Controlling Selectivity in N-Heterocycle Directed Borylation of Indoles

Supporting Information

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1. General experimental

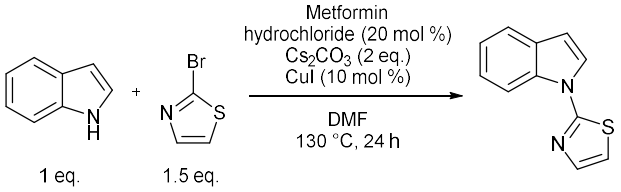
All reactions were performed under an inert atmosphere using standard Schlenk techniques unless otherwise stated. All chemicals were purchased from commercial sources and used without further purification unless stated otherwise. BCl_3 and BBr_3 solutions were transferred to Schlenks fitted with J. Youngs valves prior to use. Dry solvents were obtained from an Inert PureSolv MD5 SPS machine or dried over CaH_2 and stored over 3 Å molecular sieves.

Bruker 300, Bruker 400 and Bruker 500 MHz NMR spectrometers were used to obtain $^{13}C\{^1H\}$, ^1H, ^{11}B NMR spectra. $CDCl_3$ or CD_2Cl_2 was used as the solvent in all cases and the residual $CHCl_3$ or CH_2Cl_2 was used as reference (δ_{1H} 7.26 ppm and 5.32 ppm respectively) for $^{13}C\{^1H\}$ and ^1H NMR spectra. ^{11}B NMR spectra were referenced to external BF_3-Et_2O. NMR Spectroscopy was undertaken at room temperature (~20 °C), spin-spin J coupling constants are reported in hertz (Hz) and the chemical shifts δ are reported in ppm. The multiplicity of the signals is given as s, d, t, q, dd, dt, td and m, for singlet, doublet, triplet, quartet, doublet of doublets, doublet of triplets, triplet of doublets and multiplet respectively. C-B bonded and C-$(N)_3$ ^{13}C resonances were not detected in the $^{13}C\{^1H\}$ NMR spectra presumably due to broad resonances due to quadrupolar effects.

Column chromatography was performed on 40-63 μm silica gel manually or using a CombiFlash NextGen 300+ Autocolumn system. Mass spectrometry was performed by the mass spectrometry services at either the University of Manchester or the University of Edinburgh using electrospray or APCI ionisation modes.

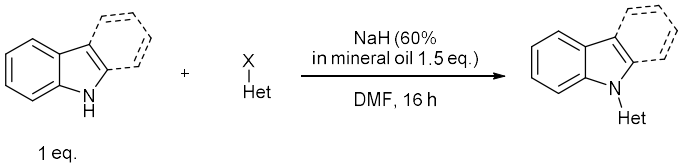
Cyclic voltammetry measurements were conducted under an N_2 atmosphere using a CH-Instrument 1110C Electrochemical/Analyser potentiostat. THF (1 mM) was used as the solvent in all cases and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the electrolyte. A glassy carbon working electrode was used and platinum wire as the counter and reference electrodes. All potentials were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

2. Synthesis of *N*-substituted starting materials

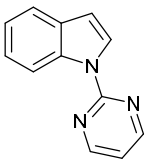


To an ampule containing indole (1.170 g, 10 mmol), CuI (0.190 g, 1 mmol), metformin hydrochloride (0.331 g, 2 mmol), and Cs_2CO_3 (6.516 g, 20 mmol) was added dry DMF (20 mL) and 2-bromothiazole (1.35 mL, 15 mmol). The reaction was heated to 130 °C and stirred for 24 hours. The reaction mixture was then diluted with EtOAc and the solid was removed by filtration. The filtrate was washed with water and brine, dried over $MgSO_4$ and purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product, **1-(2-thiazolyl)-1H-indole (12)** (0.656 g, 33%) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.69 (d, *J* = 3.5 Hz, 1H), 7.65 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.61 (d, *J* = 3.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.28 – 7.23 (m, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.72 (dd, *J* = 3.5, 0.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.8, 140.2, 135.2, 130.3, 126.6, 124.2, 122.4, 121.4, 113.3, 113.1, 107.2. Analytical data are in accordance with the literature.[S1]

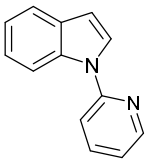
2.1 Synthesis of N-substituted indole starting materials: GP1



A solution of indole or carbazole (10 mmol) in DMF (10 mL) was slowly added to a mixture of 60% NaH in mineral oil (0.599 g, 15 mmol) in DMF (10 mL). The reaction was stirred for 15 minutes after which the appropriate 2-haloheterocycle in dry DMF (5 mL) was added. The reaction was heated to 100 °C or 130 °C and stirred overnight. The reaction was cooled to room temperature and quenched with H_2O (50 mL). EtOAc (50 mL) was added and the organic phase was washed with water (3 x 50 mL). The aqueous washings were back extracted with EtOAc (2 x 50 mL). The combined organic fractions were dried over $MgSO_4$ and the product was purified by column chromatography on silica gel (EtOAc/Hexanes) to yield the pure product

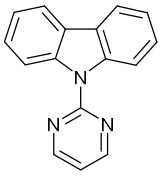


***N*-(2-pyrimidyl)indole (1)** was prepared following GP1 using 2-chloropyrimidine (1.718 g, 15 mmol), indole (1.171 g, 10 mmol) and stirred at 130 °C to give the pure product (1.734 g, 89%) as an off-white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 4.8 Hz, 2H), 8.28 (d, J = 3.7 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 4.8 Hz, 1H), 6.71 (d, J = 3.7 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ. 158.3, 158.0, 135.5, 131.5, 125.9, 123.8, 122.3, 121.0, 116.4, 116.3, 107.1. Analytical data are in accordance with the literature.[S2]

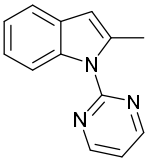


***N*-(2-pyridyl)indole (3)** was prepared following GP1 using 2-bromopyridine (1.14 mL, 12 mmol), indole (1.171 g, 10 mmol) and stirred at 130 °C to give the pure product (0.829 g, 43%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.73 (d, *J* = 3.5 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H),

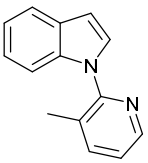
7.51 (d, *J* = 8.4 Hz, 1H), 7.30 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 (m, 1H), 6.72 (d, *J* = 3.5 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.7, 149.2, 138.1, 135.2, 130.6, 126.1, 123.3, 121.4, 121.2, 120.2, 114.8, 113.1, 105.7. Analytical data are in accordance with the literature.[S3]



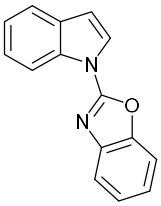
9-(Pyrimidin-2-yl)-9H-carbazole (5) was prepared following GP1 using 2-chloropyrimidine (1.370 g, 12 mmol), carbazole (1.670 g, 10 mmol) and stirred at 130 °C to give the pure product (2.040 g, 83%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.89 – 8.80 (m, 4H), 8.14 – 8.03 (m, 2H), 7.51 (m, 2H), 7.42 – 7.34 (m, 2H), 7.13 (t, *J* = 4.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.3, 158.0, 139.3, 126.8, 126.0, 122.4, 119.7, 116.4, 116.1. Analytical data are in accordance with the literature.[S2]



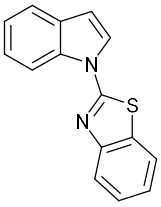
***N*-(2-pyrimidyl)-2-methylindole (7)** was prepared following GP1 using 2-chloropyrimidine (1.718 g, 15 mmol), 2-methylindole (1.312 g, 10 mmol) and stirred at 130 °C to give the product (1.317 g, 63%) as a yellow solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.15 (m, 2H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.48 – 6.40 (m, 1H), 2.76 – 2.69 (m, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.6, 158.2, 137.9, 137.0, 129.6, 122.5, 121.9, 119.6, 117.04, 114.1, 106.8, 16.7. Analytical data are in accordance with the literature.[S4]



3-methyl-2-indolylpyridine (9) was prepared following GP1 using 2-bromo-3-methylpyridine (1.34 mL, 12 mmol), indole (1.171 g, 10 mmol) and stirred at 130 °C to give the pure product (0.642 g, 31%) as an orange solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.77 (m, 1H), 7.71 – 7.66 (m, 1H), 7.36 (d, *J* = 3.3 Hz, 1H), 7.32 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.24 – 7.14 (m, 3H), 6.71 (dd, *J* = 3.3, 0.8 Hz, 1H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 150.9, 146.9, 141.0, 136.3, 129.3, 129.0, 127.7, 123.0, 122.7, 121.2, 120.7, 111.3, 104.1, 18.1. Analytical data are in accordance with the literature.[S5]

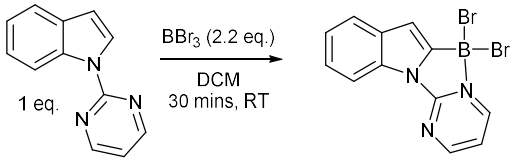


***N*-(2-benzoxazolyl)indole (15)** was prepared following GP1 using 2-chlorobenzoxazole (1.37 mL, 12 mmol), indole (1.171 g, 10 mmol) and stirred at 130 °C to give the pure product (2.063 g, 88%) as a white solid **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.89 (d, *J* = 3.6 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.55 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.45 (m, 1H), 7.36 (td, *J* = 7.7, 1.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 6.79 (dd, *J* = 3.6, 0.8 Hz, 1H)**. ^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 154.9, 148.7, 141.7, 134.9, 130.3, 125.1, 124.9, 124.8, 123.8, 123.2, 121.4, 119.0, 114.7, 110.1, 108.7. Analytical data are in accordance with the literature.[S6]



***N*-(2-benzothiazolyl)indole (16)** was prepared following GP1 using 2-bromobenzothiazole (2.360 g, 11 mmol), indole (1.171 g, 10 mmol) and stirred at 100 °C to give the pure product (1.260 g, 50%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.66 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.49 (m, 1H), 7.43 (m, 1H), 7.35 (m, 1H), 7.30 (m, 1H), 6.78 (d, *J* = 3.5 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.1, 151.4, 135.6, 131.5, 130.6, 126.8, 126.7, 124.6, 124.5, 123.0, 122.1, 121.5, 121.3, 114.4, 108.4. Analytical data are in accordance with the literature.[S7]

3. Directed borylation with BX_3



To an ampule fitted with a J-Youngs tap was added compound **1** (0.039 g, 0.2 mmol) which was dissolved in DCM (0.7 mL). BBr_3 (0.44 mL, 1M in DCM) was added, the ampule was sealed and the mixture was stirred at room temperature for 0.5 hours. The solvent/volatiles were removed under vacuum and the solid dried. The product was dissolved in DCM, passed through a filter and the volatiles were removed to give a solid which was washed with pentane and dried to give the pure product, **2-Br** (0.054 g, 74%) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.97 (dd, J = 4.7, 2.2 Hz, 1H), 8.82 (dd, J = 6.1, 2.3 Hz, 1H), 8.19 – 8.10 (m, 1H), 7.60 (dt, J = 7.4, 1.0 Hz, 1H), 7.40 – 7.26 (m, 3H), 6.93 (d, J = 0.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.9, 151.8, 135.7, 132.7, 125.1, 124.8, 122.4, 114.8, 113.9, 113.3. **^{11}B NMR** (160 MHz, $CDCl_3$) δ -6.82. **[Acc. Mass]** Calculated $[M+H]^+$: 363.92508, Observed $[M+H]^+$: 363.92830. For spectra of **2-Br** see section 8.

When conducting the borylation of **1** with BCl_3, a hindered base is required to sequester HCl by products and drive the reaction to completion. C2 is always the major product (**2-Cl).**

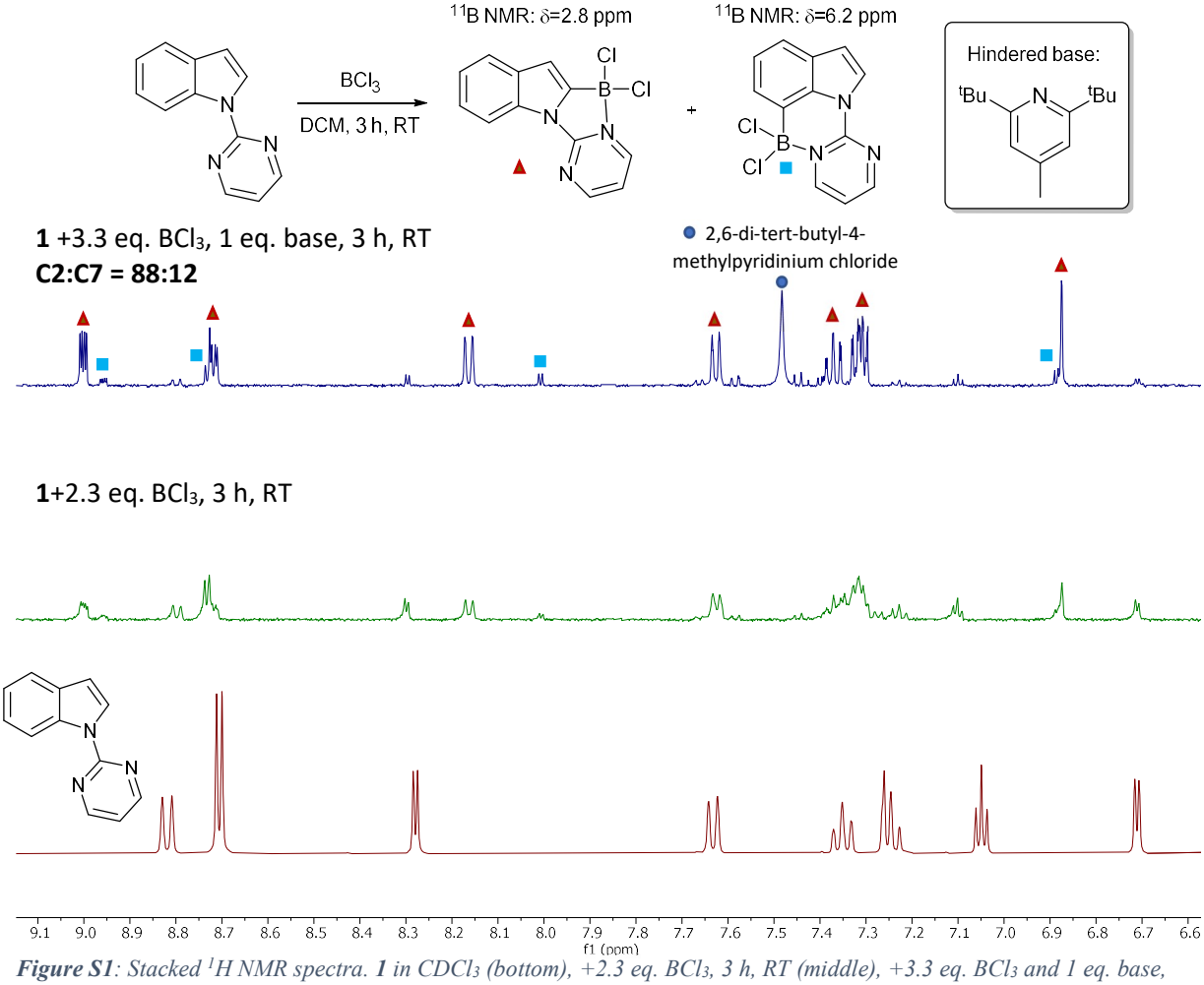


***Figure S1**: Stacked ^{1}H NMR spectra. **1** in $CDCl_3$ (bottom), +2.3 eq. BCl_3, 3 h, RT (middle), +3.3 eq. BCl_3 and 1 eq. base, 3 h, RT (top).* **Note: only those resonances that are clearly distinguishable from the C2-BCl_2 product or compound 1 have been labelled as C7-BCl_2.**

Synthesis of 2-Cl

To an ampule fitted with a J-Youngs tap was added compound **1** (0.020 g, 0.1 mmol) which was dissolved in DCM (0.35 mL). BBr_3 (0.32 mL, 1M in DCM) was added, the ampule was sealed and the mixture was stirred at room temperature for 3 hours. The solvent/volatiles were removed under vacuum and the solid dried. The major species was identified as **2-Cl** by a diagnostic singlet at 6.9 ppm attributed to the C3-H. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 9.00 (dd, *J* = 4.8, 2.2 Hz, 1H), 8.74 – 8.69 (m, 1H), 8.16 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 6.88 (s, 1H). **^{11}B NMR** (160 MHz, CD_2Cl_2) δ 2.69.

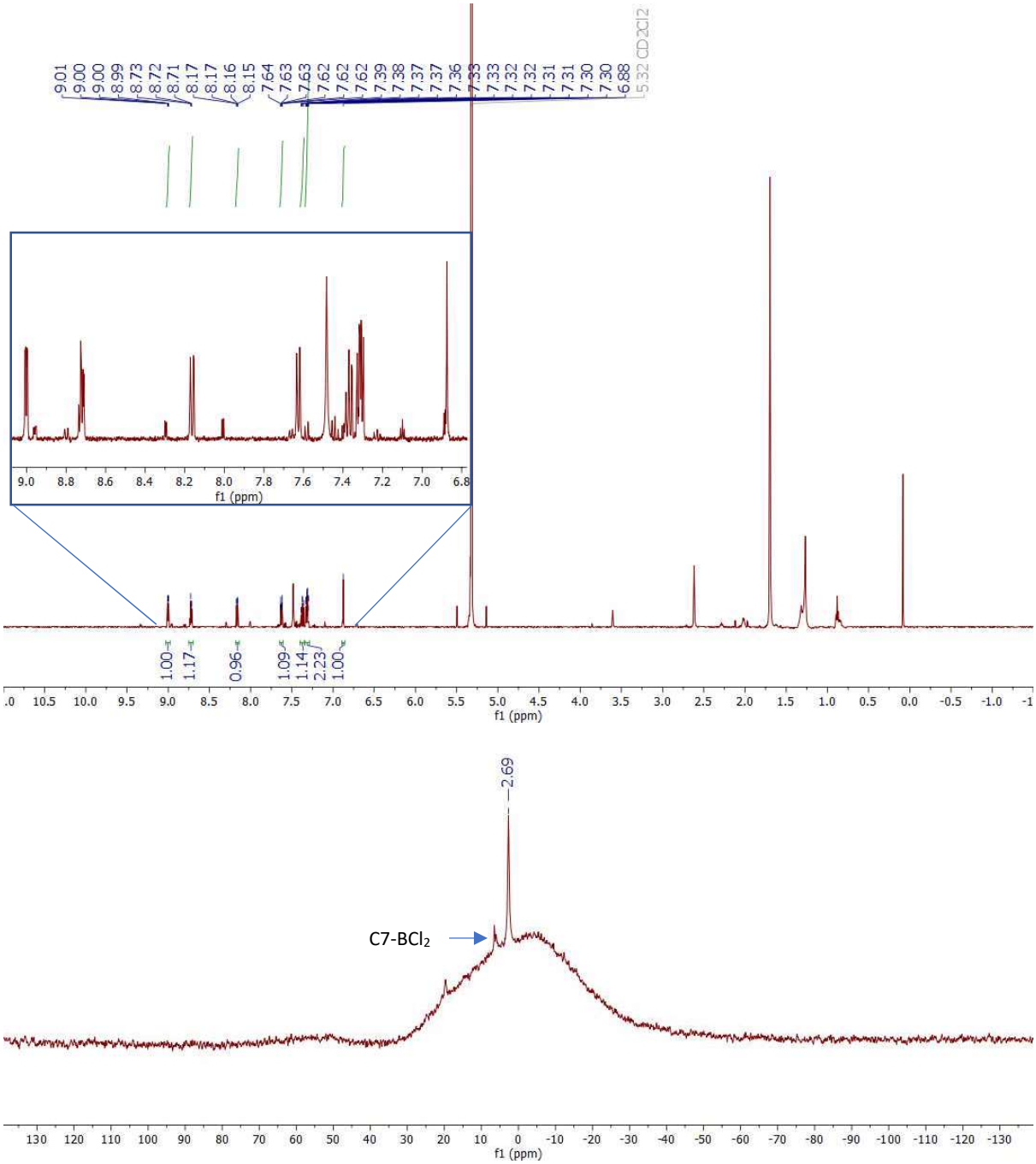
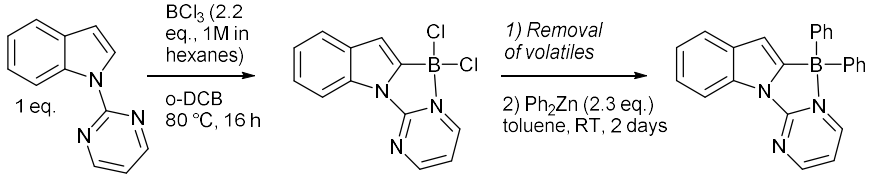


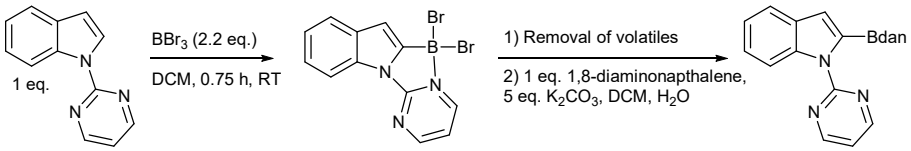
***Figure S2**: Crude ^{1}H (top) and ^{11}B (bottom) NMR spectra of **2-Cl** (major product) formed by reaction of **1** with BCl_3 in the presence of hindered base, 2,6-Di-tert-butyl-4-methylpyridine.*

Synthesis of 2-Ph



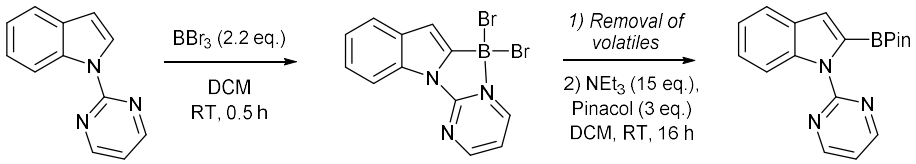
To an ampule fitted with a J-Youngs tap was added compound **1** (0.030 g, 0.15 mmol) which was dissolved in *o*-DCB (0.5 mL). BCl_3 1M in hexanes (0.33 mL, 0.33 mmol) was added, the tube was sealed and the mixture was heated to 80 °C for 16 hours. The solvents and excess BCl_3 were removed under vacuum and Ph_2Zn (0.077 g, 0.35 mmol) was added followed by toluene (0.5 mL). The reaction mixture was stirred for 2 days at room temperature. The product was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the pure product, **2-Ph** (0.011 g, 22%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.8, 2.3 Hz, 1H), 8.54 (dd, *J* = 5.8, 2.3 Hz, 1H), 8.31 – 8.22 (m, 1H), 7.62 – 7.52 (m, 1H), 7.42 – 7.31 (m, 4H), 7.29 – 7.26 (m, 2H), 7.25 – 7.16 (m, 6H), 7.11 (dd, *J* = 5.8, 4.8 Hz, 1H), 6.67 (d, *J* = 0.9 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, CDCl3) δ 163.3, 154.6, 152.4, 136.7, 133.0, 127.8, 126.5, 123.9, 122.6, 120.8, 113.8, 113.6, 108.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 0.36. **[Acc. Mass]** Calculated $[M+H]^+$: 360.1667, Observed $[M+H]^+$: 360.1655.

Synthesis of 2-Dan



To an ampule fitted with a J-Youngs tap was added compound **1** (0.028 g, 0.14 mmol) which was dissolved in DCM (0.35 mL). BBr_3 (0.33 mL, 1M in DCM) was added and the ampule was sealed and stirred at room temperature for 0.75 hours. The solvent/volatiles were removed under vacuum and the product dried. A mixture of 1,8-diaminonapthalene (0.025 g, 0.14 mmol) in DCM (1 mL) and K_2CO_3 (0.020 g, 0.7 mmol) in H_2O (0.7 mL) was prepared and stirred vigorously for 1 hour and then added to the reaction ampule containing the borylated indole at 0 °C, after stirring at 0 °C for 10 minutes the ampule was warmed to room temperature and stirred for a further 2 hours. The reaction mixture was poured into a conical flask and dried over $MgSO_4$, the crude product was purified by column chromatography on silica-gel (EtOAc/Petroleum ether) to give the pure product, **2-Dan** (0.016 g, 31%) as an off-white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.68 (d, *J* = 4.8 Hz, 2H), 7.66 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.45 – 7.34 (m, 1H), 7.34 – 7.24 (m, 1H), 7.19 – 7.11 (m, 2H), 7.07 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.04 (t, *J* = 4.7 Hz, 1H), 6.95 (s, 1H), 6.32 (dd, *J* = 7.1, 1.0 Hz, 2H), 5.80 (br s, 2H, N-H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.0, 141.7, 137.5, 136.6, 131.6, 127.7, 124.3, 122.5, 120.9, 119.6, 117.5, 116.4, 115.8, 114.7, 105.8.**^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.64. **[Acc. Mass]** Calculated $[M+H]^+$: 362.15715, Observed $[M+H]^+$: 362.15720.

Synthesis of 2-Pin



To an ampule fitted with a J-Youngs tap was added compound **1** (0.019 g, 0.1 mmol) which was dissolved in DCM (0.35 mL). BBr_3 (0.22 mL, 1M in DCM) was added, the ampule was sealed and stirred for 0.5 hours after which the volatiles were removed under vacuum and the compound was dried. NEt_3 (0.2 mL, 1.5 mmol) was added followed by pinacol (0.035 g, 0.3 mmol) and DCM (1 mL), the ampule was sealed and the reaction mixture was stirred overnight at room temperature. ^{1}H and ^{11}B NMR analysis of the crude reaction mixture showed the major species to be **2-Pin**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (d, J = 4.9 Hz, 2H), 8.61 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 – 7.14 (m, 1H), 7.02 (t, J = 4.9 Hz, 1H), 6.84 (s, 1H), 1.37 (s, 12H). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 26.30.

*Purification of **2-Pin** using flash chromatography was not possible in our hands using either silica gel or alumina as the stationary phase.*

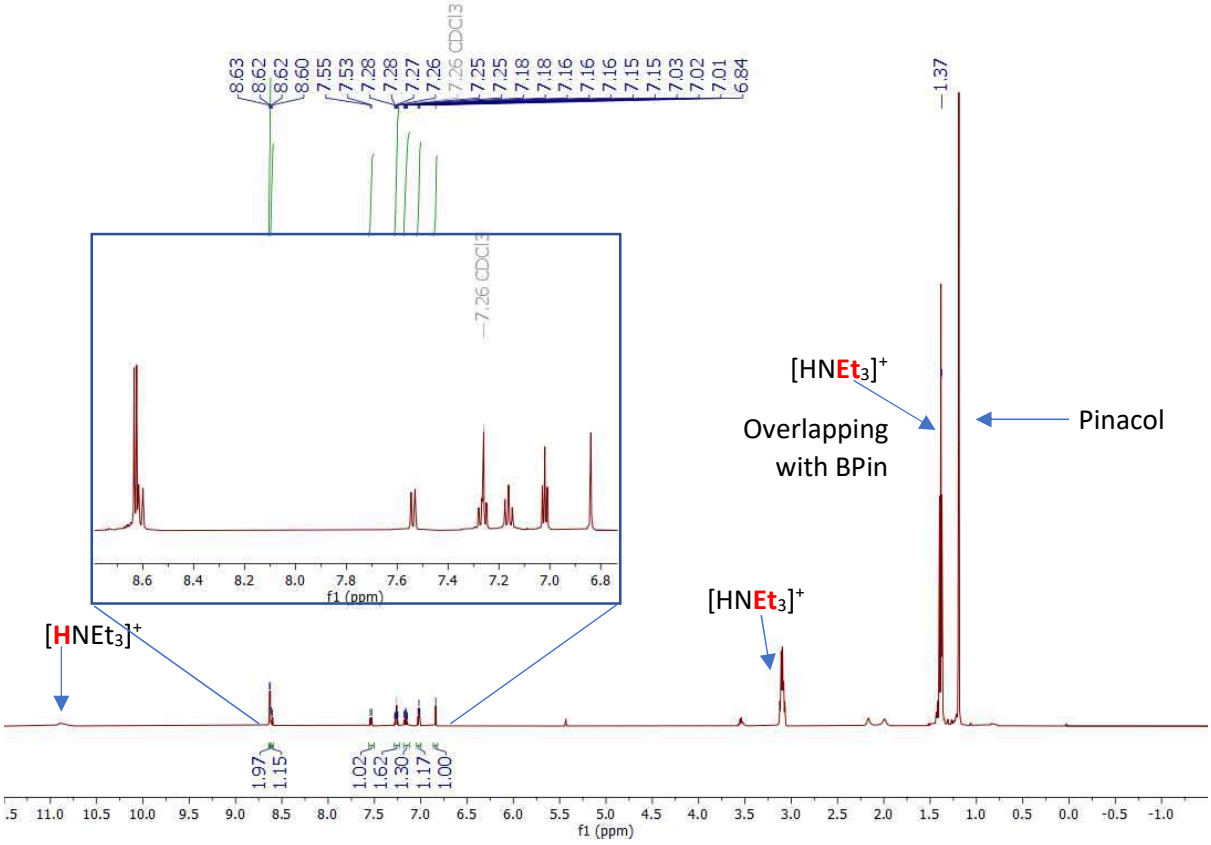


***Figure S3**: Crude ^{1}H NMR spectrum of **2-Pin**.*

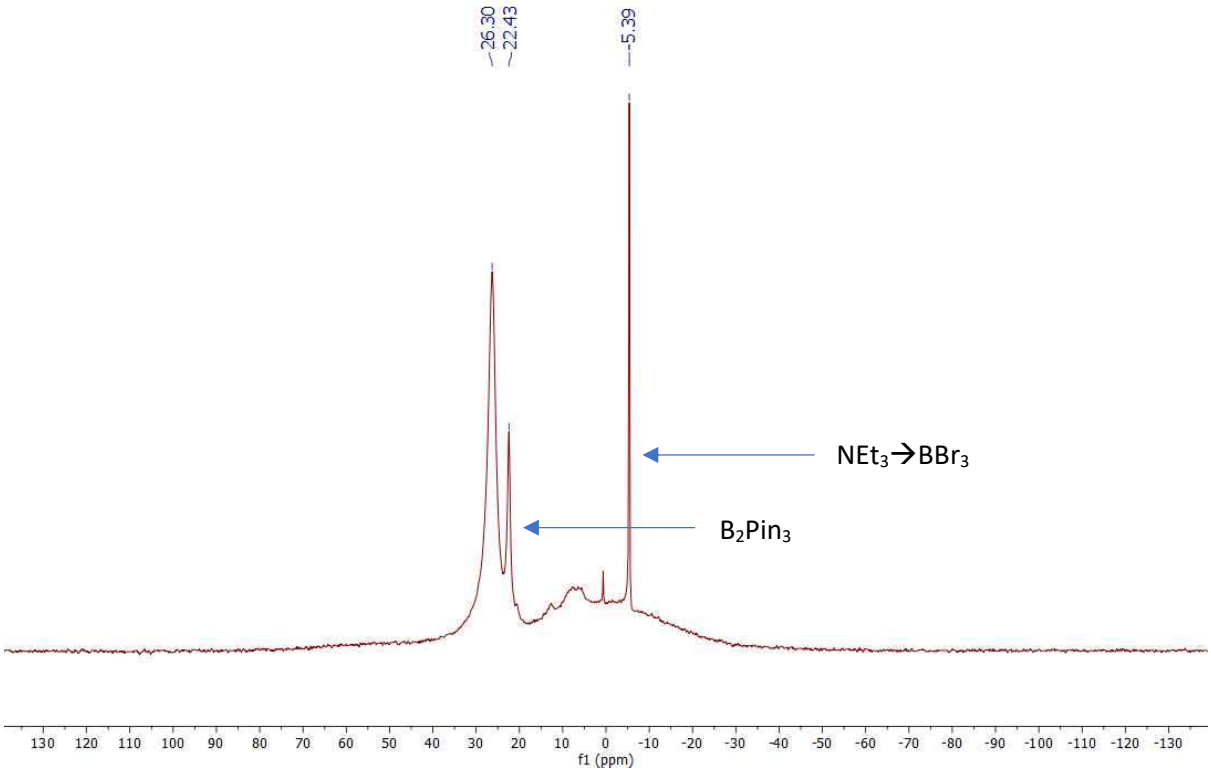
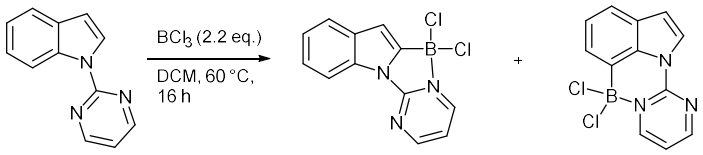


***Figure S4**: Crude ^{11}B NMR spectrum of **2-Pin**. The major resonance at +26.3 is attributed to **2-Pin**.*

Attempted isomerisation to C7 product by heating in a sealed tube.



To an ampule fitted with a J-Youngs tap was added compound **1** (0.020 g, 0.10 mmol) which was dissolved in DCM (0.35 mL). BCl_3 (0.33 mL, 1M in DCM) was added to and the ampule was sealed and stirred at 60 °C for 16 hours. The solvent/volatiles were removed under vacuum and a small portion of solid was dissolved in dry DCM.

