Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

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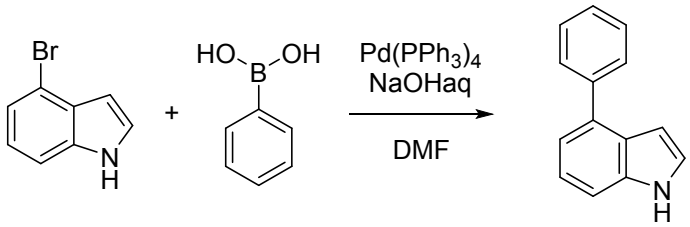
General Considerations

Unless otherwise indicated all reagents were purchased from commercial sources and were used without further purification. $[LutBCl_2][AlCl_4]$ was synthesized by a previously reported method.[1] All appropriate manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 / H_2O levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents and amines were distilled from NaK, CaH_2, or K and degassed prior to use. ^1H NMR and ^{13}C NMR spectra were recorded using 400 and 500 MHz spectrometers with chemical shift values being reported in ppm relative to residual protio solvent (e.g. in $CHCl_3$ in $CDCl_3$ δH = 7.27 or δC = 77.2) as internal standards. All coupling constants (J) are reported in Hertz (Hz). Other NMR spectra were recorded with a 400 MHz Bruker AV-400 spectrometer (^{11}B; 162 MHz, ^{27}Al 104.3 MHz). ^{11}B NMR spectra were referenced to external BF_3:Et_2O, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(D_2O)_6^{3+}$). Unless otherwise stated all NMR spectra are recorded at 293 K. Carbon atoms directly bonded to boron are not always observed in the $^{13}C\{^1H\}$ NMR spectra due to quadrupolar relaxation leading to signal broadening. All UV-Vis absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and the solution emission spectra were recorded on a Varian Cary Eclipse fluorometer at room temperature in spectroscopic grade solvents exciting at the relative absorbance maxima. Absolute quantum yield values were recorded on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer and determined using a calibrated Edinburgh Instruments integrating sphere. Cyclic voltammetry was performed using a CH-Instrument 1110C Electrochemical/Analyzer potentiostat under a nitrogen flow. Measurements were made using a 0.001 M analyte solution with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka ≥99.0%) as the supporting electrolyte in THF that had been degassed and dried prior to use. A glassy carbon electrode served as the working electrode and a platinum wire as the counter electrode. An $Ag/AgNO_3$ non-aqueous reference electrode was used. All scans were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) redox couple, which in this work is taken to be 5.39 eV below vacuum. The half-wave potential of the ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2, Fc,Fc+}$) was estimated from $E_{1/2, Fc,Fc+} = (E_{ap} + E_{cp})/2$, where E_{ap} and E_{cp} are the anodic and cathodic peak potentials, respectively.

[1] A. Del Grosso, M. D. Helm, S. A. Solomon, D. Caras-Quintero, M. J. Ingleson, *Chem. Commun.,* 2011, **47**, 12459

Synthesis of Indole Precursors

Synthesis of 4-phenyl-1*H*-indole



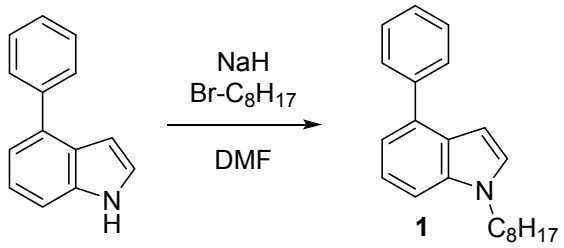
To a Schlenk, the phenylboronic acid (1.46 g, 12 mmol) and the 4-bromoindole (1 mL, 7.97 mmol) were introduced and the reagents were degassed. A degassed mixture of DMF (40 mL) and aqueous NaOH (0.64 g in 6.5 mL of H_2O) was transferred via cannula to the reagents. This was followed by the addition of $Pd(PPh_3)_4$ (370 mg, 0.32 mmol). The reaction mixture was heated for 18 h at 100°C. The reaction was cooled to room temperature and the DMF was removed under reduced pressure. The crude was washed and extracted three times with H_2O/CH_2Cl_2. The organic layers were collected and concentrated. The mixture was purified by silica gel column chromatography with pentane then pentane/CH_2Cl_2 (80/20) as eluent. A white solid of 4-phenyl-1*H*-indole was obtained in a yield of 46% (0.714 g, 3.69 mmol).

^{1}H (400 MHz, CD_2Cl_2): δ 8.16 (broad, NH), 7.87 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 2H), 7.51 (tt, *J* = 7.3 Hz, *J* = 1.3 Hz, 1H), 7.38 (m, 3H), 7.24 (dd, *J* = 2.5 Hz, *J* = 3.3 Hz, 1H), 6.85 (m, 1H);

All NMR spectra are consistent with that previously reported.[2]

[2] J. F. P. Andrews, P. M. Jackson, C. J. Moody, *Tetrahedron*, 1993, 49, 7353-7312

Synthesis of **1**: 1-octyl-4-phenyl-1*H*-indole



4-phenyl-1*H*-indole (0.741 g, 3.83 mmol) was placed in a round-bottom flask to be solubilised in DMF (6 mL). The sodium hydride (60% dispersed in oil) (230 mg, 5.75 mmol) was washed in pentane. The oil-free sodium hydride was added portionwise into the solution of 4-phenyl-1H-indole (caution: exothermic reaction). The mixture was stirred for 15 min at ambient temperature. The 1-bromooctane was then added. The reaction was followed by TLC and was stopped after 1 h 30 of stirring. The mixture was washed with water (10 mL) then extracted with CH_2Cl_2 (3x20 mL). The organic layers were concentrated and the crude was purified by silica gel column chromatography with PET 100% as eluent. A colourless oil of 1-octyl-4-phenyl-1*H*-indole was obtained (0.936 g, 3.06 mmol, 80%). **Caution: use DMF and NaH in small scale and at room temperature!**

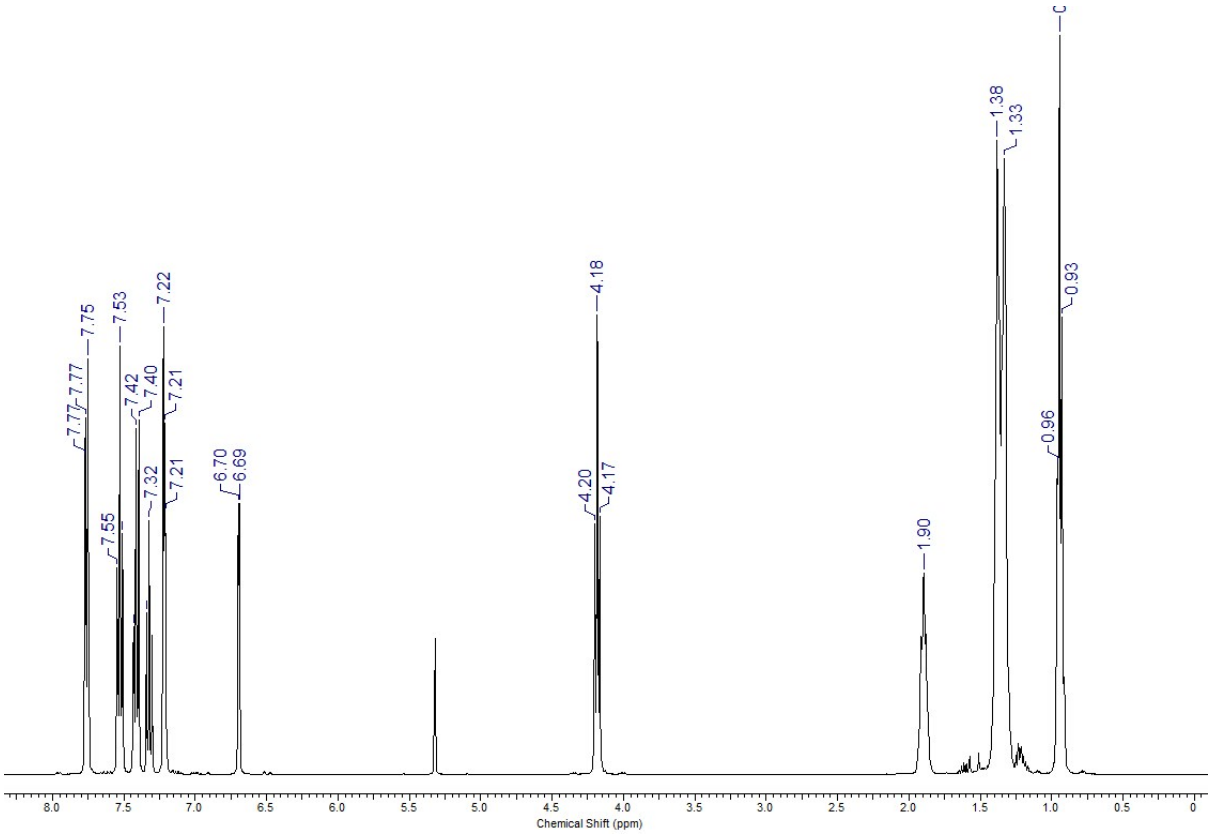
1 ^{1}H (400 MHz, CD_2Cl_2): δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.42 (m, 2H), 7.32, (t, *J* = 7.3 Hz, 1H), 7.22 (m, 2H), 6.70 (d, *J* = 3.0 Hz, 1H), 4.18 (t, *J* = 7.3 Hz, 2H), 1.90 (quin, *J* = 7.0 Hz, 2H), 1.38 (m, 10H), 0.94 (t, J = 8 Hz, 3H);

1 ^{13}C{^{1}H} (101 MHz, CD_2Cl_2): δ 142.0, 137.1, 134.9, 129.3, 129.1, 128.9, 127.5, 127.3, 122.2, 119.6, 109.3, 100.6, 47.2, 32.4, 30.9, 29.9, 29.8, 27.6, 23.3, 14.5;

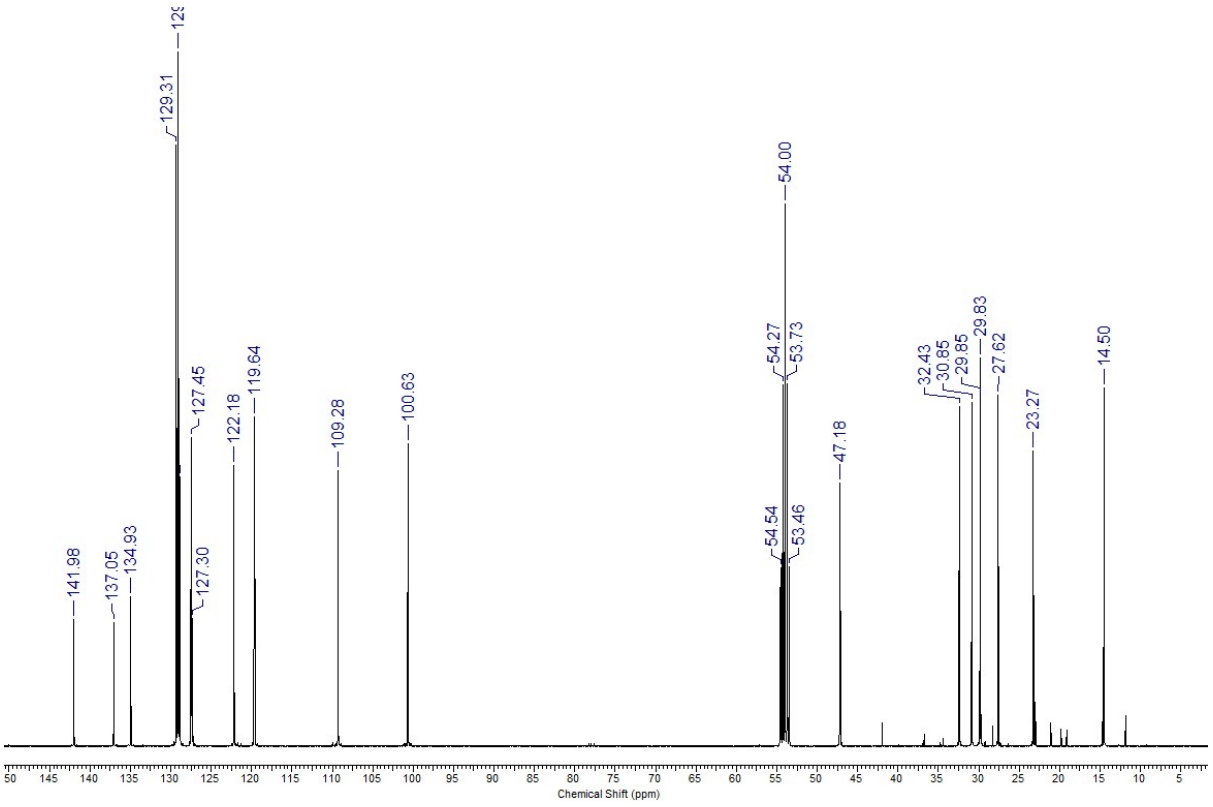
MS (APCI): calc. for $[M+H]^+$306.22, found 306

Accurate mass: calc. for $[M+H]^+$ $C_{22}H_{28}N$ 306.2216, found 306.2209

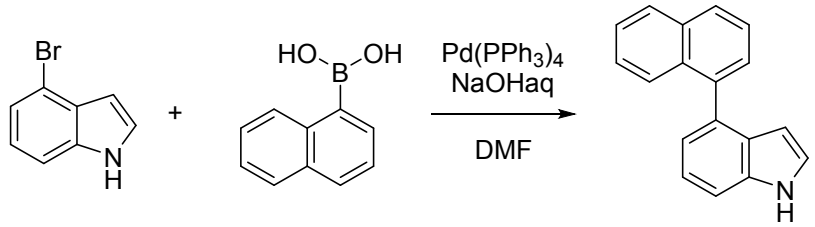
^{1}H NMR spectrum **1** (CD_2Cl_2)



^{13}C{^{1}H} NMR spectrum for **1** (CD_2Cl_2)



Synthesis of 4-(naphthalene-1-yl)-1*H* indole



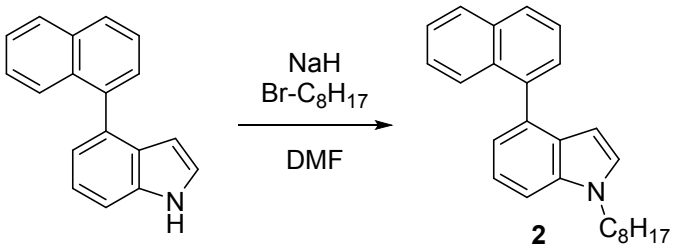
To a Schlenk, the 1-naphthylboronic acid (2.06 g, 12 mmol) and the 4-bromo-1H-indole (1 mL, 7.97 mmol) were introduced and the reagents were degassed. A degassed mixture of DMF (40 mL) and aqueous NaOH (0.64 g in 6.5 mL of H_2O) was transferred via cannula to the reagents. $Pd(PPh_3)_4$ (370 mg, 0.32 mmol) was then added. The reaction mixture was heated for 18 h at 100°C. The reaction was cooled to room temperature and the DMF was removed under reduced pressure. The crude was washed with H_2O (40 mL) and then extracted three times with CH_2Cl_2 (3x40 mL). The organic layers were collected and concentrated. The mixture was purified by silica gel column chromatography with pentane then pentane/CH_2Cl_2 (90/10) as eluent. A white powder of 4-(naphthalene-1-yl)-1*H* indole was obtained (1.004 g, 4.12 mmol, 52%).

^{1}H (400 MHz, CD_2Cl_2): δ 8.43 (broad, NH), 7.93 (m, 2H), 7.75 (dd, *J* = 8.6 Hz, *J* = 1.0 Hz, 1H), 7.58 (q, *J* = 7.1 Hz, 1H), 7.56 (d, *J* = 0.8 Hz, 1H), 7.50 (m, 2H), 7.34 (m, 2H), 7.21 (dd, *J* = 3.0 Hz, 1H), 7.16 (dd, *J* = 7.q Hz, *J* = 1.0 Hz, 1H), 6.14 (m, 1H);

All NMR spectra are consistent with that previously reported.[3]

[3] H. Muratake, M. Natsume, Heterocycles, 31, 1990, 683-690

Synthesis of **2**: 4-(naphthalene-1-yl)-1-octyl-1*H*-indole



2

The 4-(1-naphthlen-1-yl)-1*H*-indole (0.991 g, 4.07 mmol) was placed in a round-bottom flask and solubilised in DMF (6 mL). The sodium hydride (60% dispersed in oil) (245 mg, 6.13 mmol) was washed in pentane. The oil-free sodium hydride was added portionwise into the solution of 4-(1-naphthlen-1-yl)-1*H*-indole (caution: exothermic reaction). The mixture was stirred for 30 min at ambient temperature. The 1-bromooctane (0.98 mL, 5.7 mmol) was then added. The reaction was followed by TLC and was stopped after 1 h 30 of stirring. The mixture was washed with water (10 mL) then extracted with CH_2Cl_2 (3x20 mL). The organic layers were concentrated and the crude was purified by silica gel column chromatography with PET 100% as eluent. A colourless oil of 4-(naphthalene-1-yl)-1-octyl-1*H*-indole was obtained (1.356 g, 3.81 mmol, 94%). **Caution: use DMF and NaH in small scale and at room temperature!**

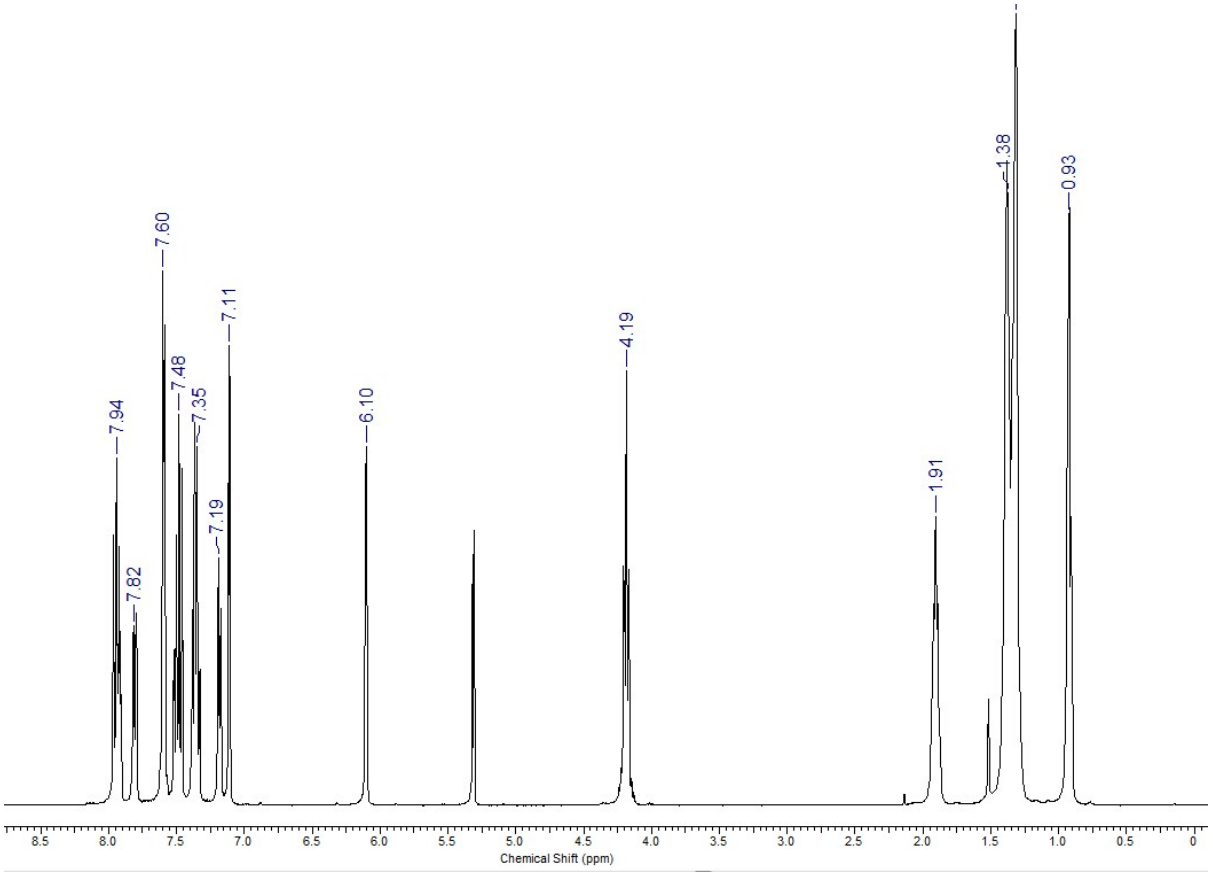
2 ^{1}H (400 MHz, CD_2Cl_2): δ 7.95 (dd, *J* = 8.3 Hz, *J* = 7.57 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 2H), 7.49, (m, 2H), 7.37 (q, *J* = 7.1 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 6.11 (m, 1H), 4.18 (dt, *J* = 7.1 Hz, *J* = 2.0 Hz, 2H), 1.92 (quin, *J* = 6.8 Hz, 2H), 1.38 (m, 10H), 0.93 (m, 3H);

2 ^{13}C (101 MHz, CD_2Cl_2): δ 139.8, 136.7, 134.4, 133.7, 132.6, 129.2, 128.7, 128.6, 128.0, 127.9, 127.1, 126.2, 126.1, 126.0, 121.8, 121.4, 109.3, 101.1, 47.2, 32.4, 30.9, 29.9, 29.8, 27.6, 23.2, 14.5;

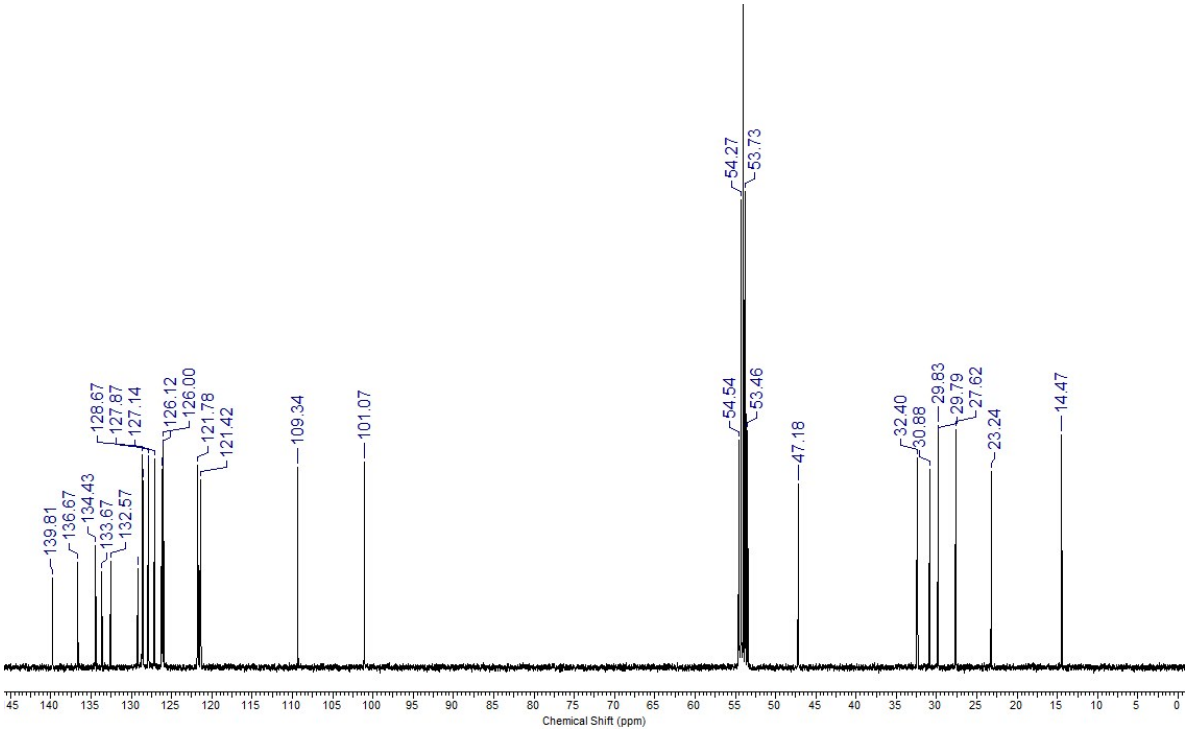
MS (APCI): calc. for $[M+H]^+$ $C_{26}H_{30}N$ 356.24, found 356.3

Accurate mass: calc. for $[M+H]^+$ $C_{26}H_{30}N$ 356.2373, found 356.2374

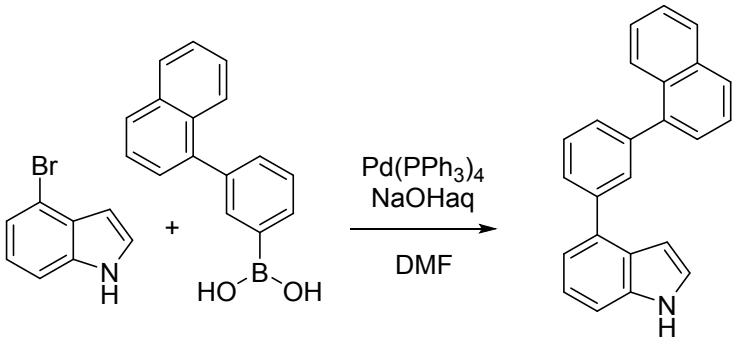
^{1}H NMR spectrum for **2** (CD_2Cl_2)



^{13}C{^{1}H} NMR spectrum for **2** (CD_2Cl_2)



Synthesis of 4-(3-(naphthalen-1-yl)phenyl)-1*H*-indole

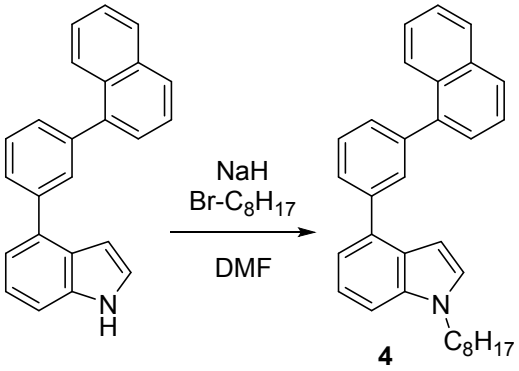


To a Schlenk, 3-(1-naphthyl)benzeneboronic acid (500 mg, 2.02 mmol) and 4-bromo-1H-indole (0.17 mL, 1.43 mmol) were introduced and the reagents were degassed. A degassed mixture of DMF (7 mL) and aqueous NaOH (0.11 g in 1 mL of H_2O) was transferred via cannula to the reagents. This was followed by the addition of $Pd(PPh_3)_4$ (62 mg, 0.054 mmol). The reaction mixture was heated for 18 h at 100°C. The reaction was cooled to room temperature and the DMF was removed under reduced pressure. The crude was washed and extracted three times with H_2O/CH_2Cl_2. The organic layers were collected, dried over $MgSO_4$ and concentrated. The mixture was purified by silica gel column chromatography with PET then PET/CH_2Cl_2 (90/10→60/40) as eluent. A white solid was obtained in a yield of 37% (4-(3-(naphthalen-1-yl)phenyl)-1*H*-indole, 0.167 g, 0.52 mmol).

