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The effects of alkylthio chains on the properties of symmetric liquid crystal dimers

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Materials and Methods

Reagents

All reagents and solvents that were available commercially were purchased from Sigma Aldrich, Fisher Scientific or Fluorochem and were used without further purification unless otherwise stated.

Thin Layer Chromatography

Reactions were monitored using thin layer chromatography, and the appropriate solvent system, using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica which were purchased from Merck KGaA. The spots on the plate were visualised by UV light (254 nm).

Column Chromatography

For normal phase column chromatography, the separations were carried out using silica gel grade 60 Å, 40-63 µm particle size, purchased from Fluorochem and using an appropriate solvent system.

Structure Characterisation

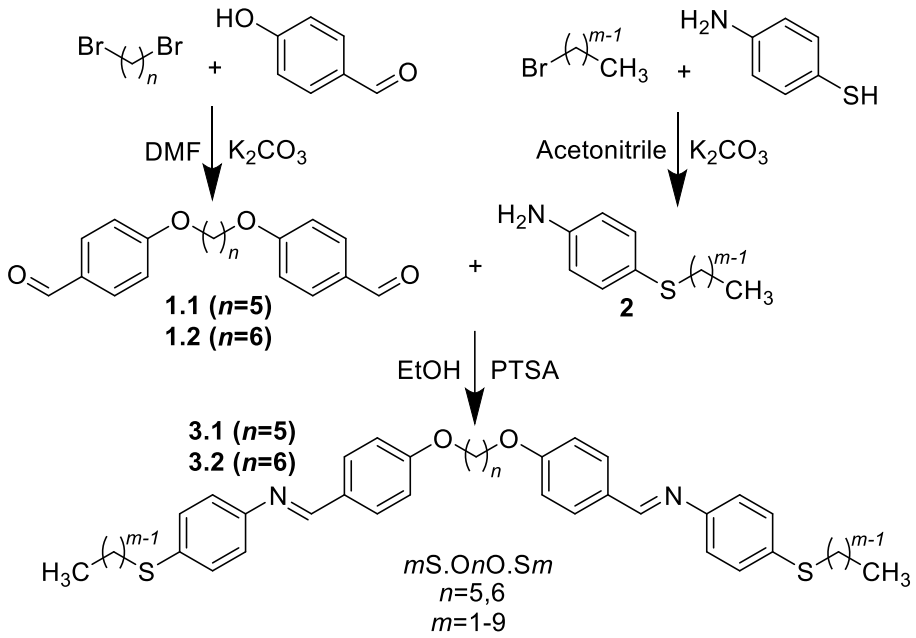
All final products and intermediates that were synthesised were characterised using ^{1}H NMR, ^{13}C NMR and infrared spectroscopies. The NMR spectra were recorded on a 400 MHz Bruker Avance III HD NMR spectrometer. The infrared spectra were recorded on a Perkin Elmer Spectrum Two FTIR with an ATR diamond cell.

Purity Analysis

In order to determine the purity of the final products, elemental analysis or high-resolution mass spectrometry was used. C, H, N, S microanalysis were carried out by the Sheffield Analytical and Scientific Services Elemental Microanalysis Service at the University of Sheffield using an Elementar Vario MICRO Cube or by the Elemental Analysis Service at OEA Laboratories Limited using a CE Instruments EA1110 CHNS-O Elemental Analyser. The instruments were calibrated using series of different masses of sulphanilamide and acetanilide.

Synthesis and Analytical Data

*m*S.O*n*O.S*m* Series



Scheme 1. Synthesis of the *m*S.O*n*O.S*m* series.

The synthesis of the *m*S.O*n*O.S*m* series follows the steps outlined in **Scheme 6.1**. The 4,4'-[alkane-1,ω-diylbis(oxy)]dibenzaldehyde)s (**1.1** and **1.2**) were synthesised using a Williamson ether reaction.[1] A modified Williamson ether reaction[2] was used to generate the 4-(alkylthio)anilines (**2**). Compounds **1.1/1.2** and **2** were subsequently combined in a Schiff's base reaction[3] to form the desired product.

4,4'-[Alkane-1,ω-diylbis(oxy)]dibenzaldehyde)s (1)

To a pre-dried flask flushed with argon and fitted with a condenser, 4-hydroxybenzaldehyde (2 eq, 4.88 g, 0.04 mol) and potassium carbonate (4 eq, 11.1 g, 0.08 mol) were added. Dimethylformamide (60 mL) was added with the appropriate 1,ω-dibromoalkane (1 eq) and stirred. The quantities of the 1,ω-dibromoalkanes used in each reaction are listed in **Table 1.1**. The reaction was heated to 90 °C, left overnight and the extent of the reaction monitored by TLC using dichloromethane as the solvent system (RF values quoted in the product data). The reaction mixture was cooled to room temperature, and poured into water (150 mL). The resulting white precipitate was vacuum filtered and recrystallised from hot ethanol (140 mL).

Table 1.1. Quantities of 1,ω-dibromoalkanes used in the syntheses of 4,4'-[alkane-1,ω-diylbis(oxy)]dibenzaldehydes (**1.1**).

n	1,ω-Dibromoalkane
5	2.72 mL, 4.60 g, 0.02 mol
6	3.08 mL, 4.88 g, 0.02 mol

4,4'-[Pentane-1,5-diylbis(oxy)]dibenzaldehyde (1.1)

Yield: 6.02 g, 96.3 %. RF: 0.20. MP: 84 °C

ν_{max}/cm^{-1}: 2944, 2844, 1689, 1601, 1575, 1510, 1471, 1426, 1379, 1303, 1251, 1213, 1154, 1108, 1030, 985, 928, 833, 802, 650, 618, 509

δ_H/ppm (400 MHz, $CDCl_3$): 9.88 (2 H, s, (C=O)-H), 7.83 (4 H, d, J 8.2 Hz, Ar-H), 6.99 (4 H, d, J 8.2 Hz, Ar-H), 4.08 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.2 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.70 (2 H, quin, J 7.2 Hz, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 190.78, 164.07, 132.00, 129.89, 114.73, 68.08, 28.81, 22.69

Data consistent with reported values.[4]

4,4'-[Hexane-1,6-diylbis(oxy)]dibenzaldehyde (1.2)

Yield: 5.72 g, 87.6 %. RF: 0.22. MP: 112 °C

ν_{max}/cm^{-1}: 2945, 2845, 1685, 1595, 1507, 1479, 1399, 1304, 1250, 1212, 1153, 1111, 1008, 831, 803, 793, 729, 638, 612, 530, 512, 459

δ_H/ppm (400 MHz, $CDCl_3$): 9.88 (2 H, s, (C=O)-H), 7.82 (4 H, d, J 8.1 Hz, Ar-H), 6.99 (4 H, d, J 8.1 Hz, Ar-H), 4.06 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 1.86 (4 H, tt, J 6.8 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.57 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)

δ_C/ppm (100 MHz, $CDCl_3$): 190.79, 164.14, 132.00, 129.84, 114.73, 68.18, 29.00, 25.79

Data consistent with reported values.[4]

4-(Alkylthio)anilines (2)

To a pre-dried flask flushed with argon and fitted with a condenser, 4-aminothiophenol (1 eq, 3.00 g, 0.024 mol) and potassium carbonate (2 eq, 6.63 g, 0.048 mol) were added. Acetonitrile (50 mL) was added with the appropriate 1-bromoalkane (1.1 eq) and stirred. The quantities of 1-bromoalkanes used in each reaction are listed in **Table 1.2**. The reaction was refluxed overnight, and the extent of the reaction monitored by TLC using dichloromethane as the

solvent system (RF values quoted in the product data). The reaction mixture was vacuum filtered, and the solvent removed under vacuum to give a brown oil. The crude product was purified using a 50 g Biotage column (program: 25 % dichloromethane and 75 % 40:60 petroleum ether for 1.5 column volumes, 30 % dichloromethane and 70 % 40:60 petroleum ether for 2 column volumes, 37 % dichloromethane and 63 % 40:60 petroleum ether for 3.5 column volumes, 97 % dichloromethane and 3 % 40:60 petroleum ether for 3 column volumes). The eluent fractions of interest were evaporated under vacuum to give a brown oil or solid. The collected brown solids were recrystallised from hot ethanol (50 mL).

Table 1.2. Quantities of 1-bromoalkanes used in the syntheses of 4-(alkylthio)anilines (**2**).

m	1-Bromoalkane
2	1.97 mL, 2.88 g, 0.0264 mol
3	2.40 mL, 3.25 g, 0.0264 mol
4	2.83 mL, 3.62 g, 0.0264 mol
5	3.27 mL, 3.99 g, 0.0264 mol
6	3.71 mL, 4.36 g, 0.0264 mol
7	4.15 mL, 4.73 g, 0.0264 mol
8	4.56 mL, 5.10 g, 0.0264 mol
9	5.04 mL, 5.47 g, 0.0264 mol

4-(Methylthio)aniline **-** Was purchased commercially from Sigma Aldrich and used without further purification.

4-(Ethylthio)aniline (2.1)

Brown oil. Yield: 1.40 g, 38.1 %. RF: 0.30

ν_{max}/cm^{-1}: 3461, 3550, 3211, 2971, 2923, 1618, 1594, 1493, 1448, 1277, 1257, 1176, 819, 763, 621, 511

δ_H/ppm (400 MHz, $CDCl_3$): 7.24 (2 H, d, J 8.5 Hz, Ar-H), 6.62 (2 H, d, J 8.5 Hz, Ar-H), 3.69 (2 H, br, NH_2), 2.79 (2 H, quart, J 7.4 Hz, S-$\underline{CH_2}$-CH_3), 1.23 (3 H, t, J 7.4 Hz, S-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.85, 133.95, 123.34, 115.55, 30.37, 14.72

Data consistent with reported values.[5]

4-(Propylthio)aniline (2.2)

Brown oil. Yield: 1.19 g, 29.6 %. RF: 0.34

ν_{max}/cm^{-1}: 3462, 3352, 3210, 2959, 2870, 1618, 1596, 1493, 1459, 1278, 1235, 1176, 819, 672, 623, 511

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.0 Hz, Ar-H), 6.61 (2 H, d, J 8.0 Hz, Ar-H), 3.65 (2 H, br, NH_2), 2.74 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.58 (2 H, sext, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_3), 0.97 (3 H, t, J 7.3 Hz, S-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.59, 133.78, 123.83, 115.54, 38.42, 22.71, 13.31

Data consistent with reported values.[6]

4-(Butylthio)aniline (2.3)

Brown oil. Yield: 0.740 g, 17.0 %. RF: 0.35

ν_{max}/cm^{-1}: 3462, 3354, 3211, 2955, 2927, 2870, 1618, 1596, 1493, 1463, 1273, 1175, 819, 727, 623, 513

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.4 Hz, Ar-H), 6.61 (2 H, d, J 8.4 Hz, Ar-H), 3.69 (2 H, br, NH_2), 2.77 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.55 (2 H, quin, J 7.4 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.41 (2 H, sext, J 7.4 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_3), 0.90 (3 H, t, J 7.4 Hz, S-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.78, 133.69, 123.76, 115.58, 36.10, 31.54, 21.85, 13.72

Data consistent with reported values.[7]

4-(Pentylthio)aniline (2.4)

Brown oil. Yield: 1.62 g, 34.6 %. RF: 0.38

ν_{max}/cm^{-1}: 3465, 3356, 3210, 2954, 2925, 2856, 1618, 1595, 1493, 14645, 1275, 1175, 818, 728, 624, 515

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.6 Hz, Ar-H), 6.61 (2 H, d, J 8.6 Hz, Ar-H), 3.68 (2 H, br, NH_2), 2.76 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.57 (2 H, quin, J 7.4 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.32 (4 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (3 H, t, J 7.2 Hz, S-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.69, 133.69, 123.86, 115.57, 36.39, 30.90, 29.11, 22.29, 14.01

Data consistent with reported values.[8]

4-(Hexylthio)aniline (2.5)

Brown oil. Yield: 2.30 g, 45.8 %. RF: 0.33

ν_{max}/cm^{-1}: 3465, 3357, 3215, 2953, 2924, 2854, 1618, 1596, 1494, 1465, 1278, 1176, 820, 724, 623, 515

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 7.9 Hz, Ar-H), 6.59 (2 H, d, J 7.9 Hz, Ar-H), 3.68 (2 H, br, NH_2), 2.76 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.55 (2 H, quin, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (6 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.87 (3 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.54, 133.67, 123.96, 115.55, 36.41, 31.42, 29.39, 28.40, 22.57, 14.05

Data consistent with reported values.[9]

4-(Heptylthio)aniline (2.6)

Brown oil. Yield: 1.23 g, 22.9 %. RF: 0.37

ν_{max}/cm^{-1}: 3465, 3356, 3208, 2953, 2924, 2853, 1619, 1596, 1494, 1465, 1276, 1176, 819, 723, 624, 514

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.5 Hz, Ar-H), 6.62 (2 H, d, J 8.5 Hz, Ar-H), 3.68 (2 H, br, NH_2), 2.76 (2 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.56 (2 H, quin, J 7.4 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.29 (8 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.87 (3 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.66, 133.69, 123.91, 115.56, 36.42, 31.75, 29.42, 28.88, 28.68, 22.61, 14.09

4-(Octylthio)aniline (2.7)

Brown oil. Yield: 2.50 g, 43.9 %. RF: 0.33

ν_{max}/cm^{-1}: 3459, 3362, 3215, 2923, 2852, 1618, 1596, 1494, 1464, 1276, 1176, 820, 722, 623, 515

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.5 Hz, Ar-H), 6.62 (2 H, d, J 8.5 Hz, Ar-H), 3.67 (2 H, br, NH_2), 2.76 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.55 (2 H, quin, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.27 (10 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.86 (3 H, t, J 7.1 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.54, 133.67, 123.97, 115.54, 36.41, 31.82, 29.41, 29.20, 29.17, 28.72, 22.65, 14.11

Data consistent with reported values.[7]

4-(Nonylthio)aniline (2.8)

Brown solid. Yield: 1.62 g, 26.8 %. RF: 0.37. MP: 30 °C

ν_{max}/cm^{-1}: 3465, 3362, 3212, 2923, 2852, 1619, 1597, 1494, 1465, 1278, 1176, 820, 721, 624, 515

δ_H/ppm (400 MHz, $CDCl_3$): 7.23 (2 H, d, J 8.5 Hz, Ar-H), 6.62 (2 H, d, J 8.5 Hz, Ar-H), 3.67 (2 H, br, NH_2), 2.76 (2 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.55 (2 H, quin, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_2-), 1.25 (12 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (3 H, t, J 7.2 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)

δ_C/ppm (100 MHz, $CDCl_3$): 145.65, 133.68, 123.92, 115.55, 36.42, 31.88, 29.49, 29.42, 29.27, 29.22, 28.72, 22.68, 14.13

Data consistent with reported values.[9]

(*E,E*)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{*N*-[(alkylthio)phenyl]methanimine}s (*m*S.O5O.S*m*) (3.1)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.1** (1 eq, 0.150 g, 4.80×10^{-4} mol) and compound **2** (3 eq) of the appropriate chain length were added along with ethanol (20 mL) and the mixture was stirred. The quantities of 4-(alkylthio)anilines used in each reaction are listed in **Table 1.3**. The reaction was heated to reflux, *p*-toluenesulfonic acid (catalytic amount) was added, and left overnight. The reaction mixture was cooled to room temperature and a yellow precipitate formed which was collected by vacuum filtration. The yellow solid was recrystallised from hot ethanol (15 mL).

Table 1.3. Quantities of 4-(alkylthio)anilines used in the syntheses of (E,E)-[pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(alkylthio)phenyl]methanimine}s (**3.1**).

m	(**2**)
1	0.179 mL, 0.200 g, 1.44×10^{-3} mol
2	0.221 g, 1.44×10^{-3} mol
3	0.241 g, 1.44×10^{-3} mol
4	0.261 g, 1.44×10^{-3} mol
5	0.281 g, 1.44×10^{-3} mol
6	0.301 g, 1.44×10^{-3} mol
7	0.322 g, 1.44×10^{-3} mol

8	0.342 g, 1.44×10^{-3} mol
9	0.362 g, 1.44×10^{-3} mol

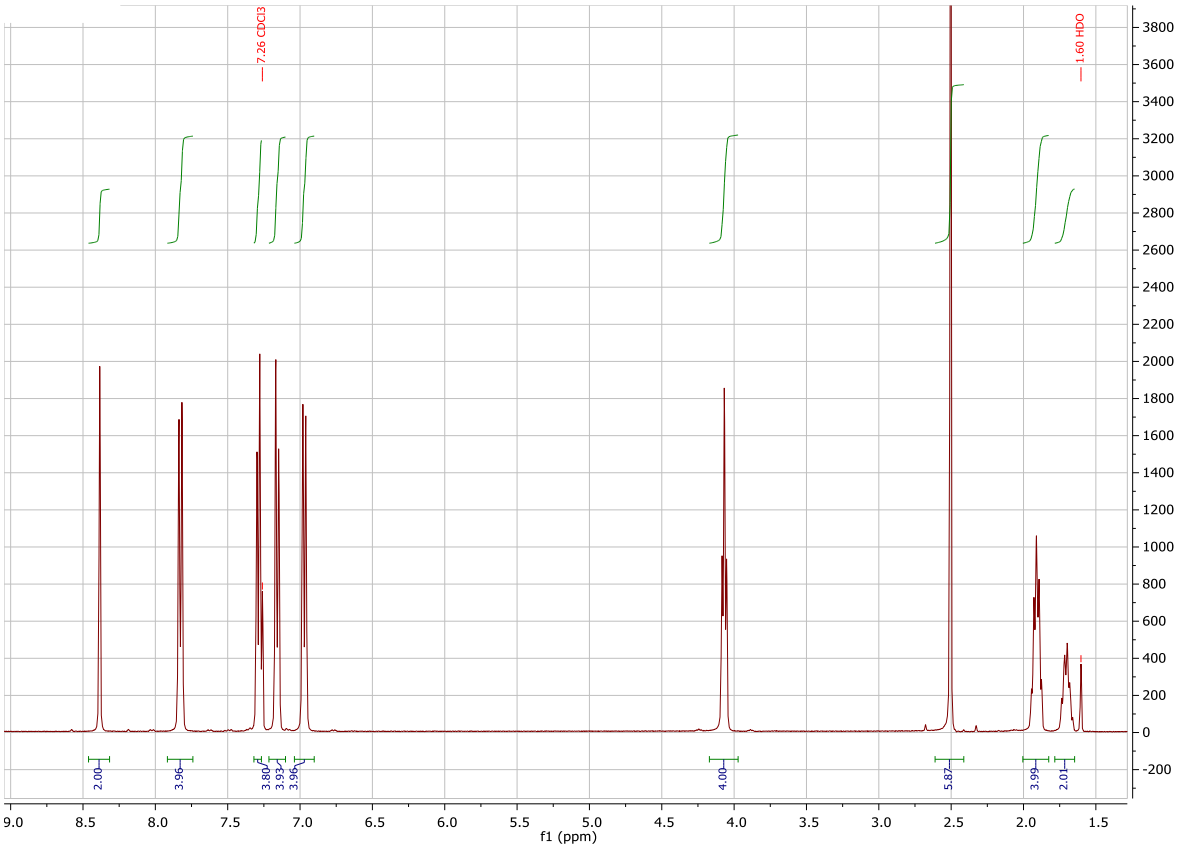
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(methylthio)phenyl]methanimine} (1S.O5O.S1) (3.1.1)

Yield: 0.240 g, 90.1 %

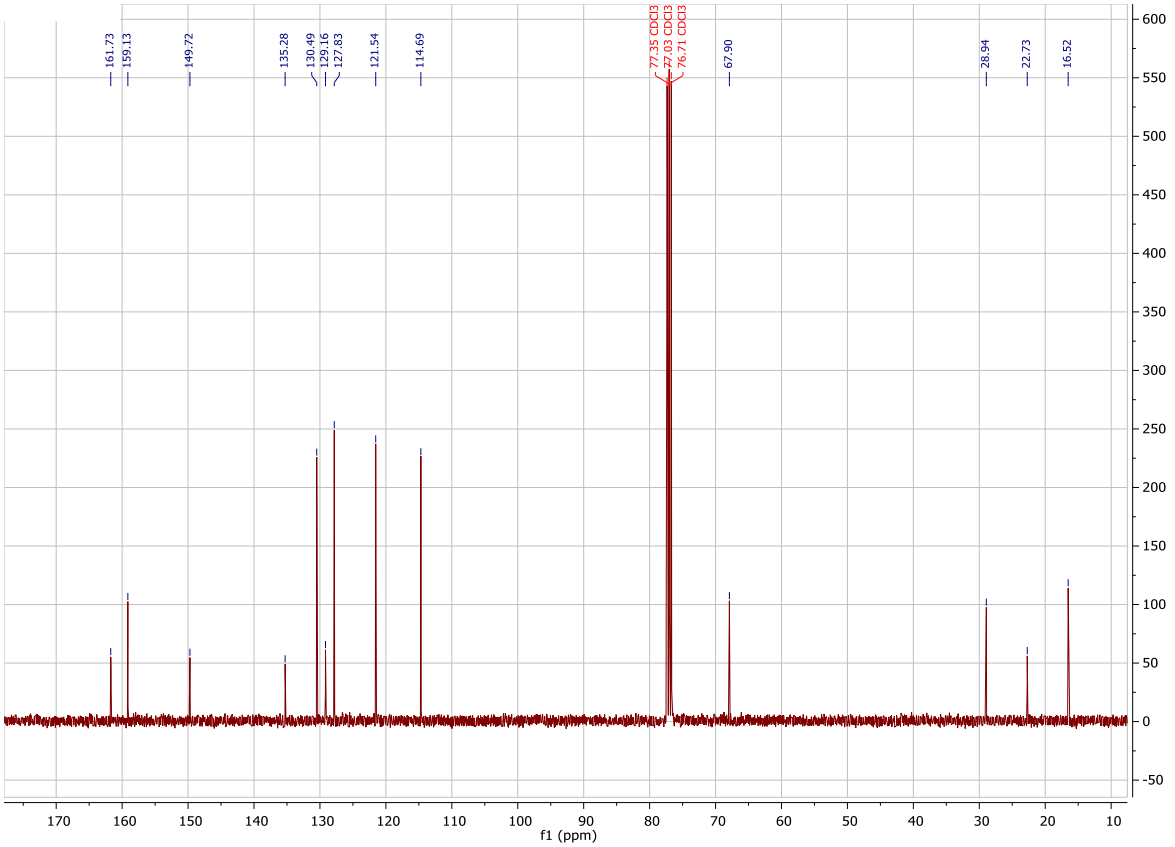
T_{CrI} 165 °C T_{NI} (158 °C)

ν_{max}/cm^{-1}: 2952, 2932, 2861, 1618, 1603, 1571, 1506, 1483, 1421, 1398, 1304, 1240, 1196, 1170, 1112, 1089, 1050, 1026, 1008, 965, 884, 839, 726, 677, 585, 542

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.0 Hz, Ar-H), 7.29 (4 H, d, J 7.8 Hz, Ar-H), 7.16 (4 H, d, J 7.8 Hz, Ar-H), 6.97 (4 H, d, J 8.0 Hz, Ar-H), 4.06 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.50 (6 H, s, S-$\underline{CH_3}$), 1.91 (4 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.71 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)



δ_C/ppm (100 MHz, $CDCl_3$): 161.73, 159.13, 149.72, 135.28, 130.49, 129.16, 127.83, 121.54, 114.69, 67.90, 28.94, 22.73, 16.52



EA: Calculated for $C_{33}H_{34}N_2O_2S_2$: C = 71.45 %, H = 6.18 %, N = 5.05 %, S = 11.56 %; Found: C = 71.43 %, H = 6.20 %, N = 4.92 %, S = 11.50 %

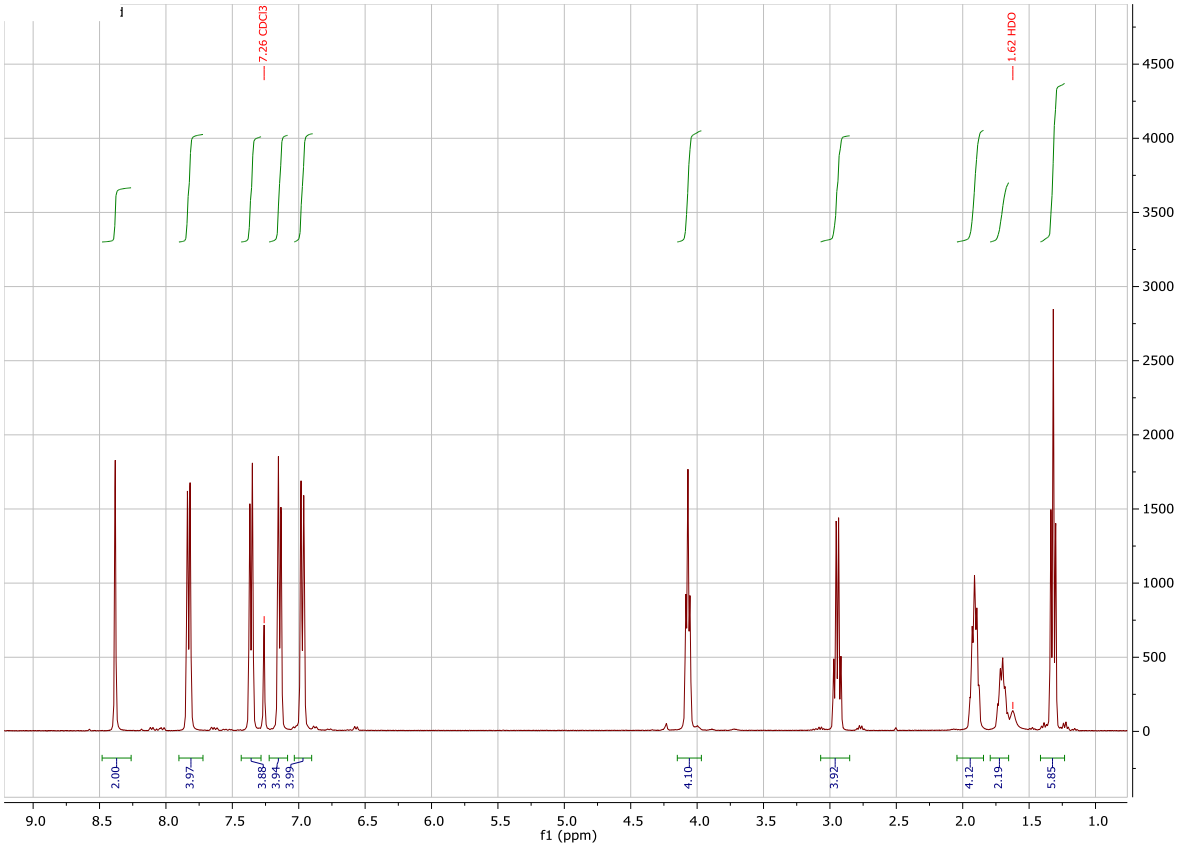
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(ethylthio)phenyl]methanimine} (2S.O5O.S2) (3.1.2)

Yield: 0.193 g, 69.0 %

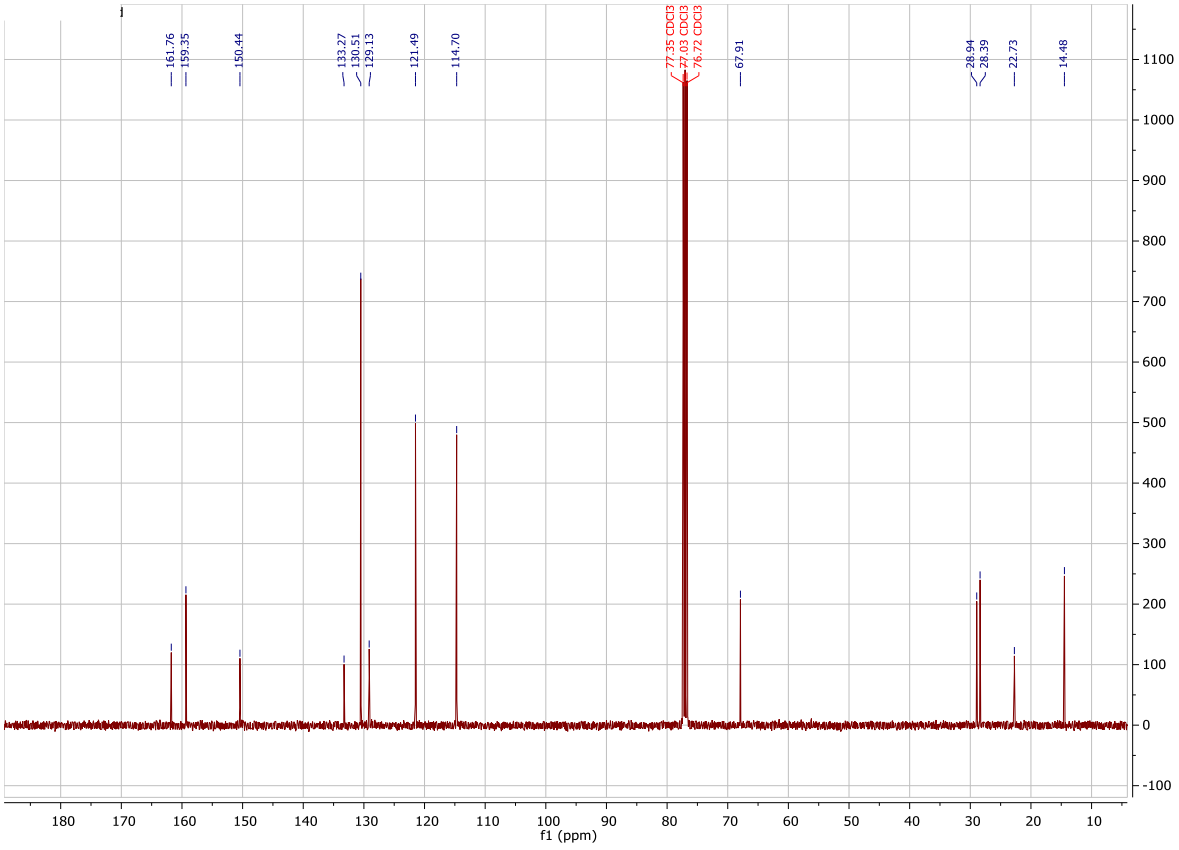
T_{Crl} 150 °C T_{NI} (121 °C)

ν_{max}/cm^{-1}: 2952, 2932, 2862, 1618, 1603, 1571, 1506, 1484, 1420, 1398, 1305, 1242, 1196, 1170, 1112, 1089, 1050, 1027, 1008, 965, 885, 840, 726, 678, 586, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.3 Hz, Ar-H), 7.36 (4 H, d, J 8.0 Hz, Ar-H), 7.14 (4 H, d, J 8.0 Hz, Ar-H), 6.97 (4 H, d, J 8.3 Hz, Ar-H), 4.07 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.94 (4 H, quart, J 7.2 Hz, S-$\underline{CH_2}$-CH_3), 1.91 (4 H, tt, J 7.1 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.32 (6 H, t, J 7.2 Hz, S-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.76, 159.35, 150.44, 133.27, 130.52, 130.51, 129.13, 121.49, 114.70, 67.91, 28.94, 28.39, 22.73, 14.48



EA: Calculated for $C_{35}H_{38}N_2O_2S_2$: C = 72.13 %, H = 6.57 %, N = 4.81 %, S = 11.00 %; Found: C = 72.19 %, H = 6.53 %, N = 4.49 %, S = 11.02 %

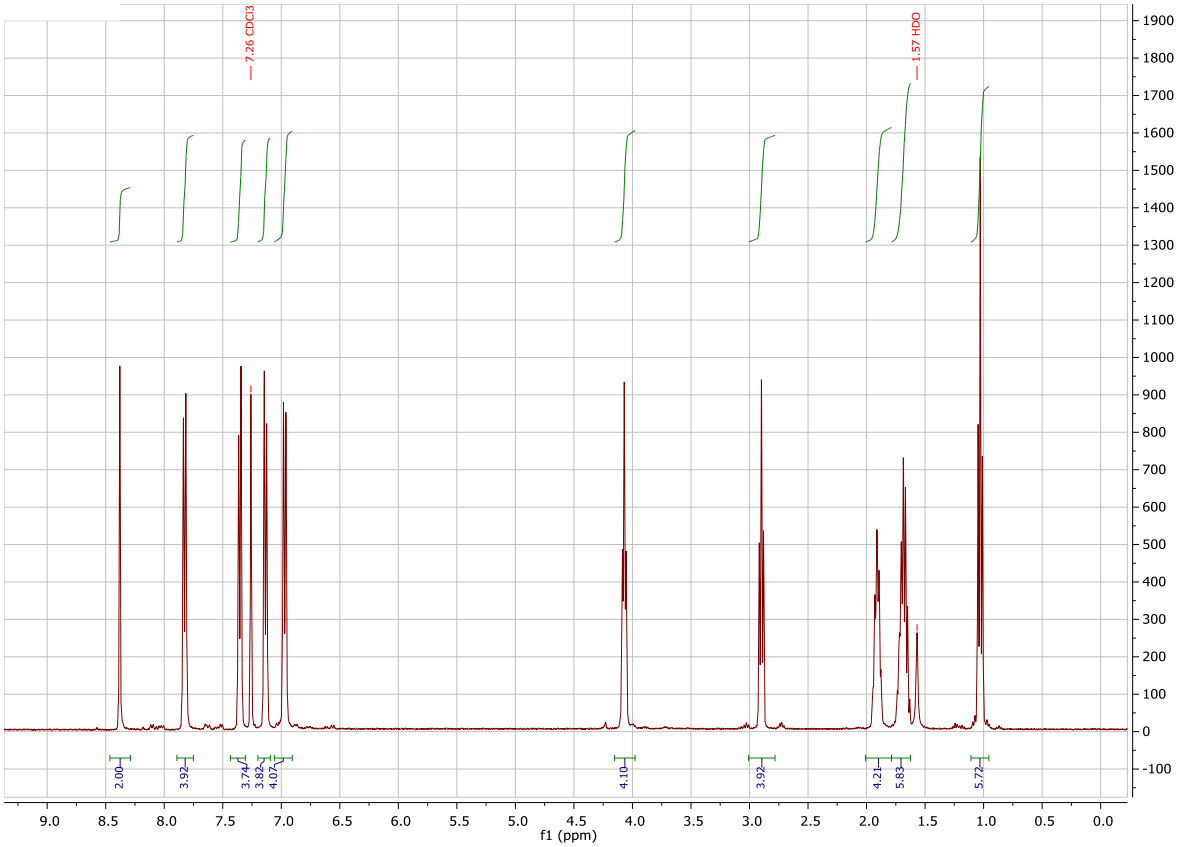
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(propylthio)phenyl]methanimine} (3S.O5O.S3) (3.1.3)

Yield: 0.229 g, 78.1 %

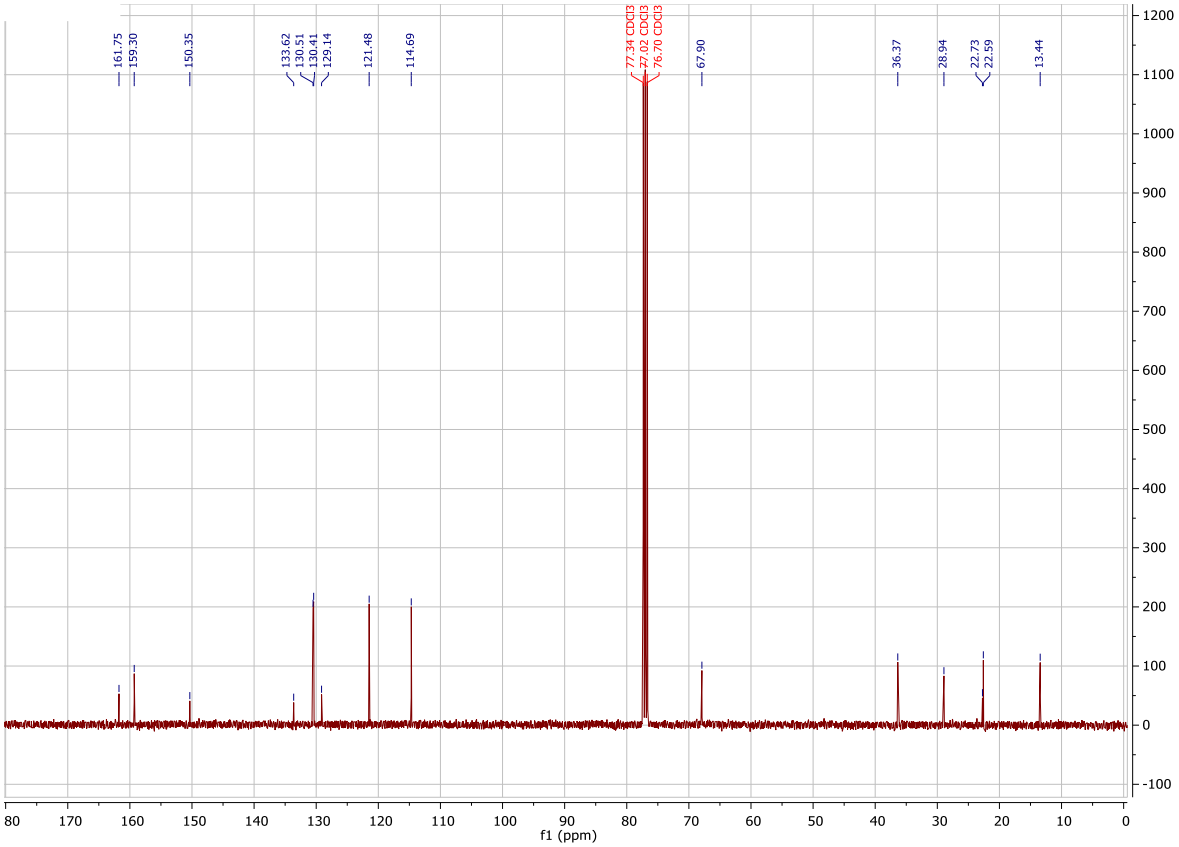
T_{CrI} 119 °C T_{NI} (84 °C)

ν_{max}/cm^{-1}: 2954, 2931, 2872, 1618, 1604, 1571, 1506, 1483, 1421, 1397, 1304, 1242, 1197, 1169, 1112, 1089, 1050, 1026, 1008, 965, 884, 839, 726, 678, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.3 Hz, Ar-H), 7.35 (4 H, d, J 7.8 Hz, Ar-H), 7.14 (4 H, d, J 7.8 Hz, Ar-H), 6.97 (4 H, d, J 8.3 Hz, Ar-H), 4.07 (4 H, t, J 6.6 Hz, O-$\underline{CH_2}$-CH_2-), 2.90 (4 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2), 1.91 (4 H, tt, J 7.2 Hz, 6.6 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_3), 1.03 (6 H, t, J 7.3 Hz, S-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.30, 150.35, 133.62, 130.51, 130.41, 129.14, 121.48, 114.69, 67.90, 36.37, 28.94, 22.73, 22.59, 13.44



EA: Calculated for $C_{37}H_{42}N_2O_2S_2$: C = 72.75 %, H = 6.93 %, N = 4.59 %, S = 10.50 %; Found: C = 72.55 %, H = 6.93 %, N = 4.55 %, S = 10.55 %

