Supporting Information

Visible-Light-Triggered Organophotoredox-catalyzed Oxidation of 3-(benzylidine)indoline to Indole-3-carbinols and 3-acyl indoles

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General information:

^{1}H NMR spectra were recorded in $CDCl_3$ solutions with a Bruker (300 MHz, 400 MHz). Spectrometer Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.28 ppm) as an internal standard. All coupling constants are absolute values and are expressed in hertz. Signal description: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, brs = broad singlet. ^{13}C NMR spectra were recorded in $CDCl_3$ solutions with the help of Bruker Spectrometer (75 MHz, 101 MHz) complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. High-resolution mass spectra (HRMS) were performed in dichloromethane solvent. The molecular fragments are quoted as the relation between mass and charge (m/z). Crystallographic data were collected at room temperature on a Bruker D8 quest microfocus single crystal XRD machine. The routine monitoring of reactions was performed with silica gel coated glass slides and pre coated Al plates, which were analyzed with iodine, UV light, and alkaline $KMnO_4$, respectively. Solvents, reagents, and chemicals were purchased from Aldrich, Alfa aesar, Merck, SRL, Spectrochem, and Process Chemicals. Melting points were determined in a capillary melting point apparatus and are uncorrected. The final products were purified by column chromatography on Merck silica gel (60-120) mesh). All reactions involving moisture-sensitive reactants were executed with oven-dried glassware.

The Material of the Irradiation Vessel

Model：Tornado-G-5M

Broadband source：λ_{max} = 545 nm

Emission spectrum (figure S1)

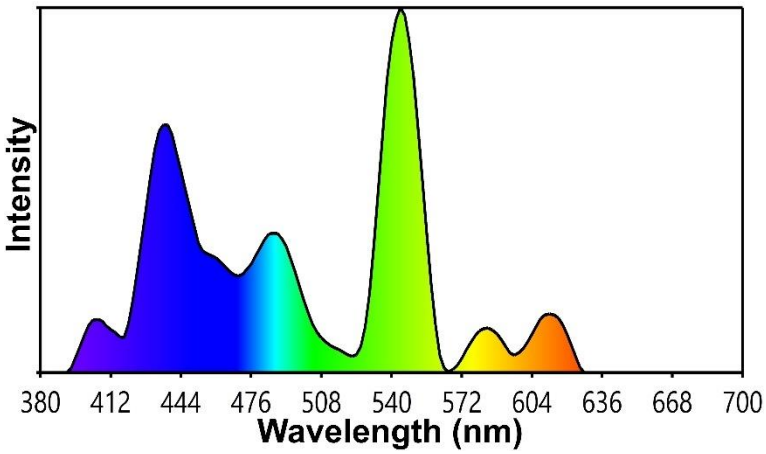


Figure S1: The spectrum of our lamp (32 W CFL)

Material of the irradiation vessel：Borosilicate reaction tube

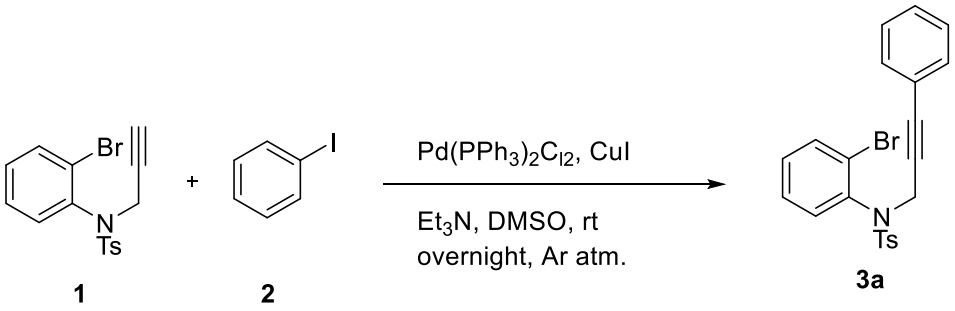
Distance from the light source to the irradiation vessel：3.0 cm

Not use any filters

Experimental Section

General Procedure 1 (GP1):

Representative experimental procedure for the synthesis and Characterization of N-(2-bromophenyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (3a):

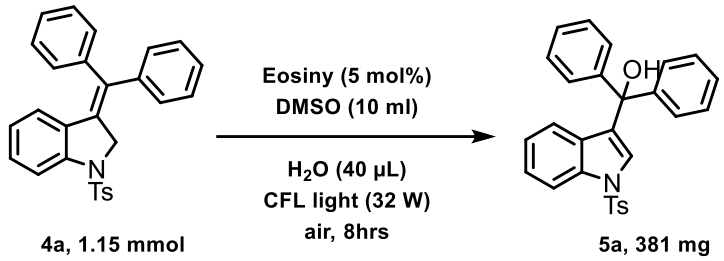


Compound **3a** was synthesized by following our previous reported procedure[1].

To a solution of **1** (500 mg, 1.38 mmol) in dimethylsulfoxide (DMSO) (4 mL), iodobenzene (**2**) (310 mg, 1.52 mmol), triethylamine (279 mg, 2.76 mmol), CuI (6 mg, 0.028 mmol) and $Pd(PPh_3)_2Cl_2$ (20 mg, 0.028 mmol) were added successively. The resulting solution was stirred at room temperature under argon atmosphere for overnight. After the completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with ethyl acetate. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated. The product was subjected to column chromatography (silica gel, 60-120 mesh), eluting with hexane/EtOAc 95:5 (v/v) to afford the product **3a** as a yellow semisolid (455 mg, 1.035 mmol, 75%).

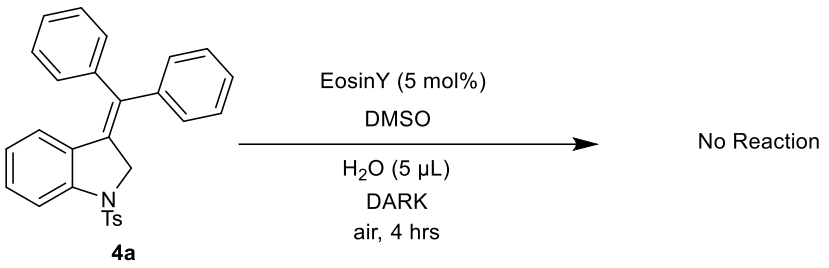
Compounds **3b-3o** were synthesized by following the above method.

Scale-up synthesis of diphenyl(1-tosyl-1*H*-indol-3-yl)methanol (5a)

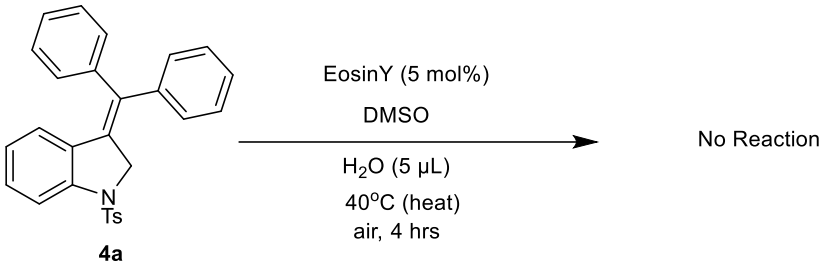


An oven dried reaction tube (50 mL) equipped with a magnetic stir bar was charged with *3-(diphenylmethylene)-1-tosylindoline* (**4a**) (503 mg, 1.15 mmol), Eosin Y (40 mg, 0.05 equiv.), H_2O (40 µL) and DMSO (10 mL). Then the mixture was irradiated with 32 W household CFL bulb under air atmosphere for 8 hrs. After completion of the reaction (monitored by TLC), the mixture was extracted with EtOAc (3x40 mL). The organic phase was dried by Na_2SO_4 and evaporated to leave the crude product, which was purified by silica gel (60-120 mesh) column chromatography (hexane /EtOAc, 95:5) to provide the pure *diphenyl(1-tosyl-1H-indol-3-yl)methanol* (**5a**) as a white solid ; yield: 381 mg (73%).

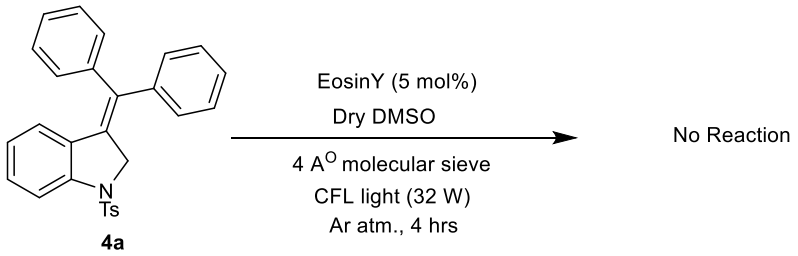
Control experiments:



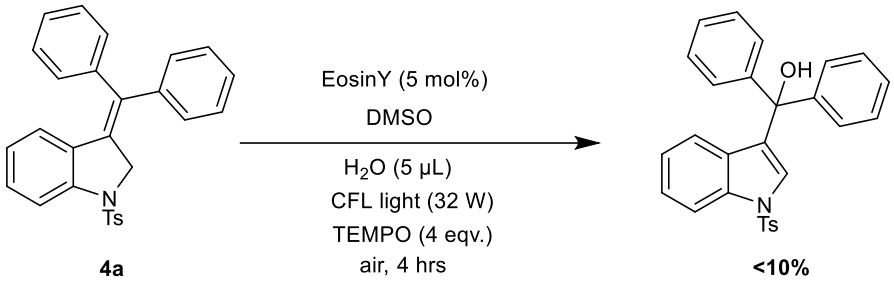
An oven dried reaction tube (20 mL) equipped with a magnetic stir bar was charged with **4a** (66 mg, 0.15 mmol), Eosin Y (5 mg, 0.05 equiv.), H_2O (5µL) and DMSO (1 mL). Then the mixture was stirred in dark for 4 hrs under air atmosphere and the reaction was not initiated at all.



An oven dried reaction tube (20 mL) equipped with a magnetic stir bar was charged with **4a** (66 mg, 0.15 mmol), Eosin Y (5 mg, 0.05 equiv.), H_2O (5µL) and DMSO (1 mL). Then the mixture was stirred in 40 °C for 4 hrs under air atmosphere and the reaction was not initiated at all.



An oven dried reaction tube (20 mL) equipped with a magnetic stir bar and activated molecular sieve was charged with **4a** (66 mg, 0.15 mmol), Eosin Y (5 mg, 0.05 equiv.), and dry DMSO (1 mL). Then the mixture was irradiated with 32 W household CFL bulb under air atmosphere for 4 hrs and the reaction was not initiated at all.

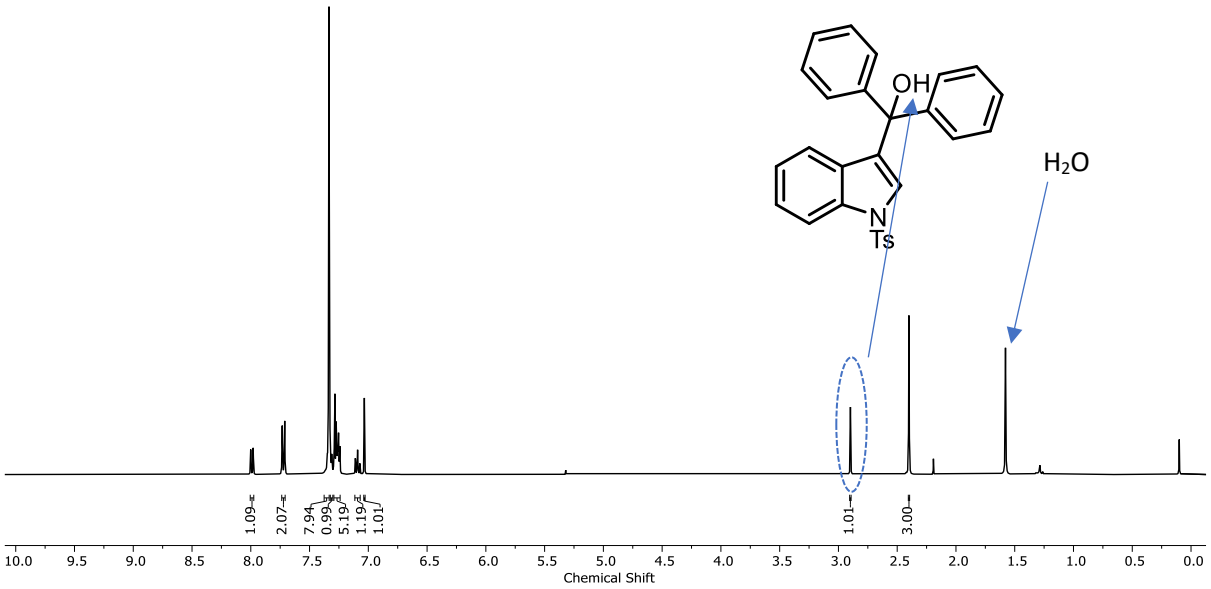


4a **<10%**

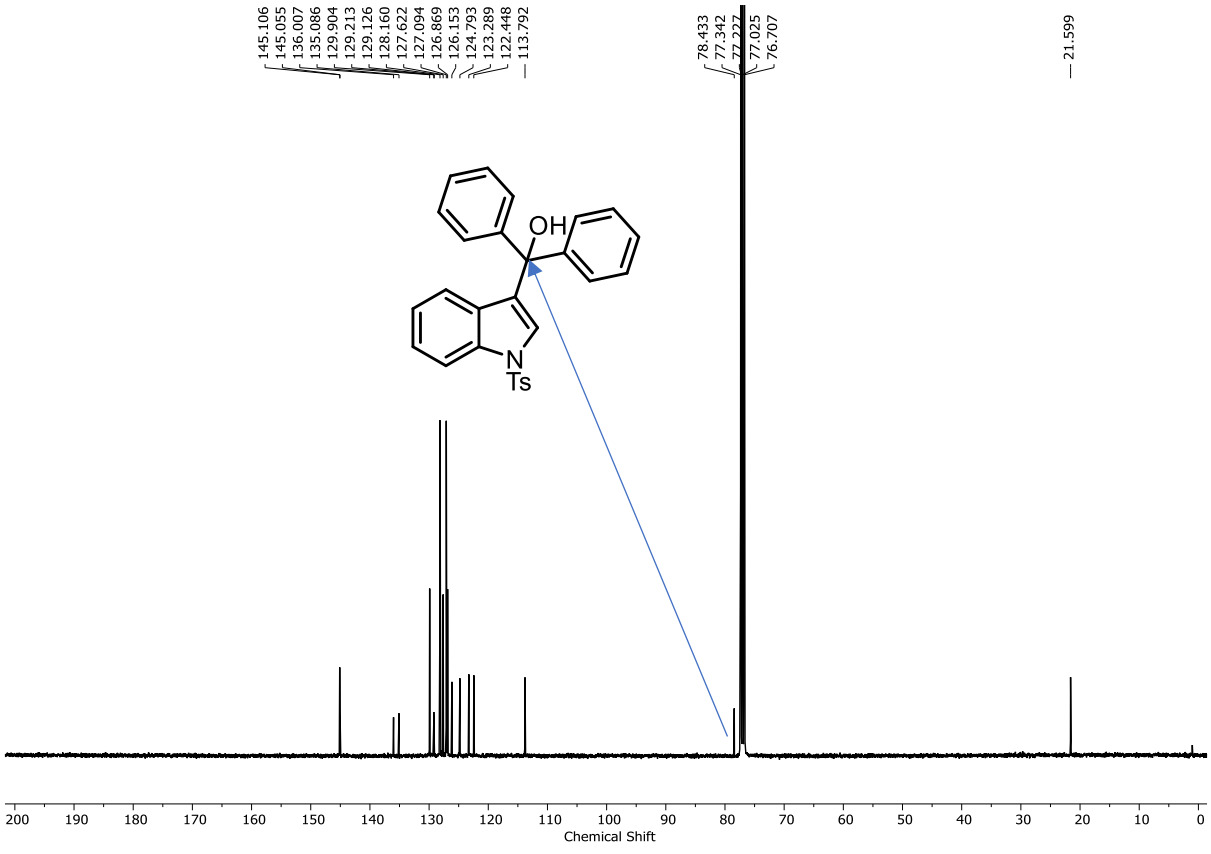
An oven dried reaction tube (20 mL) equipped with a magnetic stir bar was charged with **4a** (66 mg, 0.15 mmol), Eosin Y (5 mg, 0.05 equiv.), TEMPO (94 mg, 4 equiv.), H_2O (5µL) and DMSO (1 mL). Then the mixture was irradiated with 32 W household CFL bulb under air atmosphere for 4 hrs. After completion of the reaction (monitored by TLC), the mixture was extracted with EtOAc (3x20 mL). The organic phase was dried by Na_2SO_4 and evaporated to leave the crude product, which was purified by silica gel (60-120 mesh) column chromatography (hexane /EtOAc, 95:5) to provide the pure **5a** as a white solid; which was yielded in less than 10%.

NMR [^{1}H, $^{13}C\{^{1}H\}$, ^{19}F] spectra of synthesized products:

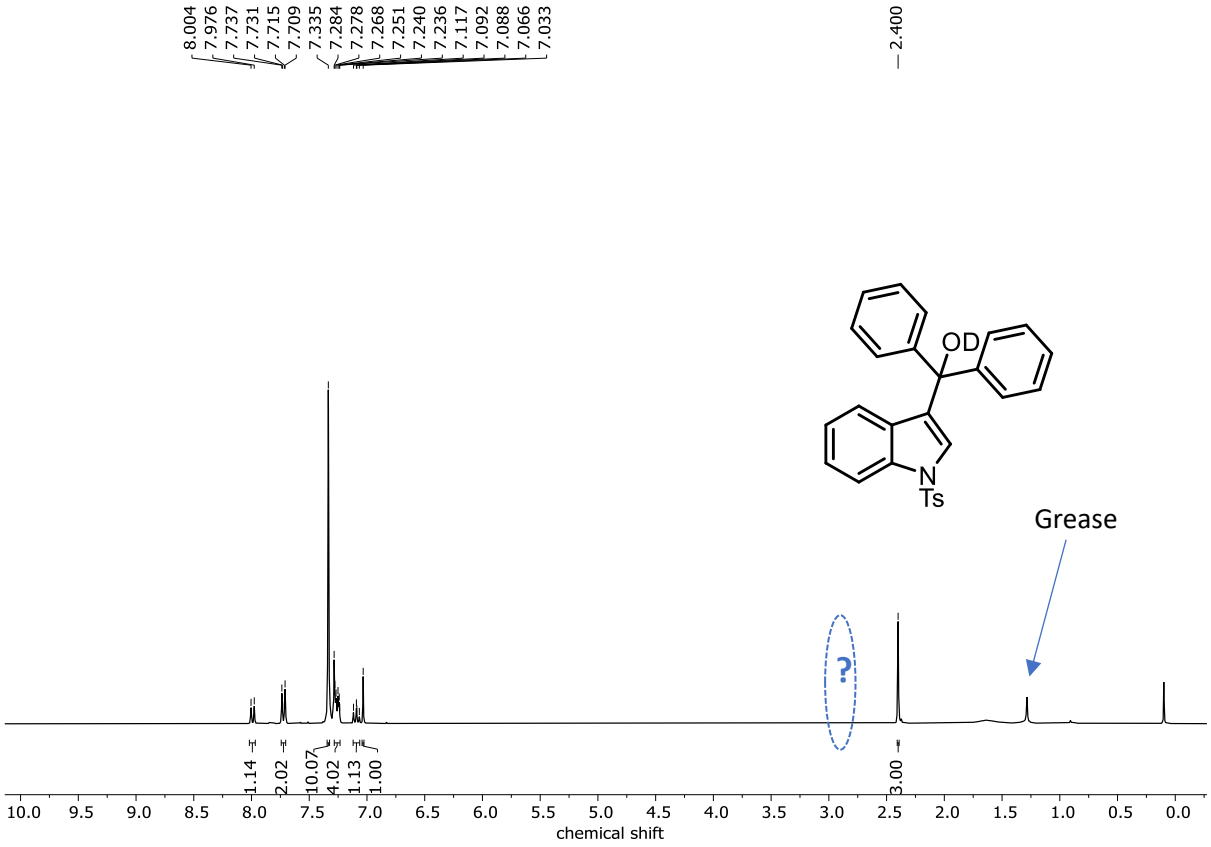
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5a



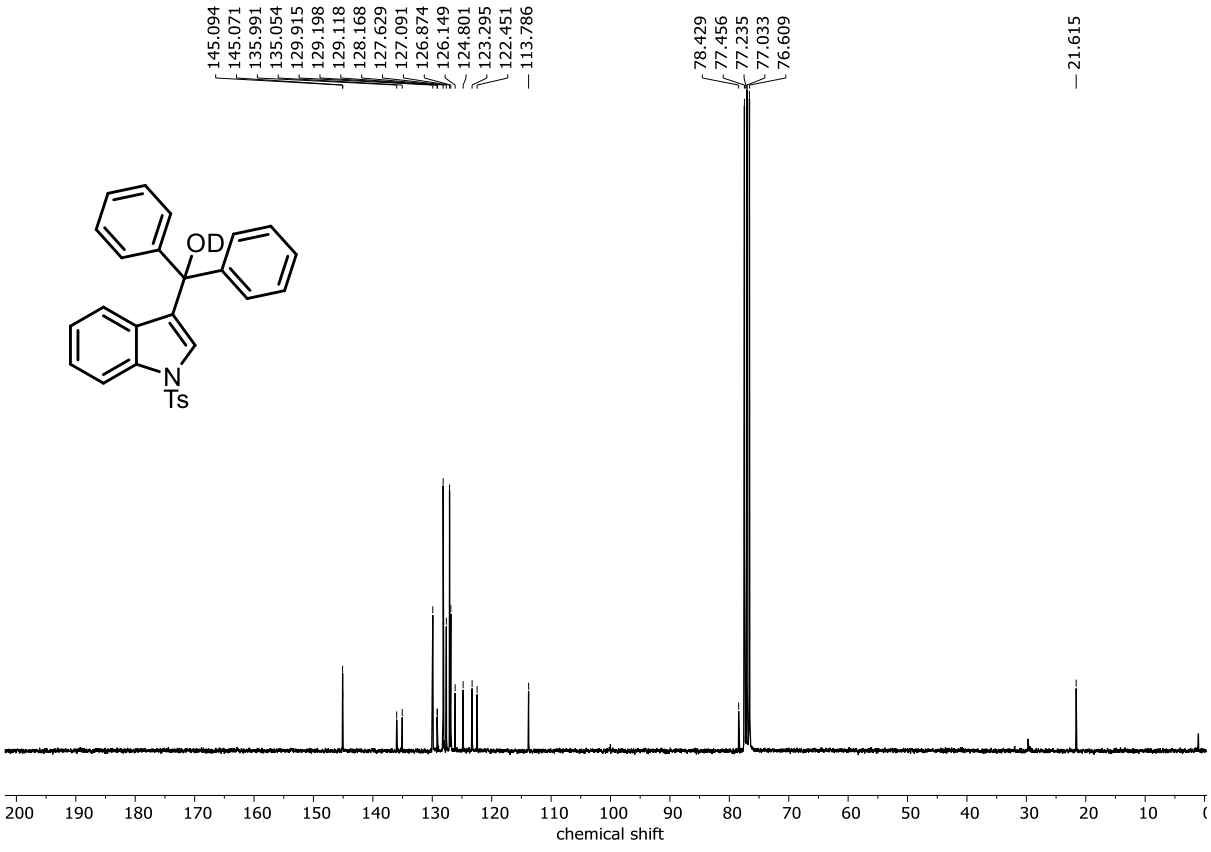
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of 5a



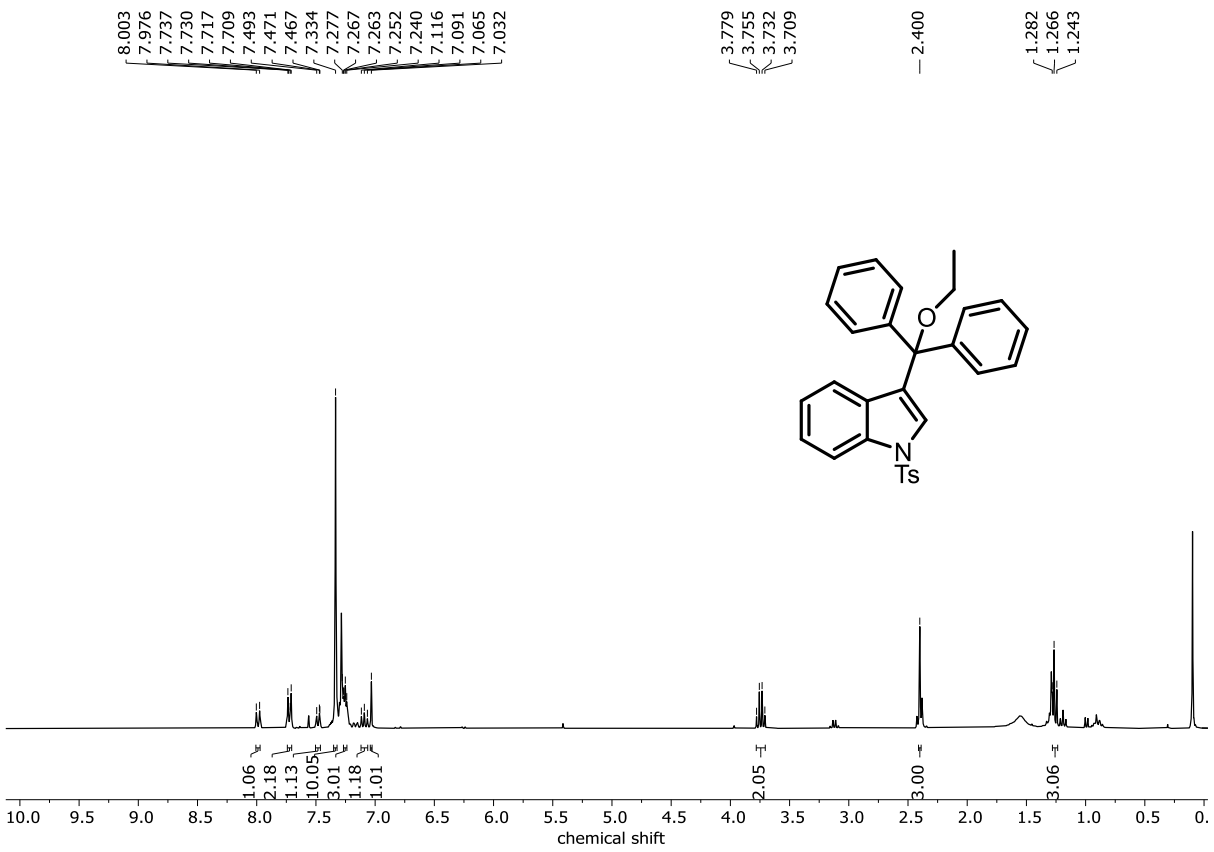
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5aa



