Supporting Information for

Tandem Prins Cyclization for the Synthesis of Indole Fused Spiro-1,4-Diazocane Scaffolds

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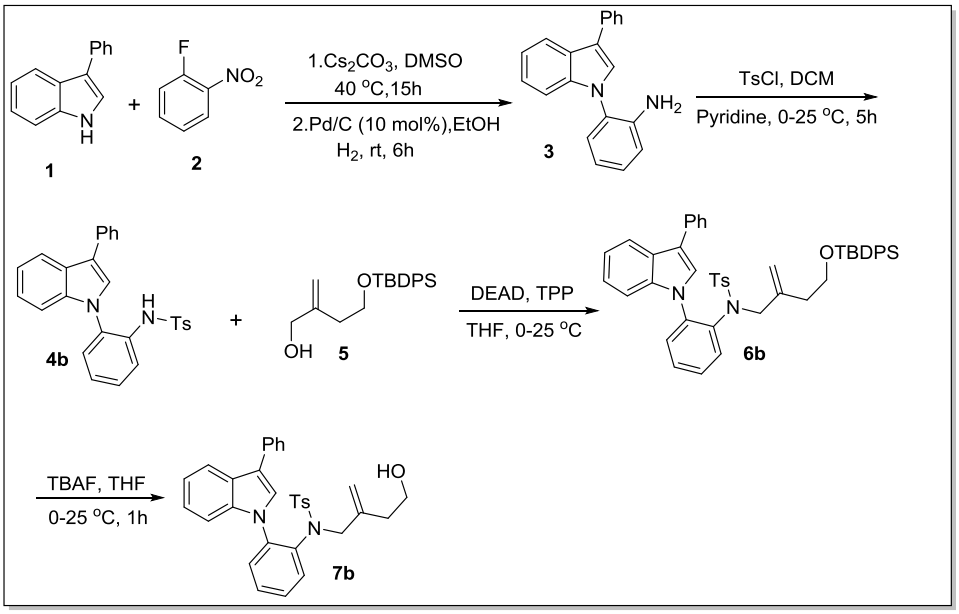
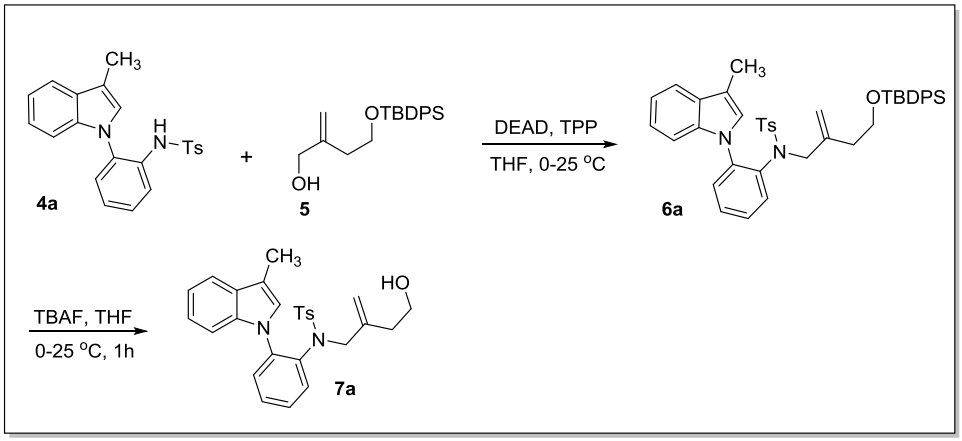
1. Experimental procedures

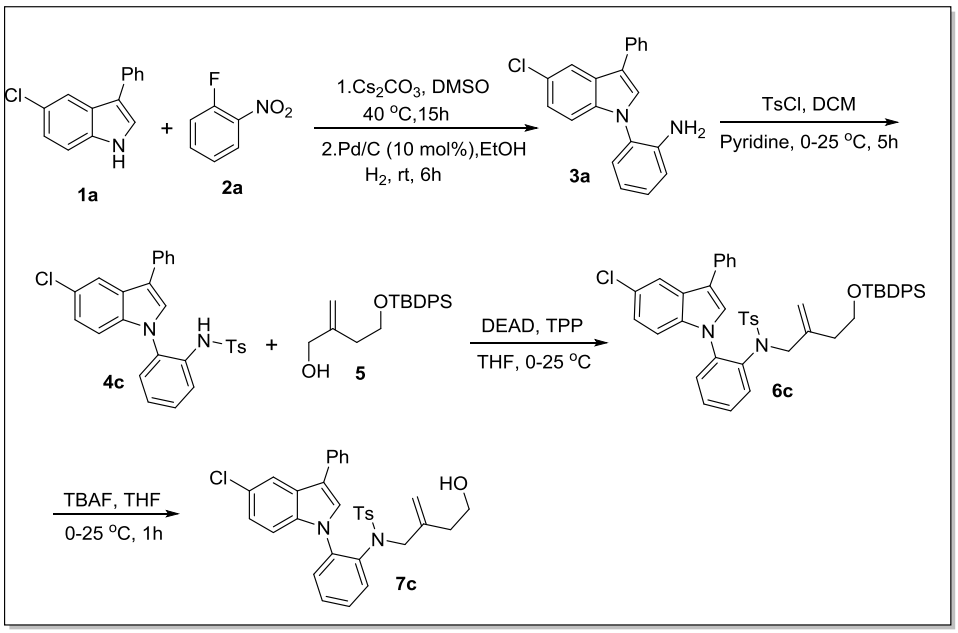
General

All solvents were dried according to standard literature procedures. Reactions were performed in oven-dried round-bottom flasks, and the flasks were fitted with rubber septa; the reactions were conducted under nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel 60−120 or 100−200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on a rotary evaporator at 35−40 °C. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 101 MHz (C), respectively. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (J) are quoted in hertz (Hz). Mass spectra were recorded on a mass spectrometer by electrospray ionization (ESI) or an atmospheric pressure chemical ionization (APCI) technique.

Preparation of starting materials (Ref 9)







Preparation of compound 3 & 3a: To a stirred solution of 3-phenylindole (2 g, 10.3 mmol) in DMSO was added Cs_2CO_3 (6.73 g, 20.7 mmol) and stirred for 15 min at room temperature and then 1-fluoro-2-nitrobenzene (1 mL, 10.3 mmol) was added slowly and stirred at 40 ^oC under air for 15h. Then the reaction was quenched with ice water (2×20 mL) and then extracted with dichloromethane. The combined organic phase was washed with brine (25 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting compound was dissolved in EtOH (10 mL), and then Pd/C was added. The resulting suspension was stirred under hydrogen pressure using hydrogen balloon for 6h. The mixture was filtered over celite and rinsed with EtOH. The solvent was removed under vaccum and the crude product was purified

by column chromatography using 10% ethyl acetate in hexanes as eluent to afford compound **3/3a.**

2-(3-Phenyl-1*H*-indol-1-yl)aniline (3): Yield (2.5 g, 85%), Orange liquid, R_f 0.46 (10% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3476.2, 3382.3, 1616.2, 1509.6, 1461.3, 1312.8, 1220.6, 749.4, 700.7 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.26 – 7.20 (m, 6H), 6.89 – 6.84 (m, 2H), 3.63 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 137.2, 135.2, 129.4, 128.9, 128.7, 127.5, 126.2, 122.7, 120.1, 118.7, 116.4, 111.2. **HRMS** (Orbitrap ESI): calcd. for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1392; found 285.1381.

2-(5-Chloro-3-phenyl-1*H*-indol-1-yl)aniline (3a): Yield (2.3 g, 83%), Orange liquid, R_f 0.47 (10% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3539.4, 1620.1, 1509.0, 1461.2, 799.8, 757.4 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.5 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.34 – 7.28 (m, 2H), 7.23 – 7.18 (m, 2H), 7.11 (d, *J* = 8.7 Hz, 1H), 6.91 – 6.85 (m, 2H), 3.63 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 135.6, 134.5, 129.6, 129.0, 128.9, 128.6, 127.5, 126.7, 126.5, 126.2, 124.1, 123.0, 122.7, 120.7, 120.1, 119.6, 118.7, 118.5, 116.4, 112.3, 111.2. **HRMS** (Orbitrap ESI): calcd. for $C_{20}H_{16}N_2Cl$ $[M+H]^+$ 319.1002; found 319.1001.

Preparation of compound 4b & 4c: To a solution of compound **3**/ **3a** (2 g, 7.04 mmol) in anhydrous dichloromethane, pyridine (1.13 mL, 14.08 mmol) was added at 0 ^oC and stirred it for 15 min at the same temperature and then *p*-toluenesulfonyl chloride (2 g, 10.5 mmol) was added and stirred it for another 5h at room temperature. After completion, the reaction was quenched with 10% HCl solution (2×20 mL) and extracted with ethyl acetate, dried over sodium sulphate. Removal of the solvent followed by purification on silica gel column chromatography using 20% ethyl acetate in hexanes as a eluent to afford pure compound **4b/4c**.

4-Methyl-*N*-(2-(3-phenyl-1*H*-indol-1-yl)phenyl)benzenesulfonamide (4b): Yield (2.7 g, 90%), Colorless viscous liquid, R_f 0.40 (20% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3345.5, 3068.6, 1602.1, 1503.4, 1460.0, 1341.3, 1167.3, 755.8, 669.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 3H), 7.36 (d, *J* = 8.2 Hz, 3H), 7.26 (t, *J* = 9.9 Hz, 4H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.48 (s, 1H), 6.30 (s, 1H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 133.7,

129.8, 128.9, 128.8, 127.5, 127.0, 126.5, 126.1, 125.5, 123.5, 123.3, 121.4, 120.5, 110.0, 21.5. **HRMS** (Orbitrap ESI): calcd. for $C_{27}H_{23}N_2O_2S$ $[M+H]^+$ 439.148; found 439.1471.

***N*-(2-(5-Chloro-3-phenyl-1*H*-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (4c):** Yield (2. g, 89%), Colorless viscous liquid, R_f 0.42 (20% ethyl acetate in hexanes); **IR** (neat) ṽ = 3248.2, 1506.4 , 1460.7, 1165.6, 762.7, 670.4 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.3 Hz, 2H), 7.56 – 7.50 (m, 5H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.10 – 7.03 (m, 3H), 6.64 (d, *J* = 8.7 Hz, 1H), 6.56 (s, 1H), 6.26 (s, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 130.0, 129.8, 129.0, 128.7, 127.5, 127.0, 126.9, 126.6, 126.2, 123.7, 123.5, 119.9, 111.1, 21.5. **HRMS** (Orbitrap ESI): calcd. for $C_{27}H_{22}N_2O_2SCl$ $[M+H]^+$ 473.1091; found 473.1089.

Preparation of compounds 6a,6b&6c: To a stirred solution of compound **4a/4b/4c** (5.7 mmol), **5** (5.7 mmol), and triphenylphosphine (6.3 mmol) in THF at 0 ^oC was added diethyl azodi carboxylate (6.3 mmol) dropwise over 10 min and it was allowed to stir at room temperature for 6 h. After completion, as monitored by TLC, the solvent was removed under reduced pressure, and the resulting crude product was purified by column chromatography using 15% ethyl acetate in hexanes as a eluent to afford pure compound **6a/6b/6c**.

***N*-(4-((tert-Butyldiphenylsilyl)oxy)-2-methylenebutyl)-4-methyl-*N*-(2-(3-methyl-1*H*-indol-1-yl)phenyl)benzenesulfonamide (6a):** Yield 85%, colorless liquid, R_f 0.5 (15% ethyl acetate in hexanes); **IR** (neat) ṽ = 3069.1, 2930.2, 2860.1, 1598.6, 1499.1, 1461.9, 1350.0, 1162.1, 1105.2, 747.7, 702.7, 665.2 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 4H), 7.41 – 7.38 (m, 4H), 7.35 – 7.27 (m, 8H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.11 – 70.6 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 4.42 (s, 1H), 4.30 (s, 1H), 3.54 (s, 2H), 3.17 (t, *J* = 6.3 Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H), 1.40 (s, 2H), 0.90 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 140.0, 139.0, 137.2, 136.8, 135.6, 135.4, 133.9, 130.5, 129.7, 129.5, 129.3, 129.1, 129.0, 128.3, 127.7, 127.6, 121.8, 119.7, 118.8, 117.2, 112.0, 110.2, 61.7, 57.0, 35.0, 26.8, 21.6, 19.2, 9.6. **HRMS** (Orbitrap ESI): calcd. for $C_{43}H_{47}N_2O_3SSi$ $[M+H]^+$ 699.30712; found 699.31142.

***N*-(4-((*tert*-Butyldiphenylsilyl)oxy)-2-methylenebutyl)-4-methyl-*N*-(2-(3-phenyl-1*H*-indol-1-yl)phenyl)benzenesulfonamide (6b):** Yield 82%, colorless liquid, R_f 0.46 (15% ethyl acetate in hexanes); **IR** (neat) ṽ = 2924.6, 2864.5, 1597.9, 1504.3, 1407.0, 1340.2, 1219.1, 1156.8, 1093.3, 750.7, 665.7 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 7.7 Hz,

2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 8H), 7.38 – 7.34 (m, 3H), 7.31 (s, 4H), 7.19 (d, *J* = 10.2 Hz, 4H), 7.14 – 7.08 (m, 2H), 4.39 (s, 1H), 4.29 (s, 1H), 3.59 (s, 2H), 3.09 (t, *J* = 5.1 Hz, 2H), 2.38 (s, 3H), 1.55 (s, 2H), 0.90 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 139.9, 139.0, 137.8, 136.4, 135.9, 135.6, 135.4, 133.9, 130.1, 129.7, 129.5, 129.2, 129.1, 128.8, 128.3, 128.0, 127.8, 127.5, 126.7, 126.0, 122.2, 120.8, 119.9, 118.5, 117.4, 110.7, 61.6, 57.5, 34.7, 26.8, 21.6, 19.1. **HRMS** (Orbitrap ESI): calcd. for $C_{48}H_{48}N_2O_3SSi$ [M + H] $^+$ 761.32 33; found 761.3259.

***N*-(4-((*tert*-Butyldiphenylsilyl)oxy)-2-methylenebutyl)-*N*-(2-(5-chloro-3-phenyl-1*H*-indol-1-yl)phenyl)-4-methylbenzenesulfonamide (6c):** Yield 85%, colorless liquid, R_f 0.46 (15% ethyl acetate in hexanes); **IR** (neat) ṽ = 3850.3, 3812.9, 2921.7, 1462.8, 1110.4, 767.2, 708.1 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.8 Hz, 1H), 7.90 (s, 1H), 7.71 – 7.63 (m, 4H), 7.50 – 7.45 (dd, *J* = m, 7H), 7.41 – 7.30 (m, 8H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.38 (s, 1H), 4.29 (s, 1H), 3.72 – 3.52 (m, 2H), 3.14 (t, *J* = 5.6 Hz, 2H), 2.39 (s, 3H), 1.26 (s, 2H), 0.92 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 139.9, 138.7, 136.3, 136.1, 135.9, 135.5, 134.6, 133.8, 130.0, 129.7, 129.5, 129.3, 128.9, 128.6, 128.4, 127.7, 127.6, 126.5, 126.3, 122.4, 119.3, 118.2, 117.6, 111.8, 61.7, 57.6, 34.7, 26.8, 21.6, 19.1. **HRMS** (Orbitrap ESI): calcd. for $C_{48}H_{48}N_2O_3SClSi$ $[M+H]^+$ 795.2843; found 795.2834.

Preparation of compound 7a,7b&7c: To a solution of **6a/6b/6c** (1 mmol) in THF at 0 °C was added TBAF (2 mmol) drop wise under N_2 atmosphere and the resulting mixture was allowed to stir at rt for 1h. After complete consuption of starting material, the reaction was quenched with a sat. solution of $NaHCO_3$, and the aqueous layer was extracted with ethyl acetate. Removal of the solvent under reduced pressure followed by purification on silica gel column chromatography using 40% ethyl acetate in hexanes as a eluent to afford pure compound **7a/7b/7c**.

***N*-(4-Hydroxy-2-methylenebutyl)-4-methyl-*N*-(2-(3-methyl-1*H*-indol-1-yl)phenyl)benzene sulfonamide (7a):** Yield 90%, white viscous liquid, R_f 0.50 (40% ethyl acetate in hexanes); **IR** (neat) ṽ = 3768.0, 3550.9, 3420.2, 3071.7, 1600.6, 1500.4, 1460.7, 1346.5, 1162.3, 1091.8, 858.5, 754.8, 701.3, 665.6 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.42 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.16 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.13 – 7.09 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 4.43 (s, 1H), 4.38 (s, 1H), 3.67 (s, 2H), 3.09 (t, *J* = 5.7 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H), 1.39 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 140.2, 139.1, 137.3, 136.4, 135.6, 129.8, 129.3, 128.3, 121.8, 119.8,

118.8, 116.8, 112.0, 110.2, 60.3, 57.5, 34.9, 21.7, 9.7. **HRMS** (Orbitrap ESI): calcd. for $C_{27}H_{29}N_2O_3S$ $[M + H]^+$ 461.1893; found 461.1903.

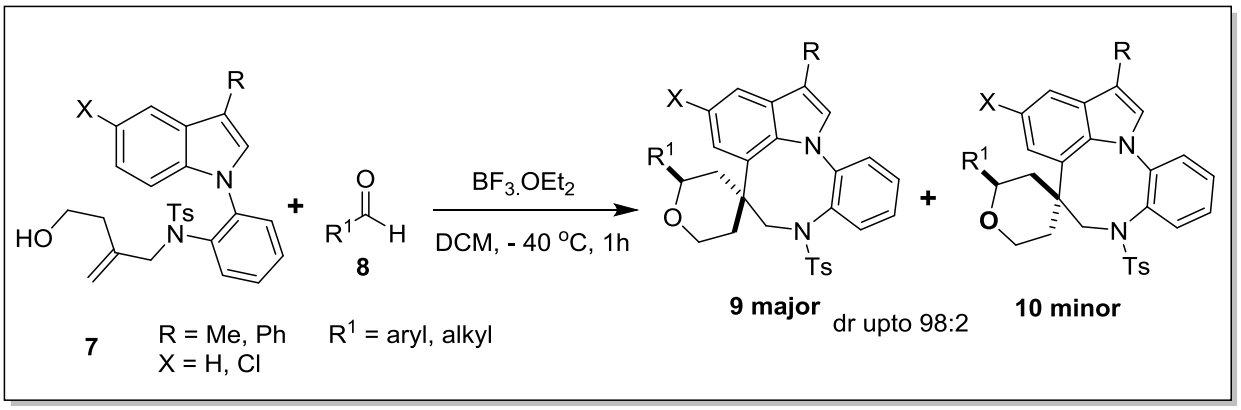
***N*-(4-Hydroxy-2-methylenebutyl)-4-methyl-N-(2-(3-phenyl-1*H*-indol-1-yl)phenyl)benzene sulfonamide (7b):** Yield 91%, white viscous liquid, R_f 0.50 (40% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3558.4, 3419.5, 3069.1, 2925.2, 1596.9, 1500.3, 1457.6, 1347.6, 1161.1, 1046.0, 859.0, 750.4, 660.0 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.78 – 7.71 (m, 4H), 7.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 3H), 7.40 – 7.36 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.24 – 7.19 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.38 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 2H), 3.03 (t, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 1.59 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 140.1, 139.0, 138.0, 136.1, 135.3, 129.9, 129.8, 129.4, 129.3, 128.9, 128.4, 127.7, 126.1, 110.7, 60.3, 58.0, 34.7, 21.7. **HRMS** (Orbitrap ESI): calcd. for $C_{32}H_{31}N_2O_3S$ $[M + H]^+$ 523.2055; found 523.2043.

***N*-(2-(5-Chloro-3-phenyl-1*H*-indol-1-yl)phenyl)-*N*-(4-hydroxy-2-methylenebutyl)-4-methylbenzenesulfonamide (7c)**: Yield 92%, white viscous liquid, R_f 0.50 (40% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3735.5, 2915.3, 1500.4, 1460.9, 1346.6, 1162.1, 762.6, 703.27, 662.2 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.93 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 4H), 7.49 (t, *J* = 7.0 Hz, 4H), 7.41 – 7.37 (m, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 1H), 4.40 (d, *J* = 15.7 Hz, 2H), 3.93 (s, 2H), 3.14 (s, 2H), 2.45 (s, 3H), 1.58 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 140.1, 138.8, 136.4, 136.1, 135.9, 134.6, 129.9, 129.5, 129.1, 129.0, 128.8, 128.4, 127.6, 126.4, 111.8, 60.4, 57.9, 34.7, 21.7. **HRMS** (Orbitrap ESI): calcd. for $C_{32}H_{30}N_2O_3SCl$ $[M + H]^+$ 557.1666; found 557.1669.

Typical procedure for Prins/Friedel-Crafts cyclization:

To a mixture of **7a/7b/7c** (0.448 mmol) and aldehyde **8** (0.672 mmol) in anhydrous DCM was added $BF_3.OEt_2$ (1.5 equiv) at – 40 ^oC. The mixture was allowed to stir at the same temperature for 1h under nitrogen atmosphere. After completion, the reaction was quenched with a sat. solution of $NaHCO_3$ (5 mL) and then extracted with dichloromethane (2 × 5 mL). The organic layer was washed with brine (3 × 2 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using 15% ethyl acetate in hexanes gradient mixture to afford the pure product **9** or **10.**

2. Characterization data for the products:



7-Methyl-2'-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino [7,8,1-hi]indole-11,4'-pyran] (9a): Yield 85%, white solid, mp 190-193 ^{o}C; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2924.9, 2864.7, 1595.8, 1502.7, 1408.7, 1353.4, 1161.3, 1095.5, 759.8, 669.5 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.37 – 7.34 (m, 7H), 7.31 (dd, *J* = 8.7, 4.4 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.77 – 6.72 (m, 5H), 4.69 (dd, *J* = 9.2, 4.5 Hz, 1H), 4.38 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.4 Hz, 1H), 3.51 – 3.40 (m, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.20 (d, *J* = 9.1 Hz, 2H), 1.47 (d, *J* = 14.3 Hz, 1H), 1.39 – 1.33 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.8, 142.5, 135.8, 135.0, 132.2, 131.9, 130.6, 130.5, 128.8, 128.6, 127.8, 127.0, 126.7, 126.5, 125.9, 123.9, 120.0, 118.4, 114.2, 75.5, 62.8, 51.6, 47.9, 40.2, 34.5, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{34}H_{33}N_2O_3S$ $[M + H]^+$ 549.2206; found 549.2227.

2'-(4-Isopropylphenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9b): Yield 82%, white solid, mp 220-222 ^{o}C; R_f 0.45 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2960.5, 2868.8, 1505.3, 1409.9, 1355.9, 1163.2, 1096.3, 763.8, 669.8 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.02 – 7.00 (m, 2H), 6.73 (t, *J* = 5.6 Hz, 5H), 4.66 (dd, *J* = 8.7, 4.9 Hz, 1H), 4.37 (d, *J* = 13.4 Hz, 1H), 3.93 (d, *J* = 13.4 Hz, 1H), 3.44 (td, *J* = 12.1Hz, 2.5 2H), 2.91 (td, *J* = 13.8, 2.7Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 2.20 (d, *J* = 8.1 Hz, 2H), 1.48-1.36 (m, 2H), 1.26 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 143.1, 142.4, 140.1, 135.7, 135.0, 132.2, 131.9, 130.6, 128.8, 126.9,

126.6, 126.5, 125.9, 123.9, 120.0, 118.3, 114.2, 75.2, 62.8, 51.6, 47.7, 40.2, 34.5, 33.9, 24.0, 21.5, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{37}H_{39}N_2O_3S$ $[M + H]^+$ 591.2675; found 591.2704.

2'-(4-Bromophenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9c): Yield 91%, white solid, mp 160-162 ^oC; R_f 0.52 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2926.0, 2869.3, 1501.0, 1408.5, 1353.2, 1162.3, 1096.4, 760.3, 666.4 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 3H), 7.37 (d, *J* = 7.8 Hz, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.76 – 6.72 (m, 5H), 4.66 (d, *J* = 10.3 Hz, 1H), 4.35 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 3.47 – 3.41 (m, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.18 – 2.01 (m, 2H), 1.49 – 1.26 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 142.5, 141.9, 135.7, 134.9, 132.1, 131.9, 131.6, 130.7, 130.3, 128.8, 128.3, 127.6, 127.0, 126.7, 126.4, 123.9, 121.5, 120.0, 119.8, 118.4, 114.2, 74.6, 62.8, 51.5, 47.8, 40.1, 34.4, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{34}H_{32}N_2O_3BrS$ $[M + H]^+$ 627.1311; found 627.1346.

2'-(2,4-Dichlorophenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9d): Yield 87%, light yellow solid, mp 230-232 ^oC; R_f 0.42 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2923.3, 2868.1, 1593.7, 1502.1, 1407.6, 1353.5, 1161.3, 1094.8, 758.8, 666.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.33 (m, 4H), 7.26 (d, *J* = 8.9 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 4.7 Hz, 3H), 6.76 (s, 1H), 5.02 (d, *J* = 11.4 Hz, 1H), 4.35 (d, *J* = 13.5 Hz, 1H), 4.04 (d, *J* = 13.5 Hz, 1H), 3.52 – 3.41 (m, 2H), 2.37 (d, *J* = 12.6 Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 1.91 (t, *J* = 12.3 Hz, 1H), 1.49 (d, *J* = 14.4 Hz, 1H), 1.38 – 1.32 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.5, 139.1, 135.9, 134.9, 133.7, 132.2, 131.9, 131.7, 130.6, 130.3, 129.0, 128.9, 128.1, 127.6, 127.0, 126.7, 126.6, 123.8, 120.0, 119.9, 118.5, 114.2, 71.7, 63.1, 51.1, 46.0, 40.4, 34.5, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{34}H_{31}N_2O_3Cl_2S$ $[M + H]^+$ 617.1432; found 617.1434.

7-Methyl-2'-(p-tolyl)-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino [7,8,1-hi]indole-11,4'-pyran] (9e): Yield 85%, white solid, mp 210-213 ^oC; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2921.3, 1487.6, 1402.1, 1353.6, 1123.4, 1046.4, 758.3, 668.9 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.26 (d, *J* = 4.5 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.77 – 6.72 (m, 5H), 4.66 (t, *J* = 6.7 Hz, 1H), 4.37 (d, *J* = 13.4 Hz, 1H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.49

– 3.39 (m, 2H), 2.36 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.18 (d, *J* = 7.3 Hz, 2H), 1.47 – 1.33 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.4, 139.9, 137.5, 135.8, 135.0, 132.2, 131.9, 130.6, 129.2, 128.8, 126.9, 126.6, 126.5, 125.8, 123.9, 120.0, 118.3, 114.2, 75.1, 62.8, 51.6, 47.9, 40.2, 34.5, 21.6, 21.2, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{35}H_{35}N_2O_3S$ $[M + H]^+$ 563.2362; found 563.2384.

7-Methyl-2'-(o-tolyl)-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino [7,8,1-hi]indole-11,4'-pyran] (9f): Yield 83%, white solid, mp 205-207 ^oC; R_f 0.48 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2924.6, 1501.8, 1408.1, 1353.6, 1160.4, 1093.4, 758.3, 668.7 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.36 (d, *J* = 5.2 Hz, 3H), 7.22 – 7.18 (m, 3H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.77 – 6.72 (m, 5H), 4.89 (d, *J* = 10.1 Hz, 1H), 4.40 (d, *J* = 13.3 Hz, 1H), 3.98 (d, *J* = 13.3 Hz, 1H), 3.52 – 3.41 (m, 2H), 2.41 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H), 2.20 – 2.12 (m, 2H), 1.50 – 1.35 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.5, 140.8, 135.8, 135.0, 134.0, 132.1, 131.9, 130.7, 130.4, 128.8, 127.5, 127.0, 126.7, 126.5, 125.4, 123.9, 120.0, 118.4, 114.2, 71.9, 63.1, 51.4, 46.5, 40.3, 34.6, 21.6, 19.2, 9.6. **HRMS** (Orbitrap ESI): calcd. for $C_{35}H_{35}N_2O_3S$ $[M + H]^+$ 563.2362; found 563.2384.

2'-(4-Butylphenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9g): Yield 87%, white solid, mp 190-192 ^oC; R_f 0.54 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2925.7, 2860.5, 1503.2, 1408.1, 1350.5, 1160.0, 1094.7, 758.7, 668.5 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.00 (s, 2H), 6.77 – 6.74 (m, 5H), 4.66 (s, 1H), 4.37 (d, *J* = 13.1 Hz, 1H), 3.93 (d, *J* = 13.2 Hz, 1H), 3.43 (d, *J* = 12.3 Hz, 2H), 2.61 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.19 (d, *J* = 5.7 Hz, 2H), 1.48 – 1.26 (m, 6H), 0.92 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.6, 142.4, 140.0, 135.8, 135.0, 132.2, 131.9, 130.6, 128.8, 128.6, 126.9, 126.6, 126.5, 125.8, 123.9, 120.0, 118.3, 114.2, 75.2, 62.8, 51.6, 47.8, 40.2, 35.4, 34.5, 33.7, 22.4, 21.6, 14.0, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{38}H_{41}N_2O_3S$ $[M + H]^+$ 605.2832; found 605.2860.

2'-(3-Fluorophenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9h): Yield 76%, yellow solid, mp 200-203 ^oC; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2924.2, 2868.4, 1594.0, 1501.1, 1408.6, 1351.9, 1160.5, 1095.8, 764.6, 670.1 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.38 – 7.32 (m, 4H), 7.14 – 7.09 (m, 2H), 7.03 – 6.97 (m, 3H), 6.77 – 6.74 (m,

5H), 4.69 (d, *J* = 10.9 Hz, 1H), 4.35 (d, *J* = 13.3 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 3.50 – 3.39 (m, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.20 – 2.14 (m, 2H), 1.47 (d, *J* = 14.1 Hz, 1H), 1.39 – 1.32 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.3 (d, J_{C-F} = 245.7 Hz), 161.8, 145.5 (d, J_{C-F} = 6.9 Hz), 143.1, 142.5, 135.7, 135.0, 132.1, 131.9, 130.7, 130.3, 130.1 (d, J_{C-F} = 8.1 Hz), 128.8, 127.0, 126.7 (d, J_{C-F} = 28.9 Hz), 126.5, 123.9, 121.4, 120.0, 119.9, 118.4, 114.7 (d, J_{C-F} = 21.1 Hz), 114.5, 114.2, 113.0, 112.8 (d, J_{C-F} = 22.3 Hz), 74.6, 62.8, 51.5, 47.8, 40.1, 34.5, 21.4, 9.6. **HRMS** (Orbitrap ESI): calcd. for $C_{35}H_{32}FN_2O_3S$ $[M + H]^+$ 567.2118; found 567.2124.

7-Methyl-2'-(naphthalen-2-yl)-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9i): Yield 84%, white solid, mp 240-243 ^oC; Rf 0.40 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2923.1, 2863.7, 1502.5, 1407.5, 1339.8, 1159.3, 1094.3, 753.0, 666.8 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 4H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 4H), 7.39 – 7.35 (m, 3H), 7.00 (d, *J* = 6.3 Hz, 2H), 6.77 (d, *J* = 11.5 Hz, 5H), 4.88 (d, *J* = 9.5 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 4.01 (d, *J* = 13.3 Hz, 1H), 3.56 – 3.47 (m, 2H), 2.29 (s, 5H), 2.26 (s, 3H), 1.51 (d, *J* = 14.7 Hz, 1H), 1.44 – 1.38 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 142.5, 140.2, 135.8, 135.0, 133.4, 133.1, 132.2, 131.9, 130.7, 130.5, 128.8, 128.3, 128.1, 127.7, 127.0, 126.7, 126.5, 126.2, 125.9, 124.6, 124.0, 123.9, 120.0, 118.4, 114.2, 75.4, 62.9, 51.6, 48.0, 40.2, 34.5, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{38}H_{35}N_2O_3S$ $[M + H]^+$ 599.2362; found 599.2392.

2'-(4-Ethylphenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9j): Yield 79%, white solid, mp 155-157 ^oC; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2942.6, 1567.8, 1438.1, 1396.6, 1172.4, 1120.4, 758.8, 668.1 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.29 – 7.19 (m, 4H), 7.00 (s, 2H), 6.75 (d, *J* = 10.2 Hz, 5H), 4.68 – 4.65 (m, 1H), 4.37 (d, *J* = 13.4 Hz, 1H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.48 – 3.39 (m, 2H), 2.65 (dd, *J* = 14.8, 7.3 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.19 (d, *J* = 6.4 Hz, 2H), 1.46 (d, *J* = 14.3 Hz, 1H), 1.39 – 1.31 (m, 1H), 1.23 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 143.1, 142.4, 140.1, 135.8, 135.0, 132.2, 131.9, 130.6, 128.8, 128.0, 127.4, 126.9, 126.6, 126.5, 125.9, 125.0, 123.9, 120.0, 118.3, 114.2, 75.2, 62.8, 51.6, 47.8, 40.2, 34.5, 28.6, 21.6, 15.7, 9.6. **HRMS** (Orbitrap ESI): calcd. for $C_{36}H_{37}N_2O_3S$ $[M + H]^+$ 577.2525; found 577.2541.

