SUPPORTING INFORMATION

^{13}C NMR Investigations of Hairy-Rod Like π -Conjugated Mesogens

A. A. Boopathi[†⊥], K. Janani[†], Nitin P. Lobo[‡⊥] and T. Narasimhaswamy[†⊥*]

[†]Polymer Science and Technology, [‡]Inorganic and Physical Chemistry,

CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India

[⊥]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, Uttar Pradesh 201002, India

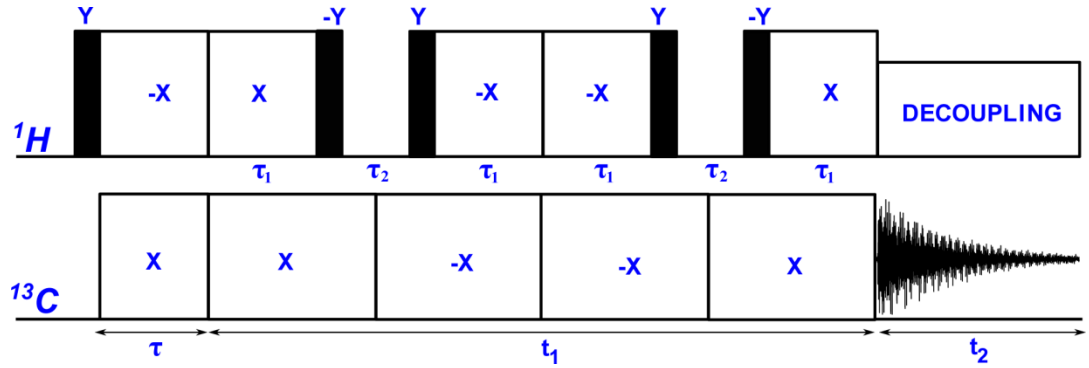

Figure S1: Pulse sequence for SAMPI-4 experiment, which is a CP based SLF scheme provides the 2D correlation spectrum between ^{13}C chemical shift (in F2 dimension) and related ^{13}C-^{1}H dipolar frequency (F1 dimension). Experiment starts with a cross-polarization (CP) block with a polarization inversion for a contact time τ, then during the t_1 period high resolution heteronuclear ^{13}C-^{1}H dipolar couplings evolves under the absence of homonuclear ^{1}H-^{1}H dipolar couplings (suppressed by "magic sandwich" pulses) and finally ^{13}C signals are acquired by employing SPINAL-64 heteronuclear decoupling pulse scheme during t_2 period. Here the darker boxes represent 90° pulses.

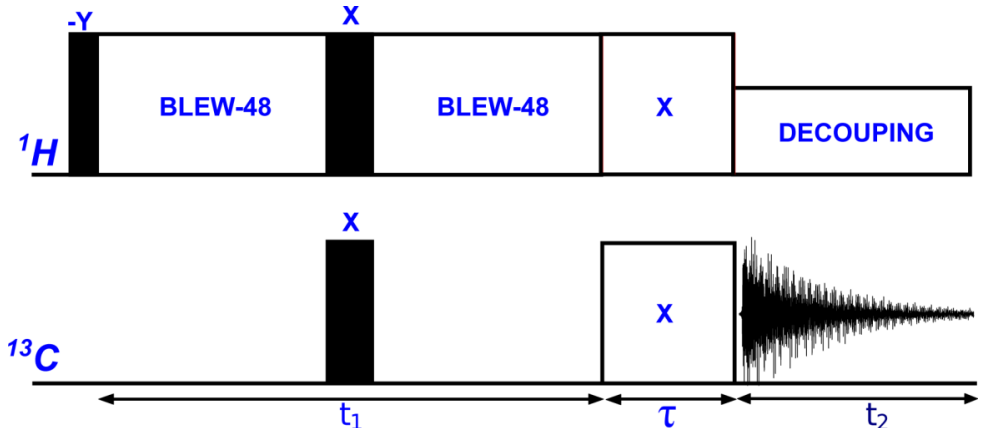

Figure S2: Pulse sequence for 2D Proton Encoded Local Field (PELF) experiment. During t_1 heteronuclear ^{13}C-^{1}H dipolar couplings evolves under BLEW-48 homonuclear decoupling sequence to suppress the homonuclear ^{1}H-^{1}H dipolar couplings and SPINAL-64 heteronuclear decoupling sequence is applied during t_2 period to acquire ^{13}C signals. CP step with a contact time, τ was used to transfer proton magnetization to carbon. Here, thin and thick rectangular darker boxes represent 90° and 180° pulses, respectively.

