Supporting information

π-Conjugated indole dyads with strong blue emission made possible by Stille cross-coupling and double Fisher indole cyclisation

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Content

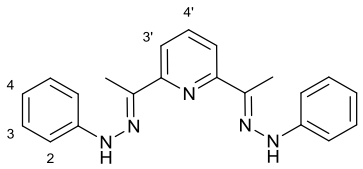
General Information

All reagents were obtained from Sigma Aldrich, Alfa Aesar, VWR and Across and used without further purification. All the reactions were carried out under a nitrogen atmosphere and were stirred with a magnetic stirrer unless otherwise stated. Anhydrous solvents were obtained from a PureSolv MD6 solvent purification system. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 300, a Bruker AV3-400 or a Bruker Advanced 500 spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual solvent peak, and peaks are described as singlet (s), doublet (d), triplet (t),quartet (q), quintet (qui), sextet (sex), multiplet (m), broad singlet (br), and coupling constants (J) are quoted in Hertz (Hz). Spectra were recorded in deuterated chloroform, deuterated dichloromethane or deuterated dimethyl sulfoxide and were measured at room temperature unless otherwise stated. Where needed, two dimensional correlation spectroscopy (2D-COSY), heteronuclear single quantum coherence spectroscopy (HSQC) and heteronuclear multiple bond correlation spectroscopy (HMBC) were used in order to aid assignment. The progress of reactions was monitored by TLC and by ultraviolet light and purified by column chromatography employing silica gel 60 (40-63µm). High resolution mass spectrometry was performed on Bruker MaXis Impact (EI+) by positive and negative electrospray ionisation. The accepted experimental error is <4 ppm.

High performance liquid chromatography (HPLC) was performed on an Agilent 1100 Infinity Series equipped with a UV detector and Ascentis Express C_{18} reverse phase column using MeCN/water (50-95%) containing 0.1% TFA, at a flow rate of 0.5 mL min^{-1} over a period of 12 minutes. Infrared spectra (IR) were recorded in solid phase on a Bruker Alpha Platinum ATR FTIR spectrometer with vibrational frequencies given in cm^{-1}. Melting points were measured on a Stuart SMP30. The electronic absorption spectra were recorded on a Cary 100 UV-Vis scanning spectrophotometer. The fluorescence spectra were recorded on a FluoroMax-3 spectrofluorimeter. Quantum yields of fluorescence were measured by the relative method using optically dilute solutions.

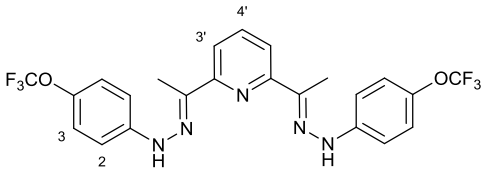
Experimental Procedures

2,6-Diactetylpyridine-bis(phenylhydrazone) (1)[1]



A solution of 2,6-diacetylpyridine (915 mg, 5.6 mmol) and phenylhydrazine (1.10 mL, 11.2 mmol) in dry EtOH (10 mL) was refluxed for 45 min. The reaction mixture was cooled to room temperature. The resulting white powder was collected by suction filtration, washed with cold ethanol and dried under vacuum to yield compound **1** as a pale yellow-white solid (1.66 g, 86%). **^{1}H NMR** (500 MHz, DMSO) δ ppm 9.49 (s, 2H, NH), 8.01 (d, *J* = 7.9 Hz, 2H, 3'-H), 7.76 (t, *J* = 7.9 Hz, 1H, 4'-H), 7.33 (dd, *J* = 7.9, 1.2 Hz, 4H, 2-H), 7.26 (t, *J* = 7.9 Hz, 4H, 3-H), 6.81 (tt, *J* = 7.9, 1.2 Hz, 2H, 4-H), 2.45 (s, 6H, CH_3). **^{13}C NMR** (125 MHz, DMSO) δ ppm 154.9, 145.6, 141.5, 136.2, 128.9, 119.3, 117.4, 113.0, 11.0; **m/z (ES+):** Found: 366.1692 [M+Na], requires: 366.1689; **IR ν_{max}/cm^{-1} (solid):** 3341, 3012, 2927, 1600, 1561, 1245, 1162, 1139, 746, 693; **M.pt:** 218-220.5 °C.

2,6-Diactetylpyridine-bis(4-trifluoromethoxyphenylhydrazone) (2)

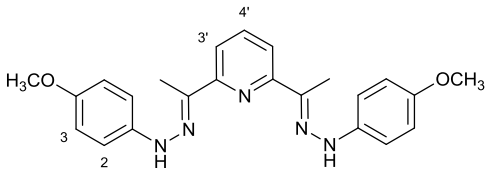


The same procedure as described for compound **1** using 4-trifluoromethoxyphenylhydrazine hydrochloride (2.29 g, 10.0 mmol) and 2,6-diacetylpyridine (816 mg, 5.0 mmol). Compound **3** was isolated by gravity filtration as a bright orange solid (2.40 g, 93%). **^{1}H NMR** (500 MHz, MeOD) δ ppm 8.49 (t, *J* = 8.1 Hz, 1H, 4'-H), 8.01 (d, *J* = 8.1 Hz, 2H, 3'-H), 7.60 – 7.27 (m, 4H, 3-H), 7.06 (d, *J* = 9.0 Hz,

[1] J. D. Curry, M. A. Robinson, D. H. Busch, Inorg. Chem., 1967, 8, 1570-1574.

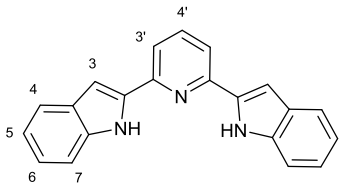
4H, 2-H), 2.44 (s, 6H, CH_3); **^{13}C NMR** (125 MHz, MeOD) δ ppm 149.1, 148.4, 145.2, 144.1, 132.6, 123.5, 122.0 (q, J_{F-C} = 254.9 Hz),121.8, 116.6, 11.5; **m/z (ES+):** Found: 534.1333 [M+Na], requires: 534.1335; **IR ν_{max}/cm^{-1} (solid):** 3150, 3073, 2955, 2906, 1540, 1504, 1439, 1248, 1193, 1159, 1142, 844; **M.pt:** 271.3-272.8 °C.

2,6-Diactetylpyridine-bis(4-methoxyphenylhydrazone) (3)



The same procedure as described for compound **1** using 4-methoxyphenylhydrazine hydrochloride (664 mg, 3.8 mmol) and 2,6-diacetylpyridine (310 mg, 1.9 mmol). Compound **2** was isolated as a dark purple solid (785 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$ + EtOH) δ ppm 11.14 (s, 2H, NH), 7.80 (t, *J* = 8.1 Hz, 1H, 4'-H), 7.39 (d, *J* = 9.0 Hz, 4H, 3-H), 7.02 (d, *J* = 8.1 Hz, 2H, 3'-H), 6.43 (d, *J* = 9.0 Hz, 4H, 2-H), 3.66 (s, 6H, OCH_3), 2.38 (s, 6H, CH_3); **^{13}C NMR** (125 MHz, DMSO) δ ppm 154.2, 138.0, 118.9, 115.4, 114.5, 55.2, 11.6; **m/z (ES+):** Found: 426.1905 [M+Na], requires: 426.1900; **IR ν_{max}/cm^{-1} (solid):** 3393, 3187, 2994, 2831, 1502, 1412, 1270, 1231, 816; **M.pt:** 178-181 °C.

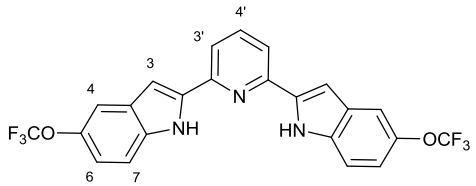
2,6-Bis(1H-indol-2-yl)pyridine (4)[2]



A solution of compound **1** (175 mg, 0.51 mmol) in 1 g of polyphosphoric acid (PPA) was heated at 100°C overnight. The reaction mixture was cooled to room temperature, neutralised with 10% NaOH aqueous solution and extracted with DCM (3 × 75 mL). The combined organic phases were washed with water and dried over anhydrous Na_2S0_4. The solvents were removed under reduced pressure to yield compound **4** as a yellow-camel solid (64.3 mg, 41%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 9.65 (s, 2H, NH), 7.73 (m, 1H, 4'-H), 7.65 (m, 4H, 4-H and 7-H), 7.50 (d, *J* = 8.1 Hz, 2H, 3'-H), 7.25-7.13 (m, 4H, 5-Hand 6-H), 7.07 (s, 2H, 3-H); **m/z (ES+):** Found: 310.1366, requires: 310.1266; **IR ν_{max}/cm^{-1} (solid):** 3433, 3047, 1595, 1564, 1449, 1334, 1300, 786, 743, 612; **M.pt:** 248 °C.

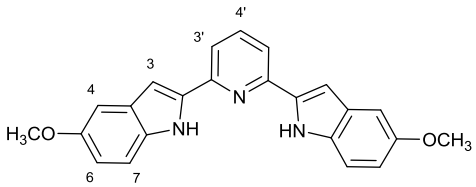
[2] R. P. Thummel and V. Hegde, *J. Org. Chem*., **1989**, 54, 1720-1725.

2,6-Bis[(5-trifluoromethoxy)-1H-indol-2-yl]pyridine (5)



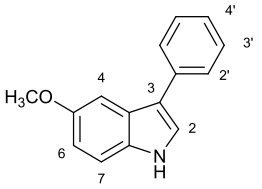
The same procedure as described for compound **4** starting from compound **2** (1.13 g, 2.2 mmol) dissolved in 1 g of polyphosphoric acid (PPA) heated at 100 °C overnight. Compound **5** was isolated as a yellow solid (446 mg, 43%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 9.56 (s, 2H, NH), 7.80 (dd, *J* = 8.4, 7.2 Hz, 1H, 4'-H), 7.71 (dd, *J* = 7.2 Hz, 0.6 Hz, 2H, 3'-H), 7.53 (s, 2H, 4-H), 7.48 (d, *J* = 8.8 Hz, 2H, 7-H), 7.14 (dd, *J* = 8.8, 1.4 Hz, 2H, 6-H), 7.08 (d, *J* = 1.4 Hz, 2H, 3-H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.5, 143.6, 138.1, 137.7, 134.9, 129.3, 121.0 (q, J_{F-C} = 255.6 Hz), 119.1, 117.6, 113.7, 112.1, 101.7; **m/z (ES+):** Found: 495.1254 [$M+NH_4^+$], requires: 495.1250; **IR ν_{max}/cm^{-1} (solid):** 3465, 3314, 1693, 1595, 1564, 1453, 1252, 1191, 1131, 868, 782; **M.pt:** 226 °C.

2,6-Bis[(5-methoxy)-1H-indol-2-yl]pyridine (6)



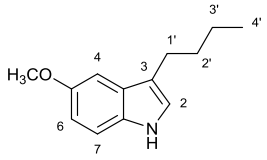
To a solution of **19** (400 mg, 0.61 mmol) in dry THF (20 mL), 1.83 mL of 1M TBAF in THF (1.9 mmol) was added. The reaction was refluxed for 2.5 h. The reaction mixture was hydrolysed with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. The solvents were removed under reduced pressure. Compound **6** was purified by column chromatography on Silica (Hex:EtOAc with a gradient from 9:3 to 7:3) yielding a yellow solid (54 mg, 24%). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ ppm 9.68 (s, 2H, NH), 7.78 (dd, *J* = 8.2, 7.1 Hz, 1H, 4'-H), 7.69 (dd, *J* = 8.2, 0.7 Hz, 2H, 3'-H), 7.43 (d, *J* = 8.8 Hz, 2H, 7-H), 7.11 (d, *J* = 2.5 Hz, 2H, 4-H), 7.02 (dd, *J* = 2.0, 0.7 Hz, 2H, 3-H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 2H, 6-H), 3.86 (s, 6H, OCH_3); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ ppm 155.1, 150.3, 137.7, 137.6, 132.3, 130.0, 118.4, 114.4, 112.6, 102.7, 101.1, 56.1; **m/z (ES+):** Found: 370.1561, requires 370.1550; **IR ν_{max}/ cm^{-1} (solid):** 3430, 3446, 2922, 2853, 1623, 1594, 1562, 1540, 1450, 1211, 781; **M.pt:** 295 °C.

5-Methoxy-3-phenyl-1H-indole (7)[3]



4-Methoxyphenylhydrazine hydrochloride (980 mg, 5.6 mmol) was dissolved in a heated solution of sodium acetate (1.18 g, 14.4 mmol) in glacial acetic under a nitrogen atmosphere. Phenylacetaldehyde (1.00 mL, 8.6 mmol) was added dropwise. The reaction mixture was stirred overnight at 75°C, than after cooling was poured into water (20 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (3 × 30 mL) until the pH was adjusted to 7 and dried over Na_2SO_4. The solvents were removed under reduced pressure, the residue was passed through a silica plug and purified by column chromatography on Silica (Hexane:Diethyl ether, 1:7) to yield compound **7** as a yellow solid (0.81 g, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.15 (br s, 1H, NH), 7.65 (dd, *J* = 7, 1.2 Hz, 2H, 2'-H), 7.46 (t, *J* = 7.0 Hz, 2H, 3'-H), 7.38 (d, *J* = 2.4 Hz, 1H, 4-H), 7.36 – 7.28 (m, 3H, 2-H and 7-H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H, 6-H), 3.87 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 154.8, 135.9, 132.0, 128.9, 127.4, 126.2, 126.0, 122.8, 118.2, 112.7, 112.3, 101.7, 56.1; **m/z (ES+):** Found: 224.1069 [M+H], requires 224.1075; **IRν_{max}/cm^{-1}:** 3402, 3006, 2956, 2827, 1613, 1598, 1580, 1537; **M.pt:** 69.8-70.8 °C.

3-*n*-Butyl-5-methoxy-1H-indole (8)[4]

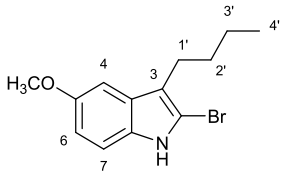


The same procedure as described for compound **7** using hexanal (2 mL, 16.7 mmol), NaOAc (3 g, 36.14 mmol) and 4-methoxyphenylhydrazine hydrochloride (2.43 g, 13.9 mmol). The residue was passed through a silica plug and then purified by column chromatography on Silica (Hexane:DCM, 1:9) to yield the compound **8** as a yellow oil (2.00 g, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.78 (br s, 1H, NH), 7.24 (d, *J* = 8.8 Hz, 1H, 7-H), 7.05 (d, *J* = 2.5 Hz, 1H, 4-H), 6.95 (d, *J* = 2.2 Hz, 1H, 2-H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H, 6-H), 3.88 (s, 3H, OCH_3), 2.72 (t, *J* = 7.4 Hz, 2H, 1'-H), 1.69 (dt, *J* = 15.3, 7.4 Hz, 2H, 2'-H), 1.43 (sex, *J* = 7.4 Hz, 2H, 3'-H), 0.96 (t, *J* = 7.4 Hz, 3H, 4'-H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 154.0, 131.7, 128.2, 122.0, 117.1, 112.1, 111.8, 101.2, 56.2, 32.3, 25.0, 22.8, 14.2; **m/z (ES+):**

[3] Z. Zhang, Z. Hu, Z. Yu, P. Lei, H. Chi, Y. Wangb, R. He, Tetrahedron Letters, 2007, 48, 2415–2419
[4] J. B. Baudin, M. G. Commenil, S. A. Julia and L. Mauclarie, Bulletin de la Societe chimique de France, 1996, 133, 329-350.

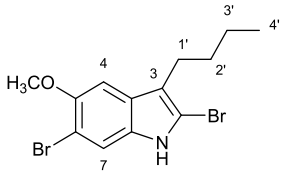
Found: 204.1390 [M+H], requires 204.1310; **IRν_{max}/cm^{-1}(liquid):** 3414, 2954, 2926, 2855, 1623, 1582, 1482.

2-Bromo-3-*n*-butyl-5-methoxy-1H-indole (10)



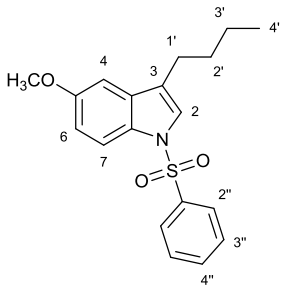
N-bromosuccinimide (415 mg, 2.5 mmol) in small portions was added to an ice cooled solution of compound **8** (515 mg, 2.5 mmol) in chloroform (80 mL). The reaction was wrapped with foil and allowed to react for 1h at room temperature. The reaction mixture was diluted in DCM (20 mL) and washed with water (3 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvents were evaporated under reduced pressure yielding compound **10**. **^{1}H NMR (300 MHz, $CDCl_3$)** δ ppm 7.80 (s, 1H, NH), 7.17 (d, *J* = 8.8 Hz, 1H, 6-H), 6.97 (d, *J* = 2.5 Hz, 1H, 4-H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H, 7-H), 3.86 (s, 3H, OCH_3), 2.68 (t, *J* = 7.5 Hz, 2H, 1'-H), 1.64 (dt, *J* = 14.7, 7.5 Hz, 2H, 2'-H), 1.39 (td, *J* = 14.7, 7.5 Hz, 2H, 3'-H), 0.94 (t, *J* = 7.5 Hz, 3H, 4'-H); **m/z (ES+):** Found: 282.0480 [M+H], requires 282.0415.

2,6-Dibromo-3-*n*-butyl-5-methoxy-1H-indole (11)



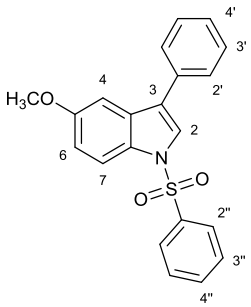
The same procedure as described for compound **10** using N-bromosuccinimide (111 mg, 0.67 mmol) and compound **8** (126 mg, 0.61 mmol). Compound **11** was purified by column chromatography on Silica (Hex:DCM, 4:3) and isolated as a brown oil (13 mg, 5.8%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ ppm 7.81 (s, 1H, NH), 7.47 (s, 1H, 7-H), 6.97 (s, 1H, 4-H), 3.93 (s, 3H, OCH_3) 2.67 (t, *J* = 7.5 Hz, 2H, 1'-H), 1.61 (dt, *J* = 14.7, 7.5 Hz, 2H, 2'-H), 1.38 (dq, *J* = 14.7, 7.5 Hz, 2H, 3'-H), 0.94 (d, *J* = 7.5 Hz, 3H, 4'-H).

3-*n*-Butyl-5-methoxy-1-phenylsulfonylindole (12)



NaH (240 mg, 5.9 mmol, 60% dispersion in oil) was charged with nitrogen, washed with 2 mL of Hexane twice before being dissolved in THF (7 mL) and then, a solution of compound **8** (401 mg, 2.0 mmol) in THF (4 mL) was added dropwise at 0°C. The reaction mixture was left to stir for 1h at room temperature. Benzenesulfonyl chloride (0.50 mL, 3.9 mmol) was added dropwise at the same temperature and the reaction was stirred for 7h. The reaction mixture was hydrolysed with water (10 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvents were evaporated under reduced pressure. Compound **12** was purified by column chromatography on Silica (Hex:DCM, 1:3) yielding a rose-white solid (230 mg, 57%).**^{1}H NMR** (500 MHz, CD_2Cl_2) δ ppm 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H, 7-H), 7.81 (dd, *J* = 7.5, 1.2 Hz, 2H, 2''-H), 7.53 (t, *J* = 7.5 Hz, 1H, 4''-H), 7.42 (t, *J* = 7.5 Hz, 2H, 3''-H), 7.28 (s, 1H, 2-H), 6.91 (d, *J* = 8.1, 1H, 6-H) 6.89 (s, 1H, 4-H), 3.81 (s, 3H, OCH_3), 2.61 (t, *J* = 7.5 Hz, 2H, 1'-H), 1.64 (dt, *J* = 14.7, 7.4 Hz, 2H, 2'-H), 1.39 (dq, *J* = 14.7, 7.4 Hz, 2H, 3'-H), 0.94 (t, *J* = 7.4 Hz, 3H, 4'-H); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ ppm 156.9, 138.4, 134.0, 132.9, 130.5, 129.5, 127.0, 124.8, 123.9, 115.0, 113.7, 102.7, 56.0, 31.3, 24.9, 22.8, 14.0; **m/z (ES+)**: Found: 344.1317 [M+H], requires 344.1242; **IRν_{max}/cm^{-1}(solid)**: 3005, 2955, 2928, 2869, 2833, 1609, 1446, 1251; **M.pt**: 77.1-77.8 °C.

