SUPPORT INFORMATION SECTION

Bromine-terminated azobenzene liquid crystals.

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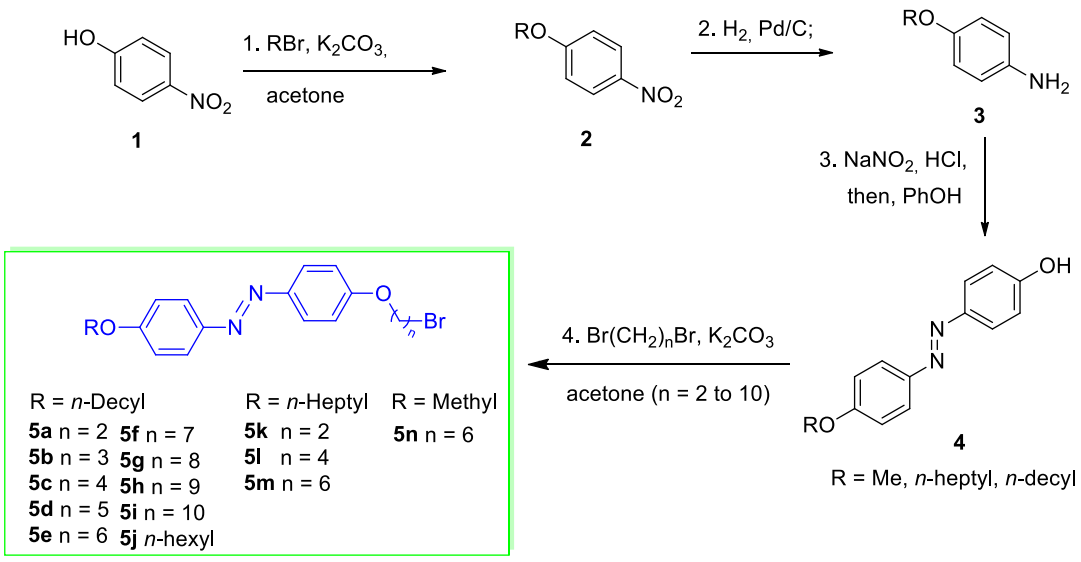
Instrumentation

Differential scanning calorimetry (DSC) analyses were obtained on a DSC 2910 TA instruments.^{1}H NMR and ^{13}C NMR spectra were obtained with $CDCl_3$ as a solvent on a Varian 300 MHz spectrometer. Chemical shifts are given in parts per million (δ) and are relative to the signal of tetramethylsilane (δ = 0 ppm for ^{1}H) as internal reference for solutions in $CDCl_3$. FT-IR/ATR spectra were measured using a Varian 640-IR spectrometer between 4000 and 500 cm^{-1} and with a resolution of 4 cm^{-1}. All spectra were performed with 16 scans and are given in wavenumbers (cm^{-1}).CHN analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The melting points, phase transition temperatures and mesomorphic textures were taken using a polarizing optical microscrope (POM) Olympus BX43, equipped with a Mettler Toledo FP82HT Hot Stage with an FP90 Central Processor at a heating/cooling rate of 10 °C min^{-1} (magnification: 10x).X-ray diffraction (XRD) experiments were performed with the X'Pert-PRO (PANalytical) diffractometer system using the linear monochromatic Cu $K\alpha_1$ beam (λ = 1.5405 Å), with an applied power of 1.2 kVA. The scans were performed in continuous mode from 2º to 30º (2θ angle) and diffracted radiation collected with the X'Celerator detector. The powder was placed on a glass plate and the patterns collected at the mesophase temperature, by cooling from the isotropic. The experimental procedure is described following the Scheme I.



Scheme I. Preparation of Azobenzenes LC.

Synthesis of 1-(decyloxy)-4-nitrobenzene (**2**)

In a round bottom flask with a reflux system dissolve 4-nitrophenol (**1**) (15 mmol) and K_2CO_3 (33 mmol) in acetone. Heat the solution for 30 min. Add a small amount of KI and the 1-bromodecane is slowly added. The reaction mixture is kept in reflux and monitored by TLC. After the 20 h, the mixture is cooled and filtered, washing with heated acetone; the solvent is removed via rotary evaporator and the resultant material is dissolved in DCM and washed with H_2O. The resulting yellow liquid is purified via column chromatography (ether/petroleum ether 5:95) yielded a white solid. Yield: 53%. Melting point = 37°C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (d, 2H, J = 8.8 Hz); 6.93 (d, 2H, J = 9.4 Hz); 4.04 (t, 2 H, J = 6.7 Hz); 1.81 (m, 2 H); 1.53 – 1,21 (m,14 H); 0.87 (t, 3 H, J = 6.4 Hz).

Synthesis of 4-(decyloxy)aniline (**3**)

In a inox reactor with 50 ml of dry methanol, add 4,5 mmol of nitrocompound 1-(decyloxy)-4-nitrobenzene (**2**) and 10% in weight of Pd/C. Close the reactor and load with 9 bar of H_2. Keep the system under agitation until the total use of H_2 (from 24 to 48h). After the reaction completion, the reaction mixture is filtered with celite. The produced reddish liquid is distillated in a rotary evaporator, resulting in quantitative reddish brown solid.^{1}H NMR (300 MHz, $CDCl_3$): 6.77(d, 2 H, J = 9.0 Hz); 6.66 (d, 2 H, J = 9.0 Hz); 3.90 (t, 2 H, J = 6.6 Hz); 2.98 (s broad, NH_2); 1.76 (m, 2 H); 1.59 –1.17 (m, 14 H); 0.91 (t, 3 H, J = 6.7 Hz)

*General procedure to the synthesis of (E)-4-((4-(alkoxy)phenyl)diazenyl)phenols (**4a-c**).*

3,0 mmol of 4-alkoxyaniline (**3**) was dissolved in 4mL of HCl 6 M at 0°C. Maintaining the temperature at 0 – 5°C, add a cold $NaNO_2$ (4.8 mmol) on water (1.5 mL) under agitation to the solution. The diazonium salt formation can be control by starch iodide paper. After the formation of diazonium salt, add, carefully, a cold phenol solution (3.6 mmol) into 2.5 mL NaOH 7 M maintaining the temperature between 0 – 5°C. Let stir for around 30 min (at least) and acidify the resulting mixture with concentrated HCl; the resulting precipitate is filtered, washed with water and dry naturally. After the solid is dried, it's washed with petroleum ether. Produces a reddish brown solid.

(E)-4-(4-(methoxyphenyldiazenyl)phenol (**4a**). Yield: 92%. Melting point = 137-140 °C. IR (KBr, υ_{max}, cm^{-1}): 3414, 2846, 1599, 1490, 1435, 1460, 1240. ^{1}H NMR (300 MHz, $CDCl_3$): 7.90-7.85 (m, 4H), 7.02-6.97 (m, 4H), 3.88 (s, 3H).

(E)-4-(4-(heptyloxyphenyldiazenyl)phenol (**4b**). Yield: 54%. Melting point = 92-94 °C. IR (KBr, υ_{max}, cm^{-1}): 3465, 2921, 1600, 1584, 1473, 1249. ^{1}H NMR (300 MHz, $CDCl_3$): 7.79-7.71 (m, 4H), 7.10-6.85 (m, 4H), 3.93-3.89 (t, 2H, 7.5 Hz), 1.74-1.69 (m, 2H), 1.40-1.23 (m, 8H). 0.83-0.79 (t, 3H, j + 7.3 Hz).

(E)-4-(4-(decyloxyphenyldiazenyl)phenol (**4c**). Yield: 70%. Melting point = 98-104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.88 (d, 2 H, J = 8.8 Hz); 7.84 (d, 2 H, J = 7.9 Hz); 7.01 (d, 2H, J = 8.8 Hz); 6.95 (d, 2H, J = 7.6 Hz); 4.05 (t, 2 H, J = 6.6 Hz); 1.84 (m, 2H); 1.59 – 1.20 (m, 14 H); 0.92 (t, 3 H, J = 6.6 Hz).

*General procedure to the synthesis of (E)-1-(4-(bromoalkoxy)phenyl)-2-(4-(alkoxyphenyl)diazenes (**5a-i**).*

(E)-4-(4-(alkoxyphenyl)diazenyl)phenol (**4**) (0.5 mmol) and anhydrous K_2CO_3 (1.6 mmol) were dissolved into acetone in a round bottom flask with reflux system under stirred for 15 minutes. α,ω-dibromoalkane (3 mmol) was added drop wise in the reaction mixture and the system was refluxed from 15 to 48h (monitored by TLC). After the reaction is done, the still hot solution is filtered and washed with hot acetone. The filtrate was collected and evaporated in rotary evaporator; added cold petroleum ether to the concentrated extracts and the resulting precipitate was filtered and washed three times with this same solvent. Recrystallization in ethanol with a few drops of water.

(E)-1-(4-(2-bromoethyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5a**): Yield: 61%. Melting point = 96.0 °C. IR (KBr, υ_{max}, cm^{-1}): 2985, 2935, 2854, 1600, 1265, 748, 704. ^1H NMR (300 MHz, $CDCl_3$): 7.92 (m, 4 H); 7.03 (m, 4 H); 4.39 (t, 2 H, J = 6.3 Hz); 4.06 (t, 2H, J = 6.6 Hz); 3.70 (t, 2H, J = 6.3 Hz); 1.84 (m, 2 H); 1.57 - 1.22 (m, 14 H); 0.92 (t, 3 H, J = 6.7 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.3; 159.8; 147.4; 146.7; 124.4; 124.3; 114.8; 114.6; 68.3; 67.9; 31.8; 29.5; 29.4; 29.3; 29.2; 28.8; 26.0; 22.6; 14.1.

(E)-1-(4-(3-bromopropyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5b**): Yield: 54%.Cr 83.5 SmA 101.6 I. IR (KBr, υ_{max}, cm^{-1}): 3053, 2985, 2927, 1597, 1500, 1265, 748, 704.^1H NMR (300 MHz, $CDCl_3$): 7.90 (m, 4H); 7.03 (m, 4 H); 4.21 (t, 2 H, J = 5.8 Hz); 4.05 (t, 2 H, J = 6.6 Hz); 3.65 (t, 2 H, J = 6.4 Hz); 2.38 (m, 2 H); 1.84 (m, 2 H); 1.57-1.20 (m, 14 H); 0.91 (t, 3 H, J = 6.9 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 160.6; 147.2; 146.8; 124.4; 124.3; 114.7; 114.6; 68.3; 65.6; 32.3; 31.9; 29.9; 29.6; 29.5; 29.4; 29.3; 29.2; 26.0; 22.7; 14.2.

(E)-1-(4-(4-bromobutyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5c**): Yield: 59%. Cr 96.0 SmA 106.0 N 108 I. IR (KBr, υ_{max}, cm^{-1}): 3053, 2985, 2927, 1597, 1500, 1265, 748, 704. ^1H NMR (300 MHz, $CDCl_3$): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.08 (m, 4 H); 3.53 (t, 2 H, J = 6.4 Hz); 2.12 (m, 2 H); 2.02 (m, 2 H); 1.84 (m, 2 H); 1.55-1.23 (m, 14 H); 0.92 (t, 3 H, J = 6.4 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 160.8; 147.1; 146.9; 124.3; 124.3;114.7; 114.6; 68.3; 67.1; 33.4; 31.9; 29.6; 29.5; 29.4; 29.3; 29.2; 27.8; 26.0; 22.7; 14.2.

(E)-1-(4-(5-bromopentyloxyphenyl)-2-(4-(decyloxyphenyl)diazene(**5d**): Yield: 32%. Cr 77.5 SmA 111.5 I. IR (KBr, υ_{max}, cm^{-1}): 3093, 2935, 2920, 1600 1581, 1498,1265, 748, 704. ^1H NMR (300 MHz, $CDCl_3$): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.06 (m, 4 H); 3. 47 (t, 2H, J = 6.8 Hz); 1.98 (m, 2 H); 1,86 (m, 4H); 1.68 (m, 2 H); 1.56-1.26 (m, 14 H); 0.92 (t, 3 H, J = 7.0 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 160.9; 147.0; 146.9; 124.3; 114.7; 114.6; 68.3; 67.9; 33.5; 32.5; 31.9; 29.6; 29.5; 29.4; 29,3; 29.2; 28.4; 26.0; 24.8; 22.7; 14.1.

(E)-1-(4-(6-bromohexyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5e**): Yield: 57%. Cr 80.0 SmA 104.5 N 109.0 I. IR (KBr, υ_{max}, cm^{-1}): 2940, 2905, 1610, 1588, 1475,1285, 748, 704. ^1H NMR (300 MHz, $CDCl_3$): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.05 (m; 4 H); 3.46 (t, 2 H); 2.00-1.76 (m, 6 H); 1.65-1.24 (m, 18 H); 0.98-0.87 (m, 3 H). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 161.0; 147.0; 146.9; 124.3 114.7; 114.6; 68.3; 68.0; 33.8; 32.7;

31.9; 31.8; 29.6; 29.5; 29.4; 29.3; 29.2; 29.1; 29.0; 27.9; 26.0; 26.0;25.3; 22.7; 22.,6; 14.1; 14,1.

(E)-1-(4-(7-bromoheptyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5f**): Yield: 60%. Cr 64.6 SmA 109 I. IR (KBr, υ_{max}, cm^{-1}): 3053, 2985, 2927, 1597, 1500, 1265, 748, 704. ^{1}H NMR (300 MHz, CDCl3): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.05 (m, 4 H); 345 (t, 2 H, J = 6.8 Hz); 1.96 – 1.79 (m, 6 H); 1.58 – 1.23 (m, 20 H); 0.92 (t, 3H, J = 6.9 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 161.1; 146.9; 146.8; 124.3; 114.6; 114.6; 68.3; 68.1; 33.9; 32.7; 31.9; 29.6; 29.5; 29.4; 29.3; 29.2; 29.1; 28.5; 28.1; 26.0; 25.9; 22.7; 14.1.

(E)-1-(4-(8-bromooctyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5g**): Yield: 38%. Cr 88.2 SmA 107.6 I. IR (KBr, υ_{max}, cm^{-1}): 2987, 2922, 2870, 1602, 1423, 1265, 748, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.05 (m, 4 H); 3.44 (t, 2 H, J = 6.7 Hz); 1.98 -1.74 (m, 7 H); 1.62 - 1,19 (m, 21 H); 0.92 (t, 3H, J = 6.7 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 161.1; 146.9; 146.9; 124.3; 114.6; 68.3; 68.2; 34.2; 28.7; 28.1; 26.0; 25.9; 22.7; 14.1.

(E)-1-(4-(9-bromononyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5h**): Yield: 78%. Cr 55.4 SmA 101.6 I. IR (KBr, υ_{max}, cm^{-1}): 3093, 2935, 2920, 1600, 1581, 1498, 1265, 748, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.88 (m, 4 H); 7.01 (m, 4 H); 4.05 (m, 4 H); 3.44 (t, 2 H, J = 6.8 Hz); 1.93-1.79 (m, 5 H); 1.55 – 1.24 (m, 25 H); 0.92 (t, 3 H, J = 6.9 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 161.1; 147.0; 146.9; 124.3; 114.6; 68.3; 68.2; 34.0; 32.8; 31.9; 29.6; 29.5; 29.4; 29.3; 29.3; 29.2; 29.2; 29.2; 28.7; 28.1; 26.1; 26.0; 22.7; 14.2.

(E)-1-(4-(10-bromodecyloxyphenyl)-2-(4-(decyloxyphenyl)diazene (**5i**): Yield: 39%. Cr 96.0 SmA 106.2 I. IR (KBr, υ_{max}, cm^{-1}): 3093, 2987, 2935, 2920, 1600, 1581, 1498, 1265, 894, 748, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 (m, 4 H); 7.01 (m, 4 H); 4.05 (m, 4 H); 3.43 (t, 2 H); 1.95 – 1.76 (m, 6 H); 1.57–1.24 (m, 26 H); 0.92 (t, 3 H, J = 6.9 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.1; 161.1; 146.9; 146.9; 124.3; 114.6; 68.3; 68.3; 34.0; 32.8; 31.9; 29.6; 29.5; 29.4; 29.4; 29.3; 29.3; 29.2; 29.2; 28.7; 28.2; 26.0; 26.0; 22.7; 14.1.

