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Room temperature columnar liquid crystalline self-assembly of acidochromic, luminescent, star-shaped molecules with cyanovinylene chromophores

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Supporting information

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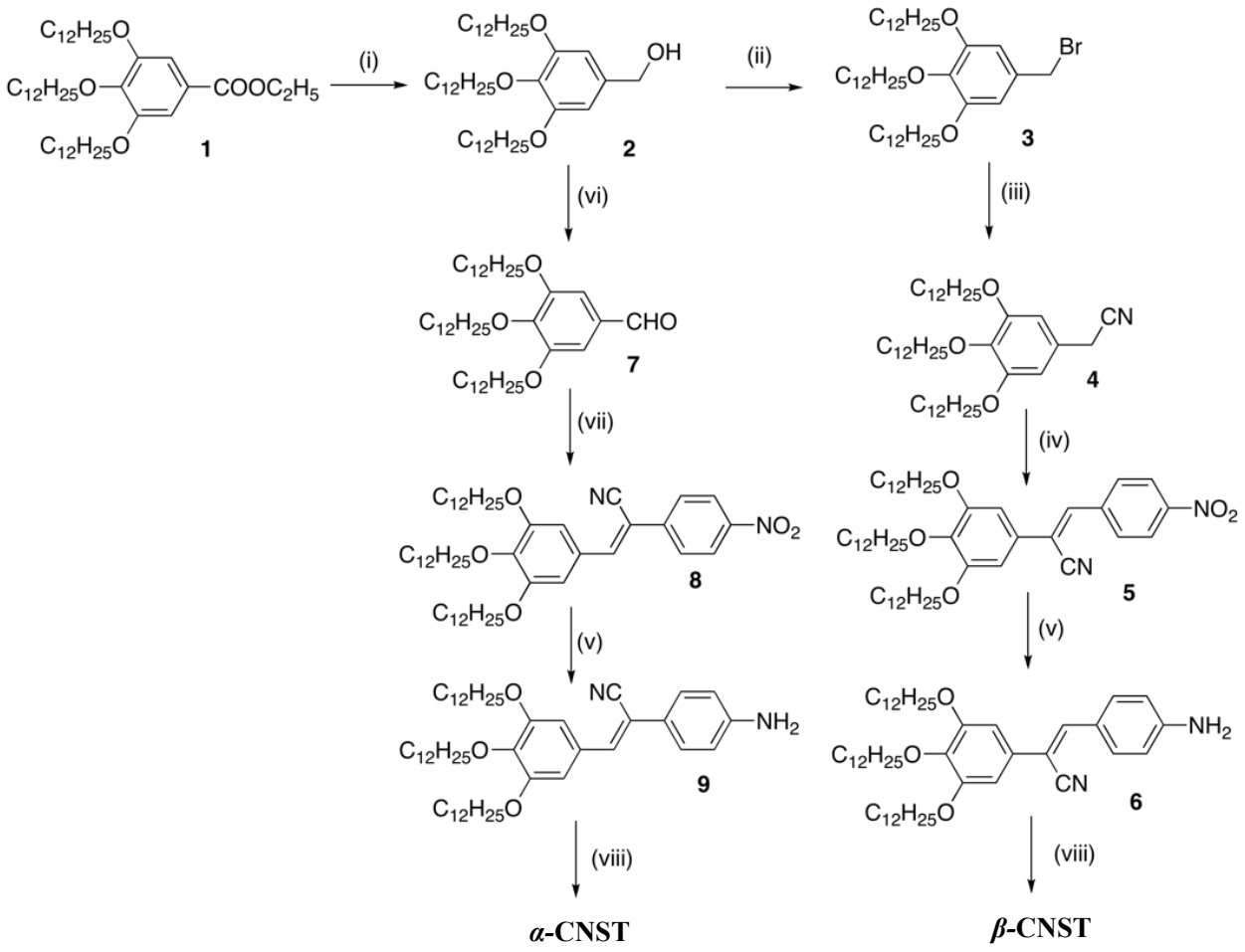
1. Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Aluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer.Polarizing optical microscope (POM) (Nikon Eclipse LV100POL) in conjunction with a controllable hot stage (Mettler Toledo FP90) was used for the characterization of mesogens. The phase transitions, associated enthalpy changes were obtained by differential scanning calorimeter (DSC) (Mettler Toledo DSC1). X-ray diffraction (XRD) studies were carried out using image plate and a detector. This setup had CuKα (0.15418 nm) radiation from a source (GeniX3D, Xenocs) operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to irradiate the sample. Glass capillaries containing the sample were used for the measurements. Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state and solid thin film state respectively. Time resolved lifetime measurements were done on time correlated single photon counter from Horiba JobinYvon spectrophotometer.

2. Experimental Section

Scheme 1. Synthesis of star-shaped TSANs



Reagents and Conditions: (i) LAH, THF, RT, 2 h (95 %); (ii) $SOCl_2$, dry dichloromethane, room temperature (95%); (iii) NaCN, benzyltriethylammonium chloride, Dry DMF, 65 ^oC, 72 h (75%); (iv) 4-Nitrobenzaldehyde, dry ethanol+chloroform (1:1), NaOEt, room emperature, 3 h (70 %); (v) Zinc powder, $HCOONH_4$, THF-CH_3OH (2:1), room temperature, 1 h (60-70 %); (vi) (PCC)pyridinium chlorochromate:silica gel, dichloromethane, room temperature, 1 h (81 %); (vii) 4-nitrophenylacetonitrile, ethanol, piperidine (75%); (viii) 1,3,5-triformylphloroglucinol, Methanol, reflux, 6 h (67 -68%).

Procedure for the synthesis of ethyl 3,4,5-tri(dodecyloxy) benzoate (**1**)[1]

A mixture of ethyl gallate (25.2 mmol, 1equiv.), anhyd. K_2CO_3 (166.5 mmol, 6.6 equiv.), *n*-bromododecane (83.3 mmol, 3.3 equiv.) were taken in dry DMF (20 ml) and heated at 80 ^oC for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The combined extract was washed with water and brine and later dried over anhyd. Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethylacetate-hexanes yielded the desired product.

R_f = 0.61(10% EtOAc-hexanes); Low melting white solid; yield: 90%; IR (KBr pellet): ν_{max} in cm^{-1} 2924, 2853, 1716, 1590, 1504, 1465, 1432, 1333, 1222, 1119; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.25 (s, 2H, Ar), 4.35 (q, 2H, J = 6 Hz, $COOCH_2$), 4.01 (m, 6H, 3 × OCH_2), 1.23-1.83 (m, 60H, 30 × CH_2), 0.87-0.89 (m, 12H, 4 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 166.66, 153.01, 142.57, 125.26, 108.24, 73.68, 69.40, 61.14, 32.14, 30.54, 29.95, 29.92, 29.85, 29.79, 29.61, 29.54, 26.30, 22.90, 14.30; HRMS (ESI+) exact mass calculated for $C_{45}H_{83}O_5$ (M+1): 703.6235, Found: 703.6199.

Procedure for the synthesis of 3,4,5- tridodecyloxy benzyl alcohols (**2**):[1]

To a stirred suspension of lithium aluminium hydride (LAH) (21.3 mmol, 1.5 equiv.) in dry THF (20 ml) under nitrogen atmosphere, added the solution of ethyl 3,4,5-tri(dodecyloxy) benzoate (14.2 mmol, 1 equiv.) in dry THF drop wise at 0 ^oC. Then the reaction mixture was allowed to reach room temperature and stirred for 2 h. Excess LAH present was quenched by the addition of moist sodium sulphate. Reaction mixture was extracted with EtOAc (6 × 30 ml). The combined extracts were washed with water, dried over anhyd. Na_2SO_4 and concentrated *in vaccuo*. Purification was done by column chromatography over silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f = 0.15 (10% EtOAc-hexanes), white solid, yield: 95%; IR (KBr pellet): ν_{max} in cm^{-1} 3417.27, 2922.36, 2852.51, 1590.29, 1467.09, 1438.45, 1334.39, 1231.90, 1124.64, 806.80, 722.27, 466.28; ^1H NMR ($CDCl_3$, 600 MHz): δ 6.55 (s, 2H, Ar), 4.59-4.60 (d, 2H, $ArCH_2$), 3.92- 3.98 (m, 6H, 3 × OCH_2), 1.26- 1.81 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 153.47, 137.75, 136.24, 105.52, 73.65, 69.30, 65.88, 32.16, 32.15, 30.54, 29.98,

29.96, 29.92, 29.88, 29.87, 29.84, 29.63, 29.62, 29.59, 26.36, 26.32, 22.91, 14.33.; HRMS (ESI+) exact mass calculated for $C_{43}H_{80}O_4$ (M+1): 661.6129, Found: 661.6128.

Procedure for the synthesis of 3,4,5- tridodecyloxy benzyl chloride (**3**):[2]

3,4,5- tridodecyloxy benzyl alcohol (4.5mmol, 1equiv.) was dissolved in Dry DCM (20 mL) with stirring and cooled to 0 ^oC under Ar atmosphere. $SOCl_2$ (3.18 equiv.) was added to the above reaction mixture and stirred at the room temperature for 2 h. The reaction mixture was slowly quenched with saturated $NaHCO_3$. Reaction mixture was extracted with methylene chloride and the organic layer was washed with saturated brine solution, and dried over Na_2SO_4. A light yellowish white solid was obtained on removal of solvent. used without further purification for next step reaction.

R_f = 0.5 (5% EtOAc-hexanes), light yellowish white solid, yield: 95%; IR (KBr pellet): ν_{max} in cm^{-1} 2954, 2921, 2849, 1594, 1506, 1466, 1441, 1393, 1334, 1246, 1125, 830; ^1H NMR ($CDCl_3$, 600 MHz): δ 6.56 (s, 2H, Ar), 4.51 (s, 2H, $ArCH_2$), 3.92-3.98 (m, 6H, 3 × OCH_2), 1.26- 1.80 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 153.21, 138.28, 132.32, 107.06, 73.47, 69.14, 47.01, 31.95, 30.34, 30.3, 29.77, 29.72, 29.66, 29.39, 26.11, 22.72, 14.14; LRMS (ESI+) molecular mass calculated for $C_{43}H_{80}ClO_3$ (M+1): 680.55, Found: 680.77.

Procedure for the synthesis of 2-(3,4,5-tris(dodecyloxy)phenyl) acetonitrile (**4**):

3,4,5-tridodecyloxy benzyl chloride (2.76 mmol, 1equiv.) was dissolved in DMF (11 mL). Sodium cyanide (13.81 mmol, 5 equiv.) and benzyltriethylammonium chloride (0.13 mmol, 0.05 equiv.) were added. The mixture was stirred at 65 ^oC for 72 h. The reaction mixture was poured into water and extracted with DCM. The combined organic layers were washed with water, brine, dried Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography using 5-10% ethyl acetate-hexane system to get pure product as a white solid (1.38 g, 75%).

R_f = 0.53 (10% EtOAc-hexanes), white solid, yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 2954, 2920, 2850, 2249, 1595, 1506, 1467, 1443, 1393, 1337, 1250, 1236, 1124, 816, 722; ^1H NMR ($CDCl_3$, 600 MHz): δ 6.47 (s, 2H, Ar), 3.91-3.97 (m, 6H, 3 × OCH_2), 3.66 (s, 2H, $ArCH_2$), 1.26-1.82 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 153.77, 137.97,

124.87, 118.24, 111.20, 106.41, 73.69, 69.42, 32.15, 30.51, 29.93, 29.86, 29.62, 29.55, 26.29, 23.99, 22.92, 14.35; HRMS (ESI+) exact mass calculated for $C_{44}H_{80}NO_3$ (M+1): 670.6133, Found: 670.6138.

Procedure for the synthesis of (Z)-2-(3,4,5-tris(dodecyloxy)phenyl)-3-(4-nitrophenyl) acrylonitrile (**5**):

A solution of 4-nitro benzaldehyde (1.55 mmol, 2equiv.) and 2-(3,4,5-tris(dodecyloxy)phenyl) acetonitrile (0.77 mmol., 1equiv.) in ethanol+chloroform (1:1) (20 mL) was stirred at room temperature and then NaOEt (3.87mmol., 5 equiv.) was added. After 2 h, large amounts of yellow solids were separated out from the solution the solution was filtered and washed with ethanol. Further purification done by recrystallization from DCM-Methanol.

R_f = 0.79 (10% EtOAc-hexanes), yellow solid, yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 2221, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30,720.33, 645.33, 579.48; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (d, 2H, *J* = 6 Hz, Ar), 8.0 (d, 2H, *J* = 12 Hz, Ar), 7.47 (s, 1H, Ar), 6.86 (s, 2H, Ar), 3.99 - 4.04 (m, 6H, 3 × OCH_2), 1.26-1.85 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 153.80, 148.26, 140.42, 139.98, 137.98, 130.06, 128.67, 124.4, 117.44, 116.27, 105.19, 73.89, 69.61, 32.16, 30.54, 29.91, 29.86, 29.62, 29.61, 29.56, 26.30, 22.92, 14.35; HRMS (ESI+) exact mass calculated for $C_{51}H_{83}N_2O_5$ (M+1): 803.6296, Found: 803.6302.

Procedure for the synthesis of (Z)-2-(3,4,5-tris(dodecyloxy)phenyl)-3-(4-aminophenyl) acrylonitrile (**6**):

To a solution of nitro compound **5** (0.37 mmol, 1 equiv.) in THF + CH_3OH (2:1) was added Zn powder (2.28 mmol., 6.1equiv.) and $HCOONH_4$ (2.28mmol., 6.1 equiv.). This mixture was stirred for 1 h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent yielded a residue, which was column chromatographed with a mixture of DCM-heaxane (5-20 %) as eluents to provide the desired amine. Further purification done by recrystallization from DCM-methanol system yields the pure product.

R_f = 0.21 (10% EtOAc-hexanes), light yellow solid, yield: 60%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 2220, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30,720.33; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.75 (d, 2H, *J* = 12 Hz, Ar), 7.28 (s,

1H, Ar), 6.78 (s, 2H, Ar), 6.71 (d, 2H, J = 6 Hz, Ar), 3.96 - 4.03 (m, 6H, 3 × OCH_2), 4.05 (s, 2H, N**H**$_2$), 1.26-1.84 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 153.58, 148.91, 141.87, 138.79, 131.47, 130.65, 124.26, 119.35, 114.9, 106.56, 104.56, 73.78, 69.49, 32.17, 32.15, 30.54, 29.99, 29.97, 29.94, 29.89, 29.87, 29.83, 29.65, 29.6, 26.34, 26.32, 22.93, 14.36; HRMS (ESI+) exact mass calculated for $C_{51}H_{85}N_2O_3$ (M+1): 773.6554, Found: 773.6557.

