Electronic Supplementary Information (ESI)

Effect of Alkyl Chain and Linking Units on Mesophase Transitions and Molecular Order of Rod-Like Thiophene Mesogens: ^{13}C NMR Investigation

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Synthesis of 5-octylthiophene-2-carboxylic acid: (1)

To a solution of 5-octylthiophene-2-carbaldehyde (14.1g, 63 mmol, 1 equiv) in Tetrahydrofuran (THF) (150 mL) was added freshly prepared aqueous solutions of sodium chlorite (34.1 g, 378 mmol, 6 equiv) and sodium dihydrogen orthophosphate dihydrate (29.4 g, 189 mmol, 3 equiv) drop wise to get a pale yellow solution at 0 °C. The reaction mixture was then stirred at same temperature for 12 hrs. The volatile compounds were removed in vacuum. The residue was dissolved in 150 mL of distilled water and the aqueous solution was acidified to pH 3 by adding one molar HCl, the obtained white precipitate was filtered and dissolved in chloroform and washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography using chloroform as an eluent. The similar procedure was followed for the synthesis of 5-hexylthiophene-2-carboxylic acid and 5-bromothiophene-2-carboxylic acid compounds.

Yield: 84%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 3.6 Hz, 1H), 6.74 (d, J = 3.6 Hz, 1H), 2.77 (t, J = 7.6 Hz, 2H), 1.71 – 1.51 (m, 2H), 1.47 – 1.05 (m, 10H), 0.81 (t, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 167.83, 156.09, 135.31, 129.85, 125.55, 31.83, 31.39, 30.59, 29.26, 29.18, 29.03, 22.65, 14.09.

Synthesis of 5-hexylthiophene-2-carboxylic acid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.8 Hz, 1H), 6.84 (d, *J* = 3.8 Hz, 1H), 2.87 (t, *J* = 7.7 Hz, 2H), 1.80 – 1.65 (m, 2H), 1.58 – 1.23 (m, 6H), 0.92 (t, *J* = 6.3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.00, 156.13, 135.34, 129.84, 125.56, 31.49, 31.35, 30.59, 28.70, 22.54, 14.05.

Synthesis of 5-bromothiophene-2-carboxylic acid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.31, 133.89, 131.30, 122.22.

Synthesis of 4-formylphenyl 5-octylthiophene-2-carboxylate: (2)

A mixture of 5-octylthiophene-2-carboxylic acid (12.5g, 52 mmol, 1 equiv) and 4-hydroxybenzaldehyde (6.4 g, 52 mmol, 1 equiv) were dissolved in 100 mL dichloromethane To this solution, was added a solution of DCC (16 g, 78 mmol, 1.5 equiv) and a catalytic amount of DMAP (0.64 g, 5.2 mmol, and 0.1equiv) in DCM (30 mL). The reaction mixture were then stirred at 0 °C for 24 hrs. The precipitated dicyclohexylurea was filtered off, and the filtrate was concentrated. The residue was dissolved in DCM, washed with 5% cold KOH (aq) solution, water, and brine, dried over anhydrous Na_2SO_4, and concentrated. This solid was purified by column chromatography using ethyl acetate and hexane as eluents (v/v 2:8). Finally white color solid compound obtained. The similar procedure was followed for the synthesis of 4-formylphenyl thiophene-2-carboxylate, 4-formylphenyl 5-hexylthiophene-2-carboxylate and 4-formylphenyl 5-bromothiophene-2-carboxylate compounds.

Yield: 79%

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 3.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 3.4 Hz, 1H), 2.79 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.48 – 1.03 (m, 10H), 0.80 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.98, 159.86, 156.43, 155.44, 135.61, 133.96, 131.24, 128.96, 125.76, 122.48, 31.84, 31.44, 30.61, 29.27, 29.20, 29.04, 22.54, 14.13.

Synthesis of 4-formylphenyl 5-hexylthiophene-2-carboxylate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 3.8 Hz, 1H), 7.44 – 7.34 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 3.8 Hz, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.72 (m, 2H), 1.58 – 1.15 (m, 6H), 0.84 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.89, 159.80, 156.38, 155.43, 135.57, 133.97, 131.19, 128.98, 125.75, 122.44, 31.59, 31.48, 30.58, 28.69, 22.54, 14.06.

Synthesis of 4-formylphenyl 5-bromothiophene-2-carboxylate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.88, 158.71, 154.99, 135.51, 134.23, 133.15, 131.43, 131.30, 122.39, 122.35.

Synthesis of 4-formylphenyl thiophene-2-carboxylate:

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 8.06 – 7.93 (m, 3H), 7.73 (d, *J* = 4.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.97, 159.86, 155.26, 135.27, 134.24, 134.11, 132.13, 131.28, 128.27, 122.47.

Synthesis of 4-(5-octylthiophene-2-carbonyloxy) benzoic acid: (5)

To a solution of 5-octylthiophene-2-carbaldehyde (14.7 g, 41 mmol, 1 equiv) in Tetrahydrofuran (THF) (150 mL) was added freshly prepared aqueous solutions of sodium chlorite (22.2 g, 246 mmol, 6 equiv) and sodium dihydrogen orthophosphate dihydrate (19.1 g, 123 mmol, 3 equiv) drop wise to get a pale yellow solution at 0 °C. The reaction mixture was then stirred at same temperature for 12 hrs. The volatile compounds were removed in vacuum. The residue was dissolved in 150 mL of distilled water and the aqueous solution was acidified to pH 3 by adding one molar HCl, the obtained white precipitate was filtered and dissolved in chloroform and washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography using ethyl acetate as an eluent. The similar procedure was followed for the synthesis of 4-(thiophene-2-carbonyloxy) benzoic acid, 4-(5-hexylthiophene-2-carbonyloxy) benzoic acid and 4-(5-bromothiophene-2-carbonyloxy) benzoic acid compounds.

Yield: 81%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 3.6 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.29 (s, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 1.84 – 1.65 (m, 2H), 1.37 (m, 10H), 0.91 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86, 159.95, 156.28, 155.10, 135.50, 131.90, 129.13, 126.72, 125.69, 121.87, 31.83, 31.43, 30.61, 29.26, 29.17, 29.03, 22.65, 14.09.

Synthesis of 4-(thiophene-2-carbonyloxy) benzoic acid:

^{1}H NMR (400 MHz, DMSO) δ 8.00 (m, 4H), 7.34 (m, 2H), 7.27 (t, 1H).

Synthesis of 4-(5-hexylthiophene-2-carbonyloxy) benzoic acid:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 3.7 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 3.7 Hz, 1H), 2.90 (t, *J* = 7.6 Hz, 2H), 1.75 (m, 2H), 1.31-1.42 (m, 6H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86, 160.00, 156.30, 155.04, 135.52, 131.87, 129.10, 126.82, 125.71, 121.87, 31.49, 31.39, 30.60, 28.69, 22.54, 14.06.

Synthesis of 4-((4-(dodecyloxy) phenoxy) carbonyl) phenyl 5-octylthiophene-2-carboxylate: (7)

A mixture of 4-(5-octylthiophene-2-carbonyloxy) benzoic acid (11.9 g, 33 mmol, 1 equiv) and 4-(dodecyloxy) phenol (9.2 g, 33 mmol, 1 equiv) were dissolved in 100 mL dichloromethane To this solution, was added a solution of DCC (10.2 g, 49.5 mmol, 1.5 equiv) and a catalytic amount of DMAP (0.4 g, 3.3 mmol, and 0.1equiv) in DCM (30 mL). The reaction mixture were then stirred at 0 °C for 24 hrs. The precipitated dicyclohexylurea was filtered off, and the combined filtrate was concentrated. The residue was dissolved in DCM, washed with 5% cold KOH (aq) solution, water, and brine, dried over anhydrous Na_2SO_4, and concentrated. This solid was purified by column chromatography using ethyl acetate and hexane as eluents (v/v 2:8). Finally white color solid compound obtained. The similar procedure was followed for the synthesis of KTC, HTC and BRTC compounds.

Yield: 74%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 3.8 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 3.8 Hz, 1H), 3.96 (t, *J* = 6.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.86 – 1.64 (m, 4H), 1.64 – 1.05 (m, 28H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.81, 159.98, 156.98, 156.25, 154.84, 144.21, 135.47, 131.75,

129.17, 127.20, 125.69, 122.36, 121.91, 115.15, 68.47, 31.94, 31.84, 31.43, 30.61, 29.68, 29.65, 29.62, 29.60, 29.42, 29.37, 29.30, 29.27, 29.18, 29.03, 26.06, 22.71, 22.66, 14.13, 14.10.

Synthesis of 4-((4-(dodecyloxy) phenoxy) carbonyl) phenyl 5-hexylthiophene-2-carboxylate: (HTC)

1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, J = 3.8 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 3.8 Hz, 1H), 3.96 (t, J = 6.6 Hz, 2H), 2.89 (t, J = 7.6 Hz, 2H), 1.86 – 1.64 (m, 4H), 1.58 – 1.18 (m, 24H), 0.89 (m, 6H). 13C NMR (101 MHz, $CDCl_3$) δ 164.82, 160.00, 156.97, 156.25, 154.83, 144.19, 135.48, 131.76, 129.15, 127.19, 125.69, 122.36, 121.91, 68.47, 31.93, 31.49, 31.39, 30.61, 29.68, 29.65, 29.62, 29.60, 29.41, 29.36, 29.29, 28.69, 26.05, 22.70, 22.54, 14.13, 14.05.

Synthesis of 4-((4-(dodecyloxy)phenoxy)carbonyl)phenyl 5-bromothiophene-2-carboxylate: (BRTC)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 4.0 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.80 – 1.76 (m, 2H), 1.45 – 1.32 (m, 18H), 0.88 (t, *J* = 6.5 Hz, 3H).

Synthesis of 4-((4-(dodecyloxy)phenoxy)carbonyl)phenyl 2,2'-bithiophene-5-carboxylate: (BTC)

To a solution of thiophene 2-boronic acid (0.65 g, 5.1 mmol, 1.5 eqiv), and BRTC (2 g, 3.4 mmol, 1 eqiv), dissolved in tetrahydrofuran (60 mL) was added a 2M solution of potassium carbonate K_2CO_3 dissolved in water (10 mL). The mixture was bubbled with nitrogen for 10 minutes. Then, tetrakis(triphenylphosphine) palladium $Pd(PPh_3)_4$ (0), (196 mg, 5 mol%) was added. The reaction maintained further 16 hrs at 75 ^{o}C. The completion of reaction checked by TLC and reaction cooled

to room temperature. The mixture was filtered off and the solvent was removed washed with 10% HCl and the residue was purified by column chromatography using hexane and ethyl acetate (v/v, 8:2) as eluents, colorless solid obtained which was further recrystallized from Acetonitrile.

Yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 4.0 Hz, 1H), 7.39 – 7.34 (m, 4H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.07 – 7.12 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.57 – 1.09 (m, 18H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.79, 159.79, 156.99, 154.68, 146.03, 144.17, 136.03, 136.00, 131.82, 129.76, 128.31, 127.36, 126.67, 125.74, 124.24, 122.36, 121.87, 115.15, 68.47, 31.94, 29.68, 29.66, 29.62, 29.60, 29.42, 29.37, 29.29, 26.06, 22.71, 14.14.

Synthesis of 4 – bromo – 4'- (dodecyloxy) biphenyl: (11)

In a 250 mL round bottom flask, (10 g, 28 mmol) 4'-bromo biphenyl -4-ol and (3.86g, 28 m mol) K_2CO_3 were taken and 100 mL DMF was added. The mixture was stirred while heating at 90°C followed by dropwise addition of (6.97g, 28 mmol) 1-bromo dodecane. The reaction was continued for 5h. Then the reaction mixture was poured into 1L distilled water and transferred to a separating funnel and extracted with chloroform. The chloroform layer was washed using 5% NaOH solution and distilled water, and the organic layer was dried over anhydrous sodium sulfate. Upon removal of solvent using rotary evaporator under reduced pressure, white solid was obtained. It was further purified by recrystallization from acetonitrile.

Yield: 86% ^{1}H NMR (400 MHz, CDCl3) δ 7.52 – 7.50 (d, 2H), 7.45 – 7.47 (d, 2H), 7.39 – 7.41 (d, 2H), 6.96 – 6.94 (m, 2H), 3.98 (t, J = 6.6 Hz, 2H), 1.75 – 1.81 (m, 2H), 1.53 (d, J = 39.9 Hz, 2H), 1.49– 1.26 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H).

Synthesis of 2-(4'-(dodecyloxy) biphenyl-4-yl)-5-octylthiophene: (OTPC)

A 100 mL round bottom flask equipped with a magnetic stirrer, (0.62g, 4.5 mmol) K_2CO_3, (20.2 mg, 0.9m mol) Pd $(OAc)_2$, (52.6 mg, 0.18 m mol) PCy_3HBF_4 and (45.95 mg) pivalic acid were placed. The reaction flask was purged with nitrogen gas and (0.59g, 3 mmol) 2-octyllthiophene and (1.88 g, 4.5 m mol) 4 -bromo - 4' - (octyloxy) biphenyl in 50 mL dimethyl acetamide were added. The reaction mixture was then vigorously stirred at 110 °C for 10 h. After that the solution was cooled to room temperature, diluted with dichloromethane and distilled water. The aqueous phase was extracted with dichloromethane and the combined organic layer was dried over anhydrous $MgSO_4$ and removed the solvent under vacuum. The white color crude solid obtained was purified by column chromatography using ethyl acetate and hexane as eluents (v/v 2:8).

Yield:74% ^{1}H NMR (400 MHz, CDCl3) δ 7.53 – 7.44 (m, 6H), 7.07 (d, J = 3.5 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 3.3 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 1.75 – 1.69 (m, 2H), 1.65 – 1.59 (m, 2H), 1.19 – 1.40 (m, 28H), 0.81 (t, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 158.85, 145.64, 141.44, 139.44, 133.20, 133.00, 127.80, 126.91, 125.80, 124.98, 122.51, 114.93, 68.20, 31.89, 31.84, 31.61, 30.27, 29.63, 29.60, 29.57, 29.38, 29.31, 29.18, 29.11, 26.05, 22.64, 22.61, 14.01.

HRMS data of mesogens

1) KTC: $[M+H]^+$=509.2375; Calculated=509.2362
2) HTC: $[M+Na]^+$=615.3143; Calculated=615.3120
3) OTC: $[M+H]^+$=621.3636; Calculated=615.3614

Table S1: 2D PELF data of aliphatic chains for three mesogen in solution and mesophases. The first entry values are coupling from directly bonded C–H pairs; the second entry values are from indirectly bonded C–H pairs. The errors on the values of D_{CH} are about ±0.03 kHz. (Soln.: Solution chemical shift; CS: chemical shift; AIS: alignment induced shift; D_{CH}: Dipolar coupling; S_{CH}: Bond order parameter)
For dodecyloxy chain carbon numbers are assigned sequentially from *A* to *L*, proceeding from phenyl ring to methyl unit
For alkyl chain carbons numbers are assigned sequentially from *a* to *h*, proceeding from thiophene ring to methyl unit

C. No.	KTC					HTC					OTC				
	Soln (ppm)	98 °C				Soln (ppm)	85 °C				Soln (ppm)	96 °C			
		CS (ppm)	AIS (ppm)	D_{CH} (kHz)	S_{CH}		CS (ppm)	AIS (ppm)	D_{CH} (kHz)	S_{CH}		CS (ppm)	AIS (ppm)	D_{CH} (kHz)	S_{CH}
A	68.47	61.7	-6.77	4.82, 0.67	-0.212	68.47	60.4	-8.07	5.97, 0.80	-0.263	68.47	60.8	-7.67	6.27,0.92	-0.276
B	29.36	22.5	-6.86	3.5	-0.154	29.36	21.0	-8.36	3.95	-0.174	29.37	20.8	-8.57	4.46	-0.197
C	26.05	19.4	-6.65	3.56, 0.4	-0.157	26.05	18.6	-7.45	4.47, 0.57	-0.197	26.06	19.3	-6.76	6.2	-0.273
D	29.28	22.1	-7.18	4.59	-0.202	29.28	20.4	-8.88	5.55, 0.46	-0.245	29.30	20.8	-8.50	4.46	-0.197
E	29.61	23.2	-6.41	3.11	-0.137	29.61	22.0	-7.61	4.38	-0.193	29.62	22.1	-7.52	4.46	-0.197
F	29.67	25.0	-4.67	2.63	-0.116	29.67	23.2	-6.47	3.11	-0.137	29.68	23.7	-5.98	2.91	-0.128
G	29.4	22.5	-6.90	3.97	-0.175	29.40	21.2	-8.20	4.27	-0.188	29.42	21.0	-8.42	5.20,0.34	-0.229
H	29.59	22.7	-6.89	3.54	-0.156	29.59	21.4	-8.19	4.91	-0.216	29.60	21.0	-8.60	5.20,0.34	-0.229
I	29.64	23.6	-6.04	2.72	-0.12	29.64	22.3	-7.34	3.68	-0.162	29.65	22.1	-7.55	4.46	-0.197
J	31.93	26.4	-5.53	2.57	-0.113	31.93	26.4	-5.53	2.94	-0.130	31.94	26.9	-5.04	2.73	-0.120
K	22.7	19.4	-3.30	1.94	-0.086	22.70	18.3	-4.40	3.35	-0.148	22.71	18.8	-3.91	3.1	-0.137
L	14.12	11.0	-3.12	0.77	-0.034	14.12	11.1	-3.02	0.94, 0.30	-0.041	14.13	11.5	-2.63	0.83	-0.037
a						30.61	22.3	-8.31	3.68	-0.162	30.61	22.4	-8.21	3.63	-0.160
b						31.48	23.3	-8.18	3.62	-0.160	31.84	24.3	-7.54	3.48	-0.153
c						28.68	19.7	-8.98	2.18	-0.096	29.03	19.8	-9.23	4.73	-0.209
d						31.39	23.2	-8.19	3.11	-0.137	31.43	23.7	-7.73	3.57	-0.157
e						22.53	18.3	-4.23	3.35	-0.148	29.27	20.6	-8.67	6.09	-0.268
f						14.05	11.1	-2.95	0.94, 0.30	-0.041	29.18	20.1	-9.08	1.91	-0.084
g											22.66	18.4	-4.26	4.8	-0.212
h											14.10	11.5	-2.60	0.3	-0.013

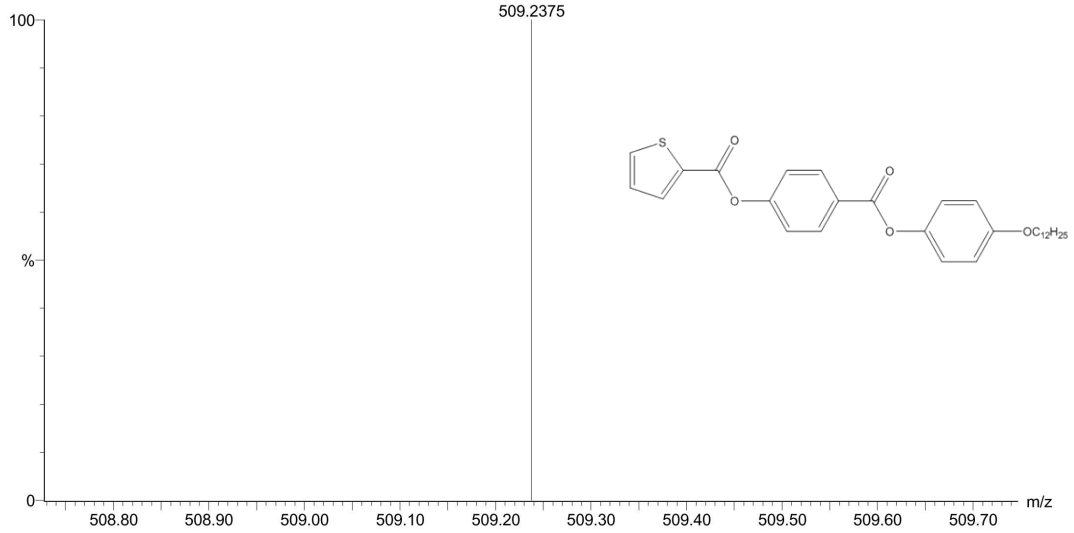
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-30 H: 0-37 O: 0-5 S: 0-1

RD-KTC
211117-09-RD-KTC 1 (0.025) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (1:2)

TOF MS ES+
1.25e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
509.2375	509.2362	1.3	2.6	12.5	n/a	C30 H37 O5 S

Figure S1: HRMS plot of KTC.

