

Supporting information for

## **Synthesis of Hydrophobic Carbohydrate Polymers and Their Formation of Thermotropic Liquid Crystalline Phases**

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## I. General methods and instrumentation.

All reactions were carried out under nitrogen using standard techniques, unless otherwise noted.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian 400 or 500 MHz spectrometer. Samples for IR were prepared by drop-casting a solution of the sample in dichloromethane on a KBr plate or with a horizontal attenuated total reflectance (ATR) adapter on a Nicolet FT-IR. Polymer molecular weights were determined by gel permeation chromatography (GPC) versus polystyrene standards using THF as the eluent at a flow rate of 1 mL/min through a Styragel column (4EHR) with a refractive index detector. Specific rotations were determined using a Rudolph Autopol II polarimeter operating at 589 nm in a 50 mm pathlength cell. Unless otherwise mentioned, all chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, or Acros and used as received. Thermogravimetric analysis of GOE-PAS<sub>n</sub> was recorded on a TGA Q50 V6.7 TA instrument with a ramp of 20 °C/min from 27 °C to 700 °C. X-Ray diffractograms of GOE-PAS<sub>n</sub> polymers were obtained with a linear focalized monochromatic Cu-K $\alpha$ 1 beam ( $\alpha=1.5404$  Å), using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. In all cases, about 10 mm long sample cylinders were introduced in Lindemann capillaries of 1 mm diameter and 10  $\mu\text{m}$  wall thickness. The diffraction patterns were recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer (periodicities up to 70 Å) and on image plates, scanned by STORM 820 from Molecular Dynamics with 50  $\mu\text{m}$  resolution (periodicities up to 120 Å). The sample temperature was controlled within  $\pm 0.01$  °C and exposure times were typically of 6 hours.

For GOE-PAS<sub>n</sub> POM textures, samples were observed between glass slides with a Leitz Orthoplan polarizing microscopy equipped with a Mettler FP82 hot stage and a FP80 control unit. Images were acquired with a Moticam Pro camera and a magnification of 300.

The transition temperatures and enthalpies were measured by differential scanning calorimetry with TA Instruments DSCQ1000 instrument operated at a scanning rate of 10°C/min on heating and cooling.

## II. Polymerization procedure.

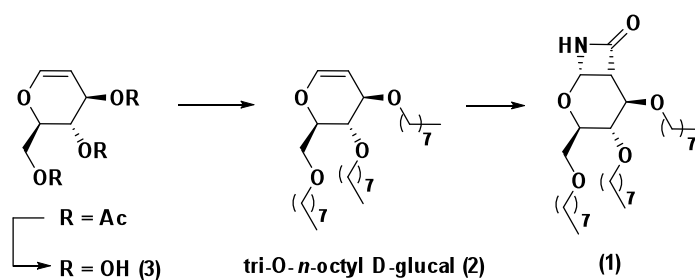
**GOE-PAS<sub>20</sub>.** In an oven-dried flask, lactam **1** (0.5 g, 0.951 mmol) was dissolved in 5 mL of distilled tetrahydrofuran dried over 4 Å molecular sieves. The reaction flask was cooled to 0 °C in an ice bath and 4-nitrobenzoyl chloride (0.0088 g, 0.0475 mmol, 5.0 mol %) was added as a solution in THF (0.10 mL). Next, 0.48 mL of a 0.25 M solution of LiHMDS in THF (0.119 mmol, 12.5 mol%) was added and the solution was stirred for 1 hour, at which time a drop of saturated NH<sub>4</sub>Cl solution was added. The THF was removed and the resulting solid was redissolved in ethyl acetate (25 mL) and washed with 1 M HCl, saturated NaHCO<sub>3</sub>, and brine. After drying the organic phase over sodium sulfate, the solution was filtered, concentrated and dried under high vacuum to obtain the polymer as a gummy white solid (0.453 g; 91%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.26 (d,  $J = 10$  Hz, *end group* 2H), 8.07 (d,  $J = 10$  Hz, *end group* 2H), 7.85-7.50 (br, 1H), 5.81-5.34 (br, 1H), 3.91-3.18 (m, 11H), 2.62 (bs, 1H), 1.52-1.26 (m, 36H), 0.88 (m, 9H);  $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm)

171.2, 149.7, 128.9, 123.5, 78.8, 77.0, 76.8, 76.7, 76.5, 75.8, 73.1, 72.8, 72.5, 71.6, 71.3, 68.8, 51.5, 31.9, 31.64, 31.60, 30.5, 30.3, 30.1, 29.9, 29.7, 29.6, 29.4, 29.0, 26.4, 26.3, 26.2, 26.0, 25.7, 22.7, 22.66, 22.4, 22.3, 14.04, 14.02, 13.7; IR (ATR): 3348, 2955, 2924, 2855, 1687, 1529, 1467, 1095  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}} = +77.9$  (5.04 mg/mL in  $\text{CHCl}_3$ , 26.7°C); GPC(THF)  $M_{\text{n}} = 11.3$  kDa,  $M_{\text{w}} = 12.1$  kDa,  $\text{Đ} (M_{\text{w}}/M_{\text{n}}) = 1.1$ .

**GOE-PAS<sub>50</sub>**. In an oven-dried flask, lactam **1** (0.5 g, 0.951 mmol) was dissolved in 5 mL of distilled tetrahydrofuran dried over 4 Å molecular sieves. The reaction flask was cooled to 0 °C in an ice bath and 4-nitrobenzoyl chloride (0.0035 g, 0.019 mmol, 2.0 mol %) was added as a solution in THF (0.10 mL). Next, 0.2 mL of a 0.25 M solution of LiHMDS in THF (0.0475 mmol, 5 mol%) was added and the solution was stirred for 1 hour, at which time a drop of saturated  $\text{NH}_4\text{Cl}$  solution was added. The THF was removed and the resulting solid was redissolved in ethyl acetate (25 mL) and washed with 1 M HCl, saturated  $\text{NaHCO}_3$ , and brine. After drying the organic phase over sodium sulfate, the solution was filtered, concentrated and dried under high vacuum to obtain the polymer as a gummy white solid (0.425 g; 85%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.26 (d,  $J = 10$  Hz, *end group* 2H), 8.07 (d,  $J = 10$  Hz, *end group* 2H), 7.71 (br, 1H), 5.81-5.43 (br, 1H), 3.65-3.31 (m, 11H), 2.66 (bs, 1H), 1.56-1.18 (m, 36H), 0.88 (m, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 171.4, 78.9, 77.6, 77.3, 77.0, 76.1, 73.2, 72.7, 71.7, 68.9, 51.7, 32.05, 32.0, 30.5, 30.3, 30.2, 30.0, 29.75, 29.7, 29.5, 29.4, 26.45, 26.4, 26.2, 26.1, 22.8, 22.76, 22.74, 14.15, 14.14, 14.10; IR (ATR): 3348, 2955, 2924, 2855, 1687, 1529, 1467, 1095  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}} = +84.5$  (5.13 mg/mL in  $\text{CHCl}_3$ , 26.7°C); GPC(THF)  $M_{\text{n}} = 26.3$  kDa,  $M_{\text{w}} = 27.7$  kDa,  $\text{Đ} (M_{\text{w}}/M_{\text{n}}) = 1.1$ .