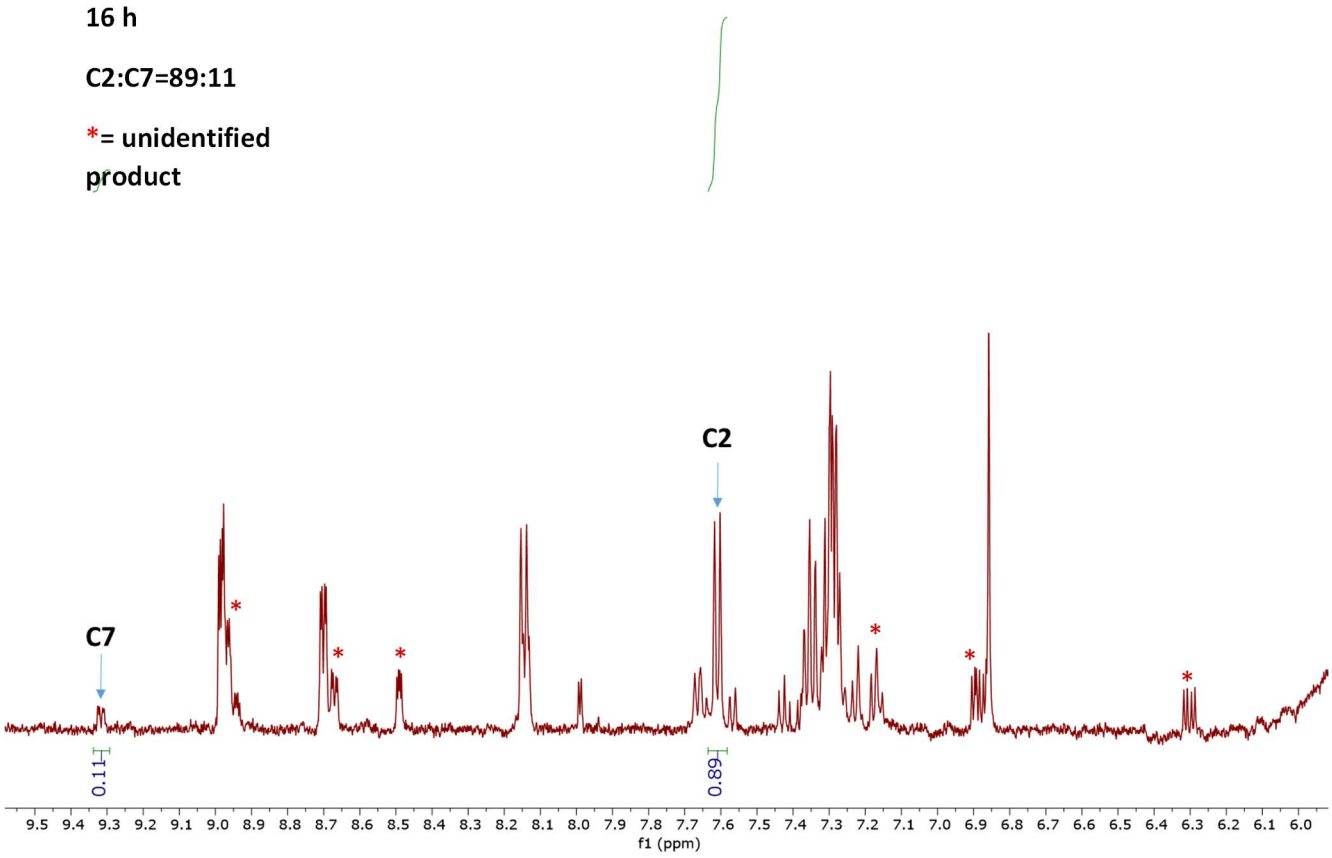


***Figure S5**: [1]H NMR spectra showing the ratio of C2:C7 borylation after 16 h along with an unidentified product (asterisked)*

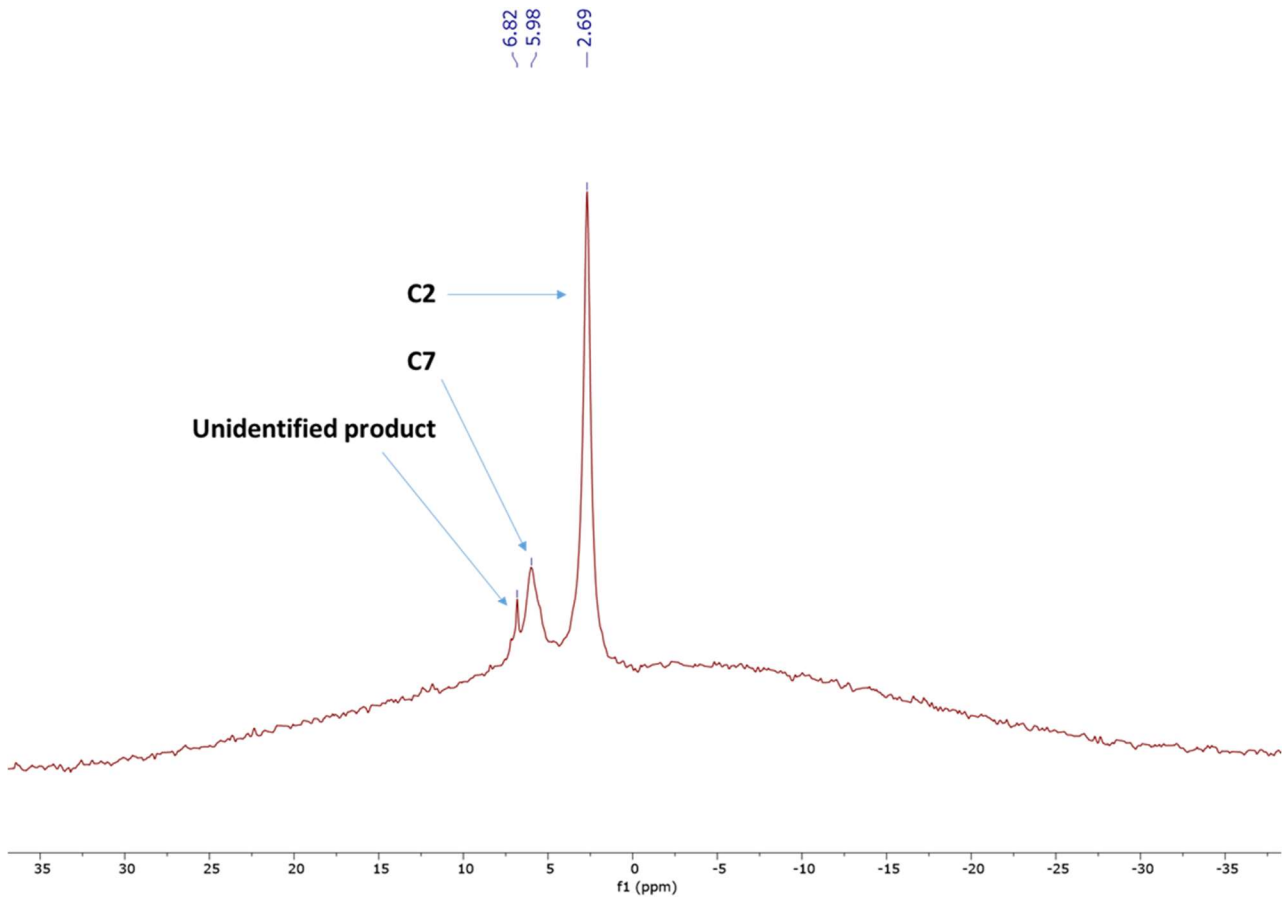
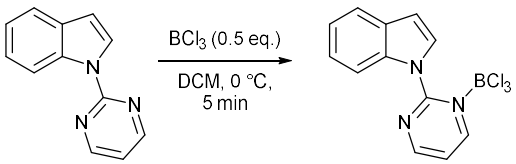


***Figure S6**: [11]B NMR spectra showing the chemical shifts for the C2 borylated and C7 borylated products after 16 h and an unidentified side product*

1-BCl_3 adduct



To an NMR tube fitted with a J-Youngs tap was added compound **1** (0.020 g, 0.1 mmol) which was dissolved in DCM (1 mL). BCl_3 (0.05 mL, 1M in DCM) was added at 0 °C, the tube was shaken, and the NMR measurement taken within 5 minutes. The observed new species at 7.16 ppm is assigned as the Lewis adduct, and is completely consumed at longer reaction times.

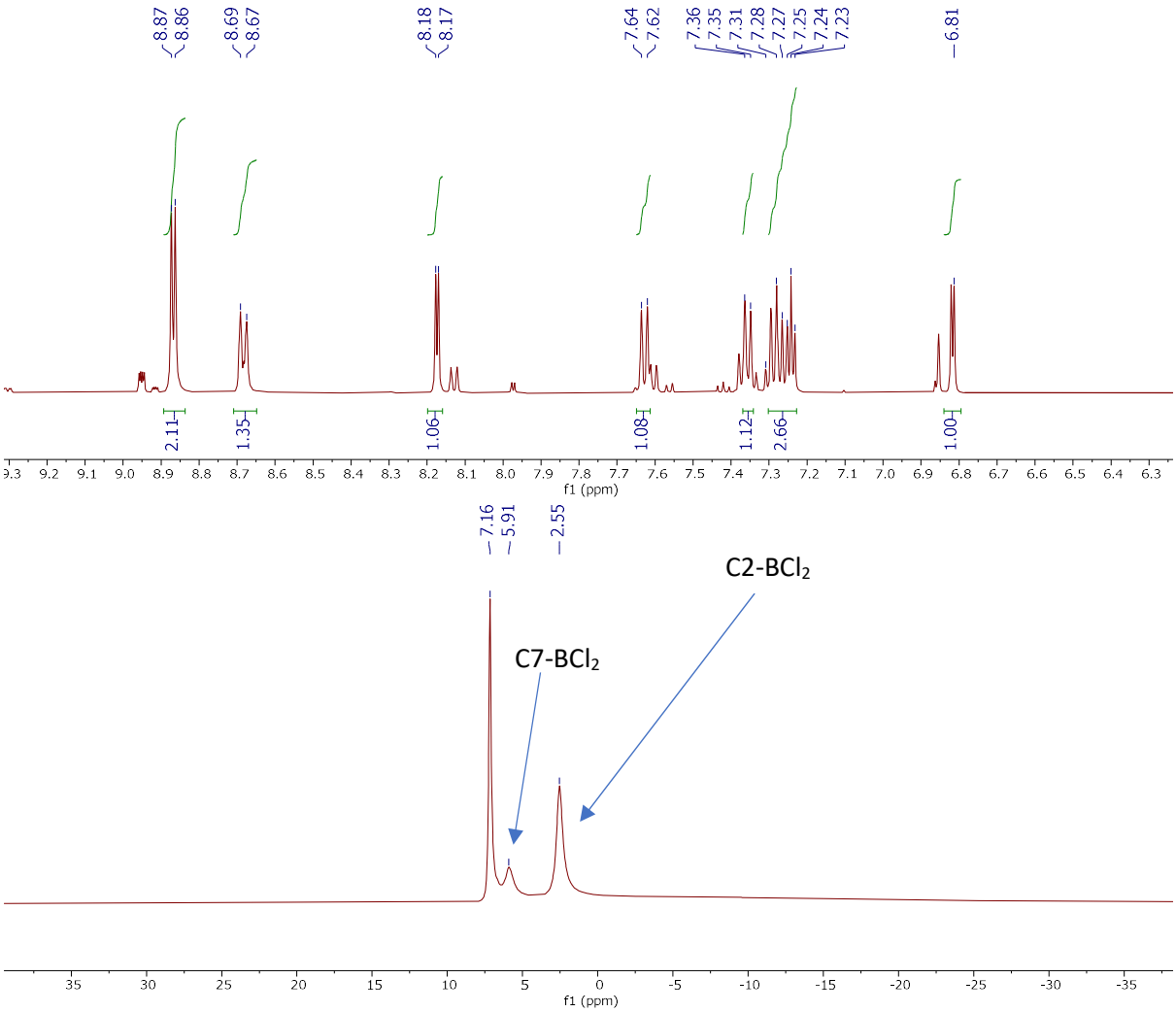
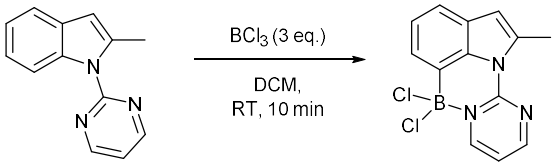


***Figure S7**: In-situ ^{1}H (top) and ^{11}B (bottom) NMR spectra of the crude mixture containing **1-BCl_3** adduct.*

Borylation of *N*-pyrimidin-2-yl-2-methylindole - *In-situ* NMR



To an NMR tube fitted with a J-Youngs tap was added compound **7** (0.01 g, 0.05 mmol) which was dissolved in DCM (0.4 mL). BCl_3 (0.15 mL, 1M in DCM) was added and the mixture was immediately submitted for NMR analysis. A single species was observed in the ^{1}H and ^{11}B NMR spectra assigned as the C7-borylated product.

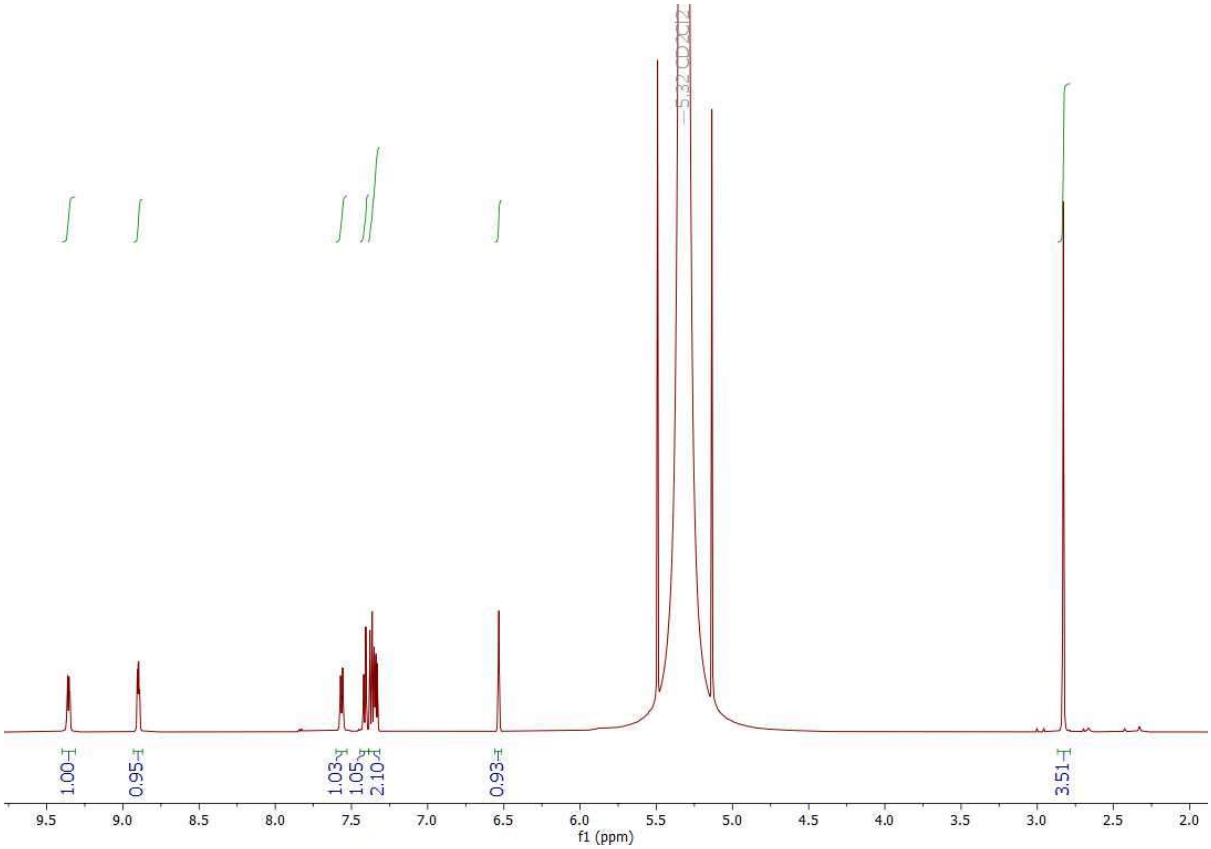


***Figure S8**: In-situ ^{1}H NMR spectrum of reaction between **7** and BCl_3* after 10 minutes*, the single product observed by ^{1}H NMR is assigned as **8-Cl**.*

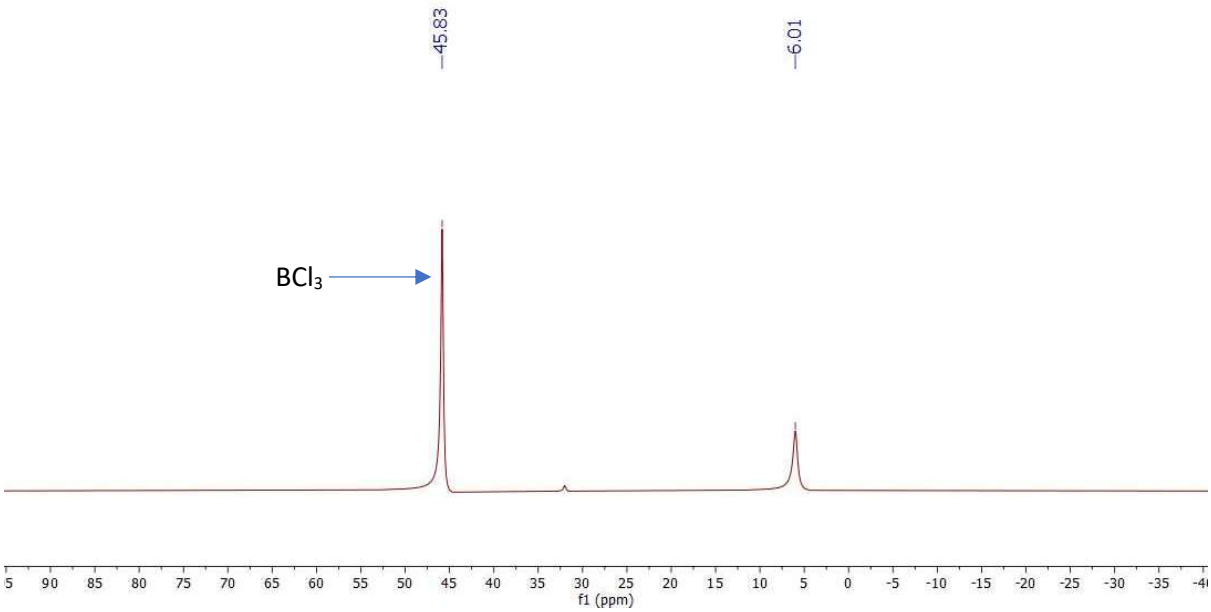


***Figure S9**: In-situ ^{11}B NMR spectrum of reaction between **7** and BCl_3 after 10 minutes, the single product observed by ^{1}H NMR is assigned as **8-Cl**.*

The *in-situ* ^{1}H-^{1}H COSY spectrum (below) shows a clear cross peak between the C(2)-CH_3 protons with a signal at 6.5 ppm which can be assigned as the C3-H. Therefore, borylation has not occurred at C(3)-H

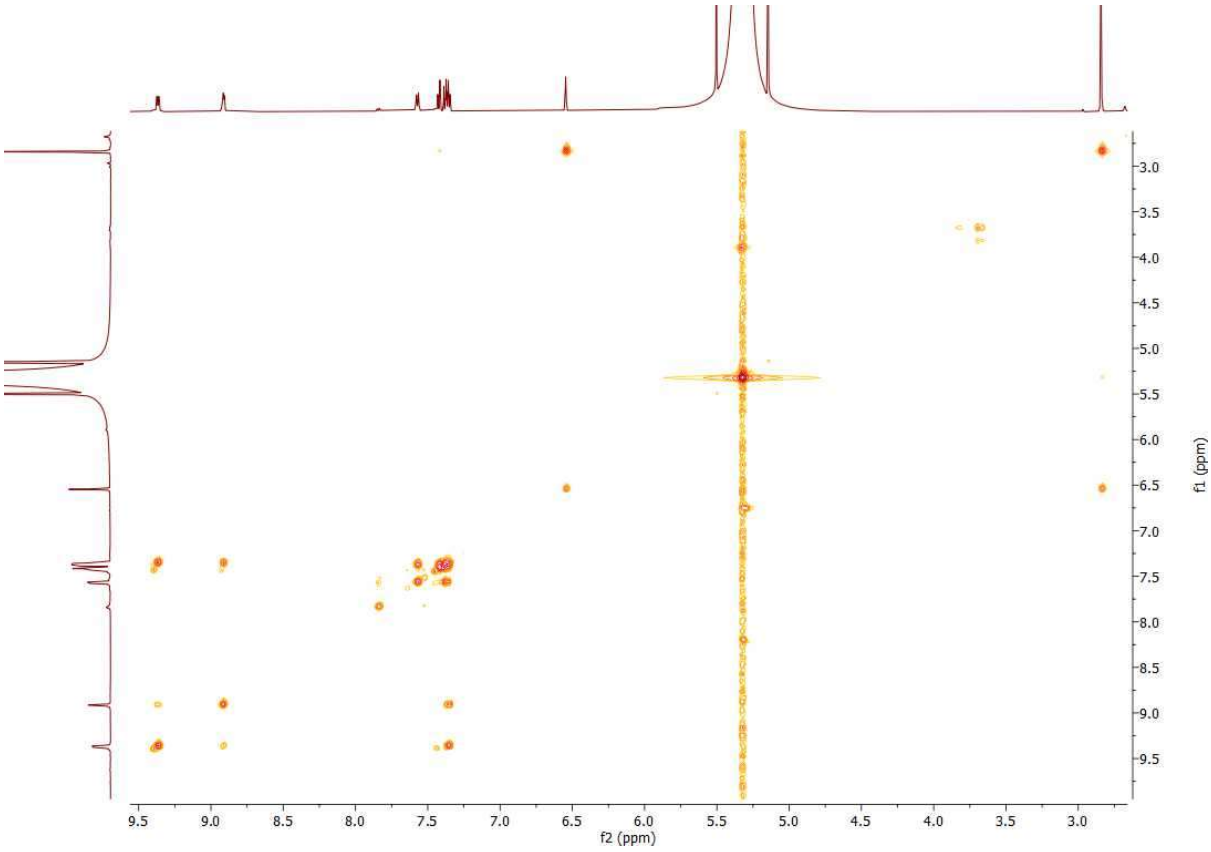
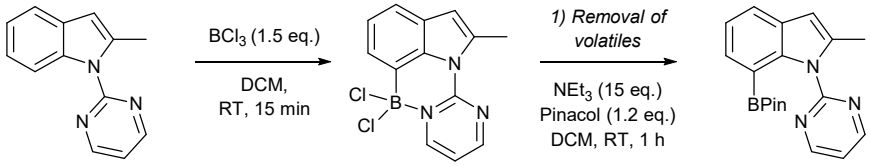


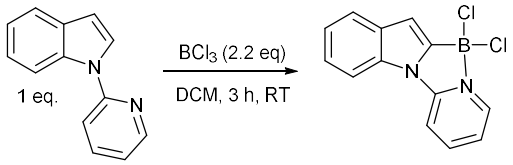
***Figure S10**: In-situ ^{1}H- ^{1}H COSY spectrum of **8-Cl**.*

Synthesis of 8-Pin

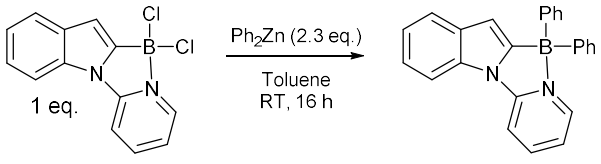


To an ampule fitted with a J-Youngs tap was added compound **7** (0.042 g, 0.2 mmol) which was dissolved in DCM (1.6 mL). BCl_3 (0.3 mL, 1M in DCM) was added and the ampule was sealed and stirred at room temperature for 0.25 hours. The volatiles were removed and the crude $–BCl_2$ product dried under vacuum. NEt_3 (0.42 mL, 3 mmol) was added followed by pinacol (0.029 g, 0.24 mmol) and DCM (2.5 mL), the ampule was sealed and stirred for 1 h. The crude product was purified by flash chromatography on silica gel (EtOAc/ Petroleum ether) to give the pure product, **8-Pin** (0.054 g, 80%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 5.1 Hz, 2H), 7.55 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 (t, *J* = 5.1 Hz, 1H), 6.48 – 6.45 (m, 1H), 2.84 (d, *J* = 1.2 Hz, 3H), 1.31 (s, 12H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.2, 154.1, 139.9, 138.0, 127.3, 126.5, 124.6, 118.9, 114.3, 111.5, 81.1, 26.8, 17.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 11.19. **[Acc. Mass]** Calculated $[M]^+$ 335.17996, Observed $[M]^+$: 335.18117.

3.2. Directed borylation of pyridyl-substituted indole, 3.



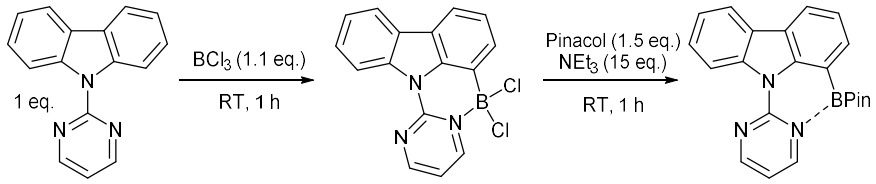
To an ampule fitted with a J-Youngs tap was added compound **3** (0.019 g, 0.10 mmol) which was dissolved in DCM (0.35 mL). BCl_3 (0.33 mL, 1M in DCM) was added to and the ampule was sealed and stirred at room temperature for 3 hours. The solvent/volatiles were removed under vacuum until dryness to give the pure product, **4-Cl** (0.024 g, 87%) as a yellow solid. Crystals were grown by slow evaporation of a DCM/pentane solution of the product**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.8 Hz, 1H), 8.22 – 8.06 (m, 1H), 7.72 – 7.59 (m, 3H), 7.36 – 7.18 (m, 3H), 6.91 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.8, 145.3, 142.3, 136.0, 132.7, 124.3, 123.7, 122.8, 118.4, 111.4, 110.7, 109.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 3.03. **[Acc. Mass]** Calculated $[M+Na]^+$: 297.01281, Observed $[M+Na]^+$: 297.01270. For spectra of **4-Cl** see section 8.



To an ampule fitted with a J-Youngs tap was added compound **4-Cl** (0.056 g, 0.2 mmol) and Ph_2Zn (0.100 g, 0.46 mmol) followed by toluene (1.5 mL). The ampule was sealed and the reaction was stirred at room temperature for 16 hours. The crude product was purified by column chromatography on silica-gel (EtOAc: Petroleum ether) to give the pure product, **4-Ph** (0.011 g, 15%) as a brown solid. **^{1}H NMR**

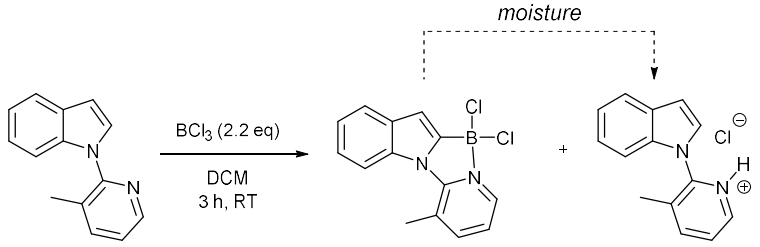
(400 MHz, $CDCl_3$) δ 8.34 – 8.30 (m, 1H), 8.10 – 8.00 (m, 1H), 7.80 (dt, *J* = 8.6, 1.1 Hz, 1H), 7.77 – 7.66 (m, 1H), 7.66 – 7.53 (m, 1H), 7.35 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.29 – 7.15 (m, 8H), 7.17 – 7.08 (m, 1H), 6.66 (d, *J* = 0.9 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 150.3, 143.9, 142.8, 136.9, 133.1, 132.8, 127.7, 126.2, 122.8, 121.9, 121.3, 117.3, 111.2, 109.6, 107.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 0.02. **[Acc. Mass]** Calculated $[M+H]^+$: 359.17141, Observed $[M+H]^+$: 359.17100.

3.3. Directed borylation of pyrimidine-substituted carbazole, 5.



BCl_3 (0.11 mL, 1M in DCM) was added to a solution of compound **5** (0.024 g, 0.1 mmol) in DCM (1 mL) and the reaction mixture was stirred at room temperature for 1 hour. Pinacol (0.018 g, 0.15 mmol) and NEt_3 (0.21 mL, 1.5 mmol) were added and the mixture was stirred for 1 hour. Volatiles were removed under vacuum and the crude product was purified by column chromatography on silica-gel (EtOAc: hexane) to yield the pure product, **6-Pin** (0.025 g, 67%) as a white solid. **^1H NMR** (400 MHz, CD_2Cl_2) δ 9.10 (d, *J* = 5.2 Hz, 2H), 8.83 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.57 – 7.41 (m, 3H), 7.28 (t, *J* = 5.2 Hz, 1H), 1.31 (s, 12H). **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_2Cl_2) δ 156.8, 154.0, 141.5, 138.9, 129.9, 128.6, 127.2, 125.3, 124.6, 124.0, 120. 8, 119.0, 119.0, 114.8, 81.4, 27.1. **^{11}B NMR** (128 MHz, CD_2Cl_2) δ 9.90. **[Acc. Mass]** Calculated $[M+H]^+$: 372.1878, Observed $[M+H]^+$: 372.1869.

3.4. Borylation of 3-methylpyridine substituted indole, **9**:



To an ampule fitted with a J-Youngs tap was added compound **9** (0.031 g, 0.15 mmol) which was dissolved in DCM (0.4 mL) followed by addition of BCl_3 (0.33 mL, 1M in DCM,). The mixture was stirred at room temperature for 3 hours after which the solvent/volatiles were removed under inert conditions by vacuum and the product dried. Crude NMR spectra in $CDCl_3$ showed an initial mixture of C2-BCl_2 borylated indole, **10-Cl,** and the chloride salt of the protonated starting material (see scheme above). Leaving the mixture in 'wet' $CDCl_3$ resulted in protodeborylation of the C2-BCl_2 indole **10-Cl** to the protonated 3-methyl-2-indolylpyridine. The sensitivity to moisture of **10-Cl** made isolation as a clean material challenging in our hands, thus in-situ spectra only are reported.

The formation of the protonated chloride-salt by-product was confirmed by the addition of HCl (2.5 eq, 2M in Et_2O) to 3-methyl-2-indolylpyridine.

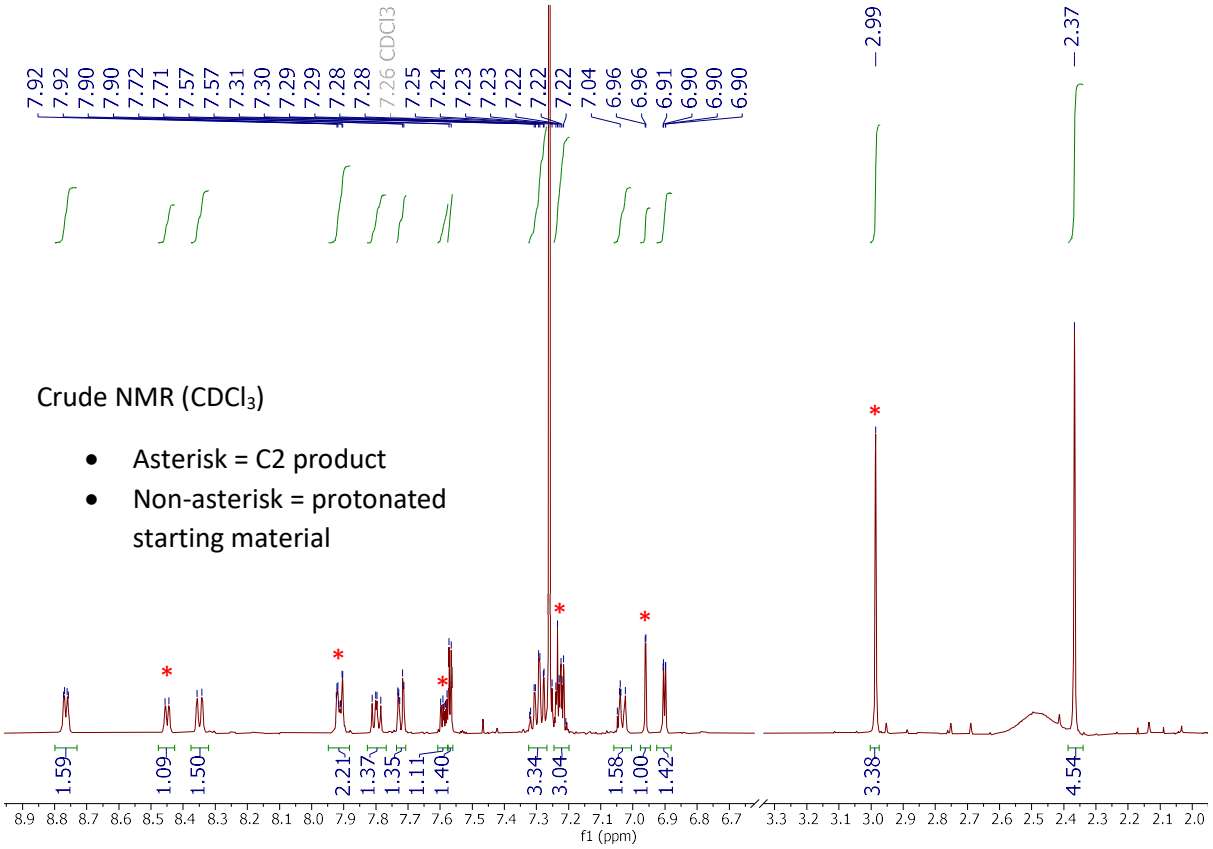


***Figure S11**: Crude ^{1}H NMR spectrum of the reaction between **9** and BCl_3 after 3 hours at room temperature. Spectrum shows a mixture of C2-borylated product and protonated starting material by-product*

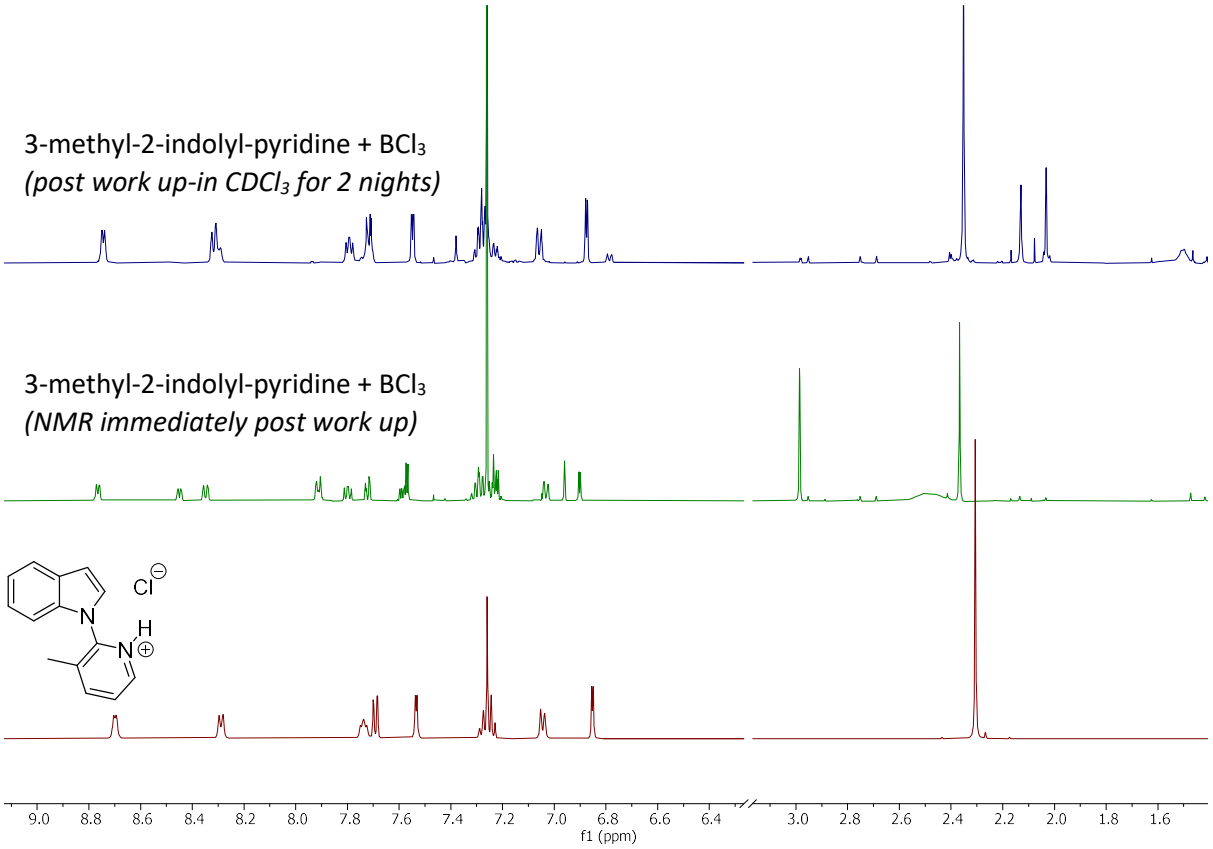
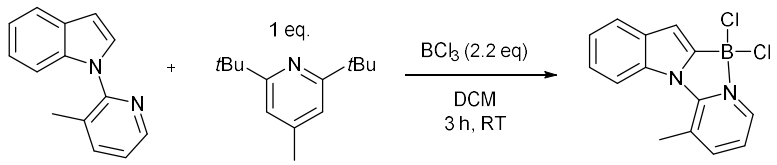


***Figure S12**: Stacked spectra showing the decomposition of C2-borylated product into protonated starting material. NMR spectrum of 3-methyl-2-indolyl-pyridiniumchloride (bottom). NMR spectrum after post-workup (middle) and 2 nights (top)*



To an ampule fitted with a J-Youngs tap was added compound **9** (0.020 g, 0.1 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.21 g, 0.01 mmol) which were dissolved in DCM (0.35 mL) followed by addition of BCl_3 (3.2 eq., 1M in DCM, 0.33 mL). The mixture was stirred at room temperature for 3 hours after which the solvent/volatiles were removed under inert conditions by vacuum and the product dried. Crude NMR spectra in $CDCl_3$ showed the major product as **10-Cl** (88% yield determined by ^{1}H NMR. 55 mg crude solid obtained, 1 mg dissolved in CD_2Cl_2 and 1 µL mesitylene internal standard added for yield determination). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.43 (d, J = 5.7 Hz, 1H), 8.05 – 7.90 (m, 2H), 7.68 – 7.53 (m, 1H), 7.34 – 7.21 (m, 3H), 6.91 (s, 1H), 2.98 (s, 3H).**^{11}B NMR** (128 MHz, $CDCl_3$) δ 2.45. **[Acc. Mass]** Calculated $[M]^+$: 288.03869, Observed $[M]^+$: 288.03925. **^{13}C{^{1}H} NMR** spectrum unobtainable due to poor solubility of **8-Cl** in CD_2Cl_2.

