Supporting Information

Pd-Catalyzed Three-Component [2+2+1] Cycloamination to Carbazoles

Mingzhu Shen,† Min Li,† Jingxun Yu*

School of College of Chemistry & Materials Science, Northwest University, 1 Xue Fu Avenue, Chang'an Zone, Xi'an 710127, China.

E-mail: yujx@nwu.edu.cn.

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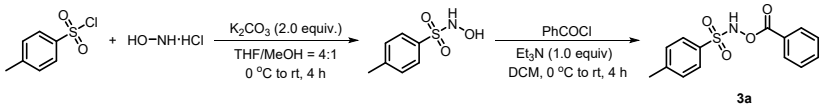
A. General information:

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines or a glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. MeCN, DCE and DMF were dried over CaH_2. Toluene and 1,4-dioxane were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); Visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquiredat on Bruker Ascend 400 (400 MHz) spectrometer. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; q, quartet; m, multiplet; Coupling constants *J* are quoted in Hz. Chemical shifts are reported in delta (δ) units. ^{1}H NMR spectra were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm; DMSO-d_6: 2.50 ppm). Carbon nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer; Chemical shifts are reported in ppm relative to the center line of a triplet at 77.16 ppm for chloroform-*d*. Phosphine nuclear magnetic resonance (^{31}P NMR) data were acquired at 162 MHz on a JEOL Ascend 400 spectrometer. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal cetimeters (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. Hydroxylamines **3a**-**b**,[1] **3c**,[2] **3d**,[1] **3e**[3] and **3f** [4]were prepared according to literature methods.

B. Preparation of substrates:



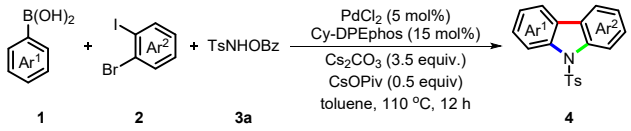
Hydroxylamine hydrochloride (12.0 mmol, 2.0 equiv.) was added to a 100 mL round-bottomed flask under an open environment, and distilled water (5 mL) was added to dissolve it. K_2CO_3 (12.0 mmol, 2.0 equiv.) previously dissolved in distilled water (6 mL) was then added to the above aqueous hydroxylamine hydrochloride solution in batches at 0 °C. After that, THF (12 mL) and MeOH (3 mL) were added, and Tosyl chloride (6.0 mmol, 1.0 equiv.) was added dropwise. The temperature of the system was slowly raised to room temperature with stirring for 4 h. At the end, the mixture was extracted with ethyl acetate three times, and the organic layer was dried with a desiccant (anhydrous $MgSO_4$) to eliminate the water and then concentrated to remove the solvent to provide *N*-tosyl hydroxylamine.

Subsequently, to a solution of *N*-tosyl hydroxylamine (5.0 mmol, 1.0 equiv.) in DCM (25 mL), Et_3N (5.0 mmol, 1.0 equiv.) was added, followed by the gradual dropwise addition of benzoyl chloride (5.0 mmol, 1.0 equiv.) to the system

under the condition of an ice-water bath. The reaction mixture was stirred at room temperature until completion as indicated by TLC (about 4 h). To the reaction mixture was quenched with water, the organic layer was separated and the aqueous layer was extracted with DCM three times, and the combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was then chromatographed on silica gel to afford the product **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.94 (d, J = 7.9 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.41 (s, 3H). Analytical data are in accordance with the literature values.[1]

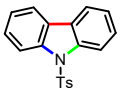
(Note: All secondary hydroxylamine reagents covered in the article were prepared using this method.)

C. General procedures for the [2+2+1] cycloamination to carbazoles:



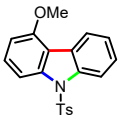
In a glovebox, a 5.0 mL barotolerant vial equipped with a stirring bar was charged with $PdCl_2$ (1.8 mg, 0.01 mmol), Cy-DPEphos (16.9 mg, 0.03 mmol), **1** (0.24 mmol), **2** (0.20 mmol), hydroxylamine **3a** (87.4 mg, 0.30 mmol), Cs_2CO_3 (0.23 g, 0.70 mmol,), CsOPiv (23.4 mg, 0.10 mmol,) and toluene (2.0 mL) was then added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ℃ for 12 h. After the reaction vessel was cooled to room temperature, the crude reaction mixture was filtered with celite and washed with ethyl acetate. The solvent was removed under reduced pressure. Then the residue was chromatographed on silica gel to afford the desired product **4**.

D. Identification of compounds:



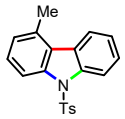
9-Tosyl-9*H*-carbazole (4a)

White solid (PE:EA = 50:1, R_f = 0.32, 48.8 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.57 - 7.41 (m, 2H), 7.36 (t, J = 7.5, 2H), 7.09 (d, J = 8.2 Hz, 2H), 2.25 (s, 3H). Analytical data are in accordance with the literature values.[6]



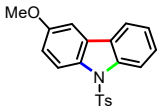
4-Methoxy-9-tosyl-9*H*-carbazole (4b)

White solid (PE:EA = 50:1, R_f = 0.32, 44.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.53 - 7.31 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.01 (s, 3H), 2.24 (s, 3H). Analytical data are in accordance with the literature values.[6]



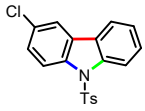
4-Methyl-9-tosyl-9*H*-carbazole (4c)

White solid (PE:EA = 50:1, R_f = 0.32, 45.6 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.53 - 7.46 (m, 1H), 7.42 - 7.34 (m, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.76 (s, 3H), 2.25 (s, 3H). Analytical data are in accordance with the literature values.[7]



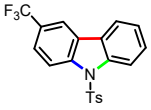
3-Methoxy-9-tosyl-9*H*-carbazole (4d)

White solid (PE:EA = 50:1, R_f = 0.22, 50.6 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.40 - 7.27 (m, 2H), 7.14-6.99 (m, 3H), 3.88 (s, 3H), 2.21 (s, 3H). Analytical data are in accordance with the literature values.[6]



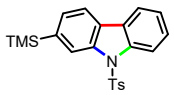
3-Chloro-9-tosyl-9*H*-carbazole (4e)

White solid (PE:EA = 50:1, R_f = 0.31, 49.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.86 - 7.82 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.56 - 7.47 (m, 1H), 7.44 (dd, *J* = 8.9, 2.2 Hz, 1H)), 7.37 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.26 (s, 3H). Analytical data are in accordance with the literature values.[6]



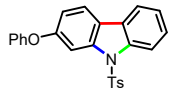
9-Tosyl-3-(trifluoromethyl)-9*H*-carbazole (4f)

White solid (PE:EA = 50:1, R_f = 0.22, 47.5 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.7 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.17 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.80 - 7.65 (m, 3H), 7.62 - 7.50 (m, 1H), 7.47 - 7.36 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H). Analytical data are in accordance with the literature values.[6]



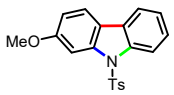
9-Tosyl-2-(trimethylsilyl)-9*H*-carbazole (4g)

Pale yellow oil (PE:EA = 50:1, R_f = 0.30, 64.5 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.52 - 7.47 (m, 2H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.26 (s, 3H), 0.38 (s, 9H). Analytical data are in accordance with the literature values.[7]



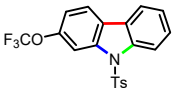
2-phenoxy-9-tosyl-9H-carbazole (4h)

White solid (PE:EA = 50:1, R_f = 0.30, 70.2 mg, 85% yield). Melting point: 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.86 - 7.81 (m, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 8.5 Hz, 1H), 7.42 - 7.33 (m, 3H), 7.18 - 7.03 (m, 6H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.0, 145.1, 139.4, 138.9, 134.9, 129.9, 129.8, 126.9, 126.7, 126.2, 124.2, 123.5, 122.2, 120.9, 119.7, 118.8, 115.9, 115.2, 106.5, 21.6 ppm. IR (KBr): 3054, 1621, 1591, 1487, 1456, 1371, 1174, 990, 720, 543 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{19}NO_3NaS$ $[M+Na]^+$ 436.0978, found 436.0978.



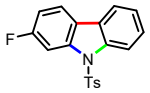
2-Methoxy-9-tosyl-9*H*-carbazole (4i)

White solid (PE:EA = 50:1, R_f = 0.31, 58.3 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.44 - 7.36 (m, 1H), 7.36 - 7.27 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.95 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.95 (s, 3H), 2.25 (s, 3H). Analytical data are in accordance with the literature values.[6]



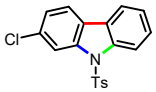
9-Tosyl-2-(trifluoromethoxy)-9*H*-carbazole (4j)

White solid (PE:EA = 50:1, R_f = 0.21, 59.1 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.23 (s, 3H). Analytical data are in accordance with the literature values.[7]



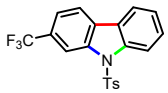
2-Fluoro-9-tosyl-9*H*-carbazole (4k)

White solid (PE:EA = 50:1, R_f = 0.32, 59.0 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.07 (dd, *J* = 10.3, 2.2 Hz, 1H), 7.87 - 7.78 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.51 - 7.43 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.15 - 7.05 (m, 3H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[6]



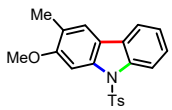
2-Chloro-9-tosyl-9*H*-carbazole (4l)

White solid (PE:EA = 40:1, R_f = 0.29, 57.5 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[6]



9-Tosyl-2-(trifluoromethyl)-9*H*-carbazole (4m)

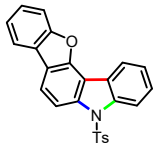
White solid (PE:EA = 50:1, R_f = 0.20, 55.2 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 15.6, 8.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.65 - 7.53 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[7]



2-Methoxy-3-methyl-9-tosyl-9*H*-carbazole (4n)

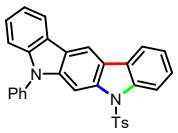
White solid (PE:EA = 50:1, R_f = 0.25, 50.4 mg, 69% yield). Melting point: 153-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.84 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.36 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.01 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 144.8, 138.3, 138.1, 135.0, 129.7, 126.9, 126.5, 125.8, 124.0, 123.9, 121.2, 119.1, 115.2, 97.4, 55.9, 21.5, 16.7 ppm. IR

(KBr): 3056, 2359, 1625, 1463, 1367, 1274, 1168, 1042, 988, 680, 571 cm^{-1}. HRMS (ESI) m/z calculated for $C_{21}H_{19}NO_3NaS$ $[M+Na]^+$ 388.0978, found 388.0980.



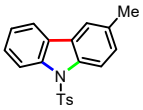
5-Tosyl-5H-benzofuro[3,2-c]carbazole (4o)

White solid (PE:EA = 30:1, R_f = 0.25, 74.8 mg, 91% yield). Melting point: 175-176 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 - 8.30 (m, 3H), 7.95 (dd, *J* = 17.4, 8.1 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.60 - 7.51 (m, 1H), 7.51 -2 7.40 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 150.2, 145.1, 138.4, 138.3, 134.9, 129.7, 127.3, 126.6, 126.5, 124.5, 124.1, 124.1, 123.2, 122.7, 120.4, 120.3, 119.1, 115.2, 112.1, 111.8, 110.3, 21.5 ppm. IR (KBr): 3434, 3059, 2922, 1646, 1420, 1371, 1174, 1065, 811, 657, 573 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{17}NO_3NaS$ $[M+Na]^+$ 434.0821, found 434.0817.



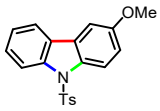
5-phenyl-7-tosyl-5,7-dihydroindolo[2,3-b]carbazole (4p)

White solid (PE:EA = 30:1, R_f = 0.30, 81.7 mg, 84% yield). Melting point: 181-182 ℃. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.46 - 8.34 (m, 2H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.77 - 7.64 (m, 6H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 - 7.32 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 142.0, 141.4, 139.0, 138.0, 137.5, 134.8, 130.2, 129.5, 127.9, 127.3, 127.1, 126.5, 126.3, 126.1, 124.1, 123.1, 121.3, 120.9, 120.3, 120.2, 119.4, 115.4, 111.0, 109.8, 96.2, 21.4 ppm. IR (KBr): 3059, 1633, 1597, 1448, 1368, 1172, 765, 663, 571 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{23}N_2O_2S$ $[M+H]^+$ 487.1475, found 487.1475.



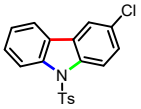
3-Methyl-9-tosyl-9*H*-carbazole (4aa)

White solid (PE:EA = 50:1, R_f = 0.32, 51.6 mg, 77% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.71 - 7.66 (m, 3H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.37 - 7.28 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.20 (s, 3H). Analytical data are in accordance with the literature values.[6]



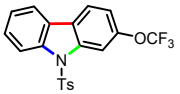
3-Methoxy-9-tosyl-9*H*-carbazole (4ab)

White solid (PE:EA = 50:1, R_f = 0.22, 58.3 mg, 83% yield). HNMR data was identicial with **4d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.40-7.27 (m, 2H), 7.14-6.99 (m, 3H), 3.88 (s, 3H), 2.21 (s, 3H). Analytical data are in accordance with the literature values.[6]



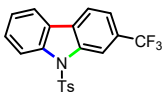
3-Chloro-9-tosyl-9*H*-carbazole (4ac)

White solid (PE:EA = 50:1, R_f = 0.31, 63.2 mg, 89% yield). HNMR data was identicial with **4e**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.86 - 7.82 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.56 - 7.47 (m, 1H), 7.44 (dd, *J* = 8.9, 2.2 Hz, 1H)), 7.37 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.26 (s, 3H). Analytical data are in accordance with the literature values.[6]



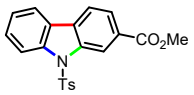
9-Tosyl-2-(trifluoromethoxy)-9*H*-carbazole (4ad)

White solid (PE:EA = 50:1, R_f = 0.21, 58.3 mg, 72% yield). HNMR data was identicial with **4j.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.23 (s, 3H). Analytical data are in accordance with the literature values.[7]



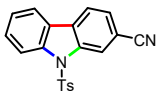
9-Tosyl-2-(trifluoromethyl)-9*H*-carbazole (4ae)

White solid (PE:EA = 50:1, R_f = 0.20, 62.3 mg, 80% yield). HNMR data was identicial with **4m.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 15.6, 8.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.65 - 7.53 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[7]



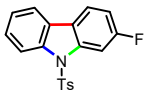
Methyl 9-tosyl-9*H*-carbazole-2-carboxylate (4af)

White solid (PE:EA = 30:1, R_f = 0.20, 63.7 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.01 (s, 3H), 2.25 (s, 3H). Analytical data are in accordance with the literature values.[7]



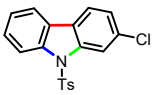
9-Tosyl-9*H*-carbazole-2-carbonitrile (4ag)

White solid (PE:EA = 30:1, R_f = 0.22, 50.5 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.00 - 7.91 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.64 -7.55 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H) ppm. Analytical data are in accordance with the literature values.[7]



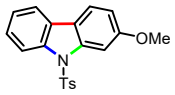
2-Fluoro-9-tosyl-9*H*-carbazole (4ah)

White solid (PE:EA = 50:1, R_f = 0.32, 61.0 mg, 90% yield). HNMR data was identicial with **4k**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.07 (dd, *J* = 10.3, 2.2 Hz, 1H), 7.87 - 7.78 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.51 - 7.43 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.15 - 7.05 (m, 3H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[6]



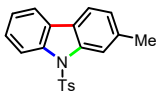
2-Chloro-9-tosyl-9*H*-carbazole (4ai)

White solid (PE:EA = 40:1, R_f = 0.29, 66.7 mg, 94% yield). HNMR data was identicial with **4l**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.40 - 7.30 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). Analytical data are in accordance with the literature values.[6]



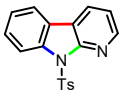
2-Methoxy-9-tosyl-9*H*-carbazole (4aj)

White solid (PE:EA = 50:1, R_f = 0.31, 62.5 mg, 89% yield). HNMR data was identicial with **4i**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.44 - 7.36 (m, 1H), 7.36 - 7.27 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.95 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.95 (s, 3H), 2.25 (s, 3H). Analytical data are in accordance with the literature values.[6]



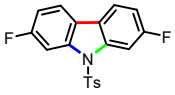
2-methyl-9-tosyl-9H-carbazole (4ak)

White solid (PE:EA = 50:1, R_f = 0.35, 58.3 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.19 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 15.4, 8.1 Hz, 3H), 7.50 - 7.42 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.58 (s, 3H), 2.21 (s, 3H). Analytical data are in accordance with the literature values.[5]



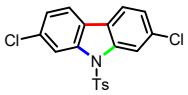
9-tosyl-9H-pyrido[2,3-b]indole (4al)

White solid (PE:EA = 20:1, R_f = 0.20, 46.4 mg, 72% yield). Melting point: 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.61 - 7.52 (m, 1H), 7.44 - 7.35 (m, 1H), 7.28 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.0, 145.0, 137.8, 136.0, 129.6, 128.4, 128.3, 127.6, 123.9, 122.9, 120.7, 119.1, 118.8, 115.1, 21.6 ppm. IR (KBr): 3059, 1590, 1447, 1394, 1253, 1176, 971, 775, 665, 578 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{15}N_2O_2S$ $[M+H]^+$ 323.0849, found 323.0853.