Procedure for the synthesis of 3,4,5- tridodecyloxy benzaldehydes (**7**):[1]

An appropriate 3,4,5- tridecyloxy benzyl alcohol (11.3 mmol, 1 equiv.) was taken in CH_2Cl_2 (10 vol.). To this pyridinium chlorochromate (11.3 mmol, 1 equiv.) adsorbed over equal amount of silica gel is added and stirred at room temperature for 1 h. The reaction mixture was filtered over celite bed and concentrated to get the crude product, which was further purified by column chromatography on silica gel (60-120) with 10% EtOAc-hexanes as eluent.

R_f = 0.53 (10% EtOAc-hexanes), white solid, yield: 81%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 1695.12, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30, 720.33, 645.33, 579.48; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.83 (s, 1H, CHO), 7.08 (s, 2H, Ar), 4.02 - 4.06(m, 6H, 3 × OCH_2), 1.26-1.84 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 191.52, 153.74, 144.08, 131.66, 108.07, 73.85, 69.45, 32.14, 30.56, 29.97, 29.94, 29.92, 29.88, 29.85, 29.76, 29.60, 29.47, 26.29, 26.25, 22.92, 14.33; HRMS (ESI+) exact mass calculated for $C_{43}H_{79}O_4$ (M+1): 659.5973, Found: 659.5975.

Procedure for the synthesis of (Z)-3-(3,4,5-tris(dodecyloxy)phenyl)-2-(4-nitrophenyl) acrylonitrile (**8**):

A solution of 3,4,5- tridodecyloxy benzaldehydes (0.76 mmol, 1equiv.) and 4-nitrophenylacetonitrile (0.99 mmol., 1.3equiv.) in ethanol (20 mL) was heated to dissolve and then 1 mL of piperidine was added. After 2 h the solution was cooled down to room temperature and a large amounts of yellow solids were separated out from the solution. Pure product could be obtained by the vacuum filtration and washing with ethanol.

R_f = 0.8 (10% EtOAc-hexanes), yellow solid, yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 2221, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30,720.33, 645.33, 579.48; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.30 (d, 2H, J = 12 Hz, Ar), 7.82

(d, 2H, J = 12 Hz, Ar), 7.55 (s, 1H, Ar), 7.20 (s, 2H, Ar), 4.07 - 4.03 (m, 6H, 3 × OCH_2), 1.26-1.86 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 153.46, 147.83, 145.94, 141.79, 141.15, 127.9, 126.69, 124.55, 117.86, 108.64, 107.53, 73.93, 69.48, 32.16, 32.14, 30.56, 29.98, 29.95, 19.92, 29.88, 29.86, 29.78, 29.62, 29.59, 29.50, 26.32, 26.26, 22.91, 14.34; HRMS (ESI+) exact mass calculated for $C_{51}H_{83}N_2O_5$ (M+1): 803.6296, Found: 803.6301.

Procedure for the synthesis of (Z)-3-(3,4,5-tris(dodecyloxy)phenyl)-2-(4-aminophenyl) acrylonitrile (**9**):

To a solution of nitro compound **8** (0.9 mmol, 1 equiv.) in THF + CH_3OH (2:1) was added Zn powder (3.04 mmol., 6.1equiv.) and $HCOONH_4$ (3.04 mmol., 6.1 equiv.) and stirred for 1 h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent yielded the residue. This residue was purified by column chromatography over neutral alumina with DCM-heaxane (5-20 %) as eluents to provide the desired amine. Further purification done by recrystallization from DCM-methanol system yields the pure product.

R_f = 0.2 (10% EtOAc-hexanes), light yellow solid, yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 3441.06, 2956.36, 2919.21, 2849.30, 2729.23, 2221, 1584.10, 1439.42, 1381.82, 1336.74, 1226.84, 1119.30,720.33, 645.33, 579.48; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (d, 2H, J = 6 Hz, Ar), 7.24 (s, 1H, Ar) 7.09 (s, 2H, Ar), 6.72 (d, 2H, J = 6 Hz, Ar), 4.00 - 4.04 (m, 6H, 3 × OCH_2), 3.87 (s, 2H, NH_2), 1.26-1.84 (m, 60H, 30 × CH_2), 0.88 (t, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 153.29, 147.5, 140.03, 139.04, 129.35, 127.29, 125.02, 118.88, 115.3, 110.1, 107.74, 73.79, 69.37, 32.16, 32.14, 30.55, 29.97, 29.95, 29.92, 29.88, 29.86, 29.81, 29.63, 29.61, 29.58, 29.55, 26.33, 22.91, 14.33; HRMS (ESI+) exact mass calculated for $C_{51}H_{85}N_2O_3$ (M+1): 773.6554, Found: 773.6556.

Procedure for the synthesis of **α-CNST**:

A mixture of triformylphloroglucinol (0.07 mmol, 1 equiv.) and aniline **9** (0.22 mmol, 3.2 equiv.) in absolute methanol (50 ml) was heated to reflux under inert atmosphere for 6 h with vigorous stirring. The dull yellow solid separated upon cooling the reaction mixture was collected by filtration, repeatedly washed with methanol, and air-dried. The crude product was purified by repeated recrystallizations by DCM-methanol system.

R_f = 0.6 (30% EtOAc-hexanes), yellowish orange solid, yield: 68%; IR (KBr pellet): ν_{max} in cm^{-1} 3424, 3087, 3062, 3028, 2954, 2924, 2852, 2212, 1621, 1602, 1580, 1453, 1333, 1291, 1263, 1113, 1027, 698; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 13.52-13.50 (m, =CNH), 13.46-13.43 (m, =CNH), 13.06-13.09 (m, =CNH), 8.76-8.86 (m, 3H, =CHN), 7.71-7.73 (m, 6H, Ar), 7.36-7.43 (m, 9H, =CH, Ar), 7.15-7.16 (m, 6H, Ar), 4.04 (t, 18H, 9×OCH_2) and 1.26-1.84 (m, 180H, 90×CH_2), 0.88 (t, 27H, 9×CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.39, 185.56, 182.45, 153.39, 153.17, 148.71, 144.93, 142.26, 140.94, 140.91, 140.86, 140.30, 139.50, 139.42, 132.24, 132.18, 131.18, 128.56, 128.22, 127.55, 123.72, 120.29, 118.40, 118.12, 118.09, 118.00, 116.09, 114.28, 111.66, 108.70, 108.61, 108.50, 108.15, 107.59, 107.41, 73.85, 69.42, 69.23, 34.04, 32.17, 32.16, 31.84, 30.61, 30.52, 30.00, 29.98, 29.97, 29.95, 29.94, 29.90, 29.84, 29.83, 29.77, 29.73, 29.68, 29.66, 29.63, 29.61, 29.58, 29.41, 29.38, 29.17, 26.37, 26.32, 26.25, 22.92, 14.35.; MALDI-TOF exact mass calculated for $C_{162}H_{253}N_6O_{12}$ (M+1): 2474.9366, Found: 2475.019.

Procedure for the synthesis of **β-CNST**:

A mixture of triformylphloroglucinol (0.042 mmol, 1 equiv.) and aniline **6** (0.13 mmol, 3.2 equiv.) in absolute methanol (50 ml) was heated to reflux under inert atmosphere for 6 h with vigorous stirring. The dull yellow solid separated upon cooling the reaction mixture was collected by filtration, repeatedly washed with methanol, and air-dried. The crude product was purified by repeated recrystallizations by DCM-methanol system.

R_f = 0.6 (30% EtOAc-hexanes), yellowish orange solid, yield: 67%; IR (KBr pellet): ν_{max} in cm^{-1} 3444, 2924, 2852, 2211, 1625, 1588, 1510, 1461, 1435, 1338, 1291, 1254, 1181, 1118, 1033, 902, 826, 720; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 13.50-13.52 (m, =CNH), 13.45-13.47 (m, =CNH), 13.10-13.12 (m, =CNH), 8.78-8.88 (m, 3H, =CHN), 7.96-7.99 (m, 6H, Ar), 7.38-7.40 (m, 9H, =CH, Ar), 6.83 (s, 6H, Ar), 3.98-4.04 (m, 18H, 9×OCH_2), 1.26-1.84 (m, 180H, 90×CH_2), 0.88(t, 27H, 9×CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.35, 185.45, 182.22, 153.93, 153.67, 148.30, 147.70, 140.27, 139.69, 139.66, 139.62, 139.48, 131.24, 131.17, 129.41, 124.27, 123.71, 118.44, 117.74, 116.07, 114.27, 111.22, 111.17, 107.88, 107.69, 107.60, 107.14, 104.74, 73.77, 69.52, 69.39, 34.97, 34.46, 34.03, 32.27, 32.17, 32.15, 32.04, 31.84, 30.61, 30.01, 29.96, 29.94, 29.91, 29.83, 29.72, 29.68, 29.63, 29.61, 29.57, 29.48, 29.37, 29.16, 26.37, 26.28, 23.02, 22.91, 22.79, 14.44, 14.33.; MALDI-TOF exact mass calculated for $C_{162}H_{253}N_6O_{12}$ (M+1): 2474.9366, Found: 2475.072.