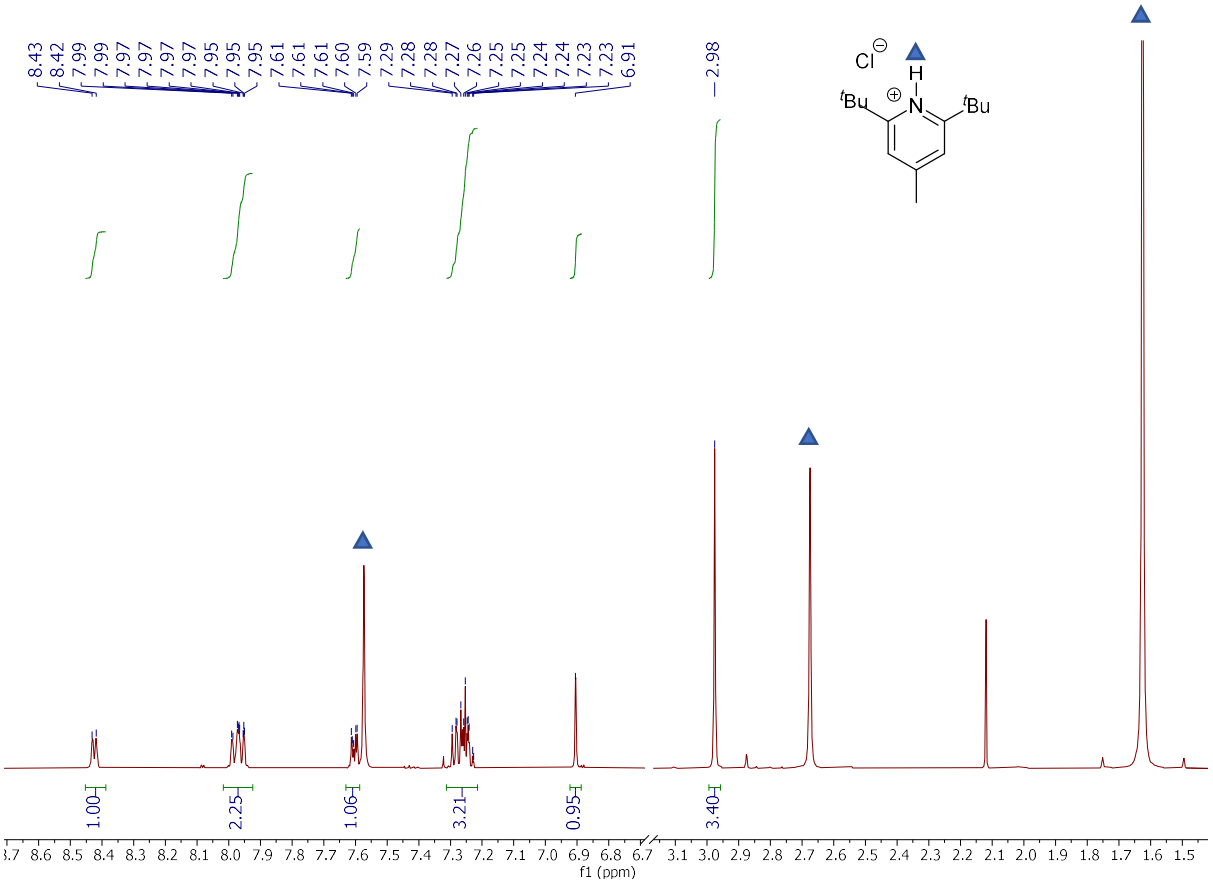
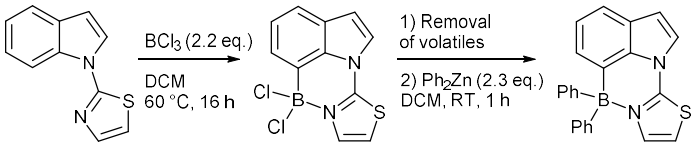
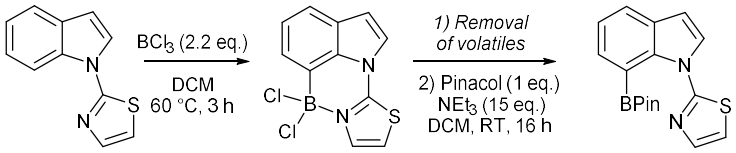


***Figure S13**: Crude ^{1}H NMR spectrum of reaction between 7 and BCl_3 in the presence of 2,6-Di-tert-butyl-4-methylpyridine.*

3.5. Directed borylation of thiazole substituted indole, 12:

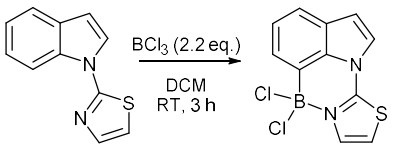


To an ampule fitted with a J-Youngs tap was added compound **12** (0.029 g, 0.15 mmol) which was dissolved in DCM (0.4 mL). BCl_3 1M (0.33 mL, 0.33 mmol) was added, the ampule was sealed and the mixture was stirred at 60 °C for 3 hours. The solvents and excess BCl_3 were removed under vacuum and Ph_2Zn (0.077 g, 0.35 mmol) was added followed by DCM (1.5 mL). The reaction mixture was stirred for 1 hour at room temperature. The solids were filtered off and the crude product was purified by column chromatography on silica gel (EtOAc/Petroleum ether) to give the product, **14-Ph** (0.035 g, 66%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.0 Hz, 1H), 7.35 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.29 (m, 6H), 7.24 – 7.18 (m, 5H), 7.18 – 7.11 (m, 2H), 6.82 (dd, *J* = 7.5, 3.8 Hz, 2H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 159.2, 137.2, 136.2, 133.7, 129.39, 127.4, 125.9, 125.7, 125.4, 121.6, 117.9, 112.7, 108.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 0.22. **[Acc. Mass]** Calculated $[M+H]^+$: 365.1278, Observed $[M+H]^+$: 365.1269.



To an ampule fitted with a J-Youngs tap was added compound **12** (0.037 g, 0.18 mmol). DCM (0.4 mL) was added followed by BCl_3 (0.22 mL, 1M in DCM). The ampule was sealed and the reaction mixture was stirred for 3 hours at 60 °C after which the solvent/volatiles were removed under vacuum. NEt_3 (0.38 mL, 2.7 mmol) was added followed by pinacol (0.021 g, 0.18 mmol) and the reaction mixture was stirred vigorously overnight at room temperature. The crude product was purified on silica-gel (EtOAc/Petroleum ether) to give the pure product, **14-Pin** (0.032 g, 55%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 4.0 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H), 1.37 (s, 12H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.1, 138.8, 136.5, 129.8, 127.1, 124.6, 123.8, 120.8, 111.4, 110.5, 81.3, 27.1. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 13.75. **[Acc. Mass]** Calculated $[M+H]^+$: 327.1333, Observed $[M+H]^+$: 327.1324.

In-situ studies of reaction show conversion to 12-Cl boracycle after 2-3 hours.



To an NMR tube fitted with a J-Youngs tap was added compound **12** (0.030 g, 0.15 mmol) which was dissolved in DCM (0.5 mL). BCl_3 1M (0.33 mL, 0.33 mmol) was added, the tube was sealed, and the mixture was stirred at room temperature for 3 hours and monitored periodically via NMR spectroscopy. Conversion to **14-Cl** was observed between 2-3 hours at room temperature, analysis of precipitate in

the NMR tube showed some adduct remains, thus heating was required for further conversion. **^{1}H NMR** (400 MHz, CH_2Cl_2) δ 8.03 (d, *J* = 4.3 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.16 (d, *J* = 4.3 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, CH_2Cl_2) δ 158.6, 134.6, 134.4, 129.3, 126.6, 126.3, 122.6, 121.8, 113.8, 110.8. **^{11}B NMR** (128 MHz, CH_2Cl_2) δ 6.22

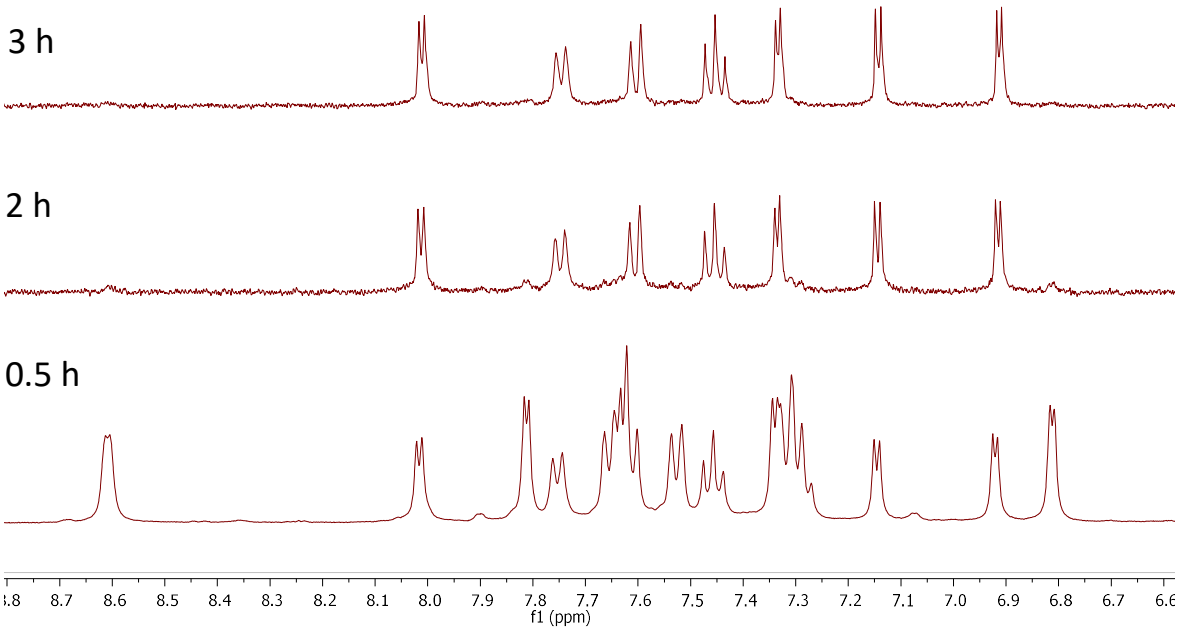


***Figure S14**: Stacked in-situ ^{1}H NMR spectrum showing conversion to **12-Cl** in reaction between **12** and BCl_3 after 3 hours.*

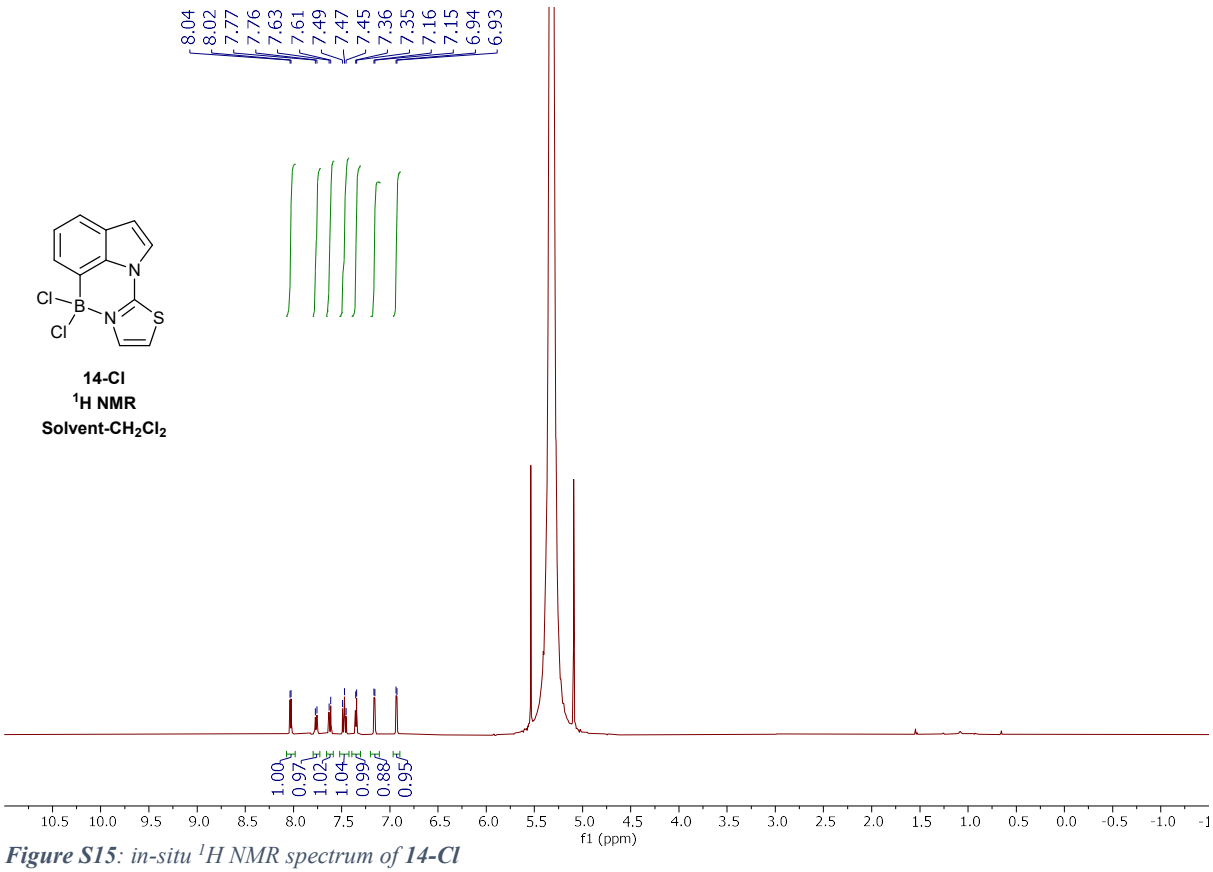


Figure S15**: in-situ ^{1}H NMR spectrum of **14-Cl

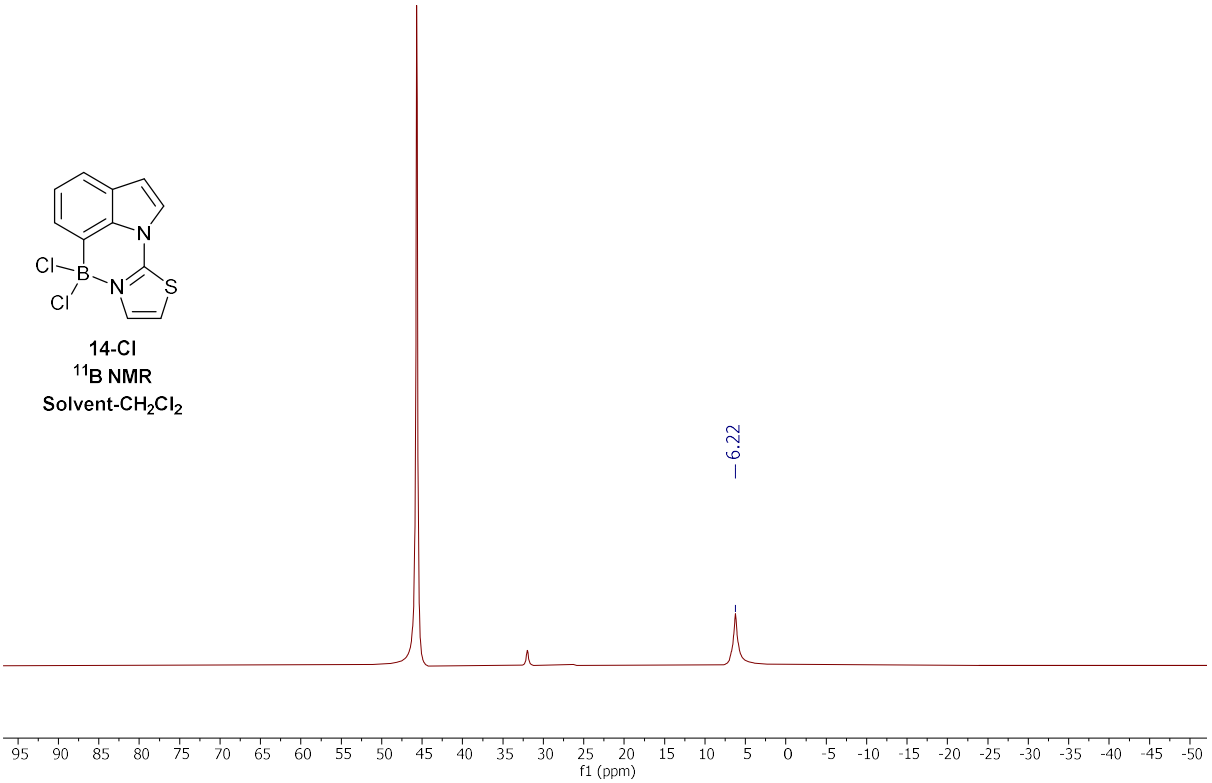


***Figure S16**: in-situ ^{11}B NMR spectrum of **14-Cl.** Resonance at 46 ppm is BCl_3*

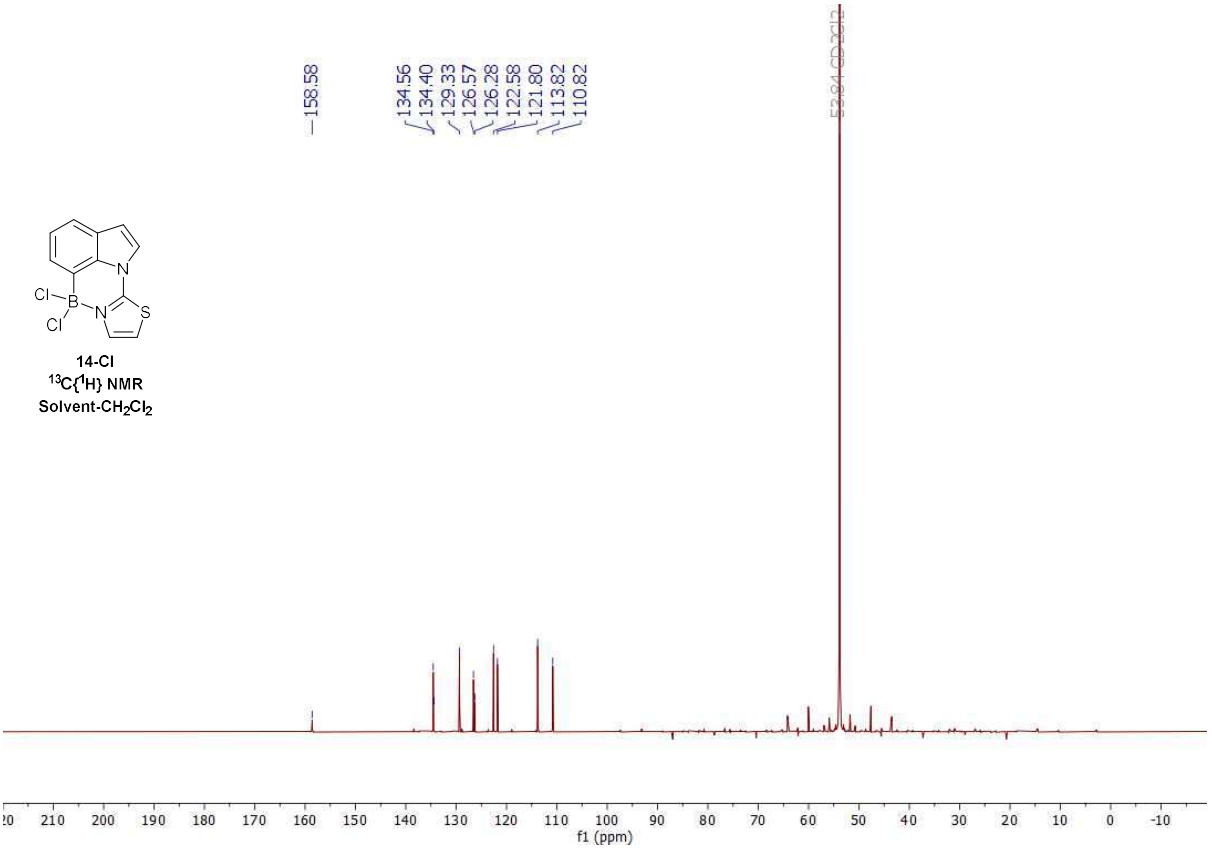
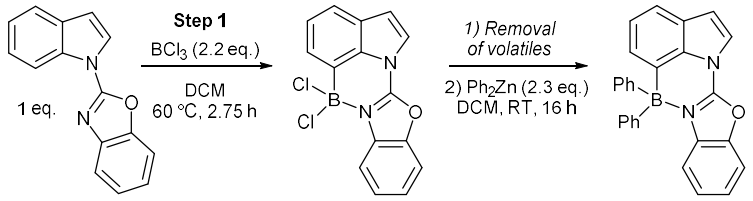


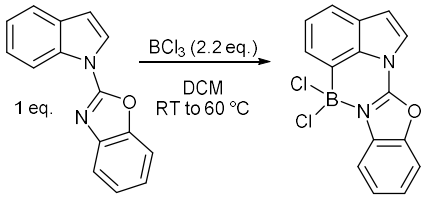
Figure S17**: in-situ $^{13}C\{^1H\}$ NMR spectrum of **14-Cl

3.6. Directed borylation of benzoxazole substituted indole, 15



To an NMR tube fitted with a J-Youngs tap was added compound **15** (0.024 g, 0.1 mmol). DCM (0.35 mL) was added followed by BCl_3 1M in DCM (0.22 mL, 0.22 mmol). The tube was sealed and heated to 60 °C for 2.75 hours after which it was cooled and excess BCl_3 and DCM were removed under vacuum. Ph_2Zn (0.050 g, 0.23 mmol) was added followed by DCM (0.5 mL) and the reaction mixture was left overnight at room temperature. The crude product was purified by column chromatography on silica gel (EtOAc/Hexanes) to give the pure product, **17-Ph** (0.026 g, 64%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.42 – 7.38 (m, 5H), 7.34 – 7.27 (m, 3H), 7.25 – 7.18 (m, 6H), 7.17 – 7.11 (m, 2H), 6.89 (d, J = 3.6 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 152.2, 146.9, 136.6, 134.0, 134.0, 129.7, 127.3, 126.5, 126.5, 126.1, 125.6, 125.0, 119.7, 118.3, 118.3, 114.1, 110.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 0.08. **[Acc. Mass]** Calculated $[M+H]^+$: 399.16632, Observed $[M+H]^+$: 399.16540.
Slow cooling of the reaction mixture after step 1 produces crystals suitable for x-ray diffraction.

In-situ NMR studies showing clean conversion to BCl_2 boracycle after 3h, 60 °C.



To an NMR tube fitted with a J-Youngs tap was added compound **15** (0.024 g, 0.1 mmol). DCM (0.35 mL) was added followed by BCl_3 1M in DCM (0.22 mL, 0.22 mmol). The tube was sealed and rotated overnight at room temperature during which periodic NMR measurements of the solution were taken. The reaction mixture was heated to 60 °C for 3 hours after which complete conversion to a single product, **17-Cl** was observed by NMR spectroscopy. Note: Poor solubility of an intermediate, which we assume is the BCl_3 adduct of **15** resulted in some precipitation which went back into solution upon formation of **17-Cl**.

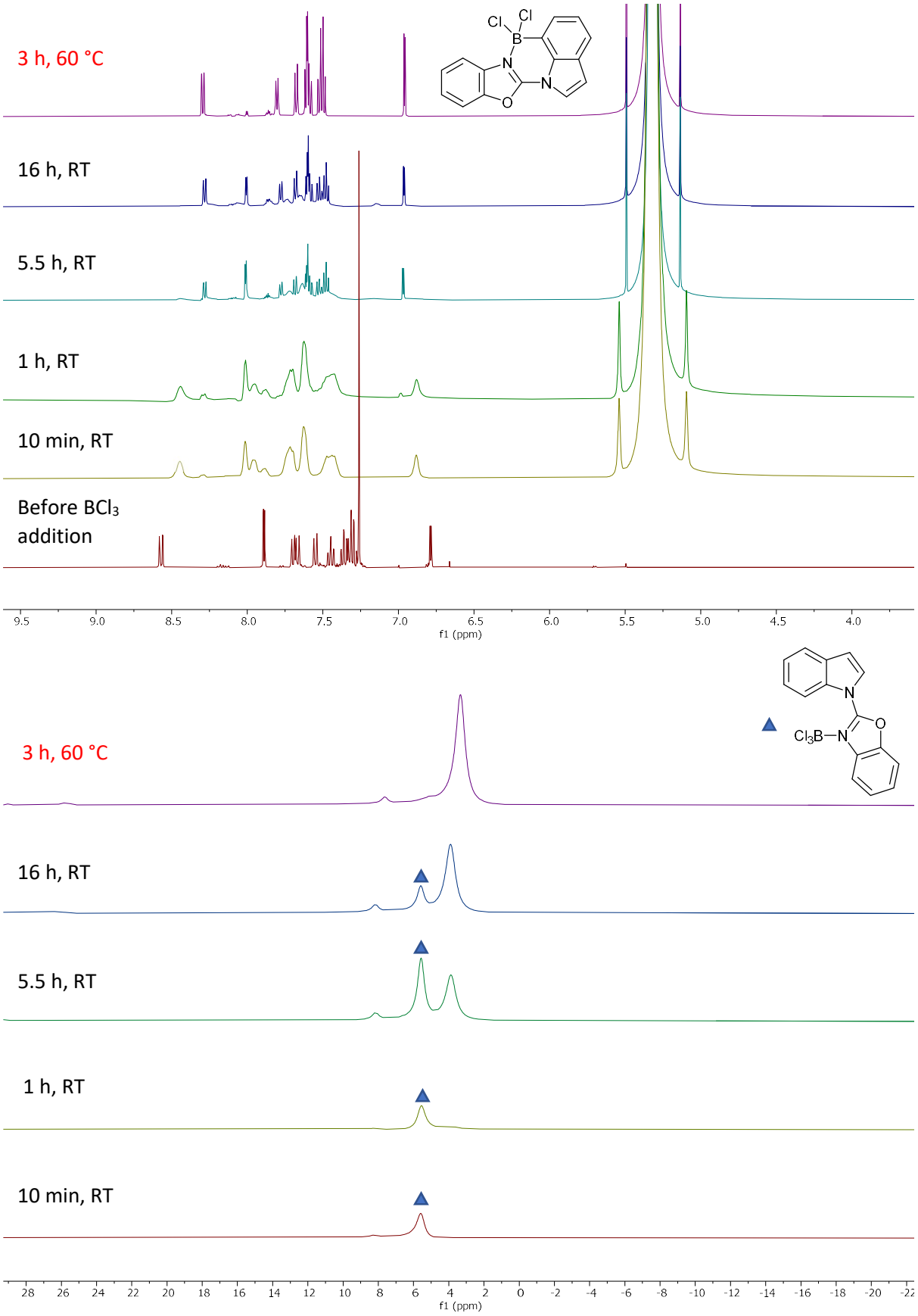
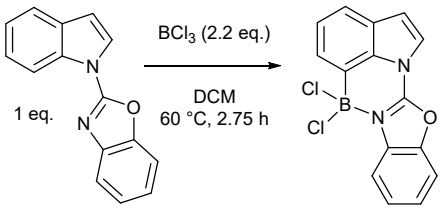
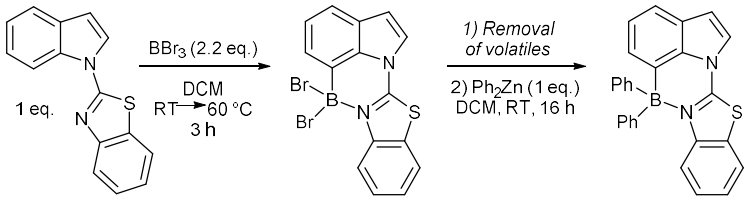


***Figure S18**: Stacked ^{1}H (top) and ^{11}B (bottom) NMR spectra showing conversion of **15** into **17-Cl** upon heating*



To an ampule fitted with a J-Youngs tap was added compound **15** (0.024 g, 0.1 mmol). DCM (0.35 mL) was added followed by BCl_3 (0.22 mL, 1M in DCM). The ampule was sealed and the reaction mixture was heated to 60 °C for 2.75 hours, after which it was cooled and the solvent/volatiles removed under vacuum and the solid dried to give the pure product, **17-Cl** (0.030 g, 73%) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (m, *J* = 8.2, 1.3, 0.6 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.65 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.56 – 7.46 (m, 2H), 6.97 (d, *J* = 3.7 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 149.9, 146.8, 134.3, 131.2, 129.9, 127.6, 127.5, 126.8, 126.4, 121.6, 119.9, 118.7, 115.4, 111.3. **^{11}B NMR** (128 MHz, CDCl3) δ 3.92. **[Acc. Mass]** Calculated $[M]^+$: 314.01795, Observed $[M]^+$: 314.01728.

3.7. Directed borylation of benzothiazole substituted indole, 16



To an NMR tube fitted with a J-Youngs tap was added compound **16** (0.0250 g, 0.1 mmol DCM (0.35 mL) was added followed by BBr_3 (0.22 mL, 1M in DCM), the tube was sealed, and the reaction mixed for 2 hours at room temperature followed by 1 hour at 60 °C. The solvent/volatiles were removed under vacuum and the crude material dried. Ph_2Zn (20 mg, 0.1 mmol) was added followed by DCM (1 mL), the tube was sealed and mixed overnight at room temperature. The product was purified on silica-gel (EtOAc/Petroleum ether) to give the pure product, **18-Ph** (0.012 g, 29%) as a grey solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 1H), 7.60 (dt, *J* = 8.4, 0.7 Hz, 1H), 7.44 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.33 – 7.25 (m, 3H), 7.23 – 7.14 (m, 7H), 7.14 – 7.08 (m, 2H), 6.85 (d, *J* = 3.7 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 144.7, 135.4, 133.8, 129.4, 127.5, 127.3, 126.5, 125.5, 125.5, 125.4, 125.2, 122.4, 122.2, 121.7, 117.8, 114.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 0.88. **[Acc. Mass]** Calculated $[M+H]^+$: 415.14348, Observed $[M+H]^+$: 415.14370.

4. Cyclic voltammetry

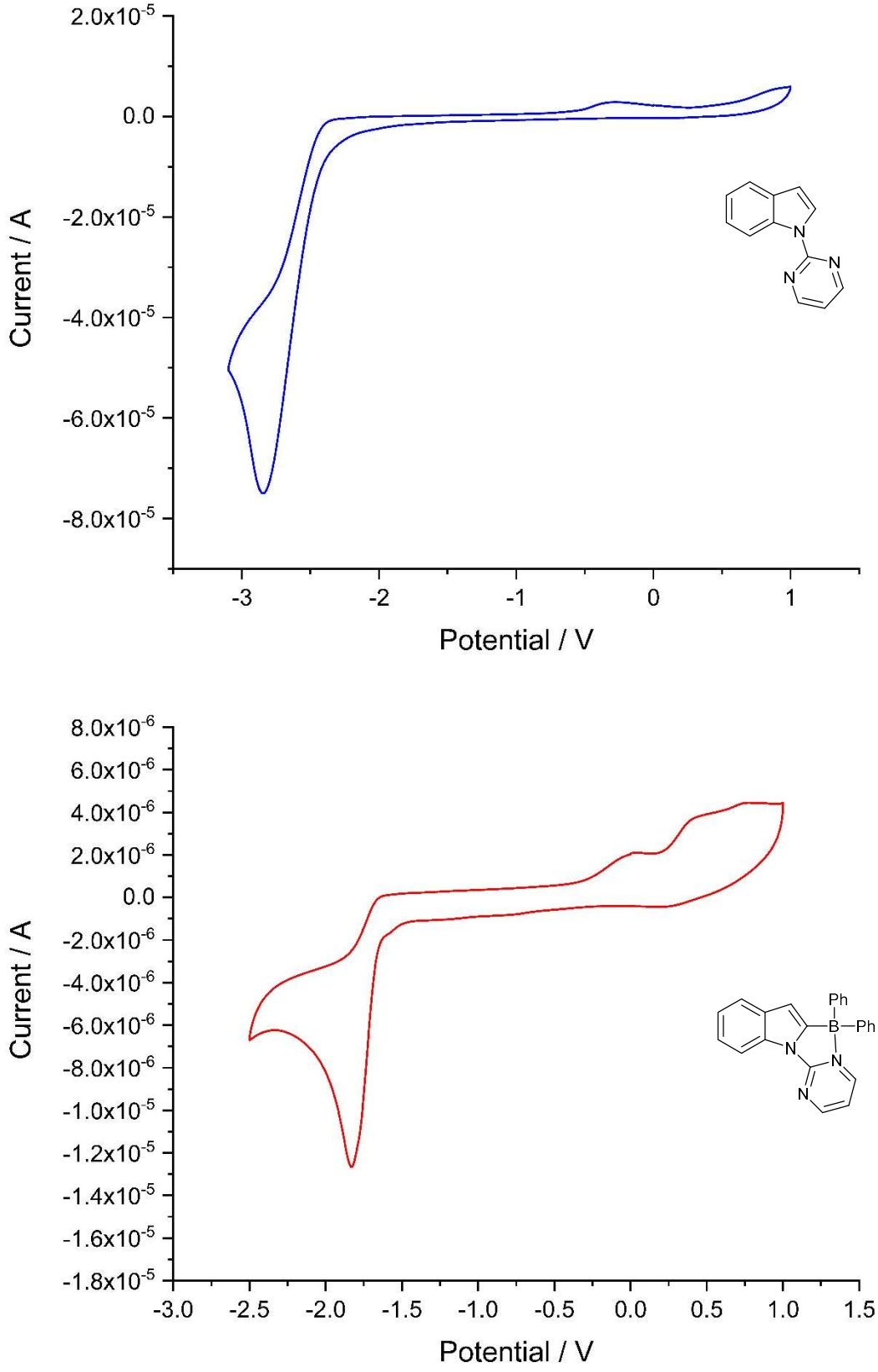


***Figure S19**: Cyclic voltammetry diagram of **1** (top) and **2-Ph** (bottom). Measured in THF (1 mM) with [nBu$_4$N][PF$_6$] (0.1M) as the supporting electrolyte*

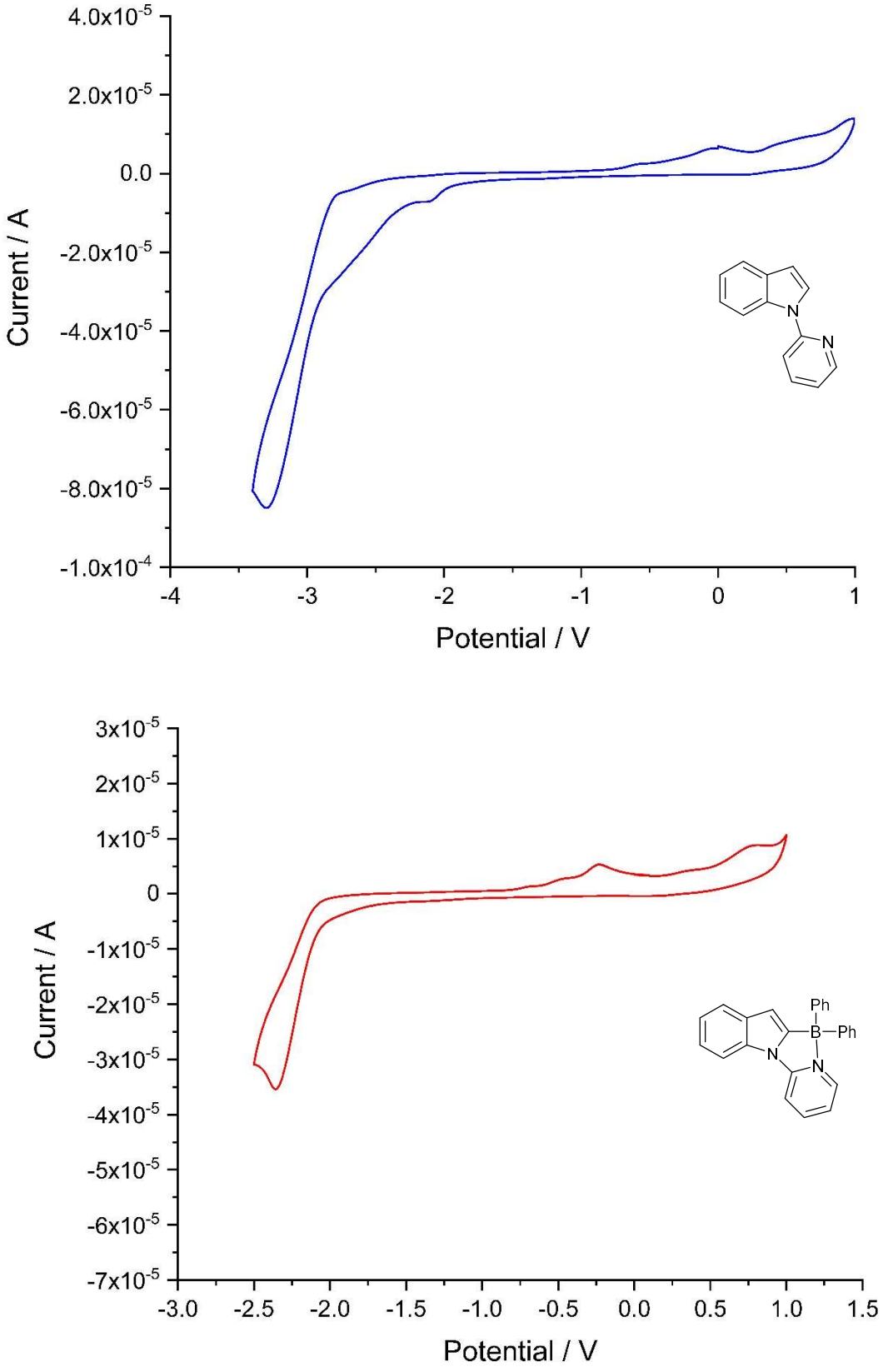


***Figure S20**: Cyclic voltammetry diagram of **3** (top) and **4-Ph** (bottom). Measured in THF (1 mM) with [nBu$_4$N][PF$_6$] (0.1M) as the supporting electrolyte*