**GOE-PAS<sub>100</sub>**. In an oven-dried flask, lactam **1** (0.5 g, 0.951 mmol) was dissolved in 5 mL of distilled tetrahydrofuran dried over 4 Å molecular sieves. The reaction flask was cooled to 0 °C in an ice bath and 4-nitrobenzoyl chloride (0.0018 g, 0.0095 mmol, 1.0 mol %) was added as a solution in THF (0.10 mL). Next, 0.1 mL of a 0.25 M solution of LiHMDS in THF (0.024 mmol, 2.5 mol %) was added and the solution was stirred for 2 hours, at which time a drop of saturated  $\text{NH}_4\text{Cl}$  solution was added. The THF was removed and the resulting solid was redissolved in dichloromethane (25 mL) and washed with 1 M HCl, saturated  $\text{NaHCO}_3$ , and brine. After drying the organic phase over sodium sulfate, the solution was filtered, concentrated and dried under high vacuum to obtain the polymer as a gummy white solid (0.484 g; 97%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.26 (d,  $J = 10$  Hz, *end group* 2H), 8.07 (d,  $J = 10$  Hz, *end group* 2H), 7.70 (br, 1H), 5.94-5.43 (br, 1H), 3.70-3.31 (m, 11H), 2.66 (bs, 1H), 1.56-1.18 (m, 36H), 0.88 (m, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 171.1, 78.5, 77.3, 76.8, 72.7, 71.6, 69.0, 51.1, 31.9, 30.3, 29.4, 26.2, 22.7, 14.0; IR (ATR): 3348, 2955, 2924, 2855, 1687, 1529, 1467, 1095  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}} = +80.6$  (4.79 mg/mL in  $\text{CHCl}_3$ , 26.7°C); GPC(THF)  $M_{\text{n}} = 47.4$  kDa,  $M_{\text{w}} = 51.4$  kDa,  $\text{Đ} (M_{\text{w}}/M_{\text{n}}) = 1.1$ .

### III. Small molecule synthetic procedures.



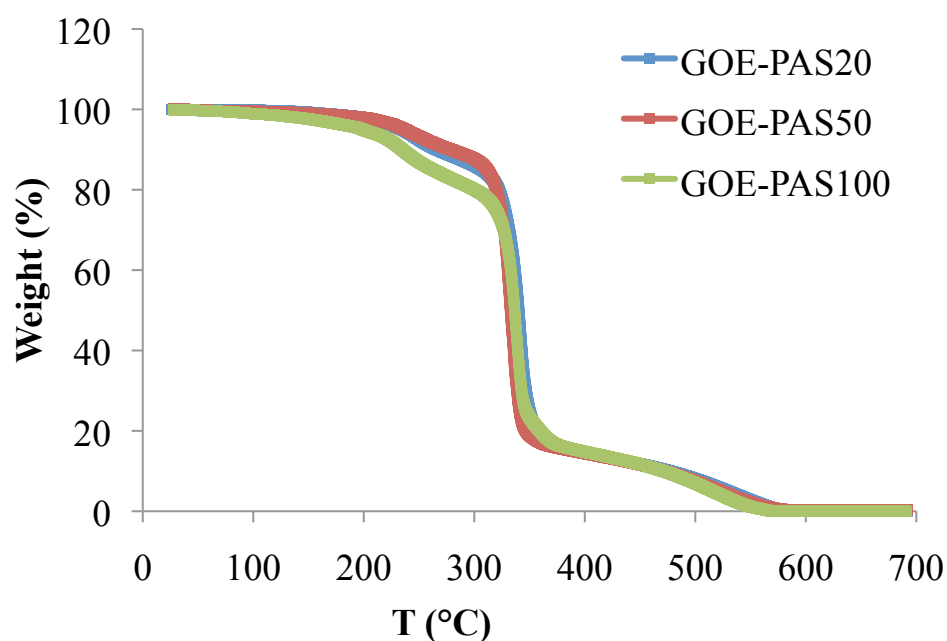
**D-Glucal (3).** To a solution of Triacetyl-D-Glucal (10 g, 36.7 mmol) in methanol (200 mL), sodium hydroxide (150 mg, 3.67 mmol) was added. The mixture was stirred at room temperature for 24 hours. The solvent was then evaporated and D-Glucal (3) was used in the next step without further purification;  $^1\text{H}$  NMR (400 MHz, MeOD):  $\delta$  (ppm) 6.31 (m, 1H), 4.65 (m, 1H), 4.09 (m, 1H), 3.88-3.67 (m, 3H), 3.53 (m, 1H).

**3,4,6-tri-*O*-octyl-D-Glucal (2).** A solution of D-Glucal (3) (3g, 20.5 mmol) in DMF (30 mL) was added dropwise at 0 °C to a solution of NaH (2.95 g, 123 mmol) in DMF (80 mL). The solution was stirred for 15 minutes at room temperature. 1-iodooctane (22 mL, 123 mmol) was then added dropwise and the reaction mixture was stirred at 60°C for 16 hours. The solution was then concentrated and ethyl acetate was added. The organic phase was washed with water and brine, then dried over sodium sulfate, filtered and concentrated. The crude was purified by silica gel flash chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  from 60/40 to 20/80) and yielded (2) as colorless oil (54%);  $^1\text{H}$ -NMR and IR matched those reported in the literature.<sup>1</sup>

