Supporting Information

Dual-Sate Emission and Two-wavelength Amplified Spontaneous Emission Behaviors Observed from Symmetric Dyes Based on Functionalized Fluorene and Benzotriazole Units

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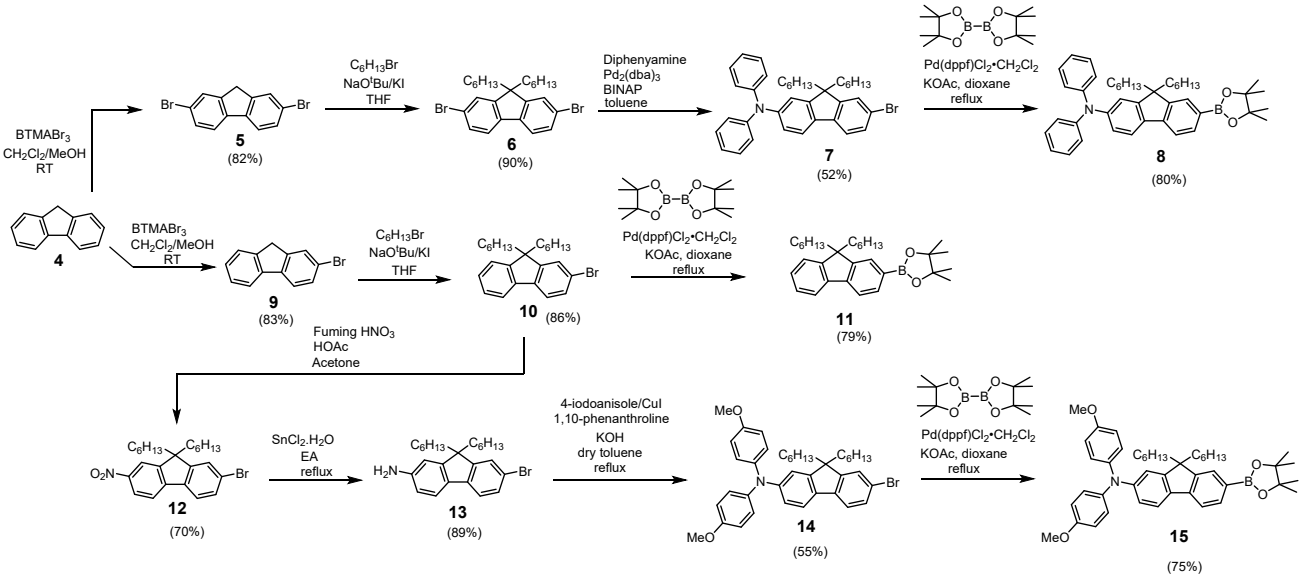
1. Synthesis

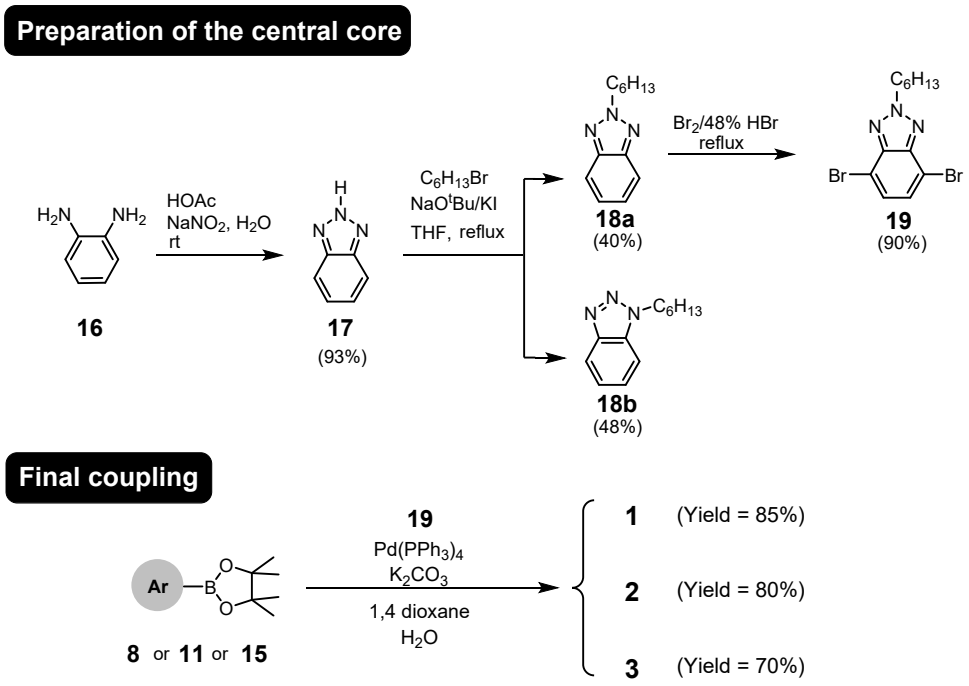
1.1 General

Fluorene, 1,2-diaminobenzene and all the other reagents utilized for the preparation of the intermediates and final structures were purchased from various commercial sources and were used as received. Compounds **5**-**7** were synthesized according to the established procedures.[1] A 500 MHz NMR spectrometer was employed to measure the ^{1}H NMR and ^{13}C NMR spectra for all the intermediates and final structures using TMS or residual $CHCl_3$ signals as the internal standards. The detailed syntheses for the intermediates and the final chromophores are presented in the next section. High-resolution mass spectra (HRMS) were measured by using an ESI-TOF mass spectrometer (Waters LCT) and MALDI-TOF MS spectra were measured by using a Voyager DE-PRO mass spectrometer (Applied Biosystem, USA).

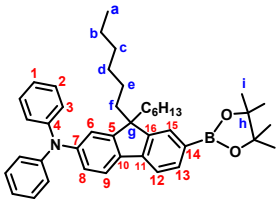
1.2 Synthesis

Preparation of the end-groups



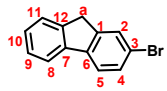


Scheme S1. The synthetic procedures for the preparation of building units and the final coupling toward target model chromophores.

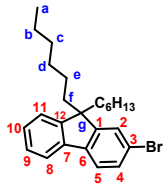


9,9-Dihexyl-*N*,*N*-diphenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-amine (8) To a mixture of compound **7** (3.26 g, 5.61 mmol) and bis(pinacolato)diboron (1.57 g, 6.17 mmol) in DMF (35 mL) was added potassium acetate (1.68 g, 0.017 mol) and Pd(dppf)Cl_2·CH_2Cl_2 (0.14 g, 0.17 mmol) and the resulting solution was stirred at 90 °C under N_2 for 18 h. After cooled down to r.t, the reaction mixture was extracted with ethyl acetate (30 mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate: hexane (1:30) as the eluent to give the target product (3.0 g) with a yield of 85.0 %. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 1H; H_{13}), 7.68 (s, 1H; H_{15}), 7.61-7.55 (m, 2H; H_9, H_{12}), 7.26-7.21 (m, 4H; H_2), 7.12-7.10 (m, 5H; H_3, H_6), 7.02-6.97 (m, 3H; H_1, H_8), 1.92-1.78 (m, 4H; H_f), 1.37 (s, 12H; H_i), 1.03-1.01 (m, 12H; H_c, H_d, H_e), 0.88 (t, 6H, H_a), 0.59 (br, 4H, H_b); ^{13}C NMR: (75 MHz, $CDCl_3$):

δ 152.69 (C_{16}), 149.73 (C_5), 147.89 (C_4), 147.45 (C_7), 143.90 (C_{11}), 136.03 (C_{10}), 133.76 (C_{15}), 129.10 (C_2), 128.58 (C_{13}), 123.78 (C_3), 123.35 (C_{12}), 122.46 (C_1), 120.75 (C_6), 119.21 (C_9), 118.36 (C_8), 83.60 (C_h), 55.03 (C_g), 40.05 (C_f), 31.46 (C_e), 29.55 (C_d), 24.90 (C_i), 23.63 (C_c), 22.52 (C_b), 14.03 (C_a); HRMS (EI): *m/z*: calcd for $C_{43}H_{54}BNO_2$: 627.4255 $[M]^+$; found: 627.4249.

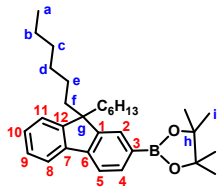


2-Bromofluorene (9) To a mixture of compound **4** (7 g, 42.1 mmol) and $ZnCl_2$ (6.88 g, 50.52 mmol) in acetic acid (110 mL) was added $BTMABr_3$ (16.42 g, 42.1 mol) and the resulting solution was stirred at r.t. for 4 h. After reaction was completed, saturated $NaHSO_{3(aq)}$ was added into the reaction mixture and stirred for 20 min. The white precipitate was collected and dried in vacuum oven. The product was obtained as white solid (8.58 g) with a yield of 83.1%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*= 7.5 Hz, 1H; H_3), 7.68 (s, 1H; H_2), 7.64 (d, *J*= 8 Hz, 1H; H_5), 7.54 (d, *J*= 7.5 Hz, 1H, H_4), 7.38 (t, *J*= 7.5 Hz, 1H; H_9), 7.33 (t, *J*= 7.5 Hz, 1H; H_{11}), 3.89 (s, 2H, H_a); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 145.18 (C_1), 142.82 (C_{12}), 140.68 (C_7), 130.14 (C_6), 129.86 (C_2), 128.23 (C_5), 127.10 (C_4), 126.93 (C_{10}), 125.03 (C_9), 121.16 (C_{11}), 121.08 (C_3), 119.91 (C_8), 36.73 (C_a).

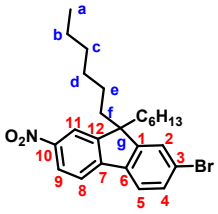


2-Bromo-9,9-dihexyl-9*H*-fluorene (10) A mixture of compound **9** (8 g, 32.64 mmol), NaO^{t}Bu (12.5 g, 130.56 mmol), KI (0.54 g, 0.326 mmol) in THF (70 mL) was refluxed for 30 min and cooled down to r.t. before the addition of bromohexane (10.76 mL, 83.56 mmol). The whole system was then heated to reflux for overnight. After the reaction was completed, 9 mL of pyridine was added and the mixture was refluxed for another 1 h. After cooled down to r.t., 1N $HCl_{(aq)}$ (30 mL) was added and stirred for 30 min. The above solution was extracted with ethyl acetate (50 mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the residue was purified by column chromatography on silica gel using *n*-hexane as eluent to afford the target product as a yellow

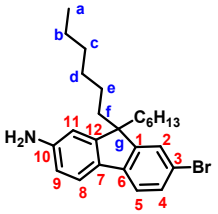
liquid (11.6 g; yield = 85.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (s, 1H, H_2), 7.56 (d, *J*= 8 Hz, 1H; H_4), 7.47 (d, *J*= 8 Hz, 2H; H_5, H_{11}), 7.34 (t, *J*= 2.5 Hz, 3H; H_8, H_9, H_{10}), 1.94-1.98 (m, 4H; H_f), 1.06-1.16 (m, 12H; H_c, H_d, H_e); 0.78 (t, *J*=7 Hz, 6H; H_a), 0.62-0.63 (m, 4H; H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.88 (C_1), 150.20 (C_{12}), 140.08 (C_7), 139.97 (C_6), 129.84 (C_2), 127.38 (C_5), 126.85 (C_4), 126.07 (C_{10}), 122.76 (C_9), 120.92 (C_{11}), 119.67 (C_3), 55.29 (C_8), 40.27 (C_g), 31.56 (C_f), 29.61 (C_e), 23.62 (C_d), 22.63 (C_c), 22.52 (C_b), 13.93 (C_a). HRMS (EI): *m/z*: calcd for $C_{12}H_{18}N_3$: 412.1768 $[M]^+$; found 412.1760.



2-(9,9-Dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxadiborolane) (11) To a mixture of compound **10** (2.83 g, 6.85 mmol) and bis(pinacolacto)diboron (2.09 g, 8.22 mmol) in DMF (30 mL) was added potassium acetate (2.01 g, 20.55 mmol) and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.31 g, 0.34 mmol) and the resulting solution was stirred at 90 °C for overnight. After cooled down to r.t., the solution was filtered through a pad of Celite 545 and the filtrate was extracted with dichloromethane (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the residue was purified by column chromatography on silica gel using *n*-hexane as eluent to give product as a yellow liquid (2.5 g) with a yield of 79.3%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 1H; H_4), 7.76 (s, 1H, H_2), 7.73-7.70 (m, 2H; H_5, H_{11}), 7.34-7.32 (m, 4H; H_8, H_9), 2.02-1.96 (m, 4H; H_f), 1.39 (s, 12H; H_i), 1.11-1.03 (m, 12H; H_b, H_c, H_d), 0.76 (t, *J* = 7 Hz, 6H; H_a) 0.61-0.59 (m, 4H; H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.26 (C_1), 149.83 (C_{12}), 144.09 (C_7), 140.90 (C_6), 133.66 (C_2, C_5), 128.81 (C_4), 127.42 (C_{10}), 126.61 (C_9), 122.89 (C_{11}), 120.03(C_3), 118.89 (C_8), 83.63 (C_h) 55.03 (C_g), 40.19 (C_f), 31.42(C_e), 29.62 (C_d), 24.90 (C_i), 23.61 (C_c), 22.51 (C_b), 13.93 (C_a).

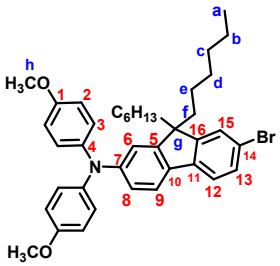


2-Bromo-9,9-dihexyl-7-nitro-9*H*-fluorene (12) A mixture of compound **10** (7.86 g, 19.01 mmol) in acetone (20 mL) and acetic acid (20 mL) was stirred in ice bath. To this mixture was added very slowly with fuming nitric acid. The resulting solution was stirred at r.t. for 2 h. When the reaction is completed, 1N $NaOH_{(aq)}$ was added and stirred, and the mixed solution was extracted by ethyl acetate (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane: ethyl acetate (100:1) as eluent to give target product as a yellow liquid (6.1 g) with a yield of 70.2%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.26 (dd, J_1= 8.5 Hz, J_2=1.5 Hz, 1H, H_9), 8.19 (s, 1H, H_{11}), 7.76 (d, J= 8.5 Hz, 1H, H_8), 7.63-7.65 (m, 2H, H_2, H_4), 1.94-2.08 (m, 4H, H_f), 1.02-1.13 (m, 12H, H_c, H_d, H_e); 0.76 (t, J=7 Hz, 6H, H_a), 0.55-0.59 (m, 4H, H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.33 (C_1), 151.56 (C_{12}), 147.36 (C_{10}), 146.38 (C_7), 137.66 (C_6), 130.67 (C_2), 126.52 (C_5), 123.63 (C_4), 123.36 (C_8), 122.41 (C_9), 119.89 (C_{11}), 118.23 (C_3), 55.94 (C_g), 39.91 (C_f), 31.35 (C_e), 29.41 (C_d), 23.64 (C_c), 22.44 (C_b), 13.87 (C_a).

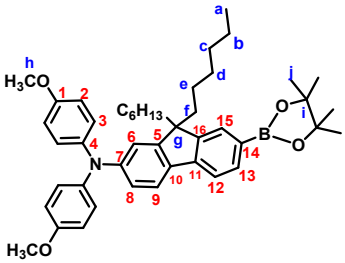


7-Bromo-9,9-dihexyl-9*H*-fluoren-2-amine (13) A mixture of compound **12** (5.4 g, 11.78 mmol) and $SnCl_2 \cdot 2H_2O$ in ethyl acetate (130 mL) was refluxed for overnight. After reaction was completed, saturated $NaHCO_{3(aq)}$ was added to quench the reaction. The above solution was extracted by ethyl acetate (50 mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the residue was purified by column chromatography using ethyl acetate: *n*-hexane (1: 25) as eluent to afford desired product as brown liquid (4.5 g) with a yield of 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, J = 8 Hz, 1H, H_4), 7.37-7.41 (m, H_8, H_5), 6.70 (dd,

J_1 = 9.5 Hz, J_2=1.5 Hz, 2H, H_9, H_{11}), 4.28 (s, NH, 2H), 1.85-1.89 (m, 4H, H_f), 1.05-1.14 (m, 12H, H_c, H_d, H_e); 0.78 (t, J = 7.5 Hz, 6H, H_a), 0.62 (m, 4H, H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.32 (C_1), 152.09 (C_{12}), 145.41 (C_7), 140.49 (C_6), 131.79 (C_{10}), 129.65 (C_2), 125.79 (C_5), 120.59 (C_4), 119.70 (C_8), 119.14 (C_9), 114.44 (C_{11}), 109.98 (C_3), 55.12 (C_g), 40.49 (C_f), 31.48 (C_e), 29.66 (C_d), 23.62 (C_c), 22.58 (C_b), 13.96 (C_a).