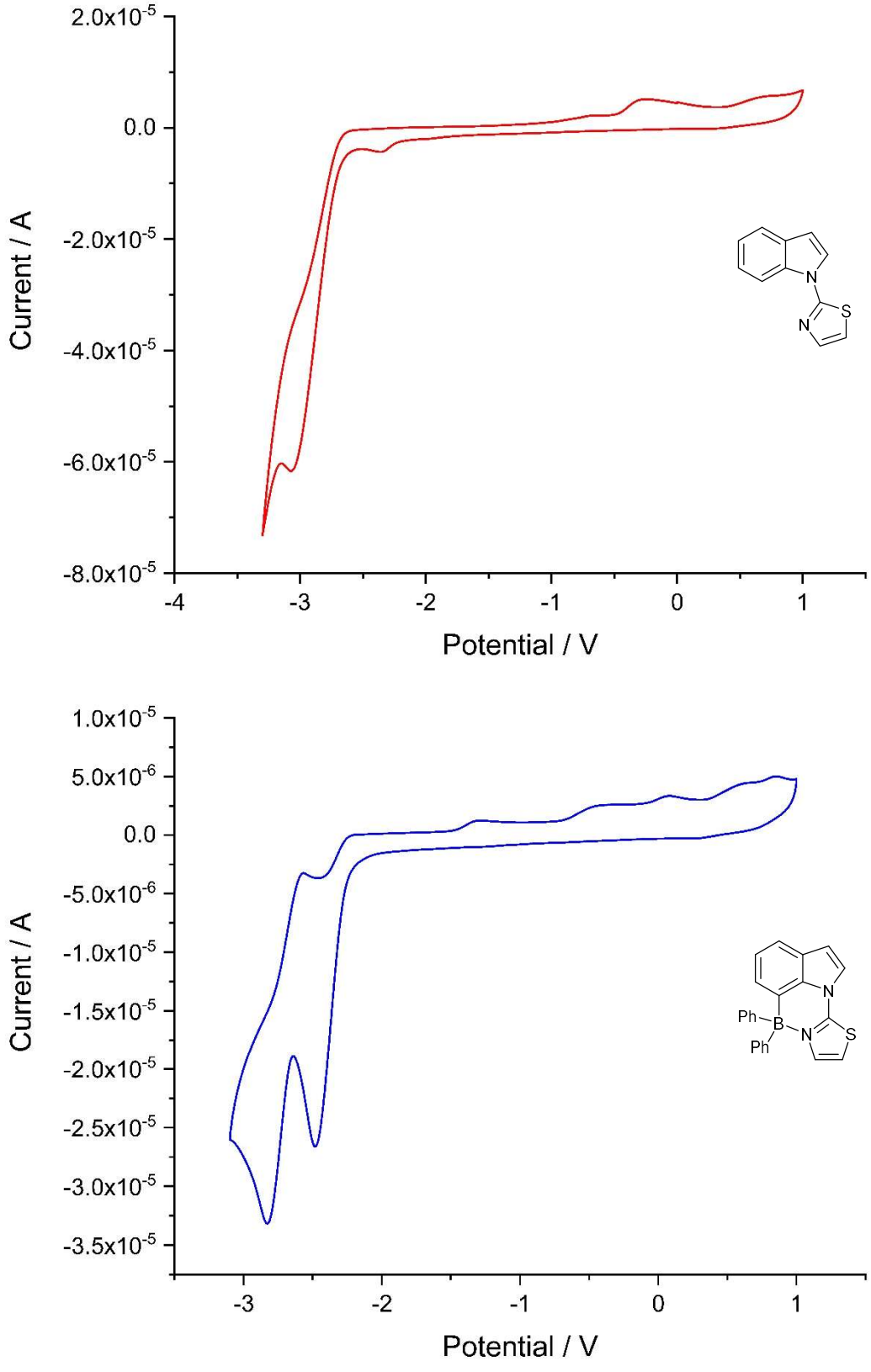


***Figure S61**: Cyclic voltammetry diagram of **12** (top) and **14-Ph** (bottom). Measured in THF (1 mM) with [nBu4N][PF6] (0.1 M) as the supporting electrolyte*

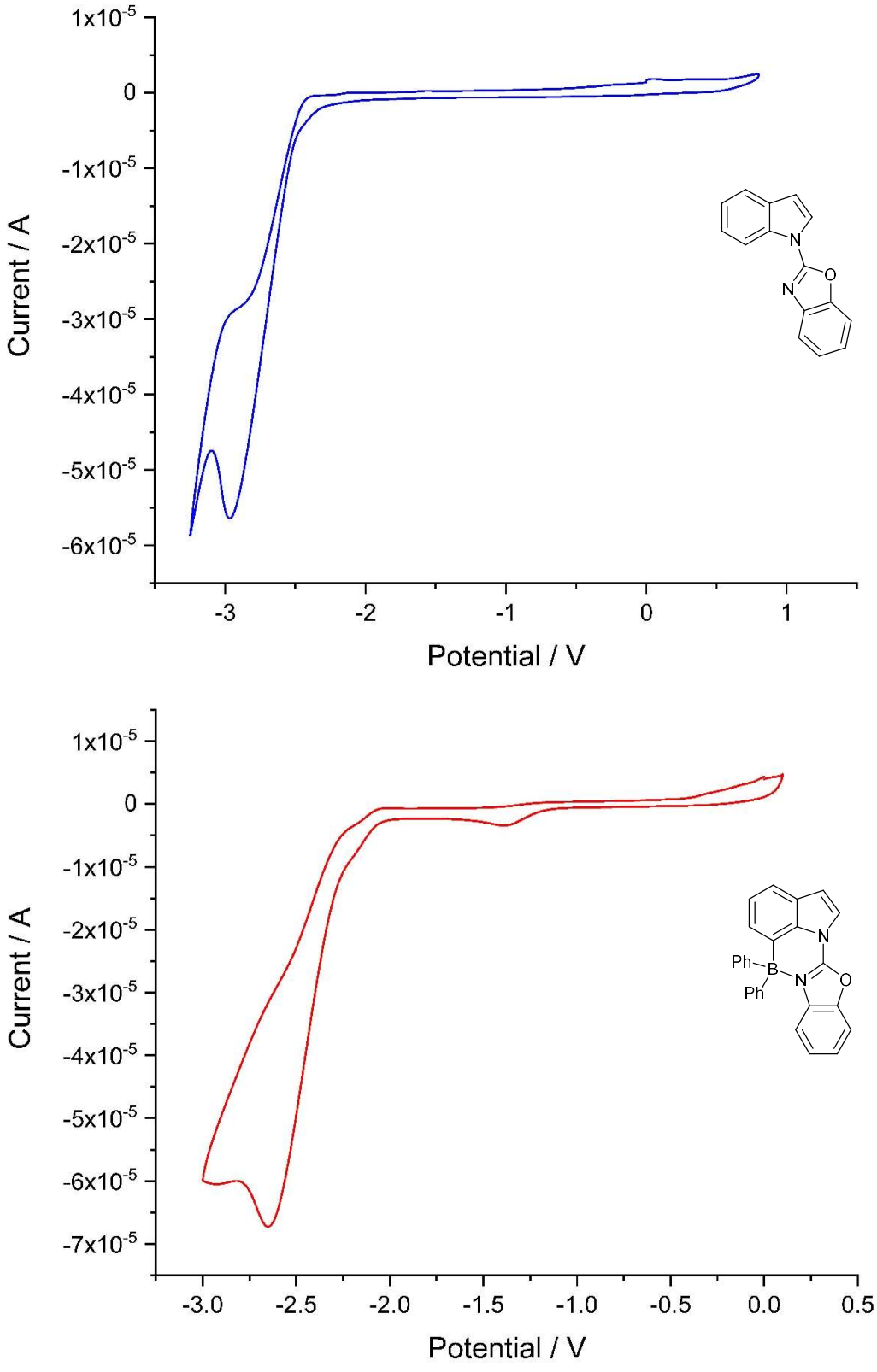


***Figure S22**: Cyclic voltammetry diagram of **15** (top) and **17-Ph** (bottom). Measured in THF (1 mM) with [nBu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte*

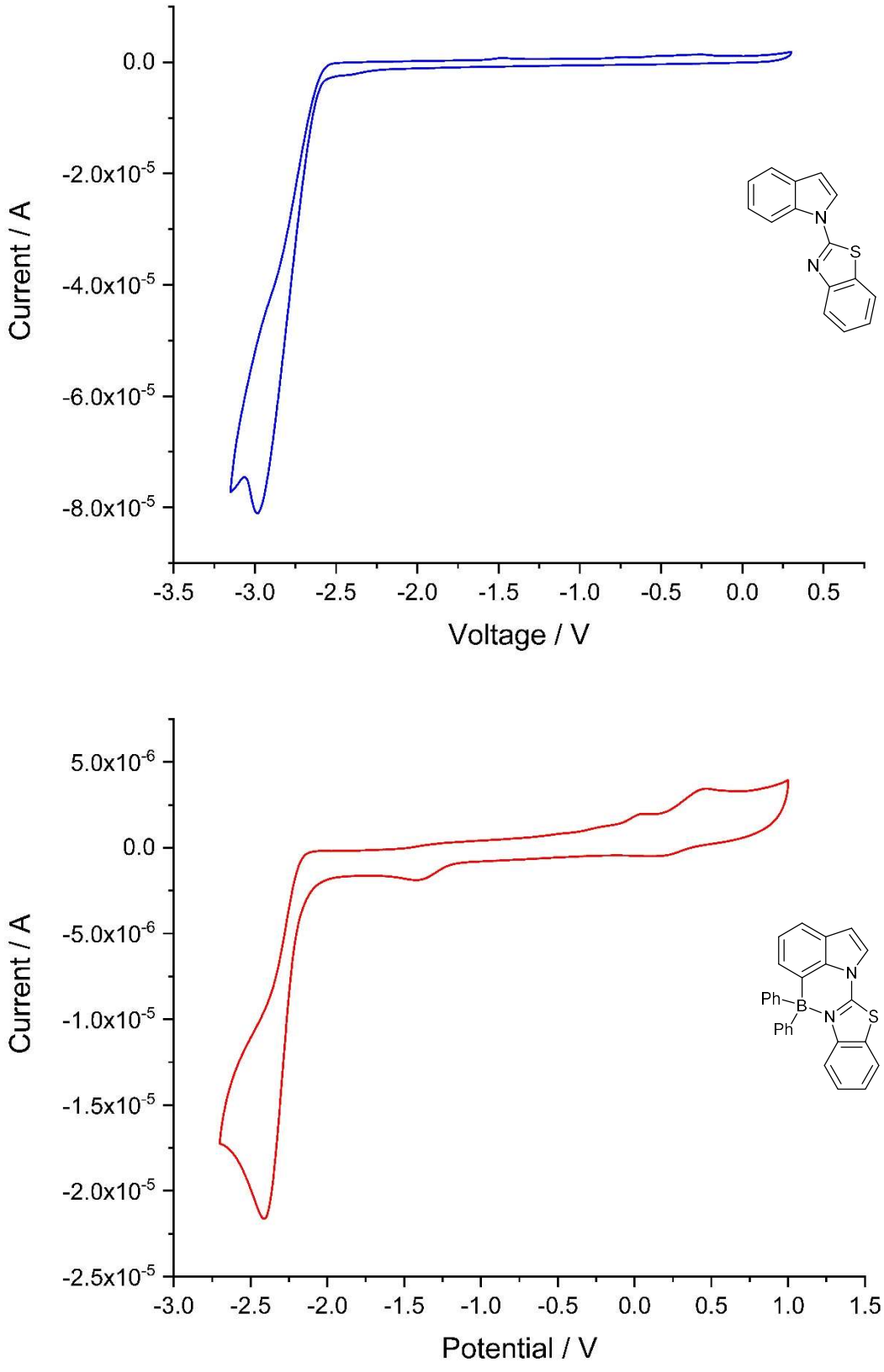


***Figure S23**: Cyclic voltammetry diagram of **16** (top) and **18-Ph** (bottom). Measured in THF (1 mM) with [nBu4N][PF6] (0.1 M) as the supporting electrolyte*

5. References

S1) J. K. Kwon, J. H. Lee, T. S. Kim, E. K. Yum, H. J. Park, *Bull. Korean Chem. Soc*., **2016**, 37, 1927–1933

S2) V. P. Reddy, R. Qiu, T. Iwasaki, N. Kambe, *Org. Lett*., **2013**, 15, 1290-1293

S3) I. D. Inaloo, S. Majnooni, H. Eslahi, M. Esmaeilpour, *New J. Chem.*, **2020**, 44, 13266-13278

S4) D.–G. Yu, F. de Azambuja, F. Glorius, *Angew. Chem. Int. Ed*., **2014**, 126, 2792-2796

S5) X. Hong, Q. Tan, B. Liu, B. Xu, *Angew. Chem. Int. Ed.,* **2017**, 56, 3691-3695

S6) S. G. Rull, J. F. Blandez, M. R. Fructos, T. R. Belderrain, M. C. Nicasio, *Adv. Synth. Catal.,* **2015**, 357, 907-911

S7) Y. Zi, F. Schömberg, K. Wagner, I. Vilotijevic, *Org. Lett.,* **2020**, 22, 3407-3411

6. X-Ray Crystallographic data

Crystal structure of 17-Cl. Using the program Olex2,[S1] the structure was solved by Direct Methods (ShelXT)[S2] and refined by Least Squares minimisation with ShelXL.[S3] The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

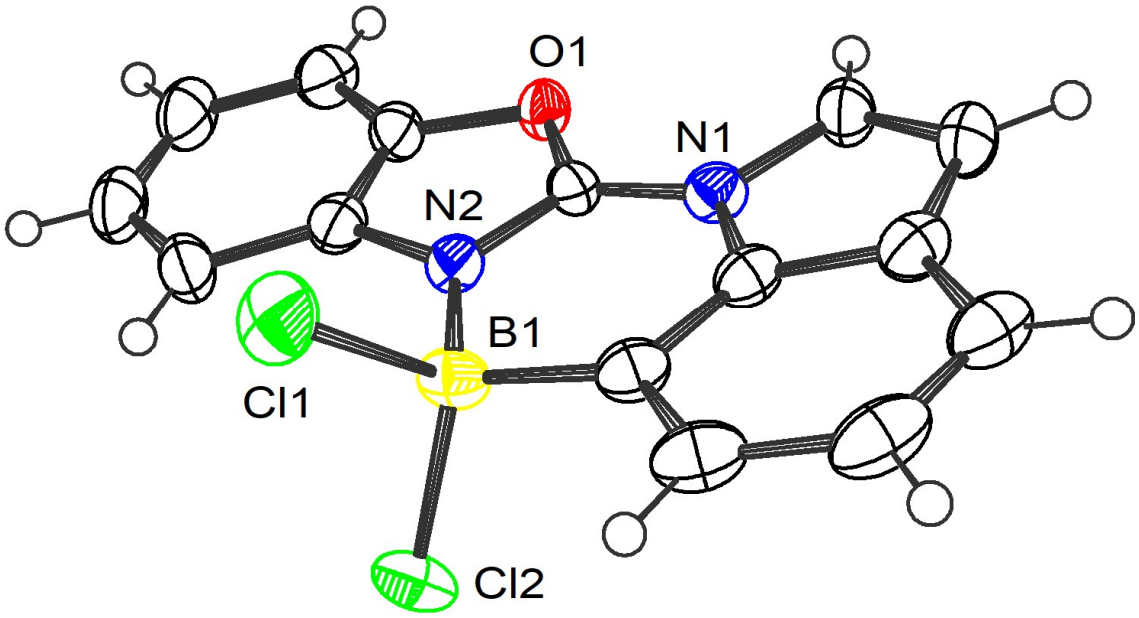


Figure S24. *ORTEP plot (50% probability) for* ***17-Cl***

Table 1 Crystal data and structure refinement for **17-Cl**	
Identification code	2051058
Empirical formula	$C_{15}H_9BN_2OCl_2$
Formula weight	314.95
Temperature/K	120.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.2660(2)
b/Å	11.4559(3)
c/Å	12.8747(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1366.65(6)
Z	4
ρ_{calc}g/cm^3	1.531
μ/mm^{-1}	4.252

F(000)	640.0
Crystal size/mm^3	0.392 × 0.05 × 0.031
Crystal color/shape	Colorless/needle
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.336 to 152.594
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 10, -16 ≤ l ≤ 15
Reflections collected	14822
Independent reflections	2851 [R_{int} = 0.0707, R_{sigma} = 0.0486]
Data/restraints/parameters	2851/0/190
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1398
Final R indexes [all data]	R_1 = 0.0604, wR_2 = 0.1470
Largest diff. peak/hole / e Å^{-3}	0.43/-0.51
Flack parameter	0.021(13)

Crystal structure of 4-Cl. Using the program Olex2,[S1] the structure was solved by Direct Methods (ShelXT)[S2] and refined by Least Squares minimisation with ShelXL.[S3] The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

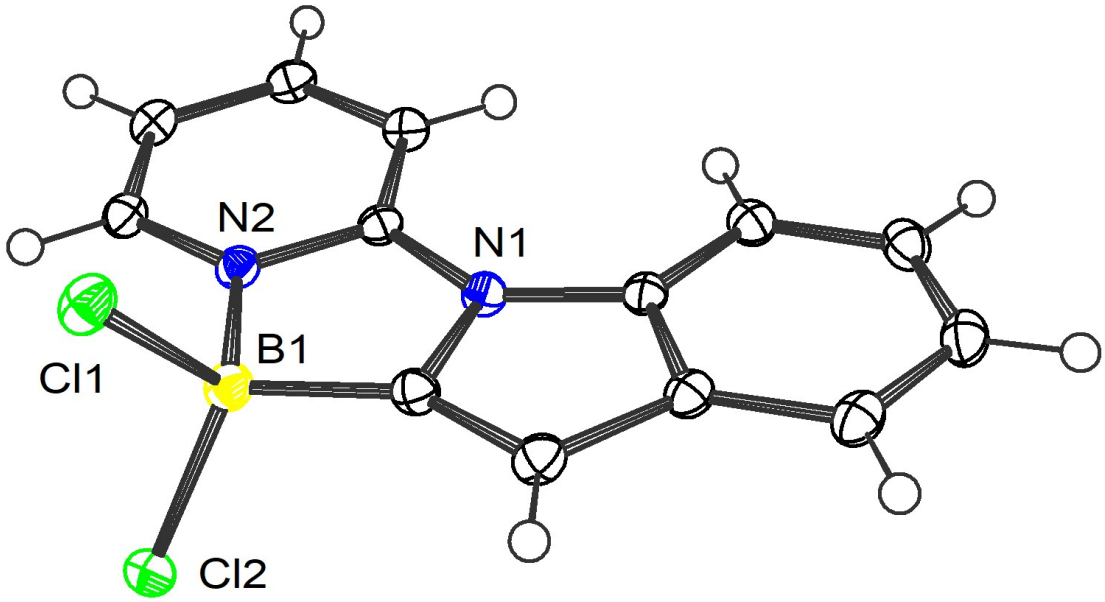


Figure S25. *ORTEP plot (50% probability) for* ***4-Cl****.*

Table 1 Crystal data and structure refinement for **4-Cl**.	
Identification code	2051059
Empirical formula	$C_{13}H_9BN_2Cl_2$
Formula weight	274.93
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.2198(4)
b/Å	8.3969(5)
c/Å	19.8689(9)
α/°	90
β/°	97.203(2)
γ/°	90
Volume/Å^3	1195.02(11)
Z	4
ρ_{calc}g/cm^3	1.528
μ/mm^{-1}	0.521
F(000)	560.0
Crystal size/mm^3	0.453 × 0.096 × 0.076
Crystal color/shape	Colorless/block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.274 to 61.054
Index ranges	$-9 \le h \le 10$, $-12 \le k \le 11$, $-28 \le l \le 27$
Reflections collected	18777
Independent reflections	3636 [R_{int} = 0.0590, R_{sigma} = 0.0436]
Data/restraints/parameters	3636/0/163
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0874
Final R indexes [all data]	R_1 = 0.0424, wR_2 = 0.0928
Largest diff. peak/hole / e Å^{-3}	0.43/-0.30

(S1) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

(S2) G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3-8.

(S3) G. M. Sheldrick, *Acta Cryst A.* **2008**, *64*, 112-122.

7. Computational data

All of the calculations were performed using the Gaussian09 series of programs.[S1] Geometries optimisation were completed with the DFT method using the M06-2X functional[S2] and the 6-311+G(d,p) as a basis set. All geometry optimizations were full, with no restrictions. Stationary points located in the potential energy surface were characterized as minima (no imaginary frequencies) or as transition states (one and only one imaginary frequency) by vibrational analysis. The transition state was further confirmed by IRC calculations. Solvent effects of dichloromethane were introduced using the self consistent field approach, by means of the integral equation formalism polarizable continuum model (IEFPCM).[S3]

[S1] 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.
[S2] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.
[S3] Mennucci B.; Cancès E.; Tomasi J., *J. Phys. Chem. B* **1997**, *101*, 10506-10517.

N-thiazole indole

C	2.1266610	0.8850940	0.0000490
C	1.1346910	-0.1201050	0.0000030
C	1.4588960	-1.4787890	-0.0001100
C	2.8070350	-1.8070850	-0.0001760
C	3.8078830	-0.8220400	-0.0001260
C	3.4782940	0.5229590	-0.0000160
C	1.4514650	2.1583950	0.0001610
C	0.1209900	1.9051470	0.0001780
H	0.6894590	-2.2355650	-0.0001320
H	3.0917610	-2.8527460	-0.0002590
H	4.8491700	-1.1217360	-0.0001730
H	4.2482890	1.2858690	0.0000230
H	1.9076970	3.1353800	0.0002400
H	-0.7101140	2.5930640	0.0002680
C	-2.8941060	-1.6353670	0.0002320
C	-3.7281570	-0.5695030	-0.0000400
H	-3.2132410	-2.6680490	0.0004090
H	-4.8058070	-0.5466480	-0.0001260
C	-1.3547680	-0.0707130	0.0000720
S	-2.8100320	0.8974670	-0.0002650
N	-1.5453970	-1.3510140	0.0003020
N	-0.1046050	0.5285870	0.0000720

BCl_3

B	0.0000000	0.0000000	0.0000000
Cl	0.0000000	1.7426300	0.0000000
Cl	1.5091620	-0.8713150	0.0000000
Cl	-1.5091620	-0.8713150	0.0000000

INT1 (N-thiazole indole-BCl_3 adduct)

C	2.8362910	-0.8341530	0.6405880

C	2.0471170	0.1557930	0.0261670
C	2.4720590	0.8837460	-1.0826530
C	3.7446700	0.6120280	-1.5603750
C	4.5606430	-0.3591220	-0.9554810
C	4.1179910	-1.0876310	0.1357380
C	2.0589080	-1.3954260	1.7187140
C	0.8599160	-0.7664330	1.7322040
H	1.8400960	1.6223710	-1.5609410
H	4.1129930	1.1562790	-2.4213970
H	5.5490270	-0.5433200	-1.3588530
H	4.7461390	-1.8444340	0.5905980
H	2.3662290	-2.1717710	2.4010840
H	0.0042440	-0.8854670	2.3764510
C	-2.2671610	1.7991410	-0.0820110
C	-1.6632860	2.9784220	0.1729340
H	-3.2921850	1.6533190	-0.3774020
H	-2.0914420	3.9656820	0.1112610
C	-0.2111570	1.0486520	0.4303570
S	-0.0281670	2.7370570	0.6246060
N	-1.4319590	0.7001150	0.0376620
N	0.8280710	0.1892560	0.7087140
B	-1.9446540	-0.7859900	-0.2845500
Cl	-0.6045690	-1.7592400	-1.0875560
Cl	-3.3824460	-0.6657220	-1.4457840
Cl	-2.4935670	-1.5309980	1.3207820

INT2 (N-thiazole indole-BCl_2 cation)

C	-2.5932760	-0.8493960	0.1918730
C	-1.3899840	-0.3660870	-0.3445060
C	-1.3327380	0.6977800	-1.2391700
C	-2.5355870	1.3171790	-1.5503730
C	-3.7477290	0.8763270	-0.9997370

C	-3.7906260	-0.2094280	-0.1395360
C	-2.2792620	-2.0093560	0.9996780
C	-0.9469000	-2.2090030	0.9419890
H	-0.4114770	1.0243550	-1.7090840
H	-2.5337850	2.1524550	-2.2392570
H	-4.6649550	1.3866120	-1.2657100
H	-4.7313240	-0.5654120	0.2628320
H	-2.9776320	-2.6099580	1.5604760
H	-0.3153580	-2.9403400	1.4218070
C	2.9374590	-0.0078530	-0.5166470
C	3.3087100	-1.2802150	-0.7194560
H	3.5527390	0.8746840	-0.5890380
H	4.2858680	-1.6498990	-0.9855650
C	0.9614940	-1.0678720	-0.0984370
S	1.9809480	-2.3674060	-0.5124350
N	1.5996480	0.1190210	-0.1204500
N	-0.3626360	-1.1991630	0.1478410
B	1.1076940	1.3863330	0.5073600
Cl	1.6546770	2.8773120	-0.1712140
Cl	0.1308420	1.3275640	1.9276780

$[BCl_4]^-$

B	0.0000000	0.0000000	0.0000000
Cl	1.0752560	1.0752560	1.0752560
Cl	-1.0752560	-1.0752560	1.0752560
Cl	-1.0752560	1.0752560	-1.0752560
Cl	1.0752560	-1.0752560	-1.0752560

$TS^{‡}$1B (N-thiazole-indole-TS1-C2)

C	-2.2103500	-0.8084460	-0.6292360
C	-1.6355380	0.4640830	-0.4133980
C	-2.2957940	1.4820280	0.2717250

C	-3.5770040	1.2000250	0.7072500
C	-4.1866600	-0.0530600	0.4815620
C	-3.5185960	-1.0609270	-0.1780950
C	-1.2374680	-1.6199670	-1.2810570
C	-0.0863280	-0.8855260	-1.4152540
H	-1.8420280	2.4494230	0.4464050
H	-4.1314710	1.9668160	1.2342800
H	-5.1942580	-0.2182250	0.8410590
H	-3.9777340	-2.0272440	-0.3460570
H	-1.3697150	-2.6344280	-1.6272820
C	2.8260690	1.0331380	0.4699070
C	2.6439810	2.3646640	0.3587710
H	3.6860620	0.5120780	0.8622270
H	3.3184460	3.1559500	0.6436680
C	0.7490910	1.0898800	-0.4308230
S	1.1048110	2.7438530	-0.3429390
N	1.7259390	0.3180080	0.0281140
N	-0.3451770	0.4380130	-0.9470220
B	1.3813180	-1.1650830	0.2434320
Cl	0.3741340	-1.4602380	1.6601210
Cl	2.5500330	-2.3501570	-0.3002330
H	0.7225100	-1.0313650	-2.1182900

INT3B (N-thiazole-indole-Wheland-C2)

C	-2.2133650	-0.9826880	-0.4434390
C	-1.7212020	0.3659810	-0.3649110
C	-2.5227530	1.4131960	0.1008160
C	-3.8162610	1.0852130	0.4374930
C	-4.3448110	-0.2365400	0.3338500
C	-3.5673120	-1.2680120	-0.0998740
C	-1.1704530	-1.7968540	-0.8270330
C	0.0283500	-1.0078200	-1.0165450

H	-2.1602990	2.4289610	0.1799200
H	-4.4723420	1.8707610	0.7939930
H	-5.3770500	-0.4054910	0.6098720
H	-3.9442780	-2.2793850	-0.1822740
H	-1.2164080	-2.8648710	-0.9964040
C	2.7684830	1.2184590	0.3566260
C	2.4851250	2.5385100	0.3134970
H	3.6949910	0.7492780	0.6513080
H	3.1208900	3.3711840	0.5678320
C	0.6337620	1.1518190	-0.3535280
S	0.8608460	2.8273200	-0.2302010
N	1.6961430	0.4424530	-0.0213170
N	-0.4225430	0.3679160	-0.7706070
B	1.3637470	-1.1040270	0.0145760
Cl	0.8623520	-1.5326430	1.7359060
Cl	2.7291480	-2.1169850	-0.6218190
H	0.4341640	-1.1039300	-2.0316330

TS‡2B (N-thiazole-indole-TS2-C2)

C	0.7940390	1.8160100	-1.4771380
C	0.2795460	2.0190260	-0.1830120
C	0.8401730	2.9008710	0.7310990
C	1.9623720	3.5987930	0.3073970
C	2.4936290	3.4187260	-0.9780120
C	1.9228260	2.5302360	-1.8779610
C	-0.0158940	0.7783790	-2.1173050
C	-1.0223350	0.4399720	-1.2339880
H	0.4332340	3.0422520	1.7246760
H	2.4364500	4.2965800	0.9864300
H	3.3705630	3.9837740	-1.2691540
H	2.3435030	2.3894130	-2.8662180
H	0.0091500	0.5025860	-3.1632790

C	-3.3467760	-0.5999230	1.5368380
C	-3.1412060	0.0567510	2.6969360
H	-4.0659280	-1.3808220	1.3419140
H	-3.6457260	-0.0667310	3.6411280
C	-1.6772290	0.7753370	0.9208840
S	-1.8692390	1.2397750	2.5420160
N	-2.5041240	-0.1784060	0.5316220
N	-0.8299120	1.1765550	-0.0767160
B	-2.2774790	-0.5484340	-0.9940420
Cl	-3.7699820	-0.0582090	-1.9662820
Cl	-1.8728780	-2.3325030	-1.1722990
H	0.7810960	-0.4944310	-1.6539330
B	2.2958540	-1.3724960	0.4964150
Cl	0.7308160	-1.2755030	1.4315410
Cl	1.7475870	-1.6038870	-1.4659490
Cl	3.2684030	0.1547160	0.5663630
Cl	3.2464650	-2.8785260	0.8381290

HCl

Cl	0.0000000	0.0000000	0.0713290
H	0.0000000	0.0000000	-1.2125870

13 (N-thiazole-indole-prod-C2)

C	-2.2942720	-1.2033250	-0.0003320
C	-1.9414070	0.1643270	-0.0003800
C	-2.8761910	1.1921720	-0.0000530
C	-4.2153180	0.8200230	0.0003560
C	-4.5952520	-0.5296920	0.0003630
C	-3.6483800	-1.5453220	0.0000000
C	-1.0672610	-1.9835330	-0.0005260
C	-0.0206870	-1.1239640	-0.0007670
H	-2.5849420	2.2358910	-0.0000620

H	-4.9777820	1.5892220	0.0007000
H	-5.6489990	-0.7811100	0.0006820
H	-3.9517660	-2.5857250	0.0000270
H	-1.0030390	-3.0608070	-0.0004610
C	2.6428390	1.5444400	-0.0007040
C	2.1691210	2.8053150	-0.0003300
H	3.6762680	1.2321150	-0.0007740
H	2.7173840	3.7326330	-0.0001430
C	0.4269480	1.1222070	-0.0008700
S	0.4200770	2.8273990	-0.0004470
N	1.6441430	0.5935580	-0.0010820
N	-0.5516800	0.1919070	-0.0007680
B	1.5796140	-0.9885070	-0.0001570
Cl	2.4113180	-1.6377470	1.5305420
Cl	2.4137120	-1.6406180	-1.5281660

TS‡1A (N-thiazole-indole-TS1-C7)

C	-2.0936370	-1.5056560	-0.0140750
C	-1.0304330	-0.8068610	-0.5976410
C	-1.1658580	0.4331280	-1.2316440
C	-2.4549240	0.9881910	-1.2321670
C	-3.5229360	0.3315250	-0.6264740
C	-3.3609220	-0.9242160	-0.0401800
C	-1.5387080	-2.7062560	0.5788540
C	-0.2024620	-2.6754450	0.4005050
H	-2.6151140	1.9395390	-1.7244010
H	-4.5017850	0.7931160	-0.6319900
H	-4.2063190	-1.4314230	0.4094320
H	-2.0836960	-3.4815790	1.0933440
H	0.5707940	-3.3567860	0.7181870
C	2.6872060	0.9633880	-0.0228080
C	3.6108220	-0.0040320	-0.1541640

H	2.8581190	2.0194490	0.1156730
H	4.6841960	0.0929340	-0.1425250
C	1.3346450	-0.8404730	-0.2438270
S	2.8713310	-1.5511590	-0.3817410
N	1.3809470	0.4815770	-0.0605710
N	0.1432120	-1.5048190	-0.3213890
B	0.1740130	1.3560300	0.3309310
Cl	0.2537550	3.0243150	-0.2237420
Cl	-0.5691590	0.9921130	1.8874420
H	-0.4015620	0.8267940	-1.8919750

INT3A (N-thiazole-indole-Wheland-C7)

C	-2.1899710	-1.5469900	-0.0792500
C	-1.0779110	-0.7907010	-0.4670530
C	-1.0916630	0.5946600	-0.8650260
C	-2.4280070	1.1755710	-0.8373380
C	-3.5256490	0.4624700	-0.4414810
C	-3.4192630	-0.9022210	-0.0707300
C	-1.6924870	-2.8398100	0.3458620
C	-0.3462980	-2.8009300	0.2513820
H	-2.5305160	2.2067010	-1.1569300
H	-4.4991880	0.9329840	-0.4180430
H	-4.3099800	-1.4354710	0.2442970
H	-2.2768890	-3.6739900	0.6983340
H	0.4058010	-3.5364040	0.4884680
C	2.6768940	0.8224040	-0.0373920
C	3.5678690	-0.1885610	-0.0903880
H	2.8864270	1.8766470	0.0529100
H	4.6436940	-0.1358330	-0.0528420
C	1.2744820	-0.9191130	-0.2166710
S	2.7748230	-1.7131200	-0.2545600
N	1.3626380	0.3986580	-0.1133210

N	0.0356900	-1.5299210	-0.2485000
B	0.0813890	1.3341730	0.0878730
Cl	0.4386870	3.0209980	-0.5111430
Cl	-0.3666360	1.2887910	1.8763170
H	-0.6246170	0.7561770	-1.8493040

TS‡2A (N-thiazole-indole -TS2-C7)

C	0.6089540	2.4927560	1.4854820
C	0.9121470	1.3184160	0.7885670
C	1.1810210	1.2093050	-0.5862890
C	1.2386360	2.4582380	-1.2595900
C	0.9332820	3.6501640	-0.6080700
C	0.6185830	3.6819100	0.7547800
C	0.3752090	2.1075790	2.8623260
C	0.5310000	0.7652450	2.9435450
H	1.4634550	2.4626870	-2.3212460
H	0.9458910	4.5760400	-1.1682200
H	0.3858970	4.6254690	1.2345510
H	0.1242360	2.7585510	3.6840260
H	0.4460840	0.0960440	3.7853840
C	1.4993960	-2.6452990	-0.2371910
C	1.1667960	-3.3987950	0.8249740
H	1.8101660	-2.9876280	-1.2118500
H	1.1500490	-4.4729310	0.9077970
C	1.0168440	-1.0169940	1.2340780
S	0.7140030	-2.4098650	2.1737260
N	1.4092870	-1.2812820	-0.0049930
N	0.8692020	0.2667610	1.6731170
B	1.8287480	-0.1791720	-1.0657590
Cl	1.2763820	-0.7010420	-2.7538660
Cl	3.7012480	-0.0817810	-1.0100880
H	-0.1855370	1.1167750	-1.0349380

Cl	-2.3949360	0.4184540	1.3485360
Cl	-1.6871060	1.0260830	-1.5689500
Cl	-4.3594970	-0.2092530	-0.8919980
Cl	-1.8328450	-1.8741270	-0.5642680
B	-2.6207660	-0.2372950	-0.3456170

14 (N-thiazole-indole-prod-C7)

C	-2.5882600	1.1800710	-0.0035180
C	-1.3438550	0.5384240	-0.0026010
C	-1.1166810	-0.8266910	-0.0152380
C	-2.2790980	-1.5994180	-0.0329750
C	-3.5516450	-1.0102870	-0.0349310
C	-3.7266100	0.3719110	-0.0194680
C	-2.3195850	2.6072230	0.0123670
C	-0.9769070	2.7827580	0.0200930
H	-2.1961250	-2.6812270	-0.0445690
H	-4.4256170	-1.6508060	-0.0479620
H	-4.7201520	0.8036650	-0.0208110
H	-3.0478460	3.4027840	0.0179500
H	-0.3865700	3.6856950	0.0311380
C	2.7319610	-0.1958730	-0.0351990
C	3.3778530	0.9800180	-0.0350040
H	3.1672160	-1.1834220	-0.0461300
H	4.4391740	1.1644710	-0.0453100
C	0.9541490	1.1880300	-0.0055300
S	2.2563770	2.3082780	-0.0141000
N	1.3468920	-0.0814950	-0.0190970
N	-0.3536040	1.5238150	0.0114250
B	0.3839640	-1.3370710	0.0043540
Cl	0.7905850	-2.3083890	1.5640600
Cl	0.8110100	-2.3964050	-1.4861040

N-Pyrimidine-indole

C	-1.0956790	-0.0920960	0.0000740
C	-2.1562860	0.8436140	-0.0002430
C	-3.4823680	0.3985740	-0.0002960
C	-3.7303290	-0.9637660	0.0000040
C	-2.6690050	-1.8815590	0.0003720
C	-1.3437940	-1.4688040	0.0003970
C	-0.2275040	2.0033290	0.0000100
C	-1.5720310	2.1606910	-0.0003400
H	-4.2972450	1.1134470	-0.0005480
H	-4.7509010	-1.3275610	-0.0000230
H	-2.8851480	-2.9435070	0.0006370
H	-0.5342610	-2.1807230	0.0006620
H	-2.0993340	3.1015290	-0.0006310
H	0.5665300	2.7296590	0.0000680
C	1.4117250	0.1738150	0.0003030
N	2.3655590	1.1065020	0.0005830
N	1.5919870	-1.1436140	-0.0003830
C	3.6184270	0.6634650	0.0002690
C	2.8573420	-1.5624380	-0.0007010
C	3.9342550	-0.6895860	-0.0002940
H	4.3956720	1.4213680	0.0006400
H	3.0052180	-2.6376520	-0.0010300
H	4.9562610	-1.0396540	-0.0004170
N	0.0959810	0.6444910	0.0002720

INT4 (N-Pyrimidine-indole-BCl_3)

C	-2.1809030	0.2310580	-0.0679310
C	-2.8909610	-0.8629940	-0.5955660
C	-4.2230440	-1.0625520	-0.2185570
C	-4.8019930	-0.1750520	0.6739280
C	-4.0697850	0.9014920	1.1982220