^{1}H (400 MHz, CD_2Cl_2): δ 8.41 (broad, NH), 8.04 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.64, (t, *J* = 7.8 Hz, 1H), 7.53 (m, 6H), 7.28 (m, 3H), 6.80 (m, 1H);

^{13}C{^{1}H} (101 MHz, CD_2Cl_2): δ 141.8, 141.5, 140.8, 136.9, 134.5, 134.4, 132.2, 130.9, 129.2, 129.1, 128.8, 128.2, 127.6, 126.7, 126.6, 126.5, 126.3, 126.0, 125.3, 122.8, 120.3, 111.0, 102.3;

Synthesis of **4**: 4-(3-(naphthalen-1-yl)phenyl)-1-octyl-1*H*-indole



4

4-(3-(naphthalen-1-yl)phenyl)-1*H*-indole (0.167 g, 0.52 mmol) was placed in a round-bottom flask and solubilised in DMF (3 mL). Sodium hydride (60% dispersed in oil) (32 mg, 0.79 mmol) was washed in pentane and added portionwise into the solution of 4-(3-(naphthyl)phenyl-1H-indole (caution: exothermic reaction). The mixture was stirred for 30 min at ambient temperature and 1-bromooctane (0.13 mL, 0.73 mmol) was then added. The reaction was followed by TLC and was stopped after 1 h 30 of stirring. The mixture was washed with water (5 mL) then extracted with CH_2Cl_2 (3x10 mL). The organic layers were dried over $MgSO_4$, then concentrated and the crude was purified by silica gel column chromatography with PET then PET/CH_2Cl_2 (99/1→95/5) as eluent. A colourless oil was obtained (4-(3-(naphthalen-1-yl)phenyl)-1-octyl-1*H*-indole, 0.194 g, 0.45 mmol, 86%). **Caution: use DMF and NaH in small scale and at room temperature!**

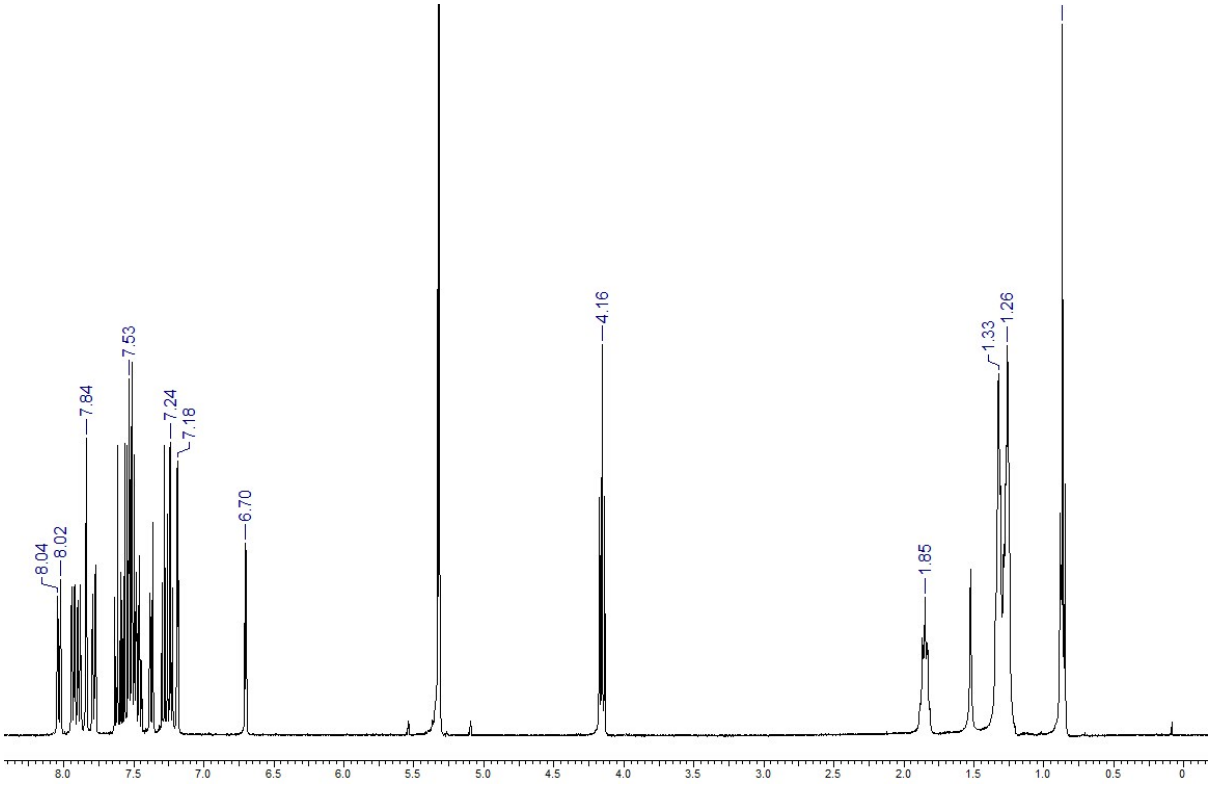
4 ^{1}H (400 MHz, CD_2Cl_2): δ 8.02 (dd, *J* = 8.3 Hz, *J* = 0.8 Hz, 1H), 7.92 (dd, *J* = 8.1 Hz, *J* = 0.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 1.8 Hz, 1H), 7.79 (dt, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (m, 5H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.24 (m, 3H), 6.70 (dd, *J* = 3.3 Hz, *J* = 0.8 Hz, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 1.85 (quint, *J* = 7.1 Hz, 2H), 1.29 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H);

4 ^{13}C{^{1}H} (101 MHz, CD_2Cl_2): δ 141.9, 141.5, 140.9, 137.0, 134.6, 134.4, 132.2, 130.9, 129.1, 129.0, 128.9, 128.8, 128.2, 128.1, 127.6, 127.2, 126.6, 126.5, 126.3, 126.0, 122.1, 119.7, 109.4, 100.6, 47.2, 32.3, 30.8, 29.8, 29.7, 27.5, 23.2, 14.4;

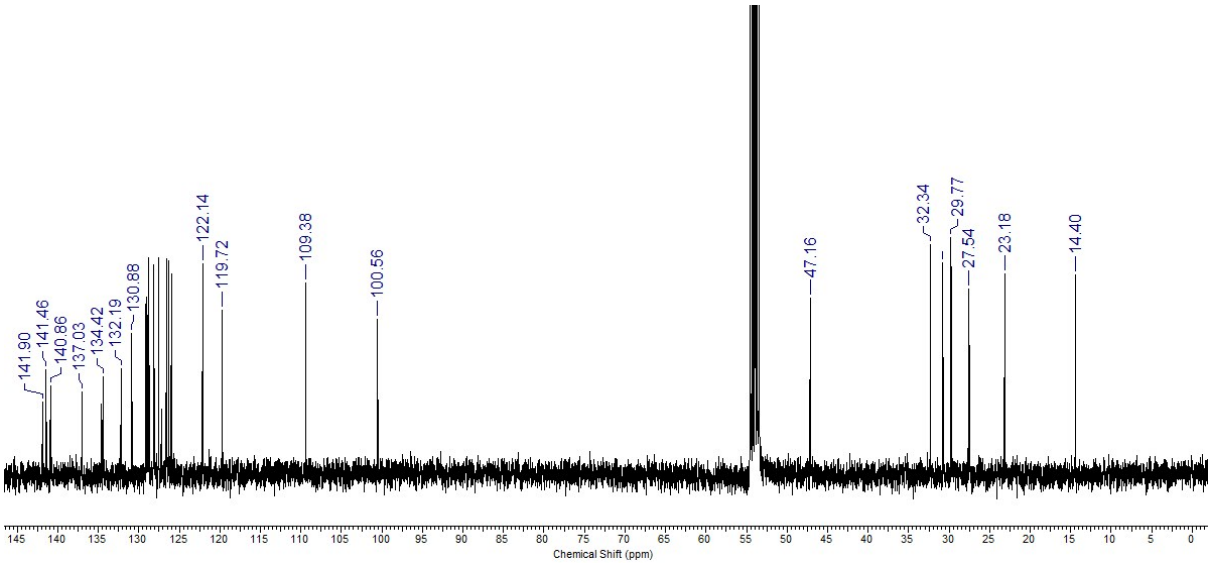
MS (APCI): calc. for $[M+H]^+$ $C_{32}H_{34}N$ 432.27, found 432.3

Accurate mass: calc. for $[M+H]^+$ $C_{32}H_{34}N$ 432.2686, found 432.2683

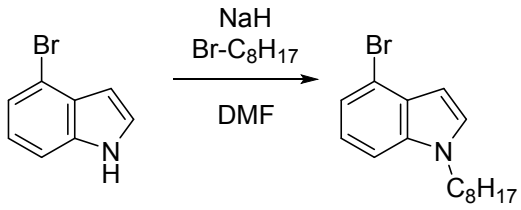
^{1}H NMR spectrum for **4** (CD_2Cl_2)



^{13}C{^{1}H} NMR spectrum for **4** in CD_2Cl_2.



Synthesis of 4-Br-1-octyl-Indole



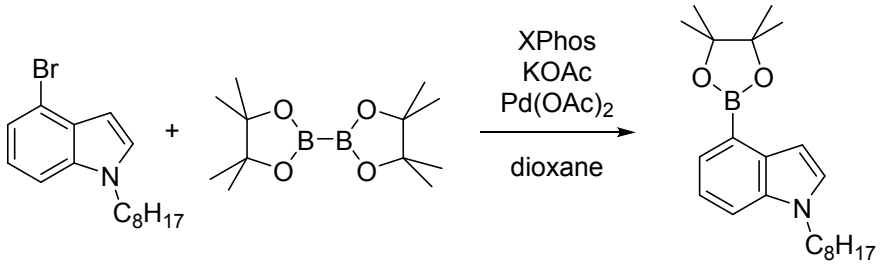
4-bromo-1*H*-indole (0.500 g, 2.82 mmol) was placed in a round-bottom flask to be solubilised in DMF (3 mL). The sodium hydride (60% dispersed in oil) (135 mg, 3.38 mmol) was washed in pentane. The oil-free sodium hydride was added portion wise into the solution of 4-bromo-1H-indole (caution: exothermic reaction). The mixture was stirred for 15 min at ambient temperature. The 1-bromooctane was then added (0.653 g, 3.38 mmol). The reaction was followed by TLC and was stopped after 1 h 30 of stirring. The mixture was washed with water (10 mL) then extracted with CH_2Cl_2 (3x10 mL). The organic layers were concentrated and the crude was purified by silica gel column chromatography with PET 100% as eluent. A colourless oil of 4-bromo-1-octyl-indole was obtained (0.619 g, 2.01 mmol, 71%). **Caution: use DMF and NaH in small scale and at room temperature!**

^{1}H (400 MHz, CD_2Cl_2): δ 7.31 – 7.18 (m 4H) 6.51 (m, 1H), 4.11 (dt, *J* = 7.3, 1 Hz Hz, 2H), 1.81 (quin, *J* = 7.0 Hz, 2H), 1.27 (m, 10H), 0.87 (t, J = 8 Hz, 3H);

^{13}C{^{1}H} (101 MHz, CD_2Cl_2): δ 137.0, 129.7, 129.2, 122.7, 122.5, 115.1, 109.4, 101.5, 47.4, 32.4, 30.8, 29.8, 29.6, 27.5, 23.2, 14.4;

MS (APCI): calc. for $[M+H]^+$308.1, found 308

Synthesis of 1-octyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole



To an ampoule, bis(pinacolato)diboron (3.13 g, 12.3 mmol), 4-Br-*N*-octyl-indole (1.9 g, 6.16 mmol), XPhos (587 mg, 1.23 mmol), potassium acetate (1.81 g, 18.5 mmol) and palladium acetate (138 mg, 0.62 mmol) were introduced. The reagents were degassed and suspended in degassed dioxane (18 mL). The reaction mixture was heated for 18 h at 90°C. The reaction was cooled to room temperature and the dioxane was removed under reduced pressure. The crude was washed with H_2O (40 mL) and then extracted three times with CH_2Cl_2 (3x40 mL). The organic layers were collected and concentrated. The mixture was purified by silica gel column chromatography with PET then PET/CH_2Cl_2 (90/10 to 50/50) as eluent. A colourless oil was obtained (1-octyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole, 1.50 g, 4.22 mmol, 69%).

^{1}H (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 7.1 Hz, *J* = 1.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 8.3 Hz, *J* = 7.0 Hz, 1H), 7.41, (d, *J* = 3.3 Hz, 1H), 7.25 (dd, *J* = 3.3 Hz, *J* = 1.0 Hz, 1H), 4.37 (t, *J* = 7.1 Hz, 2H), 2.06 (quint, *J* = 7.1 Hz, 2H), 1.65 (s, 12H), 1.55 (m, 10H), 1.13 (t, *J* = 7.1 Hz, 3H);

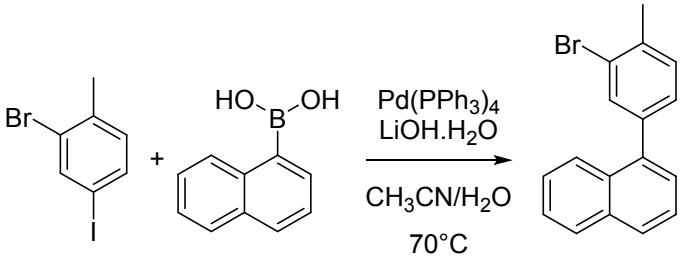
^{13}C{^{1}H} (101 MHz, $CDCl_3$): δ 135.2, 133.2, 128.3, 127.2, 120.6, 112.2, 102.6, 83.2, 46.3, 31.7, 30.3, 29.2, 29.1, 26.9, 24.9, 22.6, 14.0;

^{11}B (128 MHz, $CDCl_3$): δ 31.4 (br);

MS (APCI): calc. for $[M+H]^+$ $C_{22}H_{35}O_2NB$ 356.28, found 356.3

Accurate mass: calc. for $[M+H]^+$ $C_{22}H_{35}O_2NB$ 356.2755, found 356.2759

Synthesis of 1-(3-bromo-4-methylphenyl)naphthalene



In a Schlenk, the solvent CH_3CN/H_2O (110/10 mL) was degassed via four successive freeze-pump-thaw cyclings. In another Schlenk, 2-bromo-5-iodo-1-methylenebenzene (0.3 mL, 2.08 mmol), 1-naphthylboronic acid (0.358 g, 2.08 mmol), lithium hydroxide (0.349 g, 8.32 mmol) and $Pd(PPh_3)_4$ (120 mg, 1.04 10^{-4} mol) were degassed. The solvent mixture was transferred via cannula to the Schlenk containing the reagents. The reaction mixture was stirred at 70°C for 18 h during which it turned into a yellow solution with a white suspension. The desired compound was extracted with pentane (100 mL). 1-(3-bromo-4-methylphenyl)naphthalene was purified by flash silica gel column chromatography with pentane as eluent (0.546 g, 88%).

^{1}H (400 MHz, $CDCl_3$): δ 7.88-7.93 (m, 3H), 7.72 (s, 1H), 7.41-7.56 (m, 4H), 7.37 (s, 2H), 2.42 (s, 3H);

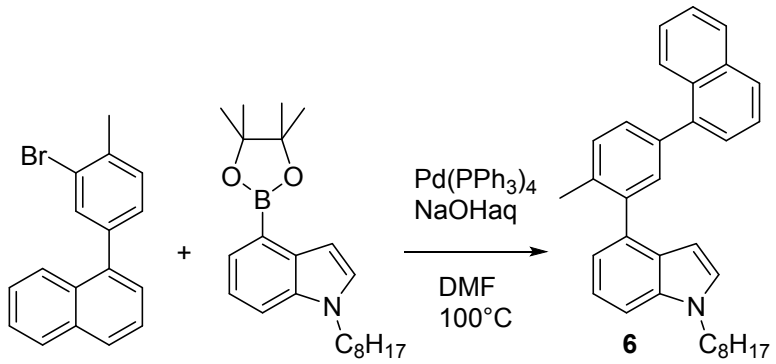
^{13}C (101 MHz, $CDCl_3$): δ 140.0, 138.5, 136.7, 133.7, 133.5, 131.4, 130.5, 128.9, 128.3, 127.9, 126.9, 126.2, 125.8, 125.6, 125.3, 124.7, 22.7;

MS (ESI): calc. for $[M]^+$ $C_{17}H_{13}Br$ 296.02, found 296.0

The NMR spectra are consistent with that previously reported.[4]

[4] O. Lafon, P. Lesot, C.-A. Fan, H. B. Kagan, Chem. Eur. J. 2007, 13, 3772 – 3786

Synthesis of **6**: 4-(2-methyl-5-(naphthalen-1-yl)phenyl)-1-octyl-1*H*-indole



In a Schlenk, 1-(3-bromo-4-methylphenyl)naphthalene (0.546 g, 1.84 mmol), N-octylindole-4-boronic ester (0.653 g, 1.84 mmol), $Pd(PPh_3)_4$ (0.213 g, 1.84 10^{-4} mol), NaOHaq (0.15g in 1.5 mL of H_2O) and DMF (10 mL) were degassed. The reaction mixture was heated for 2 d at 100°C. The reaction was cooled to room temperature and the DMF was removed under reduced pressure. The crude was washed and extracted three times with H_2O/CH_2Cl_2. The organic layers were collected, dried over $MgSO_4$ and concentrated. The mixture was purified by silica gel column chromatography with PET then PET/CH_2Cl_2 (90/10) as eluent. Compound **6** was obtained as a colourless oil in a yield of 46% (0.380 g, 0.85 mmol).

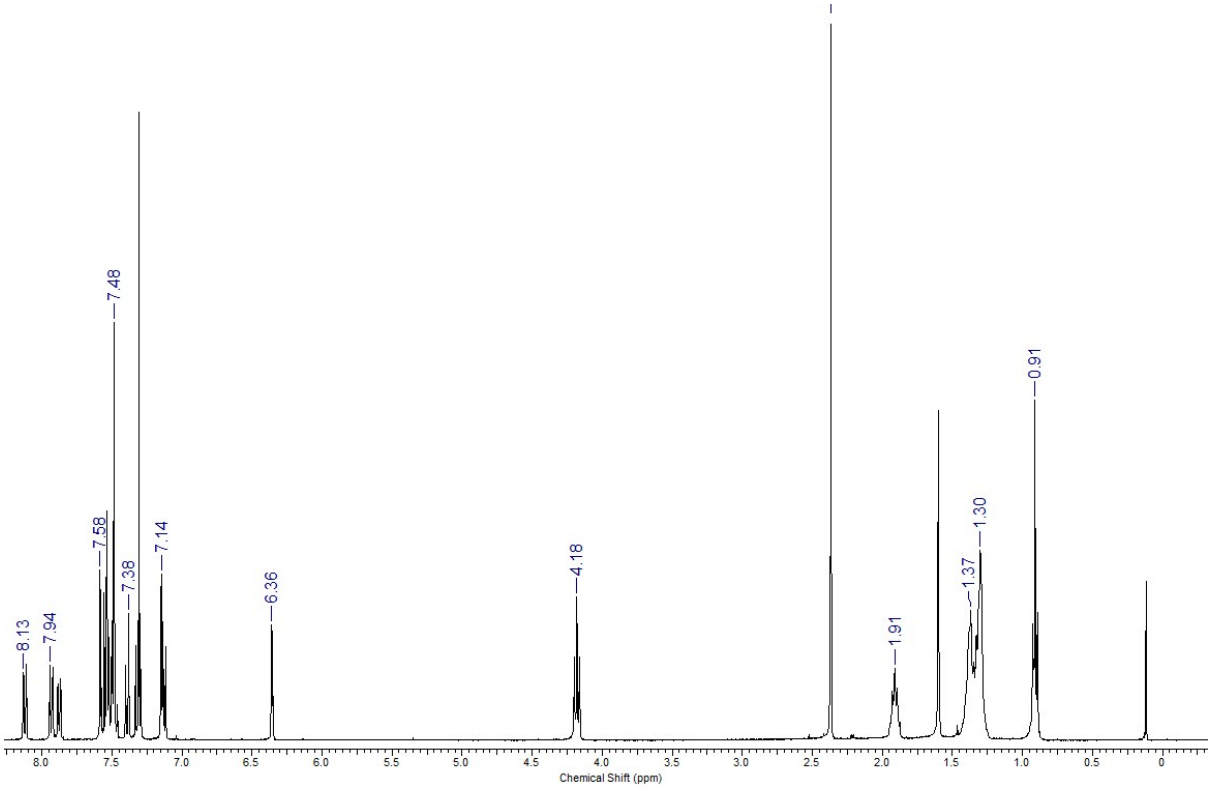
6 ^{1}H (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.82 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.87 (m, 1H), 7.61 (s, 1H), 7.58-7.47 (m, 6H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.33 (m, 1H), 7.15 (m, 2H), 6.38 (d, *J* = 2.8 Hz, 1H), 4.18 (t, *J* = 6.81 Hz, 2H), 2.39 (s, 3H), 1.91 (quint, *J* = 6.3 Hz, 2H), 1.31 (m, 10H), 0.93 (t, *J* = 6.8 Hz, 3H);

6 ^{13}C{^{1}H} (101 MHz, $CDCl_3$): δ 140.8, 140.2, 137.8, 135.9, 135.2, 134.4, 133.8, 131.8, 130.0, 128.7, 128.2, 127.8, 127.3, 127.0, 126.2, 125.9, 125.4, 121.1, 120.1, 108.3, 100.7, 46.6, 31.8, 30.2, 29.2, 29.2, 27.0, 22.6, 20.1, 14.1;

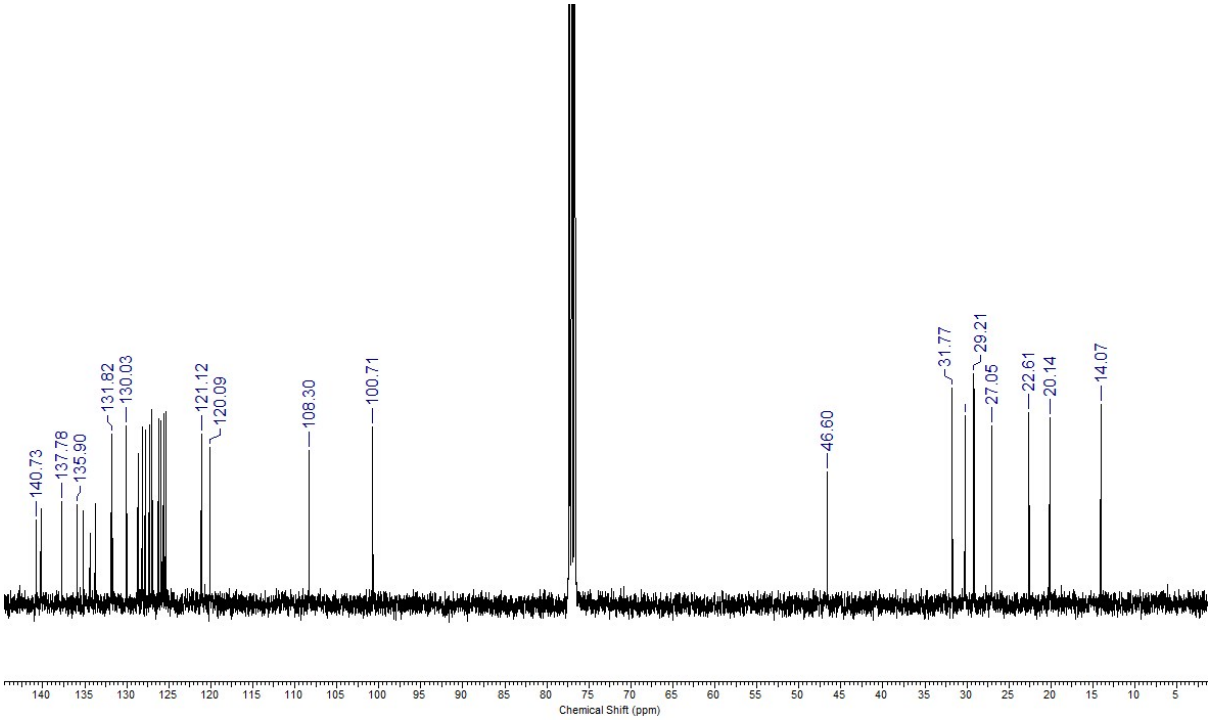
MS (APCI): calc. for $[M+H]^+$ $C_{33}H_{36}N$ 446.28, found 446.27

Accurate mass: calc. for $[M+H]^+$ $C_{33}H_{36}N$ 446.2842, found 446.2839

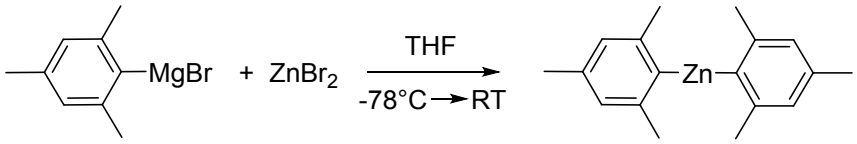
1H NMR spectrum for **6** ($CDCl_3$)



$^{13}C\{^1H\}$ NMR spectrum for **6** ($CDCl_3$)



Synthesis of bis(2,4,6-trimethylphenyl)-zinc



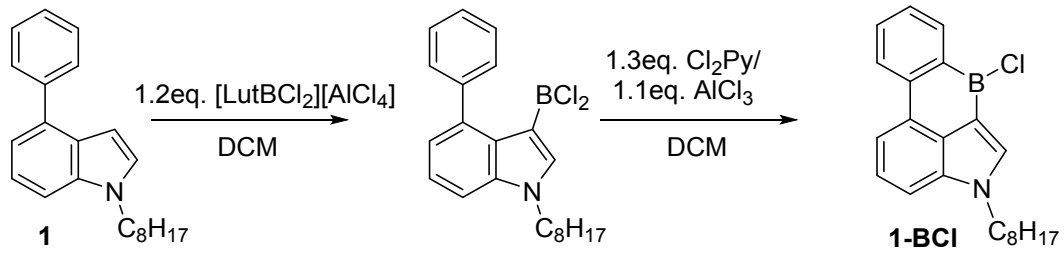
Dry $ZnBr_2$ (1 g, 4.44 mmol) was solubilised in dry THF (8 mL) in a Schlenk. A solution of MesMgBr (8 mL, 1 M in THF, 8.88 mmol) was added dropwise to the $ZnBr_2$ solution at -78°C. The mixture was warmed slowly to room temperature and stirred overnight. A slight excess of 1,4-dioxane (0.8 mL, 9.38 mmol) was introduced into the mixture and stirred for 18 h to allow the precipitation of magnesium salts. The mixture was filtered and rinsed with THF (6 mL). The solution was transferred via cannula into another Schlenk. The light yellow solution was concentrated under reduced pressure. Dimesitylzinc was solubilised in toluene and the residual magnesium precipitated. The solution was transferred via cannula into another Schlenk. Dimesitylzinc was recrystallized by evaporation of the toluene until precipitation and by heating until dissolution of the precipitate. The solution was cooled at room temperature. White needles were obtained. The same process (filtration, evaporation, precipitation, heat, cool and crystallisation) was repeated several times. The ether free crystals (bis(2,4-trimethylphenyl)-zinc, 344 mg, 26%) were dried under vacuum.

The synthesis was based on that previously reported.[5]

[5] M. Irwin, T. Krämer, J. E. McGrady, J. M. Goicoechea, *Inorg. Chem.*, **2011**, *50*, 5006–5014

Synthesis of Fused Indoles

Synthesis of **1-BCl**



A J. Young's NMR tube was charged with **1** (0.007 mL, 2.05 10^{-5} mol). The compound was solubilised in dry CH_2Cl_2 (0.7 mL) and $[LutBCl_2][AlCl_4]$ (9 mg, 2.52 10^{-5} mol) was added. The solution was stirred for 5 min at room temperature. After a near quantitative formation of the intermediate assigned as indoleBCl_2 (by NMR spectroscopy see Fig S1–S3), 2,6-dichloropyridine (4 mg, 2.70 10^{-5} mol) and $AlCl_3$ (3 mg, 2.25 10^{-5} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain a new compound assigned as **1-BCl**.