3. NMR Spectra

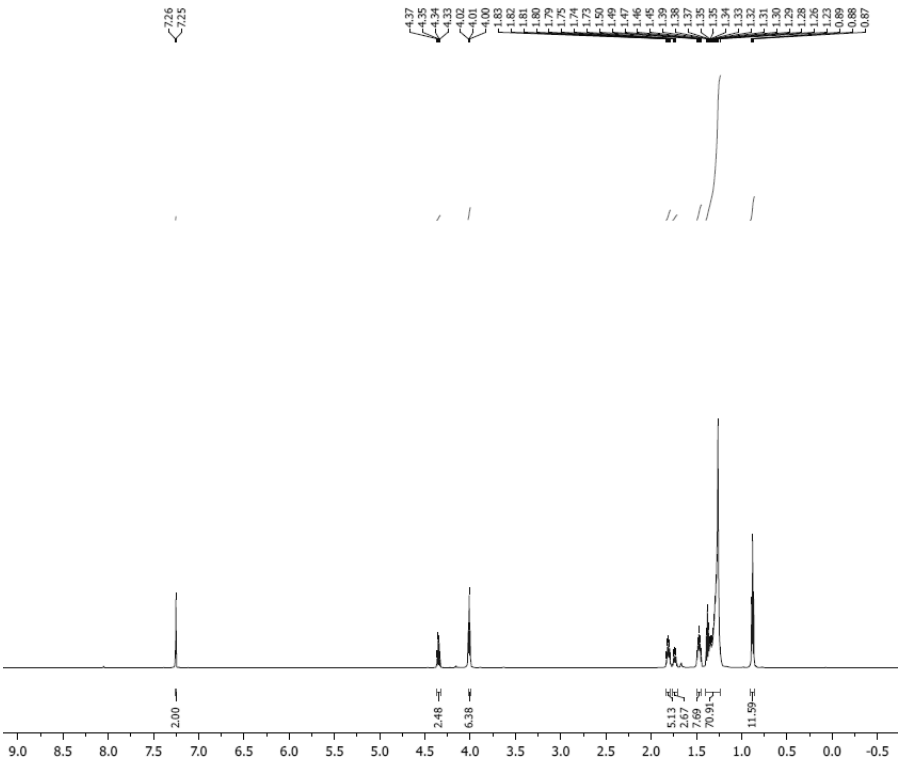


Figure S1. ^{1}H NMR (600 MHz) spectra of **1** in $CDCl_3$

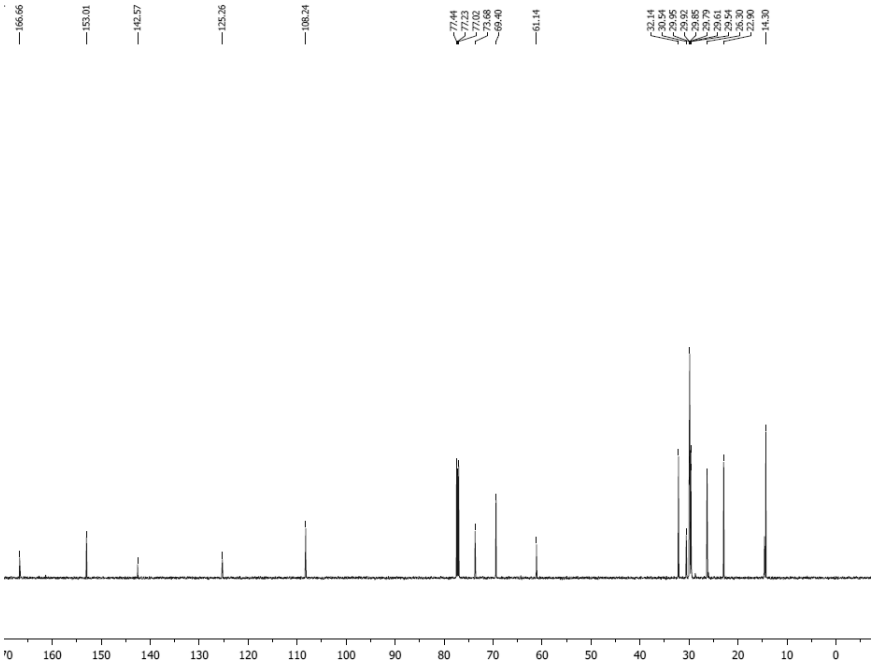


Figure S2. ^{13}C NMR (150 MHz) spectra of **1** in $CDCl_3$

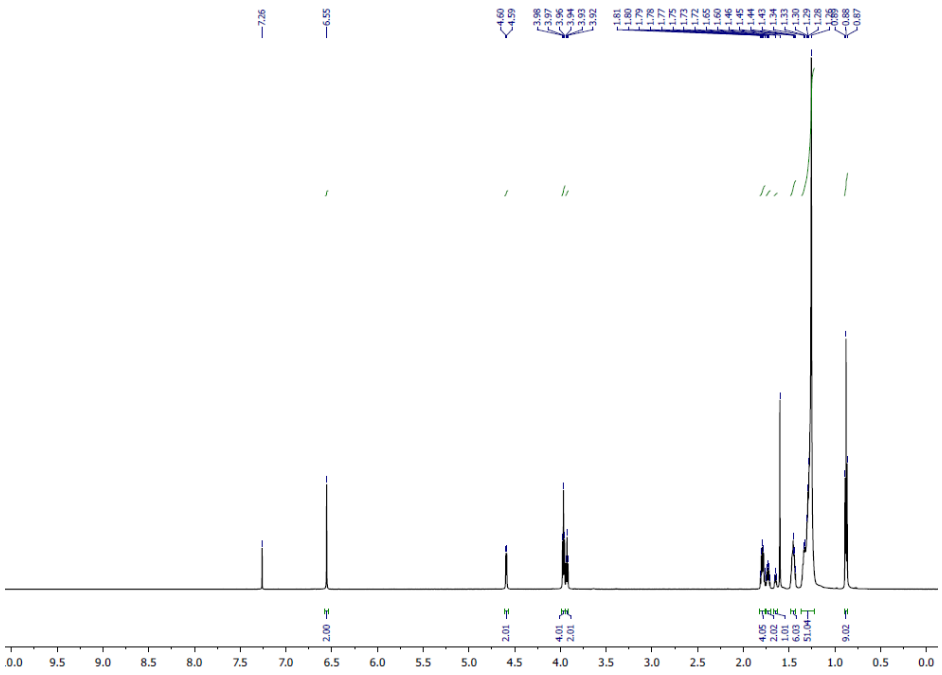


Figure S3. ^{1}H NMR (600 MHz) spectra of **2** in $CDCl_3$

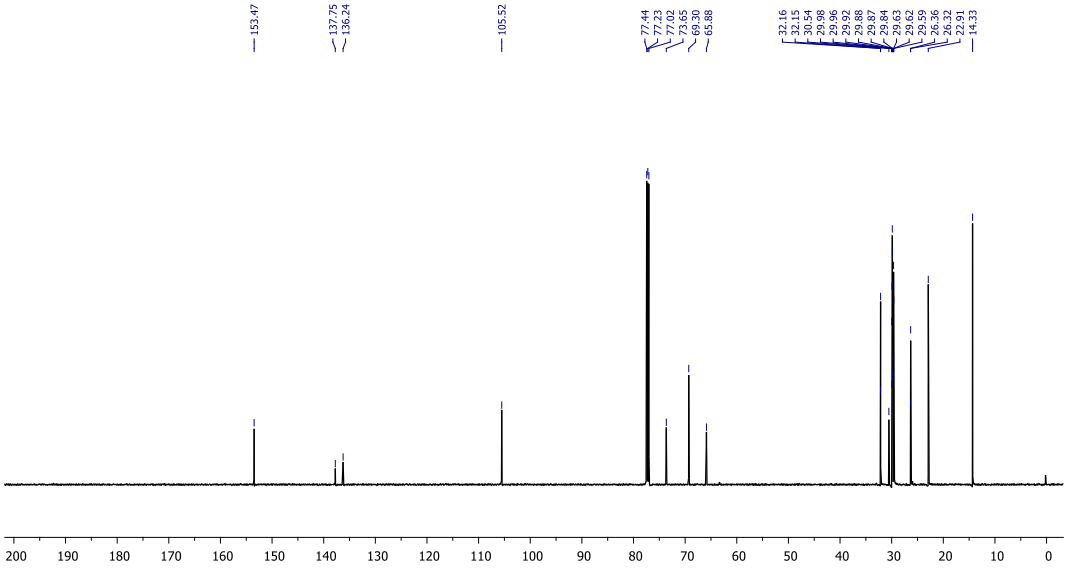


Figure S4. ^{13}C NMR (150 MHz) spectra of **2** in $CDCl_3$

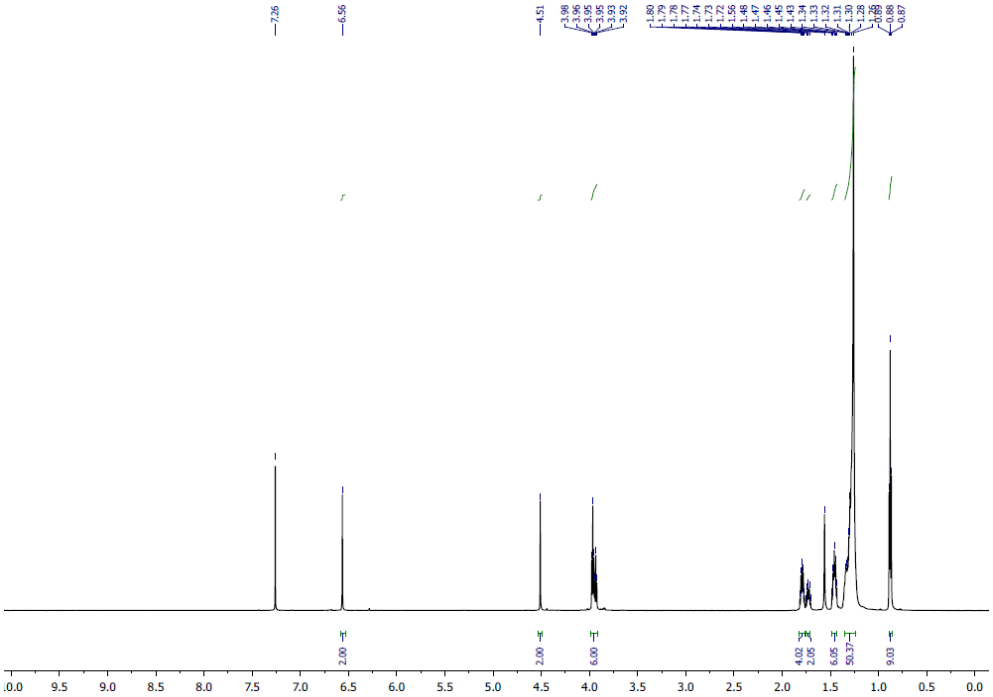


Figure S5. ^{1}H NMR (600 MHz) spectra of **3** in $CDCl_3$

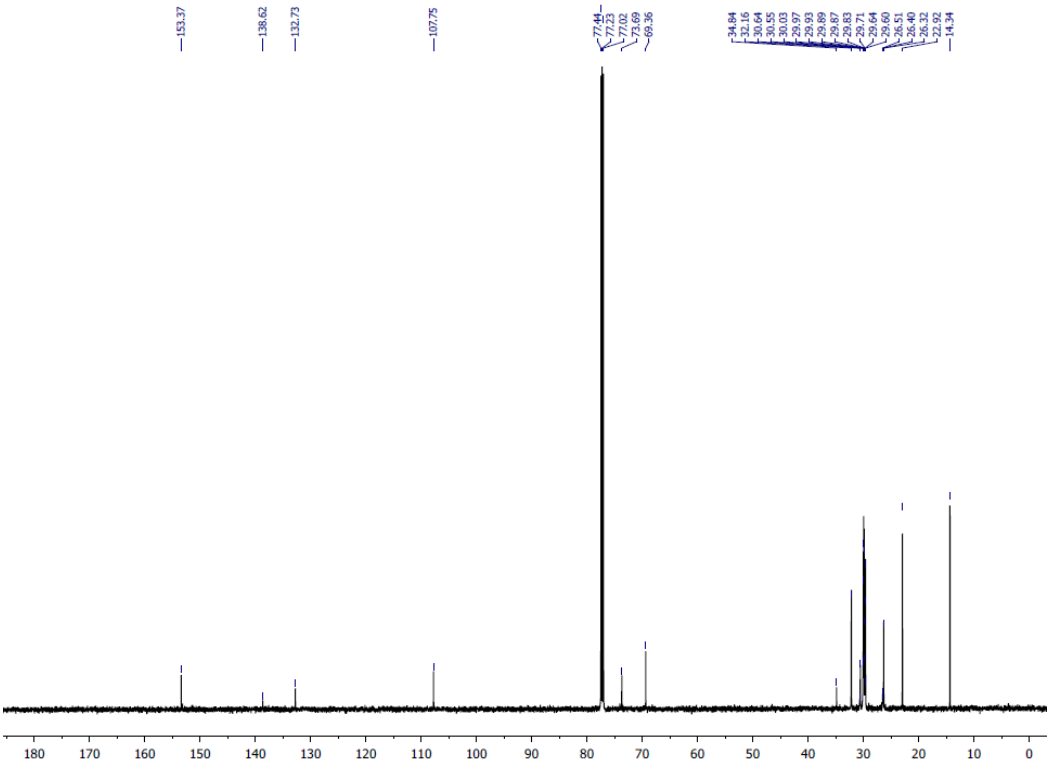


Figure S6. ^{13}C NMR (100 MHz) spectra of **3** in $CDCl_3$

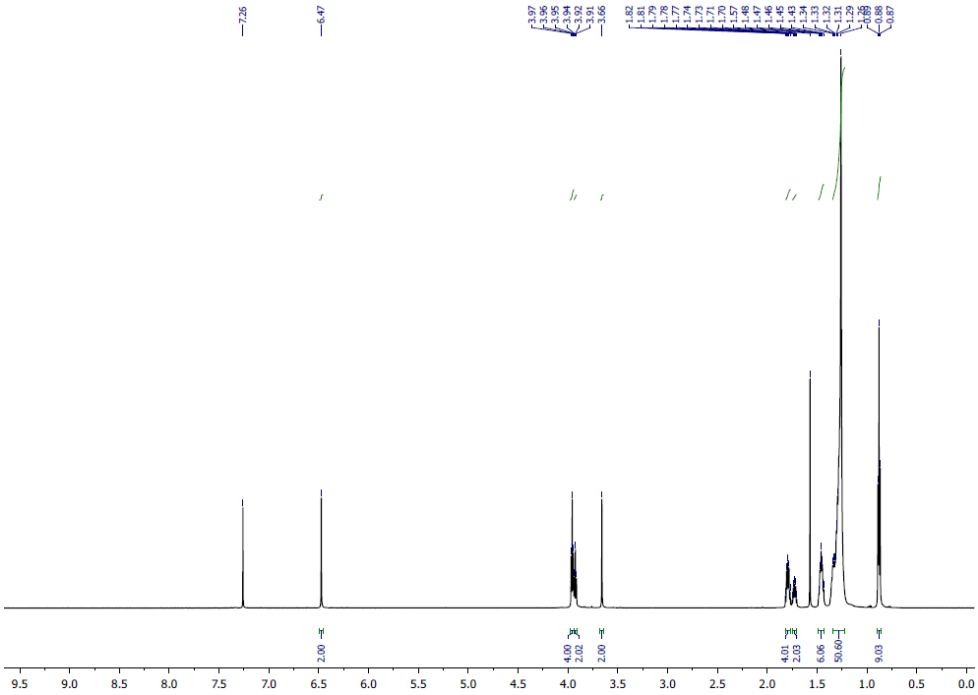