C	-2.7482270	1.1229370	0.8389510
C	-0.7968530	-0.9567080	-1.4327240
C	-1.9919520	-1.5838770	-1.4679780
H	-4.7846390	-1.9001140	-0.6151040
H	-5.8325070	-0.3136300	0.9776380
H	-4.5441770	1.5778990	1.8988790
H	-2.1905300	1.9569770	1.2408120
H	-2.2246280	-2.4583590	-2.0547470
H	0.1241710	-1.1704320	-1.9498670
C	0.1238330	1.0753230	-0.3849380
N	-0.2262290	2.3534250	-0.3582200
N	1.4137910	0.6597890	-0.2703240
C	0.7244240	3.2688310	-0.4276380
C	2.3721200	1.5990510	-0.4923020
C	2.0639270	2.9262080	-0.6205980
H	0.4086930	4.3044180	-0.3619730
H	3.3906950	1.2385090	-0.5173220
H	2.8335070	3.6642770	-0.7886760
N	-0.8768860	0.1577080	-0.5833570
B	1.9420710	-0.7671710	0.3052450
Cl	3.3428900	-0.3898930	1.4718680
Cl	2.5772090	-1.7472170	-1.1302280
Cl	0.6358310	-1.6371520	1.2530790

INT5 (N-Pyrimidine-indole-BCl_2-cation)

C	-1.8745250	0.2559230	-0.1887330
C	-2.5205370	-0.9080020	-0.6391200
C	-3.8765850	-1.0938020	-0.3632690
C	-4.5426280	-0.1182680	0.3616370
C	-3.8744130	1.0293070	0.8114470
C	-2.5276990	1.2397110	0.5465530
C	-0.3630300	-1.0692700	-1.2899020

C	-1.5443800	-1.7123130	-1.3440510
H	-4.3888410	-1.9847450	-0.7052920
H	-5.5946210	-0.2420130	0.5870400
H	-4.4199270	1.7763100	1.3746670
H	-2.0209120	2.1322950	0.8831000
H	-1.7281620	-2.6421710	-1.8586690
H	0.5771010	-1.2979730	-1.7700470
C	0.4839830	1.0054780	-0.2842150
N	0.2383110	2.2991870	-0.1862460
N	1.7430680	0.4791700	-0.1280890
C	1.2692370	3.1229530	-0.1070530
C	2.8087240	1.3399650	-0.1712910
C	2.6005830	2.6865450	-0.1981700
H	1.0376680	4.1759820	0.0106760
H	3.7918850	0.8890090	-0.1308980
H	3.4300120	3.3769160	-0.2183430
N	-0.5198940	0.1426820	-0.5760300
B	1.9752670	-0.9258300	0.3690850
Cl	0.9791000	-1.5262400	1.6435220
Cl	3.3136450	-1.8073540	-0.2663510

TS‡3B (N-Pyrimidine-indole-TS1-C2)

C	-1.6951840	0.4782650	-0.3902550
C	-2.3099950	-0.7728950	-0.6078320
C	-3.6317640	-0.9733400	-0.1777700
C	-4.2759450	0.0648160	0.4626420
C	-3.6290960	1.2975640	0.6864040
C	-2.3306800	1.5290710	0.2701060
C	-0.1921860	-0.9241380	-1.3877970
C	-1.3566790	-1.6217000	-1.2580270
H	-4.1235980	-1.9234290	-0.3458240
H	-5.2952360	-0.0632860	0.8044250

H	-4.1667250	2.0900050	1.1927380
H	-1.8397420	2.4796400	0.4297760
H	-1.5277730	-2.6231760	-1.6225540
C	0.6856160	1.1204860	-0.4599440
N	0.6795470	2.4319590	-0.4385460
N	1.7413850	0.3570600	-0.0710480
C	1.8222970	3.0290640	-0.1046280
C	2.9256150	0.9582220	0.1933090
C	3.0027060	2.3273220	0.1574720
H	1.8019790	4.1120950	-0.0621160
H	3.7531790	0.3123650	0.4594200
H	3.9300320	2.8367880	0.3719650
N	-0.3930470	0.3880470	-0.8885160
B	1.4521750	-1.1068340	0.2969280
Cl	2.5834030	-2.3124990	-0.2390740
Cl	0.4329130	-1.3277960	1.6987410
H	0.6461990	-1.1176960	-2.0421230

INT6A (N-Pyrimidine-indole-Wheland-C2)

C	-1.7438550	0.4337860	-0.3836180
C	-2.2744520	-0.9038090	-0.4073480
C	-3.6350550	-1.1354600	-0.0462230
C	-4.3785490	-0.0648580	0.3482540
C	-3.8121770	1.2462250	0.3926310
C	-2.5126800	1.5251710	0.0376770
C	-0.0361920	-1.0069100	-0.9905500
C	-1.2561020	-1.7597660	-0.7614660
H	-4.0415460	-2.1378690	-0.0857270
H	-5.4134150	-0.1920640	0.6367560
H	-4.4460200	2.0639740	0.7157310
H	-2.1069400	2.5264890	0.0642240
H	-1.3320350	-2.8314700	-0.8929660

C	0.6079420	1.2003430	-0.4065870
N	0.5418820	2.5052110	-0.3644700
N	1.6860710	0.4520580	-0.0948390
C	1.6761370	3.1235730	-0.0150340
C	2.8331290	1.0665640	0.2226120
C	2.8624820	2.4458230	0.2592600
H	1.6319880	4.2052110	0.0370010
H	3.6796610	0.4309450	0.4542450
H	3.7675080	2.9762870	0.5145510
N	-0.4453590	0.3788910	-0.7779130
B	1.3024920	-1.0959880	0.0036310
Cl	2.6433290	-2.1605490	-0.5952670
Cl	0.8243900	-1.4153720	1.7550250
H	0.3351900	-1.1481240	-2.0149480

TS‡4A (N-Pyrimidine-indole-TS2-C2)

C	0.3491130	2.0363560	0.0217830
C	0.8621920	1.9386760	-1.2855280
C	2.0087760	2.6577600	-1.6231580
C	2.5975290	3.4501950	-0.6491860
C	2.0676510	3.5269820	0.6476750
C	0.9306990	2.8190980	1.0116430
C	-0.9896170	0.6007150	-1.1688670
C	0.0263020	0.9886160	-2.0190410
H	2.4265970	2.5936150	-2.6205890
H	3.4872850	4.0189300	-0.8906470
H	2.5579730	4.1508090	1.3848800
H	0.5181880	2.8662740	2.0100040
H	0.0506410	0.8038660	-3.0845030
C	-1.6324800	0.7808540	1.0389060
N	-1.5880780	1.1844760	2.2851470
N	-2.5074600	-0.1171200	0.5312660

C	-2.4893250	0.6259830	3.0994060
C	-3.4083460	-0.6747720	1.3458000
C	-3.4244070	-0.3175640	2.6788100
H	-2.4593510	0.9493860	4.1337520
H	-4.0872200	-1.3925150	0.9005790
H	-4.1360340	-0.7519200	3.3644330
N	-0.7810120	1.2137520	0.0494450
B	-2.2777190	-0.3451800	-1.0350910
Cl	-1.9732240	-2.1252160	-1.3658550
Cl	-3.7510350	0.2978100	-1.9437930
H	0.7813530	-0.3617660	-1.6523910
B	2.2736380	-1.4443820	0.4129950
Cl	3.1989850	-2.9881380	0.6231250
Cl	0.7330780	-1.3792380	1.3904910
Cl	3.2790120	0.0540000	0.5502650
Cl	1.6677890	-1.5353350	-1.5533800

(N-Pyrimidine-indole-prod-C2)

C	-1.9708860	0.2800130	0.0001400
C	-2.3792250	-1.0722680	0.0000440
C	-3.7464120	-1.3620550	-0.0000740
C	-4.6517540	-0.3101060	-0.0000920
C	-4.2173350	1.0238160	0.0000060
C	-2.8653110	1.3447410	0.0001310
C	-0.1078270	-1.0797730	0.0001530
C	-1.1855040	-1.9008640	0.0001110
H	-4.0903410	-2.3897250	-0.0001330
H	-5.7147200	-0.5193330	-0.0001750
H	-4.9495810	1.8221150	-0.0000110
H	-2.5183580	2.3692860	0.0002120
H	-1.1625450	-2.9796840	0.0000990
C	0.4062470	1.1827180	0.0000960

N	0.2125370	2.4886650	0.0001200
N	1.6219580	0.5771480	-0.0000690
C	1.3180140	3.2327830	-0.0000900
C	2.7263030	1.3305480	-0.0002710
C	2.6103970	2.7038970	-0.0003130
H	1.1659350	4.3066430	-0.0000410
H	3.6714820	0.8000070	-0.0003410
H	3.4824280	3.3397400	-0.0005050
N	-0.5792930	0.2506940	0.0002390
B	1.4853460	-1.0157210	0.0000350
Cl	2.3022480	-1.6803310	-1.5280010
Cl	2.3025950	-1.6800630	1.5279800

TS‡3A (N-Pyrimidine-indole-TS1-C7)

C	-1.1090920	-0.6937320	-0.5907660
C	-2.2435190	-1.3002570	-0.0306490
C	-3.4570920	-0.6176260	-0.0842020
C	-3.4999360	0.6446960	-0.6760730
C	-2.3693630	1.2050630	-1.2656150
C	-1.1358550	0.5396060	-1.2450170
C	-0.4777520	-2.6614500	0.3607130
C	-1.8112700	-2.5613290	0.5391640
H	-4.3533350	-1.0550310	0.3392250
H	-4.4364300	1.1866370	-0.7054200
H	-2.4409050	2.1611260	-1.7692680
H	-2.4342330	-3.2882920	1.0351510
H	0.2322290	-3.4162660	0.6569040
C	1.2779730	-1.0588910	-0.2706270
N	2.2573740	-1.9329790	-0.3525780
N	1.4707300	0.2862900	-0.1228590
C	3.5010490	-1.4700350	-0.3737200
C	2.7441830	0.7571760	-0.2183030

C	3.7964320	-0.1053570	-0.3693190
H	4.2901340	-2.2129320	-0.4136570
H	2.8691610	1.8285290	-0.1380410
H	4.8079820	0.2641650	-0.4419500
N	-0.0144560	-1.5084070	-0.3145480
B	0.3579500	1.2375050	0.3996630
Cl	-0.3396840	0.8111650	1.9515290
Cl	0.4989470	2.9231150	-0.0580430
H	-0.3219000	0.8802670	-1.8741450

INT6A (N-Pyrimidine-indole-Wheland-C7)

C	1.1591690	0.7025250	-0.4555650
C	2.3552560	1.3392150	-0.0959820
C	3.5035630	0.5621520	-0.0898060
C	3.4526030	-0.8150360	-0.4361060
C	2.2807560	-1.4084220	-0.8091900
C	1.0159410	-0.6771400	-0.8476620
C	0.6622250	2.7944300	0.2161880
C	2.0057370	2.6880970	0.3030700
H	4.4533740	0.9970900	0.2037040
H	4.3684150	-1.3899650	-0.4136390
H	2.2651140	-2.4497020	-1.1112060
H	2.6812530	3.4595420	0.6349600
H	-0.0142800	3.6042470	0.4327300
C	-1.1940450	1.1607160	-0.2281950
N	-2.1091260	2.0959750	-0.2616610
N	-1.4338270	-0.1716220	-0.1492280
C	-3.3832950	1.7045430	-0.2241220
C	-2.7244300	-0.5594290	-0.1209770
C	-3.7441230	0.3649210	-0.1663080
H	-4.1288450	2.4910800	-0.2460260
H	-2.9012420	-1.6243970	-0.0550750

H	-4.7765290	0.0491710	-0.1473630
N	0.1410330	1.5574660	-0.2372070
B	-0.2313280	-1.2483730	0.0913940
Cl	0.1661290	-1.1846230	1.8894340
Cl	-0.7468940	-2.9110000	-0.4567760
H	0.5596700	-0.7817830	-1.8456410

TS‡4A (N-Pyrimidine-indole-TS2-C7)

C	0.4695270	1.2966200	0.8448420
C	-0.2646580	2.2420940	1.5656900
C	-0.7001600	3.3708240	0.8697200
C	-0.3988270	3.4991790	-0.4889590
C	0.3444120	2.5355160	-1.1680850
C	0.7872330	1.3575530	-0.5190780
C	0.2812470	0.5477640	2.9637460
C	-0.3686900	1.7350560	2.9189130
H	-1.2771240	4.1394470	1.3708760
H	-0.7437900	4.3735460	-1.0258200
H	0.5615350	2.6620940	-2.2236420
H	-0.8698710	2.2059280	3.7493660
H	0.4303920	-0.1549670	3.7659680
C	1.3867210	-0.8988500	1.2601570
N	1.4389340	-1.9057380	2.1134880
N	1.8361300	-0.9502770	-0.0221280
C	1.9244180	-3.0578500	1.6732390
C	2.3129410	-2.1364110	-0.4598440
C	2.3584530	-3.2350230	0.3609980
H	1.9658240	-3.8687840	2.3921310
H	2.6598750	-2.1555730	-1.4837240
H	2.7358720	-4.1808890	0.0028590
N	0.8252000	0.2759530	1.6947540
B	1.9794270	0.3787010	-0.9381840

Cl	3.6336420	1.1116310	-0.4625190
Cl	1.9677400	-0.0586510	-2.7314980
H	-0.3176680	0.5789230	-1.1151770
Cl	-1.7872230	-1.5723970	0.9948090
Cl	-1.3007030	-0.4047870	-1.7967100
Cl	-3.2121310	0.9797640	0.1594130
Cl	-3.9630790	-1.6773020	-1.1306270
B	-2.6579800	-0.6803990	-0.3463020

(N-Pyrimidine-indole-prod-C7)

C	-1.3846850	0.4979160	-0.0012380
C	-2.6736060	1.0477800	-0.0011680
C	-3.7512610	0.1611550	-0.0044970
C	-3.4803340	-1.2061390	-0.0079970
C	-2.1696210	-1.7036920	-0.0077010
C	-1.0678060	-0.8471840	-0.0039660
C	-1.1786840	2.7589540	0.0039390
C	-2.5056630	2.4904900	0.0025150
H	-4.7726760	0.5224130	-0.0045290
H	-4.3073860	-1.9062010	-0.0108500
H	-2.0092600	-2.7766950	-0.0101680
H	-3.2895210	3.2315050	0.0040260
H	-0.6396590	3.6911350	0.0064290
C	0.8789450	1.3693040	-0.0015680
N	1.6468650	2.4573150	-0.0020470
N	1.3615970	0.0997400	-0.0043670
C	2.9556400	2.2838460	-0.0053220
C	2.7067080	-0.0551510	-0.0074030
C	3.5531560	1.0197970	-0.0082610
H	3.5598640	3.1848490	-0.0055290
H	3.0557190	-1.0798400	-0.0088450
H	4.6244670	0.8896360	-0.0107480

N	-0.4682410	1.5462960	0.0017580
B	0.4596840	-1.2388350	0.0009930
Cl	0.9563190	-2.2221890	-1.5167930
Cl	0.9496670	-2.2006660	1.5358430

TS-1A-distortion

C	2.11986400	0.86600000	0.10844500
C	1.08359800	0.01150700	-0.28559000
C	1.25076300	-1.35540000	-0.53356600
C	2.54284200	-1.86529700	-0.33275700
C	3.58339900	-1.04476900	0.09467700
C	3.39129500	0.32314800	0.29158200
C	1.53526100	2.17623900	0.31451400
C	0.20666800	2.07285800	0.10844500
H	2.72755600	-2.91471400	-0.52672000
H	4.56500300	-1.47184900	0.25373100
H	4.21613800	0.95206700	0.60495500
H	2.05565600	3.07544200	0.60340900
H	-0.58242400	2.80318800	0.19225800
C	-2.64007200	-1.58429300	0.64862500
C	-3.56502300	-0.71068200	0.21562400
H	-2.80853200	-2.55957500	1.07769300
H	-4.63740100	-0.81867800	0.21909300
C	-1.29300100	0.10421200	-0.03440900
S	-2.82856200	0.71943600	-0.42047900
N	-1.33670900	-1.11101200	0.51773600
N	-0.10420900	0.73905900	-0.25941600
H	0.51386600	-1.93432100	-1.07853600

TS-1B-distortion

C	2.10595900	0.83986300	-0.05726700
C	1.09407600	-0.13021000	-0.23440400

C	1.31747200	-1.49327900	-0.05087900
C	2.60617200	-1.86614000	0.28219100
C	3.64318700	-0.92117700	0.43866500
C	3.40849700	0.42632400	0.27614300
C	1.51503500	2.12307400	-0.24196700
C	0.17417400	1.94855000	-0.47470700
H	0.53254500	-2.22888800	-0.17350900
H	2.82728300	-2.91706900	0.42297300
H	4.63528600	-1.26933100	0.69615300
H	4.19792700	1.15657600	0.40389000
H	2.02137900	3.07678300	-0.21854000
C	-3.26540100	0.61003100	0.97265100
C	-3.59400500	-0.55149100	0.37152300
H	-3.87194200	1.20835500	1.63531600
H	-4.51881900	-1.10088400	0.44286700
C	-1.35102900	0.17603300	-0.15659500
S	-2.30121700	-1.14874700	-0.61701600
N	-1.97271900	1.00471200	0.67252200
N	-0.08665400	0.54687300	-0.54729500
H	-0.51338600	2.62384300	-0.96561300

TS-3A-distortion

C	-1.10909200	-0.69373200	-0.59076600
C	-2.24351900	-1.30025700	-0.03064900
C	-3.45709200	-0.61762600	-0.08420200
C	-3.49993600	0.64469600	-0.67607300
C	-2.36936300	1.20506300	-1.26561500
C	-1.13585500	0.53960600	-1.24501700
C	-0.47775200	-2.66145000	0.36071300
C	-1.81127000	-2.56132900	0.53916400
H	-4.35333500	-1.05503100	0.33922500
H	-4.43643000	1.18663700	-0.70542000

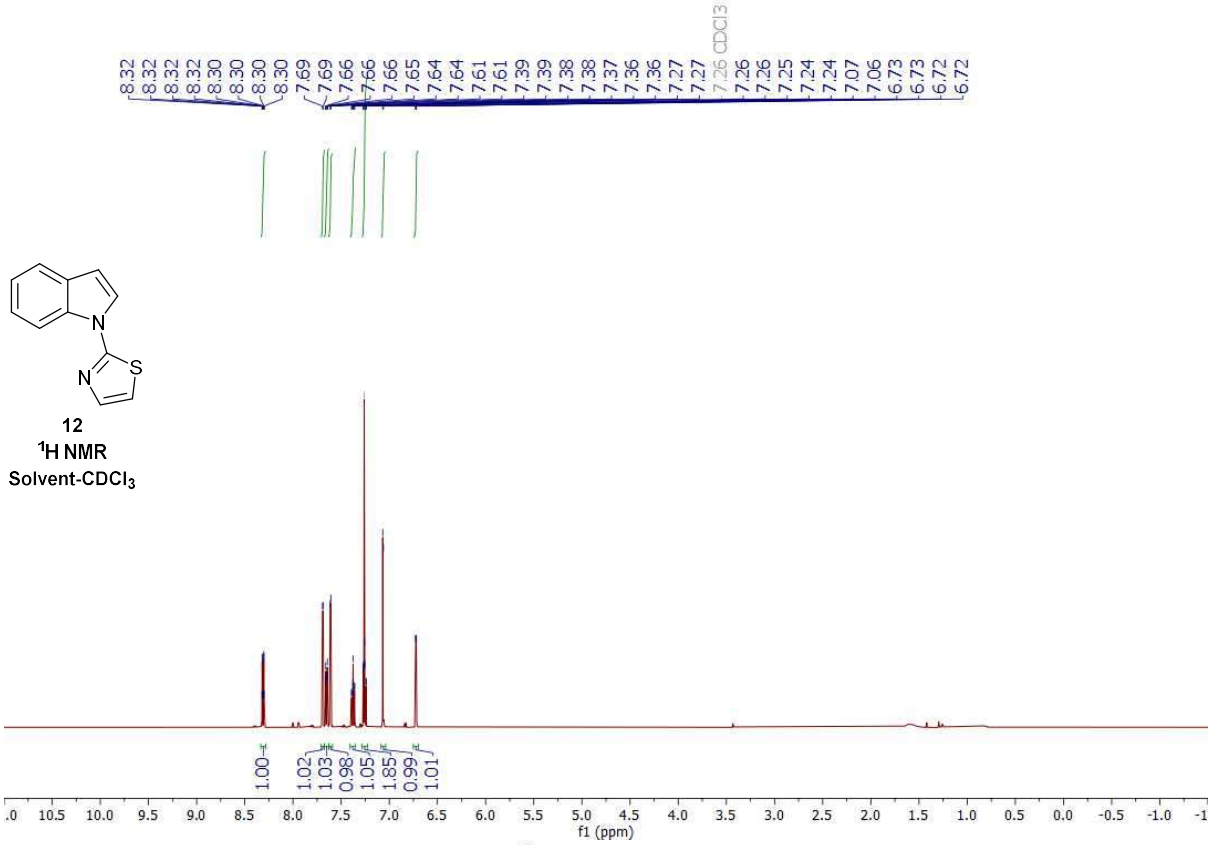
H	-2.44090500	2.16112600	-1.76926800
H	-2.43423300	-3.28829200	1.03515100
H	0.23222900	-3.41626600	0.65690400
C	1.27797300	-1.05889100	-0.27062700
N	2.25737400	-1.93297900	-0.35257800
N	1.47073000	0.28629000	-0.12285900
C	3.50104900	-1.47003500	-0.37372000
C	2.74418300	0.75717600	-0.21830300
C	3.79643200	-0.10535700	-0.36931900
H	4.29013400	-2.21293200	-0.41365700
H	2.86916100	1.82852900	-0.13804100
H	4.80798200	0.26416500	-0.44195000
N	-0.01445600	-1.50840700	-0.31454800
H	-0.32190000	0.88026700	-1.87414500

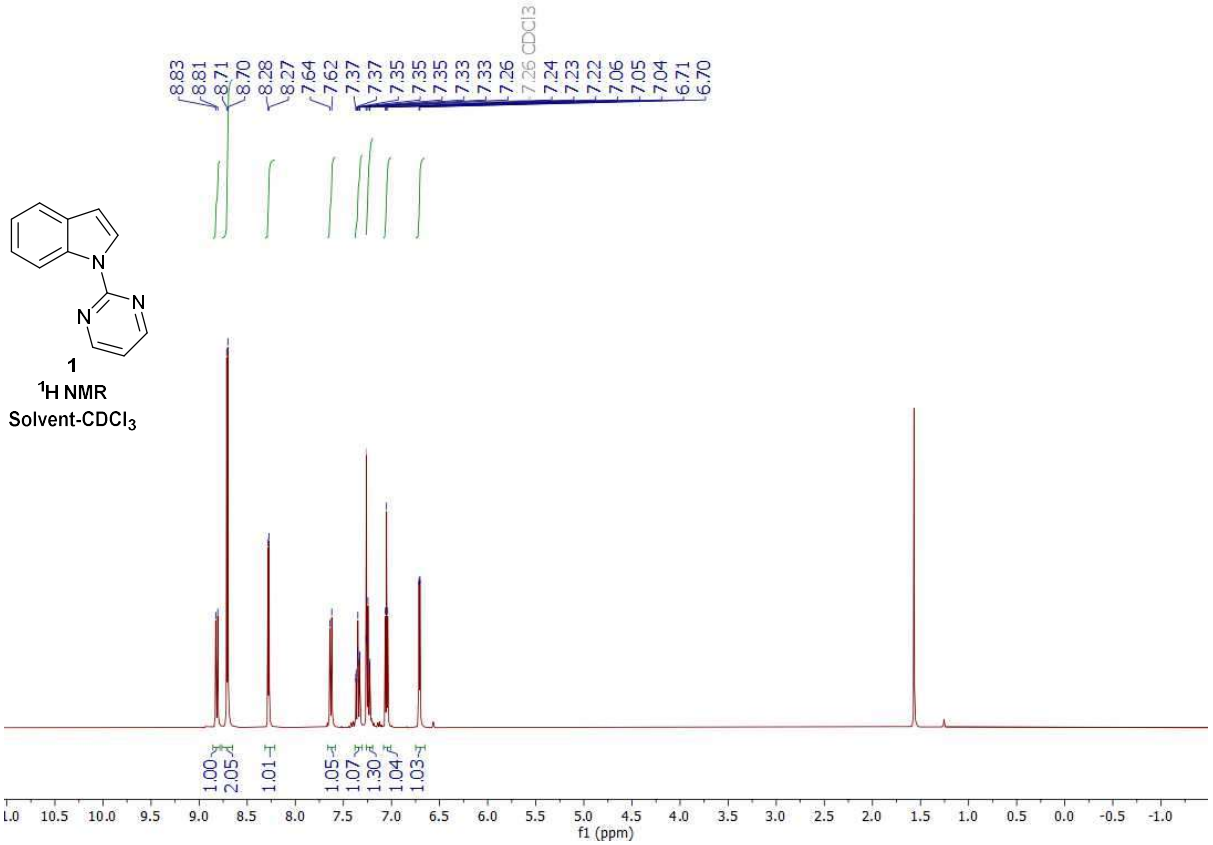
TS-3B-distortion

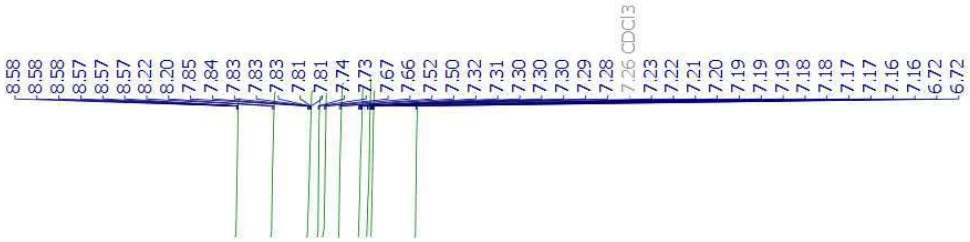
C	1.11625000	-0.14209000	-0.20489200
C	2.11891600	0.83718800	-0.04238000
C	3.43145100	0.43462400	0.25325100
C	3.68652400	-0.91387200	0.39239000
C	2.66000000	-1.86942100	0.24635300
C	1.35891700	-1.50643800	-0.05064600
C	0.17612900	1.92800400	-0.43230000
C	1.50873700	2.12137400	-0.21726000
H	4.21631500	1.17150500	0.37075600
H	4.68973100	-1.25120500	0.62034200
H	2.89793800	-2.91976700	0.36272200
H	0.57470700	-2.24084100	-0.17619800
H	2.00880800	3.07794100	-0.22119400
C	-1.34132200	0.07110400	-0.18491300
N	-1.78112700	-1.08092800	-0.63196000
N	-2.07373400	0.91938800	0.58495400

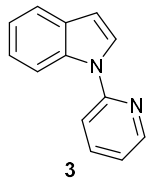
C	-3.05775600	-1.36930200	-0.38503500
C	-3.39096300	0.66683200	0.77151000
C	-3.92873200	-0.48763800	0.26193800
H	-3.40648200	-2.33487100	-0.73323200
H	-3.94906000	1.38774600	1.35599200
H	-4.97333800	-0.72195700	0.40119100
N	-0.07927300	0.53326800	-0.46292500
H	-0.54859100	2.60715500	-0.85895000

