

Supporting Information

Syntheses of New Liquid Crystals Derived From Thiophene Connected to Heterocyclic 1,2,3-Triazole

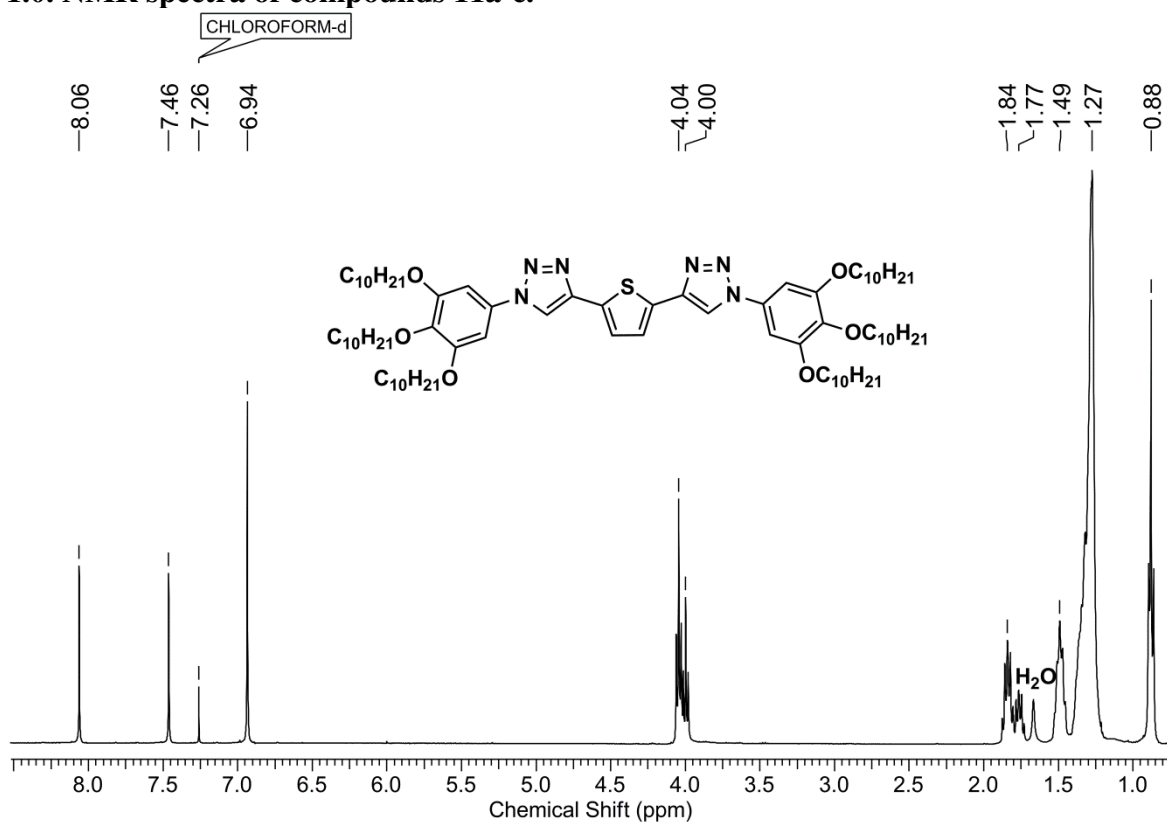
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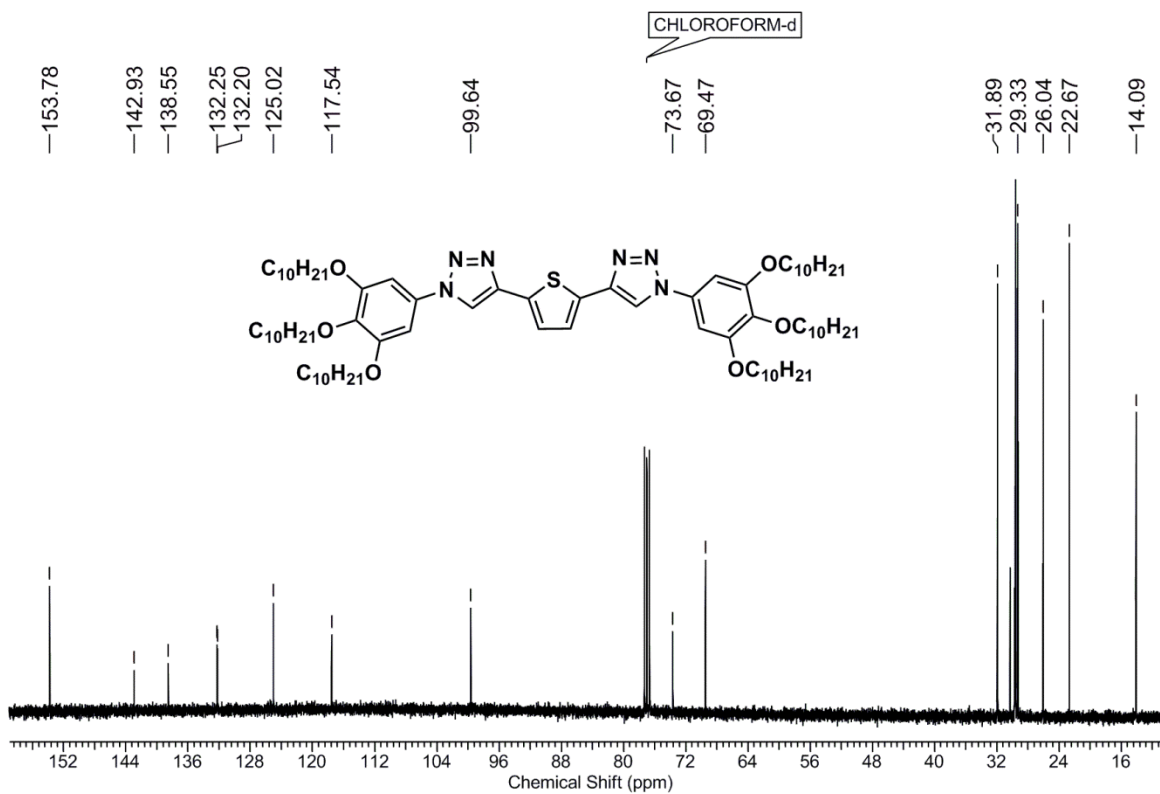
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Experimental

1.0. NMR spectra of compounds 11a-c.





b)

Figure S1. (a) ^1H NMR spectrum of compound **11a** (CDCl_3) and (b) ^{13}C NMR spectrum of compound **11c** (CDCl_3).

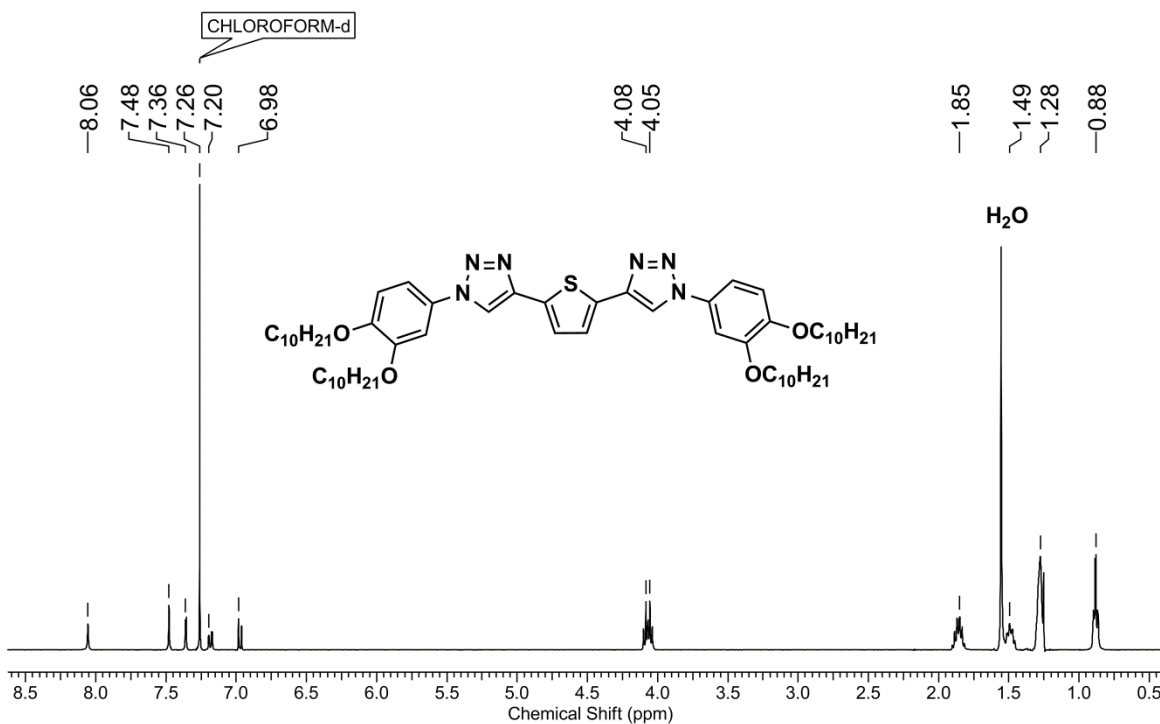


Figure S2. (a) ^1H NMR spectrum of compound **11b** (CDCl_3).