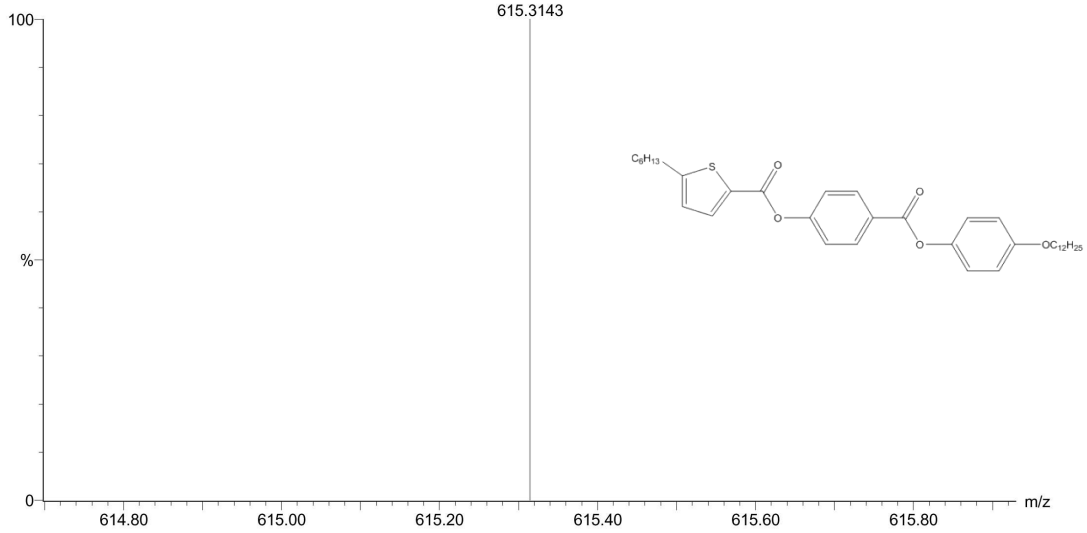
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-36 H: 0-48 O: 0-5 Na: 0-1 S: 0-1

RD-HTC
211117-10-RD-HTC 64 (1.610) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (61:64)

TOF MS ES+
3.14e+001



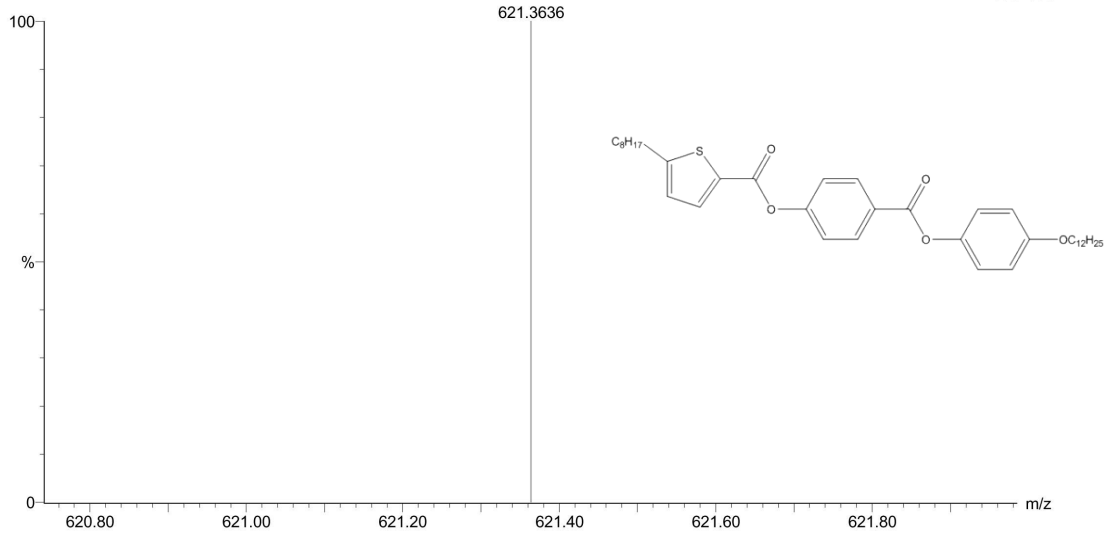
Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
615.3143	615.3120	2.3	3.7	12.5	n/a	C36 H48 O5 Na S

Figure S2: HRMS plot of HTC.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
56 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-38 H: 0-53 O: 0-5 S: 0-4
RD-OTC
221117-01-RD-OTC 47 (1.182) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (41:47) TOF MS ES+
2.89e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
621.3636	621.3614	2.2	3.5	12.5	n/a	C38 H53 O5 S

Figure S3: HRMS plot of OTC.

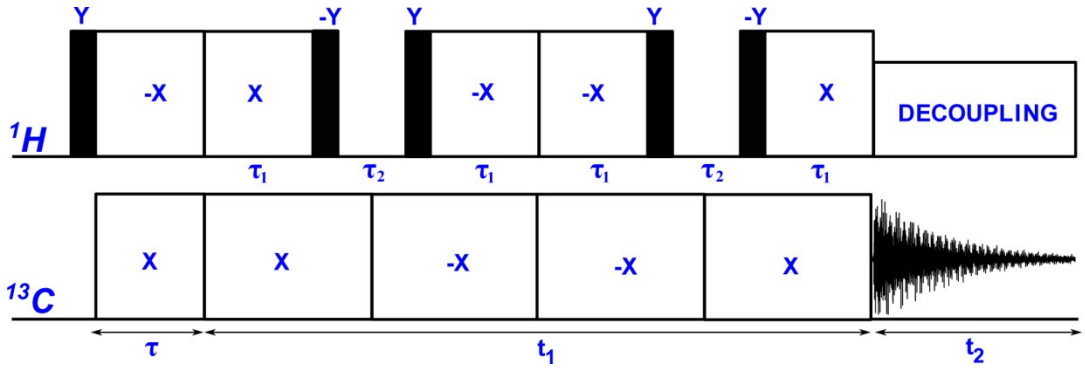


Figure S4: Pulse sequence for SAMPI-4 experiment, belongs to the family of CP based SLF techniques provides the 2D correlation spectrum between ^{13}C chemical shift (in F2 dimension) with the associated ^{13}C-^{1}H dipolar frequency (F1 dimension). Experiment starts with a cross-polarization (CP) block with a polarization inversion for a contact time τ, then the evolution of high resolution heteronuclear ^{13}C-^{1}H dipolar couplings monitored under the absence of homonuclear ^{1}H-^{1}H dipolar couplings (suppressed by "magic sandwich" pulses) during the t_1 period 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.

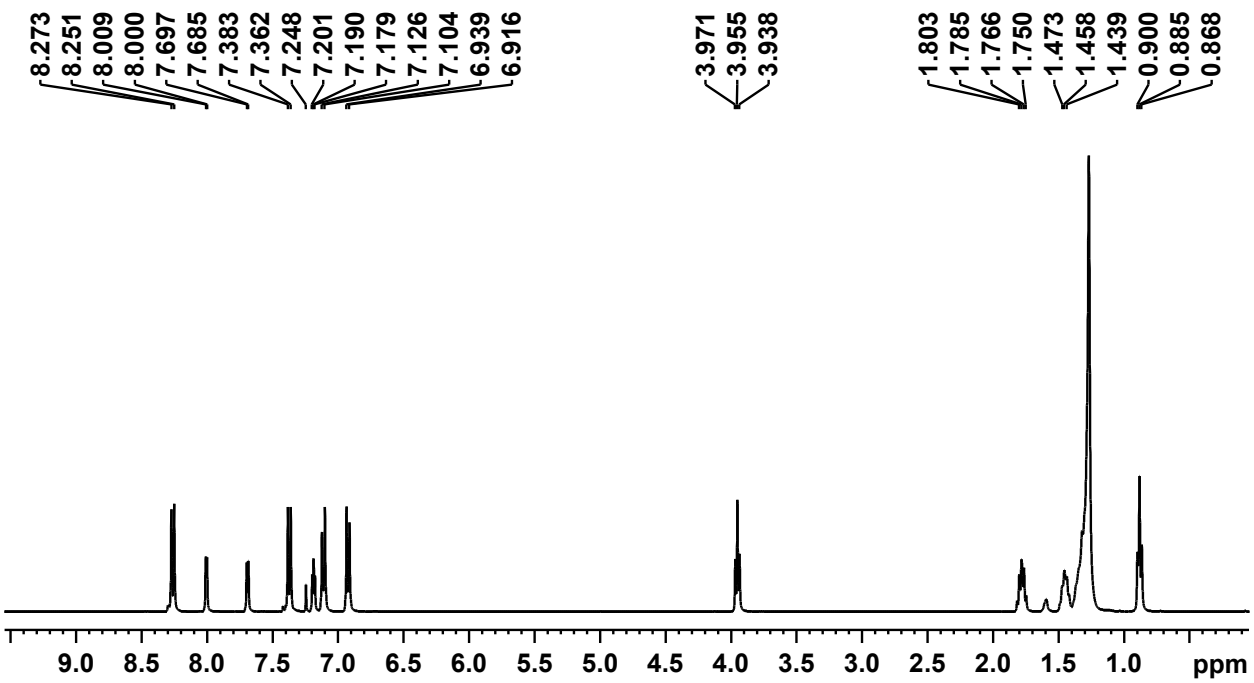
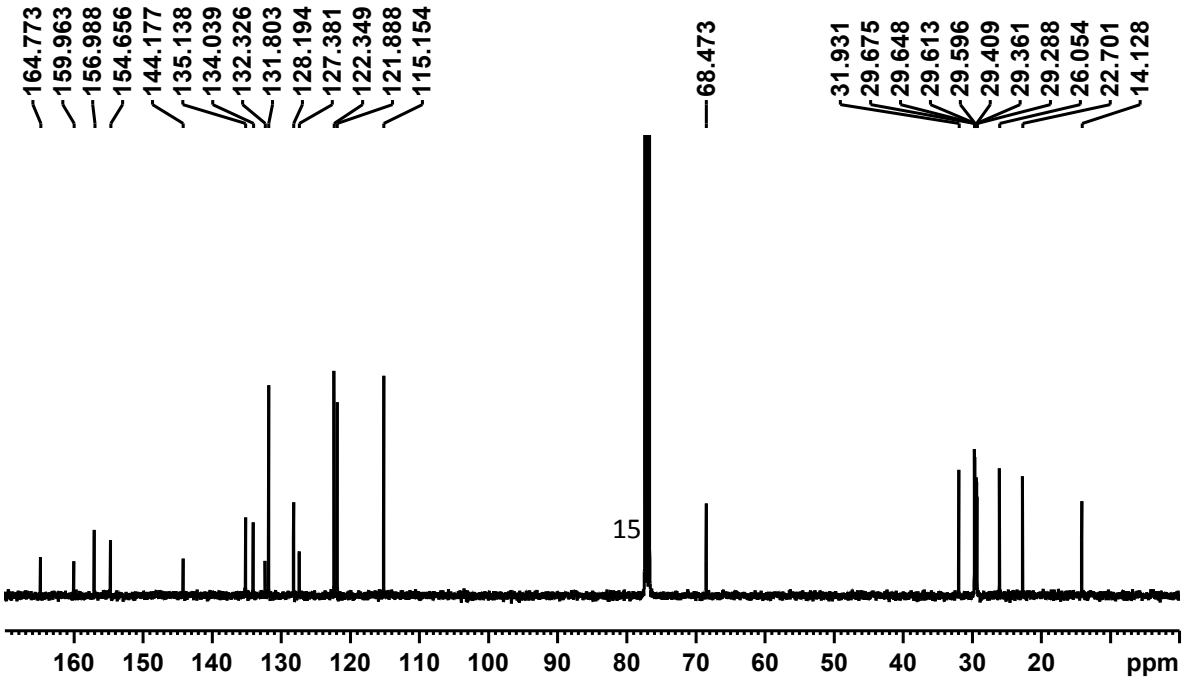


Figure S5: ^{1}H NMR Spectrum of KTC Mesogen



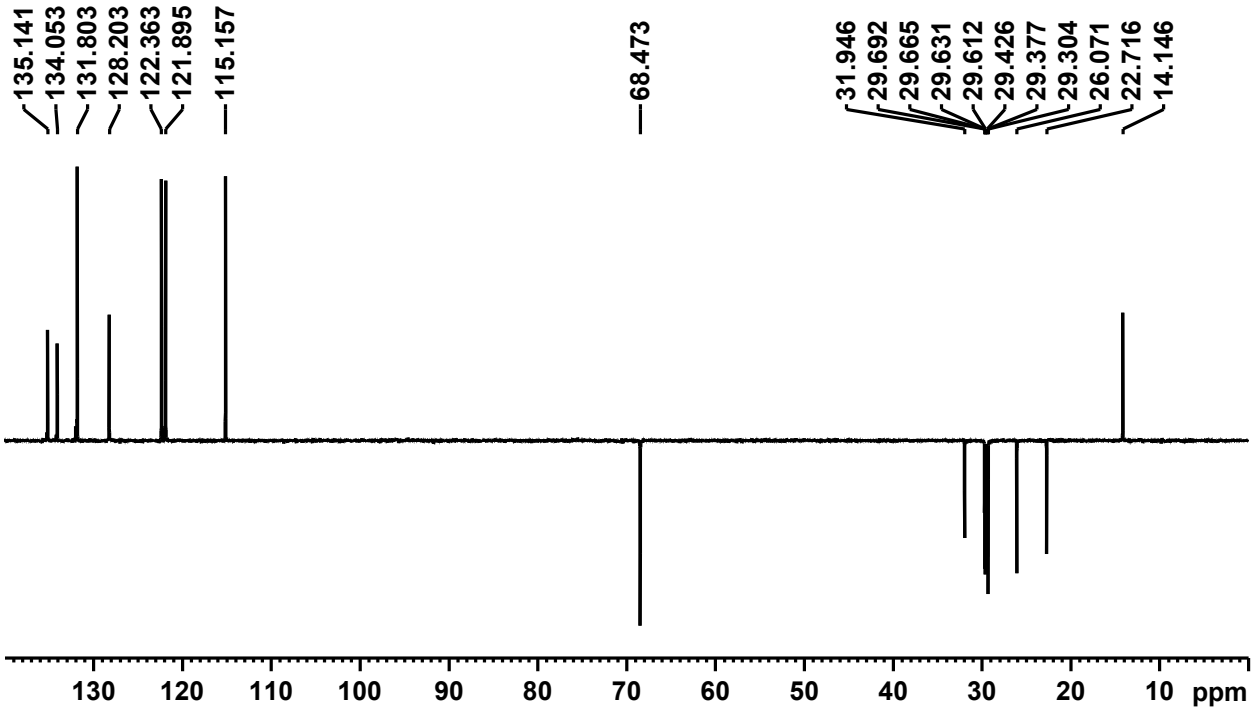


Figure S7: DEPT-135 ^{13}C NMR Spectrum of KTC Mesogen

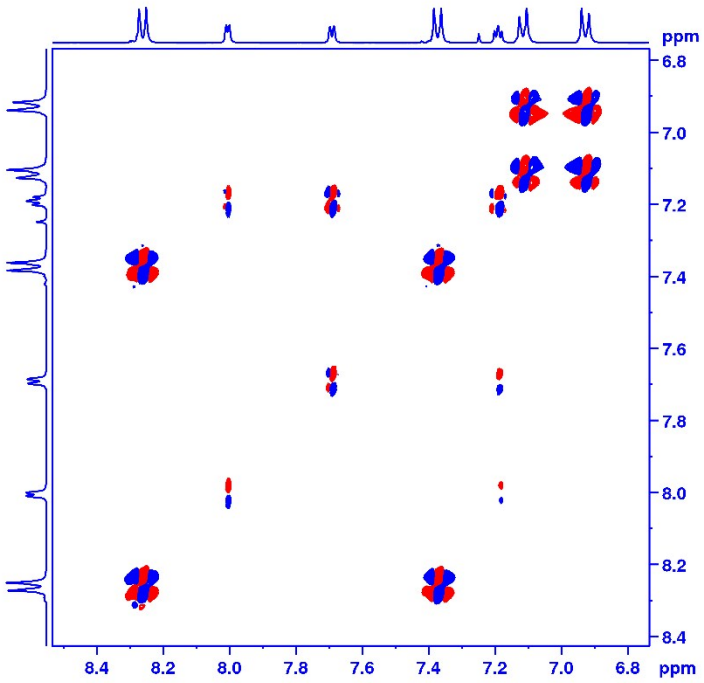


Figure S8: ^{1}H - ^{1}H DQF COSY NMR Spectrum aromatic region of KTC mesogen

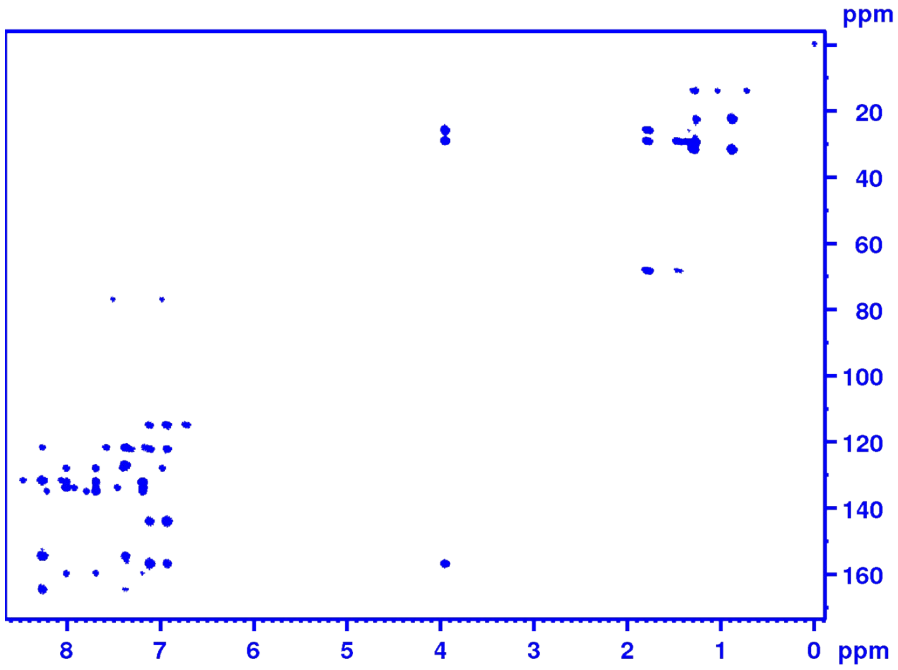


Figure S9: ^{1}H - ^{13}C HMBC NMR Spectrum of KTC Mesogen

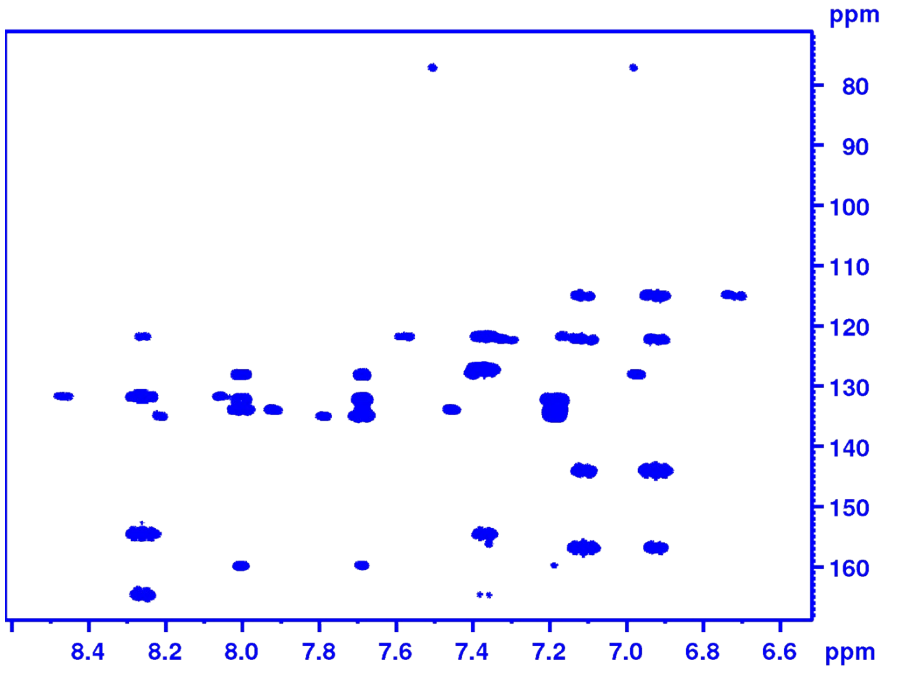


Figure S10: Expanded plot of ^{1}H - ^{13}C HMBC spectrum aromatic region of KTC mesogen.

