Synthesis and Molecular Properties of Methoxy-Substituted Diindolo[3,2-*b*:2',3'-*h*]carbazoles for Organic Electronics Obtained by a Consecutive Twofold Suzuki and Twofold Cadogan Reaction

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Content

1. General Remarks

Commercially available reagents were used without further purification; solvents and gases were dried by standard procedures. Organic solvents were evaporated using a rotary evaporator. Flash chromatography was performed using silica gel 60, particle size 40-63 μm. Thin-layer chromatography was performed using commercially Merck pre-coated aluminium backed TLC Silica gel 60 F_{254}, with spot detection under UV light.

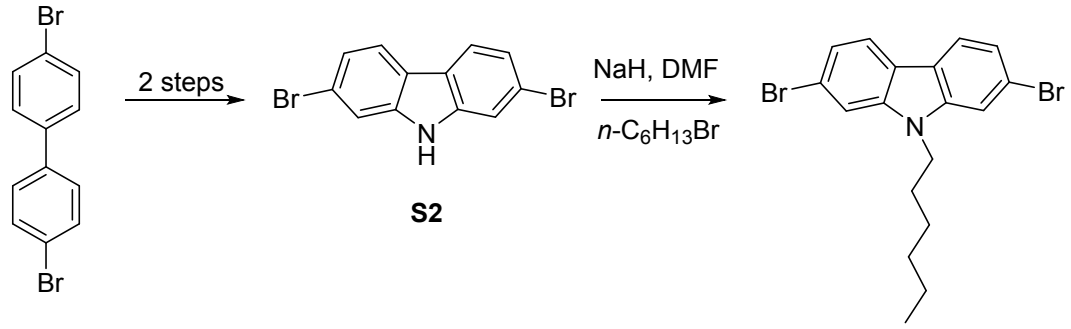
Melting points (mp) were determined on the Electrothermal IA9000 Series Digital Melting Point Apparatus and are uncorrected. NMR spectra were recorded in deuterated solvent on a 400 MHz or 500 MHz Bruker Avance III apparatus. The chemical shifts are calibrated to residual proton resonance of TMS (δ_H 0 ppm) and DMSO-d_6 (δ_H 2.50 ppm) and carbon resonance of the solvents $CDCl_3$ (δ_C 77.16 ppm) and DMSO-d_6 (δ_C 39.52 ppm). ^{1}H NMR data are presented as follow: chemical shift, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, qt = quintuplet, sex = sextuplet, m = multiplet), coupling constant (*J*, Hz), integration. ^{13}C NMR data are presented as follows: chemical shift, (C-H coupling patterns refer to the corresponding DEPT spectra; s = C_{quat}, d = CH, t = CH_2, q = CH_3). Mass spectra (MS) and high-resolution mass data (HRMS) under electron spray ionization (ESI) mode were obtained on a Q-TOF Micro WATERS spectrometer; mass spectra under electronic impact (EI) were obtained with direct probe at 70 eV on a JEOL GCmate spectrometer.

UV spectra were recorded on a JASCO V-660 spectrophotometer and fluorescence spectra on a Perkin Elmer LS55 fluorescence spectrometer. Infrared spectra were made on a Perkin Elmer SPECTRUM ONE FT-IR spectrometer. Absolute photoluminescence quantum yields as well as luminescence spectra of solids were recorded with the Hamamatsu CC9920 integration sphere set-up at room temperature. For quantum yield measurements sample solutions (10^{-5} M) were purged with argon prior to measurement. Electrochemical studies were carried out at room temperature using a GAMRY Ref600 potentiostat. The working electrode was a platinum electrode, the auxiliary electrode a platinum wire. The reference electrode was an aqueous saturated (KCl) calomel electrode. Under the conditions used, the reversible potential for the ferrocenium/ferrocene couple at 298 K is +0.46 V, and for the Fc^{*+}/Fc^{*} -0.13 V in a $1x10^{-1}$ M Bu_4NPF_6 /CH_2Cl_2 electrolyte solution. Sample solutions (10^{-4} M) in a $1x10^{-1}$ M Bu_4NPF_6 /CH_2Cl_2 electrolyte solution were used. TGA measurements were recorded on a Perkin Elmer thermogravimetric analyzer TGA7. DSC curves were made on a Perkin Elmer Differential Scanning Calorimeter DSC7.

2. Experimental Part.

***N*-*n*-hexyl-2,7-dibromocarbazole (S3)**

The 2,7-dibromocarbazole **S3** was obtained from 2,7-dibromocarbazole (**S2**),[1] that was synthesized according to literature procedures from the dibromobiphenyl **S1** in two steps.

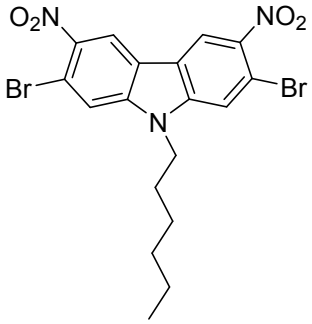


S1 **S2** **S3**

To a solution of 2,7-dibromocarbazole (**S2**) (7.050 g, 21.69 mmol) in dry DMF (65 mL) was added NaH (1.21 g, 60% w/w in mineral oil, 30 mmol) and the reaction mixture stirred for 30 min under an atmosphere of nitrogen. Thereafter, *n*-hexylbromide (4.655 g, 3.96 mL, 28.20 mmol) was added dropwise and the resulting solution stirred at room temperature overnight. The reaction mixture was diluted with water and extracted with dichloromethane and washed with brine. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated under reduced pressure. Flash chromatography on silica gel (SiO_2, heptane/ethyl acetate = 8:2 (v/v)) gave carbazole **S3** (8.694 g, 21;25 mmol, 98% yield) as a colorless powder, mp. 74-75 °C ($CHCl_3$/*n*-pentane). R_f 0.62 (SiO_2, heptane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 1.6 Hz, 2H), 7.33 (dd, *J* = 6.4 Hz, *J* = 1.6 Hz, 2H), 4.16 (t, *J* = 7.2 Hz, 2H), 1.85-1.78 (m, 2H), 1.40-1.25 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4 (s), 122.5 (d), 121.5 (d), 121.3 (s), 119.7 (s), 112.0 (d), 43.4 (t), 31.5 (t), 28.8 (t), 26.9 (t), 22.6 (t), 14.0 (q). MS [ESI (+)]: m/z (%) = 409 (100), 407 (50), 338 (30), 336 (15); HRMS: calcd for $C_{18}H_{19}NBr_2$ 406.9884; found 406.9889.

[1] F. Dierschke, A.C. Grimsdale, K. Müllen, *Synthesis*, 2003, 2470-2472.

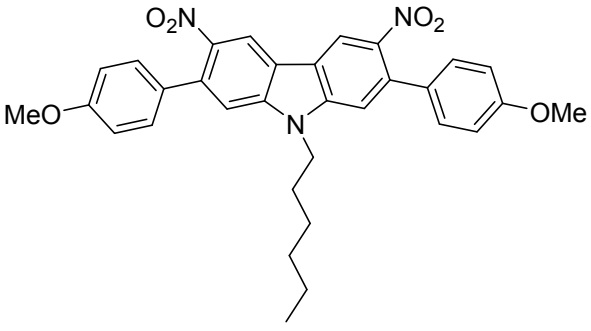
***N*-*n*-hexyl-2,7-dibromo-3,6-dinitrocarbazole (1)**



1

In a three-necked flask equipped with reflux condenser, thermometer and dropping funnel, *N*-*n*-hexyl-2,7-dibromocarbazole (**S3**) (7.140 g, 17.45 mmol) was dissolved in acetic acid (50 mL) at 80 °C and fuming nitric acid (6.9 mL, 10.395 g, 165 mmol) was added dropwise. The reaction mixture was heated to 100 °C for 1h and thereafter cooled down to room temperature, diluted with water and extracted with dichloromethane. The combined organic layers were washed with brine, dried with $MgSO_4$ and the solvents removed under reduced pressure. Crystallization of the product from hot $CHCl_3$ yielded the bis-nitro product **1** (7.627 g, 15.28 mmol, 88% yield) as yellow needles, mp 207-211 °C; R_f 0.3 (SiO_2, heptane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 2H), 8.31 (s, 2H), 4.51 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.71 (m, 2H), 1.29-1.21 (m, 6H), 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 143.1 (s), 142.6 (s), 120.4 (s), 120.3 (d), 116.2 (d), 112.4 (s), 43.3 (t), 30.8 (t), 28.4 (t), 25.7 (t), 22.0 (t), 13.8 (q). MS [ESI (+)]: m/z (%) = 500 (100), 499 (60), 483 (20), 428 (10); HRMS: calcd for $C_{18}H_{17}Br_2N_3O_4$ 496.9586; found 496.9589.

***N*-hexyl-3,6-dinitro-2,7-bis(4'-methoxyphenyl)carbazole (11):**



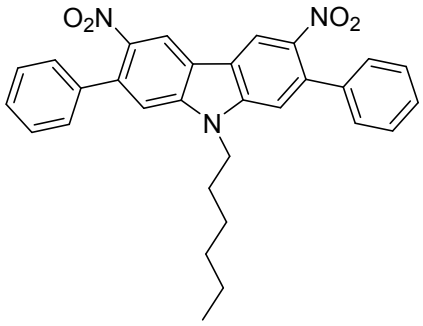
11

General procedure for a twofold Suzuki reaction under microwave heating: Dibromo-dinitrocarbazole **1** (300 mg, 0.60 mmol, 1 equiv.), 4-methoxyphenylboronic acid (**3**) (237.5 mg, 1.56 mmol, 2.6 equiv.), and $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 5 mol%) were placed in a microwave tube under nitrogen, followed by addition of N_2-purged DMF (8 mL) and a N_2-purged solution of Na_2CO_3 (1 M, 3.6 mL). The tube was sealed with a Teflon cap and heated under microwave irradiation (300 W) for 10

minutes at 140 °C. Thereafter, brine was added and the product was extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and concentrated. The crude product was purified by flash chromatography (silica gel, ethyl acetate/*n*-pentane = 2:8 to 6:4 (v/v)) to afford **11** (282 mg, 0.51 mmol, 85% yield) as a yellow powder.

General procedure for a twofold Suzuki reaction with conventional heating: 2,7-Dibromo-3,6-dinitrocarbazole (**1**) (500 mg, 1 mmol, 1 equiv.), 4-methoxyphenylboronic acid (**3**) (396 mg, 2.6 mmol, 2.6 equiv.), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 5 mol%) and cesium fluoride (604 mg, 4 mmol, 4 equiv.) were combined in a dry Schlenk tube under argon, dry THF was then added, and the mixture stirred until dissolution. The solution was then heated at 70 °C for 2 days. The compound was diluted with water, extracted with dichloromethane. The organic layer was washed with brine and dried over magnesium sulfate; the solvent was then removed under vacuum. The crude product was filtered through a plug of silica gel with 30% to 50% ethyl acetate in heptane as the eluent to afford compound **11** (481 mg, 0.87 mmol, 87% yield) as a yellow powder, mp 246-248 °C ($CHCl_3$/*n*-pentane), R_f 0.32 (SiO_2, heptane/ethyl acetate = 7:3 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 2H), 7.36-7.34 (m, 6H), 7.01 (m, 4H), 4,34 (t, *J* = 7.2, 2H), 3.88 (s, 6H), 1.89 (m, 2H), 1.38-1.27 (m, 6H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (s), 143.35 (s), 143.30 (s), 136.4 (s), 131.1 (s), 129.5 (d), 121.0 (s), 118.6 (d), 114.4 (d), 112.2 (d), 55.5 (q), 44.1 (t), 31.5 (t), 29.0 (t), 27.0 (t), 22.6 (t), 14.1 (q). IR (neat, ATR): ν = 2924, 1509, 1460, 1335, 1238, 1172, 1105, 1024, 891 cm^{-1}. MS [ESI (+)]: m/z (%) = 554 ([M+H]$^+$, 26), 537 (38), 520 (100), 508 (10); HRMS: calcd for $C_{32}H_{32}N_3O_6$ ([M+H]$^+$) 554.229; found 554.2307.

***N*-hexyl-3,6-dinitro-2,7-bis-phenylcarbazole (10):**

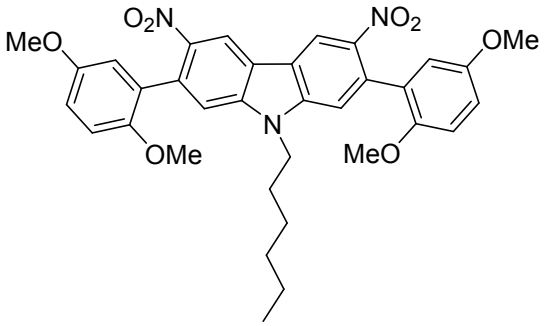


10

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and phenylboronic acid (**2**): Carbazole **10** (295 mg, 0.48 mmol, 83% yield) was obtained as yellow solid after being washed with CH_2Cl_2; mp 136-138 °C ($CHCl_3$/*n*-pentane); R_f 0.13 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 2H), 7.49-7.42 (m, 10H), 7.39 (s, 2H), 4.36 (t, *J* = 7.2 Hz, 2H), 1.89 (m, 2H), 1.39-1.26 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (s), 143.2 (s), 139,0 (s), 136.9 (s), 128.8

(d), 128.3 (d), 128.2 (d), 121.3 (s), 118.7 (d), 112.4 (d), 44.2 (t), 31.5 (t), 29.0 (t), 26.9 (t), 22.6 (t), 14.0 (q). IR (neat, ATR): ν = 2930, 1600, 1514, 1500, 1463, 1449, 1338, 1314, 888, 811, 770 cm^{-1}. MS [ESI (+)]: m/z (%) = 494 ($[M+H]^+$, 57), 477 (50), 460 (100), 431 (23), 416 (14), 406 (7); HRMS: calcd for $C_{30}H_{28}N_3O_4$ ($[M+H]^+$) 494.2080; found 494.2057.

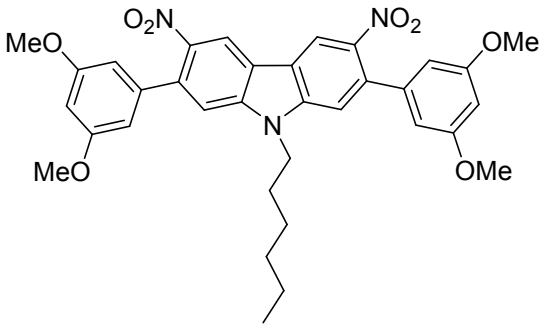
***N*-hexyl-3,6-dinitro-2,7-bis(2',5'-dimethoxyphenyl)carbazole (12):**



12

Synthesized according to the general procedure for a twofold Suzuki reaction under conventional heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and 2,5-dimethoxyphenylboronic acid (**4**): Carbazole **12** (1763 mg, 2.87 mmol, 96% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 8:2 to 7:3 (v/v)) as a yellow solid, mp 210-212 °C ($CHCl_3$/*n*-pentane); R_f 0.50 (SiO_2, *n*-pentane/ethyl acetate = 7:3 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 2H), 7.36 (s, 2H), 7.03 (d, *J* = 3.0 Hz, 2H), 6.95 (dd, *J* = 8.9 Hz, *J* = 3.0 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.33 (t, *J* = 7.4 Hz, 2H), 3.87 (s, 6H), 3.69 (s, 6H), 1.89 (m, 2H), 1.39-1.26 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1(s), 150.4 (s), 143.7 (s), 143.5 (s), 132.9 (s), 129.4 (s), 121.4 (s), 118.2 (d), 116.6 (d), 113.5 (d), 112.6 (d), 111.7 (d), 56.0 (q), 55.9 (q), 44.2 (t), 31.5 (t), 29.1 (t), 27.0 (t), 22.6 (t), 14.1 (q). IR (neat, ATR): ν = 2936, 1516, 1500, 1461, 1335, 1279, 1265, 1218, 1186, 1170, 1140, 1048, 1019, 881, 859, 811, 800, 736 cm^{-1}. MS [EI (+)]: m/z (%) = 613 ($[M]^+$,100), 598 (8), 583 (33), 566 (7), 554 (15), 420 (7), 307 (7); HRMS: calcd for $C_{34}H_{36}N_3O_8$ ($[M+H]^+$) 614.2502; found 614.2490.

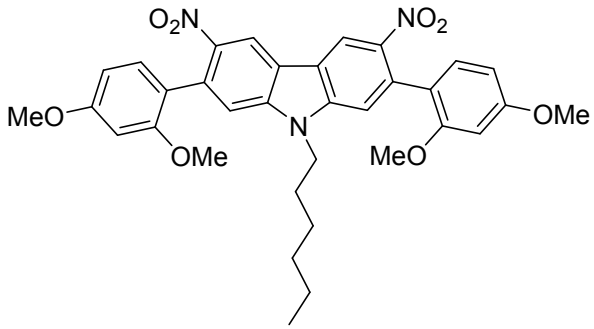
***N*-hexyl-3,6-dinitro-2,7-bis(3',5'-dimethoxyphenyl)carbazole (13):**



13

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and 3,5-dimethoxyphenylboronic acid (**5**): Carbazole **13** (221 mg, 0.36 mmol, 90% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 8:2 to 7:3 (v/v)), yellow crystals with mp 152-154 °C (CH_2Cl_2/*n*-pentane); R_f 0.26 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 2H), 7.40 (s, 2H), 6.56-6.54 (m, 6H), 4.34 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 12H), 1.87 (m, 2H), 1.37-1.25 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (s), 143.2 (s), 143.1 (s), 140.9 (s), 136.7 (s), 121.3 (s), 118.6 (d), 112.1 (d), 106.6 (d), 100.0 (d), 55.6 (q), 44.2 (t), 31.5 (t), 29.0 (t), 27.0 (t), 22.6 (t), 14.1 (q). IR (neat, ATR): ν = 2932, 1595, 1514, 1455, 1336, 1241, 1203, 1154, 1063, 1035, 840 cm^{-1}. HRMS: calcd for $C_{34}H_{36}N_3O_8$ ([M+H]$^+$) 614.2502; found 614.2505.

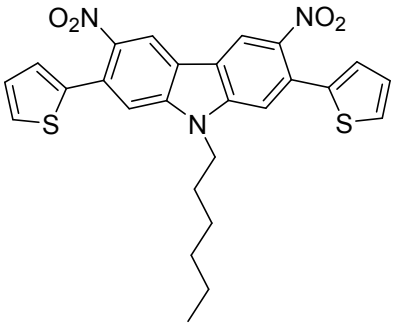
***N*-hexyl-3,6-dinitro-2,7-bis(2',4'-dimethoxyphenyl)carbazole (14):**



14

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and 2,4-dimethoxyphenylboronic acid (**6**): Carbazole **14** (190 mg, 0.31 mmol, 78% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 8:2 to 7:3 (v/v)) as an orange solid, mp 151-153 °C (CH_2Cl_2/*n*-pentane); R_f 0.38 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.32 (s, 2H), 6.67 (dd, *J* = 8.3 Hz, *J* = 2.3 Hz, 2H), 6.88 (d, *J* = 2.3 Hz, 2H), 4.32 (t, *J* = 7.2 Hz, 2H), 3.89 (s, 6H), 3.73 (s, 6H), 1.88 (m, 2H), 1.38-1.25 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (s), 157.3 (s), 143.8 (s), 143.5 (s), 132.8 (s), 130.3 (d), 121.2 (s), 121.1 (s), 118.1 (d), 112.5 (d), 105.2 (d), 98.8 (d), 55.6 (q), 55.5 (q), 44.1 (t), 31.6 (t), 29.1 (t), 27.0 (t), 22.7 (t), 14.1 (q). IR (neat, ATR): ν = 2931, 1607, 1584, 1509, 1462, 1455, 1339, 1304, 1284, 1250, 1206, 1157, 1135, 1028, 817 cm^{-1}. HRMS: calcd for $C_{34}H_{36}N_3O_8$ ([M+H]$^+$) 614.2502; found 614.2489.

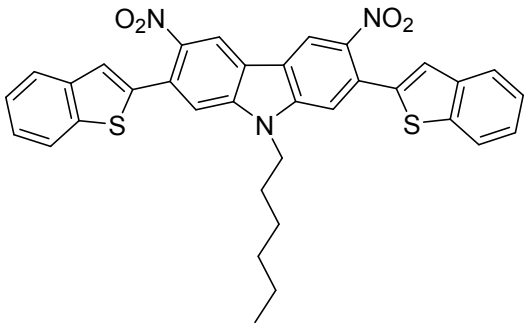
***N*-hexyl-3,6-dinitro-2,7-bis(2'-thiophenyl)carbazole (15):**



15

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and thiophene-2-boronic acid (**7**): Carbazole **15** (230 mg, 0.45 mmol, 91% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 to 8:2 (v/v)) as a solid; mp 141-144 °C ($CHCl_3$/*n*-pentane); R_f 0.70 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 7.50 (s, 2H), 7.47 (dd, *J* = 4.9 Hz, *J* = 1.2 Hz, 2H), 7.16-7.12 (m, 4H), 4.36 (t, *J* = 7.2 Hz, 2H), 1.90 (m, 2H), 1.38-1.25 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6 (s), 142.9 (s), 138.7 (s), 128.8 (s), 127.9 (d), 127.5 (d), 127.2 (d), 121.5 (s), 118.5 (d), 113.0 (d), 44.2 (t), 31.5 (t), 29.0 (t), 26.9 (t), 22.6 (t), 14.0 (q). IR (neat, ATR): ν = 2928, 1604, 1520, 1464, 1337, 847, 716 cm^{-1}. HRMS: calcd for $C_{26}H_{24}N_3O_4S_2$ ($[M+H]^+$) 506.1208; found 506.1185.

***N*-hexyl-3,6-dinitro-2,7-bis(2'-benzothiophenyl)carbazole (16):**

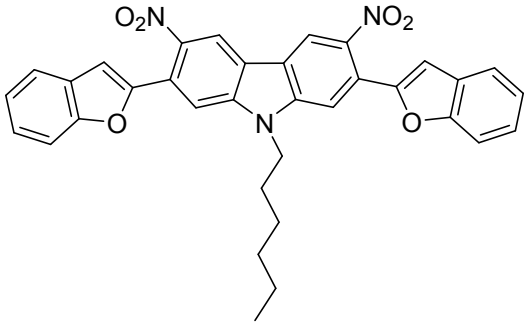


16

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and benzo[b]thien-2-ylboronic acid (**8**): Carbazole **16** (44 mg, 0.07 mmol, 72% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 to 8:2 (v/v)) as a solid; mp 250-252 °C ($CHCl_3$/*n*-pentane); R_f 0.27 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79(s, 2H), 7.89 (dd, *J* = 6.9 Hz, *J* = 1.4 Hz, 2H), 7.89 (dd, *J* = 6.5 Hz, *J* = 2.1 Hz, 2H), 7.61 (s, 2H), 7.44-7.39 (m, 4H), 7.38 (s, 2H), 4.39 (t, *J* = 7.2 Hz, 2H), 1.91 (m, 2H), 1.38-1.25 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5 (s), 143.0

(s), 140.6 (s), 140.0 (s), 139.1 (s), 129.2 (s), 125.1 (d), 125.0 (d), 124.2 (d), 124.1 (d), 122.3 (d), 121.8 (s), 118.8 (d), 113.3 (d), 44.3 (t), 31.5 (t), 29.1 (t), 27.0 (t), 22.6 (t), 14.1 (q). IR (neat, ATR): ν = 2927, 1602, 1515, 1464, 1314, 885, 796, 748, 725 cm^{-1}. HRMS: calcd for $C_{34}H_{27}N_3O_4S_2$ ($[M+H]^+$) 605.1437; found 605.1423.

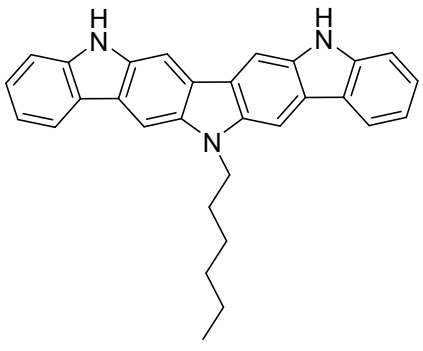
***N*-hexyl-3,6-dinitro-2,7-bis(2'-benzofuranyl)carbazole (17):**



17

Synthesized according to the general procedure for a twofold Suzuki reaction under microwave heating from 2,7-dibromo-3,6-dinitrocarbazole (**1**) and 2-benzofuranylboronic acid (**9**): Carbazole **17** (151 mg, 0.26 mmol, 88% yield) was obtained by flash chromatography (silica, *n*-pentane/ethyl acetate = 8:2 to 5:5 (v/v)) as a solid, mp 240-242 °C; R_f 0.21 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 2H), 7.82 (s, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 8.3 Hz, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 8.3 Hz, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 0.6 Hz, 2H), 4.48 (t, *J* = 7.2 Hz, 2H), 1.97 (m, 2H), 1.44-1.26 (m, 6H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 (s), 151.7 (s), 143.1 (s), 142.6 (s), 128.8 (s), 125.5 (d), 124.7 (s), 123.5 (d), 121.8 (s), 121.7 (d), 118.8 (d), 111.6 (d), 111.0 (d), 106.4 (d), 44.3 (t), 31.5 (t), 29.1 (t), 27.0 (t), 22.6 (t), 14.1 (q). IR (neat, ATR): ν = 2926, 2857, 1716, 1606, 1517, 1454, 1337, 1256, 1163, 887, 807, 746 cm^{-1}. HRMS: calcd for $C_{34}H_{28}N_3O_6$ ($[M+H]^+$) 574.1978; found 574.1978.

5,8-dihydro-14-hexyl-diindolo[3,2-*b*:2',3'-*h*]carbazole (18):

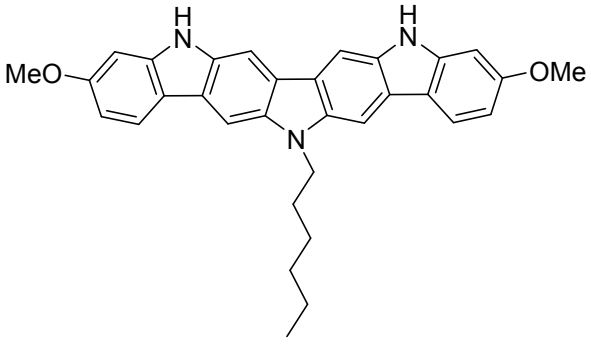


18

Twofold Cadogan reaction under conventional heating: Dinitrocarbazole **10** (100 mg, 0.20 mmol, 1 equiv.) was dissolved in 1,2-dichlorobenzene (5 mL) in a Schlenk-tube and then $P(OEt)_3$ (0.42 mL, 2.45 mmol, 12 equiv.) was added under nitrogen. The tube was sealed placed into an oil bath and heated to 230 °C for 24 hours. The resulting reaction mixture was then evaporated and the crude product was precipitated from CH_2Cl_2 and *n*-pentane to afford **18** (22 mg, 0.05 mmol, 25% yield) as a yellow powder; R_f 0.04 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)).

Twofold Cadogan reaction under microwave heating: Dinitrocarbazole **10** (200 mg, 0.41 mmol, 1 equiv.) was dissolved in 1,2-dichlorobenzene (6 mL) and placed in a microwave tube under nitrogen. Then $P(OEt)_3$ (0.83 mL, 4.84 mmol, 12 equiv.) was added and the tube was sealed and heated under microwave irradiation (300 W) for 1,5 hours at 230 °C. The resulting mixture was evaporated and the product was precipitated from CH_2Cl_2 and *n*-pentane to afford **18** (116 mg, 0.27 mmol, 66 % yield) as a yellow powder, mp 270-275 °C (CH_2Cl_2/*n*-pentane); R_f 0.04 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 2H), 8.25 (d, *J* = 7.8 Hz, 2H), 8.24 (s, 2H), 8.21 (s, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 2H), 7.14 (dd, *J* = 7.8 Hz, *J* = 7.2 Hz, 2H), 4.54 (t, *J* = 7.0 Hz, 2H), 1.93 (m, 2H), 1.47-1.25 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 141.0 (s), 136.9 (s), 134.5 (s), 125.2 (s), 122.7 (s), 122.5 (d), 122.3 (d), 120.3 (d), 117.5 (s), 110.4 (d), 100.8 (d), 98.2 (d), 42.6 (t), 31.0 (t), 28.0 (t), 26.2 (t), 22.0 (t), 13.7 (q). IR (neat, ATR): ν = 3402, 2919, 1504, 1457, 1226, 1022, 979, 839, 746, 729; cm^{-1}. HRMS: calcd for $C_{30}H_{27}N_3$ 429.5670; found 429.5634.

3,10-dimethoxy-5,8-dihydro-14-hexyl-diindolo[3,2-*b*:2',3'-*h*]carbazole (19):

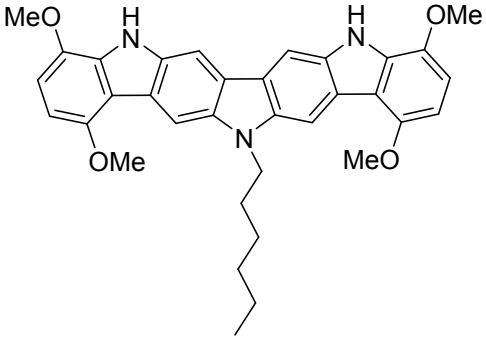


19

The reaction was carried out with dinitrocarbazole **11** according to the general procedure for a twofold Cadogan reaction under microwave heating: The obtained product was washed with CH_2Cl_2 and pentane then filtrated through a plug of silica gel to afford **19** (74 mg, 0.15 mmol, 50% yield) as a yellow powder, mp 270-275 °C (CH_2Cl_2/*n*-pentane); R_f 0.05 (SiO_2, *n*-pentane/ethyl acetate = 7:3 (v/v)). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.89 (bs, 2H), 8.68 (s, 2H), 8.52 (d, *J* = 8.5 Hz, 2H), 8.06 (s, 2H), 6.96 (d, *J* = 2.2 Hz, 2H), 6.76 (dd, *J* = 8.5 Hz , *J* = 2.2 Hz, 2H), 4.49 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 6H), 1.90 (m, *J* = 6.7 Hz, 2H), 1.45-1.19 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.4 (s), 142.3

(s), 136.7 (s), 134.5 (s), 122.5 (s), 121.1 (s), 120.7 (d), 116.6 (s), 106.5 (d), 100.3 (d), 97.4 (d), 94.3 (d), 55.2 (q) 42.5 (t), 31.0 (t), 28.0 (t), 26.2 (t), 22.0 (t), 13.7 (q). IR (neat, ATR): ν = 3397, 3379, 2924, 1629, 1616, 1500, 1449, 1436, 1376, 1283, 1252, 1223, 1194, 1162, 1104, 1025, 951, 837 cm^{-1}. HRMS calcd for $C_{32}H_{31}N_3O_2$ 489.2411; found 489.2402.

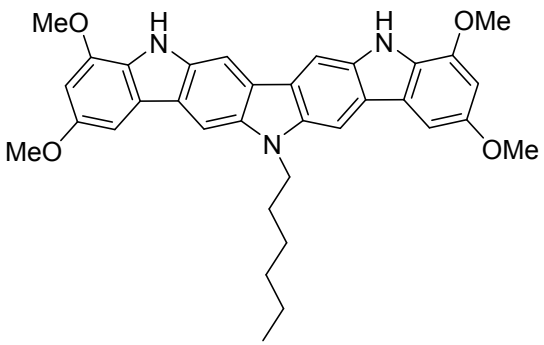
1,4,9,12-tetramethoxy-5,8-dihydro-14-hexyl-diindolo[3,2-*b*:2',3'-*h*]carbazole (20):



20

The reaction was carried out with dinitrocarbazole **12** according to the general procedure for a twofold Cadogan reaction under microwave heating: Compound **20** (93 mg, 0.17 mmol, 52% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 to 7:3 (v/v)) as a yellow solid, mp 129-134 °C (CH_2Cl_2/pentane); R_f 0.23 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (500 MHz, DMSO-d_6, 40 °C) δ 11.06 (s, 2H), 8.15 (s, 2H), 8.13 (s, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 4.46 (t, *J* = 7.0 Hz, 2H), 4.05 (s, 6H), 3.97 (s, 6H), 1.94 (m, 2H), 1.46-1.40 (m, 4H), 1.30 (sex, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, , DMSO-d_6, 40 °C) δ 149.9 (s), 139.8 (s), 136.7 (s), 133.9 (s), 131.8 (s), 121.9 (s), 121.4 (s), 112.8 (s), 106.5 (d), 100.6 (d), 100.0 (d), 98.0 (d), 55.7 (q), 55.5 (q), 42.3 (t), 30.7 (t), 27.6 (t), 26.1 (t), 21.8 (t), 13.7 (q). IR (neat, ATR) ν = 3419, 2933, 1598, 1515, 1462, 1305, 1252, 1163, 1109, 1091, 1017, 843, 778, 719 cm^{-1}. HRMS calcd for $C_{34}H_{36}N_3O_4$ 550.2706; found 550.2698.

