Supporting Information

Tailor-designed polyphilic promotors for stabilizing dispersions of carbon nanotubes in liquid crystals

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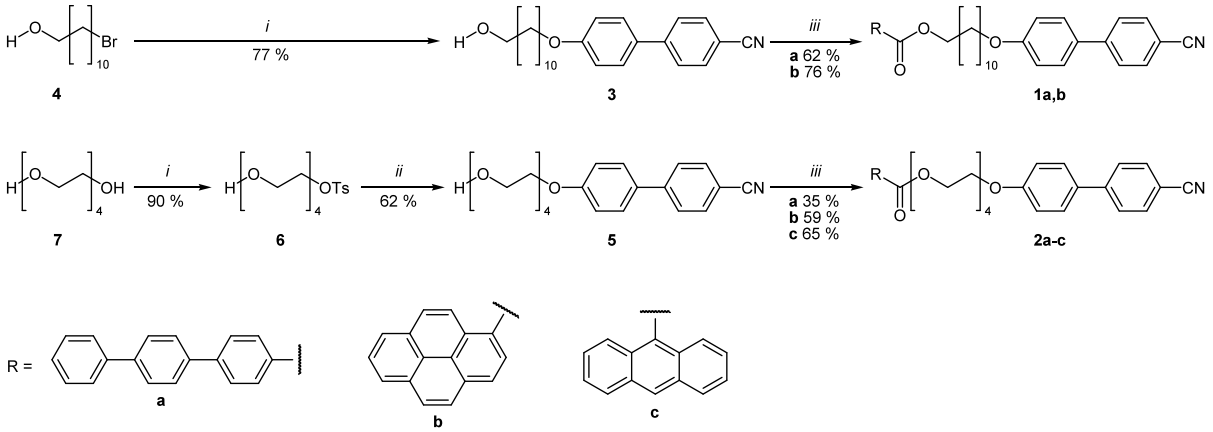
Content

1. Synthesis and analytical data



Scheme S1: Synthesis of compounds **1a,b** and **2a-c**, respectively. *Reagents and conditions.*
i: TsCl, aq. NaOH, THF, 5 °C *ii*: K_2CO_3, 4-hydroxy-4'-cyanobiphenyl, TBAF, butanone, reflux; *iii*: 1. $SOCl_2$, reflux, 2. piperidine, R-COOH, DMAP, CH_2Cl_2, reflux.

General remarks:
4-Hydroxy-4'-cyanobiphenyl, 11-bromo-1-undecanol, tetraethylene glycol, 4-toluenesulfonyl chloride, *N,N*-dimethylaminopyridine (DMAP), *p*-terphenyl-4-carboxylic acid, pyrene-1-carboxylic acid, anthracene-9-carboxylic acid were obtained from Sigma Aldrich and used as obtained.

4'-(11-Hydroxyundecyloxy)biphenyl-4-carbonitrile 3[S1]
A mixture of 4-hydroxy-4'-cyanobiphenyl (2.00 g, 10.2 mmol), K_2CO_3 (2.83 g, 20.5 mmol), 11-bromo-1-undecanol (2.57 g, 10.2 mmol) and tetrabutylammonium iodide (10 mg) in 2-butanone (150 mL) was refluxed for 48 h under an argon atmosphere. After evaporation of the solvent under reduced pressure the residue was dissolved in chloroform (100 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$ and evaporated in vacuo. The obtained product was crystallized twice from methanol yielding **3** (2.9 g, 7.9 mmol, 77 %) as colorless leaflets (phase sequence see below).
^{1}H-NMR (400 MHz, $CDCl_3$) d = 7.66 (*d,* 2H, J = 8.5 Hz, Ar-*H*), 7.61 (*d*, 2H, J = 8.5 Hz, Ar-*H*), 7.50 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 6.97 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 3.98 (*t*, 2H, J = 6.5 Hz, Ar-OCH_2), 3.62 (*t*, 2H, J = 6.6 Hz, CH_2-OH), 1.79 (*m*, 2H, CH_2), 1.55 (*m*, 2H, CH_2), 1.45 (*m*, 2H, CH_2), 1.39-1.21 (*m*, 17H, CH_2).

2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate 6[S2]
To a chilled mixture of tetraethylene glycol (175.6 g, 0.90 mol), NaOH (5.47 g, 0.14 mol), THF (25 mL) and water (30 mL) a solution of 4-toluenesulfonyl chloride (16.70 g, 87.5 mmol) in THF (100 mL) was added over a period of 1 h. After addition was completed the mixture was stirred at 5°C for 2 h, poured into ice water (500 mL) and extracted with dichloromethane (3 x 150 mL). The combined organic layers were washed with water (5 x 200 mL), and dried over $MgSO_4$. Evaporation of the solvent yields **6** (27.4 g, 78.5 mmol, 90 %) as a colorless oil which was used without further purification.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.77 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.31 (*d*, 2H, J = 8.0 Hz, Ar-*H*), 4.14 (*m*, 2H, Ar-OCH_2), 3.71-3.55 (*m*, 16H, OCH_2), 2.42 (*s*, 3H, Ar-CH_3), 2.23 (*s*, br, 2H, CH_3-O*H*).

4'-(2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethoxy)biphenyl-4-carbonitrile 5[S1]
A mixture of 4-hydroxy-4'-cyanobiphenyl (4.00 g, 20.5 mmol), K_2CO_3 (5.66 g, 41.0 mmol), tosylate **6** (7.14 g, 20.5 mmol) and tetrabutylammonium iodide (20 mg) in 2-butanone (200 mL) was refluxed for 24 h under an argon atmosphere. After evaporation of the solvent under reduced pressure, the residue was dissolved in diethylether (100 mL) and carefully washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$ and evaporated in vacuo. Purification of the obtained product by column chromatography (eluent: ethyl acetate) yields **5** (4.7 g, 12.7 mmol, 62 %) as a slightly yellowish oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.67 (*d*, 2H, J = 8.5 Hz, Ar-*H*), 7.61 (*d*, 2H, J = 8.5 Hz, Ar-*H*), 7.50 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 7.00 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 4.17 (*m*, 2H, Ar-OCH_2-CH_2), 3.87 (*m*, 2H, Ar-OCH_2-CH_2), 3.74-3.66 (*m*, 10H, OCH_2), 3.59 (*m*, 2H, CH_2-OH).

General procedure for esterification:
All reactions were carried out in an argon atmosphere. A mixture of the corresponding carboxylic acid (1.0 eq.) and thionyl chloride (5 mL per mmol carboxylic acid) was refluxed until all solid was dissolved followed by additional

heating for 24 h. After evaporation of excess thionyl chloride at reduced pressure the obtained acid chloride was carefully dried in vacuo and finally flushed with argon. The acid chloride was then treated with a solution of the corresponding alcohol (1.0 eq.), dry pyridine (10 eq.) and DMAP (5 mol-%) in dry dichloromethane (5 mL per mmol alcohol). After refluxing for 24 h the mixture was washed with water, 10 % HCl, conc. $NaHCO_3$-solution and dried over $MgSO_4$ (**1a** was worked up in a different way). The product obtained by evaporation of the solvent was purified as described below.

11-(4'Cyanobiphenyl-4-yloxy)undecyl *p*-terphenyl-4-carboxylate 1a
Prepared from p-terphenyl-4-carboxylic acid (0.20 g, 0.73 mmol), thionylchloride (3.6 mL), **3** (0.27 g, 0.73 mmol), pyridine (0.6 mL, 0.58 g, 7.29 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (3.6 mL). The precipitated raw product was filtrated an washed with methanol and pentane. Crystallization (first from chloroform, then from ethyl acetate) yields **1a** (0.28 g, 0.45 mmol, 62%) as colorless needles (phase sequence, see Table S1, for copies of NMR spectra, see Figures S1 and S2).
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.11 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.72-7.58 (*m*, 12H, Ar-*H*), 7.52-7.41 (*m*, 4H, Ar-*H*), 7.36 (*m*, 1H, Ar-*H*), 6.96 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 4.33 (*t*, 2H, J = 6.6 Hz, COO-CH_2), 3.98 (*t*, 2H, J = 6.6 Hz, Ar-OCH_2), 1.38-1.73 (*m*, 4H, CH_2), 1.53-1.28 (*m*, 14H, CH_2); ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 166.5, 159.8, 145.2, 145.0, 141.0, 140.4, 138.8, 132.5, 131.2, 130.1, 129.3, 128.9, 128.3, 127.6, 127.0, 126.8, 119.1, 115.1, 110.0, 68.1, 65.1, 29.5, 29.5, 29.3, 29.2, 28.7, 26.0.