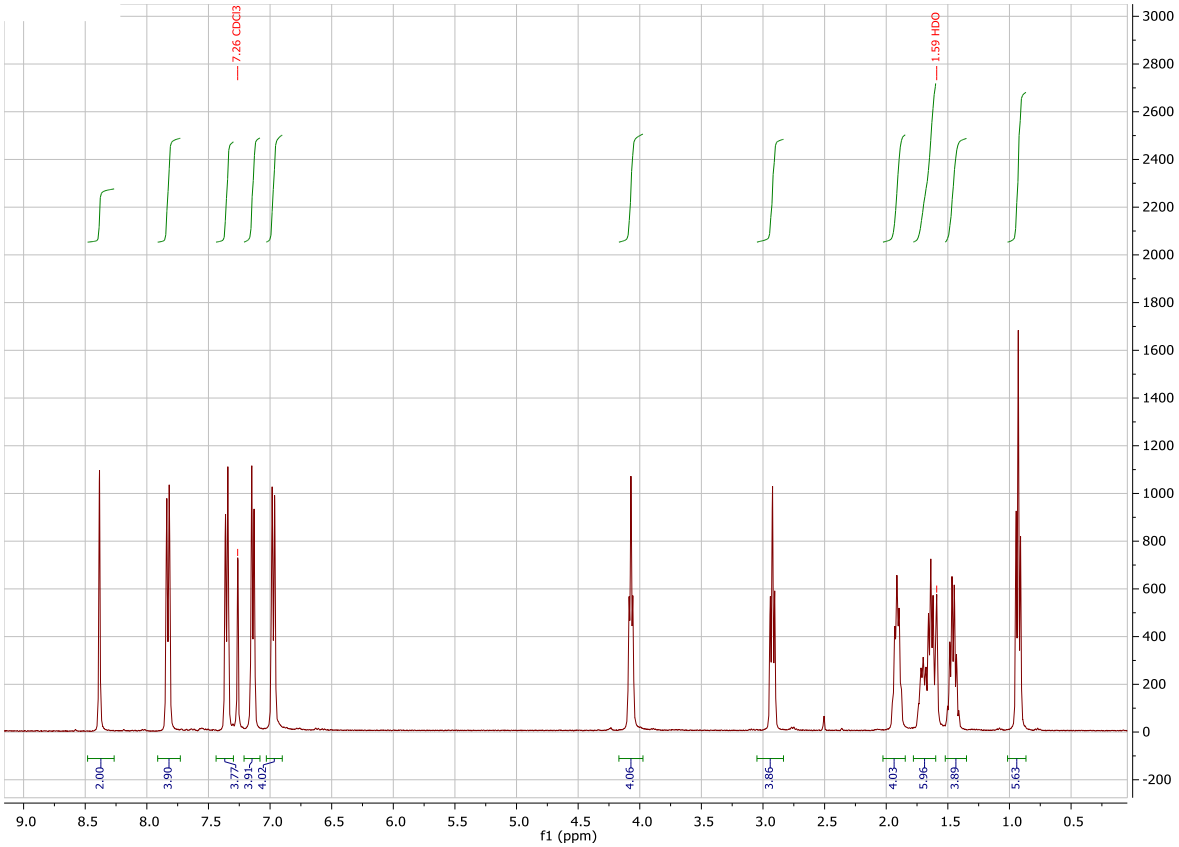
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(butylthio)phenyl]methanimine} (4S.O5O.S4) (3.1.4)

Yield: 0.238 g, 77.6 %

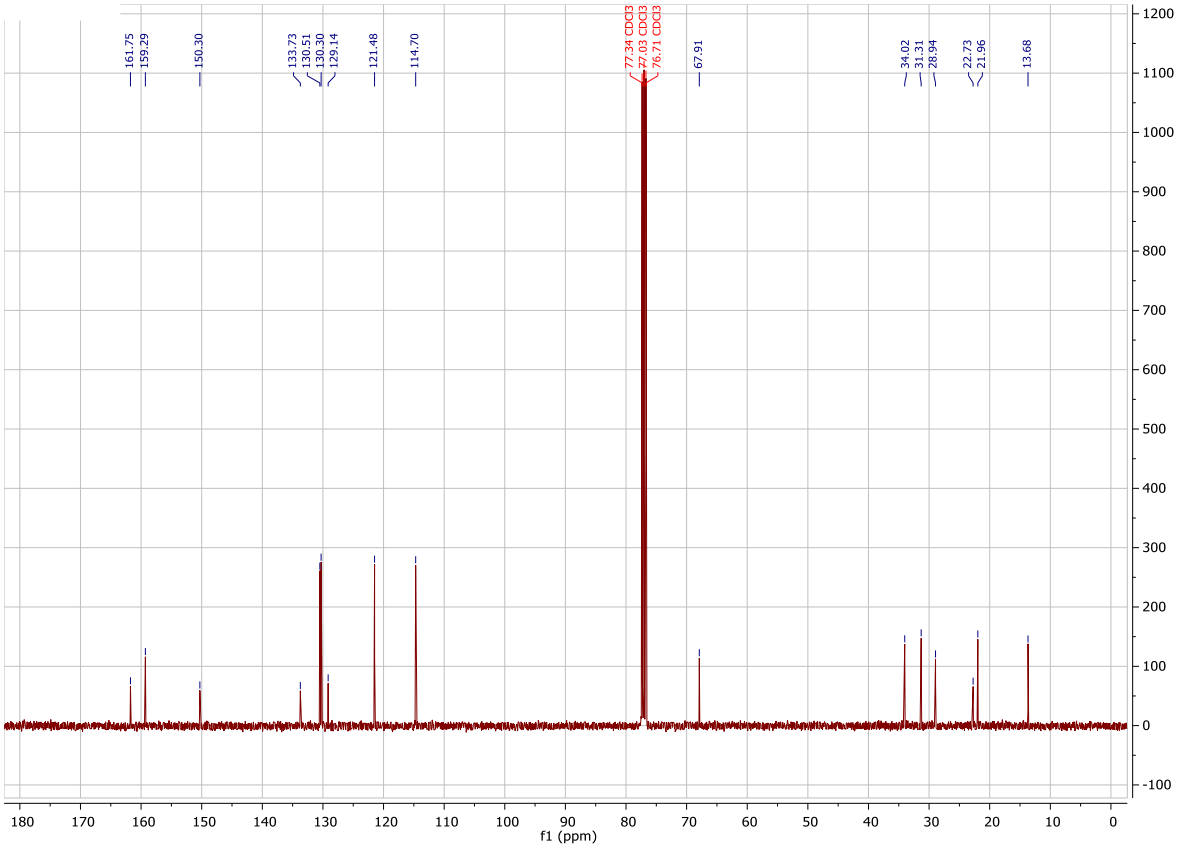
T_{CrI} 122 °C T_{NI} (95 °C)

ν_{max}/cm^{-1}: 2954, 2931, 2872, 1617, 1604, 1571, 1506, 1483, 1421, 1398, 1305, 1242, 1196, 1169, 1112, 1089, 1050, 1026, 1008, 965, 884, 839, 815, 726, 678, 587, 544

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.0 Hz, Ar-H), 7.35 (4 H, d, J 7.8 Hz, Ar-H), 7.14 (4 H, d, J 7.8 Hz, Ar-H), 6.97 (4 H, d, J 8.0 Hz, Ar-H), 4.07 (4 H, t, J 6.2 Hz, O-$\underline{CH_2}$-CH_2-), 2.92 (4 H, t, J 7.0 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.1 Hz, 6.2 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.46 (4 H, sext, J 7.0 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_3), 1.03 (6 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.29, 150.30, 133.73, 130.51, 130.30, 129.14, 121.48, 114.70, 67.91, 34.02, 31.31, 28.94, 22.73, 21.96, 13.68



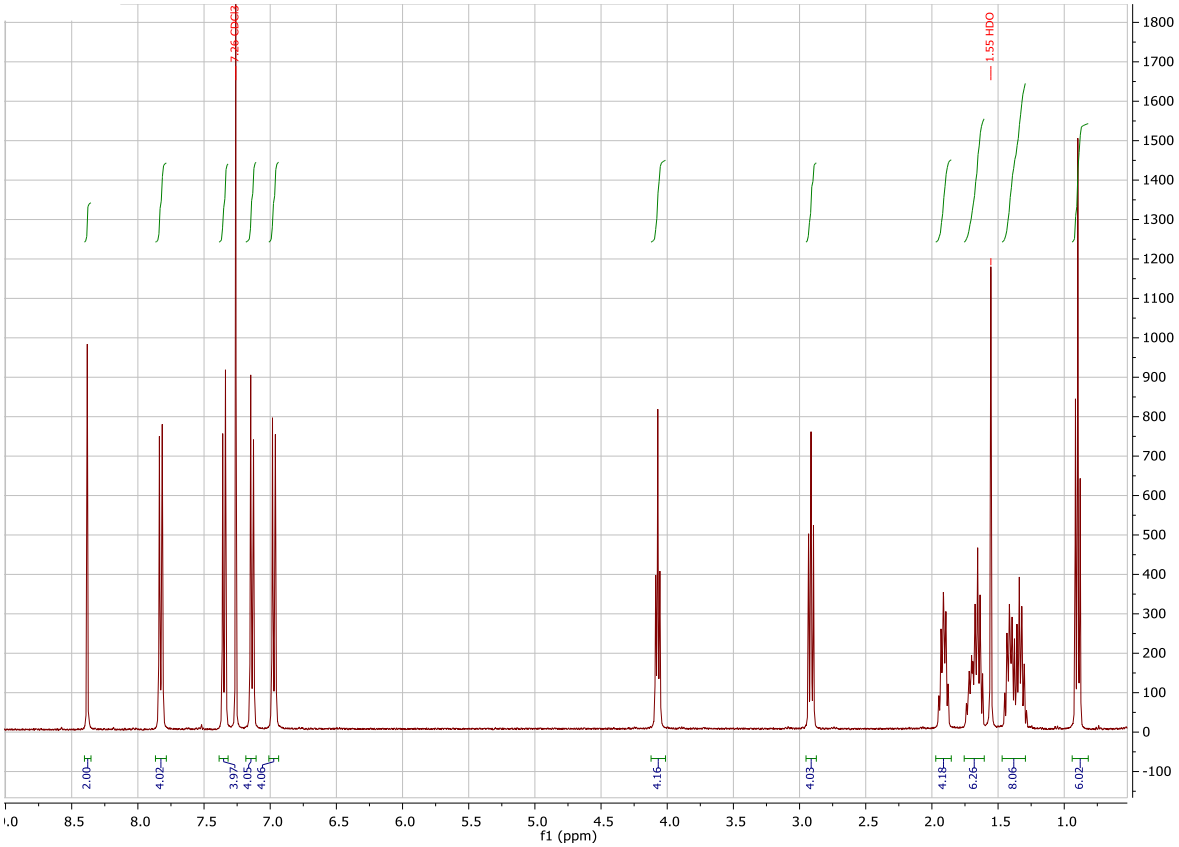
EA: Calculated for $C_{39}H_{46}N_2O_2S_2$: C = 73.31 %, H = 7.26 %, N = 4.38 %, S = 10.04 %; Found: C = 73.18 %, H = 7.20 %, N = 4.06 %, S = 10.06 %

(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(pentylthio)phenyl]methanimine} (5S.O5O.S5) (3.1.5)

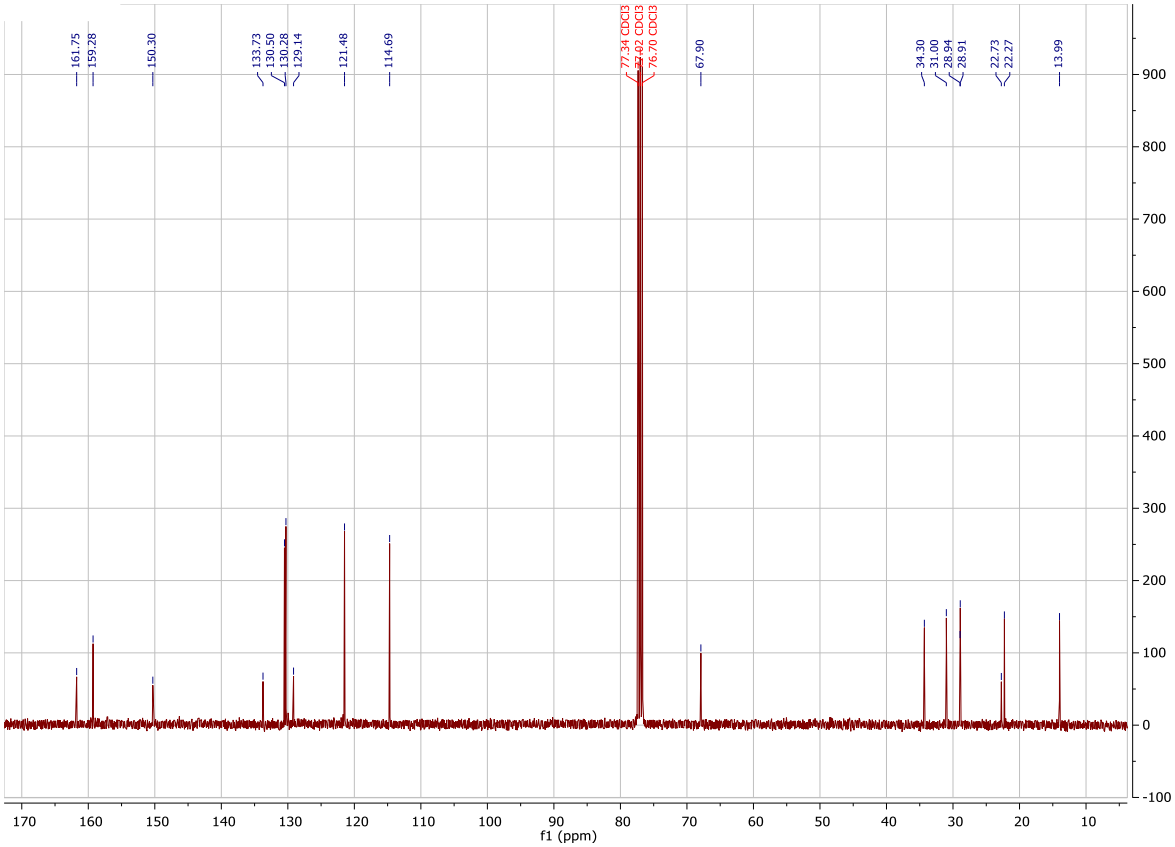
Yield: 0.251 g, 78.4 %. M.P: 124 °C

ν_{max}/cm^{-1}: 2953, 2931, 2871, 1618, 1604, 1571, 1506, 1483, 1421, 1399, 1305, 1242, 1197, 1170, 1112, 1089, 1051, 1027, 1008, 965, 885, 840, 813, 726, 679, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.4 Hz, Ar-H), 7.14 (4 H, d, J 8.4 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.07 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.2 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.68 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.37 (8 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.90 (6 H, t, J 7.4 Hz, S-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.28, 150.30, 133.73, 130.50, 130.28, 129.14, 121.48, 114.69, 67.90, 34.30, 31.00, 28.94, 28.91, 22.73, 22.27, 13.99



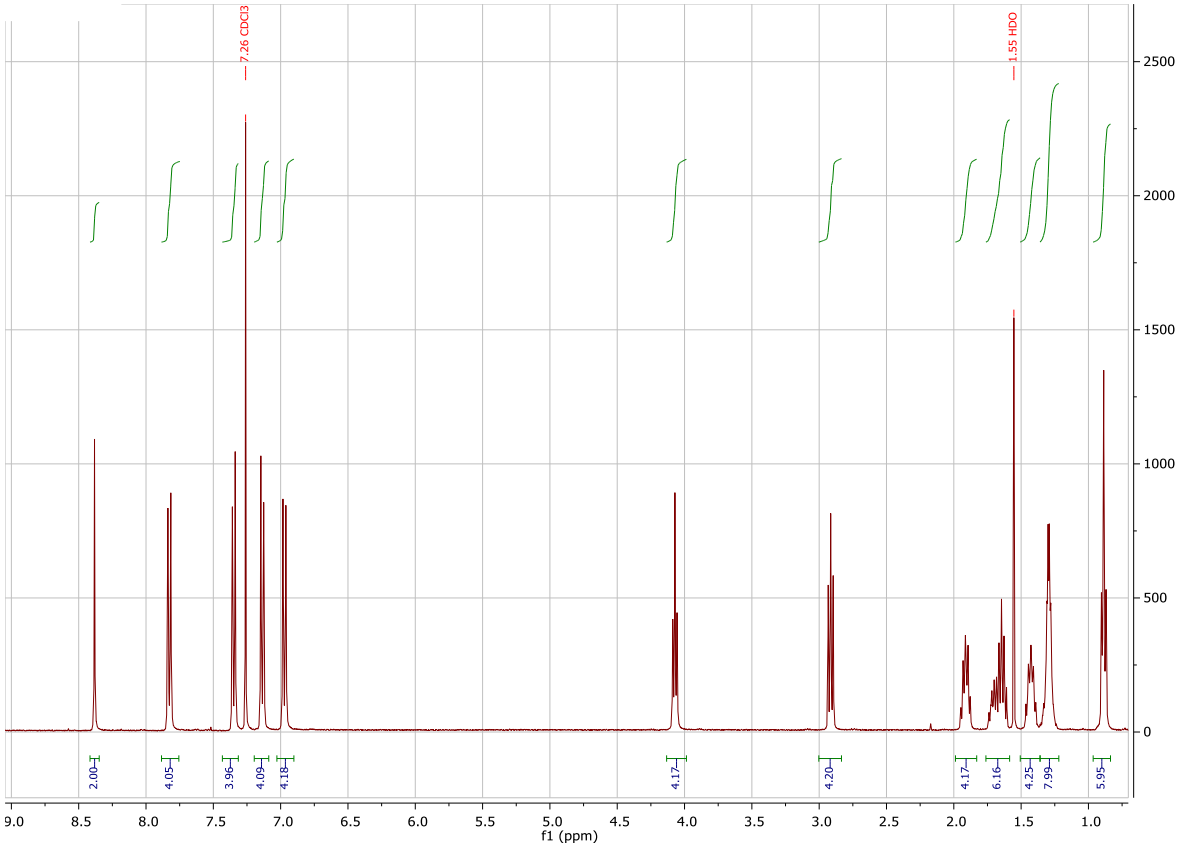
EA: Calculated for $C_{41}H_{50}N_2O_2S_2$: C = 73.83 %, H = 7.56 %, N = 4.80 %, S = 9.61 %; Found: C = 73.94 %, H = 7.52 %, N = 4.15 %, S = 9.13 %

(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(hexylthio)phenyl]methanimine} (6S.O5O.S6) (3.1.6)

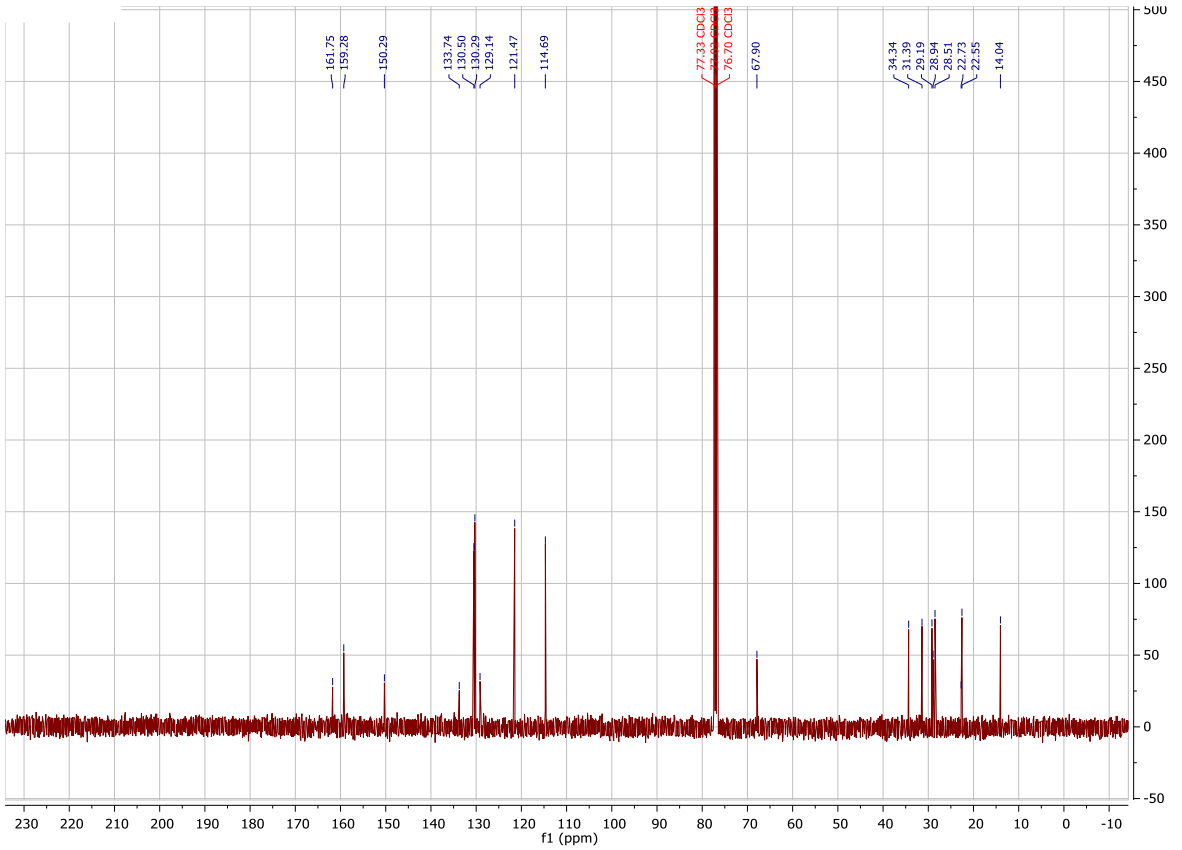
Yield: 0.220 g, 65.9 %. M.P: 126 °C

ν_{max}/cm^{-1}: 2953, 2930, 2871, 1617, 1604, 1571, 1506, 1483, 1420, 1398, 1304, 1241, 1196, 1169, 1112, 1089, 1051, 1027, 1007, 964, 884, 840, 813, 726, 679, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.6 Hz, Ar-H), 7.35 (4 H, d, J 8.4 Hz, Ar-H), 7.14 (4 H, d, J 8.4 Hz, Ar-H), 6.97 (4 H, d, J 8.6 Hz, Ar-H), 4.07 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 6.9 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (4 H, quin, J 7.3 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (8 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.89 (6 H, t, J 7.3 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.28, 150.29, 133.74, 130.50, 130.29, 129.14, 121.47, 114.69, 67.90, 34.34, 31.39, 29.19, 28.94, 28.51, 22.73, 22.55, 14.04



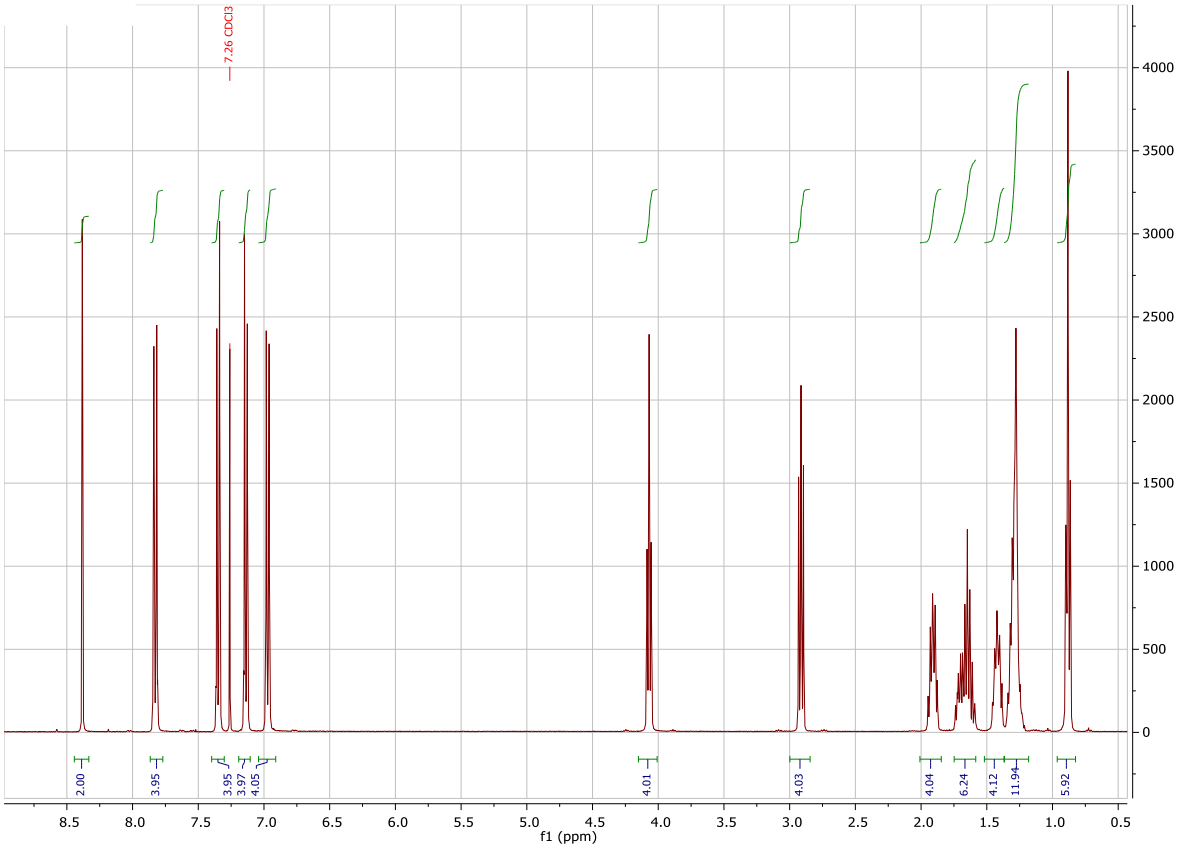
EA: Calculated for $C_{43}H_{54}N_2O_2S_2$: C = 74.31 %, H = 7.83 %, N = 4.03 %, S = 9.23 %; Found: C = 74.26 %, H = 7.87 %, N = 3.96 %, S = 9.19 %

(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(heptylthio)phenyl]methanimine} (7S.O5O.S7) (3.1.7)

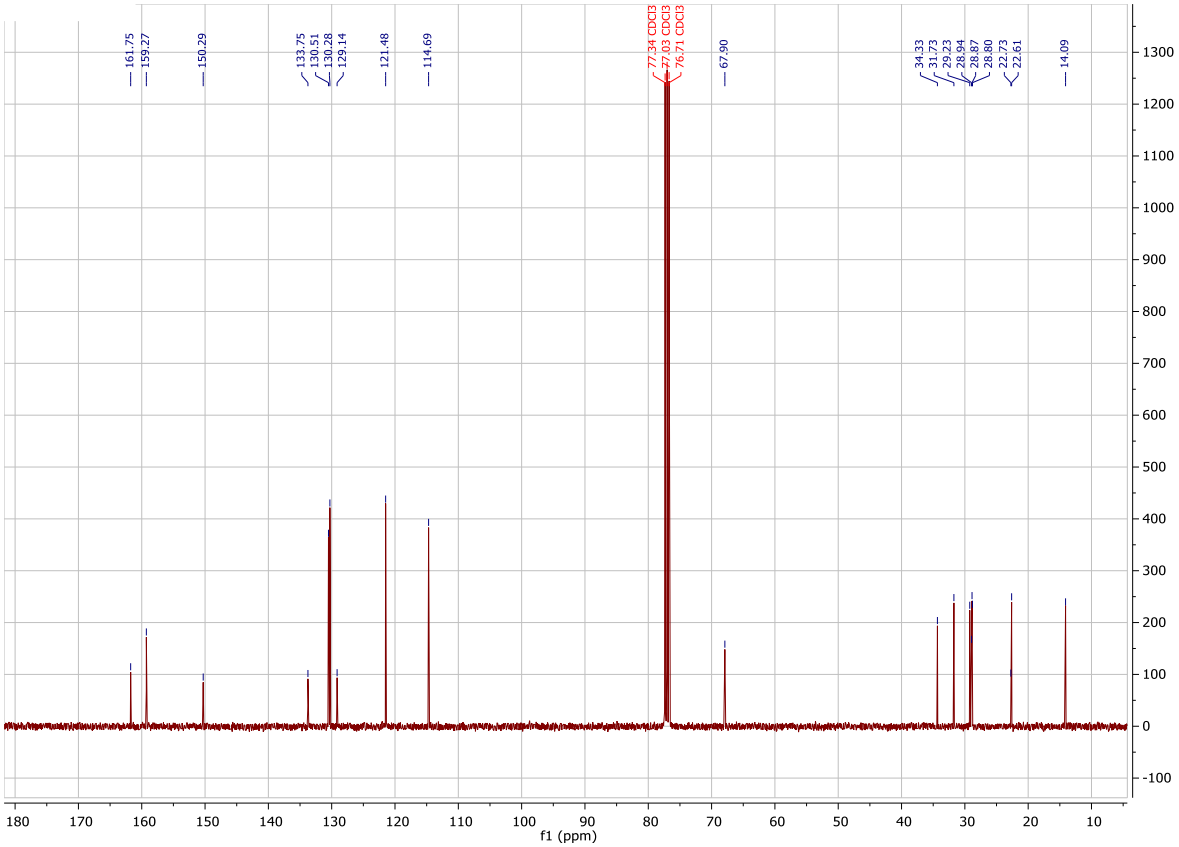
Yield: 0.285 g, 82.1 %. M.P: 122 °C

ν_{max}/cm^{-1}: 2953, 2930, 2871, 1618, 1604, 1571, 1506, 1483, 1421, 1398, 1305, 1242, 1197, 1170, 1112, 1089, 1051, 1027, 1008, 965, 885, 840, 813, 726, 679, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.6 Hz, Ar-H), 7.14 (4 H, d, J 8.6 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.07 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (4 H, quin, J 7.0 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.27 (12 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.87 (6 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.27, 150.29, 133.75, 130.51, 130.28, 129.14, 121.48, 114.69, 67.90, 34.33, 31.73, 29.23, 28.94, 28.87, 28.80, 22.73, 22.61, 14.09



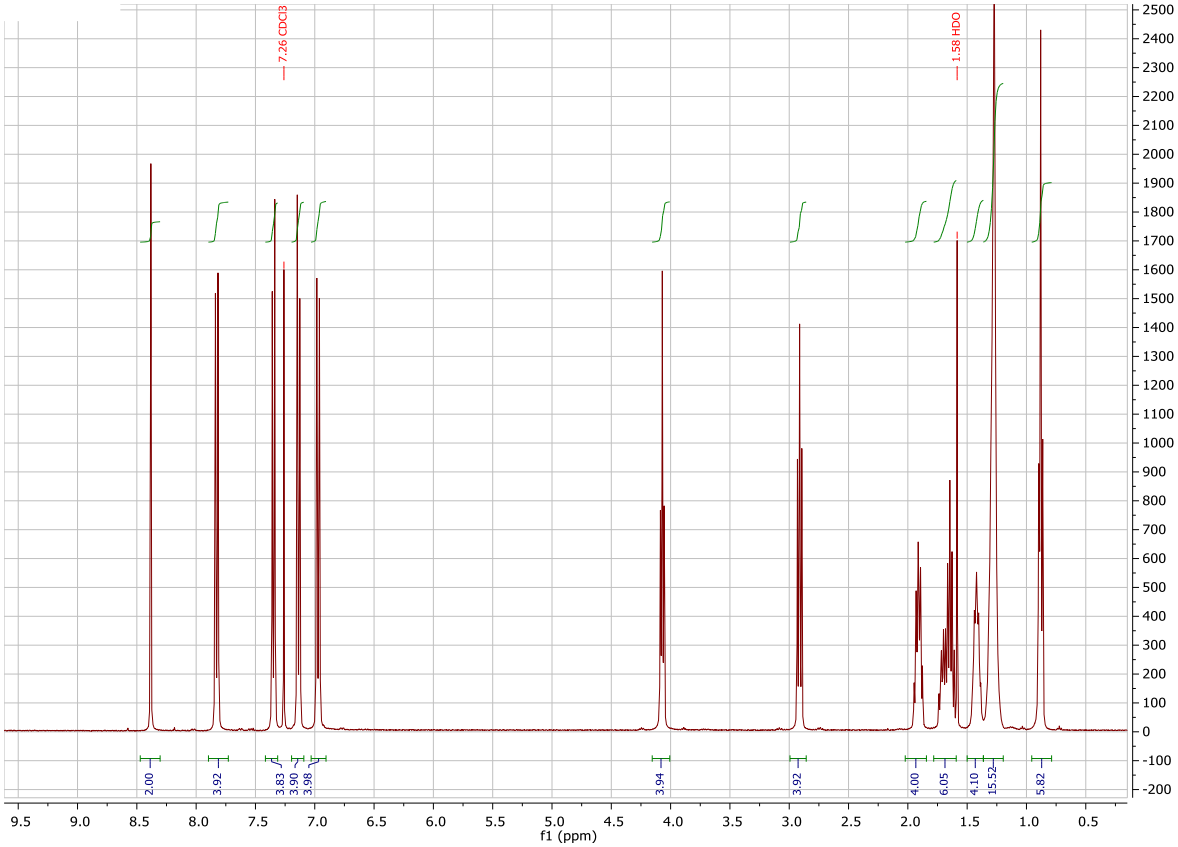
EA: Calculated for $C_{45}H_{58}N_2O_2S_2$: C = 74.75 %, H = 8.09 %, N = 3.87 %, S = 8.87 %; Found: C = 74.37 %, H = 8.09 %, N = 3.76 %, S = 8.87 %

(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(octylthio)phenyl]methanimine} (8S.O5O.S8) (3.1.8)

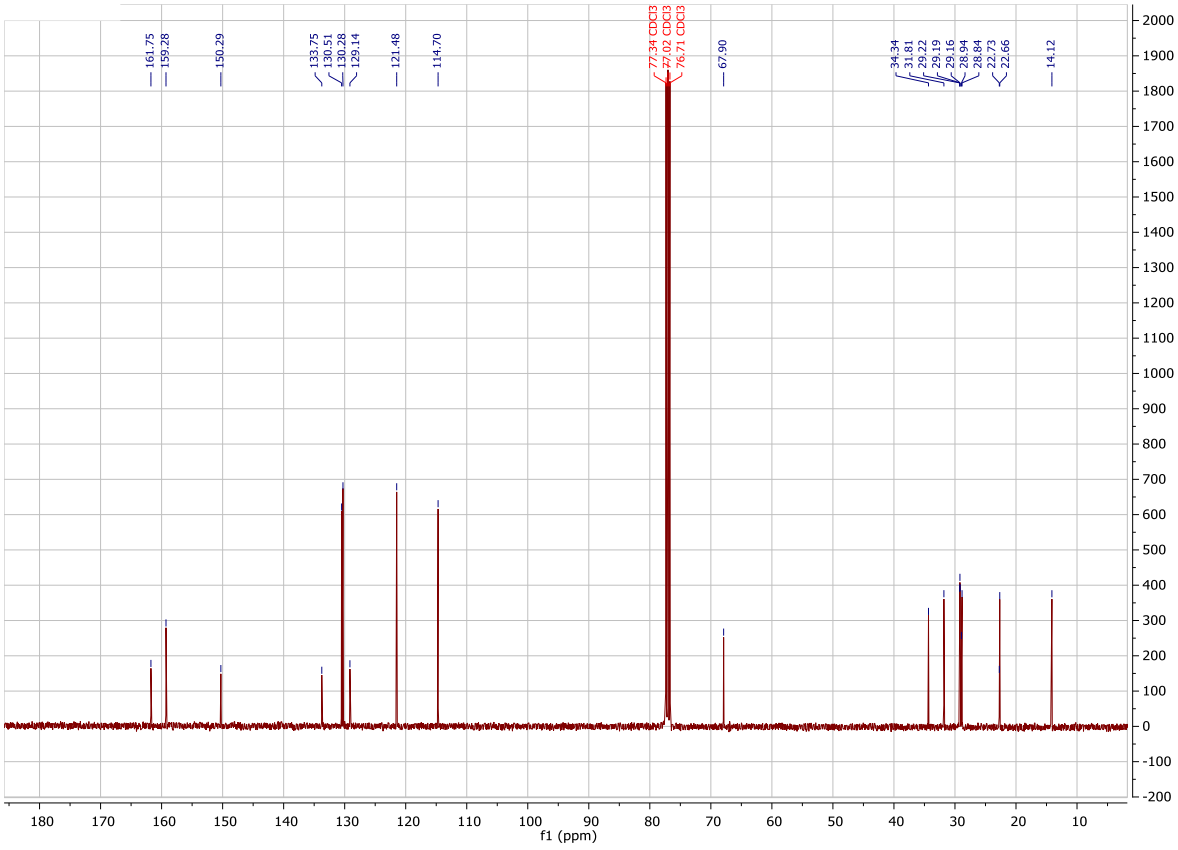
Yield: 0.281 g, 77.9 %. M.P: 120 °C

ν_{max}/cm^{-1}: 2953, 2930, 2871, 1618, 1604, 1571, 1507, 1483, 1421, 1399, 1305, 1242, 1197, 1170, 1112, 1089, 1051, 1027, 1008, 965, 885, 840, 813, 755, 678, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.4 Hz, Ar-H), 7.13 (4 H, d, J 8.4 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.07 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.1 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.64 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (4 H, quin, J 7.4 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.28 (16 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.28, 150.29, 133.75, 130.51, 130.28, 129.14, 121.48, 114.70, 67.90, 34.34, 31.81, 29.22, 29.19, 29.16, 28.94, 28.84, 22.73, 22.66, 14.12



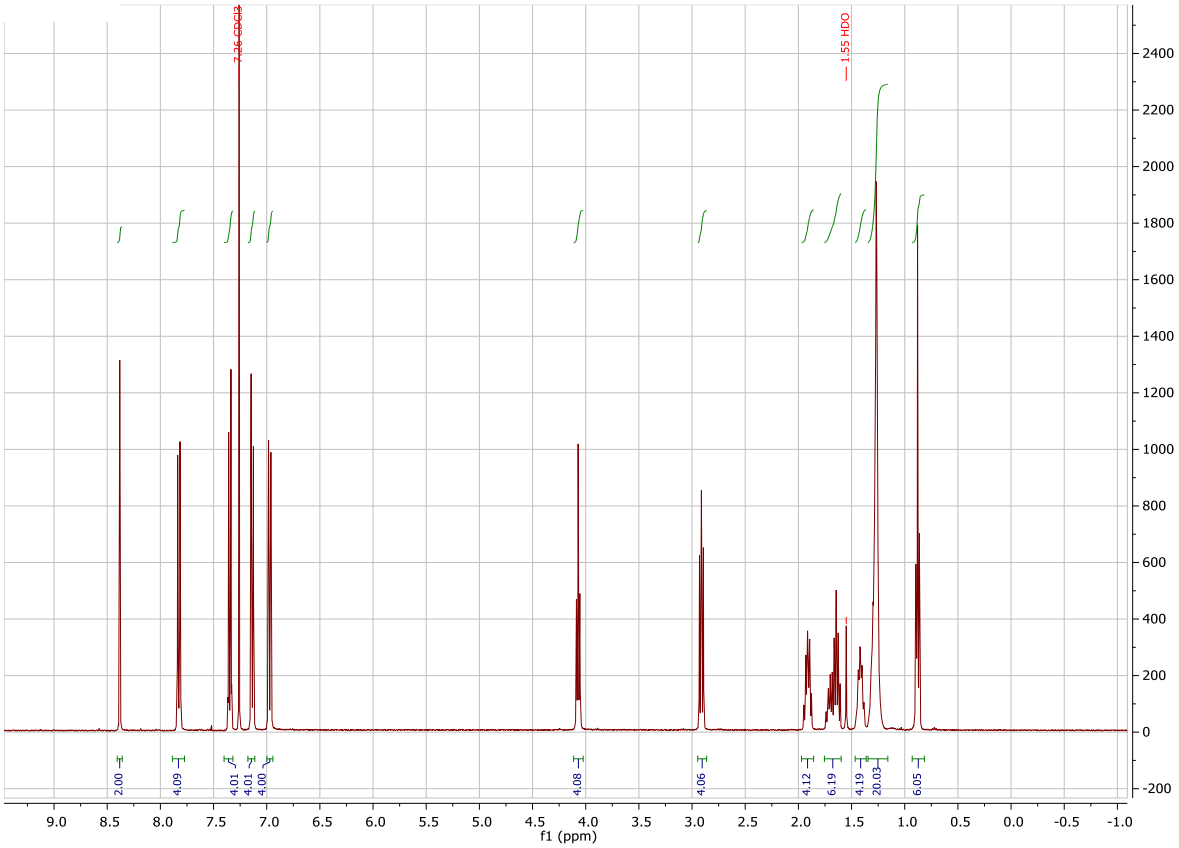
EA: Calculated for $C_{47}H_{62}N_2O_2S_2$: C = 75.15 %, H = 8.32 %, N = 3.73 %, S = 8.54 %; Found: C = 75.43 %, H = 8.34 %, N = 3.80 %, S = 8.08 %