2'-(3-Bromophenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9k): Yield 72%, light yellow solid, mp 175-177 ^oC; R_f

0.50 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2923.8, 2868.5, 1502.6, 1408.7, 1352.0, 1159.9, 1094.7, 756.0, 668.5 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.3 Hz, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 3H), 7.27 (s, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.77 – 6.75 (m, 5H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 13.6 Hz, 1H), 3.94 (d, *J* = 13.4 Hz, 1H), 3.48 (s, 1H), 3.42 (d, *J* = 11.7 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 2.19 (s, 1H), 2.14 (d, *J* = 11.8 Hz, 1H), 1.46 (s, 1H), 1.34 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 143.1, 142.5, 135.7, 134.9, 132.1, 131.9, 130.8, 130.7, 130.3, 130.1, 129.0, 128.8, 127.0, 126.7, 126.5, 124.5, 123.9, 122.7, 120.0, 119.9, 118.5, 114.2, 74.5, 62.8, 51.5, 47.9, 40.2, 34.4, 21.6, 9.6. **HRMS** (Orbitrap ESI): calcd. for $C_{34}H_{32}BrN_2O_3S$ $[M + H]^+$ 627.1317; found 627.1315.

2'-(4-Fluorophenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9l): Yield 78%, white solid, mp 180-183 ^{o}C; R_f 0.55 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2925.2, 1508.5, 1353.0, 1223.1, 1161.7, 1095.6, 764.0, 668.8 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.38 – 7.33 (m, 5H), 7.08 – 6.98 (m, 4H), 6.77 – 6.72 (m, 5H), 4.69 – 4.66 (m, 1H), 4.36 (d, *J* = 13.3 Hz, 1H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.50 – 3.39 (m, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 2.20 – 2.15 (m, 2H), 1.49 – 1.46 (m, 1H), 1.39 – 1.31 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5 (d, $J_{C\text{-}F}$ = 245.9 Hz), 161.1, 143.4, 143.1, 142.5, 138.6, 135.7, 135.0, 132.1, 131.9, 130.6, 130.4, 128.8, 127.6, 127.5 (d, $J_{C\text{-}F}$ = 7.9 Hz), 127.0, 126.7, 126.5, 123.9, 120.0, 119.9 (d, $J_{C\text{-}F}$ = 10.2 Hz), 118.4, 115.5, 115.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.2, 74.6, 62.8, 51.5, 47.9, 40.2, 34.4, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{34}H_{32}FN_2O_3S$ $[M + H]^+$ 567.2112; found 567.2136.

2'-(3-Methoxyphenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9m): Yield 87%, white solid, mp 225-228 ^{o}C; R_f 0.25 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2932.6, 2950.5, 1640.7, 1420.5, 1349.2, 1175.8, 1072.8, 760.8, 669.6 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.50 (s, 1H), 7.38 – 7.36 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.00 (s, 2H), 6.96 – 6.92 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.73 (m, 5H), 4.67 (d, *J* = 8.0 Hz, 2H), 4.37 (d, *J* = 13.4 Hz, 2H), 3.95 (d, *J* = 13.4 Hz, 2H), 3.83 (s, 3H), 3.50 – 3.39 (m, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.19 (d, *J* = 10.6 Hz, 2H), 1.46 (d, *J* = 13.3 Hz, 1H), 1.38 – 1.32 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 144.5, 143.1, 142.5, 135.8, 135.0, 132.2, 131.9, 130.6, 130.5, 129.6, 128.8, 127.0, 126.7, 126.5,

123.9, 120.0, 118.4, 118.2, 114.2, 113.6, 111.2, 75.2, 62.8, 55.4, 51.6, 47.9, 40.2, 34.5, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{35}H_{35}N_2O_4S$ [M + H] $^+$ 579.2318; found 579.2317.

2'-(3,5-Dimethoxyphenyl)-7-methyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo [2,3][1,4]diazocino[7,8,1-hi]indole-11,4'-pyran] (9n): Yield 86%, white solid, mp 235-240 ^{o}C; R_f 0.2 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2953.6, 2925.2, 1601.4, 1461.8, 1355.2, 1157.8, 1095.3, 760.3, 668.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.01 (dd, *J* = 7.2, 1.3 Hz, 2H), 6.74 (dd, *J* 7.6, 1.4 Hz, 5H), 6.53 (s, 2H), 6.40 (s, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 4.35 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 3.81 (s, 6H), 3.49 – 3.38 (m, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.19 – 2.17 (m, 2H), 1.45 (d, *J* = 13.3 Hz, 1H), 1.37 – 1.31 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 145.3, 143.1, 142.5, 135.8, 135.0, 132.2, 131.9, 130.6, 130.5, 128.8, 127.0, 126.7, 126.5, 123.9, 120.0, 118.4, 114.2, 103.7, 100.0, 75.3, 62.8, 55.5, 51.6, 47.9, 40.2, 34.4, 21.6, 9.5. **HRMS** (Orbitrap ESI): calcd. for $C_{36}H_{37}N_2O_5S$ [M + H] $^+$ 609.2423; found 609.2423.

2'-(4-Bromophenyl)-12-phenyl-6-tosyl-2',3',5',6,6',10b-hexahydro-5*H*-spiro[benzo[b]indeno [1,7-de]azocine-4,4'-pyran] (9o): Yield 93%, white solid, mp 230-232 ^{o}C; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2925.2, 2866.3, 1504.3, 1409.1, 1353.0, 1161.6, 1095.5, 761.2, 668.8 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.43 (m, 7H), 7.37 – 7.33 (m, 1H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.11 – 7.04 (m, 3H), 6.76 – 6.70 (m, 4H), 4.69 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 13.3 Hz, 1H), 4.03 (d, *J* = 13.2 Hz, 1H), 3.51 – 3.40 (m, 2H), 2.24 – 2.11 (m, 2H), 2.02 (s, 3H), 1.49 – 1.36 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 141.8, 135.6, 135.5, 134.3, 132.5, 132.2, 131.7, 130.8, 130.7, 129.4, 129.0, 128.8, 127.9, 127.6, 127.4, 127.0, 126.6, 126.4, 124.1, 121.6, 120.9, 120.5, 120.4, 119.4, 74.6, 62.8, 51.6, 48.0, 40.3, 34.5, 21.3. **HRMS** (Orbitrap ESI): calcd. for $C_{39}H_{34}BrN_2O_3S$ [M + H] $^+$ 689.1474; found 689.1458.

12-Phenyl-2'-(*p*-tolyl)-6-tosyl-2',3',5',6,6',10b-hexahydro-5*H*-spiro[benzo[b]indeno[1,7-de]azocine-4,4'-pyran] (9p): Yield 91%, white solid, mp 200-203 ^{o}C; R_f 0.47 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 3031.1, 2924.0, 1503.0, 1407.6, 1341.2, 1159.6, 1096.5, 760.9, 667.3 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 5.7 Hz, 2H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.53 – 7.43 (m, 5H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.08 (s, 3H), 6.76 – 6.70 (m, 4H), 4.70 – 4.68 (m, 1H), 4.42 (d, *J* = 13.3 Hz, 1H), 4.02 (d, *J* = 13.3 Hz, 1H), 3.45 (dd, *J* = 21.6, 8.5 Hz, 2H), 2.36 (s, 3H), 2.22 (d, *J* = 5.3 Hz, 2H), 2.02 (s, 3H),

1.44 (t, *J* = 13.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 142.8, 139.8, 137.5, 135.7, 135.6, 134.3, 132.5, 132.2, 131.0, 130.8, 129.4, 129.2, 129.0, 128.8, 127.9, 127.3, 127.0, 126.6, 126.4, 125.8, 124.1, 120.9, 120.6, 120.5, 119.3, 75.2, 62.6, 51.7, 48.1, 40.3, 34.6, 21.2. **HRMS** (Orbitrap ESI): calcd. for $C_{40}H_{37}N_2O_3S$ $[M + H]^+$ 625.2525; found 625.2513.

12-Phenyl-2'-(o-tolyl)-6-tosyl-2',3',5',6,6',10b-hexahydro-5*H*-spiro[benzo[b]indeno[1,7-de]azocine-4,4'-pyran] (9q): Yield 88%, white solid, mp 180-183 ^oC; R_f 0.50 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2983.6, 1552.8, 1438.1, 1323.7, 1127.8, 1082.6, 762.4, 668.4 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (t, *J* = 5.7 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.48 – 7.44 (m, 5H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.21 (dd, *J* = 14.3, 7.6 Hz, 3H), 7.09 (d, *J* = 6.0 Hz, 2H), 7.03 (s, 1H), 6.73 (q, *J* = 8.2 Hz, 4H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.45 (d, *J* = 13.3 Hz, 1H), 4.06 (d, *J* = 13.3 Hz, 1H), 3.54 – 3.44 (m, 2H), 2.43 (s, 3H), 2.24 – 2.17 (m, 2H), 2.01 (s, 3H), 1.50 – 1.43 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 142.8, 140.8, 135.7, 135.5, 134.3, 134.0, 132.5, 132.2, 131.0, 130.8, 130.4, 129.3, 129.0, 128.8, 127.9, 127.5, 127.3, 127.0, 126.5, 125.4, 124.1, 120.9, 120.6, 120.5, 119.3, 71.9, 63.0, 51.4, 46.7, 40.4, 34.7, 21.2, 19.2. **HRMS** (Orbitrap ESI): calcd. for $C_{40}H_{37}N_2O_3S$ $[M + H]^+$ 625.2525; found 625.2514.

2'-(3-Fluorophenyl)-12-phenyl-6-tosyl-2',3',5',6,6',10b-hexahydro-5*H*-spiro[benzo[b]indeno [1,7-de]azocine-4,4'-pyran] (9r): Yield 87%, ligth yellow solid, mp 185-187 ^oC; R_f 0.55 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 3066.4, 1595.0, 1500.0, 1342.0, 1159.7, 1097.6, 764.7, 699.5 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 6.6 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.44 (m, 5H), 7.37 – 7.31 (m, 2H), 7.15 – 7.07 (m, 5H), 7.02 – 6.98 (m, 1H), 6.73 (q, *J* = 8.0 Hz, 4H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.40 (d, *J* = 13.3 Hz, 1H), 4.03 (d, *J* = 13.3 Hz, 1H), 3.53 – 3.41 (m, 2H), 2.27 – 2.14 (m, 2H), 2.02 (s, 3H), 1.49 – 1.37 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.3 (d, $J_{C\text{-}F}$ = 246.0 Hz), 161.8, 145.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 142.9, 130.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.0, 128.8, 127.9, 127.4 (d, $J_{C\text{-}F}$ = 33.8 Hz), 127.0, 126.6, 126.5, 120.4, 119.4, 114.8 (d, $J_{C\text{-}F}$ = 21.1 Hz), 114.5, 113.0, 112.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 74.6, 62.7, 51.6, 47.9, 40.3, 34.5, 21.3. **HRMS** (Orbitrap ESI): calcd. for $C_{39}H_{34}FN_2O_3S$ $[M + H]^+$ 629.2274; found 629.2264.

2'-Isopropyl-7-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino [7,8,1-hi]indole-11,4'-pyran] (9s): Yield 85%, white solid, mp 175-177 ^oC; R_f 0.65 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2960.1, 1503.5, 1342.8, 1221.3, 1160.6, 1091.0, 765.8, 668.5 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.60 (d, *J* = 6.7 Hz, 2H), 7.48 (s, 4H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.73 (s, 4H), 4.24 (d, *J* = 13.1 Hz, 1H), 4.03 – 3.90

(m, 2H), 3.78 (t, *J* = 11.7 Hz, 1H), 2.89 (s, 1H), 2.28 (s, 1H), 2.04 (s, 4H), 1.70 (d, *J* = 11.5 Hz, 1H), 1.18 (s, 1H), 0.98 – 0.90 (m, 1H), 0.53 (d, *J* = 6.0 Hz, 3H), 0.34 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 142.7, 135.6, 134.4, 132.7, 132.3, 131.5, 130.9, 129.4, 128.9, 128.8, 128.0, 127.3, 127.1, 126.6, 126.4, 123.8, 121.0, 120.6, 120.5, 119.2, 63.7, 52.2, 40.1, 40.0, 36.6, 32.7, 21.3, 18.5, 17.9. **HRMS** (Orbitrap ESI): calcd. for $C_{36}H_{37}N_2O_3S$ $[M + H]^+$ 577.2525; found 577.252.

2'-Isopropyl-7-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino [7,8,1-hi]indole-11,4'-pyran] (10s): Yield 5%, white solid, mp 178-181 ^oC; R_f 0.61 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 3027.4, 2929.3, 1501.9, 1405.4, 1342.6, 1219.7, 1163.0, 1099.3, 771.0, 698.8, 672.9 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.8 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.59 (d, *J* = 5.9 Hz, 2H), 7.49 (d, *J* = 6.1 Hz, 3H), 7.43 – 7.35 (m, 3H), 7.17 (s, 2H), 7.05 (s, 1H), 6.74 (s, 4H), 4.26 – 4.23 (m, 1H), 3.90 – 3.86 (m, 1H), 3.36 – 3.23 (m, 3H), 2.03 (s, 3H), 1.95 – 1.89 (m, 1H), 1.69 (d, *J* = 7.0 Hz, 1H), 1.39 – 1.26 (m, 3H), 0.99 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 142.7, 135.8, 135.7, 134.4, 132.5, 132.1, 131.5, 130.7, 129.3, 129.0, 128.8, 127.9, 127.2, 127.0, 126.5, 126.4, 124.0, 120.9, 120.4, 119.2, 62.5, 51.9, 42.4, 39.8, 34.9, 33.8, 21.3, 18.6, 18.3. **HRMS** (Orbitrap ESI): calcd. for $C_{36}H_{37}O_3N_2S$ $[M + H]^+$ 577.2519; found 577.2530.

2'-Butyl-7-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino[7,8,1-hi]indole-11,4'-pyran] (9t): Yield 82%, white solid, mp 182-185 ^oC; R_f 0.69 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2925.9, 2854.8, 1505.1, 1458.7, 1353.8, 1165.0, 1092.57, 746.2, 710.3, 662.5 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.41 – 7.34 (m, 3H), 7.15 (d, *J* = 4.5 Hz, 2H), 7.06 (s, 1H), 6.73 (q, *J* = 8.2 Hz, 4H), 4.24 (d, *J* = 13.5 Hz, 1H), 3.88 (d, *J* = 13.4 Hz, 1H), 3.64 – 3.60 (m, 1H), 3.35 – 3.23 (m, 2H), 2.03 (s, 3H), 1.94 – 1.88 (m, 1H), 1.36 – 1.33 (m, 3H), 1.26 (s, 6H), 0.94 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 142.7, 135.7, 134.4, 132.5, 132.1, 131.3, 130.7, 129.3, 128.9, 128.8, 127.9, 127.2, 127.0, 126.5, 126.4, 124.0, 120.9, 120.5, 120.4, 119.2, 72.7, 62.4, 51.8, 45.7, 39.9, 37.0, 34.9, 27.7, 22.8, 21.3, 14.1. **HRMS** (Orbitrap ESI): calcd. for $C_{37}H_{39}N_2O_3S$ $[M + H]^+$ 591.2681; found 591.2682.

2'-Butyl-7-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4]diazocino[7,8,1-hi]indole-11,4'-pyran] (10t): Yield 7%, white solid, mp 187-189 ^oC; R_f 0.65 (25% ethyl acetate in hexanes); **IR** (neat) ṽ = 2929.0, 2864.1, 1602.1, 1502.3, 1407.3, 1342.3, 1219.5, 1160.2,

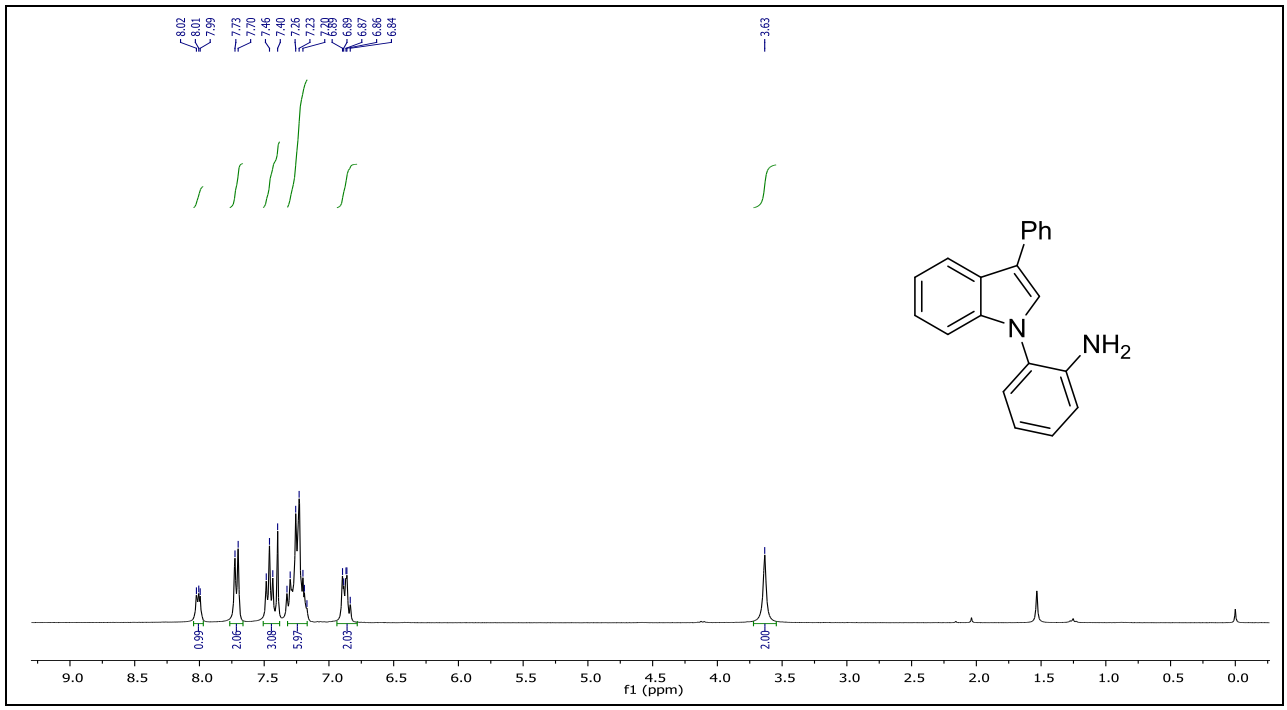
1089.4, 768.4, 669.9 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 5.3 Hz, 4H), 7.42 – 7.33 (m, 2H), 7.15 (d, *J* = 3.6 Hz, 2H), 7.08 (s, 1H), 6.73 (d, *J* = 4.5 Hz, 4H), 4.24 (d, *J* = 13.3 Hz, 1H), 4.00 (d, *J* = 9.3 Hz, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.80 (t, *J* = 12.2 Hz, 1H), 3.13 (d, *J* = 8.7 Hz, 1H), 2.28 (t, *J* = 12.0 Hz, 1H), 2.04 (s, 3H), 1.63 – 1.59 (m, 2H), 1.26 (s, 2H), 1.13 – 1.08 (m, 3H), 0.97 – 0.88 (m, 2H), 0.78 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 142.7, 135.6, 134.4, 132.6, 132.2, 131.3, 130.7, 129.4, 128.9, 128.8, 127.9, 127.2, 127.0, 126.5, 126.4, 124.0, 121.0, 120.5, 119.2, 71.7, 63.7, 52.2, 40.3, 40.0, 39.8, 35.6, 27.3, 22.6, 21.3, 14.0. **HRMS** (Orbitrap ESI): calcd. for $C_{37}H_{39}O_3N_2S$ $[M + H]^+$ 591.2676; found 591.2690.

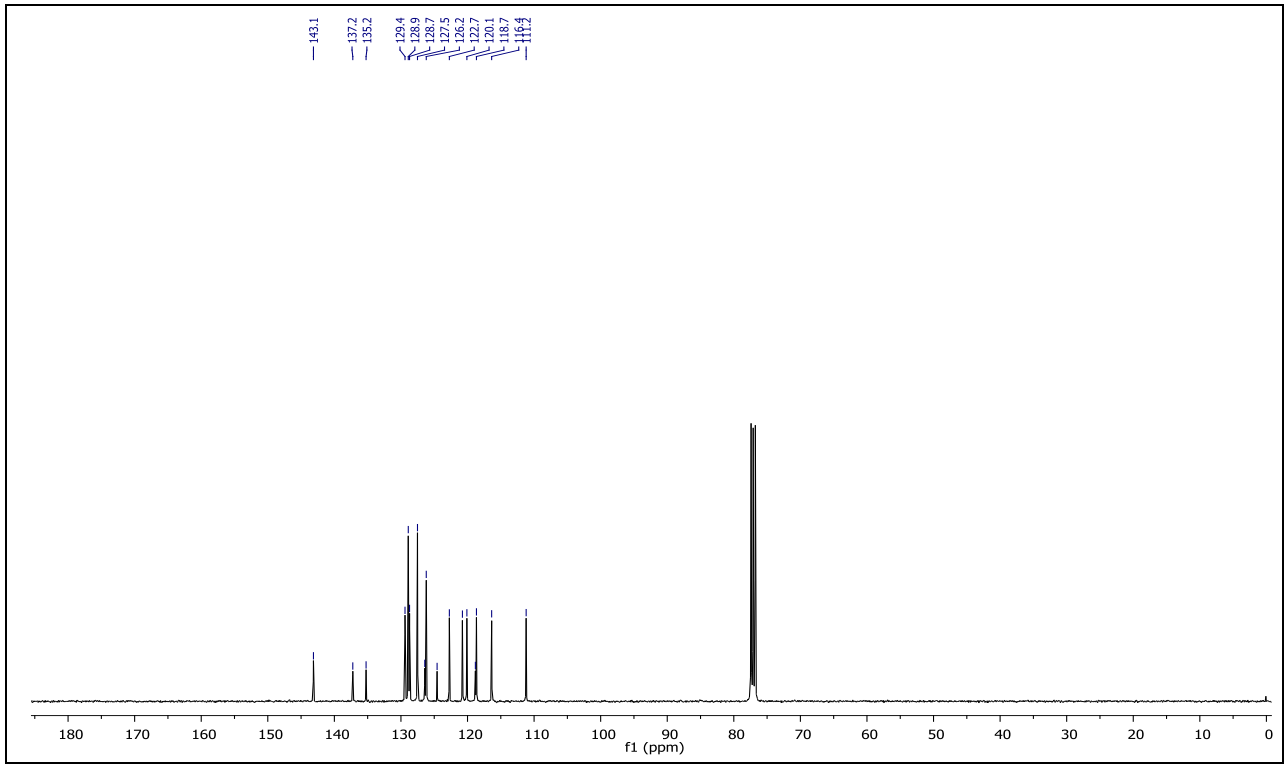
9-Chloro-7-phenyl-2'-(p-tolyl)-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9u): Yield 90%, white solid, mp 213-216 ^{o}C; R_f 0.49 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 3848.9, 3667.8, 3539.9, 3250.2, 2956.0, 2925.8, 1555.71, 1512.4, 1462.1, 769.3, 644.3 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) (racemic mixture, dr 1:0.9) δ 7.89 – 7.83 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.37 (m, 11H), 7.30 (d, *J* = 6.5 Hz, 2H), 7.15 (s, 2H), 7.09 – 7.02 (m, 8H), 6.97 (d, *J* = 7.5 Hz, 4H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 5.0 Hz, 4H), 4.53 (dd, *J* = 28.2, 12.7 Hz, 4H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.25 (d, *J* = 11.2 Hz, 1H), 3.76 – 3.56 (m, 5H), 2.28 (s, 3H), 2.23 (s, 2H), 2.01 (s, 5H), 1.90 – 1.87 (m, 2H), 1.67 – 1.64 (m, 2H), 1.53 – 1.48 (m, 3H), 1.38 – 1.28 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 138.7, 138.4, 137.6, 137.5, 136.1, 135.6, 133.4, 133.3, 133.2, 132.0, 131.4, 131.3, 131.2, 131.1, 130.2, 130.1, 128.9, 128.8, 128.7, 128.3, 128.0, 127.9, 127.7, 127.6, 127.5, 127.3, 126.4, 126.3, 126.2, 125.9, 125.1, 124.6, 124.5, 122.9, 119.1, 116.6, 110.8, 110.7, 74.0, 73.2, 63.4, 63.2, 57.5, 57.1, 45.1, 41.7, 39.4, 39.3, 39.2, 33.8, 21.2, 21.1. **HRMS** (Orbitrap ESI): calcd. for $C_{40}H_{36}N_2O_3SCl$ $[M + H]^+$ 659.2135; found 659.2137.

9-Chloro-2'-isopropyl-7-phenyl-13-tosyl-2',3',5',6',12,13-hexahydrospiro[benzo[2,3][1,4] diazocino[7,8,1-hi]indole-11,4'-pyran] (9v): Yield 87%, white solid, mp 193 - 195 ^{o}C; R_f 0.69 (25% ethyl acetate in hexanes); **IR** (neat) $\tilde{\nu}$ = 2965.1, 2852.3, 1648.5, 1509.5, 1483.9, 1342.8, 1261.3, 1182.6, 1069.0, 752.8, 672.5 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) (racemic mixture dr 1:0.6) δ 7.83 – 7.80 (m, 2H), 7.55 (dt, *J* = 7.9, 5.0 Hz, 3H), 7.47 – 7.38 (m, 7H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 7.10 – 7.01 (m, 7H), 6.90 (dd, *J* = 7.4, 1.7 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 3H), 4.37 (dd, *J* = 13.9, 5.0 Hz, 3H), 3.56 (dd, *J* = 12.3, 5.2 Hz, 1H), 3.47 – 3.36 (m, 2H), 3.00 – 2.93 (m, 2H), 2.01 (s, 5H), 1.76 – 1.73 (m, 1H), 1.45 – 1.37

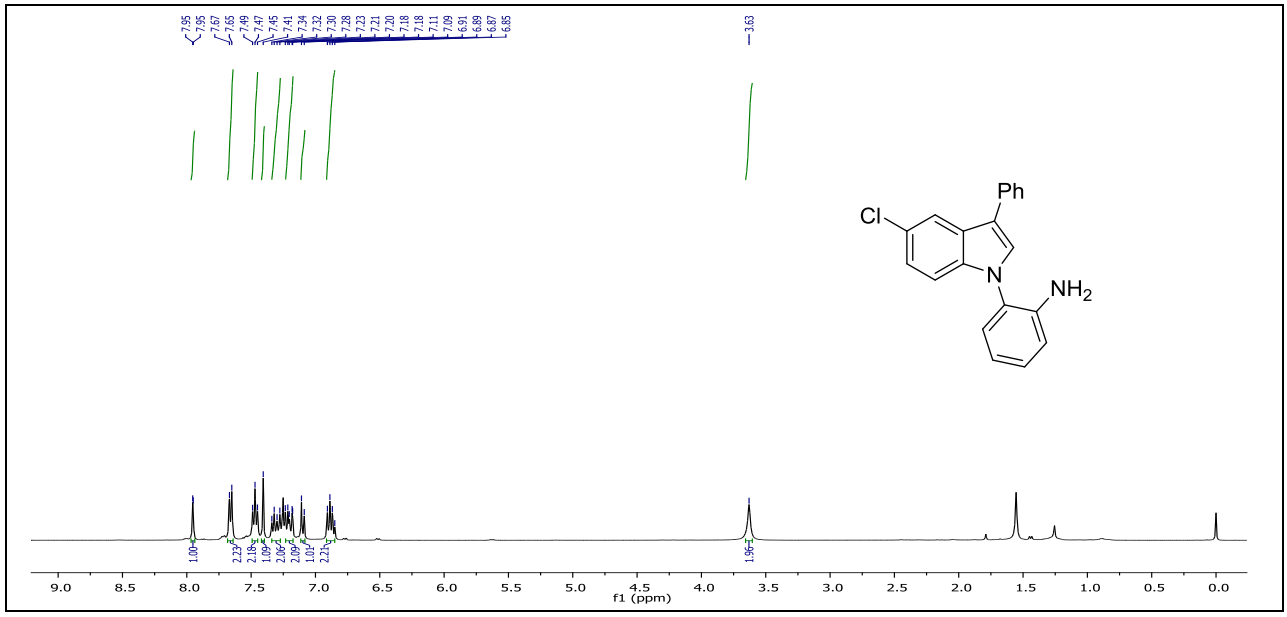
(m, 2H), 1.33 – 1.23 (m, 2H), 1.16 (d, *J* = 12.4 Hz, 1H), 1.04 – 0.98 (m, 1H), 0.64 (d, *J* = 6.8 Hz, 2H), 0.61 (d, *J* = 6.8 Hz, 3H), 0.46 (d, *J* = 6.8 Hz, 3H), 0.42 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 139.5, 139.2, 138.6, 138.4, 136.1, 135.7, 133.4, 132.1, 131.9, 131.4, 131.3, 131.1, 130.1, 130.0, 128.7, 128.3, 127.8, 127.6, 127.4, 126.3, 125.9, 125.8, 124.5, 122.9, 122.8, 119.1, 116.5, 116.4, 110.7, 63.1, 62.6, 57.5, 57.3, 42.5, 39.6, 38.8, 36.1, 33.9, 33.0, 32.7, 21.2, 18.5, 18.0, 17.7, 17.4. **HRMS** (Orbitrap ESI): calcd. for $C_{36}H_{36}N_2O_3SCl$ $[M + H]^+$ 611.2135; found 611.2133.

