# A Borylative Cyclisation Towards Indole Boronic Esters

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# *1. General Information*

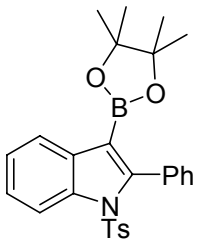
All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of dry nitrogen. Flash chromatography was performed on silica gel (BDH Silica Gel 60 43-60, or Fluorochem Davisil silica gel 43-60). The solvent system used was a gradient of petroleum ether or cyclohexane/ ethyl acetate (90-10), increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F254), which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate. $^{1}H/^{13}C$ NMR spectra were recorded on Bruker AC-250 or Av1-250 instruments or AMX-400 or AV1-400 instruments. $^{1}H$: Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), integration, coupling constants (J) in Hz, and assignment. $^{13}C$ NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). Infrared (FTIR) spectra in the range of 4000-450 $cm^{-1}$ were recorded on a Perkin Elmer Paragon 100 FTIR spectrometer ($\nu_{max}$ in $cm^{-1}$). Bands are characterized as broad (br), strong (s), medium (m) and weak (w). Samples were recorded as thin films using sodium chloride plates, as a DCM solution or as a KBr disc. Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Bench top GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES+) or a MicroMass Prospec operating in either FAB (FAB+), EI (EI+) or CI (CI+) mode. Melting points were performed on recrystallised solids and recorded on a Gallenkamp melting point apparatus and are uncorrected. All *o*-alkynylanilines were prepared according to literature procedures.[1]

[1] Yin, W. Ma, Z. Chai and G. Zhao, *J. Org. Chem*., 2007, **72**, 5731.

## *2. Synthesis of Indole Boronic Esters*

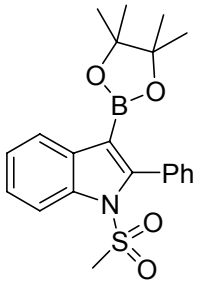
**General procedure:**

A solution of amino alkyne (0.1 mmol), $Pd_2dba_3$ (5 mol%), $AsPh_3$ (10 mol%), $Cs_2CO_3$ (0.2 mmol), $B_2Pin_2$ (0.2 mmol) in DMA (to make up a 0.5 M solution) was heated at 60 $^oC$ under a nitrogen atmosphere. After 30 minutes, the reaction mixture was allowed to cool to room temperature and diethyl ether (10 mL) was added. The organic extract was washed with $H_2O$ (5 mL x 3), dried ($MgSO_4$) and the solvents removed under reduced pressure to provide the crude product. Purification of the residue by flash chromatography on silica gel using a solvent gradient of petroleum ether / ethyl acetate (90:10), increasing in polarity to ethyl acetate gave the desired products.




**2**

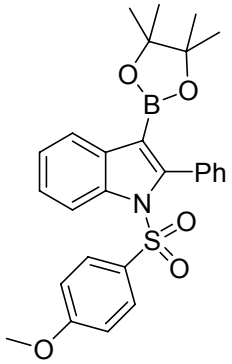
Following the general procedure, a solution of the amino alkyne (104 mg, 0.3 mmol), $Pd_2dba_3$ (13.8 mg, 5 mol%), $AsPh_3$ (9.3 mg, 10 mol%), $Cs_2CO_3$ (195.6 mg, 0.6 mmol), $B_2Pin_2$ (153.6 mg, 0.6 mmol) in DMA (0.6 mL) gave indole boronic ester **2** as a colourless oil (102 mg, 72%). $^1H$ NMR (400 MHz, $CDCl_3$) δ; 8.35-8.31 (1 H, m, ArH), 7.90-7.87 (1 H, m, ArH), 7.49-7.32 (9 H, m, ArH), 7.07 (2 H, d, *J* = 8.0 Hz, ArH), 2.32 (3 H, s, $CH_3$), 1.18 (12 H, s, $CH_3$). $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ; 148.7, 144.6, 137.6, 135.7, 133.4, 132.2, 131.7, 129.3, 128.6, 126.9, 126.6, 124.6, 124.0, 122.2, 115.5, 83.3, 24.6, 21.5. FTIR 2983 (m), 1598 (s), 1556 (s), 1400 (s), 1379 (s), 1181 (s), 1084 (s), 1038 (s), 734 (s). HRMS (EI+) calculated for $C_{27}H_{28}BNO_4S$: 473.1832. Found: 473.1849.




**3**

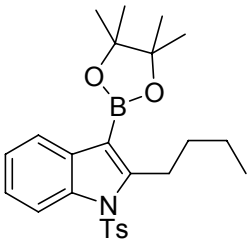
Following the general procedure, a solution of the amino alkyne (54 mg, 0.2 mmol), $Pd_2dba_3$ (9.2 mg, 5 mol%), $AsPh_3$ (6.2 mg, 10 mol%), $Cs_2CO_3$ (130.4 mg, 0.4 mmol), $B_2Pin_2$ (102.4 mg, 0.4 mmol) in DMA (0.4 mL) gave indole boronic ester **3** (50 mg, 63%) as a colourless oil. $^1H$ NMR (250 MHz, $CDCl_3$) δ; 8.15-8.08 (1 H, m, ArH), 8.03-7.96 (1 H, m, ArH), 7.52-7.36 (7 H, m, ArH), 2.85 (3 H, s, $CH_3$), 1.23 (12 H, s, $CH_3$). $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ; 148.6, 137.4, 133.3, 132.1, 131.2, 128.9,

127.0, 124.9, 124.3, 122.6, 114.9, 83.4, 40.8, 24.7. FTIR 2983 (m), 2932 (m), 1404 (s), 1368 (s), 1316 (s), 1174 (s), 1091 (s), 812 (s), 772 (s). HRMS (EI+) calculated for $C_{21}H_{25}BNO_4S$: 398.1597. Found: 398.1614.



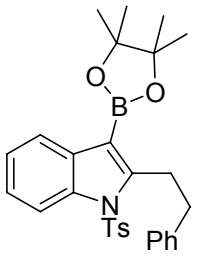

**4**

Following the general procedure, a solution of the amino alkyne (71 mg, 0.2 mmol), $Pd_2dba_3$ (9.2 mg, 5 mol%), $AsPh_3$ (6.2 mg, 10 mol%), $Cs_2CO_3$ (130.4 mg, 0.4 mmol), $B_2Pin_2$ (102.4 mg, 0.4 mmol) in DMA (0.4 mL) gave indole boronic ester **4** (62 mg, 65%) as a colourless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ; 8.33 (2 H, d, *J* = 8.0 Hz, ArH), 7.89 (1 H, d, *J* = 7.0 Hz, ArH), 7.47-7.42 (1 H, m, ArH), 7.39-7.36 (7 H, m, ArH), 7.31 (1 H, td, *J* = 7.0, 1.0 Hz, ArH), 6.74 (2 H, d, *J* = 8.0 Hz, ArH), 3.79 (3 H, s, $CH_3$), 1.18 (12 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 163.6, 148.7, 137.7, 133.4, 132.3, 131.7, 130.3, 129.1, 128.6, 126.6, 124.6, 123.9, 122.2, 115.5, 113.9, 83.2, 55.6, 24.6. FTIR 2979 (m), 2844 (m), 1598 (s), 1501 (s), 1269 (s), 1173 (s), 1088 (s), 916 (s), 734 (s). HRMS (EI+) calculated for $C_{27}H_{29}BNO_5S$: 490.1860. Found: 490.1860.



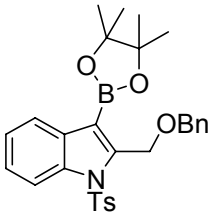

**5**

Following the general procedure, a solution of the amino alkyne (33 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (12.4 mg, 40 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **5** (33 mg, 73%) as a colourless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ; 8.16-8.12 (1 H, m, ArH), 7.96-7.93 (1 H, m, ArH), 7.65 (2 H, d, *J* = 8.0 Hz, ArH), 7.25-7.23 (2 H, m, ArH), 7.19 (2 H, d, *J* = 8.0 Hz, ArH), 3.33-3.29 (2 H, m, $CH_2$), 2.35 (3 H, s, $CH_3$), 1.74-1.67 (2 H, m, $CH_2$), 1.47-1.36 (2 H, m, $CH_2$), 1.36 (12 H, s, $CH_3$), 0.96 (3 H, t, *J* = 7.0 Hz, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 153.0, 144.6, 137.2, 136.5, 133.4, 129.8, 126.4, 123.6, 123.5, 122.1, 114.5, 83.1, 34.2, 28.1, 24.9, 22.7, 21.5, 13.8. FTIR 2987 (m), 2941 (m), 1564 (m), 1408 (s), 1374 (s), 1324 (s), 1181 (s), 1093 (s), 1046 (s), 776 (s), 545 (s). HRMS (EI+) calculated for $C_{25}H_{33}BNO_4S$: 454.2223. Found: 454.2222.



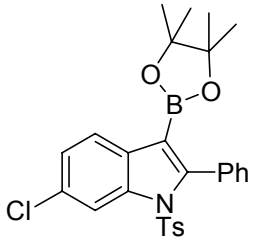

**6**

Following the general procedure, a solution of the amino alkyne (37.5 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (12.4 mg, 40 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **6** (35 mg, 70%) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.21-8.17 (1 H, m, ArH), 8.00-7.96 (1 H, m, ArH), 7.69 (2 H, d, *J* = 8.0 Hz, ArH), 7.43-7.35 (4 H, m, ArH), 7.28-7.17 (3 H, m, ArH), 7.19 (2 H, d, *J* = 8.0 Hz, ArH), 3.60-3.53 (2 H, m, $CH_2$), 3.08-3.02 (2 H, m, $CH_2$), 2.33 (3 H, s, $CH_3$), 1.39 (12 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 151.5, 144.8, 142.3, 137.1, 136.4, 133.2, 129.9, 128.7, 128.4, 126.4, 125.9, 123.9, 123.6, 122.2, 114.4, 83.2, 38.6, 31.5, 25.1, 21.5. FTIR 2983 (m), 1602 (m), 1402 (s), 1372 (s), 1174 (s), 1141 (s), 1060 (s), 703 (s), 573 (s). HRMS (EI+) calculated for $C_{29}H_{33}BNO_4S$: 502.2223. Found: 502.2225.