Synthesis of (E)-1-(4-decyloxyphenyl)-2-(4-hexyloxyphenyl)diazene (**5j**): **4**(0.5 mmol) and anhydrous K_2CO_3 (1.6 mmol) were dissolved into acetone in a round bottom flask with reflux system under agitation for 15 minutes. 6-bromohexane (3 mmol) was added drop wise and the system was refluxed from 15 to 48h (monitored by TLC). After the reaction is done, the still hot solution was filtered and washed with hot acetone. The filtrate wasconcentrated in rotary evaporator, cold petroleum ether was added to the concentrated extract, and the resulting precipitate was filtered and washed three times with petroleum ether. Recrystallization in ethanol with a few drops of water.
Yield: 64%. Cr 88.0 SmA 109.0 I. IR (KBr, υ_{max}, cm^{-1}): 2987, 2922, 2870, 1602, 1423, 1265, 748, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 (d, 4 H, J = 8.8 Hz); 7.01 (d, 4 H, J = 9.1 Hz); 4.05 (m, 4 H); 1.84 (m, 4 H); 1.64 (s,1 H); 1.51 (m, 4 H); 1.44 – 1.23 (m, 16 H); 0.93 (t, 6 H, J = 7.0 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): 161.1; 146.9; 124.3; 114.6; 68.3; 31.9; 31.6; 29.6; 29.4; 29.3; 29.2; 29.2; 26.0; 25.7; 22.7; 22.6; 14.1; 14.0.

(E)-1-(4-(2-bromoethyloxy)phenyl)-2-(4-(heptyloxy)phenyl)diazene (**5k**):

Yield: 61%. Cr 105 N (103) I. IR (KBr, υ_{max}, cm^{-1}): 2987, 2922, 2870, 1602, 1423, 1265, 748, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.80 (m, 4 H); 7.01 (m, 4 H); 4.30 (t, 2H, J = 6.4Hz); 4.02 (t, 2H, J = 6.6 Hz); 3.70 (t, 2H, J = 6.5 Hz); 1.80 (m, 2H); 1.40 (m, 8H);, 16 H); 0.93 (t, 3H, J = 7.3 Hz).^{13}C NMR (300 MHz, $CDCl_3$): 161.4; 160.0; 147.5; 146.8; 124.4; 124.3; 68.4; 68.0; 31.9; 29.3; 29.0; 28.9; 26.0; 22.6; 14.2.

(E)-1-(4-(4-bromobutoxy)phenyl)-2-(4-(heptyloxyphenyl)diazene (**5l**):
Yield: 36%. Cr 96.4 SmA (96.5) N 114.0 I °C IR (KBr, υ_{max}, cm^{-1}): 2942, 1610, 1590, 1480, 1250, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.85 (m, 4H); 6.99 (m, 4H);4.02 (m, 4H); 3.52 (t, 2H, J = 6.0 Hz);2.15 (m, 2H); 2.00 (m, 2H); 1.80 (m, 2H) 1.4 (m, 8H). 0.90 (t, 3H, 7.5 Hz).^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 160.8; 147.1; 146.9; 124.4; 124.3; 114.7; 114.6; 68.4; 67.2; 33.5; 31.8; 29.4; 29.3; 29.1; 27.9; 26.0; 22.6; 14.1.

(E)-1-(4-(6-bromohexyloxy)phenyl)-2-(4-(heptyloxy)phenyl)diazene (**5m**):
Yield: 46%. Cr 103 SmA (102) N 111.0 I °C IR (KBr, υ_{max}, cm^{-1}): 2942, 1610, 1590, 1480, 1250, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.85 (dd, 4H); 6.99 (m, 4H); 3.99 (m, 4H); 3.52 (t, 2H, J = 7.5 Hz); 1.83- (m, 6H); 1.50 (m, 6H); 1.40 (m, 6H); 0.88 (t, 3H, 7.4 Hz).^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 160.8; 147.0; 146.9; 124.4; 124.3; 114.7; 114.6; 68.4; 68.0; 33.8; 32.7; 31.8; 29.2; 29.1 29.0; 27.9; 26.0; 22.6; 25.3; 22.6; 14.1.

(E)-1-(4-(6-bromohexyloxy)phenyl)-2-(4-(methoxy)phenyl)diazene (**5n**):
Yield: 80%. Cr1 102.0 Cr 106.0 N (99.5) I. IR (KBr, υ_{max}, cm^{-1}): 2965, 1618, 1593, 1473, 1254, 704. ^{1}H NMR (300 MHz, $CDCl_3$): 7.92 (m, 4H); 7.05 (m, 4H); 4.12 (t, 2H, J = 7.7 Hz); 3.90 (s, 3H);3.56 (t, 2H, J = 7.2 Hz)); 1.90 (m, 4H);1.44 (m, 4H).^{13}C NMR (300 MHz, $CDCl_3$): 161.2; 161.1; 147.1 (2C); 124.4 (2C); 114.2 (2C); 68.1; 55.6; 33.8; 32.7; 29.1; 27.9; 25.3.

Anexos

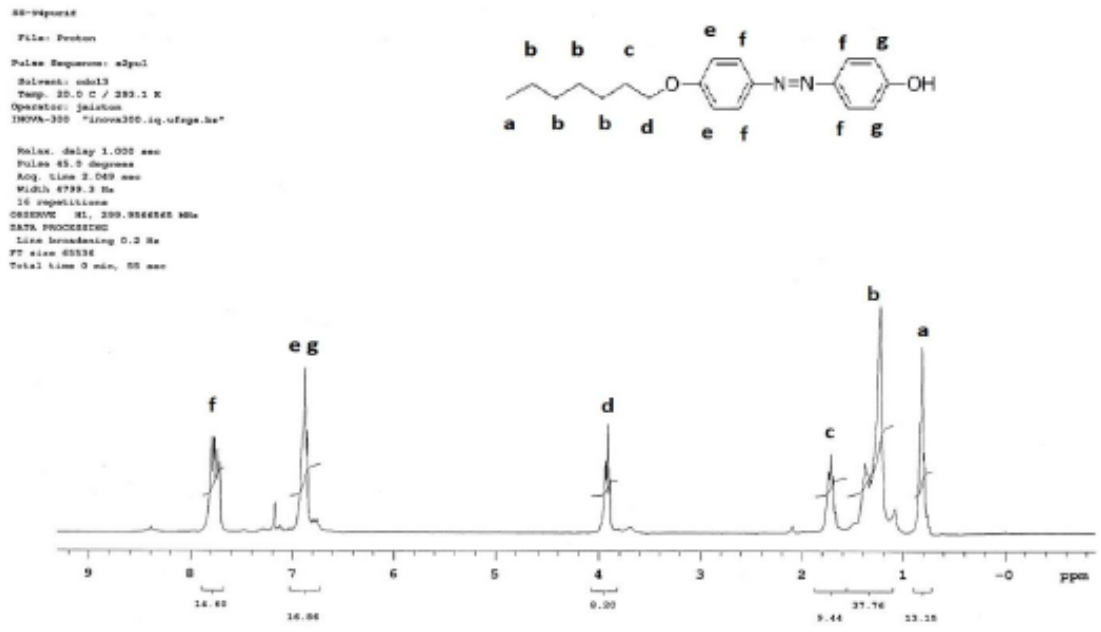


Figure SI1. ^{1}H NMR of **4a** in $CDCl_3$ (300 MHz)

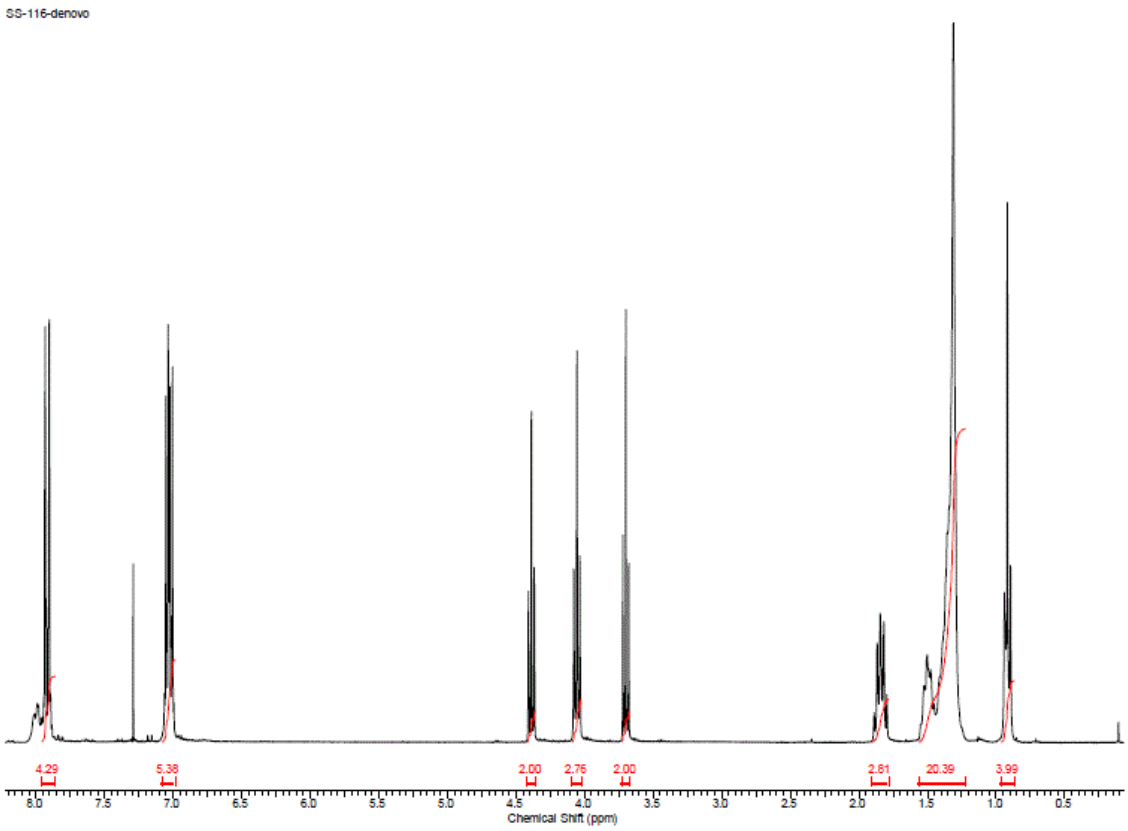


Figure SI2. ^{1}HNMR of **5a** in $CDCl_3$ (300 MHz).

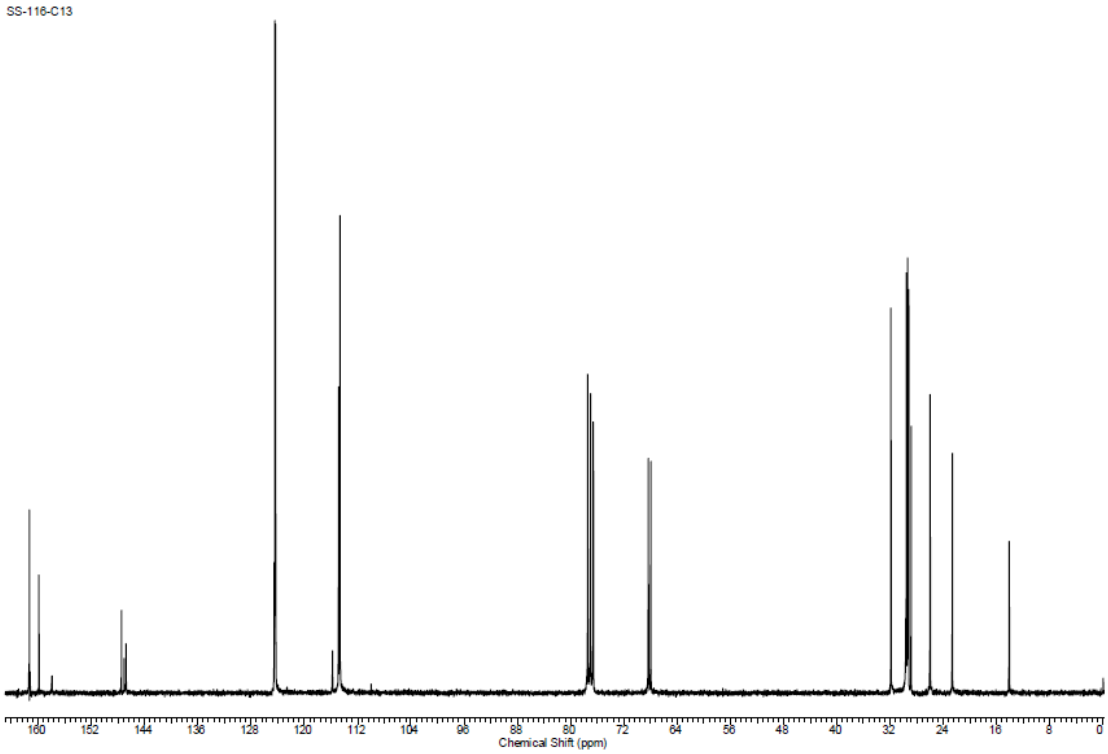


Figure SI3. ^{13}C NMR of **5a** in $CDCl_3$ (75 MHz).

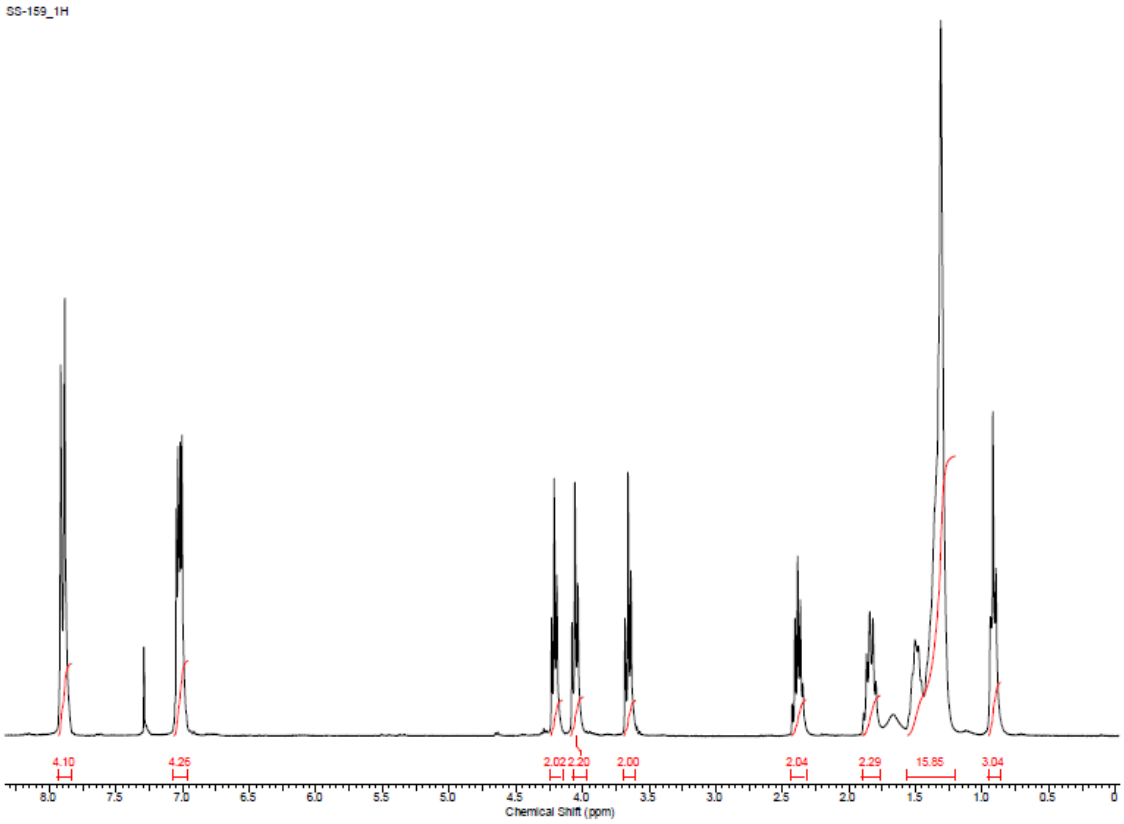


Figure SI4. ^{1}HNMR of **5b** in $CDCl_3$ (300 MHz).

