Supporting Information

Efficient Synthesis of Dipyrrolobenzenes and Dipyrrolopyrazines *via* Bidirectional Gold-Catalysis – A Combined Synthetic and Photophysical Study

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1 Experimental Procedures

1.1 General Information

Chemicals were bought from commercial suppliers (abcr, Acros, Alfa Aesar, Carbolution, Chempur, Fluka, Merck, Sigma Aldrich and TCI) and used as delivered. Anhydrous solvents were dispensed from a solvent purification system MB SPS-800. Solvents were degassed by freeze-pump-thaw technique. Deuterated solvents were bought from Eurisotop and Sigma Aldrich.

Melting points (mp) were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and are uncorrected.

R_f-values were determined by analytical thin layer chromatography (TLC) on aluminum sheets coated with silica gel produced by Macherey-Nagel (ALUGRAM® Xtra SIL G/25 UV_{254}). Detection was accomplished using UV-light (254 and 365 nm) or a TLC staining solution (vanillin and ninhydrine).

Nuclear magnetic resonance (NMR) spectra were, if not mentioned otherwise, recorded at room temperature at the organic chemistry department of Heidelberg University under the supervision of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Fourier 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz), Bruker Avance NEO 700 (700 MHz). $CDCl_3$ was filtered through a plug of aluminum oxide (alox) to remove acid impurities. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Spectra were referenced to residual solvent protons according to Fulmer *et al*.[1] or for TCE-d_2 to 6.00 ppm (^{1}H) and 73.8 ppm (^{13}C), respectively. The following abbreviations were used to describe the observed multiplicities: for ^{1}H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext =sextet, sept = septet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad signal; for ^{13}C{^{1}H} NMR spectra: s = quaternary carbon, d = CH carbon, t = CH_2 carbon and q = CH_3 carbon. ^{13}C{^{1}H} NMR spectra are proton decoupled and interpreted with help of DEPT- and 2D spectra. All spectra were integrated and processed using Bruker TopSpin 4.1.1 software.

High-resolution mass spectra (HR-MS) were recorded at the chemistry department of Heidelberg University under the supervision of Dr. J. Gross on the following spectrometers: JEOL AccuTOF GCx (EI)**,** Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, MALDI, DART), Finnigan LCQ (ESI), Bruker AutoFlex Speed (MALDI) and Bruker timsTOFfleX (ESI, MALDI).

UPLC-MS were recorded on a Waters UPLC-SQD2 equiped with BEH C18 column. Various combinations of acetonitrile/water were used as eluent. All spectra were adapted with Spectrus Processor software from ACDLabs.

Infrared spectra were recorded from a neat powder or oil on a FT-IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal. For the most significant bands the wave numbers are given.

UV-Vis spectra were recorded on a Jasco UV-VIS V-670. Fluorescence spectra were recorded on a Jasco FP6500. Quantum yields (QY) were recorded on a Jasco FP-8600 fluorescence spectrometer equipped with a ILF-835 100 mm dia. integrating sphere or determined according to the Publication from C. Würth *et al*. using quinine sulfate dihydrate as standard.[2]

X-ray crystallography was carried out at the chemistry department of Heidelberg University under the supervision of Dr. F. Rominger on the following instruments: Bruker Smart APEX II Quazar (with Mo-microsource) and Stoe Stadivari (with Co-microsource and Pilatus detector). The structures were processed with Mercury 4.3.0.

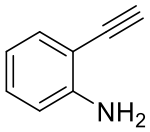
For flash column chromatography silica gel (Sigma-Aldrich, pore size 60 Å, 70–230 mesh, 63–200 µm) or aluminum oxide (Honeywell, pore size 60 Å, activated, neutral) was used as stationary phase. As eluents different mixtures of petroleum ether (PE), ethyl acetate (EA) or dichloromethane (DCM) were used.

1.2 Catalyst Screening for the Synthesis of *m*DPB

To a solution of **1a** (10.0 mg, 32.4 µmol) in 2 mL solvent the catalyst (5 mol%) was added and the solution was stirred at room temperature. As internal standard hexamethylbenzene (5.00 mg) was added from a stock solution. After 4 h a 100 µL sample was taken and mixed with 200 µL dimethylformamide and 1.50 mL acetonitrile. The reaction was quantified using a UPLC-MS approach (positive ionization, column BEH C18, acetonitrile/water 70% → 90%, 3 µL injection) by monitoring the TIC+ trace. The concentrations of **1a** and ***m*DPBa** were determined according to a standard curve and normalized to the internal standard.

1.3 Synthesis of Compounds

2-Ethynylaniline (S1)

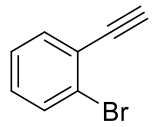


A Schlenk flask containing 2-iodoaniline (15.0 g, 68.5 mmol) and $(PPh_3)_2PdCl_2$ (240 mg, 342 µmol) was evacuated and refilled with nitrogen three times. Degassed Et_3N (200 mL) and ethynyltrimethylsilane (10.1 g, 103.7 mmol) were added and the mixture was stirred at rt for 5 min. CuI (130 mg, 685 µmol) was added and the mixture was stirred at rt for 2 h. The mixture was filtered through a plug of Celite® (eluted with EA), the solvents were removed under reduced pressure and the residue was dissolved in MeOH (150 mL). K_2CO_3 (18.9 g, 137 mmol) was added and the resulting mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 20:1 to 5:1). The product was obtained as a pale yellow oil (6.62 g, 56.5 mmol, 82%).

R_f: 0.24 (silica gel, PE:EA = 10:1); **^{1}H NMR** (301 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H), 7.17–7.12 (m, 1H), 6.71–6.65 (m, 2H), 4.24 (br, 2H), 3.38 (s, 1H).

The spectroscopic data correspond to those previously reported in the literature.[3]

1-Bromo-2-ethynylbenzene (S2)

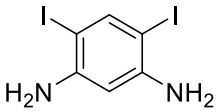


A Schlenk flask containing 1-bromo-2-iodobenzene (4.24 g, 15.0 mmol) and $(PPh_3)_2PdCl_2$ (52.6 mg, 75.0 µmol) was evacuated and refilled with nitrogen three times. Degassed Et_3N (40 mL), degassed THF (20 mL) and ethynyltrimethylsilane (1.47 g, 15.0 mmol) were added and the mixture was stirred at rt for 5 min. CuI (14.3 mg, 75.0 µmol) was added and the mixture was stirred at rt for 12 h. The mixture was filtered through a plug of Celite® (eluted with EA), the solvents were removed under reduced pressure and the residue was dissolved in MeOH (20 mL). K_2CO_3 (4.15 g, 30.0 mmol) was added and the resulting mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE). The product was obtained as a pale yellow oil (1.87 g, 10.3 mmol, 69%).

R_f: 0.90 (silica gel, PE:EA = 20:1); **^{1}H NMR** (301 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.53 (dd, *J* = 7.5 Hz, *J* = 1.8 Hz, 1H), 7.30–7.25 (m, 1H), 7.19 (td, *J* = 7.7 Hz, *J* = 1.9 Hz, 1H), 3.38 (s, 1H).

The spectroscopic data correspond to those previously reported in the literature.[4]

4,6-Diiodobenzene-1,3-diamine (S3)

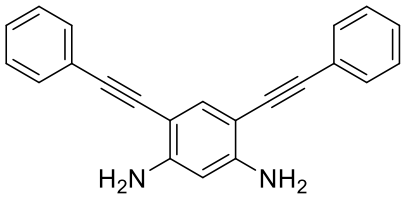


According to a procedure by Iskra *et al*.,[5] *m*-phenylenediamine (10.0 g, 92.5 mmol) and KI (30.7 g, 185 mmol) were added to a solution of concentrated sulfuric acid (7.40 mL, 139 mmol) in MeOH (450 mL). H_2O_2 (35 wt%, 35.9 g, 370 mmol) was added drop wise at 0 °C and the mixture was stirred rigorously for 40 min. The mixture was poured into DCM (1 L) and the organic phase was washed twice with 0.1 M $NaHSO_3$ (450 mL). The aqueous layer was extracted with DCM (300 mL). The combined organic layers were concentrated at 25 °C under reduced pressure to one third of the volume and crystallized at −20 °C. The product was obtained as a grey-greenish solid (9.10 g, 25.2 mmol, 27%).

R_f: 0.30 (silica gel, PE:EA = 1:1); **^{1}H NMR** (500 MHz, DMSO-d_6): δ = 7.52 (s, 1H), 6.23 (s, 1H), 5.05 (br, 4H).

The spectroscopic data correspond to those previously reported in the literature.[5]

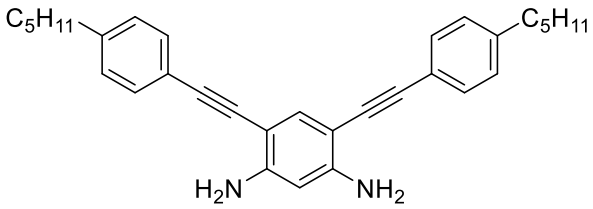
4,6-Bis(phenylethynyl)benzene-1,3-diamine (1a)



S3 (1.80 g, 5.00 mmol), $(PPh_3)_2PdCl_2$ (176 mg, 250 µmol) and CuI (47.6mg, 250 µmol) were added to a solution of phenylacetylene (1.12 g, 11.0 mmol) in degassed tetrahydrofuran/diisopropylamine (35 mL, 6:1) and the mixture was stirred at rt for 2 h. Water was added, the aqueous phase was extracted with diethyl ether, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1, 1% Et_3N). The product was obtained as a pale yellow solid (1.25 g, 4.05 mmol, 81%).

Mp: 154 °C; $\mathbf{R_f}$: 0.50 (silica gel, DCM); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 4H), 7.45 (s, 1H), 7.33 (m, 6H), 6.04 (s, 1H), 4.36 (br, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 149.41 (s, 2C), 136.44 (d, 1C), 131.35 (d, 4C), 128.47 (d, 2C), 127.92 (d, 4C), 123.77 (s, 2C), 99.04 (d, 1C), 98.58 (s, 2C), 93.14 (s, 2C), 85.84 (s, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{22}H_{17}N_2]^+$, $[M+H]^+$: 309.13862, found: 309.13870; **IR** (ATR): ν [cm^{-1}] = 3482, 3446, 3370, 3344, 3031, 2190, 1625, 1591, 1544, 1507, 1483, 1443, 1357, 1333, 1279, 1265, 1213, 1153, 1085, 1069, 1025, 914, 900, 845, 751, 690, 627; **UV-Vis** (DCM): λ_{max} [nm] = 268, 296, 333, 352; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 420; **quantum yield** (DCM): Φ = 1%.

4,6-Bis((4-pentylphenyl)ethynyl)benzene-1,3-diamine (1b)

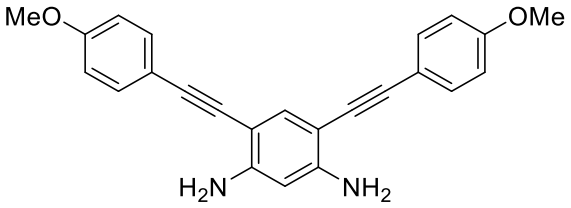


S3 (500 mg, 1.39 mmol), $(PPh_3)_2PdCl_2$ (48.8 mg, 69.5 µmol) and CuI (13.2 mg, 69.5 µmol) were added to a solution of 1-ethynyl-4-pentylbenzene (526 mg, 3.06 mmol) in degassed tetrahydrofuran/diisopropylamine (15 mL, 6:1) and the mixture was stirred at rt for 16 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1, 1% Et_3N). The product was obtained as a pale yellow solid (561 mg, 1.25 mmol, 90%).

Mp: 129 °C; $\mathbf{R_f}$: 0.77 (silica gel, DCM); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.41 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 6.05 (s, 1H), 4.33 (br, 4H), 2.60 (t, *J* = 7.7 Hz, 4H), 1.61 (quint, *J* = 7.4 Hz, 4H), 1.32 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 149.22 (s, 2C), 143.09 (s, 2C), 136.28 (d, 1C), 131.30 (d, 4C), 128.60 (d, 4C), 120.93 (s, 2C), 99.35 (d, 1C), 98.61 (s, 2C), 93.25 (s, 2C), 85.10 (s, 2C), 35.99 (t, 2C), 31.58 (t, 2C), 31.12 (t, 2C), 22.67 (t, 2C), 14.18 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{32}H_{37}N_2]^+$, $[M+H]^+$: 449.29513, found: 449.29533; **IR** (ATR): ν [cm^{-1}] = 3466, 3372, 2952, 2926, 2855, 2190, 1620, 1548, 1512, 1444, 1358, 1332, 1265, 1218, 1181, 1115,

1082, 1018, 909, 836, 801, 727, 667, 618; **UV-Vis** (DCM): λ_{max} [nm] = 271, 297, 336, 358; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 424; **quantum yield** (DCM): Φ = 4%.

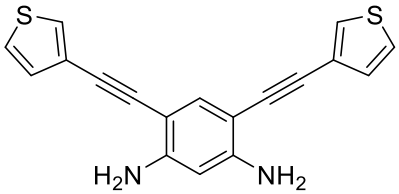
4,6-Bis((4-methoxyphenyl)ethynyl)benzene-1,3-diamine (1c)



S3 (619 mg, 1.72 mmol), $(PPh_3)_2PdCl_2$ (60.4 mg, 86.0 µmol) and CuI (16.4 mg, 86.0 µmol) were added to a solution of 4-ethynylanisole (500 mg, 3.78 mmol) in degassed tetrahydrofuran/diisopropylamine (12 mL, 20:3) and the mixture was stirred at rt for 2 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1 to 1:1, 1% Et_3N). The product was obtained as a pale yellow solid (534 mg, 1.45 mmol, 84%).

Mp: 187 °C; $\mathbf{R_f}$: 0.14 (silica gel, DCM); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.8 Hz, 4H), 7.39 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 4H), 6.05 (s, 1H), 4.31 (br, 4H), 3.82 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 159.41 (s, 2C), 149.06 (s, 2C), 136.12 (d, 1C), 132.85 (d, 4C), 115.97 (s, 2C), 114.11 (d, 4C), 99.45 (d, 1C), 98.68 (s, 2C), 92.87 (s, 2C), 84.35 (s, 2C), 55.46 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{24}H_{21}N_2O_2]^+$, $[M+H]^+$: 369.15975, found: 369.15995; **IR** (ATR): ν [cm^{-1}] = 3462, 3368, 2970, 2838, 2195, 1731, 1621, 1567, 1549, 1510, 1445, 1413, 1361, 1333, 1300, 1277, 1245, 1171, 1106, 1028, 909, 827, 793, 756, 644, 615; **UV-Vis** (DCM): λ_{max} [nm] = 274, 295, 354; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 416; **quantum yield** (DCM): Φ = 2%.

4,6-Bis(thiophen-3-ylethynyl)benzene-1,3-diamine (1d)

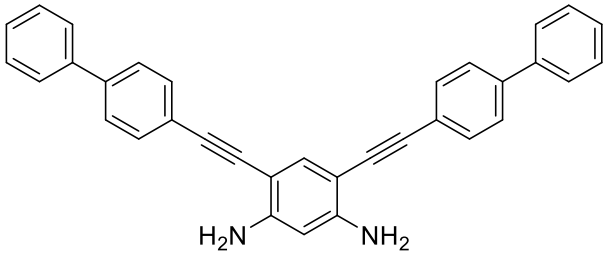


S3 (756 mg, 2.10 mmol), $(PPh_3)_2PdCl_2$ (73.7 mg, 105 µmol) and CuI (20.0 mg, 105 µmol) were added to a solution of 3-ethynylthiophene (500 mg, 4.62 mmol) in degassed tetrahydrofuran/diisopropylamine (12 mL, 20:3) and the mixture was stirred at rt for 24 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1 to 1:1, 1% Et_3N). The product was obtained as a colorless solid (618 mg, 1.93 mmol, 92%).

Mp: 148 °C; $\mathbf{R_f}$: 0.31 (silica gel, DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 3.0 Hz, *J* = 1.2 Hz, 2H), 7.39 (s, 1H), 7.29 (dd, *J* = 4.9 Hz, *J* = 2.9 Hz, 2H), 7.16 (dd, *J* = 5.0 Hz, *J* = 1.1 Hz, 2H), 6.03 (s,

1H), 4.31 (br, 4H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ = 149.41 (s, 2C), 136.43 (d, 1C), 130.01 (d, 2C), 127.84 (d, 2C), 125.42 (d, 2C), 122.82 (s, 2C), 99.09 (d, 1C), 98.64 (s, 2C), 88.05 (s, 2C), 85.25 (s, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{18}H_{13}N_2S_2]^+$, $[M+H]^+$: 321.05147, found: 321.05170; **IR** (ATR): ν [cm^{-1}] = 3438, 3349, 3102, 1620, 1555, 1524, 1496, 1439, 1414, 1324, 1297, 1270, 1216, 1187, 1073, 936, 903, 864, 844, 766, 686, 643, 619; **UV-Vis** (DCM): λ_{max} [nm] = 266, 292, 315, 354; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 390; **quantum yield** (DCM): Φ = 2%.

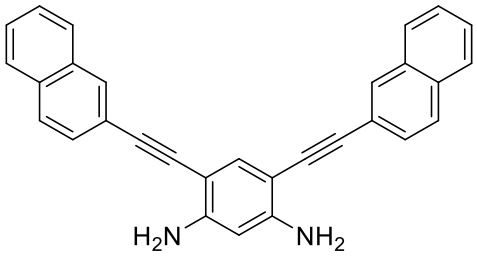
4,6-Bis([1,1'-biphenyl]-4-ylethynyl)benzene-1,3-diamine (1e)



S3 (459 mg, 1.28 mmol), $(PPh_3)_2PdCl_2$ (44.8 mg, 63.8 µmol) and CuI (12.1 mg, 63.8 µmol) were added to a solution of 4-ethynylbiphenyl (500 mg, 2.81 mmol) in degassed tetrahydrofuran/diisopropylamine (12 mL, 20:3) and the mixture was stirred at rt for 2 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1 to EA, 1% Et_3N). The product was obtained as a yellow solid (545 mg, 1.18 mmol, 93%).

Mp: decomposition >250 °C; **R_f**: 0.54 (silica gel, DCM); **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.70 (m, 8H), 7.64 (d, *J* = 8.4 Hz, 4H), 7.48 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.22 (s, 1H), 6.07 (s, 1H), 5.67 (br, 4H).; **$^{13}C\{^{1}H\}$ NMR** (151 MHz, DMSO-d_6): δ = 151.18 (s, 2C), 139.36 (s, 2C), 138.89 (s, 2C), 135.96 (d, 1C), 131.32 (d, 4C), 129.01 (d, 4C), 127.66 (d, 2C), 126.63 (d, 4C), 126.54 (d, 4C), 122.78 (s, 2C), 96.73 (d, 1C), 95.66 (s, 2C), 91.87 (s, 2C), 89.29 (s, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{34}H_{25}N_2]^+$, $[M+H]^+$: 461.20123, found: 461.20148; **IR** (ATR): ν [cm^{-1}] = 3485, 3381, 3057, 3034, 2239, 2183, 1892, 1821, 1737, 1672, 1626, 1603, 1542, 1523, 1449, 1405, 1365, 1336, 1292, 1266, 1208, 1159, 1118, 1085, 1038, 1004, 987, 964, 909, 842, 759, 719, 668, 624; **UV-Vis** (DCM): λ_{max} [nm] = 286, 312, 370; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 446; **quantum yield** (DCM): Φ = 29%.

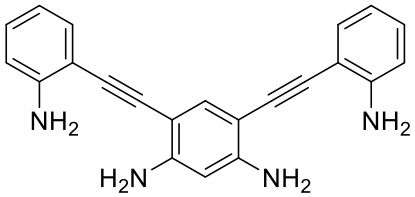
4,6-Bis(naphthalen-2-ylethynyl)benzene-1,3-diamine (1f)



S3 (100 mg, 278 µmol), $(PPh_3)_2PdCl_2$ (9.75 mg, 13.9 µmol) and CuI (2.65 mg, 13.9 µmol) were added to a solution of 2-ethynylnaphthalene (93.0 mg, 611 µmol) in degassed tetrahydrofuran/diisopropylamine (6 mL, 20:3) and the mixture was stirred at rt for 24 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1 to EA, 1% Et_3N). The product was obtained as a yellow solid (112 mg, 273 µmol, 98%).

Mp: decomposition >249 °C; $\mathbf{R_f}$: 0.56 (silica gel, DCM); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (s, 2H), 7.81 (m, 6H), 7.55 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.52 (s, 1H), 7.49 (m, 4H), 6.10 (s, 1H), 4.43 (br, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 149.57 (s, 2C), 136.65 (d, 1C), 133.26 (s, 2C), 132.72 (s, 2C), 130.86 (d, 2C), 128.47 (d, 2C), 128.14 (d, 2C), 127.92 (d, 2C), 127.83 (d, 2C), 126.70 (d, 2C), 126.60 (d, 2C), 121.17 (s, 2C), 99.25 (d, 1C), 98.62 (s, 2C), 93.68 (s, 2C), 86.30 (s, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{30}H_{21}N_2]^+$, $[M+H]^+$: 409.16993, found: 409.17016; **IR** (ATR): ν [cm^{-1}] = 3463, 3372, 3053, 2183, 1736, 1614, 1592, 1567, 1544, 1503, 1441, 1368, 1331, 1263, 1191, 1143, 1129, 1070, 1016, 951, 898, 862, 821, 740, 651, 629; **UV-Vis** (DCM): λ_{max} [nm] = 281, 313, 371; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 442; **quantum yield** (DCM): Φ = 22%.

4,6-Bis((2-aminophenyl)ethynyl)benzene-1,3-diamine (1g)

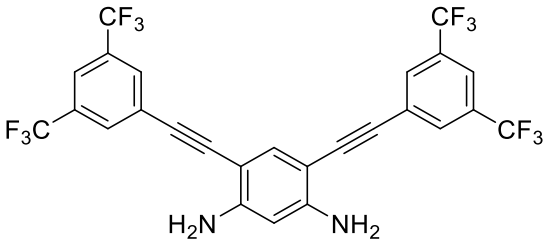


S3 (1.40 g, 3.89 mmol), $(PPh_3)_2PdCl_2$ (137 mg, 195 µmol) and CuI (37.0 mg, 195 µmol) were added to a solution of 2-ethynylaniline (**S1**, 1.00 g, 8.56 mmol) in degassed tetrahydrofuran/diisopropylamine (23 mL, 20:3) and the mixture was stirred at rt for 2 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 3:1 to 1:1, 1% Et_3N) and further by washing with a small amount of ice-cold MeOH. The product was obtained as a pale yellow solid (1.05 g, 3.10 mmol, 80%).

Mp: 135 °C; $\mathbf{R_f}$: 0.83 (silica gel, EA); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.36 (s, 1H), 7.26 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 2H), 7.03–6.99 (m, 2H), 6.70 (dd, *J* = 8.1 Hz, *J* = 0.6 Hz, 2H),), 6.52 (td, *J* = 7.4 Hz,

J = 1.0 Hz, 2H), 6.05 (s, 1H), 5.47 (br, 4H), 5.32 (br, 4H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, DMSO-d_6): δ = 150.2 (s, 2C), 148.6 (s, 2C), 136.0 (d, 1C), 131.5 (d, 2C), 128.6 (d, 2C), 115.8 (d, 2C), 113.8 (d, 2C), 107.3 (s, 2C), 97.1 (d, 1C), 96.5 (s, 2C), 91.6 (s, 2C), 88.9 (s, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{22}H_{19}N_4]^+$, $[M+H]^+$: 339.16042, found: 339.16042; **IR** (ATR): ν [cm^{-1}] = 3418, 3331, 3192, 3031, 2193, 1729, 1619, 1511, 1492, 1454, 1434, 1356, 1318, 1267, 1155, 1033, 929, 896, 849, 834, 783, 742, 667, 632; **UV-Vis** (DCM): λ_{max} [nm] = 248, 278, 356; **fluorescence** (DCM): λ_{ex} [nm] = 360, λ_{max} [nm] = 420; **quantum yield** (DCM): Φ = 5%.

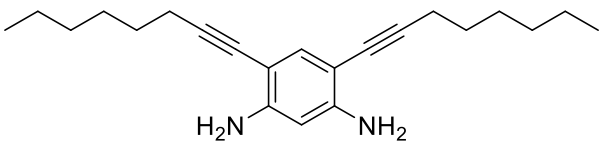
4,6-Bis((3,5-bis(trifluoromethyl)phenyl)ethynyl)benzene-1,3-diamine (1h)



S3 (343 mg, 953 µmol), $(PPh_3)_2PdCl_2$ (33.4 mg, 47.7 µmol) and CuI (9.07 mg, 47.7 µmol) were added to a solution of 1-ethynyl-3,5-bis(trifluoromethyl)benzene (500 mg, 2.10 mmol) in degassed tetrahydrofuran/diisopropylamine (12 mL, 20:3) and the mixture was stirred at rt for 18 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 4:1 to EA, 1% Et_3N). The product was obtained as a yellow solid (540 mg, 930 µmol, 98%).

Mp: 163 °C; **R_f**: 0.67 (silica gel, DCM); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.89 (s, 4H), 7.78 (s, 2H), 7.48 (s, 1H), 6.05 (s, 1H), 4.44 (br, 4H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ = 150.5 (s, 2C), 137.7 (d, 1C), 132.2 (q, *J* = 33.6 Hz, 2C), 131.0 (q, *J* = 3.4 Hz, 4C), 126.1 (d, 4C), 124.5 (d, 2C), 121.8 (d, 2C), 121.2 (sept, *J* = 3.8 Hz, 2C), 98.4 (d, 1C), 97.9 (s, 2C), 90.7 (s, 2C), 89.6 (s, 2C); **$^{19}F\{^{1}H\}$ NMR** (283 MHz, $CDCl_3$): −63.11 (s, 6F); **HR-MS** (ESI+): *m/z* calculated for $[C_{26}H_{13}F_{12}N_2]^+$, $[M+H]^+$: 581.08816, found: 581.08883; **IR** (ATR): ν [cm^{-1}] = 3499, 3397, 3089, 2198, 1631, 1614, 1542, 1506, 1452, 1382, 1334, 1276, 1254, 1176, 1128, 1106, 927, 912, 894, 846, 828, 758, 716, 698, 683, 628; **UV-Vis** (DCM): λ_{max} [nm] = 256, 275, 308, 373; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 444; **quantum yield** (DCM): Φ = 12%.

4,6-Di(oct-1-yn-1-yl)benzene-1,3-diamine (1i)



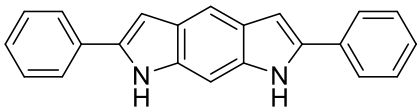
S3 (743 mg, 2.06 mmol), $(PPh_3)_2PdCl_2$ (72.5 mg, 103 µmol) and CuI (19.7 mg, 103 µmol) were added to a solution of oct-1-yne (500 mg, 4.54 mmol) in degassed tetrahydrofuran/diisopropylamine (12 mL, 20:3) and the mixture was stirred at rt for 2 h. Water was added, the aqueous phase was extracted with DCM, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by

flash column chromatography (silica gel, EA, 1% Et_3N). The product was obtained as a brown liquid (356 mg, 1.10 mmol, 53%).

R_f: 0.34 (silica gel, DCM); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.16 (s, 1H), 5.98 (s, 1H), 4.14 (br, 4H), 2.41 (t, *J* = 7.1 Hz, 4H), 1.60–1.55 (m, 4H), 1.46–1.41 (m, 4H), 1.33–1.29 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 148.5 (s, 2C), 136.0 (d, 1C), 99.9 (d, 1C), 98.9 (s, 2C), 93.6 (s, 2C), 76.7 (s, 2C), 31.5 (t, 2C), 29.2 (t, 2C), 28.8 (t, 2C), 22.7 (t, 2C), 19.8 (t, 2C), 14.2 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{22}H_{33}N_2]^+$, $[M+H]^+$: 325.26383, found: 325.26472; **IR** (ATR): ν [cm^{-1}] = 3471, 3376, 3200, 2954, 2928, 2856, 2215, 1621, 1557, 1503, 1464, 1438, 1376, 1319, 1264, 1184, 1118, 896, 834, 722, 694.

The compound is not stable in solution.

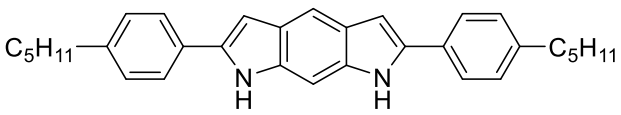
2,6-Diphenyl-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBa)



IPrAuNTf$_2$ (14.0 mg, 16.2 µmol) was added to a solution of **1a** (100 mg, 324 µmol) in ethanol (20 mL) and the solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a pale yellow solid (87.0 mg, 282 µmol, 87%).

Mp: >300 °C; **R_f**: 0.36 (silica gel, DCM); **^{1}H NMR** (500 MHz, DMSO-d_6): δ = 11.06 (br, 2H), 7.84 (d, *J* = 7.3 Hz, 4H), 7.59 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.34 (s, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 6.87 (s, 2H); **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6): δ = 137.09 (s, 2C), 136.25 (s, 2C), 132.70 (d, 2C), 128.86 (d, 4C), 126.89 (s, 2C), 125.33 (s, 2C), 124.58 (d, 4C), 109.09 (d, 1C), 98.03 (d, 2C), 91.11 (d, 1C); **HR-MS** (ESI+): *m/z* calculated for $[C_{22}H_{17}N_2]^+$, $[M+H]^+$: 309.13862, found: 309.13866; **IR** (ATR): ν [cm^{-1}] = 3416, 3103, 3054, 1881, 1803, 1740, 1637, 1604, 1584, 1554, 1490, 1452, 1417, 1367, 1350, 1315, 1279, 1252, 1188, 1153, 1133, 1075, 1048, 1028, 923, 874, 836, 788, 759, 742, 689; **UV-Vis** (DCM): λ_{max} [nm] = 254, 317, 355; (DMSO): λ_{max} [nm] = 326, 364; (THF): λ_{max} [nm] = 324, 360; (PhMe): λ_{max} [nm] = 321, 357; (MeOH): λ_{max} [nm] = 260, 319, 357; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 420; (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 440; (THF): λ_{ex} [nm] = 350, λ_{max} [nm] = 426; (PhMe): λ_{ex} [nm] = 350, λ_{max} [nm] = 416; (MeOH): λ_{ex} [nm] = 350, λ_{max} [nm] = 430; **quantum yield** (DCM): Φ = 79%; (DMSO): Φ = 71%; (THF): Φ = 96%; (PhMe): Φ = 81%; (MeOH): Φ = 65%.

2,6-Bis(4-pentylphenyl)-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBb)

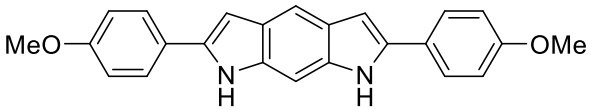


IPrAuNTf$_2$ (21.3 mg, 24.6 µmol) was added to a solution of **1b** (220 mg, 491 µmol) in ethanol (44 mL) and the solution was stirred at room temperature for 2 h. The solvent was removed under reduced

pressure and the residue was washed with methanol. The product was obtained as a pale yellow solid (218 mg, 486 µmol, 99%).

Mp: >300 °C; **R_f**: 0.89 (silica gel, DCM); **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 10.97 (br, 2H), 7.74 (d, *J* = 8.2 Hz, 4H), 7.55 (s, 1H), 7.31 (s, 1H), 7.26 (d, *J* = 8.2 Hz, 4H), 6.79 (s, 2H), 2.60 (t, *J* = 7.9 Hz, 4H), 1.61 (dt, *J* = 7.8 Hz, *J* = 7.4 Hz, 4H), 1.31 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 141.11 (s, 2C), 137.18 (s, 2C), 136.00 (s, 2C), 130.23 (s, 2C), 128.75 (d, 4C), 125.31 (s, 2C), 124.53 (d, 4C), 108.70 (d, 1C), 97.35 (d, 2C), 91.02 (d, 1C), 34.84 (t, 2C), 30.94 (t, 2C), 30.59 (t, 2C), 22.00 (t, 2C), 13.98 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{32}H_{37}N_2]^+$, $[M+H]^+$: 449.29513, found: 449.29542; **IR** (ATR): ν [cm^{-1}] = 3423, 2927, 1663, 1504, 1425, 1363, 1120, 827, 746, 623; **UV-Vis** (DCM): λ_{max} [nm] = 261, 316, 356; (DMSO): λ_{max} [nm] = 325, 365; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 416; (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 434; **quantum yield** (DCM): Φ = 69%; (DMSO): Φ = 82%.

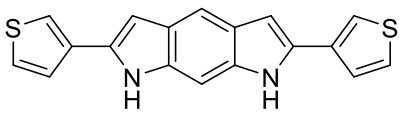
2,6-Bis(4-methoxyphenyl)-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBc)



IPrAuNTf$_2$ (11.8 mg, 13.6 µmol) was added to a solution of **1c** (100 mg, 271 µmol) in ethanol (60 mL) and the solution was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a pale yellow solid (97.0 mg, 263 µmol, 97%).

Mp: >300 °C; **R_f**: 0.36 (silica gel, DCM); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 10.87 (br, 2H), 7.76 (d, *J* = 8.8 Hz, 4H), 7.51 (s, 1H), 7.29 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 4H), 6.70 (s, 2H), 3.81 (s, 6H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 158.34 (s, 2C), 136.96 (s, 2C), 135.71 (s, 2C), 125.83 (d, 4C), 125.50 (s, 2C), 125.30 (s, 2C), 114.24 (d, 4C), 108.20 (d, 1C), 96.51 (d, 2C), 90.87 (d, 1C), 55.12 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{24}H_{21}N_2O_2]^+$, $[M+H]^+$: 369.15975, found: 369.15987; **IR** (ATR): ν [cm^{-1}] = 3438, 3421, 2958, 2837, 1632, 1608, 1583, 1555, 1502, 1454, 1434, 1361, 1311, 1293, 1248, 1179, 1112, 1049, 1026, 922, 868, 829, 781, 745, 717, 683, 651; **UV-Vis** (DCM): λ_{max} [nm] = 307, 355; (DMSO): λ_{max} [nm] = 256, 313, 319, 363; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 412; (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 426; **quantum yield** (DCM): Φ = 54%; (DMSO): Φ = 14%.

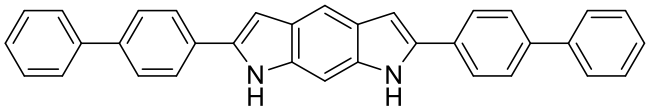
2,6-Di(thiophen-3-yl)-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBd)



IPrAuNTf$_2$ (13.5 mg, 15.6 µmol) was added to a solution of **1d** (100 mg, 312 µmol) in ethanol (20 mL) and the solution was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a yellow solid (94.0 mg, 293 µmol, 94%).

Mp: >300 °C; **R_f**: 0.88 (silica gel, DCM); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 10.93 (br, 2H), 7.78 (dd, *J* = 2.9 Hz, *J* = 1.2 Hz, 2H), 7.63 (dd, *J* = 4.9 Hz, *J* = 2.9 Hz, 2H), 7.59 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 2H), 7.55 (s, 1H), 7.26 (d, *J* = 0.9 Hz, 1H), 6.71 (d, *J* = 1.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ = 135.55 (s, 2C), 134.69 (d, 2C), 133.54 (d, 2C), 126.74 (s, 2C), 125.78 (s, 2C), 124.96 (s, 2C), 118.42 (d, 2C), 108.82 (d, 1C), 97.83 (d, 2C), 90.63 (d, 1C); **HR-MS** (ESI+): *m/z* calculated for $[C_{18}H_{13}N_2S_2]^+$, $[M+H]^+$: 321.05147, found: 321.05155; **IR** (ATR): ν [cm^{-1}] = 3412, 3095, 1740, 1633, 1580, 1524, 1485, 1453, 1423, 1342, 1235, 1199, 1122, 1088, 1050, 957, 868, 835, 766, 743, 681, 604; **UV-Vis** (DCM): λ_{max} [nm] = 314, 348; (DMSO): λ_{max} [nm] = 259, 272, 320, 355; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 410; (DMSO): λ_{ex} [nm] = 370, λ_{max} [nm] = 422; **quantum yield** (DCM): Φ = 37%; (DMSO): Φ = 83%.

2,6-Di([1,1'-biphenyl]-4-yl)-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBe)

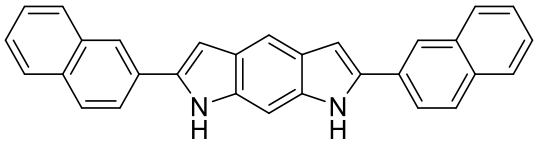


IPrAuNTf$_2$ (9.40 mg, 10.9 µmol) was added to a solution of **1e** (100 mg, 217 µmol) in ethanol (60 mL) and the solution was stirred at 60 °C for 18 h. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a yellow solid (92.0 mg, 200 µmol, 92%).

Mp: >300 °C; **R_f**: 0.05 (silica gel, DCM); **^{1}H NMR** (500 MHz, DMSO-d_6): δ = 11.13 (br, 2H), 8.31 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 4H), 7.77 (m, 8H), 7.64 (s, 1H), 7.50 (m, 6H), 6.95 (s, 2H); **HR-MS** (ESI+): *m/z* calculated for $[C_{34}H_{25}N_2]^+$, $[M+H]^+$: 461.20123, found: 461.20140; **IR** (ATR): ν [cm^{-1}] = 3439, 3421, 3054, 3033, 1633, 1595, 1569, 1547, 1525, 1483, 1450, 1417, 1362, 1316, 1268, 1246, 1216, 1119, 1039, 1003, 909, 868, 832, 785, 760, 743, 717, 685, 649; **UV-Vis** (DMSO): λ_{max} [nm] = 272, 385; **fluorescence** (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 470, 498; **quantum yield** (DMSO): Φ = 32%.

No ^{13}C NMR was recorded due to low solubility of the compound. The structure was confirmed by derivatization to ***m*DPBe`**.

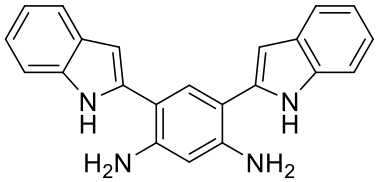
2,6-Di(naphthalen-2-yl)-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBf)



IPrAuNTf$_2$ (5.30 mg, 6.12 µmol) was added to a solution of **1f** (50.0 mg, 122 µmol) in ethanol (40 mL) and the solution was stirred at 60 °C for 18 h. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a yellow solid (46.0 mg, 113 µmol, 92%).

Mp: >300 °C; **R_f**: 0.05 (silica gel, DCM); **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 11.26 (br, 2H), 8.34 (s, 2H), 8.04 (dd, *J* = 8.6 Hz, *J* = 1.5 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.94–7.91 (m, 4H), 7.68 (s, 1H), 7.57–7.54 (m, 2H), 7.51–7.48 (m, 2H), 7.40 (s, 1H), 7.05 (d, *J* = 1.5 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 137.12 (s, 2C), 136.70 (s, 2C), 133.39 (s, 2C), 132.11 (d, 2C), 130.14 (d, 2C), 128.32 (d, 2C), 127.79 (s, 2C), 127.71 (d, 2C), 126.68 (d, 2C), 125.78 (s, 2C), 125.49 (d, 2C), 123.76 (d, 2C), 122.07 (s, 2C), 109.38 (d, 1C), 99.11 (d, 2C), 91.09 (d, 1C); **HR-MS** (ESI+): *m/z* calculated for $[C_{30}H_{21}N_2]^+$, $[M+H]^+$: 409.16992, found: 409.17023; **IR** (ATR): ν [cm^{-1}] = 3422, 3055, 2967, 2928, 1950, 1707, 1624, 1600, 1576, 1555, 1509, 1466, 1441, 1416, 1393, 1371, 1345, 1327, 1291, 1259, 1232, 1191, 1161, 1147, 1132, 1046, 1018, 960, 894, 859, 827, 785, 746, 683, 671, 625; **UV-Vis** (DMSO): λ_{max} [nm] = 288, 297, 343, 383; **fluorescence** (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 474, 502; **quantum yield** (DMSO): Φ = 43%.

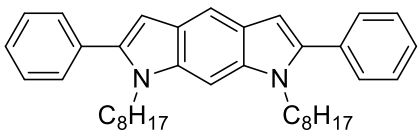
4,6-Di(1*H*-indol-2-yl)benzene-1,3-diamine (1g`)



IPrAuNTf$_2$ (12.8 mg, 14.8 µmol) was added to a solution of **1g** (100 mg, 296 µmol) in ethanol (30 mL) and the solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was washed with methanol. The product was obtained as a pale green solid (80.0 mg, 236 µmol, 80%).

Mp: 223 °C; **R_f**: 0.29 (silica gel, DCM); **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 11.03 (br, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.48 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 1.6 Hz, 2H), 6.26 (s, 1H), 5.17 (br, 4H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 146.07 (d, 2C), 136.86 (s, 2C), 136.01 (s, 2C), 129.61 (d, 1C), 128.94 (s, 2C), 120.39 (d, 2C), 119.23 (d, 2C), 118.84 (d, 2C), 110.74 (d, 2C), 107.76 (d, 2C), 101.08 (s, 1C), 98.53 (d, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{22}H_{19}N_4]^+$, $[M+H]^+$: 339.16042, found: 339.16052; **IR** (ATR): ν [cm^{-1}] = 3402, 3357, 3308, 3157, 1737, 1627, 1572, 1503, 1454, 1433, 1412, 1348, 1294, 1230, 1204, 1148, 1116, 1058, 1008, 943, 898, 867, 822, 795, 776, 749, 702, 669, 607; **UV-Vis** (DCM): λ_{max} [nm] = 297, 330; (DMSO): λ_{max} [nm] = 258, 303, 332, 353; **fluorescence** (DCM): λ_{ex} [nm] = 330, λ_{max} [nm] = 418; (DMSO): λ_{ex} [nm] = 360, λ_{max} [nm] = 442; **quantum yield** (DCM): Φ = 41%; (DMSO): Φ = 95%.

1,7-Dioctyl-2,6-diphenyl-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBa`)

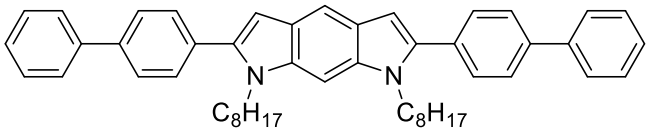


NaH (8.14 mg, 204 µmol, 60% dispersion in mineral oil) was added to a solution of ***m*DPBa** (29.9mg, 97.0 µmol) and 1-bromooctane (37.5 mg, 194 µmol) in dry dimethylformamide (20 mL) at 0 °C and the

mixture was stirred at rt for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 40:1). The product was obtained as a pale yellow solid (16.0 mg, 30.0 µmol, 31%).

Mp: 70 °C; **R_f**: 0.65 (silica gel, PE:EA = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.54 (d, *J* = 7.4 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.20 (s, 1H), 6.56 (s, 2H), 4.20 (t, *J* = 7.4 Hz, 4H), 1.74 (t, *J* = 7.4 Hz, 4H), 1.23 (m, 4H), 1.17 (m, 16H), 0.85 (t, *J* = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 141.58 (s, 2C), 136.63 (s, 2C), 134.08 (s, 2C), 129.53 (d, 4C), 128.62 (d, 4C), 127.70 (d, 2C), 124.96 (s, 2C), 110.60 (d, 1C), 101.80 (d, 2C), 89.69 (d, 1C), 44.38 (t, 2C), 32.01 (t, 2C), 29.50 (t, 2C), 29.38 (t, 4C), 27.08 (t, 2C), 22.87 (t, 2C), 14.34 (q, 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{38}H_{49}N_2]^+$, $[M]^+$: 533.38903, found: 533.38913; **IR** (ATR): ν [cm^{-1}] = 3059, 2920, 2852, 1627, 1603, 1545, 1483, 1452, 1363, 1318, 1268, 1247, 1210, 1154, 1141, 1118, 1070, 1028, 913, 885, 803, 770, 758, 723, 700, 633; **UV-Vis** (DCM): λ_{max} [nm] = 318, 356; (DMSO): λ_{max} [nm] = 357, 314, 339; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 416; (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 437; **quantum yield** (DCM): Φ = 98%; (DMSO): Φ = 71%.

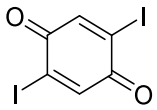
2,6-Di([1,1'-biphenyl]-4-yl)-1,7-dioctyl-1,7-dihydropyrrolo[3,2-*f*]indole (*m*DPBe`)



NaH (14.6 mg, 365 µmol, 60% dispersion in mineral oil) was added to a solution of ***m*DPBe** (80.1 mg, 174 µmol) and 1-bromooctane (67.2 mg, 348 µmol) in dry dimethylformamide (20 mL) at 0 °C and the mixture was stirred at rt for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 40:1). The product was obtained as a pale yellow solid (47.2 mg, 68.9 µmol, 40%).

Mp: 223 °C; **R_f**: 0.55 (silica gel, PE:EA = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 4H), 7.69 (d, *J* = 7.6 Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 4H), 7.50–7.47 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.23 (s, 1H), 6.62 (s, 2H), 4.26 (t, *J* = 7.3 Hz, 4H), 1.79 (m, 4H), 1.20 (m, 20H), 0.83 (t, *J* = 7.0 Hz, 6H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 141.16 (s, 2C), 140.81 (s, 2C), 140.30 (s, 2C), 136.76 (s, 2C), 132.91 (s, 2C), 129.72 (d, 4C), 129.01 (d, 4C), 127.57 (d, 2C), 127.24 (d, 4C), 127.20 (d, 4C), 124.96 (s, 2C), 110.56 (d, 1C), 101.91 (d, 2C), 89.66 (d, 1C), 44.40 (t, 2C), 31.94 (t, 2C), 29.46 (t, 2C), 29.33 (t, 2C), 29.32 (t, 2C), 27.01 (t, 2C), 22.78 (t, 2C), 14.23 (q 2C); **HR-MS** (ESI+): *m/z* calculated for $[C_{50}H_{57}N_2]^+$, $[M]^+$: 685.45163, found: 685.45253; **IR** (ATR): ν [cm^{-1}] = 3062, 3028, 1953, 1924, 1852, 1736, 1630, 1610, 1556, 1481, 1446, 1363, 1263, 1245, 1192, 1151, 1135, 1102, 1073, 1039, 1007, 910, 887, 835, 808, 763, 732, 697, 668, 645, 617; **UV-Vis** (DCM): λ_{max} [nm] = 254, 268, 342; (DMSO): λ_{max} [nm] = 266, 340; **fluorescence** (DCM): λ_{ex} [nm] = 350, λ_{max} [nm] = 464; (DMSO): λ_{ex} [nm] = 350, λ_{max} [nm] = 472, 503; **quantum yield** (DCM): Φ = 39%; (DMSO): Φ = 16%.