11-(4'Cyanobiphenyl-4-yloxy)undecyl pyrene-1-carboxylate 1b
Prepared from pyrene-1-carboxylic acid (0.20 g, 0.81 mmol), thionylchloride (4.1 mL), **3** (0.30 g, 0.81 mmol), pyridine (0.7 mL, 0.64 g, 8.12 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (4.1 mL). Column chromatography (eluent: chloroform) followed by crystallization (acetonitrile) yields **1b** (0.19 g, 0.32 mmol, 76 %) as colorless needles (phase sequence see Table S1; for copies of NMR spectra, see Figures S3 and S4).
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.25 (*d*, 1H, J = 9.4 Hz, Ar-*H*), 8.61 (*d*, 1H, J = 8.1 Hz, Ar-*H*), 8.27-8.20 (*m*, 3H, Ar-*H*), 8.18-8.14 (*m*, 2H, Ar-*H*), 8.09-8.02 (*m*, 2H, Ar-*H*), 7.65 (*d*, 2H, J = 8.5 Hz, Ar-*H*), 7.60 (*d*, 2H, J = 8.6 Hz, Ar-*H*), 7.48 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 6.95 (*d*, 2H, J = 8.8 Hz, Ar-*H*), 4.49 (*t*, 2H, J = 6.7 Hz, COO-CH_2), 3.97 (*t*, 2H, J = 6.5 Hz, Ar-OCH_2), 1.89 (*m*, 2H, CH_2), 1.78 (*m*, 2H, CH_2), 1.61-1.23 (*m*, 14H, CH_2); ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 168.1, 159.8, 145.2, 134.2, 132.5, 131.2, 131.1, 131.0, 130.4, 129.5, 129.3, 128.3, 127.1, 127.0, 126.3, 126.2, 126.1, 124.9, 124.8, 124.2, 124.1, 123.9, 119.1, 115.1, 110.0, 68.1, 65.4, 29.5, 29.4, 29.3, 29.2, 28.8, 26.2.

2-(2-(2-(2-(4'-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethyl *p*-terphenyl-4-carboxylate 2a
Prepared from *p*-terphenyl-4-carboxylic acid (0.20 g, 0.73 mmol), thionylchloride (3.6 mL), **5** (0.27 g, 0.73 mmol), pyridine (0.6 mL, 0.58 g, 7.29 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (3.6 mL). The product was crystallized twice from methanol, yielding **2a** (0.16 g, 0.26 mmol, 35 %) as colorless needles (melting point see Table S1; for copies of NMR spectra, see Figures S5 and S6).
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.11 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.69-7.55 (*m*, 12H, Ar-*H*), 7.48-7.43 (*m*, 4H, Ar-*H*), 7.36 (*m*, 1H, Ar-*H*), 6.96 (*d*, 2H, J = 8.5 Hz, Ar-*H*), 4.49 (*m*, 2H, COO-CH_2), 4.13 (dd, 2H, J = 4.3 Hz, J = 5.0 Hz, Ar-OCH_2), 3.85 (*m*, 4H, OCH_2CH_2), 3.70 (*m*, 8H, OCH_2CH_2O); ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 166.4, 159.4,

145.1, 141.0, 140.3, 138.7, 132.5, 131.6 130.2, 128.8, 128.3, 127.6, 127.1, 127.0, 126.8, 119.0, 115.3, 110.1, 70.9, 70.8, 70.7, 69.7, 69.3, 67.6, 64.2.

2-(2-(2-(2-(4'-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethyl pyrene-1-carboxylate 2b

Prepared from pyrene-1-carboxylic acid (0.20 g, 0.81 mmol), thionylchloride (4.0 mL), alcohol **5** (0.30 g, 0.81 mmol), pyridine (0.7 mL, 0.64 g, 8.12 mmol), DMAP (5 mg, 0.04 mmol) in dichloromethane (4.0 mL). The product was first subjected to column chromatography (eluent: chloroform) followed by an additional column chromatography (eluent: diethylether). **2b** (0.29 g, 0.48 mmol, 59 %) was obtained as a greenish highly viscous fluid, which crystallizes after a few days (melting point see Table S1; for copies of NMR spectra, see Figure S7 and S8).
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.23 (*d*, 1H, J = 9.4 Hz, Ar-*H*), 8.63 (*d*, 1H, J = 8.1 Hz, Ar-*H*), 8.25-8.18 (*m*, 3H, Ar-*H*), 8.15-8.12 (*m*, 2H, Ar-*H*), 8.05-8.01 (*m*, 2H, Ar-*H*), 7.60 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.51 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.38 (*d*, 2H, J = 8.7 Hz, Ar-*H*), 6.88 (*d*, 2H, J = 8.7 Hz, Ar-*H*), 4.64 (*m*, 2H, COO-CH_2), 4.06 (*m*, 2H, Ar-OCH_2), 3.95 (*m*, 2H, OCH_2), 3.82-3.69 (*m*, 10H, OCH_2CH_2O); ^{13}C-NMR (200 MHz, $CDCl_3$) δ = 167.9, 159.3, 145.1, 134.3, 132.4, 131.5, 131.2, 131.0, 130.3, 129.6, 129.4, 128.5, 128.2, 127.1, 127.0, 126.3, 126.2, 124.9, 124.8, 124.2, 124.1, 123.5, 119.1, 115.1, 110.0, 70.8, 69.6, 69.3, 67.5, 64.3.

2-(2-(2-(2-(4'-Cyanobiphenyl-4-yloxy)ethoxy)ethoxy)ethoxy)ethyl anthracene-9-carboxylate 2c

Prepared from anthracene-9-carboxylic acid (0.20 g, 0.90 mmol), thionylchloride (4.5 mL), alcohol **5** (0.33 g, 0.90 mmol), pyridine (0.73 mL, 0.71 g, 9.00 mmol), DMAP (6 mg, 0.05 mmol) in dichloromethane (4.5 mL). Purification of the product by column chromatography (eluent: diethylether) yields **2c** (0.34 g, 0.59 mmol, 65 %) as a yellowish highly viscous fluid which crystallizes after a few days (melting point see Table S1; for copies of NMR spectra, see Figures S9 and S10).
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.49 (*s*, 1H, Ar-*H*), 8.11 (*d*, 2H, J = 8.6 Hz, Ar-*H*), 7.98 (*d*, 2H, J = 8.2 Hz, Ar-*H*), 7.64 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.57 (*d*, 2H, J = 8.3 Hz, Ar-*H*), 7.54-7.43 (*m*, 6H, Ar-*H*), 6.92 (*d*, 2H, J = 8.6 Hz, Ar-*H*), 4.75 (*m*, 2H, COO-CH_2), 4.07 (*m*, 2H, Ar-OCH_2), 3.92 (*m*, 2H, OCH_2), 3.79 (*m*, 2H, OCH_2), 3.70 (*m*, 8H, OCH_2); ^{13}C-NMR (200 MHz, $CDCl_3$) δ =174.2, 169.4, 159.4, 145.1, 142.5, 141.8, 132.5, 131.6, 131.5, 130.9, 129.4, 128.5, 128.3, 128.2, 128.1, 127.7, 127.1, 127.0, 126.9, 126.5, 126.1, 125.6, 125.4, 125.2, 119.0, 115.2, 115.1, 110.1, 110.0, 70.8, 70.7, 70.6, 70.5, 69.6, 69.1, 68.6, 67.5, 66.1, 64.6, 64.5, 55.0.

