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EFFICIENT AND STRAIGHFORWARD CLICK SYNTHESIS OF STRUCTURALLY RELATED DENDRITIC TRIAZOLES

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Contenido

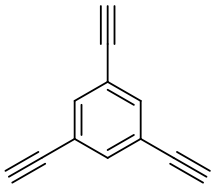
1 General Experimental Methods:

Melting points were taken on a Leitz Wetzlar Microscope Heating Stage, Model 350 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-300 spectrometer with Me_4Si as the internal standard and chloroform-*d* as solvent. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet expected but not resolved. The structure of the products were determined by a combination of spectroscopic methods such as IR, 1D and 2D NMR (including COSY, HSQC and HMBC experiments) and HRMS. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer using potassium bromide disk technique. Absorbance frequencies are recorded in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF Q II (Q-TOF), nebulizer pressure 0.4 Bar, dry gas 4.0 l/min at 180 ºC, source ESI positive mode, capillary voltaje 4500V, scan 50-1500 m/z or by ultraviolet matrix assisted laser desorption-ionization mass spectrometry (UV−MALDI MS) and by ultraviolet laser desorption-ionization mass spectrometry (UV−LDI MS) performed on the Bruker Ultraflex Daltonics TOF/TOF mass spectrometer Mass spectra were acquired in linear positive and negative ion modes. Stock solutions of samples were prepared in chloroform. External mass calibration was made using β-cyclodextrin (MW 1134) with nHo as matrix in positive and negative ion mode. Sample solutions were spotted on a MTP 384 target plate polished steel from Bruker Daltonics (Leipzig, Germany). For UV−MALDI MS matrix solution was prepared by dissolving GA (gentisic acid, 1 mg/mL) in water. For UV-LDI MS experiments two portions of analyte solution (0.5 μL × 2) were loaded on the probe and dried successively (two dry layers). Desorption/ Ionization was obtained by using the frequency-tripled Nd:YAG laser (355-nm). The laser power was adjusted to obtain high signal-to-noise ratio (S/N) while ensuring minimal fragmentation of the parent ion sand each mass spectrum was generated by averaging 100 lasers pulses per spot. Spectra were obtained and analyzed with the programs FlexControl and FlexAnalysis, respectively. Reactions were monitored by TLC on 0.25 mm E. Merck Silica Gel Plates (60F254), using UV light (254 nm) and 7% of phosphomolybdic acid in ethanol as developing agent. Flash column chromatography using E. Silica Gel 60H was performed by gradient elution of mixture of *n*-hexane and increasing volumes of dichloromethane. Reactions were run under an argon atmosphere with dry, freshly anhydrous distilled solvents, unless otherwise noted. Reagents as copper (I) bromide, triphenylamine, sodium azide, hydrazine monohydrate, carbazole, triphenylphosphine, K_2CO_3, copper-bronze, 18-crown-6, $Pd(PPh_3)_2Cl_2$, copper (I) iodide, trimethylsilylacetylene, Pd/C 10%, KI and KIO_3 were commercially available in standard quality and used as received. *Tert*-butyl chloride was prepared according reference.[1] Solvents were purified according to standard procedures.[2]

2 Synthetic Procedures and Characterization Data

2.1 Synthesis of cores

2.1.1 Synthesis of 1,3,5-triethynylbenzene (4)

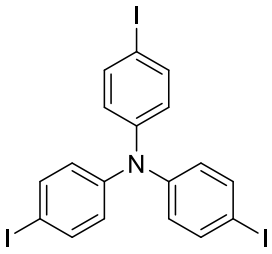


To a solution of commercial 1,3,5-tribromobenzene **11** (503.0 mg, 1.59 mmole) in dry triethylamine (9.0 mL) were added $Pd(PPh_3)Cl_2$ (36.1 mg, 0.05 mmole) and CuI (10.0 mg, 0.05 mmole) and the mixture was stirred for 15 minutes under argon atmosphere. Commercial TMSA (0.9 mL, 6.33 mmole) was added and the reaction was heated to 65°C and stirred for 16 hours. Hexane (25 mL) was added to the reaction mixture, and subjected to shot path column chromatography on silica gel. After evaporation of solvent, the residue was purified by column chromatography on silica gel eluted with hexane to give 583.0 mg (1.59 mmole, 100%) of 1,3,5-*tris*(trimethylsilylethynyl)benzene **11-TMS** as pale yellow solid. This product was dissolved in tetrahydrofuran (7.0 mL) and methanol (2.0 mL) and a solution of anhydrous potassium carbonate (26.9 mg in 0.4 mL of H_2O) was added and the mixture was stirred at room temperature for 6 h. Then water (12 mL) was added and the organic solvents were evaporated. The residue was extracted with dichloromethane, washed with water and brine, and dried over anhydrous sodium sulfate to give 220.8 mg (1.47 mmole, 92% in two steps) of **1** as white off solid. The ^{1}H NMR data are according to reference.[3]

^{1}H NMR: δ (300 MHz, $CDCl_3$): 3.10 (3H, s), 7.57 (3H, s, alkyne).

^{13}C NMR: δ (75.4 MHz, $CDCl_3$): 78.67, 81.59, 122.93, 135.64.

2.1.2 Synthesis of *tris* (4-iodophenyl) amine (16)

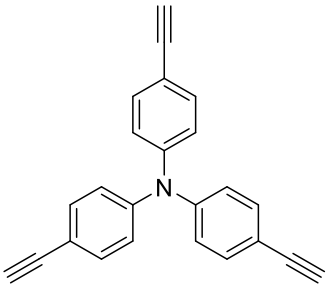


Triphenylamine **12** (1.00 g, 4.09 mmoles) was suspended in glacial acetic acid (30 mL). KI (1.49 g, 9.0 mmoles) and KIO_3 (0.97 g, 4.52 mmoles) were added and the mixture was heated to 110° C for 5 hours. The mixture was cooled in an ice-bath and the solid formed was filtered by suction and washed with water. This crude product was dissolved in dichloromethane (30 mL) and washed with H_2O (20 mL), 5%aqueous $NaHCO_3$ (2 x 20 mL) and brine (20 mL). the organic layer was treated with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford **16** as a light pink solid (948.2 mg, 1.52 mmoles, 37%). The obtained product was characterized by ^{1}H NMR in $CDCl_3$ and the data observed were according to reference.[4]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 6.81 (6H, d, *J* 8.8 Hz), 7.53 (6H, d, *J* 8.8 Hz).

2.1.3 Synthesis of *tris* (4-ethynylphenyl) amine (5)

In dried reflux equipment compound 16 (503.8 mg, 0.87 mmol), $Pd(PPh_3)_2Cl_2$ (56.3 mg, 0.08 mmol) and CuI (15.1 mg, 0.08 mmol) were charged and the system was purged with three vaccum-argon cycles. THF (6.5

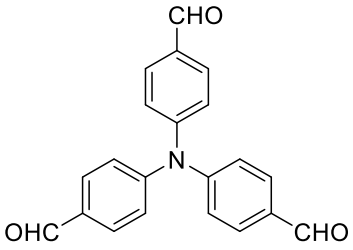


mL) was added and after 5 minutes, trimethylamine (1.5 mL) was added. The mixture was stirred for 10 minutes at room temperature and TMSA (0.6 mL, 4.25 mmol) was added and the mixture color turned black. The reaction was stirred 16 h at rt and then diluted with Et_2O and filtered over a Celite pad. Solvents were concentrated under reduced pressure and the crude product **17** was used in the next step without purification. Crude **17** was dissolved in a mixture of dichloromethane (9.0 mL) and methanol (9.0 mL) at rt under argon atmosphere. Anhydrous K_2CO_3 (242.5 mg, 1.75 mmol) was added and the resulting black suspension was stirred 2 h at rt. The reaction was diluted with H_2O (7 mL) and organic solvents were evaporated. This aqueous layer was extracted with dichloromethane (25 mL). Organic layer was separated and washed with brine (15 mL), treated with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by flash chromatography in SiO_2 (hexane/dichloromethane, 90/10) yielding **5** as a light yellow solid (193.5 mg, 70%, 2 steps).[5]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 3.06 (3H, s, alkyne), 7.01 (6H, d, *J* 8.7 Hz), 7.38 (6H, d, *J* 8.6 Hz).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 77.20 (C≡CH), 83.40 (C≡CH), 116.87, 123.94, 133.37.

2.1.4 Synthesis of *tris* (4-formylphenyl) amine 13

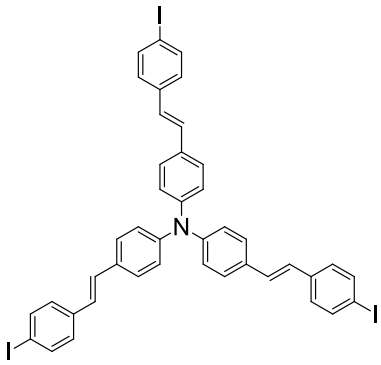


In dried reflux equipment adapted with an addition funnel was charged dried *N*,*N*-dimethylformamide (7.3 mL, 94.28 mmol) and cooled to 0° C in an ice bath. Phosphorous oxychloride (9.5 mL, 101.92 mmol) was added by the addition funnel in 30 minutes. The mixture was stirred 1 h at 0° C, triphenylamine **12** (1.01 g, 4.11 mmol) was added and the reaction was stirred at 95° C for 4 hours. After cooling to rt, the reaction mixture was poured into ice-water (200 mL) and basified to pH 8-9 with NaOH 3N (185 mL). Water layer was extracted with dichloromethane (200 mL), the organic phase was washed with H_2O (3 x 50 mL), treated with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by flash chromatography (hexane/dichloroethane, 50/50) affording *tris*-formyl derivative **13** (215.4 mg, 0.65 mmol) and *bis*-formyl derivative (379.7 mg, 1.26 mmol). This last compound was submitted to formylation with and ice-cooled mixture of *N*,*N*-dimethylformamide (2.3 mL, 29.70 mmol) and phosphorous oxychloride (3.01 mL, 32.29 mol) and stirred at 95° C for 2 hours. After cooling to rt, the reaction mixture was poured into ice-H_2O (100 mL) and basified with NaOH 3N (59 mL). Aqueous layer was extracted with dichloromethane (100 mL) and the organic phase was washed with H_2O (3 x 20 mL), treated anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by flash chromatography (hexane/dichloromethane, 50/50) affording **13** as light yellow solid (315.8 mg, 0.96 mmol, 76%). Overall yield of **13**: 531.2 mg, 1.61 mmol, 39%. Bi- and *tris*-formyl derivatives were characterized by ^{1}H and ^{13}C NMR and the data collected were in according to ref.[6]

Bis-formyl triphenyalmine: ^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.12 – 7.21 (6H, m), 7.21 – 7.29 (1H, m), 7.38 (2H, dd, *J*1 = *J*2 7.7 Hz), 7.76 (4H, d, *J* 8.6 Hz). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 122.76, 126.27, 127.07, 130.16, 131.28, 131.31, 145.50, 152.00, 190.51 (CHO).

Tris-formyl triphenyalmine **13**: ^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.23 (6H, d, *J* 8.6 Hz), 7.81 (6H, d, *J* 8.6 Hz), 9.90 (3H, s, CHO). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 124.54, 131.48, 132.56, 151.18, 190.49 (CHO).

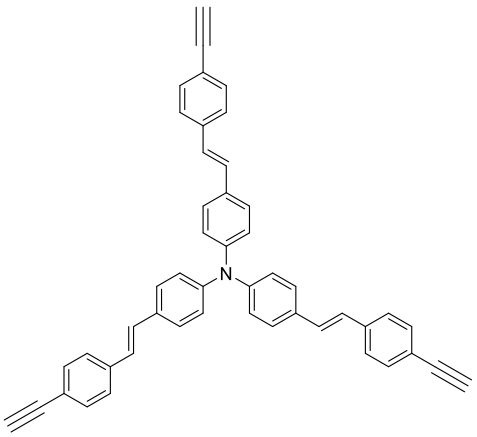
2.1.5 Synthesis of compound 15



Dimethyl 4-iodobenzylphosphonate (609.7 mg, 1.87 mmol)[3] and *tris*(4-formylphenyl)amine **13** (150.7 mg, 0.46 mmol) were dissolved in 30 mL of dry THF. After the reaction mixture was heated to reflux, solid potassium *tert*-butoxide (286.3 mg, 2.55 mmol) was added in portions. The mixture was further refluxed under dry argon for 2 hours. The resulting dark green mixture was diluted of dichloromethane (100 mL) and of H_2O (100 mL). The phases were separated and the organic one was washed H_2O (3 x 40 mL), dried over anhydrous Na_2SO_4, filtered and solvents concentrated under reduced pressure. Crude product was purified by flash chromatrography (hexane/dichloromethane, 80/20) yielding **15** as light yellow solid (381.6 mg, 0.41 mmol, 89%). ^{1}H NMR spectrum were in according with our previous published data.[3]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 6.92 (3H, d, *J* 16.3 Hz, vinylic), 7.07 (3H, d, *J* 16.1 Hz, vinylic), 7.10 (6H, d, *J* 8.5 Hz), 7.23 (6H, d, *J* 8.3 Hz), 7.41 (6H, d, *J* 8.6 Hz), 7.67 (6H, d, *J* 8.3 Hz).

2.1.6 Synthesis of *tris*-ethynyl derivative 6



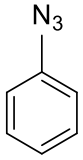
In dried reflux equipment compound **15** (381.6 mg, 0.41 mmol), $Pd(PPh_3)_2Cl_2$ (15.9 mg, 0.01 mmol) and CuI (15.0 mg, 0.08 mmol) were charged and the system was purged with three vaccum-argon cycles. Toluene (35 mL) was added and after 5 minutes, trimethylamine (35 mL) was added. The mixture was stirred for 10 minutes at room temperature and TMSA (0.35 mL, 2.48 mmol) was added and the mixture color turned orange. The reaction was stirred 16 h at 70° C and then solvents were concentrated under reduced pressure. Crude product was diluted with hexane and filtered over a pad of SiO_2. Crude TMS derivative was used in the next step without purification. Crude TMS-product was dissolved in a mixture of dichloromethane (5.0 mL) and methanol (5.0 mL) at rt under argon atmosphere. Anhydrous K_2CO_3 (121.7 mg, 0.88 mmol) was added and the resulting yellow suspension was stirred 2 h at rt. The reaction was diluted with H_2O (20 mL) and organic solvents were evaporated. This aqueous layer was

extracted with dichloromethane (2 x 50 mL). Combined organic layer was separated and washed with brine (15 mL), treated with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by flash chromatography in SiO_2 (hexane/dichloromethane, 80/20) yielding **6** as a light yellow solid (260.4 mg, 100%, 2 steps).

Mp: 132 – 133°C (dichloromethane/hexane). IR: 548, 831 (Ph), 962, 1277, 1501, 1589 (Ph), 2102 (C≡C), 3287 (C≡H) cm^{-1}. ^1H NMR: δ (300 MHz, $CDCl_3$, TMS): 3.13 (3H, s, alkyne), 6.99 (3H, d, *J* 16.3 Hz, vinylic), 7.10 (3H, d, *J* 16.5 Hz, vinylic), 7.11 (6H, d, *J* 8.5 Hz, 2-H), 7.42 (6H, d, *J* 8.6 Hz, 3-H), 7.44 – 7.48 (12H, m, 8-H, 9-H). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 77.89 (C≡CH), 83.82 (C≡CH), 120.77 (C-10), 124.31 (C-2), 126.19 (C-8), 126.60 (C-6 vinylic), 127.67 (C-3), 129.19 (C-5 vinylic), 131.96 (C-4), 132.48 (C-9), 138.02 (C-7), 146.84 (C-1). MS (DI): m/z 623 (M^+).

2.2 Synthesis of dendrons:

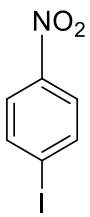
2.2.1 Synthesis of phenyl azide (7)



In a two-neck round-bottom flask were charged ice (50.0 g), concentrated HCl (24.0 mL), H_2O (24.0 mL) and freshly distilled aniline **18** (4.9 mL, 54.0 mmol) and the mixture was cooled in an ice-bath. A solution of $NaNO_2$ (4.08 g, 59.1 mmol) in H_2O (20 mL) was slowly added so the temperature was less than 10° C. the orange solution was left to stir for 10 minutes at 0° C. a solution of NaN_3 (3.86 g, 594 mmol) in H_2O (10 mL) was added (maximum temperature 10° C), the color disappeared and evolution of gases was observed. The reaction was left 10 minutes at 0° C and then 2 h at rt. The mixture was extracted with Et_2O (3 x 40 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na_2SO_4, filtered and the solvents were concentrated under reduced pressure. The resulting crude product was protected from light. Crude **7** was obtained as a light brown oil (6.4 g, 100%). 1H NMR spectrum was according to reference.[7]

^1H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.06 (2H, dd, *J* 8.7, *J* 1.1 Hz), 7.17 (1H, dd, *J1 = J2* 7.4 Hz), 7.38 (2H, ddd, *J* 8.2, *J* 7.5, *J* 1.7 Hz).

2.2.2 Synthesis of 4-nitro-1-iodobenzene



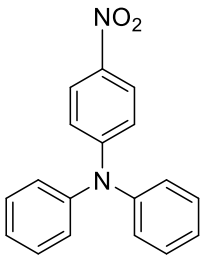
In a two-neck round-bottom flask concentrated HNO_3 (15.0 mL) was cooled in an ice-salt and concentrated H_2SO_4 was added slowly by an addition funnel so temperature was below 20° C. After cooling again to 0° C, iodobenzene (1.65 mL, 14.7 mmol) was slowly added. Blue color of reaction mixture was observed after each aliquot of iodobenzene. When the addition was completed the reaction was left at rt for 30 minutes and a yellow solid appeared. The reaction mixture was poured into an ice-water bath and the solid formed was filtered and washed with H_2O. Crude product was dissolved in dichloromethane (50.0 mL) and basified with saturated aqueous $NaHCO_3$ until pH 8-9. Organic layer was treated with anhydrous Na_2SO_4, filtered and solvents were concentrated under reduced pressure affording

crude **4-nitro-1-iodobenzene** (2.80 g) as a yellow solid). Crude solid was crystallized in ethanol (50.0 mL) yielding crystalline product (1.67 g, 46%) as yellow solid. ^{1}H and ^{13}C NMR data are according to reference.[8]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.88 - 7.97 (4H, m).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 102.65 (C-I), 124.85, 138.67, 147.89 (C-NO_2).

2.2.3 Synthesis of nitro-triphenylamine (19)

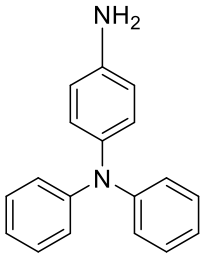


In a reflux equipment was charged commercial triphenyalmine **12** (505.3 mg, 2.07 mmol) in a mixture of glacial acetic acid (18 mL) and chloroform (6 mL). $NaNO_3$ (171.6 mg, 2.02 mmol) was added and the reaction mixture was stirred at 90° C for 2 hs. After cooling to rt the mixture was diluted with H_2O (50 mL) and extracted with dichloromethane (50 mL). Organic layer was washed with 5% aqueous $NaHCO_3$ (3 x 25 mL), brine (25 mL), treated with anhydrous Na_2SO_4, filtered and solvent concentrated under reduced pressure. Crude oily compound **19** was crystallized from ethanol:H_2O (25mL, 1:1) affording **19** as crystalline yellow solid (586.0 mg, 2.02 mmol, 100%). ^{1}H and ^{13}C NMR data are according to reference.[9]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 6.92 (2H, d, *J* 9.3 Hz, 3-H), 7.16 – 7.24 (6H, m, 5-H, 7-H), 7.37 (4H, dd, *J1 = J2* 7.7 Hz, 6-H), 8.04 (2H, d, *J* 9.3 Hz, 2-H).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 118.14 (C-3), 125.46 (C-2), 125.73 (C-8), 126.52 (C-6), 129.92 (C-7), 140.17 (C-NO_2), 145.66 (C-5), 153.48 (C-4).

2.2.4 Synthesis of amino-triphenylamine (20)



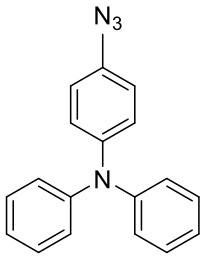
In a reflux equipment was charged compound **19** (598.0 mg, 2.06 mmol) and Pd/C 10% (29.7 mg) in anhydrous ethanol (5.0 mL) and the mixture was refluxed. Hydrazine monohydrate (0.62 mL) was added dropwise to the hot solution. The reaction was refluxed for 2 hs. Hot reaction was filtered over a Celite pad washing with dichloromethane. The filtrate was dried with anhydrous Na_2SO_4, filtered and solvents concentrated under reduced pressure. Crude amine **20** was crystallized from ethanol:H_2O affording **20** as crystalline gray solid (465.2 mg, 1.79 mmol, 87%). ^{1}H and ^{13}C NMR data are according to reference.[10]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 3.60 (2H,bs, NH_2), 6.65 (2H, d, *J* 8.7 Hz, 2-H), 6.90 (2H, d, *J* 7.3 Hz, 8-H), 6.96 (2H, d, *J* 8.7 Hz, 3-H), 7.03 (4H, d, *J* 7.6 Hz, 6-H), 7.20 (4H, dd, *J1 = J2* 7.9 Hz, 7-H).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 116.18 (C-2), 121.46 (C-8), 122.52 (C-6), 127.84 (C-3), 128.97 (C-7), 138.95 (C-4), 143.01 (C-NH_2), 148.27 (C-5).

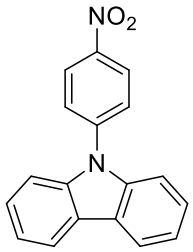
2.2.5 Synthesis of triphenylamine-azide (8)

In a two-neck round-bottom flask was suspended amine **20** (460.0 mg, 1.77 mmol) in a mixture of concentrated HCl (0.37 mL) and H_2O (5 mL) and cooled to 0° C in an ice-bath. A solution of $NaNO_2$ (134.54



mg, 1.95 mml) in H_2O (2 mL) was slowly added and the mixture turned dark red. After stirring 15 minutes at 0° C, a solution of NaN_3 (142.4 mg, 2.19 mmol) in H_2O (2 mL) was added and the decolored mixture was stirred at 0° C for 1 h. The reaction mixture was extracted with dichloromethane and washed with H_2O. Organic layer was dried with anhydrous Na_2SO_4, filtered and solvent concentrated under reduce pressure protected from light yielding azide **8** as a brown solid (498.5 mg, 1.74mmol, 98%). ^1H and ^{13}C NMR data are according to reference.[11] IR (KBr, film): 754, 1275 (azide), 1587, 2122 (azide), 2913 cm^{-1}. ^1H NMR: δ (300 MHz, $CDCl_3$, TMS): 6.91 (2H, d, *J* 9.1 Hz, 2-H), 6.98 – 7.07 (6H, m, 6-H, 8-H), 7.08 (2H, d, *J* 8.8 Hz, 3-H), 7.25 (4H, dd, *J* 8.5, *J* 7.4 Hz, 7-H). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 119.89 (C-2), 122.86 (C-8), 123.96 (C-6), 125.56 (C-3), 129.30 (C-7), 134.12 (C-N_3), 145.01 (C-4), 147.62 (C-5).

2.2.6 Synthesis of N-(4-nitrophenyl) carbazole (22a)

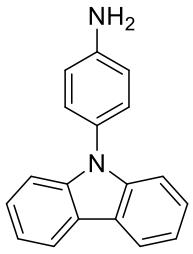


In a reflux equipment was charged commercial carbazole **21a** (505.2 mg, 3.02 mmol), **4-nitro-1-iodobenzene** (905.9 mg, 3.64 mmol), anhydrous K_2CO_3 (521.6 mg, 3.77 mmol) and cooper-bronze (21.3 mg) in anhydrous nitrobenzene (25 mL). The resulting mixture was purged by 3 cycles vaccumm-argon and then refluxed for 48 h. After cooling to rt, the reaction was filtered over a Celite pad, washing with chloroform. Filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash chromatography **22a** as slightly impure solid (1.01 g). This compound was crystallized in AcOEt (14 mL) yielding **22a** as a bright yellow solid (705.6 mg, 2.45 mmol, 81%). ^1H and ^{13}C NMR data are according to reference.[12]

^1H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.35 (2H, ddd, *J1 = J2* 7.9, *Jw* 1.3 Hz, 8-H), 7.45 (2H, ddd, *J1 = J2* 8.1, *Jw* 1.2 Hz, 7-H), 7.50 (2H, d, *J* 8.0 Hz, 6-H), 7.81 (2H, d, *J* 9.0 Hz, 3-H), 8.15 (2H, bd, *J* 7.7 Hz, 9-H), 8.49 2H, (d, *J* 9.0 Hz, 2-H).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 109.61 (C-6), 120.64 (C-9), 121.21 (C-8), 124.18 (C-10), 125.55 (C-2), 126.48 (C-7), 126.76 (C-3), 139.86 (C-5), 143.87(C-4), 145.84 (C-NO_2).

2.2.7 Synthesis of N-(4-aminophenyl) carbazole (23a)

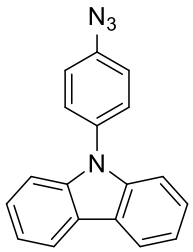


Compound **22a** was reduced in the same conditions as **20** affording **23a** as a light yellow solid (632.9 mg, 2.45 mmol, 100%). Crude **23a** was sufficiently pure and it was used in the next step without further purification. ^1H and ^{13}C NMR data are according to reference.[13]

^1H NMR: δ (300 MHz, $CDCl_3$, TMS): 3.85 (2H, bs, NH_2), 6.87 (2H, d, *J* 8.6, 2-H), 7.26 (2H, dd, *J* 8.4, *J* 7.0 Hz, 8-H), 7.30 (2H, d, *J* 8.5 Hz, 3-H), 7.32 (2H, d, *J* 8.4 Hz, 6-H), 7.40 (2H, ddd, *J* 8.2, *J* 6.9, *Jw* 1.2 Hz, 7-H), 8.14 (2H, bd, *J* 7.7 Hz, 9-H).

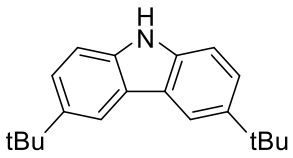
^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 109.78 (C-6), 115.91 (C-2), 119.42 (C-8), 120.18 (C-9), 122.98 (C-10), 125.72 (C-7), 128.20 (C-4), 128.53 (C-3), 141.52(C-5), 145.95 (C-NH_2).

2.2.8 Synthesis of N-(4-azidophenyl) carbazole (9)



Compound **23a** (632.9 mg, 2.45 mmol) was suspended in 6 M HCl/ THF (9:1, 25 mL) and cooled in an ice-salt bath. $NaNO_2$ (203.7 mg, 3.03 mmol) was added portion wise so temperature was less than 10° C. Bright orange mixture was stirred at 0° C for 2 h. A solution of NaN_3 (320.1 mg, 4.92 mmol) in H_2O (3 mL) was added under good stirring. Subsequently, a solution of NaOAc.3 H_2O (18.1 g) in H_2O (22 mL) and additional THF (9 mL) were added and the reaction mixture was stirred overnight at rt. The mixture was extracted with EtOAc (2 x 50 mL) and combined organic layers were washed with water (3 x 20 mL). resulting organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure yielding **9** as a light yellow solid (690.5 mg, 2.43 mmol, 99%). ^{1}H and ^{13}C NMR data are according to reference.[14] IR (KBr disk): 754, 831, 1290 (azide), 1450, 1508, 2116 (azide) cm^{-1}. ^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.26 (2H, d, *J* 8.8 Hz, 2-H), 7.29 (2H, ddd, *J1 = J2* 7.9, *Jw* 1.3 Hz, 8-H), 7.35 (2H, d, *J* 7.6 Hz, 6-H), 7.42 (2H, ddd, *J* 8.2, *J* 6.9, *Jw* 1.2 Hz, 7-H), 7.56 (2H, d, *J* 8.8 Hz, 3-H), 8.15 (2H, bd, *J* 7.8 Hz, 9-H). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 109.55 (C-6), 120.06 (C-8), 120.37 (C-2), 120.43 (C-9), 123.37 (C-10), 126.02 (C-7), 128.62 (C-3), 134.44 (C-4), 139.21(C-N_3), 140.88 (C-5).

2.2.9 Synthesis of 3,6-di-*tert*-butyl carbazole (21b)

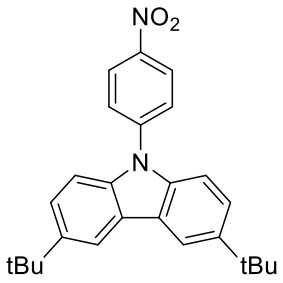


In a dried round-bottom flask were charge commercial carbazole **21a** (2.51g, 15.0 mmol), anhydrous $AlCl_3$ (2.01 g, 15.0 mmol) and anhydrous dichloromethane (60 mL). The suspension was cooled to 0° C in an ice-bath and a solution of *tert*-butyl chloride (3.9 mL, 35.6 mmol) in anhydrous dichloromethane (10 mL) was added by a dropping funnel. After 15 minutes at 0° C the reaction was stirred for 24 h at rt. The brown solutions was diluted with dichloromethane (100 mL) and poured into ice-H_2O (200 mL). Phases were separated and the organic one was washed 5% aqueous $NaHCO_3$ until neutral pH (2 x 20 mL). Aqueous layer was extracted with dichloromethane and combined organic layers were washed with brine (30 mL). Organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford crude **21b** as a white solid. Crystallization from petroleum ether (50 mL) yielding crystalline **21b** (2.57 g, 9.21 mmol, 61%). ^{1}H NMR data is according to reference.[15]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 7.33 (2H, d, *J* 8.5 Hz, 1-H, 8-H), 7.47 (2H, dd, *J* 8.5, *J* 1.8 Hz, 2-H, 7-H), 7.83 (1H, bs, NH), 8.08 (2H, d, *J* 1.3 Hz, 4-H, 5-H5).

2.2.10 Synthesis of *N*-(4-nitrophenyl) 3,6-di-*tert*-butyl carbazole (22b)

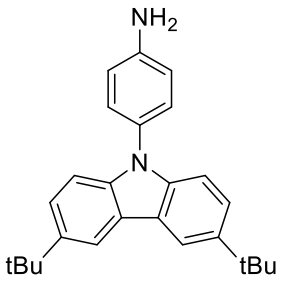
Compound **22b** was obtained according the synthetic procedure applied for **22a** starting from 3,6-di-*tert*-butyl carbazole **21b** (500.0 mg, 1.79 mmol). Yield: 459.0 mg (1.15 mmol, 64%) as yellow solid. ^{1}H and ^{13}C NMR data are according to reference.[12]



^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 1.47 (18H, s, ^{t}Bu), 7.45 (2H, d, *J* 8.7 Hz, 6-H), 7.50 (2H, dd, *J* 8.7, *Jw* 1.8 Hz, 7-H), 7.79 (2H, d, *J* 9.0 Hz, 3-H), 8.14 (2H, d, *Jw* 1.8 Hz, 9-H), 8.46 (2H, d, *J* 9.0 Hz, 2-H).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 31.92 (CH_3), 34.81 ($\underline{C}Me_3$), 109.18 (C-6), 116.59 (C-9), 124.12 (C-7), 124.29 (C-10), 125.50 (C-2), 126.02 (C-3), 138.14 (C-5), 144.38 (C-4, C-8), 145.31($\underline{C}$-NO_2).

2.2.11 Synthesis of *N*-(4-aminophenyl) 3,6-di-*tert*-butyl carbazole (23b)

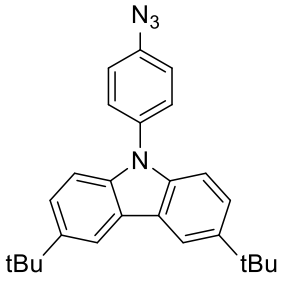


Compound **23b** was obtained according the synthetic procedure applied for **22b** starting from **22b** (408.9 mg, 1.02 mmol). Yield: 343.0 mg (0.93 mmol, 91%) as light yellow solid. ^{1}H and ^{13}C NMR data are according to reference.[12]

^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 1.46 (18H, s, CH_3), 3.84 (2H, bs, NH_2), 6.85 (2H, d, *J* 8.8 Hz, 2-H), 7.24 (2H, d, *J* 8.6 Hz, 6-H), 7.28 (2H, d, *J* 8.7 Hz, 3-H), 7.44 (2H, dd, *J* 8.6, *Jw* 1.9 Hz, 7-H), 8.12 (2H, d, *Jw* 1.7 Hz, 9-H).

^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 32.05 (CH_3), 34.70 (CMe_3), 109.13 (C-6), 115.87 (C-2), 116.09 (C-9), 122.90 (C-10), 123.38 (C-7), 128.27 (C-3), 128.78 (C-4), 139.92 (C-5), 142.24(C-8), 145.58 ($\underline{C}$-NH_2).

2.2.12 Synthesis of *N*-(4-azidophenyl) 3,6-di-*tert*-butyl carbazole (10)



Compound **10** was obtained according the synthetic procedure applied for **9** starting from **23b** (345.7 mg, 0.93 mmol). Yield: 395.3 mg (0.93 mmol, 100%) as light yellow solid. ^{1}H and ^{13}C NMR data are according to reference.[16] IR (KBr disk): 810, 1292 (azide), 1508, 2126 (azide), 2960 (C-H alkane) cm^{-1}. ^{1}H NMR: δ (300 MHz, $CDCl_3$, TMS): 1.47 (18H, s, CH_3), 7.24 (2H, d, *J* 8.8 Hz, 2-H), 7.29 (2H, d, *J* 8.7 Hz, 6-H), 7.46 (2H, dd, *J* 8.7, *Jw* 1.8 Hz, 7-H), 7.54 (2H, d, *J* 8.6 Hz, 3-H), 8.14 (2H, d, *Jw* 1.9 Hz, 9-H). ^{13}C NMR: δ (75 MHz, $CDCl_3$, TMS): 32.01 (CH_3), 34.74 (CMe_3), 108.97 (C-6), 116.30 (C-9), 120.33 (C-2), 123.35 (C-10), 123.67 (C-7), 128.26 (C-3), 134.97 (C-4), 138.66 ($\underline{C}$-N_3), 139.24(C-5), 143.01 (C-8).