2,5-Diiodocyclohexa-2,5-diene-1,4-dione (2)

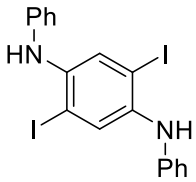


According to a procedure by Menéndez *et al*.,[6] 1,4-diiodo-2,5-dimethoxybenzene (3.00 g, 7.69 mmol) was dissolved in CH_3CN (60 mL) and a solution of cerium ammonium nitrate (10.5 g, 19.2 mmol) in water (40 mL) was added. The mixture was stirred at 100 °C for 30 min. After cooling to rt, water (50 mL) was added and the precipitated solid was filtered off and washed with water. The product was obtained as an orange solid (2.46 g, 6.84 mmol, 89%).

^{1}H NMR (301 MHz, $CDCl_3$): δ = 7.89 (s, 2H); **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$): δ = 177.8 (s, 2C), 143.8 (d, 2C), 119.9 (s, 2C).

The spectroscopic data correspond to those previously reported in the literature.[6]

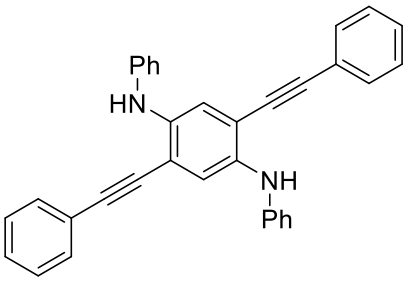
2,5-Diiodo-*N*^{1},*N*^{4}-diphenylbenzene-1,4-diamine (3)



According to a modified procedure by Yamamoto *et al*.,[7] titanium(IV) chloride (1.94 g, 10.2 mmol) was added dropwise to a stirred solution of aniline (9.51 g, 102 mmol) in chlorobenzene (40 mL) under nitrogen at 90 °C. To this mixture was added dropwise over 15 min a solution of **2** (2.45 g, 6.81 mmol) in chlorobenzene (40 mL) and stirring was continued at 135 °C for 16 h. The precipitate was removed by filtration through a pad of Celite® and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (alox, PE:DCM = 5:1 to 1:1). The product was obtained as a red solid with approximately 3% of dark red impurities and was used without further purification (1.83 g, 3.57 mmol, 52%). An analytically pure sample was obtained as an off-white solid by preparative thin layer chromatography (silica gel, PE:DCM = 3:1).

Mp:171 °C; **R_f**: 0.63 (silica gel, PE:EA = 20:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.64 (s, 2H), 7.31 (t, *J* = 7.8 Hz, 4H), 7.03–6.97 (m, 6H), 5.61 (br, 2H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 143.0 (s, 2C), 139.1 (s, 2C), 129.7 (d, 4C), 128.1 (d, 2C), 122.0 (d, 2C), 118.4 (d, 4C), 91.4 (s, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{18}H_{14}I_2N_2]^+$, $[M]^+$: 511.92409, found: 511.92399; **IR** (ATR): ν [cm^{-1}] = 3395, 2923, 2851, 1594, 1509, 1494, 1460, 1430, 1364, 1304, 1268, 1225, 1176, 1079, 1042, 993, 884, 868, 816, 748, 696, 631.

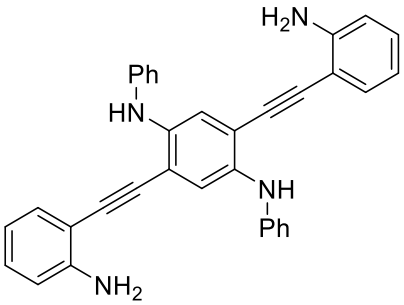
N^1,N^4-Diphenyl-2,5-bis(phenylethynyl)benzene-1,4-diamine (4a)



A Schlenk flask containing **3** (200 mg, 391 µmol) and $(PPh_3)_2PdCl_2$ (5.48 mg, 7.81 µmol) was evacuated and refilled with argon three times. Degassed THF (5 mL), degassed Et_3N (5 mL) and phenylacetylene (120 mg, 1.17 mmol) were added and the mixture was stirred at rt for 5 min. CuI (2.98 mg, 15.6 µmol) was added and the mixture was stirred at rt for 12 h. The solvents were removed under reduced pressure and 15 mL water was added. The mixture was extracted with DCM, the combined organic layers were washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was recrystallized from DCM/pentane. The product was obtained as a yellow solid (143 mg, 310 µmol, 80%).

Mp: decomposition >218 °C; **R_f**: 0.29 (silica gel, PE:DCM = 5:1); **^{1}H NMR** (700 MHz, $CDCl_3$): δ = 7.50–7.48 (m, 4H), 7.44 (s, 2H), 7.35–7.32 (m, 10H), 7.17 (d, *J* = 7.8 Hz, 4H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.21 (br, 2H); **^{13}C{^{1}H} NMR** (176 MHz, $CDCl_3$): δ = 142.9 (s, 2C), 137.8 (s, 2C), 131.7 (d, 4C), 129.6 (d, 4C), 128.8 (d, 2C), 128.6 (d, 4C), 122.9 (s, 2C), 121.7 (d, 2C), 119.3 (d, 2C), 118.9 (d, 4C), 113.4 (s, 2C), 96.8 (s, 2C), 85.9 (s, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{34}H_{24}N_2]^+$, $[M]^+$: 460.19340, found: 460.19192; **IR** (ATR): ν [cm^{-1}] = 3393, 3052, 3013, 1598, 1531, 1493, 1473, 1445, 1415, 1315, 1270, 1232, 1178, 1084, 1030, 910, 871, 745, 685, 629; **UV-Vis** (DCM): λ_{max} [nm] = 310, 427; **fluorescence** (DCM): λ_{ex} [nm] = 330, λ_{max} [nm] = 518; **quantum yield** (DCM): Φ = 28%.

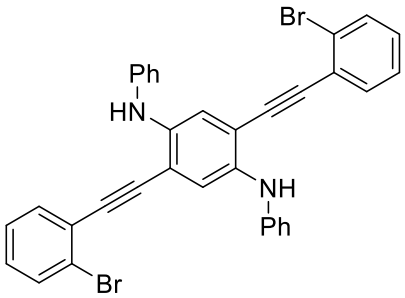
2,5-Bis((2-aminophenyl)ethynyl)-N^1,N^4-diphenylbenzene-1,4-diamine (4b)



A Schlenk flask containing **3** (1.00 g, 1.95 mmol) and $(PPh_3)_2PdCl_2$ (13.7 mg, 19.5 µmol) was evacuated and refilled with argon three times. Degassed THF (20 mL), degassed Et_3N (10 mL) and 2-ethynylaniline (**S1**, 572 mg, 4.88 mmol) were added and the mixture was stirred at rt for 5 min. CuI (7.44 mg, 39.1 µmol) was added and the mixture was stirred at rt for 16 h. The mixture was filtered through a short plug of silica gel eluted with 10% MeOH in DCM and the solvent was removed under reduced pressure. The product already partly cyclized on the silica gel and was therefore used without further purification in the next step.

The compound is not stable in solution.

2,5-Bis((2-bromophenyl)ethynyl)-*N*^{1},*N*^{4}-diphenylbenzene-1,4-diamine (4c)

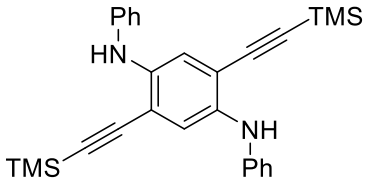


A Schlenk flask containing **3** (109 mg, 213 µmol) and $(PPh_3)_2PdCl_2$ (7.48 mg, 10.7 µmol) was evacuated and refilled with argon three times. Degassed THF (10 mL), degassed Et_3N (10 mL) and 1-bromo-2-ethynylbenzene (**S2**, 88.7 mg, 490 µmol) were added and the mixture was stirred at rt for 5 min. CuI (4.06 mg, 21.3 µmol) was added and the mixture was stirred at rt for 4 h. The solvents were removed under reduced pressure and 15 mL water was added. The mixture was extracted with DCM, the combined organic layers were washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, the residue was filtered through a short plug of silica gel eluted with a 5:1 mixture of PE/DCM and the solvents were removed under reduced pressure. After recrystallization from DCM/pentane, the product was obtained with minor impurities, mostly due to already cyclized portions of the product. The crude product was used without further purification in the next step.

R_f: 0.63 (silica gel, PE:EA = 5:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.63–7.62 (m, 2H), 7.55 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 2H), 7.51 (s, 2H), 7.36–7.33 (m, 4H), 7.32–7.30 (m, 2H), 7.22–7.18 (m, 6H), 7.00 (t, *J* = 7.3 Hz, 2H), 6.70 (br, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 142.6 (s, 2C), 138.0 (s, 2C), 133.2 (d, 2C), 132.5 (d, 2C), 129.8 (d, 2C), 129.6 (d, 4C), 127.4 (d, 2C), 125.4 (s, 2C), 125.1 (s, 2C), 121.7 (d, 2C), 119.0 (d, 4C), 118.1 (d, 2C), 112.7 (s, 2C), 95.5 (s, 2C), 90.9 (s, 2C); **HR-MS** (DART+): *m/z* calculated for $[C_{34}H_{23}Br_2N_4]^+$, $[M+H]^+$: 617.0223, found: 617.0220.

The compound is not stable in solution.

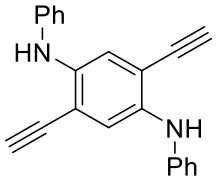
***N*^{1},*N*^{4}-Diphenyl-2,5-bis((trimethylsilyl)ethynyl)benzene-1,4-diamine (4d-TMS)**



A Schlenk flask containing **3** (1.03 g, 2.00 mmol) and $(PPh_3)_2PdCl_2$ (70.3 mg, 100 µmol) was evacuated and refilled with argon three times. Degassed THF (20 mL), degassed Et_3N (20 mL) and ethynyltrimethylsilane (590 mg, 6.01 mmol) were added and the mixture was stirred at rt for 5 min. CuI (38.2 mg, 200 µmol) was added and the mixture was stirred at rt for 1 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 100:1 to 10:1). After further purification by recrystallization from DCM/MeOH, the product was obtained as a yellow solid (802 mg, 1.77 mmol, 88%).

Mp: 181 °C; **R_f**: 0.52 (silica gel, PE:EA = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 6H), 7.12–7.10 (m, 4H), 7.00–6.97 (m, 2H), 6.17 (br, 2H), 0.25 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 142.8 (s, 2C), 138.0 (s, 2C), 129.6 (d, 4C), 121.7 (d, 2C), 118.8 (d, 2C), 118.8 (d, 4C), 113.0 (s, 2C), 102.6 (s, 2C), 101.4 (s, 2C), 0.1 (q, 6C); **HR-MS** (DART+): *m/z* calculated for $[C_{28}H_{33}N_2Si_2]^+$, $[M+H]^+$: 453.2177, found: 453.2173; **IR** (ATR): ν [cm^{-1}] = 3395, 3047, 2960, 2898, 2139, 1598, 1515, 1494, 1470, 1438, 1406, 1279, 1246, 1195, 1173, 1076, 1025, 921, 839, 758, 743, 694, 628.

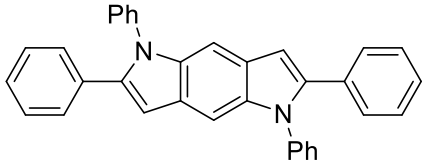
2,5-Diethynyl-*N*^{1},*N*^{4}-diphenylbenzene-1,4-diamine (4d-H)



4d-TMS (721 mg, 1.59 mmol) was dissolved in DCM (30 mL) and MeOH (30 mL). K_2CO_3 (1.10 g, 7.96 mmol) was added and the resulting mixture was stirred at rt for 2 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 50:1 to 5:1). After further purification by recrystallization from DCM/MeOH, the product was obtained as a yellow-orange solid (437 mg, 1.42 mmol, 89%).

Mp: decomposition >183 °C; **R_f**: 0.30 (silica gel, PE:EA = 20:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.37 (s, 2H), 7.32–7.30 (m, 4H), 7.12–7.11 (m, 4H), 7.00–6.98 (m, 2H), 6.12 (br, 2H), 3.45 (s, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 142.5 (s, 2C), 138.3 (s, 2C), 129.6 (d, 4C), 122.0 (d, 2C), 119.5 (d, 2C), 119.0 (d, 4C), 112.2 (s, 2C), 84.6 (d, 2C), 80.2 (s, 2C); **HR-MS** (DART+): *m/z* calculated for $[C_{22}H_{17}N_2]^+$, $[M+H]^+$: 309.1386, found: 309.1390; **IR** (ATR): ν [cm^{-1}] = 3395, 3261, 3044, 2096, 1947, 1735, 1595, 1510, 1466, 1438, 1405, 1281, 1239, 1194, 1167, 1151, 1074, 1024, 913, 871, 750, 694, 682, 618.

1,2,5,6-Tetraphenyl-1,5-dihydropyrrolo[2,3-*f*]indole (*p*DPBa)

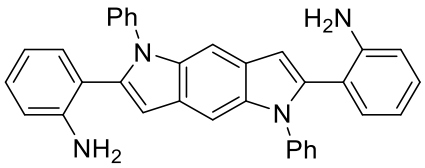


4a (30.0 mg, 65.1 µmol) and $IPrAuNTf_2$ (584 µg, 651 nmol) were dissolved in DCM (5 mL) and the mixture was stirred at rt for 2 h. The solvent was removed under reduced pressure and the residue was washed with MeOH and DCM/pentane (1:1) and pentane. The product was obtained as a pale yellow solid (28.6 mg, 62.1 mmol, 95%).

Mp: >300 °C; **R_f**: 0.47 (silica gel, PE:DCM = 5:1); **^{1}H NMR** (300 MHz, TCE-d_2): δ = 7.53–7.45 (m, 6H), 7.40–7.25 (m, 16H), 6.80 (s, 2H); **^{13}C{^{1}H} NMR** (176 MHz, TCE-d_2, 140 °C): δ = 141.7 (s, 2C), 139.8 (s, 2C), 137.6 (s, 2C), 133.1 (s, 2C), 128.9 (d, 4C), 128.6 (d, 4C), 128.2 (d, 4C), 127.8 (d, 4C), 126.8 (d, 2C), 126.6 (s, 2C), 126.6 (d, 2C), 103.5 (d, 2C), 99.8 (d, 2C); **HR-MS** (DART+): *m/z* calculated for $[C_{34}H_{25}N_2]^+$, $[M+H]^+$: 461.2012, found: 461.2014; **IR** (ATR): ν [cm^{-1}] = 3049, 1946, 1880, 1597, 1498,

1449, 1432, 1401, 1357, 1261, 1236, 1206, 1169, 1071, 1027, 916, 853, 842, 775, 757, 699, 666; **UV-Vis** (DCM): λ_{max} [nm] = 299, 342, 375; **fluorescence** (DCM): λ_{ex} [nm] = 340, λ_{max} [nm] = 418, 438, 468; **quantum yield** (DCM): Φ = 59%.

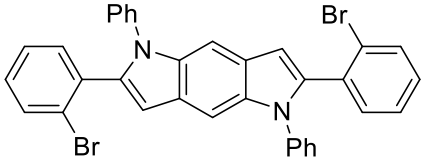
2,2'-(1,5-Diphenyl-1,5-dihydropyrrolo[2,3-*f*]indole-2,6-diyl)dianiline (*p*DPBb)



The crude product **4b** (theoretical yield: 1.95 mmol) and $IPrAuNTf_2$ (16.9 mg, 19.5 µmol) were dissolved in DCM (20 mL) and the mixture was stirred at rt for 16 h. Pentane (40 mL) was added and the mixture was cooled to −20 °C for 1 h. The precipitate was filtered off and recrystallized again from DCM/pentane. The product was obtained as a pale yellow solid (730 mg, 1.49 mmol, 76% over two steps).

Mp: decomposition >205 °C; **R_f**: 0.17 (silica gel, PE:EA = 5:1); **^{1}H NMR** (301 MHz, DMSO-d_6): δ = 7.46–7.42 (m, 6H), 7.33–7.29 (m, 6H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.71 (s, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.42 (t, *J* = 7.2 Hz, 2H), 4.95 (br, 4H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ = 146.6 (s, 2C), 138.8 (s, 2C), 138.4 (s, 2C), 135.6 (s, 2C), 131.1 (d, 2C), 129.1 (d, 4C), 128.8 (d, 2C), 127.3 (d, 4C), 126.6 (d, 2C), 125.9 (s, 2C), 116.5 (s, 2C), 115.7 (d, 2C), 114.7 (d, 2C), 103.5 (d, 2C), 99.3 (d, 2C); **HR-MS** (DART+): *m/z* calculated for $[C_{34}H_{27}N_4]^+$, $[M+H]^+$: 491.2230, found: 491.2224; **IR** (ATR): ν [cm^{-1}] = 3433, 3346, 3063, 1613, 1596, 1573, 1488, 1448, 1432, 1399, 1353, 1315, 1279, 1260, 1230, 1204, 1169, 1059, 1025, 920, 851, 765, 750, 695, 659; **UV-Vis** (DCM): λ_{max} [nm] = 296, 345; **fluorescence** (DCM): λ_{ex} [nm] = 295, λ_{max} [nm] = 407, 421; **quantum yield** (DCM): Φ = 49%.

2,6-Bis(2-bromophenyl)-1,5-diphenyl-1,5-dihydropyrrolo[2,3-*f*]indole (*p*DPBc)

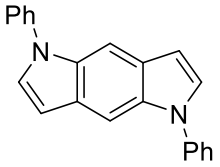


The crude product **4c** (theoretical yield: 213 µmol) and $IPrAuNTf_2$ (1.85 mg, 2.13 µmol) were dissolved in MeCN (10 mL) and the mixture was stirred at rt for 16 h. The resulting precipitate was filtered off and washed with MeOH, DCM/pentane (1:1) and pentane. The product was obtained as a colorless solid (115 mg, 186 µmol, 87% over two steps).

Mp: >300 °C; **R_f**: 0.48 (silica gel, PE:DCM = 5:1); **^{1}H NMR** (700 MHz, TCE-d_2, 80 °C): δ = 7.62 (s, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.42–7.39 (m, 4H), 7.36–7.35 (m, 4H), 7.33–7.29 (m, 4H), 7.25 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 2H), 7.18–7.15 (m, 2H), 6.80 (s, 2H); **^{13}C{^{1}H} NMR** (176 MHz, TCE-d_2, 80 °C): δ = 139.8 (s, 2C), 138.7 (s, 2C), 135.7 (s, 2C), 134.4 (s, 2C), 132.8 (d, 2C), 132.7 (d, 2C), 129.2 (d, 2C), 128.8 (d, 4C), 127.7 (d, 4C), 126.5 (d, 2C), 126.5 (d, 2C), 126.1 (s, 2C), 124.5 (s, 2C), 120.2 (s, 2C), 104.9 (d, 2C), 100.0 (d, 2C), 99.5 (s, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{34}H_{22}Br_2N_2]^+$, $[M]^+$: 616.01443, found:

616.01417; **IR** (ATR): ν [cm^{-1}] = 3071, 3042, 1596, 1560, 1496, 1434, 1397, 1350, 1252, 1228, 1200, 1139, 1090, 1040, 958, 919, 848, 838, 761, 725, 694, 658, 640; **UV-Vis** (DCM): λ_{max} [nm] = 298, 329, 351; **fluorescence** (DCM): λ_{ex} [nm] = 330, λ_{max} [nm] = 468, 498; **quantum yield** (DCM): Φ = 2%.

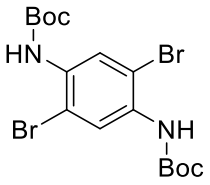
1,5-Diphenyl-1,5-dihydropyrrolo[2,3-*f*]indole (*p*DPBd)



4d-TMS (41.5 mg, 91.7 µmol) and $IPrAuNTf_2$ (794 µg, 917 µmol) were dissolved in MeCN (3 mL) and the mixture was stirred at 75 °C for 12 h. The solvent was removed under reduced pressure and the residue was filtered through a plug of alox eluted with DCM. The solvent was removed under reduced pressure and the residue was washed with MeOH. The product was obtained as a colorless solid (24.5 mg, 79.5 µmol, 87%).

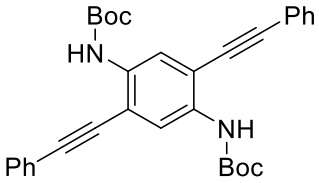
Mp: 244 °C; **R_f**: 0.38 (silica gel, PE:EA = 5:1); **^{1}H NMR** (301 MHz, $CDCl_3$): δ = 7.84 (s, 2H), 7.62–7.52 (m, 8H), 7.38 (d, *J* = 3.3 Hz, 2H), 7.37–7.32 (m, 2H), 6.69 (d, *J* = 3.3 Hz, 2H); **^{13}C{^{1}H} NMR** (176 MHz, $CDCl_3$): δ = 140.7 (s, 2C), 133.3 (s, 2C), 129.7 (d, 4C), 128.9 (d, 2C), 127.6 (s, 2C), 126.0 (d, 2C), 124.2 (d, 4C), 103.1 (d, 2C), 100.5 (d, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{22}H_{16}N_2]^+$, $[M]^+$: 308.13080, found: 308.12927; **IR** (ATR): ν [cm^{-1}] = 3102, 3043, 1596, 1528, 1499, 1445, 1398, 1332, 1302, 1218, 1173, 1120, 1066, 909, 848, 812, 744, 697, 670, 620; **UV-Vis** (DCM): λ_{max} [nm] = 288, 337, 347; **fluorescence** (DCM): λ_{ex} [nm] = 330, λ_{max} [nm] = 358, 372; **quantum yield** (DCM): Φ = 5%.

Di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (5)



Di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate was synthesized according to a literature procedure.[8]

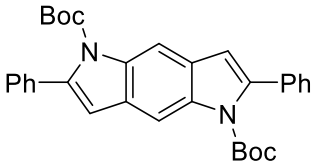
Di-*tert*-butyl (2,5-bis(phenylethynyl)-1,4-phenylene)dicarbamate (6)



A Schlenk flask containing **5** (250 mg, 536 µmol) and $(PPh_3)_2PdCl_2$ (18.8 mg, 26.8 µmol) was evacuated and refilled with argon three times. Degassed THF (10 mL), degassed Et_3N (10 mL) and phenylacetylene (164 mg, 1.61 mmol) were added and the mixture was stirred at rt for 5 min. CuI (5.11 mg, 26.8 µmol) was added and the mixture was stirred at 80 °C for 1 d. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:DCM = 5:1 to 2:1). The product was obtained as a pale yellow solid (255 mg, 501 µmol, 93%).

Mp: decomposition >220 °C; **R_f**: 0.29 (silica gel, PE:DCM = 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.32 (s, 2H), 7.56–7.52 (m, 4H), 7.40–7.37 (m, 6H), 7.23 (s, 2H), 1.55 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 152.7 (s, 2C), 134.2 (s, 2C), 131.8 (d, 4C), 129.0 (d, 2C), 128.7 (d, 4C), 122.6 (s, 2C), 120.7 (d, 2C), 112.7 (s, 2C), 97.5 (s, 2C), 84.8 (s, 2C); 81.1 (s, 2C), 28.5 (q, 6C); **HR-MS** (MALDI+): *m/z* calculated for $[C_{32}H_{32}N_2O_4]^+$, $[M]^+$: 508.2357, found: 508.2355; **IR** (ATR): ν [cm^{-1}] = 3409, 2982, 2935, 1723, 1597, 1532, 1494, 1427, 1390, 1366, 1285, 1231, 1152, 1055, 1029, 888, 857, 771, 753, 689; **UV-Vis** (DCM): λ_{max} [nm] = 268, 313, 323, 365; **fluorescence** (DCM): λ_{ex} [nm] = 320, λ_{max} [nm] = 414, 426; **quantum yield** (DCM): Φ = 59%.

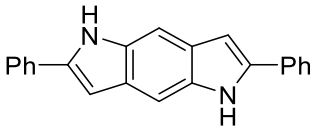
Di-*tert*-butyl 2,6-diphenylpyrrolo[2,3-*f*]indole-1,5-dicarboxylate (*p*DPBe`)



6 (58.5 mg, 115 µmol) and $IPrAuNTf_2$ (996 mg, 1.15 µmol) were dissolved in DCM (10 mL) and the mixture was stirred at rt for 8 h. The solvent was removed under reduced pressure and the residue was washed with MeOH and DCM/pentane (1:1) and pentane. The product was obtained as a colorless solid (55.0 mg, 108 µmol, 94%).

Mp: decomposition >241 °C; **R_f**: 0.57(silica gel, PE:EA = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.38 (s, 2H), 7.48–7.45 (m, 4H), 7.43–7.33 (m, 6H), 6.65 (s, 2H), 1.31 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 150.8 (s, 2C), 141.0 (s, 2C), 135.5 (s, 2C), 135.1 (s, 2C), 128.8 (d, 4C), 127.9 (d, 4C), 127.9 (s, 2C), 127.6 (d, 2C), 111.1 (d, 2C), 106.3 (d, 2C), 83.3 (s, 2C), 27.7 (q, 6C); **HR-MS** (MALDI+): *m/z* calculated for $[C_{32}H_{32}N_2O_4]^+$, $[M]^+$: 508.2357, found: 508.2357; **IR** (ATR): ν [cm^{-1}] = 2983, 1712, 1606, 1571, 1475, 1435, 1384, 1367, 1302, 1260, 1232, 1212, 1177, 1147, 1118, 1073, 1040, 1017, 875, 843, 822, 772, 734, 706, 676, 619; **UV-Vis** (DCM): λ_{max} [nm] = 265, 327; **fluorescence** (DCM): λ_{ex} [nm] = 325, λ_{max} [nm] = 391, 403; **quantum yield** (DCM): Φ = 59%.

2,6-Diphenyl-1,5-dihydropyrrolo[2,3-*f*]indole (*p*DPBe)

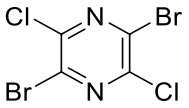


***p*DPBe`** (27.2 mg, 53.5 µmol) was heated under an atmosphere of Argon at 200 °C for 4 h. and the residue was washed with MeOH. The product was obtained as a pale yellow solid (16.1 mg, 52.2 µmol, 98%).

R_f: 0.35 (silica gel, PE:EA = 5:1); **^{1}H NMR** (301 MHz, DMSO-d_6): δ = 11.03 (s, 2H), 7.86 (d, *J* = 7.6 Hz, 4H), 7.48–7.43 (m, 6H), 7.29 (t, *J* = 7.1 Hz, 2H), 6.89 (s, 2H); **UV-Vis** (DCM): λ_{max} [nm] = 260, 286, 351, 392; (DMSO): λ_{max} [nm] = 285, 361, 384, 408; **fluorescence** (DCM): λ_{ex} [nm] = 390, λ_{max} [nm] = 413, 436, 462; (DMSO): λ_{ex} [nm] = 360, λ_{max} [nm] = 427, 451; **quantum yield** (DCM): Φ = 47%; (DMSO): Φ = 54%.

The spectroscopic data correspond to those previously reported in the literature.[9]

2,5-Dibromo-3,6-dichloropyrazine (7)

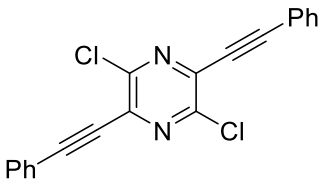


According to a procedure by Gong *et al*.,[10] to a solution of 5-Bromo-6-chloropyrazin-2-amine (4.92 g, 23.6 mmol) in MeOH (100 mL) was added *N*-chlorosuccinimide (3.15 g, 23.6 mmol) in portions and the resulting mixture was stirred at 50 °C for 16 h. Water (100 mL) was added, the resulting precipitate was collected by filtration and dried under reduced pressure. The compound was dissolved in HBr (48 wt%, 120 mL) and THF (170 mL) at 0 °C, $NaNO_2$ (4.07 g, 59.0 mmol) was added in small portions and the mixture was stirred at rt for 1 h. KOH was added until neutralization of the mixture and the crude product was extracted with EA, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, PE:EA = 50:1). The product was obtained as a colorless solid (4.43 g, 14.4 mmol, 61%).

R_f: 0.50 (silica gel, PE:EA = 50:1); **^{13}C{^{1}H} NMR** (76 MHz, $CDCl_3$): δ = 146.8 (s, 2C), 136.5 (s, 2C).

The spectroscopic data correspond to those previously reported in the literature.[10]

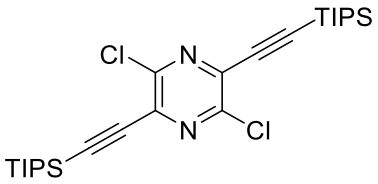
2,5-Dichloro-3,6-bis(phenylethynyl)pyrazine (8a)



A Schlenk flask containing **7** (388 mg, 1.26 mmol) and $(PPh_3)_2PdCl_2$ (17.8 mg, 25.3 µmol) was evacuated and refilled with argon three times. Degassed THF (10 mL), degassed Et_3N (10 mL) and phenylacetylene (273 mg, 2.59 mmol) were added and the mixture was stirred at rt for 5 min. CuI (9.64 mg, 50.6 µmol) was added and the mixture was stirred at rt for 12 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:DCM = 10:1 to 1:1). The product was obtained a pale yellow solid (396 mg, 1.13 mmol, 90%).

Mp: 219 °C; **R_f**: 0.60 (silica gel, PE:EA = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.8 Hz, 4H), 7.47–7.45 (m, 2H), 7.43–7.40 (m, 4H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 147.7 (s, 2C), 136.0 (s, 2C), 132.6 (d, 4C), 130.5 (d, 2C), 128.8 (d, 4C), 121.0 (s, 2C), 100.5 (s, 2C), 84.5 (s, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_{10}Cl_2N_2]^+$, $[M]^+$: 348.02156, found: 348.02078; **IR** (ATR): ν [cm^{-1}] = 3068, 2225, 2193, 1571, 1496, 1444, 1422, 1303, 1242, 1224, 1168, 1105, 1071, 1025, 918, 849, 757, 689, 669; **UV-Vis** (DCM): λ_{max} [nm] = 306, 380; **fluorescence** (DCM): λ_{ex} [nm] = 305, λ_{max} [nm] = 415; **quantum yield** (DCM): Φ = 20%.

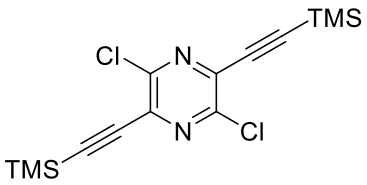
2,5-Dichloro-3,6-bis((triisopropylsilyl)ethynyl)pyrazine (8b)



A Schlenk flask containing **7** (2.00 g, 6.52 mmol) and $(PPh_3)_2PdCl_2$ (91.5 mg, 130 µmol) was evacuated and refilled with argon three times. Degassed THF (20 mL), degassed Et_3N (20 mL) and ethynyltriisopropylsilane (2.44 g, 13.4 mmol) were added and the mixture was stirred at rt for 5 min. CuI (37.3 mg, 196 µmol) was added and the mixture was stirred at rt for 16 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 200:1). The product was obtained as a colorless solid (2.93 g, 5.75 mmol, 88%).

Mp: 117 °C; **R_f**: 0.75 (silica gel, PE:EA = 100:1); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.21–1.14 (m, 42H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 148.0 (s, 2C), 135.7 (s, 2C), 106.0 (s, 2C), 100.2 (s, 2C), 18.7 (q, 12C), 11.3 (d, 6C); **HR-MS** (EI+): *m/z* calculated for $[C_{26}H_{42}Cl_2N_2Si_2]^+$, $[M]^+$: 508.22581, found: 508.22712; **IR** (ATR): ν [cm^{-1}] = 2945, 2891, 2866, 2168, 1461, 1393, 1333, 1297, 1252, 1157, 1122, 1074, 1018, 996, 920, 883, 830, 682, 611.

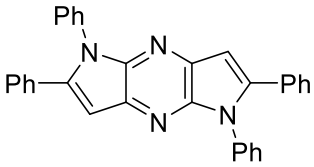
2,5-Dichloro-3,6-bis((trimethylsilyl)ethynyl)pyrazine (8c)



A Schlenk flask containing **7** (1.65 g, 5.38 mmol) and $(PPh_3)_2PdCl_2$ (189 mg, 269 µmol) was evacuated and refilled with argon three times. Degassed THF (15 mL), degassed Et_3N (10 mL) and ethynyltrimethylsilane (1.11 g, 11.3 mmol) were added and the mixture was stirred at rt for 5 min. CuI (102 mg, 538 µmol) was added and the mixture was stirred at rt for 4 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 100:1). The product was obtained as an off-white solid (1.59 g, 4.66 mmol, 87%).

Mp: 103 °C; **R_f**: 0.75 (silica gel, PE:EA = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.30 (s, 18H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 147.8 (s, 2C), 135.8 (s, 2C), 108.6 (s, 2C), 98.2 (s, 2C), –0.5 (q, 6C); **HR-MS** (EI+): *m/z* calculated for $[C_{14}H_{18}Cl_2N_2Si_2]^+$, $[M]^+$: 340.03801, found: 340.03713; **IR** (ATR): ν [cm^{-1}] = 2963, 2899, 1392, 1298, 1249, 1156, 1123, 842, 763, 706, 635.

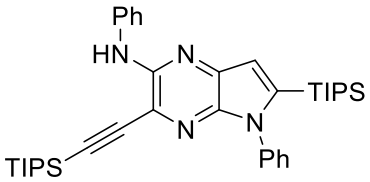
1,2,5,6-Tetraphenyl-1,5-dihydrodipyrrolo[2,3-*b*:2',3'-*e*]pyrazine (*p*DPPa)



A Schlenk flask containing **8a** (250 mg, 716 µmol), $Pd_2(dba)_3$ (8.52 mg, 9.31 µmol), *rac*-BINAP (11.6 mg, 18.6 µmol) and NaO^tBu (241 mg, 2.51 mmol) was evacuated and refilled with argon three times. Degassed toluene (15 mL) and aniline (667 mg, 7.16 mmol) were added and the mixture was stirred at 115 °C for 16 h. The solvents were removed under reduced pressure and the residue was transferred on a fritted glass filter, washed with water, MeOH and DCM and then eluted with a large amount of THF to yield 174 mg (376 µmol, 53%) of the product as a bright yellow solid. The washing solution was extracted with DCM and the combined organic phased where washed with water, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue and $PdCl_2(MeCN)_2$ (8.80 mg, 33.9 µmol) were dissolved in chlorobenzene (20 mL) and the mixture was stirred at 110 °C for 2 d. The solvent was removed under reduced pressure and the residue was treated as above to yield additional 84.0 mg (182 µmol, 25%).

Mp: >300 °C; **R_f**: 0.26 (silica gel, PE:DCM = 1:2); **^{1}H NMR** (700 MHz, TCE-d_2, 120 °C): δ = 7.50–7.48 (m, 4H), 7.47–7.46 (m, 4H), 7.43–7.40 (m, 6H), 7.35–7.33 (m, 6H), 6.98 (s, 2H); **^{13}C{^{1}H} NMR** (176 MHz, TCE-d_2, 120 °C): δ = 144.0 (s, 2C), 143.0 (s, 2C), 137.3 (s, 2C), 135.4 (s, 2C), 132.2 (s, 2C), 128.8 (d, 4C), 128.6 (d, 4C), 128.5 (d, 4C), 128.1 (d, 4C), 127.8 (d, 2C), 126.9 (d, 2C), 102.1 (d, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{32}H_{22}N_4]^+$, $[M]^+$: 462.18390, found: 462.18520; **IR** (ATR): ν [cm^{-1}] = 3051, 1954, 1888, 1594, 1547, 1496, 1454, 1443, 1396, 1326, 1309, 1241, 1200, 1173, 1091, 1029, 973, 924, 846, 832, 787, 757 717, 695, 666, 652, 620; **UV-Vis** (DCM): λ_{max} [nm] = 263, 388; **fluorescence** (DCM): λ_{ex} [nm] = 390, λ_{max} [nm] = 442, 462; **quantum yield** (DCM): Φ = 56%.

***N*,5-Diphenyl-6-(triisopropylsilyl)-3-((triisopropylsilyl)ethynyl)-5*H*-pyrrolo[2,3-*b*]pyrazin-2-amine (9)**

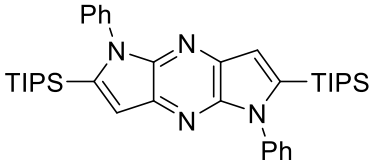


A Schlenk flask containing **8b** (500 mg, 981 µmol), $Pd_2(dba)_3$ (18.0 mg, 19.6 µmol), *rac*-BINAP (24.4 mg, 39.2 µmol) and NaO^tBu (330 mg, 3.43 mmol) was evacuated and refilled with argon three times.

Degassed toluene (15 mL) and aniline (914 mg, 9.81 mmol) were added and the mixture was stirred at 115 °C for 16 h. The solvents were removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 40:1 to 20:1) to yield the single-cyclized product **9** as a yellow solid (473 mg, 758 µmol, 77%) alongside with the double-cyclized product ***p*DPPb** as a pale yellow solid (52.5 mg, 84.3 µmol, 9%).

Mp: 232 °C; **R_f**: 0.57 (silica gel, PE:EA = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.8 Hz, 2H), 7.54 (s, 1H), 7.49–7.47 (m, 3H), 7.41–7.34 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 1.34–1.14 (m, 21H), 1.12–1.02 (m, 21H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 149.6 (s, 1C), 145.5 (s, 1C), 140.7 (s, 1C), 140.2 (s, 1C), 138.7 (s, 1C), 135.4 (s, 1C), 129.6 (d, 2C), 129.2 (d, 2C), 128.9 (d, 3C), 121.9 (d, 1C), 120.2 (s, 1C), 118.6 (d, 2C), 113.3 (d, 1C), 103.3 (s, 1C), 99.8 (s, 1C), 19.1 (q, 6C), 18.9 (q, 6C), 12.4 (d, 3C), 11.5 (d, 3C); **HR-MS** (ESI+): *m/z* calculated for $[C_{38}H_{55}N_4Si_2]^+$, $[M+H]^+$: 623.3960, found: 623.3966; **IR** (ATR): ν [cm^{-1}] = 3402, 2944, 2864, 2365, 2140, 1596, 1563, 1542, 1517, 1493, 1461, 1439, 1417, 1402, 1351, 1251, 1227, 1167, 1104, 1071, 996, 945, 921, 883, 800, 775, 746, 698, 686, 662, 636.

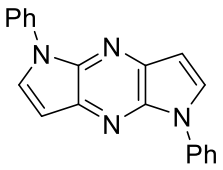
1,5-Diphenyl-2,6-bis(triisopropylsilyl)-1,5-dihydrodipyrrolo[2,3-*b*:2',3'-*e*]pyrazine (*p*DPPb)



9 (255 mg, 409 µmol) and $IPrAuNTf_2$ (35.4 mg, 40.9 µmol) were dissolved in chlorobenzene (20 mL) and the mixture was stirred at 110 °C for 2 d. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE:EA = 40:1 to 10:1). The product was obtained as a pale yellow solid (235 mg, 377 µmol, 92%).

Mp: >300 °C; **R_f**: 0.24 (silica gel, PE:EA = 20:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.54–7.48 (m, 6H), 7.46–7.45 (m, 4H), 7.09 (s, 2H), 1.11–1.03 (m, 6H), 1.01–0.99 (m, 36H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 144.3 (s, 2C), 144.1 (s, 2C), 139.4 (s, 2C), 135.4 (s, 2C), 129.7 (d, 4C), 129.1 (d, 4C), 128.9 (d, 2C), 113.6 (d, 2C), 19.1 (q, 12C), 12.4 (d, 6C); **HR-MS** (DART+): *m/z* calculated for $[C_{38}H_{55}N_4Si_2]^+$, $[M+H]^+$: 623.3960, found: 623.3973; **IR** (ATR): ν [cm^{-1}] = 2947, 2866, 1596, 1499, 1459, 1385, 1292, 1199, 1110, 1072, 1019, 996, 932, 880, 830, 790, 762, 724, 701, 684, 666, 650, 624; **UV-Vis** (DCM): λ_{max} [nm] = 267, 355, 397; **fluorescence** (DCM): λ_{ex} [nm] = 400, λ_{max} [nm] = 438; **quantum yield** (DCM): Φ = 23%.

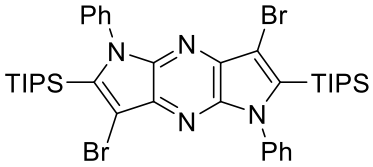
1,5-Diphenyl-1,5-dihydrodipyrrolo[2,3-*b*:2',3'-*e*]pyrazine (*p*DPPc)



Tetra-*n*-butylammonium fluoride (1 M solution in THF, 675 µL, 675 µmol) was added to a solution of ***p*DPPPb** (84.1 mg, 135 µmol) in DCM (10 mL) and the mixture was stirred for 6 h. Water (10 mL) was added and the mixture was extracted with DCM and the combined organic layers were washed with water and brine and dried over Na_2SO_4. The solution was filtered through a plug of silica gel eluted with DCM and the solvent was removed under reduced pressure. The product was obtained as an off-white solid (41.4 mg, 133 µmol, 99%).

Mp: 244 °C; **R_f**: 0.38 (silica gel, PE:EA = 5:1); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 7.89–7.86 (m, 6H), 7.59–7.55 (m, 4H), 7.40–7.36 (m, 2H), 6.82 (d, *J* = 3.8 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 140.1 (s, 2C), 139.0 (s, 2C), 136.3 (s, 2C), 131.3 (d, 2C), 129.7 (d, 4C), 126.6 (d, 2C), 123.9 (d, 4C), 102.2 (d, 2C); **HR-MS** (EI+): *m/z* calculated for $[C_{20}H_{14}N_4]^+$, $[M]^+$: 310.12130, found: 310.12163; **IR** (ATR): ν [cm^{-1}] = 3128, 3106, 3041, 1720, 1597, 1530, 1512, 1494, 1453, 1389, 1362, 1285, 1256, 1213, 1175, 1164, 1105, 1072, 1025, 1003, 962, 917, 894, 852, 802, 765, 755, 740, 693, 669; **UV-Vis** (DCM): λ_{max} [nm] = 275, 337, 373; **fluorescence** (DCM): λ_{ex} [nm] = 335, λ_{max} [nm] = 419; **quantum yield** (DCM): Φ = 14%.

3,7-Dibromo-1,5-diphenyl-2,6-bis(triisopropylsilyl)-1,5-dihydrodipyrrolo[2,3-*b*:2',3'-*e*]pyrazine (*p*DPPd)



To a solution of ***p*DPPPb** (10.8 mg, 17.3 µmol) in DCM (2 mL) *N*-bromosuccinimide (7.71 mg, 43.3 µmol) was added and the reaction mixture was stirred at rt for 8 h. A saturated aqueous solution of Na_2SO_3 (3 mL) and water (5 mL) was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was recrystallized from DCM/pentane. The product was obtained as a pale yellow solid (12.4 mg, 15.9 µmol, 92%).

Mp: >300 °C; **R_f**: 0.45 (silica gel, PE:EA = 20:1); **^{1}H NMR** (600 MHz, CD_2Cl_2): δ = 7.59–7.54 (m, 6H), 7.47–7.45 (m, 4H), 1.32 (sept, *J* = 7.5 Hz, 6H), 1.05 (d, *J* = 7.5 Hz, 36H); **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2): δ = 144.2 (s, 2C), 143.5 (s, 2C), 139.4 (s, 2C), 134.7 (s, 2C), 130.5 (d, 4C), 129.6 (d, 2C), 129.1 (d, 4C), 103.4 (s, 2C), 19.5 (q, 12C), 13.0 (d, 6C); **HR-MS** (MALDI+): *m/z* calculated for $[C_{38}H_{52}Br_2N_4Si_2]^+$, $[M]^+$: 778.2092, found: 778.2092; **IR** (ATR): ν [cm^{-1}] = 2945, 2863, 1595, 1497, 1455, 1381, 1297, 1260, 1211, 1160, 1071, 1032, 1019, 997, 927, 912, 882, 803, 765, 738, 703, 694, 669, 647, 629; **UV-Vis** (DCM): λ_{max} [nm] = 267, 359, 405; **fluorescence** (DCM): λ_{ex} [nm] = 360, λ_{max} [nm] = 454, 464, 502; **quantum yield** (DCM): Φ = 1%.

2 NMR Spectra

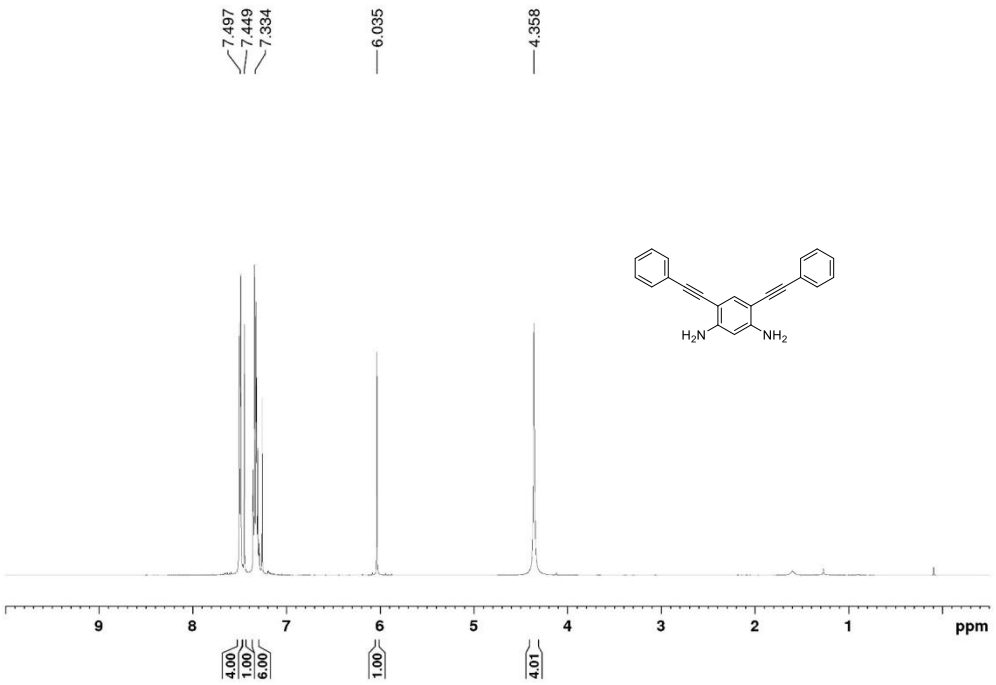


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1a**.