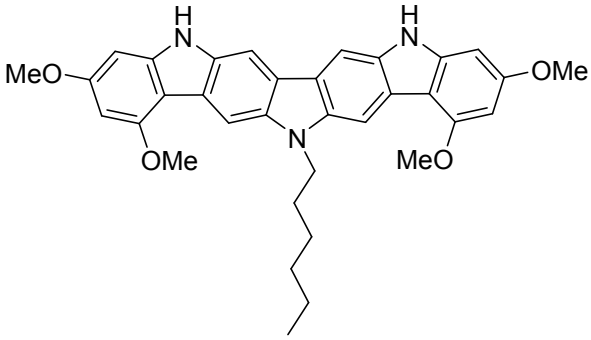
2,4,9,11-tetramethoxy-5,8-dihydro-14-hexyl-diindolo[3,2-*b*:2',3'-*h*]carbazole (21):



21

The reaction was carried out with dinitrocarbazole **13** according to the general procedure for a twofold Cadogan reaction under microwave heating: Compound **21** (59 mg, 0.11 mmol, 50% yield) was precipitated from CH_2Cl_2 and *n*-pentane to afford a yellow powder, mp 272-274 °C (CH_2Cl_2/*n*-pentane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 2H), 8.11 (s, 2H), 8.10 (s, 2H), 7.40 (s, 2H), 6.65 (s, 2H), 4.49 (t, J = 6.1 Hz, 2H), 3.99 (s, 6H), 3.90 (s, 6H), 1.92 (m, 2H), 1.46-1.24 (m, 6H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.3 (s), 145.8 (s), 136.8 (s), 135.0 (s), 125.9 (s), 123.0 (s), 123.9 (s), 122.4 (s), 101.2 (d), 98.0 (d), 97.4 (d), 94.4 (d), 55.7 (q), 55.4 (q), 42.7 (t), 31.2 (t), 28.2 (t), 26.5 (t), 22.2 (t), 14.0 (q). IR (neat, ATR) ν = 3429, 3408, 2925, 1593, 1500, 1457, 1272, 1195, 1148, 1047, 1024 cm^{-1}. HRMS calcd for $C_{34}H_{35}N_3O_4$ 549.2622; found 549.2617.

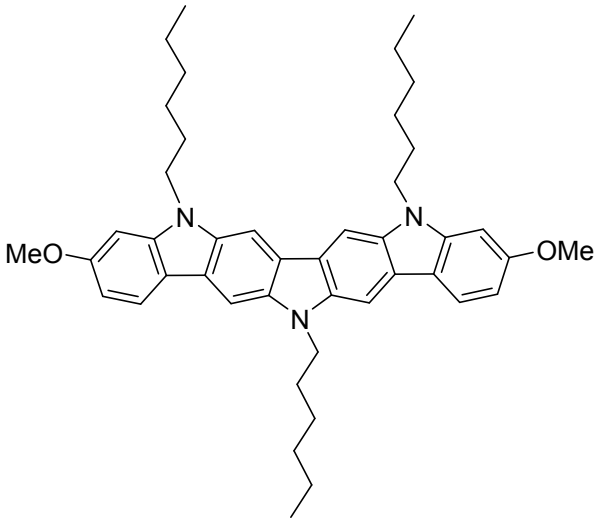
1,3,10,12-tetramethoxy-5,8-dihydro-14-hexyl-diindolo[3,2-*b*:2',3'-*h*]carbazole (22):



22

The reaction was carried out with dinitrocarbazole **14** according to the general procedure for a twofold Cadogan reaction under microwave heating: Compound **22** (59 mg, 0.11 mmol, 48% yield) was precipitated from CH_2Cl_2 and *n*-pentane to afford a yellow powder, mp 332-334 °C (CH_2Cl_2/*n*-pentane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.94 (s, 2H), 8.10 (s, 2H), 7.98 (s, 2H), 6.59 (s, 2H), 6.31 (s, 2H), 4.43 (br t, 2H), 4.05 (s, 6H), 3.86 (s, 6H), 1.90 (m, 2H), 1.40-1.27 (m, 6H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, , DMSO-d_6, 70 °C) δ 159.5 (s), 155.9 (s), 142.8 (s), 136.6 (s), 133.7 (s), 121.5 (s), 120.2 (s), 105.9 (s), 99.5 (d), 99.0 (d), 89.7 (d), 87.2 (d), 55.2 (q), 55.2 (q), 42.3 (t), 30.5 (t), 27.5 (t), 25.8 (t), 21.5 (t), 13.3 (q). IR (neat, ATR) ν = 3372, 2927, 1593, 1504, 1455, 1264, 1205, 1148, 1120, 843 cm^{-1}. HRMS calcd for $C_{34}H_{35}N_3O_4$ 549.2622; found 549.2611.

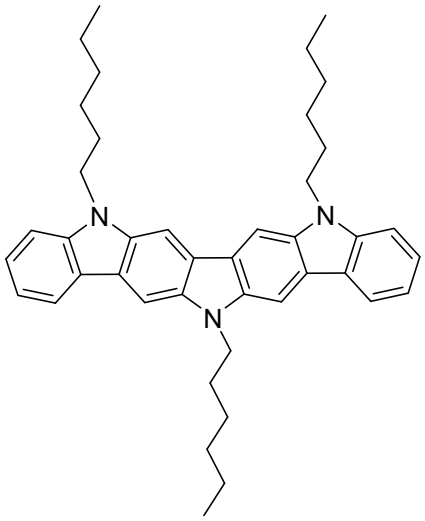
3,10-dimethoxy-tris-(N-*n*-hexyl)-diindolo[3,2-*b*:2',3'-*h*]carbazole (27):



27

General procedure for the twofold N-alkylation of the di-indolocarbazoles **26-30**. Under nitrogen atmosphere, the diindolocarbazole **19** (114 mg, 0.23 mmol, 1 equiv.) was dissolved in dry dimethylformamide (10 mL), sodium hydride (60% dispersion in oil, 28 mg, 0.70 mmol, 3 equiv.) was then introduced by portions. After stirring 30 minutes at room temperature, 1-bromohexane (0.19 mL, 1.38 mmol, 6 equiv.) was added drop wise and the reaction mixture was stirred at room temperature for 1 hour. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layers were combined, washed with brine, dried with $MgSO_4$; and the solvent was removed under vacuum. The obtained product was crystallized from CH_2Cl_2/*n*-pentane to afford compound **27** (135 mg, 0.21 mmol, 91% yield) as a brown powder; R_f 0.51 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v). Flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v) followed by filtration through a plug of ALOX III/N) gave an analytical pure sample of **27**, mp 191-193 °C (CH_2Cl_2/*n*-pentane). ^{1}H NMR (500 MHz, C_6D_6) δ 8.29 (d, *J* = 0.6 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 8.13 (s, *J* = 0.6 Hz, 2H), 7.02-6.99 (m, 4H), 4.26 (t, *J* = 7.4 Hz, 2H), 4.04 (t, *J* = 7.3 Hz, 4H), 3.61 (s, 6H), 1.85 (m, 2H), 1.72 (m, 4H), 1.33-1.30 (m, 2H), 1.20-1.06 (m, 16H), 0.81-0.78 (m, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.0 (s), 143.8 (s), 138.2 (s), 136.6 (s), 123.8 (s), 122.7 (s), 121.4 (d), 117.9 (s), 106.5 (d), 99.0 (d), 98.5 (d), 94.0 (d), 55.3 (q), 43.7 (t), 43.6 (t), 31.9 (t), 31.8 (t), 29.0 (t), 28.9 (t), 27.4 (t), 27.3 (t), 22.9 (t), 22.8 (t), 14.3 (q), 14.2 (q); IR (neat, ATR) ν = 2922, 2855, 1633, 1614, 1503, 1470, 1448, 1377, 1290, 1264, 1220, 1169, 1135, 1066, 1034, 942 cm^{-1}; MS [ESI (+)]: m/z (%) = 658 ([M+H]$^+$, 70), 657 ([M]$^+$, 100), 573 (25); HRMS calcd for $C_{44}H_{56}N_3O_2$ 658.4359 [M+H]$^+$; found 658.4373. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 449 nm (3.87), 425 (3.98), 386 (5.05), 365 (4.80), 346 (4.36, sh), 296 (4.79).

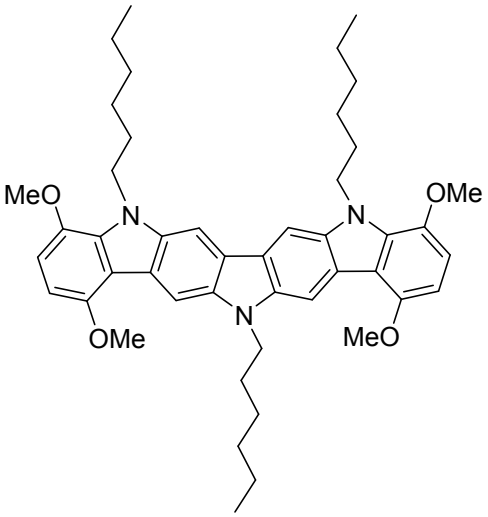
Tris-(N-*n*-hexyl)-diindolo[3,2-*b*:2',3'-*h*]carbazole (26):



26

According to the general procedure for the twofold *N*-alkylation of di-indolocarbazoles, diindolocarbazole **26** was obtained from **18**, after purification by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a yellow powder (60 mg, 0.10 mmol, 95% yield); mp 165-170 °C (CH_2Cl_2/*n*-pentane); R_f 0.84 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (500 MHz, C_6D_6, 10 °C) δ 8.34 (m, 4H), 8.20 (s, 2H), 7.54 (dd, *J* = 8.1 Hz, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.21 (t, *J* = 7.3 Hz, 2H), 4.06 (t, *J* = 7.3 Hz, 4H), 1.81 (m, *J* = 7.3 Hz, 2H), 1.68 (m, *J* = 7.3 Hz, 4H), 1.36-1.25 (m, 6H), 1.20-1.02 (m, 8H), 0.94-0.91 (m, 4H), 0.81-0.78 (m, 9H); ^{13}C NMR (125 MHz, C_6D_6, 10 °C) δ 142.3 (s), 138.1 (s), 136.2 (s), 126.0 (d), 123.8 (s), 123.7 (s), 123.6 (s), 120.8 (d), 118.5 (d), 108.9 (d), 99.3 (d), 99.1 (d), 43.6 (t), 43.3 (t), 31.9 (t), 31.8 (t), 29.0 (t), 28.9 (t), 27.4 (t), 27.3 (t), 23.0 (t), 22.9 (t), 14.4 (q), 14.3 (q); IR (neat, ATR) ν = 2921, 2853, 1500, 1469, 1264, 1227, 826 cm^{-1}. HRMS calcd for $C_{42}H_{52}N_3$ $[M+H]^+$: 598.4161; found 598.4158. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 466 nm (3.66), 440 (3.53), 379 (4.79), 368 (4.43), 356 (4.51), 338 (4.08), 324 (3.81), 294 (4.50).

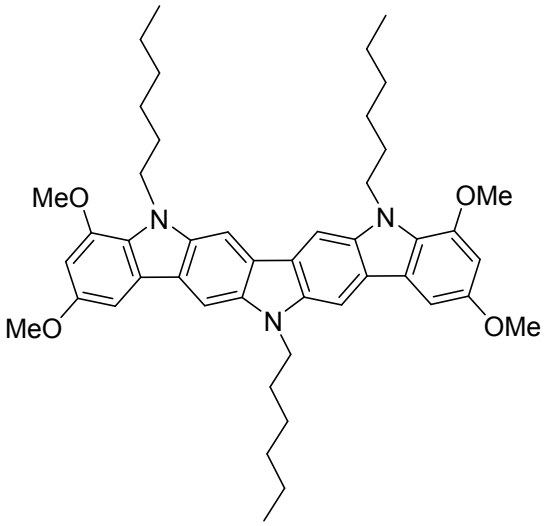
1,4,9,12-tetramethoxy-tris-(N-*n*-hexyl)-diindolo[3,2-*b*:2',3'-*h*]carbazole (28):



28

According to the general procedure for the twofold *N*-alkylation of di-indolocarbazoles, diindolocarbazole **28** was obtained from **20**, after purification by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9.5:0.5 (v/v)). Crystallization from CH_2Cl_2/*n*-pentane gave **28** as yellow micro crystals (34 mg, 0.05 mmol, 52% yield); mp 163-164 °C (CH_2Cl_2/*n*-pentane); R_f 0.77 (SiO_2, *n*-pentane/ethyl acetate = 8:2 (v/v)). ^{1}H NMR (400 MHz, C_6D_6) δ 8.85 (s, 2H), 8.42 (s, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.5 Hz, 2H), 4.73 (t, *J* = 7.0 Hz, 4H), 4.39 (t, *J* = 6.3 Hz, 2H), 3.80 (s, 6H), .3.60 (s, 6H), 1.94-1.87 (m, 6H), 1.34-1.31 (m, 6H), 1.19-1.12 (m, 12H), 0.84-0.81 (m, 9H); ^{13}C NMR (125 MHz, C_6D_6, 10 °C) δ 151.6 (s), 141.8 (s), 138.6 (s), 136.0 (s), 132.6 (s), 127.5 (s), 123.2 (s), 114.9 (s), 107.6 (d), 102.2 (d), 99.1 (d), 98.4 (d), 55.8 (q), 55.4 (q), 45.6 (t), 43.5 (t), 31.9 (t), 31.8 (t), 30.5 (t), 28.8 (t), 27.3 (t), 27.1 (t), 23.0 (t), 22.9 (t), 14.3 (q), 14.3 (q). IR (neat, ATR): ν = 2924, 1594, 1499, 1467, 1369, 1262, 1223, 1170, 1143, 1108, 1054, 1025, 928 cm^{-1}. MS [ESI (+)]: m/z (%) = 717 ([M]$^+$, 100), 687 (65), 646 (92), 616 (20); HRMS calcd for $C_{46}H_{59}N_3O_4$ 717.4506; found 717.4485. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 458 nm (4.03), 433 (3.95), 3.84 (4.87), 363 (4.75), 350 (4.61), 317 (4.61), 279 (4.74).

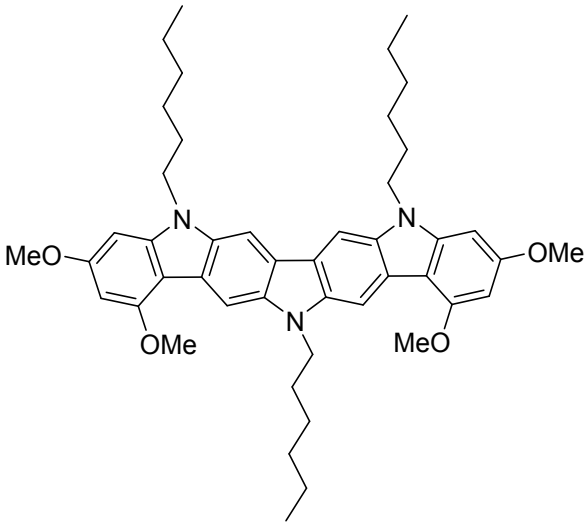
2,4,9,11-tetramethoxy-tris-(N-*n*-hexyl)-diindolo[3,2-*b*:2',3'-*h*]carbazole (29):



29

According to the general procedure for the twofold *N*-alkylation of di-indolocarbazoles, diindolocarbazole **29** was obtained from **21**, after purification by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) followed by precipitation from CH_2Cl_2/*n*-pentane as a yellow solid (38.3 mg, 0.05 mmol, 49% yield); mp 231-235 °C (CH_2Cl_2/*n*-pentane); R_f 0.82 (SiO_2 *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (500 MHz, C_6D_6, 40 °C) δ 8.39 (s, 2H), 8.14 (s, 2H), 7.52 (d, *J* = 2.0 Hz, 2H), 6.78 (d, *J* = 2.0 Hz, 2H), 4.68 (br t, 4H), 4.30 (br t, 2H), 3.71 (s, 6H), .3.51 (s, 6H), 1.93-1.86 (m, 6H), 1.35-1.32 (m, 6H), 1.21-1.13 (m, 12H), 0.82 (t, *J* = 7.60 Hz, 6H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6, 40 °C) δ 154.7 (s), 147.9 (s), 138.3 (s), 137.5 (s), 127.1 (s), 125.3 (s), 124.4 (s), 124.2 (s), 100.0 (d), 99.3 (d), 98.4 (d), 95.2 (d), 55.8 (q), 55.3 (q), 45.8 (t), 43.9 (t), 32.0 (t), 32.0 (t), 30.6 (t), 28.9 (t), 27.5 (t), 27.1 (t), 22.9 (t), 22.9 (t), 14.2 (q), 14.2 (q). IR (neat, ATR) ν = 2921, 2853, 1587, 1496, 1468, 1372, 1298, 1218, 1203, 1158, 1134, 1354, 1028, 827cm^{-1}. HRMS calcd for $C_{46}H_{60}N_3O_4$ ($[M+H]^+$) 718.4584; found 718.4602. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 476 nm (4.12), 447 (3.96), 379 (4.93), 369 (4.96), 361 (4.96), 332 (4.58), 287 (4.87), 276 (4.82, sh).

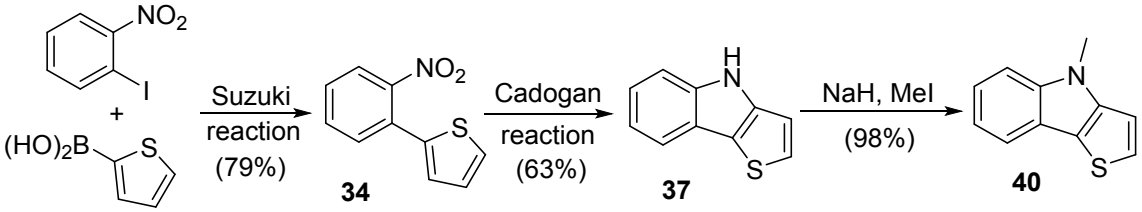
1,3,10,12-tetramethoxy-tris-(N-*n*-hexyl)-diindolo[3,2-*b*:2',3'-*h*]carbazole (30):



30

According to the general procedure for the twofold *N*-alkylation of di-indolocarbazoles, diindolocarbazole **30** was obtained from **22**, after purification by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9.5:0.5 (v/v)) and crystallization from CH_2Cl_2/*n*-pentane yielding yellow crystals (58.2 mg, 0.08 mmol, 84% yield); mp 168-171 ˚C (CH_2Cl_2/*n*-pentane); R_f 0.76 (SiO_2, *n*-pentane/ethyl acetate = 9:1). ^{1}H NMR (500 MHz, C_6D_6, 40 °C): δ 8.67 (s, 2H), 8.28 (s, 2H), 6.61 (s, 2H), 6.47 (s, 2H), 4.39 (br t, 4H), 4.10 (br t, 2H), 3.71 (s, 6H), .3.66 (s, 6H), 1.94 (m, 2H), 1.78 (m, 4H), 1.36-1.30 (m, 2H), 1.28-1.22 (m, 4H), 1.19-1.12 (m, 12H), 0.84-0.81 (m, 9H); ^{13}C NMR (125 MHz, C_6D_6, 40 °C) δ 160.6 (s), 157.2 (s), 144.1 (s), 138.1 (s), 135.4 (s), 122.8 (s), 121.6 (s), 107.1 (s), 101.2 (d), 97.9 (d), 90.0 (d), 85.9 (d), 55.0 (q), 54.8 (q), 43.2 (t), 43.1 (t), 31.5 (t), 31.4 (t), 28.6 (t), 28.5 (t), 26.9 (t), 26.8 (t), 22.5 (t), 22.4 (t), 13.8 (q), 13.7 (q); IR (neat, ATR) ν = 2922, 2853, 1612, 1590, 1469, 1434, 1374, 1261, 1205, 1148, 1127, 1058, 824 cm^{-1}. HRMS calcd for $C_{46}H_{59}N_3O_4$ 717.4500; found 717.4519. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 438 nm (3.95), 414 (4.18), 382 (5.05), 363 (4.80), 345 (4.42, sh), 307 (4.61, sh), 287 (4.78), 268 (4.68).

4*H*-4-methyl-thieno[3,2-*b*]indole (40)[2]



[2] M. Mézlovà, J.J. Aaron, J. Svoboda, A. Adenier, F. Maurel, K. Chane-Ching, *J. Electroanal. Chem.* 2005, **581**, 93-103.

2-ortho-nitrophenylthiophene (34)[3] was obtained by a microwave accelerated Suzuki reaction of 2-iodonitrobenzene and thiophene-2-boronic acid. 2-iodo-nitrobenzene (300 mg, 1.20 mmol), thiophene-2-boronic acid (185 mg, 1.45 mmol), and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 2.5 mol%) were placed in a microwave reaction vessel, flushed with nitrogen and N_2-purged DMF (4 mL) and a N_2-purged solution of Na_2CO_3 (3.6 mL of a 1 M solution in water) was added. The tube was sealed and placed in a microwave oven for 10 min. (300 W, 140 °C). Brine was added, the product extracted with CH_2Cl_2 and the combined organic layers dried with $MgSO_4$ and concentrated. Thiophene **34** (194 mg, 0.95 mmol, 79% yield) was thereafter obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as an oil; R_f 0.64 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.60-7.54 (m, 2H), 7.47 (ddd, J = 8.0 Hz, J = 6.4 Hz, J = 2.5 Hz, 1H), 7.41 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 7.10-7.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6 (s), 137.3 (s), 132.4 (d), 132.0 (d), 128.7 (d), 128.5 (s), 127.9 (d), 127.3 (d), 127.2 (d), 124.0 (d). IR (neat, ATR) ν = 3075, 2963, 1522, 1477, 1437, 1355, 1263, 1118, 1090, 1027, 849 cm^{-1}.

4*H*-thieno[3,2-*b*]indole (37):[2,4] In a microwave reaction vessel, compound **34** (200 mg, 0.97 mmol) was dissolved in 1,2-dichlorobenzene (5 mL). Then triethylphosphite (2.0 mL, 11.7 mmol) was added. The tube was sealed and heated under microwave irradiation (300 W, 230 °C) for 1,5 hours. The solvents were evaporated and the crude product was purified by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9.5:0.5 to 9:1 (v/v)). Indole **37** (110 mg, 0.64 mmol, 66% yield) was obtained as yellow solid, mp 176-178 °C (ethyl acetate/*n*-pentane); R_f 0.35 (SiO_2, pentane/ethyl acetate = 7:3 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 5.2 Hz, 1H), 7.26 (dd, J = 8.2 Hz, J = 7.2 Hz, , 1H), 7.18 (dd, J = 7.8 Hz, J = 7.2 Hz, 1H), 7.02 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1 (s), 141.3 (s), 127.1 (d), 123.0 (d), 122.3 (s), 119.9 (d), 119.0 (d), 118.2 (d), 112.0 (d), 111.6 (s). IR (neat, ATR): ν = 3389, 1508, 1500, 1452, 1375, 1301, 1235, 1091, 1048, 926, 814 cm^{-1}. HRMS calcd for $C_{10}H_8NS$ ([M+H]$^+$) 174.0377; found 174.0379.

4*H*-4-methyl-thieno[3,2-*b*]indole (40):[2]

The Cadogan reaction product **37** (80 mg, 0.46 mmol) was dissolved in dry DMF (10 mL) and then sodium hydride (60% dispersion in oil, 55 mg, 1.38 mmol) was added by portions. After stirring 30 min at room temperature, iodomethane (0.17 mL, 2.73 mmol) was added dropwise and the mixture stirred at room temperature for 1h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layers were combined, washed with brine and dried with $MgSO_4$. Compound **40** (85 mg, 0.45 mmol, 98% yield) was obtained after flash chromatography (silica gel *n*-*n*-

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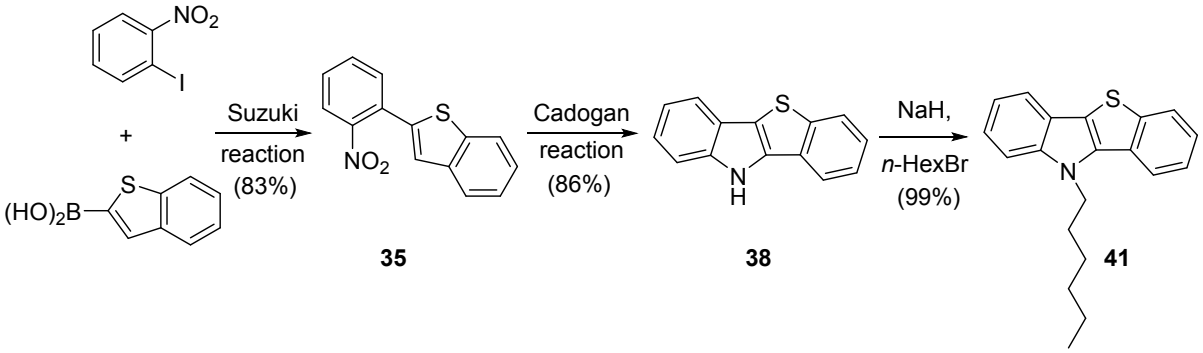
[3] P. Appukkuttan, E. Van der Eycken, W. Dehaen, *Synlett,* 2005, 127-133.

[4] R.A. Abramovitch, T. Chellathurai, I.T. McMaster, T. Takaya, Ch.I. Azogu, D.P. Vanderpool, *J. Org. Chem.,* 1977, **42**, 2914.

pentane/ethyl acetate = 9:1 (v/v)) as a white solid, mp 79-81 °C ($CHCl_3$/*n*-pentane); R_f 0.54 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (ddd, *J* = 7.8 Hz, *J* = 1.2 Hz, *J* = 0.8 Hz, 1H), 7.38 (ddd, *J* = 8.3 Hz, *J* = 1.1 Hz, *J* = 0.8 Hz, 1H), 7.37 (d, *J* = 5.2 Hz, 1H), 7.31 (ddd, *J* = 8.3 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 1H), 7.17 (ddd, *J* = 7.8 Hz, *J* = 7.1 Hz, *J* = 1.1 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.06 (s), 142.08 (s), 126.89 (d), 122.55 (d), 121.85 (s), 119.16 (d), 119.02 (d), 115.93 (s), 110.20 (d), 109.79 (d), 31.39 (q). IR (neat, ATR): ν = 3337, 2973, 1513, 1463, 1429, 1393, 1364, 1351, 1318, 1250, 1168, 1081, 1047, 742 cm^{-1}. HRMS calcd for $C_{11}H_{10}NS$ ([M+H]$^+$) 188.0534; found 188.0543.

10*H*-10-hexyl-benzothieno[3,2-*b*]indole (41):



2-ortho-nitrophenylbenzothiophene (35)[5] was prepared by a microwave accelerated Suzuki coupling reaction of 2-iodonitrobenzene and benzothiophene-2-boronic acid. 2-iodonitrobenzene (200 mg, 0.8 mmol), benzothiophene-2-boronic acid (157 mg, 0.88 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 2.5 mol%) were placed in a microwave reaction vessel, flushed with nitrogen and N_2-purged DMF (7 mL) and a N_2-purged solution of Na_2CO_3 (2.4 mL of a 1 M solution in water) was added. The tube was sealed and placed in a microwave oven for 10 min. (300 W, 140 °C). Brine was added, the product extracted with CH_2Cl_2 and the combined organic layers dried with $MgSO_4$ and concentrated. The cross-coupling product **35** (169 mg, 0.66 mmol, 83% yield) was thereafter obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a solid, mp 83-86 °C (CH_2Cl_2/*n*-pentane); R_f 0.67 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.77 (m, 3H), 7.65-7.59 (m, 2H), 7.51 (ddd, *J* = 8.0 Hz, *J* = 6.2 Hz, *J* = 2.7 Hz, 1H), 7.40-7.34 (m, 2H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (s), 140.5 (s), 139.9 (s), 137.6 (s), 132.6 (d), 132.2 (d), 129.3 (d), 128.7 (s), 125.1 (d), 124.9 (d), 124.2 (d), 124.1 (d), 123.9 (d), 122.3 (d). IR (neat, ATR) ν = 2918, 1608, 1516, 1472, 1352, 1301, 1168, 1063, 946, 859, 845, 828 cm^{-1}. HRMS calcd for $C_{14}H_9NO_2SNa$ ([M+Na]$^+$) 278.0252; found 272.0247.

[5] E. David, S. Pellet-Rostaing, M. Lemaire, *Tetrahedron*, 2007, **63**, 8999-9006.

10*H*-[1]Benzothieno[3,2-*b*]indole (38)[6,7,8] was prepared by a microwave accelerated Cadogan reaction. Compound **35** (35 mg, 0.14 mmol) was dissolved in 1,2-dichlorobenzene (4 mL). Then triethylphosphite (0.3 mL, 1.75 mmol) was added. The tube was sealed and heated under microwave irradiation (300 W, 230 °C) for 1,5 h. The solvents were evaporated and the crude product was purified by flash chromatography (silica gel, pentane/ethyl acetate = to 9:1 (v/v)) to give *10H*-[1]benzothieno[3,2-*b*]indole (**38**) (27 mg, 0.12 mmol, 86% yield) was obtained as a colourless solid, mp 254-256 °C ($CHCl_3$/*n*-pentane); R_f 0.36 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 7.8 Hz, *J* = 7.3 Hz, 1H), 7.35 (dd, *J* = 8.0 Hz, *J* = 7.3 Hz, 1H), 7.32 (dd, *J* = 8.1 Hz, *J* = 7.1 Hz, 1H), 7.24 (dd, *J* = 7.8 Hz, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.0 (s), 140.7 (s), 137.0 (s), 126.8 (s), 124.6 (d), 124.4 (d), 124.3 (d), 123.5 (d), 122.7 (s), 120.4 (d), 119.5 (d), 119.4 (d), 116.8 (s), 112.3 (d). IR (neat, ATR) ν = 3406, 2979, 1475, 1451, 1432, 1370, 1344, 1301, 1230, 1103, 1057, 1017, 927 cm^{-1}. HRMS calcd for $C_{14}H_{10}NS$ ($[M+H]^+$) 224.0534; found 224.0542.

N-*n*-hexyl-benzothieno[3,2-*b*]indole (41) was obtained through *N*-alkylation of **38** with *n*-hexyl bromide. The Cadogan reaction product **38** (25 mg, 0.11 mmol) was dissolved in dry DMF (7 mL) and then sodium hydride (60% dispersion in oil, 6.7 mg, 0.17 mmol) was added. After stirring 30 min at room temperature, *n*-hexylbromide (0.47 mL, 0.34 mmol) was added and the mixture stirred at room temperature for 1h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layers were combined, washed with brine and dried with $MgSO_4$. N-*n*-hexyl-benzothieno[3,2-*b*]indole (**41**) (33 mg, 0.11 mmol, 99% yield) was obtained after flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a colourless solid; mp 45-47 °C (ethyl acetate/*n*-pentane); R_f 0.08 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.48-7.42 (m, 2H), 7.37-7.31 (m, 2H), 7.20 (ddd, *J* = 7.9 Hz, *J* = 7.1 Hz, *J* = 0.9 Hz, 1H), 4.39 (t, *J* = 7.5 Hz, 2H), 1.92 (m, 2H), 1.45 (m, 2H), 1.37-1.19 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4 (s), 141.6 (s), 137.5 (s), 127.2 (s), 124.7 (d), 124.4 (d), 123.9 (d), 122.9 (d), 121.7 (s), 120.0 (d), 119.5 (d), 119.4 (d), 115.4 (s), 110.0 (d), 45.2 (t), 31.7 (t), 30.7 (t), 26.9 (t), 22.7 (t), 14.1 (q). MS [ESI (+)]: m/z (%) = 308 ($[M+H]^+$, 71), 238 (13), 224 (100), 223 (51); HRMS calcd for $C_{20}H_{22}NS$ ($[M+H]^+$) 308.1480; found 308.1473.

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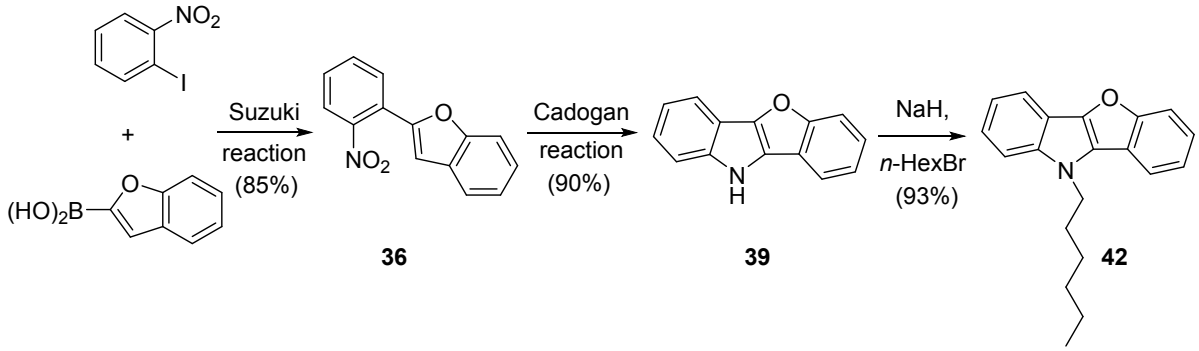
[6] K.E. Chippendale, B. Iddon, H. Suschitzky, *J. Chem. Soc. Perkin Trans. I*, 1972, 2023-2030.

[7] K. Takamatsu, K. Hirano, T. Satoh, M. Miura, *Org. Lett.*, 2014, **16**, 2892-2895.

[8] Y.B. KIM, H.M. KIM, Y. BEAK, T.H. KIM, ORGANIC COMPOUND AND ORGANIC ELECTROLUMINESCENT ELEMENT INCLUDING SAME, WIPO Patent Application WO/2014/104665.

N-*n*-hexyl-benzofuro[3,2-*b*]indole (42):



2-*o*-nitrophenylbenzofuran (36)[9] was prepared by a microwave accelerated Suzuki cross-coupling reactions of benzofurane-2-boronic acid and 2-bromonitrobenzene. 2-iodonitrobenzene (100 mg, 0.4 mmol), benzofurane-2-boronic acid (72 mg, 0.44 mmol), and $Pd(PPh_3)_4$ (14 mg, 0.012 mmol, 3 mol%) were placed in a microwave reaction vessel, flushed with nitrogen and N_2-purged DMF (5 mL) and a N_2-purged solution of Na_2CO_3 (1.2 mL of a 1 M solution in water) was added. The tube was sealed and placed in a microwave oven for 10 min. (300 W, 140 °C). Brine was added, the product extracted with CH_2Cl_2 and the combined organic layers dried with $MgSO_4$ and concentrated. The Suzuki cross-coupling product **36** (81 mg, 0.34 mmol, 85% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a red oil that become a solid while standing, mp 53-55 °C; R_f 0.43 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.67-7.60 (m, 2H), 7.53-7.49 (m, 2H), 7.33 (ddd, J = 7.3 Hz, J = 1.4 Hz, J = 0.7 Hz, 1H), 7.28-7.24 (m, 1H), 7.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (s), 150.5 (s), 148.3 (s), 132.1 (d), 130.0 (d), 129.4 (d), 128.5 (s), 125.4 (d), 124.3 (s), 124.1 (d), 123.3 (d), 121.6 (d), 111.5 (d), 106.1 (d). IR (neat, ATR): ν = 3415, 3053, 1520, 1442, 1350, 1298, 1255, 1164, 1107, 1022, 920 cm^{-1}. HRMS calcd for $C_{14}H_{10}NO_4$ ($[M+H]^+$) 240.0661; found 240.0667.