8. Spectroscopic data – NMR spectra of purified compounds





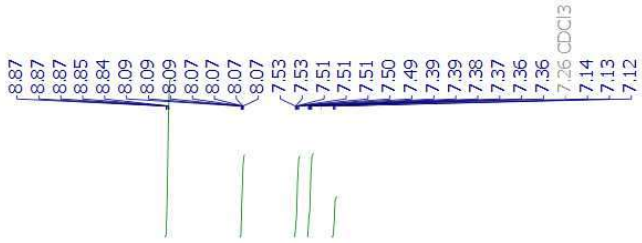


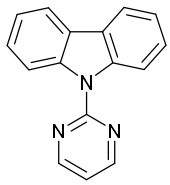


3

^{1}H NMR

Solvent-$CDCl_3$

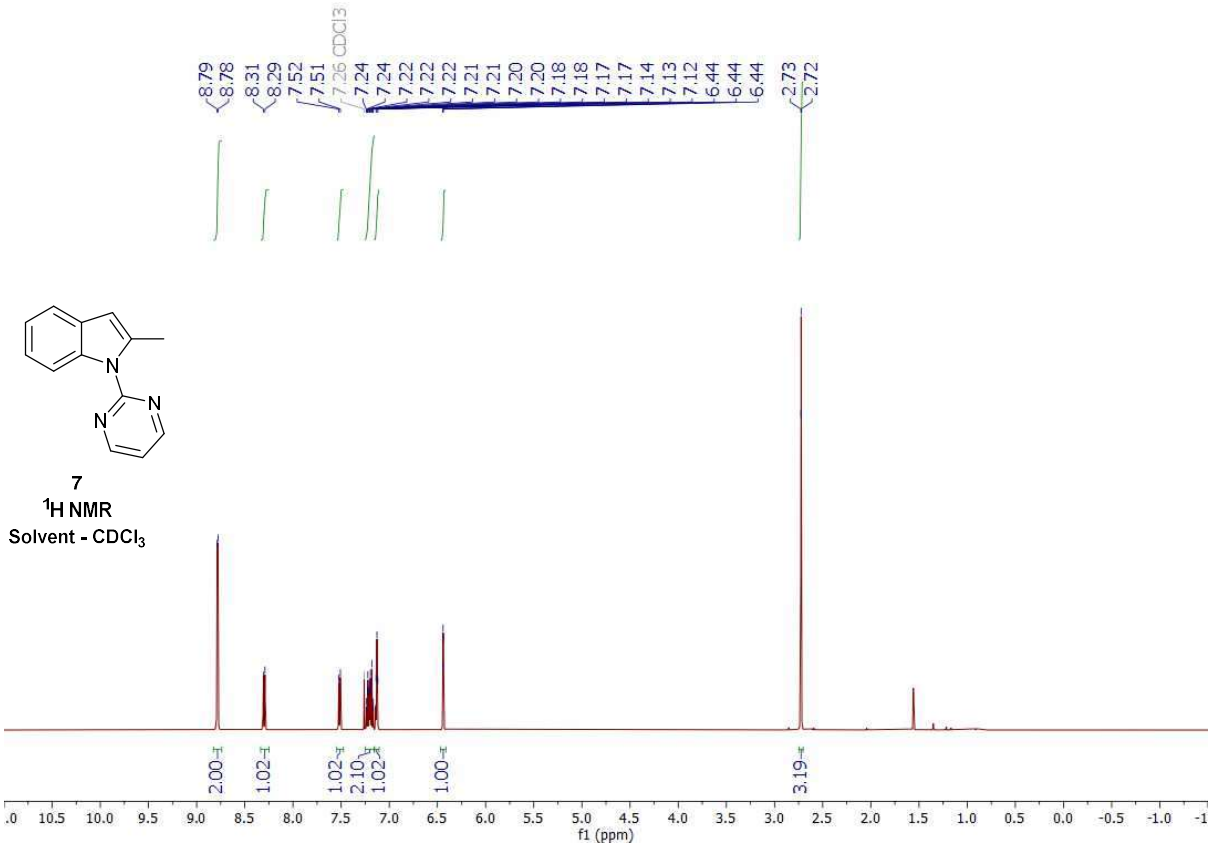




5

^{1}H NMR

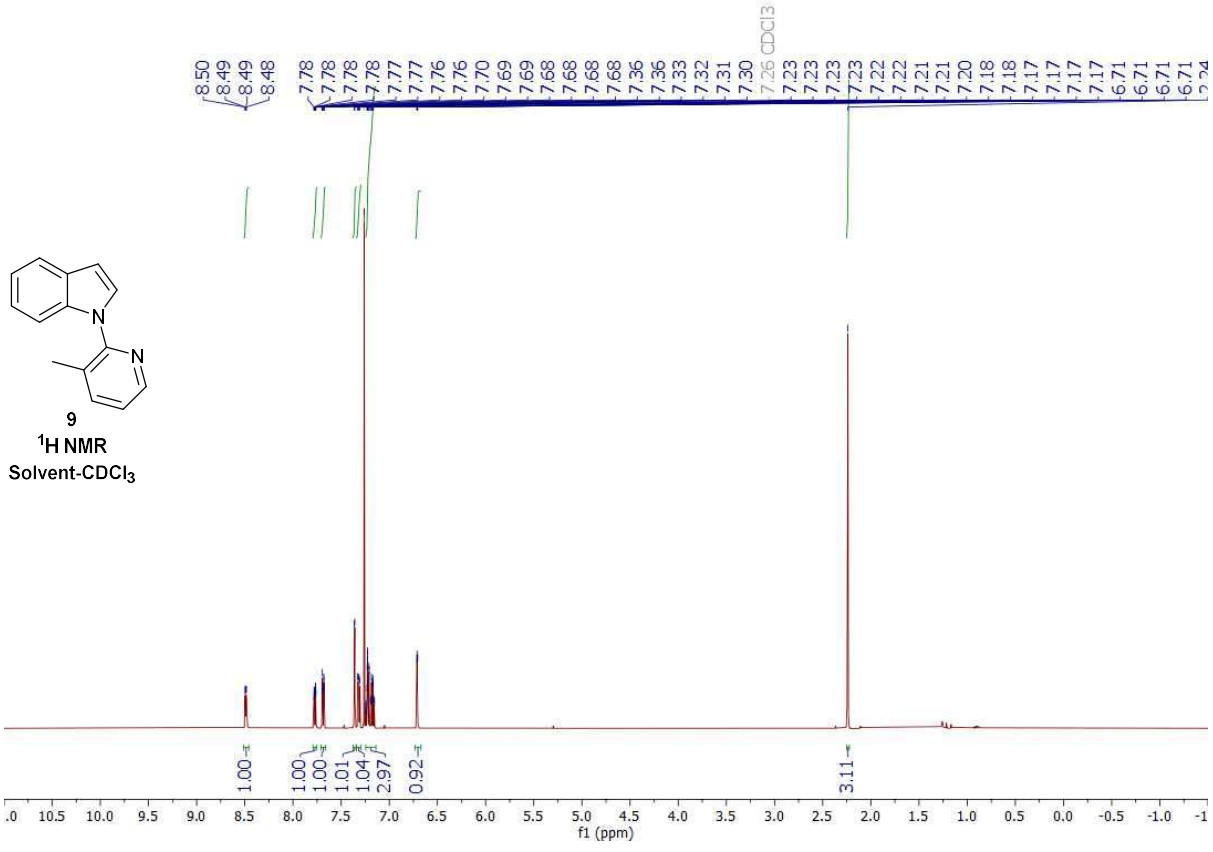
Solvent-$CDCl_3$



7

^{1}H NMR

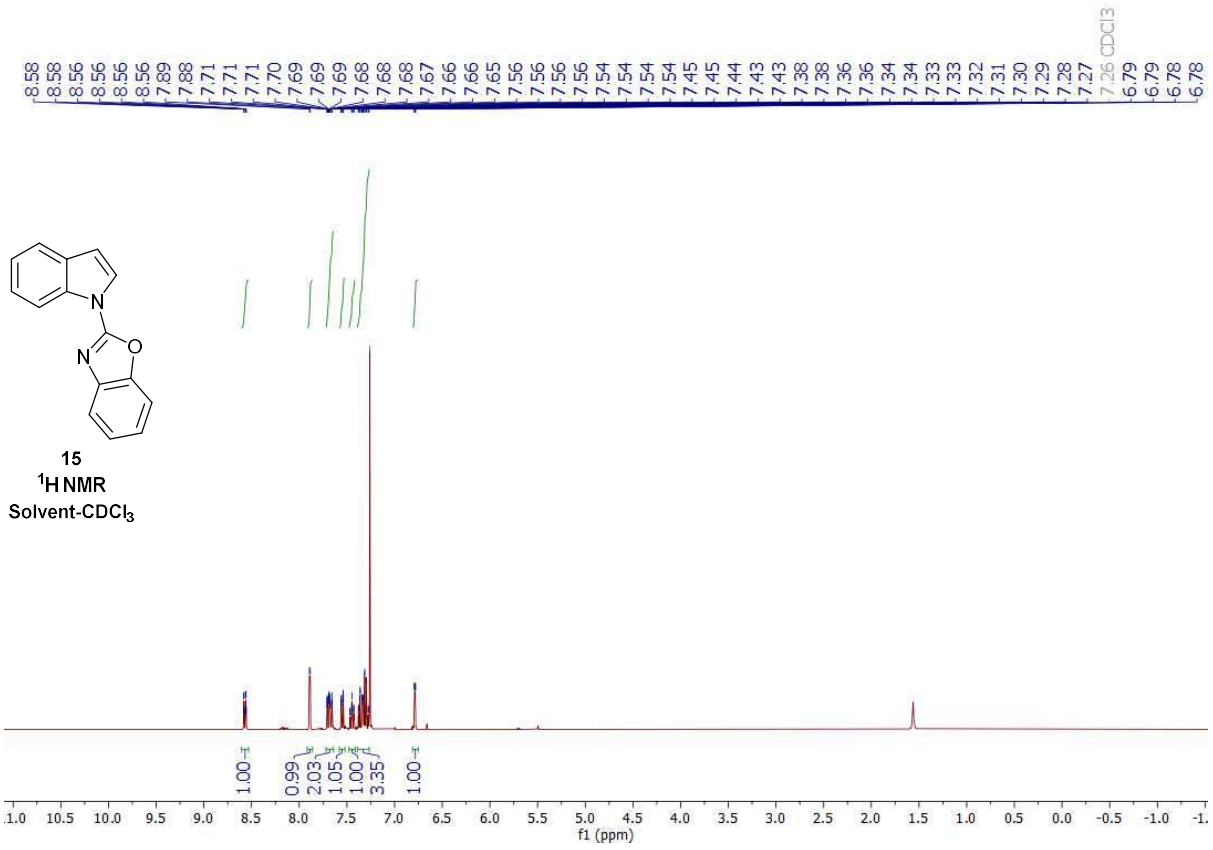
Solvent - $CDCl_3$



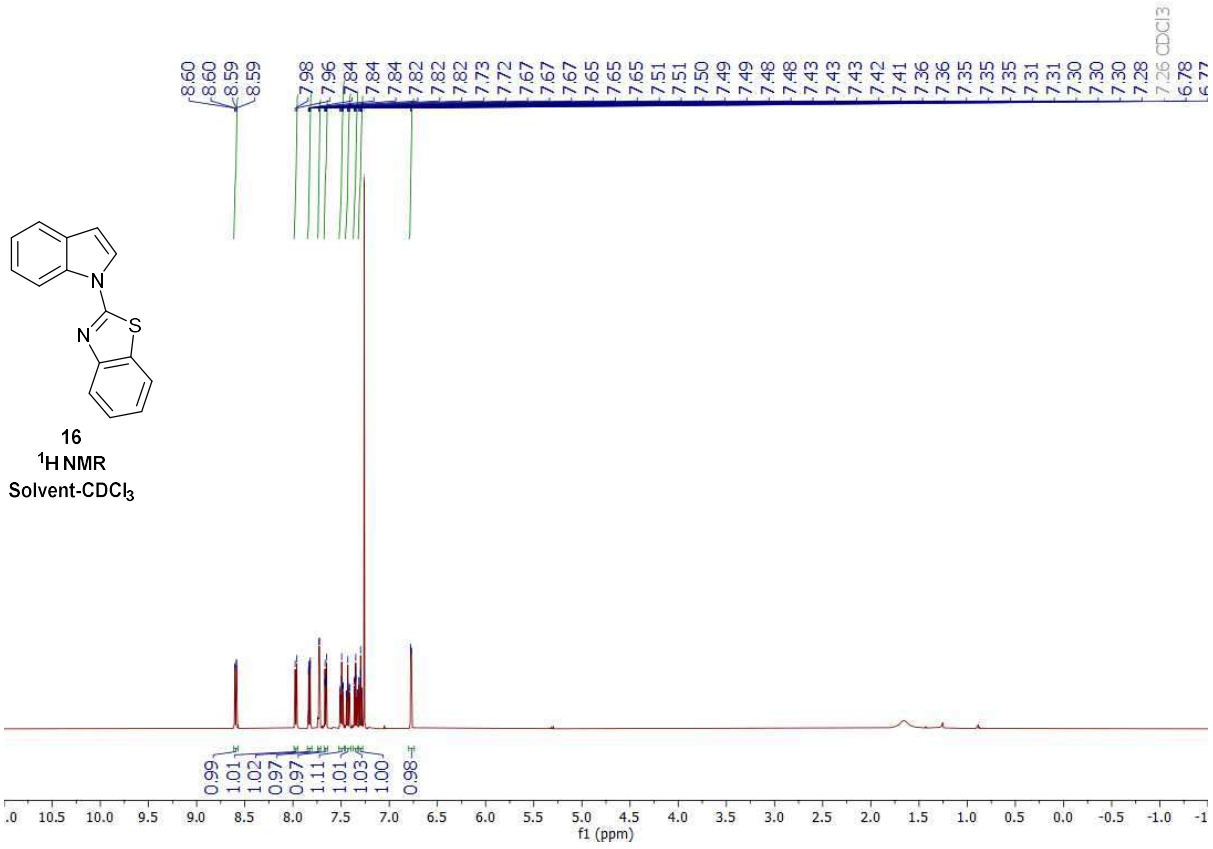
9

^{1}H NMR

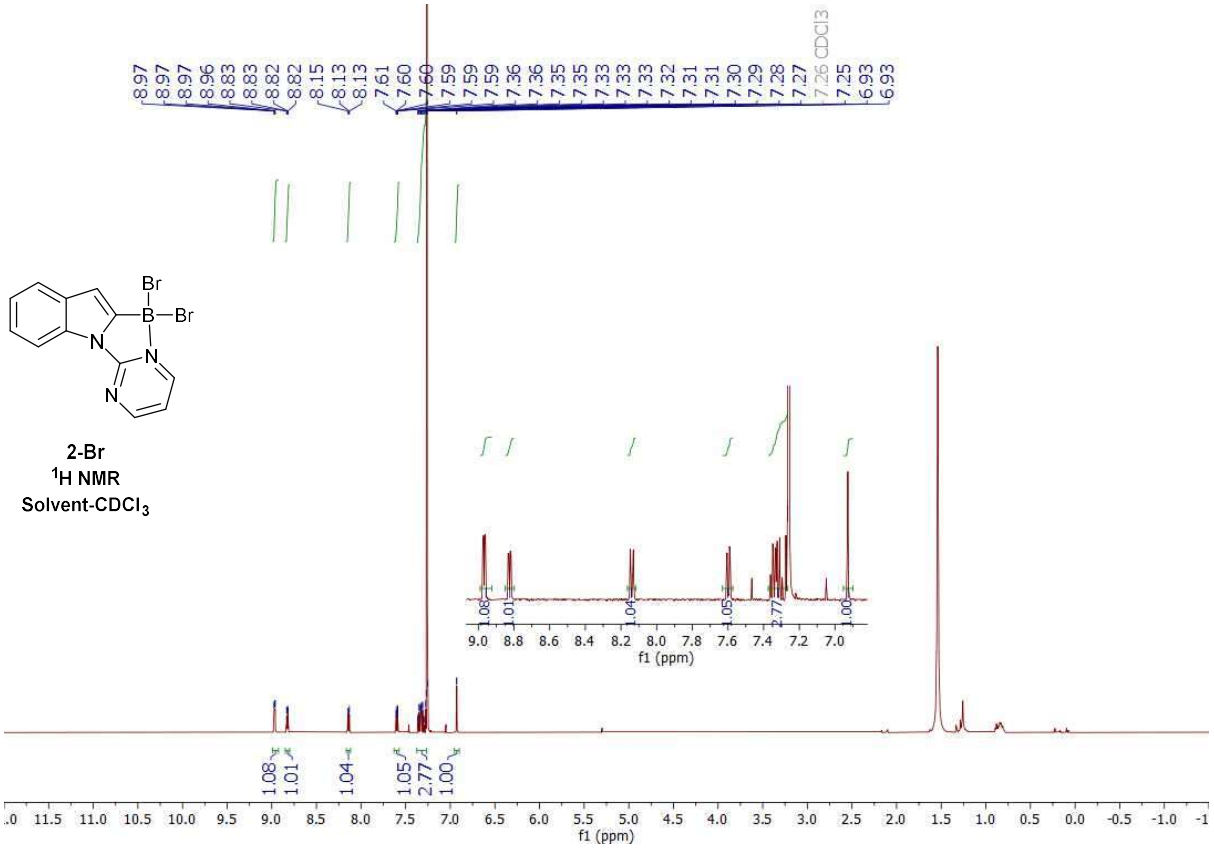
Solvent-$CDCl_3$



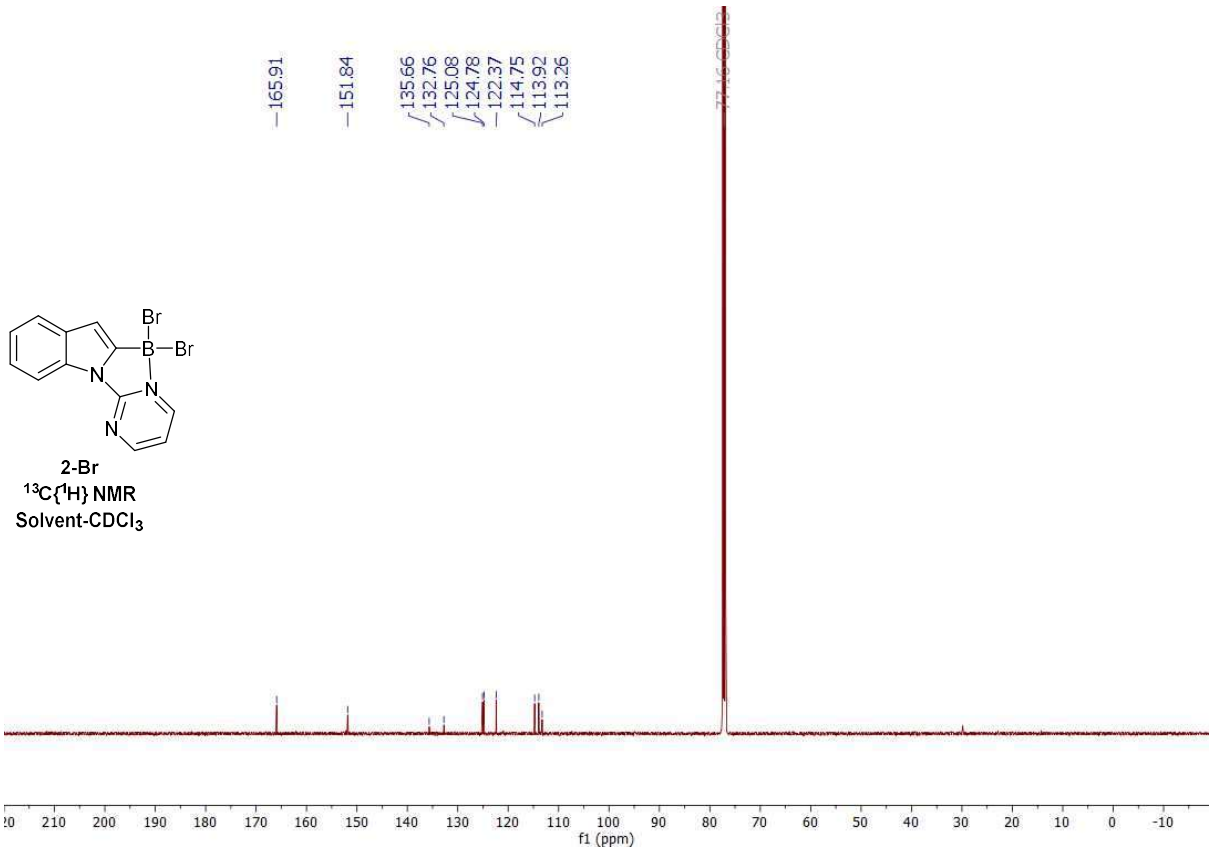
15
^{1}H NMR
Solvent-$CDCl_3$



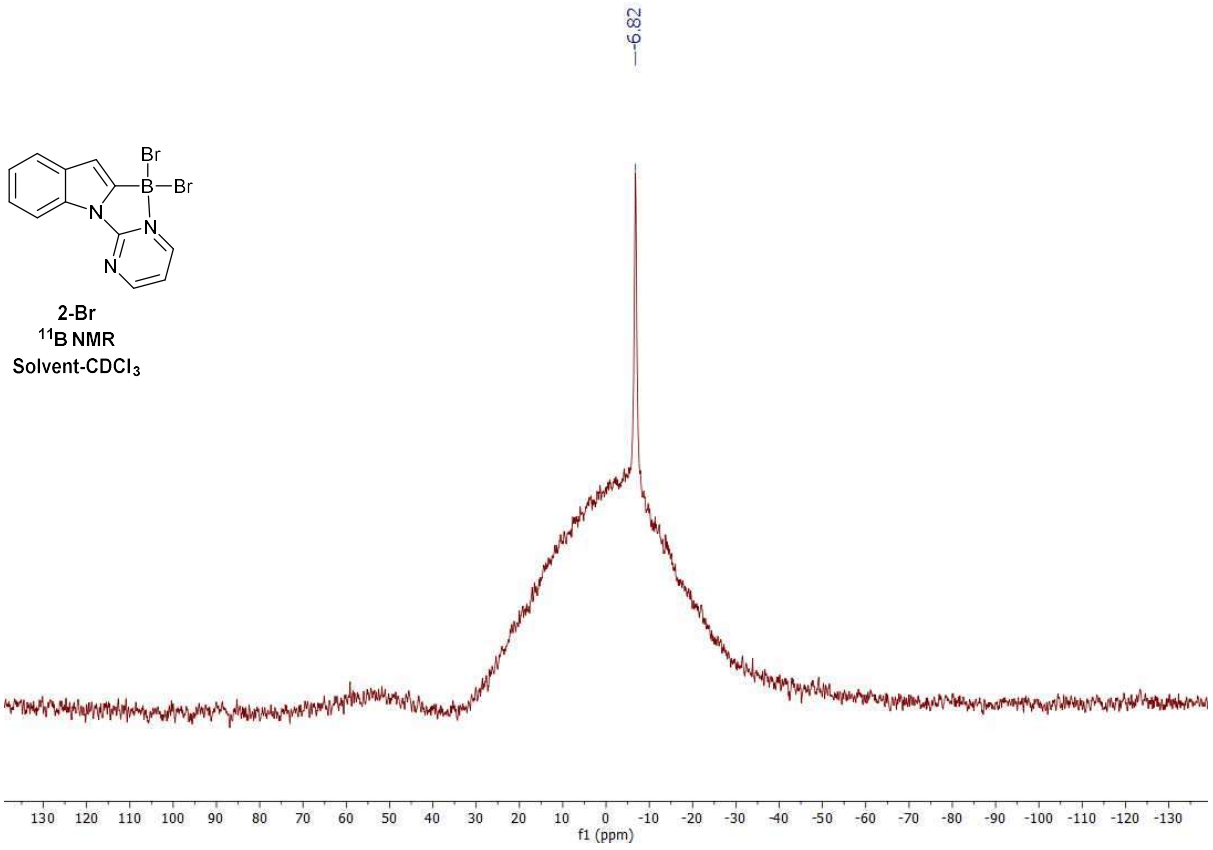
16
^{1}H NMR
Solvent-$CDCl_3$



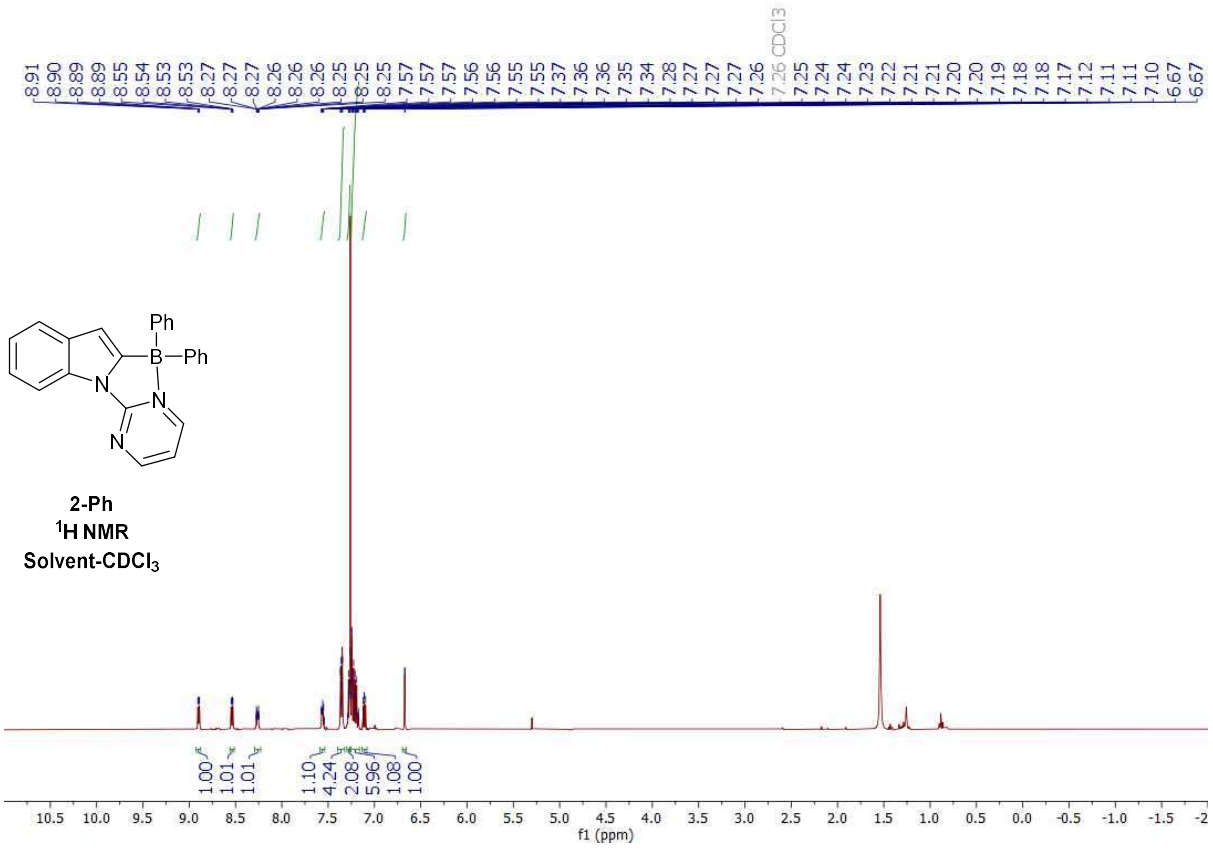
2-Br
^{1}H NMR
Solvent-$CDCl_3$



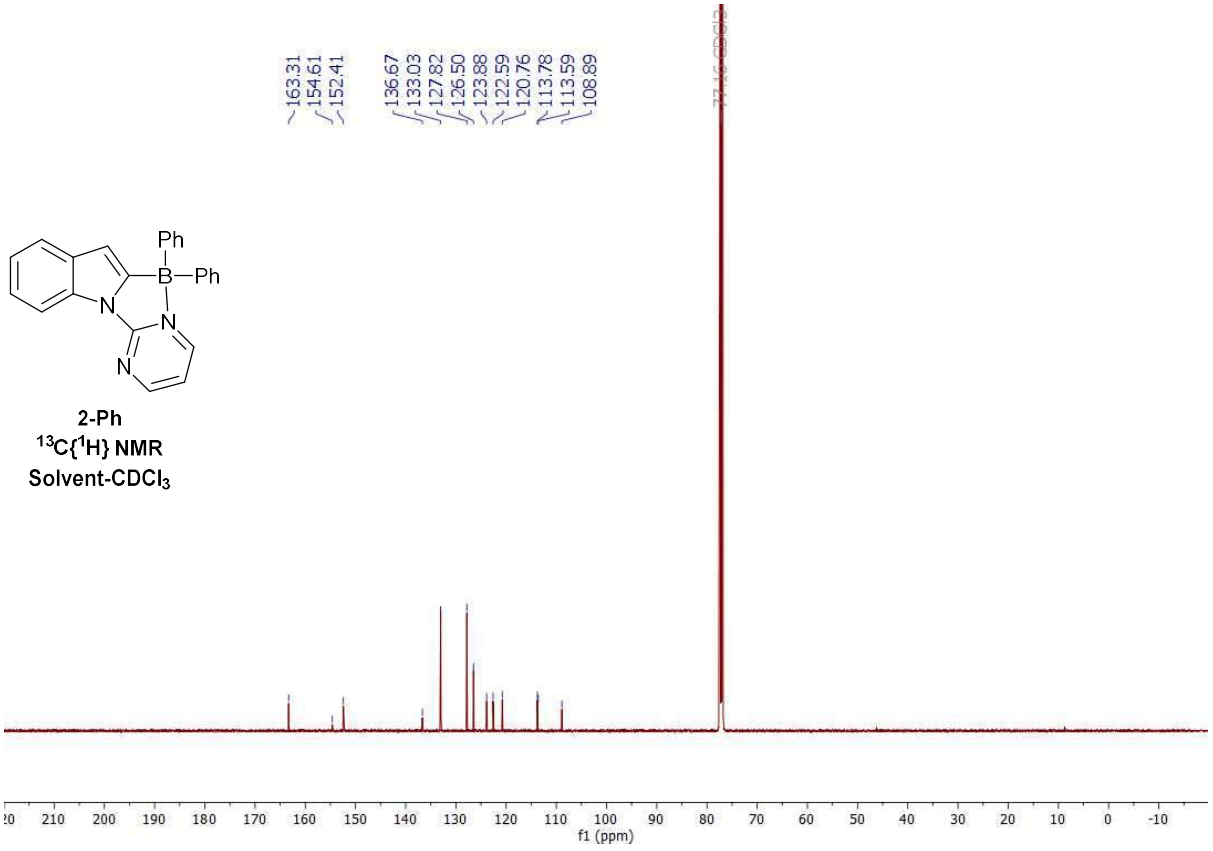
2-Br
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$



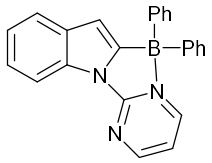
2-Br
^{11}B NMR
Solvent-$CDCl_3$



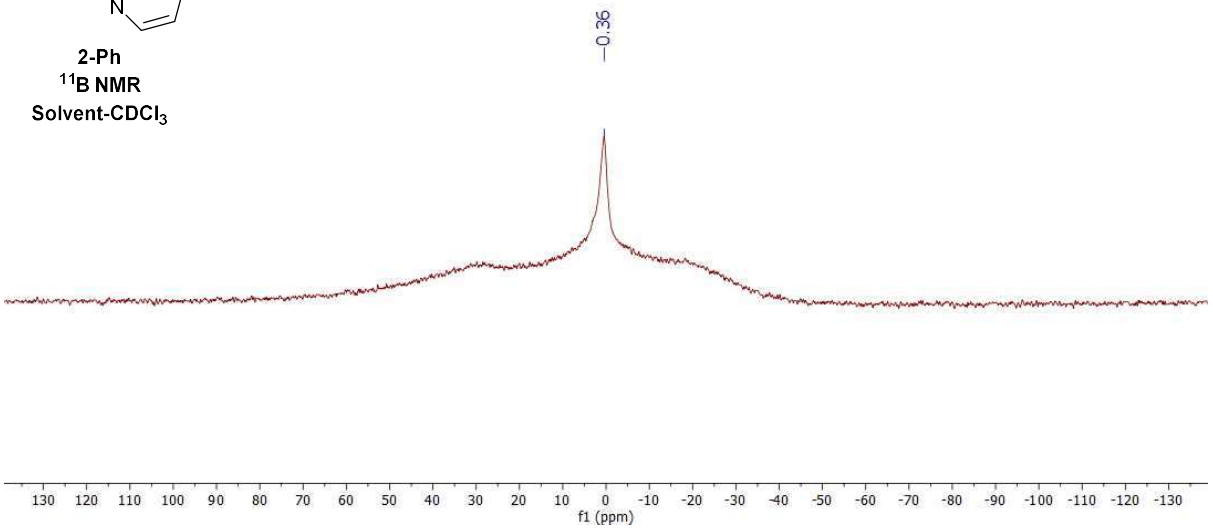
2-Ph
^{1}H NMR
Solvent-$CDCl_3$

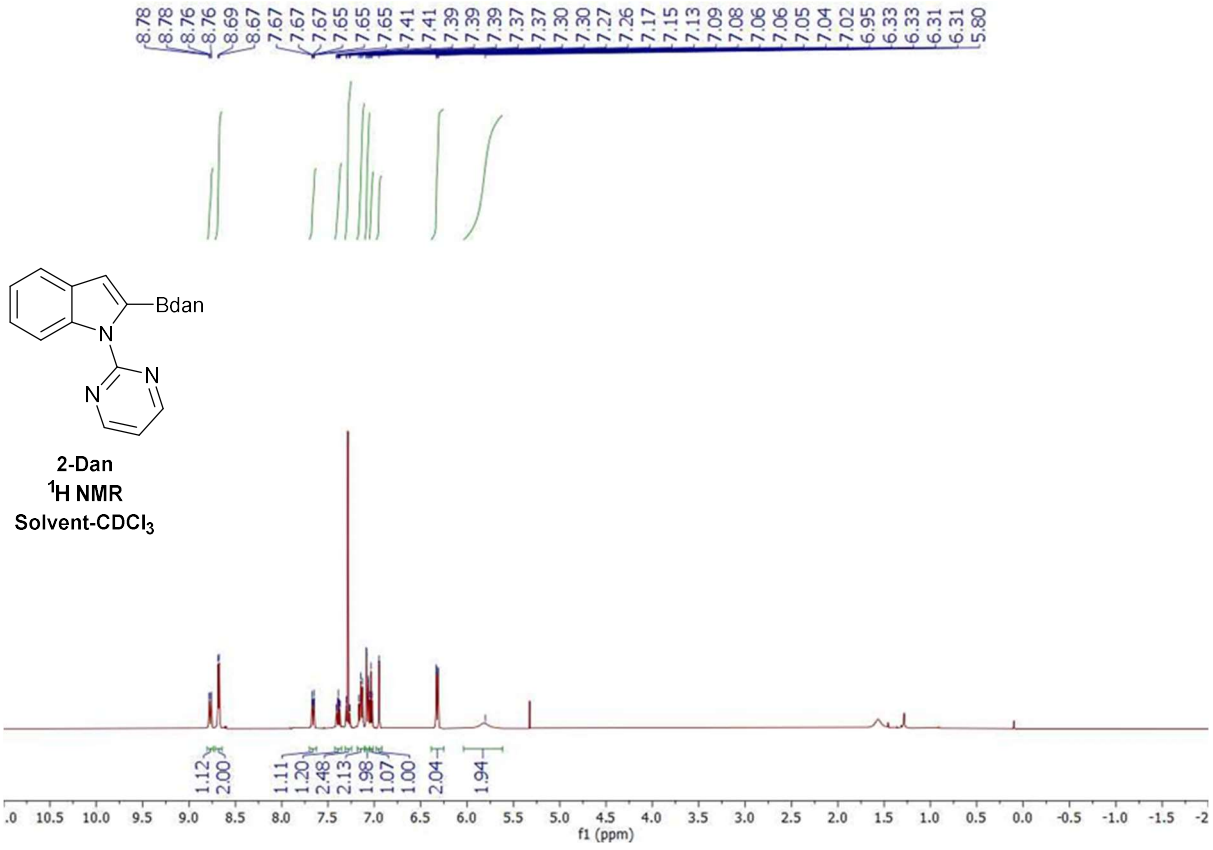


2-Ph
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$

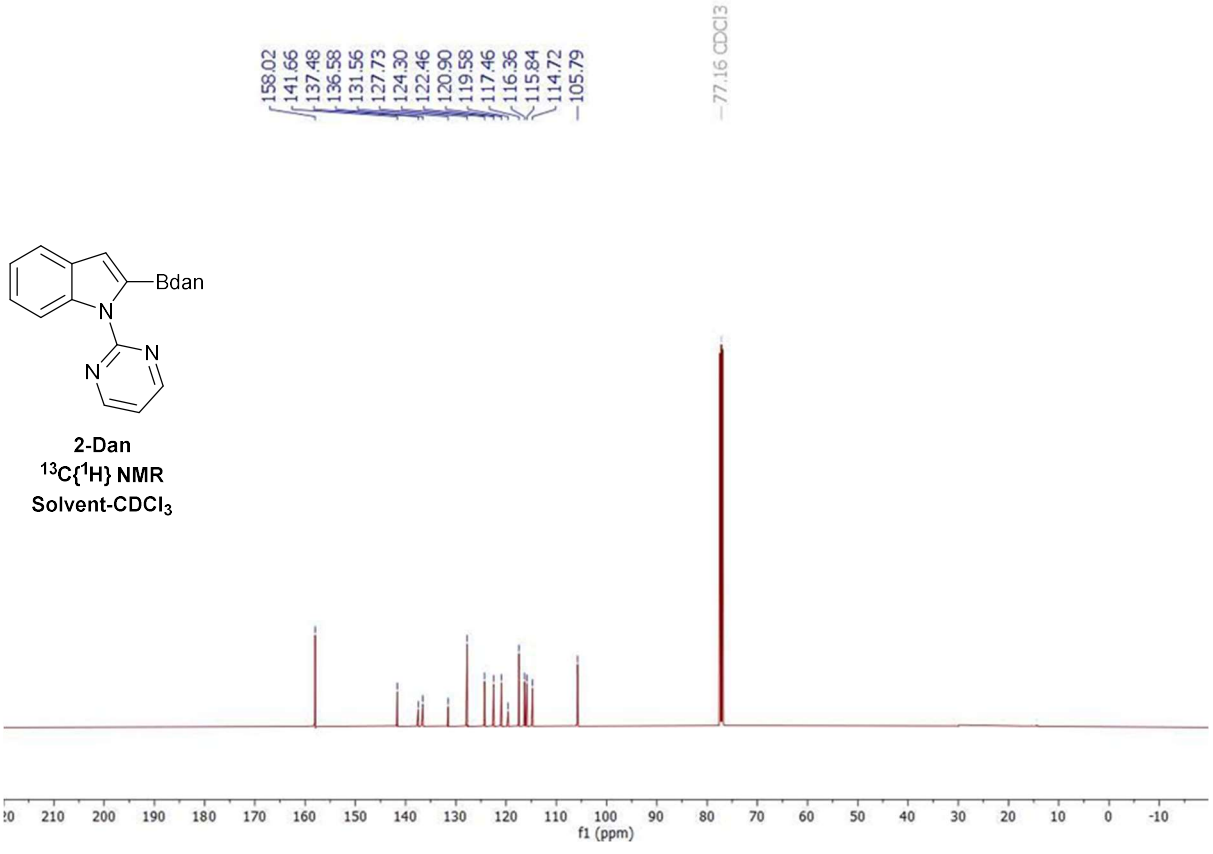


2-Ph
^{11}B NMR
Solvent-$CDCl_3$

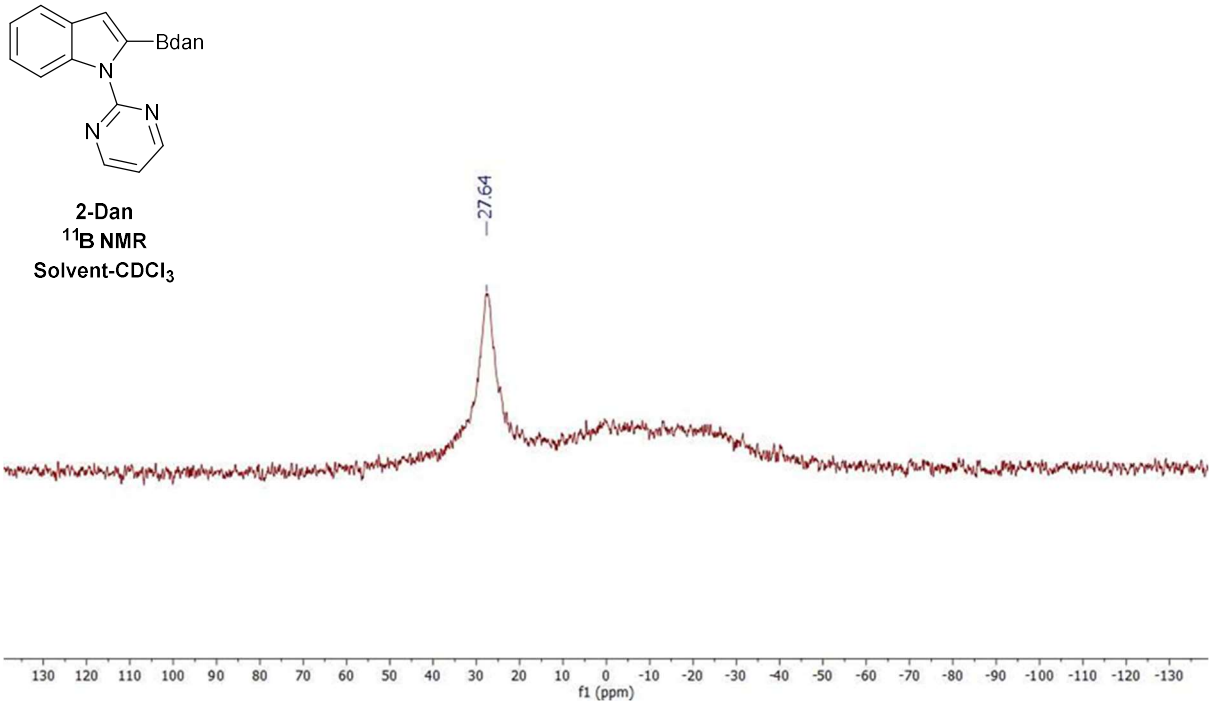




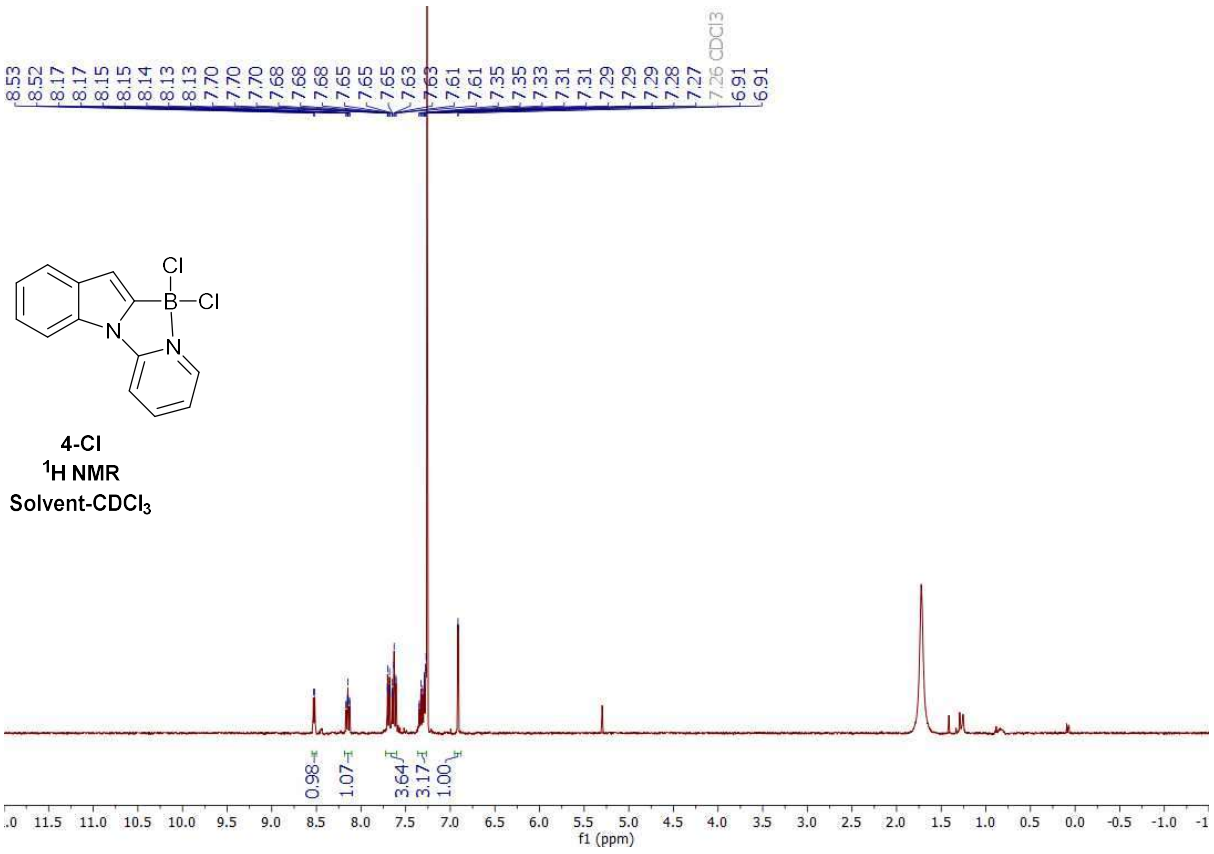
2-Dan
^{1}H NMR
Solvent-$CDCl_3$



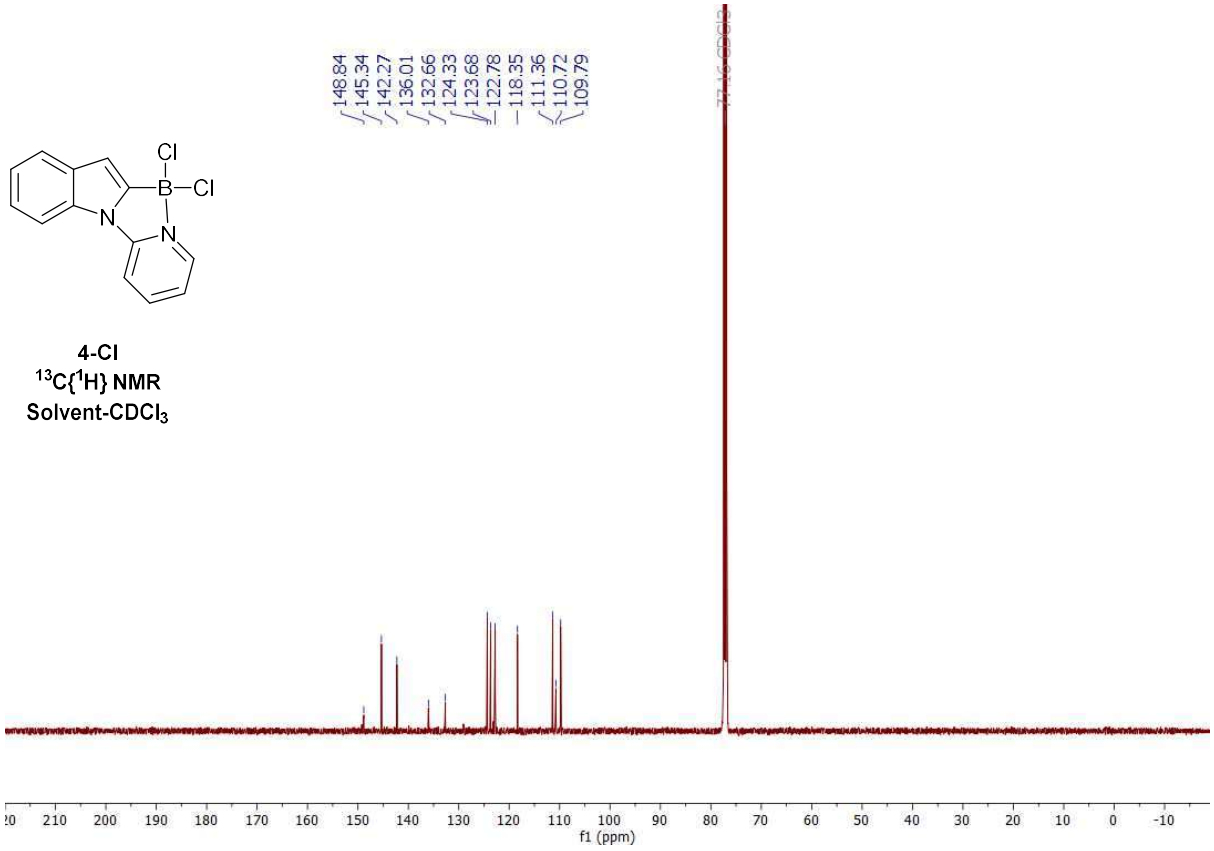
2-Dan
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$