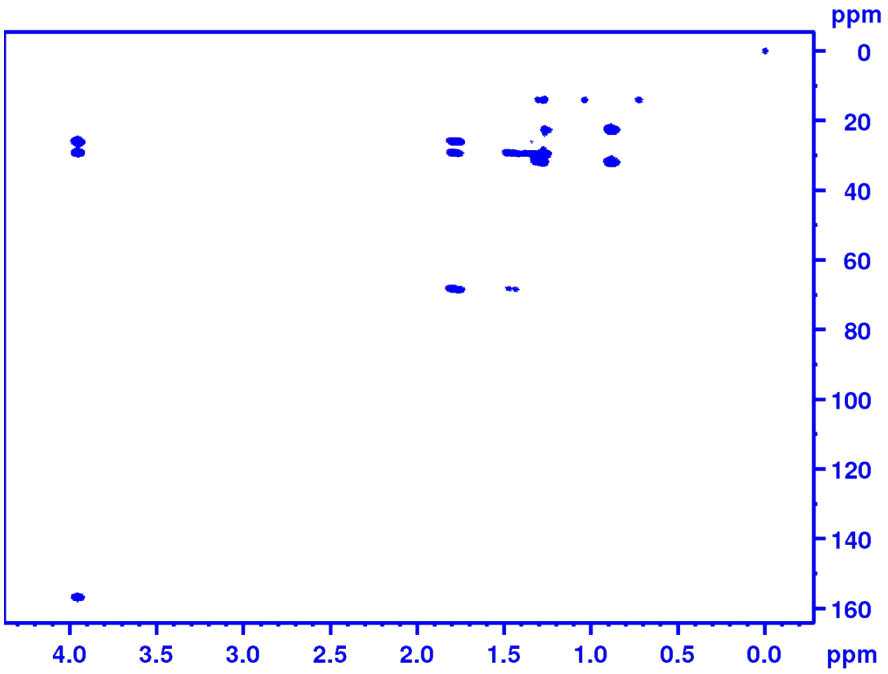


Figure S11: Expanded plot of ^{1}H -^{13}C HMBC spectrum aliphatic region of KTC mesogen.

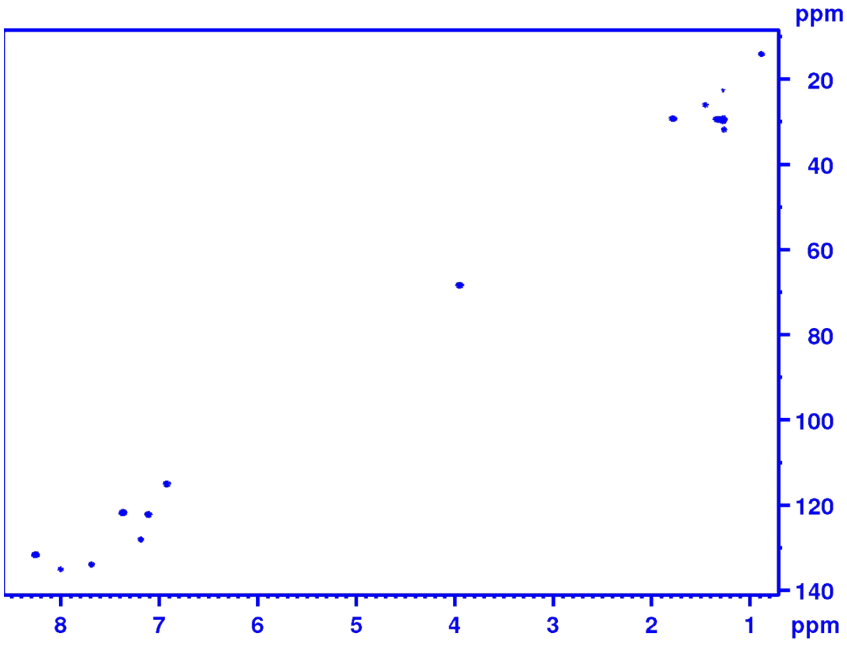


Figure S12: ^{1}H -^{13}C HSQC NMR spectrum of KTC Mesogen

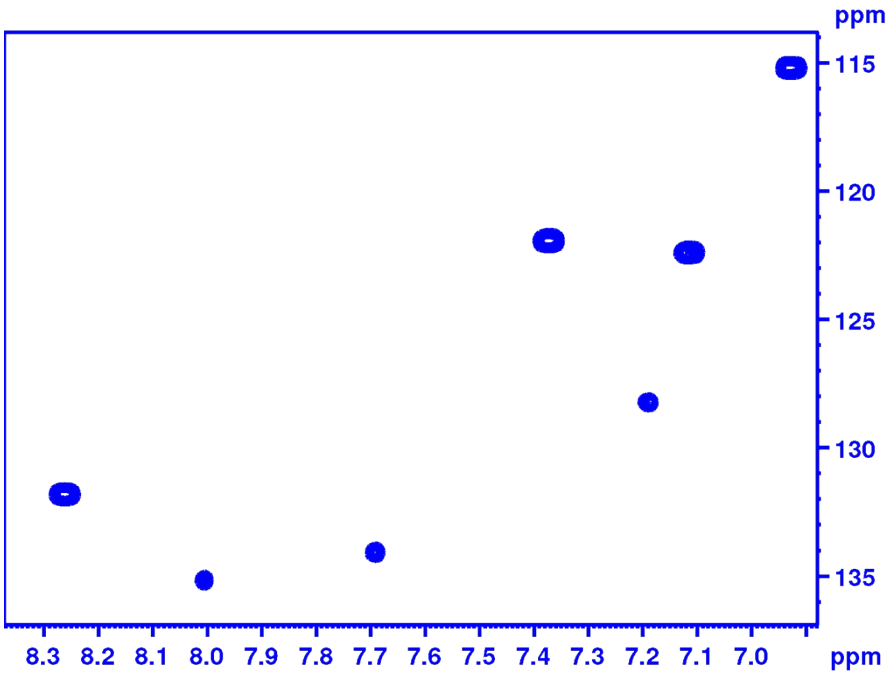


Figure S13: Expanded plot of ^{1}H-^{13}C HSQC spectrum aromatic region of KTC mesogen

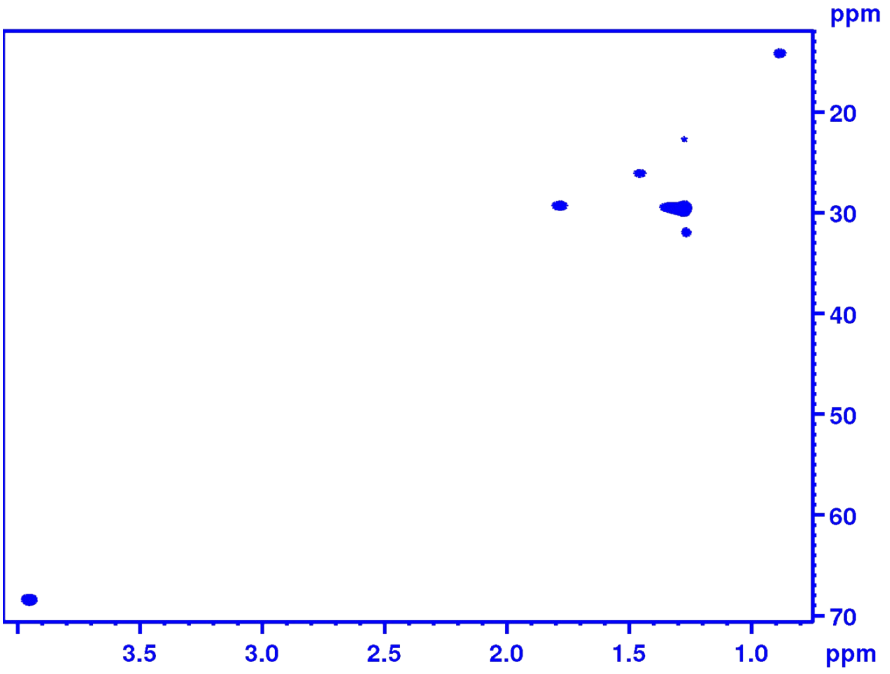


Figure S14: Expanded plot of ^{1}H -^{13}C HSQC spectrum aliphatic region of KTC mesogen

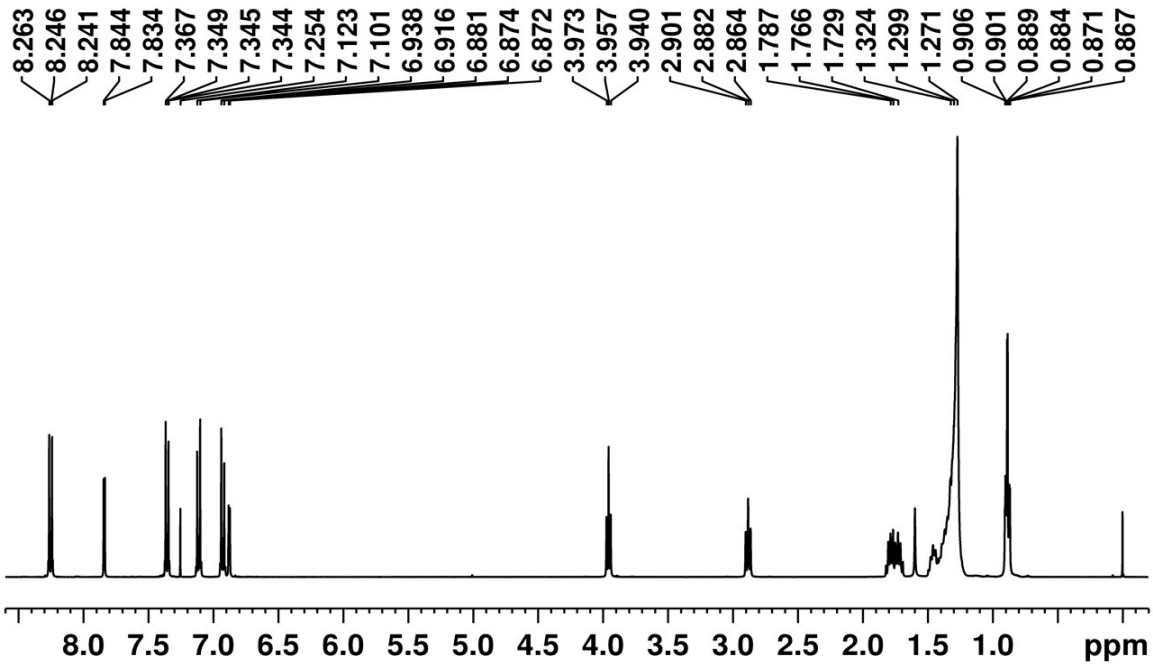


Figure S15: ^{1}H NMR Spectrum of OTC Mesogen

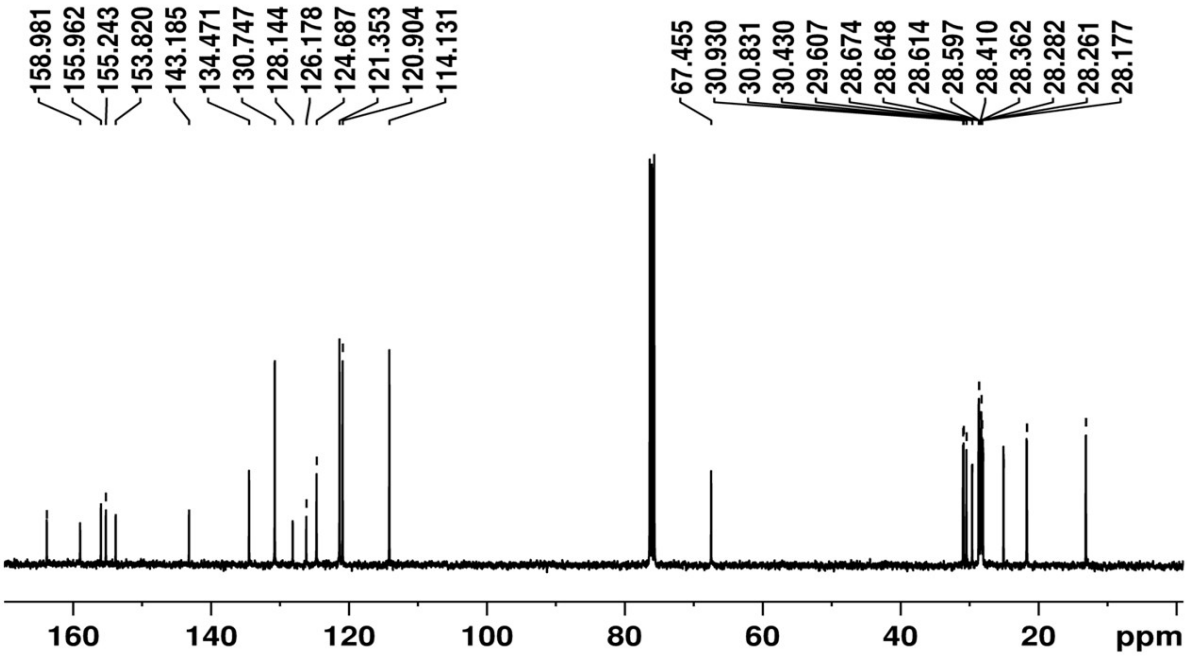


Figure S16: ^{13}C NMR Spectrum of OTC Mesogen

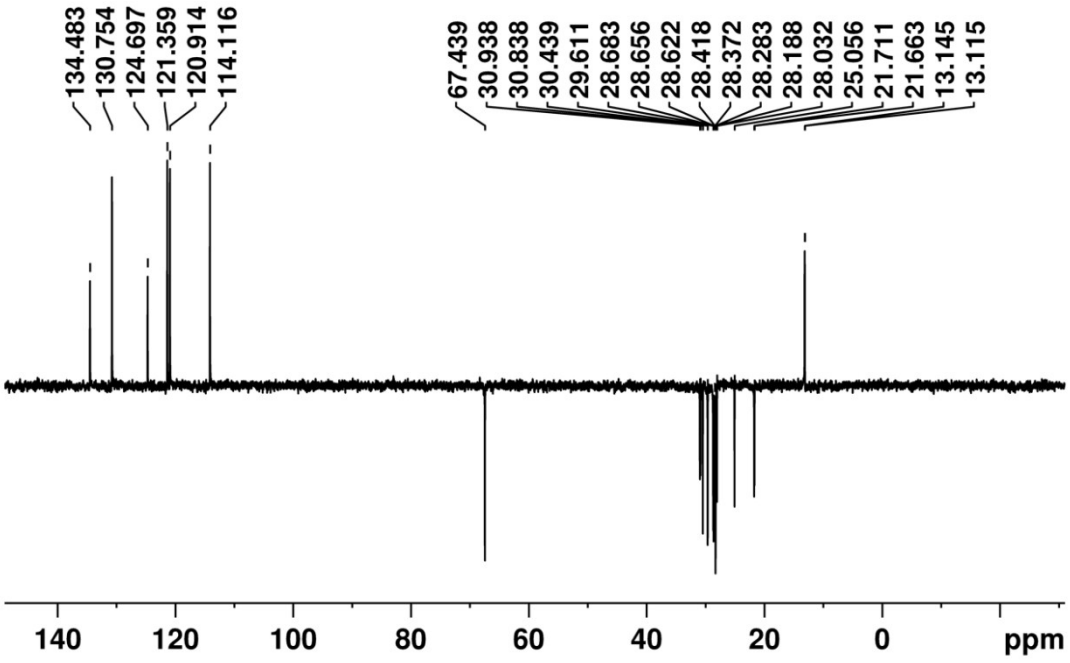


Figure S17: DEPT-135 ^{13}C NMR Spectrum of OTC Mesogen

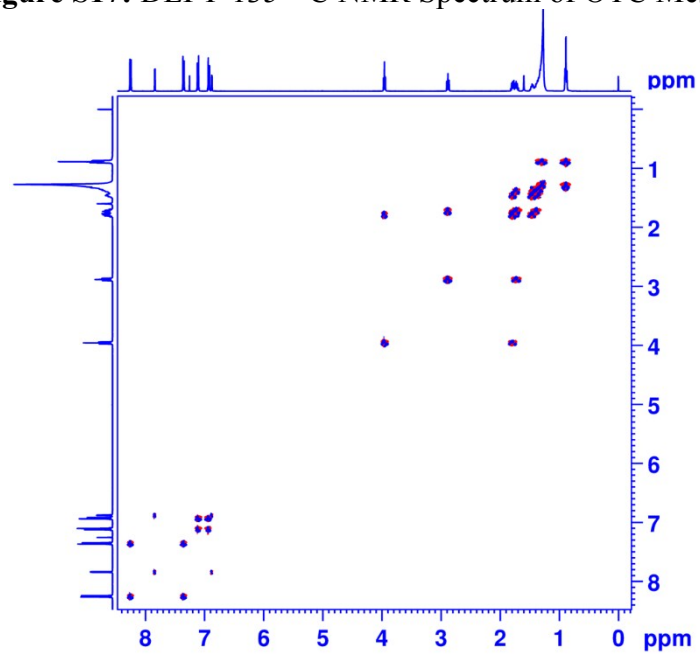


Figure S18: ^{1}H-^{1}H DQF COSY NMR Spectrum of OTC Mesogen

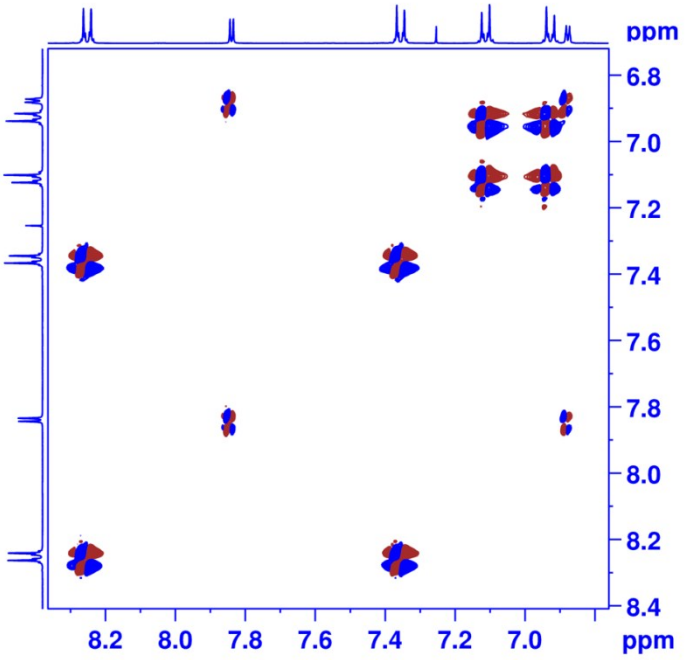


Figure S19: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aromatic region of OTC

