the gel in (+)-IPC solution to the values higher than those seen in pure CDCl₃. This process was accompanied by gradual reduce of ΔνQ until the value of 0 Hz was reached, which is characteristic for isotropic systems. Moreover, a PDMS gel contacted with (+)-IPC for more than one month shortened in length and released viscous liquid, which later became significantly fluid. The gel could either shrunk or depolymerize in the (+)-IPC solution at the concentrations of 9 mg/mL. The ²⁹Si 1D and 2D NMR examination of the liquid, released from an (+)IPC/PDMS/CDCl₃ sample, evidences for the polymer chemical degradation: both liquid and an intact gel show a ²⁹Si NMR signal of dimethylsiloxanes at -21 ppm (Fig. SI-6) A 7-month old sample became completely isotropic.

**Interaction of PDMS with IPC**

The chemical degradation of PDMS gel in the fine solutions of (+)-IPC was surprising for us, especially because similar sticks earlier were reported to be successfully applied in a number of studies[13] but not for isopinocampheol. A synthesized (+)-IPC-derivative, O-capped with acetyl group, did not prevent the reduction of the ΔνQ but degradation seemed to slow down such that we were able to get 10 RDCs (in the range -4...+2 Hz) already after two days of diffusion. The experimental and theoretical RDC values are in agreement with the spatial structure of the molecule (Table SI-4 and Fig. SI-4).

The ability of PDMS to swell differently in solvents is of great concern in the development of micro devices and their components. Alcohols are not reported to be good solvents for PDMS, i.e. do not show high values of volume increase[14]. Thus, our results showing the independence of PDMS gel extension from alcohol or ester functionalities of (+)-IPC, on the one hand, coincide well with the general data for the polymer swelling properties. On the other hand, the information on chemical incompatibility of (+)-IPC and PDMS is potentially of big importance for further applications.

**(+)-Isopinocampheol acetate ((+)‐IPC-OAc).** 1M solution of (+)-isopinocampheol in pyridine was chilled on an ice bath and 2 eq. of acetic anhydride were added via septum. The reaction mixture was stirred for 5 hrs. on the ice-bath and then kept in a fridge until reaction completion. The reaction progress was monitored via TLC. The mixture then was poured on an ice cold HCl solution and the product was extracted in diethyl ether. The combined organic extractions were washed with 1M HCl, water and brine. The final ether solution was dried over MgSO₄ and the organic solvent was removed on a rotary evaporator providing dark-yellow liquid. Yield: 80%. Rₜ (EtOAc-PE, 1:5) 0.6. ¹H NMR (400 MHz, CDCl₃, 300 K) δ = 0.89 (CH₃-9, 3H, s), 0.98 (H-7a,1H, d, 9.9 Hz), 1.02 (CH₃-10, 3H, 7.4 Hz), 1.15 (CH₃-8, 3H, s), 1.58 (H-4a, 1H, ddd, 14.3x4.2x2.8 Hz), 1.75 (H-1, 1H, dd, 5.9x2.1 Hz), 1.86 (H-5, 1H, m), 1.99 (Ac-12, 3H, s), 2.04 (H-2, 1H, m), 2.30 (H-7s, 1H, m), 2.52 (H-4s, 1H, m), 4.96 (H-3, 1H, m) ppm. ¹³C NMR (100 MHz, CDCl₃, 300 K) δ = 20.5 (CH₃-10), 21.5 (Ac-12), 23.7 (CH₃-9), 27.5 (CH₃-8), 33.4 (C-7), 35.9 (C-4), 38.3 (C-6), 41.3 (C-5), 43.6 (C-2), 47.5 (C-1), 74.1 (C-3), 177.0 (CO-11) ppm.
RDC structure elucidation for (+)IPC-OAc

**Fig. SI-4.** Fragments of a CLIP HSQC spectrum (600 MHz) of (+)-IPC-OAc in CDCl$_3$ (left) and a spectrum of (+)-IPC-OAc recorded in 2.6% PDMS equilibrated in CDCl$_3$ (right). Selected 1D-slices of the F1-domain corresponding to diastereotopic protons H7s and H7a reveal high quality of the acquired data for the anisotropic spectrum.

