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Contrasting effects of heterocycle substitution and branched tails in the arms of star-shaped molecules

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Supporting information

Table of Contents

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 Cu Kα(λ =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. Thermogravimetric analysis (TGA) was accomplished with a thermogravimetric analyzer (Mettler Toledo, model TG/SDTA 851 e).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.

2. Experimental Section

3,4,5-Trimethoxy-N'-(4-nitrobenzoyl)benzohydrazide (2)[1]

A mixture of 4-nitrobenzohydrazide (5.5 mmol, 1 equiv.) and dry pyridine (15 ml, 3 vol.) was stirred under nitrogen atmosphere at 0 ^{o}C. To this, a solution of trimethoxybenzoyl chloride (5.8 mmol, 1.05 equiv.) in dry THF was added drop wise. The reaction mixture was stirred at room temperature for 12 h and then poured into cold water. The whole mass (a mixture of solid and water) was extracted with ethyl acetate (2 × 100 ml). The combined extracts were given water

wash, brine wash, dried over anhyd. Na_2SO_4 and concentrated. The solid obtained was recrystallized from hot ethanol.

R_f = 0.35 (30% EtOAc-hexanes); off white solid; Yield : 75%; IR (KBr pellet): ν_{max} in cm^{-1} 3105, 3002, 1733, 1641, 1528, 1433, 1345, 1277, 1030, 998, 870, 714, 507;^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.21 (s, 1H, CONH), 9.82 (s, 1H, CONH), 8.23 (d, 2H, J = 8Hz, Ar), 8.02 (d, 2H, J = 8Hz, Ar), 7.07 (s, 2H, Ar), 3.89-3.84 (2s, 9H, 3 × OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 166.24, 164.54, 153.41, 150.20, 142.16, 136.56, 128.87, 125.68, 123.87, 104.97, 61.105, 56.39. HRMS (ESI+) exact Mass calculated for $C_{17}H_{18}N_3O_7$(M+1): 376.1139, found: 376.1149.

2-(4-Nitrophenyl)-5-(3,4,5-trimethoxyphenyl)-1,3,4-oxadiazole (3a) [1]

A mixture of **2** (4.8 mmol, 1 equiv.) and phosphorous oxychloride (72.5 mmol, 5 equiv.) was heated at 100 ^{o}C for 5 h. The excess $POCl_3$ was distilled off under reduced pressure. Traces of $POCl_3$ in the reaction mixture were quenched firstly with the very slow addition of ice-cold water followed by the addition of sodium bicarbonate solution with cooling. The yellow residue obtained was extracted with chloroform (4 × 100 ml). The combined extracts was washed with 20 % $NaHCO_3$, water, brine and dried over anhyd. Na_2SO_4. Upon removal of the solvent under reduced pressure, a yellow solid was obtained, that was purified by recrystallization in benzene.

R_f = 0.6 (20% Methanol-Chloroform); Yield: 70%; IR (KBr pellet) : ν_{max} in cm^{-1} 2947, 1596, 1556, 1522, 1497, 1462, 1341, 1323, 1239, 1131, 993, 862 & 727; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.38 (d, 2H, *J*=6 Hz, Ar), 8.31 (d, 2H, *J* = 12Hz, Ar), 7.34 (s, 2H, Ar), 3.96 (s, 6H, 2 × OCH_3), 3.92 (s, 3H, 1×OCH_3).^{13}C NMR ($CDCl_3$, 150 MHz): 165.65, 162.93, 153.94, 149.63, 141.83, 129.50, 127.94, 124.55, 118.41, 104.55, 61.22, 56.60; HRMS (ESI+) exact Mass calculated for $C_{17}H_{16}N_3O_6$(M+1): 358.1034, found: 358.1032.

2-(4-Nitrophenyl)-5-(3,4,5-trimethoxyphenyl)-1,3,4-thiadiazole (3b) [1]

A solution of compound **2** (4.8 mmol, 1 equiv.) in dry THF (30ml) was added to P_2S_5 (17.3 mmol, 3.6 equiv.) at 0 ^{o}C under Ar- atmosphere and refluxed for 48 h. Distilled out the THF and the reaction was poured on to ice water and extracted with $CHCl_3$ (3 × 50ml). The combined organic layer extracted was washed with water, brine and dried over anhyd. Na_2SO_4. Evaporation

of solvent and recrystallization with ethanol furnished the desired product.

R_f: 0.62 (20% Methanol-Chlroform); Yield: 60%; IR (KBr pellet) : ν_{max} in cm^{-1} 3002, 2975, 2948, 2844, 1596, 1584, 1522, 1452, 1427, 1401, 1337, 1246, 1124, 1090, 998, 850, 747; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, 2H, J= 8Hz, Ar), 8.19 (d, 2H, J = 8Hz, Ar), 7.25 (s, 2H, Ar), 3.97-3.93 (m, 9H, 3 × OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.76, 165.44,162.72, 153.88, 149.16, 141.26, 135.83, 128.72, 124.65, 105.44, 61.26, 56.58. HRMS (ESI+) exact Mass calculated for $C_{17}H_{16}N_3O_5S$ (M+1): 374.0805, found: 374.0809.

5-(5-(4-nitrophenyl)-1,3,4-oxadiazol-2-yl)benzene-1,2,3-triol (4) [1]

A solution of compound **3a** (1.4 mmol, 1 equiv.) in dry dichloromethane (30 ml) was cooled to -78 ^oC and stirred under nitrogen atmosphere. Then, BBr_3 (0.5 ml, 5.04 mmol, 3.6 equiv) was added drop wise to this solution and the reaction mixture was allowed to warm-up to room temperature and continued to stir for 17 h. The reaction mass was poured into ice-water with vigorous stirring to quench the excess BBr_3. The organic layer separated was collected and washed with water (4 × 100 ml), 5 % $NaHCO_3$ solution (1 × 50 ml) and dried over anhyd. Na_2SO_4. Evaporation of solvent under reduced pressure yielded a solid compound that was repeatedly washed with methanol. R_f = 0.23 (20% Methanol-$CHCl_3$); yellow solid; yield: 65%; IR (KBr pellet) : ν_{max} in cm^{-1} 3379, 1629, 1604, 1572, 1559, 1529, 1448, 1330, 1211, 1026, 857, 731, 705; ^1H NMR (DMSO-d_6, 600 MHz): δ 9.51 (broad s, 3H, 3 × OH), 8.42-8.39(m, 2H, Ar), 8.28-8.25(m, 2H, Ar), 7.09 (s, 2H, Ar).^{13}C NMR (DMSO-d_6, 150 MHz): 165.37, 161.96, 148.95, 146.56, 137.79, 129.18, 127.68, 124.64, 112.68, 106.12. HRMS (ESI+) exact Mass calculated for $C_{14}H_{10}N_3O_6$ (M+1): 316.0564, found: 316.0561.

5-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)benzene-1,2,3-triol (5)

A solution of compound **3b** (1.4mmol, 1 equiv.) in dry dichloromethane (30 ml) was cooled to -78^oC and stirred under nitrogen atmosphere. Then, BBr_3 (0.5 ml, 5.04 mmol, 3.6 equiv) was added drop wise to this solution and the reaction mixture was allowed to warm-up to room temperature and continued to stir for 17 h. The reaction mass was poured into ice-water with vigorous stirring to quench the excess BBr_3. The organic layer separated was collected and washed with water (4 × 100 ml), 5 % $NaHCO_3$ solution (1 × 50 ml) and dried over anhyd.

Na_2SO_4. Evaporation of solvent under reduced pressure yielded a solid compound that was repeatedly washed with methanol.

R_f = 0.31 (20% Methanol-$CHCl_3$); brownish yellow solid; mp: >300 ^oC; yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 3487, 2919, 1602, 1516, 1460, 1429, 1332, 1196, 1033, 852, 750; ^1H NMR (DMSO-d_6, 400 MHz): δ 8.39 (d, 2H, J = 8.8 Hz, Ar), 8.27 (d, 2H, *J* = 8.8 Hz, Ar), 7.00 (s, 2H, Ar). ^{13}C NMR (DMSO-d_6, 100 MHz): 169.93, 164.16, 148.58, 146.58, 137.36, 135.41, 128.67, 124.58, 119.27, 106.96. HRMS (ESI+) exact Mass calculated for $C_{14}H_{10}N_3O_5S$ (M+1): 332.0336, found: 332.0342.

2-(4-Nitrophenyl)-5-(3,4,5-tris(alkoxy)phenyl)-1,3,4-oxadiazole (6a)

A mixture of compound **4** (0.48 mmol, 1equiv.), 2-hexylbromodecane (1.57 mmol, 3.3 equiv.), anhyd. K_2CO_3 (3.14 mmol, 6.6 equiv.), and DMF (10 ml) was heated at 80 ^oC for 17 h under nitrogen atmosphere. Then the reaction mixture was poured on to ice-water and extracted with EtOAc (3 × 50 ml). The combined organic layer was washed with water, brine and dried over anhyd. Na_2SO_4. Evaporation of the solvent and purification of the residue over neutral alumina using hexanes followed by ethylacetate-hexanes (5%) as eluents furnished the desired product.

6a: R_f = 0.51 (10% EtOAc-hexanes); a yellow liquid; yield: 70%; IR (KBr pellet): ν_{max} cm^{-1} 2918, 2849, 1590, 1556, 1523, 1493, 1468, 1436, 1338, 1126, 1022, 861, 729, 703; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.39(d, 2H, *J*= 8.8 Hz, Ar), 8.32 (d, 2H, *J*= 8.8 Hz, Ar), 7.29 (s, 2H, Ar), 3.94-3.9 (m, 6H, 3 × OCH_2), 1.58-0.84 (m, 94H, 38× CH_2, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 166.10, 162.84, 154.10, 149.71,142.24, 129.75, 127.96, 124.58, 117.80, 105.36, 72.08, 39.56, 38.50, 32.13, 31.60, 31.49, 30.45, 30.33, 30.10, 29.98, 29.88, 29.66, 29.59, 27.31, 27.15, 22.91, 14.30. MALDI-TOF exact mass calculated for $C_{62}H_{106}N_3O_6$ (M+1): 988.8082, found: 988.835.

2-(4-Nitrophenyl)-5-(3,4,5-tris(alkoxy)phenyl)-1,3,4-thiadiazole (6b-c)

A mixture of compound **5** (0.48 mmol, 1equiv.), n-bromoalkane (1.57 mmol, 3.3 equiv.), anhyd.

K_2CO_3 (3.14 mmol, 6.6 equiv.), and DMF (10 ml) was heated at 80 ^oC for 17 h under nitrogen atmosphere. Then the reaction mixture was poured on to ice-water and extracted with EtOAc (3 × 50 ml). The combined organic layer was washed with water, brine and dried over anhyd.Na_2SO_4. Evaporation of the solvent and purification of the residue over neutral alumina using hexanes followed by ethylacetate-hexanes (5%) as eluents furnished the desired product.

6b: R_f = 0.62 (10% EtOAc-hexanes); a yellow solid; mp: >85-87 ^oC; yield: 60%; IR (KBr pellet): ν_{max} cm^{-1} 2923, 2846, 1635, 1456, 1273, 1261, 1094, 1019, 801, 762, 749; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.37 (d, 2H, *J*= 6 Hz, Ar), 8.19 (d, 2H, *J* = 6 Hz, Ar), 7.22 (s, 2H, Ar), 4.08-4.03 (m, 6H, 3 × OCH_2), 1.87-0.86 (m, 93H, 42 × CH_2, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 170.07, 165.21, 153.86, 149.21, 141.68, 136.08, 128.72, 124.66, 124.52, 106.86, 73.90, 69.66, 32.15, 30.56, 29.94, 29.88, 29.87, 29.80, 29.62, 29.59, 29.54, 26.30, 22.91, 14.32. MALDI-TOF exact mass calculated for $C_{62}H_{106}N_3O_5S$ (M+1): 1004.7853, found: 1004.782.