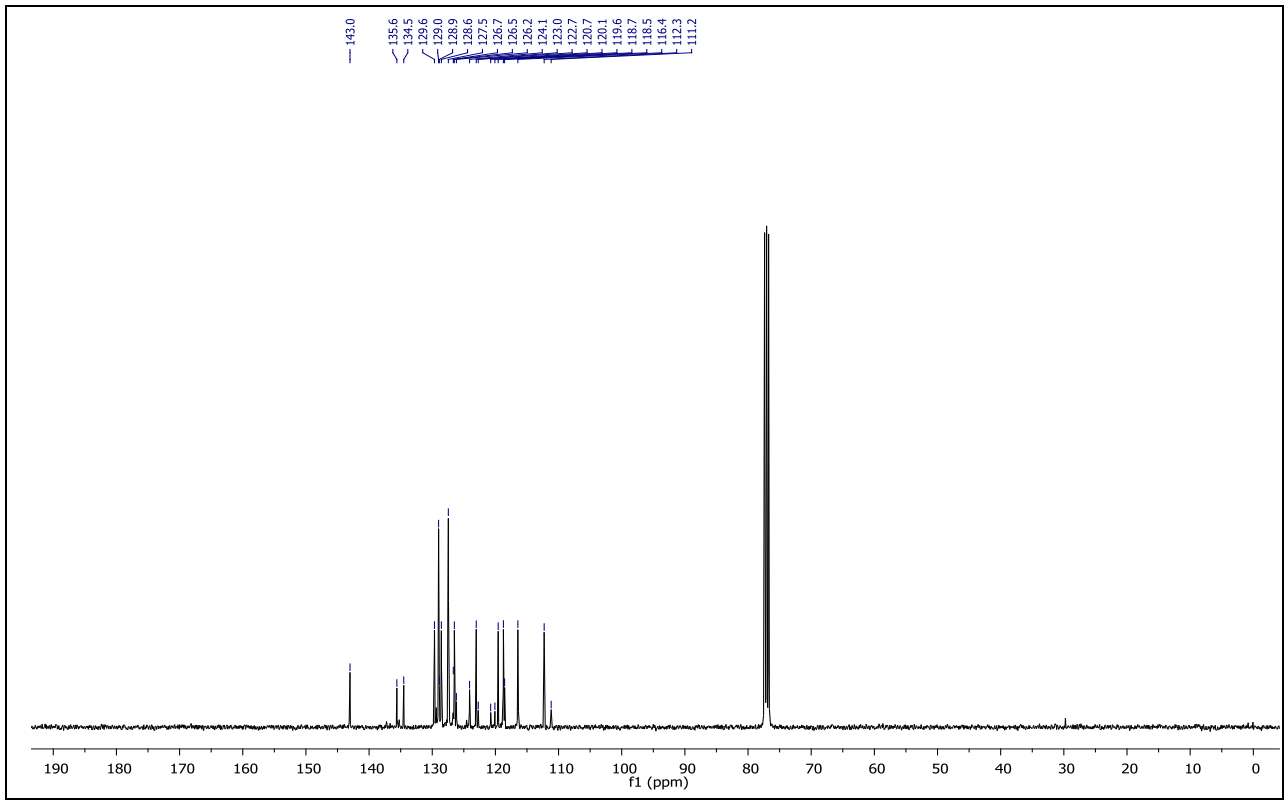
3. Copies of NMR spectra of products: ^{1}H and ^{13}C NMR spectra of compound 3



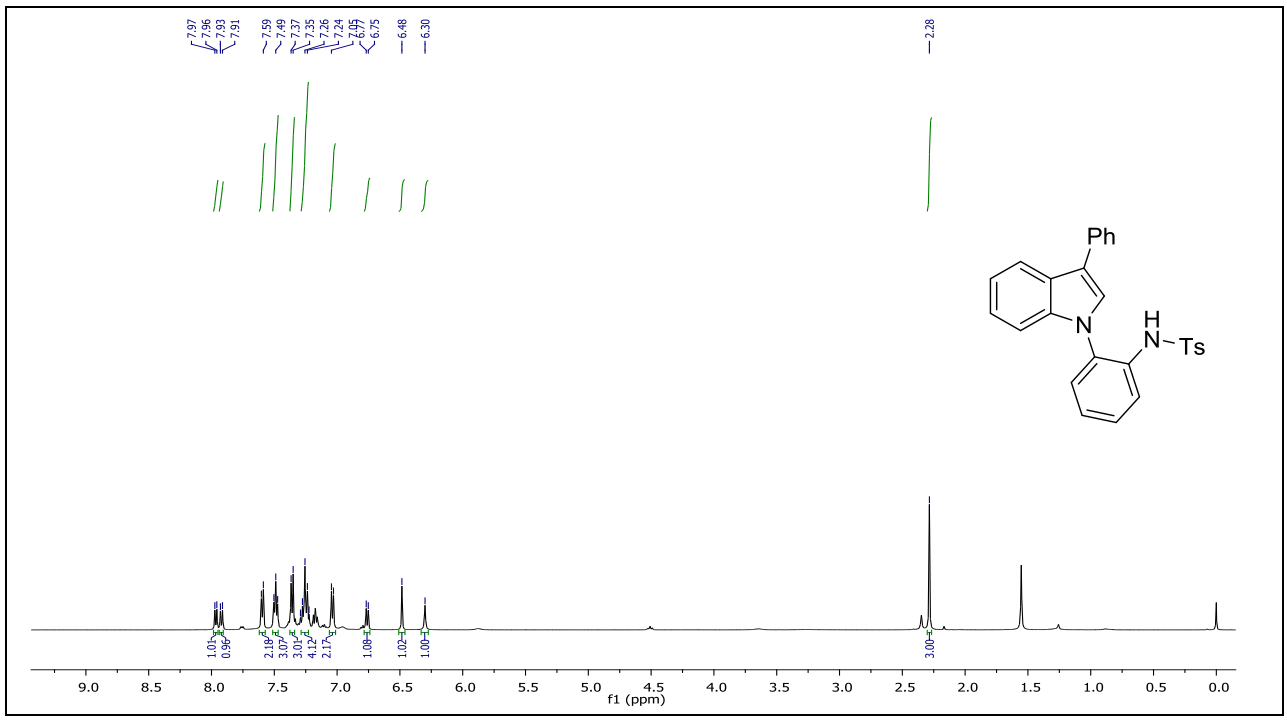


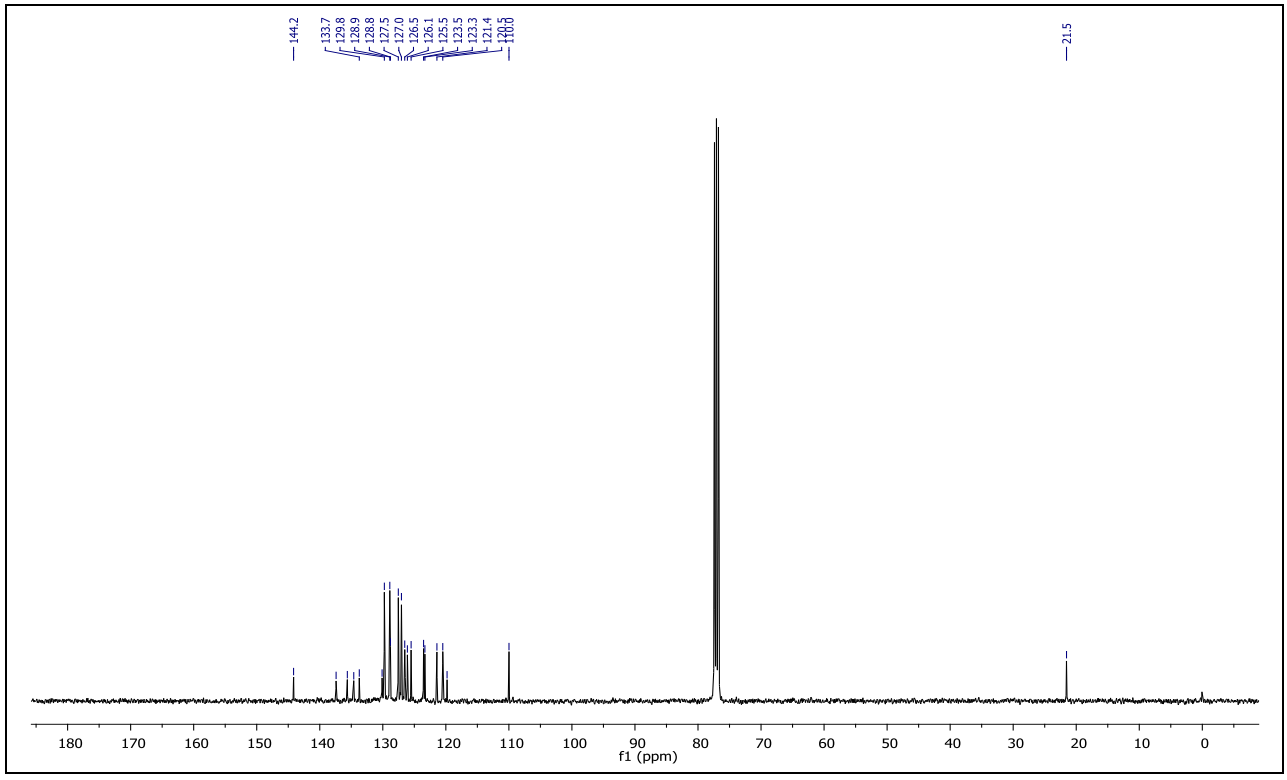
^{1}H and ^{13}C NMR spectra of compound 3a



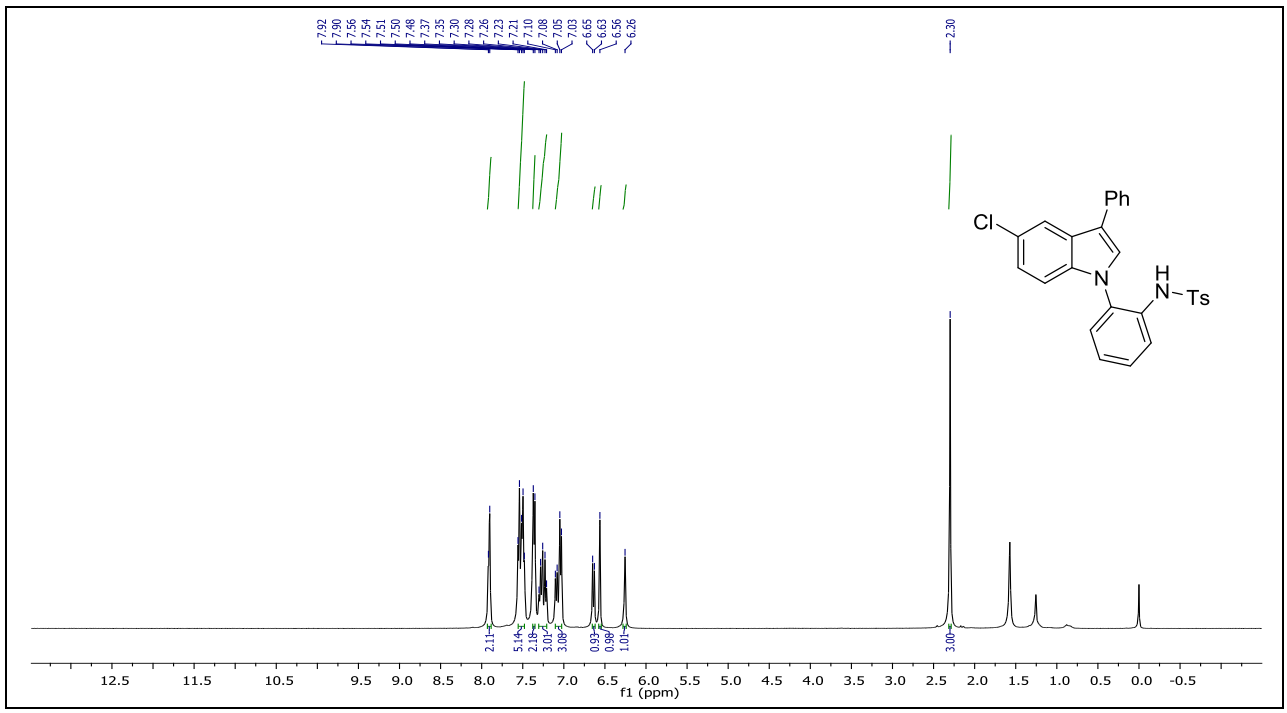


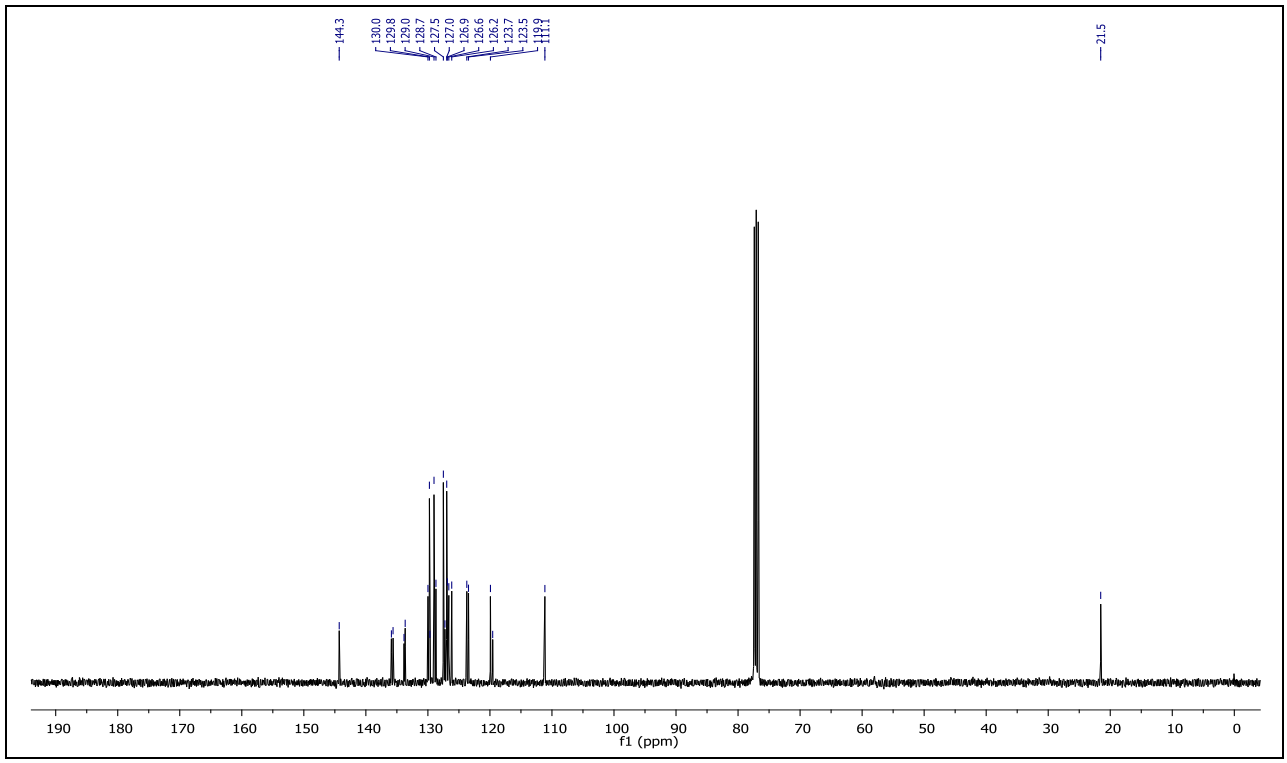
^{1}H and ^{13}C NMR spectra of compound 4b



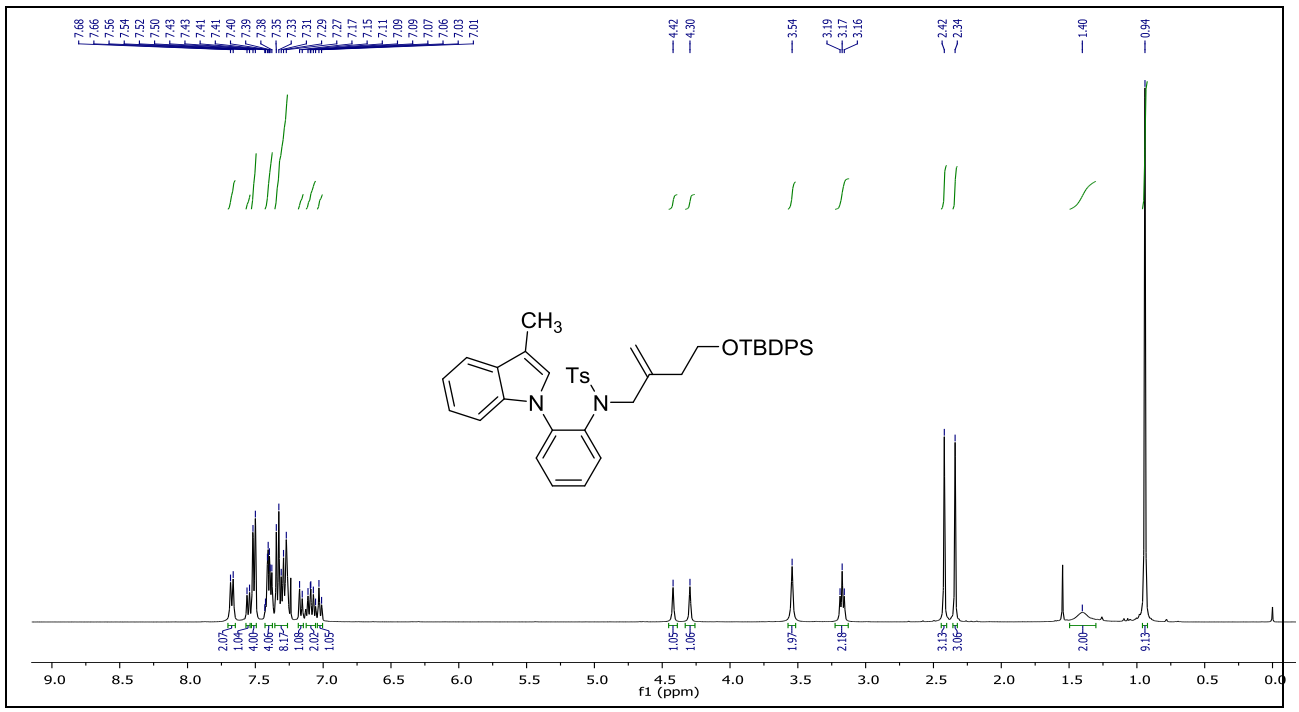


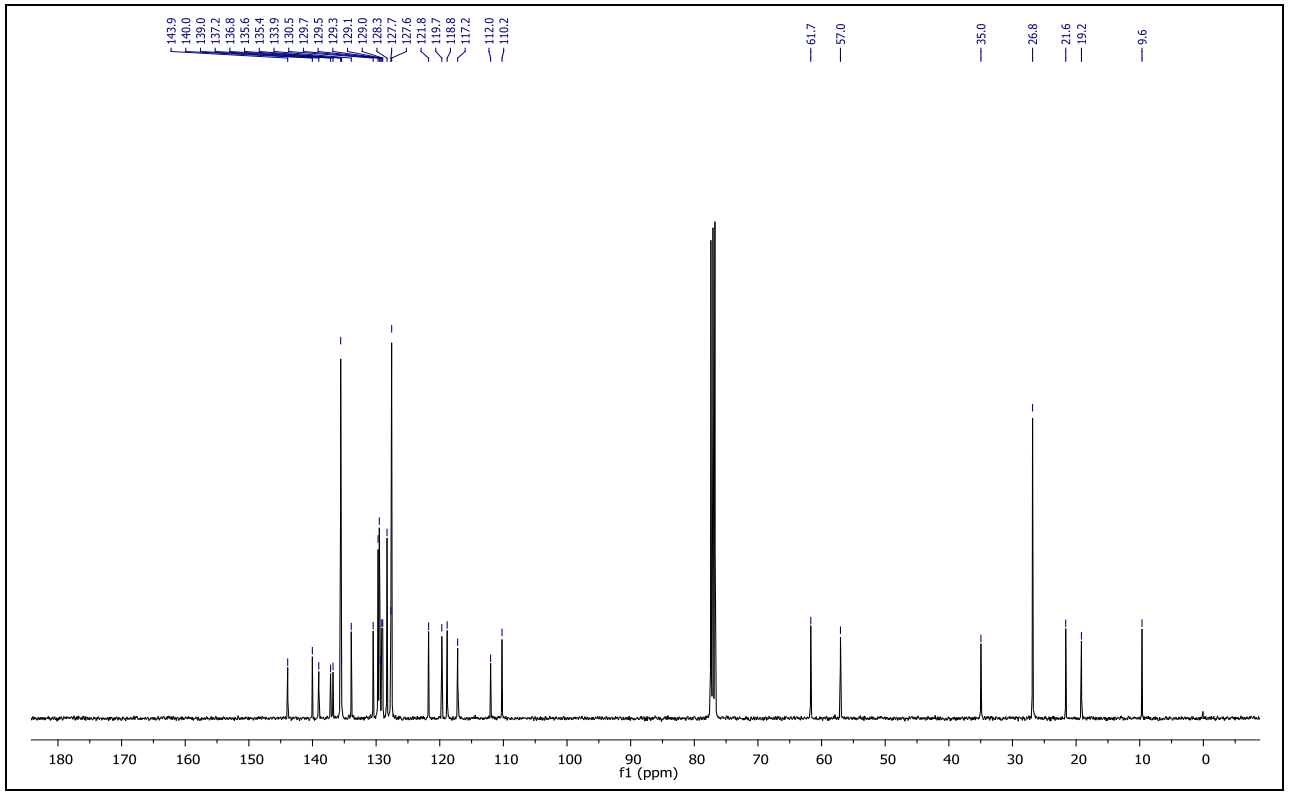
^{1}H and ^{13}C NMR spectra of compound 4c



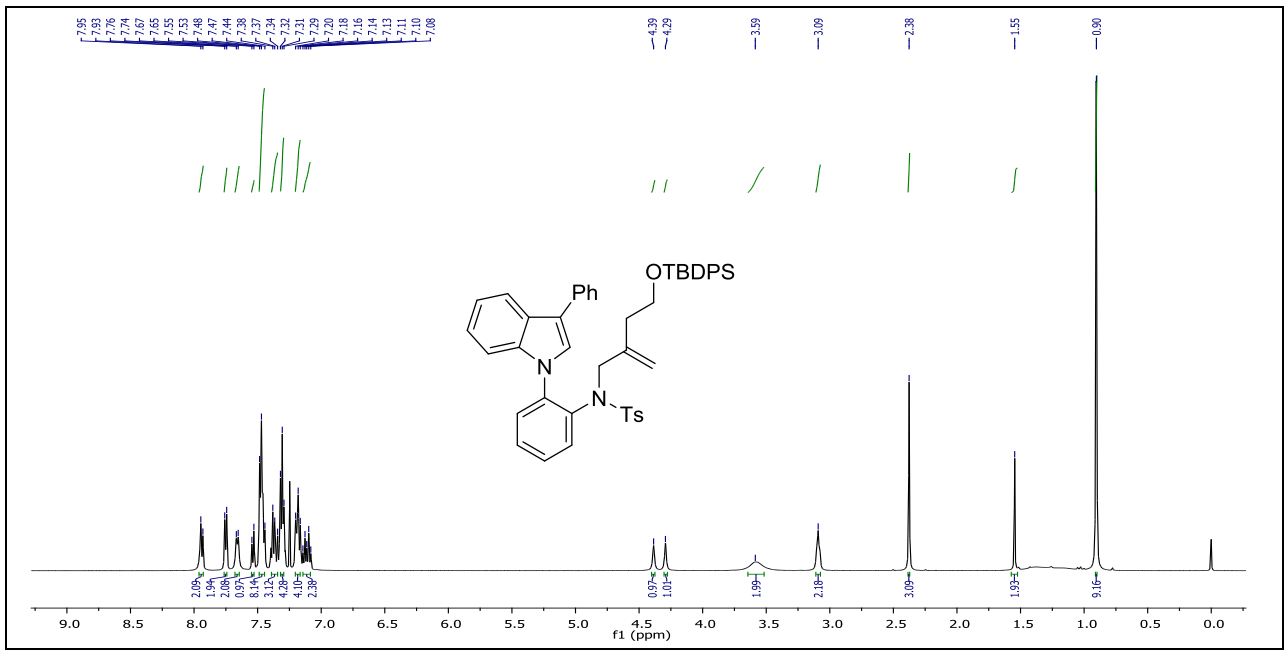


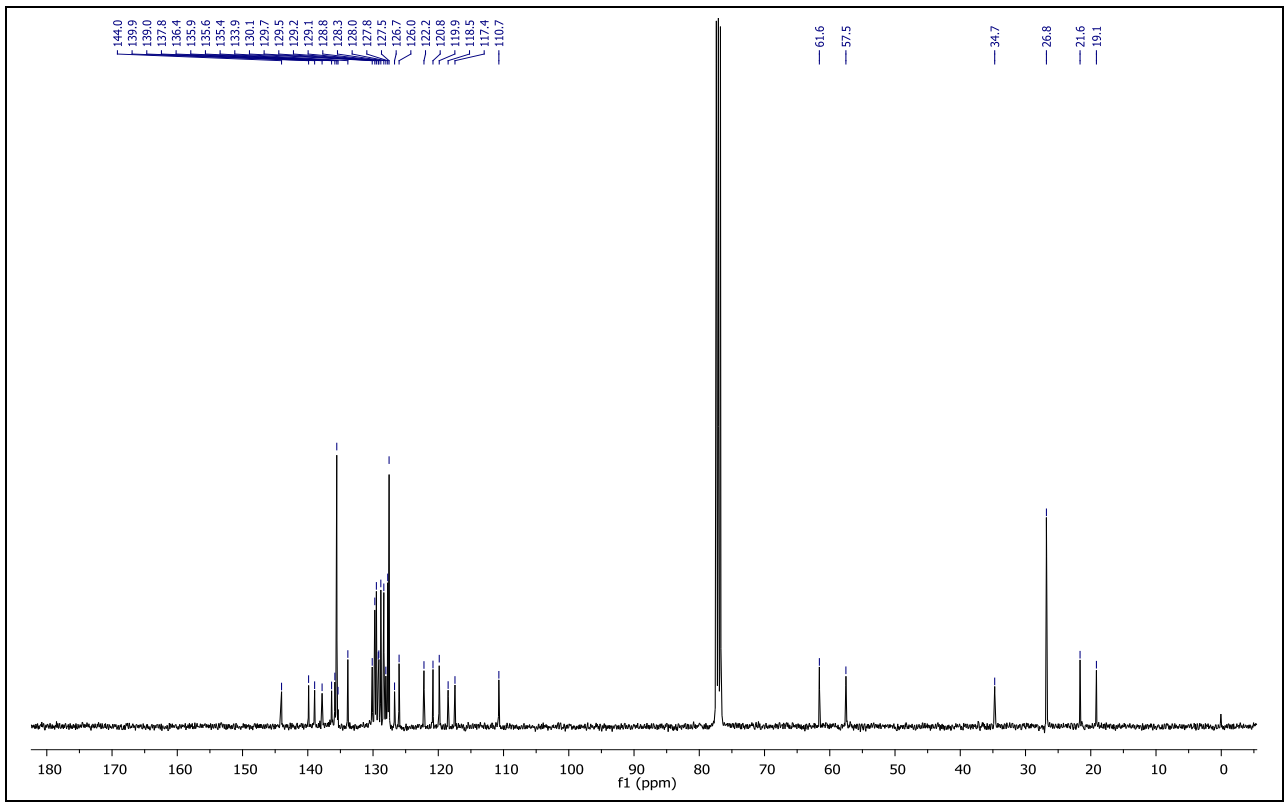
^{1}H and ^{13}C NMR spectra of compound 6a



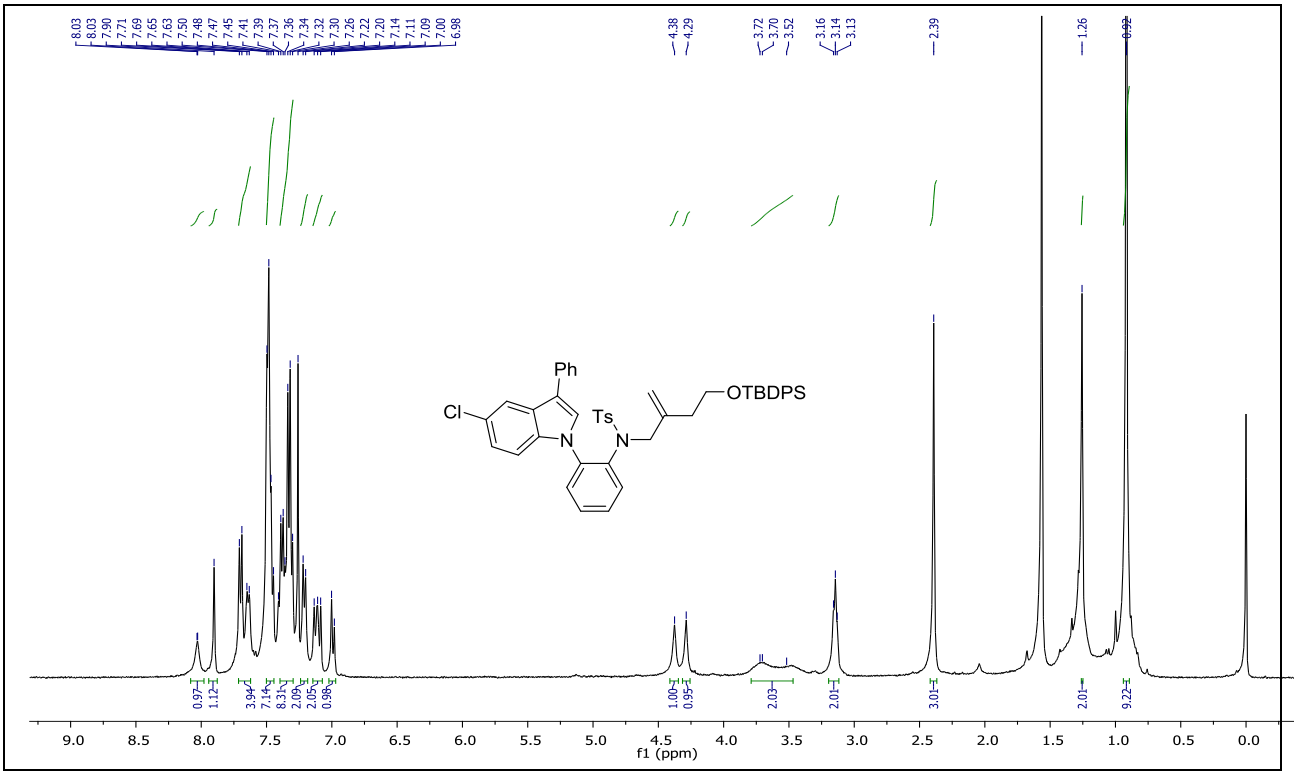


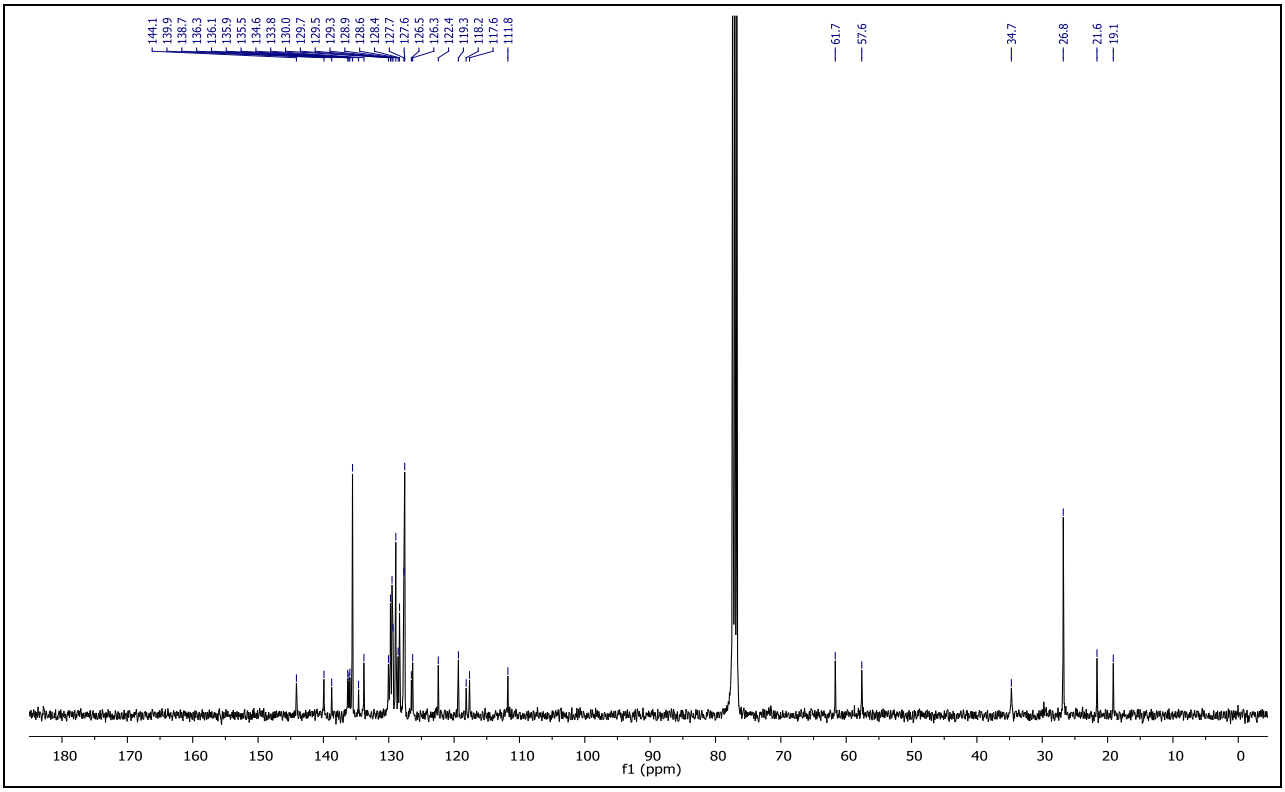
^{1}H and ^{13}C NMR spectra of compound 6b