**(1*S*,3*R*,4*S*,5*R*,6*R*)-4,5-bis(octyloxy)-3-((octyloxy)methyl)-2-oxa-8-azabicyclo[4.2.0]octan-7-one (1).** The procedure was adapted from the literature with minor changes.<sup>2</sup> At room temperature, 1.13 mL (1.84 g, 13 mmol) of chlorosulfonyl isocyanate (CSI), which had previously been stored over oven-dried sodium carbonate for > 1 week at 4 °C, was dissolved in 20 mL of anhydrous toluene, over 2.0 g of oven-dried sodium carbonate under nitrogen. The solution was cooled to -78 °C in a dry ice/acetone bath and a solution of 4.93 g (10.0 mmol) of tri-*O*-octyl-D-glucal (2) dissolved in 20 mL of anhydrous toluene was slowly added. The solution was warmed to -62 °C by transferring the reaction flask to a chloroform/dry ice cooling bath. After 30 min at -62 °C, the reaction was cooled to -78 °C and diluted with an additional 60 mL of anhydrous toluene and 4.9 mL of Red-Al (> 65 wt% solution in toluene) was added slowly. After 15 minutes at -78 °C, the reaction was warmed to -62 °C for 15 minutes and then warmed to -10 °C in an ice/saturated sodium chloride bath. After 5 minutes at -10 °C, 1.0 mL of water was added and the reaction was stirred for an additional 30 minutes while warming to 0 °C. If possible, the solution was filtered to remove solids. If an emulsion formed, a saturated solution of tartrate could be added to complex aluminum ions. After the addition of 50 mL of diethyl ether, the organic phase was washed with saturated bicarbonate and brine, dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was removed. The crude material was purified with silica gel chromatography using increasing polar mixtures of hexanes and ethyl acetate. Elution began with 5% ethyl acetate in hexanes. The proportion of ethyl acetate was increased

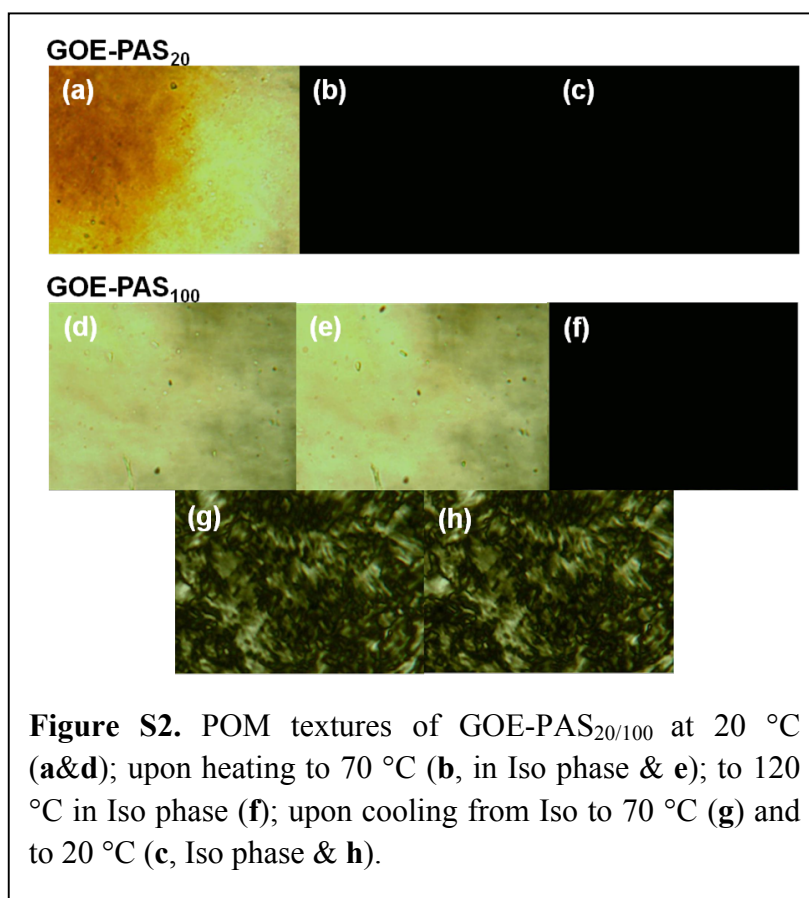
in increments of 5% until it reached 30%, at which time the product eluted. After removal of the solvent, 2.25 g (43% yield) of a clear oil (**1**) was isolated;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.0 (m, 1H), 5.51 (dd,  $J = 4.6, 1.9$  Hz, 1H), 4.12 (qd,  $J = 7.1, 0.9$  Hz, 1H), 3.90-3.84 (m, 1H), 3.80 (m, 1H), 3.74-3.70 (m, 1H), 3.66-3.58 (m, 3H), 3.51-3.41 (m, 3H), 3.35 (m, 1H), 3.28 (m, 1H), 1.60-1.51 (m, 6H), 1.27 (m, 30H), 0.88 (m, 9H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.7, 76.6, 76.4, 72.1, 71.9, 70.1, 69.7, 69.6, 55.3, 32.0, 31.9, 30.3, 29.9, 29.7, 29.62, 29.59, 29.55, 29.46, 29.4, 26.3, 26.26, 22.8, 14.2; IR (ATR): 3299, 2955, 2925, 2856, 1765, 1467, 1364, 1100  $\text{cm}^{-1}$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{31}\text{H}_{59}\text{NO}_5$ , 548.4291; found, 548.4313.

#### IV. Thermogravimetric analysis (TGA) of GOE-PAS<sub>n</sub>



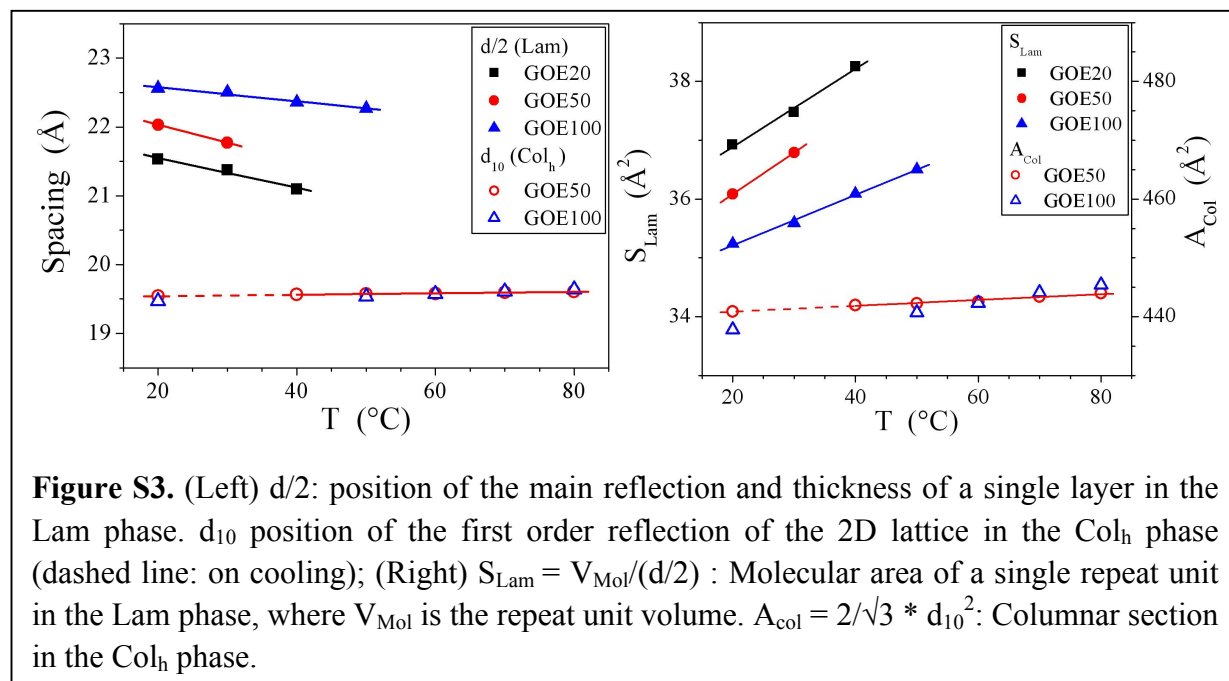
**Figure S1.** TGA analysis of GOE-PAS<sub>n</sub>. Ramp from 27°C to 700 °C, 20 °C/min.