5-Methoxy-3-phenyl-1-phenylsulfonylindole (13)[5]

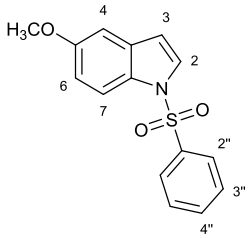


NaH (160 mg, 3.8 mmol, 57-63% dispersion in oil) was charged with nitrogen, washed with 2 mL of Hexane twice before being dissolved in THF (5 mL) and then, a solution of solution of compound **7** (573 mg, 2.6 mmol) in THF (7 mL) was added dropwise at 0°C. The reaction mixture was left to stir

[5] A. N. Campbell, E. B. Mayer and S. S. Stahl, Chem. Commun., 2011, 47, 10257-10259.

for 1h at room temperature. Benzenesulfonyl chloride (0.36 mL, 2.8 mmol) was added dropwise at the same temperature and the reaction was stirred for 45 min. The reaction mixture was hydrolysed with water (10 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4. The solvents were evaporated under reduced pressure. Compound **13** was purified by column chromatography on Silica (Hex:DCM, 1:13) yielding a white solid (808 mg, 87%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ ppm 7.96 (d, *J* = 9.0 Hz, 1H, 7-H), 7.89 (dd, *J* = 8.3, 0.9 Hz, 2H, 2''-H), 7.64 (s, 1H, 2-H), 7.60 – 7.56 (m, 2H, 2'-H), 7.56 – 7.51 (m, 1H, 4''-H), 7.45 (m, 4H, 3'-H and 3''-H), 7.40 – 7.34 (m, 1H, 4'-H), 7.20 (d, *J* = 2.5 Hz, 1H, 4-H), 6.98 (dd, *J* = 9.0, 2.5 Hz, 1H, 6-H), 3.82 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, CDCl3) δ ppm 198.0, 157.0, 155.6, 138.3, 134.0, 133.2, 129.4, 129.1, 128.0, 127.7, 126.9, 124.5, 123.9, 114.9, 114.1, 103.2, 55.9; **m/z (ES+):** Found 364.1006 [M+H]**,** requires 364.0929; **IRν_{max}/cm^{-1} (solid):** 3135, 3061, 2920, 1611, 1471, 1364; **M.pt:** 127.5-128.0 °C.

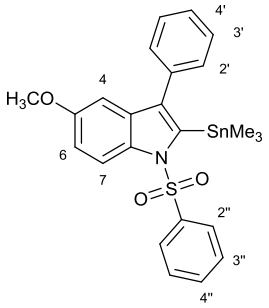
5-Methoxy-1-phenylsulfonylindole (14)[6]



To a solution of compound **9** (4.12 g, 27.9 mmol) in dry THF (20 mL) under nitrogen was added dropwise a solution of NaH (1.53 g, 36.4 mmol) in dry THF (250 mL) at 0 °C. The reaction mixture was warmed to room temperature and reacted for 1h. The mixture was cooled to 0 °C before the addition of benzenesulfonyl chloride (3.6 mL, 28.0 mmol). The reaction mixture reacted overnight. Once completed, the reaction mixture was hydrolysed with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvents were removed under reduced pressure. Compound **14** was recrystallised from EtOH and isolated as an off-white crystalline (6.34 g, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.88 (d, *J* = 9.0 Hz, 1H, 7-H), 7.84 (dd, *J* = 8.5, 1.2 Hz, 2H, 2''-H), 7.54 – 7.50 (m, 2H, 2-H and 4''-H), 7.42 (t, *J* = 7.8 Hz, 2H, 3''-H), 6.97 (d, *J* = 2.5 Hz, 1H, 4-H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 1H, 6-H), 6.59 (dd, *J* = 3.6, 0.6 Hz, 1H, 3-H), 3.81 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 133.9, 129.4, 127.3, 126.8, 114.6, 113.9, 109.5, 103.9, 55.8; **m/z (ES+):** Found: 288.0693 [M+H], requires 288.0690; **IR ν_{max}/cm^{-1} (solid):** 3136, 3103, 3000, 2949, 2839, 15832, 1445, 1436, 1370, 1141, 1120, 1090, 994; **M.pt:** 95-97 °C.

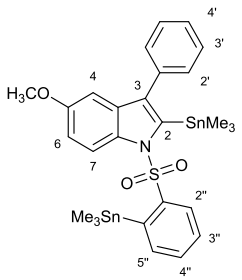
[6] I. R. Greig, G. L. Baillie, M. Abdelrahman, L. Trembleau, R. A. Ross, Bioorg. Med. Chem. Lett., 2016, 26, 4403–4407.

5-Methoxy-3-phenyl-1-phenylsulfonyl-2-trimethylstannylindole (15)



To a solution of compound **13** (1.64 g, 4.5 mmol) in THF (30 mL) was added 1.6 M hexane solution of *n*BuLi (4.48 mL, 7.2 mmol) at -78°C within 45 min. The orange solution was allowed to reach room temperature and was left sitting for 1 h. Trimethyltin chloride (7.48 mL, 7.2 mmol, 1M in THF) was added dropwise at -78°C and the reaction was left for 2h. The reaction mixture was hydrolysed with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with a saturated solution of KF, dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. Compound **15** was purified by column chromatography on Silica (Hex:EtOAc, 9:1) yielding a white solid (210 mg, 35%). **^{1}H NMR** (500 MHz, DMSO) δ ppm 7.77 (d, *J* = 9.0 Hz, 1H, 7-H), 7.70 (d, *J* = 7.3 Hz, 2H, 2''-H), 7.63 (t, *J* = 7.3 Hz, 1H, 4''-H), 7.58 – 7.49 (m, 4H, 3''-H and 3'-H), 7.47 (d, *J* = 7.3 Hz, 1H, 4'-H), 7.44 (dd, *J* = 6.7, 1.5 2H, 2'-H), 6.91 (dd, *J* = 9.0, 2.5 Hz, 1H, 6-H), 6.71 (d, *J* = 2.5 Hz, 1H, 4-H), 3.66 (s, 3H, OCH_3), 0.09 (9H, $SnMe_3$); **^{13}C NMR** (125 MHz, DMSO) δ ppm 156.5, 141.8, 138.2, 136.7, 134.2, 134.1, 132.9, 132.6, 129.8, 129.5, 128.8, 128.2, 126.2, 115.1, 113.7, 101.3, 55.3, -5.2; **m/z (ES+):** Found: 528.0655 [M+H], requires 528.0577; **IRν_{max}/cm^{-1} (solid):** 3060, 2991, 2921, 1768, 1525, 1360, 1216; **M.pt:** 112.4-113.6 °C.

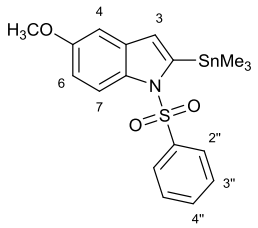
5-Methoxy-3-phenyl-1-[(2'-trimethylstannyl)phenylsulfonyl]-2-trimethylstannylindole (16)



The same procedure as described for compound **15**. Compound **16** was isolated as a violet solid (216 mg, 7%). **^{1}H NMR** (500MHz, DMSO) δ ppm 7.79 (dd, *J* = 7.7, 1.1 Hz, 1H, 2''-H), 7.60 – 7.49 (m, 7H,2'-4'H and 3''-H), 7.43 (td, *J* = 7.7, 1.1 Hz, 1H, 4''-H), 7.40 (d, *J* = 9.0 Hz, 1H, 7-H), 6.96 (dd, *J* = 7.7, 1.1 Hz, 1H, 5''-H), 6.87 (dd, *J* = 9.0, 2.5 Hz, 1H, 6-H), 6.79 (d, *J* = 2.5 Hz, 1H, 4-H), 3.70 (s, 3H, OCH_3), 0.47 (s, 9H, $SnMe_3$), 0.01 (s, 9H, $SnMe_3$); **^{13}C NMR** (125 MHz, DMSO) δ ppm 156.2, 145.2, 141.9, 141.9,

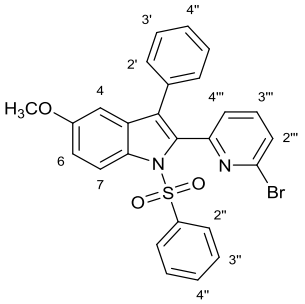
137.5, 135.8, 134.2, 132.6, 132.6, 132.4, 130.1, 129.7, 128.7, 128.0, 124.5, 114.0, 113.5, 101.5, 55.3, -5.2, -5.2; **m/z (ES+):** Found: 692.0279 [M+H], requires 692.0225; **IRν_{max}/cm^{-1} (solid):** 3053, 2957, 2918, 1738, 1606, 1487, 1431, 1345; **M.pt:** 58.2-59.0 °C.

5-Methoxy-1-phenylsulfonyl-2-trimethylstannylindole (17)



To a solution of compound **14** (3.94 g, 13.7 mmol) in THF (30 mL) was added 2M THF solution of LDA (10.3 mL, 20.5 mmol) at -20°C dropwise. The orange solution was allowed to reach room temperature and was left sitting for 1 h. Trimethyltin chloride (21.3 mL, 20.5 mmol, 1M in THF) was added dropwise at -78°C and the reaction was left for 2h. The reaction mixture was hydrolysed with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with a saturated solution of KF, dried over Na2SO4 and the solvents were evaporated under reduced pressure. Compound **17** was purified by column chromatography on Silica (Hex:DCM, 1:1) yielding a white solid (4.10 g, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* = 9.0 Hz, 1H, 7-H), 7.65 (dd, *J* = 7.9 Hz, 1.0 Hz, 2H, 2''-H), 7.49 (t, *J* = 7.9 Hz, 1H, 4''-H), 7.39 (t, *J* = 7.9 Hz, 2H, 3''-H), 6.49 (d, *J* = 2.5 Hz, 1H, 4-H), 6.82 (dd, *J* = 9.0 Hz, 2.5Hz, 1H, 6-H), 6.77 (d, *J* = 2.5 Hz, 1H, 4-H), 3.80 (s, 3H, OCH_3), 0.42 (s, 9H, $SnMe_3$); **^{13}C NMR** (100 MHz,$CDCl_3$) δ ppm 156.4, 144.6, 139.1, 133.5, 133.2, 133.0, 129.2, 126.4, 120.5, 114.5, 113.3, 102.7, 55.7, -6.6; **m/z (ES+):** Found: 474.0155 [M+Na], requires: 474.0158; **IR ν_{max}/cm^{-1} (solid):** 3068, 2972, 2913, 2833, 1586, 1506, 1586, 1506, 1448, 1422, 1362 1145, 1108, 1089; **M.pt:** 64-65°C.

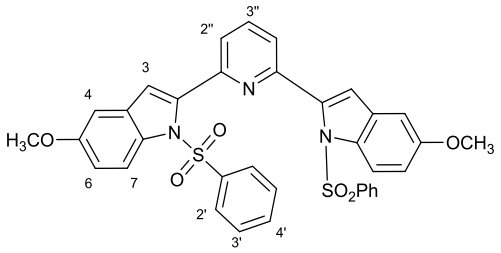
6-(5-Methoxy-3-phenyl-1-phenylsulfonylindol-2-yl)-2-bromopyridine (18)



A solution of 2,6-dibromopyridine (27 mg, 0.11 mmol), compound **15** (139 mg, 0.26 mmol) and CuI (2 mg, 10%) in THF (5 mL) was degassed and bubbled with nitrogen for 30 min. Then, $Pd(PPh_3)_4$ (13.3

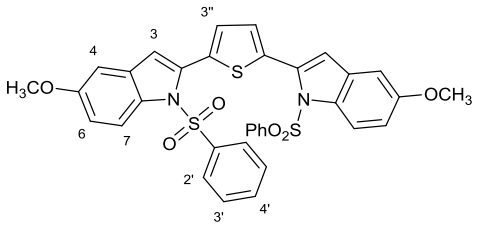
mg, 10%) dissolved in THF (2 mL) was added. The reaction mixture was transferred to a pre-heated hot-plate at 65 °C and refluxed for 4h. The reaction mixture was hydrolysed with 10 mL of water and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvents were removed under reduced pressure. Compound **18** was purified by column chromatography on Silica (Hex:EtAcO, 7:3) and/or HPLC (50:95+Formic acid 0.1%) to yield the compound as a yellow-orange solid (160 mg, 84%). **^{1}H NMR** (500 MHz, DMSO) δ ppm 8.05 (d, *J* = 9.2 Hz, 1H, 7-H), 7.95 (dd, *J* = 7.8, 1.1 Hz, 2H, 2''-H), 7.75 (t, *J* = 7.4 Hz, 1H, 3'''-H), 7.71 (m, 2H, 4''-H and 4'''-H), 7.61 (t, *J* = 7.8 Hz, 2H, 3''-H), 7.52 (dd, *J* = 7.4, 0.8 Hz, 1H, 2'''-H), 7.35 (t, *J* = 7.2 Hz, 2H, 3'-H), 7.30 (t, *J* = 7.2 Hz, 1H, 4'-H), 7.22 (dd, *J* = 7.2, 1.4 Hz, 2H, 2'-H), 7.10 (dd, *J* = 9.2, 2.5 Hz, 1H, 6-H), 6.88 (d, *J* = 2.5 Hz, 1H, 4-H), 3.72 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, DMSO) δ ppm 156.8, 151.2, 140.0, 140.0, 136.9, 134.6, 134.1, 131.0, 130.0, 129.9, 129.5, 129.5, 128.6, 127.9, 127.8, 126.9, 126.3, 125.1, 115.9, 115.0, 102.4, 55.4; **m/z (ES+):** Found: 519.0383 [M+H], requires 519.0300; **IRν_{max}/cm^{-1} (solid):** 3052, 2917, 2849, 1606, 1541, 1495, 1448, 1334; **M.pt:** 161.0-161.9°C.

2,6-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)pyridine (19)



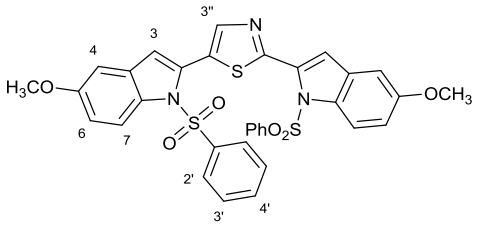
The same procedure as described for compound **18** starting from compound **17** (1.13g, 2.5 mmol), 2,6-dibromopyridine (270 mg, 1.2 mmol), CuI (40 mg, 20%), and $Pd(PPh_3)_4$ (133 mg, 10%) refluxed overnight at 90 °C. Compound **19** was purified by column chromatography (Hex:EtOAc, 7:3) and isolated as a white solid (0.70 g, 92%). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ ppm 8.06 (d, *J* = 8.9 Hz, 2H, 7-H), 7.92 (dd, *J* = 8.1, 7.5 Hz, 1H, 4''-H), 7.75 – 7.71 (m, 6H, 2'-H and 3''-H), 7.36 (t, *J* = 7.4, 1.2 Hz, 2H, 4'-H), 7.16 (dd, *J* = 8.4, 7.4 Hz, 4H, 3'-H), 7.00-6.98 (m, 4H, 4-H and 6-H), 6.87 (d, *J* = 0.7 Hz, 2H, 3-H), 3.82 (s, 6H, OCH_3); **^{13}C NMR** (125 MHz, CD_2Cl_2) δ ppm 157.7, 151.0, 142.1, 137.5, 135.8, 133.9, 133.1, 131.9, 129.0, 127.7, 125.2, 117.5, 116.0, 114.7, 104.1, 56.0; **m/z (ES+):** Found: 650.1434 [M+H], requires: 650.1414; **IR ν_{max}/cm^{-1} (solid):** 3060, 2999, 2954, 2837, 1606, 1563, 1474, 1448, 1427, 1366, 1359, 1177, 1143, 601, 570; **M.pt:** 197-200°C.

2,5-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)thiophene (20)



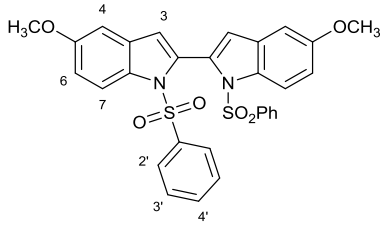
The same procedure as described from compound **18** starting from compound **17** (900 mg, 2.0 mmol), 2,5-dibromothiophene (220 mg, 0.91 mmol), CuI (35 mg, 20%) and $Pd(PPh_3)_4$ (158 mg, 15%). Compound **20** was purified by column chromatography on Silica (Hex:EtOAc, gradient from 4:1 to 7:3) and isolated as a green solid (515 mg, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.23 (d, *J* = 9.2 Hz, 2H, 7-H), 7.53 (dd, *J* = 8.4, 1.1 Hz, 4H, 2'-H), 7.47 (t, *J* = 7.6 Hz, 2H, 4'-H), 7.32 (dd, *J* = 8.4, 7.6 Hz, 4H, 3'-H), 7.27 (s, 2H, 3''-H), 7.00 (dd, *J* = 9.2, 2.6 Hz, 2H, 6-H), 6.90 (d, *J* = 2.6 Hz, 2H, 4-H), 6.63 (s, 2H, 3-H), 3.84 (s, 6H, OCH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 157.3, 137.4, 134.6, 134.2, 133.9, 133.2, 131.3, 130.3, 129.0, 127.1, 117.8, 115.2, 114.4, 103.3, 55.8; **m/z (ES+):** Found: 655.1029 [M+H], requires: 655.1026; **IR ν_{max}/cm^{-1} (solid):** 3073, 3000, 2920, 2834, 1585, 1464, 1447, 1434, 1370, 1207, 1174, 1144, 600, 569; **M.pt:** 152-156 °C.

2,5-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)thiazole (21)



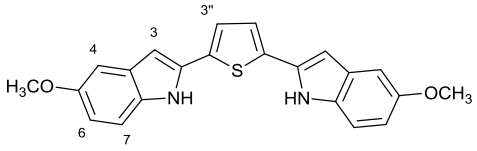
Same procedure as described from compound **18** starting from compound **17** (0.58 mmol, 2.2 equiv), 2,5-dibromothiazole (0.26 mmol), CuI (20%) and $Pd(PPh_3)_4$ (20%). Chemical conversion is quantitative; however, compound **21** rapidly decomposes. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 8.06 (d, *J* = 8.6 Hz, 2H, 7-H), 7.93 (dd, *J* = 8.3, 7.3 Hz, 1H, 3''-H), 7.77 – 7.69 (m, 4H, 2'-H), 7.40 – 7.32 (m, 4H, 4'-H), 7.16 (t, *J* = 7.9 Hz, 4H, 3'H), 6.99 (m, 4H, 4-H and 6- H), 6.88 (s, 2H, 3-H), 3.82 (s, 6H, OCH_3).