1-BCl ^{1}H (400 MHz, in CH_2Cl_2- capillary d_6-DMSO): δ 8.46 (d, *J* = 7.8 Hz, 2H), 8.18 (m, 1H), 8.12 (s, 1H), 7.70 (m, 2H), 7.51 (m, 2H), 4.19, (t, *J* = 6.8 Hz, 2H), 1.98 (t, *J* = 7.1 Hz, 2H), 1.29 (m, 10H), 0.85 (t, *J* = 6.3 Hz, 3H)

1-BCl ^{11}B (128 MHz, in CH_2Cl_2- capillary d_6-DMSO): δ very broad ~47.1;

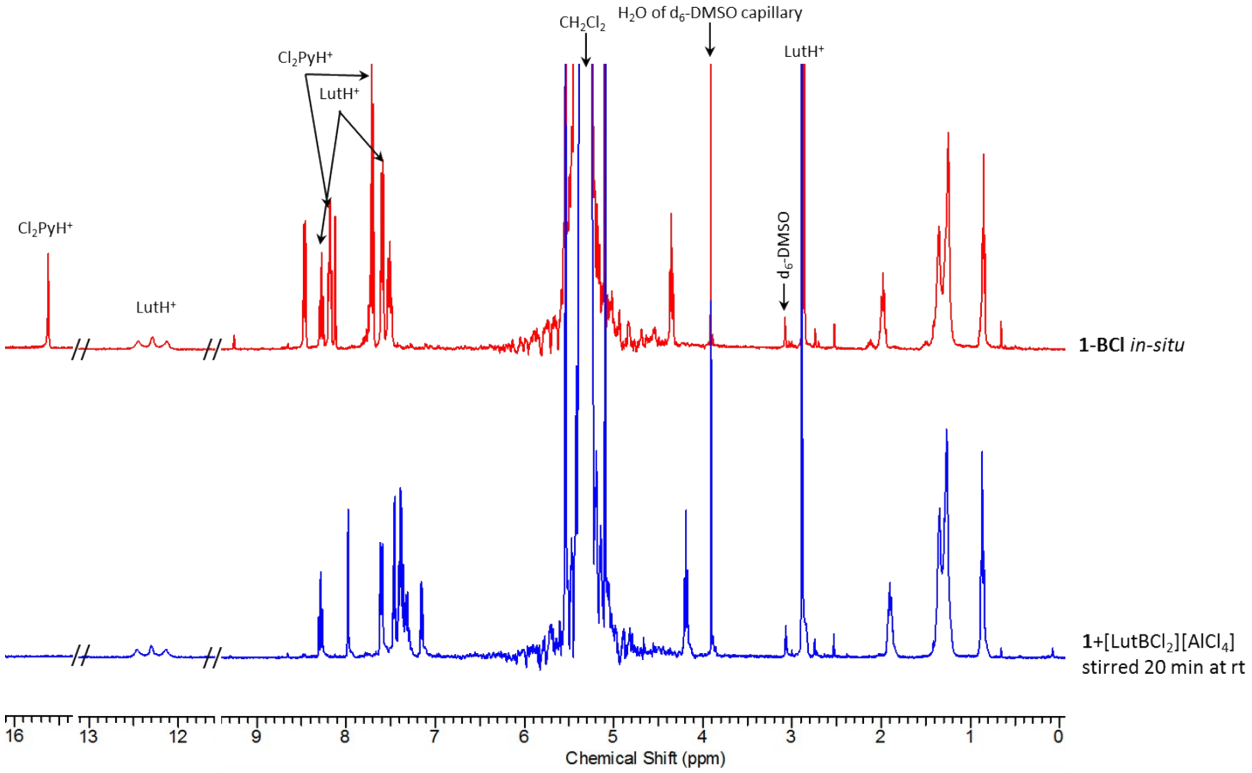


Figure S1: ^{1}H NMR spectra for the two step synthesis of **1-BCl** from **1** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added.

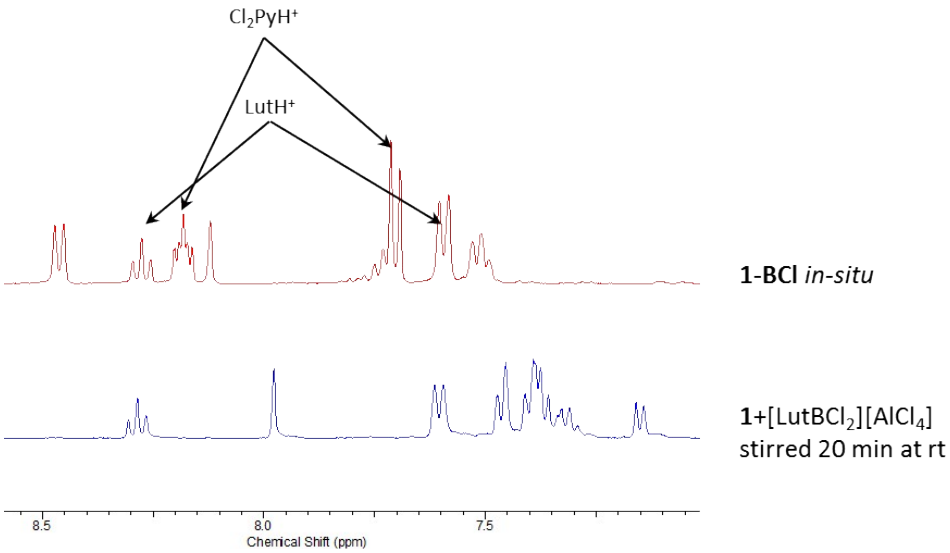


Figure S2: ^{1}H NMR spectra of the aromatic region for the two step synthesis of **1-BCl** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. Resonances for LutH and Cl_2PyH are overlapped with resonances for **1-BCl**

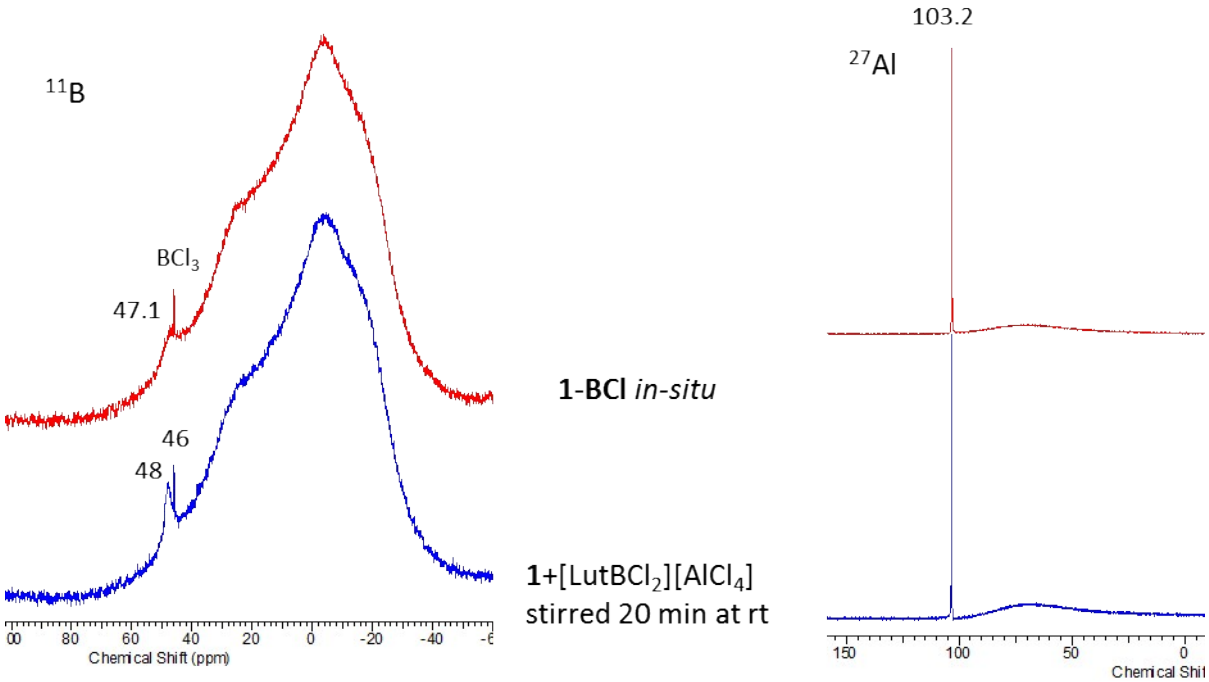
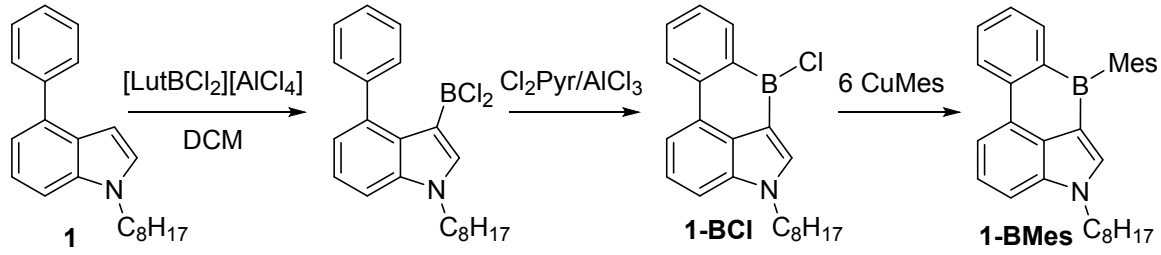


Figure S3: ^{11}B and ^{27}Al NMR spectra for the two step synthesis of **1-BCl** from **1** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. A minor impurity of BCl_3 is also observed. The sharp resonance at 103.2 in the ^{27}Al NMR spectrum is consistent with $[AlCl_4]^-$.

Attempted synthesis of **1-BMes**: 6-mesityl-4-octyl-4,6-dihydrobenzo[5,6]borinino[2,3,4-*cd*]indole



The below is a representative attempt at forming and isolating **1-BMes**, a range of syntheses were attempted over a range of scales, but pure **1-BMes** was not isolable in our hands predominantly due to its sensitivity to protodeboronation. However, its formulation is with high confidence based on *in-situ* NMR, mass spectroscopy, comparison to **2-BMes** and the formation of **3** from **1-BCl**.

A J. Young's NMR tube was charged with phenyl-indole **1** (0.007 mL, 2.29 10^{-5} mol). The compound was solubilised in dry CH_2Cl_2 (0.7 mL) and $[LutBCl_2][AlCl_4]$ (9 mg, 2.52 10^{-5} mol) was added. The solution was stirred for 20 min at room temperature. After a near quantitative formation of an intermediate consistent with **indoleBCl$_2$** (by NMR spectroscopy), 2,6-dichloropyridine (4 mg, 2.70 10^{-5} mol) and $AlCl_3$ (3 mg, 2.25 10^{-5} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain a single new compound assigned as **1-BCl**. Excess CuMes was added (26 mg, 1.42 10^{-4} mol) to the solution and the reaction mixture was stirred for 18 h at room temperature. The solution was extraction from the insoluble material via a cannula transfer. The volatile compounds/solvent were removed under reduced pressure. The mixture was then extracted with dry toluene. After evaporating toluene, compound **1-BMes** was extracted twice with dry pentane. A colourless oil containing crude 6-mesityl-4-octyl-4,6-dihydrobenzo[5,6]borinino[2,3,4-*cd*]indole, **1-BMes** was obtained with mesitylene present as an impurity along with other unidentified species (particularly observable in the 2 to 2.45 ppm region of the ^{1}H NMR spectrum). Further purification by chromatography using silica or alumina stationary phases was challenging due to the sensitivity of this compound to protodeboronation.

1-BMes ^{1}H (400 MHz, in CD_2Cl_2): δ 8.51 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 7.82 (s, 1H), 7.75 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 7.68 (m, 1H), 7.58 (m, 1H) 7.54 (m, 1H), 7.34 (dt, *J* = 7.3 Hz, *J* = 1.0 Hz, 1H), 6.92 (s, 2H, Mes), 4.31 (t, *J* = 7.1 Hz, 2H), 2.37 (s, Mes accurate integration is not possible due to overlap with other species), 2.04 (s, Mes accurate integration is not possible due to overlap with other species), 1.95 (quint, *J* = 7.1 Hz), 1.29 (m, accurate integration is not possible due to overlap with other species), 0.85 (accurate integration is not possible due to overlap with other species);

MS (APCI): calc. for $[M+H]^+$ $C_{31}H_{37}NB$ 434.3, found 434.4

HRMS (APCI) calc. for $C_{31}H_{37}BN^+$ $[M + H]^+$ = 434.3014, found 434.3021

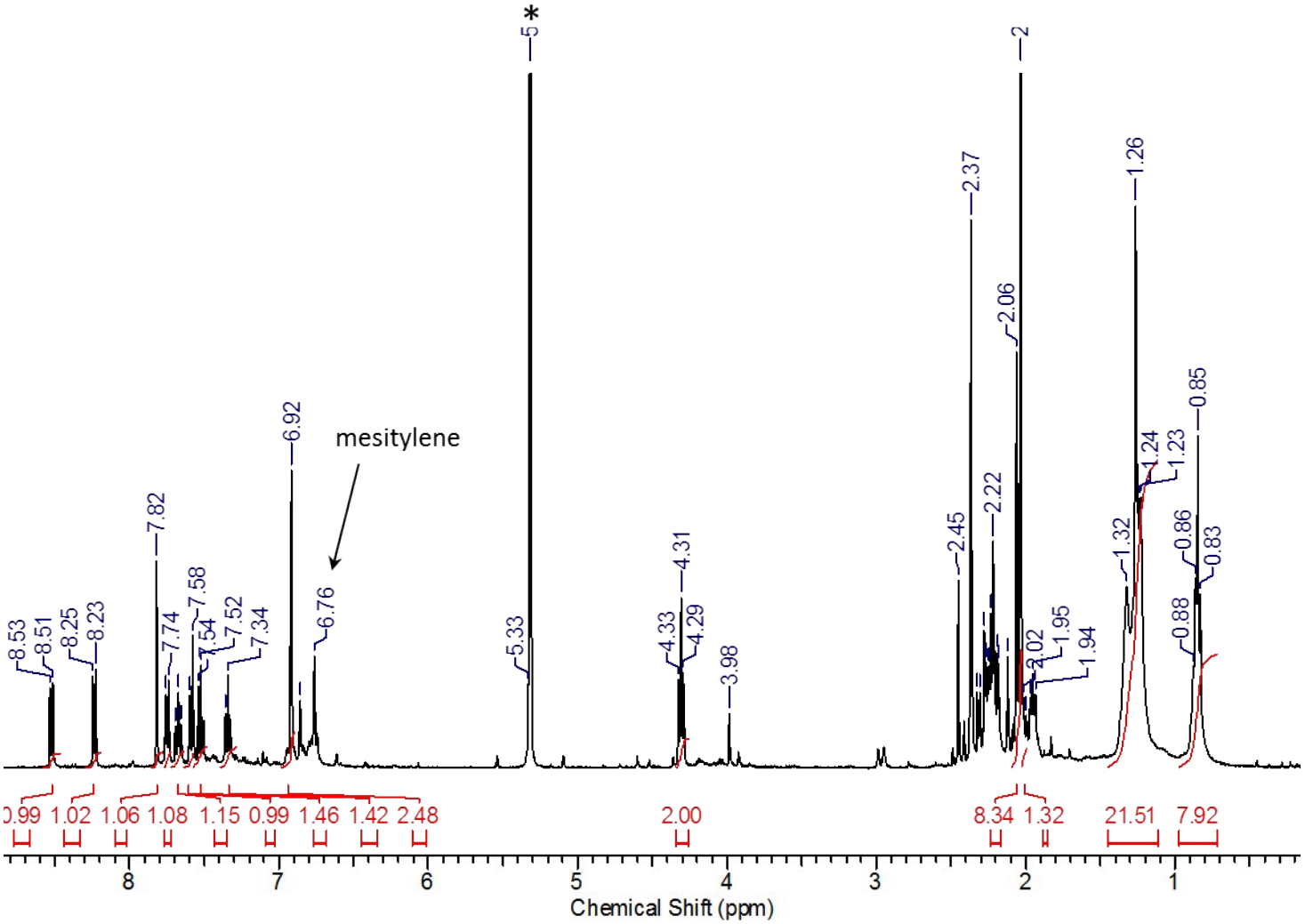


Figure S4: ^{1}H NMR spectrum of **1-BMes** in CD_2Cl_2 after attempted work up. The residual protio-solvent peak is labelled '*' Other unidentified impurities including mesitylene remain. Only one indole N-CH_2 resonance is observed indicating the other species do not contain *N*-octyl-indole

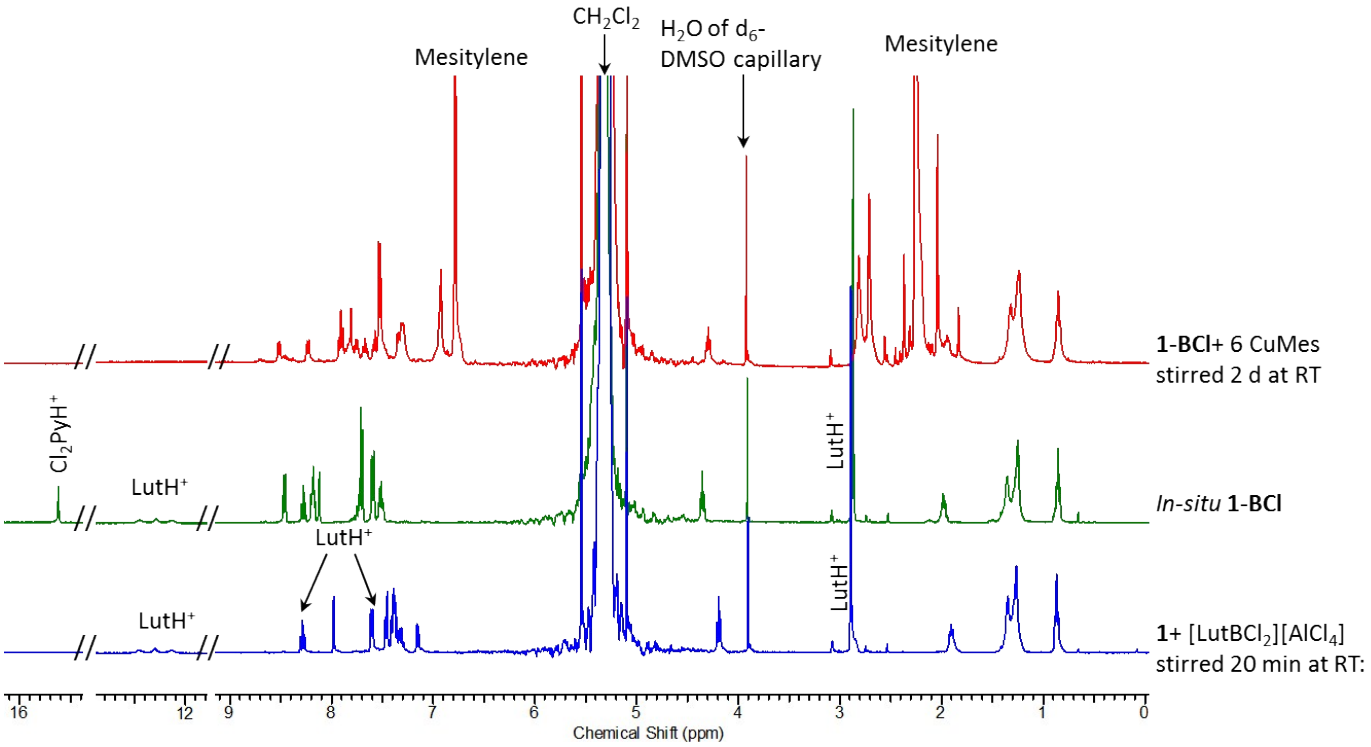


Figure S5: In-situ ^{1}H NMR spectra for the three step, one pot formation of **1-BMes** from **1**. By-products, LutH$^+$ and Cl_2PyH^+ are labelled in the blue and green traces. In the final *in-situ* spectrum the by-products include 2,6-lutidine, 2,6-dichloropyridine (from deprotonation of lutH and Cl_2PyH, respectively) and mesitylene. The in-situ conversion throughout is excellent with only one new N-CH_2 resonance observed (ca. 4.3 ppm) for each step.

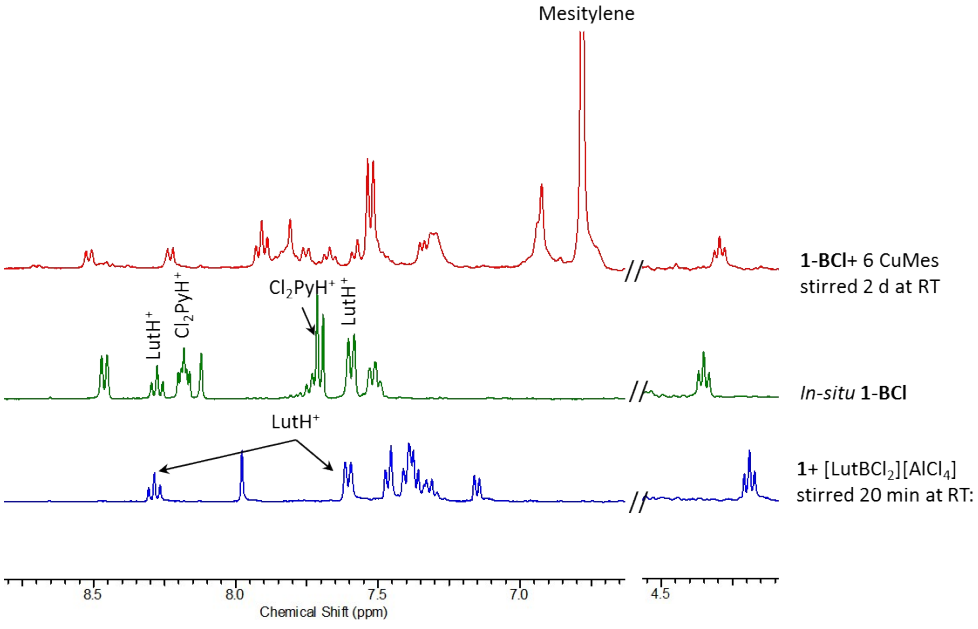


Figure S6: Partial in-situ ^{1}H NMR spectra for the three step, one pot formation of **1-BMes** from **1**. By-products, LutH and Cl_2PyH are labelled in the blue and green traces. In the final *in-situ* spectrum the by-products include 2,6-lutidine, 2,6-dichloropyridine (from deprotonation of lutH and Cl_2PyH, respectively) and mesitylene.

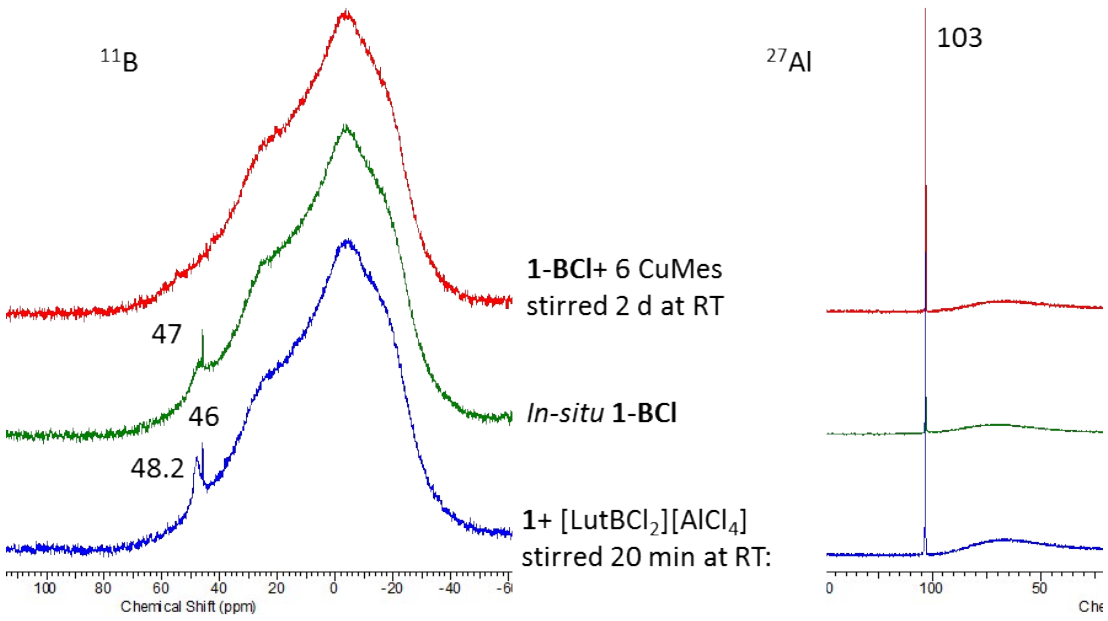
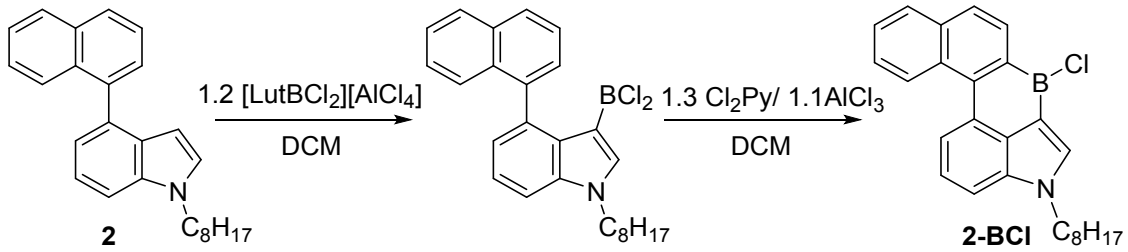


Figure S7: In-situ ^{11}B and ^{27}Al NMR spectra for the three step, one pot formation of **1-BMes** from **1**.

Synthesis of **2-BCl**



A J. Young's NMR tube was charged with **2** (0.007 mL, 2.05 10^{-5} mol). The compound was solubilised in dry CH_2Cl_2 (0.7 mL) and $[LutBCl_2][AlCl_4]$ (9 mg, 2.52 10^{-5} mol) was added. The solution was stirred for 5 min at room temperature. After a near quantitative formation of the intermediate assigned as indole-BCl_2 (by NMR spectroscopy), 2,6-dichloropyridine (4 mg, 2.70 10^{-5} mol) and $AlCl_3$ (3 mg, 2.25 10^{-5} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain **2-BCl**.

2-BCl ^{1}H (400 MHz, in CH_2Cl_2- capillary d_6-DMSO): δ 9.02 (m, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.49 (d, *J* = 8.3 Hz, 1H), 8.26 (m, 1H), 8.20 (s, 1H), 7.99 (m, 1H), 7.89 (m, 1H), 7.65 (m, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 1.95 (quint, *J* = 7.1 Hz,2H), 1.32 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H);

2-BCl ^{11}B (128 MHz, in CH_2Cl_2- capillary d_6-DMSO): δ very broad ~47.7;

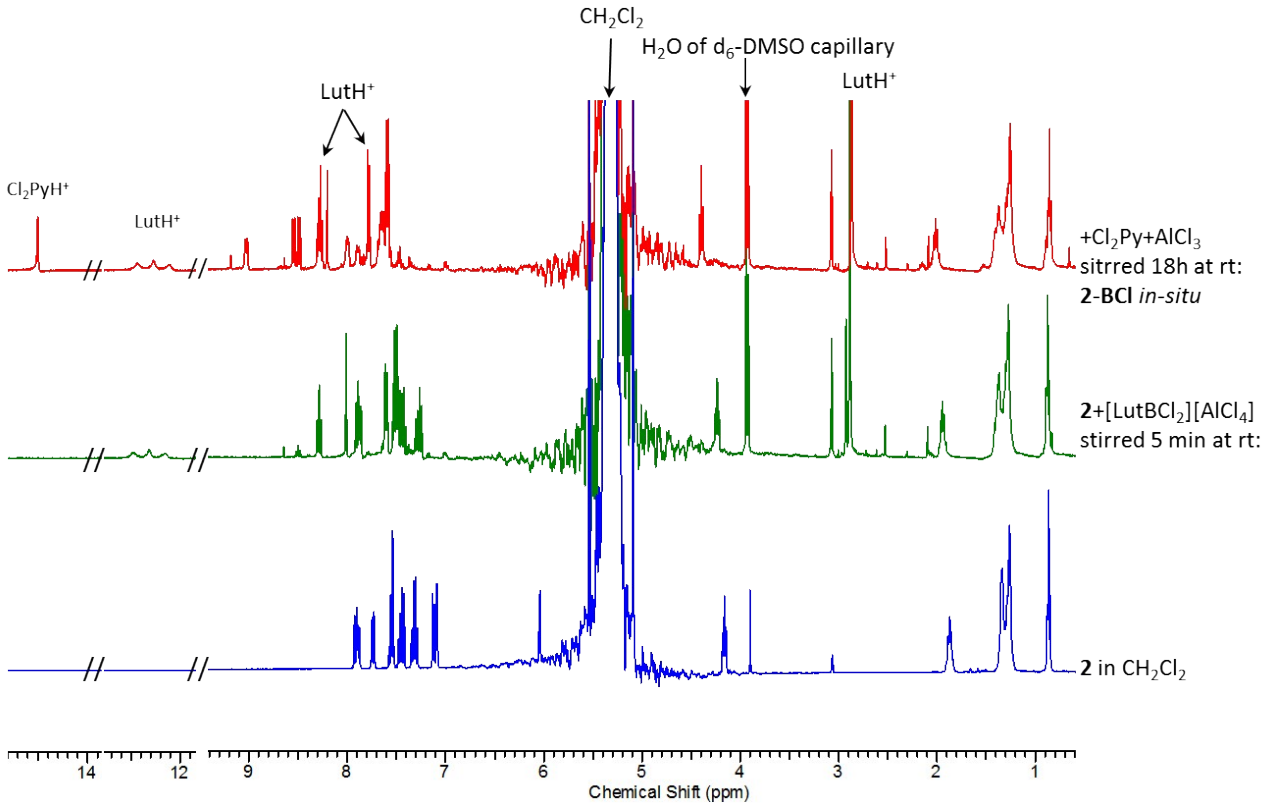


Figure S8: ^{1}H NMR spectra for the two step, one pot synthesis of **2-BCl** from **2** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. The resonances of Cl_2PyH^+ are sensitive to the amount of free Cl_2Py in solution. The chemical shift of Cl2Py<u>H</u>$^+$ varies with small changes in the ratio Cl_2Py/Cl_2PyH^+ in solution.