## V. Polarized optical microscopy (POM) images of GOE-PAS<sub>20/100</sub>

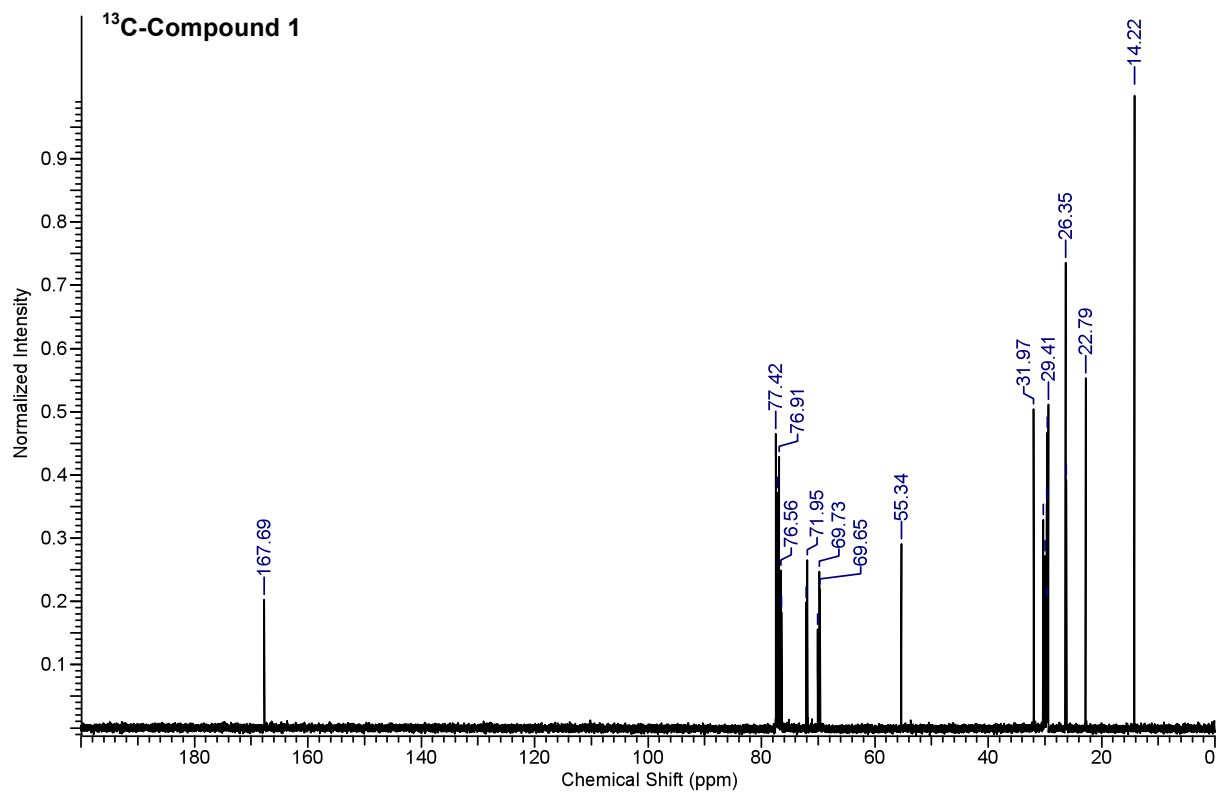
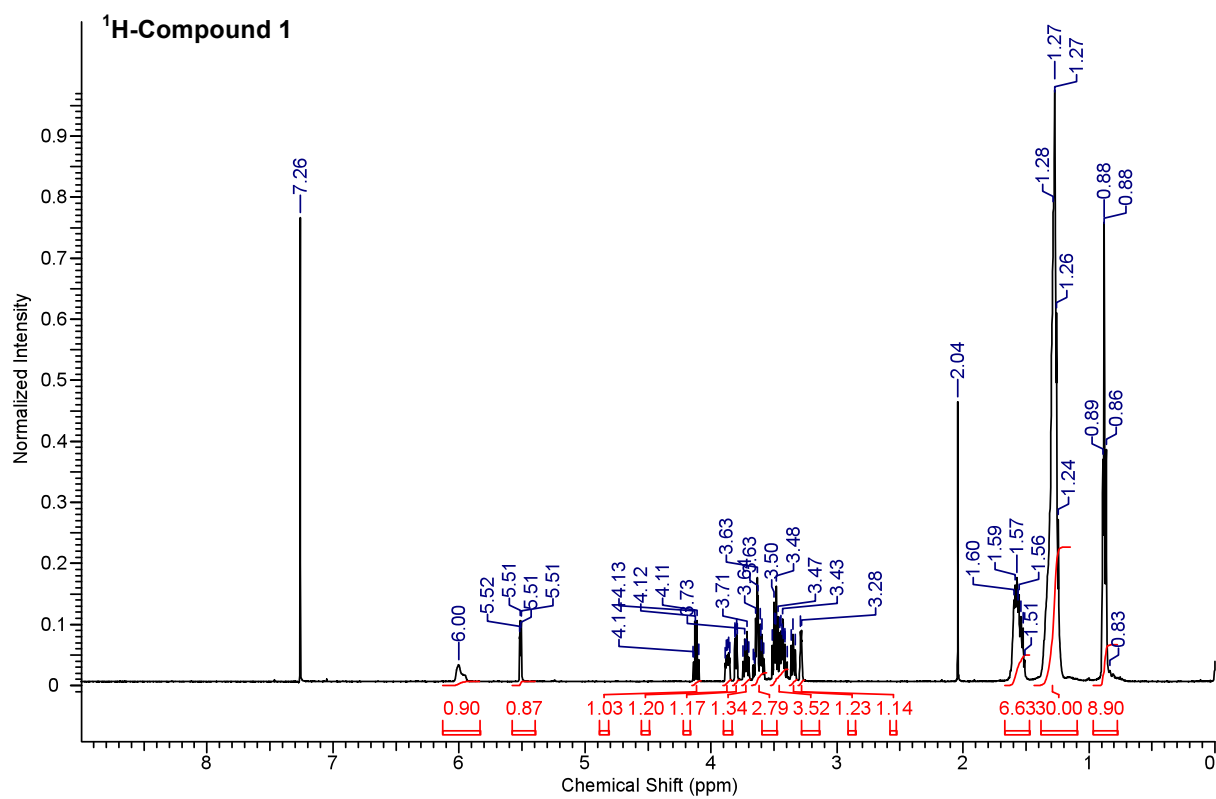


**Figure S2.** POM textures of GOE-PAS<sub>20/100</sub> at 20 °C (**a&d**); upon heating to 70 °C (**b**, in Iso phase & **e**); to 120 °C in Iso phase (**f**); upon cooling from Iso to 70 °C (**g**) and to 20 °C (**c**, Iso phase & **h**).