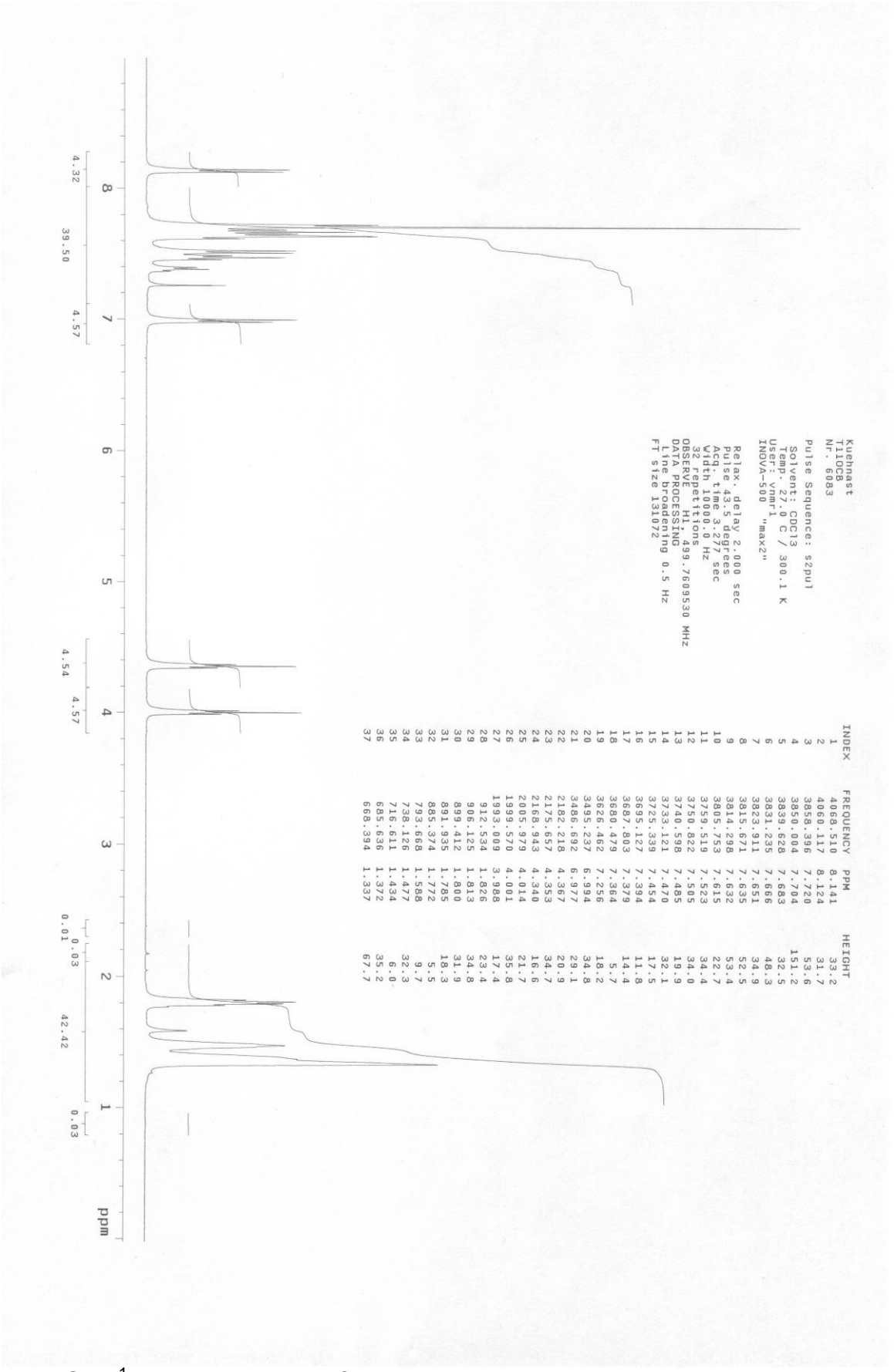


Figure S1 . ^{1}H-NMR spectrum of **1a**.

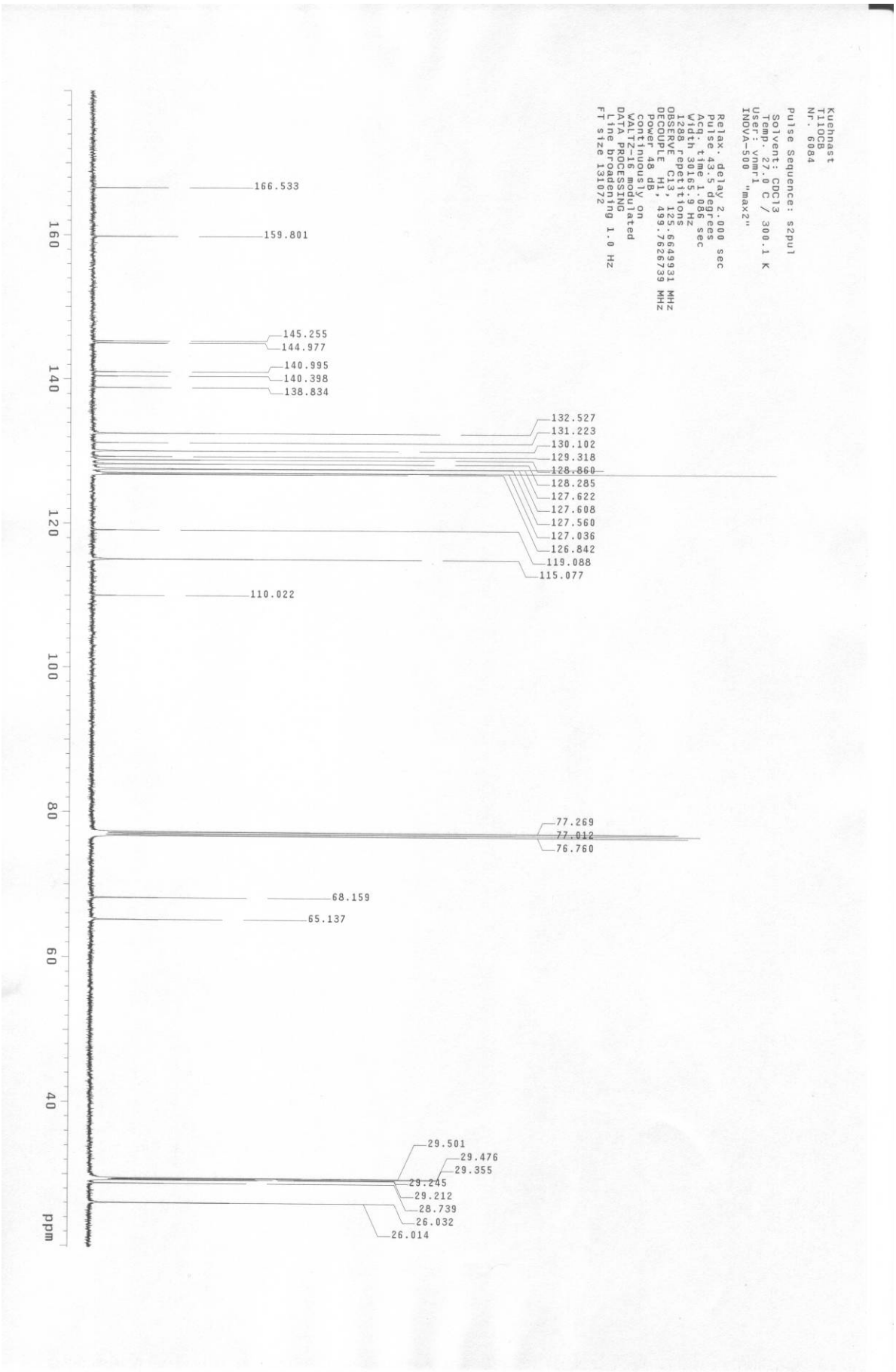


Figure S2 . ^{13}C-NMR spectrum of **1a**.