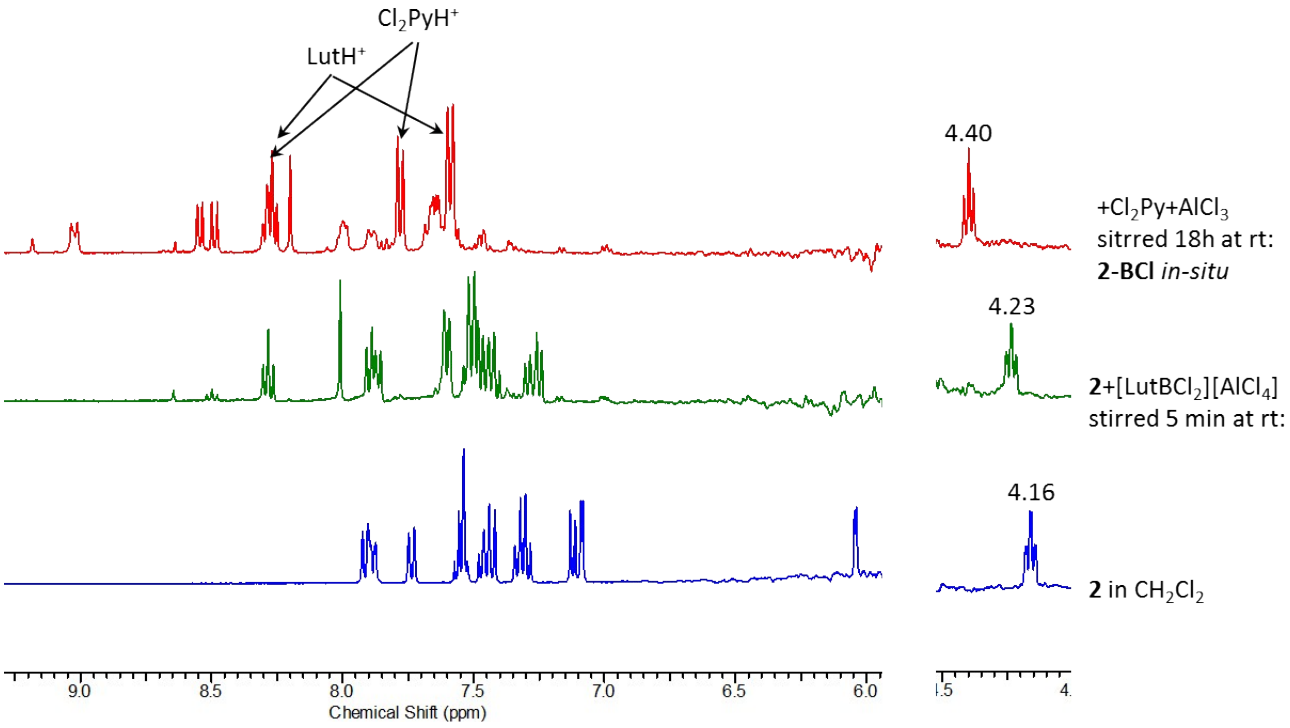


Figure S9: ^{1}H NMR spectra of the aromatic region and N-CH_2 for the two step synthesis of **2-BCl** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added.

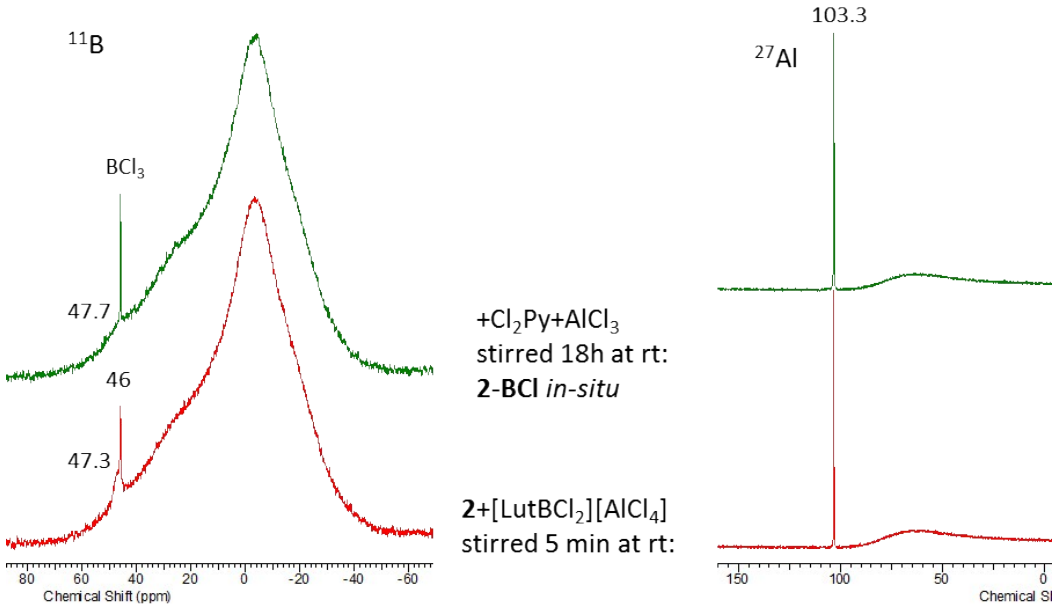
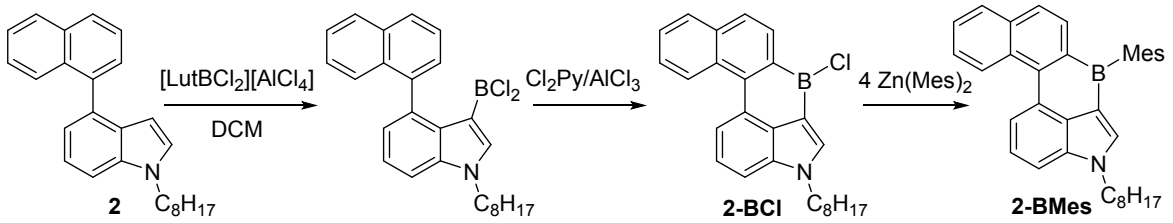


Figure S10: ^{11}B and ^{27}Al NMR spectra for the two step, one pot synthesis of **2-BCl** from **2** with $[LutBCl_2][AlCl_4]$ and then $Cl_2Py/AlCl_3$ in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. A minor impurity of BCl_3 is also observed. The sharp resonance at 103.3 in the ^{27}Al NMR spectrum is consistent with $[AlCl_4]^-$.

Formation of **2-BMes** using $ZnMes_2$

(6-mesityl-4-octyl-4,6-dihydronaphtho[1',2':5,6]borinino[2,3,4-*cd*]indole)



A J. Young's NMR tube was charged with **2** (0.007 mL, 2.05 10^{-5} mol). The compound was solubilised in dry CH_2Cl_2 (0.7 mL) and $[LutBCl_2][AlCl_4]$ (9 mg, 2.52 10^{-5} mol) was added. The solution was stirred for 1 h at room temperature. After a near quantitative formation of the intermediate assigned as indole-BCl_2 (by NMR spectroscopy), 2,6-dichloropyridine (4 mg, 2.70 10^{-5} mol) and $AlCl_3$ (3 mg, 2.25 10^{-5} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain **2-BCl**. Then excess $Zn(Mes)_2$ was added (28 mg, 9.22 10^{-5} mol) to the solution and the reaction mixture was stirred for 18 h at room temperature. The solution was filtered via a cannula transfer. Compound **2-BMes** was extracted with dry toluene. The mixture was purified by rapid silica gel plug chromatography with PET then PET/CH_2Cl_2 (90/10) as eluent. A yellow oil of 6-mesityl-4-octyl-4,6-dihydronaphtho[1',2':5,6]borinino[2,3,4-*cd*]indole, **2-BMes** was obtained. Exposure of this compound to silica or alumina stationary phases leads to increasing amount of protodeboronation products over time.

2-BMes: ^{1}H (400 MHz, in CD_2Cl_2): δ 9.11 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 7.94 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.90 (s, 1H), 7.67 – 7.58 (m, 6H), 6.95 (s, 2H, Mes), 4.36 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H, Mes), 2.04 (s, 6H, Mes), 1.99 (quint, *J* = 7.1 Hz, 2H), 1.29 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H);

2-BMes: $^{13}C\{^{1}H\}$ (101 MHz, in CD_2Cl_2): δ 143.2, 140.1, 139.4, 137.2, 136.9, 136.8, 133.9, 131.7, 130.6, 129.9, 129.2, 128.9, 127.9, 127.4, 127.0, 126.4, 126.2, 125.6, 122.9, 121.4, 111.3, 109.3, 101, 48.3, 32.3, 31.1, 30.9, 29.7, 29.6, 27.5, 23.7, 23.2, 22.9, 21.5, 14.4;

MS (APCI): calc. for $[M+H]^+$ $C_{35}H_{39}NB$ 484.32, found 484.3

Accurate mass: calc. for $[M+H]^+$ $C_{35}H_{39}BN$ 484.3170, found 484.3162

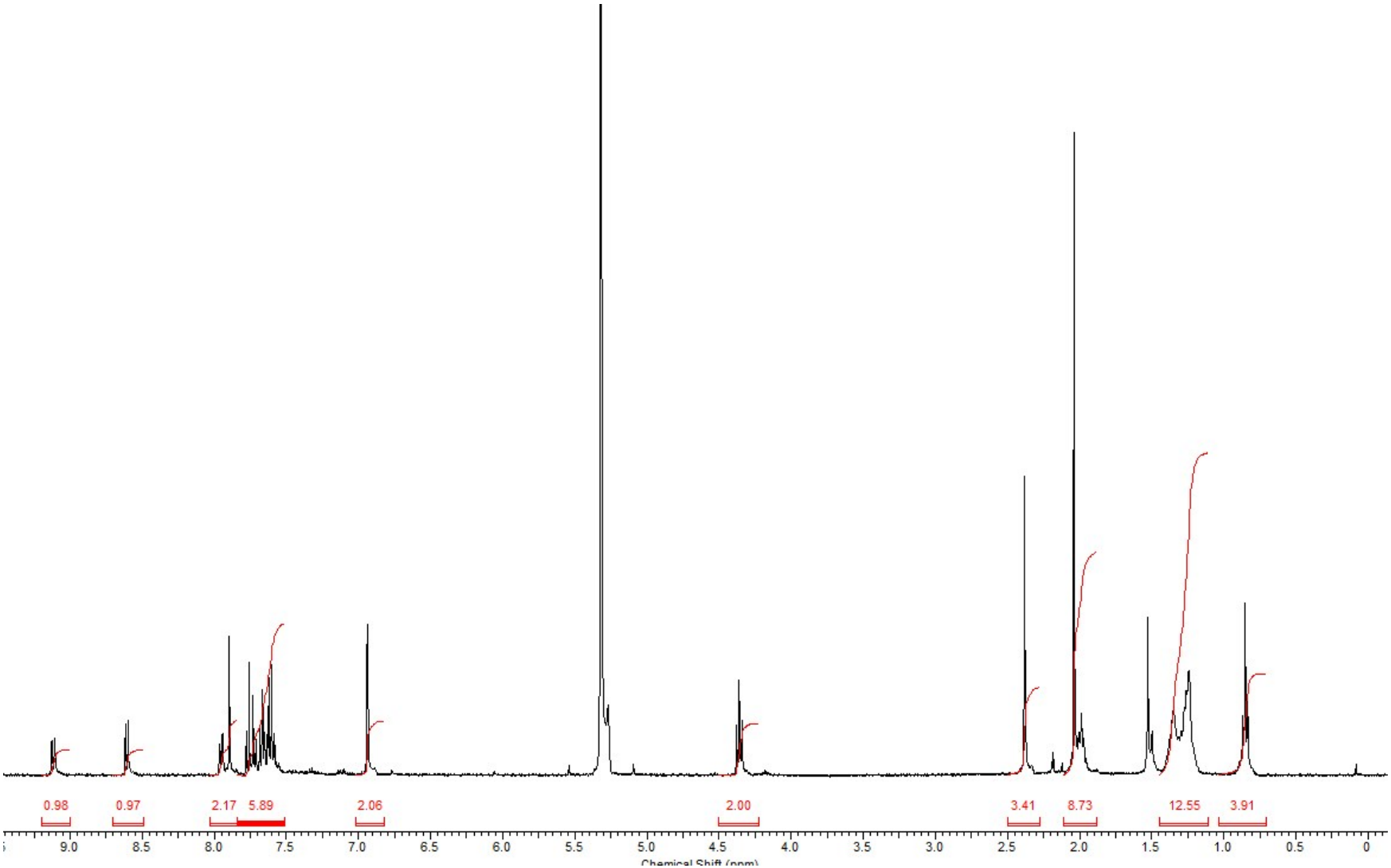


Figure S11: ^{1}H NMR spectrum of purified **2-BMes** in CD_2Cl_2. The residual protio-solvent peak is at 5.32 and the resonance at 1.5 ppm is due to H_2O / HDO

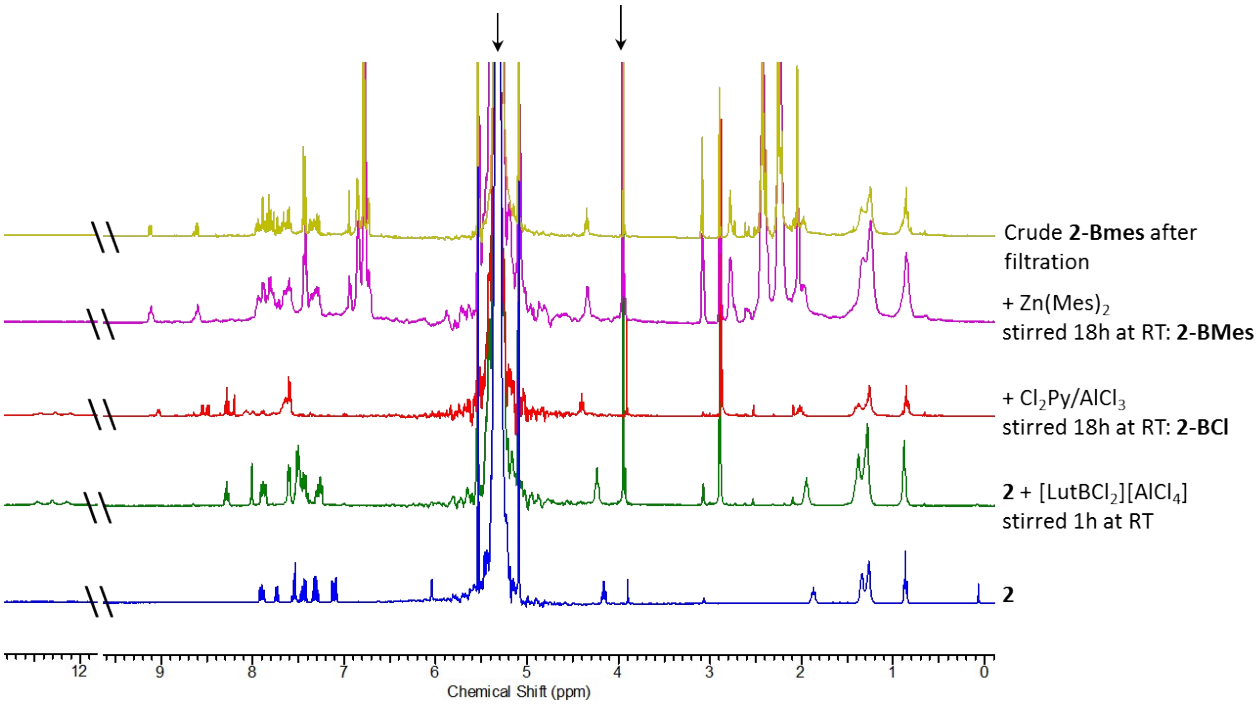


Figure S12: *In-situ* ^{1}H NMR spectra for the three step, one pot formation of **2-BMes** from **2** using $ZnMes_2$. The conversion throughout is good with only one new N-CH_2 resonance observed (ca. 4.3 ppm) for each step. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. The resonances labelled with an arrow correspond to protio DCM and water in the DMSO capillary, respectively.

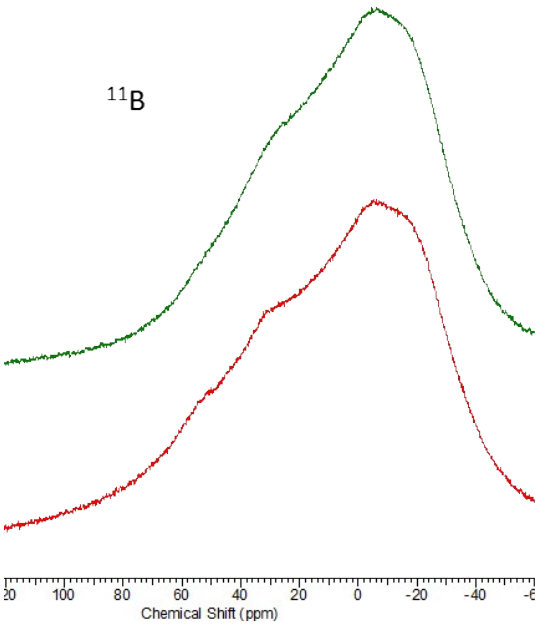
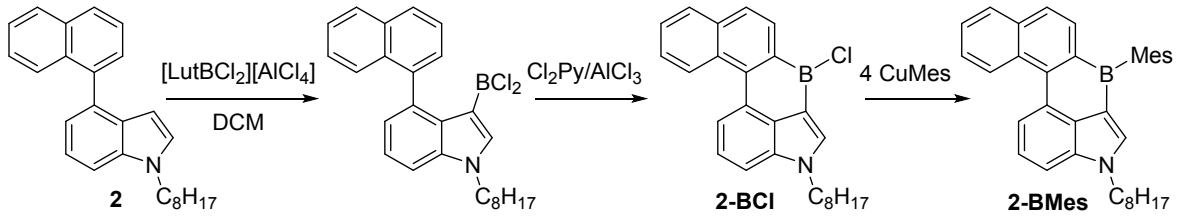


Figure S13: ^{11}B NMR spectra of **2-BMes** before and after column chromatography, in both cases no discernible resonance attributable to **2-BMes** was observable over the background for borosilicate glass.

Formation of **2-BMes** using CuMes

(6-mesityl-4-octyl-4,6-dihydronaphtho[1',2':5,6]borinino[2,3,4-*cd*]indole)



An ampoule with a J. Young's tap was charged with **2** (40 mg, 1.13 10^{-4} mol). The compound was solubilised in dry CH_2Cl_2 (4.5 mL) and $[LutBCl_2][AlCl_4]$ (40 mg, 1.13 10^{-4} mol) was added. The solution was stirred for 1 h at room temperature. Then 2,6-dichloropyridine (17 mg, 1.15 10^{-4} mol) and $AlCl_3$ (15 mg, 1.13 10^{-4} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature. Then excess CuMes was added (82 mg, 4.52 10^{-4} mol) to the solution and the reaction mixture was stirred in the dark for 18 h at room temperature. The solution was filtered from the copper salts *via* a cannula transfer. Compound **2-BMes** was extracted with dry toluene. The mixture was further purified by rapid preparative silica gel TLC with PET/CH_2Cl_2 (95/15) as eluent. A yellow oil of 6-mesityl-4-octyl-4,6-dihydronaphtho[1',2':5,6]borinino[2,3,4-*cd*]indole **2-BMes** was obtained (15.4 mg, 3.19 10^{-5} mol, 28%) with the low yield due to significant protodeboronation during purification.

2-BMes ^{1}H (400 MHz, in CD_2Cl_2): δ 9.11 (dd, *J* = 8.3 Hz, *J* = 0.76 Hz, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 7.94 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.90 (s, 1H), 7.67 – 7.58 (m, 6H), 6.94 (s, 2H, Mes), 4.36 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H, Mes), 2.04 (s, 6H, Mes), 1.99 (quint, *J* = 7.1 Hz, 2H), 1.29 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H);

2-BMes ^{13}C (101 MHz, in CD_2Cl_2): δ 143.2, 140.1, 139.4, 137.2, 136.9, 136.8, 133.9, 131.7, 130.6, 129.9, 129.2, 128.9, 127.9, 127.4, 127.0, 126.4, 126.2, 125.6, 122.9, 121.4, 111.3, 109.3, 101, 48.3, 32.3, 31.1, 30.9, 29.7, 29.6, 27.5, 23.7, 23.2, 22.9, 21.5, 14.4;

MS (APCI): calc. for $[M+H]^+$ $C_{35}H_{39}NB$ 484.32, found 484.3

Accurate mass: calc. for $[M+H]^+$ $C_{35}H_{39}BN$ 484.3170, found 484.3162

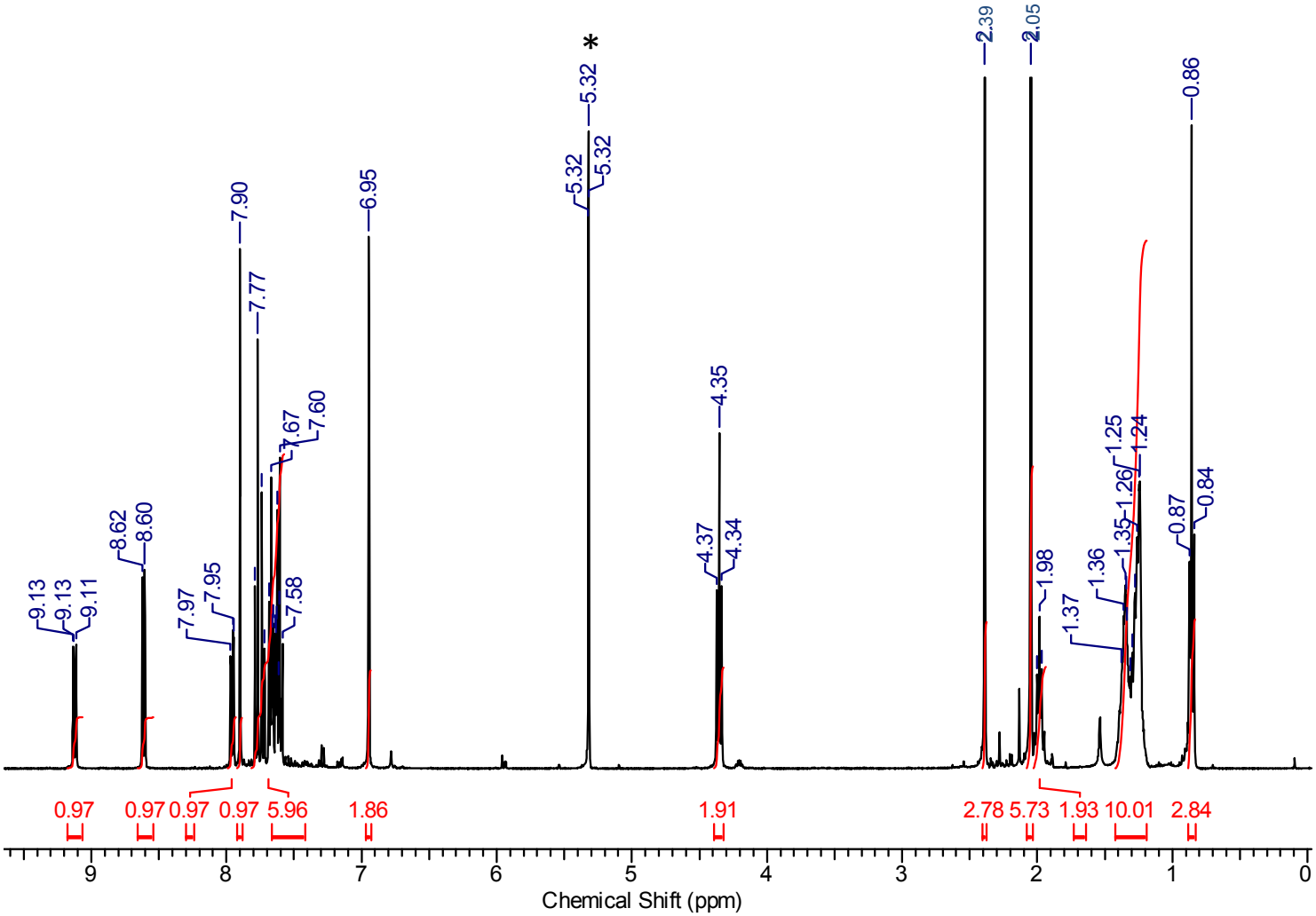


Figure S14: ^{1}H NMR spectrum of purified **2-BMes** in CD_2Cl_2. The residual protio-solvent peak is labelled '*' the resonance at 1.5 ppm is due to H_2O

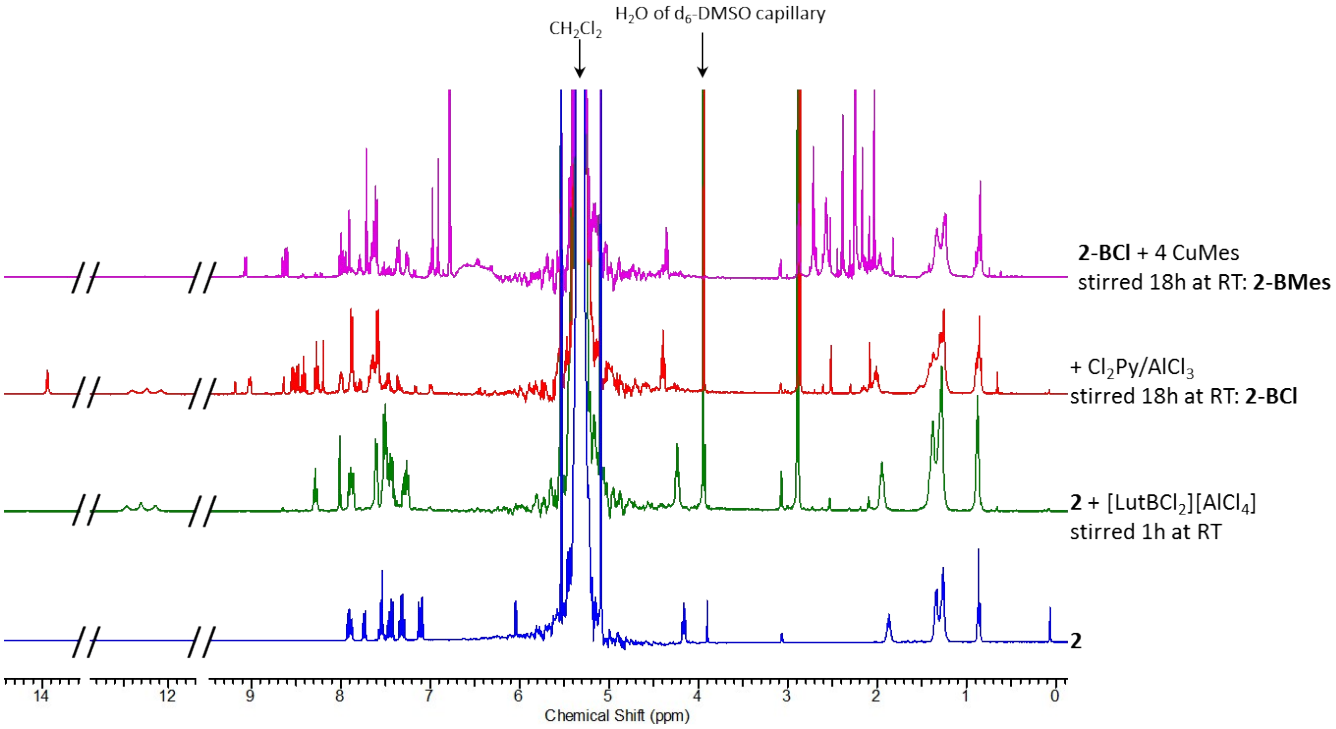


Figure S15: *In-situ* ^{1}H NMR spectra for the three step, one pot formation of **2-BMes** from **2** using CuMes. The conversion throughout is good with only one new N-CH_2 resonance observed (ca. 4.3 ppm) for each step. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added.