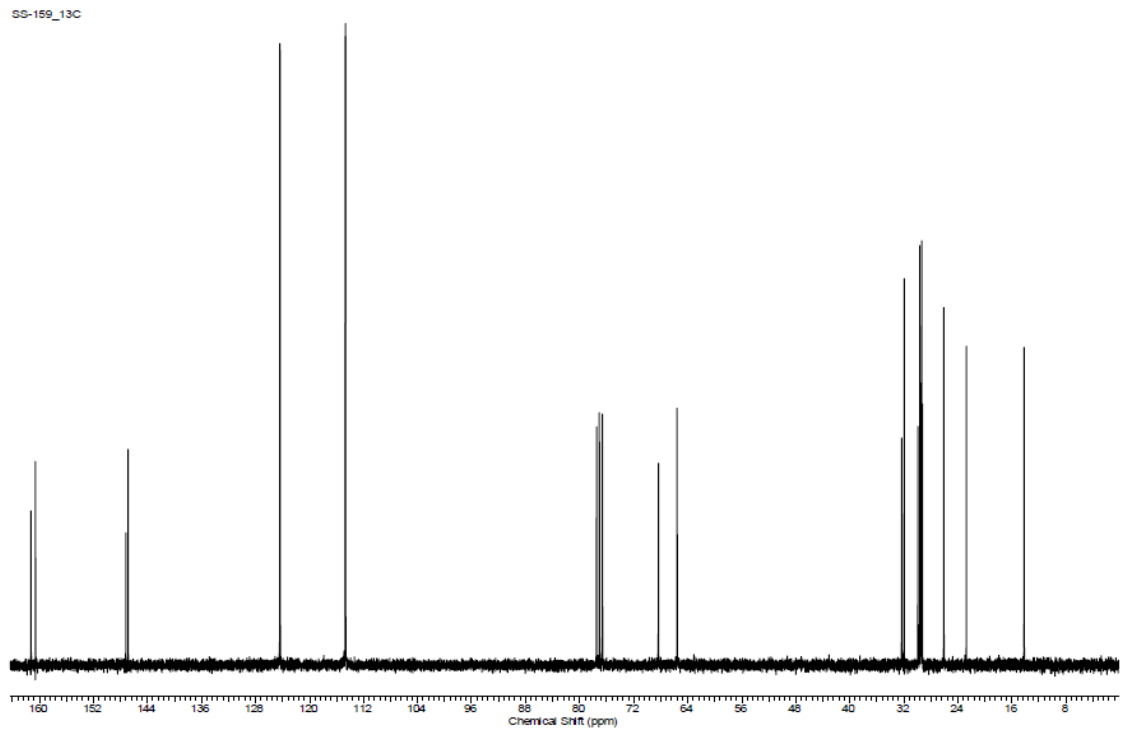


Figure SI5. ^{13}C NMR of **5b** in $CDCl_3$ (75 MHz).

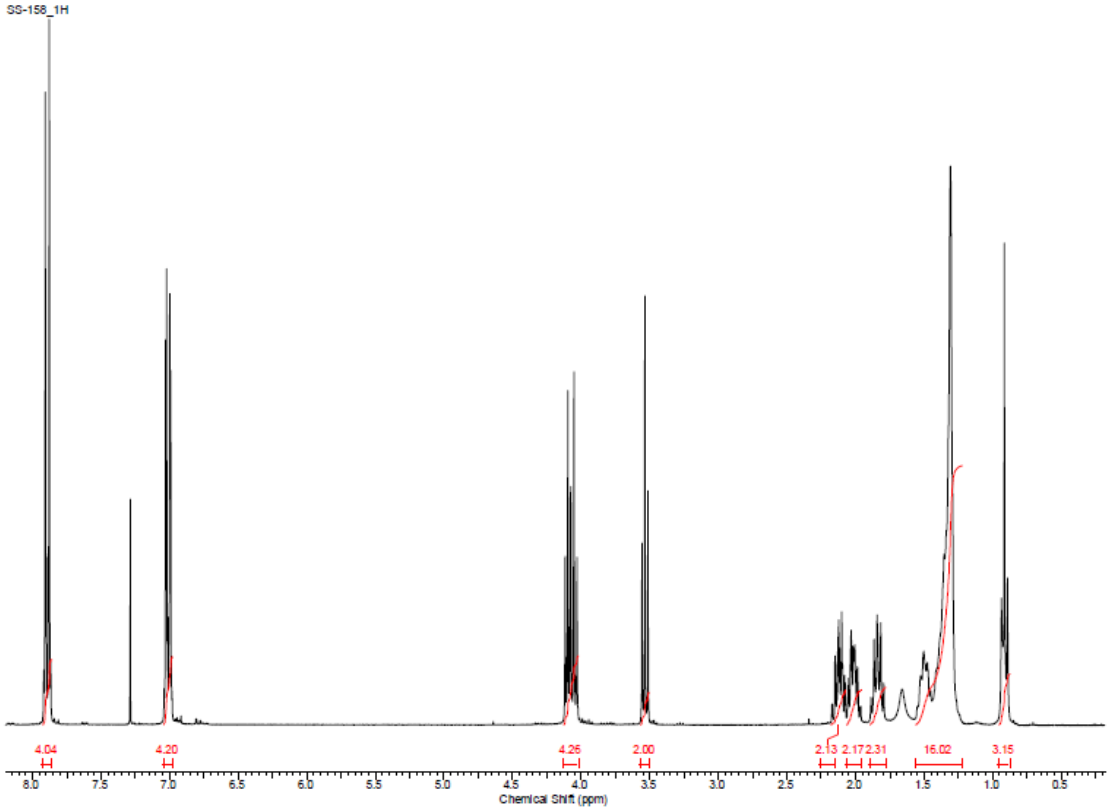


Figure SI6. ^{1}HNMR of **5c** in $CDCl_3$ (300 MHz).

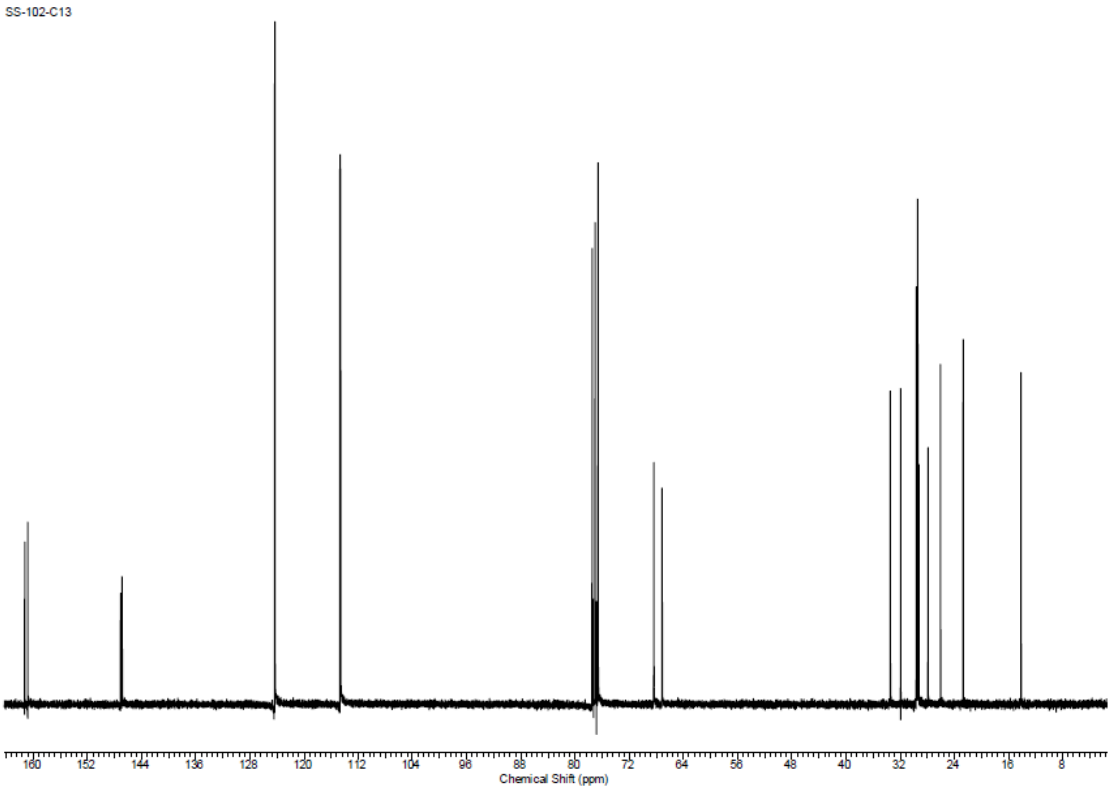


Figure SI7. ^{13}C NMR of **5c** in $CDCl_3$ (75 MHz).

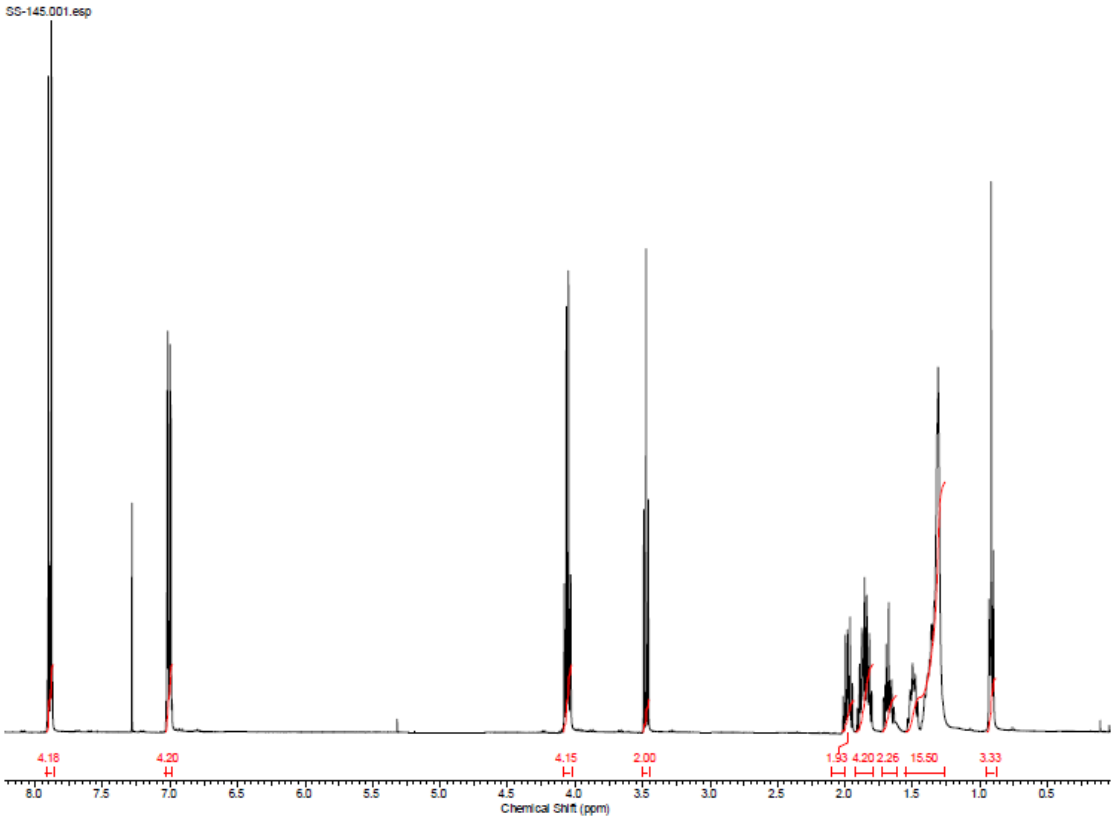


Figure SI8. ^{1}HNMR of **5d** in $CDCl_3$ (300 MHz).

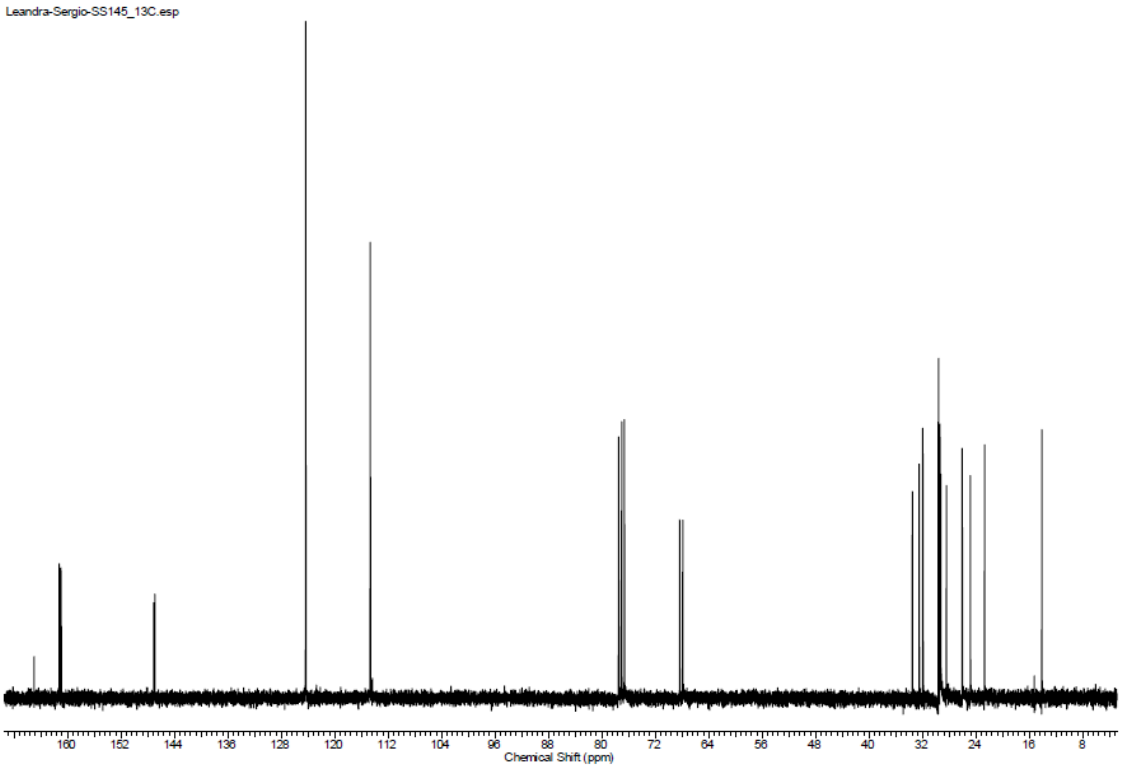


Figure SI9. ^{13}C NMR of **5d** in $CDCl_3$ (75 MHz).