Figure S7. ^{1}H NMR (600 MHz) spectra of **4** in $CDCl_3$

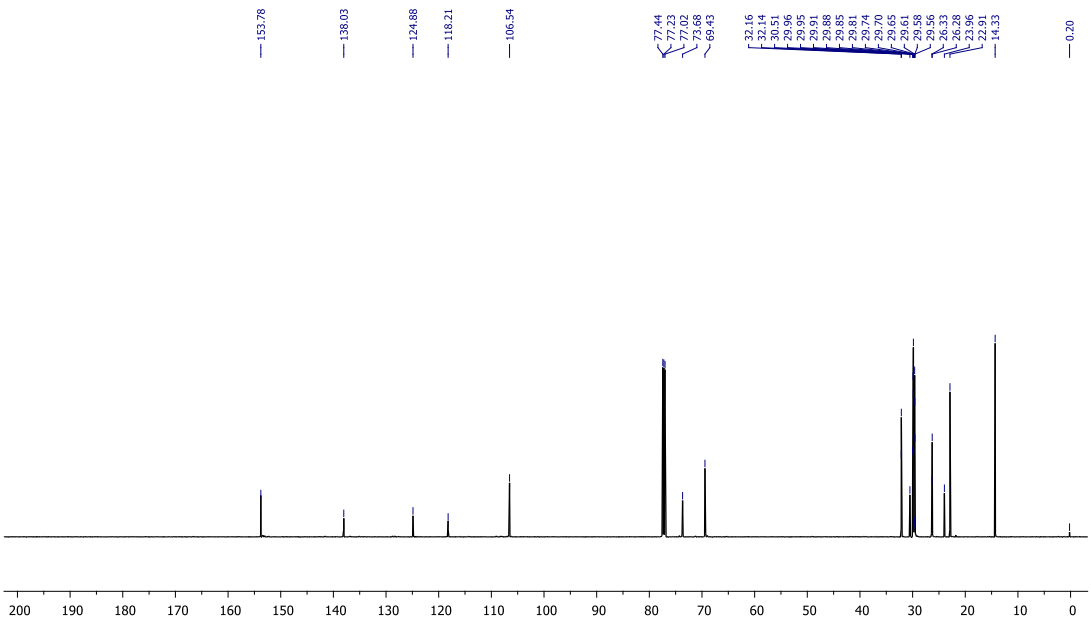


Figure S8. ^{13}C NMR (150 MHz) spectra of **4** in $CDCl_3$

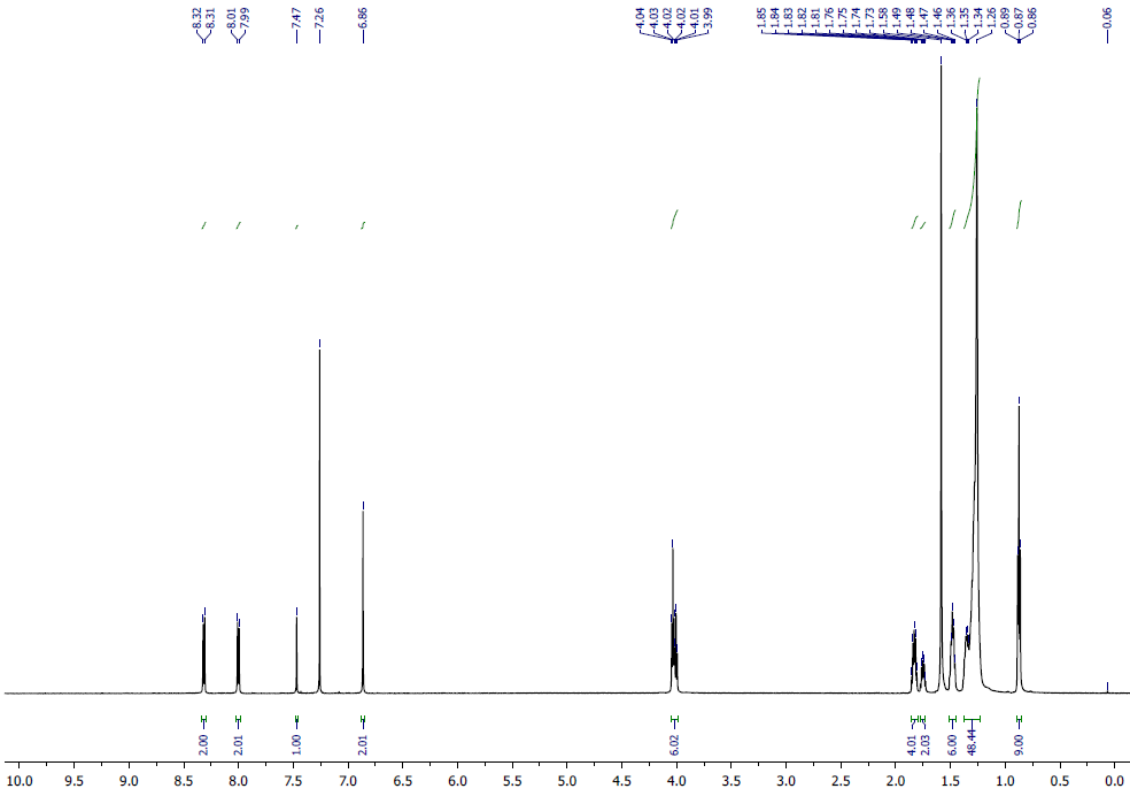


Figure S9. ^{1}H NMR (600 MHz) spectra of **5** in $CDCl_3$

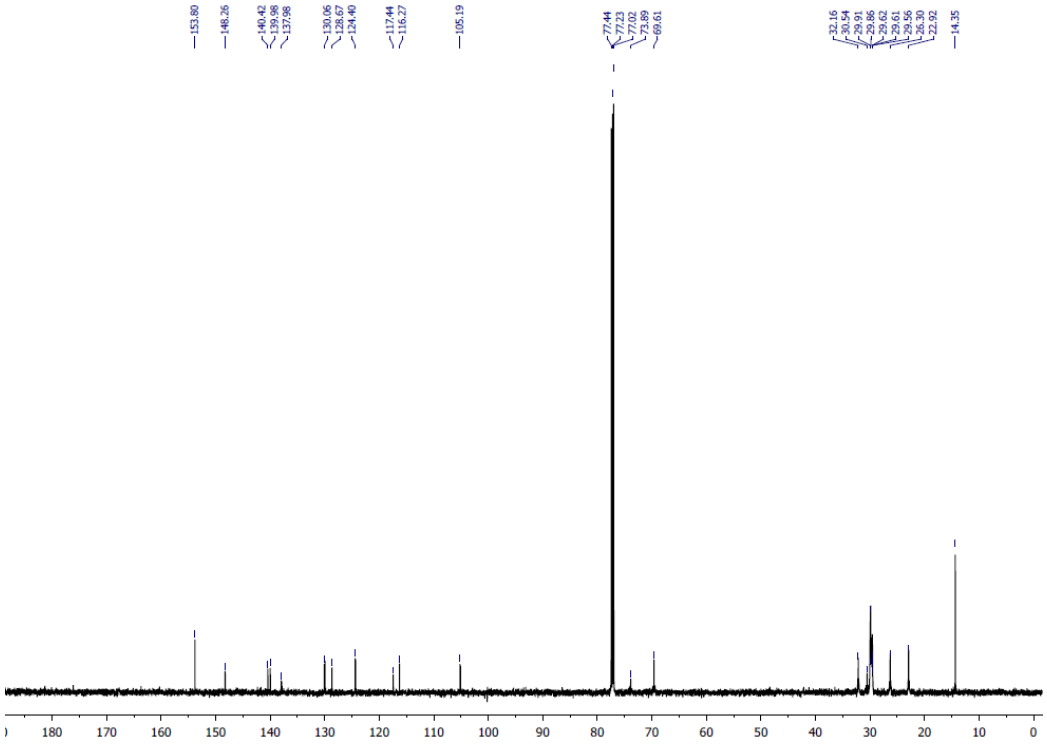


Figure S10. ^{13}C NMR (150 MHz) spectra of **5** in $CDCl_3$

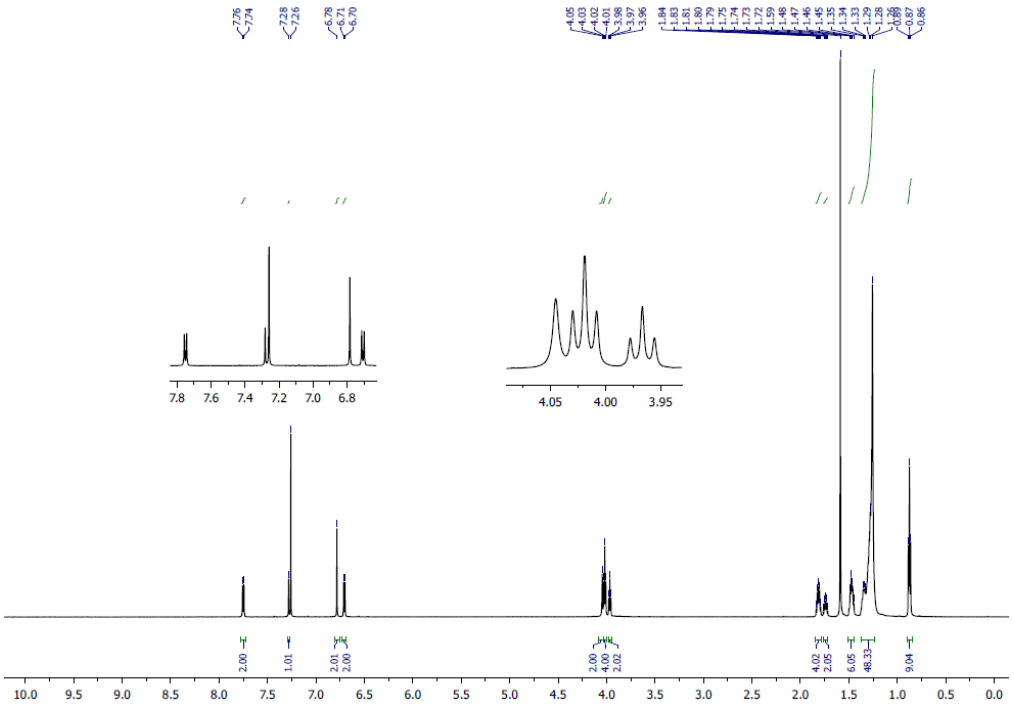


Figure S11. ^{1}H NMR (600 MHz) spectra of **6** in $CDCl_3$

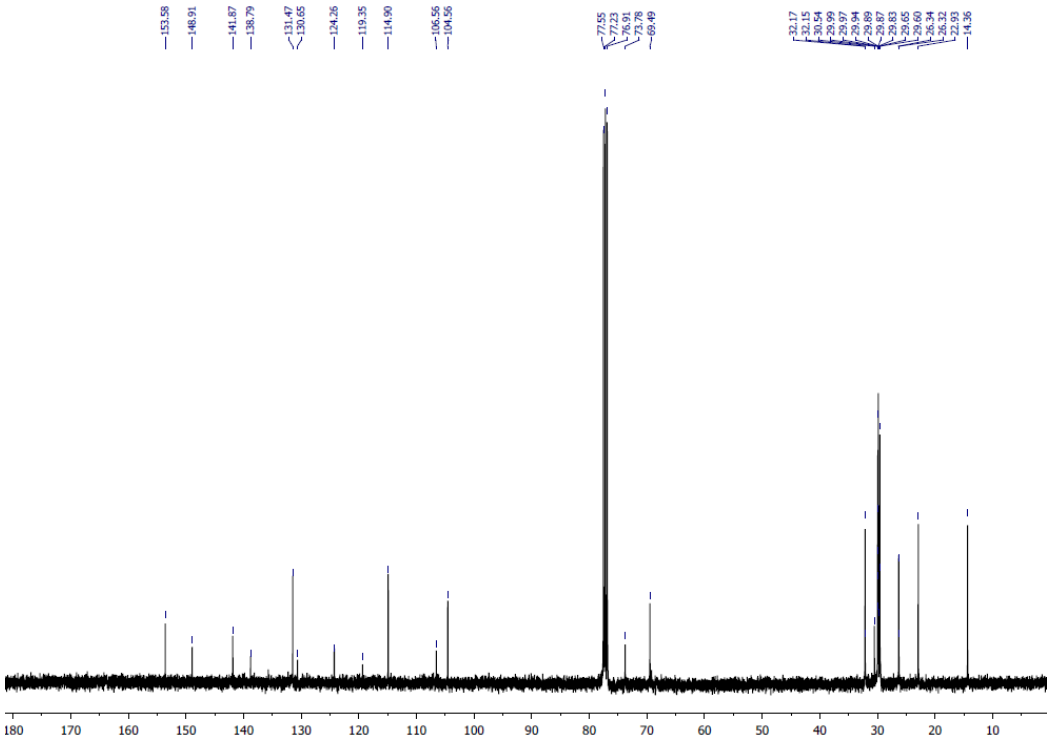


Figure S12. ^{13}C NMR (100 MHz) spectra of **6** in $CDCl_3$

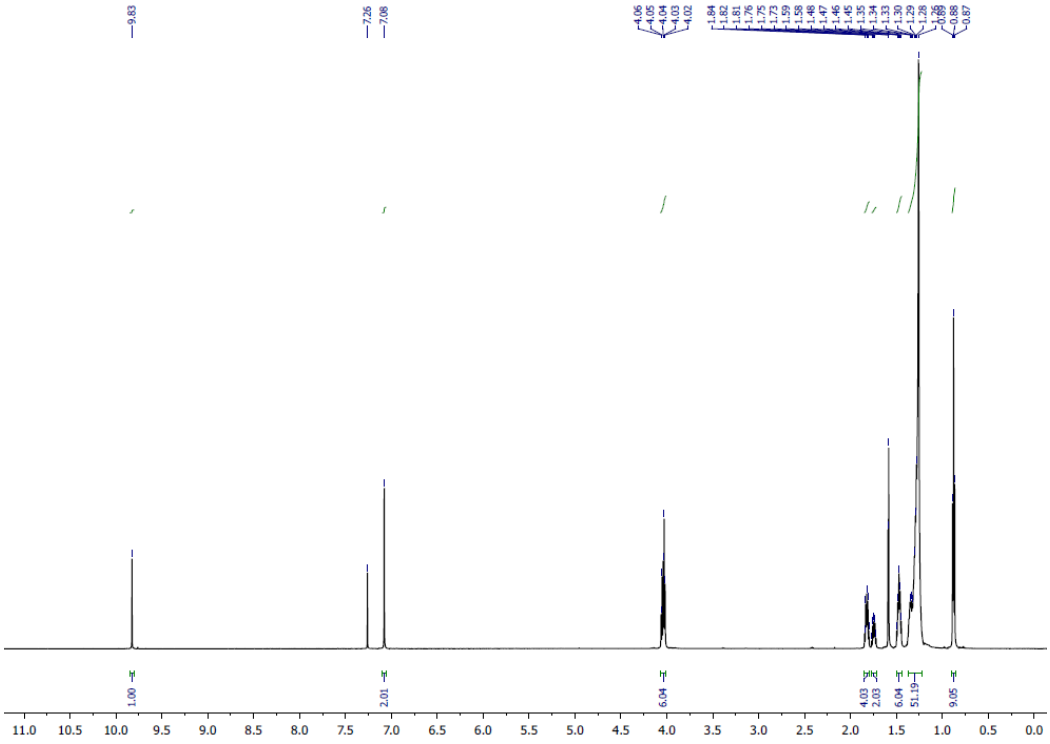


Figure S13. ^{1}H NMR (600 MHz) spectra of **7** in $CDCl_3$

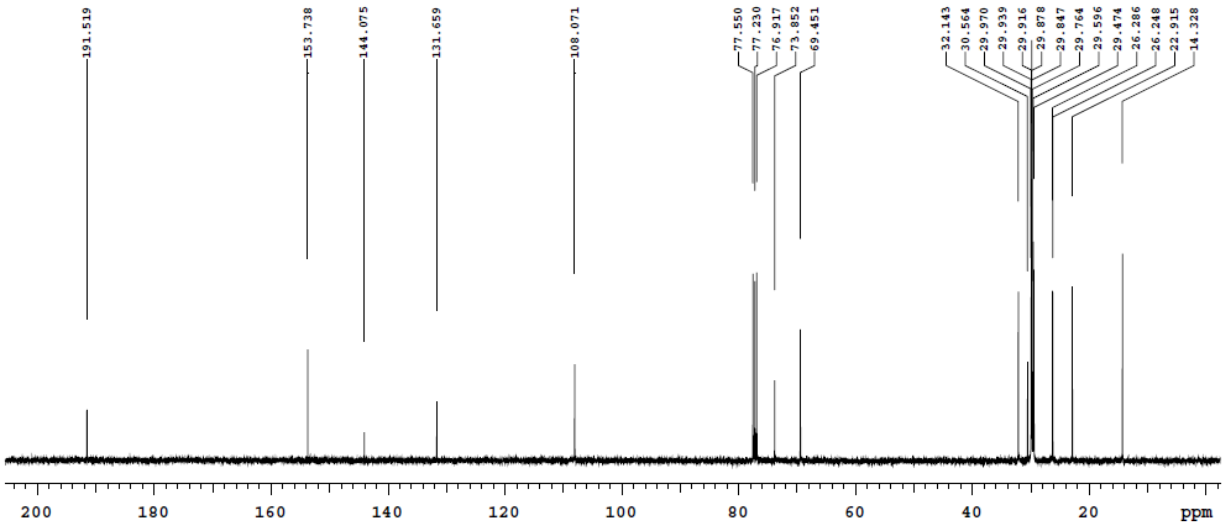