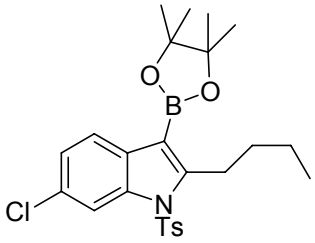

**7**

Following the general procedure, a solution of the amino alkyne (39 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (12.4 mg, 40 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **7** (35 mg, 68%) as a colourless solid. Mp 108-110 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$) δ; 8.13-8.10 (1 H, m, ArH), 8.06-8.02 (1 H, m, ArH), 7.93 (2 H, d, *J* = 8.0 Hz, ArH), 7.37-7.23 (7 H, m, ArH), 6.99 (2 H, d, *J* = 8.0 Hz, ArH), 5.32 (2 H, s, $CH_2$), 4.59 (2 H, s, $CH_2$), 2.27 (3 H, s, $CH_3$), 1.36 (12 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 145.5, 144.5, 138.5, 137.1, 136.2, 132.3, 129.4, 128.2, 127.9, 127.4, 124.8 (C x 2), 123.3, 123.0, 114.2, 83.5, 72.0, 63.4, 25.0, 21.5. FTIR 3063 (m), 2991 (m), 2937 (m), 1573 (m), 1451 (s), 1396 (s), 1375 (s), 1177 (s), 1072 (s), 857 (s), 672 (s), 574 (s). HRMS (EI+, Na added) calculated for $C_{29}H_{32}BNO_5NaS$: 540.1992. Found: 540.2017.



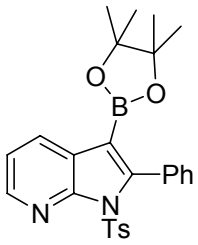

**8**

Following the general procedure, a solution of the amino alkyne (39 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (12.4 mg, 40 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **8** (40 mg, 79%) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.36 (1 H, d, *J* = 2.0 Hz, ArH), 7.79 (1 H, d, *J* = 8.0 Hz, ArH), 7.45-7.26 (8 H, m, ArH), 7.10 (2 H, d, *J* = 8.0 Hz, ArH), 2.35 (3 H, s, $CH_3$), 1.16 (12 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 149.3, 144.9, 138.0, 135.5, 131.8, 131.71, 131.66, 130.4, 129.5, 128.8, 127.0, 126.6, 124.5, 123.0, 115.6, 83.3, 24.6, 21.6. FTIR 2979 (m), 2941 (w), 1602 (m), 1459 (s), 1374 (s), 1181 (s), 1093 (s), 819 (s), 667 (s), 578 (s). HRMS (EI+) calculated for $C_{27}H_{28}NO_4S^{35}ClB$: 508.1521. Found: 508.1512.



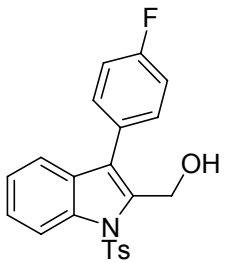

**9**

Following the general procedure, a solution of the amino alkyne (39 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (12.4 mg, 40 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **9** (36 mg, 74%) as a colourless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ; 8.19 (1 H, d, *J* = 2.0 Hz, ArH), 7.86 (1 H, d, *J* = 8.0 Hz, ArH), 7.67 (2 H, d, *J* = 8.0 Hz, ArH), 7.24-7.20 (3 H, m, ArH), 3.29-3.25 (2 H, m, $CH_2$), 2.37 (3 H, s, $CH_3$), 1.72-1.66 (2 H, m, $CH_2$), 1.47-1.41 (2 H, m, $CH_2$), 1.36 (12 H, s, $CH_3$), 0.96 (3 H, t, *J* = 7.0 Hz, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 153.6, 145.0, 137.5, 136.3, 131.9, 130.0, 129.5, 126.4, 124.0, 122.9, 114.6, 83.2, 34.2, 28.1, 24.9, 22.7, 21.6, 13.8. FTIR 2969 (m), 2935 (m), 1560 (m), 1465 (s), 1408 (s), 1173 (s), 1055 (s), 915 (s), 740 (s), 584 (s). HRMS (EI+) calculated for $C_{25}H_{32}BNO_4S^{35}Cl$: 488.1834. Found: 488.1823.



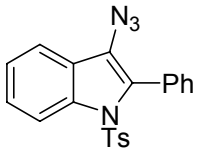

**10**

Following the general procedure, a solution of the amino alkyne (35 mg, 0.1 mmol), $Pd_2dba_3$ (9.2 mg, 10 mol%), $AsPh_3$ (6.2 mg, 20 mol%), $Cs_2CO_3$ (65.2 mg, 0.2 mmol), $B_2Pin_2$ (51.2 mg, 0.2 mmol) in DMA (0.2 mL) gave indole boronic ester **10** (24 mg, 51%) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.49 (1 H, dd, *J* = 5.0, 2.0 Hz, ArH), 8.17 (1 H, dd, *J* = 8.0, 2.0 Hz, ArH), 7.82 (2 H, d, *J* = 8.0 Hz, ArH), 7.49-7.41 (5 H, m, ArH), 7.23 (1 H, dd, *J* = 8.0, 5.0 Hz, ArH), 7.18 (2 H, d, *J* = 8.0 Hz, ArH), 2.35 (3 H, s, $CH_3$), 1.18 (12 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 149.8, 149.1, 144.8, 144.6, 136.2, 132.6, 130.9, 130.5, 129.3, 128.7, 127.9, 126.8, 125.5, 119.5, 83.3, 24.6, 21.6. FTIR 2988 (m), 29353 (m), 1594 (m), 1553 (m), 1492 (s), 1420 (s), 1382 (s), 1180 (s), 1093 (s), 1048 (s), 819 (s), 580 (s). HRMS (EI+) calculated for $C_{26}H_{28}N_2O_4SB$: 475.1863. Found: 475.1881.



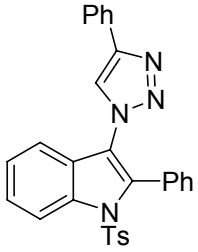

**12**

A mixture of amino alkyne **11** (108 mg, 0.2 mmol), $Pd_2dba_3$ (9.2 mg, 5 mol%), $AsPh_3$ (6.2 mg, 10 mol%), $Cs_2CO_3$ (130.4 mg, 0.4 mmol), $B_2Pin_2$ (102.4 mg, 0.4 mmol) in DMA (0.4 mL) was heated at 60 $^o$C under nitrogen. After 30 minutes, 4-fluoro-iodobenzene (88 mg, 0.4 mmol) in 1:1 DMA/$H_2O$ (0.8 mL) was added. The resulting reaction mixture was stirred at the same temperature for 16 hours. A solution of TBAF (1 M in THF) (1 mL) was added and the reaction mixture was heated at 60 $^o$C for 6 hours. After cooling to room temperature, diethyl ether (20 mL) was added and the organic phase was washed with $H_2O$ (10 mL x 3), dried ($MgSO_4$) and the organic solvents were removed under reduced pressure to give the crude product. Purification of the residue by flash chromatography on silica gel using a gradient mixture of $Et_2O$/petroleum ether (1:4) as eluent gave the indole alcohol **12** (45 mg, 57%) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.17 (1 H, d, *J* = 8.0 Hz, ArH), 7.82 (2 H, d, *J* = 8.0 Hz, ArH), 7.53-7.47 (3 H, m, ArH), 7.40 (1 H, td, *J* = 7.0, 1.0 Hz, ArH), 7.30-7.20 (5 H, m, ArH), 4.82 (2 H, d, *J* = 7.5 Hz, $CH_2$), 3.37 (1 H, t, *J* = 7.5 Hz, OH), 2.38 (3 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 162.2 (d, *J* = 247 Hz), 144.9, 135.7, 135.32, 135.26 131.4 (d, *J* = 8 Hz), 129.7, 128.9, 127.7 (d, *J* = 3 Hz), 126.2, 125.4, 124.2, 123.6, 120.0, 115.5 (d, *J* = 21 Hz), 114.2, 55.4, 21.3. FTIR 3577 (m), 2927 (m), 1511 (m), 1367 (s), 1230 (s), 1177 (s), 1097 (s), 846 (s), 713 (m). HRMS (EI+, Na added) calculated for $C_{22}H_{18}NO_3FNaS$: 418.0889. Found: 418.0873.



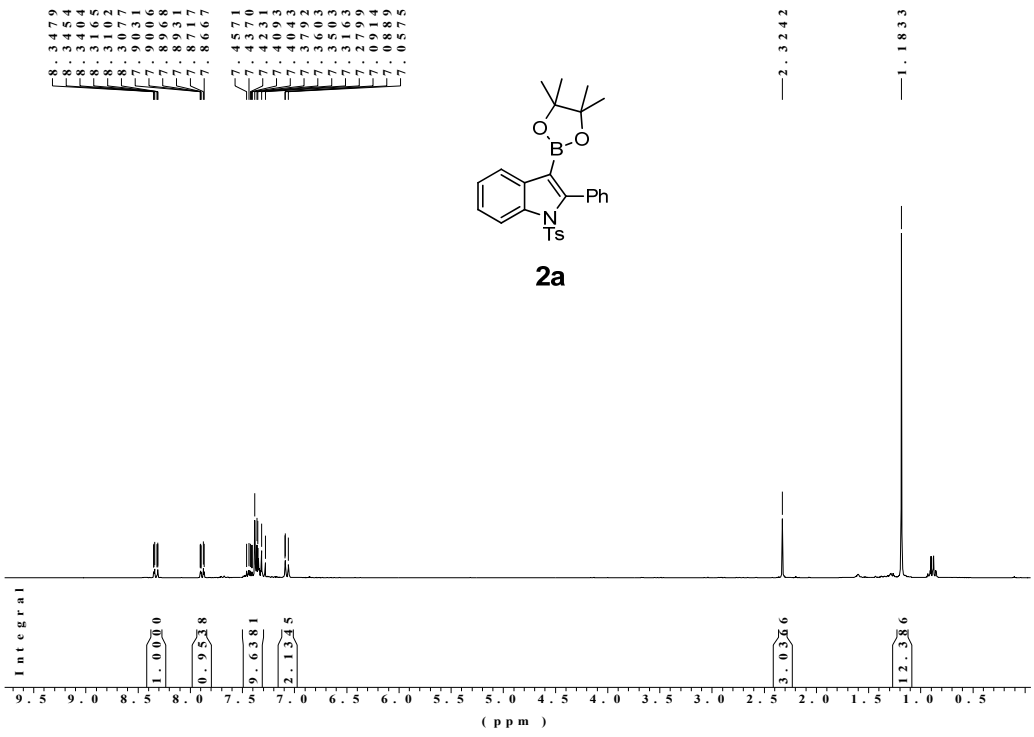

**13**

A mixture of indole boronic ester **2a** (47 mg, 0.1 mmol), $NaN_3$ (7.8 mg, 0.12 mmol) and $CuSO_4$ (1.6 mg, 0.01 mmol) in methanol (0.5 mL) was stirred at room temperature for 2 hours. The resulting dark solution was concentrated in vacuo and the crude product purified by flash chromatography on silica gel using a gradient mixture of $Et_2O$/petroleum ether as eluent to give indole azide **13** (36 mg, 93%) as a colourless oil. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.40 (1 H, d, *J* = 8.0 Hz, ArH), 7.64 (1 H, d, *J* = 8.0 Hz, ArH), 7.52-7.43 (6 H, m, ArH), 7.36 (1 H, dd, *J* = 7.0, 1.0 Hz, ArH), 7.31 (2 H, d, *J* = 8.0 Hz, ArH), 7.10 (2 H, d, *J* = 8.0 Hz, ArH), 2.34 (3 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 144.9 (C x 2), 136.4, 134.4, 131.5, 129.4, 129.2, 129.0, 127.6, 126.9, 126.0, 125.9, 124.5, 121.1, 117.9, 116.9, 21.6. FTIR 3064 (w), 2934 (w), 2111 (s), 1602 (m), 1454 (s), 1367 (s), 1177 (s), 1093 (s), 744 (s), 675 (s). HRMS (EI+) calculated for $C_{21}H_{17}N_4O_2S$: 389.1072. Found: 389.1070.