3 NMR SPECTRA

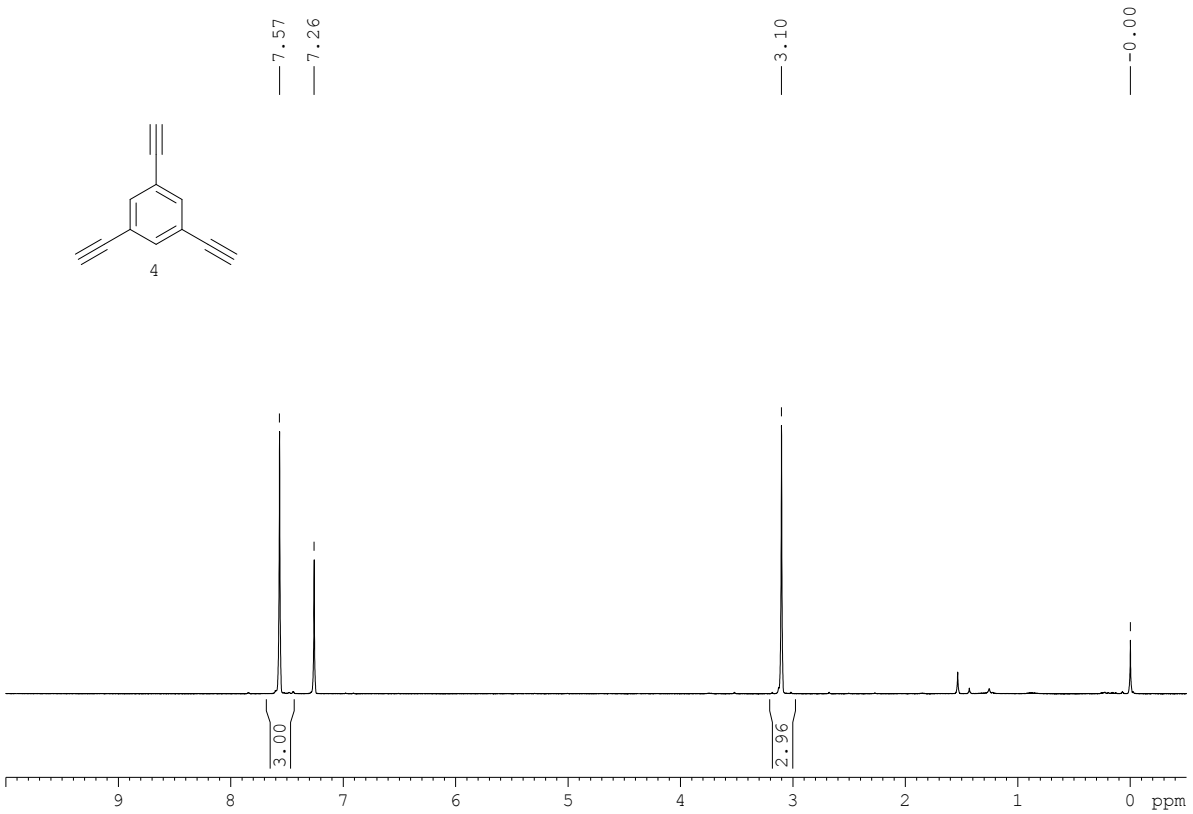


Figure S1: ^{1}H NMR (300 MHz) of triethynylbenzene **4** in $CDCl_3$

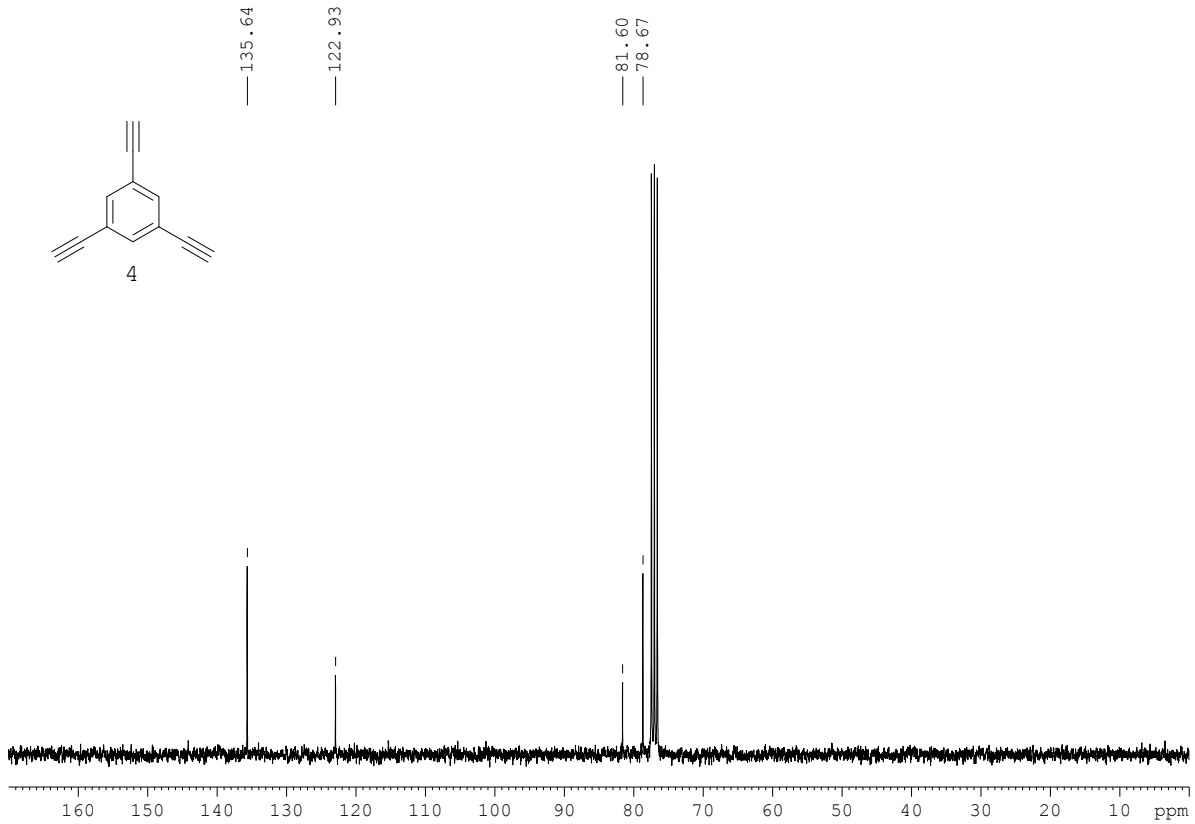


Figure S2: ^{13}C NMR(75.4 MHz) of triethynylbenzene **4** in $CDCl_3$

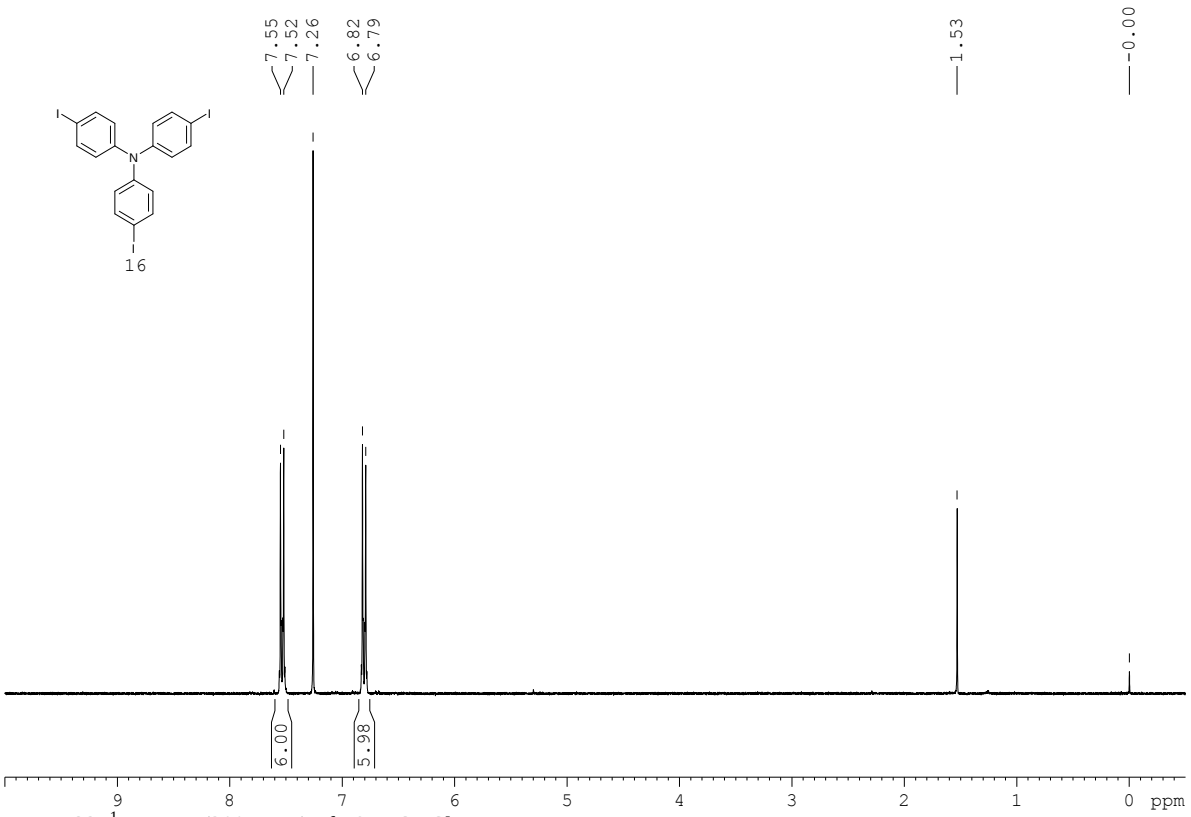


Figure S3: ^{1}H NMR (300 MHz) of **16** in $CDCl_3$

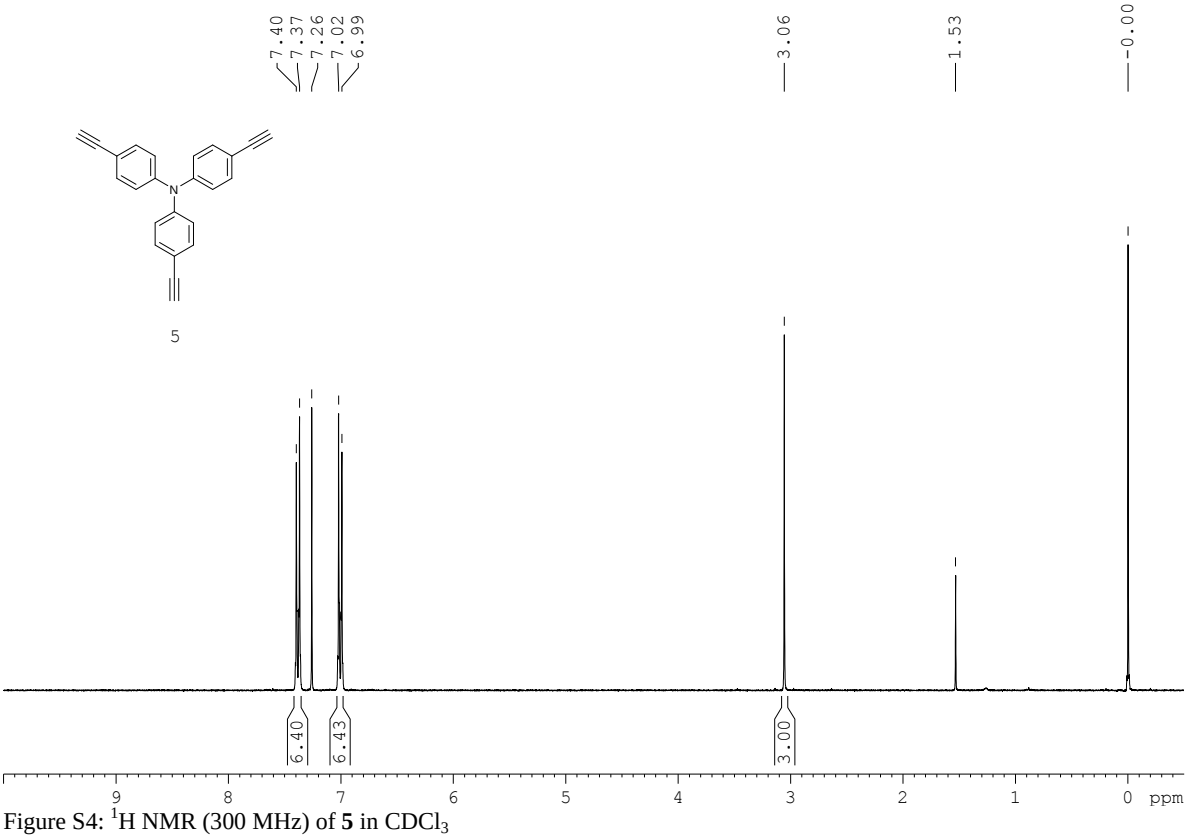


Figure S4: ^{1}H NMR (300 MHz) of **5** in $CDCl_3$

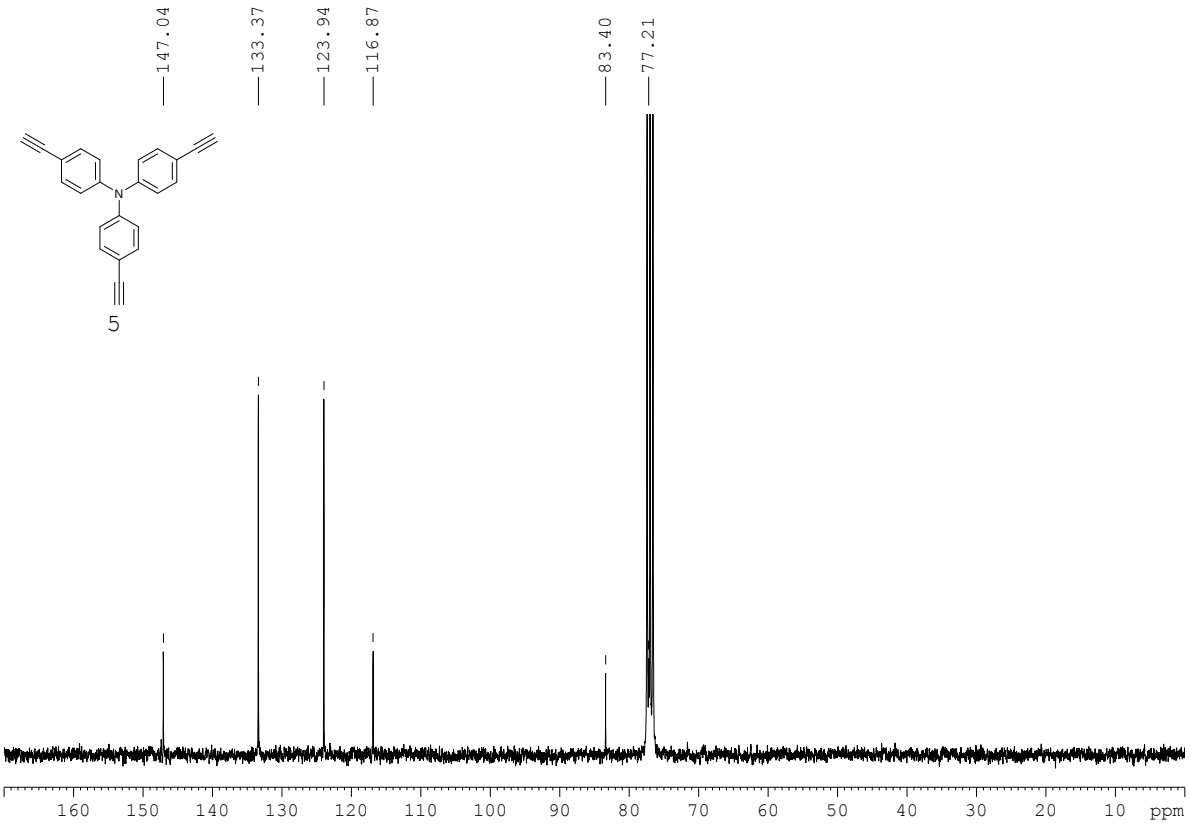


Figure S5: ^{13}C NMR (75.4 MHz) of **5** in $CDCl_3$

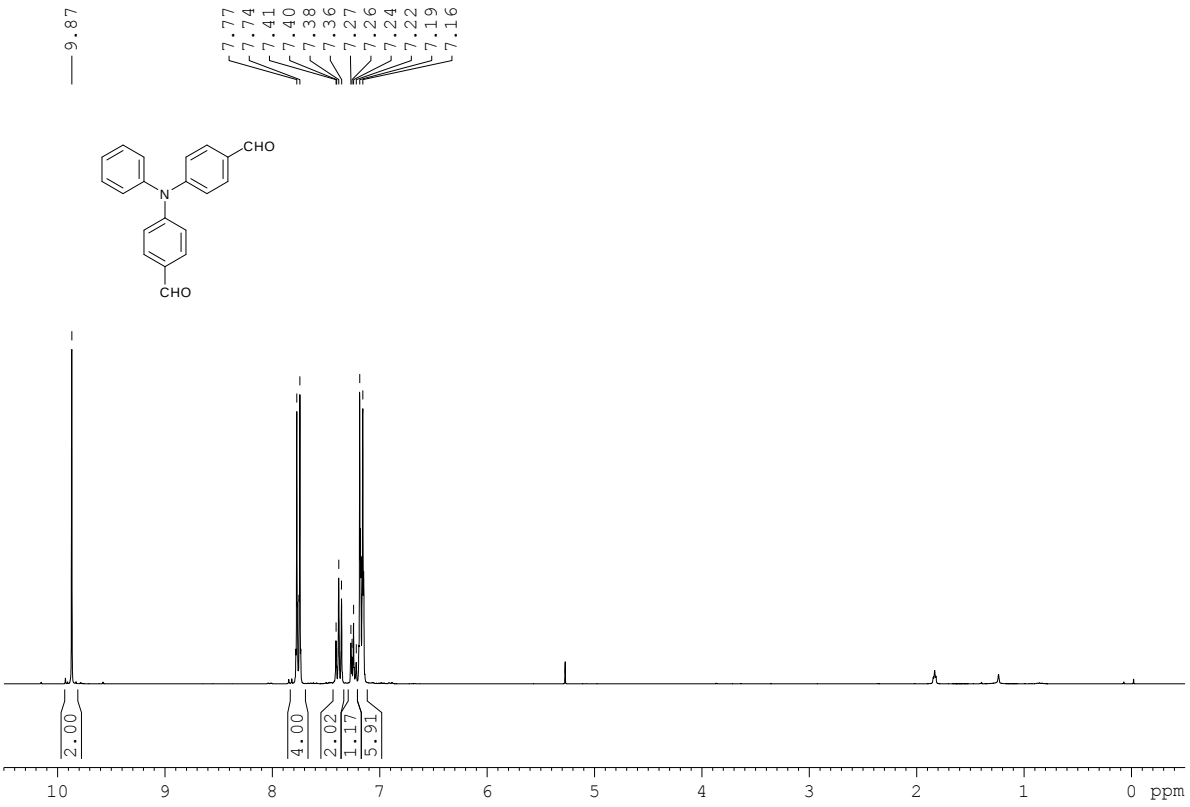


Figure S6: ^{1}H NMR (300 MHz) of **4,4'-bisformyl triphenylamine** in $CDCl_3$

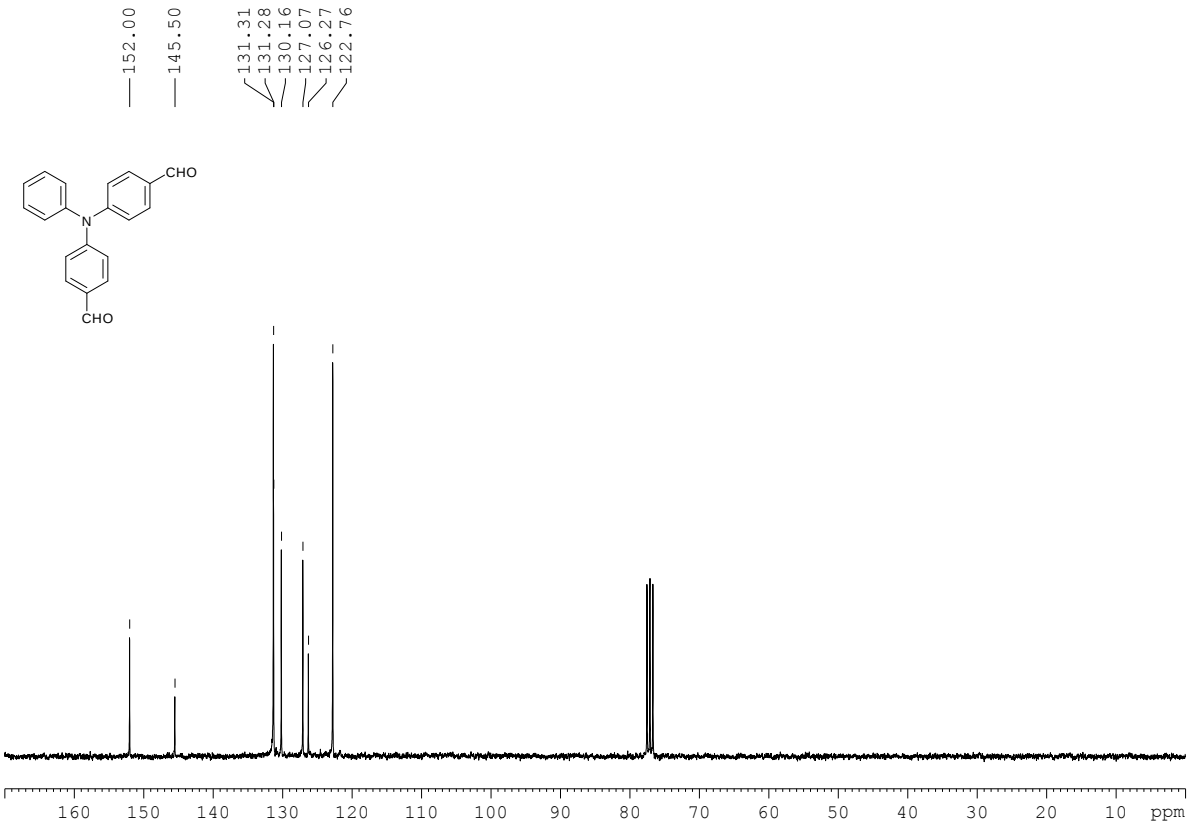


Figure S7: ^{13}C NMR (75.4 MHz) of **4,4'-bisformyl triphenylamine** in $CDCl_3$

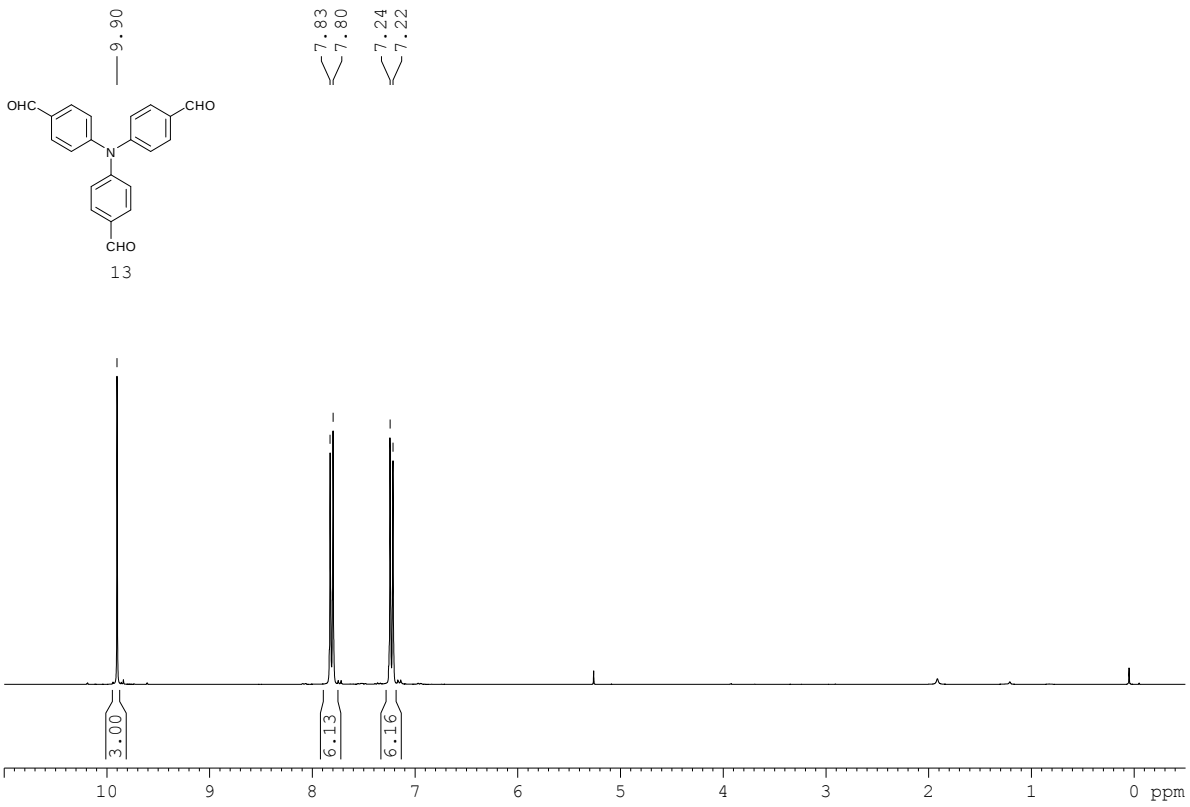


Figure S8: ^{1}H NMR (300 MHz) of **13** in $CDCl_3$

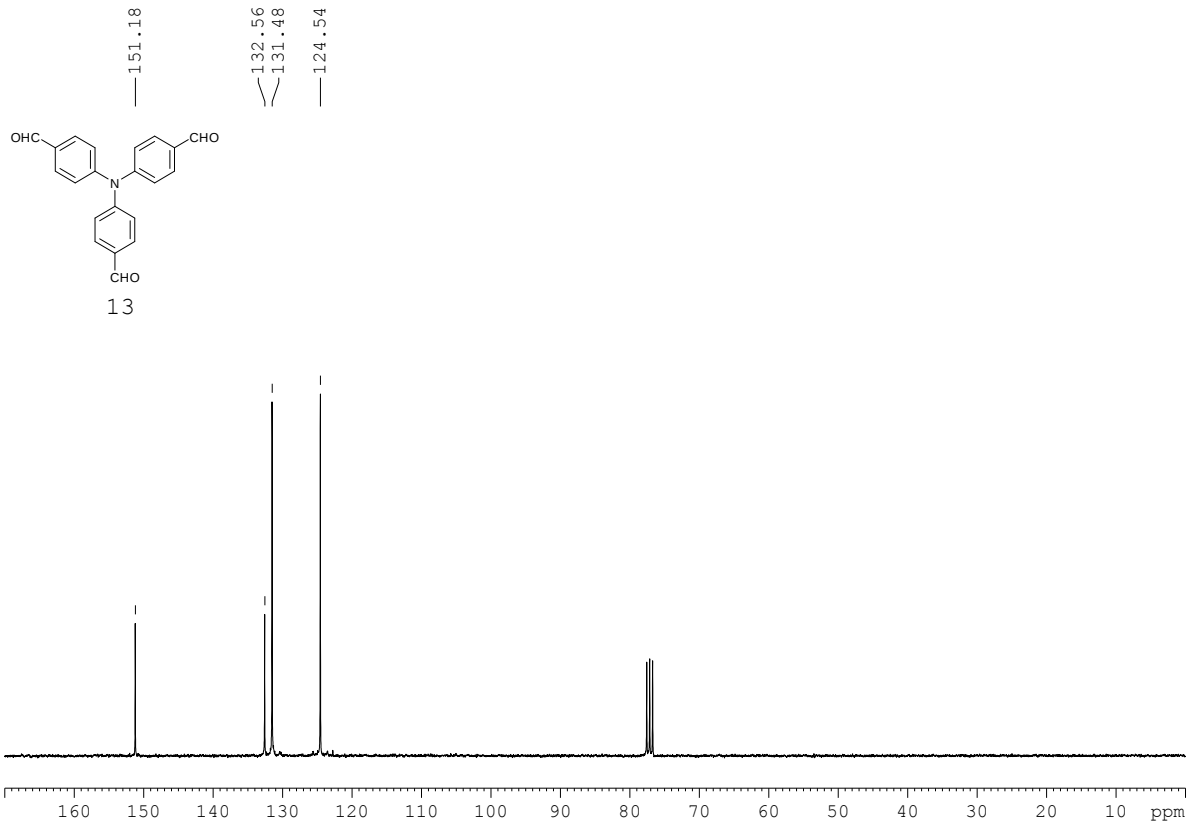


Figure S9: ^{13}C NMR (75.4 MHz) of **13** in $CDCl_3$

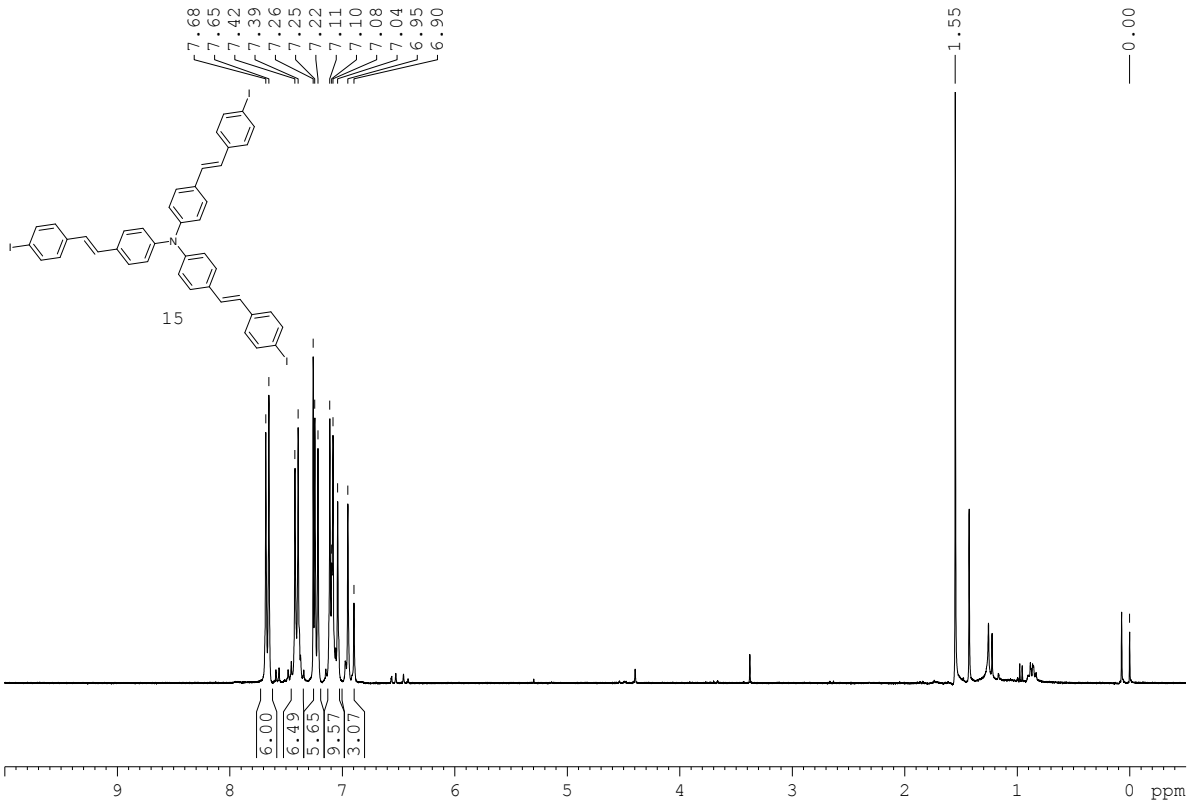


Figure S10: ^{1}H NMR (300 MHz) of **15** in $CDCl_3$

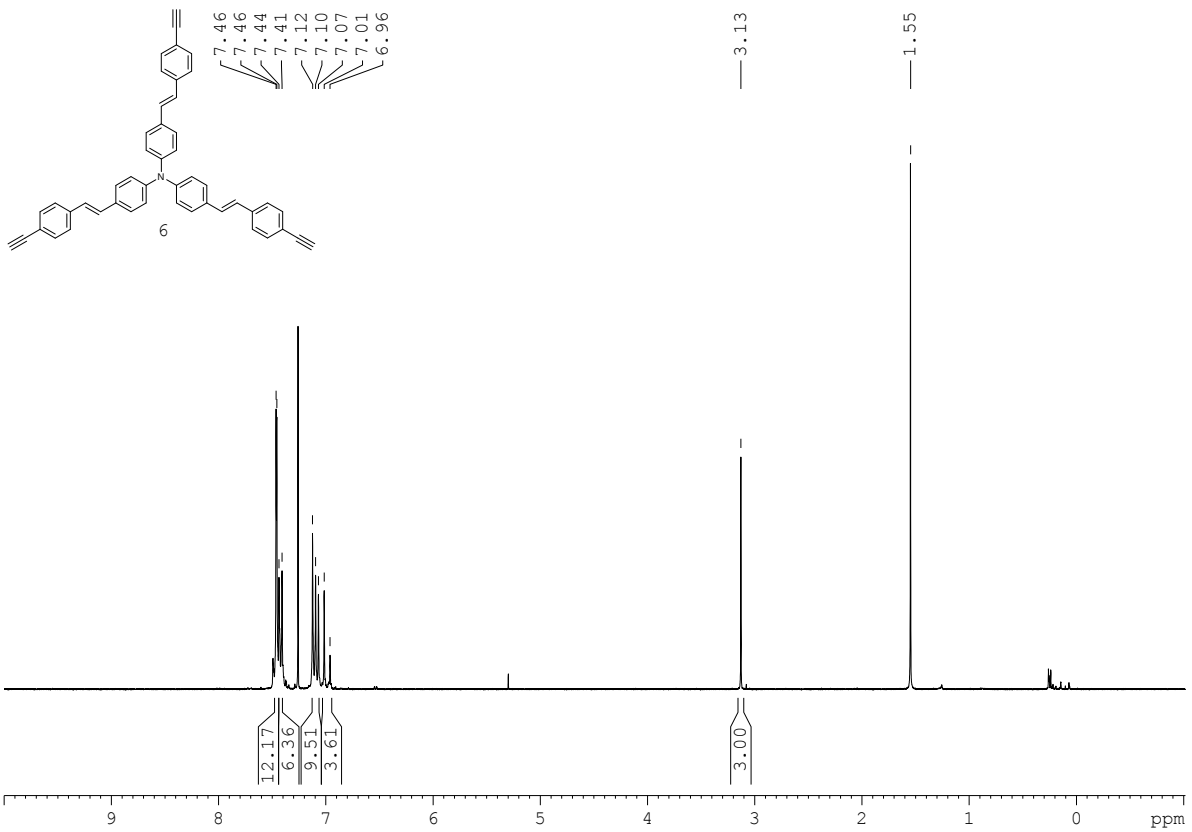


Figure S11: ^{1}H NMR (300 MHz) of **6** in $CDCl_3$

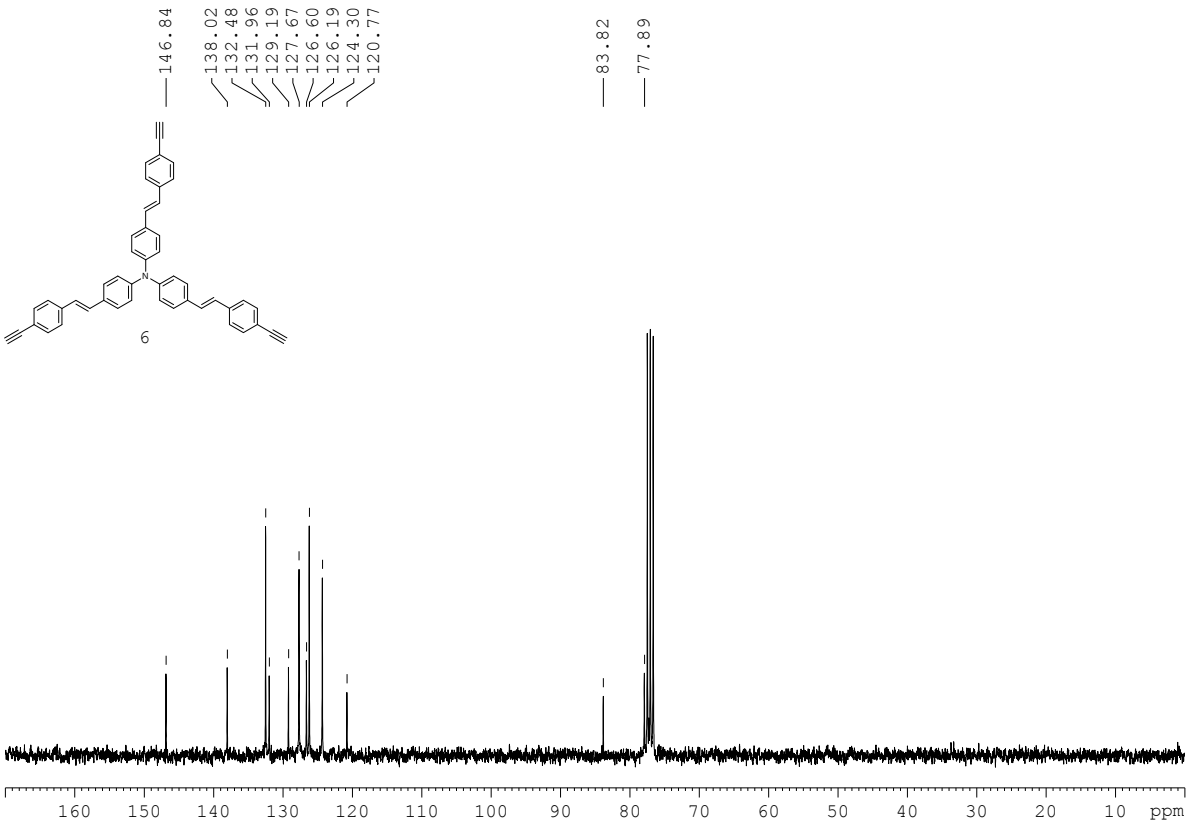


Figure S12: ^{13}C NMR (75.4 MHz) of **6** in $CDCl_3$

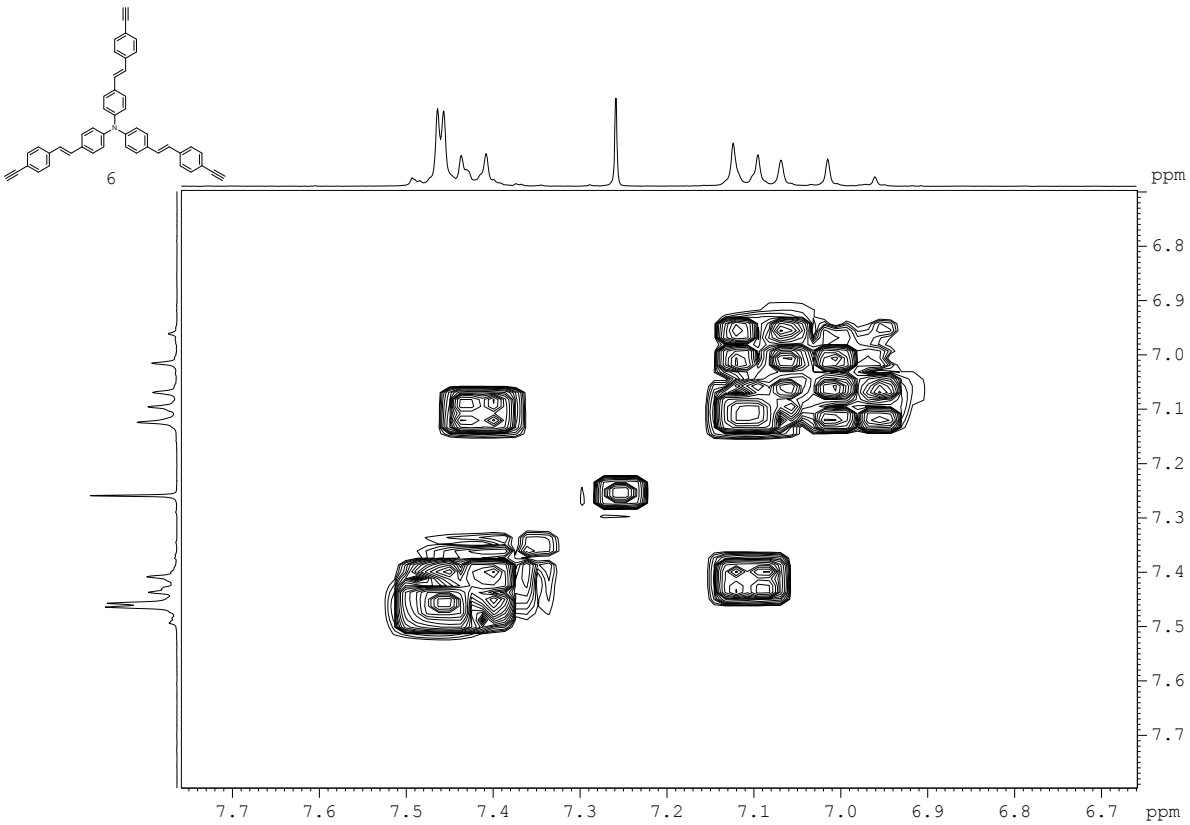


Figure S13. COSY H-H of **6** in $CDCl_3$.

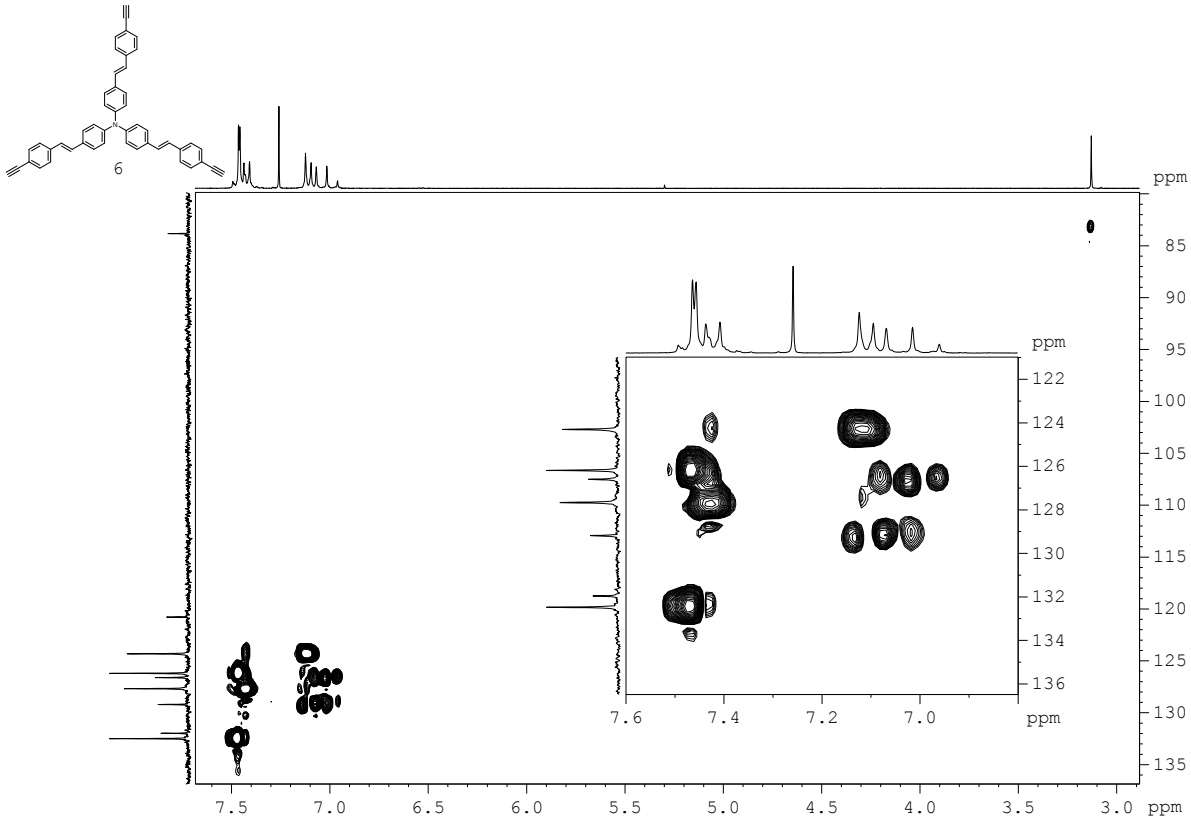


Figure S14. HSQC of **6** in $CDCl_3$.

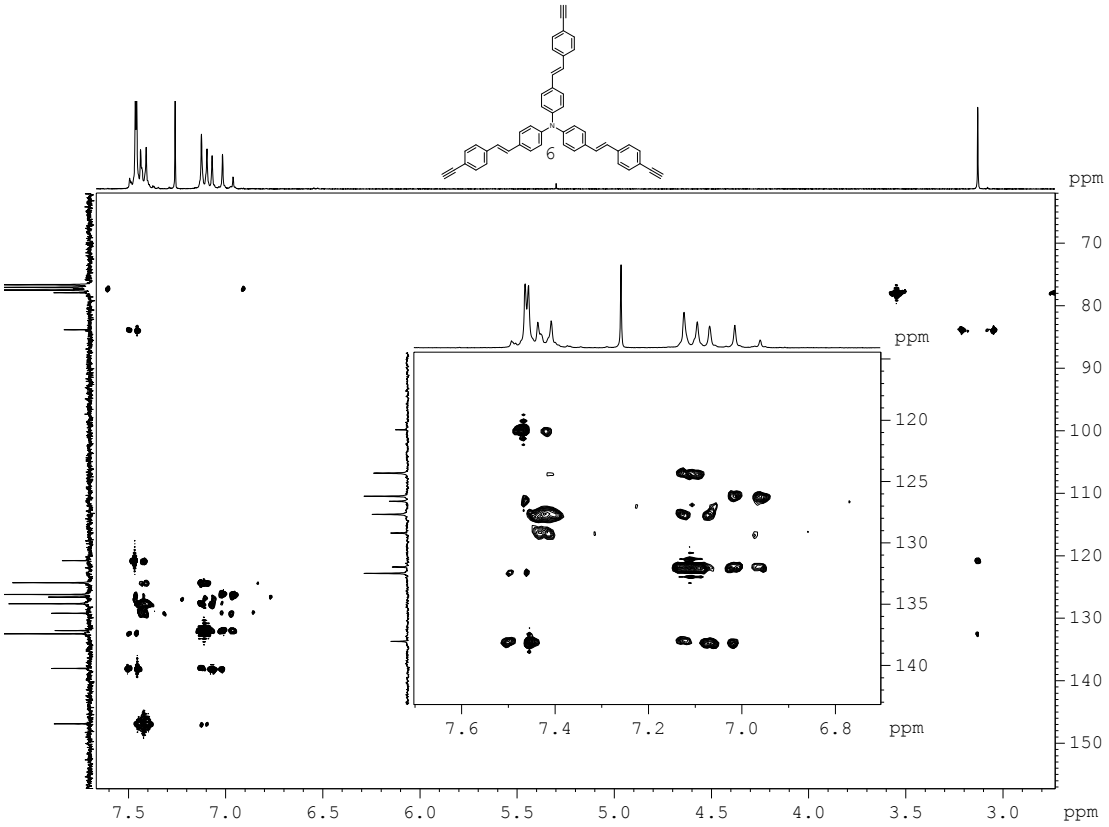


Figure S15. HMBC of **6** in $CDCl_3$.