Bis(5-methoxy-1-phenylsulfonylindol-2-yl) (22)



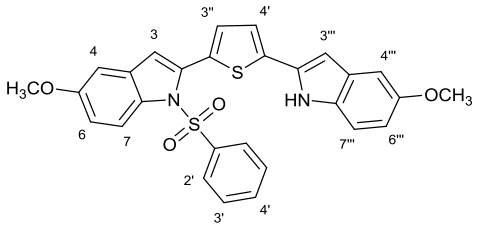
The same procedure as described for compound **18** starting from compound **17** (392 mg, 0.87 mmol), 2,5-dibromothiophene (97 mg, 0.40 mmol), CuI (15.2 mg, 20%) and $Pd(PPh_3)_4$ (92.5 mg, 20%). Compound **22** was purified by column chromatography on Silica (Hex:EtOAc, 7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.16 (d, *J* = 9.0 Hz, 2H, 7-H), 7.63 (d, *J* = 7.4 Hz, 2H, 2'-H), 7.49 (t, *J* = 7.4 Hz, 2H, 4'-H), 7.35 (t, *J* = 7.8 Hz, 4H, 3'-H), 7.04 (dd, *J* = 9.2, 2.4 Hz, 2H, 6-H), 6.99 (d, *J* = 2.1 Hz, 2H, 4-H), 6.51 (s, 2H, 3-H), 3.86 (s, 6H, OCH_3); **m/z (ES+):** Found: 595.0979 [M+Na], requires 595.0968.

2,5-Bis(5-methoxy-1H-indol-2-yl)thiophene (23)



The same procedure as described for compound **6**, starting from compound **20** (223 mg, 0.34 mmol) and TBAF (1.7 mmol, 1M in THF). Compound **23** was purified by column chromatography (Hex:EtOAc, 7:3) and isolated as a green solid (51 mg, 40%). **^{1}H NMR** (400 MHz, CD_3CN) δ ppm 9.78 (s, 2H, N-H), 7.33 (s, 2H, 3''-H), 7.28 (dt, *J* = 8.8, 0.7 Hz, 2H, 7-H), 7.05 (d, *J* = 2.5 Hz, 2H, 4-H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 2H, 6-H), 6.65 (dd, *J* = 2.2, 0.8 Hz, 2H, 3-H), 3.80 (s, 6H, OCH_3); **^{13}C NMR (125 MHz, CD_2Cl_2)** δ ppm 155.2, 134.9, 133.0, 132.3, 130.0, 123.9, 113.4, 112.0, 102.4, 101.0, 56.1; **m/z (ES+):** Found: 375.1159 [M+H], requires: 375.1162; **IR ν_{max}/cm^{-1} (solid):** 3448, 3409, 3064, 2916, 2848, 1699, 1450, 1437, 1220, 1028, 779; **M.pt:** 251 °C.

2-(5-Methoxy-1-phenylsulfonylindol-2yl)-5-(5-methoxy-1H-indol-2-yl)thiophene (24)



Compound 24 was isolated as the 2nd product following the procedure for the compound **23**. Green solid (52 mg, 30%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ ppm 8.21 (d, *J* = 9.2 Hz, 2H, 7-H and NH), 7.48 – 7.38 (m, 3H, PG), 7.31 (d, *J* = 3.8 Hz, 1H, 3''-H), 7.28 – 7.21 (m, 3H, 7-H and PG), 7.24 (d, *J* = 3.8 Hz, 1H, 4''-H), 7.06 (d, *J* = 2.5 Hz, 1H, 4'''-H), 6.99 (dd, *J* = 9.2, 2.6 Hz, 1H, 6-H), 6.88 (dd, *J* = 8.7, 2.5 Hz, 2H, 4-H and 6'''-H), 6.69 (dd, *J* = 2.1, 0.8 Hz, 1H, 3'''-H), 6.60 (d, *J* = 0.6 Hz, 1H, 3-H), 3.86 (s, 3H, OCH_3'''), 3.83 (s, 3H, OCH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 157.4, 154.9, 137.4, 137.1, 134.8, 133.8, 133.2, 132.6, 132.1, 131.4, 131.4, 131.3, 129.7, 128.9, 126.9, 122.9, 117.9, 114.9, 114.3, 113.3, 111.8, 103.2, 102.3, 101.0, 56.0, 55.8; **m/z (ES+):** Found: 515.1098 [M+H], requires: 515.1094; **IR ν_{max}/cm^{-1} (solid):** 3365, 3065, 2925, 2830, 1719, 1609, 1365, 1293, 1202, 1171, 1025; **M.pt:** 103-106 °C.

Fluorescence Data

Quantum Yield Measurements

Emission quantum yields of ligands H_2BIP(R) were determined relative to anthracene and 9,10-diphenylantracene. Firstly, two standard compounds are cross-calibrated by calculating the quantum yield of each standard relative to each other. Where Grad is the gradient obtained from plotting integrated fluorescence intensity *vs* absorbance, x and ST denote test and standard sample respectively and η is the refractive index of the solvent. This is calculated using following **Equation**.

$$\Phi_x = \Phi_{ST}\left(\frac{Grad_x}{Grad_{ST}}\right)\left(\frac{\eta_x^2}{\eta_{ST}^2}\right)$$

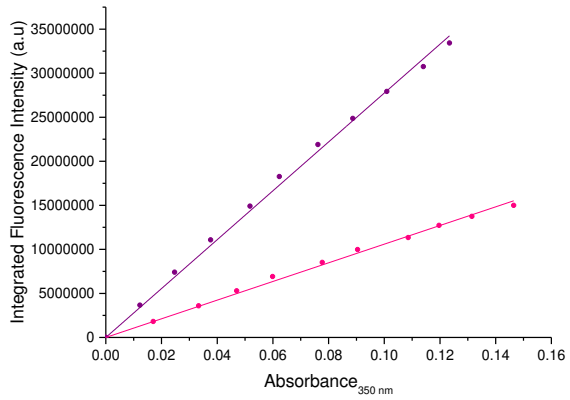
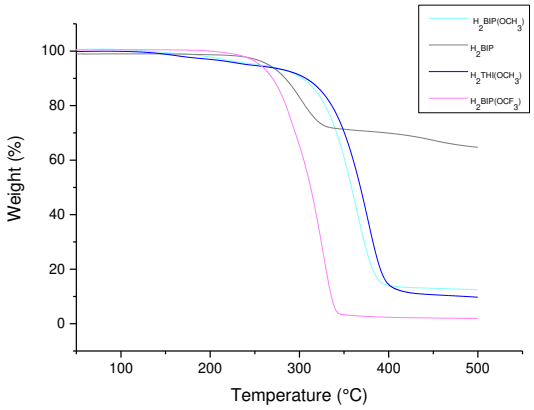


Figure: Area *vs* A_{350nm} of two standard samples: anthracene (pink) and 9,10-diphenylanthracene (purple) in cyclohexane for calibration of emission quantum yield measurement.

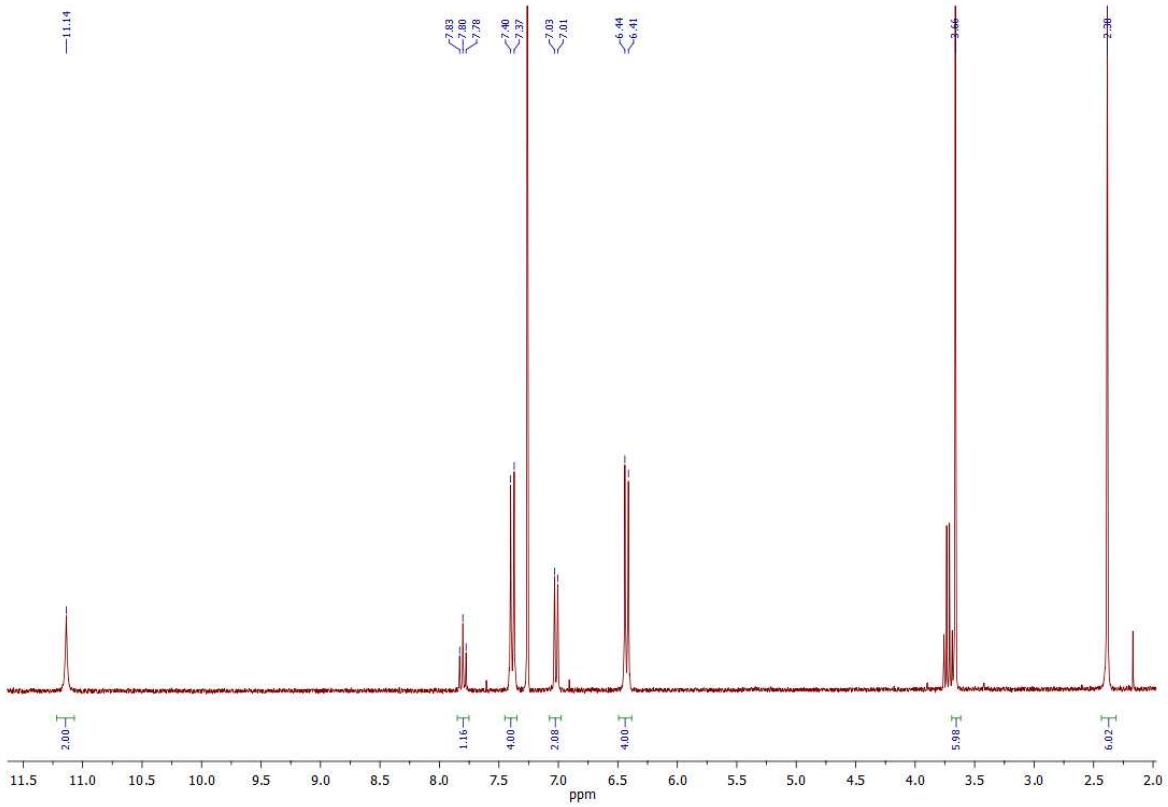
Once the quantum yields calculated for the standards relative to each other match with literature values (within ± 10%), ϕ of the test samples can then be measured and calculated using the **Equation**. The average of the two values obtained represents the quantum yield. The gradient for each sample is proportional to its fluorescence quantum yield. "Area" is the surface under the emission spectra between 365-600 nm using 350 nm as excitation wavelength and slit width of 1 nm.

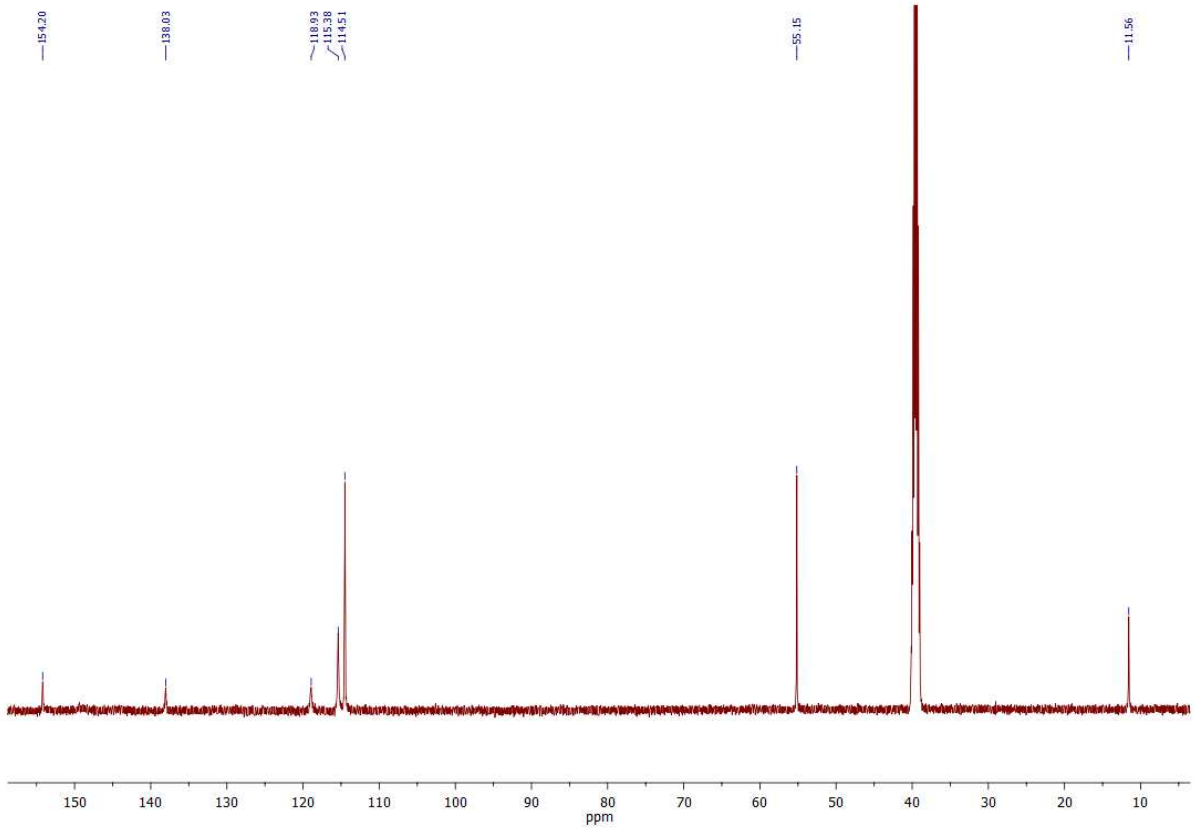
Thermogravimetric analysis (TGA) for the compounds 4-6 and 23


H2BIP(OCH3)
H2BIP
H2THI(OCH3)
H2BIP(OCF3)
Weight (%)
100
80
60
40
20
0
100
200
300
400
500
Temperature (°C)

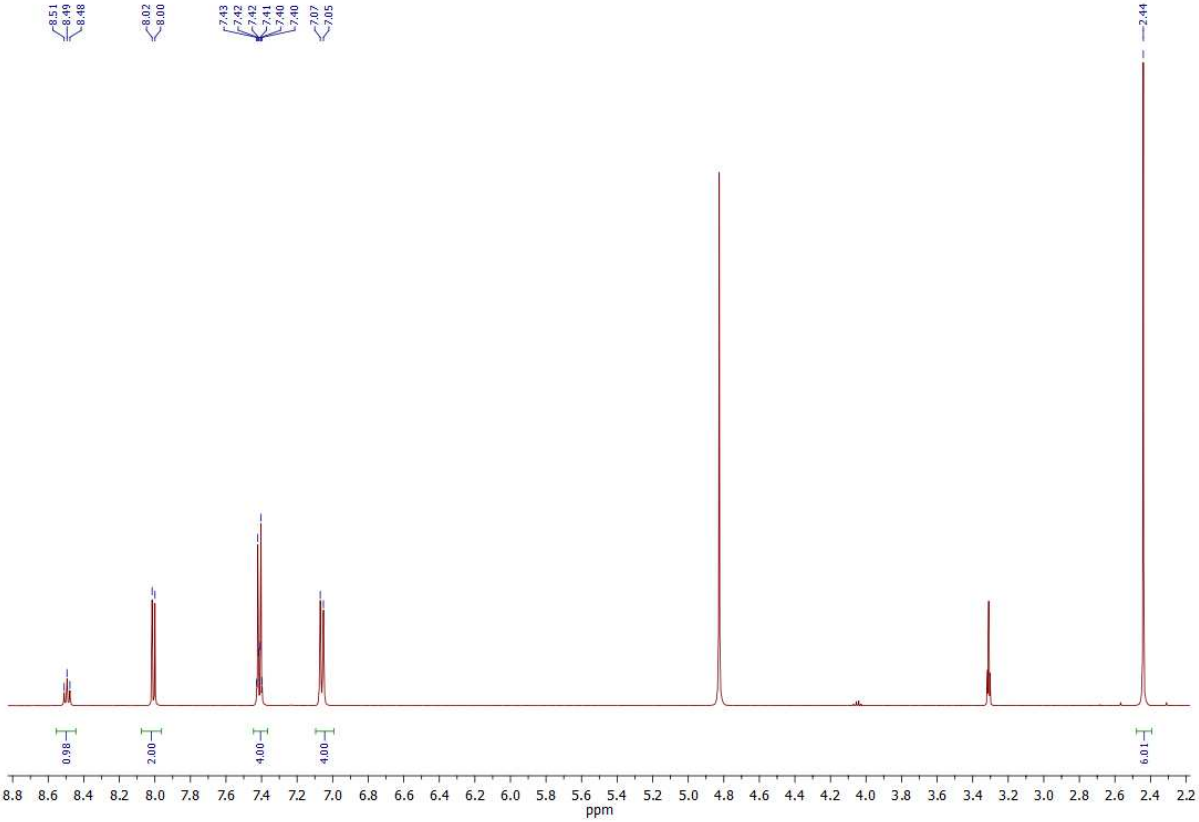
NMR Spectra

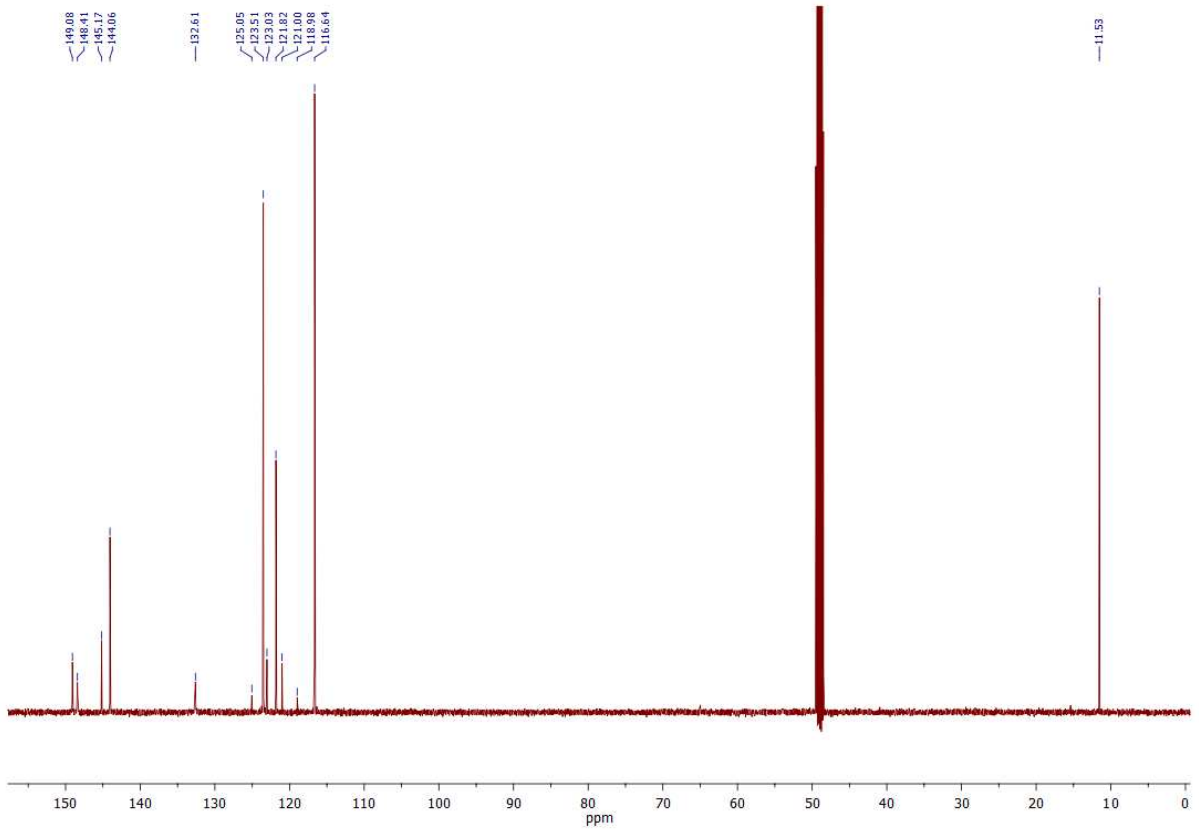
2,6-Diactetylpyridine-bis(4-trifluoromethoxyphenylhydrazone) (2)