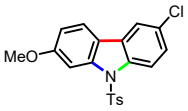
2,7-Difluoro-9-tosyl-9*H*-carbazole (4ba)

White solid (PE:EA = 50:1, R_f = 0.47, 58.6 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 10.2, 2.3 Hz, 2H), 7.80 - 7.69 (m, 4H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09 (td, *J* = 8.7, 2.3 Hz, 2H), 2.30 (s, 3H). Analytical data are in accordance with the literature values.[7]



2,7-Dichloro-9-tosyl-9*H*-carbazole (4bb)

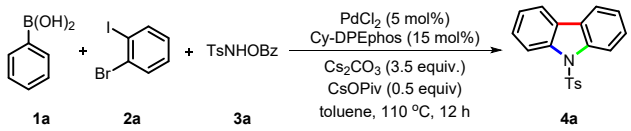
Pale yellow solid (PE:EA = 50:1, R_f = 0.45, 50.6 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.74 (dd, *J* = 16.0, 8.1 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 2.31 (s, 3H). Analytical data are in accordance with the literature values.[7]



6-Chloro-2-methoxy-9-tosyl-9*H*-carbazole (4bc)

Pale yellow solid (PE:EA = 10:1, R_f = 0.25, 62.4 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.71 - 7.65 (m, 4H), 7.37 - 7.30 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.98 - 6.91 (m, 1H), 3.95 (s, 3H), 2.26 (s, 3H). Analytical data are in accordance with the literature values.[7]

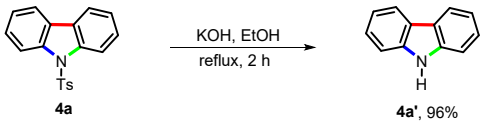
E. Gram-scale reaction:



A 150 mL barotolerant vial equipped with a stirring bar was charged with Phenylboronic acid **1a** (0.73 g, 6 mmol), 1-Bromo-2-iodobenzene **2a** (1.41 g, 5 mmol), hydroxylamine **3a** (2.18 g, 7.5 mmol), $PdCl_2$ (44.3 mg, 0.25 mmol), Cy-DPEphos (0.42 g, 0.75 mmol), Cs_2CO_3 (5.70 g, 17.5 mmol), CsOPiv (0.59 g, 2.5 mmol) and toluene (50 mL) was then added. Then the vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ºC for 12 h. After the reaction vessel was cooled to room temperature, the crude reaction mixture was filtered with celite and washed three times with ethyl acetate. The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the desired product **4a** (PE:EA = 100:1, 1.17g, 73% yield).

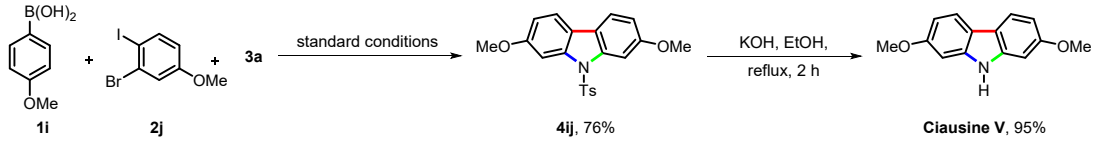
F. Synthetic application:

i) Procedure 4a for removal of tosyl group



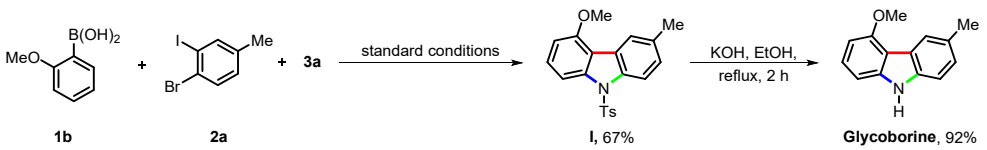
In a glovebox, a 25.0 mL barotolerant vial equipped with a stirring bar was charged with **4a** (0.32 g, 1.0 mmol, 1.0 equiv.), KOH (0.56 g, 10.0 mmol, 10.0 equiv.) and EtOH (5.0 mL). The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 80 ℃ for 2 h. After the reaction vessel was cooled to room temperature, the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford **4a'** (PE:EA = 4:1, white solid, 0.16 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 8.06 (s, 1H), 7.46 (d, J = 4.1 Hz, 4H), 7.32 - 7.23 (m, 2H). Analytical data are in accordance with the literature values.[6]

ii) Synthesis of Clausine V and Glycoborine:



1) In a glovebox, a 25.0 mL barotolerant vial equipped with a stirring bar was charged with $PdCl_2$ (8.9 mg, 0.05 mmol), Cy-DPEphos (84.4 mg, 0.15 mmol), **1i** (0.18 g, 1.2 mmol), **2j** (0.31 g, 1.0 mmol), hydroxylamine **3a** (0.44 g, 1.5 mmol), Cs_2CO_3 (1.14 g, 3.5 mmol), CsOPiv (0.12 g, 0.5 mmol) and toluene (10 mL) was then added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ℃ for 12 h. After the reaction vessel was cooled to room temperature, the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the desired product **4ij** (PE:EA = 90:1, white solid, 0.29 g, 76% yield). Melting point: 140-141 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.3 Hz, 2H), 7.66 (dd, J = 19.7, 8.5 Hz, 4H), 7.11 (d, J = 8.1 Hz, 2H), 6.91 (dd, J = 8.5, 2.3 Hz, 2H), 3.93 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 145.0, 139.8, 135.1, 129.8, 126.6, 120.1, 119.8, 112.0, 100.4, 56.0, 21.6 ppm. IR (KBr): 1606, 1475, 1368, 1280, 1161, 1045, 807, 671, 589 cm^{-1}. HRMS (ESI) m/z calculated for $C_{21}H_{19}NO_4NaS$ $[M+Na]^+$ 404.0927, found 404.0925.

2) In a glovebox, a 25.0 mL vial equipped with a stirring bar was charged with **4ij** (0.29 g, 0.8 mmol, 1.0 equiv.), KOH (0.45 g, 8.0 mmol) and EtOH (4.0 mL). The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 80 ℃ for 2 h. After the reaction vessel was cooled to room temperature, the solvent was removed under reduced pressure. Then the residue was chromatographed on silica gel to afford **Clausine V** (White solid, 0.17 g, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 2.2 Hz, 2H), 6.72 (dd, J = 8.5, 2.2 Hz, 2H), 3.81 (s, 6H). Analytical data are in accordance with the literature.[6]

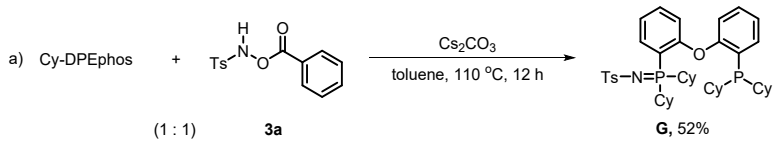


1) In a glovebox, a 25.0 mL vial equipped with a stirring bar was charged with $PdCl_2$ (8.9 mg, 0.05 mmol), Cy-DPEphos (84.4 mg, 0.15 mmol), **1b** (0.18 g, 1.2 mmol), **2a** (0.30 g, 1.0 mmol), hydroxylamine **3a** (0.44 g, 1.5 mmol),

Cs_2CO_3 (1.14 g, 3.5 mmol), CsOPiv (0.12 g, 0.5 mmol) and toluene (10 mL) was then added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ℃ for 12 h. After the reaction vessel was cooled to room temperature, the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the desired product **I** (PE:EA = 100:1, white solid, 0.24 g, 67% yield). Melting point: 139-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.01 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 8.3 Hz, 1H), 7.26 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.01 (s, 3H), 2.48 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 144.8, 140.1, 135.9, 135.1, 133.7, 129.7, 128.0, 127.7, 126.6, 126.0, 123.4, 115.7, 114.3, 107.9, 105.1, 55.6, 21.6, 21.5 ppm. IR (KBr): 1590, 1448, 1367, 1275, 1177, 1102, 810, 677, 576 cm^{-1}. HRMS (ESI) m/z calculated for $C_{21}H_{20}NO_3S$ $[M+H]^+$366.1158, found 366.1156.

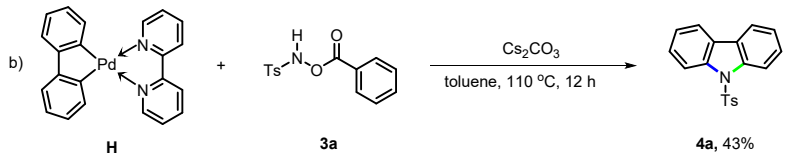
2) In a glovebox, a 25.0 mL vial equipped with a stirring bar was charged with **I** (0.24 g, 0.7 mmol), KOH (0.40 g, 7.0 mmol) and EtOH (3.5 mL). The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 80 ℃ for 2 h. After the reaction vessel was cooled to room temperature, the solvent was removed under reduced pressure. Then the residue was chromatographed on silica gel to afford **Glycoborine** (White solid 0.14 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.92 (s, 1H), 7.36 - 7.27 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.09 (s, 3H), 2.54 (s, 3H). Analytical data are in accordance with the literature values.[7]

G. Mechanistic investigation:



In a glovebox, a 15 mL barotolerant vial equipped with a stirring bar was charged with **3a** (58.2 mg, 0.2 mmol), Cy-DPEphos (112.6 mg, 0.2 mmol), Cs_2CO_3 (97.7 mg, 0.3 mmol) and toluene (2.0 mL) was then added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ℃ for 12 h. After the reaction vessel was cooled to room temperature, the crude reaction mixture was filtered with celite and washed three times with ethyl acetate. The solvent was removed under reduced pressure. Then the residue was chromatographed on silica gel to afford **G** (White solid, 76.1 mg, 52% yield). Melting point: 93-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 13.3, 7.9 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.21 (dt, *J* = 15.8, 8.0 Hz, 4H), 6.90 (dd, *J* = 8.2, 4.0 Hz, 1H), 6.75 (dd, *J* = 8.2, 5.6 Hz, 1H), 2.92 (d, *J* = 185.0 Hz, 2H), 2.40 (s, 3H), 2.21 – 0.69 (m, 42H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.3, 157.9, 157.9, 144.7, 144.6, 140.3, 137.5, 137.5, 133.5, 133.5, 130.4, 128.8, 127.9, 127.7, 125.7, 124.3, 123.3, 123.2, 118.5, 118.5, 116.9, 116.8, 116.5, 115.6, 36.0, 34.0, 33.3, 30.5,

29.7, 28.9, 27.0, 26.4, 25.7, 21.4 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.15, 37.46. IR (KBr): 2921, 2849, 1461, 1430, 1136, 1087, 731, 676, 558 cm^{-1}. HRMS (ESI) m/z calculated for $C_{43}H_{59}NO_3P_2NaS$ $[M+Na]^+$ 754.3583, found 754.3584.



H **3a** **4a**, 43%

In a glovebox, a 15 mL barotolerant vial equipped with a stirring bar was charged with **H** (83.0 mg, 0.2 mmol),[8-9] **3a** (87.3 mg, 0.3 mmol), Cs_2CO_3 (97.7 mg, 0.3 mmol) and toluene (2.0 mL) was then added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 110 ℃ for 12 h. After the reaction vessel was cooled to room temperature, the crude reaction mixture was filtered with celite and washed three times with ethyl acetate. The solvent was removed under reduced pressure. Then the residue was chromatographed on silica gel to afford **4a** (27.6 mg, 43% yield).

H. References:

[1] G. Kirby, L. Grimaud, M. R. Vitale, G. Prestat and F. Berhal, *Green Chem.*, 2021, **23**, 9428-9432.

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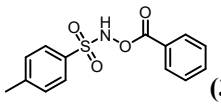
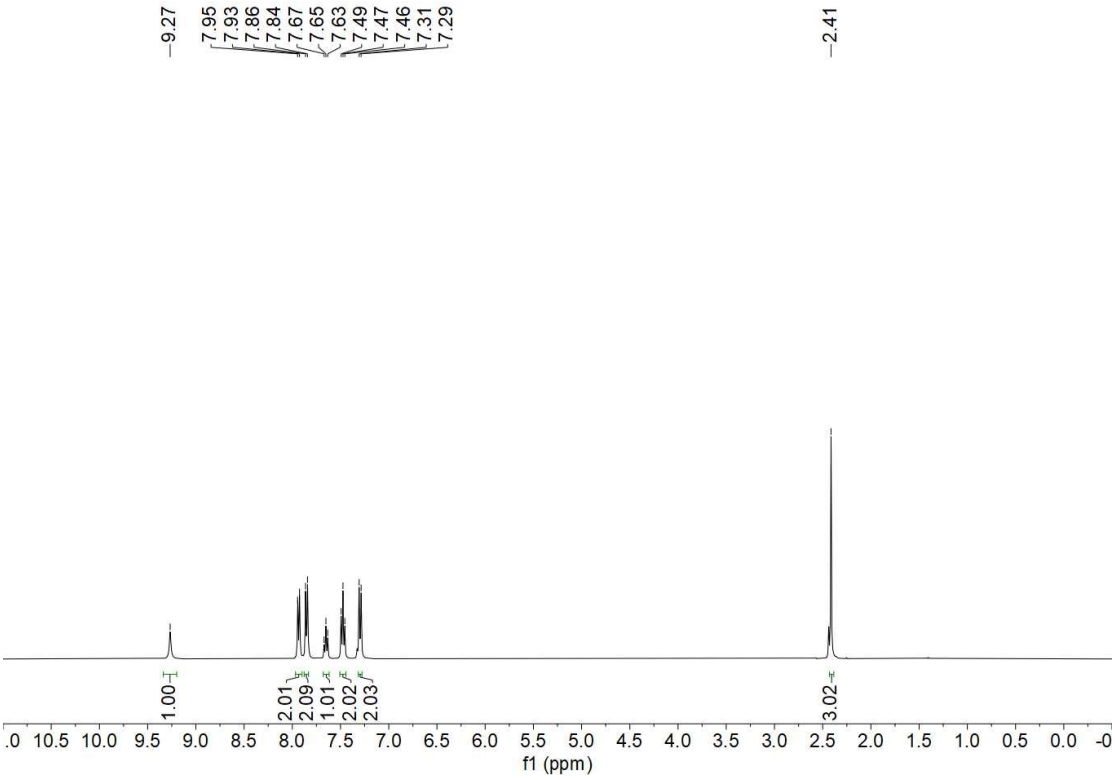
[9] A. Lu, X. Ji, B. Zhou, Z. Wu and Y. Zhang. *Angew. Chem. Int. Ed.*, 2018, **57** 3233-3237.

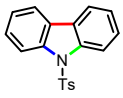
I. NMR spectra:



(3a)

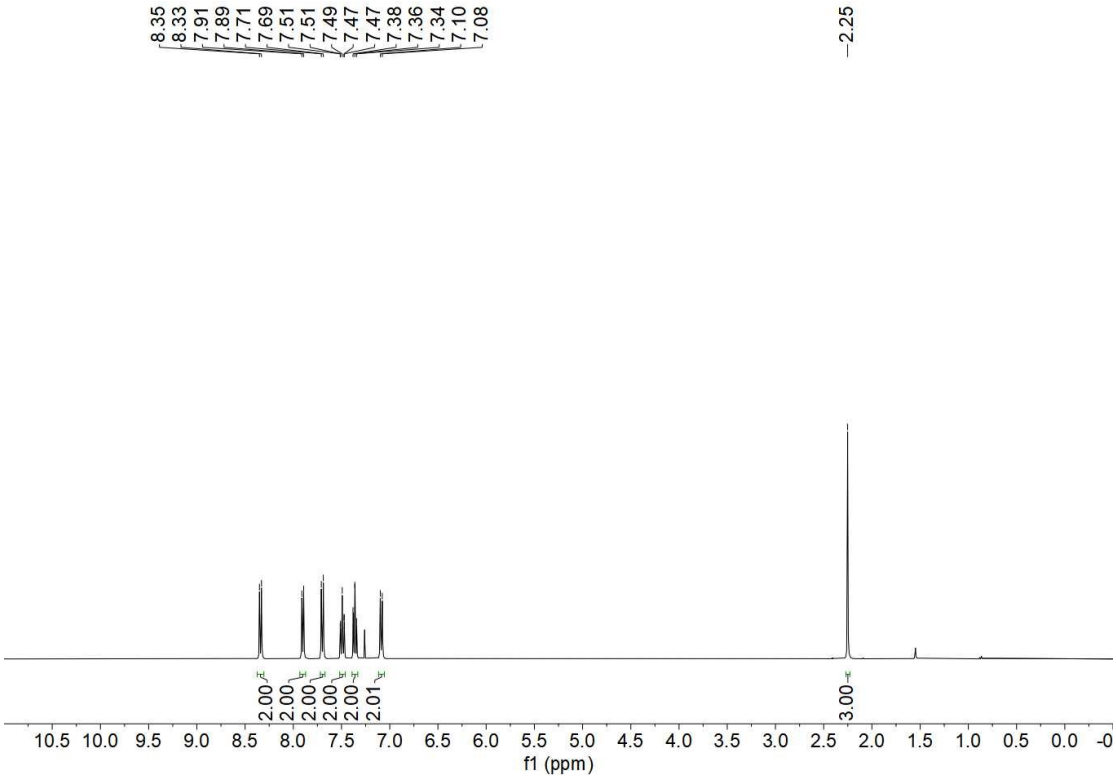
^{1}H NMR (400 MHz, Chloroform-*d*)

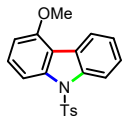




(4a)