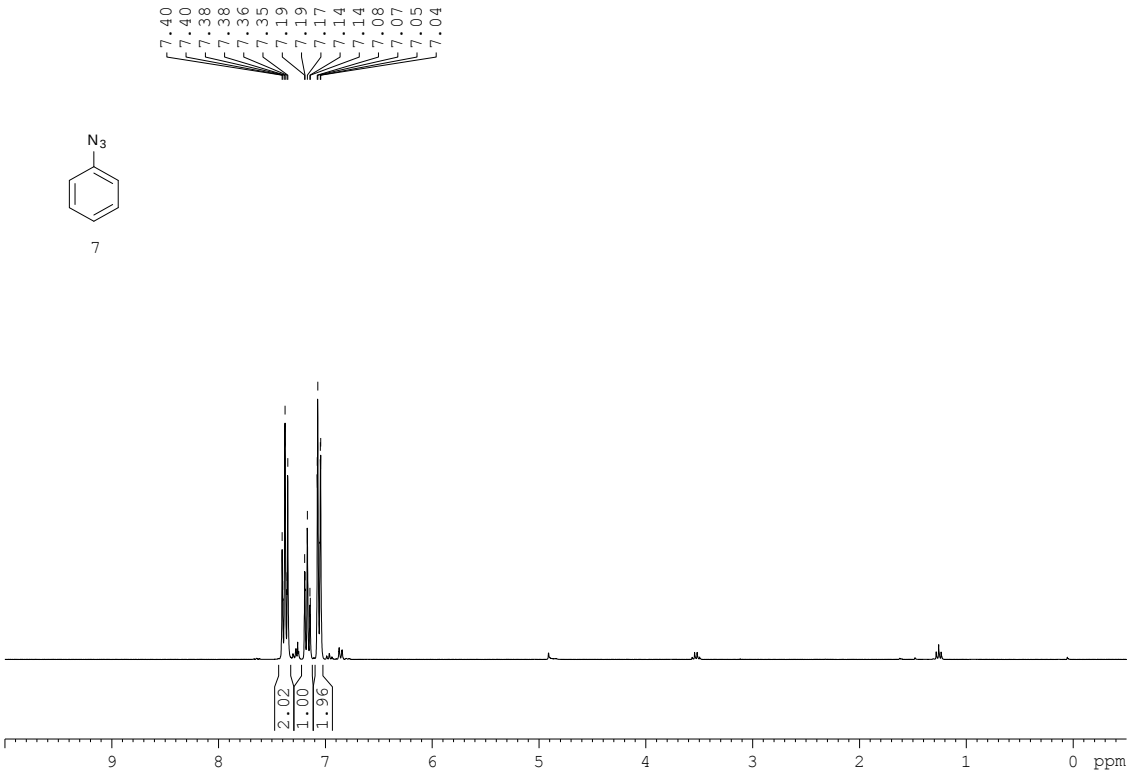


Figure S16: ^1H NMR (300 MHz) of phenylazide **7** in $CDCl_3$

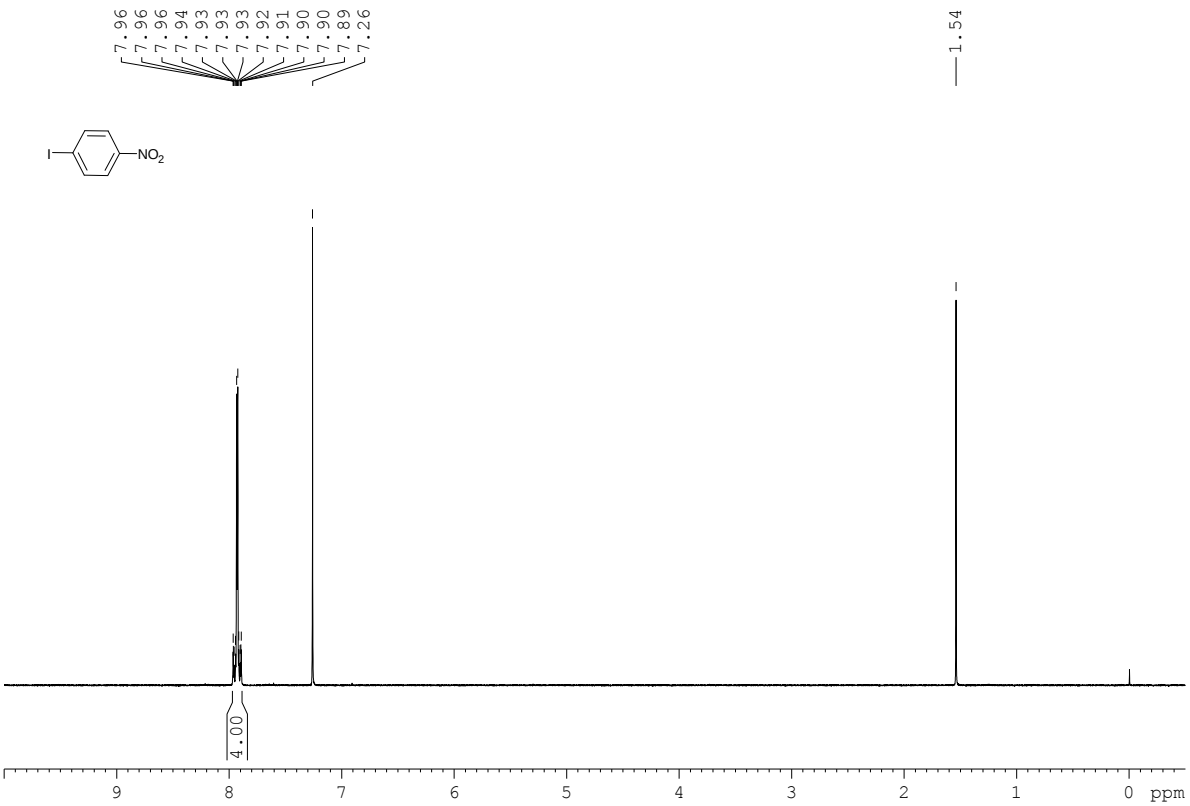


Figure S17: ^{1}H NMR (300 MHz) of **4-nitroiodobenzene** in $CDCl_3$

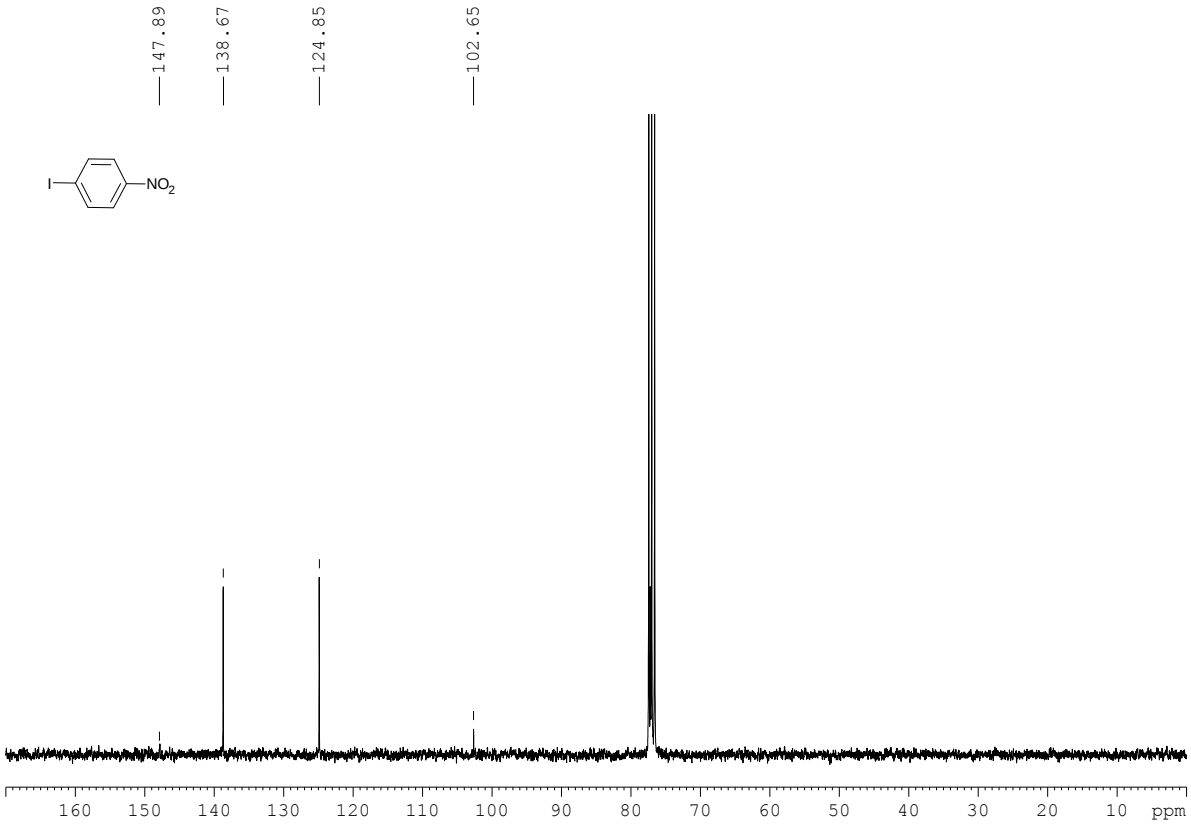


Figure S18: ^{13}C NMR (75.4 MHz) of **4-nitroiodobenzene** in $CDCl_3$

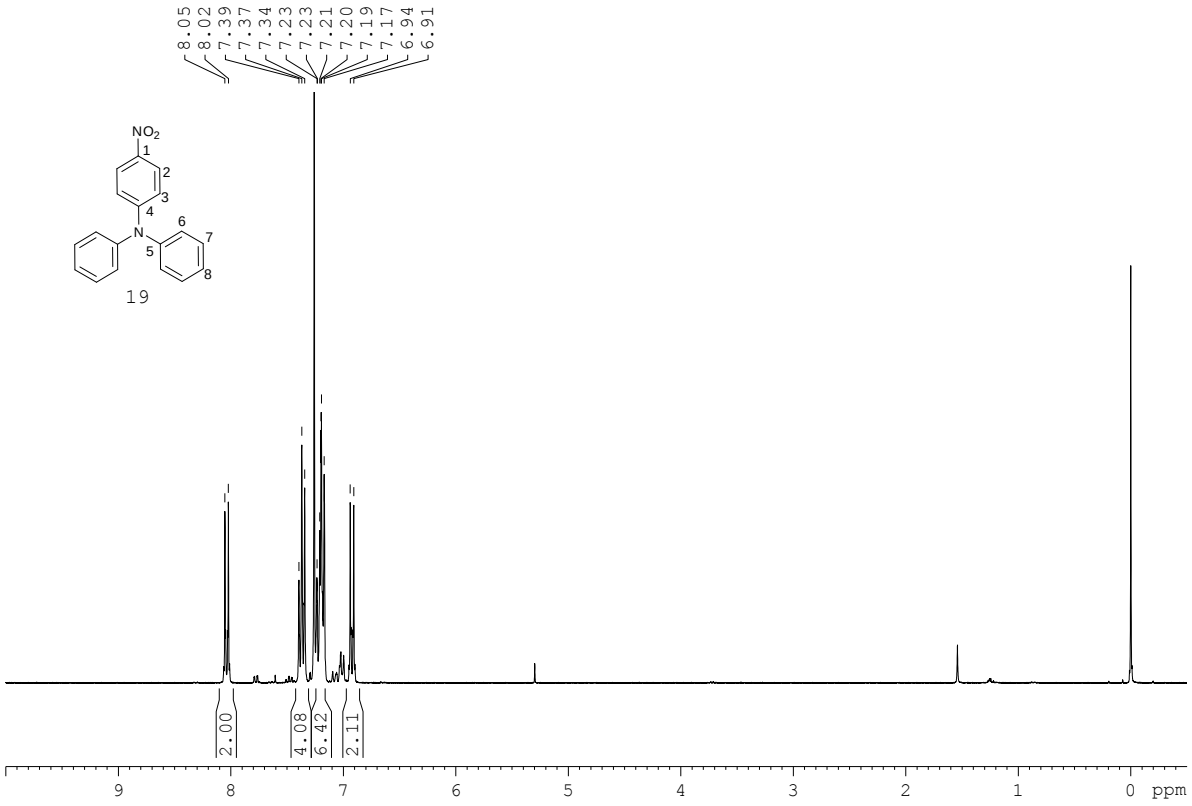


Figure S19: ^{1}H NMR (300 MHz) of **19** in $CDCl_3$

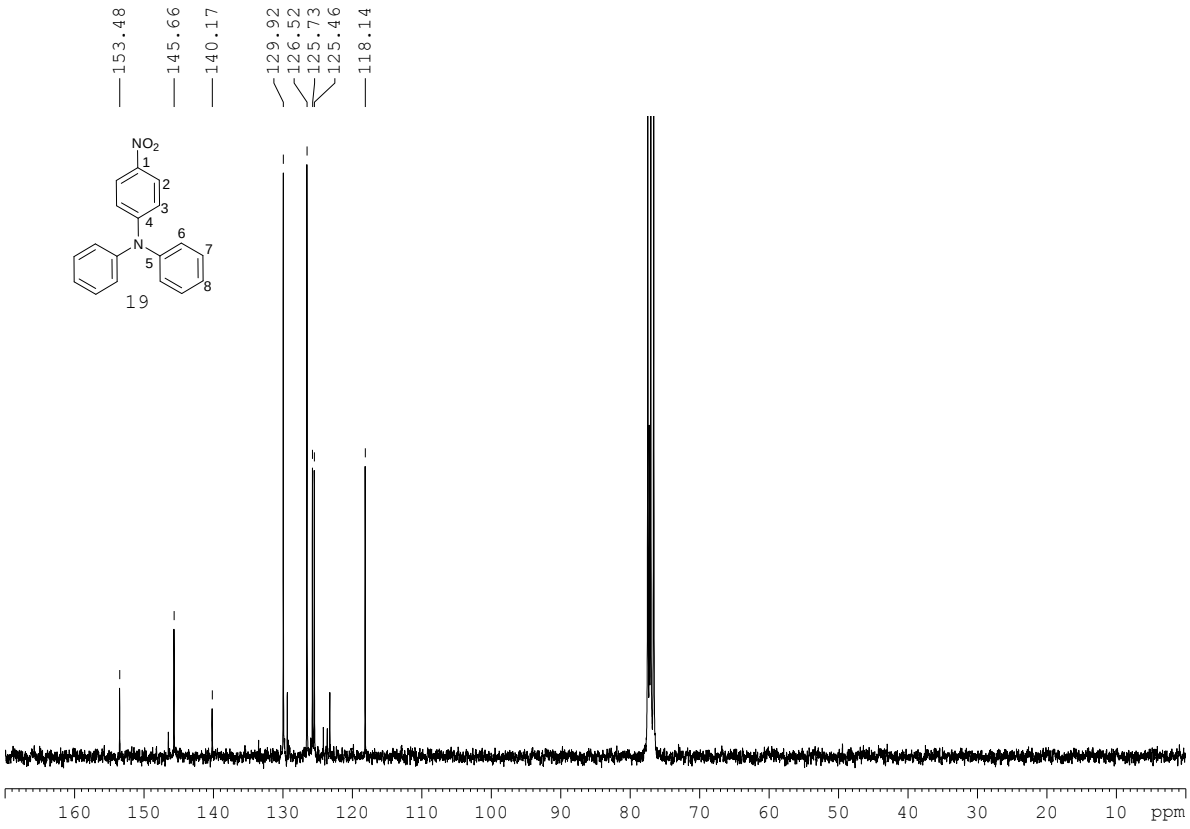


Figure S20: ^{13}C NMR (75.4 MHz) of **19** in $CDCl_3$

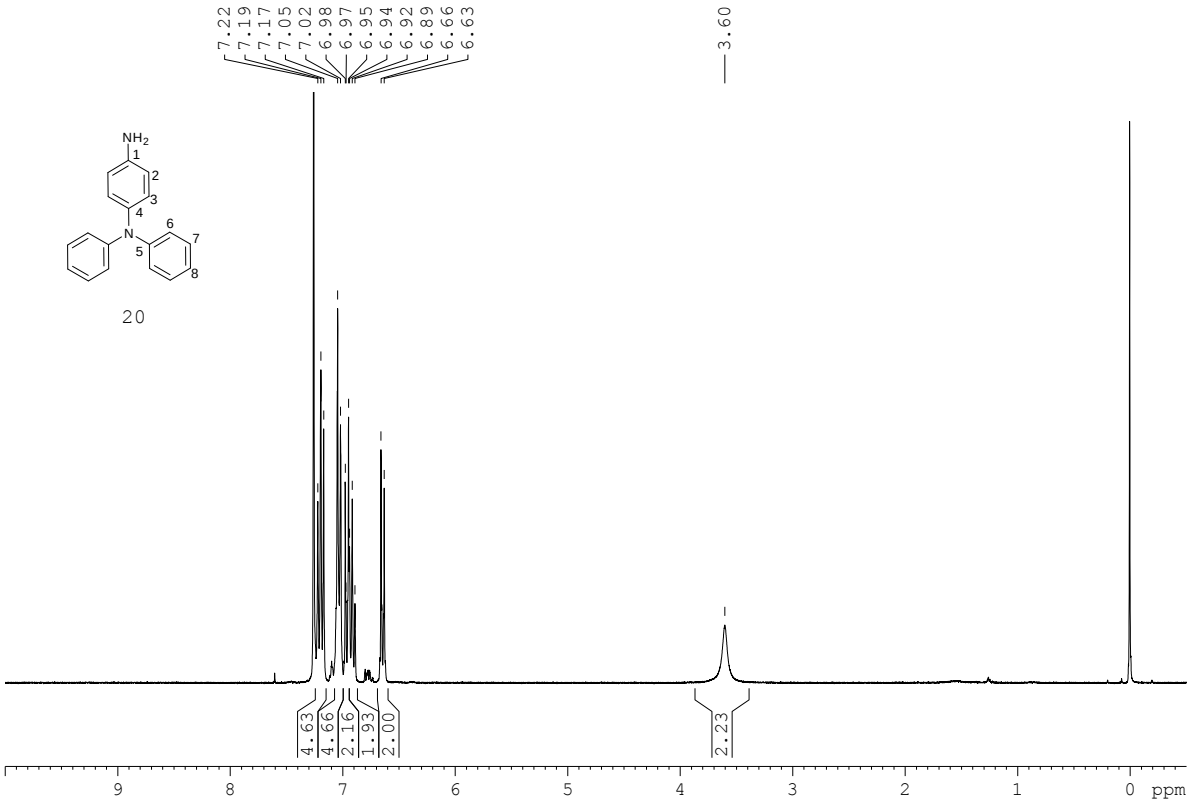


Figure S21: ^{1}H NMR (300 MHz) of **20** in $CDCl_3$

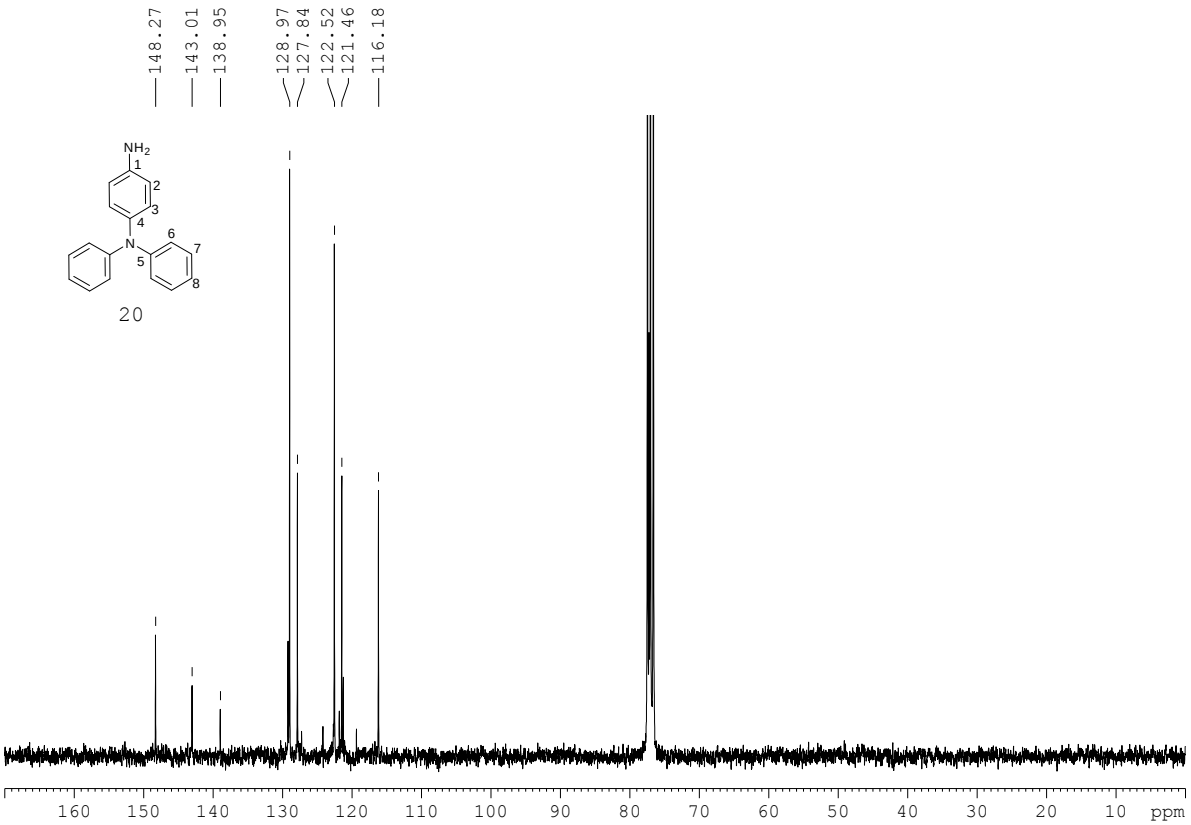


Figure S22: ^{13}C NMR (75.4 MHz) of **20** in $CDCl_3$

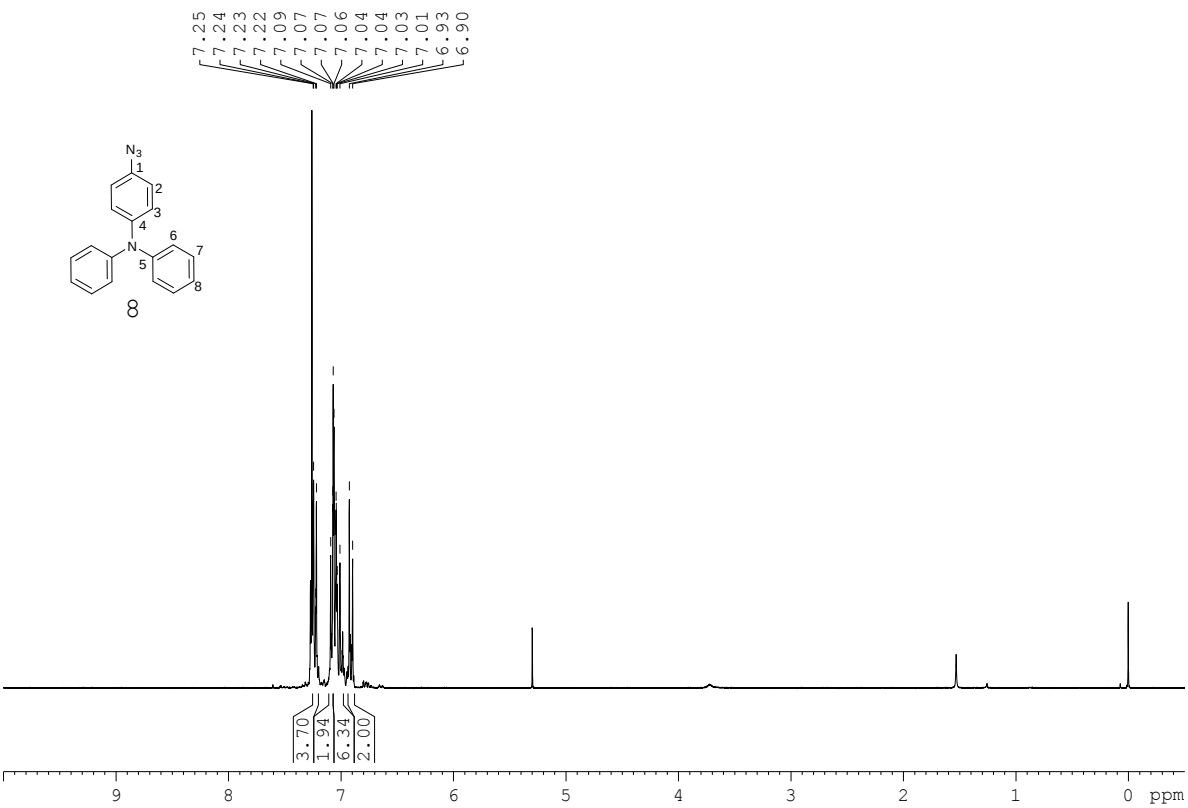


Figure S23: ^{1}H NMR (300 MHz) of **8** in $CDCl_3$

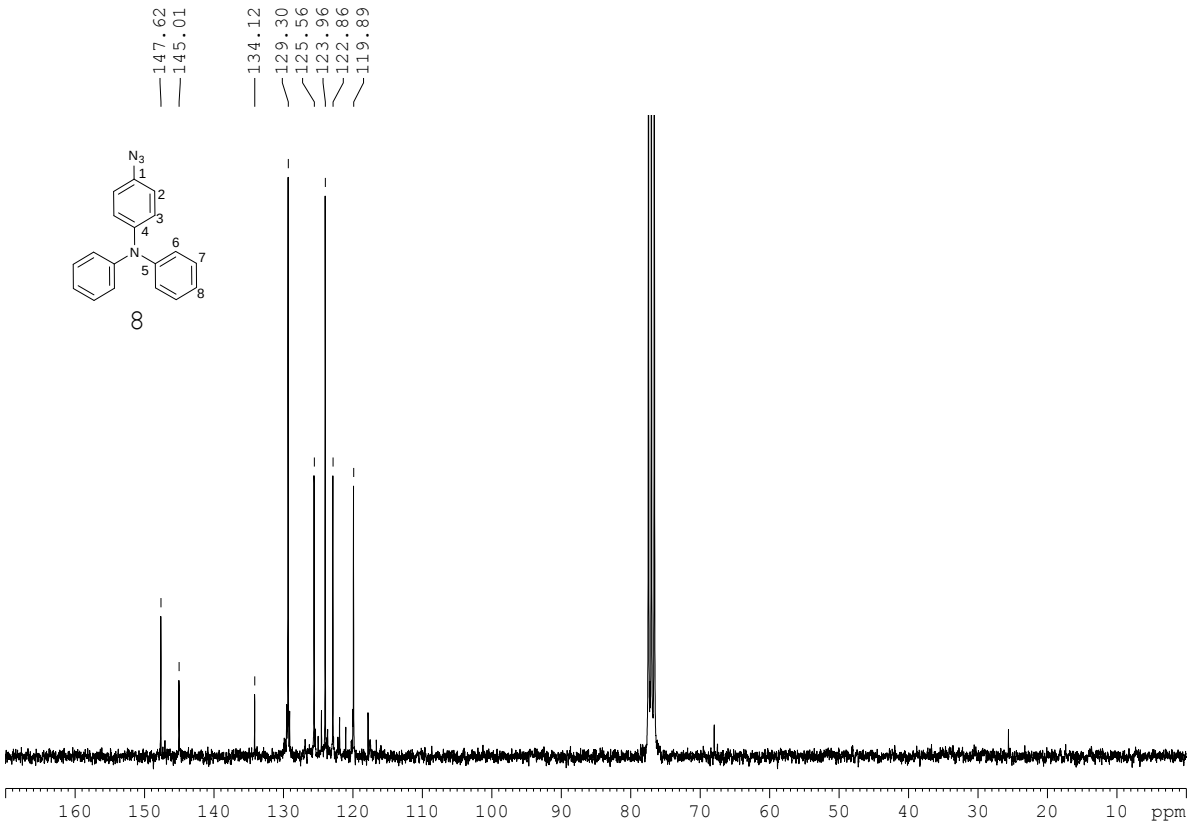


Figure S24: ^{13}C NMR (75.4 MHz) of **8** in $CDCl_3$

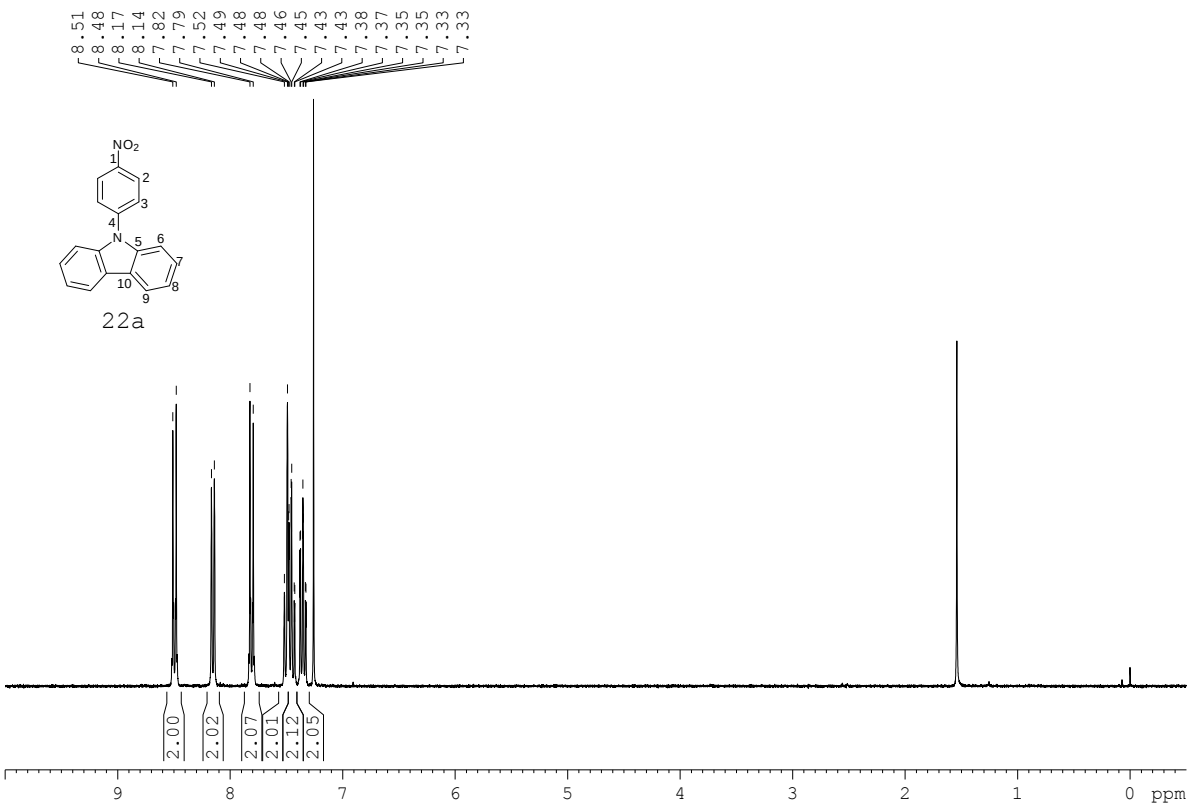


Figure S25: ^{1}H NMR (300 MHz) of **22a** in $CDCl_3$

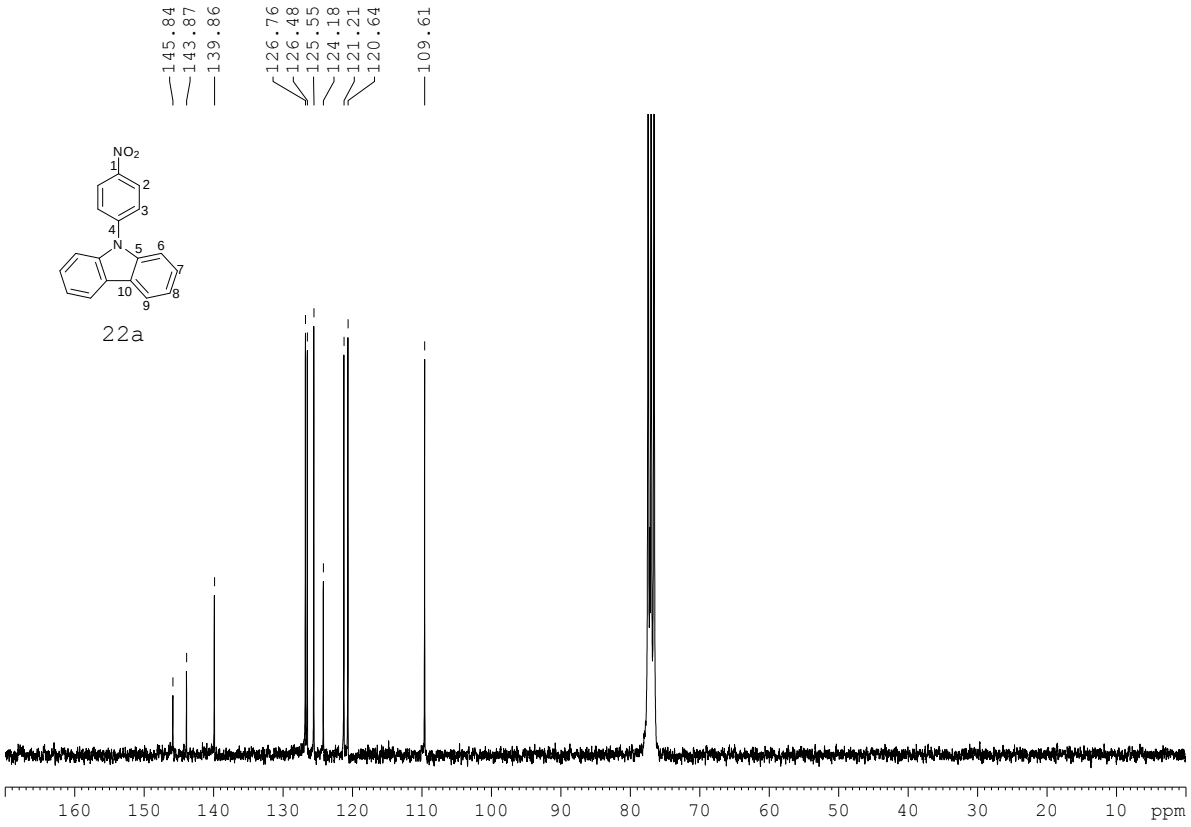


Figure S26: ^{13}C NMR (75.4 MHz) of **22a** in $CDCl_3$

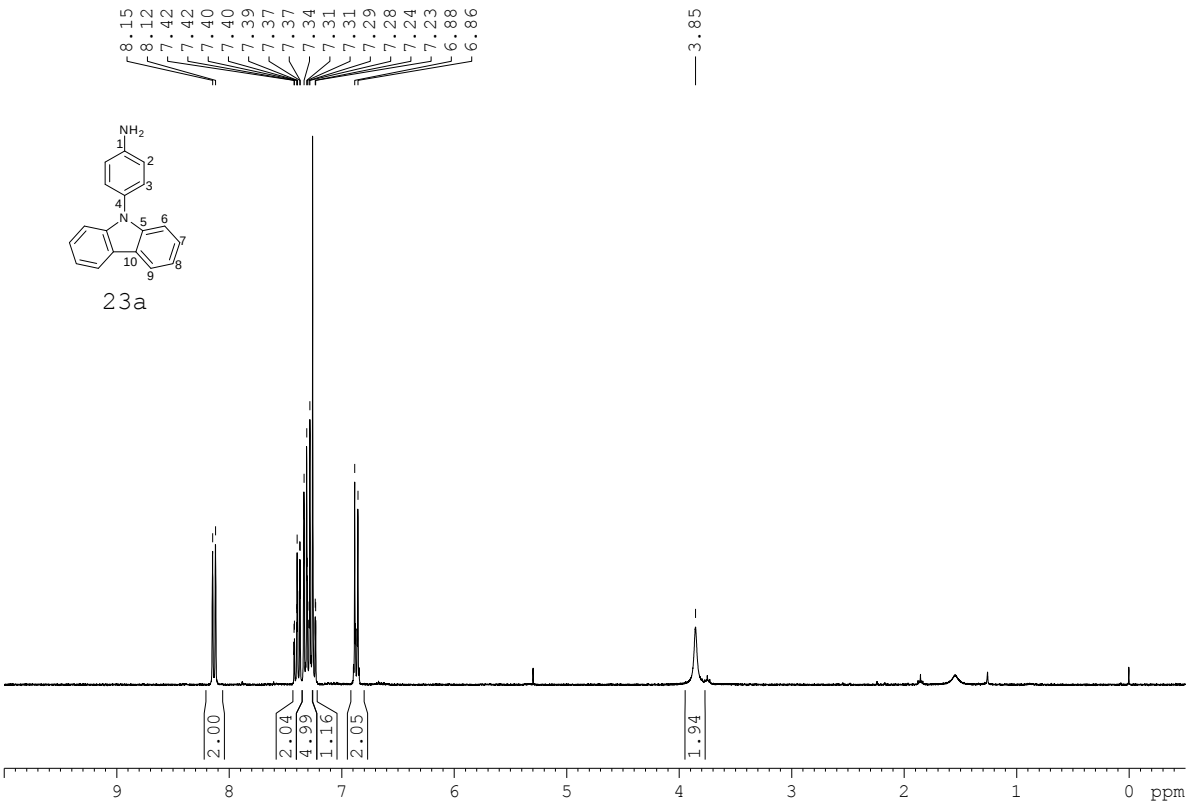


Figure S27: ^{1}H NMR (300 MHz) of **23a** in $CDCl_3$

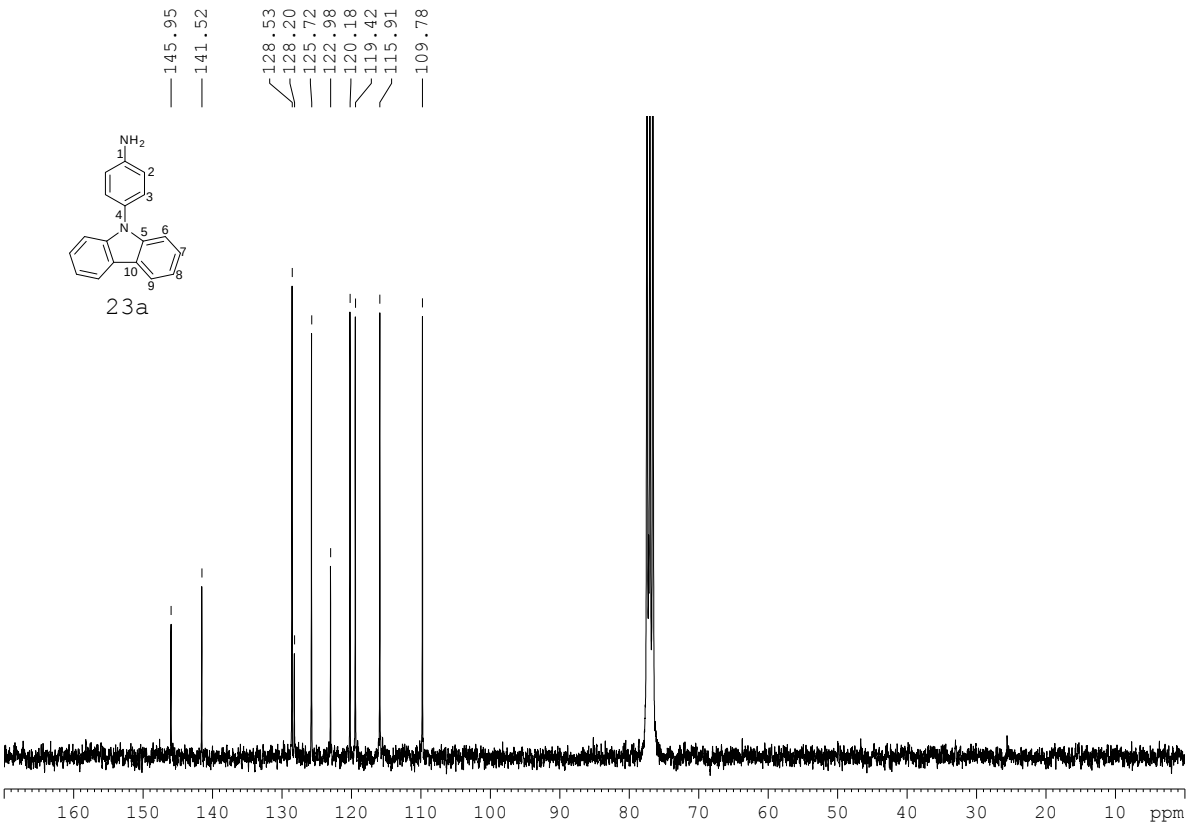


Figure S28: ^{13}C NMR (75.4 MHz) of **23a** in $CDCl_3$

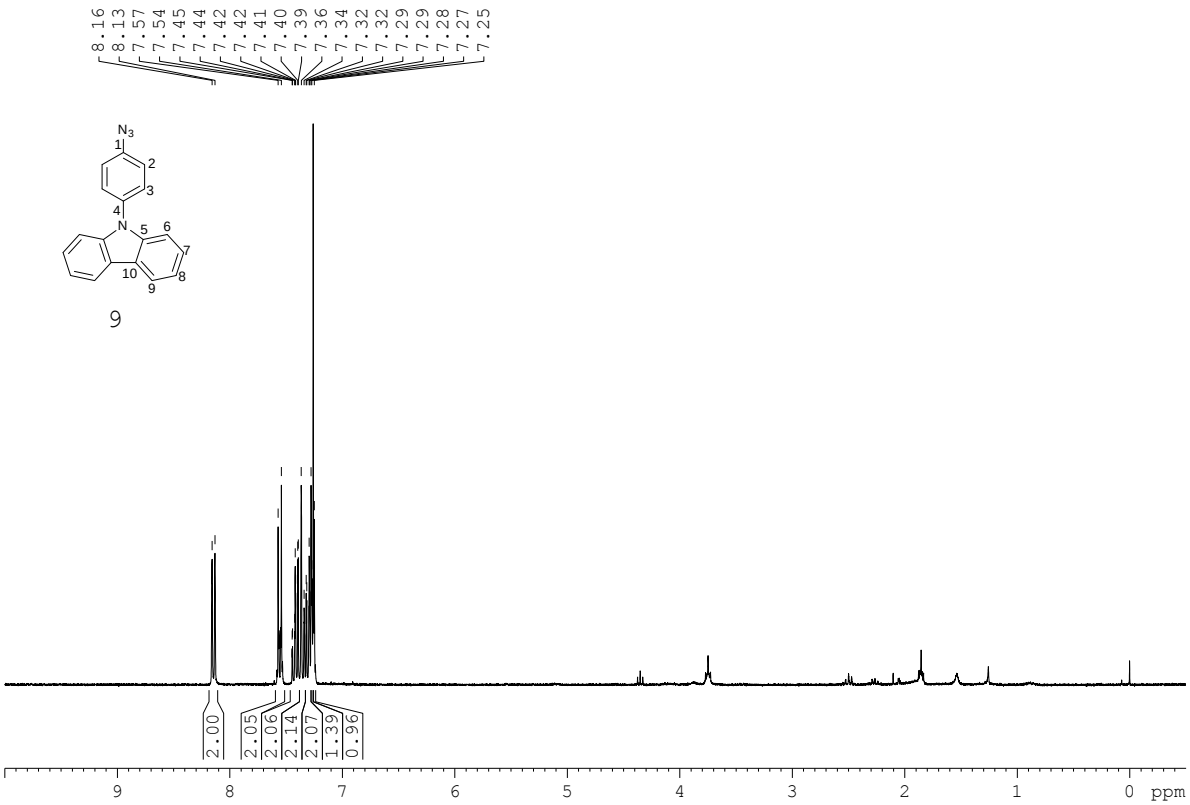


Figure S29: ^{1}H NMR (300 MHz) of **9** in $CDCl_3$

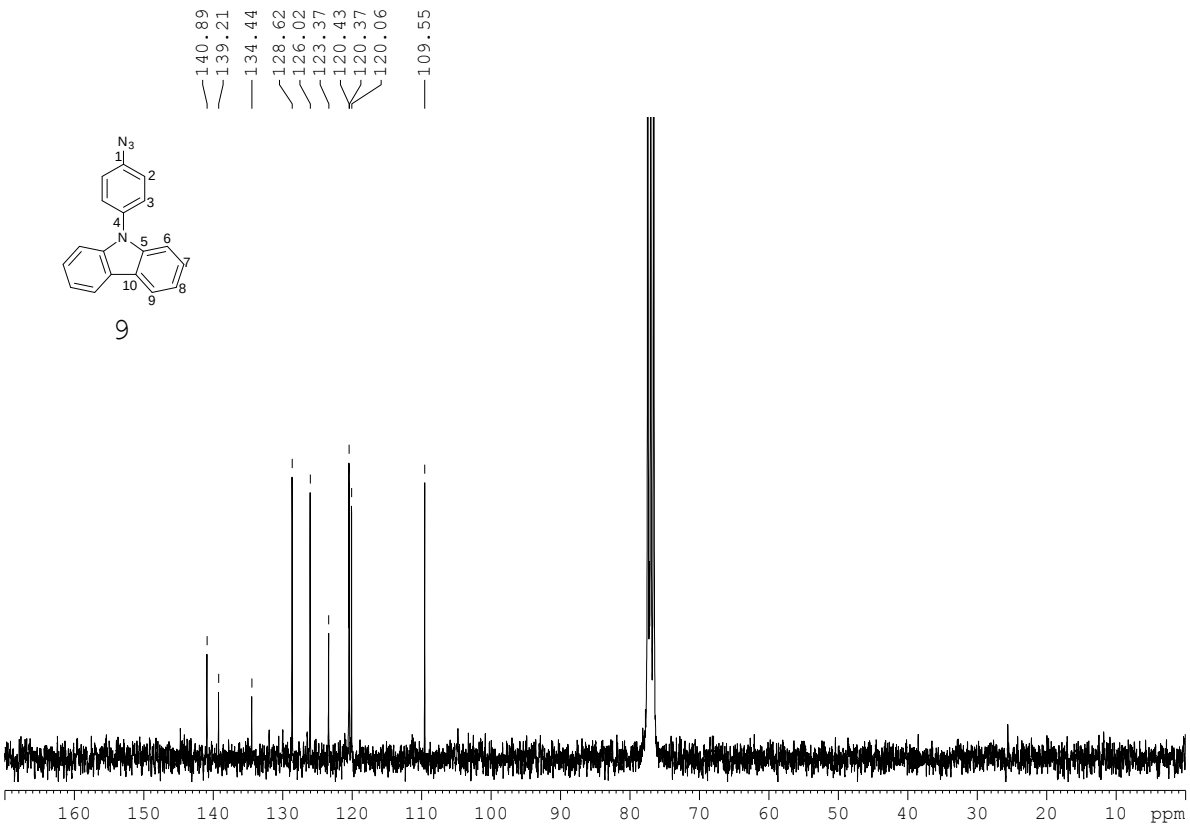


Figure S30: ^{13}C NMR (75.4 MHz) of **9** in $CDCl_3$

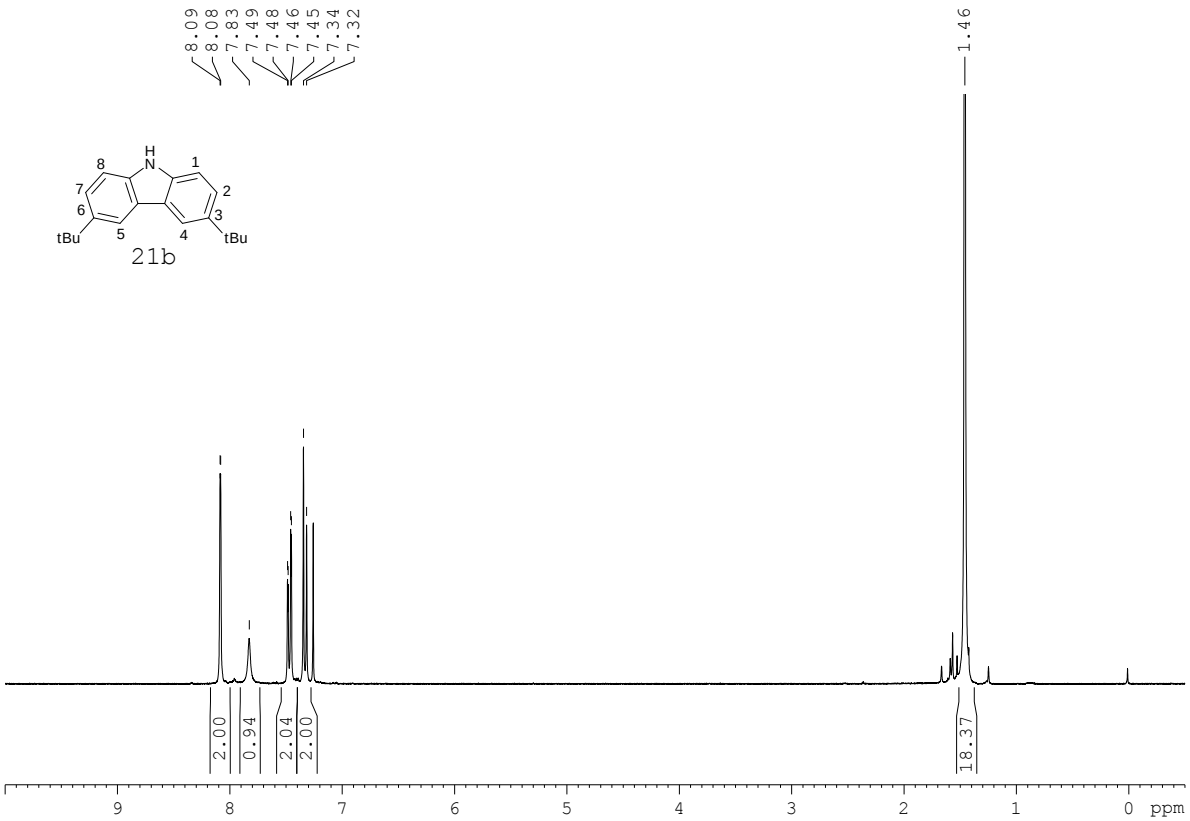


Figure S31: ^{1}H NMR (300 MHz) of **21b** in $CDCl_3$