Figure S14. ^{13}C NMR (100 MHz) spectra of **7** in $CDCl_3$

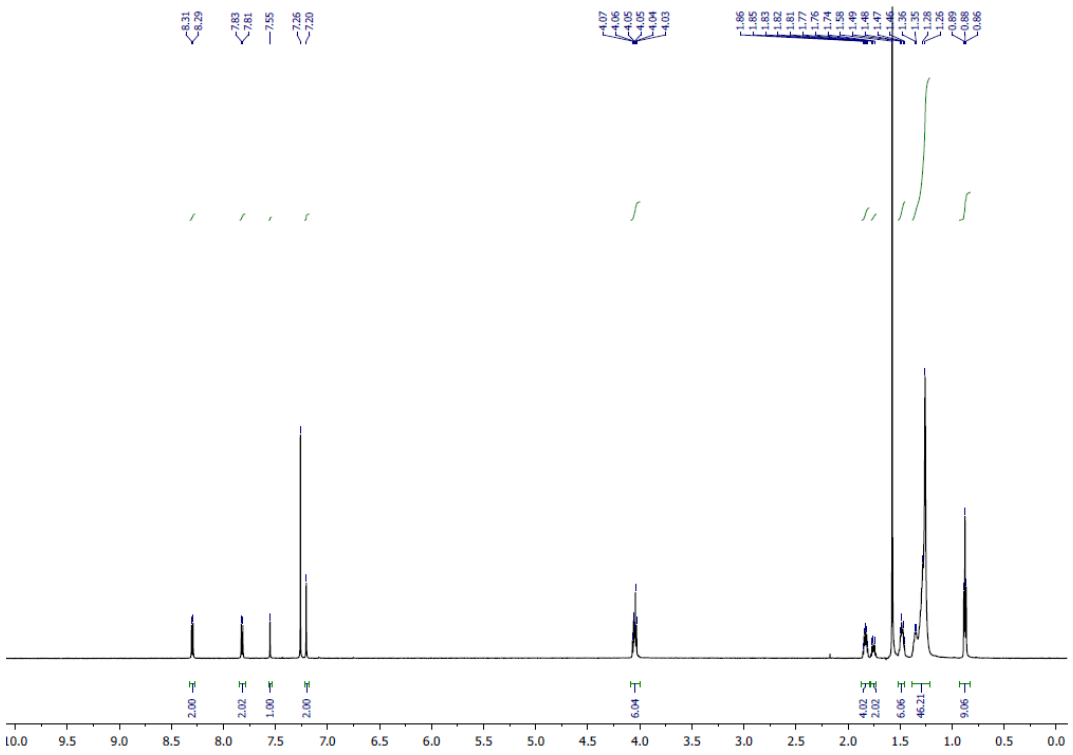


Figure S15. ^{1}H NMR (600 MHz) spectra of **8** in $CDCl_3$

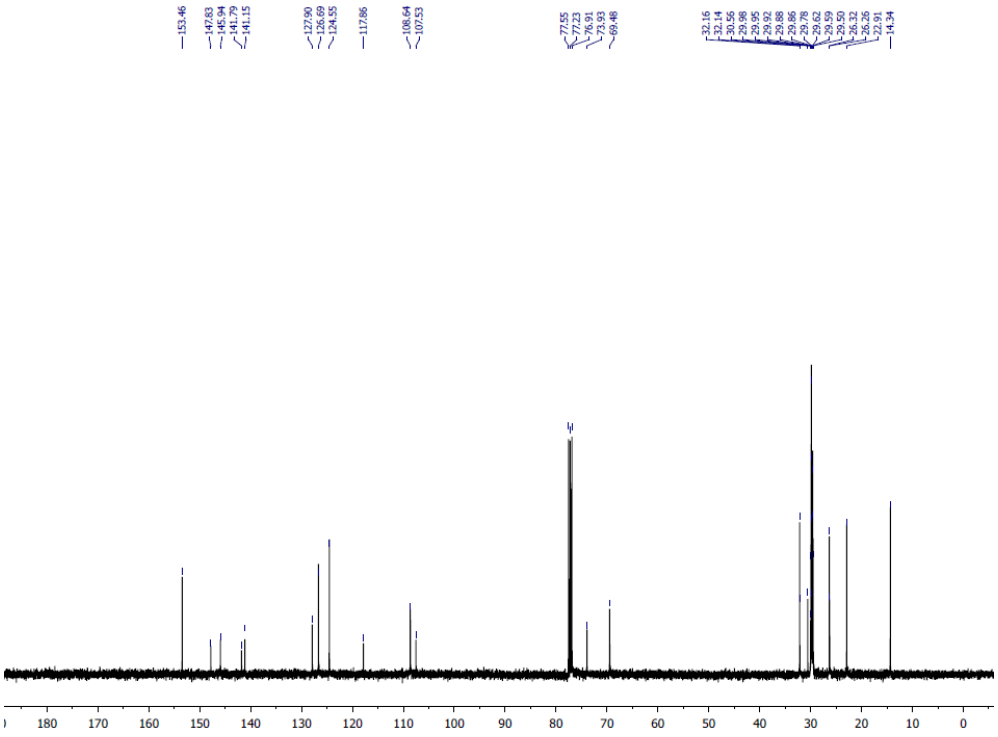


Figure S16. ^{13}C NMR (100 MHz) spectra of **8** in $CDCl_3$

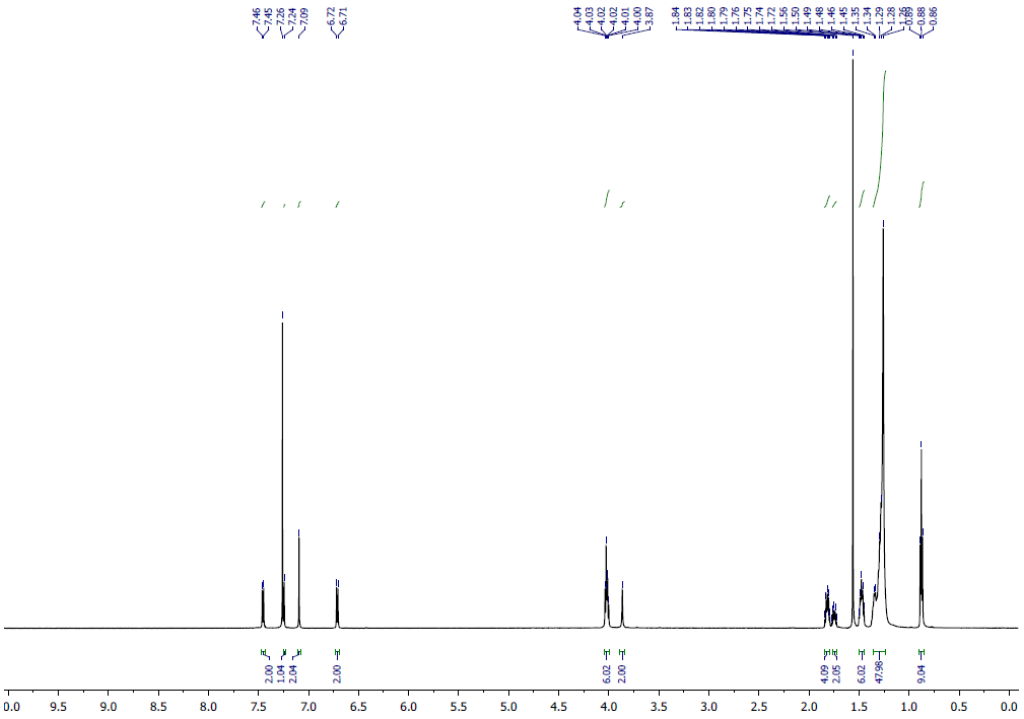


Figure S17. ^{1}H NMR (600 MHz) spectra of **9** in $CDCl_3$

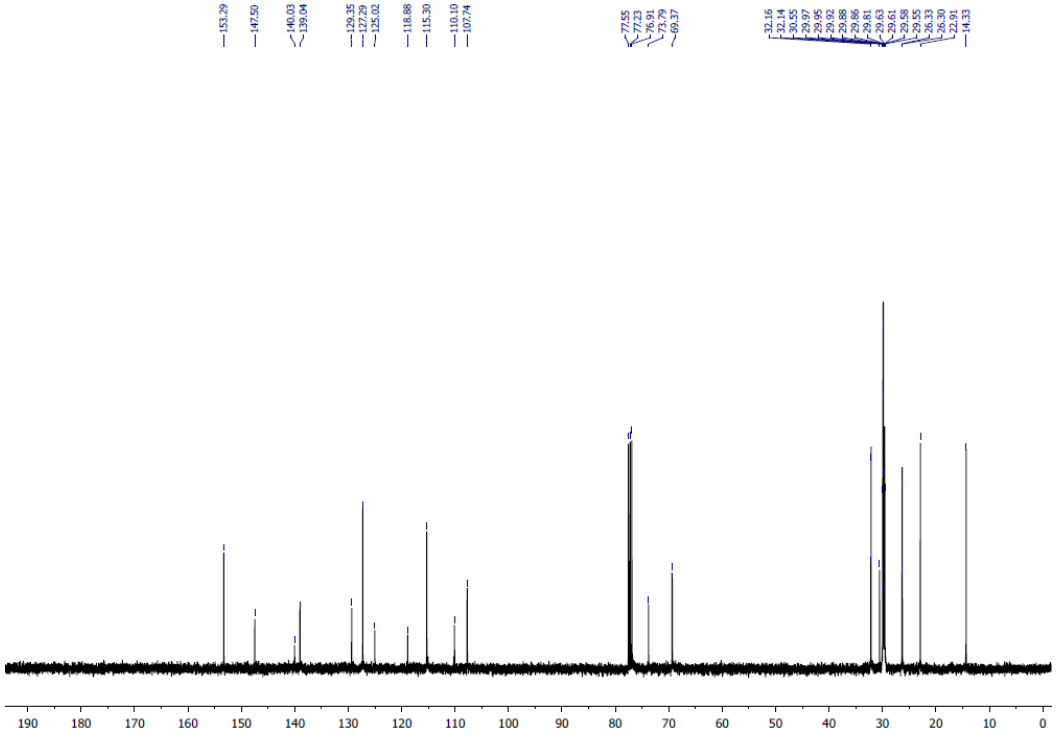


Figure S18. ^{13}C NMR (100 MHz) spectra of **9** in $CDCl_3$

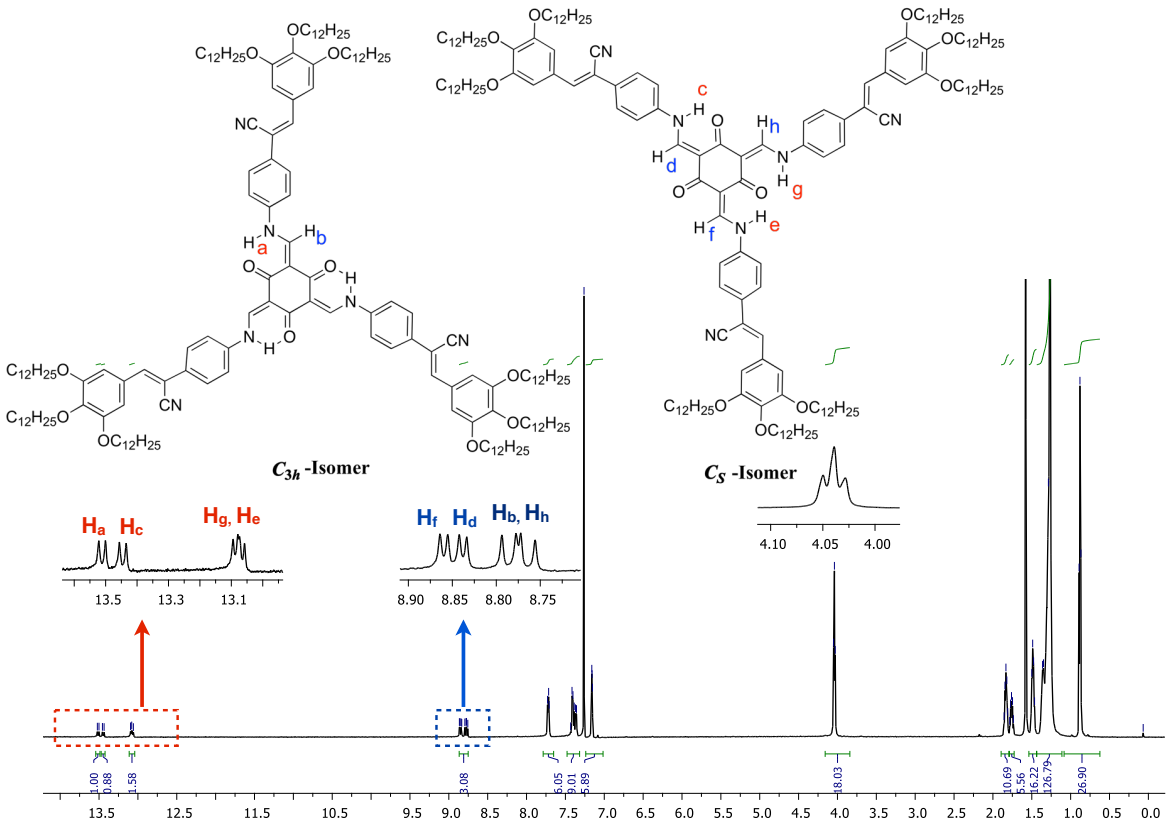


Figure S19. ^{1}H NMR (600 MHz) spectra of **α-CNST** in $CDCl_3$

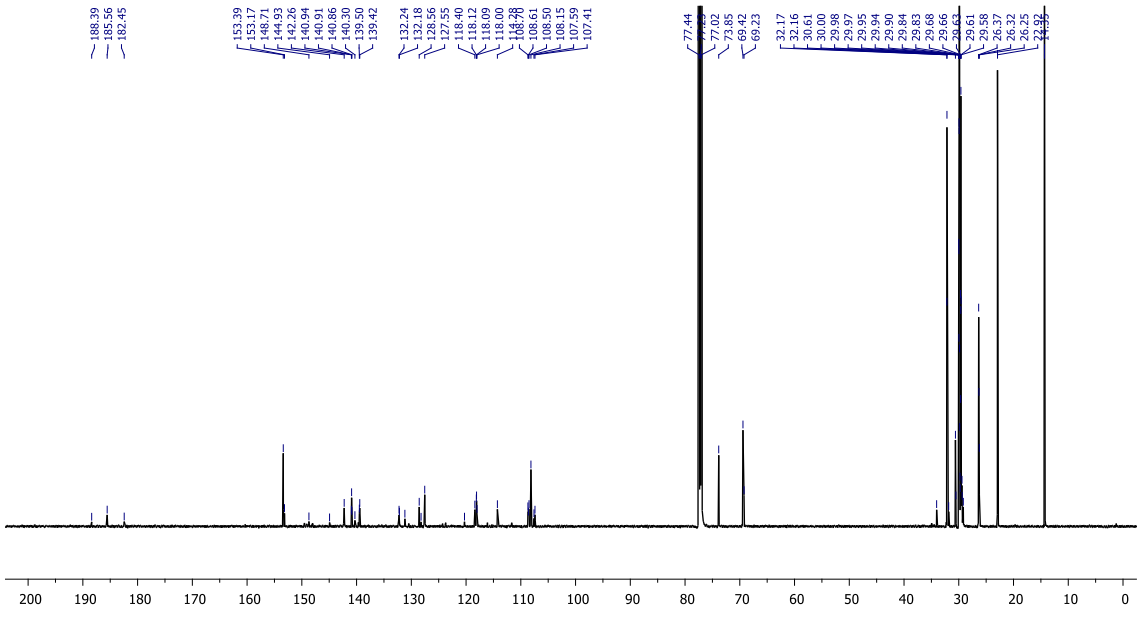


Figure S20. ^{13}C NMR (150 MHz) spectra of **α-CNST** in $CDCl_3$.