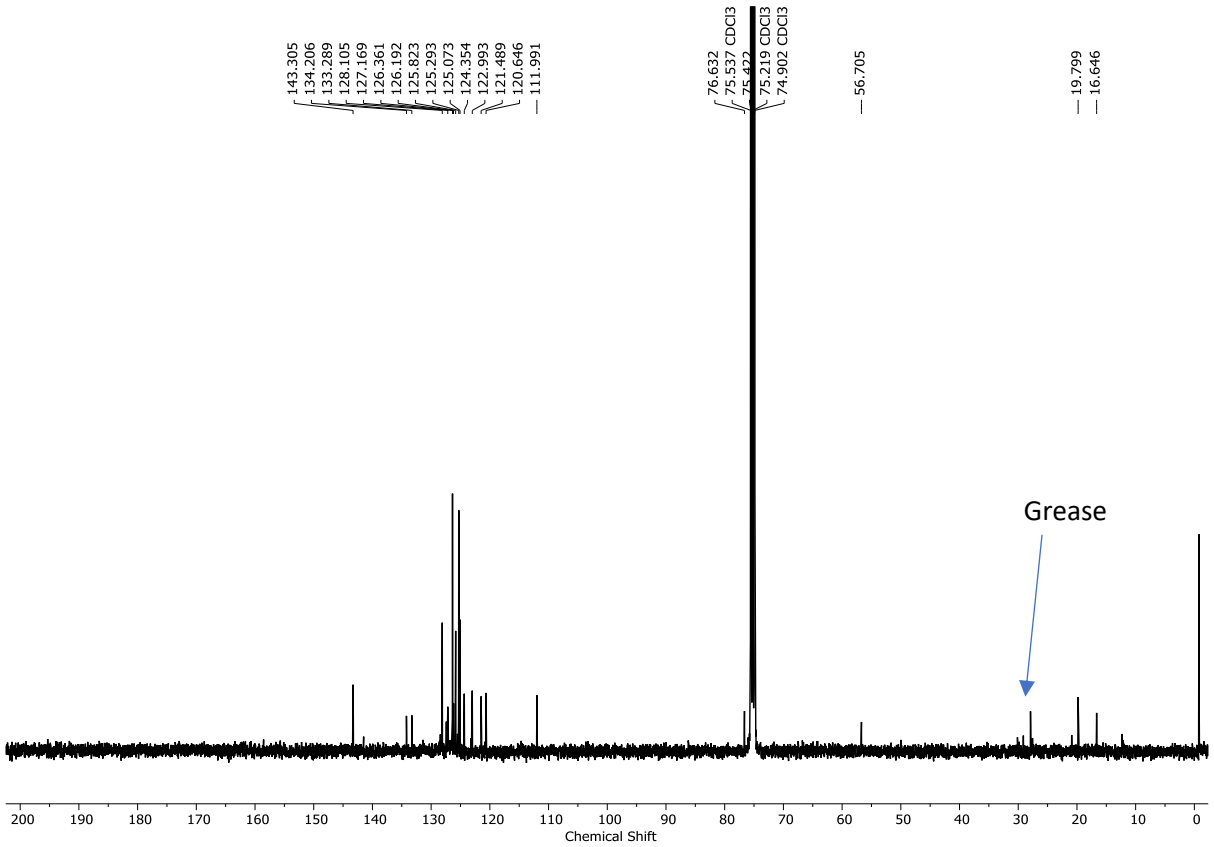
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 5aa



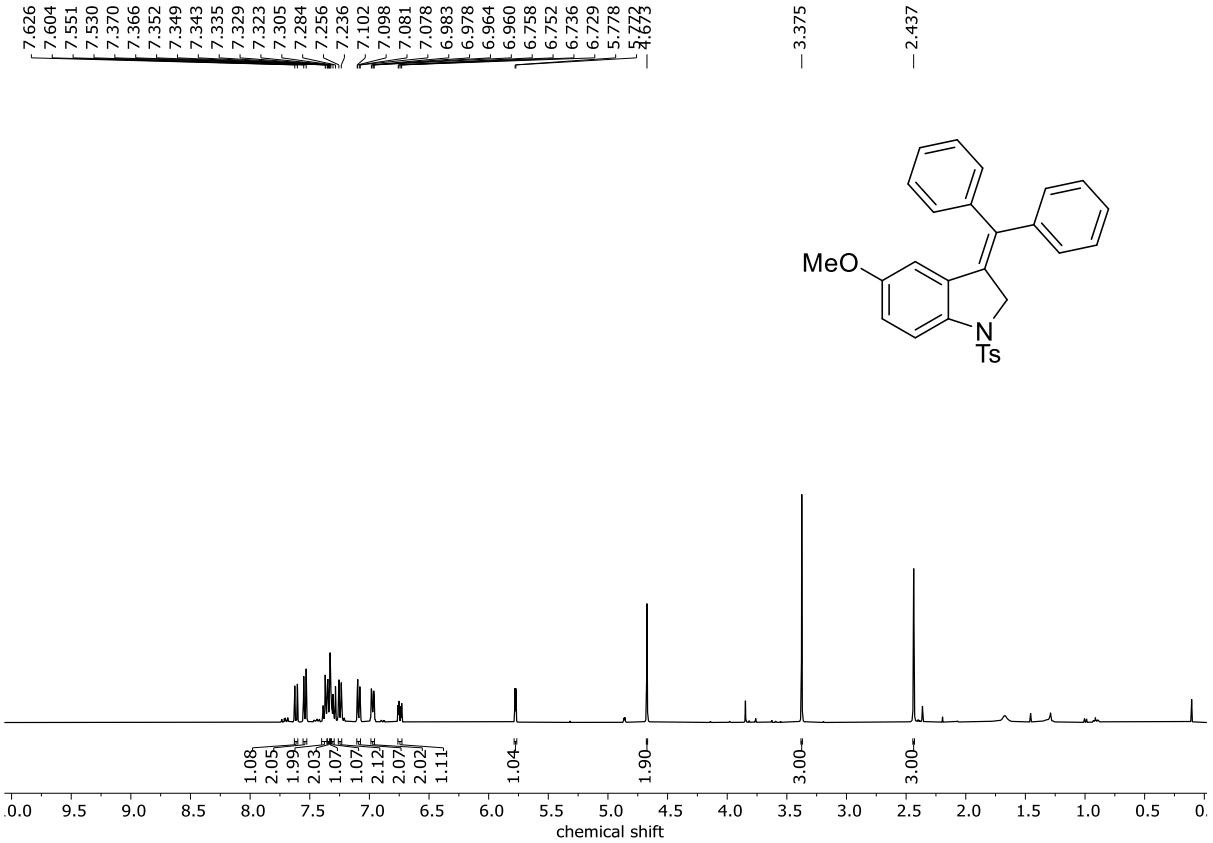
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5ab



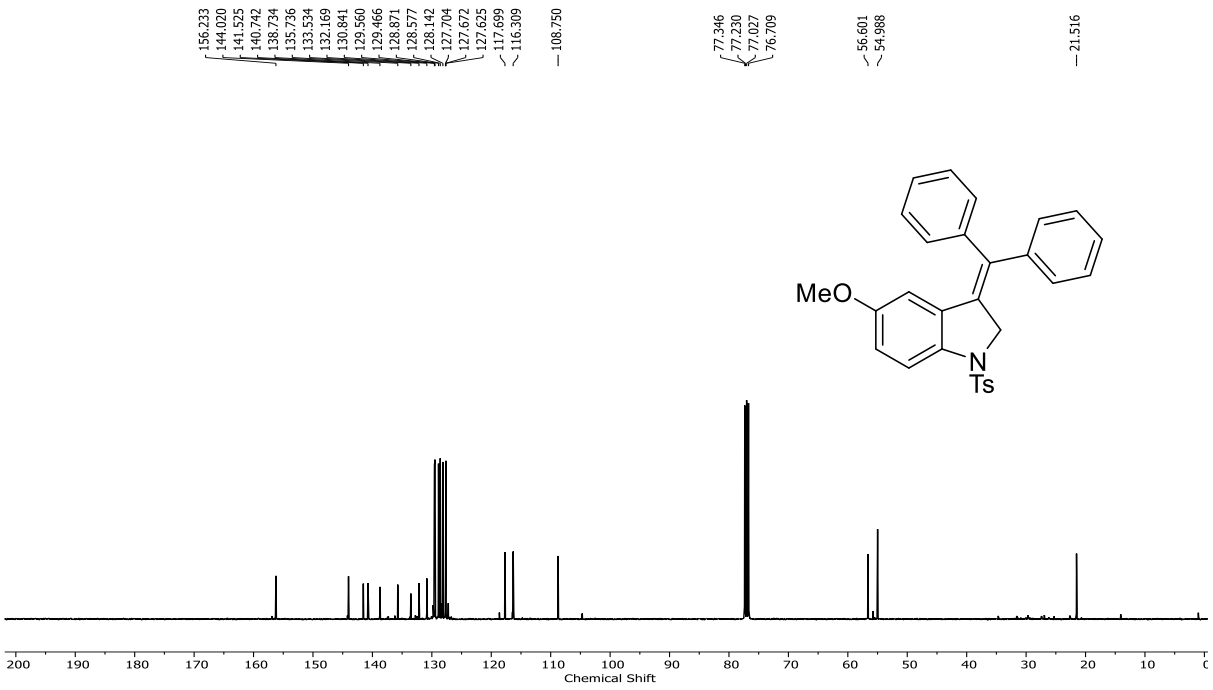
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 5ab



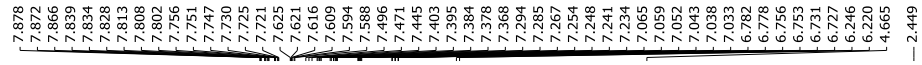
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4b

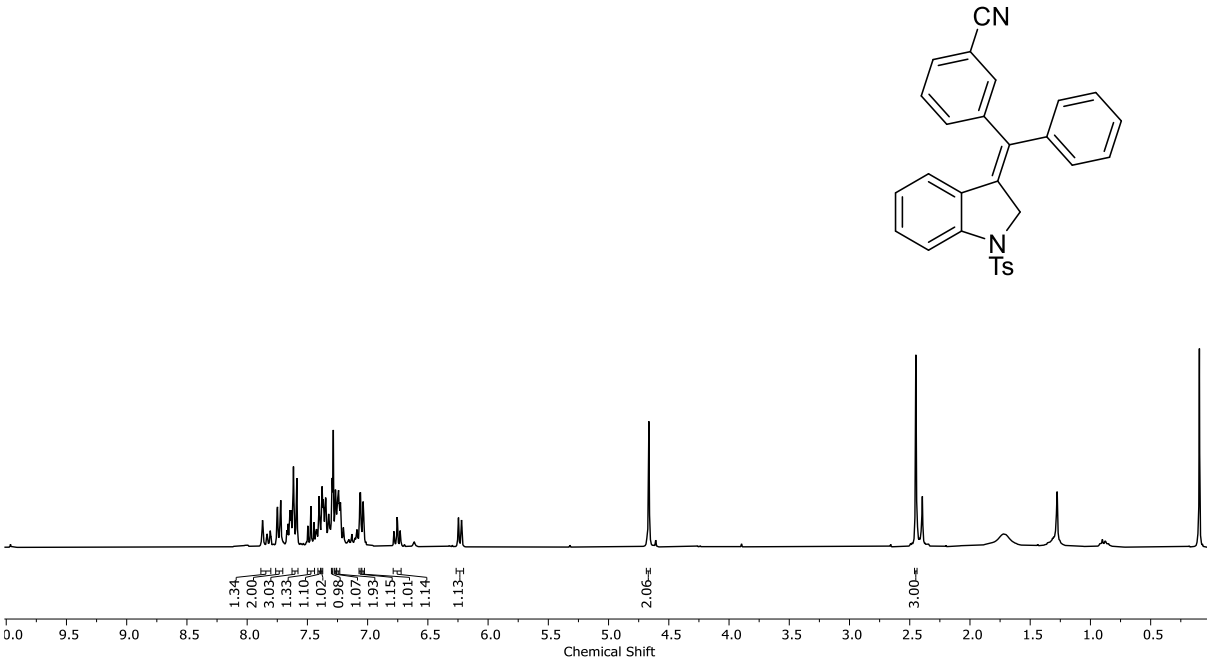


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 4b

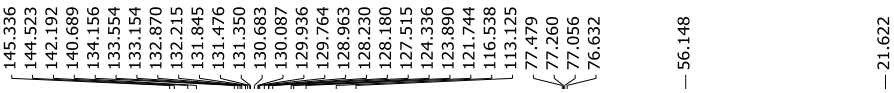


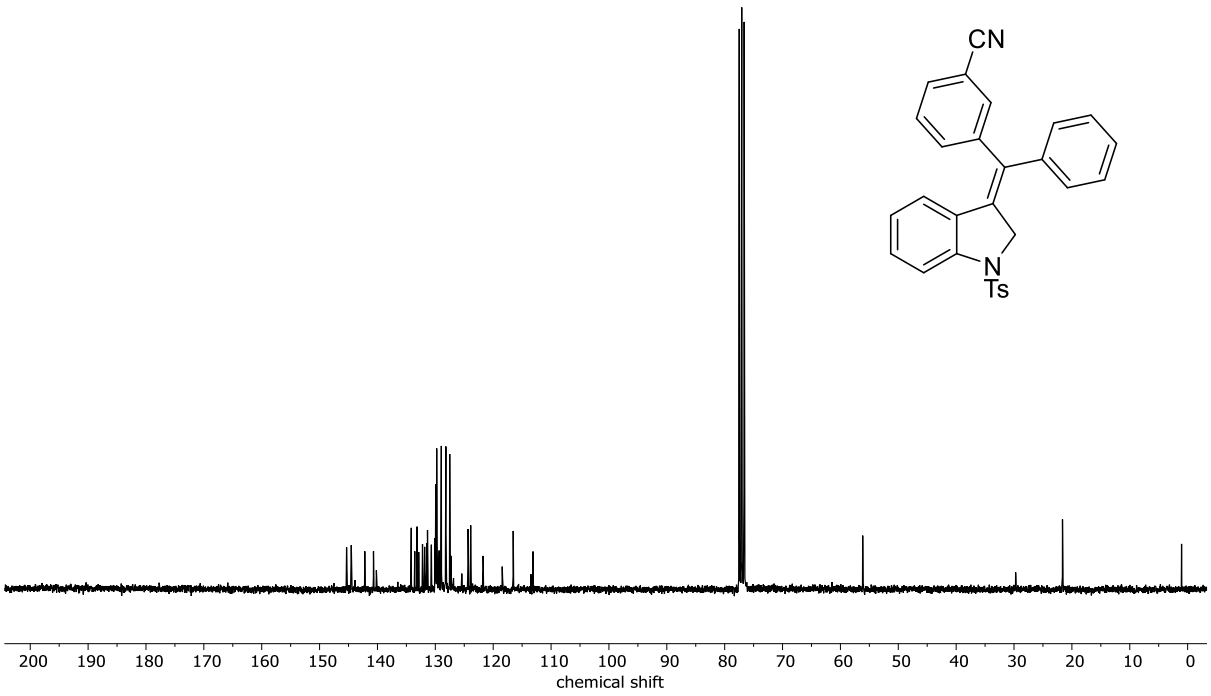
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4e



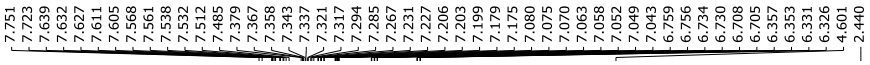


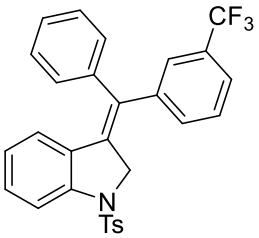
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4e

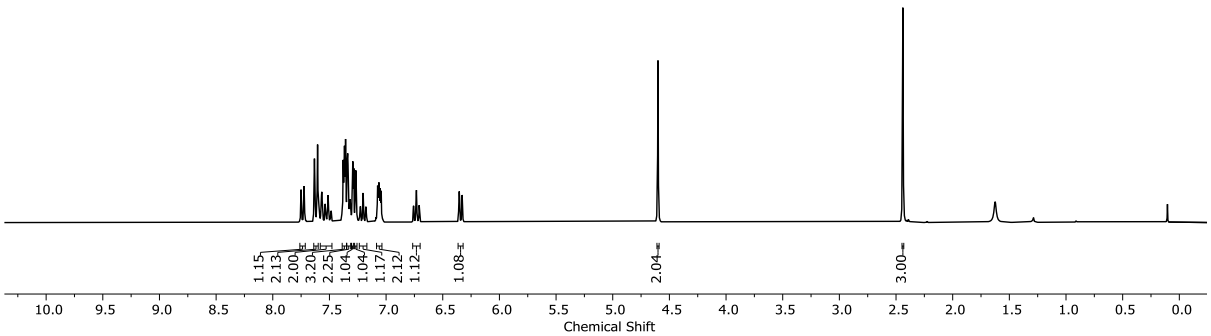




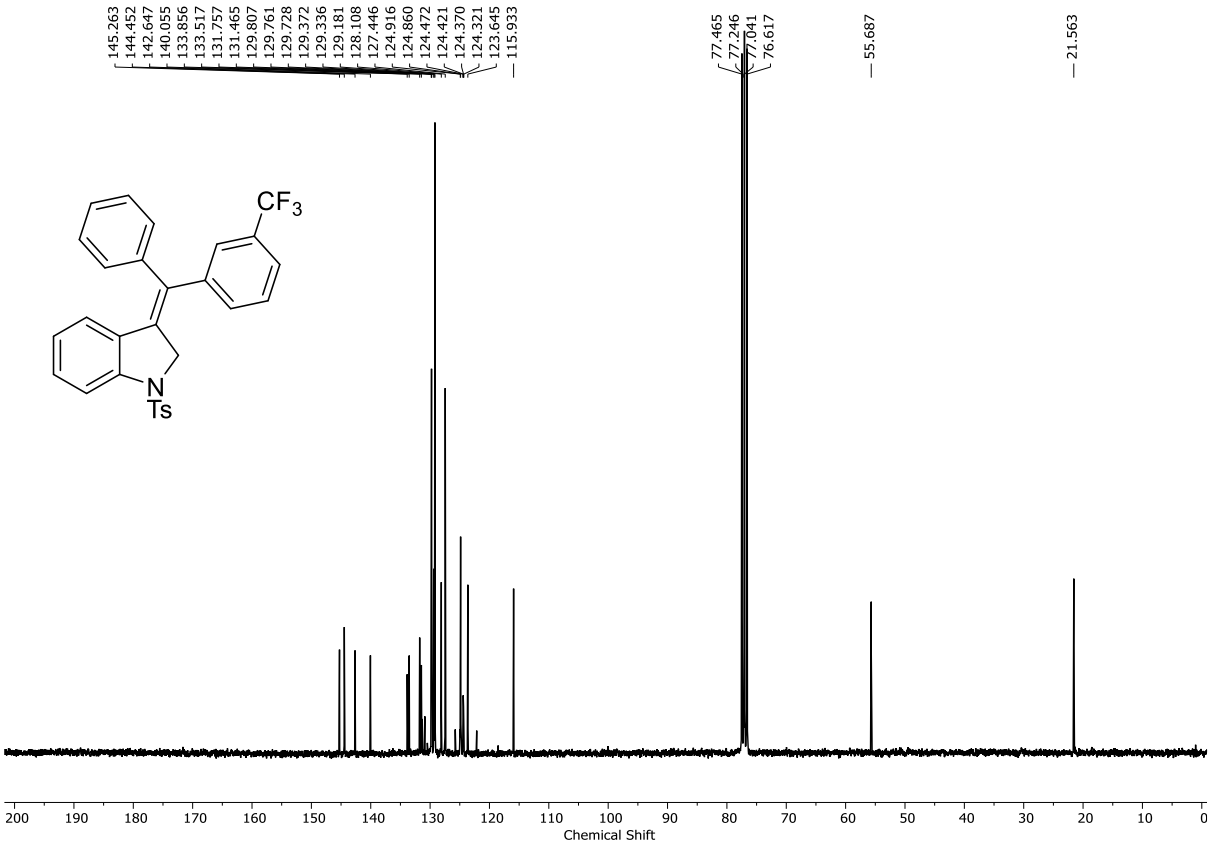
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4f



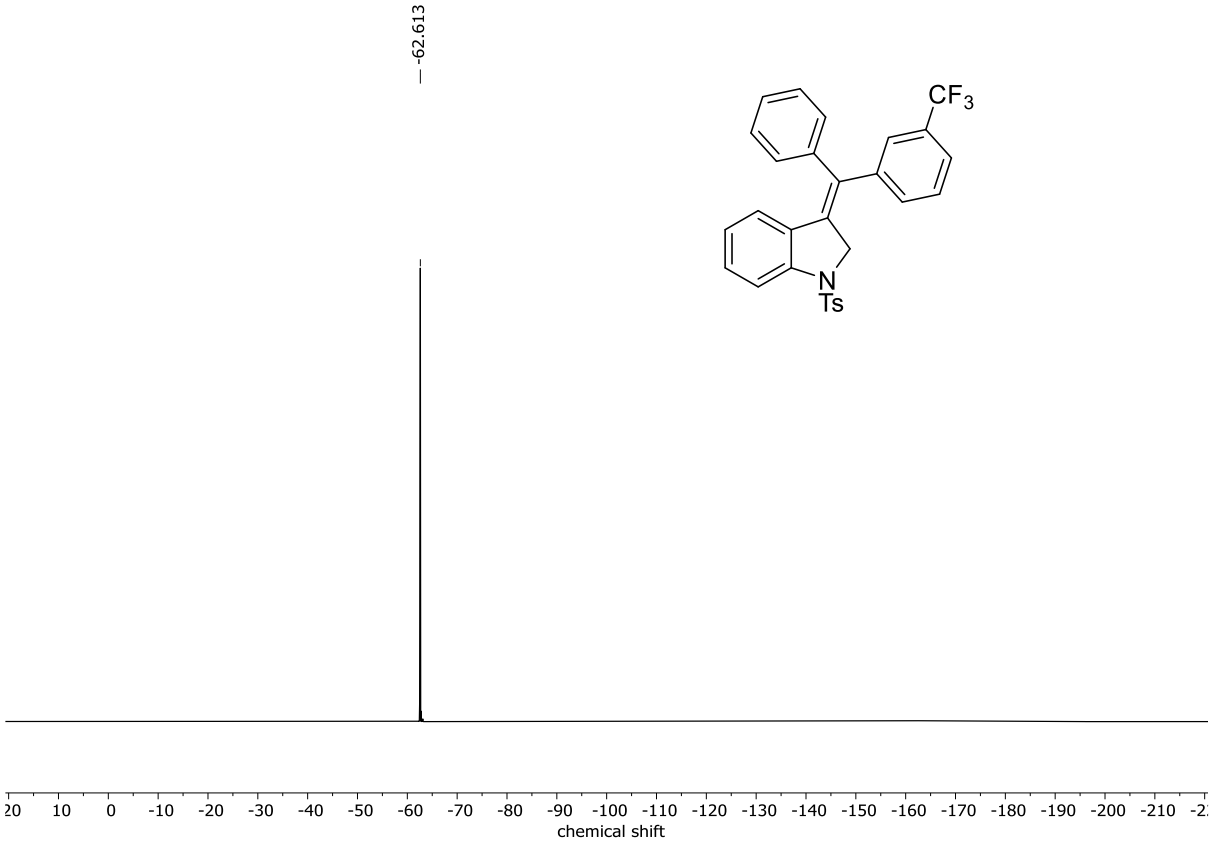




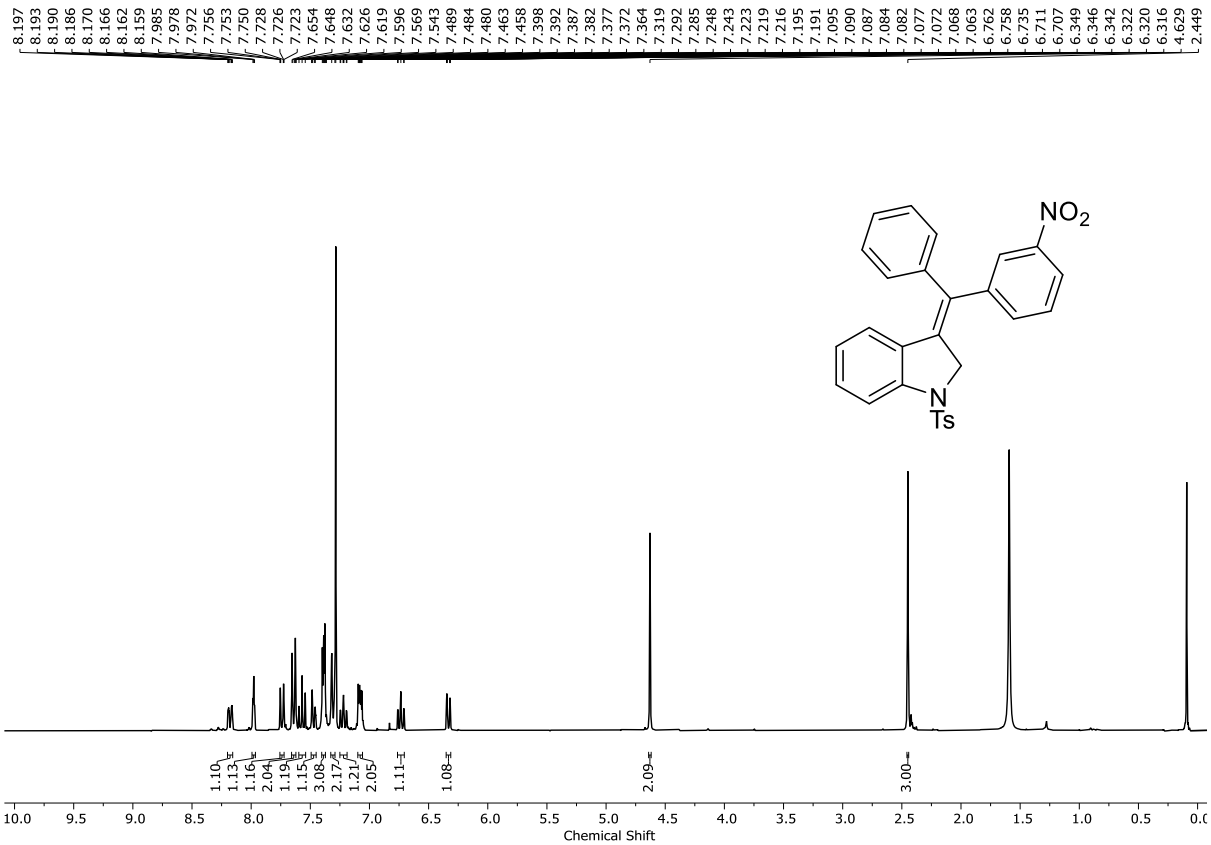
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 4f



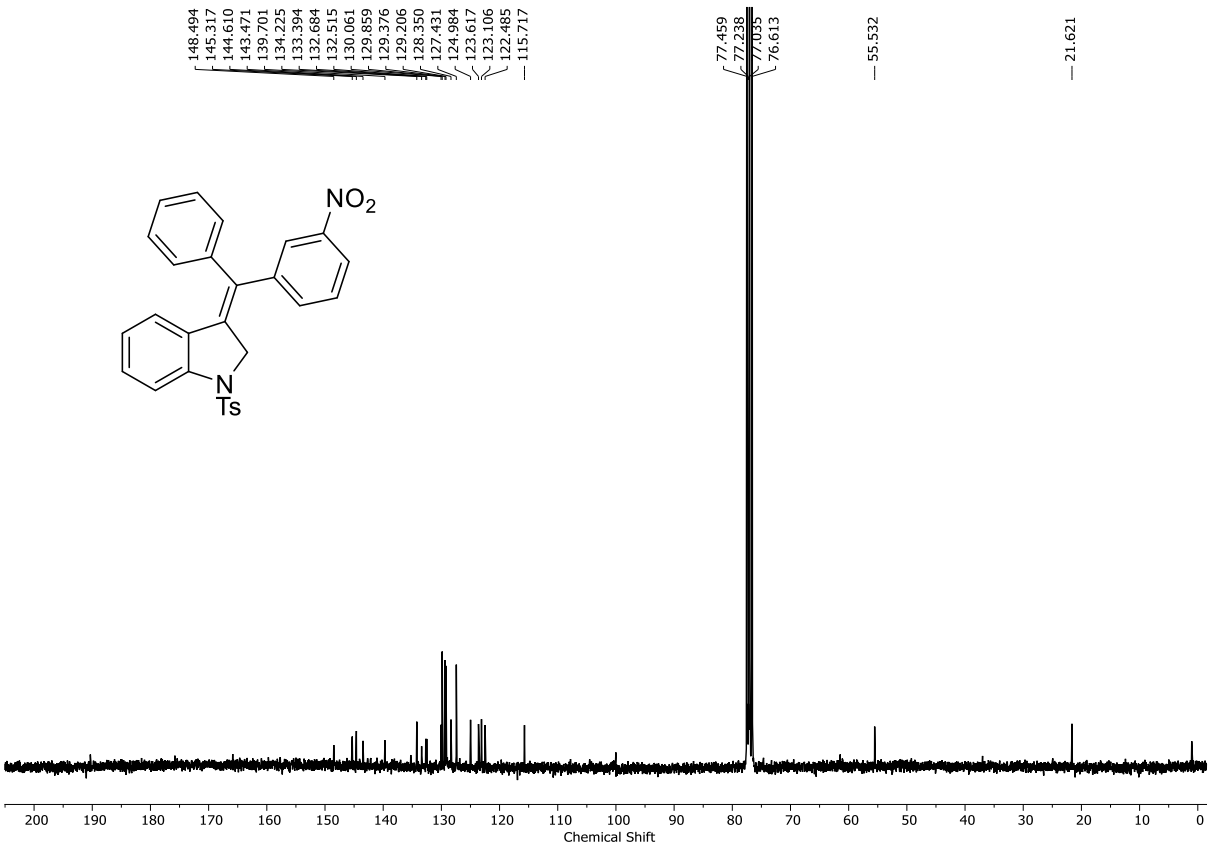
^{19}F NMR (377 MHz, $CDCl_3$) spectra of 4f