**14**

A mixture of indole boronic ester **2a** (47 mg, 0.1 mmol), $NaN_3$ (7.8 mg, 0.12 mmol) and $CuSO_4$ (1.6 mg, 0.01 mmol) in methanol (0.5 mL) was stirred at room temperature for 2 hours before a solution of phenylacetylene (20 mg, 0.2 mmol) and sodium ascorbate (10 mg, 0.05 mmol) in 1: 1 DCM/$H_2O$ (1 mL) was added. The reaction mixture was stirred at room temperature for 16 hours and then the resulting dark solution was concentrated in vacuo and the crude product purified by flash chromatography on silica gel using a gradient mixture of $Et_2O$/petroleum ether as eluent to give indole azide **14** (42 mg, 86%) as a colourless solid. Mp 204-205 $^o$C. $^1$H NMR (250 MHz, $CDCl_3$) δ; 8.48 (1 H, d, *J* = 8.0 Hz, ArH), 7.73-7.67 (3 H, m, ArH), 7.55-7.28 (13 H, m, ArH), 7.14 (2 H, d, *J* = 8.0 Hz, ArH), 2.36 (3 H, s, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ; 147.1, 145.6, 135.7, 135.0, 133.6, 131.4, 130.03, 130.00, 129.7, 128.8, 128.3, 128.1, 127.8, 127.0, 126.5, 125.7, 125.2, 125.1, 121.0, 120.8, 119.4, 116.0, 21.6. FTIR 2923 (w), 1602 (m), 1450 (s), 1381 (s), 1180 (s), 1093 (s), 1002 (s), 766 (s), 573 (s). HRMS (EI+) calculated for $C_{29}H_{23}N_4O_2S$: 491.1542. Found: 491.1522.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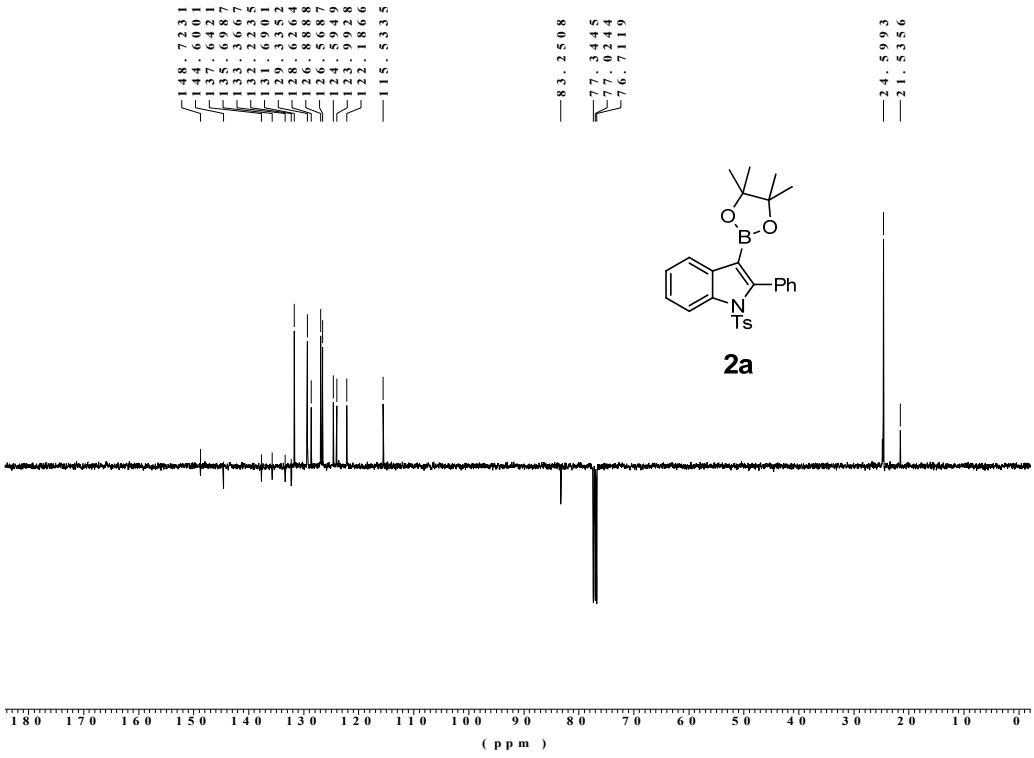
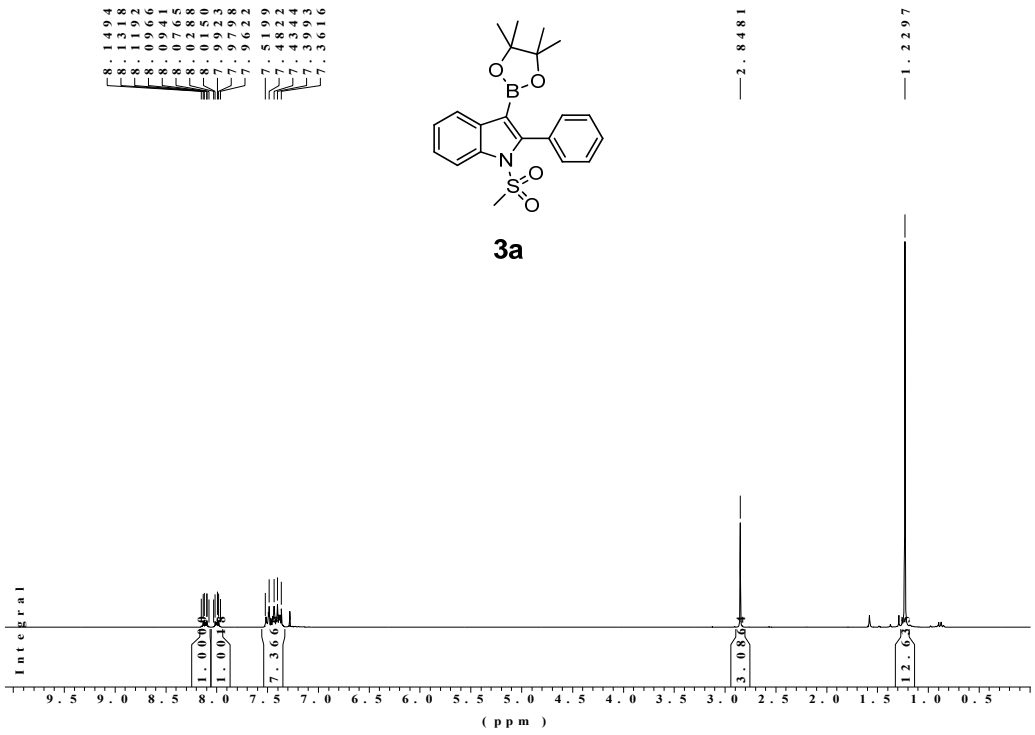
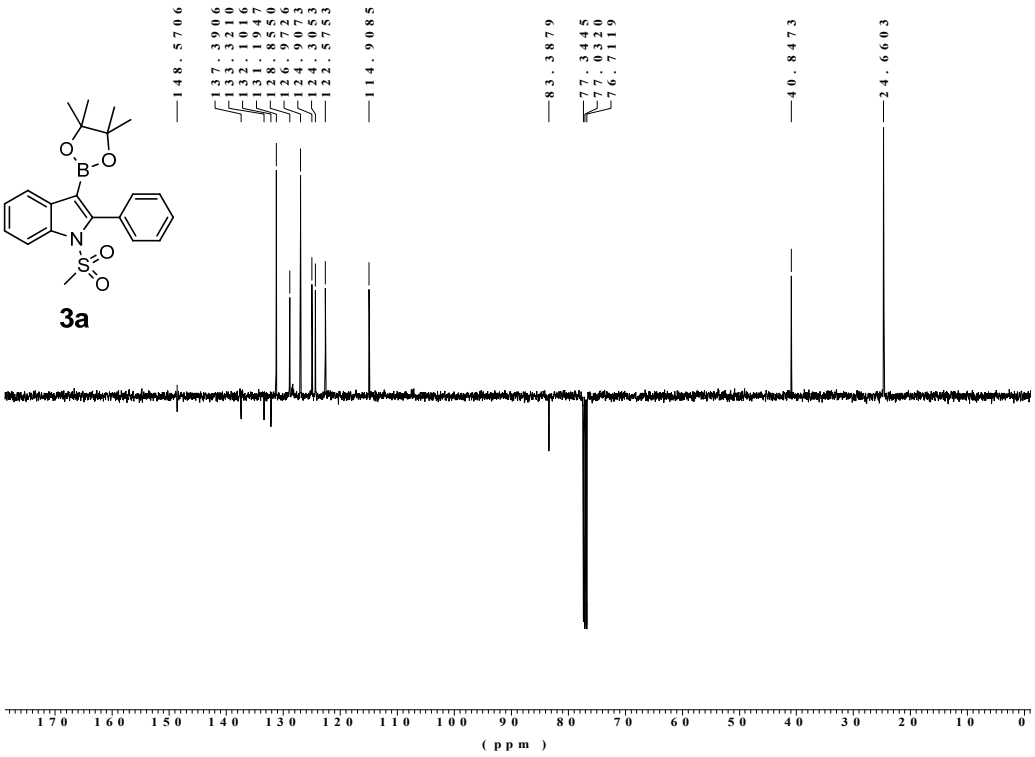
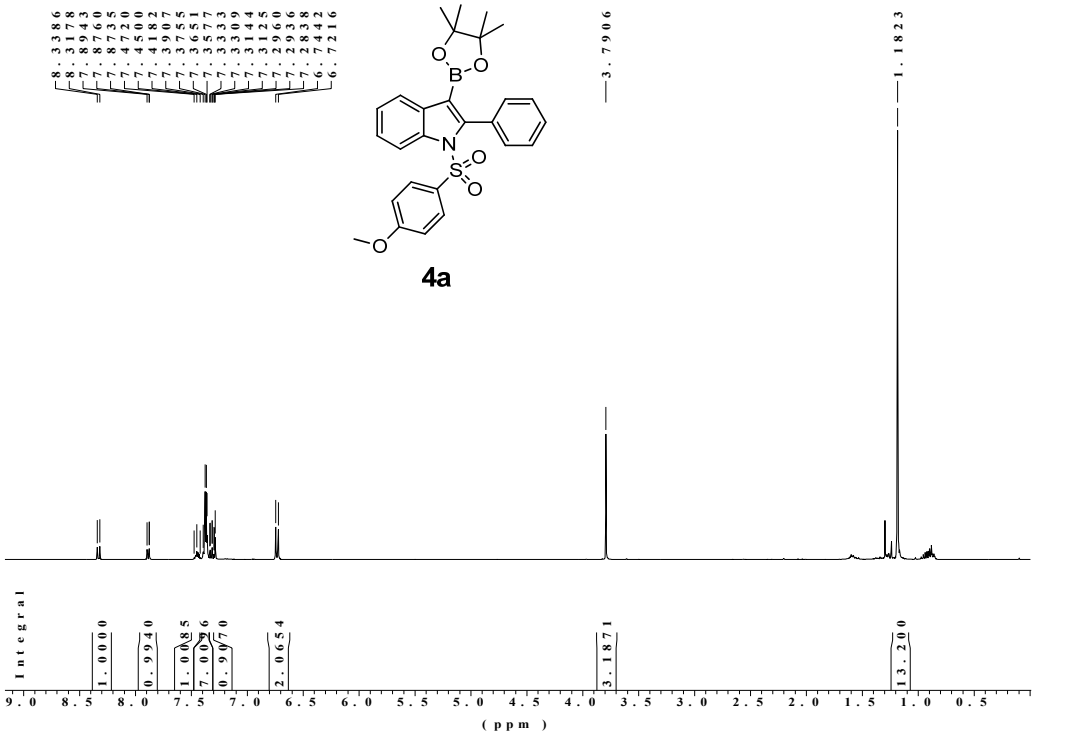
8.3404
8.3165
8.3102
8.3077
7.9031
7.9006
7.8968
7.8931
7.8717
7.8667
7.4571
7.4370
7.4231
7.4093
7.4043
7.3792
7.3603
7.3503
7.3163
7.2799
7.0914
7.0889
7.0575
2.3242
1.1833
Ph
N
Ts
2a
Integral
1.0000
0.9538
9.6381
2.1345
3.0316
12.3816
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