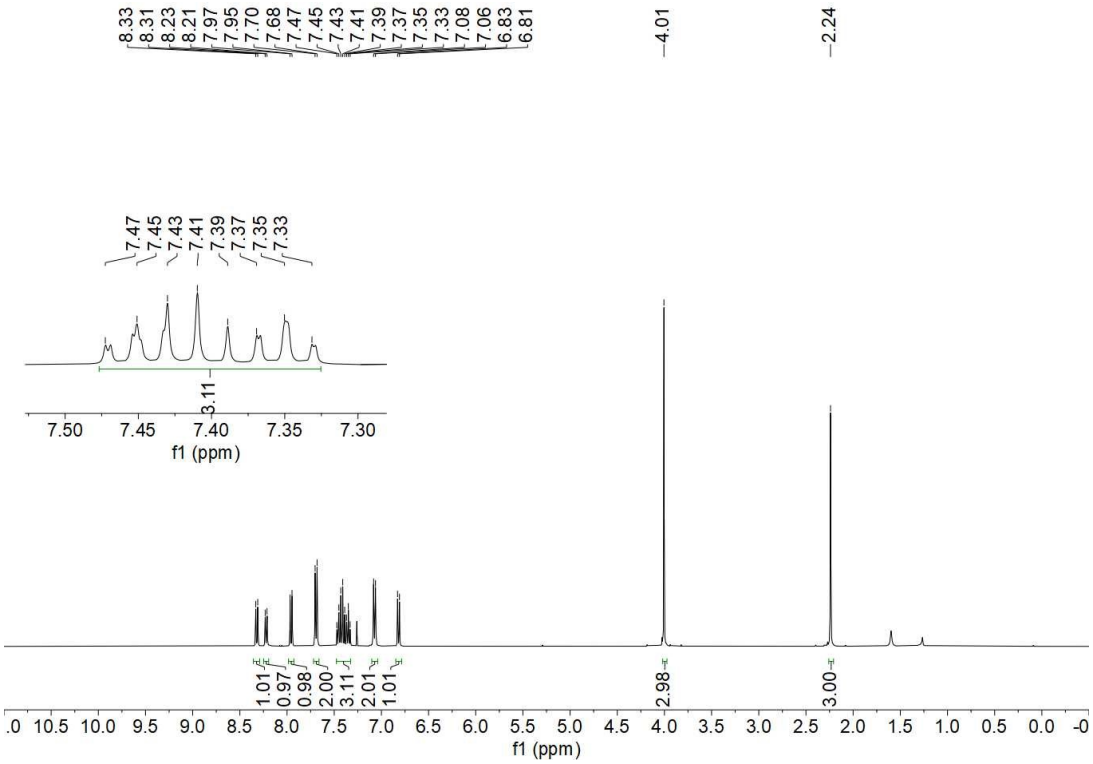
^{1}H NMR (400 MHz, Chloroform-*d*)

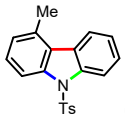




(4b)

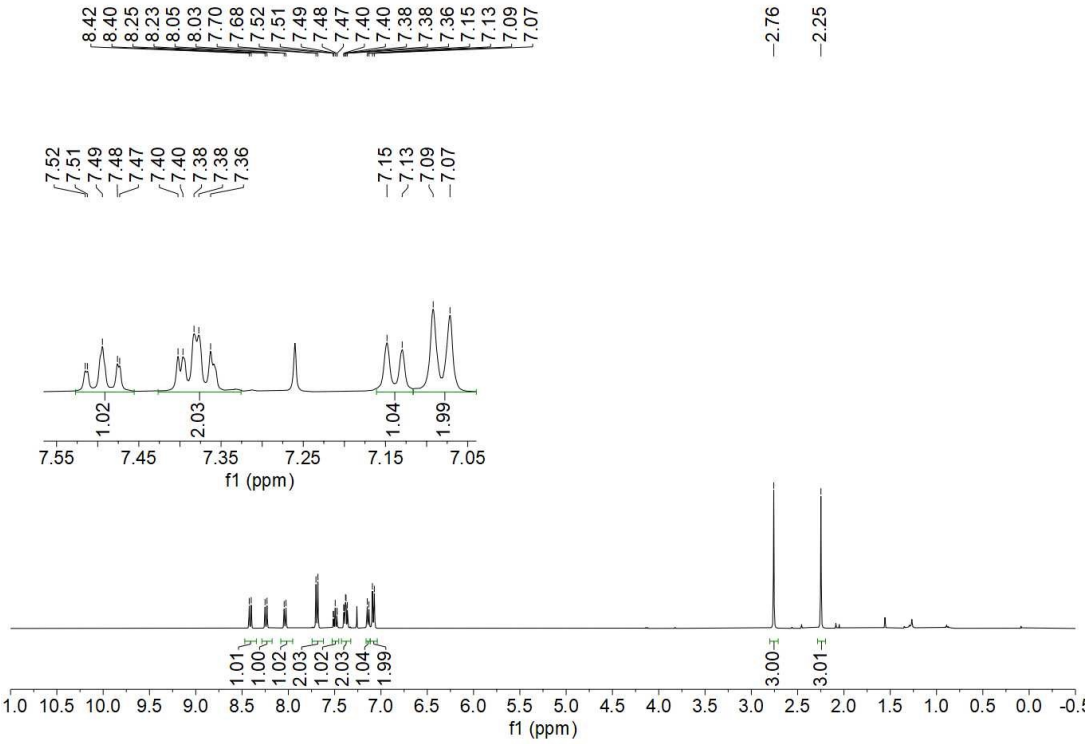
^{1}H NMR (400 MHz, Chloroform-*d*)

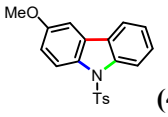




(4c)

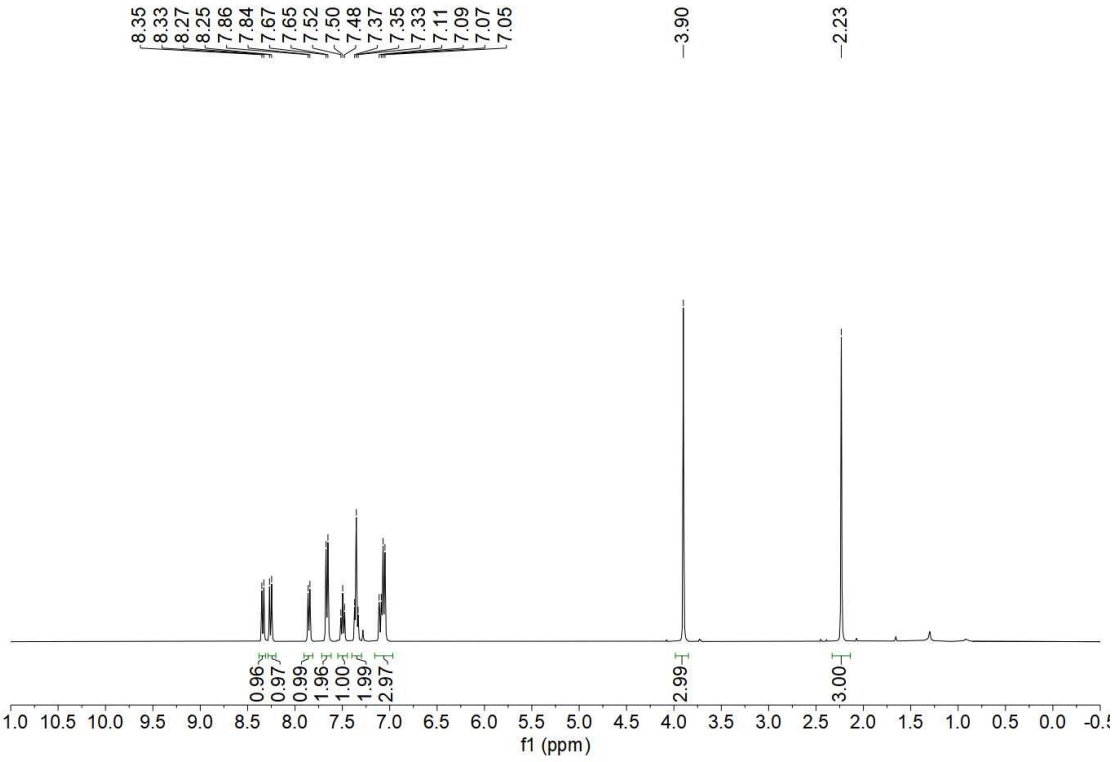
^{1}H NMR (400 MHz, Chloroform-*d*)

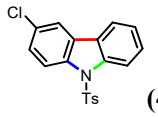




(4d)

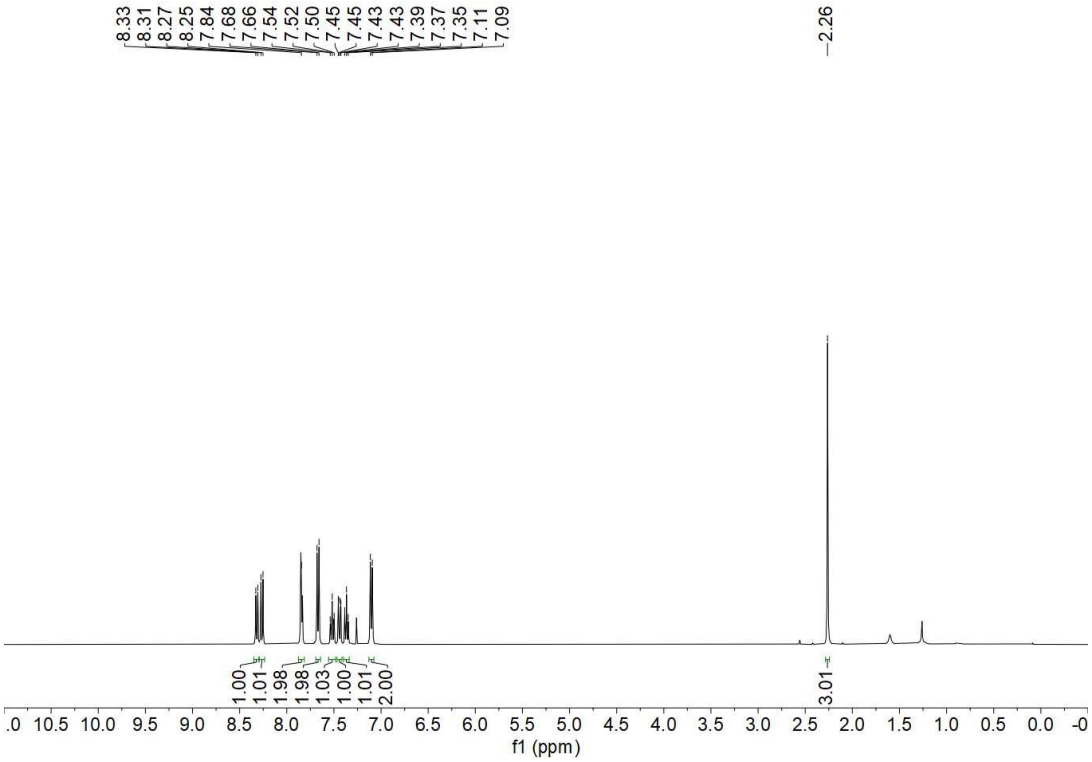
^{1}H NMR (400 MHz, Chloroform-*d*)

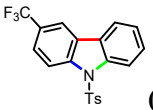




(4e)

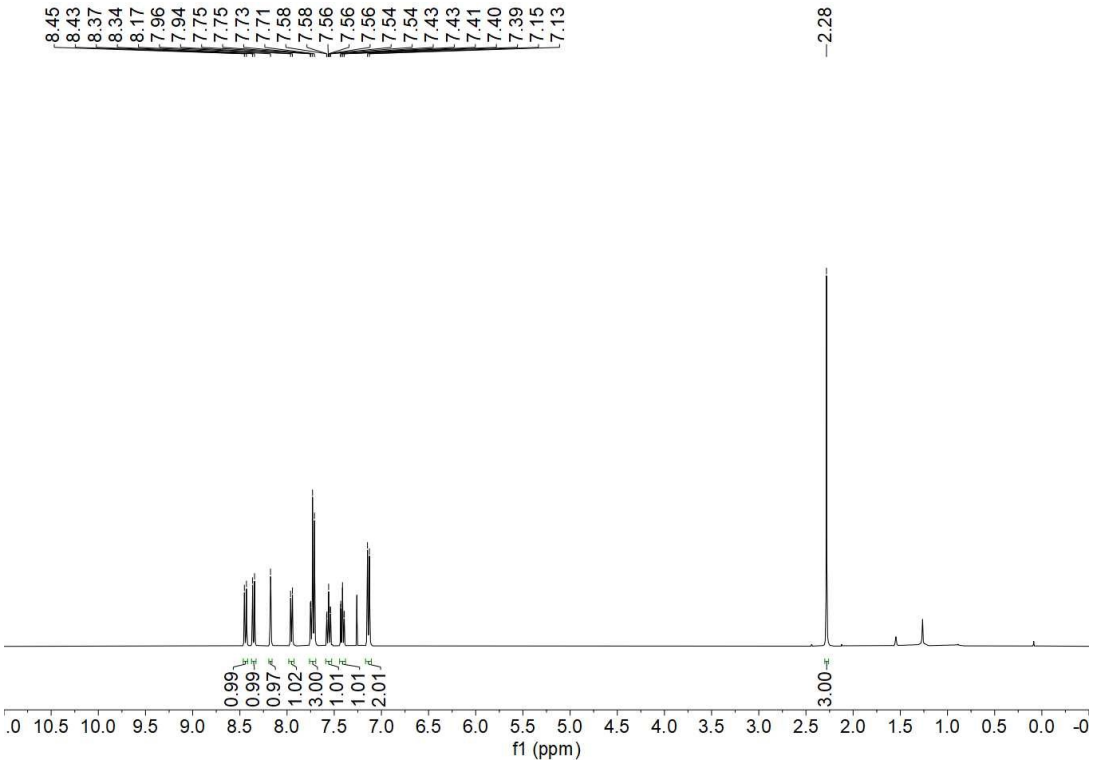
^{1}H NMR (400 MHz, Chloroform-*d*)

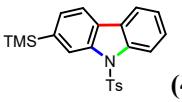




(4f)

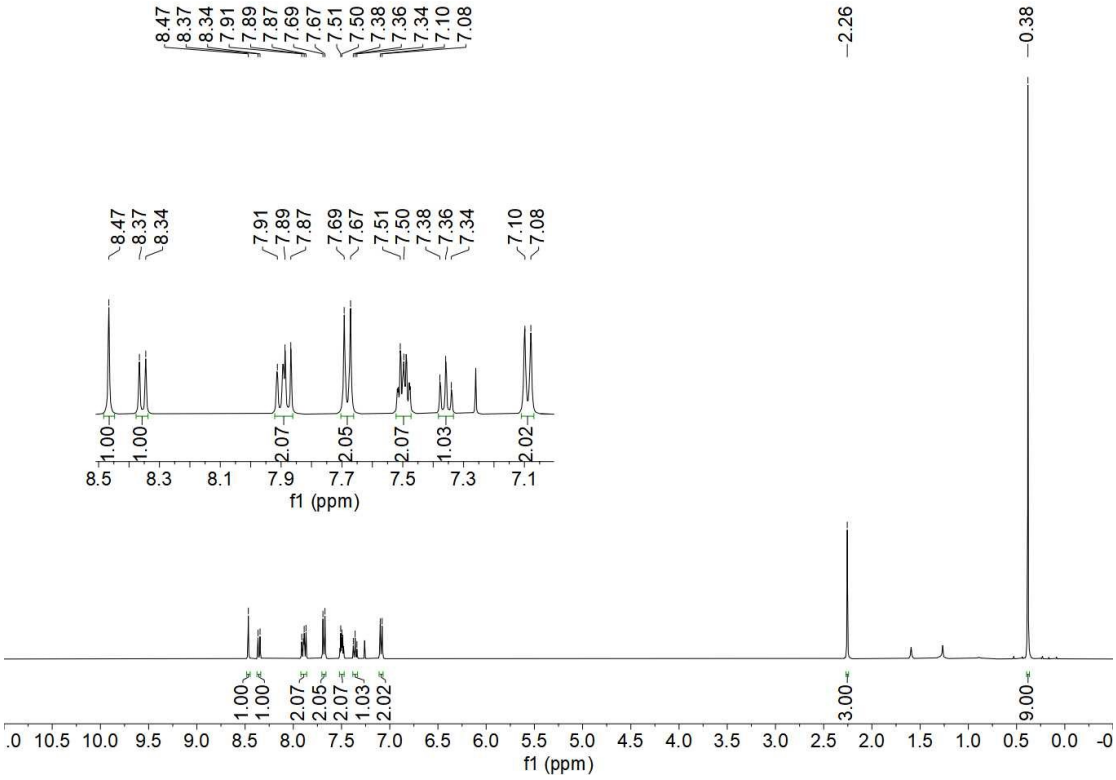
^{1}H NMR (400 MHz, Chloroform-*d*)

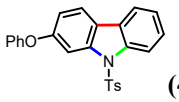




(4g)

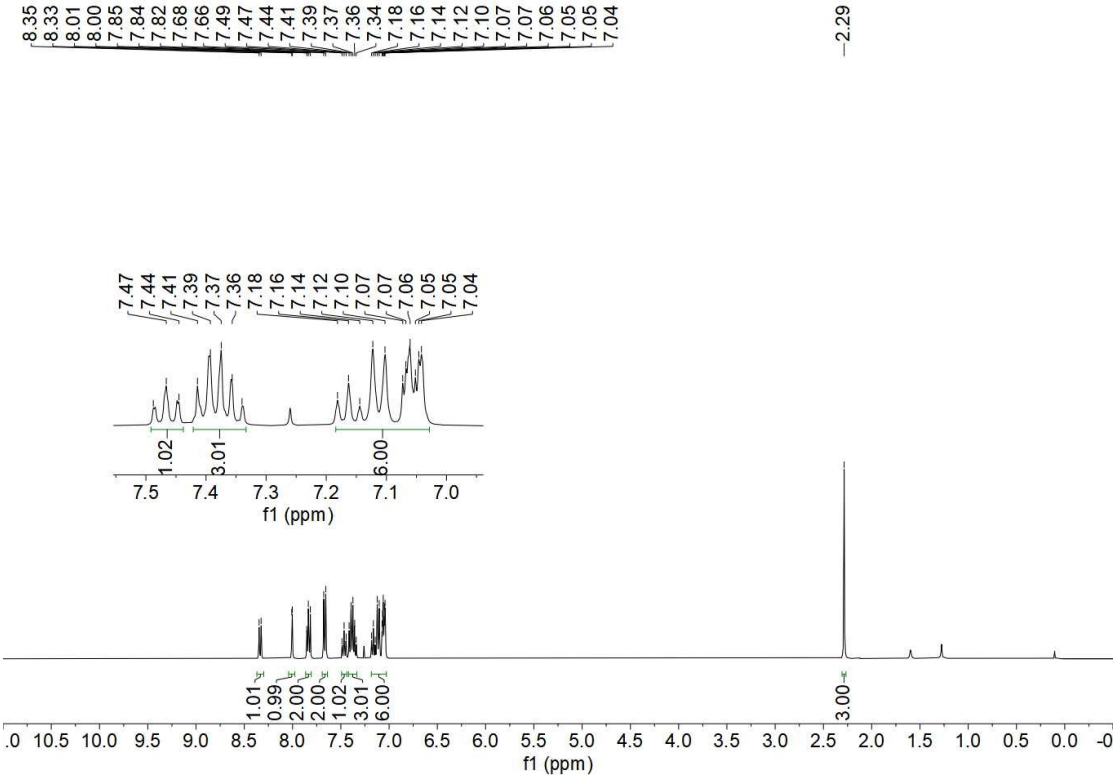
^{1}H NMR (400 MHz, Chloroform-*d*)