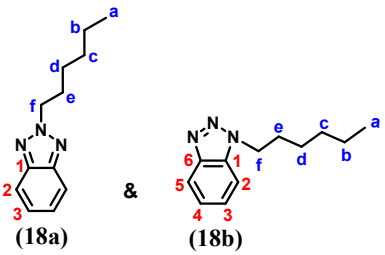
7-Bromo-9,9-dihexyl-*N*-*N*-bis(4-methoxyphenyl)-9*H*-fluoren-2-amine) (14) A solution of compound **13** (3.8 g, 8.86 mmol), 4-iodoanisole (4.56 g, 19.49 mmol), KOH (3.97 g, 70.88 mmol), CuI (0.08g, 0.44 mmol), and 1,10-phenanthroline (0.08 g, 0.44 mmol) in toluene was prepared in a 500 mL round-bottom flask and the reaction mixture was heated to 90 °C for 72 h. After cooled down to r.t., the reaction mixture was filtered through a pad of Celite 545. The filtrate was mixed with 10% $NH_4OH_{(aq)}$ (150 mL) and 0.1 N HCl (150 mL). The biphasic mixture was stirred at r.t., and then was extracted with ethyl acetate (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent, the residue was purified by column chromatography on silica gel using *n*-hexane: ethyl acetate (200:1) as eluent to give target product as a pale-yellow powder (3.12 g; yield = 54.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.40 (m, 4H; H_6, H_9, H_{12}, H_{13}), 7.10 (d, J = 8.5 Hz, 4H; H_3), 7.01 (s, 1H, H_{15}), 6.92 (d, J = 7.5 Hz, 1H; H_8), 6.86 (d, J = 8.5 Hz, 4H; H_2), 3.82 (s, 6H; H_h), 1.87-1.83 (m, 4H; H_f), 1.22-1.10 (m, 12H; H_c, H_d, H_e), 0.86-0.83 (m, 6H; H_a), 0.71-0.69 (m, 4H; H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6 (C_1), 152.7 (C_7), 151.6 (C_4), 148.5 (C_{16}), 144.4 (C_5), 140.2 (C_{11}), 133.3 (C_{10}), 129.8 (C_{13}), 125.9 (C_2), 125.9 (C_5), 120.6 (C_{12}), 120.2 (C_9), 120.0 (C_8), 119.6 (C_4), 116.2 (C_6), 114.6 (C_3), 55.4 (C_h), 55.2 (C_g), 40.1 (C_f), 31.5 (C_e), 29.6 (C_d), 23.7 (C_c), 22.6 (C_b), 14.0 (C_a); HRMS (MALDI-TOF): *m/z*: calcd for $C_{39}H_{46}BrNO_2$: 639.2706 $[M]^+$; found: 639.2687.



9,9-Dihexyl-*N*-*N*-bis(4-methoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2-dixaborolan-2-yl)-9*H*-fluoren-2-amine) (15) To a mixture of compound **14** (3.12 g, 4.84 mmol) and bis(pinacolacto)diboron (1.47 g, 5.81 mmol) in DMF (25 mL) was added potassium acetate (1.43 g, 14.5 mmol) and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.24g, 0.29 mmol) and the resulting solution was stirred at 90 °C for overnight. After cooled down to r.t., the solution was filtered through a pad of Celite 545 and the filtrate was extracted with dichloromethane (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the product was purified by column chromatography on silica gel using *n*-hexane: ethyl acetate (30:1) as eluent to give desired product as a white powder (2.49 g) with a yield of 74.6%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 1H; H_{12}), 7.69 (s, 1H; H_6), 7.58 (d, J = 8 Hz, 1H; H_9), 7.51 (d, J = 8 Hz, 1H; H_{13}), 7.07 (d, J = 8.5 Hz, 4H; H_2), 6.99 (s, 1H; H_{15}), 6.89 (d, J = 8 Hz, 1H; H_8), 6.83 (d, J = 9 Hz, 4H; H_3), 3.81 (s, 6H; H_h), 1.79-1.93 (m, 4H; H_f), 1.39 (s, 12H; H_j), 1.05-1.16 (m, 12H; H_c, H_d, H_e), 0.80 (t, J = 7.5 Hz, 6H; H_a), 0.63 (m, 4H; H_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.48 (C_1), 152.59 (C_5), 149.56 (C_{16}), 148.32 (C_{10}), 144.20 (C_7), 141.46 (C_4), 134.31 (C_{11}), 133.73 (C_{13}), 128.58 (C_{14}), 128.57 (C_{12}), 125.87 (C_2), 120.57 ($C1_5$), 120.56 (C_6), 118.05 (C_9), 116.42 (C_8), 114.56 (C_3), 83.54 (C_i), 55.43 (C_h), 54.92 (C_g), 40.06 (C_f), 31.47 (C_e), 29.58(C_d), 24.89 (C_j), 23.64 (C_c), 22.53 (C_b), 13.99 (C_a). HRMS (MALDI-TOF): *m/z*: calcd for $C_{45}H_{58}BNO_4$: 687.4509 $[M]^+$; found: 687.4453.

1*H*-Benzo[*d*][1,2,3]triazole (17) To a mixture of compound **16** (3 g, 27.70 mmol) in CH_3COOH (20 mL) was added an aqueous solution of $NaNO_2$ (4.57 g, 68.48 mmol/10 mL H_2O) and stirred at r.t for 1 h. After reaction was completed, saturated $NaHCO_{3(aq)}$ was added to neutralize the reaction mixture. The above solution was extracted with

ethyl acetate (50 mL× 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the pure product was obtained as a pale-yellow solid (3.09 g) with a yield of 93.6%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J_1 = 6.5 Hz, J_2 = 3 Hz, 2H; H_2), 7.46 (dd, J_1 = 6.5 Hz, J_2 = 3 Hz, 2H; H_3), ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.81 (C_1), 126.05 (C_2), 114.91 (C_3). HRMS-EI: *m/z*: calcd for $C_6H_6N_3$: 120.0556 $[M]^+$; found: 120.0554.



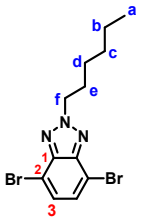
(18a) (18b)

2-Hexyl-2*H*-benzo[*d*][1,2,3]triazole & 1-Hexyl-1*H*-benzo[*d*][1,2,3]triazole (18a & 18b) To a solution of compound **17** (3.07 g, 25.7 mmol) in methanol (30 mL) was added NaO^{t}Bu (3.71 g, 38.55 mmol) and the resulting solution was stirred and refluxed for 30 min before the addition of bromohexane (5.4 mL, 38.85 mmol). The reaction mixture then was heated to reflux for overnight. After reaction was completed, 1 mL of pyridine was added into the reaction mixture and the whole system was refluxed for another 1 h. After cooled down to r.t., the solvent was removed from the reaction mixture by a rotary evaporator and the residue was re-dissolved in ethyl acetate (50 mL), which was mixed with 1 N $HCl_{(aq)}$ (10 mL) and stirred for 30 min. The above solution was extracted with ethyl acetate (50mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of solvent from the filtrate, the residue was purified by column chromatography on silica gel using EA: n-hexane (1:5) as eluent to afford two separable isomers:

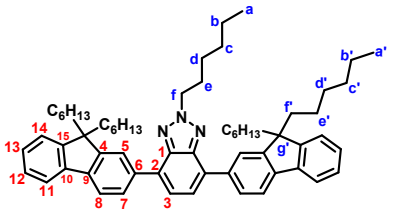
Compound 18a: Yellow liquid (2.1 g; yield = 40.1%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J_1 = 6.5 Hz, J_2 = 2.5 Hz, 2H; H_2), 7.36 (d, J_1 = 6.5 Hz, J_2 = 2.5 Hz, 2H; H_3), 4.70 (t, J = 7.5 Hz, 2H; H_f), 2.13-2.07 (m, 2H; H_e), 1.34-1.29 (m, 6H; H_b, H_c, H_d), 0.86 (t, J= 6 Hz, 3H; H_a); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.24 (C_1), 126.06 (C_2), 117.89 (C_3), 56.58 (C_f), 31.14 (C_e), 29.97(C_d), 26.18 (C_c), 22.35 (C_b), 13.88 (C_a). HRMS (EI): *m/z*: calcd for $C_{12}H_{18}N_3$: 204.1495 $[M]^+$; found: 204.1478.

Compound 18b: Orange liquid (2.52 g; yield = 48.1%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J= 8.5 Hz, 1H; H_5), 7.51 (d, J = 8 Hz, 1H; H_2), 7.45

(t, J= 8 Hz, 1H; H_4), 7.35 (t, J= 8 Hz, 1H; H_3), 4.62 (t, J= 7 Hz, 2H; H_f), 2.01-1.96 (m, 2H; H_e), 1.32-1.28 (m, 6H; H_b, H_c, H_d), 0.85 (t, J= 6.5 Hz, 3H; H_a); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.94 (C_6), 132.86 (C_1), 126.98 (C_5), 119.91 (C_2), 119.91 (C_4), 109.22 (C_3), 48.12 (C_f), 31.08 (C_e), 29.54 (C_d), 26.27 (C_c), 22.29 (C_b), 13.79 (C_a). HRMS (EI): (*m/z*): calcd for $C_{12}H_{18}N_3$: 204.1495 $[M]^+$; found: 204.1493.

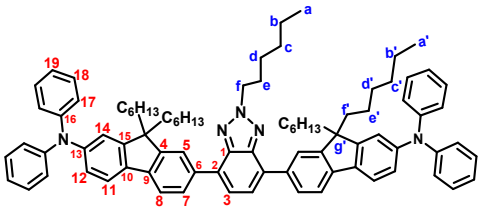


4,7-Dibromo-2-hexyl-2*H*-benzo[*d*][1,2,3]triazole (19) To a solution of compound **18a** (2.06 g, 10.1 mmol) in HBr (48%; 40 mL) was added bromine (2.4 mL, 36.44 mmol) and the resulting solution was refluxed for overnight. After reaction was completed, saturated $NaHSO_{3(aq)}$ was added to quench the reaction. The mixture was extracted using ethyl acetate (50 mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent from the filtrate, the residue was purified by column chromatography using ethyl acetate: *n*-hexane (1: 100) as eluent to afford desired product as colorless oil (3.3 g) with a yield of 90.2%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 2H; H_3), 4.77 (t, J = 7 Hz, 2H; H_f), 2.16-2.12 (m, J = 7 Hz, 2H; H_e), 1.38-1.32 (m, J = 6.5 Hz, 6H; H_b, H_c, H_d), 0.87 (t, J = 6 Hz, 3H; H_a); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.67 (C_1), 129.44 (C_3), 109.93 (C_2), 57.41 (C_f), 31.08 (C_e), 30.10 (C_d), 26.12 (C_c), 22.32 (C_b), 13.86 (C_a). HRMS (EI): (*m/z*): calcd for $C_{12}H_{15}Br_2N_3$: 358.9633 $[M]^+$; found: 358.9628.



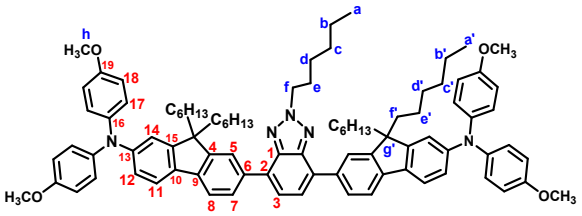
4,7-Bis(9,9-dihexyl-9*H*-fluoren-2-yl)-2-hexyl-2*H*-benzo[*d*][1,2,3]triazole (1) To a 250 mL round-bottom flask was charged compound **19** (0.8 g, 2.2 mmol), compound **11** (2.23 g, 4.84 mmol),

K_2CO_3 (2.39 g, 17.6 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol), H_2O (7 mL) and 1,4-dioxane (21 mL) and the resulting solution was refluxed for 24 h. After cooled down to r.t., the solution was filtered through a pad of Celite 545 and the filtrate was extracted with dichloromethane (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$ and after filtration and removal of the solvent, the residue was purified by column chromatography using CH_2Cl_2: *n*-hexane (1:10) as eluent to give target product as a yellow liquid (1.63 g; yield = 84.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 2H; H_7), 8.07 (s, 2H; H_5), 7.86 (d, J = 8 Hz, 2H; H_8), 7.77 (d, J = 7 Hz, 2H; H_{11}), 7.75 (s, 2H; H_3), 7.40-7.32 (m, 6H; H_{12}, H_{13}, H_{14}), 4.84 (t, J = 7 Hz, 2H; H_f), 2.25-2.22 (m, 2H; H_e), 2.11-1.99 (m, 8H; $H_{f'}$), 1.49-1.36 (m, 6H; H_b, H_c, H_d), 1.17-1.06 (m, 24H; $H_{c'}$, $H_{d'}$, $H_{e'}$); 0.93 (t, J = 7 Hz, 3H; H_a), 0.77 (t, J = 7.5 Hz, 20H; $H_{a'}$, $H_{b'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.28 (C_{15}), 151.04 (C_4), 143.68 (C_1), 140.88 (C_{10}), 140.83 (C_9), 136.18 (C_6), 130.55 (C_2), 127.43 (C_7), 127.03 (C_3), 126.75 (C_5), 124.30 (C_8), 123.17 (C_{11}), 122.89 (C_{12}), 119.79 (C_{14}, C_{13}), 56.76 (C_f), 55.10 ($C_{g'}$), 40.36 ($C_{f'}$), 31.48 ($C_{e'}$), 31.27 (C_e), 29.97 (C_d), 29.79 ($C_{d'}$), 26.34 (C_c) 23.85 ($C_{c'}$), 22.57 ($C_{b'}$), 22.49 (C_b), 13.94 ($C_{a'}$,C_a). HRMS (MALDI-TOF): *m/z*: calcd for $C_{62}H_{87}N_3$: 867.6425 $[M]^+$: found 867.6459.



7,7'-(2-Hexyl-2*H*-benzo[*d*][1,2,3]triazole-4,7-diyl)bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine) (2) To a 250 mL round-bottom flask was charged compound **19** (0.74 g, 2.04 mmol) compound **8** (2.83 g, 4.51 mmol), K_2CO_3 (2.26 g, 16.35 mmol), $Pd(PPh_3)_4$ (0.24 g, 0.21 mmol), H_2O (9 mL) and 1,4-dioxane (27 mL) and the resulting solution was stirred at 90 °C under N_2 for 18 h. After cooling to r.t., the reaction mixture was extracted with ethyl acetate (30 mL × 3) and the organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane (1:20) as the eluent to give the pure product as a yellow solid (1.00 g; yield = 41.0%). ^{1}H NMR (300 MHz,

$CDCl_3$): δ 8.14 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 2H; H_7), 8.04 (s, 2H; H_5), 7.79-7.75 (m, 4H; H_8, H_3), 7.63 (d, J = 8.1 Hz, 2H; H_{11}), 7.31-7.28 (m, 8H, H_{18}), 7.18-7.16 (m, 10H, H_{17}, H_{14}), 7.09-7.02 (m, 6H, H_{19}, H_{12}), 4.84 (t, 2H, H_f), 2.26-2.20 (m, 2H, H_e), 2.07-1.88 (m, 8H, $H_{f'}$), 1.41-1.38 (m, 4H, H_c, H_d), 1.19-1.12 (m, 24H, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.95-0.92 (m, 5H, H_a, H_b), 0.84-0.79 (m, 20H, $H_{a'}$, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.68 (C_4), 150.99 (C_{15}), 148.00 (C_{16}), 147.13 (C_{13}), 143.65 (C_1), 140.71 (C_9), 136.05 (C_6), 135.45 (C_{10}), 130.40 (C_2), 129.15 (C_{18}), 127.47 (C_5), 124.22 (C_8), 123.81 (C_{17}), 123.52 (C_3), 122.95 (C_7), 122.45 (C_{19}), 120.50 (C_{14}), 119.37 (C_{12}), 119.24 (C_{11}), 56.74 (C_f), 55.10 ($C_{g'}$), 40.26 ($C_{f'}$), 31.52 ($C_{e'}$), 31.29 (C_e), 29.97 (C_d), 29.72 ($C_{d'}$), 26.36 (C_c), 23.88 ($C_{c'}$), 22.58 ($C_{b'}$), 22.52 (C_b), 14.03 (C_a, $C_{a'}$); HRMS (MALDI-TOF): *m/z*: calcd for $C_{86}H_{99}N_5$, 1201.7895 $[M]^+$: found: 1201.7886.