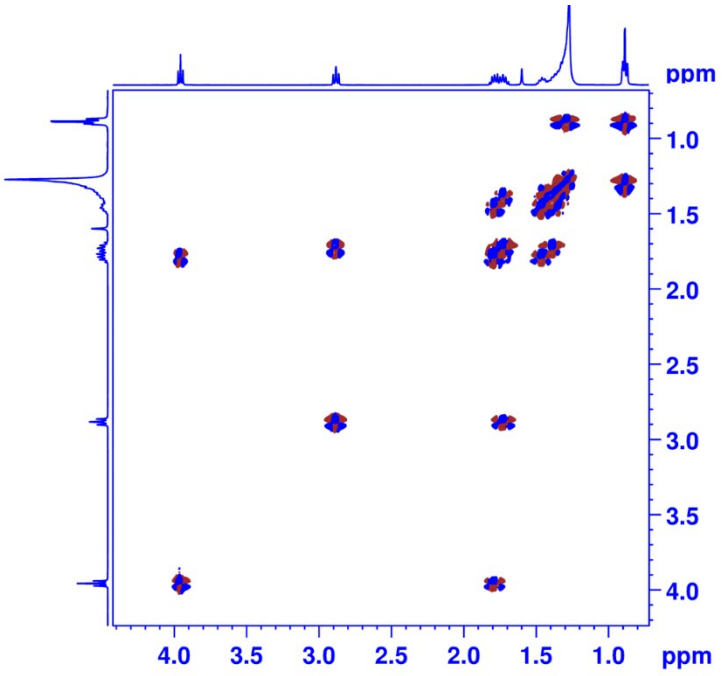


Figure S20: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aliphatic region of OTC

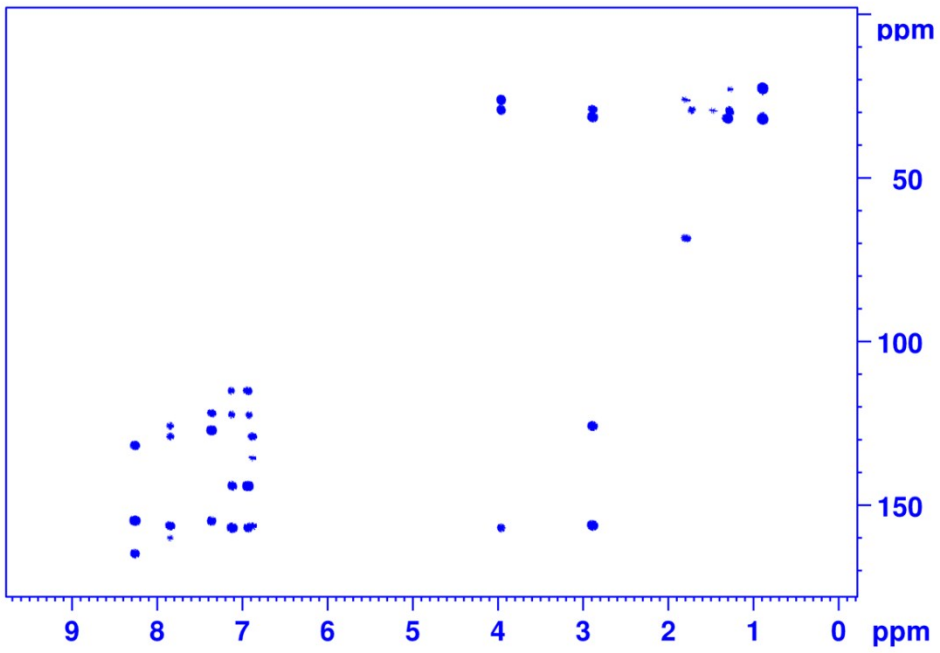


Figure S21: ^{1}H-^{13}C HMBC NMR Spectrum of OTC Mesogen

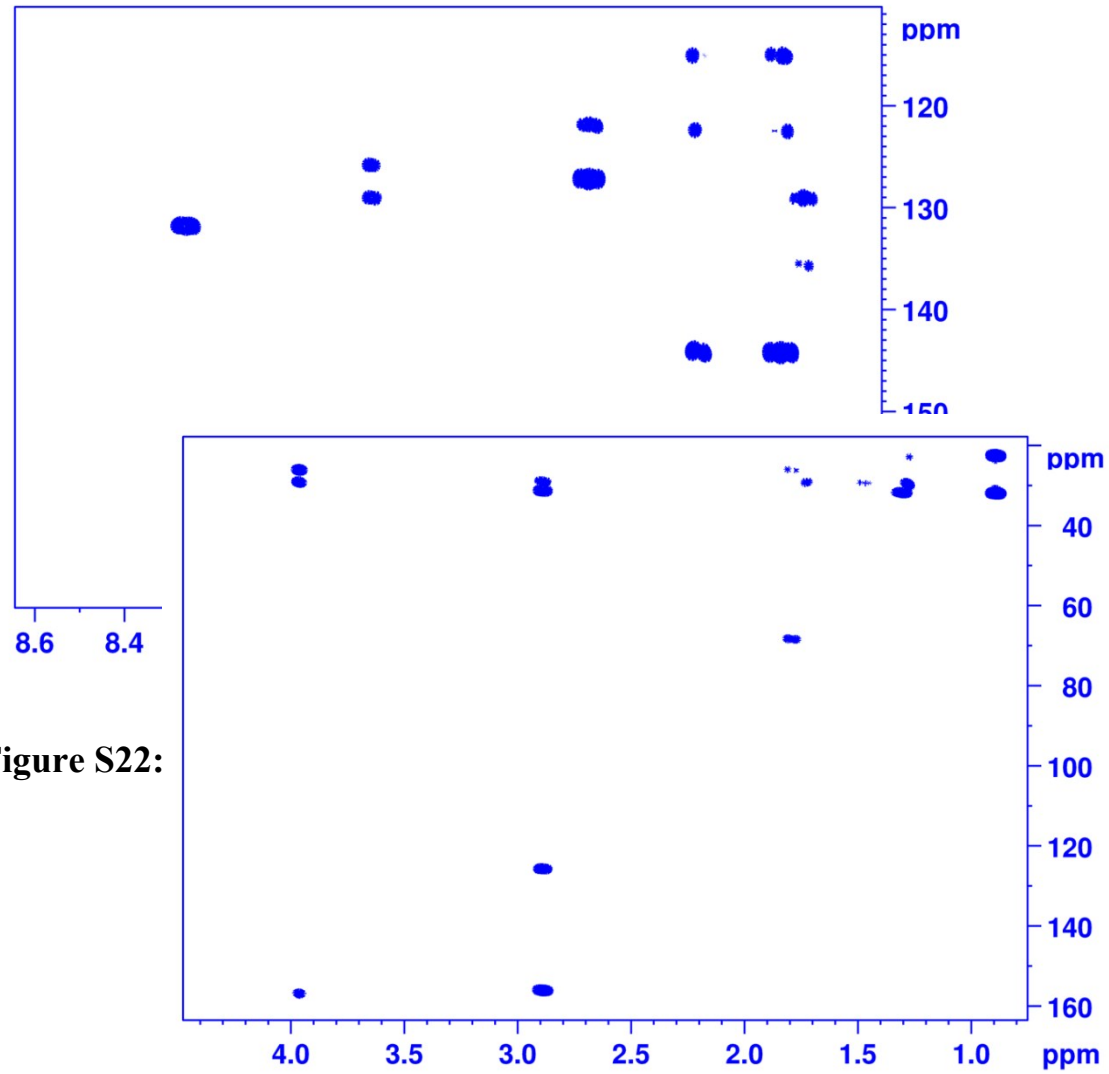


Figure S22:)TC mesogen.

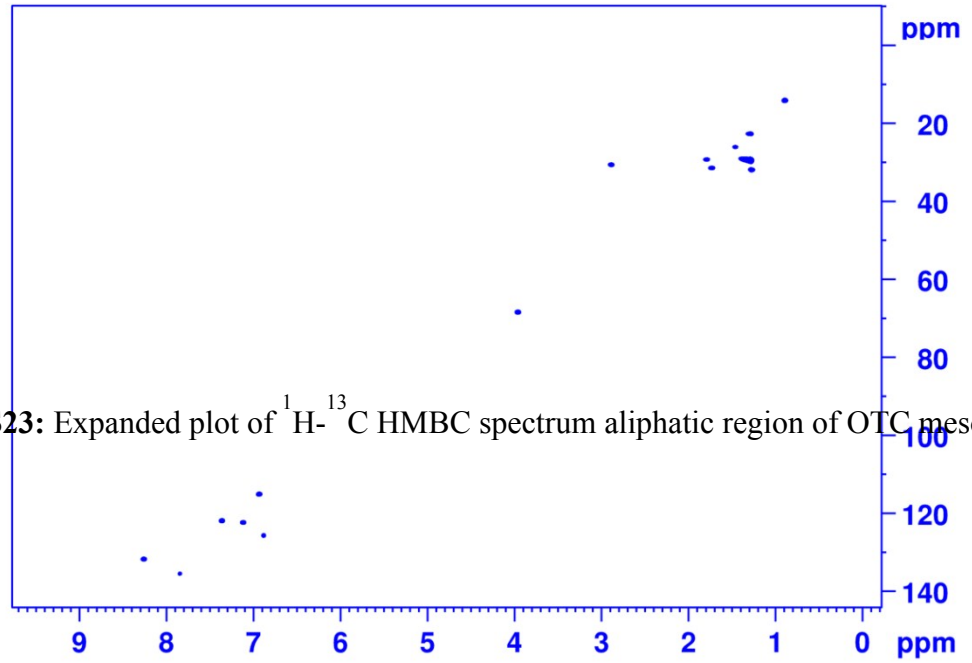


Figure S23: Expanded plot of ^{1}H-^{13}C HMBC spectrum aliphatic region of OTC mesogen.

Figure S24: ^{1}H-^{13}C HSQC NMR spectrum of OTC Mesogen

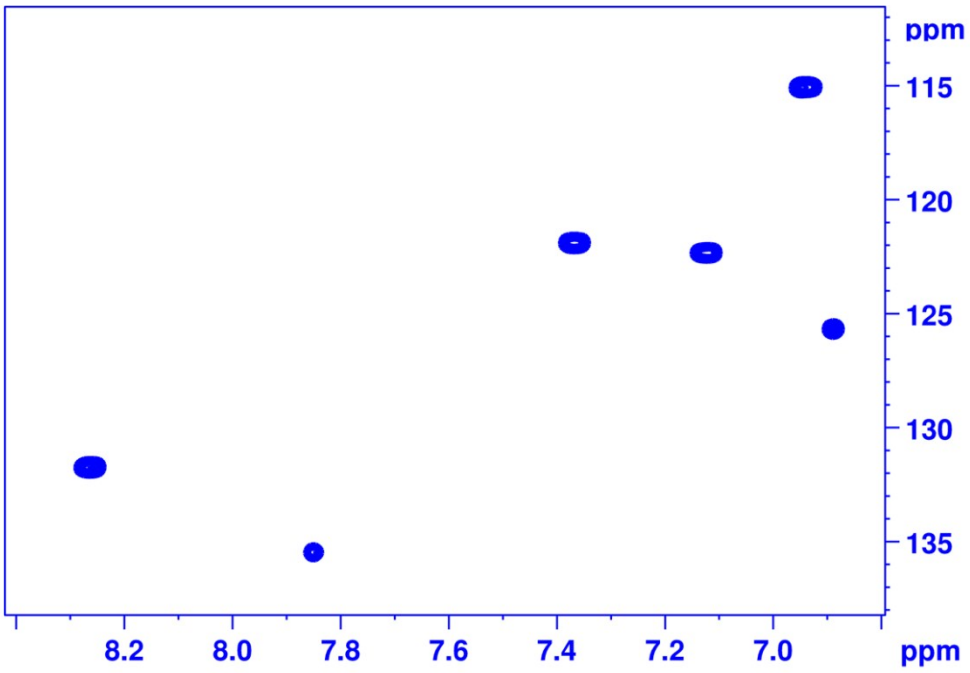


Figure S25: Expanded plot of ^{1}H-^{13}C HSQC spectrum aromatic region of OTC mesogen.

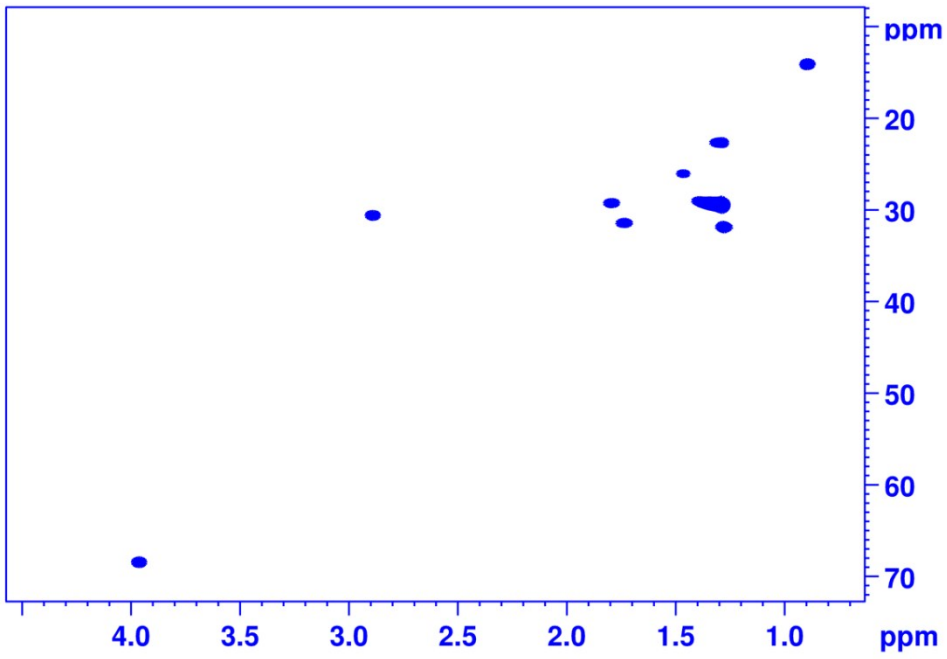


Figure S26: Expanded plot of ^{1}H-^{13}C HSQC spectrum aliphatic region of OTC mesogen.