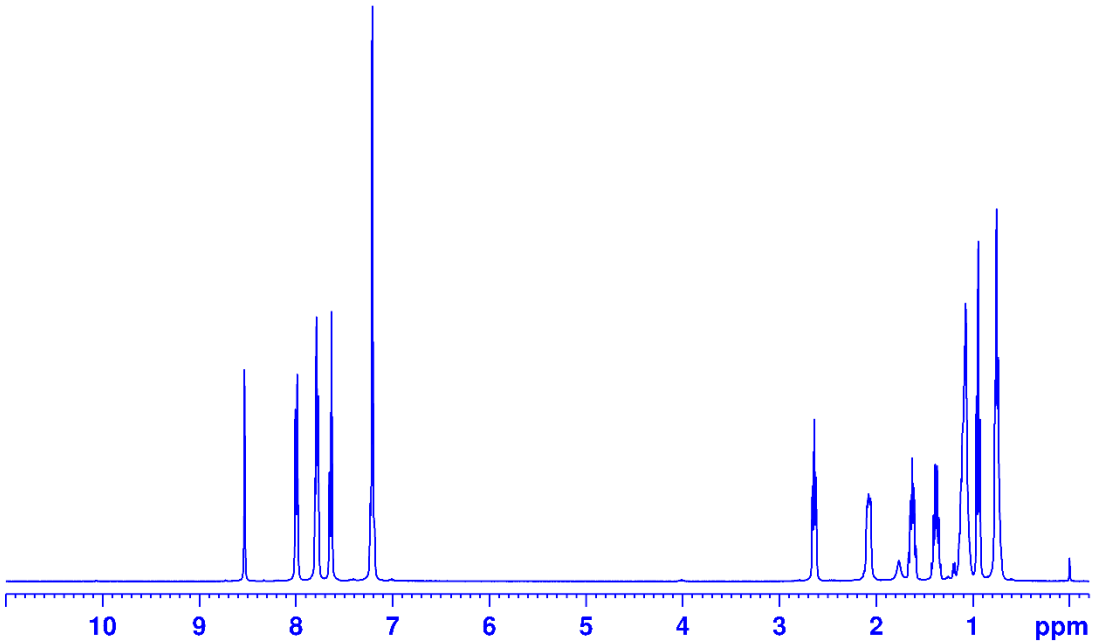

Figure S3: ^{1}H NMR Spectrum of DFDPBM

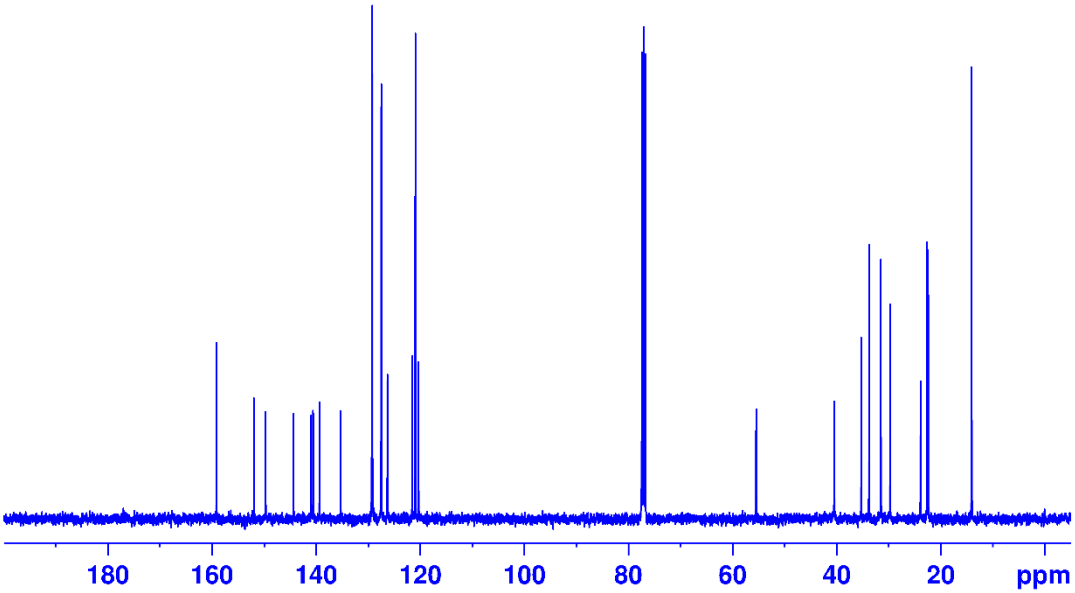

Figure S4: ^{13}C NMR Spectrum of DFDPBM

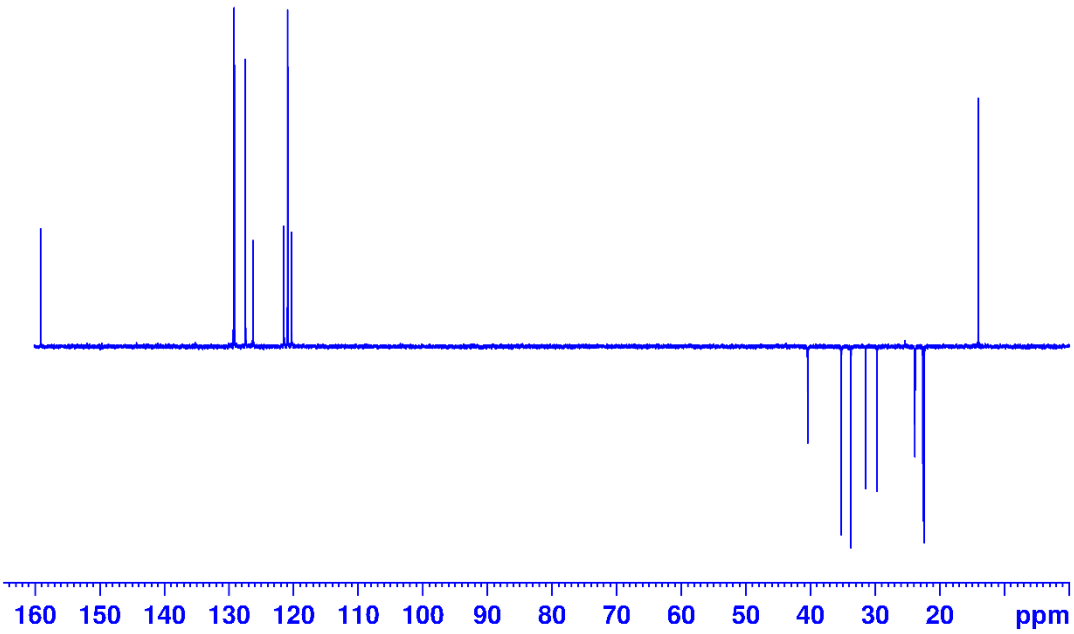

Figure S5: ^{13}C DEPT Spectrum of DFDPBM

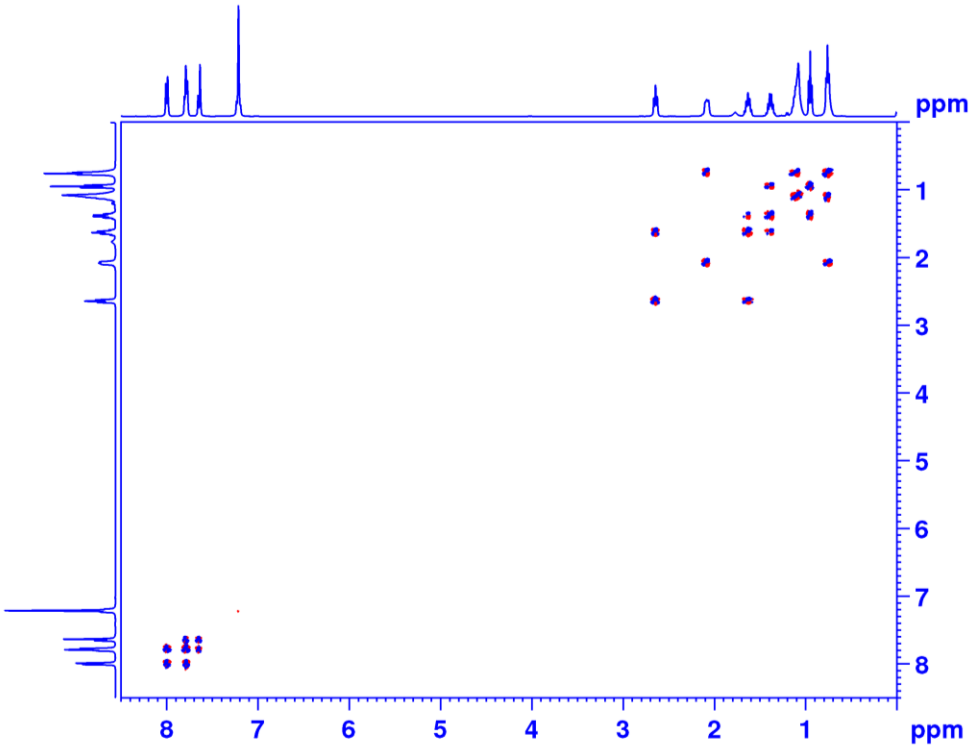

Figure S6: ^{1}H-^{1}H DQF-COSY NMR Spectrum of DFDPBM

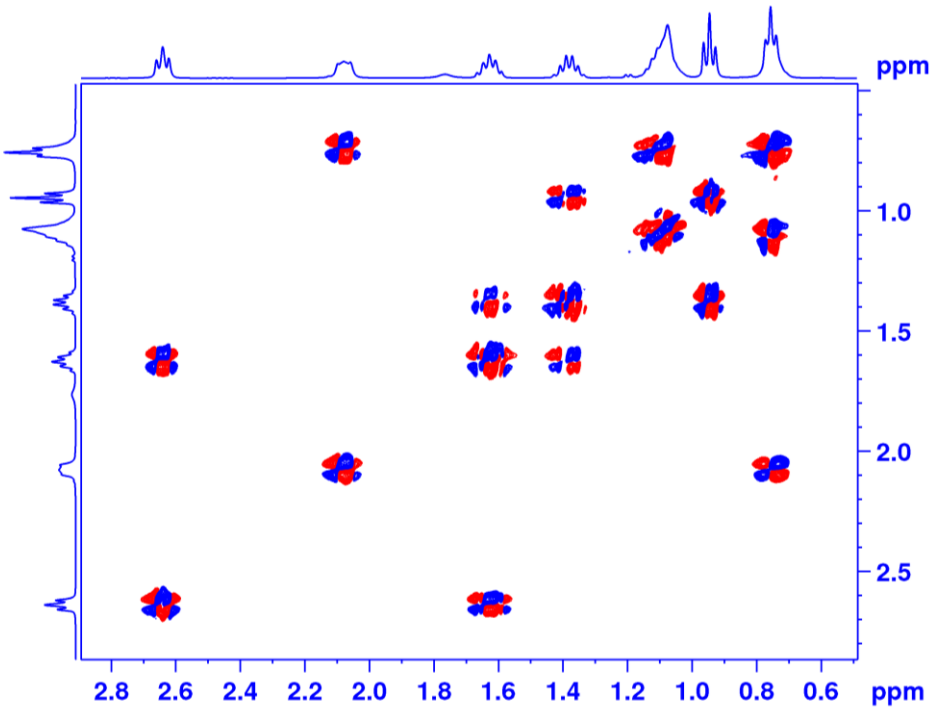

Figure S7:^{1}H-^{1}H DQF-COSY NMR Spectrum of DFDPBM: aliphatic region expansion