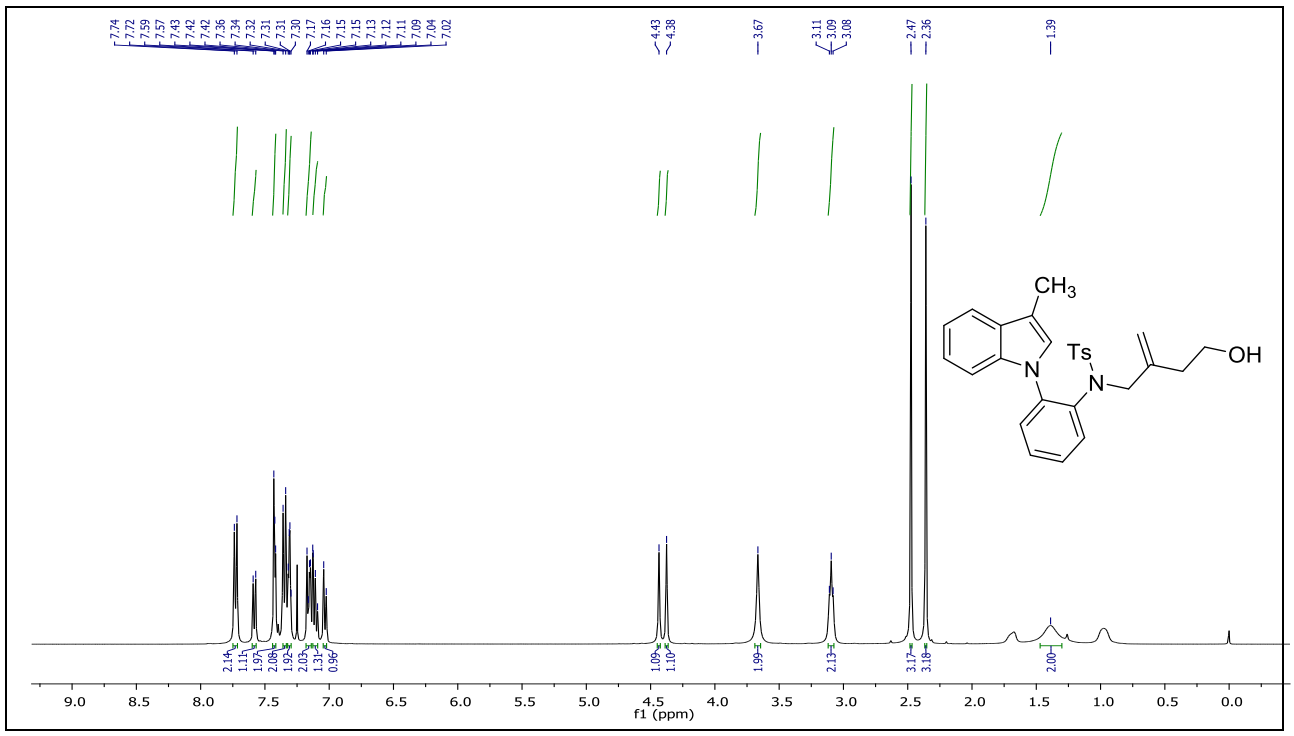


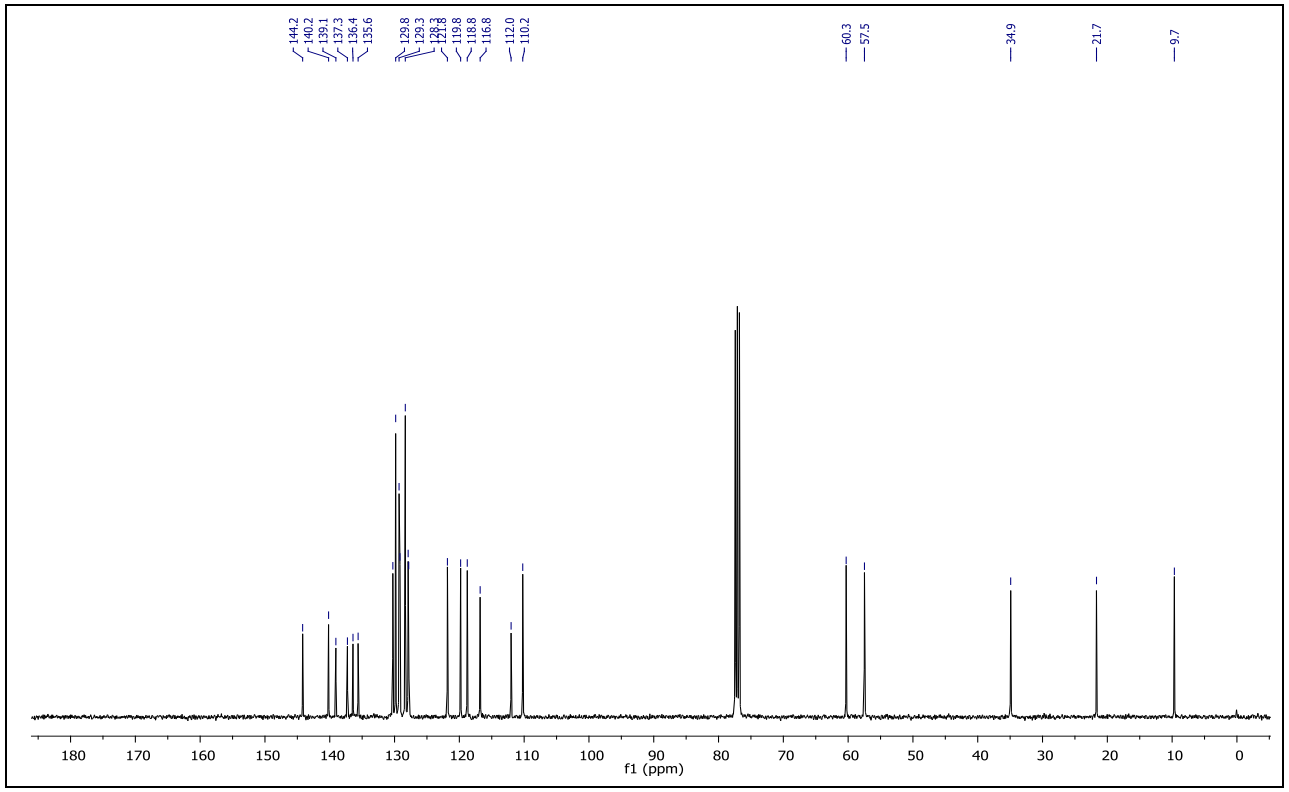
^{1}H and ^{13}C NMR spectra of compound 6c



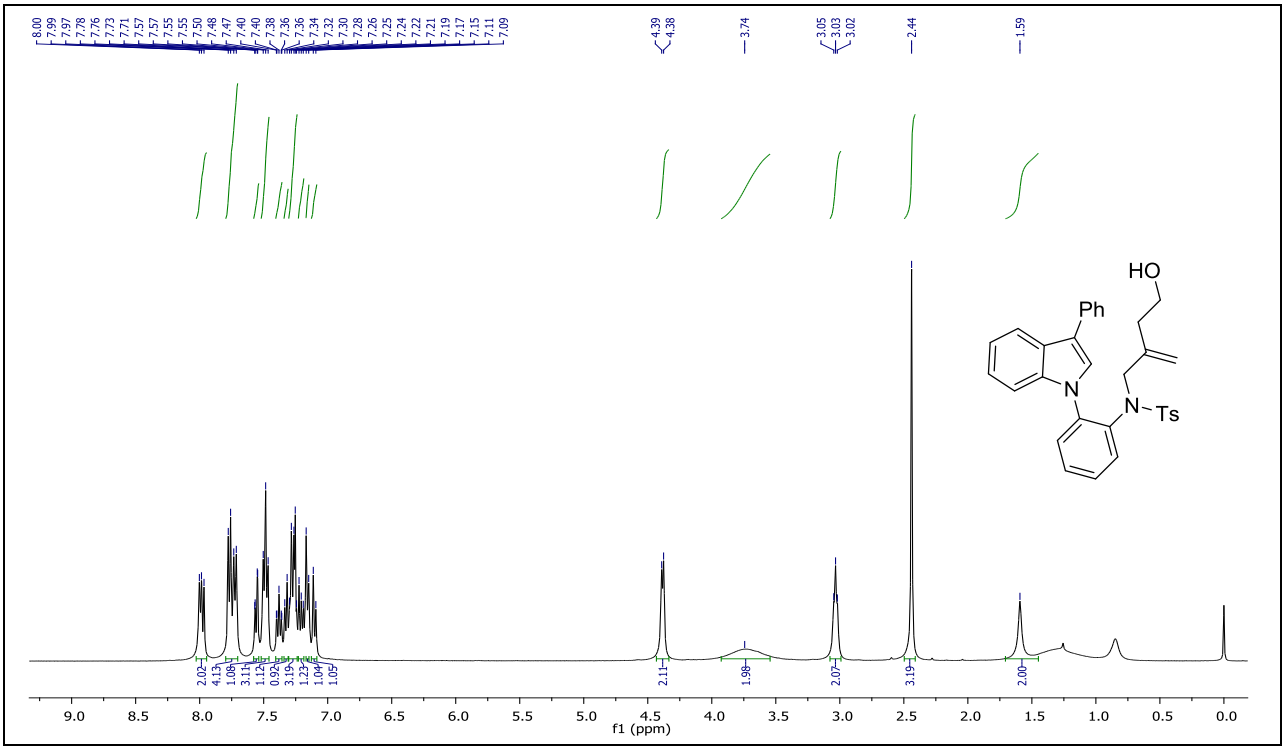


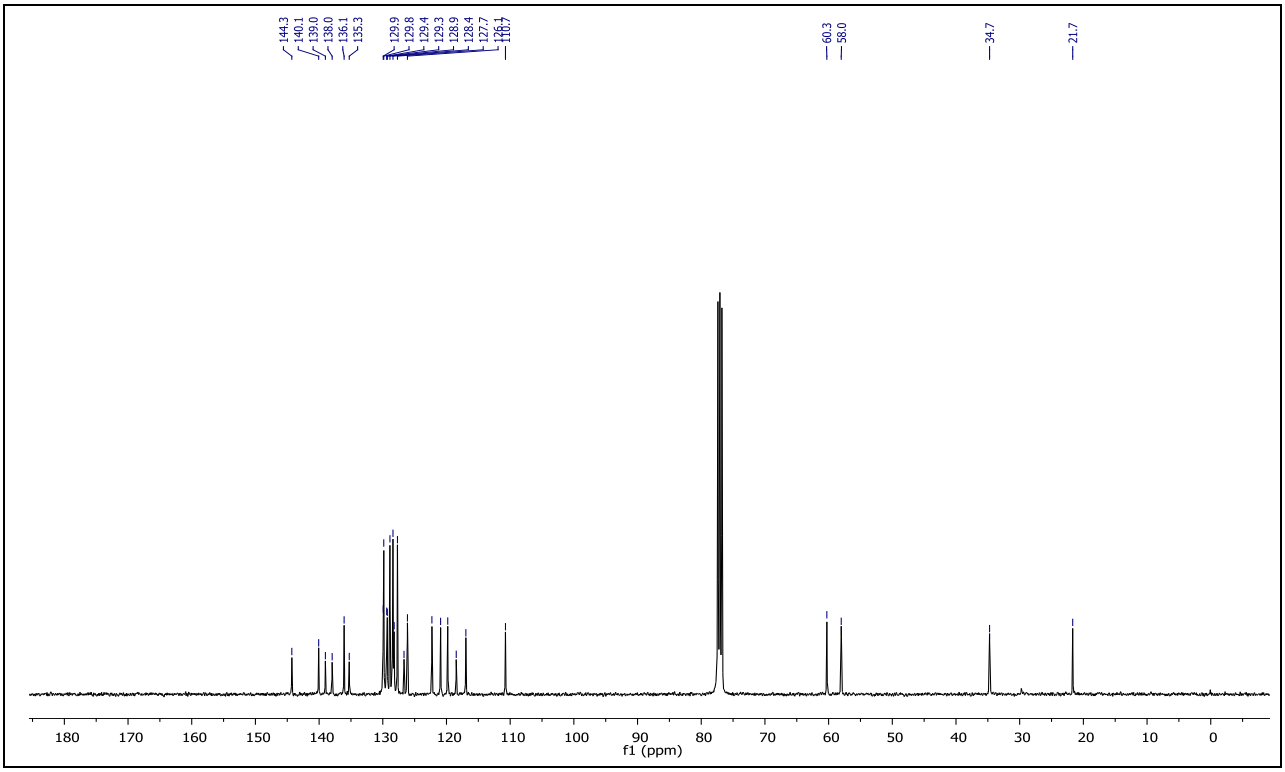
^{1}H and ^{13}C NMR spectra of compound 7a



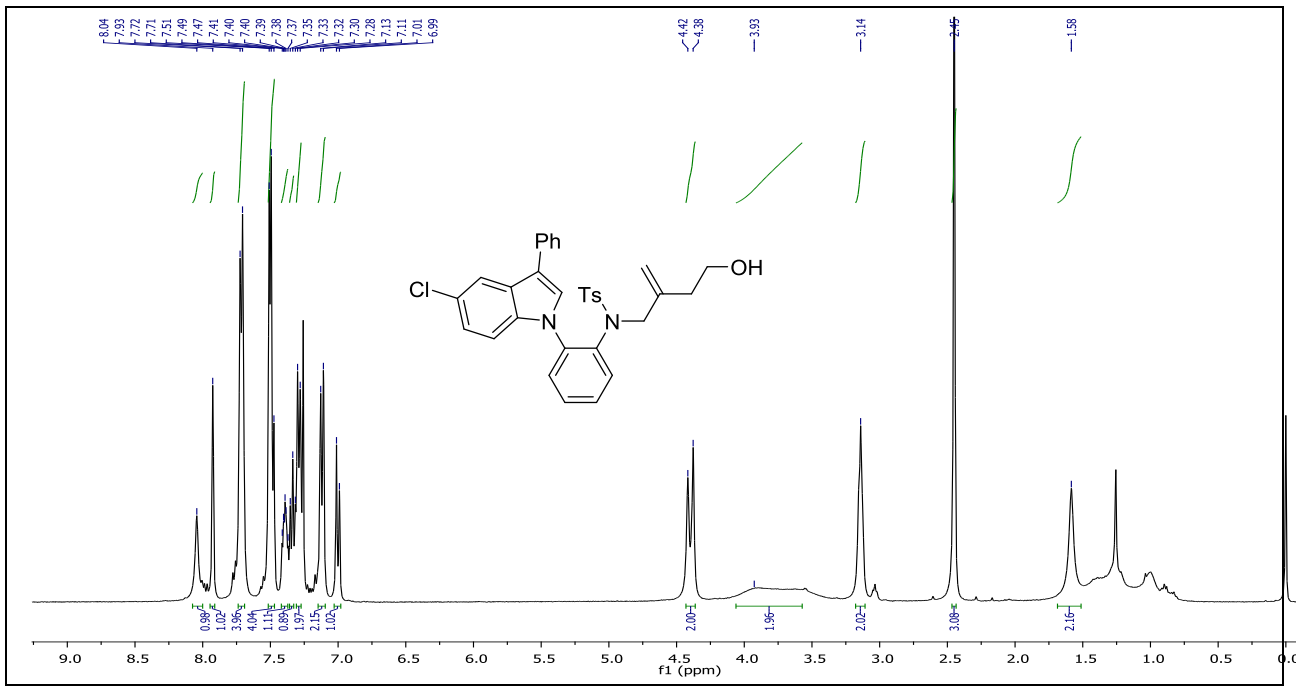


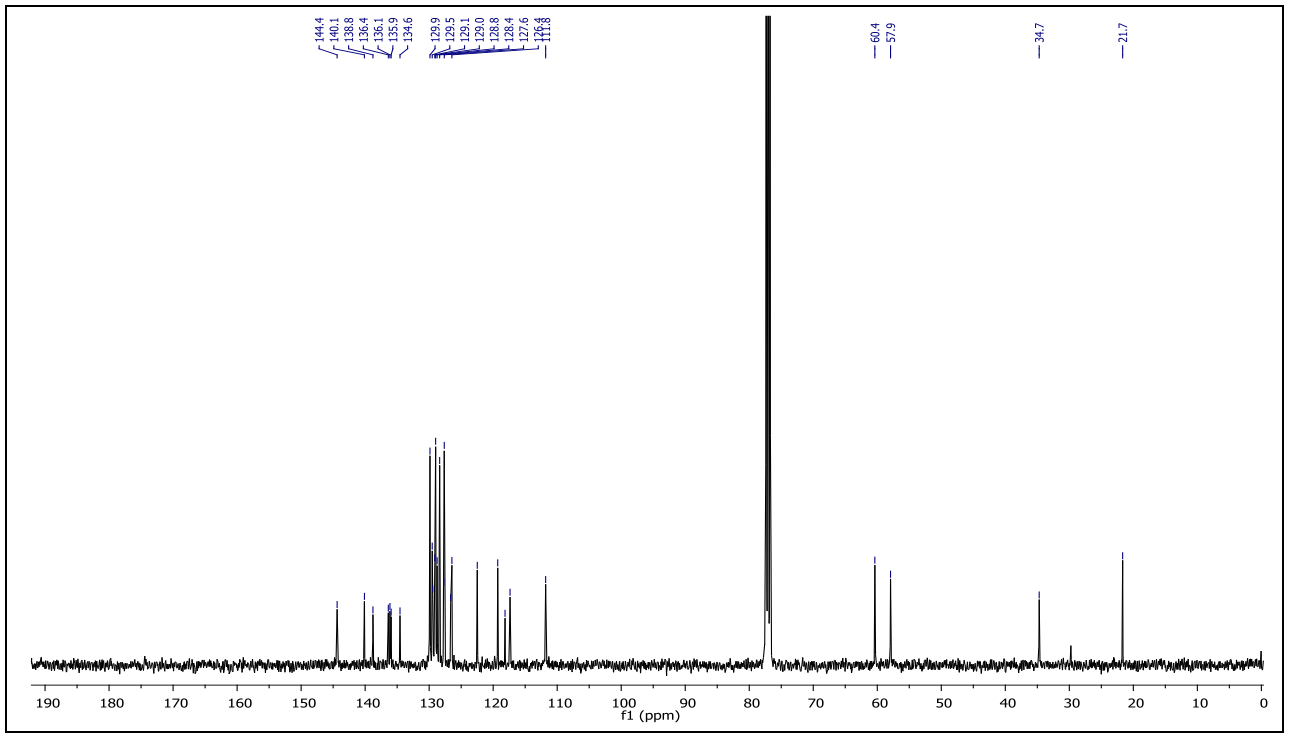
^{1}H and ^{13}C NMR spectra of compound 7b



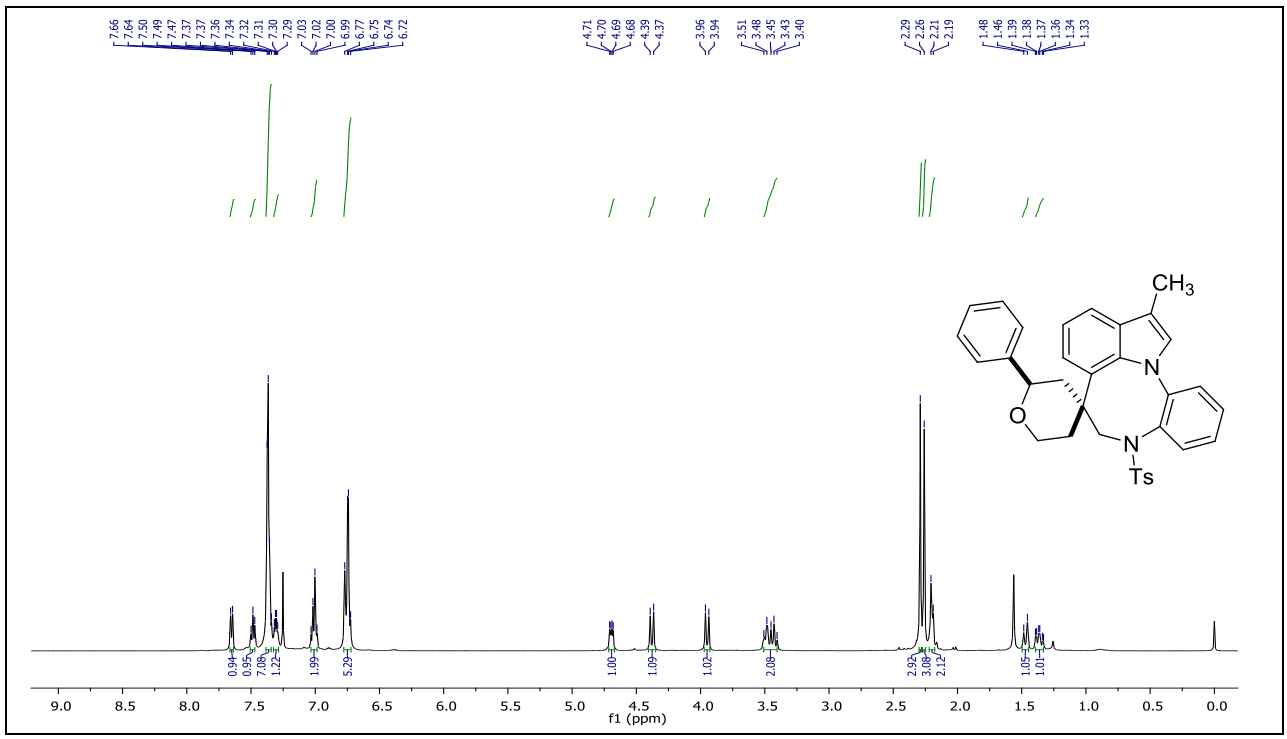


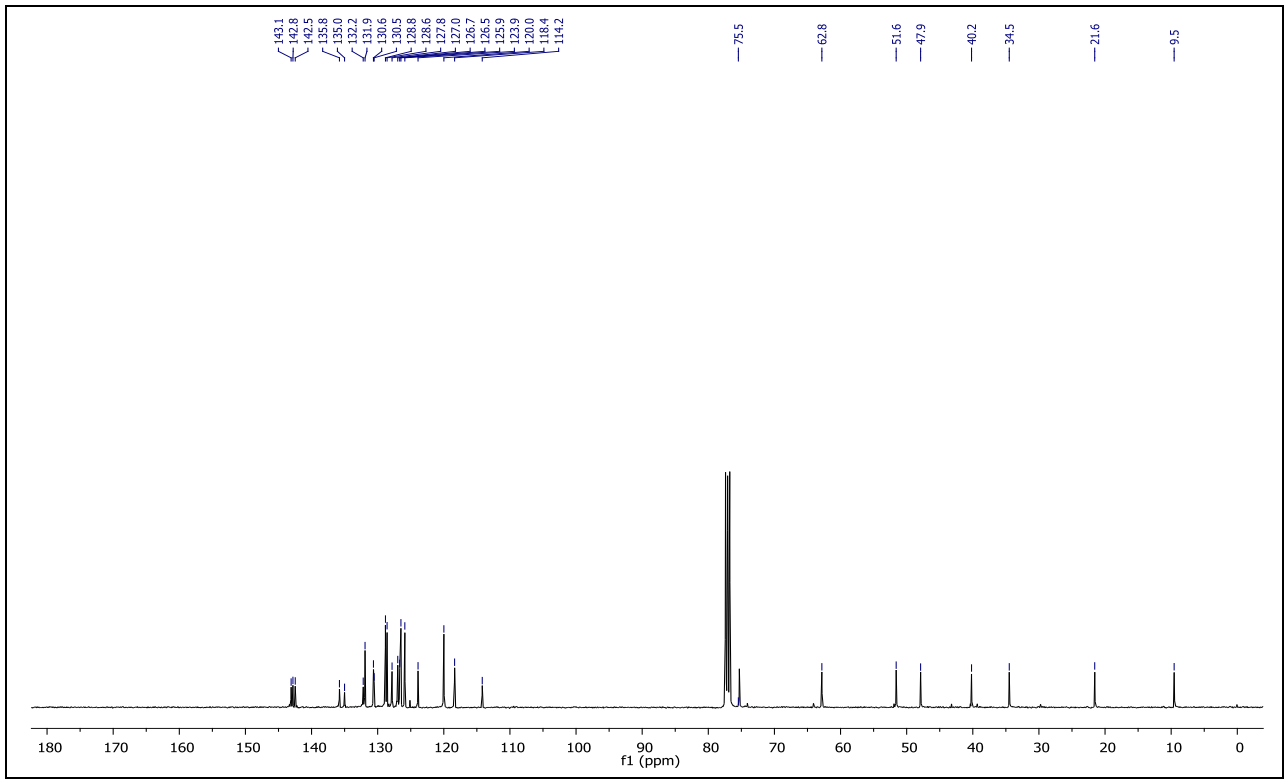
^{1}H and ^{13}C NMR spectra of compound 7c



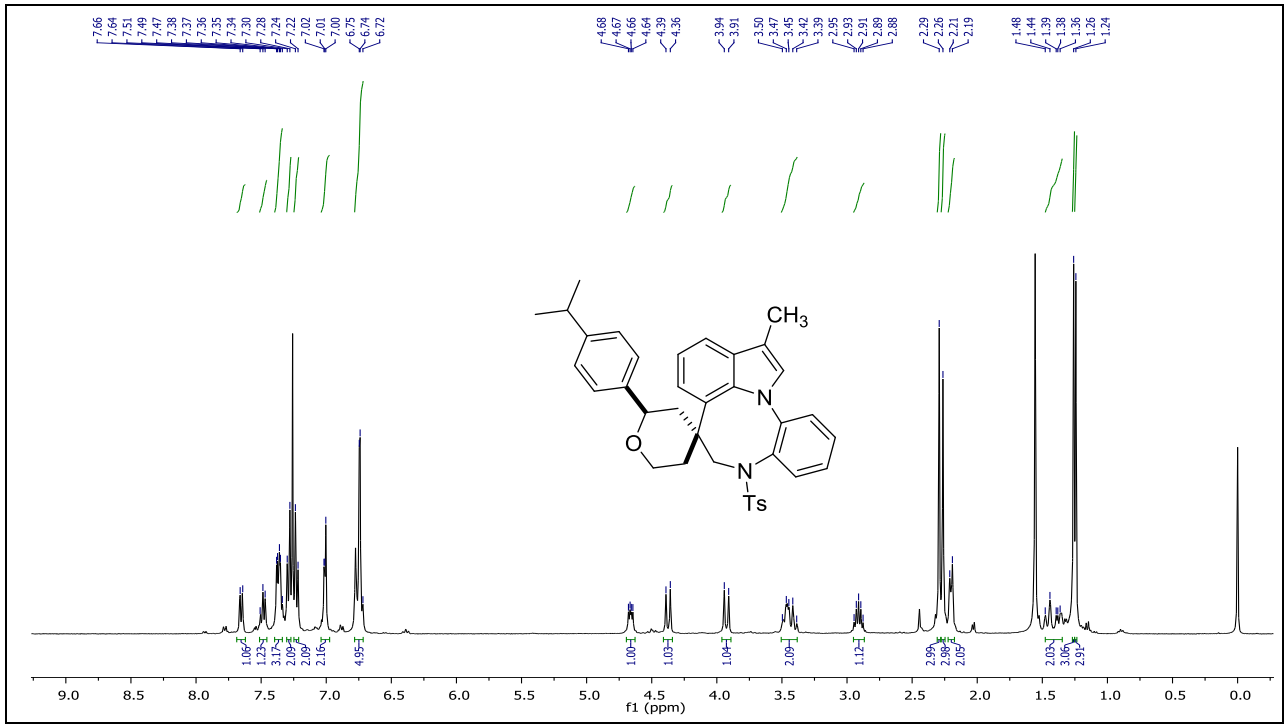


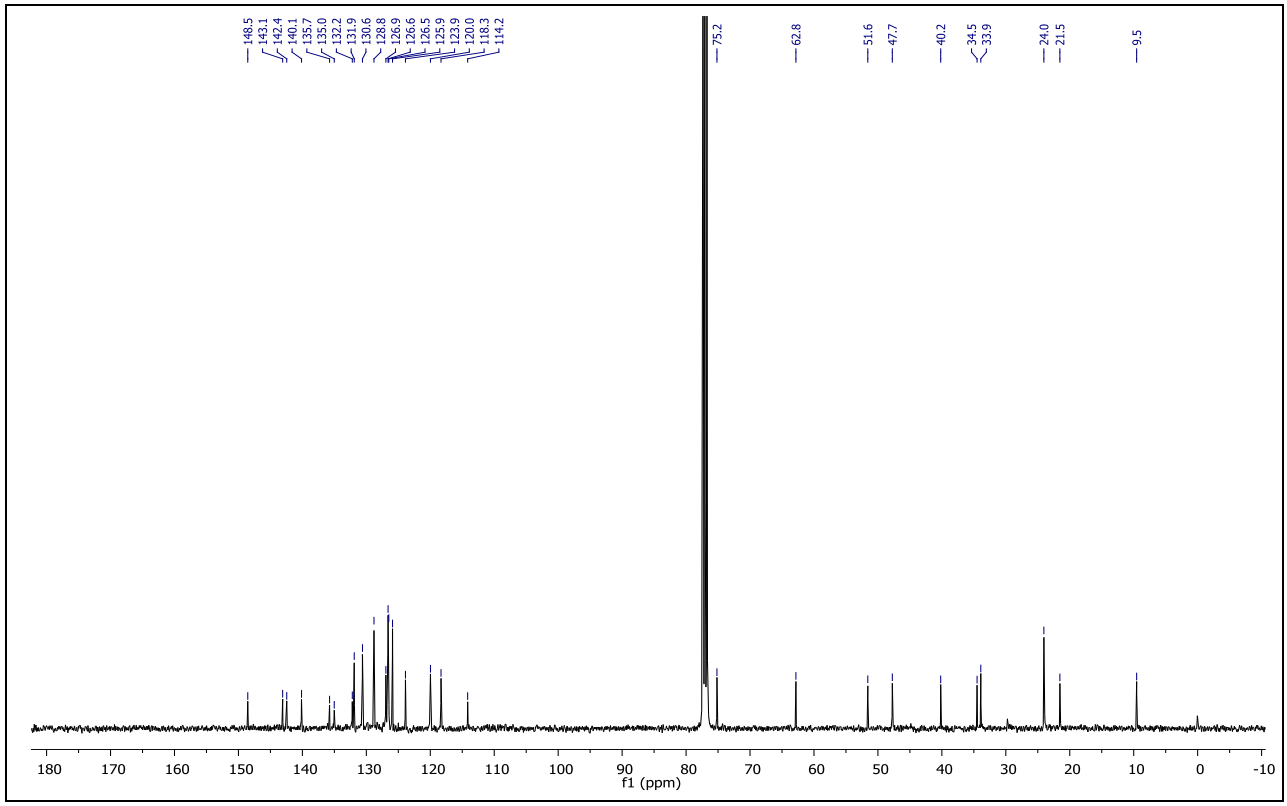
^{1}H and ^{13}C NMR spectra of compound 9a



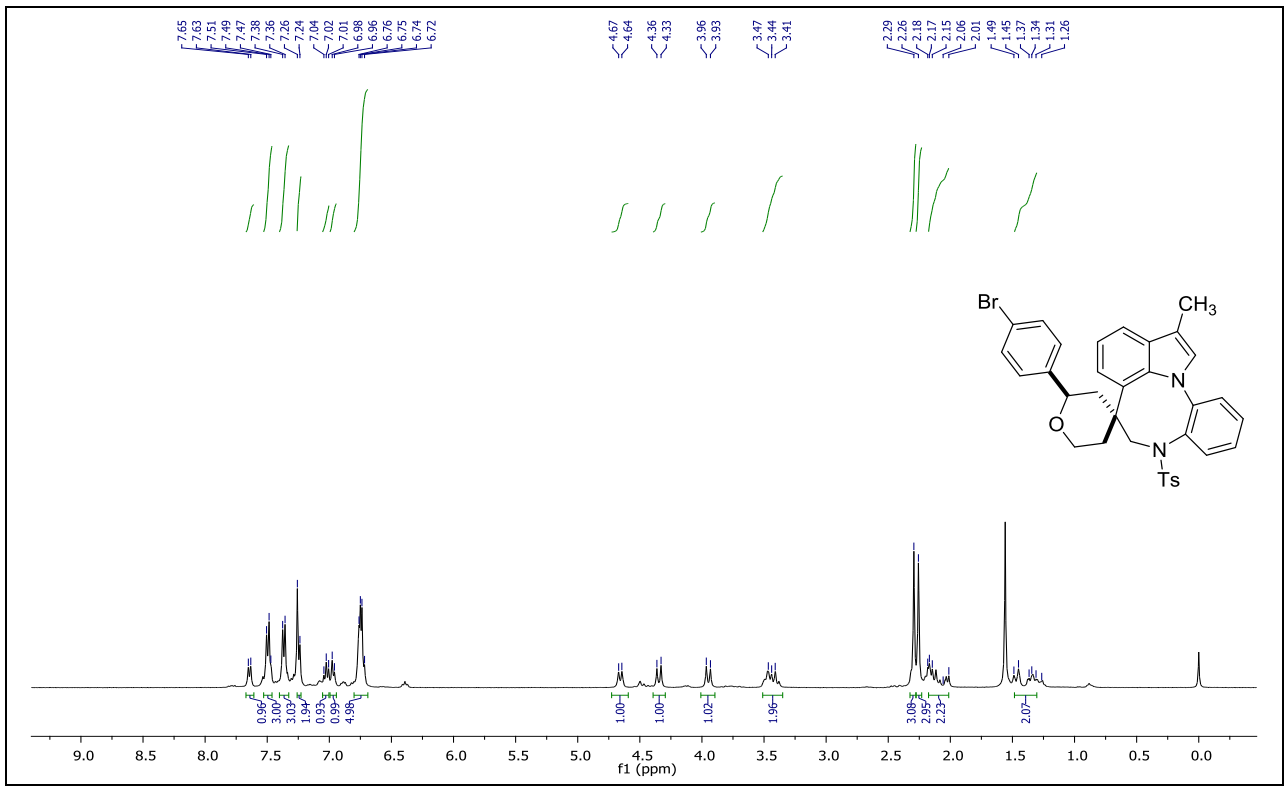


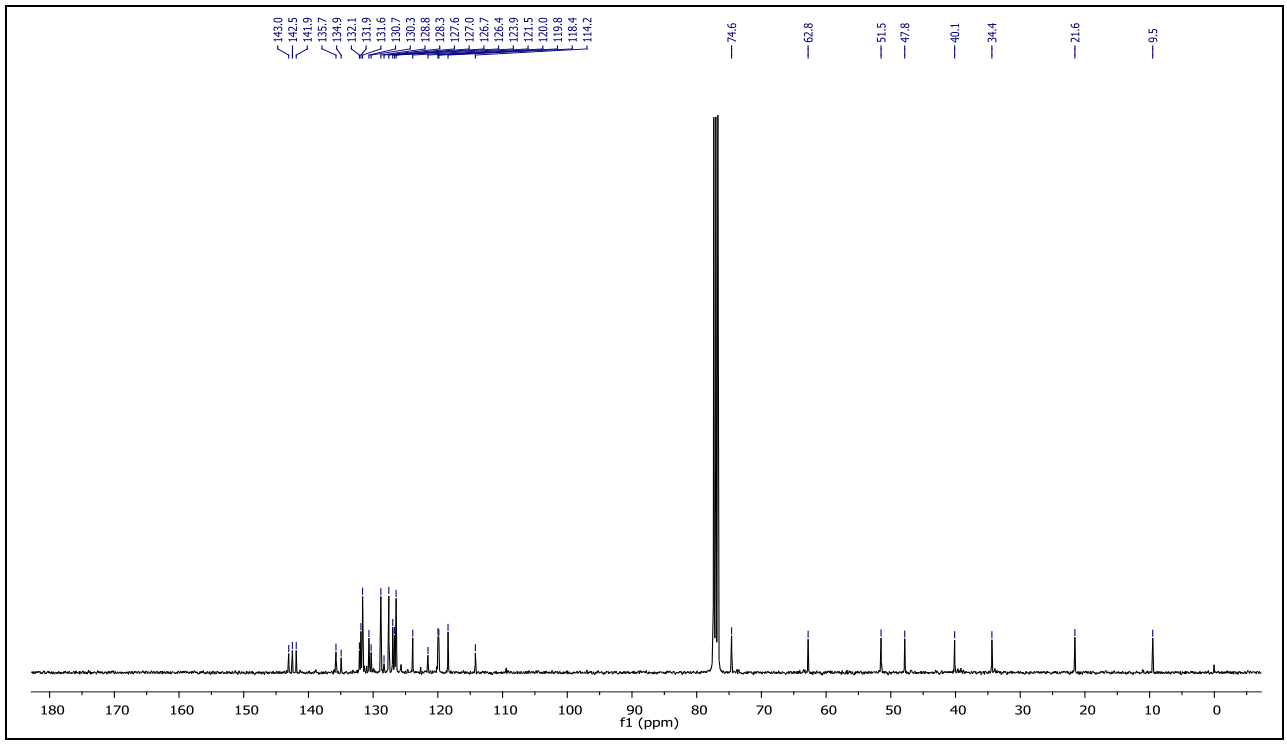
^{1}H and ^{13}C NMR spectra of compound 9b