148.7231
144.6001
137.6421
135.6987
133.3667
132.2235
131.6901
129.3352
128.6264
126.8888
126.5687
124.5949
123.9928
122.1866
115.5335
83.2508
77.3445
77.0244
76.7119
24.5993
21.5356
Ph
N
Ts
2a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


8.1494
8.1318
8.1192
8.0966
8.0941
8.0765
8.0288
8.0150
7.9923
7.9798
7.9622
7.5199
7.4822
7.4344
7.3993
7.3616
2.8481
1.2297
3a
Integral
1.00
1.00
7.36
3.08
12.6
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


148.5706
137.3906
133.3210
132.1316
131.1947
128.8550
126.9726
124.9073
124.3053
122.5753
114.9085
83.3879
77.3445
77.0320
76.7119
40.8473
24.6603
3a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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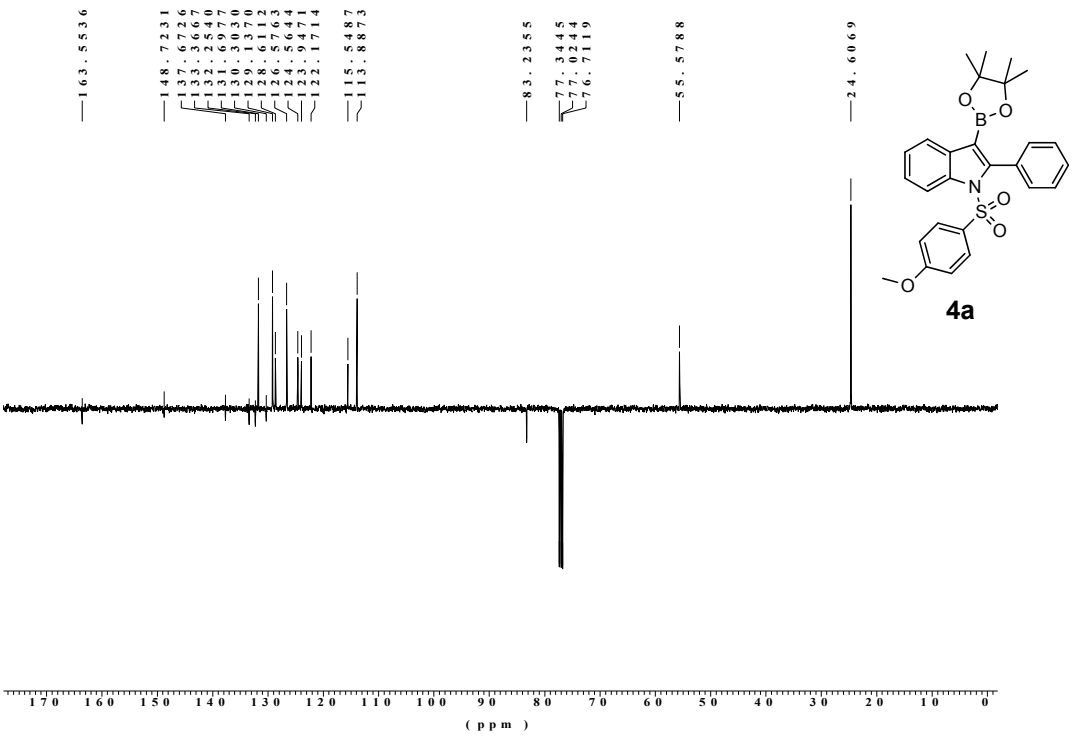
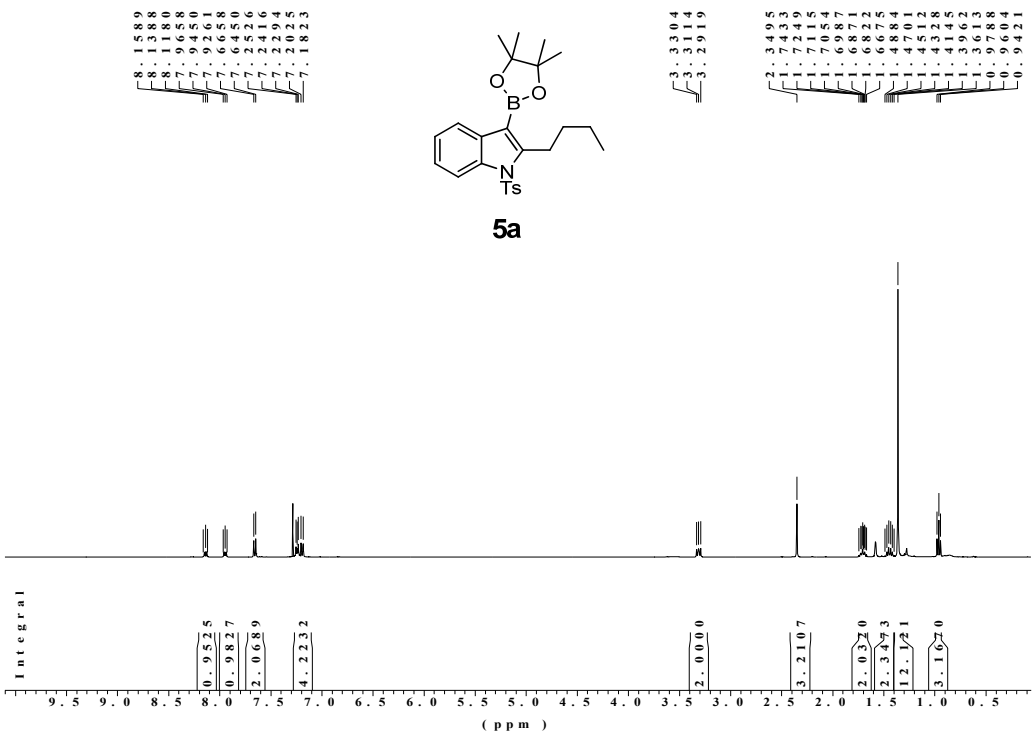
8.3178
7.8943
7.8760
7.8735
7.4720
7.4500
7.4182
7.3907
7.3755
7.3651
7.3577
7.3333
7.3309
7.3144
7.3125
7.2960
7.2936
7.2838
7.7442
6.7216
3.7906
1.1823
Integral
1.0000
0.9940
1.0085
7.0076
0.9970
2.0654
3.1871
13.200
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)
4a