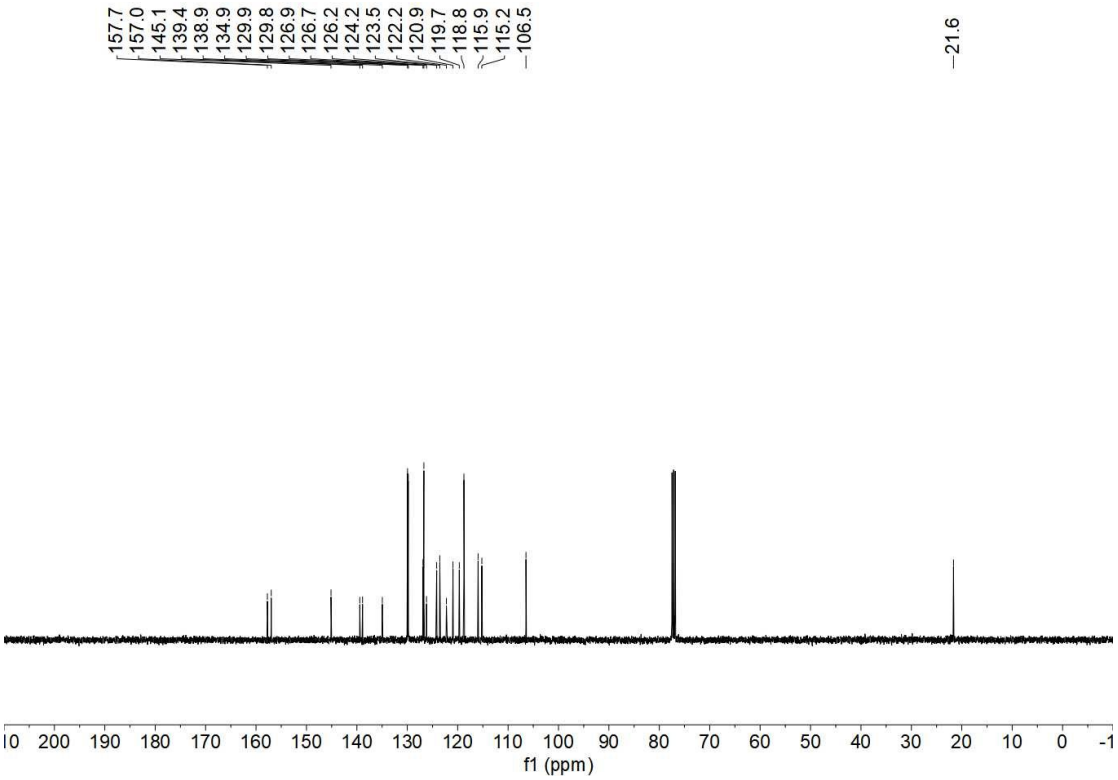


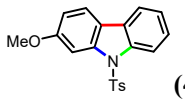
(4h)

^{1}H NMR (400 MHz, Chloroform-*d*)



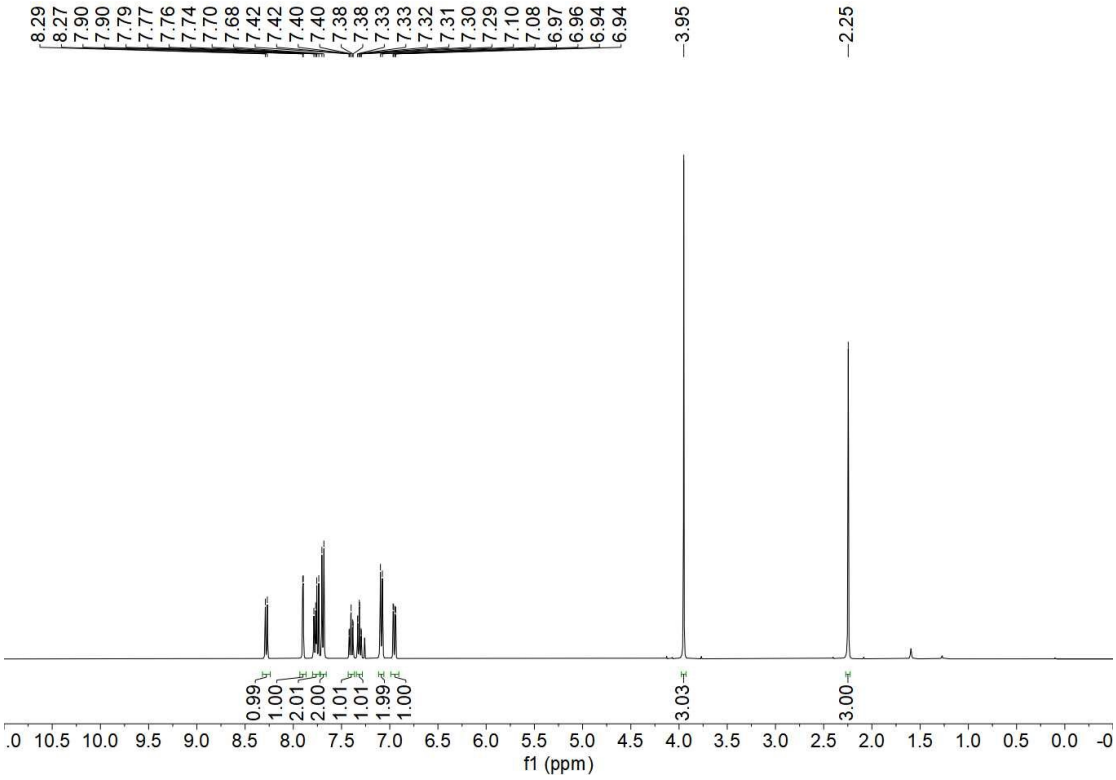
^{13}C NMR (100 MHz, Chloroform-*d*)

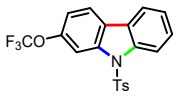




(4i)

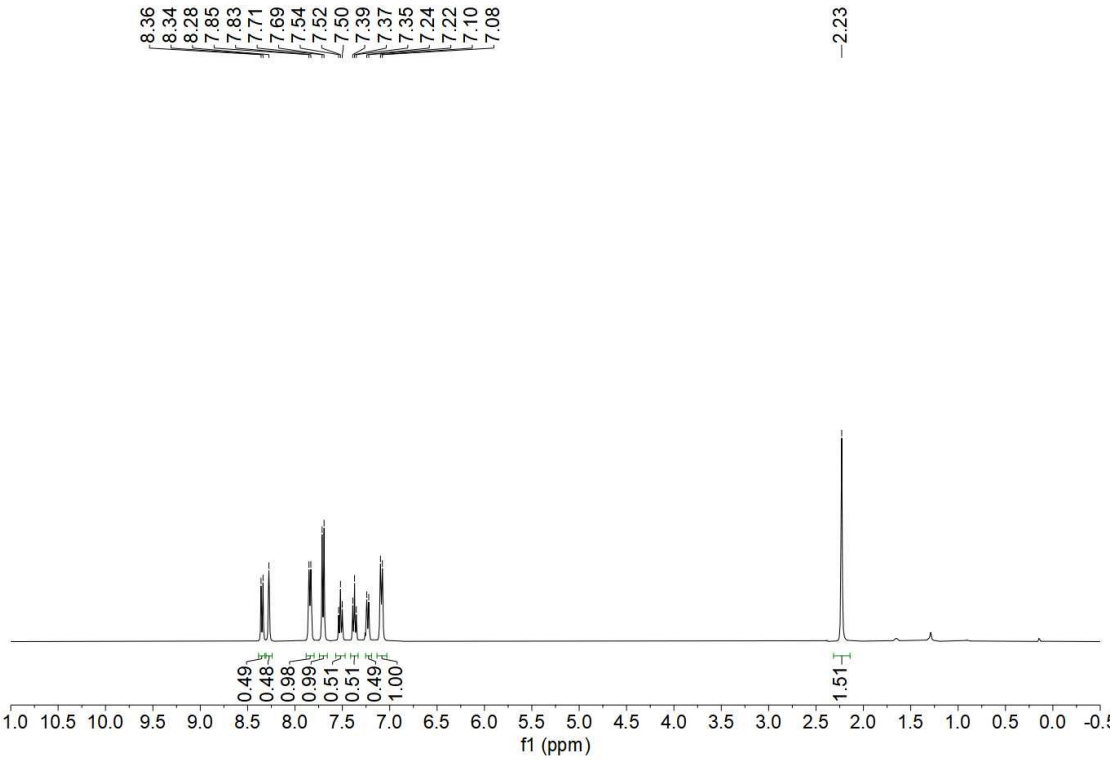
^{1}H NMR (400 MHz, Chloroform-*d*)

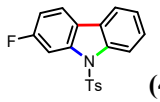




(4j)

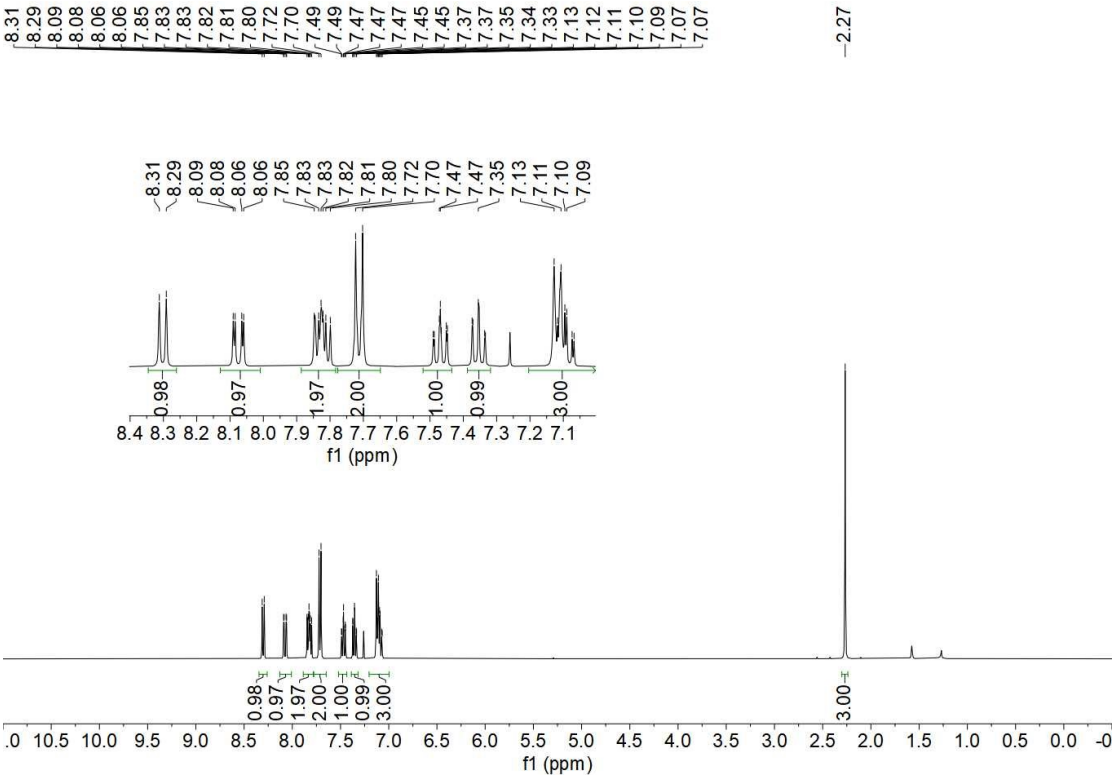
^{1}H NMR (400 MHz, Chloroform-*d*)

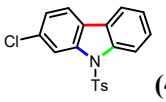




(4k)

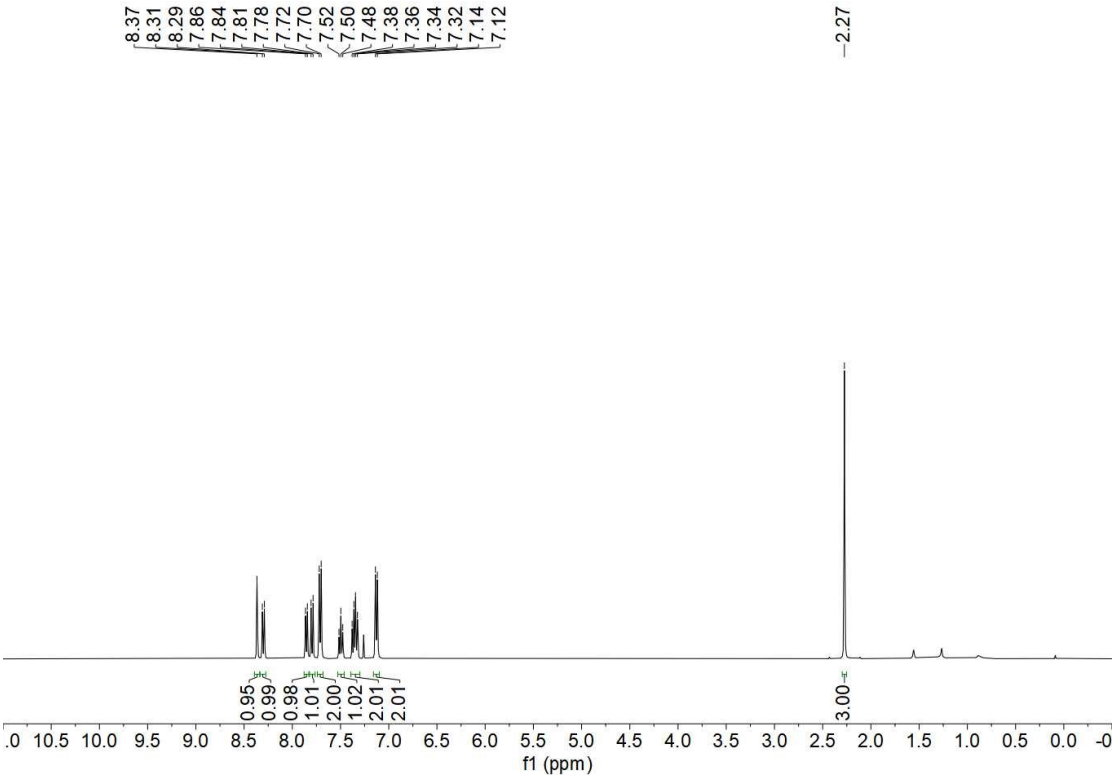
^{1}H NMR (400 MHz, Chloroform-*d*)

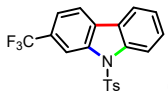




(4l)

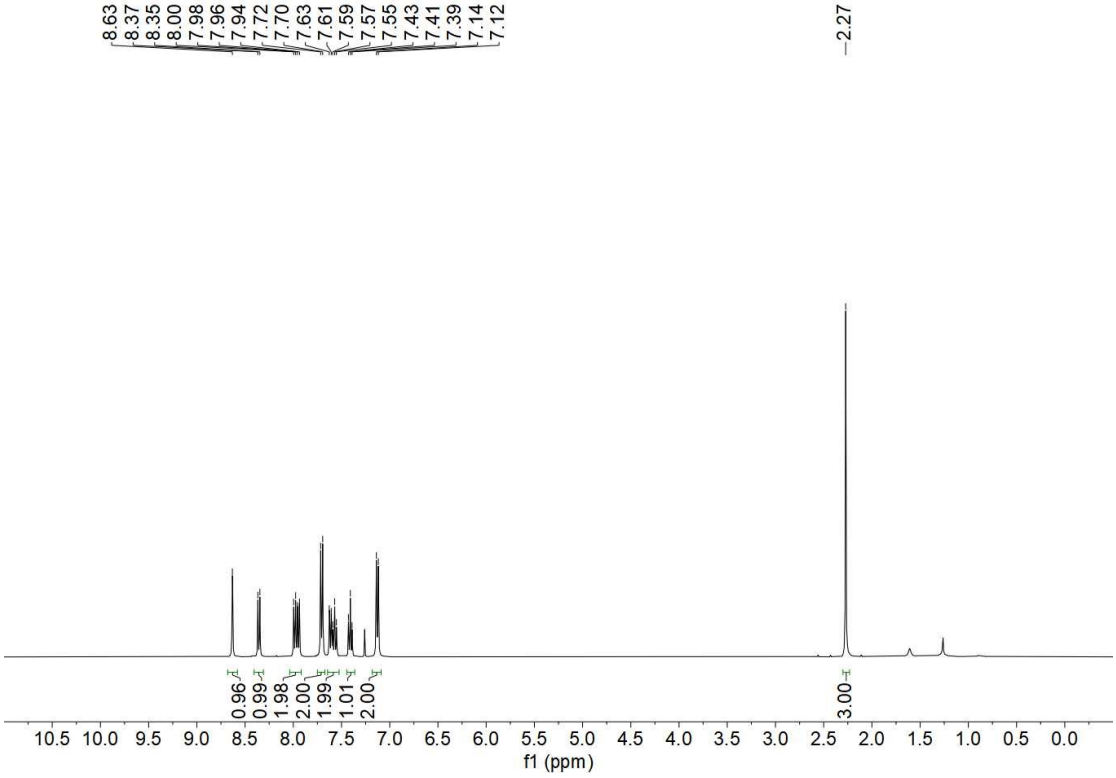
^{1}H NMR (400 MHz, Chloroform-*d*)