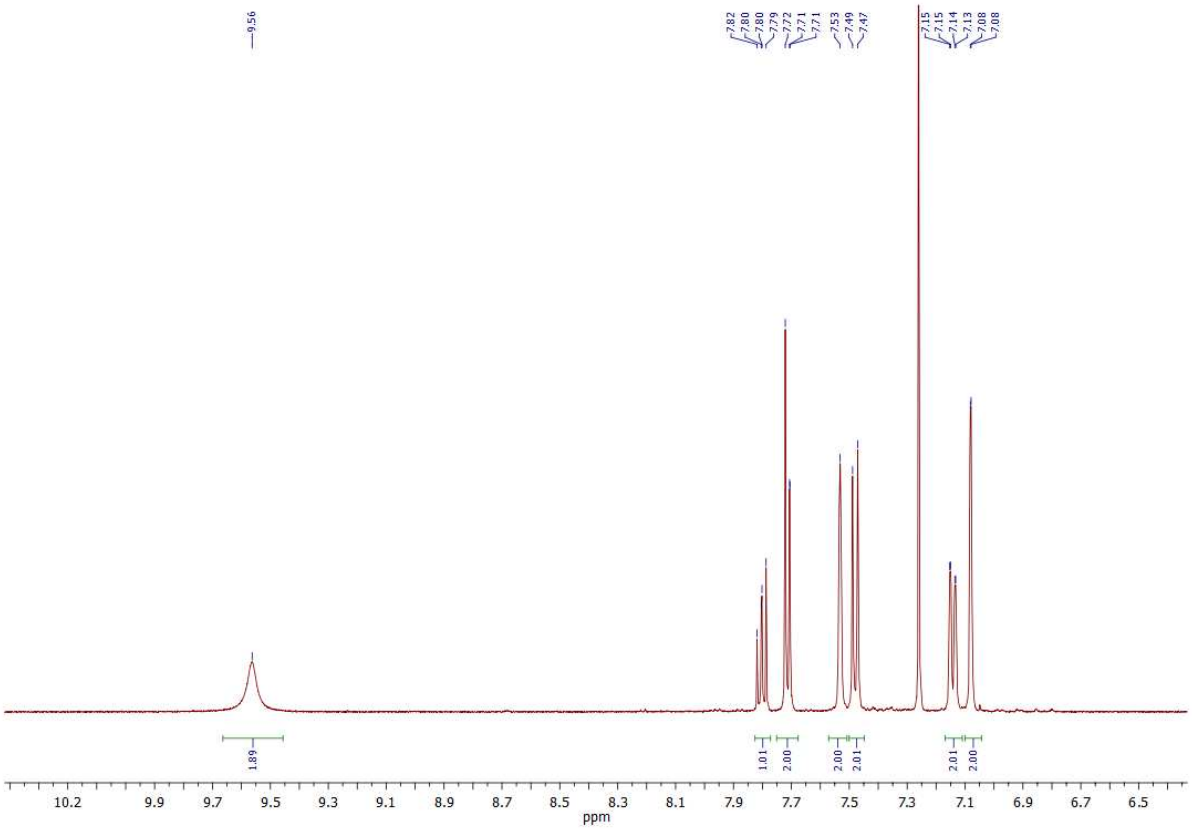


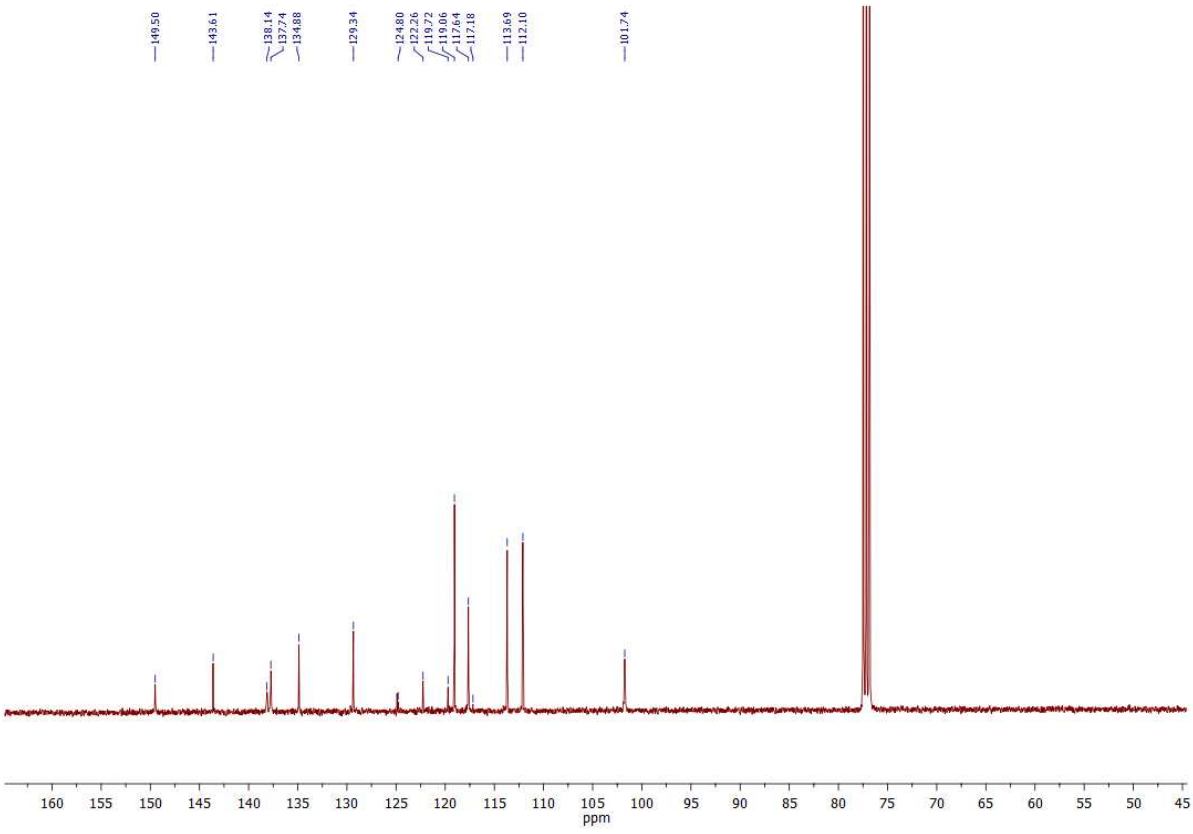
2,6-Diactetylpyridine-bis(4-methoxyphenylhydrazone) (3)



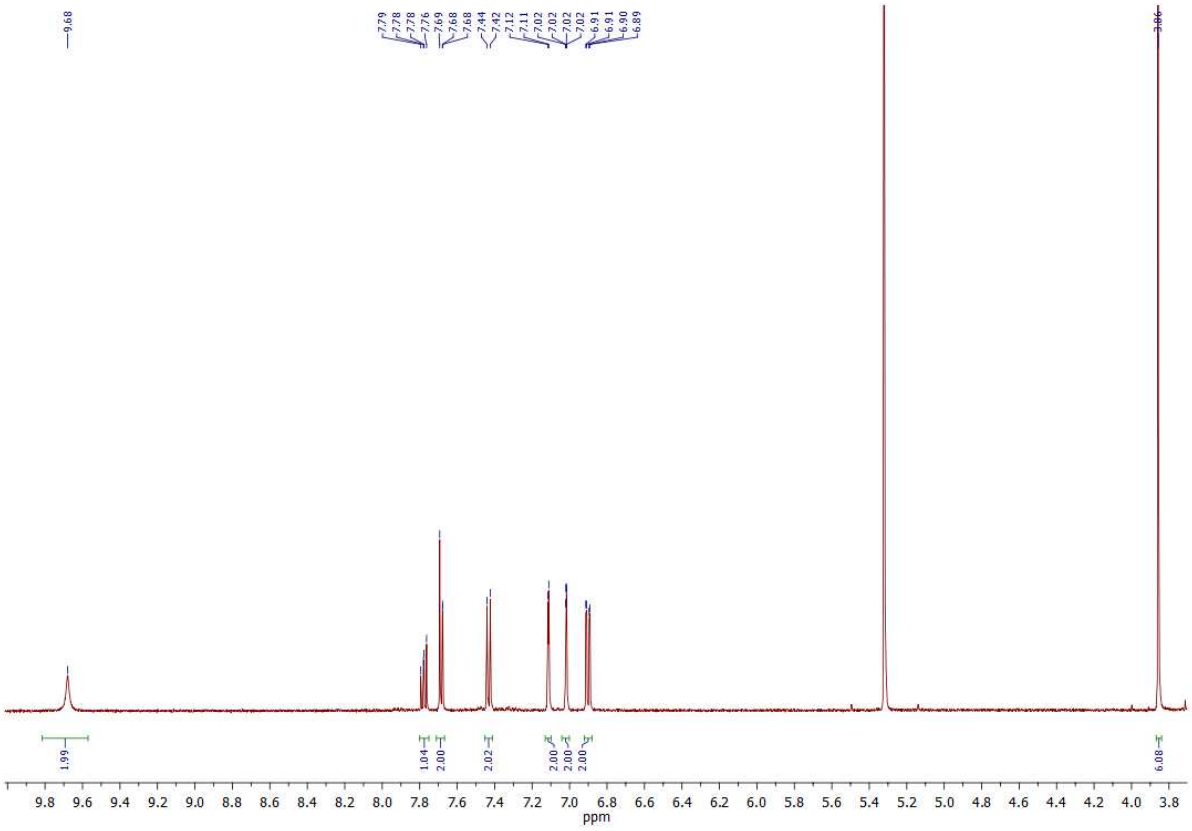


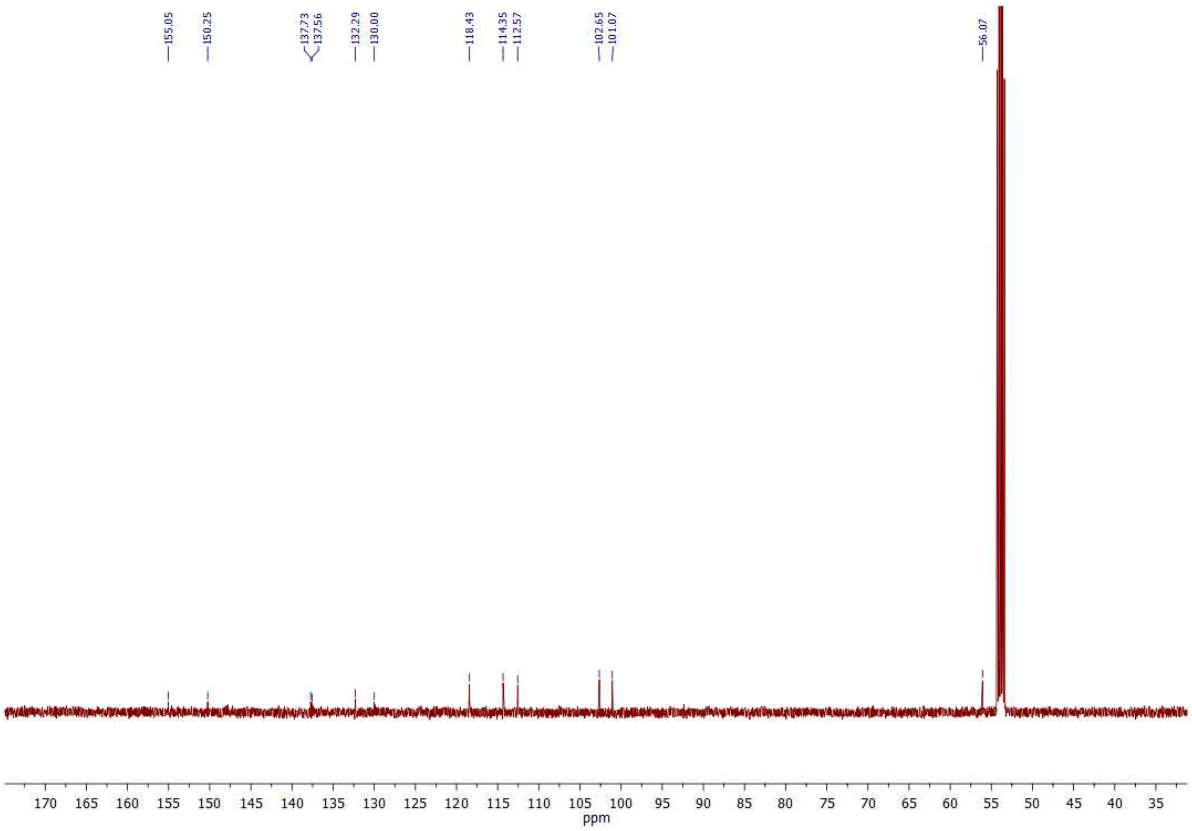
2,6-Bis[(5-trifluoromethoxy)-1H-indol-2-yl]pyridine (5)



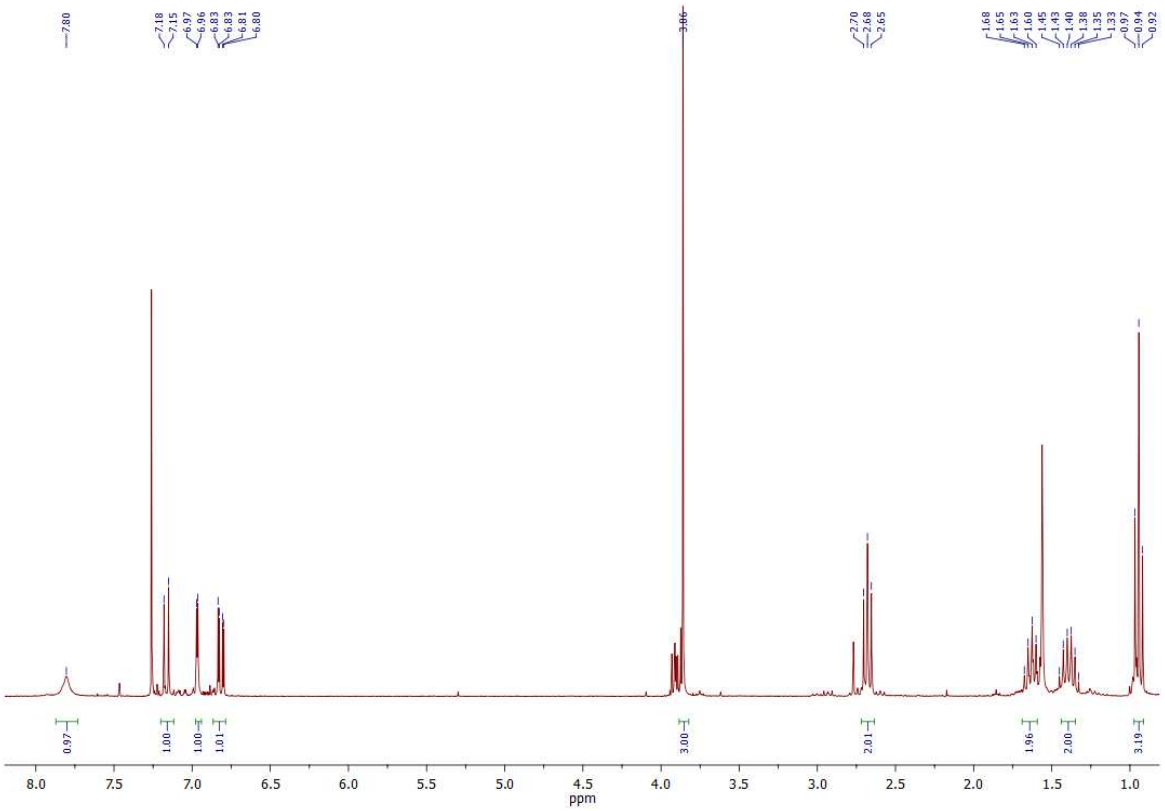


2,6-Bis[(5-methoxy)-1H-indol-2-yl]pyridine (6)

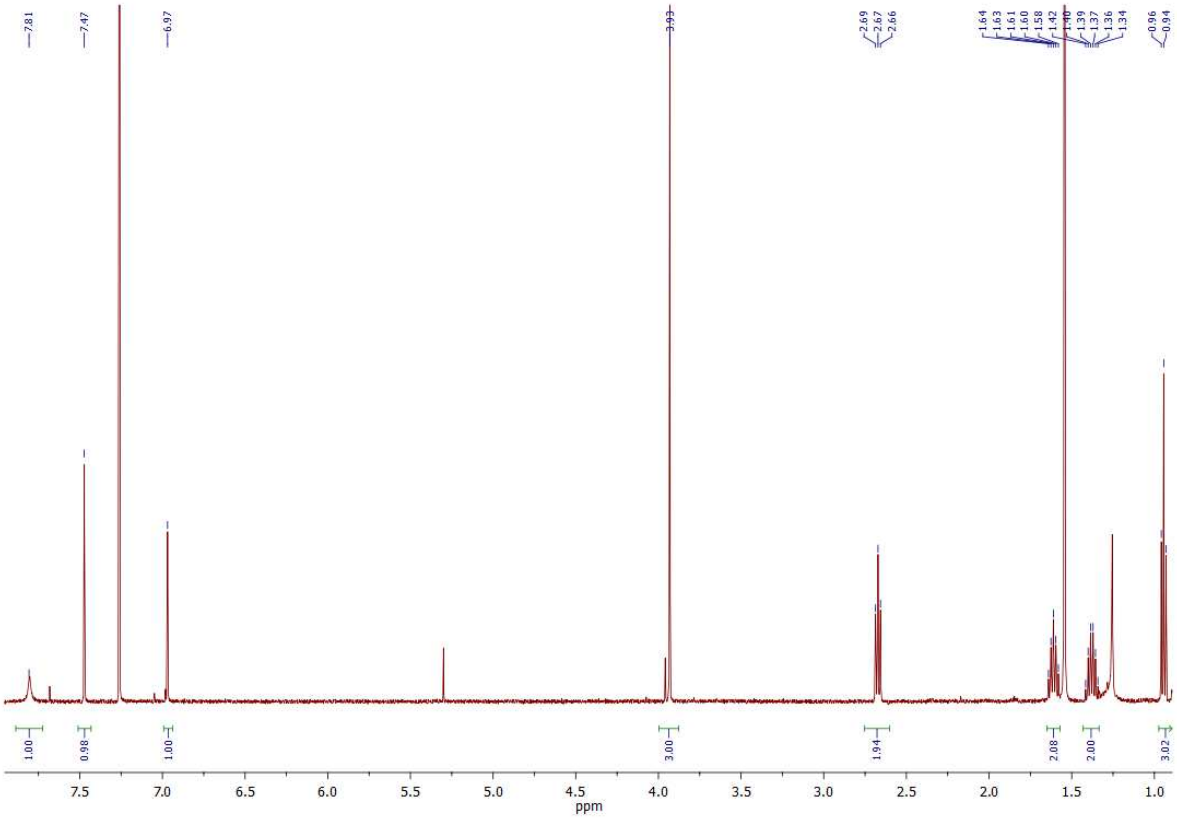




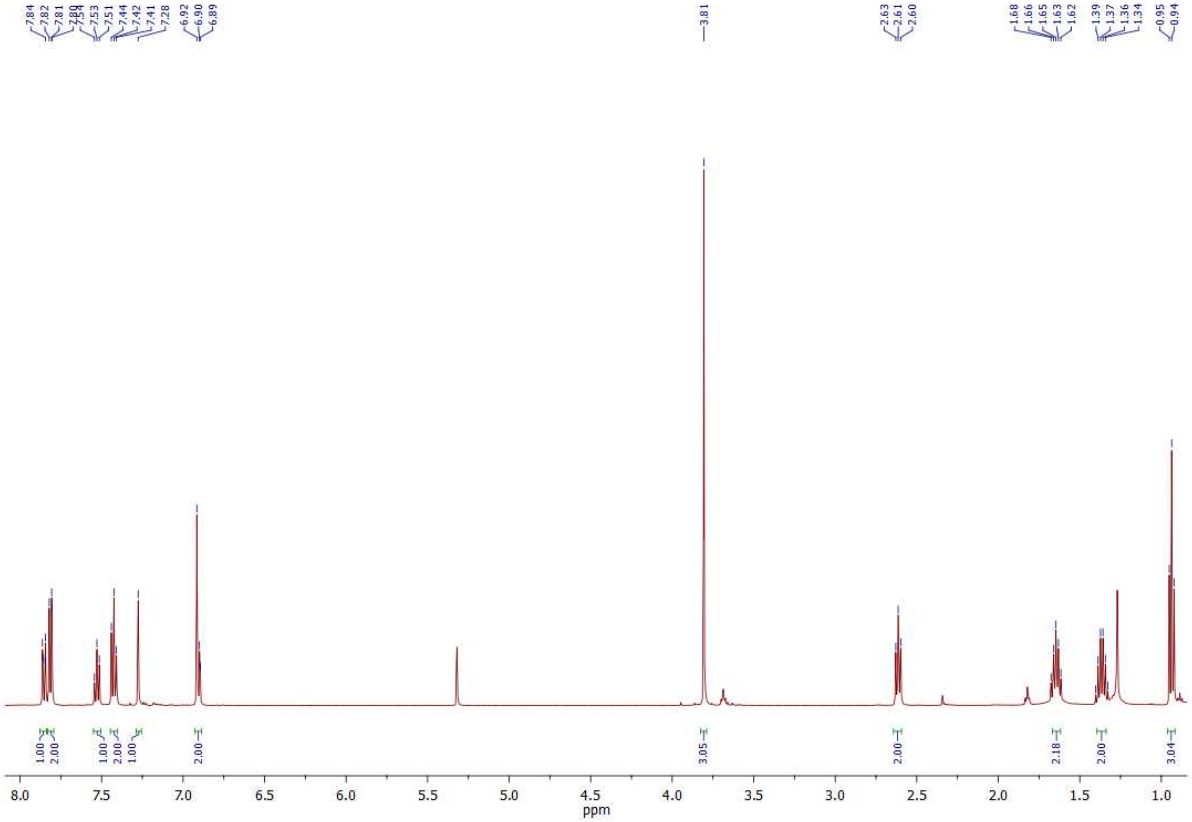
2-Bromo-3-*n*-butyl-5-methoxy-1H-indole (10)