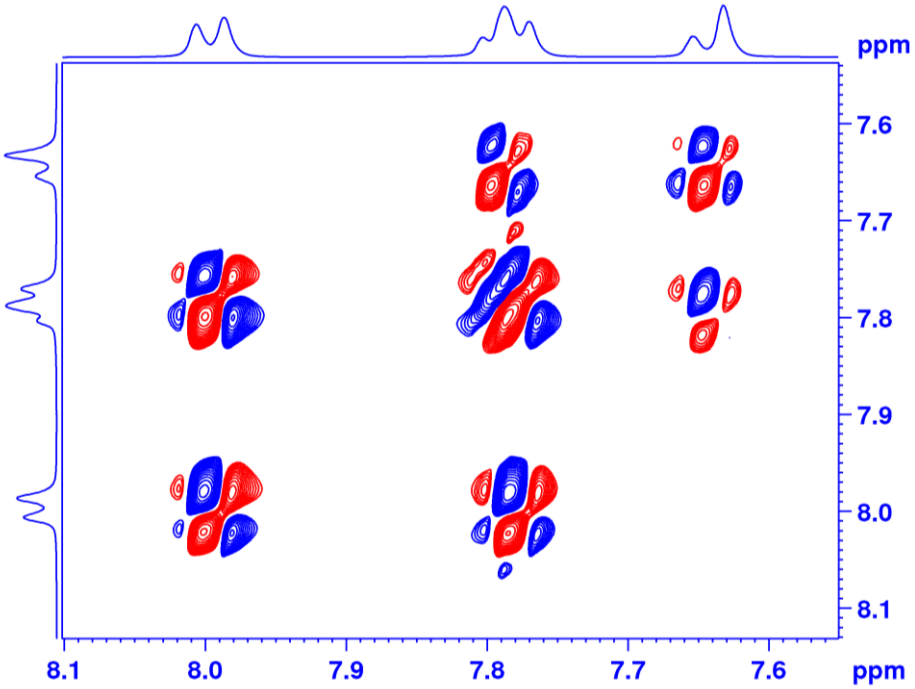

Figure S8:^{1}H-^{1}H DQF-COSY NMR Spectrum of DFDPBM: aromatic region expansion

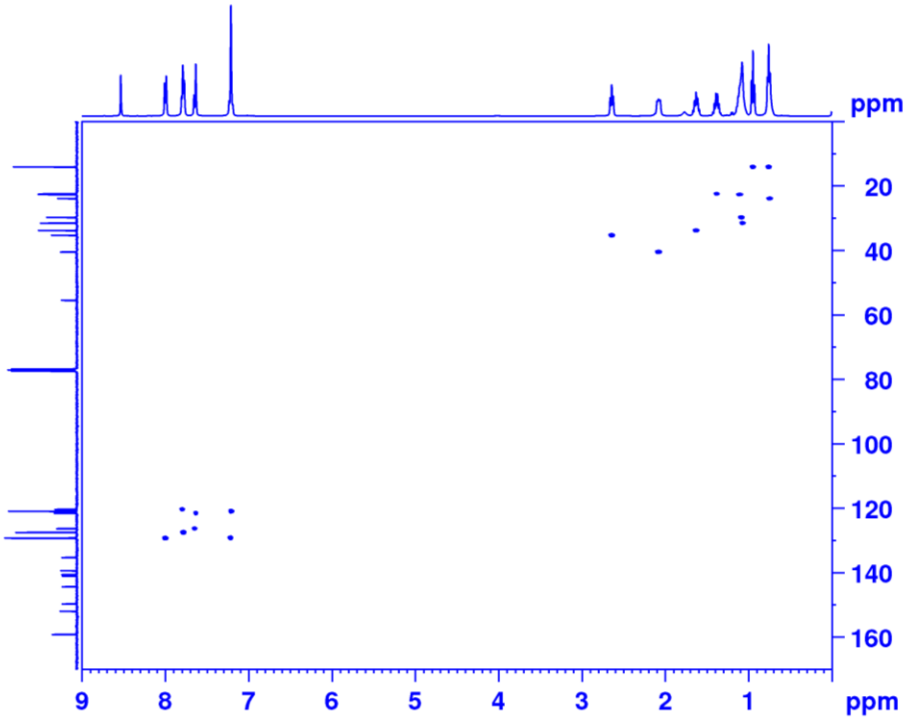

Figure S9: ^{1}H-^{13}C HSQC NMR Spectrum of DFDPBM

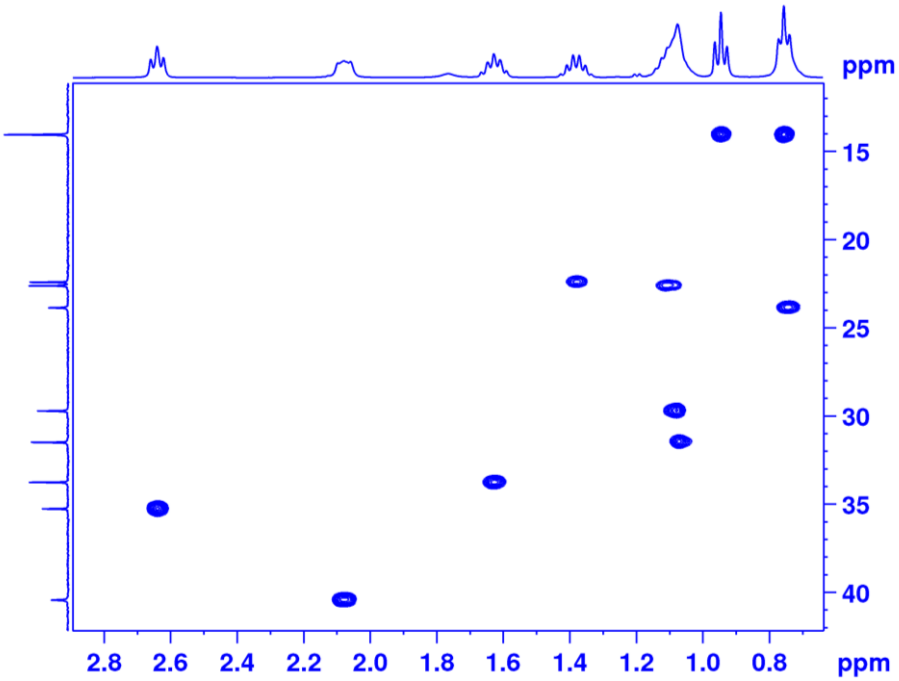

Figure S10: ^{1}H-^{13}C HSQC NMR Spectrum of DFDPBM: aliphatic region expansion