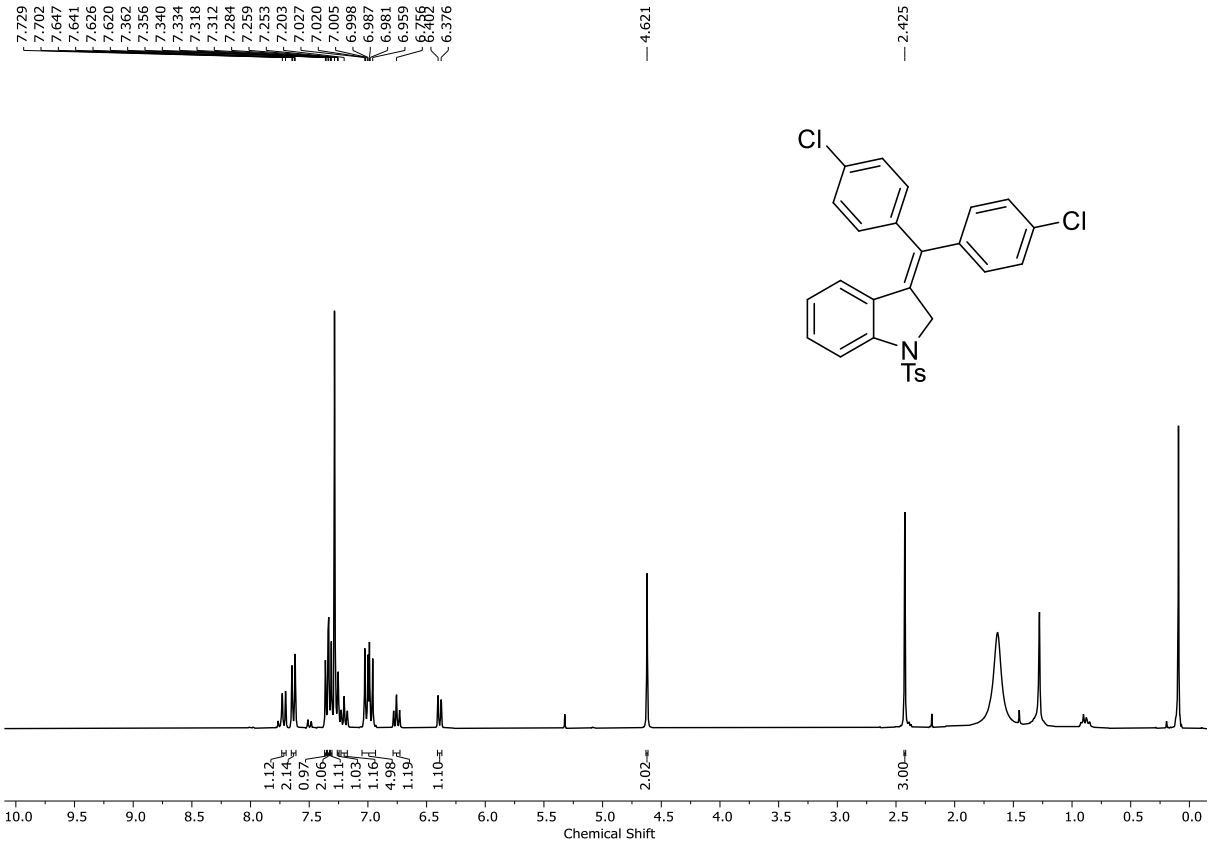
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4g



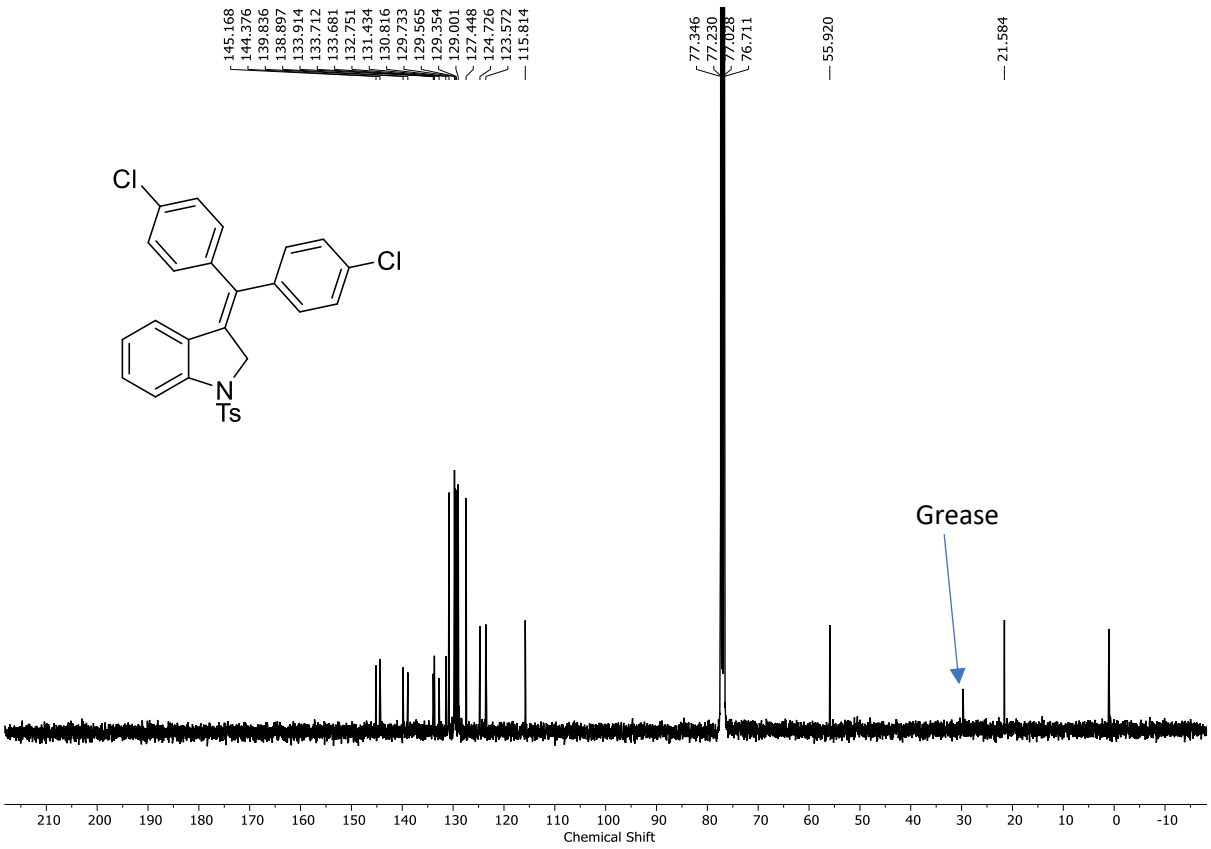
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 4g



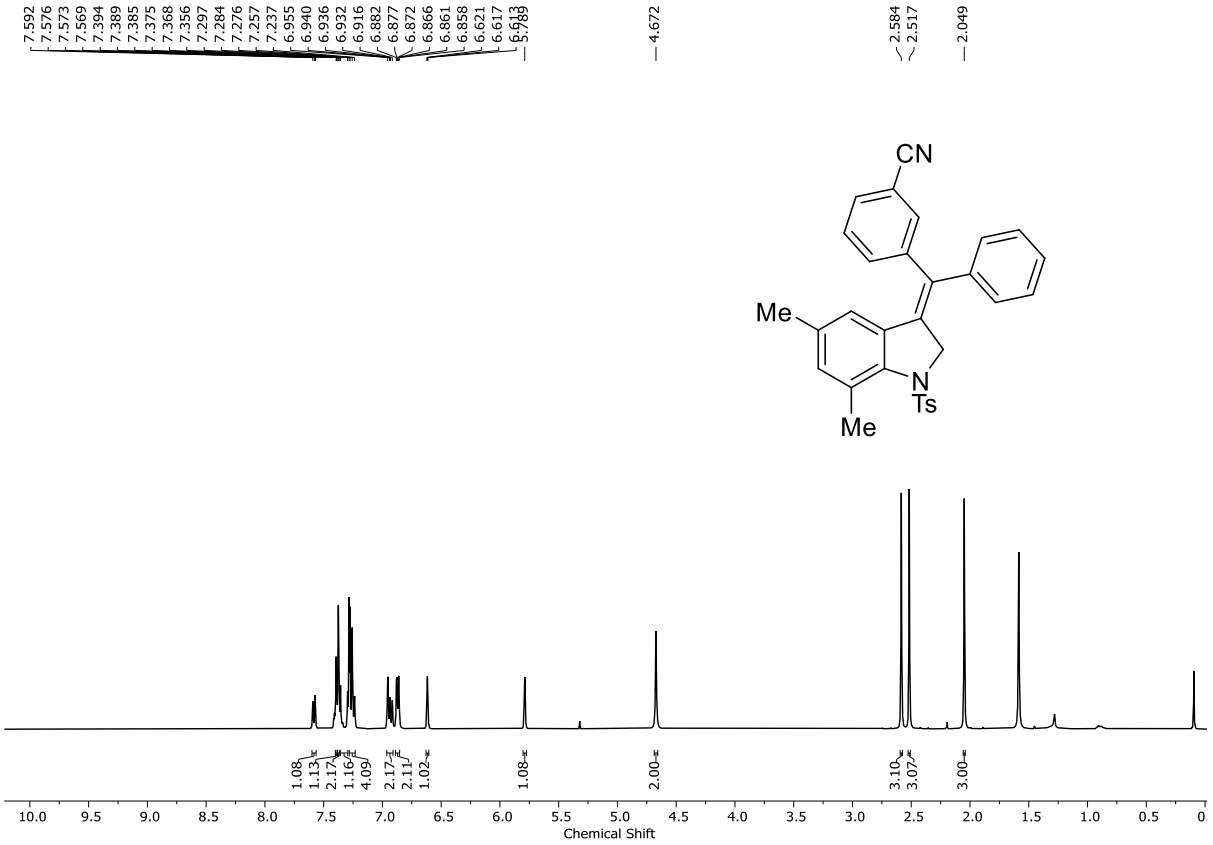
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4h



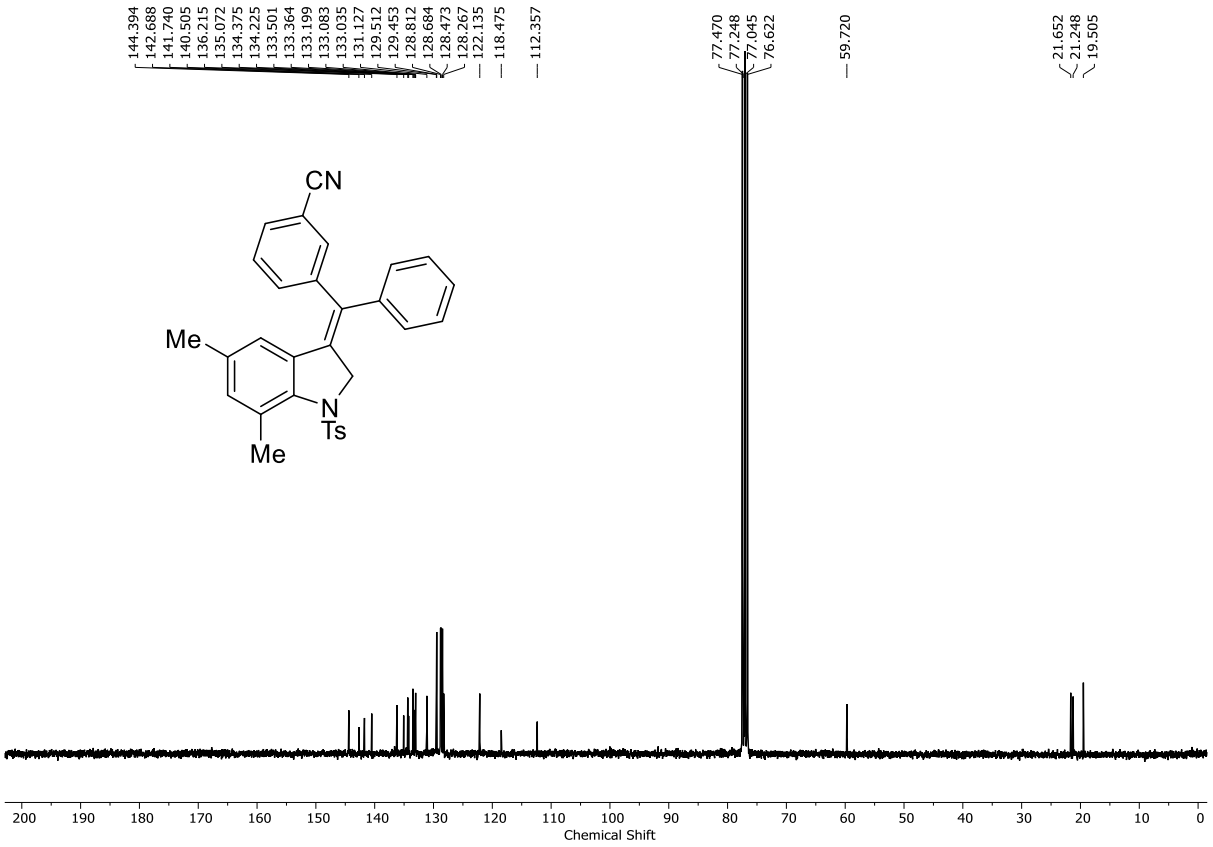
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 4h



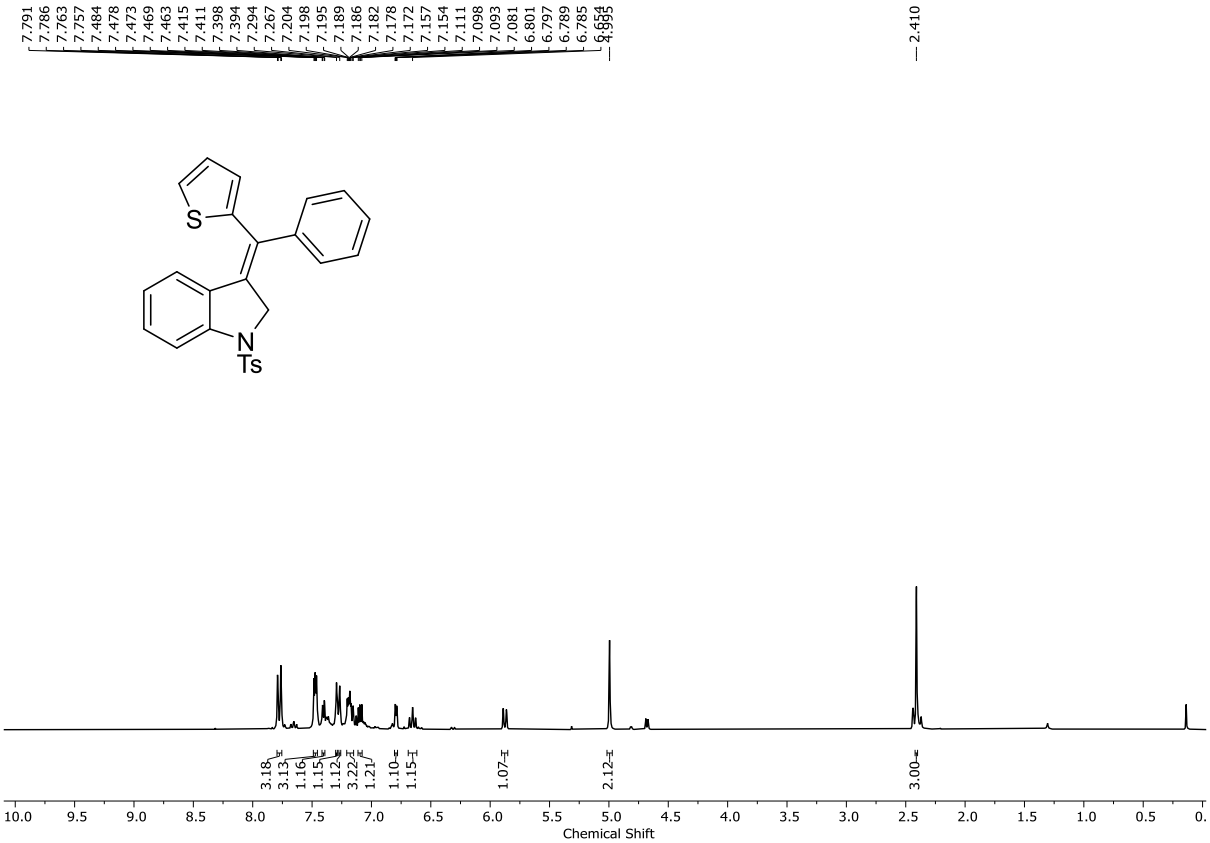
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4j



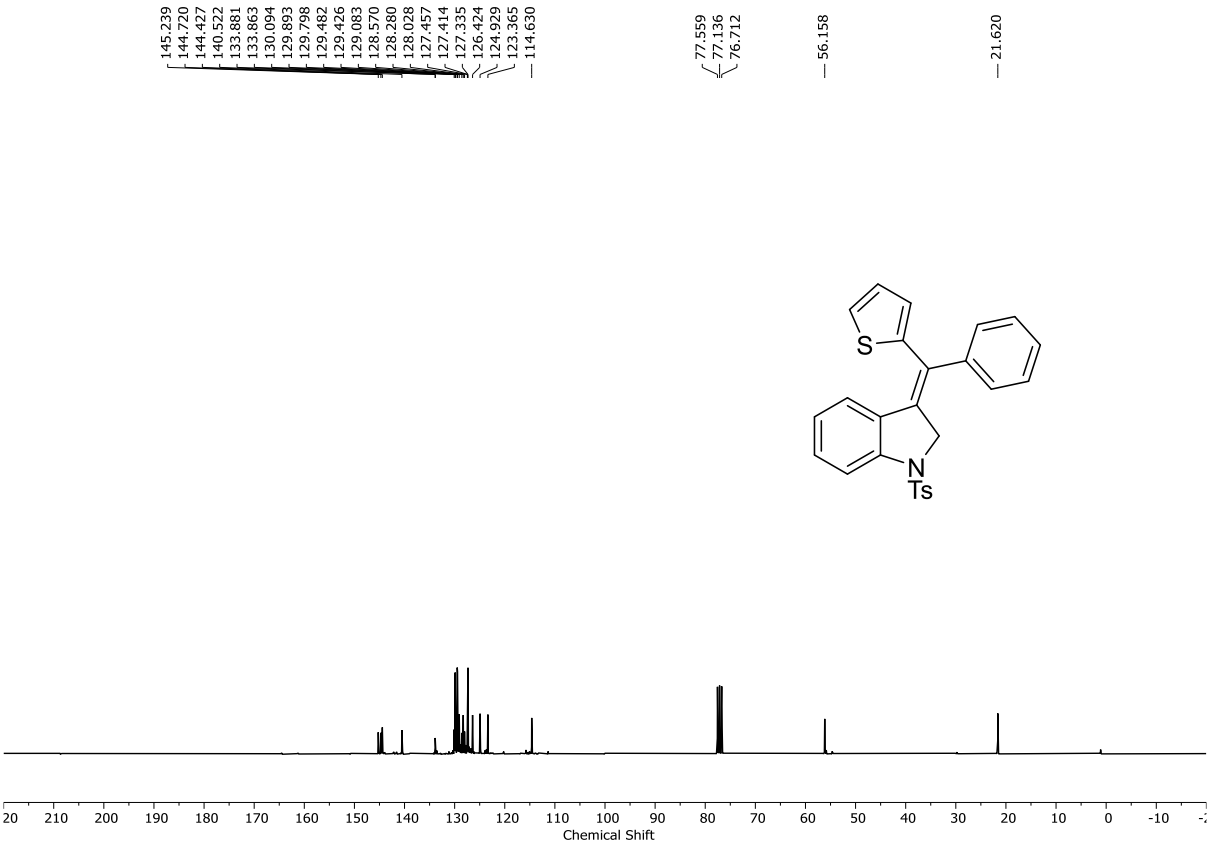
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 4j



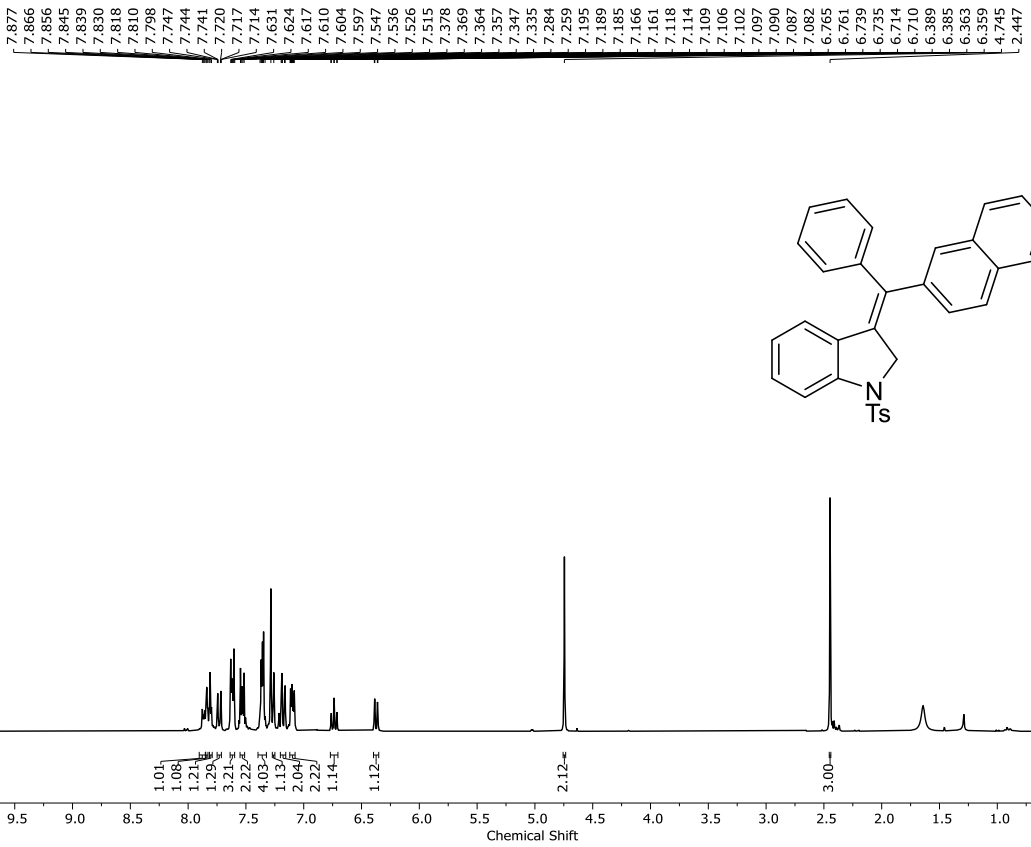
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4k



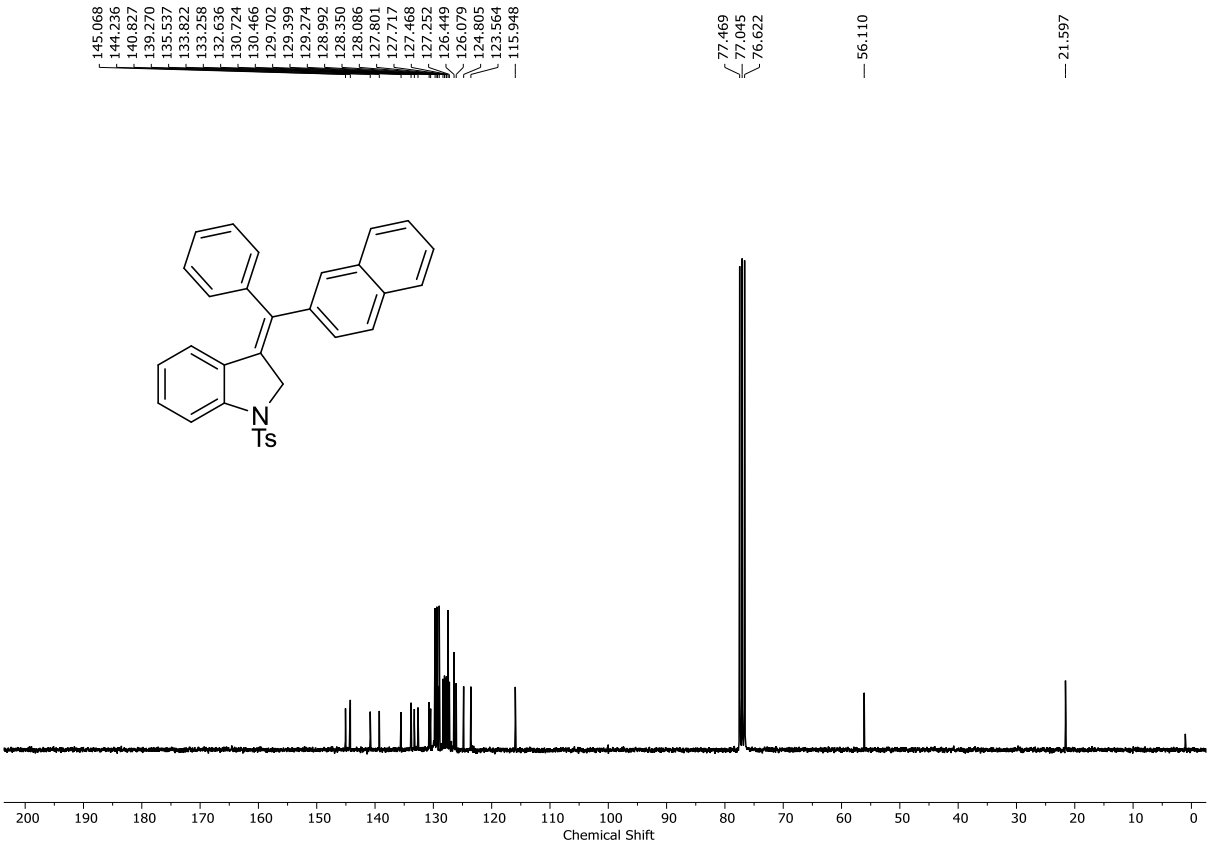
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4k



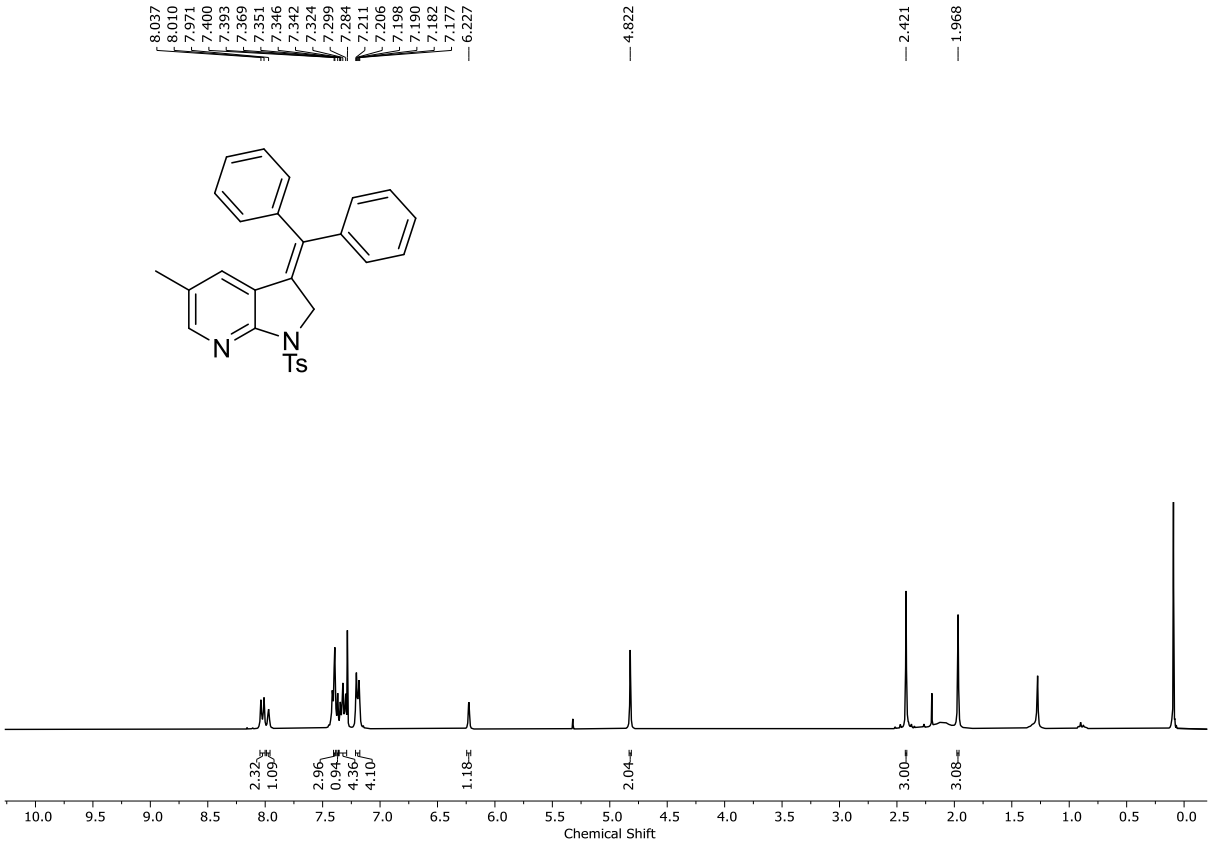
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4l