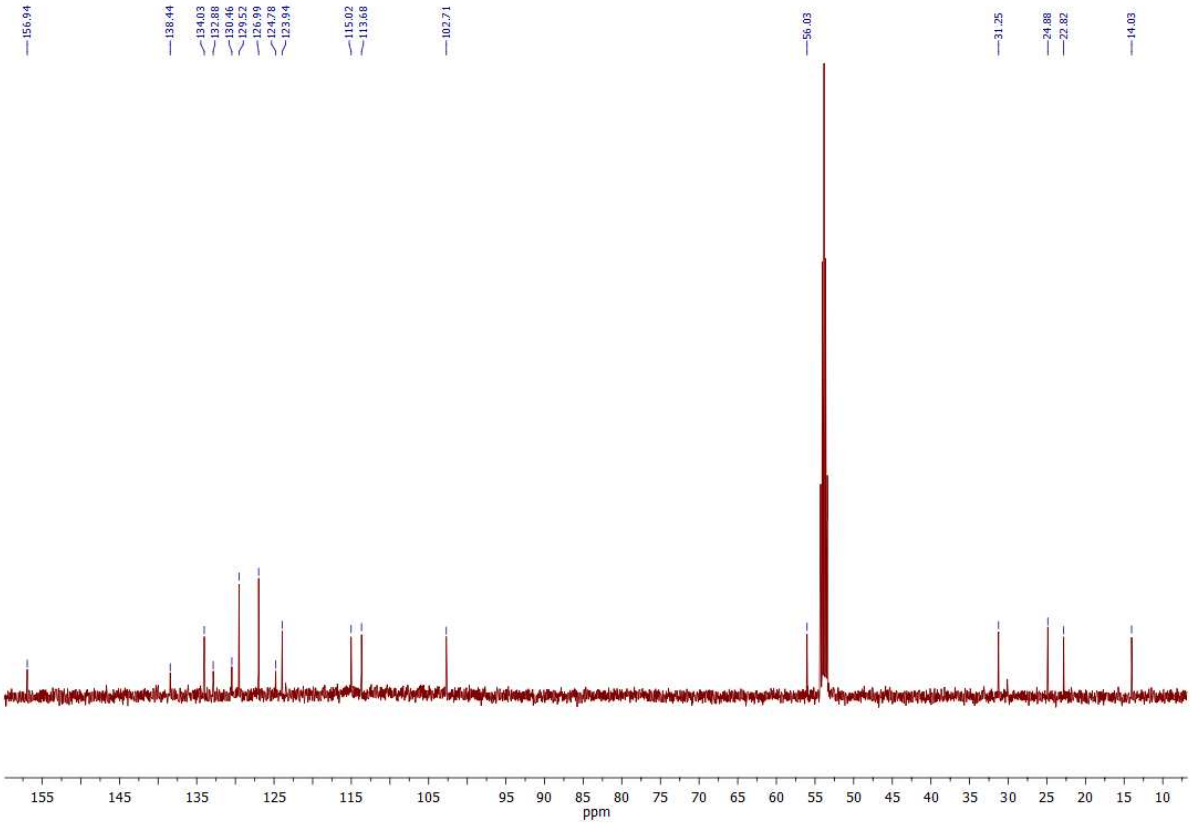


2,6-Dibromo-3-*n*-butyl-5-methoxy-1H-indole (11)

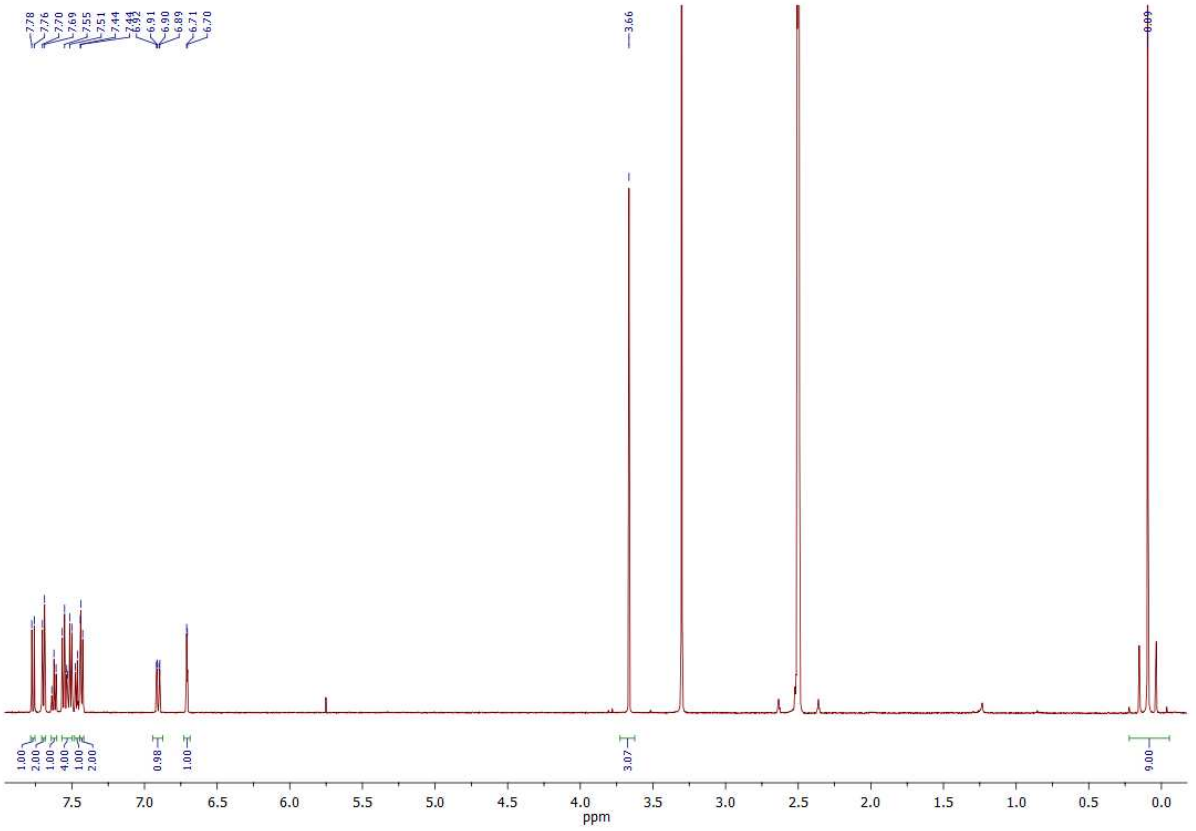


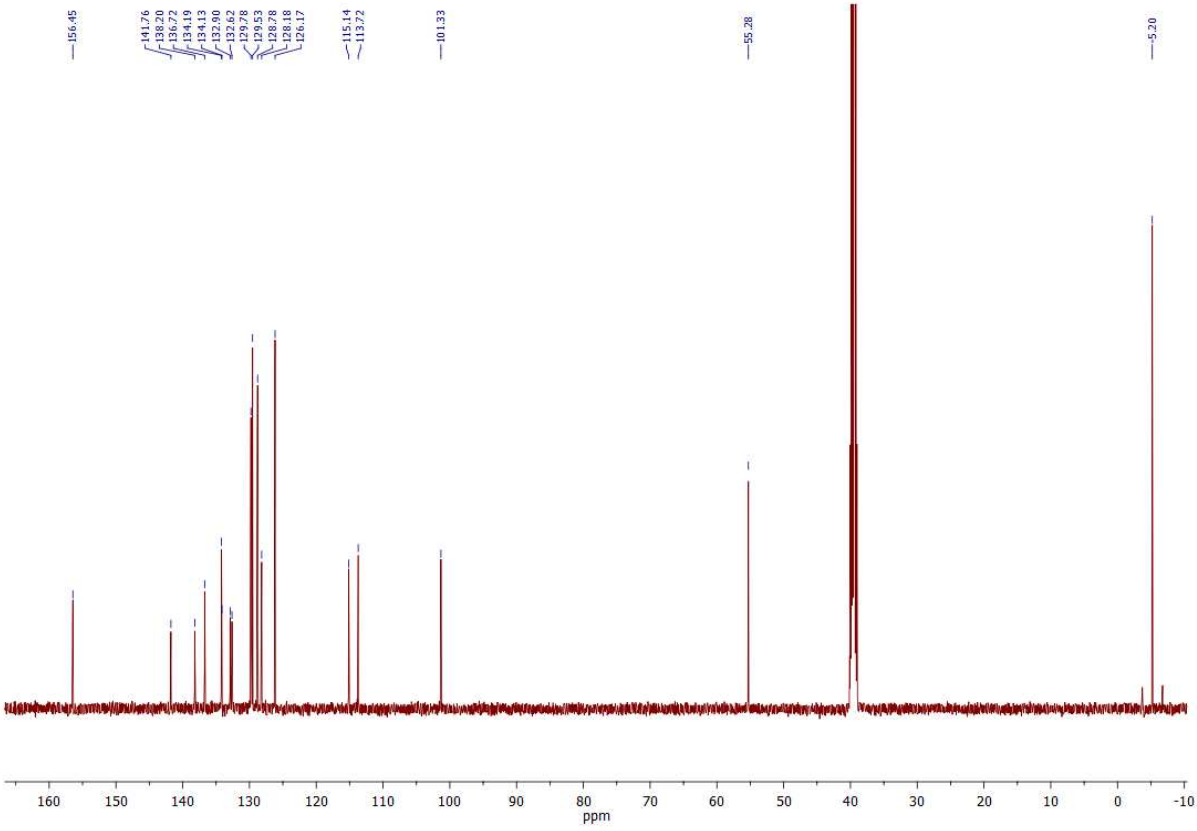
3-*n*-Butyl-5-methoxy-1-phenylsulfonylindole (12)



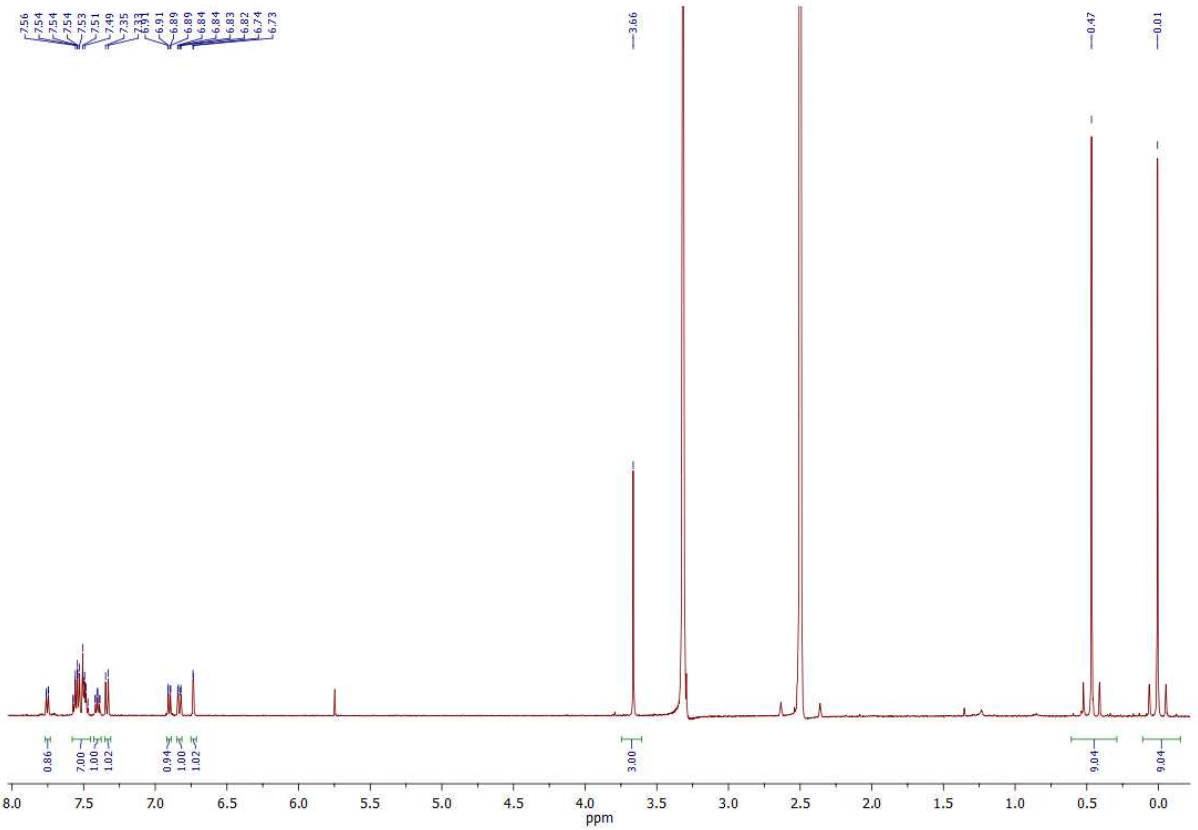


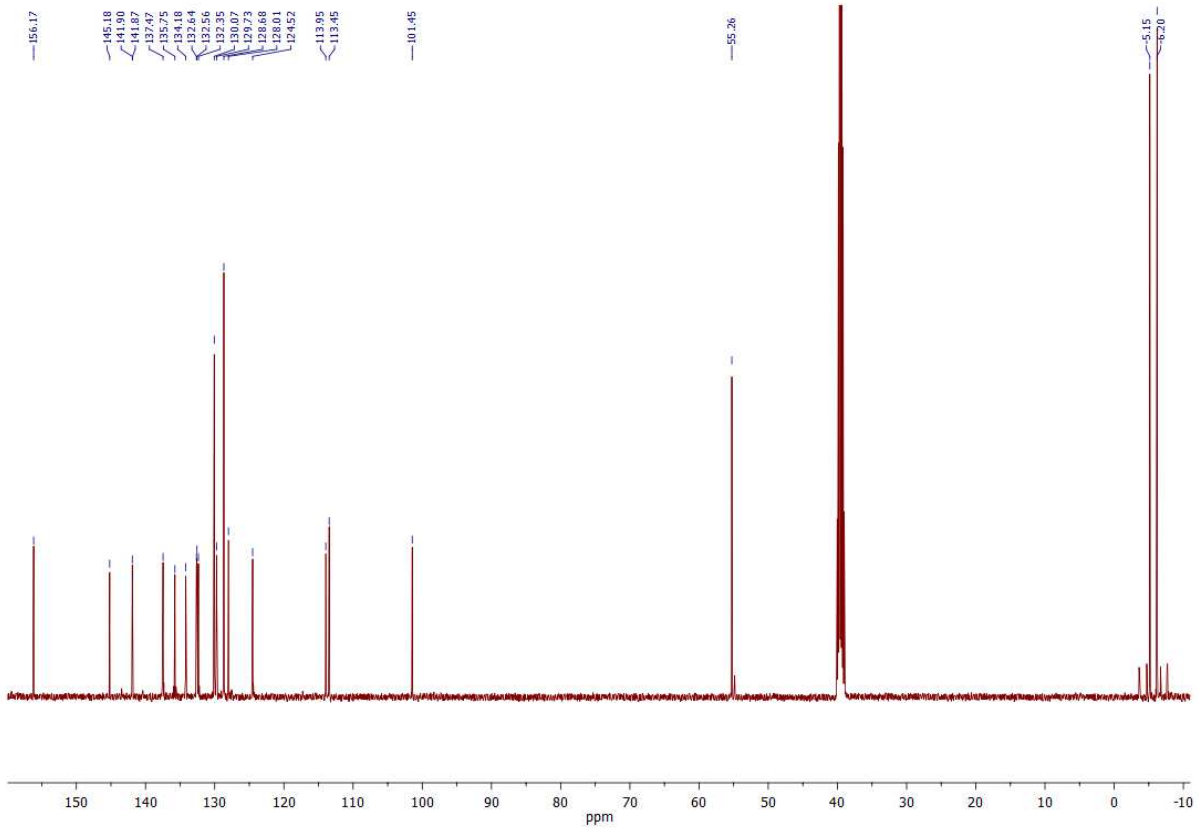
5-Methoxy-3-phenyl-1-phenylsulfonyl-2-trimethylstannylindole (15)