**Table SI-4.** RDC data for IPC-OAc

<table>
<thead>
<tr>
<th>H atom</th>
<th>C atom</th>
<th>$^{1}D_{\text{exp}}$, Hz (CLIP HSQC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.05±1.00</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1.41±0.20</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-0.21±0.30</td>
</tr>
<tr>
<td>4s</td>
<td>4</td>
<td>0.65±0.20</td>
</tr>
<tr>
<td>4a</td>
<td>4</td>
<td>1.73±0.30</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>2.32±0.70</td>
</tr>
<tr>
<td>7s</td>
<td>7</td>
<td>-3.98±0.50</td>
</tr>
<tr>
<td>7a</td>
<td>7</td>
<td>-0.02±0.20</td>
</tr>
<tr>
<td>8*</td>
<td>6</td>
<td>-0.32±0.10</td>
</tr>
<tr>
<td>9*</td>
<td>6</td>
<td>0.05±0.05</td>
</tr>
<tr>
<td>10*</td>
<td>2</td>
<td>0.20±0.40</td>
</tr>
</tbody>
</table>

* C atom

**Fig. SI-5.** Correlation between calculated and experimental RDCs for (+)-IPC-OAc (Q-factor 0.108).
NMR Studies of PDMS-decomposition

In our experiments on PDMS gels equilibration with (+)-IPC and its acetyl ester we noticed the reduction of the length and decrease of the Δν₀ of the alignment medium. The same behavior is true not only for our chemically synthesized PDMS gels but also for a sample prepared by β-irradiation \(^{[10a]}\). On the photo (Figure SI-6) one can see the first step of visible gel changes, when it starts to be fluid. To probe whether chemical degradation or gel shrinkage took place, we analysed by NMR spectroscopy methods the ‘supernatant’ – the liquid above the gel level.

Figure SI-6. Photography of dissolving PDMS gel in IPC/CDCl₃ solution

\( ^{29}\text{Si} \) NMR spectroscopy of PDMS and oligodimethylsiloxanes

The ‘supernatant’ solution in CDCl₃ was analysed by 1D and 2D \(^{29}\text{Si} \) NMR spectroscopy. In \((^{1}\text{H}^{\text{29}\text{Si}})\) HMBC spectra of the liquid released from the (+)IPC/PDMS/CDCl₃ anisotropic system (Fig. SI-7a) and spectra of the intact PDMS/CDCl₃ (Fig. SI-7b) one can clearly see that ‘supernatant’ contains dimethylsiloxanes (-22 ppm in \(^{29}\text{Si} \)), i.e. chemical changes occur leading to the loss of the anisotropic properties of the gel. Measurements were performed on Avance-III-600 NMR spectrometer.

Fig. SI-7. \((^{1}\text{H}^{\text{29}\text{Si}})\) HMBC spectra of the depolymerized PDMS (a) and an intact gel (b).
**DOSY-study of PDMS-decomposition.**

A 2D DOSY spectrum (Bruker pulse program stebpwp1s, $\Delta = 200\text{ms}$, $\delta = 2\text{ ms}$, linear gradient 2-95% in 32 incremental steps, $G_{\text{max}}$ of the probe head in the z-direction is 50 G cm$^{-1}$)[2] of the ‘supernatant’ solution of a (1% PDMS gel/(+)-IPC) was obtained at 300 K on Avance-III HD-400 spectrometer (see Figure SI-8). The self-diffusion coefficients $D$ of TMS, (+)-IPC, residual CHCl$_3$ and oligodimethylsiloxanes were determined via standard monoexponential fitting analysis in Topspin 3.2. With $D = 1.93 \cdot 10^{-9}\text{ m}^2\text{s}^{-1}$, the experimental value for TMS in CDCl$_3$ is lower as compared to the measured at the same temperature previously published[15] value of $2.92 \cdot 10^{-9}\text{ m}^2\text{s}^{-1}$, which might be due to the presence of high content of oligomers in the mixture and thus a higher viscosity. For the depolymerized PDMS gel the estimated range of $D$ is about $(2.00-2.76) \cdot 10^{-11}\text{ m}^2\text{s}^{-1}$, i.e. two orders lower values than TMS corresponding to much slower diffusion. Unfortunately, the more precise determination of the self-diffusion coefficient, which could allow a determination of the molecular weight of the depolymerisation products, was not possible due to the broad MW distribution of the oligodimethylsiloxanes.