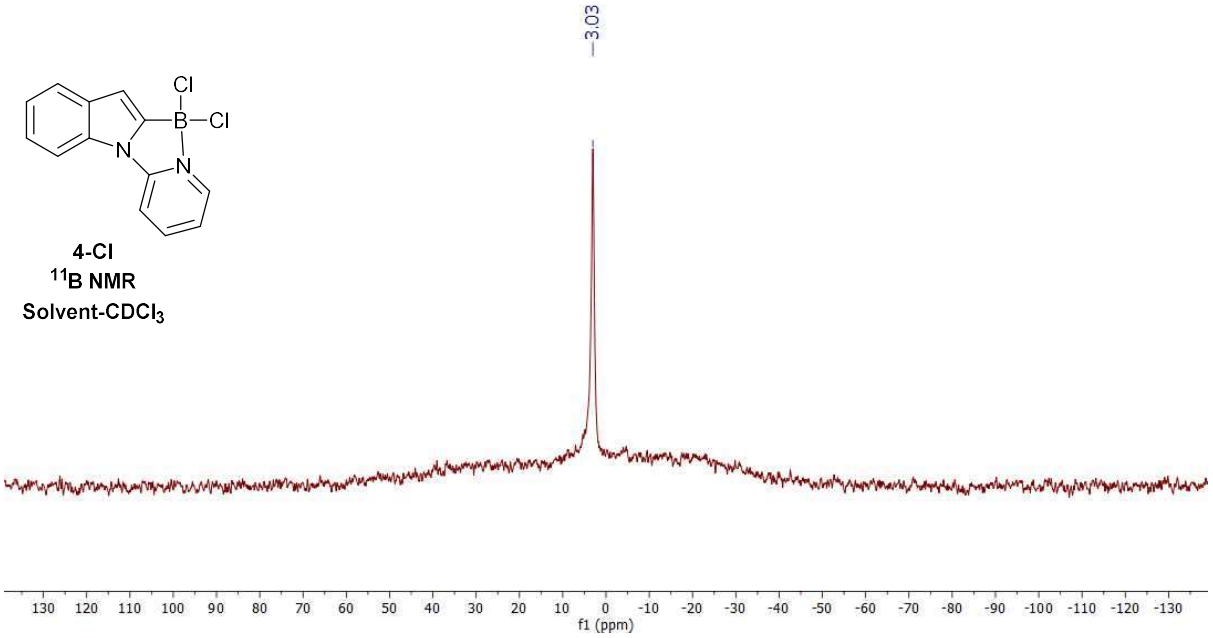
2-Dan
^{11}B NMR
Solvent-$CDCl_3$



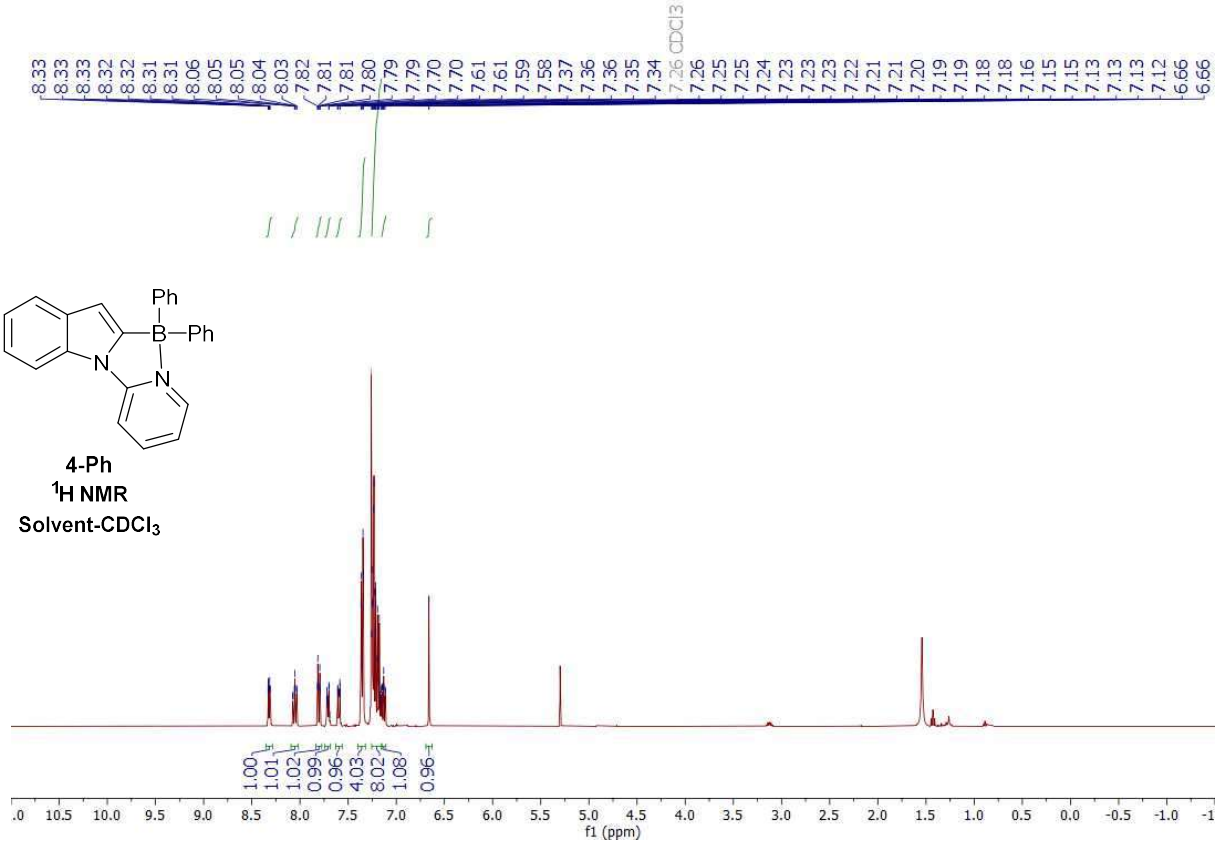
4-Cl
^{1}H NMR
Solvent-$CDCl_3$



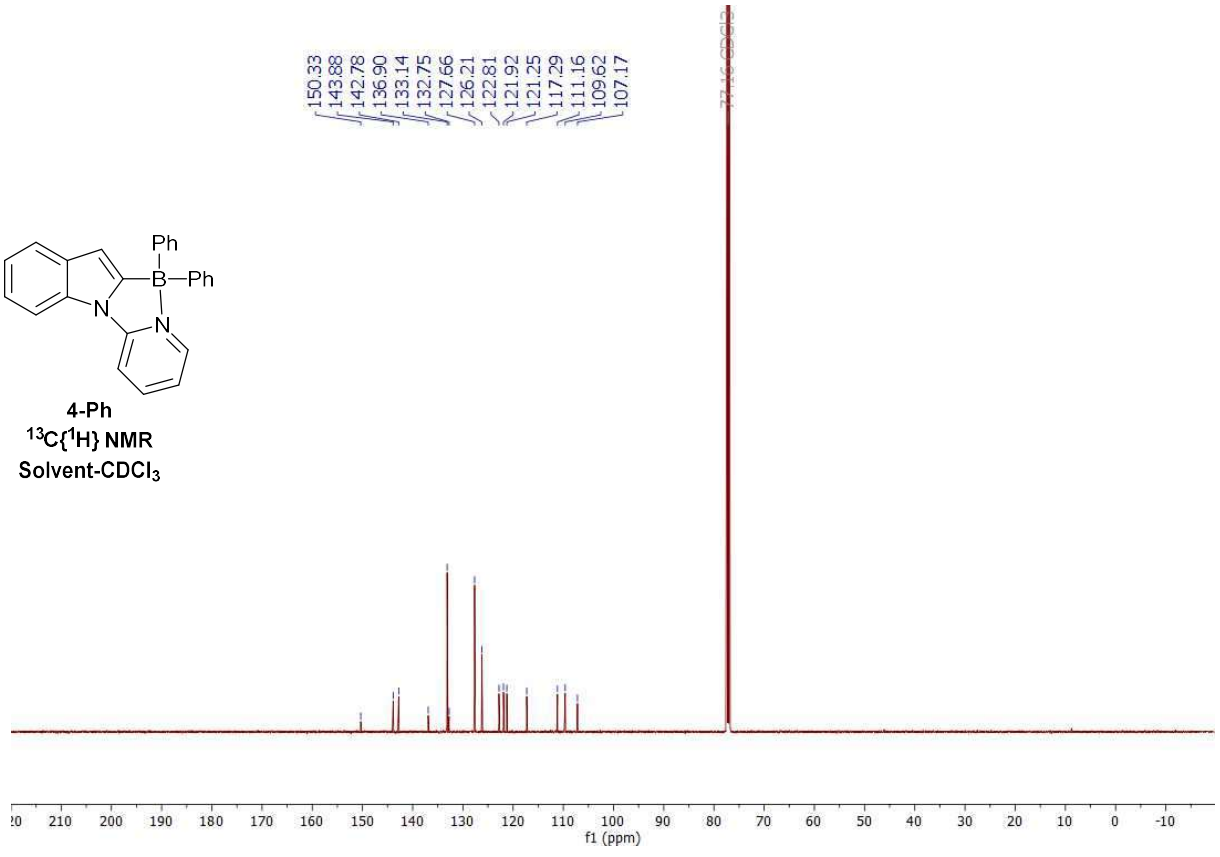
4-Cl
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$



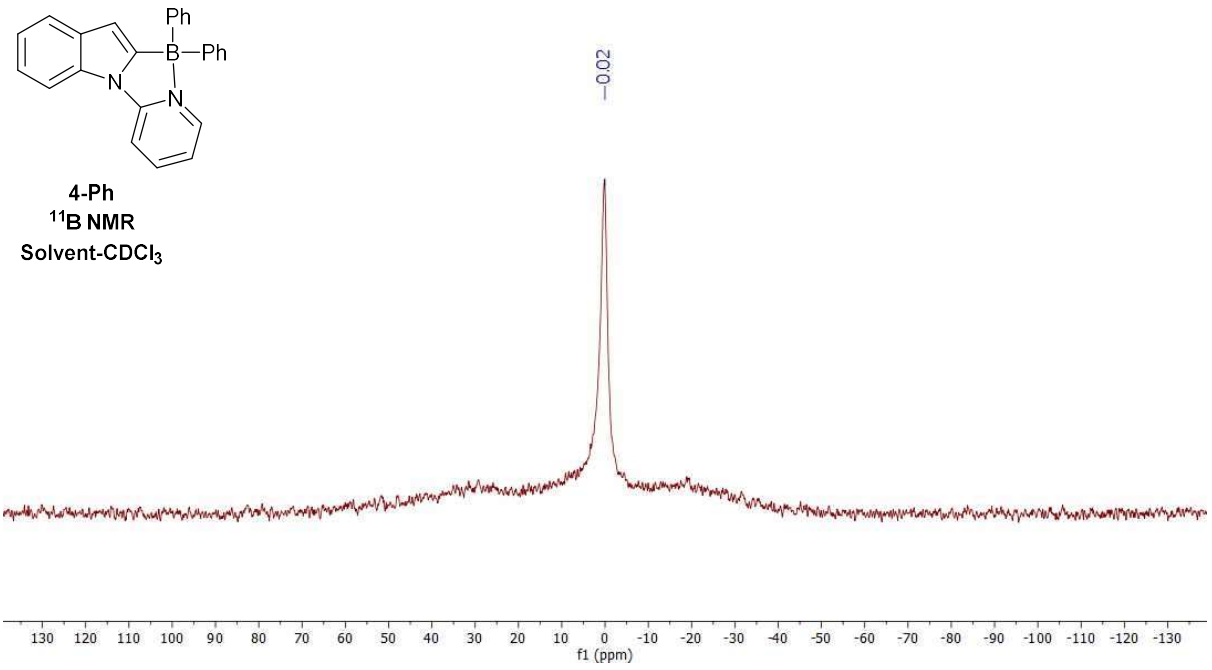
4-Cl
^{11}B NMR
Solvent-$CDCl_3$



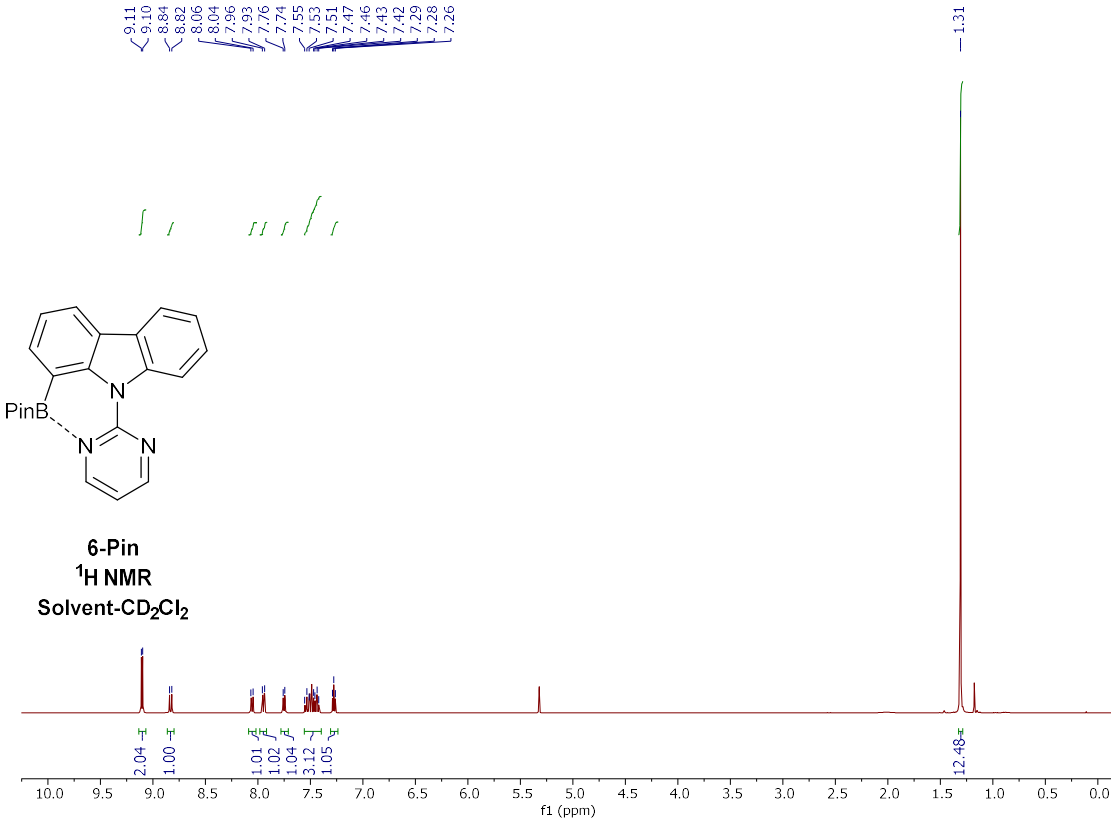
4-Ph
^{1}H NMR
Solvent-$CDCl_3$

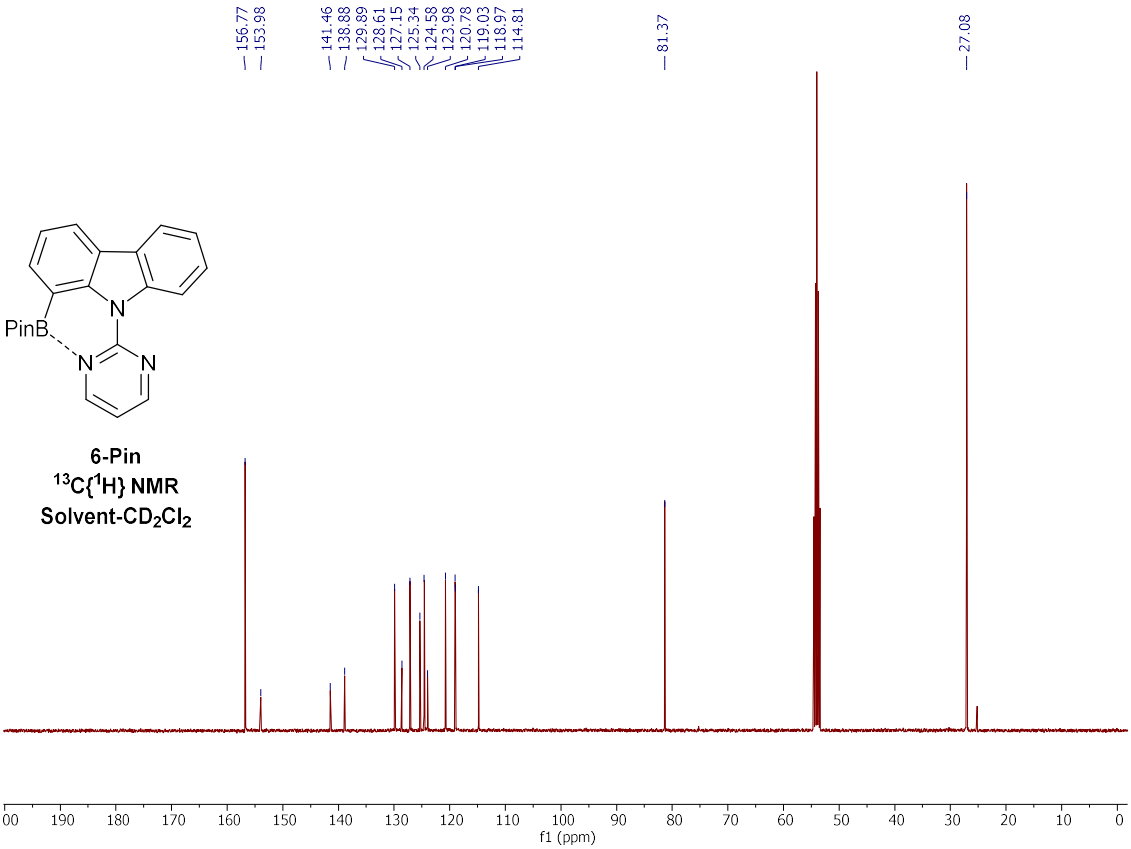


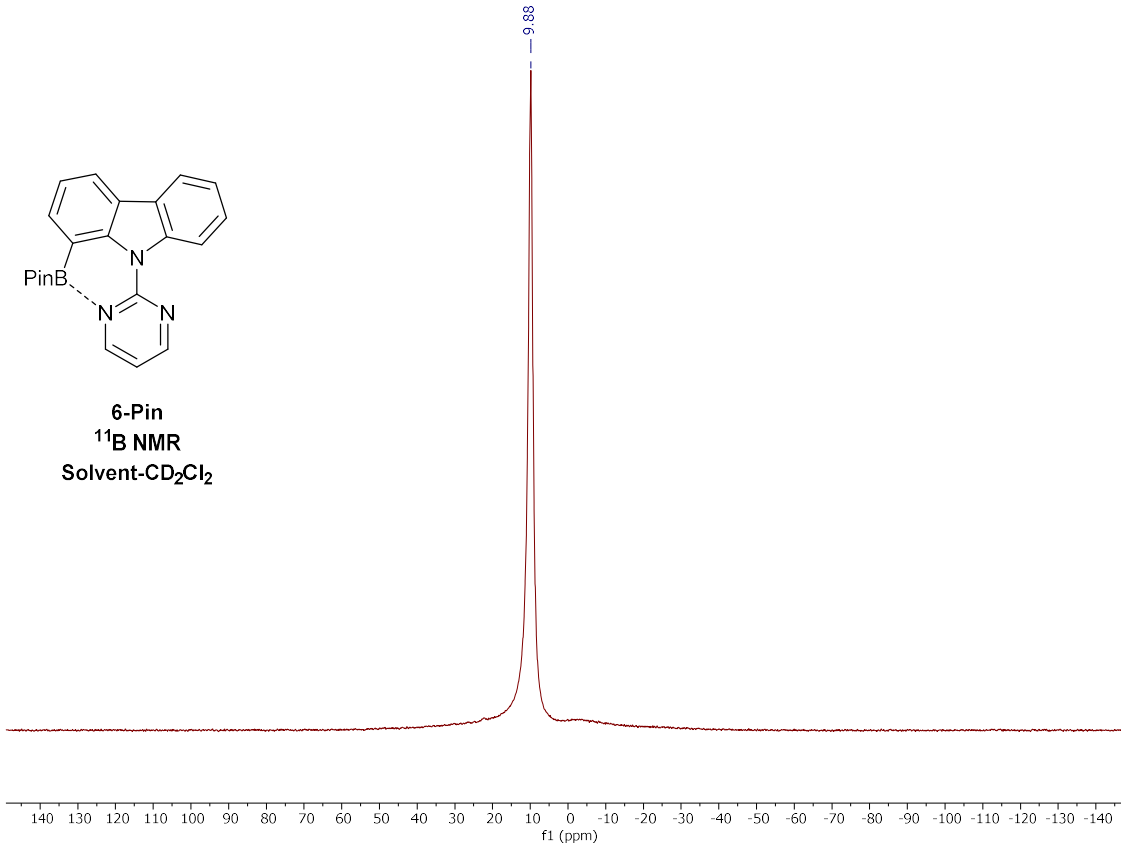
4-Ph
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$

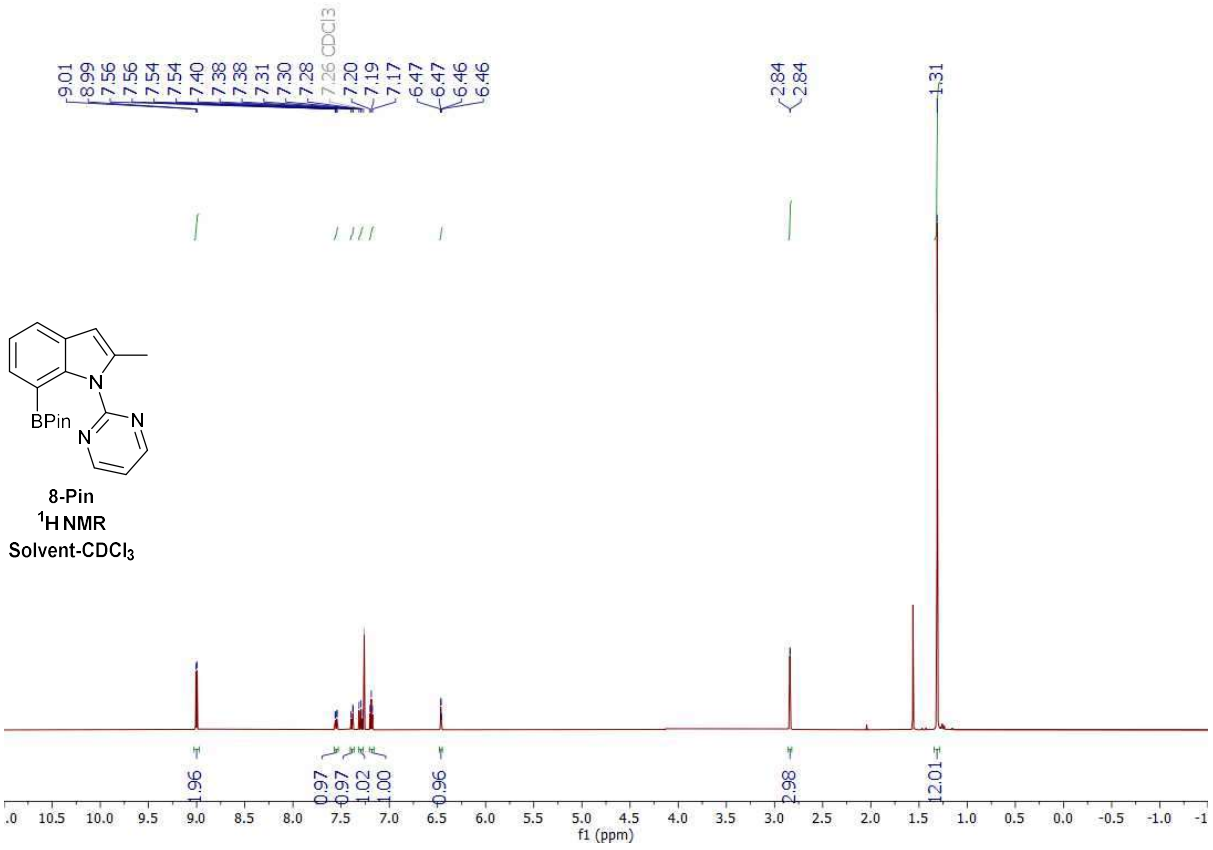


4-Ph
^{11}B NMR
Solvent-$CDCl_3$

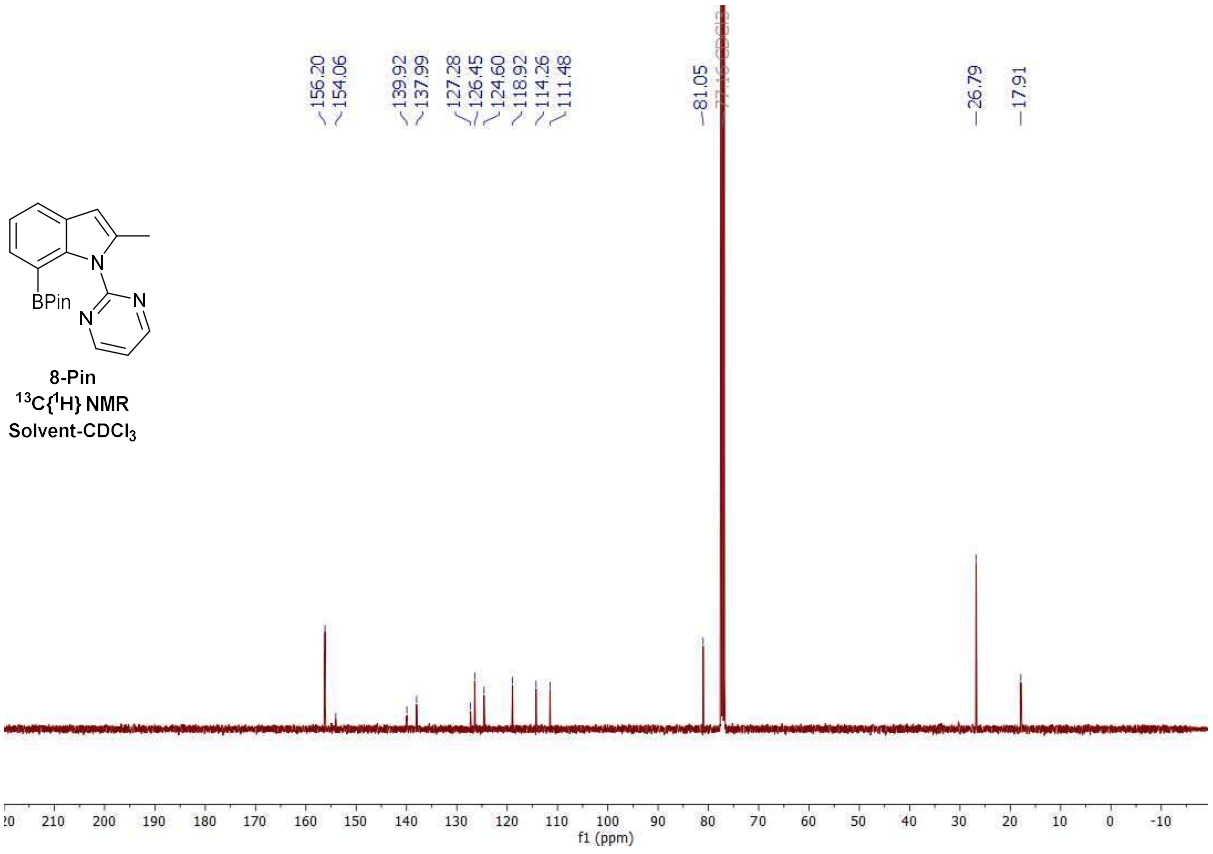

9.11
9.10
8.84
8.82
8.06
8.04
7.96
7.93
7.76
7.74
7.55
7.53
7.51
7.47
7.46
7.43
7.42
7.29
7.28
7.26
1.31
PinB
N
N
N
6-Pin
1H NMR
Solvent-CD2Cl2
2.04
1.00
1.01
1.02
1.04
3.12
1.05
12.48
f1 (ppm)


156.77
153.98
141.46
138.88
129.89
128.61
127.15
125.34
124.58
123.98
120.78
119.03
118.97
114.81
81.37
27.08
PinB
N
N
N
6-Pin
13C{1H} NMR
Solvent-CD2Cl2
f1 (ppm)

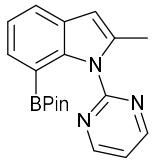

9.88
PinB
N
N
N
6-Pin
11B NMR
Solvent-CD2Cl2
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)



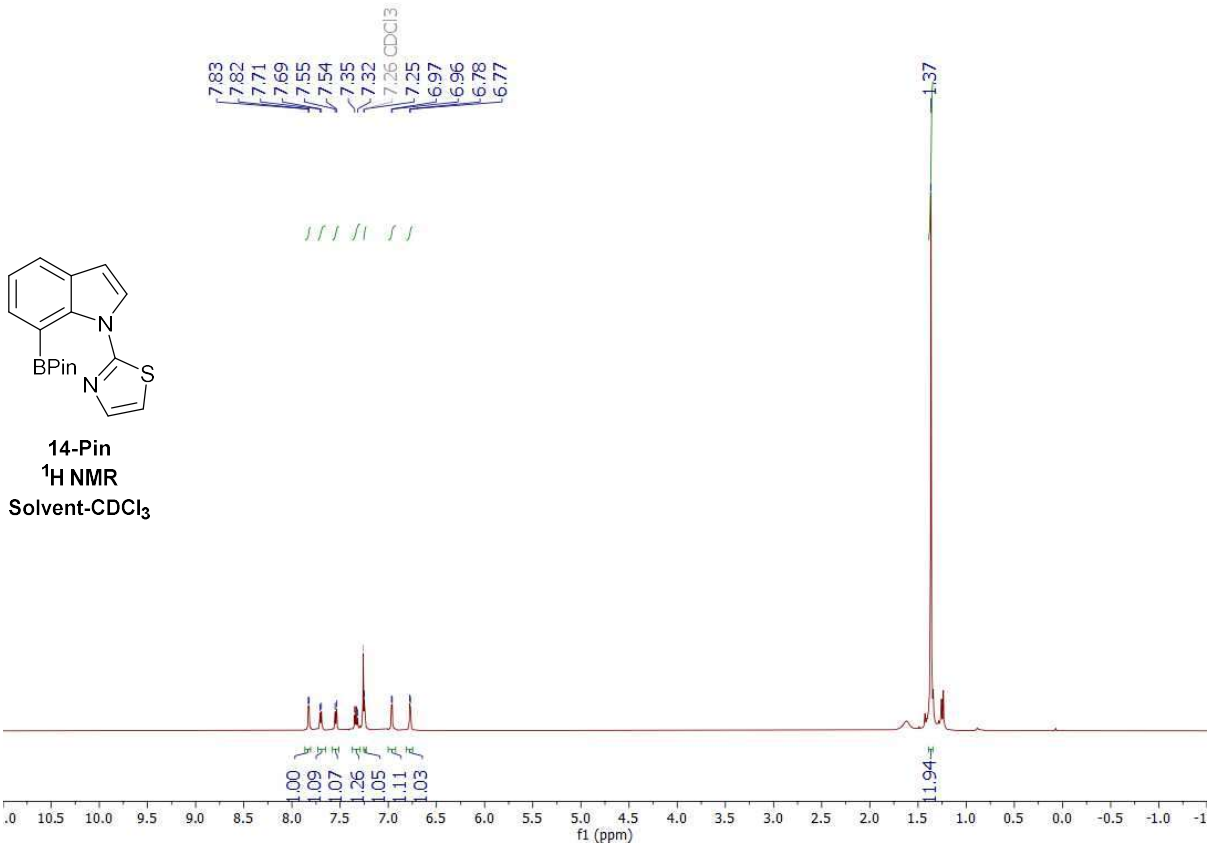
8-Pin
^{1}H NMR
Solvent-$CDCl_3$



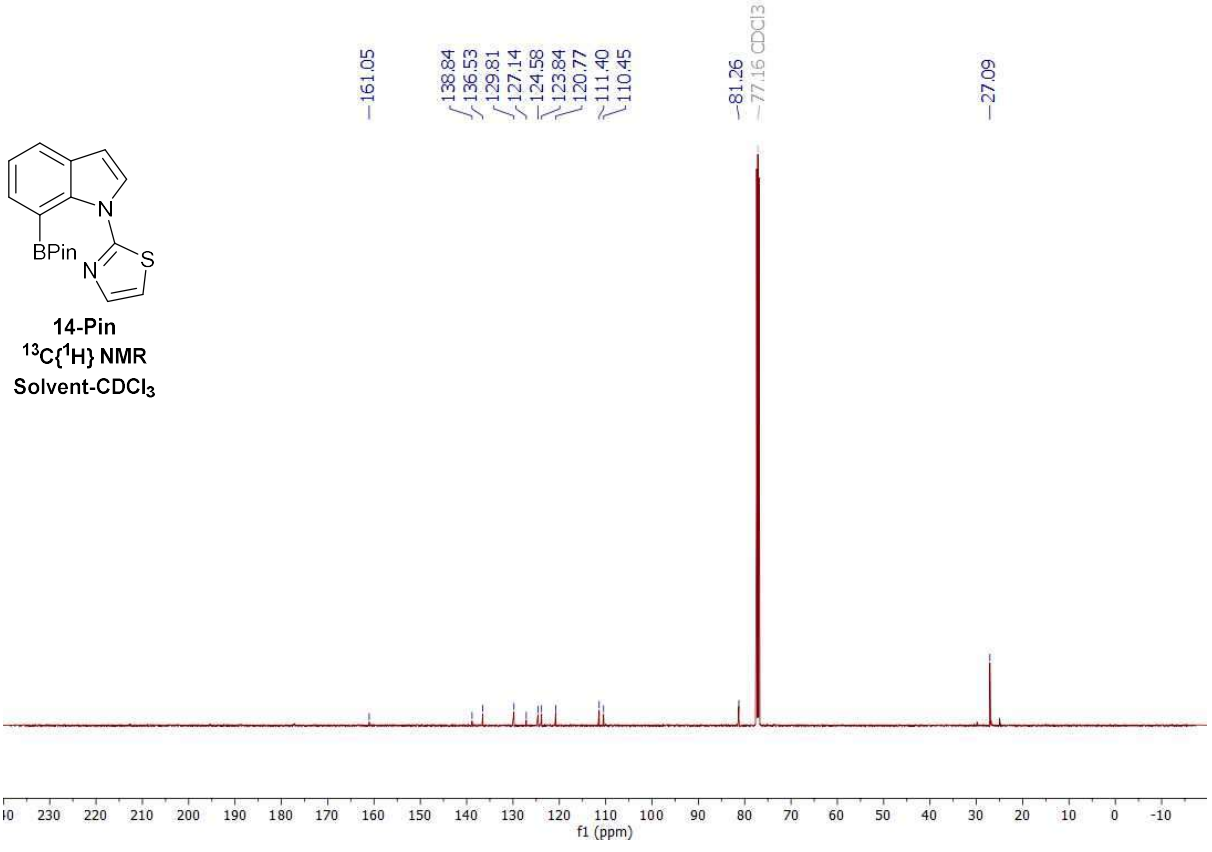
8-Pin
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$