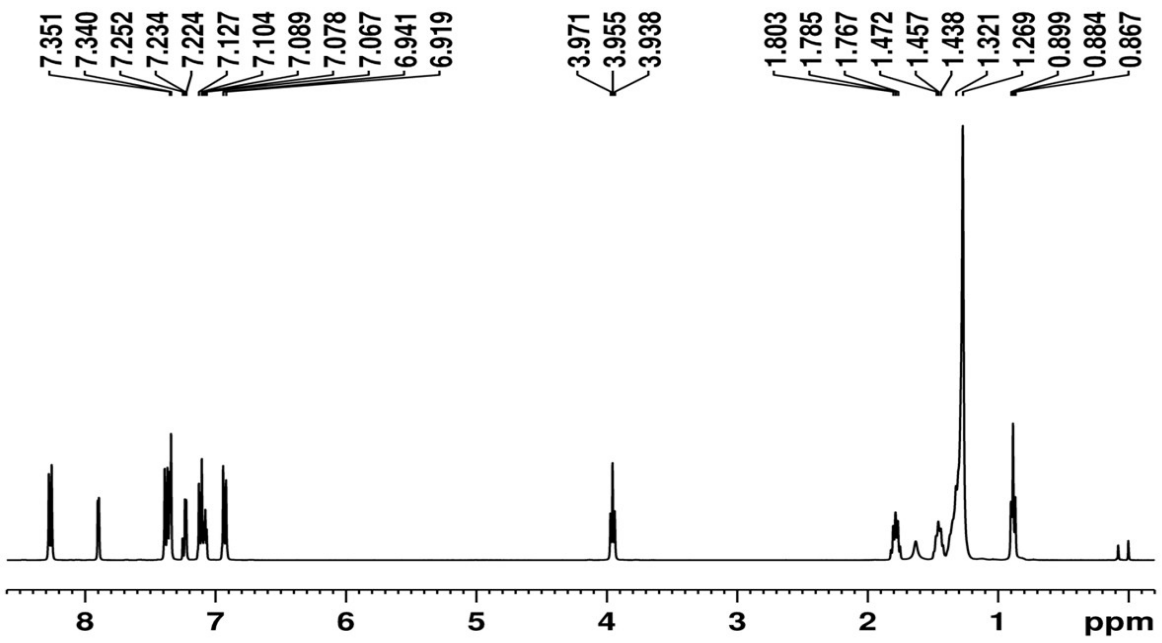


Figure S27: ^{1}H NMR Spectrum of BTC Mesogen

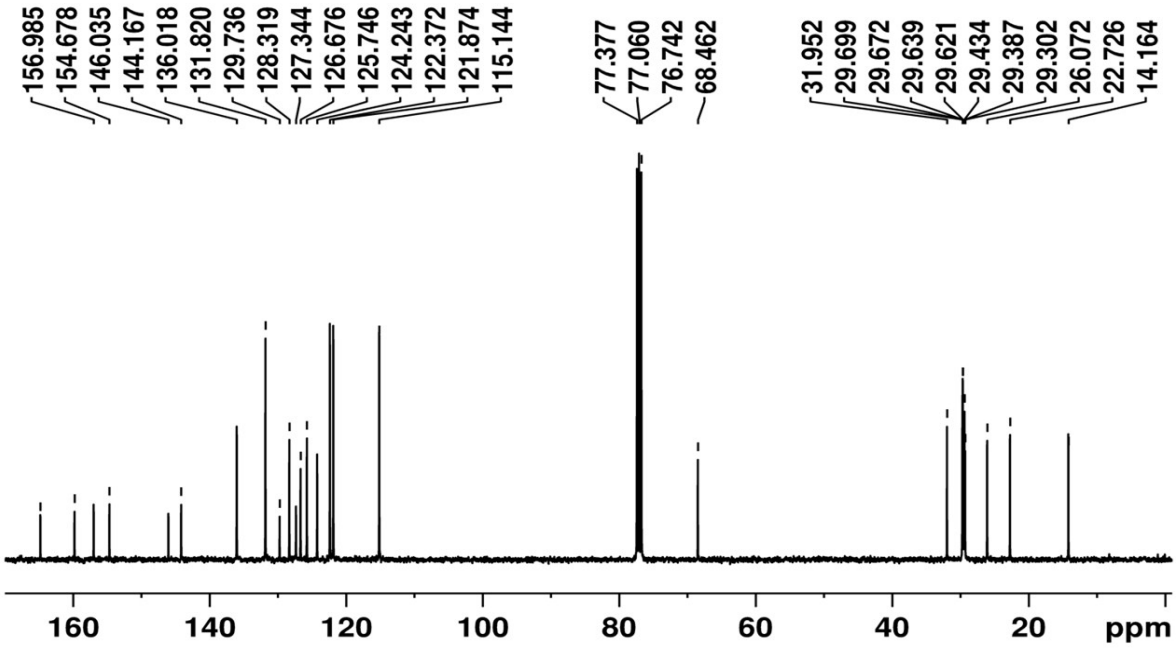


Figure S28: ^{13}C NMR Spectrum of BTC Mesogen

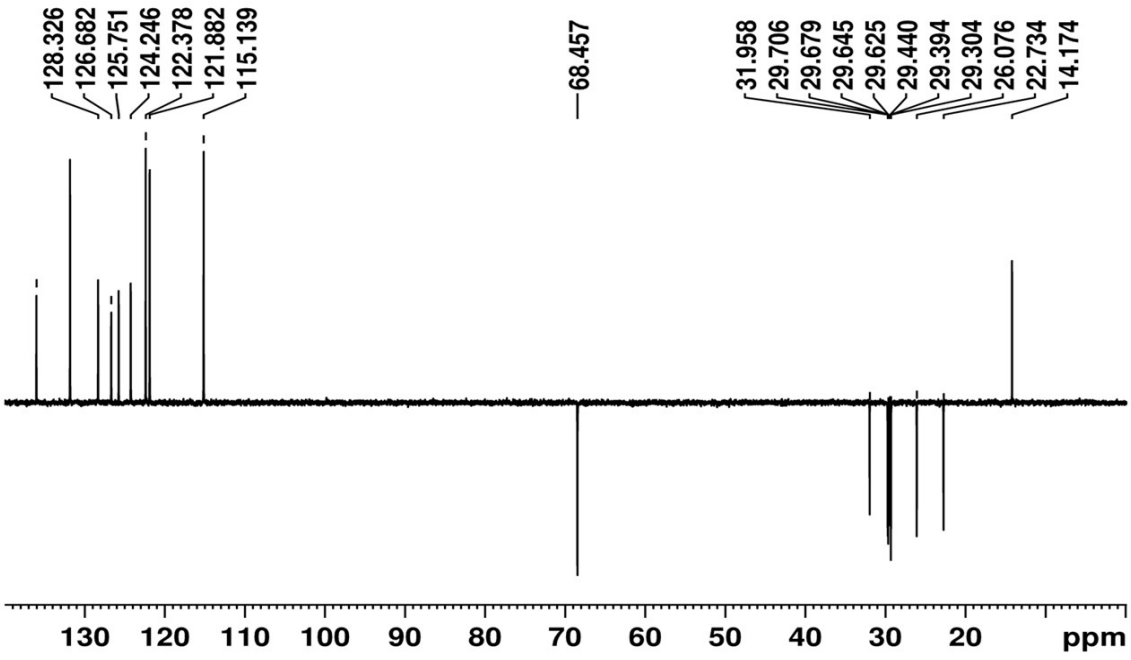


Figure S29: DEPT-135 ^{13}C NMR Spectrum of BTC Mesogen

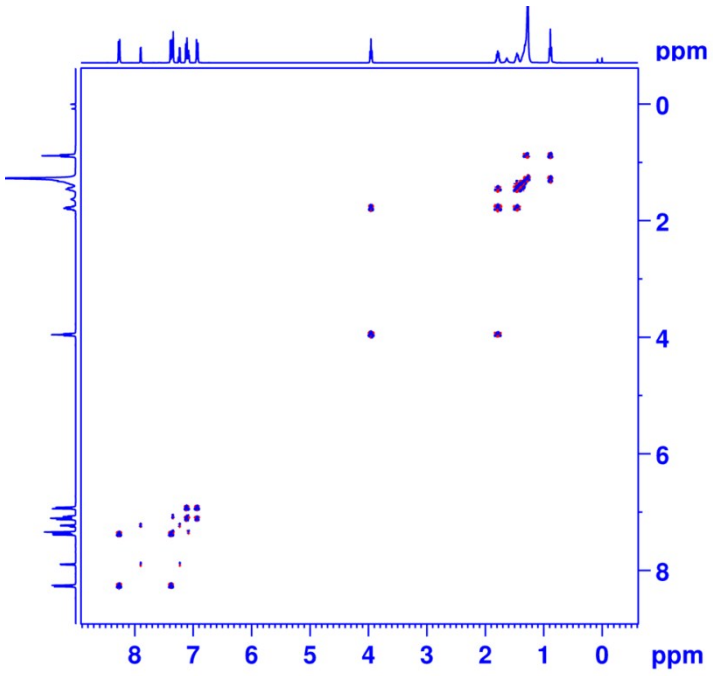


Figure S30: ^{1}H-^{1}H DQF COSY NMR Spectrum of BTC Mesogen

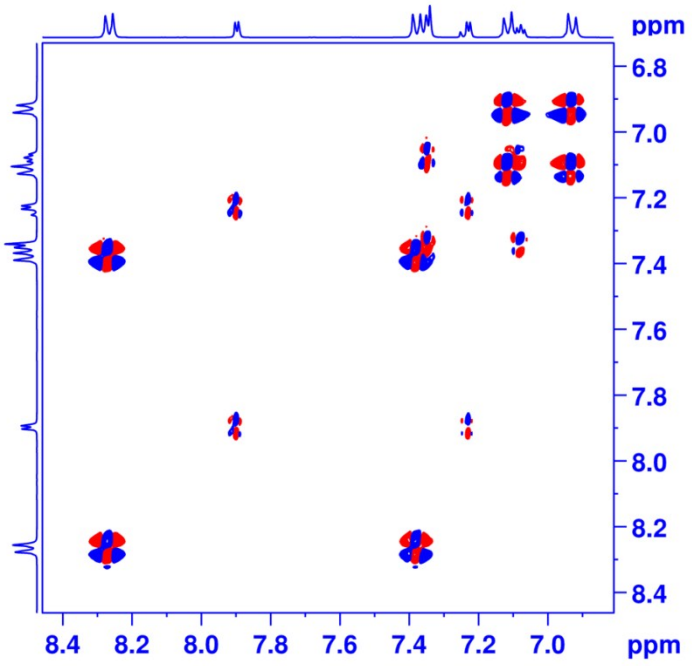


Figure S31: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aromatic region of BTC Mesogen.

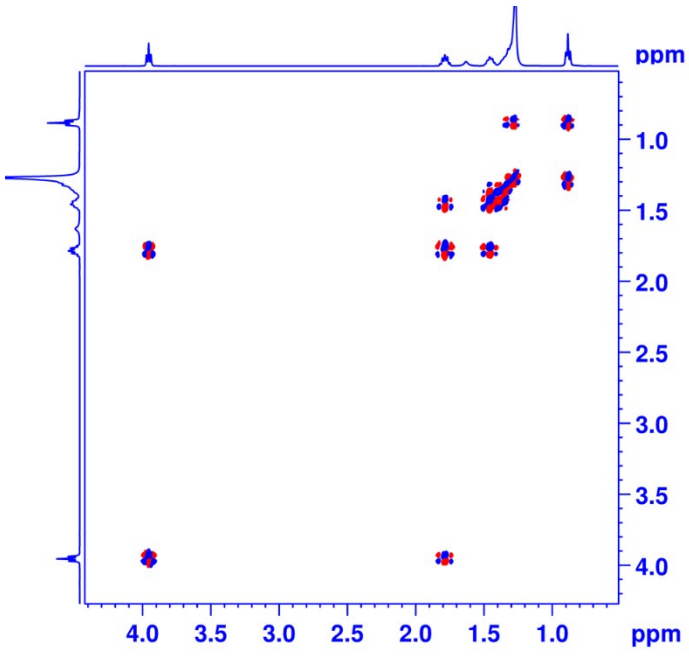


Figure S32: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aliphatic region of BTC Mesogen.

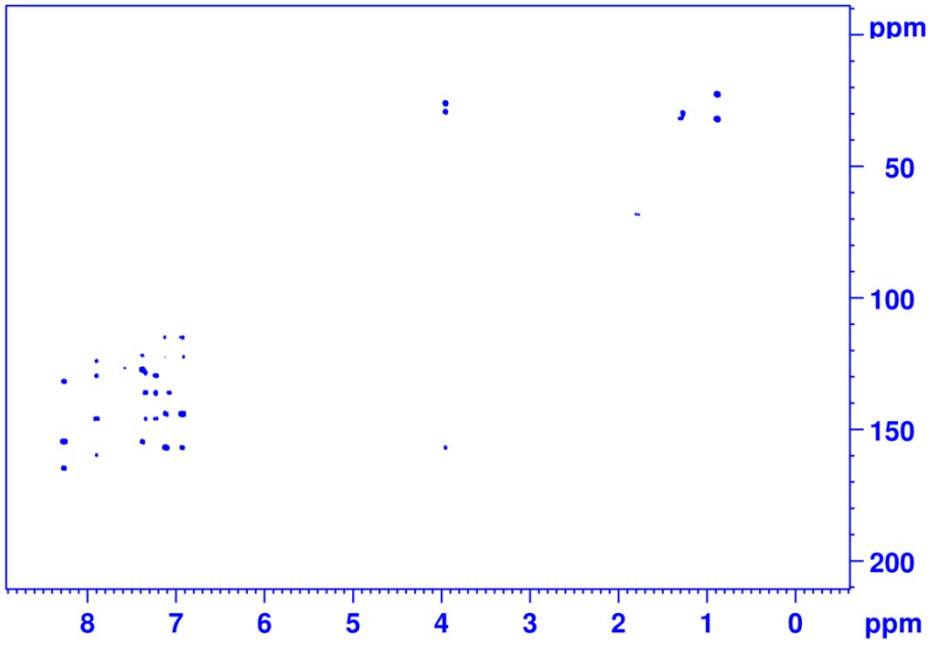


Figure S33: ^{1}H-^{13}C HMBC NMR Spectrum of BTC Mesogen

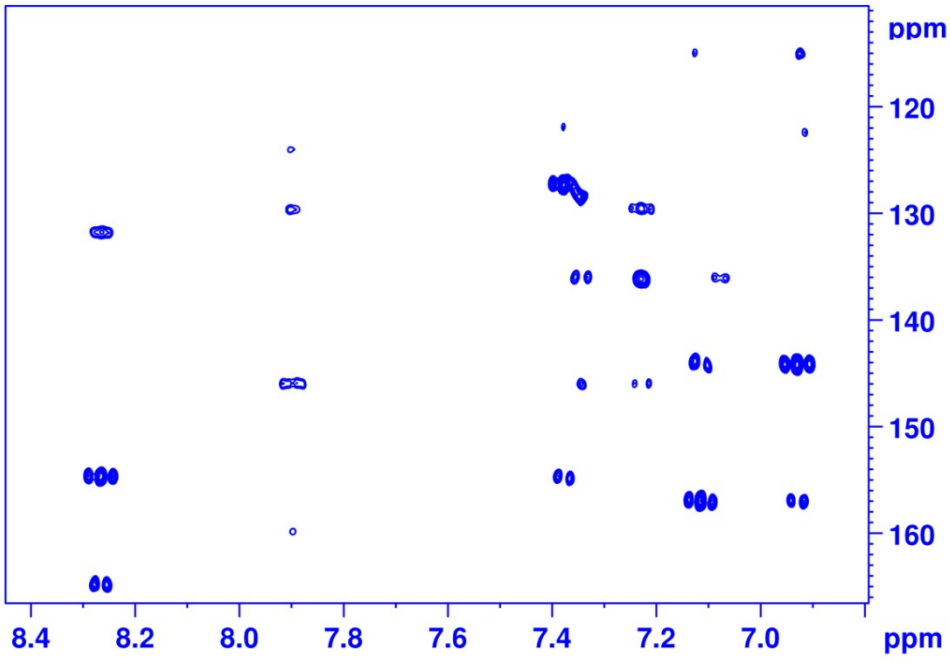


Figure S34: Expanded plot of ^{1}H-^{13}C HMBC spectrum aromatic region of BTC mesogen.

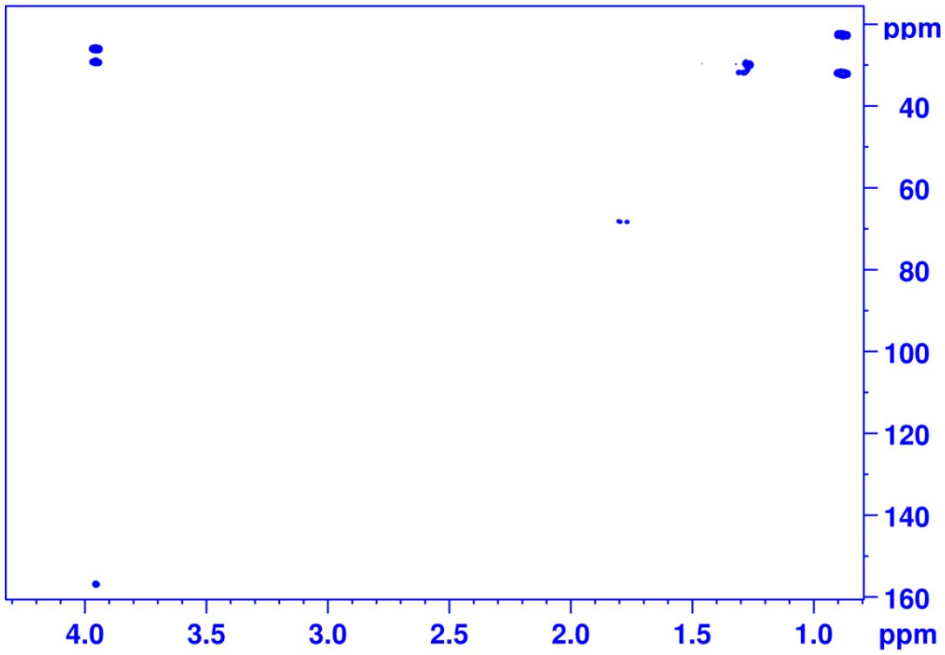


Figure S35: Expanded plot of ^{1}H -^{13}C HMBC spectrum aliphatic region of BTC mesogen.

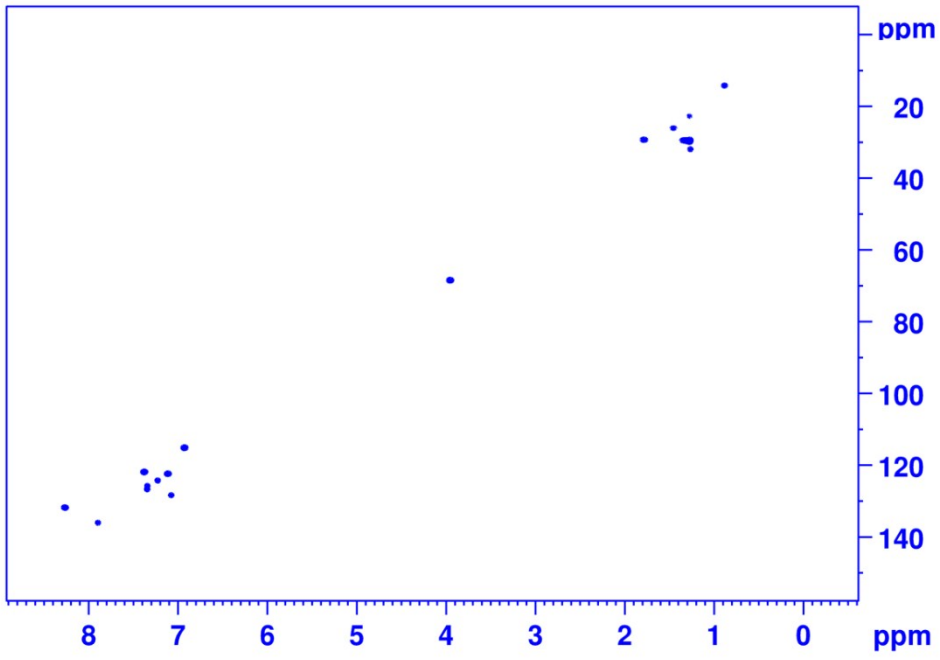


Figure S36: ^{1}H - ^{13}C HSQC NMR spectrum of BTC Mesogen

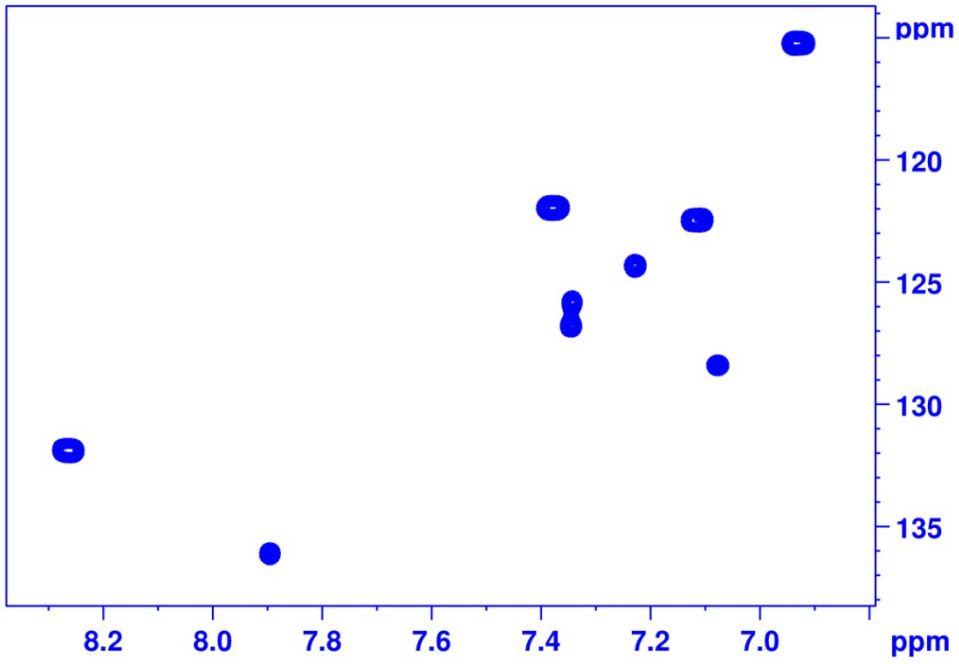


Figure S37: Expanded plot of ^{1}H -^{13}C HSQC spectrum aromatic region of BTC mesogen.

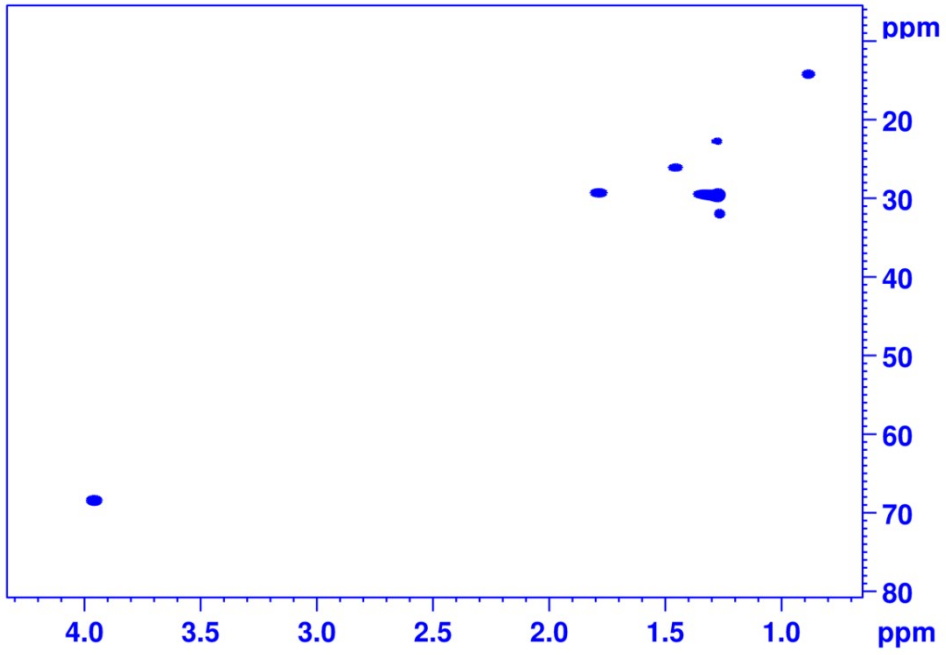


Figure S38: Expanded plot of ^{1}H-^{13}C HSQC spectrum aliphatic region of BTC mesogen