![DOSY spectrum](image)

**Fig. SI-8.** $^1\text{H}$ DOSY experiments confirm the presence of the de-polymerization products in CDCl$_3$ solution.

Thus chemical incompatibility of the PDMS gels and the bicyclic monoterpene (+)-isopinocampheol lead to chemical degradation of the gel, as seen in $^2\text{H}$ NMR, $^{29}\text{Si}$ NMR spectra and $^1\text{H}$ DOSY experiments. Esterification of the alcohol functionality allows performing RDC analysis but does not fully prevent degradation of anisotropic properties. The latter cannot be accounted for only by the alcohol functionality of the analyte. The reason for the chemical incompatibility of the polymer gel and the (+)-IPC ester is not yet known.
Predicting solvent quadrupolar splitting in a swollen gel

We consider a polymer network swollen by a deuterated solvent. Each molecule of solvent diffuses throughout the gel, interacting occasionally with the monomers of the polymer chains. During these encounters, the interactions between the partially aligned monomers of the chains and the solvent bias the orientation of the solvent molecule. The quadrupolar splitting of the solvent can thus be written as:

$$\Delta v_Q = \Delta v_Q^0 \varepsilon \phi S$$ (1)

where $\phi$ is the chain monomer volume fraction accounting for the probability of a solvent molecule to encounter a chain monomer, $S$ is the average of the second Legendre polynomial of monomer orientations, $\Delta v_Q^0$ is the quadrupolar splitting of perfectly aligned solvent molecules (for instance $\Delta v_Q^0 = 168$ kHz $^{16}$ for CDCl$_3$) and $\varepsilon$ is an efficiency factor accounting for the transfer of orientation between the monomers and the solvent molecules during a solvent-monomer encounter. Equation (1) can be equivalently understood by considering the time average of the second Legendre polynomial of solvent orientations. When the molecule diffuses freely away from the polymer chains, the molecular orientation state is described by an isotropic orientation distribution, and the measure of the second Legendre polynomial is averaged to zero. During a fraction $\phi$ of the total average time, when the solvent encounters a monomer of the polymer chain, its distribution is biased proportionally to the orientation state of the chain monomers. The efficiency of solvent orientation during this time fraction is a function of the detailed microscopic interactions between the chain monomers and the solvent molecules. Maximal quadrupolar splitting of the solvent $\Delta v_Q = \Delta v_Q^0$ would require thus small amounts of solvent $\phi \equiv 1$, completely aligned chains $S = 1$ and a perfectly efficient transfer of orientations $\varepsilon = 1$. Note that while $\phi$ and $S$ are determined by the experimental conditions, $\varepsilon$ is an intrinsic property of a given solvent/monomer pair. Tabulated values of $\varepsilon$ for different solvent/monomer pairs would therefore allow predicting the expected quadrupolar splitting for experiments performed under controlled swelling and stretching conditions. In the following we first review theoretical predictions for $S$ in stretched polymer gel networks, then provide explicit expectations in the case where gel stretching is caused by swelling in a tube. Finally, we compare our predictions with the data from the experiments discussed in this paper and extract the value of the orientation transfer efficiency for the pair PDMS/CDCl$_3$.