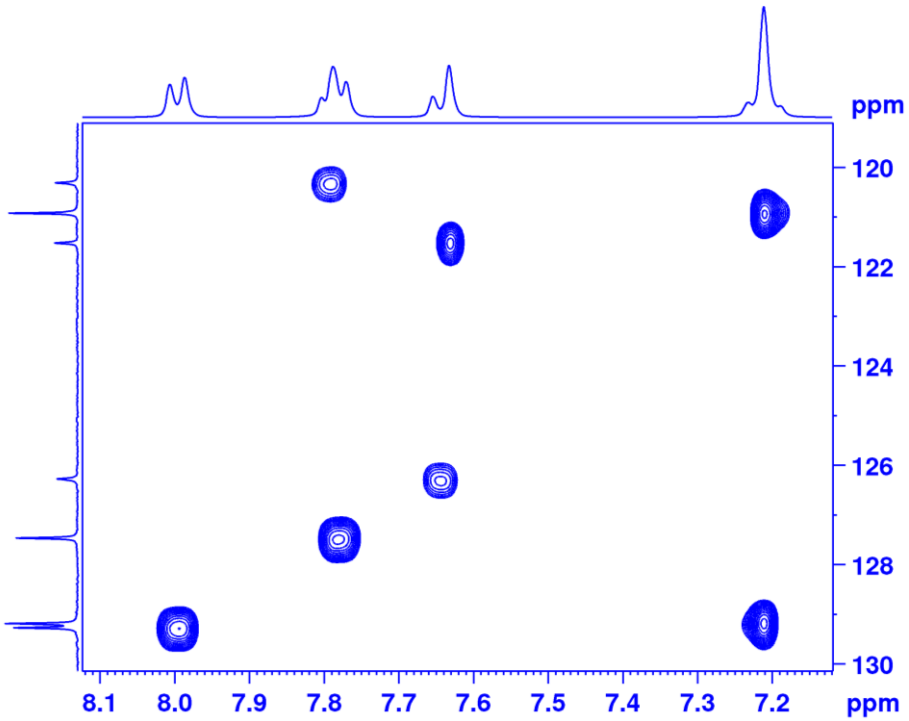

Figure S11: ^{1}H-^{13}C HSQC NMR Spectrum of DFDPBM: aromatic region expansion

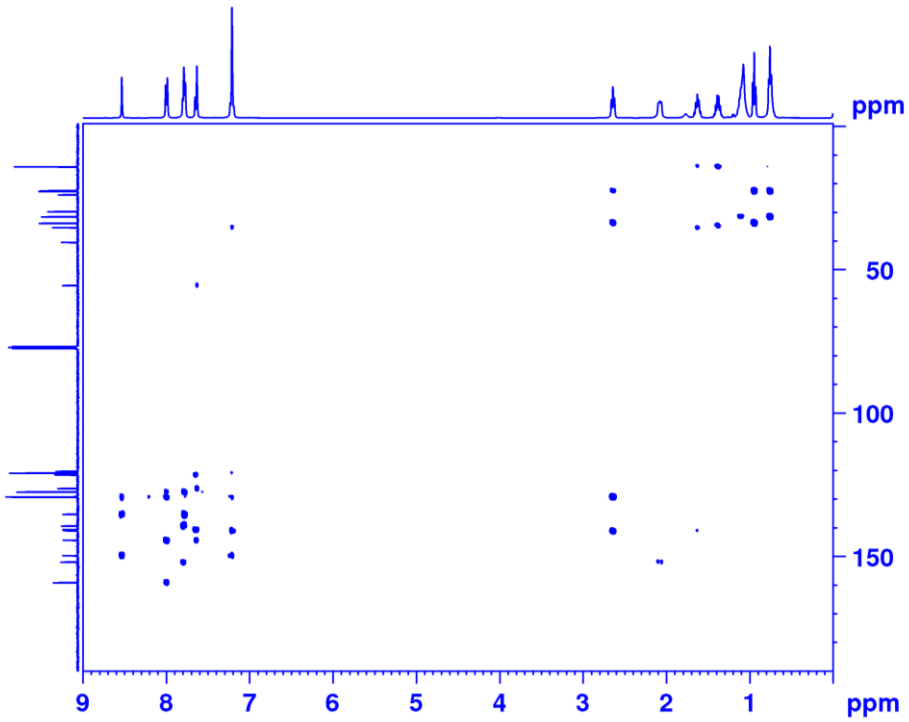

Figure S12: ^{1}H-^{13}C HMBC NMR Spectrum of DFDPBM

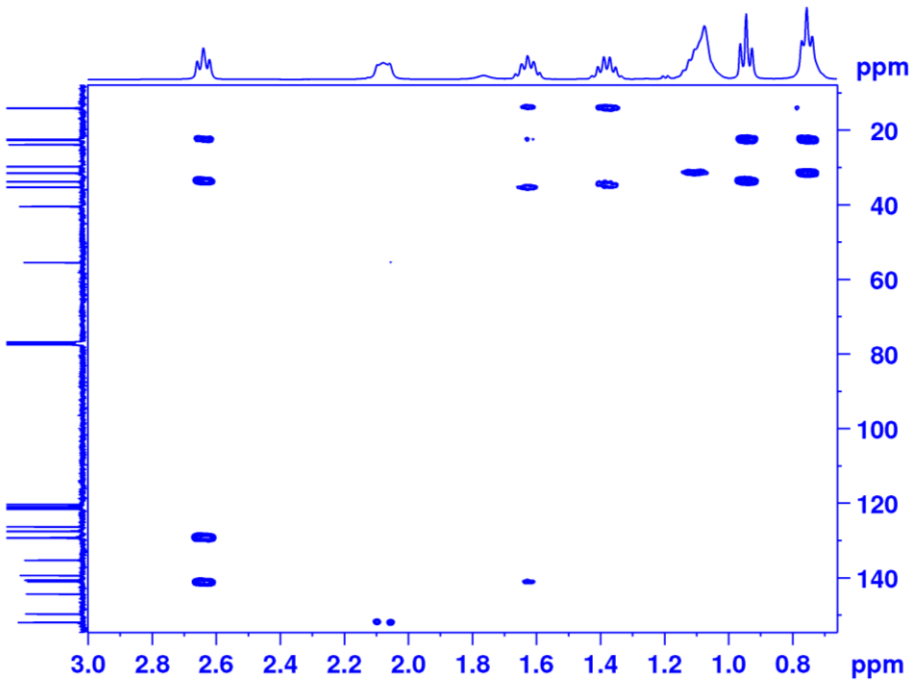

Figure S13: ^{1}H-^{13}C HMBC NMR Spectrum of DFDPBM: aliphatic region expansion

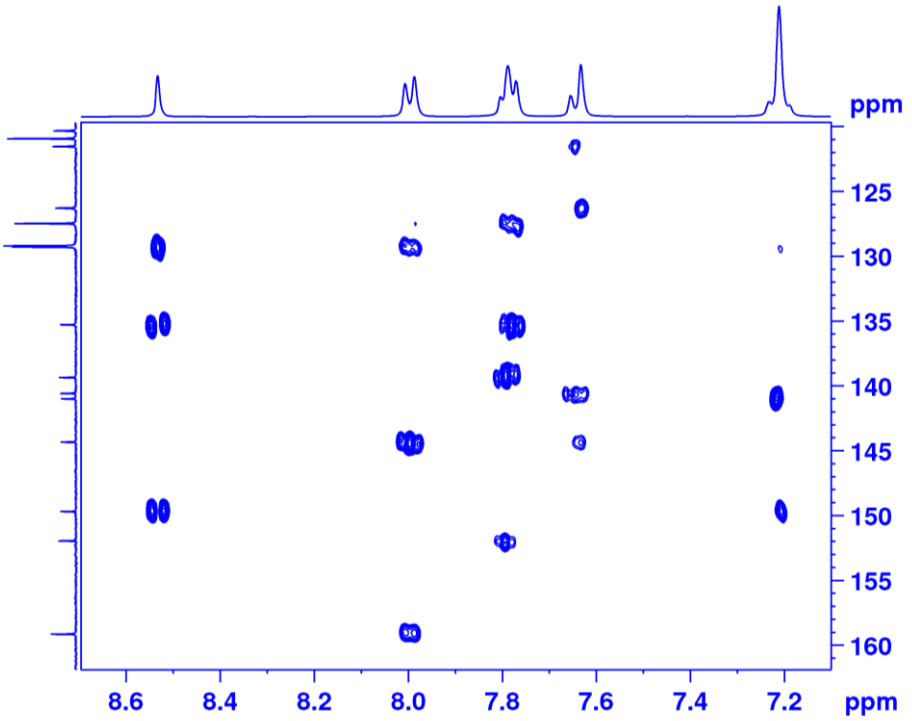