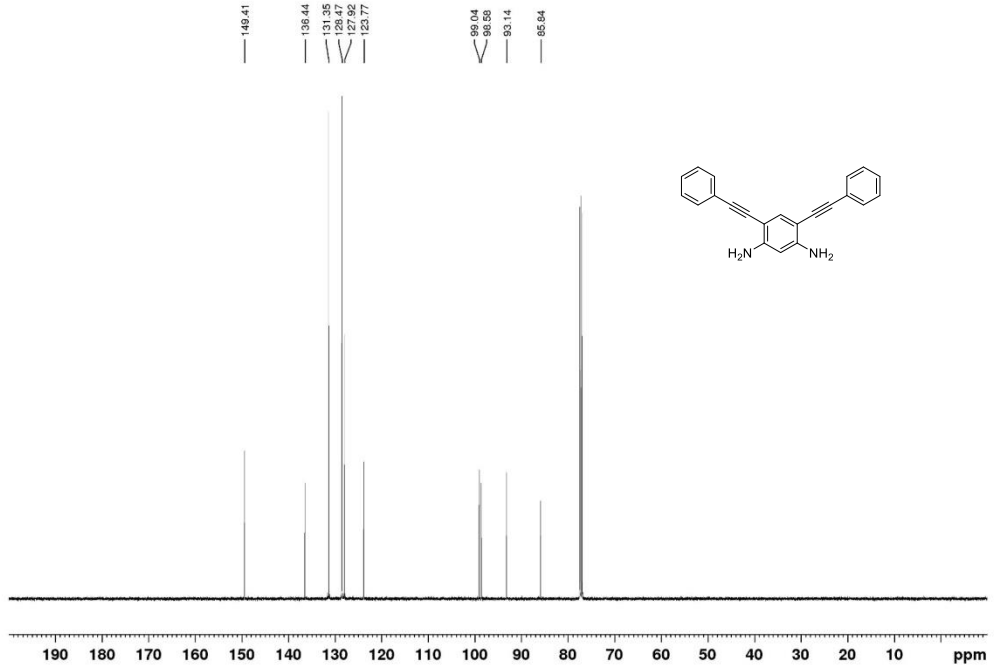


Figure S2. ^{13}H NMR spectrum (500 MHz, $CDCl_3$) of **1a**.

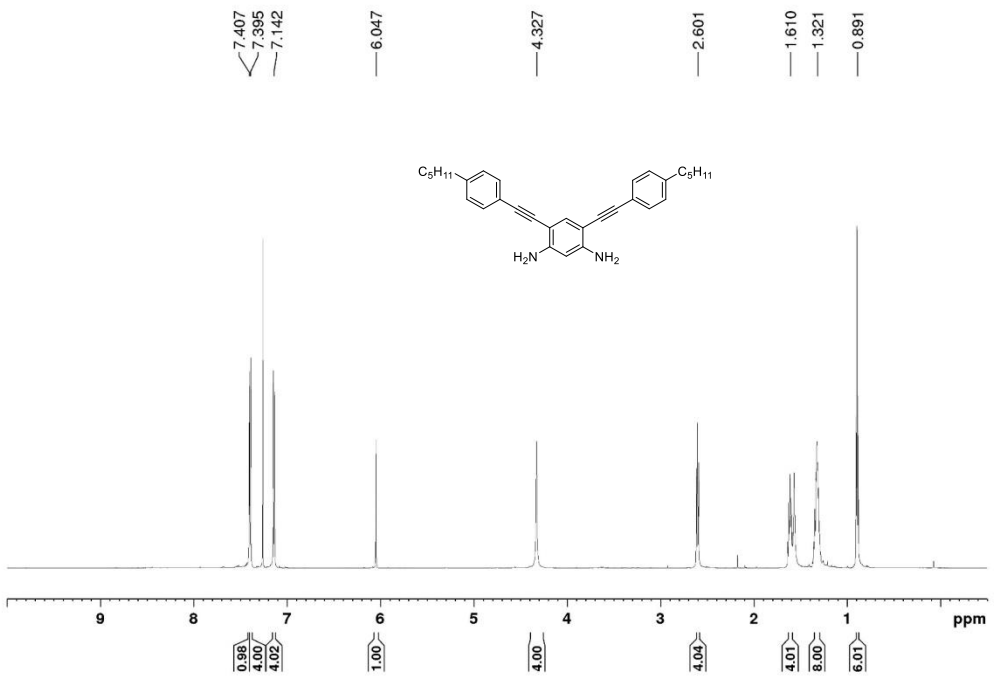


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1b**.

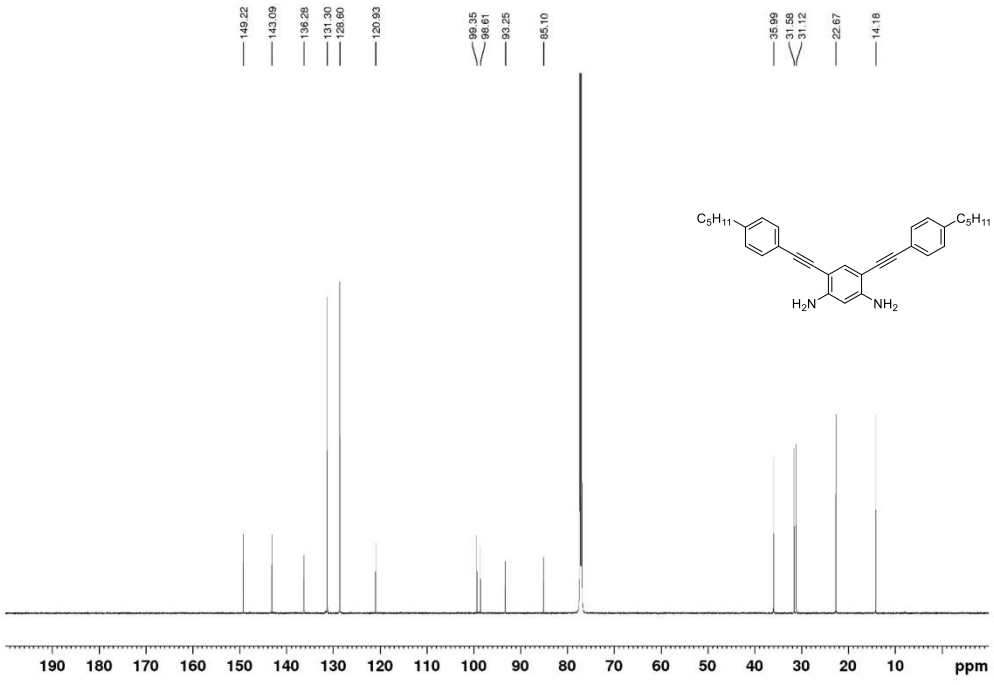


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **1b**.

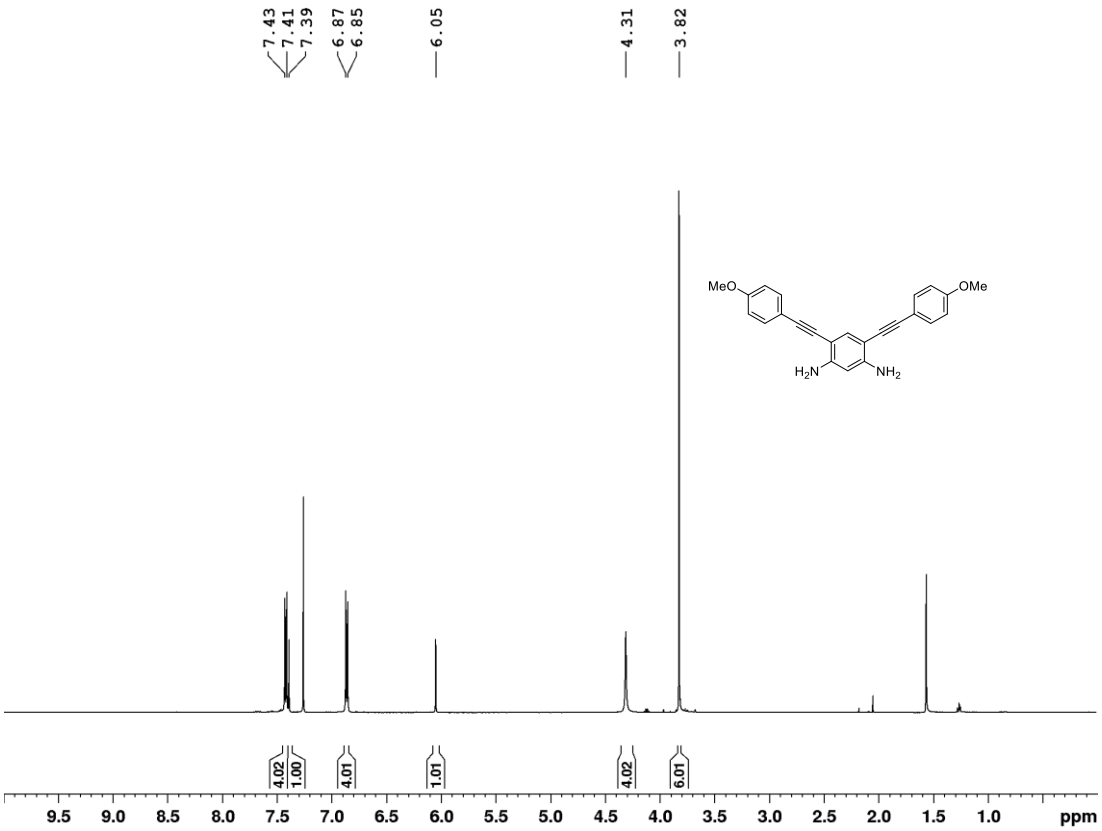


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1c**.

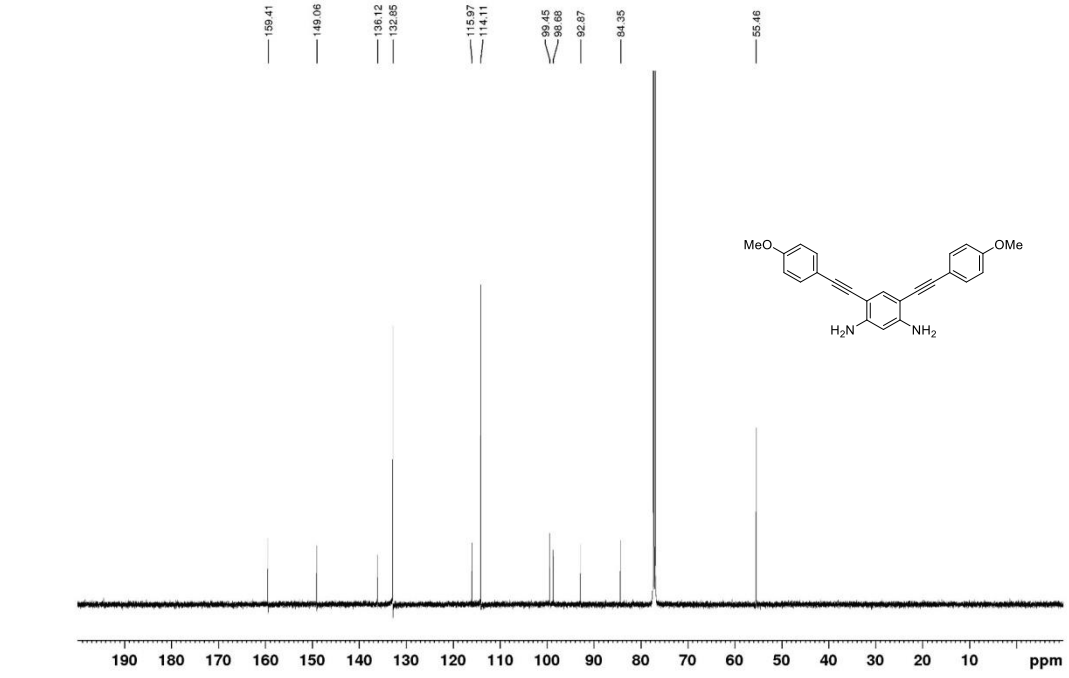


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **1c**.

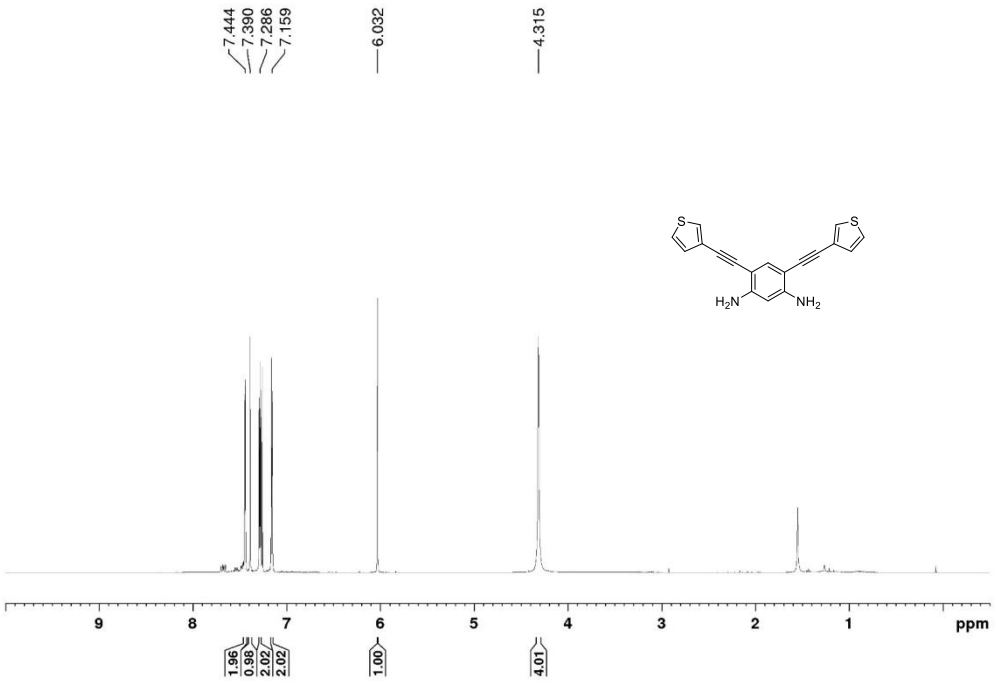


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1d**.

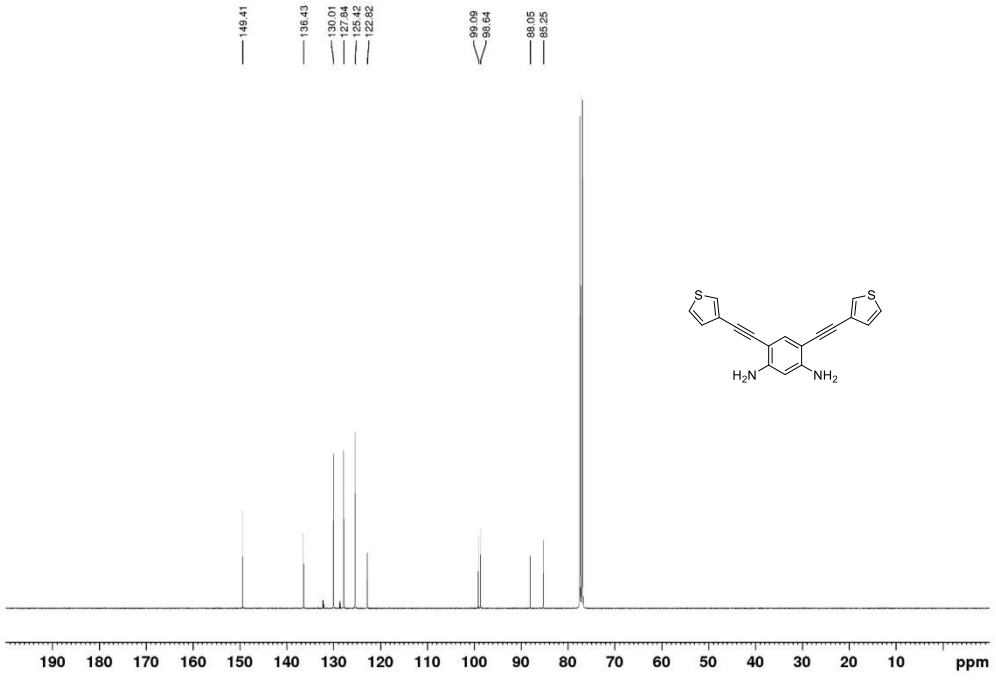


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1d**.

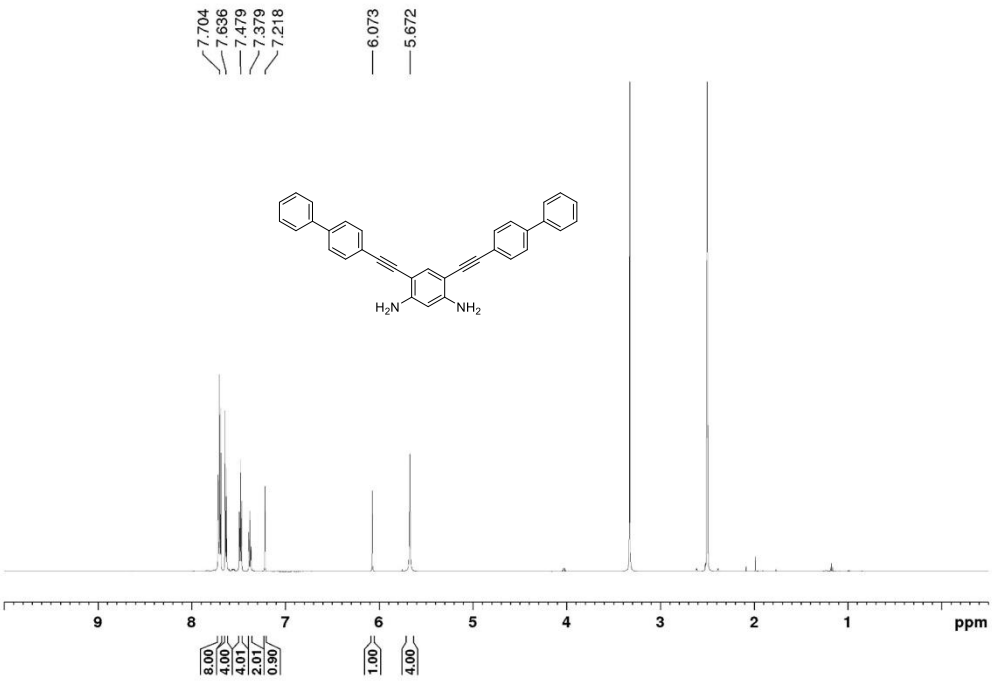


Figure S9. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **1e**.

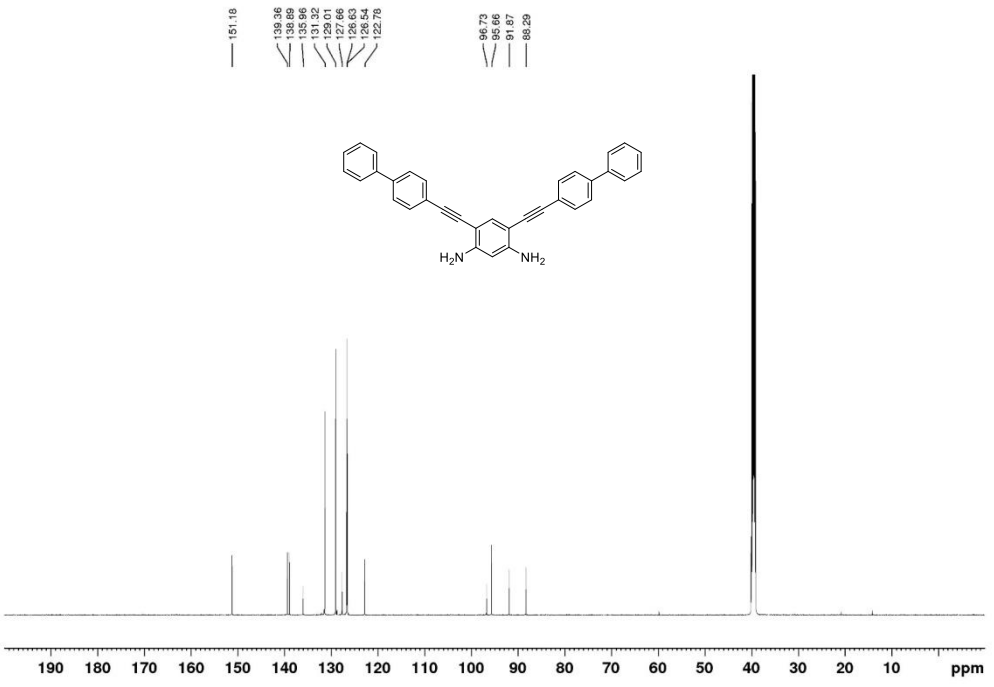


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, DMSO-d_6) of **1e**.

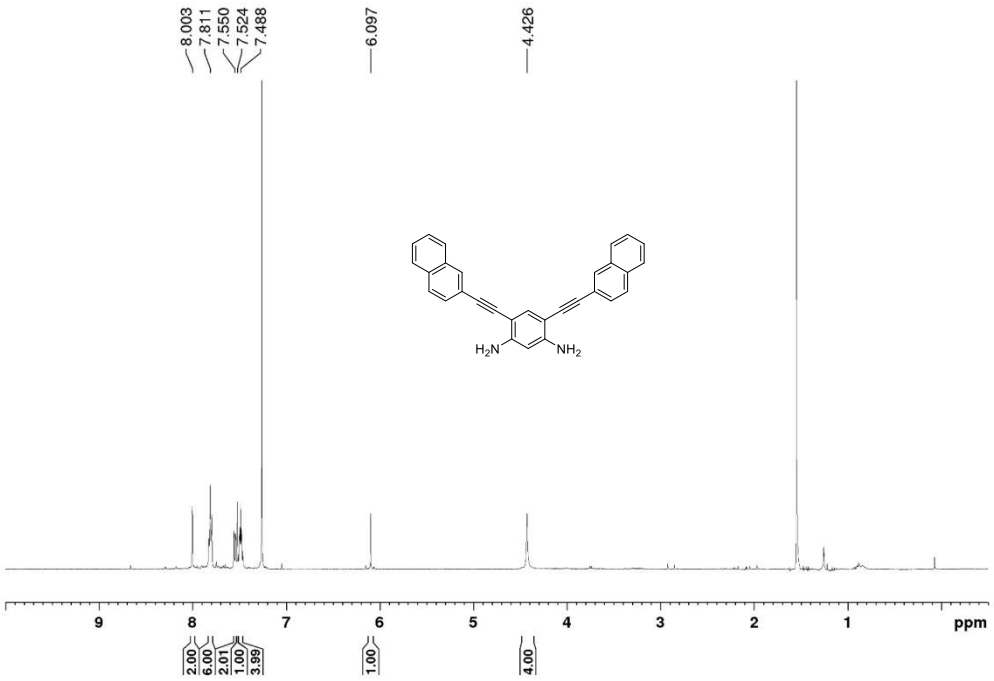


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **1f**.

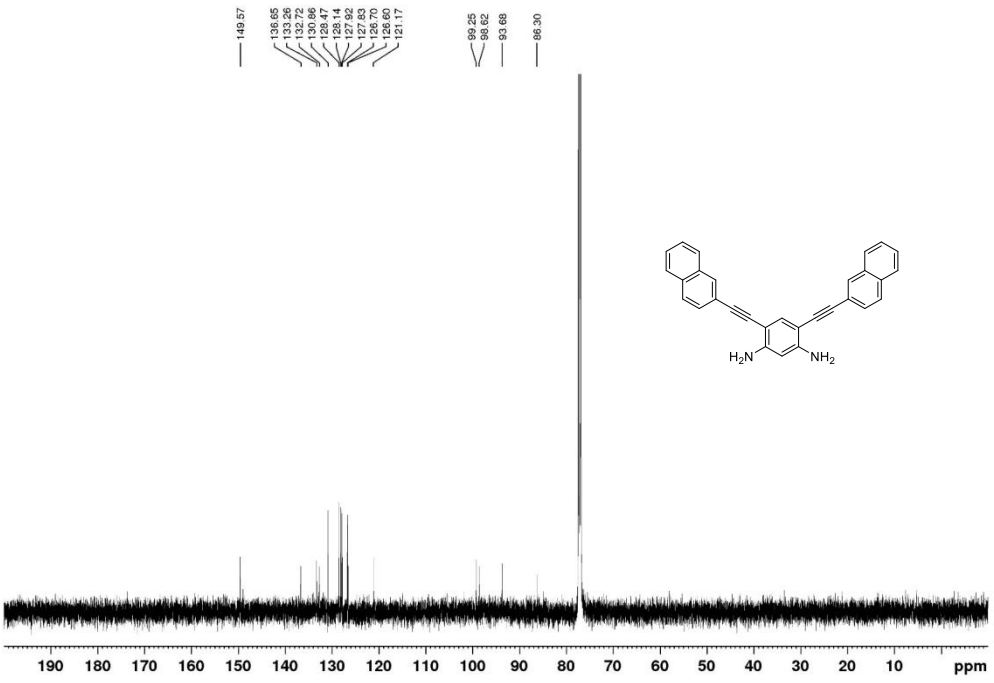


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **1f**.

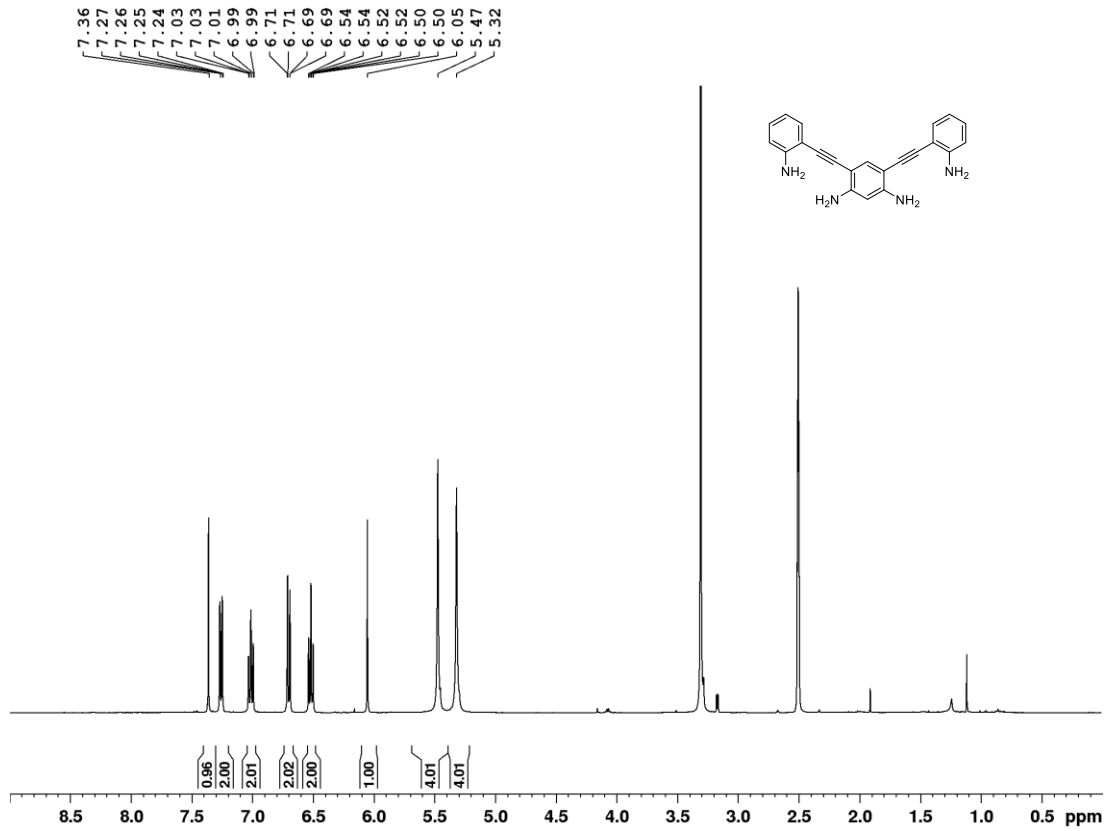


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1g**.

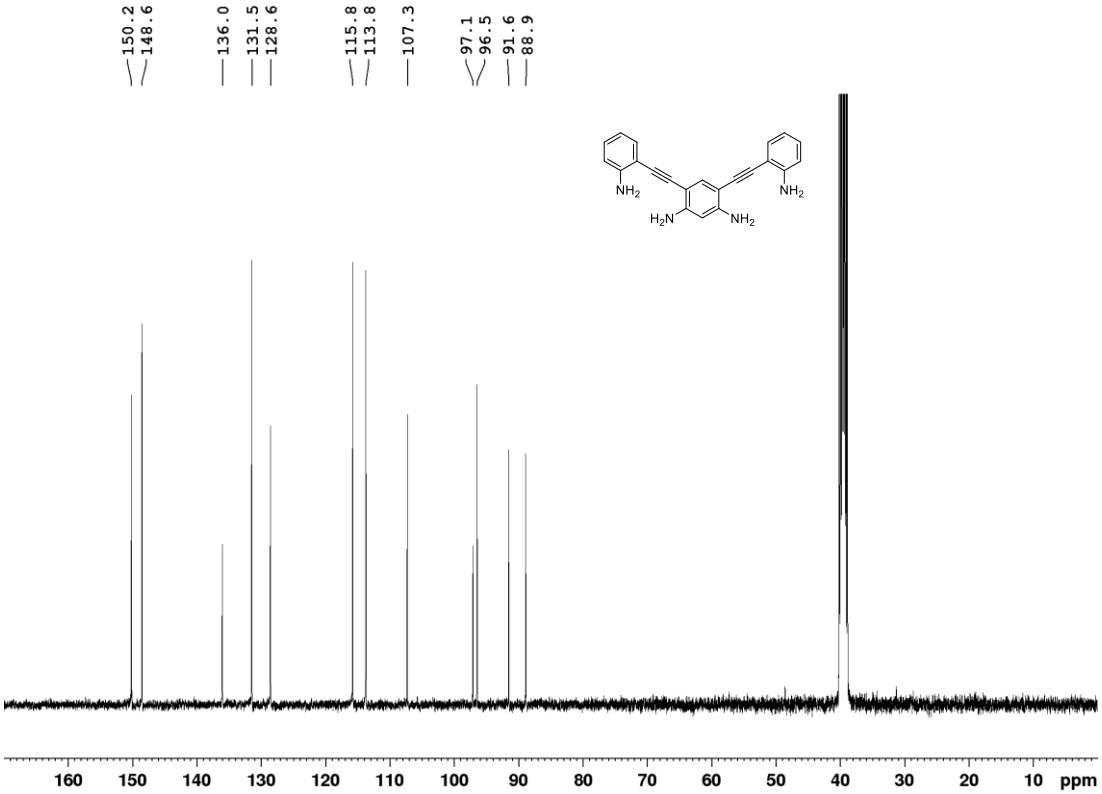


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of **1g**.

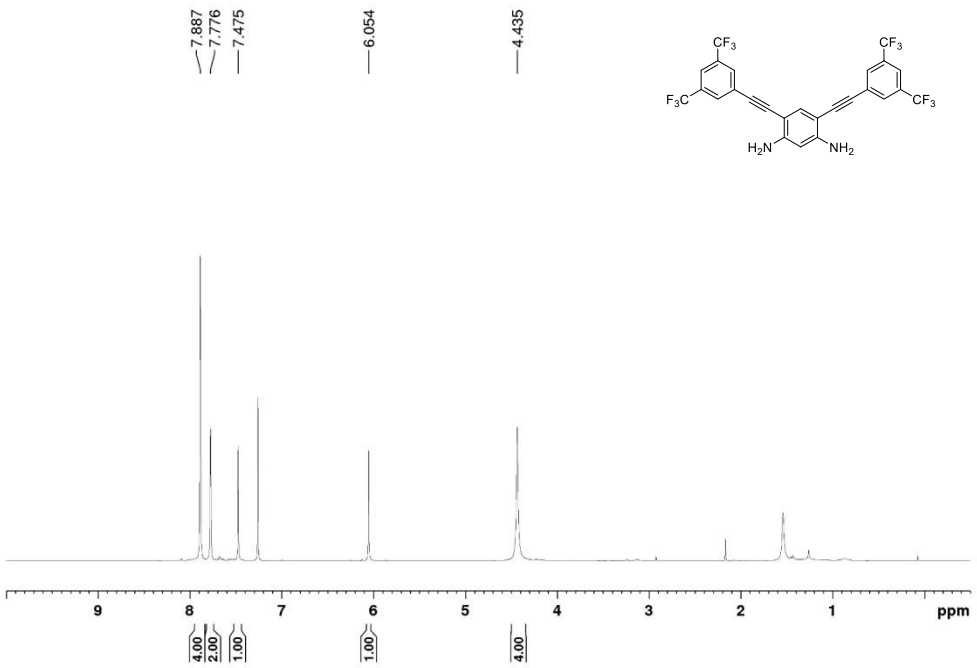


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1h**.

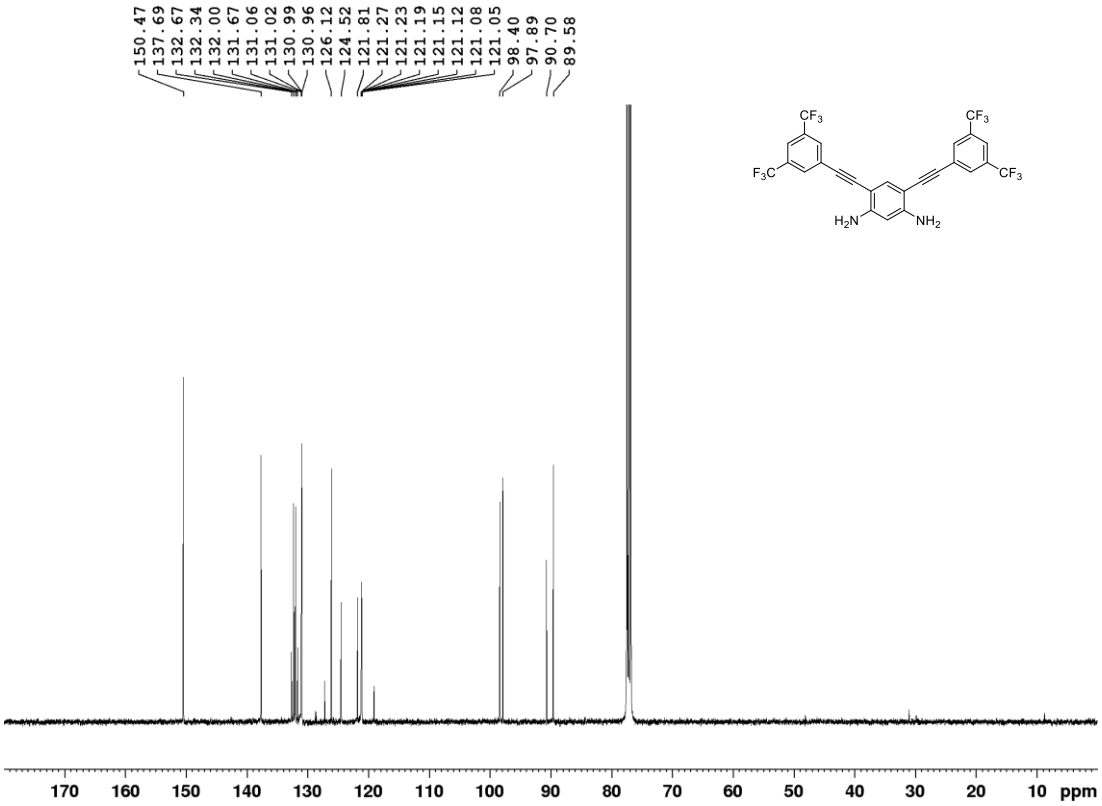


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, $CDCl_3$) of **1h**.

Figure S17. $^{19}F\{^{1}H\}$ NMR spectrum (471 MHz, $CDCl_3$) of **1h**.

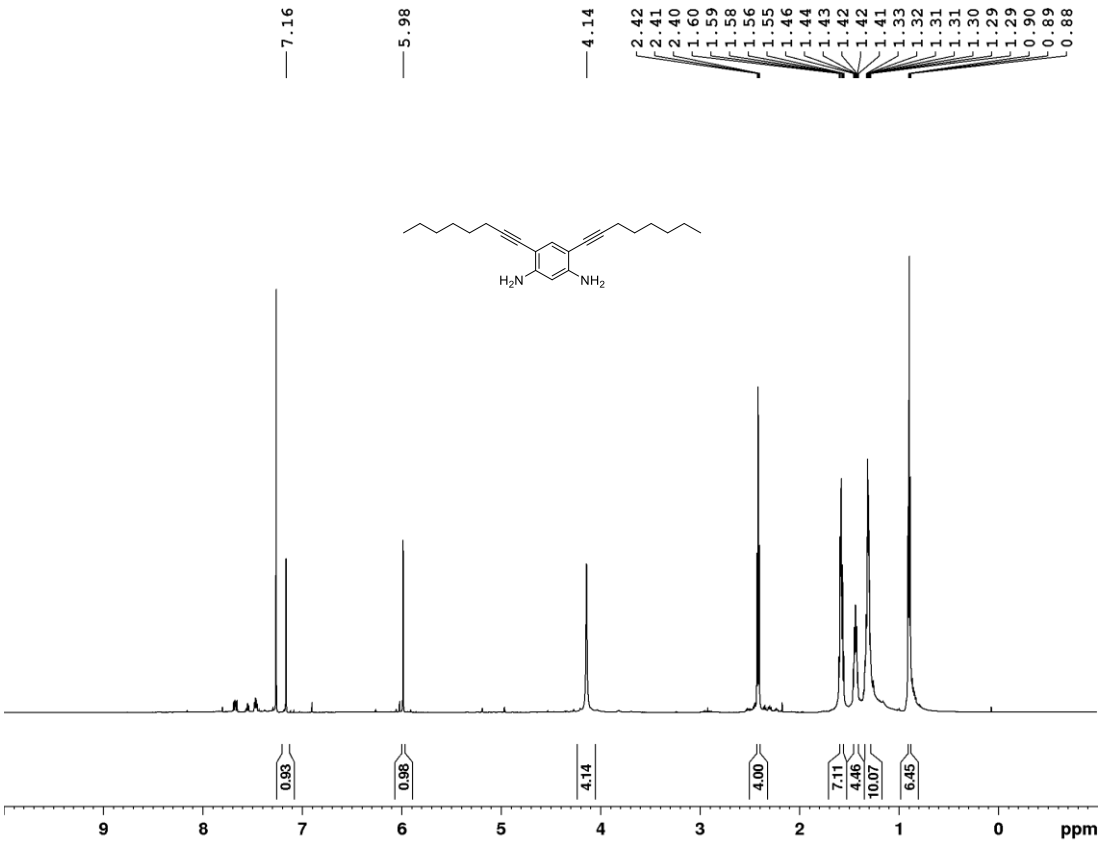


Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1i**.

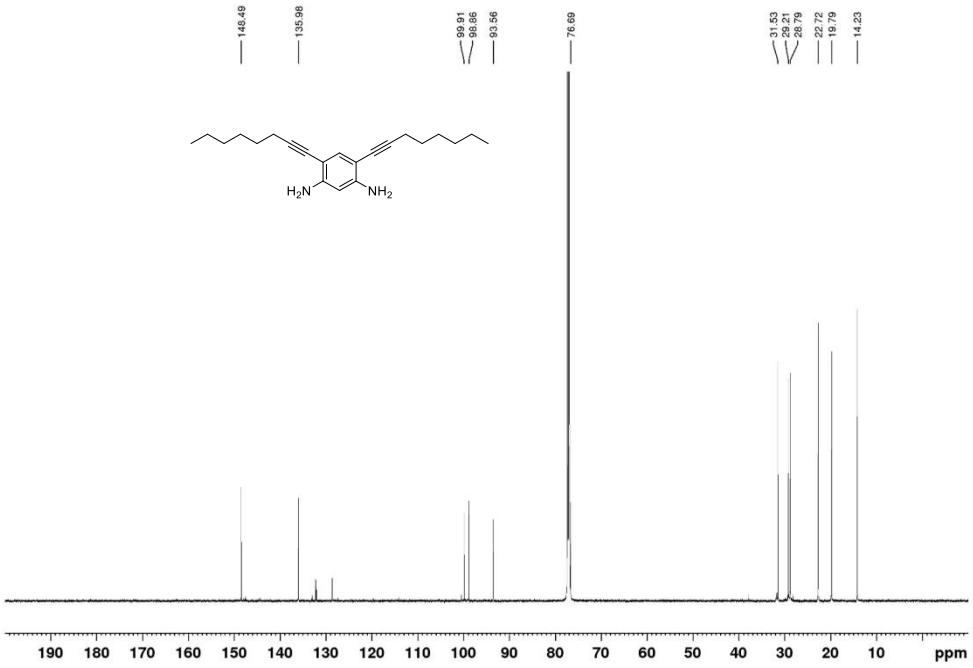


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **1i**.

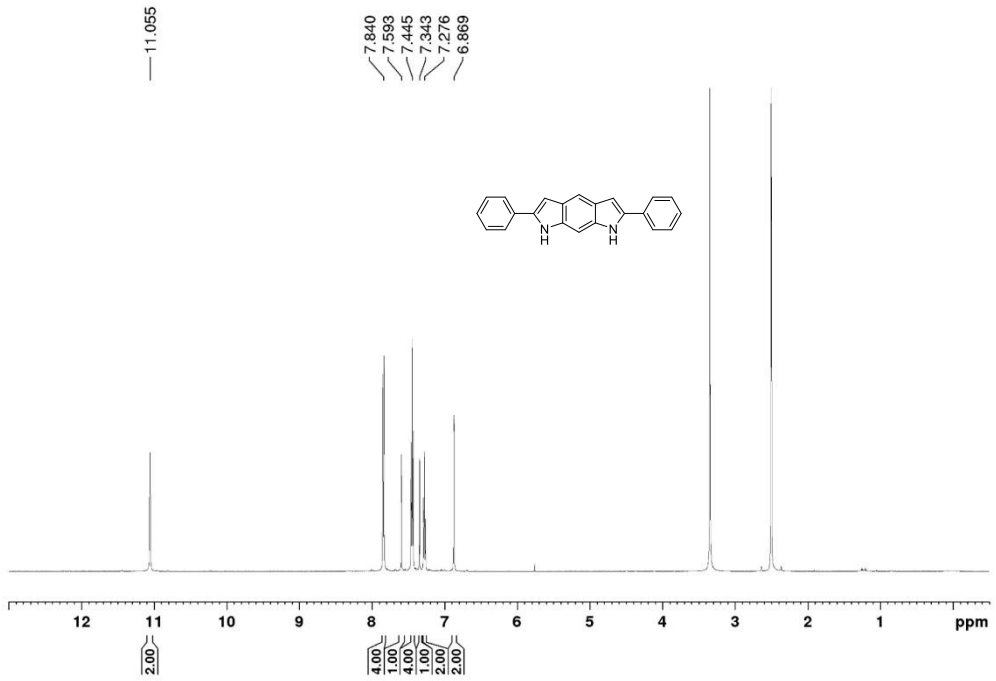


Figure S20. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of ***m*DPBa**.

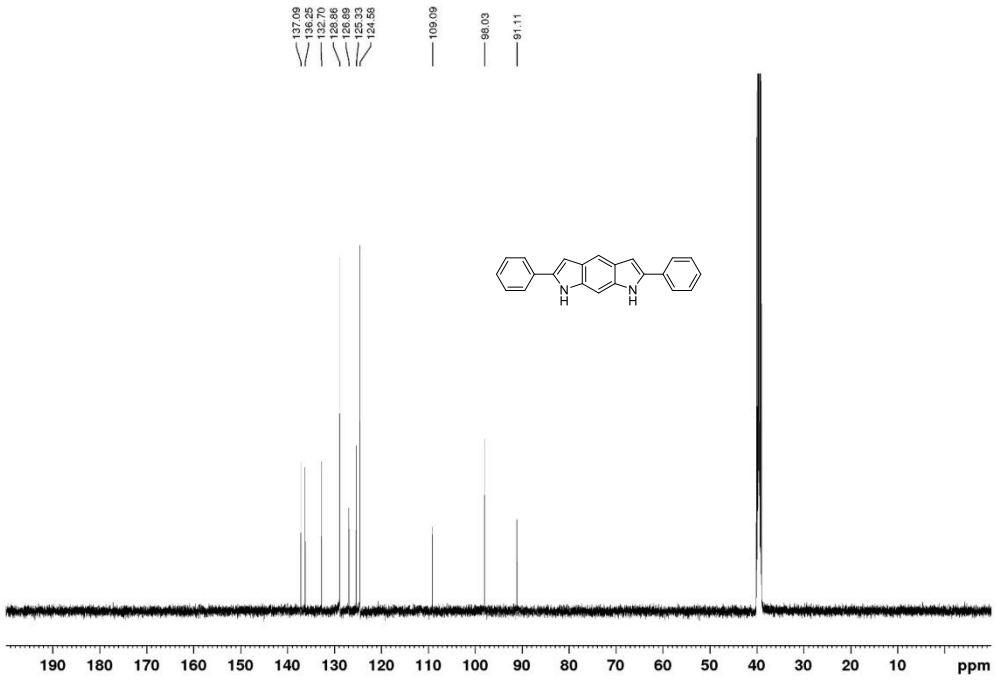


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, DMSO-d_6) of ***m*DPBa**.