6c: R_f = 0.53 (10% EtOAc-hexanes); a yellow liquid; yield: 65%; IR (KBr pellet): ν_{max} cm^{-1} 2917, 2850, 1586, 1523, 1438, 1379, 1344, 1232, 1122, 852, 720; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34(d, 2H, *J*= 8 Hz, Ar), 8.17 (d, 2H, *J*= 8 Hz, Ar), 7.21 (s, 2H, Ar), 3.96-3.90 (m, 6H, 3 × OCH_2), 1.50-0.85 (m, 94H, 38× CH_2, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 171.53, 170.19, 165.10, 153.99, 149.15, 141.60, 136.08, 128.66, 124.62, 124.32, 106.19, 71.96, 67.54, 39.50, 38.41, 37.43, 32.12, 31.55, 29.98, 29.88, 29.59, 27.11, 22.96, 22.91, 22.88, 14.30. MALDI-TOF exact mass calculated for $C_{62}H_{106}N_3O_5S$ (M+1): 1004.7853, found: 1004.735.

4-(5-(3,4,5-Trialkoxyphenyl)-1,3,4-oxadiazol-2-yl)benzenamines (7a)

To a solution of nitro compound **6a** (0.9 mmol, 1 equiv.) in dry THF was added 10 % Pd-C (10 weight % of **6a**) and stirred under hydrogen atmosphere (balloon) for 12 h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent and purification of residue over neutral alumina followed by ethylacetate-hexanes (10 %) as eluents furnished the desired amine.

7a: R_f = 0.25 (30% EtOAc-hexanes); a yellow gummy liquid; yield: 72%; IR (KBr pellet): ν_{max}

cm^{-1} 2918, 2850, 1614, 1495, 1468, 1390, 1331, 1122, 986, 835, 721; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 2H, *J*= 8.8 Hz ,Ar), 7.26 (s, 2H, Ar), 6.80 (d, 2H, *J*= 8.8 Hz, Ar), 3.93-3.88 (m, 6H, 3 × OCH_2), 1.51-0.83 (m, 76H, 38 × CH_2, 18H, 6× CH_3); ^{13}C NMR ($CDCl_3$, 100MHz): 164.89, 164.30, 153.95, 148.85, 141.39, 128.85, 118.84, 115.47, 114.62, 104.99, 71.98, 39.54, 38.49, 32.12, 31.59, 31.50, 30.46, 30.33, 30.10, 29.98, 29.87, 29.66, 29.59, 28.99, 27.27, 27.14, 26.71, 22.90, 22.59, 14.29; HRMS (ESI+) exact Mass calculated for $C_{62}H_{108}N_3O_4$ (M+1): 958.8334, found: 958.8403.

4-(5-(3,4,5-Trialkoxyphenyl)-1,3,4-thiadiazol-2-yl)benzenamines (7b-c)

To a solution of nitro compound **6b** or **6c** (0.9 mmol, 1 equiv.) in dry THF was added 10 % Pd-C (10 weight % of **6b-c**) and stirred under hydrogen atmosphere (balloon) for 12 h (monitored by TLC). The reaction mixture was then filtered through a celite bed. Evaporation of the solvent and purification of residue over neutral alumina followed by ethylacetate-hexanes (10 %) as eluents furnished the desired amine.

7b: R_f = 0.21 (15% EtOAc-hexanes); a light yellow solid; mp: 73-75 ^{o}C; yield: 65%; IR (KBr pellet): ν_{max} in cm^{-1}3456, 2961, 2928, 1634, 1459, 1034, 1016, 687; ^{1}H NMR ($CDCl_3$, 600MHz): δ 7.80 (d, 2H, *J*= 6 Hz, Ar), 7.18 (s, 2H, Ar), 6.73 (d, 2H, *J*= 12 Hz, Ar), 4.06-4.00 (m, 6H, 3 × OCH_2), 1.85-0.86 (m, 93H, 42 × CH_2, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150MHz):168.34, 166.94, 153.71, 149.44, 140.83, 129.63, 125.52, 120.61, 115.11, 106.57, 73.83, 69.57, 32.15, 30.55, 29.93, 29.88, 29.81, 29.63, 29.58, 26.30, 22.90, 14.33; HRMS (ESI+) exact Mass calculated for $C_{62}H_{108}N_3O_3S$ (M+1): 974.8106, found: 974.8088.

7c: R_f = 0.2 (15% EtOAc-hexanes); a light yellow liquid; yield: 60%; IR (KBr pellet): ν_{max} cm^{-1} 2918, 2850, 1608, 1585, 1467, 1452, 1425, 1385, 1334, 1122, 832, 653; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, 2H, *J*= 8.8Hz ,Ar), 7.16 (s, 2H, Ar), 6.73 (d, 2H, *J*= 8.8 Hz, Ar), 3.92-3.87 (m, 6H, 3 × OCH_2), 1.59-1.28 (m, 76H, 38 × CH_2), 0.87 (t, 18H, 6 × CH_3); ^{13}C NMR ($CDCl_3$, 100MHz):168.25, 167.11, 153.88 ,149.35, 140.79, 129.63, 125.35, 120.74, 115.08, 105.96, 76.92, 71.96, 39.52, 38.44, 32.23, 32.20, 32.15, 31.58, 31.50, 30.48, 30.37, 30.13, 30.02, 29.90, 29.70, 29.62, 27.32, 27.27, 27.13, 27.10, 22.98, 22.94, 22.92, 14.34. HRMS (ESI+) exact Mass calculated for $C_{62}H_{108}N_3O_3S$ (M+1): 974.8106, found: 974.8153.

Tris(*N*-salicylideneaniline)s O-b16

A mixture of triformylphloroglucinol (0.005 mmol, 1 equiv.) and aniline **7a** (0.19 mmol, 3.4 equiv.) in absolute ethanol (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 ethanol, and air-dried. The crude product was purified by repeated recrystallizations in a mixture of absolute ethanol-CH_2Cl_2.

O-b16: R_f = 0.64 (40% EtOAc – hexanes); an orange solid; Yield 80%; IR (KBr pellet): ν_{max} cm^{-1} 2956, 2925, 2854, 1626, 1598, 1584, 1492, 1456, 1285, 1252, 1179, 1115, 1010, 840, 740, 640; ^1H NMR ($CDCl_3$, 600 MHz): δ 13.57 (d, *J* = 12 Hz, =CNH), 13.52 (d, *J* = 12Hz, =CNH), 13.16-13.12 (m, =CNH), 8.93-8.83 (m, 3H, =CHN), 8.25-8.22 (m, 6H, Ar), 7.52 – 7.48 (m, 6H, Ar), 7.32 (s, 6H, Ar), 3.97-3.92 (m, 18H, 9 × OCH_2), 1.87-0.87 (m, 279H, 108 × CH_2, 9 × CH, 18 × CH_3). MALDI Tof MS for $C_{195}H_{322}N_9O_{15}$ (M+1), Calculated: 3030.4710 Found: 3030.473.

Tris(*N*-salicylideneaniline)s T-16 and T-b16

A mixture of triformylphloroglucinol (0.005 mmol, 1 equiv.) and aniline **7b** or **7c** (0.19 mmol, 3.4 equiv.) in absolute ethanol (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 ethanol, and air-dried. The crude product was purified by repeated recrystallizations in a mixture of absolute ethanol-CH_2Cl_2 in case of solid.

T-16: R_f = 0.65 (40% EtOAc-hexanes); a brick red solid; yield: 70%; IR (KBr pellet): $\nu_{max\ cm^{-1}}$ 2956, 2925, 2854, 1621, 1595, 1576, 1509, 1448, 1421, 1286, 1252, 1115, 983, 832, 723; ^1H NMR ($CDCl_3$, 600 MHz): δ 13.44 (broad s, =CNH), 13.30 (broad s, =CNH), 13.02 (broad s, =CNH), 8.74 (broad s, 3H, =CHN), 8.02 (broad d, 6H, Ar), 7.07 (broad s, 12H, Ar), 4.02 (broad s, 18H, 9 × OCH_2), 1.83-0.88 (m, 279H, 126× CH_2, 9 × CH_3). MALDI Tof MS for $C_{195}H_{322}N_9O_{12}S_3$ (M+1) Calculated: 3078.4020 Found: 3078.709.

T-b16: R_f= 0.62 (40% EtOAc – hexanes); a viscous orange liquid; Yield 65%; IR (KBr pellet): $\nu_{max\ cm^{-1}}$ 2956, 2925, 2854, 1621, 1595, 1575, 1509, 1448, 1421, 1379, 1286, 1253, 1180, 832, 772, 655; ^1H NMR ($CDCl_3$, 600 MHz): δ 13.54 (d, *J* = 12Hz, =CNH), 13.50 (d, *J* = 12 Hz,

=CNH), 13.12 (d, *J* = 12Hz, =CNH), 8.90-8.80 (m, 3H, =CHN), 8.10-8.08 (m, 6H, Ar), 7.47 – 7.43 (m, 6H, Ar), 7.20 (broad s, 6H, Ar), 3.94-3.89 (m, 18H, 9 × OCH_2), 1.86-0.87 (m, 279H, 108 × CH_2, 9 × CH, 18 × CH_3). MALDI Tof MS for $C_{195}H_{322}N_9O_{12}S_3$ (M+1) Calculated: 3078.4020 Found: 3079.895.

3. NMR Spectra

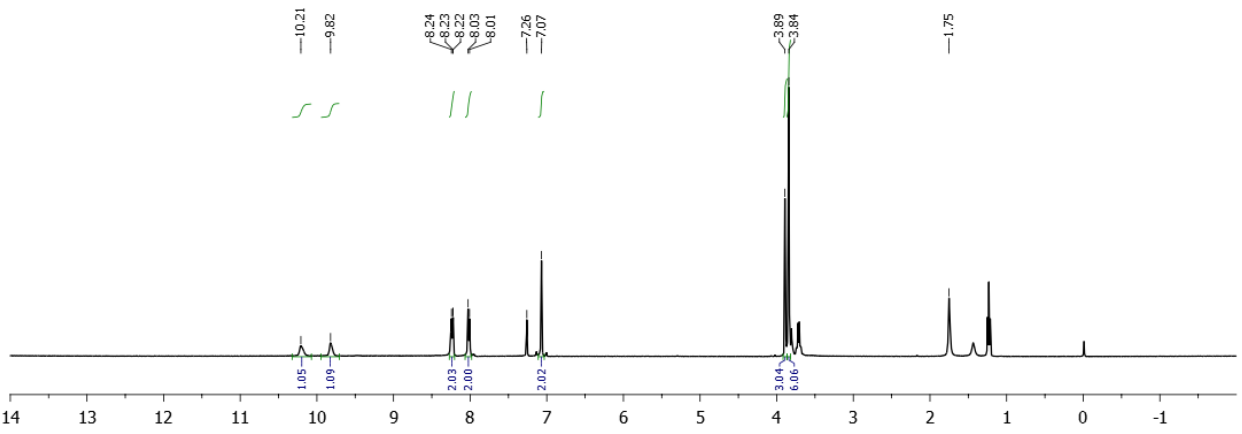


Figure S1. ^{1}H NMR of **2** (600MHz) in $CDCl_3$.