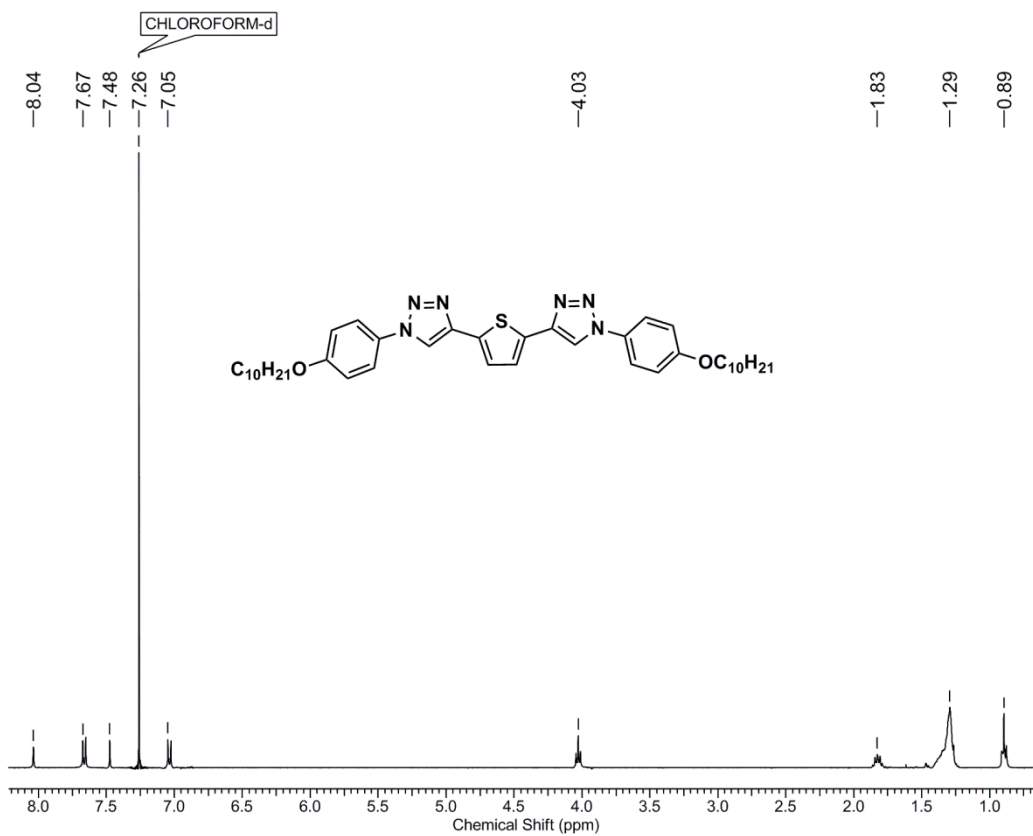
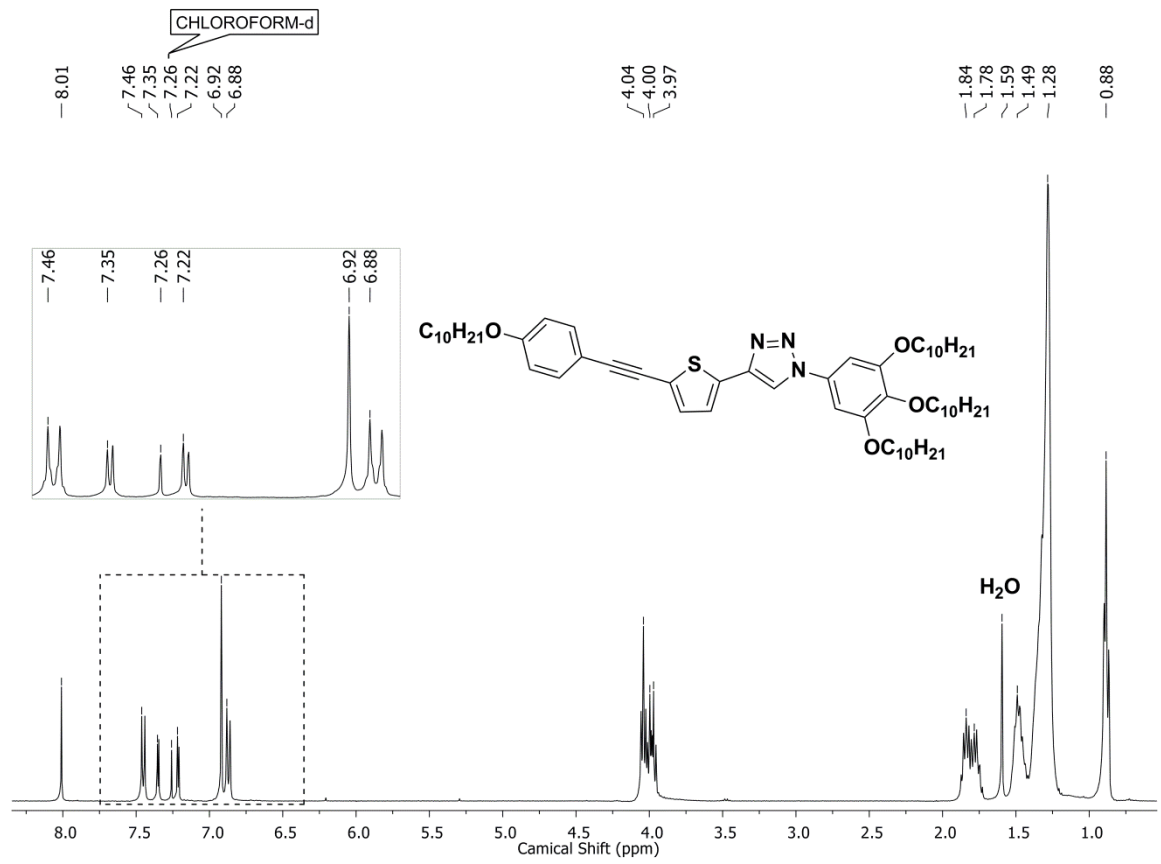
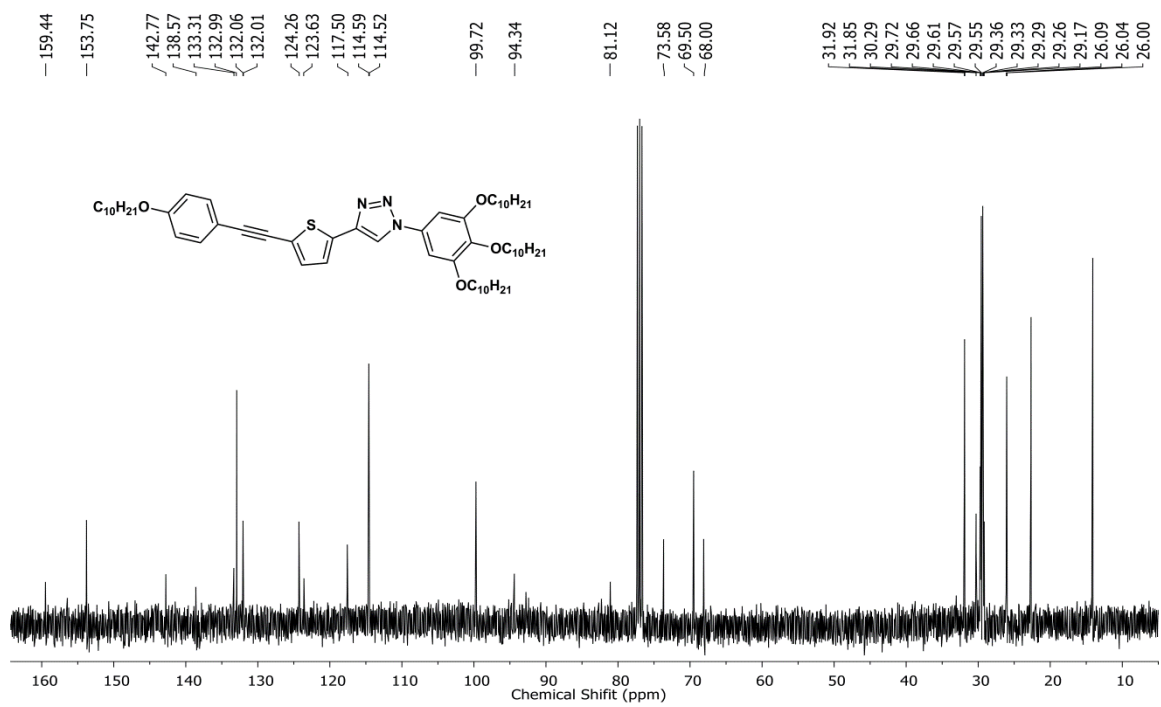


Figure S3. (a) 1H NMR spectrum of compound **11c**.