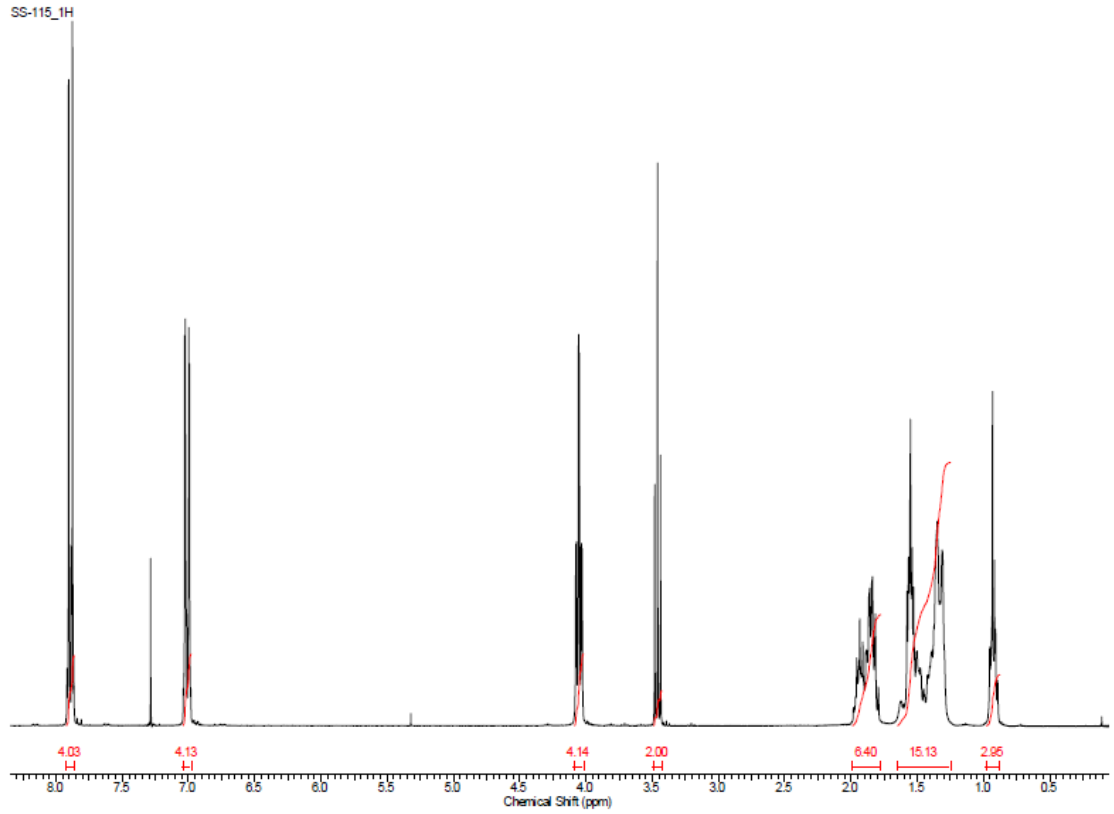


Figure SI10. ^{1}HNMR of **5e** in $CDCl_3$ (300 MHz).

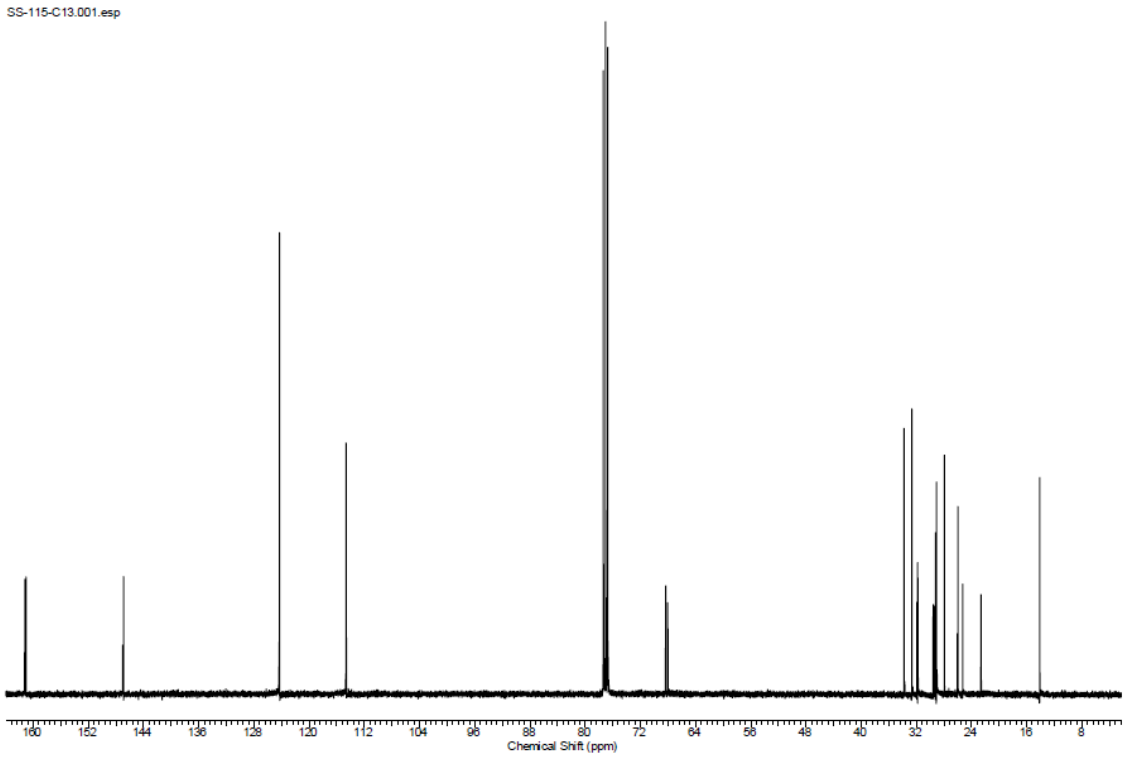


Figure SI11. ^{13}C NMR of **5e** in $CDCl_3$ (75 MHz).

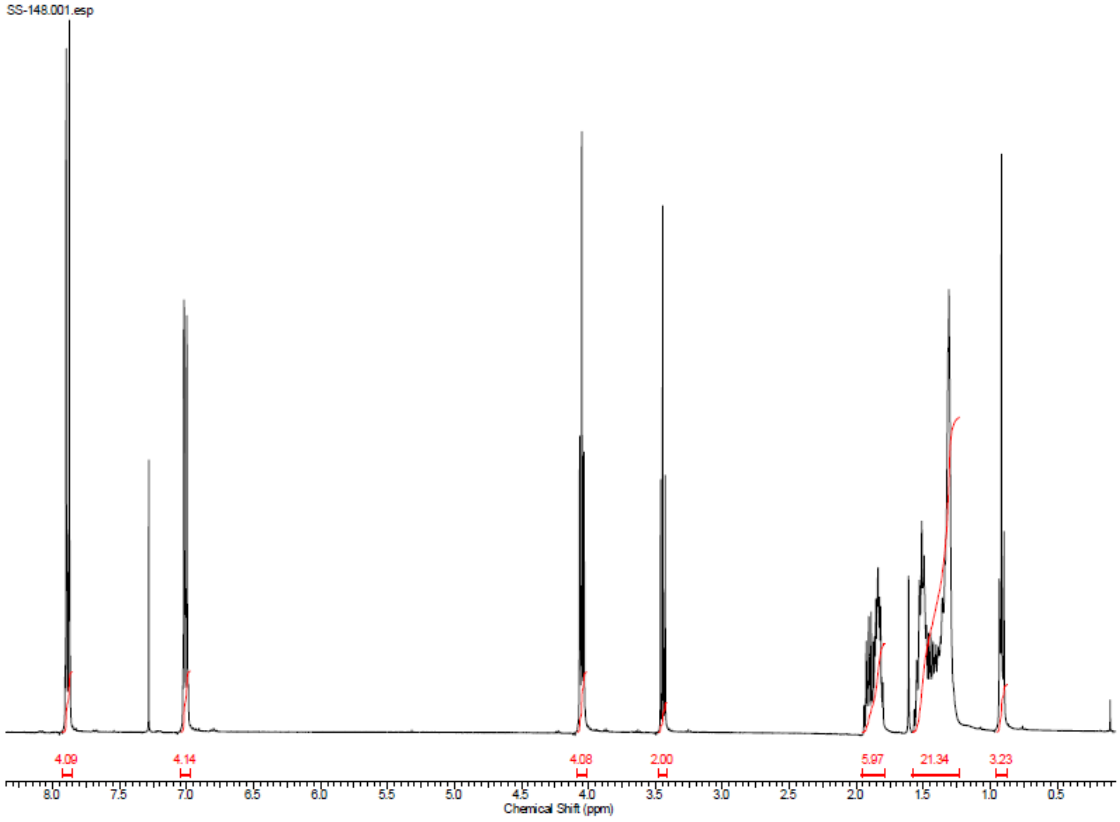


Figure SI12. ^{1}HNMR of **5f** in $CDCl_3$ (300 MHz).

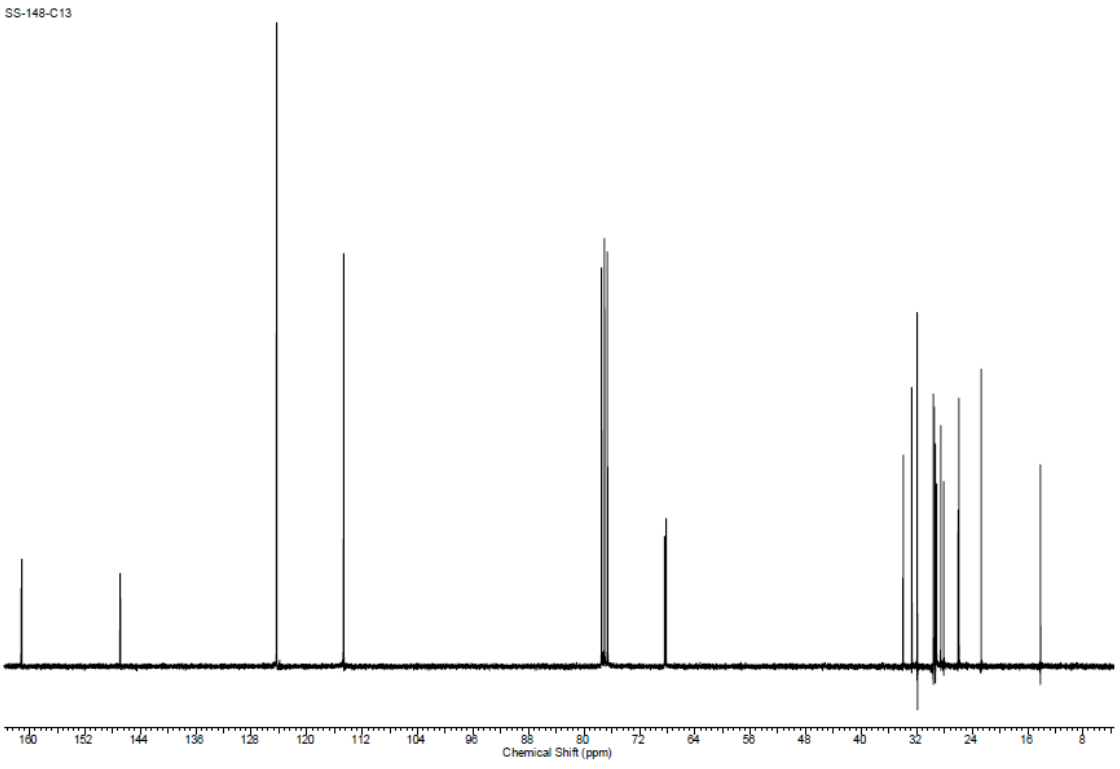


Figure SI13. ^{13}C NMR of **5f** in $CDCl_3$ (75 MHz).

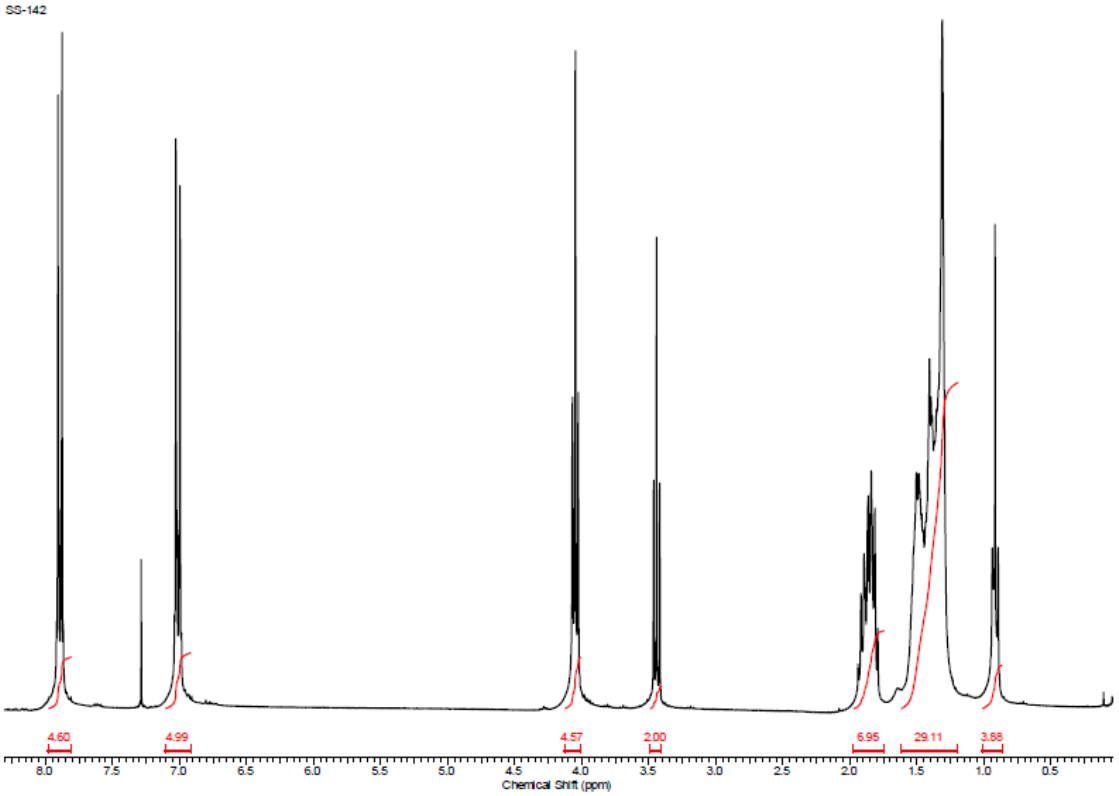


Figure SI14. ^{1}HNMR of **5g** in $CDCl_3$ (300 MHz).

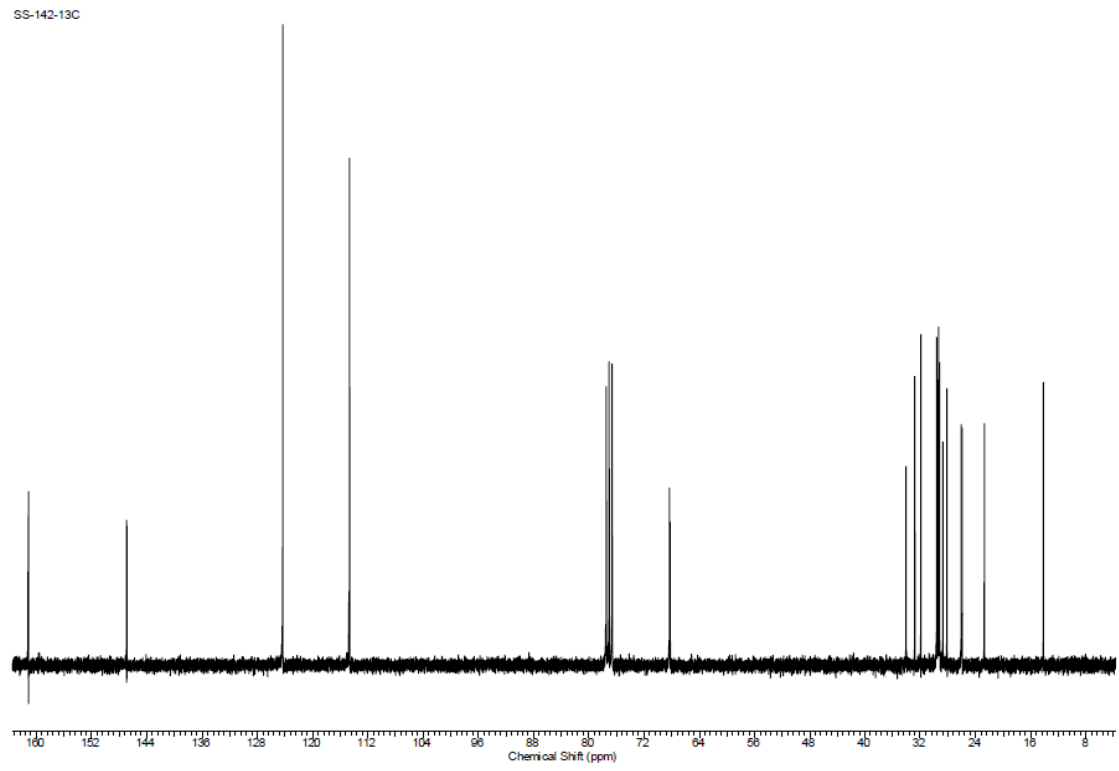


Figure SI15. ^{13}C NMR of **5g** in $CDCl_3$ (75 MHz).