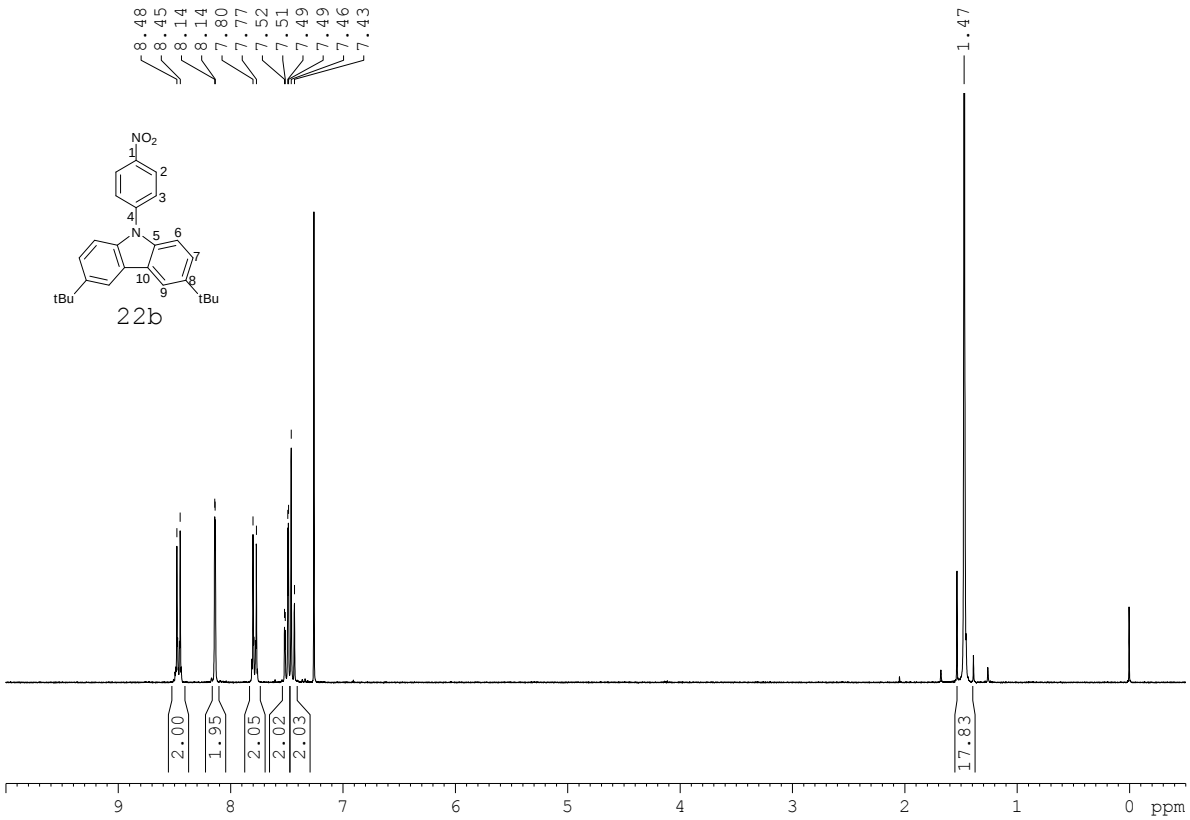


Figure S32: ^{1}H NMR (300 MHz) of **22b** in $CDCl_3$

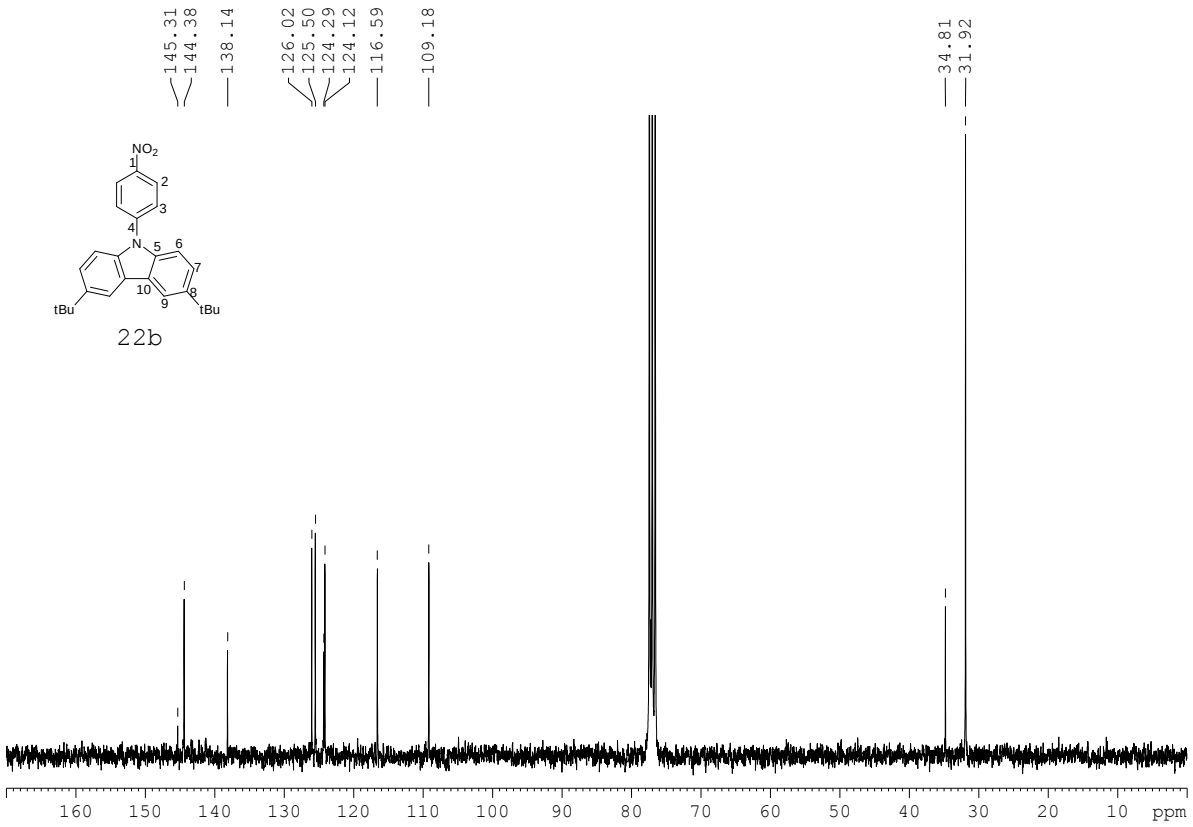


Figure S33: ^{13}C NMR (75.4 MHz) of **22b** in $CDCl_3$

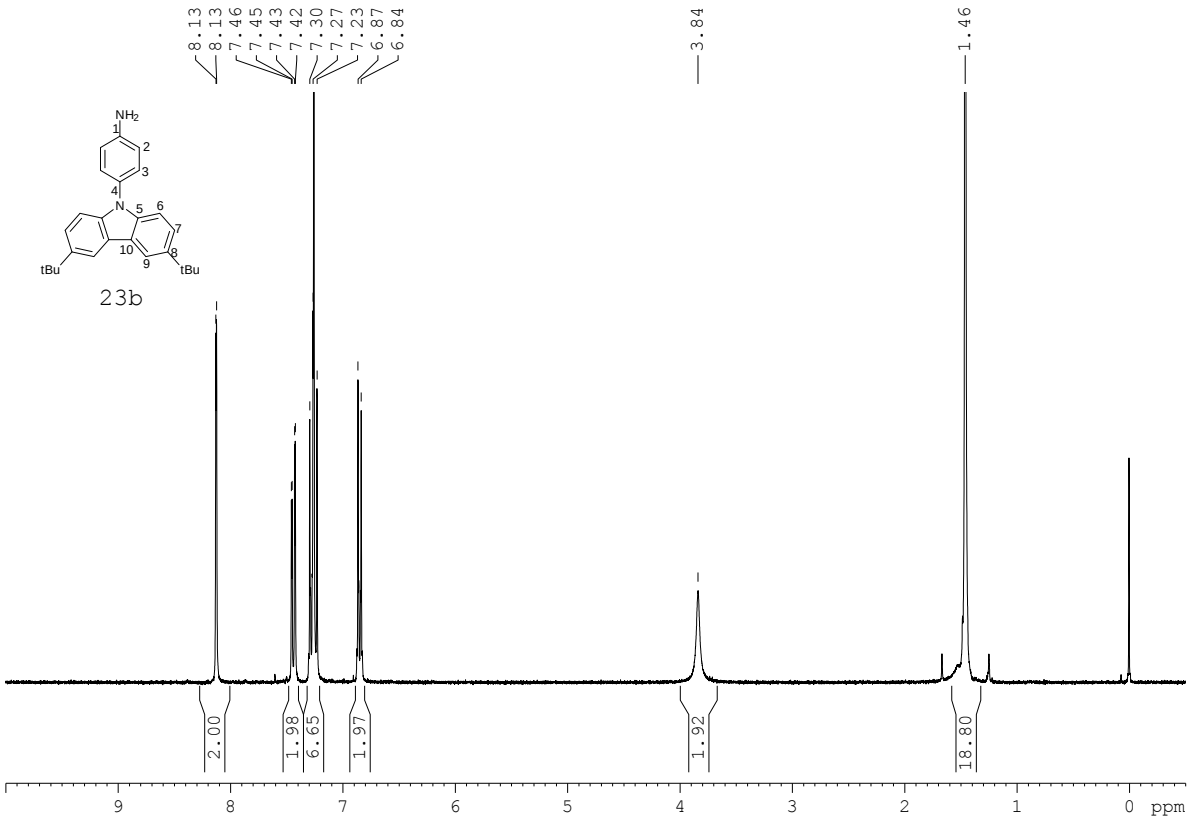


Figure S34: ^{1}H NMR (300 MHz) of **23b** in $CDCl_3$

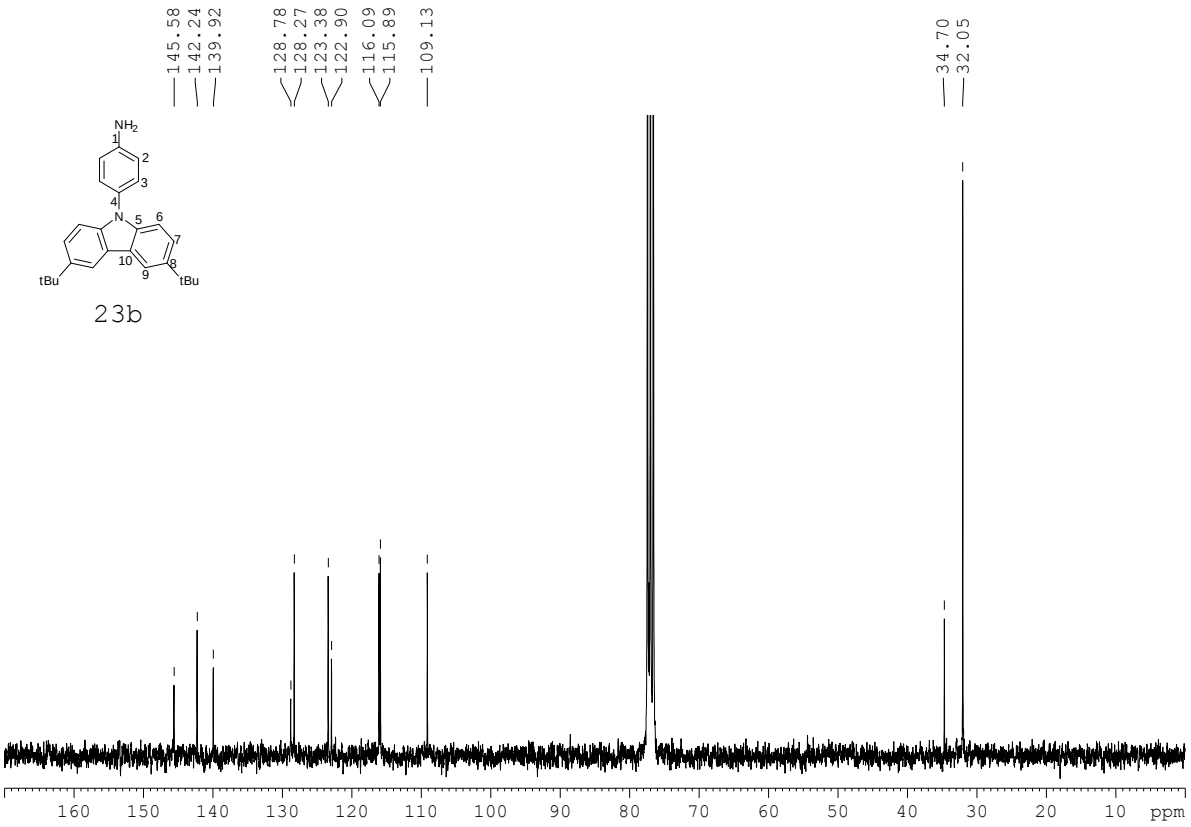


Figure S35: ^{13}C NMR (75.4 MHz) of **23b** in $CDCl_3$

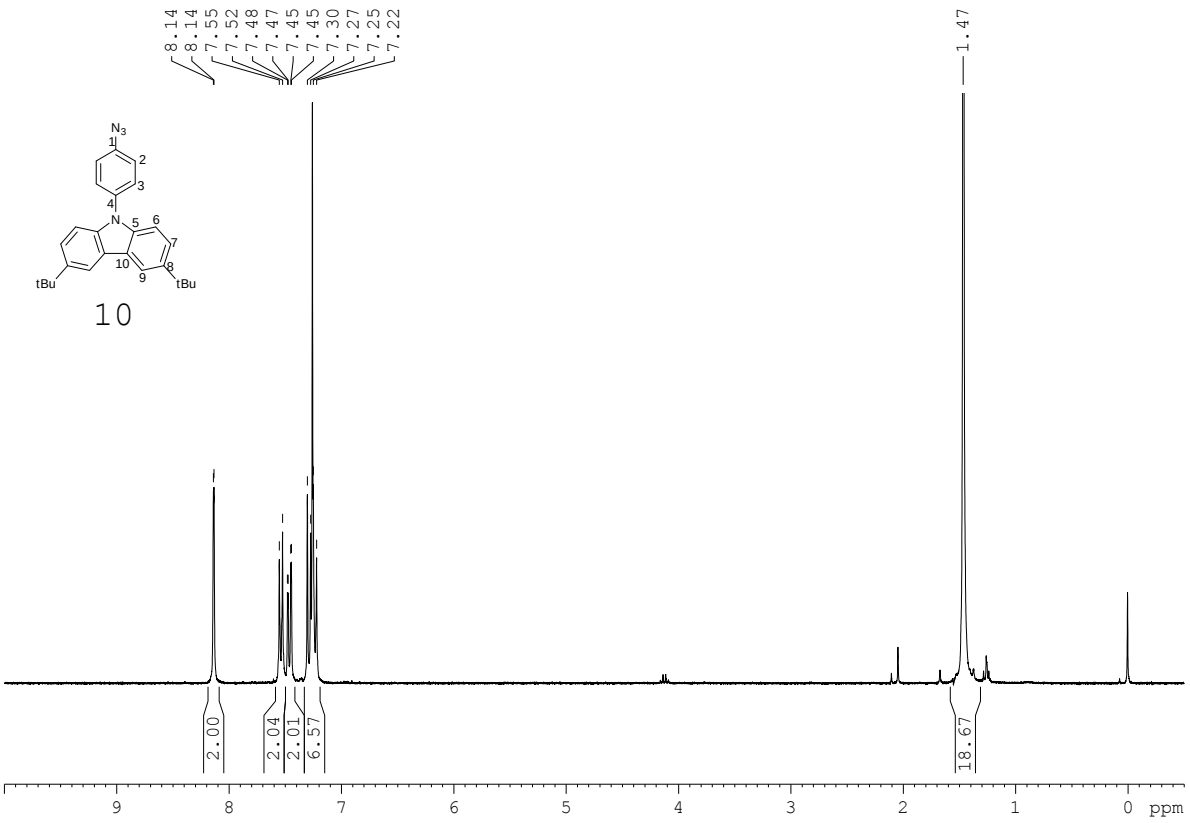


Figure S36: ^{1}H NMR (300 MHz) of **10** in $CDCl_3$

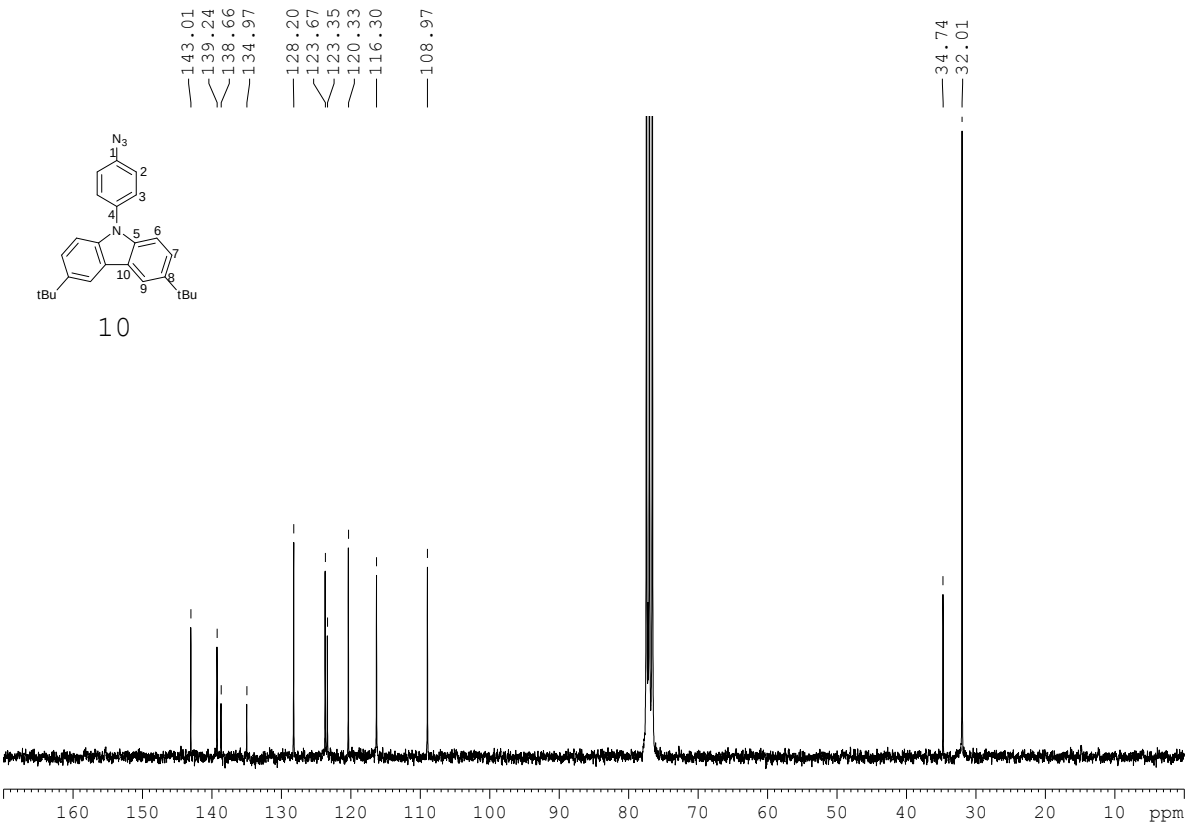


Figure S37: ^{13}C NMR (75.4 MHz) of **10** in $CDCl_3$

3.1 Triazolic dendrimers selected spectra

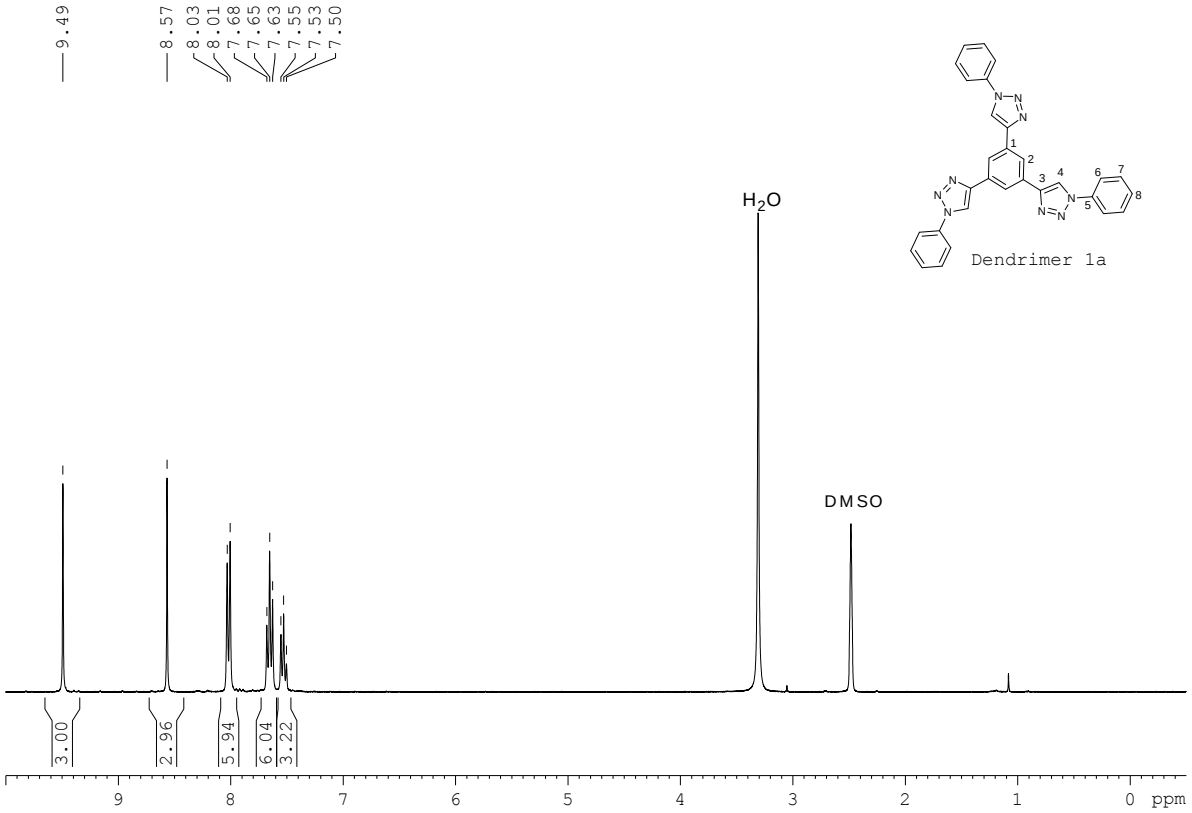


Figure S38: ^{1}H NMR (300 MHz) of **dendrimer 1a** in DMSO-d_6

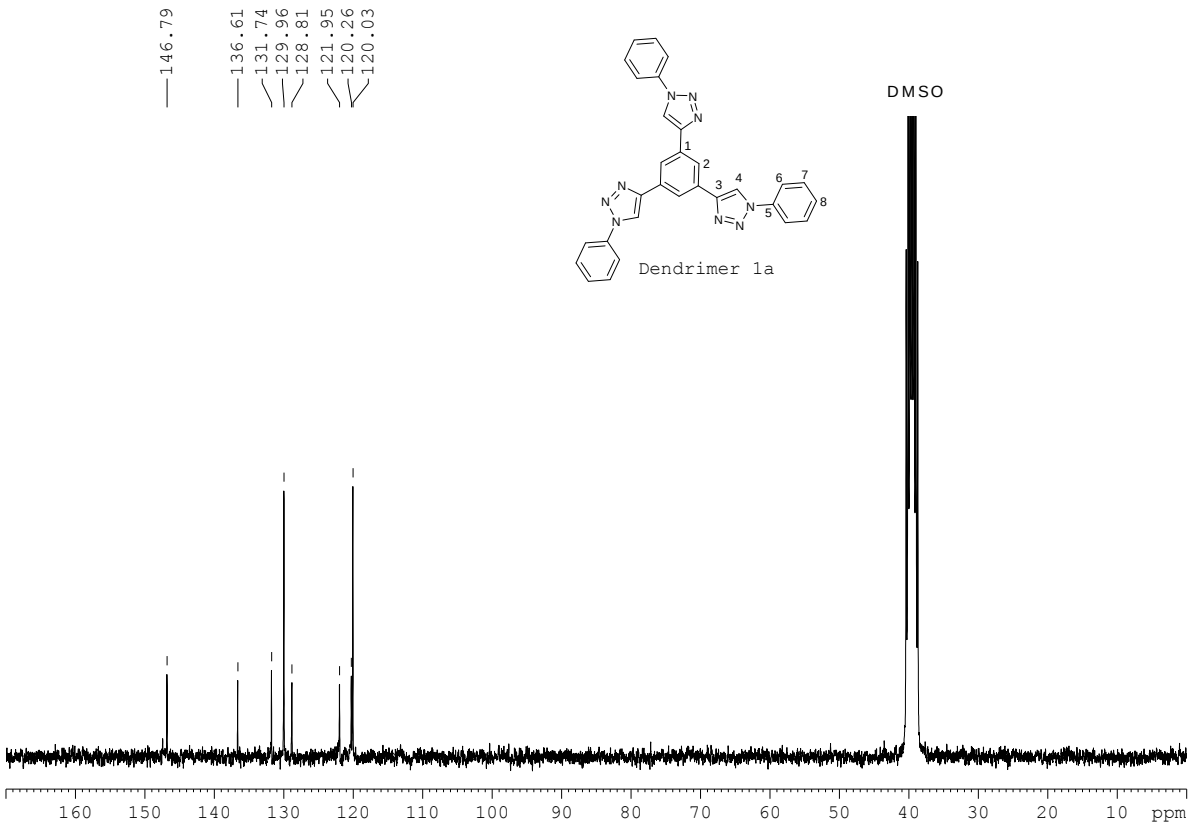


Figure S39: ^{13}C NMR (75.4 MHz) of **dendrimer 1a** in DMSO-d_6

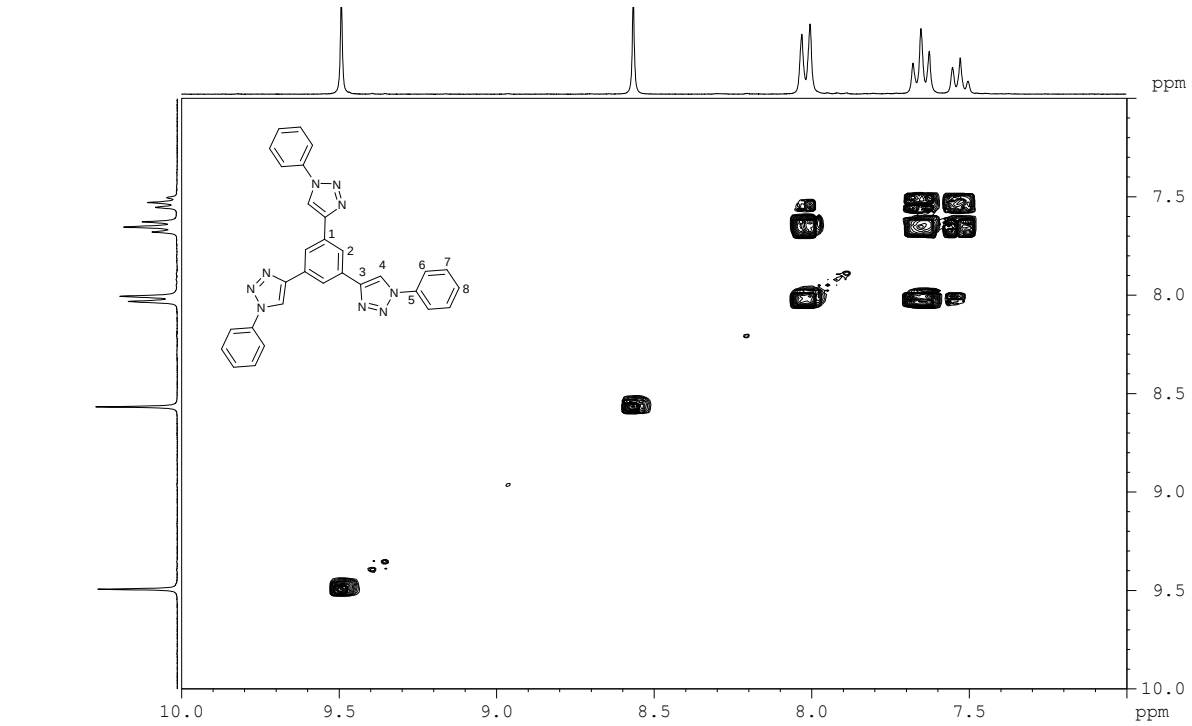


Figure S40. COSY H-H of **dendrimer 1a** in DMSO-d_6.

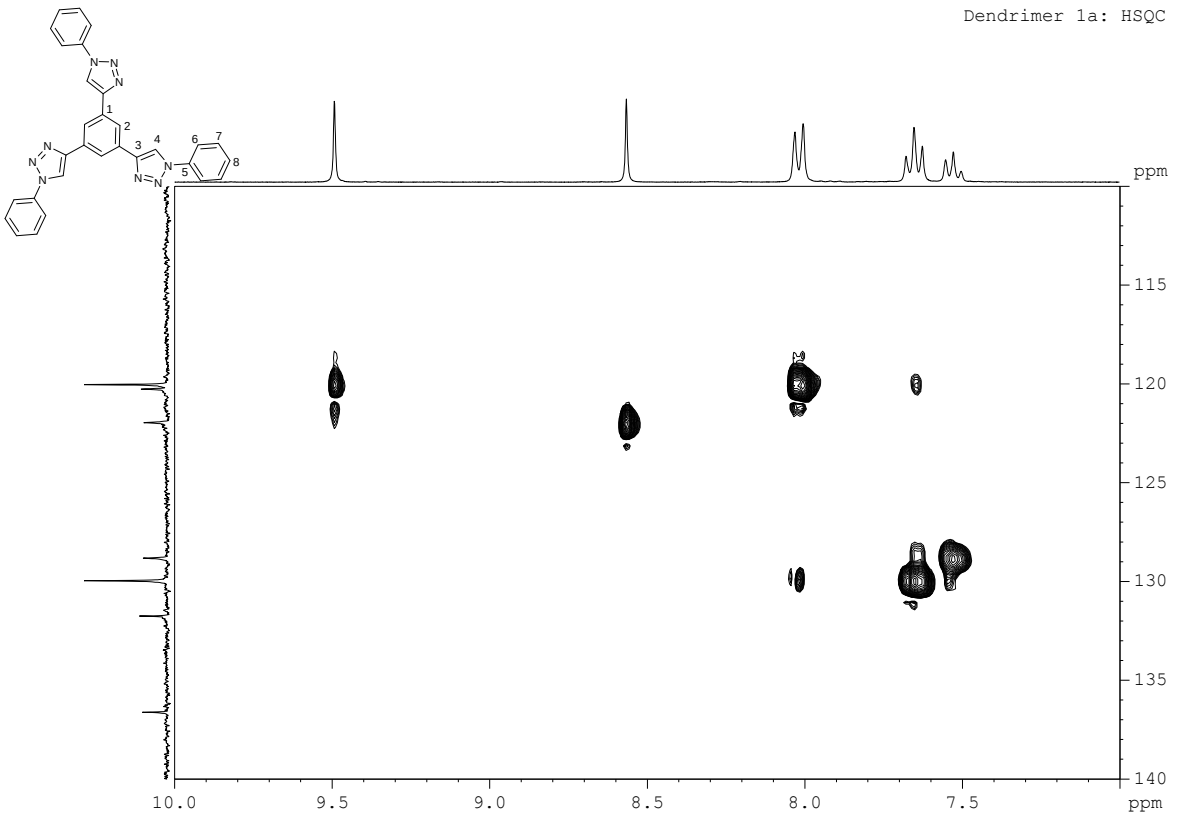


Figure S41. HSQC of **dendrimer 1a** in DMSO-d_6.

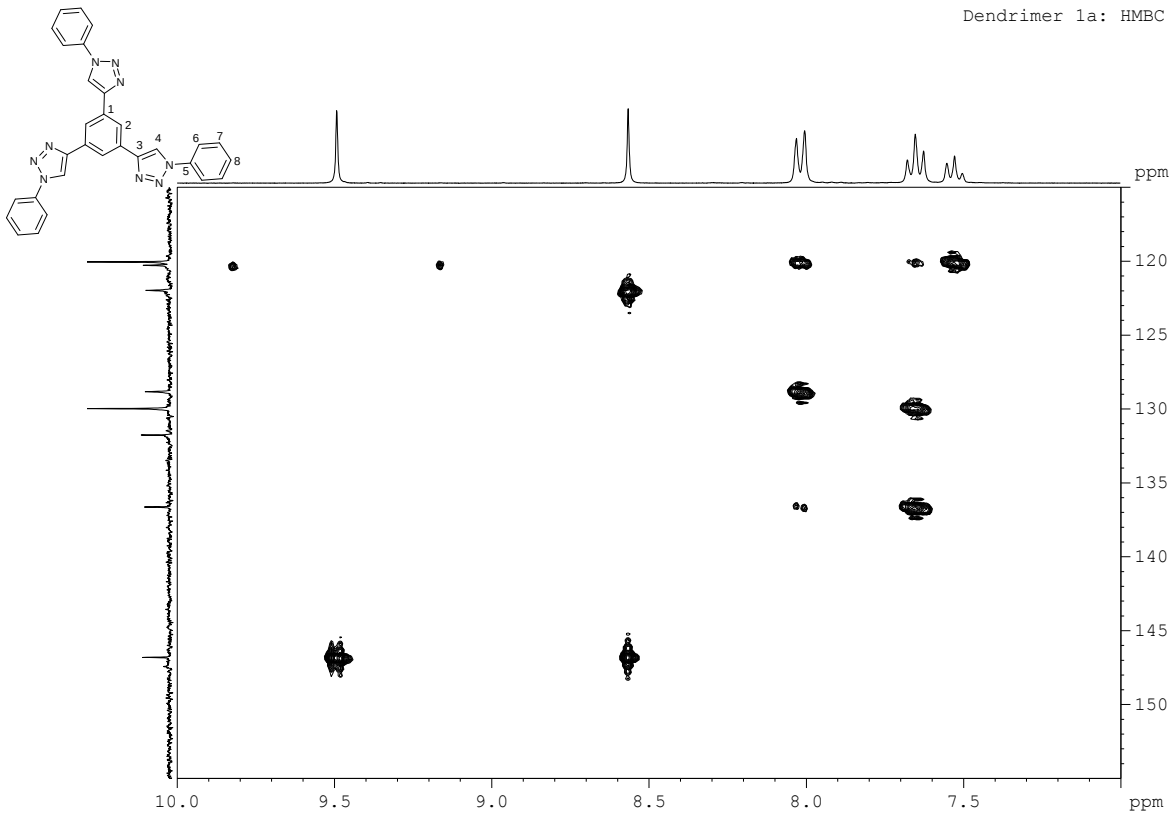


Figure S42. HMBC of **dendrimer 1a** in DMSO-d_6.

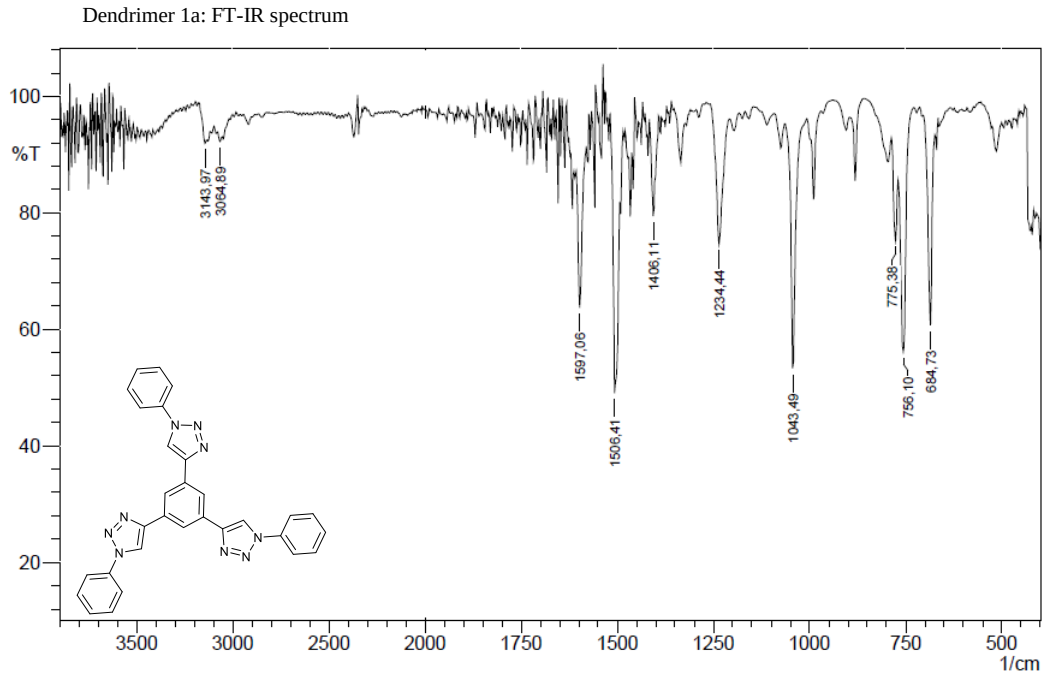


Figure S43. FT-IR (KBr disk) of **dendrimer 1a**.

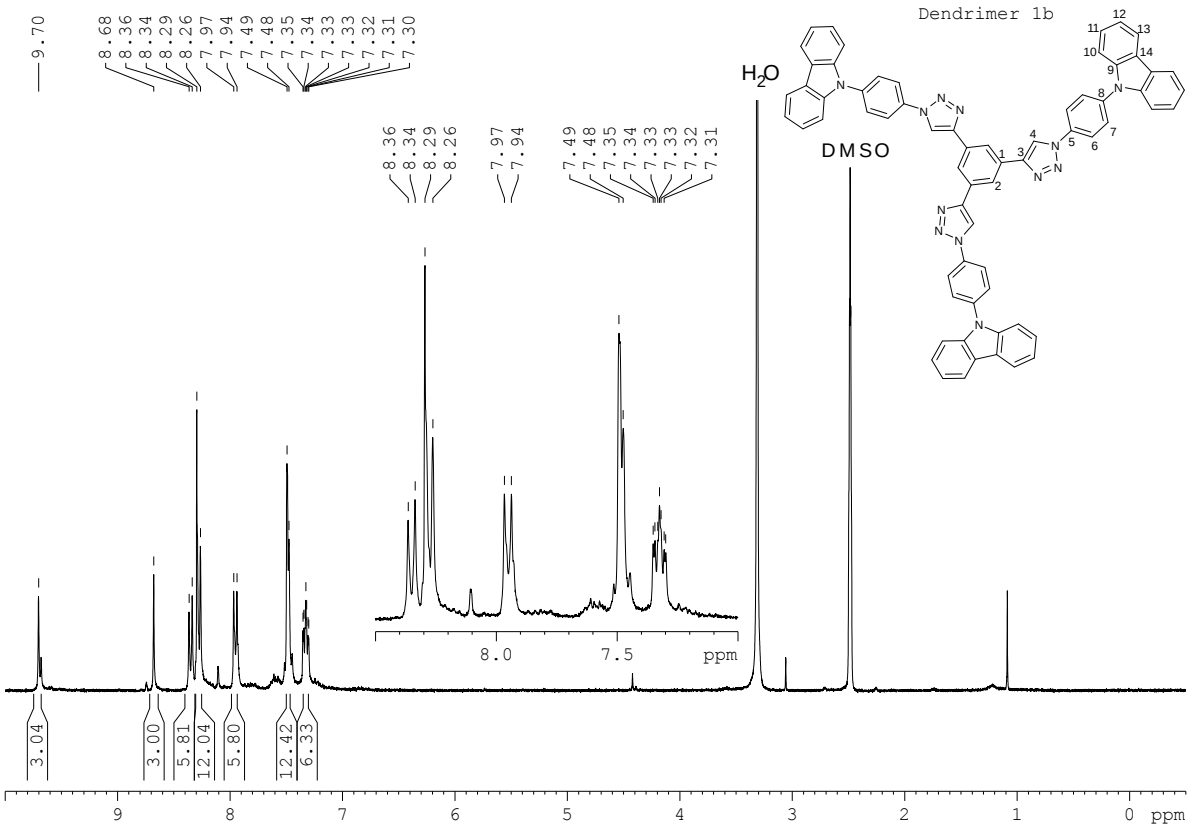


Figure S44: ^{1}H NMR (300 MHz) of **dendrimer 1b** in DMSO-d_6

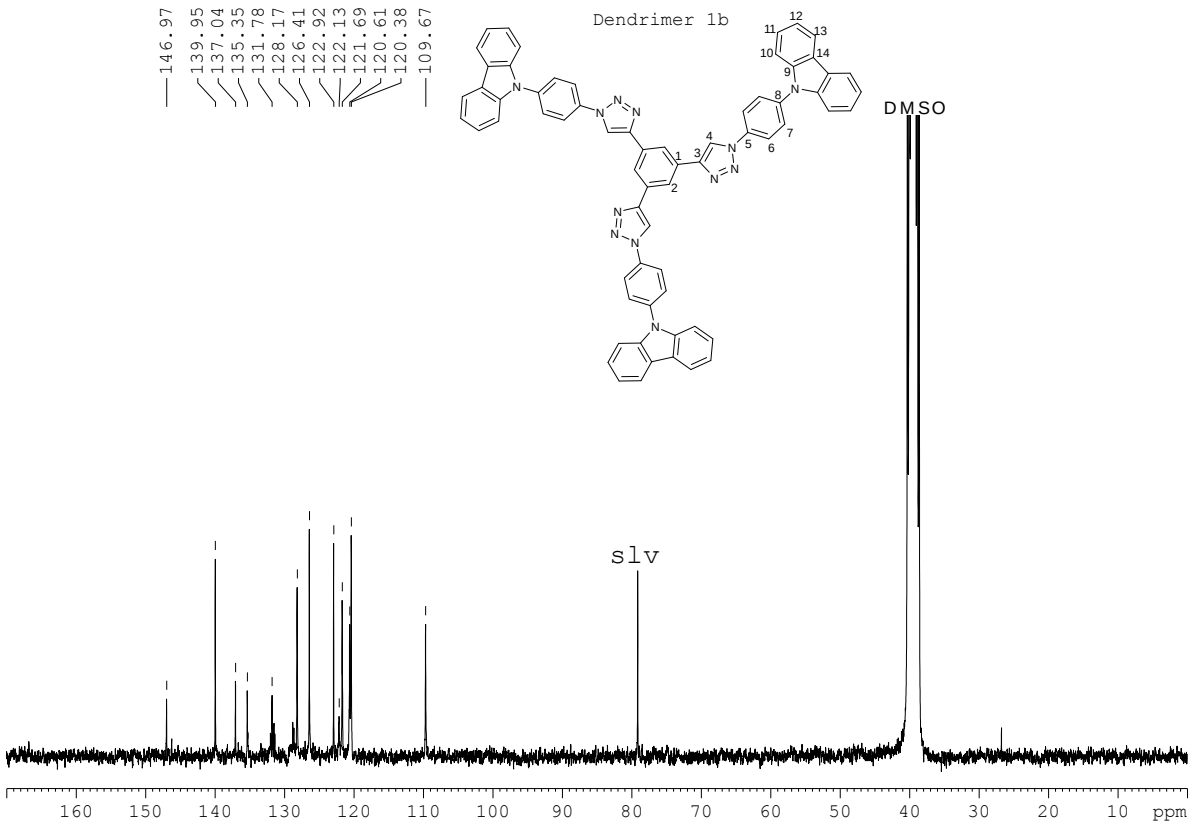


Figure S45: ^{13}C NMR (75.4 MHz) of **dendrimer 1b** in DMSO-d_6

Dendrimer 1b: COSY H-H

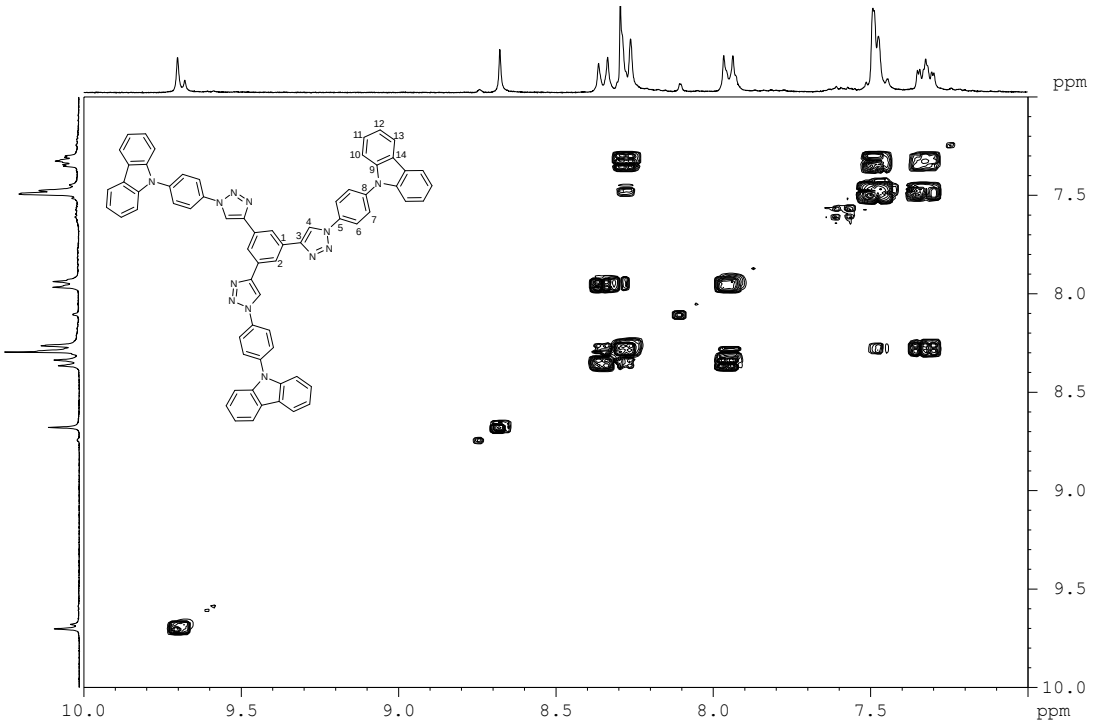


Figure S46. COSY H-H of **dendrimer 1b** in DMSO-d_6.