1.2 NMR spectra of compounds 16a-c.

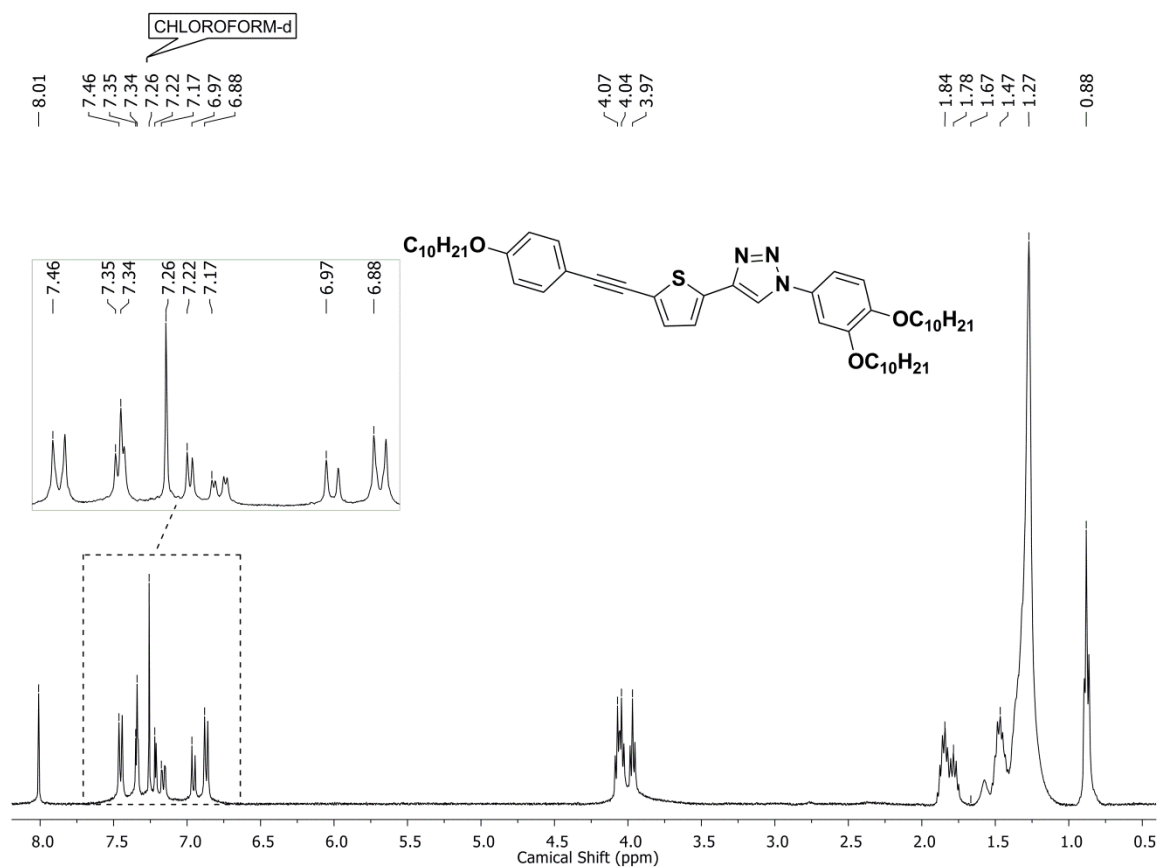


a)

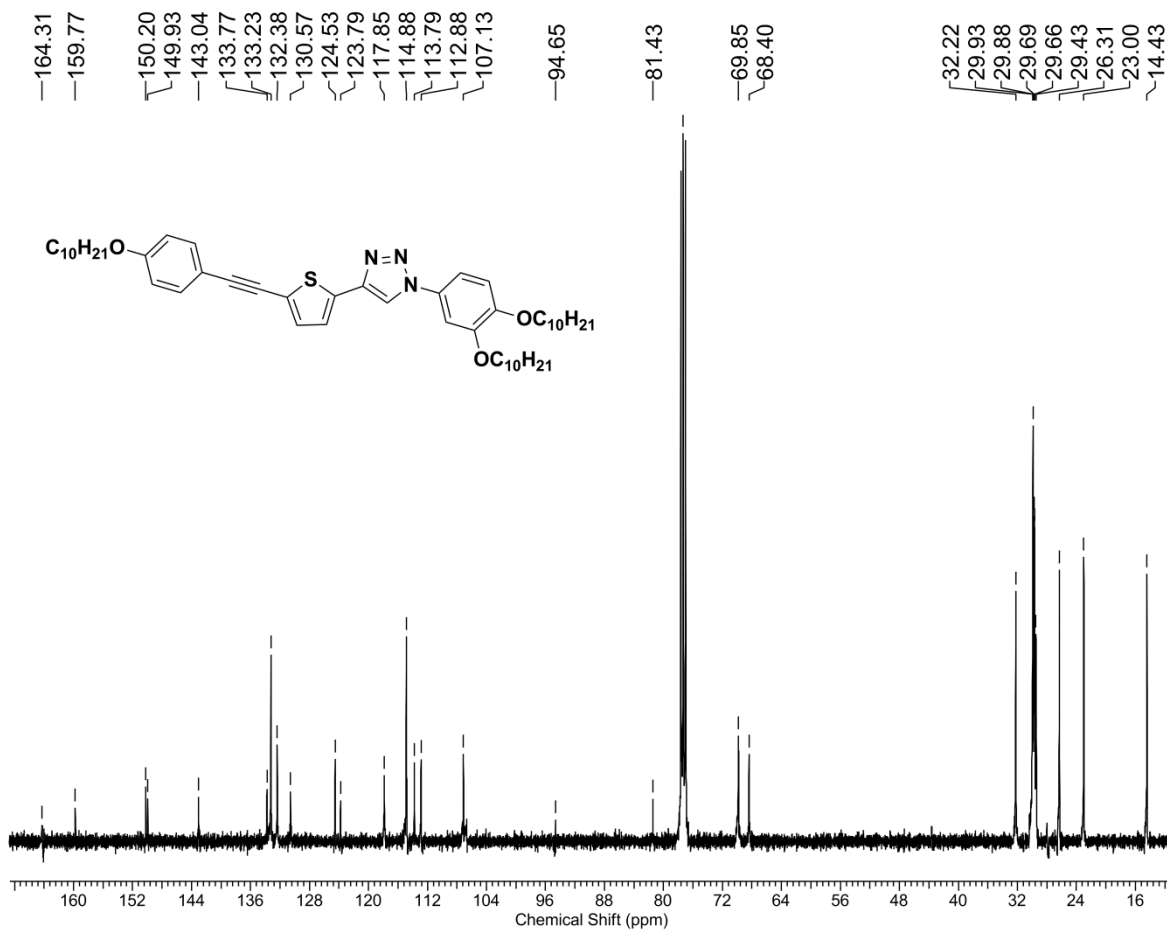


b)

Figure S4. ^1H NMR (a) and ^{13}C NMR (b) spectrum of compound **16a** (CDCl_3).