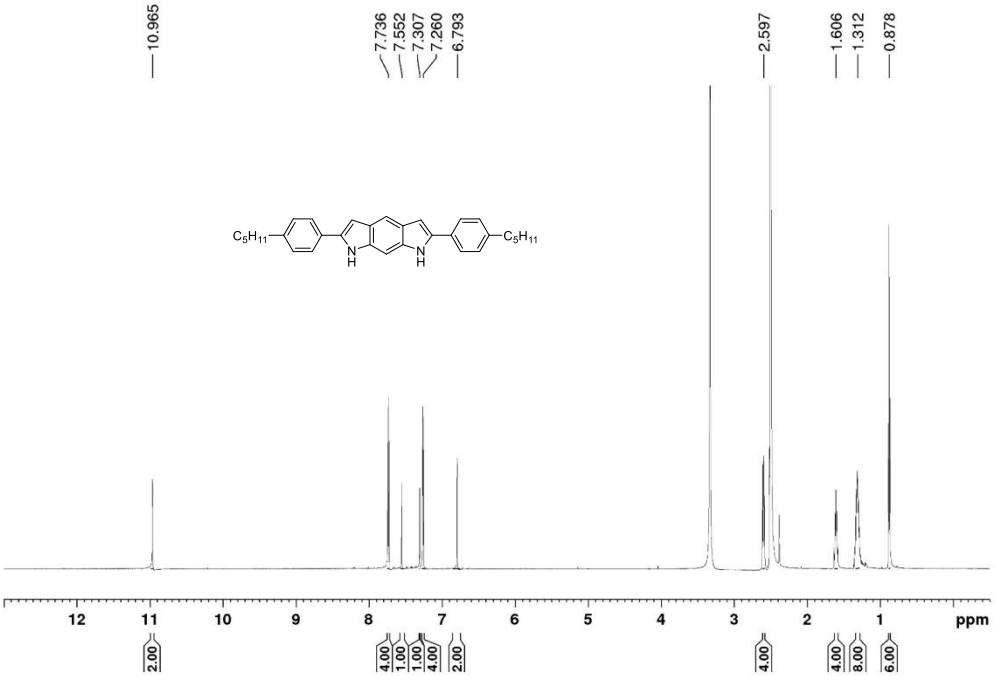


Figure S22. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of ***m*DPBb**.

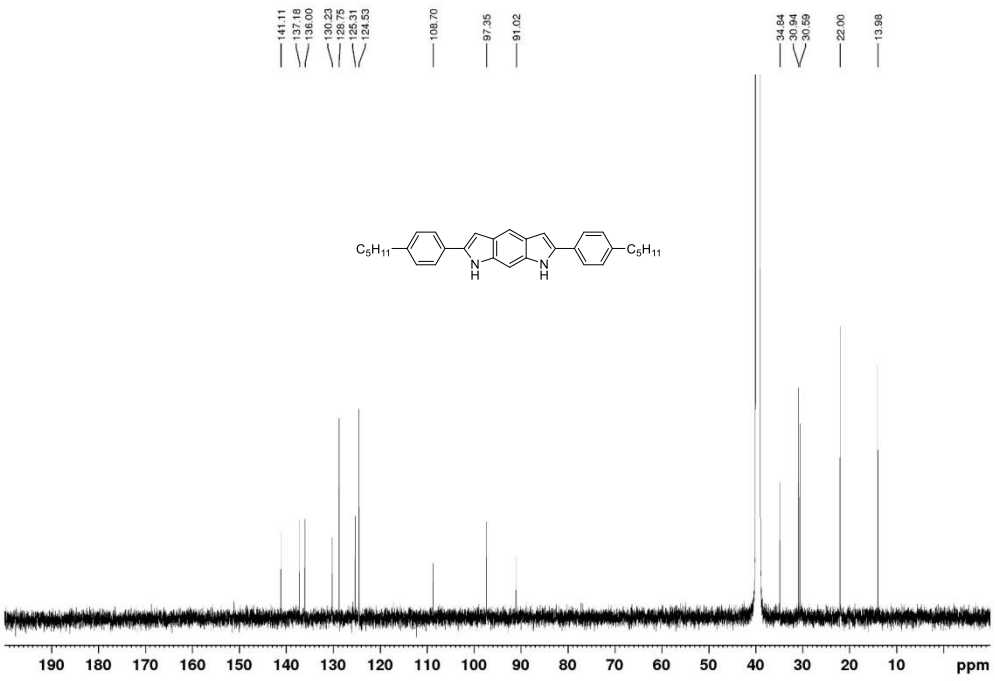


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, DMSO-d_6) of ***m*DPBb**.

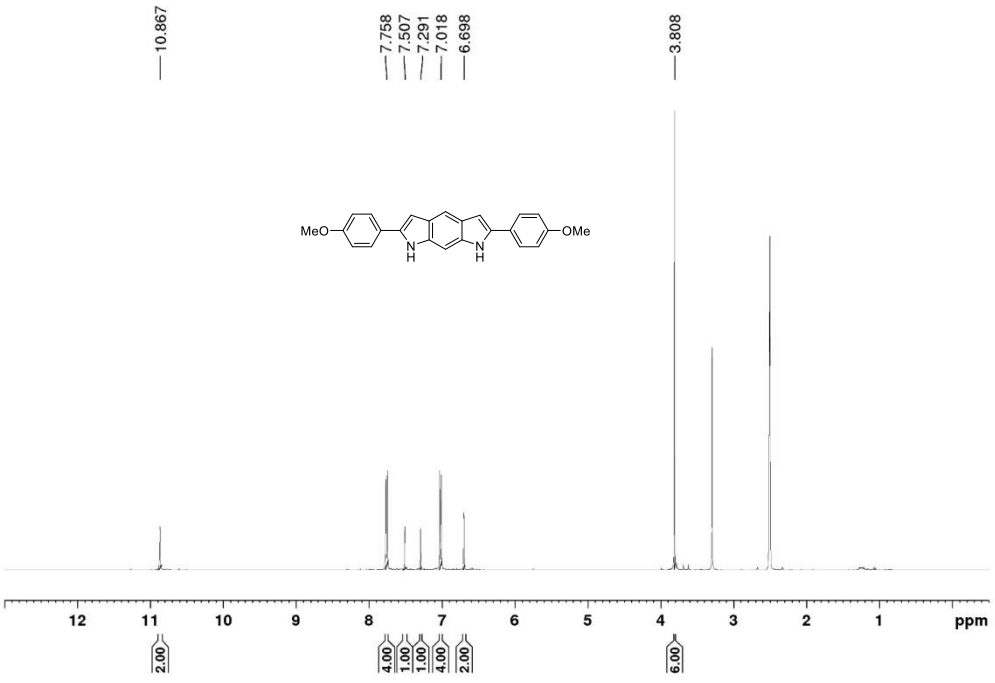


Figure S24. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of ***m*DPBc**.

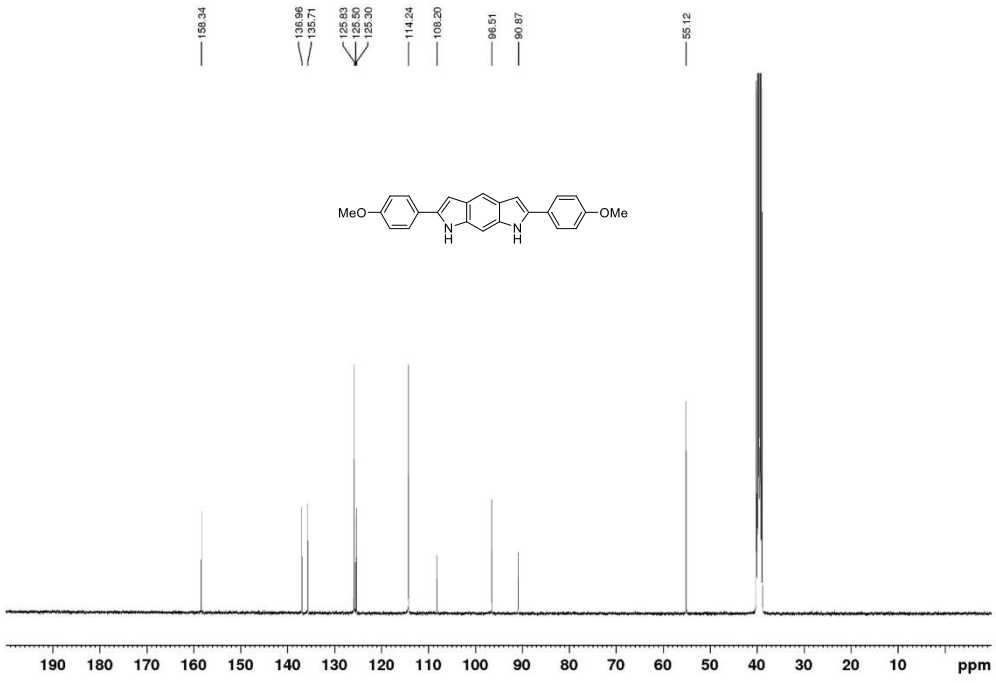


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, DMSO-d_6) of ***m*DPBc**.

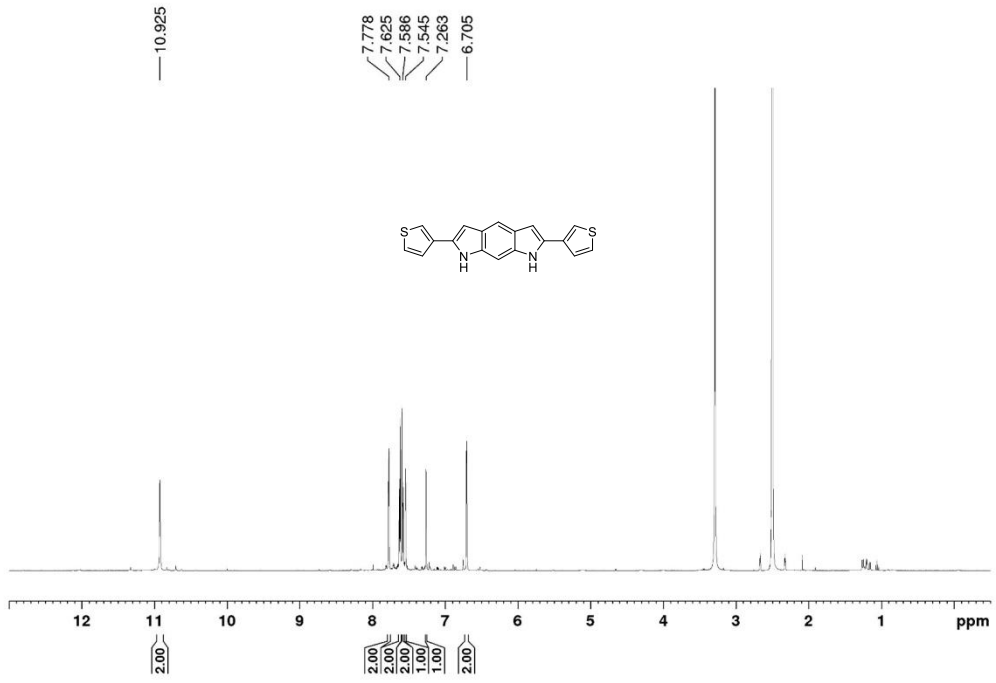


Figure S26. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of ***m*DPBd**.

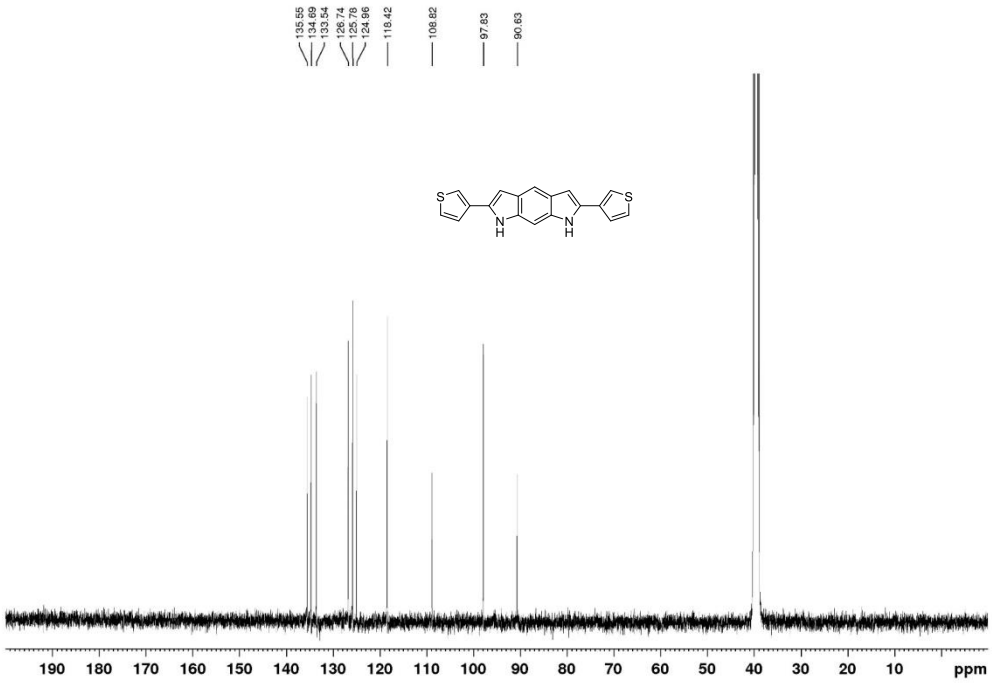


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of ***m*DPBd**.

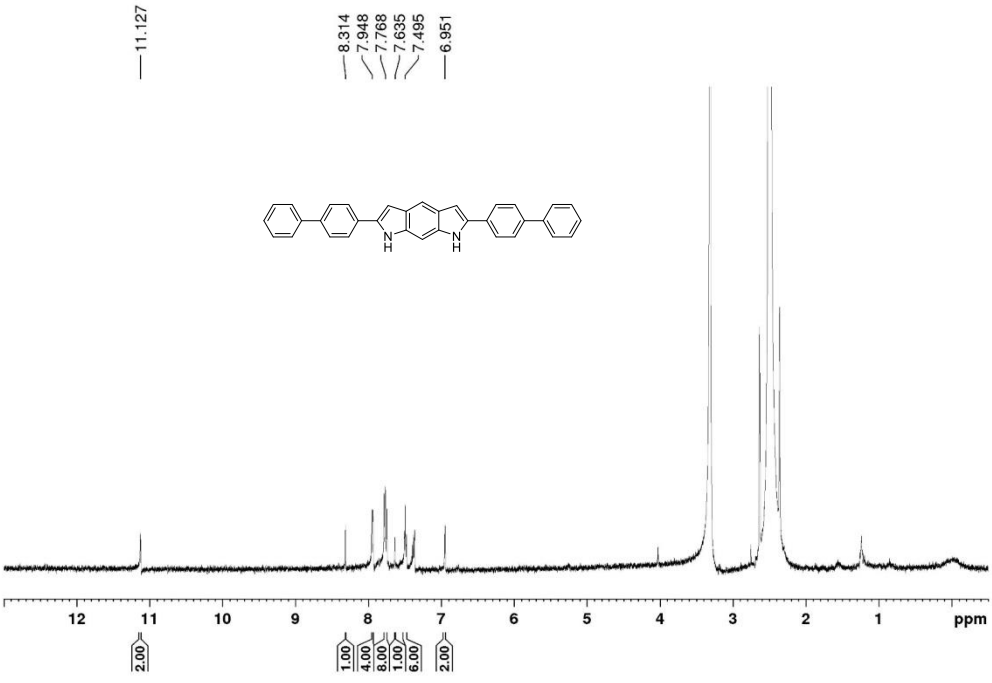


Figure S28. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of ***m*DPBe**.

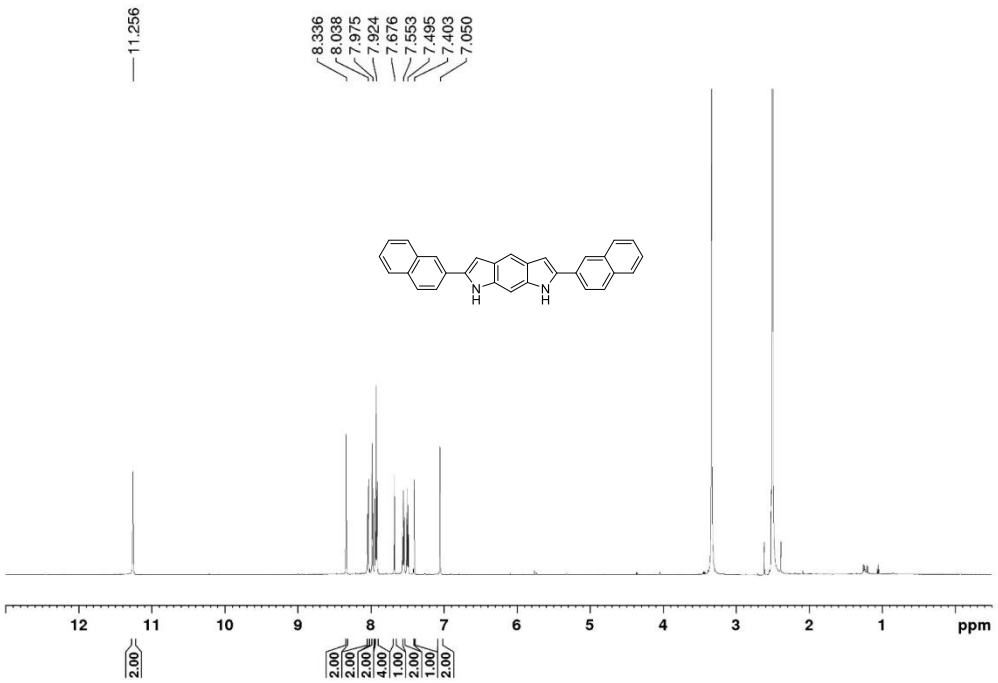


Figure S29. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of ***m*DPBBf**.

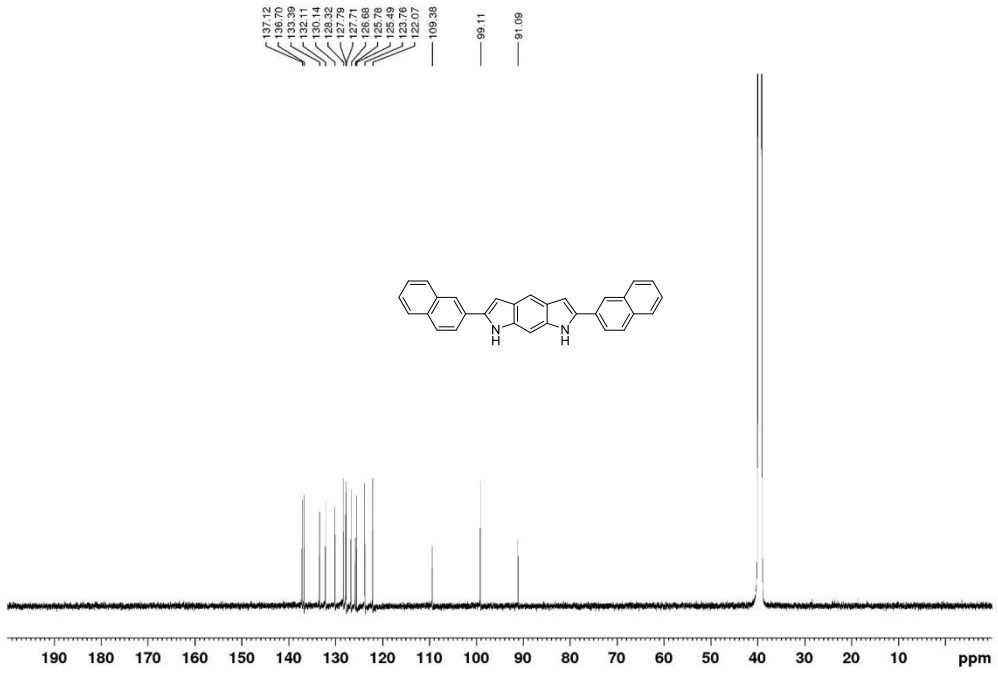


Figure S30. ^{13}C{^{1}H} NMR spectrum (151 MHz, DMSO-d_6) of ***m*DPBBf**.

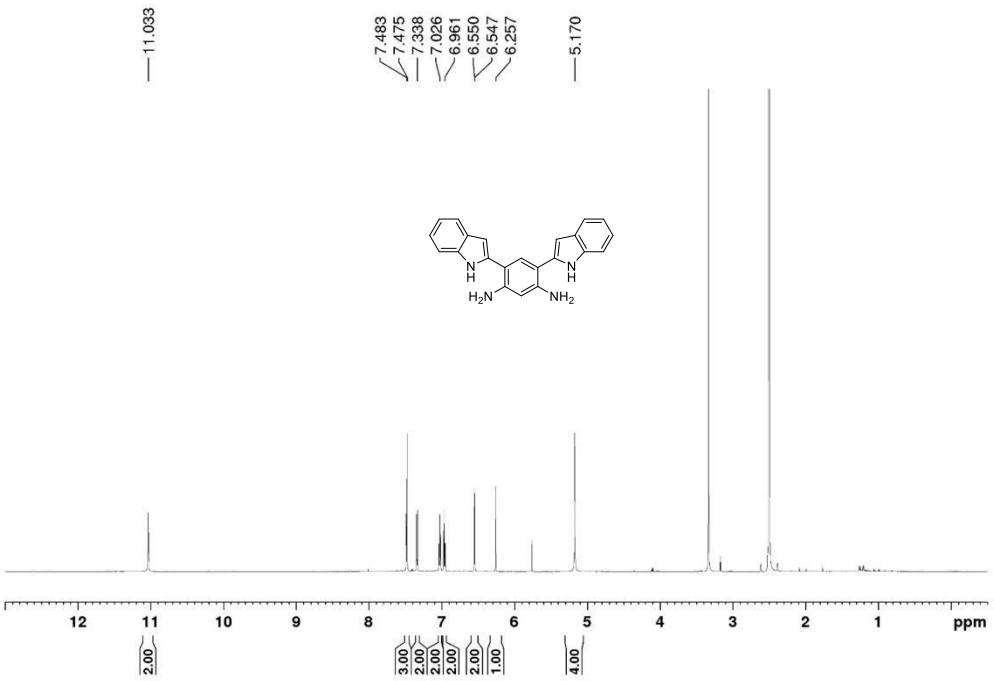


Figure S31. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **1g`**.

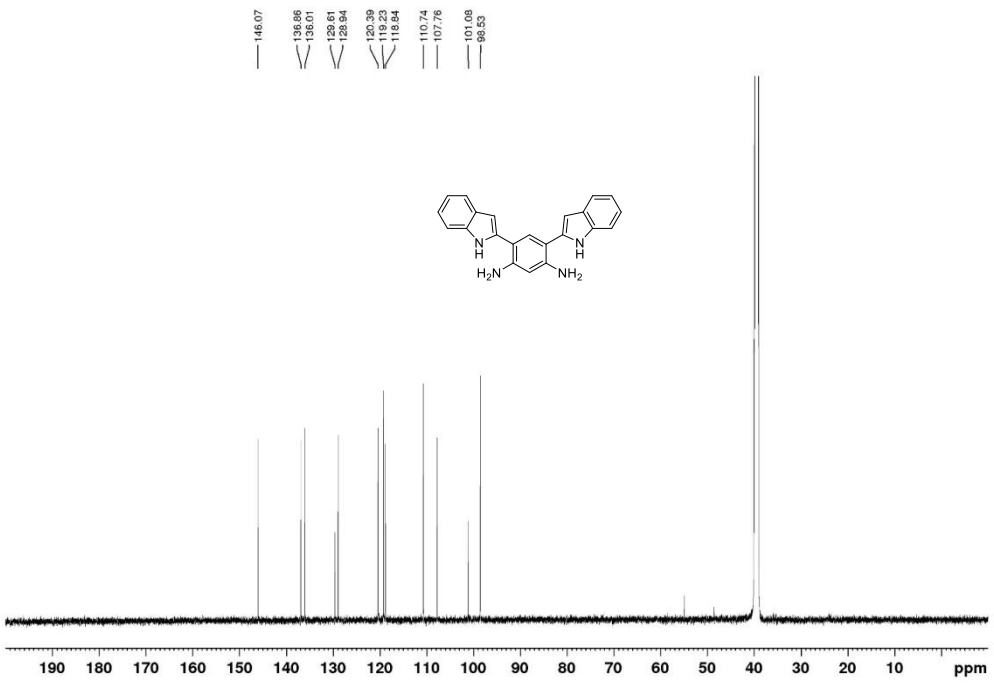


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, DMSO-d_6) of **1g`**.

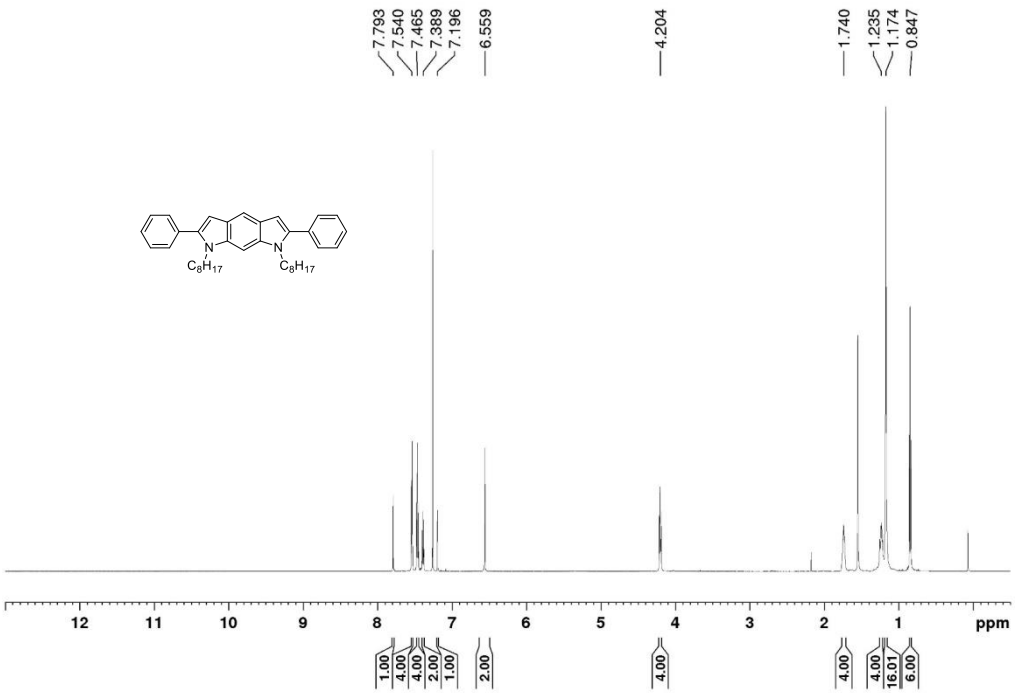


Figure S33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of ***m*DPBa`**.

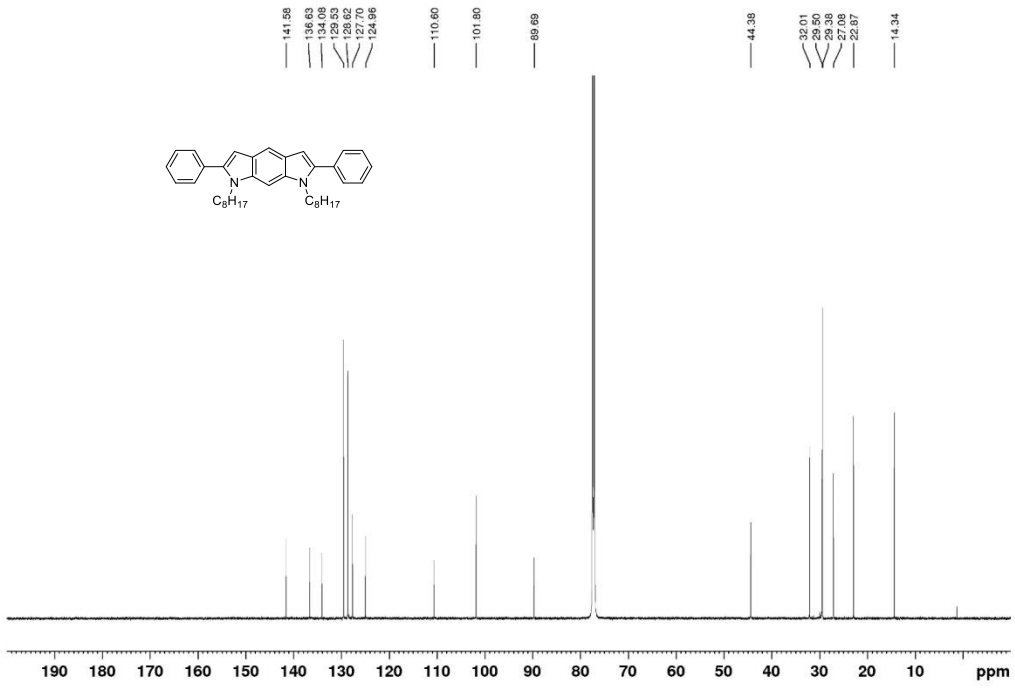


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of ***m*DPBa`**.

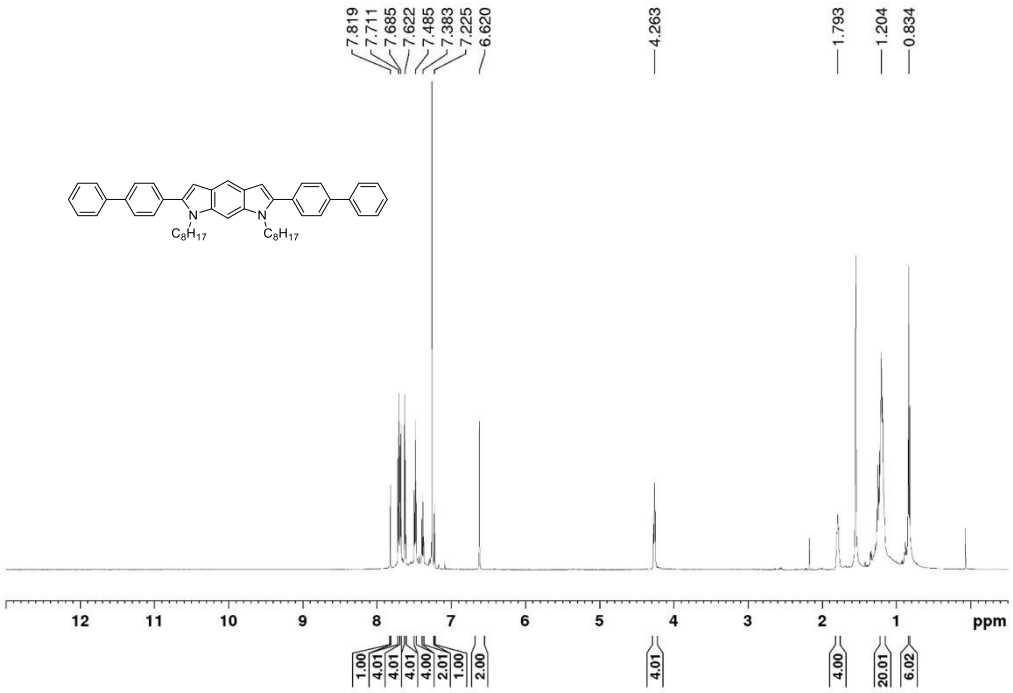


Figure S35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of ***m*DPBe`**.

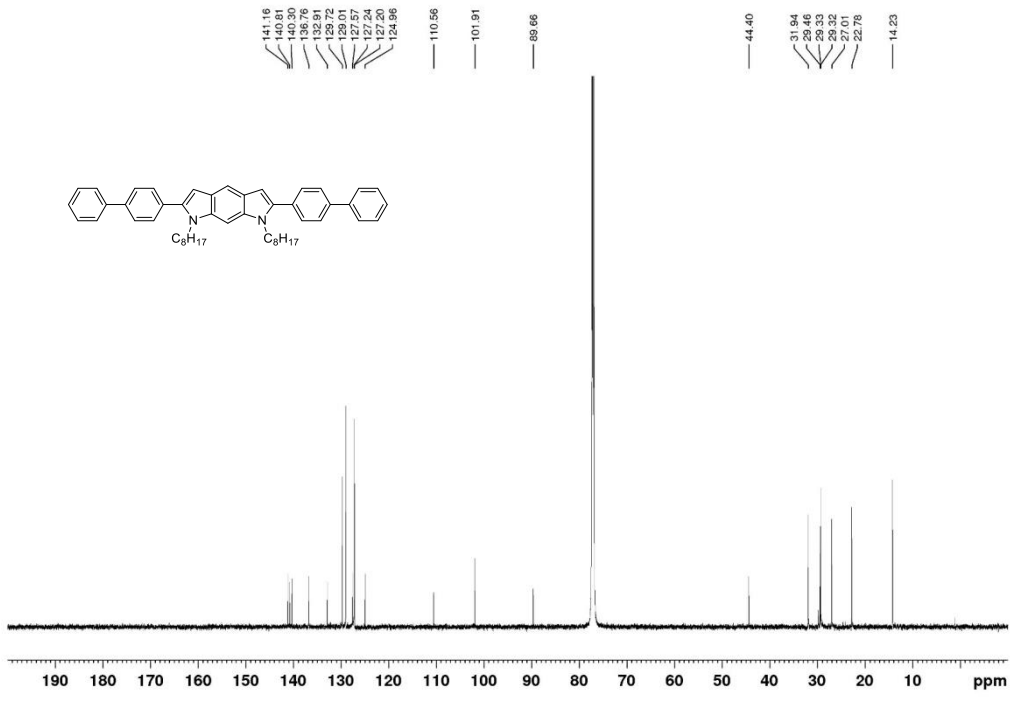


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of ***m*DPBe`**.

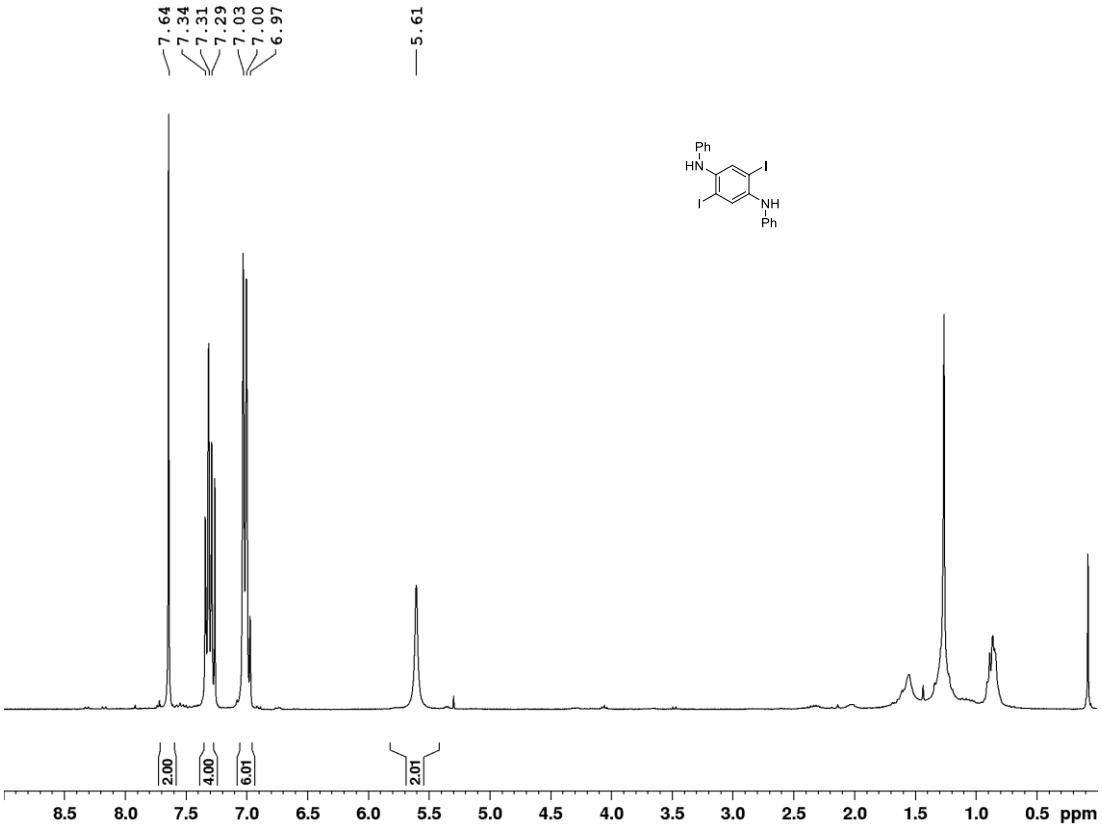


Figure S37. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3**.

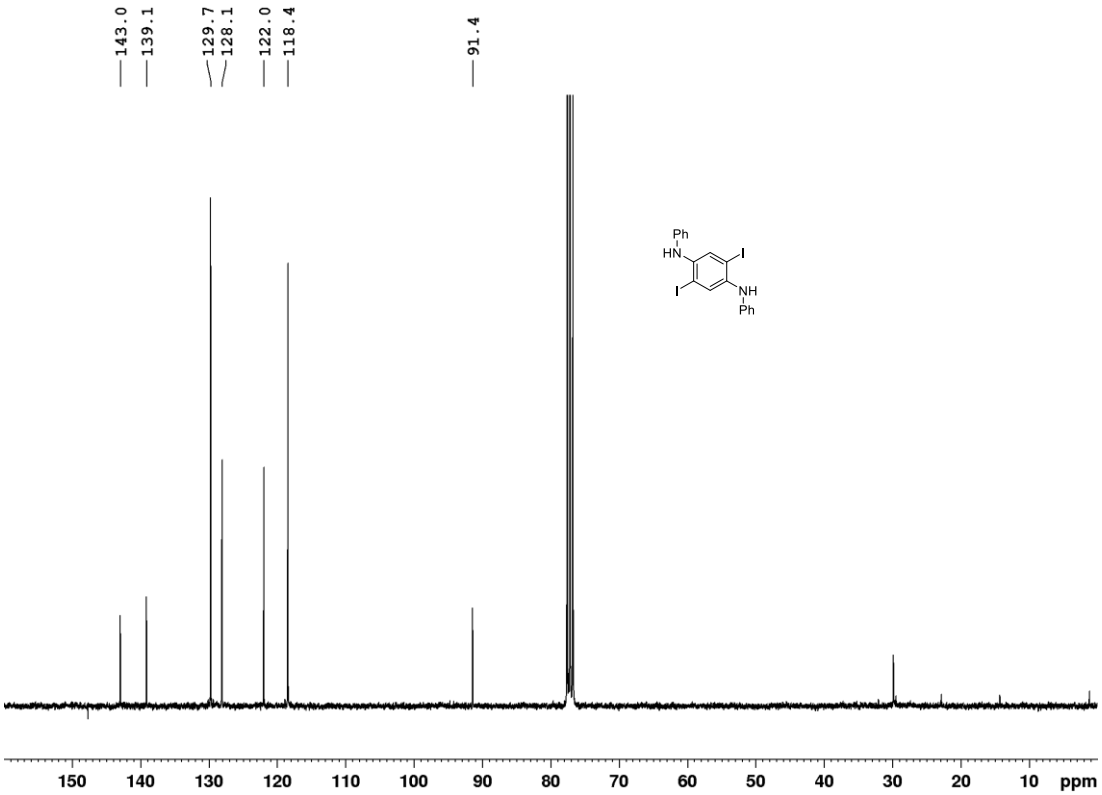


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **3**.

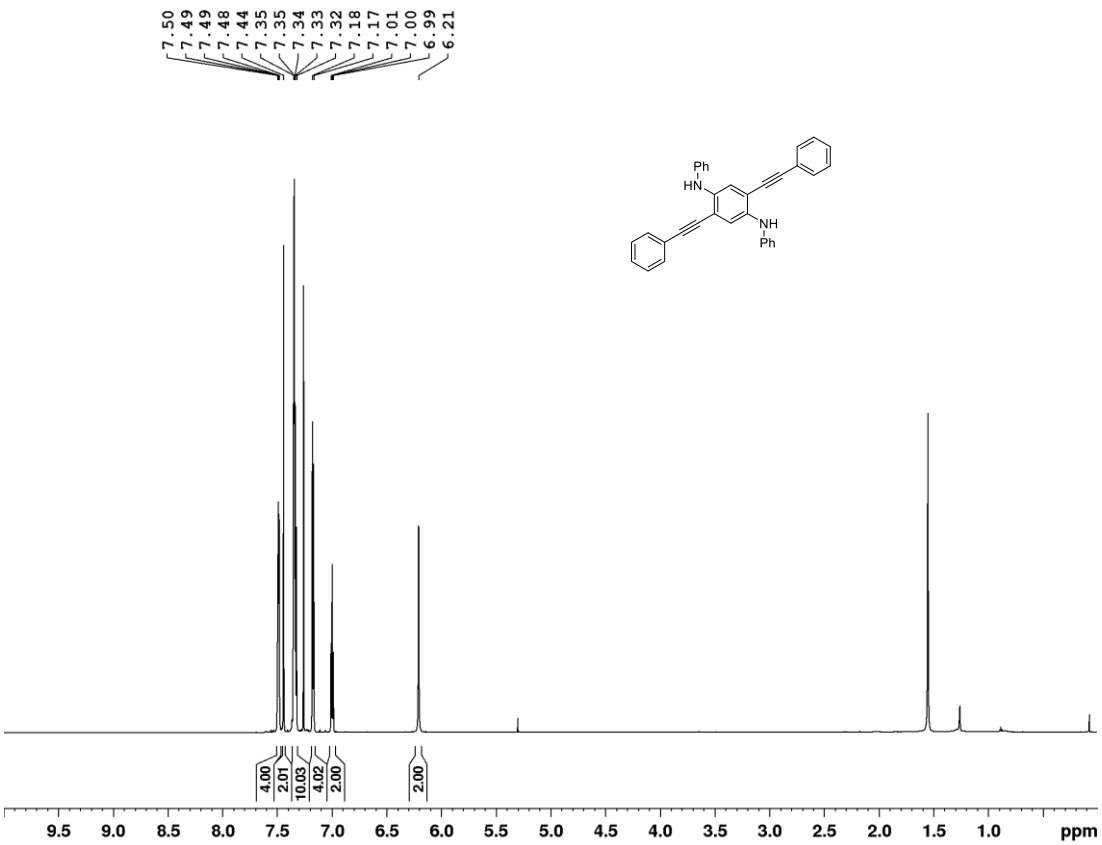


Figure S39. ^{1}H NMR spectrum (700 MHz, $CDCl_3$) of **4a**.

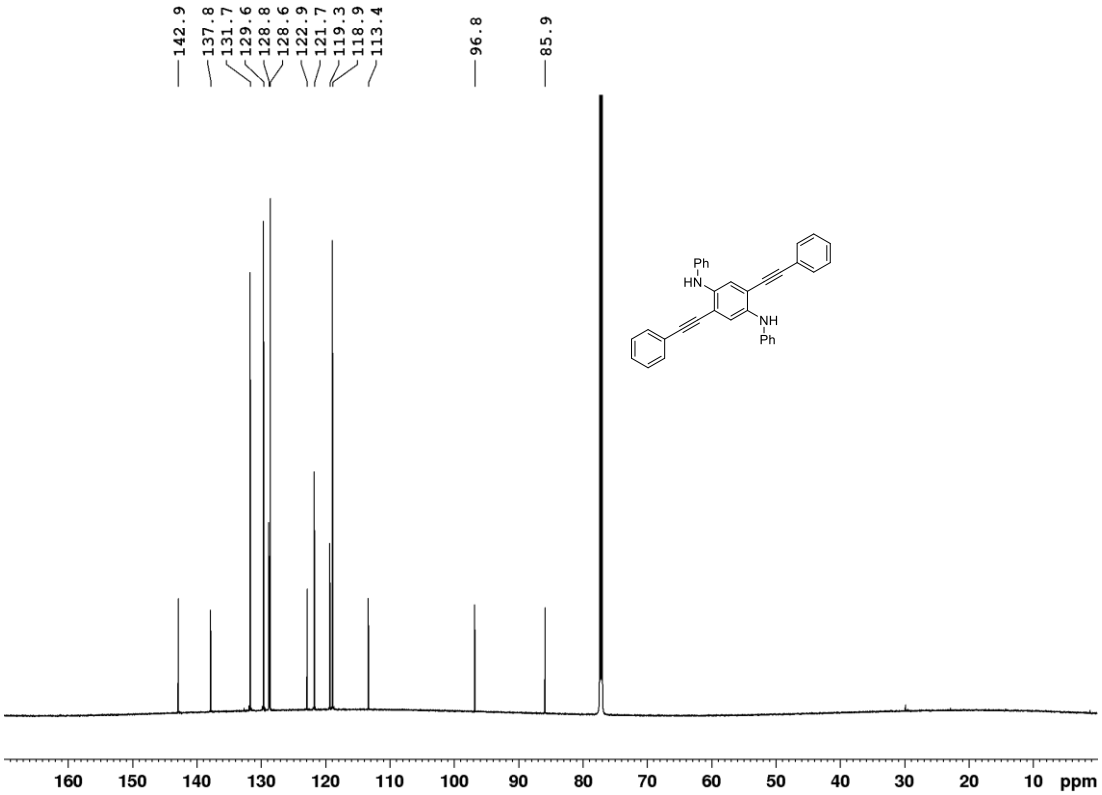


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, $CDCl_3$) of **4a**.