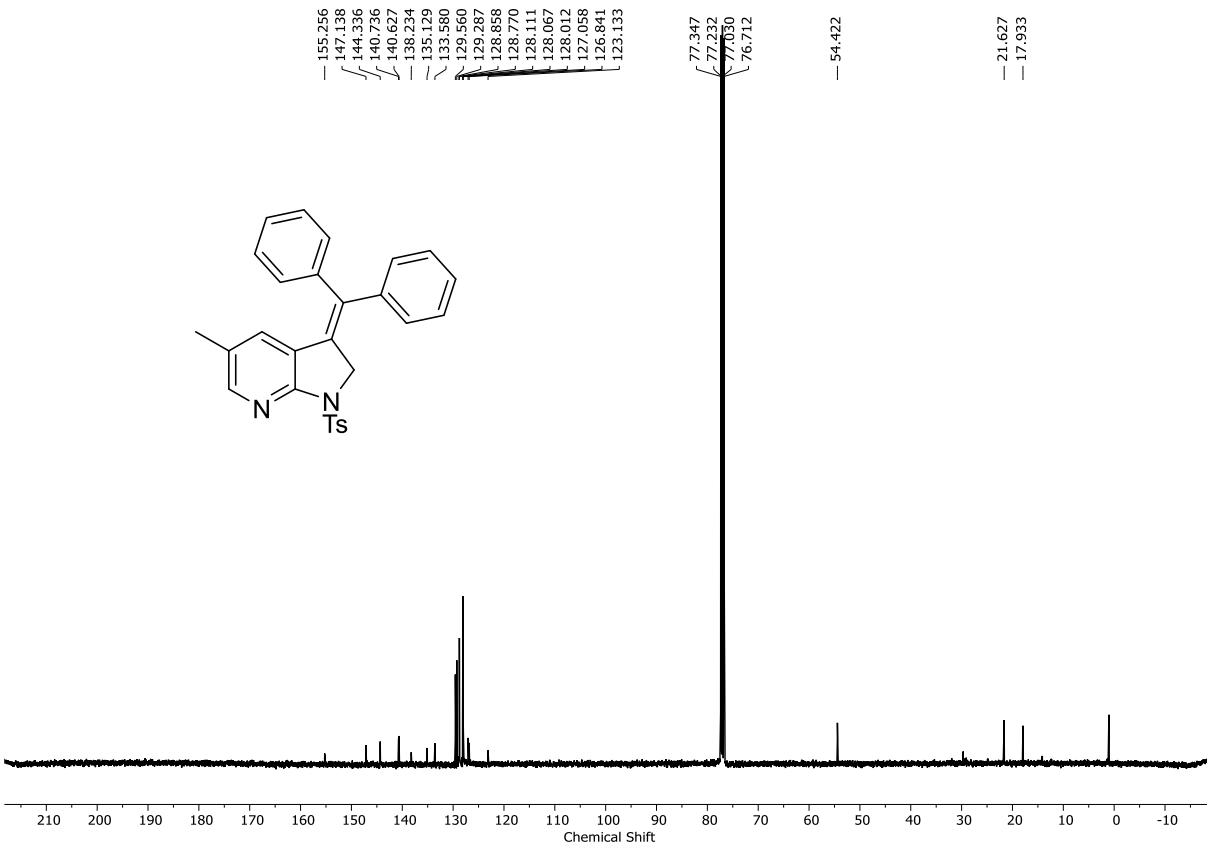
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 4l



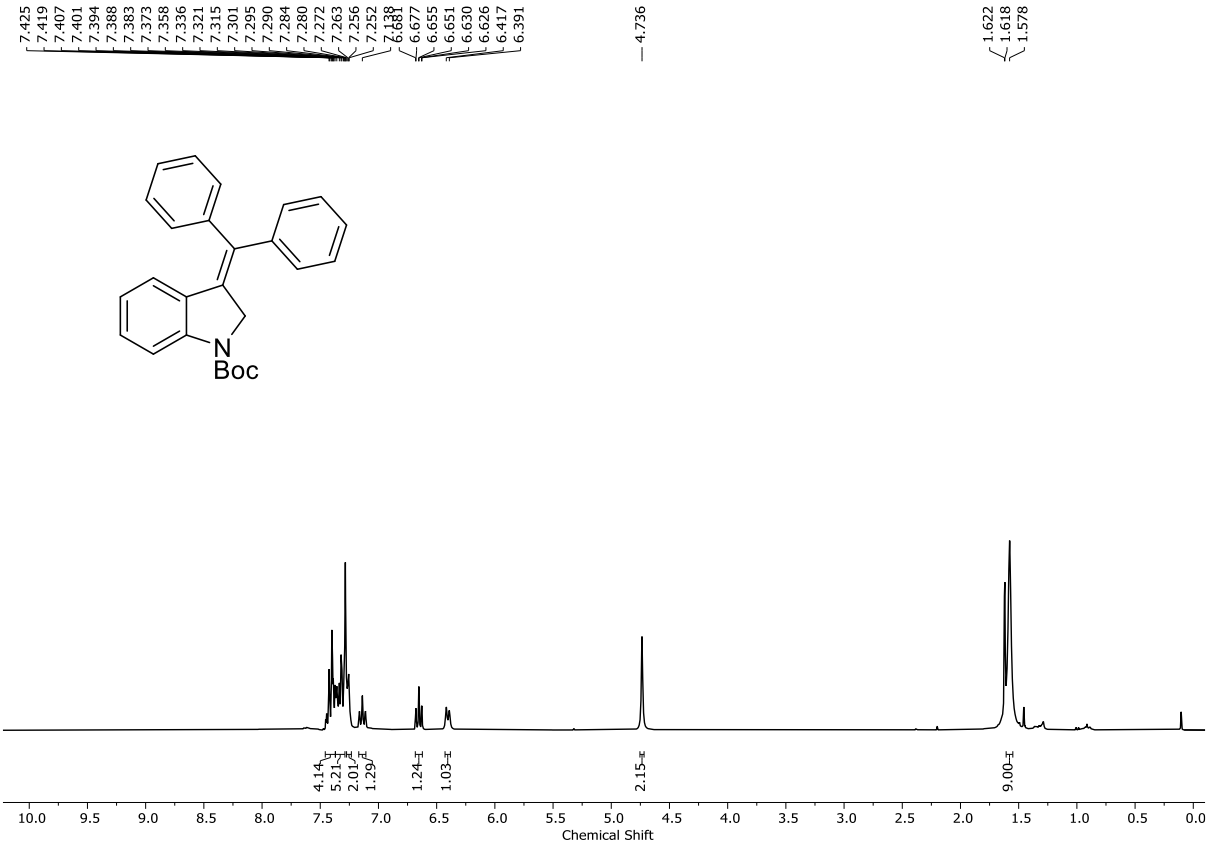
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4m



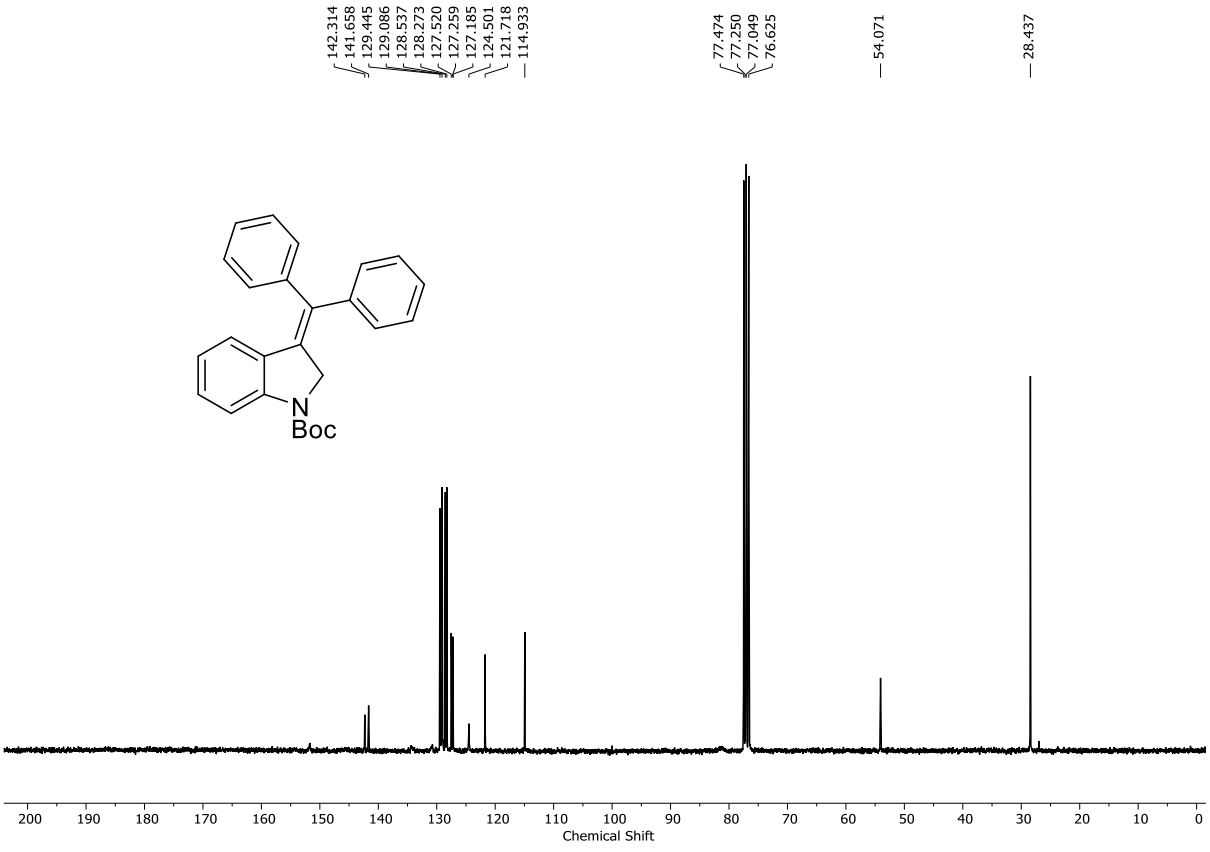
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 4m



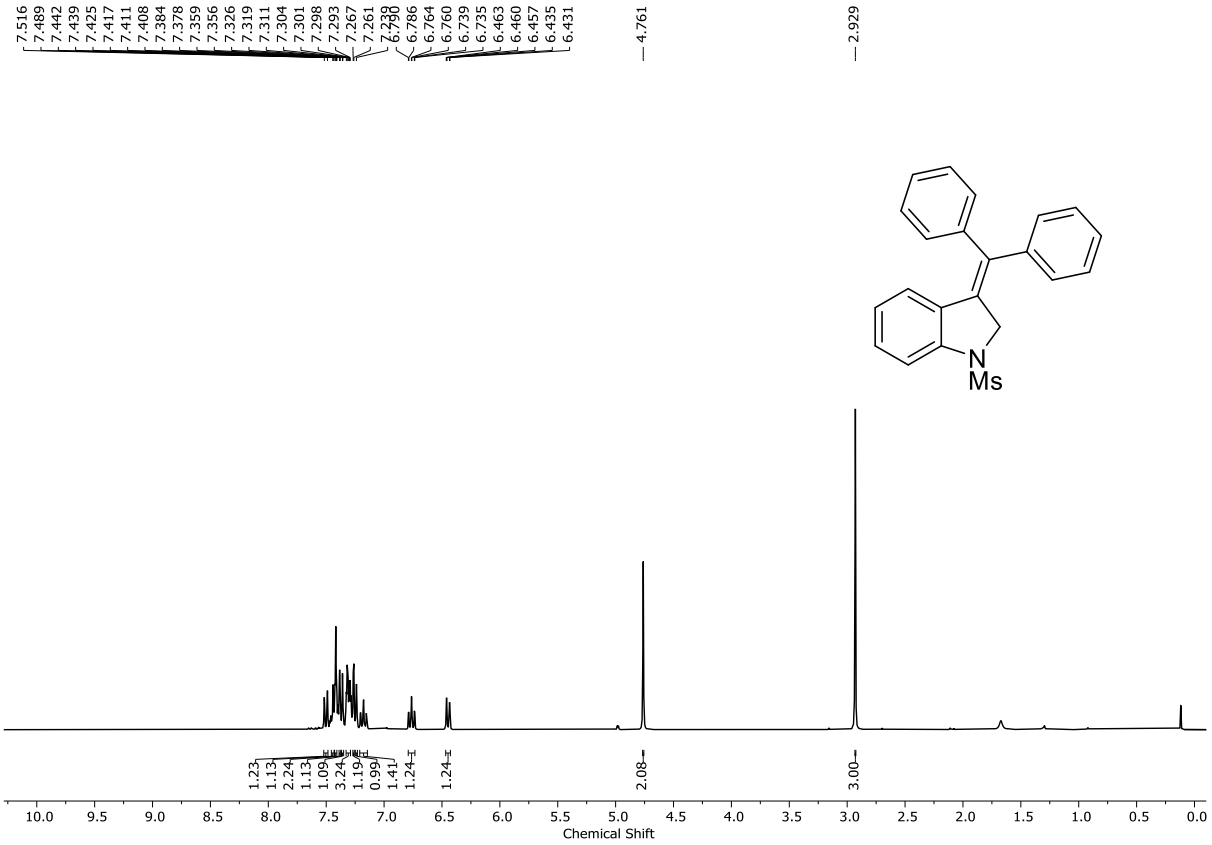
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4n



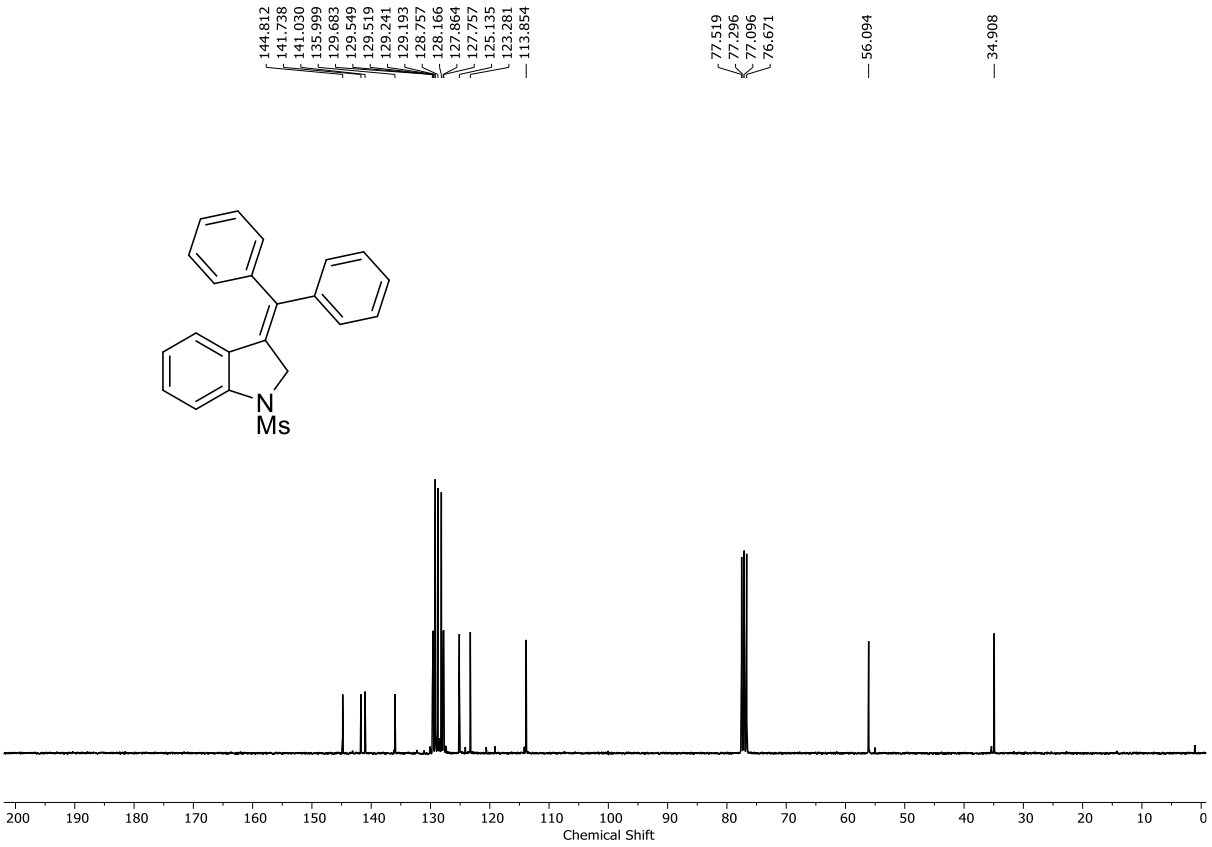
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4n



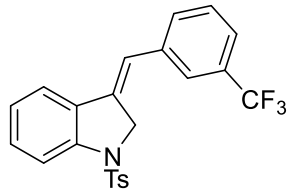
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 4o

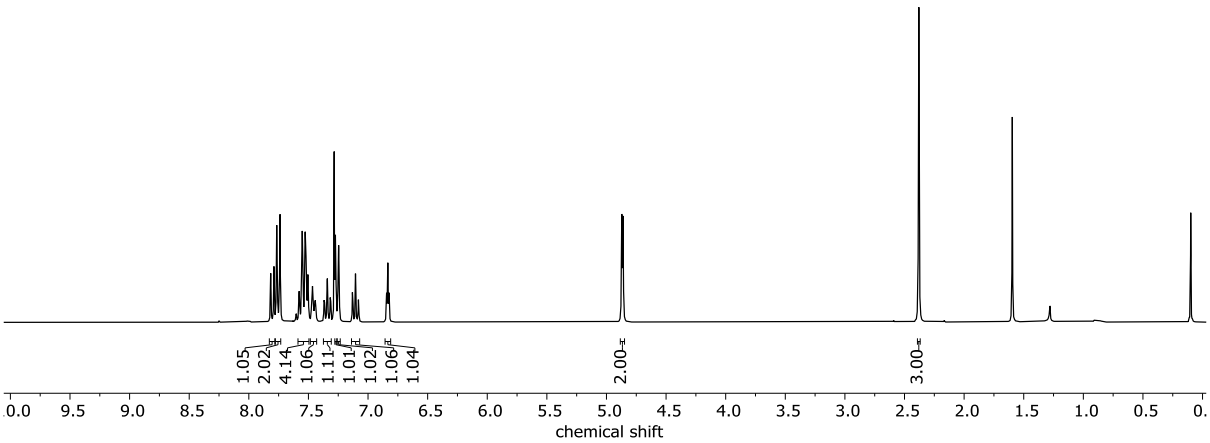


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 4o

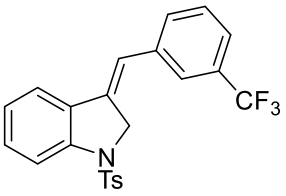


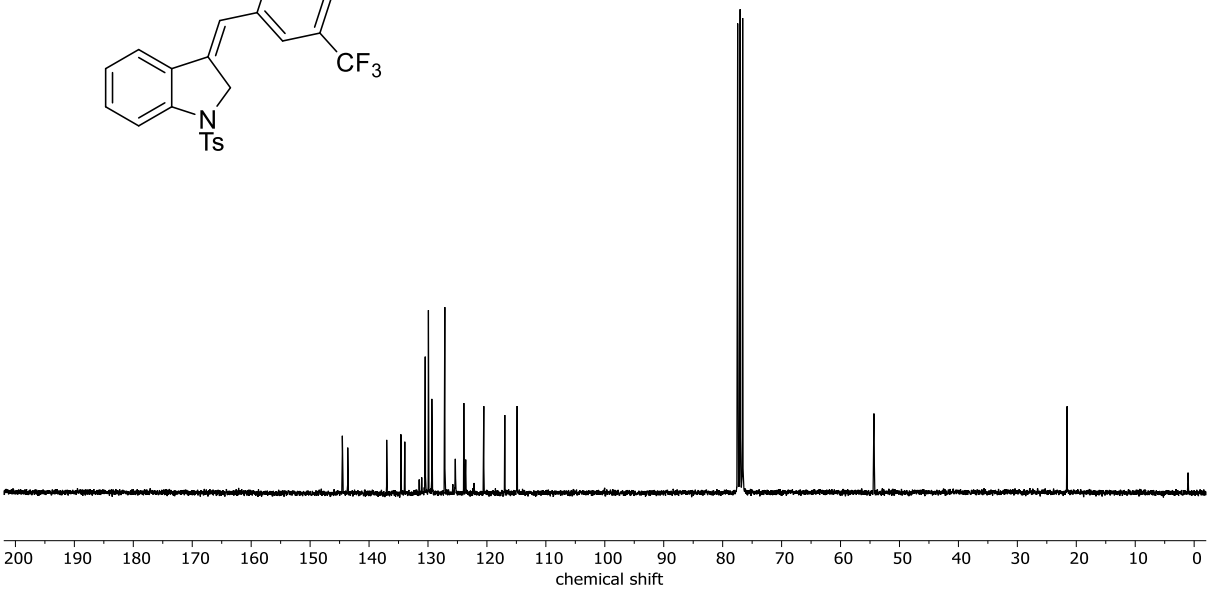
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 6e





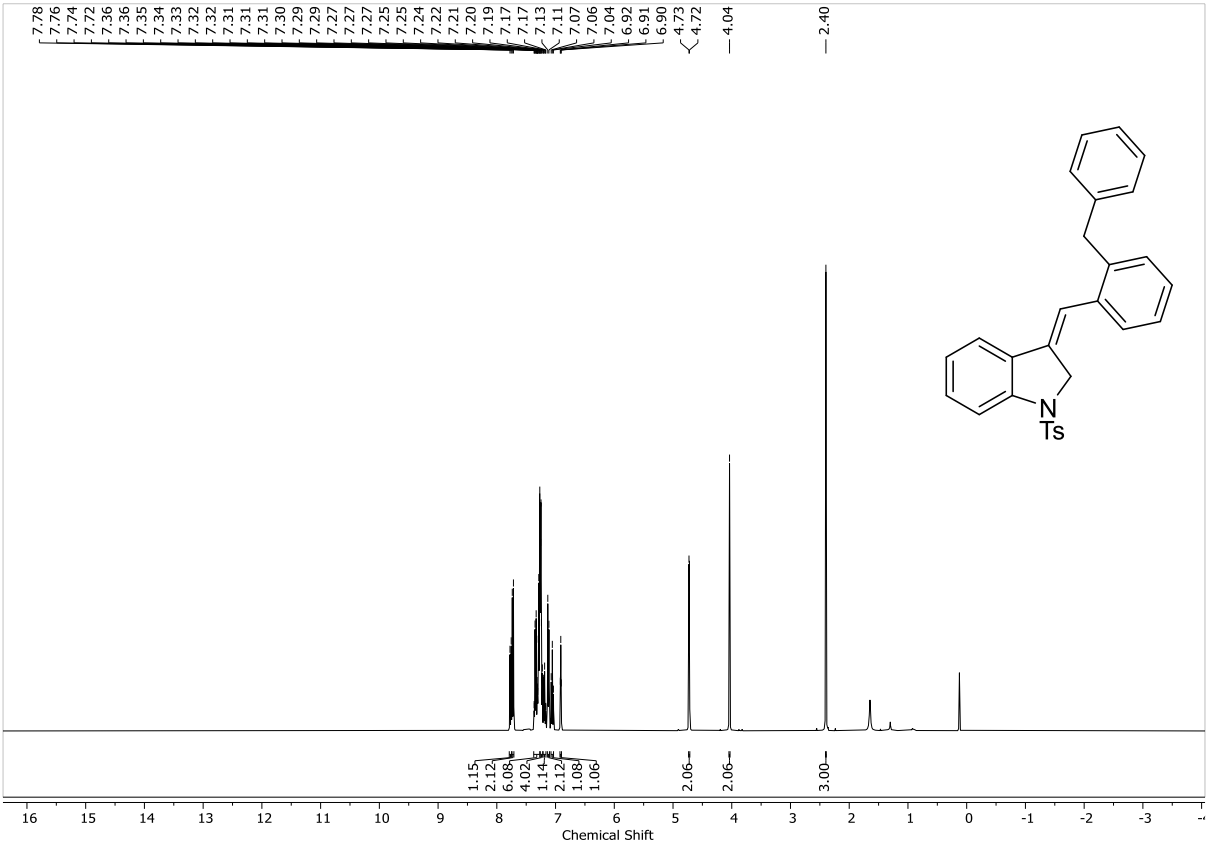
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 6e