7,7'-(2-Hexyl -2*H*-benzo[*d*] [1,2,3]triazole-4,7-diyl)bis(9,9-dihexyl-*N*,*N*-bis(4-methoxyphenyl) -9*H*-fluoren-2-amine) (3) To a 250 mL round-bottom flask was charged compound **19** (0.35 g, 0.97 mmol), compound **15** (1.48 g, 2.13 mmol), K_2CO_3 (1.05 g, 7.75 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), H_2O (7 mL) and 1,4-dioxane (21 mL) and the resulting solution was refluxed for 24 h. After cooled down to r.t., the solution was filtered through a pad of Celite 545 and the filtrate was extracted with dichloromethane (50 mL × 3). The organic layer was collected and dried over $MgSO_{4(s)}$. After filtration and removal of the solvent, the residue was purified by column chromatography using CH_2Cl_2: *n*-hexane (1:3) as eluent to give target product as a yellow powder (0.9 g; yield = 70.3%). ^{1}H NMR (500 MHz, d_8-toluene): δ 8.46 (s, J =1 Hz, 2H; H_5), 8.33 (d, J = 7.5 Hz, 2H; H_7), 7.76 (d, J = 8 Hz, 2H; H_8), 7.73 (s, 2H; H_3), 7.57 (d, J = 8.5 Hz, 2H; H_{11}), 7.39 (s, J = 2Hz, 2H; H_{14}), 7.23 (d, J = 8.5 Hz, 8H; H_{18}), 7.17 (dd, J =8 Hz, J = 2 Hz, 2H; H_{12}), 6.80 (d, J = 8.5 Hz, 8H; H_{17}), 4.49 (t, J = 7.5 Hz, 2H; H_f), 3.40 (s, 12H; $H_{h'}$), 2.19-2.14 (m, 4H; $H_{f'}$), 2.02-1.94 (m, 6H; H_e, $H_{f'}$), 1.22-1.08 (m, 38H; H_b, H_c, H_d, $H_{b'}$, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.85 (t, J = 7.5 Hz, J = 7 Hz, 15H; $H_{a'}$, H_a). ^{13}C

NMR (125 MHz, $CDCl_3$): δ 155.97 (C_{19}), 152.73 (C_1),150.77 (C_{15}), 148.69 (C_4), 144.09 (C_6), 141.70 (C_{16}), 141.24 (C_{13}), 136.94 (C_9), 135.67 (C_{10}), 134.67 (C_2), 130.66 (C_7), 1276.18 (C_{18}), 124.17 (C_5), 123.24 (C_{11}), 120.97 (C_8), 120.63 (C_3), 119.99 (C_{14}), 116.56 (C_{12}), 114.75 (C_{17}), 56.731(C_f), 55.15 ($C_{g'}$), 54.51($C_{h'}$), 40.59 ($C_{f'}$), 31.68 ($C_{e'}$), 31.29 (C_e), 30.02 ($C_{d'}$), 29.76 (C_d), 26.29 (C_c), 24.18 ($C_{c'}$), 22.77 ($C_{b'}$), 22.45 (C_b), 13.90 ($C_{a'}$), 13.82 (C_a). HRMS (MALDI-TOF) *m/z*: calcd for $C_{90}H_{107}N_5O_4$: 1321.8318 $[M]^+$: found 1321.8322.

2. Neat-film fabrication and Photophysical Methods

2.1 Neat-film fabrication

Neat films of compounds **1**, **2**, and **3** were fabricated using the spin-casting method. The materials were dissolved in toluene at a concentration of ~60 mg/mL. The spinning speed was ~2500 rpm. The thickness of the neat films was measured to be ~200 nm using a spectroscopic ellipsometer.

2.2 Linear absorption and emission spectra measurements

Linear absorption spectra were recorded on a Shimadzu 3150 PC spectrophotometer with freshly prepared sample solutions. The same sample solutions were also used for the measurement of fluorescence spectra and life-time by utilizing a Jobin-Yvon FluoroMax-4 spectrometer equipped with TCSPC accessories (FluoroHub-B + NanoLED from Jobin-Yvon). The aforementioned fluorospectrometer equipped with an integrating sphere (Labsphere from Jobin-Yvon; diameter = 100 mm) was also employed to measure the absolute photoluminescence quantum yield (PLQY) of each model compound in solution and powder phases at room temperature;[2] Coumarin 153 (Φ_F = 0.38 ± 5% at λ_{exc} = 423 nm) was used as the standard for the calibration of the integrating sphere and the instrument.[3]

As for the linear optical properties of the prepared neat-films, fluorescence spectra were measured in a front-face configuration by using a fiber-based spectrograph and a TE-cooled charge-coupled device (CCD) camera (Princeton Instruments, PIXIS 256BR), with a diode laser (λ = 375 nm) serving as the pumping source. Absolute PLQYs were detected using a calibrated integrating sphere system (Labsphere) equipped with the same CCD spectrograph. The uncertainty of the fluorescence quantum yield value was estimated to be around ±2% owing to the stability of the excitation source and the uncertainty of the radiometric calibration source. Thin film absorption spectra were measured utilizing an ultraviolet-visible spectrophotometer (Shimadzu, UV2600).

2.2 Amplifies spontaneous emission (ASE) related measurements

The experimental setup for ASE-related measurement is illustrated in Fig. S1. A frequency-tripled Q-switched Nd:YAG laser (NL204 series, EKSPLA Inc.) with a central wavelength at 355 nm was served as the excitation source. The pump pulses had a repetition rate of 10 Hz and a pulse duration of 7 ns. A combination of a polarization beam splitter (PBS) and a half-waveplate (λ/2) were

employed to regulate the pump energy. The laser beam was focused onto the front-surface of the sample to form a long line stripe using a 75 mm cylindrical lens and the side emission from the sample was collected through an optical fiber and analyzed by a spectrometer (*i*HR550, Horiba Inc.) equipped with an electrically cooled charge-coupled device (CCD) (Syncerity, Horiba Inc.). As for the samples, either a cuvette filled with the studied dye solution (1×10^{-3} M in toluene) or a neat-film of the studied model chromophores was prepared and fixed at the sample position as shown in Fig. S1 for this experiment.

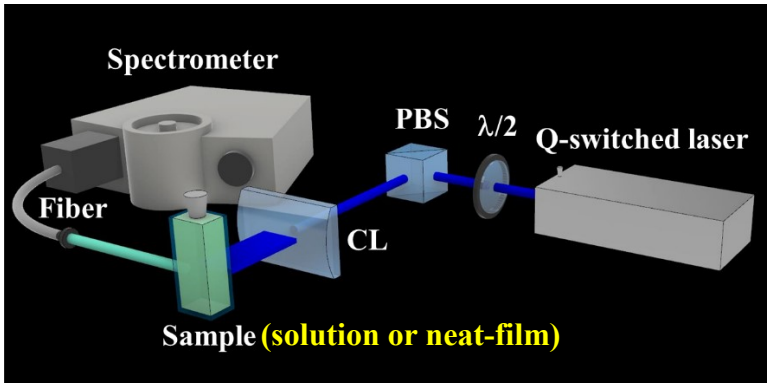


Figure S1. Optical setup for ASE-related experiments.

In addition, it should be noted that the threshold of ASE is theoretically governed by the following relationships:[4]

$$E_{Th}^{ASE} \propto \frac{1}{B}; B \propto \frac{c^3}{8\pi h\nu^3}k_r$$

where B is the Einstein constant, c is the velocity of light, h is Planck's constant, ν represents the transition frequency, and $k_r = \phi/\tau$ is the fluorescence radiative rate constant where ϕ and τ denotes PLQY and fluorescence decay lifetime, respectively.

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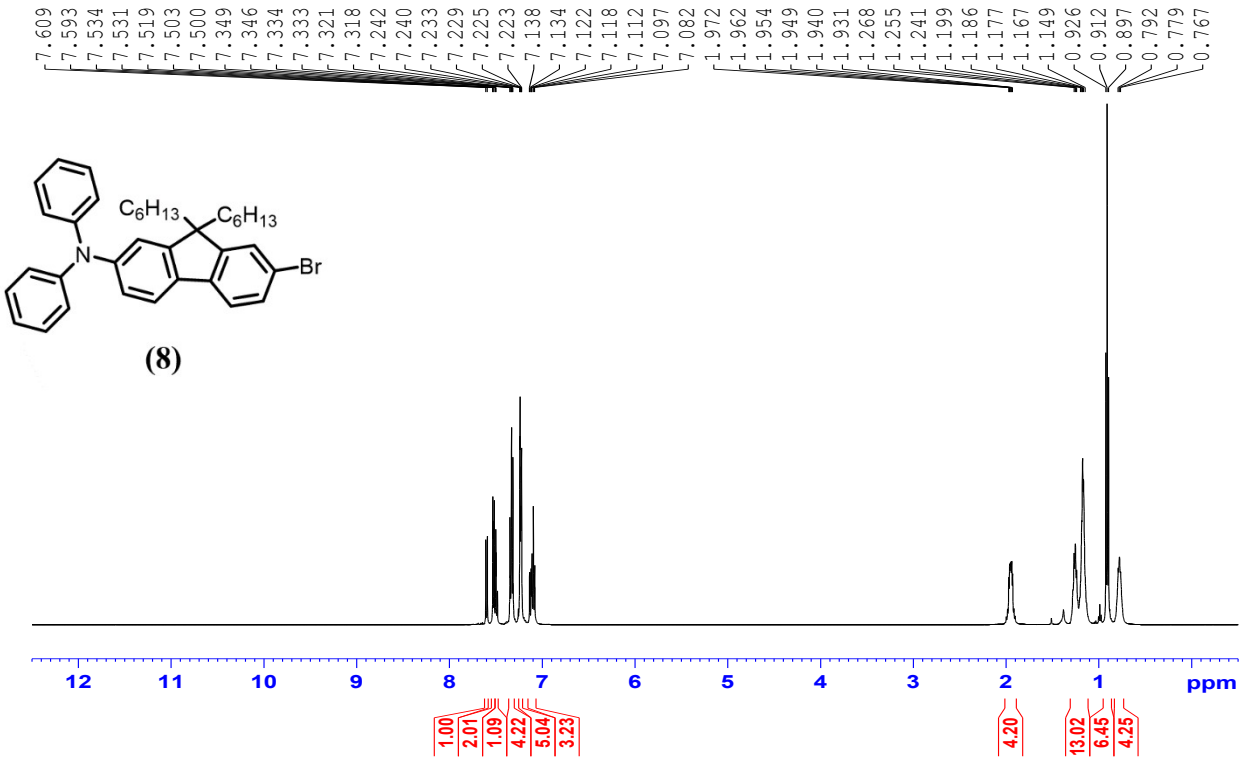
[1] T.-C. Lin, Q. Zheng, C.-Y. Chen, G. S. He, W.-J. Huang, A. I. Ryasnyanskiy and P. N. Prasad, *Chem. Commun.*, **2008**, 389-391.

[2] L. Porres, A. Holland, L.-O. Palsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.* **2006**, *16*, 267-273.

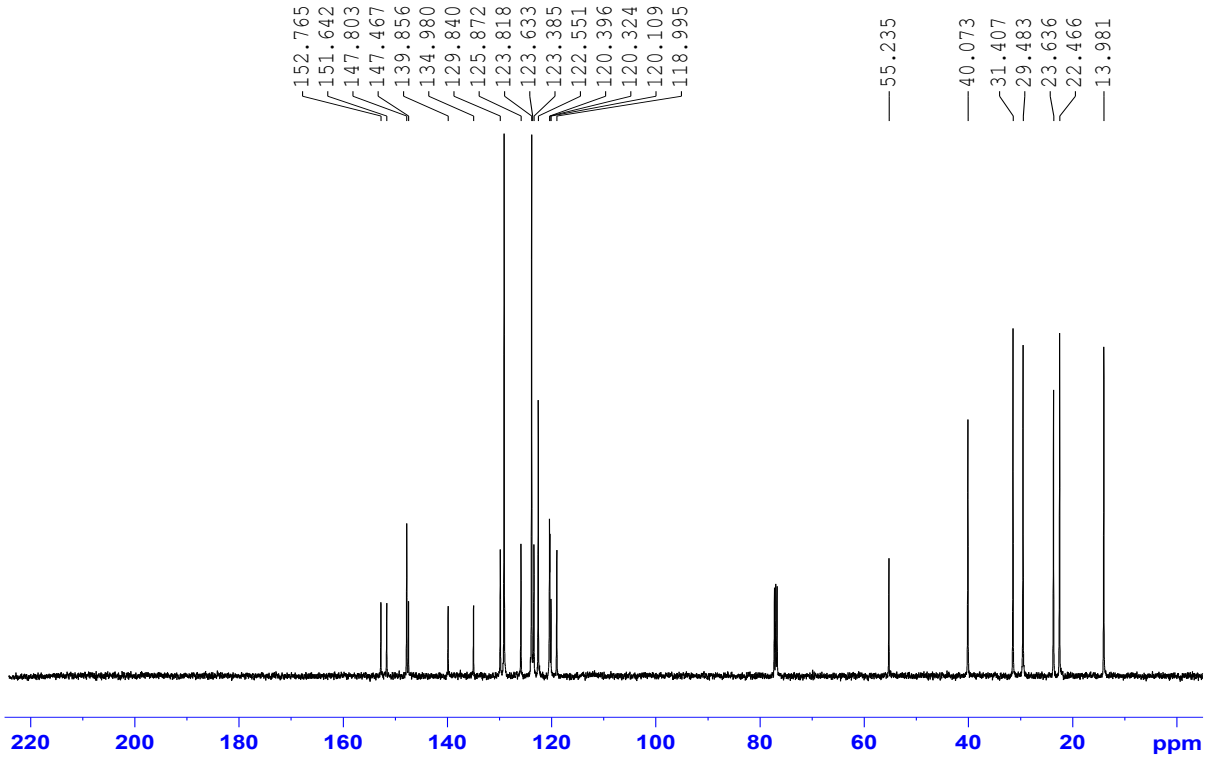
[3] a) J. A. Gardecki and M. Maroncelli, *Applied Spectroscopy* **1998**, *52*, 1179-1189; b) G. A. Reynolds and K. H. Drexhage, *Optics Communications* **1975**, *13*, 222-225.

[4] X. Tang, Y.-T. Lee, Z. Feng, S. Y. Ko, J. W. Wu, V. Placide, J.-C. Ribierre, A. D'Aléo and C. Adachi, *ACS Mater. Lett.*, **2020**, *2*, 1567-1574.

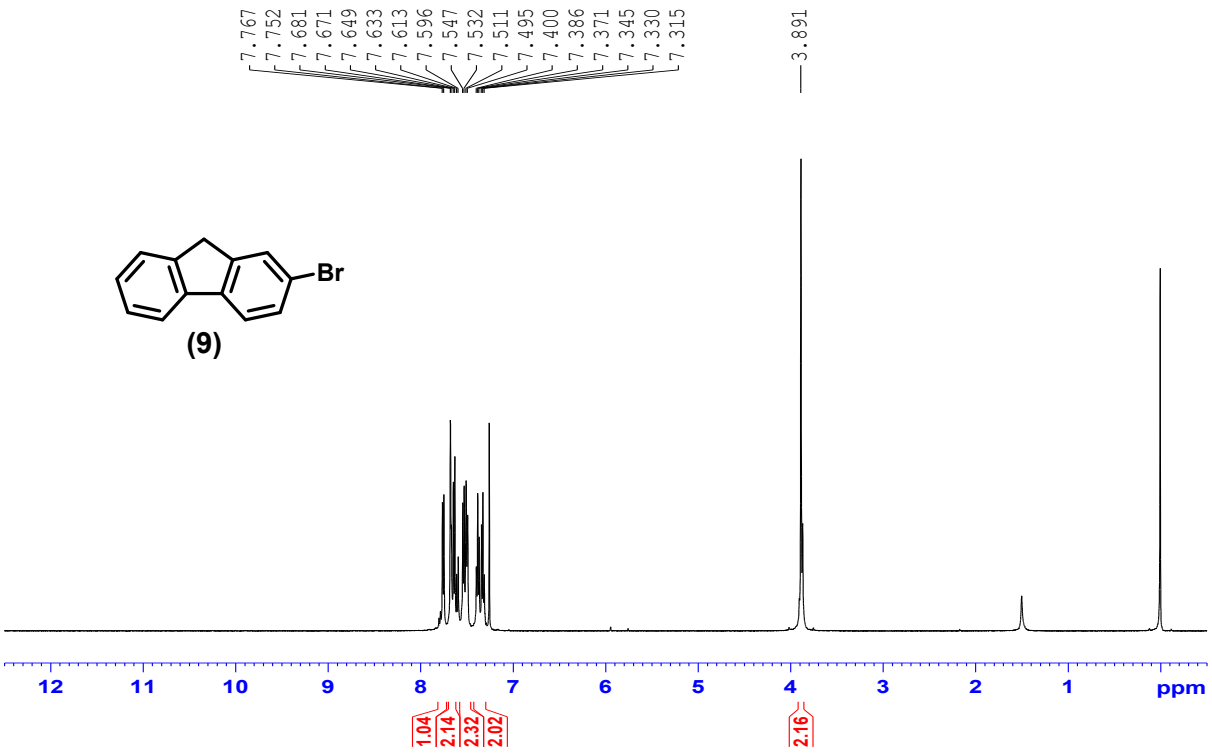
3. ^{1}H and ^{13}C NMR spectra of the precursors and final compounds