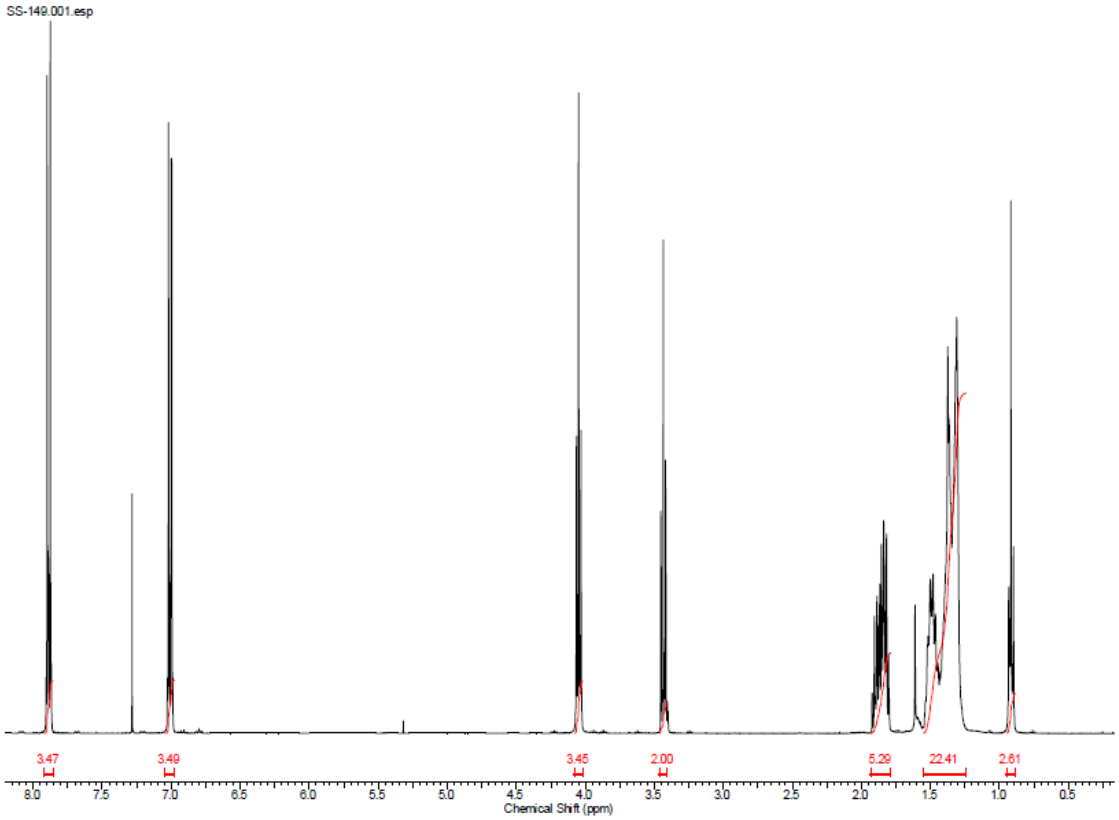


Figure SI16. ^{1}HNMR of **5h** in $CDCl_3$ (300 MHz).

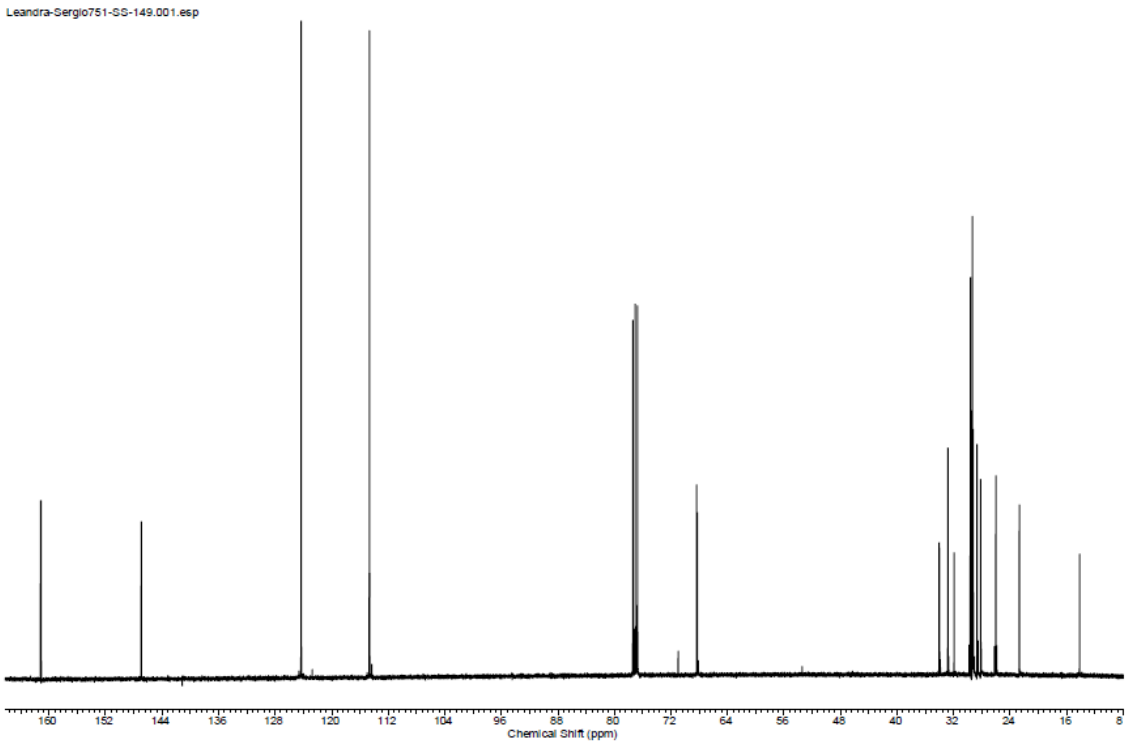


Figure SI17. ^{13}C NMR of **5h** in $CDCl_3$ (75 MHz).

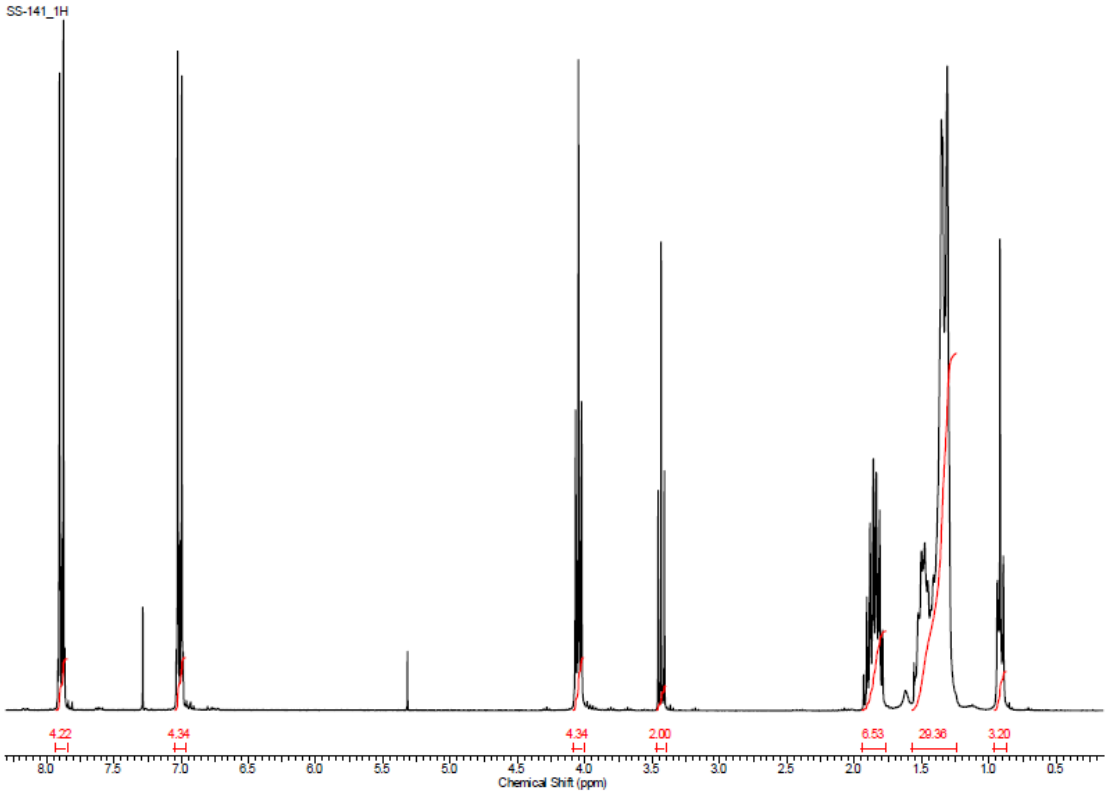


Figure SI18. ^{1}HNMR of **5i** in $CDCl_3$ (300 MHz).

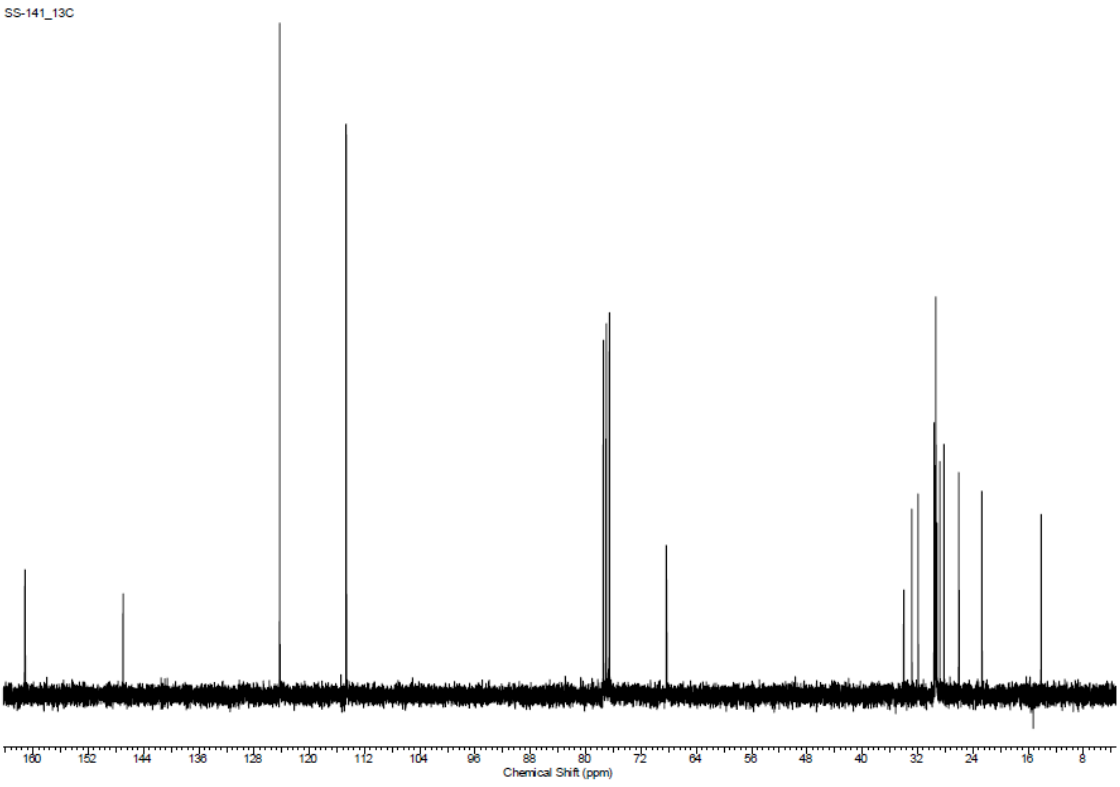


Figure SI19. ^{13}C NMR of **5i** in $CDCl_3$ (75 MHz).

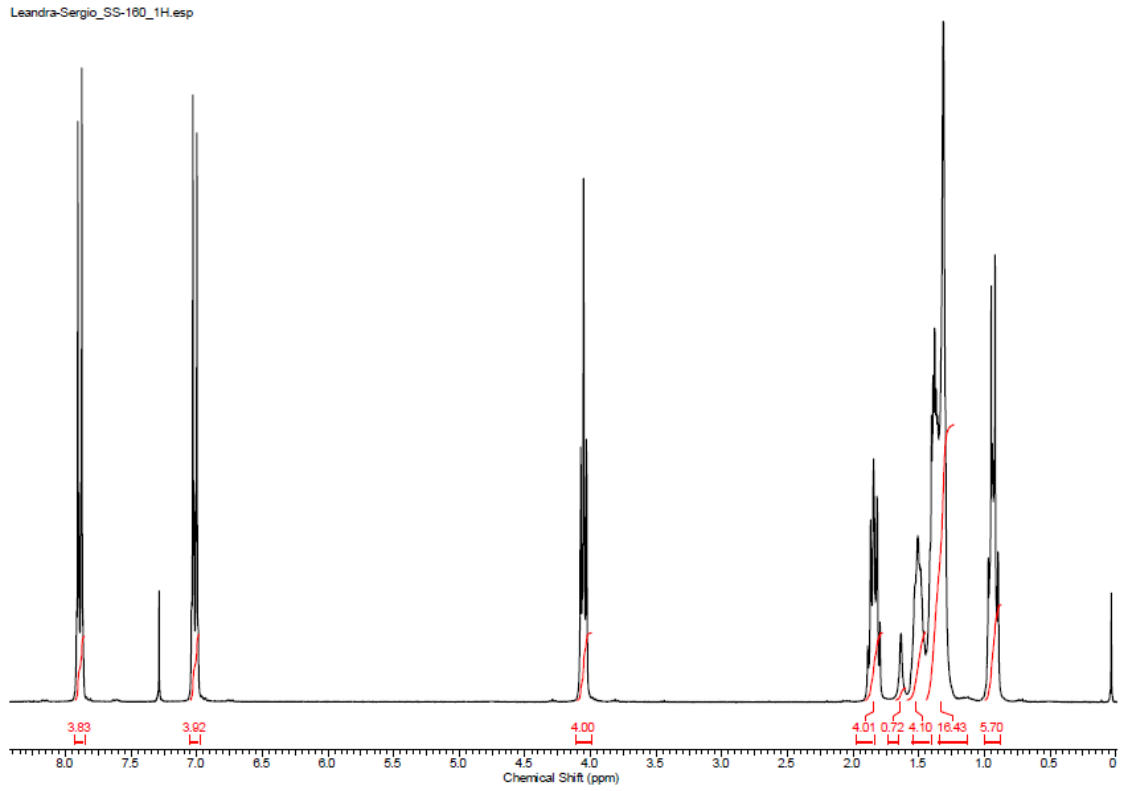


Figure SI20. ^{1}HNMR of **5j** in $CDCl_3$ (300 MHz).