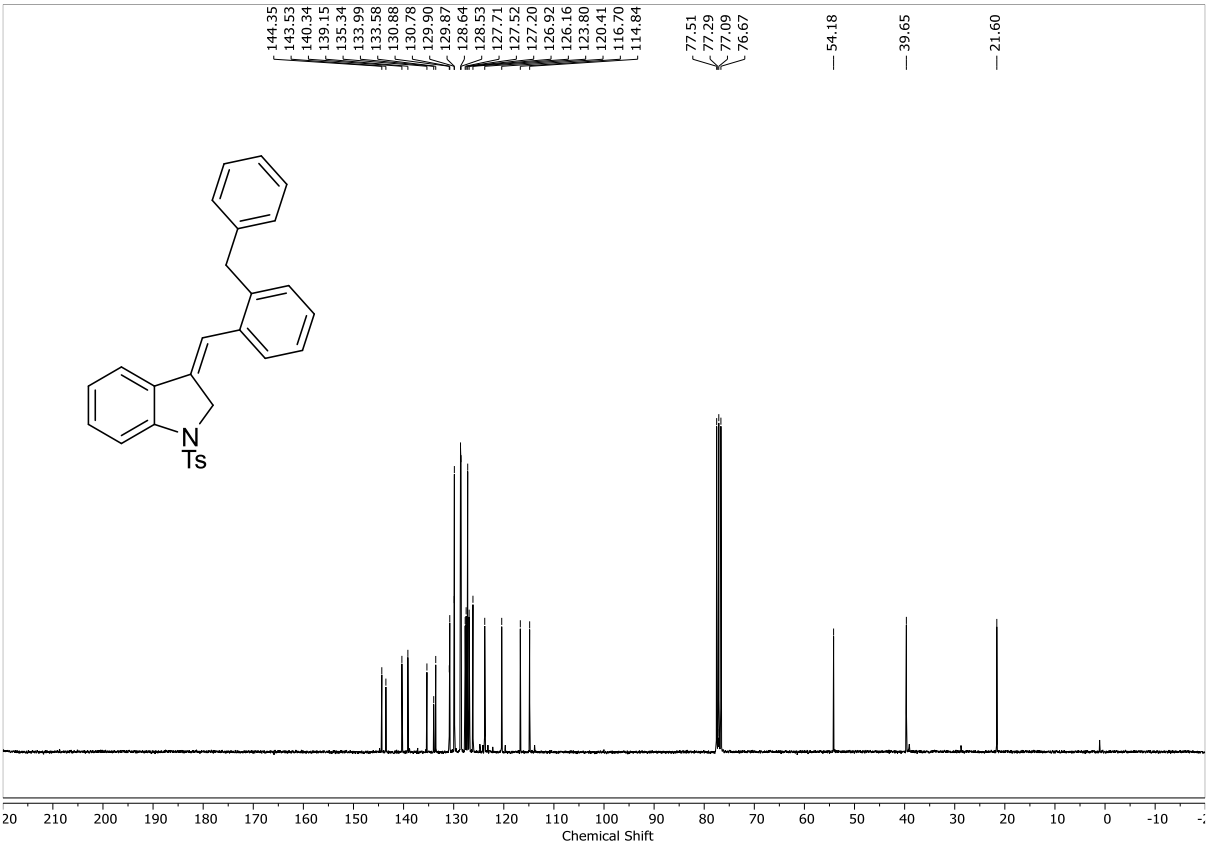


^{19}F NMR (282 MHz, $CDCl_3$) spectra of 6e

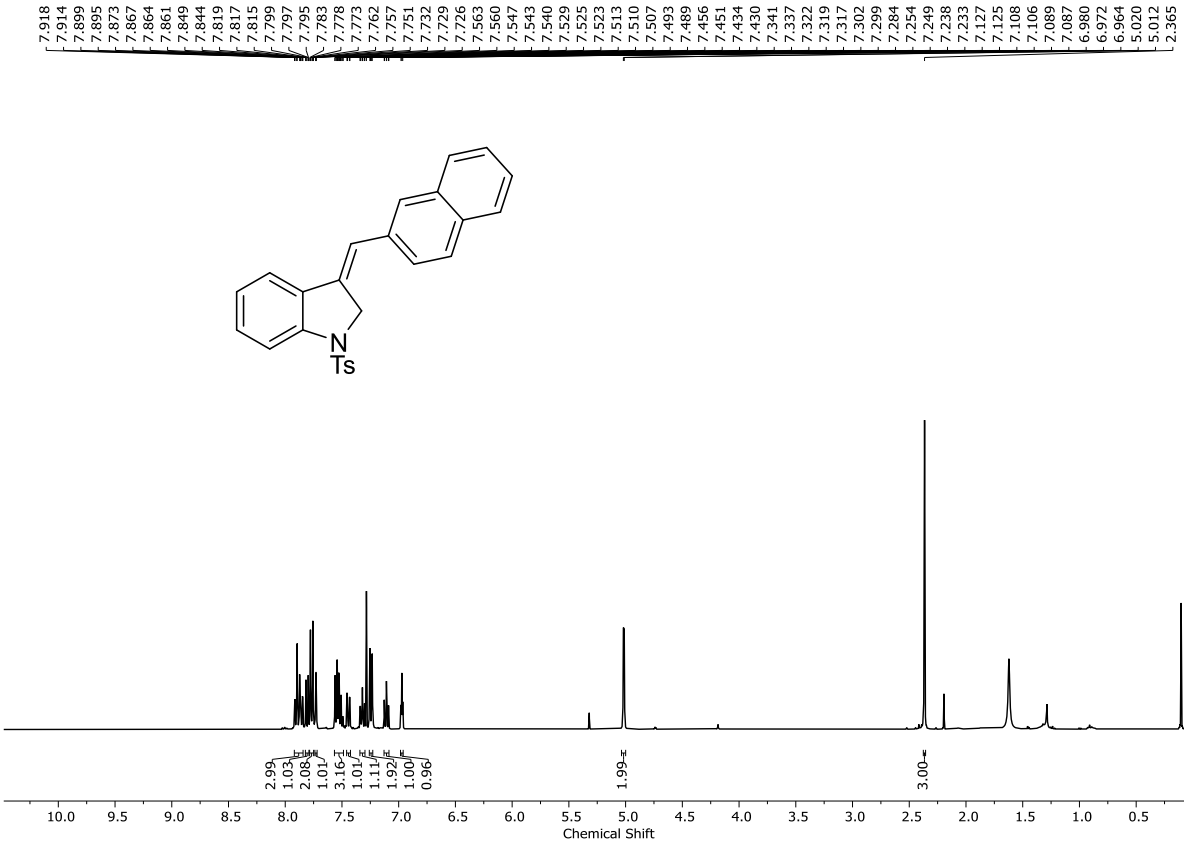
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 6j



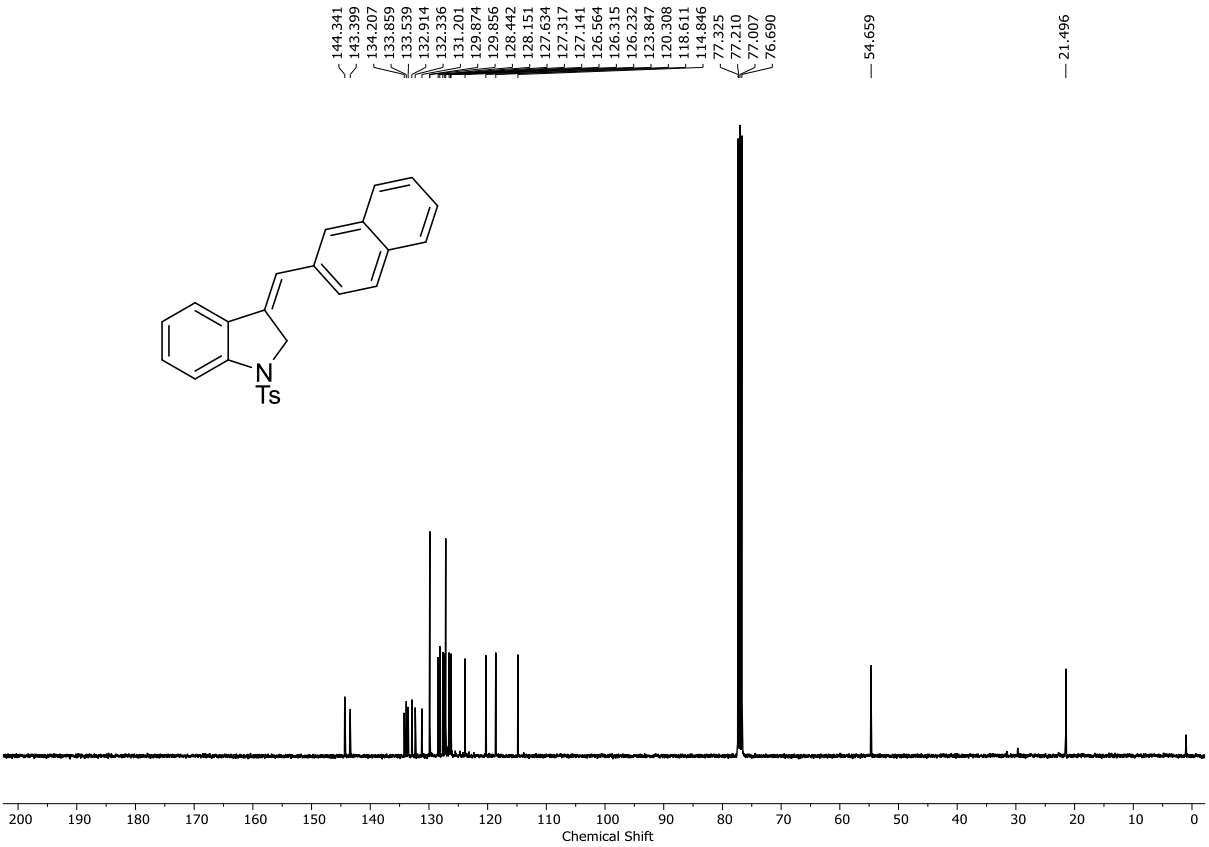
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 6j



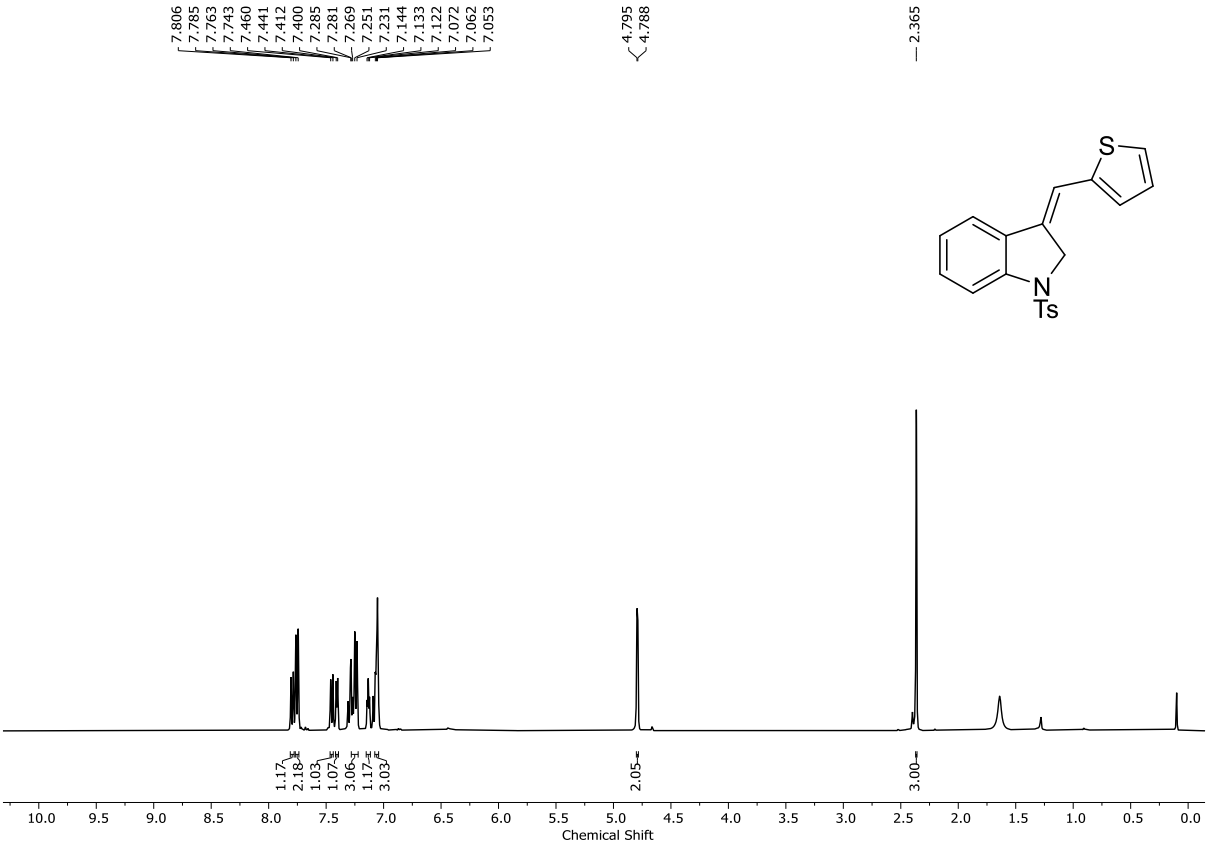
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 6k



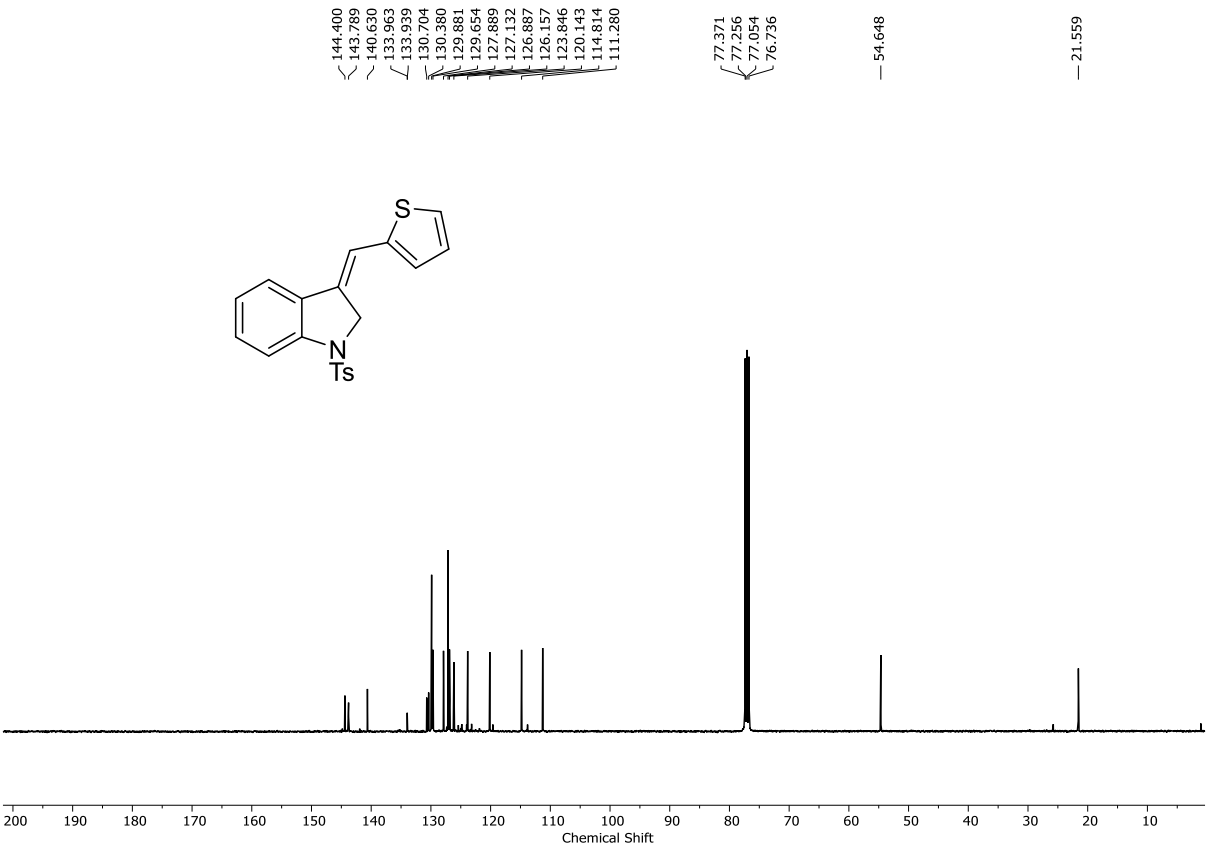
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of 6k



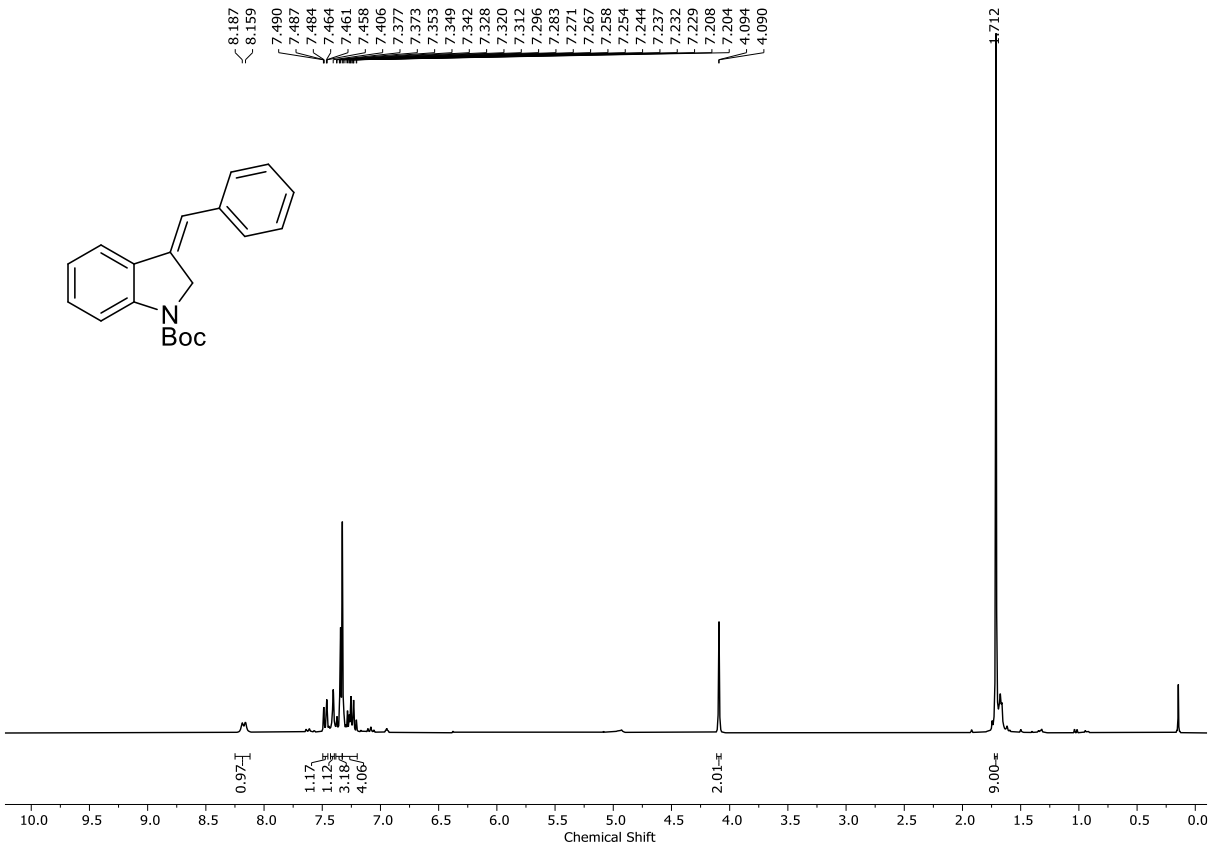
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 6l



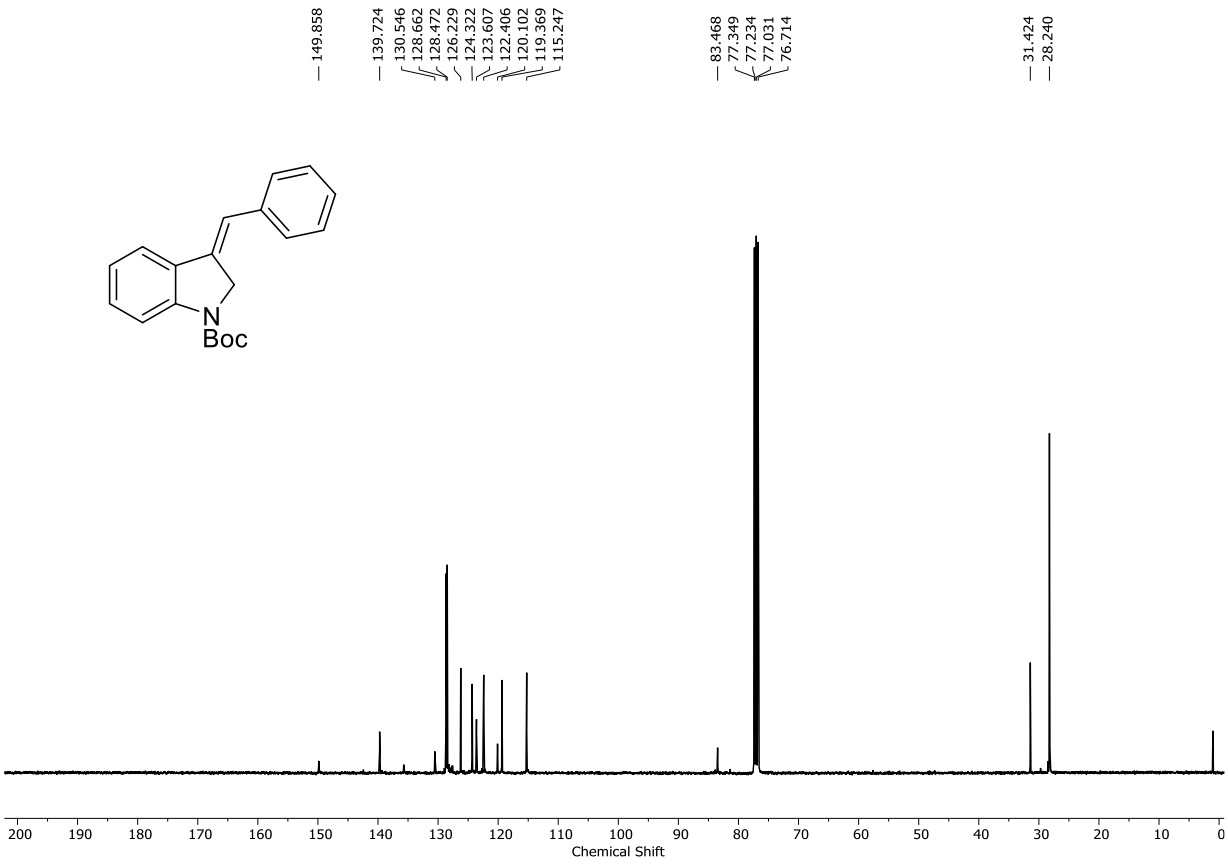
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 6l



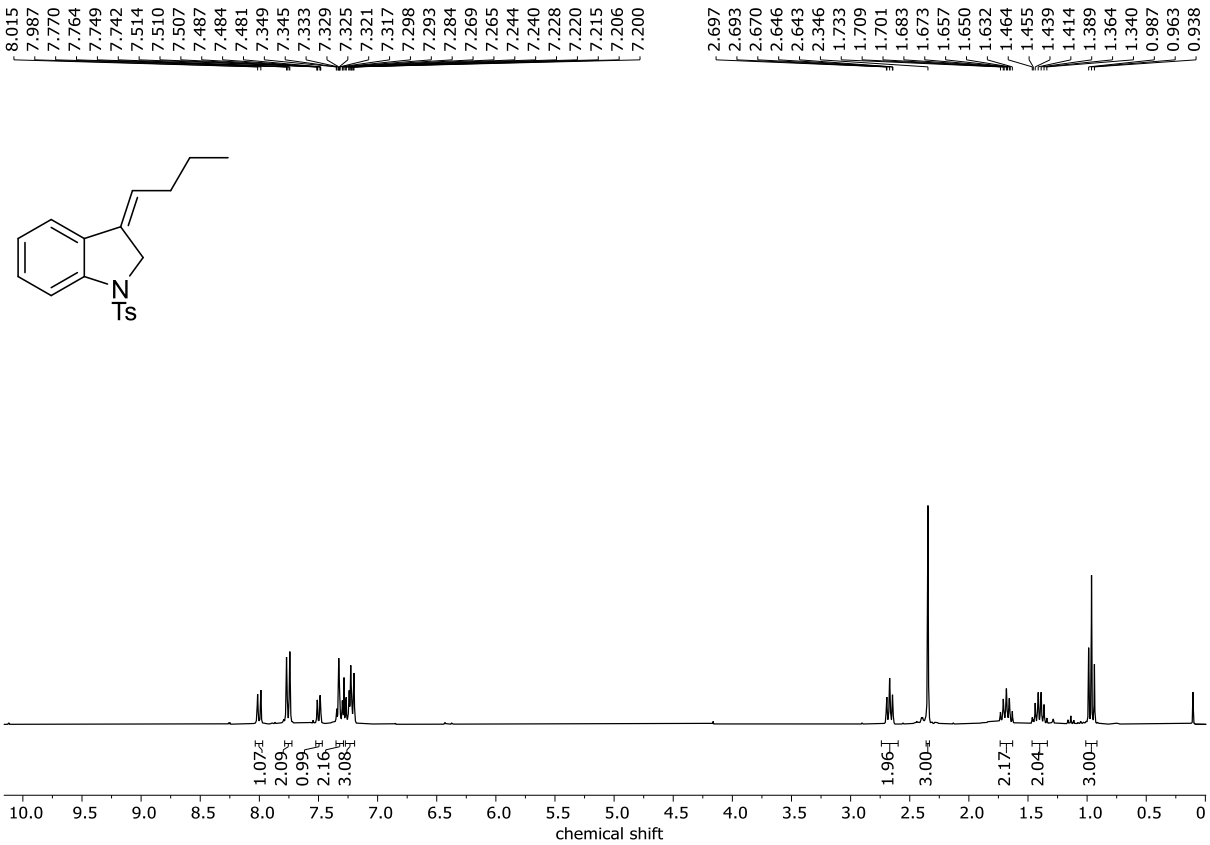
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 6m



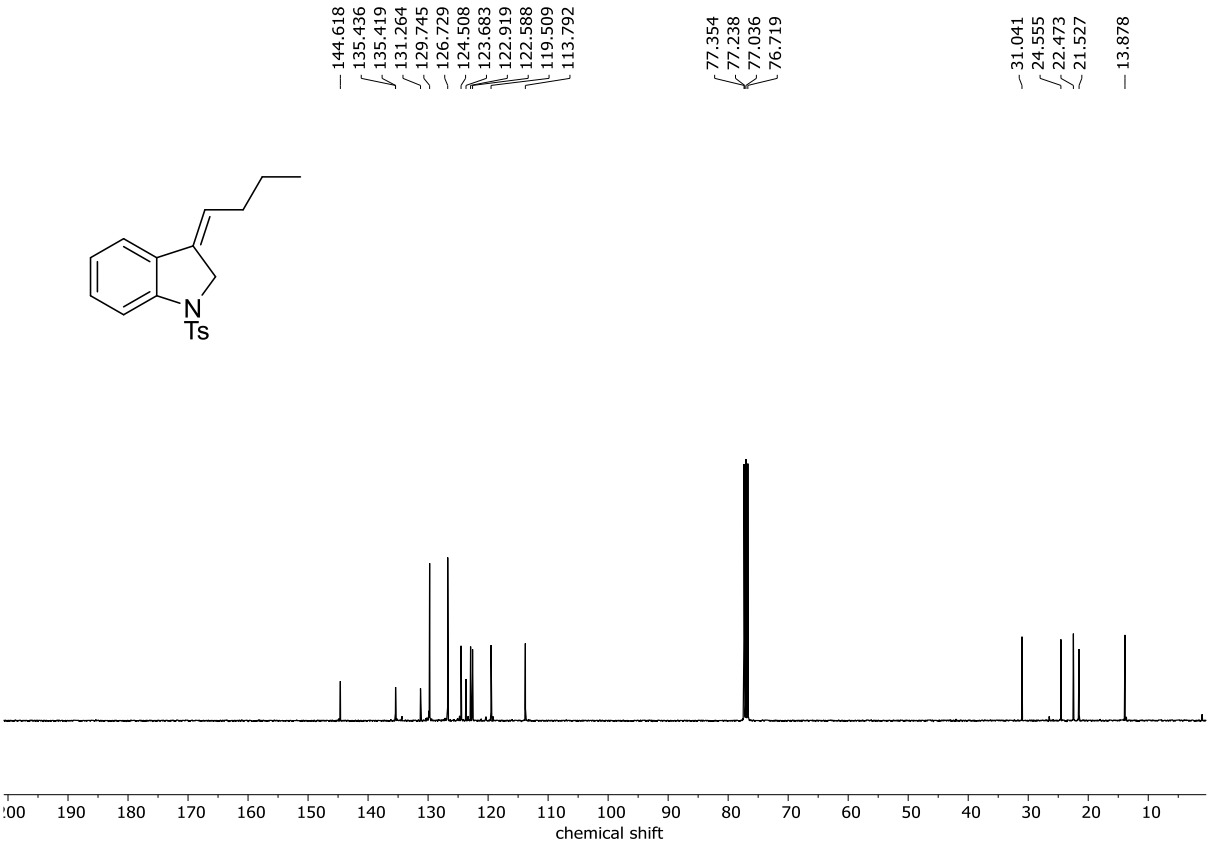
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 6m