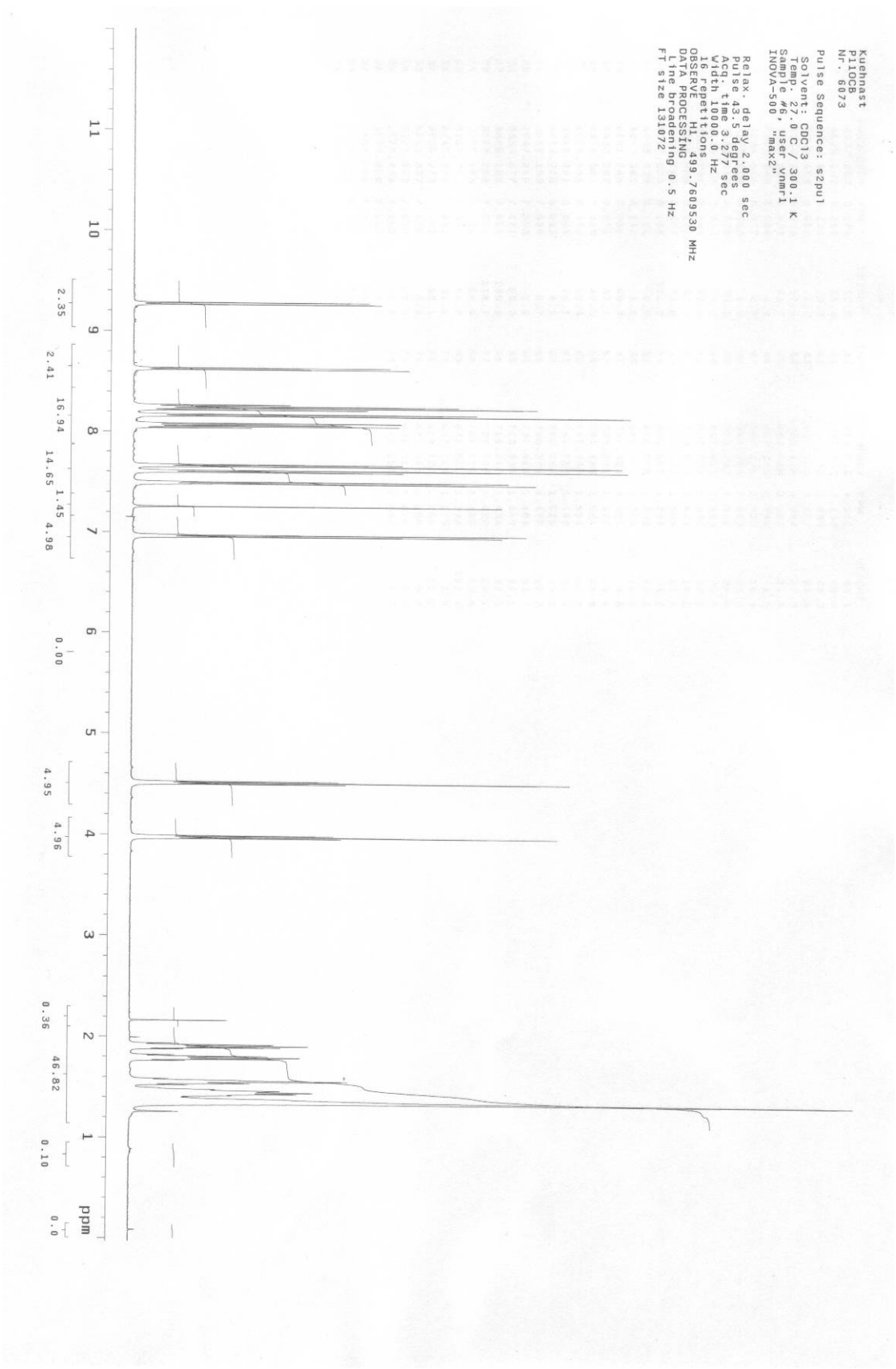


Figure S3 . ^{1}H-NMR spectrum of **1b**.

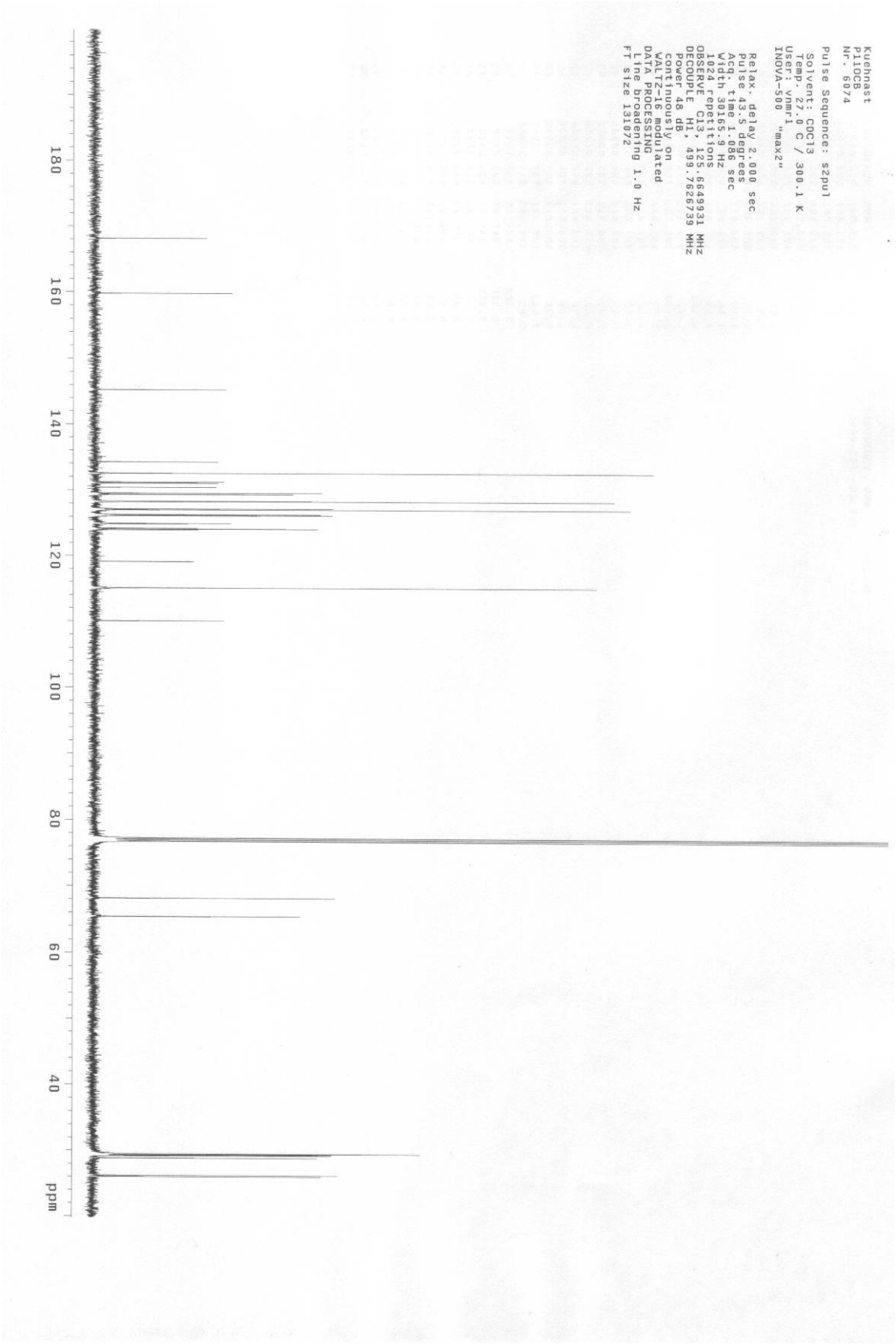


Figure S4 . ^{13}C-NMR spectrum of **1b**.

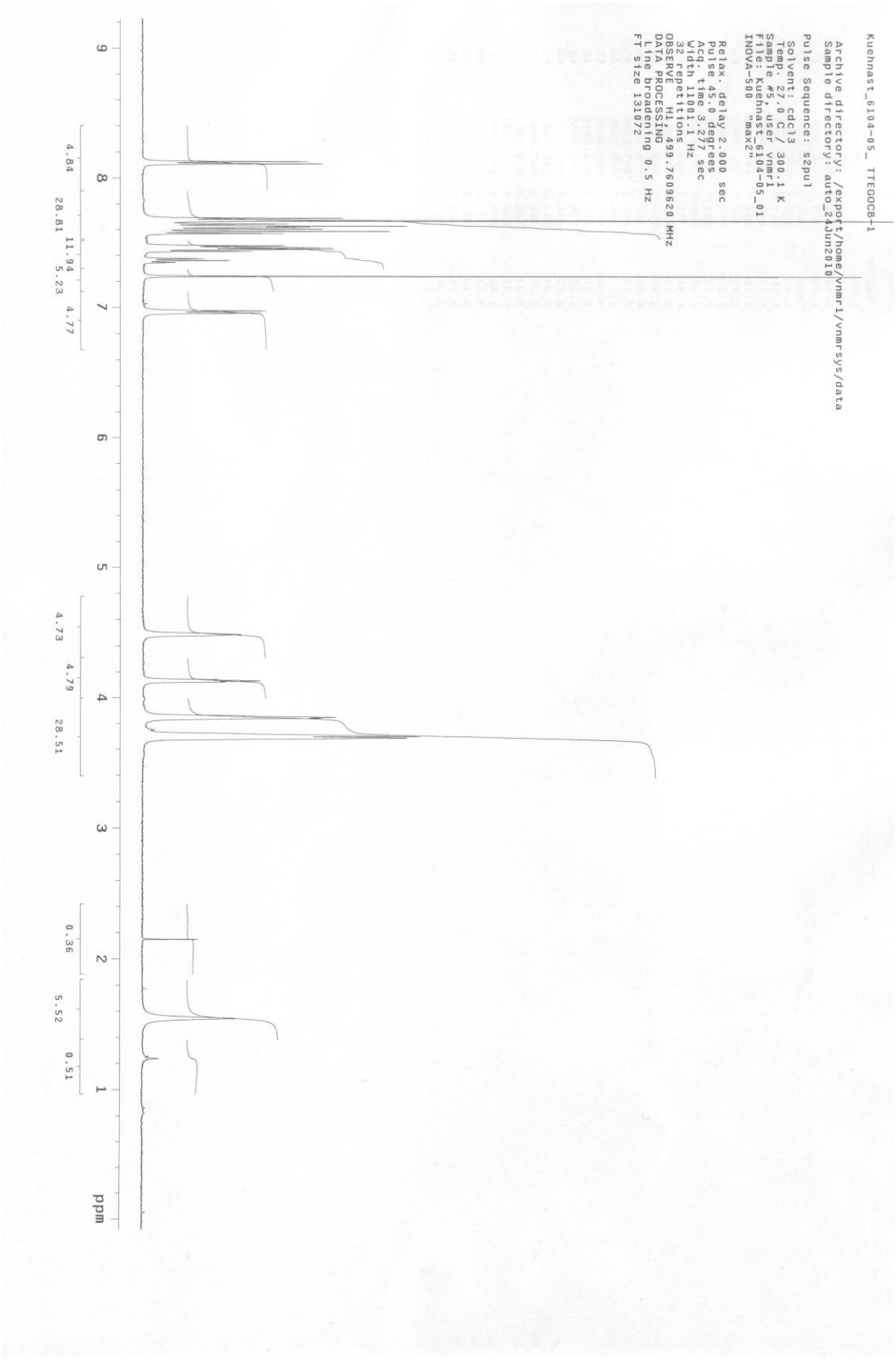


Figure S5 . ^{1}H-NMR spectrum of **2a**.