163.5536
148.7231
137.6726
133.3667
132.2540
131.6977
130.3030
129.1370
128.6112
126.5763
124.5644
123.9471
122.1714
115.5487
113.8873
83.2355
77.3445
77.0244
76.7119
55.5788
24.6069
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)
4a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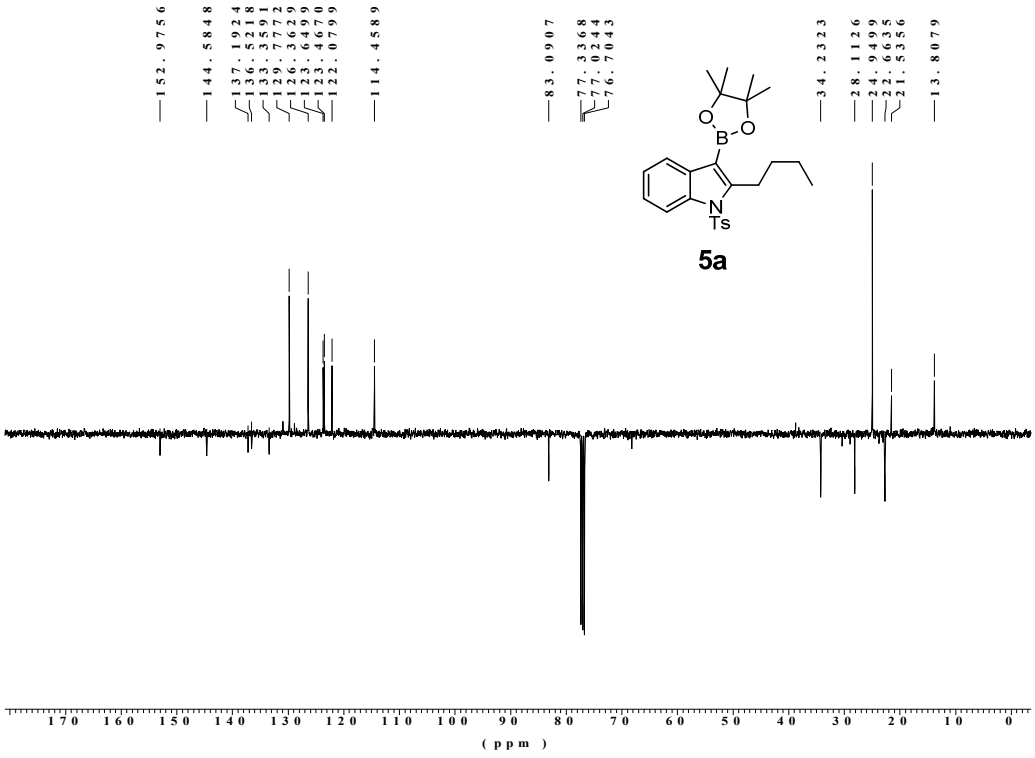
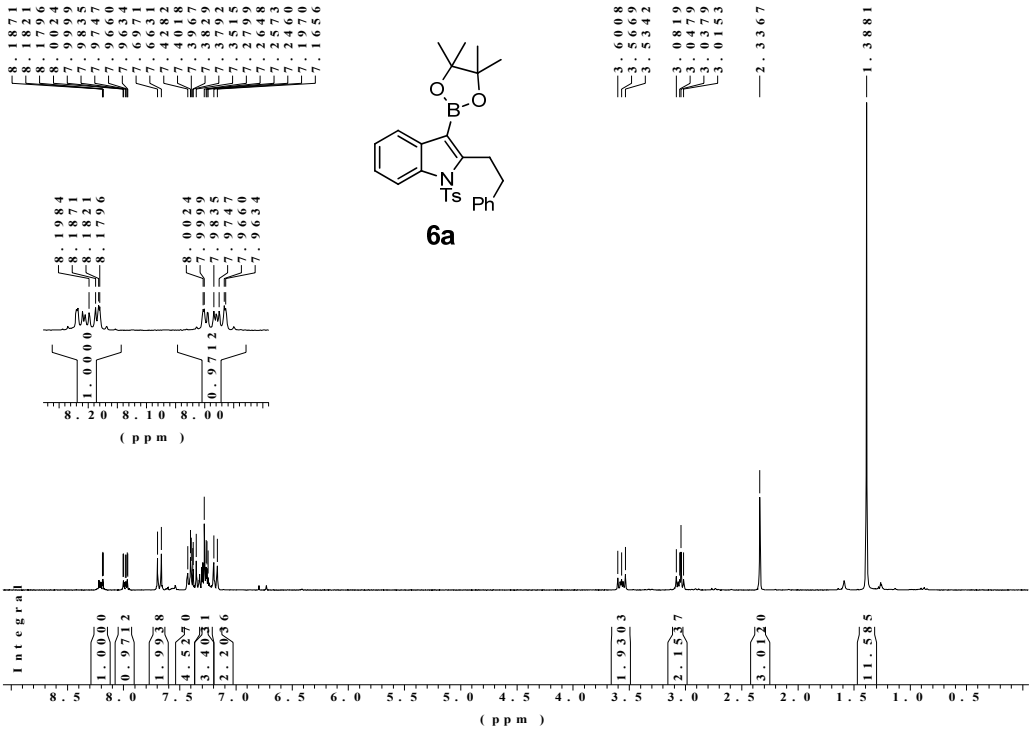
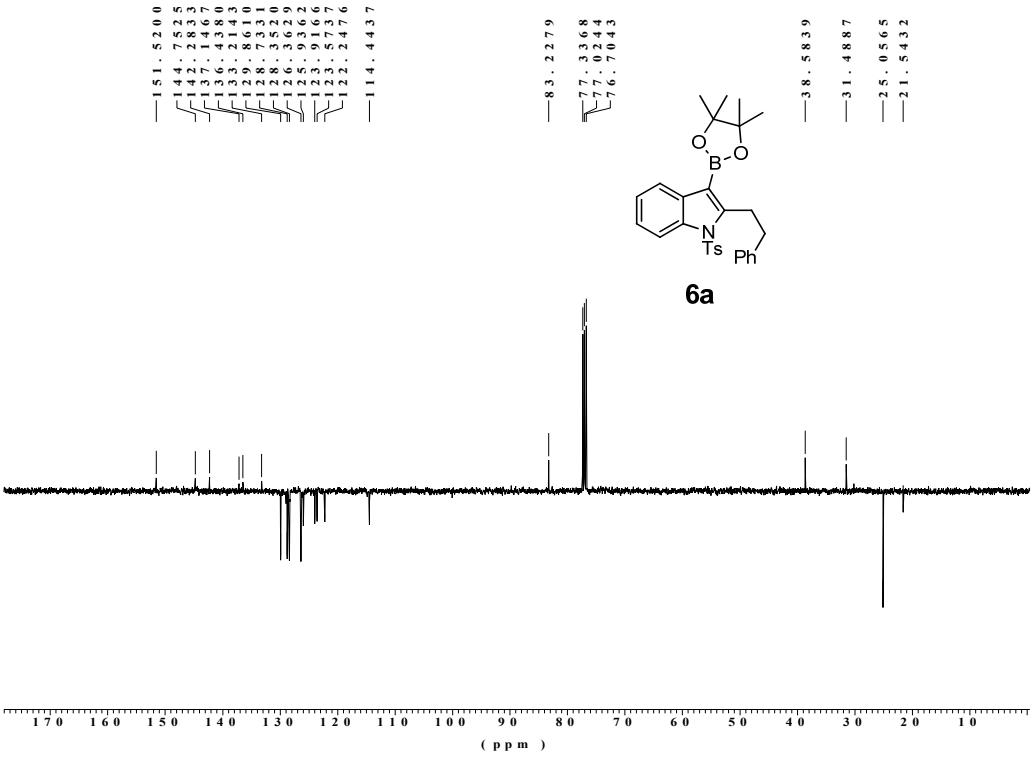
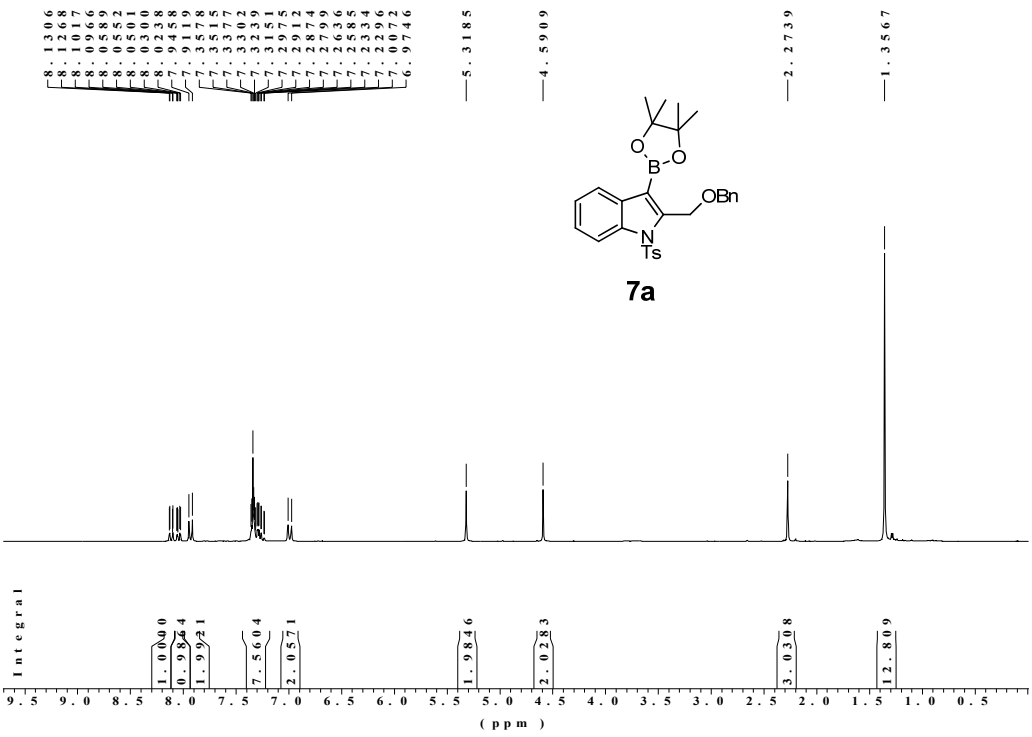
8.1388
8.1180
7.9658
7.9450
7.9261
7.6658
7.6450
7.2526
7.2416
7.2294
7.2025
7.1823
3.3304
3.3114
3.2919
2.3495
1.7433
1.7249
1.7115
1.7054
1.6987
1.6871
1.6822
1.6675
1.4884
1.4701
1.4512
1.4328
1.4145
1.3962
1.3613
0.9788
0.9604
0.9421
O
B
O
N
Ts
5a
Integral
0.9525
0.9827
2.0689
4.2232
2.0000
3.2107
2.0370
2.3473
12.1121
3.1670
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


152.9756
144.5848
137.1924
136.5218
133.3591
129.7772
126.3629
123.6499
123.4670
122.0799
114.4589
83.0907
77.3368
77.0244
76.7043
34.2323
28.1126
24.9499
22.6635
21.5356
13.8079
O
B
O
N
Ts
5a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


6a
(ppm)