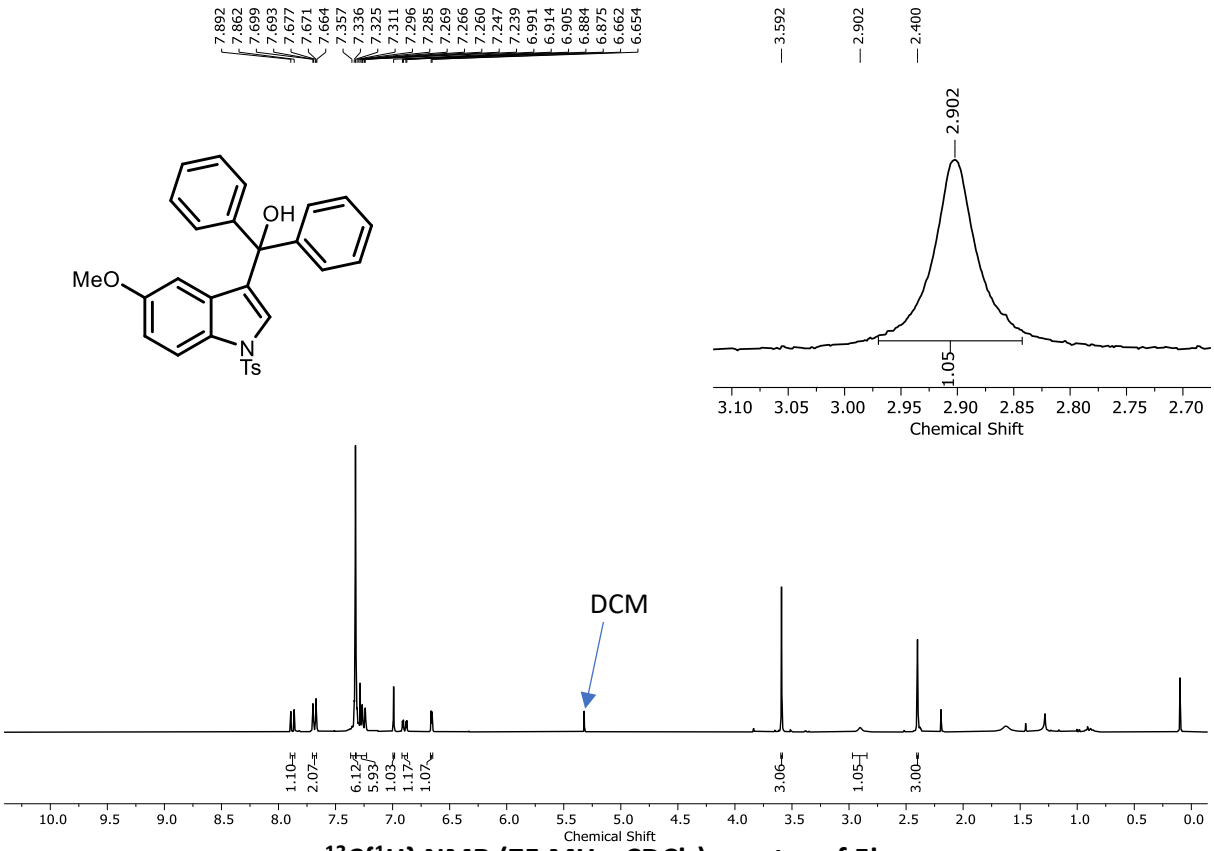
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 6n



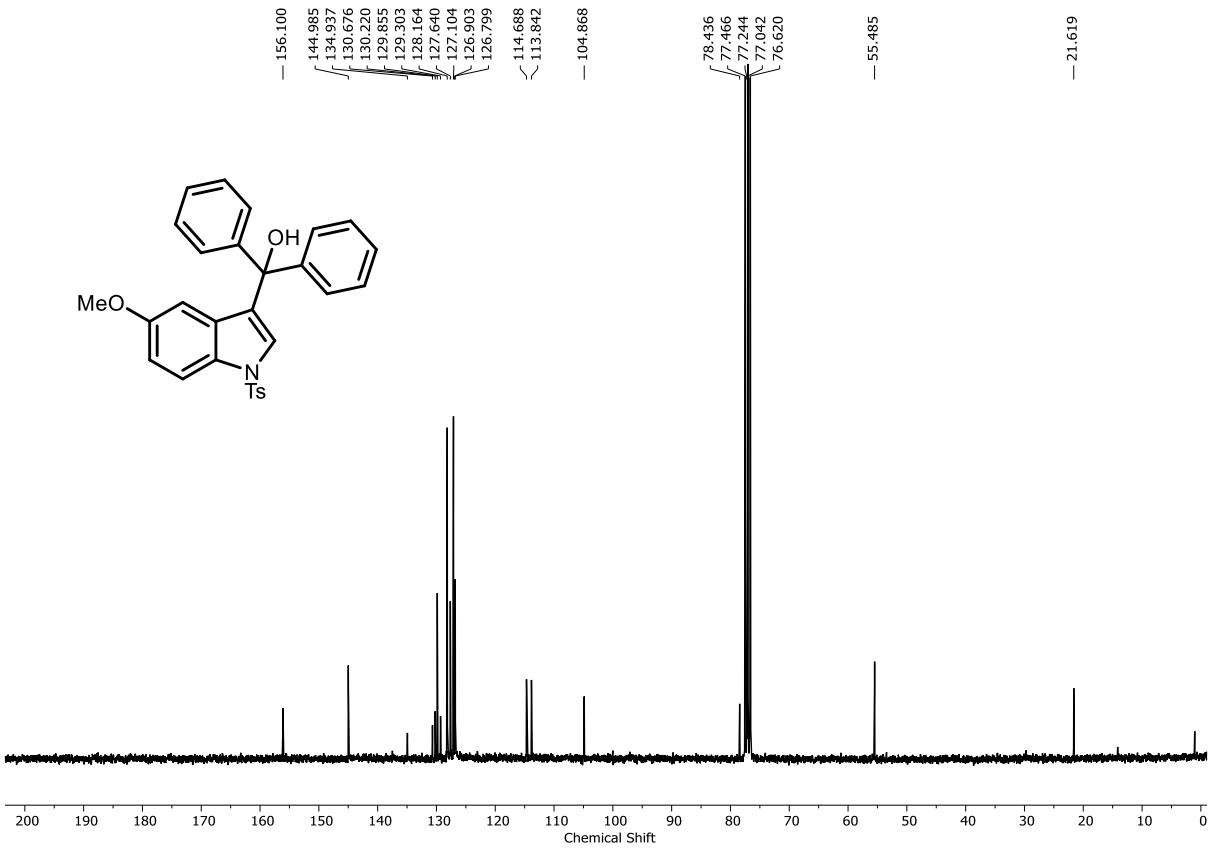
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of 6n



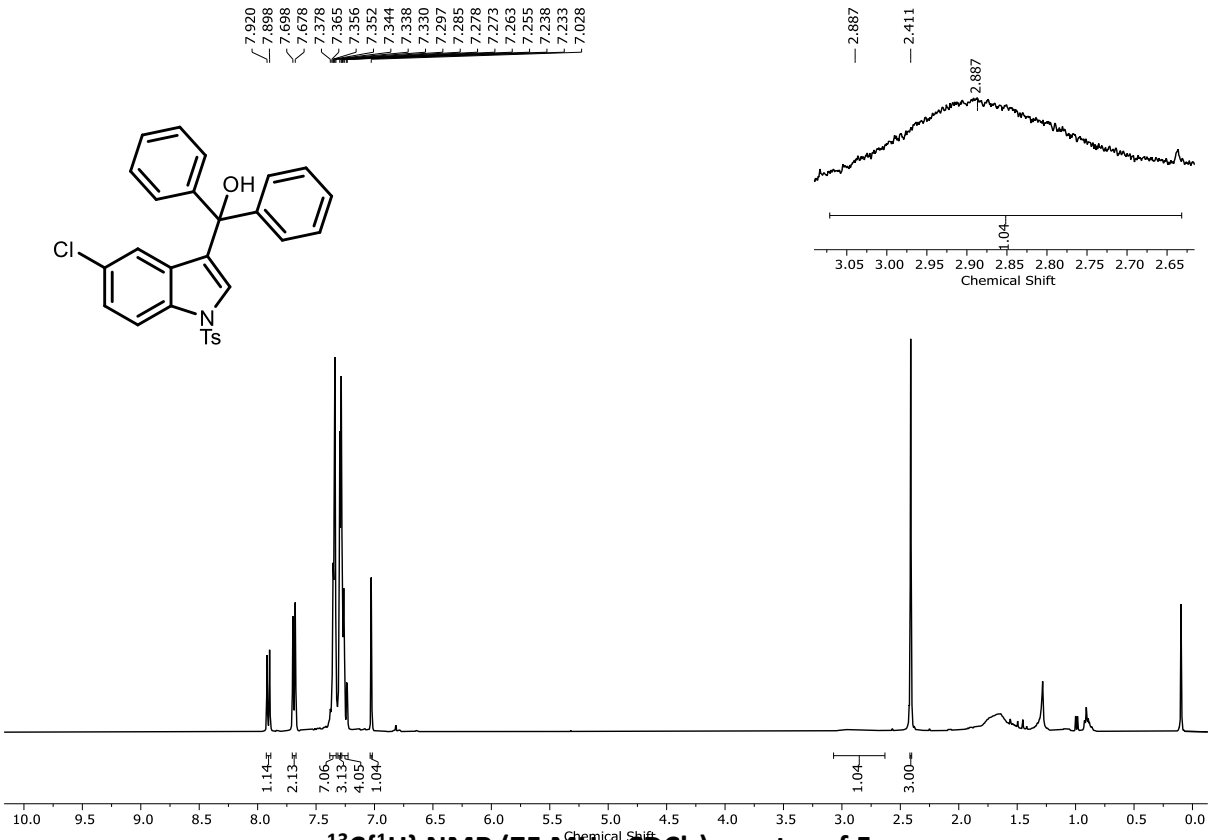
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5b



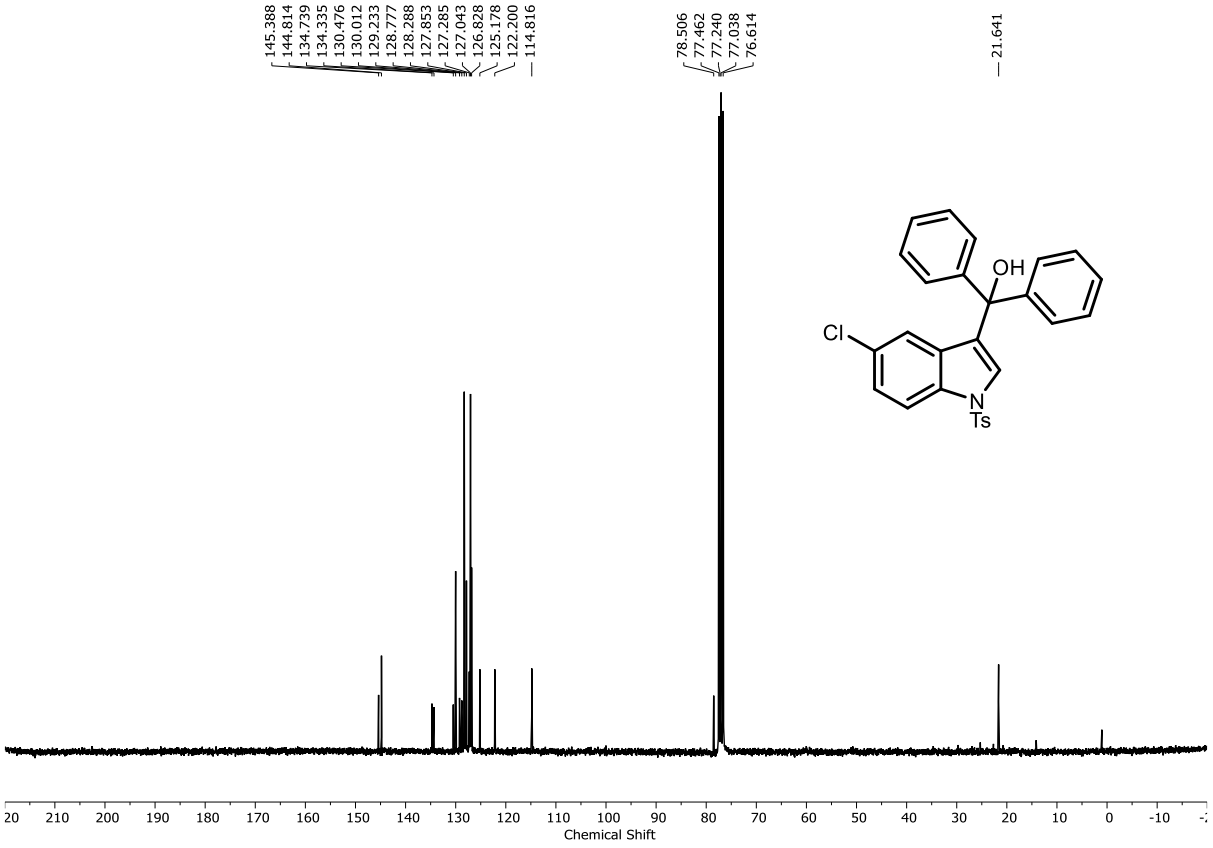
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5b



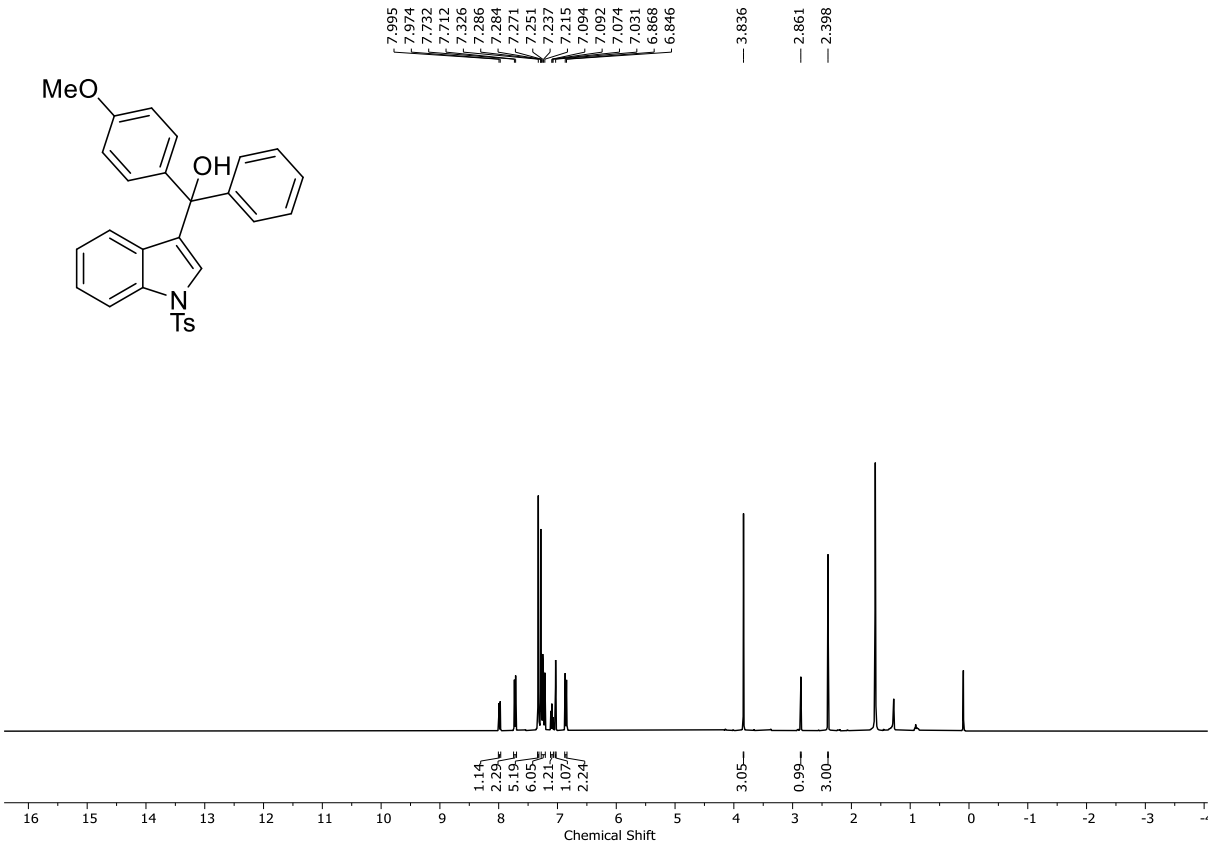
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5c



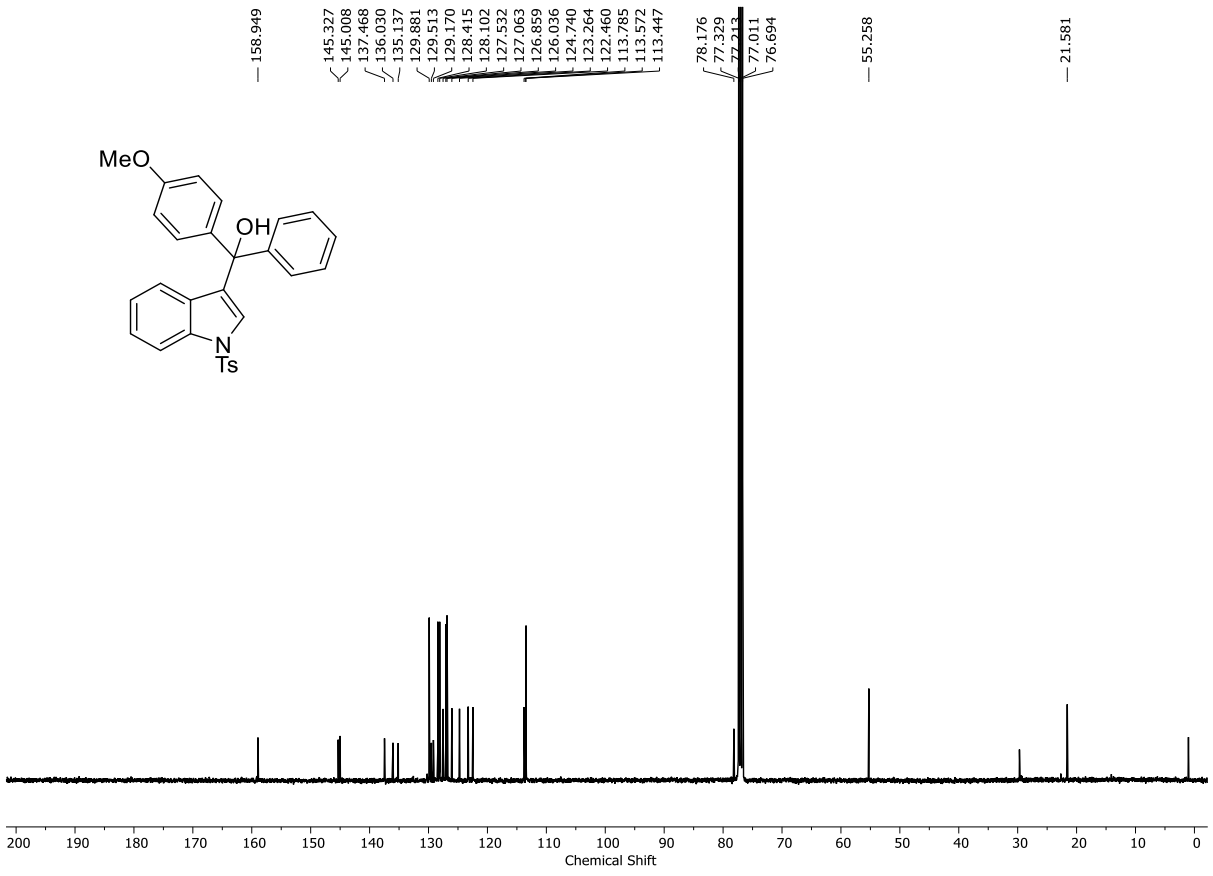
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5c



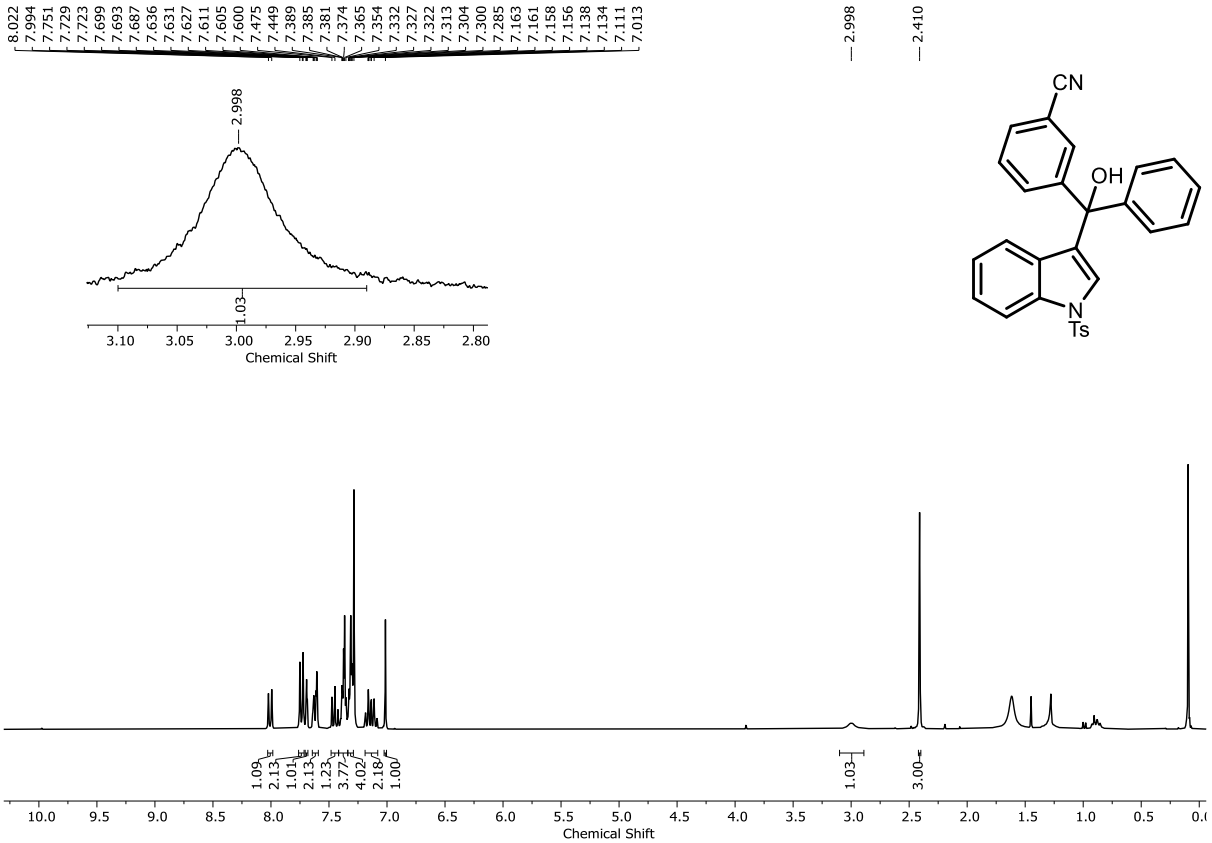
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5d



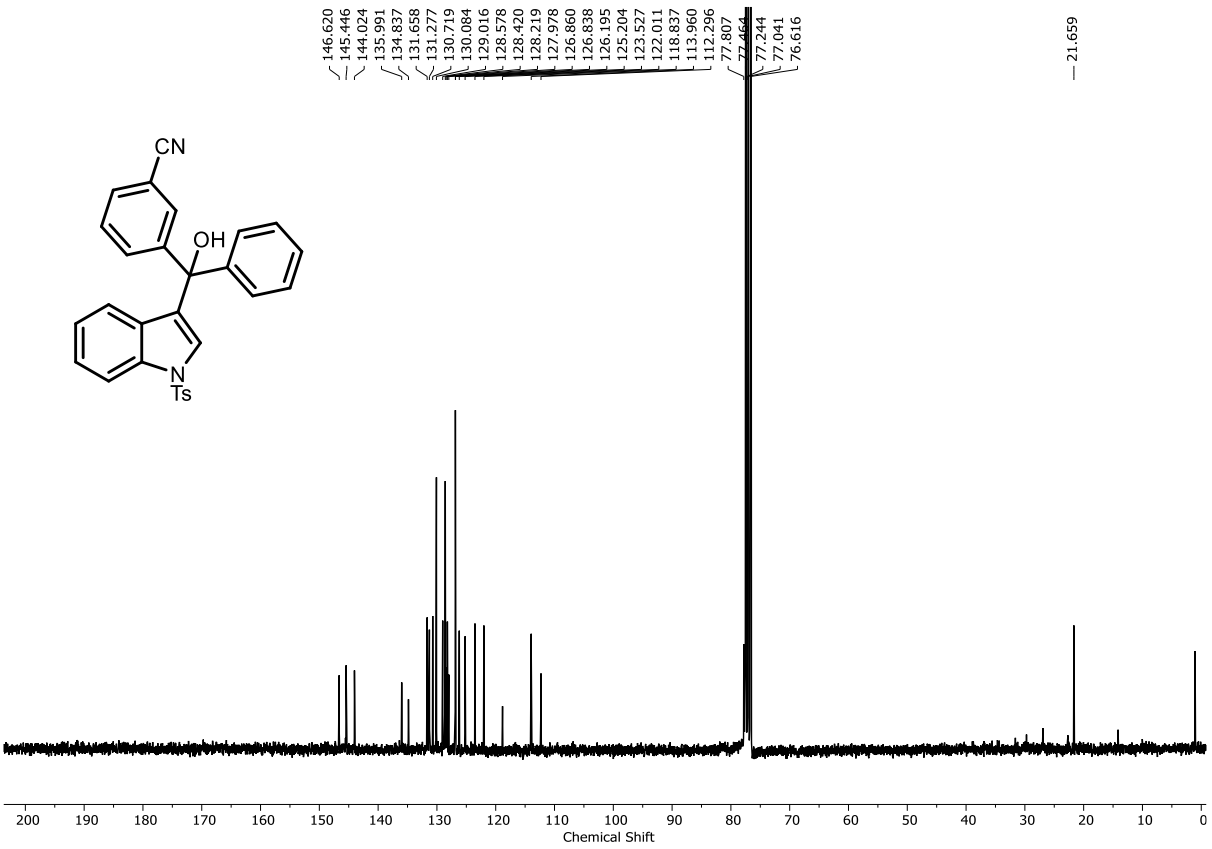
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of 5d



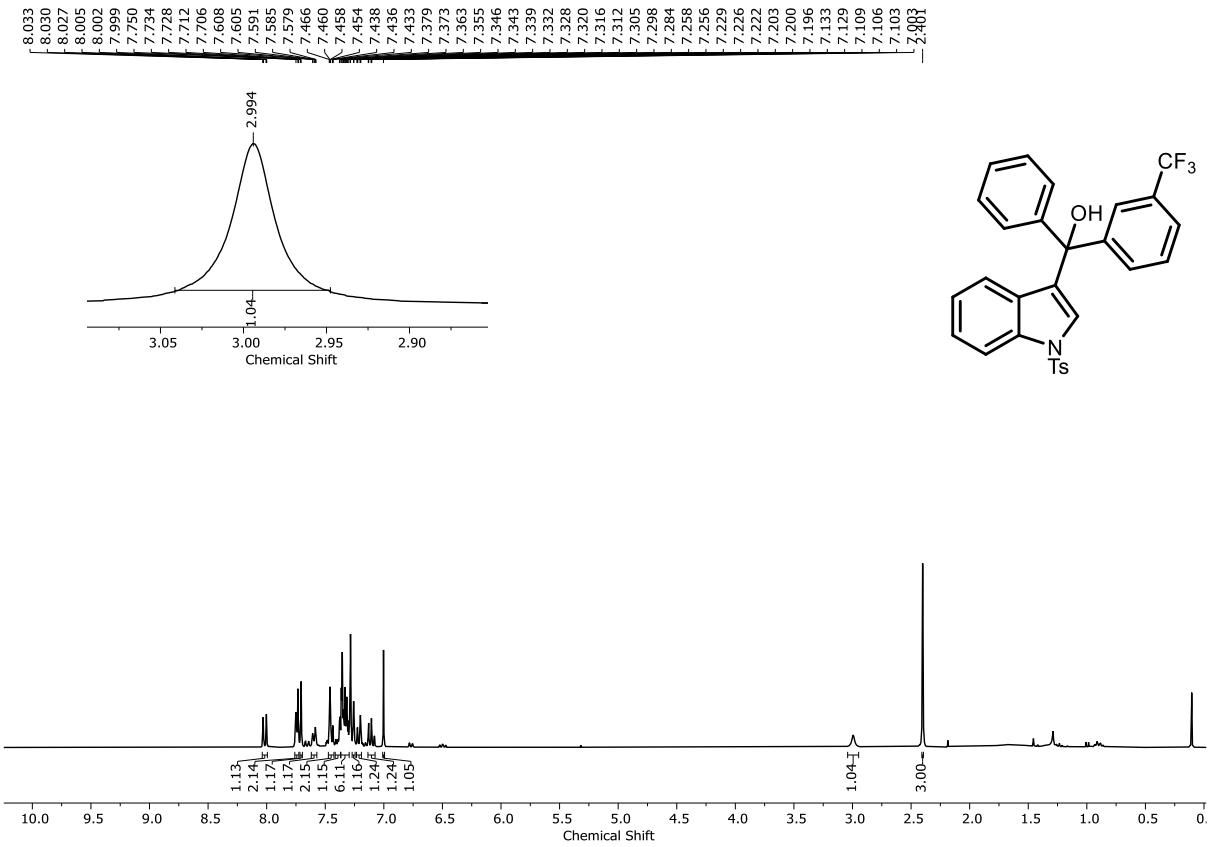
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5e