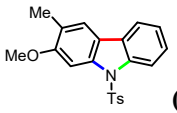




(4m)

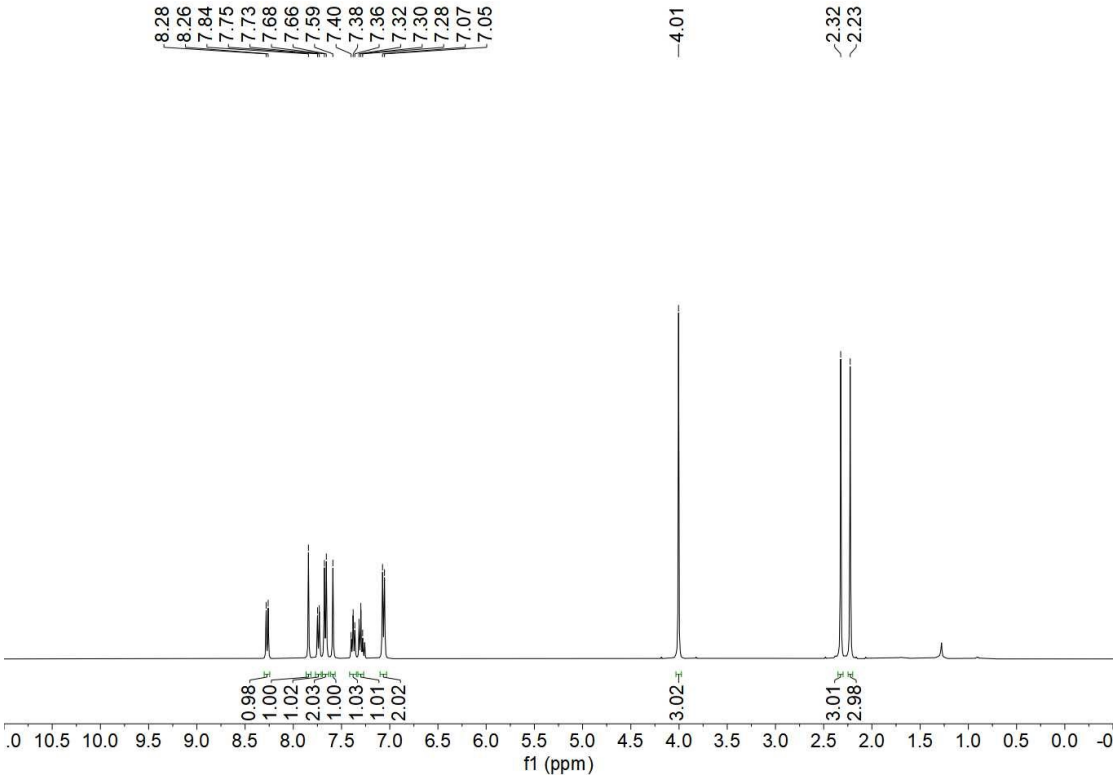
^{1}H NMR (400 MHz, Chloroform-*d*)



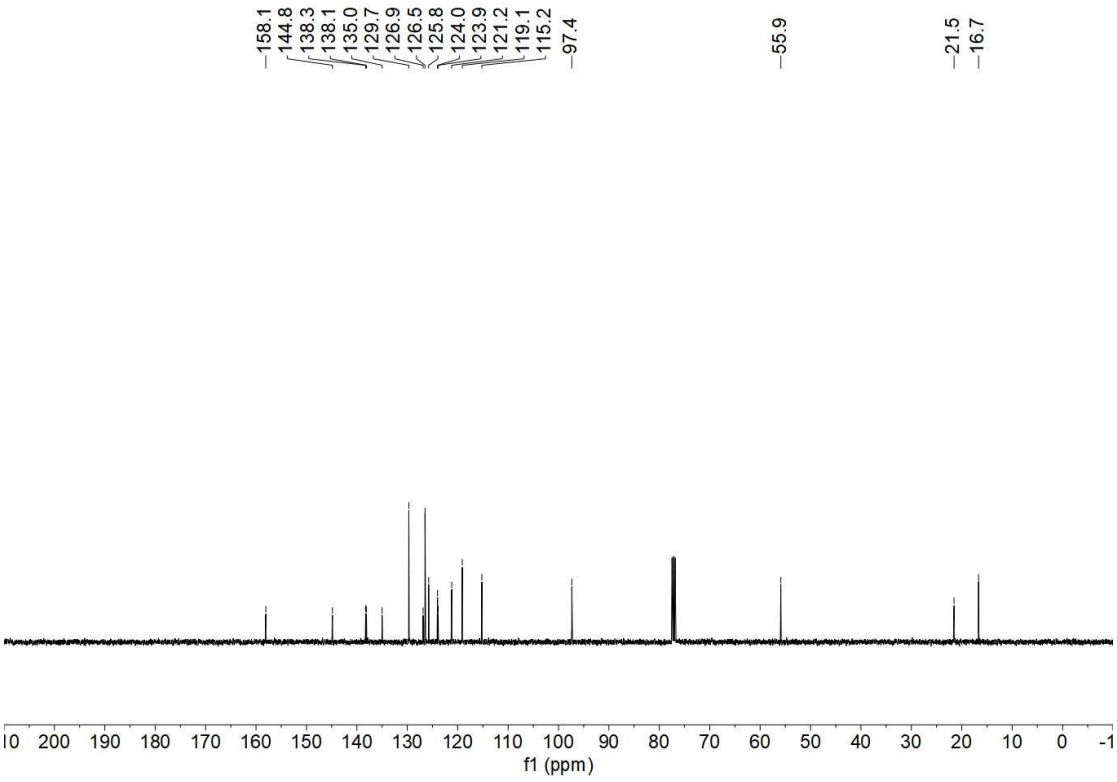


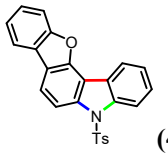
(4n)

^{1}H NMR (400 MHz, Chloroform-*d*)



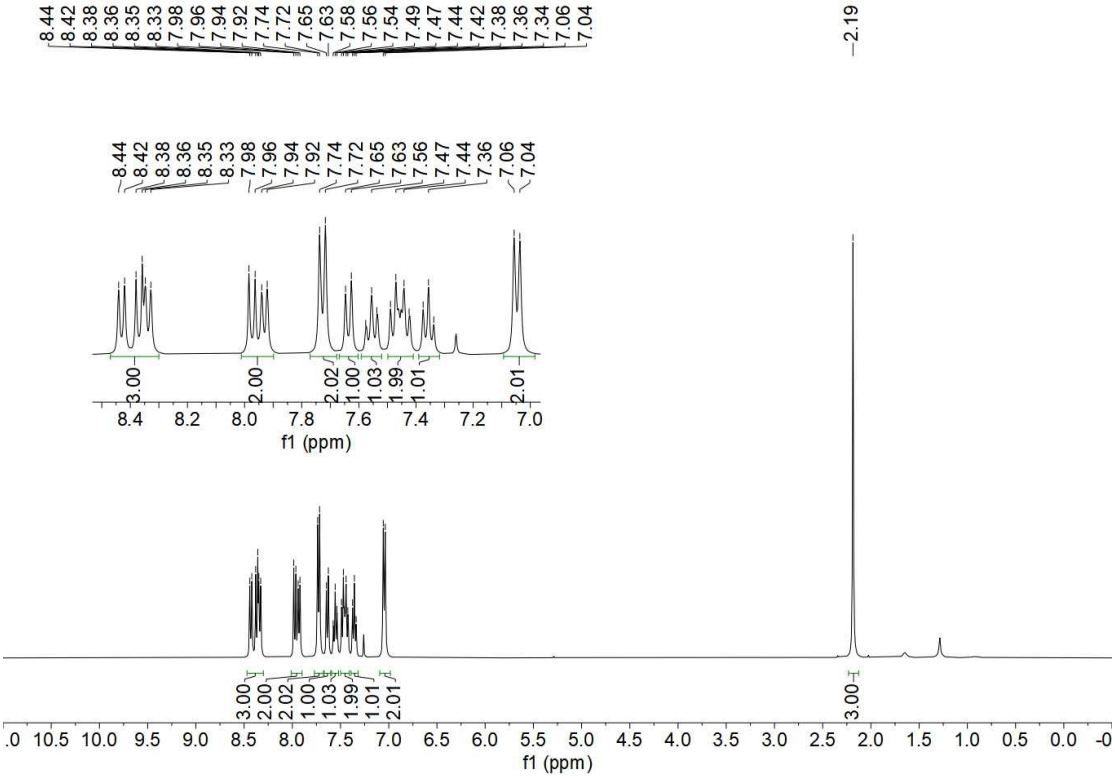
^{13}C NMR (100 MHz, Chloroform-*d*)



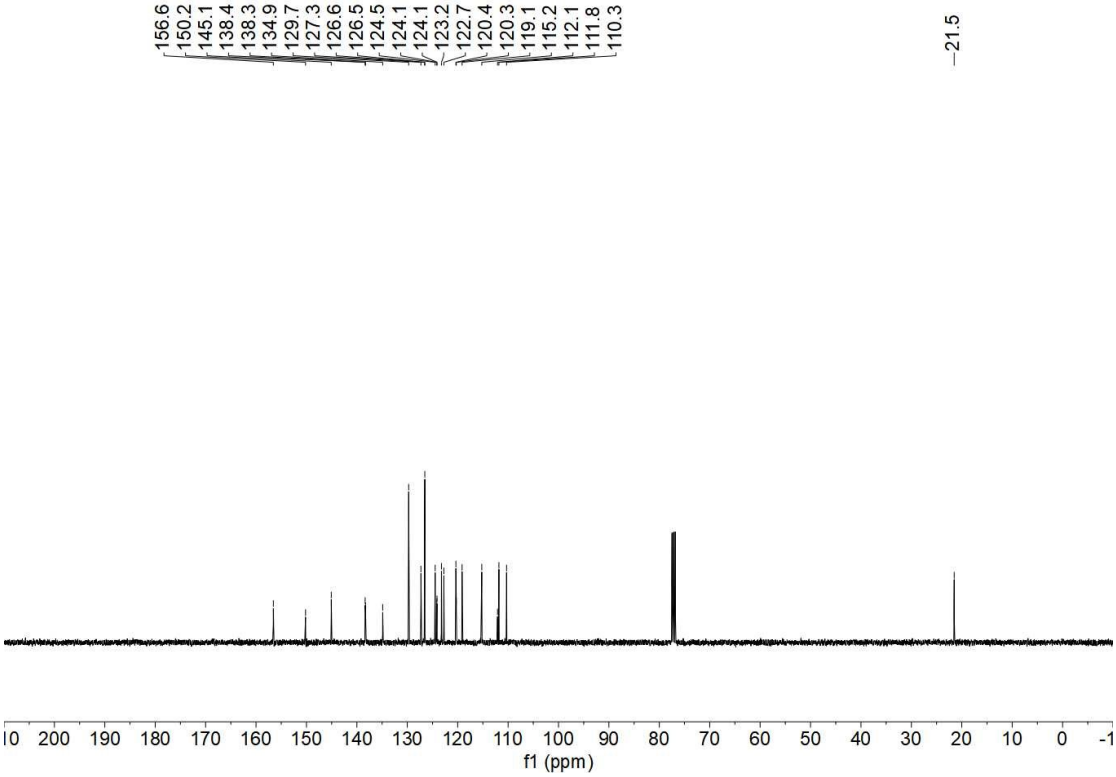


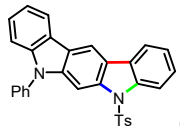
(4o)

^{1}H NMR (400 MHz, Chloroform-*d*)



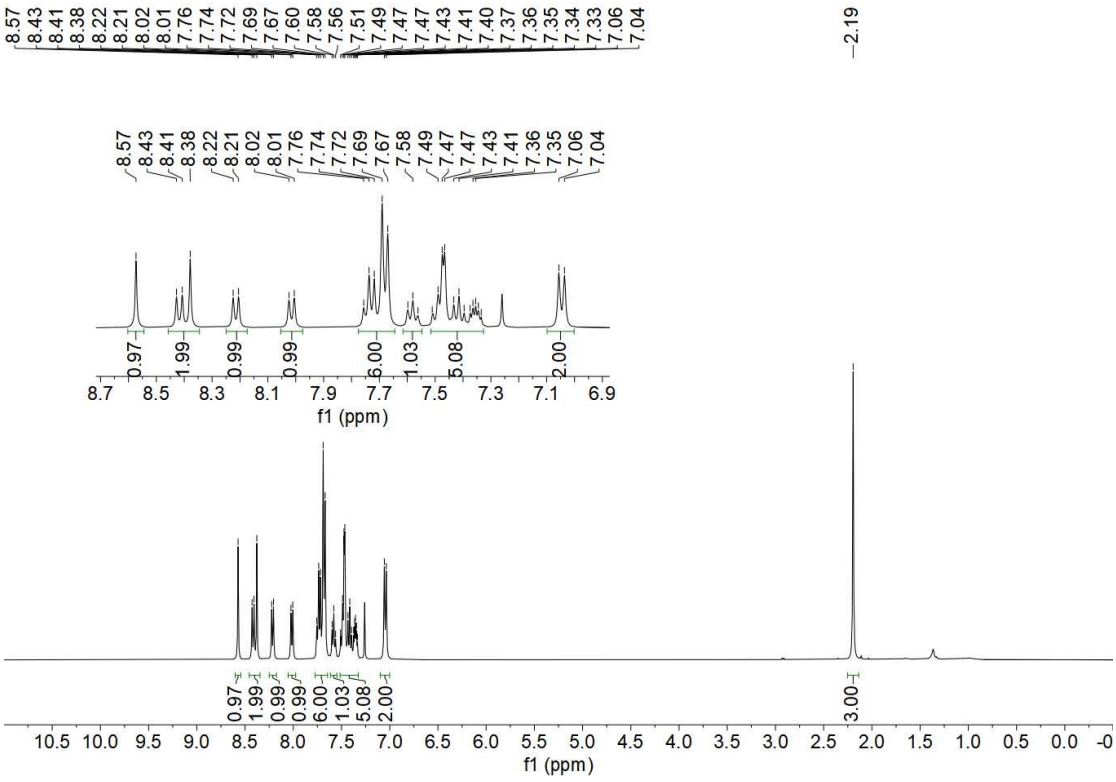
^{13}C NMR (100 MHz, Chloroform-*d*)



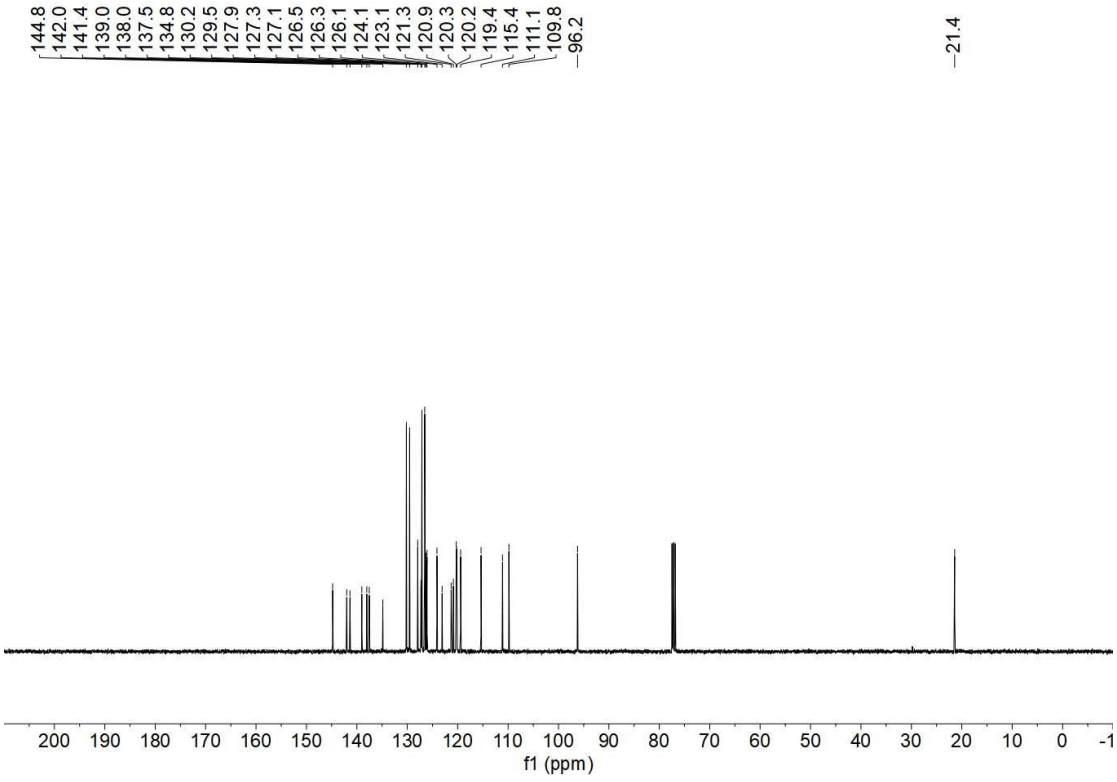


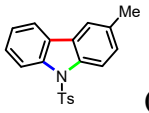
(4p)

^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (100 MHz, Chloroform-*d*)





(4aa)