Figure S14: ^{1}H-^{13}C HMBC NMR Spectrum of DFDPBM: aromatic region expansion

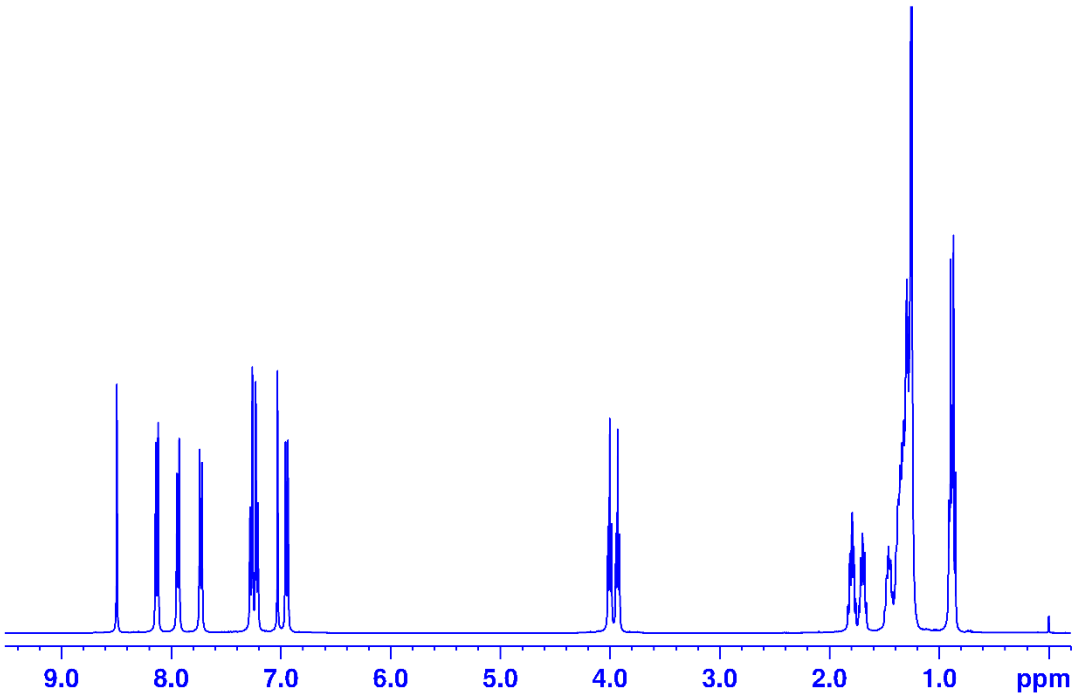

Figure S15: ^{1}H NMR Spectrum of BTMPOB

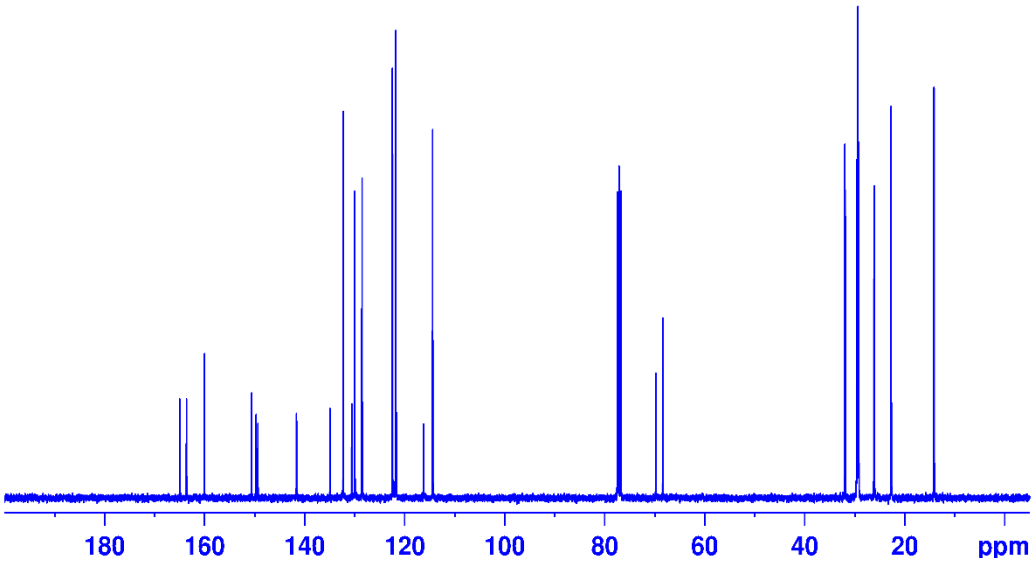

Figure S16: ^{13}C NMR Spectrum of BTMPOB

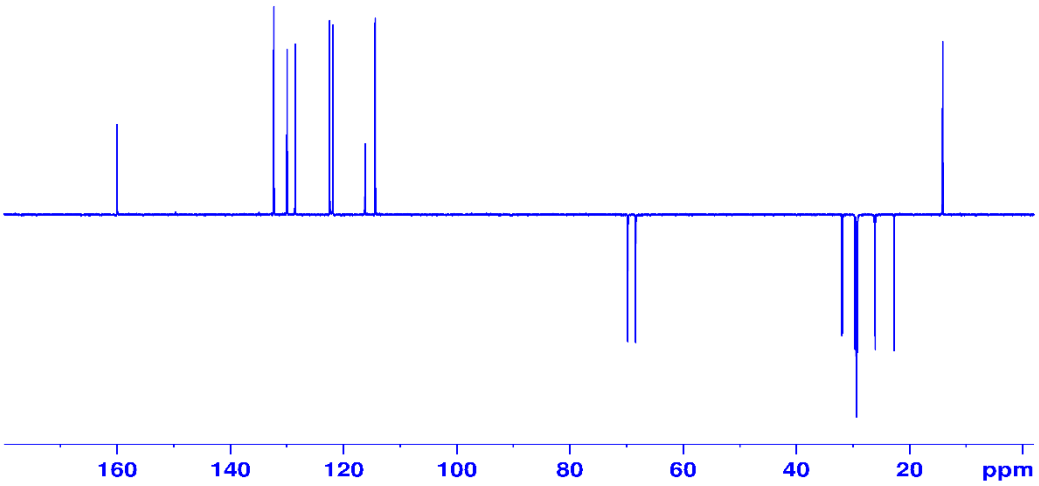

Figure S17: ^{13}C DEPT NMR Spectrum of BTMPOB