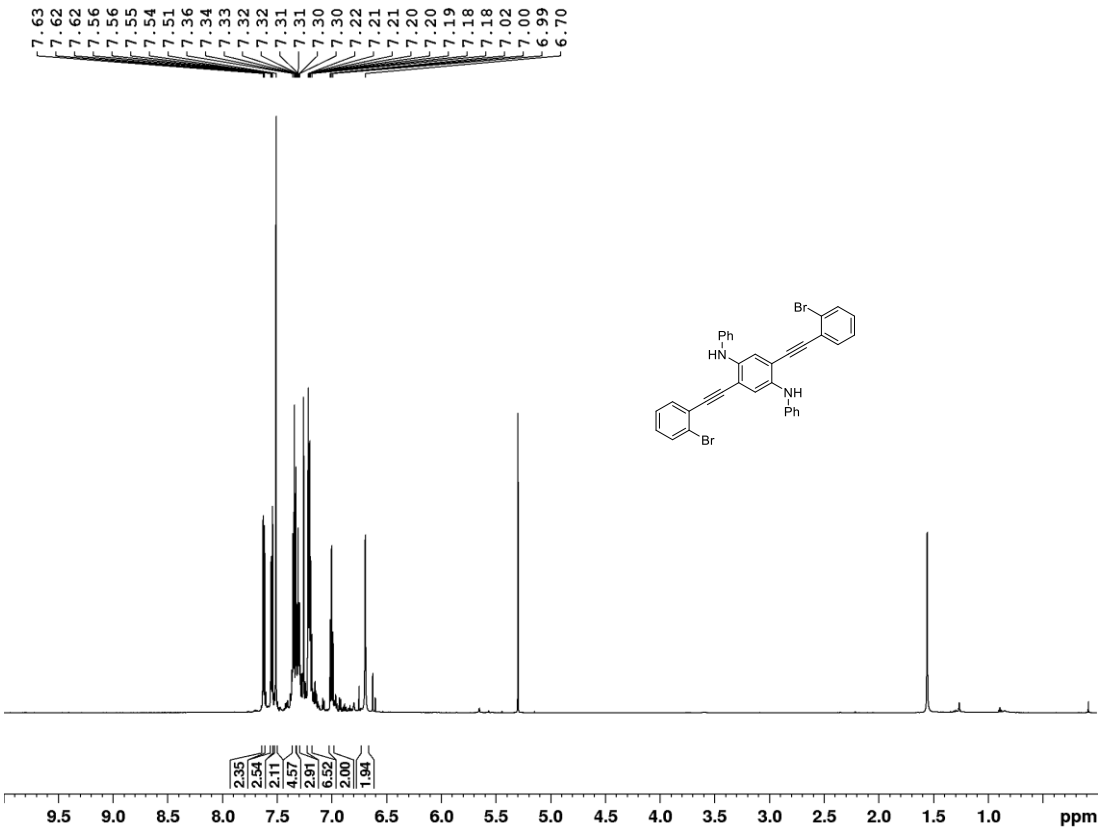


Figure S41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4c**.

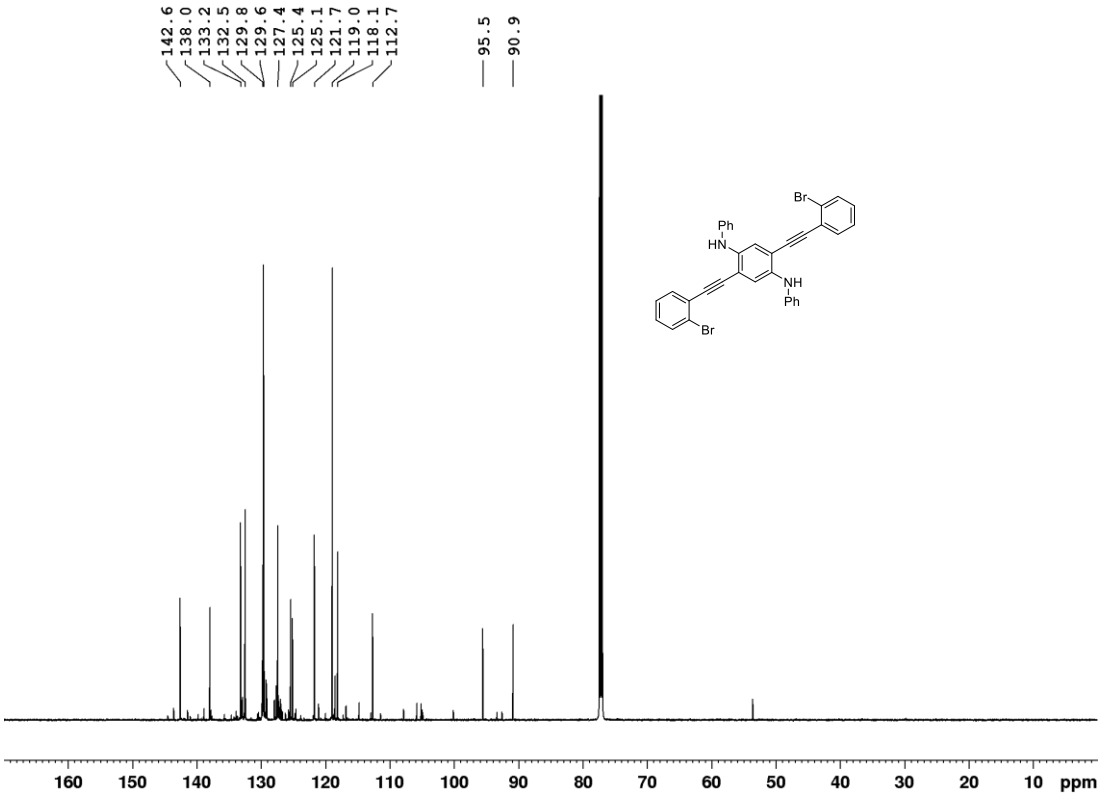


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **4c**.

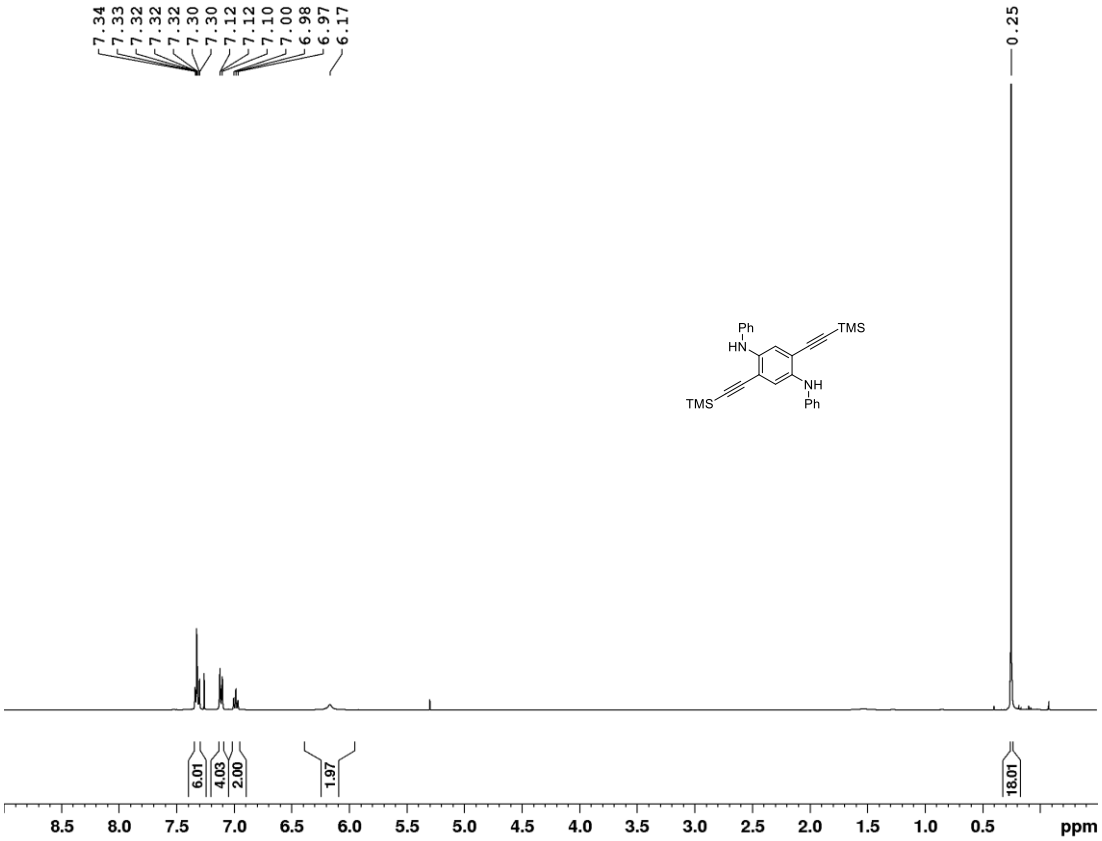


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4d-TMS**.

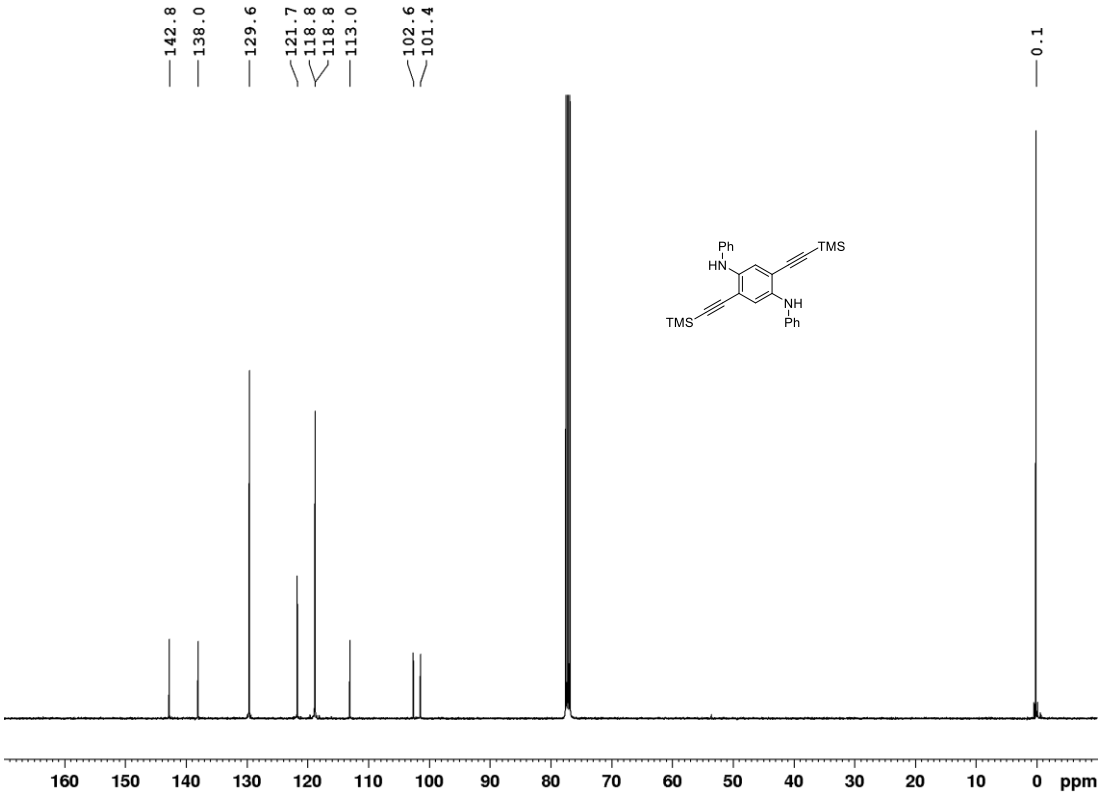


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4d-TMS**.

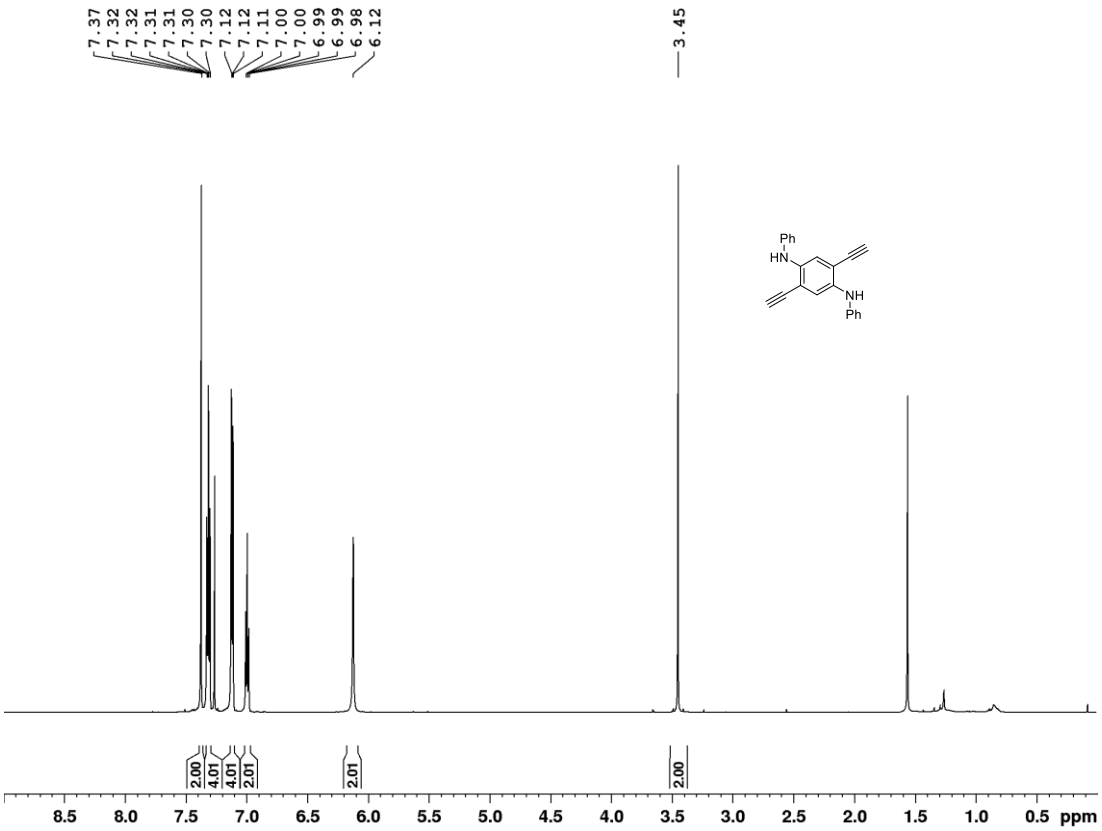


Figure S45. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4d-H**.

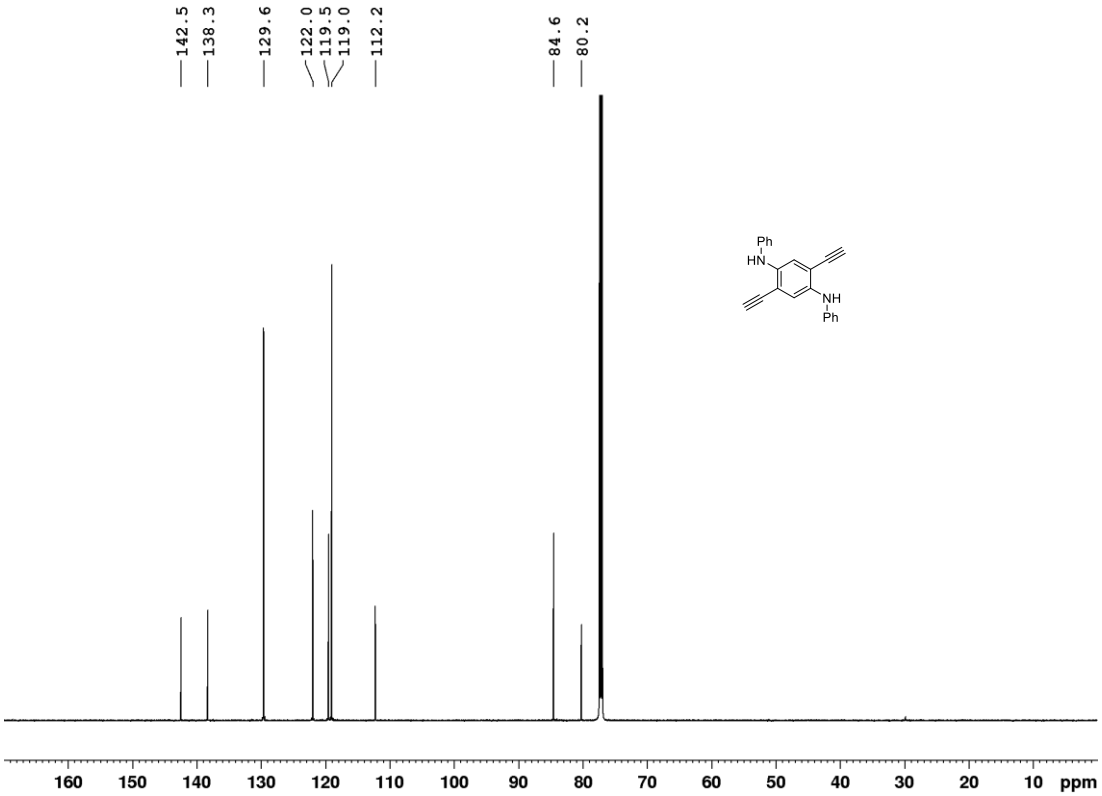


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **4d-H**.

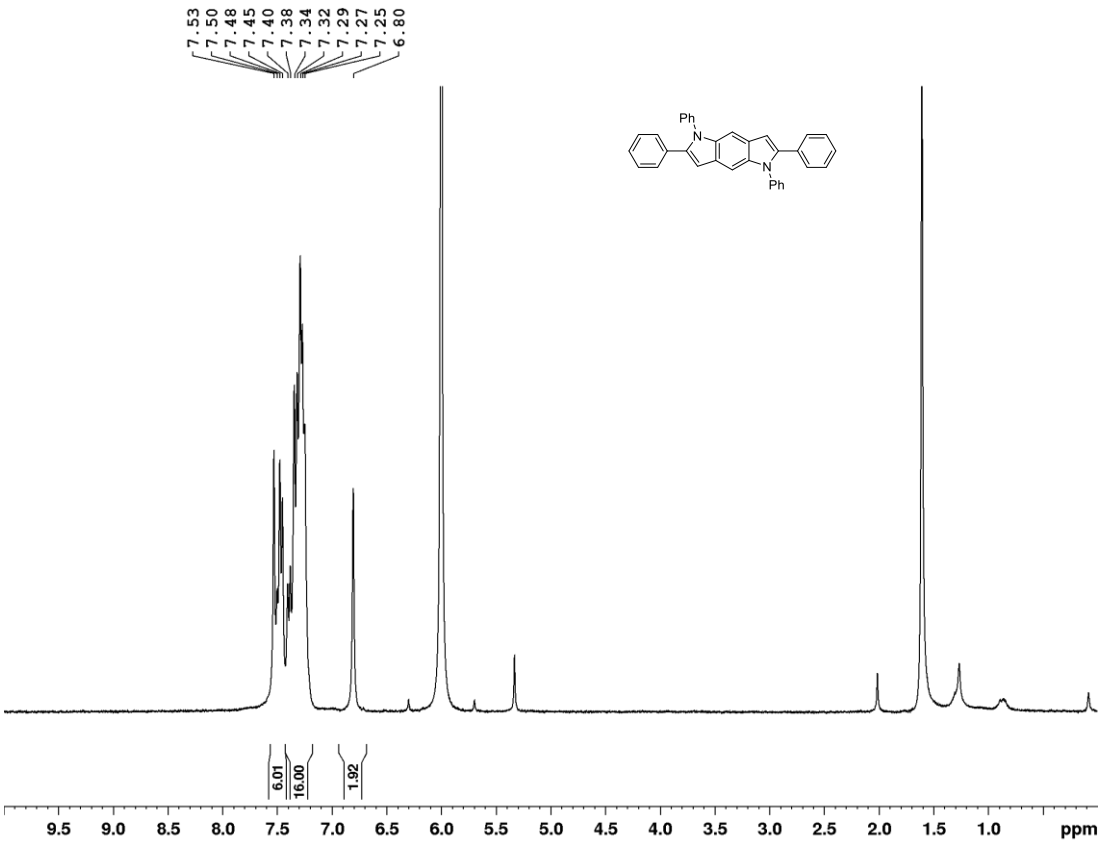


Figure S47. ^{1}H NMR spectrum (300 MHz, TCE-d_2) of ***p*DPBa**.

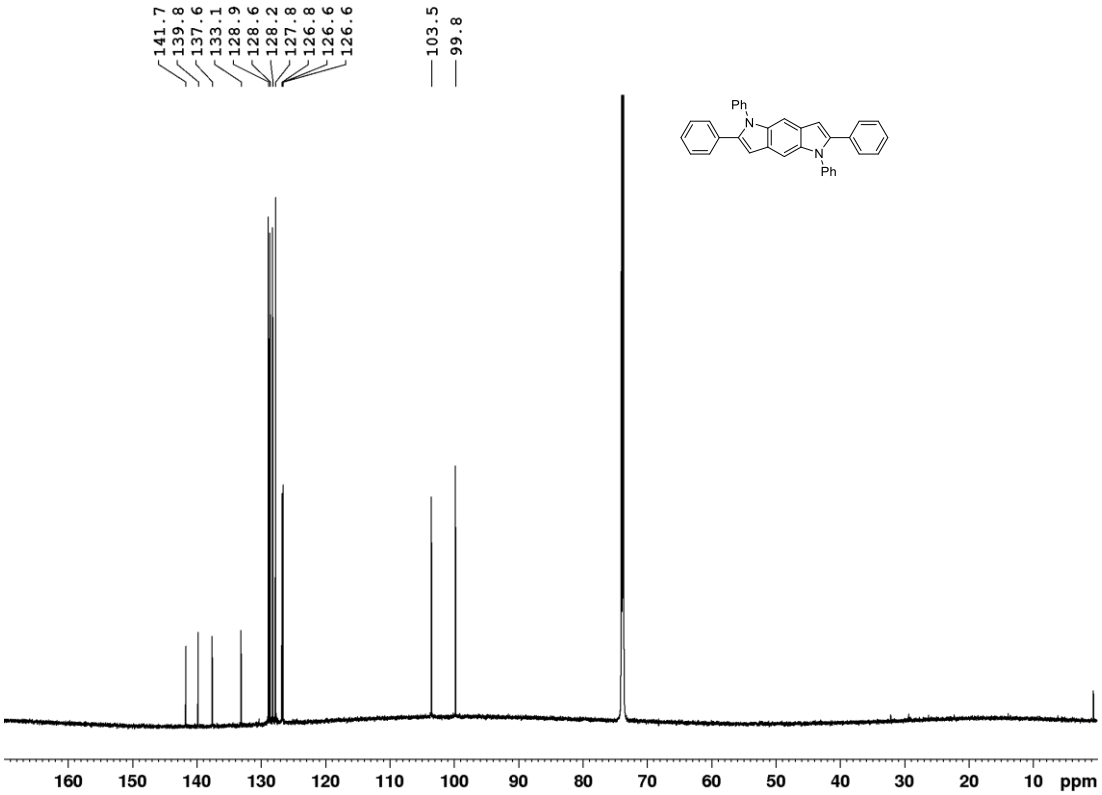


Figure S48. ^{13}C{^{1}H} NMR spectrum (176 MHz, TCE-d_2, 140 °C) of ***p*DPBa**.

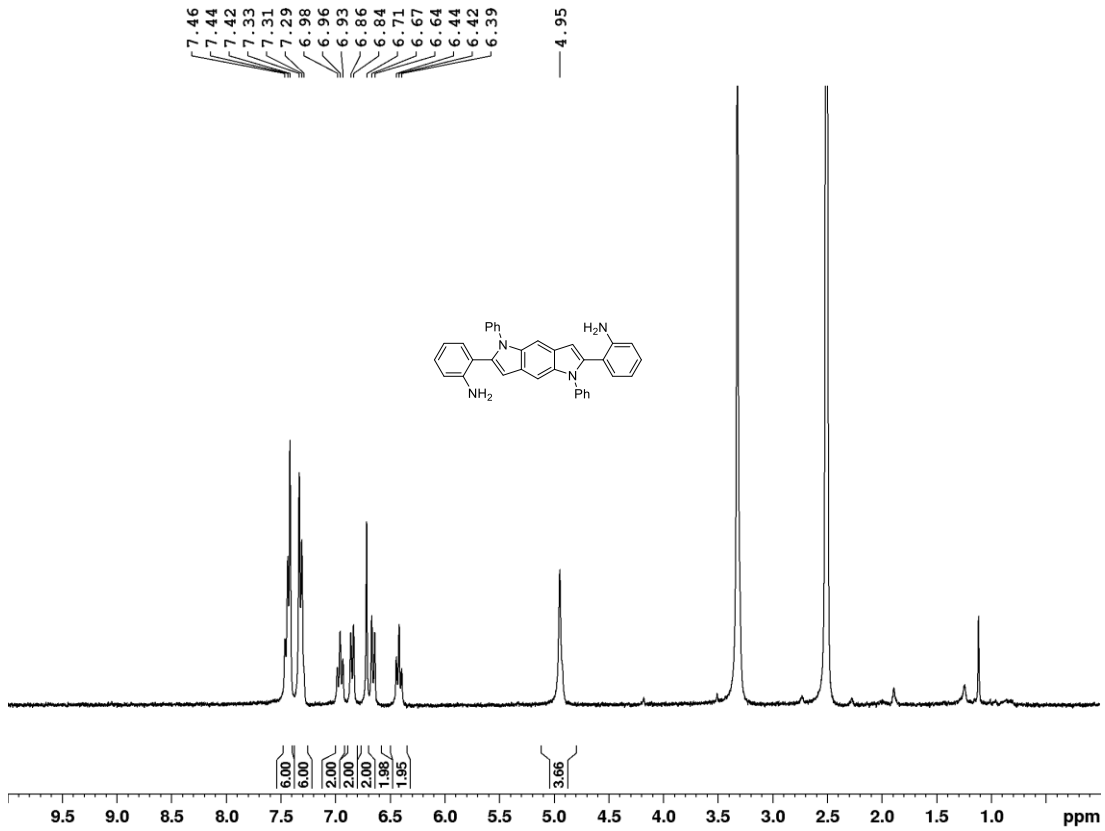


Figure S49. ^{1}H NMR spectrum (301 MHz, DMSO-d_6) of ***p*DPBb**.

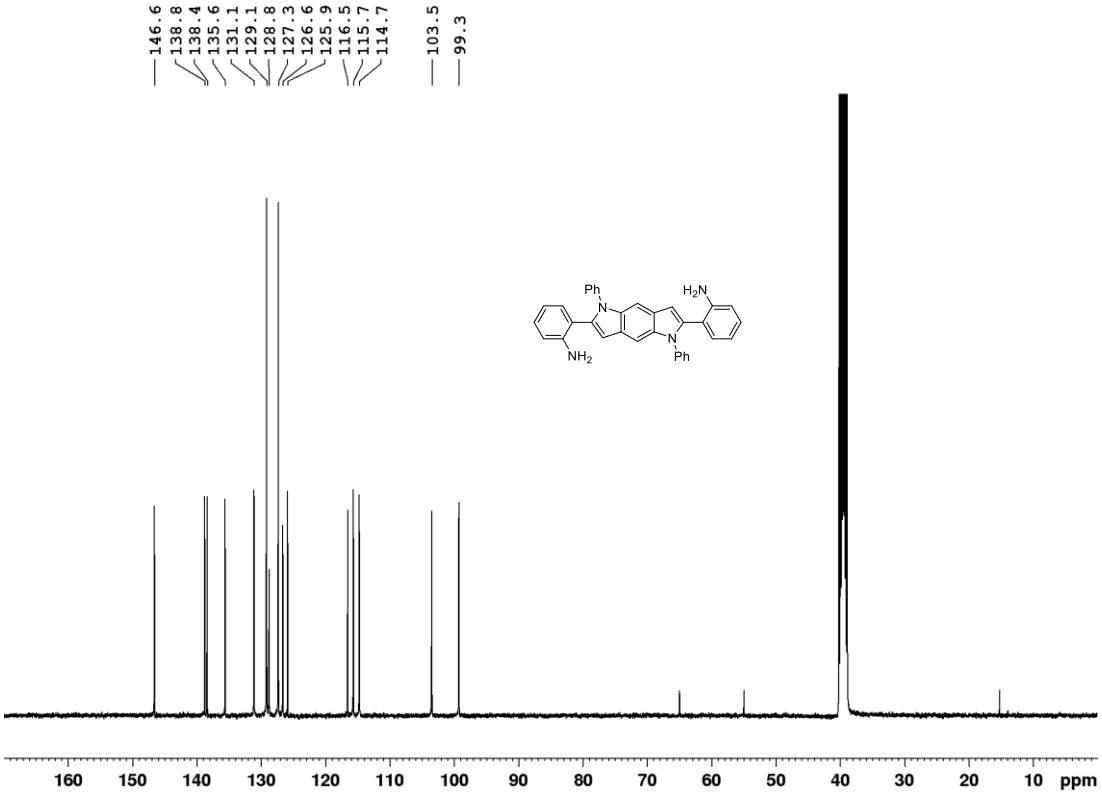


Figure S50. ^{13}C{^{1}H} NMR spectrum (101 MHz, DMSO-d_6) of ***p*DPBb**.

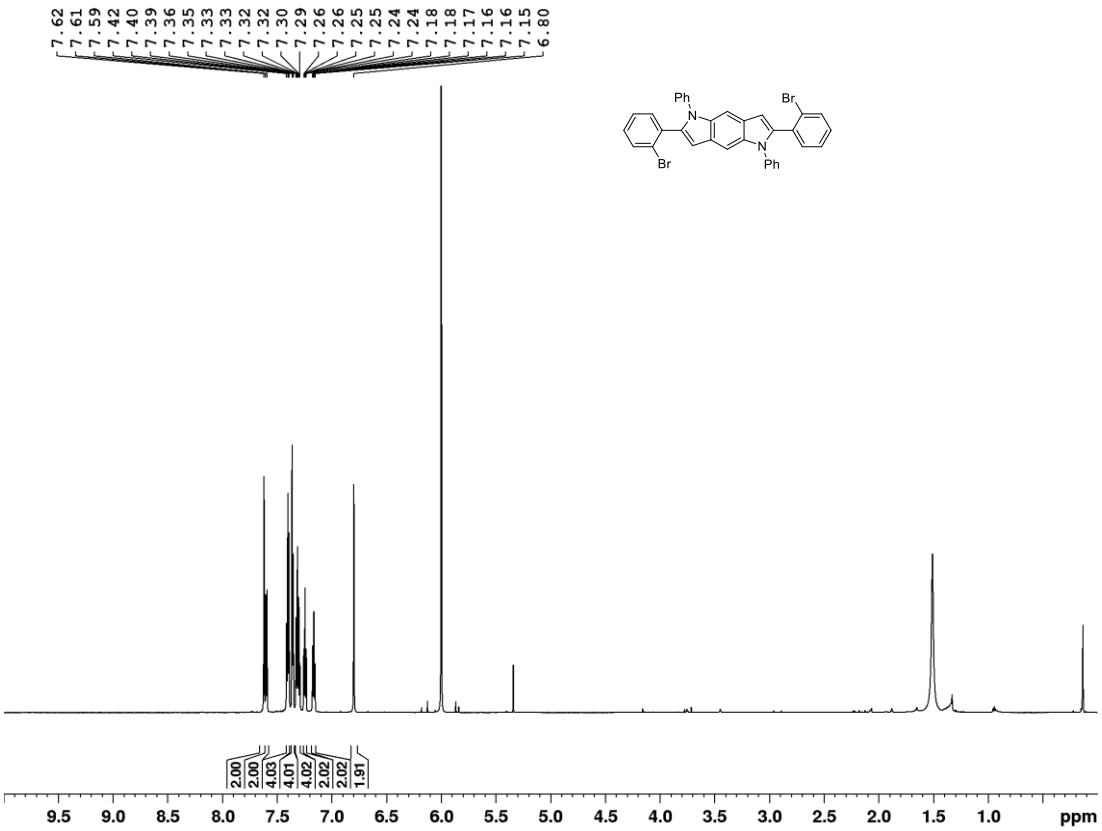


Figure S51. ^{1}H NMR spectrum (700 MHz, TCE-d_2, 80 °C) of ***p*DPBc**.

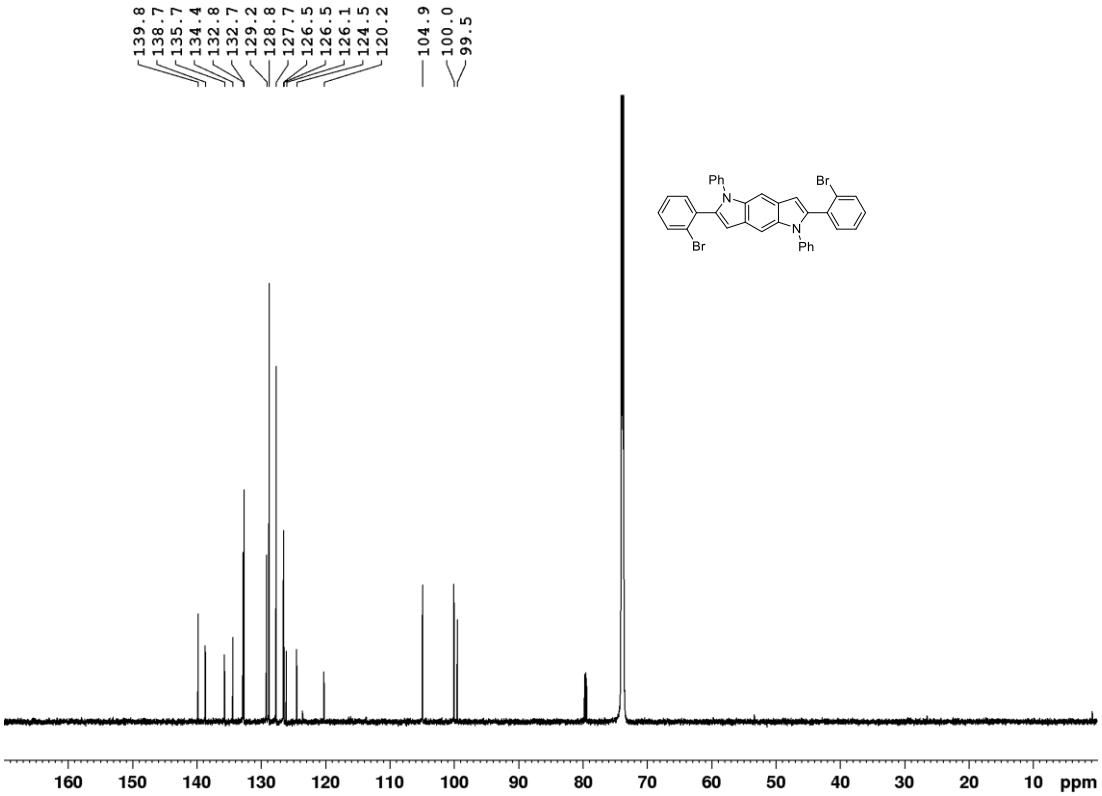


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, TCE-d_2, 80 °C) of ***p*DPBc**.

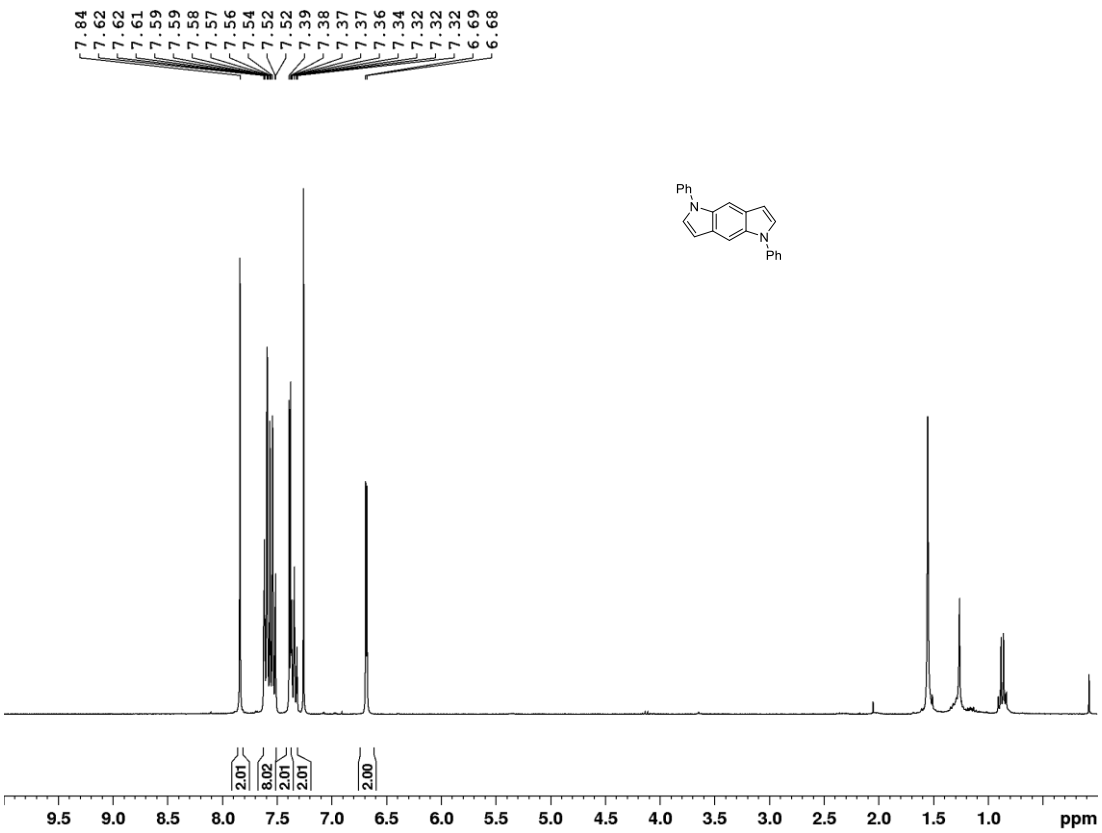


Figure S53. ^{1}H NMR spectrum (301 MHz, $CDCl_3$) of ***p*DPBd**.

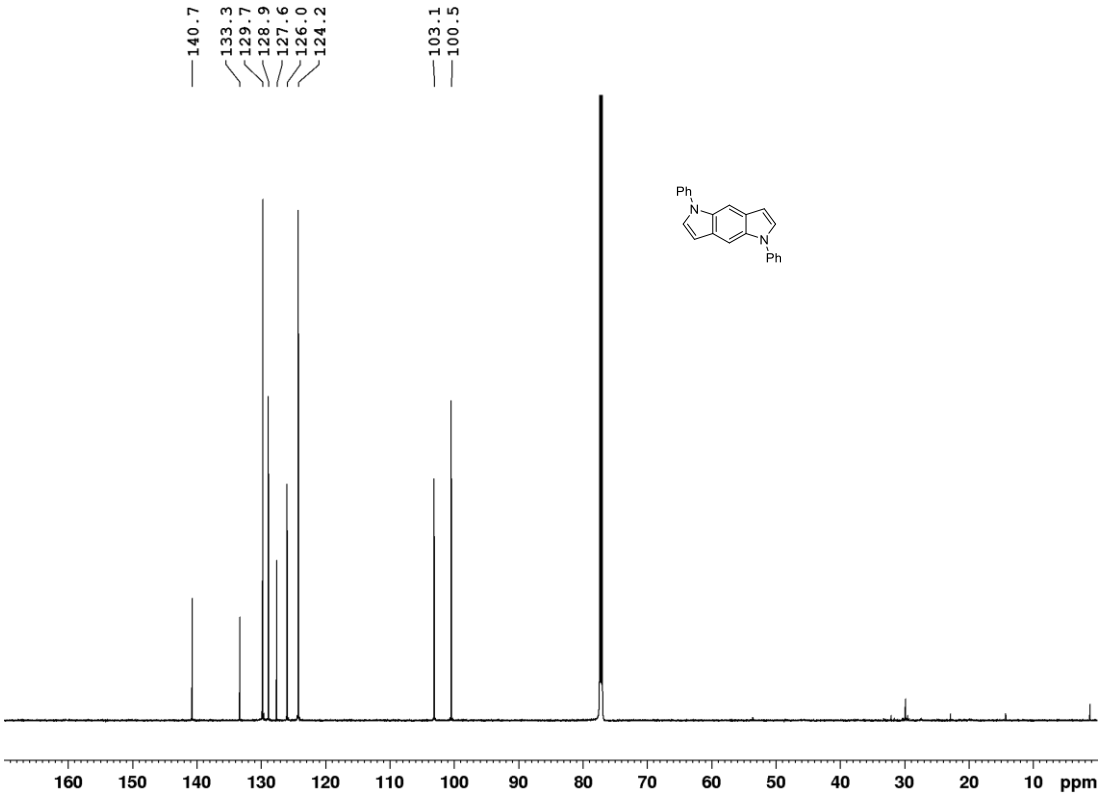


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum (176 MHz, $CDCl_3$) of ***p*DPBd**.

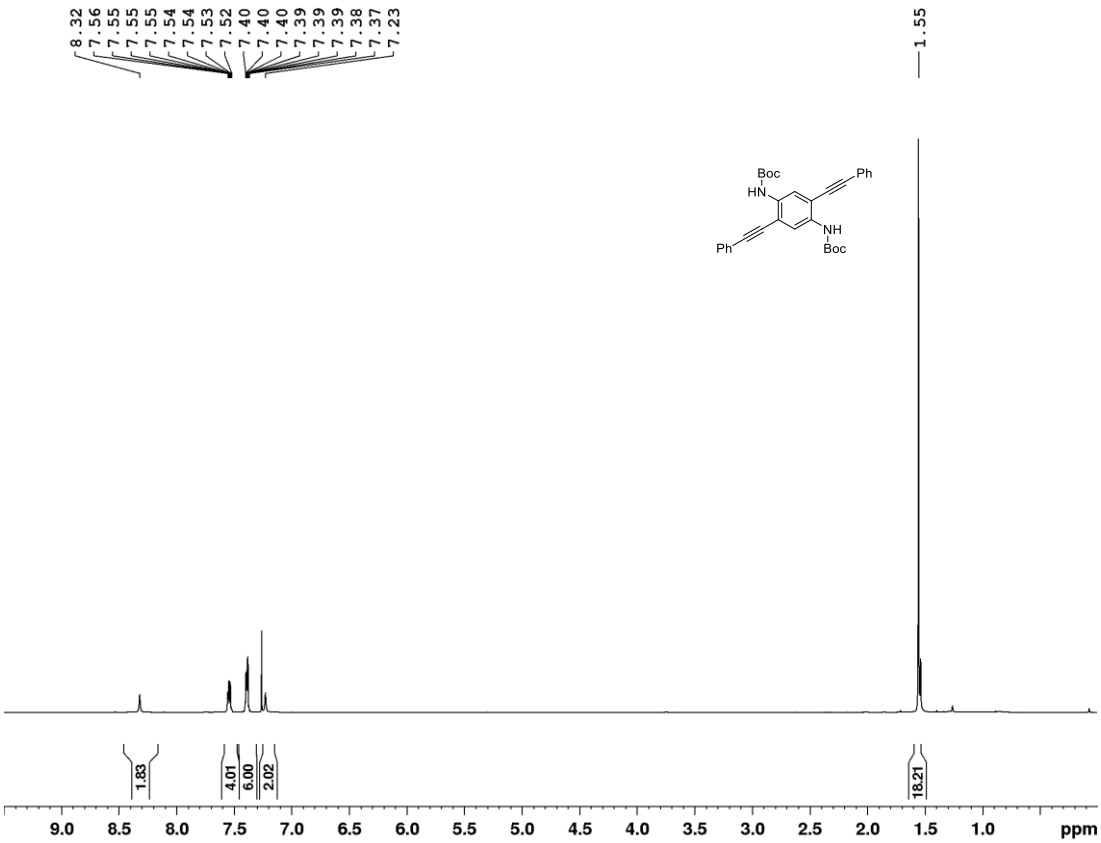


Figure S55. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**.

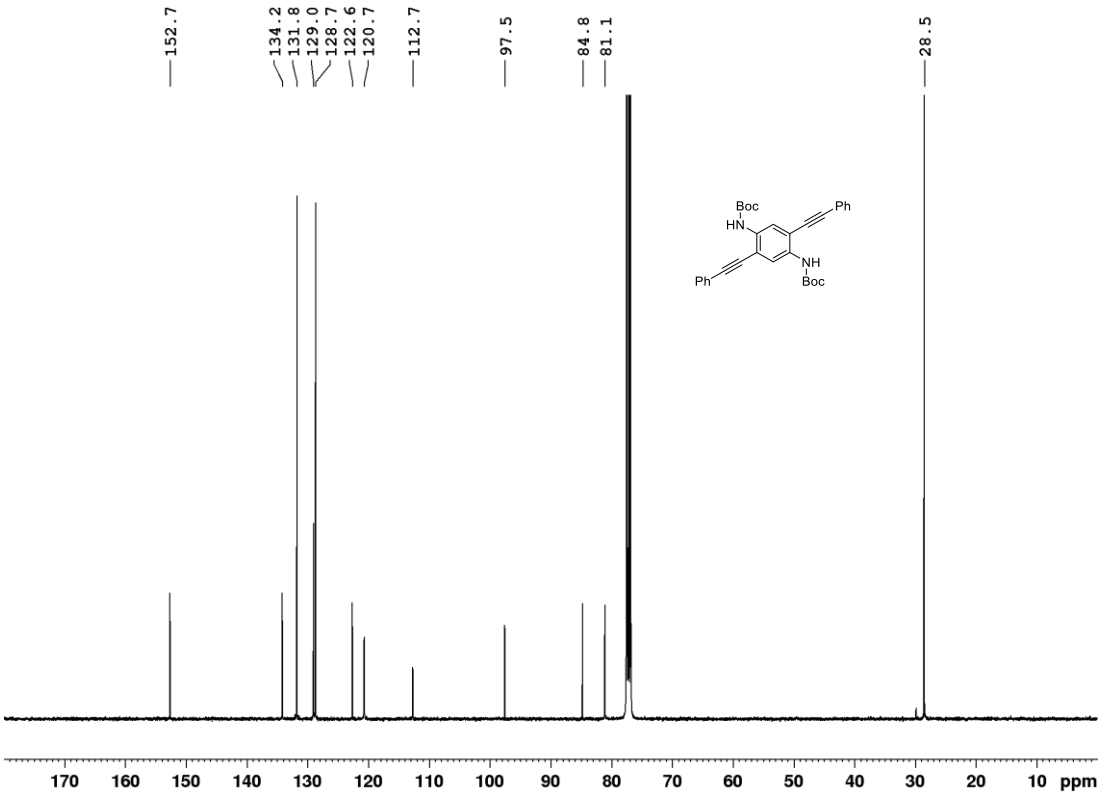


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6**.