10*H*-benzofuro[3,2-*b*]indole (39)[9, 10] was prepared by a microwave accelerated Cadogan reaction. The Suzuki cross-coupling product **36** (50 mg, 0.21 mmol) was dissolved in 1,2-dichlorobenzene (5 mL) and triethylphosphite (0.43 mL, 2.51 mmol) was added. The tube was sealed and heated under microwave irradiation (300 W, 230 °C) for 1.5 h. After evaporation of the solvents under reduced pressure the Cadogan reaction product **39** (39 mg, 0.19 mmol, 90% yield) was obtained by flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a colourless solid, mp 197-199 °C (ethyl acetate/*n*-pentane); R_f 0.43 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (ddd, J = 7.7 Hz, J = 1.3 Hz, J = 0.6 Hz, 1H), 7.69-7.64 (m, 1H), 7.63-7.60 (m, 1H), 7.47 (ddd, J = 7.8 Hz, J = 1.3 Hz, J = 0.8 Hz, 1H), 7.35-7.30 (m, 2H), 7.30-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)

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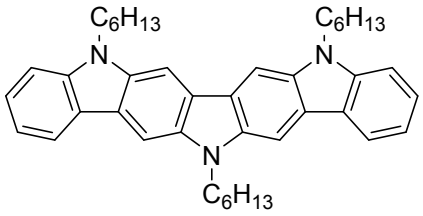
[9] H. Gao, Q.-L. Xu, M. Yousufuddin, D.H. Ess, L. Kürti, *Angew. Chem. Int. Ed.*, 2014, **53**, 2701-2705.

[10] Y. Sawada, M. Hotta, M. Matsumoto, Nitrogenated Aromatic Compound, Organic Semiconductor Material, and Organic Electronic Device, PCT Int. Appl. WO/2012/050002.

δ 159.3 (s), 143.8 (s), 139.8 (s), 125.3 (s), 124.0 (d), 123.0 (d), 122.8 (d), 120.5 (d), 118.9 (s), 118.0 (d), 117.3 (d), 114.4 (s), 112.9 (d), 112.7 (d). IR (neat, ATR) ν = 3413, 1456, 1445, 1397, 1311, 1243, 1231, 1188, 1139, 1096, 1042, 1005 cm^{-1}. MS [ESI (+)]: m/z (%) = 208 ($[M+H]^+$, 38), 180 (100), 153 (9); HRMS calcd for $C_{14}H_{10}NO$ ($[M+H]^+$) 208.0762; found 208.0755.

N-*n*-hexyl-benzofuro[3,2-*b*]indole (42) was obtained through N-alkylation of **39** with *n*-hexylbromide. Cadogan product **39** (30 mg, 0.15 mmol) was dissolved in dry DMF (8 mL) and then sodium hydride (8.7 mg, 0.22 mmol of a 60% dispersion in mineral oil) was added. After stirring 30 min at room temperature, *n*-hexylbromide (0.61 mL, 0.43 mmol) was added and the mixture stirred at room temperature for 1h. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layers were combined, washed with brine and dried with $MgSO_4$. Benzothieno[3,2-*b*]indole **42** (41 mg, 0.14 mmol, 93% yield) was obtained after flash chromatography (silica gel, *n*-pentane/ethyl acetate = 9:1 (v/v)) as a red solid; R_f 0.74 (SiO_2, *n*-pentane/ethyl acetate = 9:1 (v/v)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (ddd, *J* = 8.0 Hz, *J* = 1.1 Hz, *J* = 0.8 Hz, 1H), 7.73-7.70 (m, 1H), 7.64-7.59 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.33-7.25 (m, 3H), 7.19 (ddd, *J* = 7.7 Hz, *J* = 7.2 Hz, *J* = 0.9 Hz, 1H), 4.39 (t, *J* = 7.1 Hz, 2H), 1.92 (m, 2H), 1.41-1.19 (m, 6H), 0.83 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (s), 142.3 (s), 139.7 (s), 127.0 (s), 123.7 (d), 122.7 (d), 122.3 (d), 119.4 (d), 119.0 (s), 117.8 (d), 117.4 (d), 113.5 (s), 112.9 (d), 110.2 (d), 45.5 (t), 31.6 (t), 30.6 (t), 26.8 (t), 22.6 (t), 14.1 (q). IR (neat, ATR) ν = 2954, 2926, 2855, 1459, 1442, 1398, 1350, 1210, 1778, 1129, 1047, 1013 cm^{-1}. HRMS calc for $C_{20}H_{22}NO$ [$M+H^+$] 292.1701, found 292.1703.

3. Cyclic Voltammetry



26

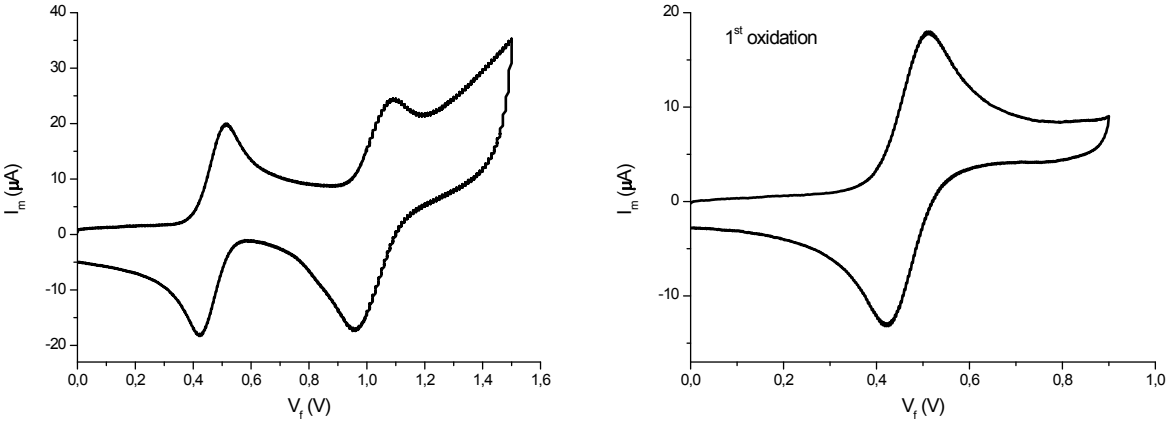
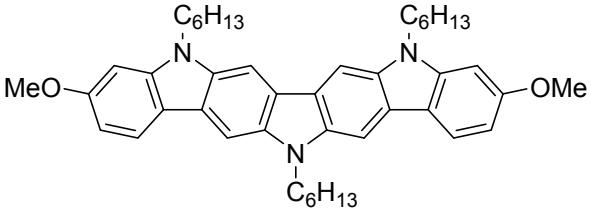


Figure 3.1. Cyclic voltammetry of **26** (10^{-3} M in CH_2Cl_2/0.1 M Bu_4NPF_6) at room temperature [left]. First oxidation potential [right]. Scan rate 100 mV/s; CV recorded vs SCE [left].



27

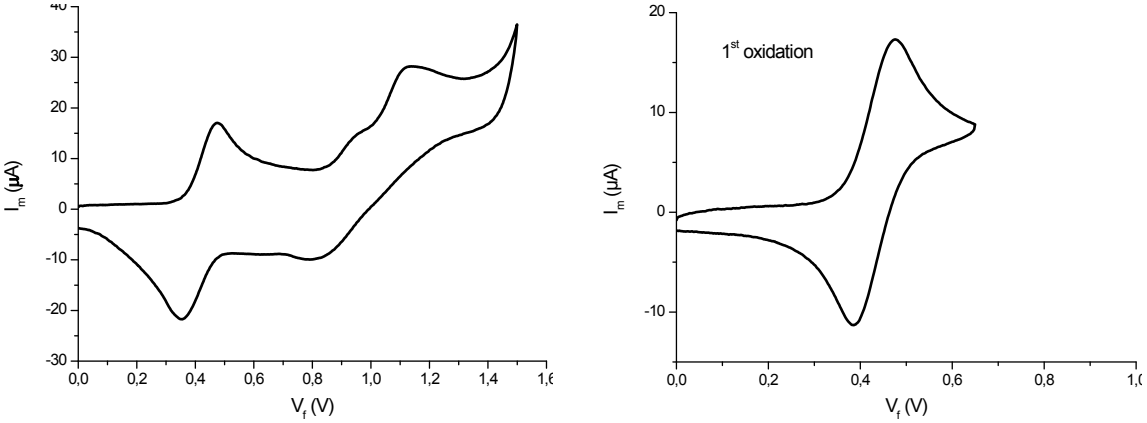
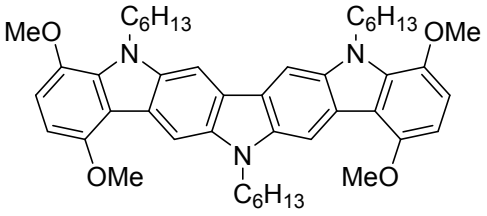


Figure 3.2. Cyclic voltammetry of **27** (10^{-3} M in CH_2Cl_2/0.1 M Bu_4NPF_6) at room temperature [left]. First oxidation potential [right]. Scan rate 100 mV/s; CV recorded vs SCE [left].



28

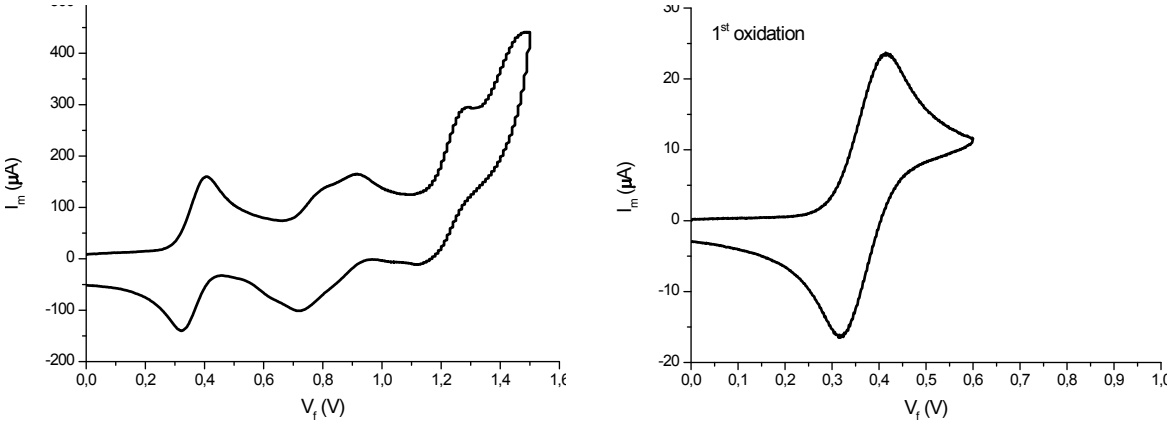
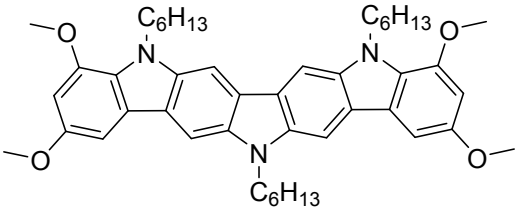


Figure 3.3. Cyclic voltammetry of **28** (10^{-3} M in CH_2Cl_2/0.1 M Bu_4NPF_6) at room temperature [left]. First oxidation potential [right]. Scan rate 100 mV/s; CV recorded vs SCE [left].



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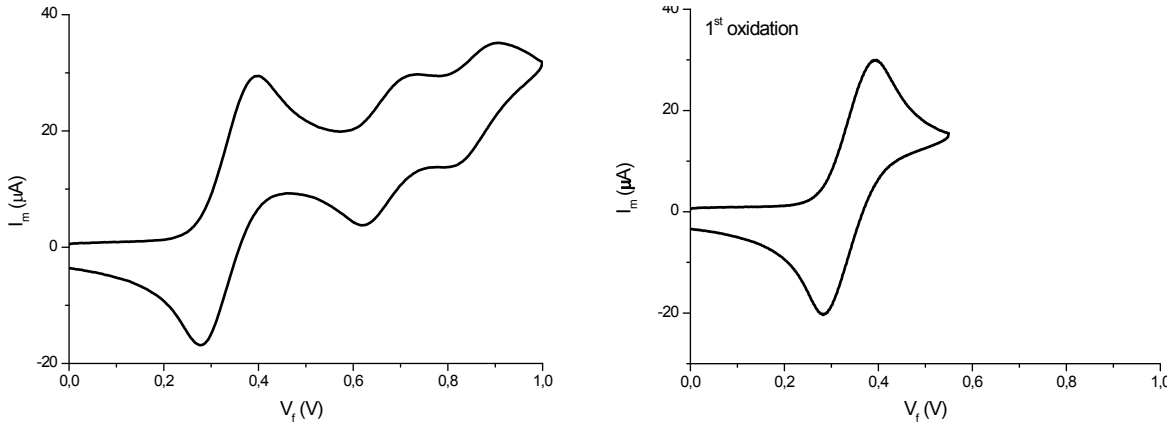
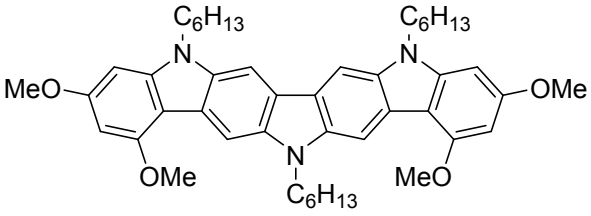


Figure 3.4. Cyclic voltammetry of **29** (10^{-3} M in CH_2Cl_2/0.1 M Bu_4NPF_6) at room temperature [left]. First oxidation potential [right]. Scan rate 100 mV/s; CV recorded vs SCE [left].



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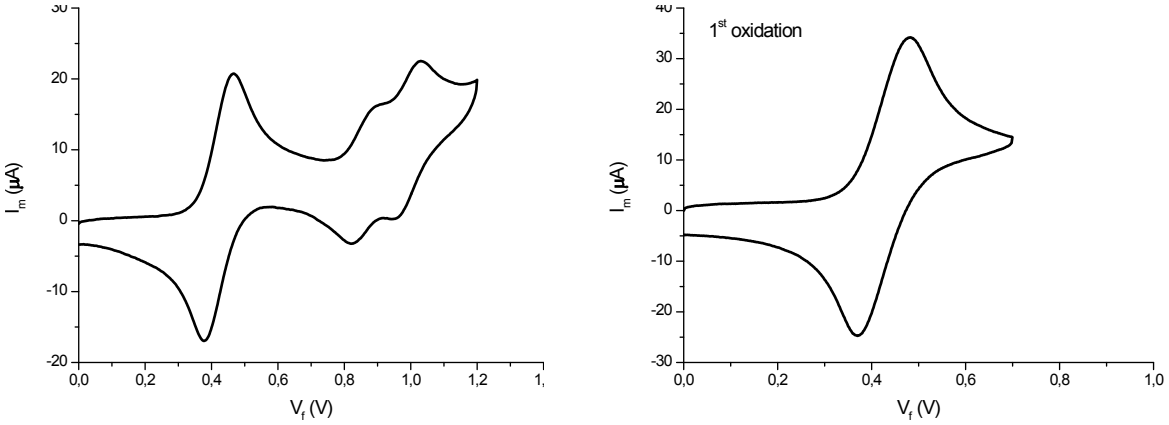
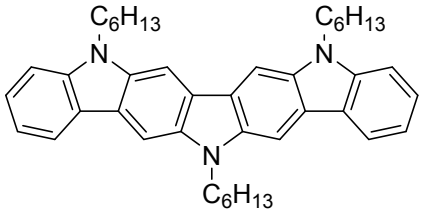


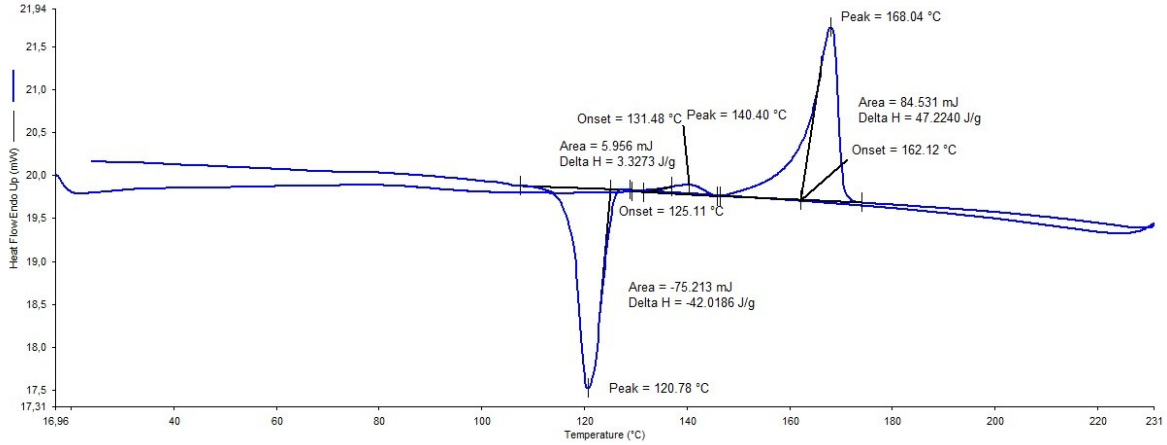
Figure 3.5. Cyclic voltammetry of **30** (10^{-3} M in CH_2Cl_2/0.1 M Bu_4NPF_6) at room temperature [left]. First oxidation potential [right]. Scan rate 100 mV/s; CV recorded vs SCE [left].

4. DSC data

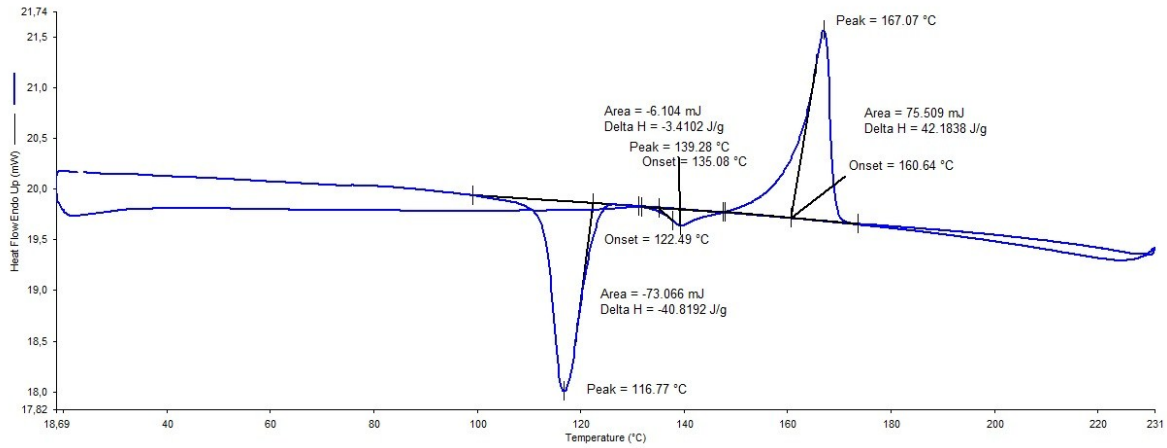


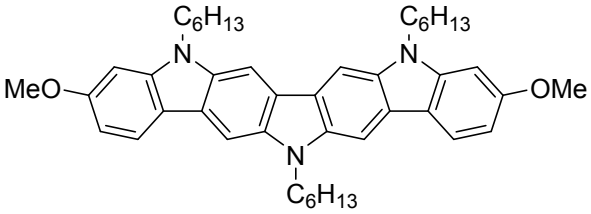
26

1er cycle



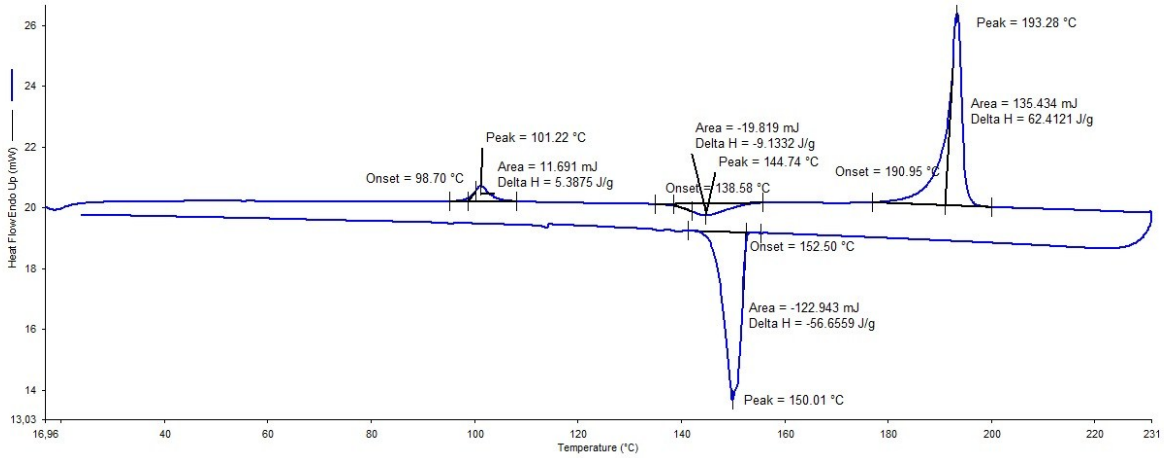
2nd cycle



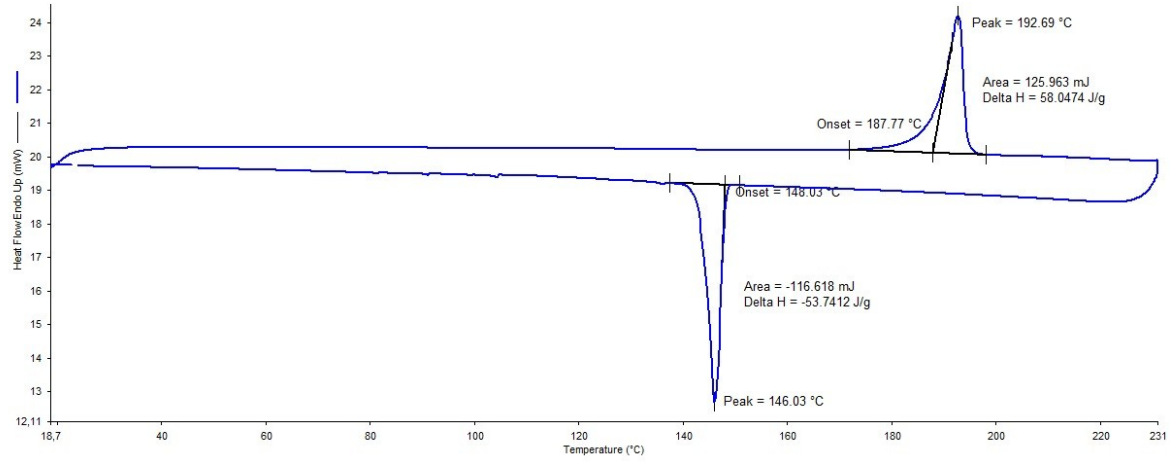


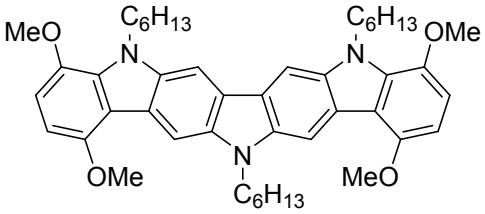
27

1er cycle



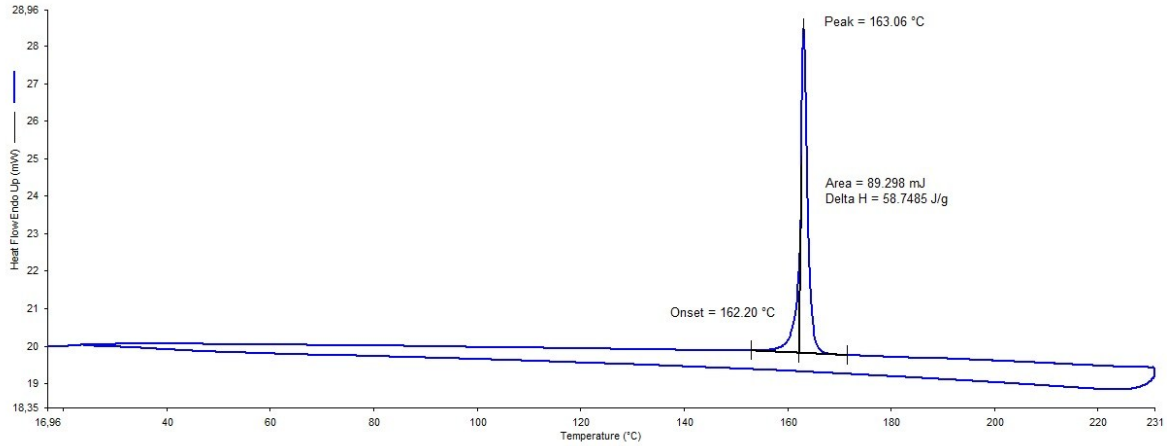
2nd cycle



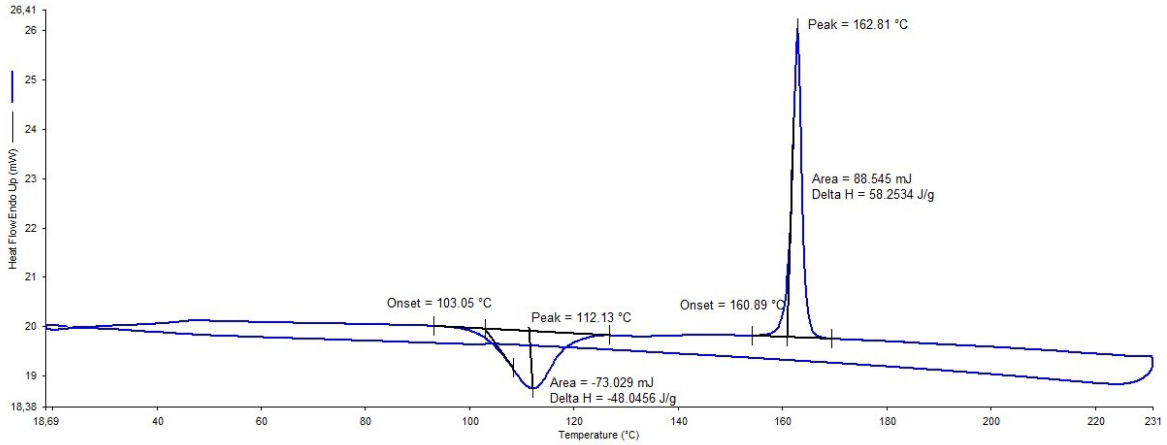


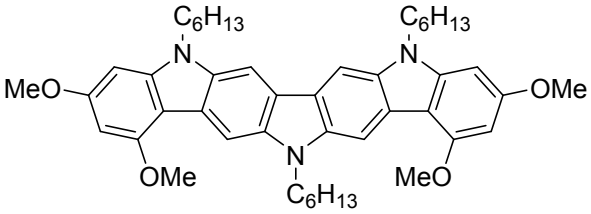
28

1er cycle



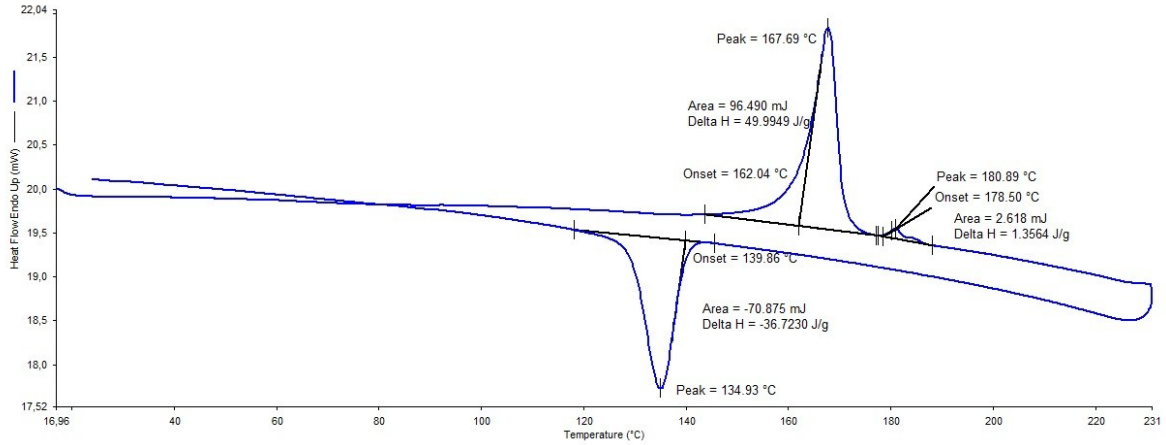
2nd cycle



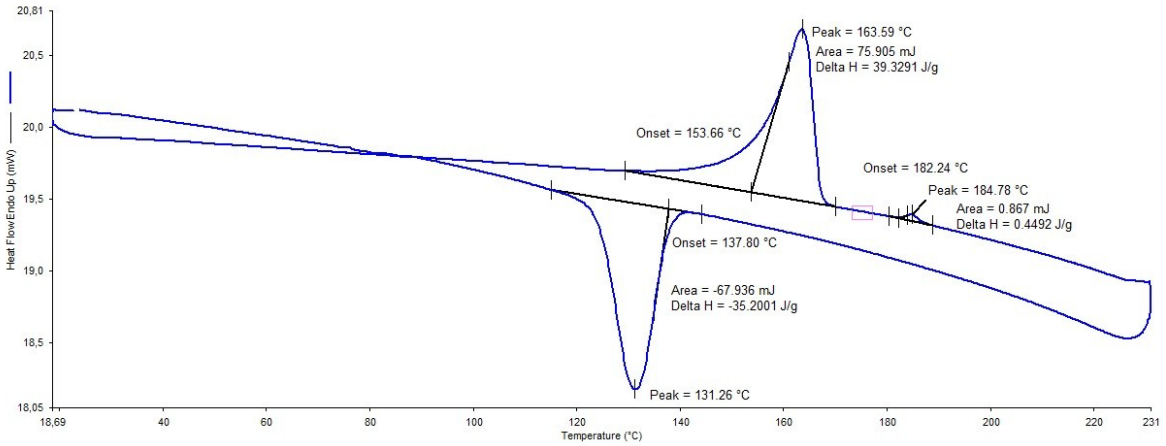


30

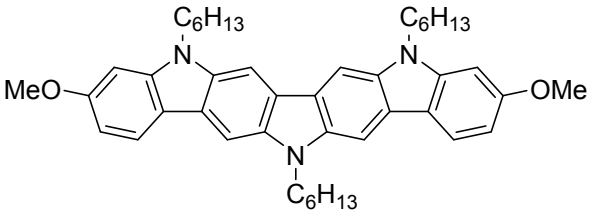
1er cycle



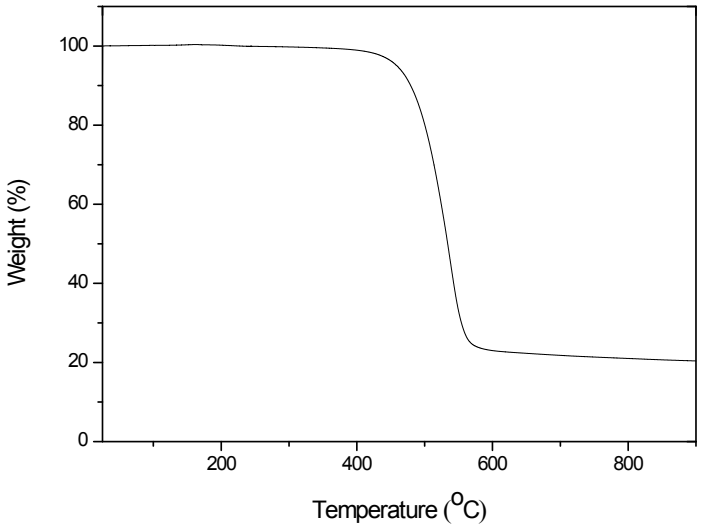
2nd cycle



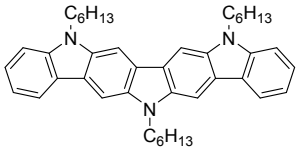
5. TGA of (27)


C6H13
C6H13
N
N
MeO
OMe
N
C6H13

27


100
80
60
40
20
0
Weight (%)
200
400
600
800
Temperature (°C)

6. UV-vis and Photoluminescence Spectra



26

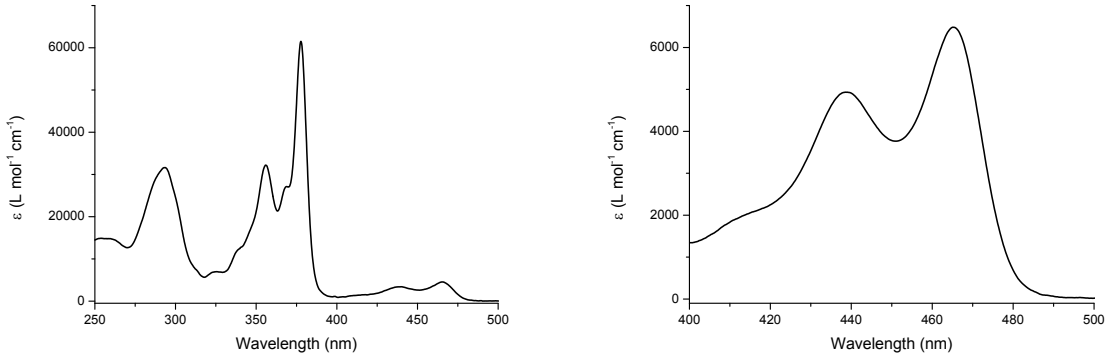


Figure 6.1: UV-vis absorption spectra of **26** in dichloromethane [left], and enlargement of the long-wavelength absorption [right].