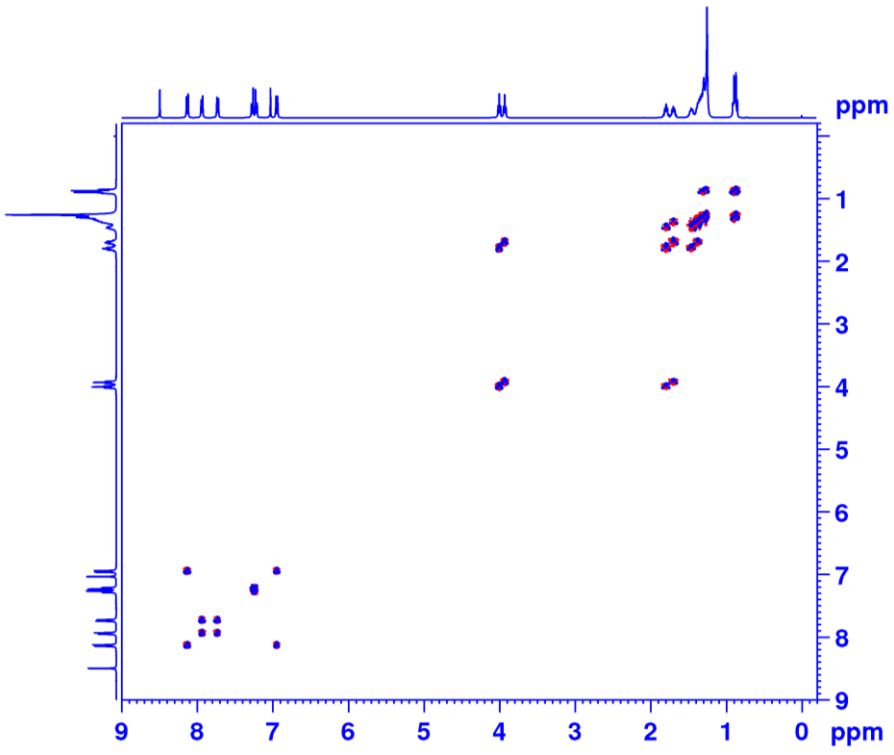

Figure S18: ^{1}H-^{1}H DQF-COSY NMR Spectrum of BTMPOB

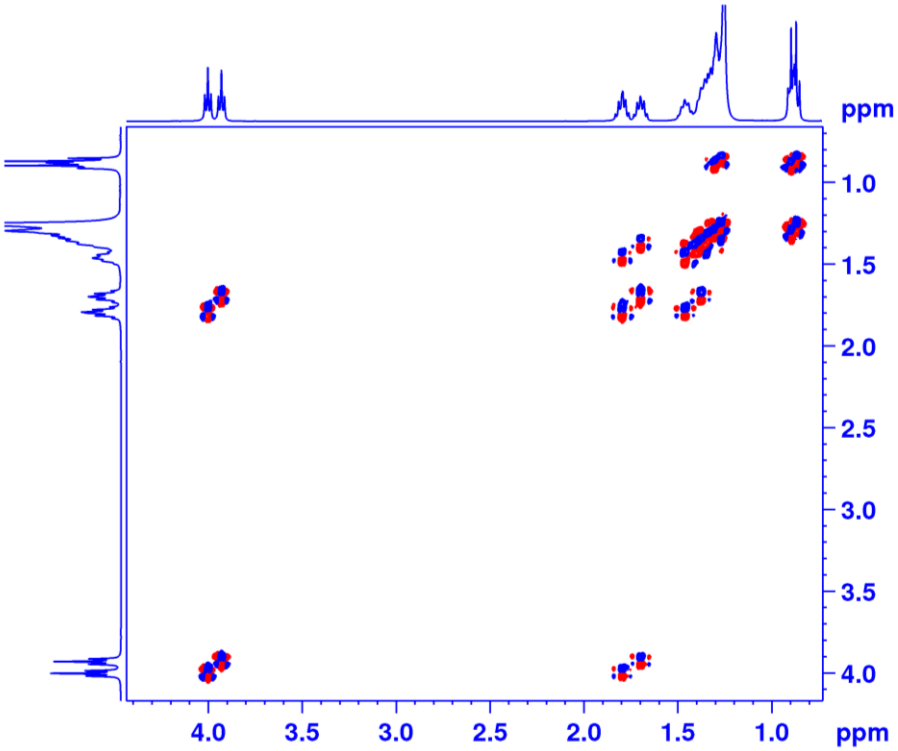

Figure S19: ^{1}H-^{1}H DQF-COSY NMR Spectrum of BTMPOB:aliphatic region expansion

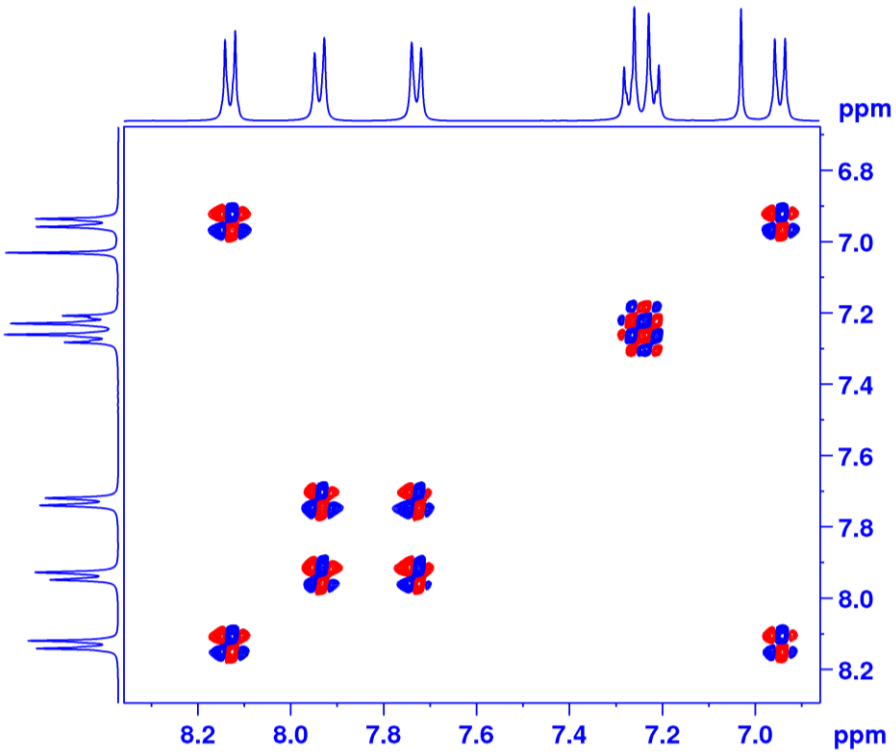

Figure S20: ^{1}H-^{1}H DQF-COSY NMR Spectrum of BTMPOB:aromatic region expansion