Dendrimer 1b: HMBC

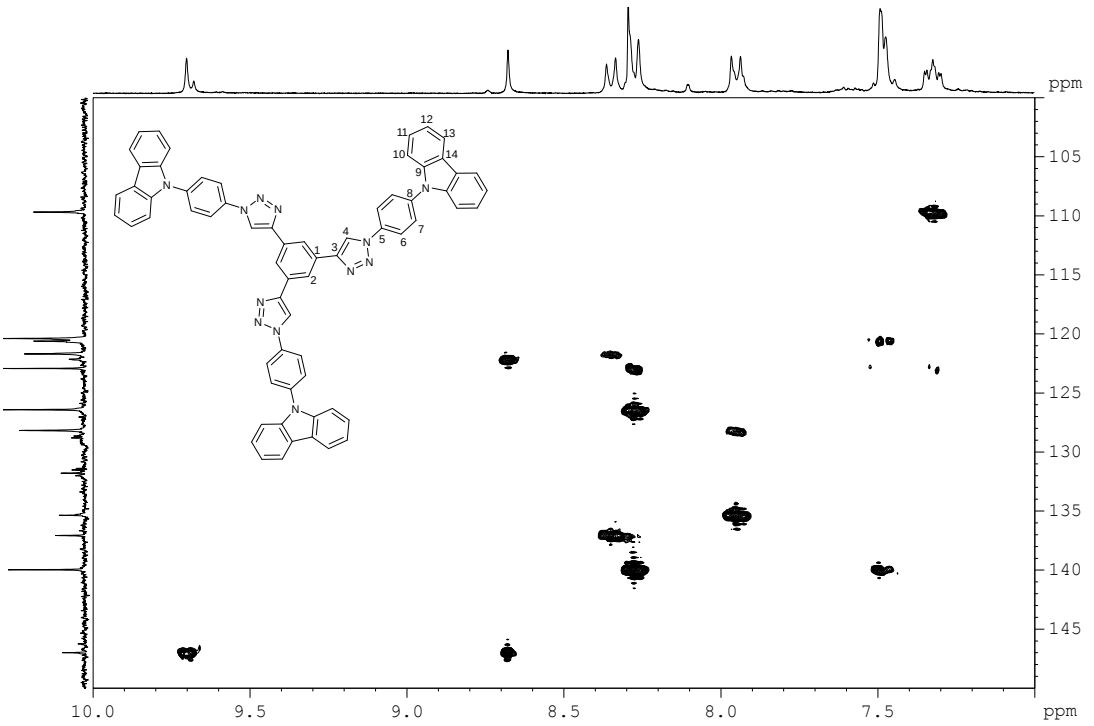


Figure S47. HMBC of **dendrimer 1b** in DMSO-d_6.

Dendrimer 1b: FT-IR spectrum

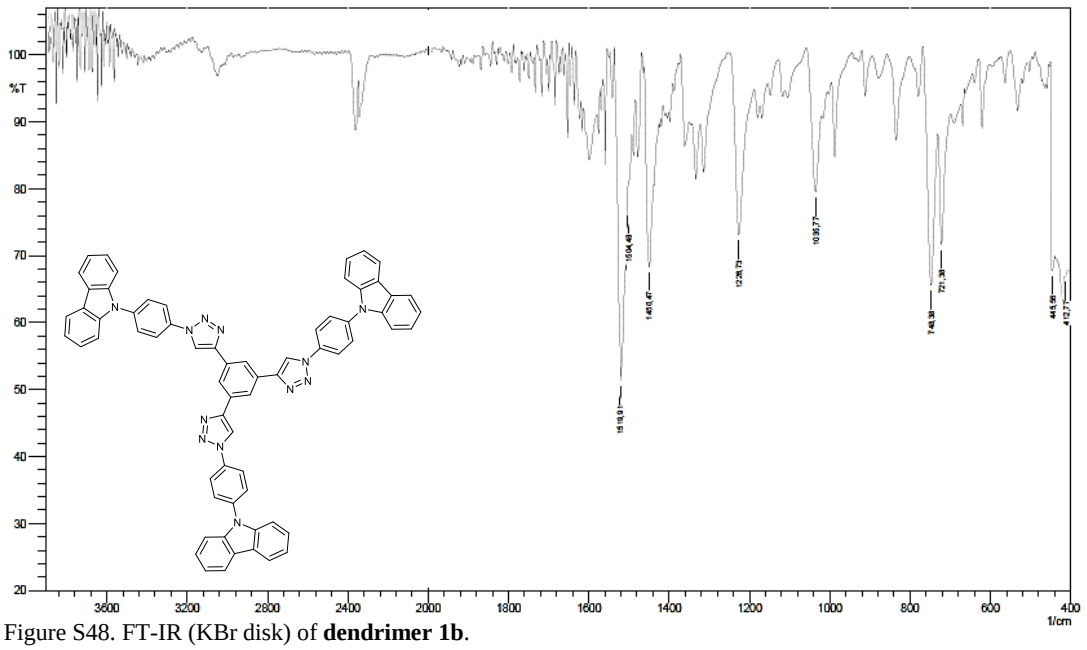


Figure S48. FT-IR (KBr disk) of **dendrimer 1b**.

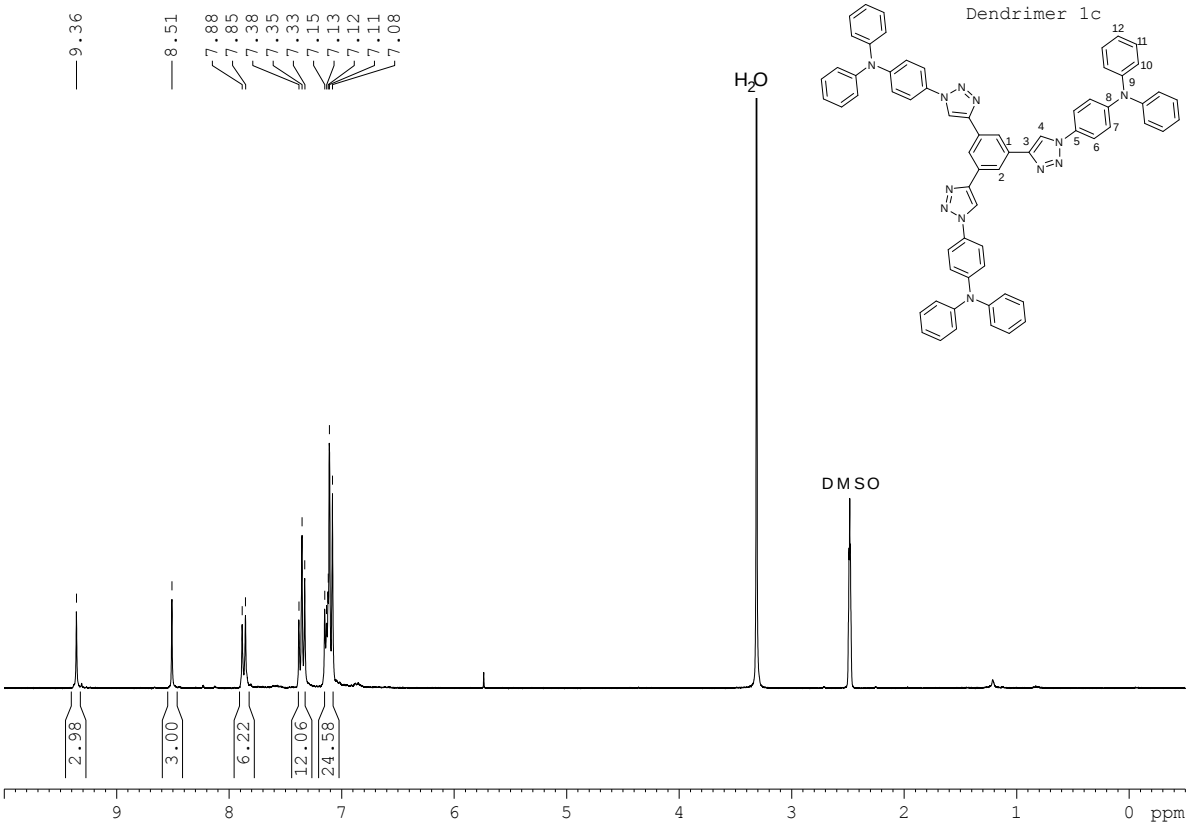


Figure S49: ^{1}H NMR (300 MHz) of **dendrimer 1c** in DMSO-d_6

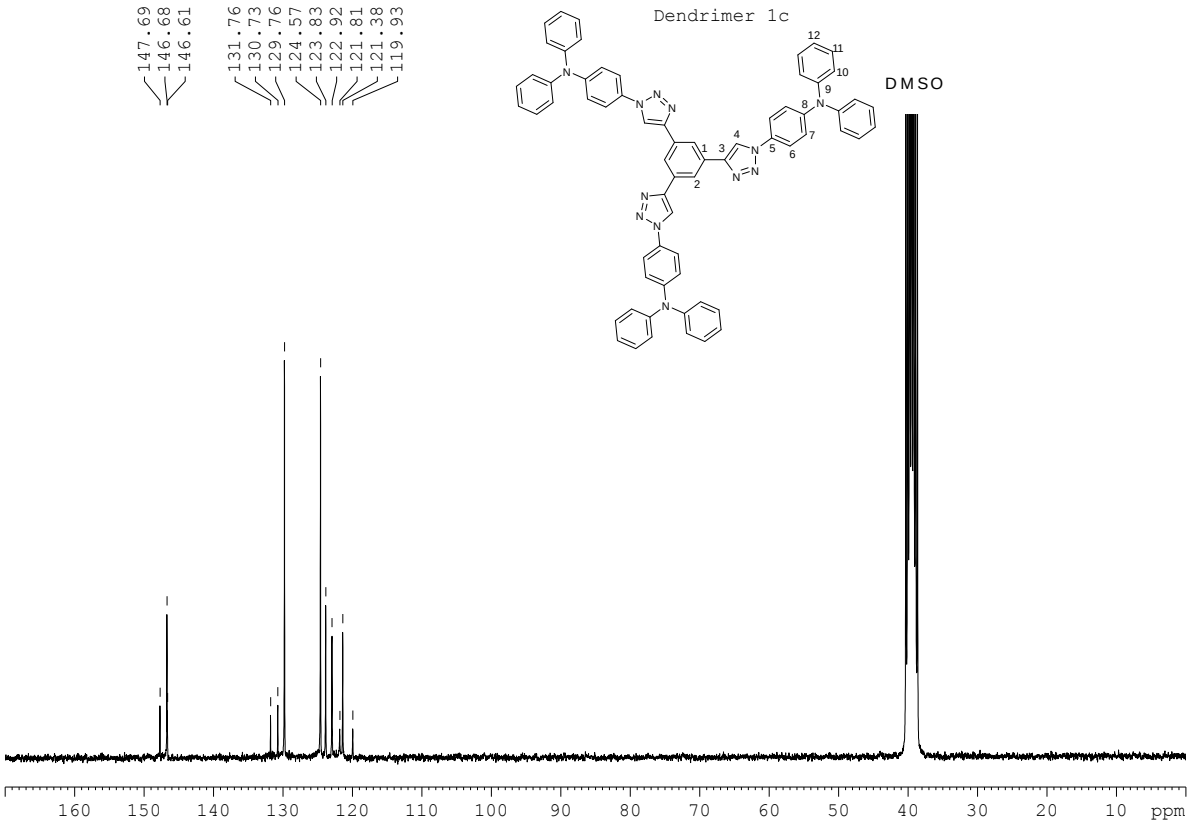


Figure S50: ^{13}C NMR (75.4 MHz) of **dendrimer 1c** in DMSO-d_6

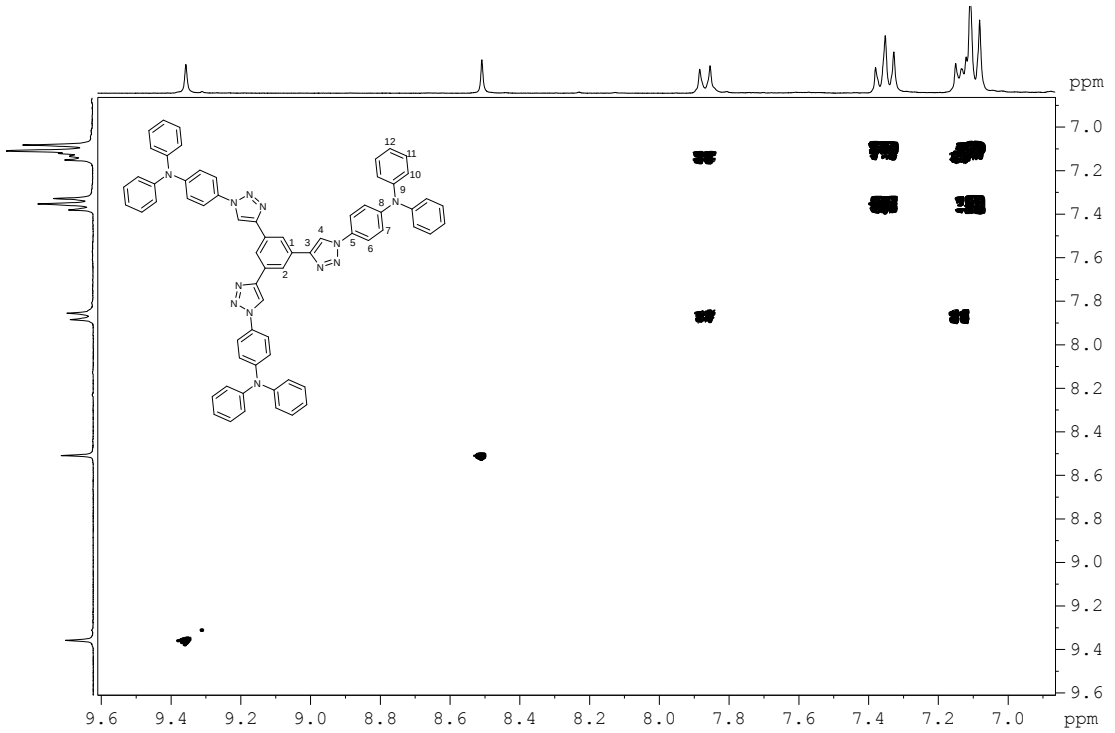


Figure S51. COSY H-H of **dendrimer 1c** in DMSO-d_6.

Dendrimer 1c: HSQC

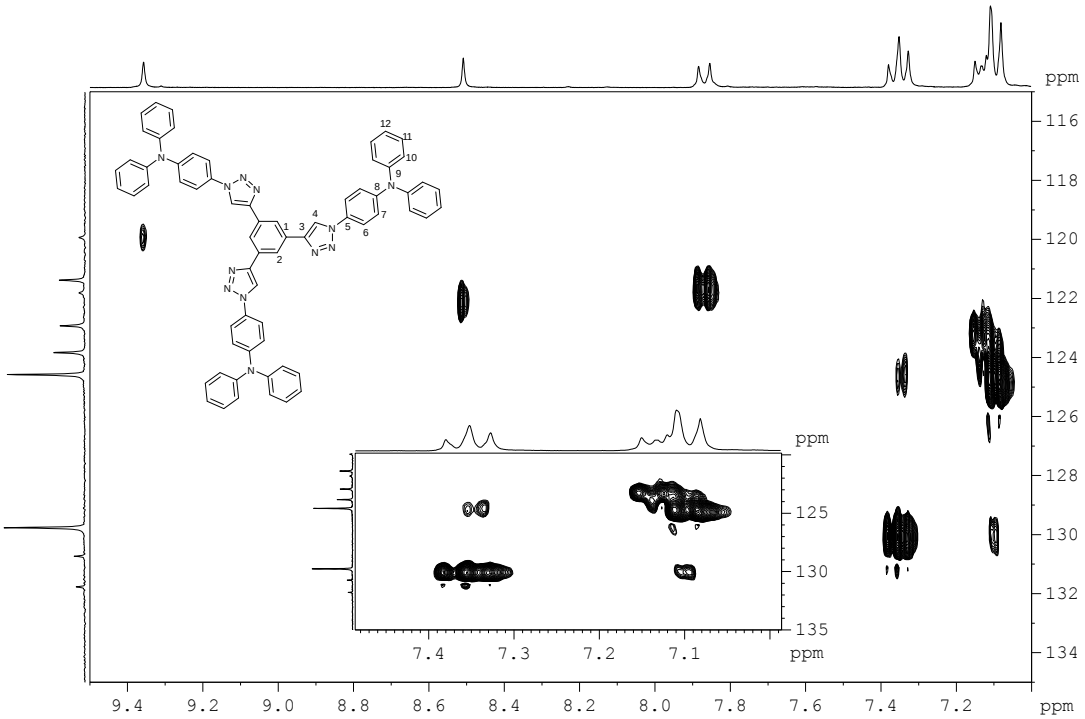


Figure S52. HSQC of **dendrimer 1c** in DMSO-d_6.

Dendrimer 1c: HMBC

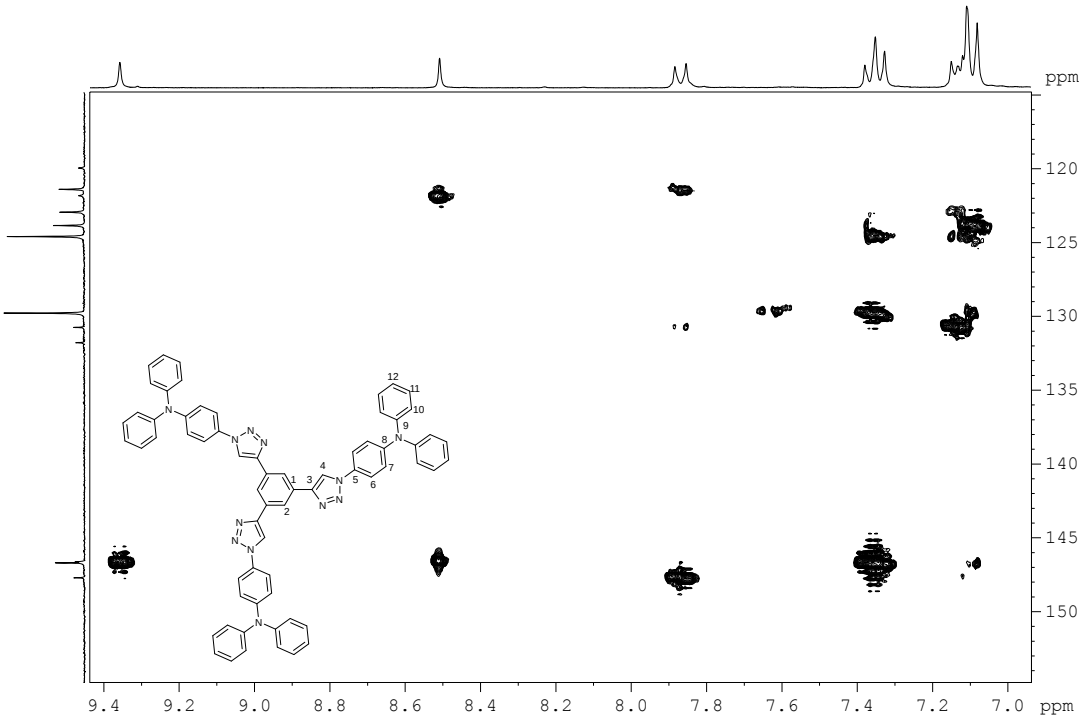


Figure S53. HMBC of **dendrimer 1c** in DMSO-d_6.

Dendrimer 1c: FT-IR spectrum

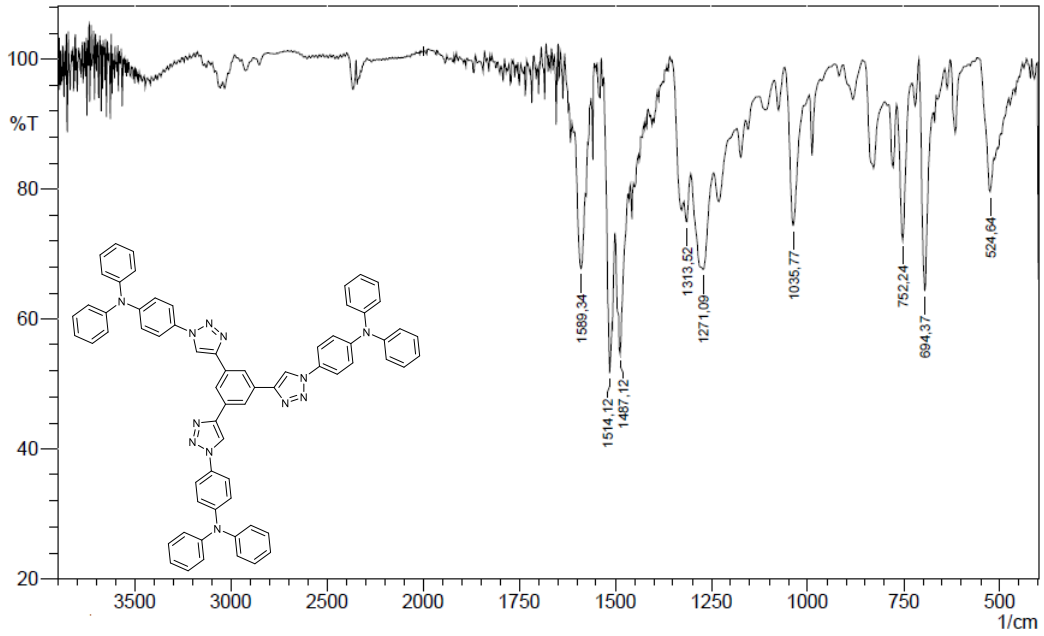


Figure S54. FT-IR (KBr disk) of **dendrimer 1c**.

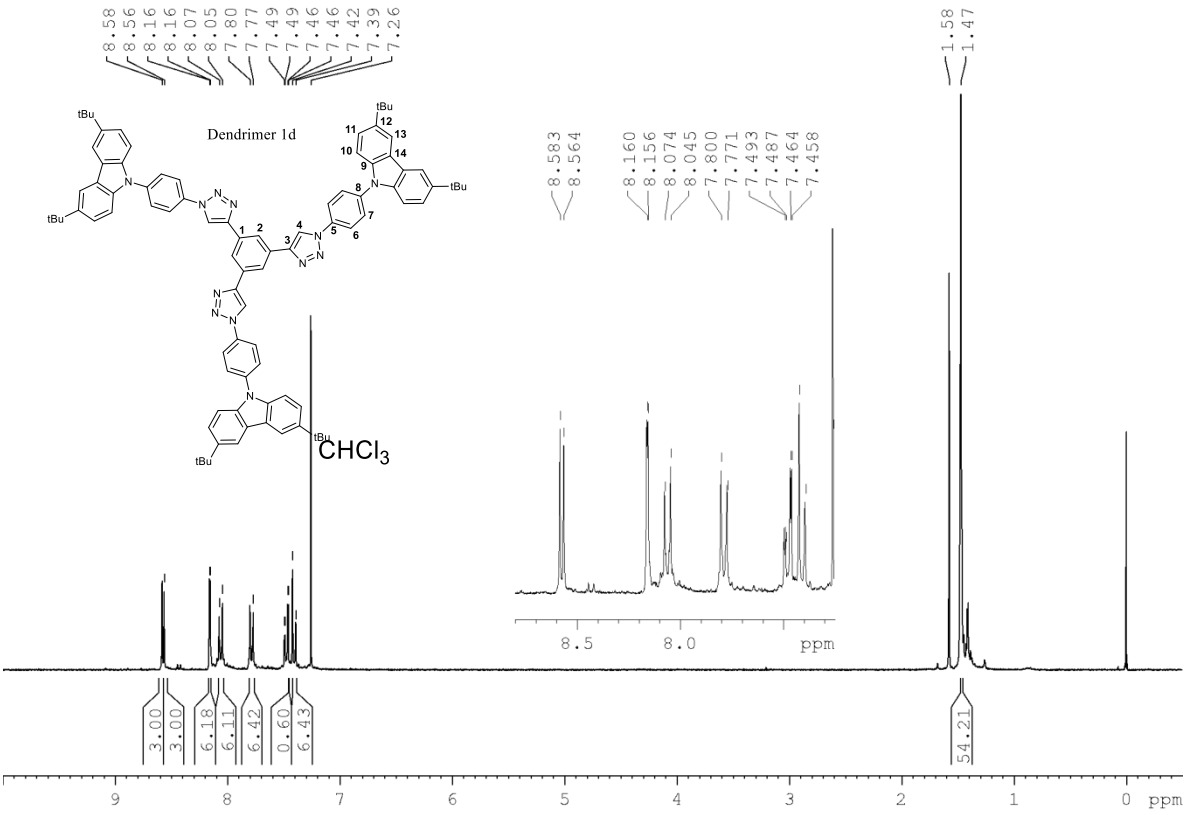


Figure S55: ^{1}H NMR (300 MHz) of **dendrimer 1d** in $CDCl_3$.

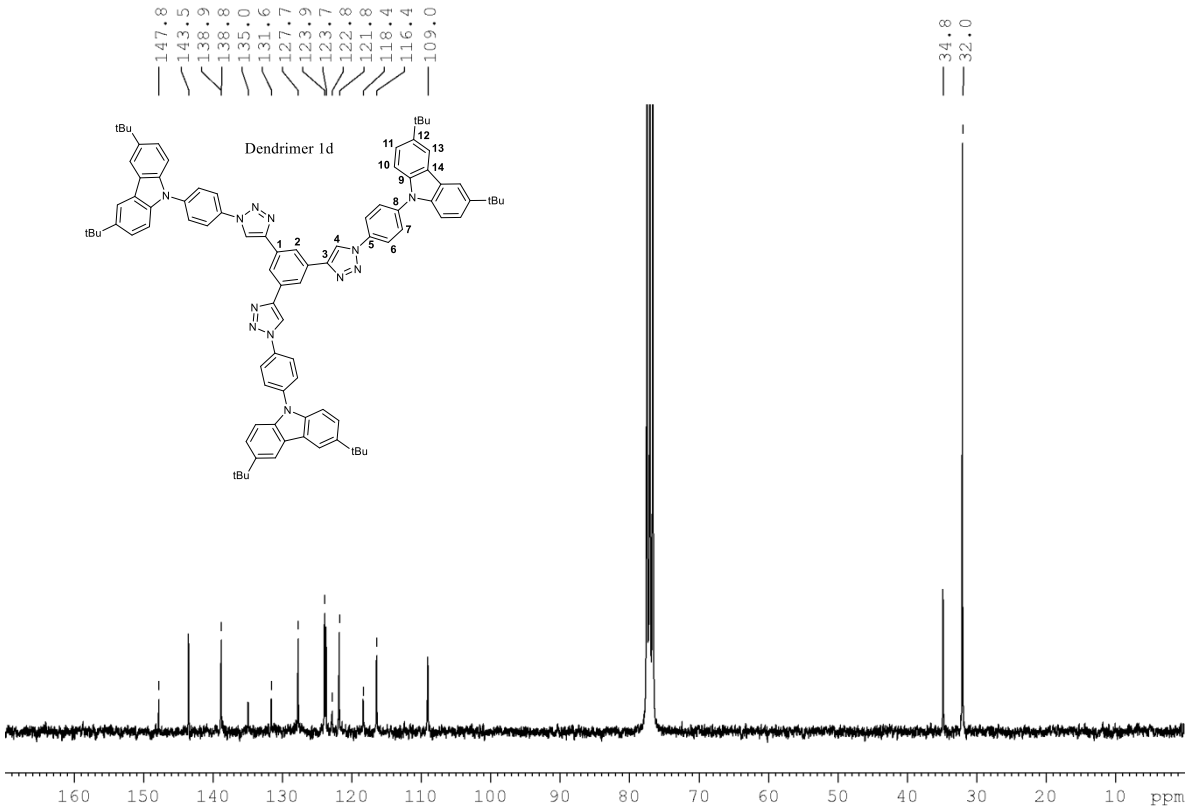


Figure S56: ^{13}C NMR (75.4 MHz) of **dendrimer 1d** in $CDCl_3$.

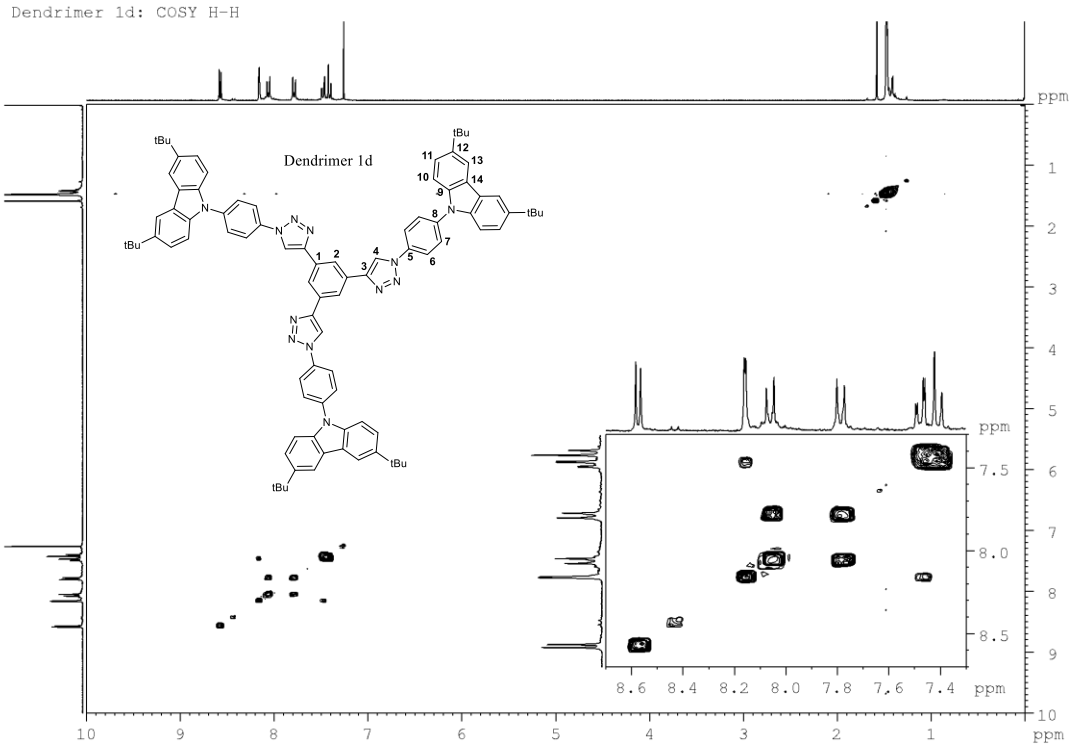


Figure S57. COSY H-H of **dendrimer 1d** in $CDCl_3$.

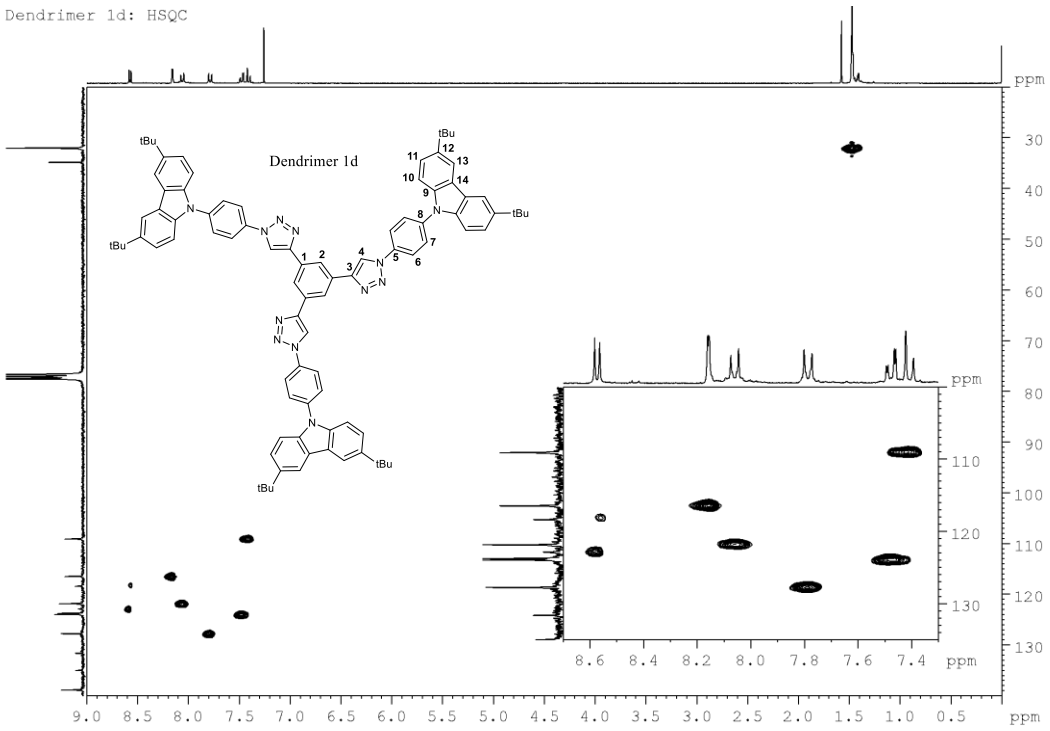


Figure S58. HSQC of **dendrimer 1d** $CDCl_3$.

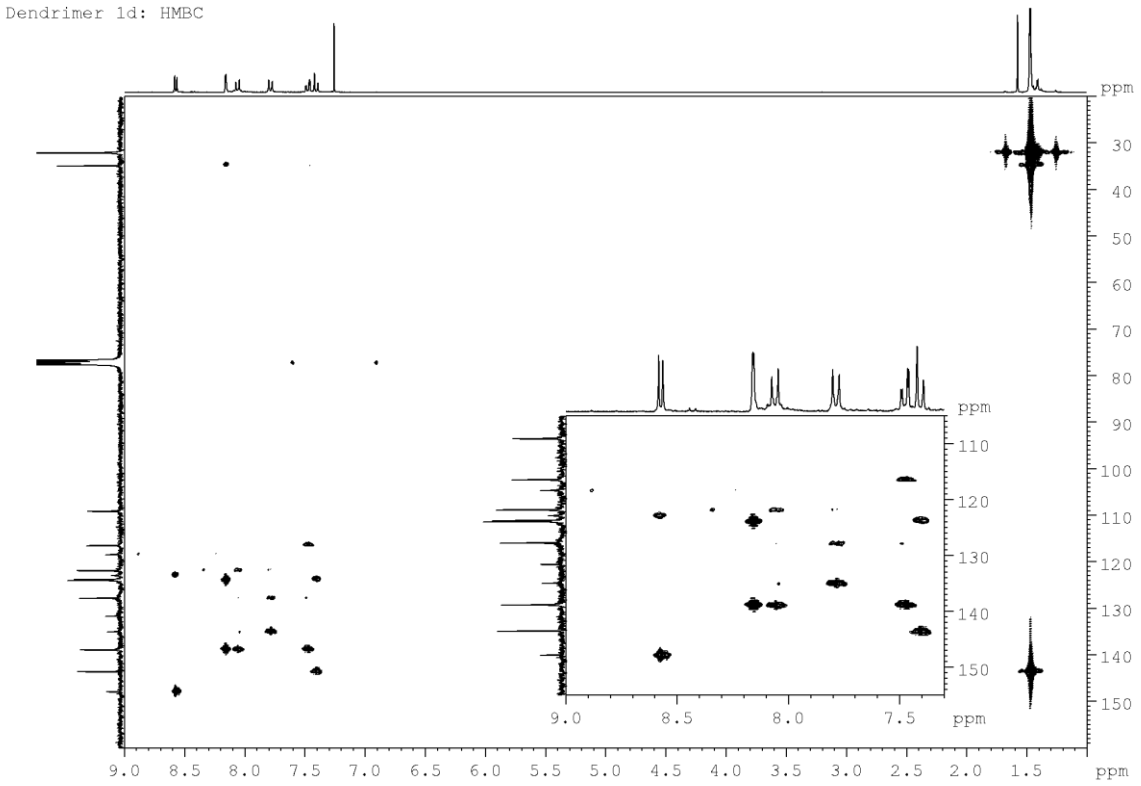


Figure S59. HMBC of **dendrimer 1d** in $CDCl_3$.

Dendrimer 1d: FT-IR spectrum

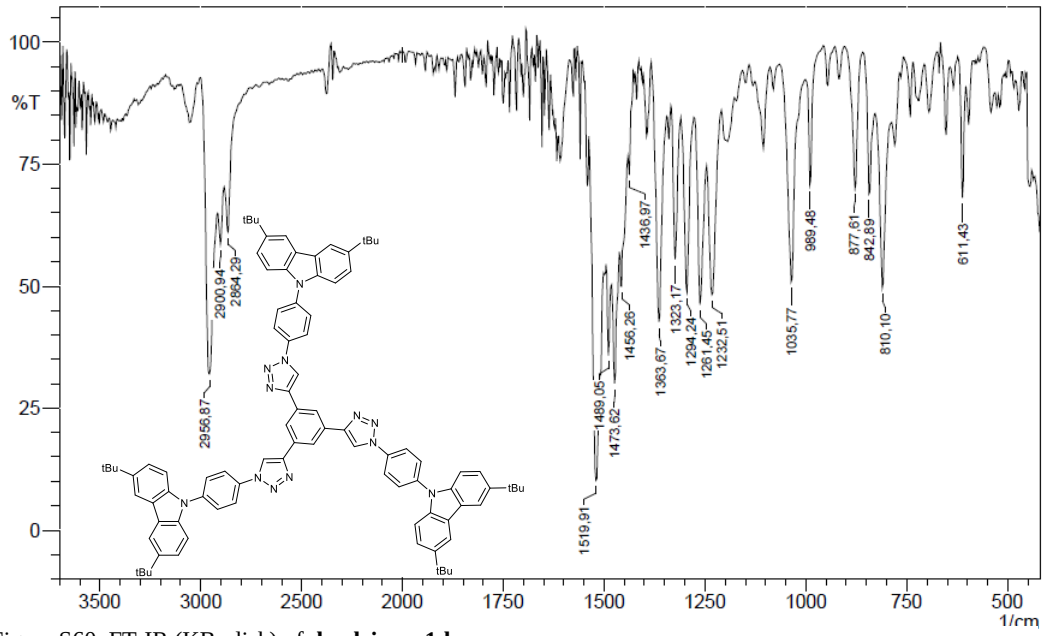


Figure S60. FT-IR (KBr disk) of **dendrimer 1d**.