(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[(nonylthio)phenyl]methanimine} (9S.O5O.S9) (3.1.9)

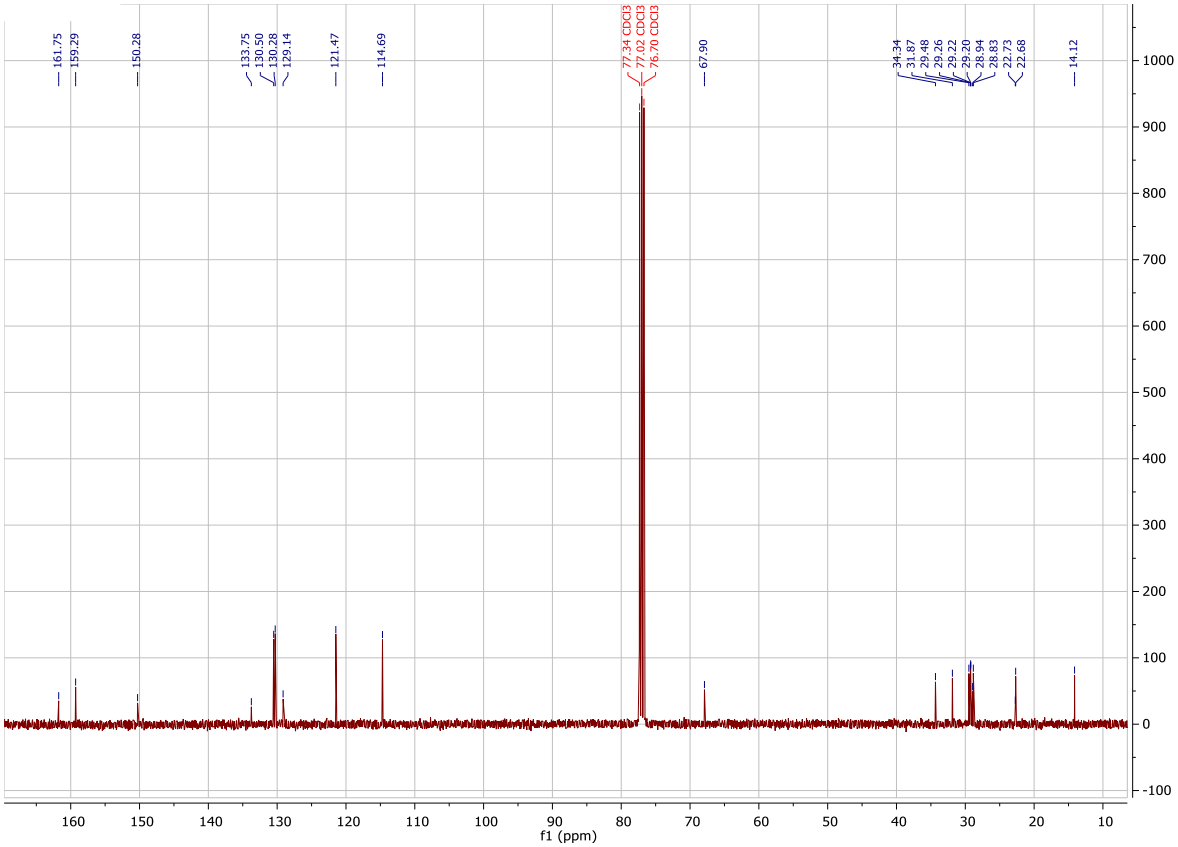
Yield: 0.354 g, 94.6 %. M.P: 121 °C

ν_{max}/cm^{-1}: 2953, 2930, 2871, 1618, 1604, 1572, 1507, 1483, 1399, 1420, 1399, 1305, 1242, 1197, 1170, 1112, 1089, 1050, 1027, 1008, 965, 885, 840, 813, 726, 679, 587, 543

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.83 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.5 Hz, Ar-H), 7.13 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.07 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.0 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.67 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (4 H, quin, J 7.1 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.26 (20 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 7.1 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.75, 159.29, 150.28, 133.75, 130.50, 130.28, 129.14, 121.47, 114.69, 67.90, 34.34, 31.87, 29.48, 29.26, 29.22, 29.20, 28.94, 28.83, 22.73, 22.68, 14.12



EA: Calculated for $C_{49}H_{66}N_2O_2S_2$: C = 75.53 %, H = 8.54 %, N = 3.60 %, S = 8.23 %; Found: C = 75.41 %, H = 8.54 %, N = 3.46 %, S = 8.16 %

(*E,E*)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{*N*-[(alkylthio)phenyl]methanimine}s (*m*S.O6O.S*m*) (3.2)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.2** (1 eq, 0.150 g, 4.60×10^{-4} mol) and compound **2** (3 eq) of the appropriate chain length were added along with ethanol (20 mL) and the mixture was stirred. The quantities of 4 (alkylthio)anilines used in each reaction are listed in **Table 1.4**. The reaction was heated to reflux, *p*-toluenesulfonic acid (catalytic amount) was added, and left overnight. The reaction mixture was cooled to room temperature and a yellow precipitate formed which was collected by vacuum filtration. The yellow solid was recrystallised from hot toluene (18 mL).

Table 1.4. Quantities of 4-(alkylthio)anilines used in the syntheses of (E,E)-[hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(alkylthio)phenyl]methanimine}s (**3.2**).

m	(**2**)
1	0.172 mL, 0.192 g, 1.38×10^{-3} mol

2	0.211 g, 1.38×10^{-3} mol
3	0.231 g, 1.38×10^{-3} mol
4	0.250 g, 1.38×10^{-3} mol
5	0.270 g, 1.38×10^{-3} mol
6	0.288 g, 1.38×10^{-3} mol
7	0.308 g, 1.38×10^{-3} mol
8	0.328 g, 1.38×10^{-3} mol
9	0.347 g, 1.38×10^{-3} mol

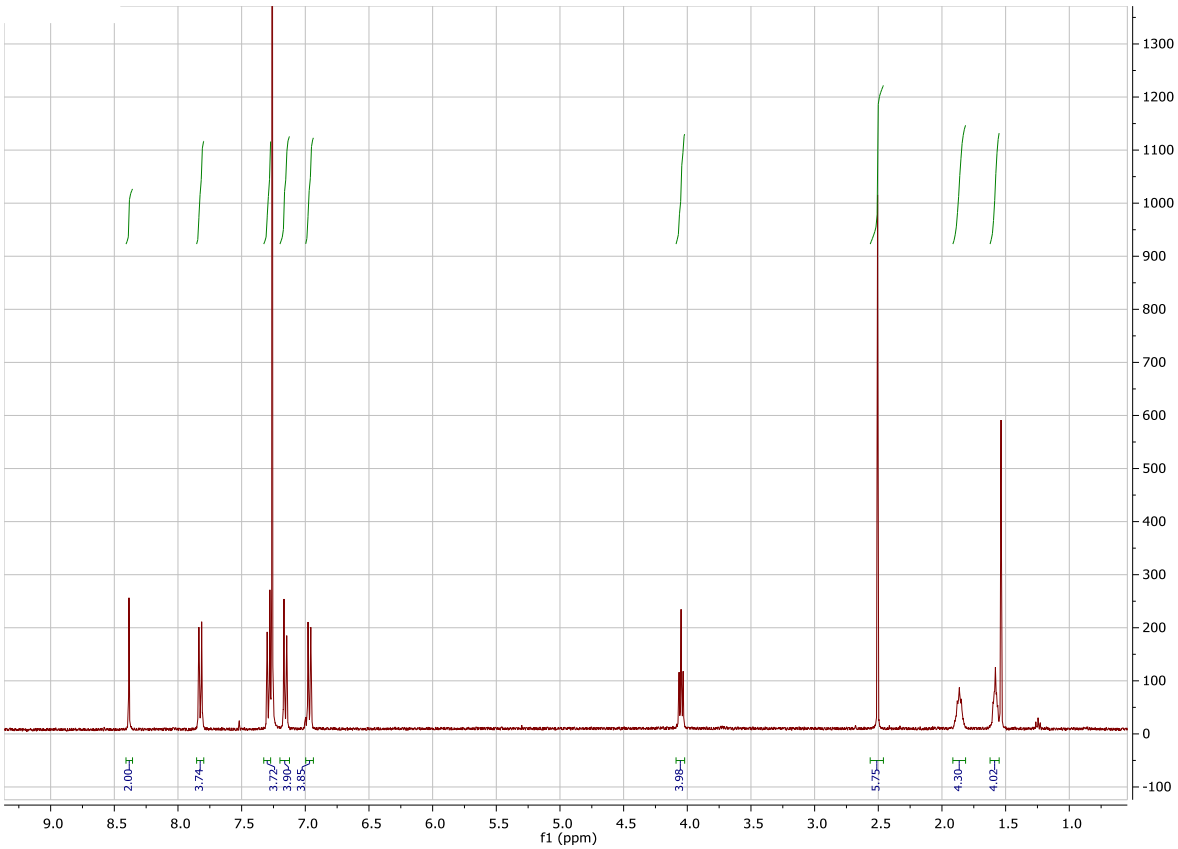
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(methylthio)phenyl]methanimine} (1S.O6O.S1) (3.2.1)

Yield: 0.235 g, 89.8 %

T_{CrN} 198 °C T_{NI} 211 °C

ν_{max}/cm^{-1}: 2939, 1618, 1604, 1571, 1507, 1474, 1396, 1304, 1244, 1197, 1169, 1111, 1087, 1025, 964, 839, 803, 725, 678, 584, 543, 436

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.29 (4 H, d, J 8.5 Hz, Ar-H), 7.16 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.51 (6 H, s, S-$\underline{CH_3}$), 1.86 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.58 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)



δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{34}H_{36}N_2O_2S_2$: C = 71.80 %, H = 6.38 %, N = 4.93 %, S = 11.27 %; Found: C = 72.08 %, H = 6.38 %, N = 4.83 %, S = 11.08 %

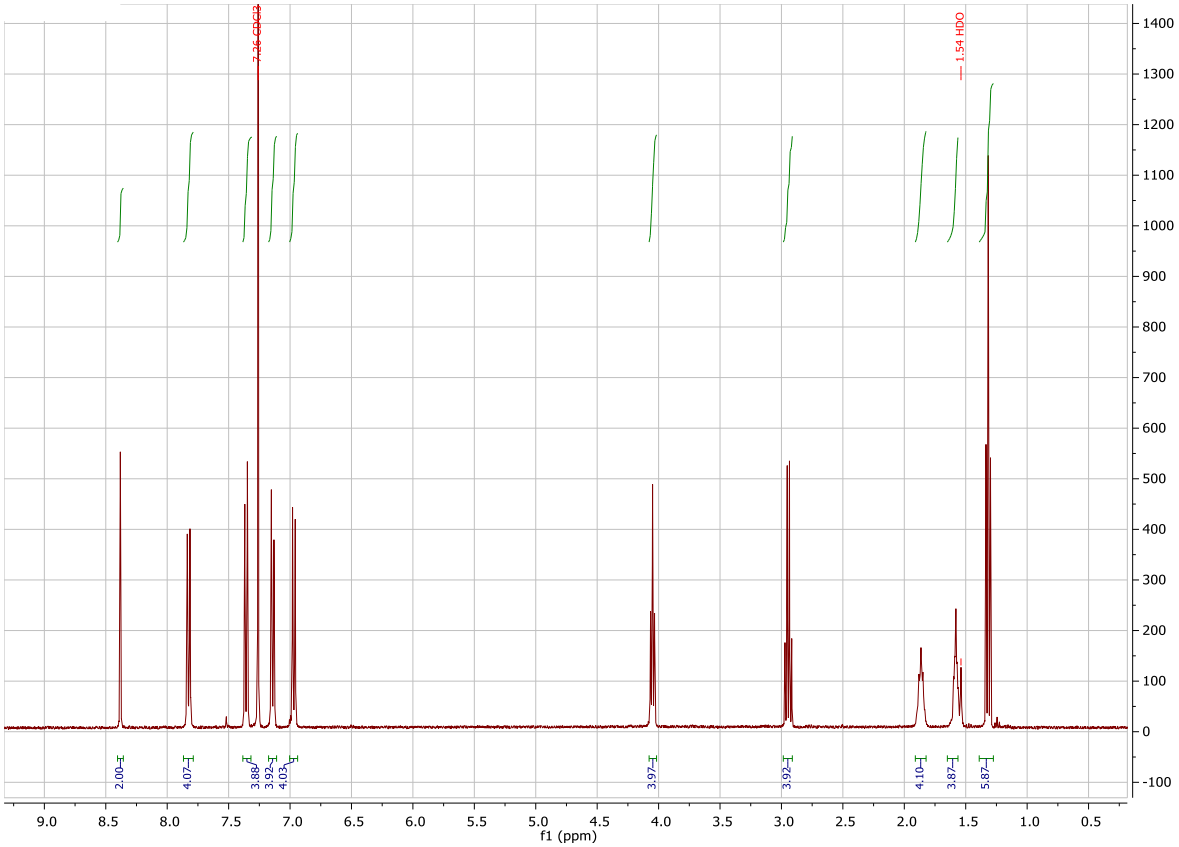
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(ethylthio)phenyl]methanimine} (2S.O6O.S2) (3.2.2)

Yield: 0.216 g, 78.7 %

T_{CrI} 184 °C T_{NI} (181 °C)

ν_{max}/cm^{-1}: 2939, 1617, 1605, 1572, 1508, 1475, 1306, 1249, 1170, 1112, 1091, 1024, 840, 803, 701, 651, 544, 495, 458, 402

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.5 Hz, Ar-H), 7.36 (4 H, d, J 8.2 Hz, Ar-H), 7.14 (4 H, d, J 8.2 Hz, Ar-H), 6.98 (4 H, d, J 8.5 Hz, Ar-H), 4.05 (4 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 2.94 (4 H, quart, J 7.3 Hz, S-$\underline{CH_2}$-CH_3), 1.86 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.58 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.31 (6 H, t, J 7.3 Hz, S-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{36}H_{40}N_2O_2S_2$: C = 72.45 %, H = 6.76 %, N = 4.69 %, S = 10.74 %; Found: C = 72.46 %, H = 6.72 %, N = 4.65 %, S = 10.75 %

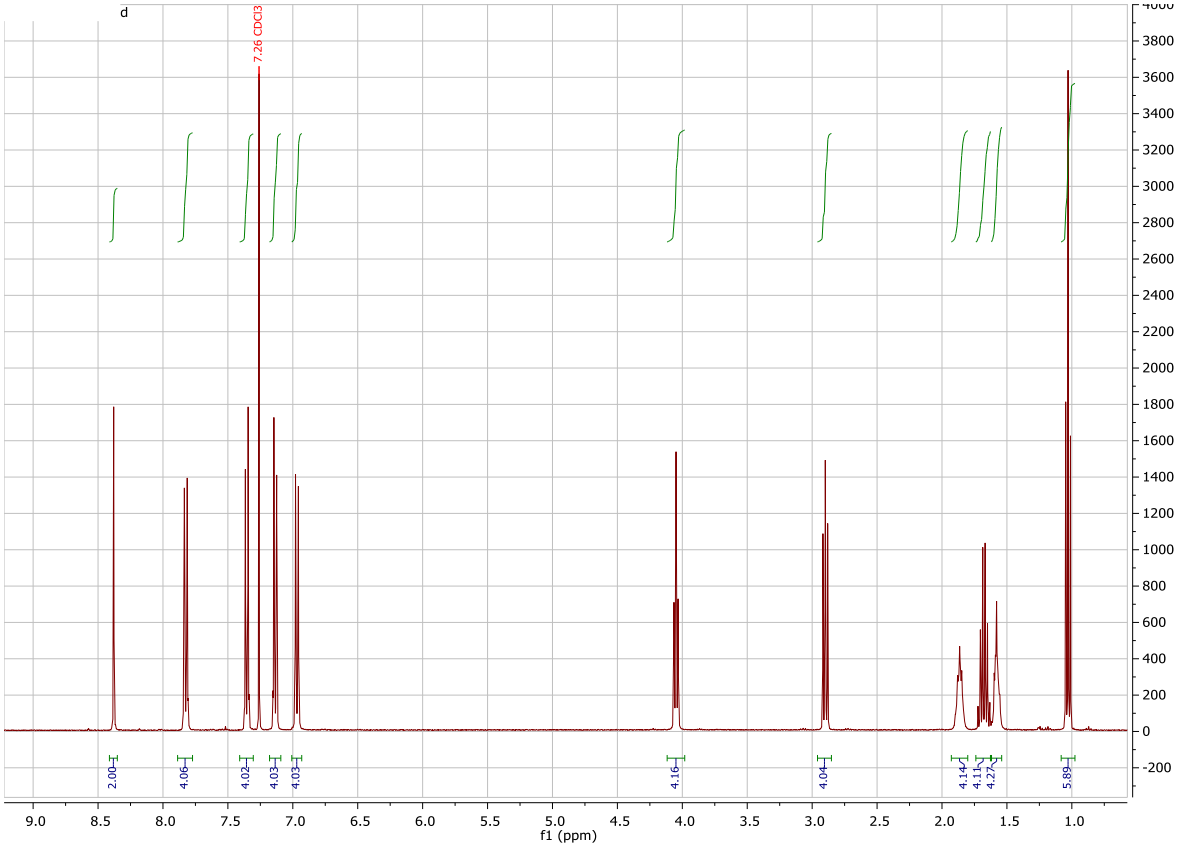
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(propylthio)phenyl]methanimine} (3S.O6O.S3) (3.2.3)

Yield: 0.256 g, 87.1 %

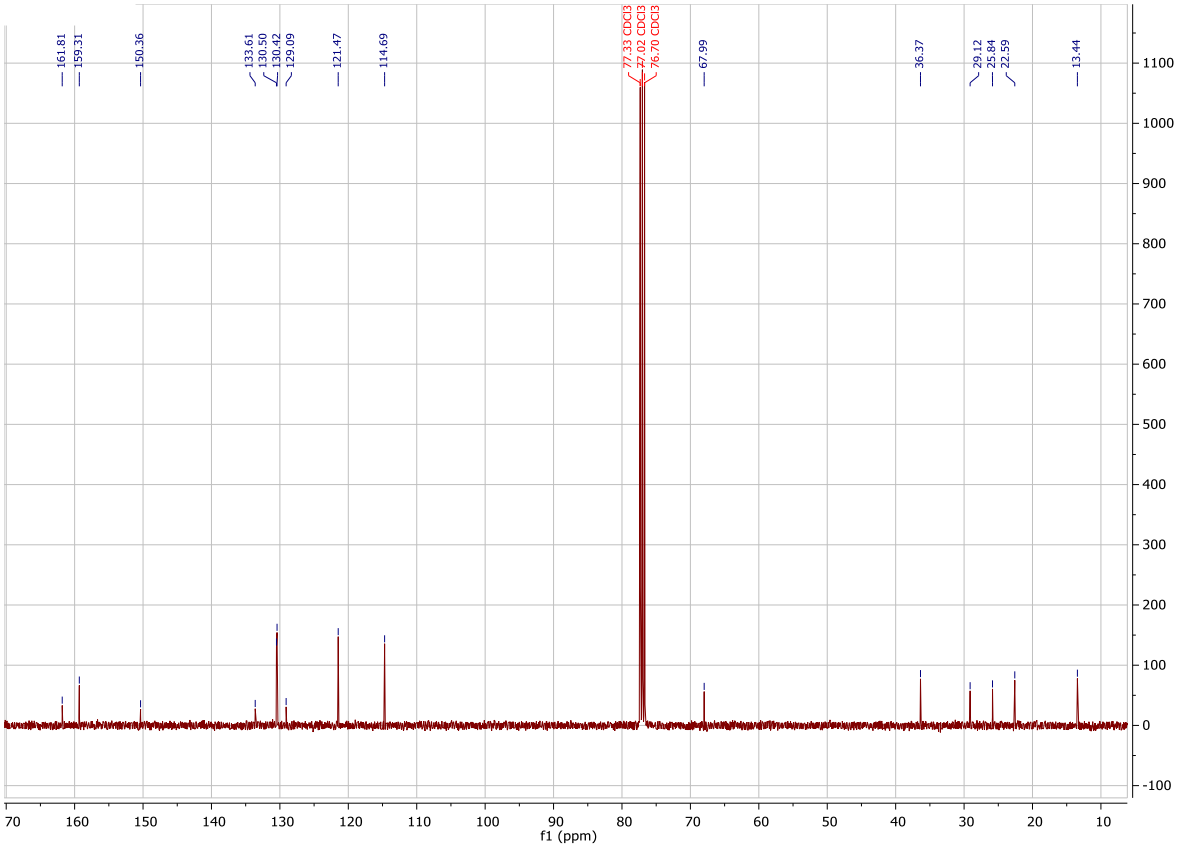
T_{CrI} 157 °C T_{NI} (152 °C)

ν_{max}/cm^{-1}: 2939, 1620, 1604, 1572, 1507, 1475, 1305, 1246, 1196, 1168, 1111, 1018, 839, 803, 689, 587, 543, 464

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.5 Hz, Ar-H), 7.14 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.90 (4 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2), 1.86 (4 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.68 (4 H, sext, J 7.3 Hz, S-CH_2-$\underline{CH_2}$-CH_3), 1.56 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.03 (6 H, t, J 7.3 Hz, S-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.81, 159.31, 150.36, 133.61, 130.50, 130.42, 129.09, 121.47, 114.69, 67.99, 36.37, 29.12, 25.84, 22.59, 13.44



EA: Calculated for $C_{38}H_{44}N_2O_2S_2$: C = 73.04 %, H = 7.10 %, N = 4.48 %, S = 10.26 %; Found: C = 73.21 %, H = 7.10 %, N = 4.43 %, S = 10.26 %

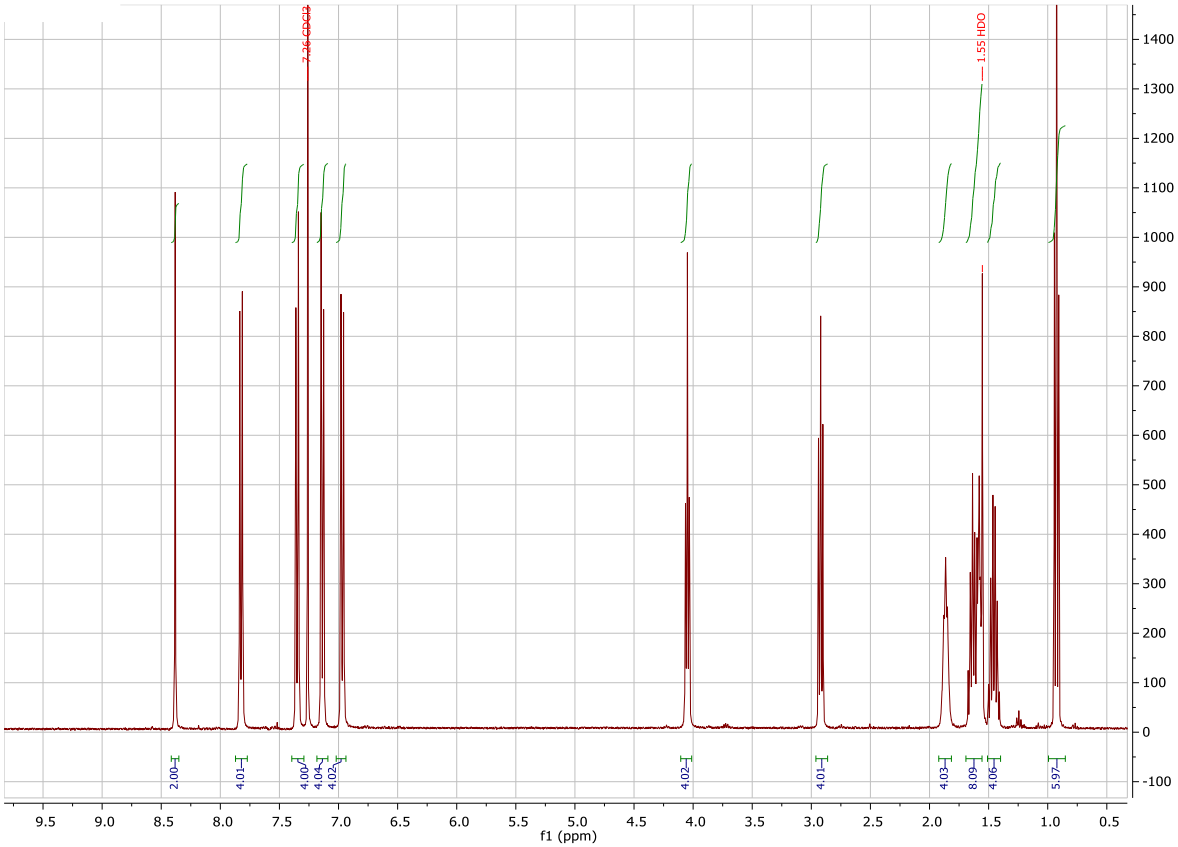
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(butylthio)phenyl]methanimine} (4S.O6O.S4) (3.2.4)

Yield: 0.292 g, 97.2 %

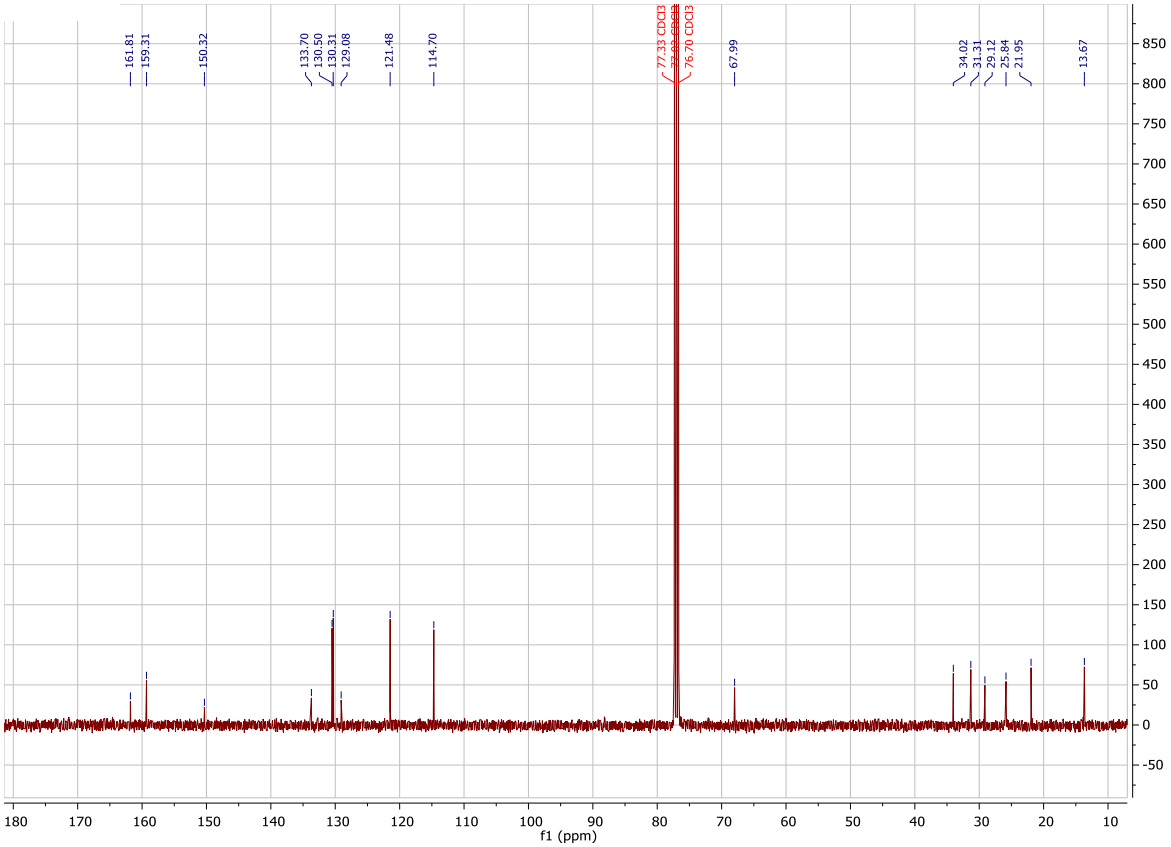
T_{CrI} 178 °C T_{NI} (158 °C)

ν_{max}/cm^{-1}: 2938, 2871, 1604, 1572, 1507, 1474, 1305, 1246, 1197, 1167, 1110, 1090, 1019, 962, 837, 803, 725, 690, 586, 542, 495, 464, 412

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.4 Hz, Ar-H), 7.13 (4 H, d, J 8.4 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.92 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.86 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.62 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.45 (4 H, sext, J 7.4 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_3), 0.93 (6 H, t, J 7.4 Hz, S-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.81, 159.31, 150.32, 133.70, 130.50, 130.31, 129.08, 121.48, 114.70, 67.99, 34.02, 31.31, 29.12, 25.84, 21.95, 13.67



EA: Calculated for $C_{40}H_{48}N_2O_2S_2$: C = 73.58 %, H = 7.41 %, N = 4.29 %, S = 9.82 %; Found: C = 73.66 %, H = 7.43 %, N = 4.23 %, S = 9.91 %

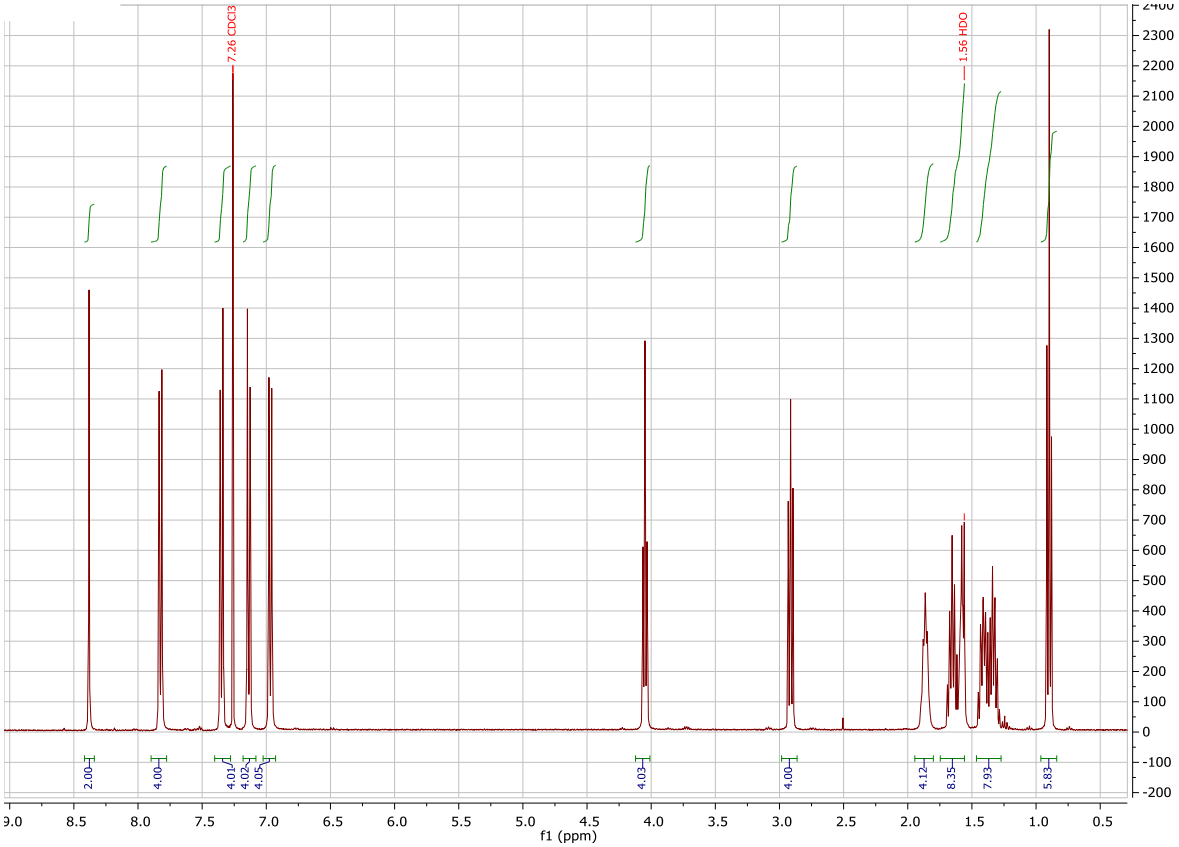
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(pentylthio)phenyl]methanimine} (5S.O6O.S5) (3.2.5)

Yield: 0.273 g, 87.1 %

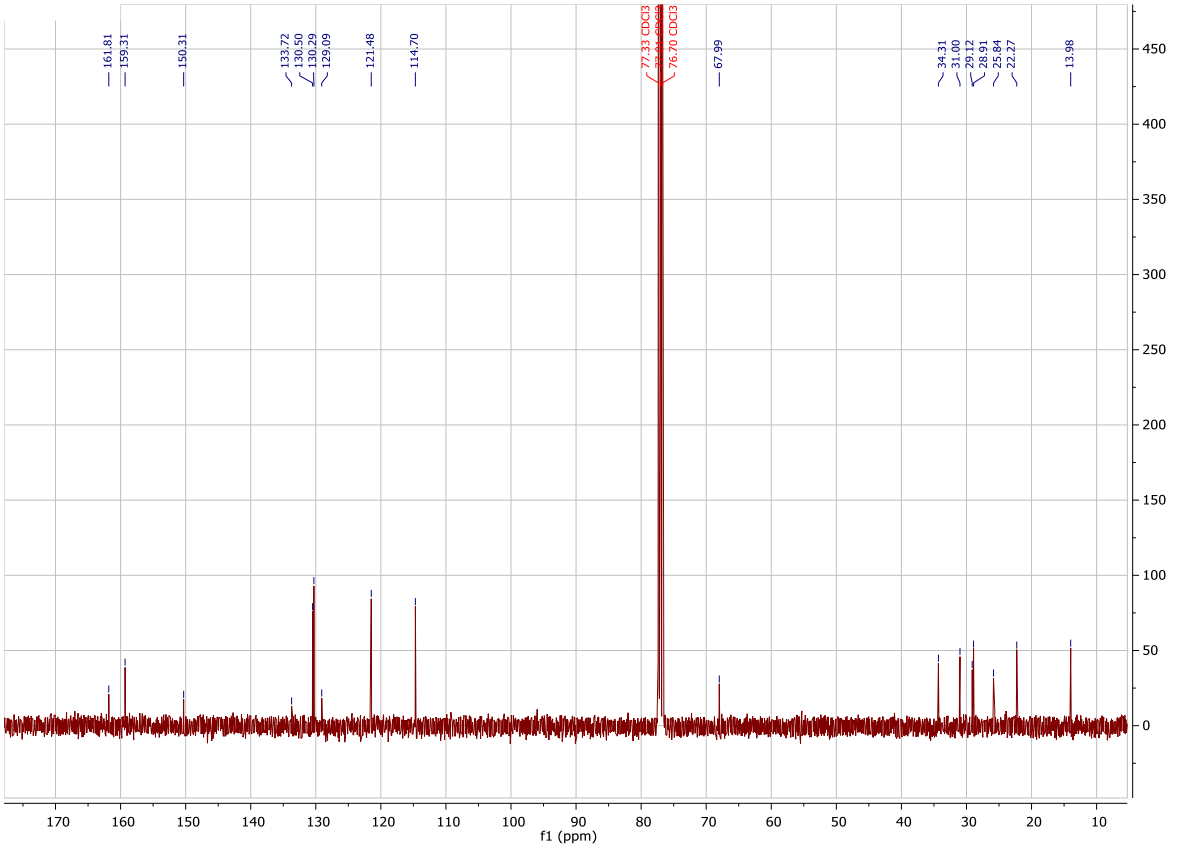
T_{CrI} 157 °C T_{NI} (149 °C)

ν_{max}/cm^{-1}: 2938, 2861, 1604, 1571, 1507, 1474, 1398, 1304, 1244, 1196, 1167, 1110, 1090, 1018, 883, 839, 802, 725, 690, 587, 542, 495, 410

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.6 Hz, Ar-H), 7.35 (4 H, d, J 8.5 Hz, Ar-H), 7.14 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.6 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.86 (4 H, tt, J 6.9 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.37 (8 H, m, S-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.90 (6 H, t, J 7.2 Hz, S-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.81, 159.31, 150.31, 133.72, 130.50, 130.29, 129.09, 121.48, 114.70, 67.99, 34.31, 31.00, 29.12, 28.91, 25.84, 22.27, 13.98



EA: Calculated for $C_{42}H_{52}N_2O_2S_2$: C = 74.08 %, H = 7.70 %, N = 4.11 %, S = 9.42 %; Found: C = 74.17 %, H = 7.73 %, N = 4.07 %, S = 9.45 %