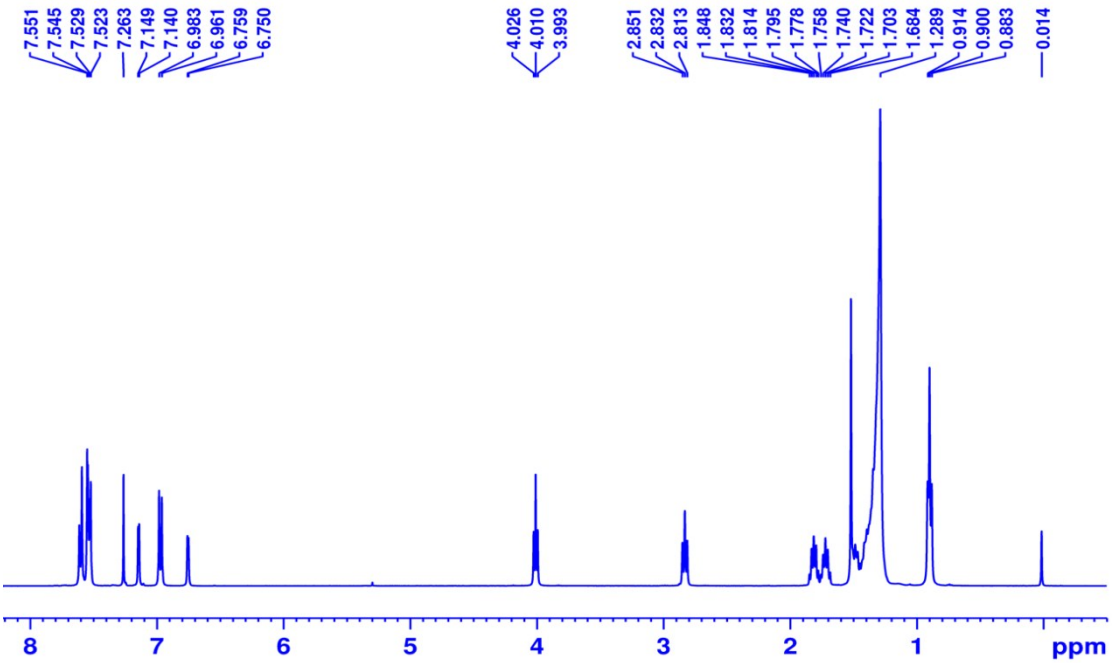


Figure S39: ^{1}H NMR Spectrum of OTPC Mesogen

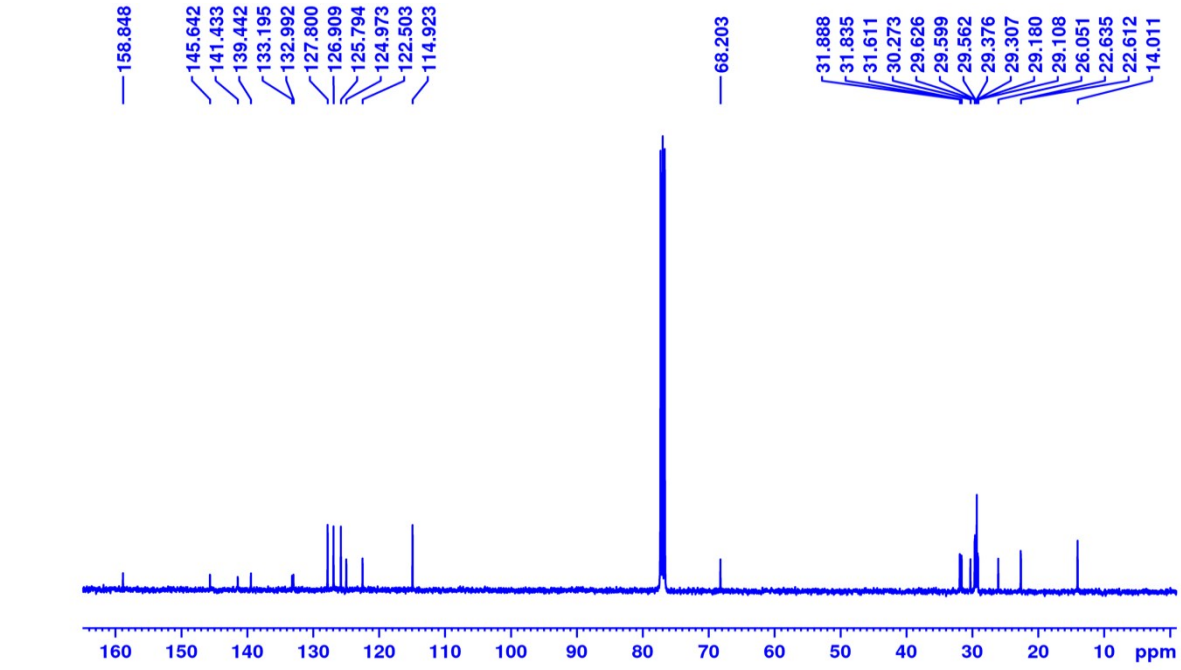


Figure S40: ^{13}C NMR Spectrum of OTPC Mesogen

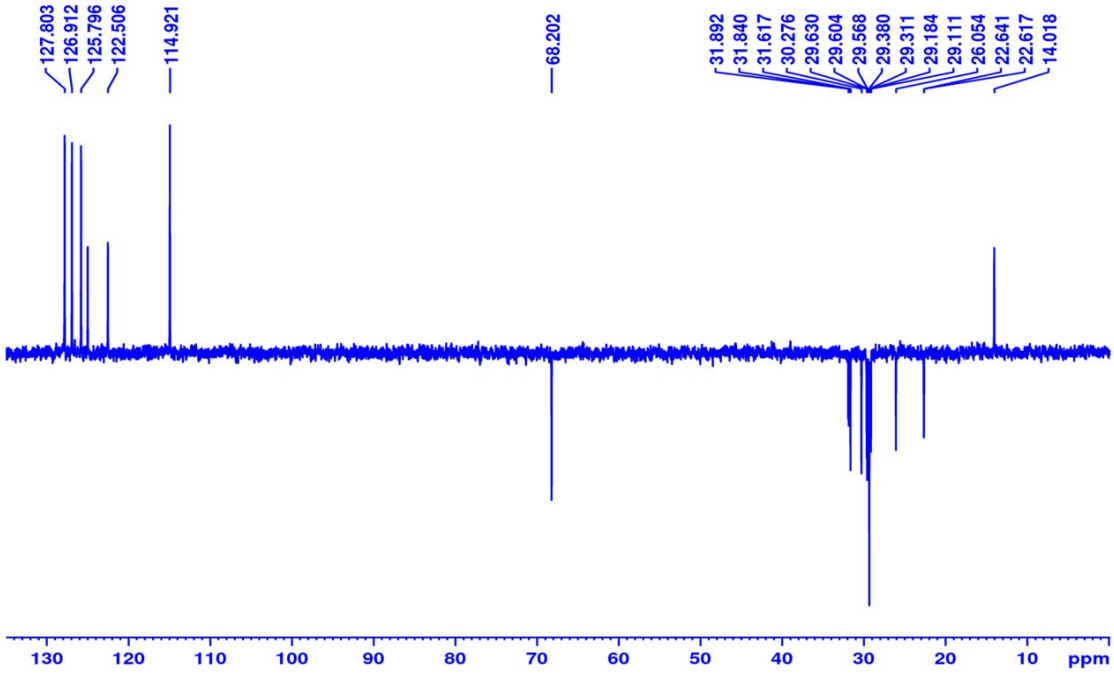


Figure S41: DEPT-135 ^{13}C NMR Spectrum of OTPC Mesogen

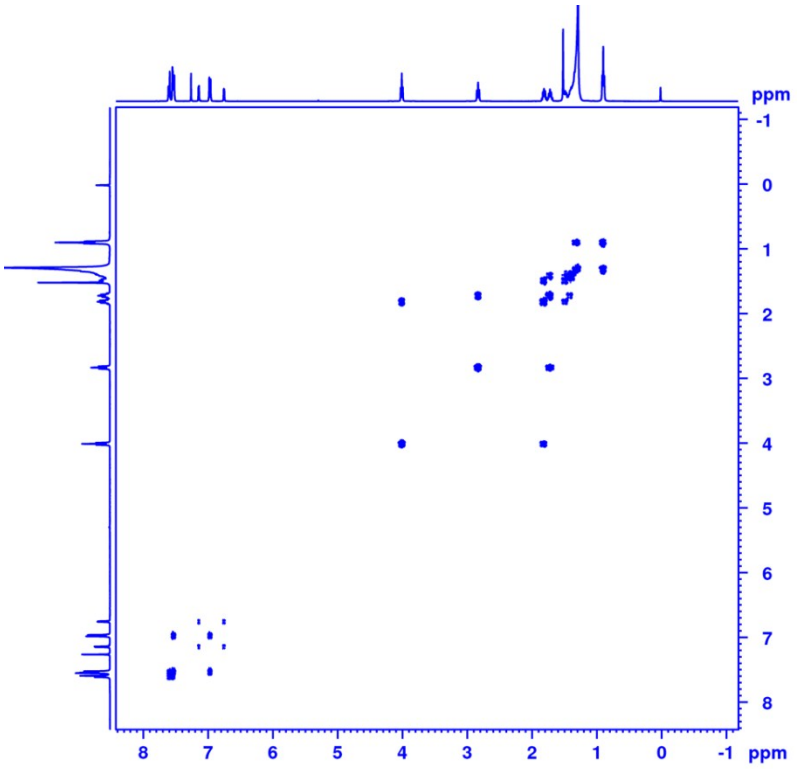


Figure S42: ^{1}H-^{1}H DQF COSY NMR Spectrum of OTPC Mesogen

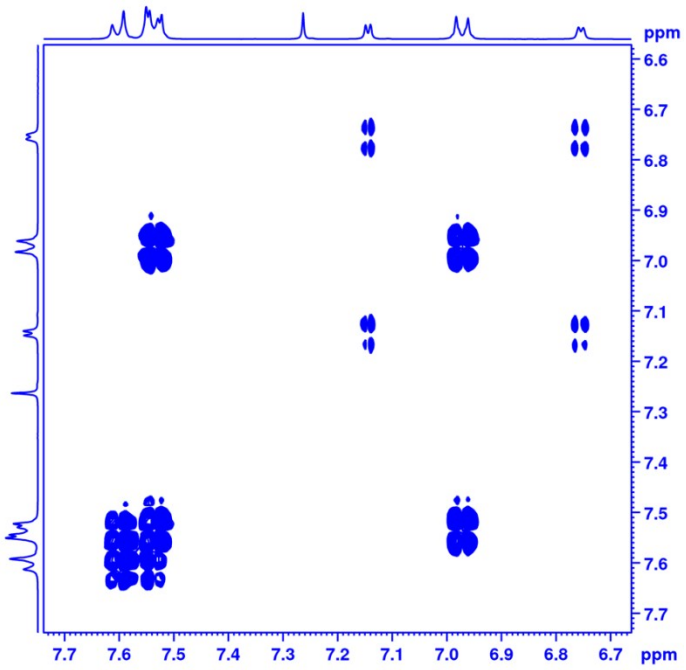


Figure S43: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aromatic region of OTPC

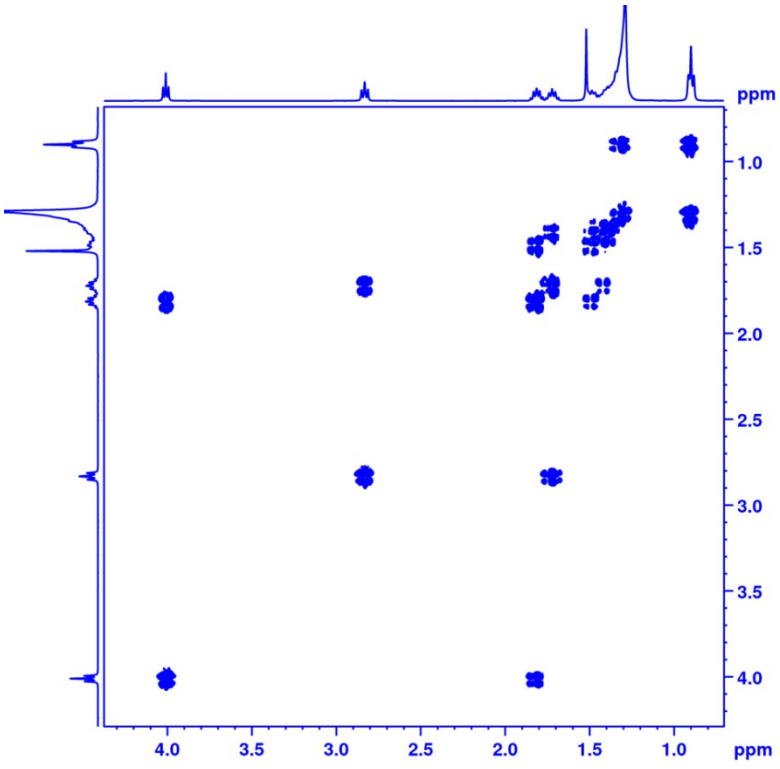


Figure S44: Expanded plot of ^{1}H-^{1}H DQF COSY spectrum aliphatic region of OTPC

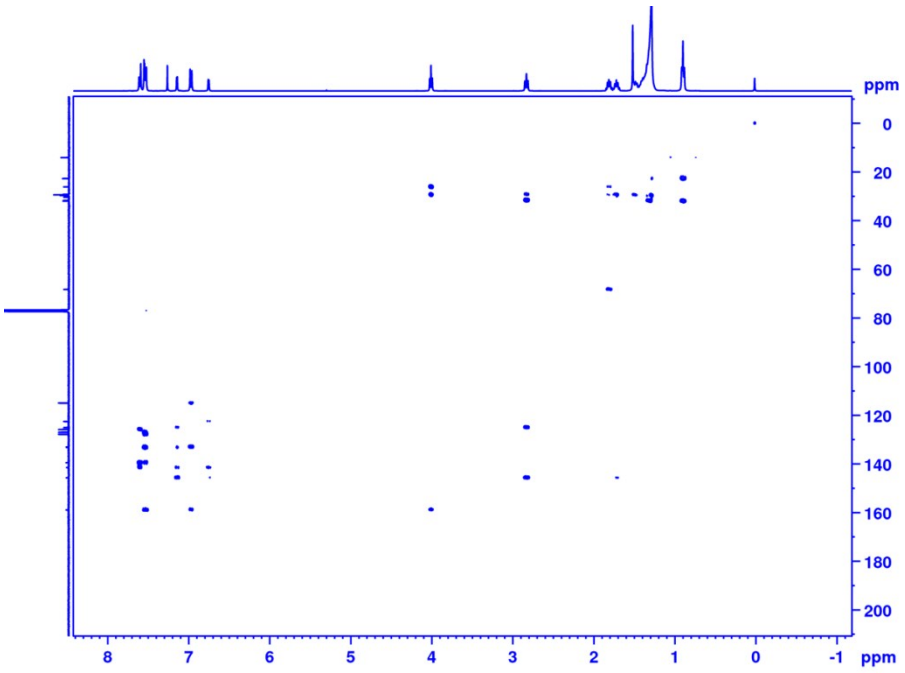


Figure S45: ^{1}H - ^{13}C HMBC NMR Spectrum of OTPC Mesogen

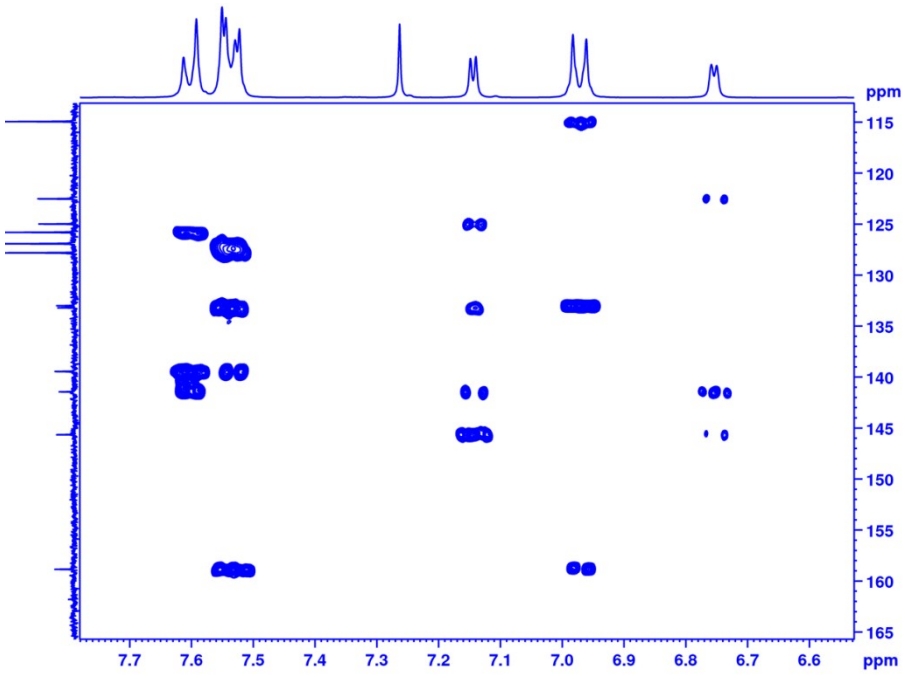


Figure S46: Expanded plot of ^{1}H-^{13}C HMBC spectrum aromatic region of OTPC mesogen.

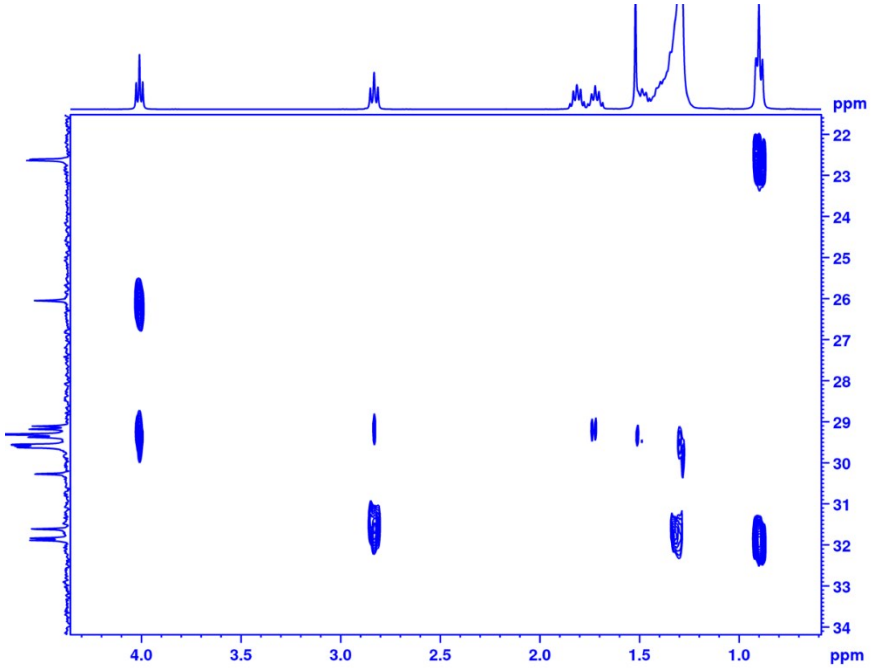


Figure S47: Expanded plot of ^{1}H-^{13}C HMBC spectrum aliphatic region of OTPC mesogen.