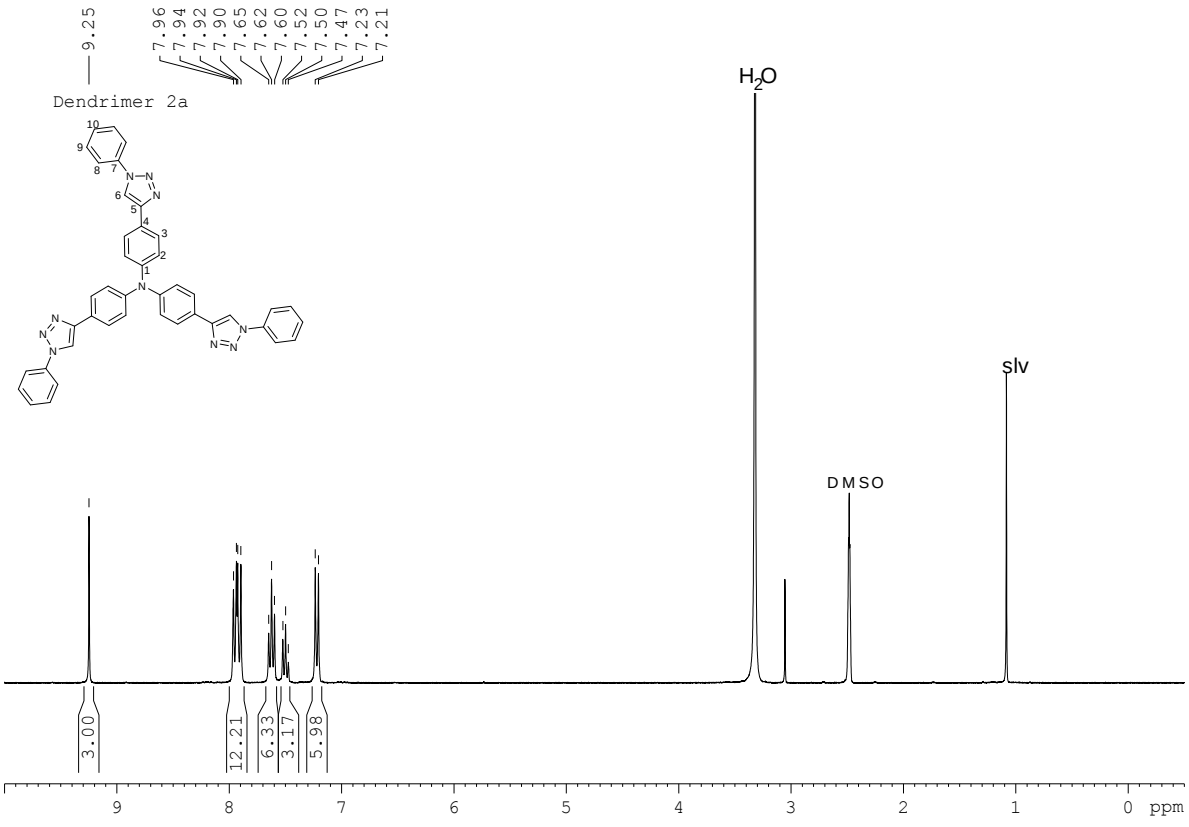


Figure S61: ^{1}H NMR (300 MHz) of **dendrimer 2a** in DMSO-d_6

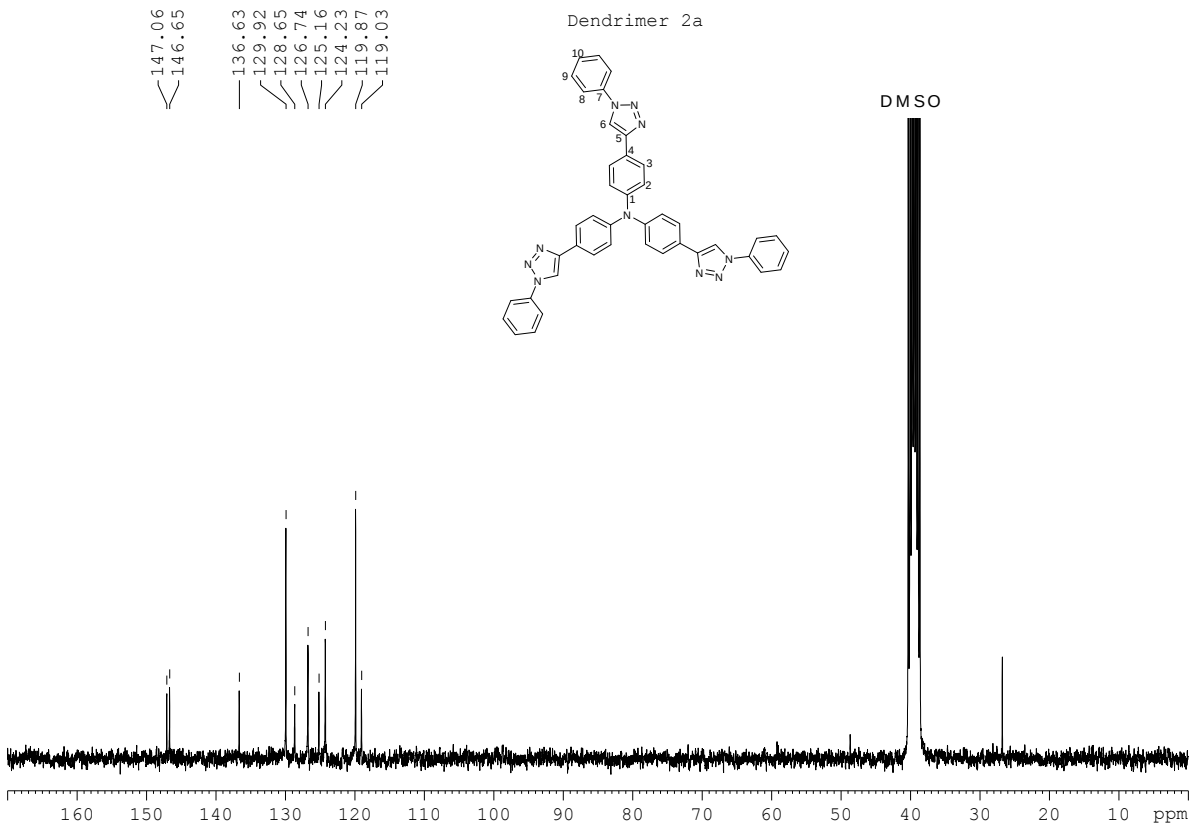


Figure S62: ^{13}C NMR (75.4 MHz) of **dendrimer 2a** in DMSO-d_6

Dendrimer 2a: COSY H-H

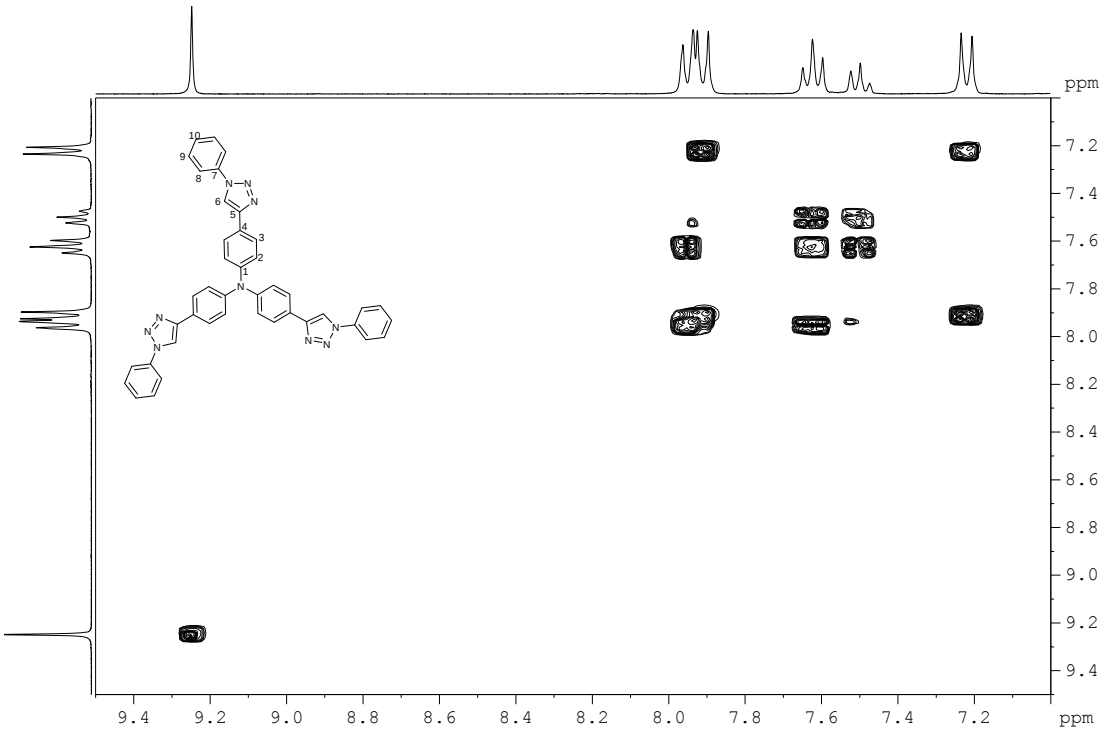


Figure S63. COSY H-H of **dendrimer 2a** in DMSO-d_6.

Dendrimer 2a: HSQC

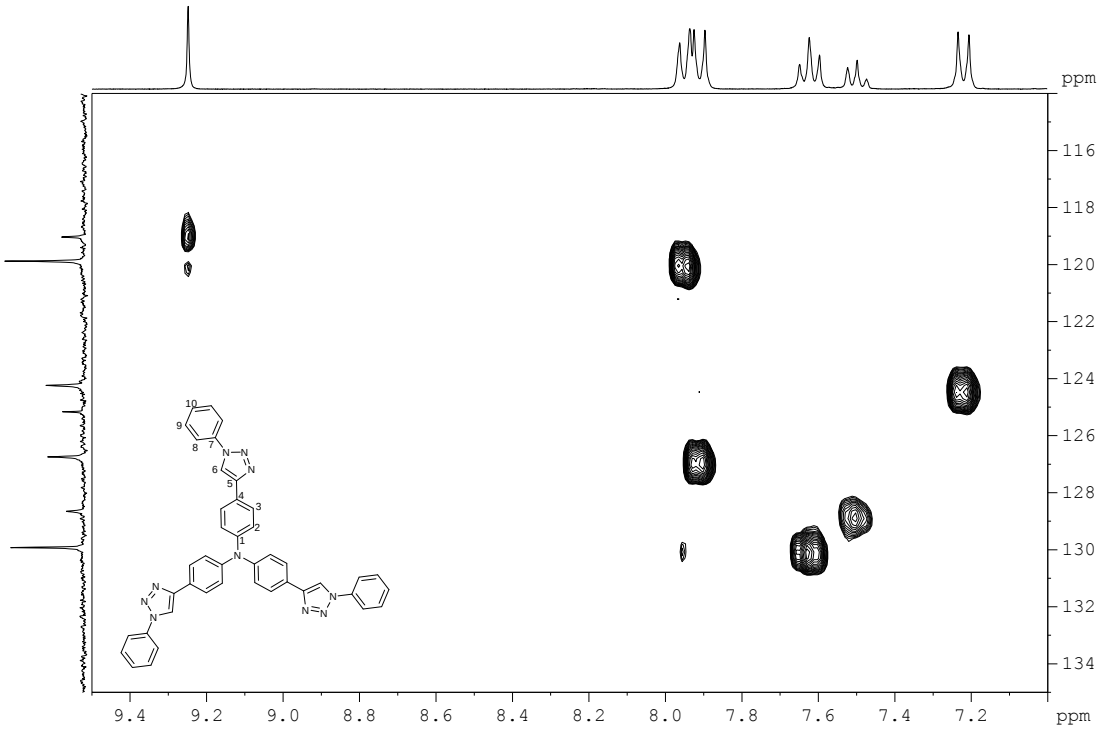


Figure S64. HSQC of **dendrimer 2a** in DMSO-d_6.

Dendrimer 2a: HMBC

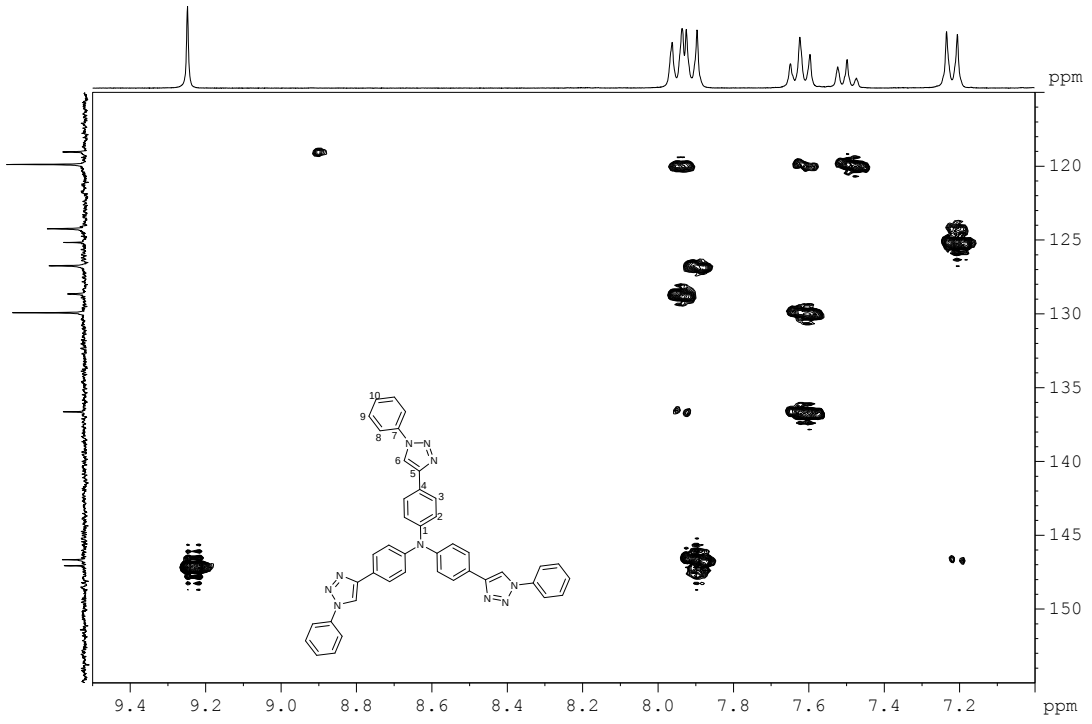


Figure S65. HMBC of **dendrimer 2a** in DMSO-d_6.

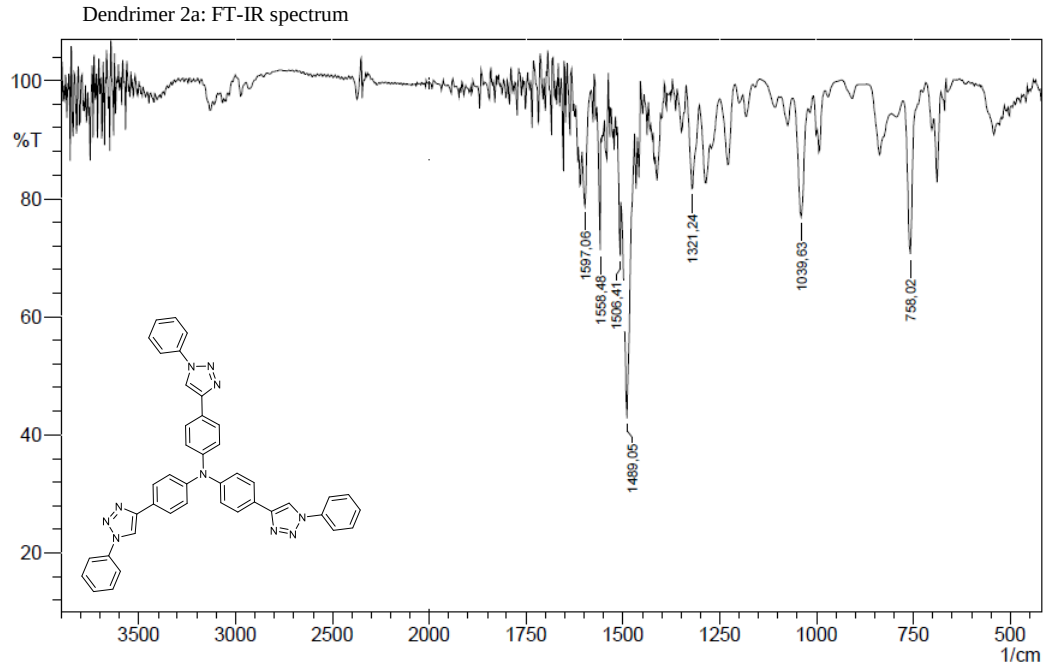


Figure S66. FT-IR (KBr disk) of **dendrimer 2a**.

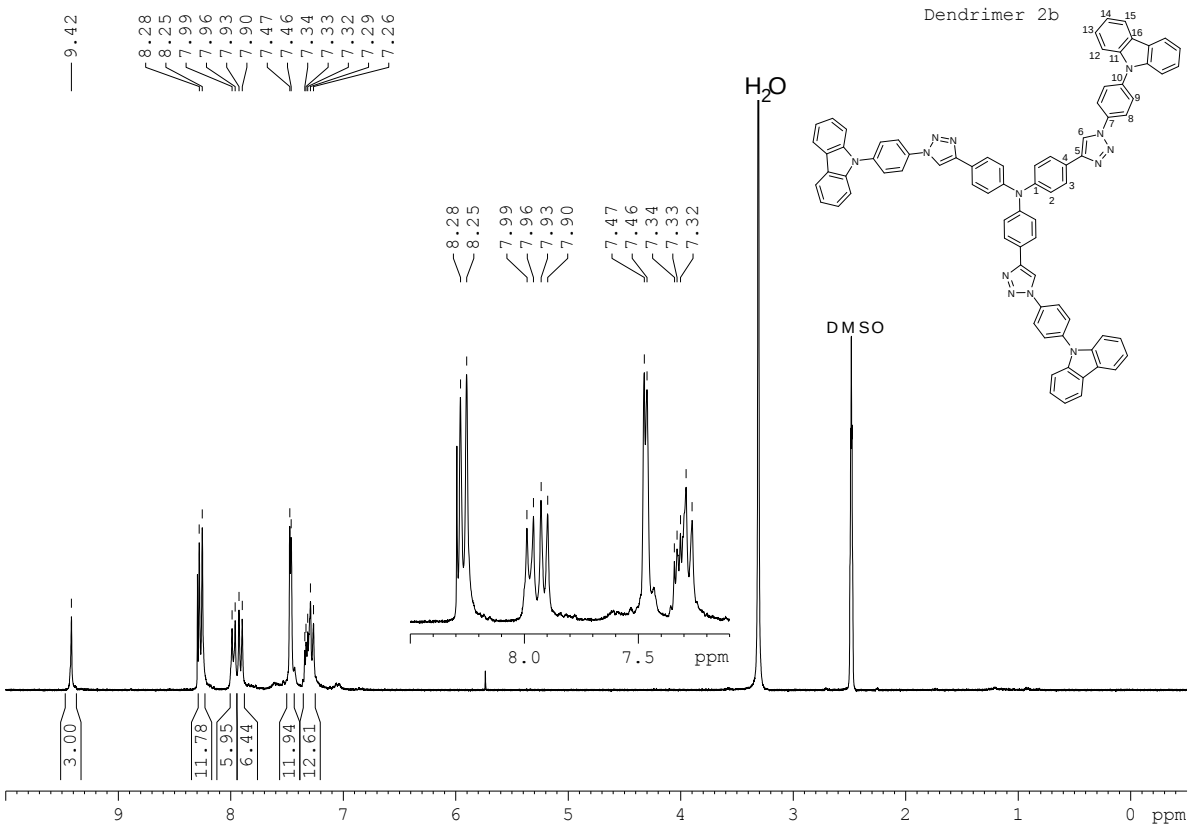


Figure S67: ^{1}H NMR (300 MHz) of **dendrimer 2b** in DMSO-d_6

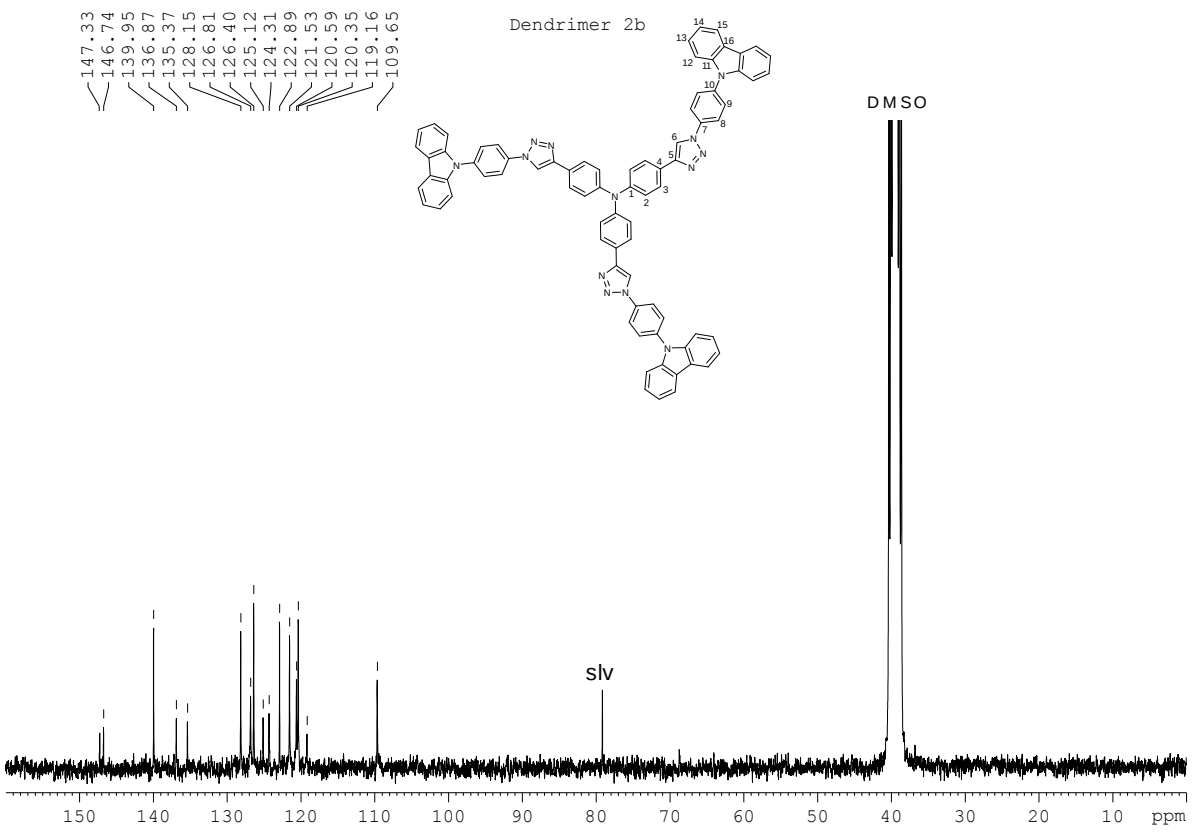


Figure S68: ^{13}C NMR (75.4 MHz) of **dendrimer 2b** in DMSO-d_6

Dendrimer 2b: COSY H-H

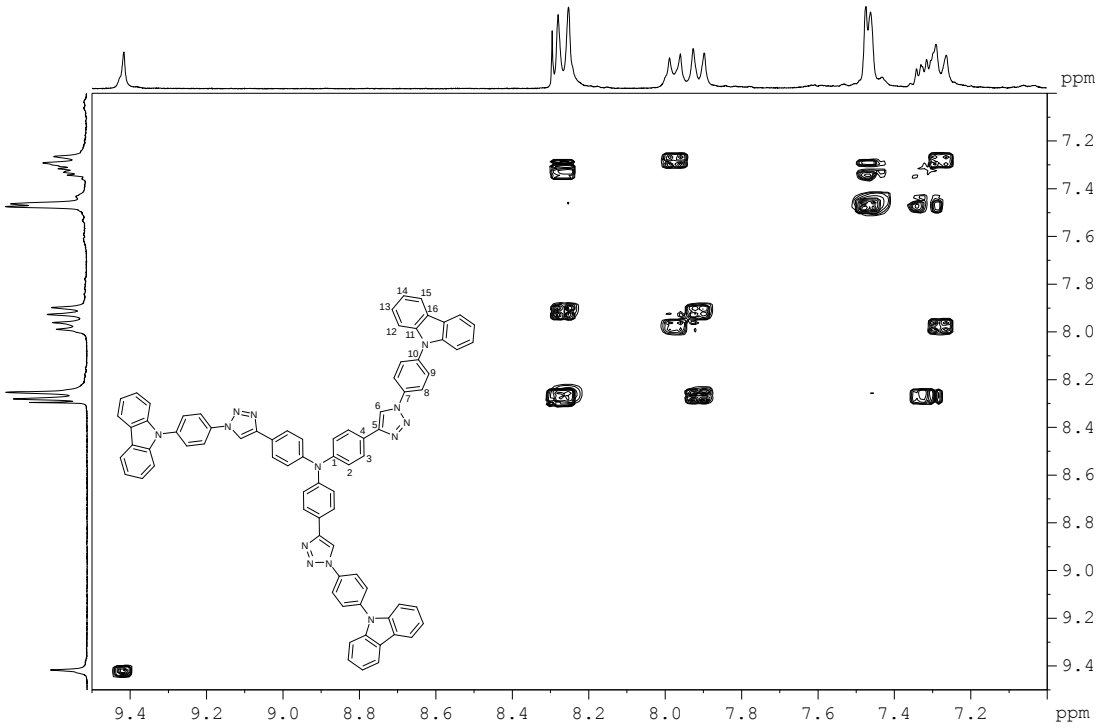


Figure S69. COSY H-H of **dendrimer 2b** in DMSO-d_6.

Dendrimer 2b: HSQC

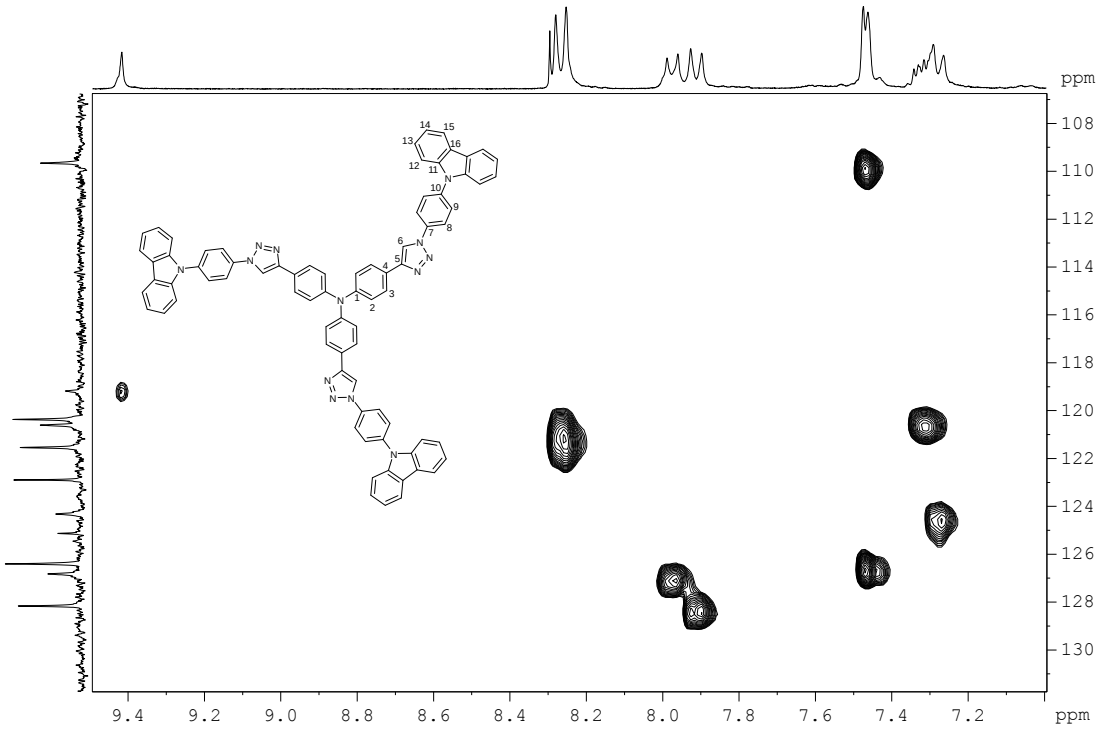


Figure S70. HSQC of **dendrimer 2b** in DMSO-d_6.

Dendrimer 2b: HMBC

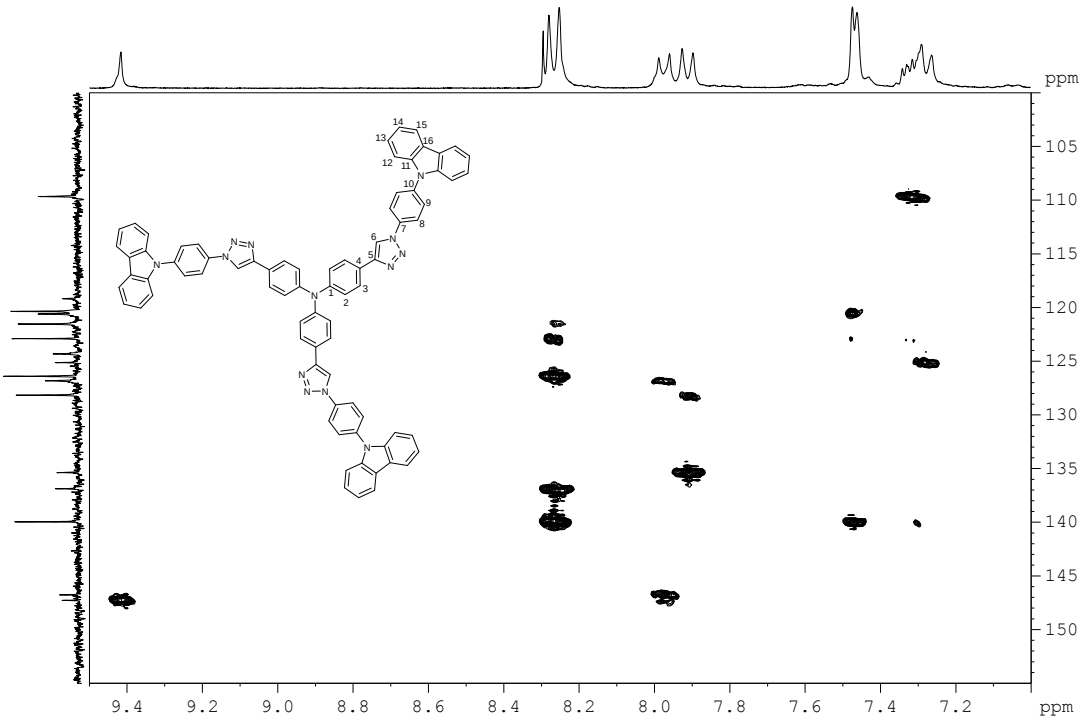


Figure S71. HMBC of **dendrimer 2b** in DMSO-d_6.

Dendrimer 2b: FT-IR spectrum

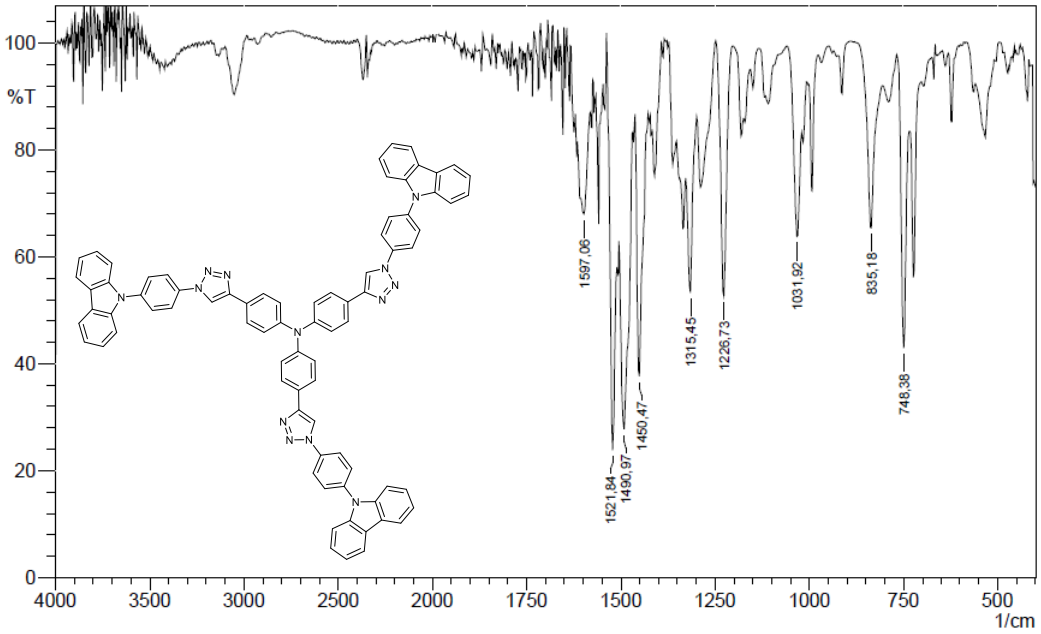


Figure S72. FT-IR (KBr disk) of **dendrimer 2b**.

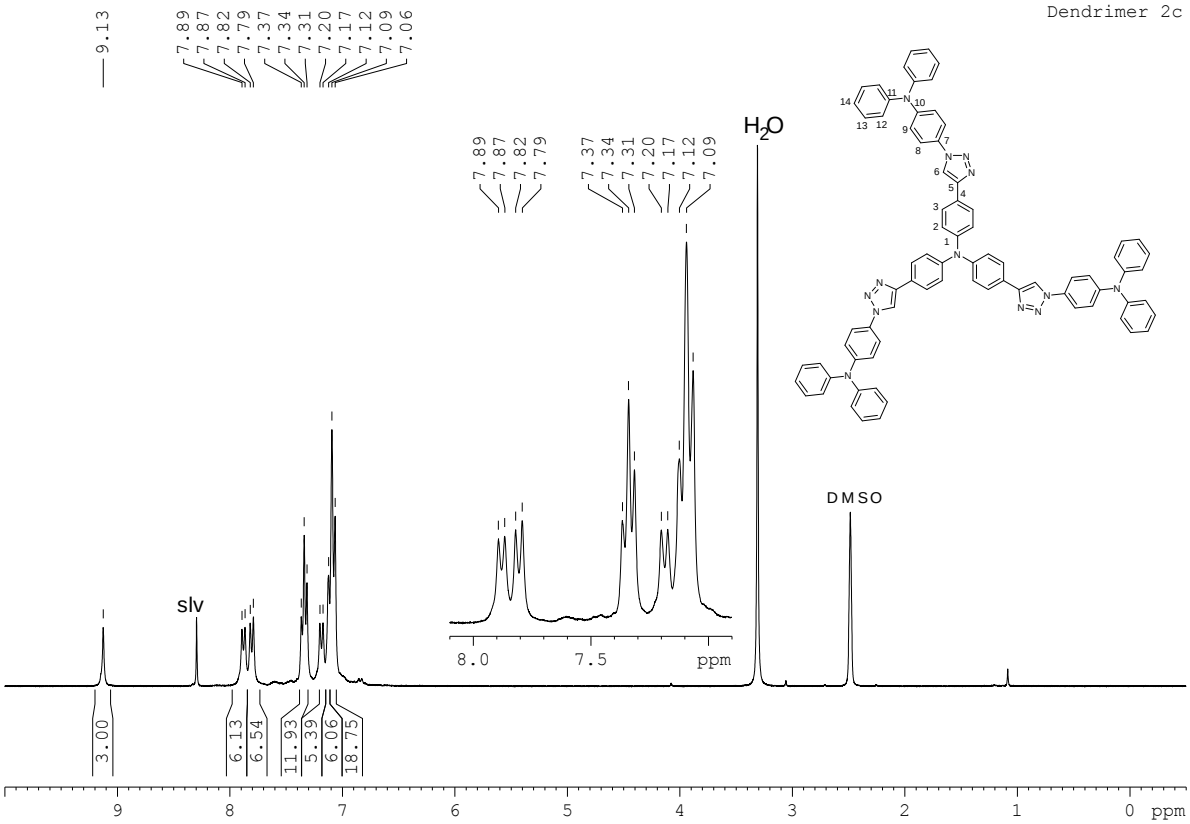


Figure S73: ^{1}H NMR (300 MHz) of **dendrimer 2c** in DMSO-d_6

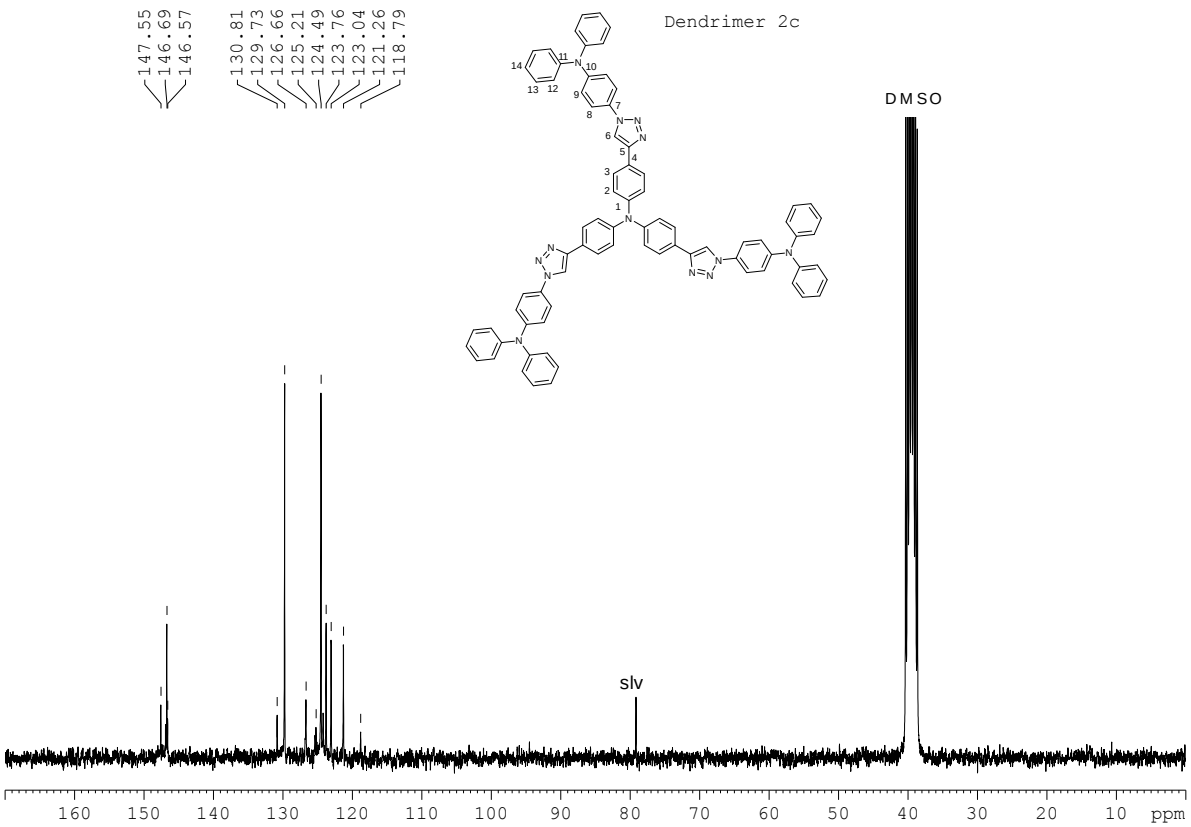


Figure S74: ^{13}C NMR (75.4 MHz) of **dendrimer 2c** in DMSO-d_6

Dendrimer 2c: COSY H-H

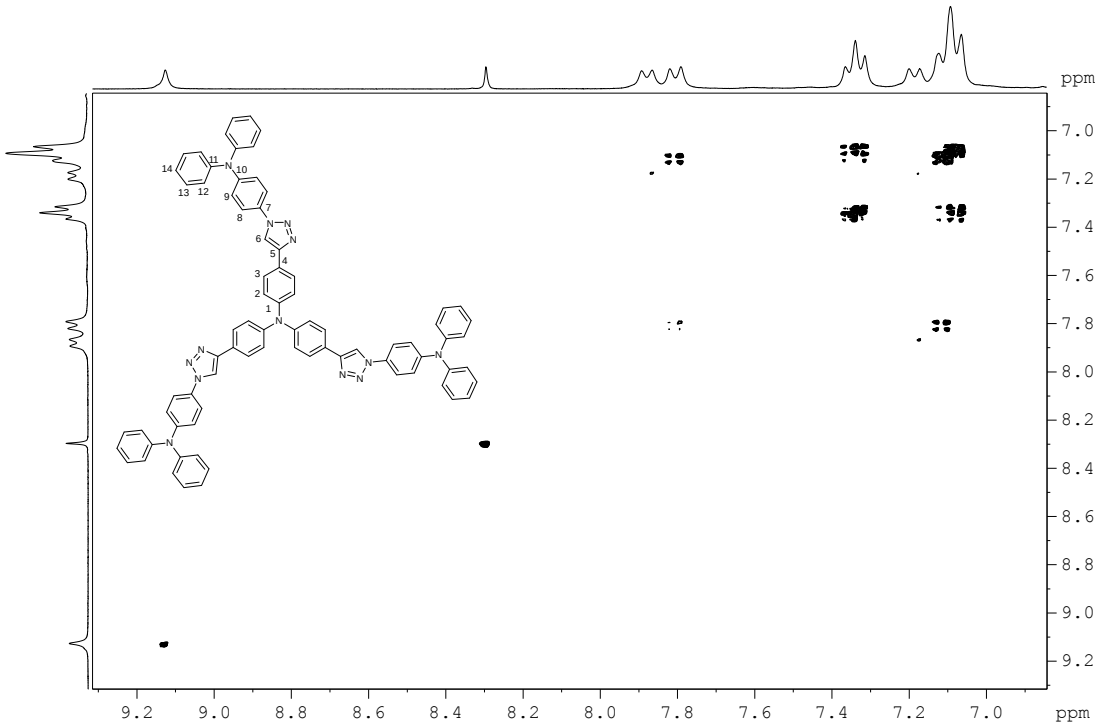


Figure S75. COSY H-H of **dendrimer 2c** in DMSO-d_6.

Dendrimer 2c: HSQC

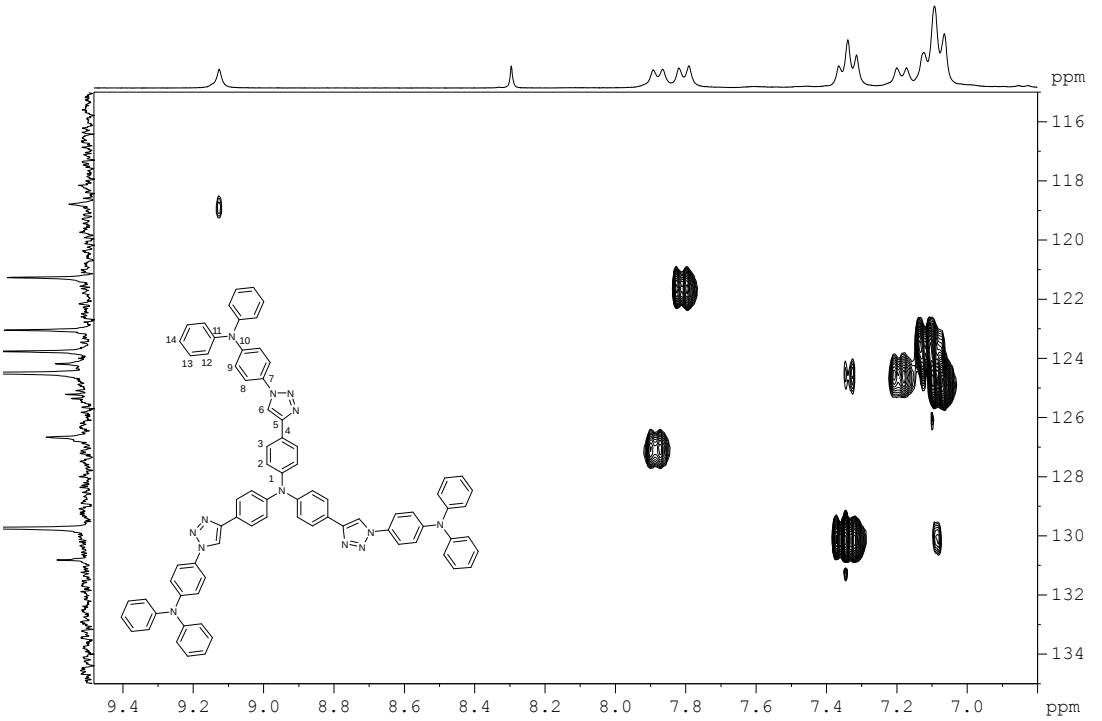


Figure S76. HSQC of **dendrimer 2c** in DMSO-d_6. 1

Dendrimer 2c: HMBC

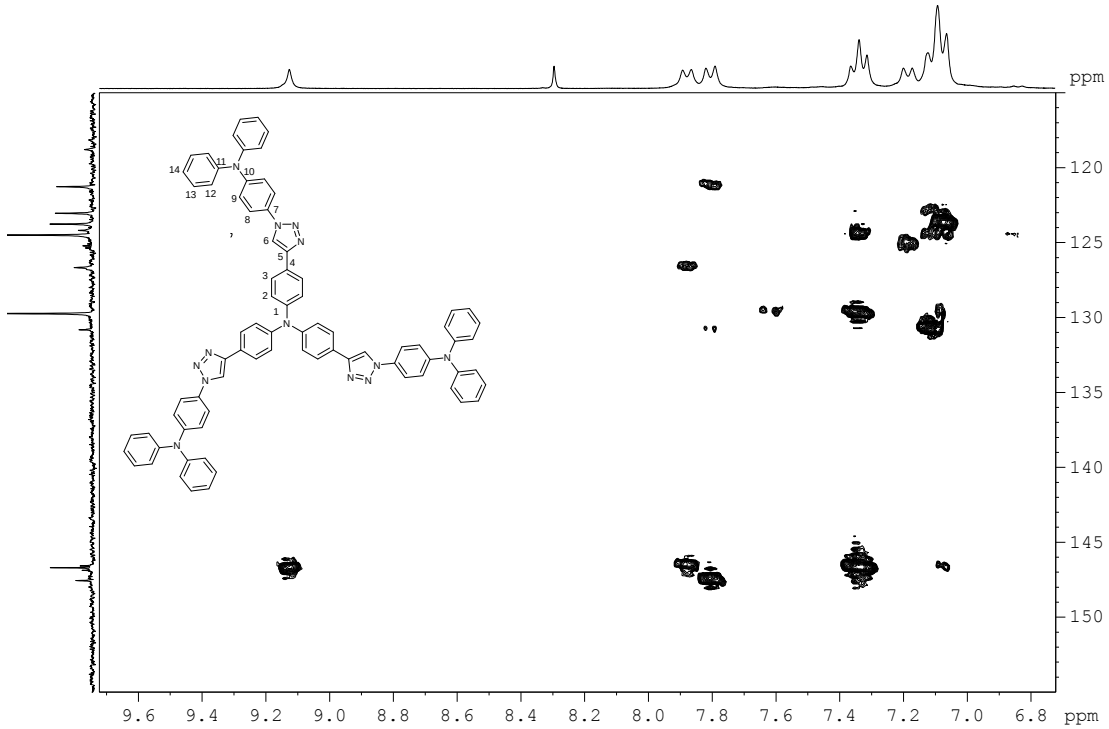


Figure S77. HMBC of **dendrimer 2c** in DMSO-d_6.