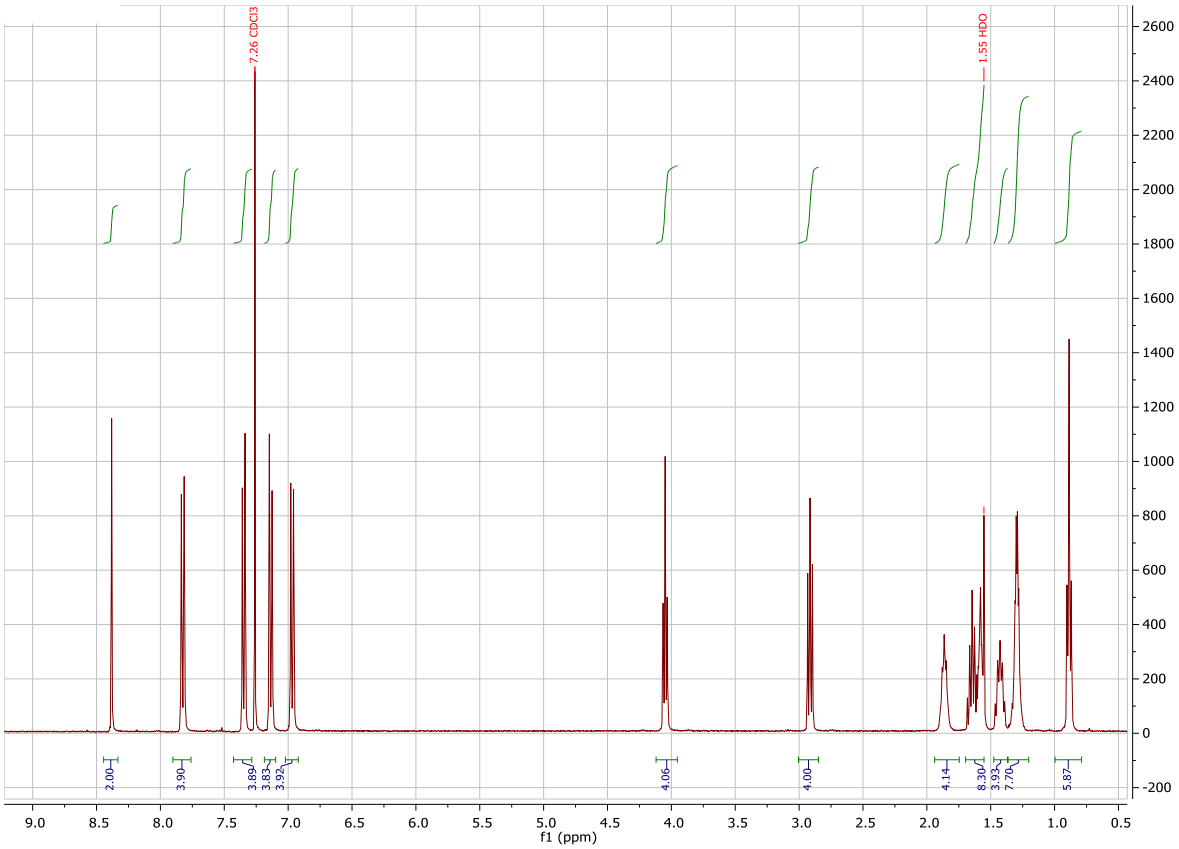
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(hexylthio)phenyl]methanimine} (6S.O6O.S6) (3.2.6)

Yield: 0.281 g, 86.2 %

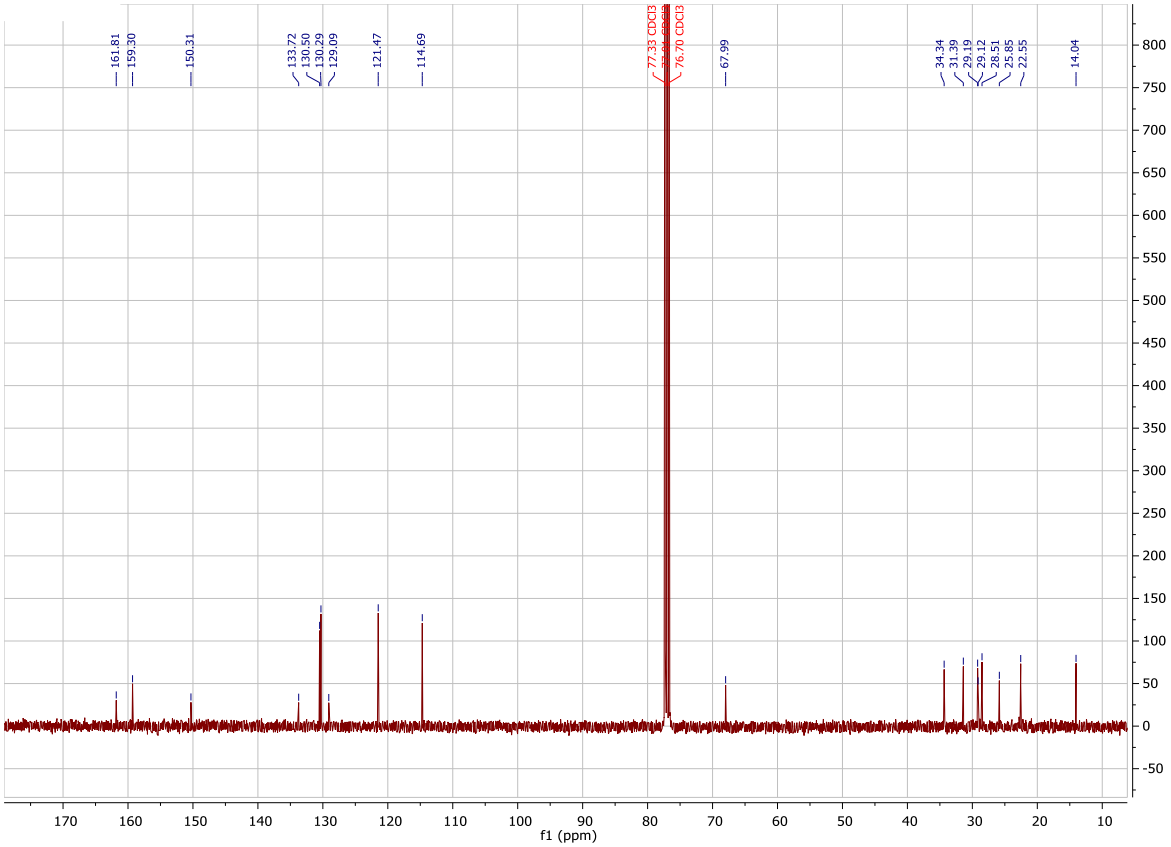
T_{CrI} 156 °C T_{NI} (150 °C)

ν_{max}/cm^{-1}: 2939, 2914, 2850, 1605, 1572, 1508, 1474, 1450, 1305, 1247, 1198, 1182, 1168, 1093, 1073, 1019, 959, 881, 838, 803, 726, 689, 586, 540, 495, 449

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.5 Hz, Ar-H), 7.14 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.86 (4 H, tt, J 6.9 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.62 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (4 H, tt, J 7.3 Hz, 7.0 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (8 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.89 (6 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.81, 159.30, 150.31, 133.72, 130.50, 130.29, 129.09, 121.47, 114.69, 67.99, 34.34, 31.39, 29.19, 29.12, 28.51, 25.85, 22.55, 14.04



EA: Calculated for $C_{44}H_{56}N_2O_2S_2$: C = 74.53 %, H = 7.96 %, N = 3.95 %, S = 9.04 %; Found: C = 74.62 %, H = 7.94 %, N = 3.91 %, S = 8.96 %

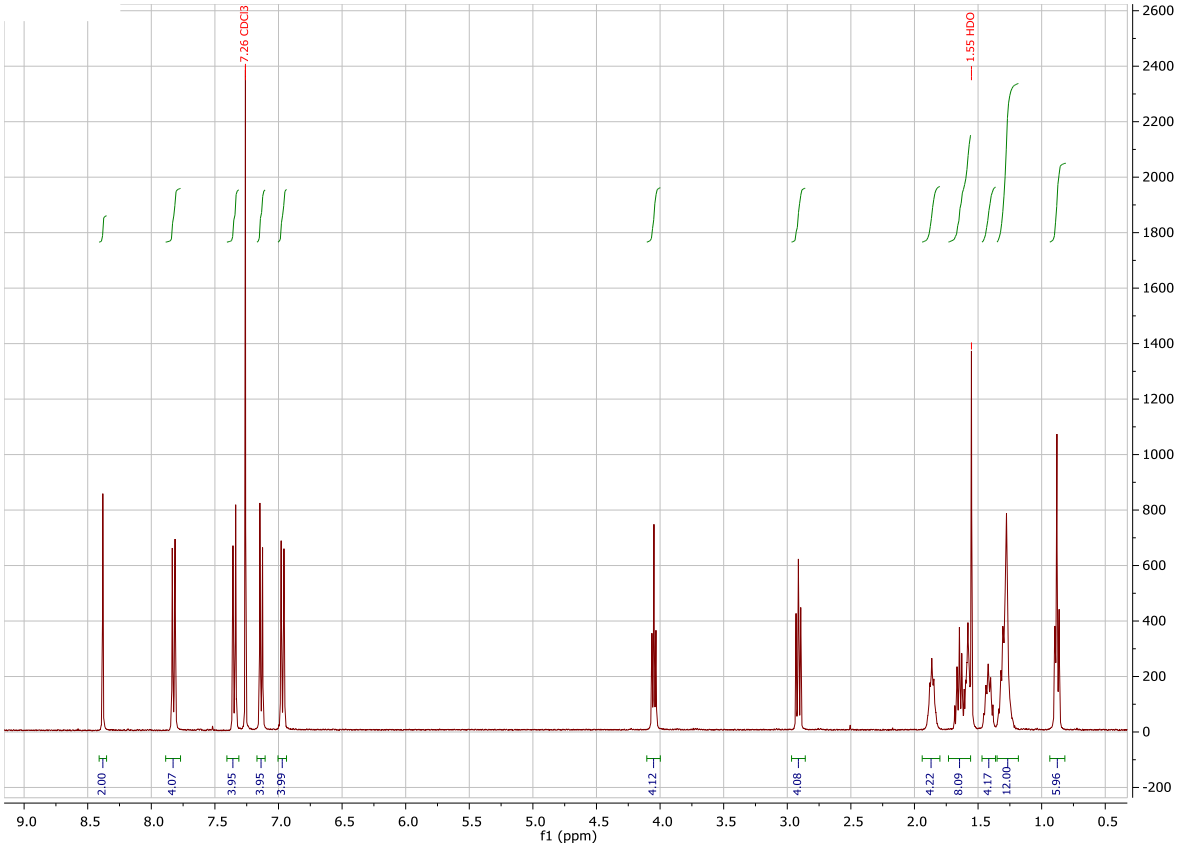
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(heptylthio)phenyl]methanimine} (7S.O6O.S7) (3.2.7)

Yield: 0.299 g, 88.2 %

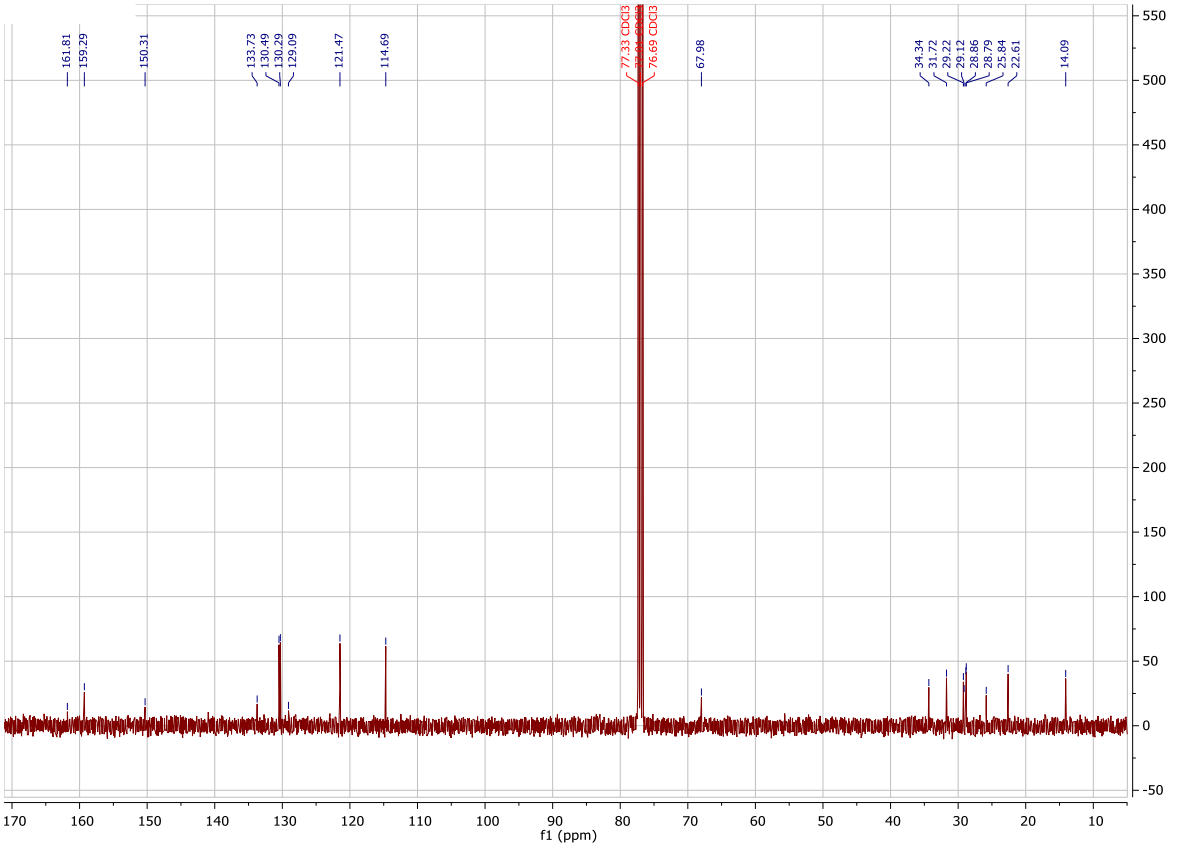
T_{CrI} 153 °C T_{NI} (148 °C)

ν_{max}/cm^{-1}: 2942, 2920, 2852, 1622, 1608, 1576, 1509, 1474, 1395, 1304, 1249, 1200, 1168, 1105, 1072, 1031, 1019, 889, 823, 803, 792, 724, 684, 585, 545, 491, 474, 420

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.8 Hz, Ar-H), 7.35 (4 H, d, J 8.4 Hz, Ar-H), 7.13 (4 H, d, J 8.4 Hz, Ar-H), 6.97 (4 H, d, J 8.8 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.86 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.63 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (4 H, tt, J 7.4 Hz, 6.9 Hz, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.30 (12 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 6.9 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.81, 159.29, 150.31, 133.73, 130.49, 130.29, 129.09, 121.47, 114.69, 67.98, 34.34, 31.72, 29.22, 29.12, 28.86, 28.79, 25.84, 22.61, 14.09



EA: Calculated for $C_{46}H_{60}N_2O_2S_2$: C = 74.95 %, H = 8.20 %, N = 3.80 %, S = 8.70 %; Found: C = 75.20 %, H = 8.15 %, N = 3.75 %, S = 8.67 %

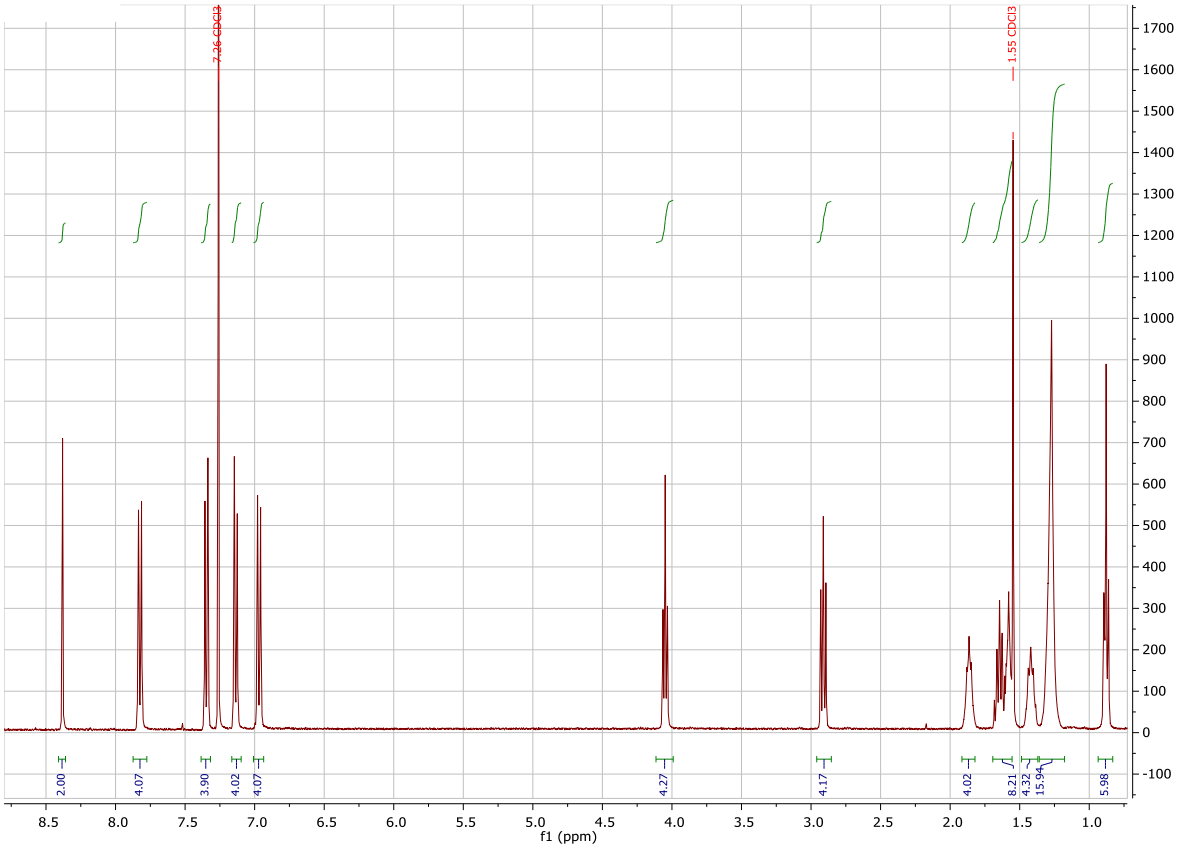
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(octylthio)phenyl]methanimine} (8S.O6O.S8) (3.2.8)

Yield: 0.246 g, 69.9 %

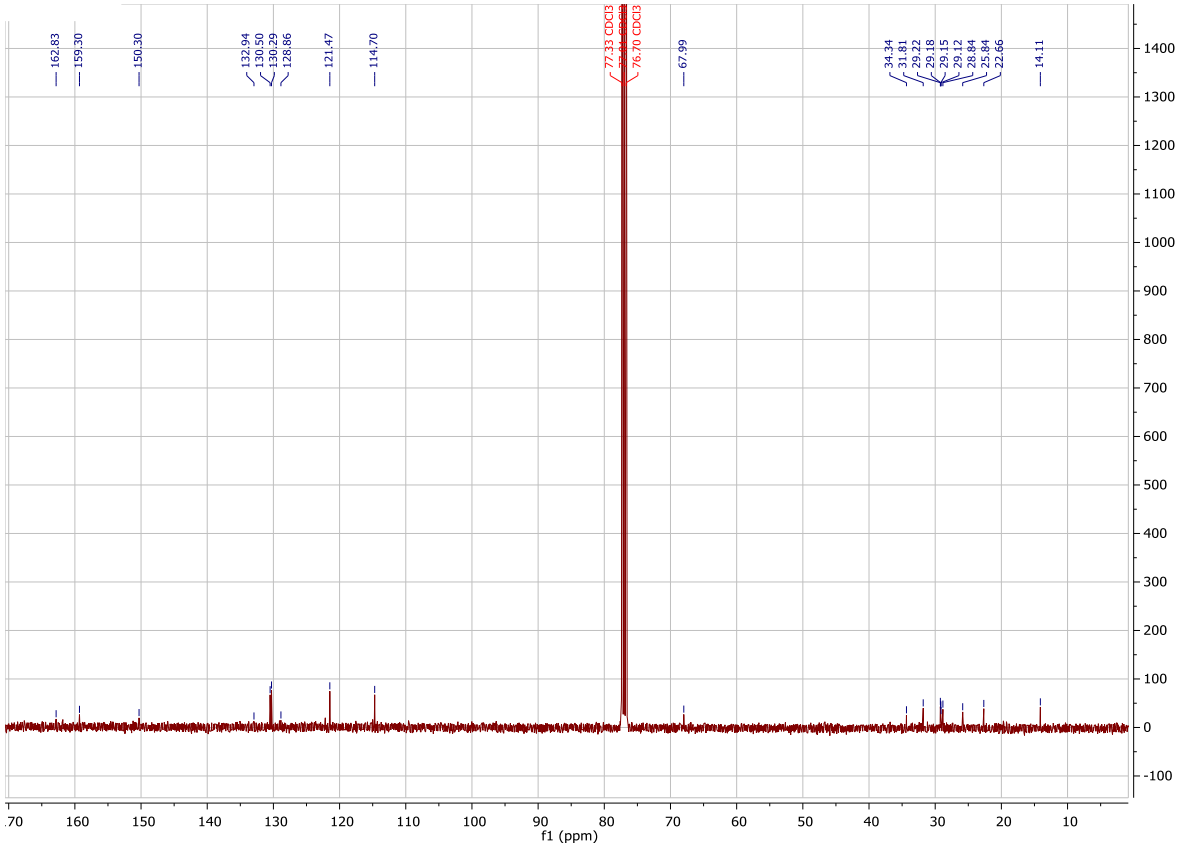
T_{CrSmC} 151 °C T_{SmCI} 154 °C

ν_{max}/cm^{-1}: 2955, 2921, 2853, 1620, 1606, 1576, 1508, 1473, 1395, 1304, 1248, 1198, 1170, 1106, 1091, 1031, 1008, 888, 839, 823, 790, 724, 684, 586, 545, 476, 443

δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.34 (4 H, d, J 8.5 Hz, Ar-H), 7.13 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.4 Hz, S-$\underline{CH_2}$-CH_2-), 1.85 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.62 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.42 (4 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.27 (16 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 7.1 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 162.83, 159.30, 150.30, 132.94, 130.50, 130.29, 128.86, 121.47, 114.70, 67.99, 34.34, 31.81, 29.22, 29.18, 29.15, 29.12, 28.84, 25.84, 22.66, 14.11



EA: Calculated for $C_{48}H_{64}N_2O_2S_2$: C = 75.35 %, H = 8.43 %, N = 3.66 %, S = 8.38 %; Found: C = 75.54 %, H = 8.45 %, N = 3.63 %, S = 8.28 %

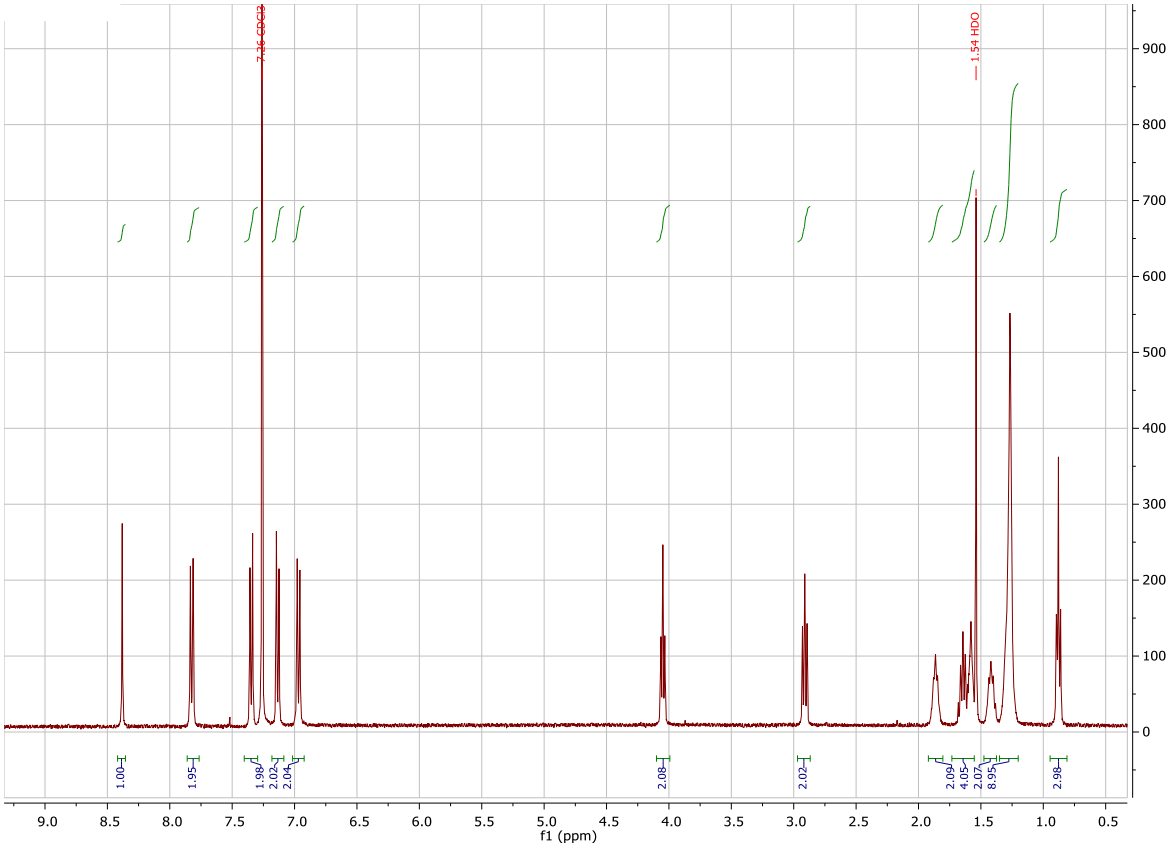
(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[(nonylthio)phenyl]methanimine} (9S.O6O.S9) (3.2.9)

Yield: 0.171 g, 46.9 %

T_{CrSmC} 149 °C T_{SmCl} 153 °C

ν_{max}/cm^{-1}: 2959, 2920, 2850, 1620, 1606, 1575, 1508, 1474, 1395, 1304, 1246, 1198, 1170, 1106, 1092, 1032, 1009, 888, 839, 823, 805, 725, 684, 586, 545, 475, 440

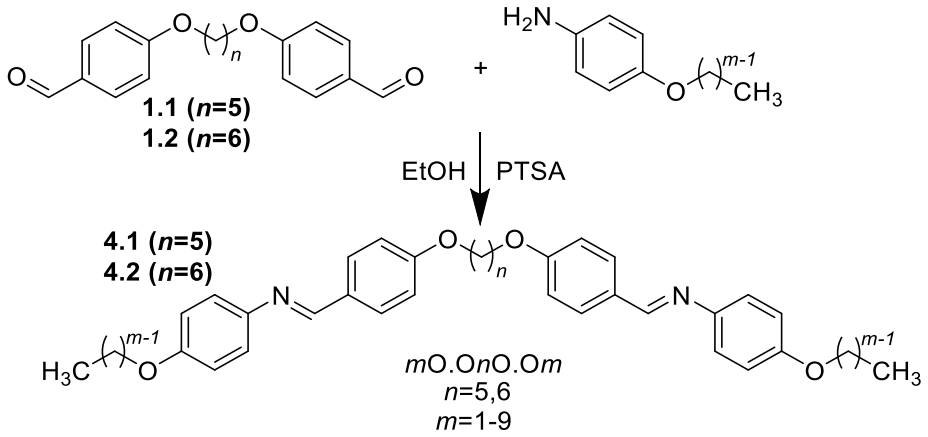
δ_H/ppm (400 MHz, $CDCl_3$): 8.38 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.7 Hz, Ar-H), 7.35 (4 H, d, J 8.5 Hz, Ar-H), 7.13 (4 H, d, J 8.5 Hz, Ar-H), 6.97 (4 H, d, J 8.7 Hz, Ar-H), 4.05 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 2.91 (4 H, t, J 7.3 Hz, S-$\underline{CH_2}$-CH_2-), 1.86 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.64 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, S-CH_2-$\underline{CH_2}$-CH_2-), 1.41 (4 H, m, S-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.27 (20 H, m, S-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 7.0 Hz, S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{50}H_{68}N_2O_2S_2$: C = 75.71 %, H = 8.64 %, N = 3.53 %, S = 8.08 %; Found: C = 75.78 %, H = 8.65 %, N = 3.50 %, S = 8.12 %

*m*O.O*n*O.O*m* Series



Scheme 2. Synthesis of the *m*O.O*n*O.O*m* series.

The synthesis of the *m*O.O*n*O.O*m* series follows the steps outlined in **Scheme 2**. The *m*O.O*n*O.O*m* series (**4.1** and **4.2**) were synthesised using the 4,4'-[alkane-1,ω-diylbis(oxy)]dibenzaldehyde)s (**1.1** and **1.2**) shown in **Scheme 1** in a Schiff's base reaction[3] to form the desired product.

(*E,E*)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{*N*-[4-(alkyloxy)phenyl]methanimine}s (*m*O.O5O.O*m*) (4.1)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.1** (1 eq, 0.250 g, 8.00×10^{-4} mol) and 4-(alkyloxy)aniline (2 eq) of the appropriate chain length were added along with ethanol (30 mL) and the mixture was stirred. The quantities of 4-(alkyloxy)anilines used in each reaction are listed in **Table 1.5**. The reaction was heated to reflux, *p*-toluenesulfonic acid (catalytic amount) was added, and left overnight. The reaction mixture was cooled to room temperature and a white precipitate formed which was collected by vacuum filtration. The white solid was recrystallised from hot ethanol (25 mL).

Table 1.5. Quantities of 4-(alkyloxy)anilines used in the syntheses of (E,E)-[pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(alkyloxy)phenyl]methanimine}s (**4.1**).

m	4-(Alkyloxy)aniline
1	0.197 g, 1.60×10^{-3} mol
2	0.206 mL, 0.219 g, 1.60×10^{-3} mol
3	0.238 mL, 0.242 g, 1.60×10^{-3} mol
4	0.267 mL, 0.264 g, 1.60×10^{-3} mol
5	0.296 mL, 0.287 g, 1.60×10^{-3} mol
6	0.309 g, 1.60×10^{-3} mol
7	0.331 g, 1.60×10^{-3} mol
8	0.354 g, 1.60×10^{-3} mol
9	0.377 g, 1.60×10^{-3} mol

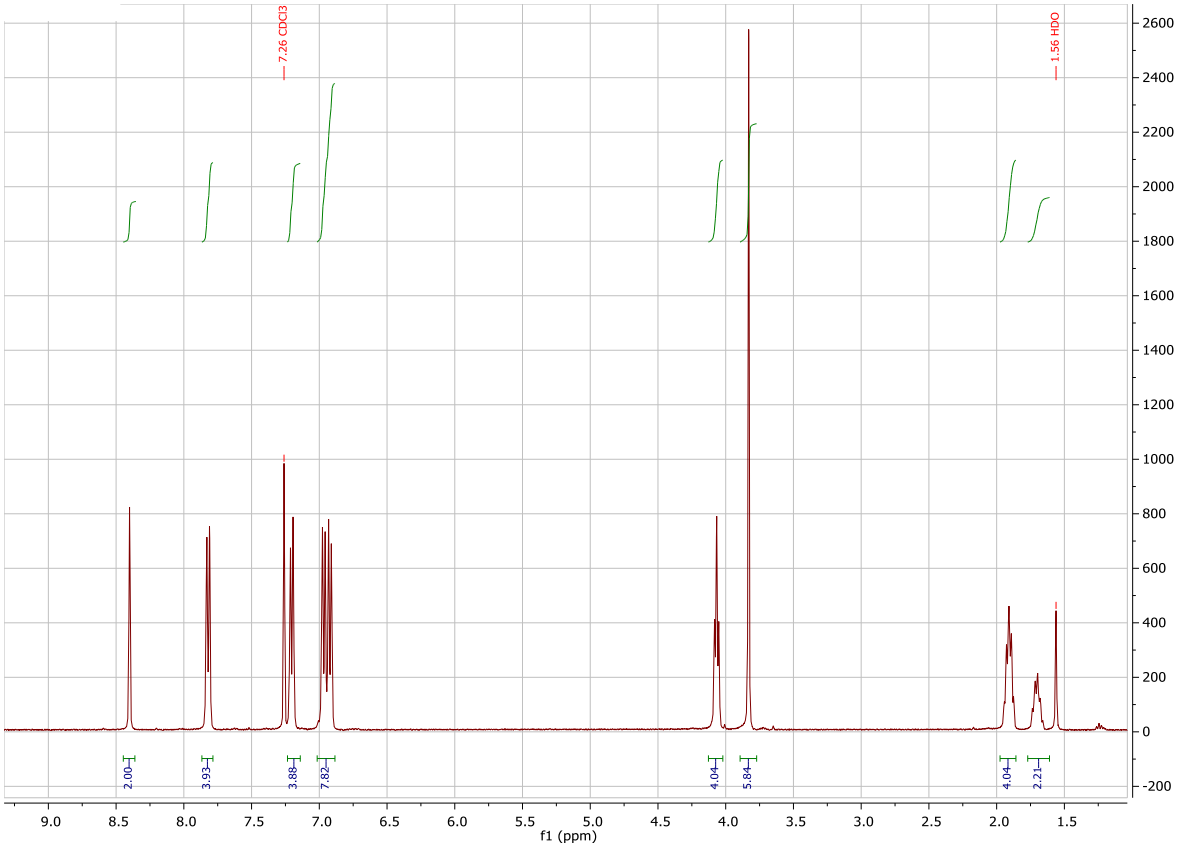
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(methoxy)phenyl]methanimine} (1O.O5O.O1) (4.1.1)

Yield: 0.187 g, 44.7 %

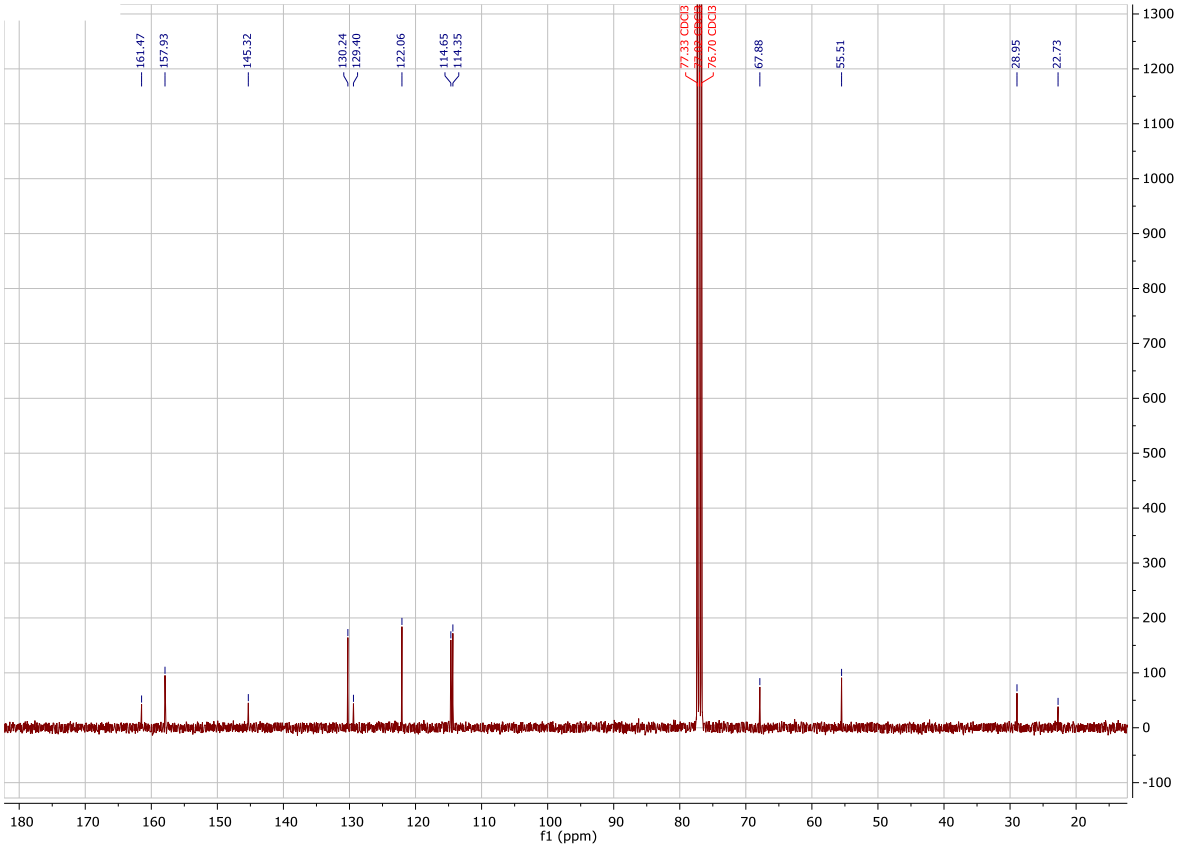
T_{CrN} 185 °C T_{NI} 195 °C

ν_{max}/cm^{-1}: 2934, 1621, 1605, 1574, 1509, 1468, 1441, 1396, 1306, 1306, 1291, 1238, 1194, 1172, 1112, 1067, 1029, 958, 947, 885, 841, 815, 744, 730, 552

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.1 Hz, Ar-H), 7.20 (4 H, d, J 8.1 Hz, Ar-H), 6.97 (4 H, d, J 8.1 Hz, Ar-H), 6.92 (4 H, d, J 8.1 Hz, Ar-H), 4.06 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 3.83 (6 H, s, O-$\underline{CH_3}$), 1.92 (4 H, tt, J 7.1 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.71 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-)



δ_C/ppm (100 MHz, $CDCl_3$): 161.47, 157.93, 157.92, 145.32, 130.24, 129.40, 122.06, 114.65, 114.35, 67.88, 55.51, 28.95, 22.73



EA: Calculated for $C_{33}H_{34}N_2O_4$: C = 75.84 %, H = 6.56 %, N = 5.36 %; Found: C = 75.65 %, H = 6.48 %, N = 5.24 %

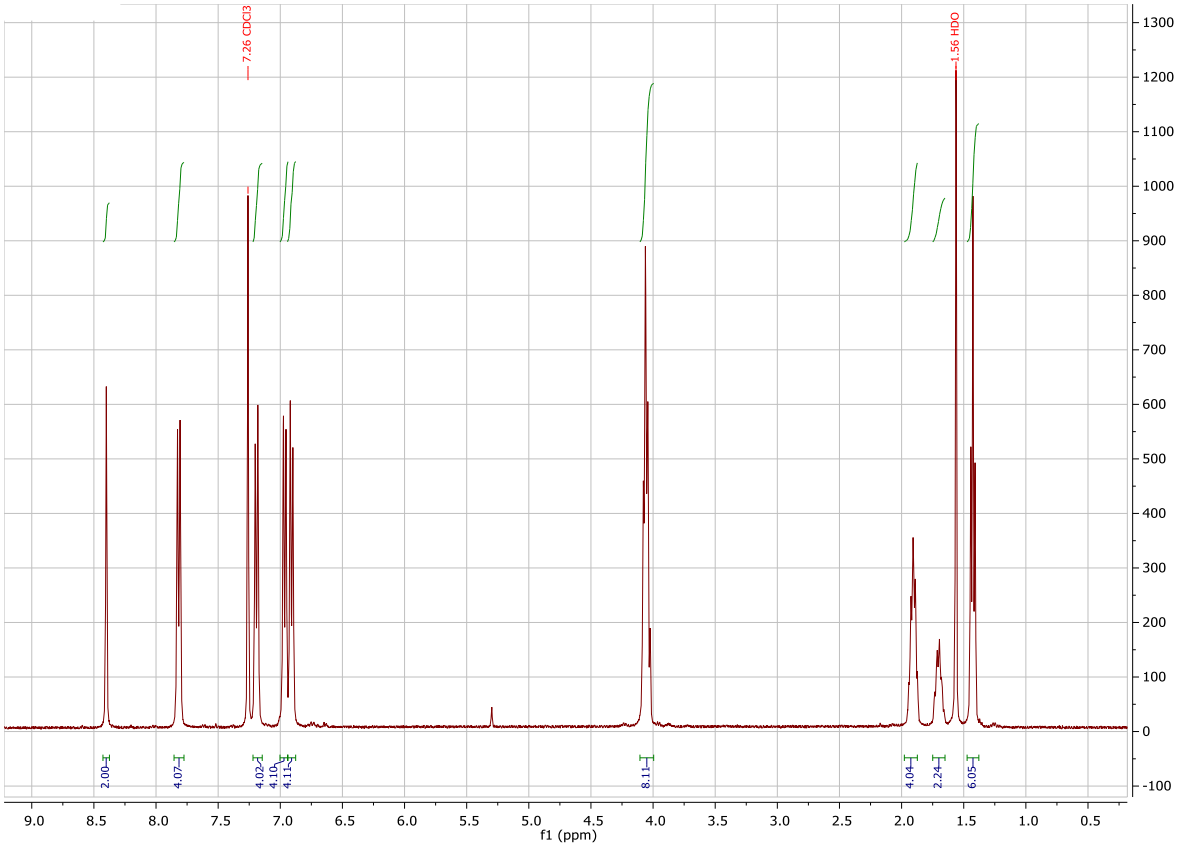
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(ethoxy)phenyl]methanimine} (2O.O5O.O2) (4.1.2)