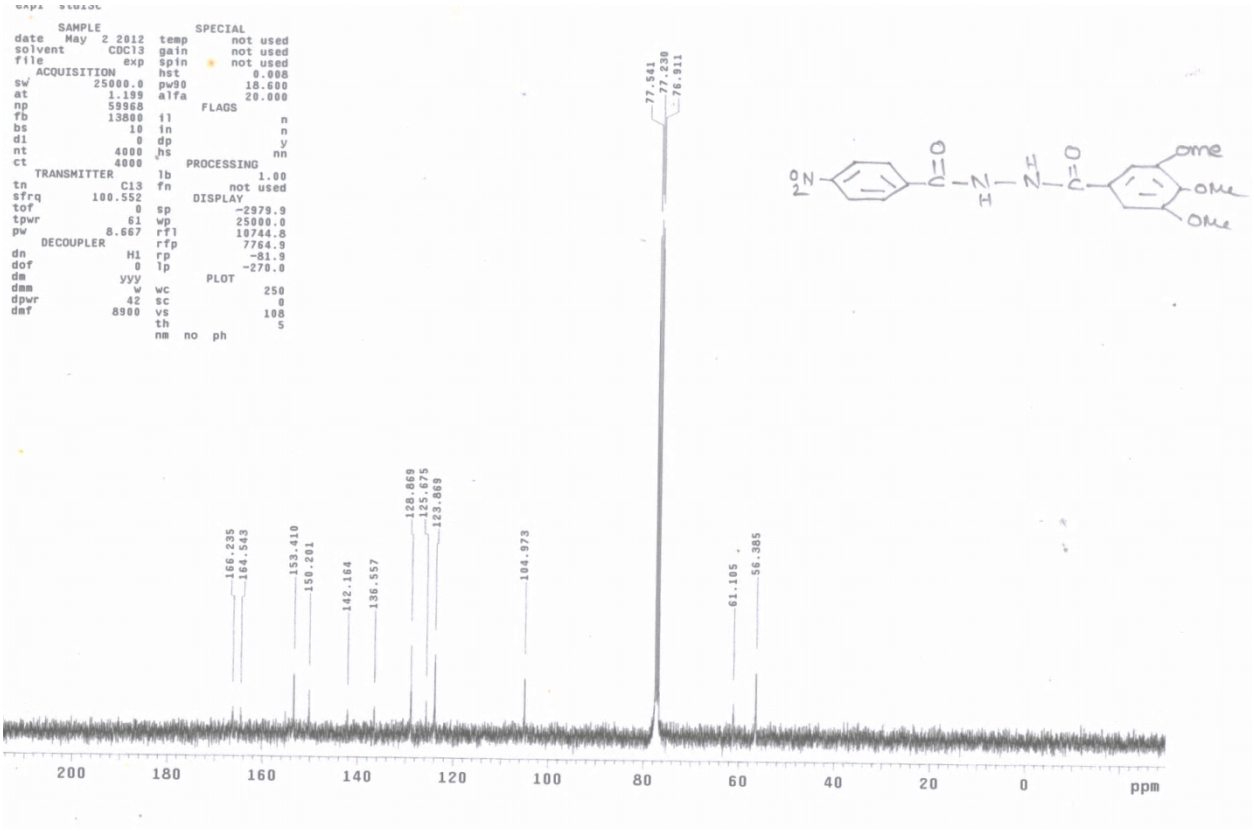


Figure S2. ^{13}C NMR of **2** (100MHz) in $CDCl_3$.

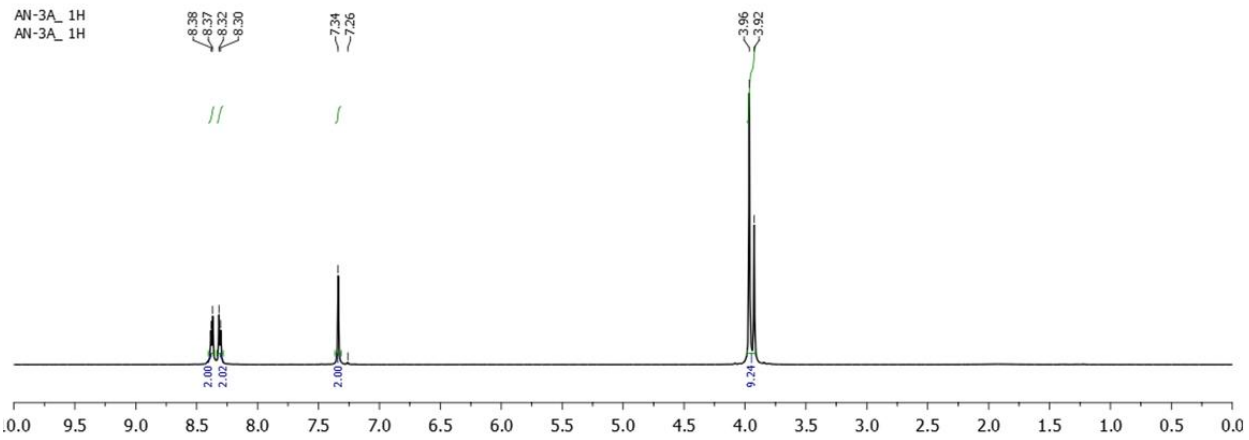


Figure S3. ^{1}H NMR of **3a** (600MHz) in $CDCl_3$.

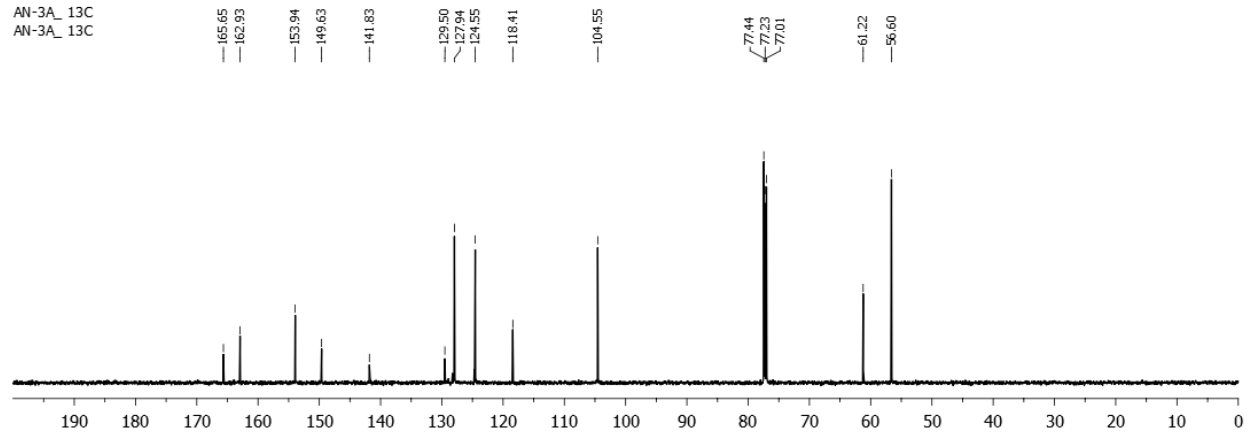


Figure S4. ^{13}C NMR of **3a** (150MHz) in $CDCl_3$.