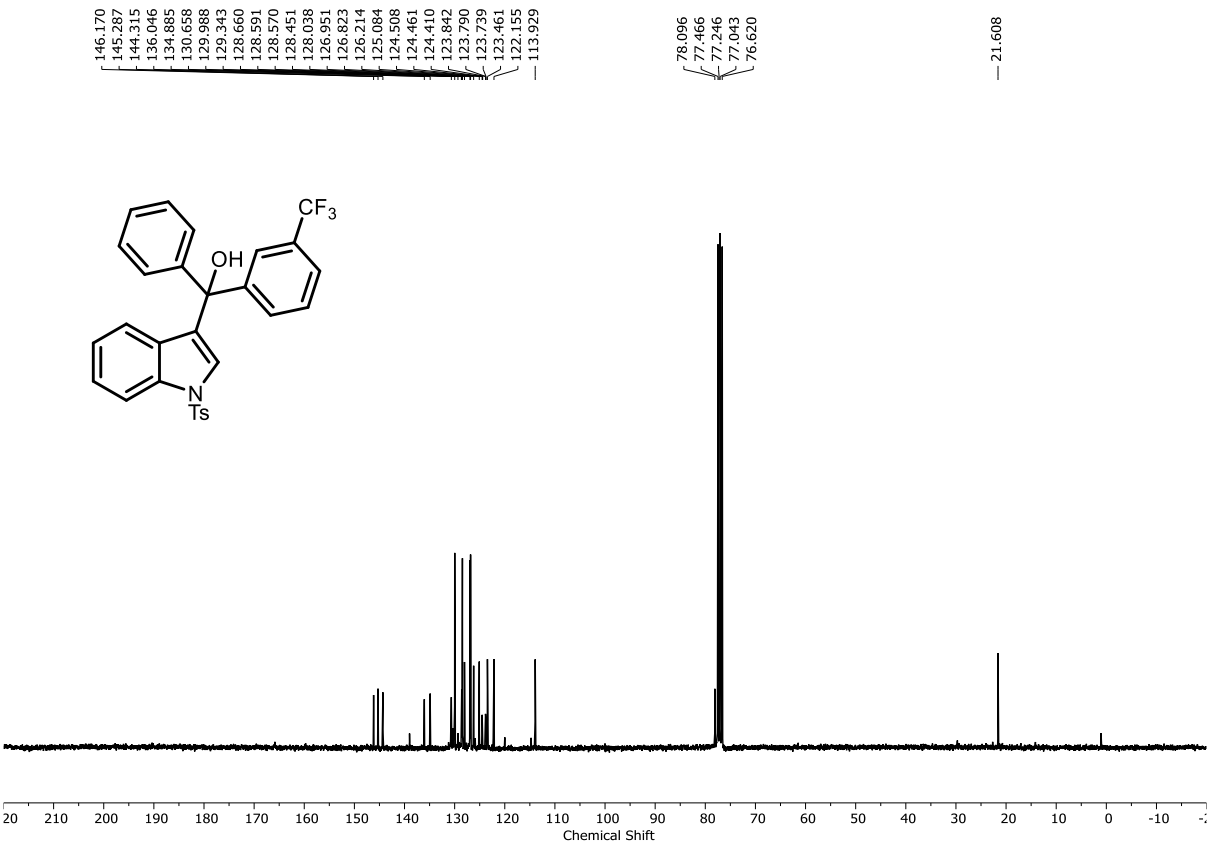
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 5e



^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5f

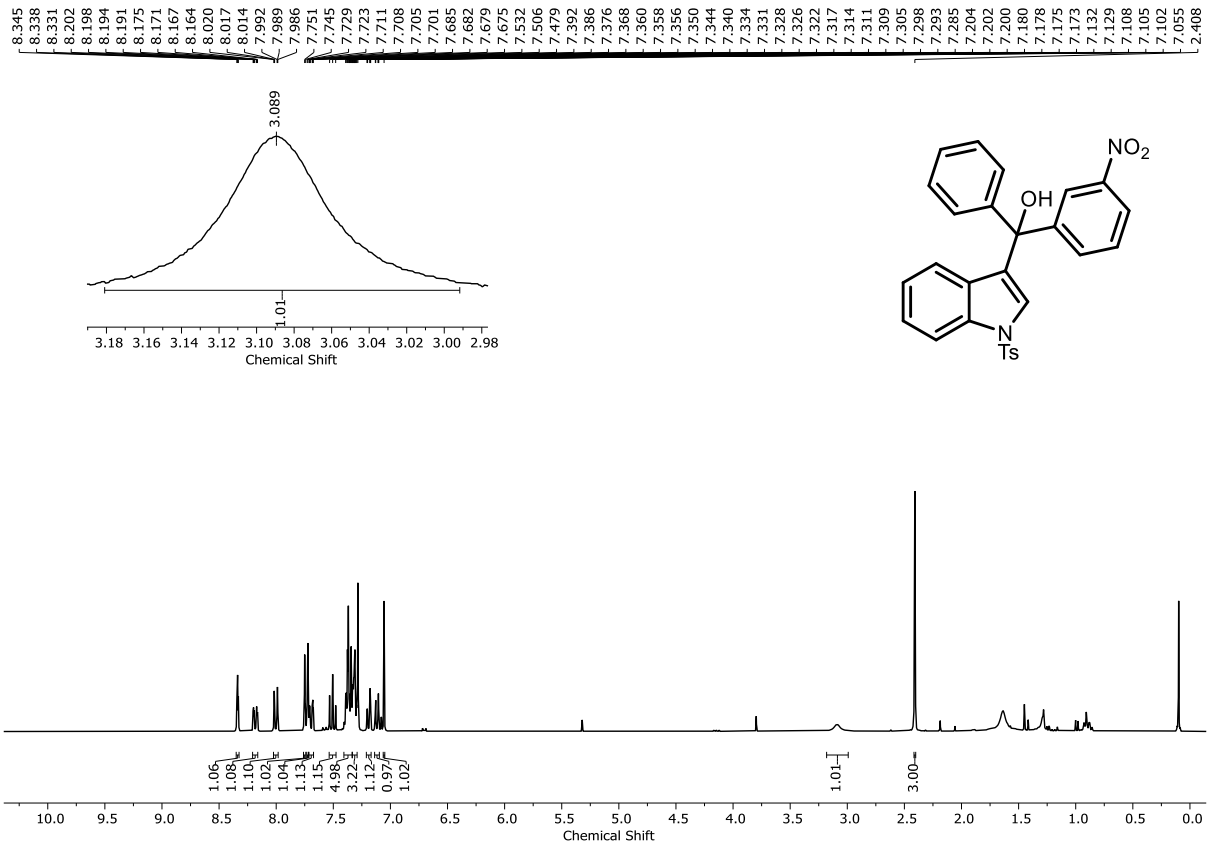


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5f

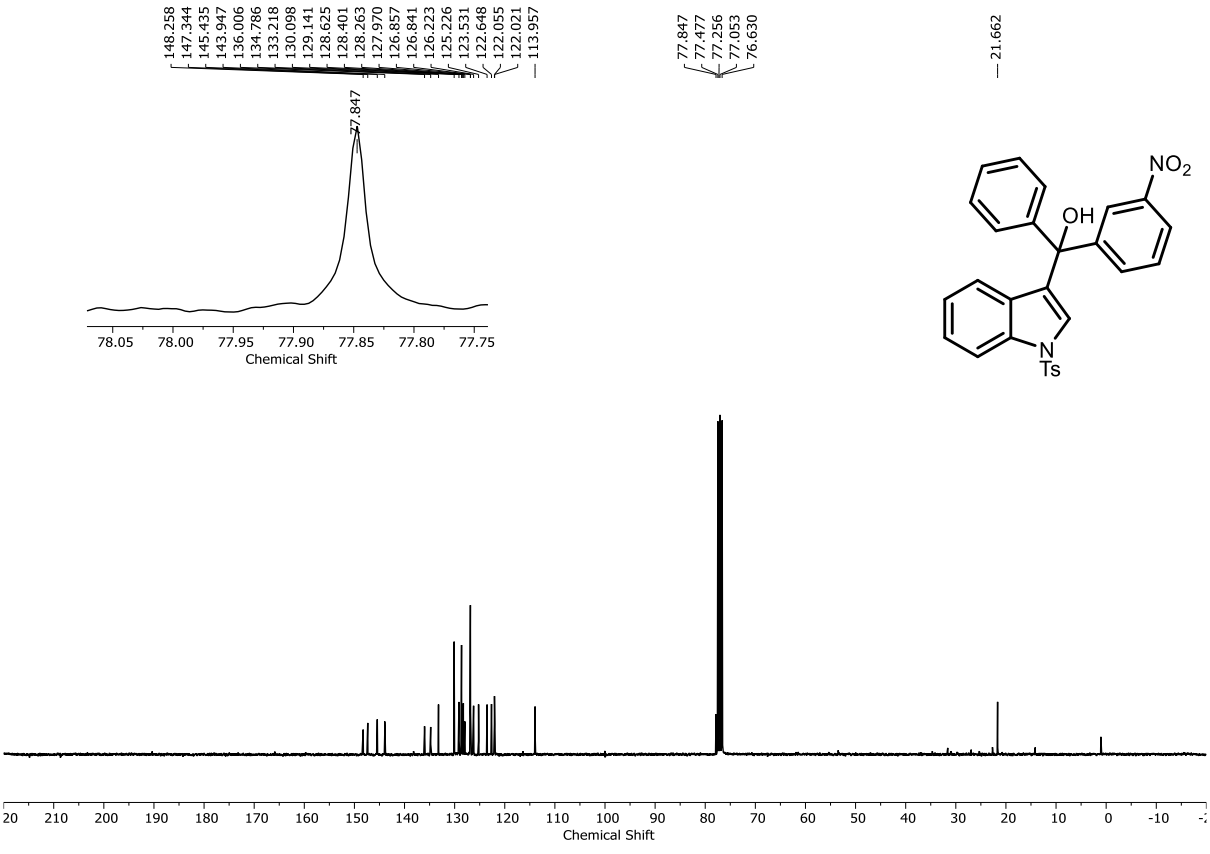


^{19}F NMR (377 MHz, $CDCl_3$) spectra of 5f

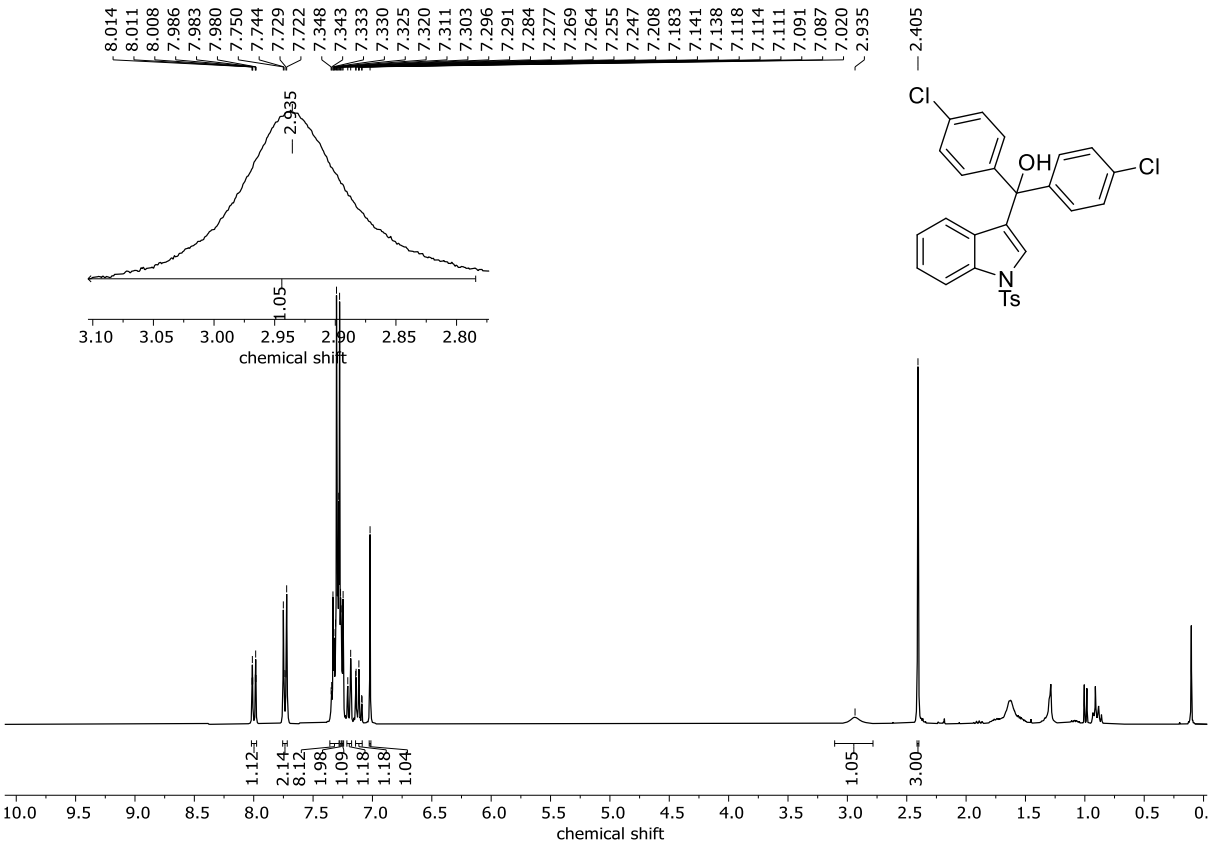
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5g



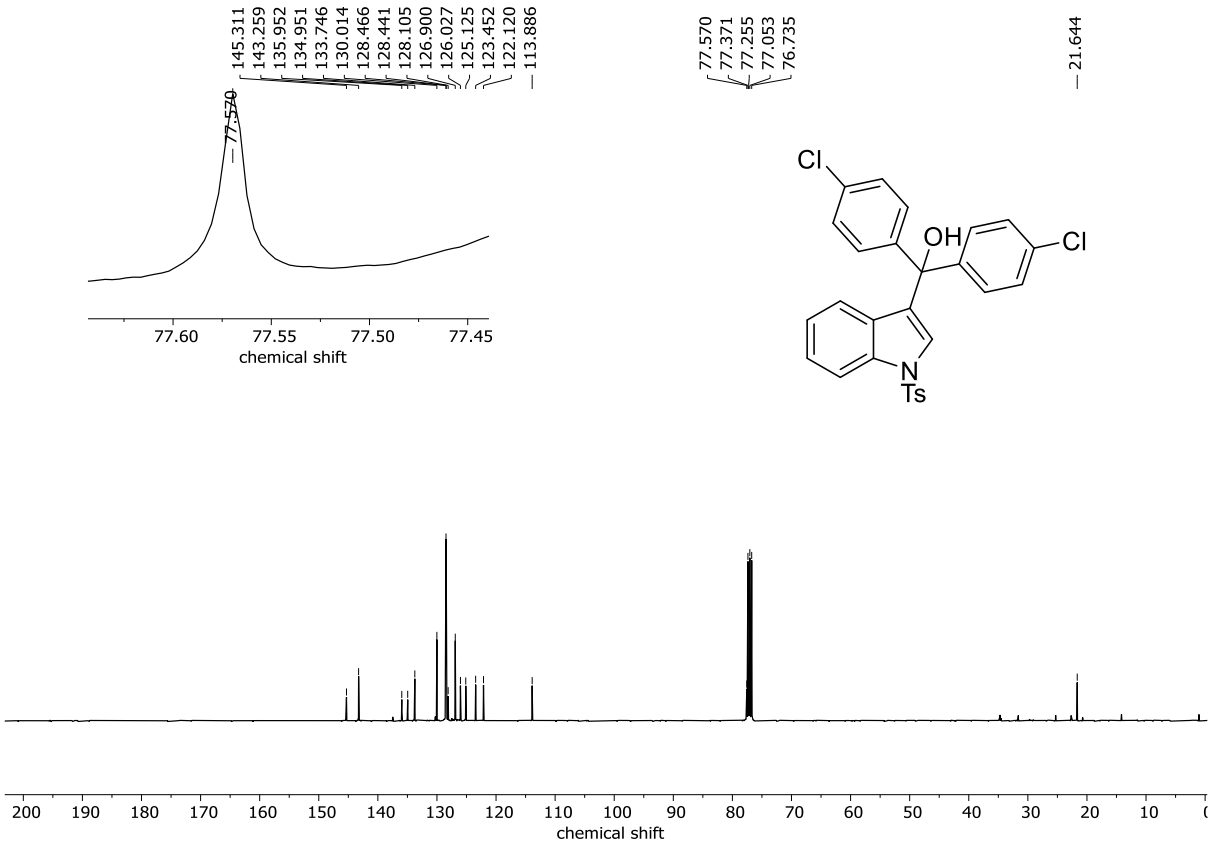
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 5g



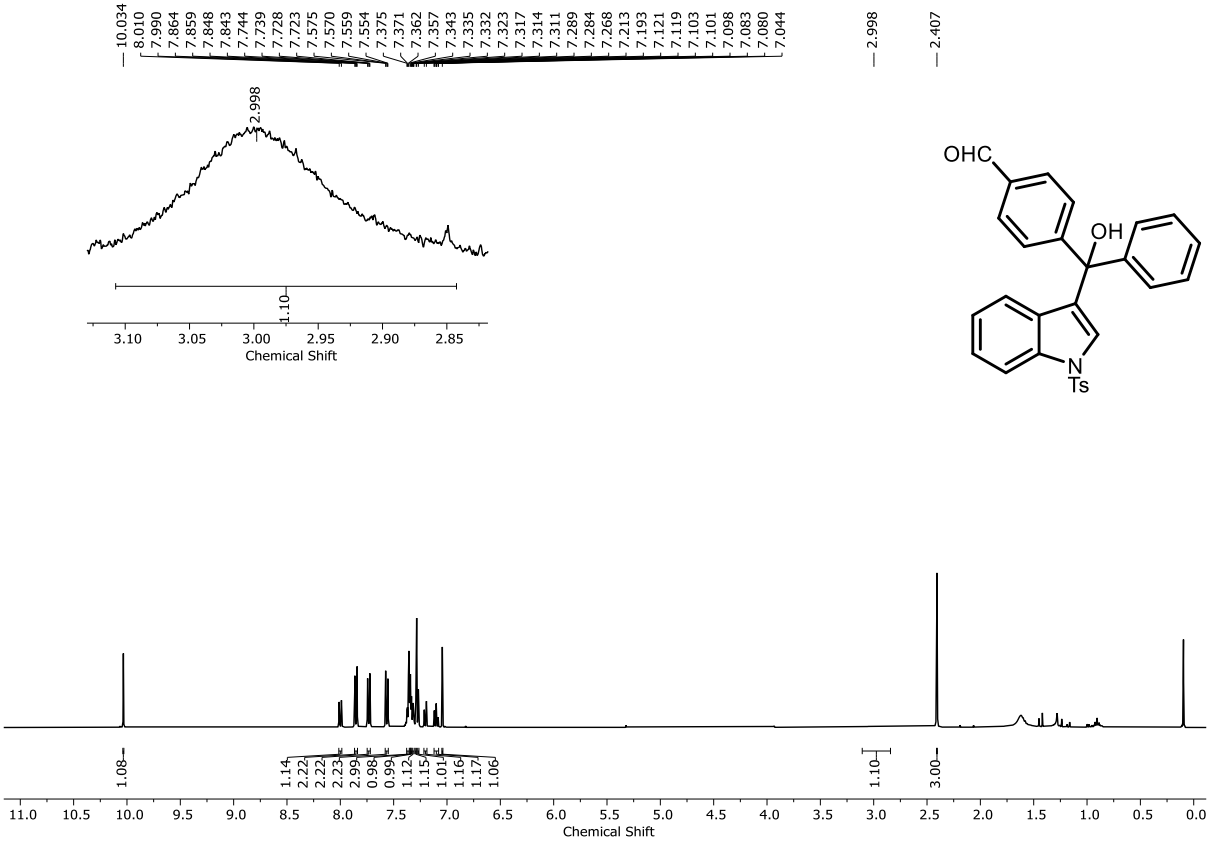
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5h



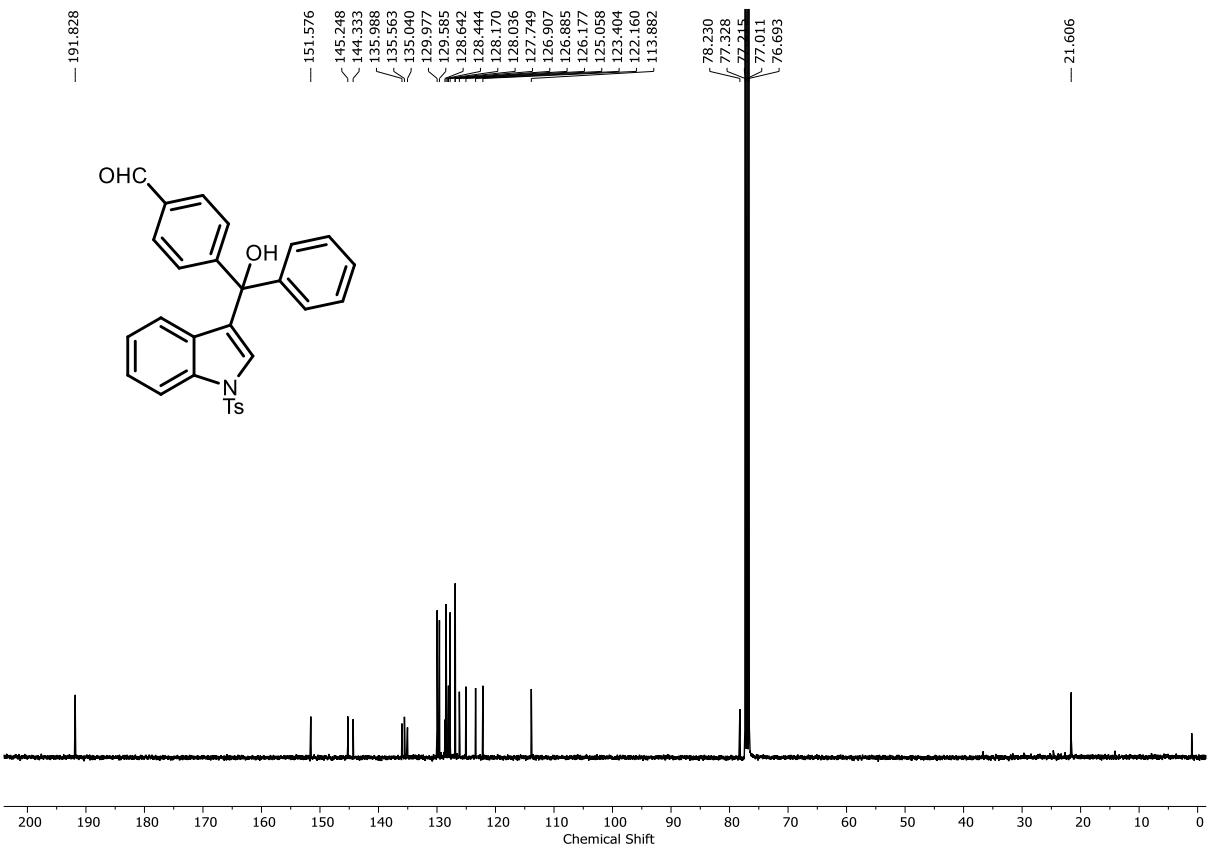
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 5h



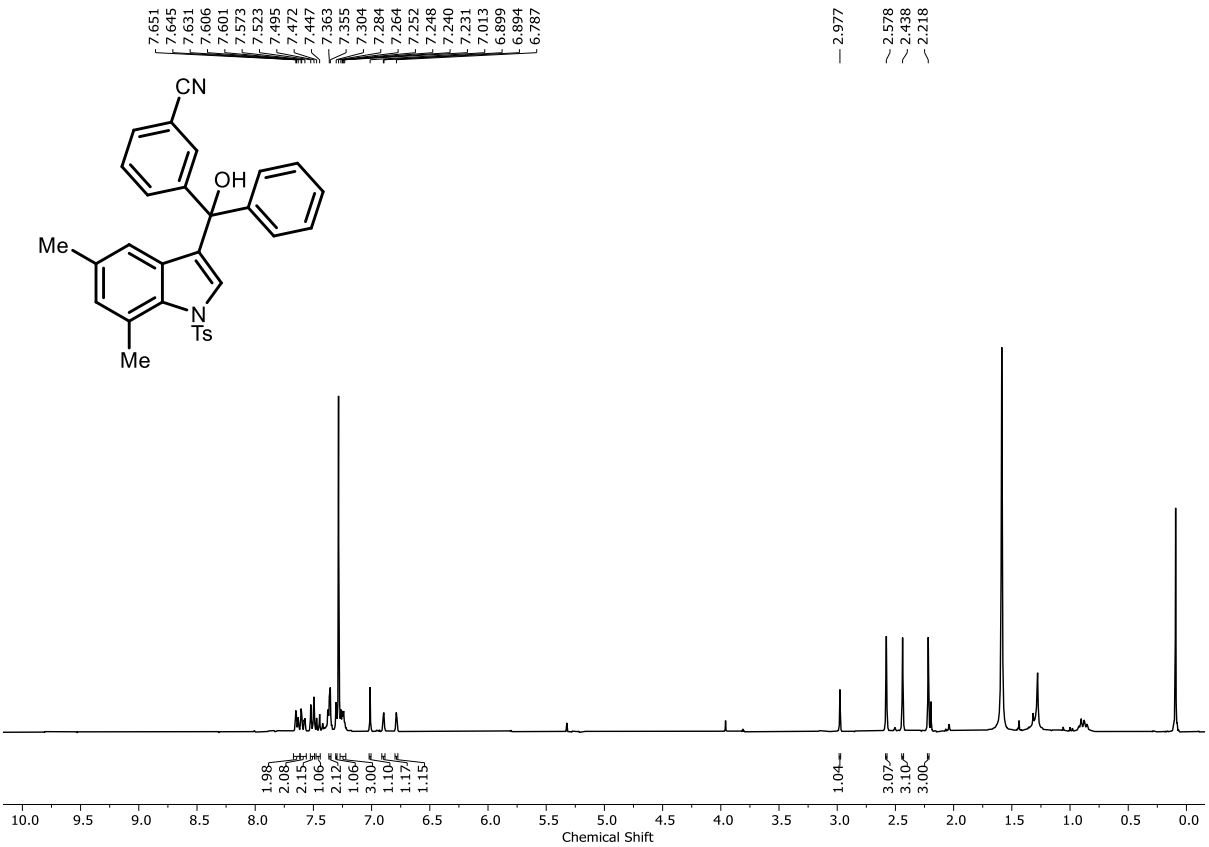
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5i