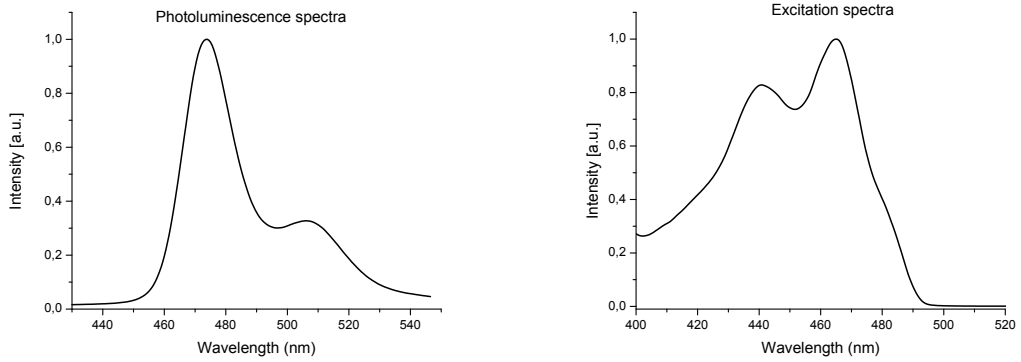


Figure 6.2: Photoluminescence spectra of **26** (10^{-5} M in CH_2Cl_2, λ_{ex} = 410 nm) [left], and excitation spectra (λ_{em} = 480 nm) [right].

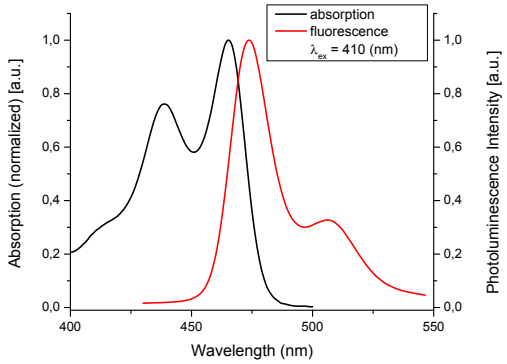
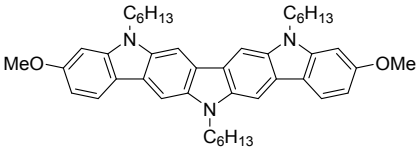


Figure 6.3: Absorption and photoluminescence (λ_{ex} = 410 nm) spectra of **26** in CH_2Cl_2.



27

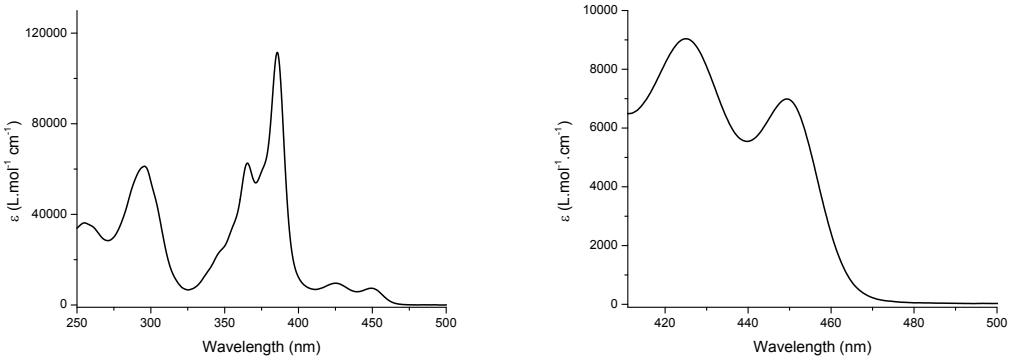


Figure 6.4: UV-vis absorption spectra of **27** in dichloromethane [left], and enlargement of the long-wavelength absorption [right].

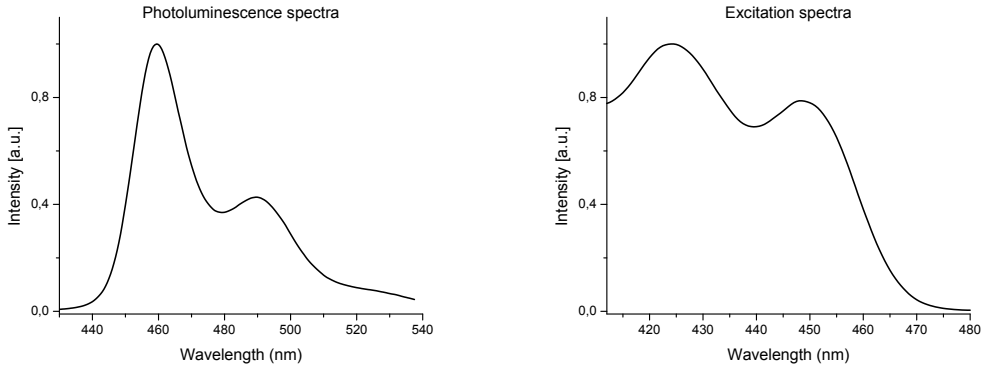


Figure 6.5: Photoluminescence spectra of **27** (10^{-5} M in CH_2Cl_2, λ_{ex} = 410 nm) [left], and excitation spectra (λ_{em} = 490 nm) [right].

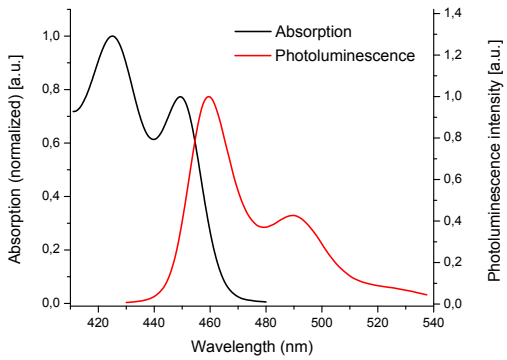
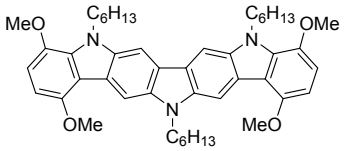


Figure 6.6: Absorption and Photoluminescence (λ_{ex} = 410 nm) spectra of **27** in CH_2Cl_2.



28

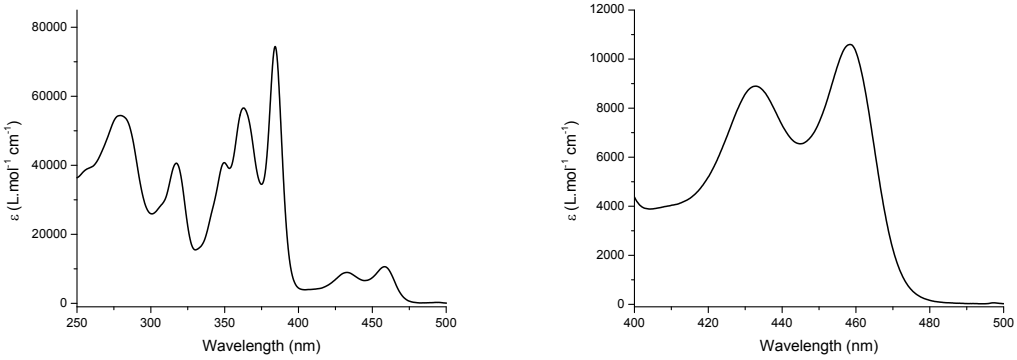


Figure 6.7: UV-vis absorption spectra of **28** in dichloromethane [left], and enlargement of the long-wavelength absorption [right].

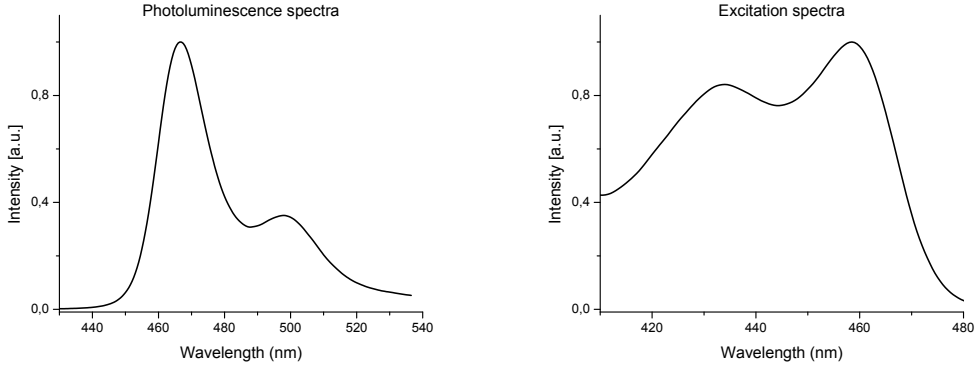


Figure 6.8: Photoluminescence spectra of **28** (10^{-5} M in CH_2Cl_2, λ_{ex} = 410 nm) [left], and excitation spectra (λ_{em} = 490 nm) [right].

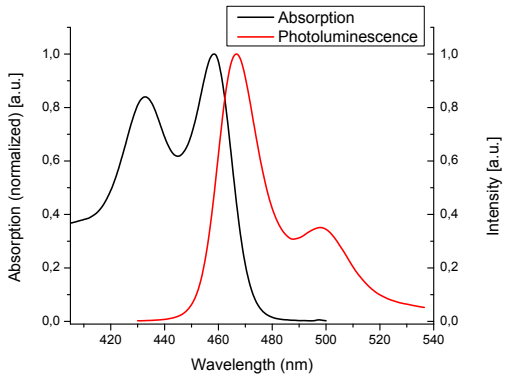
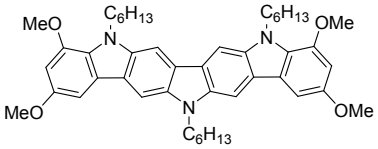


Figure 6.9: Absorption and Photoluminescence (λ_{ex} = 410 nm) spectra of **28** in CH_2Cl_2.



29

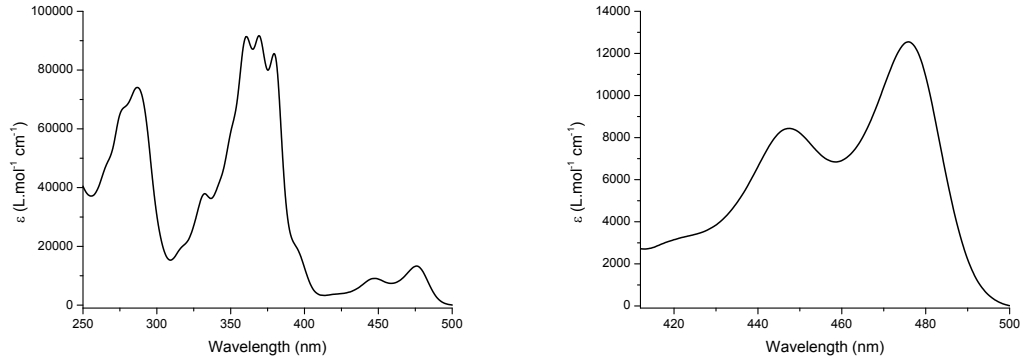


Figure 6.10: UV-vis absorption spectra of **29** in dichloromethane [left], and enlargement of the long-wavelength absorption [right].

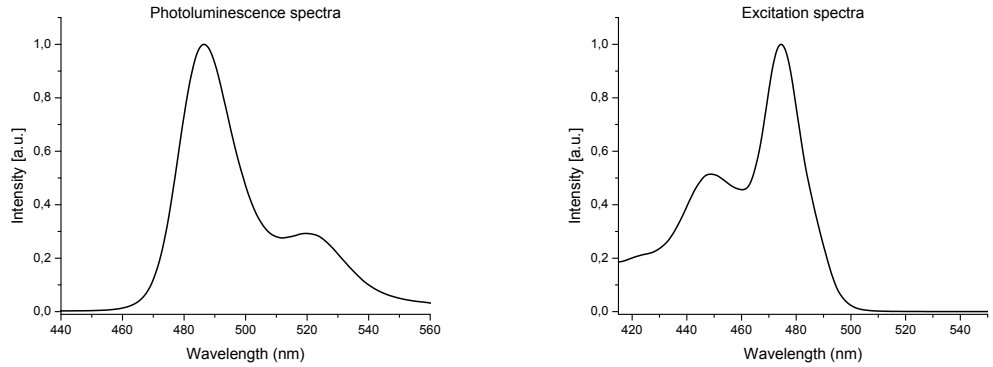


Figure 6.11: Photoluminescence spectra of **29** (10^{-5} M in CH_2Cl_2, λ_{ex} = 410 nm) [left], and excitation spectra (λ_{em} = 472 nm) [right].

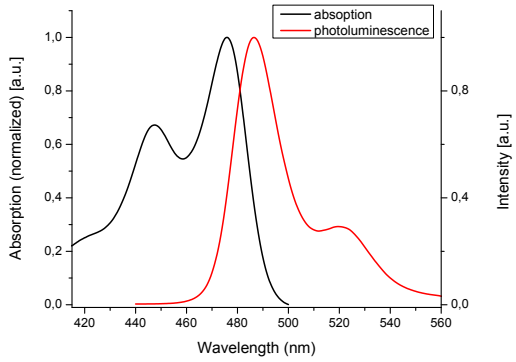
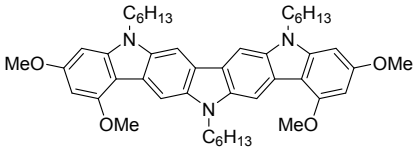


Figure 6.12: Absorption and Photoluminescence (λ_{ex} = 410 nm) spectra of **29** in CH_2Cl_2.



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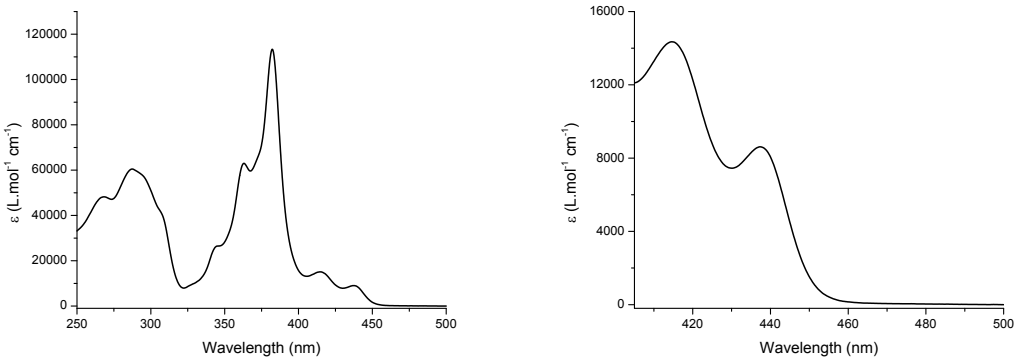


Figure 6.13: UV-vis absorption spectra of **30** in dichloromethane [left], and enlargement of the long-wavelength absorption [right].

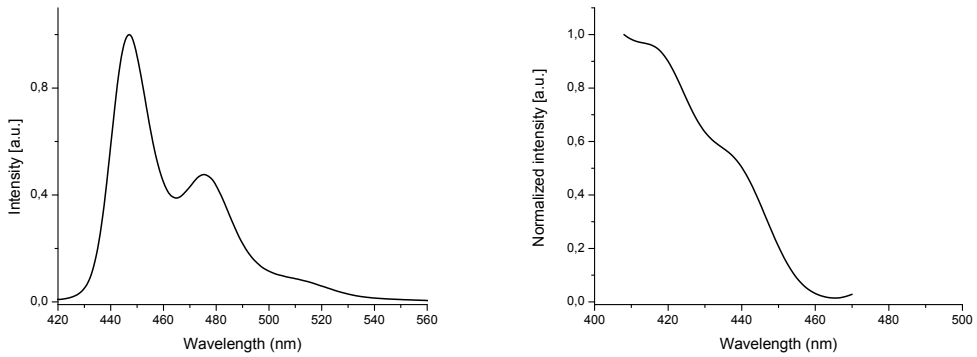


Figure 6.14: Photoluminescence spectra of **30** (10^{-5} M in CH_2Cl_2, λ_{ex} = 410 nm) [left], and excitation spectra (λ_{em} = 490 nm) [right].

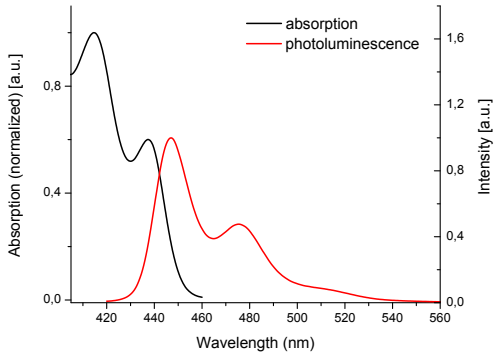
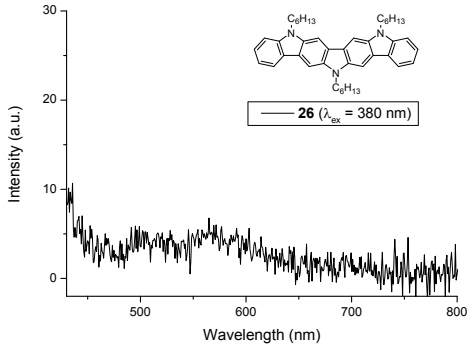
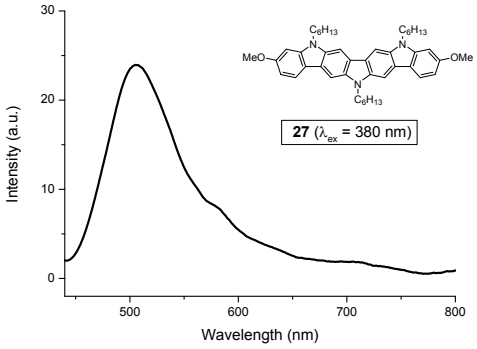
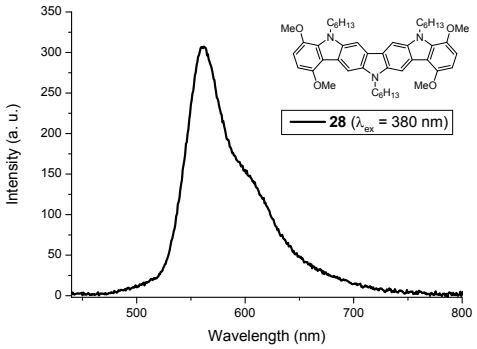


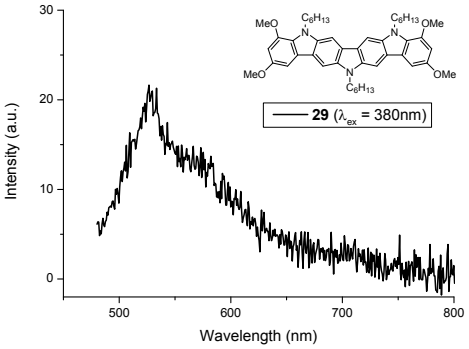
Figure 6.15: Absorption and Photoluminescence (λ_{ex} = 410 nm) spectra of **30** in CH_2Cl_2.

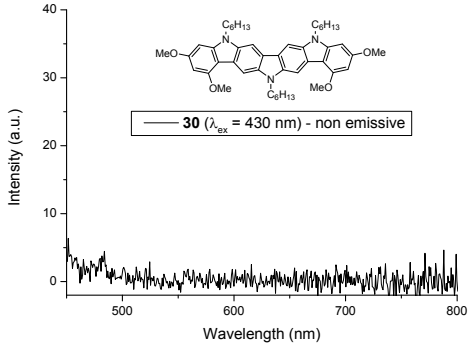
7. Solid State Photoluminescence Spectra











Compound	26	27	28	29	30
ϕ_F of solid, (λ_{ex} = [nm])	~1% (430)	2% (430)	14% (430)	2% (430)	0% (430)
ϕ_F in solution, $c = 10^{-6}$ M in CH_2Cl_2, (λ_{ex} [nm]),	22% (430)	26% (430)	22% (430)	20% (440)	27% (420)

8. Calculated HOMO-LUMO Orbitals

The molecules **26*-33*** were minimized using Gaussian 09 revision D-01 and D-02[11] with the B3LYP functional[12] and 6-31(d) basis set[13] using a PCM model[14] for dichloromethane as solvent. Vibrational analysis confirmed the stationary points as minima. The HOMO-1, HOMO, LUMO and LUMO+1 energy levels are given in the Table. Surface plots of the LUMO, HOMO and HOMO-1 (as the energy gap between the HOMO-1 and HOMO is often rather small) are given below. Each is drawn to enclose 98% of the electron density.

Table. Energies of orbitals for compounds 26*-33*.[a]

	HOMO-1	HOMO	LUMO	LUMO+1
26*	-5.21	-4.69	-1.35	-0.33
27*	-4.96	-4.66	-1.23	-0.22
28*	-4.91	-4.54	-1.17	-0.08
29*	-4.94	-4.50	-1.28	-0.19
30*	-4.75	-4.59	-1.06	0.03
31*	-4.88	-4.71	-1.27	-0.40
32*	-4.87	-4.73	-1.46	-0.73
33*	-4.80	-4.77	-1.44	-0.62

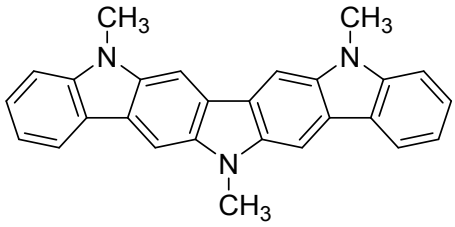
a. Energies in eV.

[11] (a) A. D. Becke *J. Chem. Phys.,* 1993, **98**, 5648. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785. (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.,* 1994, **98**, 11623.

[12] R. Ditchfield, W.J. Hehre, J.A. Pople, *J. Chem. Phys.* 1971, **54** 724.

[13] (a) V. Barone and M. Cossi, *J Phys Chem A,* **1998**, 102, 1995. (b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* 2003, **24**, 669.

[14] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.



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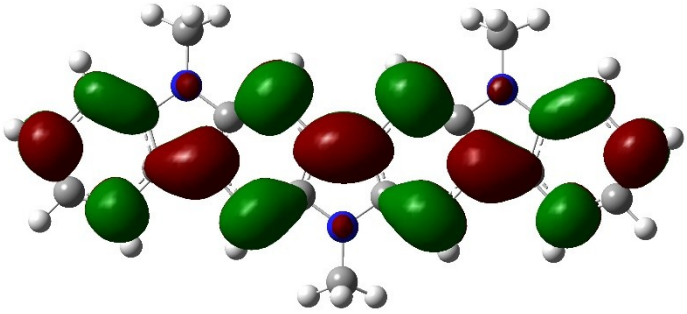


Figure 8.1.1: Calculated LUMO of **26*.**

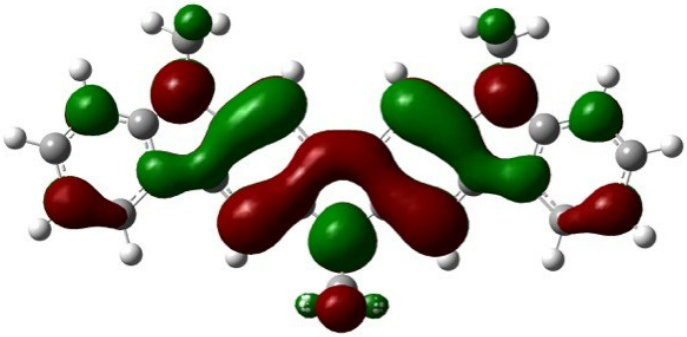


Figure 8.1.2: Calculated HOMO of **26*.**

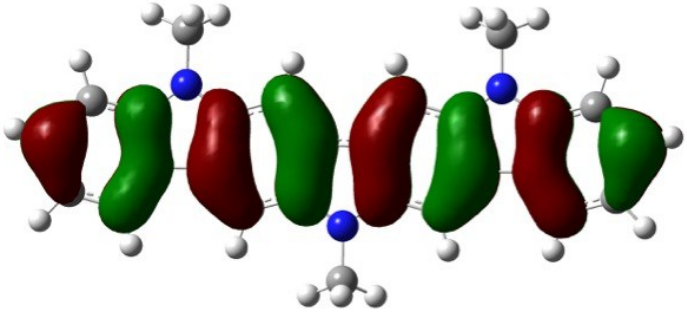
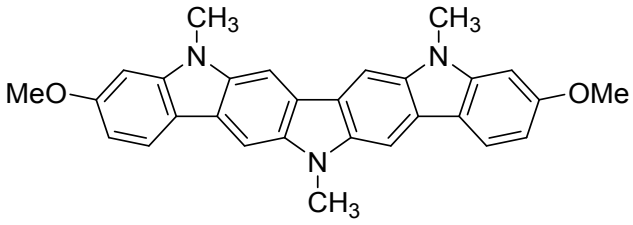


Figure 8.1.3: Calculated HOMO-1 of **26*.**



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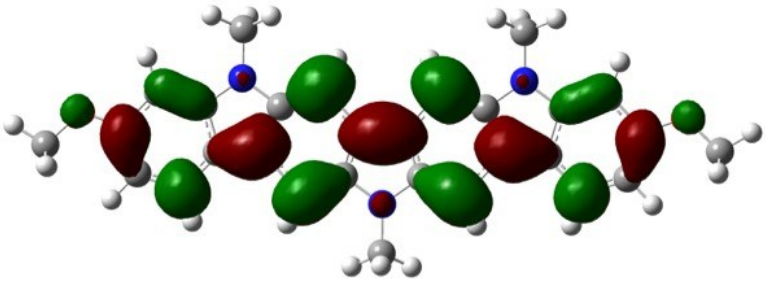


Figure 8.2.1: Calculated LUMO of **27***.

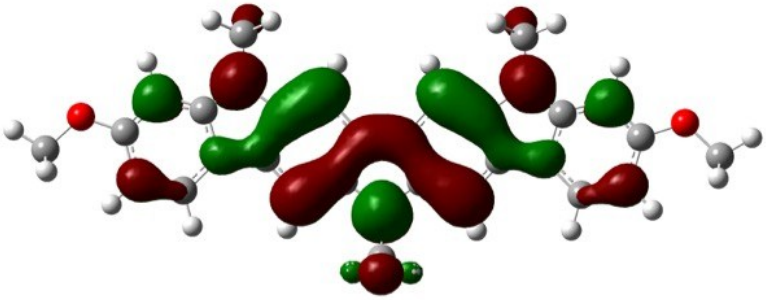


Figure 8.2.2: Calculated HOMO of **27***.

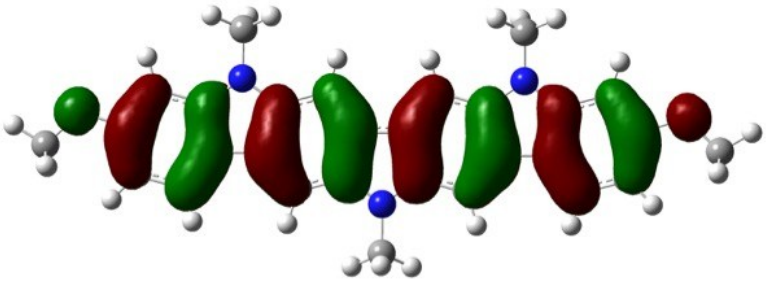
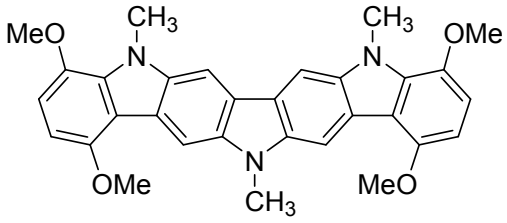


Figure 8.2.3: Calculated HOMO-1 of **27*.**



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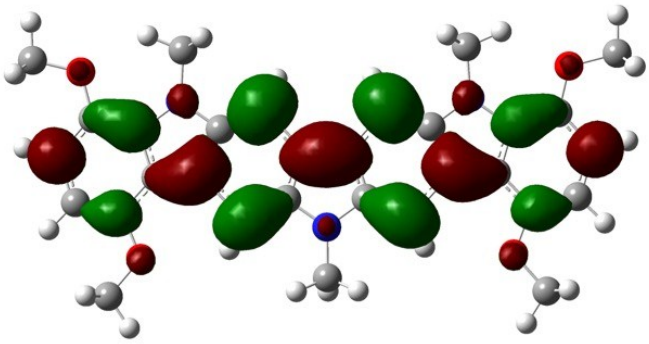


Figure 8.3.1: Calculated LUMO of **28***.

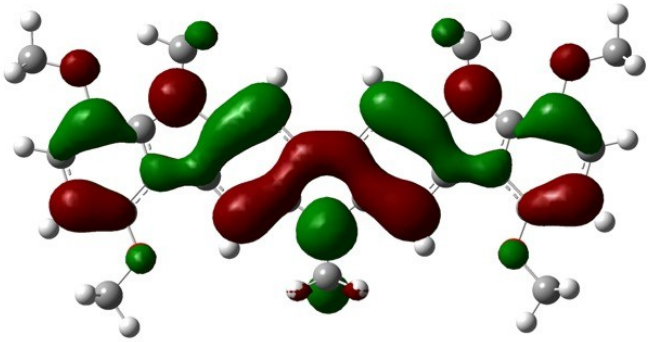


Figure 8.3.2: Calculated HOMO of **28***.

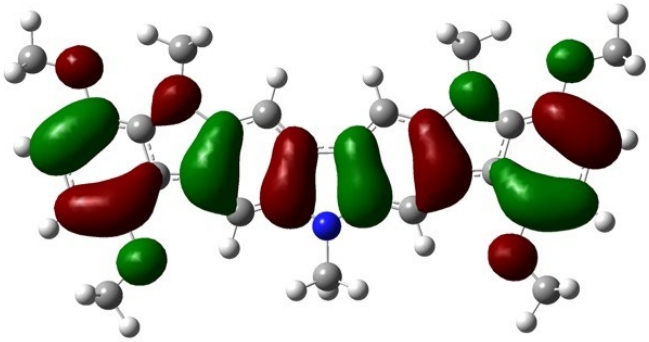
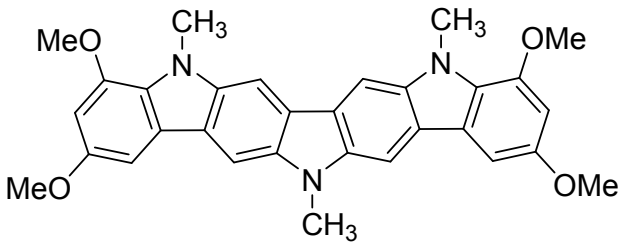


Figure 8.2.3: Calculated HOMO-1 of **28*.**



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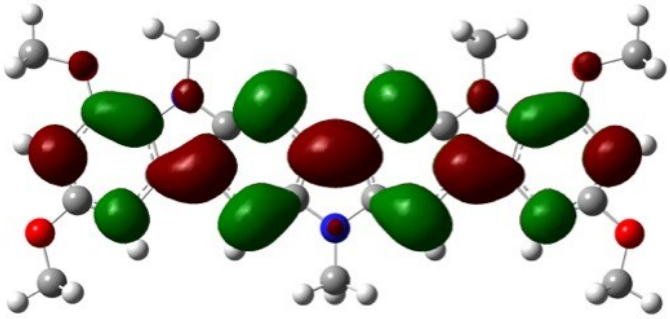


Figure 8.4.1: Calculated LUMO of **29***.

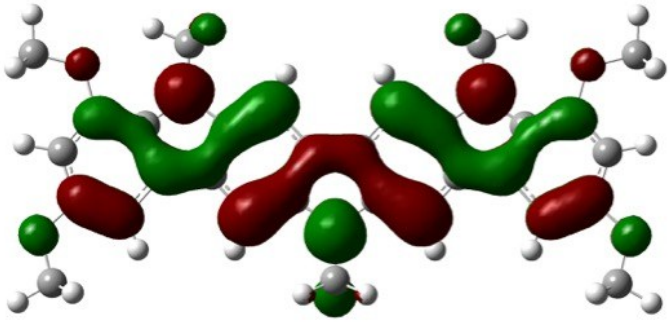


Figure 8.4.2: Calculated HOMO of **29***.

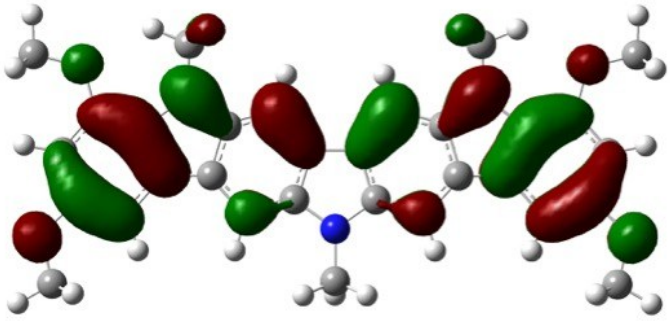
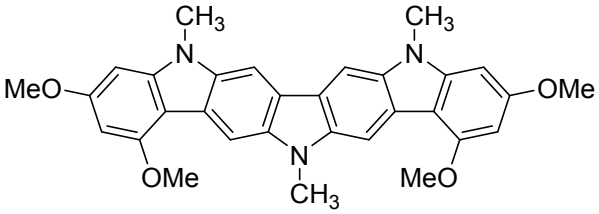


Figure 8.4.3: Calculated HOMO-1 of **29*.**



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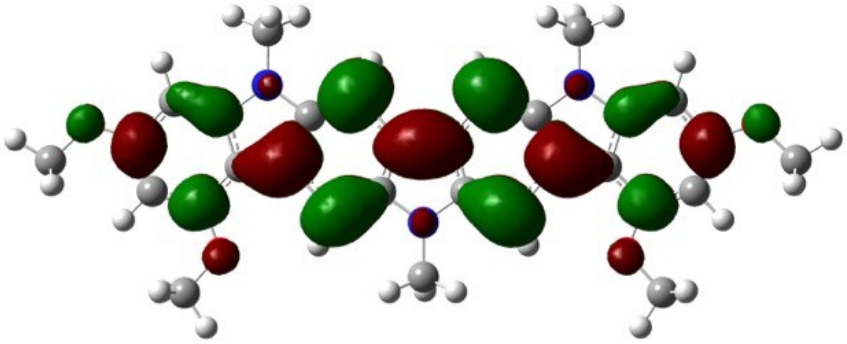


Figure 8.5.1: Calculated LUMO of **30***.