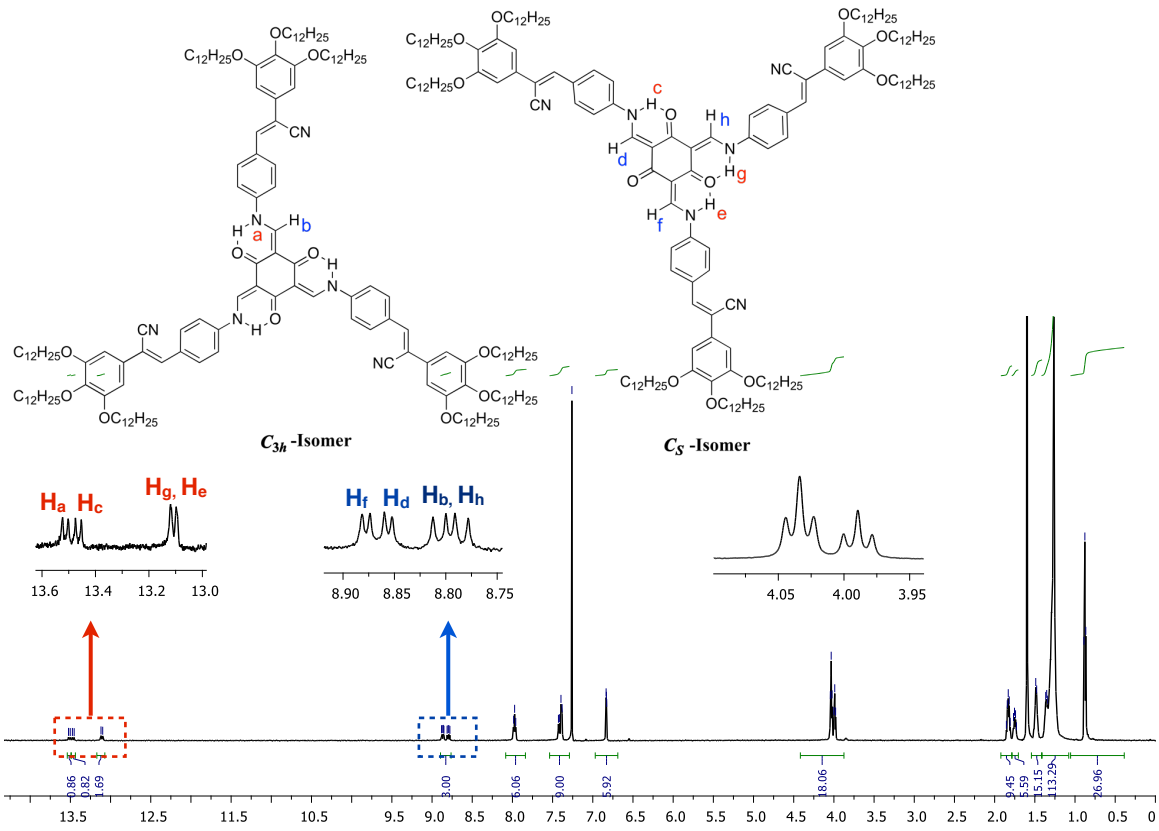


Figure S21. ^{1}H NMR (600 MHz) spectra of **β-CNST** in $CDCl_3$.

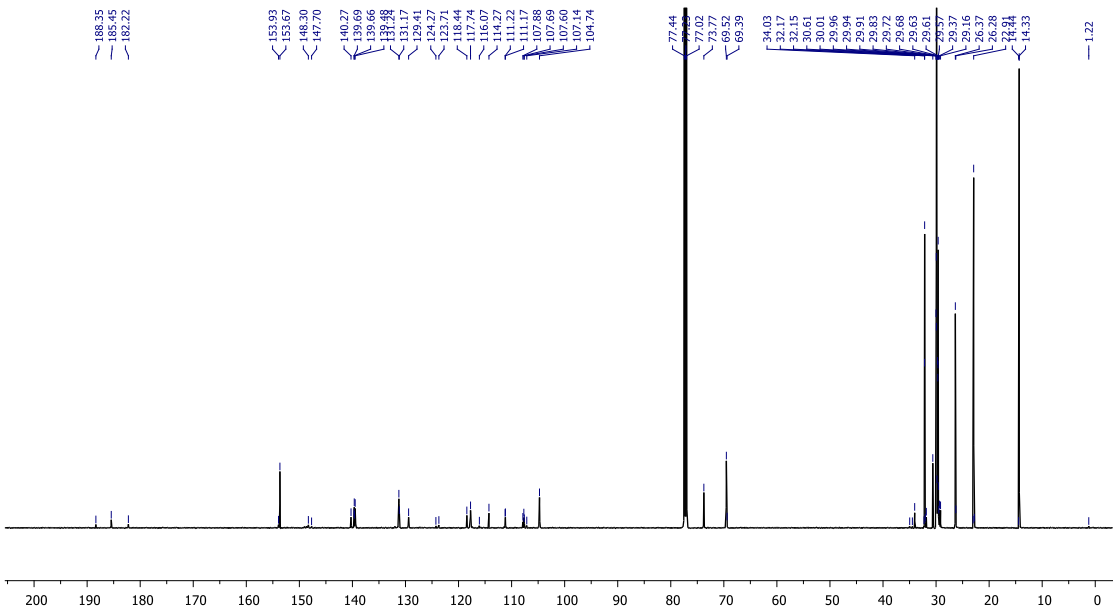


Figure S22. ^{13}C NMR (150 MHz) spectra of **β-CNST** in $CDCl_3$.

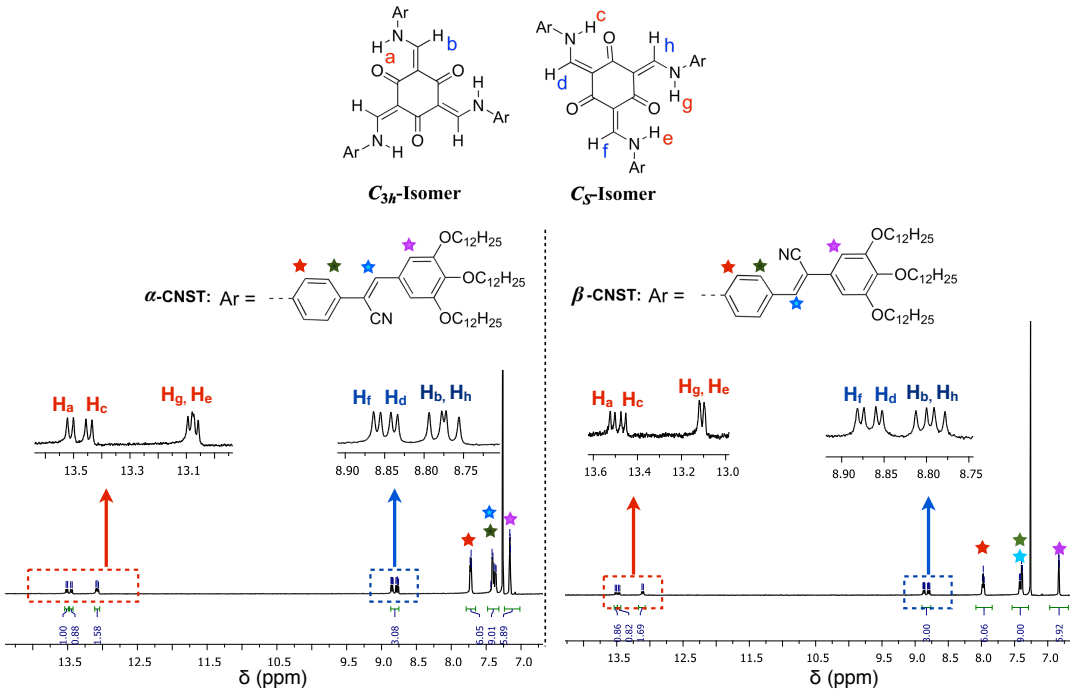


Figure S23. Expanded portions of the ^{1}H NMR spectra of TSANs ***α*-CNST** and ***β*-CNST**, in $CDCl_3$ (600 MHz).

4. MALDI-TOF mass spectra

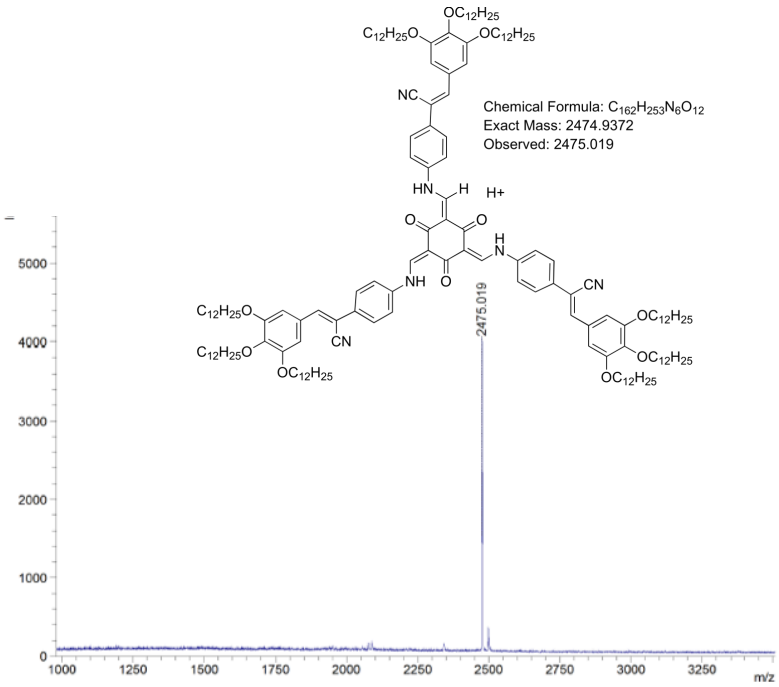


Figure S24. MALDI-TOF mass spectrum of ***α*-CNST.**

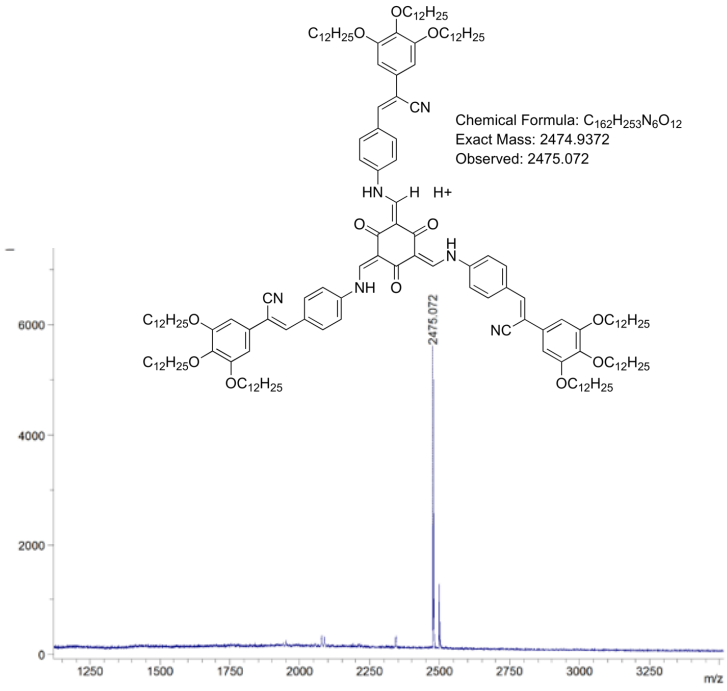


Figure S25. MALDI-TOF mass spectrum of ***β*-CNST.**

5. Thermal behavior

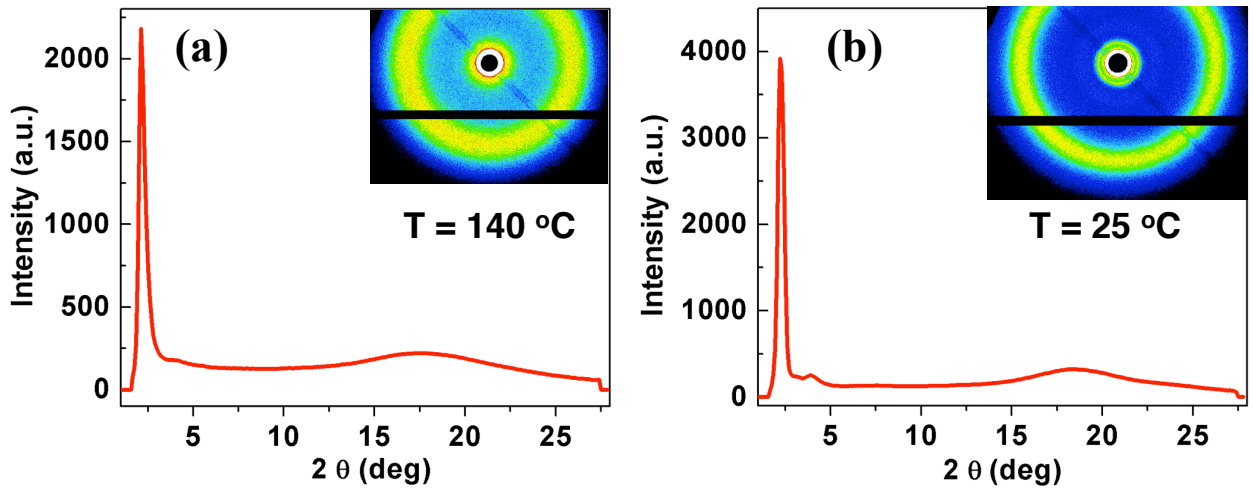


Figure S26. XRD profiles depicting the intensity against the 2θ obtained for the Col_{r2} phase of compound ***α*-CNST** at 140 °C (a) and at 25 °C (b) (inset provides the image patterns obtained).