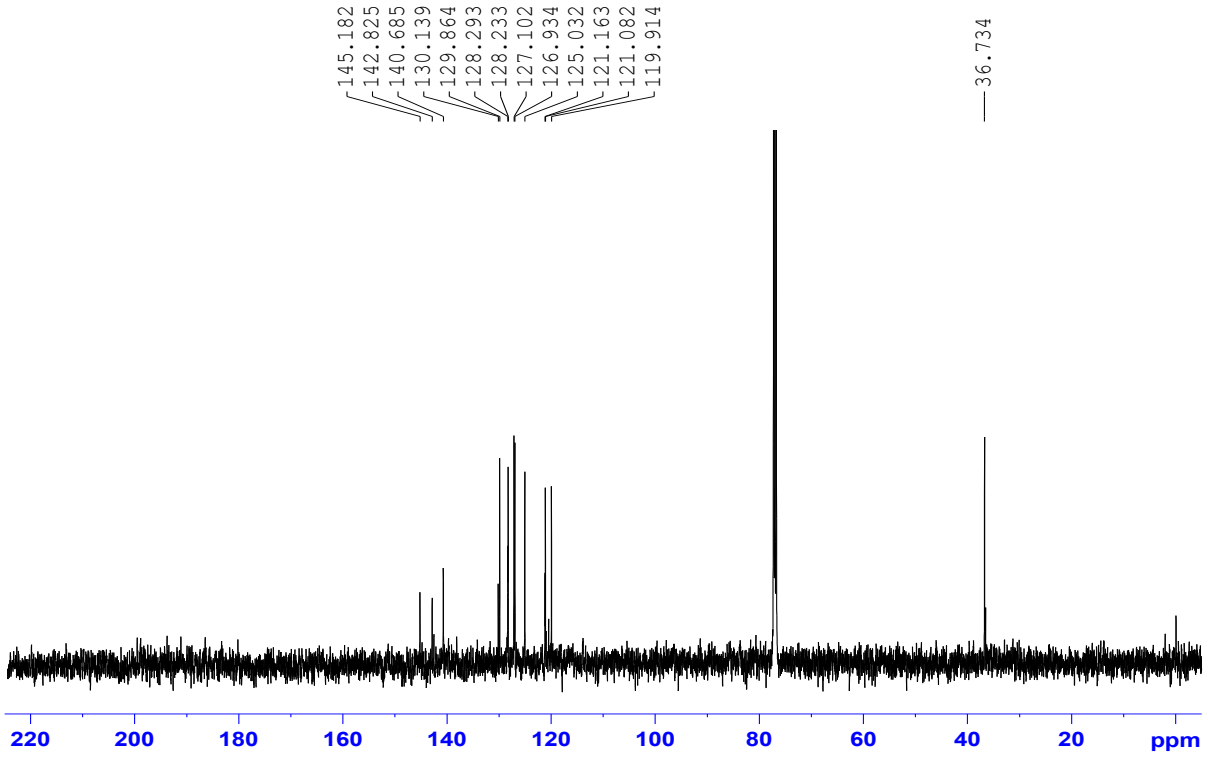
^{1}H NMR Spectrum of Compound 8 (Solvent: $CDCl_3$)



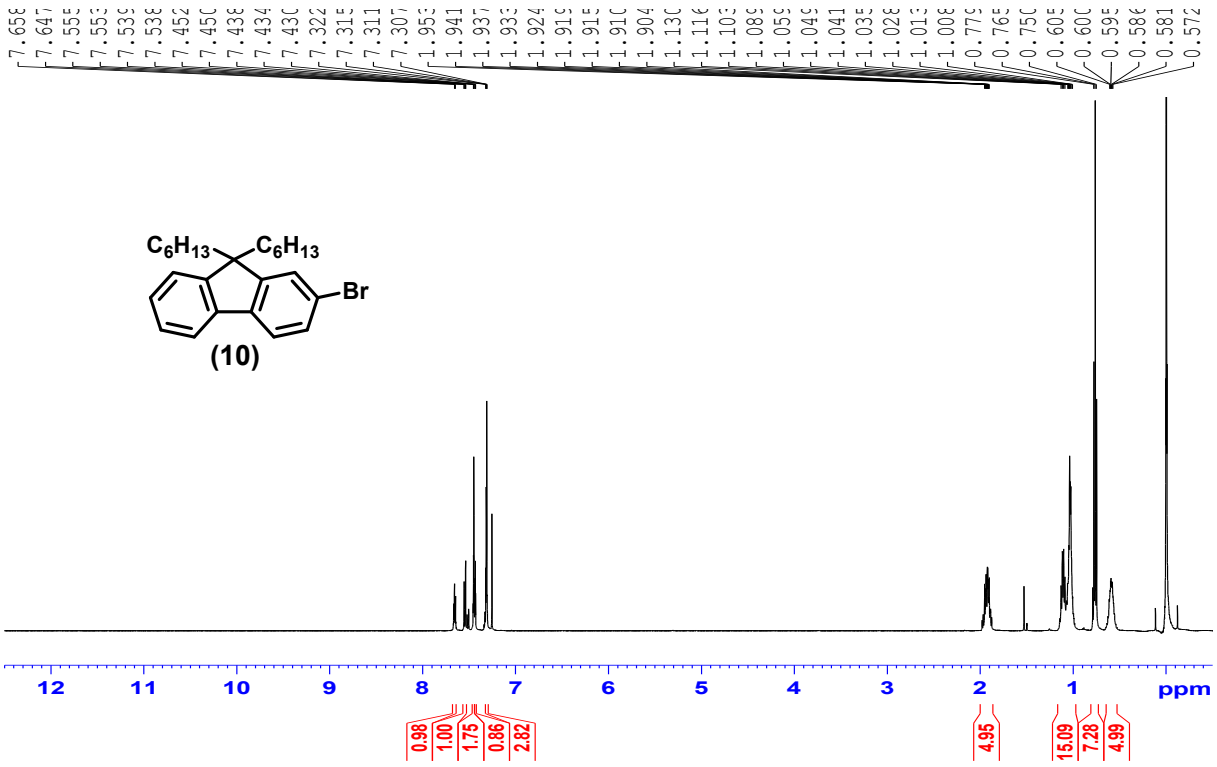
^{13}C NMR Spectrum of Compound 8 (Solvent: $CDCl_3$)



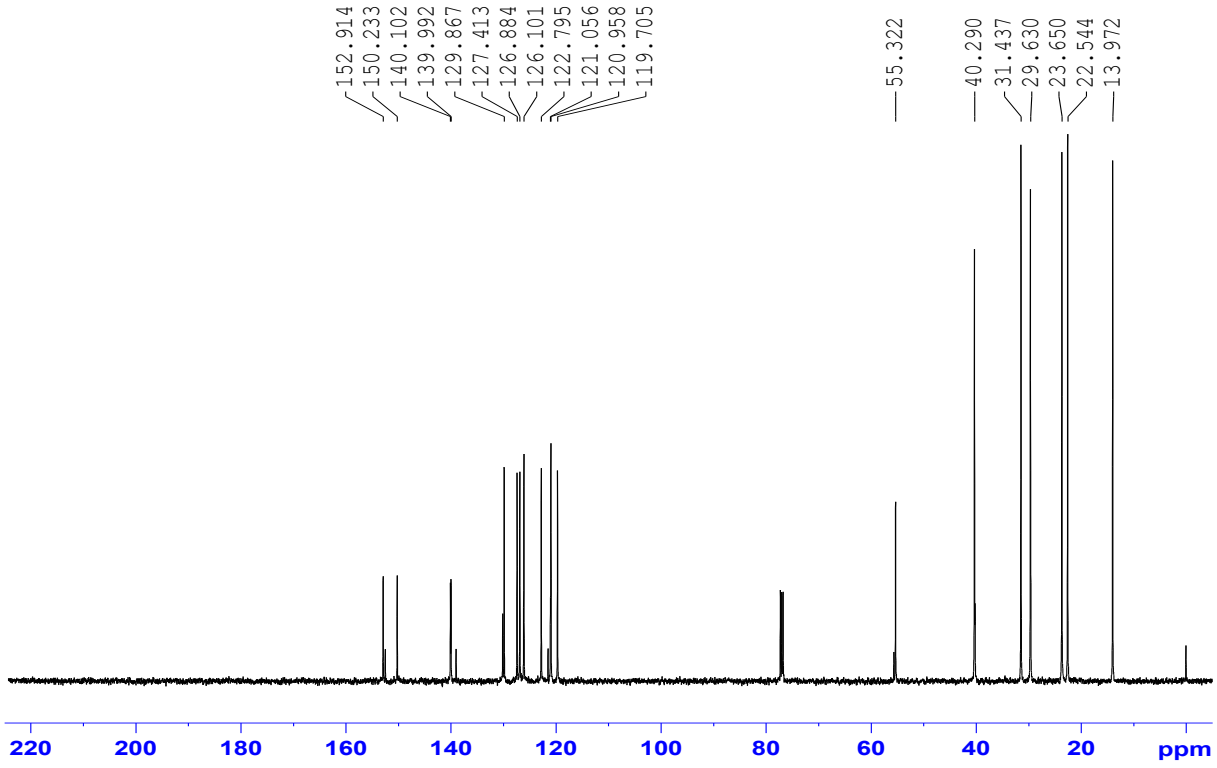
^{1}H NMR Spectrum of Compound 9 (Solvent: $CDCl_3$)



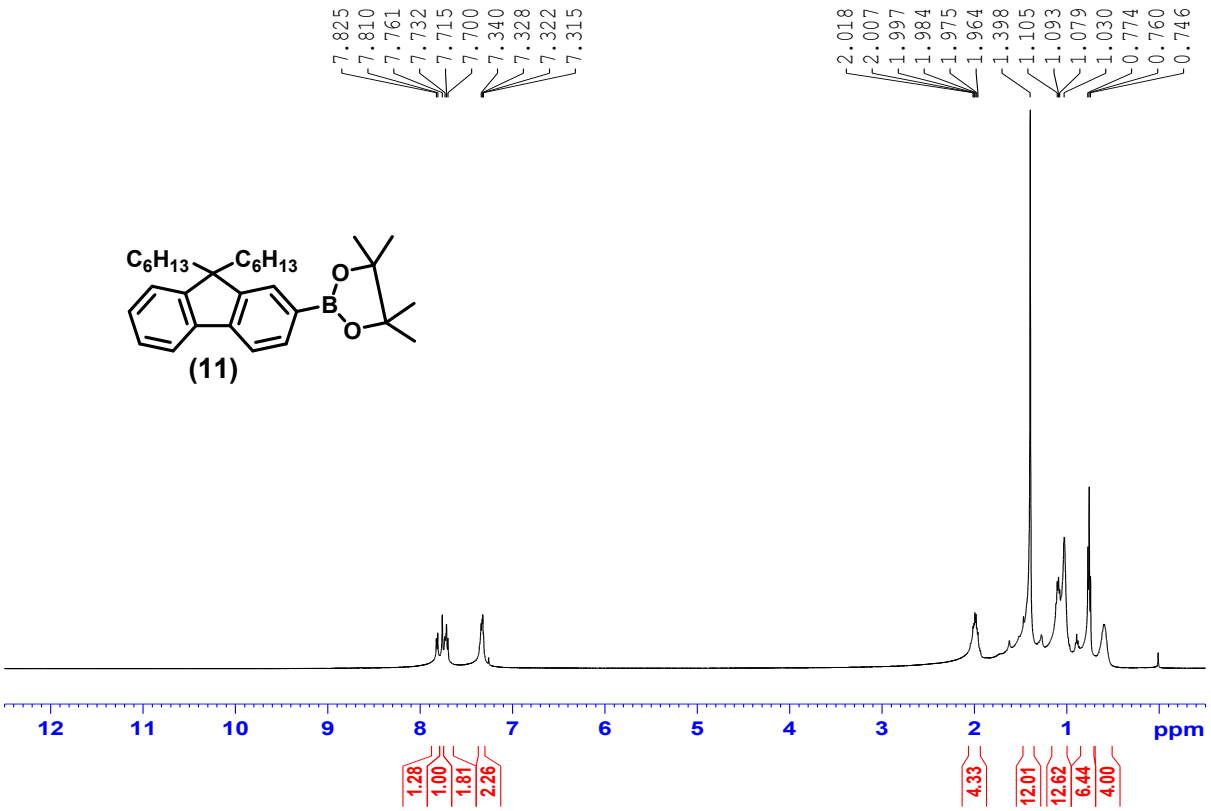
^{13}C NMR Spectrum of Compound 9 (Solvent: $CDCl_3$)



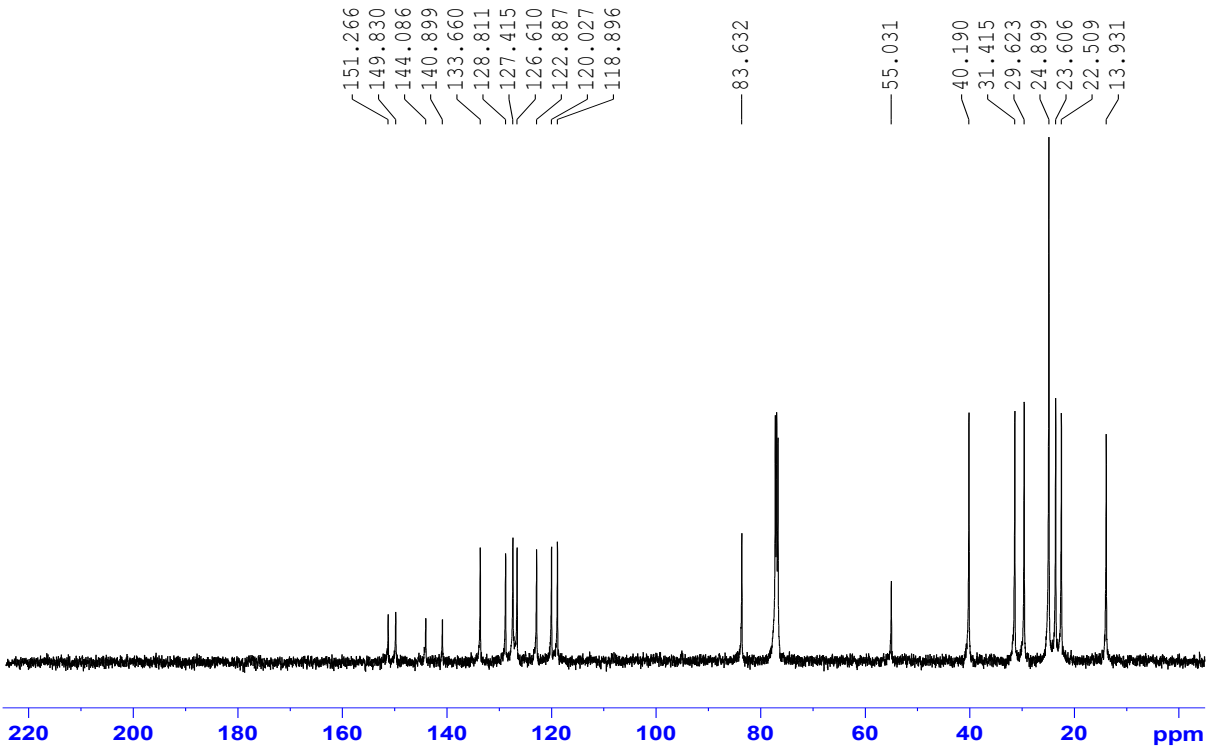
^{1}H NMR Spectrum of Compound 10 (Solvent: $CDCl_3$)