6a
(ppm)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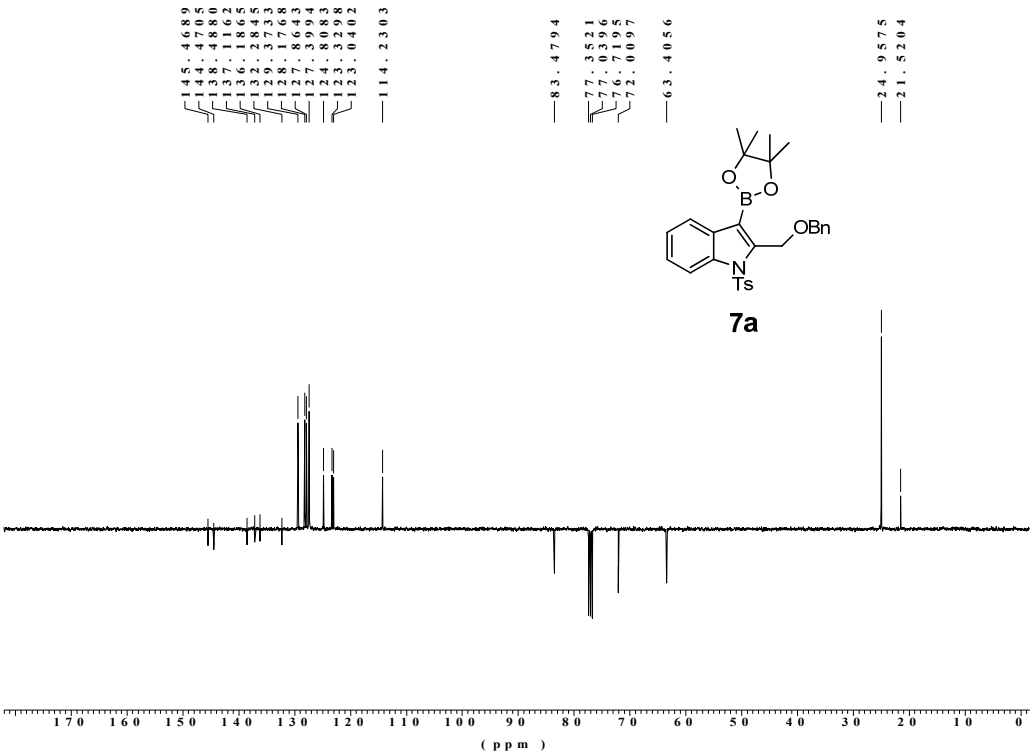
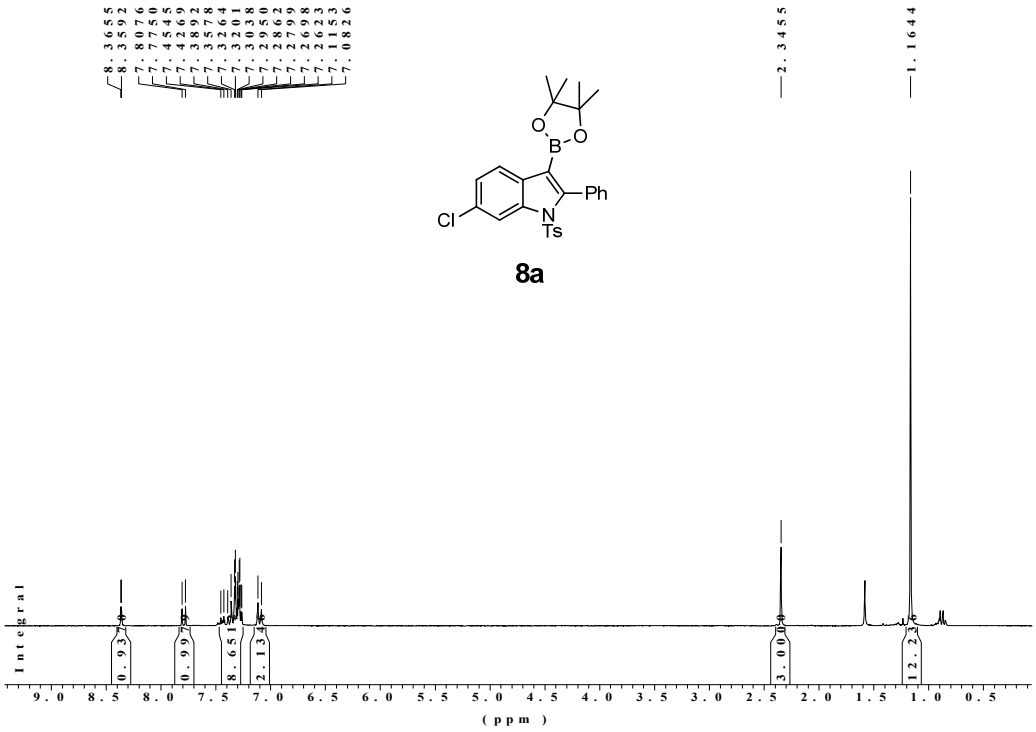
8.1017
8.0966
8.0589
8.0552
8.0501
8.0300
8.0238
7.9458
7.9119
7.3578
7.3517
7.3302
7.3249
7.3151
7.2975
7.2912
7.2874
7.2799
7.2636
7.2585
7.2334
7.2296
7.0072
6.9746
5.3185
4.5909
2.2739
1.3567
OBn
N
Ts
7a
Integral
1.0000
0.9844
1.9921
7.5604
2.0571
1.9846
2.0283
3.0308
12.8091
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


145.4689
144.4705
138.4480
137.1162
136.1865
132.2845
129.3733
128.1768
127.8643
127.3994
124.8083
123.3298
123.0402
114.2303
83.4794
77.3521
77.0396
76.7195
72.0097
63.4056
24.9575
21.5204
OBn
N
Ts
7a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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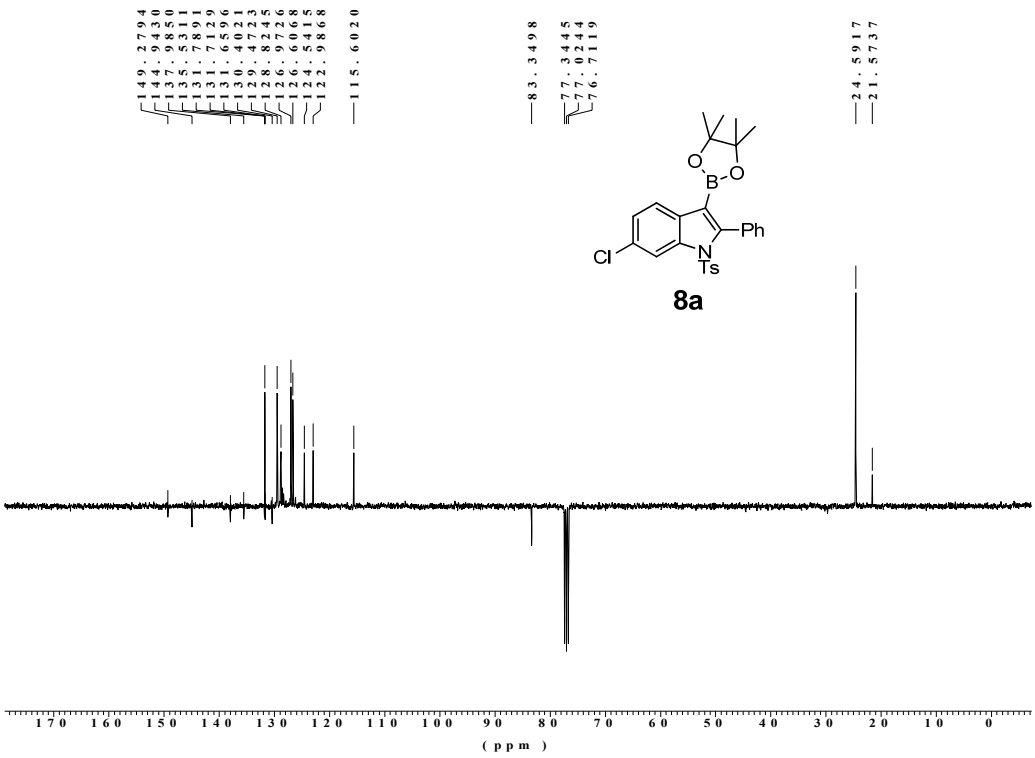
7.4545
7.4269
7.3892
7.3578
7.3264
7.3201
7.3038
7.2950
7.2862
7.2799
7.2698
7.2623
7.1153
7.0826
2.3455
1.1644
Integral
0.93
0.99
8.65
2.13
3.00
12.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)
O
B
O
Ph
Cl
N
Ts

**8a**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137.9850
135.5311
131.7891
131.7129
131.6596
130.4021
129.4723
128.8245
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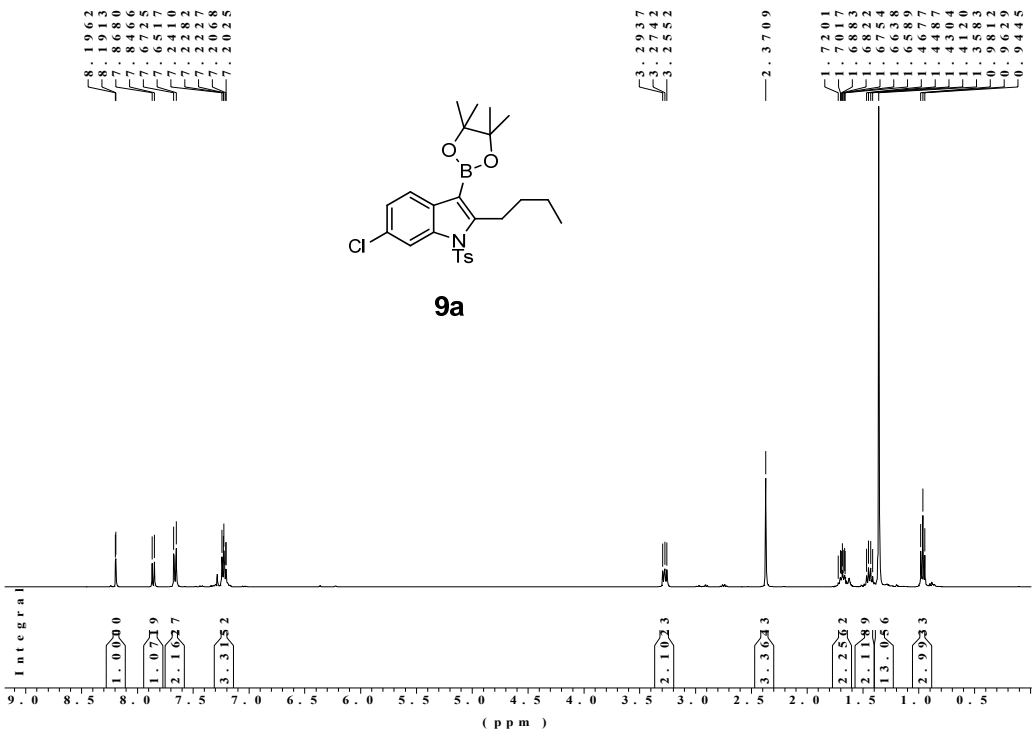
126.6068
124.5415
122.9868
115.6020
83.3498
77.3445
77.0244
76.7119
24.5917
21.5737
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)
O
B
O
Ph
Cl
N
Ts

**8a**


8.1962
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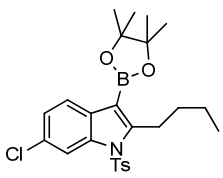
7.8466
7.6725
7.6517
7.2410
7.2282
7.2227
7.2068
7.2025
3.2937
3.2742
3.2552
2.3709
1.7201
1.7017
1.6883
1.6822
1.6754
1.6638
1.6589
1.4677
1.4487
1.4304
1.4120
1.3583
0.9812
0.9629
0.9445
Integral
1.0000
1.0719
2.1647
3.3152
2.1023
3.3643
2.2562
2.1189
13.0556
2.9933
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