Orientation of chain monomers in a polymer gel. We first write (following Sommer & Saalwächter $^{17}$) the order parameter of the chain monomers as

$$S = \frac{R^2}{R_0^4}$$ (2)

Where $R$ is the end-to-end distance of a polymer chain of $N$ monomers connecting two cross-linking points and $R_0$ the average size of that chain in a given reference polymer solution with the same monomer volume fraction. Note that the average value of $N$ is
related to the crosslinking molar fraction $X_{CR}$ by $N = 2/(z X_{CR})$ where $z$ is the crosslinker functionality. In our case where $z = 4$ one has $N = 1/(2 X_{CR})$.

We have, respectively for the ideal chain and for Flory excluded volume conditions

$$S_{id} = \frac{1}{N} \phi^{-2/3} \quad \text{and} \quad S_F = \frac{1}{N} \phi^{-1/6} \quad (3)$$

When the gel swells isotropically in an excess of solvent the prediction for the equilibrium volume fraction is

$$\phi_{id}^{eq} = N^{-3/8} \quad \text{and} \quad \phi_F^{eq} = N^{-3/5} \quad (4)$$

so that

$$S_{id}^{eq} = (\phi_{id}^{eq})^2 \quad \text{and} \quad S_F^{eq} = (\phi_{id}^{eq})^{3/2} \quad (5)$$

A molecule of solvent diffusing in a polymer gel probes many chain orientations during the NMR typical times (10⁻⁶ s), resulting in a vanishing average for the order parameter $S$. However, if one stretches the gel, a stress-induced anisotropy results that, for the case of uniaxial deformations along the Z-direction ($R_x$, $R_y$, $R_z$) → ($R_x\lambda^{-1/2}$, $R_y\lambda^{-1/2}$, $R_z\lambda$), can be written as

$$S = \frac{R^2}{R_0^2} (\lambda^2 - \frac{1}{\lambda}) \quad (6)$$

with corresponding values for $S$ resulting from different solvent conditions (ideal versus good solvent) following from (3) and (5).

**Swelling in a tube.** A typical NMR experiment is performed by inserting a cylindrical piece of a dry gel of diameter $D_0$ and length $L_0$ in an NMR tube of internal diameter $D_T$. The gel is then exposed to solvent and let swell to a length $L$. The polymer volume fraction $\phi$ is given by

$$\phi = \frac{D_0^2 L_0}{D_T^2 L} \quad (7)$$

If the cylindrical dry gel had been allowed to swell isotropically in free solvent, it would swell to dimensions

$$D_I = D_0 \phi^{-1/3}$$

$$L_I = L_0 \phi^{-1/3}$$

By measuring the deformation $\lambda$ with respect to the isotropically swollen state we get

$$\lambda = \frac{L}{L_I} = \frac{L}{L_0} \phi^{1/3} = \left(\frac{D_I}{D_T}\right)^2 = \left(\frac{D_0}{D_T}\right)^2 \phi^{-2/3} \quad (8)$$

Swelling of a gel in a tube then induces concomitantly a decrease of monomer volume fraction $\phi$ and an increase in anisotropy.

For a gel swollen in a tube we expect thus (from (1), (3), (6) and (8))
\[ \Delta v_Q^{id} = \Delta v_Q^0 \varepsilon \frac{1}{N} \phi^{1/3} \left( \frac{D_0}{D_T} \right)^4 \phi^{-4/3} - \left( \frac{D_T}{D_0} \right)^2 \phi^{2/3} \]  

(9a)

for ideal conditions and

\[ \Delta v_Q^F = \Delta v_Q^0 \varepsilon \frac{1}{N} \phi^{5/6} \left( \frac{D_0}{D_T} \right)^4 \phi^{-4/3} - \left( \frac{D_T}{D_0} \right)^2 \phi^{2/3} \]  

(9b)

for good solvent conditions. When the gel reaches maximum (equilibrium) swelling one gets

\[ \Delta v_Q^{id,eq} = \Delta v_Q^0 \varepsilon \left( \frac{D_0}{D_T} \right)^4 N^{-5/8} - \left( \frac{D_T}{D_0} \right)^2 N^{-11/8} \]  