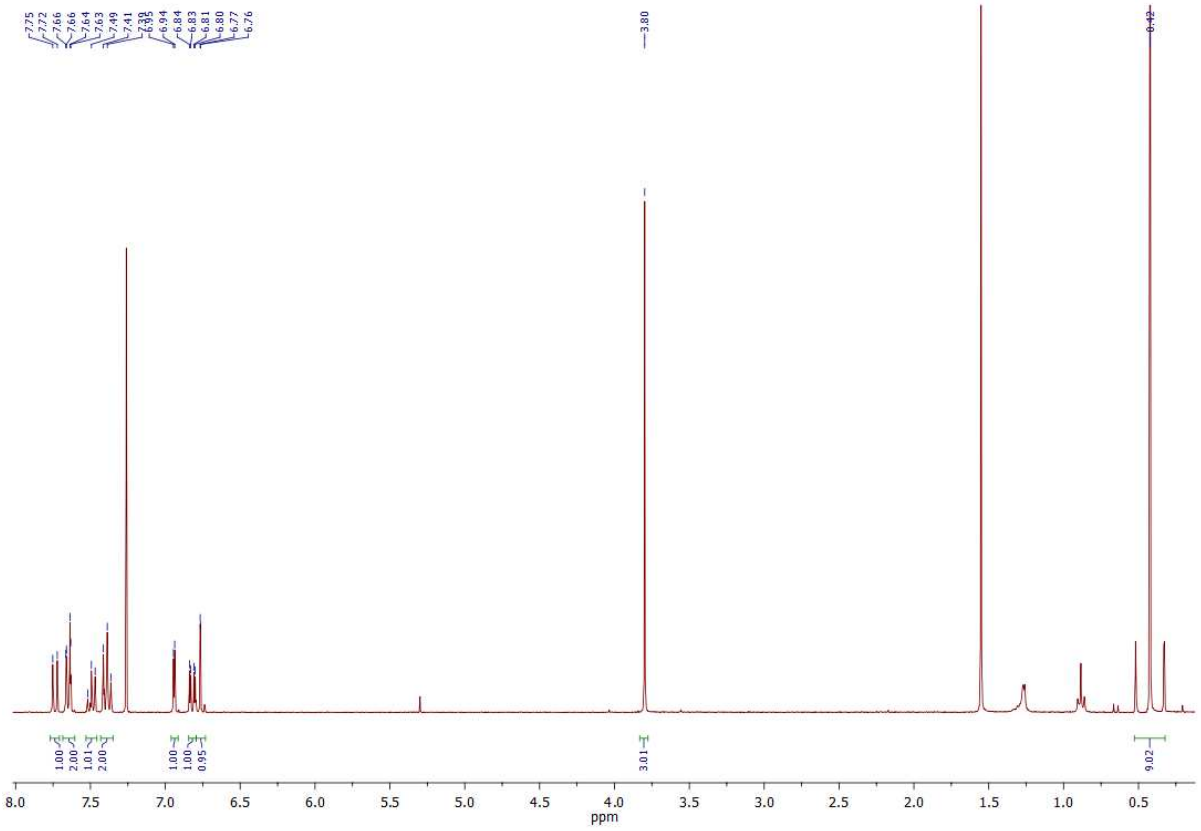


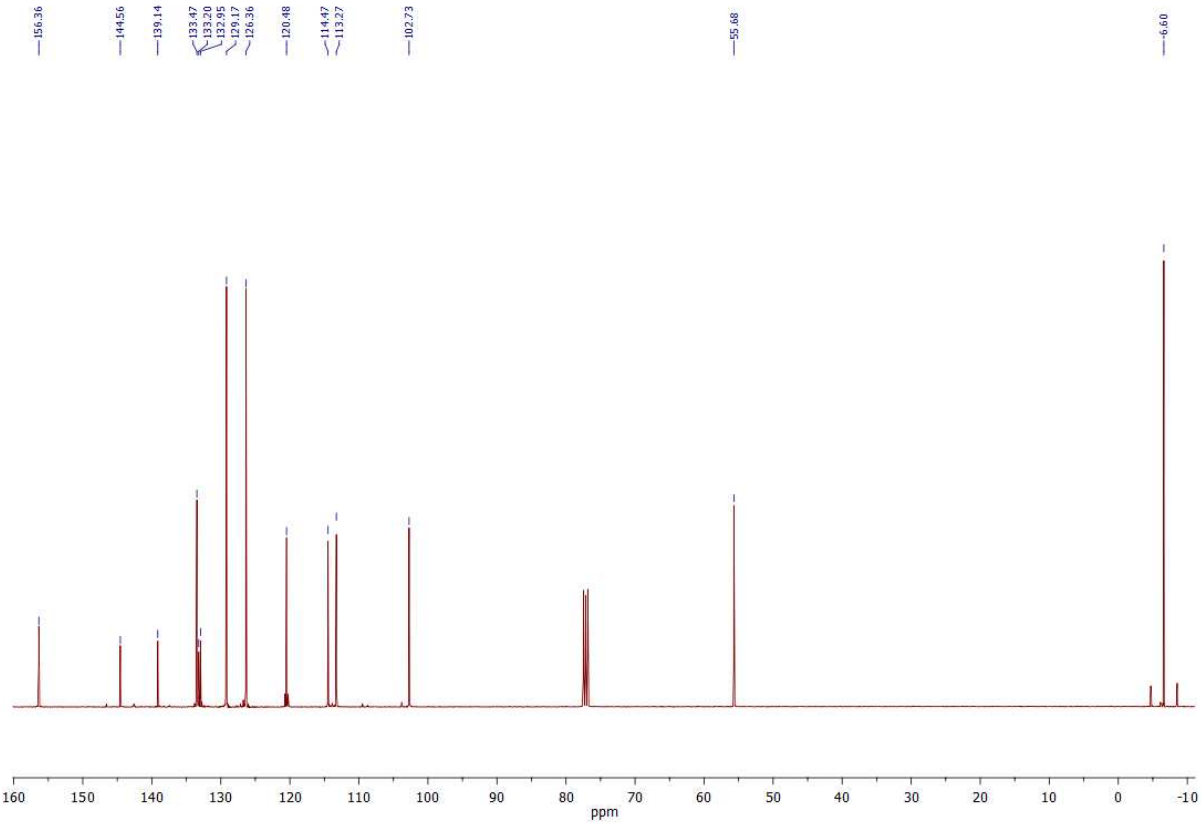
5-Methoxy-3-phenyl-1-[(2'-trimethylstannyl)phenylsulfonyl]-2-trimethylstannylindole (16)



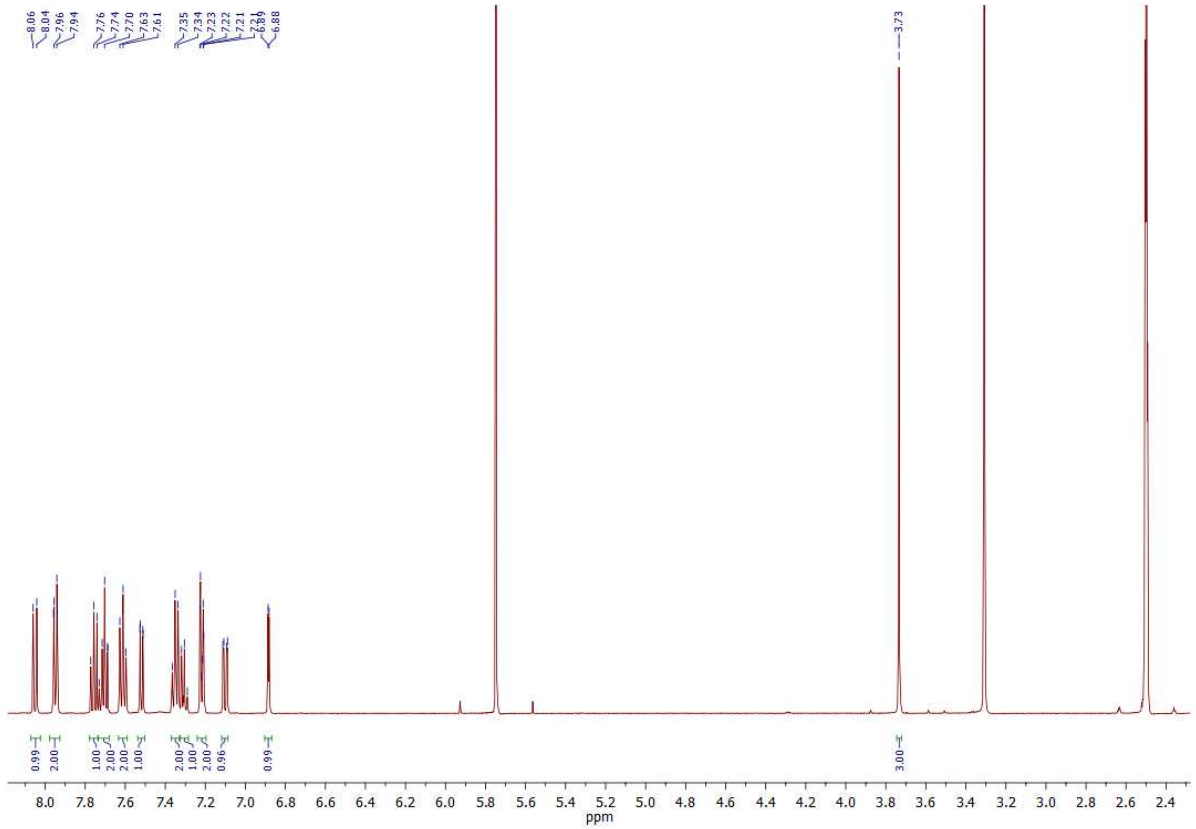


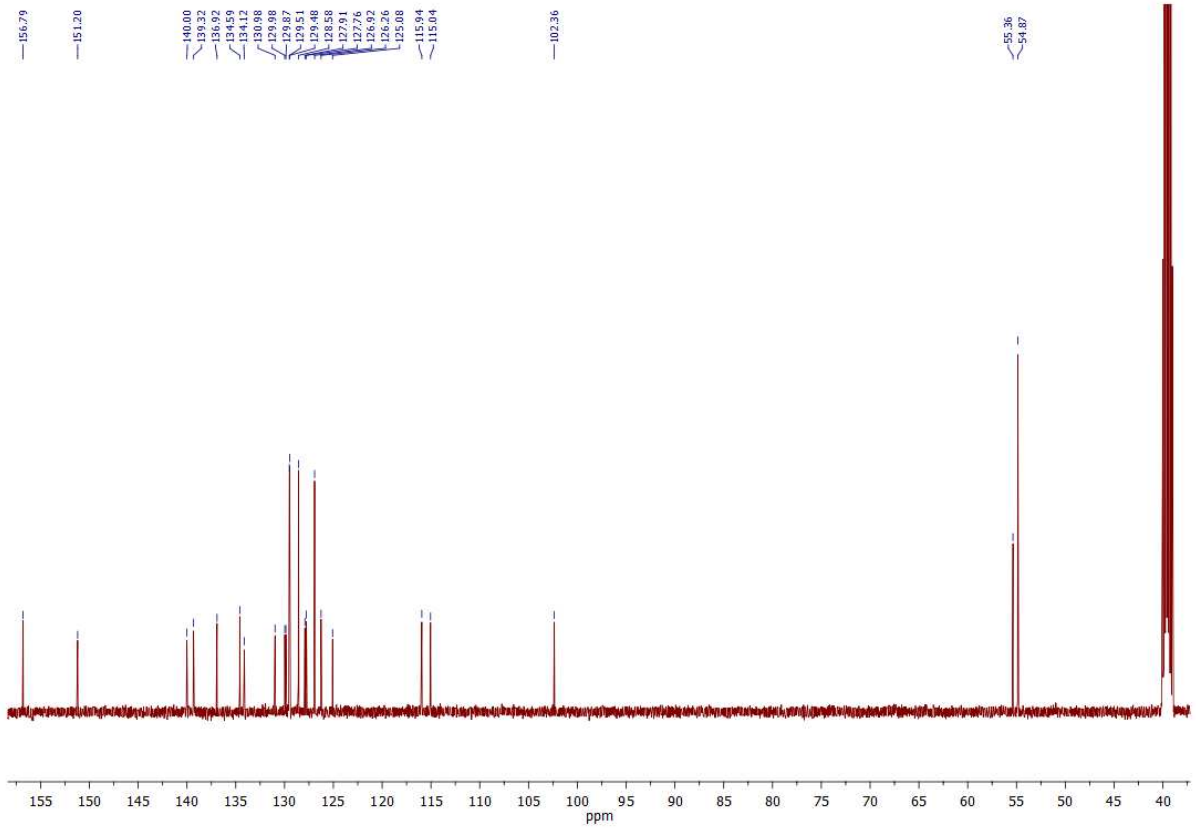
5-Methoxy-1-phenylsulfonyl-2-trimethylstannylindole (17)



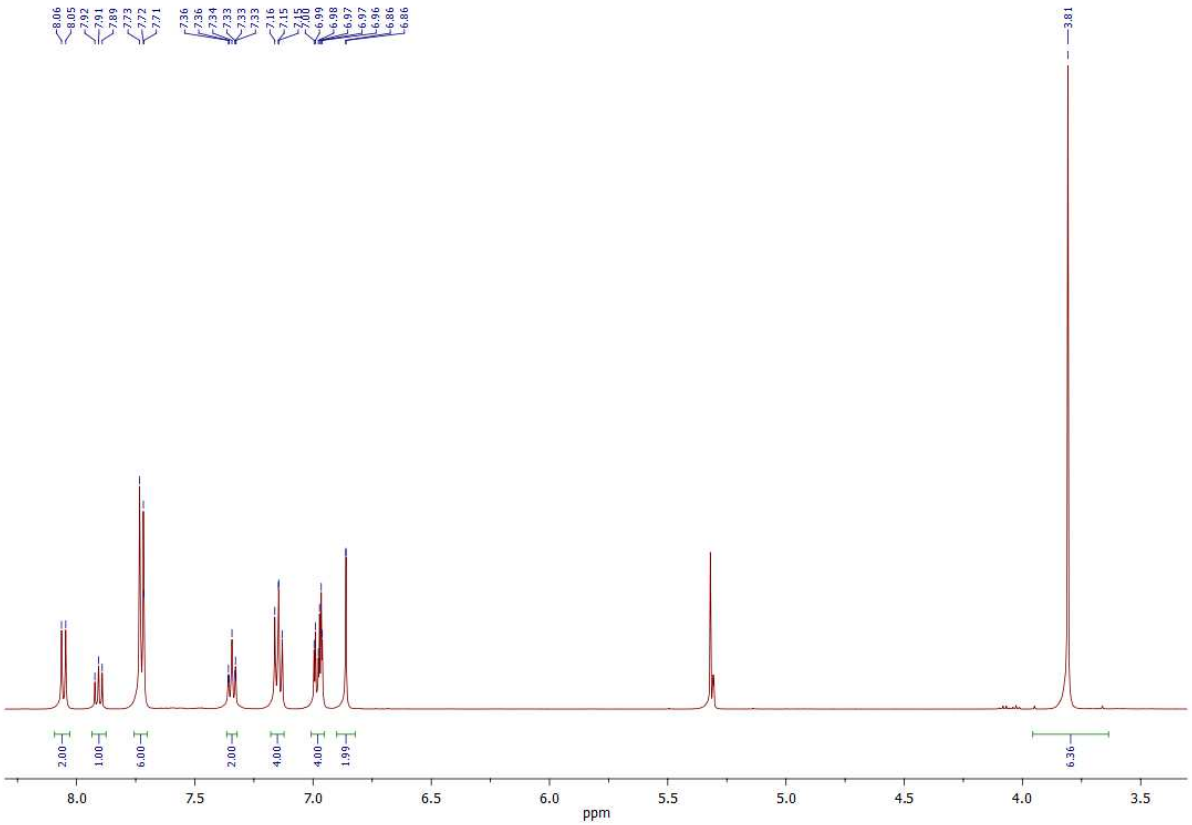


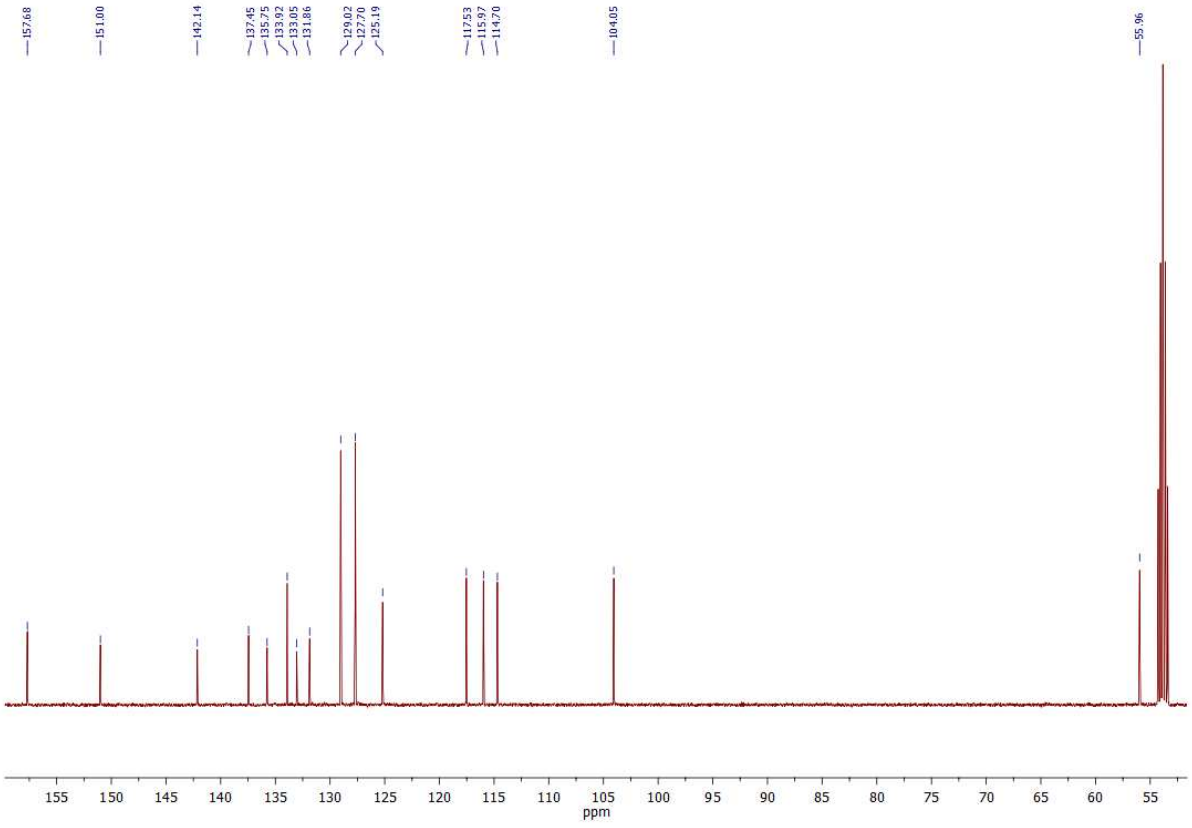
6-(5-Methoxy-3-phenyl-1-phenylsulfonylindol-2-yl)-2-bromopyridine (18)