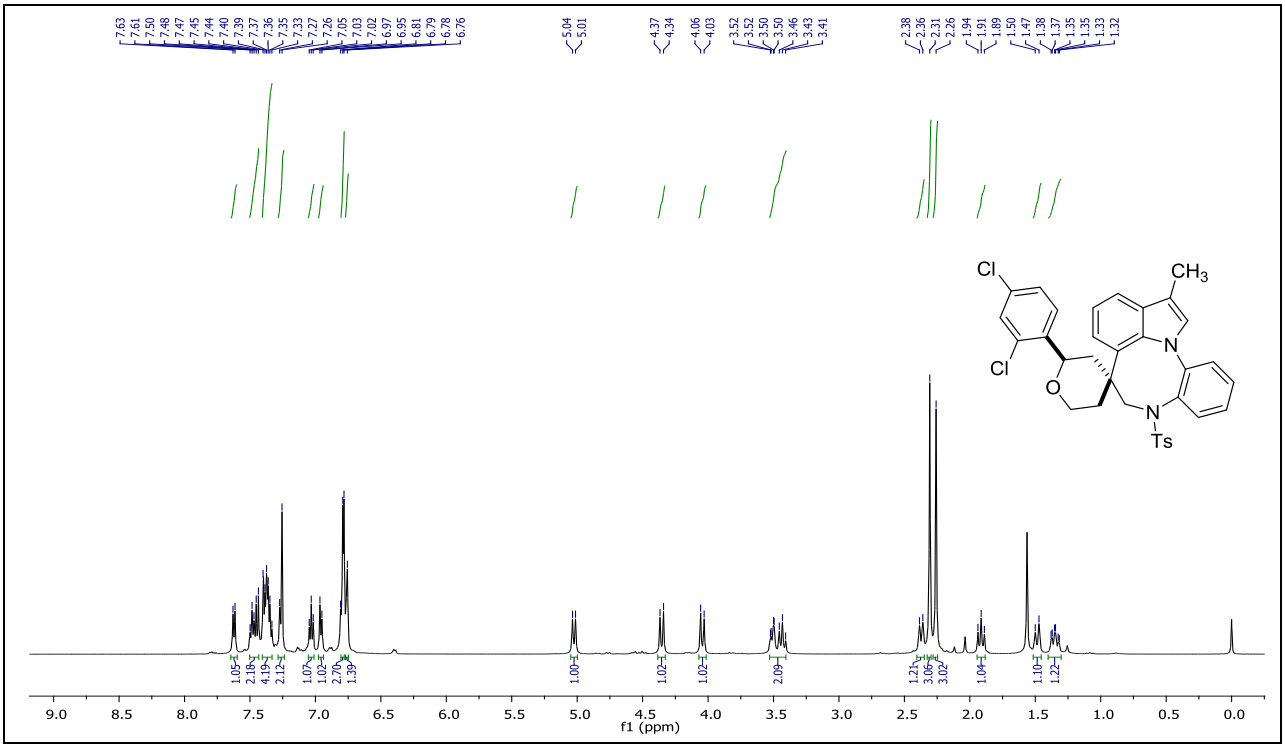


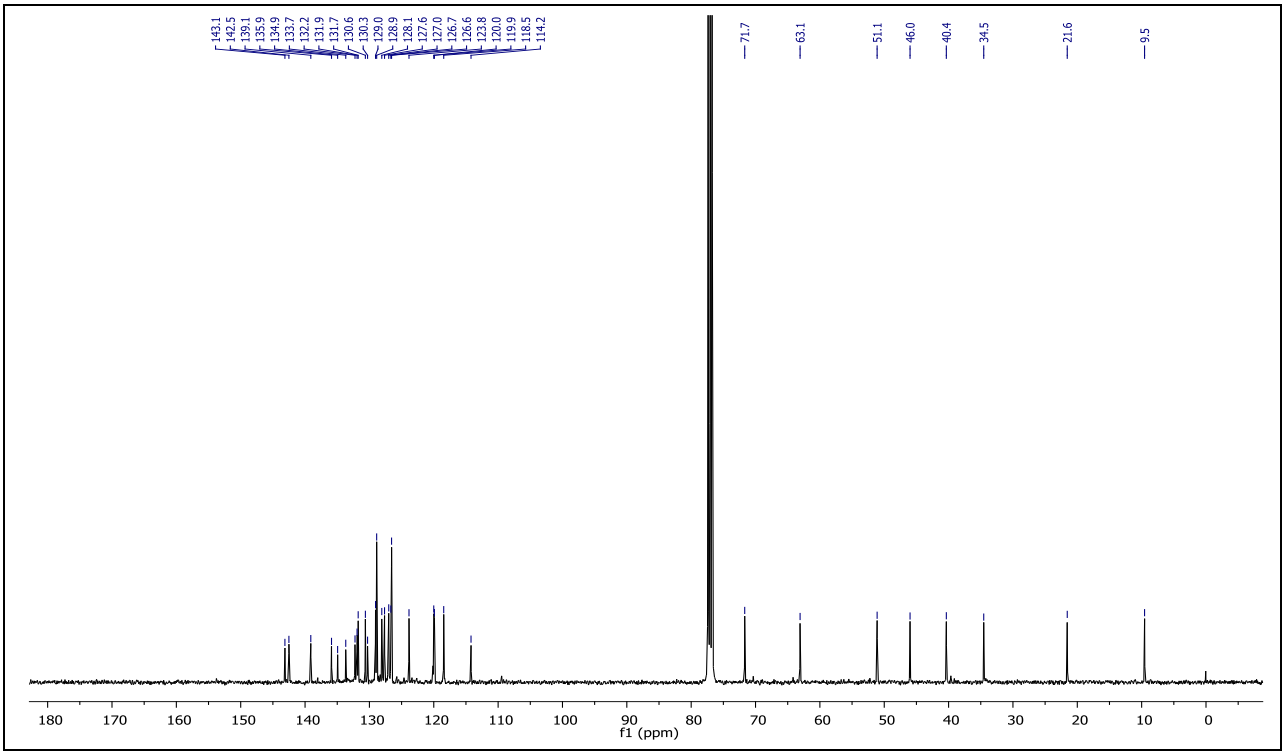
^{1}H and ^{13}C NMR spectra of compound 9c



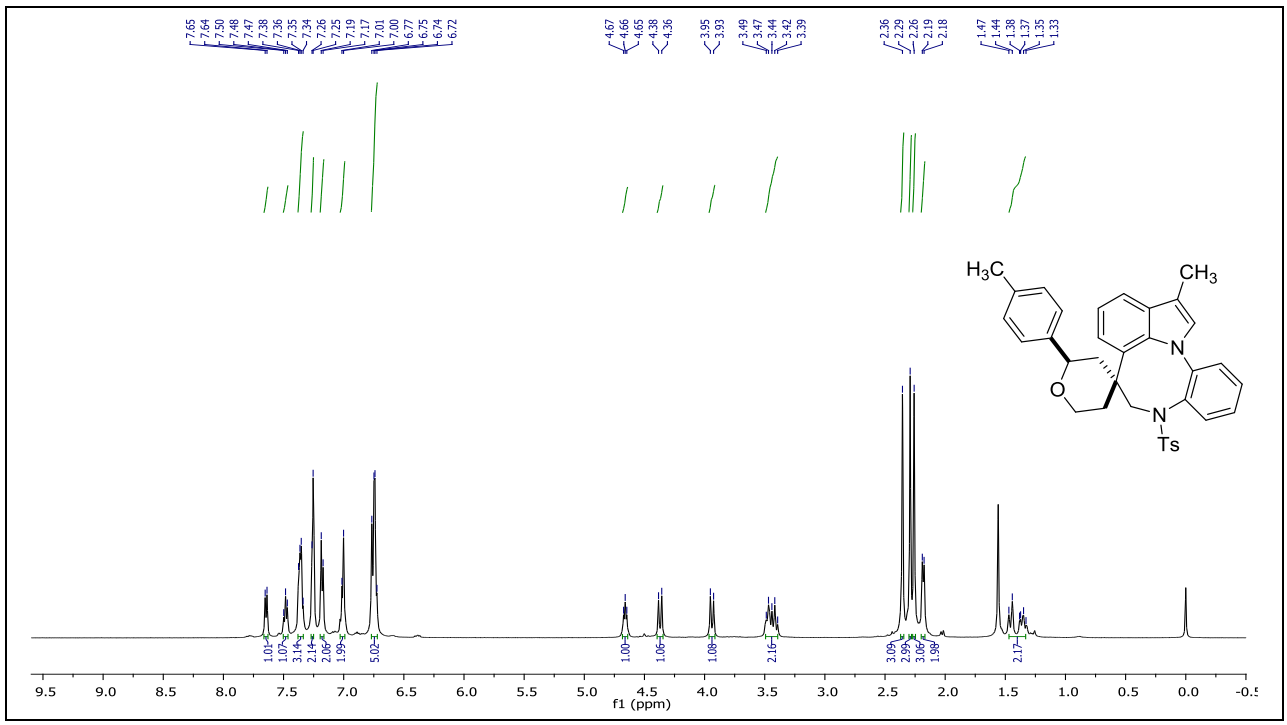


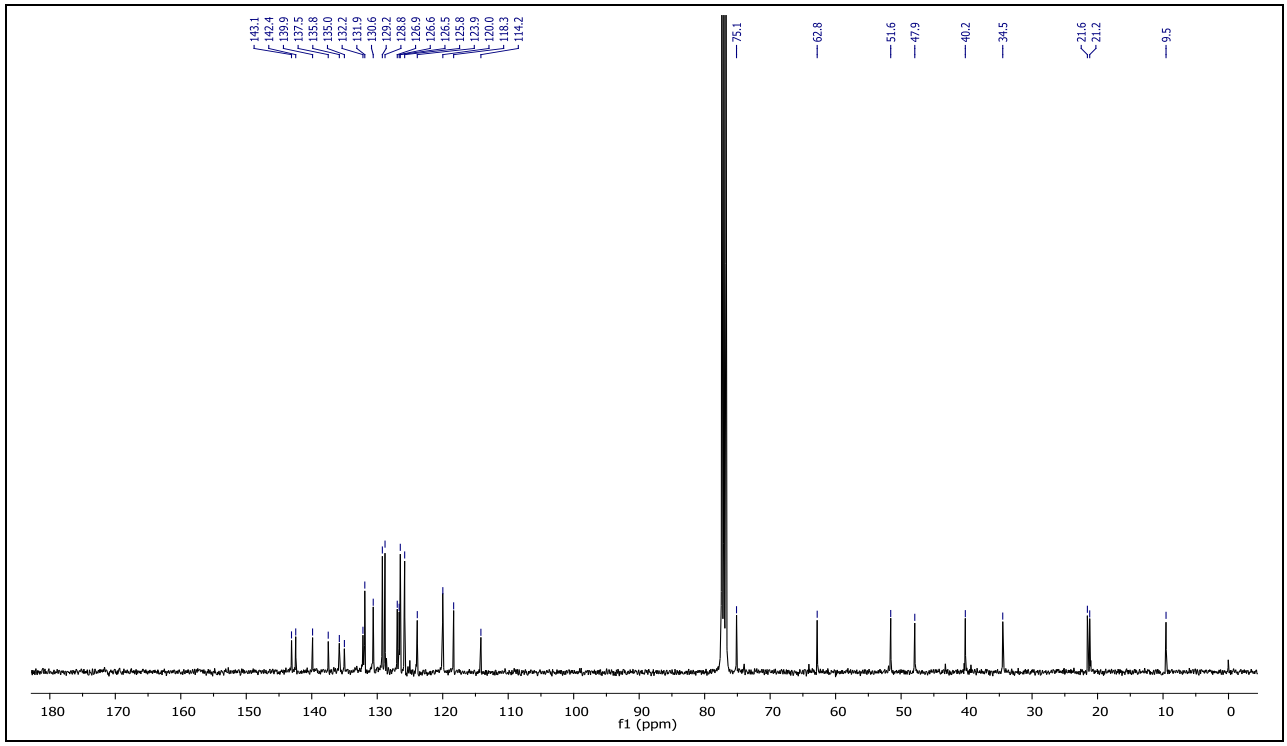
^{1}H and ^{13}C NMR spectra of compound 9d



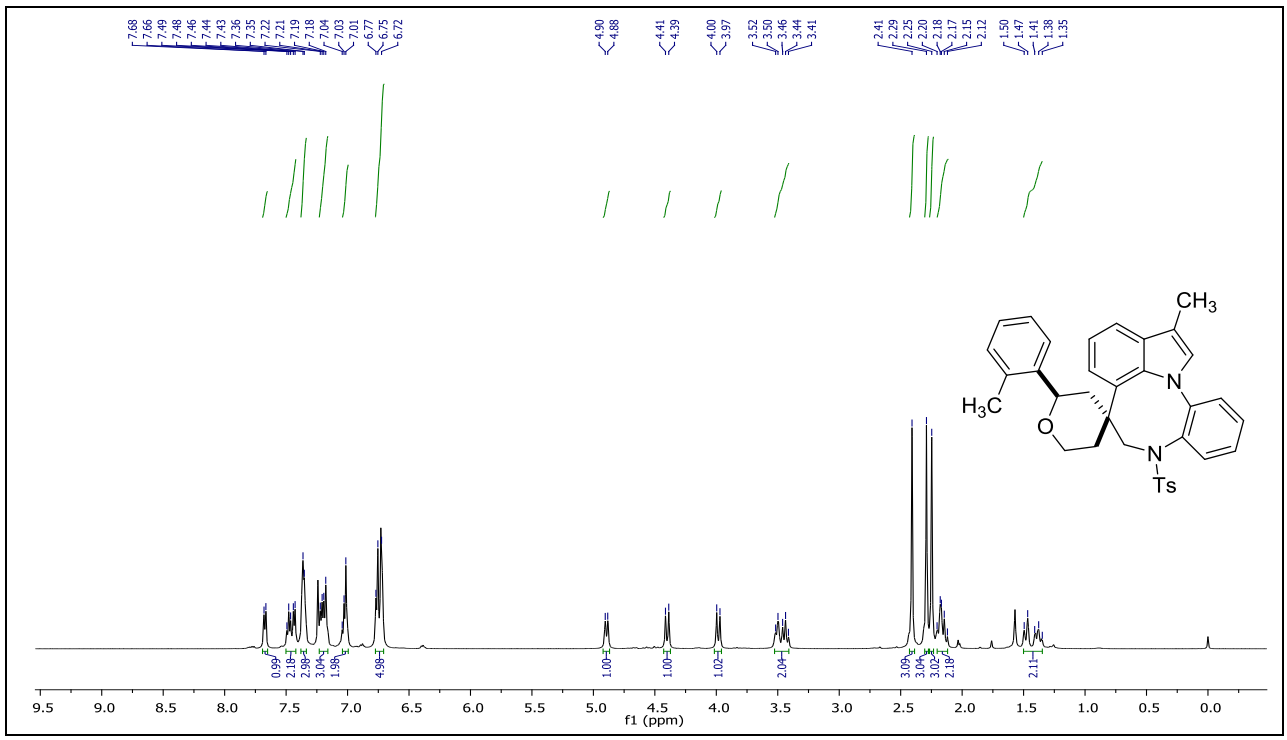


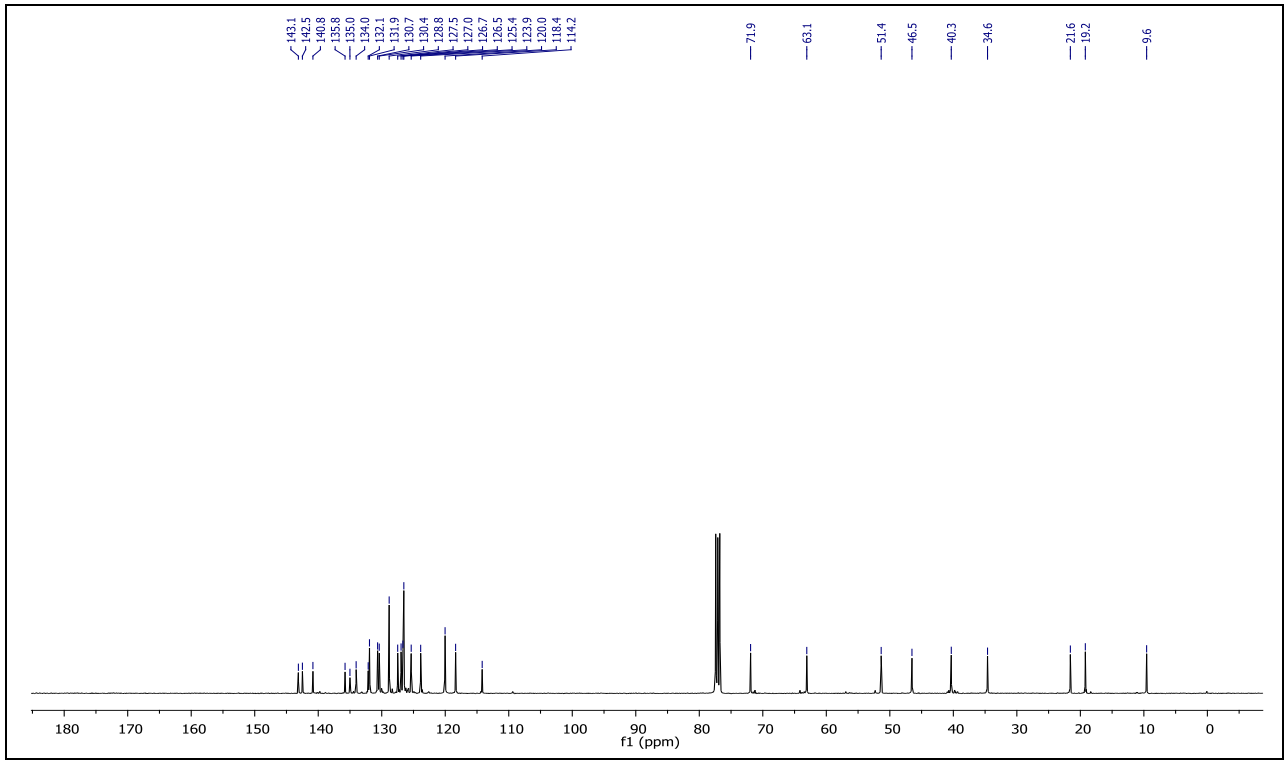
^{1}H and ^{13}C NMR spectra of compound 9e



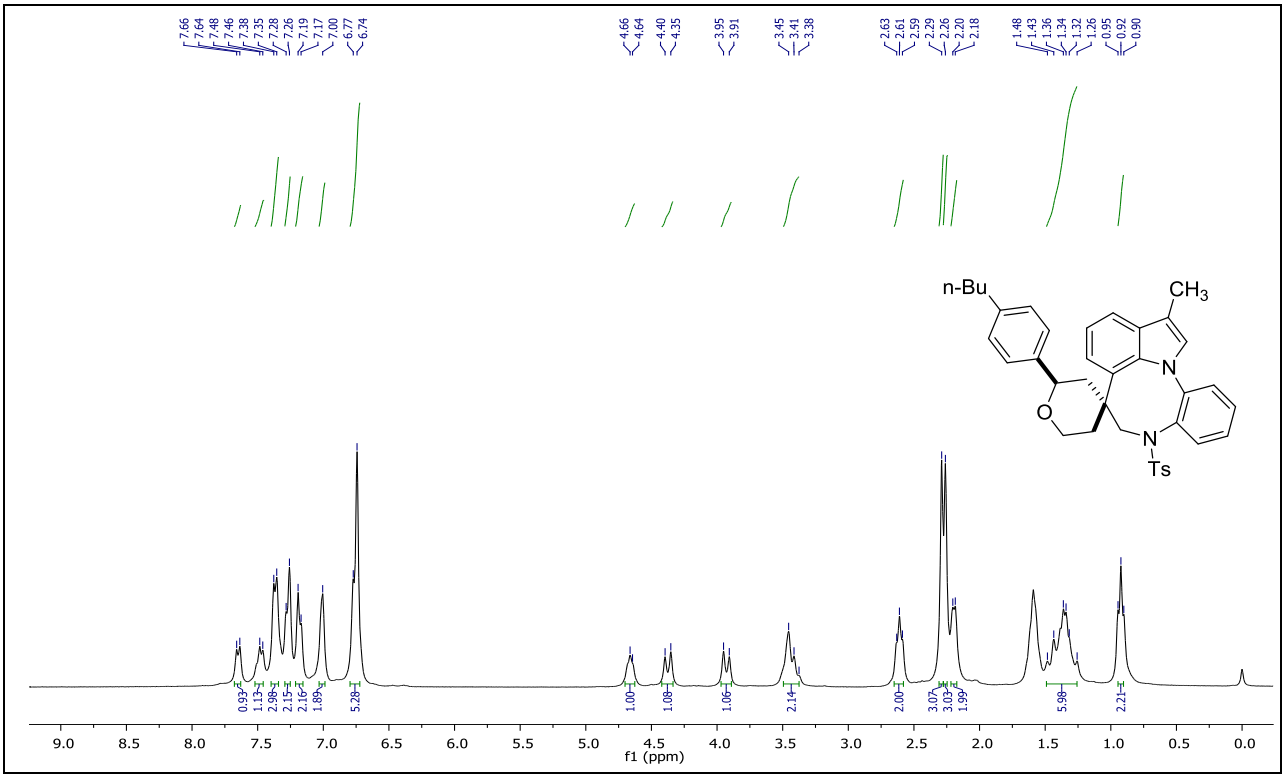


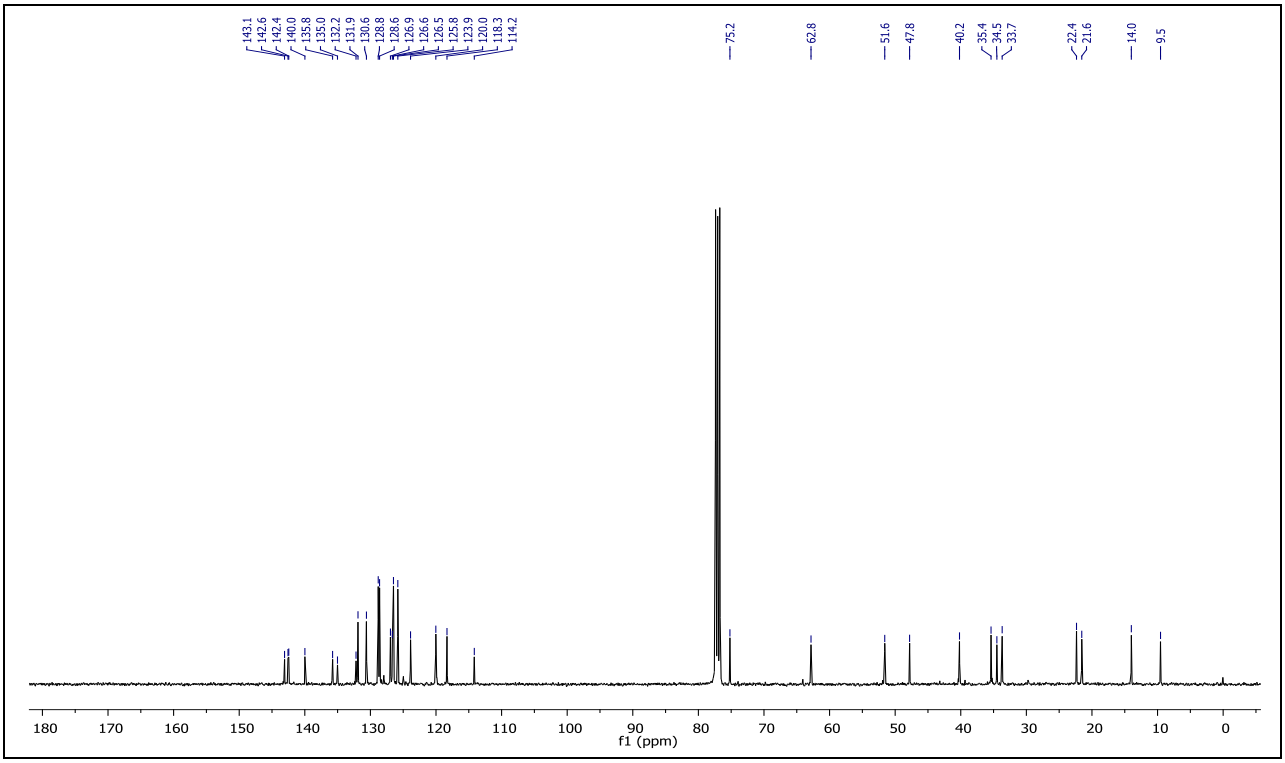
^{1}H and ^{13}C NMR spectra of compound 9f



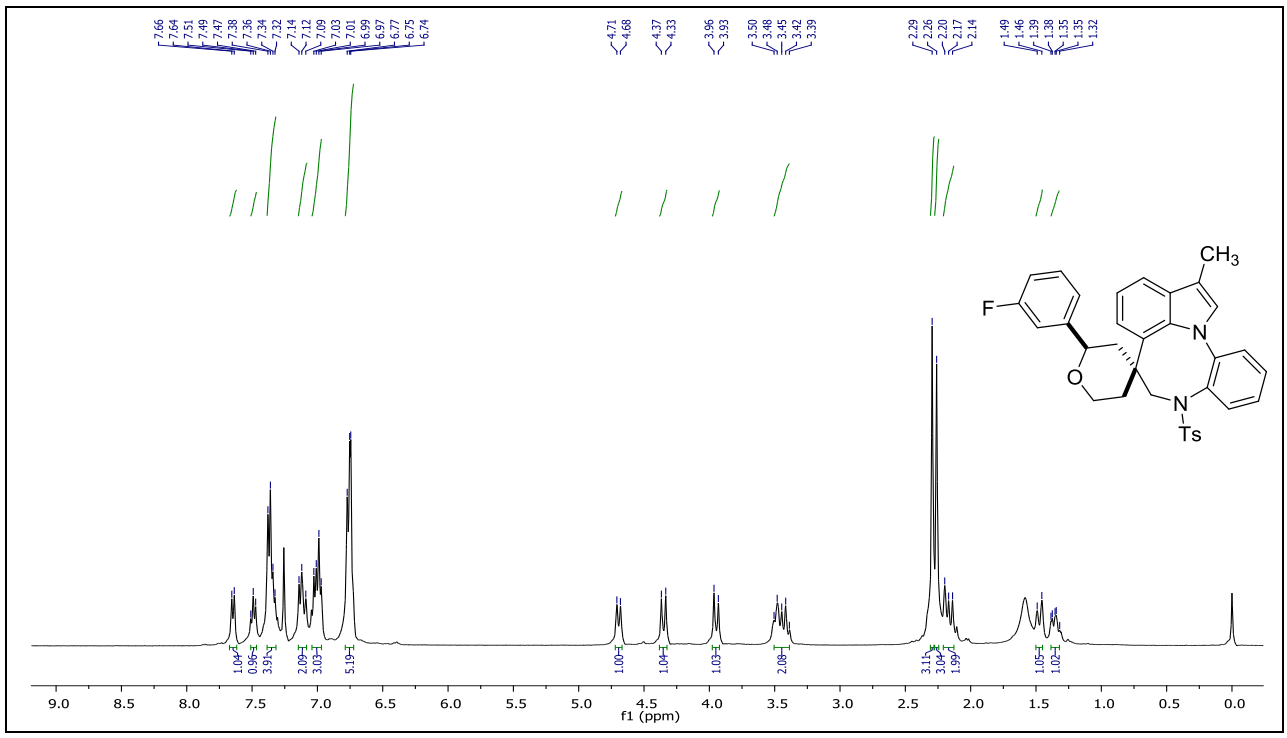


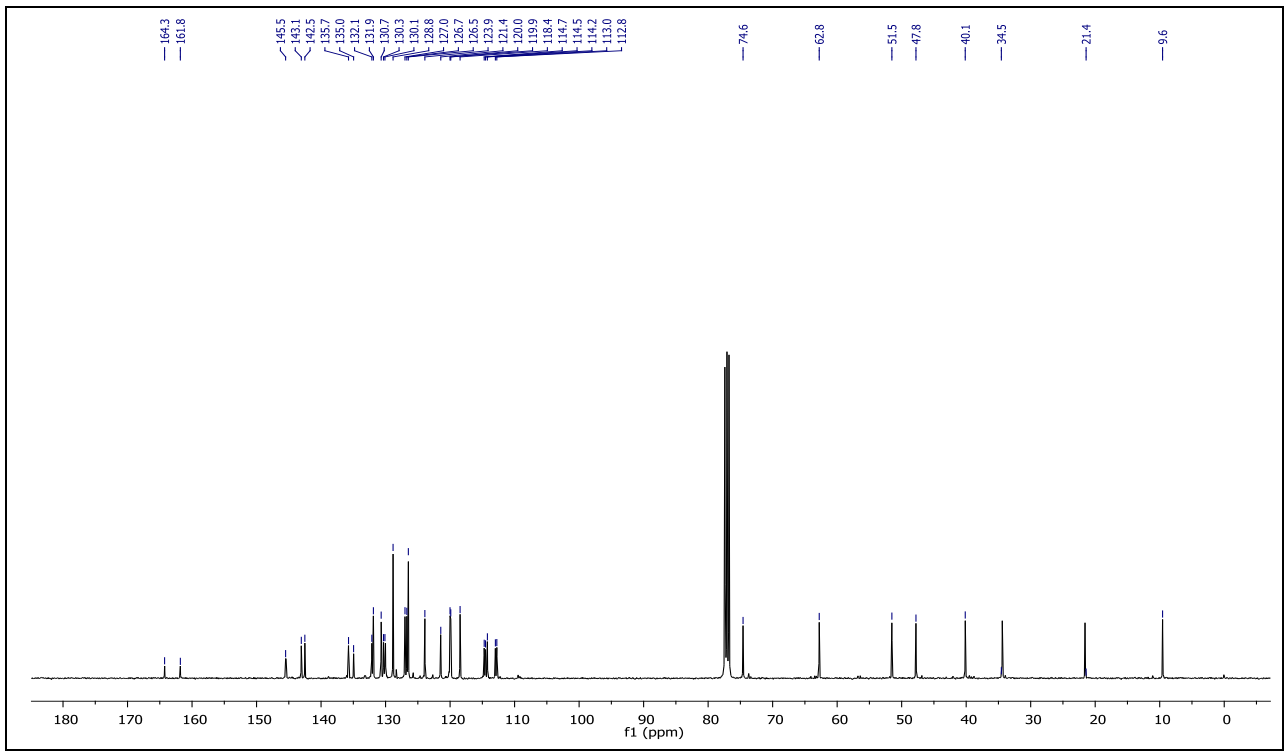
^{1}H and ^{13}C NMR spectra of compound 9g