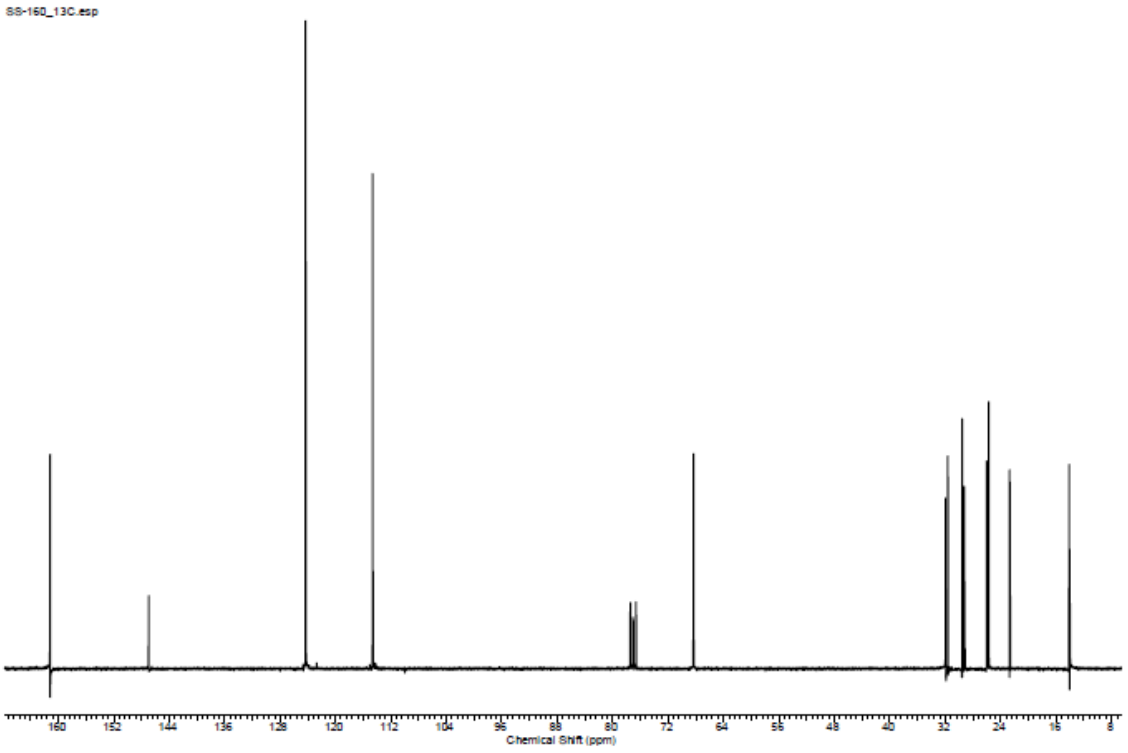


Figure SI21. ^{13}C NMR of **5j** in $CDCl_3$ (75 MHz).

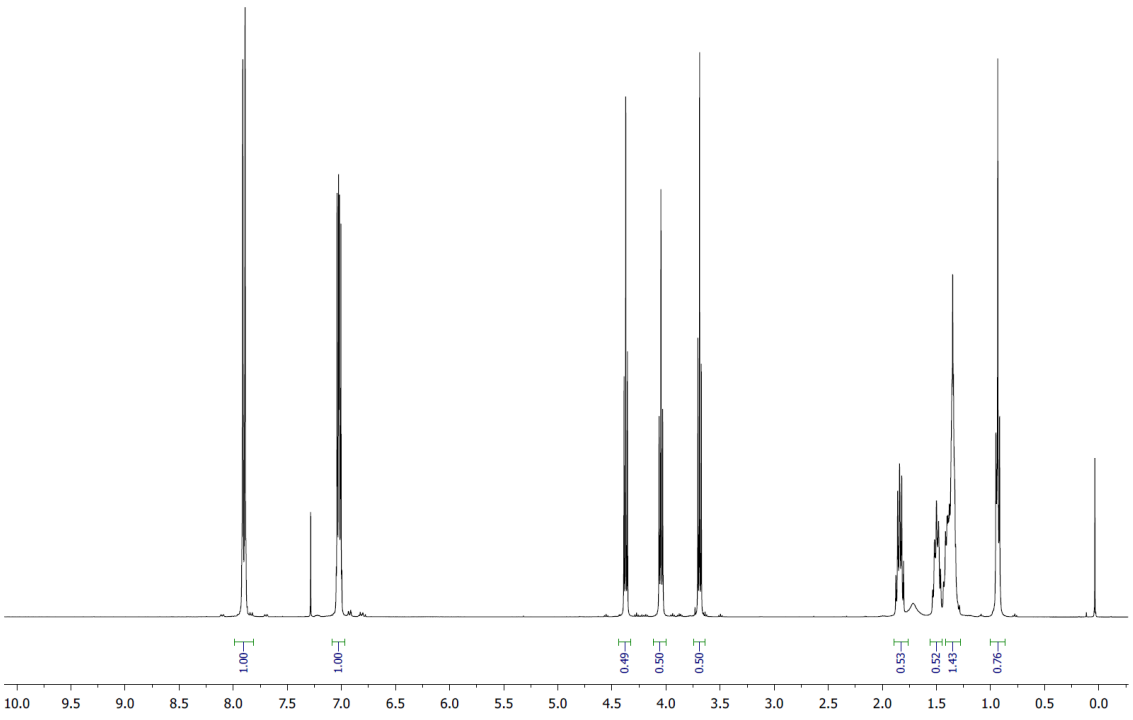


Figure SI22. ^{1}HNMR of **5k** in $CDCl_3$ (300 MHz).

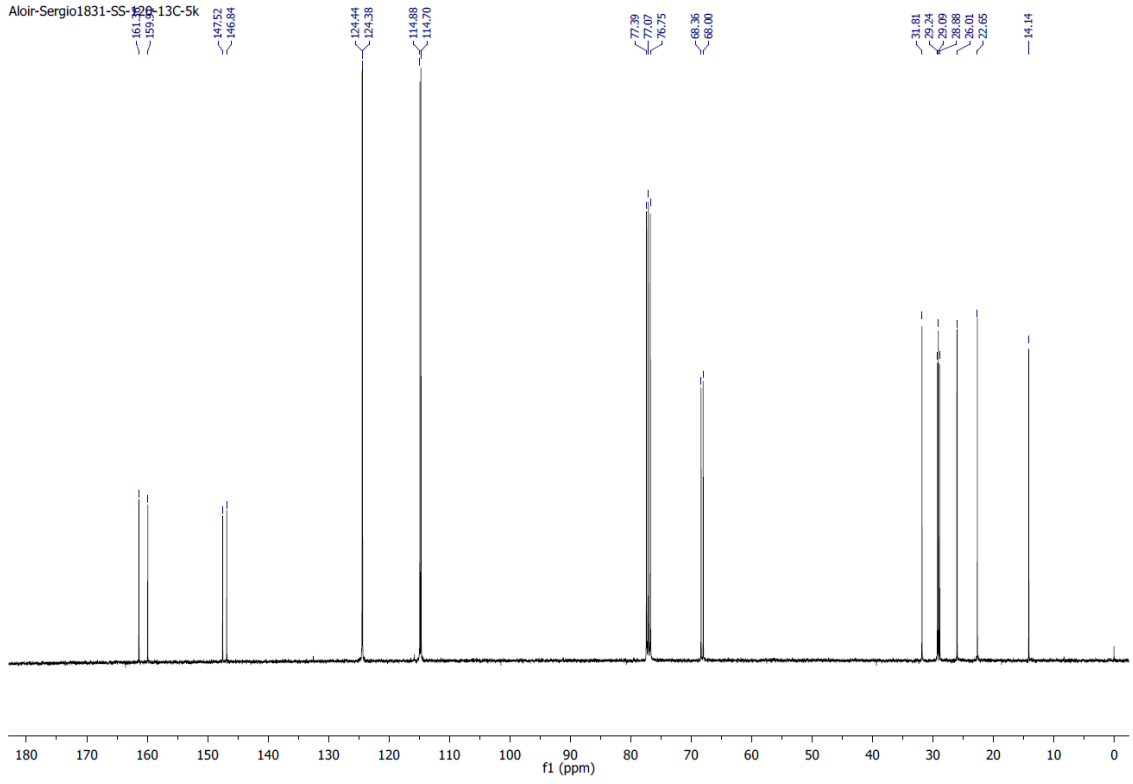


Figure SI23. ^{13}C NMR of **5k** in $CDCl_3$ (75 MHz).

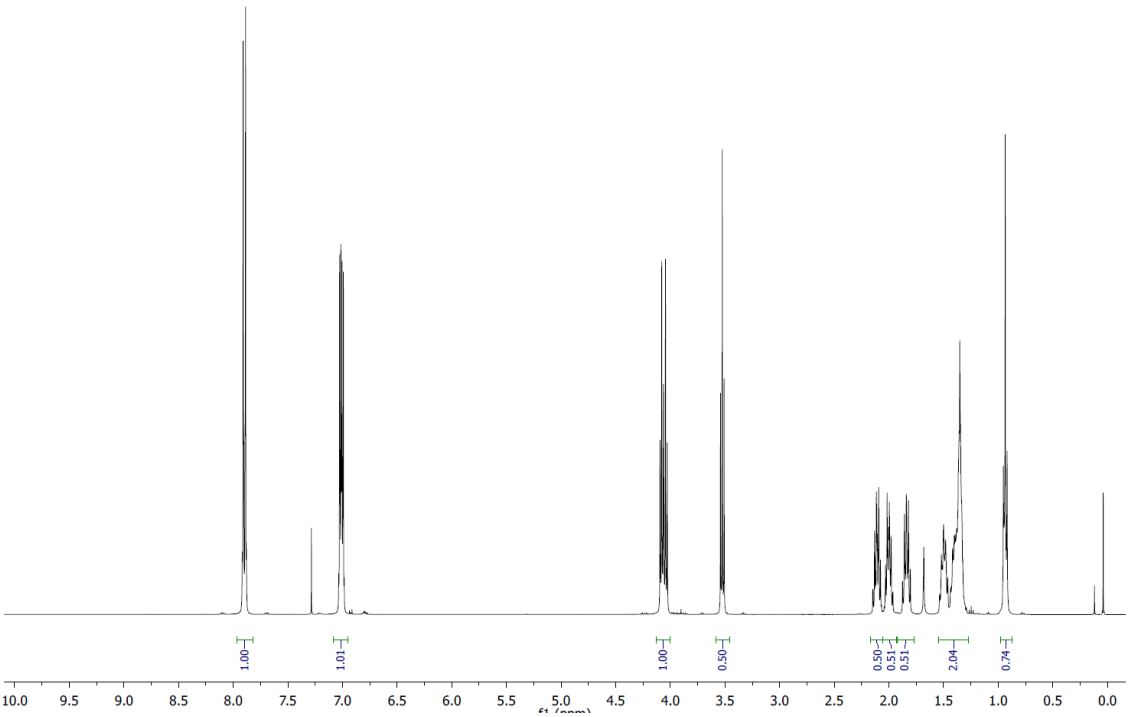


Figure SI24. ^{1}HNMR of **5l** in $CDCl_3$ (300 MHz).

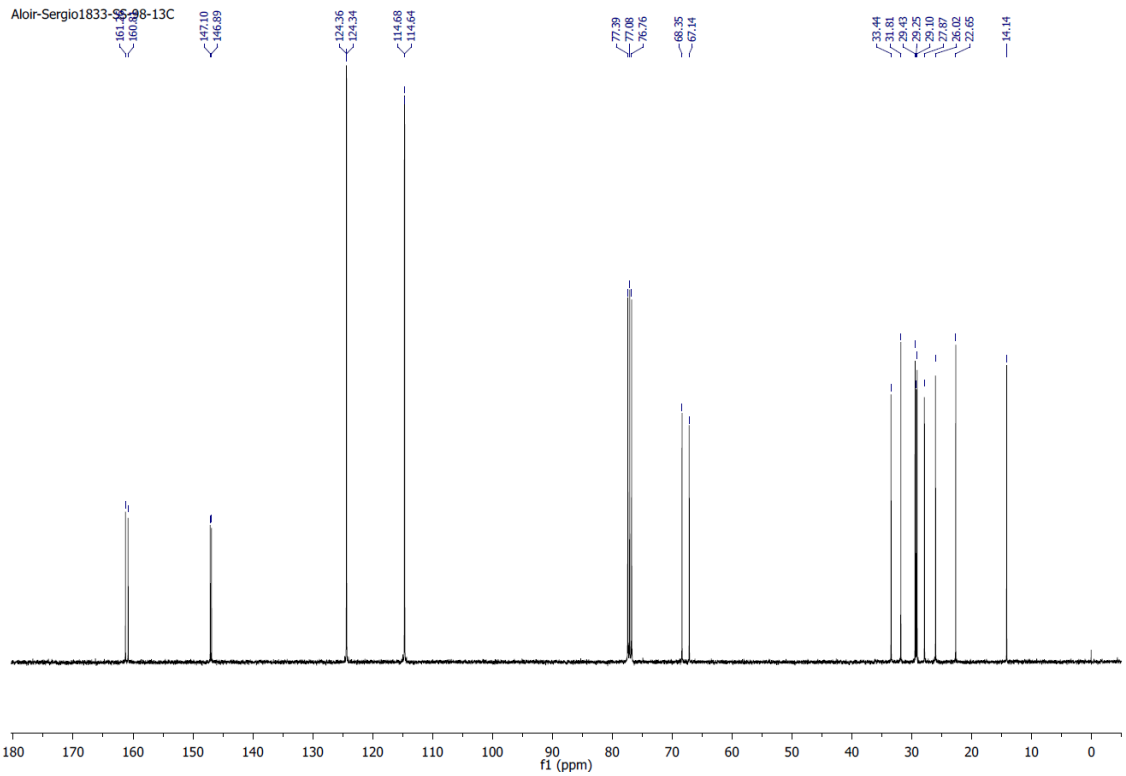


Figure SI25. ^{13}C NMR of **5l** in $CDCl_3$ (75 MHz).

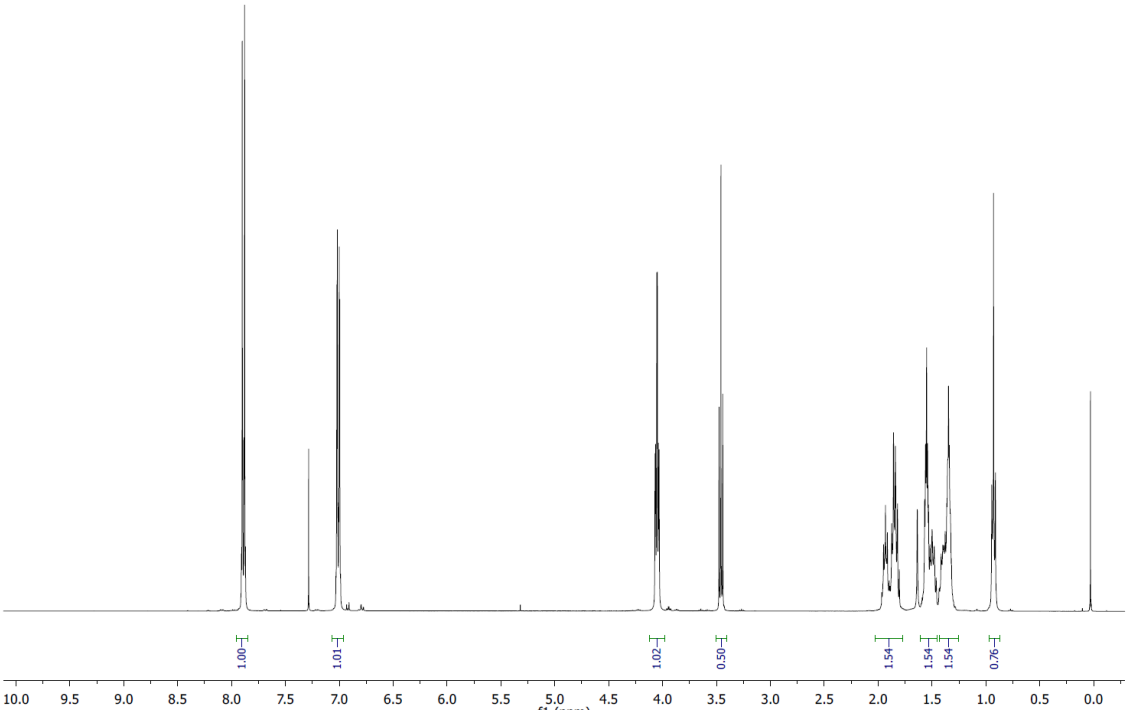


Figure SI26. ^{1}HNMR of **5m** in $CDCl_3$ (300 MHz).