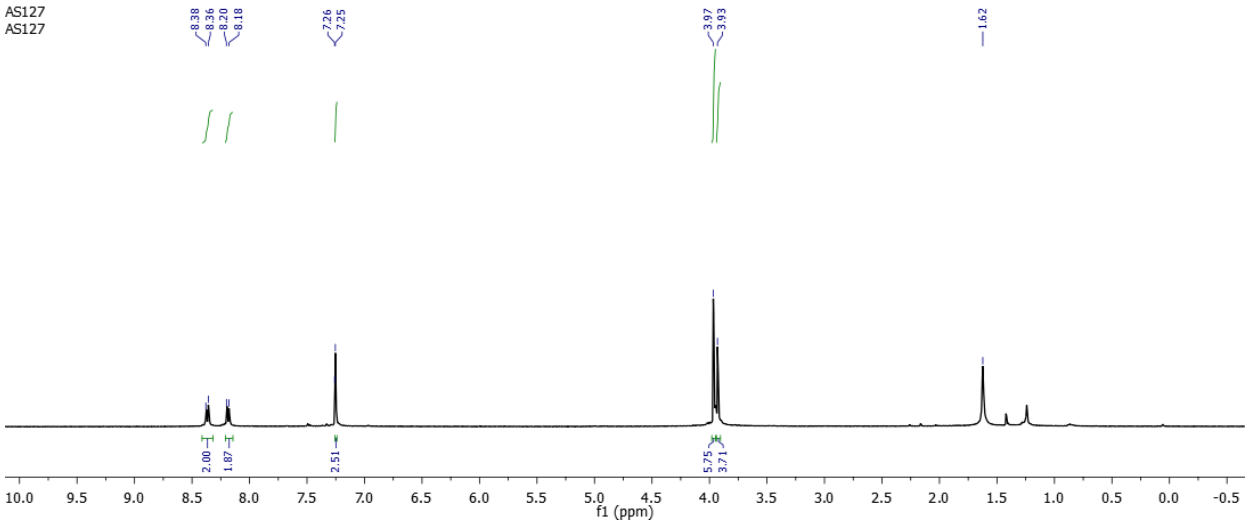


Figure S5. ^{1}H NMR of **3b**

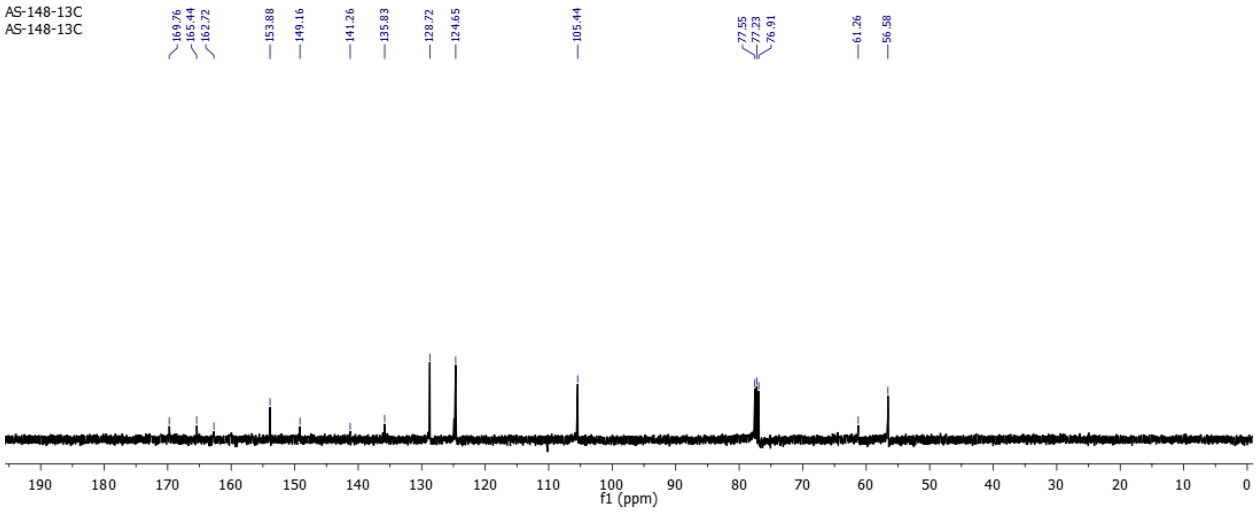


Figure S6.^{13}C NMR of **3b**

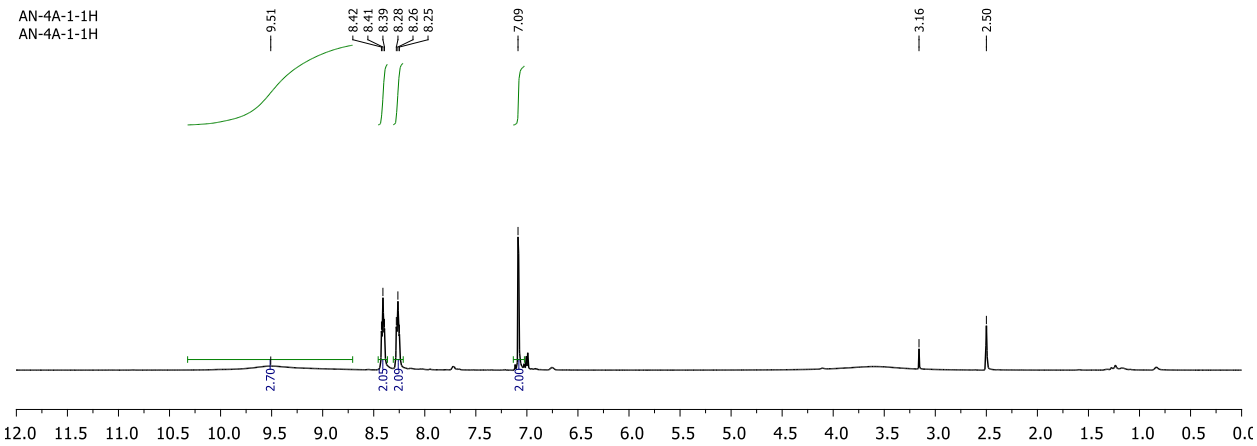


Figure S7. ^{1}H NMR of **4** (600MHz) in DMSO-d_6.

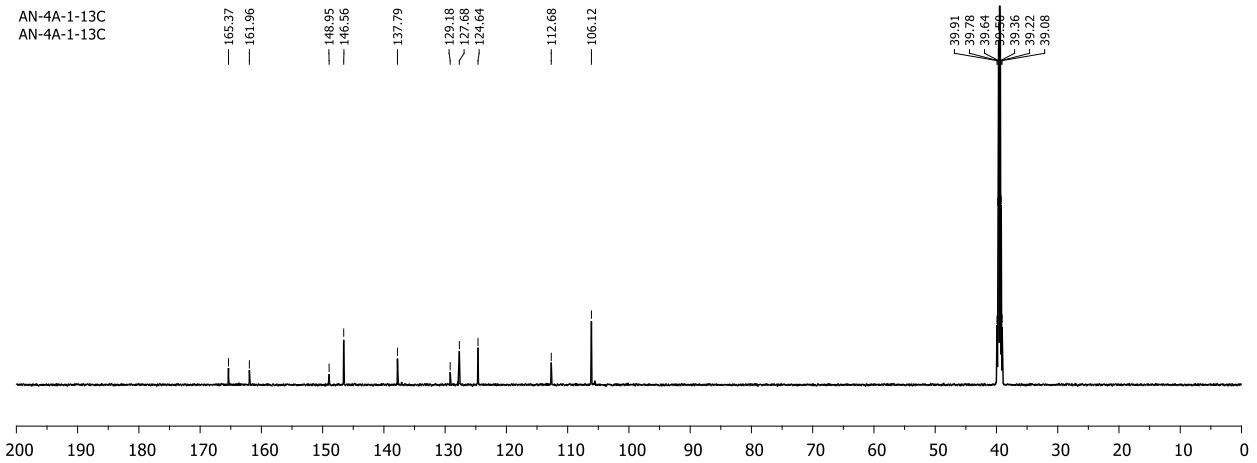


Figure S8. ^{13}C NMR of **4** (150MHz) in DMSO-d_6.

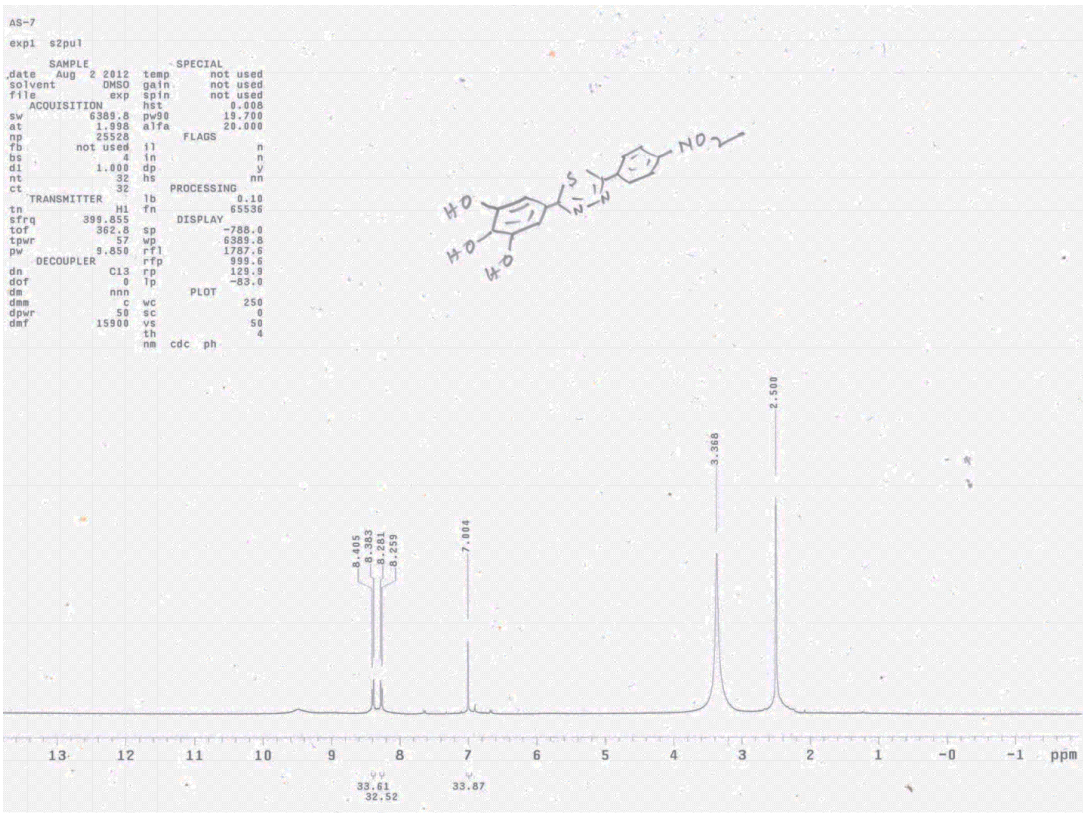


Figure S9. ^{1}H NMR of **5** (400MHz) in DMSO-d_6.

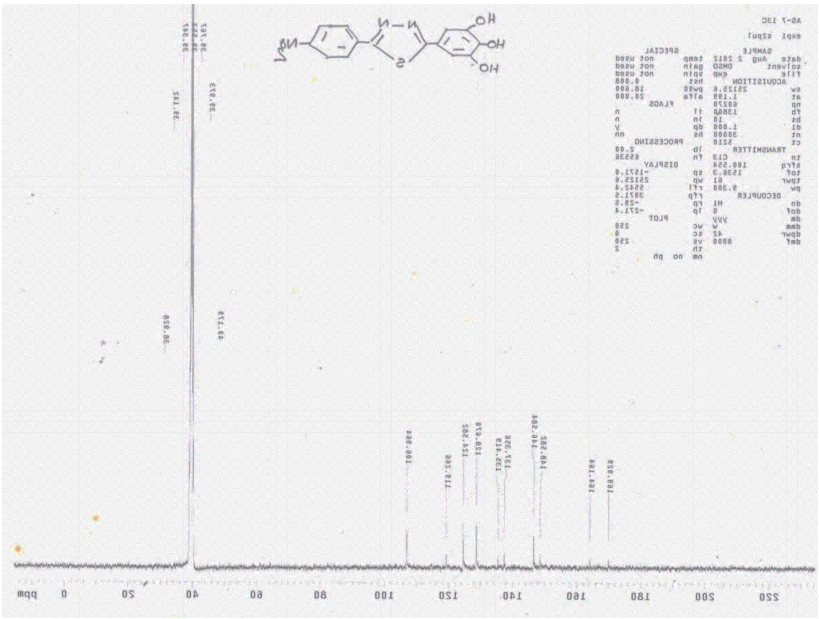


Figure S10. ^{13}C NMR of **5** (100MHz) in DMSO-d_6.

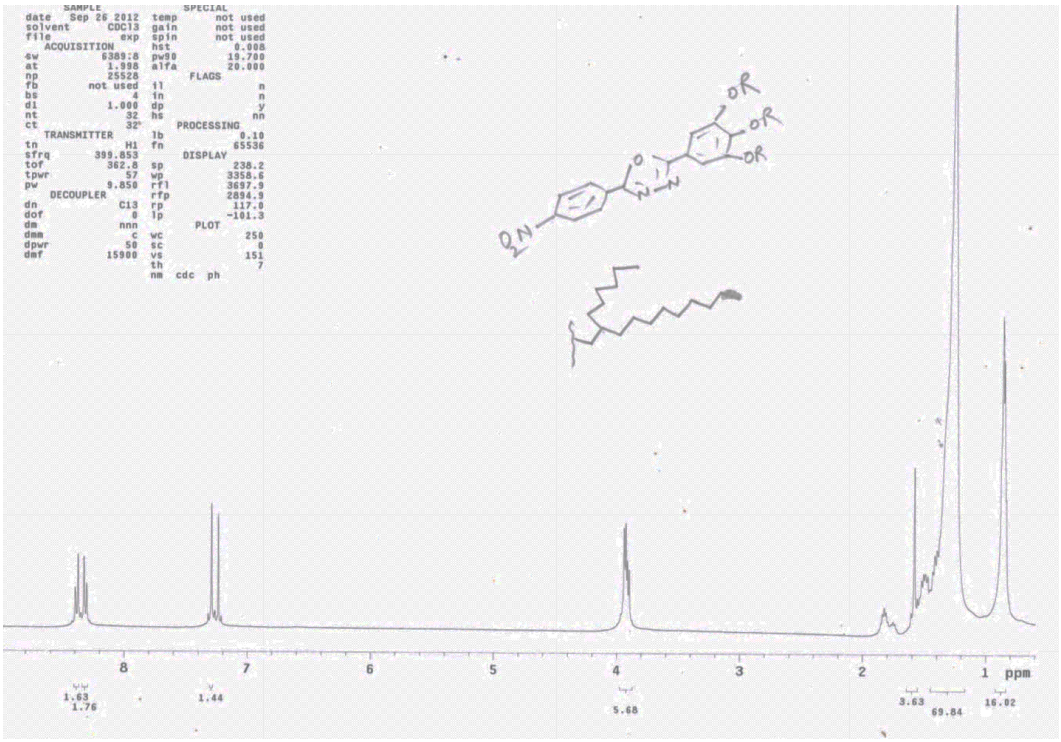


Figure S11. ^{1}H NMR of **6a** (400MHz) in $CDCl_3$.