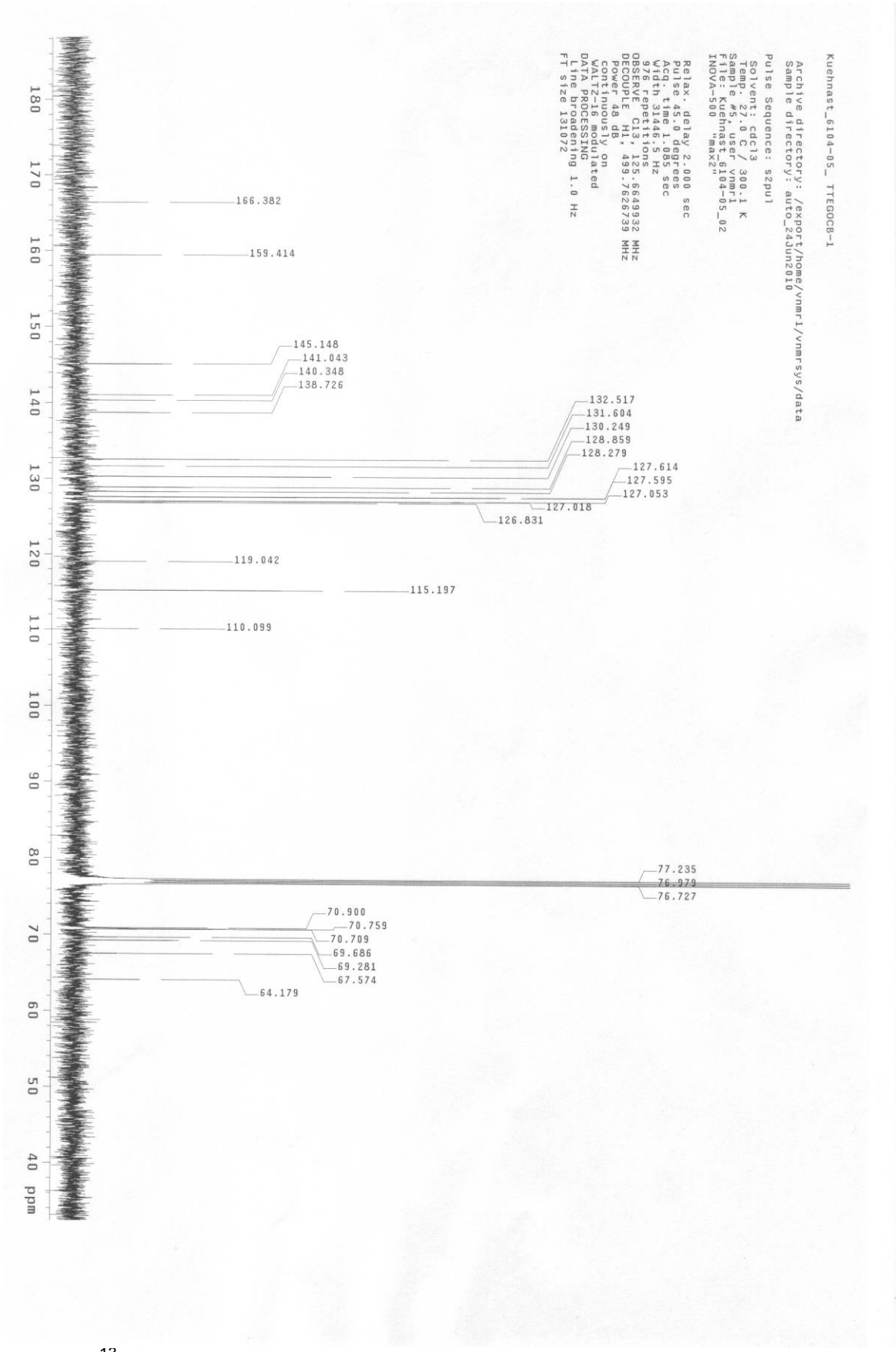


Figure S6 . ^{13}C-NMR spectrum of **2a**.

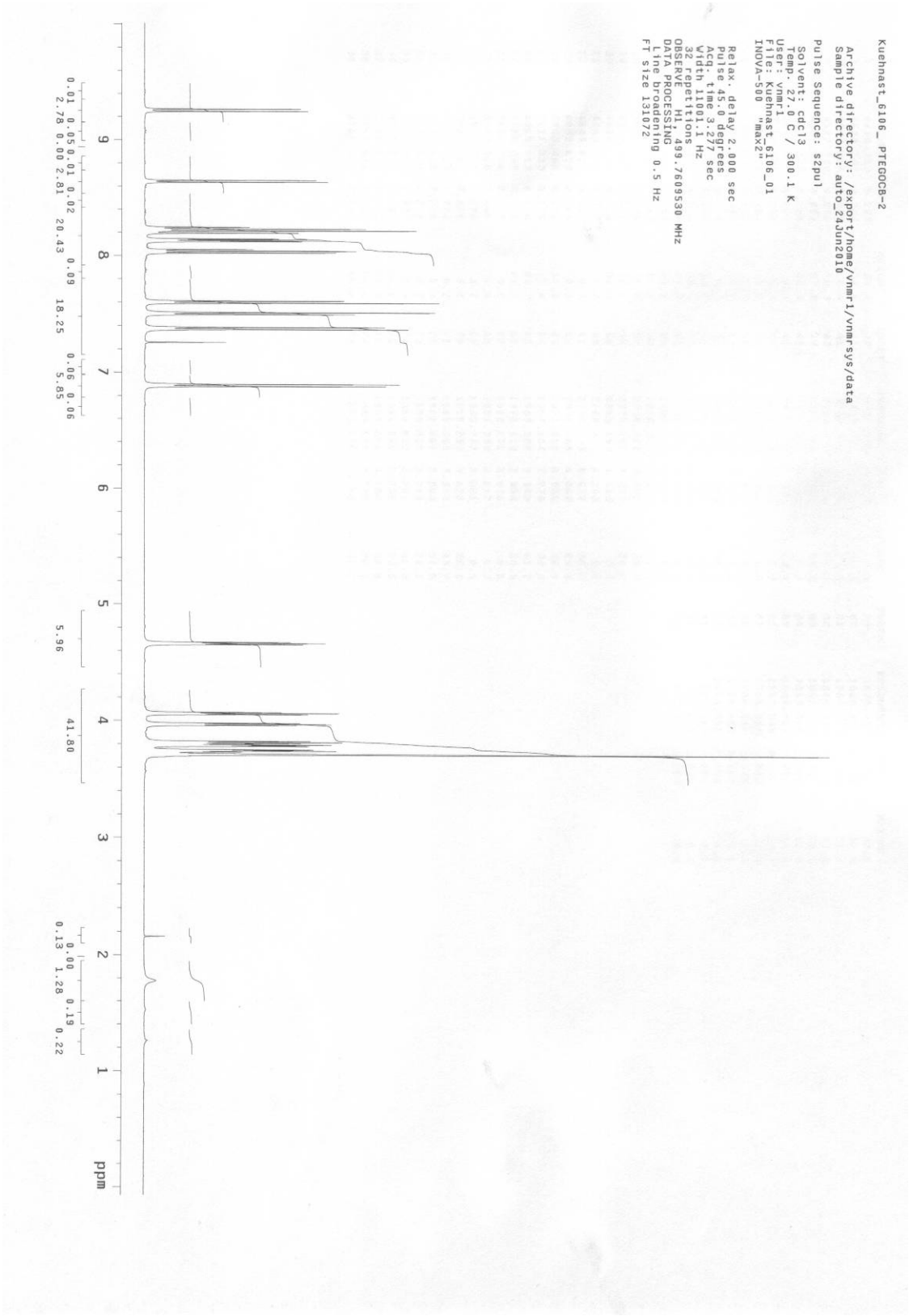


Figure S7 . ^{1}H-NMR spectrum of **2b**.