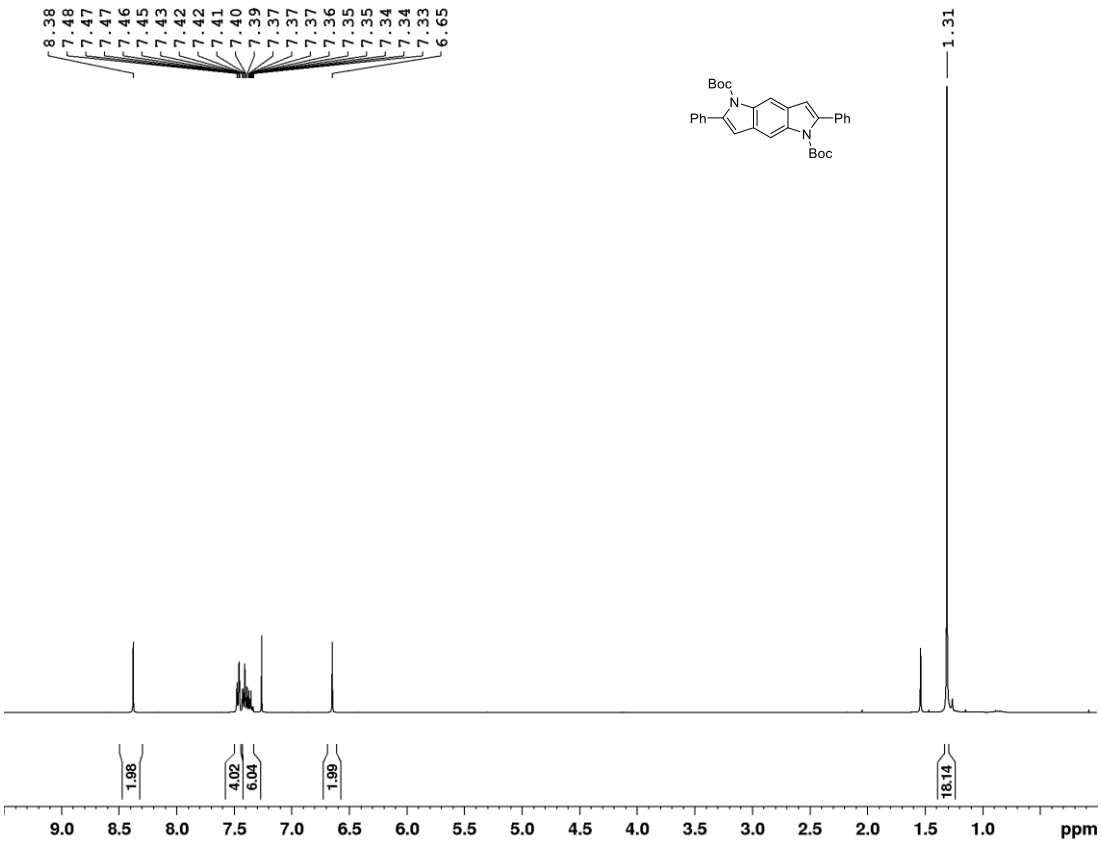


Figure S57. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ***p*DPBe`**.

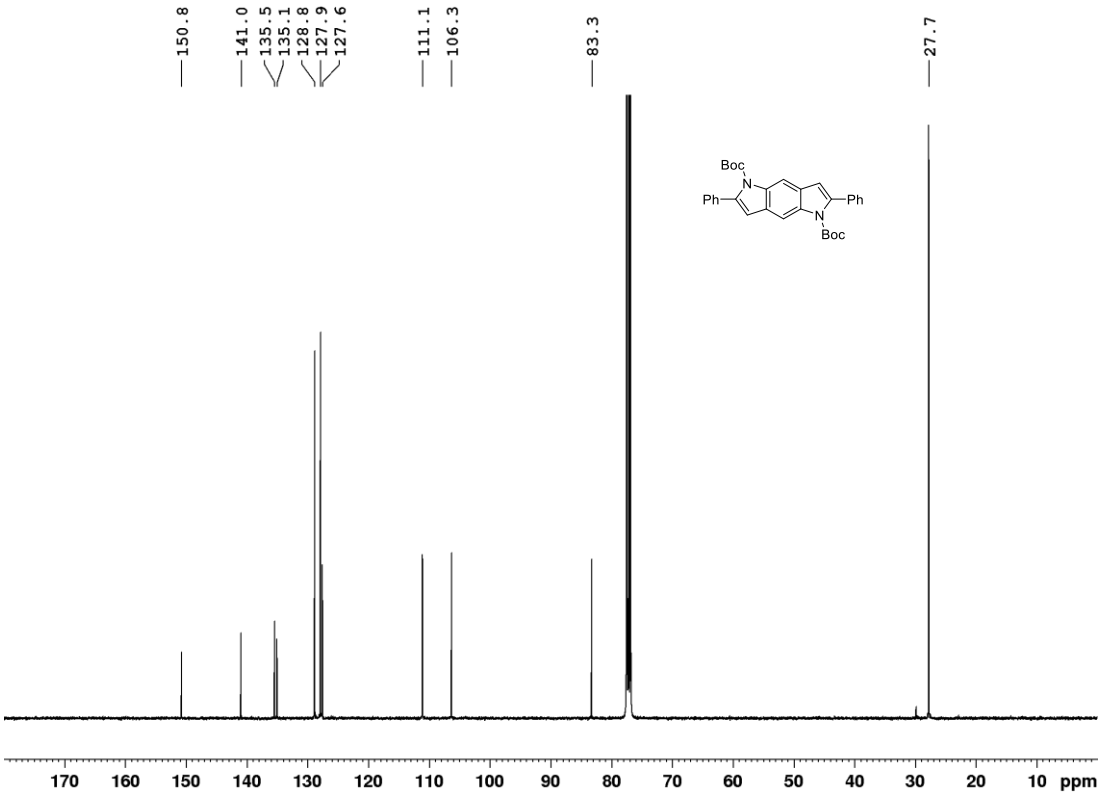


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of ***p*DPBe`**.

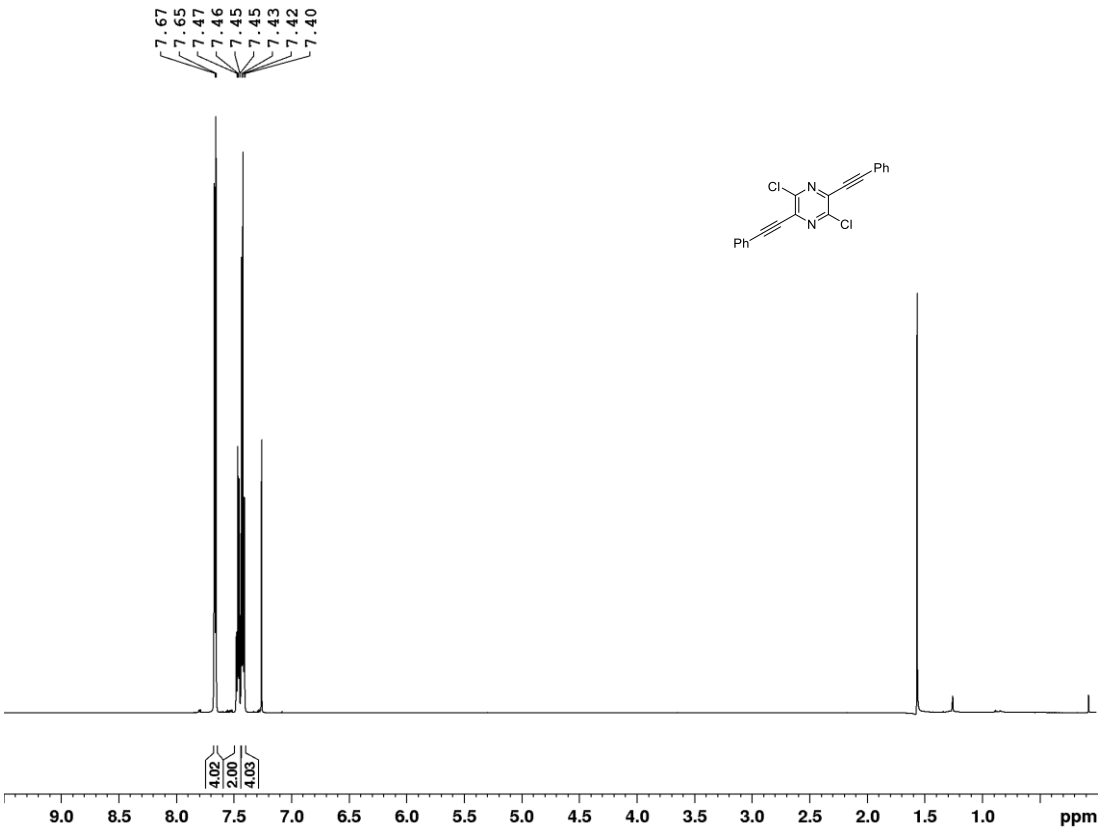


Figure S59. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **8a**.

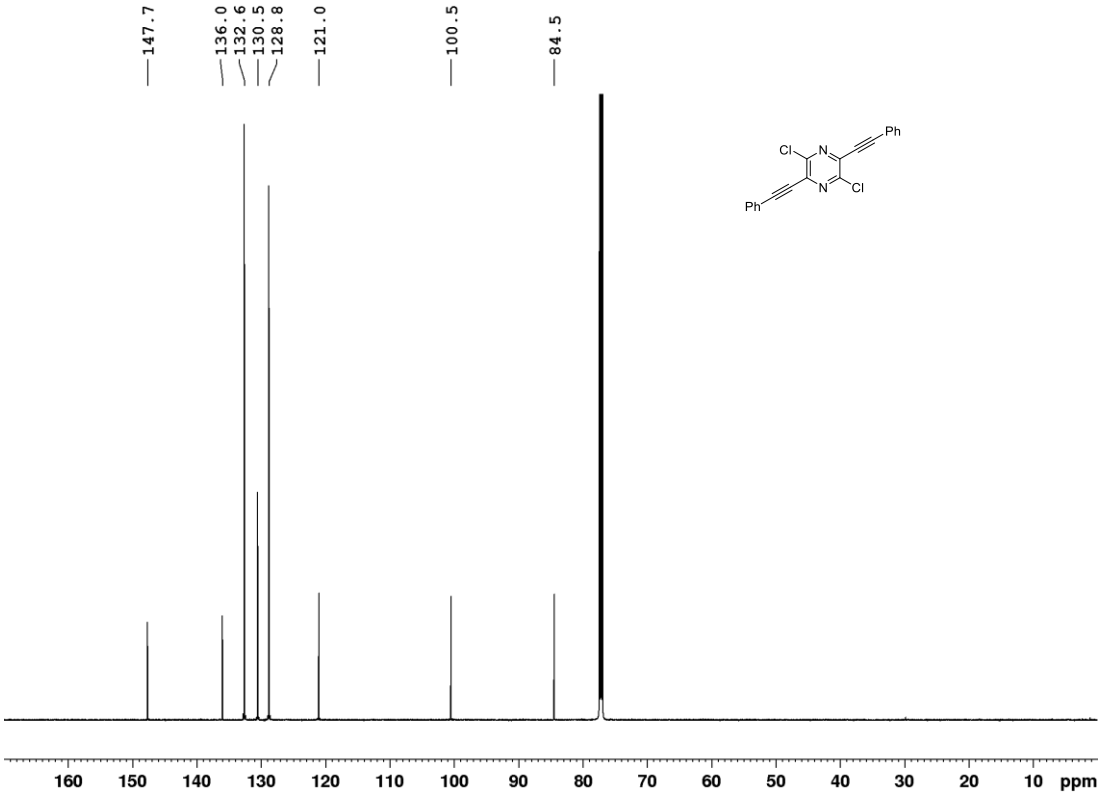


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of **8a**.

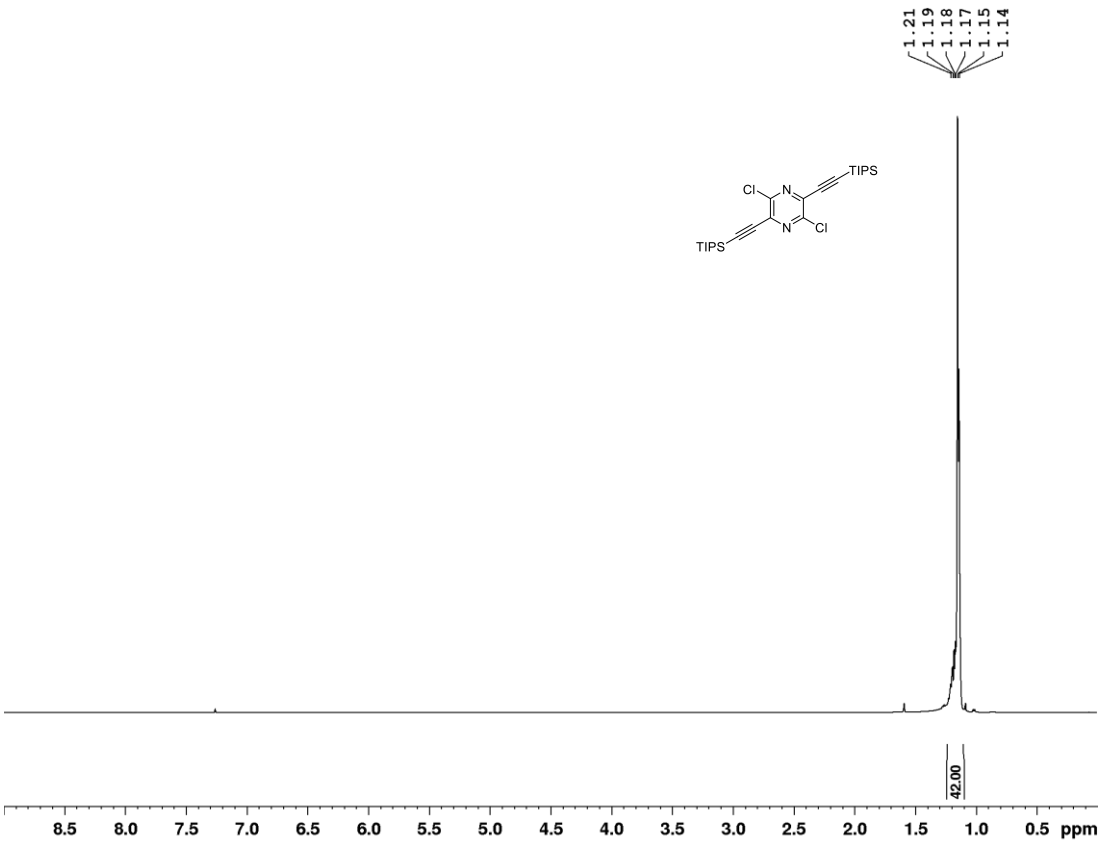


Figure S61. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8b**.

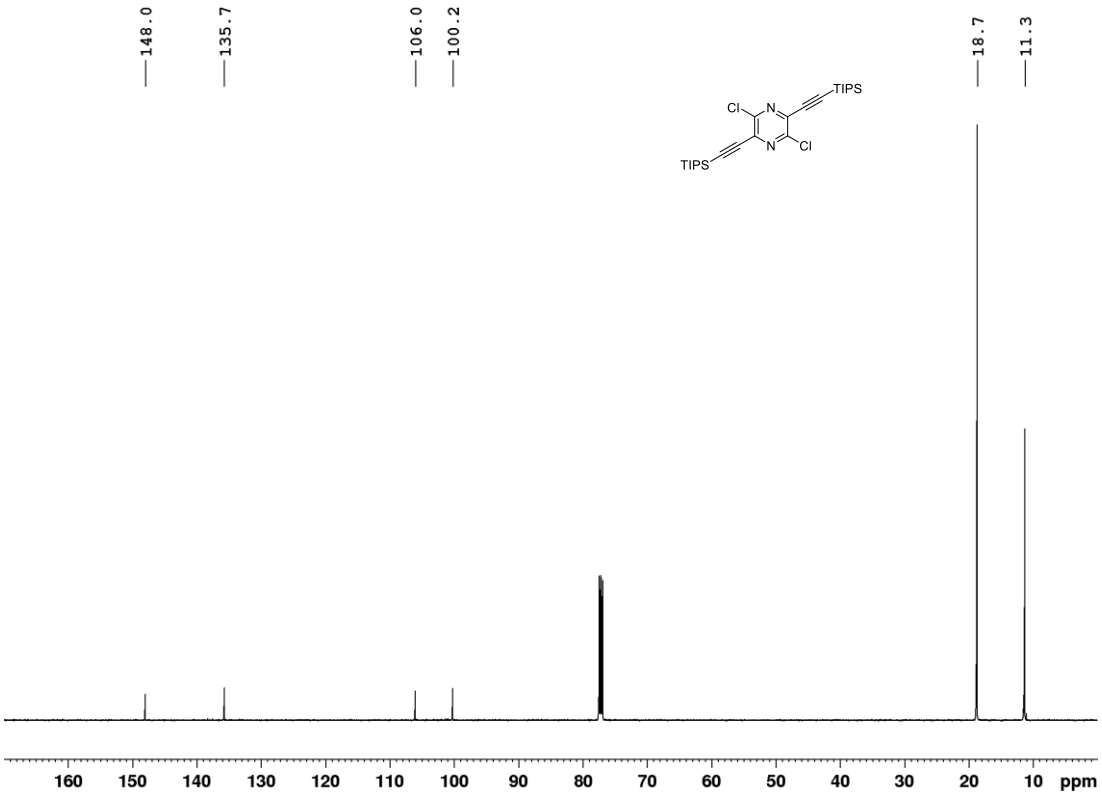


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8b**.

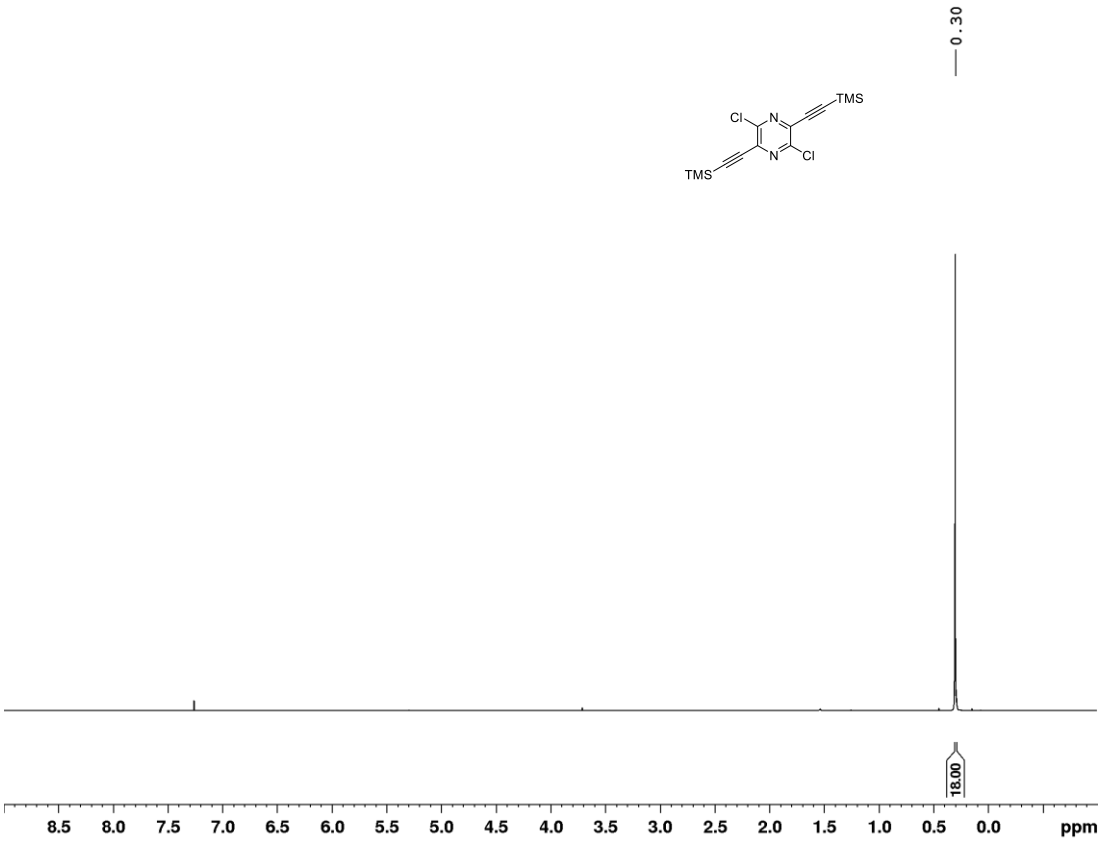


Figure S63. ^{1}H NMR spectrum (301 MHz, $CDCl_3$) of **8c**.

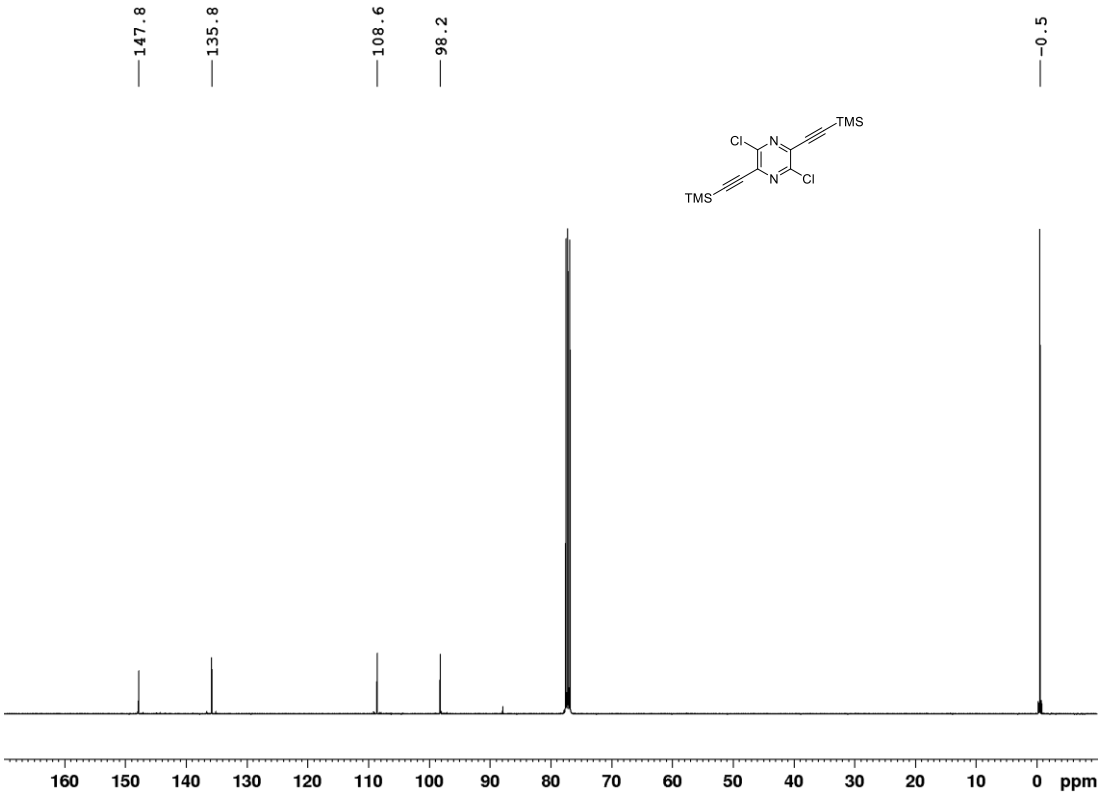


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8c**.

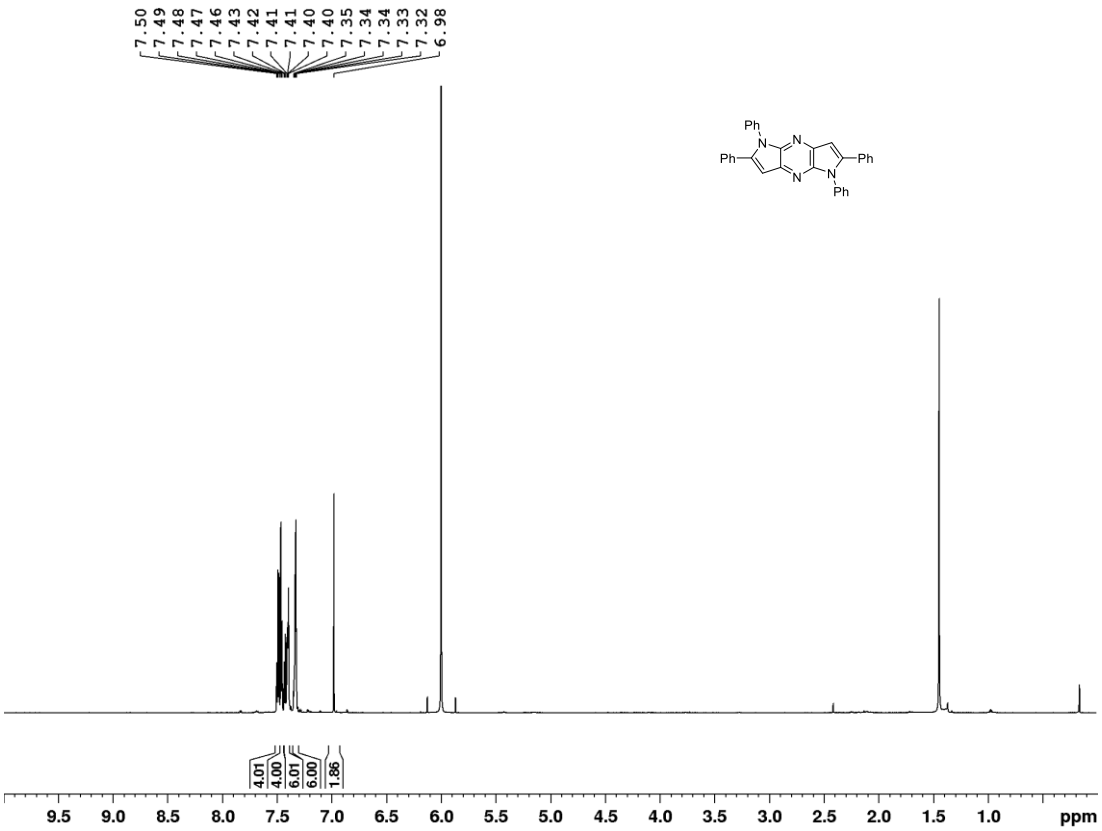


Figure S65. ^{1}H NMR spectrum (700 MHz, TCE-d_2, 120 °C) of ***p*DPPa**.

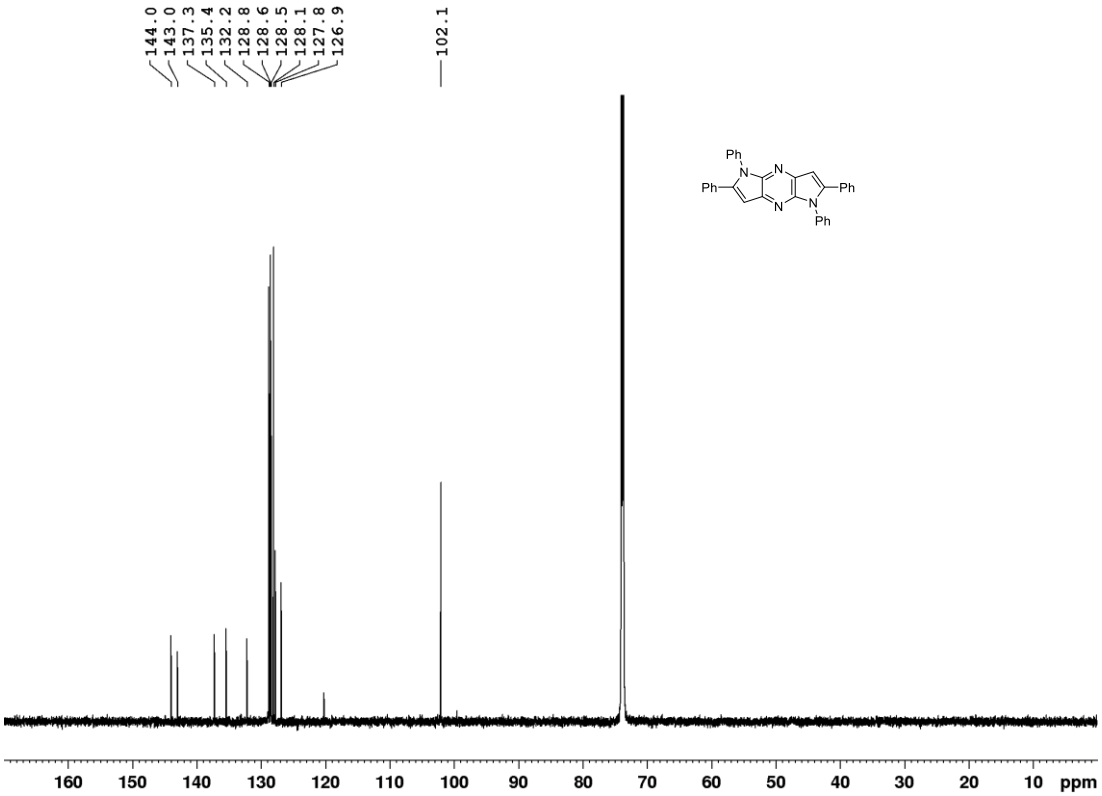


Figure S66. ^{13}C{^{1}H} NMR spectrum (176 MHz, TCE-d_2, 120 °C) of ***p*DPPa**.

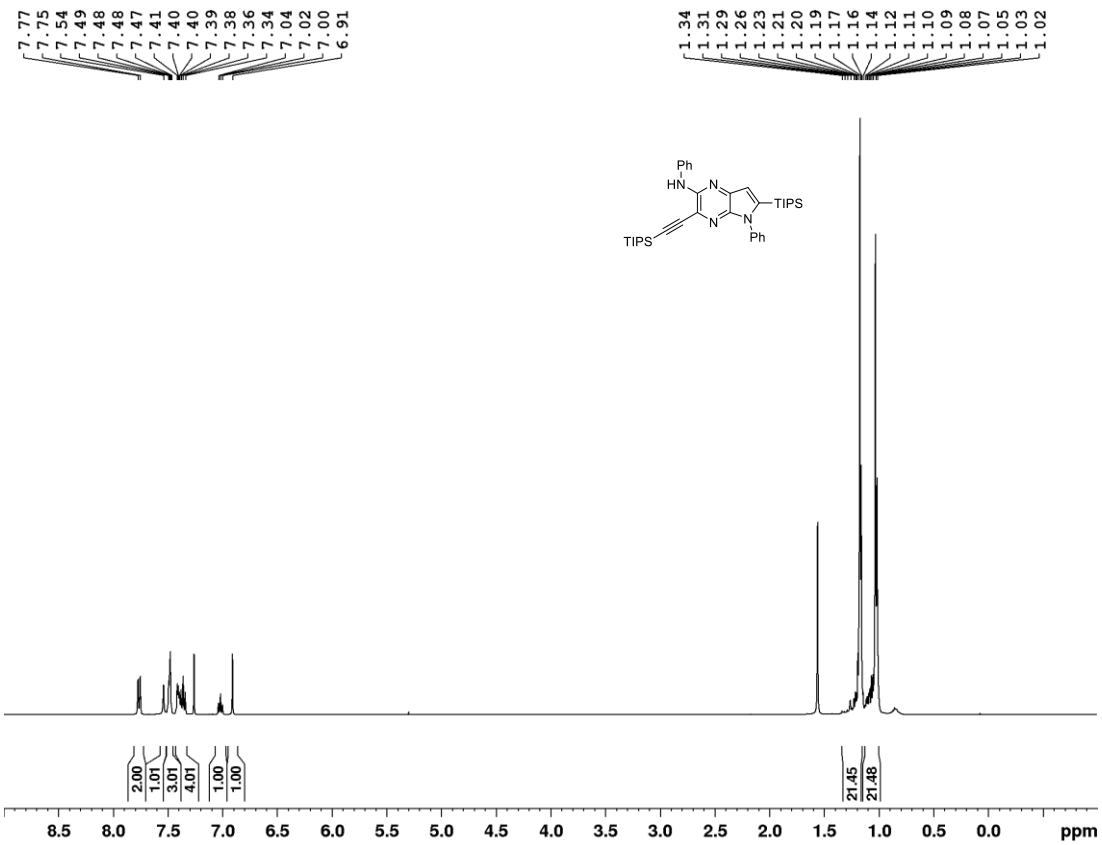


Figure S67. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9**.

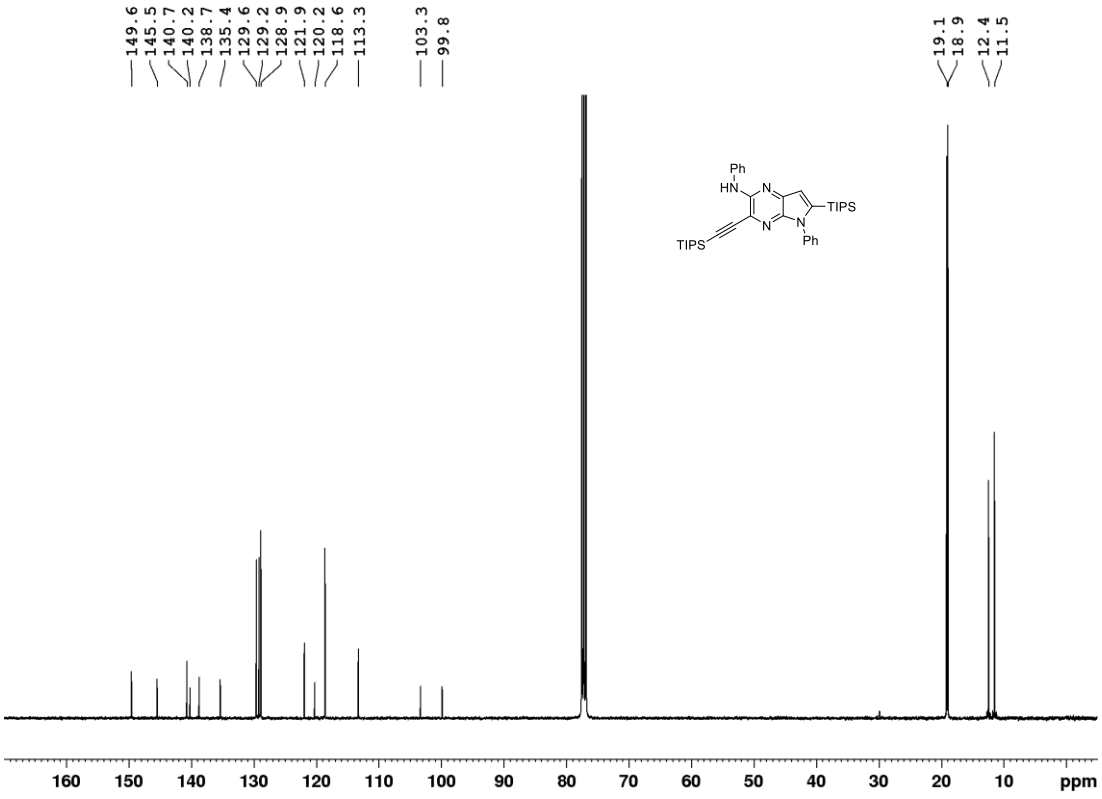


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **9**.

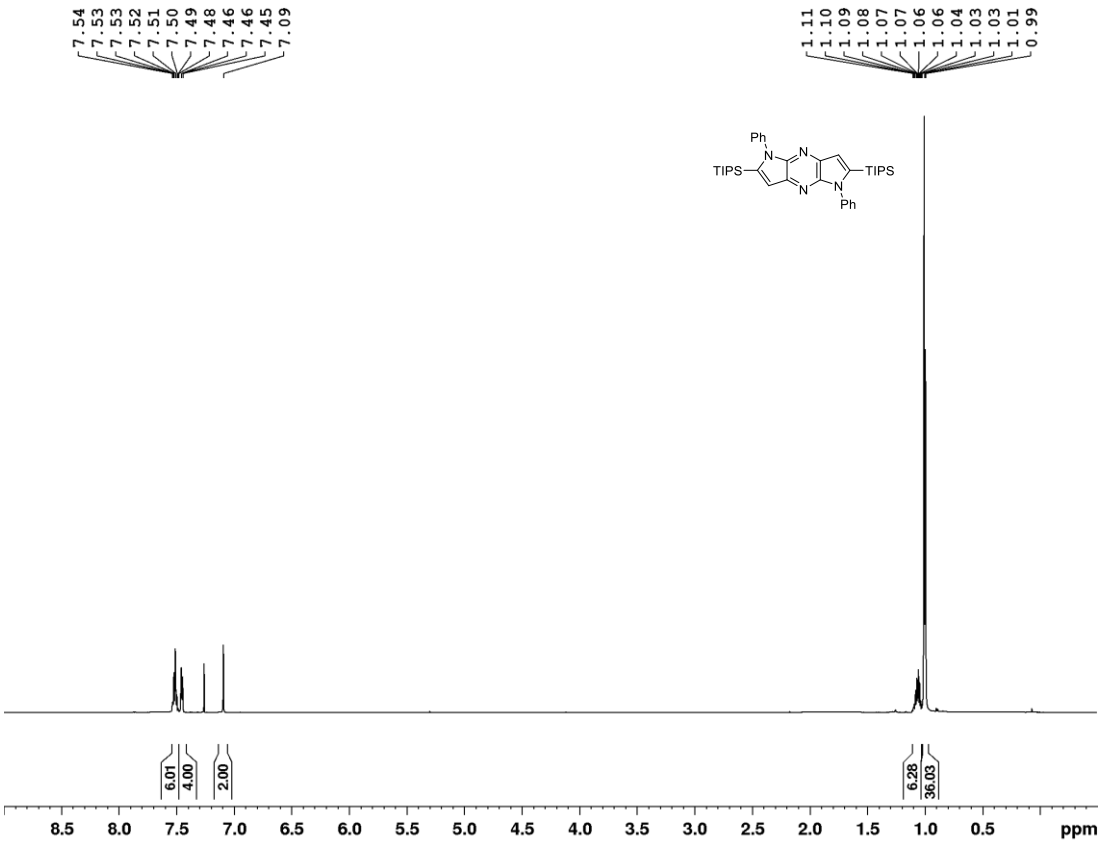


Figure S69. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of ***p*DPPBb**.

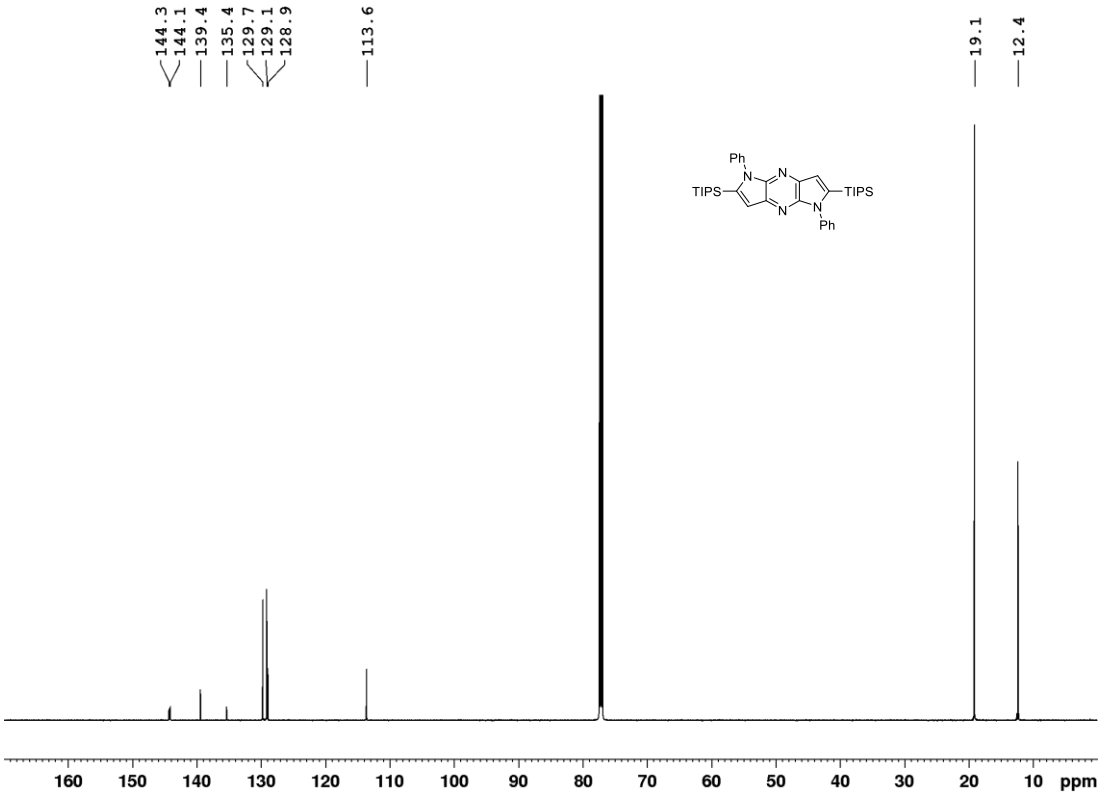


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of ***p*DPPBb**.

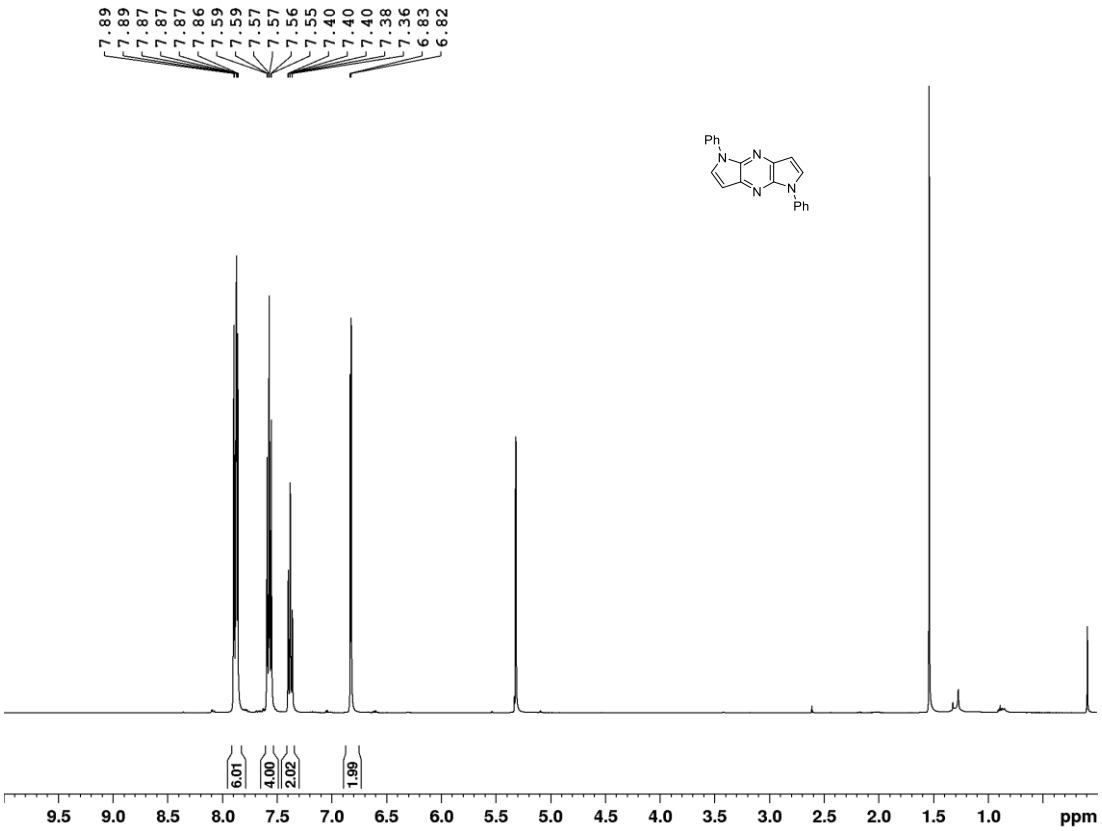


Figure S71. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ***p*DPPc**.

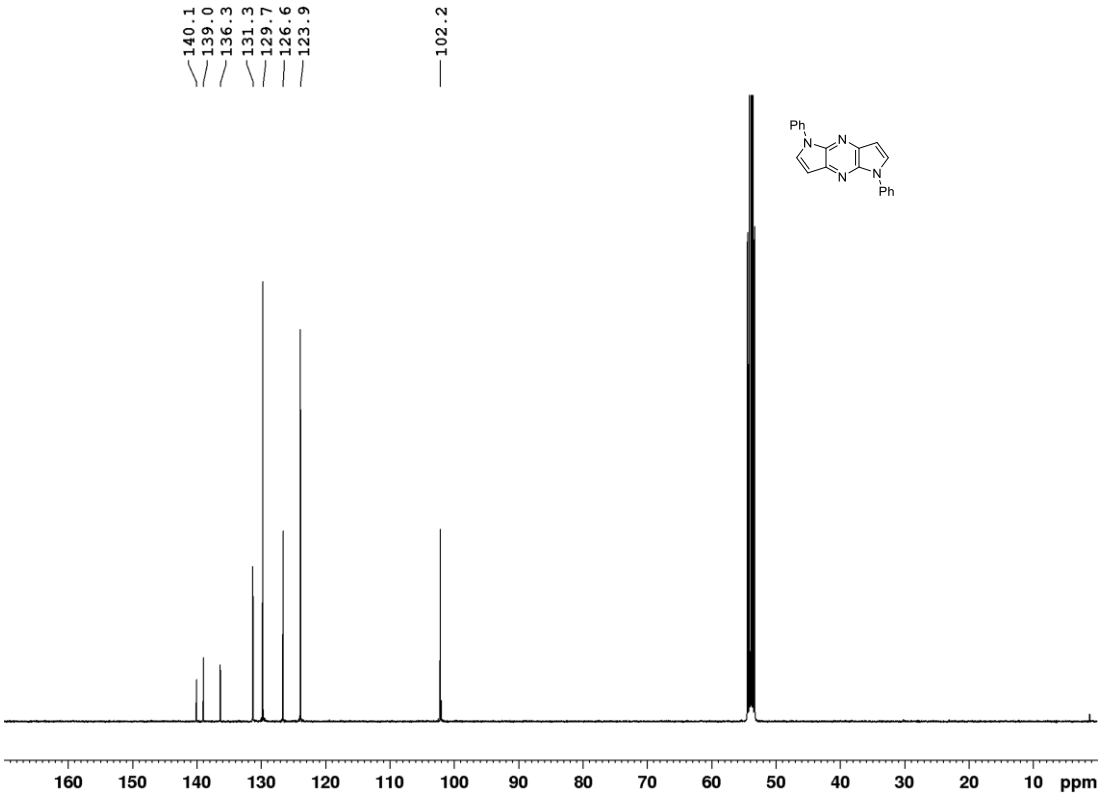


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of ***p*DPPc**.