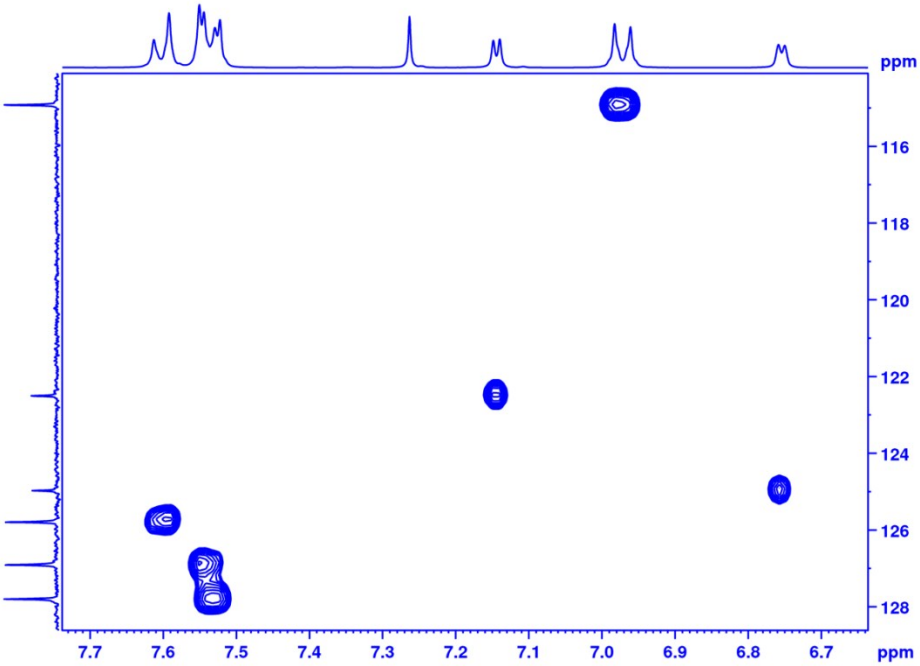


Figure S48: Expanded plot of ^{1}H-^{13}C HSQC spectrum aromatic region of OTPC mesogen

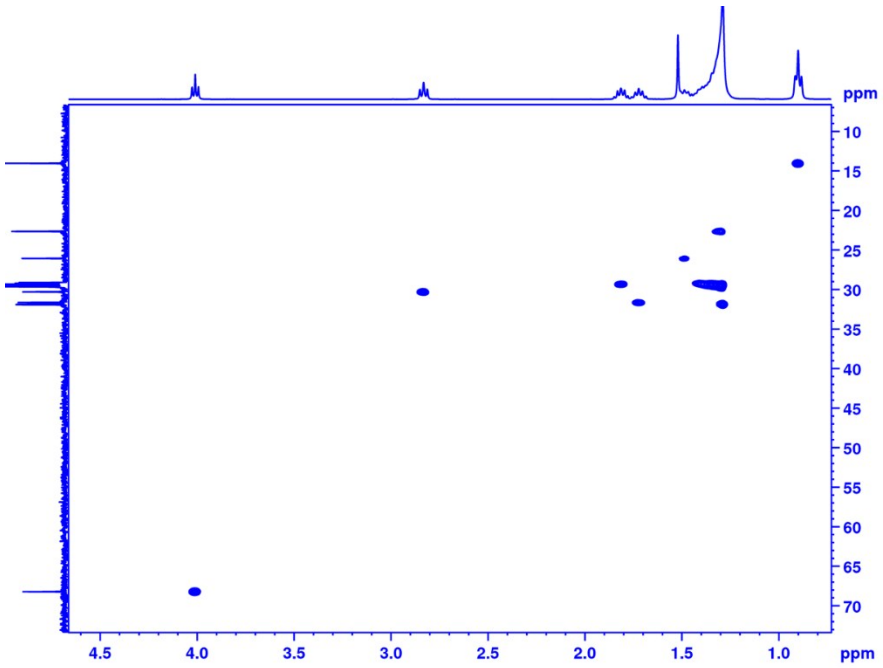


Figure S49: Expanded plot of ^{1}H-^{13}C HSQC spectrum aliphatic region of OTPC mesogen

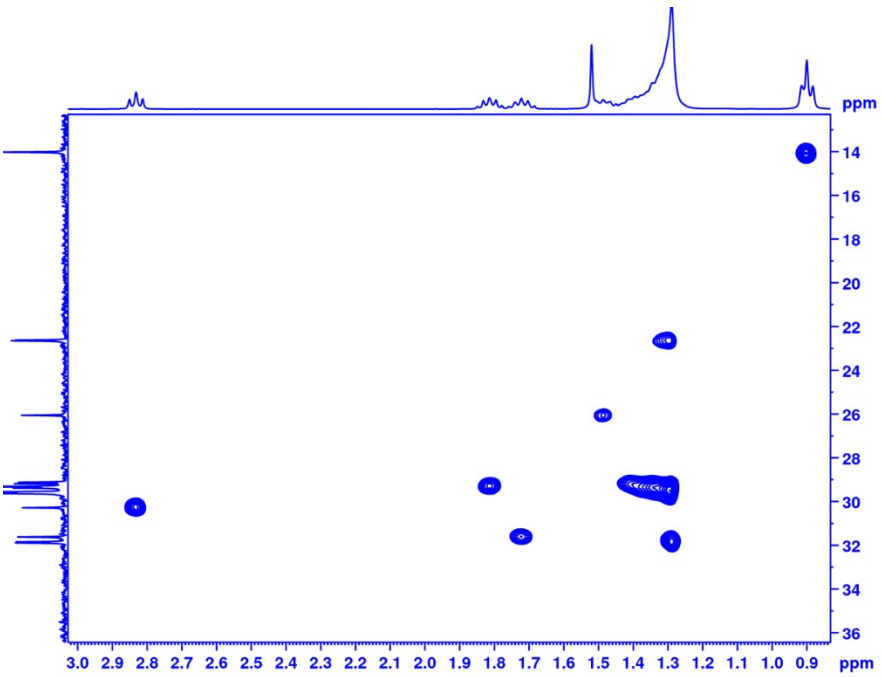


Figure S50: Expanded plot of ^{1}H-^{13}C HSQC spectrum aliphatic region of OTPC mesogen

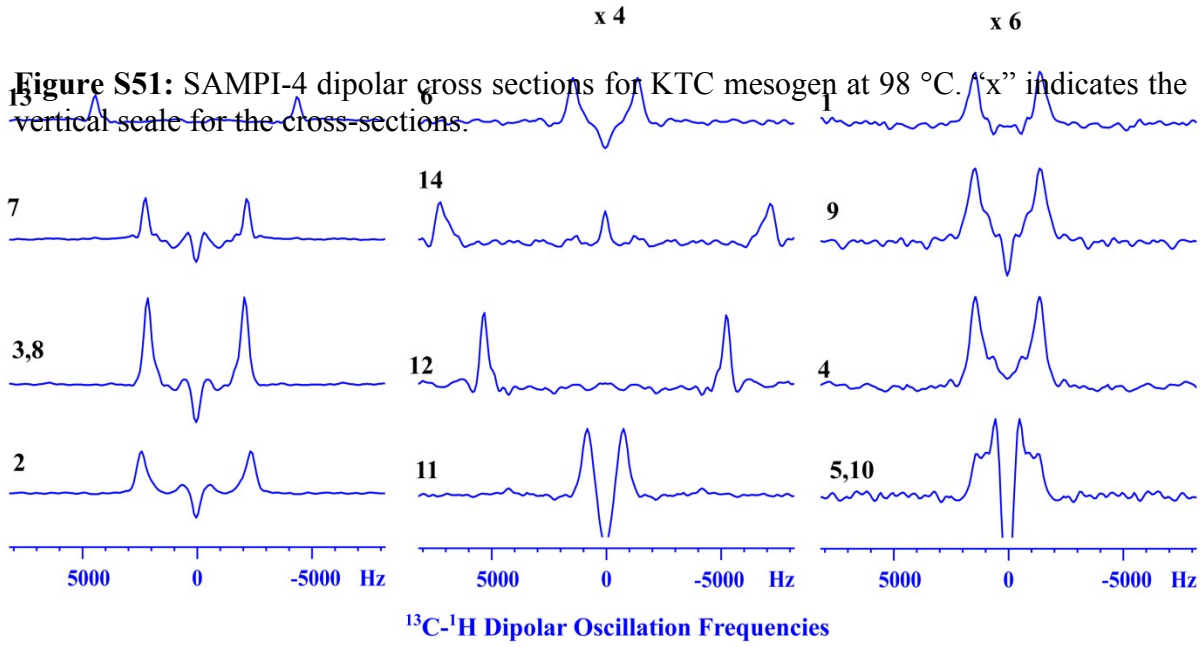


Figure S51: SAMPI-4 dipolar cross sections for KTC mesogen at 98 °C. "x" indicates the vertical scale for the cross-sections.

Figure S52: SAMPI-4 dipolar cross sections for HTC mesogen at 85 °C. "x" indicates the vertical scale for the cross-sections.

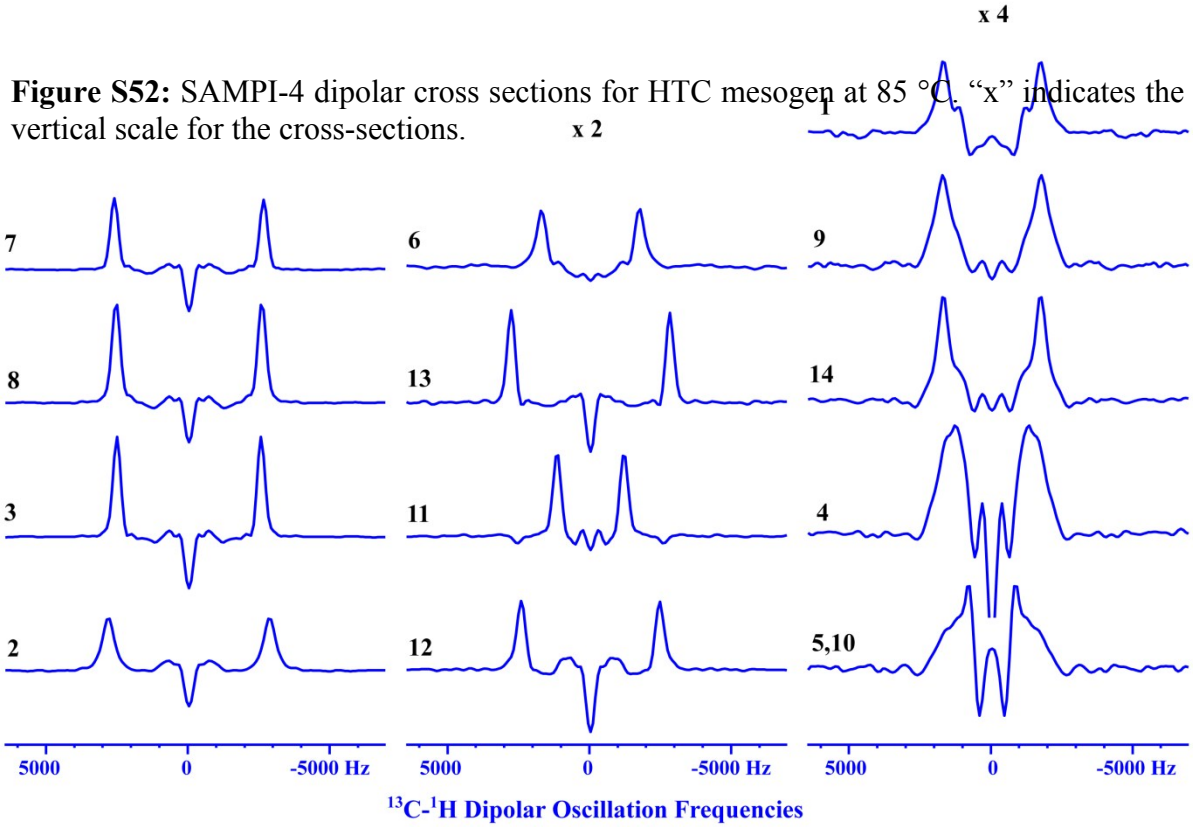
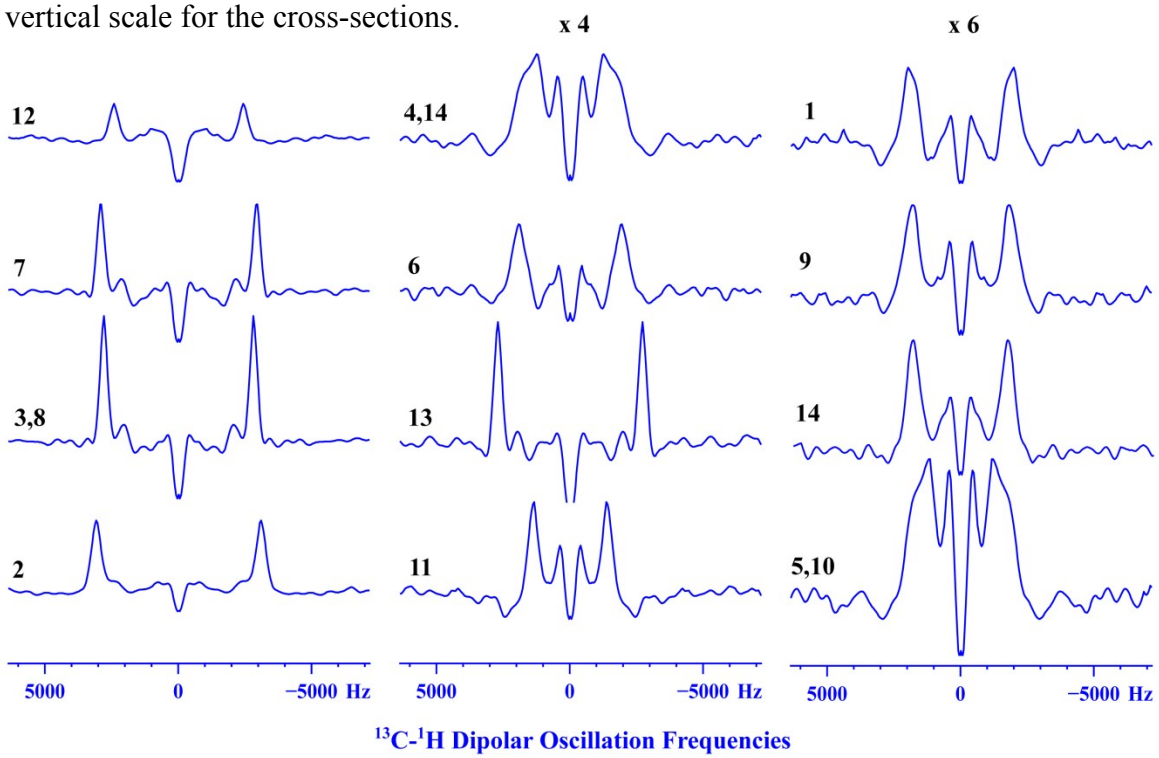


Figure S53: SAMPI-4 dipolar cross sections for OTC mesogen at 96 °C. "x" indicates the vertical scale for the cross-sections.



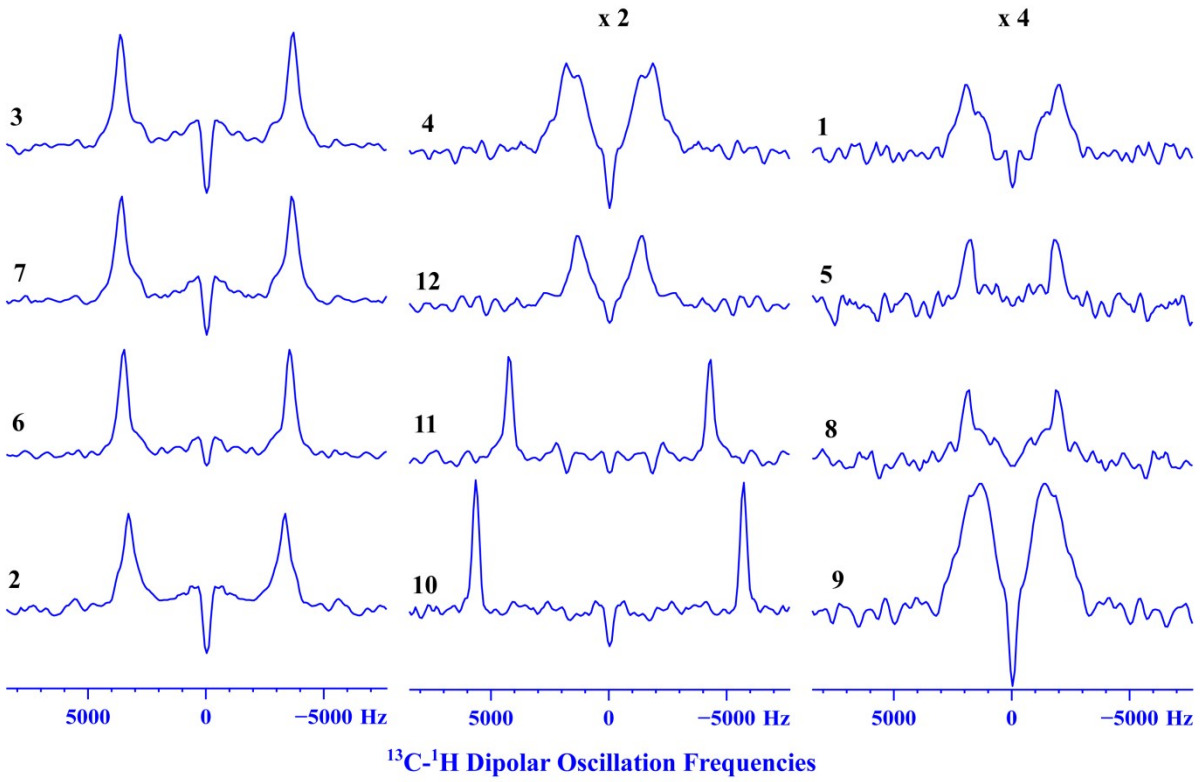


Figure S54: SAMPI-4 dipolar cross sections for OTPC mesogen at 166 °C. "x" indicates the vertical scale for the cross-sections.