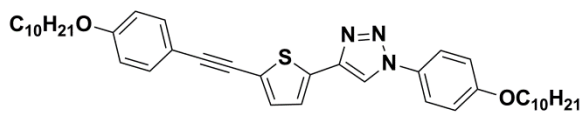
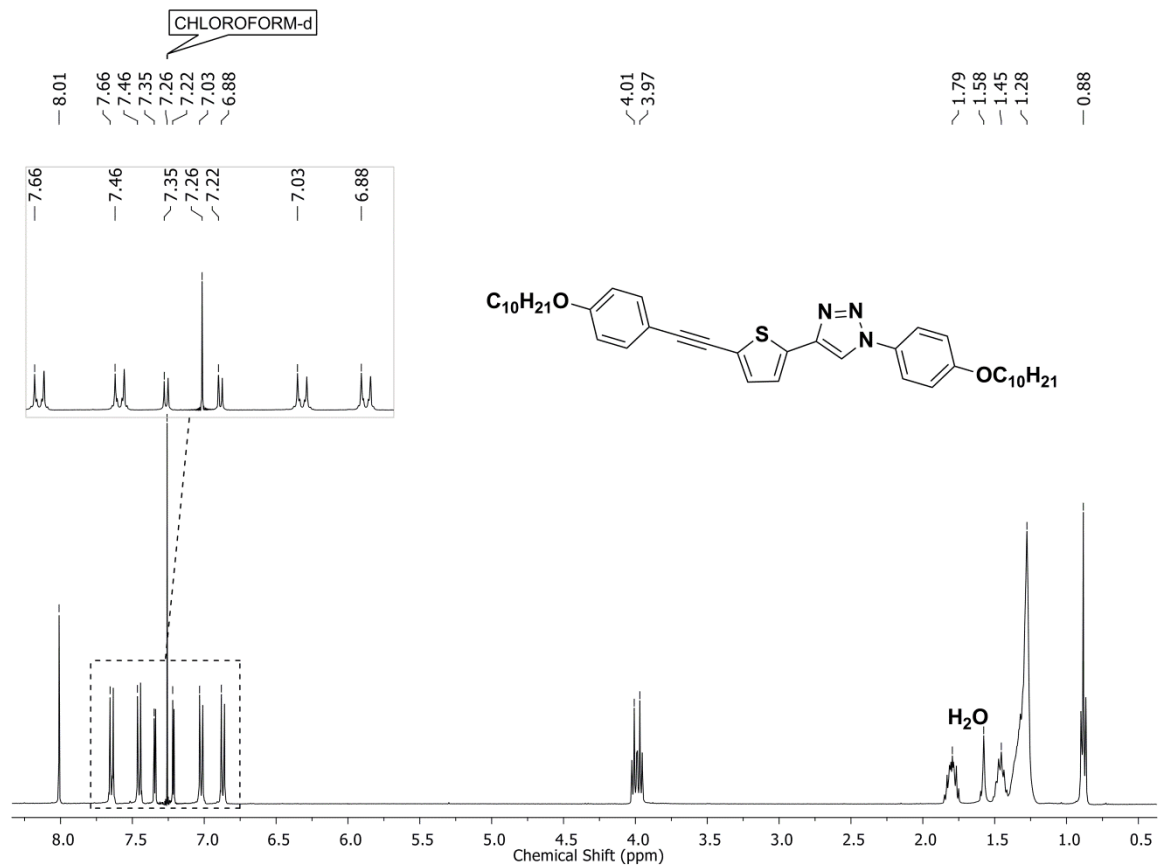


a)



b)

Figure S5. 1H NMR (a) and ^{13}C NMR (b) spectrum of compound **16b** ($CDCl_3$).



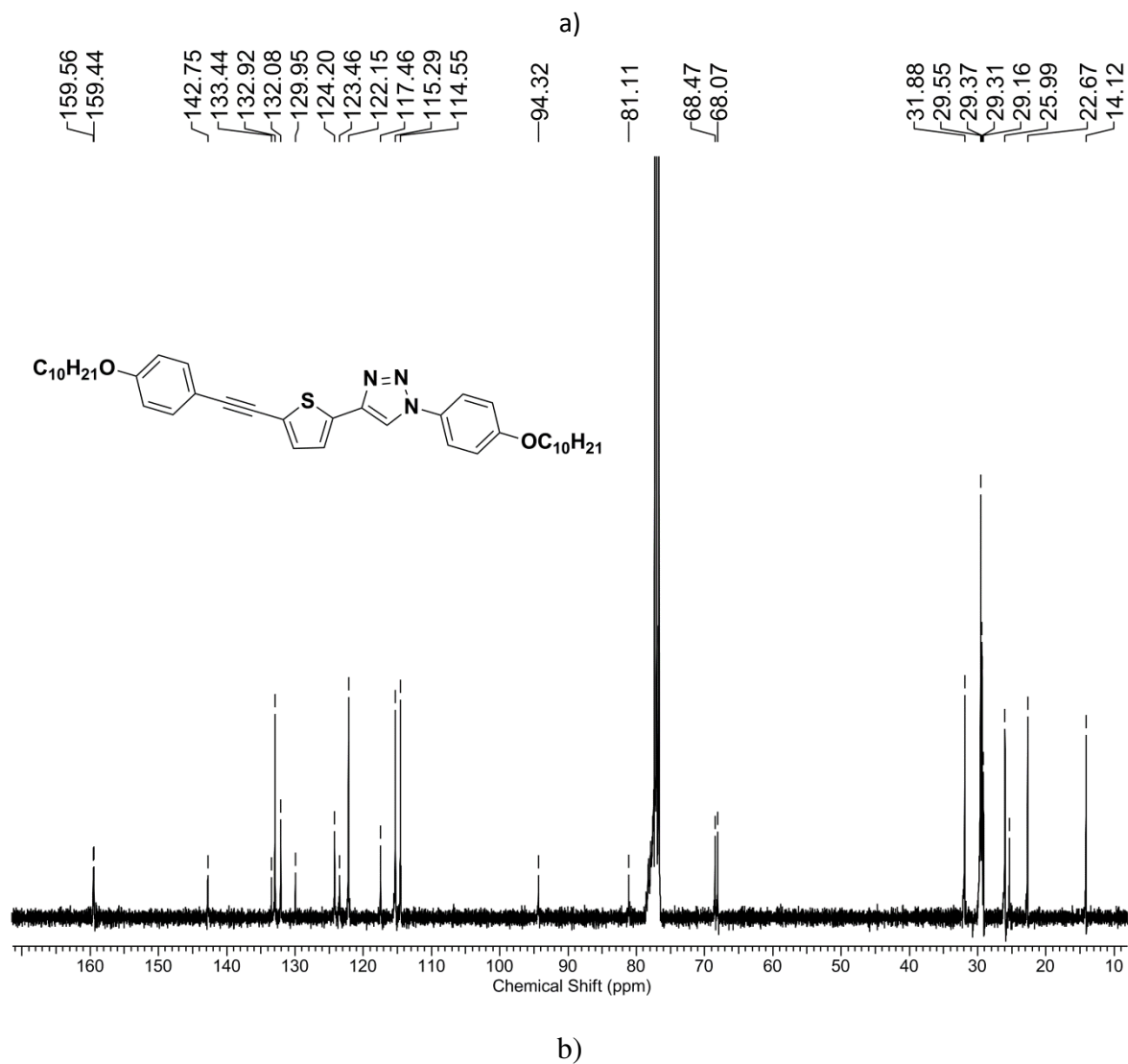


Figure S6. ^1H NMR (a) and ^{13}C NMR (b) spectrum of compound **16c** (CDCl_3).

2.0 MS spectra

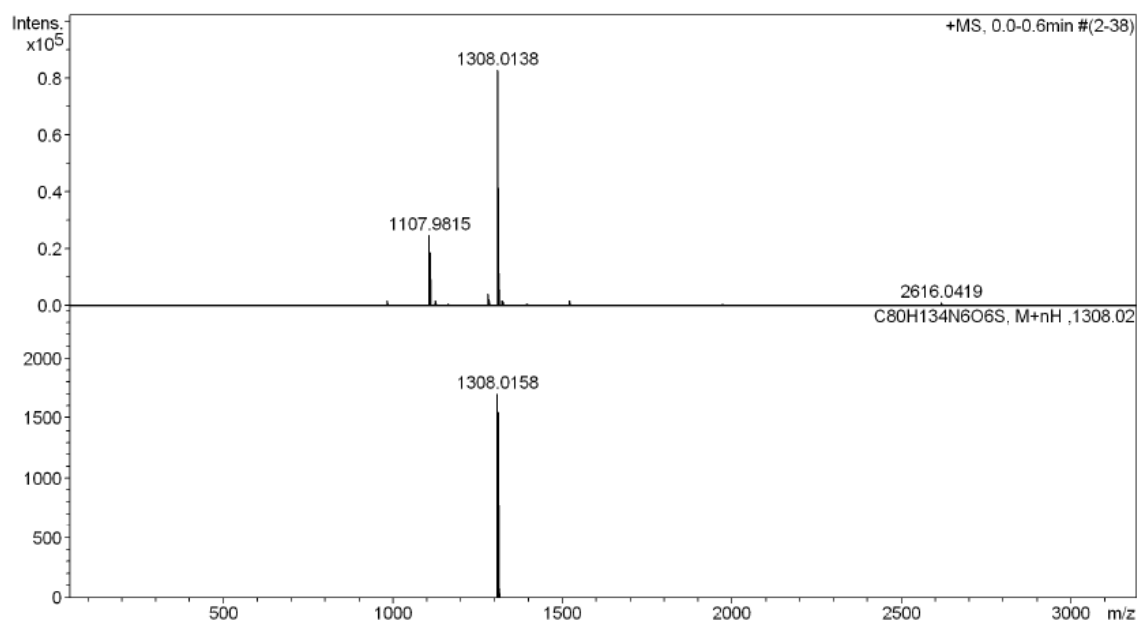


Figure S7. spectra of compound 10a.