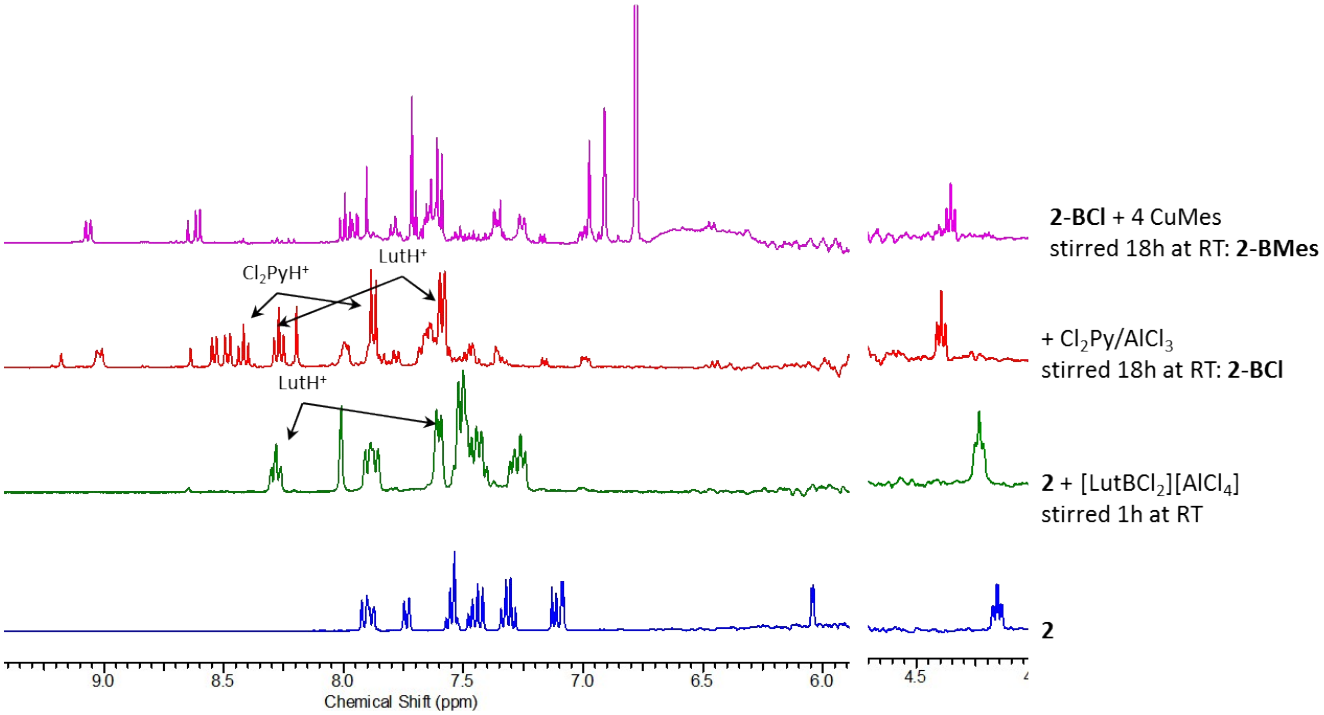
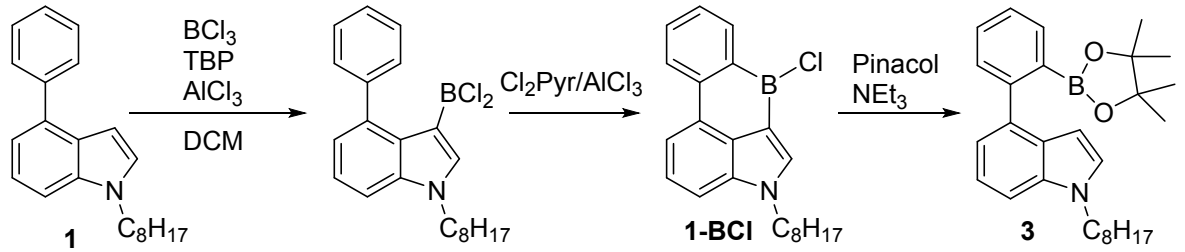


Figure S16: ^{1}H NMR spectra of the aromatic region and N-CH_2 region for the three step synthesis of **2-BMes** with $[LutBCl_2][AlCl_4]$, $Cl_2Py/AlCl_3$ and then CuMes in CH_2Cl_2. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added.

Synthesis of **3**: 1-octyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-indole



A J. Young's NMR tube was charged with **1** (50 mg, 1.64 10^{-4} mol) and TBP (2,4,6-Tri-*tert*-butylpyridine) (41 mg, 1.64 10^{-4} mol). The compound was dissolved in dry CH_2Cl_2 (0.7 mL) and BCl_3 (1 equiv. 1 M in DCM) and $AlCl_3$ (27 mg, 1.64 10^{-4} mol) was added to the solution. The solution was stirred for 20 min at room temperature. After a near quantitative formation of the indoleBCl_2 intermediate (by in-situ NMR spectroscopy), 2,6-dichloropyridine (24 mg, 1.64 10^{-4} mol) and $AlCl_3$ (27 mg 1.64 10^{-4} mol) were introduced to the solution. The reaction was stirred for 6 h at room temperature to obtain a new compound assigned as **1-BCl** (by *in-situ* NMR spectroscopy). A solution of pinacol (1 M in NEt_3) (1.3 mL, 1.3 10^{-3} mol) was then added to the reaction mixture. The volatile compounds/solvent were removed under reduced pressure, the residue was dissolved in DCM (~3 mL) and passed through a short plug of base treated (5% NEt_3 in hexane) silica gel. The crude reaction mixture was then purified by preparative silica gel TLC with PET/CH_2Cl_2 (70/30) as eluent. The desired product was isolated as a colourless oil (27 mg, 6.26 10^{-5} mol, 38%).

3 ^{1}H (500 MHz, $CDCl_3$): δ 7.80 - 7.76 (m, 1H), 7.55 - 7.60 (m, 1H), 7.55 - 7.51 (m, 1H), 7.40 (td, *J* = 7.3, 1.4 Hz, 1H), 7.37 - 7.34 (m, 1H), 7.32 - 7.28 (m, 1H), 7.13 - 7.09 (m, 2H), 6.42 (dd, *J* = 3.2, 0.6 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 1.89 (quin, *J* = 7.2 Hz, 2H), 1.44 - 1.26 (m, 10H), 1.06 (s, 12 H), 0.94 (t, 7.0 Hz, 3H);

3 ^{13}C{^{1}H} (126 MHz, $CDCl_3$): δ 146.3, 136.4, 135.8, 133.9, 129.9, 129.3, 128.2, 127.4, 126.0, 121.2, 119.7, 108.0, 100.8, 83.3, 46.5, 31.8, 30.4, 29.2, 29.2, 27.0, 24.4, 22.6, 14.1;

3 ^{11}B (128 MHz, CD_2Cl_2): δ 32.0 (br);

MS (APCI) calc. for $C_{28}H_{38}BNO_2$ = 431.29, found 431.3

Accurate mass: calc. for $[M+H]^+$ $C_{28}H_{39}BNO_2$ 432.3068, found 432.3068

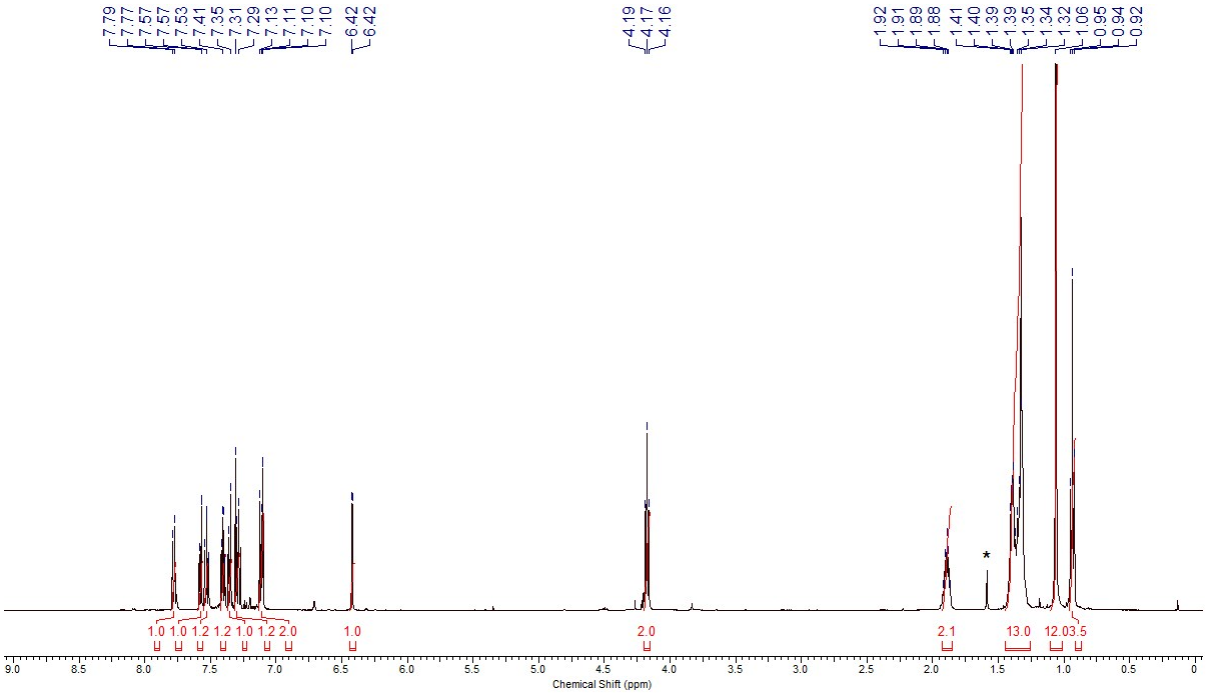


Figure S17: ^{1}H NMR spectrum of **3** in $CDCl_3$. * = H_2O

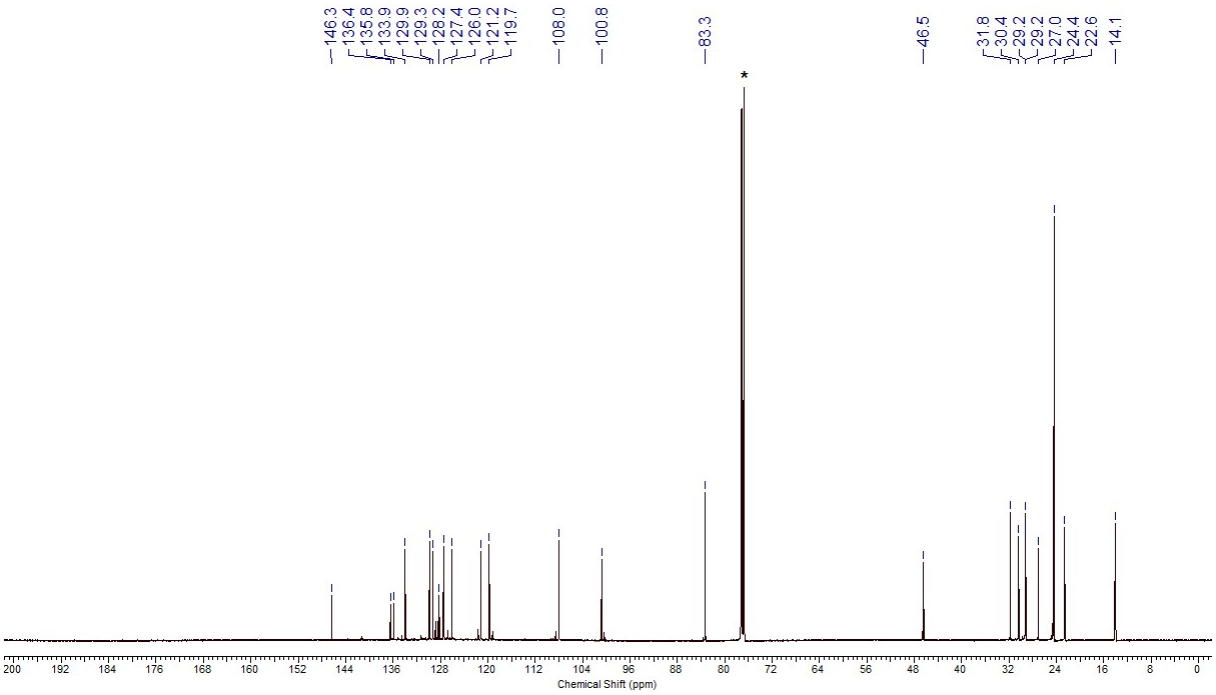


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$. * = $CHCl_3$

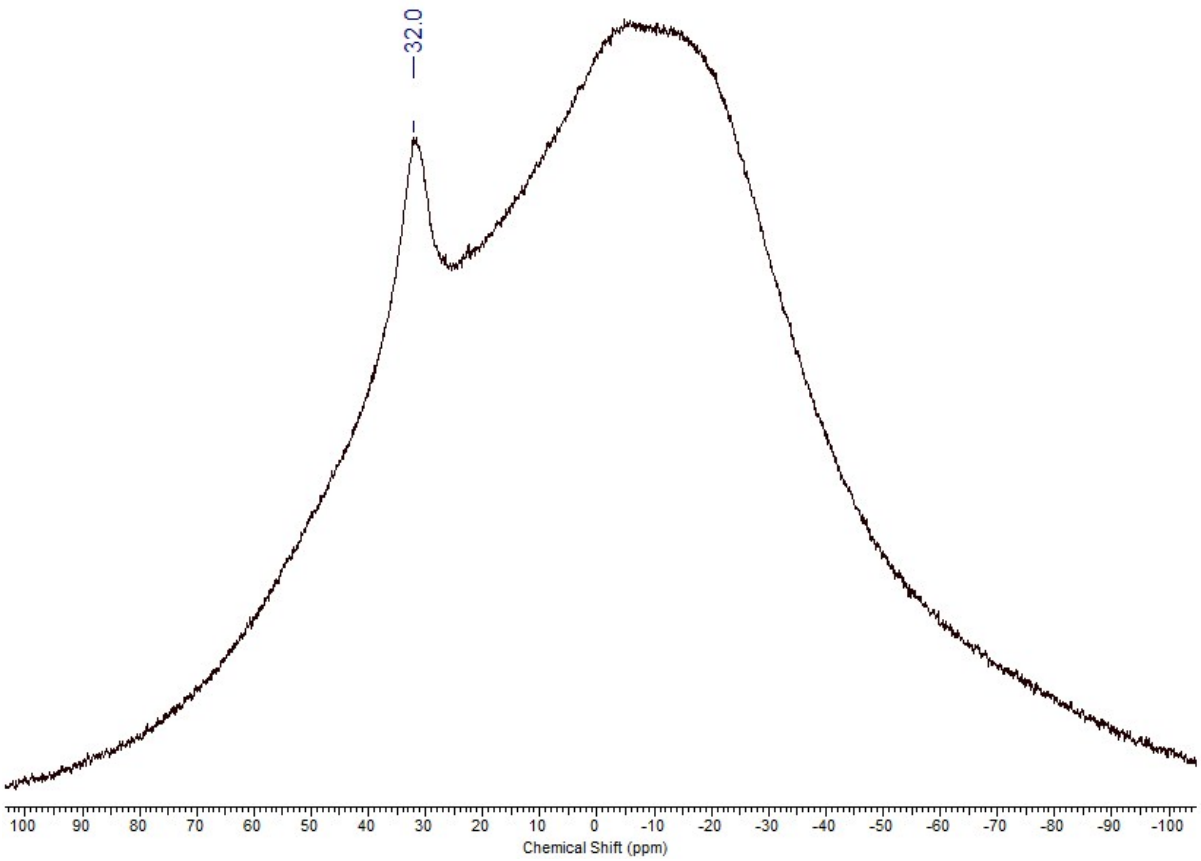


Figure S19: ^{11}B NMR spectrum of **3** in $CDCl_3$.

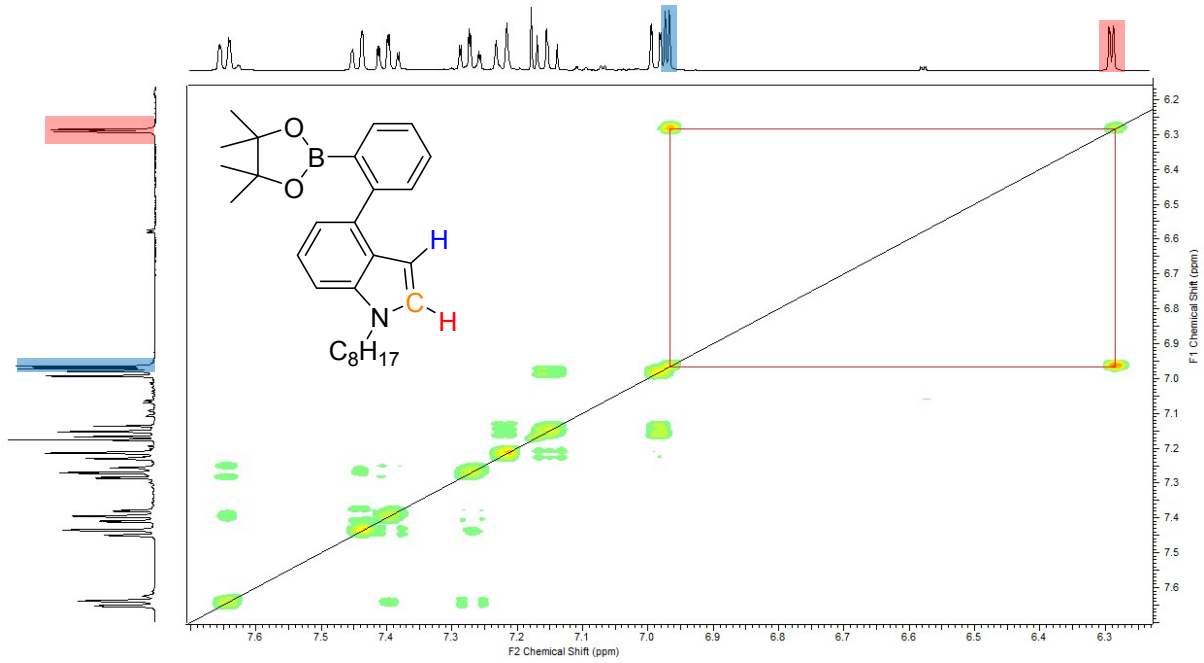


Figure S20: Partial COSY (^1H, ^1H) NMR spectrum of **3** in $CDCl_3$.

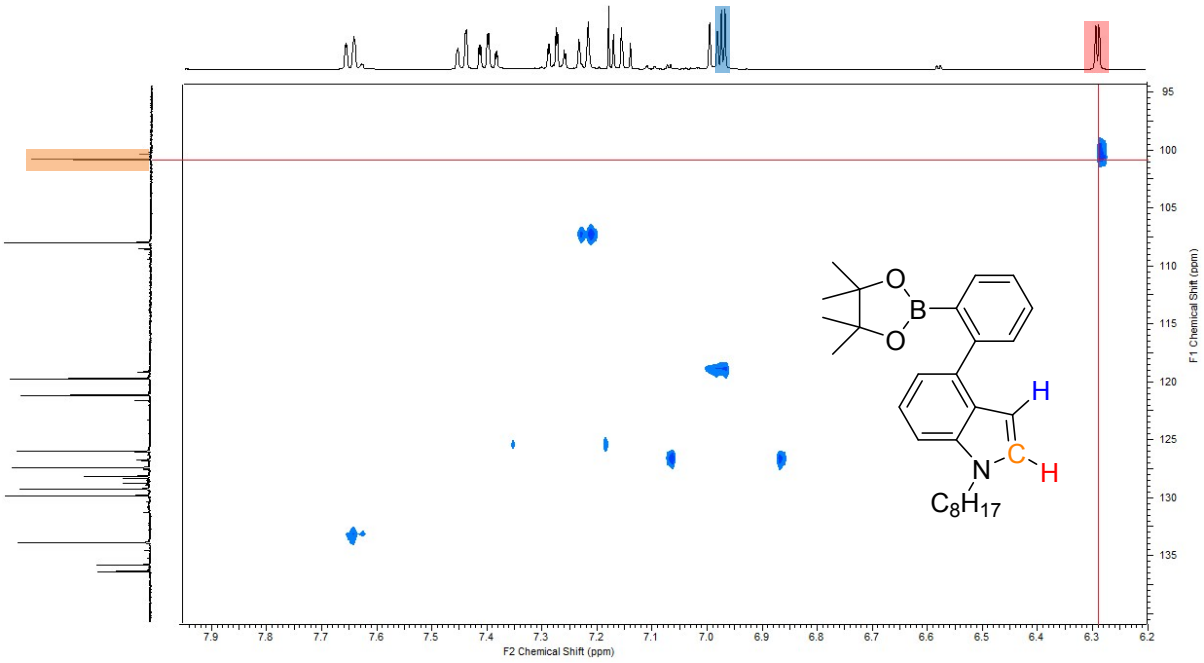


Figure S21: Partial HSQC (^{1}H, ^{13}C) NMR spectrum of **3** in $CDCl_3$.

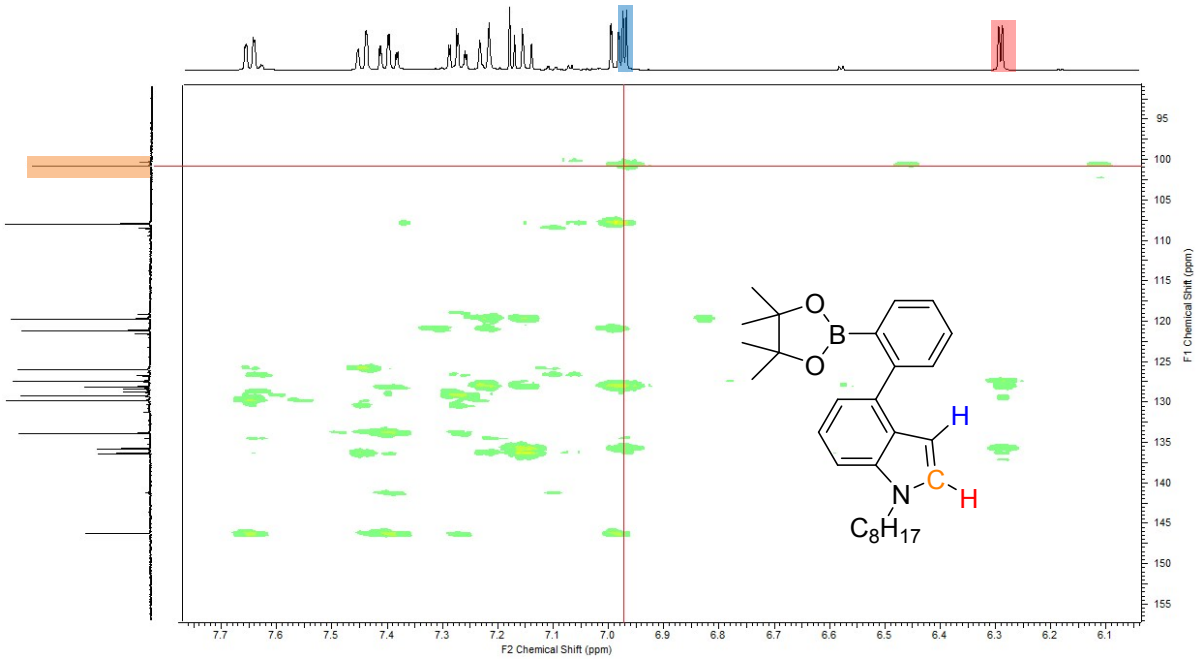
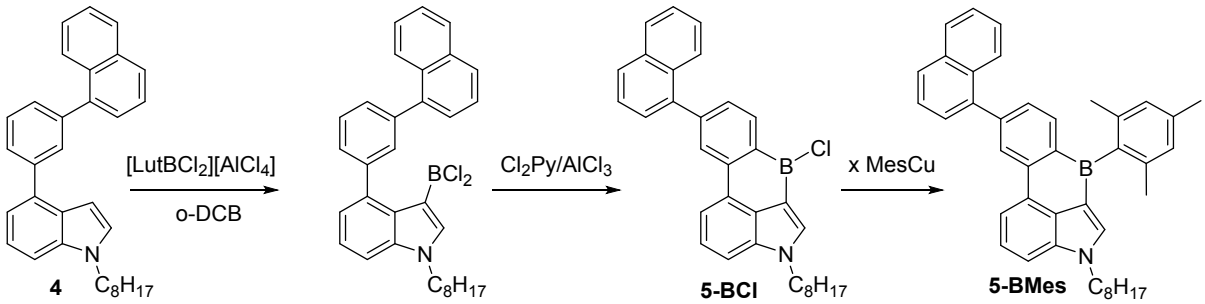


Figure S22: Partial HMBC (^{1}H, ^{13}C) NMR spectrum of **3** in $CDCl_3$.

Attempted Synthesis of **5-BMes**

6-mesityl-9-(naphthalen-1-yl)-4-octyl-4,6-dihydrobenzo[5,6]borinino[2,3,4-cd]indole



A J. Young's NMR tube was charged with 4-(3-(naphthalen-1-yl)phenyl)-1-octyl-1H-indole **4** (24 mg, 5.56 10^{-5} mol). The compound was solubilised in dry ortho-dichlorobenzene (0.8 mL) and $[LutBCl_2][AlCl_4]$ (20 mg, 5.59 10^{-5} mol) was added. The solution was stirred for 5 min at room temperature. After a near quantitative formation of a single new species assigned as the indole-BCl_2 intermediate (by in-situ NMR spectroscopy), 2,6-dichloropyridine (8.3 mg, 5.60 10^{-5} mol) and $AlCl_3$ (8 mg, 5.96 10^{-5} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain a new product that was assigned as **5-BCl** (by in-situ NMR spectroscopy). Then excess CuMes was added (61 mg, 3.34 10^{-4} mol) to the solution and the reaction mixture was stirred for 18 h at room temperature. A yellow oil tentatively assigned as 6-mesityl-9-(naphthalen-1-yl)-4-octyl-4,6-dihydrobenzo[5,6]borinino[2,3,4-cd]indole **5-BMes** was obtained contaminated with mesitylene and free pyridyl base by drying and sequential extraction with toluene (followed by further drying) and then extraction with pentane. Attempts to purify (e.g., by column chromatography) led to protodeboronation.

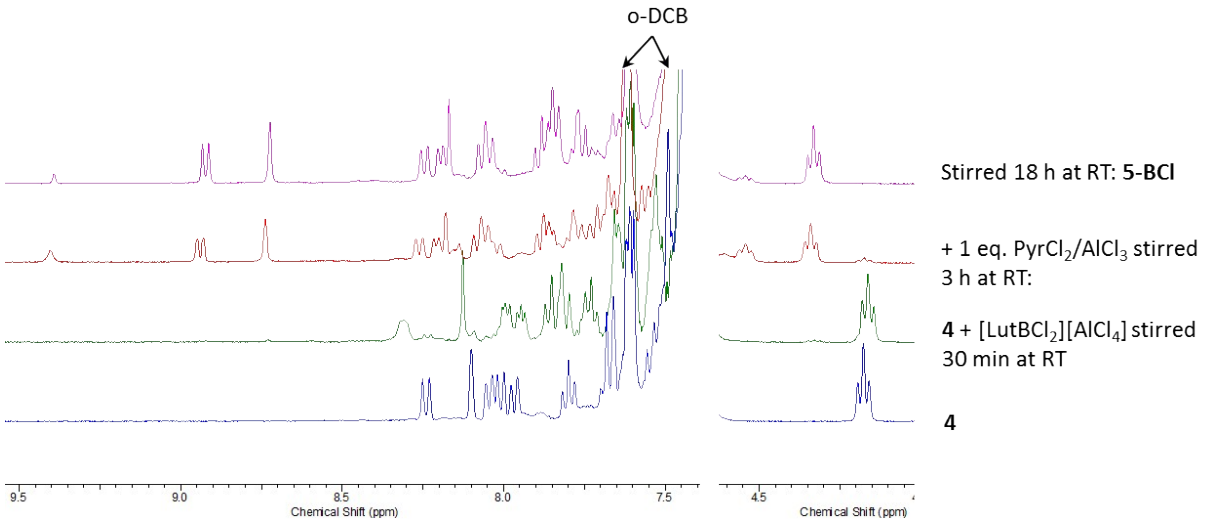


Figure S23: Partial ^{1}H NMR spectra for the two step synthesis of **5-BCl**. Spectra in protio ortho-dichlorobenzene with a "wet" d_6-DMSO capillary added. The formation of a compound containing two 1 H integral singlets is consistent with formation of **5-BCl** from borylation at the less hindered C-H position.