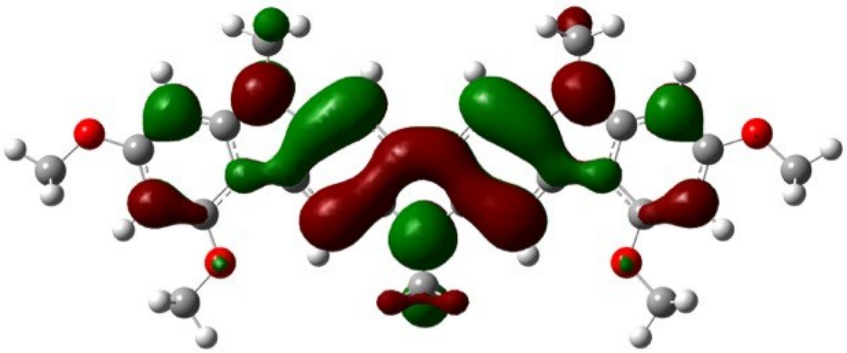


Figure 8.5.2: Calculated HOMO of **30***.

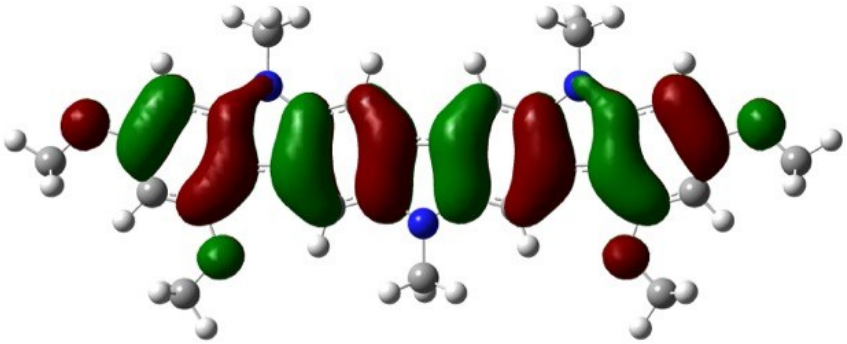
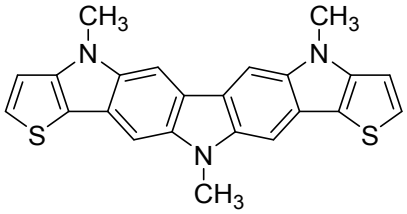


Figure 8.5.3: Calculated HOMO-1 of **30*.**



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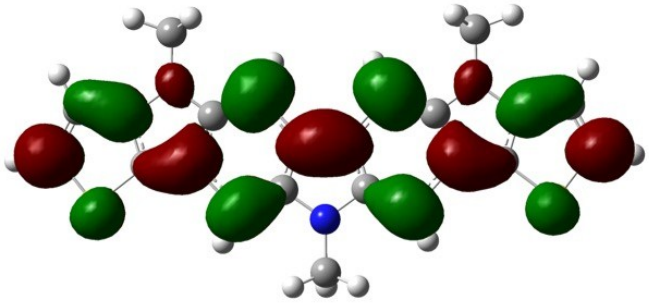


Figure 8.6.1: Calculated LUMO of **31***.

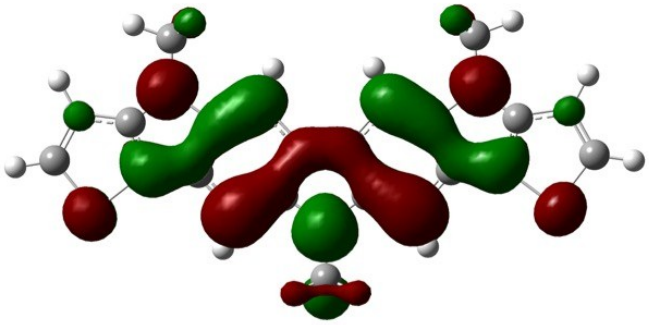


Figure 8.6.2: Calculated HOMO of **31***.

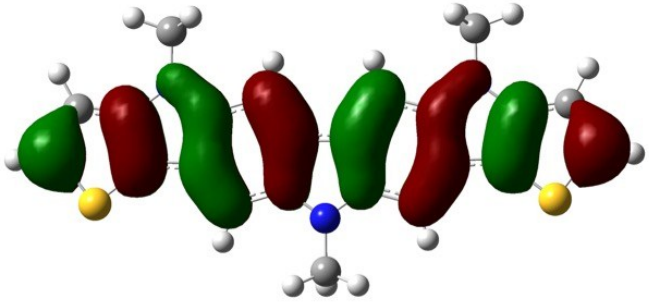
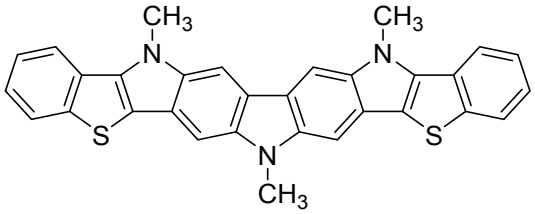


Figure 8.6.3: Calculated HOMO-1 of **31*.**



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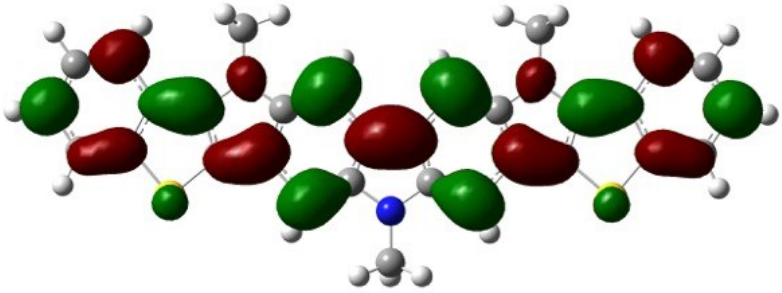


Figure 8.7.1: Calculated LUMO of **32***.

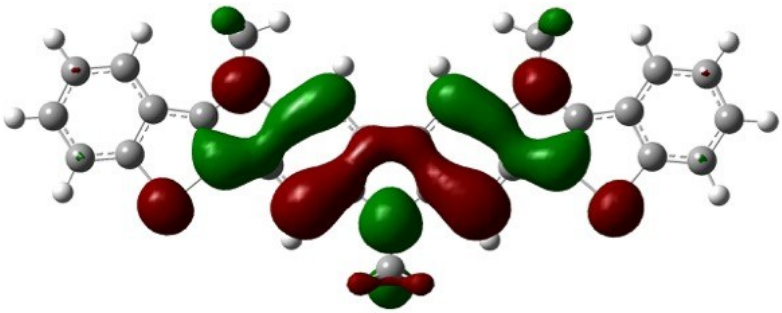


Figure 8.7.2: Calculated HOMO of **32***.

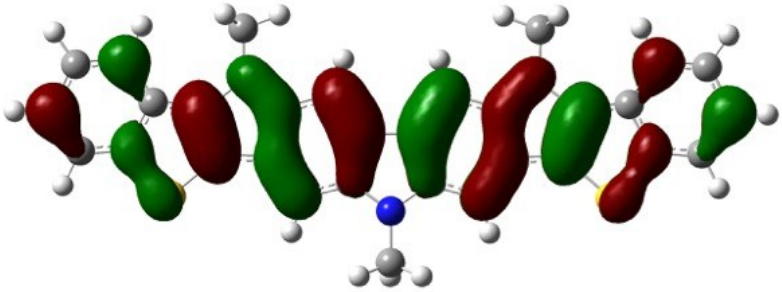
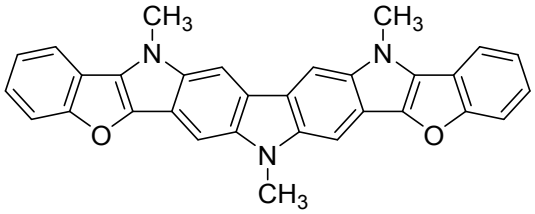


Figure 8.7.3: Calculated HOMO-1 of **32*.**



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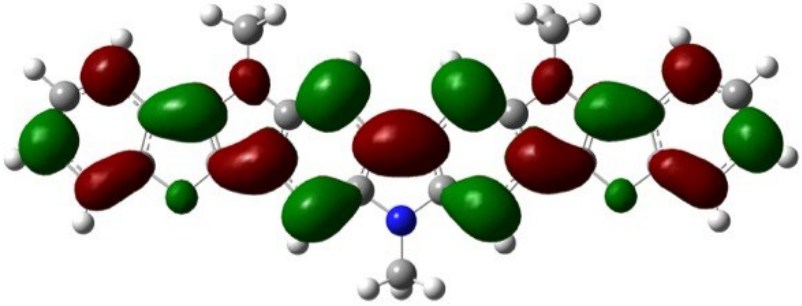


Figure 8.8.1: Calculated LUMO of **33***.

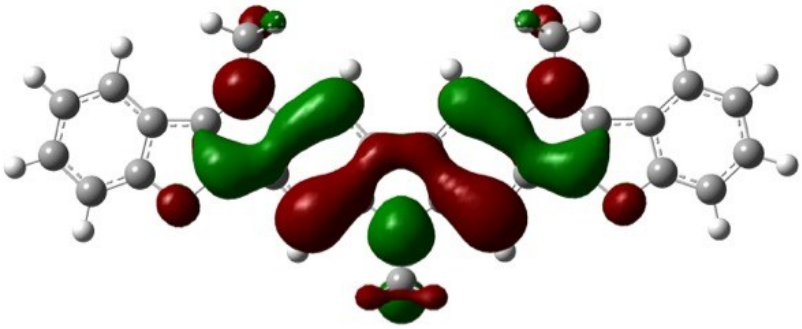


Figure 8.8.2: Calculated HOMO of **33***.

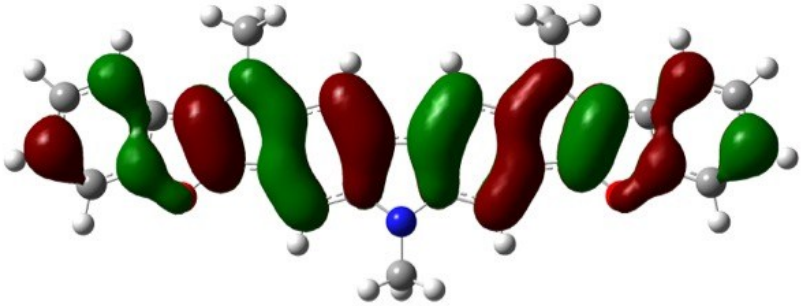
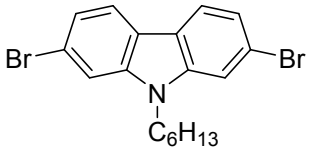


Figure 8.8.3: Calculated HOMO-1 of **33*.**

9. ^{1}H NMR and ^{13}C NMR spectra.



S3

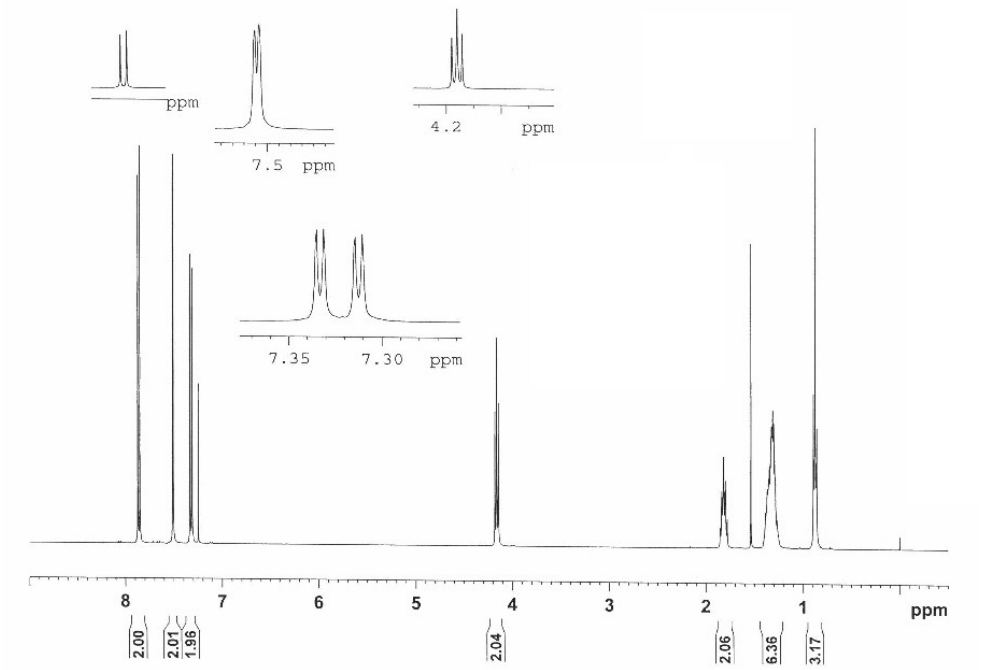


Figure 9.1: ^{1}H NMR spectrum of **S3** in $CDCl_3$, 400 MHz.

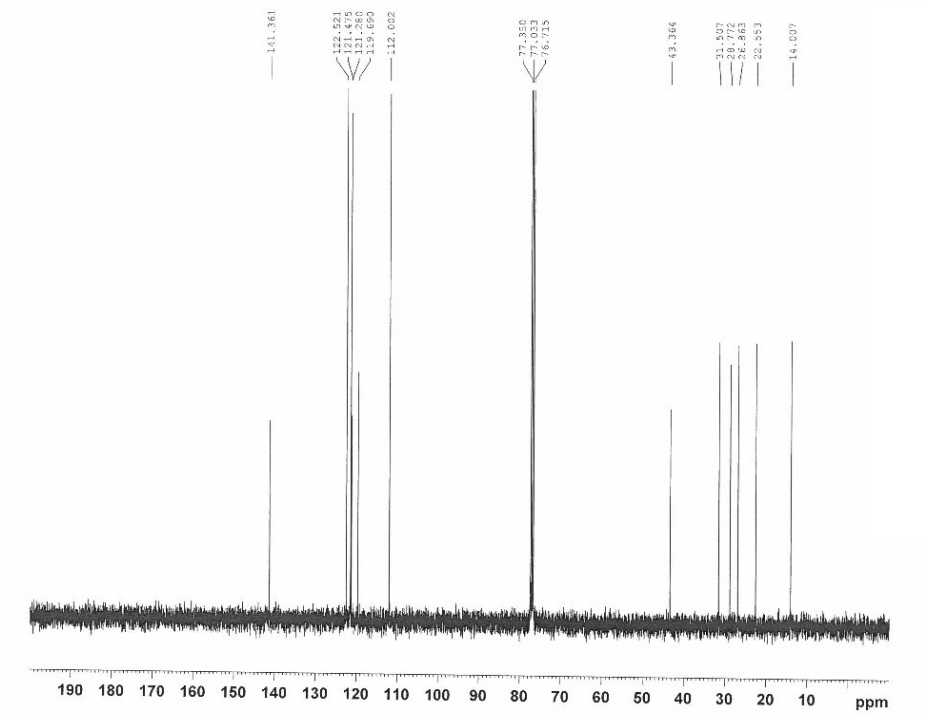
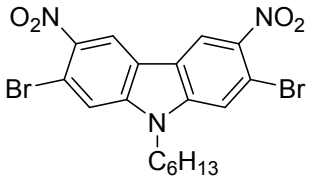


Figure 9.2: ^{13}C NMR spectrum of **S3** in $CDCl_3$, 100 MHz.



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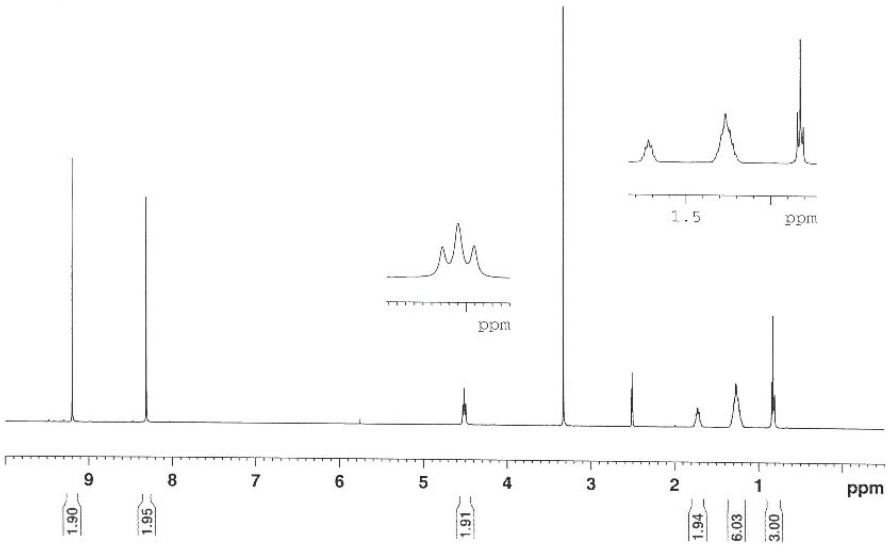


Figure 9.3: ^{1}H NMR spectrum of **1** in $CDCl_3$, 400 MHz.

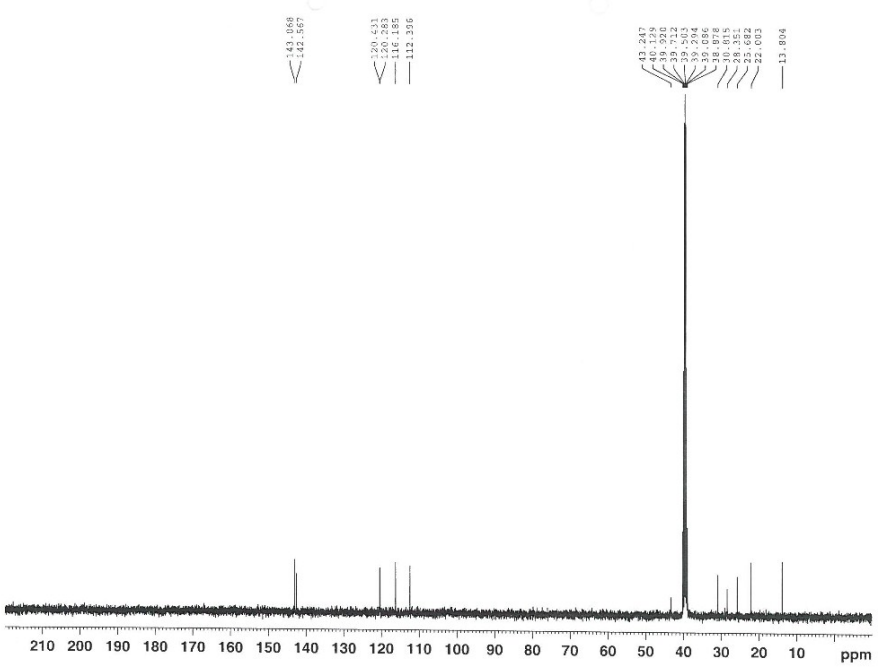
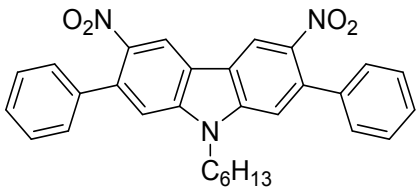


Figure 9.4: ^{13}C NMR spectrum of **1** in $CDCl_3$, 100 MHz.



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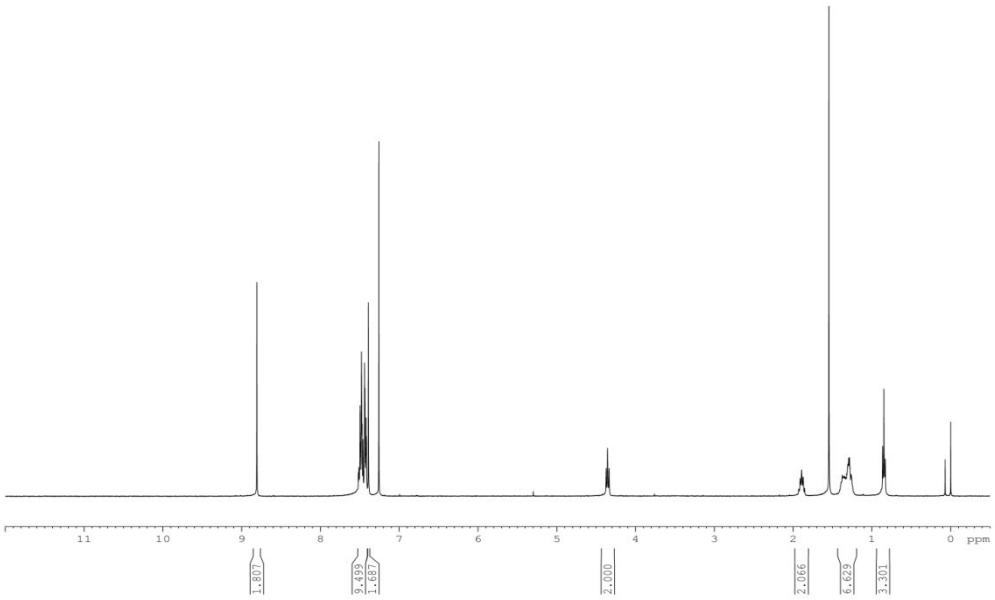


Figure 9.5: ^{1}H NMR spectrum of **10** in $CDCl_3$, 400 MHz

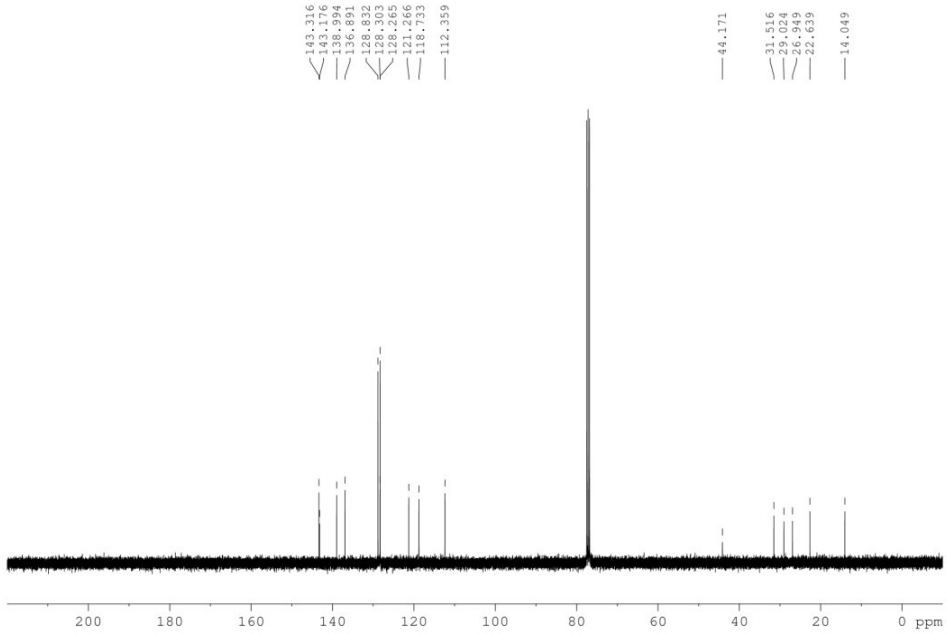
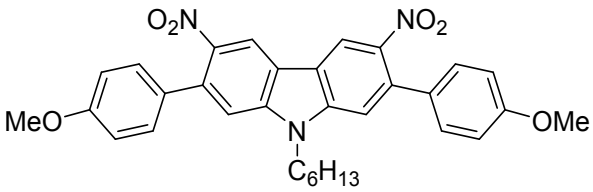


Figure 9.6: ^{13}C NMR spectrum of **10** in $CDCl_3$, 100 MHz.



11

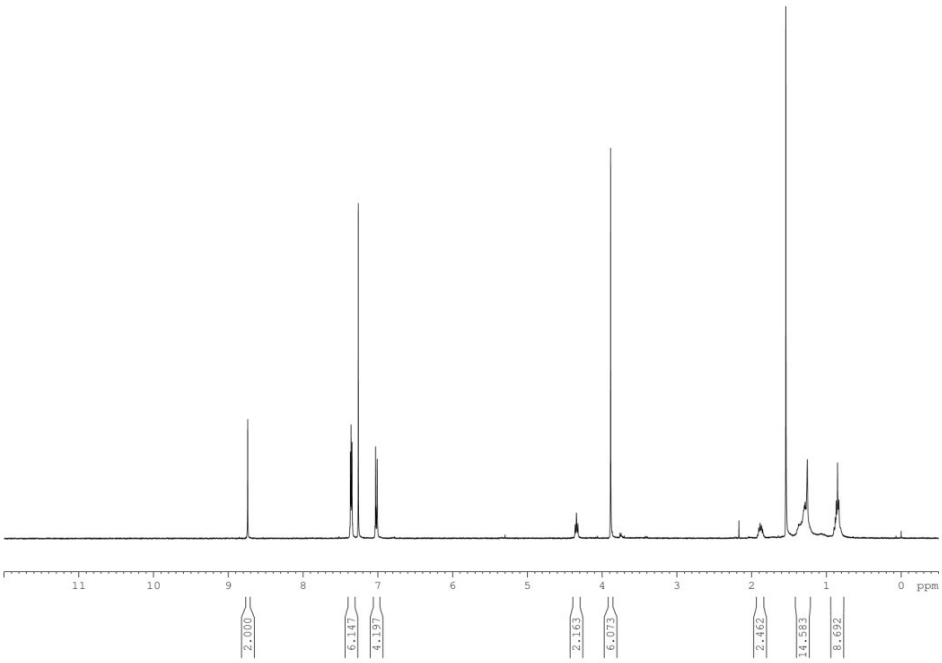


Figure 9.7: ^{1}H NMR spectrum of **11** in $CDCl_3$, 400 MHz.

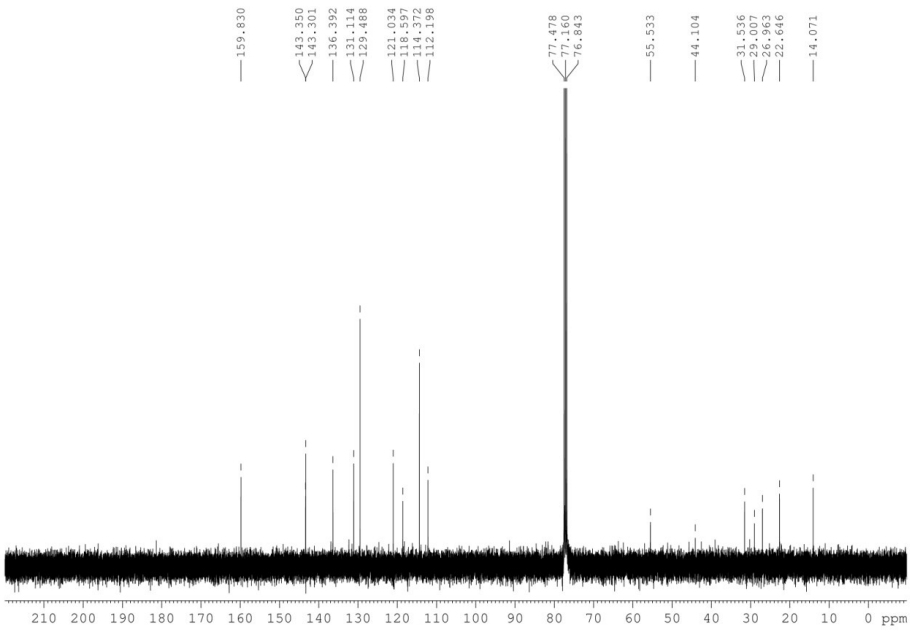
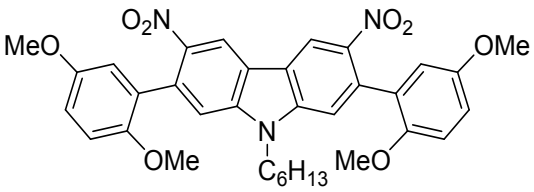


Figure 9.8: ^{13}C NMR spectrum of **11** in $CDCl_3$, 100 MHz.



12

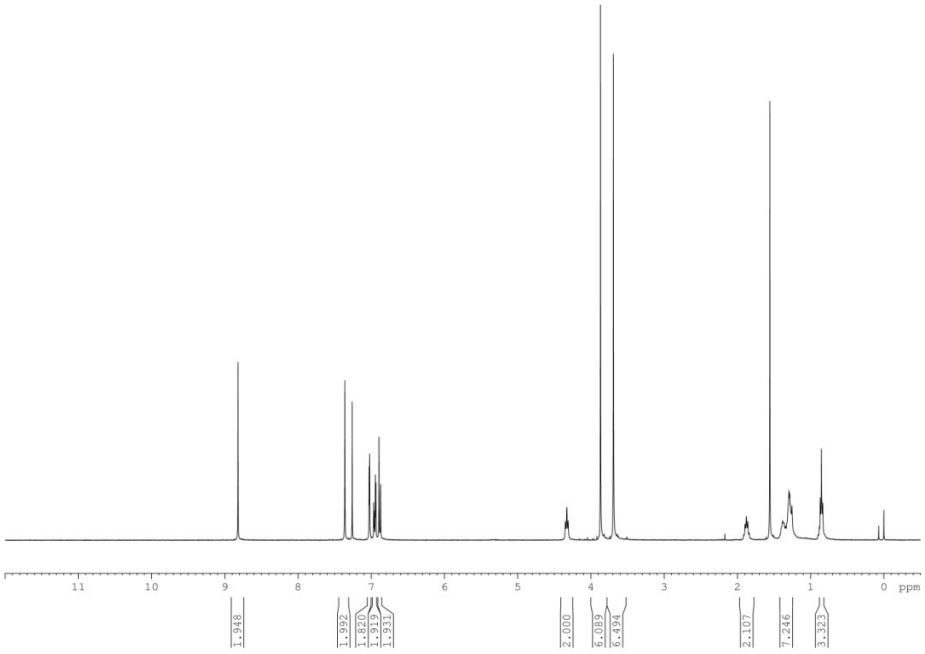


Figure 9.9: ^{1}H NMR spectrum of **12** in $CDCl_3$, 400 MHz.

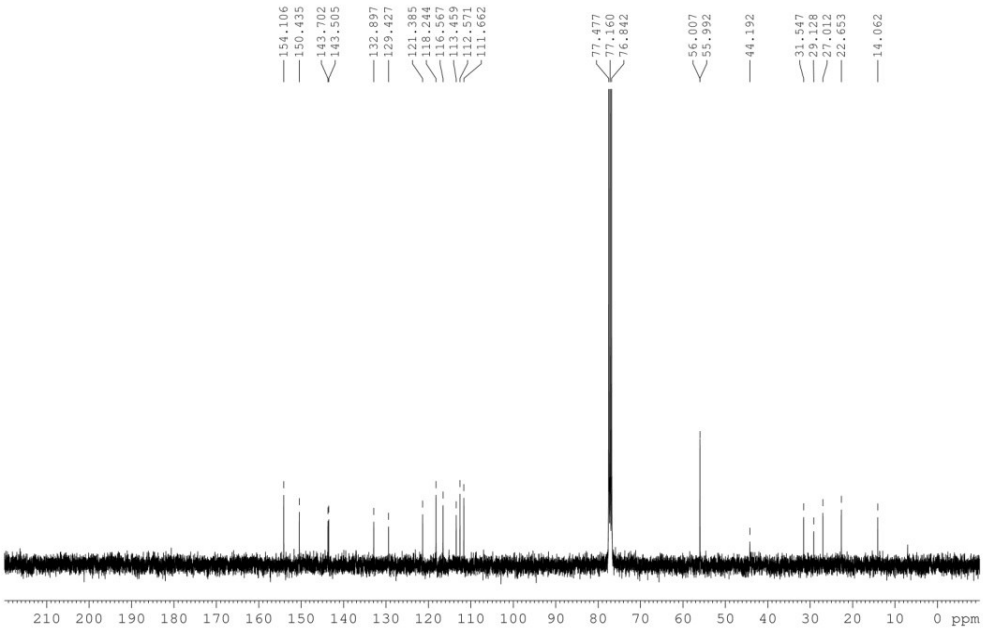
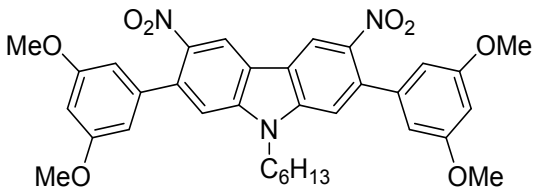


Figure 9.10: ^{13}C NMR spectrum of **12** in $CDCl_3$, 100 MHz.