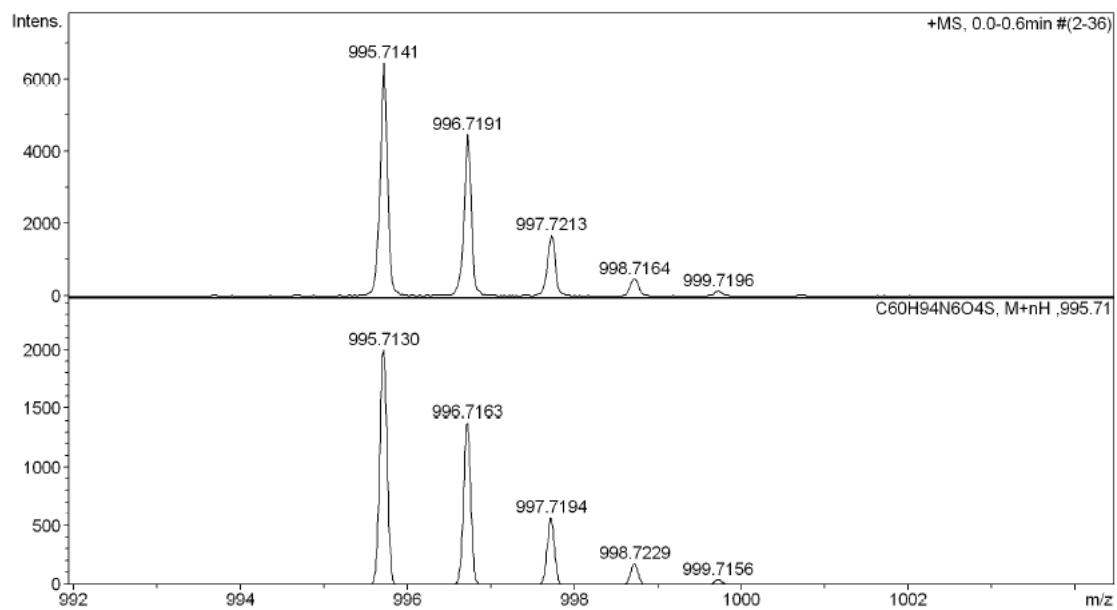


Figure S8. spectra of compound 10d.

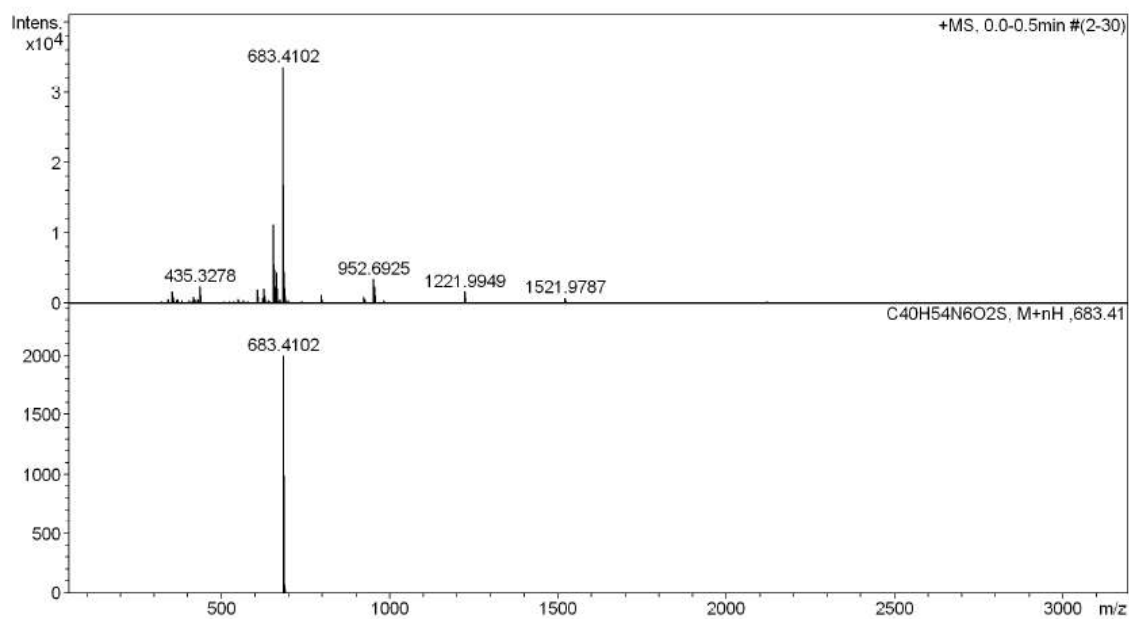


Figure S9. spectra of compound 10c.

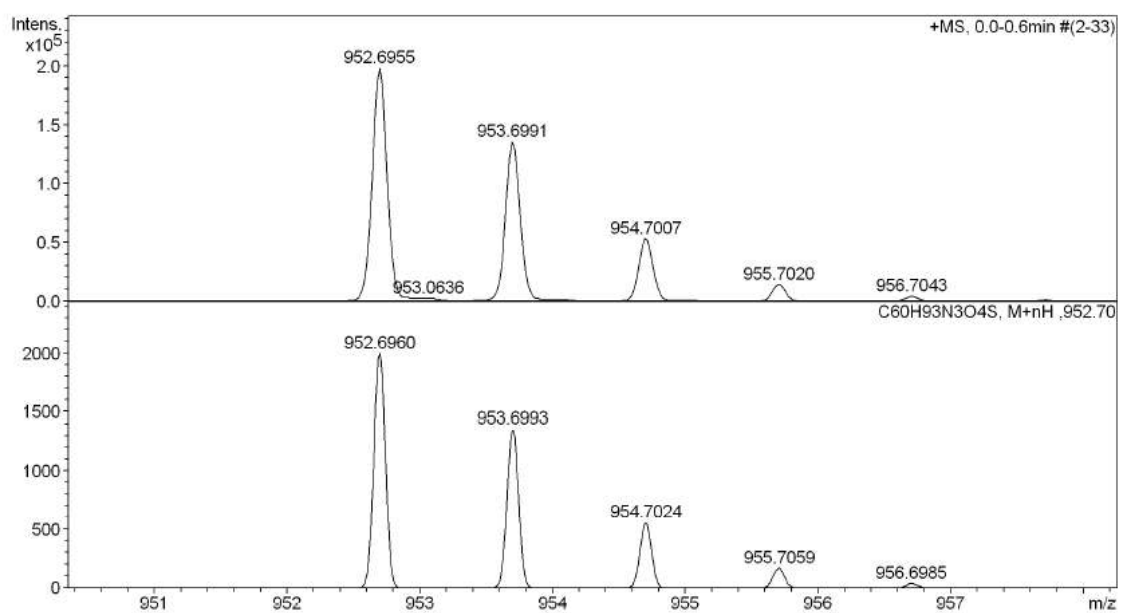


Figure S10. spectra of compound 16a.

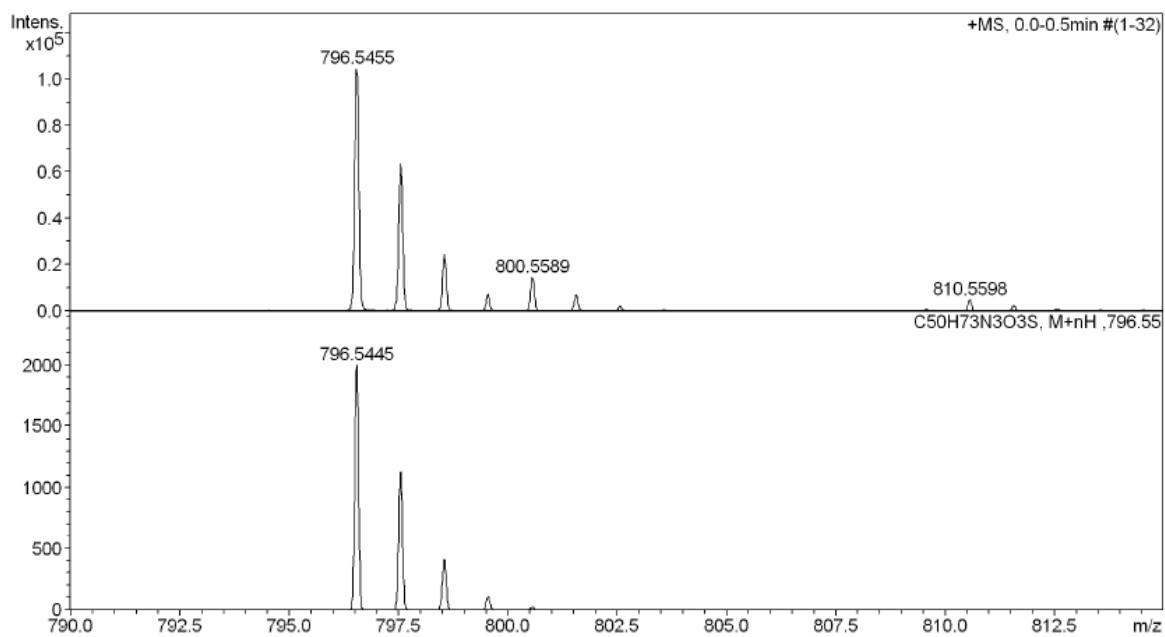


Figure S11. spectra of compound 16d.