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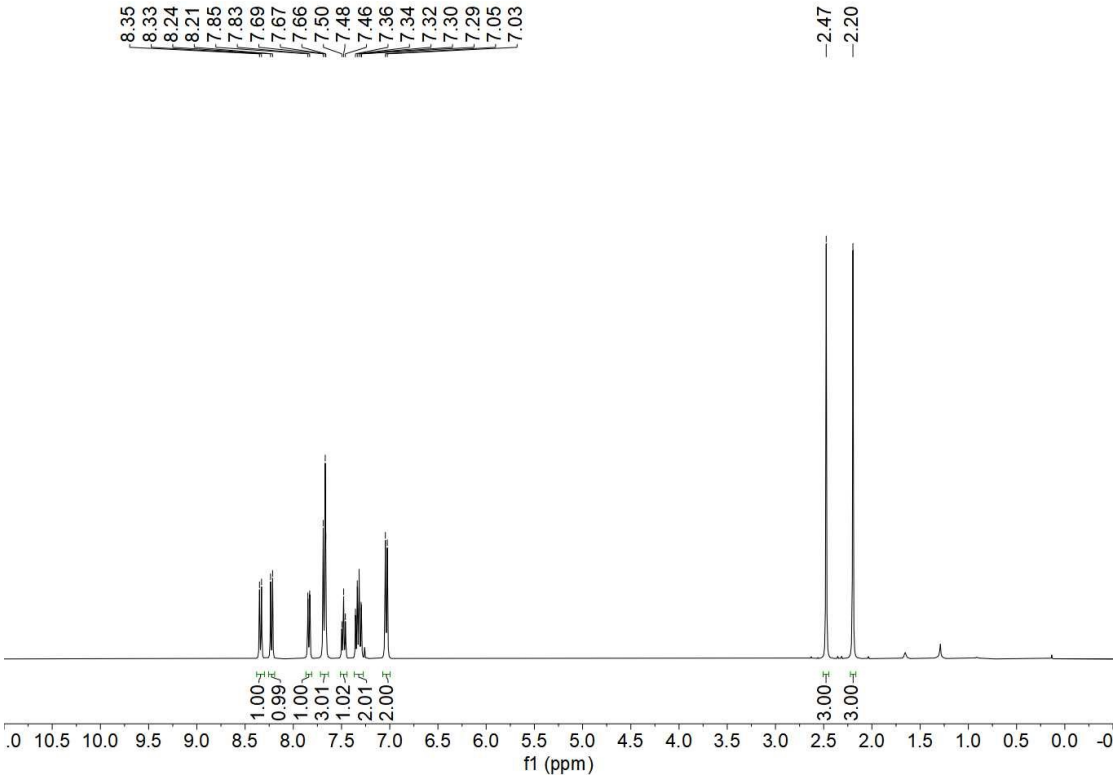
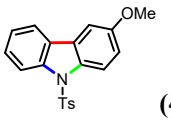
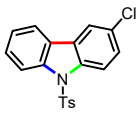




(4ab)

^{1}H NMR (400 MHz, Chloroform-*d*)



(4ac)

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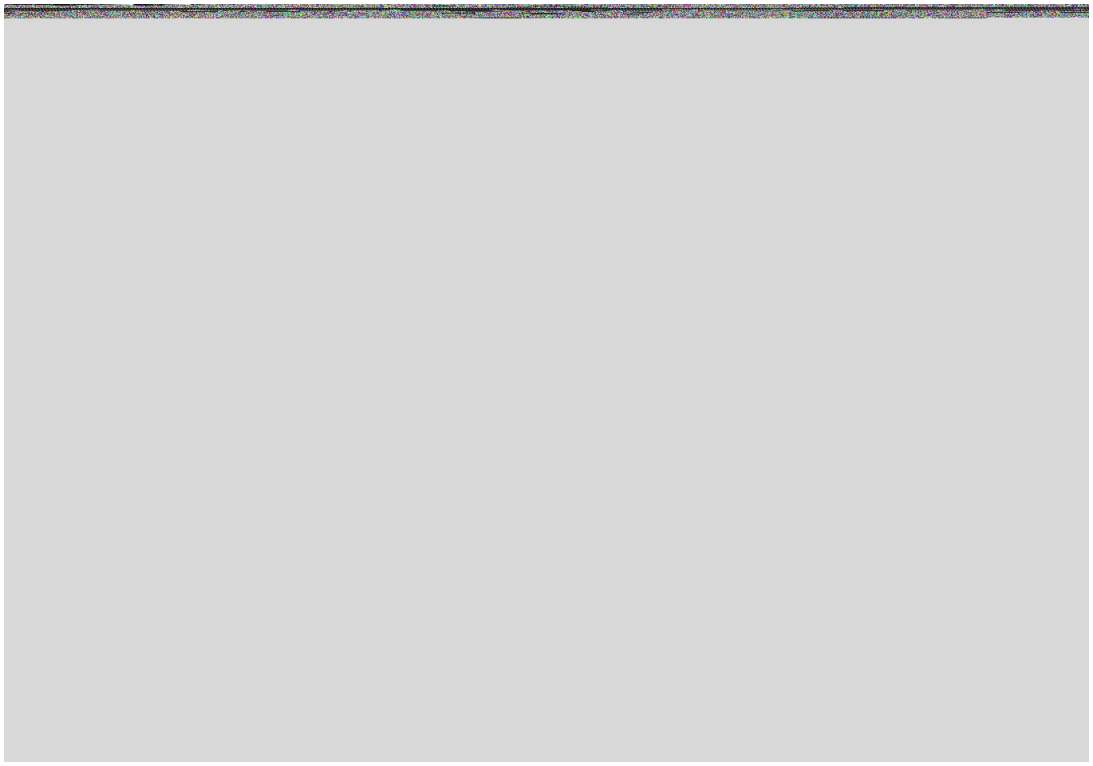
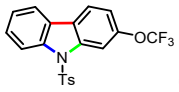
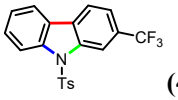




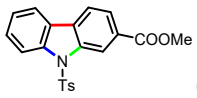
(4ad)

^{1}H NMR (400 MHz, Chloroform-*d*)



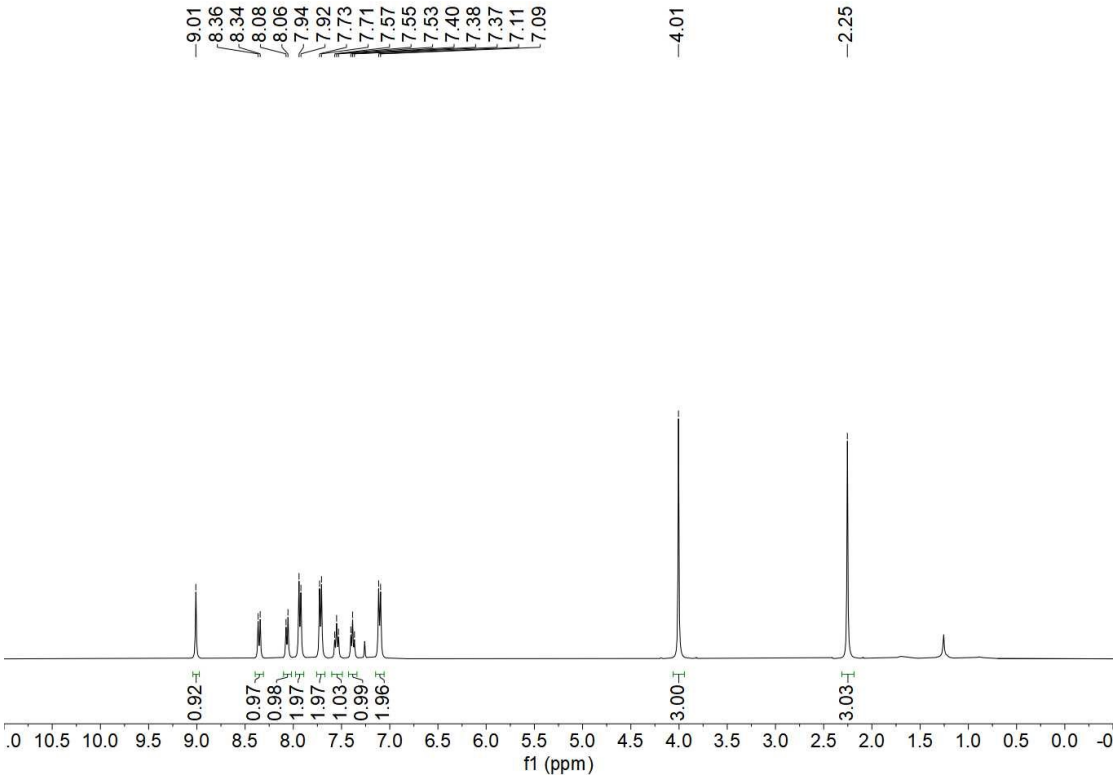
(4ae)

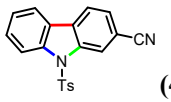
^{1}H NMR (400 MHz, Chloroform-*d*)



(4af)

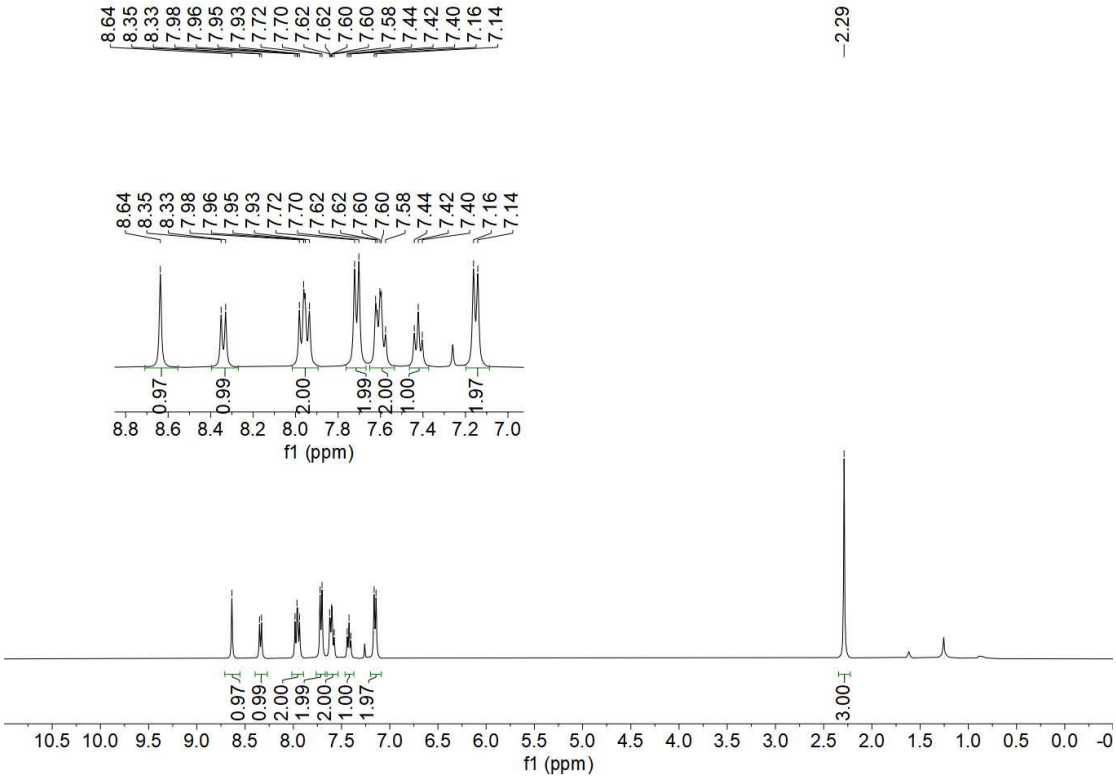
^{1}H NMR (400 MHz, Chloroform-*d*)

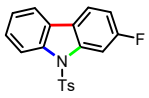




(4ag)

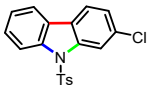
^{1}H NMR (400 MHz, Chloroform-*d*)





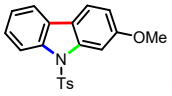
(4ah)

^{1}H NMR (400 MHz, Chloroform-*d*)



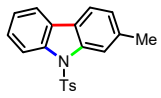
(4ai)

^{1}H NMR (400 MHz, Chloroform-*d*)



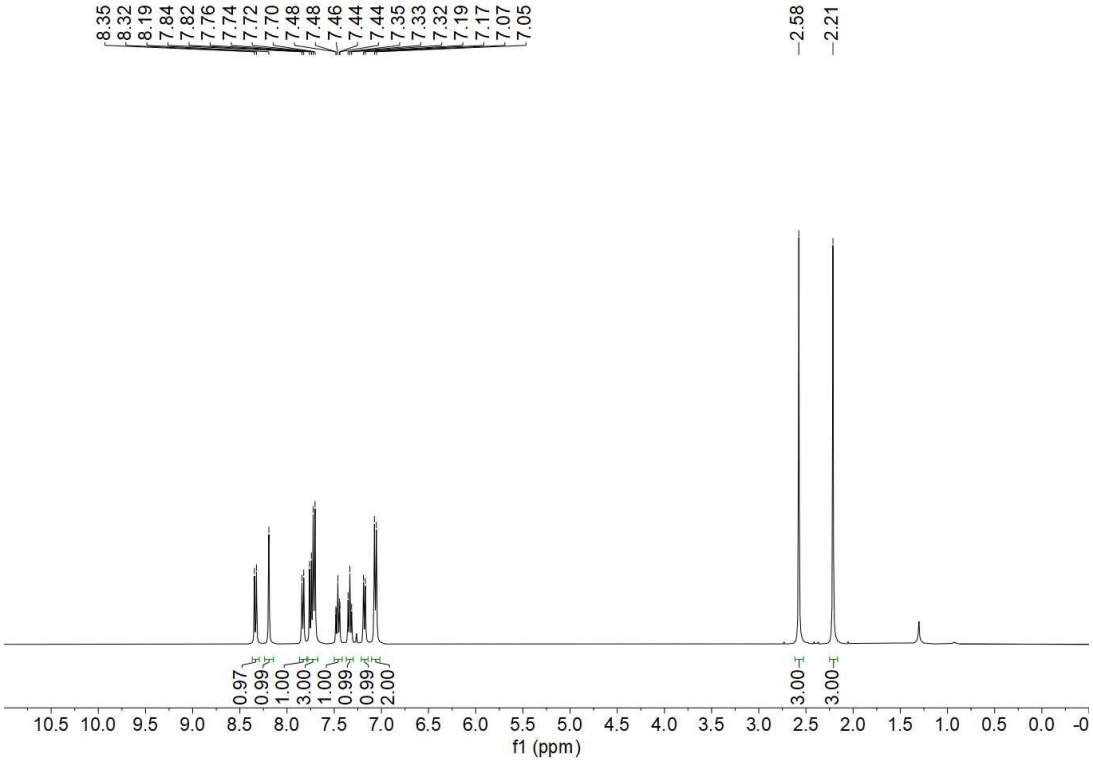
(4aj)

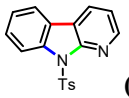
^{1}H NMR (400 MHz, Chloroform-*d*)



(4ak)

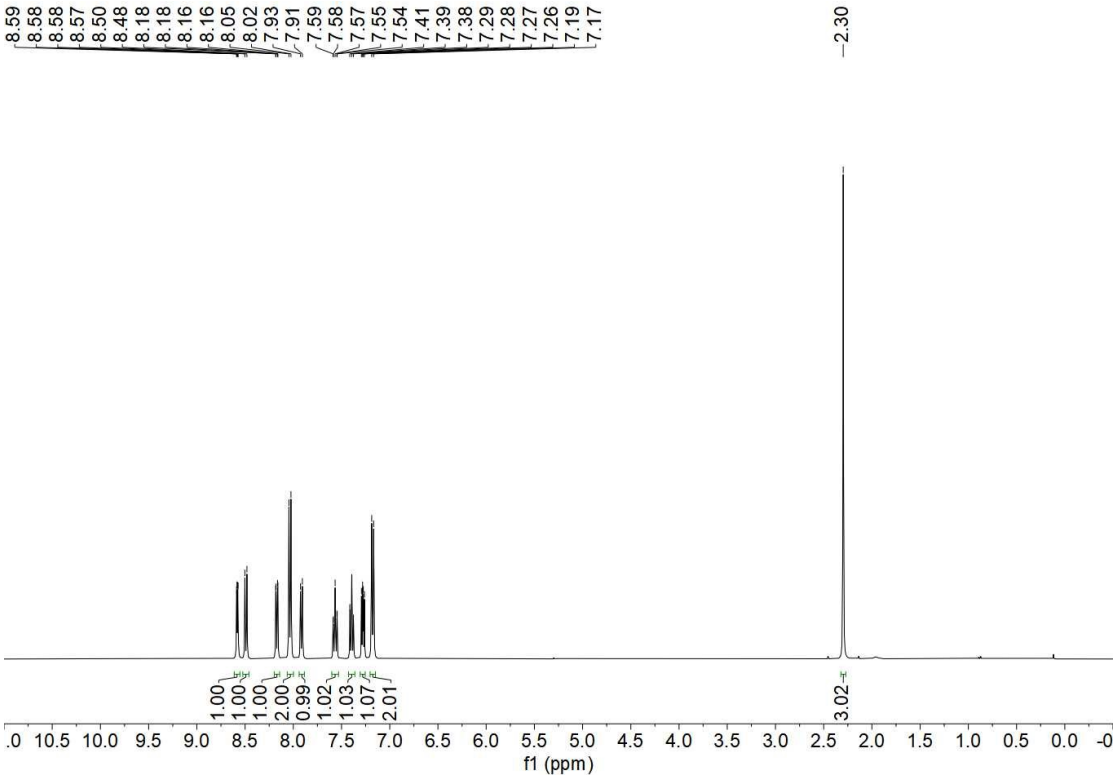
^{1}H NMR (400 MHz, Chloroform-*d*)