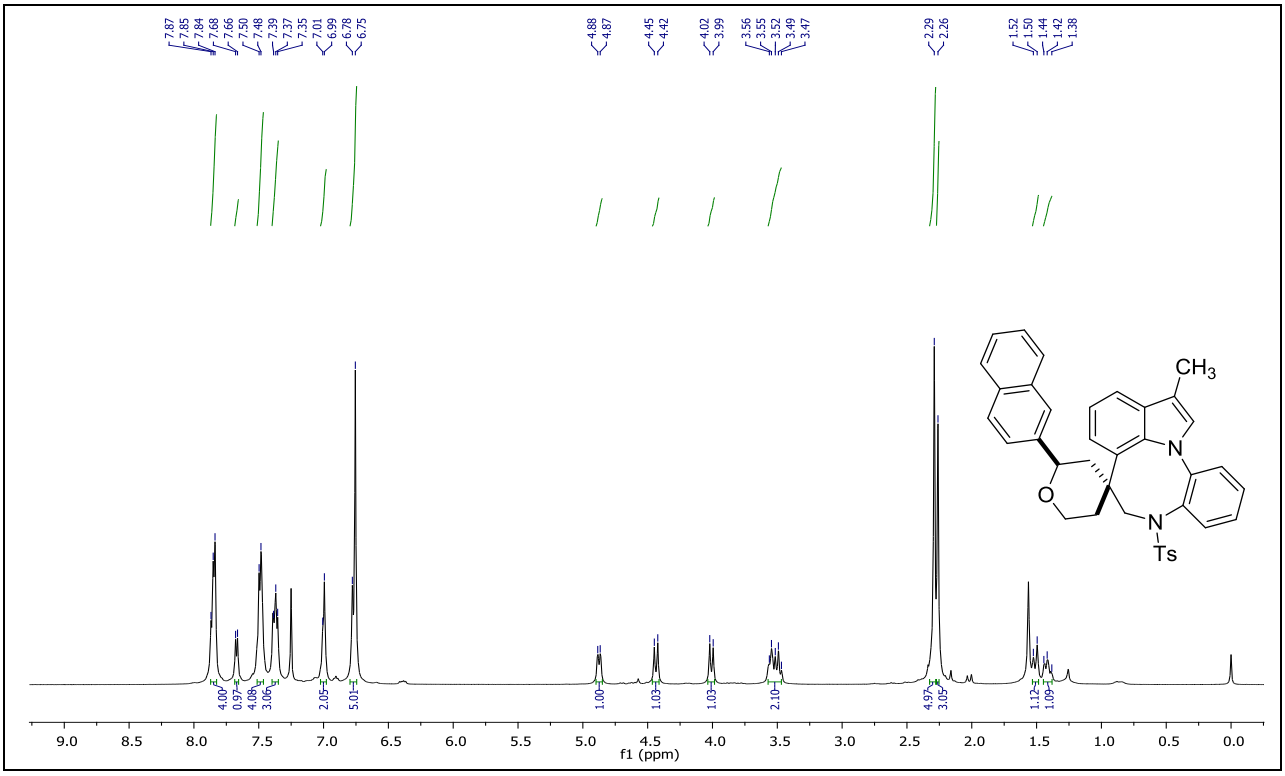


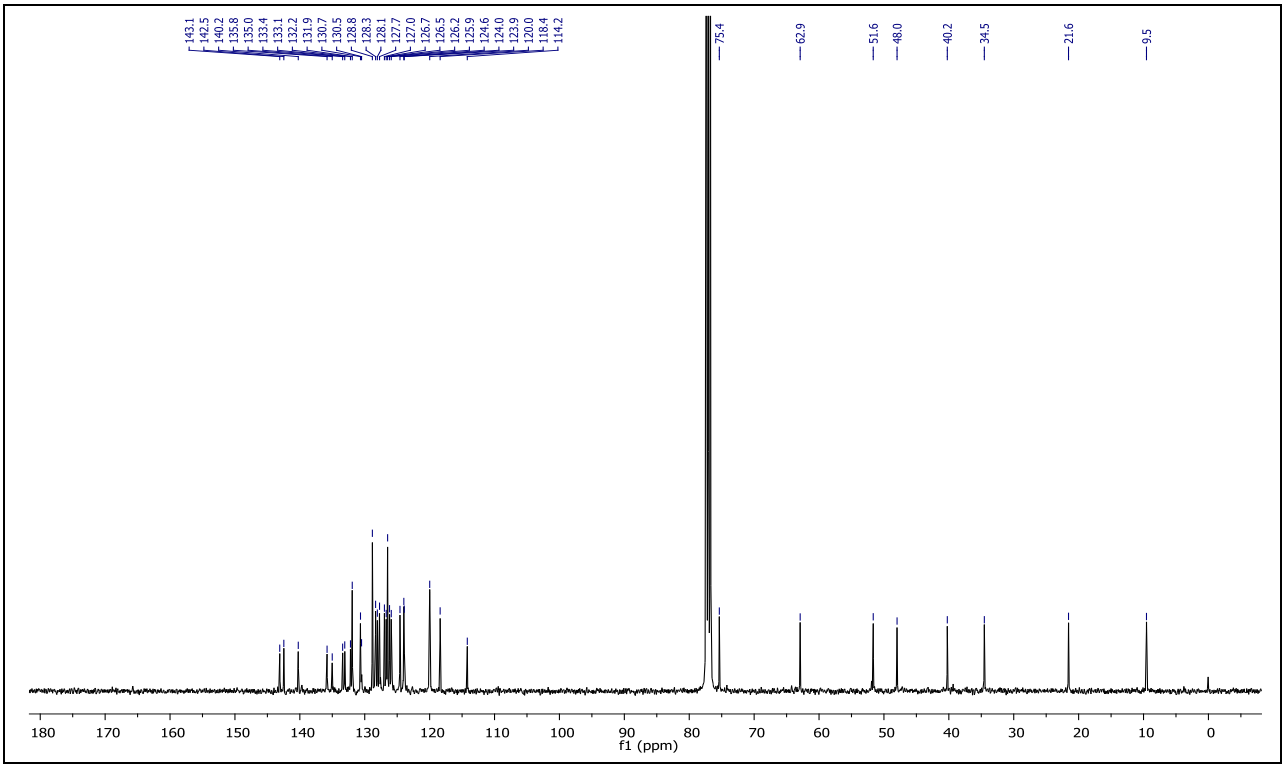
^{1}H and ^{13}C NMR spectra of compound 9h



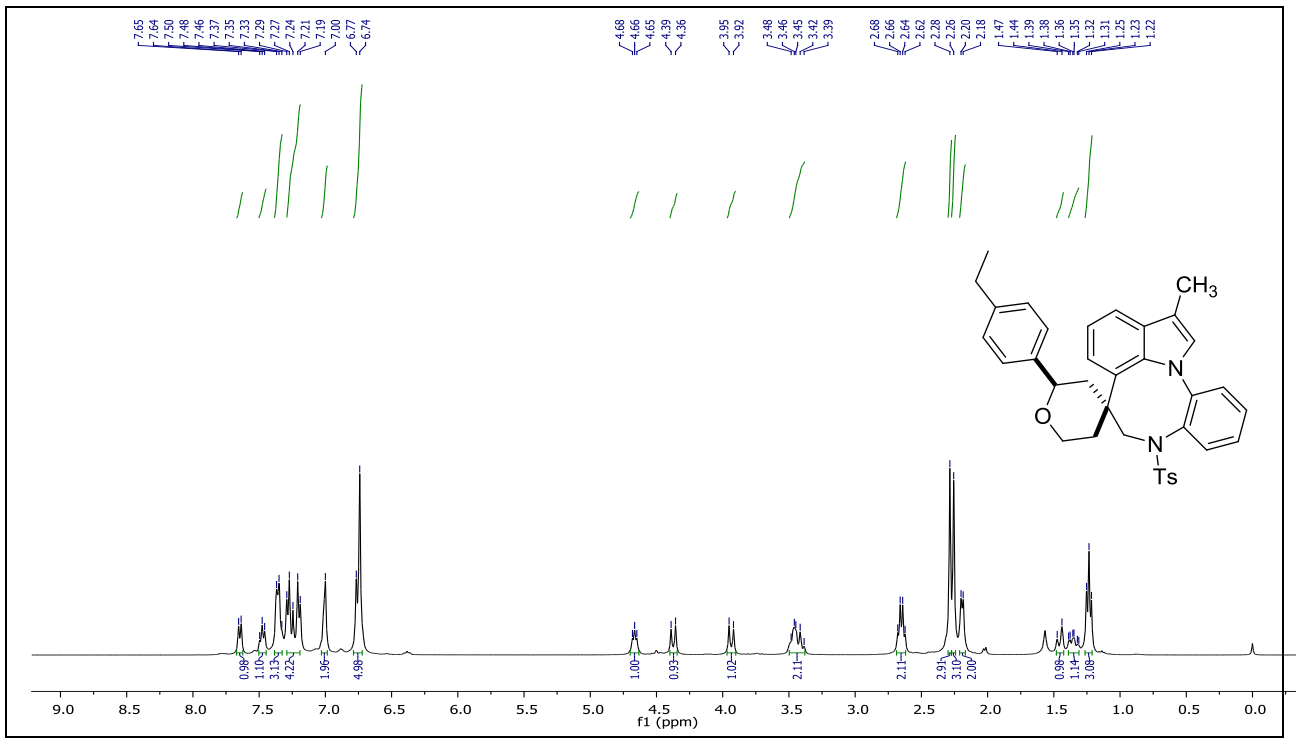


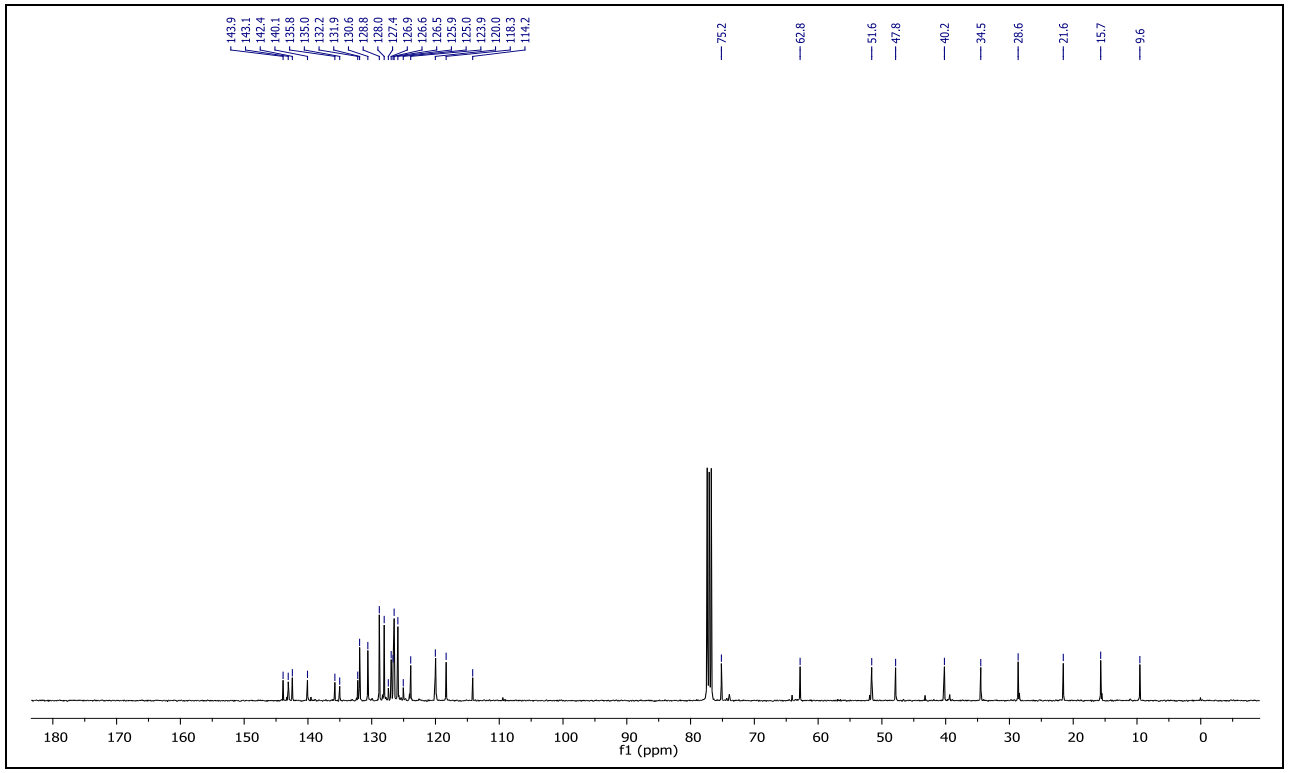
^{1}H and ^{13}C NMR spectra of compound 9i



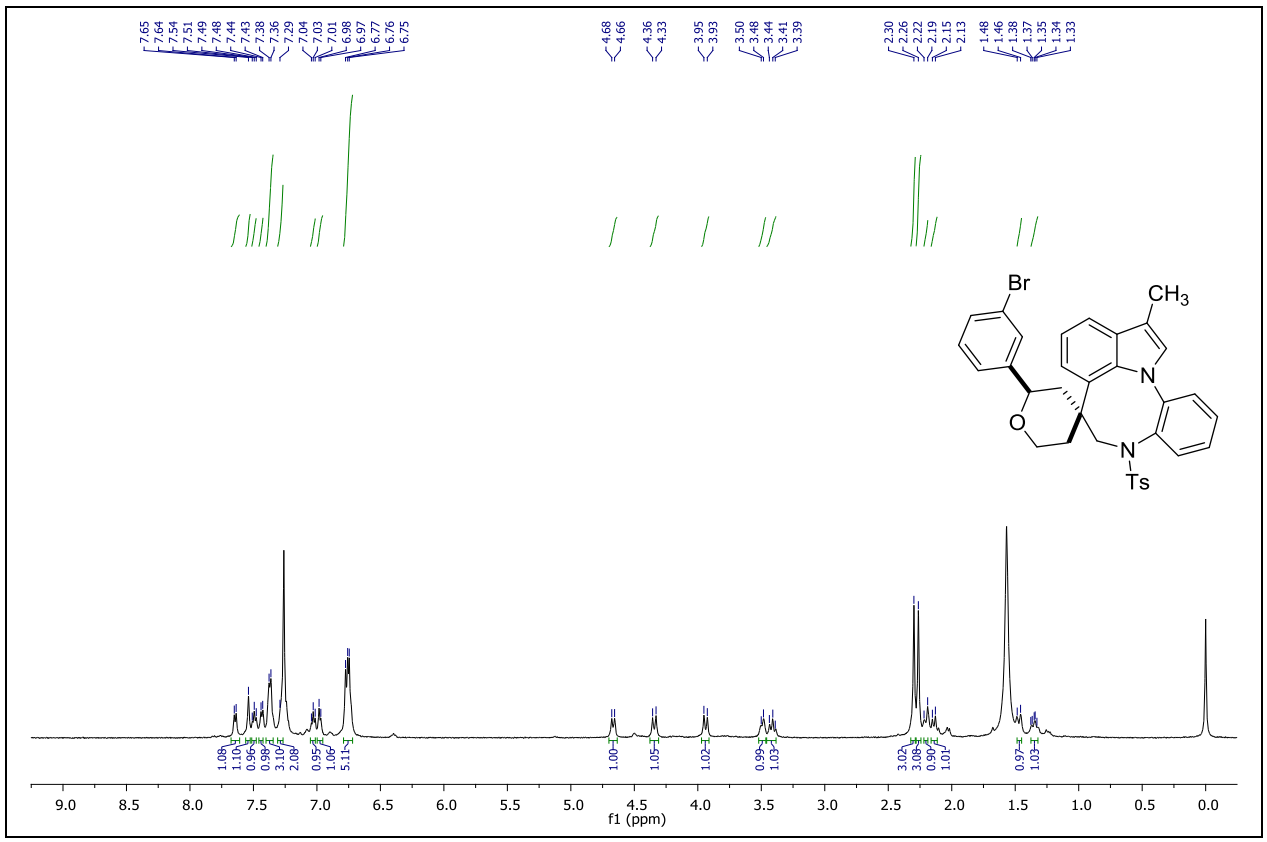


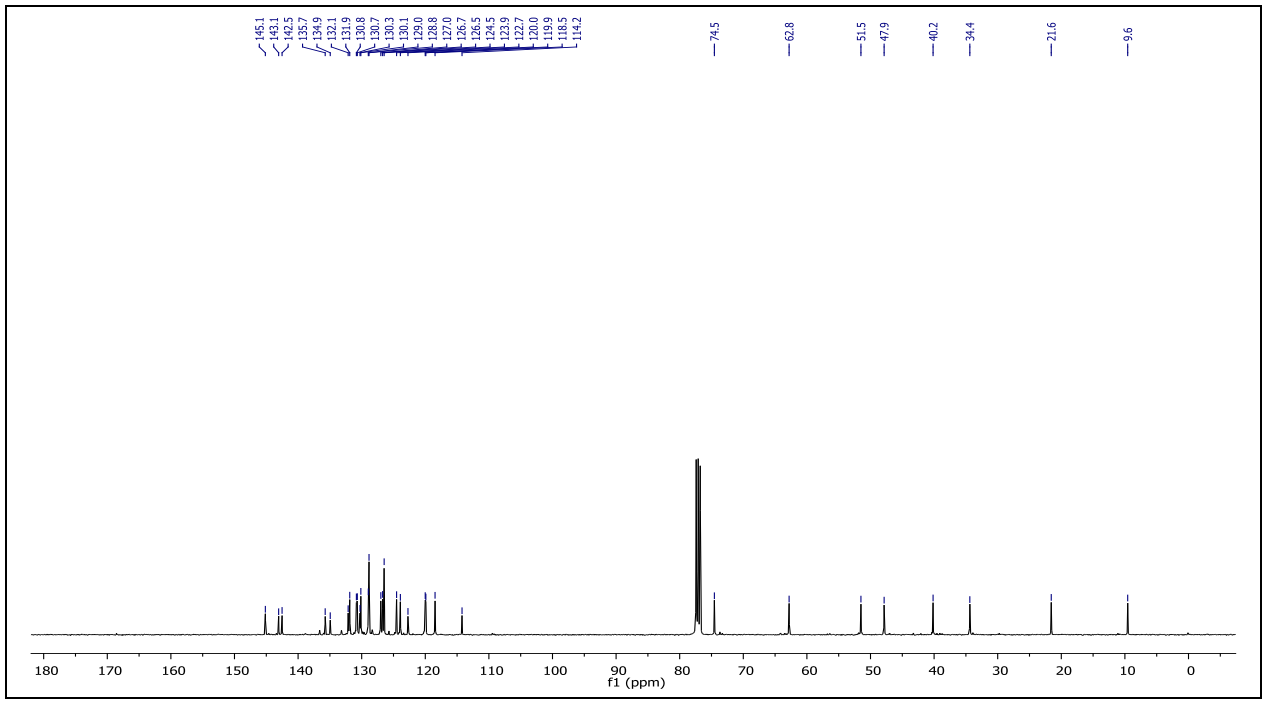
^{1}H and ^{13}C NMR spectra of compound 9j



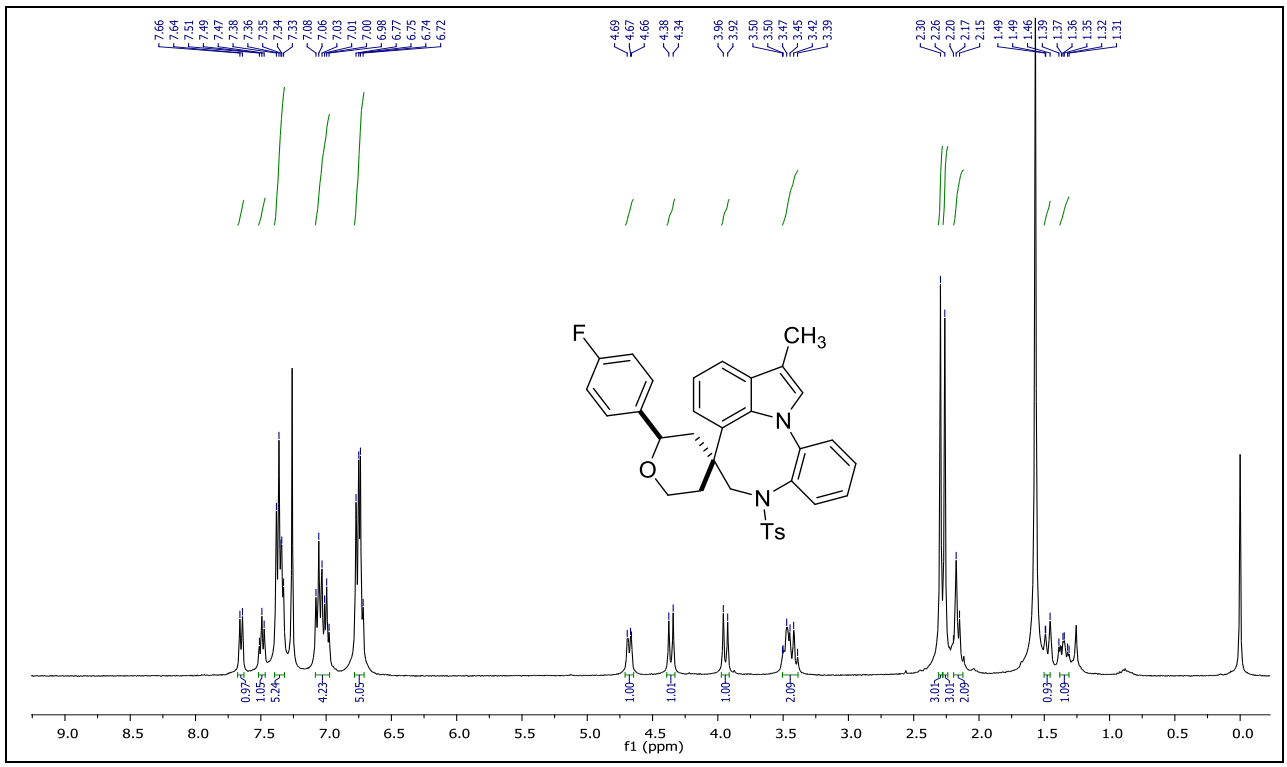


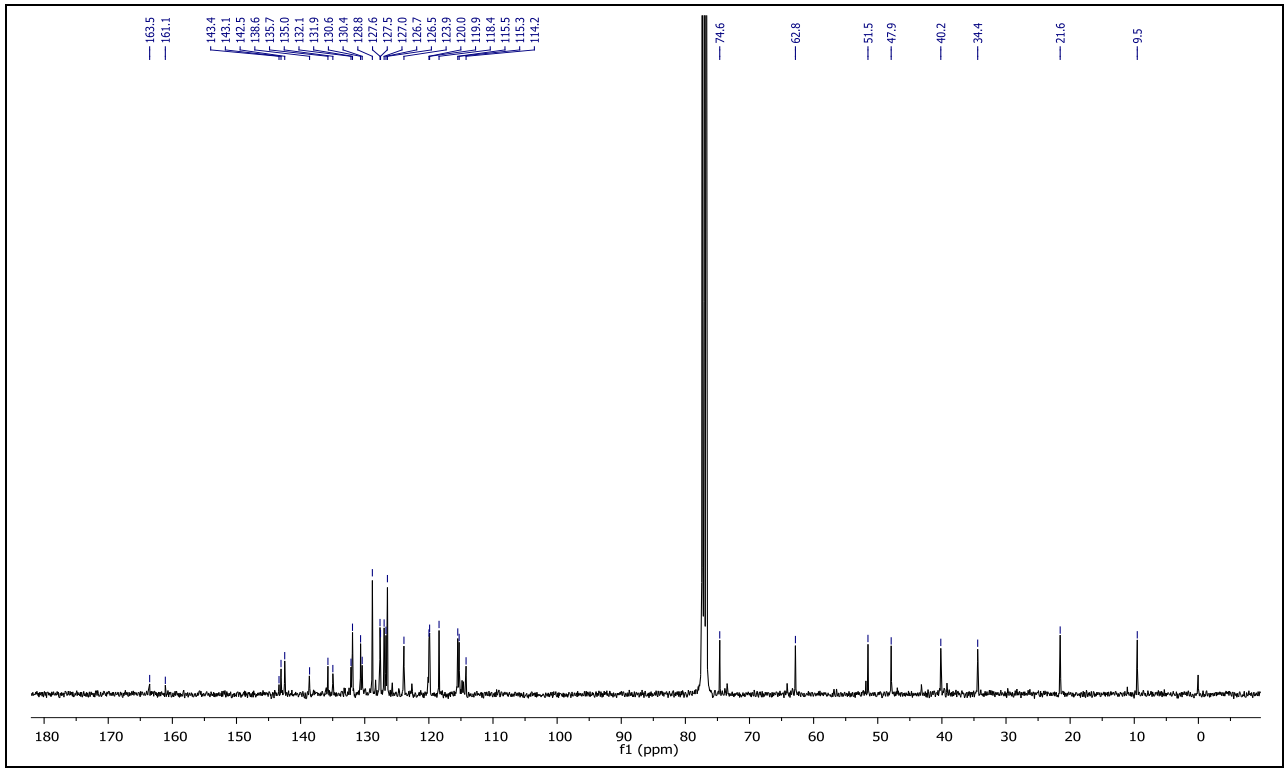
^{1}H and ^{13}C NMR spectra of compound 9k



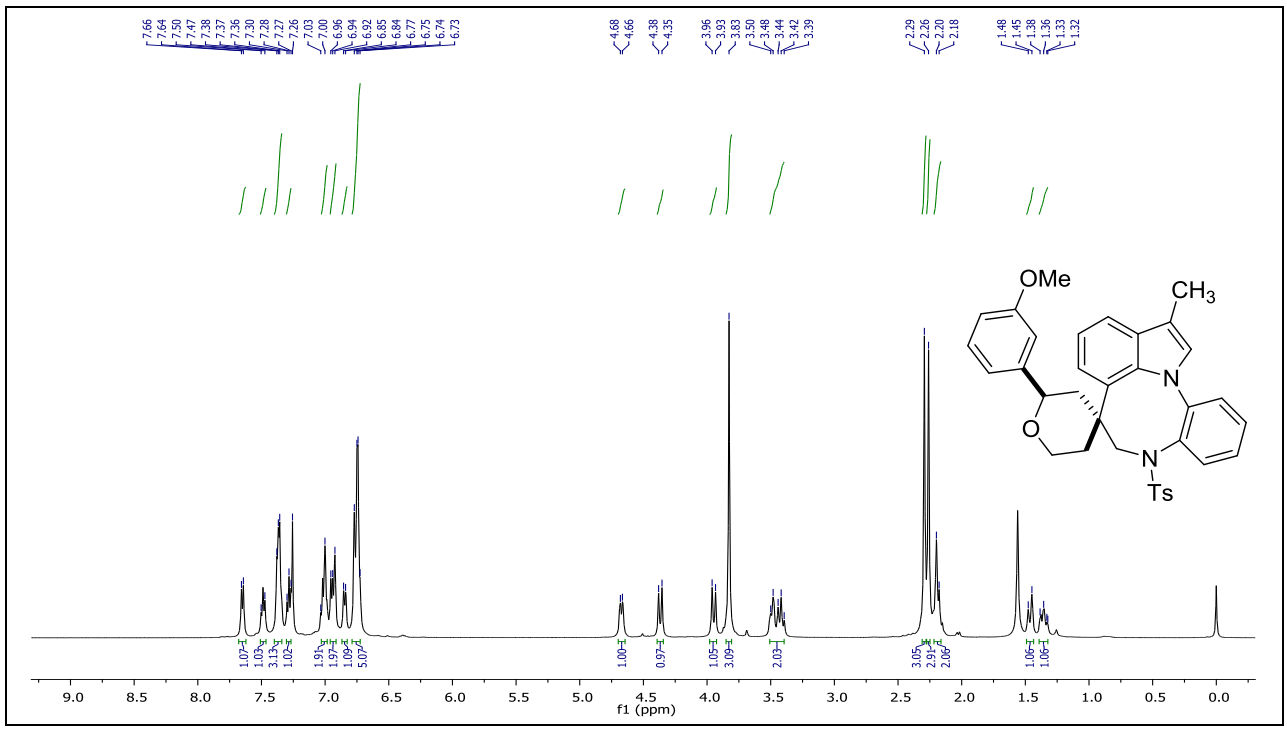


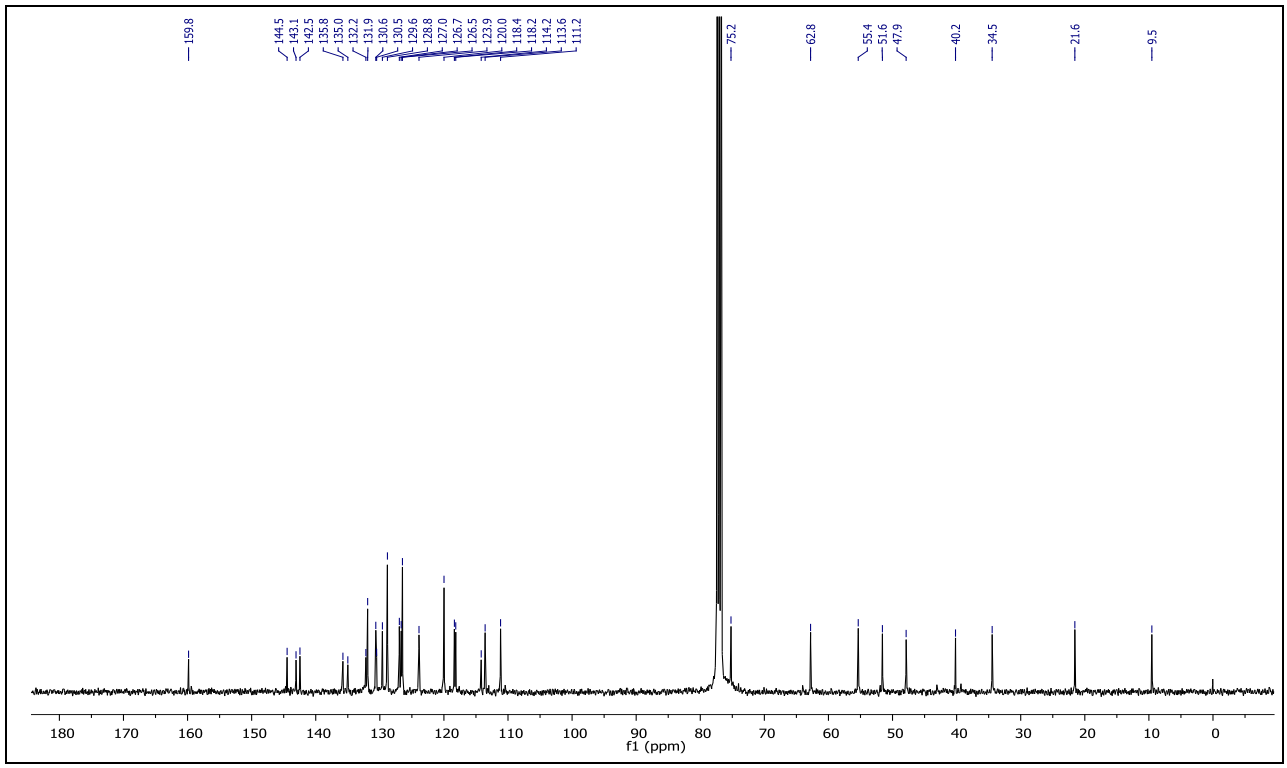
^{1}H and ^{13}C NMR spectra of compound 9l