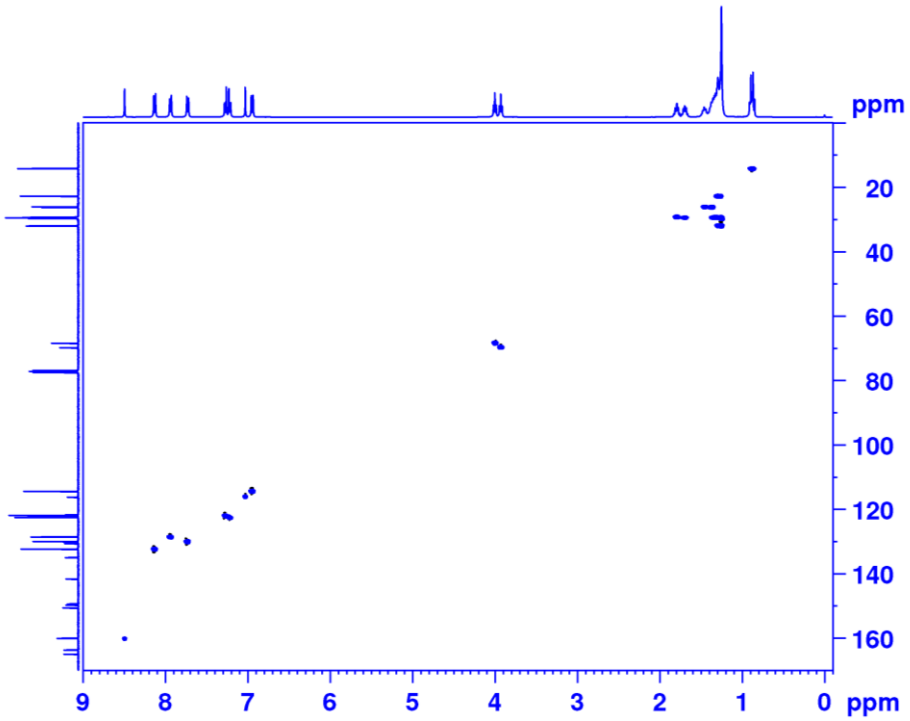

Figure S21: ^{1}H-^{13}C HSQC NMR Spectrum of BTMPOB

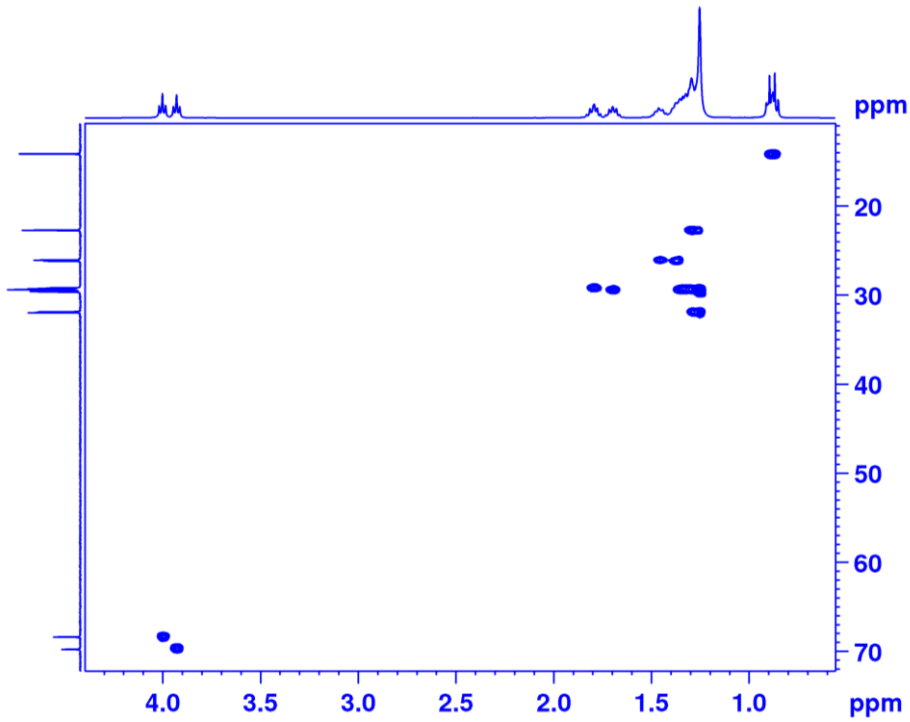

Figure S22: ^{1}H-^{13}C HSQC NMR Spectrum of BTMPOB: aliphatic region expansion

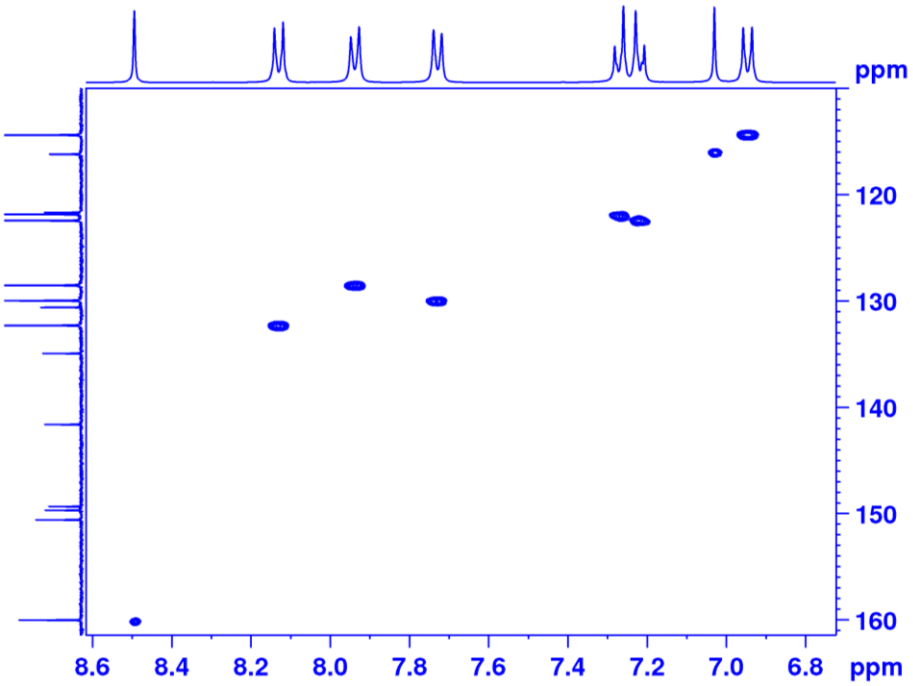

Figure S23: ^{1}H-^{13}C HSQC NMR Spectrum of BTMPOB: aromatic region expansion

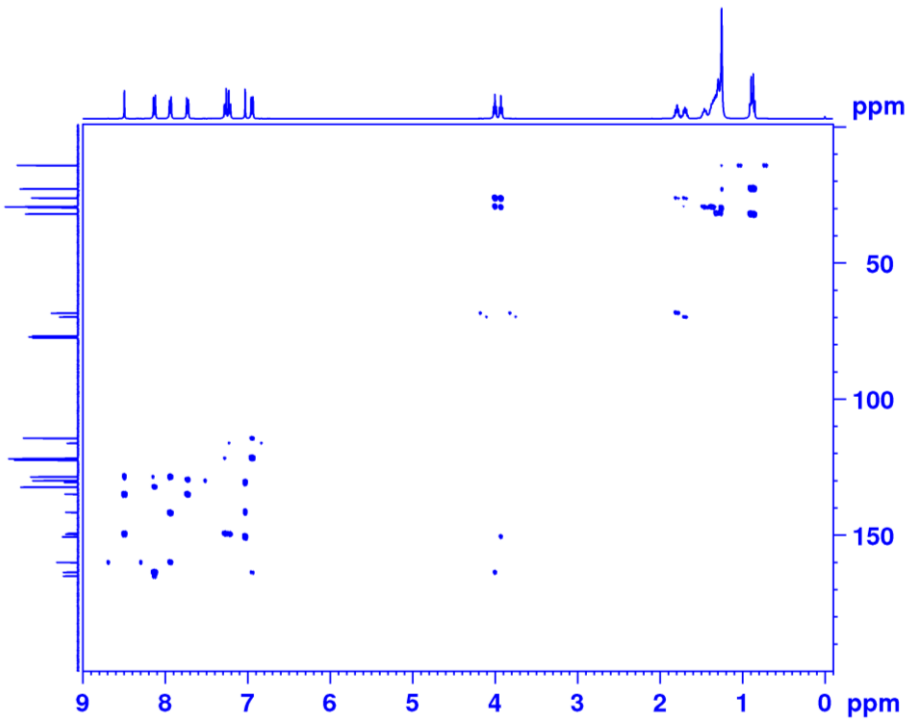

Figure S24: ^{1}H-^{13}C HMBC NMR Spectrum of BTMPOB

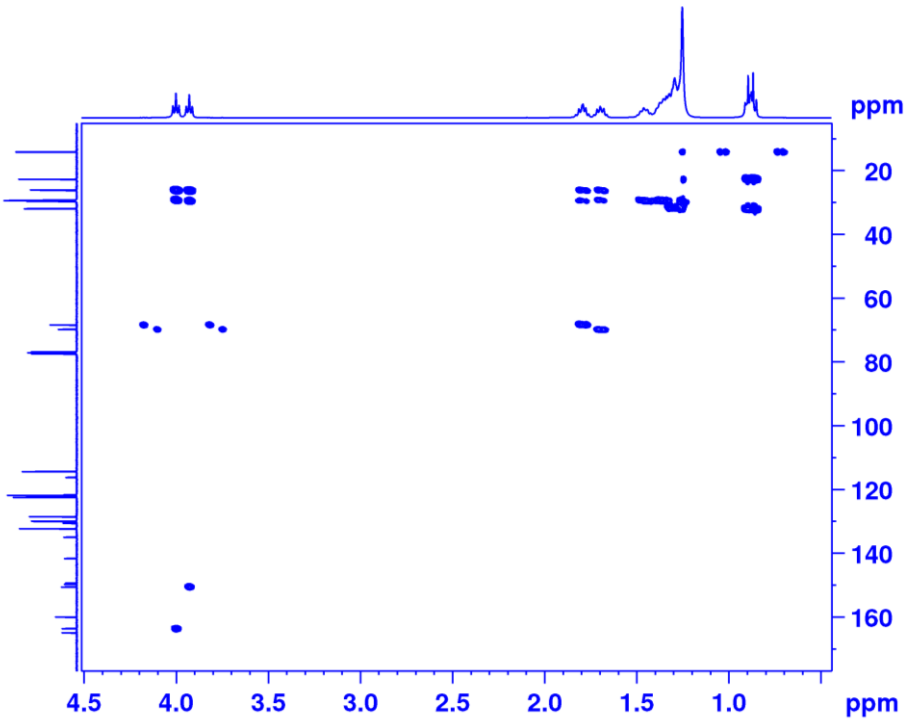

Figure S25: ^{1}H-^{13}C HMBC NMR Spectrum of BTMPOB: aliphatic region expansion

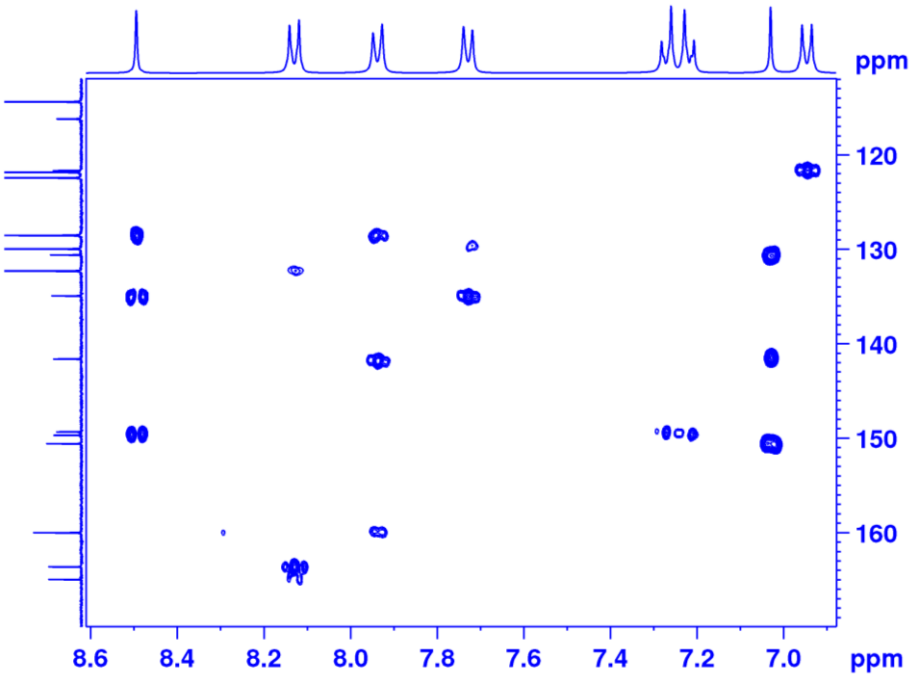

Figure S26: ^{1}H-^{13}C HMBC NMR Spectrum of BTMPOB: aromatic region expansion

Orientational Ordering of Aliphatic Chains

The 2D Proton Encoded Local Field (PELF) experiment spectrum correlates the ^{13}C chemical shift with the associated ^{13}C-^{1}H dipolar couplings. BLEW-48[1] proton homonuclear decoupling sequence was employed during t_1 period with a radio frequency (rf) field strength of 71.4 kHz and SPINAL-64 heteronuclear decoupling of strength 30 kHz was used during t_2 period. Ramp CP step with a