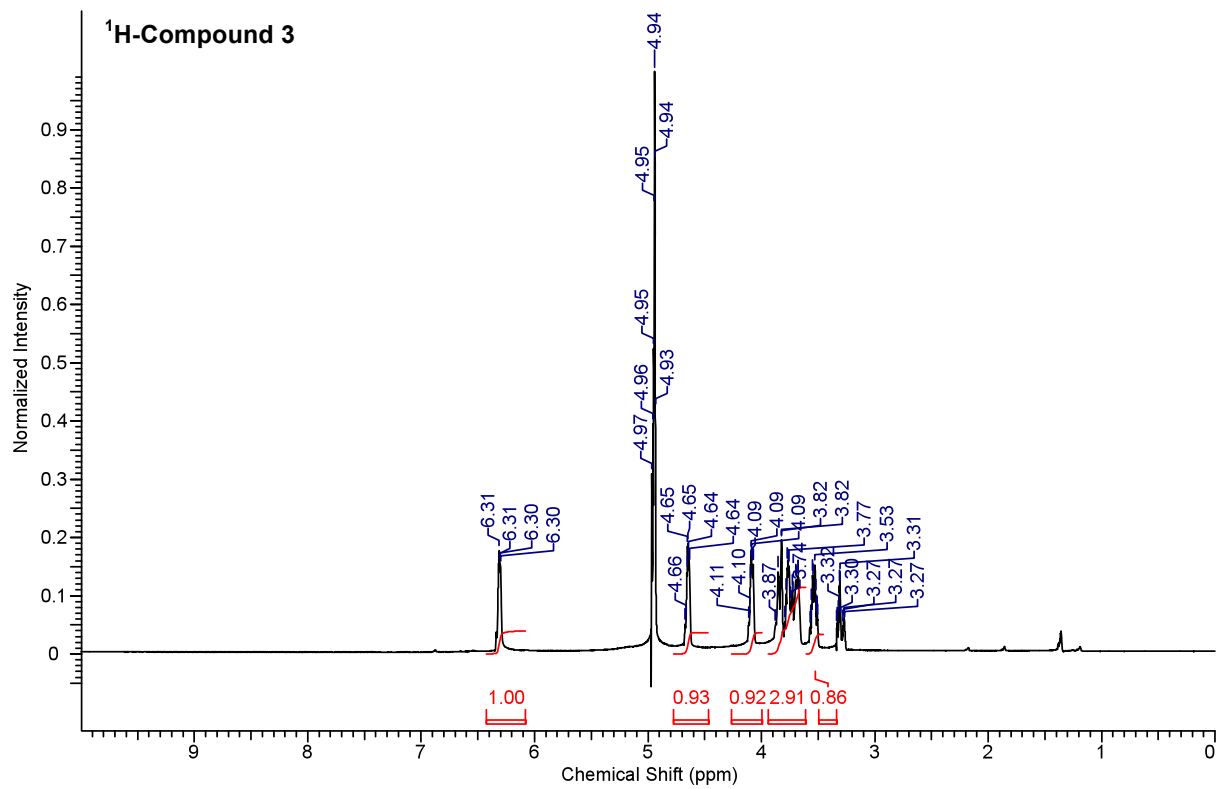
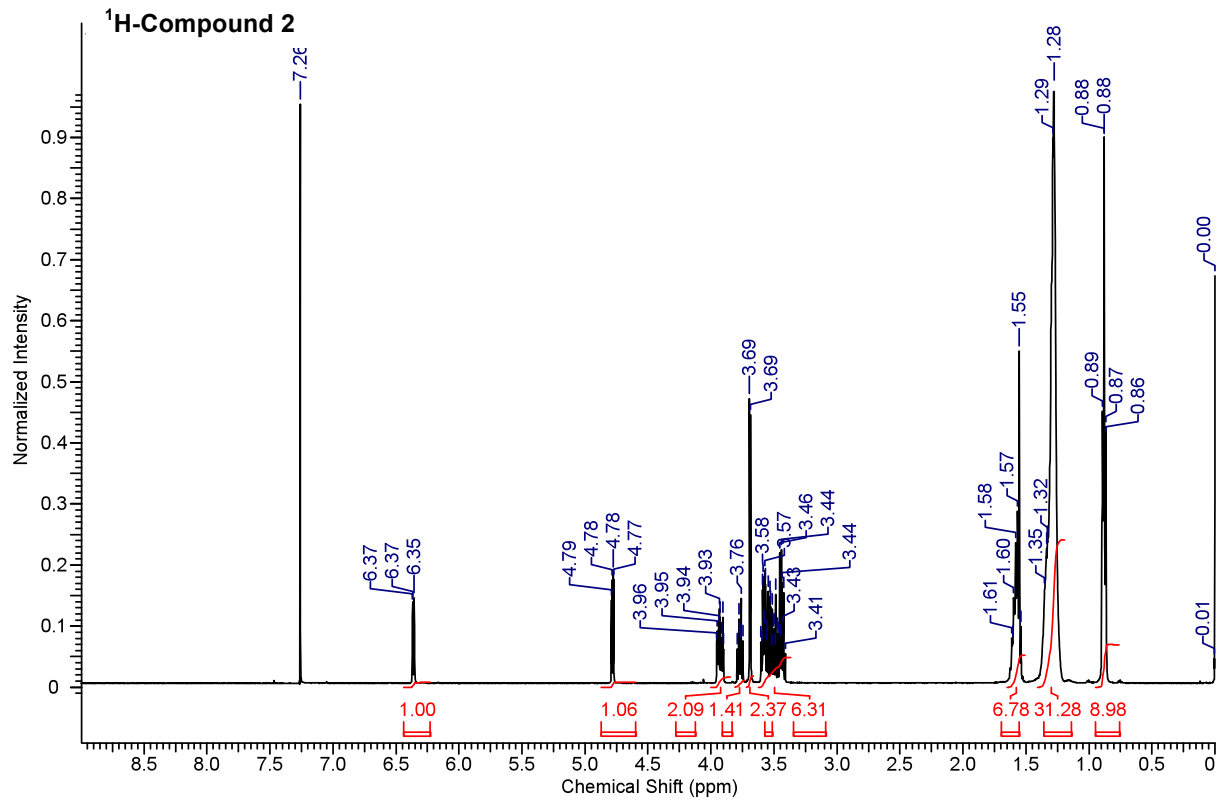
## VI. Spacing dependence on the temperature and polymer chain length in Lam and Col<sub>h</sub> mesophases.