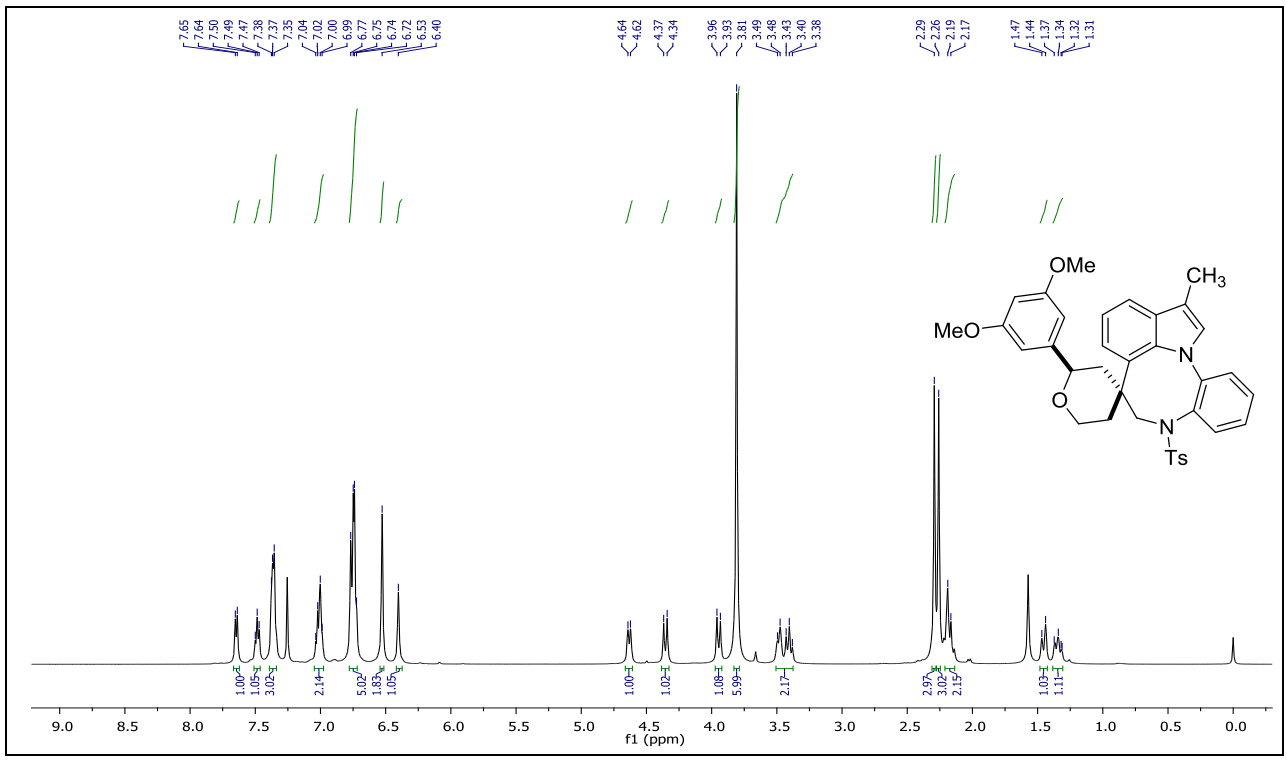


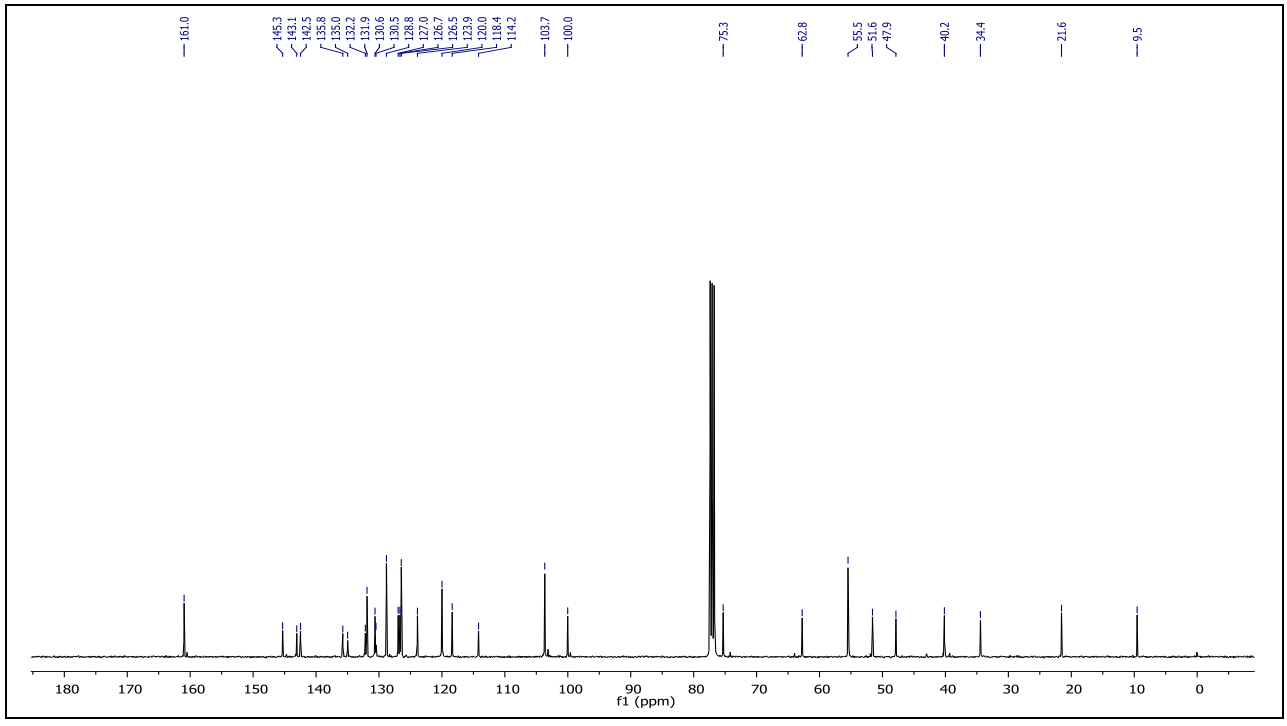
^{1}H and ^{13}C NMR spectra of compound 9m



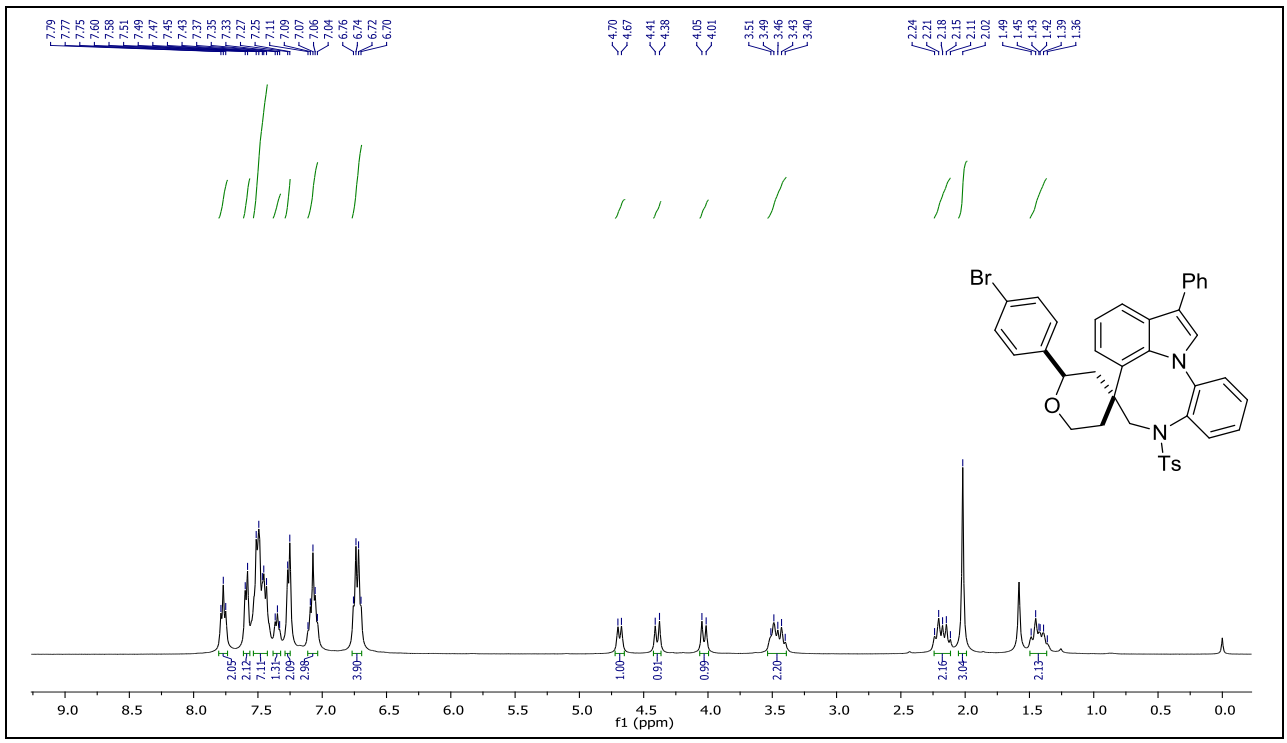


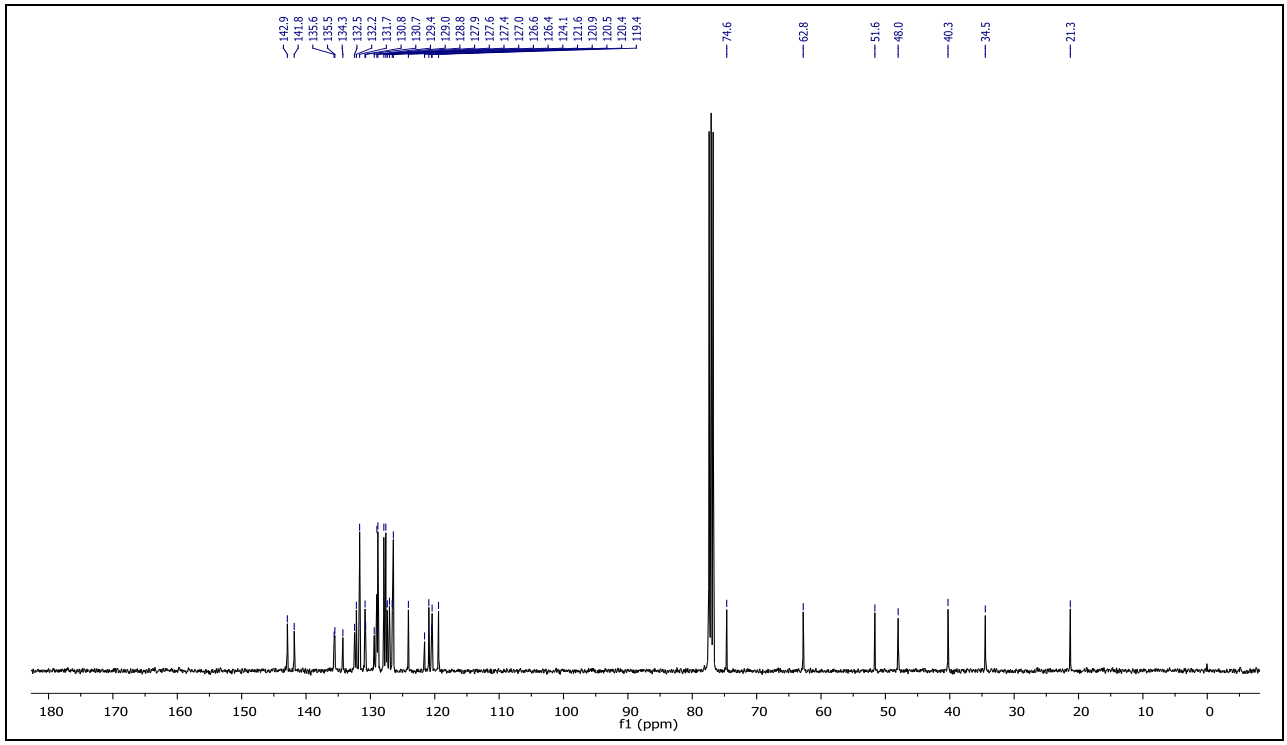
^{1}H and ^{13}C NMR spectra of compound 9n



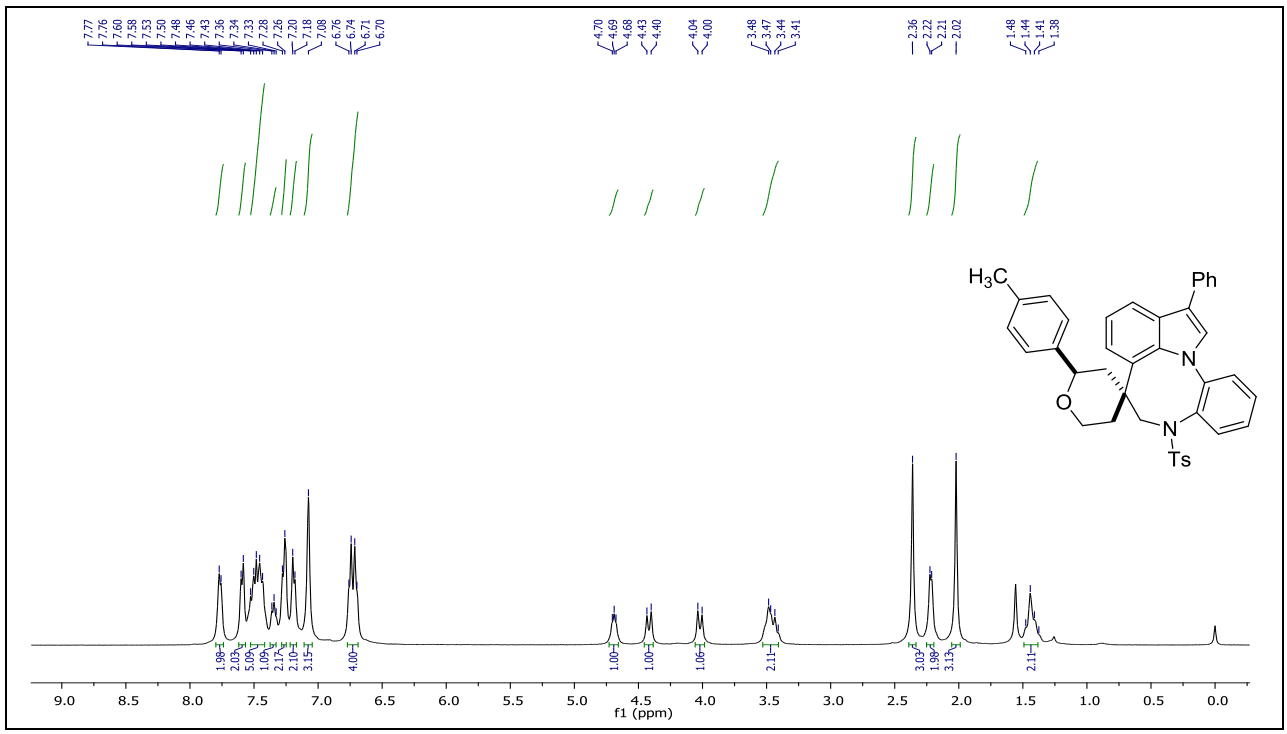


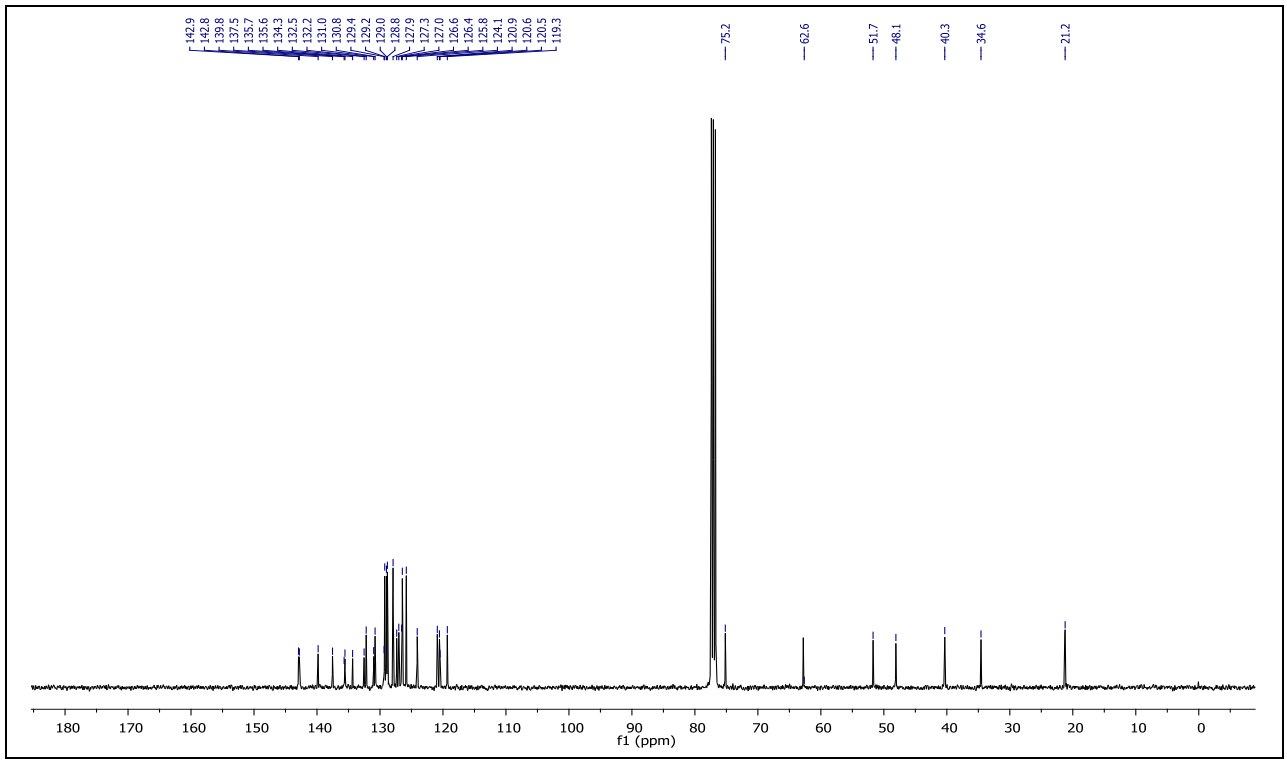
^{1}H and ^{13}C NMR spectra of compound 9o



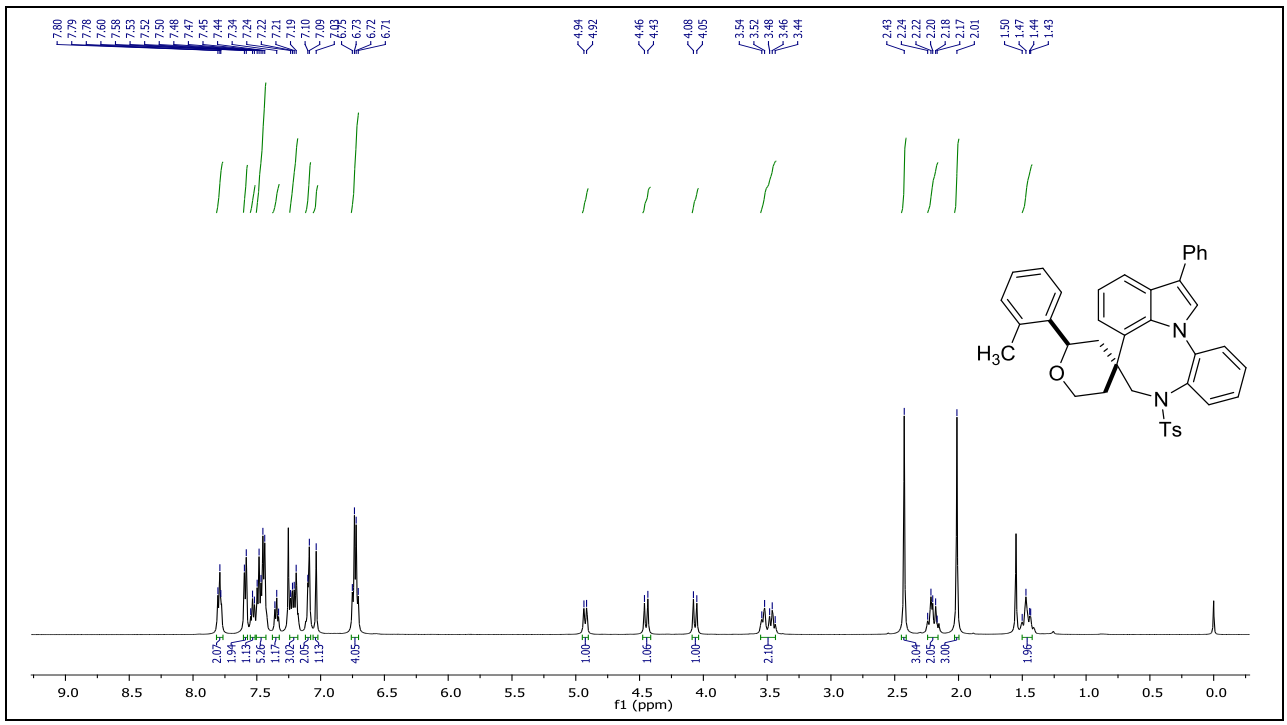


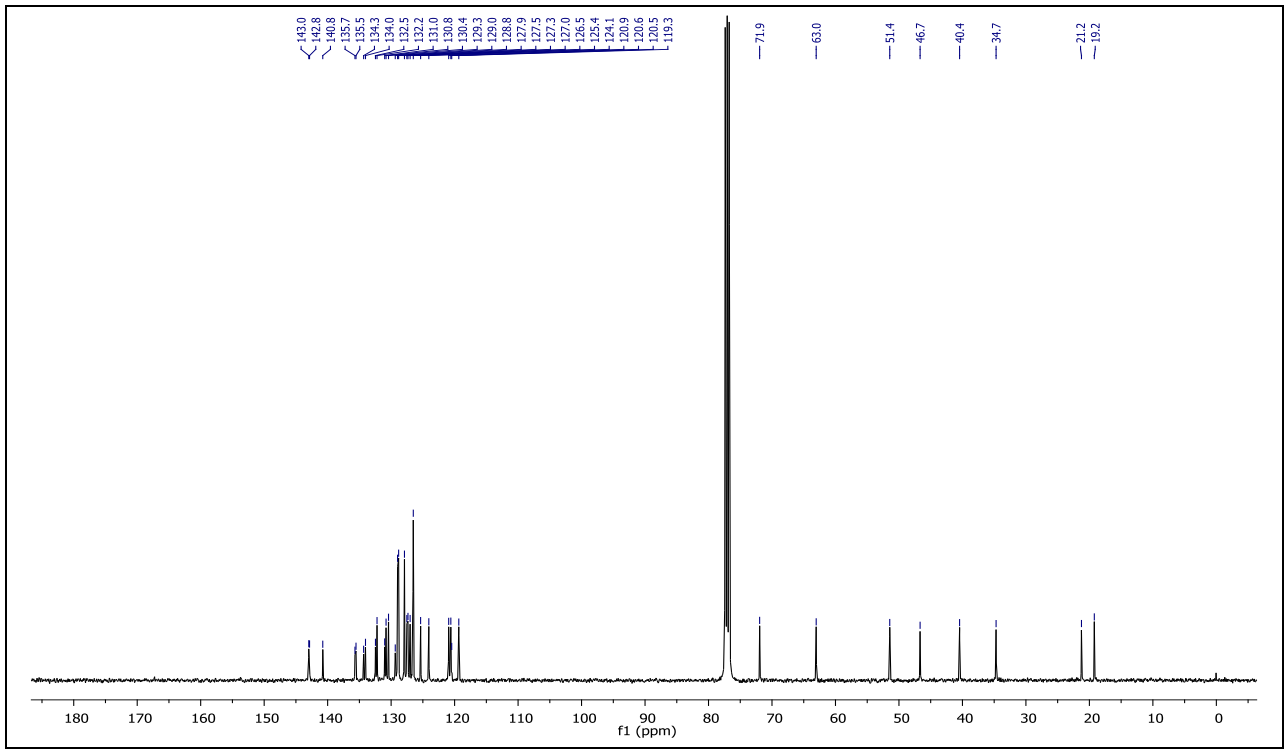
^{1}H and ^{13}C NMR spectra of compound 9p



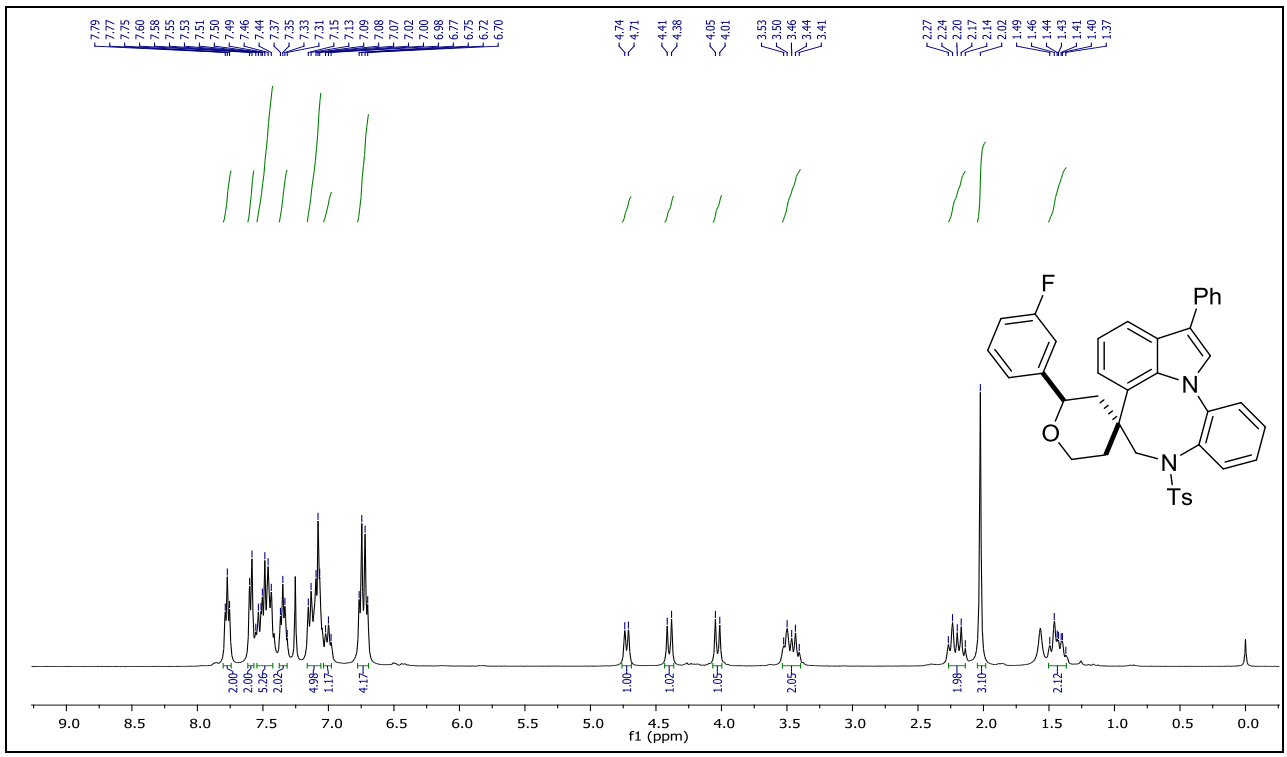


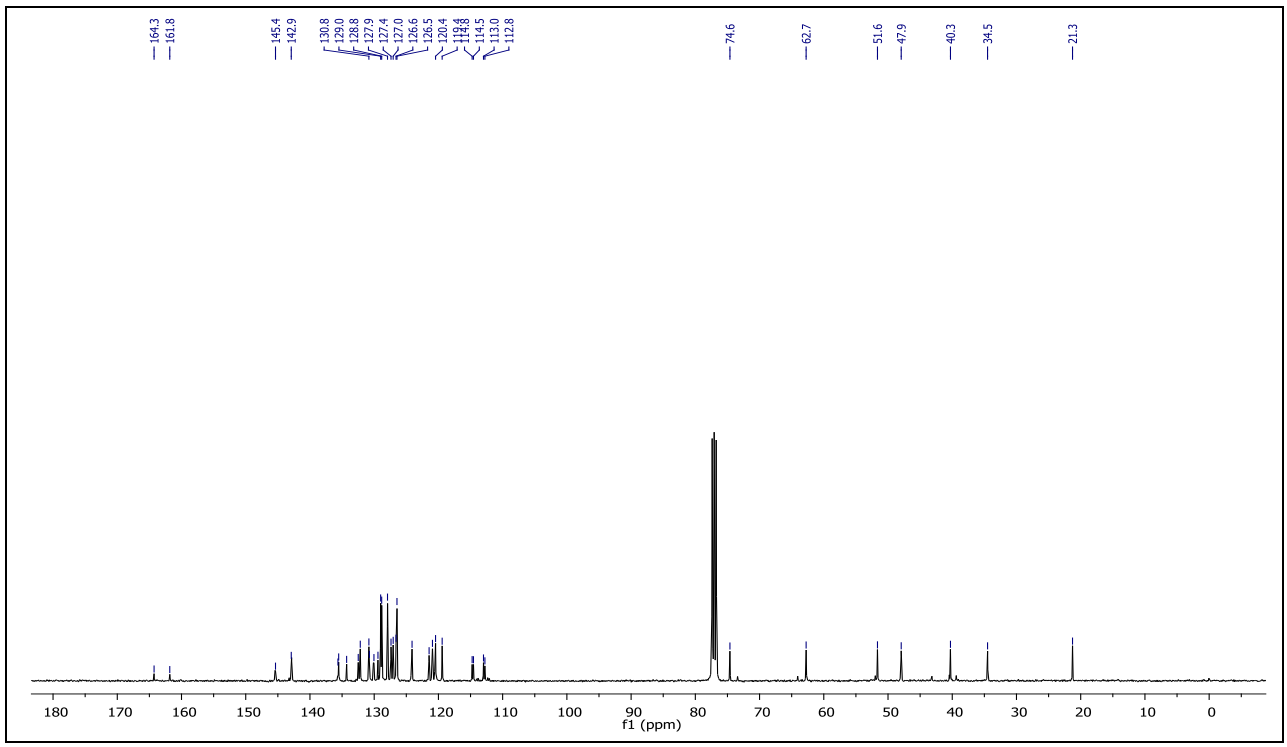
^{1}H and ^{13}C NMR spectra of compound 9q



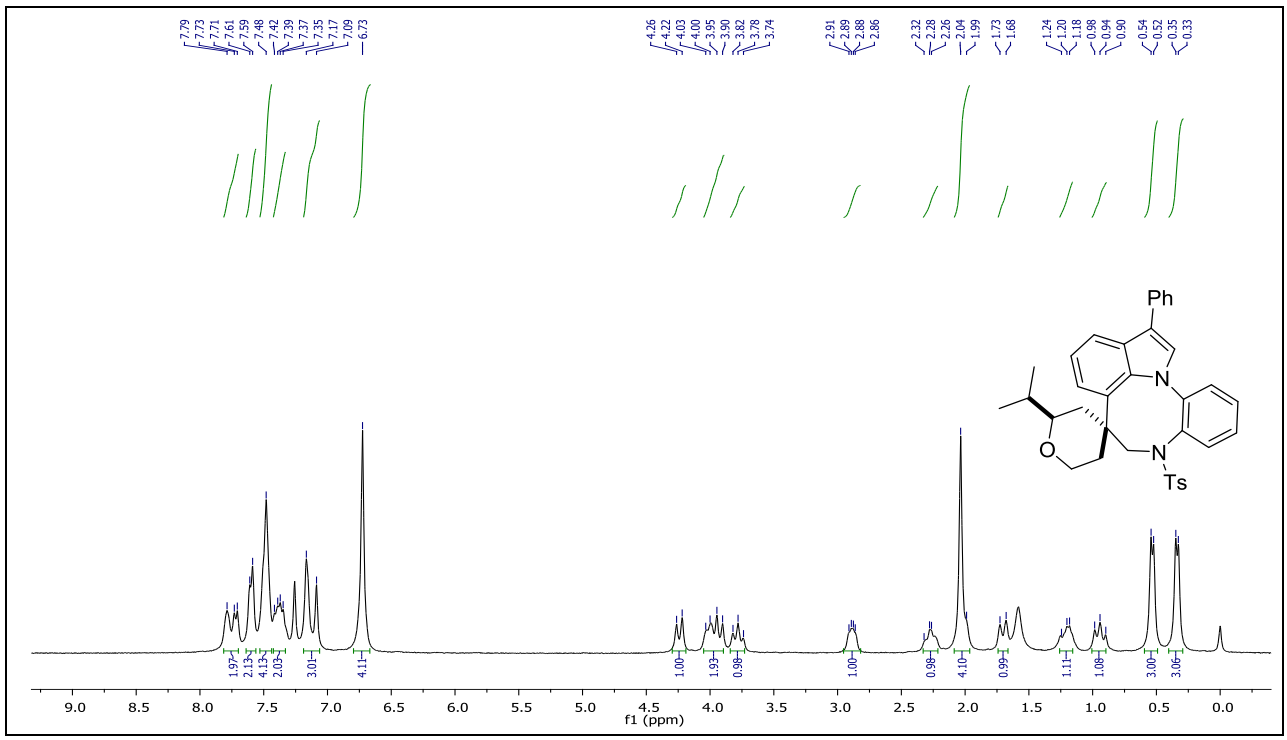


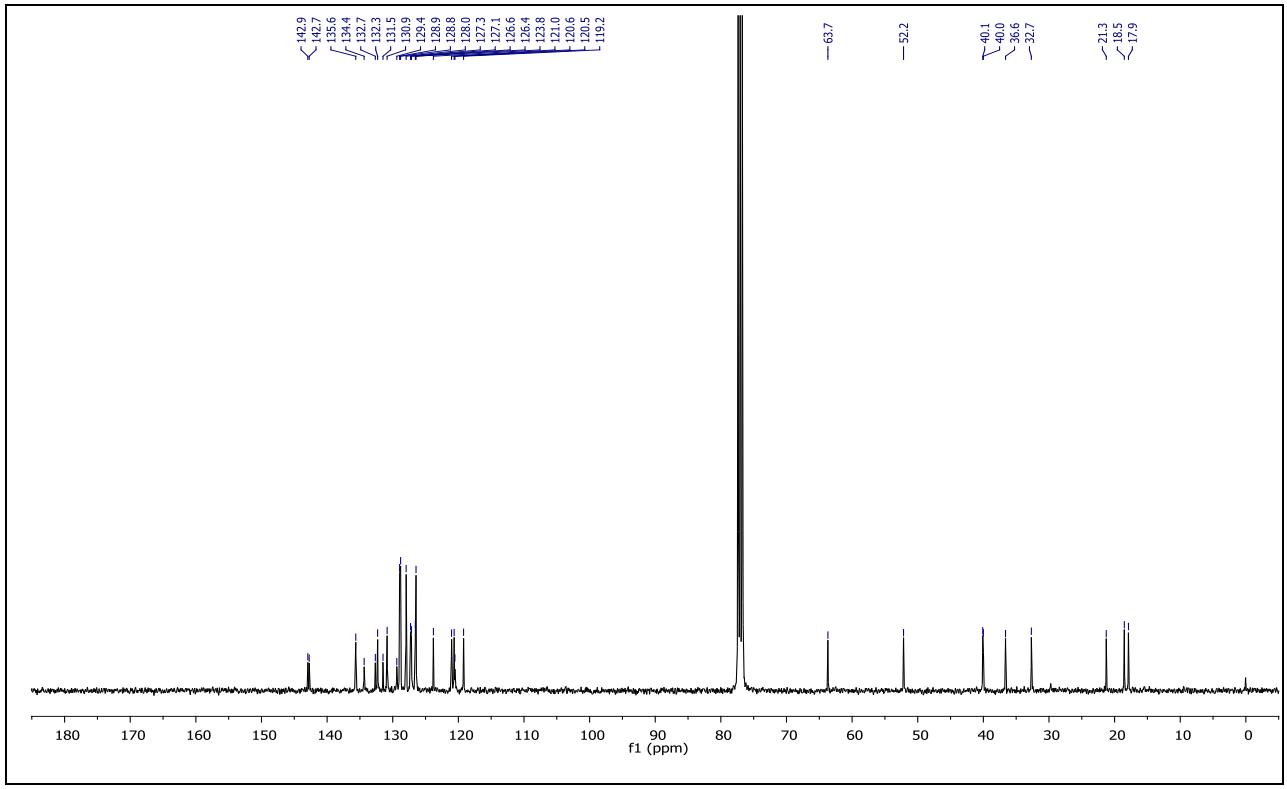
^{1}H and ^{13}C NMR spectra of compound 9r