contact time of 1.8 ms was used to transfer proton magnetization to carbon. The F_1 dimension frequency axis in the spectrum was scaled with a scaling factor of 0.42. The ^{13}C-^{1}H dipolar coupling (D_{CH}) is related to the observed splitting $\Delta\nu$ by the following equation

$$\Delta\nu = (2D_{CH} + J_{CH}) \qquad (1)$$

where J_{CH} is the scalar coupling constant and for directly bonded CH pair we considered J_{CH} =125 Hz. By assuming a axially symmetry the order parameter of each C-H bond in each segment of the chain can then be calculated by following relation[2]

$$S_{CH} = D_{CH} / K \qquad (2)$$

where $K = -h\gamma_H\gamma_C/4\pi^2 r^3_{CH}$, with γ_H and γ_C are the gyromagnetic ratios of ^{1}H and ^{13}C nuclei respectively and r_{CH} is the inter nuclear distance between them.

References

(1) Burum, D. P.; Linder, N.; Ernst, R. R. Low-Power Multipulse Line Narrowing in Solid-State NMR. *J. Magn. Reson.* **1981**, *44*, 173–188.

(2) Courtieu, J.; Bayle, J. P.; Fung, B. M. Variable Angle Sample Spinning NMR in Liquid Crystals. *Prog. Nucl. Magn. Reson. Spectrosc*. **1994**, *26*, 141-169