In-situ protection using excess CuMes

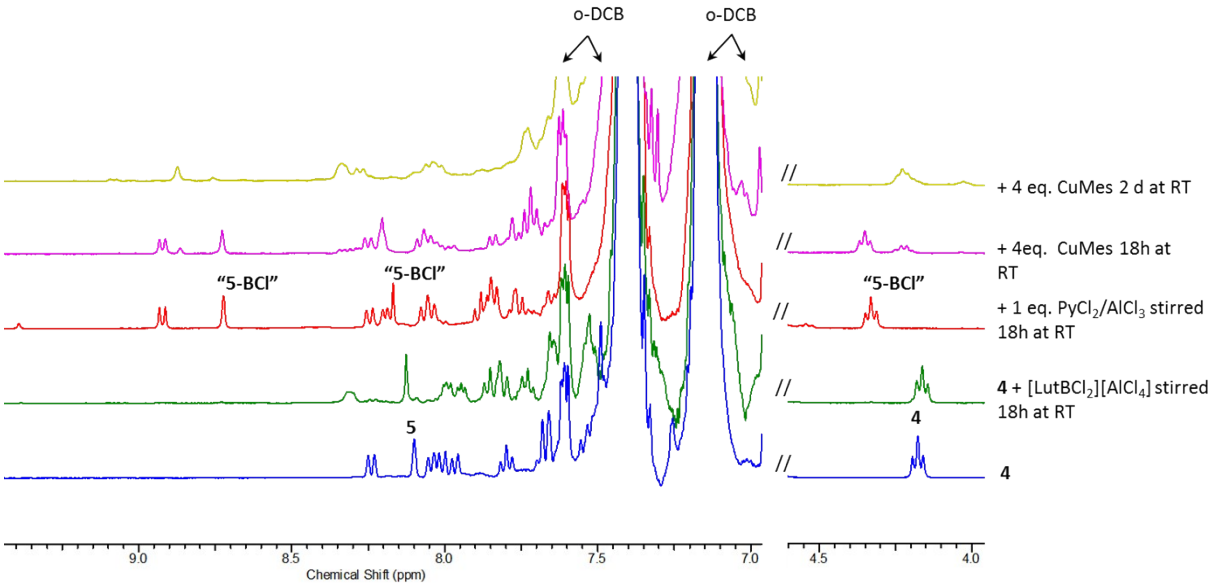


Figure S24: In-situ synthesis of **5-BMes** with $[LutBCl_2][AlCl_4]$, $Cl_2Py/AlCl_3$ and CuMes. Spectra in protio o-DCB with a "wet" d_6-DMSO capillary added.

Reactions using forcing temperatures and excess Lewis acid were attempted to determine if the second borylation was reversible and borylation at the desired position could be achieved to enable triple C-H borylation. For example, additional equivalents of $Cl_2Py/AlCl_3$ were introduced but no new species, relative to those formed after addition of the first equivalent of $Cl_2Py/AlCl_3$, were observed in the ^1H NMR spectrum. The reaction was repeated at a higher temperature in an effort to force reaction at the more sterically demanding α-position (envisaged *via* protodeboronation of **5-BCl** by Cl2PyH) and form the desired double ring closed product which was hoped to be the thermodynamic product. Compound **5-BCl** was heated in o-DCB at 140°C in presence of two equivalents of $Cl_2Py/AlCl_3$, however, only one ring closed product was formed, the previously observed **5-BCl**.

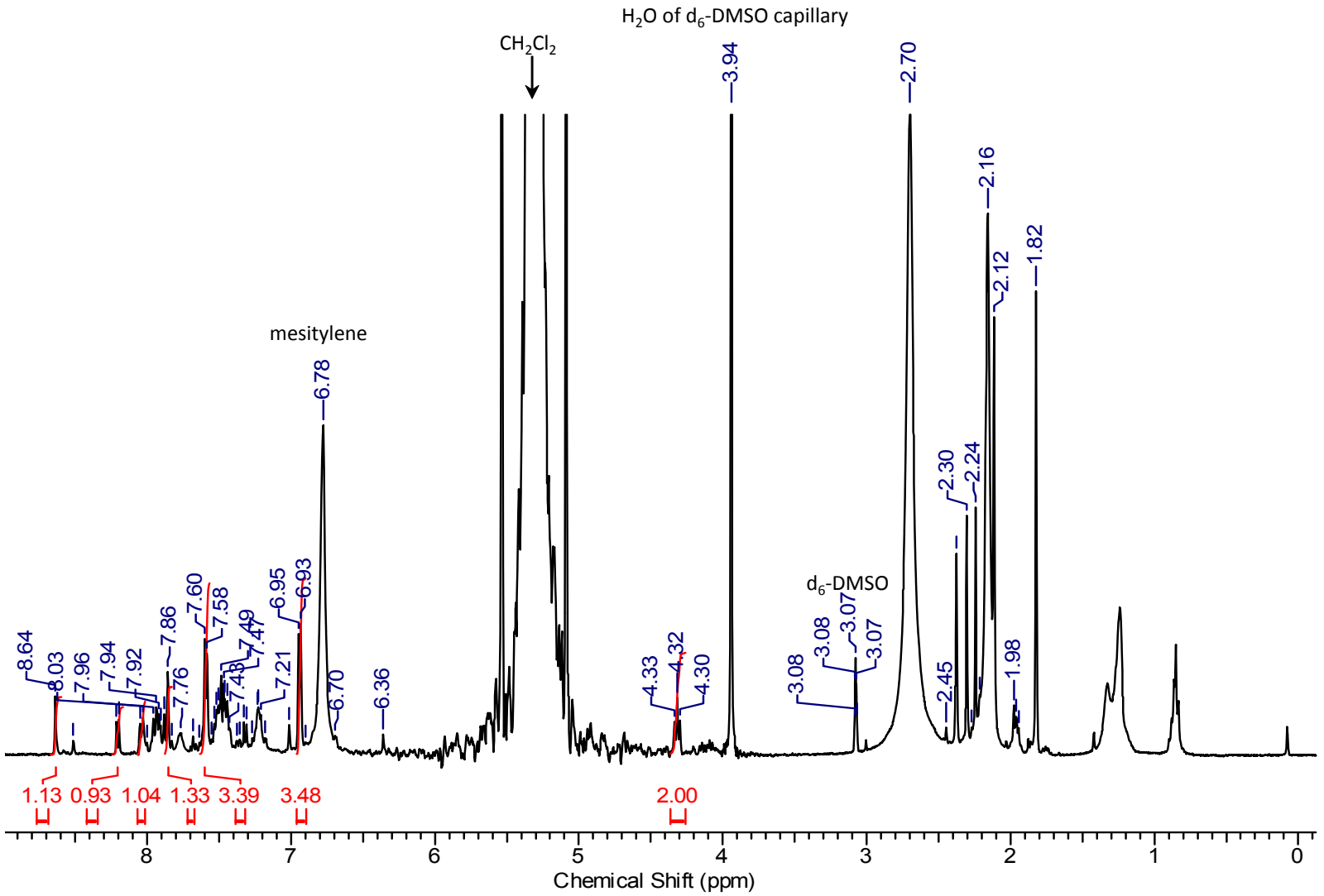


Figure S25: ^{1}H NMR spectrum from the attempted synthesis of **5-BMes** after extraction in pentane. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. Only one major *N*-octyl-indole N-CH_2 resonance is observed at 4.32 ppm suggesting only one major indole containing species is present.

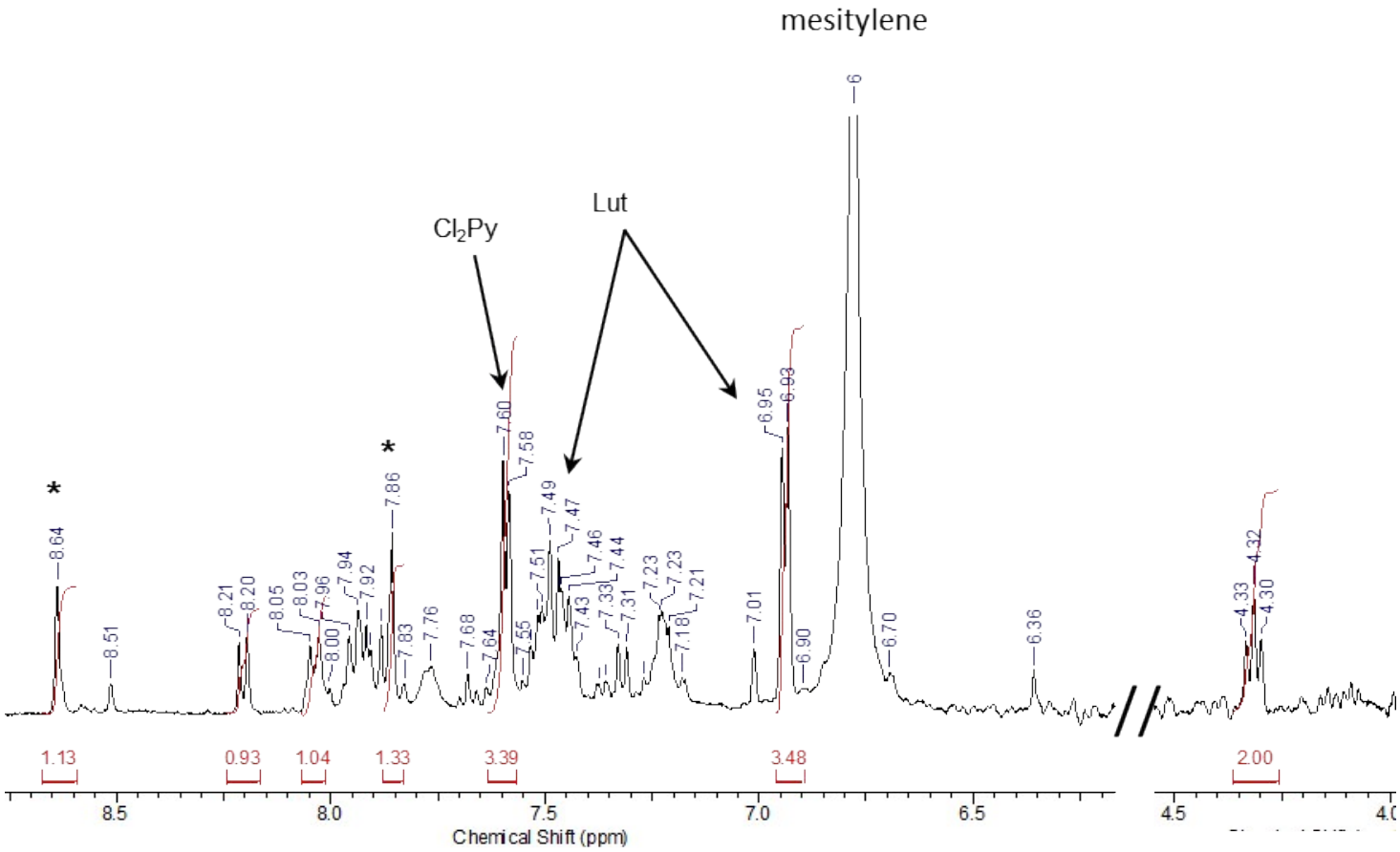
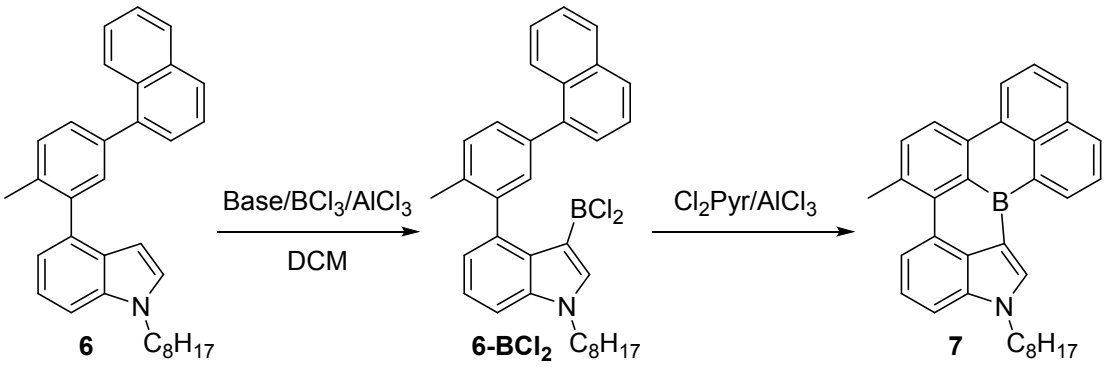


Figure S26: Partial ^{1}H NMR spectrum from the attempted synthesis of **5-BMes** after extraction in pentane. Spectra in protio CH_2Cl_2 with a "wet" d_6-DMSO capillary added. * = 1 H integral singlets (relative to NCH_2) indicating that borylation has occurred at the least hindered site

Synthesis of Compound **7**: 6-methyl-2-octyl-2H-2-aza-14b-boraindeno[1,7-ab]perylene



A Schlenk tube fitted with a J. Young's valve was charged with 4-(2-methyl-5-(naphthalen-1-yl)phenyl)-1-octyl-1H-indole, **6** (88 mg, 1.97 10^{-4} mol). The compound was solubilised in dry CH_2Cl_2 (10 mL) and BCl_3 (V=0.2 mL, C=1 mol/L in CH_2Cl_2), 2,4,6-Tri-*tert*-butylpyridine (146 mg, 5.9 10^{-4} mol) and $AlCl_3$ (26.5 mg, 1.97 10^{-4} mol) were added. The solution was stirred for 1 h at room temperature. After a near quantitative formation of a new species assigned as **6-BCl_2** (by in-situ NMR spectroscopy), 2,4,6-Tri-*tert*-butylpyridine (49 mg, 1.98 10^{-4} mol) and 2,6-dichloropyridine (29 mg, 1.97 10^{-4} mol) and $AlCl_3$ (53 mg, 3.94 10^{-4} mol) were introduced to the solution. The reaction was stirred for 18 h at room temperature to obtain **7**. The mixture was purified by preparative alumina gel TLC with PET/CH_2Cl_2 (95/15) as eluent. A yellow oil of 6-methyl-2-octyl-2H-2-aza-14b-boraindeno[1,7-ab]perylene **7** was obtained (27 mg, 5.95 10^{-5} mol, 30%). Again the low yield is due to protodeboronation during chromatography.

7 ^{1}H (400 MHz, in CD_2Cl_2): δ 9.01 (dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 8.60 (d, *J* = 7.0 Hz, 1H), 8.52 (s, 1H), 8.39 (dd, *J* = 9.0 Hz, *J* = 8.5 Hz, 2H), 8.15 (dd, *J* = 8.0 Hz, J= 1.0 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.78 (dd, *J* = 8.0 Hz, 1H), 7.68 (m, 2H), 7.60 (d, *J* = 7.3 Hz,1H), 7.50 (t, *J* = 8.03 Hz, 1H), 4.43 (t, *J* = 7.3 Hz, 2H), 3.08 (s, 3H), 2.06 (quint, *J* = 7.28 Hz, 2H), 1.49-1.25 (m, 10 H), 0.86 (t, *J* = 7.0 Hz, 3H);

7 ^{13}C{^{1}H} (101 MHz, in CD_2Cl_2): δ 140.9, 139.9, 139.6, 137.9, 137.0, 136.4, 136.1, 134.8, 133.8, 133.6, 132.6, 132.3, 131.3, 129.7, 126.6, 126.5, 124.9, 123.7, 123.1, 122.7, 110.5, 48.2, 32.4, 31.2, 29.8, 29.7, 27.6, 27.3, 23.2, 14.4; C_{ipso}-B are not observed

7 ^{11}B (128 MHz, CD_2Cl_2): δ 45.2 (br);

MS (APCI): calc. for $[M+H]^+$ $C_{33}H_{33}NB$ 454.27, found 454.6

Accurate mass: calc. for $[M+H]^+$ $C_{35}H_{39}BN$ 454.2712, found 454.2691

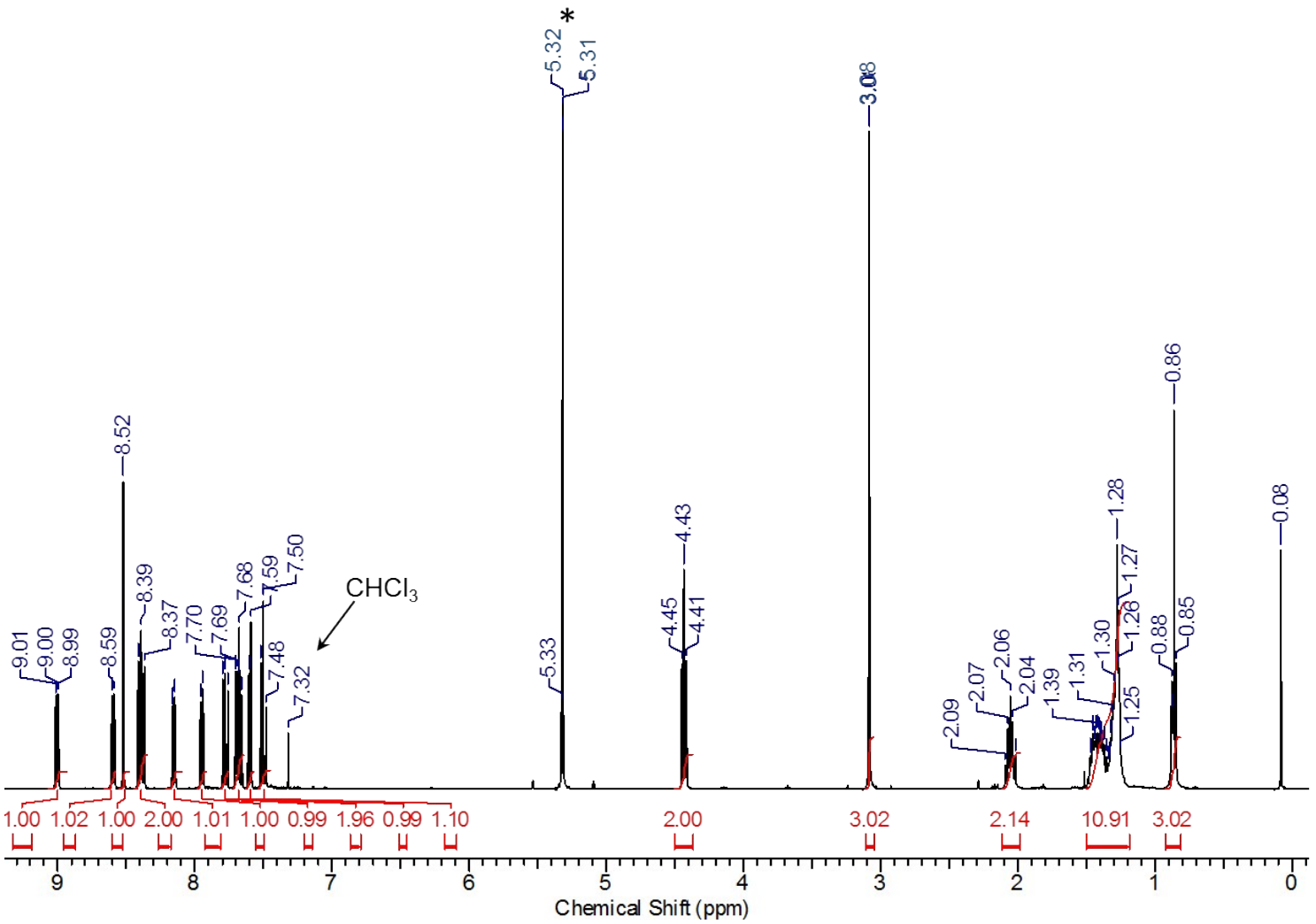


Figure S27: ^{1}H NMR of purified **7** in CD_2Cl_2. The residual protio-solvent peak is labeled '*'. Resonances between 1.5 and 1.25 ppm slightly high in integral presumably due to overlap with residual H_2O.

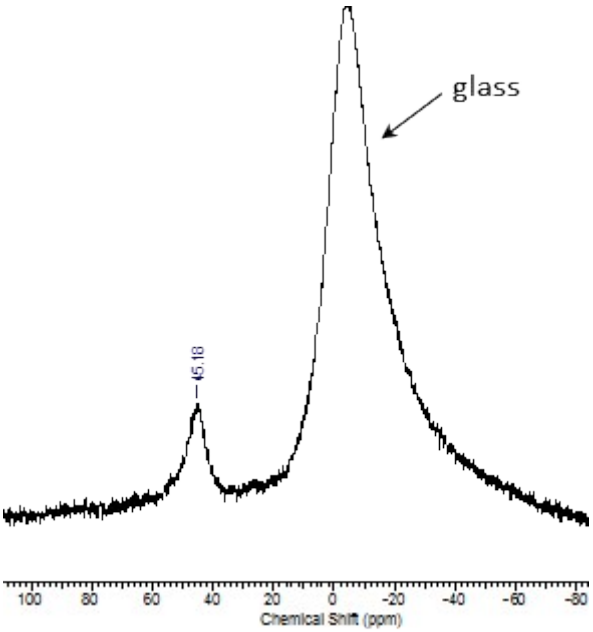


Figure S28: ^{11}B NMR spectrum of purified **7** in CD_2Cl_2.

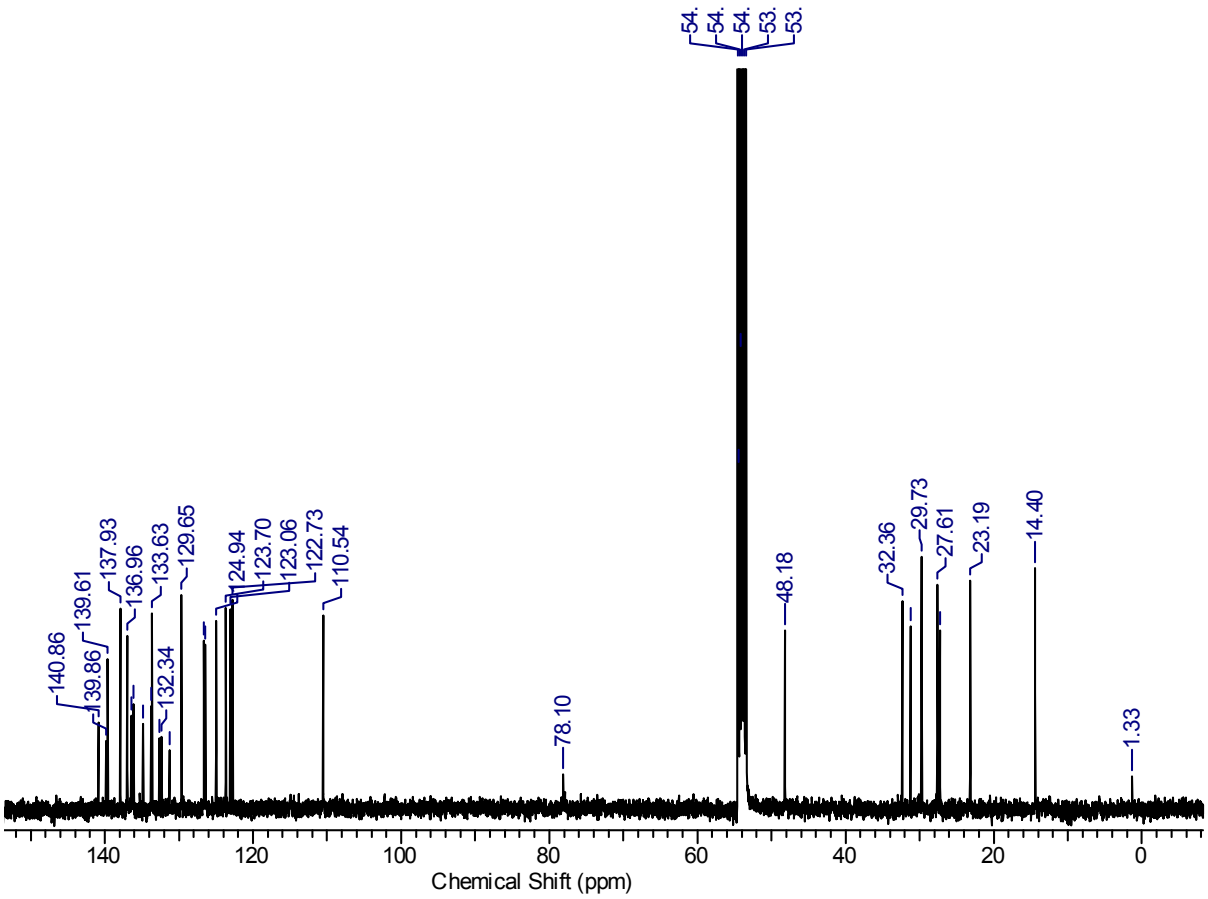


Figure S29: $^{13}C\{^1H\}$ NMR spectrum of purified **7** in CD_2Cl_2 (resonance at 78.1 ppm is due to chloroform).

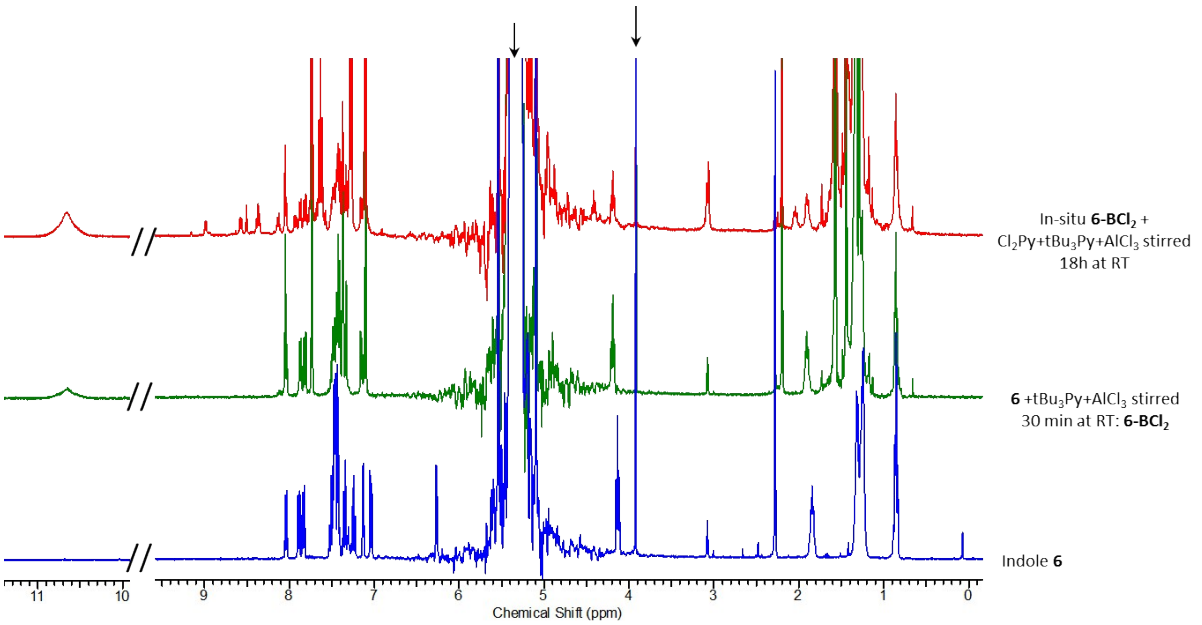


Figure S30: In-situ NMR spectra from the synthesis of **7** with $^{t}Bu_3Py$ / $AlCl_3$ / BCl_3, then $tBu_3Py/Cl_2Py/AlCl_3$. Spectra in protio DCM with a "wet" d_6-DMSO capillary added.