Yield: 0.344 g, 78.0 %

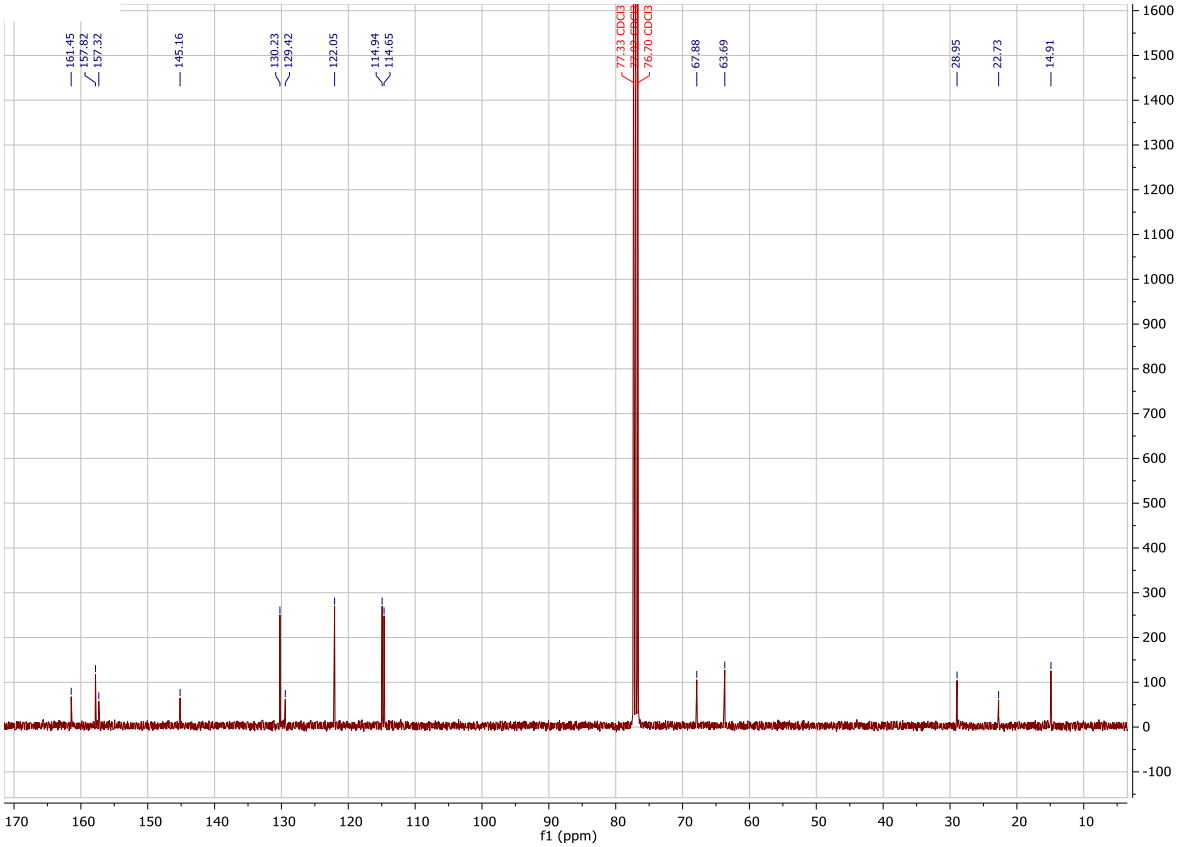
T_{CrN} 182 °C T_{NI} 204 °C

ν_{max}/cm^{-1}: 2979, 2931, 2847, 1622, 1605, 1574, 1509, 1479, 1395, 1305, 1286, 1238, 1193, 1171, 1116, 1049, 1027, 958, 946, 920, 885, 843, 815, 778, 750, 729, 550

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.3 Hz, Ar-H), 7.19 (4 H, d, J 8.3 Hz, Ar-H), 6.96 (4 H, d, J 8.3 Hz, Ar-H), 6.91 (4 H, d, J 8.3 Hz, Ar-H), 4.05 (8 H, m, O-$\underline{CH_2}$-CH_2-, O-$\underline{CH_2}$-CH_3), 1.91 (4 H, tt, J 7.1 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.71 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.43 (6 H, t, J 7.0 Hz, O-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.45, 157.82, 157.32, 145.16, 130.23, 129.42, 122.05, 114.94, 114.65, 67.88, 63.69, 28.95, 22.73, 14.91



EA: Calculated for $C_{35}H_{38}N_2O_4$: C = 76.34 %, H = 6.96 %, N = 5.09 %; Found: C = 76.36 %, H = 6.91 %, N = 4.94 %

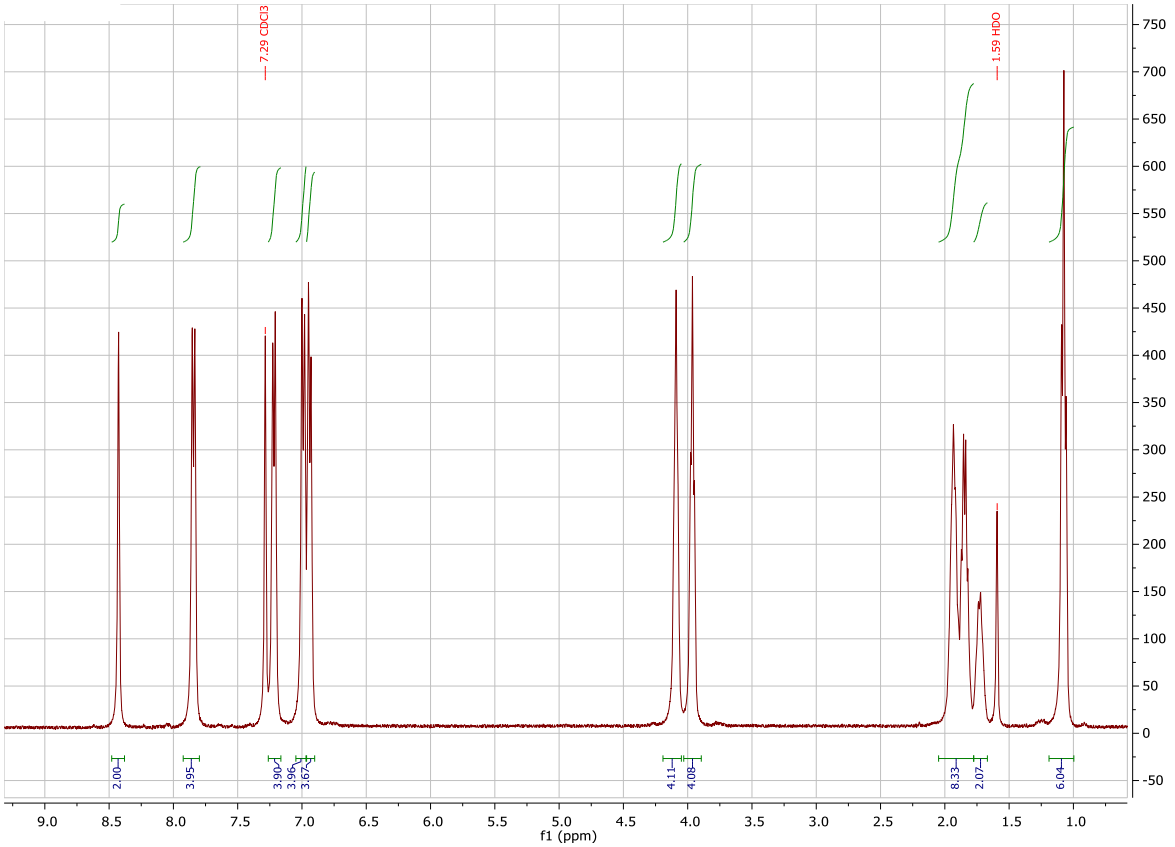
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(propoxy)phenyl]methanimine} (3O.O5O.O3) (4.1.3)

Yield: 0.345 g, 74.5 %

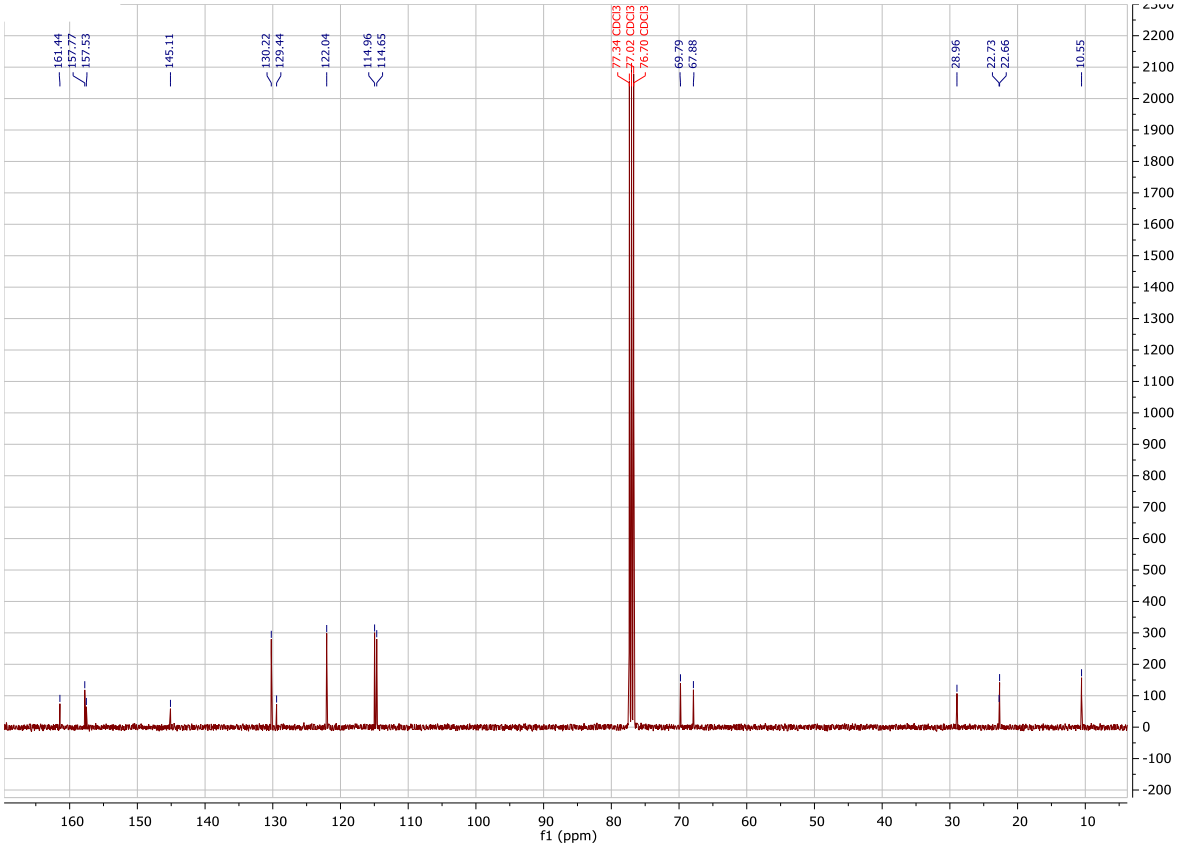
T_{CrI} 183 °C T_{NI} (176 °C)

ν_{max}/cm^{-1}: 2933, 2874, 1621, 1605, 1573, 1508, 1305, 1289, 1236, 1193, 1171, 1113, 1067, 1051, 1026, 976, 958, 946, 885, 840, 815, 741, 729, 547

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.0 Hz, Ar-H), 7.19 (4 H, d, J 8.0 Hz, Ar-H), 6.96 (4 H, d, J 8.0 Hz, Ar-H), 6.91 (4 H, d, J 8.0 Hz, Ar-H), 4.06 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 3.94 (4 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 1.86 (8 H, m, O-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_3), 1.71 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.04 (6 H, t, J 7.1 Hz, O-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.77, 157.53, 145.11, 130.22, 129.44, 122.04, 114.96, 114.65, 69.79, 67.88, 28.96, 22.73, 22.66, 10.55



EA: Calculated for $C_{37}H_{42}N_2O_4$: C = 76.79 %, H = 7.32 %, N = 4.84 %; Found: C = 76.58 %, H = 7.23 %, N = 4.69 %

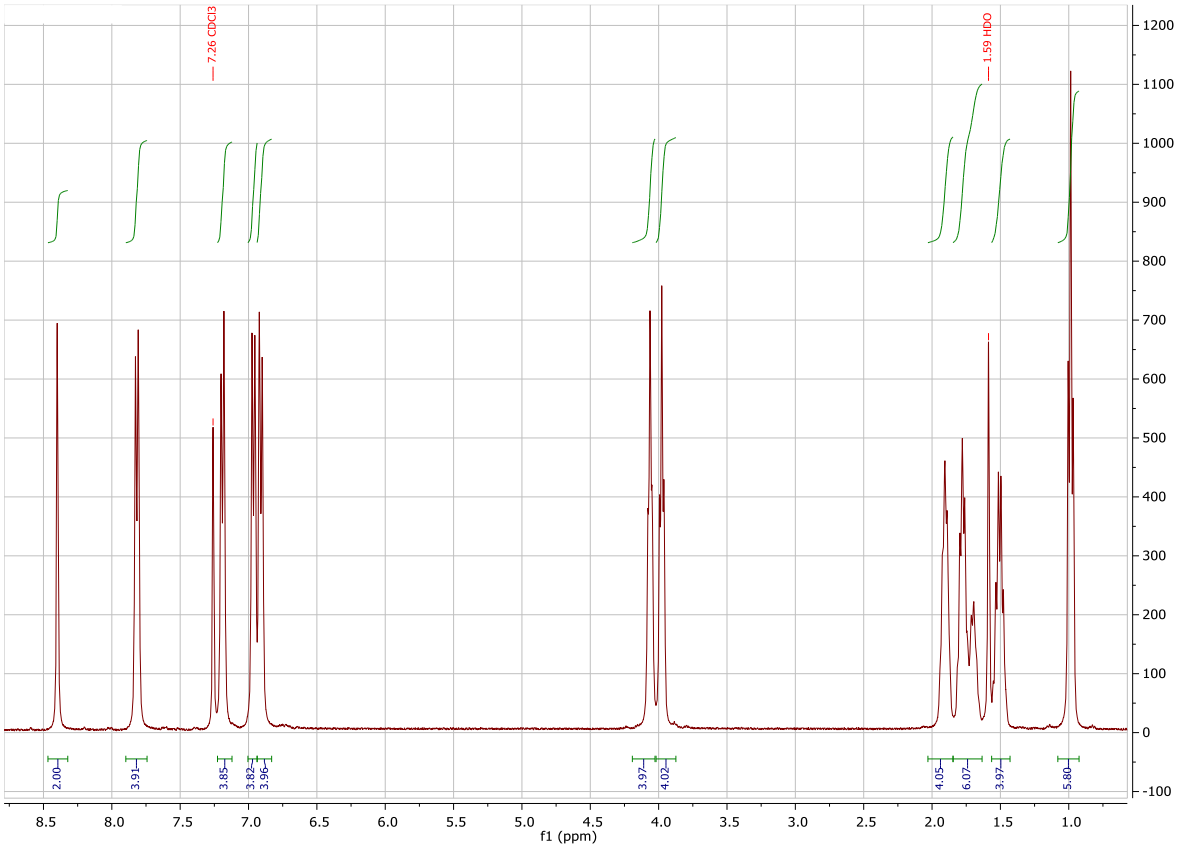
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(butoxy)phenyl]methanimine} (4O.O5O.O4) (4.1.4)

Yield: 0.393 g, 81.0 %

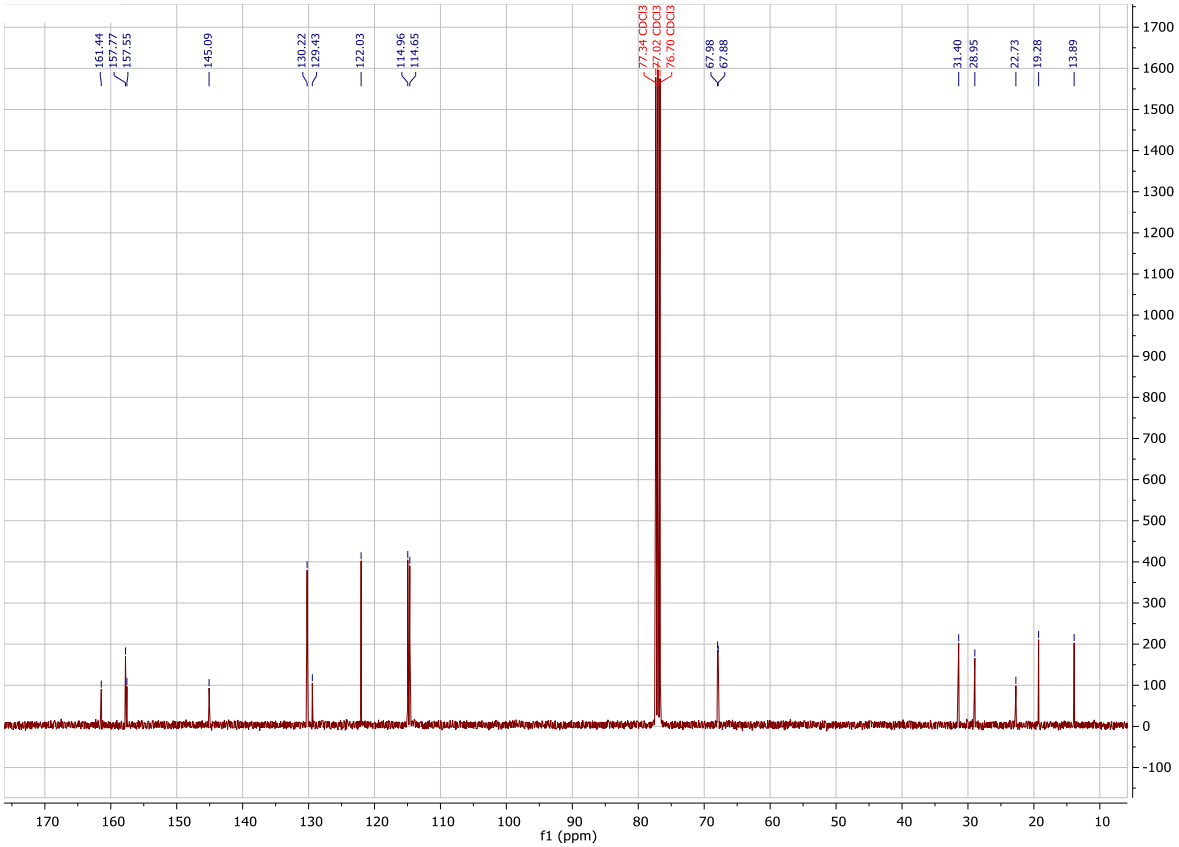
T_{CrI} 178 °C T_{NI} (176 °C)

ν_{max}/cm^{-1}: 2955, 2933, 2872, 1621, 1605, 1573, 1509, 1469, 1396, 1305, 1288, 1238, 1192, 1171, 1112, 1068, 978, 958, 946, 841, 814, 787, 754, 729, 547

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.2 Hz, Ar-H), 7.19 (4 H, d, J 8.2 Hz, Ar-H), 6.96 (4 H, d, J 8.2 Hz, Ar-H), 6.91 (4 H, d, J 8.2 Hz, Ar-H), 4.06 (4 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 3.98 (4 H, t, J 6.6 Hz, O-$\underline{CH_2}$-CH_2-), 1.90 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.74 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_2-), 1.51 (4 H, sext, J 7.2 Hz, O-CH_2-CH_2-$\underline{CH_2}$-CH_3), 0.98 (6 H, t, J 7.2 Hz, O-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.77, 157.55, 145.09, 130.22, 129.43, 122.03, 114.96, 114.65, 67.98, 67.88, 31.40, 28.95, 22.73, 19.28, 13.89



EA: Calculated for $C_{39}H_{46}N_2O_4$: C = 77.20 %, H = 7.64 %, N = 4.62 %; Found: C = 77.20 %, H = 7.63 %, N = 4.46 %

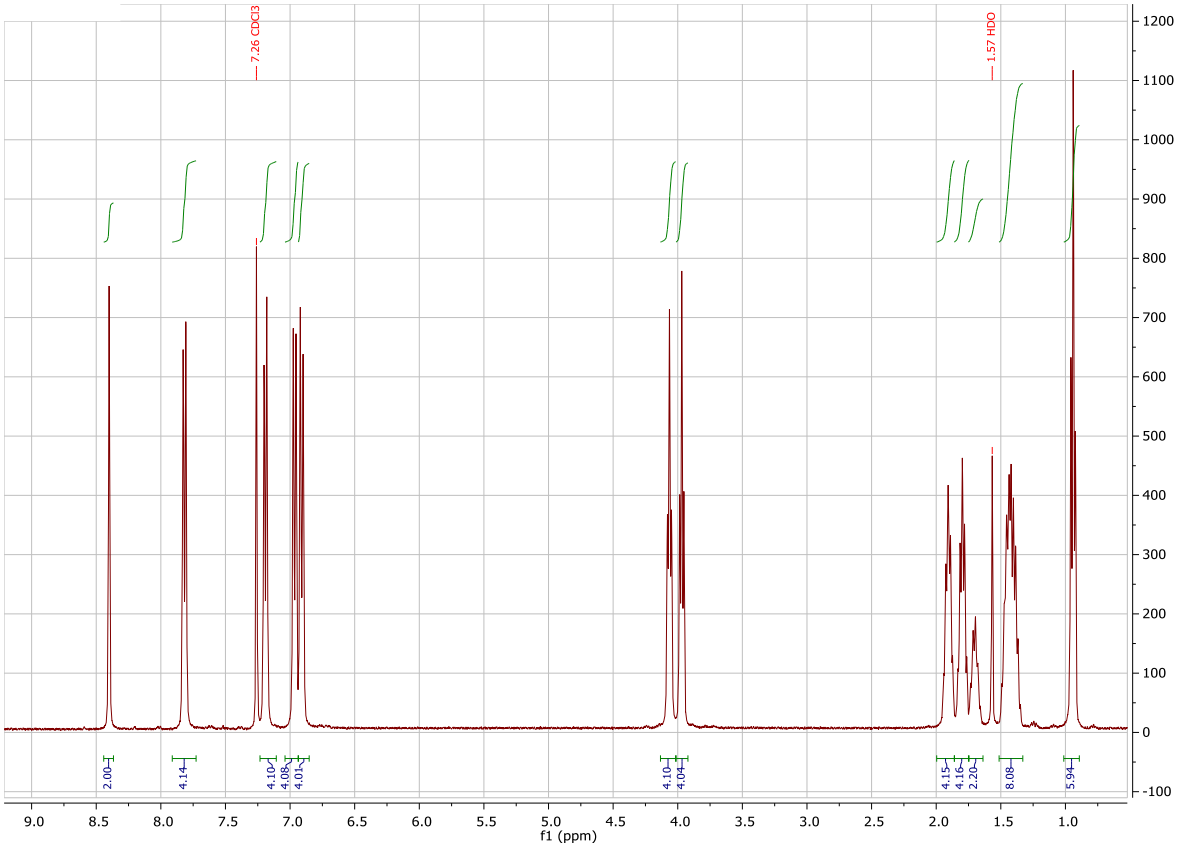
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(pentyloxy)phenyl]methanimine} (5O.O5O.O5) (4.1.5)

Yield: 0.493 g, 95.7 %

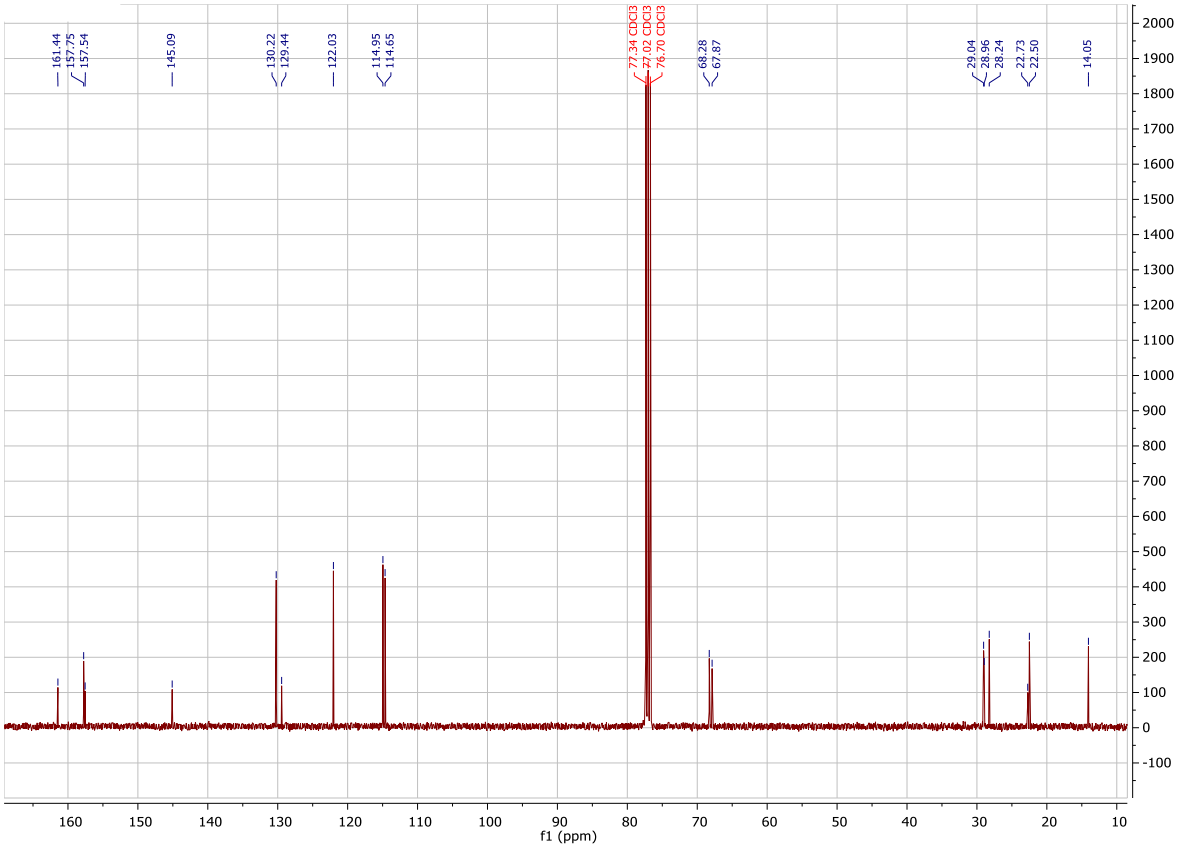
T_{CrI} 172 °C T_{SmAN} (156 °C) T_{NI} (163 °C)

ν_{max}/cm^{-1}: 2958, 2937, 2863, 1622, 1605, 1574, 1509, 1467, 1395, 1305, 1289, 1238, 1193, 1172, 1112, 1067, 1053, 1020, 957, 946, 815, 840, 815, 789, 752, 729, 547

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.3 Hz, Ar-H), 7.19 (4 H, d, J 8.3 Hz, Ar-H), 6.96 (4 H, d, J 8.3 Hz, Ar-H), 6.91 (4 H, d, J 8.3 Hz, Ar-H), 4.06 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 3.97 (4 H, t, J 6.6 Hz, O-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.80 (4 H, tt, J 7.0 Hz, 6.6 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.69 (2 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.41 (8 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.94 (6 H, t, J 7.0 Hz, O-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.75, 157.54, 145.09, 130.22, 129.44, 122.03, 114.95, 114.65, 68.28, 67.87, 29.04, 28.96, 28.24, 22.73, 22.50, 14.05



EA: Calculated for $C_{41}H_{50}N_2O_4$: C = 77.57 %, H = 7.94 %, N = 4.41 %; Found: C = 77.46 %, H = 7.94 %, N = 4.25 %

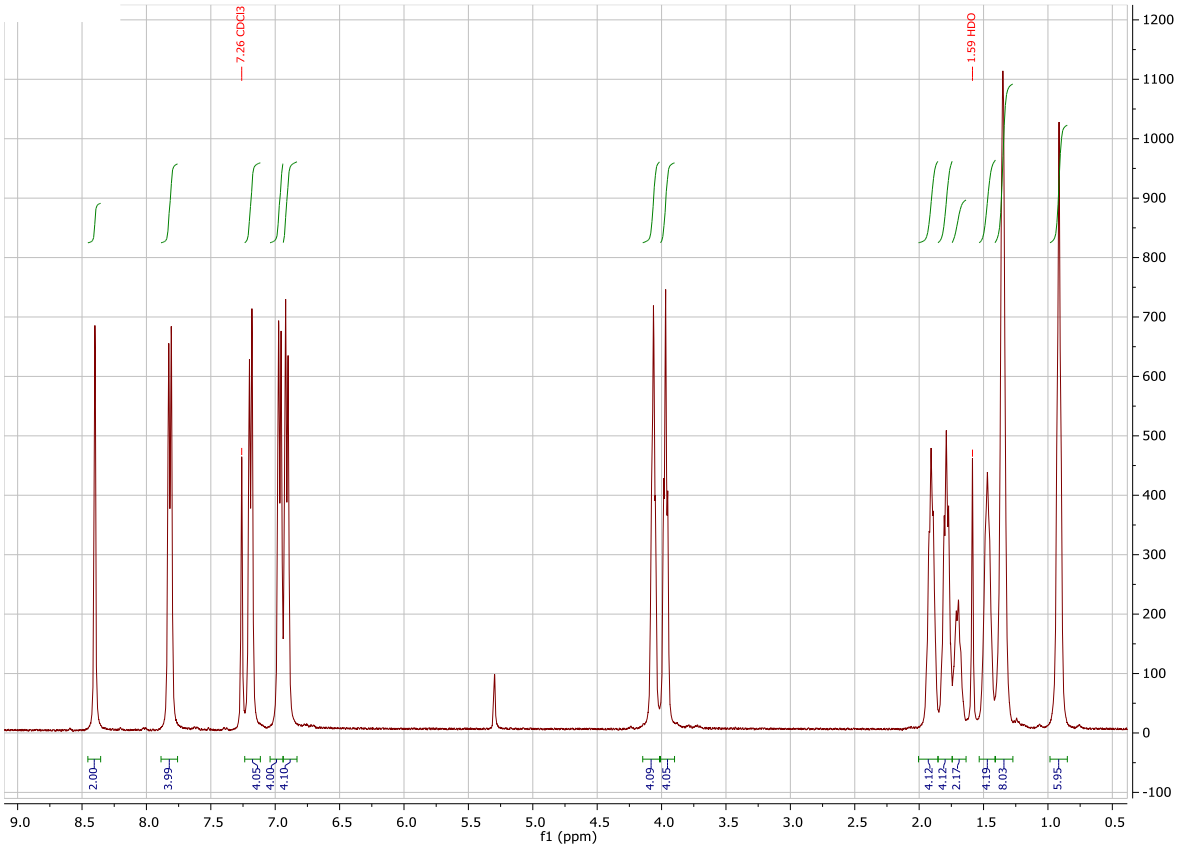
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(hexyloxy)phenyl]methanimine} (6O.O5O.O6) (4.1.6)

Yield: 0.522 g, 98.4 %

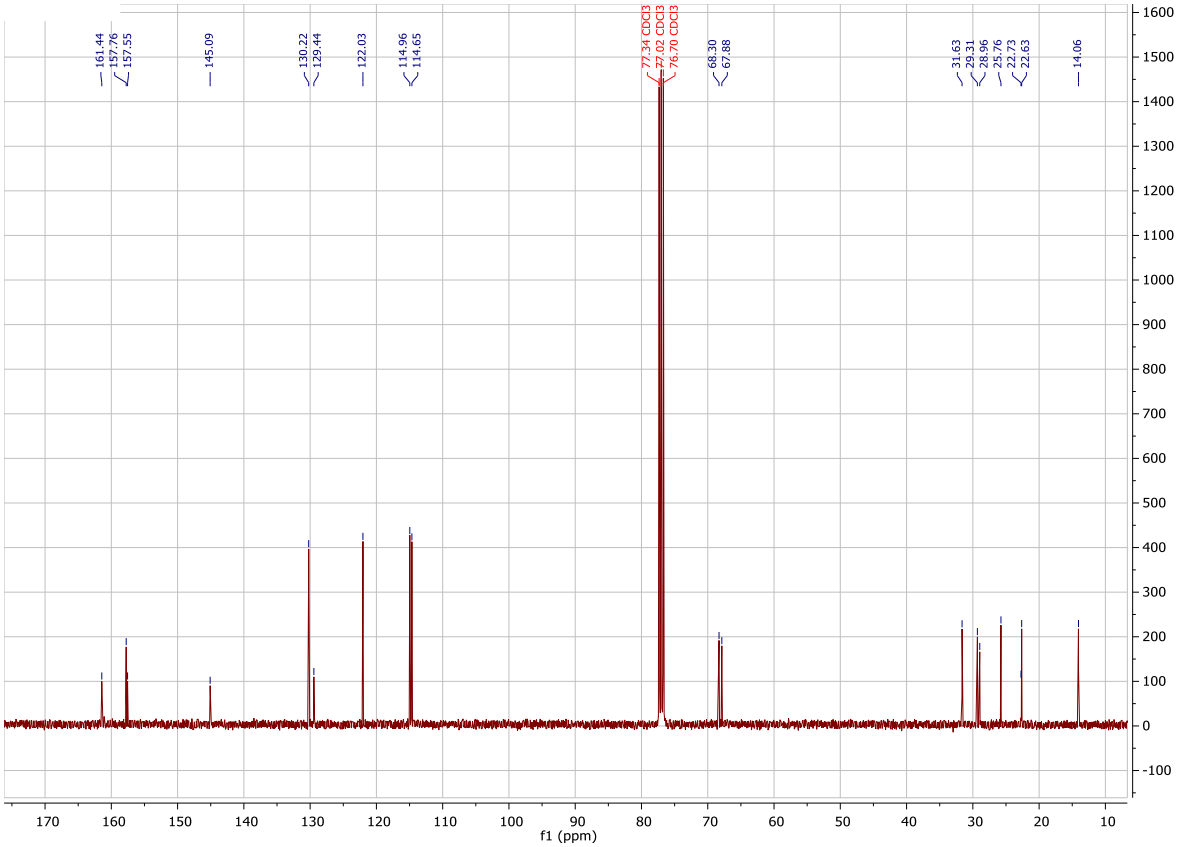
T_{CrI} 168 °C T_{SmAI} (165 °C)

ν_{max}/cm^{-1}: 2857, 2936, 2863, 1621, 1605, 1574, 1509, 1467, 1395, 1305, 1289, 1238, 1193, 1172, 1112, 1067, 1052, 1021, 957, 946, 885, 841, 815, 789, 752, 723, 547

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.1 Hz, Ar-H), 7.19 (4 H, d, J 8.1 Hz, Ar-H), 6.97 (4 H, d, J 8.1 Hz, Ar-H), 6.91 (4 H, d, J 8.1 Hz, Ar-H), 4.06 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 3.91 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 1.92 (4 H, tt, J 7.0 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.76 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_2-), 1.47 (4 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-), 1.36 (8 H, m, O-CH_2-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.92 (6 H, t, J 6.9 Hz, O-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.76, 157.55, 145.09, 130.22, 129.44, 122.03, 114.96, 114.65, 68.30, 67.88, 31.63, 29.31, 28.96, 25.76, 22.73, 22.63, 14.06



EA: Calculated for $C_{43}H_{54}N_2O_4$: C = 77.91 %, H = 8.21 %, N = 4.23 %; Found: C = 77.91 %, H = 8.26 %, N = 4.05 %

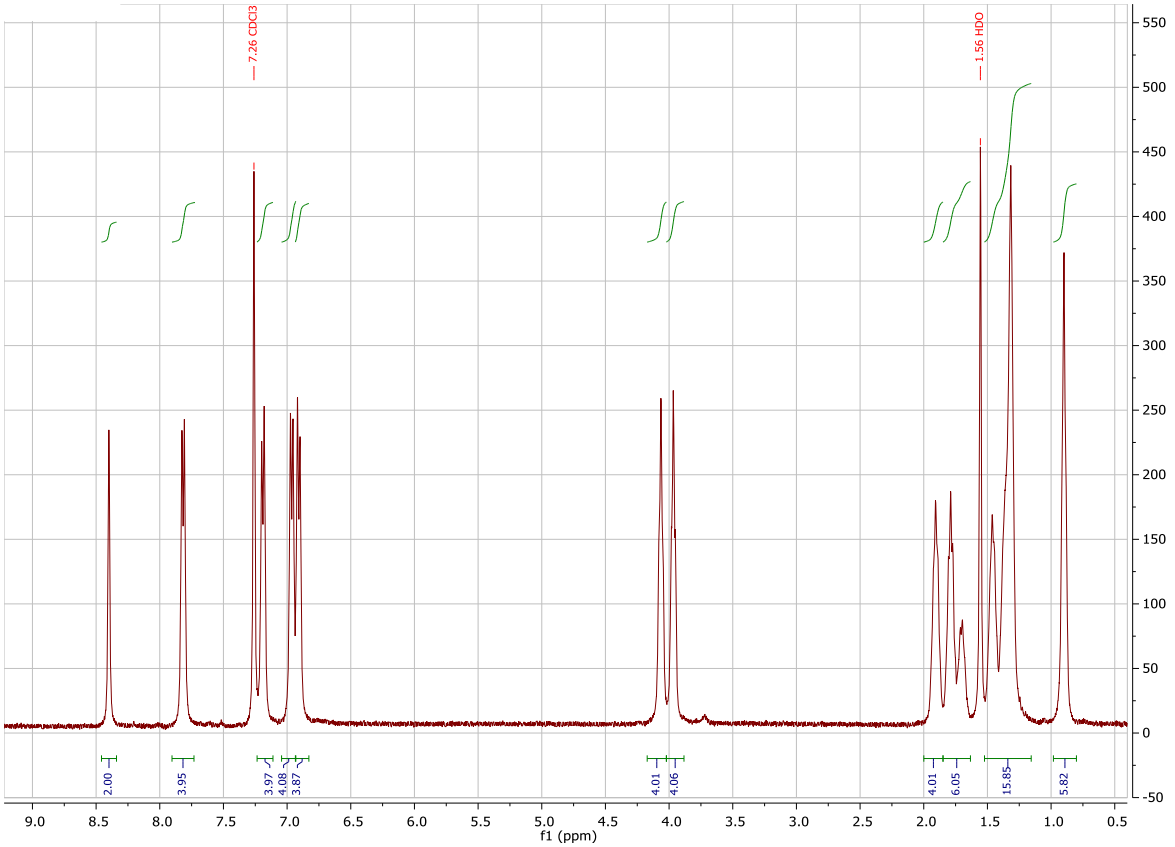
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(heptyloxy)phenyl]methanimine} (7O.O5O.O7) (4.1.7)