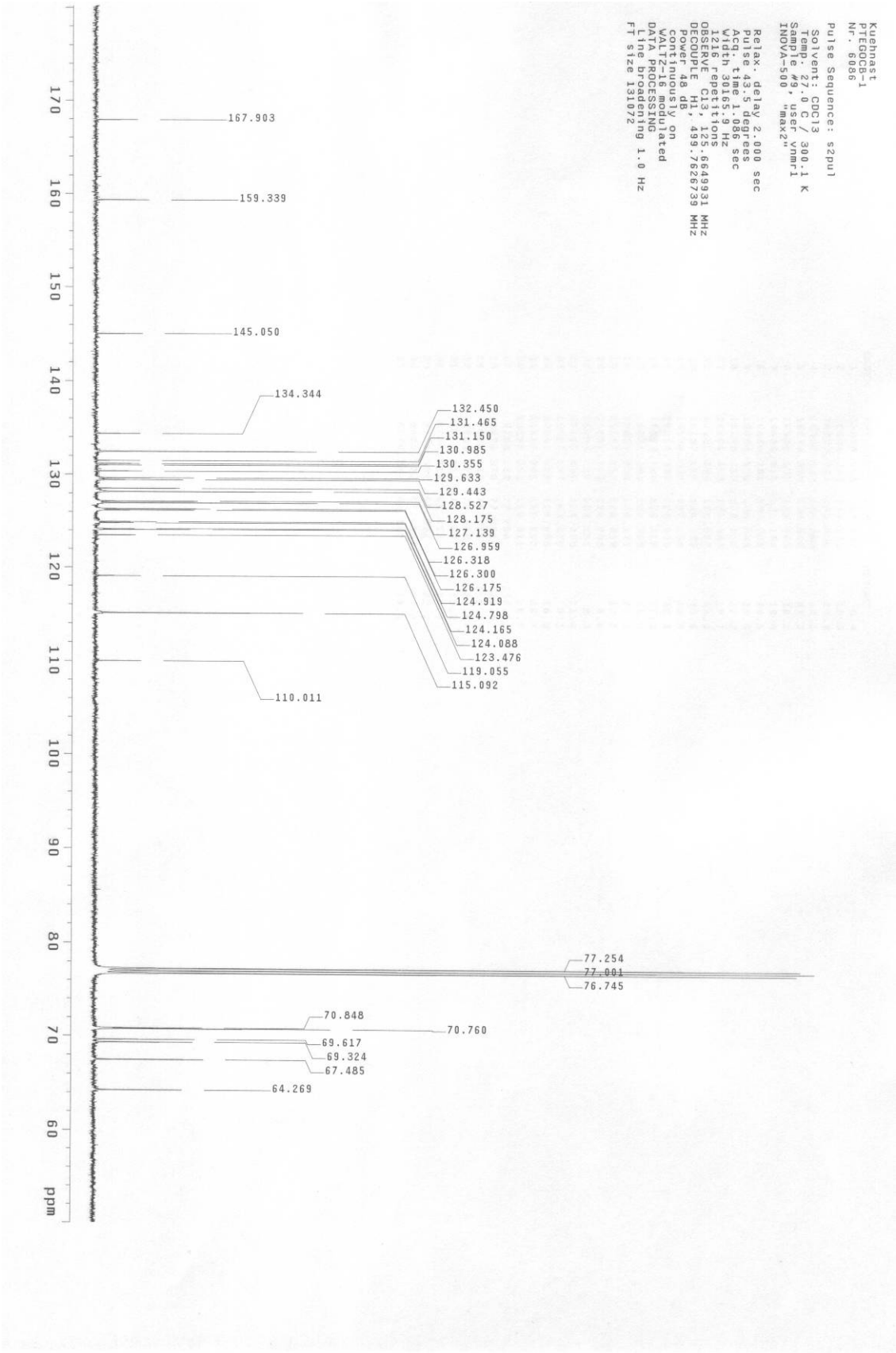


Figure S8 . ^{13}C-NMR spectrum of **2b**.

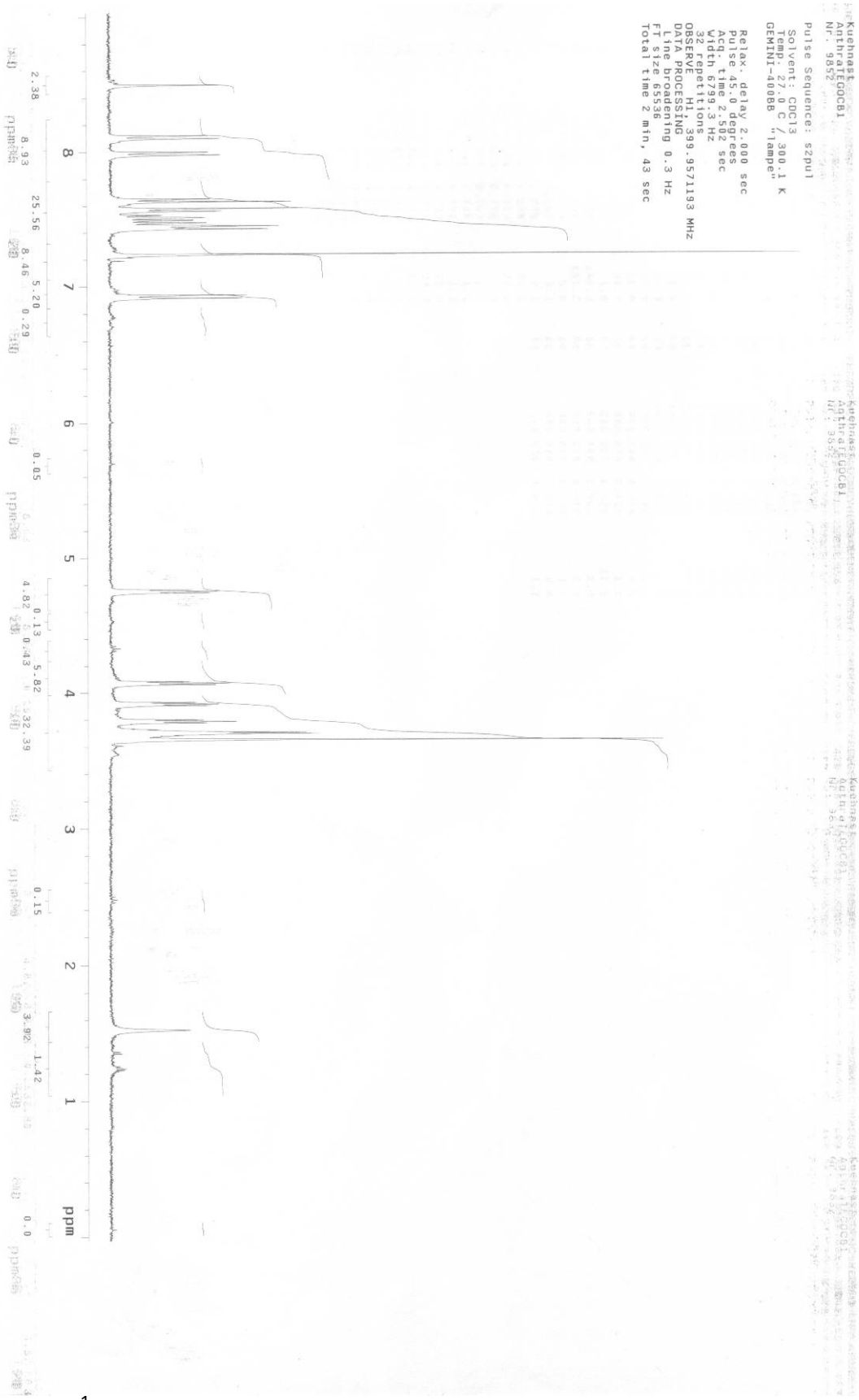


Figure S9 . ^{1}H-NMR spectrum of **2c**.