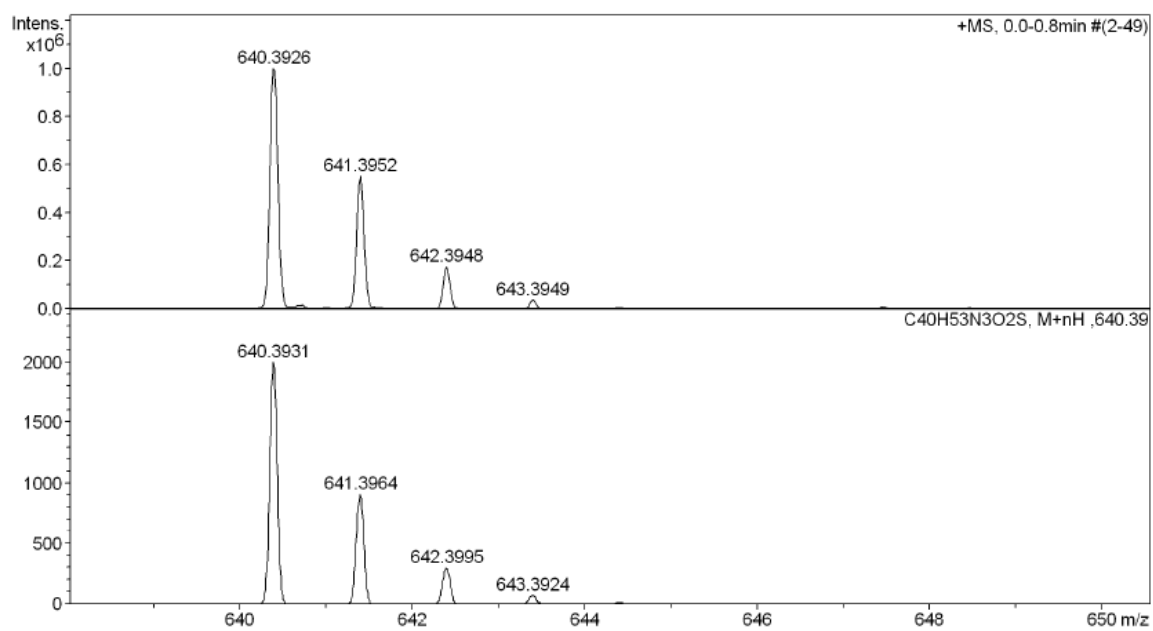


Figure S12. spectra of compound 16c.

2.0 DSC Thermograms

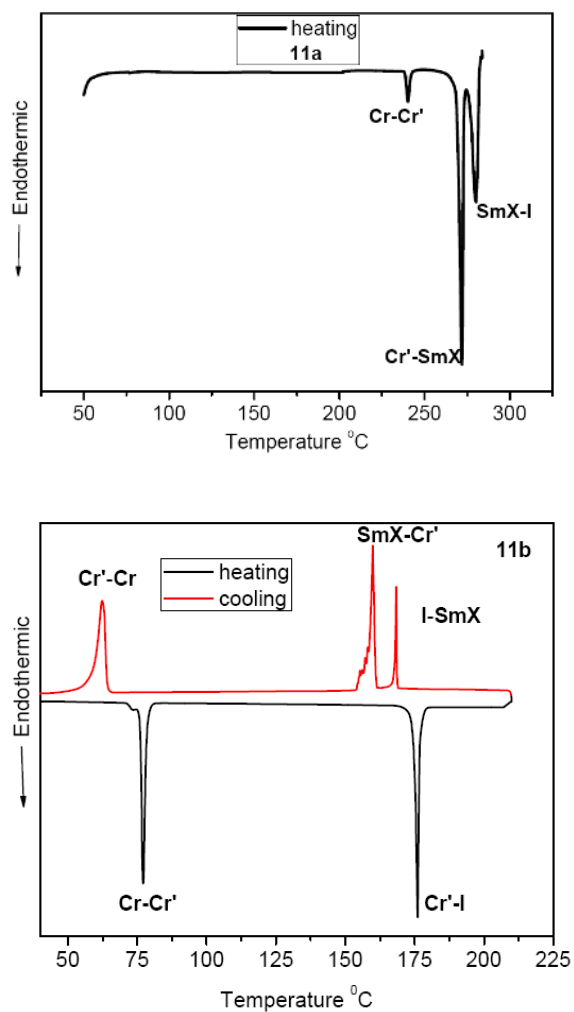


Figure S13. Thermograms obtained by DSC analysis showing the first cycle of heating and cooling ($10\text{ }^{\circ}\text{C min}^{-1}$) in nitrogen atmosphere for symmetrical compounds (**11a**, **11b**).

3.0 TGA curves

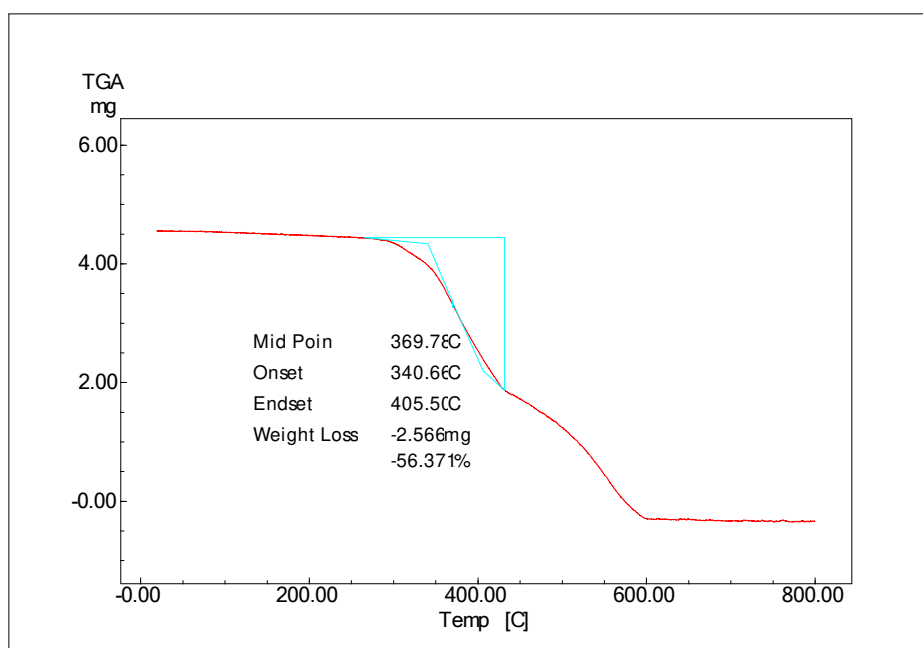


Figure S14. Thermograms of compounds 11a.

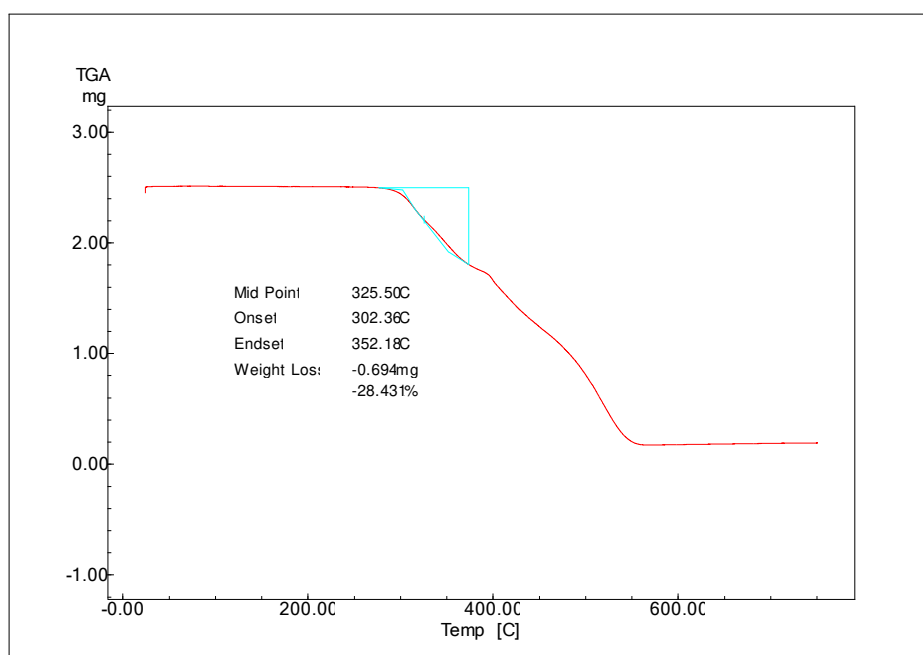


Figure S15. Thermograms of compounds 11b.