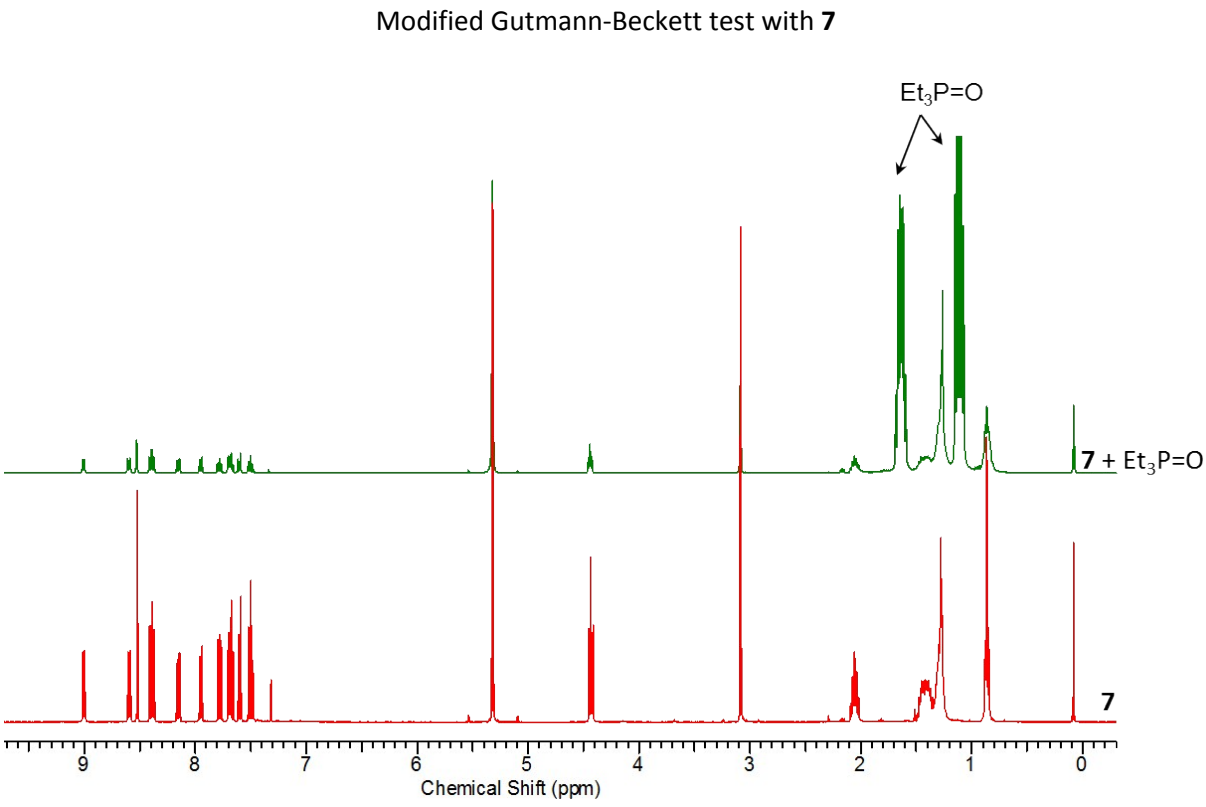


Figure S31: ^{1}H NMR spectra for **7** + $Et_3P=O$ in CD_2Cl_2. The complete lack of change in the resonances for **7** even on addition of excess (6 equivalents) Et_3PO confirms the low Lewis acidity of **7**.

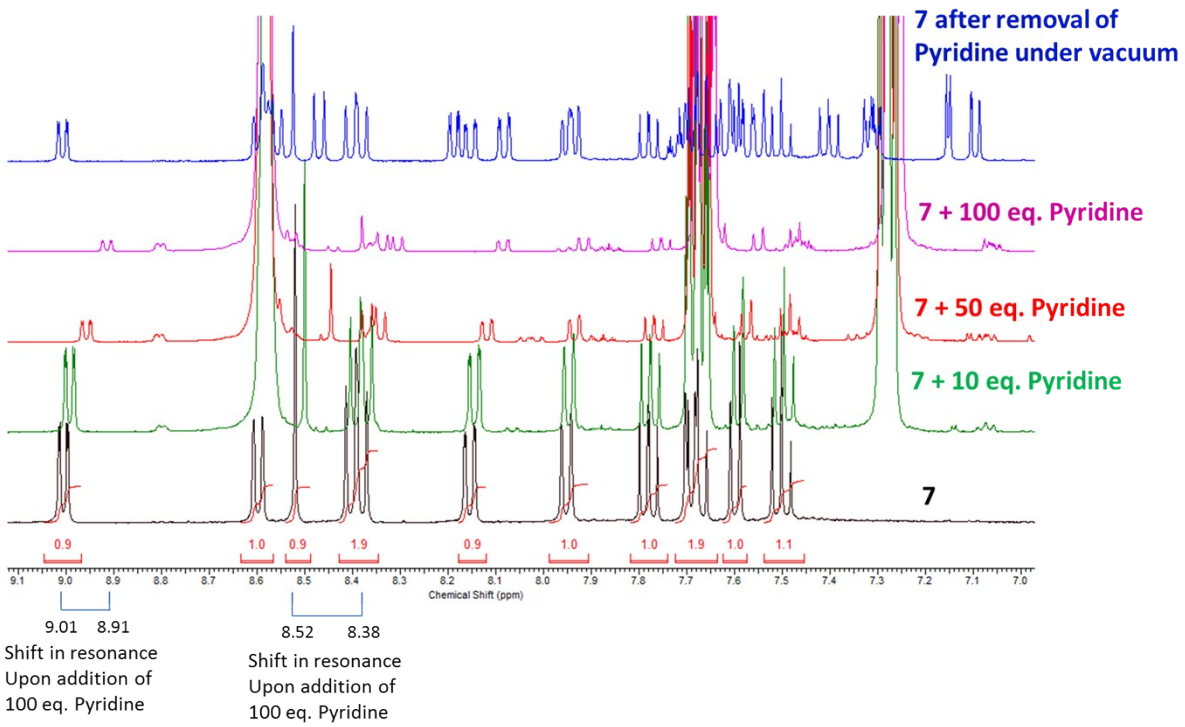


Figure S32: Partial ^{1}H NMR spectra for **7** + 10 to 100 equivalents of "wet" pyridine in "wet"CD_2Cl_2. The up field shift in resonances upon increasing concentration of pyridine suggests weak binding of pyridine and a low Lewis acidity of the boron centre of **7**. A downfield shift to the original chemical shift values is then observed upon the removal of pyridine under vacuum. Compound **7** undergoes decomposition in "wet"CD_2Cl_2 upon the addition of "wet" pyridine and a new product is observed.

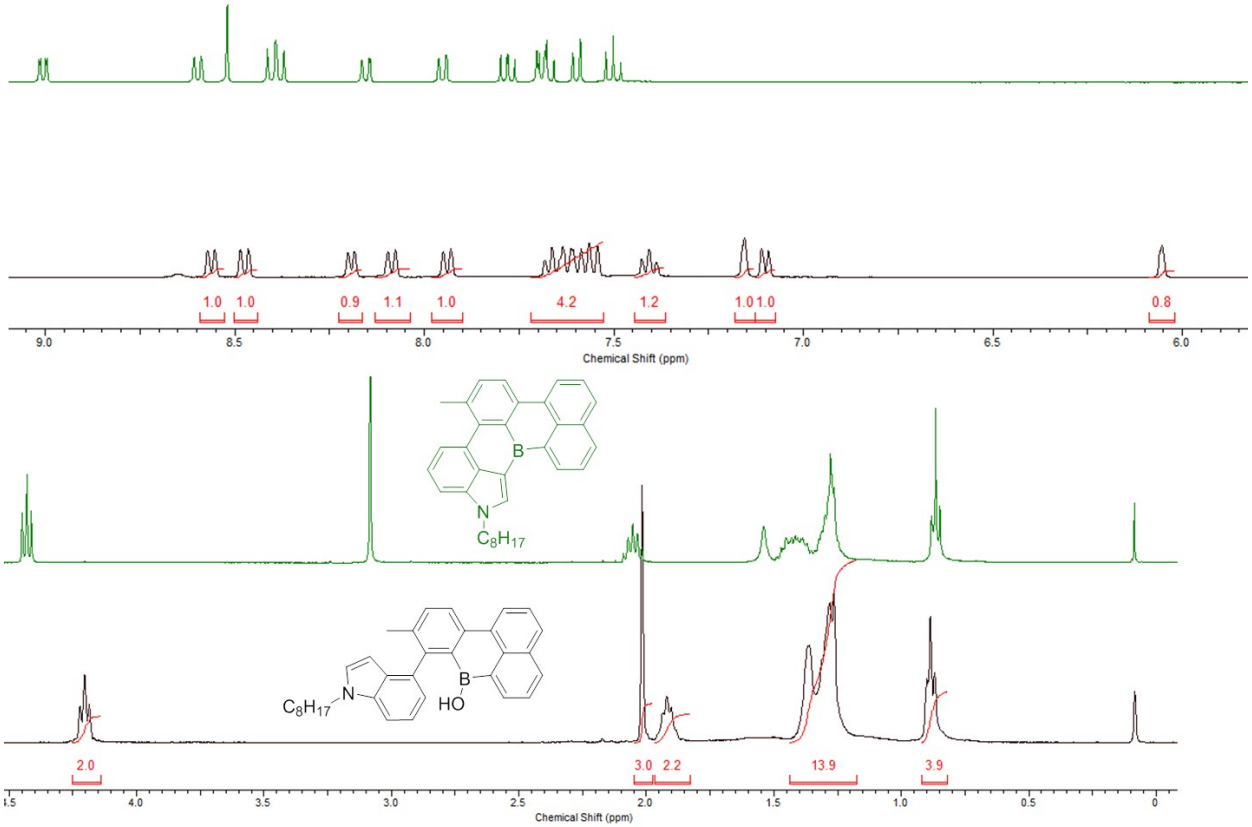


Figure S33: ^{1}H NMR spectra of **7** before (green) and after (black) 5 days in "wet" DCM with ~200 eq. Pyridine. Most notably the ^{1}H NMR spectrum shows 1 resonance consistent with a C2 indole proton at 6.1 ppm, so this product is tentatively assigned as the borinic acid formed by protodeboronation.

Stability of **7** in "wet" CH_2Cl_2

Compound **7** shows no apparent decomposition after 8 days in "wet" CH_2Cl_2.

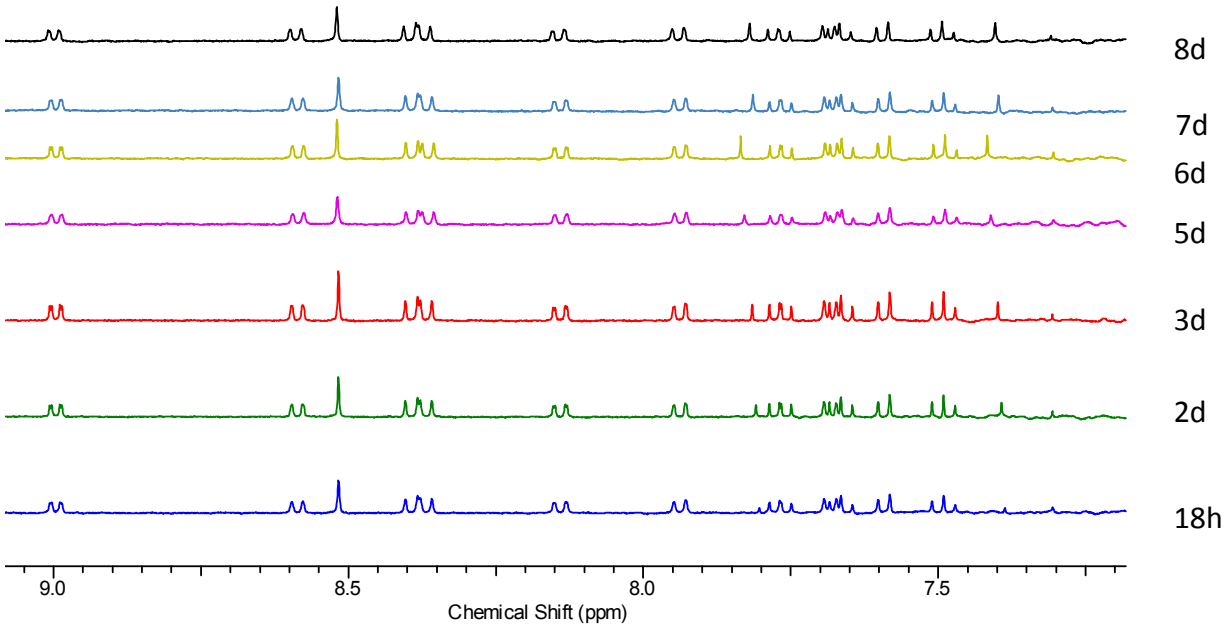


Figure S34: ^{1}H NMR spectrum of **7** in "wet" DCM ("wet" d_6-DMSO in a capillary present)

Theoretical Calculations

Calculations were performed using the Gaussian09 suite of programmes.[6] Calculations were performed at the B3LYP/6-311G(d,p) level[7]. In all cases, structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies. Full Cartesian coordinates are provided below. NICS calculations were performed using two functionals (with a 6311G(d,p) basis set) with and without a PCM (DCM) for the model compound **1-BMes'**. Only minor differences were observed thus for comparison purposes to other literature all calculations were performed at the B3LYP/6-311G(d,p) level.

Table S1: Comparison of NICS values for **1-BMes'**

Method	Ring	NICS(0)	NICS(1)	$NICS(1)_{zz}$
MO6-2X (DCM)	A	-6.02	-10.18	-25.93
	B	4.43	-0.74	2.60
	C	-7.57	-8.52	-20.45
	D	-8.93	-11.25	-28.07
MO6-2X	A	-5.99	-10.13	-25.80
	B	4.89	-0.41	3.62
	C	-7.84	-8.61	-20.78
	D	-8.92	-11.21	-27.99
B3LYP (DCM)	A	-6.45	-9.72	-24.23
	B	3.05	-1.23	1.25
	C	-7.78	-8.13	-19.08
	D	-9.21	-10.74	-26.23
B3LYP	A	-6.39	-9.66	-24.03
	B	3.51	-0.92	2.28
	C	-8.06	-8.21	-19.39
	D	-9.22	-10.73	-26.27

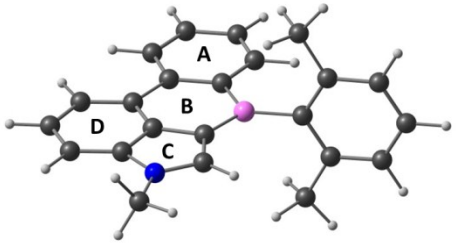
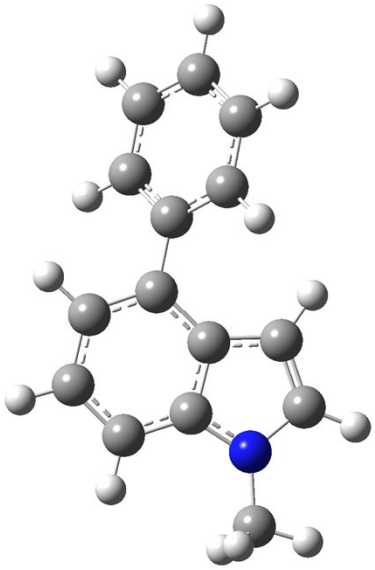


Figure S35: DFT calculated structures (at the B3LYP/6311G{d,p) level) for **1-BMes'**

[6] Gaussian 09, Revision C1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[7] http://comp.chem.umn.edu/info/DFT.htm

1' Energy(optimisation)= -398.053 10^3 kcal/mol



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C	-4.376781000	-0.636219000	0.039992000
H	-4.671683000	1.005108000	1.400331000
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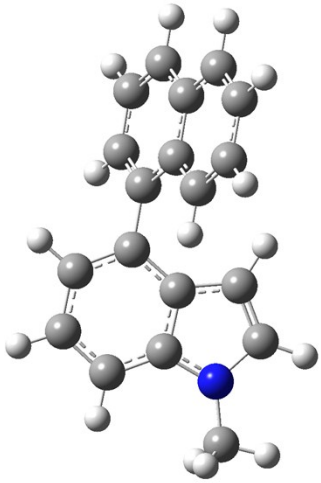
2' Energy(optimisation)= -494.484 10^3 kcal/mol



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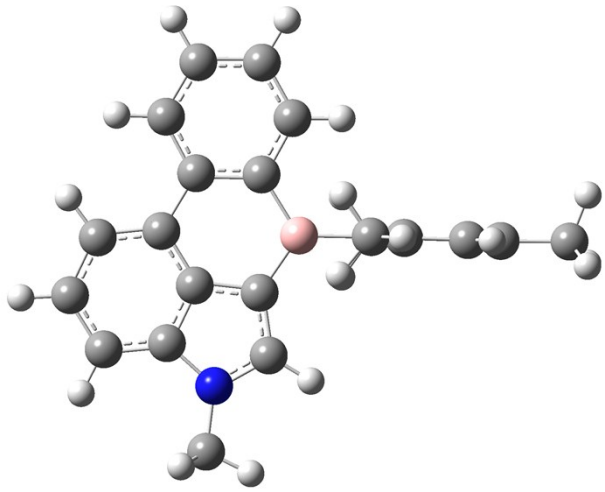
1-BMes' Energy(optimisation) = -632.347 10^3 kcal/mol



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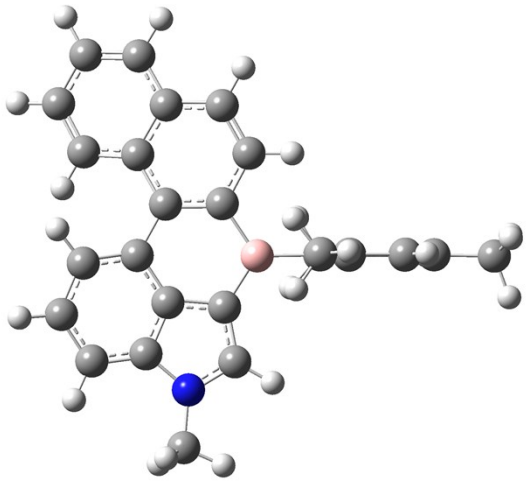
2-BMes' Energy(optimisation) = -728.774 10^3 kcal/mol



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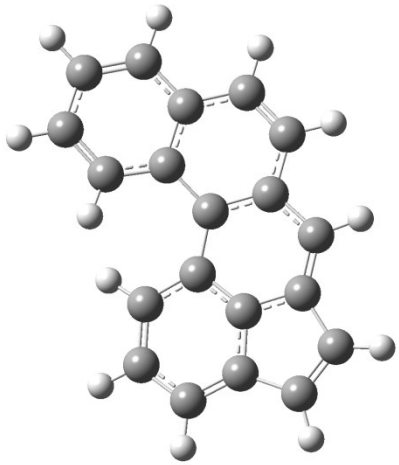

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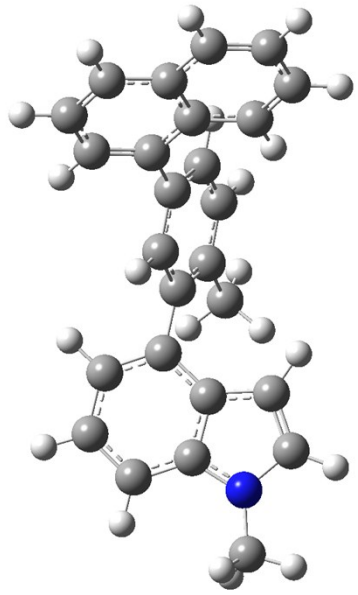
6' Energy(optimisation) = -664.184 10^3 kcal/mol



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C	1.707197000	3.309789000	4.980114000
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C	1.470154000	4.561898000	5.585967000

H	1.655878000	3.224824000	3.900495000
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7' Energy(optimisation) = -678.672 10^3 kcal/mol

NICS(1)$_{zz}$[A]=-3.42
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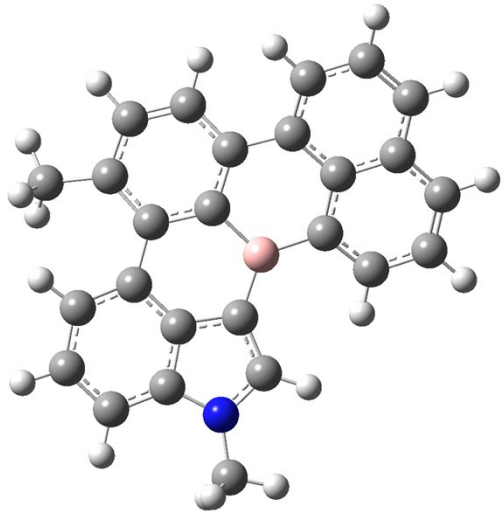

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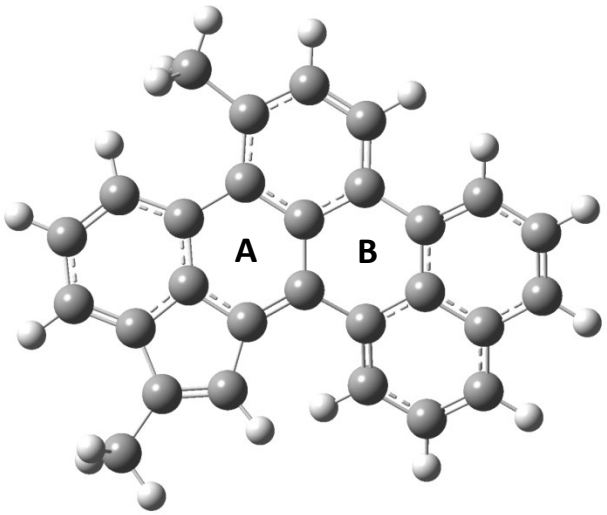
C	1.393844000	-1.593335000	-1.099098000
C	-0.447573000	0.830630000	0.842387000
H	3.715279000	-2.873100000	1.011982000
H	2.990429000	-3.008212000	-1.271938000
H	1.095133000	-1.659018000	-2.138736000
H	-1.175775000	1.626375000	0.886746000
N	-0.242123000	0.192638000	-0.352615000
C	-0.929562000	0.468824000	-1.599818000
H	-1.668688000	1.251690000	-1.433561000
H	-0.225088000	0.808263000	-2.364387000
H	-1.442922000	-0.424677000	-1.965345000
C	2.570671000	-1.284640000	3.118793000
C	1.974131000	-0.184617000	3.836074000
C	3.448578000	-2.160406000	3.807109000
C	2.400151000	0.117138000	5.157043000
C	3.791738000	-1.853990000	5.126278000
C	3.316017000	-0.736000000	5.782774000
H	4.451989000	-2.531024000	5.659073000
H	3.621573000	-0.572607000	6.807453000
C	4.015295000	-3.456133000	3.267061000
H	3.271715000	-4.037308000	2.718676000
H	4.870004000	-3.295487000	2.601569000
H	4.371334000	-4.069515000	4.097175000
C	1.872686000	1.292840000	5.897321000
C	0.696467000	1.981665000	5.456429000
C	0.069145000	1.645460000	4.216209000

C	0.147045000	3.024384000	6.270243000
C	1.982636000	2.805097000	7.822367000
C	-1.122156000	2.283892000	3.890224000
C	-1.061739000	3.646516000	5.870606000
C	0.813174000	3.421711000	7.455797000
H	2.513175000	3.119126000	8.714308000
C	-1.698215000	3.269253000	4.712120000
H	-1.636275000	2.011534000	2.976331000
H	-1.479542000	4.424804000	6.501317000
H	0.392329000	4.221920000	8.055539000
H	-2.632030000	3.739078000	4.423042000
C	0.399797000	0.331621000	1.823977000
C	2.217338000	-1.458759000	1.683847000
B	0.771997000	0.633128000	3.271127000
C	2.498724000	1.747327000	7.051231000
H	3.421453000	1.288922000	7.381032000

8 Energy(optimisation) = -676.525 10^3 kcal/mol

NICS(1)$_{zz}$[A]=-2.94
NICS(1)$_{zz}$[B]=-0.77



C	-4.821062000	-0.852653000	0.103306000
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C	-2.815900000	0.473226000	-0.044869000
C	-3.606405000	1.648082000	0.068404000
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C	-1.350911000	0.554579000	-0.220981000
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C	-1.458015000	2.960660000	0.301324000
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C	1.351732000	3.053223000	0.475934000
C	0.598283000	4.132872000	0.853090000

C	-0.806315000	4.088032000	0.765699000
H	-5.281496000	-1.833757000	0.132451000
H	-2.861396000	-1.673594000	-0.014824000
H	2.434932000	3.091490000	0.508796000
H	1.078181000	5.034823000	1.213423000
H	-1.382317000	4.944667000	1.087154000
H	3.421453000	1.288922000	7.381032000
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C	0.824247000	-0.456885000	-0.626994000
H	1.392590000	-1.332675000	-0.916689000
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C	-7.757402000	4.284049000	0.187148000
H	-7.876907000	2.208461000	0.492173000
C	-5.623090000	5.263516000	-0.185274000
C	-6.983218000	5.431602000	-0.060334000
H	-8.828507000	4.387806000	0.315422000
H	-7.450134000	6.408220000	-0.128976000
C	-3.648232000	4.067269000	-0.126972000
C	-4.501901000	6.194432000	-0.402653000
C	-3.346463000	5.486663000	-0.362751000
H	-2.364592000	5.900045000	-0.540446000
C	-7.123278000	0.010789000	0.158881000
H	-7.579587000	0.326021000	1.100079000
H	-7.633387000	0.524615000	-0.658196000
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H	-5.294046000	7.832667000	-1.529611000
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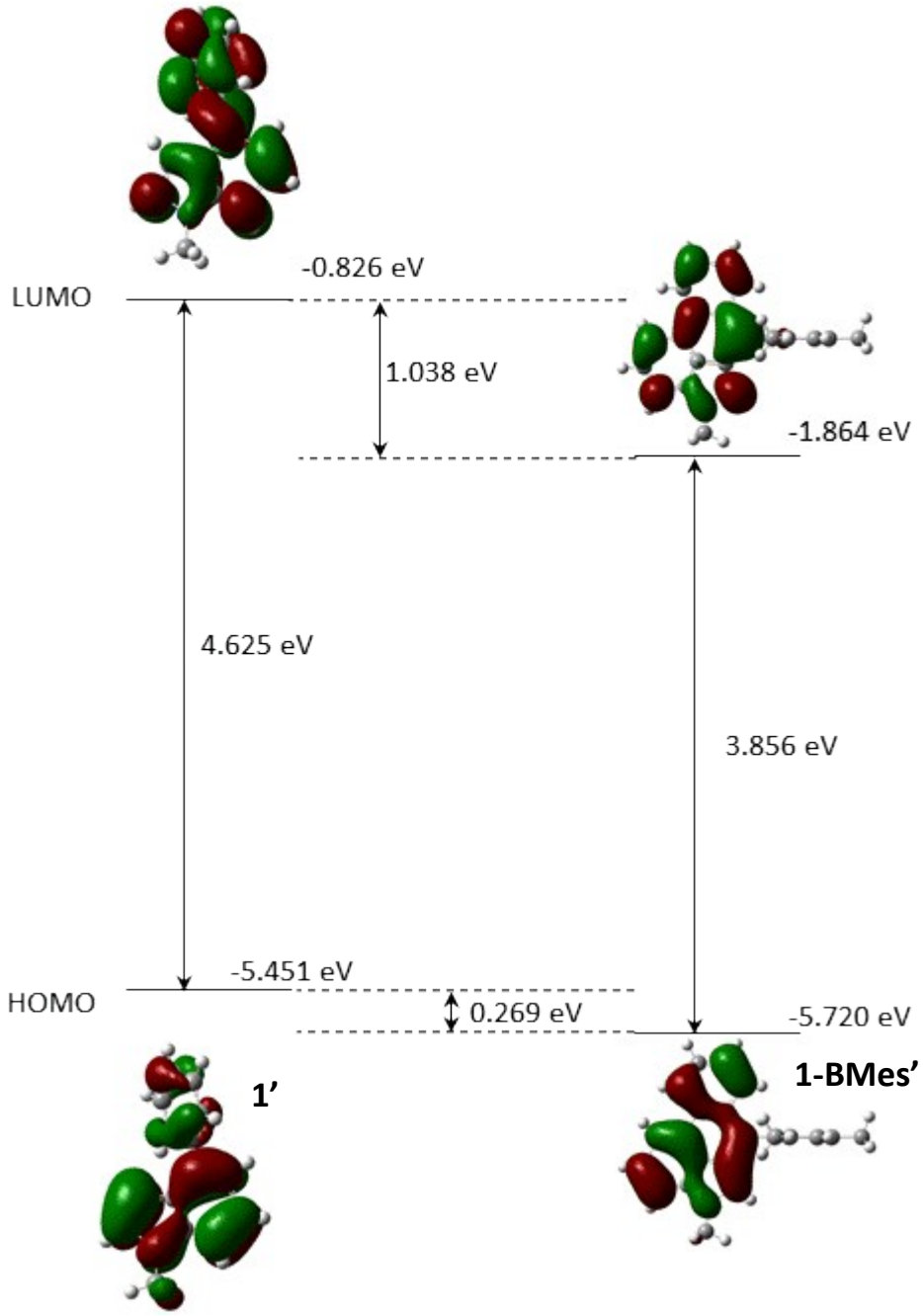