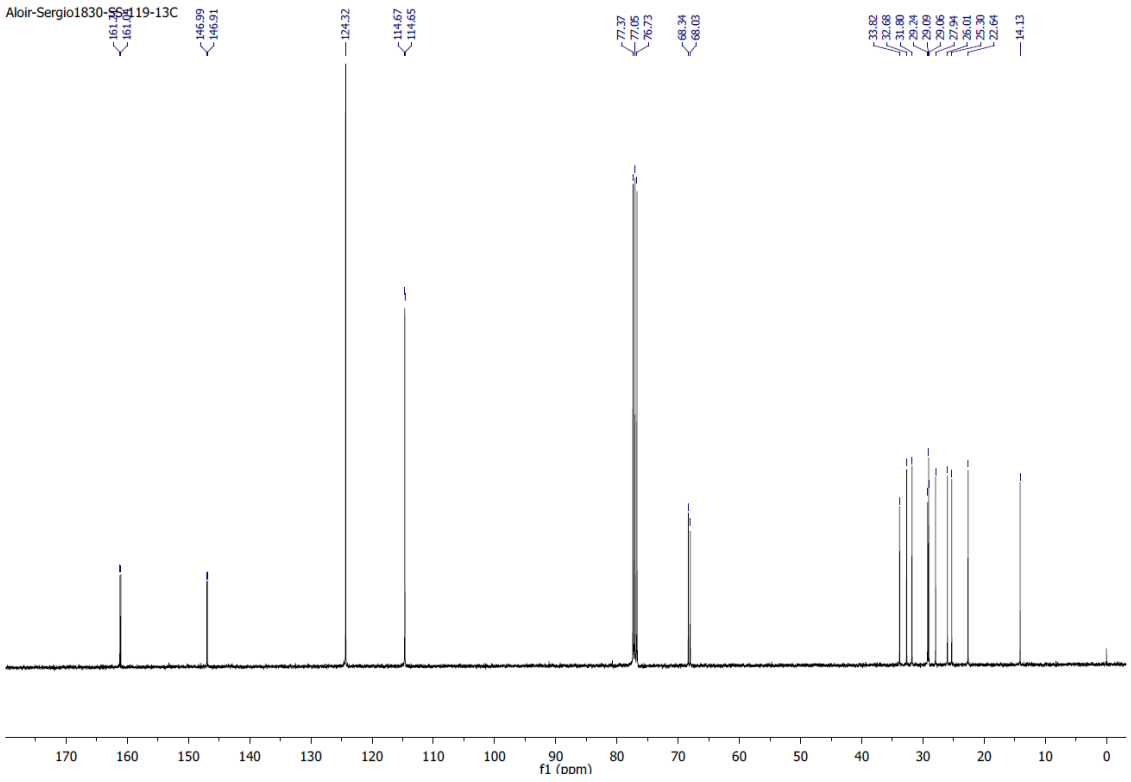


Figure SI27. ^{13}C NMR of **5m** in $CDCl_3$ (75 MHz).

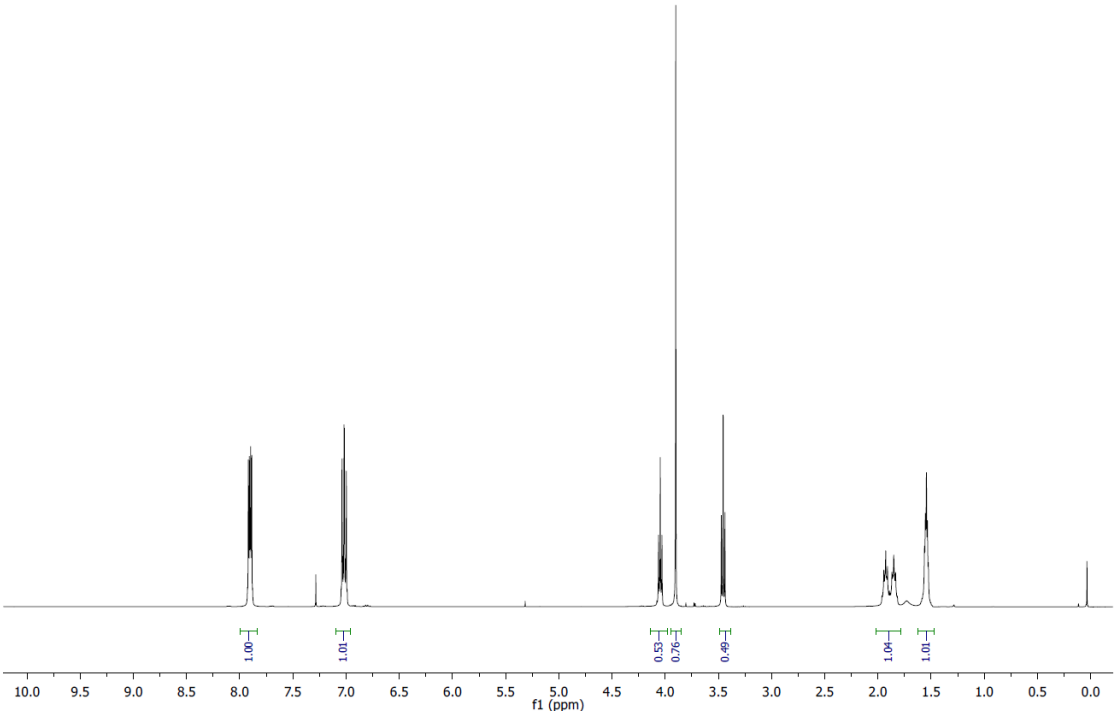


Figure SI28. ^{1}HNMR of **5n** in $CDCl_3$ (300 MHz).

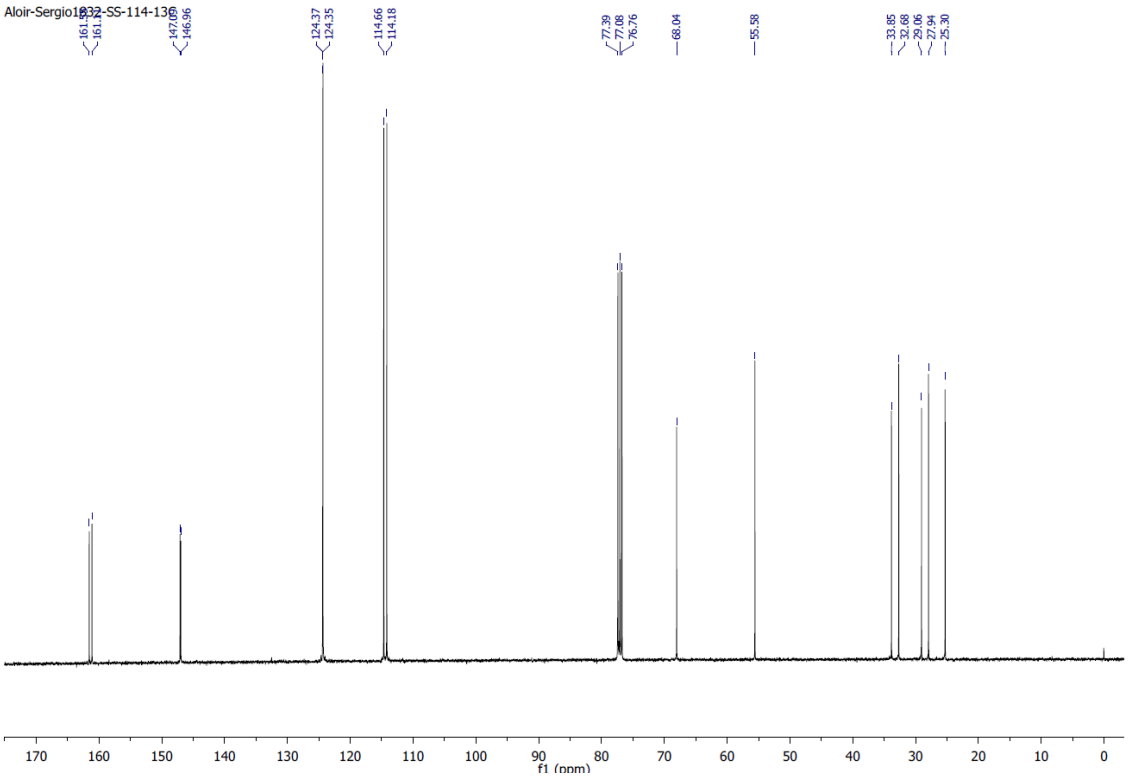


Figure SI29. ^{13}C NMR of **5n** in $CDCl_3$ (75 MHz).

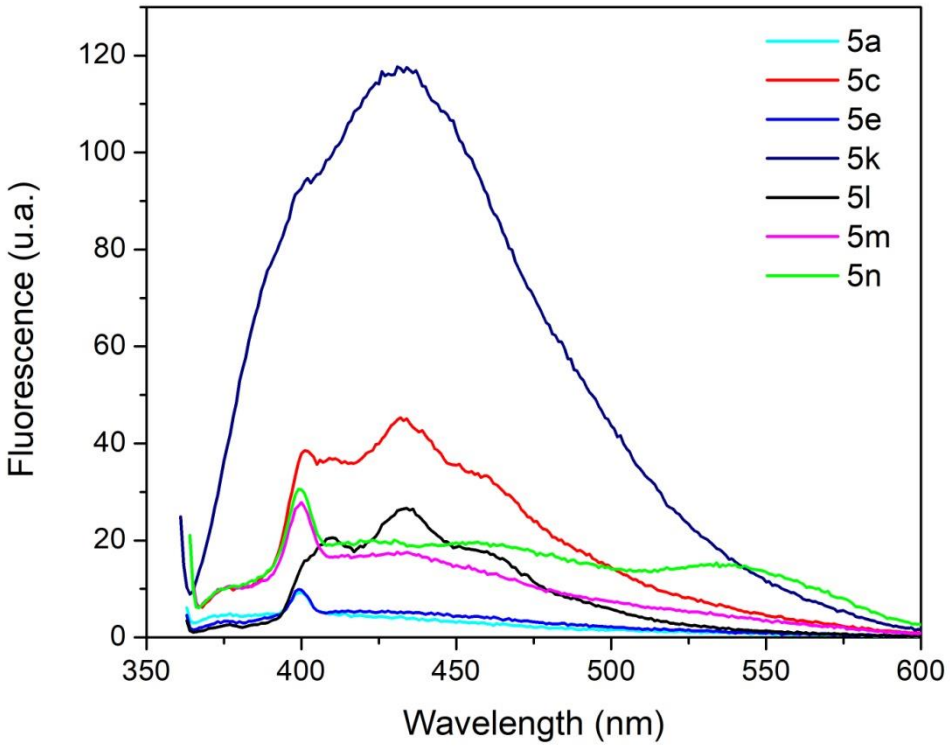


Figure SI30. Fluorescence spectra of azodyes in dioxane (1.0 x 10^{-5}M).

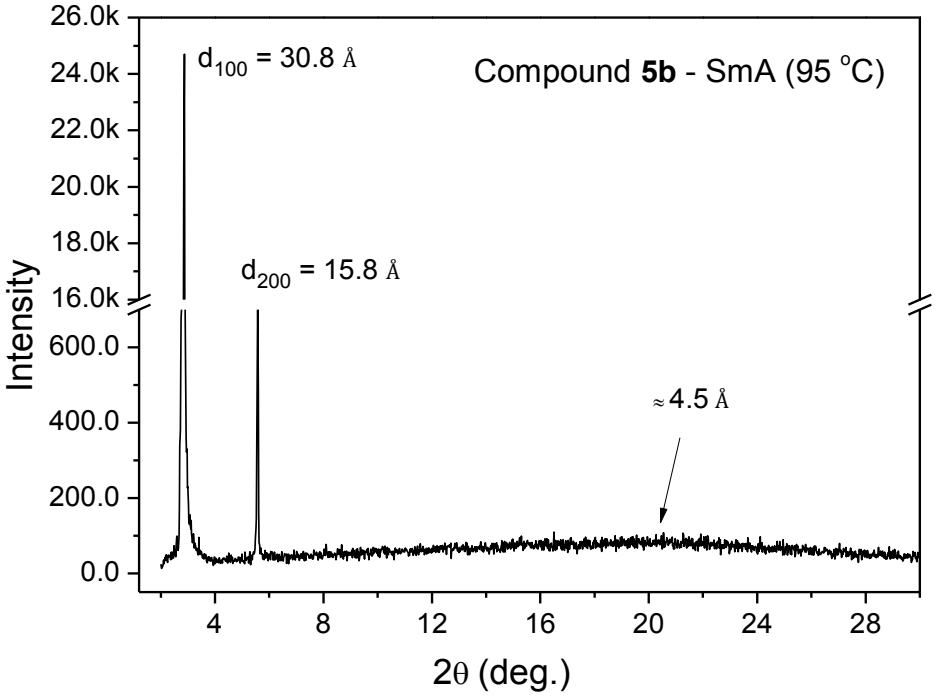


Figure SI31. Diffractogram of compound **5b** at 95 ºC.

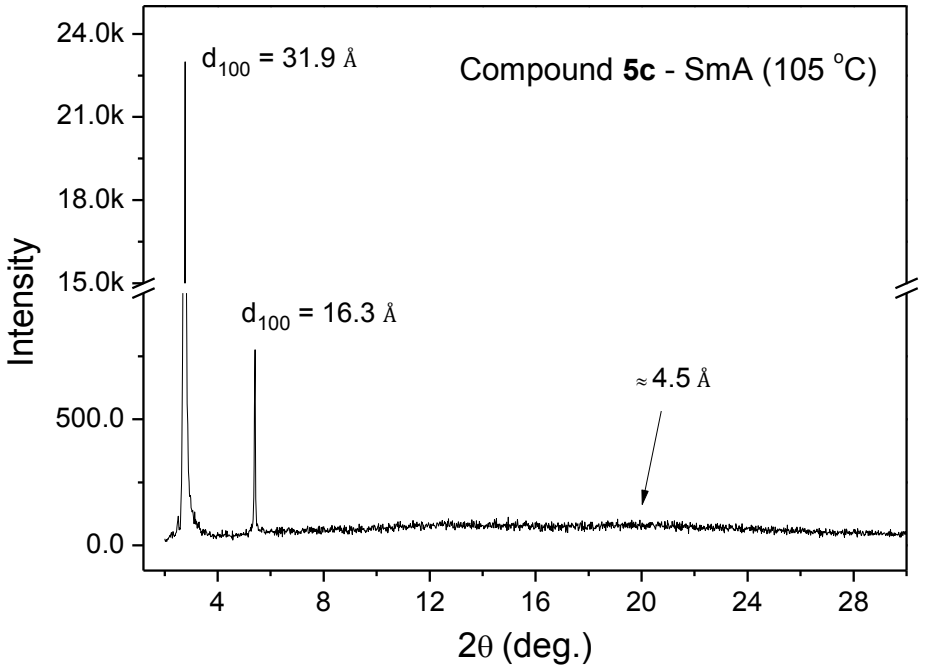


Figure SI32. Diffractogram of compound **5c** at 105 ºC.