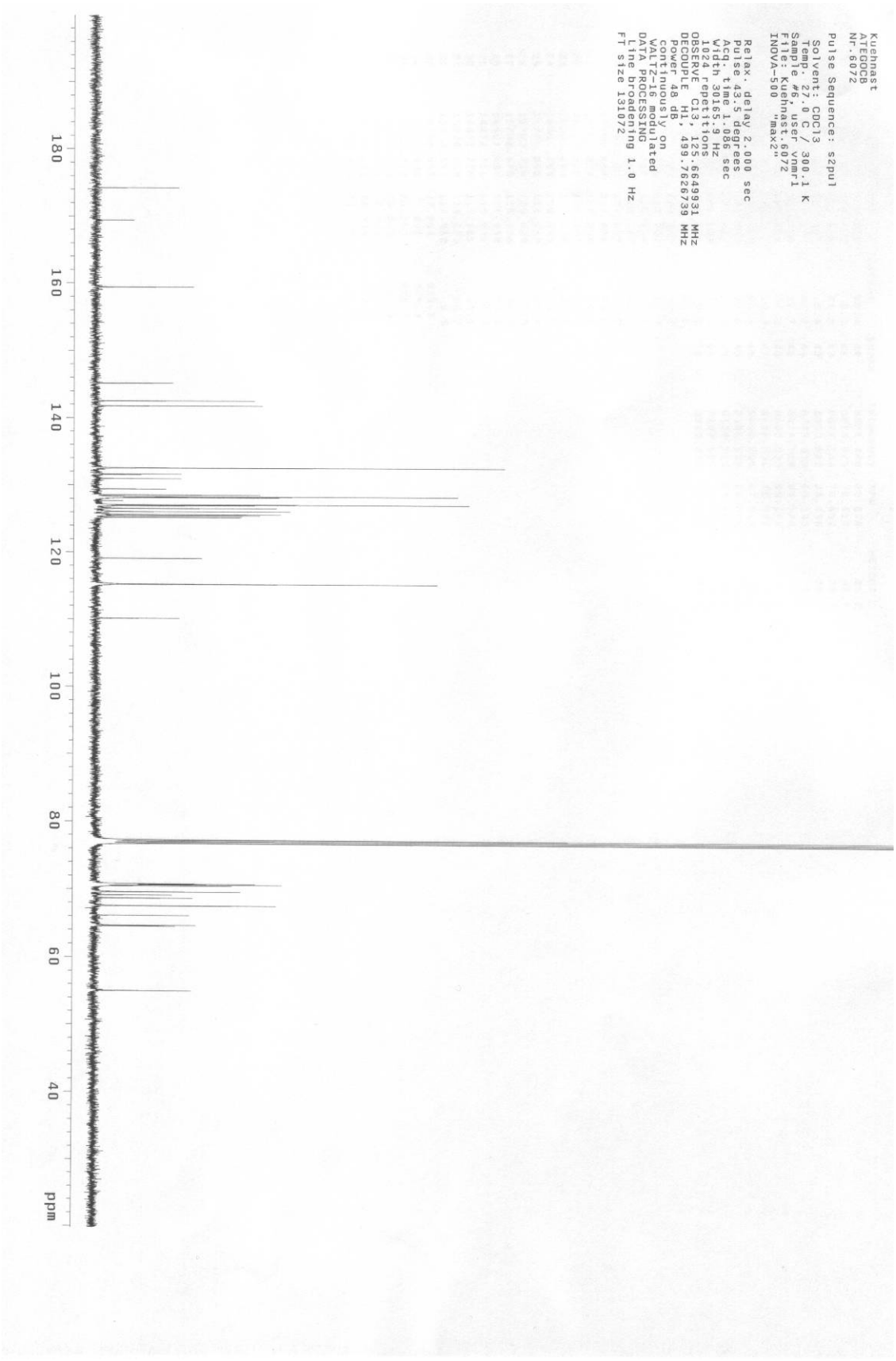
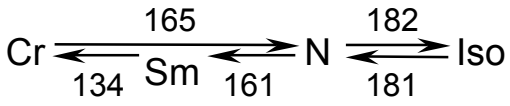
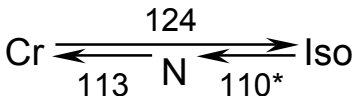
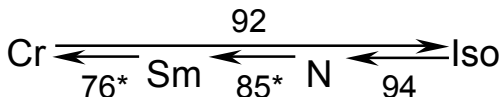


Figure S10. ^{13}C-NMR spectrum of **2c**.

2. Transition temperatures

Table S1: Transition temperatures determined by DSC (10 K/min, peak temperatures in the first heating/cooling scan) and POM (marked with *)

compound	transition temperatures (°C)
1a	
1b	
2a	mp: 133*
2b	mp: 80*
2c	mp: 125*
3	

3. Differential scanning calorimetry (DSC) curves

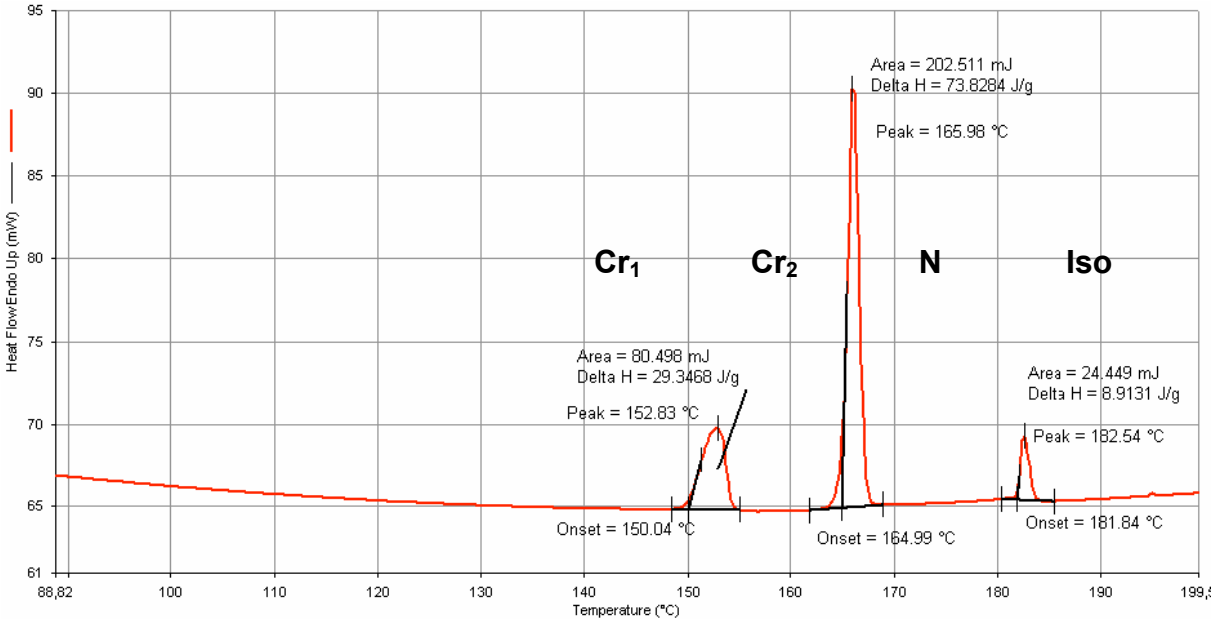


Figure S11. Second heating scan of **1a** at 10 K/min.

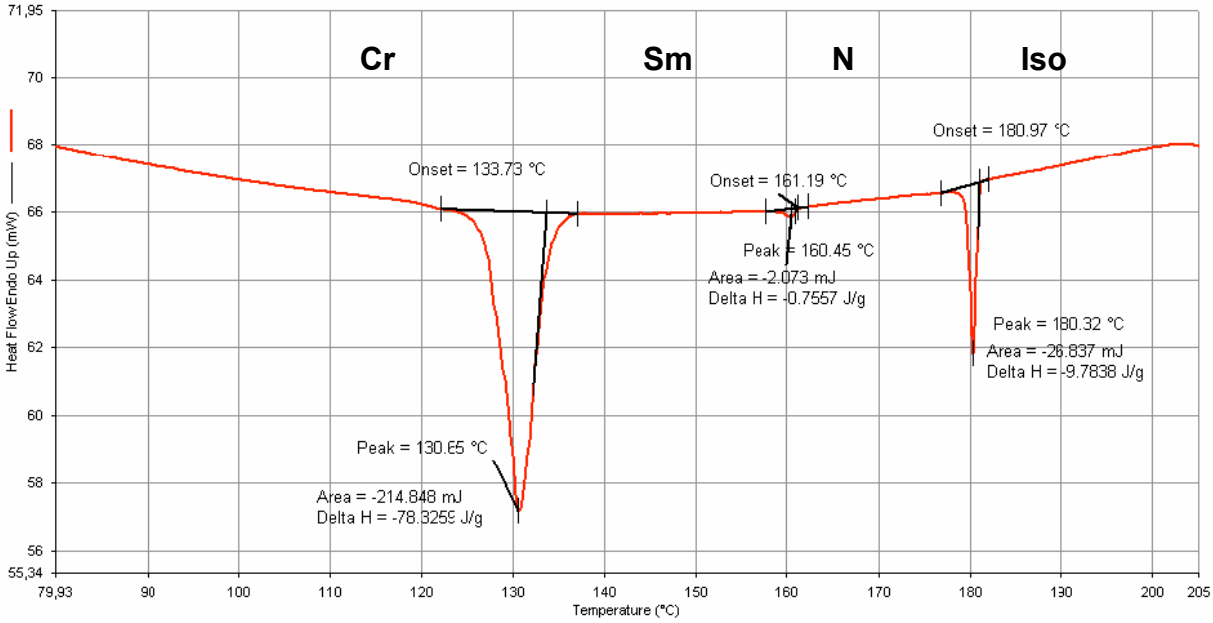


Figure S12. First cooling scan of **1a** at 10 K/min.