(10a)

for ideal swelling and

\[ \Delta v_Q^{F,eq} = \Delta v_Q^0 \varepsilon \left( \frac{D_0}{D_T} \right)^4 N^{-7/10} - \left( \frac{D_T}{D_0} \right)^2 N^{-19/10} \]  

(10b)

for swelling under excluded volume. Note, that the maximum \( \Delta v \) achievable in a tube is given by

\[ \Delta v_Q^{id,eq} = \Delta v_Q^0 \varepsilon \left( \frac{D_0}{D_T} \right)^{15/2} \frac{12}{19} \left( \frac{7}{19} \right)^{7/2} \]  

for \( N = \frac{11}{5} \) and

\[ \Delta v_Q^{F,eq} = \Delta v_Q^0 \varepsilon \left( \frac{D_0}{D_T} \right)^{15/2} \frac{12}{19} \left( \frac{7}{19} \right)^{7/2} \]  

for \( N = \frac{10}{7} \)

\((11a)\) and

\((11b)\)

**Comparison with experiments.** PDMS gels of diameter \( D_0 = 3 \) or 3.2 mm and length \( L_0 = 14 \) mm with different degrees of cross-linking (0.5, 1.0, 1.3, 1.5 and 2.0 mol\% or, equivalently, \( X_{CR} = 0.005, 0.010, 0.013, 0.015 \) and 0.020 corresponding to \( N = 100, 50, 38, 33 \) and 25) were swollen in NMR tubes with internal diameters \( D_T = 4.20 \) mm for the two most cross-linked samples and \( D_T = 4.09 \) for the three others. Swelling and equilibration of the gel is relatively fast, \( \Delta v_Q \) reaching stable values after one week for most cases. As the Fig. 1 in the main paper shows, all samples swollen for a period of four days or more exhibit homogeneous \( \Delta v_Q \) in the region captured by the NMR coil. The values of \( \Delta v_Q \) first increase with time, eventually reaching the plateau value of fully equilibrated gels.

We first plot in **Figs. SI-(9-12)** the bare data from PDMS sticks anisotropic swollen in an NMR tube, while one monitors the length of the gels and the values of quadrupolar splitting of CDCl\(_3\) in \(^2\)H NMR spectra. **Fig. SI-9** plots the increase in relative length \( L/L_0 \) of the gel sticks as a function of time. After a period of 20 to 40 days all samples have reached plateau conditions corresponding to maximum relative extensions in the range 2-4, with larger extensions being achieved for gels with smaller crosslinking fractions.
Fig. SI-9. Relative length $L/L_0$ as a function of time $t$, in days (0.5 mol% cross-linker - squares, 1.0 mol% - triangles, 1.3 mol% -circles).

For the relative extension values $L/L_0$ in Fig. SI-9, we display in Fig. SI-10 the corresponding evolution of the monomer volume fraction in the gel, as given by Eq. (7). Under the experimental conditions of this paper, as the gels swell, they span monomer volume fractions from $\phi = 1$ in the dry state down to $\phi \approx 0.15$ for the less cross-linked samples in the fully swollen state.

Fig. SI-10. Volume fraction $\phi$ of PDMS in a gel as a function of time $t$, in days (0.5 mol% cross-linker - squares, 1.0 mol% - triangles, 1.3 mol% -circles)

Fig. SI-11 shows the time evolution of the measured values for the quadrupolar splitting $\Delta v_0$. Note that the measured quadrupolar splitting values are in the range 5-25 Hz, tens of thousand times smaller than the maximum possible values ($\Delta v_0^0=168$ kHz) for perfectly aligned CDCl$_3$ molecules.
We plot also in Fig. SI-12 the evolution of quadrupolar splitting values $\Delta \nu_Q$ as a function of relative gel extension. The figure shows well that under these experimental conditions of constrained gel swelling, the measured $\Delta \nu_Q$ values are not a function of chain stretching alone, since the larger stretching ratios, achieved for less cross-linked gels, do not translate into higher $\Delta \nu_Q$ values.