13

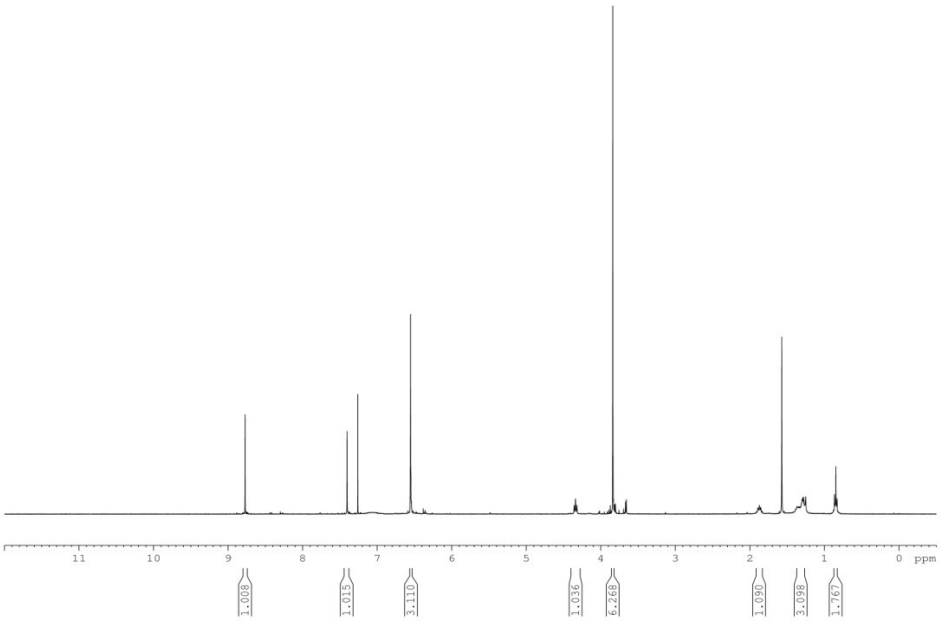


Figure 9.11: ^{1}H NMR spectrum of **13** in $CDCl_3$, 400 MHz

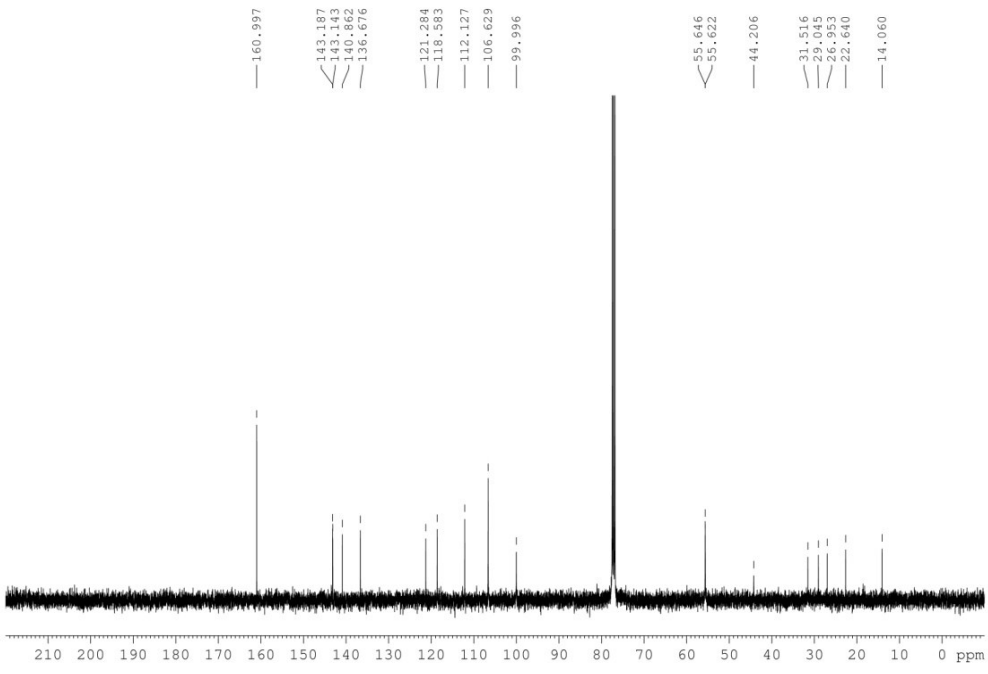
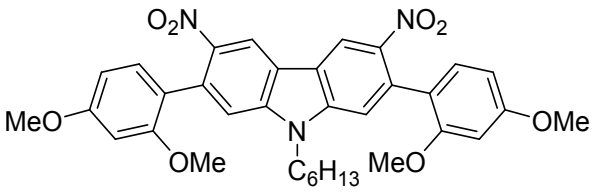


Figure 9.12: ^{1}H NMR spectrum of **13** in $CDCl_3$, 100 MHz.



14

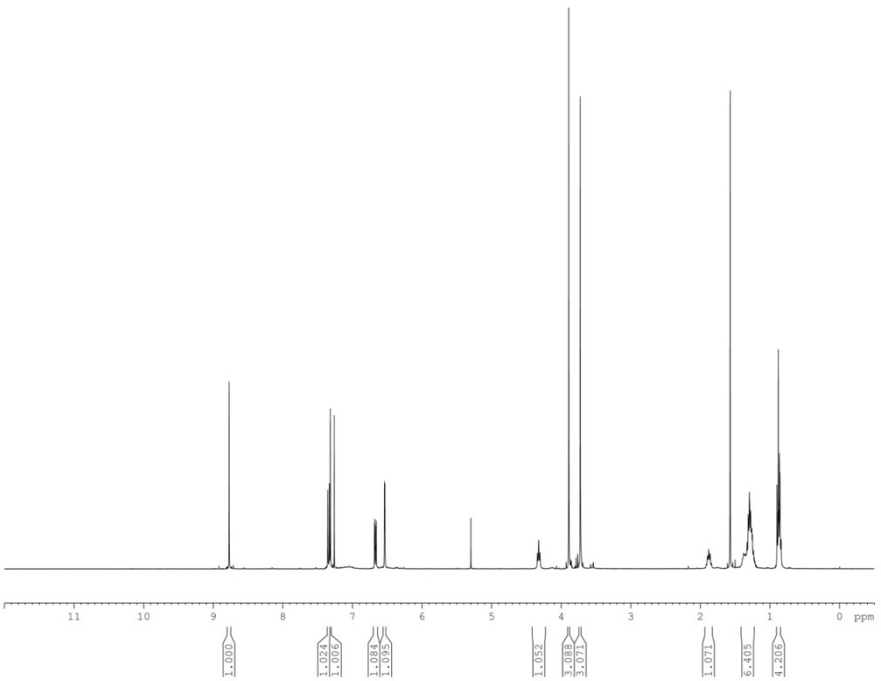


Figure 9.13: ^{1}H NMR spectrum of **14** in $CDCl_3$, 400 MHz.

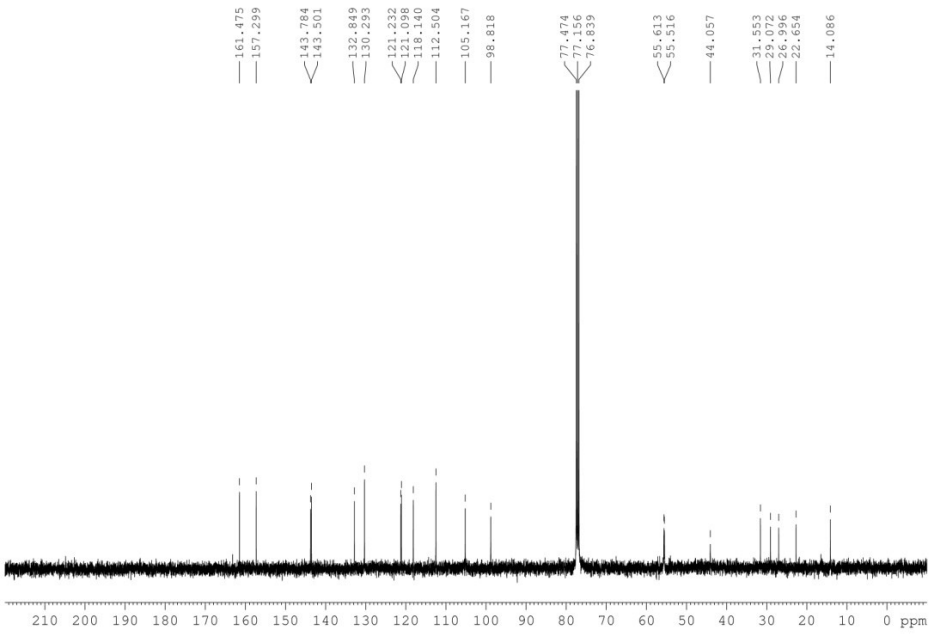
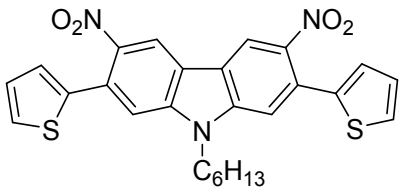


Figure 9.14: ^{13}C NMR spectrum of **14** in $CDCl_3$, 100 MHz.



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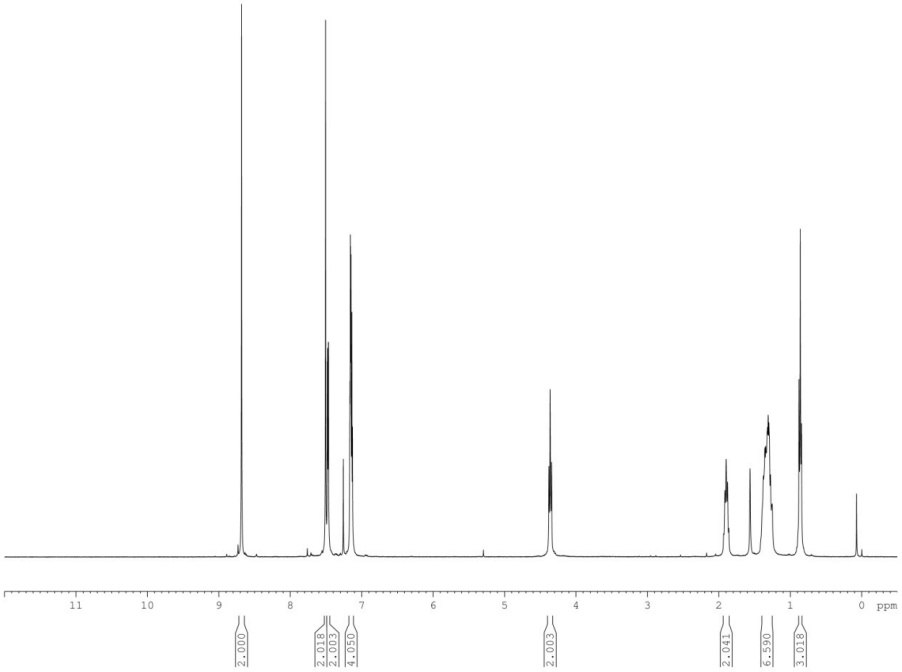


Figure 9.15: ^{1}H NMR spectrum of **15** in $CDCl_3$, 400 MHz.

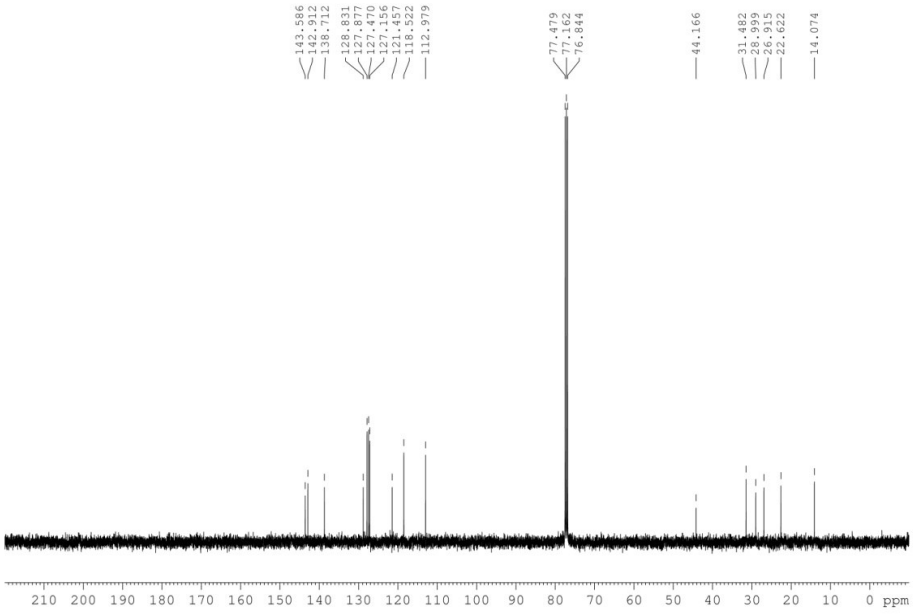
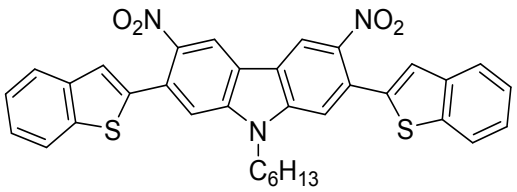


Figure 9.16: ^{13}C NMR spectrum of **15** in $CDCl_3$, 100 MHz.



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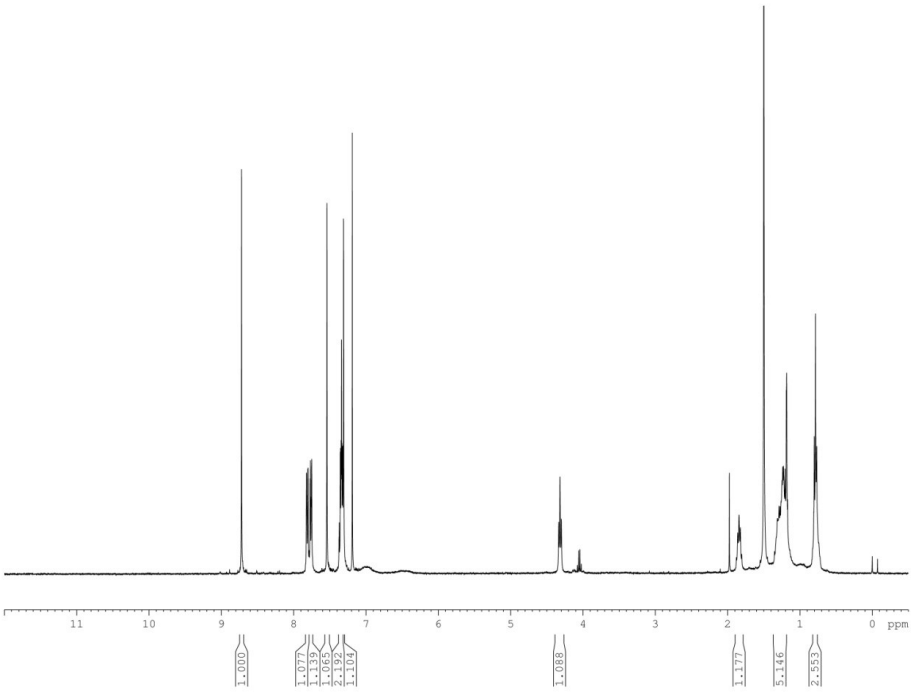


Figure 9.17: ^{1}H NMR spectrum of **16** in $CDCl_3$, 400 MHz.

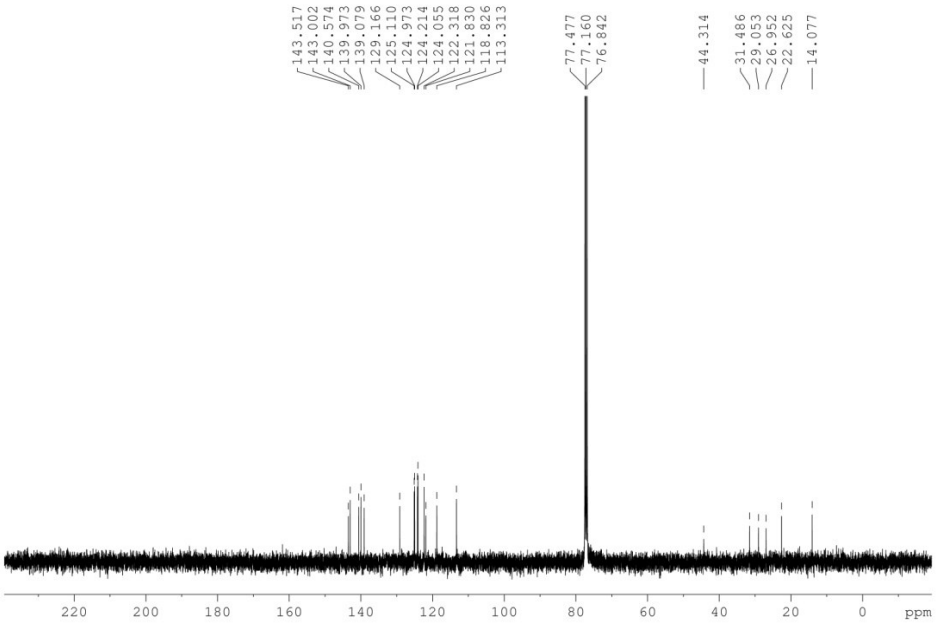
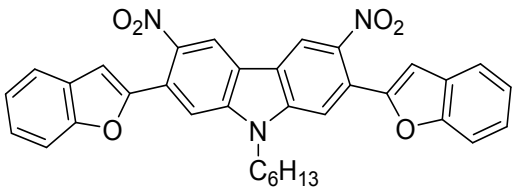


Figure 9.18: ^{13}C NMR spectrum of **16** in $CDCl_3$, 100 MHz.



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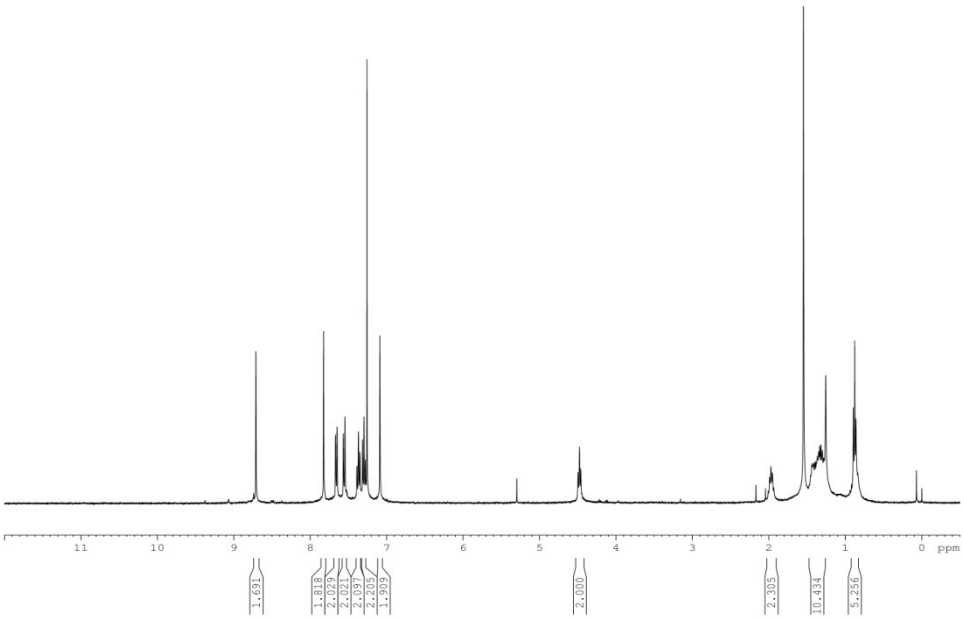


Figure 9.19: ^{1}H NMR spectrum of **17** in $CDCl_3$, 400 MHz.

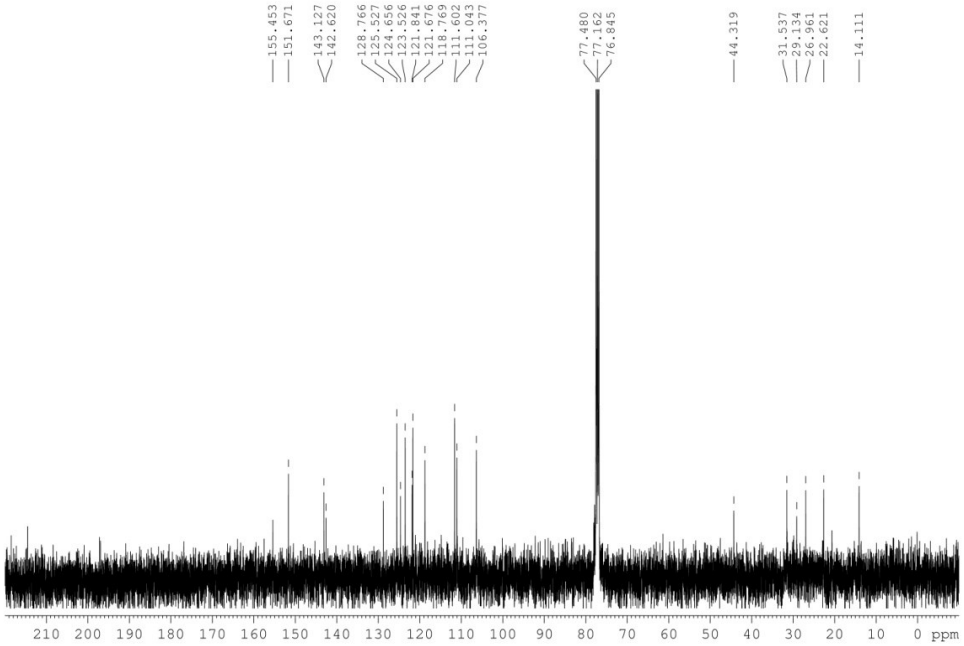
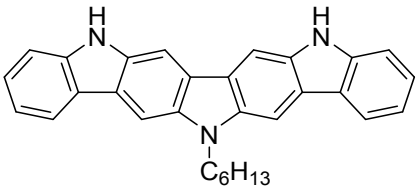


Figure 9.20: ^{13}C NMR spectrum of **17** in $CDCl_3$, 100 MHz.



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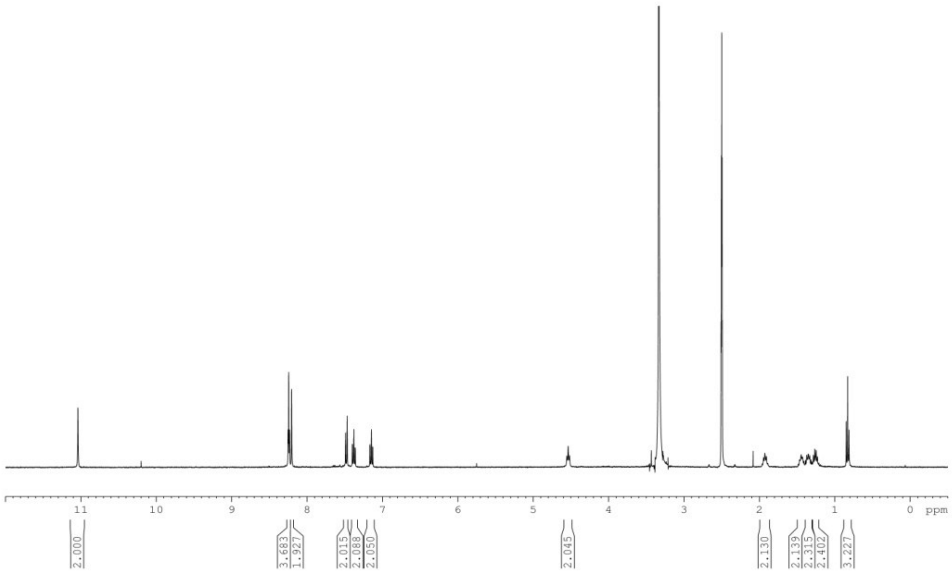


Figure 9.21: ^{1}H NMR spectrum of **18** in DMSO, 400 MHz.

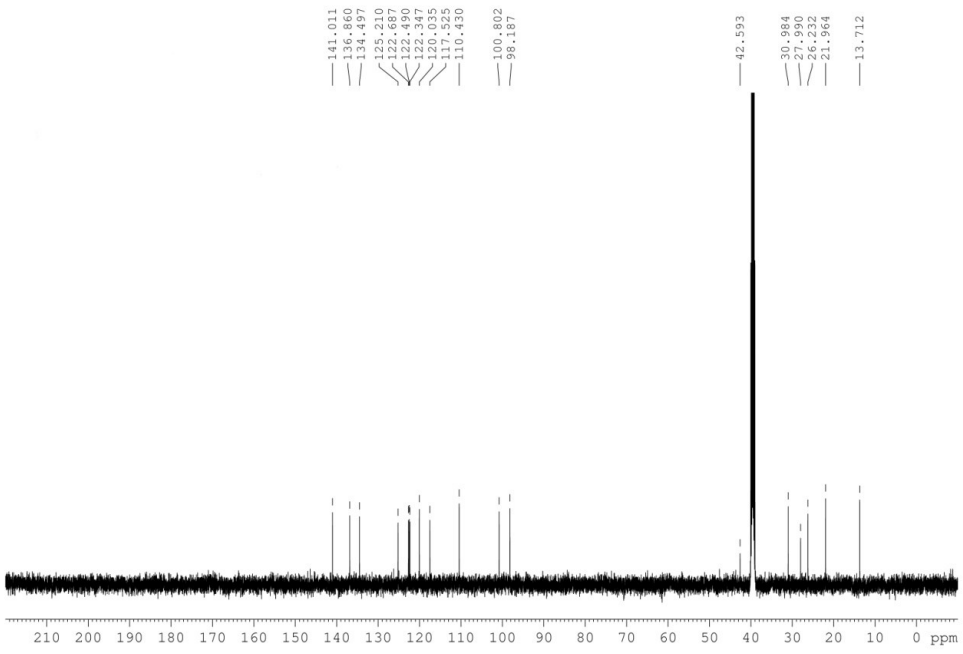
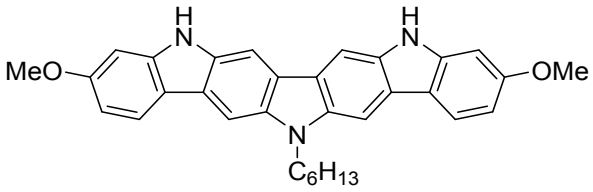


Figure 9.22: ^{13}C NMR spectrum of **18** in DMSO, 125 MHz.



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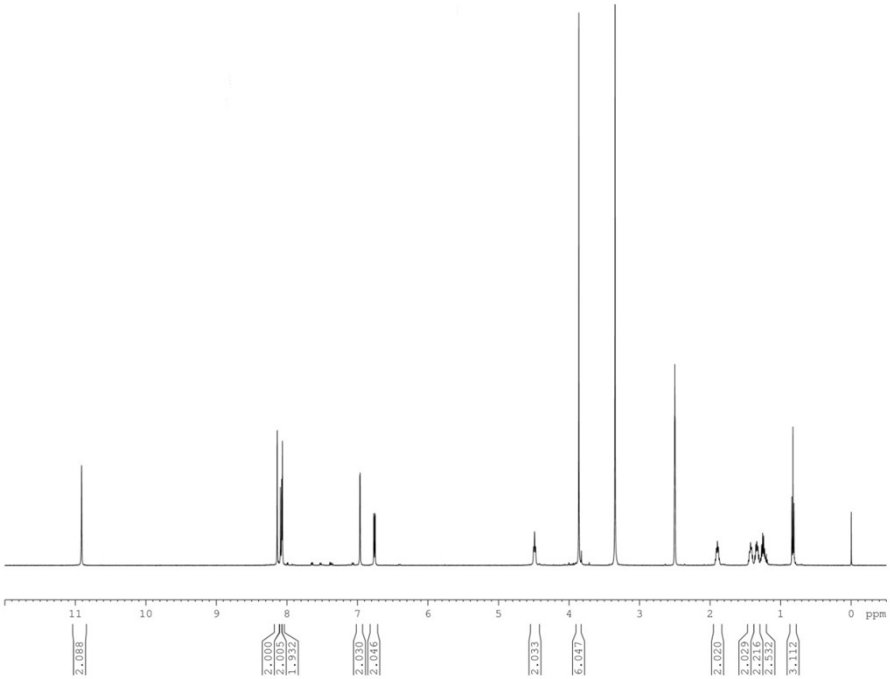


Figure 9.23: ^{1}H NMR spectrum of **19** in DMSO, 500 MHz.

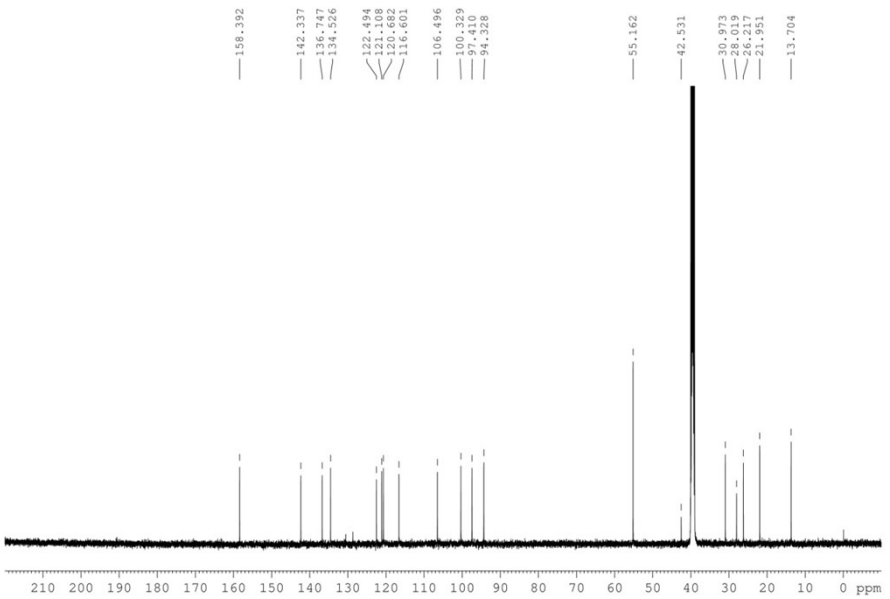
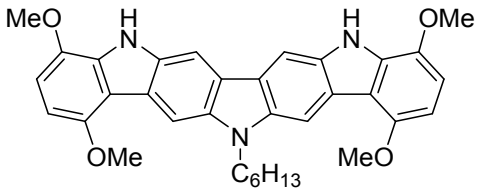


Figure 9.24: ^{13}C NMR spectrum of **19** in DMSO, 125 MHz.



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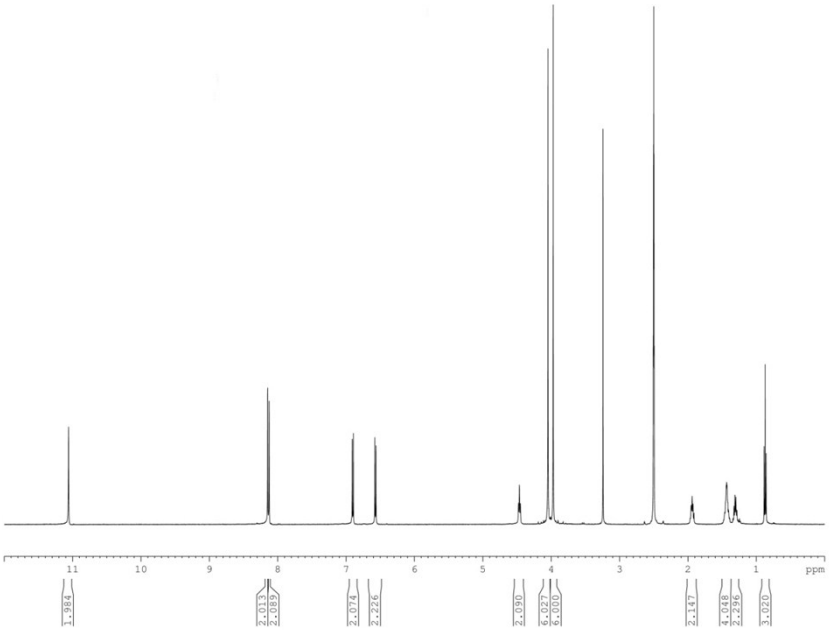


Figure 9.25: ^{1}H NMR spectrum of **20** in DMSO, 500 MHz.

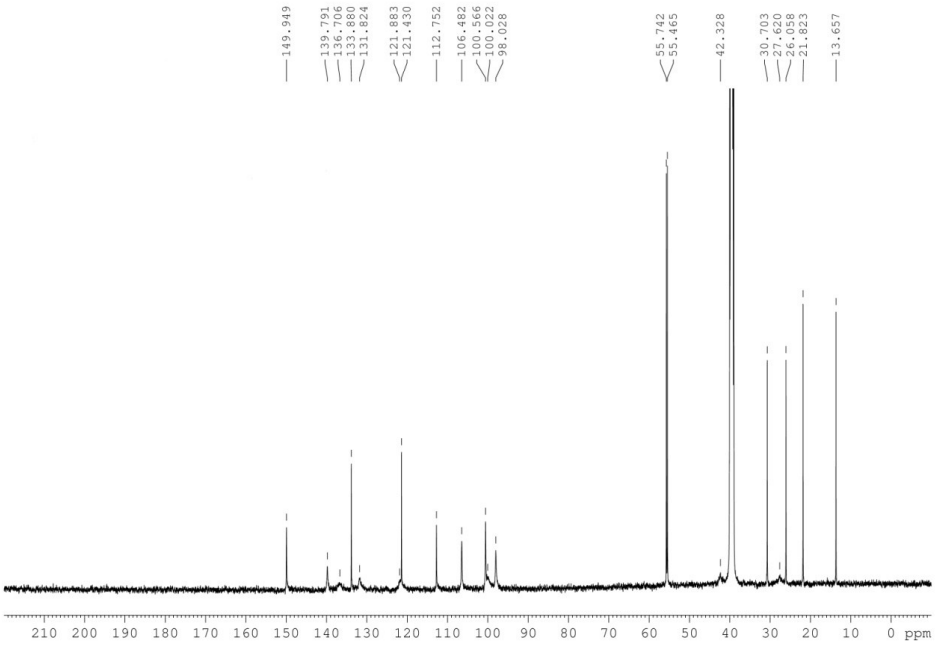
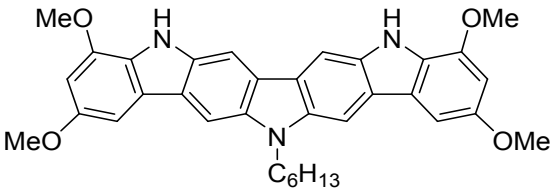


Figure 9.26: ^{13}C NMR spectrum of **20** in DMSO, 125 MHz.