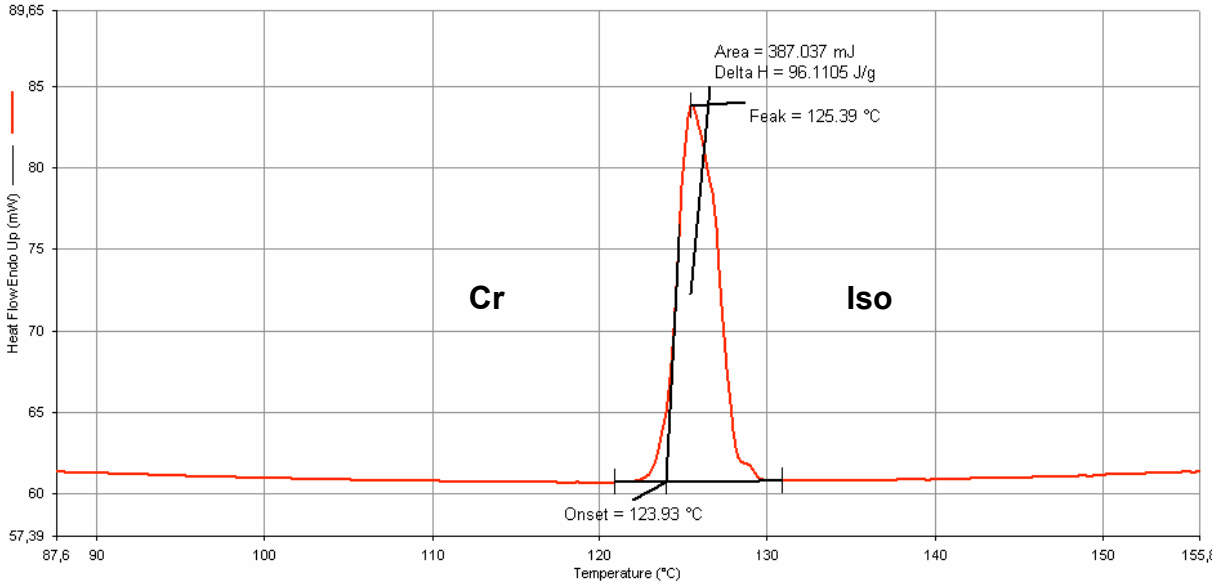


Figure S13. Second heating scan of **1b** at 10 K/min.

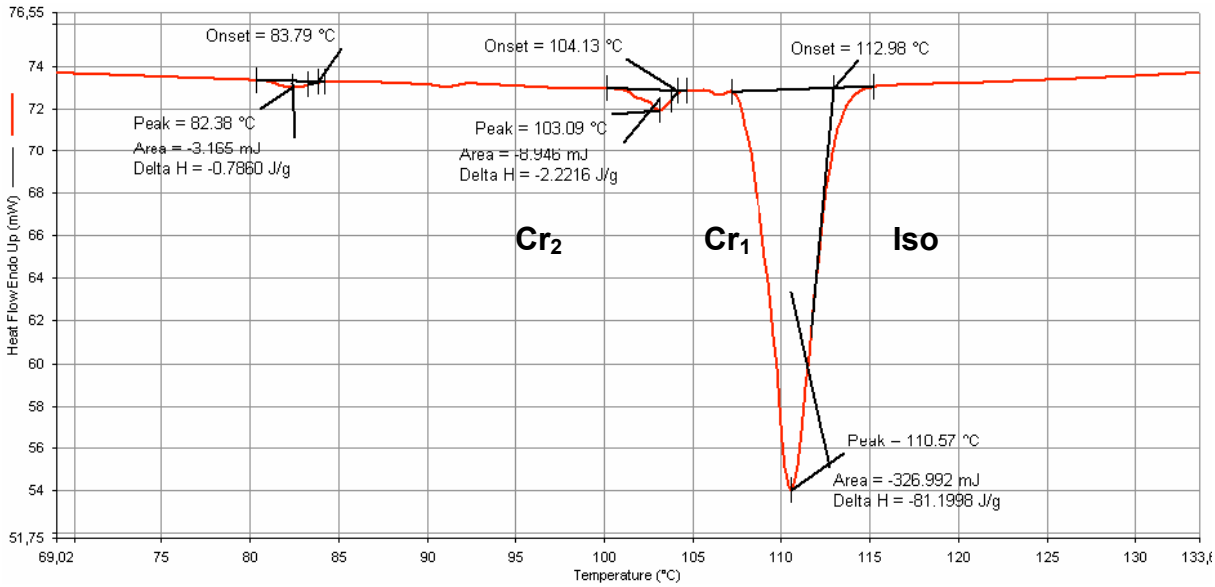


Figure S14. First cooling scan of **1b** at 10 K/min.

4. Textures of liquid crystalline compounds (POM)

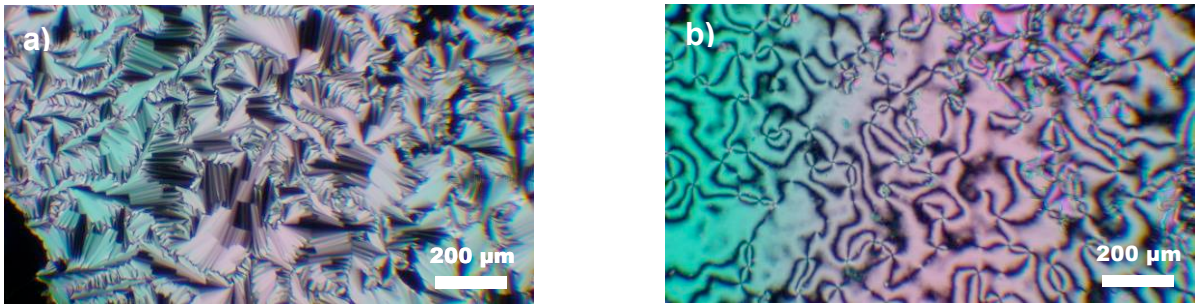


Figure S15. Micrograph of **1a** at 159 °C (a) and 187 °C (b) (crossed polarizers, on cooling).

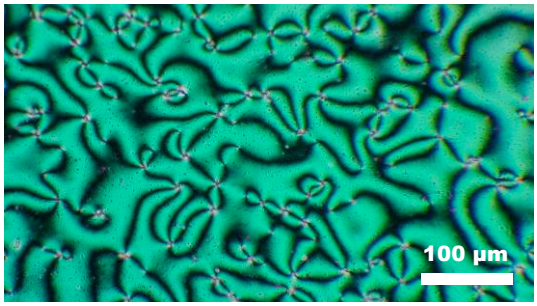


Figure S16. Micrograph of **1b** at 101 °C (crossed polarizers, on cooling).

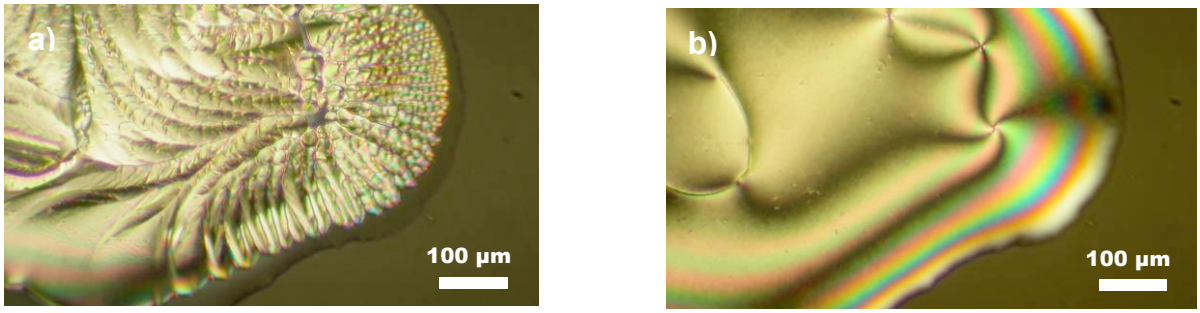


Figure S17. Micrograph of **3** at 85 °C (a) and 90 °C (b) (without cover slip, crossed polarizers, on cooling).

5. References

[S1] Cowling, S. J., Hall, A. W., Goodby, J. W., Wang, Y. Gleeson, H. F. *J. Mater. Chem.* **2006**, 16, 2181-2191.
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