We now analyze the bare data in Figs. SI-(9-12) according to the prescriptions of the theoretical arguments presented above. We first characterize the prevailing statistical conditions of the chains in the gel network, by plotting the equilibrium swelling fractions $\phi^{eq}$ in Fig. SI-13 as a function of the molar cross-link fraction $X_{CR}$: we found that they follow the standard Flory-Rehner\cite{18} predictions for the swelling of gels in an ideal solvent - see Eq. (4) $\phi^{eq} \sim X_{CR}^{3/8}$. This shows that N, the average size of polymer strands between crosslinking points, spans a value range not large enough for reaching conditions where excluded-volume statistics applies. The larger value N=100 is obtained for the lower $X_{CR} = 0.005$, while the larger cross-linking fraction $X_{CR} = 0.02$ corresponds to N=25.
**Fig. SI-13.** Equilibrium volume fraction $\phi^{eq}$ of PDMS in a gel as a function of the molar fraction of the cross-linker $X_{CR}$. Note, that the average chain length $N$ between two cross-linking points is given by $N = 1/(2X_{CR})$ and thus varies here between $N=25$ for $X_{CR} = 0.02$ and $N=100$ for $X_{CR} = 0.005$. The line is the best power-law fit to the data $\phi^{eq} = 1.05 X_{CR}^{3/8}$.

We plot in **Fig. SI-14** $\Delta\nu_Q$ as a function of polymer volume fraction for the five different $X_{CR}$ values available. Interestingly, for samples with $N=50$ and $N=38$, ideal statistics provides the best fit with Eq. (9a), while for the largest $N$ value, excluded volume statistics applies as described in Eq. (9b). This is consistent with ideal swelling conditions applying throughout most of the explored cross-linking density range, the sample with $N=100$ being at the crossover between ideal and excluded volume statistics. For the two samples where only equilibrated properties have been measured $X_{CR} = 0.015$ and $X_{CR} = 0.020$, we assumed ideal conditions and extracted the corresponding $\varepsilon$ values by assuming $\Delta\nu_Q^0=168$ kHz. Fitted $\varepsilon$ efficiencies for the five samples range from $\varepsilon = 5.9 \times 10^{-3}$ to $\varepsilon = 7.1 \times 10^{-3}$.

**Fig. SI-14.** Quadrupolar splitting $\Delta\nu_Q$ in Hz as a function of the volume fraction $\phi$. The lines are best fits according to the Eqs. (9) with $\Delta\nu_Q^0=168$ kHz, providing $\varepsilon = 6.5 \pm 0.5 \times 10^{-3}$ ((0.5 mol\% cross-linker - squares, 1.0 mol\% - triangles, 1.3 mol\% -circles), 1.5 mol\% - empty squares, 2.0 mol\% - filled triangles)

Our results are thus well described by Eq. (1) and the associated $\phi$ dependent curves of Eqs. (9), confirming the physical picture developed above. In particular, it is clear from our data, that solvent quadrupolar splitting in gels swollen in a tube cannot be understood by gel stretching alone, since larger stretching is achieved for more diluted gels, where the probability of encounters between the solvent and the chain monomers is smaller. Our arguments account for the interplay between these two opposing effects and quantitatively describe the data. The analysis further stresses the importance of $\varepsilon$, the efficiency of transfer of the orientation from the monomers to the solvent molecules. This parameter, found here for PDMS and chloroform to be of the order of 1/150, is expected for most systems to be an intrinsic property of a given solvent/monomer pair, but otherwise independent of experimental conditions. Anticipated exceptions are briefly discussed at the end of this section.
A clear picture emerges from our description that accounts for the quadrupolar splitting values observed under these experimental conditions. The reference value for solvent quadrupolar splitting, its maximum attainable value, is of order of a couple of hundred kilohertz. Dilution of the gel to the range of 10% volume fraction reduces this amount to the order of a couple of tens of kilohertz. Monomer orientation order parameters $S$, even for gels stretched in the tube by a factor four, do not rise about 0.2, bringing for these experimental conditions the maximum orientation power of the gel network to the range of a few thousand hertz. How much this orientation potential can be transferred to the solvent depends on the microscopic nature of the interactions between the monomers and the solvent during the time length of an encounter. We found here that such transfer is smaller than a percent for the PDMS/CDCl$_3$ pair, bringing thus the final observed values to the range of a few tens of hertz.