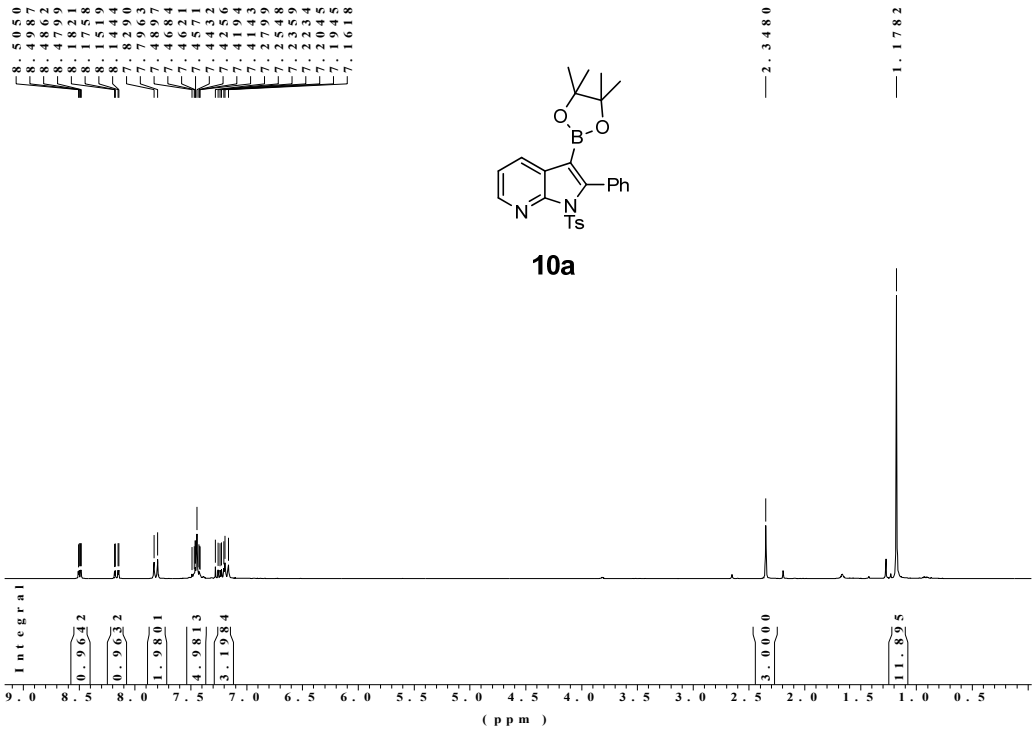


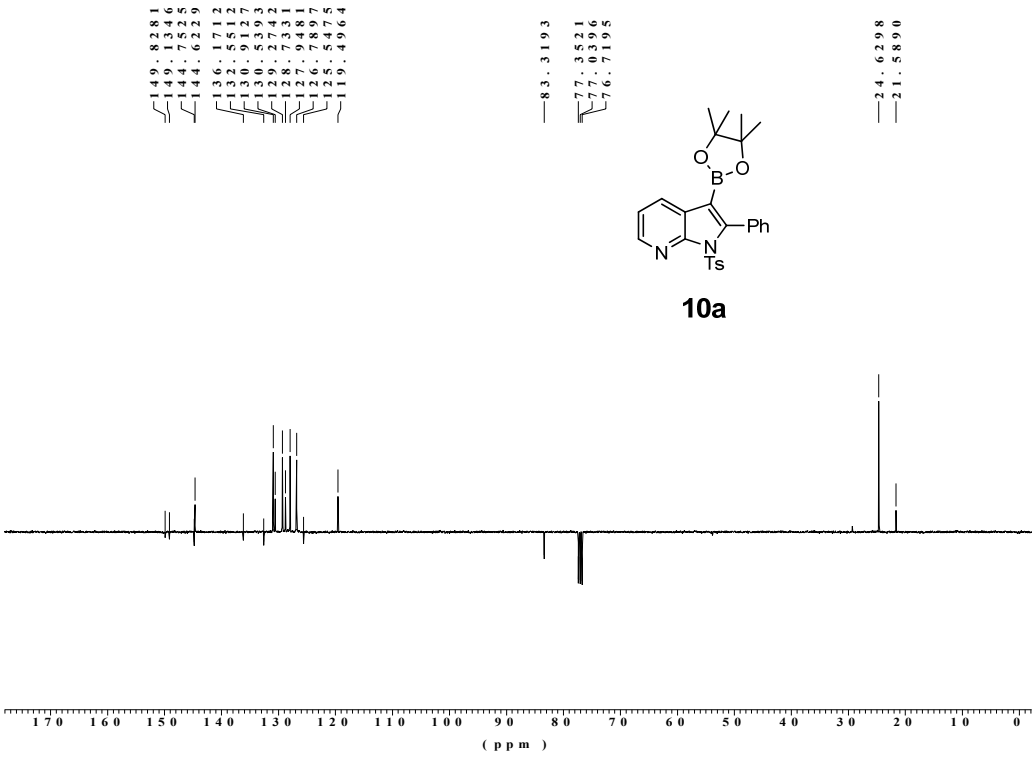
**9a**

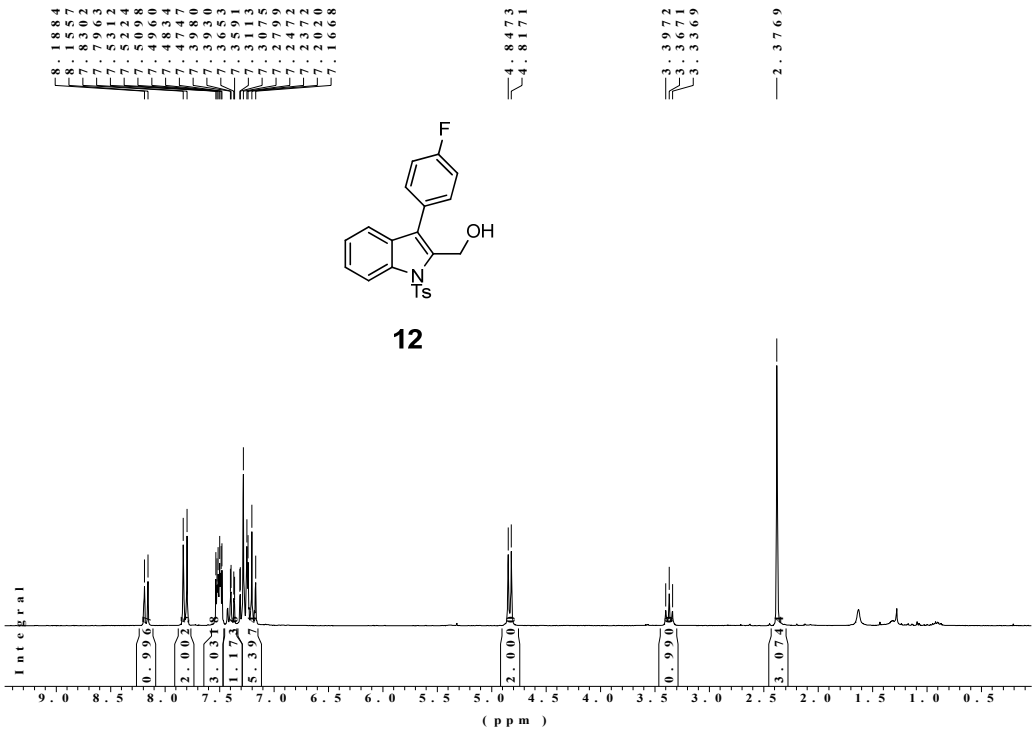

153.5624
144.9735
137.5354
136.2551
131.8806
129.9525
129.5333
126.3934
124.0233
122.8649
114.6037
83.2431
77.3521
77.0396
76.7195
34.1637
28.1050
24.9422
22.6435
21.5737
13.7774
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)



**9a**


8.5050
8.4987
8.4862
8.4799
8.1821
8.1758
8.1519
8.1444
7.8290
7.7963
7.4897
7.4684
7.4621
7.4571
7.4432
7.4256
7.4194
7.4143
7.2799
7.2548
7.2359
7.2234
7.2045
7.1945
7.1618
2.3480
1.1782
O
B
O
Ph
N
N
Ts
10a
Integral
0.9642
0.9632
1.9801
4.9813
3.1984
3.0000
11.895
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


149.8281
149.1346
144.7525
144.6229
136.1712
132.5512
130.4127
130.5393
129.2742
128.7381
127.9487
126.5475
125.9964
119.4964
83.3193
77.3521
77.0396
76.7195
24.6298
21.5890
O
B
O
Ph
N
N
Ts
10a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


8.1884
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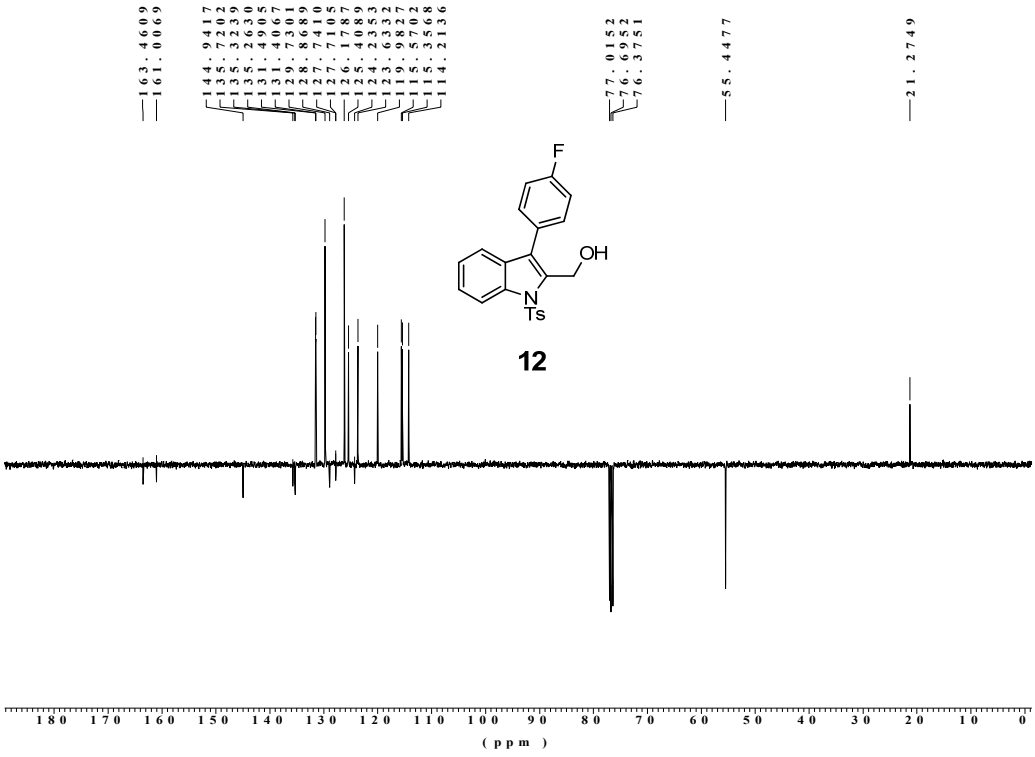
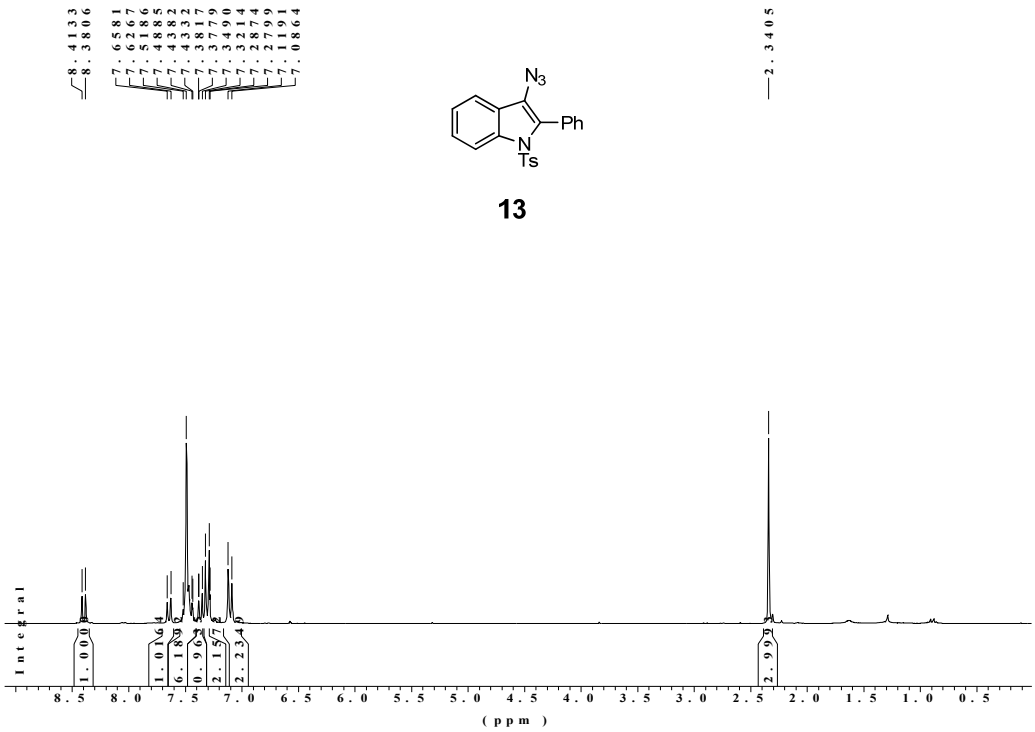
7.8302
7.7963
7.5312
7.5224
7.5098
7.4960
7.4834
7.4747
7.3980
7.3930
7.3653
7.3591
7.3113
7.3075
7.2799
7.2472
7.2372
7.2020
7.1668
4.8473
4.8171
3.3972
3.3671
3.3369
2.3769
F
OH
N
Ts
12
Integral
0.996
2.002
3.031
1.173
5.397
2.000
0.990
3.074
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