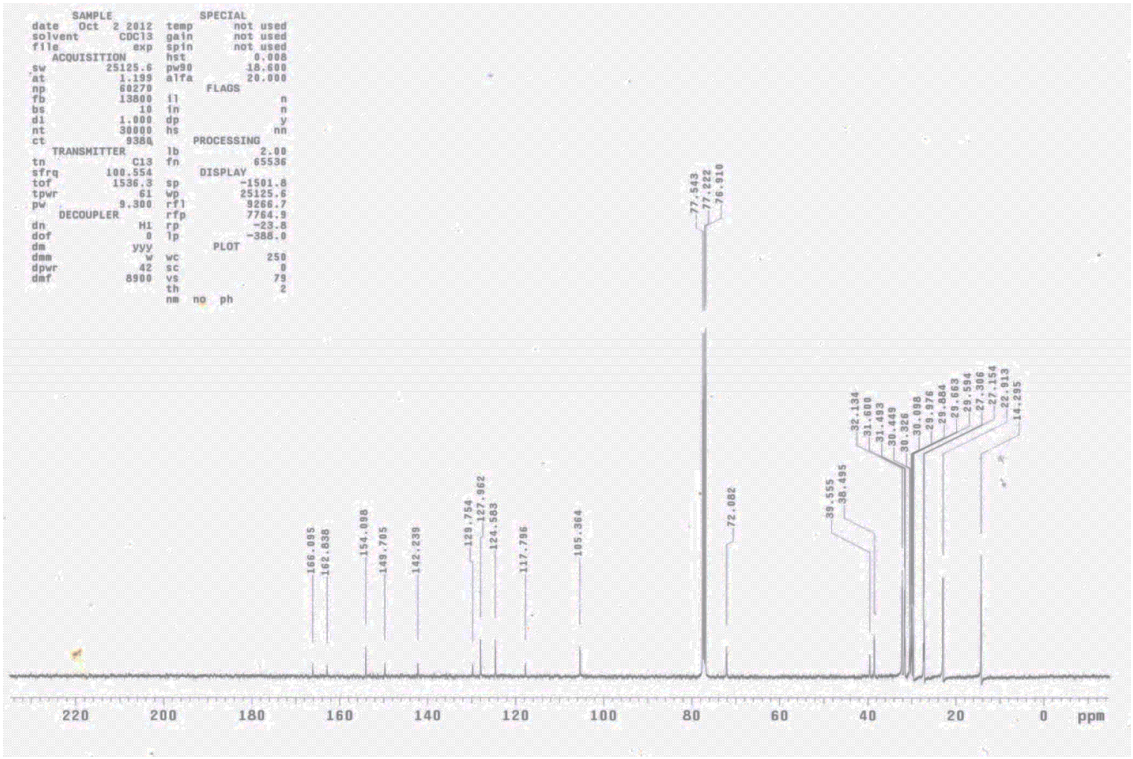


Figure S12. ^{13}C NMR of **6a** (100MHz) in $CDCl_3$.

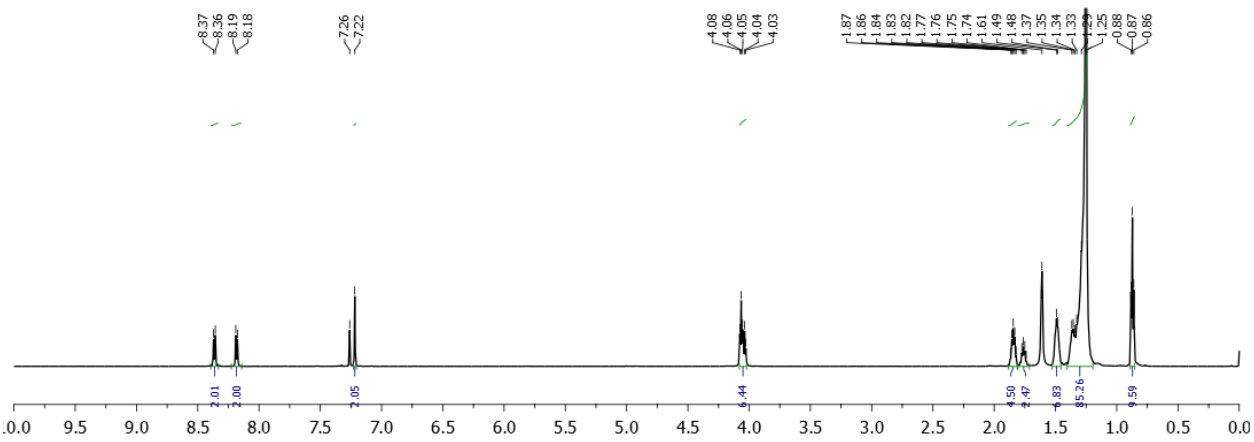


Figure S13. ^{1}H NMR of **6b** (600MHz) in $CDCl_3$.

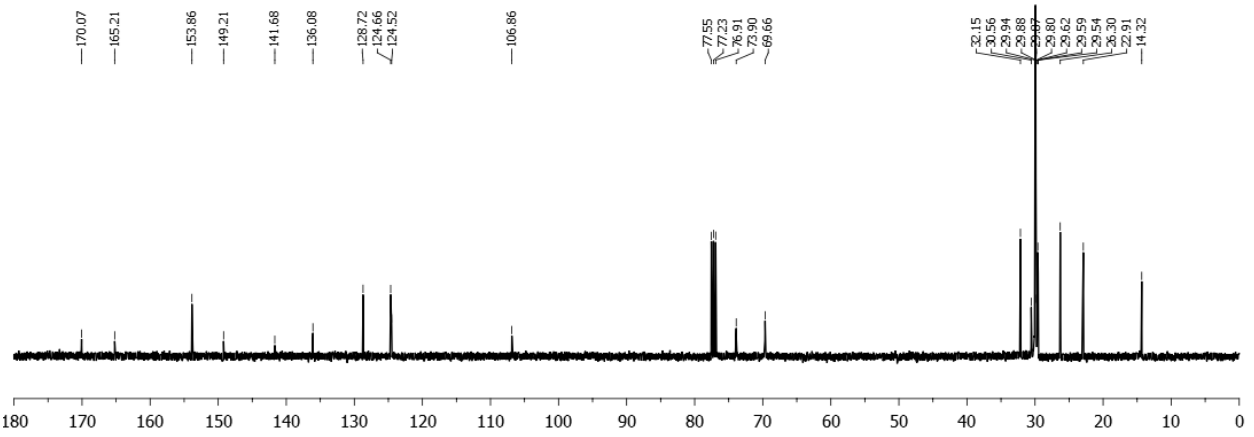


Figure S14. ^{13}C NMR of **6b** (100MHz) in $CDCl_3$.

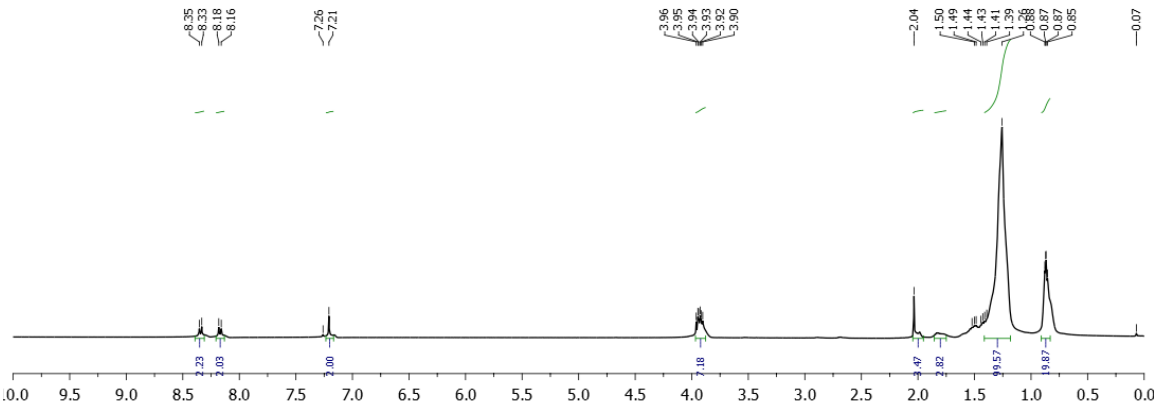


Figure S15. ^{1}H NMR of **6c** (600MHz) in $CDCl_3$.

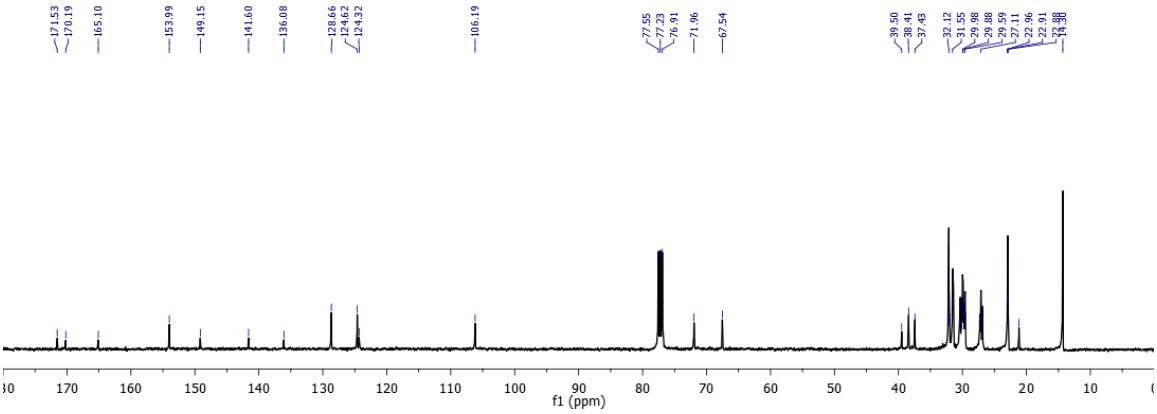


Figure S16. ^{1}H NMR of **6c** (600MHz) in $CDCl_3$.

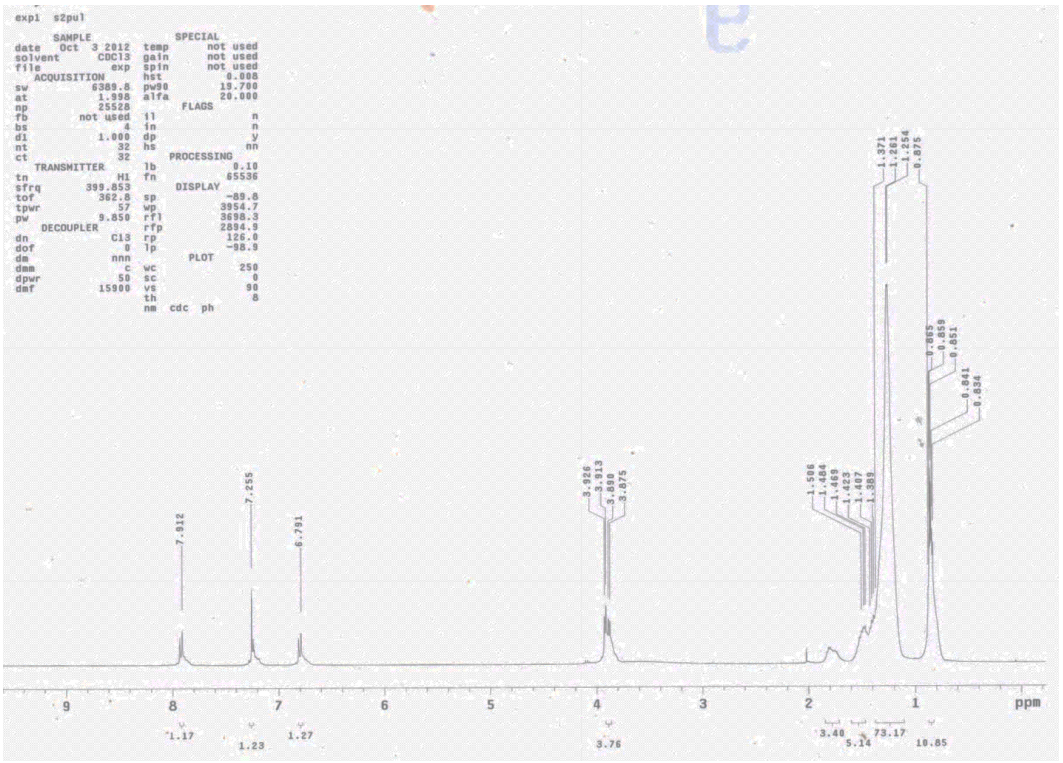


Figure S17. ^{1}H NMR of **7a** (400MHz) in $CDCl_3$.