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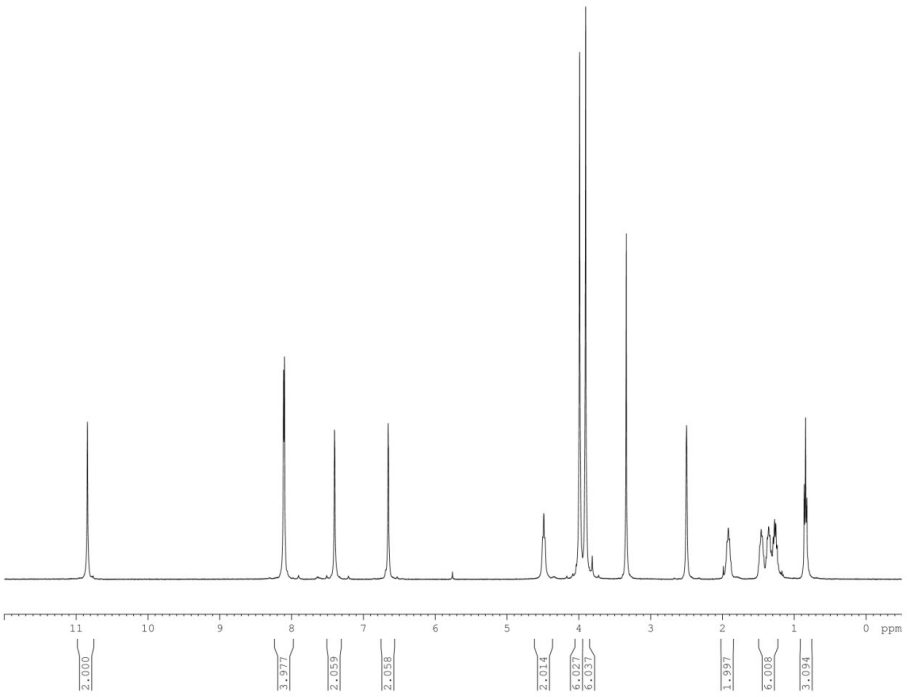


Figure 9.27: ^{1}H NMR spectrum of **21** in DMSO, 400 MHz.

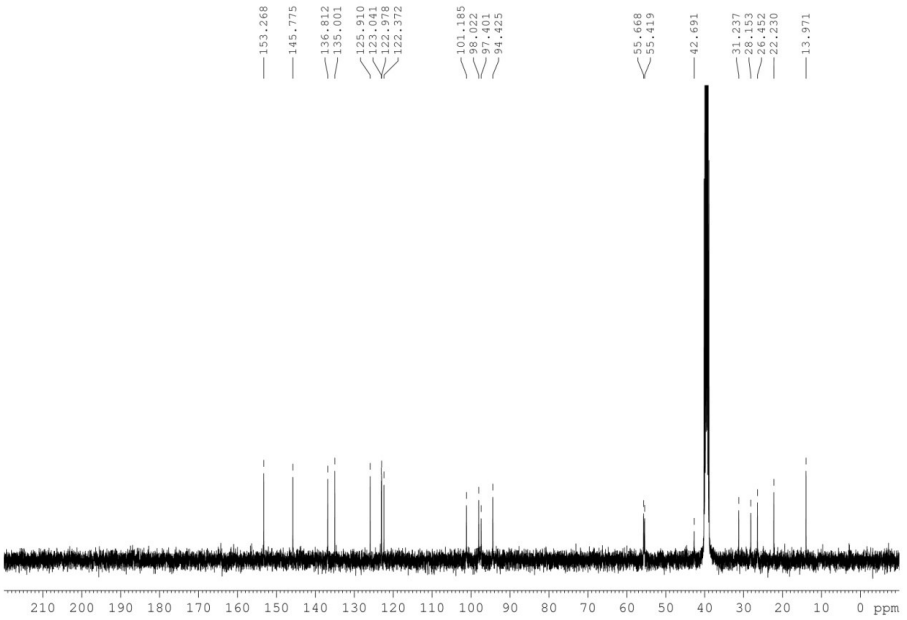
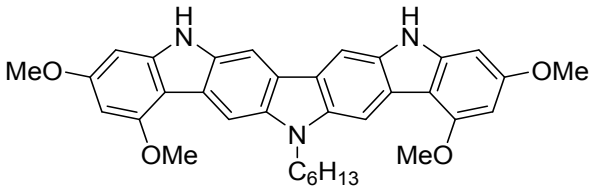


Figure 2.28: ^{13}C NMR spectrum of **21** in DMSO, 100 MHz.



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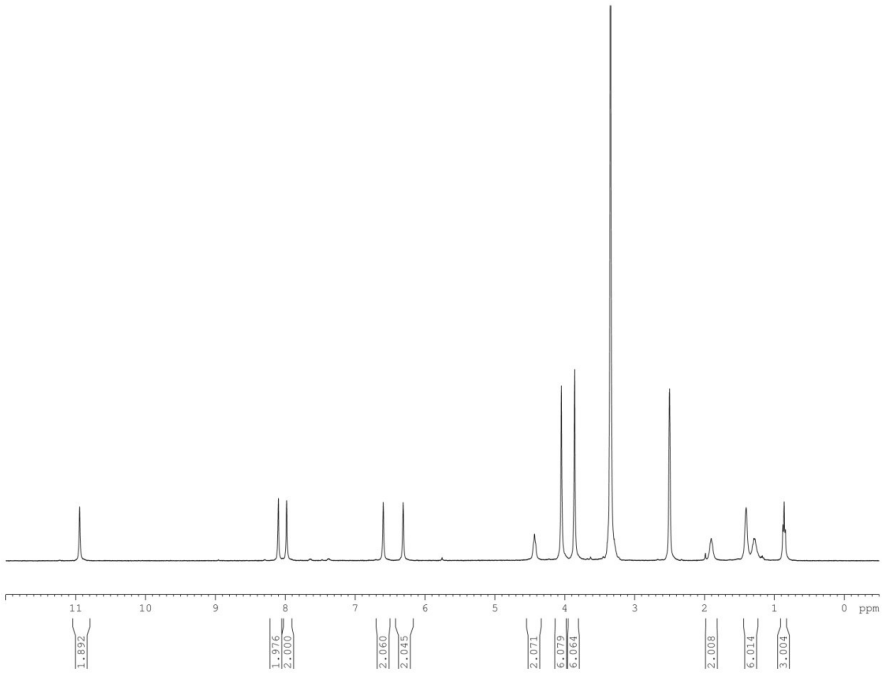


Figure 9.29: ^{1}H NMR spectrum of **22** in DMSO, 400 MHz.

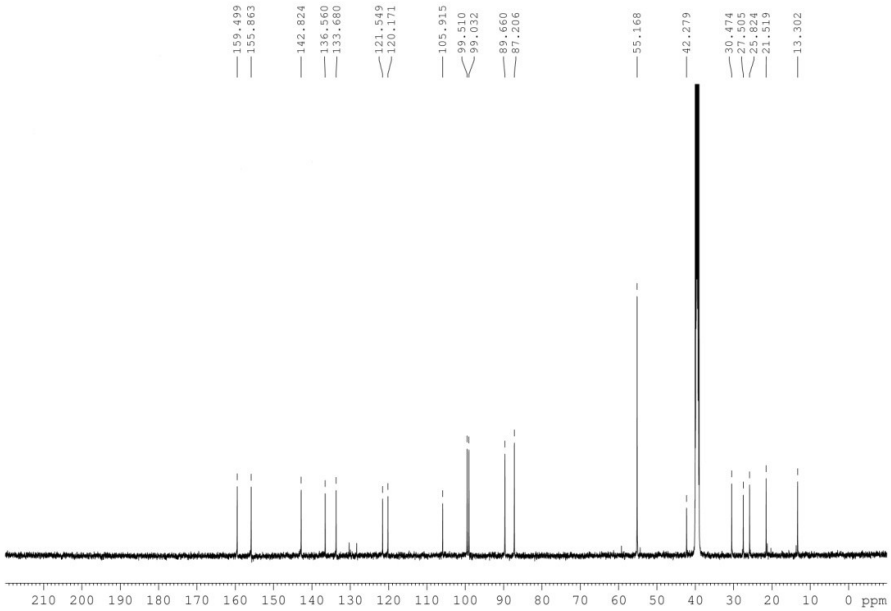
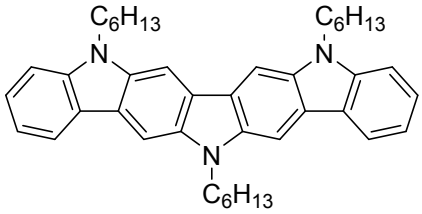


Figure 9.30: ^{13}C NMR spectrum of **22** in DMSO, 125 MHz.



26

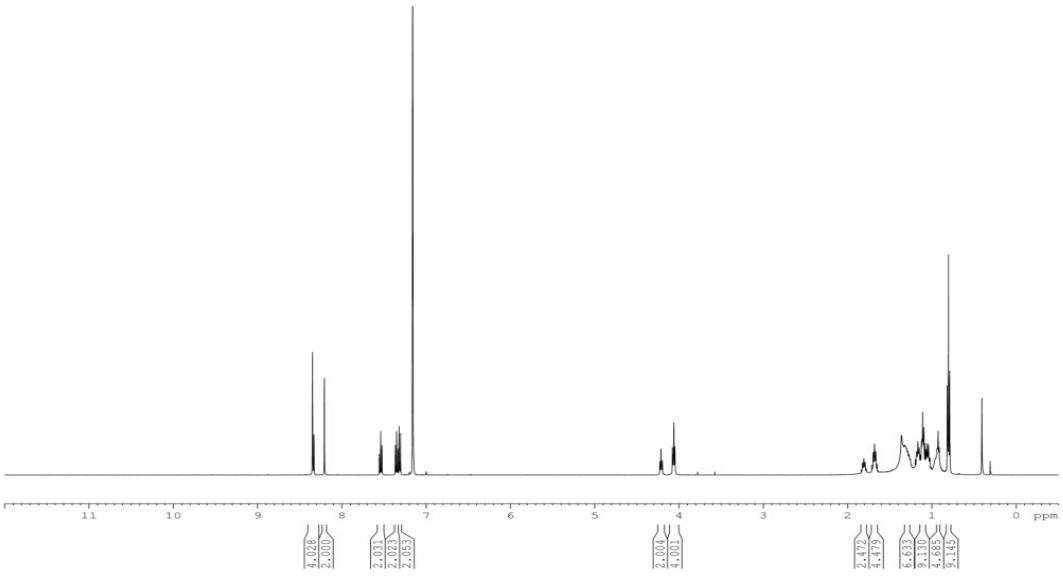


Figure 9.31: ^{1}H NMR spectrum of **26** in C_6D_6, 500 MHz.

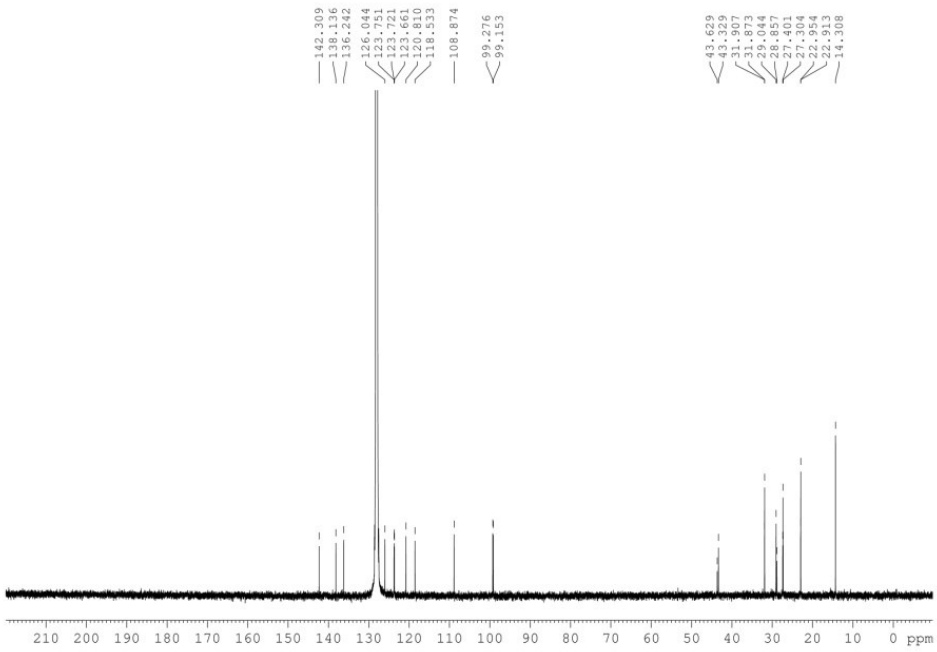
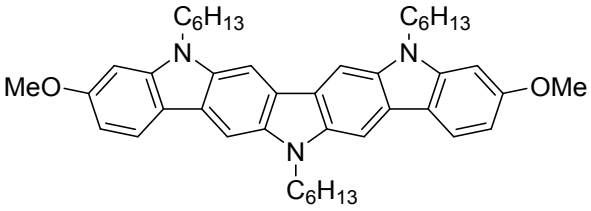


Figure 9.32: ^{13}C NMR spectrum of **26** in C_6D_6, 125 MHz.



27

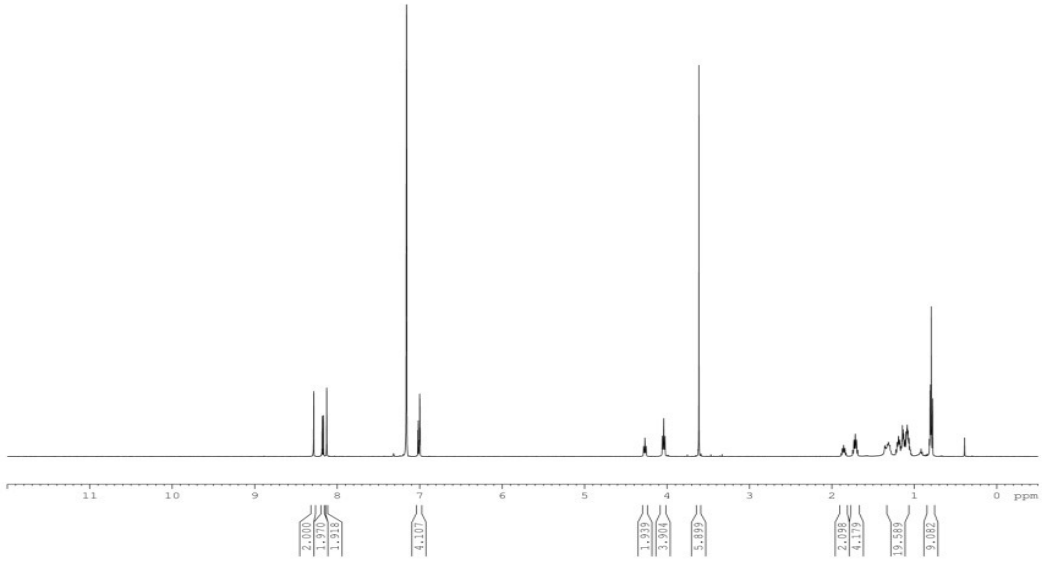


Figure 9.33: ^{1}H NMR spectrum of **27** in C_6D_6, 500 MHz.

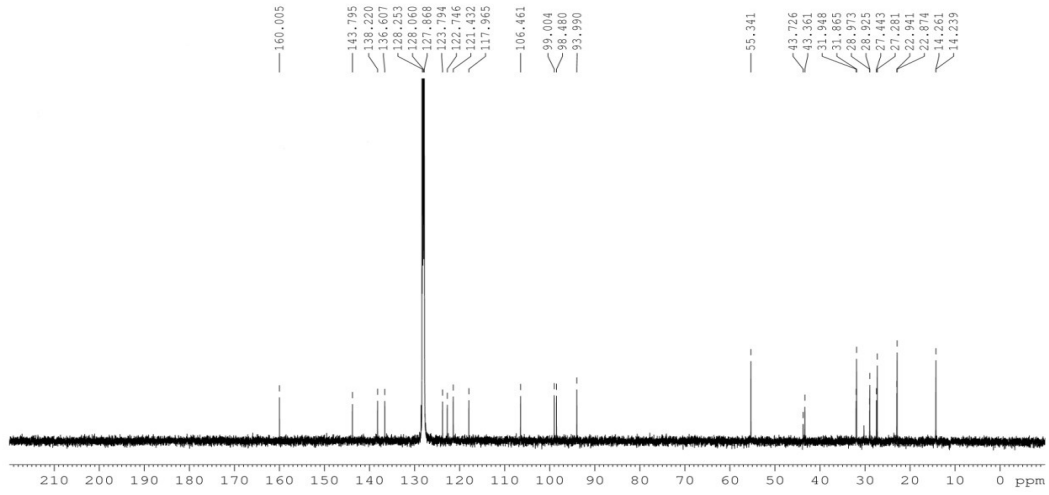
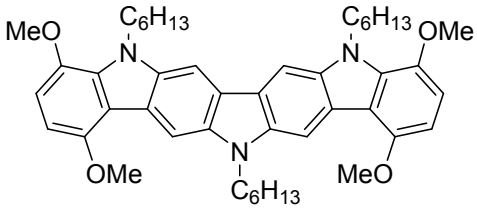


Figure 9.34: ^{13}C NMR spectrum of **27** in C_6D_6, 125 MHz.



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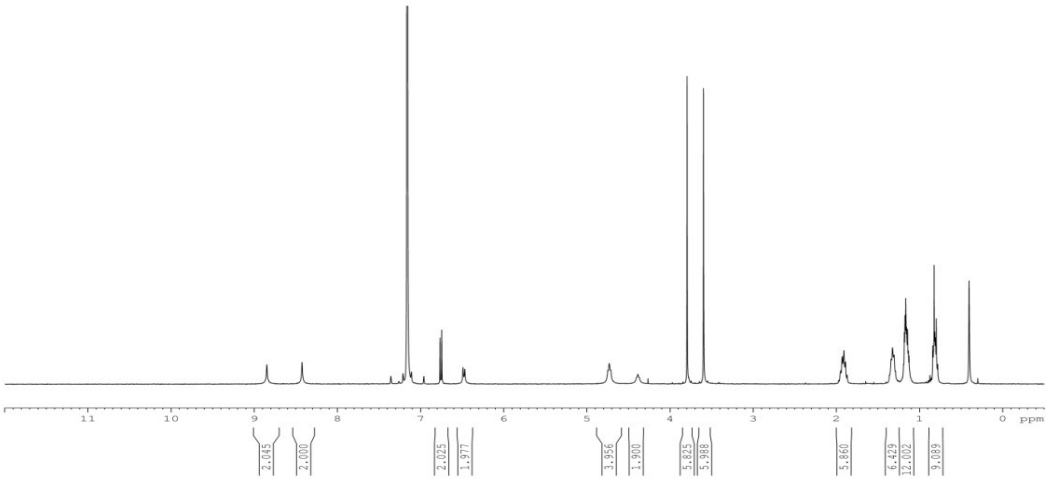


Figure 9.35: ^{1}H NMR spectrum of **28** in C_6D_6, 400 MHz.

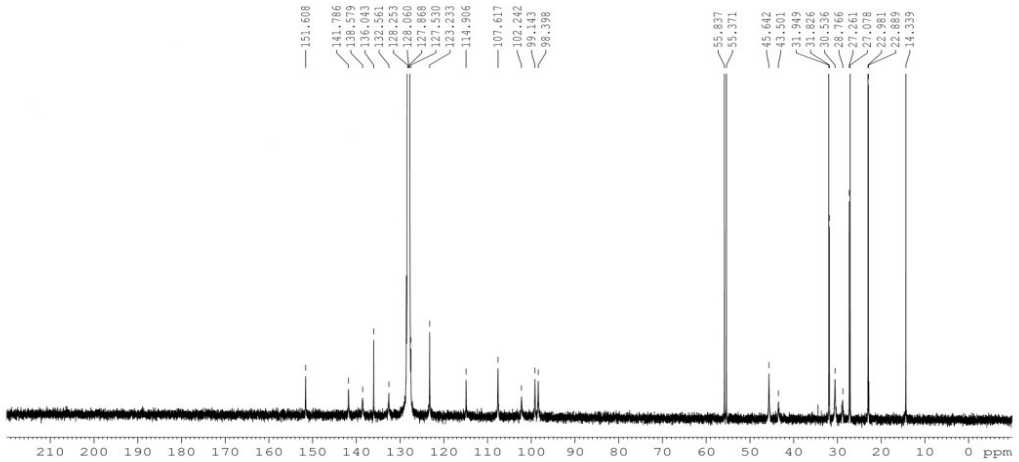
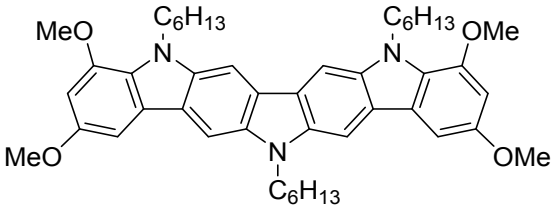


Figure 9.36: ^{13}C NMR spectrum of **28** in C_6D_6, 125 MHz.



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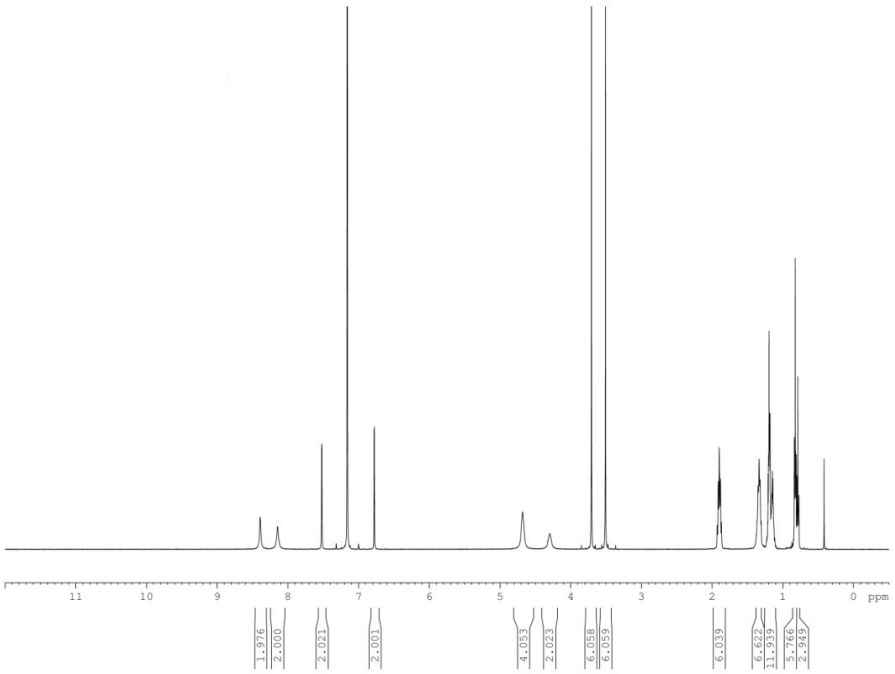


Figure 9.37: ^{1}H NMR spectrum of **29** in C_6D_6, 500 MHz.

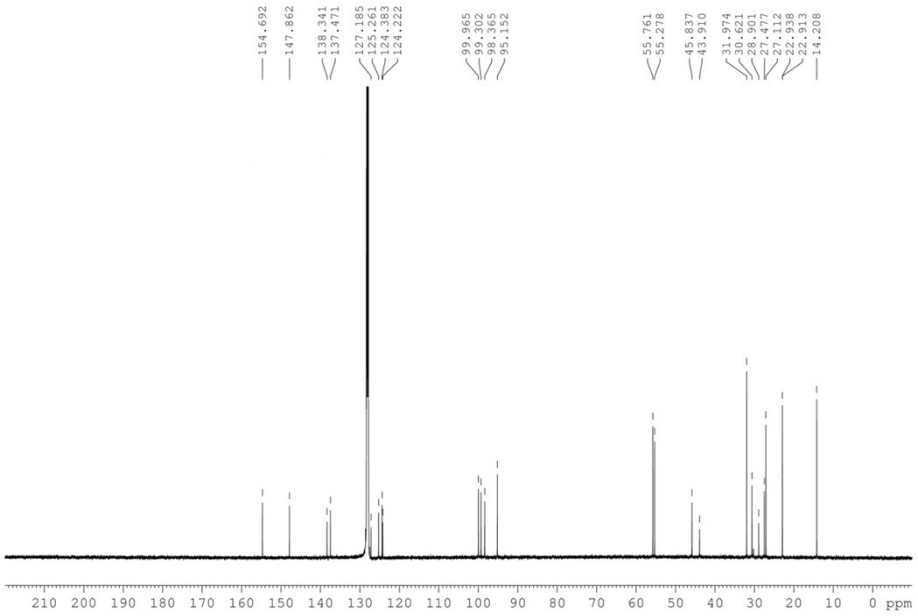
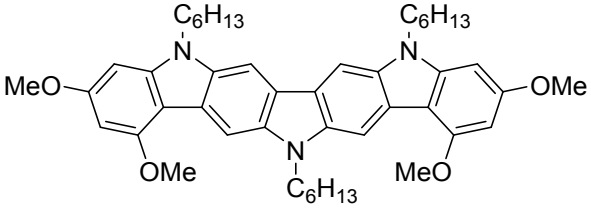


Figure 9.38: ^{13}C NMR spectrum of **29** in C_6D_6, 125 MHz.



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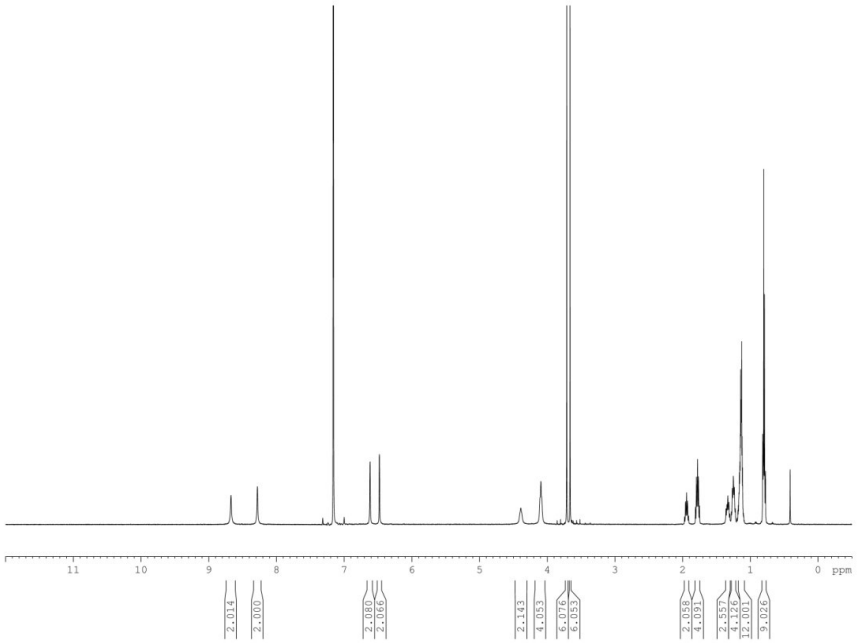

Figure 9.39: ^{1}H NMR spectrum of **30** in C_6D_6, 500 MHz.

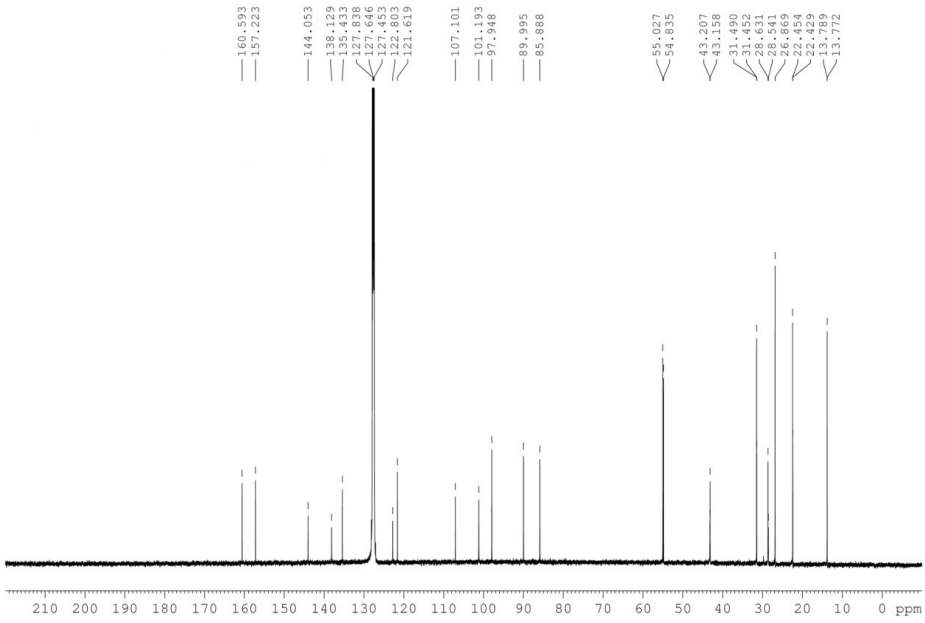

Figure 9.40: ^{13}C NMR spectrum of **30** in C_6D_6, 125 MHz.

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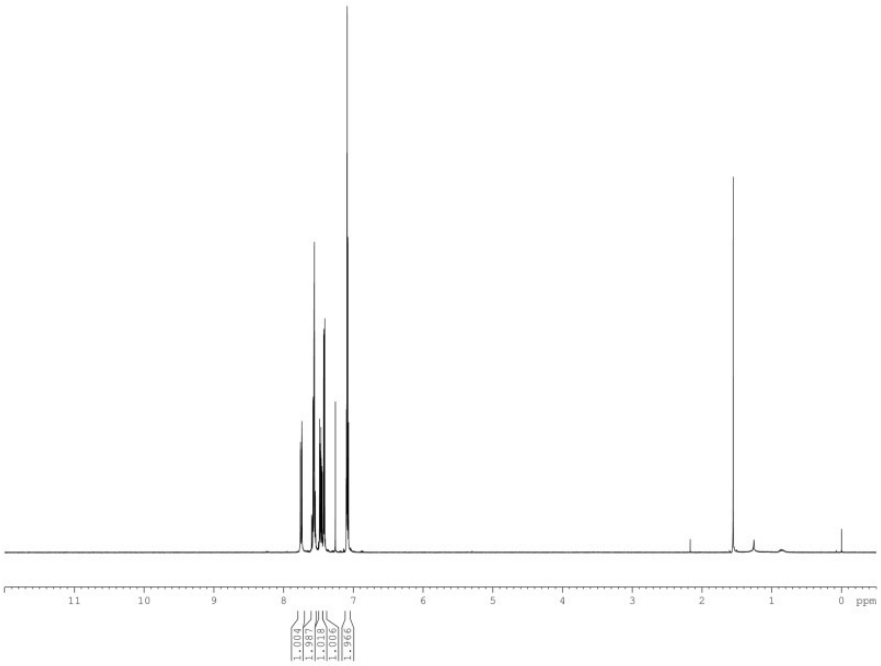


Figure 9.41: ^{1}H NMR spectrum of **34** in $CDCl_3$, 400 MHz.

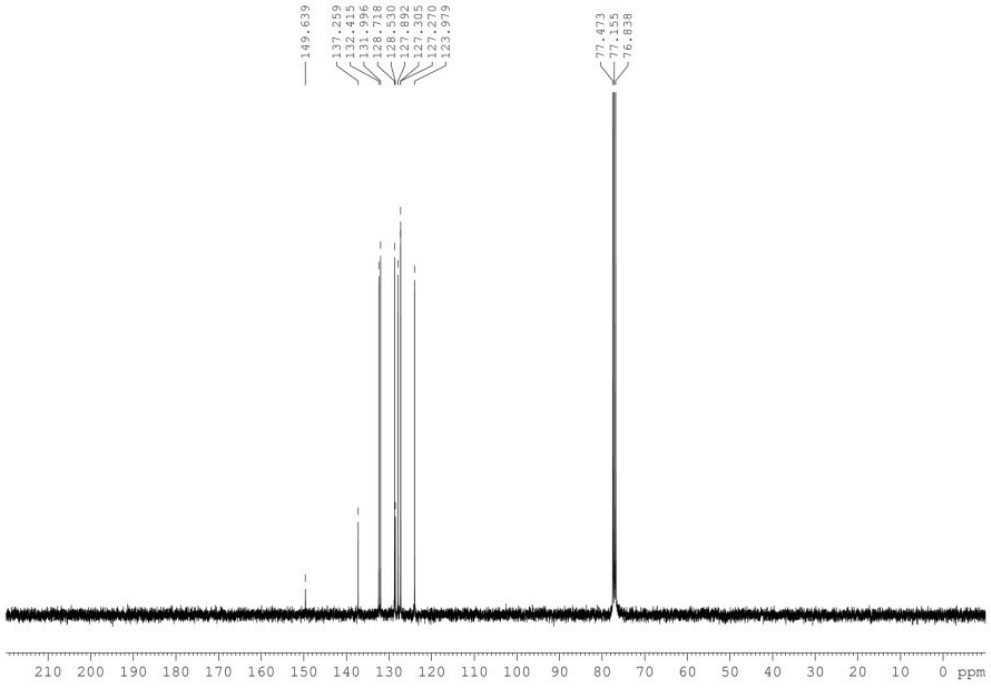
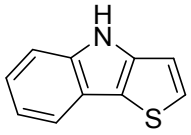


Figure 9.42: ^{13}C NMR spectrum of **34** in $CDCl_3$, 100 MHz.