In practice we expect, as values of the efficiency of orientation transfer will become available for other monomer/solvent pairs, that our approach will provide a widely applicable, quantitative pathway to understand and predict the amount of quadrupolar splitting that one can expect for a given experimental geometry. Indeed, given the efficiency of the gel/solvent pair, the simple knowledge of the gel size and cross-linking ratio will allow predicting quadrupolar splitting values.

Note that our treatment of solvent quadrupolar splitting given by Eq. (1) is similar to others$^{[20]}$, but introduces explicitly the probability of interaction between solvent and chains, given by the dilution factor $\phi$ in the equation, and identifies $\varepsilon$ the efficiency for transfer of orientation. A more in-depth study of the validity of Eq. (1), and in particular on its dependence on the order parameter $S$ of the monomers, is in principle possible by using a combination of deuterated solvents with non-deuterated chains, and deuterated chains with non-deuterated solvents. This might be crucial if, as we anticipate here, there are certain cases where $\varepsilon$ might be $S$-dependent, for instance when the size of the solvent molecule is much larger that the size of the chain monomers, and the resulting interactions between the chain monomer and the solvent lose their local character.

Being able to quantitatively treat quadrupolar splitting in anisotropically swollen gels will not only provide an operational framework for dealing with orientation media in RDC experiments, but will also open a spectrum of new interesting possibilities to study the interactions of gels with different molecules. A particularly relevant example concerns gel swelling in solvent mixtures, say for the sake of clarity, in binary solvent mixtures. Since the value of quadrupolar splitting depends explicitly on the probability of encounter between a given solvent molecule and the chain monomers, the dependence of measured values of quadrupolar splitting $\Delta \nu_Q$ as a function of $X$, the molar ratio of one of the solvents in the mixture, should be very sensitive to phenomena akin to preferential solvation. Thus, we would expect a smooth linear interpolation between two values for $\Delta \nu_Q$ as a function of $X$ if the two solvents are equally good for the polymer, while any preferential solvent character will increase its probability of contact with the chains above its average value, promoting markedly non-linear variations of $\Delta \nu_Q$ with $X$. 

\[ \text{S25} \]
NMR spectra

$^1$H NMR of BCP/CDCl$_3$, 279 K

50 ul BCP/0.5 ml CDCl$_3$

1H

279 K
$^{13}$C NMR of BCP/CDCl$_3$, 279 K
50 µl BCP/ 0.5 ml CDCl$_3$
$^{13}$C
279 K
$^1$H NMR of (+)IPC-OAc/CDCl$_3$, 279 K

IPC-OAc in CDCl$_3$
279 K
1H

Current Data Parameters
NAME         Yulia-600_IPC-OAc
EXPNO               1
PROCNO             1

F2 - Acquisition Parameters
Date          20140913
Time           8.06
INSTRUM      spect
PROBND     5 mm TBI 1H/31PUL
PULPROG        zg30
TD            65536
SOLVENT     CDCl$_3$
NS             16
DS            0
SNH          12335.526 Hz
FIDRES      0.188225 Hz
AQ               2.6563926 sec
RG             22.7
DM            48.533 usec
DE             6.50 usec
TE             279.0 K
D1       3.000000000 sec
TDO             1

--- CHANNEL f1 ---

SFO1     600.3037071 MHz
NUC1        1H
F1           9.50 usec
PLW1     14.000000000 W

F2 - Processing parameters
SI           65536
SF         600.3000447 MHz
WMW           no
SSB            0
LB            0 Hz
GB            0
PC             1.00