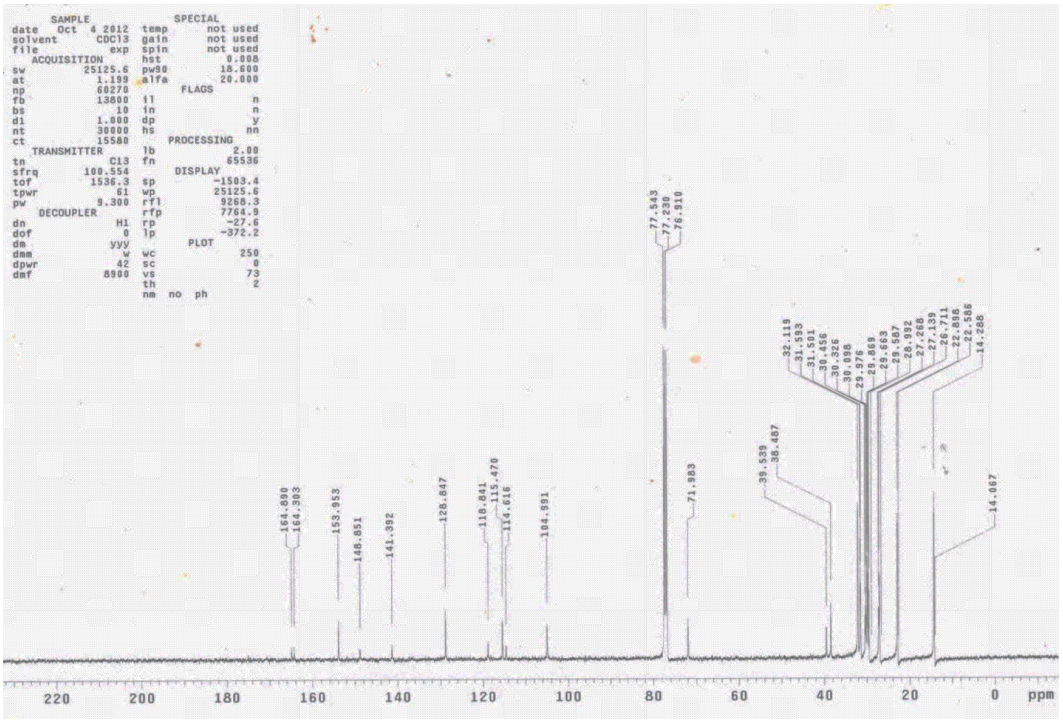


Figure S18. ^{13}C NMR of **7a** (100MHz) in $CDCl_3$.

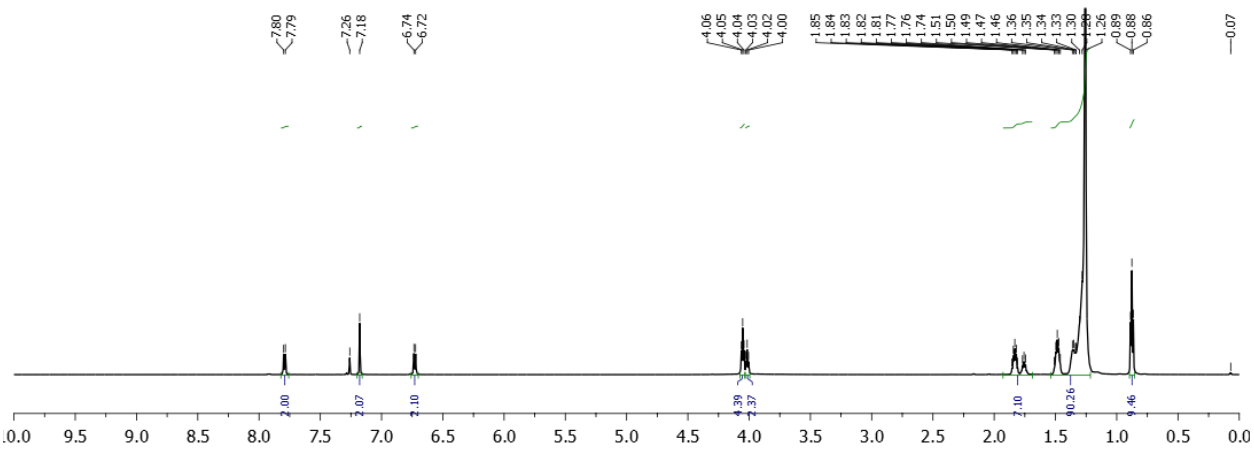


Figure S19. ^{1}H NMR of **7b** (600MHz) in $CDCl_3$.

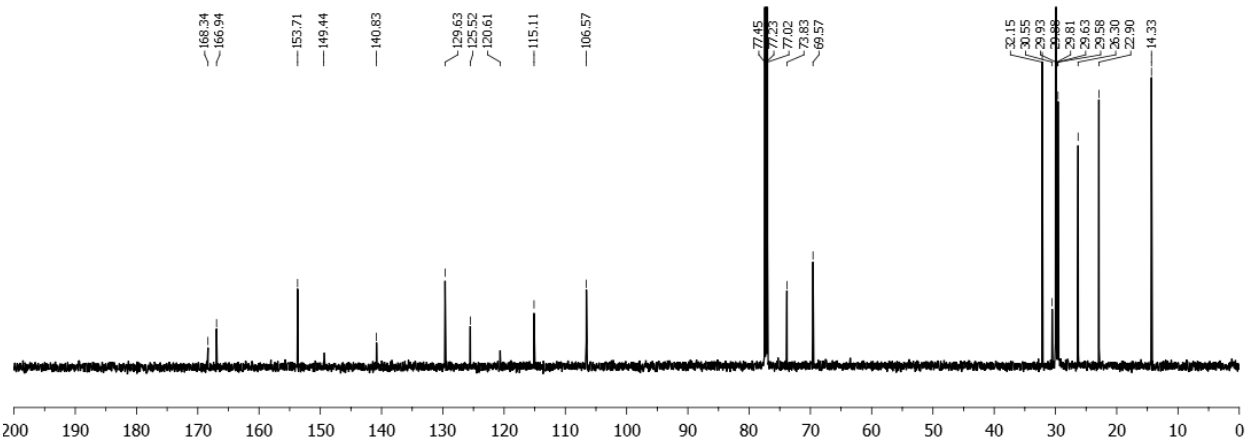


Figure S20. ^{13}C NMR of **7b** (150MHz) in $CDCl_3$.

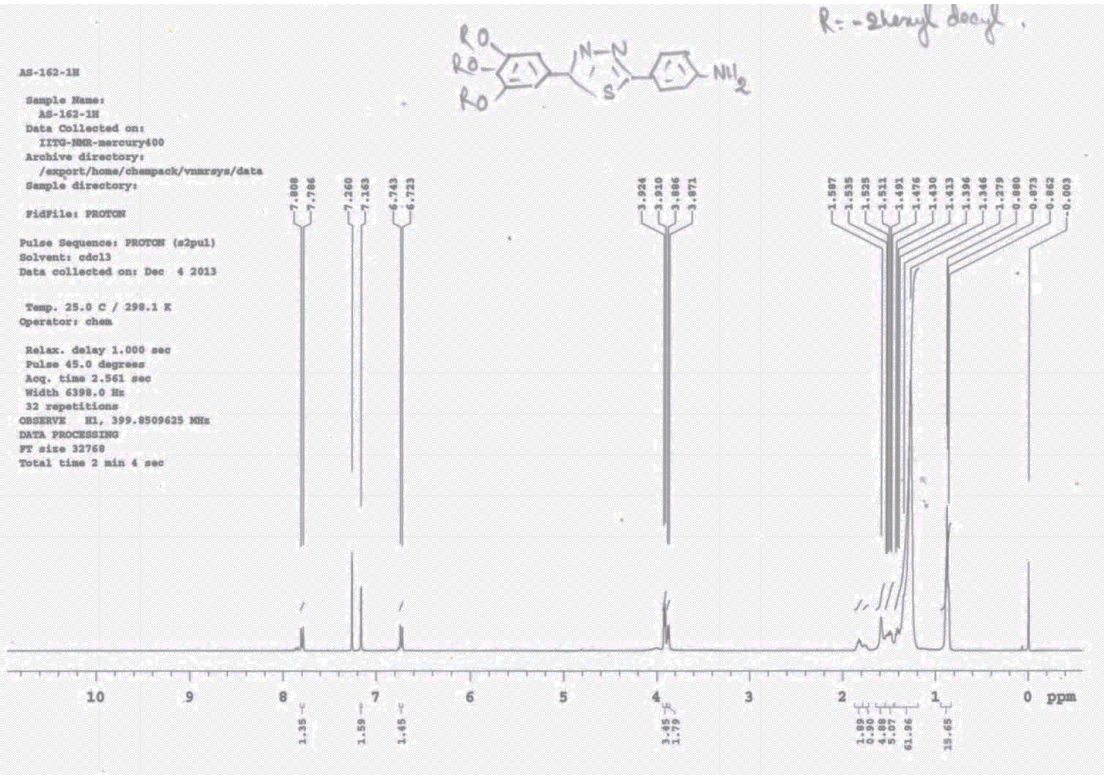


Figure S21. ^{1}H NMR of **7c** (400MHz) in $CDCl_3$.