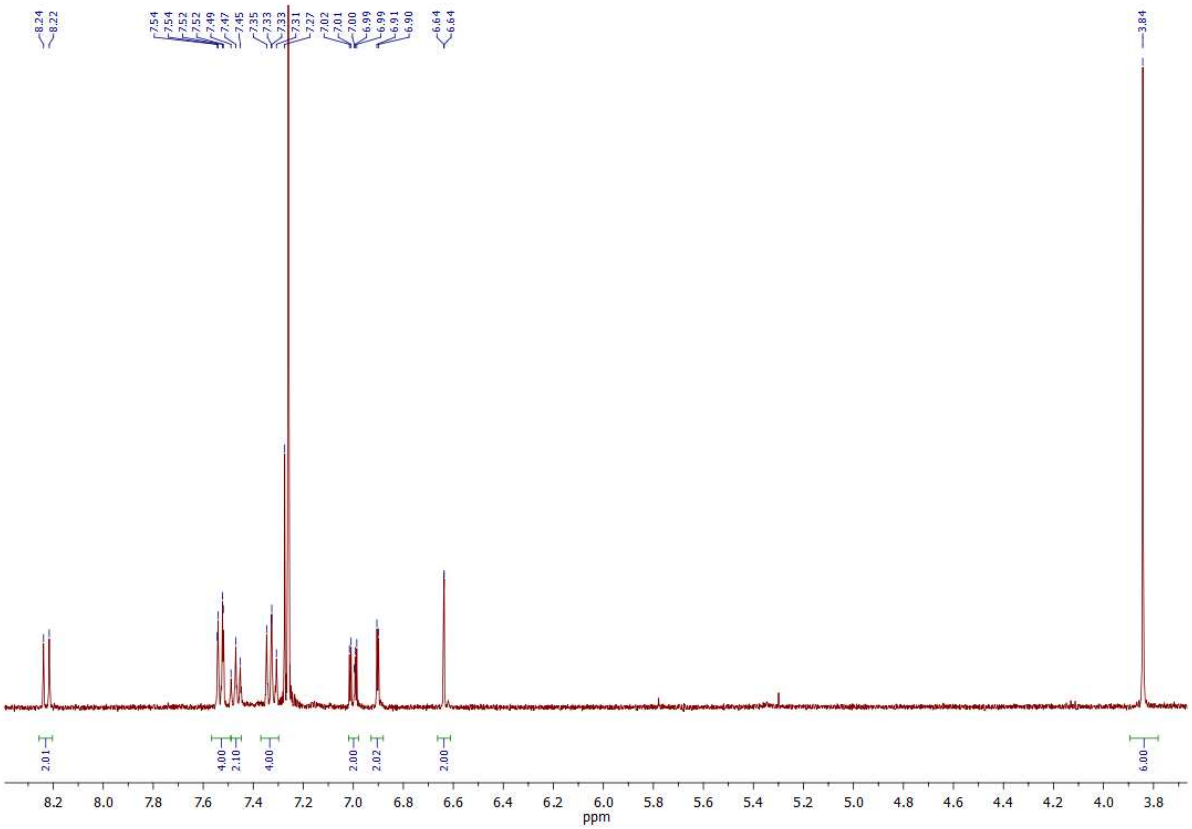


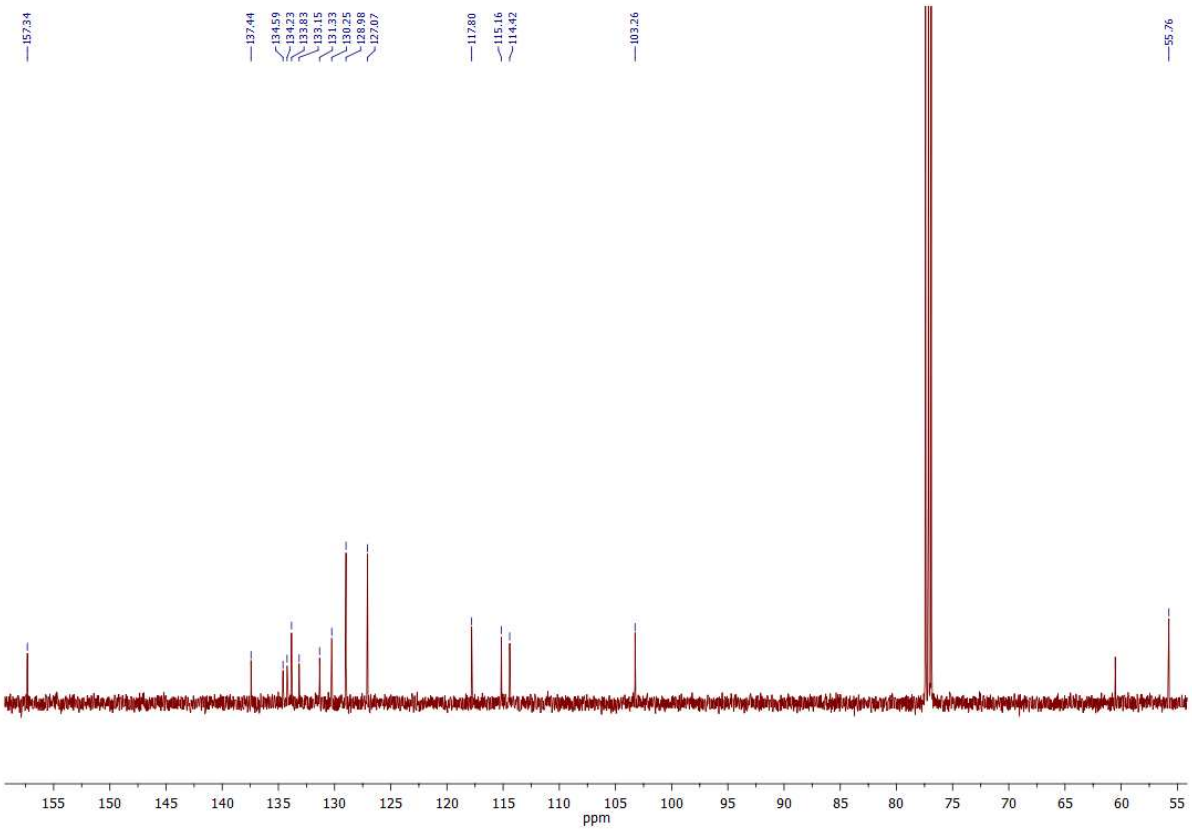
2,6-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)pyridine (19)



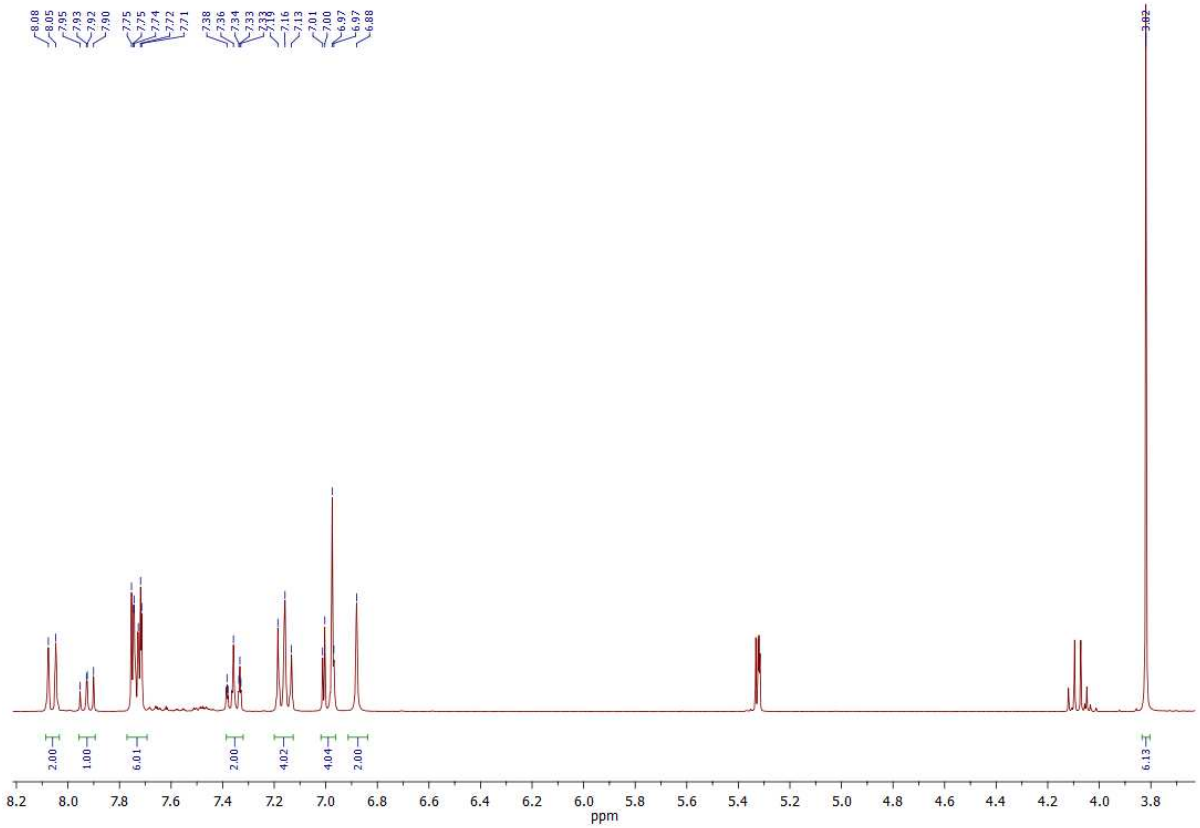


2,5-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)thiophene (20)

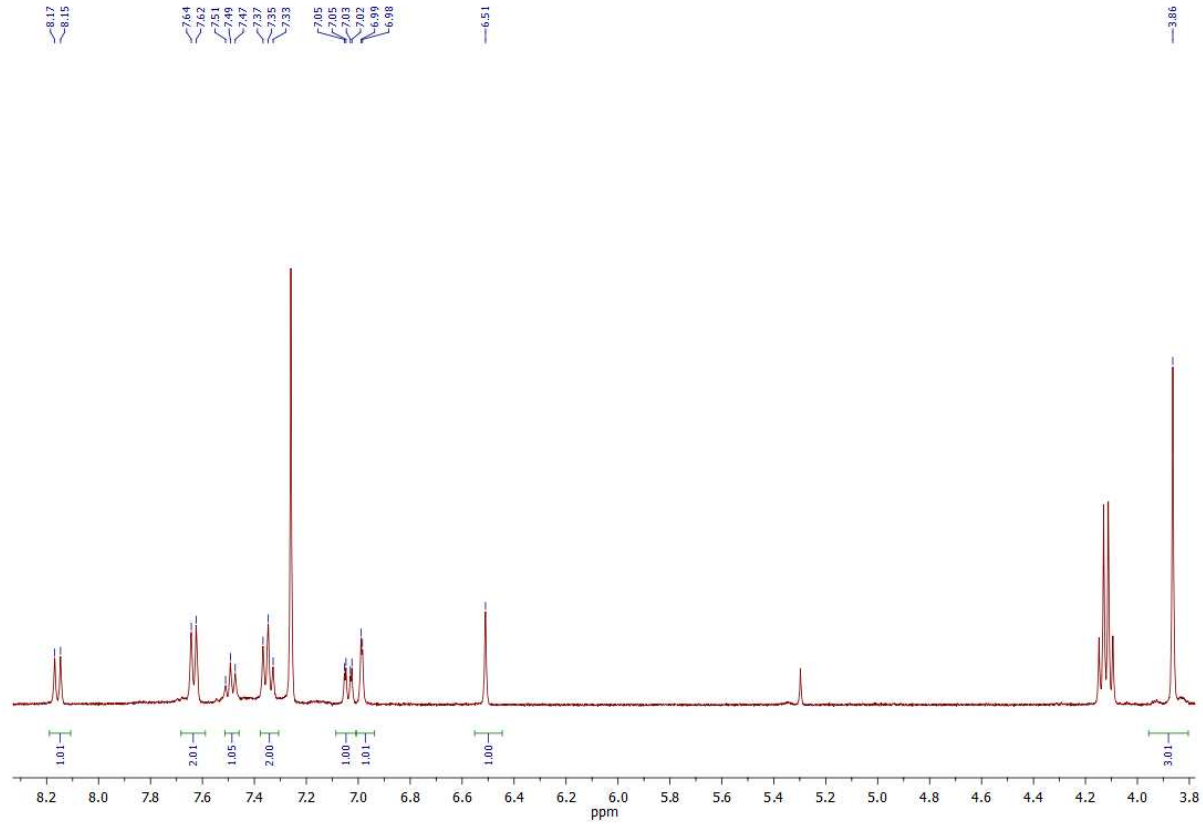




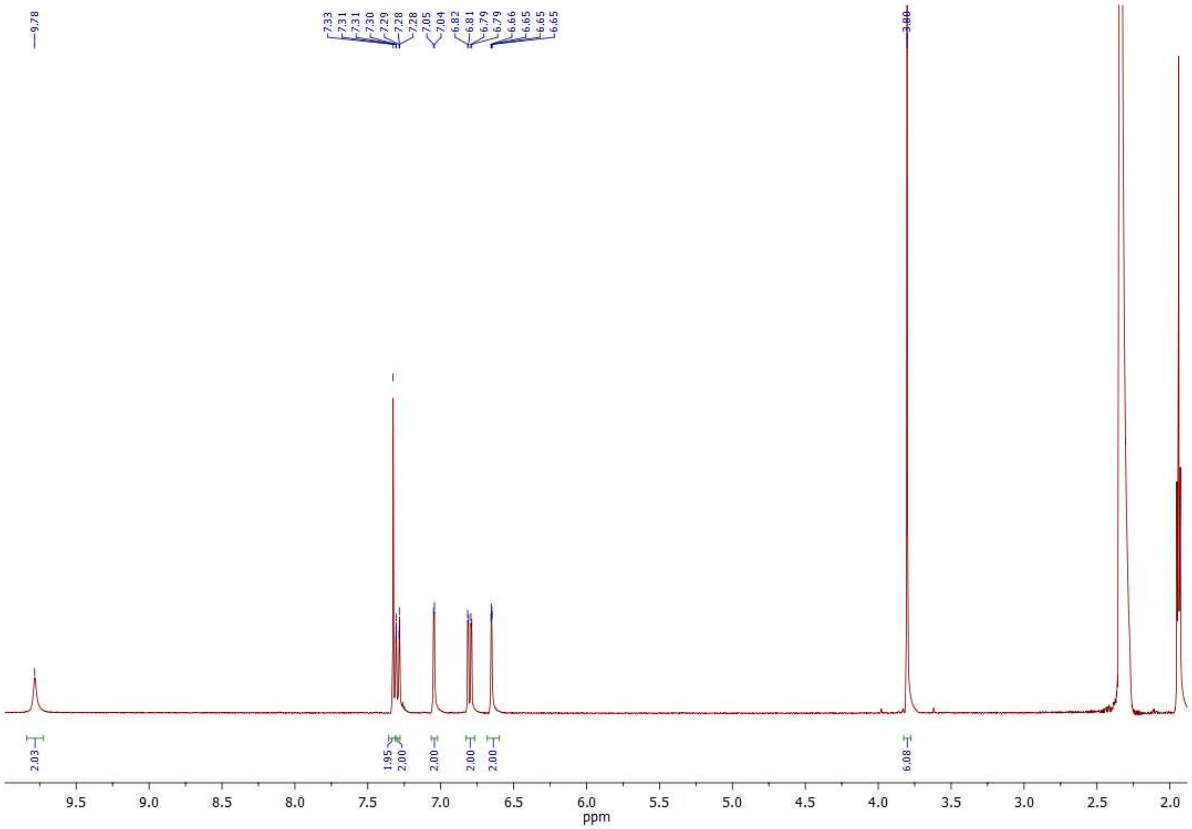
2,5-Bis(5-methoxy-1-phenylsulfonylindol-2-yl)thiazole (21) (Crude NMR spectrum)

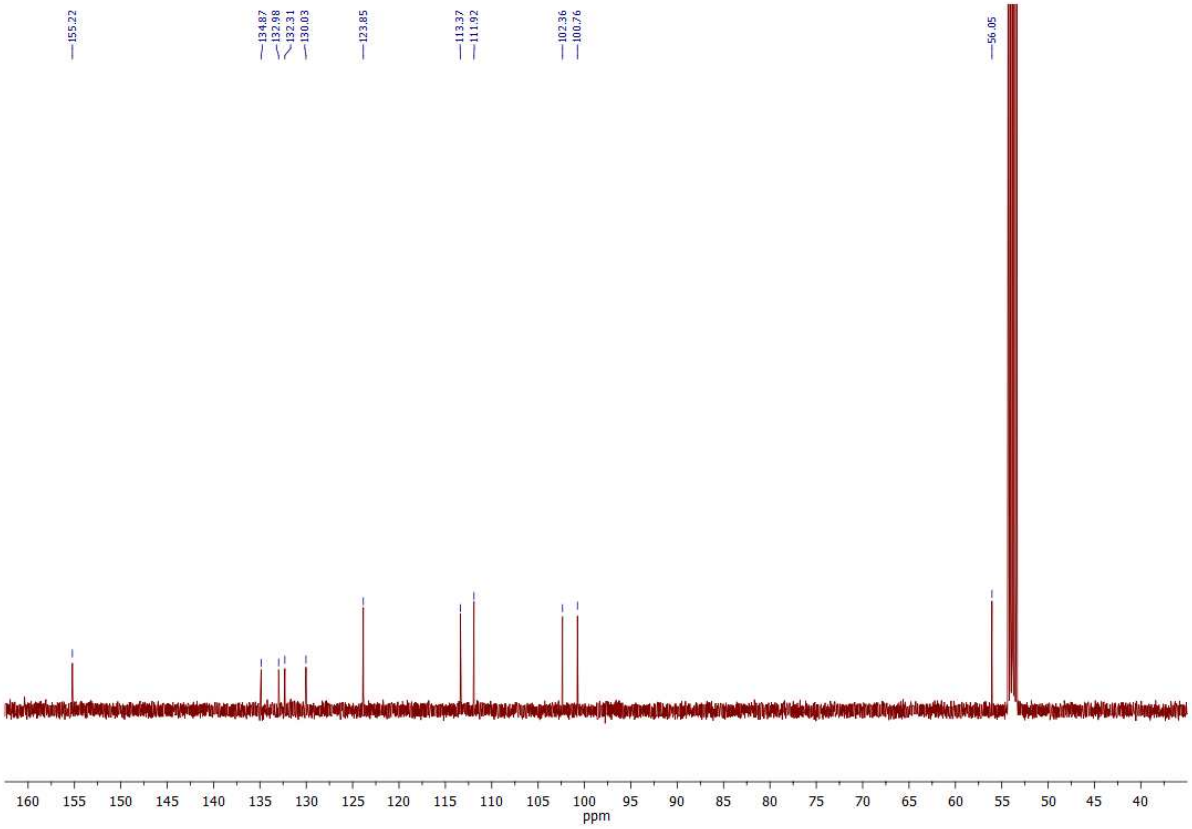


Bis(5-methoxy-1-phenylsulfonylindol-2-yl) (22)