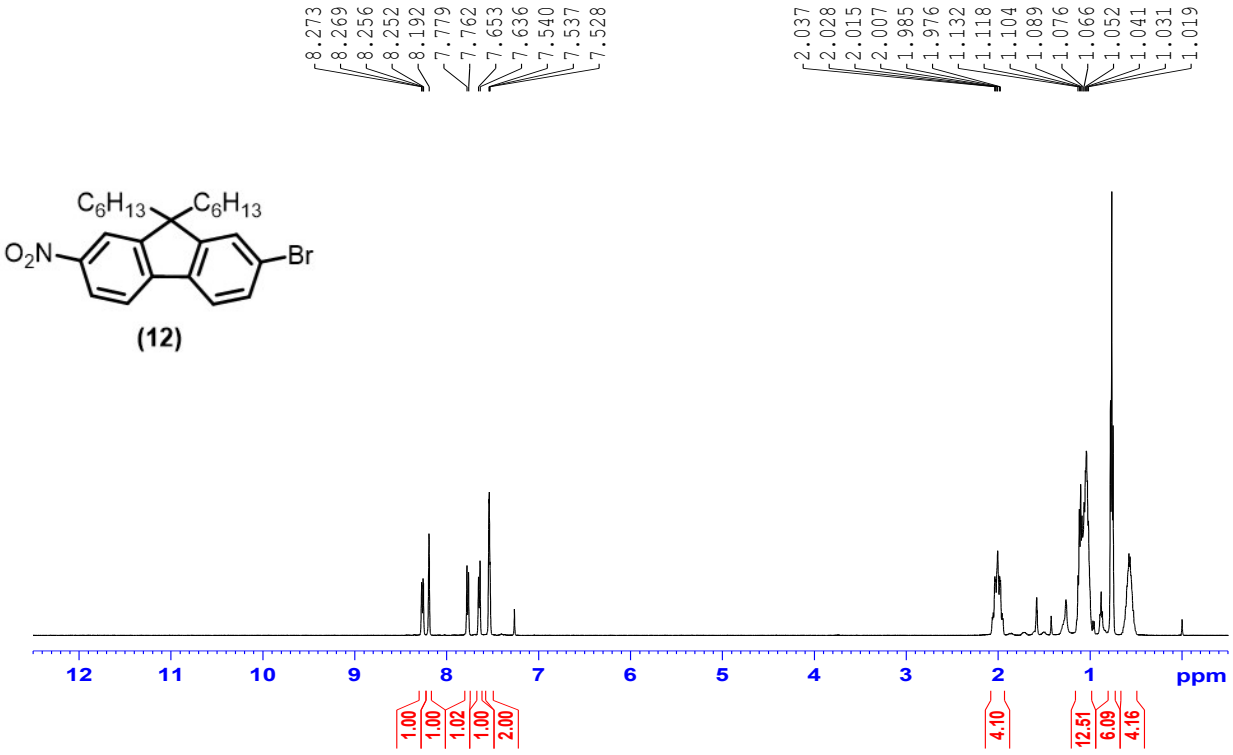
^{13}C NMR Spectrum of Compound 10 (Solvent: $CDCl_3$)



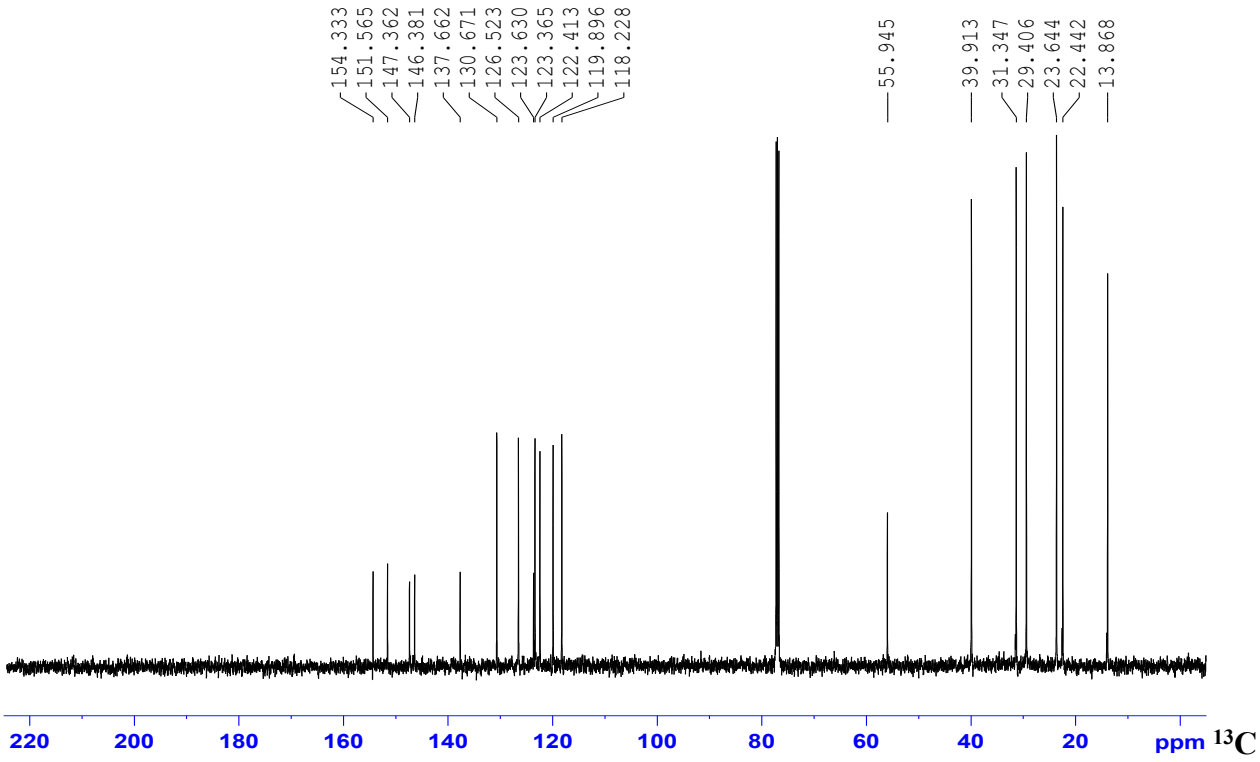
^{1}H NMR Spectrum of Compound 11 (Solvent: $CDCl_3$)



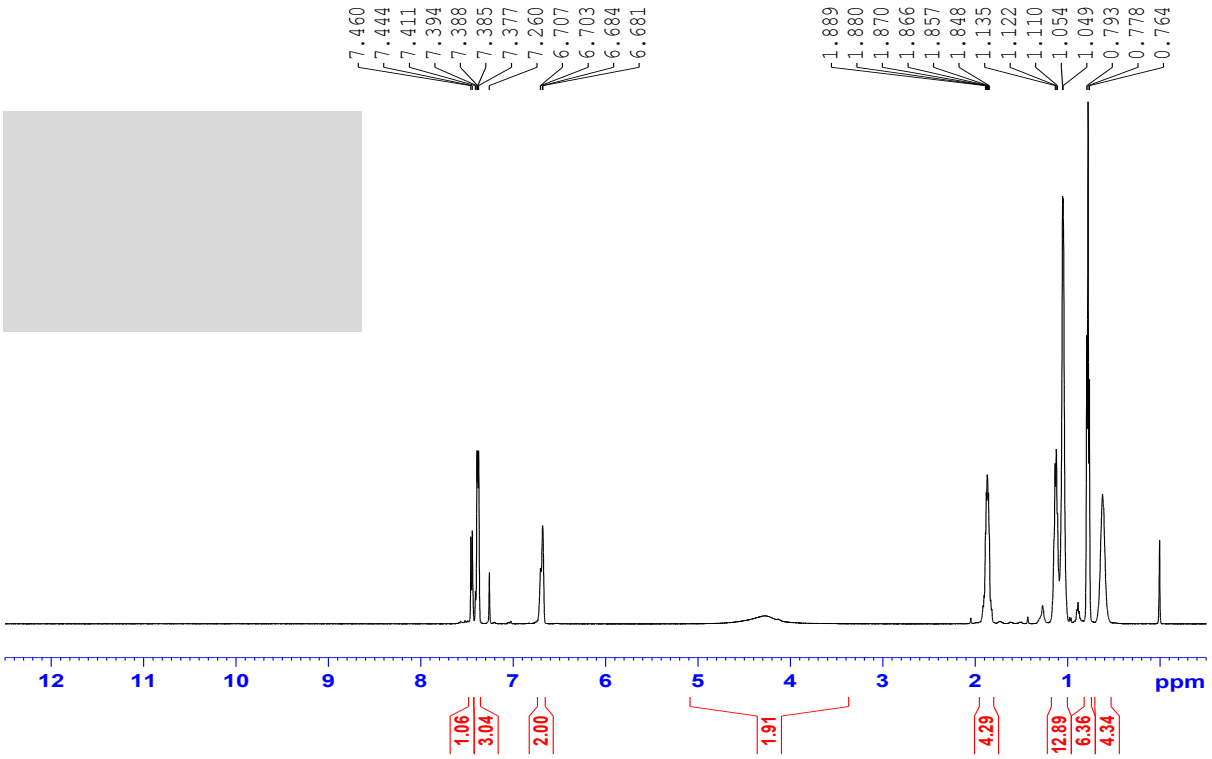
^{13}C NMR Spectrum of Compound 11 (Solvent: $CDCl_3$)



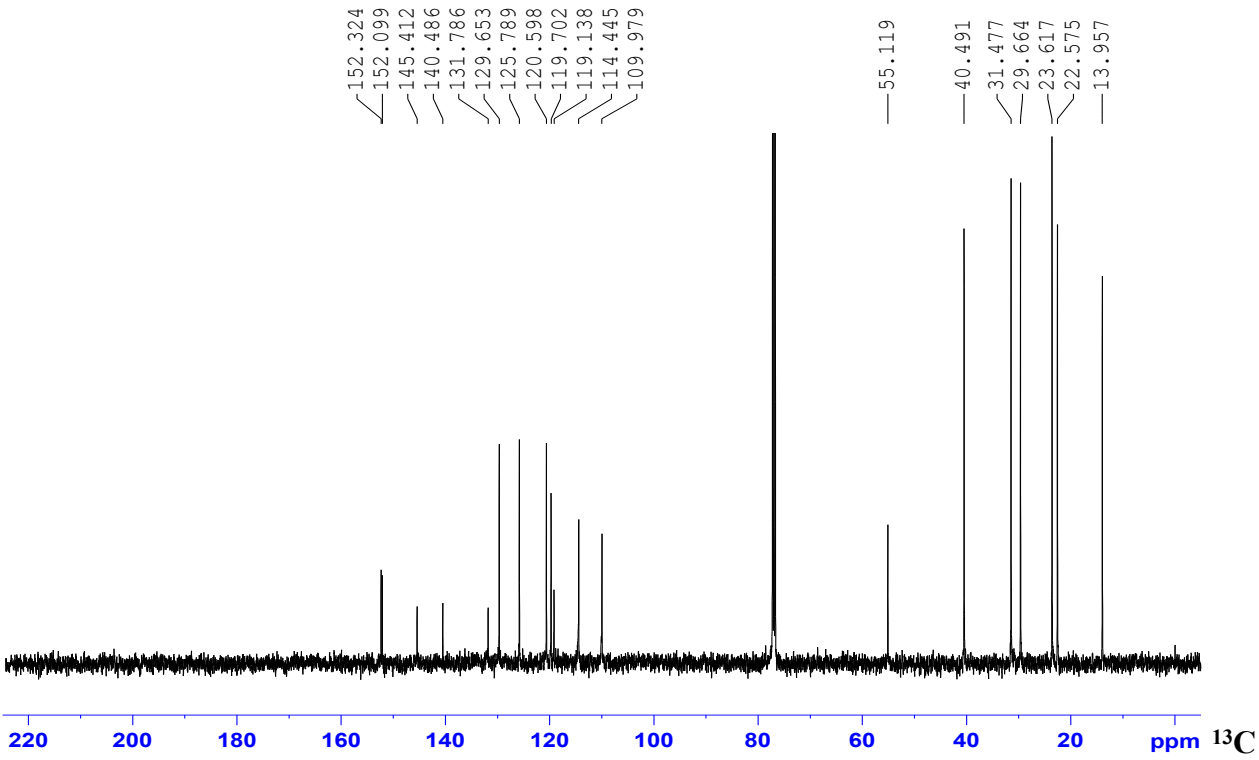
^{1}H NMR Spectrum of Compound 12 (Solvent: $CDCl_3$)



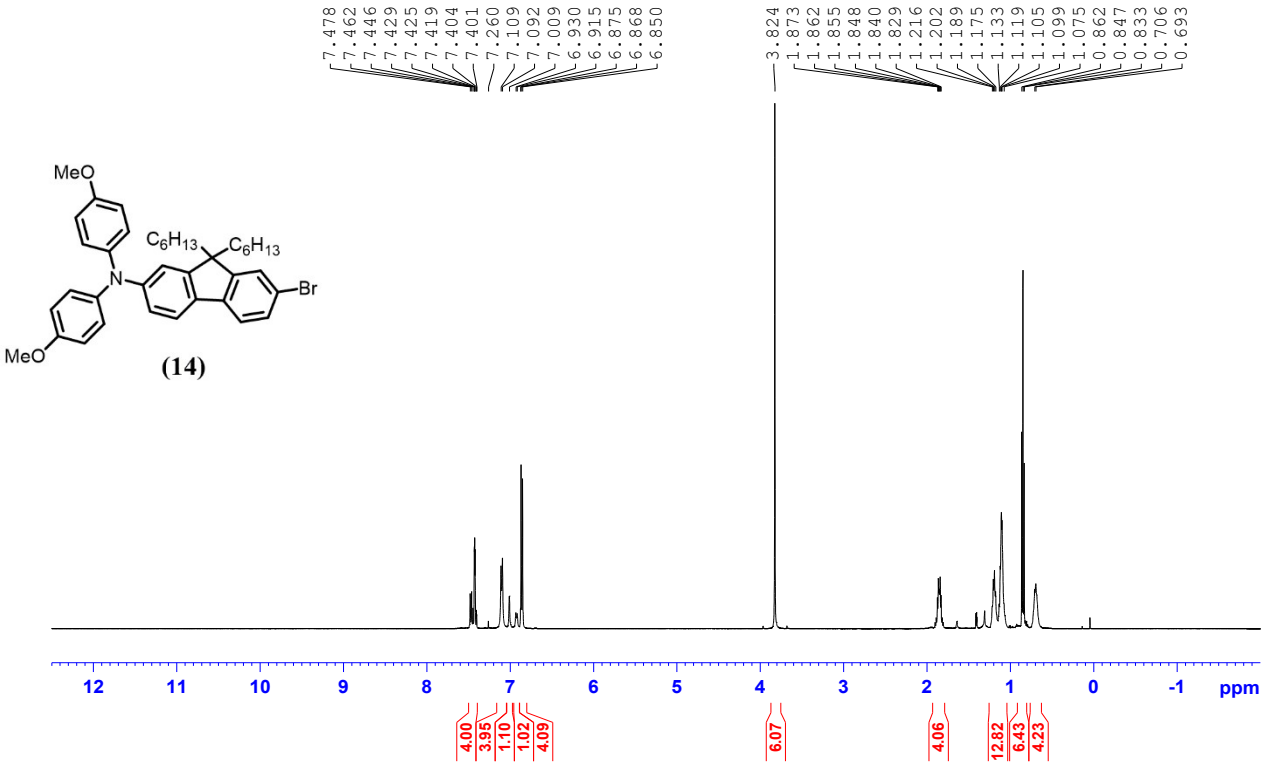
NMR Spectrum of Compound 12 (Solvent: $CDCl_3$)



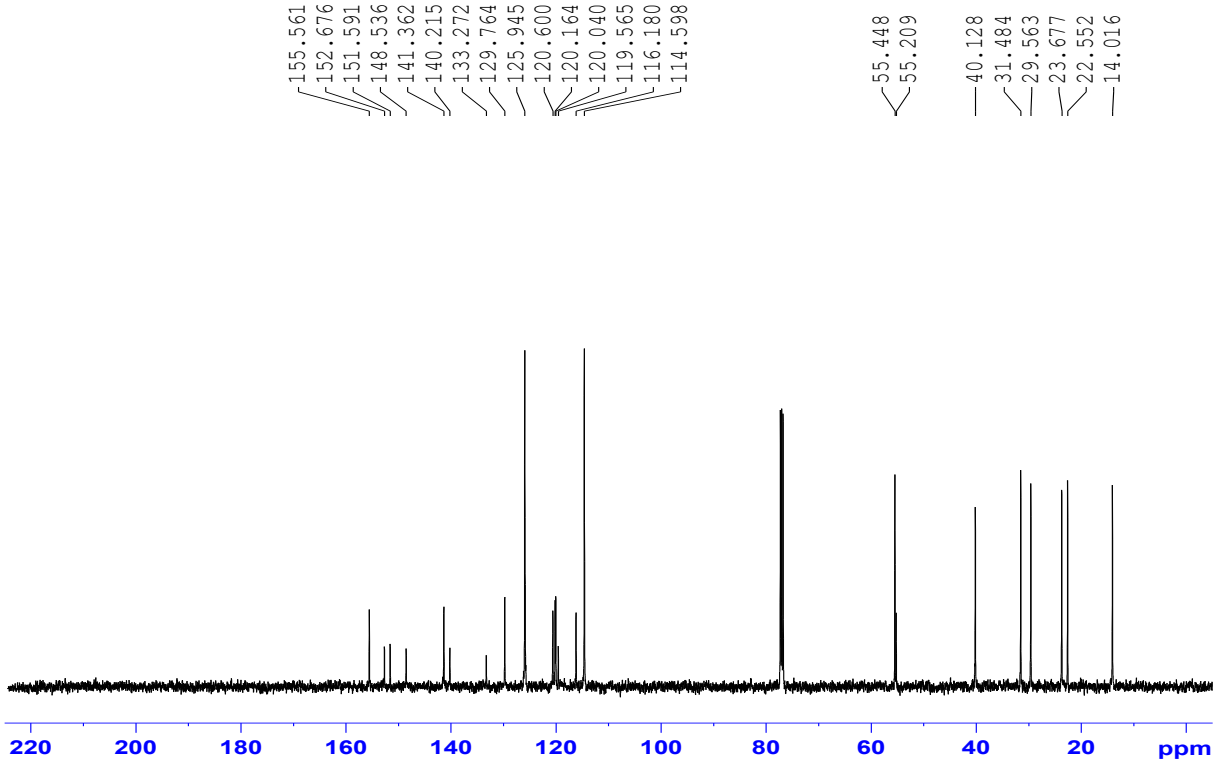
^{1}H NMR Spectrum of Compound 13 (Solvent: $CDCl_3$)