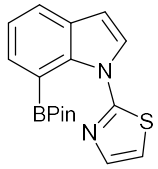
8-Pin
^{11}B NMR
Solvent-$CDCl_3$



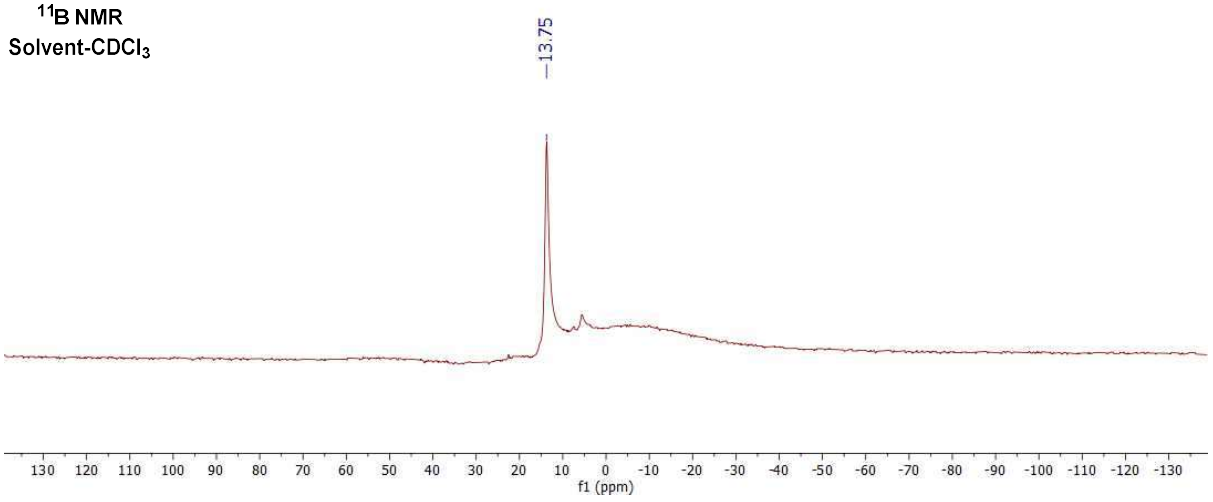
14-Pin
^{1}H NMR
Solvent-$CDCl_3$

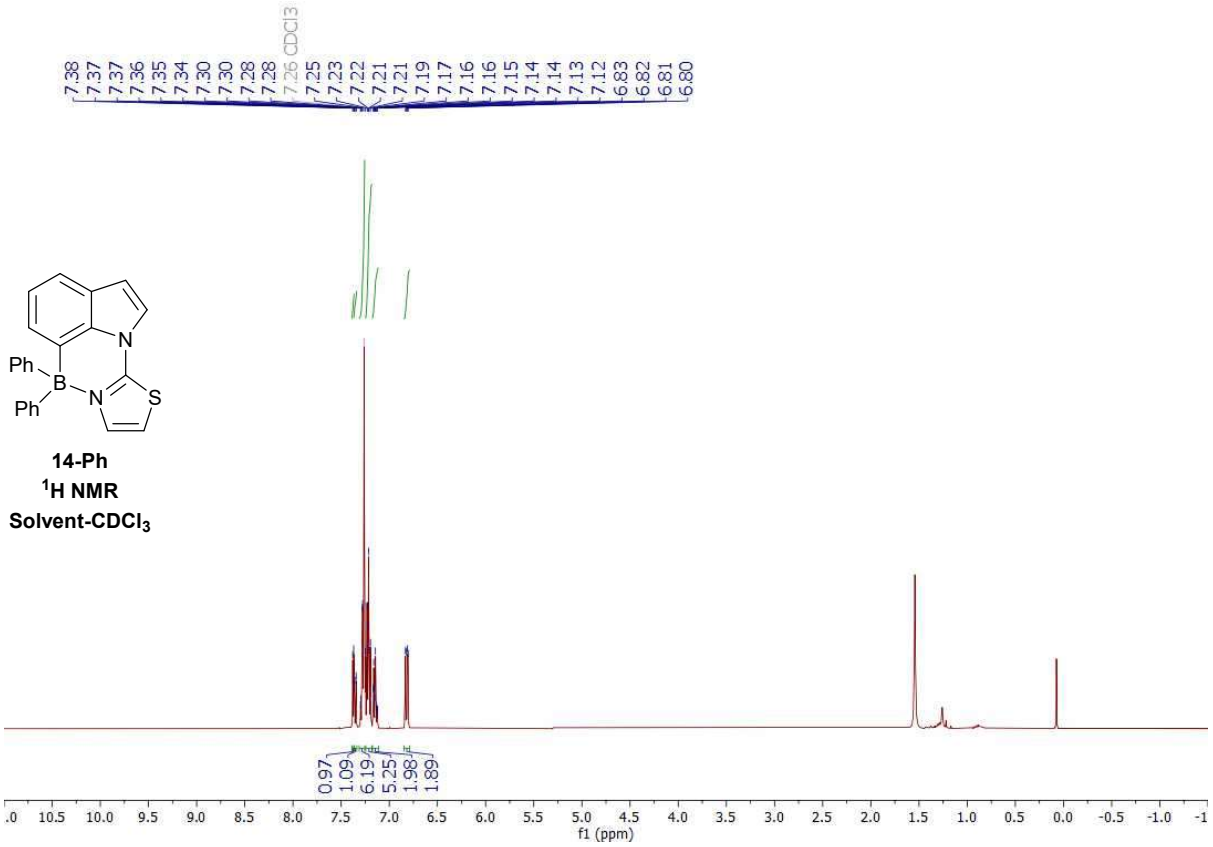


14-Pin
$^{13}C\{^{1}H\}$ NMR
Solvent-$CDCl_3$

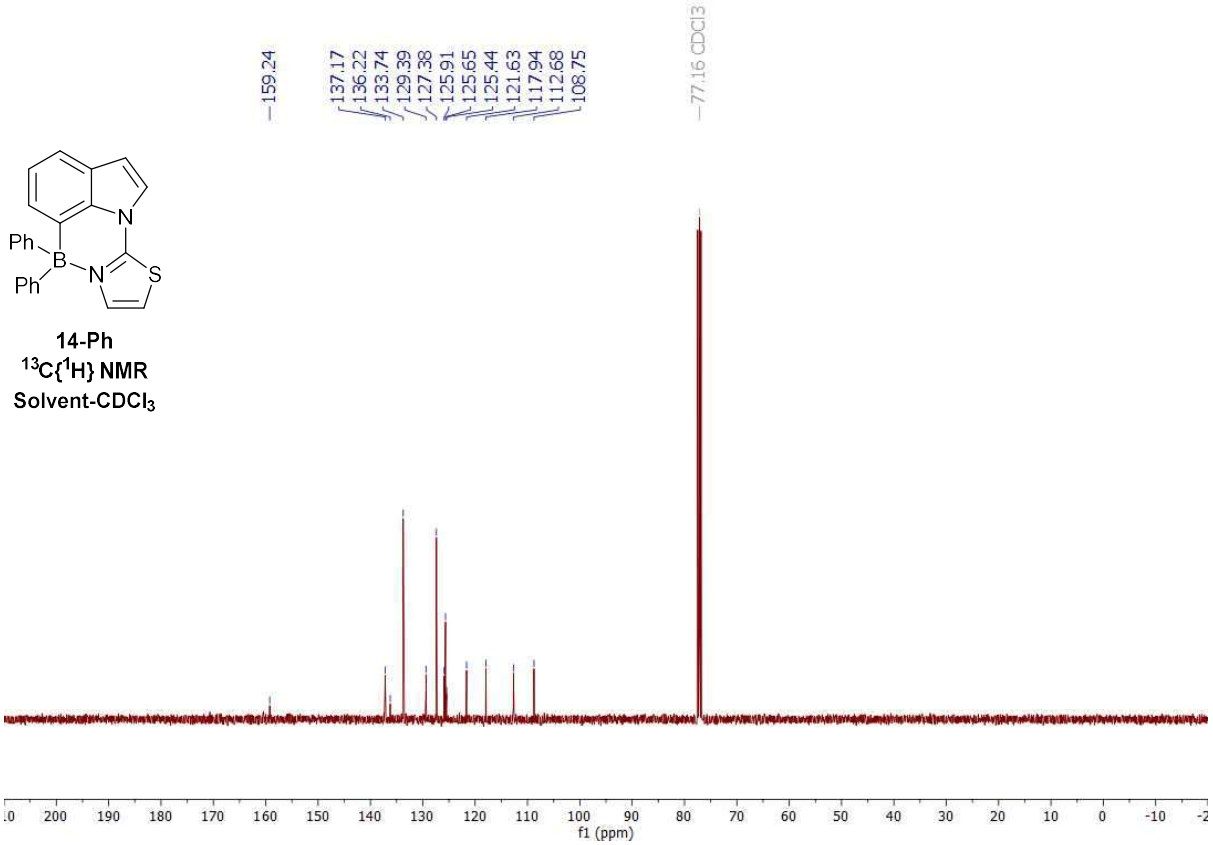


14-Pin
^{11}B NMR
Solvent-$CDCl_3$

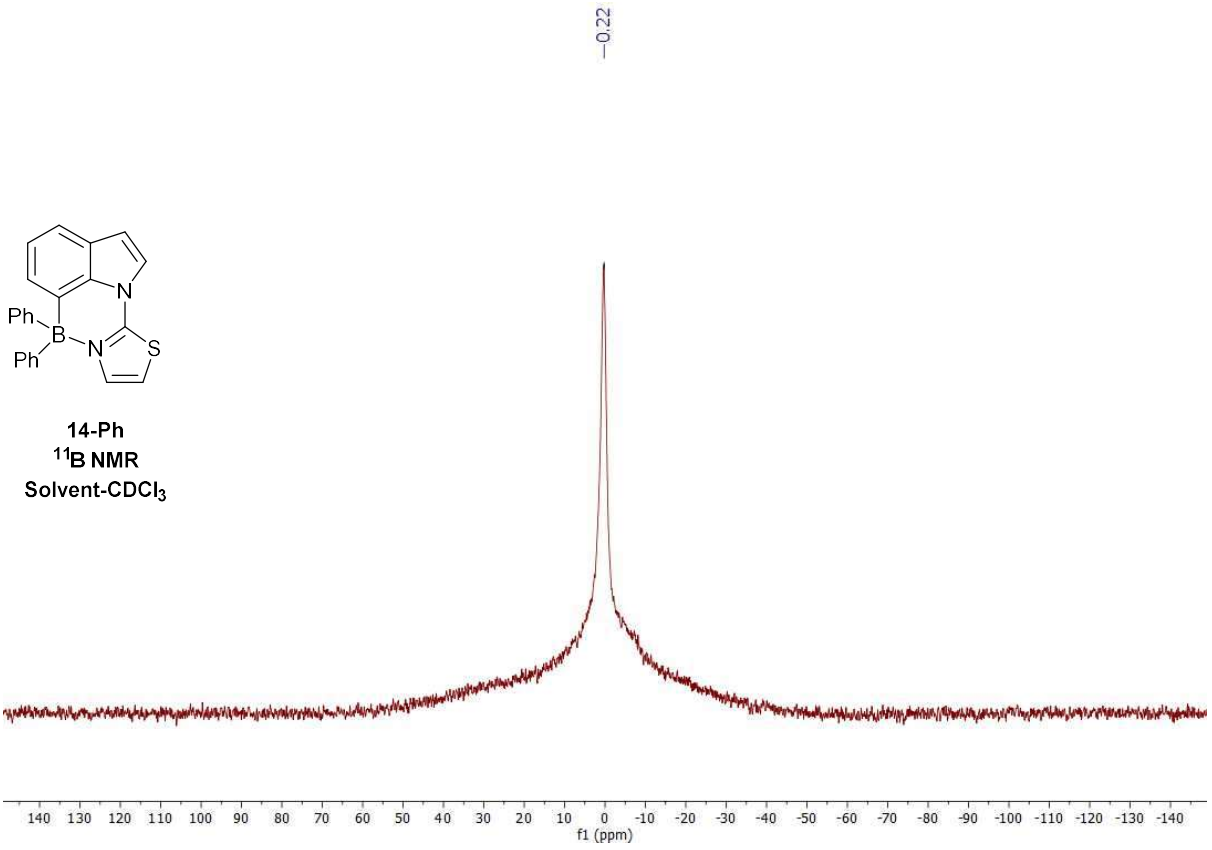




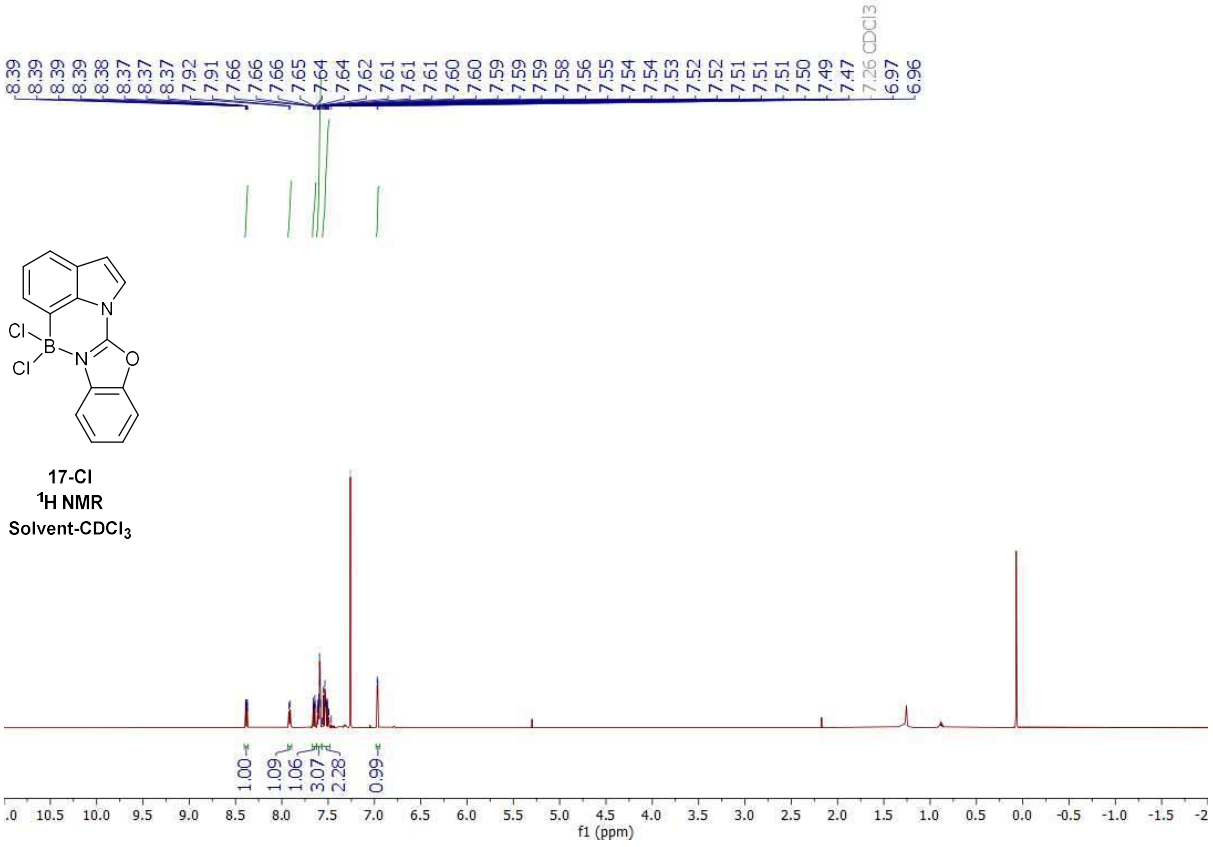
14-Ph
^{1}H NMR
Solvent-$CDCl_3$



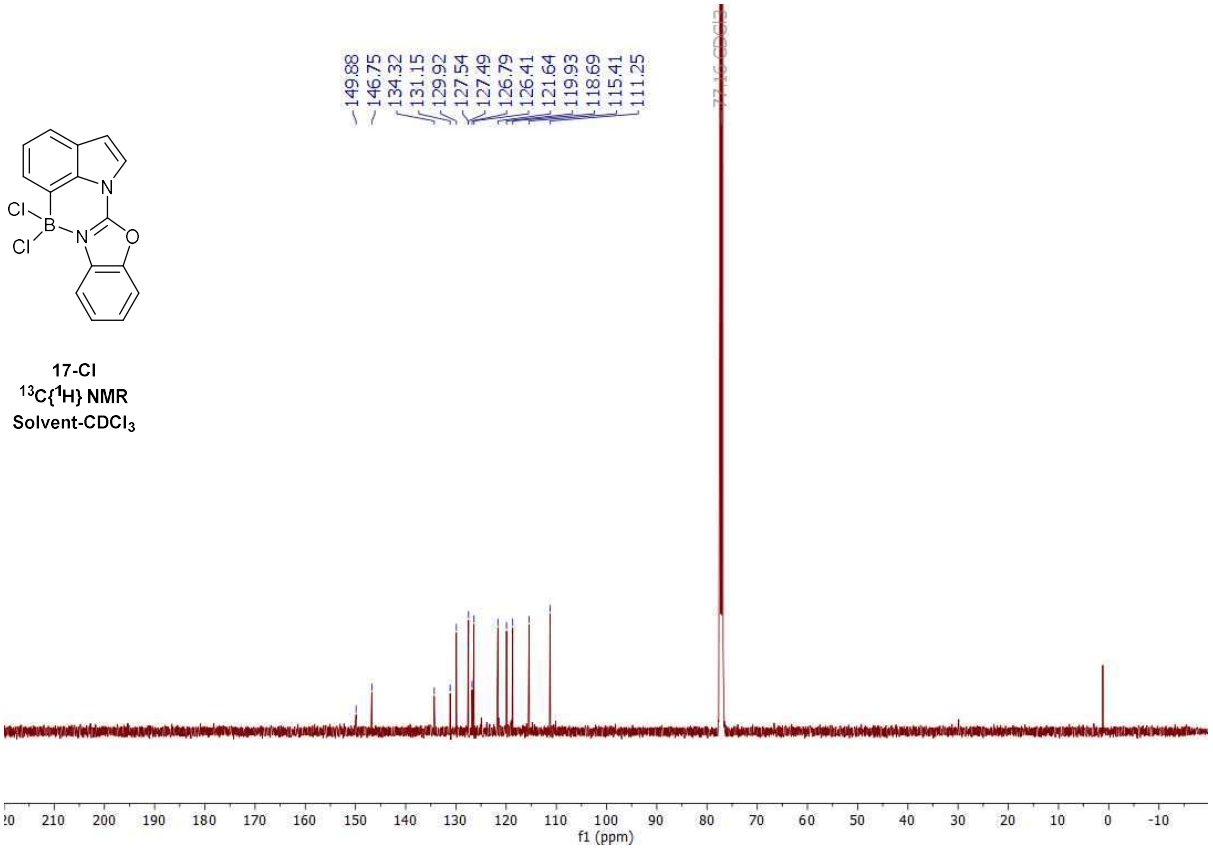
14-Ph
$^{13}C\{^{1}H\}$ NMR
Solvent-$CDCl_3$



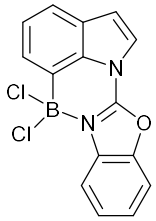
14-Ph
^{11}B NMR
Solvent-$CDCl_3$



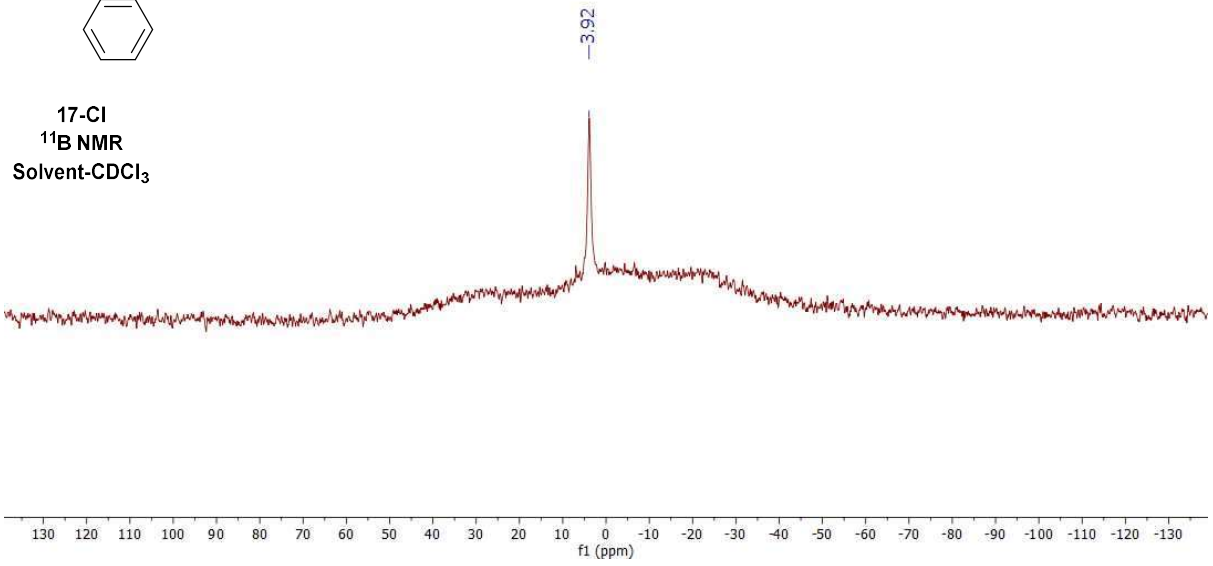
17-Cl
^{1}H NMR
Solvent-$CDCl_3$

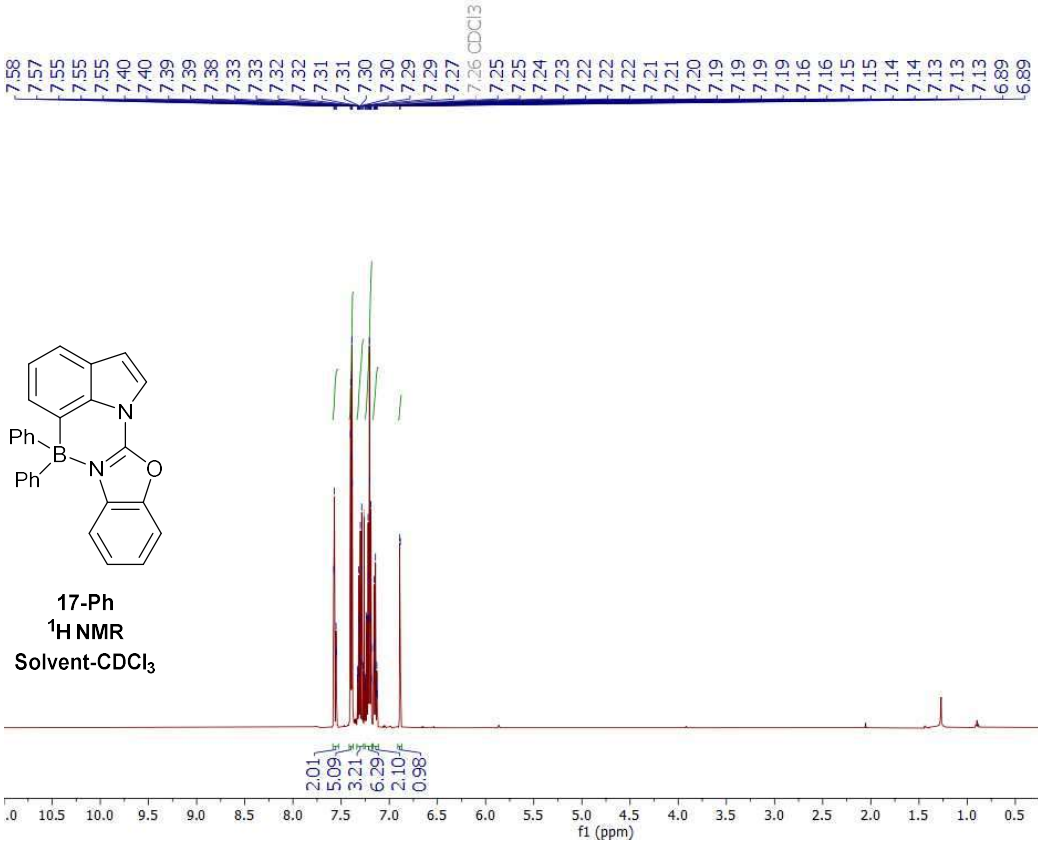


17-Cl
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$

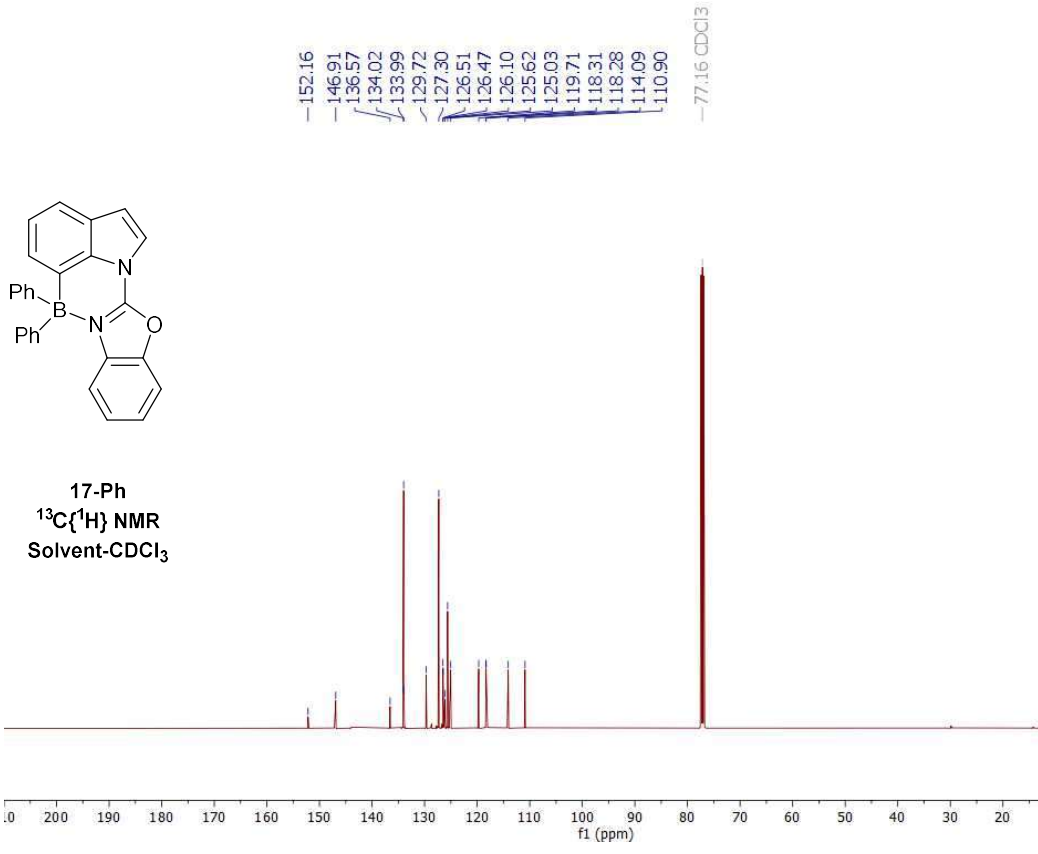


17-Cl
^{11}B NMR
Solvent-$CDCl_3$

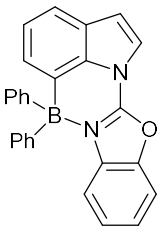




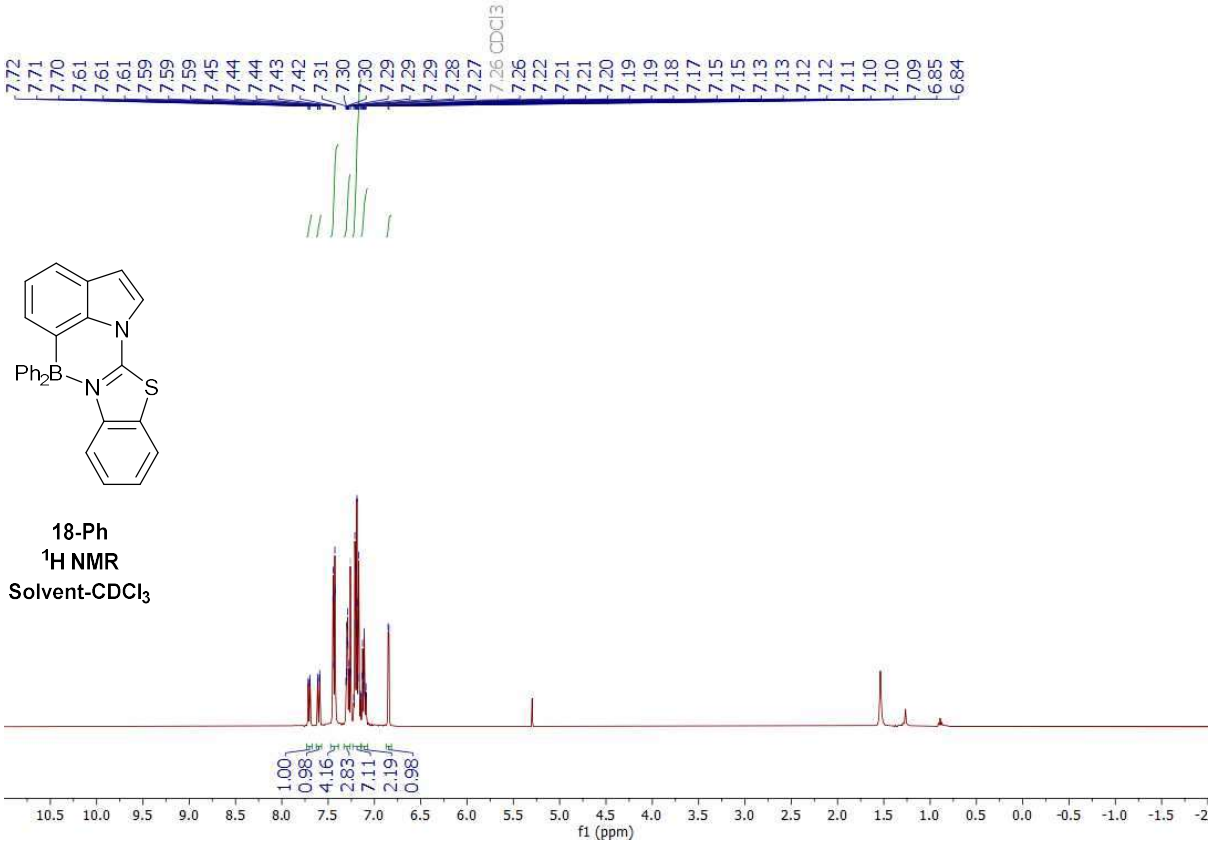
17-Ph
^{1}H NMR
Solvent-$CDCl_3$



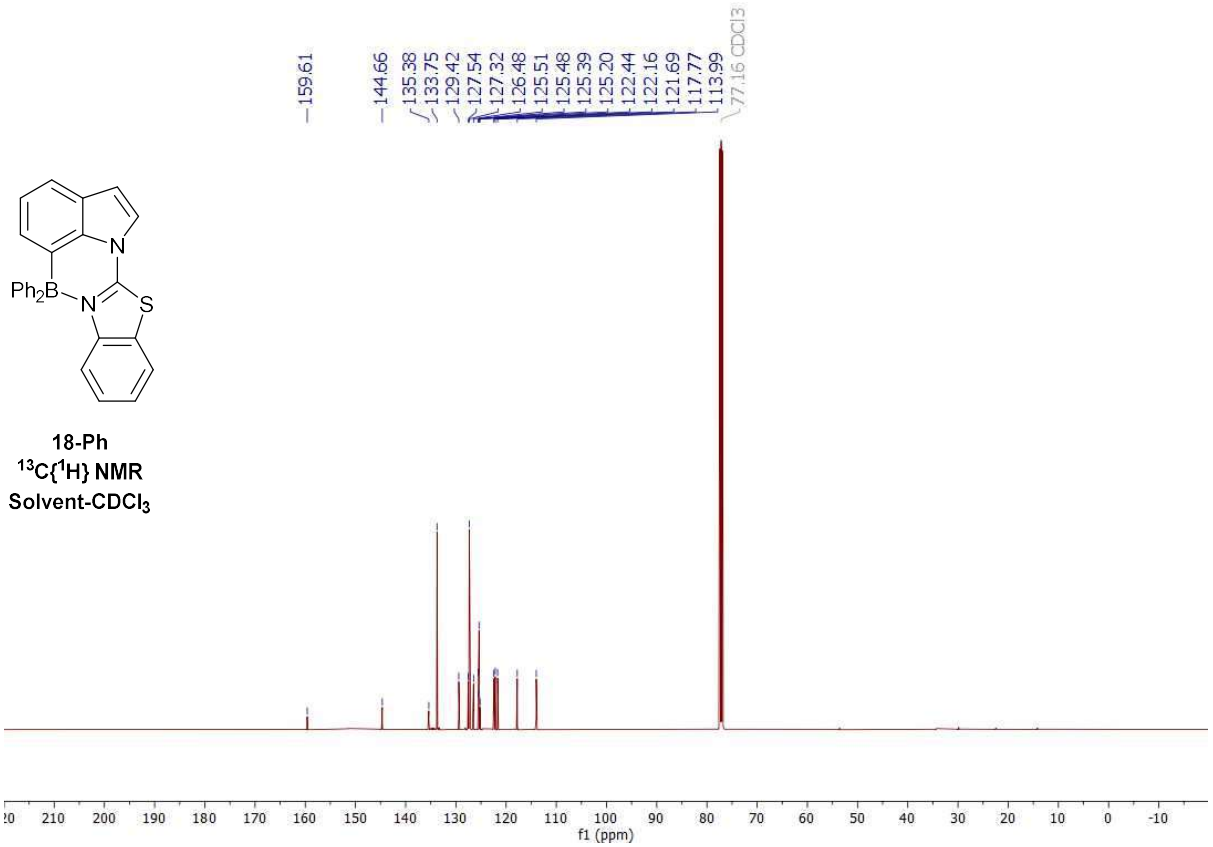
17-Ph
^{13}C{^{1}H} NMR
Solvent-$CDCl_3$



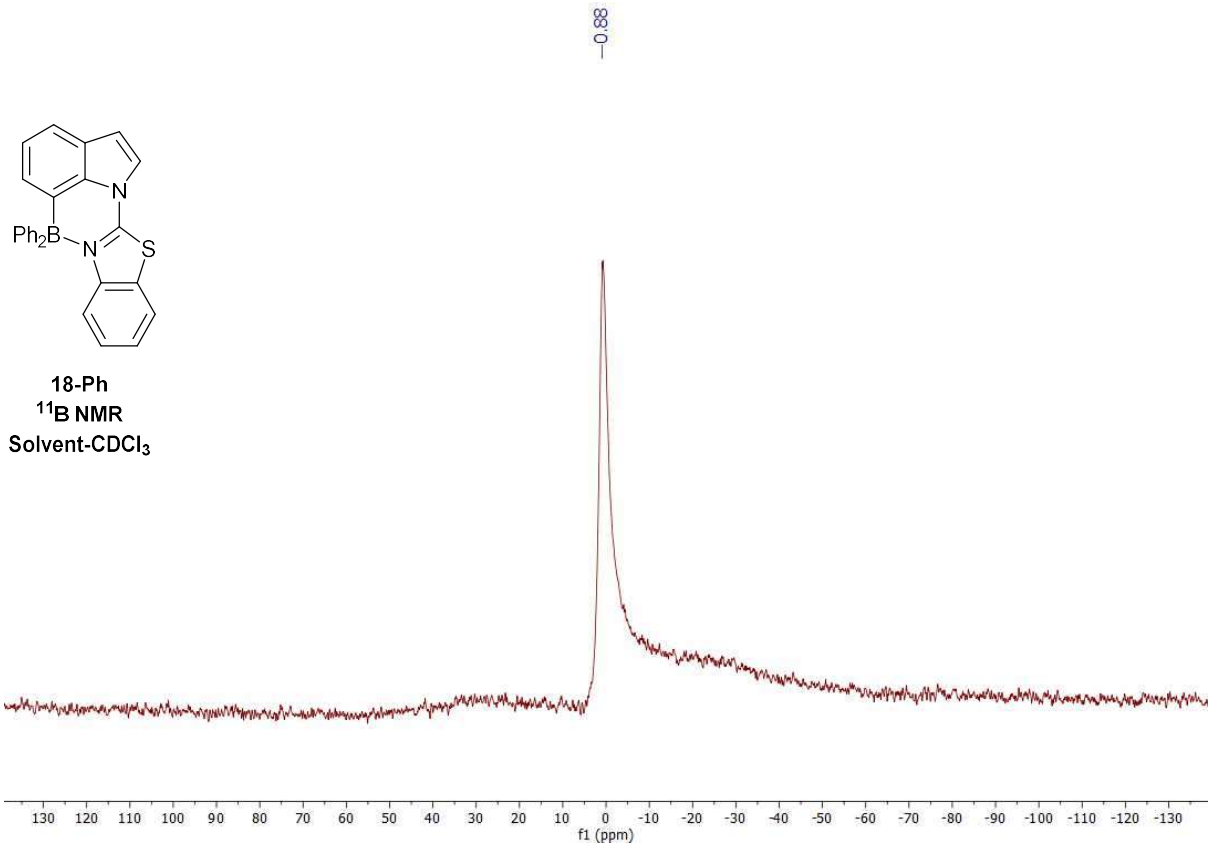
17-Ph
^{11}B NMR
Solvent-$CDCl_3$



18-Ph
^{1}H NMR
Solvent-$CDCl_3$



18-Ph
$^{13}C\{^{1}H\}$ NMR
Solvent-$CDCl_3$



18-Ph
^{11}B NMR
Solvent-$CDCl_3$