Yield: 0.500 g, 90.4 %

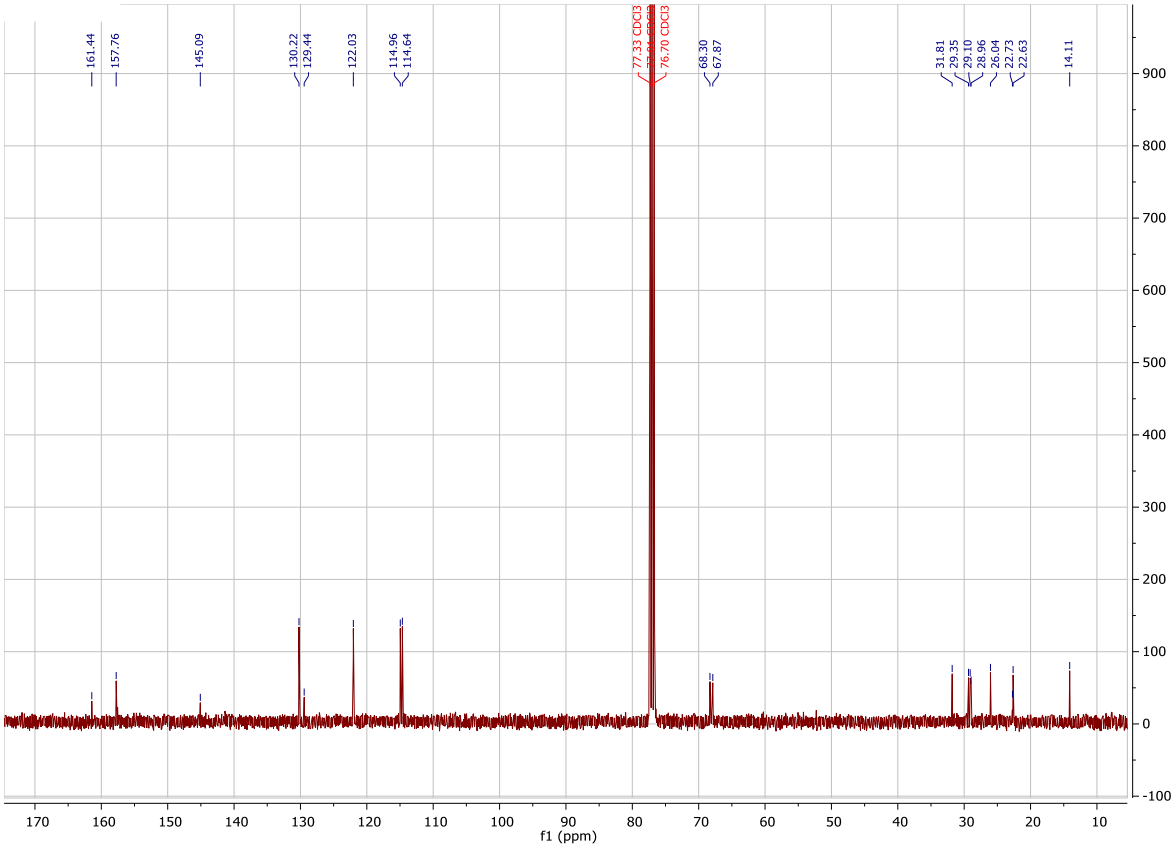
T_{CrN} 164 °C T_{SmAI} 168 °C

ν_{max}/cm^{-1}: 2955, 2935, 2860, 1622, 1606, 1574, 1509, 1467, 1395, 1306, 1291, 1238, 1112, 1173, 1112, 1067, 1017, 958, 947, 887, 840, 815, 789, 751, 729, 547

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.2 Hz, Ar-H), 7.19 (4 H, d, J 8.2 Hz, Ar-H), 6.97 (4 H, d, J 8.2 Hz, Ar-H), 6.91 (4 H, d, J 8.2 Hz, Ar-H), 4.06 (4 H, t, J 6.5 Hz, O-$\underline{CH_2}$-CH_2-), 3.97 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 1.91 (4 H, m, O-CH_2-$\underline{CH_2}$-CH_2-), 1.77 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_2-), 1.38 (16 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.90 (6 H, t, J 6.9 Hz, O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.76, 157.55, 145.09, 130.22, 129.44, 122.03, 114.96, 114.64, 68.30, 67.87, 31.81, 29.35, 29.10, 28.96, 26.04, 22.73, 22.63, 14.11



EA: Calculated for $C_{45}H_{58}N_2O_4$: C = 78.22 %, H = 8.46 %, N = 4.05 %; Found: C = 78.27 %, H = 8.49 %, N = 3.97 %

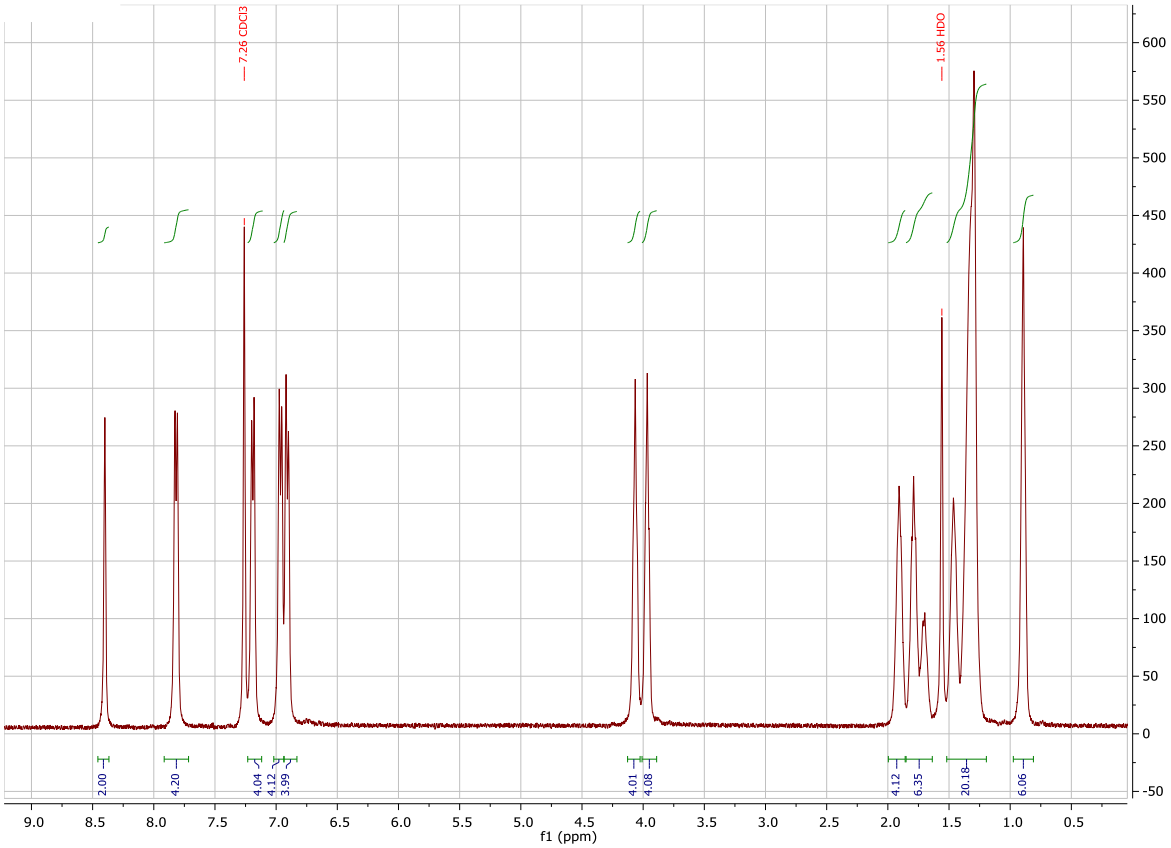
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(octyloxy)phenyl]methanimine} (8O.O5O.O8) (4.1.8)

Yield: 0.294 g, 51.1 %

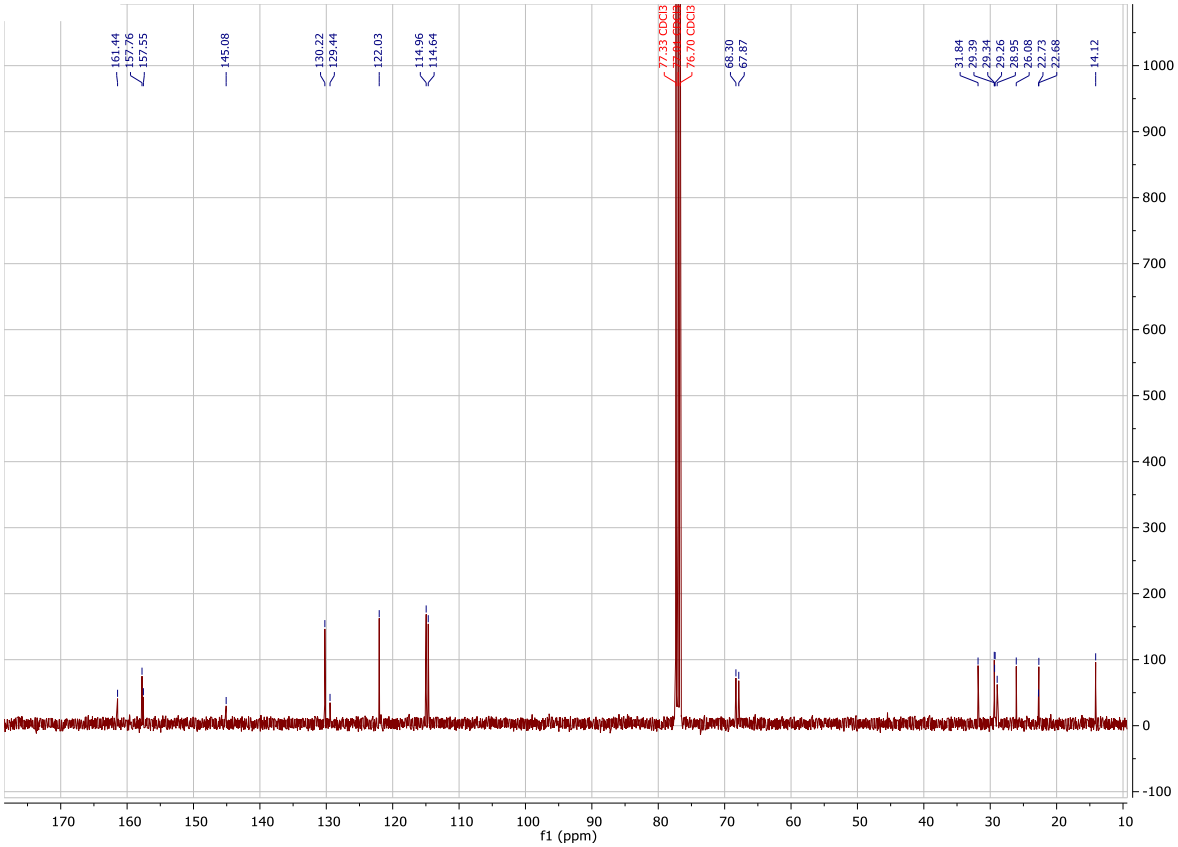
T_{CrSmA} 160 °C T_{SmAI} 171 °C

ν_{max}/cm^{-1}: 2956, 2923, 2857, 1622, 1606, 1574, 1509, 1468, 1396, 1305, 1290, 1238, 1192, 1173, 1113, 1067, 1025, 1001, 958, 946, 841, 815, 752, 729, 570, 548

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.3 Hz, Ar-H), 7.19 (4 H, d, J 8.3 Hz, Ar-H), 6.96 (4 H, d, J 8.3 Hz, Ar-H), 6.91 (4 H, d, J 8.3 Hz, Ar-H), 4.06 (4 H, t, J 6.3 Hz, O-$\underline{CH_2}$-CH_2-), 3.97 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 1.90 (4 H, tt, J 7.0 Hz, 6.3 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.77 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_2-), 1.36 (20 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-CH_3), 0.88 (6 H, t, J 6.8 Hz, O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.44, 157.76, 157.55, 145.08, 130.22, 129.44, 122.03, 114.96, 114.64, 68.30, 67.87, 31.84, 29.39, 29.34, 29.26, 28.95, 26.08, 22.73, 22.68, 14.12



EA: Calculated for $C_{47}H_{62}N_2O_4$: C = 78.51 %, H = 8.69 %, N = 3.90 %; Found: C = 78.43 %, H = 8.77 %, N = 3.70 %

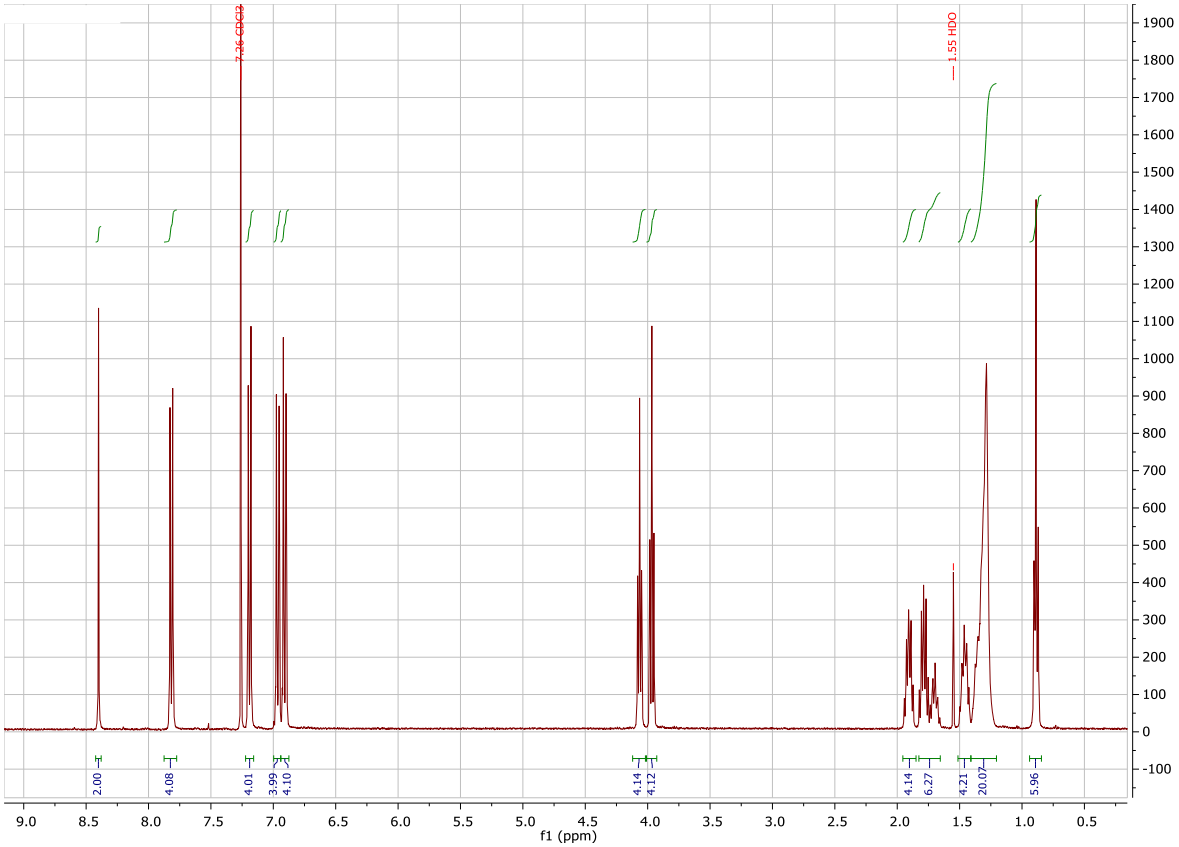
(E,E)-[Pentane-1,5-diylbis(oxy-4,1-phenylene)]bis{N-[4-(nonyloxy)phenyl]methanimine} (9O.O5O.O9) (4.1.9)

Yield: 0.228 g, 38.1 %

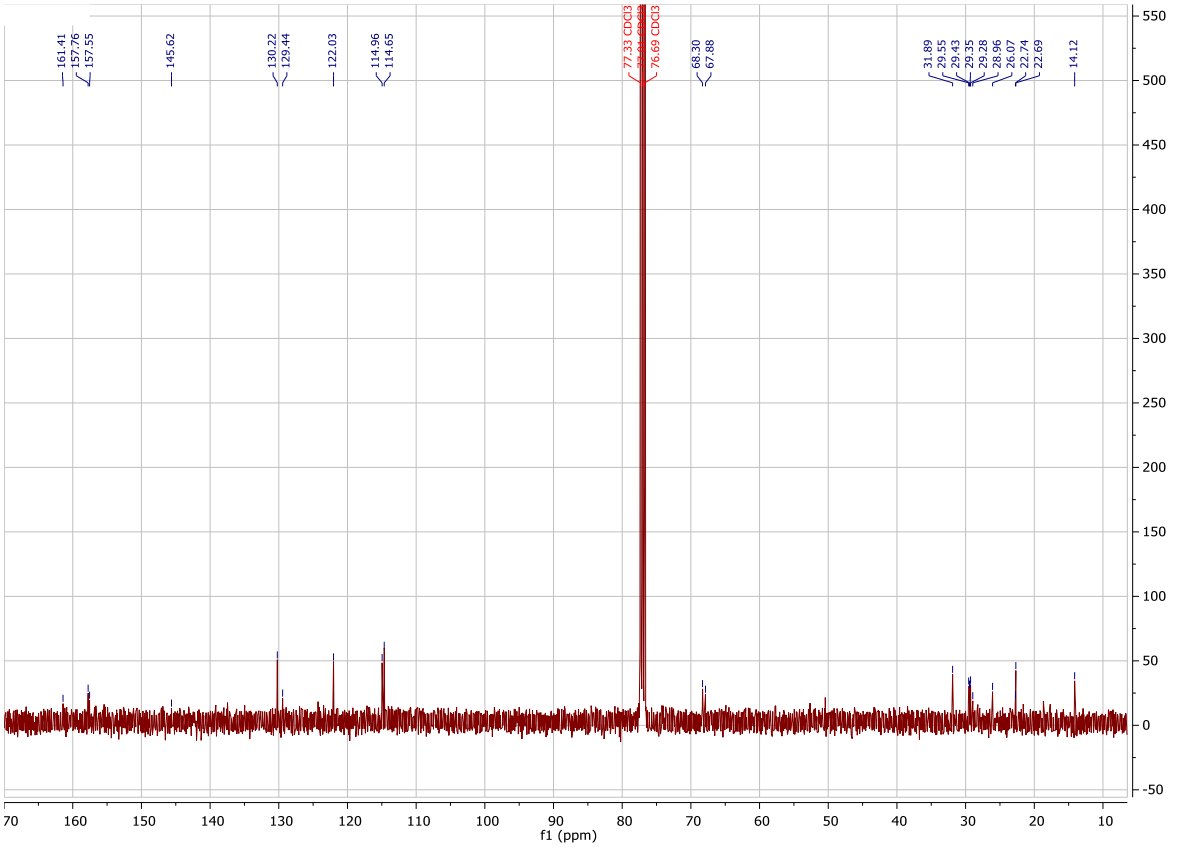
T_{CrSmA} 157 °C T_{SmAI} 171 °C

ν_{max}/cm^{-1}: 2954, 2921, 2850, 1622, 1606, 2575, 1510, 1467, 1395, 1306, 1239, 1192, 1173, 1113, 1017, 977, 957, 946, 887, 842, 816, 729, 751, 728, 570, 548

δ_H/ppm (400 MHz, $CDCl_3$): 8.40 (2 H, s, (C=N)-H), 7.82 (4 H, d, J 8.6 Hz, Ar-H), 7.19 (4 H, d, J 8.6 Hz, Ar-H), 6.97 (4 H, d, J 8.6 Hz, Ar-H), 6.92 (4 H, d, J 8.6 Hz, Ar-H), 4.06 (4 H, t, J 6.4 Hz, O-$\underline{CH_2}$-CH_2-), 3.97 (4 H, t, J 6.6 Hz, O-$\underline{CH_2}$-CH_2-), 1.91 (4 H, tt, J 6.9 Hz, 6.4 Hz, O-CH_2-$\underline{CH_2}$-CH_2-), 1.77 (6 H, m, O-CH_2-CH_2-$\underline{CH_2}$-CH_2-, O-CH_2-$\underline{CH_2}$-CH_2-), 1.35 (24 H, m, O-CH_2-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 0.88 (6 H, t, J 7.0 Hz, O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$\underline{CH_3}$)



δ_C/ppm (100 MHz, $CDCl_3$): 161.41, 157.76, 157.55, 145.62, 130.22, 129.44, 122.03, 114.96, 114.65, 68.30, 67.88, 31.89, 29.55, 29.43, 29.35, 29.28, 28.96, 26.07, 22.74, 22.69, 14.12



EA: Calculated for $C_{49}H_{66}N_2O_4$: C = 78.78 %, H = 8.91 %, N = 3.75 %; Found: C = 78.66 %, H = 8.99 %, N = 3.64 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(alkyloxy)phenyl]methanimine}s (*m*O.O6O.O*m*) (4.2)

To a pre-dried flask flushed with argon and fitted with a condenser, compound **1.2** (1 eq, 0.100 g, 3.06×10^{-4} mol) and 4-(alkyloxy)aniline (2.5 eq) of the appropriate chain length were added along with ethanol (12 mL) and the mixture was stirred. The quantities of 4-(alkyloxy)anilines used in each reaction are listed in **Table 1.6**. The reaction was heated to reflux, *p*-toluenesulfonic acid (catalytic amount) was added, and left overnight. The reaction mixture was cooled to room temperature and a white precipitate formed which was collected by vacuum filtration. The white solid was recrystallised from hot toluene (15 mL).

Table 1.6. Quantities of 4-(alkyloxy)anilines used in the syntheses of (E,E)-[hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(alkyloxy)phenyl]methanimine}s (**4.2**).

m	4-(Alkyloxy)aniline
1	0.094 g, 7.66×10^{-4} mol
2	0.099 mL, 0.105 g, 7.66×10^{-4} mol
3	0.114 mL, 0.116 g, 7.66×10^{-4} mol
4	0.128 mL, 0.127 g, 7.66×10^{-4} mol
5	0.141 mL, 0.137 g, 7.66×10^{-4} mol
6	0.148 g, 7.66×10^{-4} mol
7	0.159 g, 7.66×10^{-4} mol
8	0.170 g, 7.66×10^{-4} mol
9	0.180 g, 7.66×10^{-4} mol

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(methoxy)phenyl]methanimine} (1O.O6O.O1) (4.2.1)

Yield: 0.138 g, 84.0 %

T_{CrN} 216 °C T_{NI} 235 °C

ν_{max}/cm^{-1}: 2941, 2865, 1621, 1606, 1574, 1508, 1469, 1421, 1397, 1305, 1290, 1241, 1194, 1181, 1169, 1111, 1027, 957, 885, 840, 805, 754, 729, 640, 551, 518, 495

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{34}H_{36}N_2O_4$: C = 76.09 %, H = 6.76 %, N = 5.22 %; Found: C = 75.74 %, H = 6.79 %, N = 5.11 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(ethoxy)phenyl]methanimine} (2O.O6O.O2) (4.2.2)

Yield: 0.147 g, 85.1 %

T_{CrN} 205 °C T_{NI} 241 °C

ν_{max}/cm^{-1}: 2978, 2941, 2866, 1621, 1605, 1574, 1508, 1476, 1420, 1395, 1304, 1286, 1239, 1194, 1168, 1112, 1048, 1018, 958, 920, 889. 840, 805, 768, 729, 640, 547, 520, 499

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{36}H_{40}N_2O_4$: C = 76.57 %, H = 7.14 %, N = 4.96 %; Found: C = 76.55 %, H = 7.15 %, N = 4.85 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(propoxy)phenyl]methanimine} (3O.O6O.O3) (4.2.3)

Yield: 0.153 g, 84.3 %

T_{CrN} 209 °C T_{NI} 220 °C

ν_{max}/cm^{-1}: 2964, 2940, 2873, 1620, 1605, 1574, 1508, 1473, 1421, 1393, 1305, 1288, 1238, 1193, 1167, 1112, 1069, 1019, 976, 957, 884, 840, 804, 779, 741, 728, 639, 546, 519, 500

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{38}H_{44}N_2O_4$: C = 77.00 %, H = 7.48 %, N = 4.73 %; Found: C = 77.09 %, H = 7.41 %, N = 4.63 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(butoxy)phenyl]methanimine} (4O.O6O.O4) (4.2.4)

Yield: 0.148 g, 77.9 %

T_{CrN} 203 °C T_{NI} 218 °C

ν_{max}/cm^{-1}: 2939, 2872, 1621, 1606, 1573, 1508, 1474, 1421, 1396, 1305, 1288, 1242, 1193, 1169, 1112, 1071, 1039, 1020, 958, 885, 841, 803, 776, 729, 641, 547, 521, 473

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{40}H_{48}N_2O_4$: C = 77.39 %, H = 7.79 %, N = 4.51 %; Found: C = 77.30 %, H = 7.77 %, N = 4.40 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(pentyloxy)phenyl]methanimine} (5O.O6O.O5) (4.2.5)

Yield: 0.160 g, 80.6 %

T_{CrSmA} 196 °C T_{SmAN} 199 °C T_{NI} 205 °C

ν_{max}/cm^{-1}: 2938, 2866, 1620, 1606, 1573, 1508, 1474, 1421, 1395, 1305, 1288, 1239, 1193, 1169, 1111, 1055, 1019, 976, 956, 885, 840, 803, 777, 729, 641, 546, 521, 469

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{42}H_{52}N_2O_4$: C = 77.74 %, H = 8.08 %, N = 4.32 %; Found: C = 77.76 %, H = 8.18 %, N = 4.24 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(hexyloxy)phenyl]methanimine} (6O.O6O.O6) (4.2.6)

Yield: 0.167 g, 80.6 %

T_{CrSmA} 190 °C T_{SmAI} 205 °C

ν_{max}/cm^{-1}: 2956, 2939, 2870, 1621, 1606, 1573, 1508, 1474, 1421, 1396, 1305, 1288, 1240, 1193, 1169, 1112, 1019, 975, 957, 885, 840, 803, 776, 729, 841, 547, 520, 471

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{44}H_{56}N_2O_4$: C = 78.07 %, H = 8.34 %, N = 4.14 %; Found: C = 77.92 %, H = 8.35 %, N = 4.03 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(heptyloxy)phenyl]methanimine} (7O.O6O.O7) (4.2.7)

Yield: 0.182 g, 84.4 %

T_{CrSmA} 185 °C T_{SmAI} 203 °C

ν_{max}/cm^{-1}: 2936, 2860, 1620, 1606, 1573, 1509, 1474, 1421, 1394, 1305, 1289, 1244, 1193, 1169, 1111, 1072, 1040, 1017, 956, 886, 840, 803, 778, 729, 641, 547, 486

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{46}H_{60}N_2O_4$: C = 78.37 %, H = 8.58 %, N = 3.97 %; Found: C = 77.97 %, H = 8.57 %, N = 3.87 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(octyloxy)phenyl]methanimine} (8O.O6O.O8) (4.2.8)

Yield: 0.190 g, 84.7 %

T_{CrSmA} 181 °C T_{SmAI} 205 °C

ν_{max}/cm^{-1}: 2936, 2921, 5857, 1621, 1606, 1574, 1509, 1474, 1421, 1395, 1305, 1288, 1245, 1193, 1169, 1112, 1022, 957, 886, 840, 803, 778, 728, 641, 555, 547, 521, 481

δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

EA: Calculated for $C_{48}H_{64}N_2O_4$: C = 78.65 %, H = 8.80 %, N = 3.82 %; Found: C = 78.21 %, H = 8.85 %, N = 3.78 %

(E,E)-[Hexane-1,6-diylbis(oxy-4,1-phenylene)]bis{N-[4-(nonyloxy)phenyl]methanimine} (9O.O6O.O9) (4.2.9)

Yield: 0.182 g, 78.1 %

T_{CrSmA} 178 °C T_{SmAI} 203 °C

ν_{max}/cm^{-1}: 2920, 2856, 1621, 1606, 1575, 1509, 1474, 1421, 1395, 1305, 1288, 1244, 1193, 1169, 1112, 1018, 857, 886, 841, 803, 778, 728, 641, 556, 546

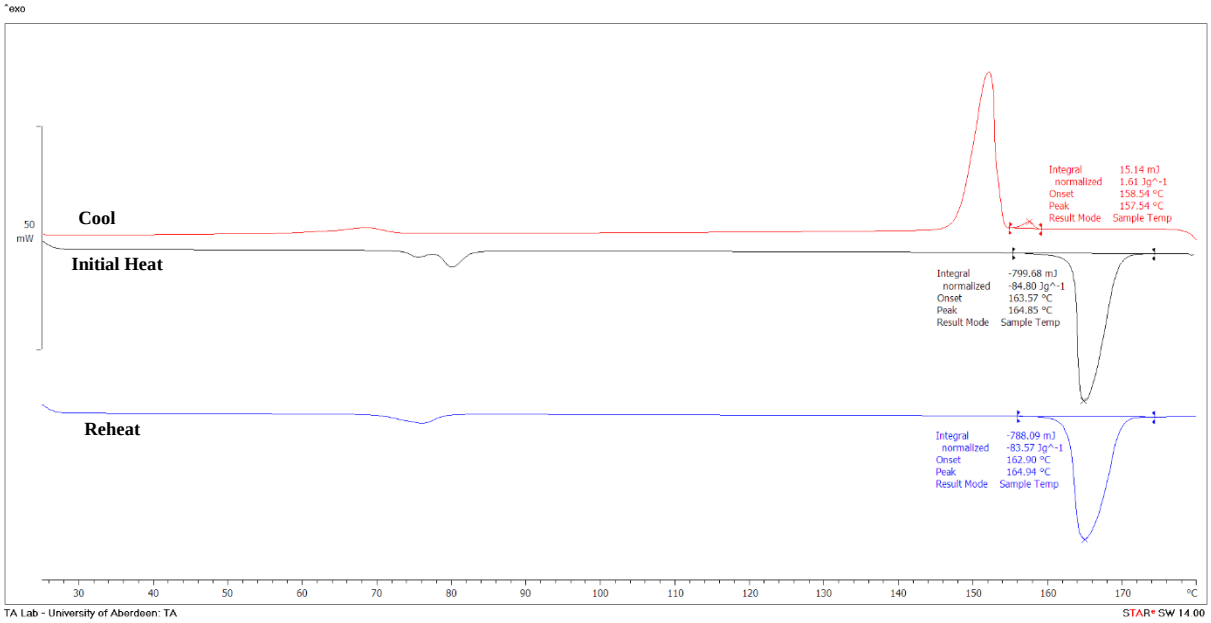
δ_H/ppm (400 MHz, $CDCl_3$): Insolubility precluded analysis

δ_C/ppm (100 MHz, $CDCl_3$): Insolubility precluded analysis

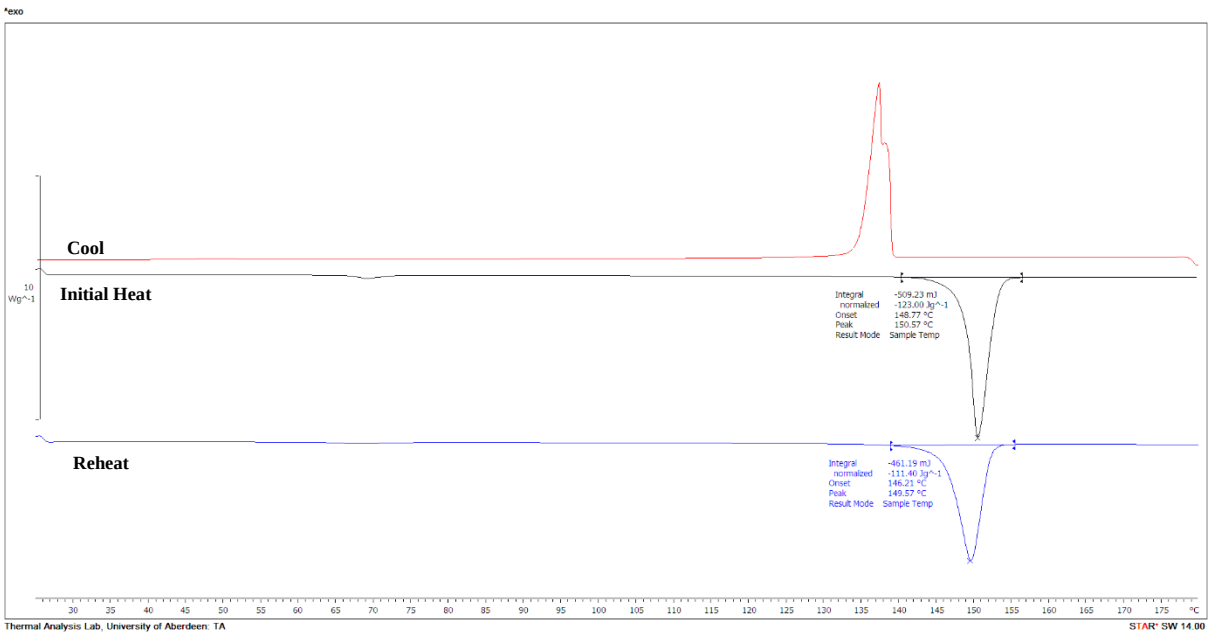
EA: Calculated for $C_{50}H_{68}N_2O_4$: C = 78.91 %, H = 9.01 %, N = 3.68 %; Found: C = 78.93 %, H = 9.02 %, N = 3.60 %