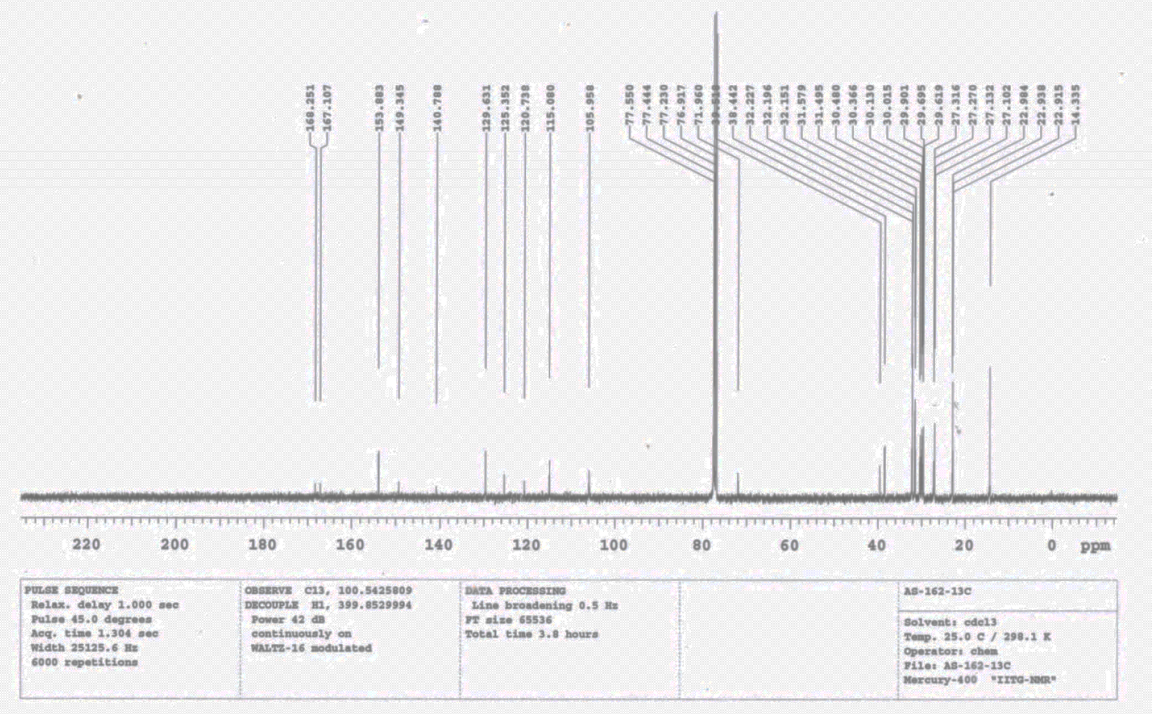


Figure S22. ^{13}C NMR of **7c** (100MHz) in $CDCl_3$.

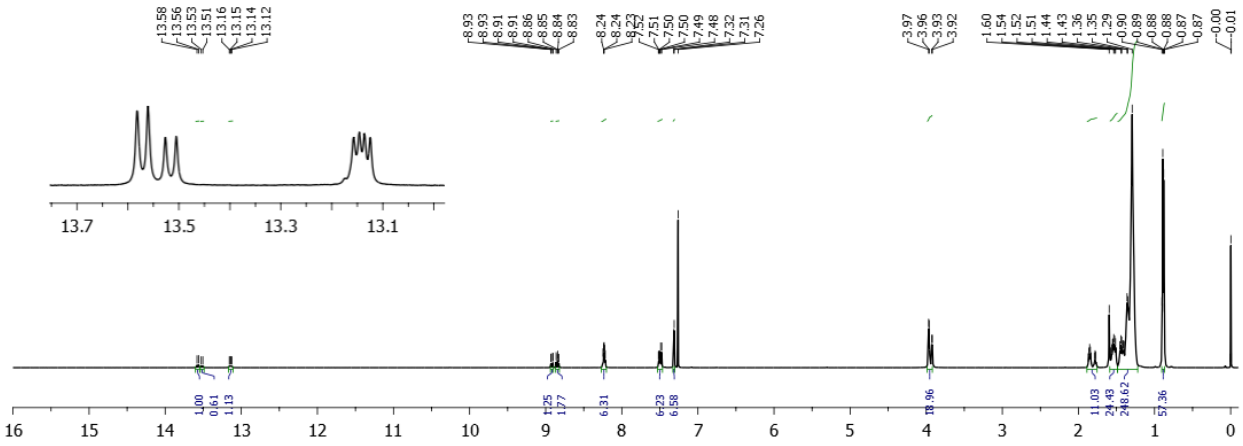


Figure S23. ^{1}H NMR of **O-b16** (600MHz) in $CDCl_3$.

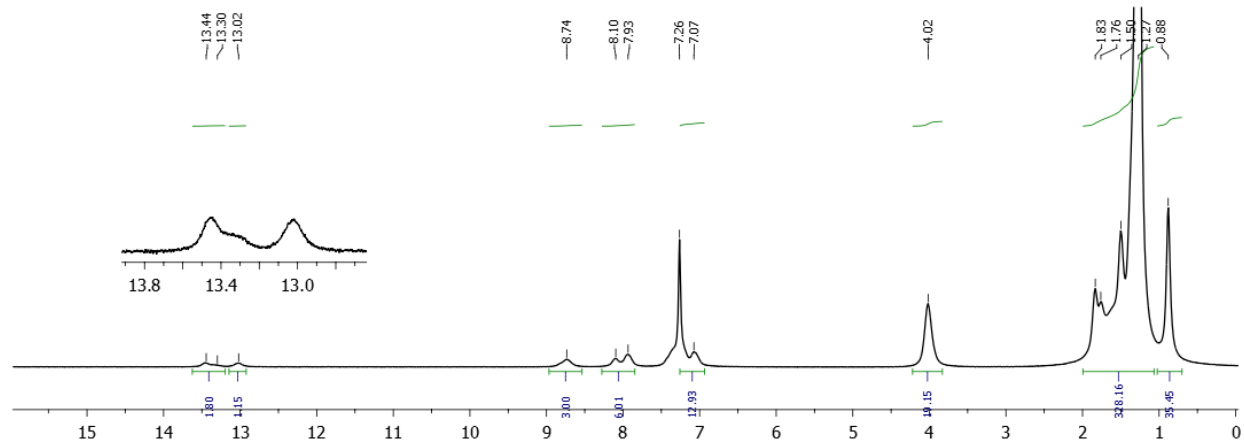


Figure S24. ^{1}H NMR of **T-16** (600MHz) in $CDCl_3$.

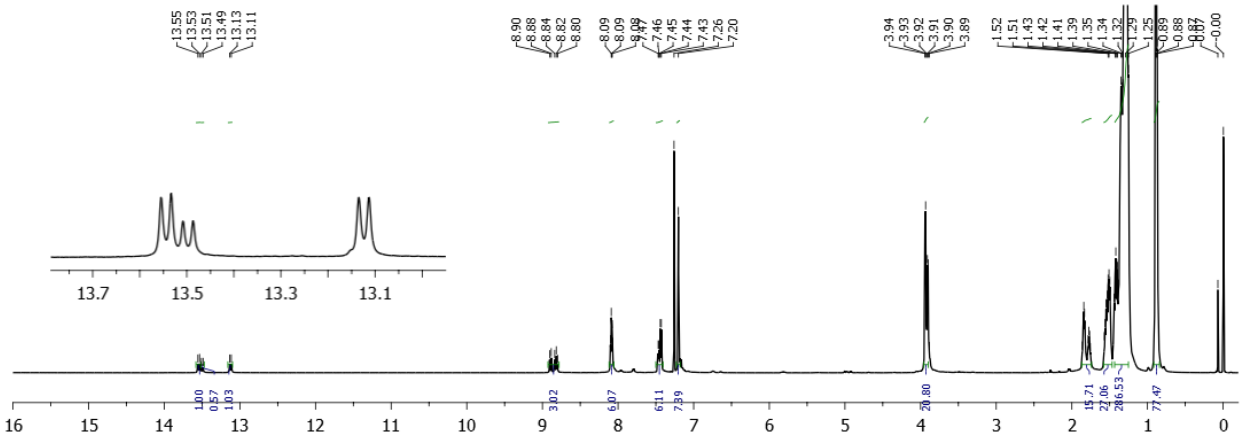


Figure S25. ^{1}H NMR of **T-b16** (600MHz) in $CDCl_3$.

4. 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 (Q_f = 0.79) in 0.1M NaOH). Absolute values were calculated according to the following equation:

$$Q_S = Q_R \times (m_S / m_R) \times (n_S / n_R)^2$$

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 re-absorption 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.

$Q_S = 1.01 \times (m_S / m_R) \times (1.407/1.407)^2$

$= 1.01 \times (m_S / m_R)$

Entry	$\mathbf{m_S}$	$\mathbf{m_R}$	$\mathbf{Q_s^{a,b,c}}$
O-16	2.63082×10^8	7.2271×10^8	0.37
O-b16	2.28589×10^8	7.2271×10^8	0.32
T-16	2.74607×10^8	7.2271×10^8	0.38
T-b16	3.15971×10^8	7.2271×10^8	0.44

[a] Measured in THF; [b]Excited at absorption maxima; [c]Standard carbazole (Q_f = 1.01) in THF solution

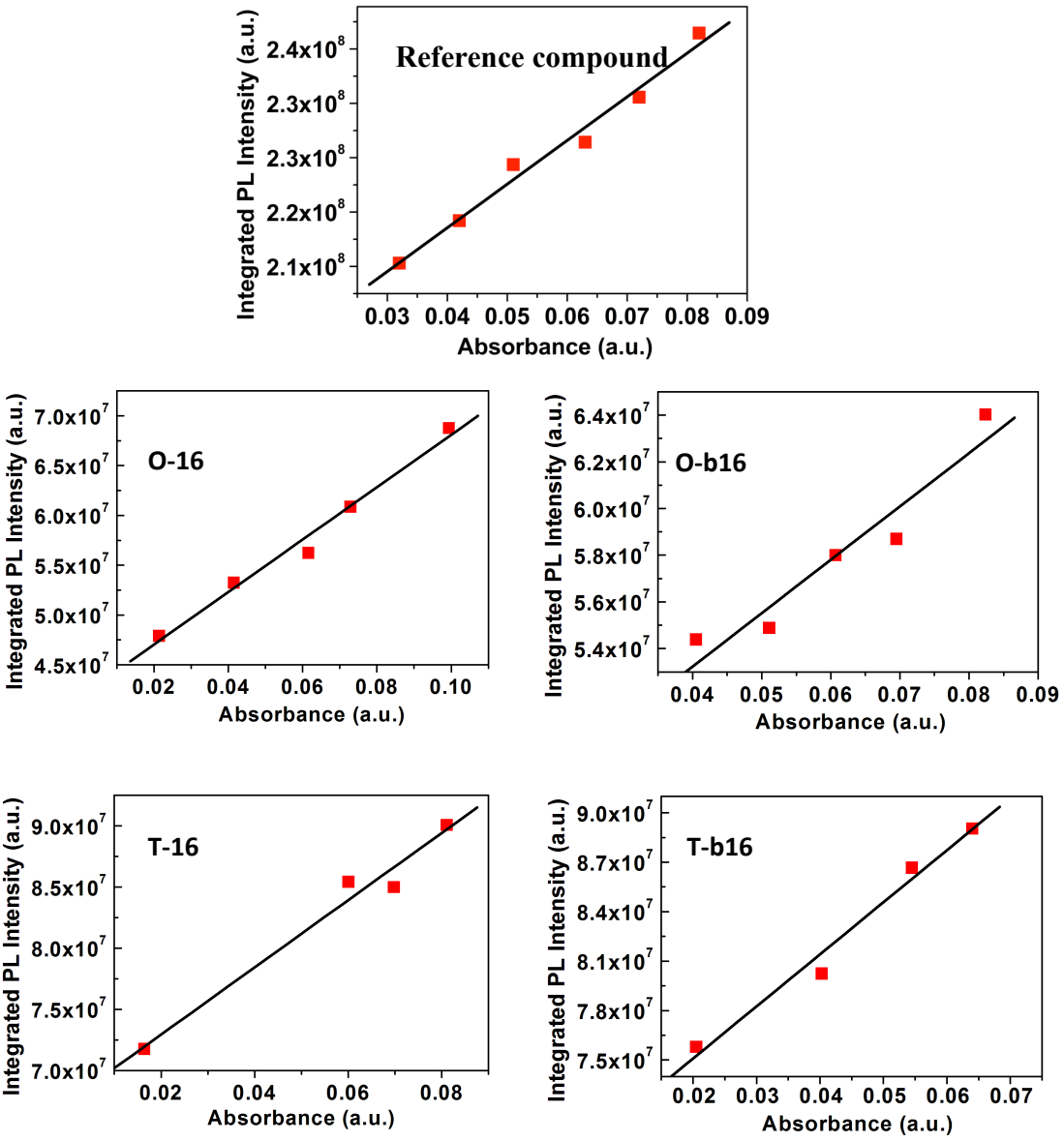


Figure S26. Plots of integrated photoluminescence intensity vs absorbance of reference compound and TSANs **O-16, O-b16, T-16** and **T-b16** (micromolar THF solution)