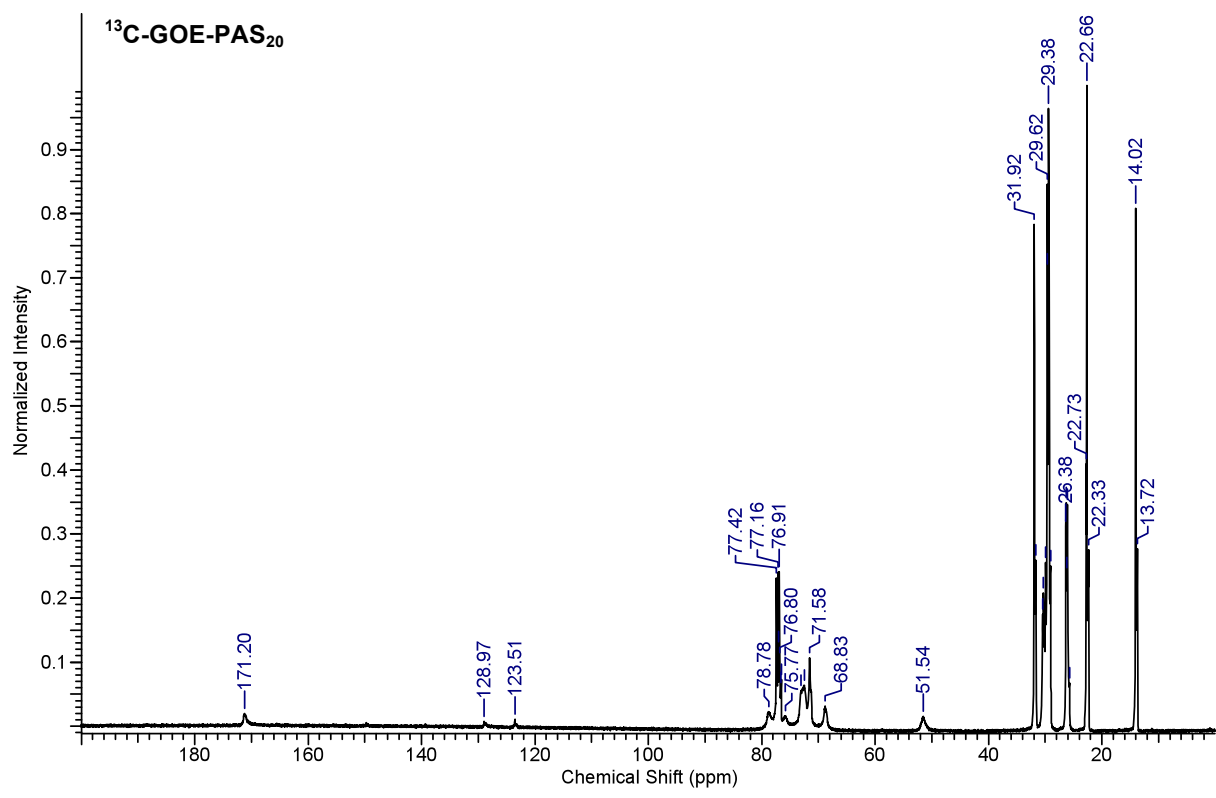
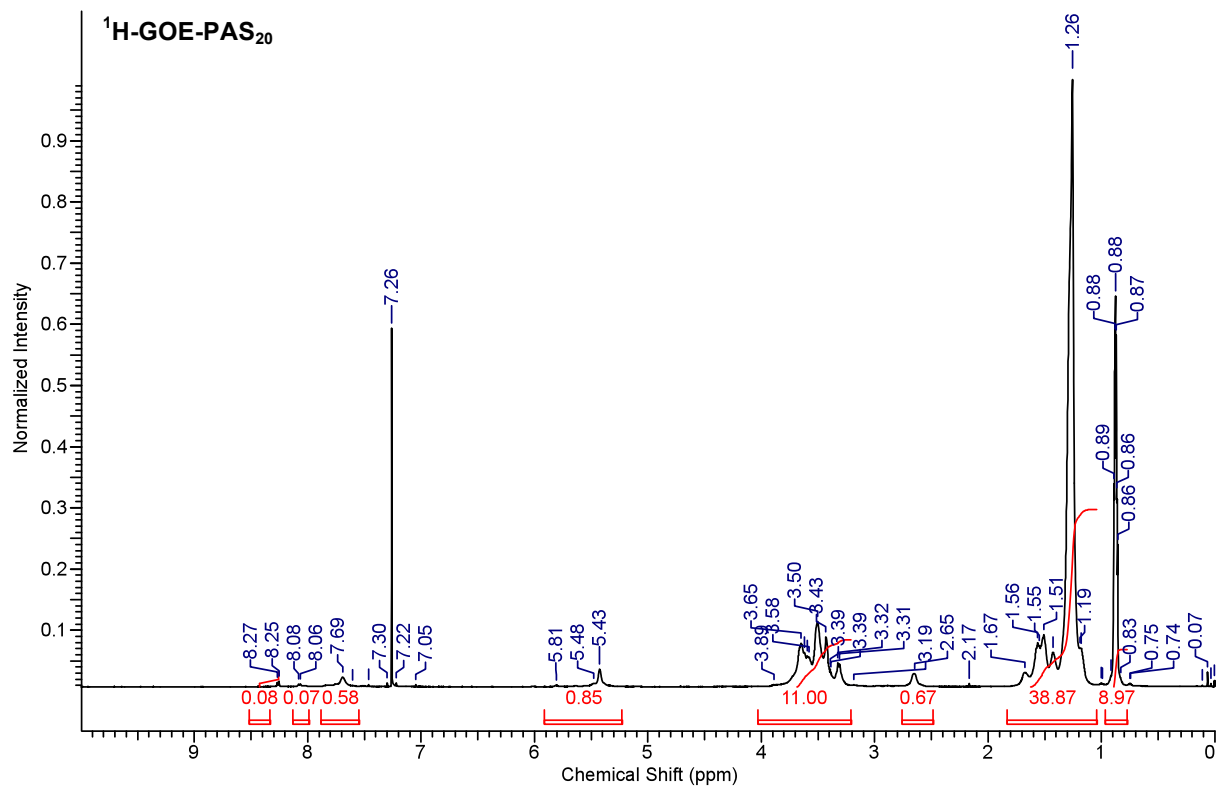