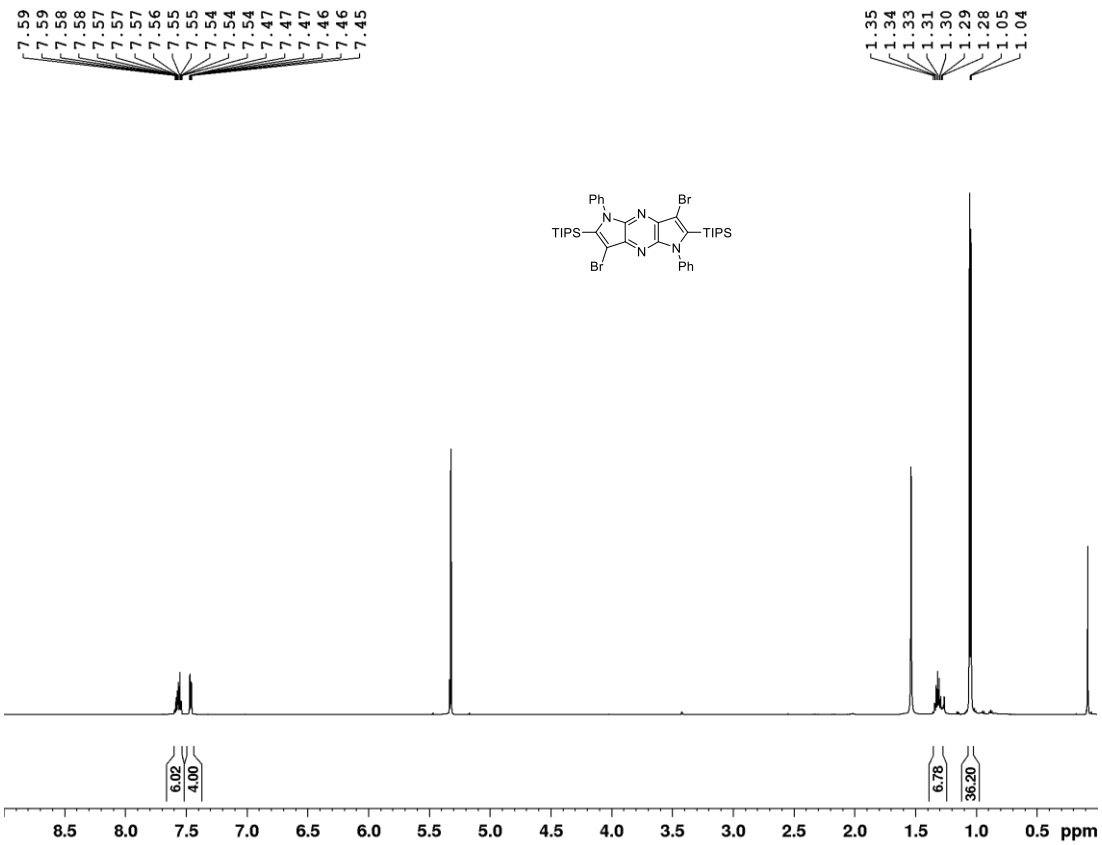


Figure S73. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) of ***p*DPPd**.

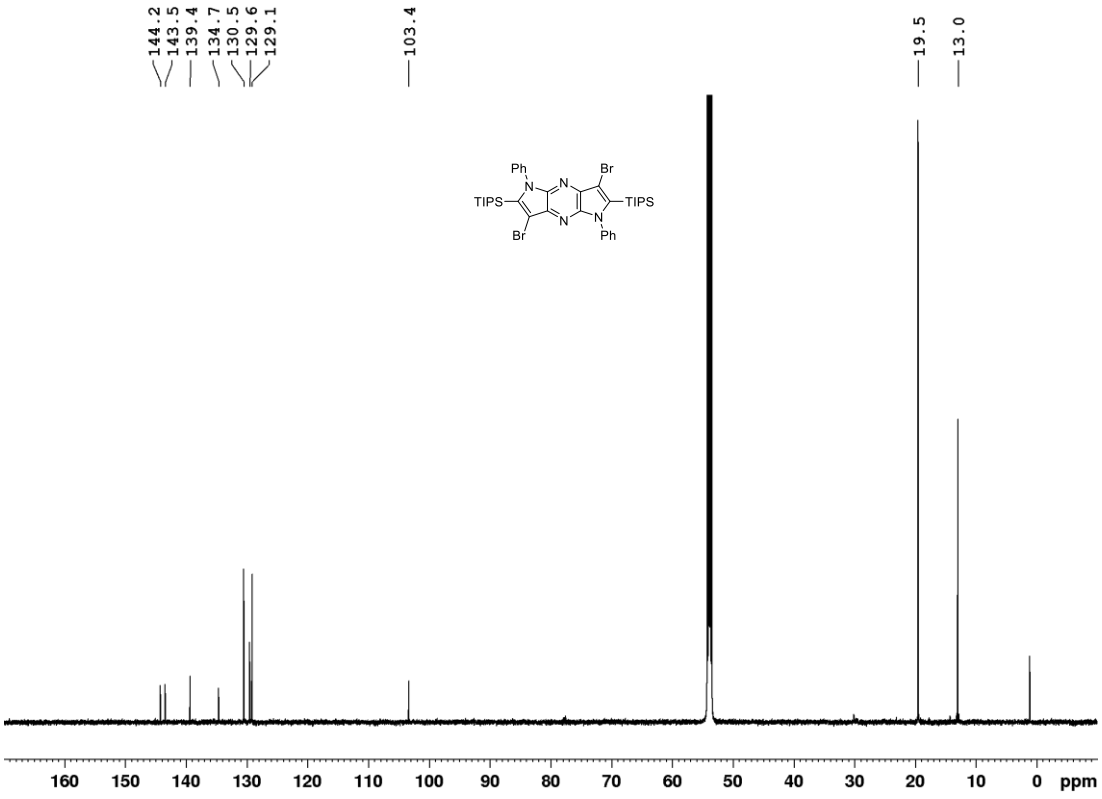


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2) of ***p*DPPd**.

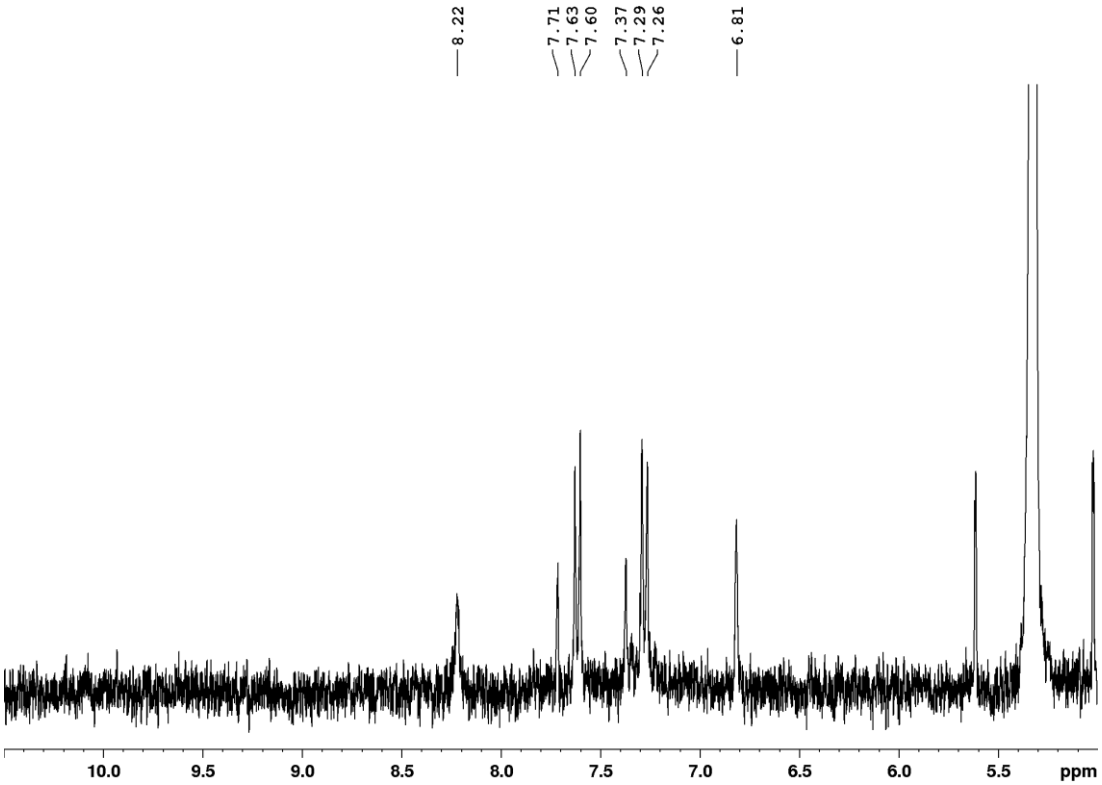


Figure S75. ^{1}H NMR spectrum (301 MHz, CD_2Cl_2) of ***m*DPBb**.

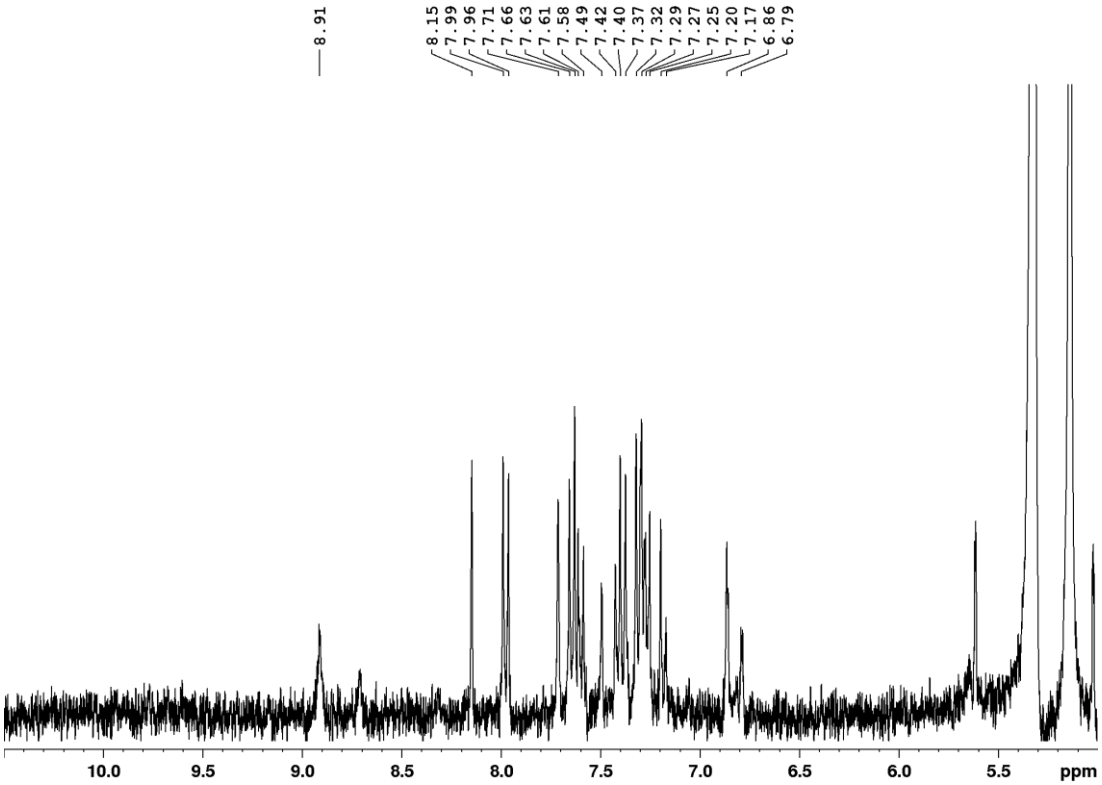


Figure S76. ^{1}H NMR spectrum (301 MHz, CD_2Cl_2) of ***m*DPBb** with addition of BH_3 (10 eq.).

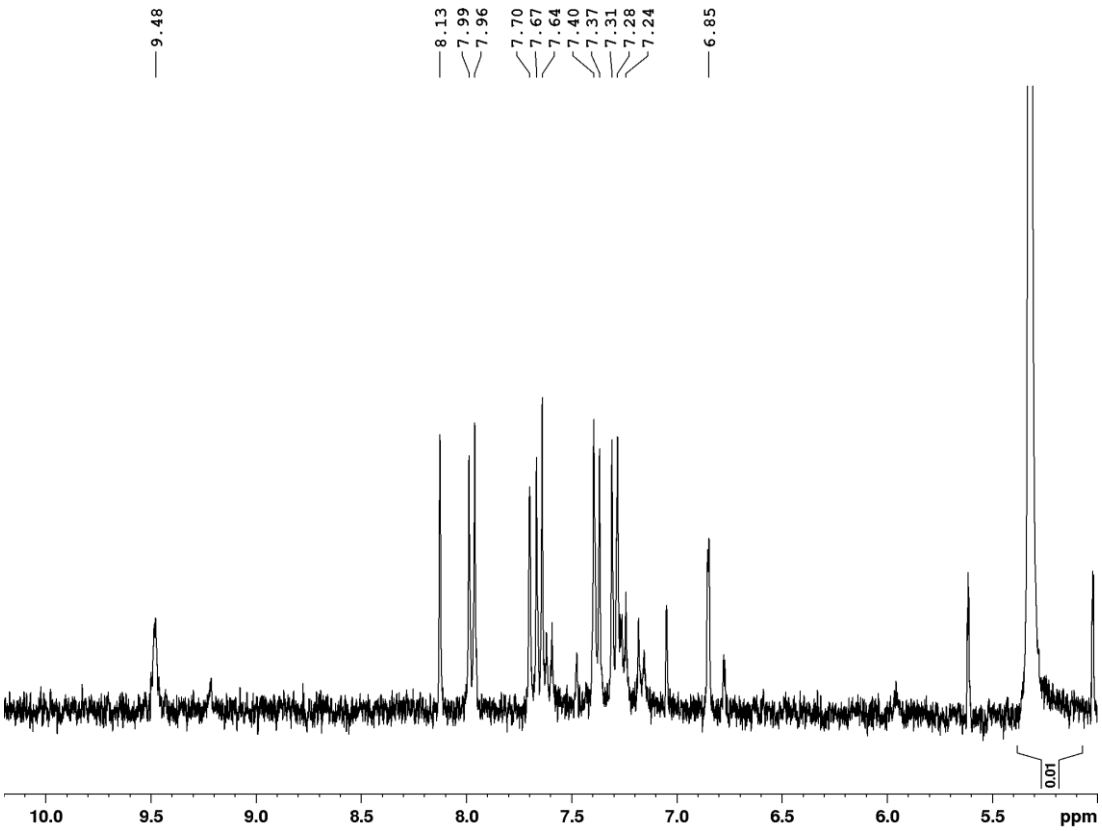


Figure S77. ^{1}H NMR spectrum (301 MHz, CD_2Cl_2) of ***m*DPBb** with addition of BH_3 (50 eq.).

3 UV-Vis and Fluorescence Spectra

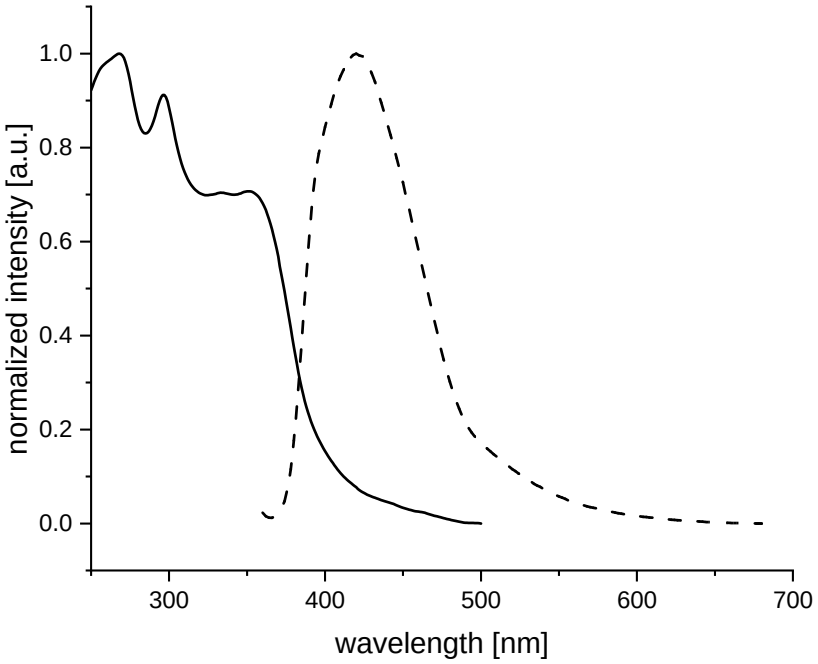


Figure S78. Absorption (solid line) and emission (dashed line) spectra of **1a** in DCM.

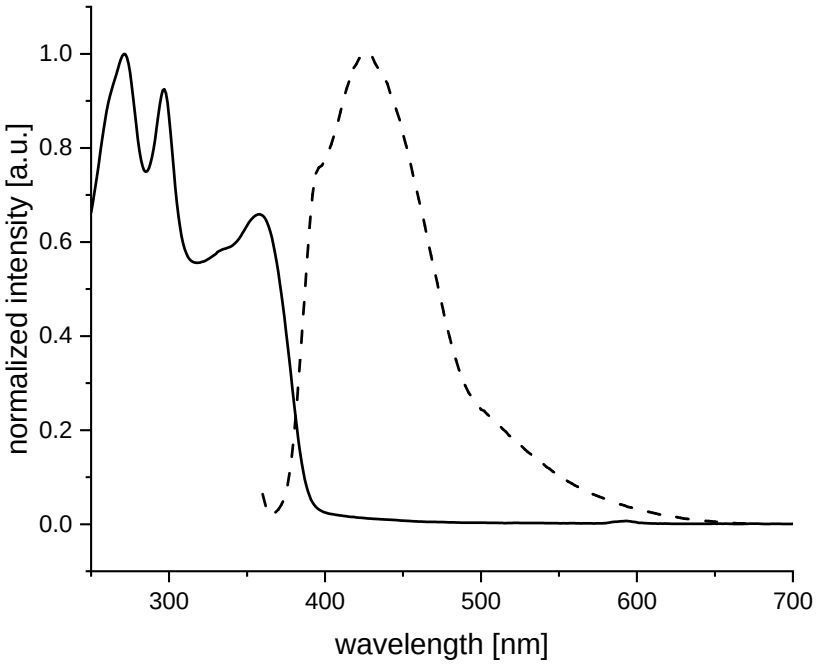


Figure S79. Absorption (solid line) and emission (dashed line) spectra of **1b** in DCM.

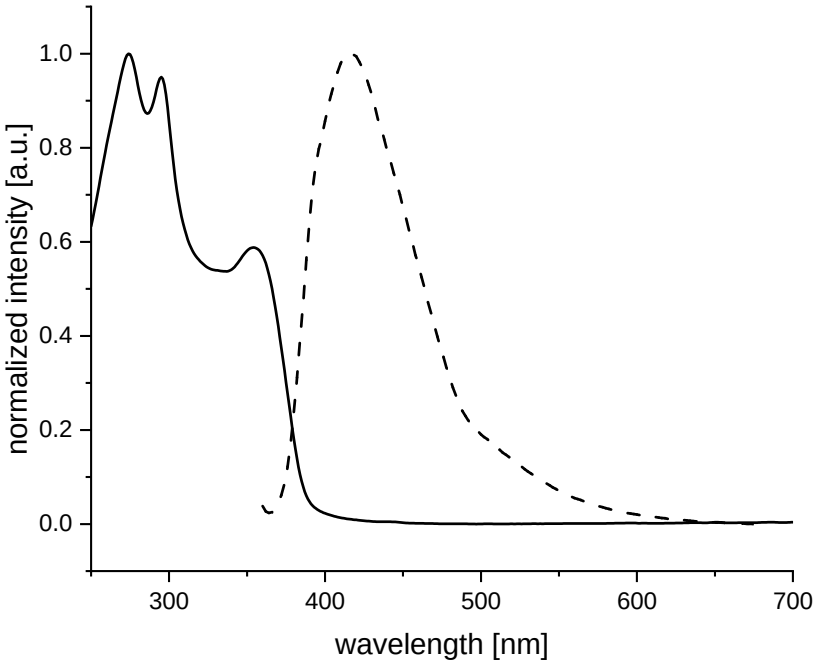


Figure S80. Absorption (solid line) and emission (dashed line) spectra of **1c** in DCM.

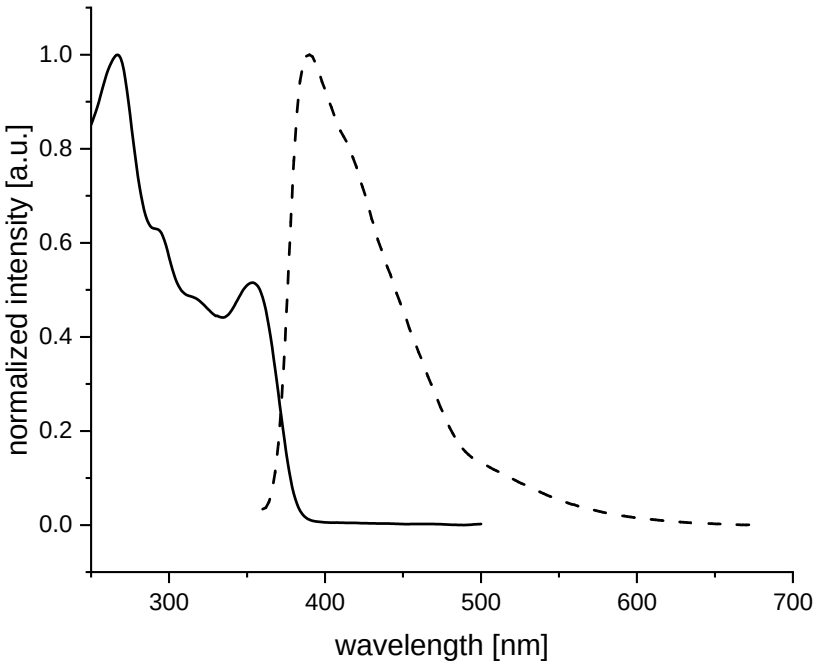


Figure S81. Absorption (solid line) and emission (dashed line) spectra of **1d** in DCM.

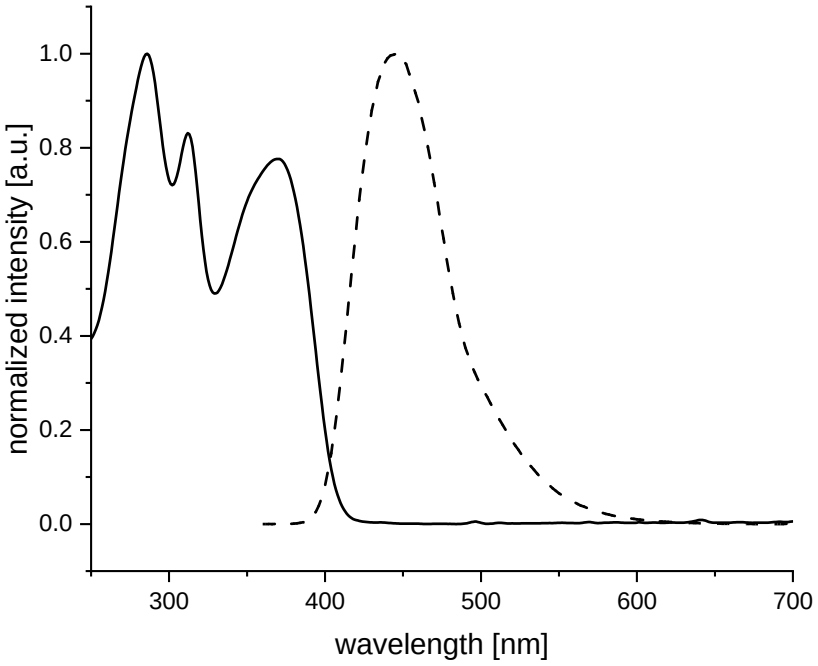


Figure S82. Absorption (solid line) and emission (dashed line) spectra of **1e** in DCM.

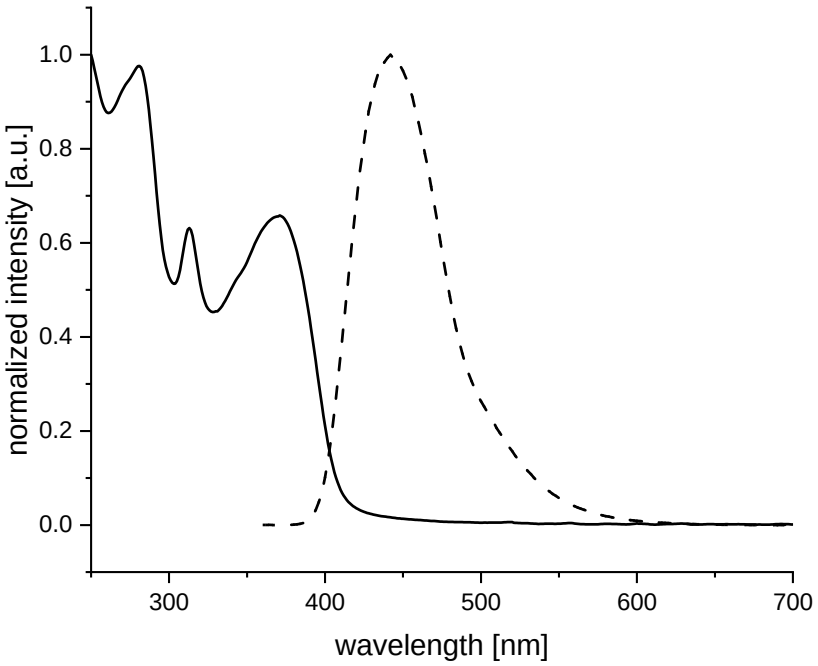


Figure S83. Absorption (solid line) and emission (dashed line) spectra of **1f** in DCM.

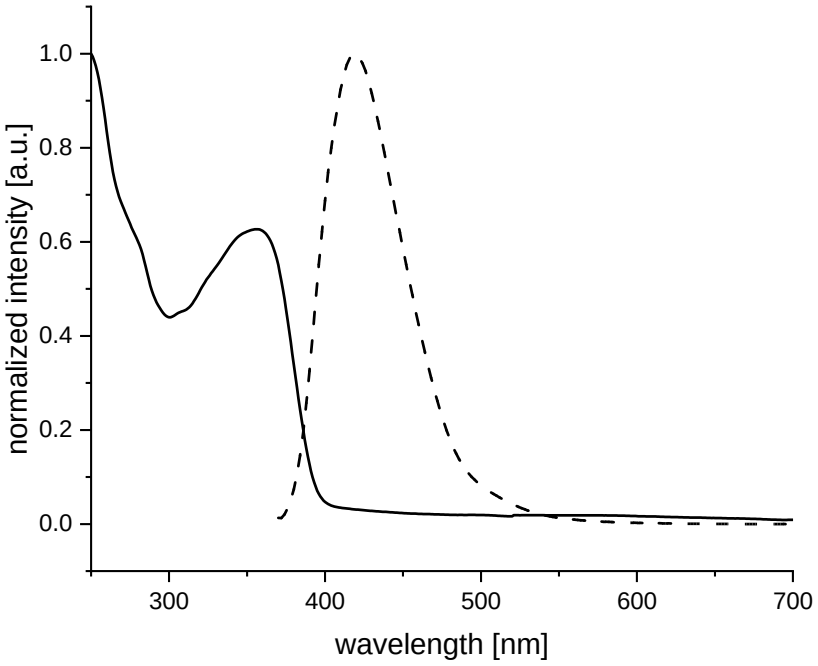


Figure S84. Absorption (solid line) and emission (dashed line) spectra of **1g** in DCM.

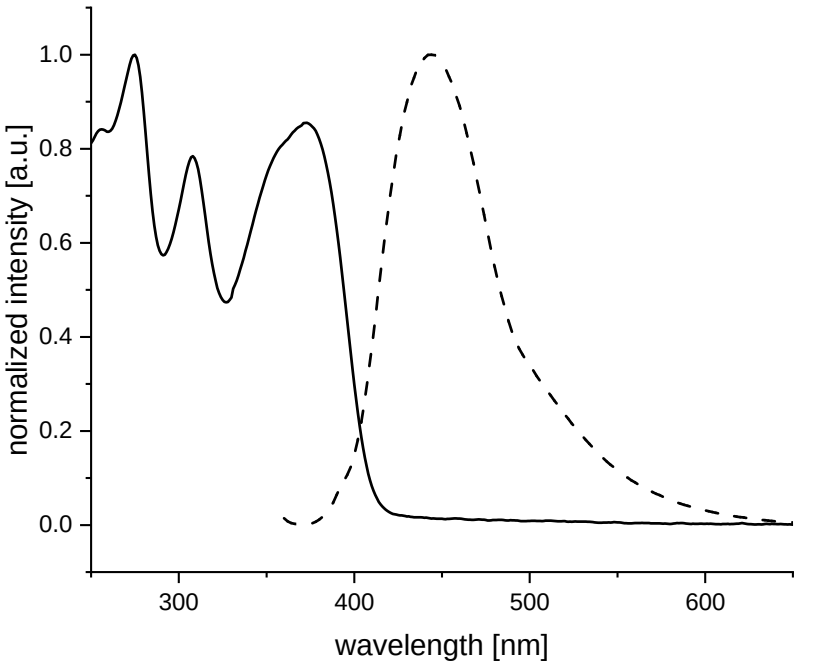


Figure S85. Absorption (solid line) and emission (dashed line) spectra of **1h** in DCM.

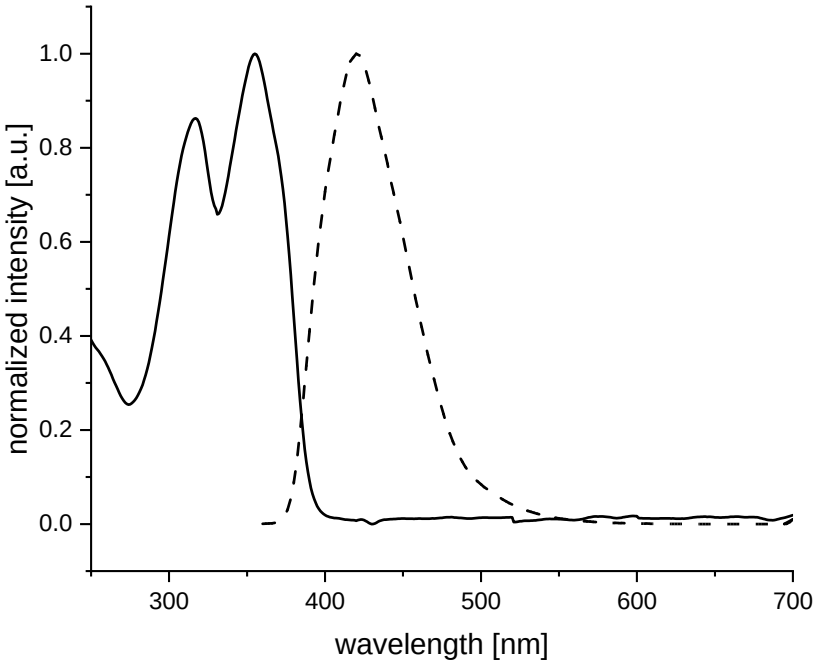


Figure S86. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa** in DCM.

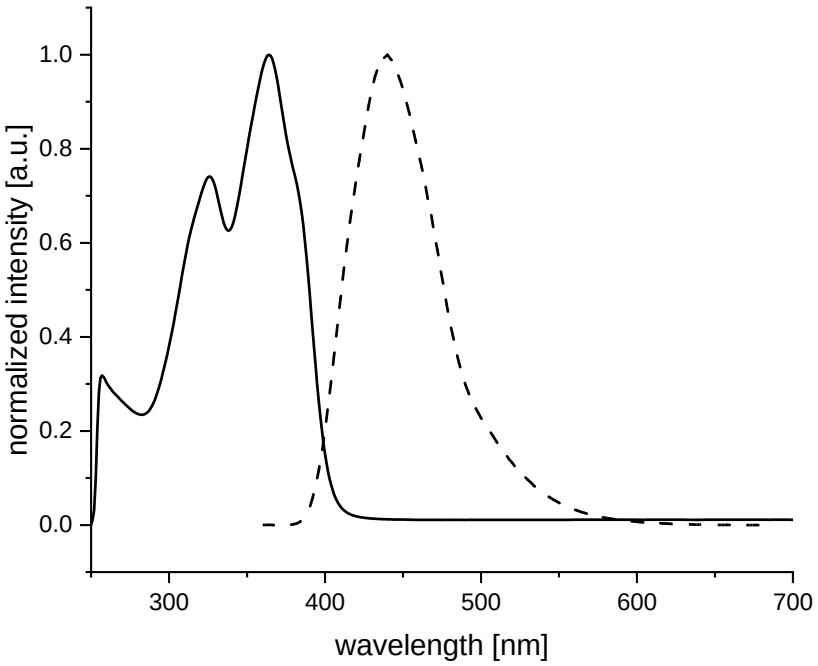


Figure S87. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa** in DMSO.

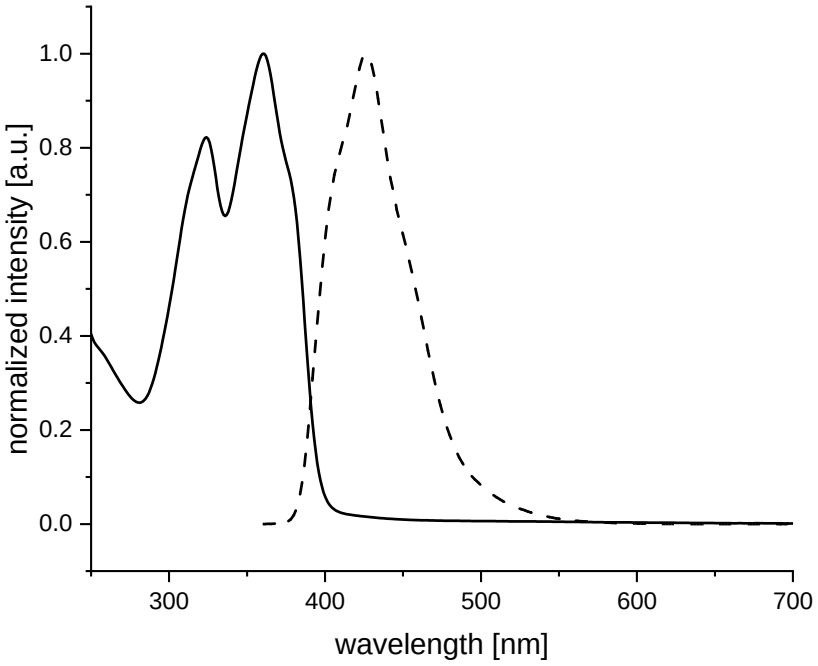


Figure S88. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa** in THF.

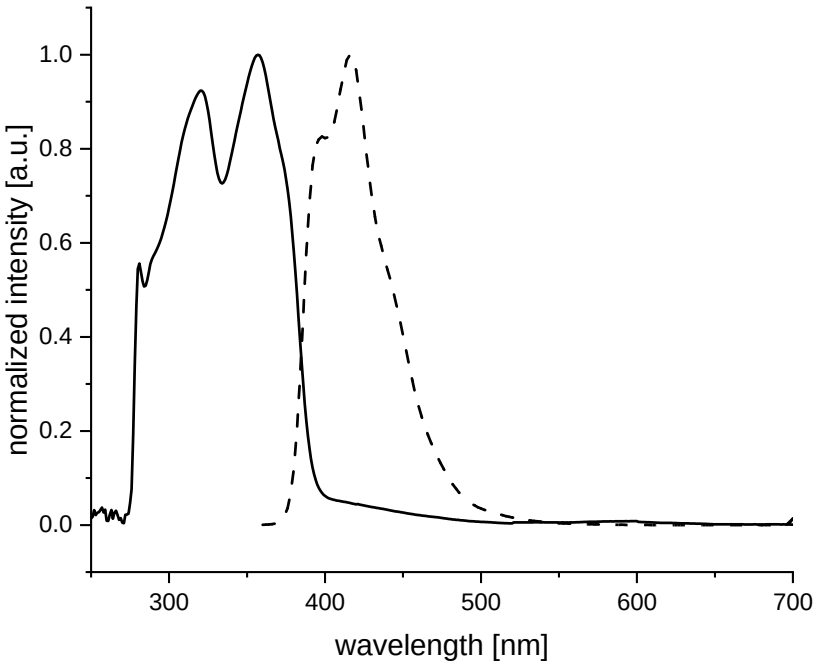


Figure S89. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa** in toluene.

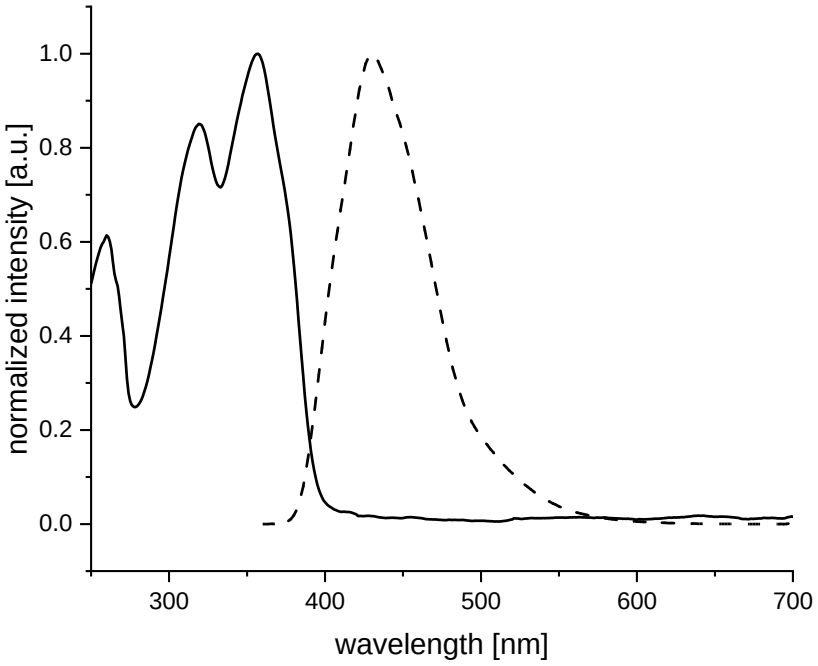


Figure S90. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa** in MeOH.

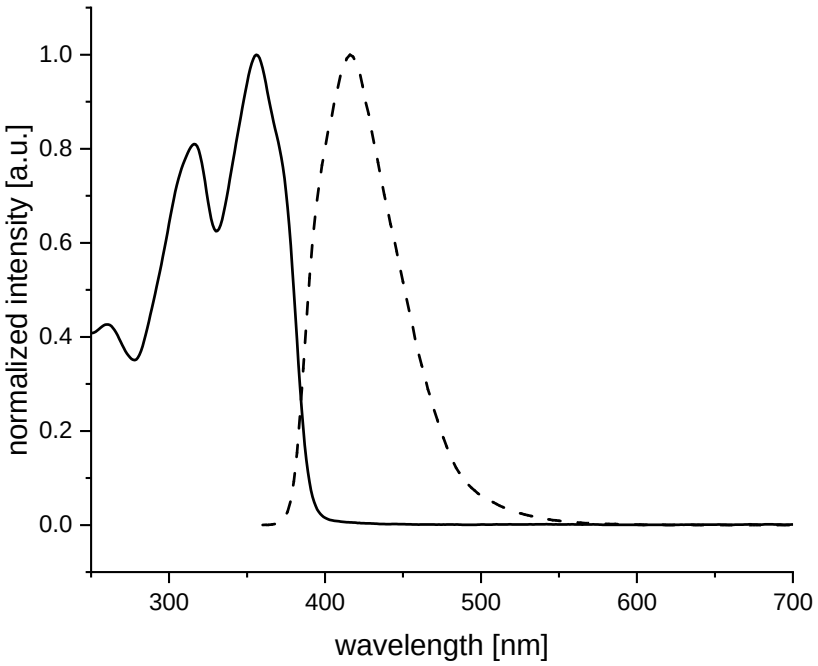


Figure S91. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBb** in DCM.

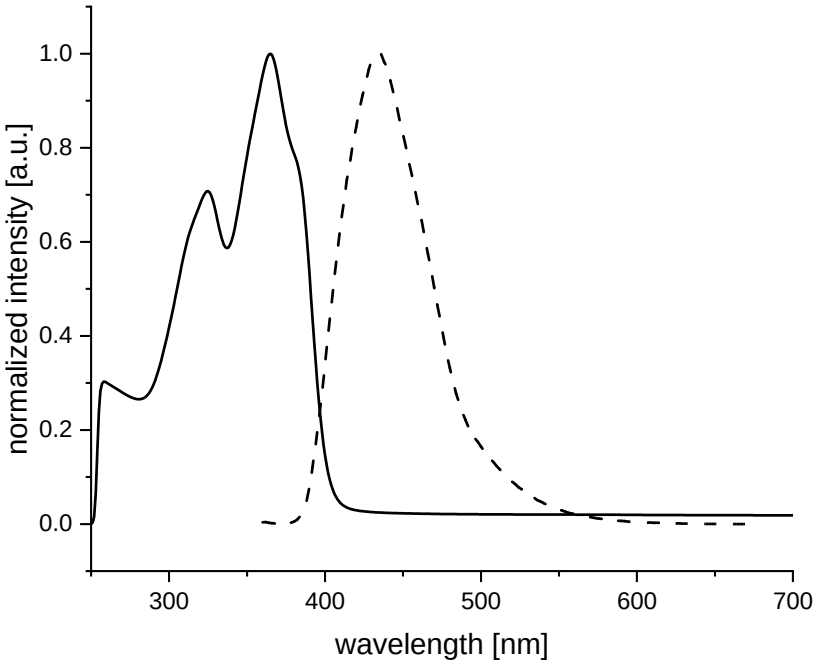


Figure S92. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBb** in DMSO.

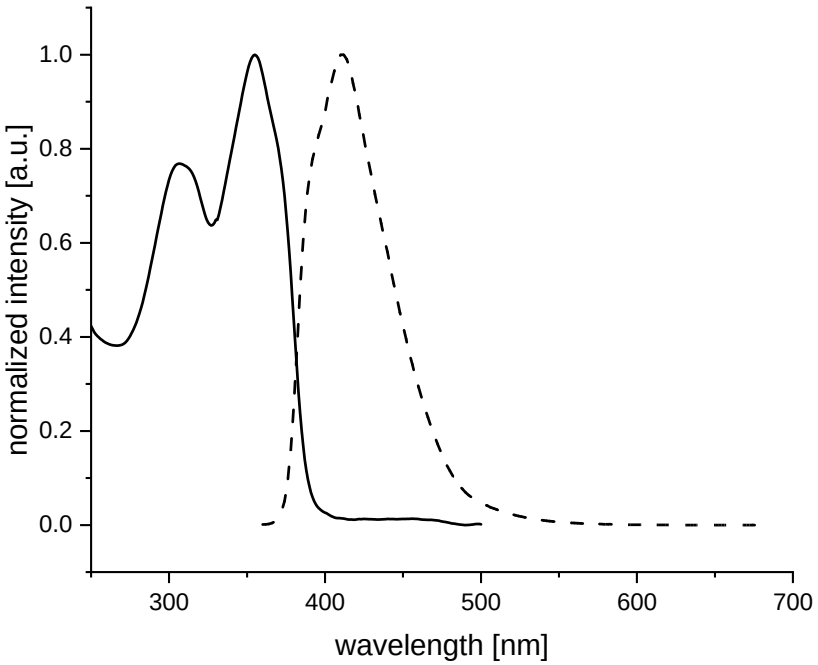


Figure S93. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBc** in DCM.

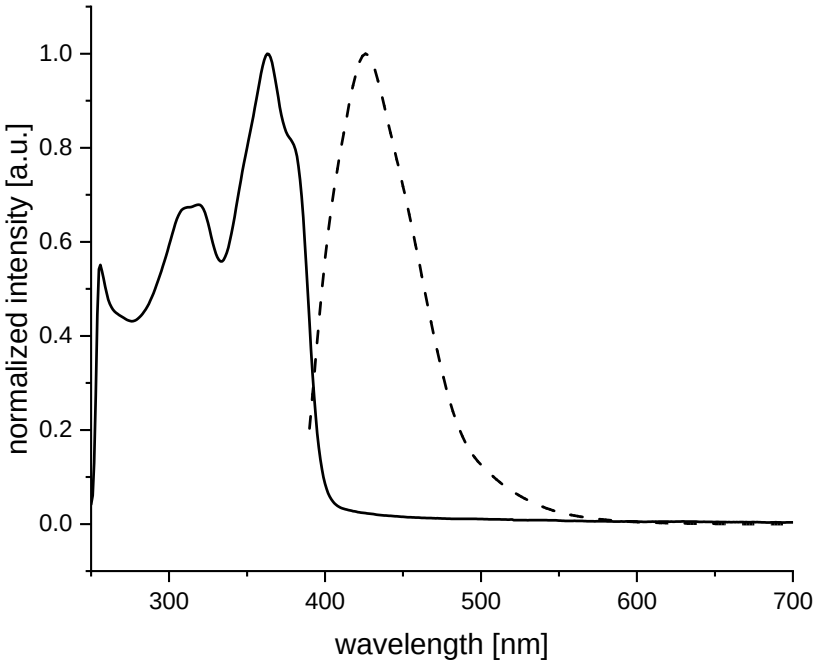


Figure S94. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBc** in DMSO.