Dendrimer 2c: FT-IR spectrum

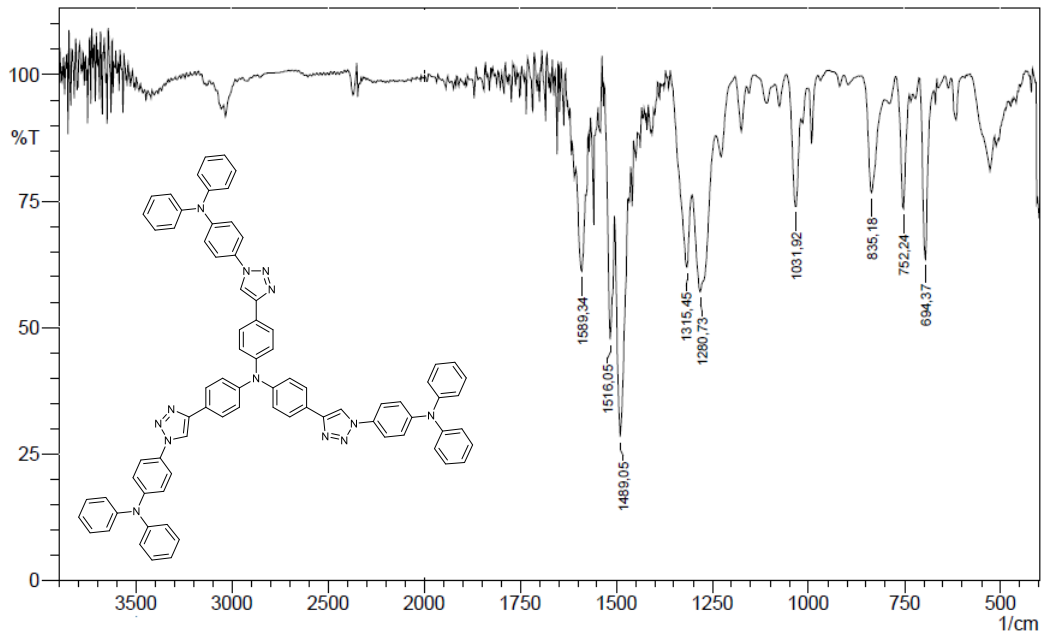


Figure S78. FT-IR (KBr disk) of **dendrimer 2c**.

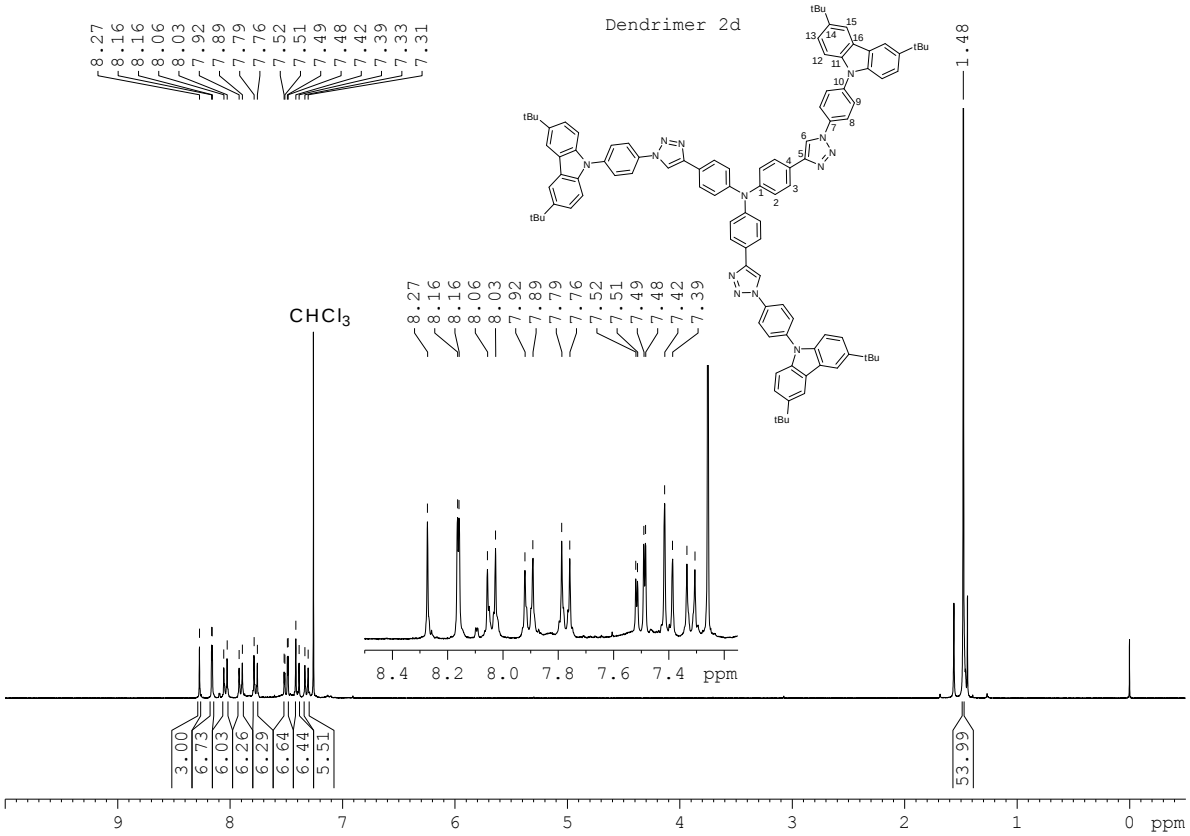


Figure S79: ^{1}H NMR (300 MHz) of **dendrimer 2d** in $CDCl_3$

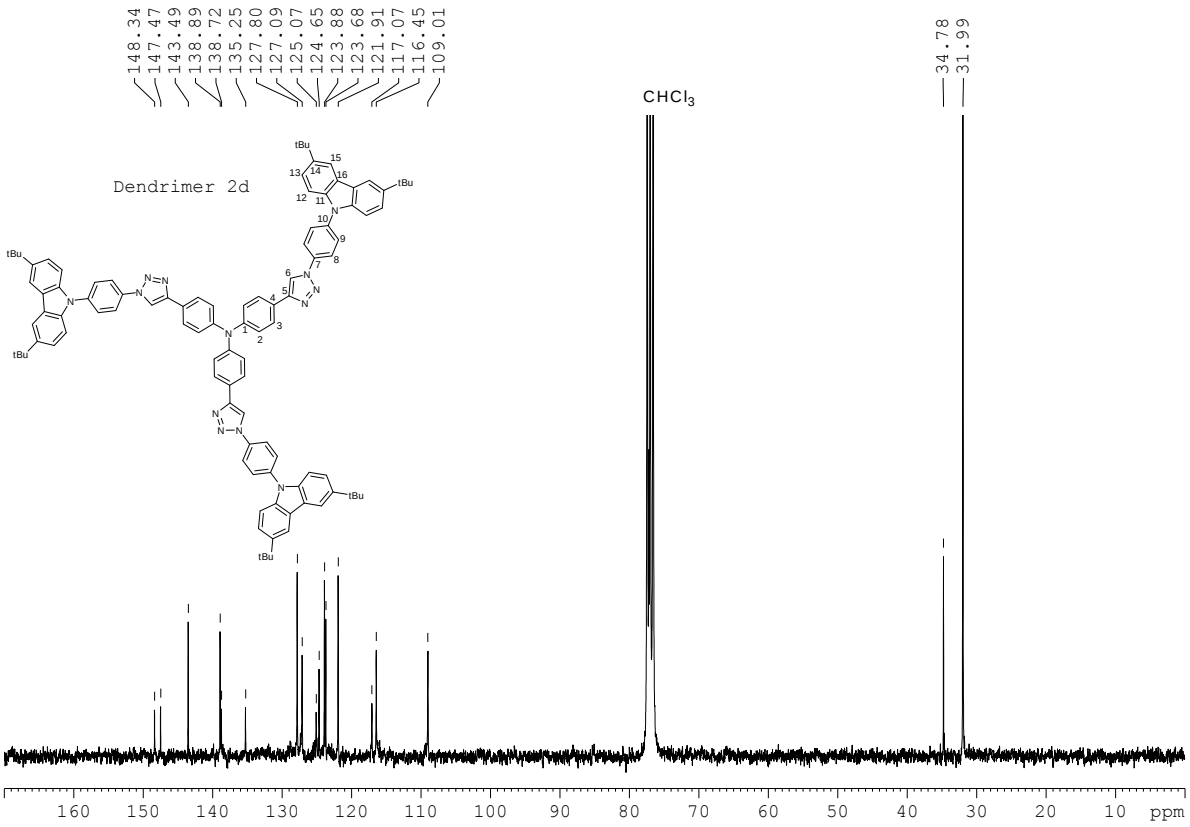


Figure S80: ^{13}C NMR (75.4 MHz) of **dendrimer 2d** in $CDCl_3$

Dendrimer 2d: COSY H-H

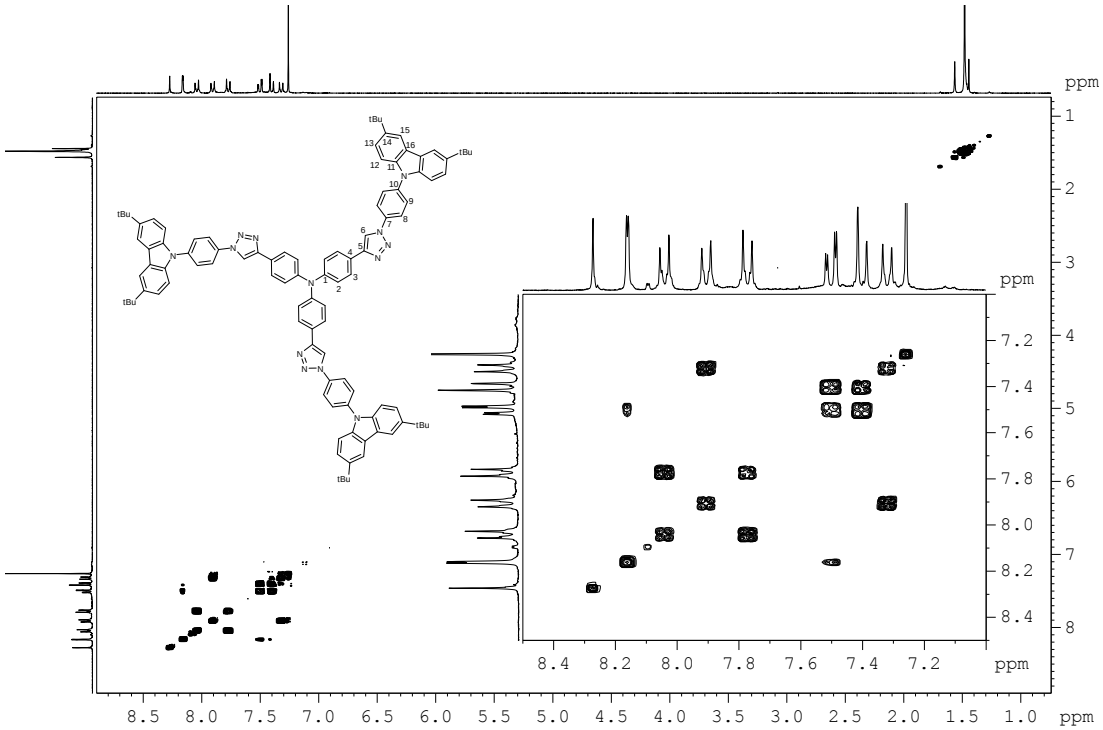


Figure S81. COSY H-H of **dendrimer 2d** in $CDCl_3$.

Dendrimer 2d: HSQC

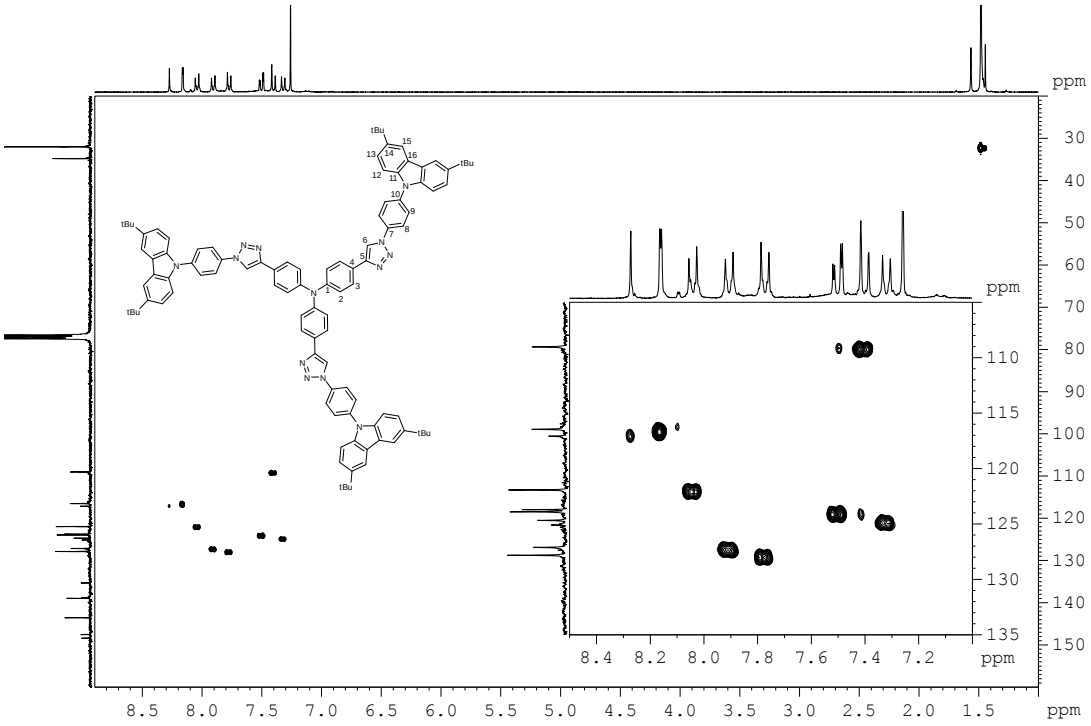


Figure S82. HSQC of **dendrimer 2d** in $CDCl_3$.

Dendrimer 2d: HMBC

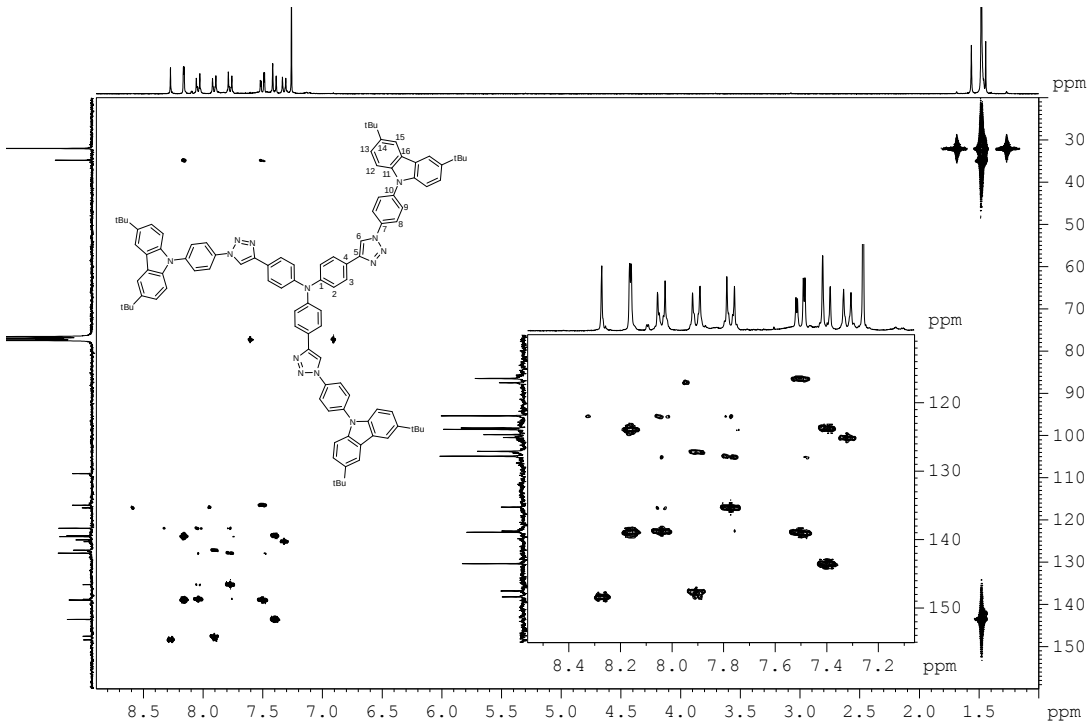


Figure S83. HMBC of **dendrimer 2d** in $CDCl_3$.

Dendrimer 2d: FT-IR spectrum

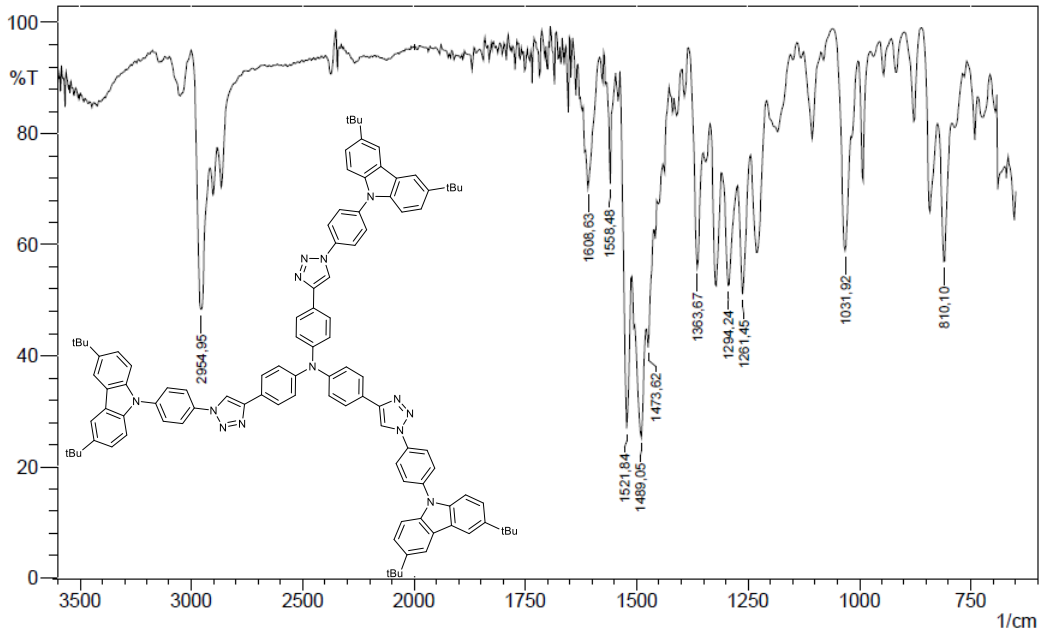


Figure S84. FT-IR (KBr disk) of **dendrimer 2d**.

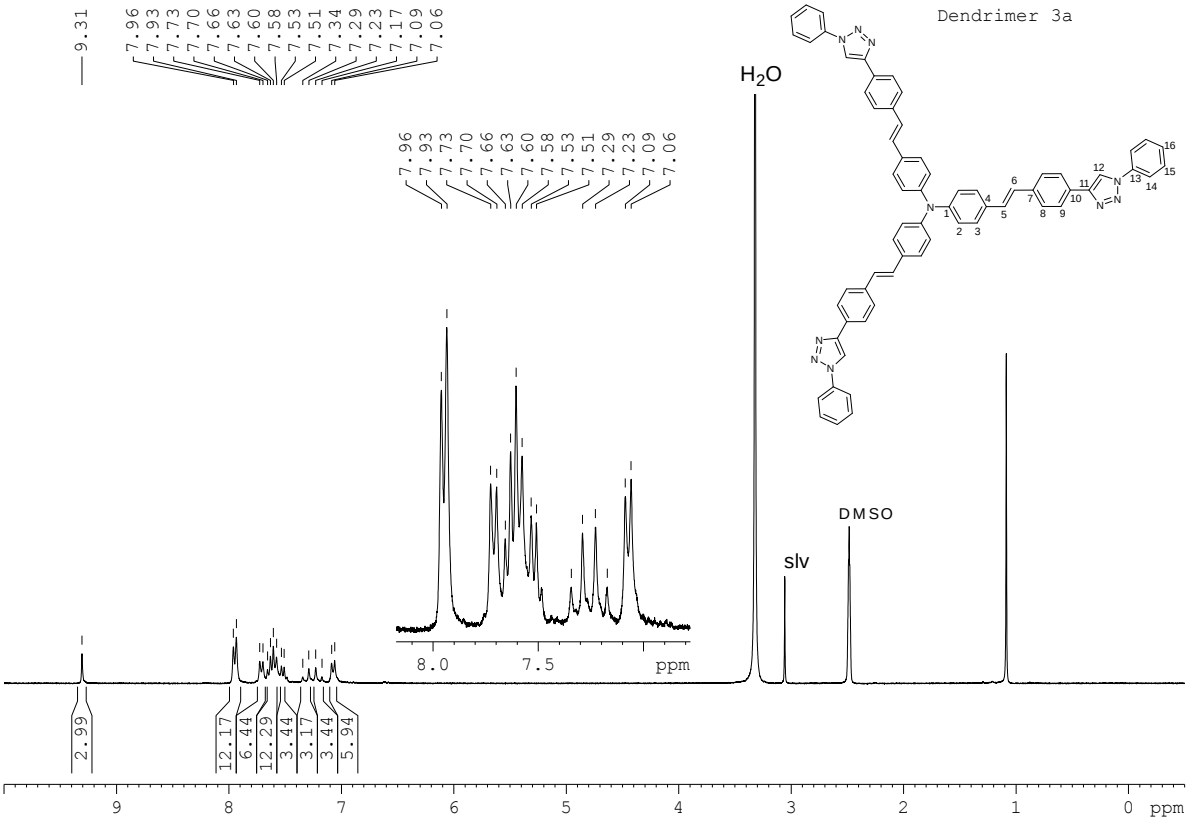


Figure S85: ^{1}H NMR (300 MHz) of **dendrimer 3a** in DMSO-d_6

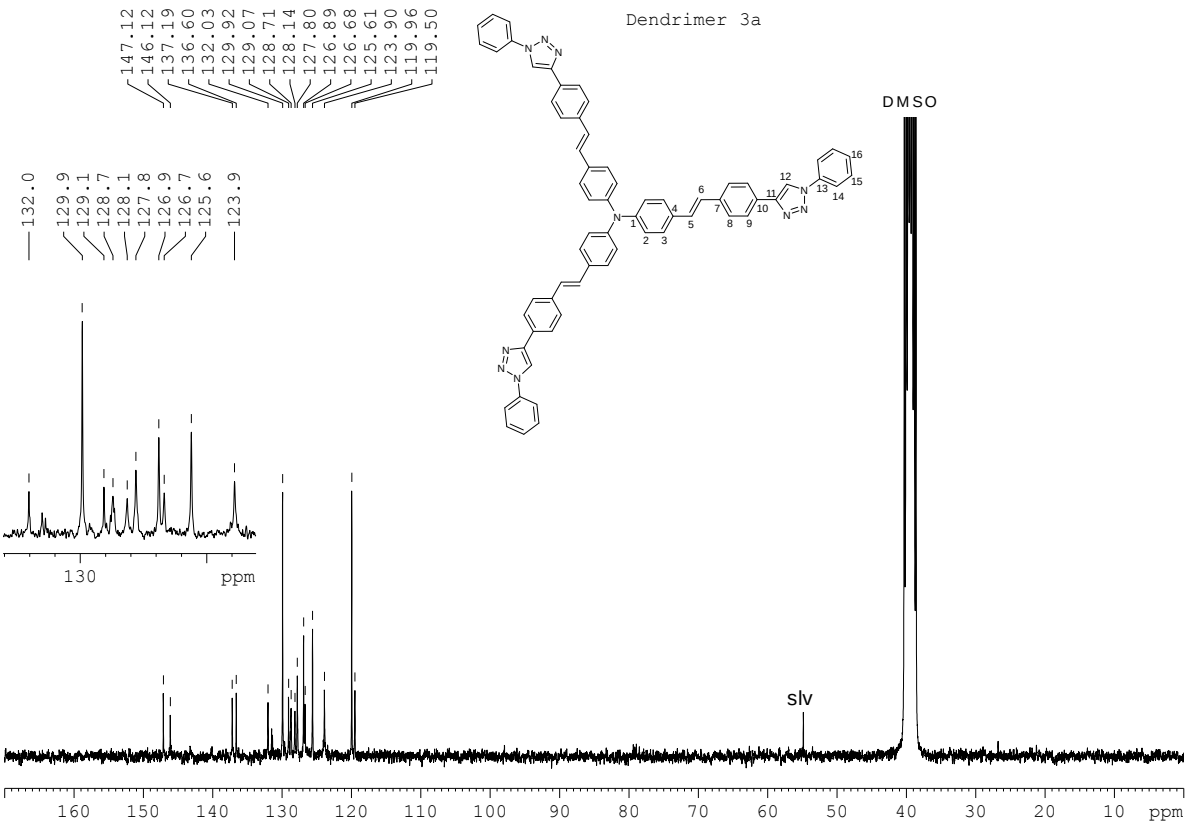


Figure S86: ^{13}C NMR (75.4 MHz) of **dendrimer 3a** in DMSO-d_6

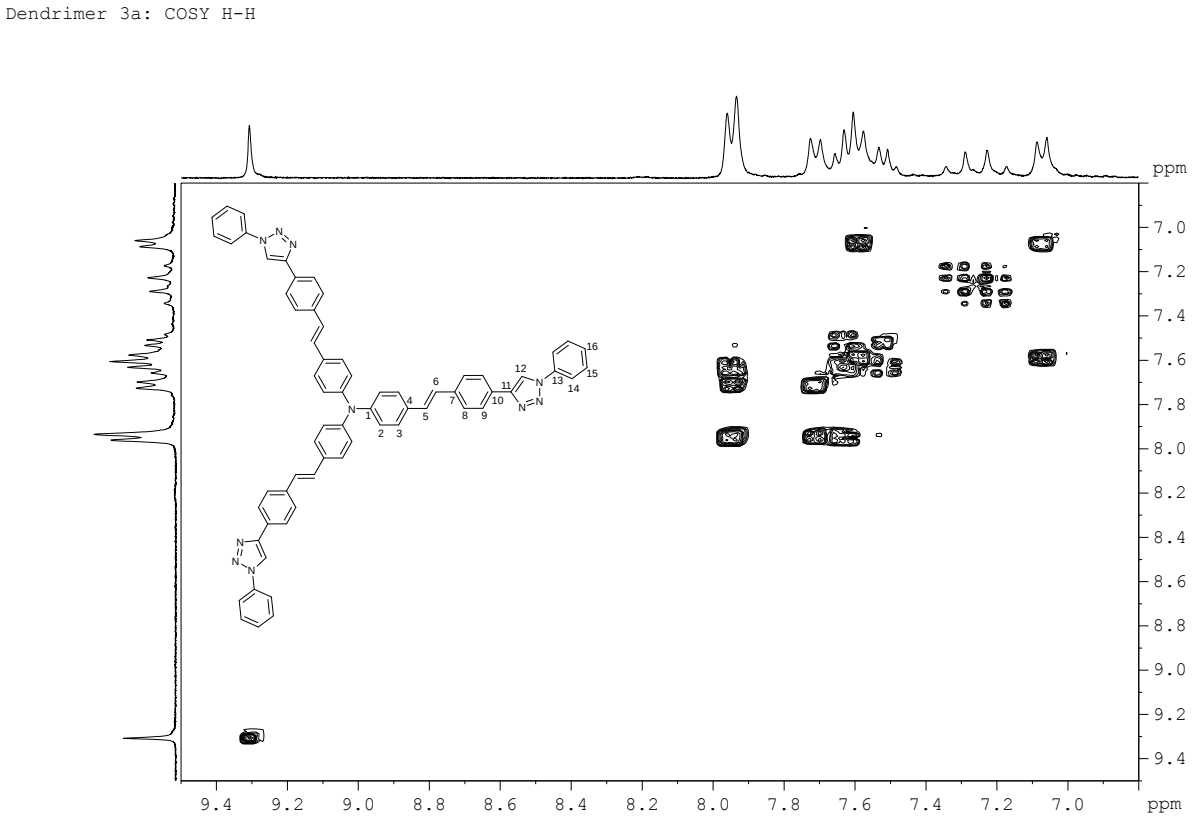


Figure S87. COSY H-H of **dendrimer 3a** in DMSO-d_6.

Dendrimer 3a: HSQC

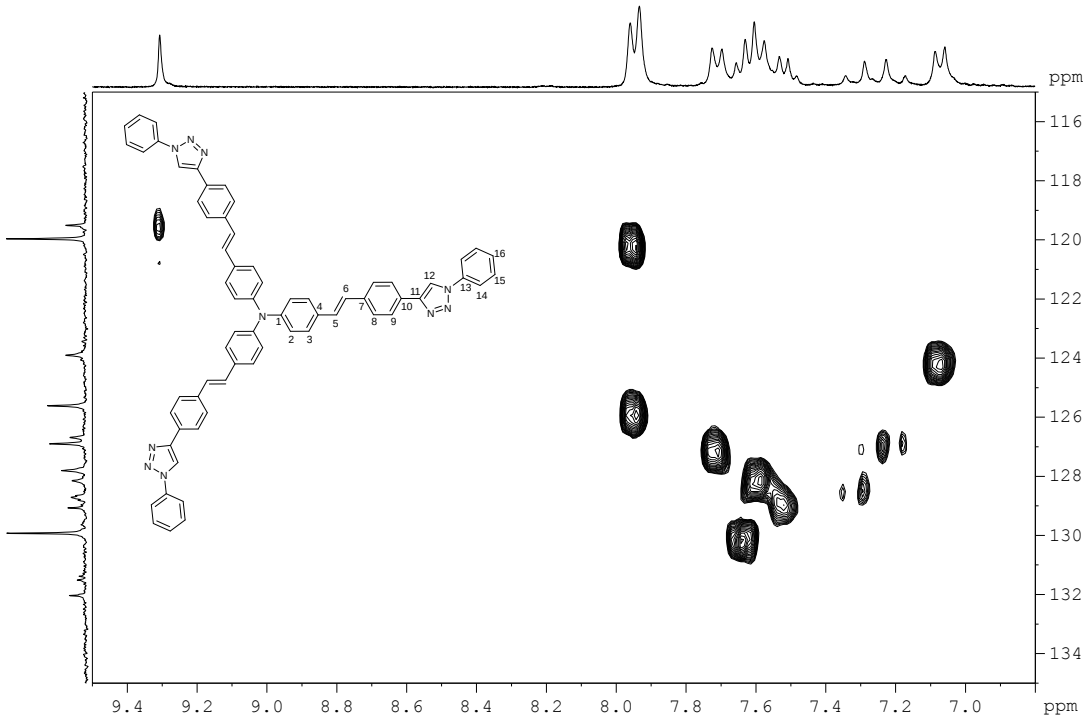


Figure S88. HSQC of **dendrimer 3a** in DMSO-d_6.

Dendrimer 3a: HMBC

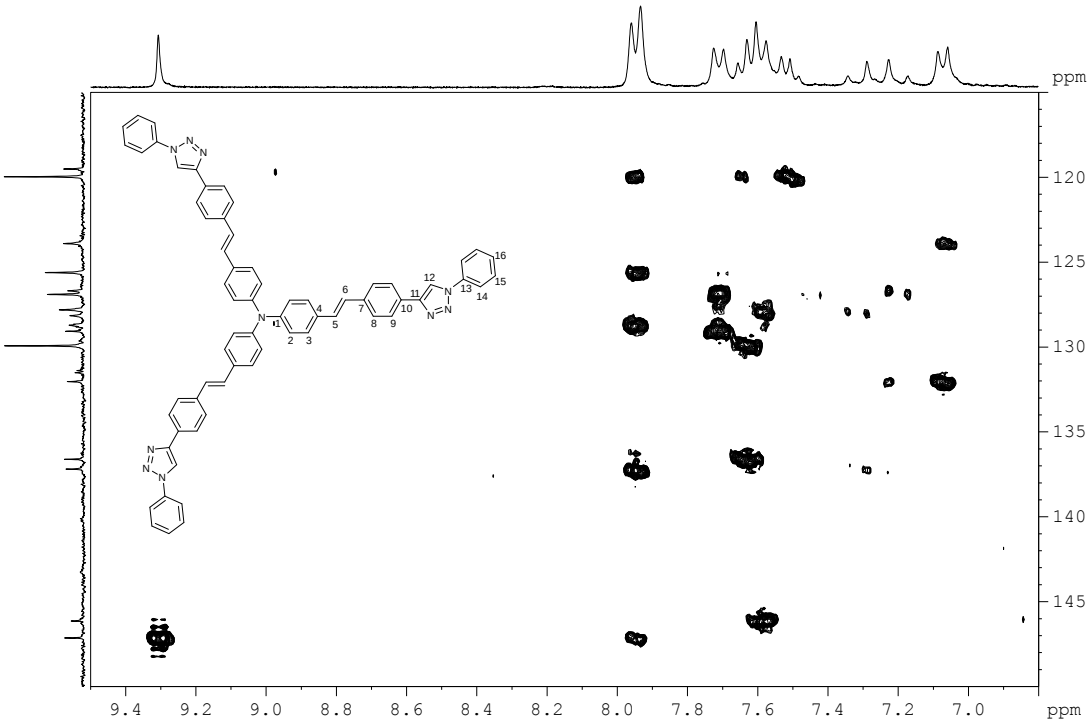


Figure S89. HMBC of **dendrimer 3a** in DMSO-d_6.

Dendrimer 3a: FT-IR spectrum

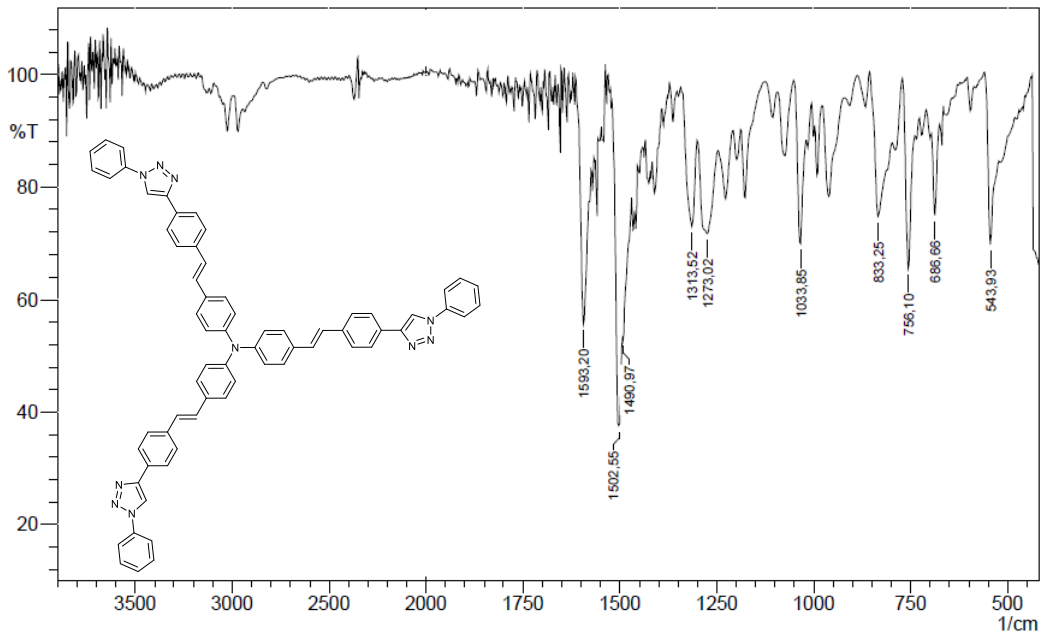


Figure S90. FT-IR (KBr disk) of **dendrimer 3a**.

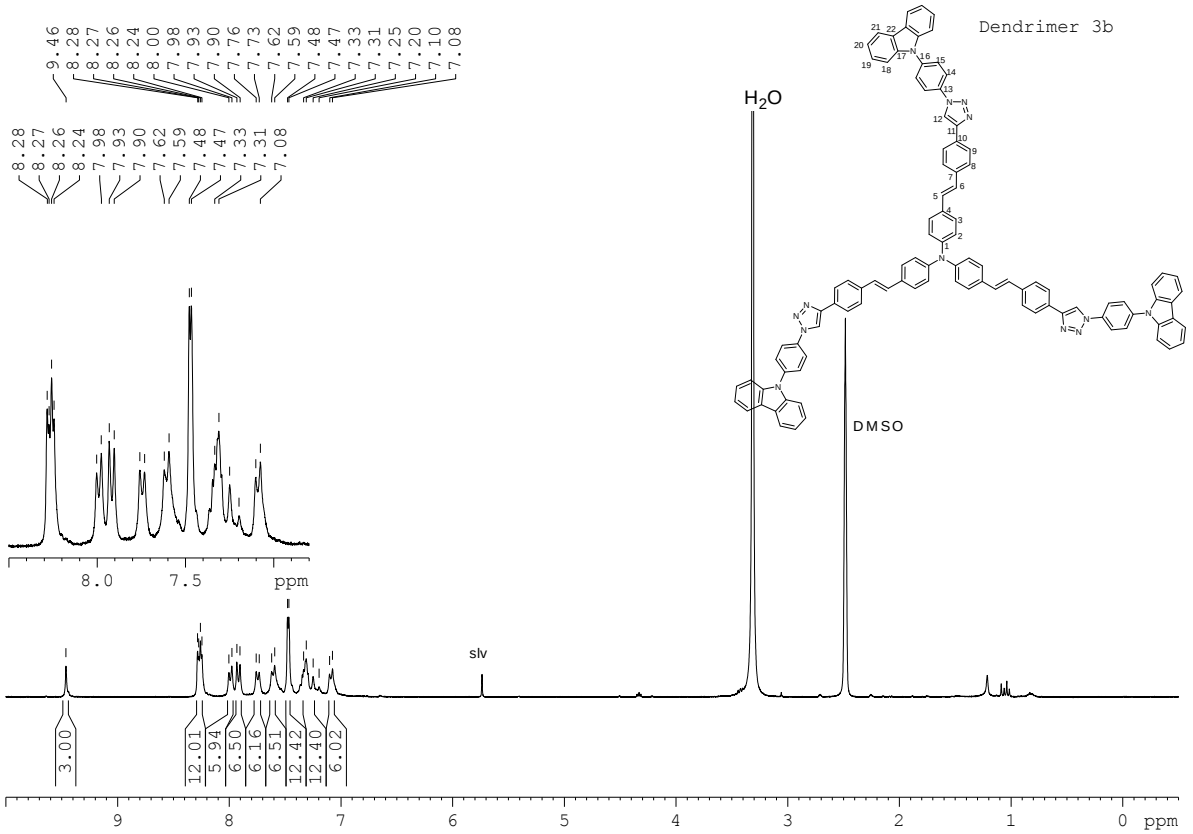


Figure S91: ^{1}H NMR (300 MHz) of **dendrimer 3b** in DMSO-d_6

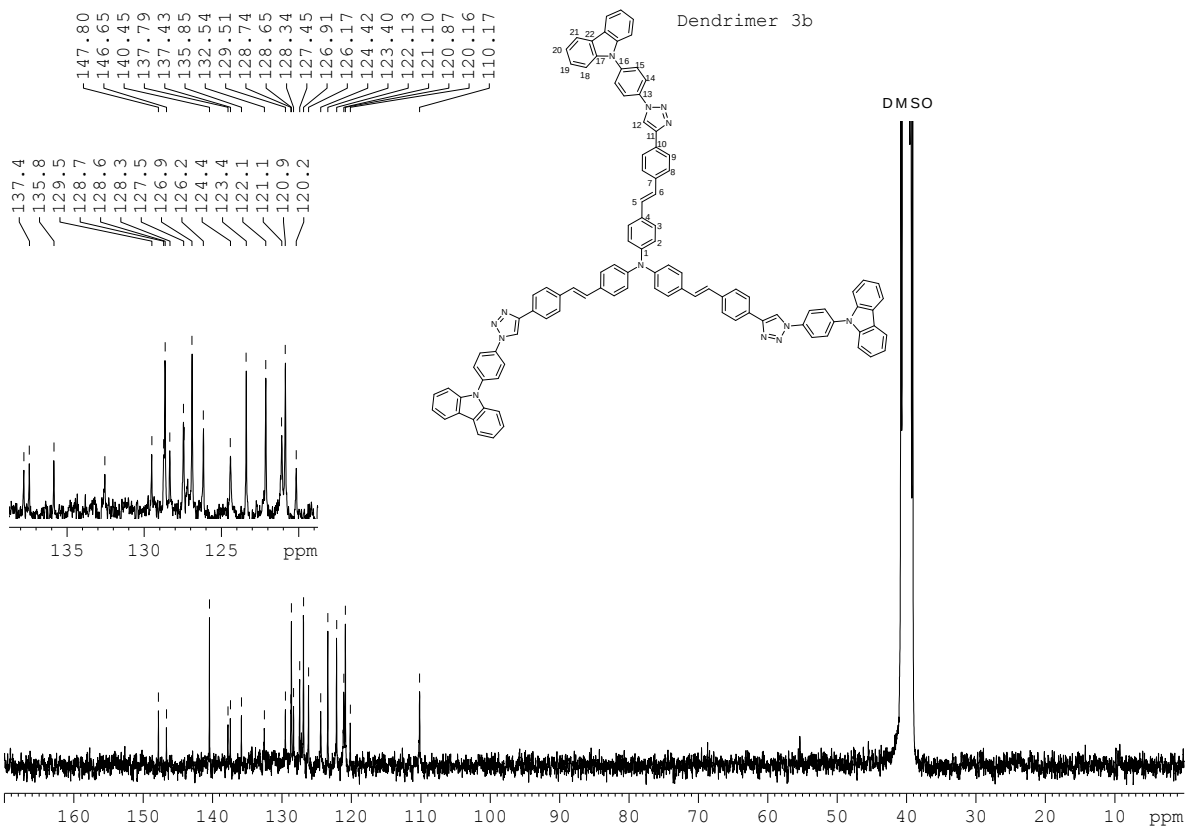


Figure S92: ^{13}C NMR (75.4 MHz) of **dendrimer 3b** in DMSO-d_6

Dendrimer 3b: COSY H-H

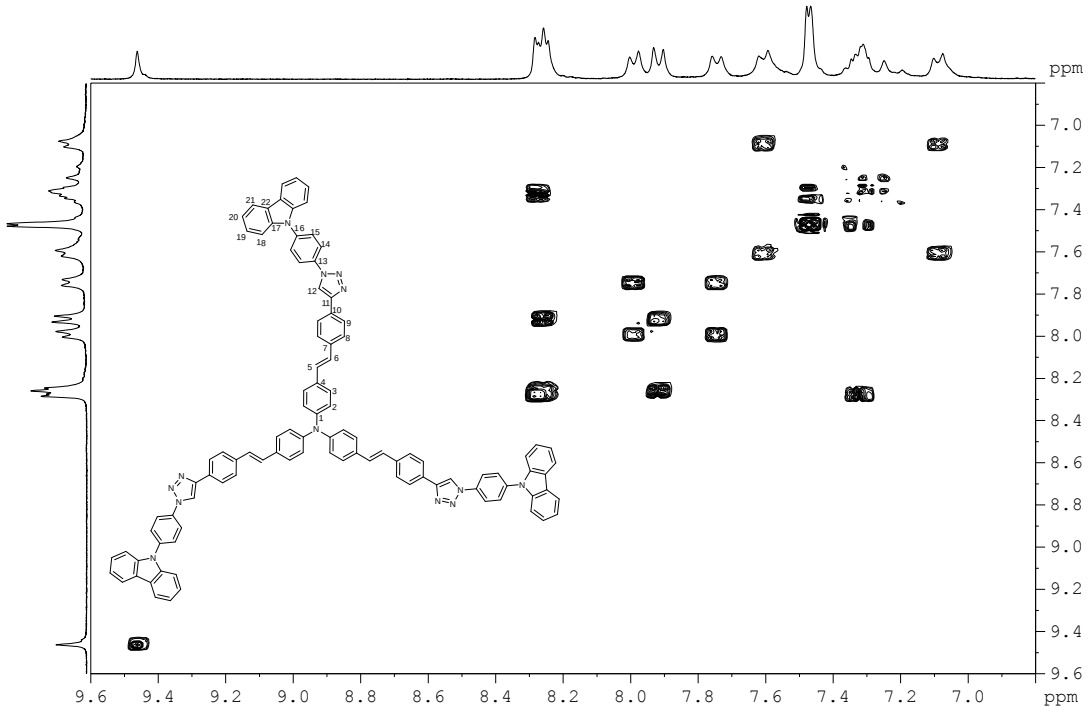


Figure S93. COSY H-H of **dendrimer 3b** in DMSO-d_6.