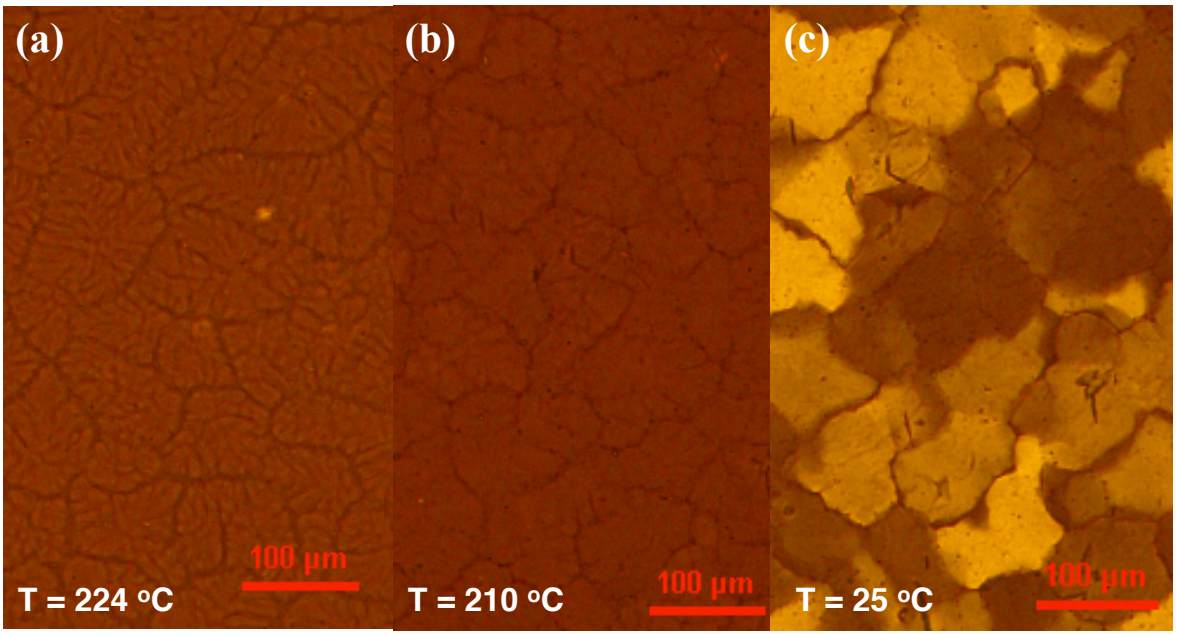


Figure S27. POM images of compound ***β*-CNST** in Col_{r1} phase at 224 °C (a); in Col_{r2} phase at 210 °C (b); frozen Col_{r2} phase at 25 °C (c).

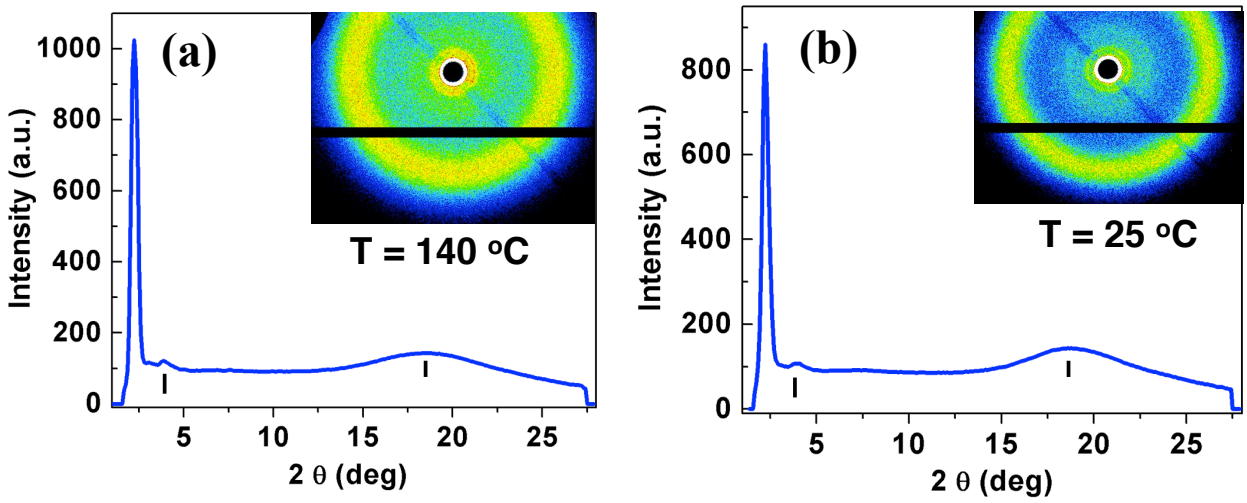


Figure S28. XRD profiles depicting the intensity against the 2θ obtained for the Col_{r2} phase of compound ***β*-CNST** at 140 °C (a) and at 25 °C (b) (inset provides the image patterns obtained).

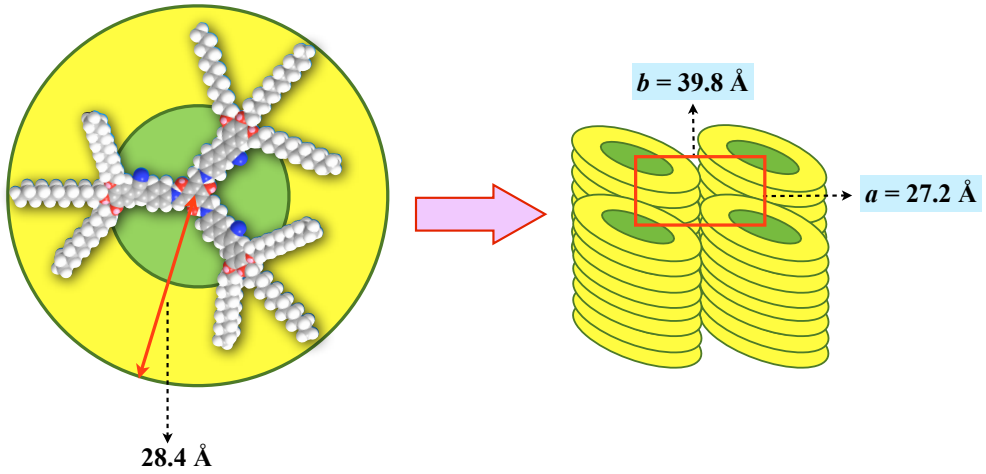


Figure S29. Schematic showing the self-assembly of compound ***β*-CNST** in Col_r phase of *p2mm* symmetry (Derived from the XRD pattern obtained at 25 °C, only C_{3h} isomer shown for the sake of clarity).

Table S1. Results of (*hkl*) indexation of XRD profiles of the compounds at a given temperature (T/°C) of mesophase.

Compounds[a] (*D*/Å)	Phase (T/°C) Symmetry	d_{obs} (Å)	d_{cal} (Å)	Miller indices *hk*	Lattice parameters (Å), Lattice area *S* (Å^2), Molecular volume *V* (Å^3)
***α*-CNST** (56.8)	Col_{r1} (200) *p2mm*	41.51 22.90 5.06 (h_a)	41.51 22.90	01 10	*a* = 22.9; b = 41.51; S = 950.6, V = 4809.9, Z = 1.2
	Col_{r2} (140) *p2mm*	39.78 28.7 23.01 11.45 4.99 (h_a)	39.78 28.7 23.27 11.64	01 10 11 22	*a* = 28.7; b = 39.78; S = 1141.69, V = 5697, Z = 1.4
	Col_{r2} (25) *p2mm*	39.68 27.75 22.55 11.64 4.99 (h_a)	39.68 27.75 22.74 11.37	01 10 11 22	*a* = 27.75; b = 39.68; S = 1101.12, V = 5494.6, Z = 1.3
***β*-CNST** (56.8)	Col_{r1} (225) *p2mm*	39.74 21.02 4.94 (h_a)	39.74 21.02	01 10	*a* = 21.02; b = 39.74; S = 835.33, V = 4126.55, Z = 1.
	Col_{r2} (140) *p2mm*	39.72 22.63 11.63 4.8 (h_a)	39.72 22.63 11.43	01 10 13	*a* = 22.63; b = 39.72; S = 898.86, V = 4314.55, Z = 1.1.
	Col_{r2} (25) *p2mm*	39.75 22.43 11.67 4.75 (h_a)	39.75 22.43 11.91	01 11 13	*a* = 27.17; b = 39.75; S = 1080.0, V = 5130.03, Z = 1.3.

[a]The diameter (D) of the disk (estimated from Chem 3D Pro 8.0 molecular model software from Cambridge Soft). d_{obs}: spacing observed; d_{cal}: spacing calculated (deduced from the lattice parameters; *a* for Col_h phase). The spacings marked h_a correspond to diffuse reflection in the wide-angle region arising from correlations between the alkyl chains. *a* and *b* are the lattice parameters obtained for Col_r phase; *Z* indicates the number of molecules per columnar slice of thickness h_a, estimated from the lattice area *S* and the volume *V*.

5. Photophysical properties

Relative Quantum Yield Calculation

Relative quantum yield of compound was measured with respect to tetrakis(octyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate in THF solution as the standard, which is having the relative quantum yield of 1 with respect to fluorescein (Qf = 0.79) in 0.1M NaOH). Absolute values were calculated according to the following equation:

$QS = QR \times (mS / mR) \times (nS / nR)^2$

Where, Q: Quantum yield; m: Slope of the plot of integrated fluorescence intensity *vs* absorbance; n: refractive index (1.407 for THF).

The subscript R refers to the reference fluorophore *i.e.* compound carbazole solution in THF and subscript S refers to the sample under investigation. In order to minimize reabsorption effects, absorbance was kept below 0.15 at the excitation wavelength of 442 nm.

Quantum Yield of compound carbazole is 1.01. Simplified equation for the calculation after substituting the appropriate values is given below and values obtained are given in table below.

$QS = 1.01 \times (mS / mR) \times (1.407/1.407)^2$

$= 1.01 \times (mS / mR)$

Entry	m_S	m_R	Q_s [a,b,c]
ST	1.5791×10^9	5.2873×10^9	0.30
α-CNST	1.45569×10^9	5.2873×10^9	0.28
β-CNST	1.34121×10^9	5.2873×10^9	0.26
[a] Measured in THF; [b]Excited at absorption maxima.; [c]Standard carbazole ($\mathbf{Q_f}$ = 1.01) in THF solution			

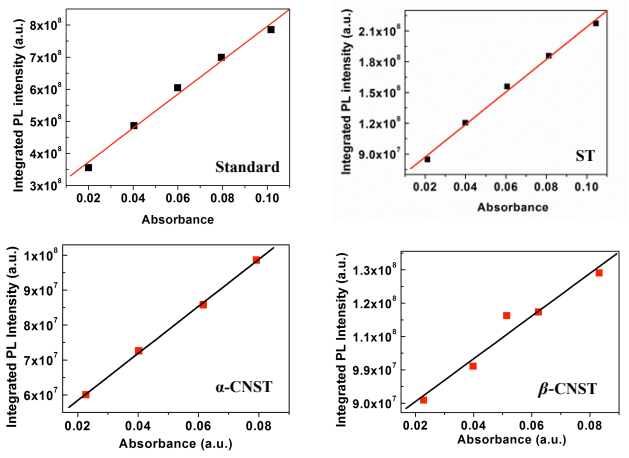


Figure S30. Plots of integrated photoluminescence intensity *vs* absorbance of reference compound and TSANs **ST, *α*-CNST** and ***β*-CNST** (micromolar THF solution)

Time resolved photoluminescence studies

Fluorescence lifetime measurements were done on using Horiba Jobin Yvon time-correlated single photon counting (TCSPC). Samples were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 405 nm (Laser) with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (Data Station Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence decay time were determined by deconvoluting the instrument response function (IRF) with bi-exponential decay using standard method of non-linear least square fitting method (DAS6 decay analysis software). The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.25) as well as the visual inspection of the residuals. Excited state fluorescence lifetimes of all compounds in the very dilute condition (micromolar solution) and in the spin coated thin film state were carried out. The decay of micromolar solution of compounds in THF and in thin films are tabulated in table 1 and table 2.

Table S2. Fluorescence life time measurements at micromolar THF solutions

Compound	Lifetime T_1 (%)	Lifetime T_2 (%)	Lifetime T_3 (%)
ST	0.3 (23.2)	1.1 (50.9)	3.3 (26)
***α*-CNST**	0.6 (23.5)	1.8 (56.5)	4.2 (20.1)
***β*-CNST**	0.4 (15.6)	1.3 (60.2)	3.1 (24.2)

Table S3. Fluorescence life time measurements of thin films.

Compound	Lifetime T_1 (%)	Lifetime T_2 (%)	Lifetime T_3 (%)
ST	0.1 (6)	0.6 (48)	1.2 (46)
***α*-CNST**	0.1 (9.1)	0.5 (31.3)	1 (59.6)
***β*-CNST**	0.1 (3.7)	0.6 (39.1)	1.2 (57.2)

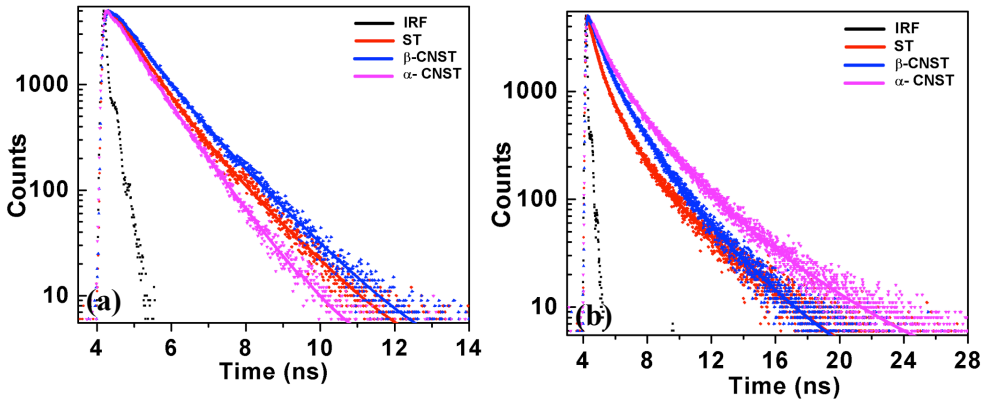


Figure S31. The fluorescence decay of TSANS **ST, *α*-CNST** and ***β*-CNST** in micromolar THF solution (a) and in annealed thin films (b) (IRF: Instrument response function).