163.4609
161.0069
144.9417
135.7202
135.3239
135.2630
131.4905
131.4067
129.7301
128.8689
127.7410
127.7105
126.1787
125.4089
124.2353
123.6332
119.9827
115.5702
115.3568
114.2136
77.0152
76.6952
76.3751
55.4477
21.2749
F
OH
N
Ts
12
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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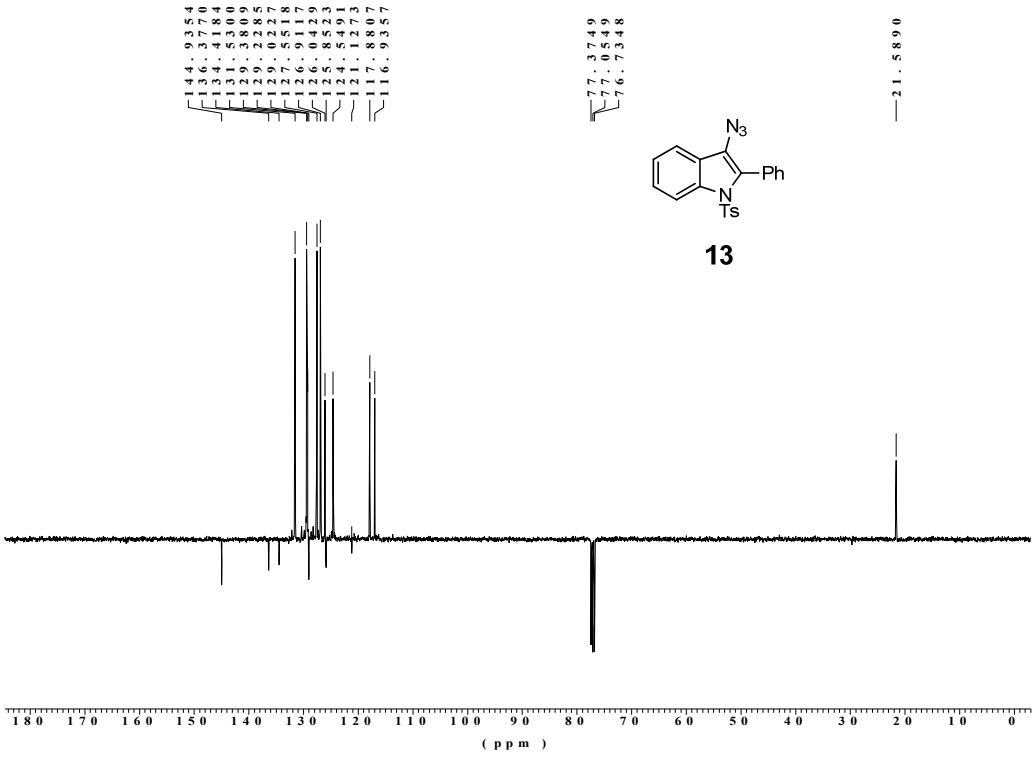
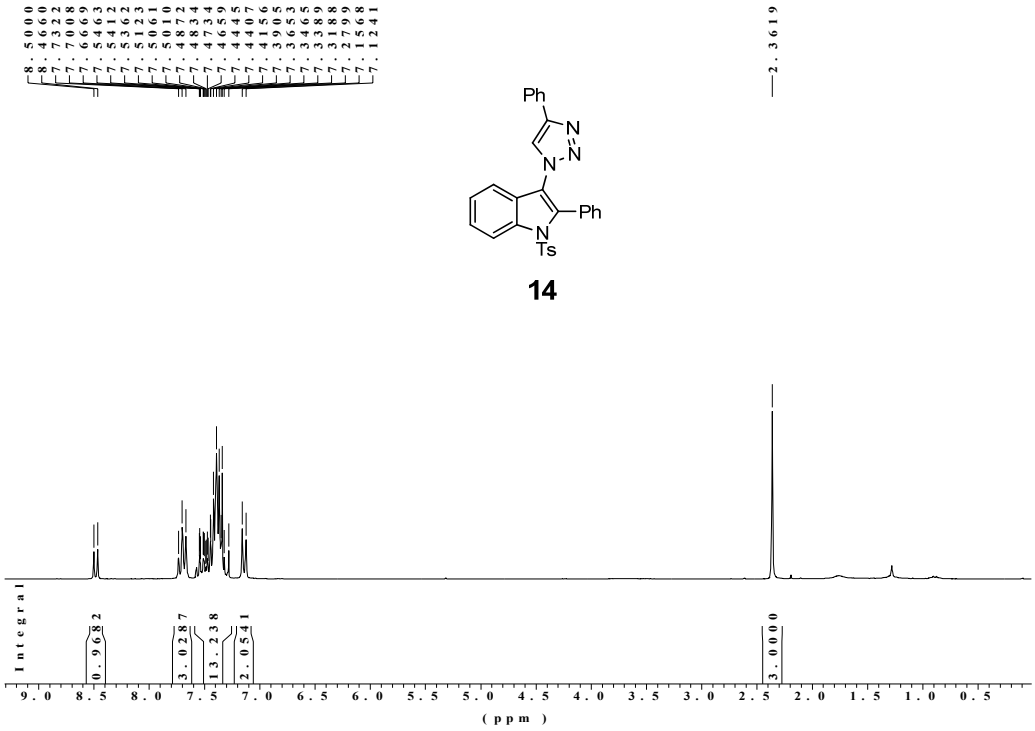
8.3806
7.6581
7.6267
7.5186
7.4885
7.4382
7.4332
7.3817
7.3779
7.3490
7.3214
7.2874
7.2799
7.1191
7.0864
2.3405
N3
Ph
N
Ts
Integral
1.000
1.014
6.189
0.967
2.157
2.234
2.993
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

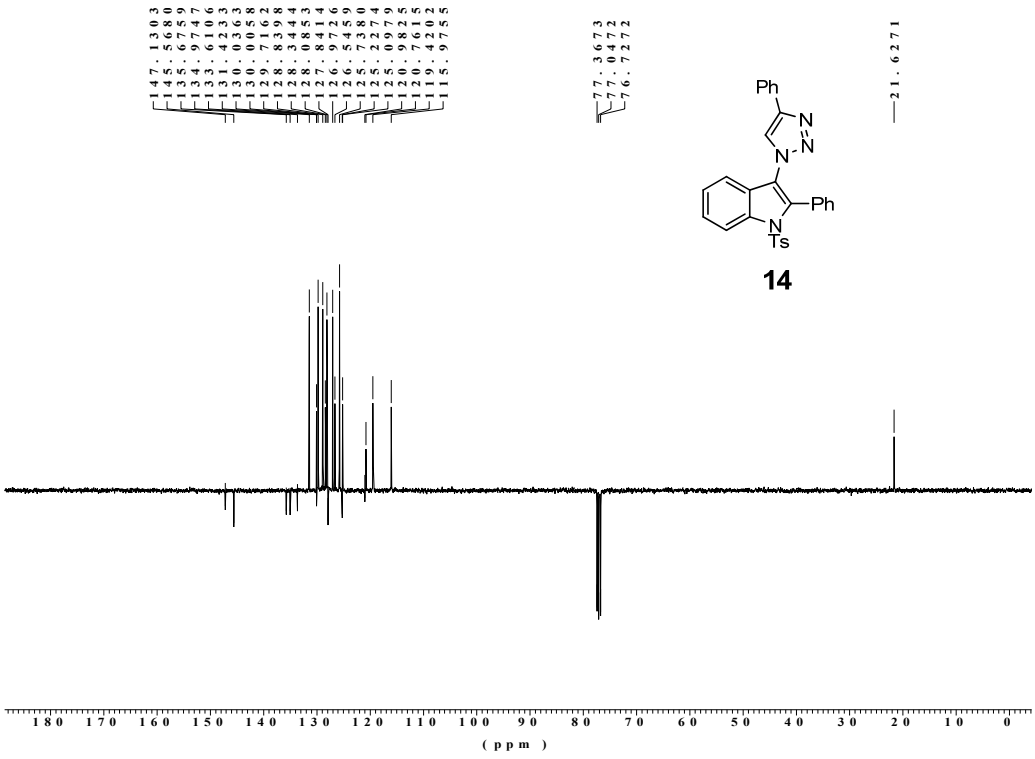
**13**


144.9354
136.3770
134.4184
131.5300
129.3809
129.2285
127.6227
127.5518
126.0417
125.8523
124.5491
121.1273
117.8807
116.9357
77.3749
77.0549
76.7348
21.5890
N3
Ph
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

**13**


8.5000
8.4660
7.7322
7.7008
7.6669
7.5463
7.5412
7.5362
7.5123
7.5061
7.5010
7.4872
7.4834
7.4734
7.4659
7.4445
7.4407
7.4156
7.3905
7.3653
7.3465
7.3389
7.3188
7.2799
7.1568
7.1241
2.3619
Ph
N
N
N
Ph
N
Ts
Integral
0.9682
3.0287
13.238
2.0541
3.0000
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

**14**


147.1303
145.5680
135.6759
134.9747
133.6106
131.4233
130.0363
130.0058
129.7162
128.8398
128.3444
128.0853
127.8814
126.9726
126.5459
125.7380
125.2274
125.0979
120.9825
120.7615
119.4202
115.9755
77.3673
77.0472
76.7272
21.6271
Ph
N
N
N
Ph
N
Ts
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

**14**