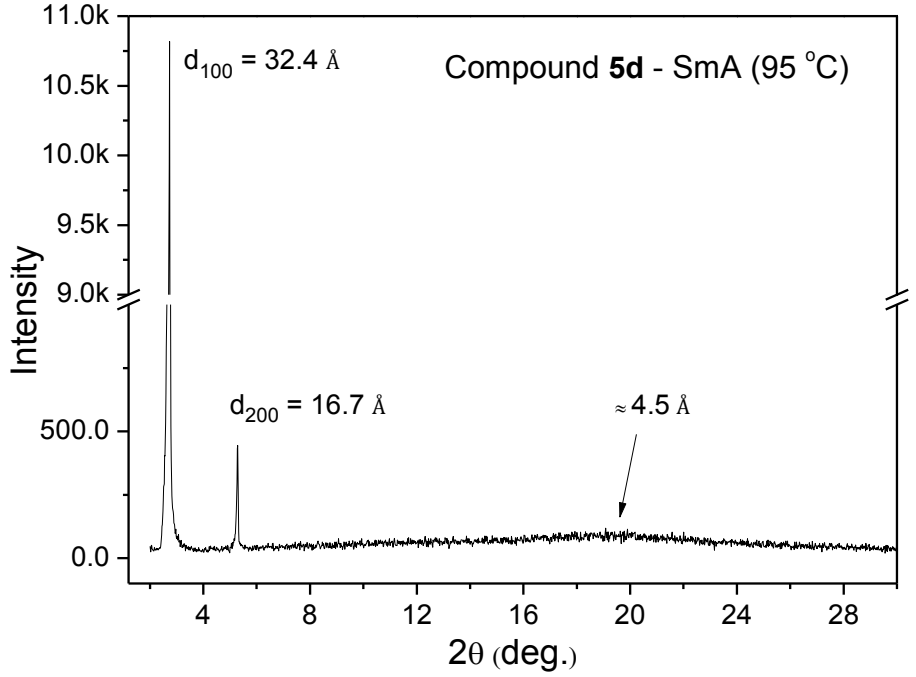


Figure SI33. Diffractogram of compound **5d** at 95 ºC.

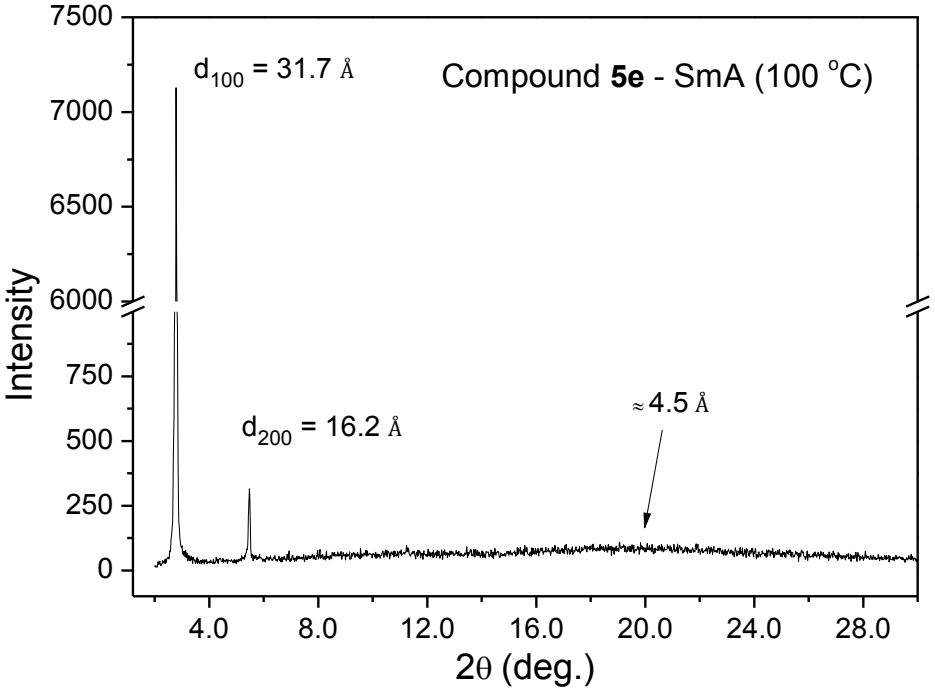


Figure SI34. Diffractogram of compound **5e** at 100 ºC.

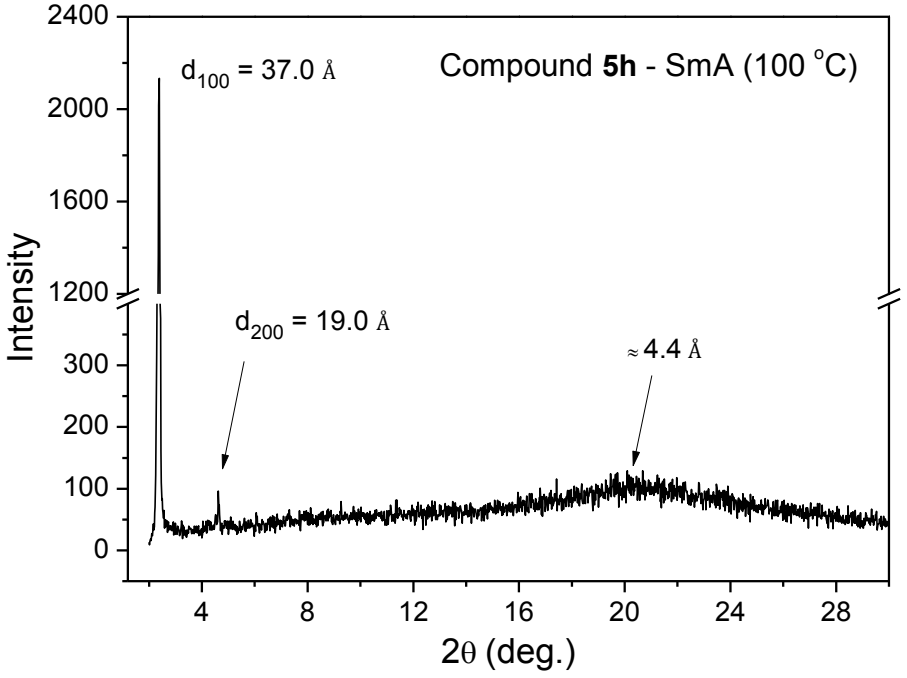


Figure SI35. Diffractogram of compound **5h** at 100 ºC)

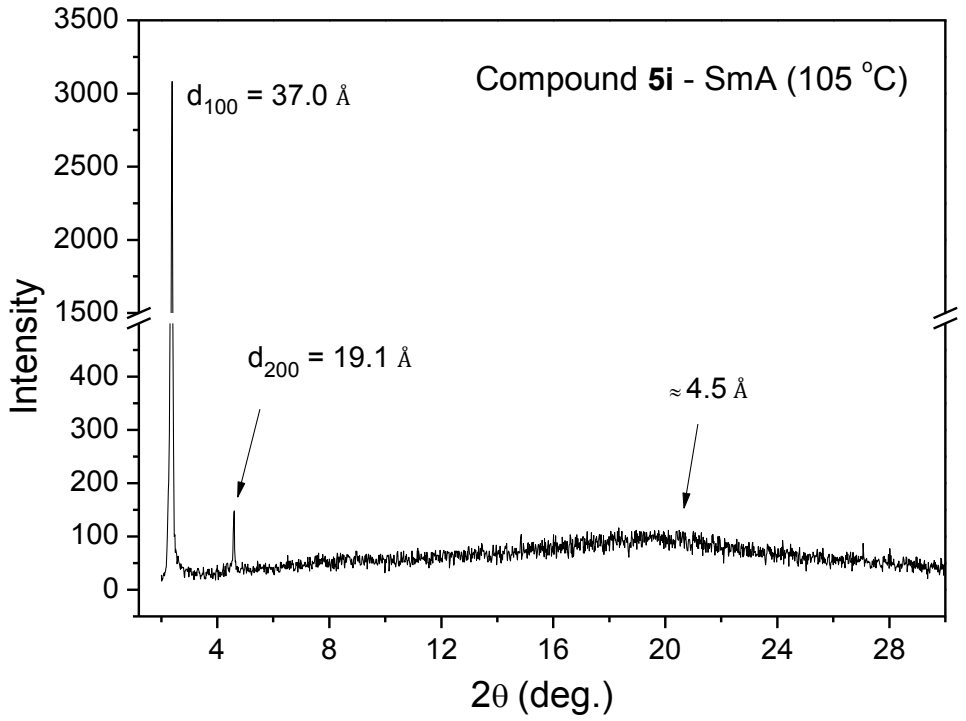
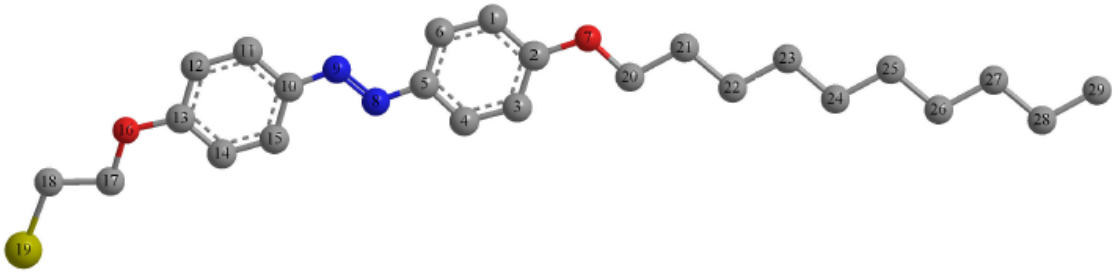


Figure SI36. Diffractogram of compound **5i** at 105 °C.

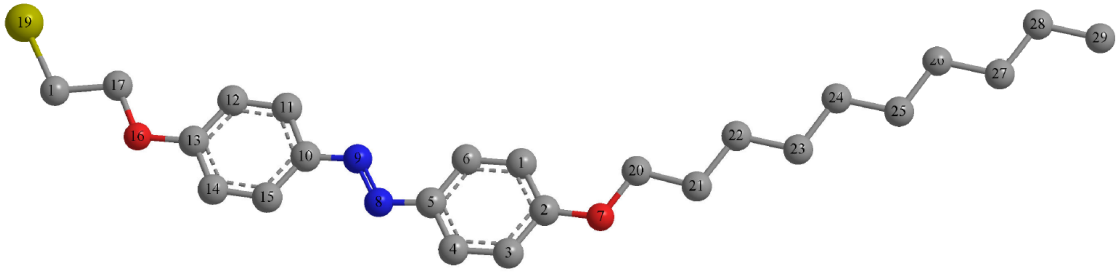
Table 1. Structural and energetic parameters of some conformers[a] extracted from **5a**, **5b** and **5c** by MM2 method.

Data	**5a**				**5b**			**5c**		
	C1	C2	C3	C4	C1	C2	C3	C1	C2	C3
E (kcal.mol^{-1})	28.55	28.46	28.80	28.10	29.15	29.20	29.10	29.55	29.60	29.40
Molecular length (Å)	27.40	28.50	26.60	27.50	29.50	30.06	28.60	30.50	30.92	29.90

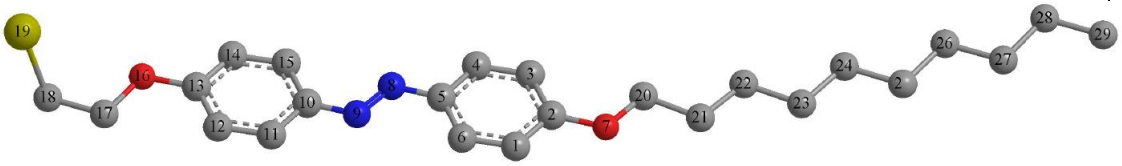


Conformer C1 for **5a**

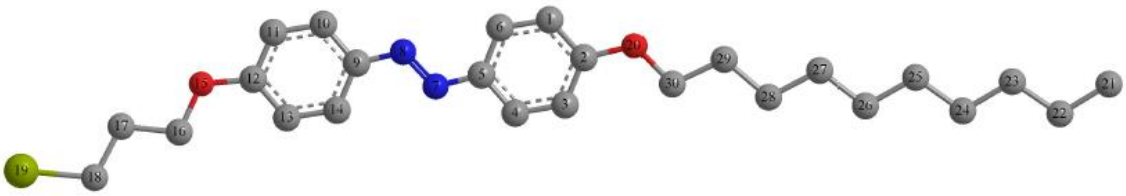
Conformer C2 for **5a**



Conformer C3 for **5a**

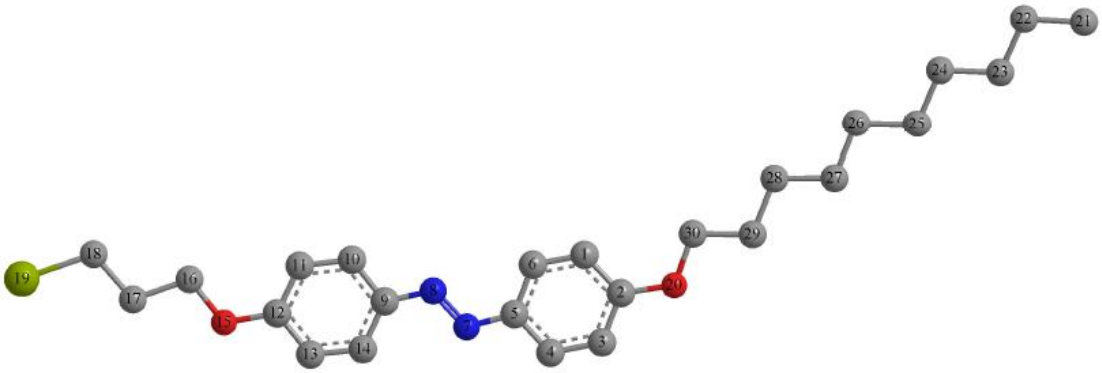


Conformer C4 for **5**[a]

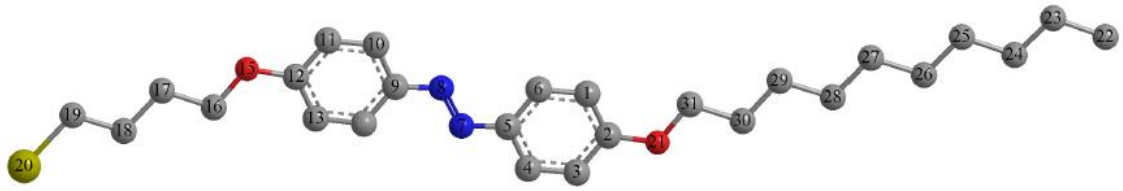


Conformer C1 for **5b**

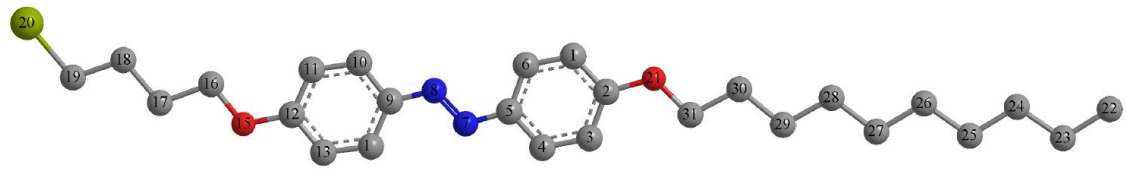
Conformer C2 for **5b**



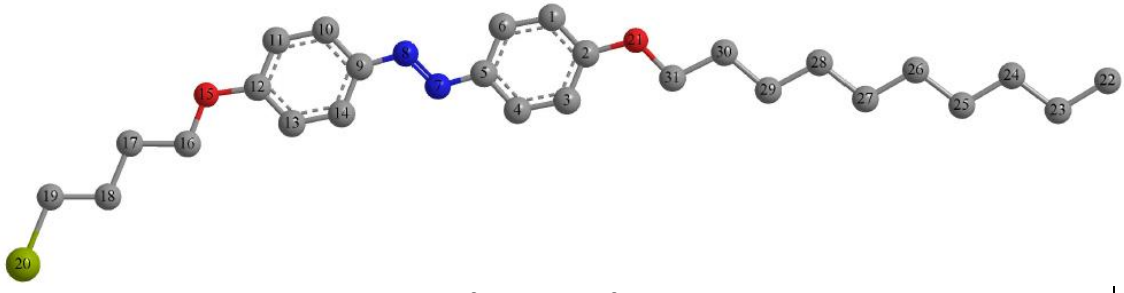
Conformer C3 for **5b**



Conformer C1 for **5c**



Conformer C2 for **5c**



Conformer C3 for **5c**

a. C1, C2, C3 and C4 refer to the conformers analysed for **5a**, **5b** and **5c**. For all conformers, see SI file.