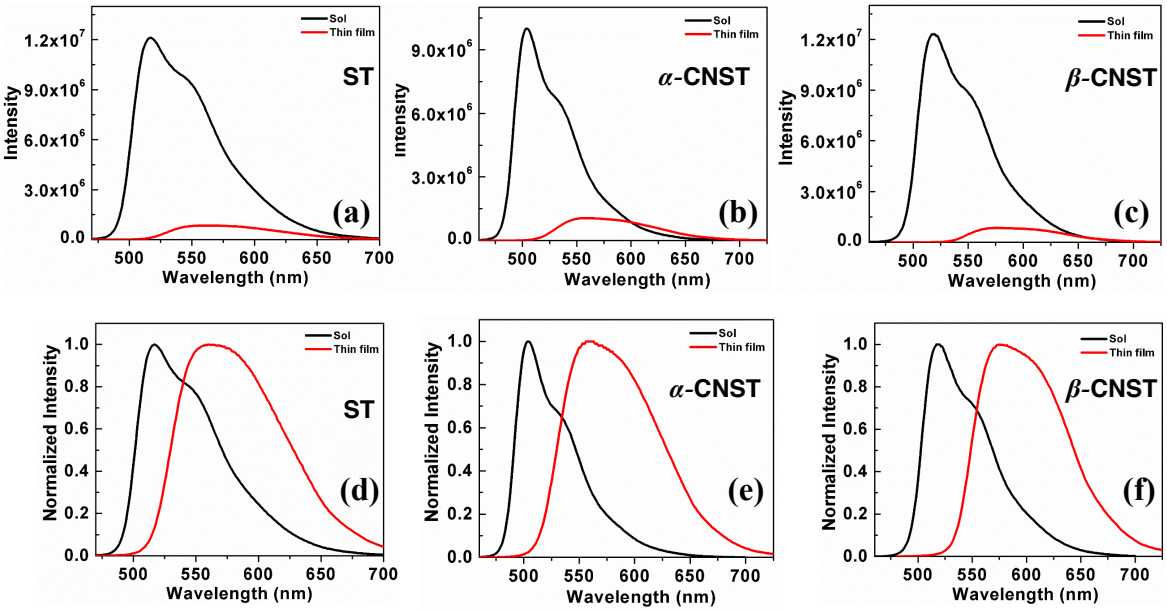


Figure S32. Overlay of the fluorescence spectra of the solutions in chloroform and in the thin film state of TSANS **ST** (a), ***α*-CNST** (b) and ***β*-CNST** (c); Normalized version of the same (d-f).

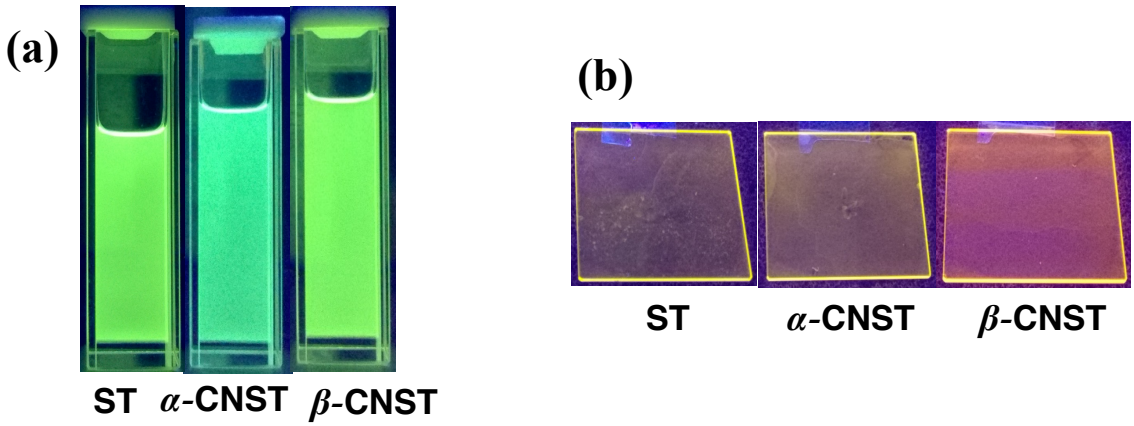


Figure S33. Pictures of micromolar solutions of stilbene based TSANs in $CHCl_3$ (a) and the spin coated thin films of compounds as seen with the UV illumination (λ = 365 nm) (b).

7. Acidochromism

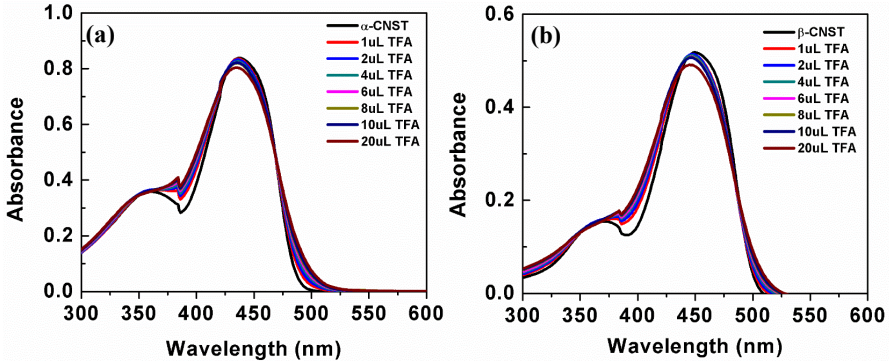


Figure S34. Absorption spectra of the TSANS (a) ***α*-CNST** and (b) ***β*-CNST** in chloroform solutions on the gradual addition of TFA.

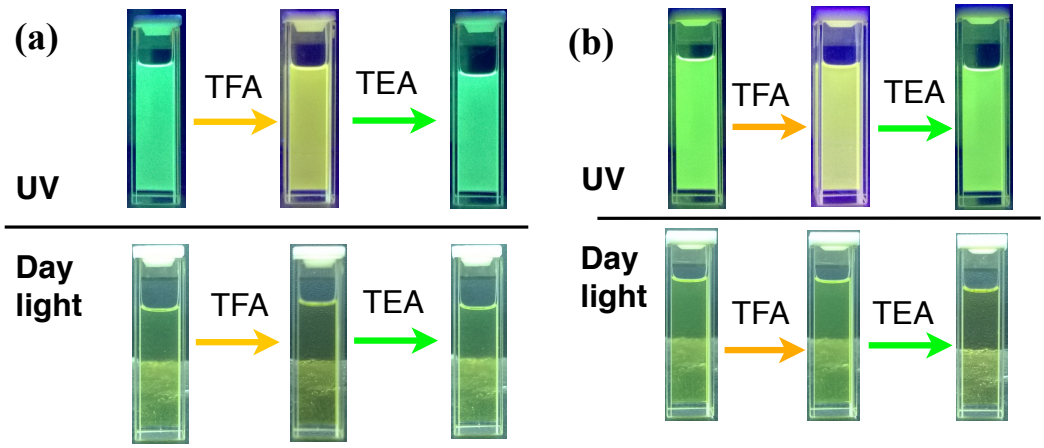


Figure S35. Images showing the change the emission of compound **α-CNST** (a) and **β-CNST** (b) with the gradual addition of TFA as visualized under UV light and normal daylight (d).

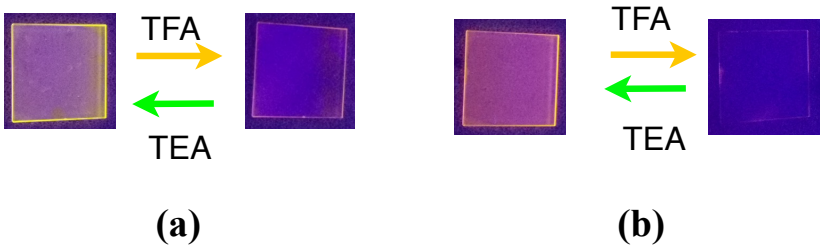


Figure S36. Images showing the change the emission of thin films of compound **α-CNST** (a) and **β-CNST** (b) on exposure to TFA vapors and recovery of the emission by neutralization with TEA vapors as visualized under UV light (λ = 365 nm)

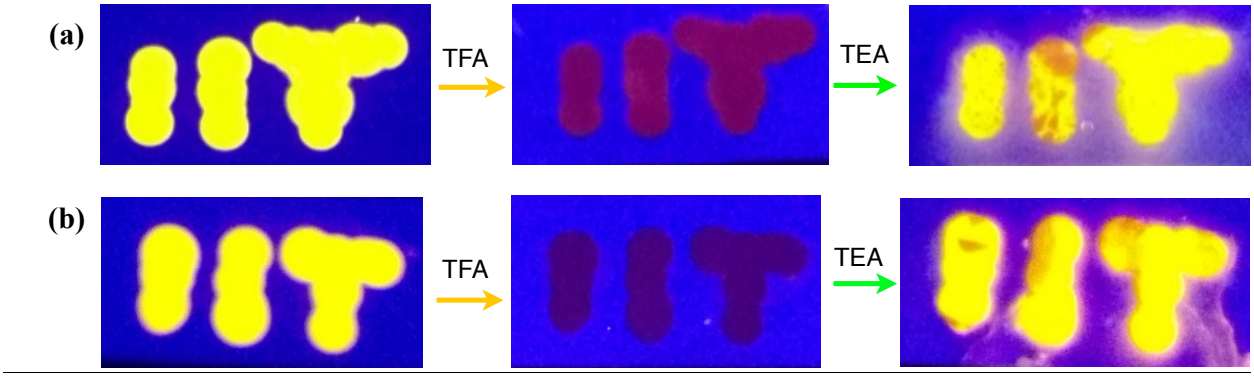


Figure S37. Images showing the change in the emission of compound **α-CNST** (a) ***β*-CNST** (b) on exposure to TFA and its recovery on neutralization with TEA. (All the images are taken under UV light of λ = 365 nm).

8. Calculation of detection limit

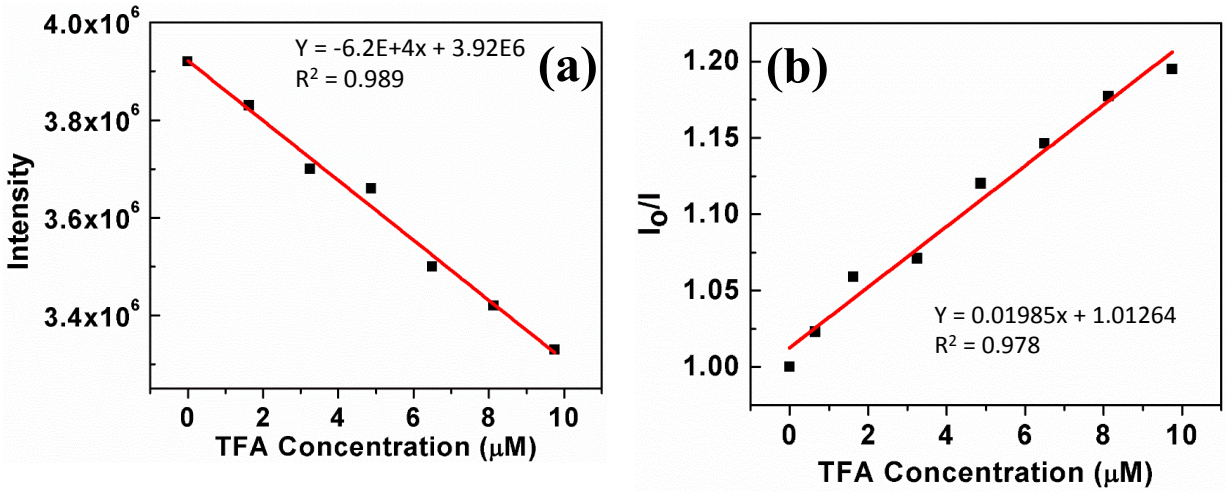


Figure S38. Fluorescence intensity of compound ***α*-CNST** (10 μM) taken in chloroform as a function of TFA concentration (a); Stern−Volmer plot for TFA (b).

For calculating detection limit, different samples of **α-CNST** (10 μM) each containing TFA solution (0 μM, 1.625 μM 3.25 μM, 4.875 μM, 6.5 μM, 8.125 μM and 9.75 μM) in 2 ml $CHCl_3$ were prepared separately and fluorescence spectrum was then recorded for each sample by exciting at 437 nm. The detection limit plot for TFA was obtained by plotting change in the fluorescence intensity vs. the concentration of TFA. The curve demonstrates a linear relationship and the correlation coefficient (R^2) via linear regression analysis were calculated to be 0.989. The limit of detection (LOD) was then calculated using the equation 3σ/K, where σ signifies the standard deviation for the intensity of **α-CNST** in the absence of TFA and K denotes slope of the equation.

LOD = 3 × σ / K
LOD = 3 × 14142.14 / 6.13 × 10^4
= 0.69 μM or **78.89 ppb**

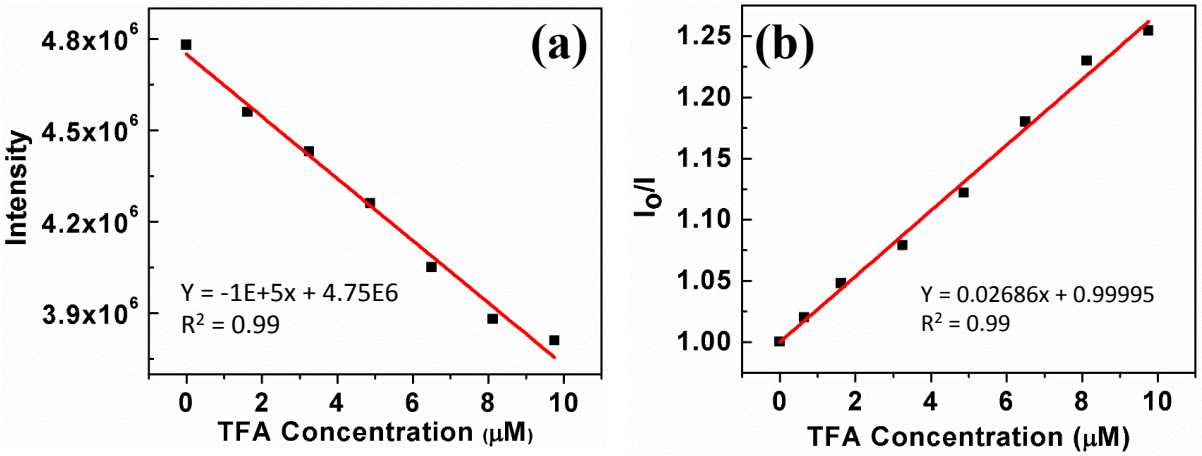


Figure S39. Fluorescence intensity of **β-CNST** (10 μM) taken in chloroform as a function of TFA concentration (a); Stern−Volmer plot for TFA (b).

For calculating detection limit, different samples of **β-CNST** (10 μM) each containing TFA solution (0 μM, 1.625 μM 3.25 μM, 4.875 μM, 6.5 μM, 8.125 μM and 9.75 μM) in 2 ml $CHCl_3$ were prepared separately and fluorescence spectrum was then recorded for each sample by exciting at 449 nm. The detection limit plot for TFA was obtained by plotting change in the fluorescence intensity vs. the concentration of TFA. The curve demonstrates a linear relationship and the correlation coefficient (R^2) via linear regression analysis were calculated to be 0.99. The limit of detection (LOD) was then calculated using the equation 3σ/K, where σ signifies the standard deviation for the intensity of **β-CNST** in the absence of TFA and K denotes slope of the equation.

LOD = 3 × σ / K
LOD = 3 × 14142.14 / 1 × 10^5
= 0.424 μM or **48.34 ppb**

9. References

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