DSC Traces

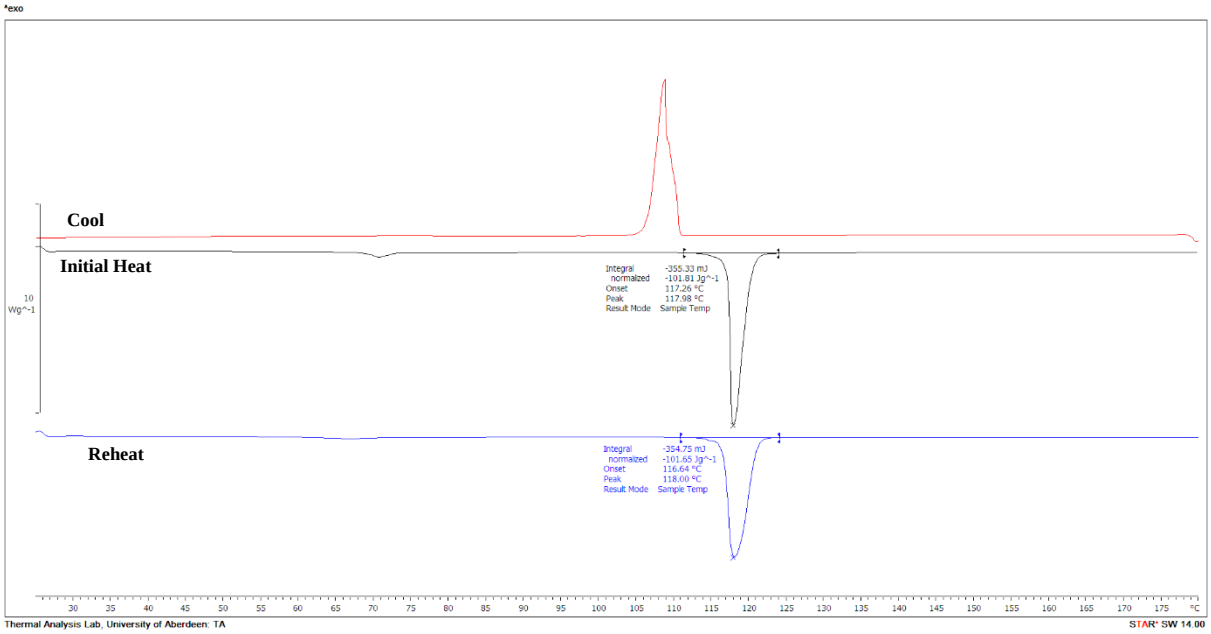
1S.O5O.S1



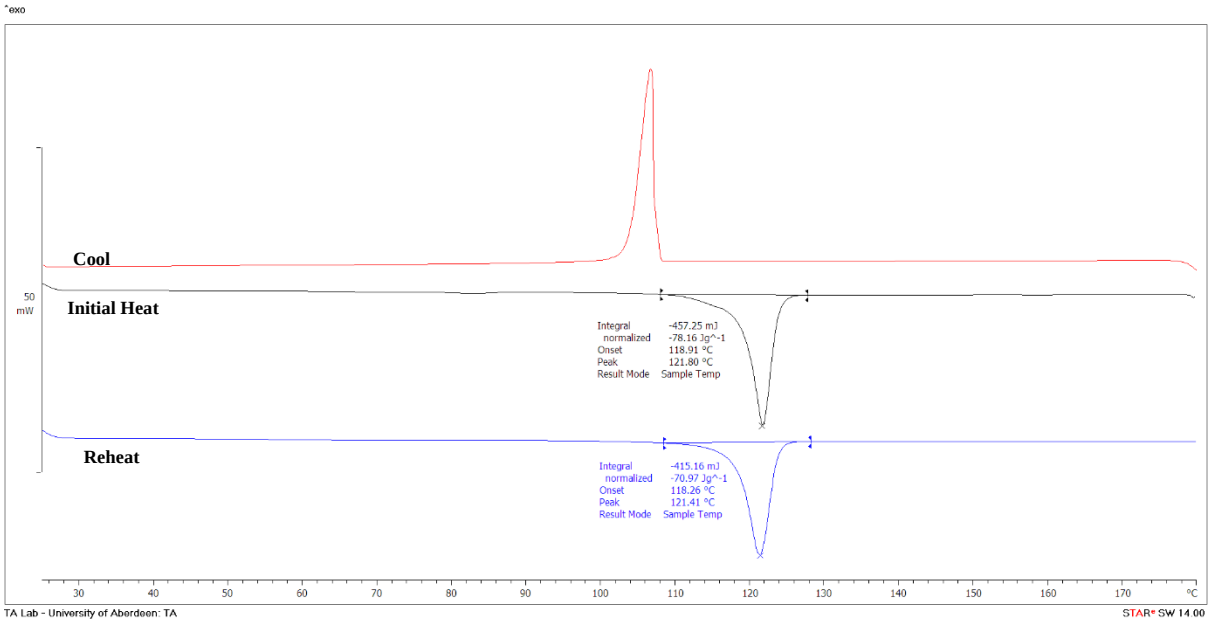
2S.O5O.S2



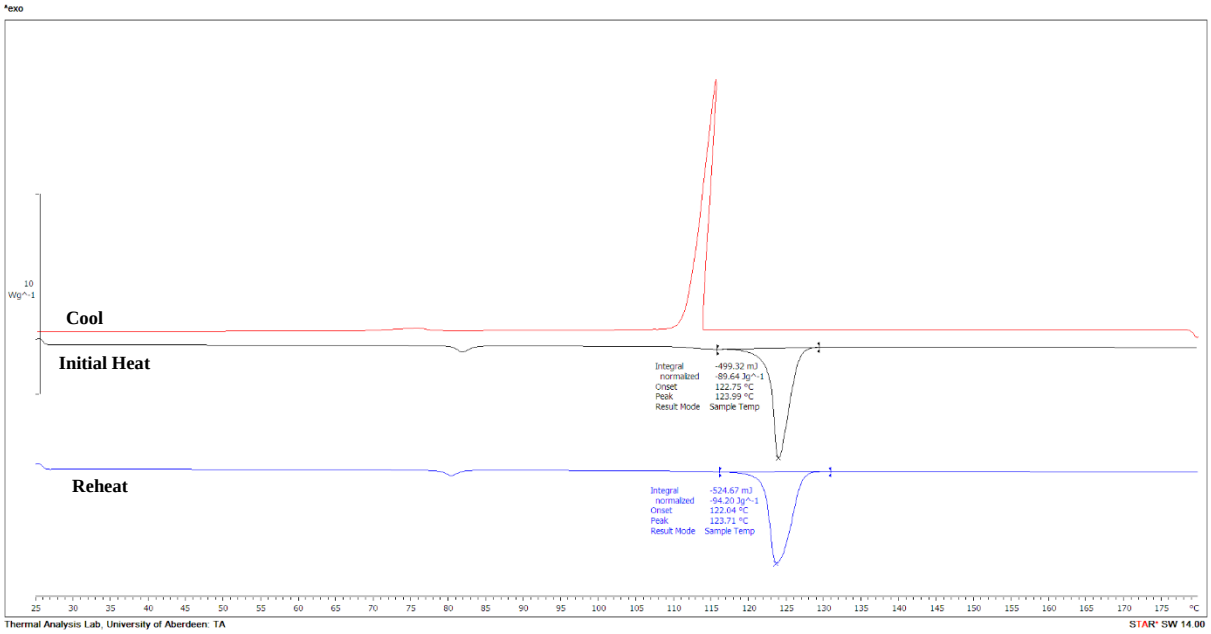
3S.O5O.S3



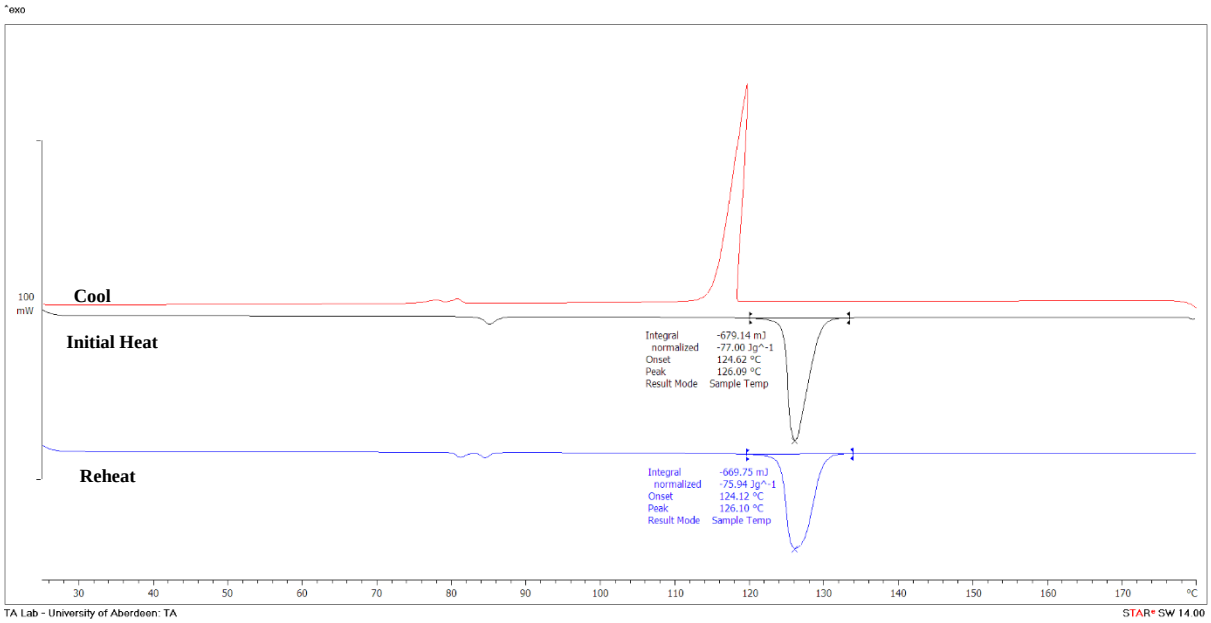
4S.O5O.S4



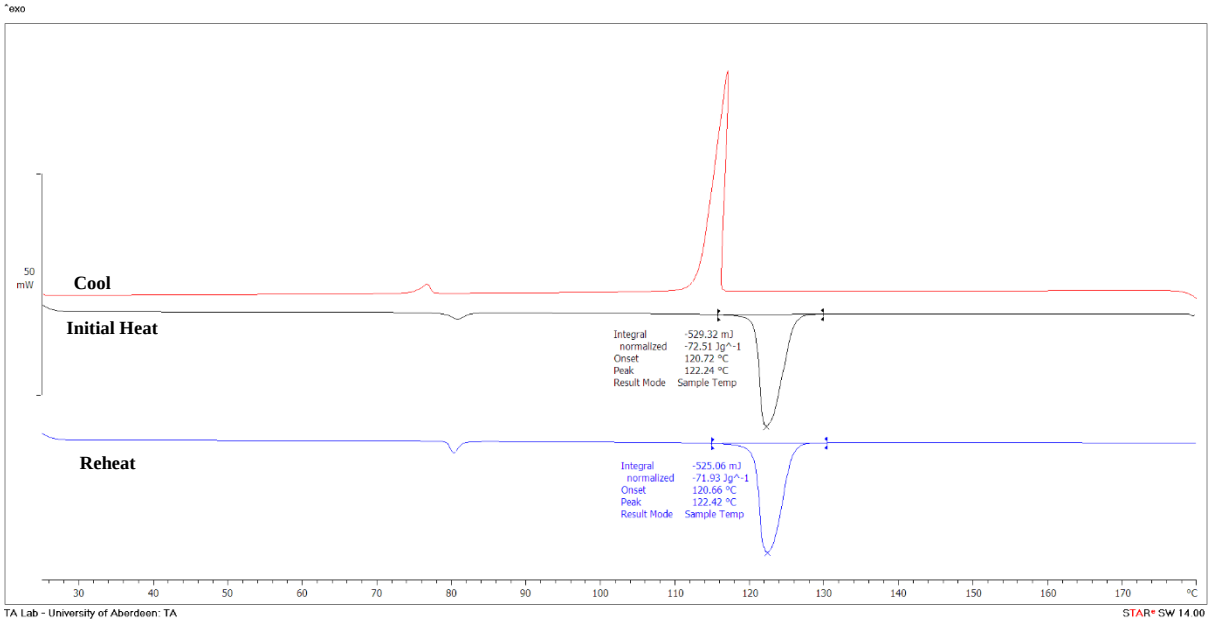
5S.O5O.S5



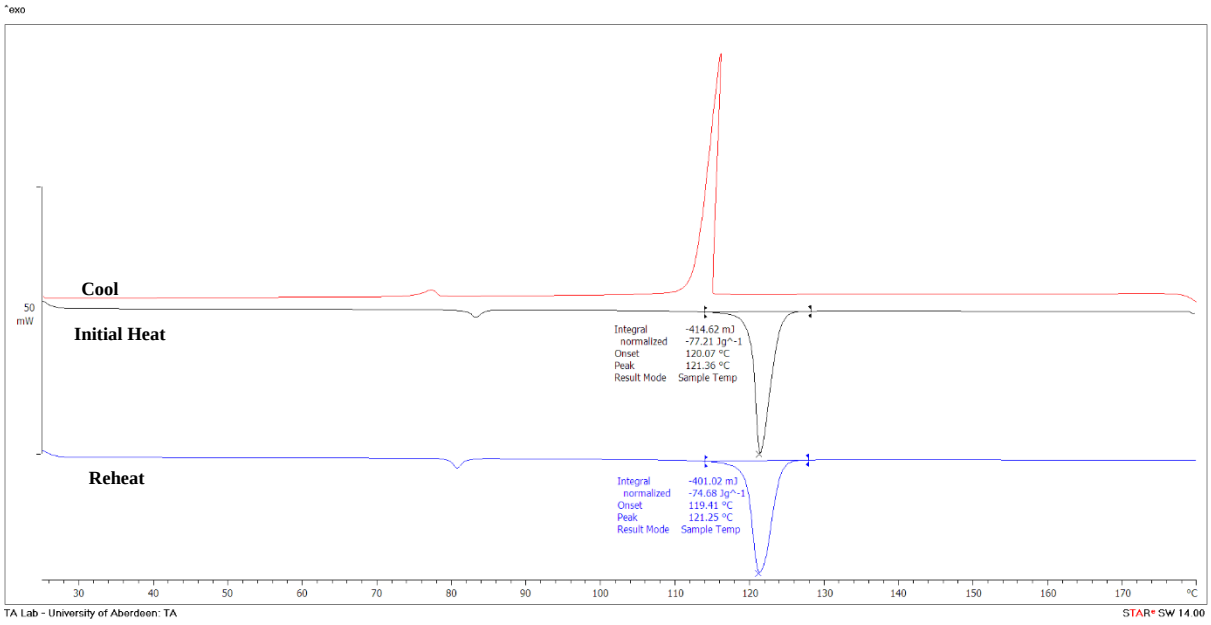
6S.O5O.S6



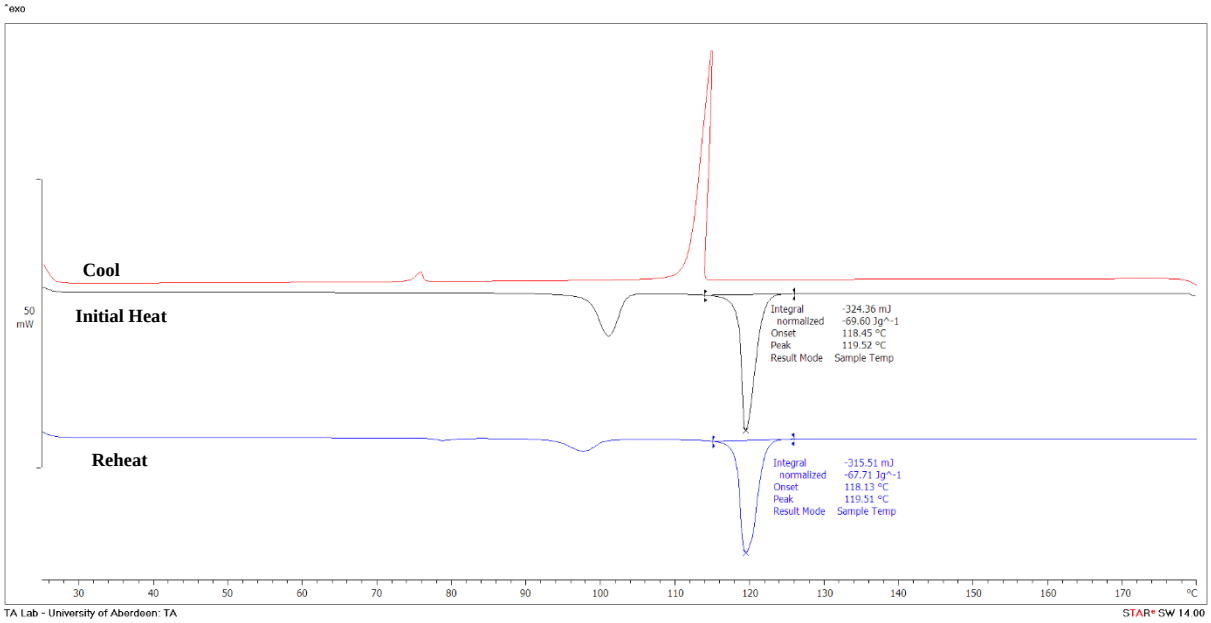
7S.O5O.S7



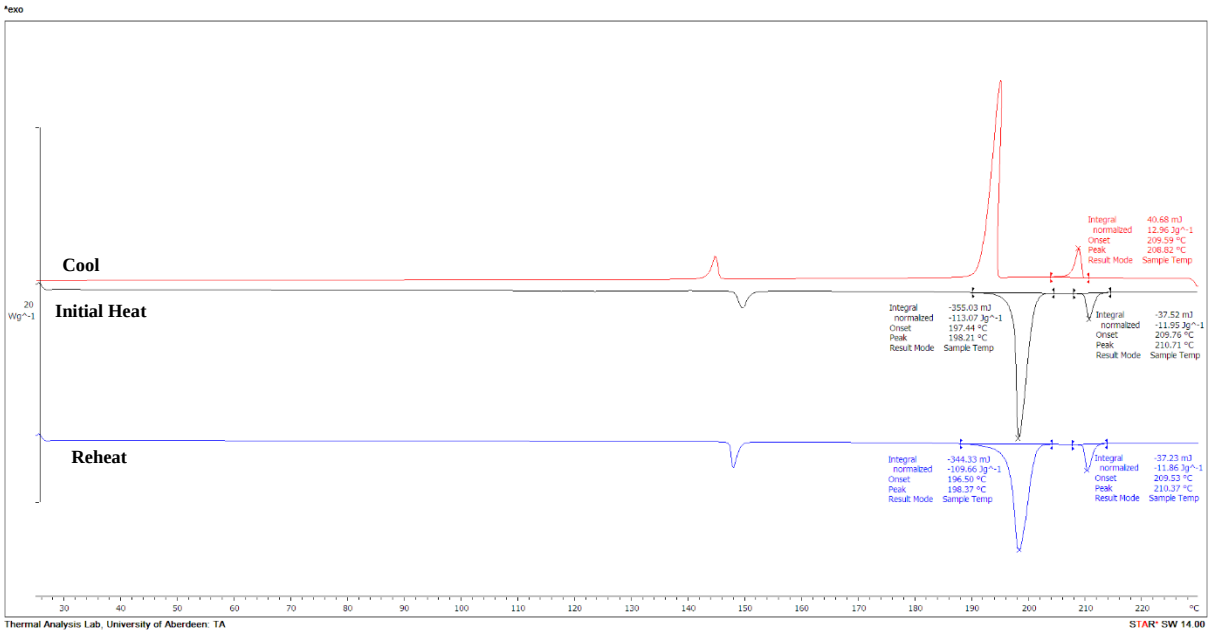
8S.O5O.S8



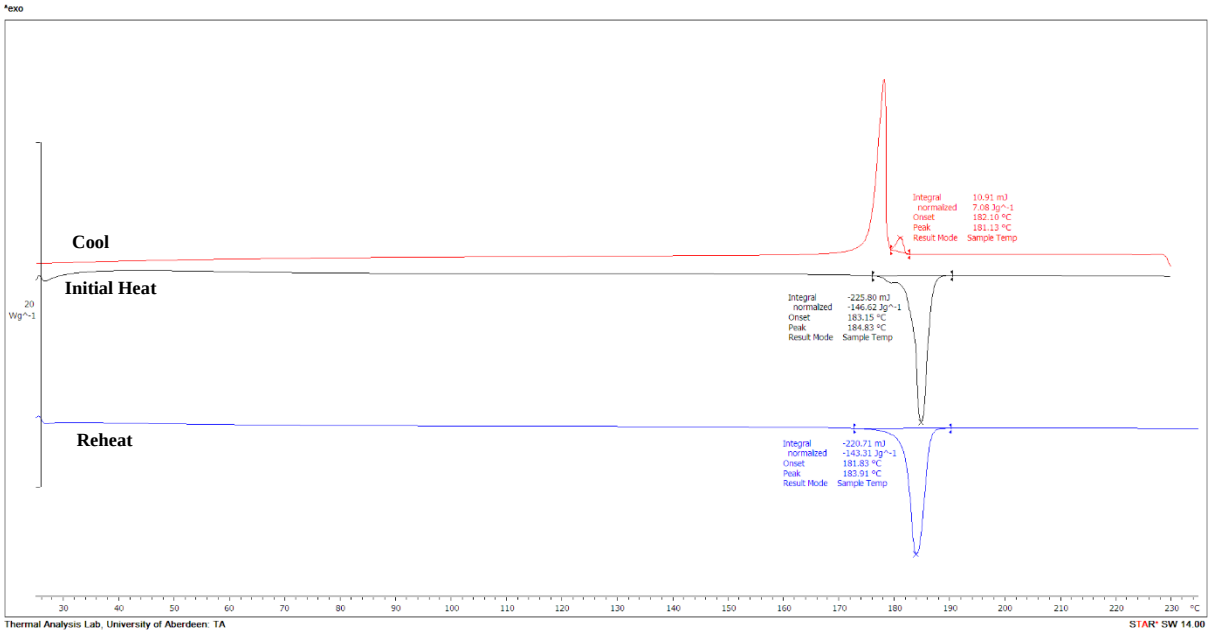
9S.O5O.S9



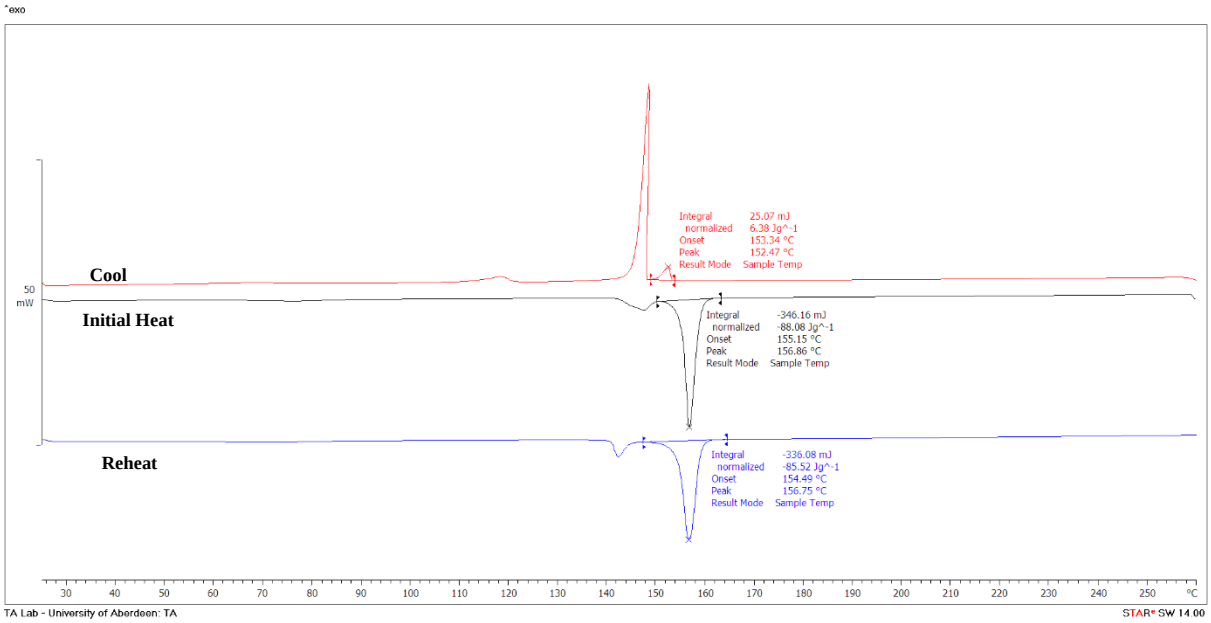
1S.O6O.S1



2S.O6O.S2



3S.O6O.S3



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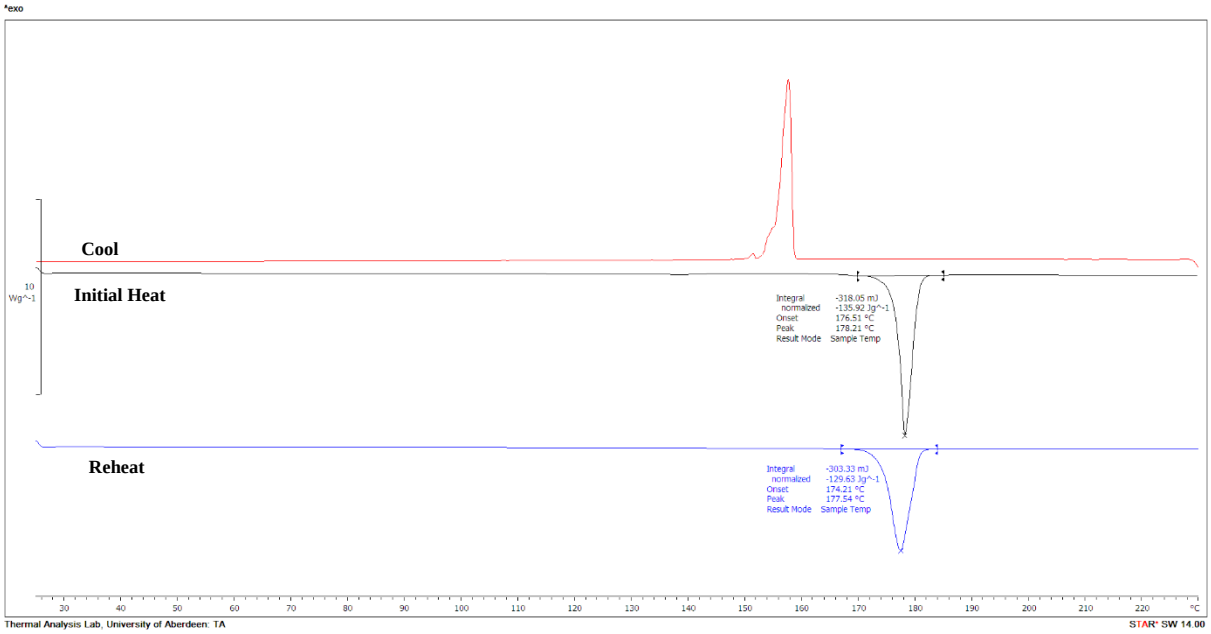
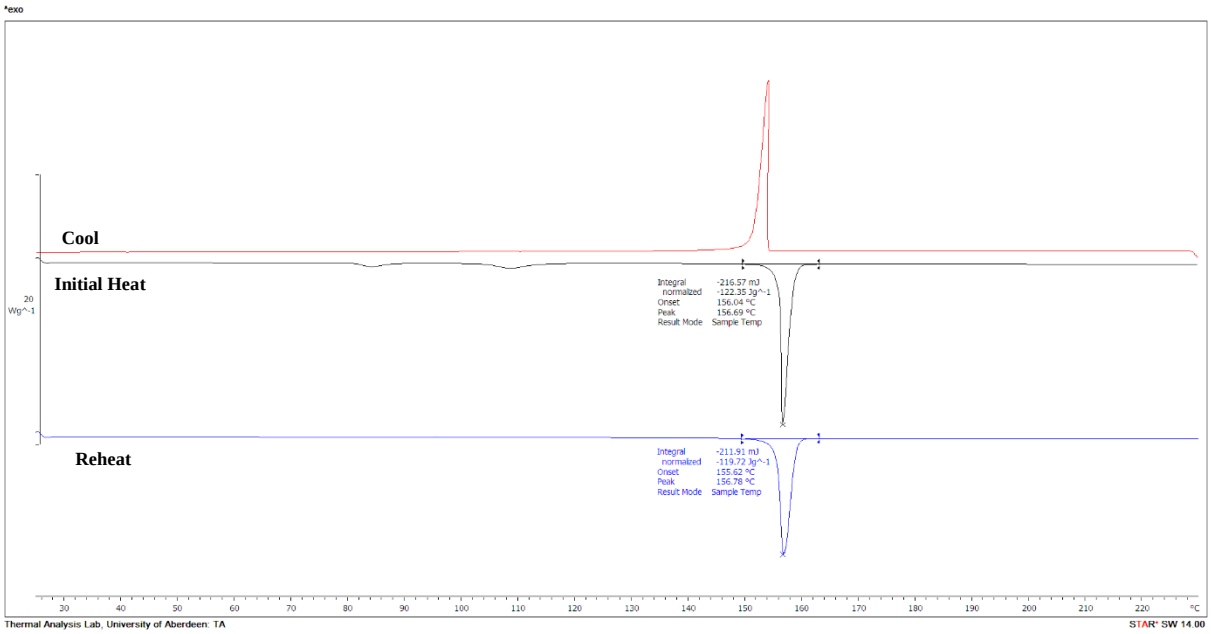
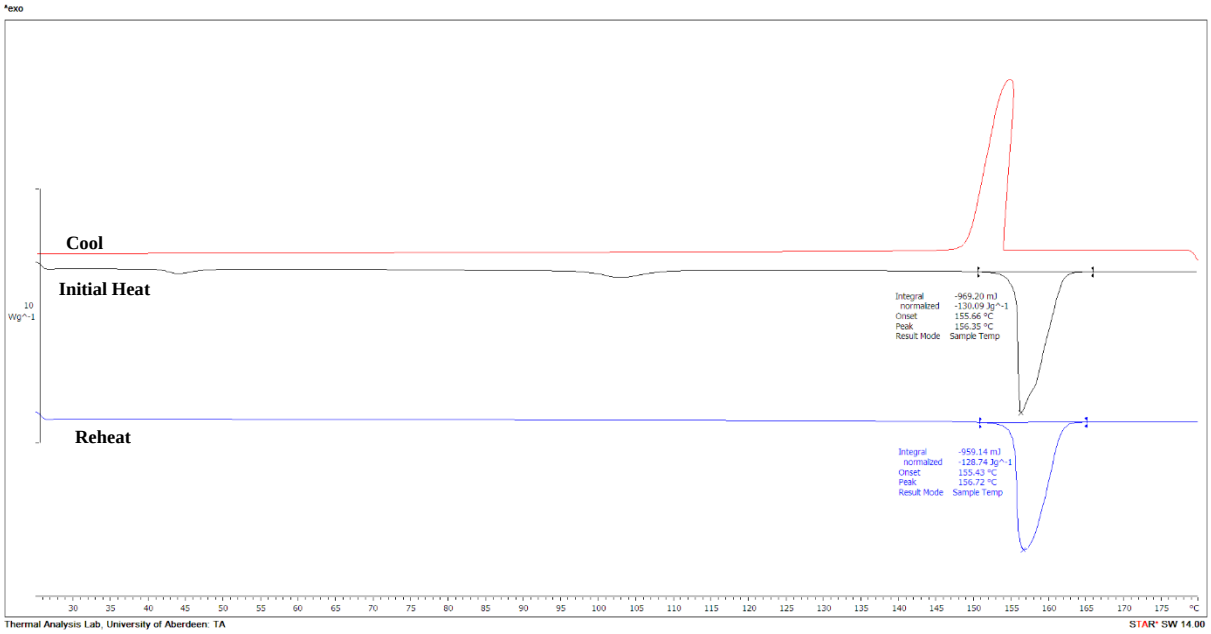


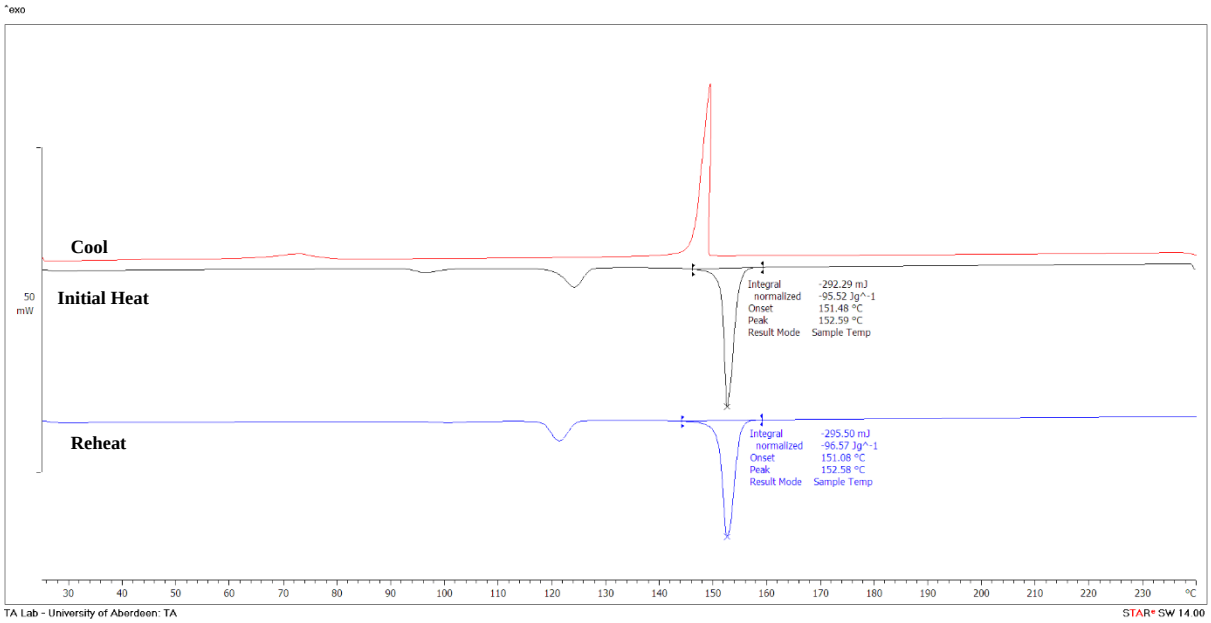
5S.O6O.S5



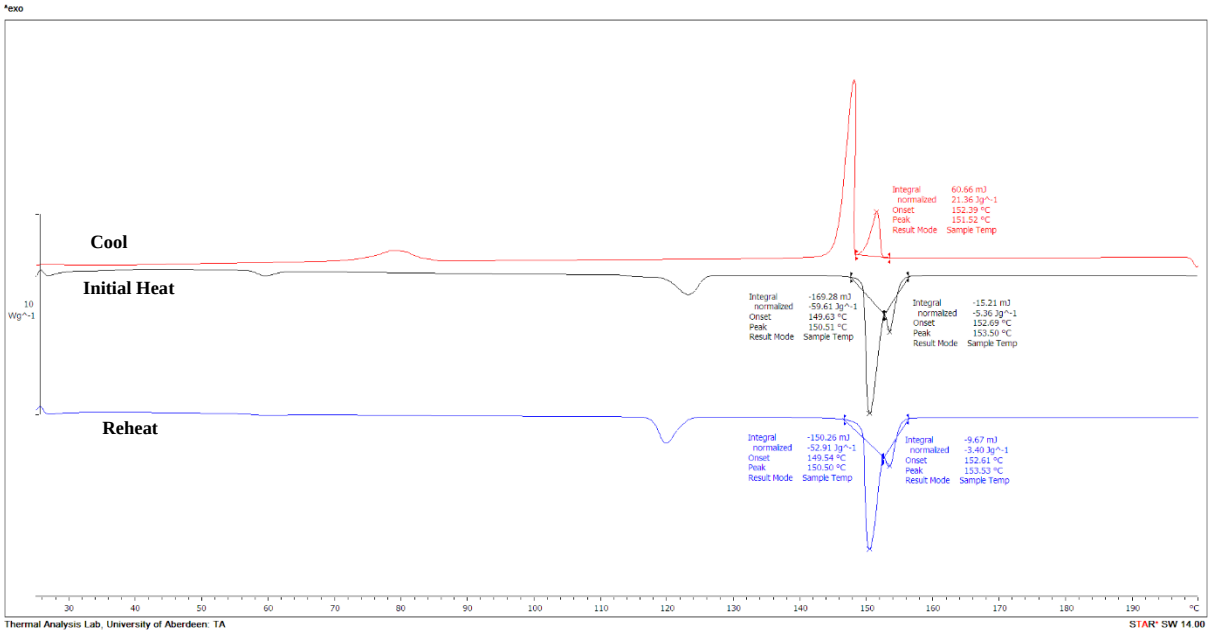
6S.O6O.S6



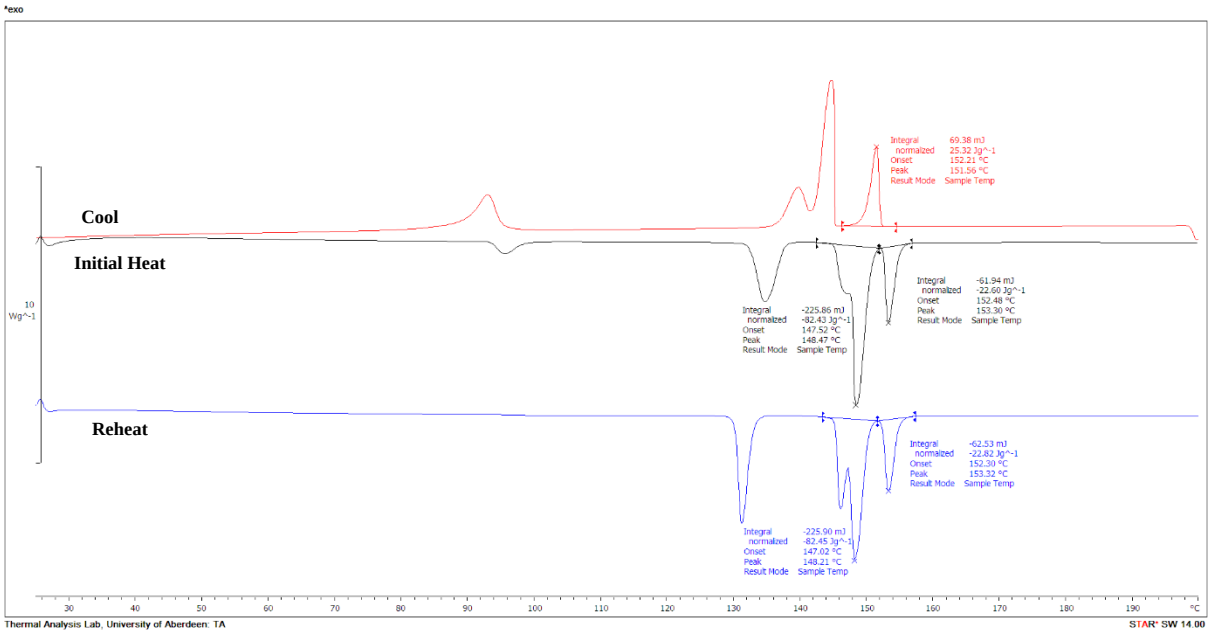
7S.O6O.S7



8S.O6O.S8



9S.O6O.S9



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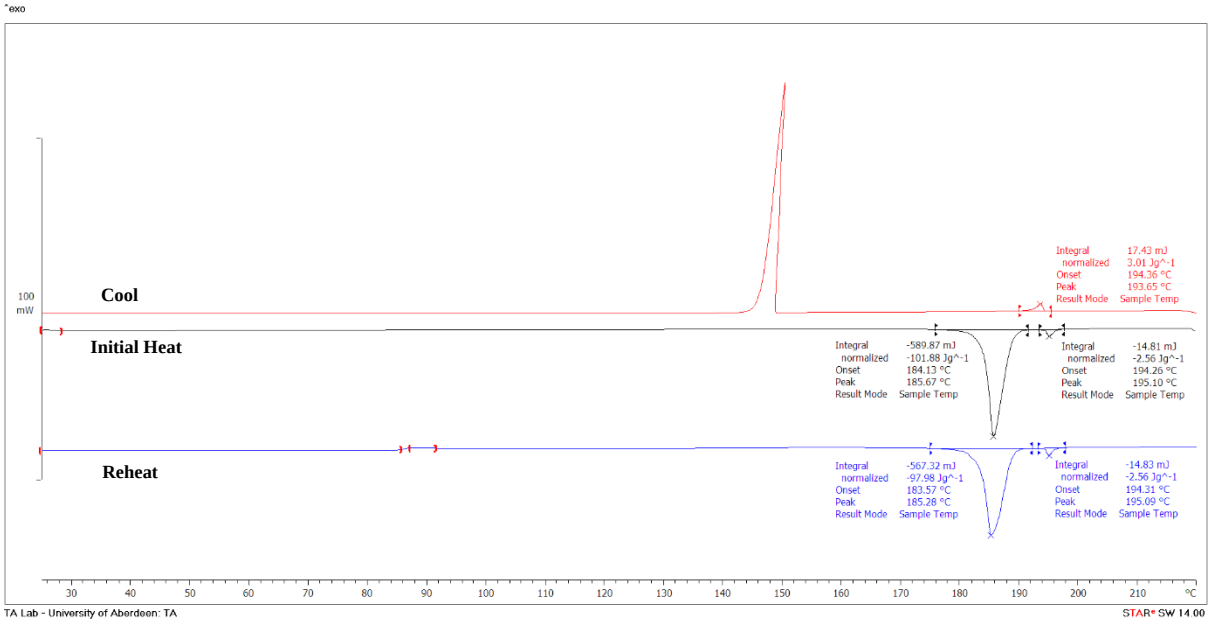
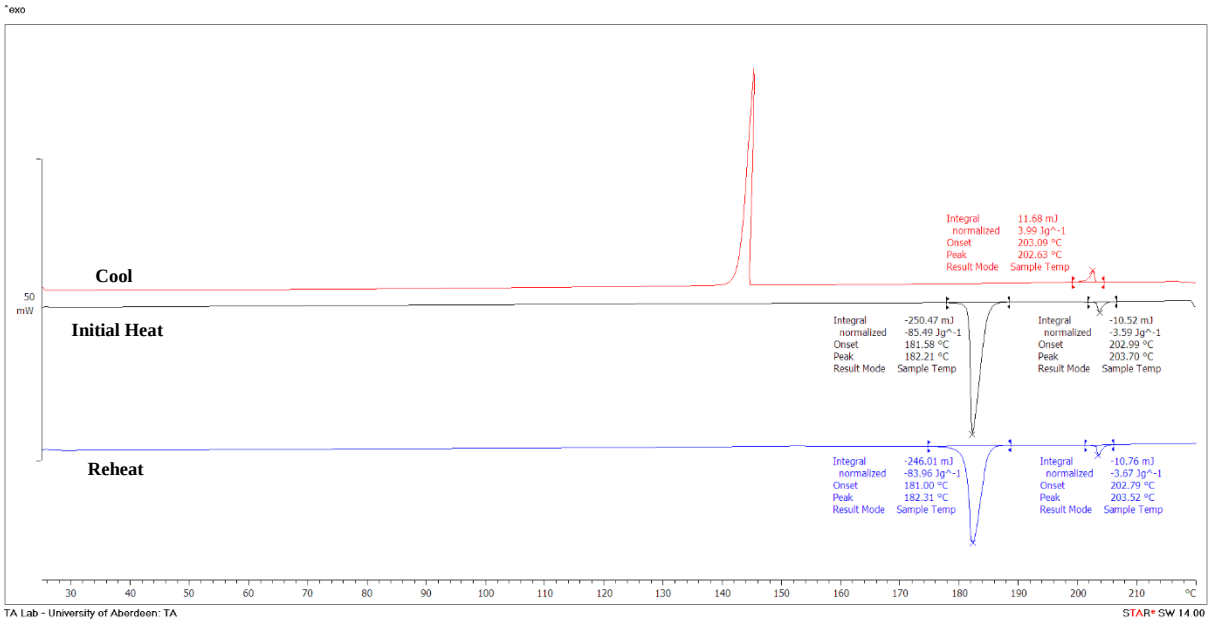
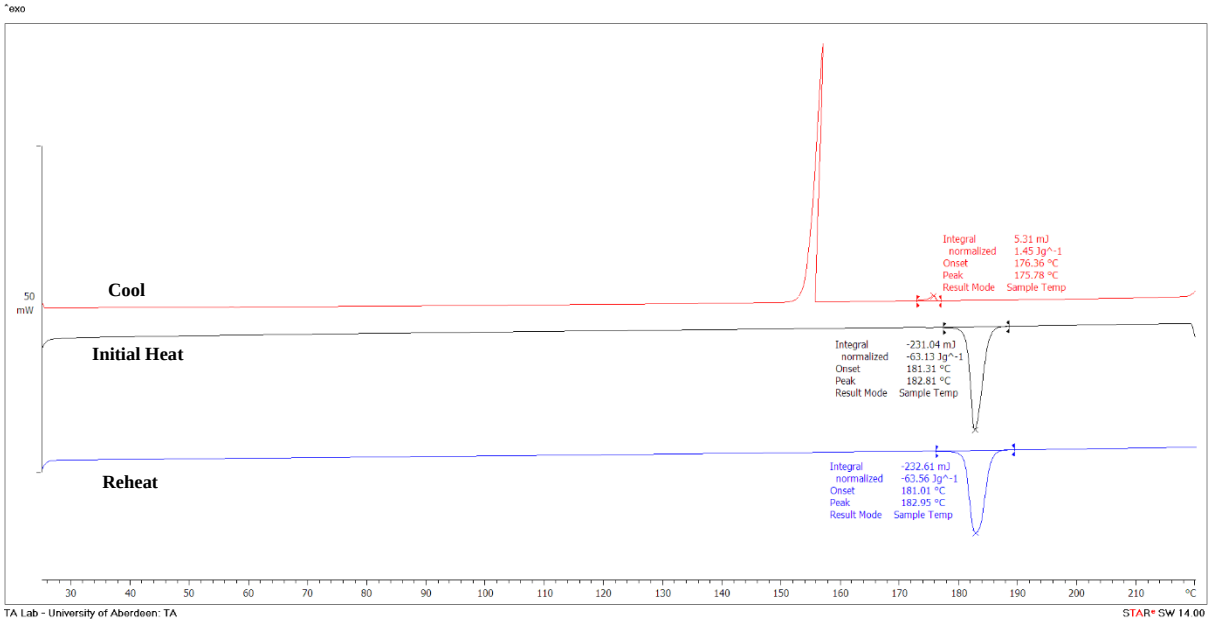