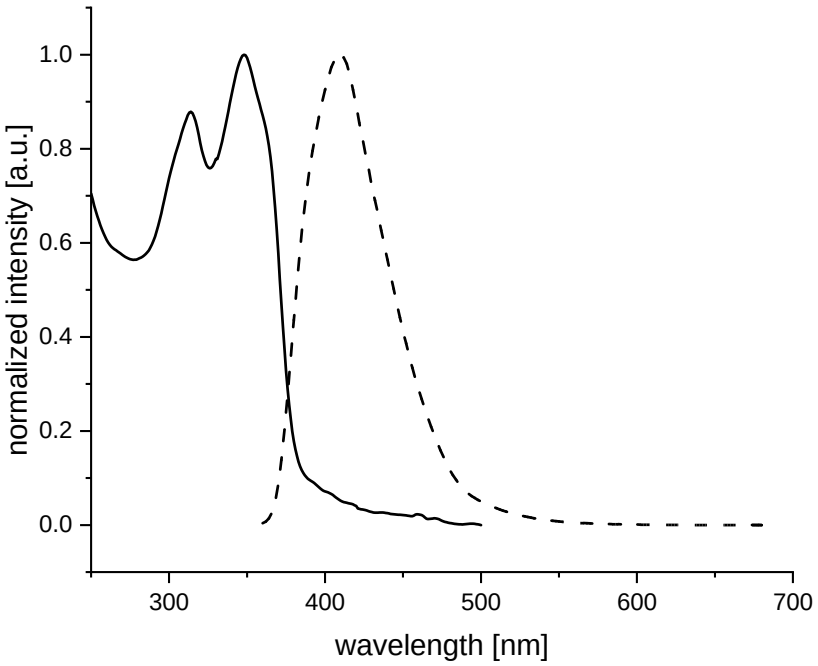


Figure S95. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBd** in DCM.

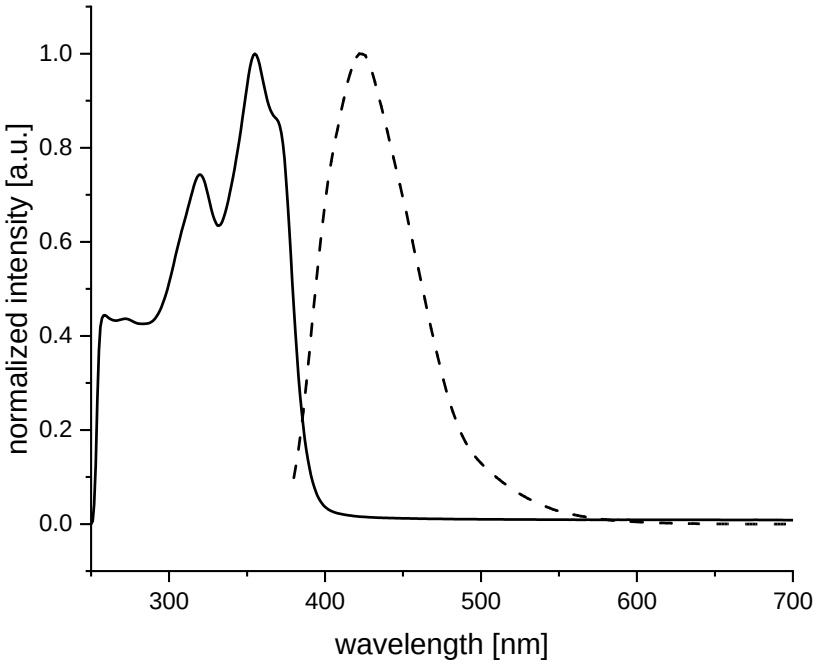


Figure S96. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBd** in DMSO.

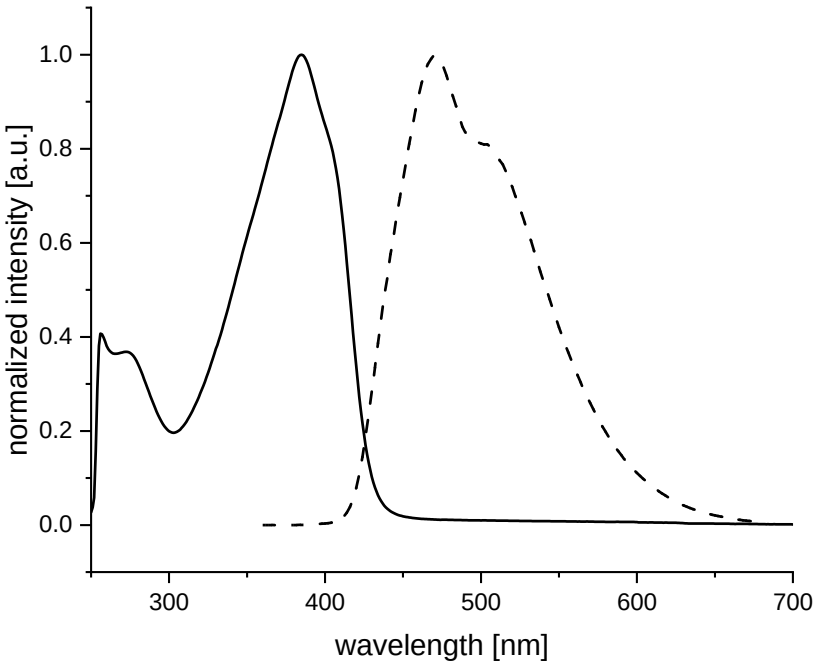


Figure S97. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBe** in DMSO.

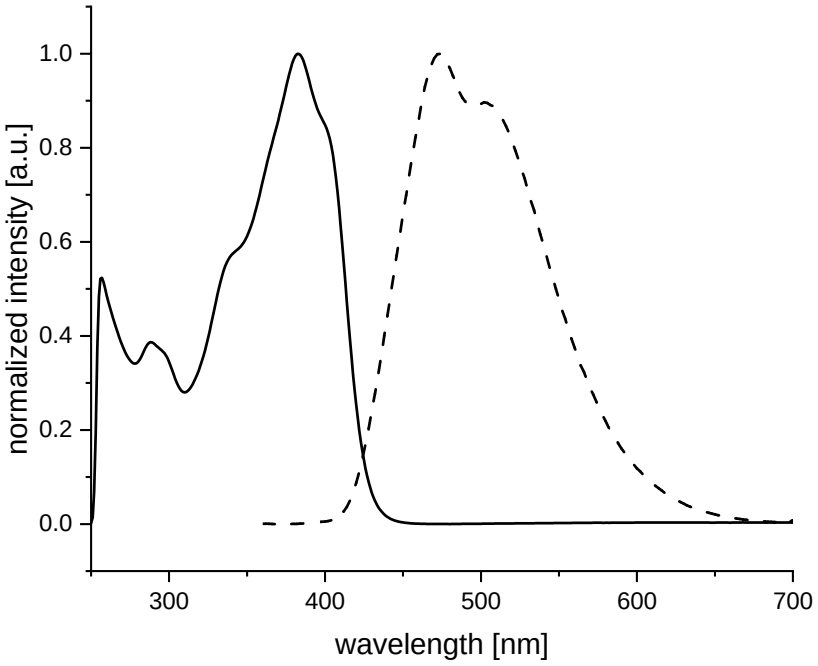


Figure S98. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBf** in DMSO.

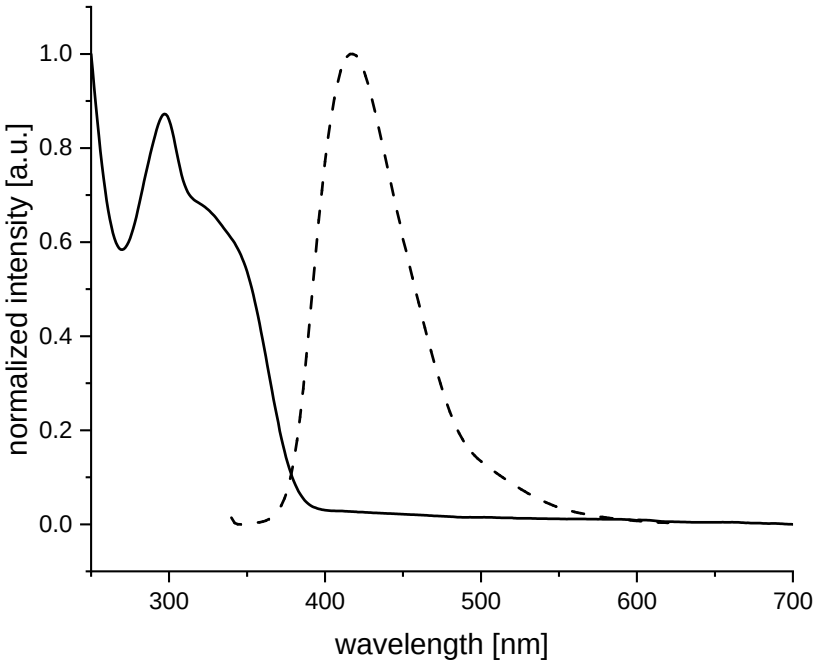


Figure S99. Absorption (solid line) and emission (dashed line) spectra of **1g`** in DCM.

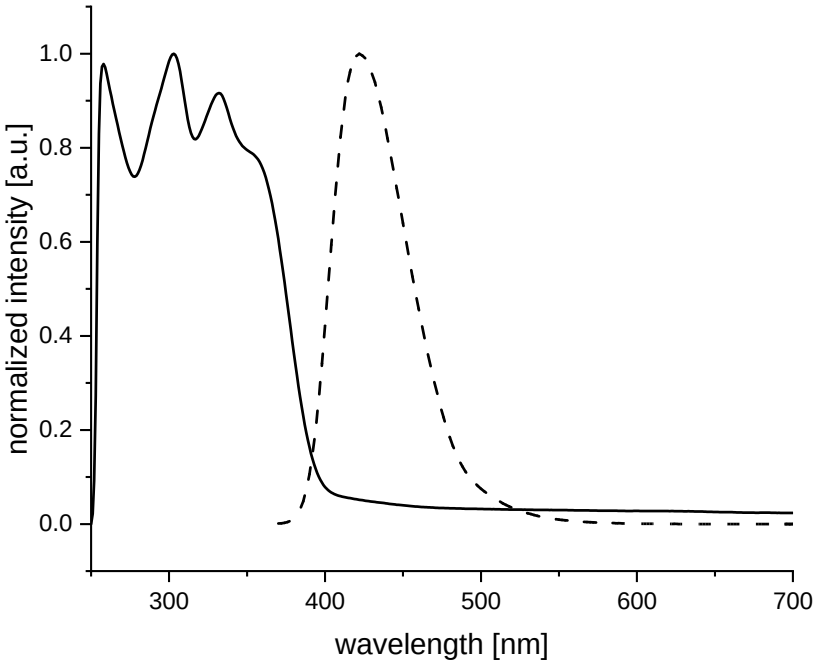


Figure S100. Absorption (solid line) and emission (dashed line) spectra of **1g`** in DMSO.

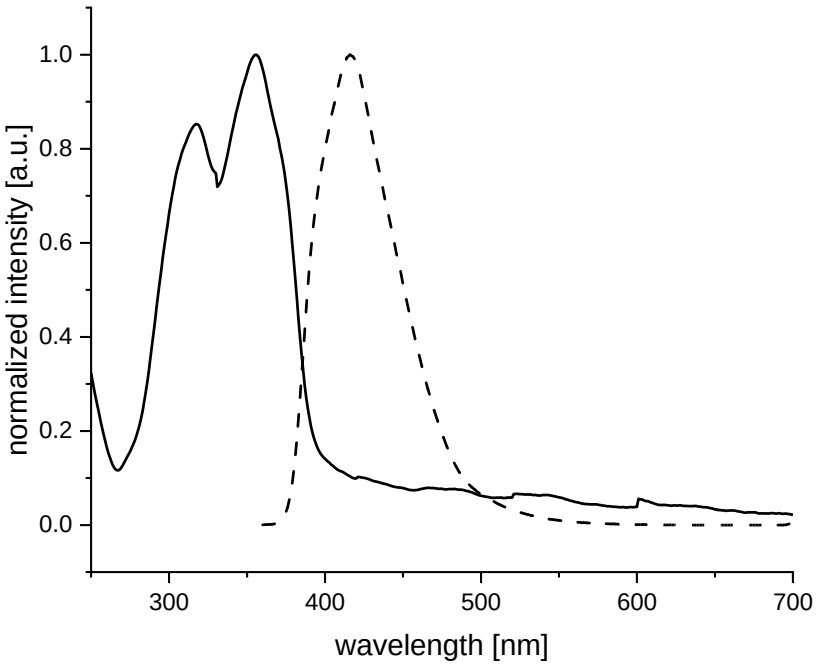


Figure S101. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa`** in DCM.

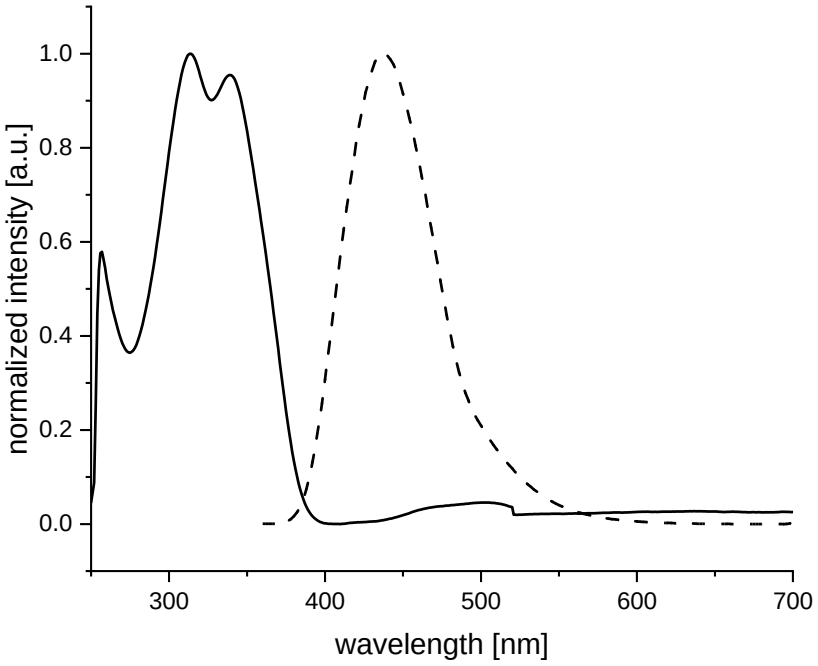


Figure S102. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBa`** in DMSO.

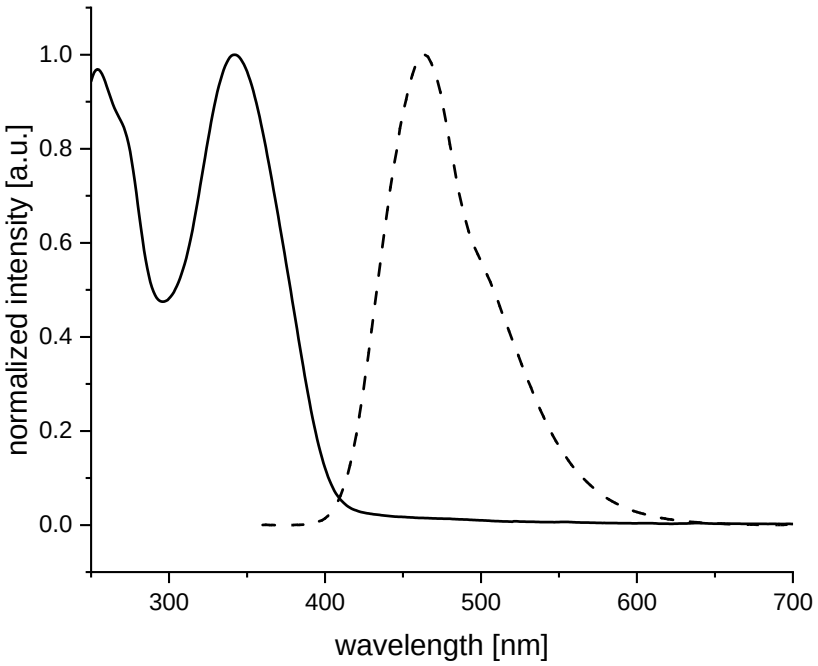


Figure S103. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBe`** in DCM.

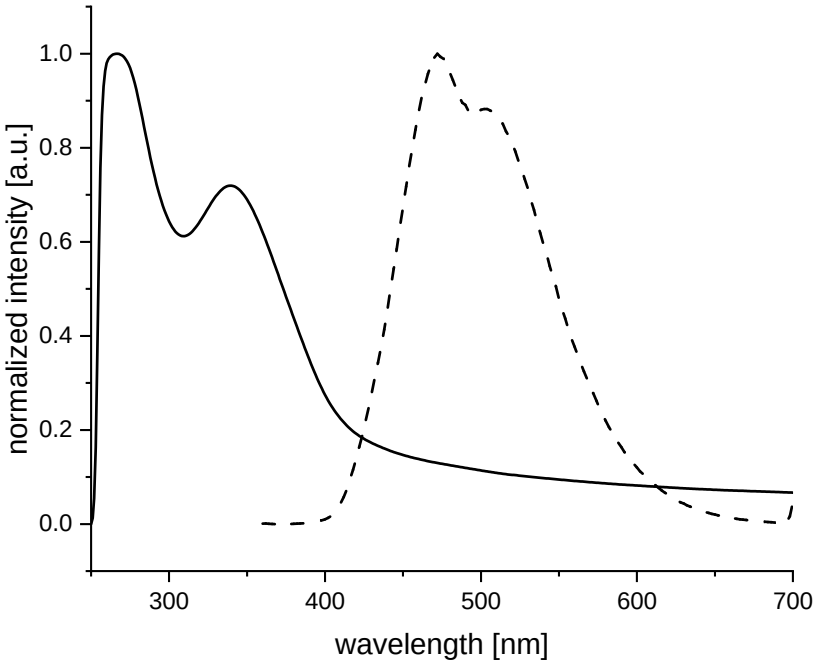


Figure S104. Absorption (solid line) and emission (dashed line) spectra of ***m*DPBe`** in DMSO.

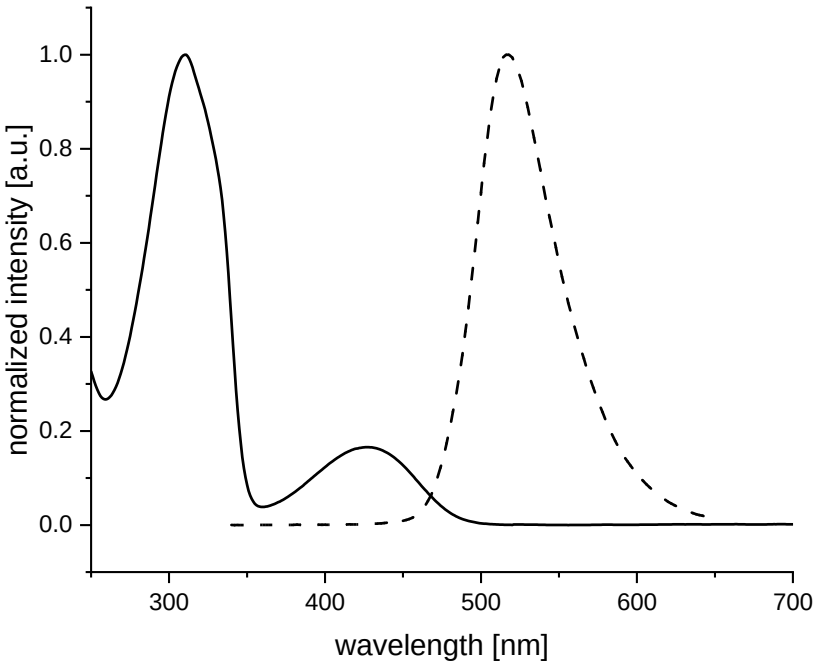


Figure S105. Absorption (solid line) and emission (dashed line) spectra of **4a** in DCM.

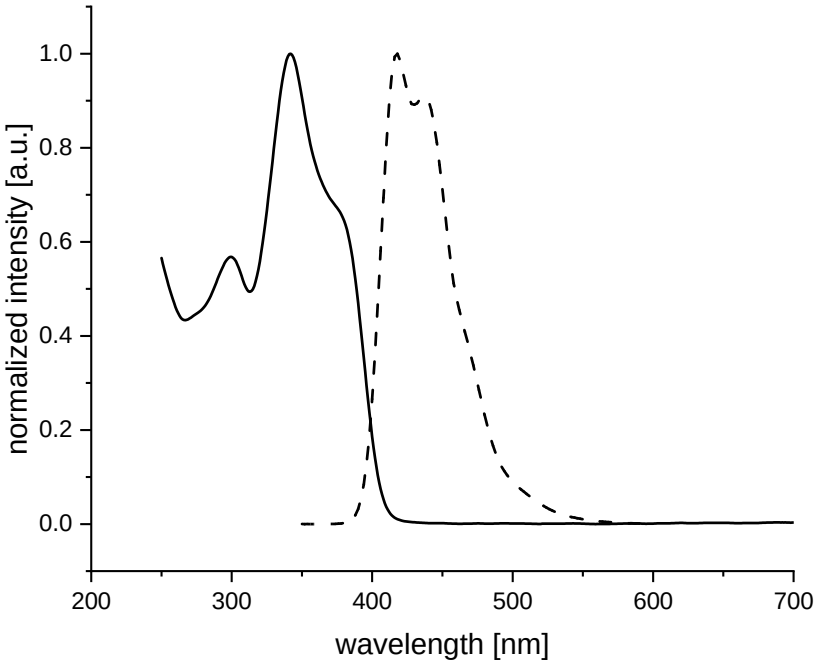


Figure S106. Absorption (solid line) and emission (dashed line) spectra of ***p*DPBa** in DCM.

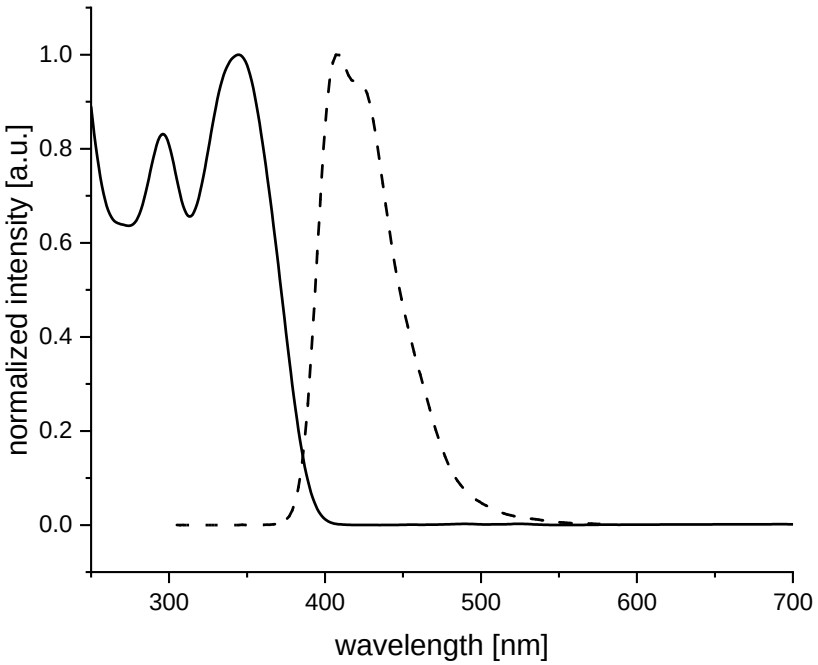


Figure S107. Absorption (solid line) and emission (dashed line) spectra of ***p*DPBb** in DCM.

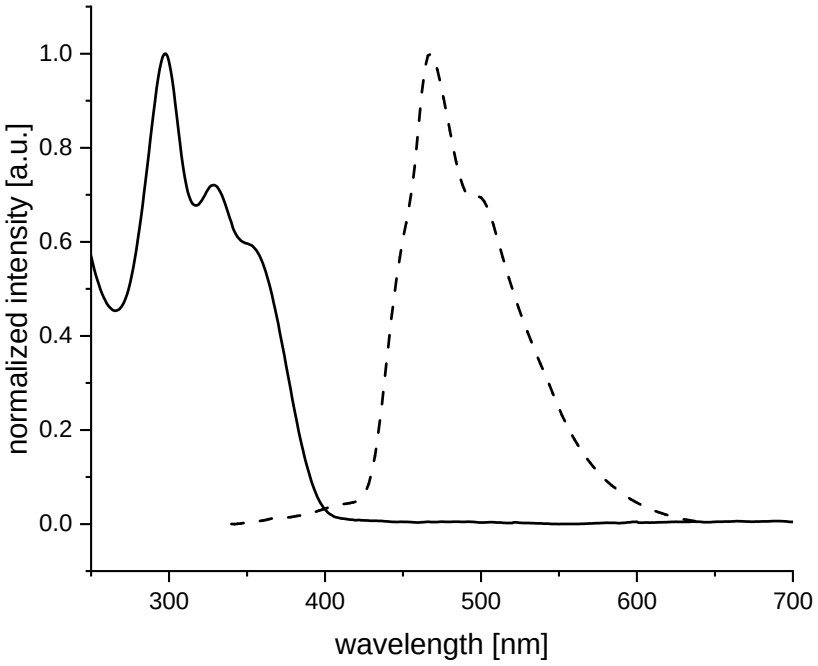


Figure S108. Absorption (solid line) and emission (dashed line) spectra of ***p*DPBBc** in DCM.

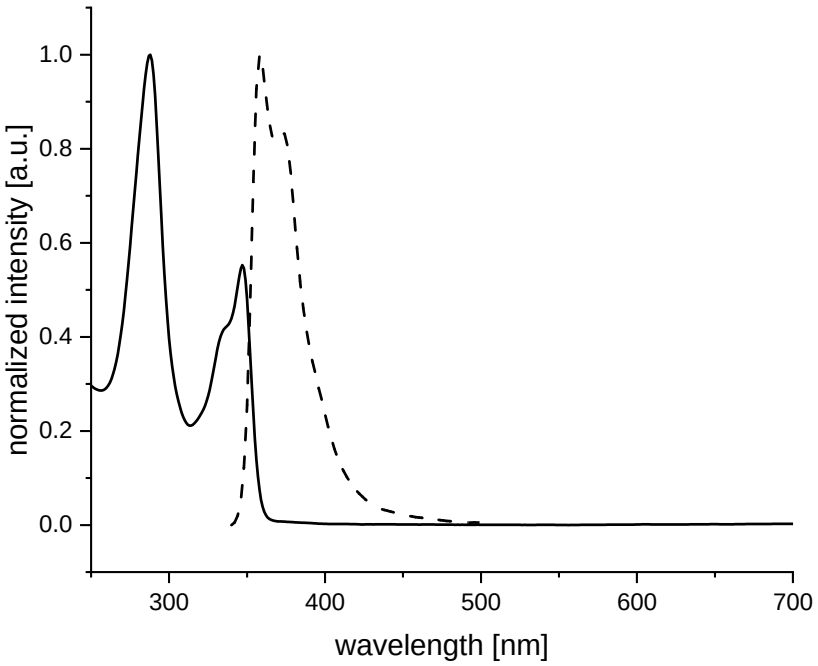


Figure S109. Absorption (solid line) and emission (dashed line) spectra of ***p*DPBBd** in DCM.

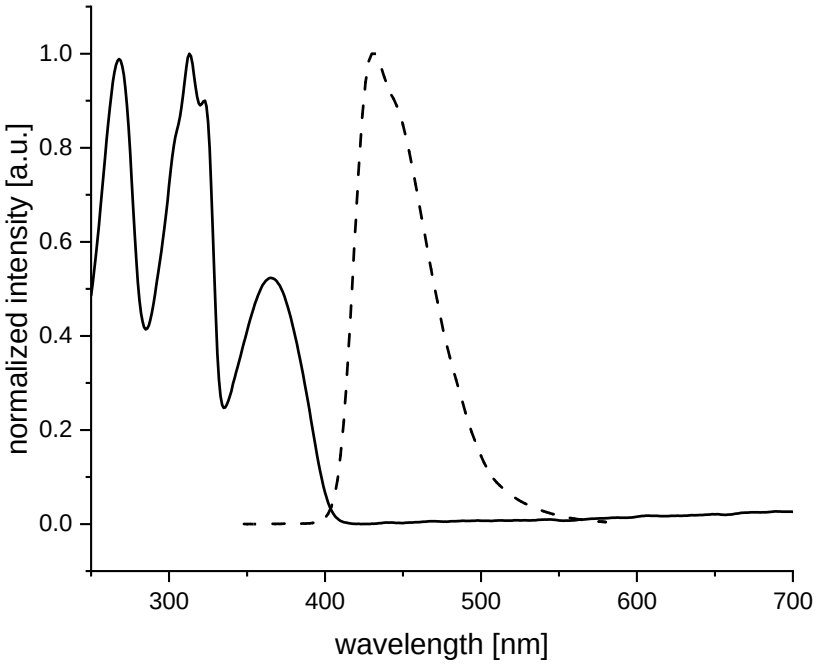


Figure S110. Absorption (solid line) and emission (dashed line) spectra of **6** in DCM.

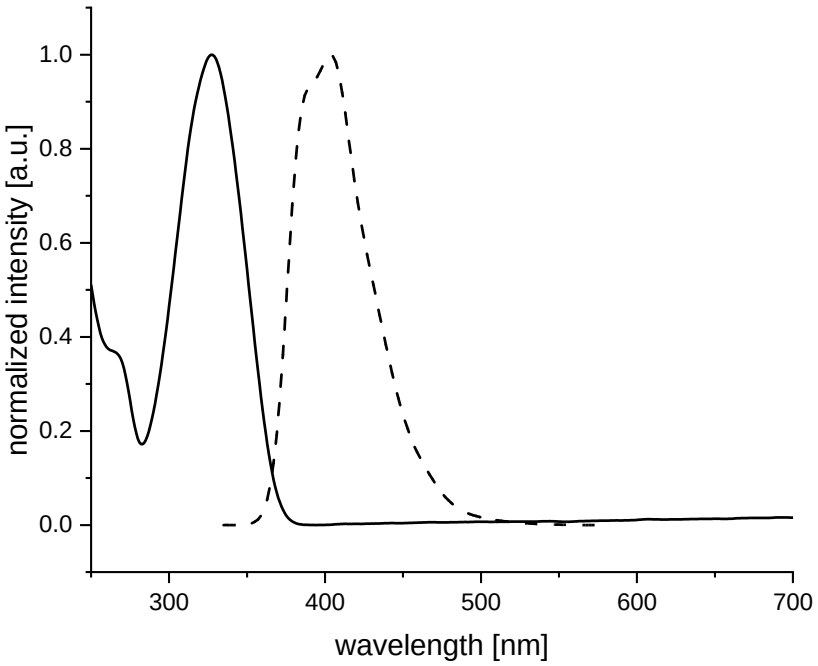


Figure S111. Absorption (solid line) and emission (dashed line) spectra of ***p*DPBe`** in DCM.

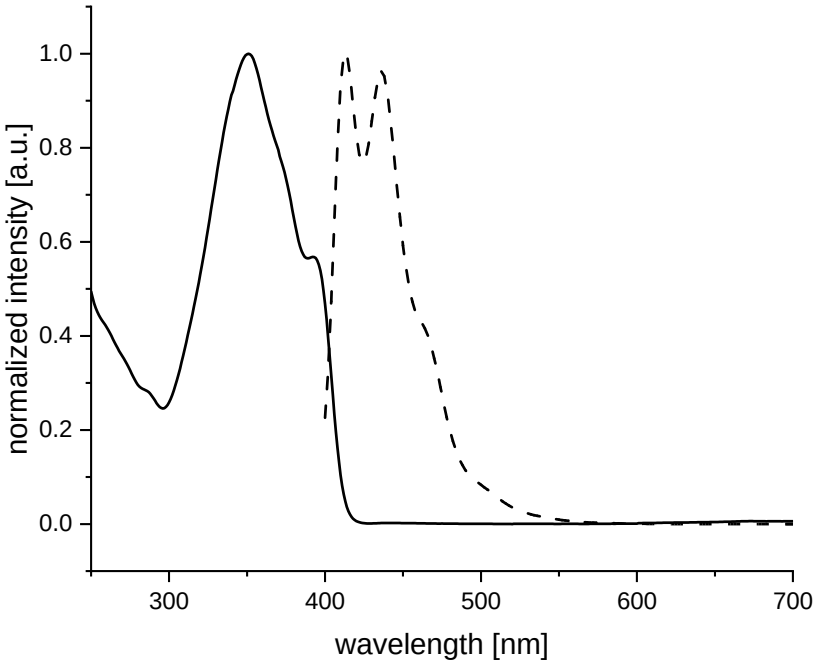


Figure S112. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPBe** in DCM.

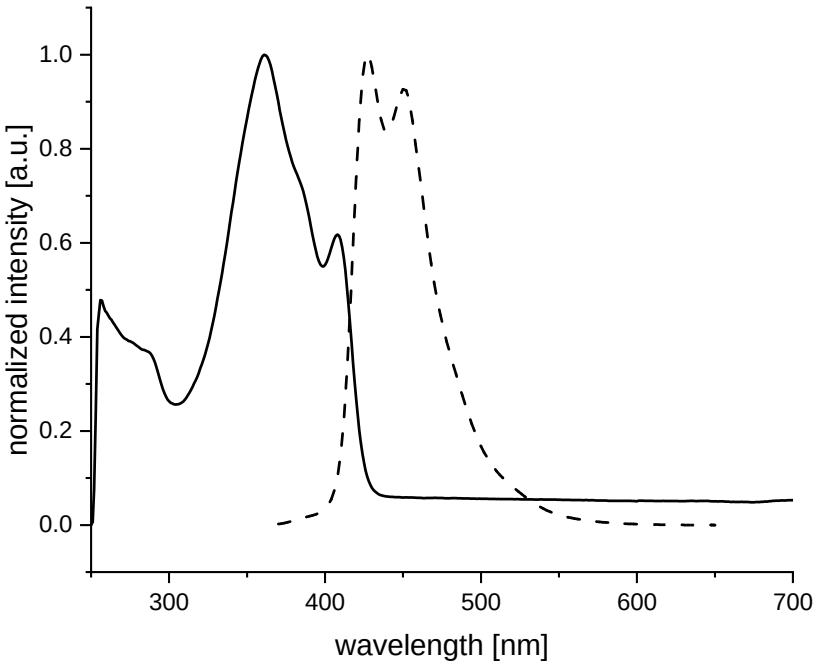


Figure S113. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPBe** in DMSO.

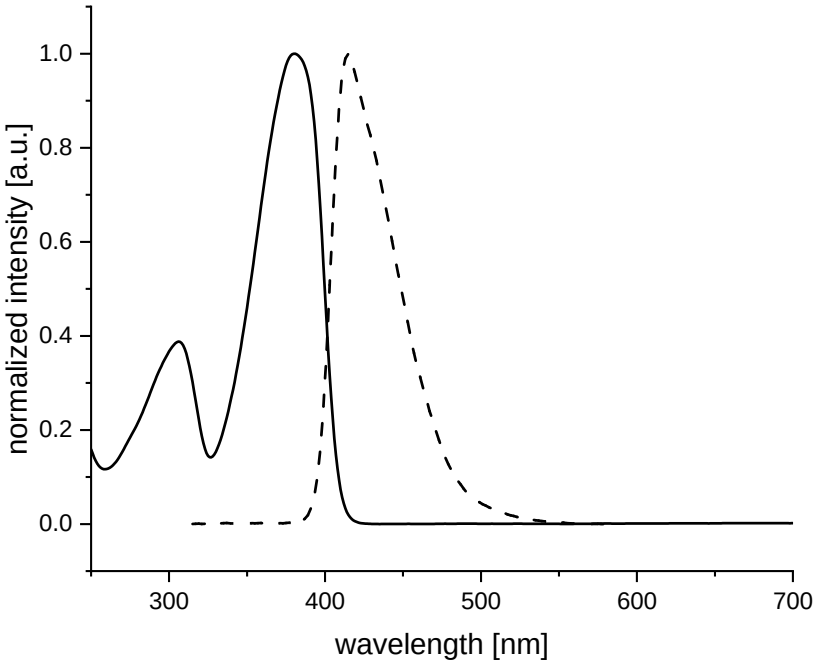


Figure S114. Absorption (solid line) and emission (dashed line) spectra of **8a** in DCM.

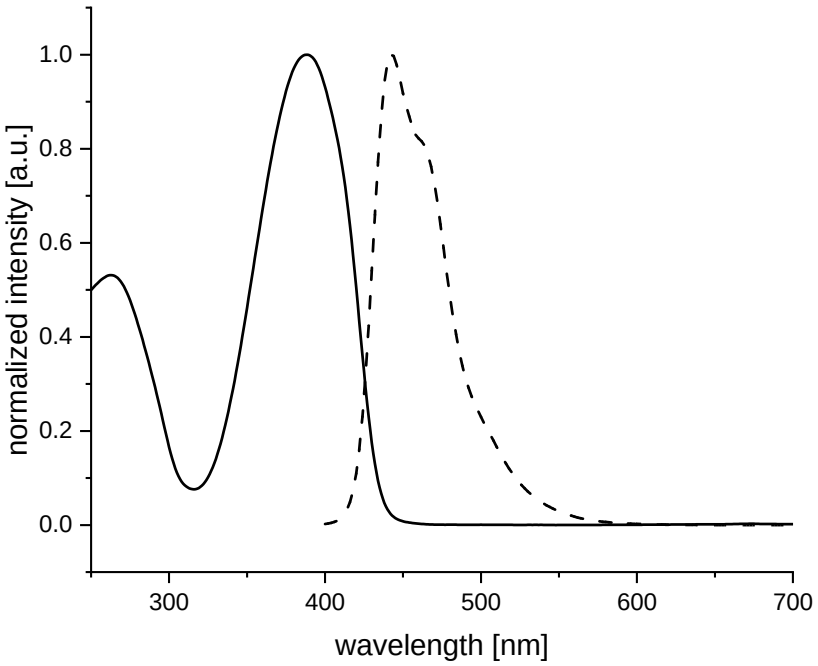


Figure S115. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPa** in DCM.

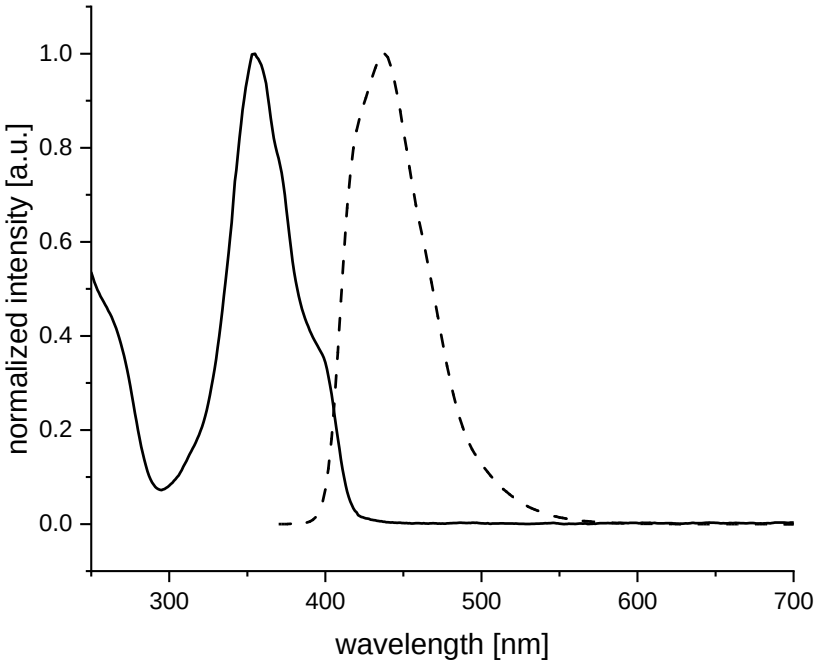


Figure S116. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPb** in DCM.

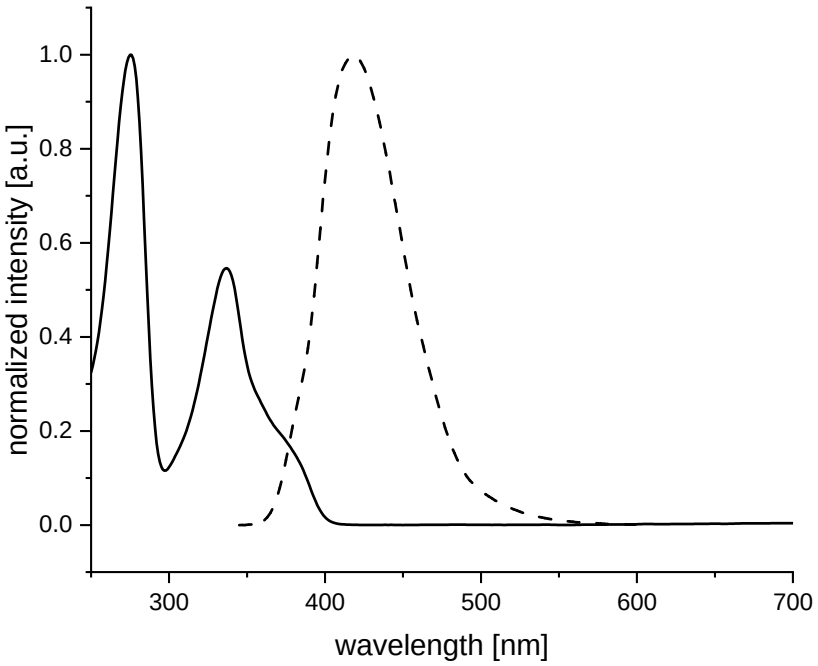


Figure S117. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPc** in DCM.

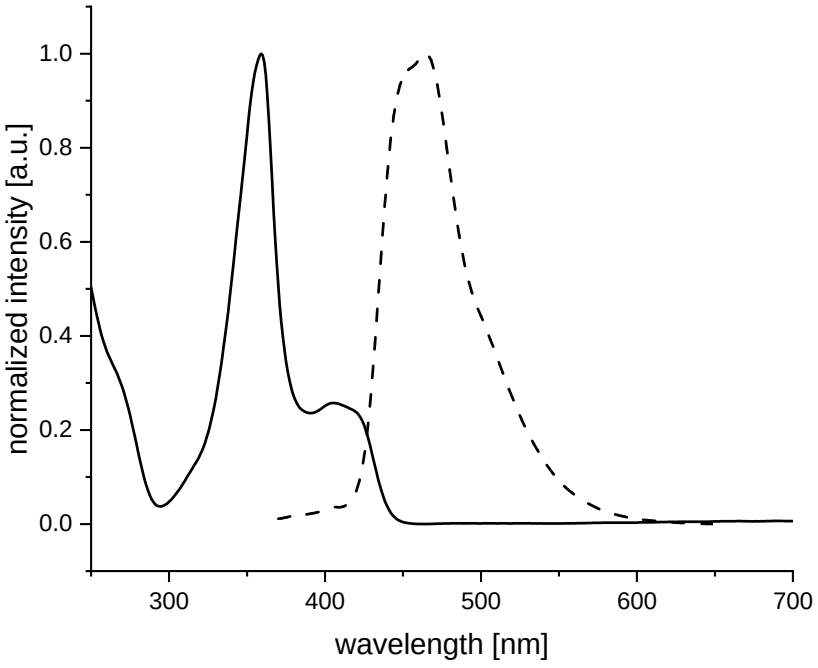
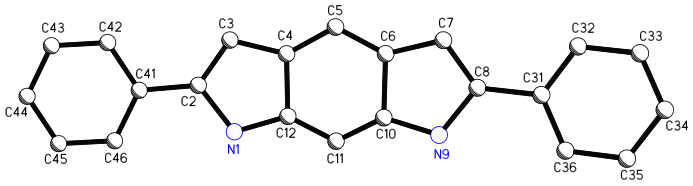


Figure S118. Absorption (solid line) and emission (dashed line) spectra of ***p*DPPPd** in DCM.

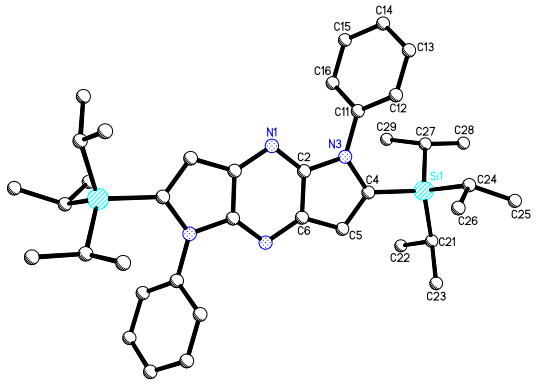
4 Crystallographic Data

Table S1. Crystal structure, crystal data and structure refinement of ***m*DPBa** (CCDC 2155478).



Empirical formula	$C_{22}H_{16}N_2$	
Formula weight	308.37	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$Pca2_1$	
Z	4	
Unit cell dimensions	a = 35.844(10) Å	α = 90 deg.
	b = 5.559(13) Å	β = 90 deg.
	c = 7.59(6) Å	γ = 90 deg.
Volume	1512(13) $Å^3$	
Density (calculated)	1.36 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	plate	
Crystal size	0.200 x 0.180 x 0.040 mm^3	
Crystal color	colorless	
Theta range for data collection	2.3 to 19.9 deg.	
Index ranges	$-33 \le h \le 17$, $-5 \le k \le 5$, $-7 \le l \le 7$	
Reflections collected	2372	
Independent reflections	1258 (R(int) = 0.1055)	
Observed reflections	852 (I I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.56	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1258 / 45 / 73	
Goodness-of-fit on F^2	1.69	
Final R indices (I>2sigma(I))	R1 = 0.175, wR2 = 0.366	
Absolute structure parameter	-10.0(10)	
Largest diff. peak and hole	0.50 and -0.55 $eÅ^{-3}$	

Table S2. Crystal structure, crystal data and structure refinement of ***p*DPPb** (CCDC 2155479).



Empirical formula	$C_{38}H_{54}N_4Si_2$
Formula weight	623.03
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Z	1
Unit cell dimensions	a = 7.9119(6) Å α = 104.4015(14) deg. b = 9.0727(7) Å β = 93.1417(15) deg. c = 15.0115(11) Å γ = 114.8680(13) deg.
Volume	931.22(12) $Å^3$
Density (calculated)	1.11 g/cm^3
Absorption coefficient	0.13 mm^{-1}
Crystal shape	plank
Crystal size	0.196 x 0.093 x 0.047 mm^3
Crystal color	colorless
Theta range for data collection	1.4 to 26.8 deg.
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-18 \le l \le 18$
Reflections collected	16718
Independent reflections	3960 (R(int) = 0.0522)
Observed reflections	3029 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.91
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3960 / 134 / 216
Goodness-of-fit on F^2	1.02
Final R indices (I>2sigma(I))	R1 = 0.047, wR2 = 0.097
Largest diff. peak and hole	0.25 and -0.23 $eÅ^{-3}$

5 References

(1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.

(2) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. Relative and absolute determination of fluorescence quantum yields of transparent samples. *Nat Protoc* **2013**, *8* (8), 1535–1550.

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