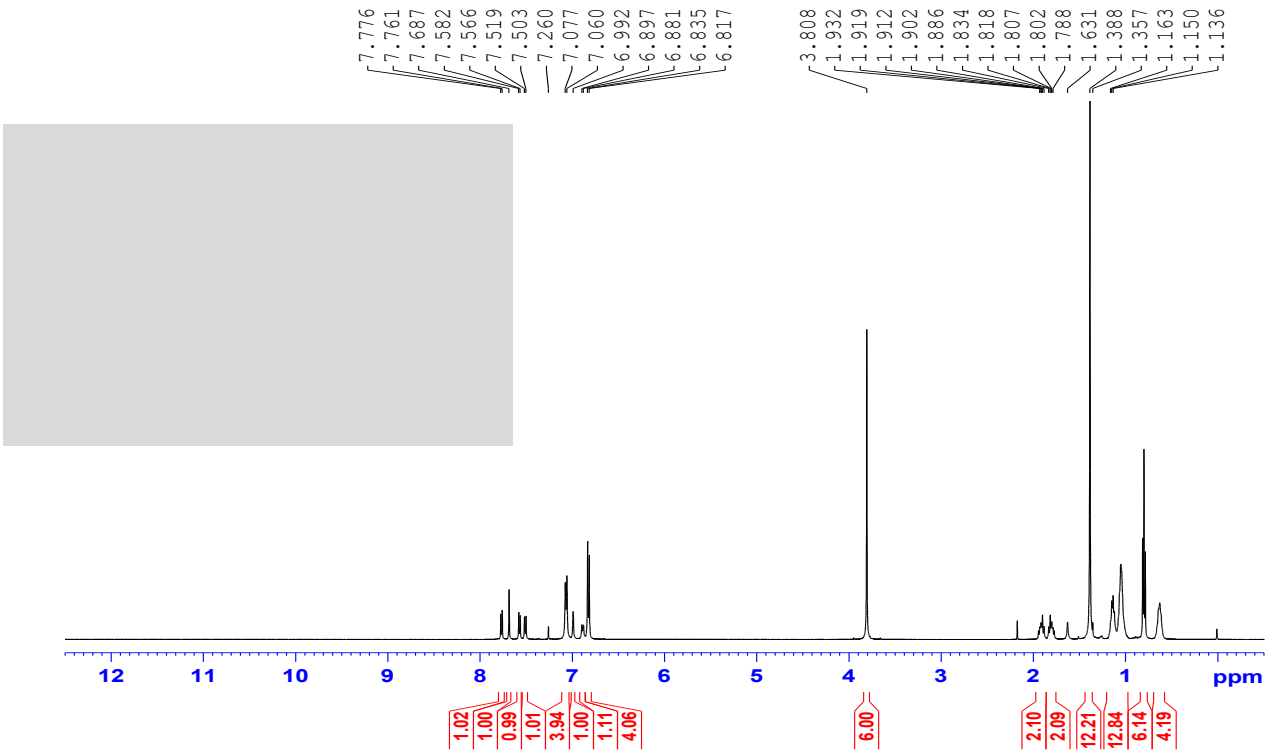
NMR Spectrum of Compound 13 (Solvent: $CDCl_3$) ^{13}C



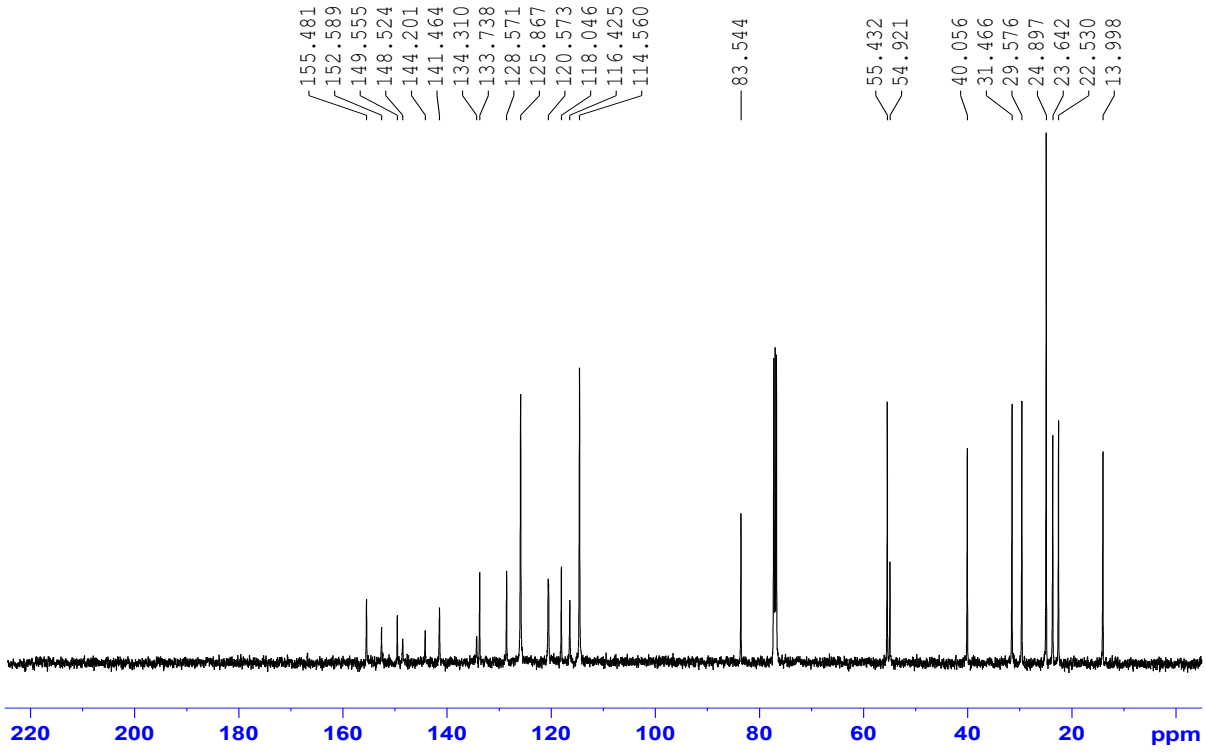
^{1}H NMR Spectrum of Compound 14 (Solvent: $CDCl_3$)



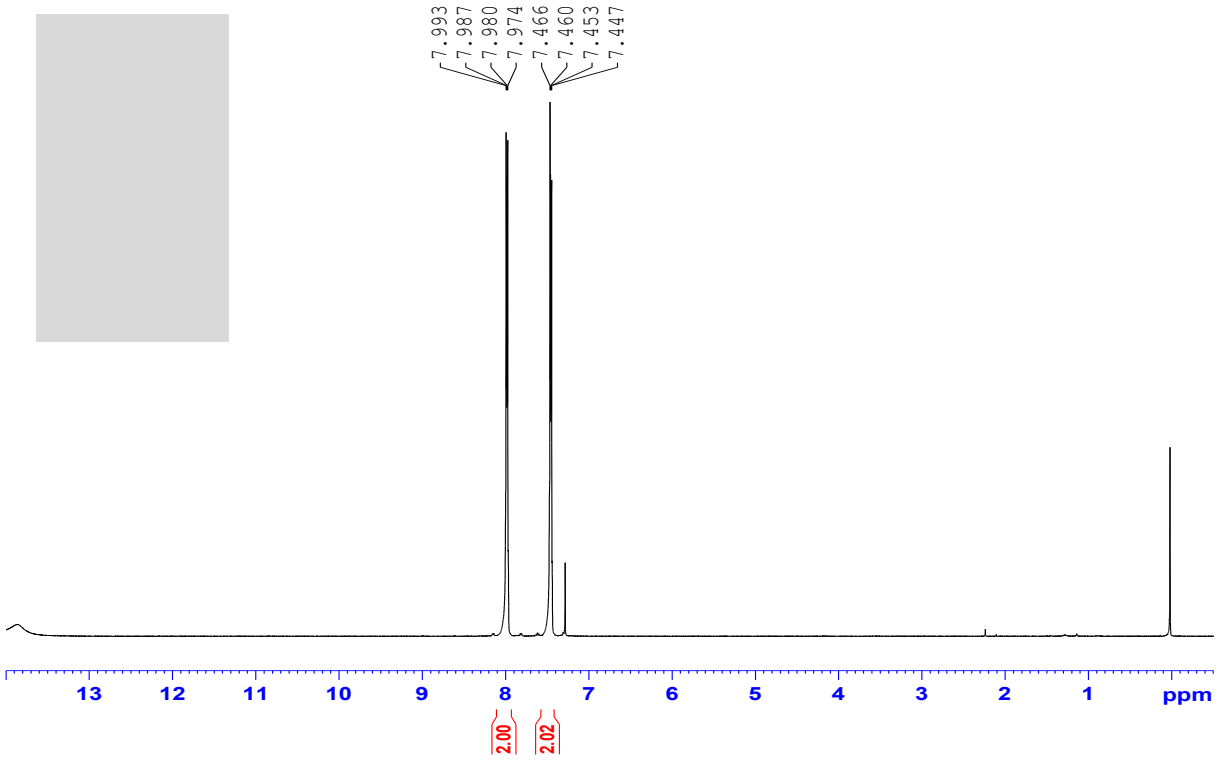
^{13}C NMR Spectrum of Compound 14 (Solvent: $CDCl_3$)



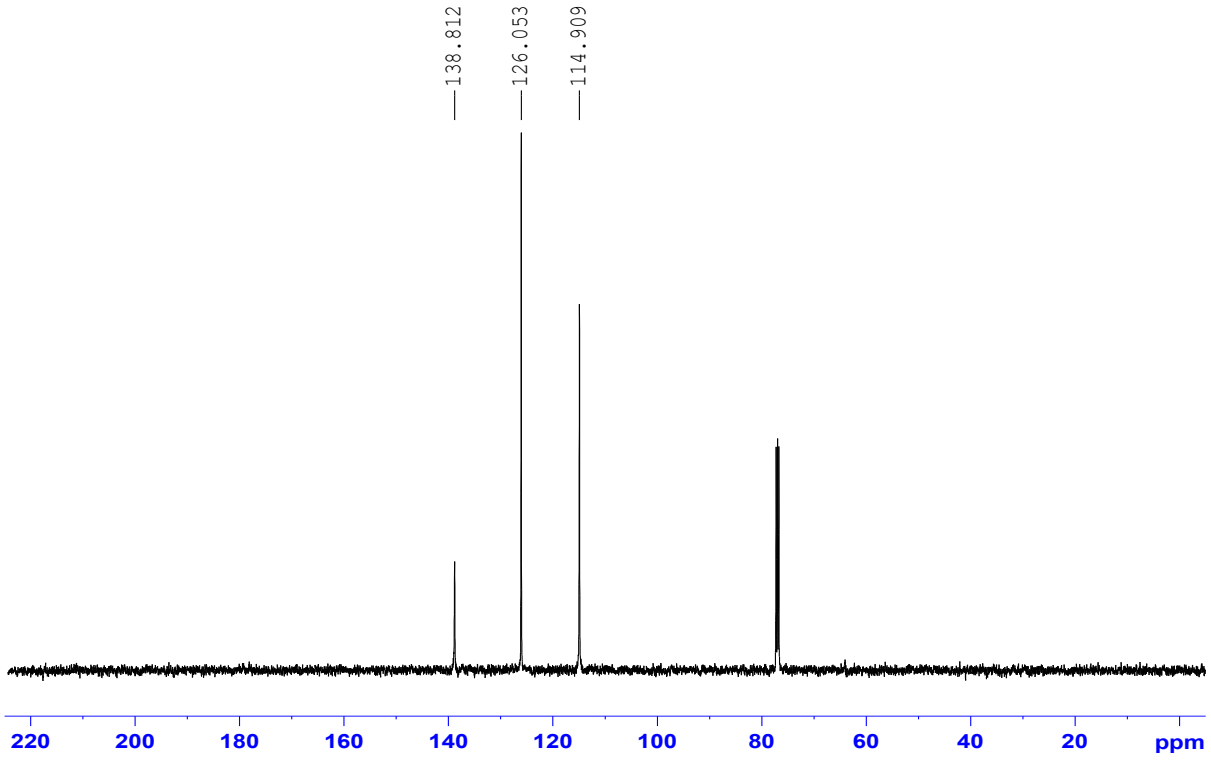
^{1}H NMR Spectrum of Compound 15 (Solvent: $CDCl_3$)



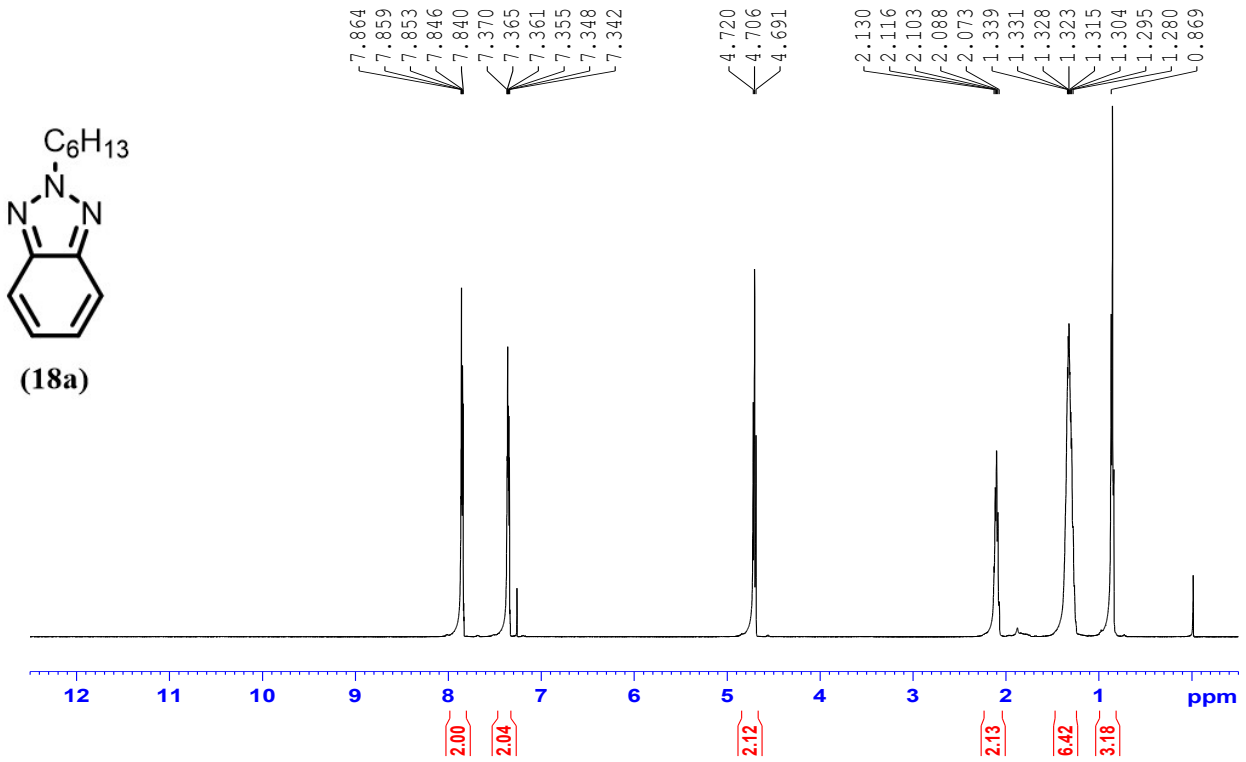
^{13}C NMR Spectrum of Compound 15 (Solvent: $CDCl_3$)