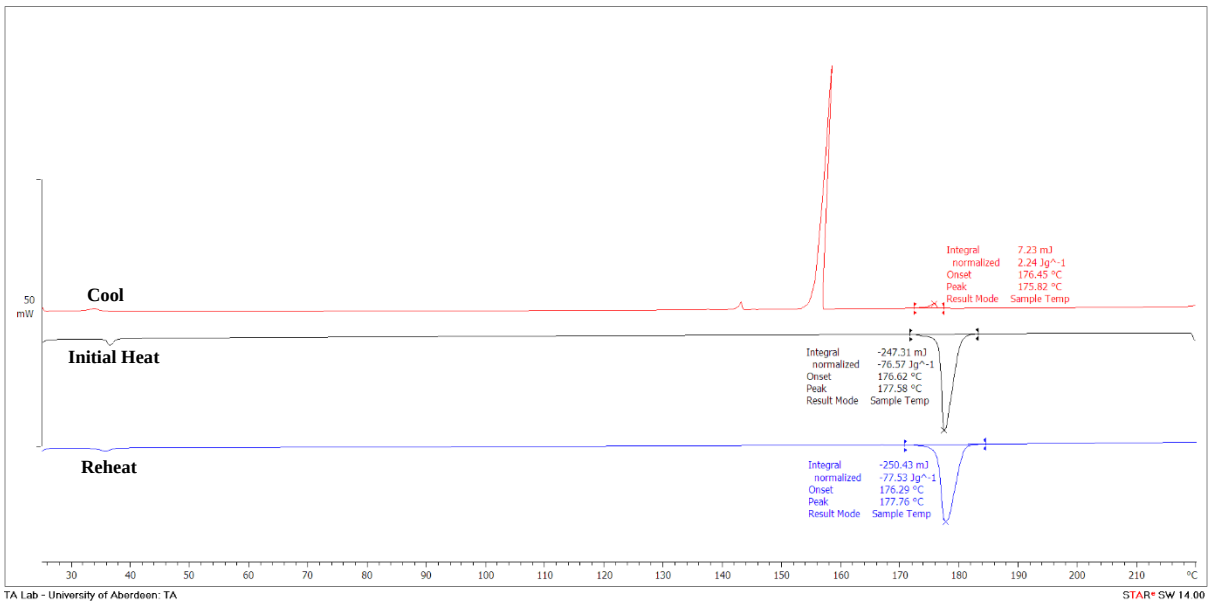
20.050.02



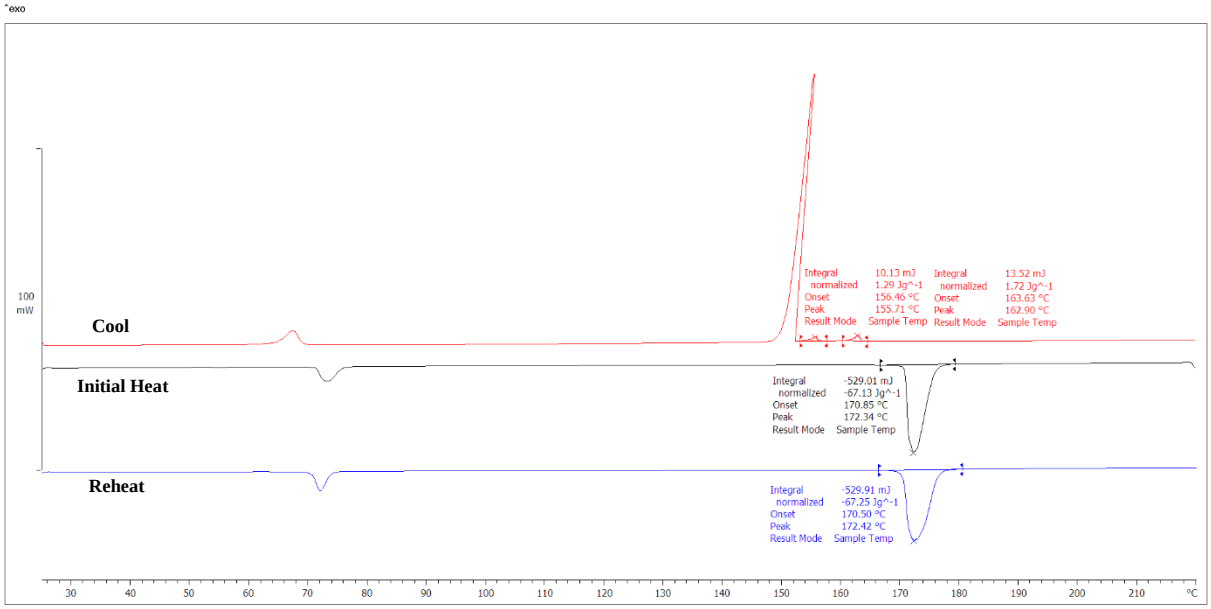
3O.O5O.O3



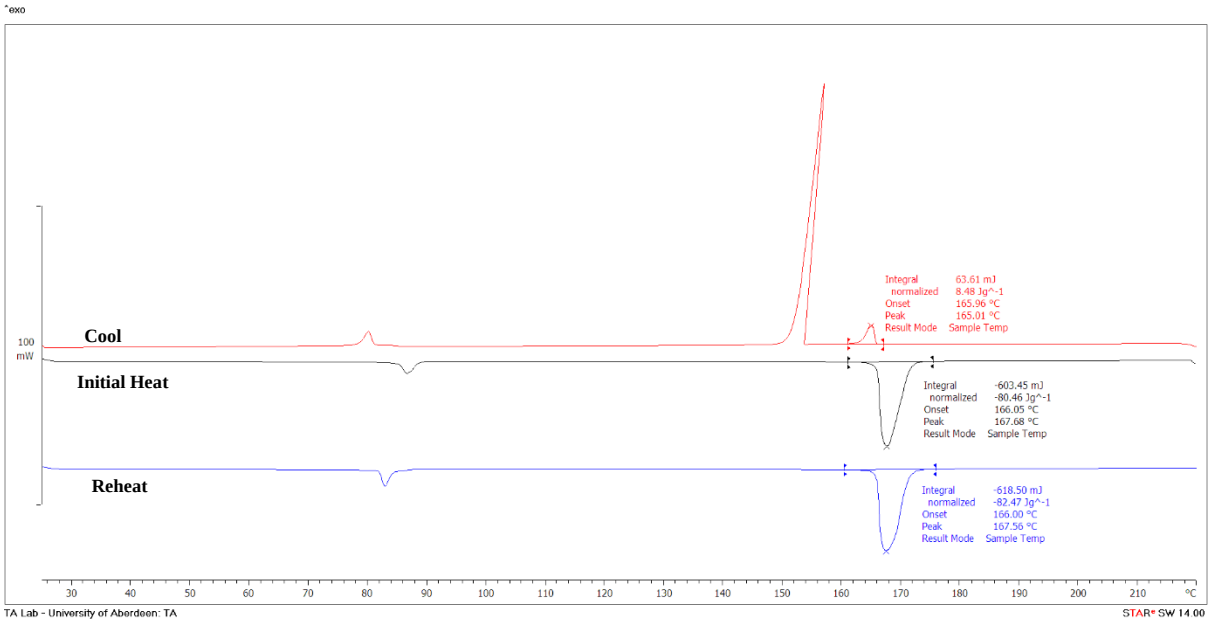
4O.O5O.O4



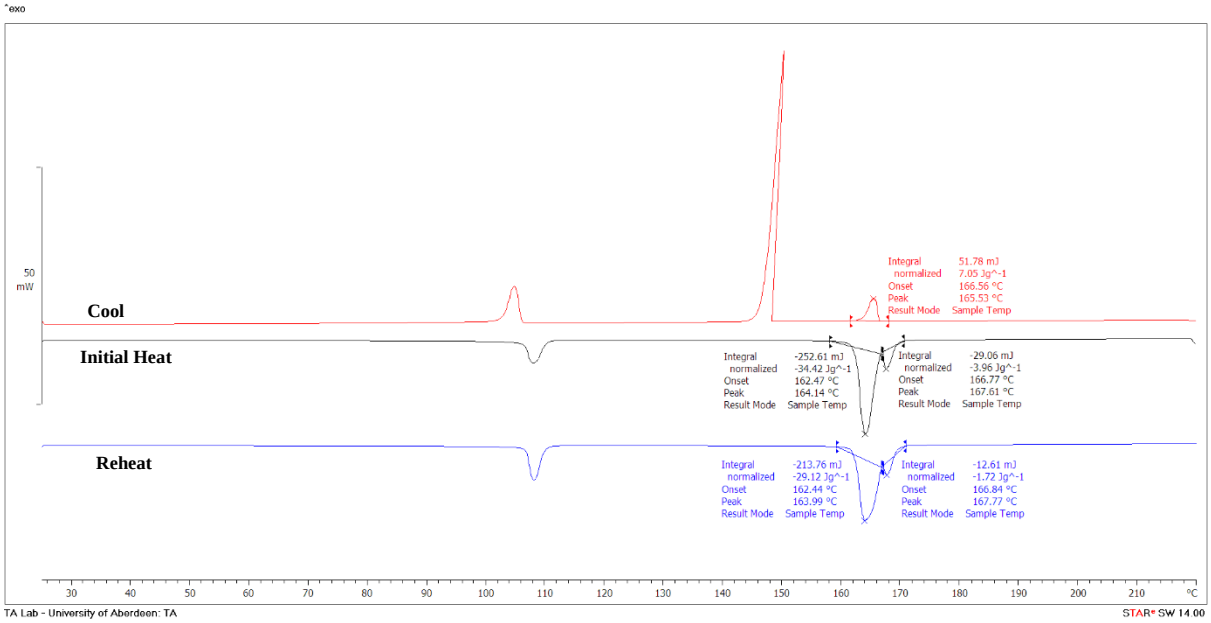
5O.O5O.O5



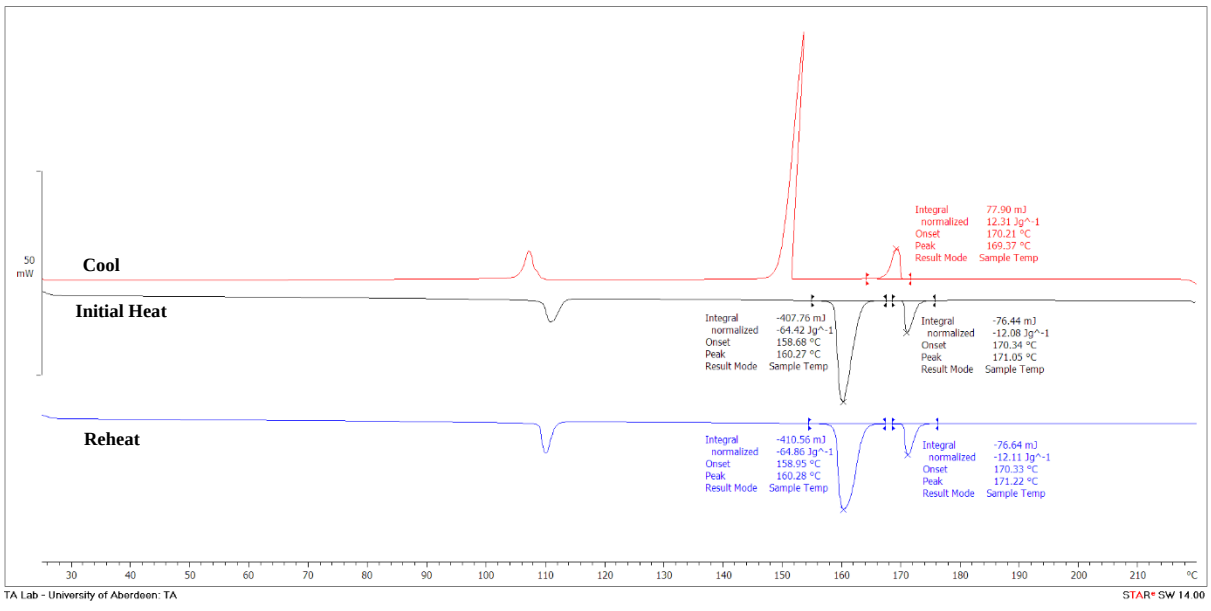
6O.O5O.O6



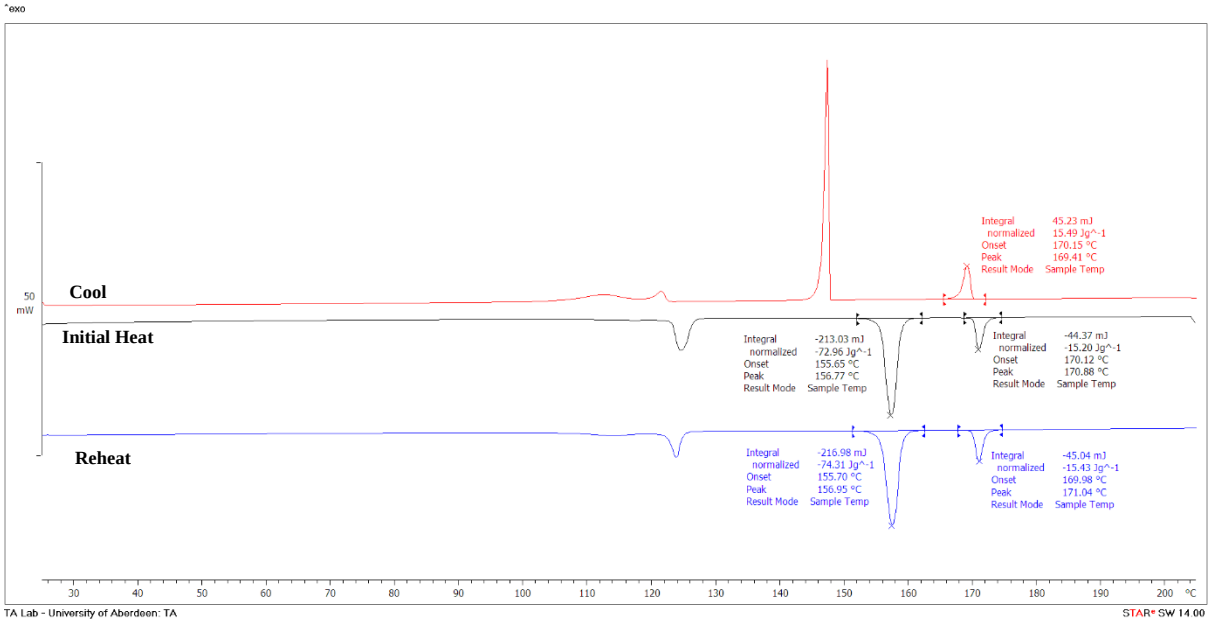
7O.O5O.O7



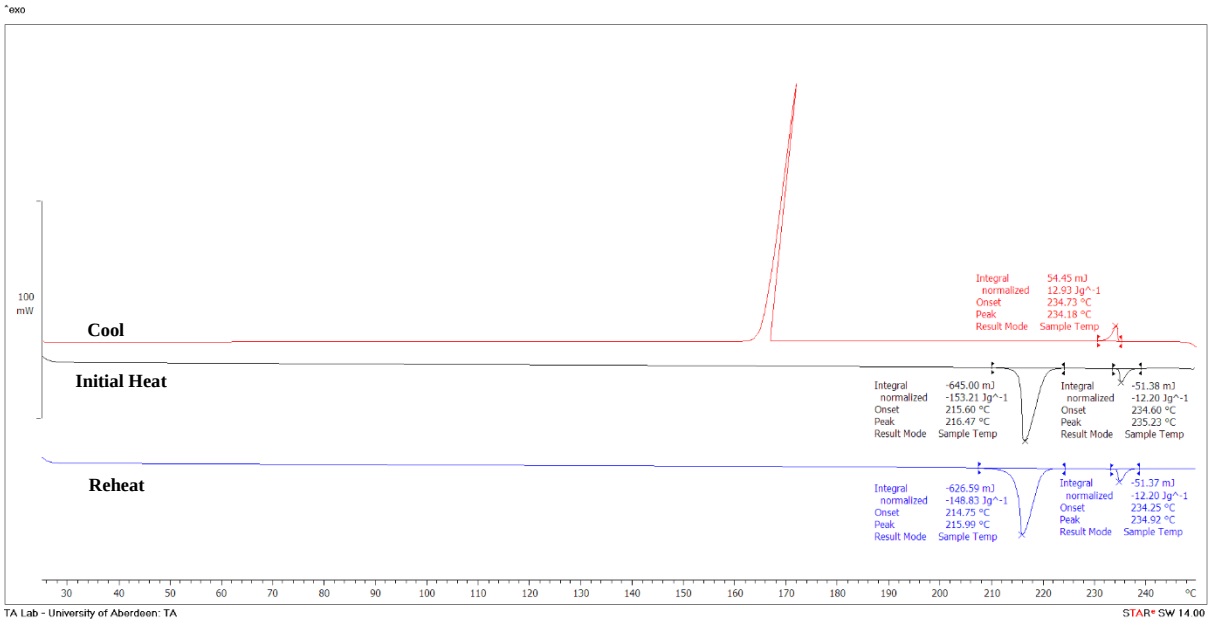
8O.O5O.O8



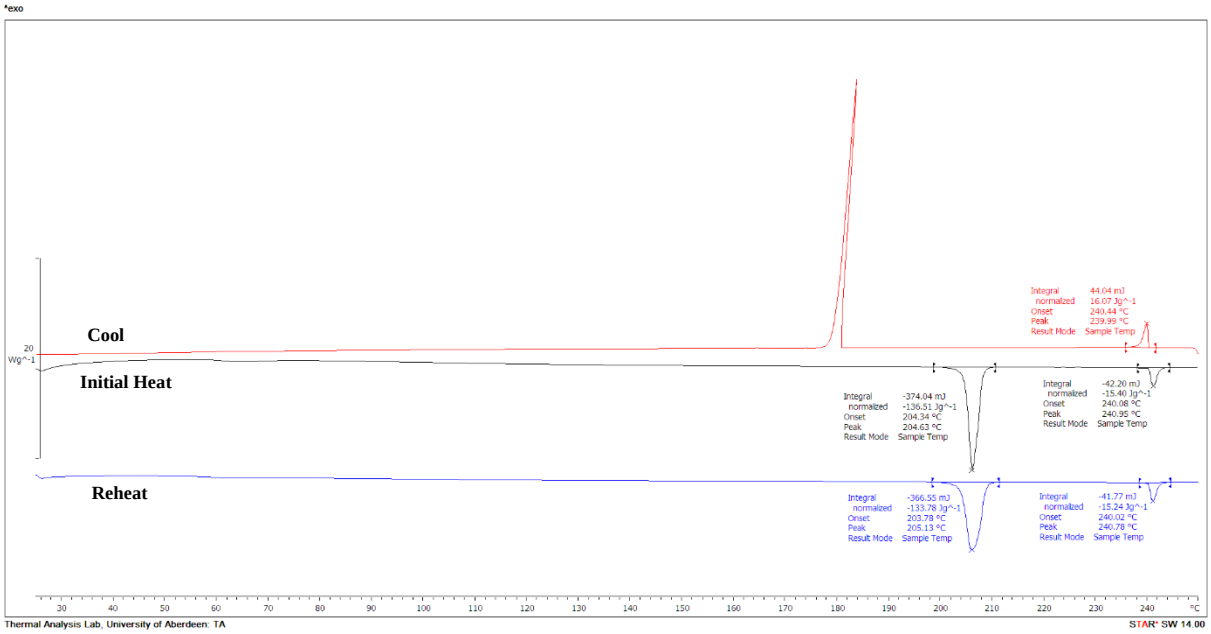
9O.O5O.O9



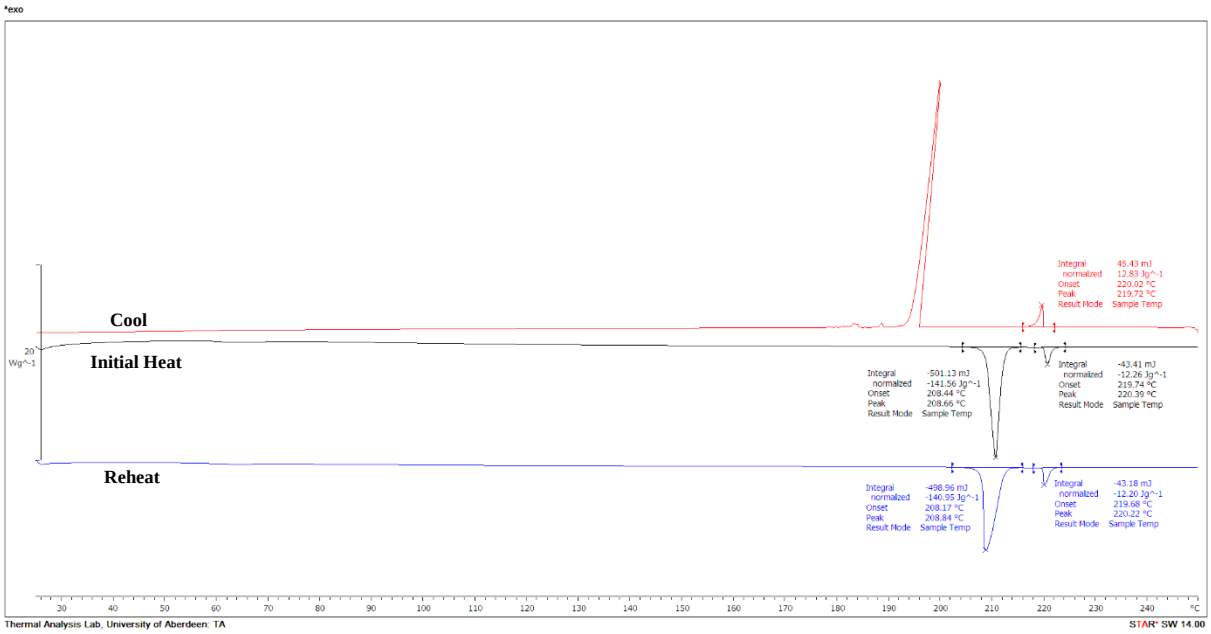
1O.O6O.O1



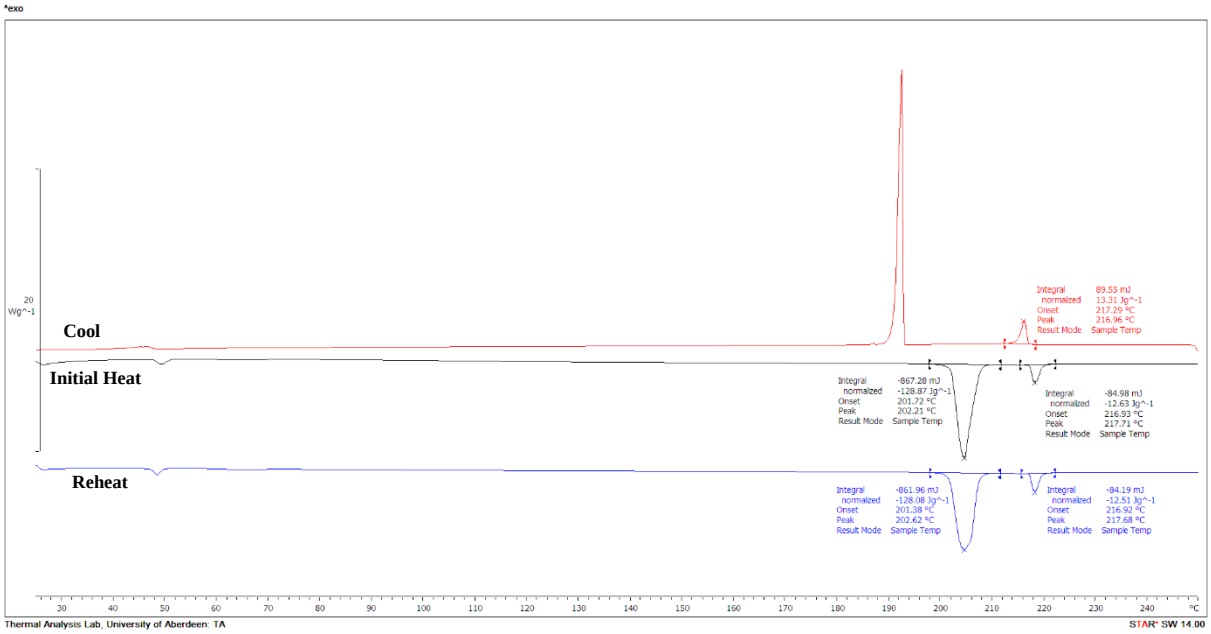
20.060.02



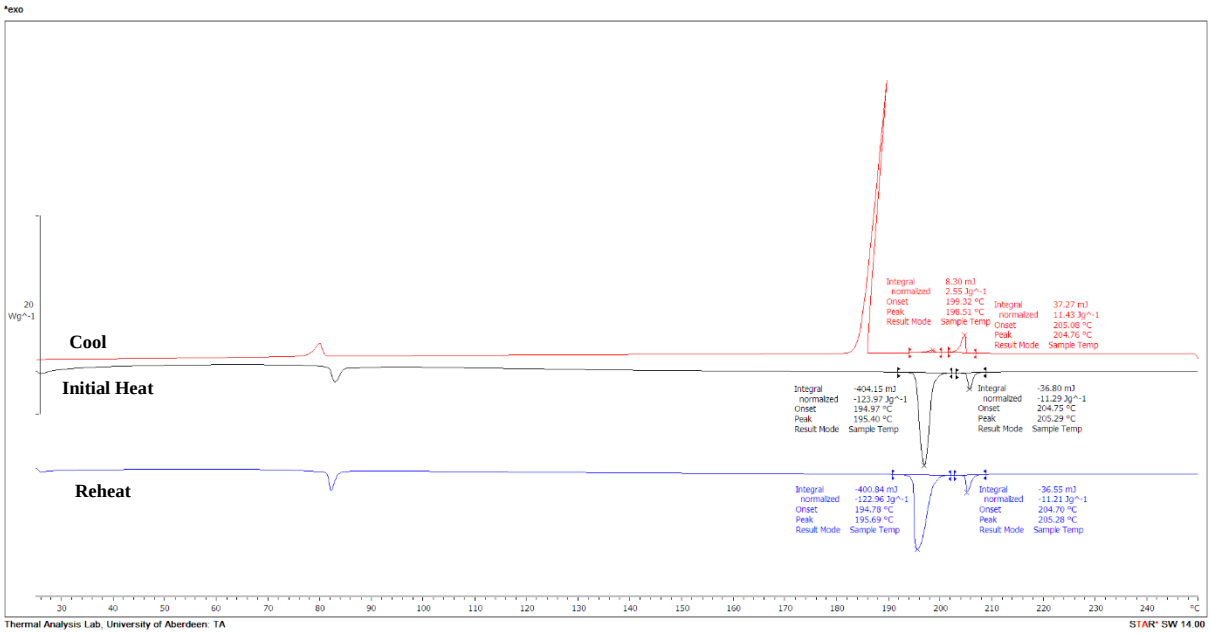
30.060.03



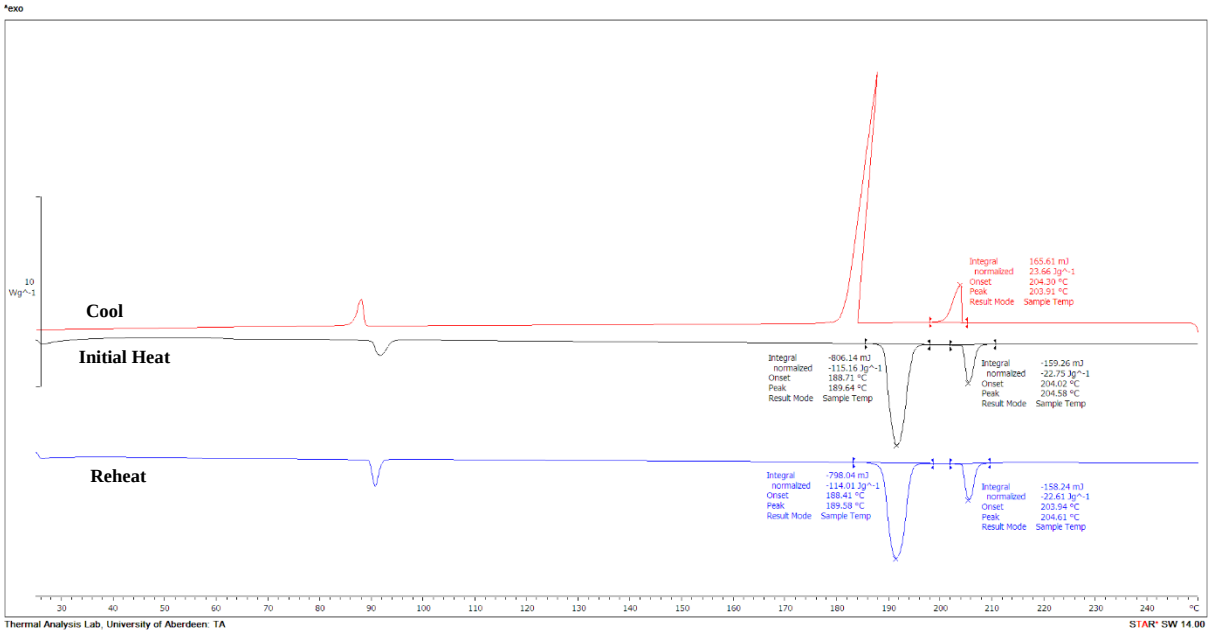
4O.O6O.O4



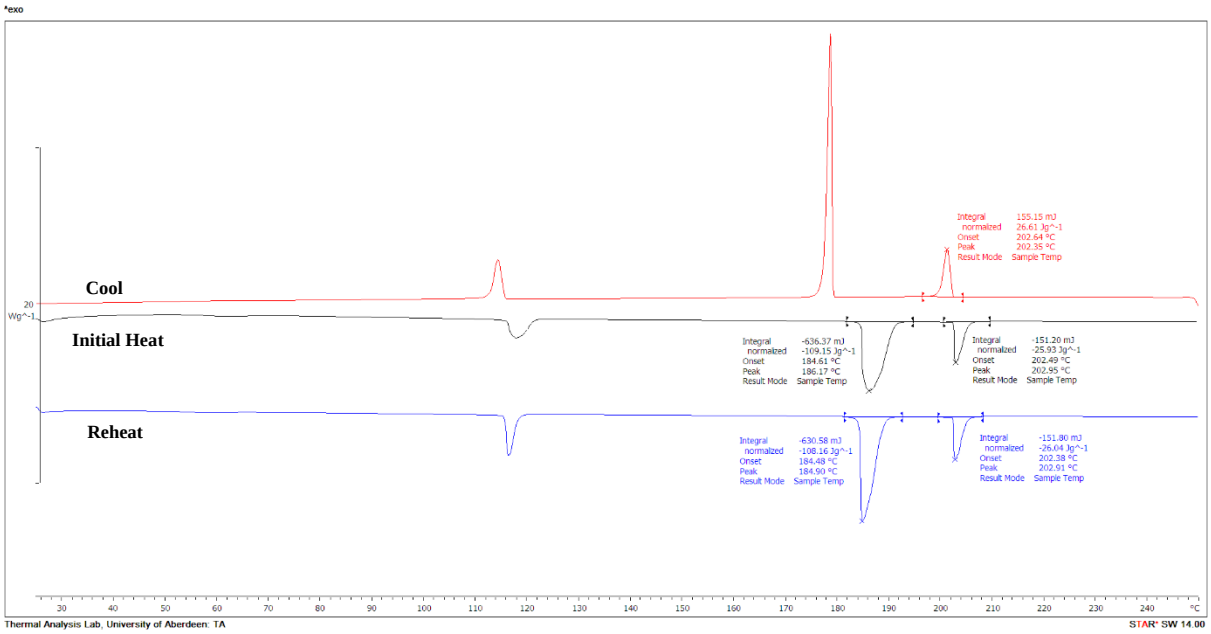
5O.O6O.O5



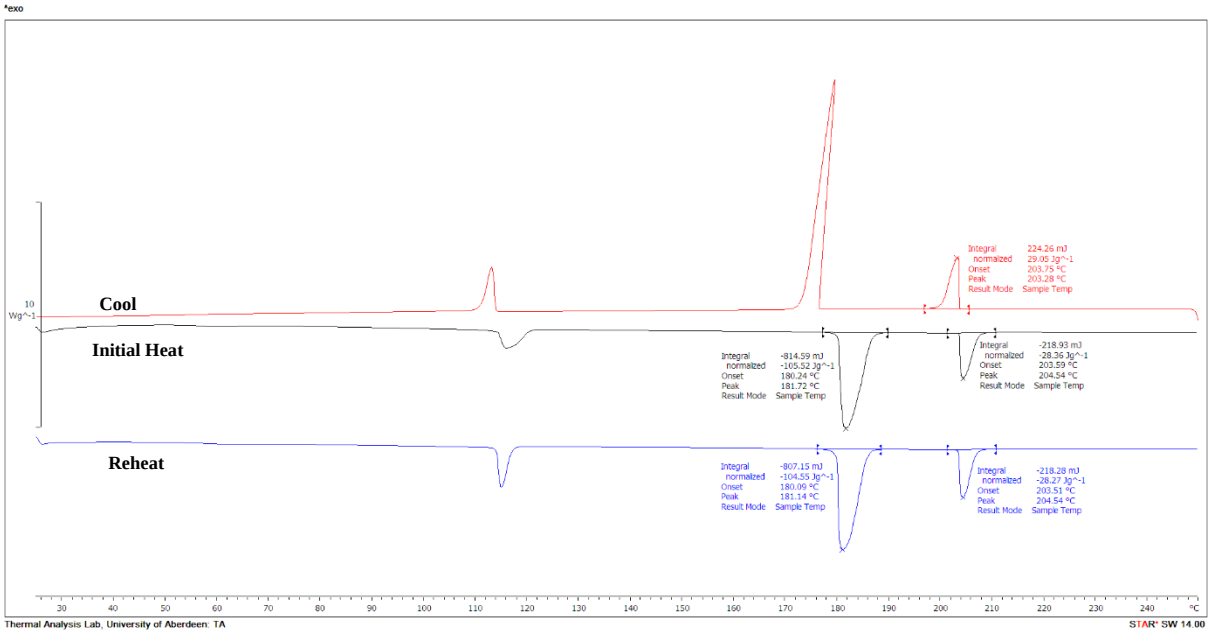
6O.O6O.O6



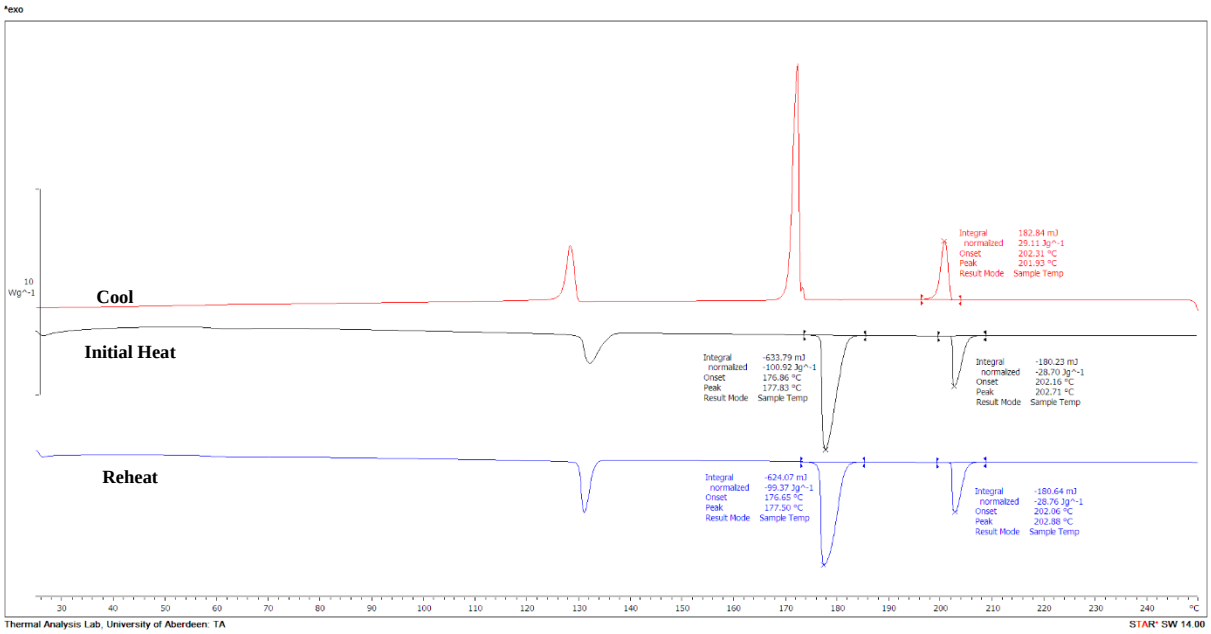
7O.O6O.O7



8O.O6O.O8



9O.O6O.O9



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4. Donahoe, H. B., Benjamin, L. E., Greiff, D. & Fennoy, L. V. Synthesis of Potential Rickettsiostatic Agents. I. 4,4′-Dicarboxy-α,ω-diphenoxyalkanes. *J. Org. Chem.* **26**, 474–476 (1961).
5. Quan, Z. J., Ren, R. G., Da, Y. X., Zhang, Z. & Wang, X. C. Alkylation of SH-heterocycles with Diethyl Phosphite using Tetrachloroethylene as an Efficient Solvent. *Heteroat. Chem.* **22**, 653–658 (2011).
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