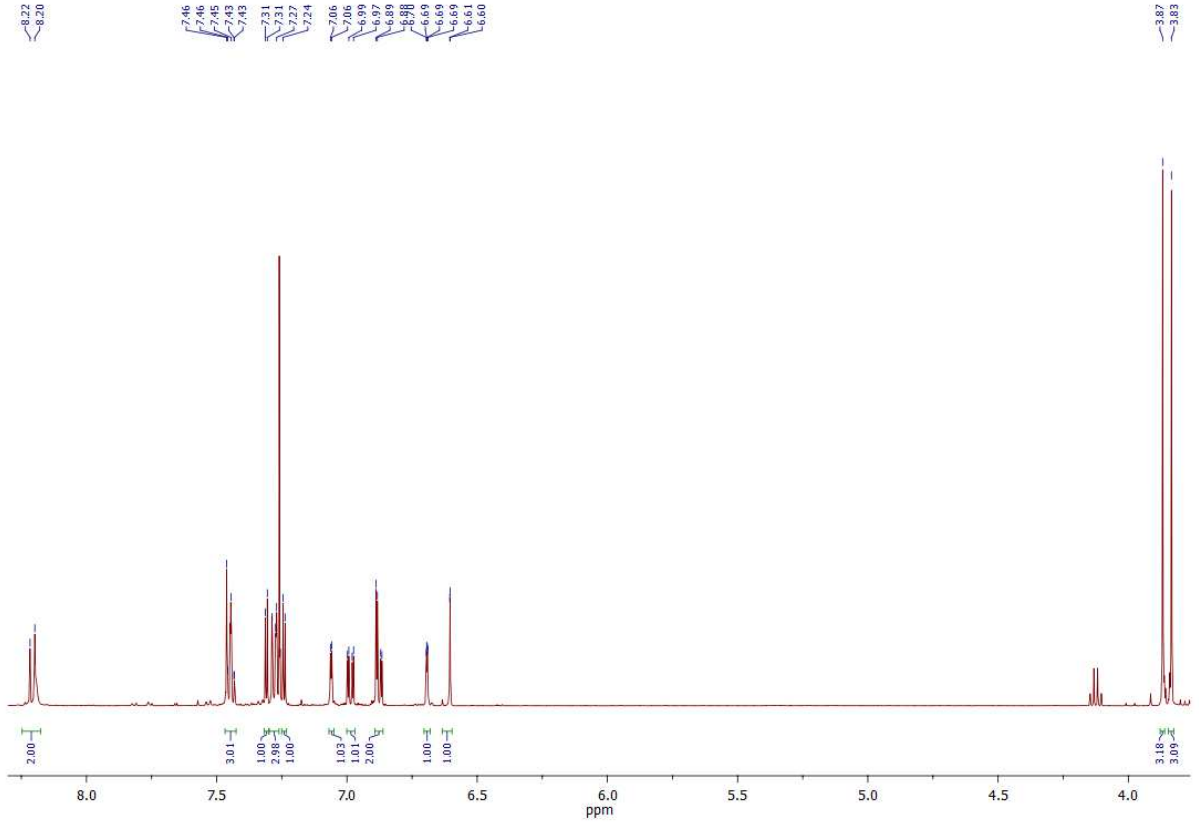


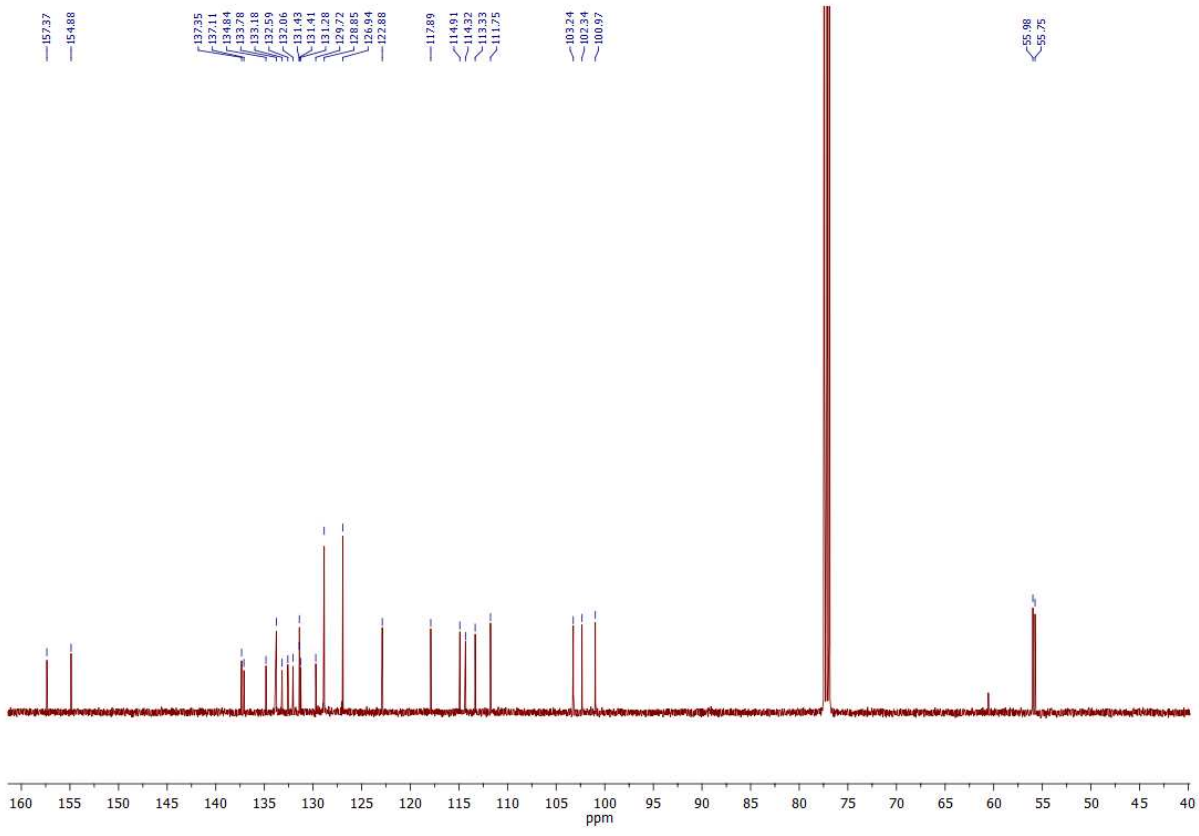
2,5-Bis(5-methoxy-1H-indol-2-yl)thiophene (23)



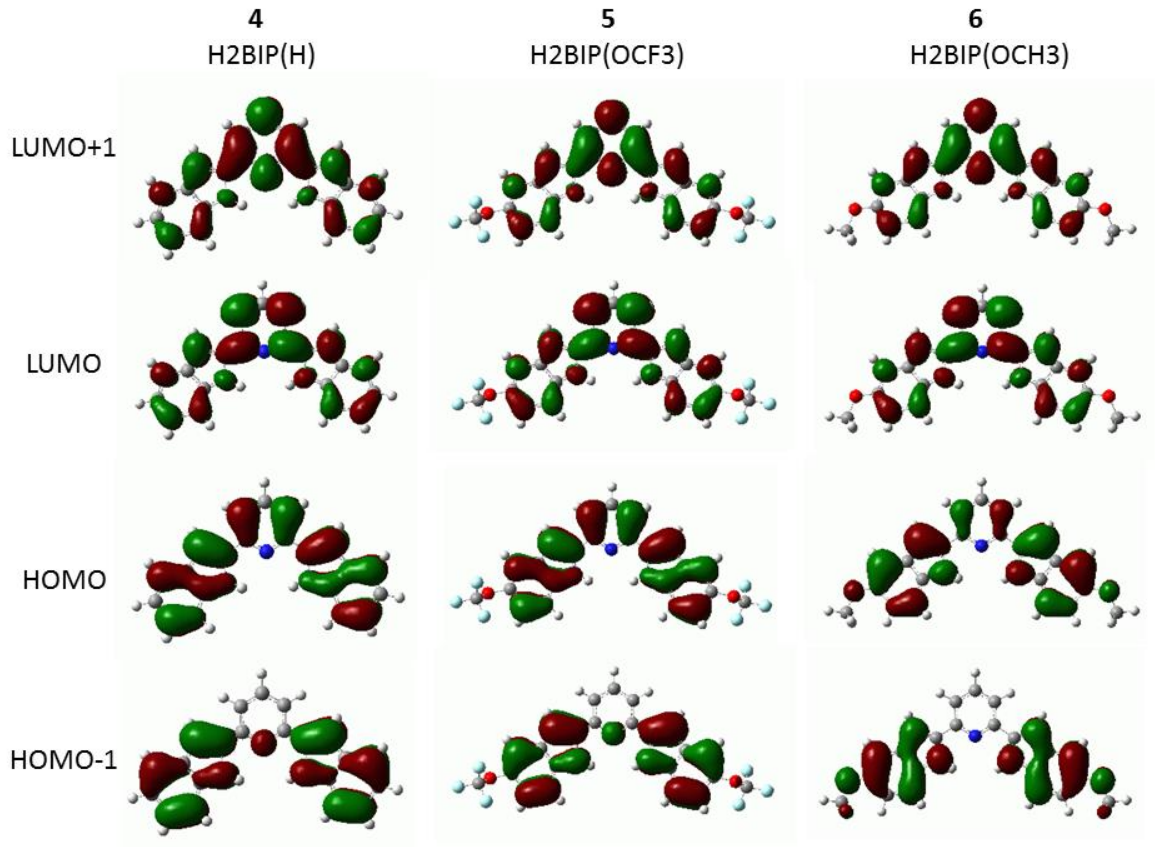


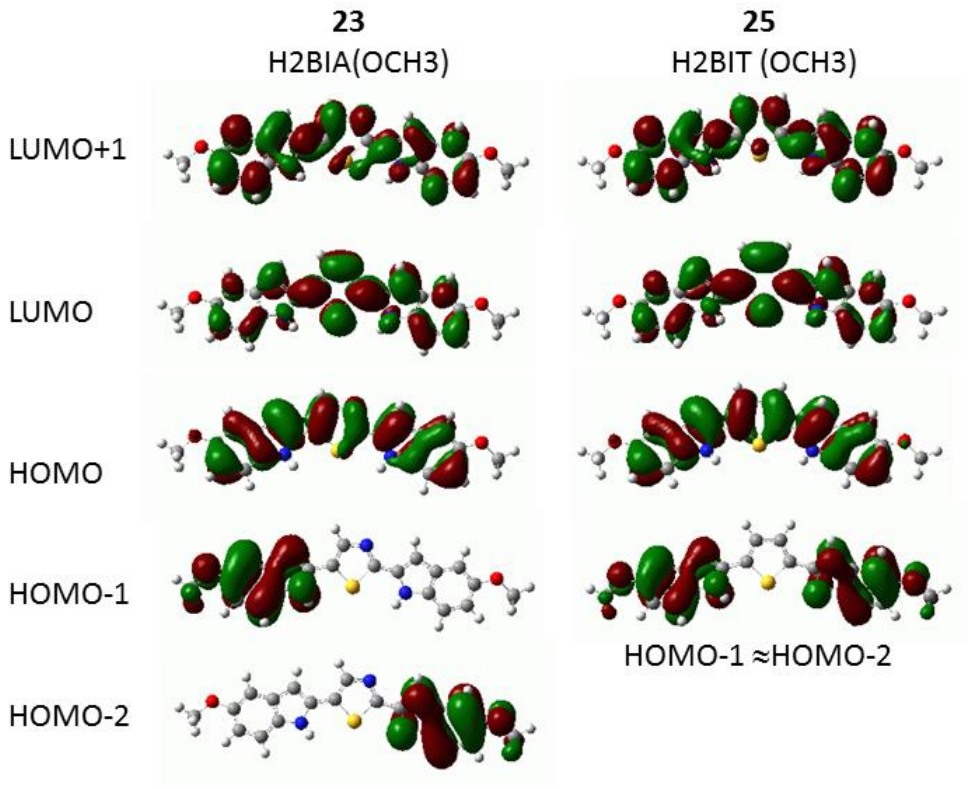
2-(5-Methoxy-1-phenylsulfonylindol-2yl)-5-(5-methoxy-1H-indol-2-yl)thiophene (24)





Enlarged images of molecular orbitals of 4-6, 23 and 25





Cartesian coordinates of optimized structures of 4-6, 23 and 25

Molecule **4**:

39 atoms

C	-0.0044	3.5619	-1.1049
C	0.0660	4.4864	-0.0216
C	0.1039	5.8649	-0.3045
C	0.0709	6.2805	-1.6260
C	0.0000	5.3471	-2.6830
C	-0.0383	3.9817	-2.4393
H	0.1582	6.5900	0.5018
H	-0.0245	5.7054	-3.7070
H	-0.0920	3.2665	-3.2535
N	-0.0260	2.3017	-0.5633
H	-0.0822	1.4261	-1.0582
C	0.0826	3.7138	1.1807
C	0.0249	2.3822	0.8153
C	0.0135	1.1599	1.6192
C	0.0129	1.2006	3.0204
N	0.0000	0.0000	0.9385
C	0.0000	0.0000	3.7191
H	0.0197	2.1467	3.5468
C	-0.0135	-1.1599	1.6192
C	-0.0129	-1.2006	3.0204
H	0.0000	0.0000	4.8036
H	-0.0197	-2.1467	3.5468
C	-0.0249	-2.3822	0.8153
C	-0.0826	-3.7138	1.1807
C	-0.0660	-4.4864	-0.0216
C	0.0044	-3.5619	-1.1049
C	-0.1039	-5.8649	-0.3045
C	0.0383	-3.9817	-2.4393
C	-0.0709	-6.2805	-1.6260

H	-0.1582	-6.5900	0.5018
C	0.0000	-5.3471	-2.6830
H	0.0920	-3.2665	-3.2535
H	0.0245	-5.7054	-3.7070
N	0.0260	-2.3017	-0.5633
H	0.0822	-1.4261	-1.0582
H	0.0995	7.3403	-1.8576
H	-0.0995	-7.3403	-1.8576
H	-0.1355	-4.0985	2.1883
H	0.1355	4.0985	2.1883

Molecule **5**:

47 atoms

C	-3.5347	-0.3759	-0.4181
C	-4.4635	0.7069	-0.4112
C	-5.8383	0.4306	-0.5116
C	-6.2195	-0.8910	-0.6122
C	-5.3057	-1.9583	-0.6297
C	-3.9458	-1.7079	-0.5308
H	-6.5814	1.2194	-0.5165
H	-5.6765	-2.9711	-0.7271
H	-3.2303	-2.5223	-0.5438
N	-2.2812	0.1660	-0.3071
H	-1.4031	-0.3281	-0.2875
C	-3.7011	1.9080	-0.2952
C	-2.3699	1.5422	-0.2337
C	-1.1535	2.3471	-0.1105
C	-1.1949	3.7477	-0.1153
N	0.0000	1.6660	0.0000
C	0.0000	4.4468	-0.0000
H	-2.1361	4.2741	-0.2114
C	1.1535	2.3471	0.1105

C	1.1949	3.7477	0.1153
H	0.0000	5.5311	-0.0000
H	2.1361	4.2741	0.2114
C	2.3699	1.5422	0.2337
C	3.7011	1.9080	0.2952
C	4.4635	0.7069	0.4112
C	3.5347	-0.3759	0.4181
C	5.8383	0.4306	0.5116
C	3.9458	-1.7079	0.5308
C	6.2195	-0.8910	0.6122
H	6.5814	1.2194	0.5165
C	5.3057	-1.9583	0.6297
H	3.2303	-2.5223	0.5438
H	5.6765	-2.9711	0.7272
N	2.2812	0.1660	0.3071
H	1.4031	-0.3281	0.2876
H	4.0923	2.9132	0.2550
H	-4.0923	2.9132	-0.2550
O	-7.5964	-1.1870	-0.7878
O	7.5964	-1.1870	0.7878
C	-8.3224	-1.4539	0.3109
C	8.3224	-1.4539	-0.3110
F	-7.8862	-2.5415	0.9828
F	-9.5813	-1.6849	-0.0743
F	-8.3361	-0.4359	1.1971
F	7.8862	-2.5415	-0.9828
F	9.5813	-1.6849	0.0743
F	8.3361	-0.4359	-1.1971

Molecule **6**:

47 atoms

C	3.5699	-0.6778	-0.0348

C	4.4923	0.4078	0.0162
C	5.8697	0.1387	0.0366
C	6.3024	-1.1824	0.0059
C	5.3734	-2.2476	-0.0452
C	4.0049	-2.0020	-0.0657
H	6.6044	0.9358	0.0759
H	5.7173	-3.2732	-0.0688
H	3.3019	-2.8273	-0.1044
N	2.3036	-0.1404	-0.0419
H	1.4292	-0.6382	-0.0833
C	3.7151	1.6073	0.0367
C	2.3829	1.2359	-0.0001
C	1.1600	2.0392	0.0012
C	1.2006	3.4405	0.0004
N	0.0000	1.3585	-0.0000
C	0.0000	4.1393	0.0000
H	2.1468	3.9668	-0.0019
C	-1.1600	2.0392	-0.0012
C	-1.2006	3.4405	-0.0004
H	0.0000	5.2238	0.0000
H	-2.1468	3.9668	0.0020
C	-2.3829	1.2359	0.0001
C	-3.7151	1.6073	-0.0367
C	-4.4923	0.4078	-0.0162
C	-3.5699	-0.6778	0.0348
C	-5.8697	0.1387	-0.0366
C	-4.0049	-2.0020	0.0657
C	-6.3024	-1.1824	-0.0059
H	-6.6044	0.9358	-0.0758
C	-5.3734	-2.2476	0.0452
H	-3.3019	-2.8273	0.1043
H	-5.7173	-3.2732	0.0687
N	-2.3036	-0.1404	0.0419
H	-1.4292	-0.6382	0.0832

H	-4.0962	2.6168	-0.0779
H	4.0962	2.6168	0.0780
O	7.6627	-1.3648	0.0284
O	-7.6627	-1.3648	-0.0284
C	8.1773	-2.6911	0.0018
H	9.2606	-2.5887	0.0269
H	7.8507	-3.2683	0.8726
H	7.8874	-3.2183	-0.9127
C	-8.1773	-2.6911	-0.0016
H	-9.2606	-2.5886	-0.0266
H	-7.8508	-3.2684	-0.8724
H	-7.8873	-3.2182	0.9129

Molecule **23**:

44 atoms

C	4.5313	-0.7613	-0.0361
C	4.9101	0.6103	0.0263
C	6.2719	0.9496	-0.0059
C	7.2196	-0.0638	-0.0924
C	6.8248	-1.4212	-0.1479
C	5.4813	-1.7775	-0.1206
H	6.6015	1.9821	0.0362
H	7.5680	-2.2048	-0.2142
H	5.1911	-2.8218	-0.1659
O	8.5286	0.3437	-0.1182
C	9.5520	-0.6411	-0.2143
H	10.4912	-0.0914	-0.2215
H	9.5395	-1.3204	0.6437
H	9.4674	-1.2209	-1.1386
N	3.1538	-0.8153	0.0005
H	2.6150	-1.6654	0.0429
C	3.7042	1.3678	0.1124

C	2.6505	0.4713	0.0988
C	1.2371	0.7692	0.1534
S	-0.0058	-0.4657	-0.0682
C	-0.6089	1.9703	0.3645
C	-1.2343	0.7621	0.1624
H	-1.1361	2.8981	0.5470
C	-2.6525	0.4859	0.0999
C	-3.6862	1.3420	-0.2329
C	-4.5527	-0.7230	0.2472
C	-4.9045	0.5994	-0.1445
C	-5.5175	-1.7102	0.4321
C	-6.2537	0.9136	-0.3661
C	-6.8513	-1.3778	0.2159
H	-5.2469	-2.7163	0.7347
C	-7.2179	-0.0730	-0.1846
H	-6.5635	1.9072	-0.6719
H	-7.6056	-2.1402	0.3585
O	-8.5140	0.3116	-0.4176
C	-9.5525	-0.6490	-0.2616
H	-10.4769	-0.1264	-0.5000
H	-9.4282	-1.4919	-0.9487
H	-9.6054	-1.0226	0.7658
N	-3.1778	-0.7680	0.3704
H	-2.6626	-1.5355	0.7715
H	3.6018	2.4407	0.1639
H	-3.5723	2.3695	-0.5451
N	0.7518	1.9699	0.3551

Molecule **25**:

45 atoms

C	4.4967	-0.6829	-0.3483
C	4.9244	0.5603	0.1974

C	6.2913	0.7727	0.4301
C	7.1982	-0.2327	0.1084
C	6.7569	-1.4564	-0.4428
C	5.4035	-1.6884	-0.6722
H	6.6592	1.7027	0.8505
H	7.4669	-2.2337	-0.6925
H	5.0746	-2.6332	-1.0917
O	8.5165	0.0523	0.3619
C	9.4990	-0.9330	0.0641
H	10.4539	-0.4938	0.3466
H	9.3392	-1.8489	0.6418
H	9.5165	-1.1755	-1.0031
N	3.1198	-0.6390	-0.4523
H	2.5634	-1.3166	-0.9492
C	3.7492	1.3495	0.3972
C	2.6655	0.5984	-0.0212
C	1.2627	0.9535	-0.0244
C	0.7068	2.2135	-0.0180
S	0.0000	-0.2656	0.0000
C	-0.7068	2.2135	0.0180
H	1.3044	3.1161	-0.0456
C	-1.2627	0.9535	0.0244
H	-1.3044	3.1161	0.0456
C	-2.6655	0.5984	0.0213
C	-3.7492	1.3495	-0.3972
C	-4.4967	-0.6829	0.3483
C	-4.9244	0.5603	-0.1974
C	-5.4035	-1.6884	0.6722
C	-6.2913	0.7727	-0.4301
C	-6.7569	-1.4563	0.4428
H	-5.0746	-2.6332	1.0918
C	-7.1982	-0.2327	-0.1084
H	-6.6591	1.7027	-0.8505
H	-7.4669	-2.2337	0.6925

O	-8.5165	0.0523	-0.3619
C	-9.4990	-0.9330	-0.0642
H	-10.4539	-0.4938	-0.3467
H	-9.3392	-1.8489	-0.6418
H	-9.5165	-1.1755	1.0031
N	-3.1198	-0.6390	0.4523
H	-2.5635	-1.3166	0.9492
H	3.6959	2.3347	0.8363
H	-3.6959	2.3346	-0.8363