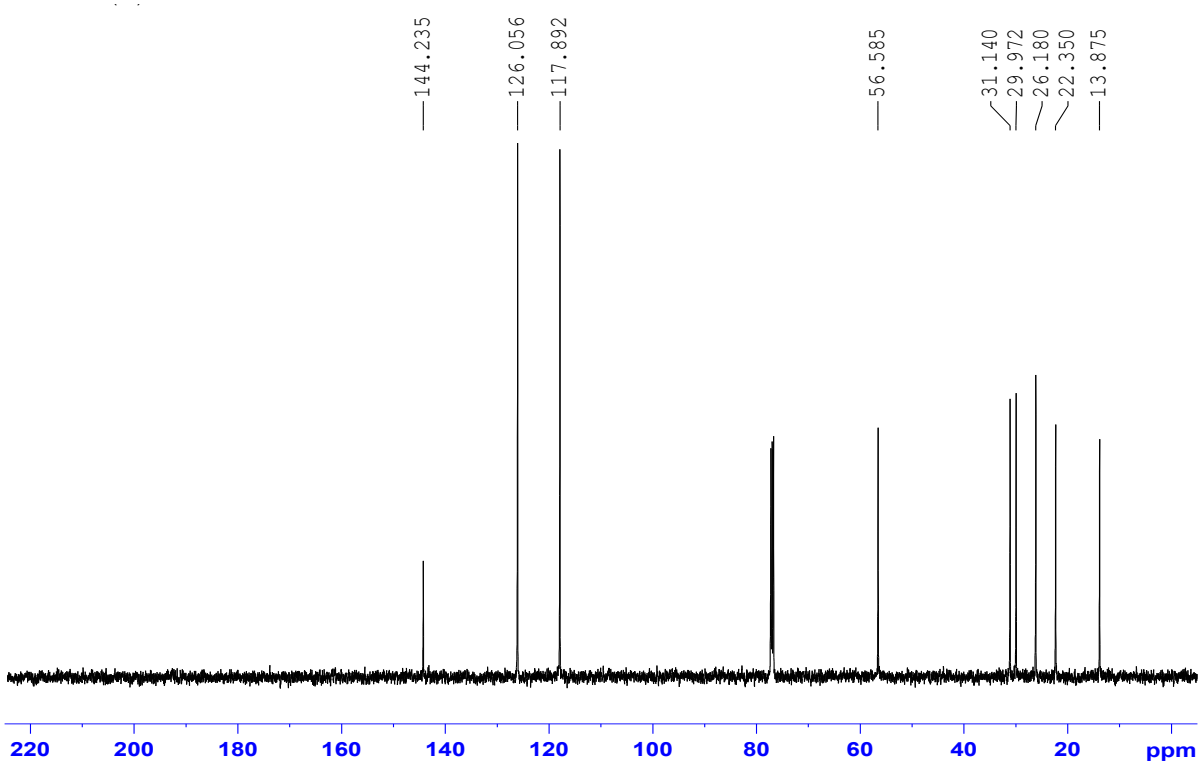
^{1}H NMR Spectrum of Compound 17 (Solvent: $CDCl_3$)



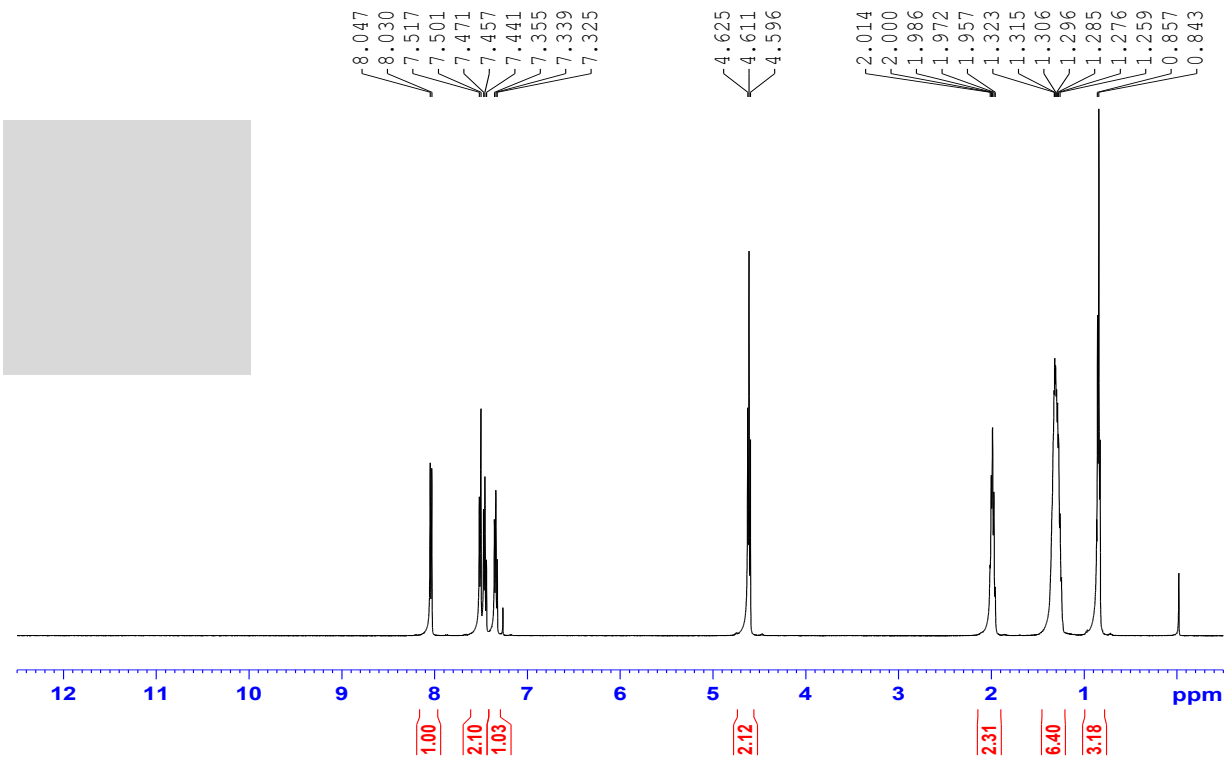
^{13}C NMR Spectrum of Compound 17 (Solvent: $CDCl_3$)



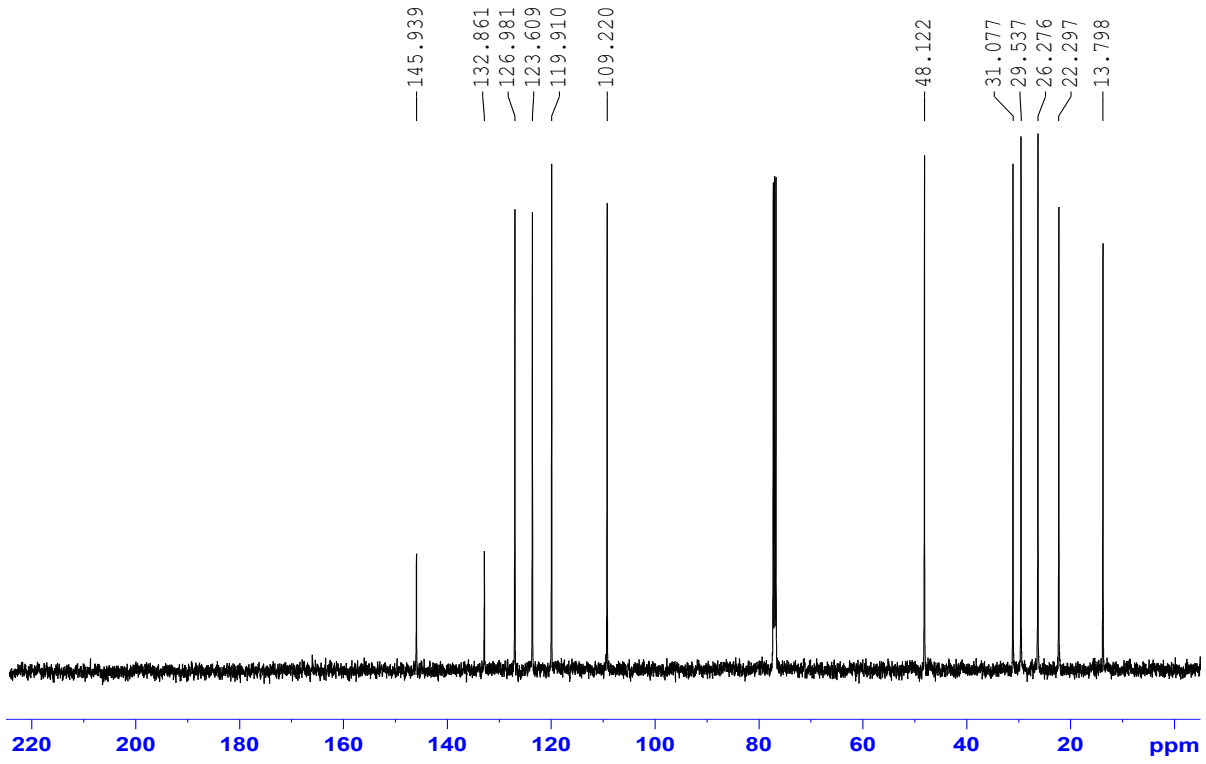
^{1}H NMR Spectrum of Compound 18a (Solvent: $CDCl_3$)



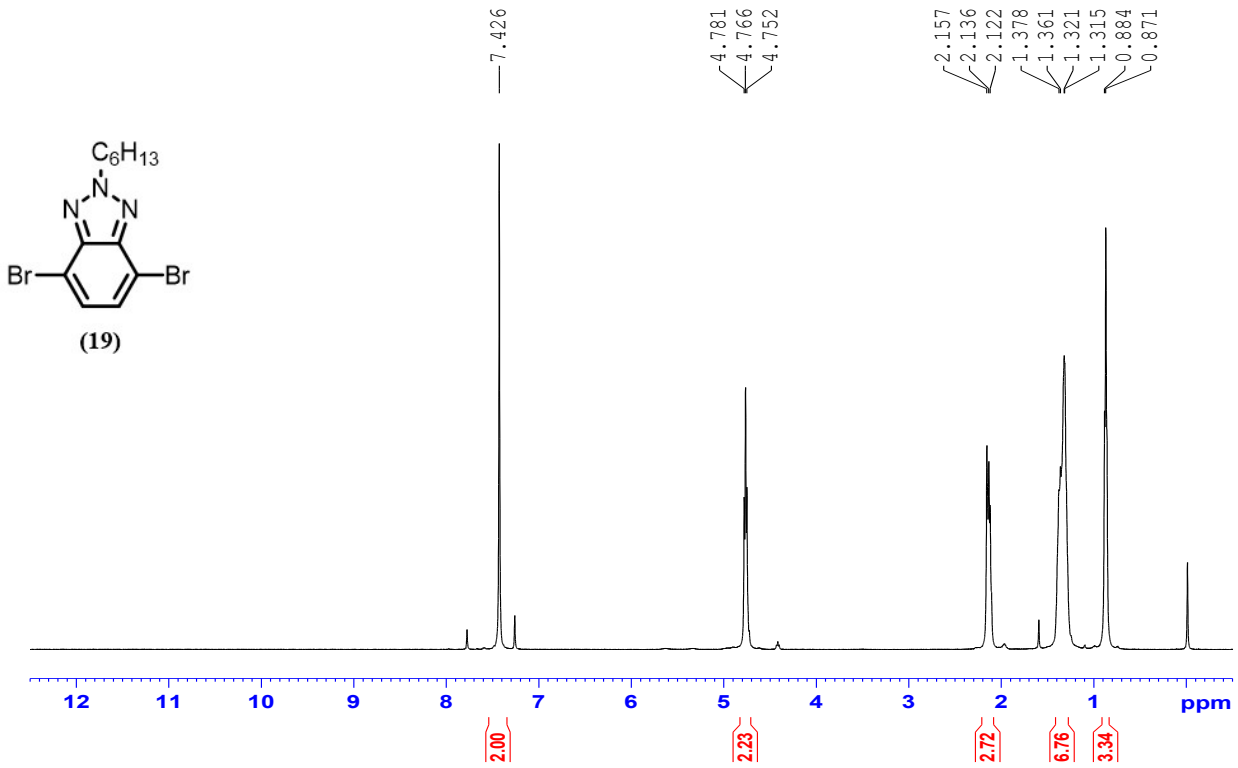
^{13}C NMR Spectrum of Compound 18a (Solvent: $CDCl_3$)



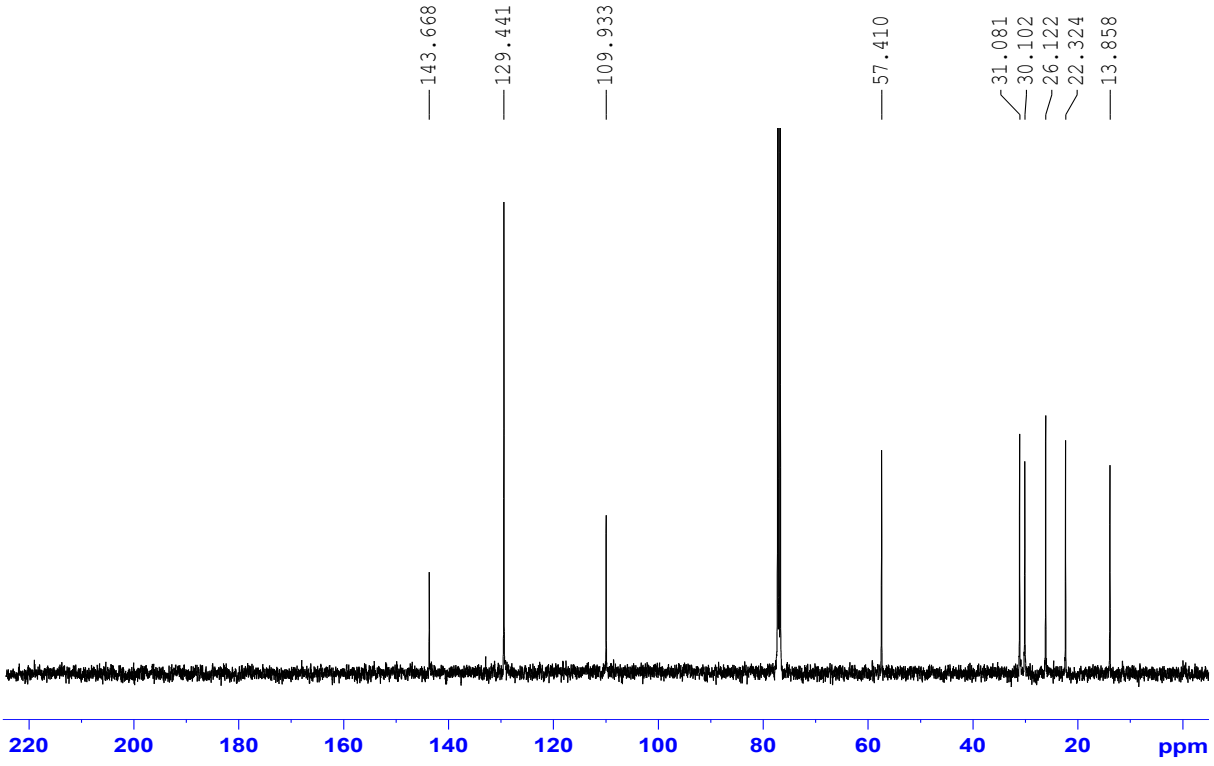
^{1}H NMR Spectrum of Compound 18b (Solvent: $CDCl_3$)



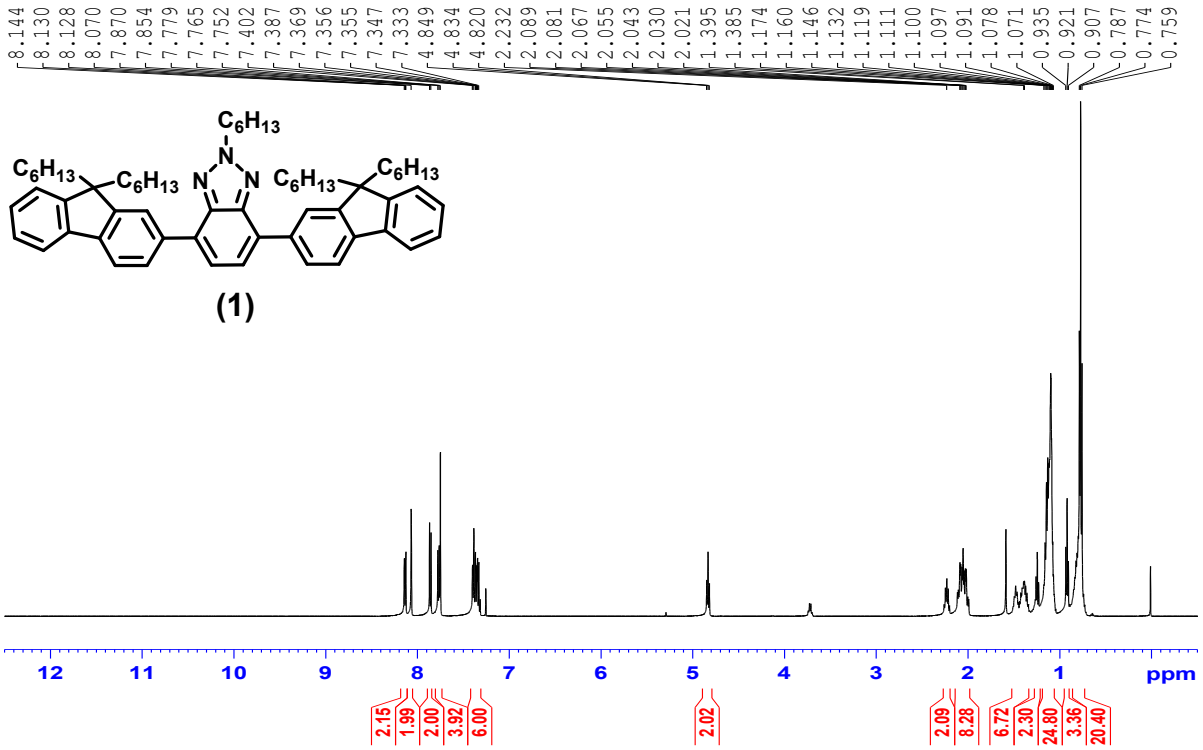
^{13}C NMR Spectrum of Compound 18b (Solvent: $CDCl_3$)