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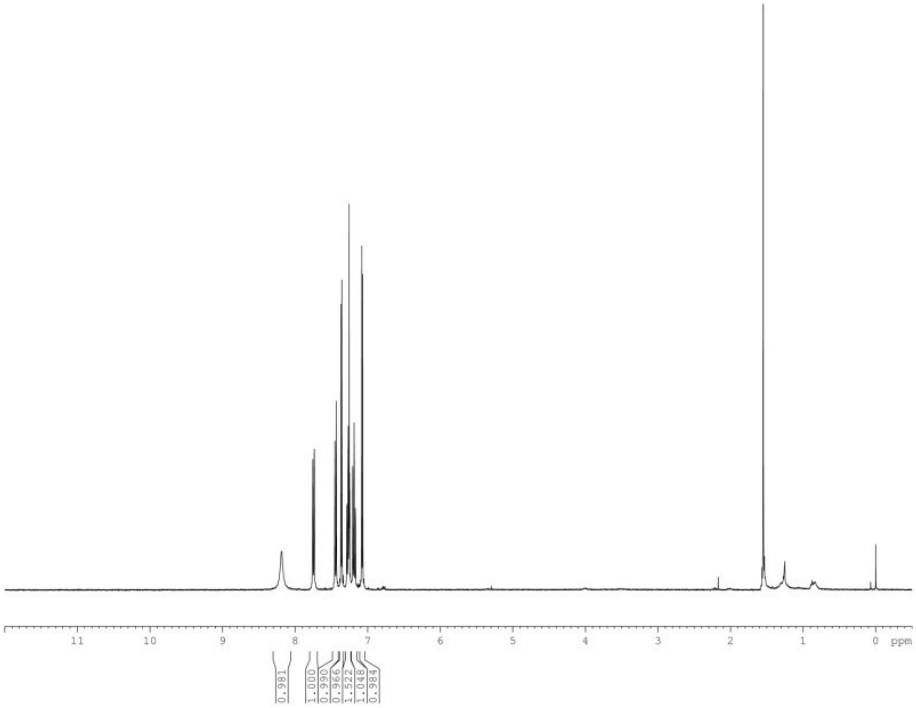


Figure 9.43: ^{1}H NMR spectrum of **37** in $CDCl_3$, 400 MHz.

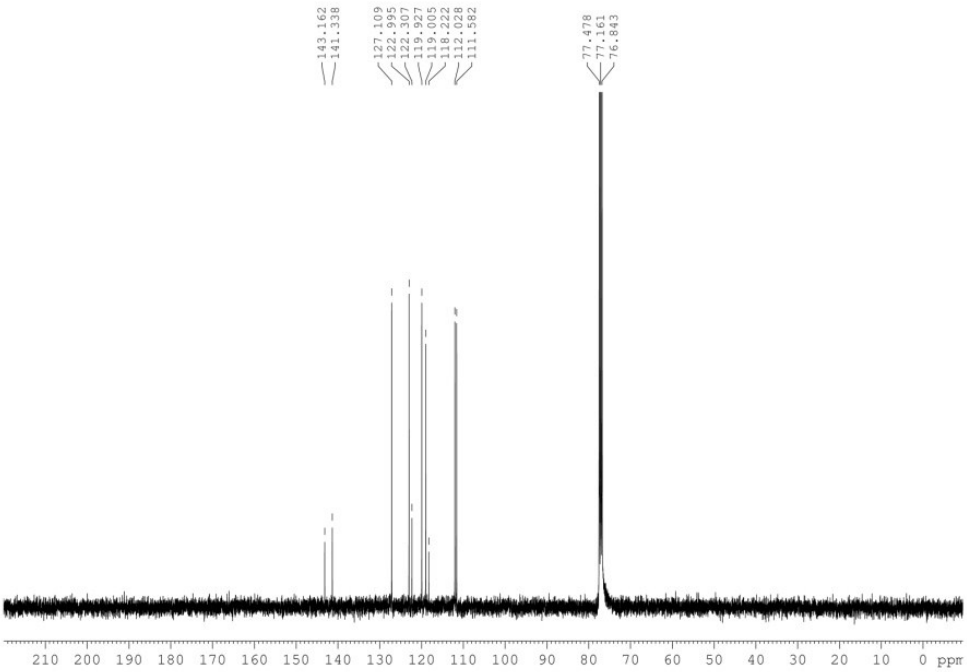
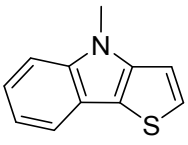


Figure 9.44: ^{13}C NMR spectrum of **37** in $CDCl_3$, 100 MHz.



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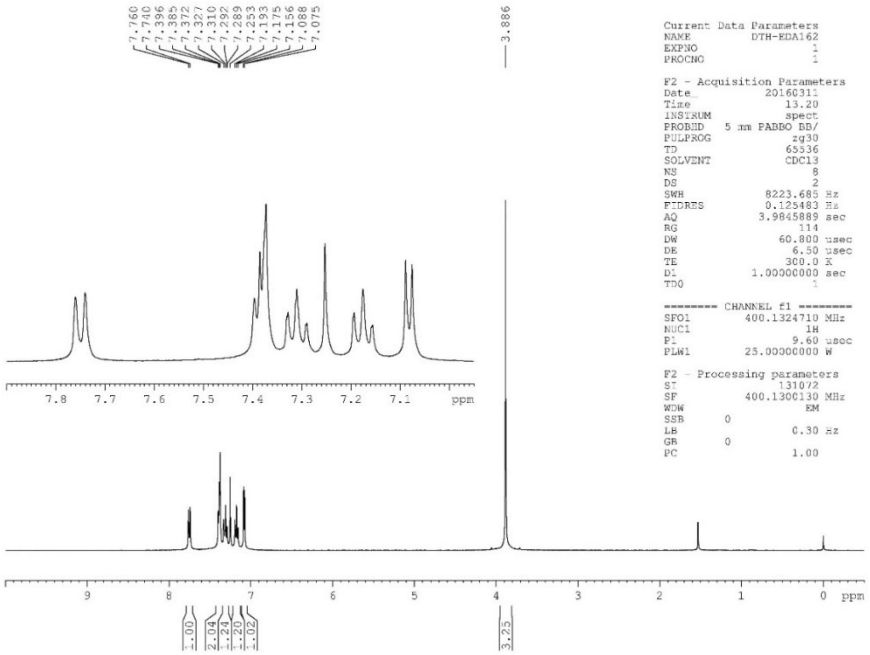


Figure 9.45: ^{1}H NMR spectrum of **40** in $CDCl_3$, 400 MHz.

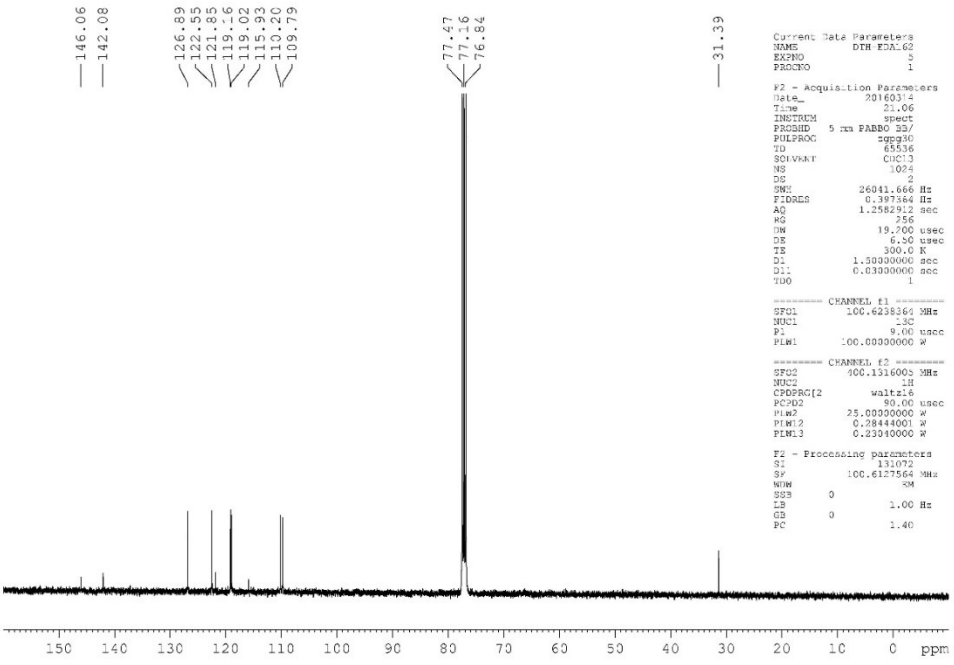
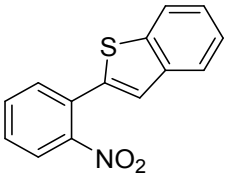


Figure 9.46: ^{13}C NMR spectrum of **40** in $CDCl_3$, 125 MHz.



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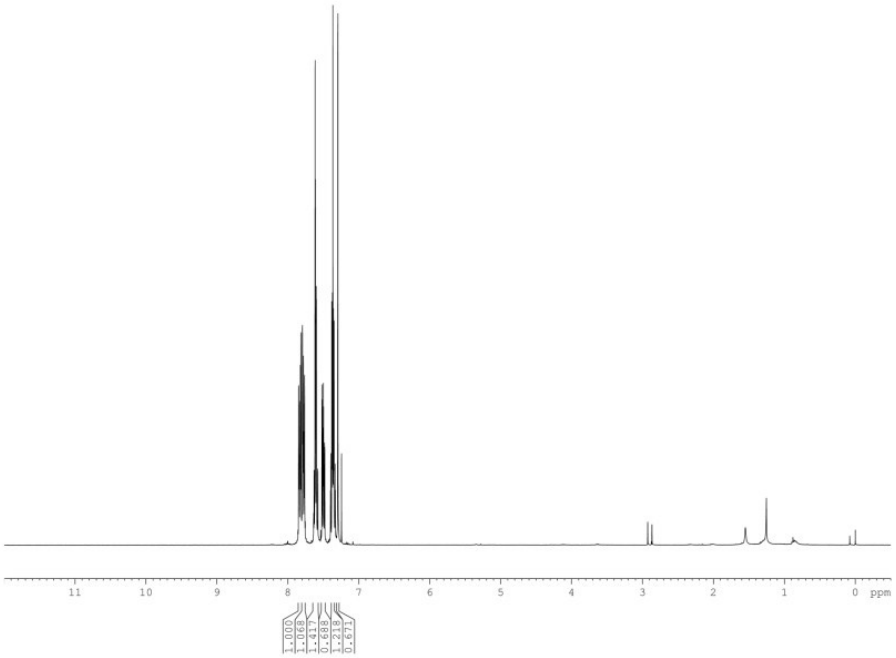


Figure 9.47: ^{1}H NMR spectrum of **35** in $CDCl_3$, 400 MHz.

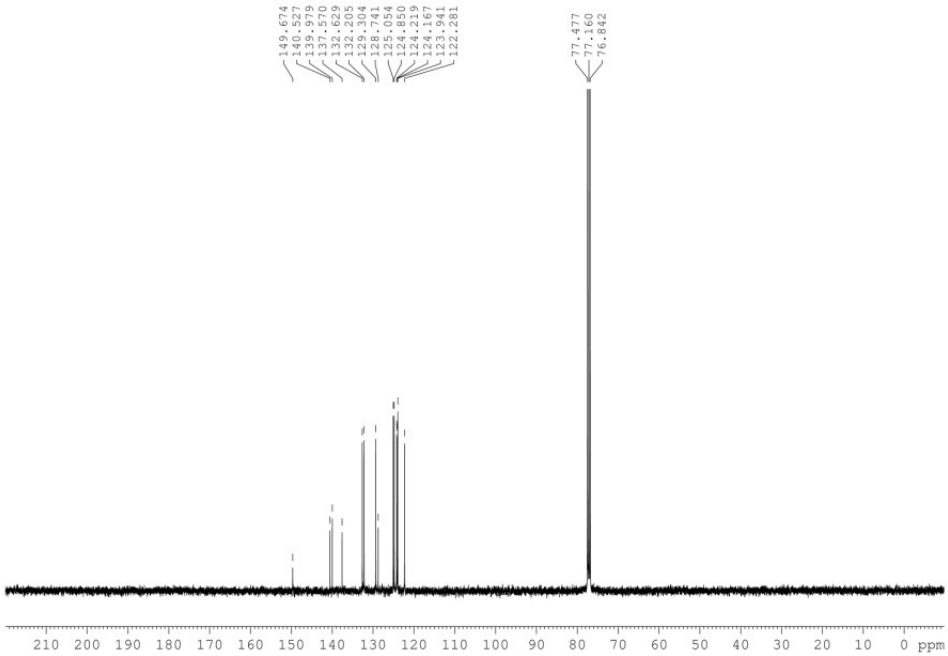
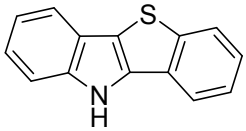


Figure 9.48: ^{13}C NMR spectrum of **35** in $CDCl_3$, 100 MHz.



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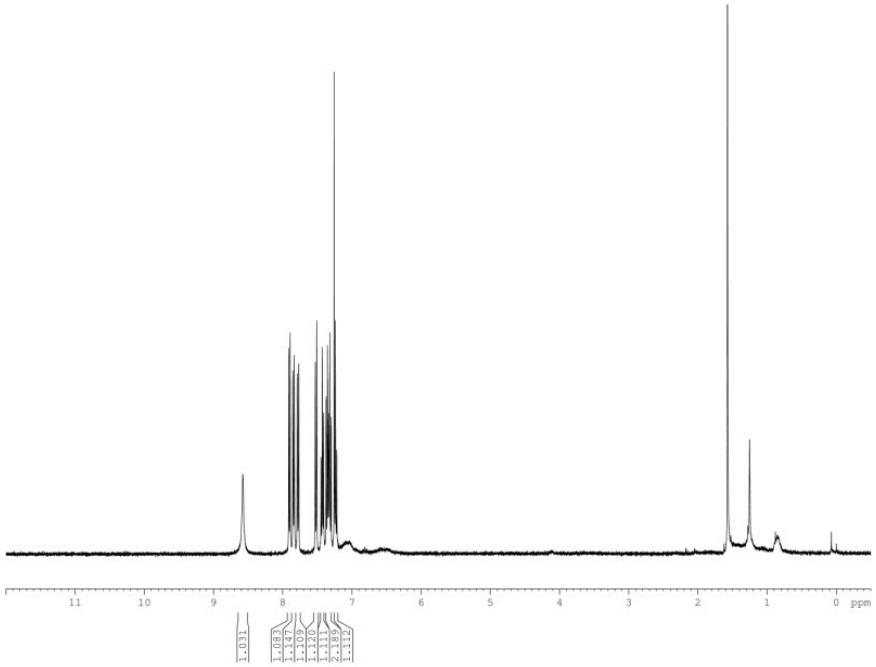


Figure 9.49: ^{1}H NMR spectrum of **38** in $CDCl_3$, 400 MHz.

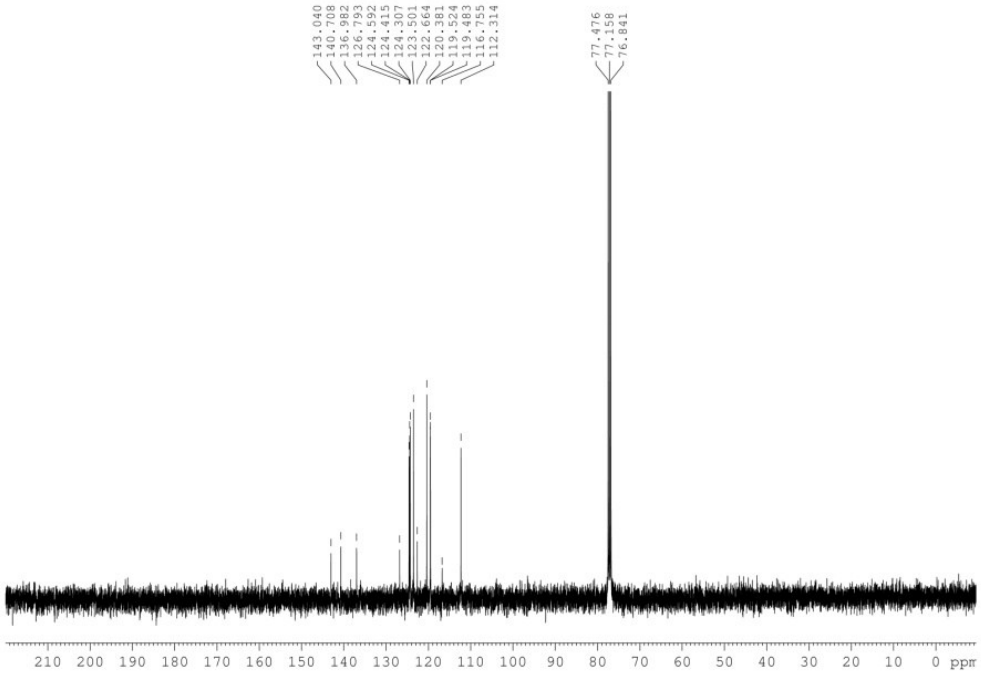
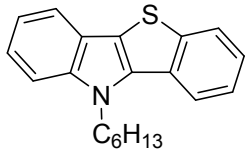


Figure 9.50: ^{13}C NMR spectrum of **38** in $CDCl_3$, 100 MHz.



41

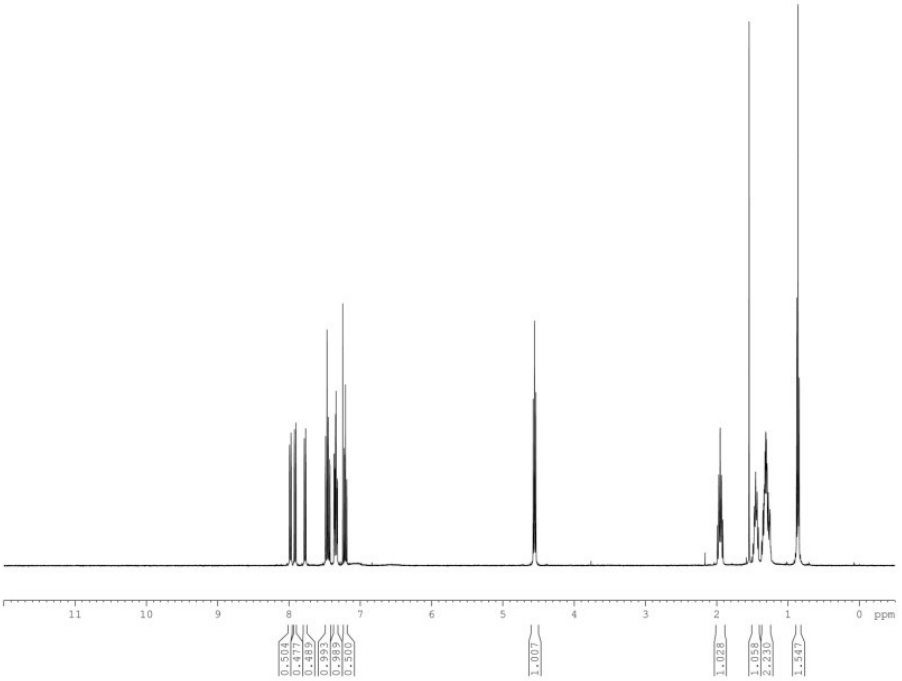


Figure 9.51: ^{1}H NMR spectrum of **41** in $CDCl_3$, 400 MHz.

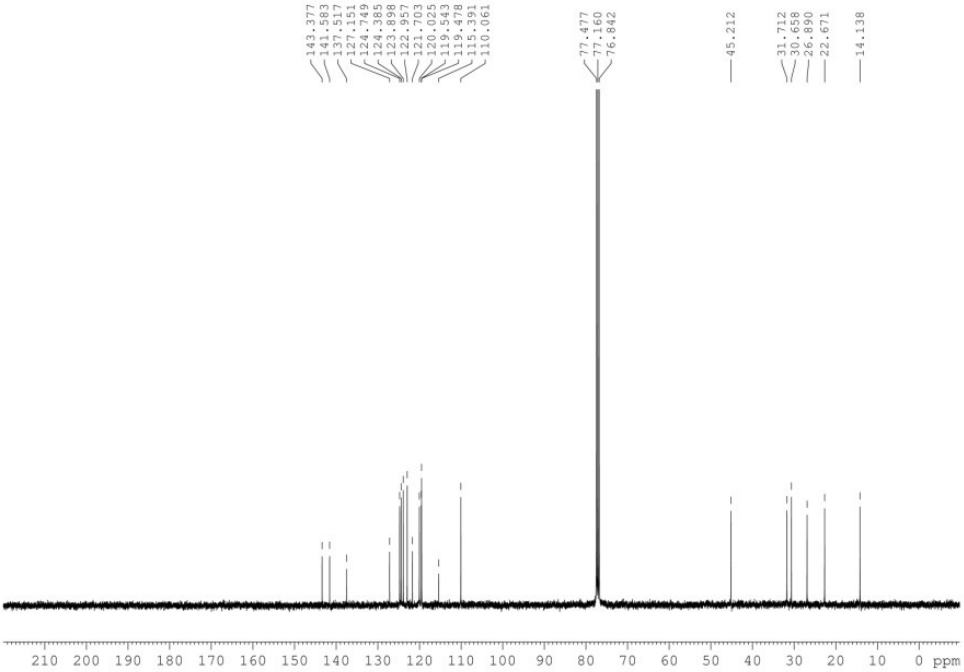
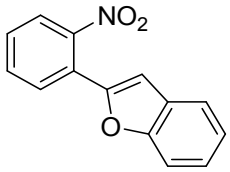


Figure 9.52: ^{13}C NMR spectrum of **41** in $CDCl_3$, 100 MHz.



36

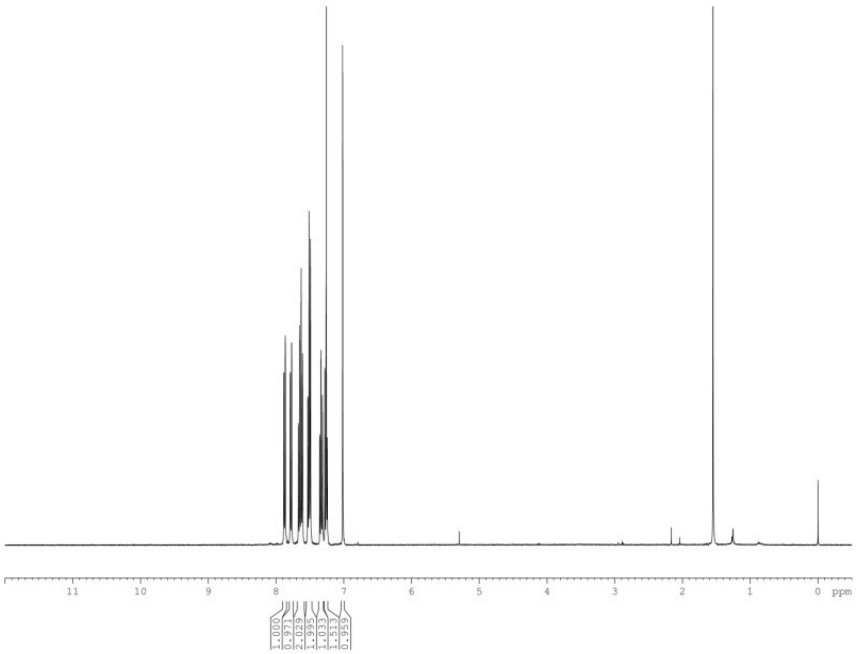


Figure 9.53: ^{1}H NMR spectrum of **36** in $CDCl_3$, 400 MHz.

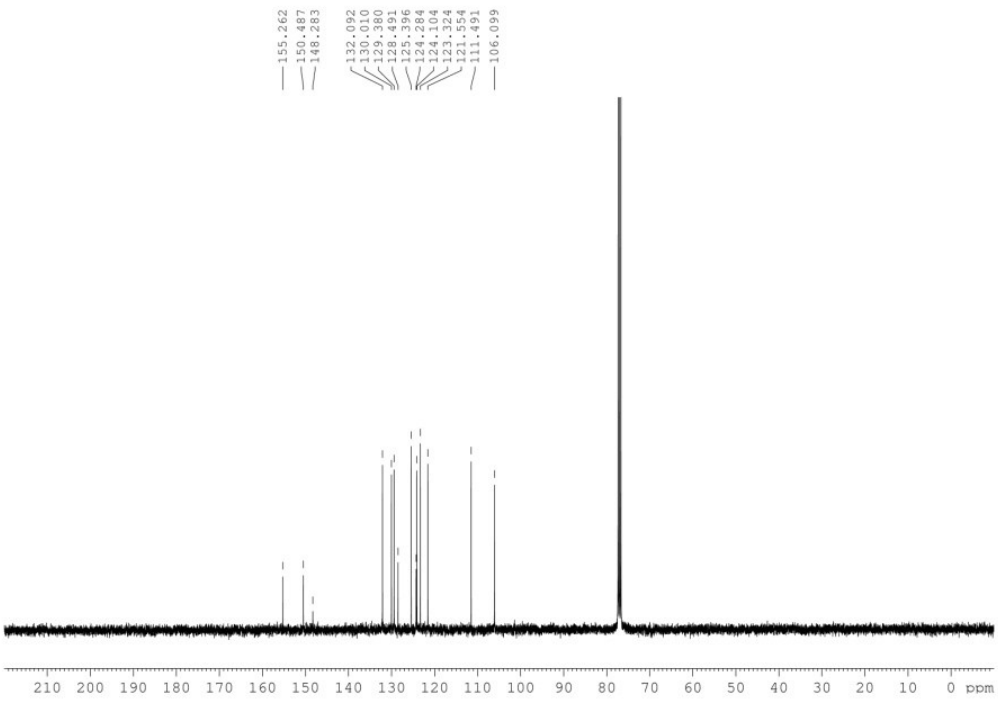
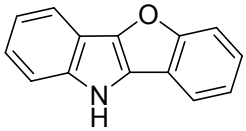


Figure 9.54: ^{13}C NMR spectrum of **36** in $CDCl_3$, 100 MHz.



39

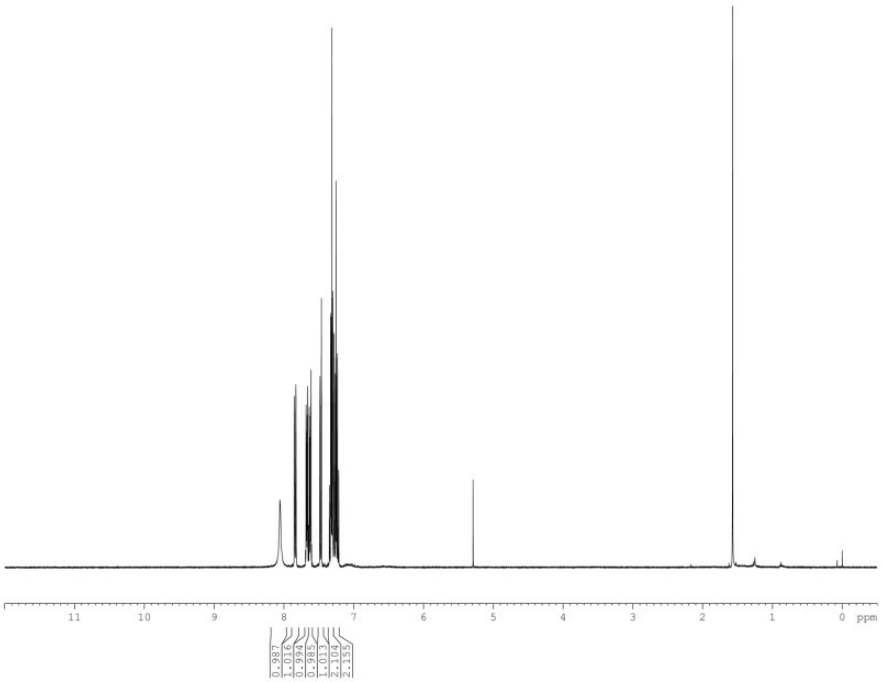


Figure 9.55: ^{1}H NMR spectrum of **39** in $CDCl_3$, 400 MHz.

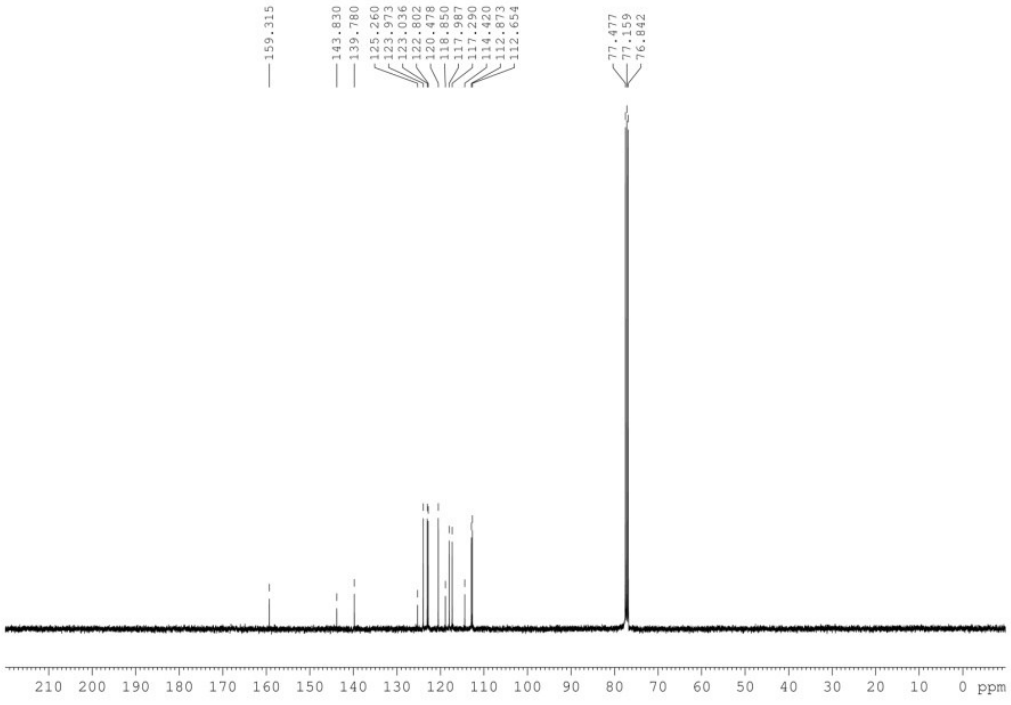
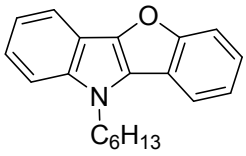


Figure 9.56: ^{13}C NMR spectrum of **39** in $CDCl_3$, 100 MHz.



42

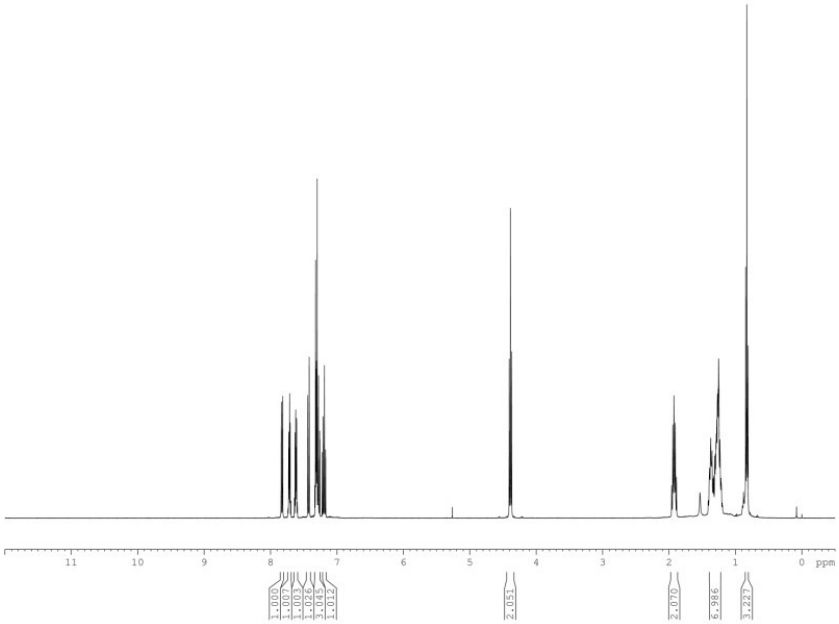


Figure 9.57: ^{1}H NMR spectrum of **42** in $CDCl_3$, 400 MHz.

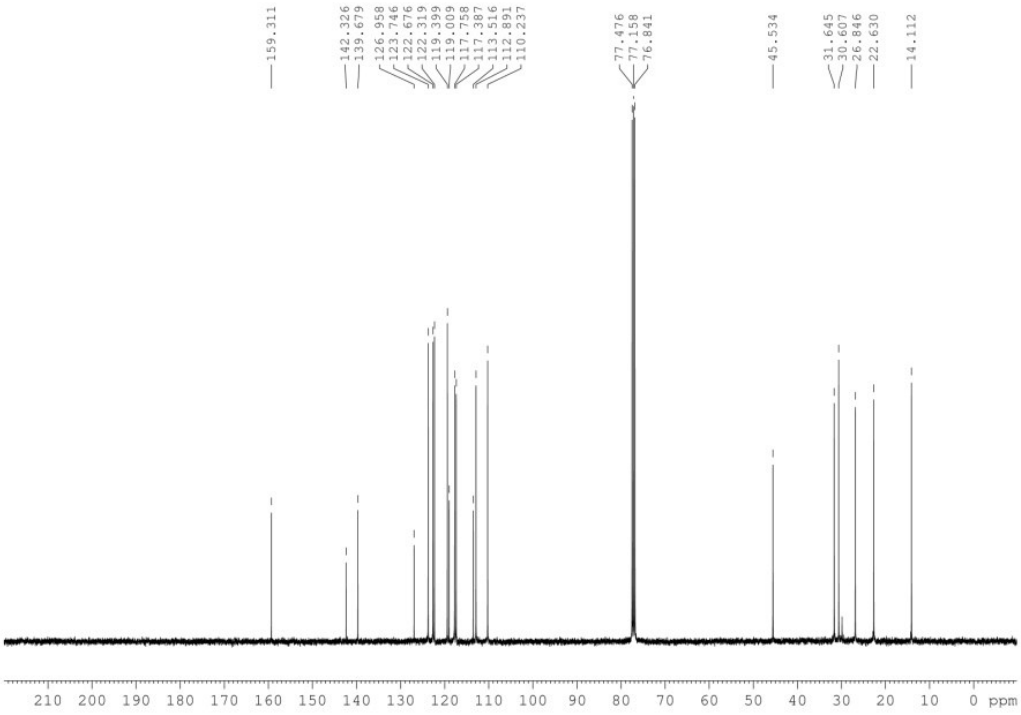


Figure 9.58: ^{13}C NMR spectrum of **42** in $CDCl_3$, 100 MHz.