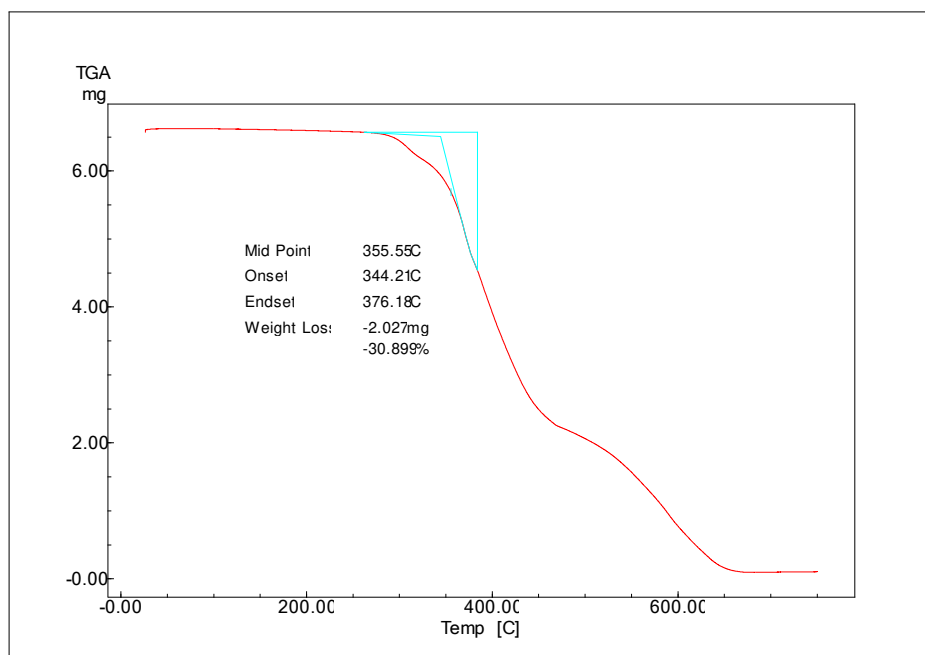


Figure S16. Thermograms of compounds **11c**.

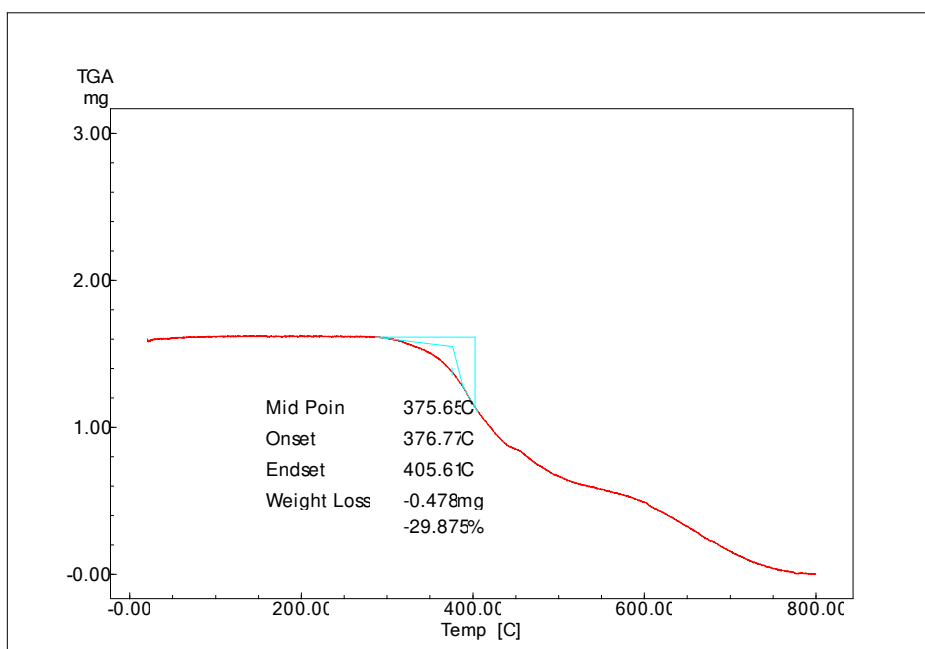


Figure S17. Thermograms of compounds **16a**.

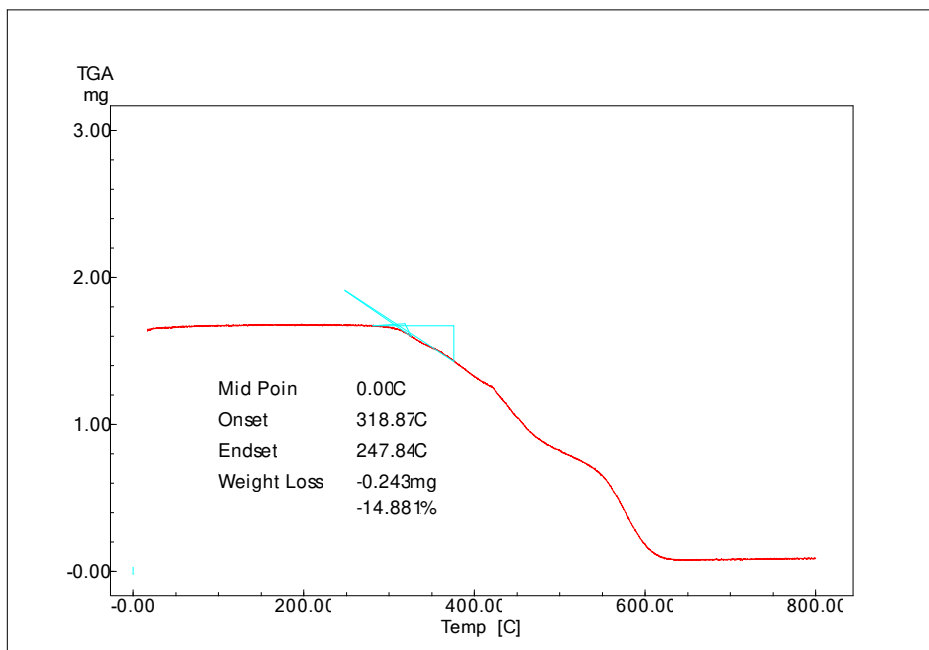


Figure S17. Thermograms of compounds **16b**.

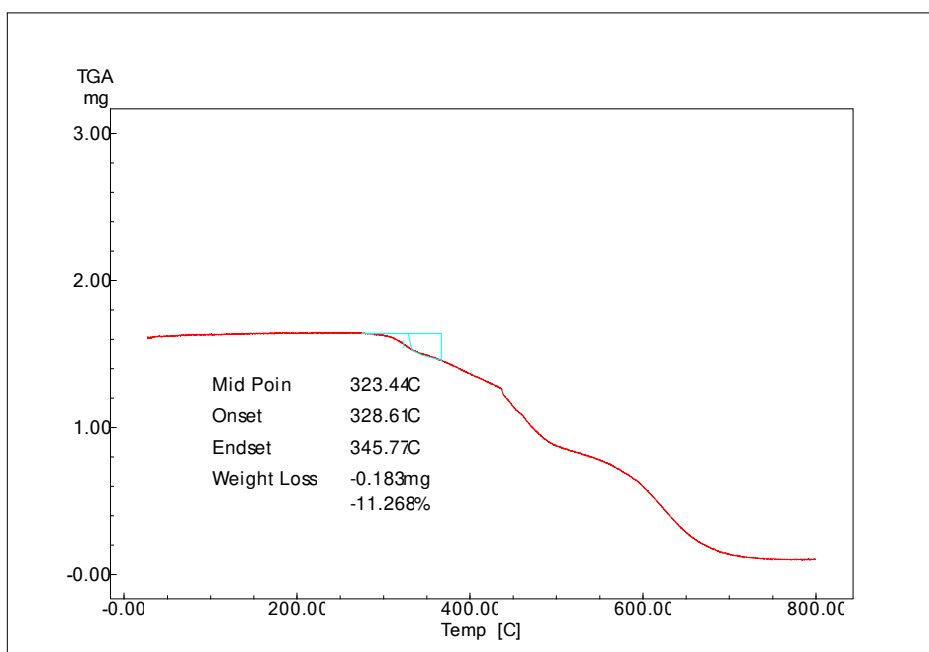


Figure S18. Thermograms of compounds **16c**.