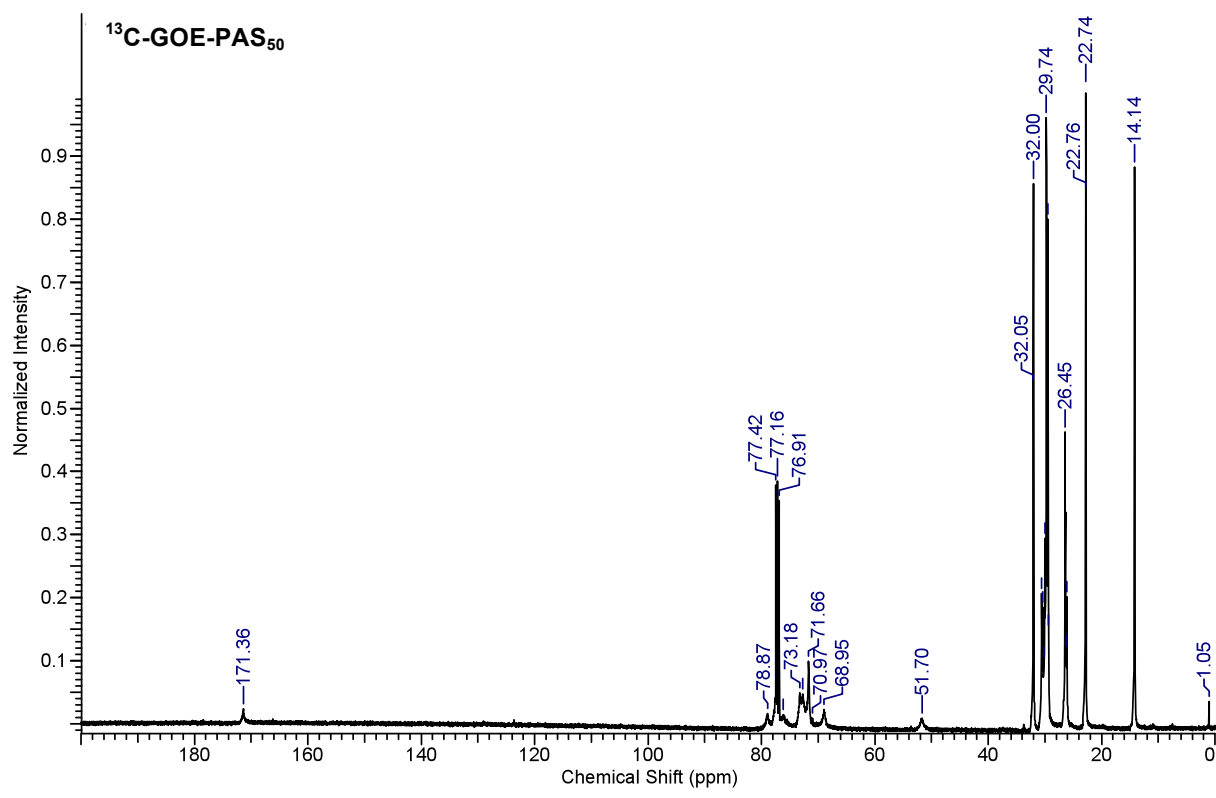
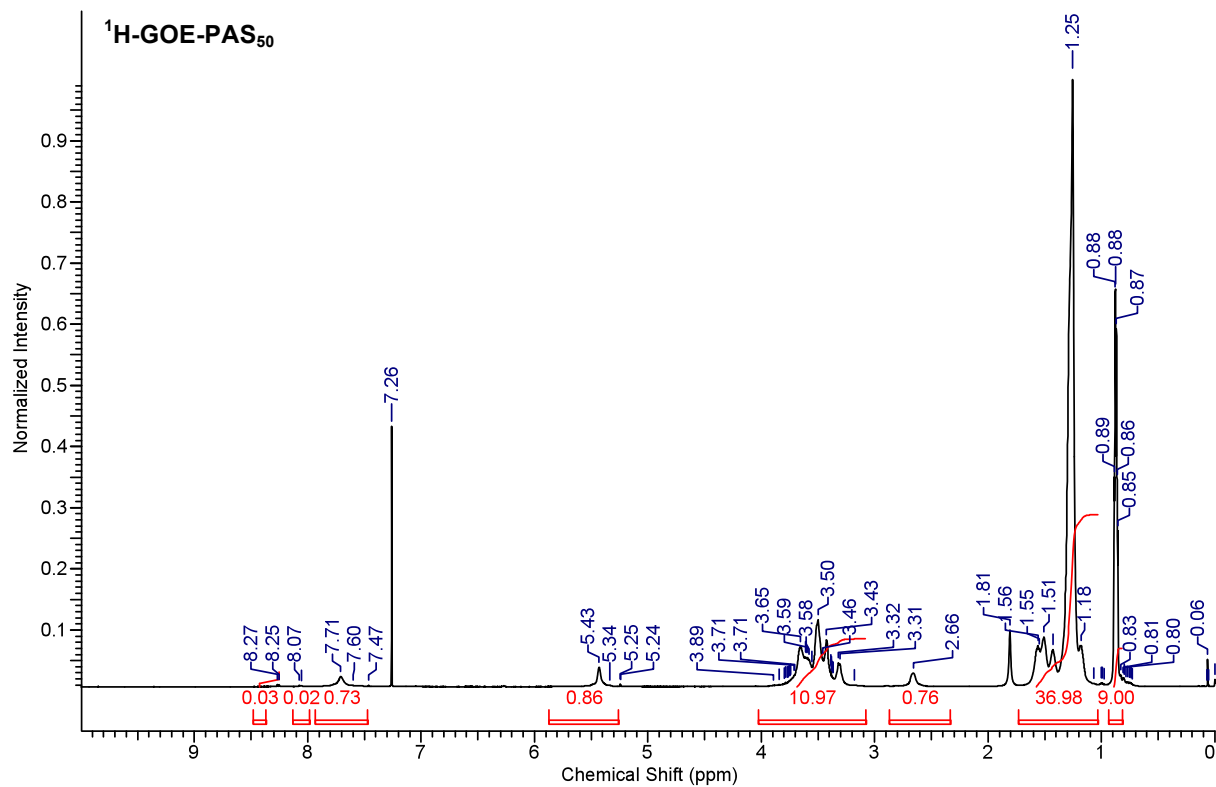
## VII. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds.