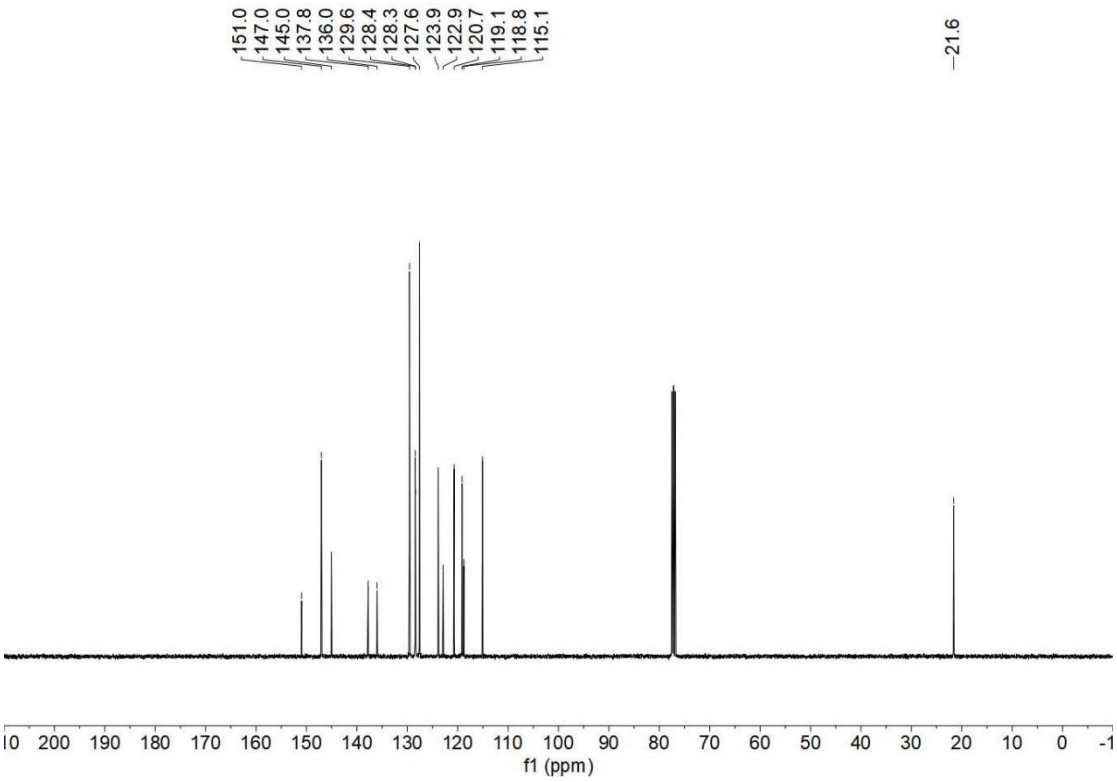


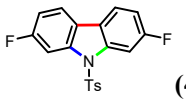


(4al)

^{1}H NMR (400 MHz, Chloroform-*d*)

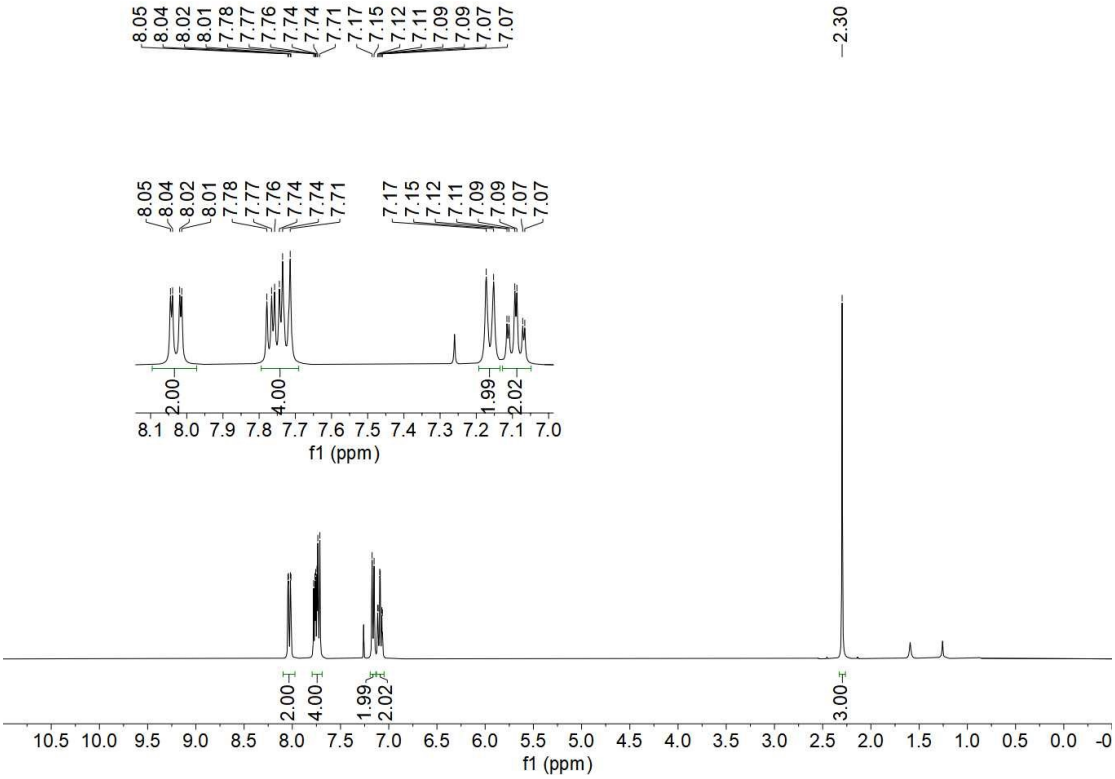


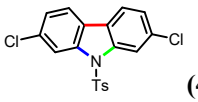




(4ba)

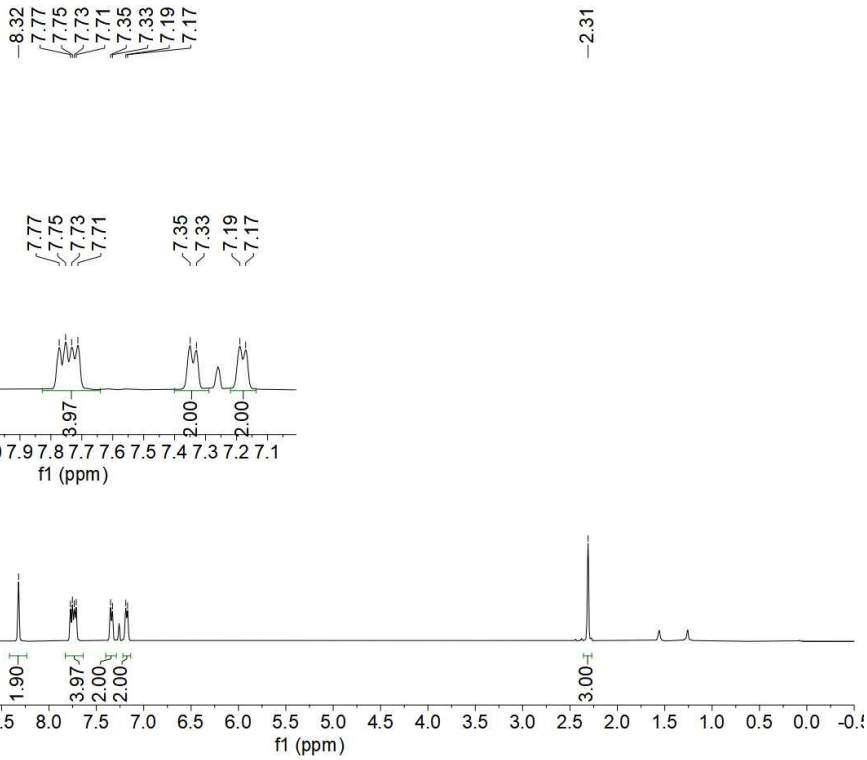
^{1}H NMR (400 MHz, Chloroform-*d*)

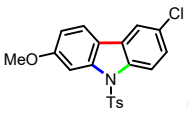




(4bb)

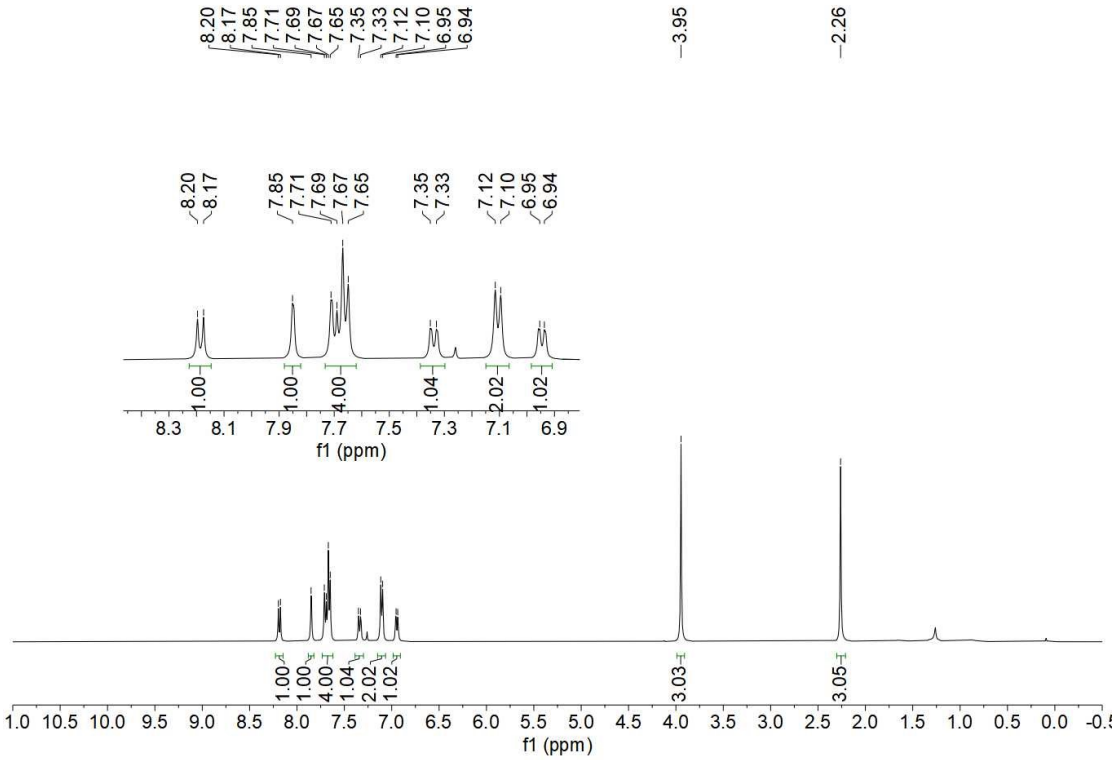
^{1}H NMR (400 MHz, Chloroform-*d*)





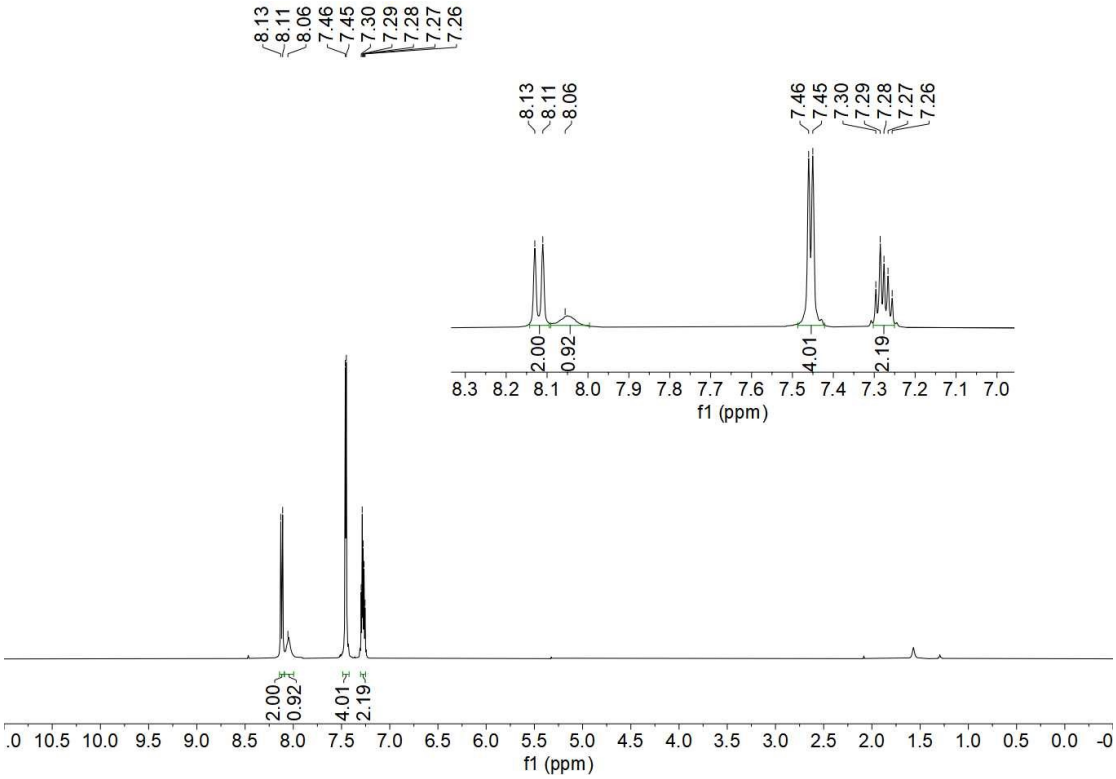
(4bc)

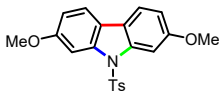
^{1}H NMR (400 MHz, Chloroform-*d*)



(4a')

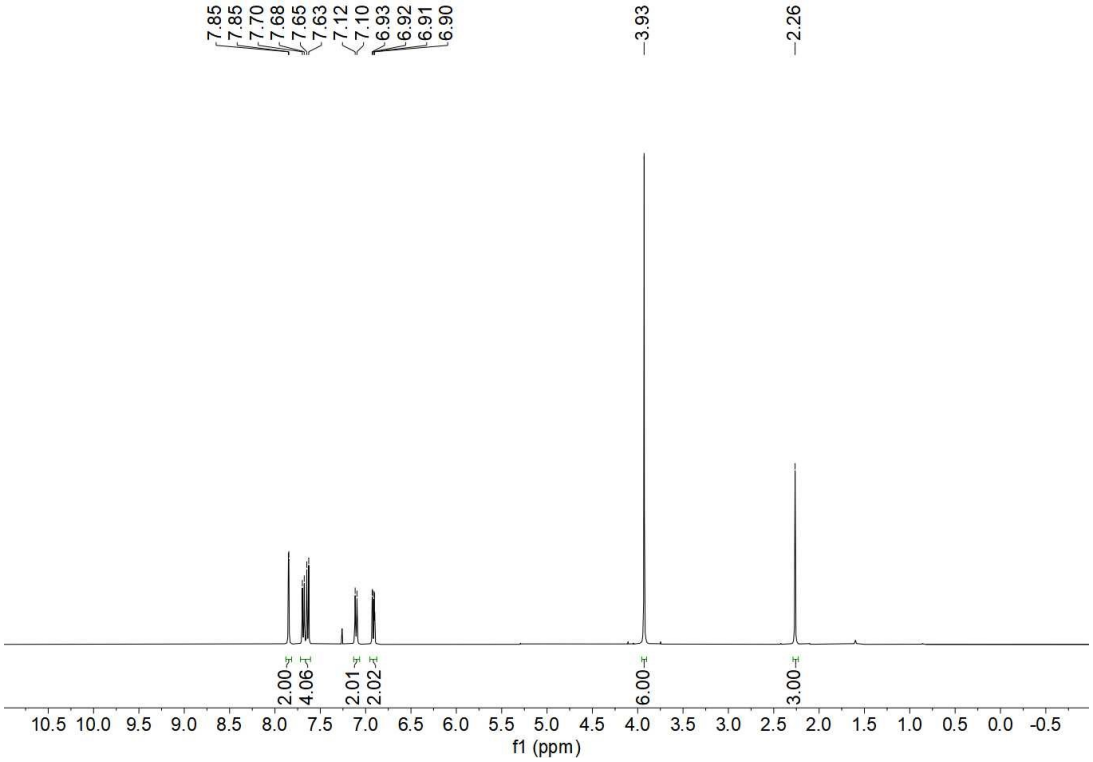
^{1}H NMR (400 MHz, Chloroform-*d*)



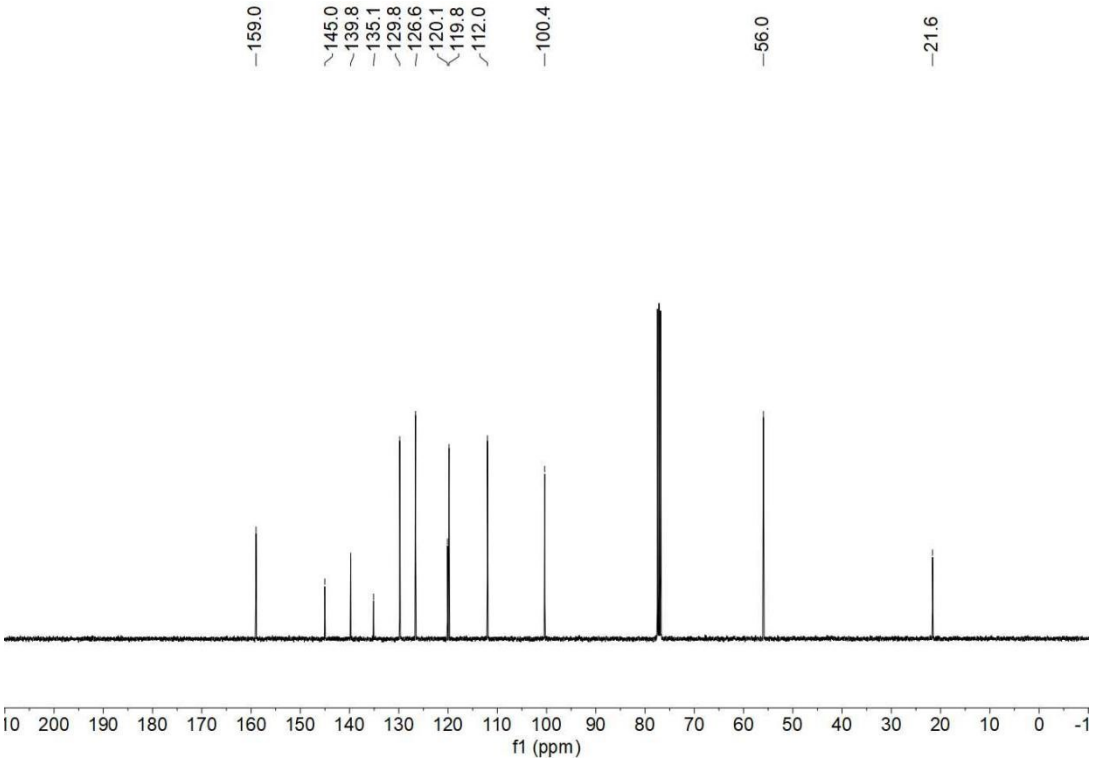


(4ij)