S19. Experimental

1,2,3-tris(decyloxy)-5-nitrobenzene (2a). Firstly, 9.0g (16.4mmol) of **1a**, 0.16g (2.3mmol) in 30mL of CH₂Cl₂ the solution was stirred for 10m at room temperature, cooled to below -5°C and 3mL of HNO₃ was added and slowly stirred for 2h at room temperature. 100mL of water was added to the solution and the organic phase was extracted with CH₂Cl₂ (3 x 40mL). The organic phase was dried over anhydrous Na₂SO₄, the solvent removed by rotary evaporation. The solid was recrystallized on ethanol affording 7.2g of pale yellow solid (65%). Mp: 39.0-40.0°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2947, 2918, 2846, 1619. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.47 (s, 2H, Ar-H), 4.0 (m, 6H, O-CH₂), 1.83 (m, 6H, -CH₂), 1.74 (m, 2H, -CH₂), 1.48 (m, 6H, -CH₂), 1.27 (m, 34H, -CH₂), 0.88 (t, J = 6.6 Hz, 9H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 152.6, 143.8, 143.1, 102.1, 73.8, 69.4, 31.9, 30.3, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.0, 25.9, 22.7, 14.1.

3,4-Didecyloxynitrobenzene (2b). It was prepared according to the procedure written for the compound **2a**. The solid was recrystallized on ethanol affording 4.1g of pale yellow solid (74%). Mp: 76-78°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 3099, 2948, 2918, 2846, 1593. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.86 (dd, J = 8.4, 2.7 Hz, 1H, Ar-H), 7.73 (d, J = 2.7Hz, 1H, Ar-H), 6.88 (d, J = 8.4Hz, 1H, Ar-H), 4.10 (m, 4H, O-CH₂), 1.85 (m, 4H, -CH₂), 1.48 (m, 4H, -CH₂), 1.27 (m, 20H, -CH₂), 0.88 (t, J = 6.6Hz, 6H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 154.7, 141.1, 117.7, 111.0, 108.0, 69.4, 31.9, 29.6, 28.9, 25.9, 22.7, 14.1.

3,4,5-tris(decyloxy)aniline (3a). In an appropriate hydrogenation flask, 3.8g (6.8mmol) of compound **2a** was added together with 0.25g of 10% Pd/C catalyst in 80mL of THF. The hydrogenation process was maintained for 20h. After this period the catalyst was removed by filtration, the solvent was removed in rotary evaporation. The solid was recrystallized on ethanol affording 3.6g of solid dark gray (95%). Mp: 41-42°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 3409, 3331, 2918, 2849, 1610. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 6.57 (s, 2H, Ar-H), 3.91 (m, 6H, O-CH₂), 1.77 (m, 6H, -CH₂), 1.45 (m, 6H, CH₂), 1.27 (m, 36H, -CH₂), 0.87 (t, J = 6.6Hz, 9H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 153.7, 142.3, 131.0, 94.4, 73.5, 68.9, 31.9, 29.6, 29.4, 29.3, 26.1, 22.7, 14.1.

3,4-bis(decyloxy)aniline (3b). It was prepared according to the procedure written for the compound **3a**. The solid was recrystallized on ethanol affording 3.5g of solid dark gray (90%). Mp: 43-45°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2955, 2849, 1725, 1609. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 6.74 (d, J = 8.4Hz, 1H, Ar-H), 6.30 (d, J = 2.7Hz, 1H, Ar-H), 6.21 (dd, J = 8.4, 2.7Hz, 1H, Ar-H), 3.93, 3.89 (m, 4H, O-CH₂), 1.76 (m, 4H, -CH₂), 1.43 (m, 4H, -CH₂), 1.27 (m, 24H, -CH₂), 0.88 (t, J = 6.8Hz, 6H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 150.6, 142.1, 141.0, 117.3, 106.9, 102.7, 71.0, 69.0, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 24.1, 22.7, 14.1.

5-azido-1,2,3-tris(decyloxy)benzene (6a). Firstly, 4.2g (7.4mmol) of compound **3a** was added to a mixture of 40mL of THF and 85mL of CH₂Cl₂. The HBF₄ was added slowly and stirred for 10m at room temperature, after that it was cooled to below -5°C and 0.99g

(14.4mmol) of NaNO₂ was dissolved in a small quantity of water and added slowly. The solution was stirred for 20m at room temperature and 100mL of ether was added. The solid was filtered off and washed with ether/methanol affording a white solid. This solid (2.6g) was added to a solution of THF/H₂O 60/20mL and cooled in a bath of icy water. The sodium azide 2.6g (3.9mmol) was dissolved in a small quantity of water and added slowly. The solution was stirred for 1h at room temperature and afterwards extracted with CH₂Cl₂ (3 x 40mL). The organic phase was removed by rotary evaporation, affording 2.2g the black oil (50.4%). IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2955, 2849, 1725, 1609. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 6.21 (s, 2H, Ar-H), 3.94-3.90 (m, 6H, O-CH₂), 1.79-1.74 (m, 6H, -CH₂), 1.46 (m, 6H, -CH₂), 1.27 (m, 24H, -CH₂), 0.88 (t, J = 6.8Hz, 9H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 153.9, 135.5, 135.0, 97.7, 73.5, 69.2, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7.

4-azido-1,2-bis(decyloxy)benzene (6b). It was prepared according to the procedure written for the compound **6a**. The purification of compound **8b** was by column chromatography on silica, hexane/ethyl acetate (95/5), affording 6.5g of the solid black red (96%). Mp: 58-61°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2955, 2918, 2849, 2113, 1599. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 6.86 (d, J = 8.4Hz, 1H, Ar-H), 6.57 (dd, J = 8.4, 3.0 Hz, 1H, Ar-H), 6.53 (d, J = 3.0Hz, 1H, Ar-H), 3.96 (m, 4H, O-CH₂), 1.79 (m, 4H, -CH₂), 1.45 (m, 4H, -CH₂), 1.27 (m, 24H, -CH₂), 0.88 (m, 6H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 115.2, 114.0, 108.4, 69.6, 69.4, 31.9, 29.9, 29.6, 29.4, 29.3, 29.1, 29.1, 26.0, 25.9, 22.7, 14.1.

N-(4-(decyloxy)phenyl)acetamide (4). The mixture of 5.0g (33.1mmol) of 4-hydroxy-*N*-methylbenzamide, 8.7mL (39.7mmol) of 1-bromododecane, 11.4g (82.7mmol) of K₂CO₃ and 250mL of butanone was refluxed and stirred for 24h. After this period, the suspension was filtered off and washed with hot butanone. The solvent was removed by rotatory evaporation and the solid obtained was macerated in hexane affording 9.2g of a white crystal (96%). Mp: 86-89°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2955, 2918, 2849, 2113, 1599. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 7.37 (d, J = 8.9Hz, 2H, Ar-H), 6.84 (d, J = 8.9Hz, 1H, Ar-H), 3.91 (t, 2H, O-CH₂), 2.13 (s, 3H, -OCCH₃), 1.75 (m, 2H, -CH₂), 1.43 (m, 2H, -CH₂), 1.27 (m, 12H, -CH₂), 0.88 (m, 6.8 Hz, 3H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 168.2, 156.0, 130.7, 130.7, 121.9, 114.7, 68.3, 31.9, 29.7, 29.62, 29.6, 29.6, 29.4, 29.3, 29.3, 26.0, 24.3, 22.7, 14.1.

4-(decyloxy)aniline (5). The suspension of 3.5g (12.0mmol) of compound **4** and 45mL of HCl on 150mL water was refluxed for 18h. After that it was basified with a solution of NaOH 20% until pH 8. The solid was filtered off and washed with water and recrystallized in hexane, affording 2.6g of gray solid (87%). Mp: 40-41°C. IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 3406, 3328, 2921, 2849, 1505. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 6.76 (m, 4H, Ar-H), 3.89 (t, J = 6.5Hz, 2H, O-CH₂), 3.21 (s, 2H, -NH₂), 1.75 (m, 2H, -CH₂), 1.44 (m, 2H, -CH₂), 1.28 (m, 12H, -CH₂), 0.89 (m, 6.8 Hz, 3H, -CH₃). ¹³C NMR (CDCl₃), δ , ppm: 153.0, 138.2, 117.1, 115.6, 68.7, 31.9, 29.6, 29.4, 29.3, 26.1, 22.7, 14.1.

1-azido-4-(decyloxy)benzene (6c). It was prepared according to the procedure written for the compound **6a**. The purification was by column chromatography on silica, hexane as the

eluent, affording 3.5g of yellow oil (70%). IR (KBr pellet) $\nu_{\max}\text{cm}^{-1}$: 2925, 2854, 2111, 1505. ^1H NMR (400 MHz, CDCl_3), δ , ppm: 6.95 (d, $J= 8.9\text{Hz}$, 2H, Ar-H), 6.89 (d, $J= 8.9\text{Hz}$, 1H, Ar-H), 3.92 (t, $J= 6.4\text{Hz}$, 2H, O- CH_2), 1.77 (m, 2H, - CH_2), 1.44 (m, 2H, - CH_2), 1.27 (m, 12H, - CH_2), 0.88 (m, 6.8 Hz, 3H, - CH_3). ^{13}C NMR (CDCl_3), δ , ppm: 156.6, 132.1, 119.9, 115.7, 68.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7.