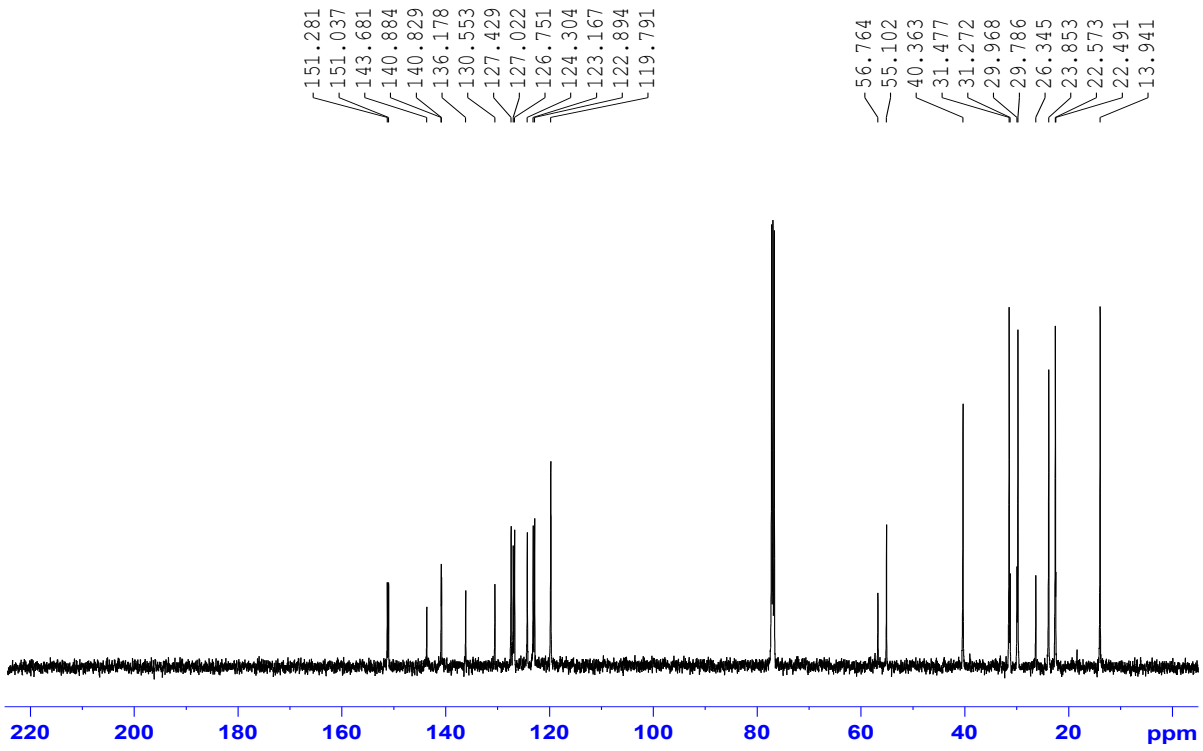
^{1}H NMR Spectrum of Compound 19 (Solvent: $CDCl_3$)



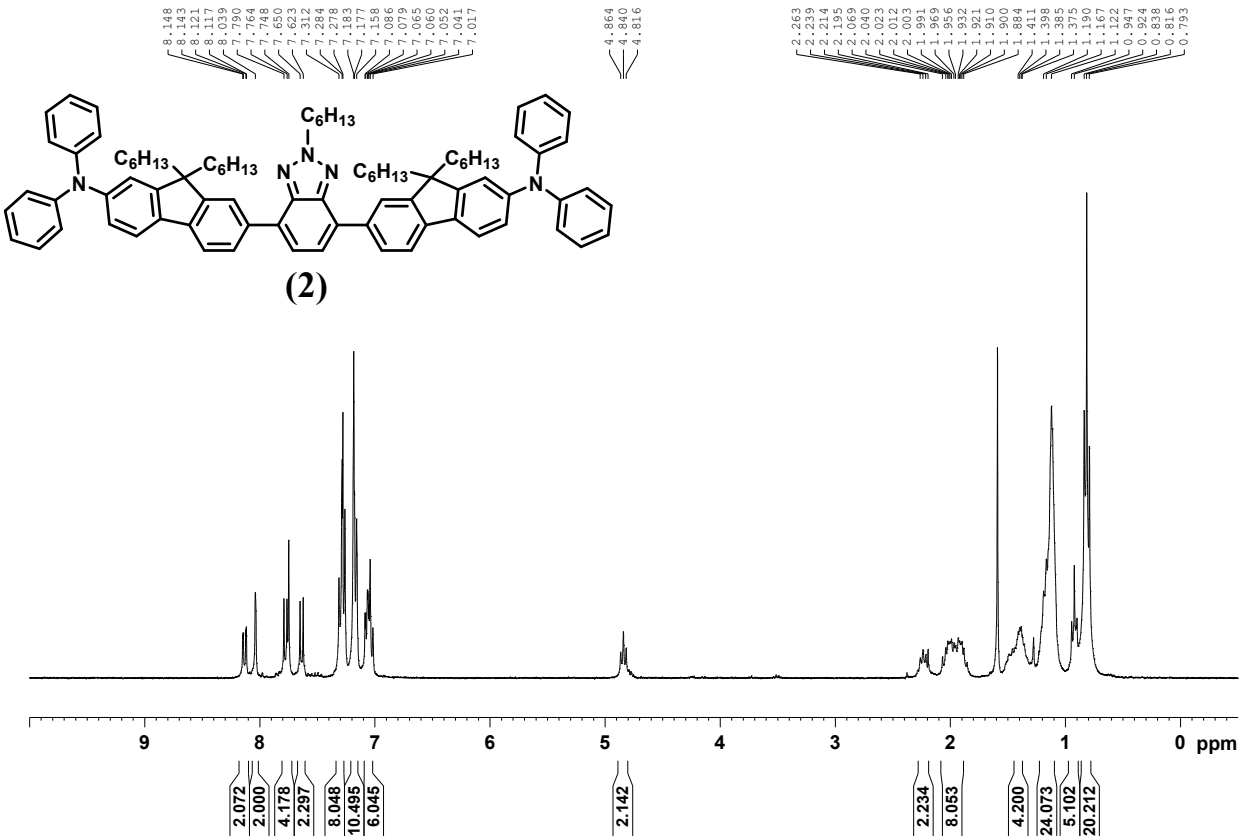
^{13}C NMR Spectrum of Compound 19 (Solvent: $CDCl_3$)



^{1}H NMR Spectrum of Compound 1 (Solvent: $CDCl_3$)

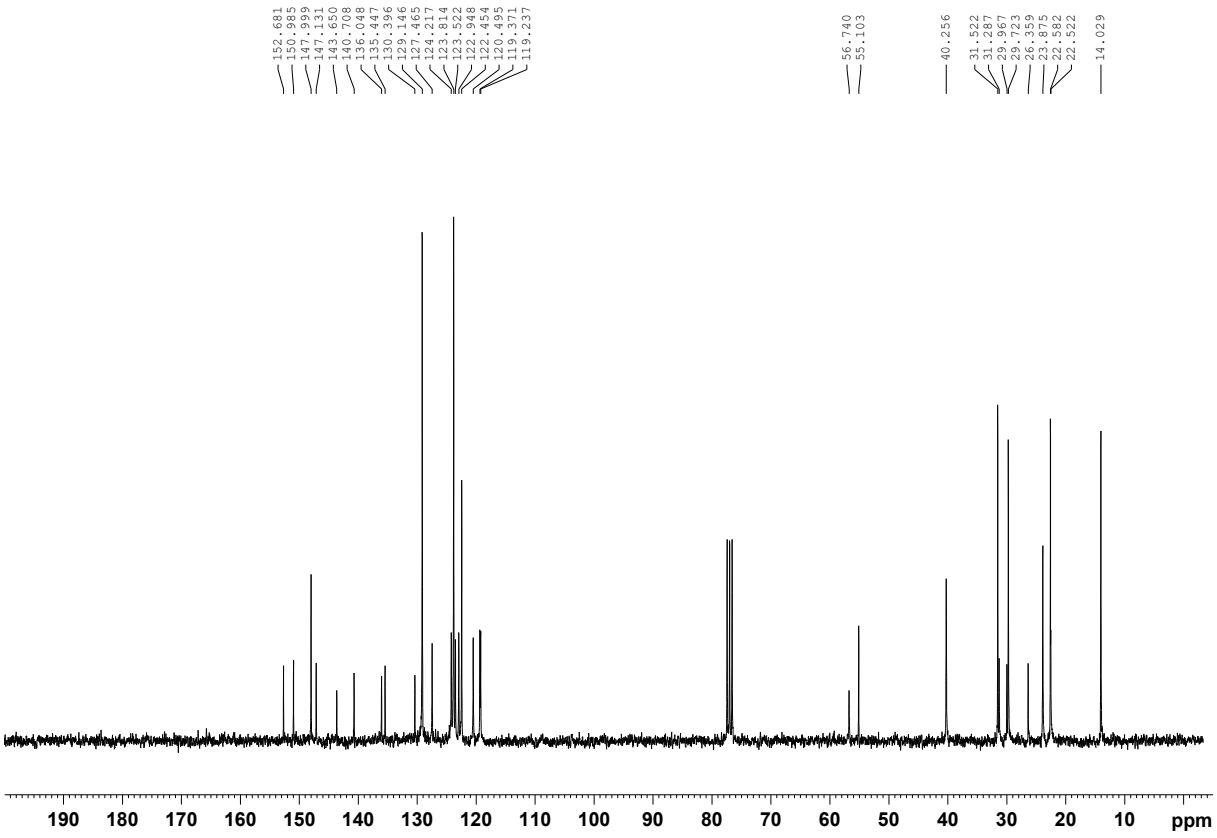


^{13}C NMR Spectrum of Compound 1 (Solvent: $CDCl_3$)

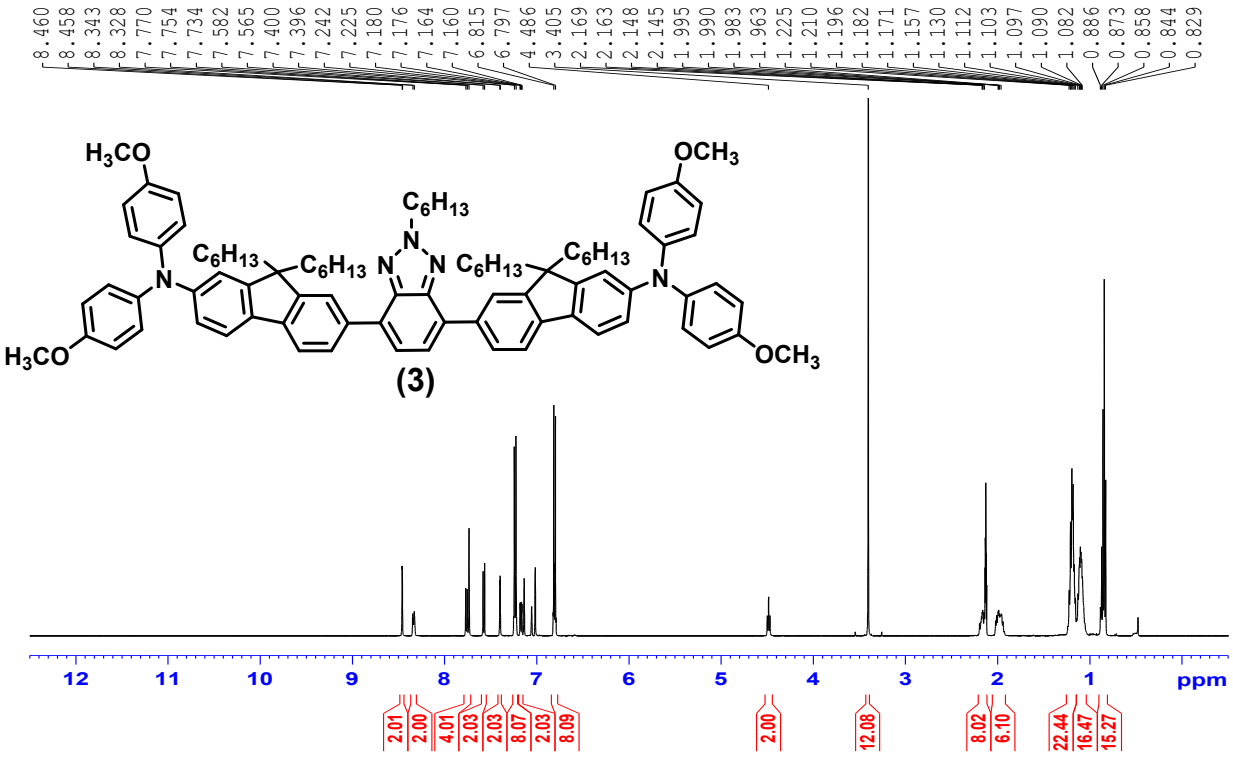


(2)

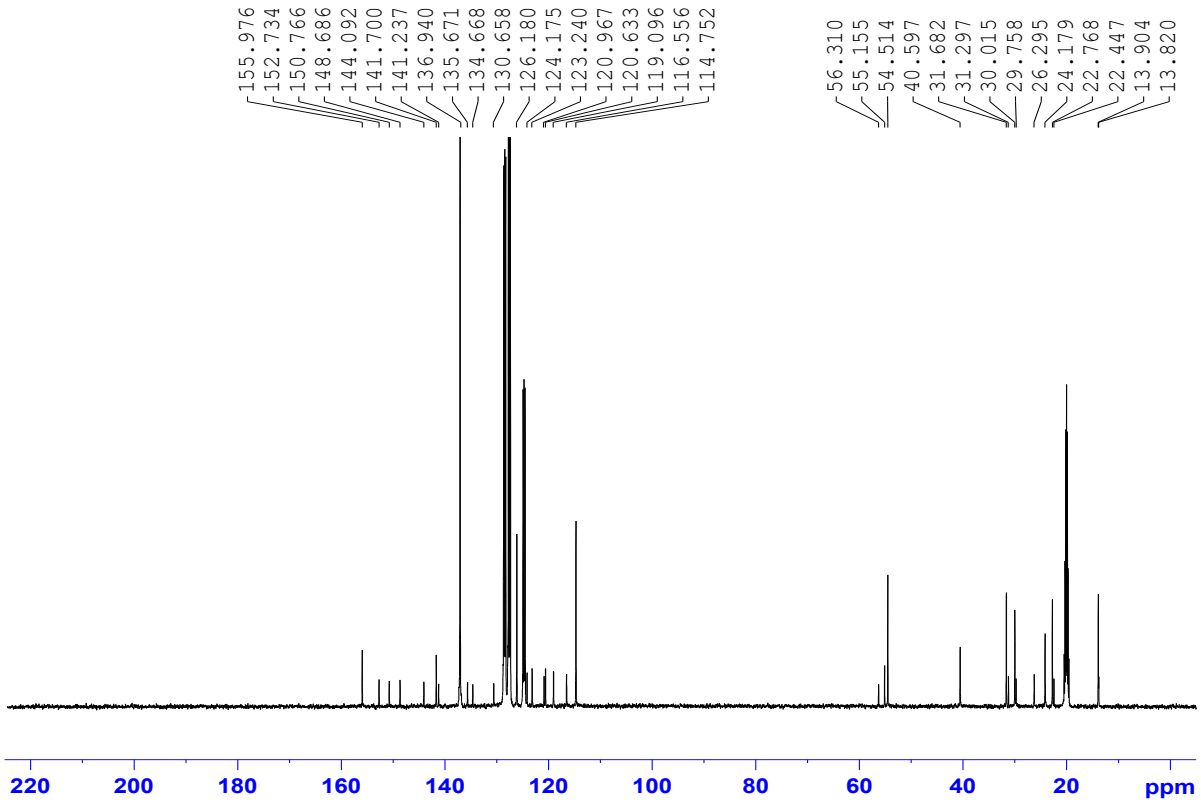
^{1}H NMR spectrum of compound 2 ($CDCl_3$)



^{13}C NMR spectrum of compound 2 ($CDCl_3$)



[1]H NMR Spectrum of Compound 3 (Solvent: d-toluene)



[13]C NMR Spectrum of Compound 3 (Solvent: d-Toluene)