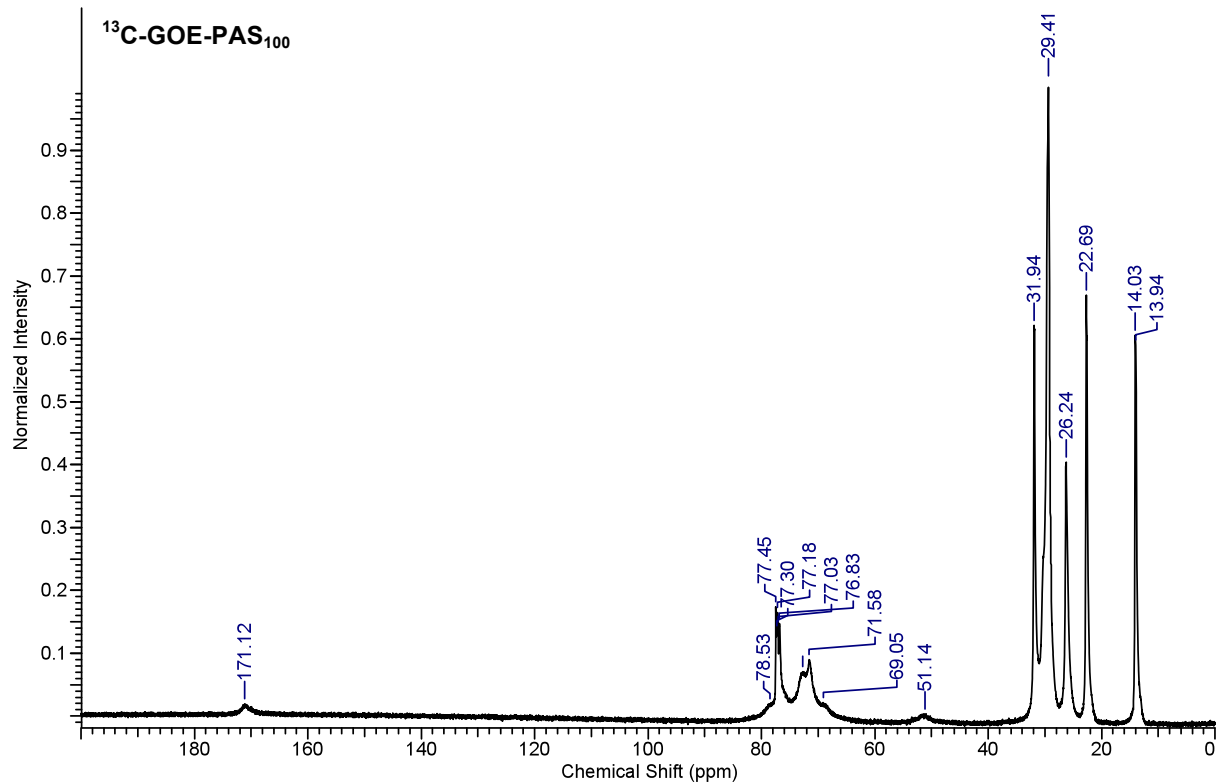
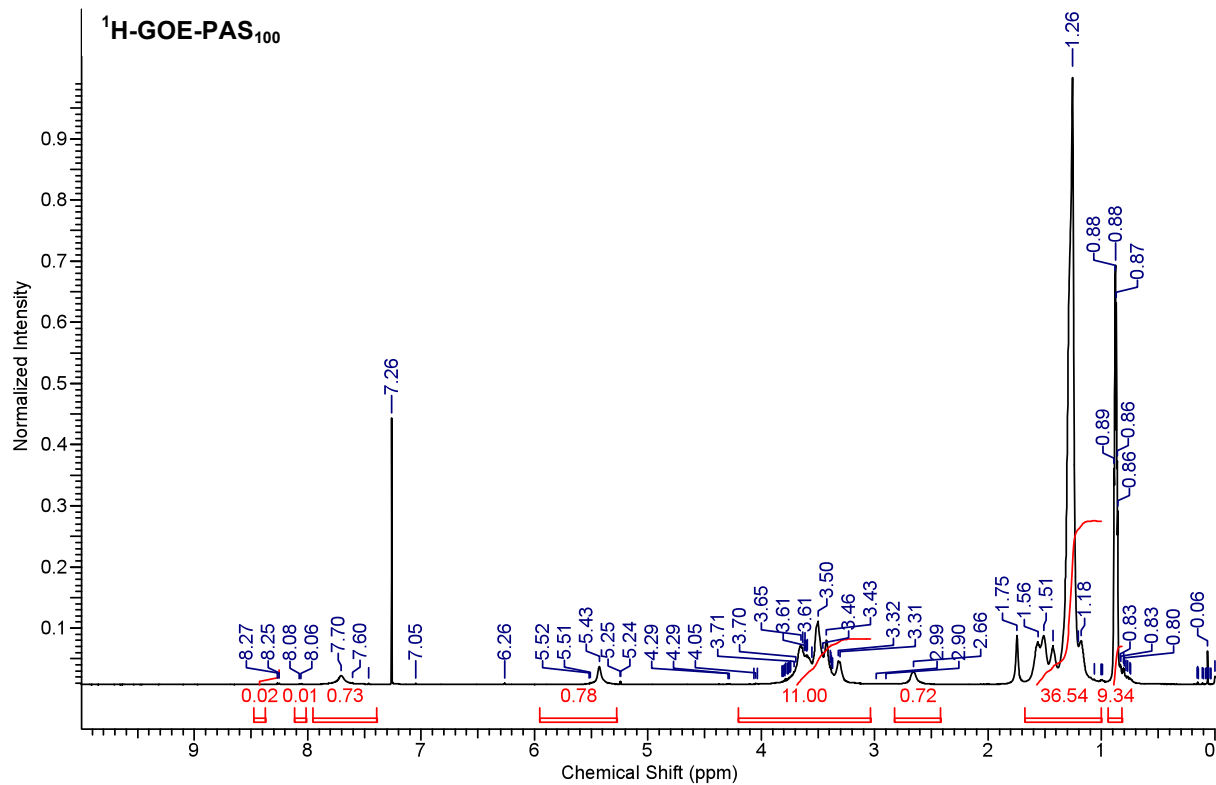












## VIII. References.

1. Seenuvasan V., Shi Min T., Hui Ping T., Shuting C., and Xue-Wei L., *Org. Lett.* **2012**, *1*, 174.
2. Kałuża, Z., Abramski, W., Bełżecki, C., Grodner, J., Mostowicz, D., Urbański, R., Chmielewski, M. *Synlett* **1994**, 539.