S28
$^{13}$C NMR of (+)IPC-OAc/CDCl$_3$, 279 K

Current Data Parameters
NAME     Yulia-600_IPC-OAc
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date          20140909
Time               7.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl$_3$
NS            1024
DG            0
SNR               24038.461 Hz
FIDRES      0.366798 Hz
AQ           1.3651488 sec
RG            2050
DM            20.800 usec
DE            6.50 usec
TE            300.0 K
D1          2.00000000 sec
D11        0.03000000 sec
TD0                 4

******* CHANNEL f1 *******
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        63.00000000 W

******* CHANNEL f2 *******
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2           90.00 usec
PLM216 16.00000000 W
PLM12          0.19753000 W
PLM13           0.16000000 W

F2 - Processing parameters
SI            32768
SF         100.6127685 MHz
WGN            EM
SSB            0
LB            1.00 Hz
CB            0
FC            1.40
CLIP HSQC of BCP/CDCl₃, 279 K

Current Data Parameters

- **NAME**: yulia-600_b-caryophyllene
- **EXPNO**: 60
- **PROCNO**: 1

**F2 - Acquisition Parameters**

- **Date**: 20150116
- **Time**: 13.15
- **INSTRUM**: spect
- **PROBHD**: 5 mm TBI 1H/31
- **PULPROG**: hsqcetgpipjcsp.2TD
- **SOLVENT**: CDCl₃
- **NS**: 8
- **DS**: 32
- **SWH**: 2000000000.0000000 sec
- **D1**: 1.50000000 sec
- **D4**: 0.00172414 sec
- **D16**: 0.00020000 sec
- **IN0**: 0.00002010 sec
- **ZGOPTNS**:

**======== CHANNEL f1 ========**

- **SFO1**: 600.3024012 MHz
- **NUC1**: 1H
- **P1**: 9.50 usec
- **P2**: 19.00 usec
- **P28**: 0 usec
- **PLW1**: 14.00000000 W

**======== CHANNEL f2 ========**

- **SFO2**: 150.9561212 MHz
- **NUC2**: 13CP
- **P14**: 500.00 usec
- **P24**: ...
- **SPW3**: 36.15000153 W
- **SPNAM[7]**: Crp60comp.4
- **SPOAL7**: 0.500
- **SPOFFS7**: 0 Hz
- **SPW7**: 36.15000153 W

**====== GRADIENT CHANNEL =====**

- **GPNAM[1]**: SMSQ10.100
- **GPNAM[2]**: SMSQ10.100
- **GPZ1**: 80.00 %
- **GPZ2**: 20.10 %
- **P16**: 1000.00 usec

**F1 - Acquisition parameters**

- **TD**: 256
- **FIDRES**: 97.170395 Hz
- **SW**: 164.787 ppm
- **FnMODE**: Echo-Antiecho

**F2 - Processing parameters**

- **SI**: 8192
- **SF**: 600.3000000 MHz
- **WDW**: QSINESSB
- **LB**: 0 Hz
- **GB**: 0
- **PC**: 1.40

**F1 - Processing parameters**

- **SI**: 2048
- **MC2**: echo-antiecho
- **SF**: 150.9455551 MHz
- **WDW**: QSINESSB
- **LB**: 0 Hz
- **GB**: 0
CLIP HSQC of BCP/2.6% PDMS/CDCl₃, 279 K
$F_1$-coupled HSQC (BIRD-filtered variant, scaling factor =8) of BCP/CDCl$_3$, 279 K
$F_1$-coupled HSQC (BIRD-filtered variant, scaling factor =8) of BCP/2.6% PDMS/CDCl$_3$, 279 K
$F_1$-coupled HSQC with MQ evolution of BCP/CDCl$_3$, 279 K
$F_1$-coupled HSQC with MQ evolution of BCP/2.6% PDMS/CDCl$_3$, 279 K
CLIP HSQC of IPC-OAc/CDCl₃, 279 K
CLIP HSQC of IPC-OAc /2.6% PDMS/CDCl₃, 279 K
References and Notes