5. MALDI-TOF Studies

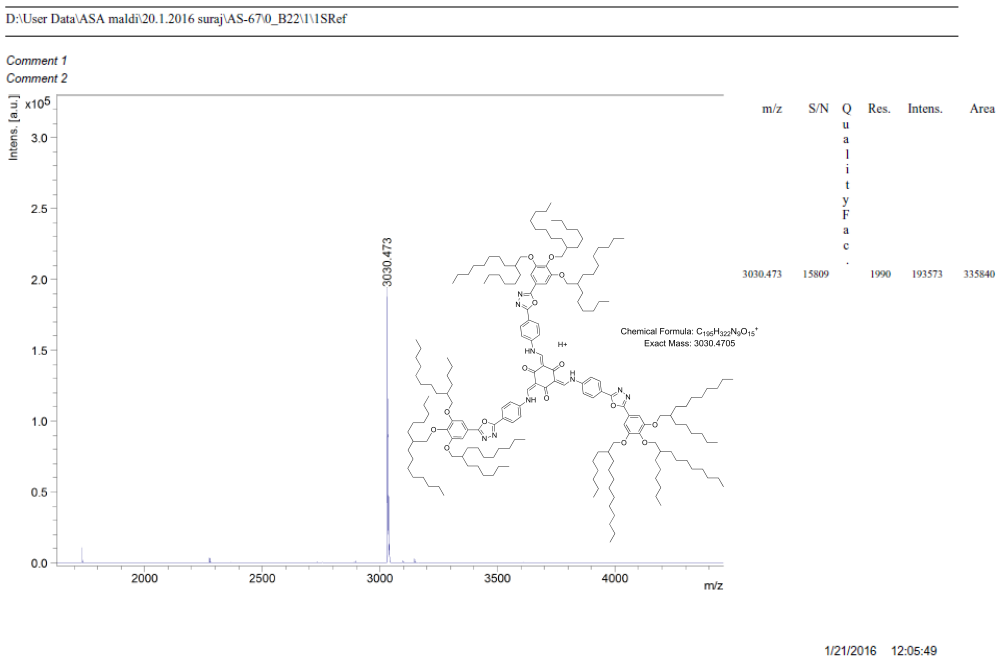


Figure S27. MALDI-TOF mass spectra of TSAN **O-b16**

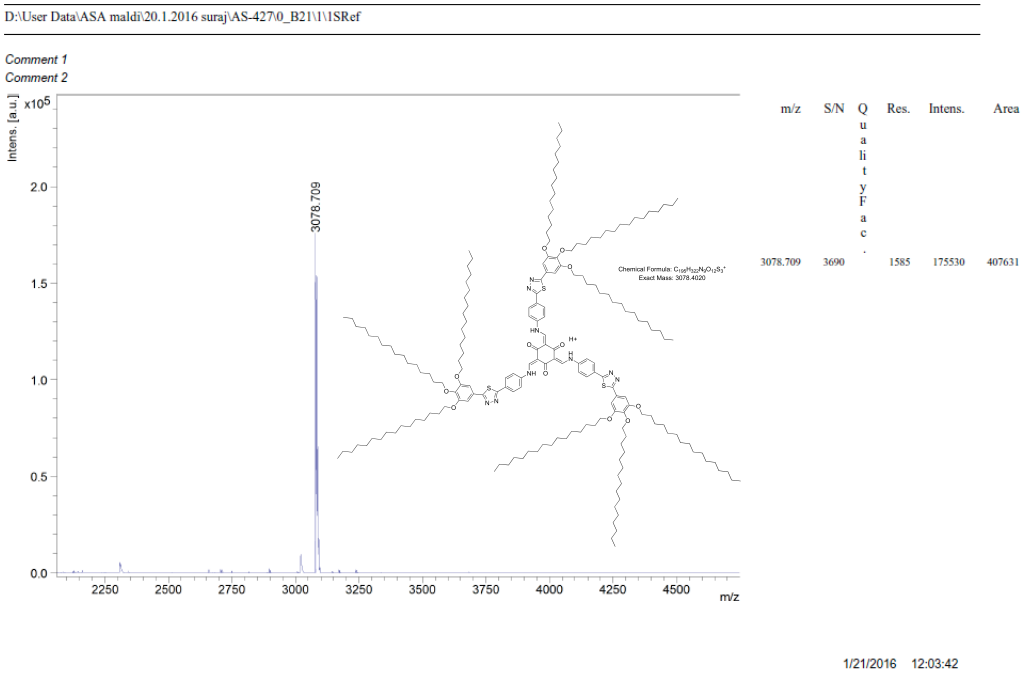
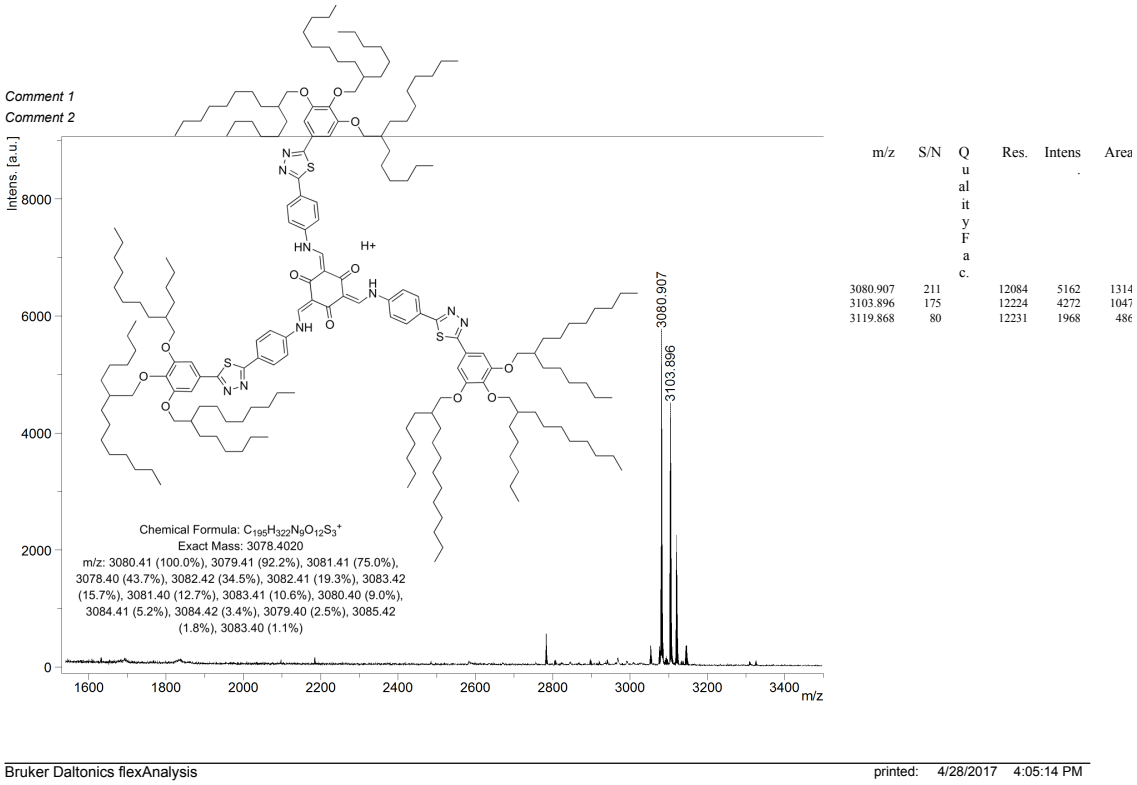
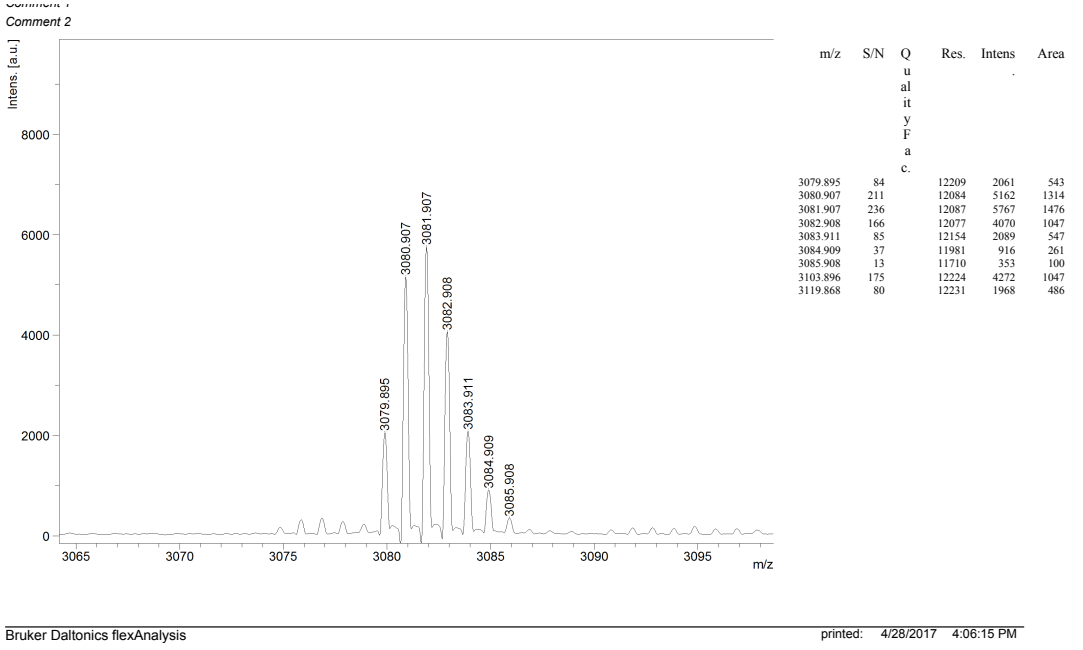


Figure S28. MALDI-TOF mass spectra of TSAN **T-16**



m/z	S/N	Quality Fac.	Res.	Intens.	Area
3080.907	211		12084	5162	1314
3103.896	175		12224	4272	1047
3119.868	80		12231	1968	486

Figure S29. MALDI-TOF mass spectra of TSAN **T-b16**



m/z	S/N	Quality Fac.	Res.	Intens.	Area
3079.895	84		12209	2061	543
3080.907	211		12084	5162	1314
3081.907	236		12087	5767	1476
3082.908	166		12077	4070	1047
3083.911	85		12154	2089	547
3084.909	37		11981	916	261
3085.908	13		11710	353	100
3103.896	175		12224	4272	1047
3119.868	80		12231	1968	486

Figure S30. Exapnded region of MALDI-TOF mass spectra of TSAN **T-b16**

5. References

1. C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao and S. K. Prasad, *J. Org. Chem.*, 2009, **74**, 3168–3171