Figure S36: HOMO and LUMO energy levels of **1'** and **1-BMes'** (isovalue 0.02)

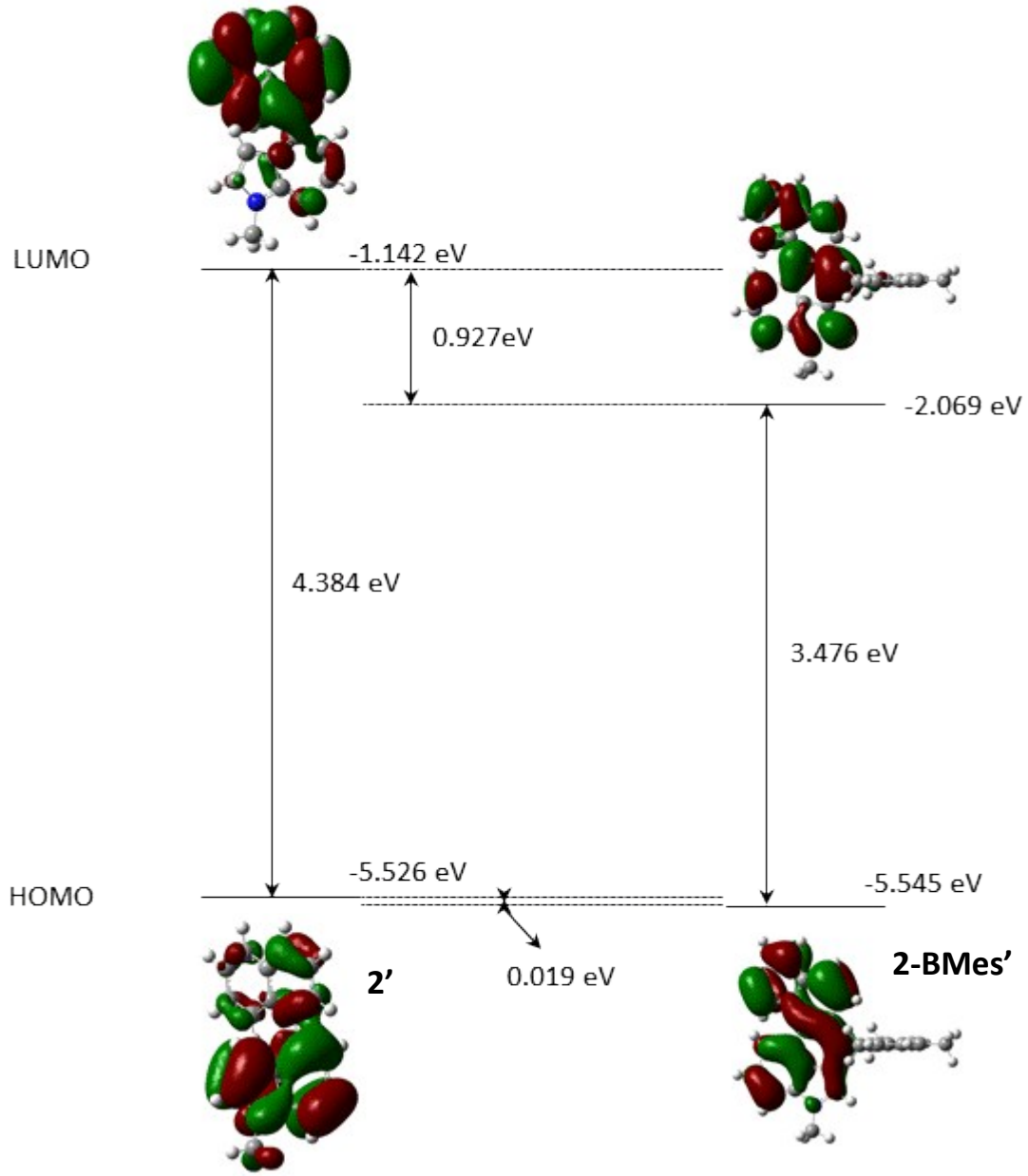

Figure S37: HOMOs and LUMOs levels of **2’** and **2-BMes’** (isovalue 0.02)

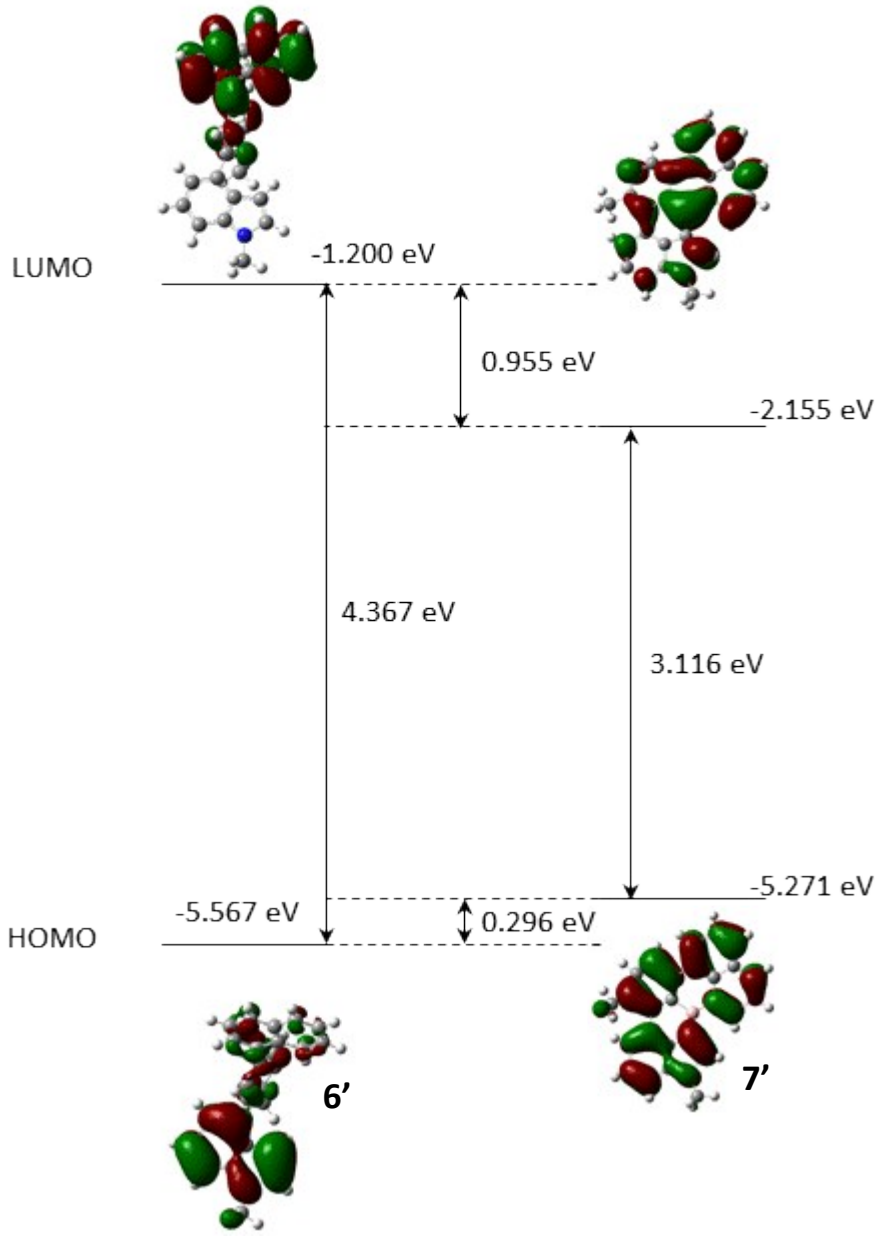

Figure S38: HOMOs and LUMOs levels of **6'** and **7'** (isovalue 0.02)

Crystallography Data

Single crystals of **7** suitable for X-ray crystallographic analysis were obtained by slow evaporation of dichloromethane. The measurement was performed at 100 K.
Data Collection. . Synchrotron X-ray data were collected at beamline I19 (λ = 0.6889 Å) Diamond Light Source[8] . Data were measured using CrystalClear-SM Expert 2.0 r5 suite of programs.

Crystal structure determinations and refinements. X-ray data were processed and reduced using CrysAlisPro suite of programs. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[9] The crystal structures were solved and refined against all F^2 values using the SHELXTL and Olex 2 suite of programs.[10] All the atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

CCDC 1494581 contains the supplementary crystallographic data for this paper.

[8] Nowell H, Barnett SA, Christensen KE, Teat SJ, Allan DR. *J Synchrotron Radiat.*,**2012,** *19***,** 435-441.
[9] (a) G. M. Sheldrick, *SADABS*, empirical absorption correction program based upon the method of Blessing. (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*. (c) R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33-38.
[10] a) Sheldrick. G. M., *Acta Crystallogr.*, **2015,** *C71*, 3-8, b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann,. J. Appl. Cryst., **2009,** *42*, 339–341

Table S2. Crystallographic information for **7**

	7
Crystal colour	Yellow
Crystal size (mm)	0.05 × 0.01 × 0.01
Crystal system	Triclinic
Space group, *Z*	P-1, *2*
a (Å)	7.8135(10)
b (Å)	12.3648(19)
c (Å)	12.4862(16)
α (°)	100.198(12)
β (°)	93.594(10)
γ (°)	92.798(11)
V (Å^3)	1182.7(3)
Density (Mg.m^{-3})	1.273
Wavelength (Å)	0.6889
Temperature (K)	100
μ(Mo-Kα) (mm^{-1})	0.068
2Θ range (°)	3.22 to 49.028
Reflns collected	9631
Independent reflns (R_{int})	4194, (0.1342)
Reflns used in refinement, *n*	4194
L.S. parameters, *p*	318
No. of restraints, *r*	0
*R*1 (*F*)[a] *I* > 2.0σ*(I)*	0.0760
*wR*2(F^2),[a] all data	00.1924
S(F^2),[a] all data	0.989

[a] $R1(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR^2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

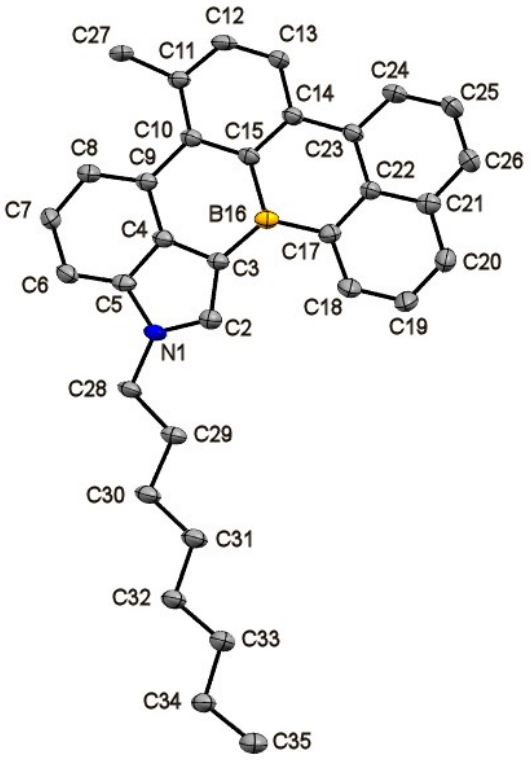

Figure S39: X-ray crystal structure of **7** with numbering (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

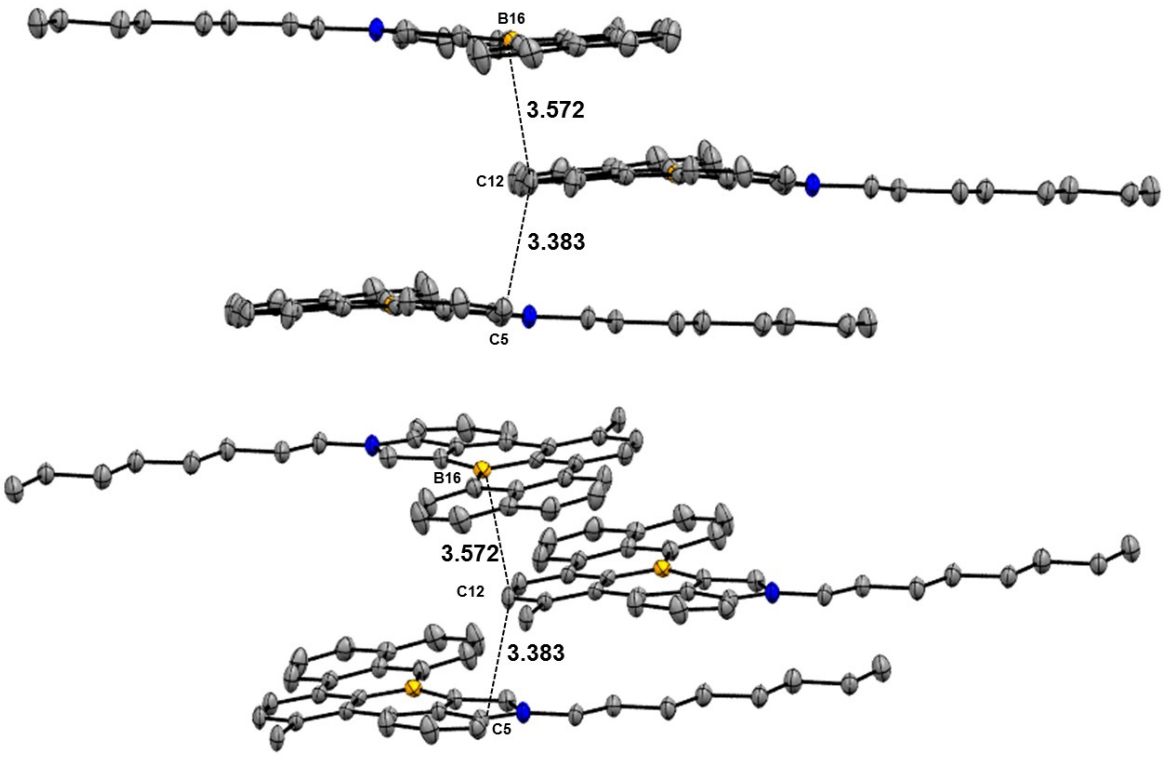

Figure S40: X-ray crystal packing structure of **7** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

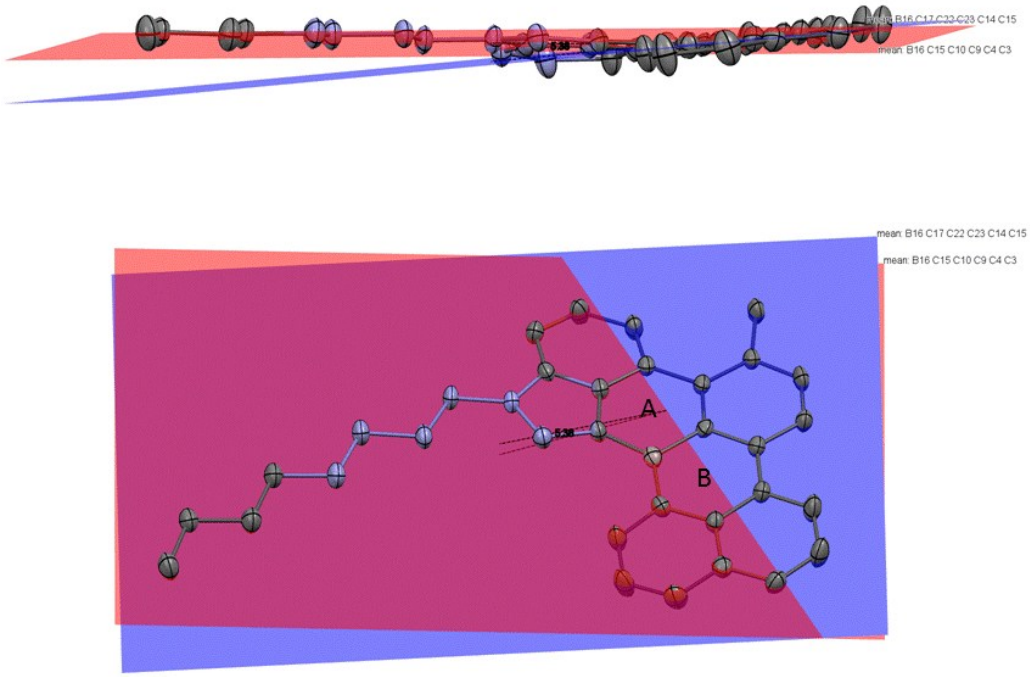

Figure S41: planes between rings A and B of the crystal structure of **7**. Hydrogen atoms are omitted for clarity.

Table S3: Selected bond distances (Å) of the crystal structure of **7**.

Bonds	Distances (Å)
N1-C2	1.355(5)
C2-C3	1.393(5)
C3-C4	1.410(5)
C4-C5	1.409(5)
C5-N1	1.397(4)
B16-C3	1.527(5)
B16-C17	1.544(5)
B16-C15	1.555(5)

Photophysical Data

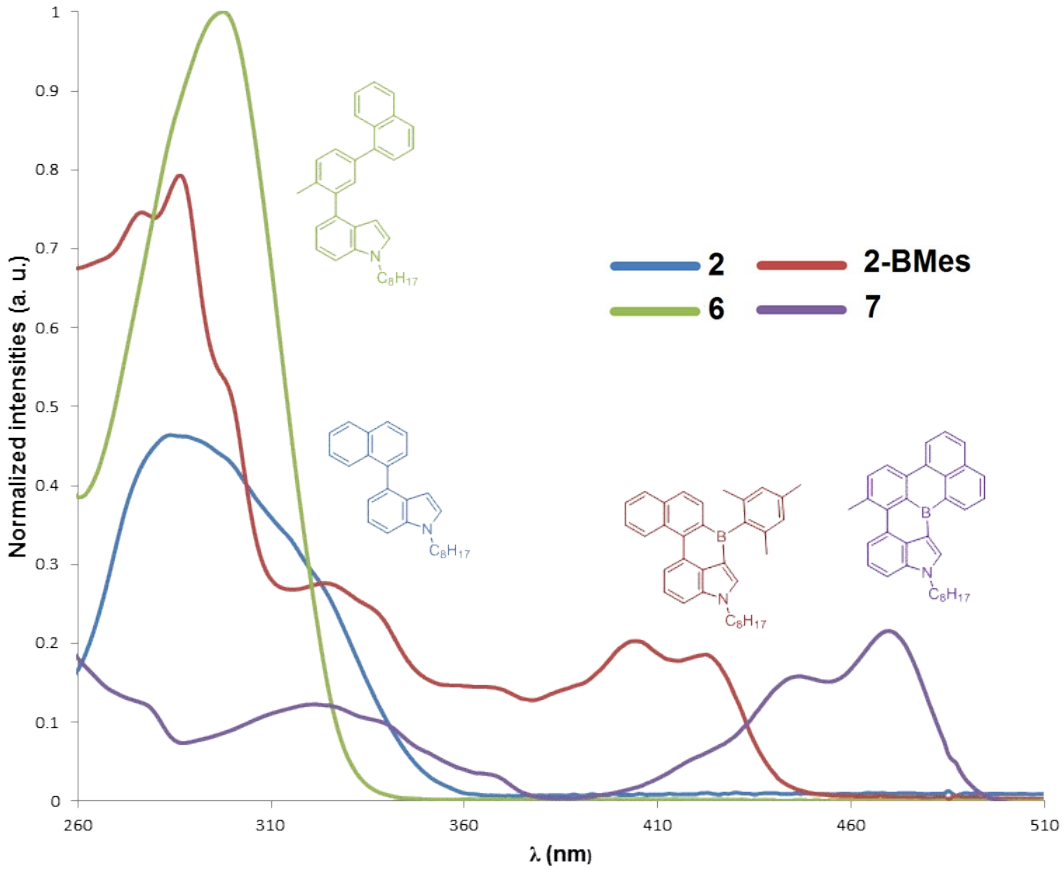

Figure S42: Normalised UV/vis absorption spectra (1 x 10^{-5} in CH_2Cl_2).

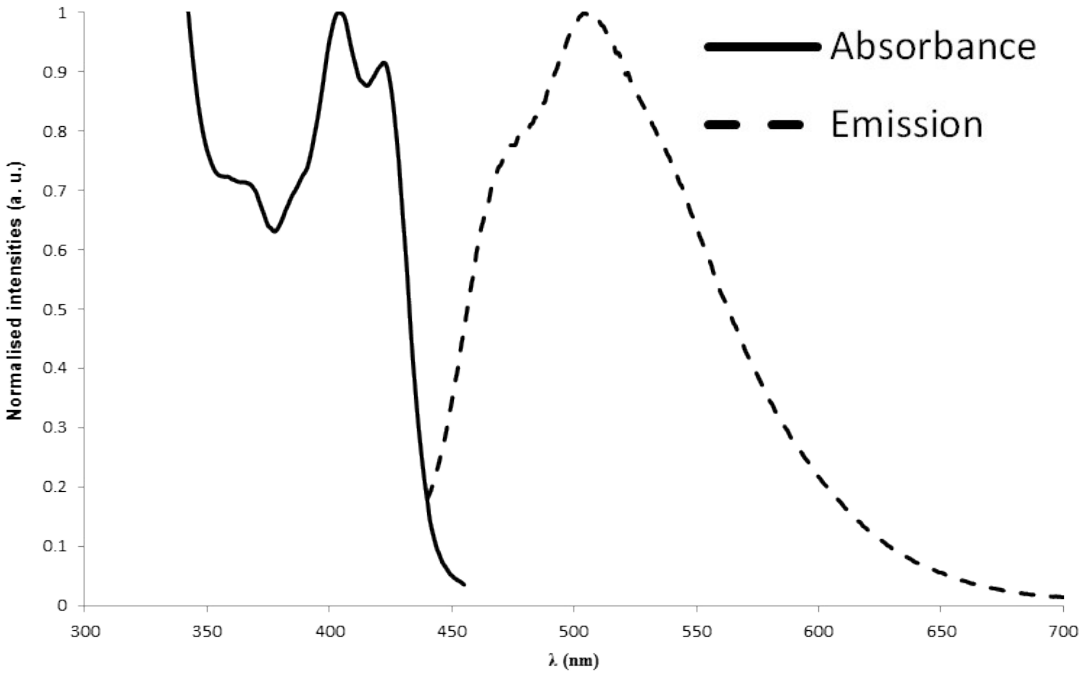

Figure S43: Normalised UV/vis absorption and emission spectra of **2-BMes** (1 x 10^{-5} CH_2Cl_2).

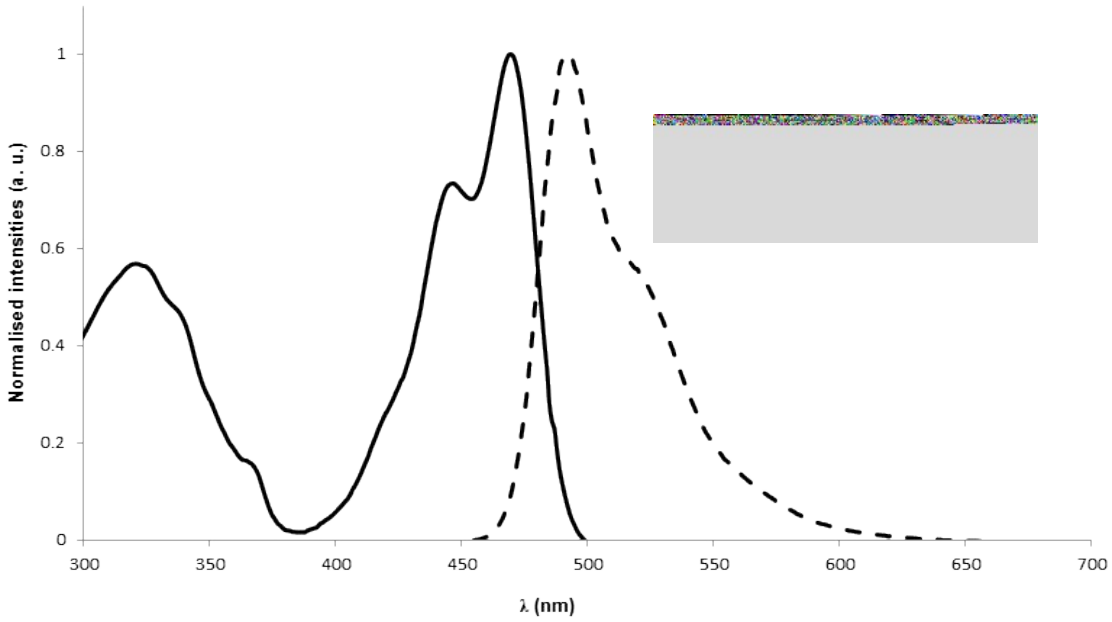

Figure S44: Normalised UV/vis absorption and emission spectra in of **7** (1 x 10^{-5} CH_2Cl_2).

Cyclic Voltammograms

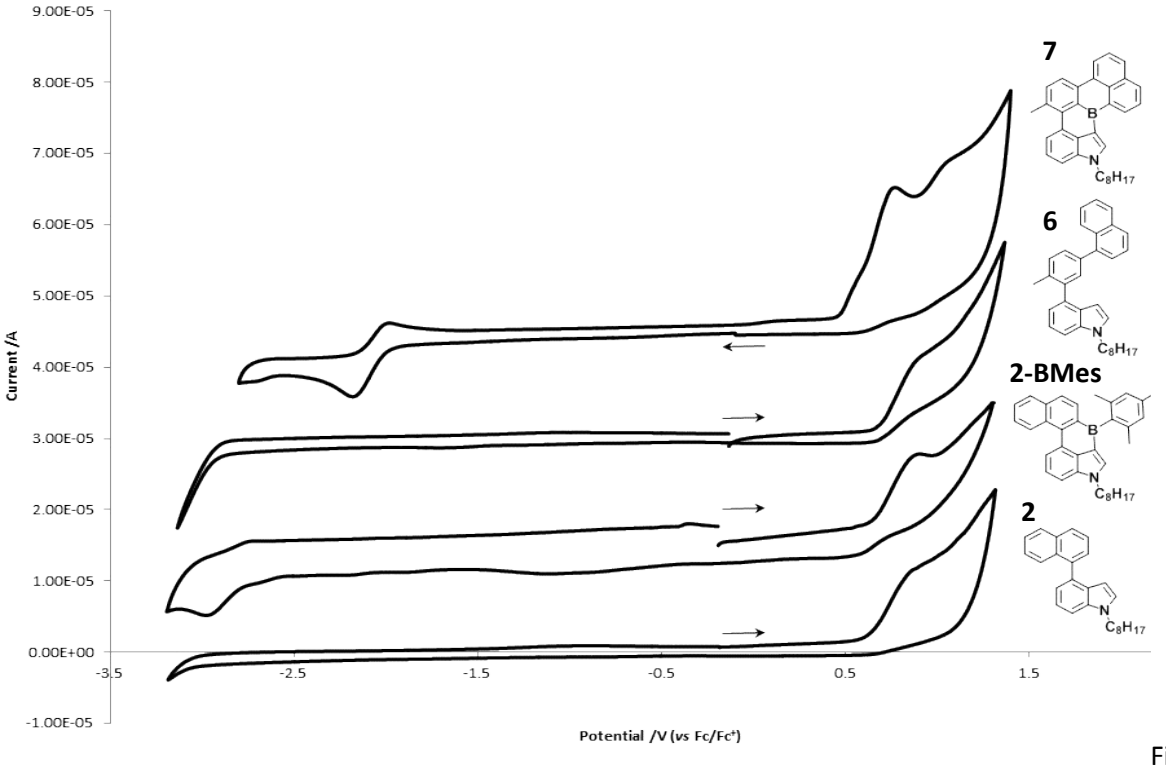

Figure S45: Cyclic voltammogram in THF (1 mM), measured with $^{n}Bu_4NPF_6$ (0.1 M) as a supporting electrolyte at a scan rate of 25 mV s^{-1}. An $Ag/AgNO_3$ non-aqueous reference electrode was used and all scans were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) redox couple.