^{1}H NMR (400 MHz, Chloroform-*d*)

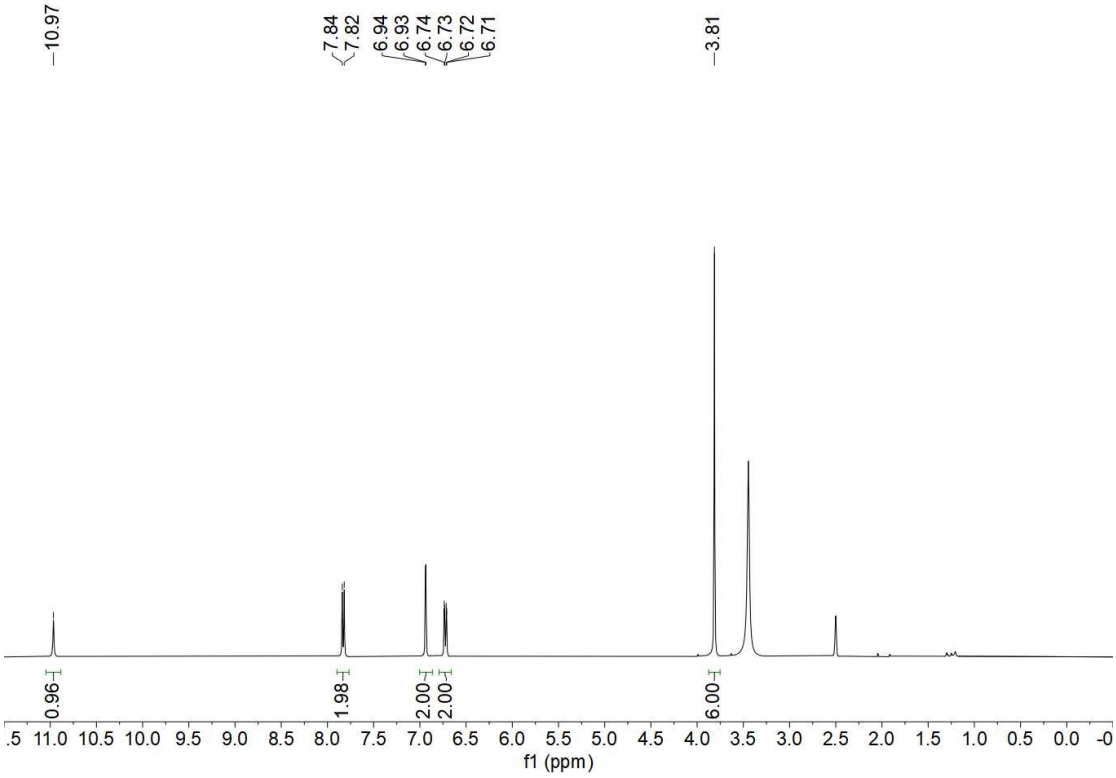


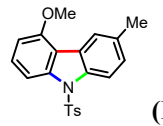
^{13}C NMR (100 MHz, Chloroform-*d*)



(Clausine V)

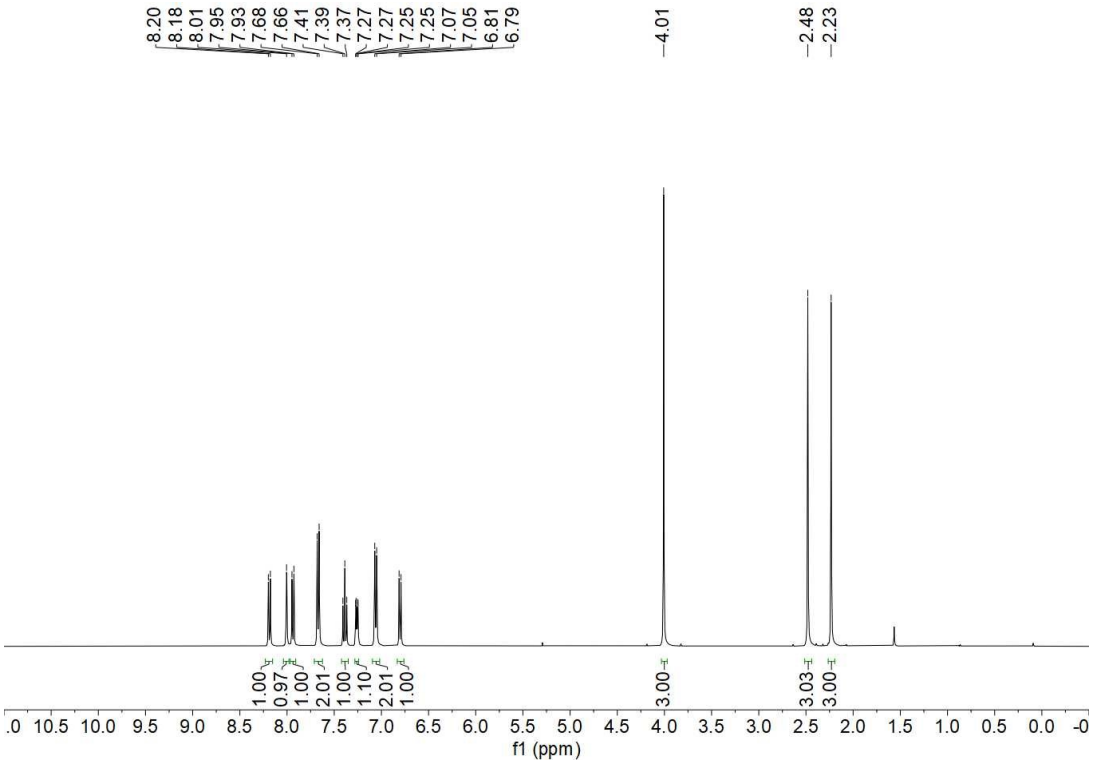
^{1}H NMR (400 MHz, DMSO-d_6)



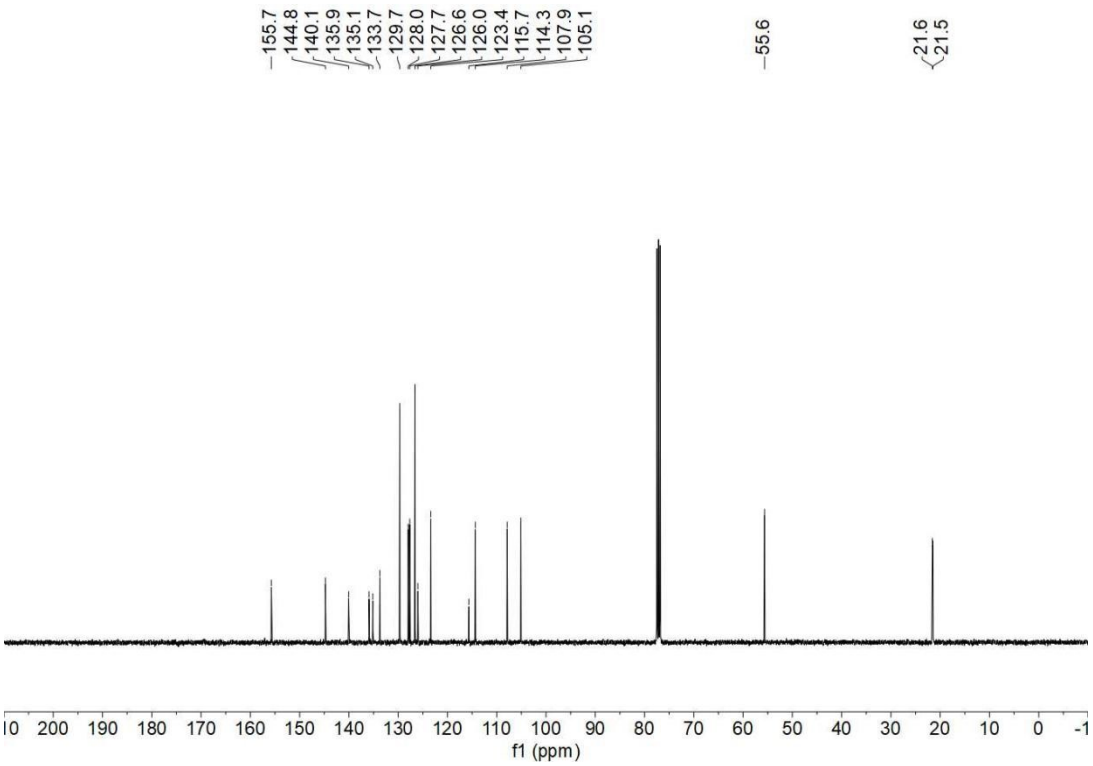


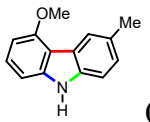
(I)

^{1}H NMR (400 MHz, Chloroform-*d*)



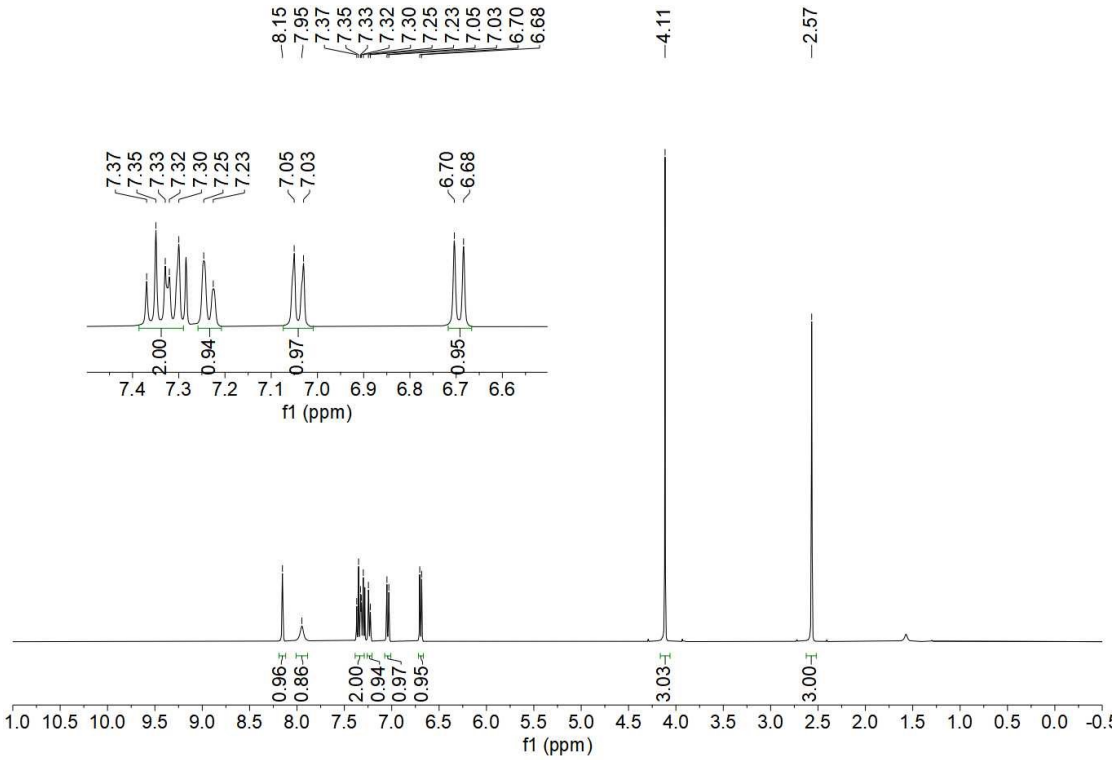
^{13}C NMR (100 MHz, Chloroform-*d*)

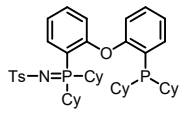




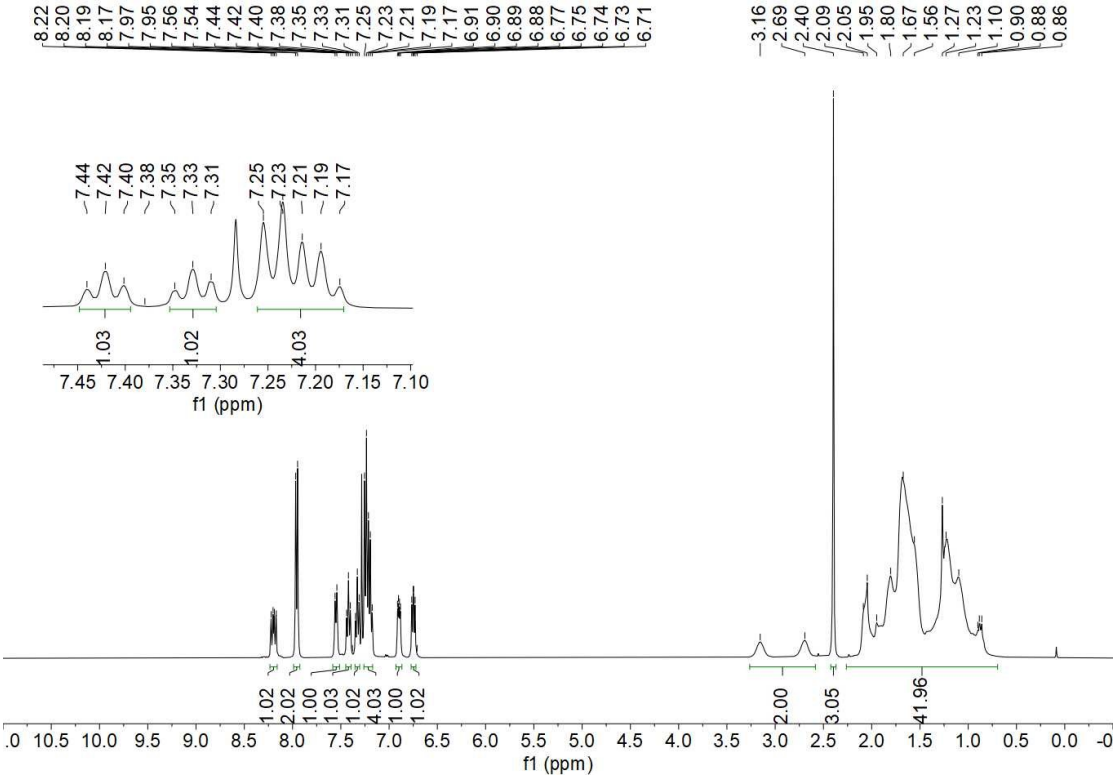
(Glycoborine)

^{1}H NMR (400 MHz, Chloroform-*d*)

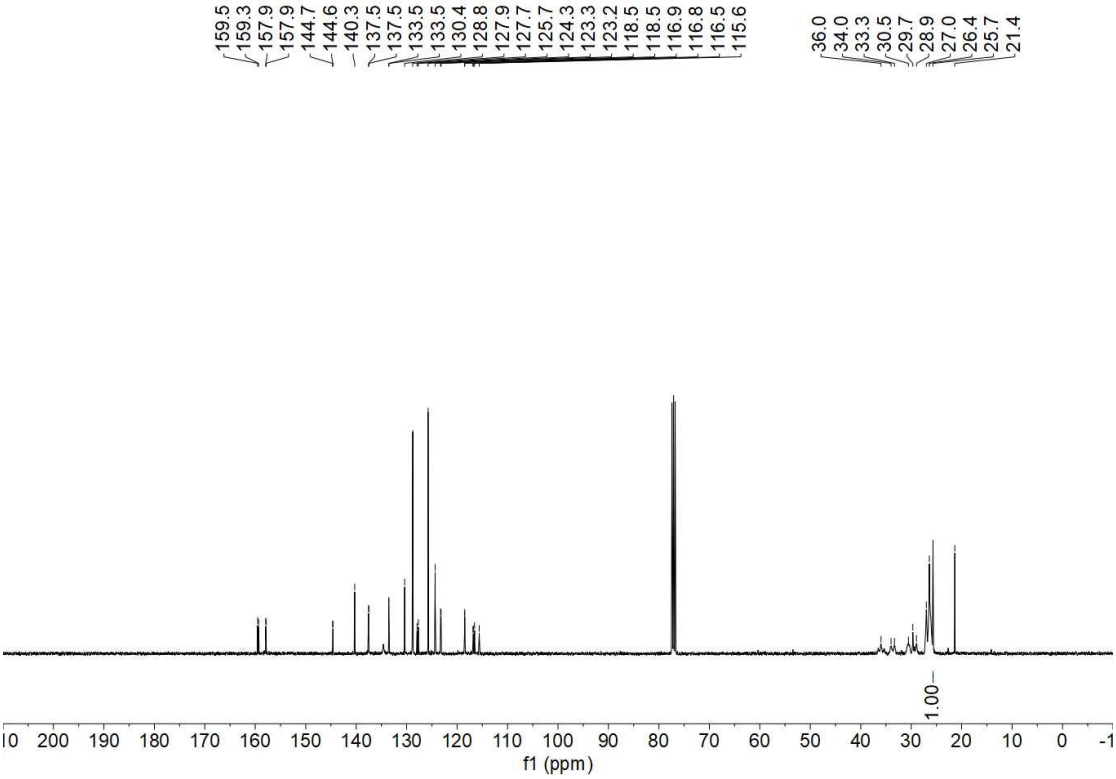




^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (100 MHz, Chloroform-*d*)



^{31}P NMR (162 MHz, Chloroform-*d*)