Dendrimer 3b: HSQC

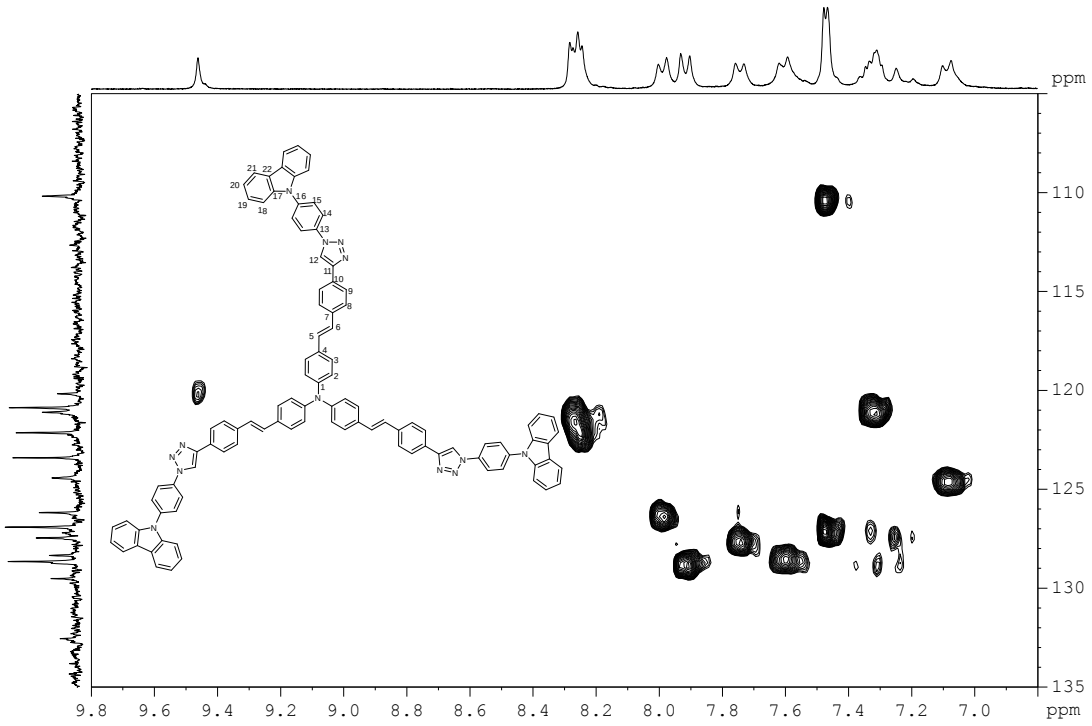


Figure S94. HSQC of **dendrimer 3b** in DMSO-d_6.

Dendrimer 3b: HMBC

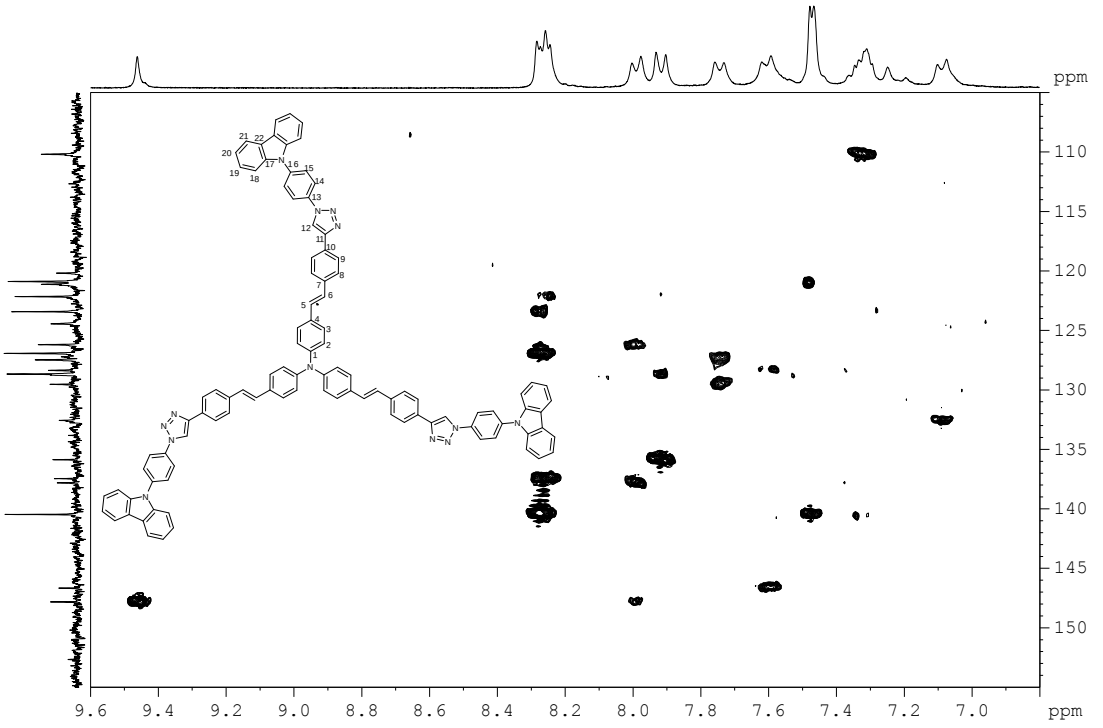


Figure S95. HMBC of **dendrimer 3b** in DMSO-d_6.

Dendrimer 3b: FT-IR spectrum

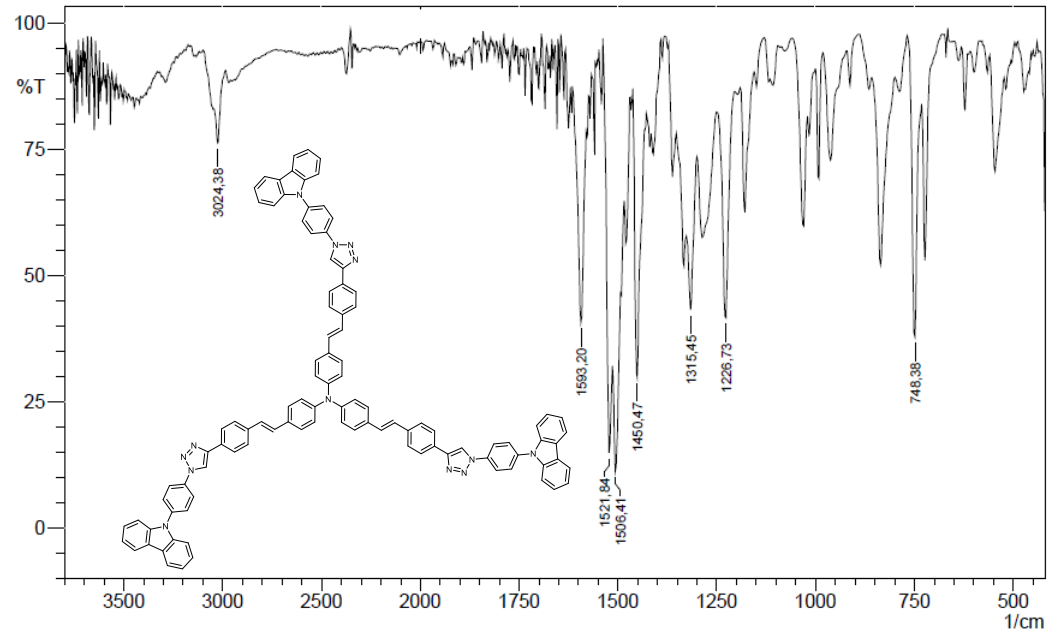


Figure S96. FT-IR (KBr disk) of **dendrimer 3b**.

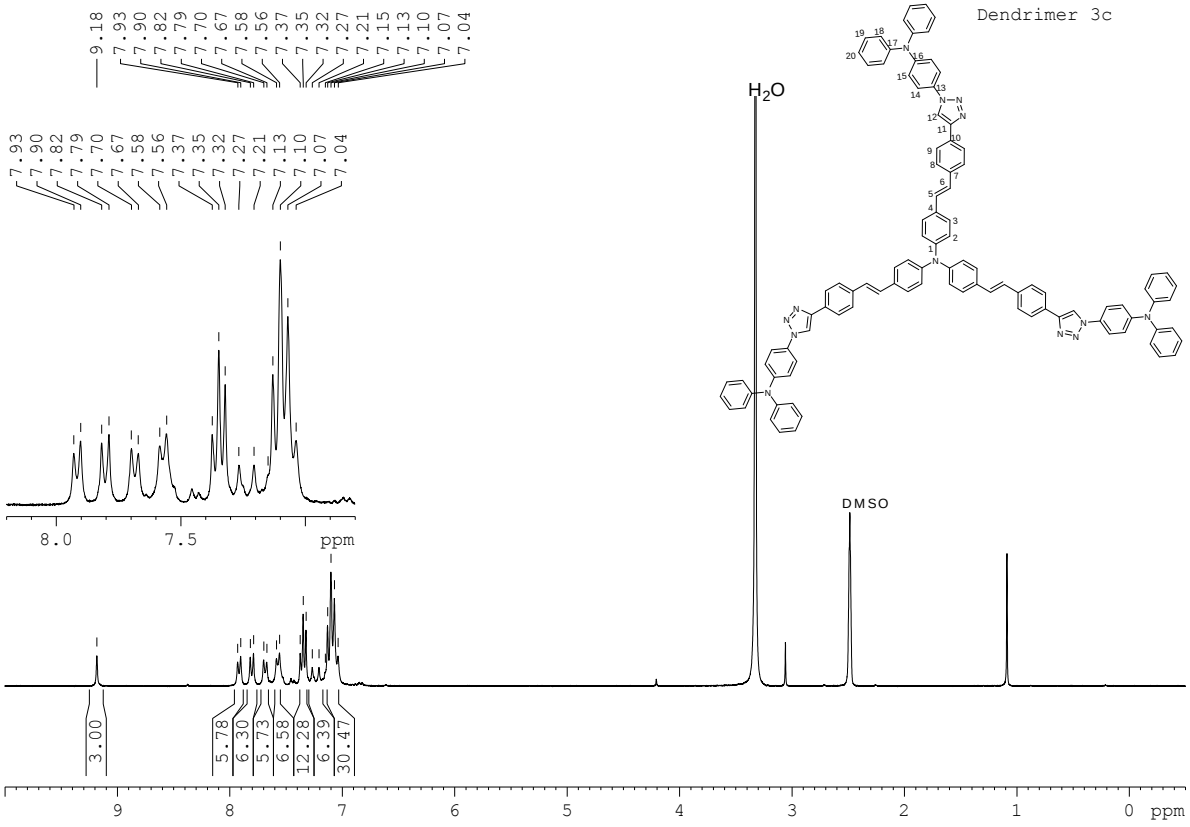


Figure S97: ^{1}H NMR (300 MHz) of **dendrimer 3c** in DMSO-d_6

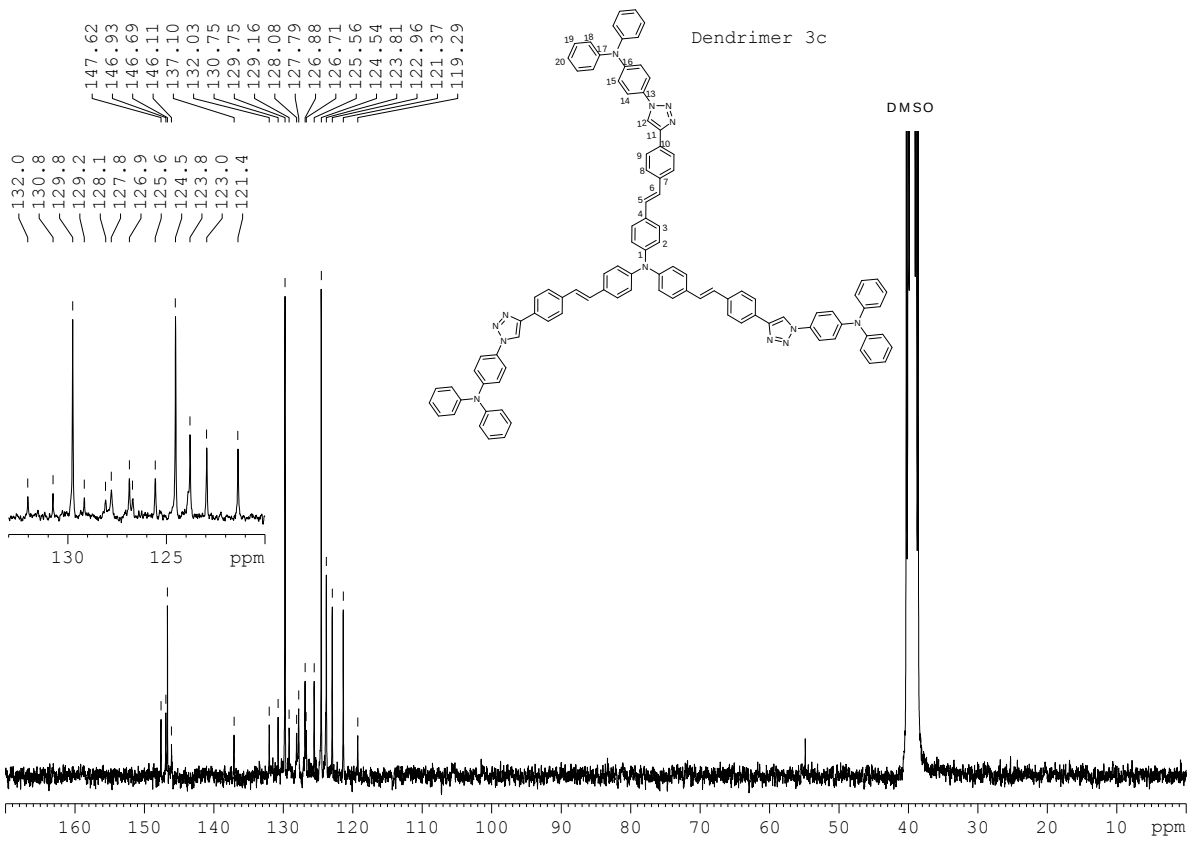


Figure S98: ^{13}C NMR (75.4 MHz) of **dendrimer 3c** in DMSO-d_6

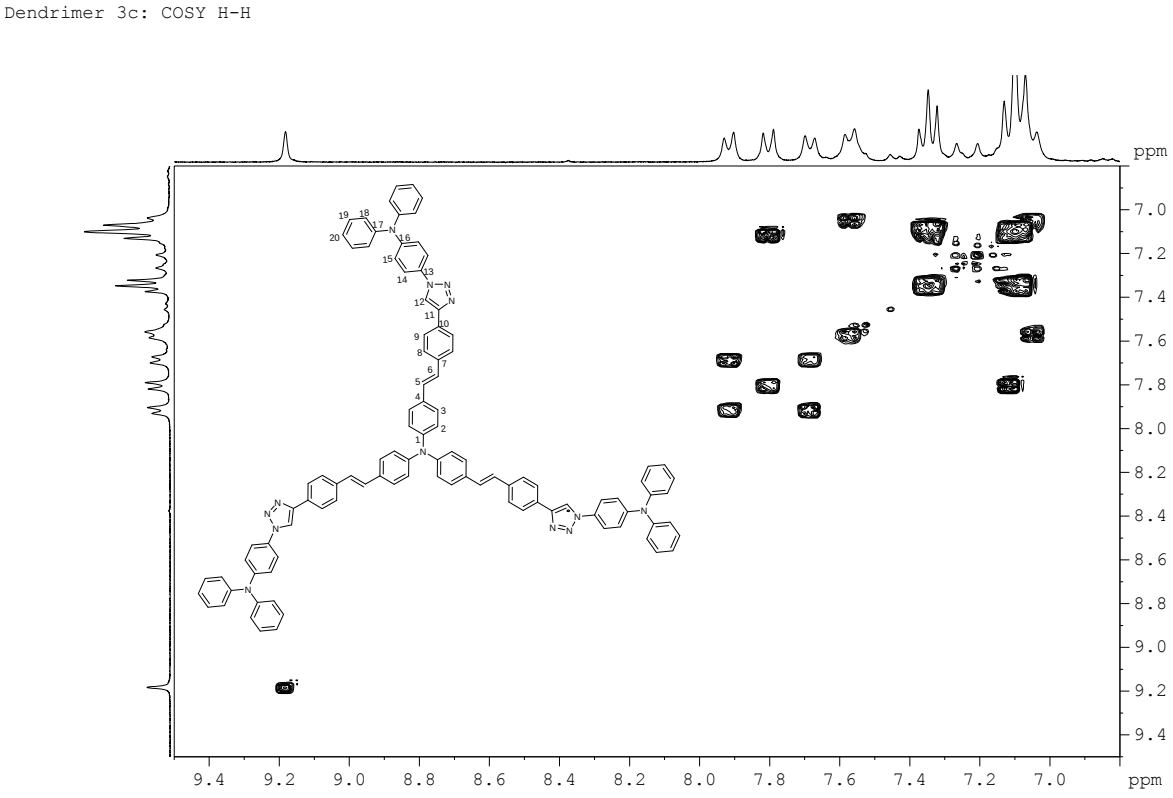


Figure S99. COSY H-H of **dendrimer 3c** in DMSO-d_6.

Dendrimer 3c: HSQC

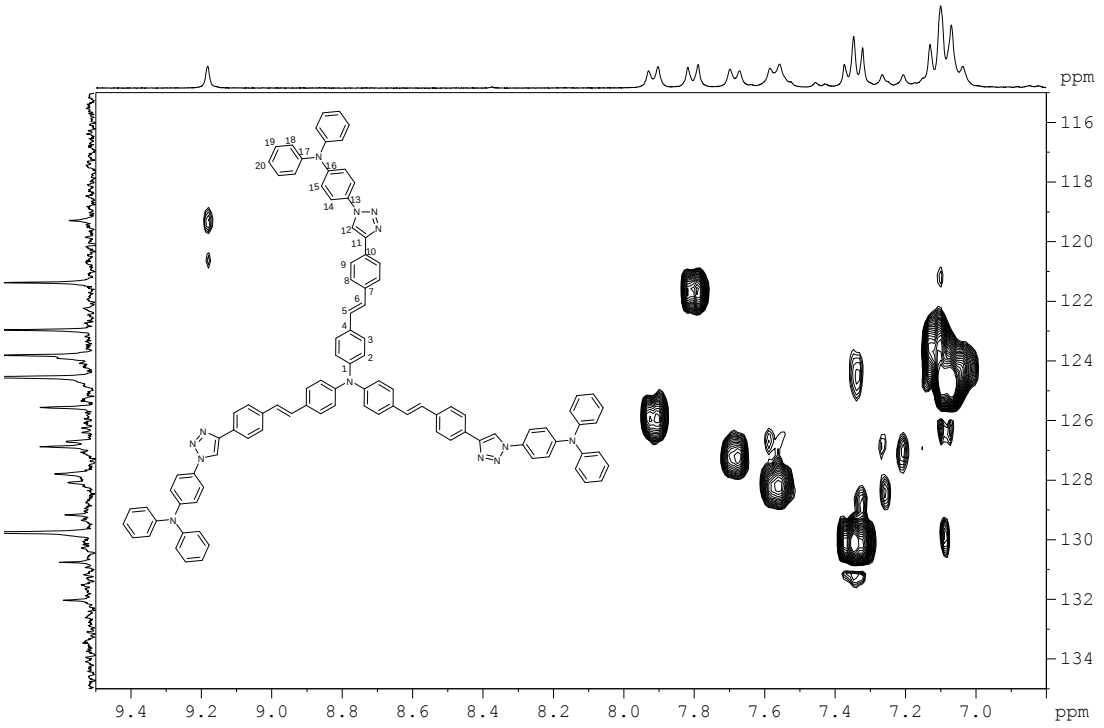


Figure S100. HSQC of **dendrimer 3c** in DMSO-d_6.

Dendrimer 3c: HMBC

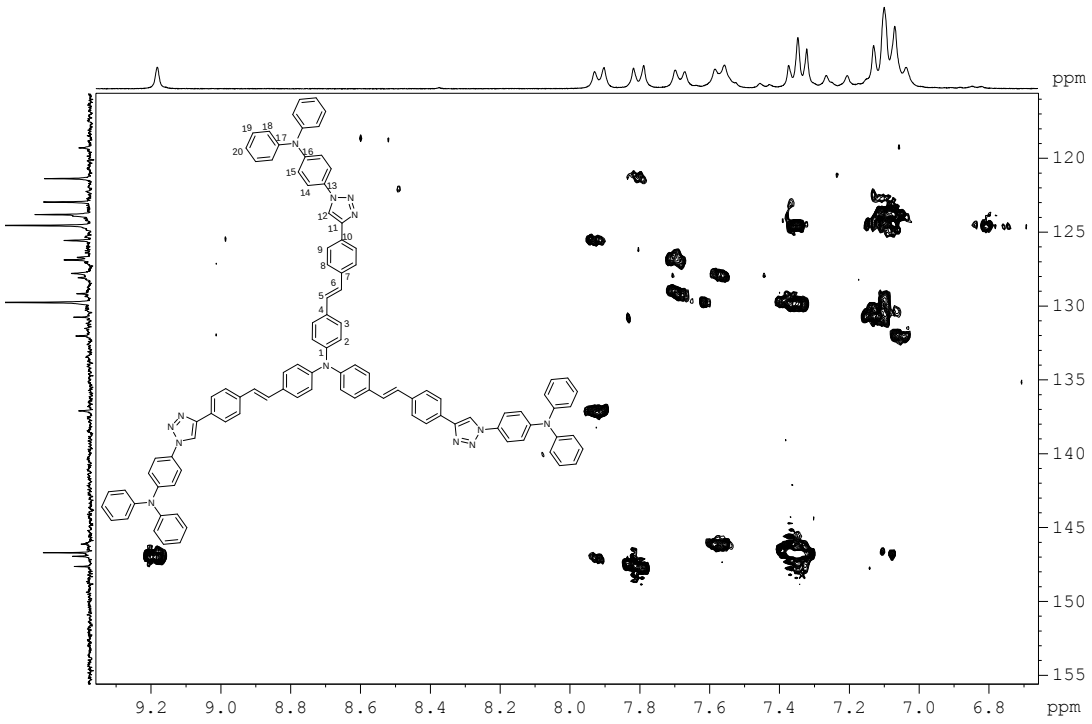


Figure S101. HMBC of **dendrimer 3c** in DMSO-d_6.

Dendrimer 3c: FT-IR spectrum

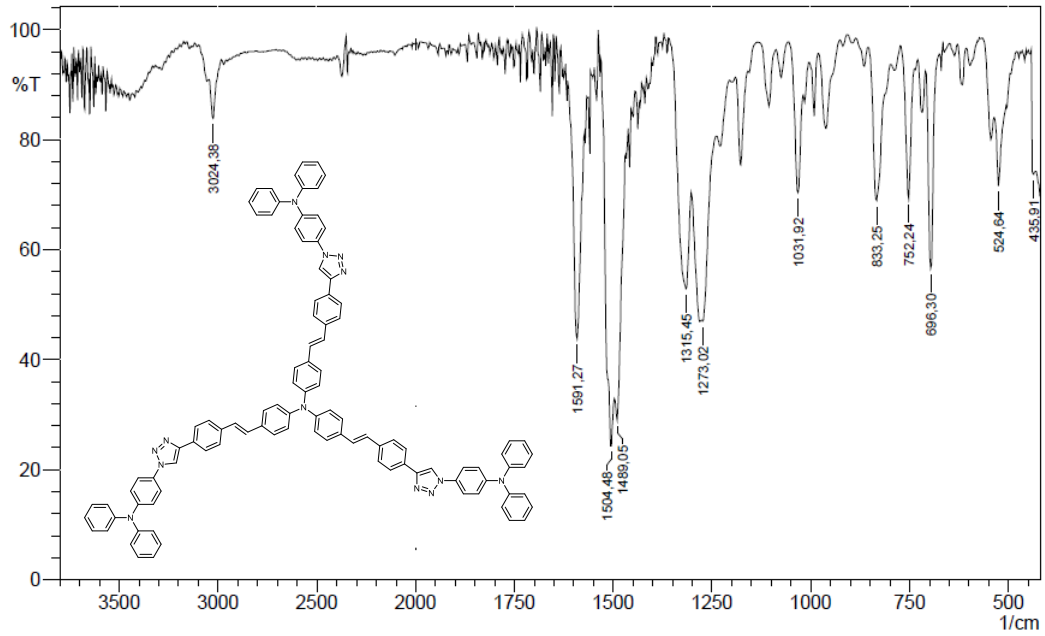


Figure S102. FT-IR (KBr disk) of **dendrimer 3c**.

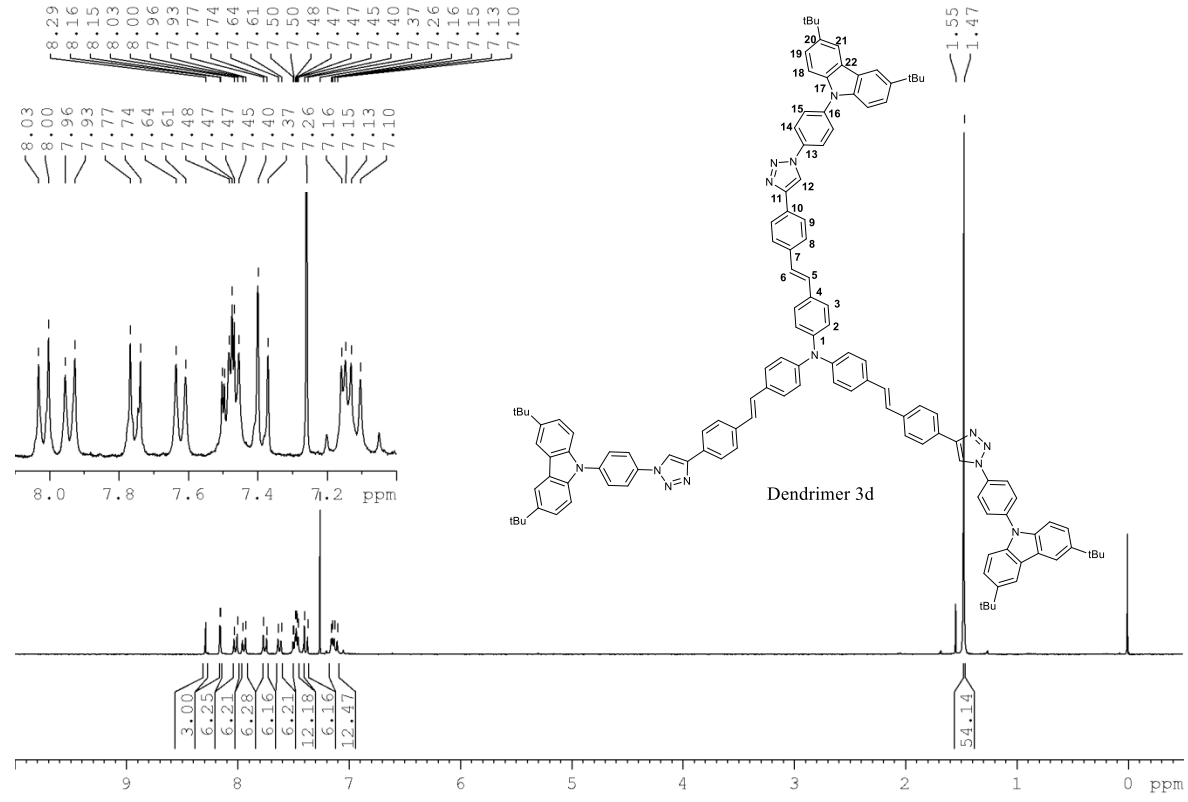


Figure S103: ^{1}H NMR (300 MHz) of **dendrimer 3d** in $CDCl_3$

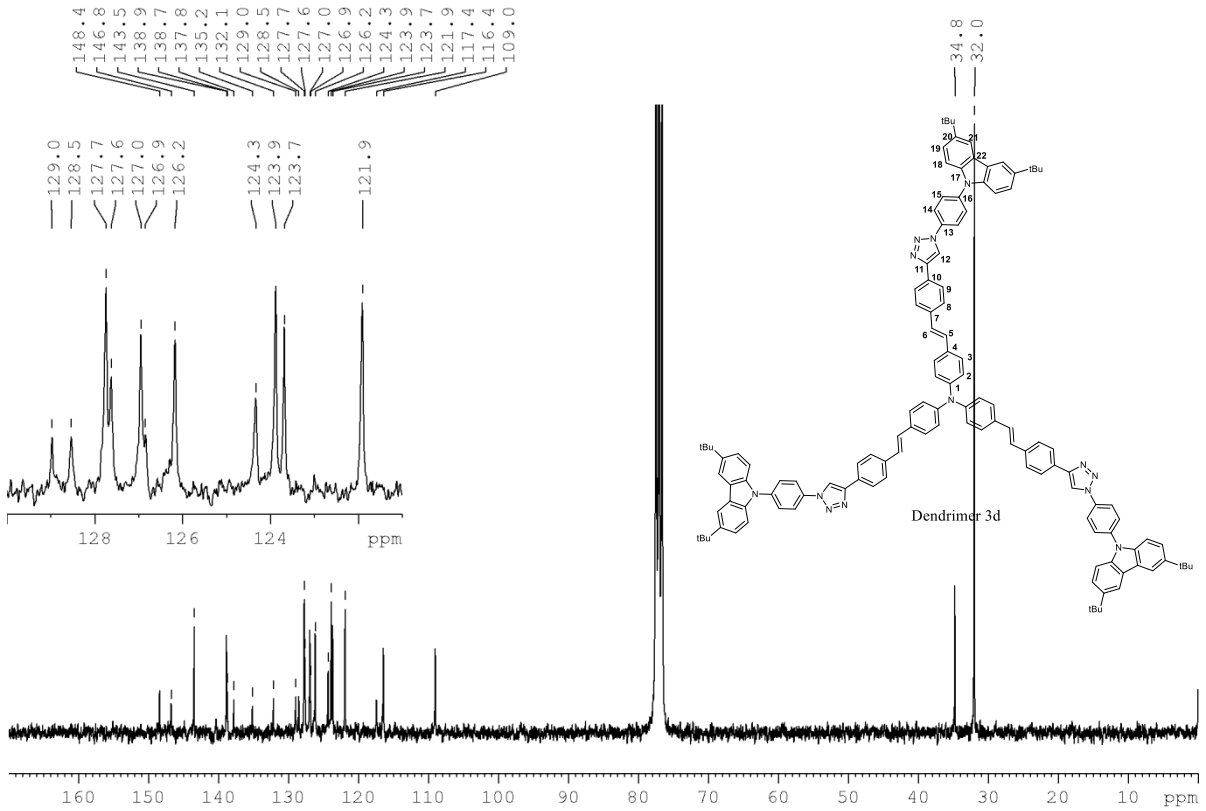


Figure S104: ^{13}C NMR (75.4 MHz) of **dendrimer 3d** in $CDCl_3$

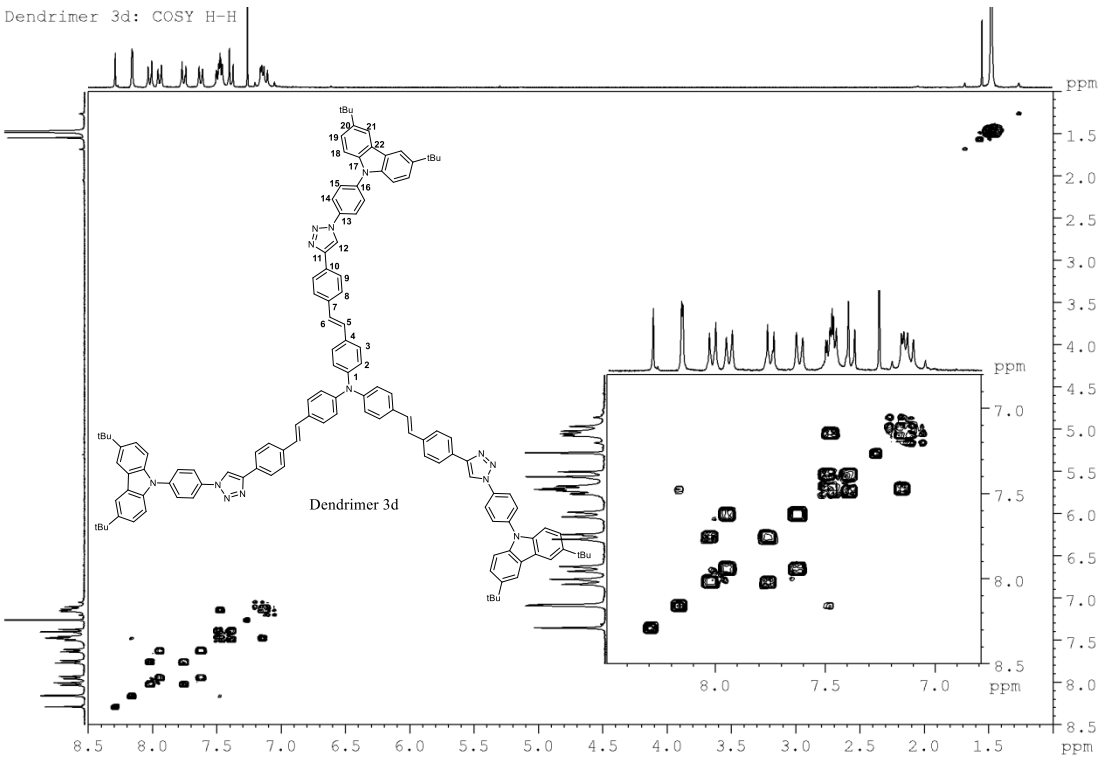


Figure S105. COSY H-H of **dendrimer 3d** in $CDCl_3$.

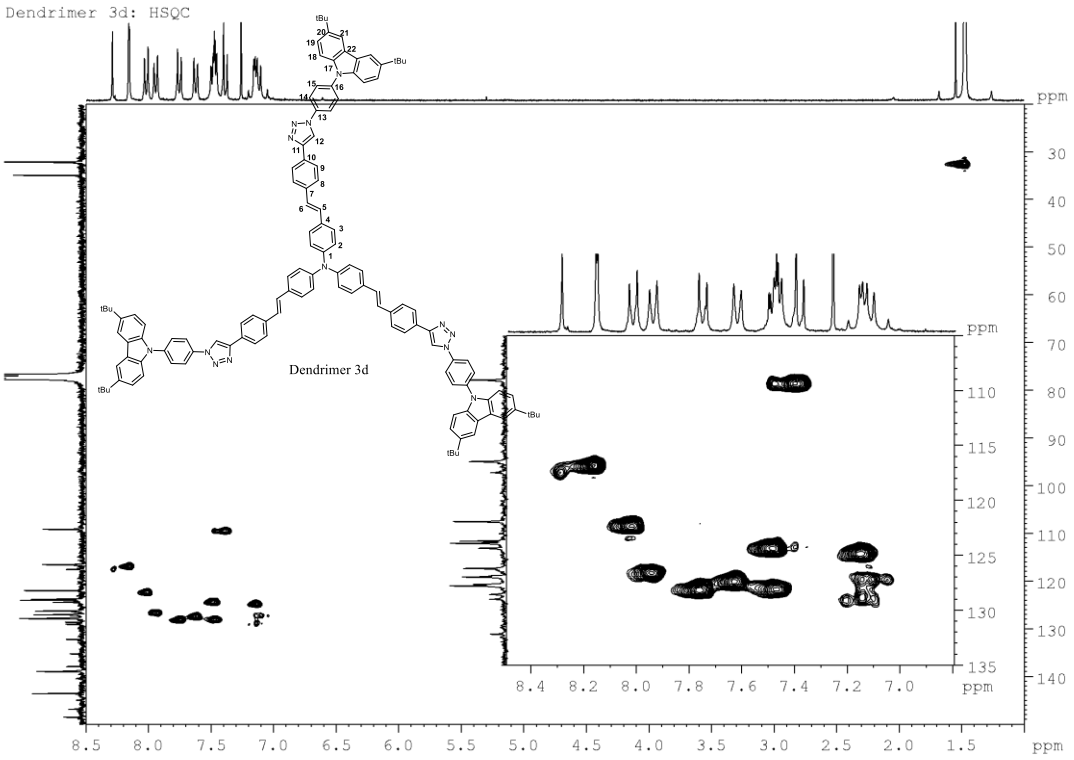


Figure S106. HSQC of **dendrimer 3d** in $CDCl_3$.

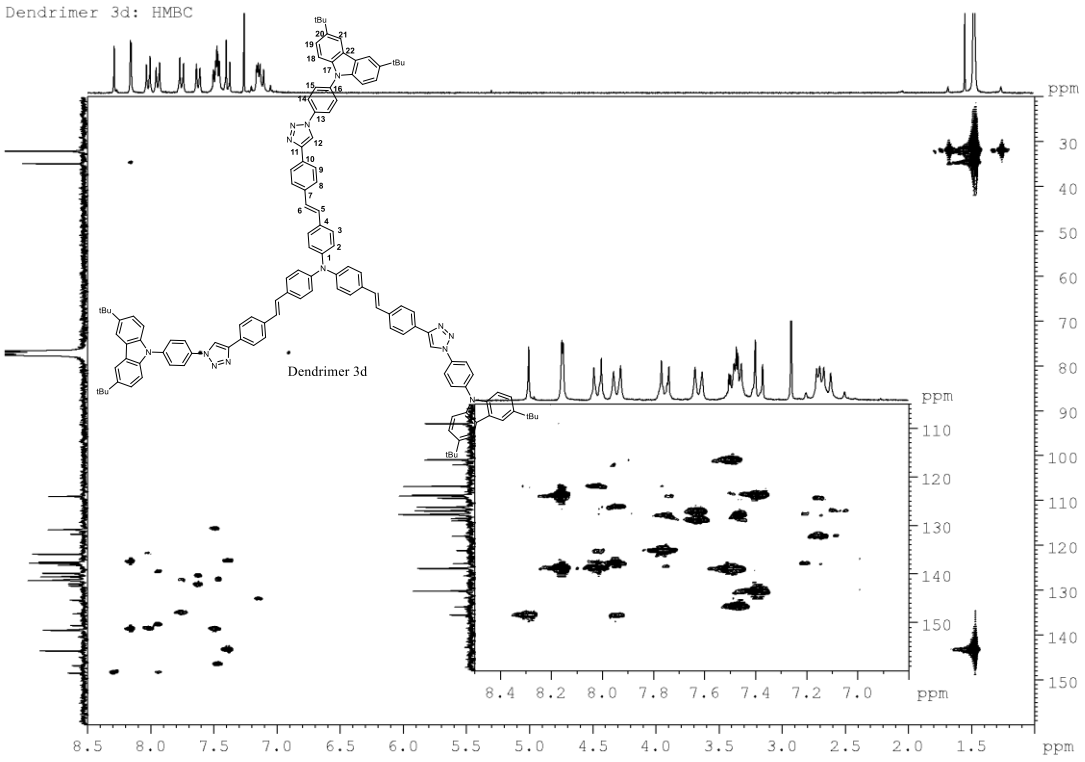


Figure S107. HMBC of **dendrimer 3d** in $CDCl_3$.

Dendrimer 3d: FT-IR spectrum

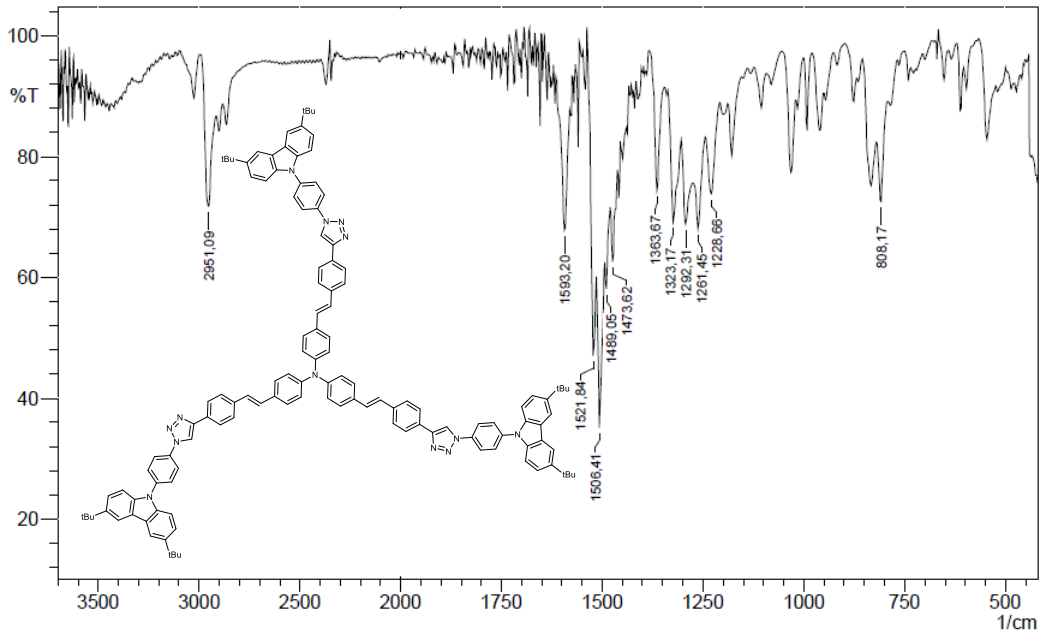


Figure S108. FT-IR (KBr disk) of **dendrimer 3d**.

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