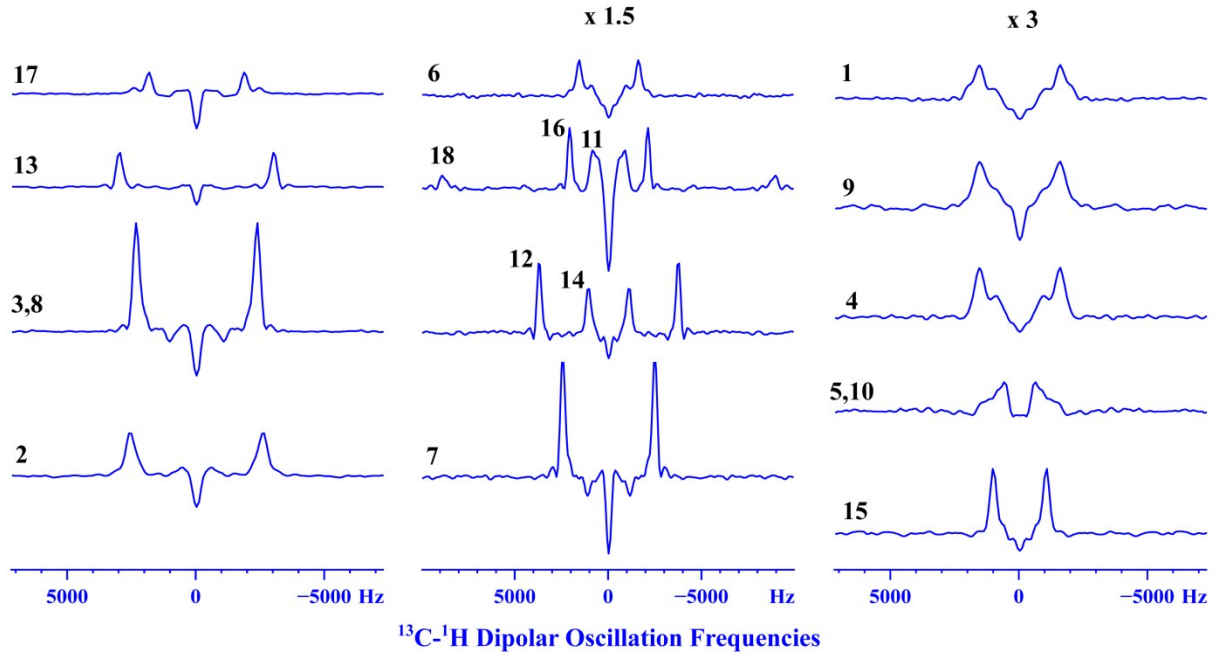


Figure S55:
vertical scal

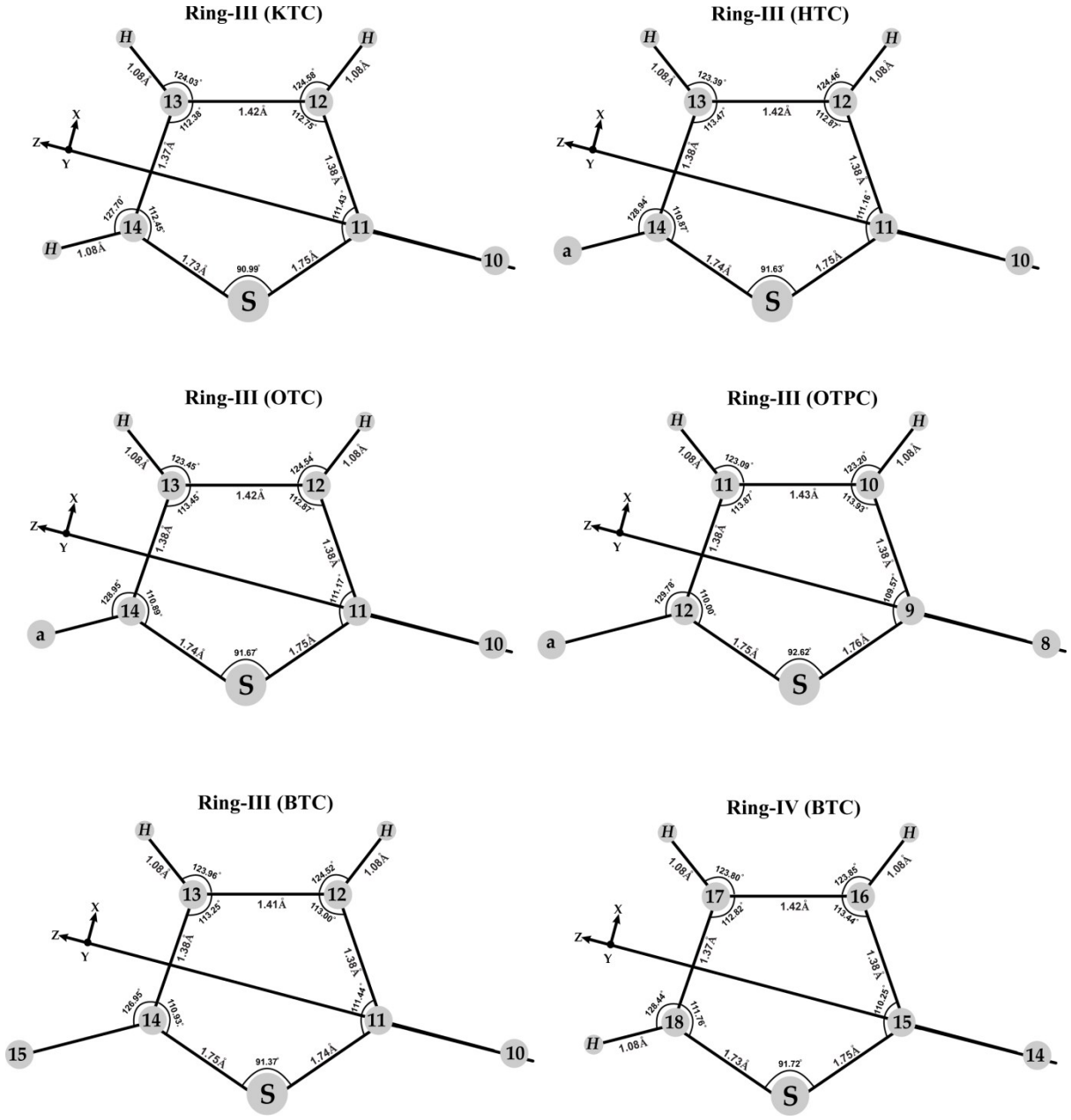


Figure S56: Model of thiophenes belongs to five mesogens with the coordinate system used for obtaining the orientational order parameters from experimental dipolar oscillation frequencies. The bond angles and bond distances obtained from the energy-minimized structure of mesogens.

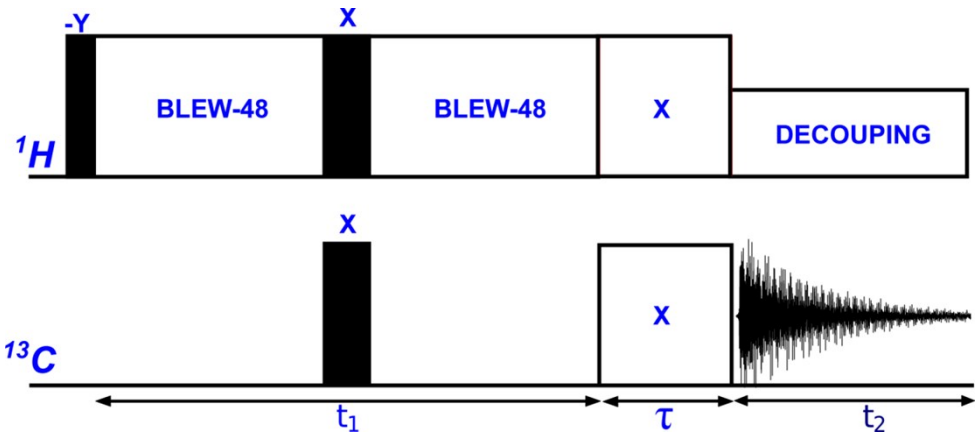


Figure S57: Pulse sequence for 2D Proton Encoded Local Field (PELF) experiment. BLEW-48 homonuclear decoupling sequence employed during t_1 period to suppress the homonuclear ^{1}H-^{1}H dipolar couplings and SPINAL-64 scheme is applied during t_2 period heteronuclear decoupling sequence to acquire ^{13}C 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.

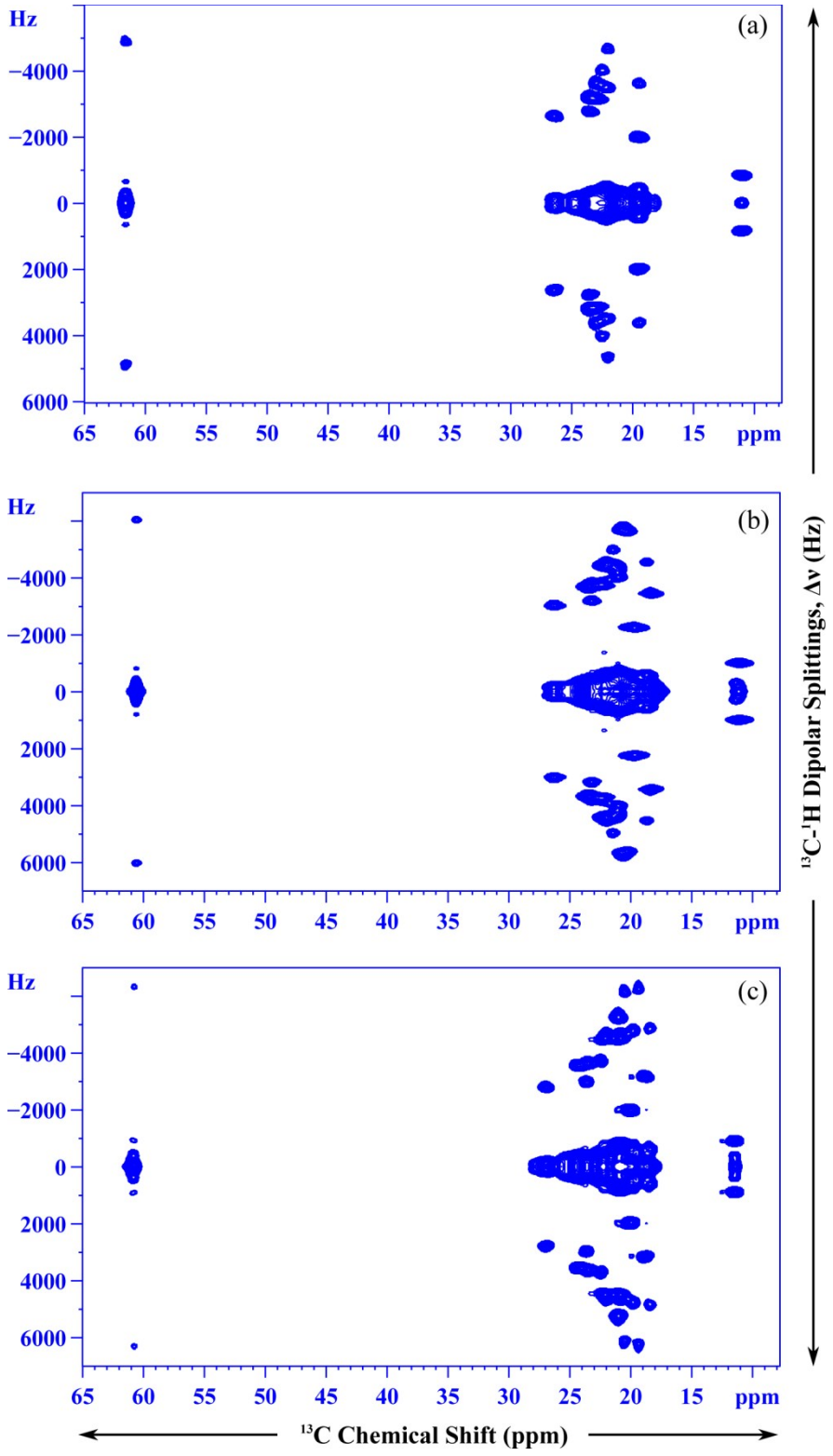


Figure S58: PELF spectra of mesogens at various phases in aliphatic region: (a) KTC in nematic (98 °C), (b) HTC in smectic C (85 °C), (c) OTC in smectic C (96 °C).

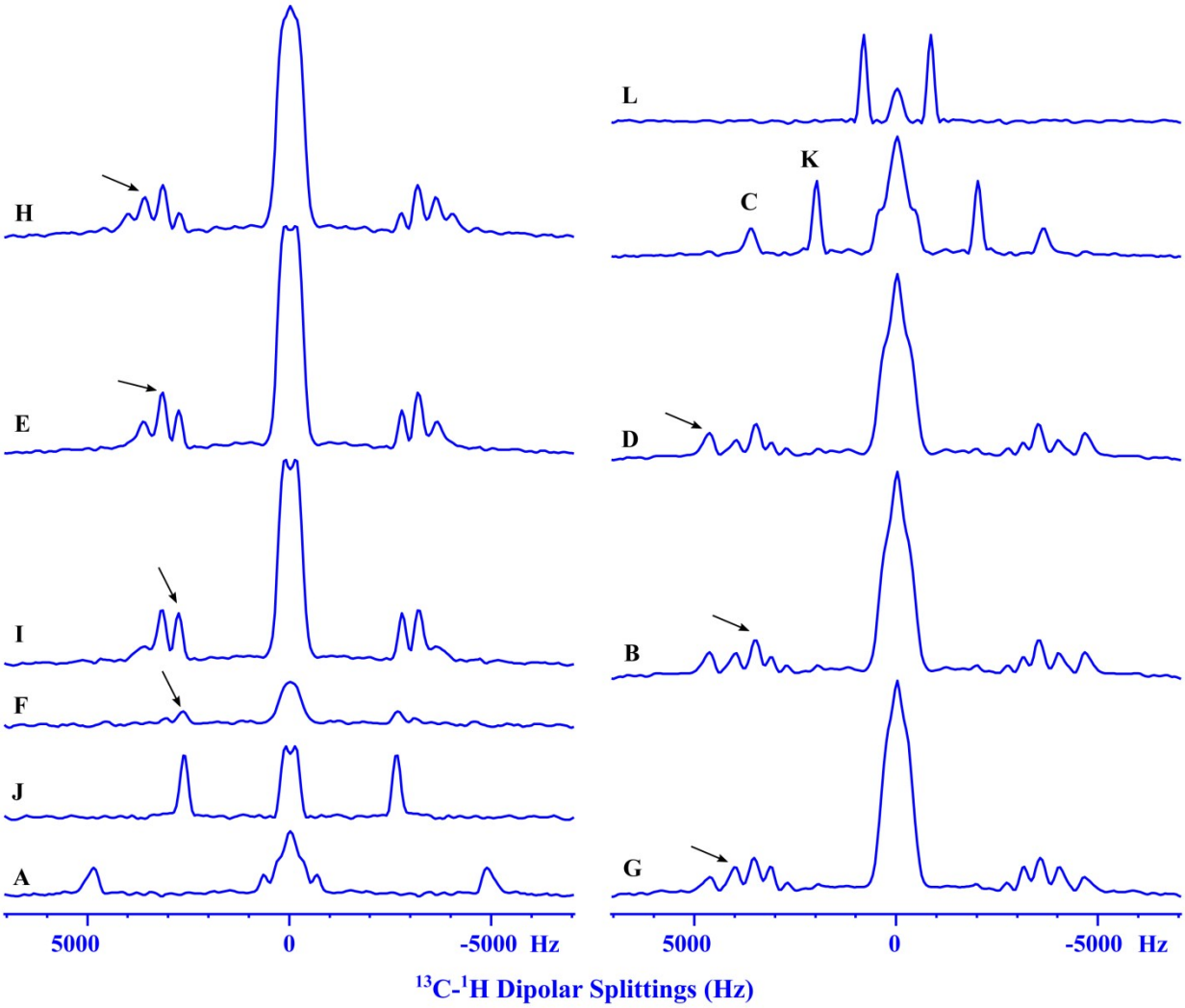


Figure S59: PELF dipolar cross sections for KTC mesogen at 98 °C.

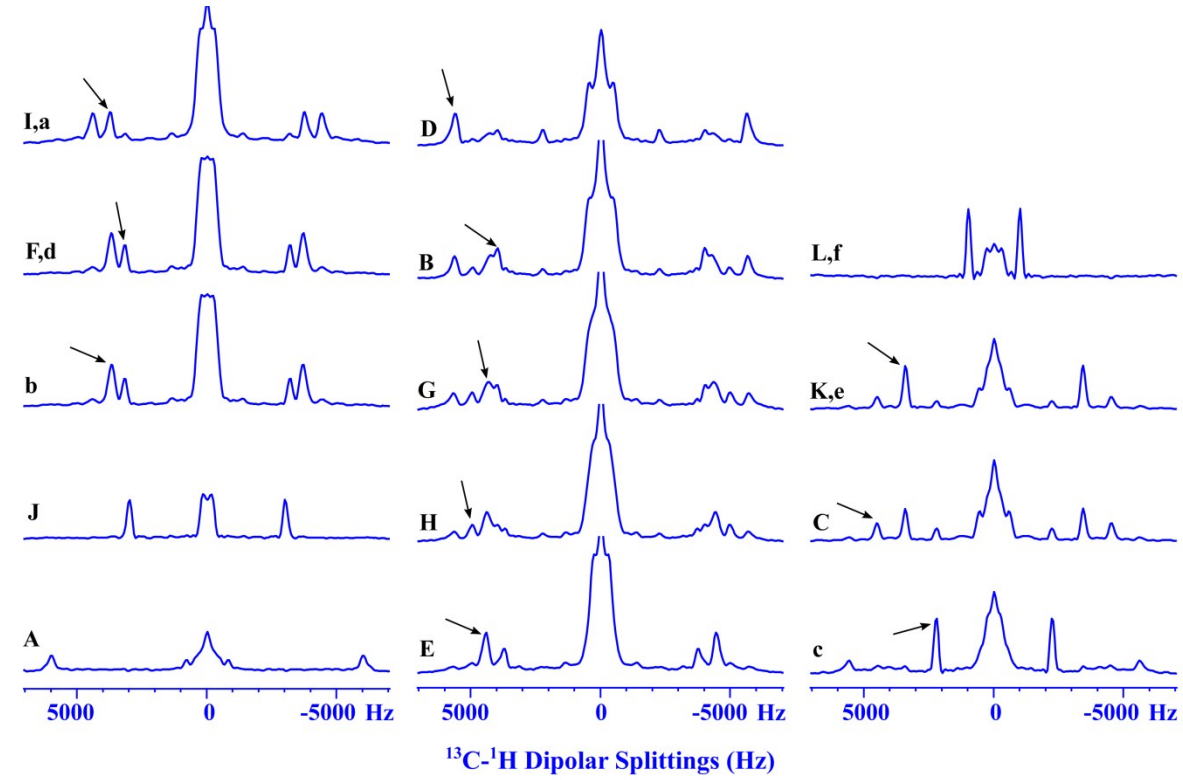


Figure S60: PELF dipolar cross sections for HTC mesogen at 85 °C.

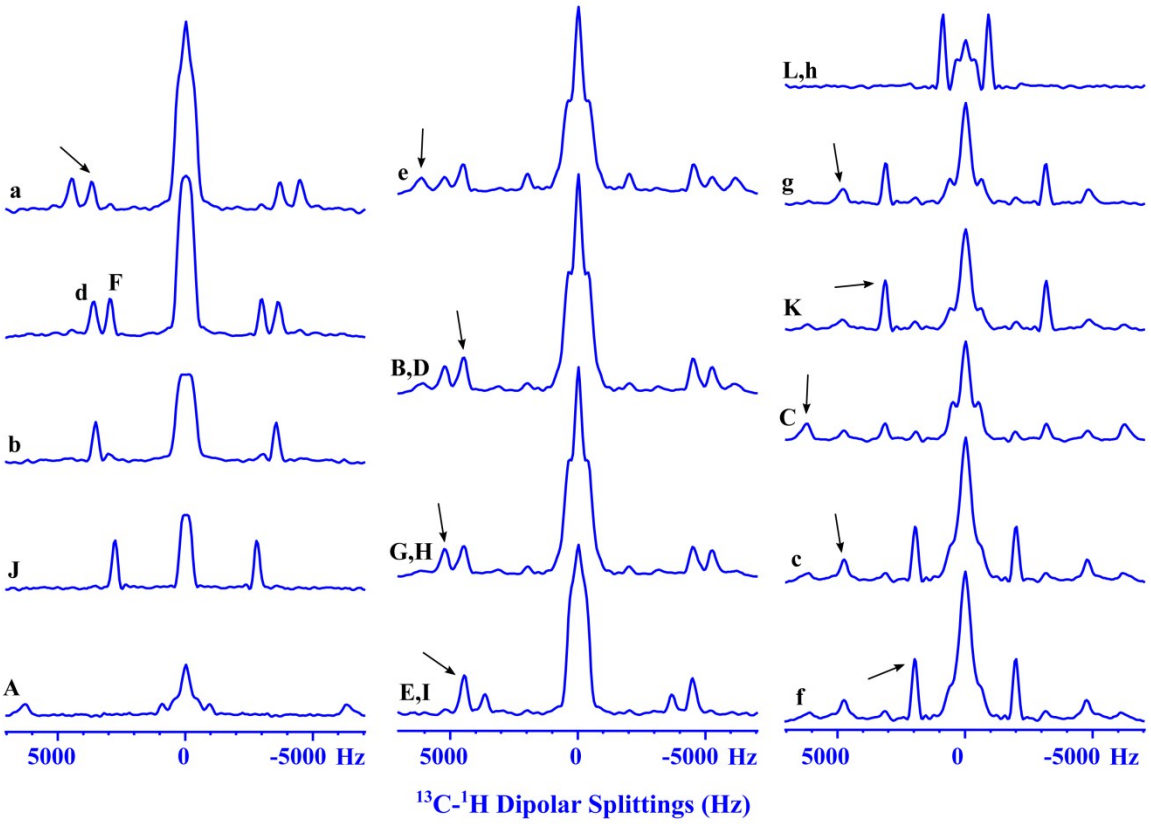


Figure S61: PELF dipolar cross sections for OTC mesogen at 96 °C.

2D PELF Experimental Details and Orientational Ordering of Aliphatic Chains

The 2D Proton Encoded Local Field (PELF)[1-3] belongs to the family of Separated Local Field (SLF) experiment. The experimental spectrum correlates the ^{13}C chemical shift with the associated ^{13}C-^{1}H dipolar couplings. BLEW-484 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. 2D PELF spectra were obtained for three mesogen under following parameters KTC/HTC/OTC: t_1 increments =128/128/100, number of scans=16, recycle delay between the scans= 12 s/ 15 s/ 14 s (to avoid rf heating effect). The F_1 dimension frequency axis in the spectrum was scaled with a scaling factor of 0.42.

The order parameter of each C-H bond in each segment of the chain can be calculated by assuming a axially symmetry and by using following relation[5]

$$S_{CH} = D_{CH} / K \qquad (1)$$

where D_{CH} is scaled dipolar coupling, $K = -h\gamma_H\gamma_C/4\pi^2r^3_{CH}$, 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.

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