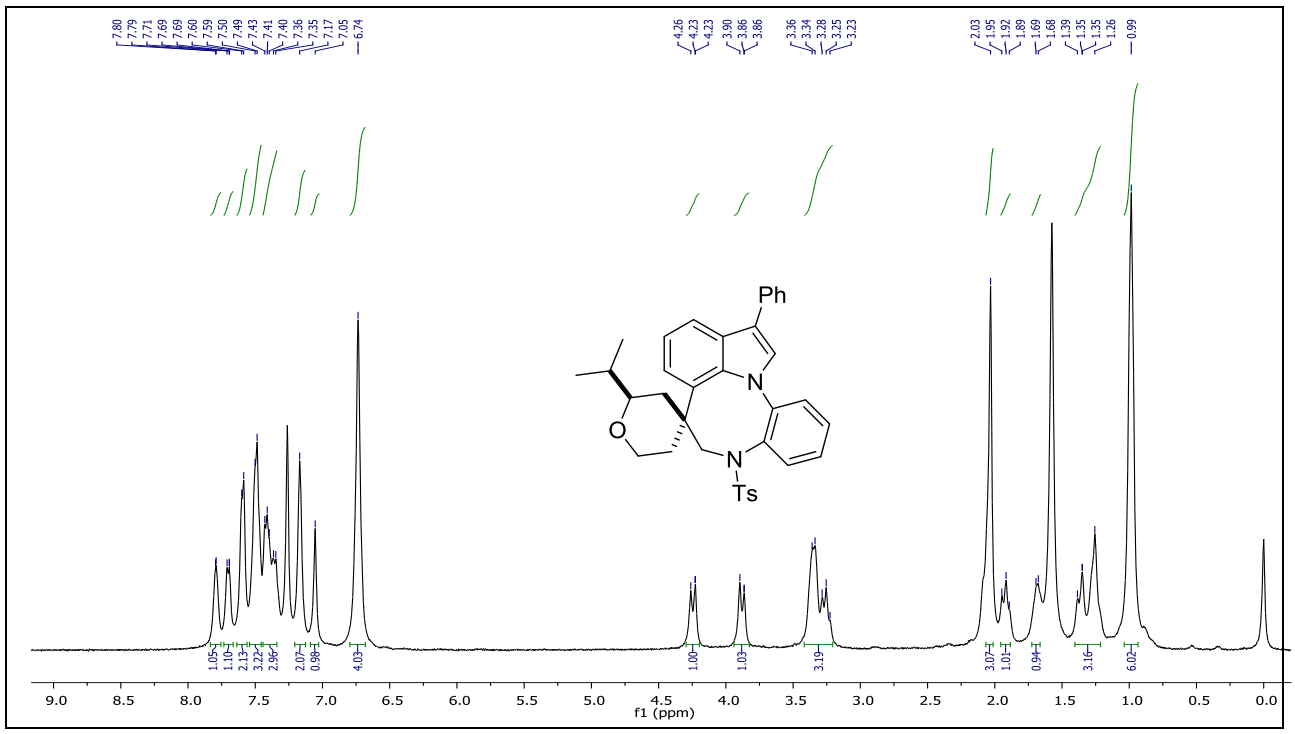


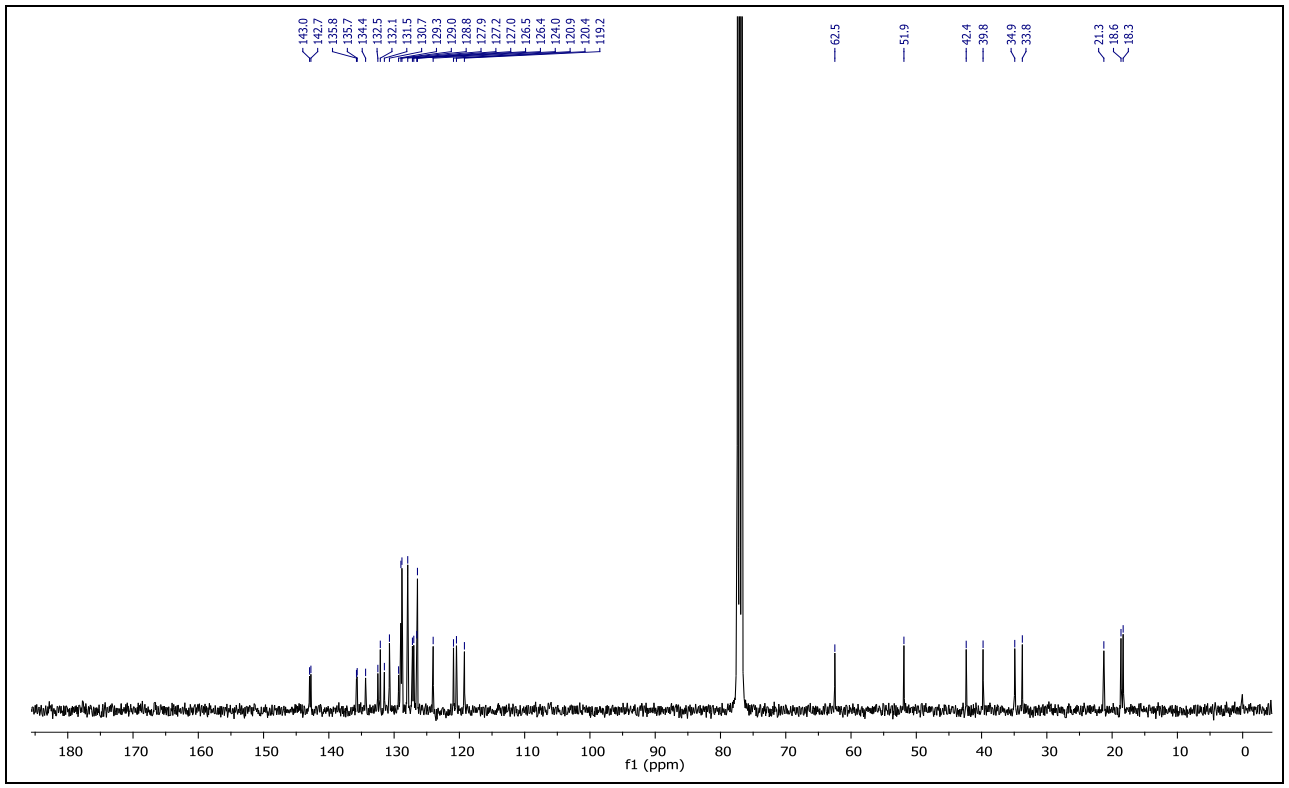
^{1}H and ^{13}C NMR spectra of compound 9s



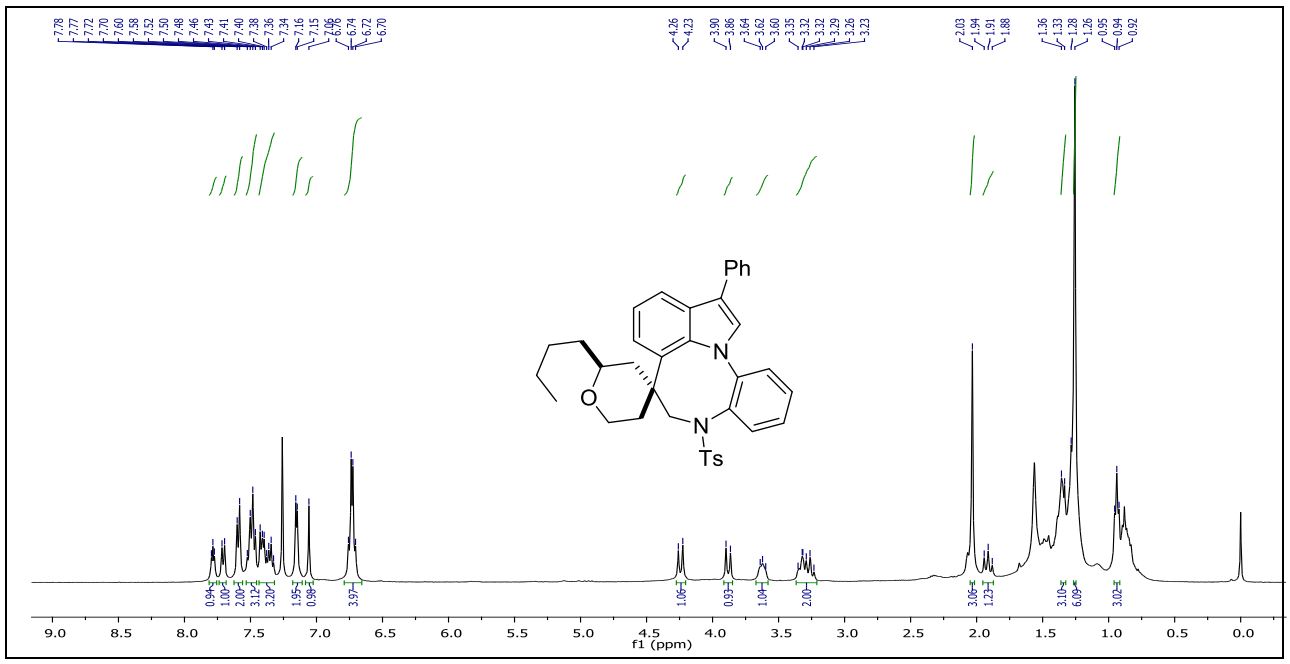


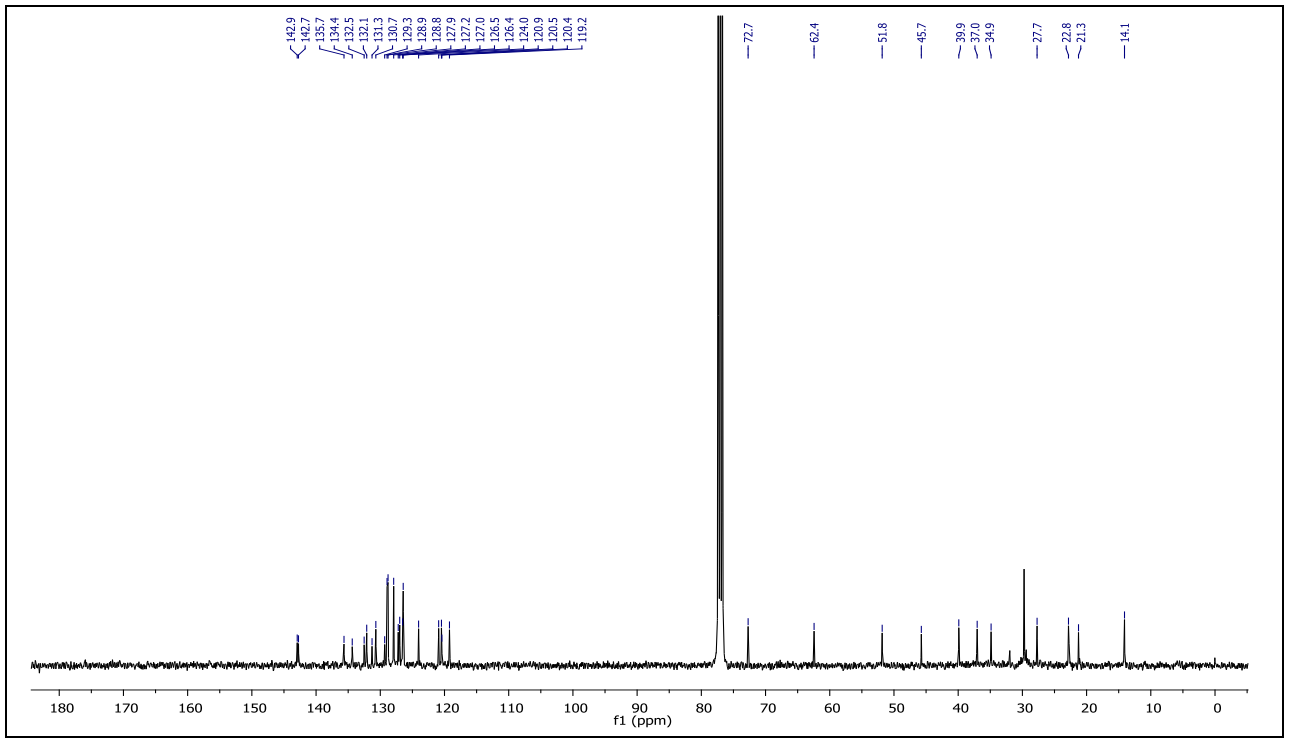
^{1}H and ^{13}C NMR spectra of compound 10s



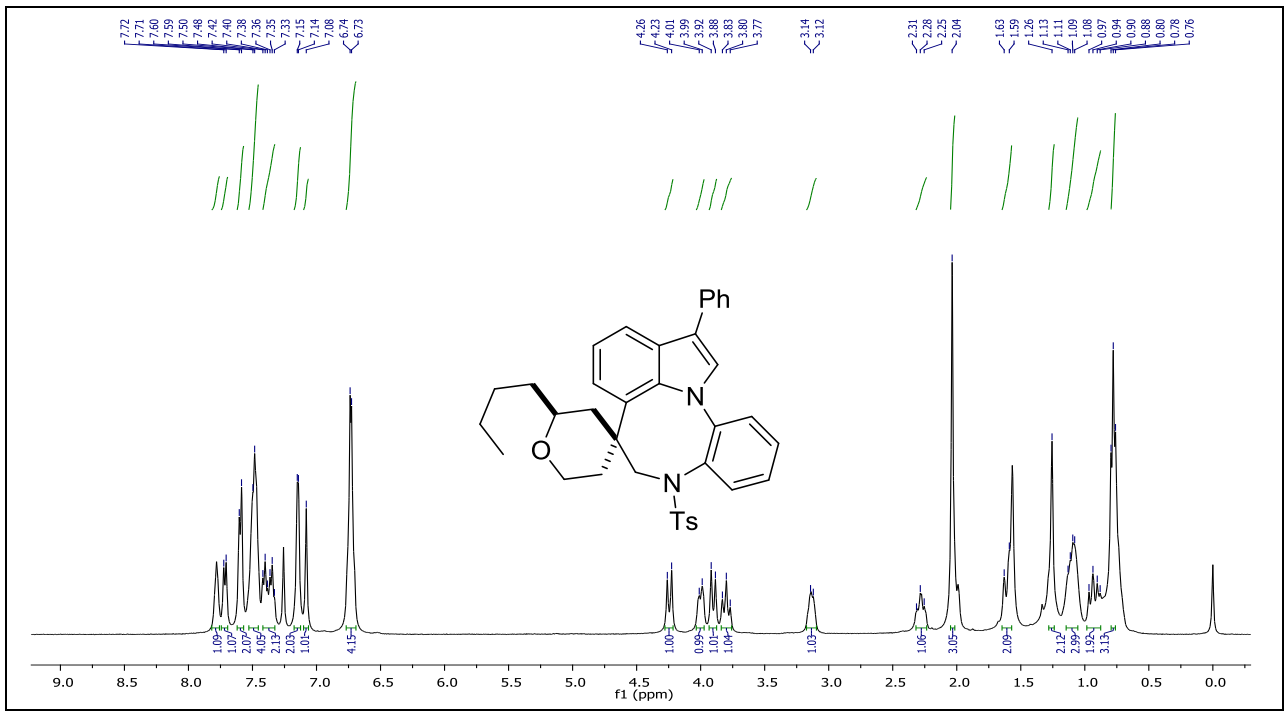


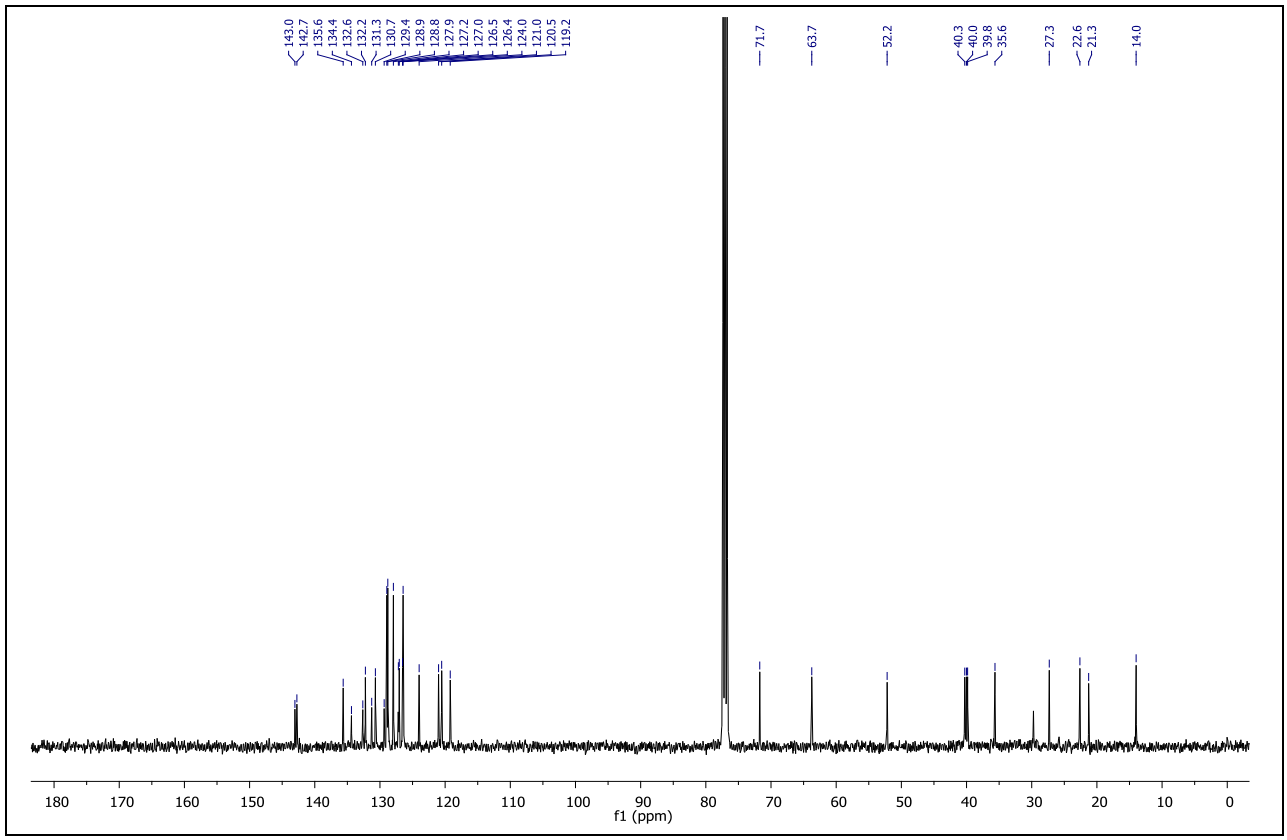
^{1}H and ^{13}C NMR spectra of compound 9t



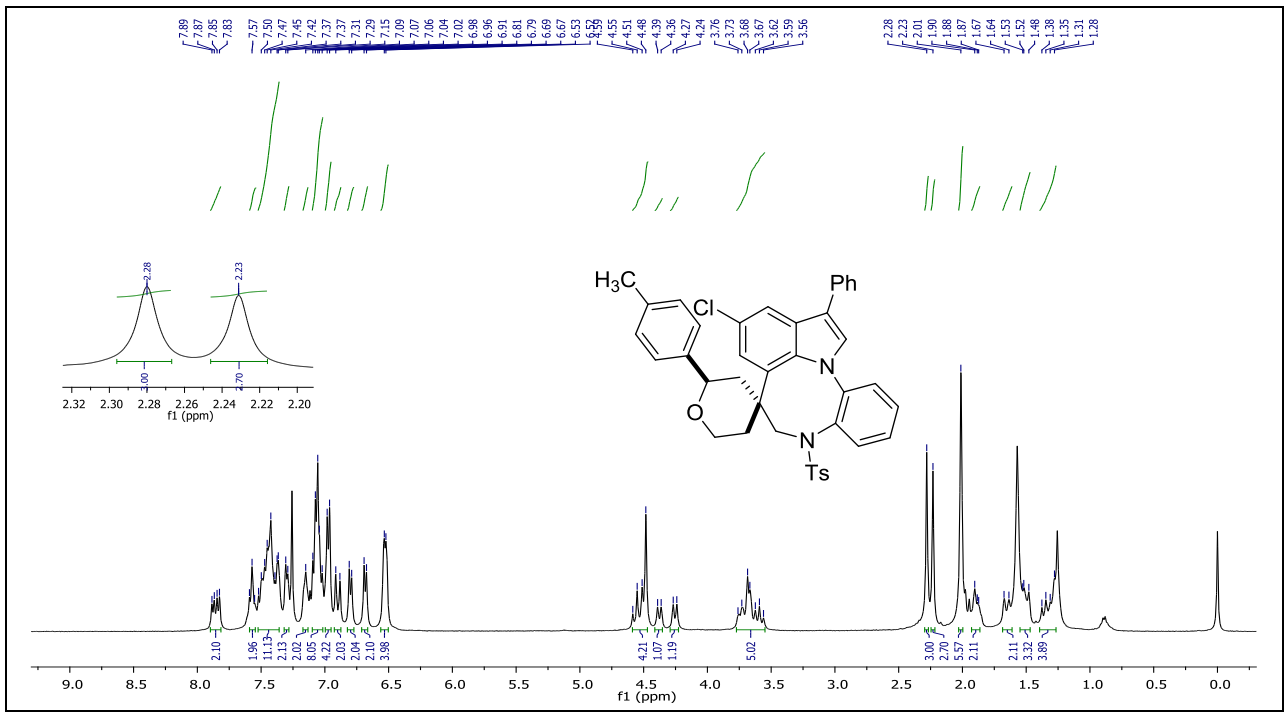


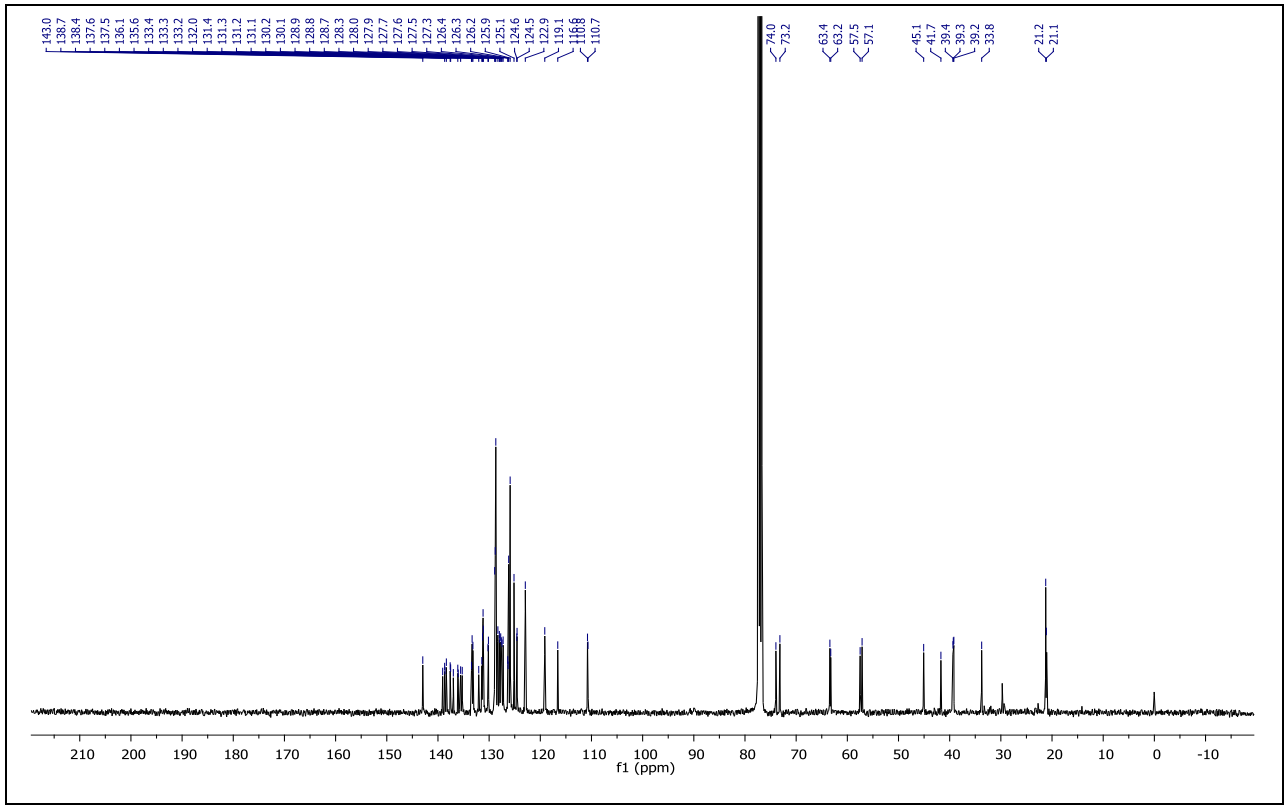
^{1}H and ^{13}C NMR spectra of compound 10t



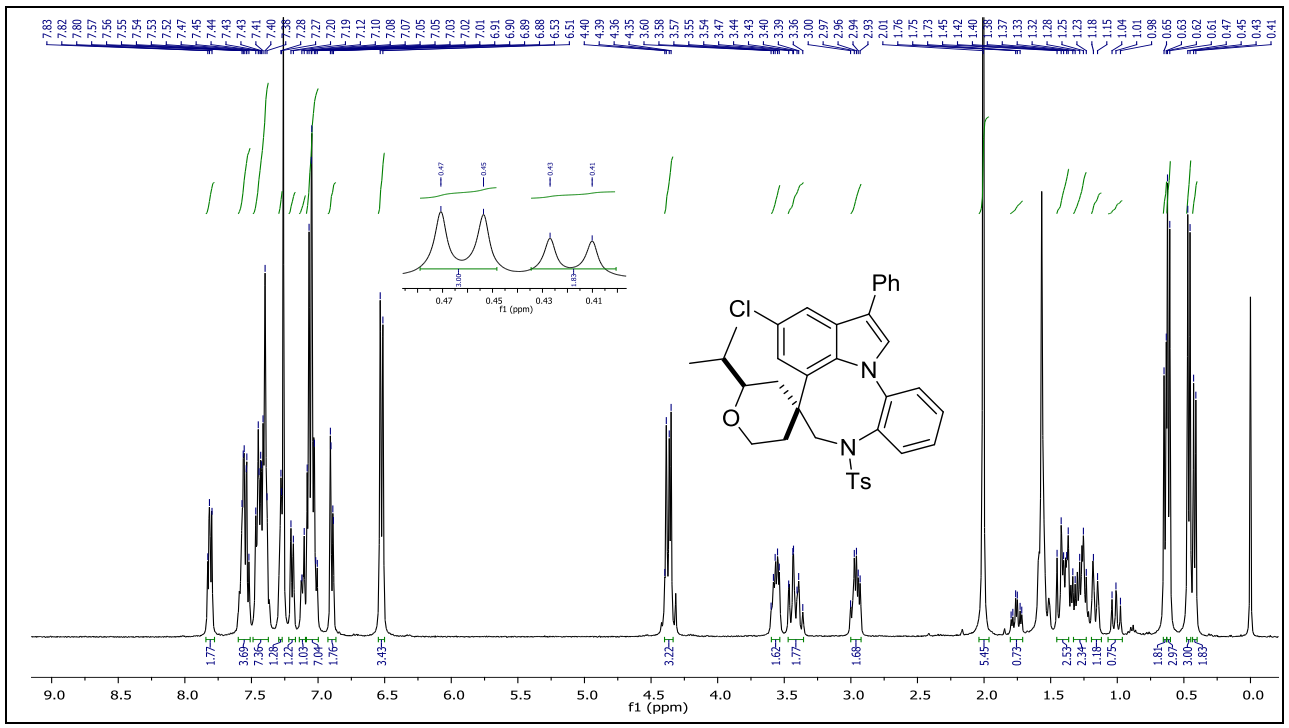


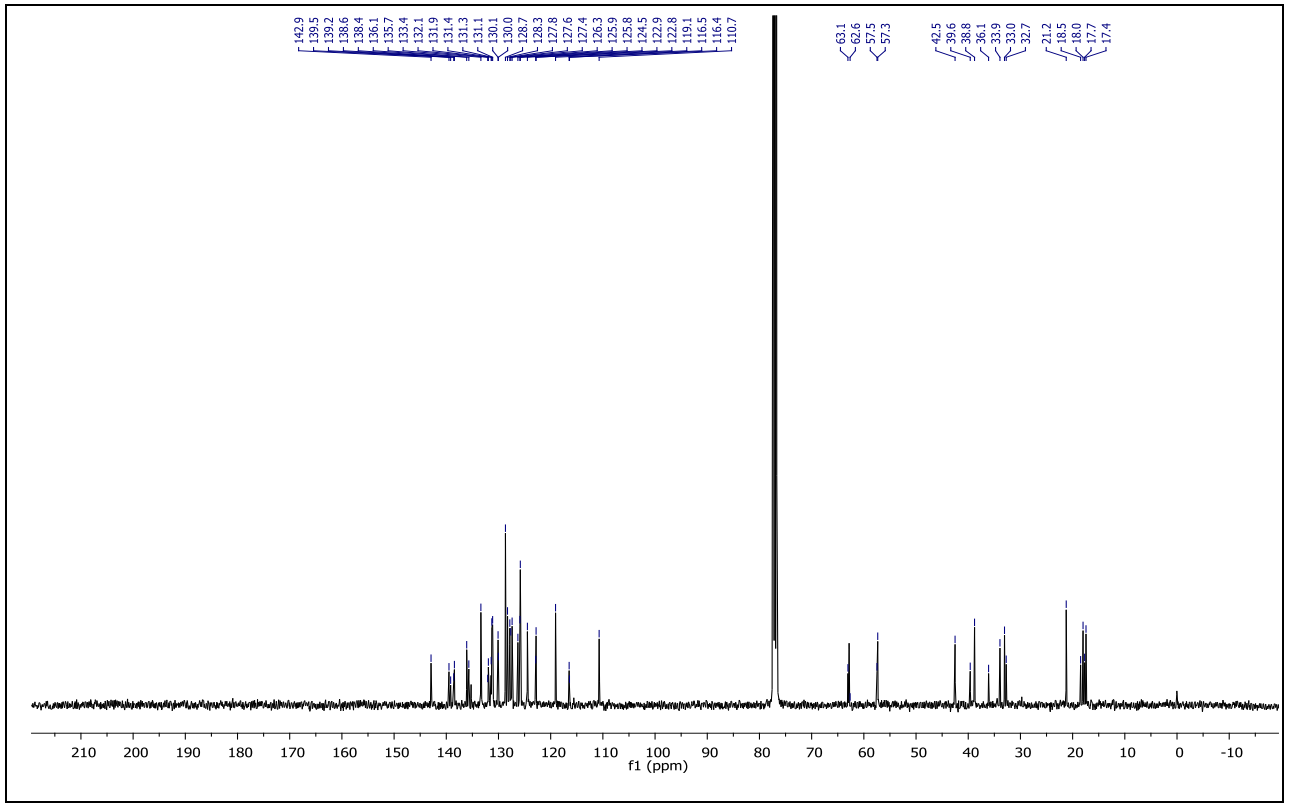
^{1}H and ^{13}C NMR spectra of compound 9u (Diastereomeric mixture, dr = 1:0.9)





^{1}H and ^{13}C NMR spectra of compound 9v (Diastereomeric mixture, dr = 1:0.6)





4. X-ray Crystallography

X-ray data for **9c** was collected at room temperatureon a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms.All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

Crystal structure determination of 9c:

Crystal Data for 9c: $C_{34}H_{31}BrN_2O_3S$, $CHCl_3$ (*M* =746.94 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.5464(3) Å, *b* = 11.3522(3) Å, *c* = 16.3209(5) Å, *α* = 79.8713(9)°, *β* = 82.8439(10)°, *γ* = 76.7777(10)°, *V* = 1688.44(9) $Å^3$, *Z* = 2, *T* = 294.15 K, μ(MoKα) = 1.555 mm^{-1}, *Dcalc* = 1.469 g/cm^3, 29864 reflections measured (4.4° ≤ 2Θ ≤ 49.994°), 5950 unique (R_{int} = 0.0865, R_{sigma} = 0.0716) which were used in all calculations. The final R_1 was 0.0939 (I > 2σ(I)) and wR_2 was 0.2488 (all data). CCDC1989601 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

A view of **9c**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii (Figure 2).

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** ActaCrystallogrC71:3-8.