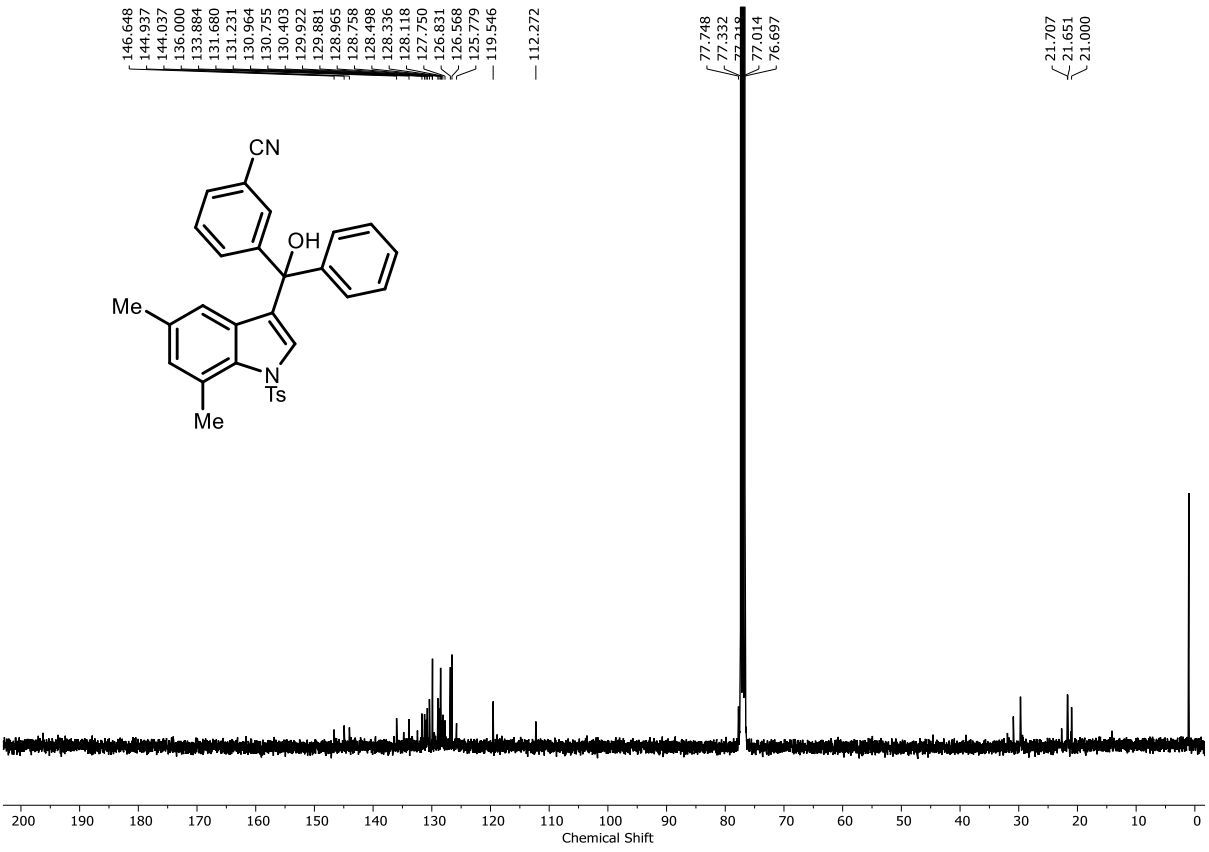
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 5i



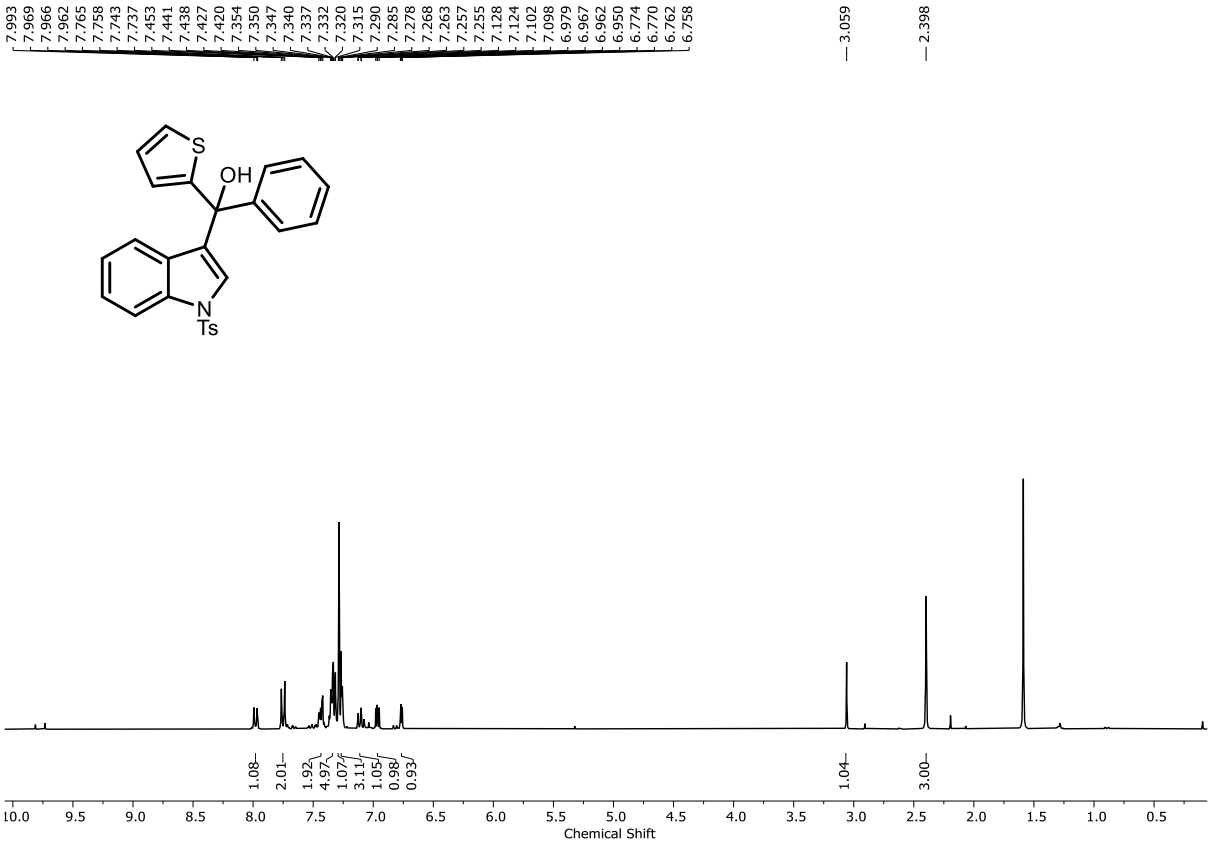
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5j



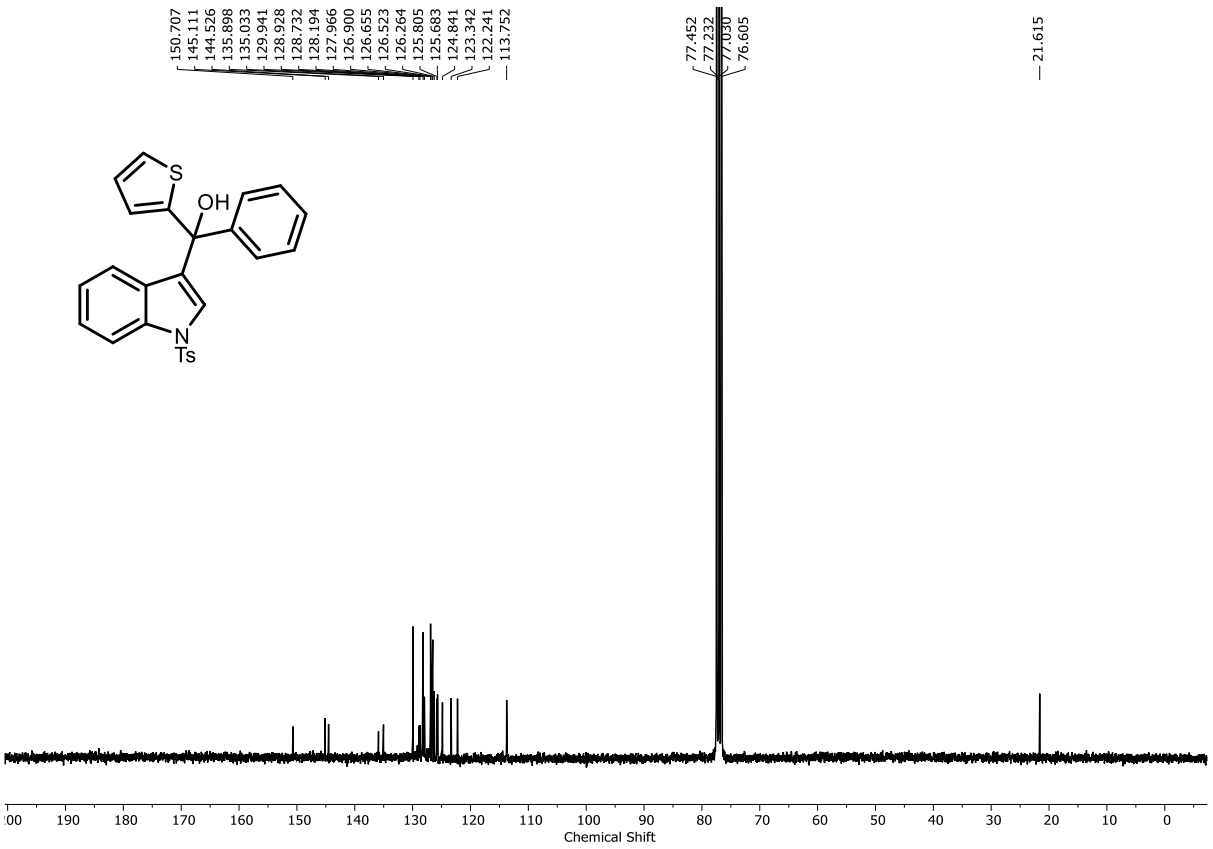
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 5j



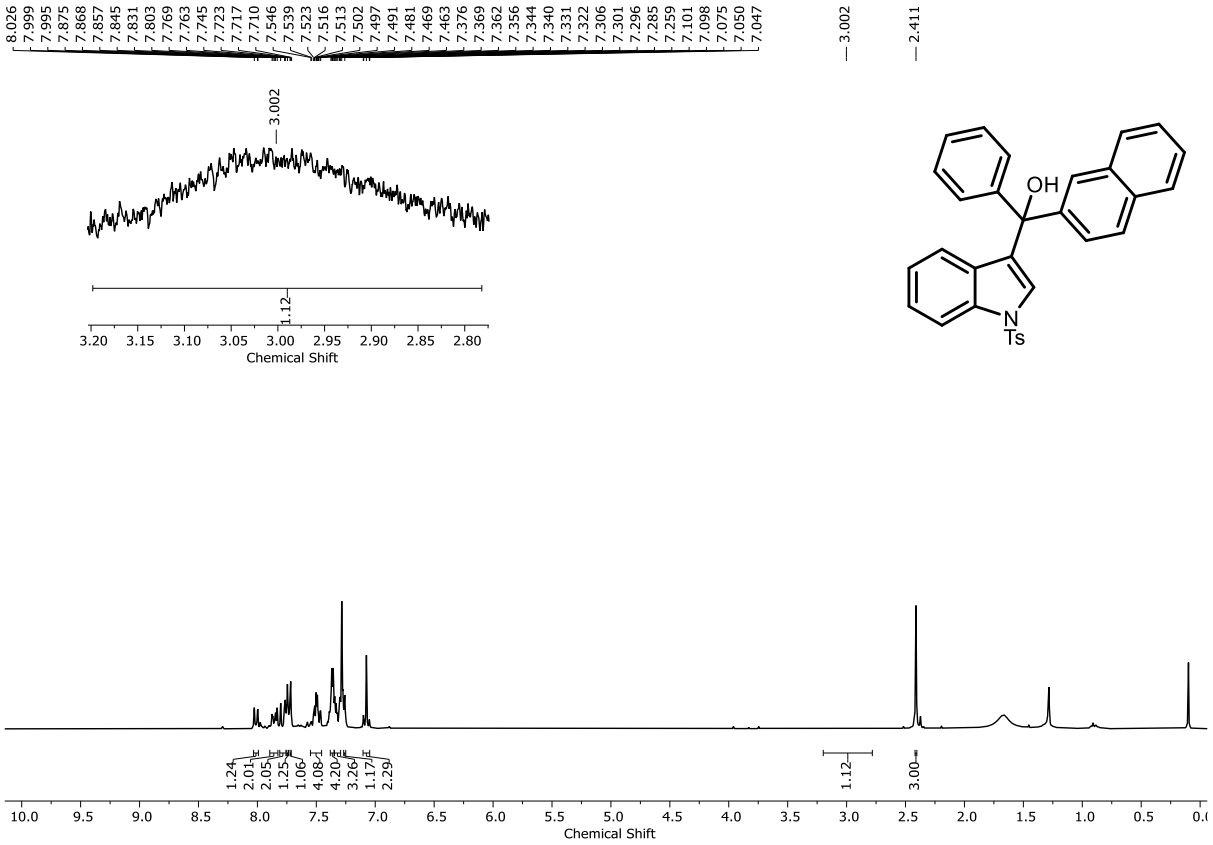
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5k



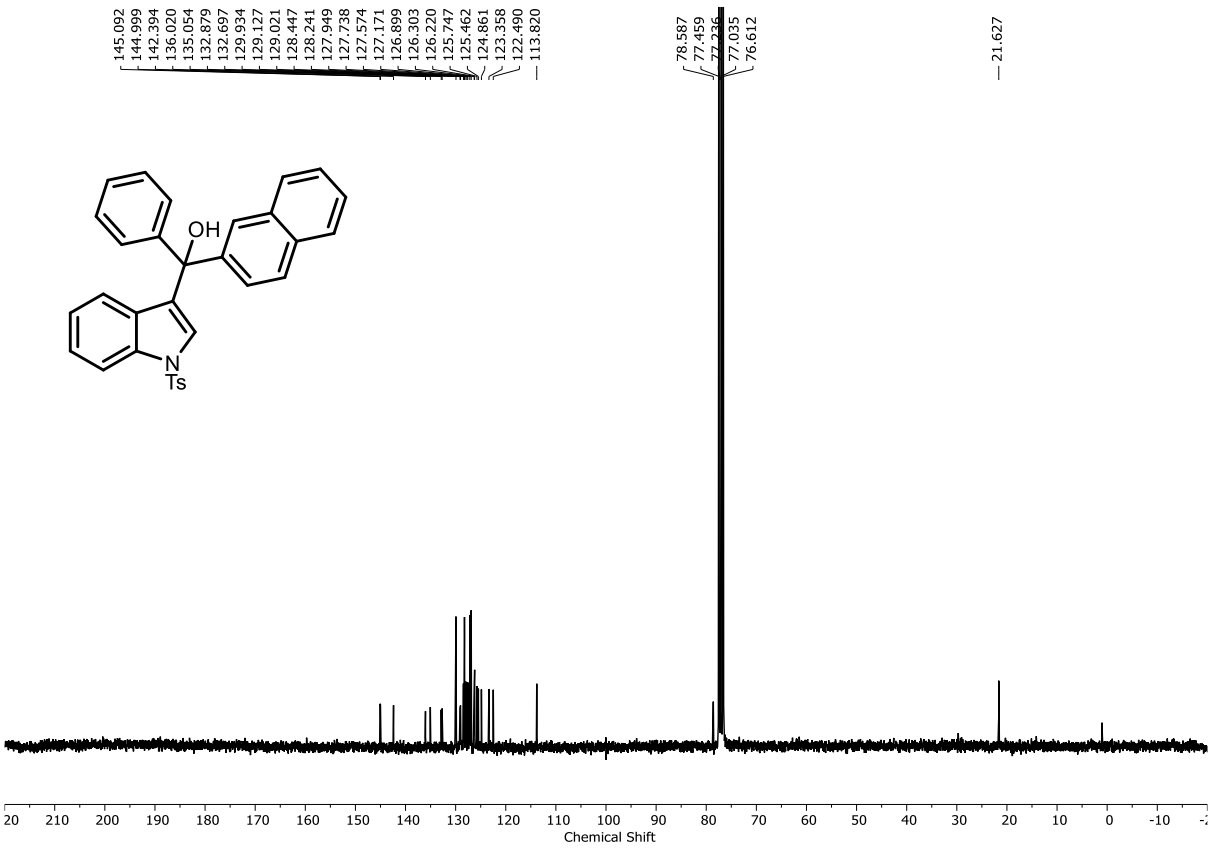
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5k



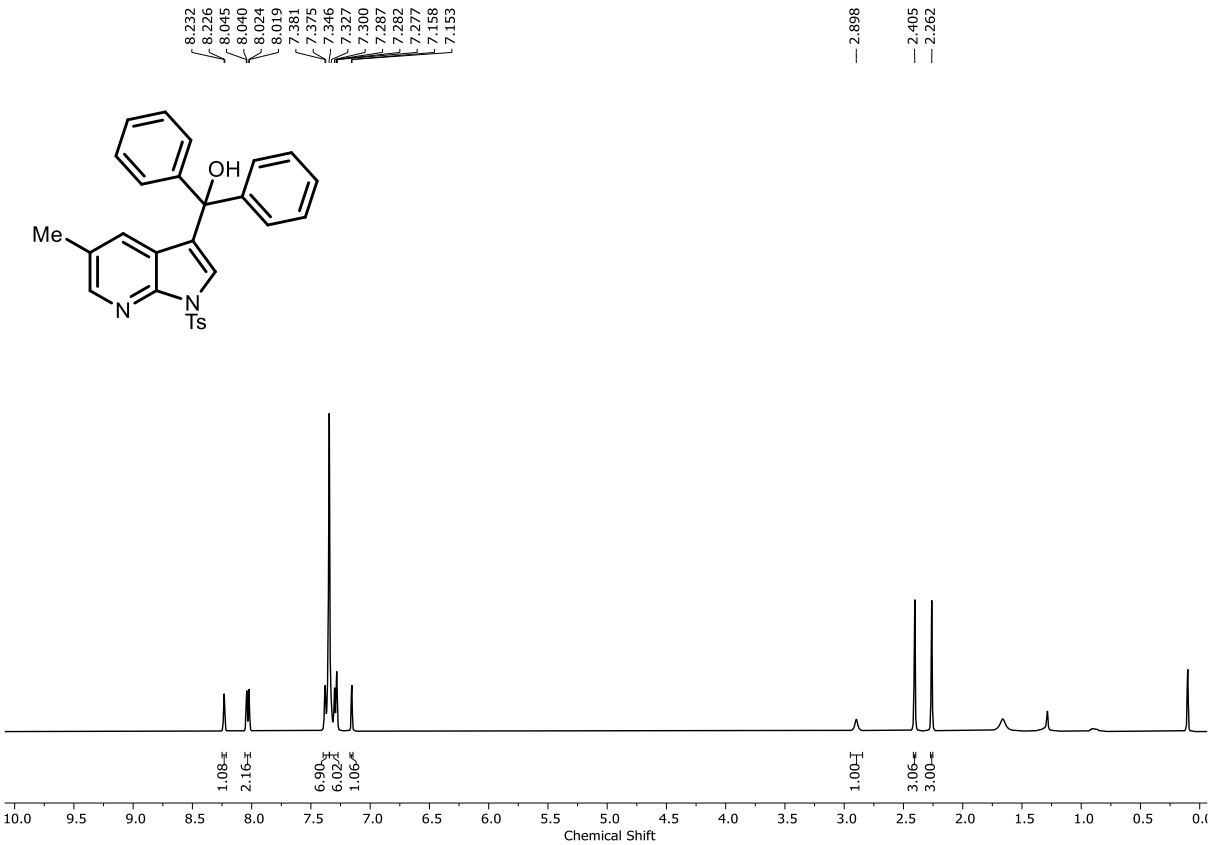
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5l



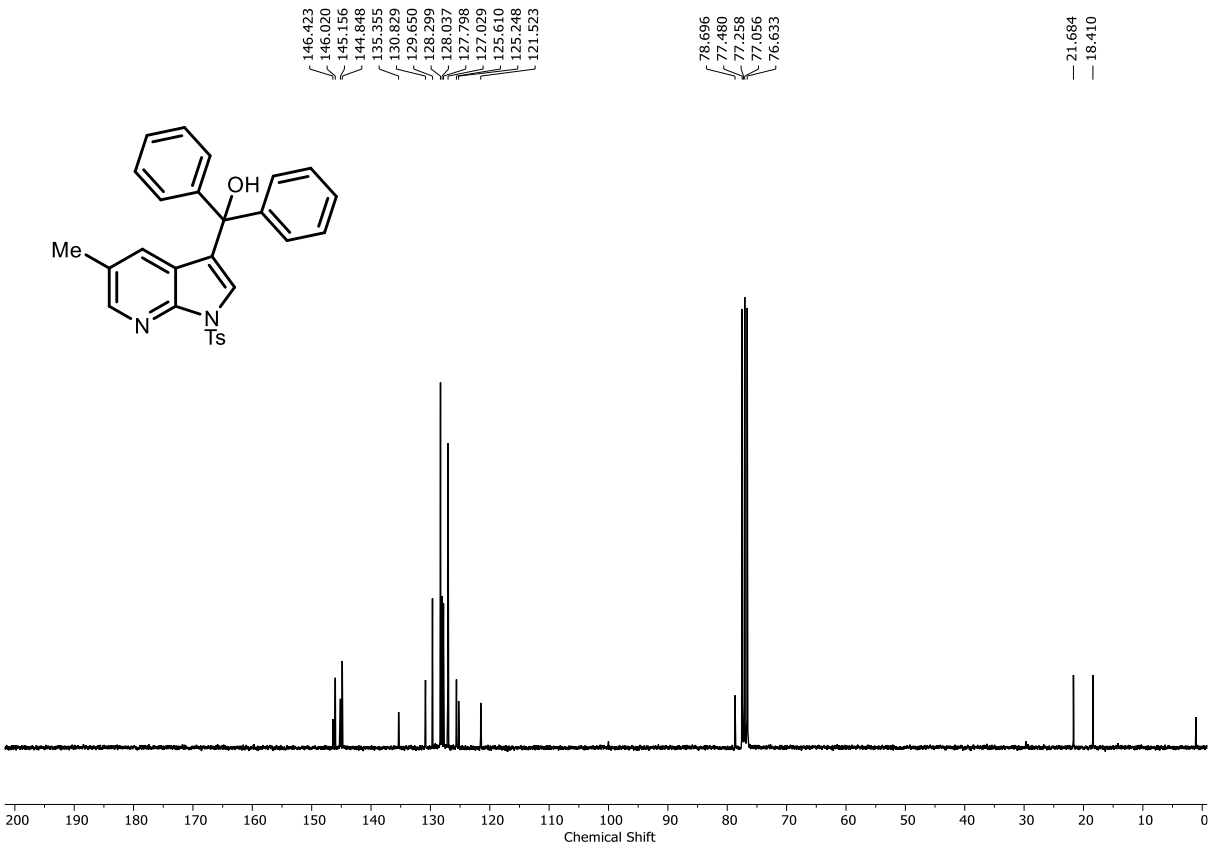
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5l



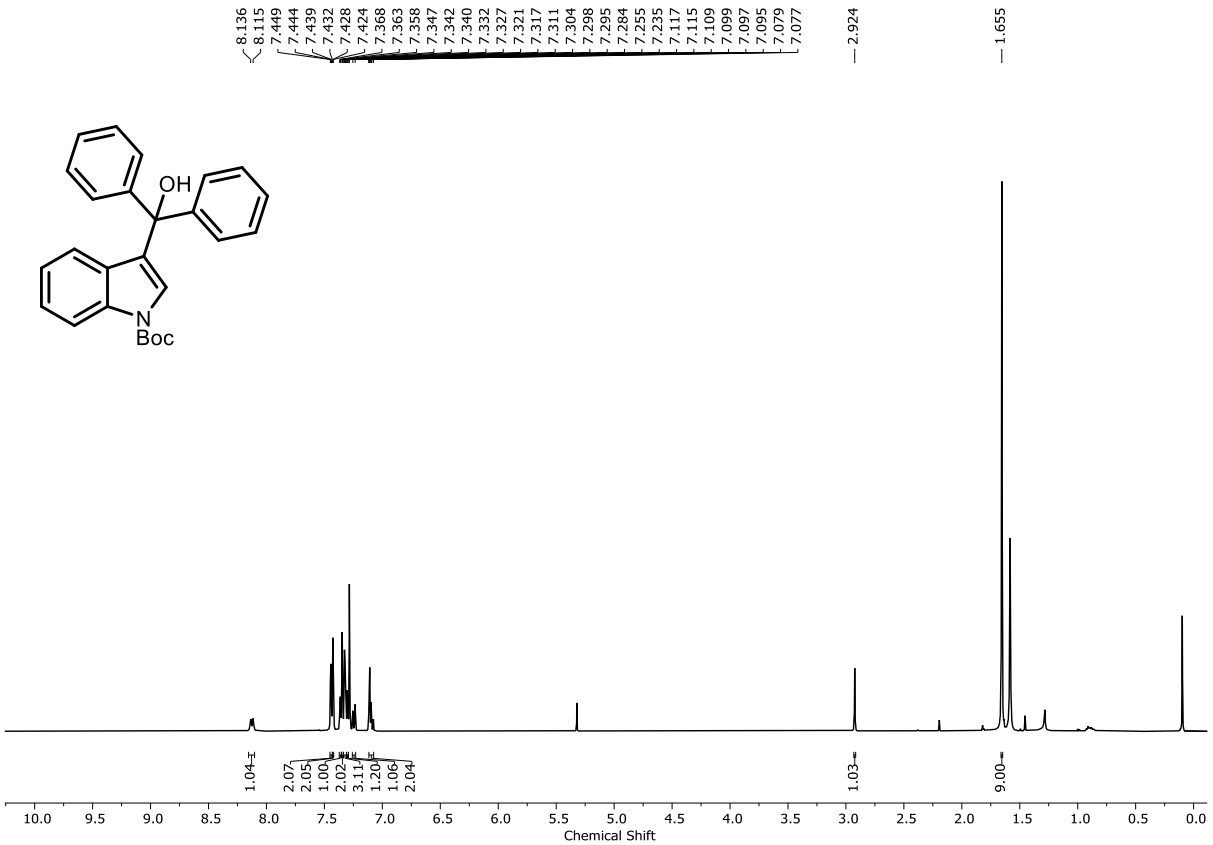
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5m



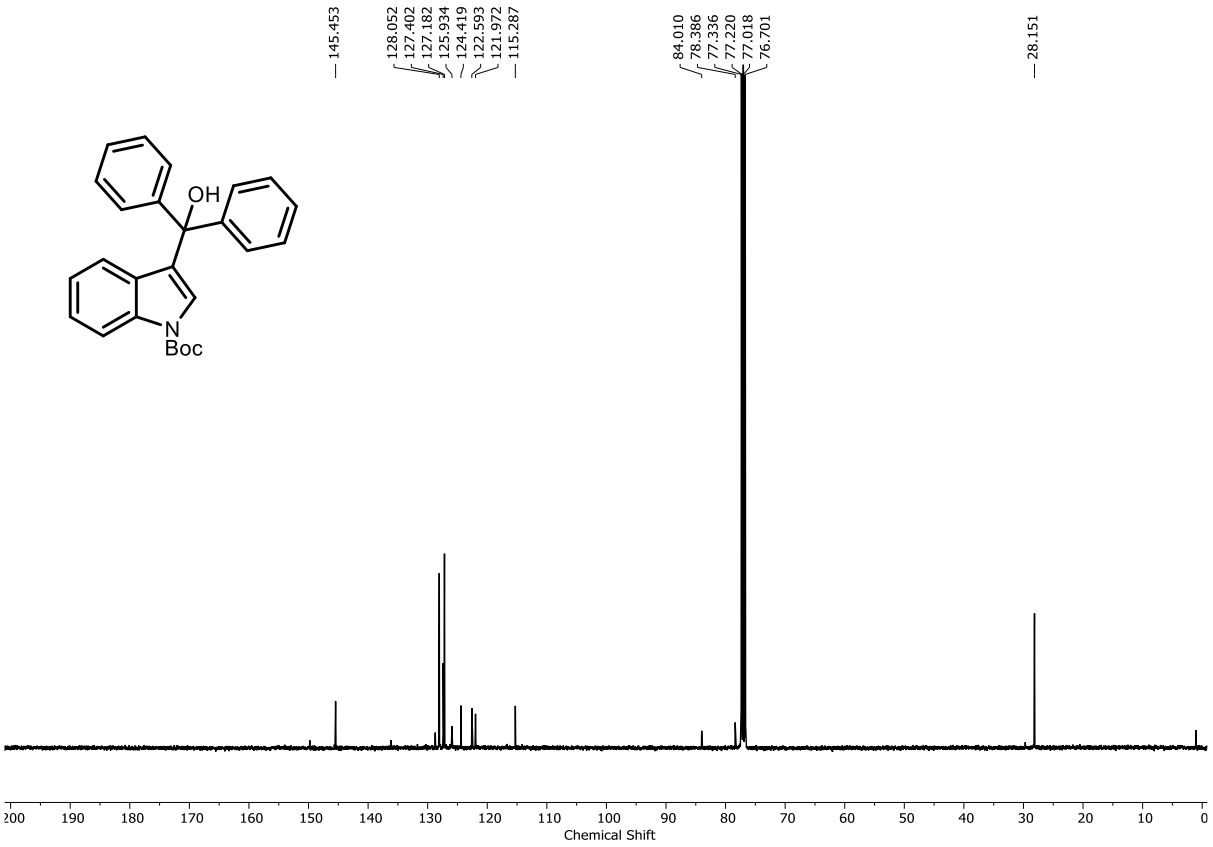
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 5m



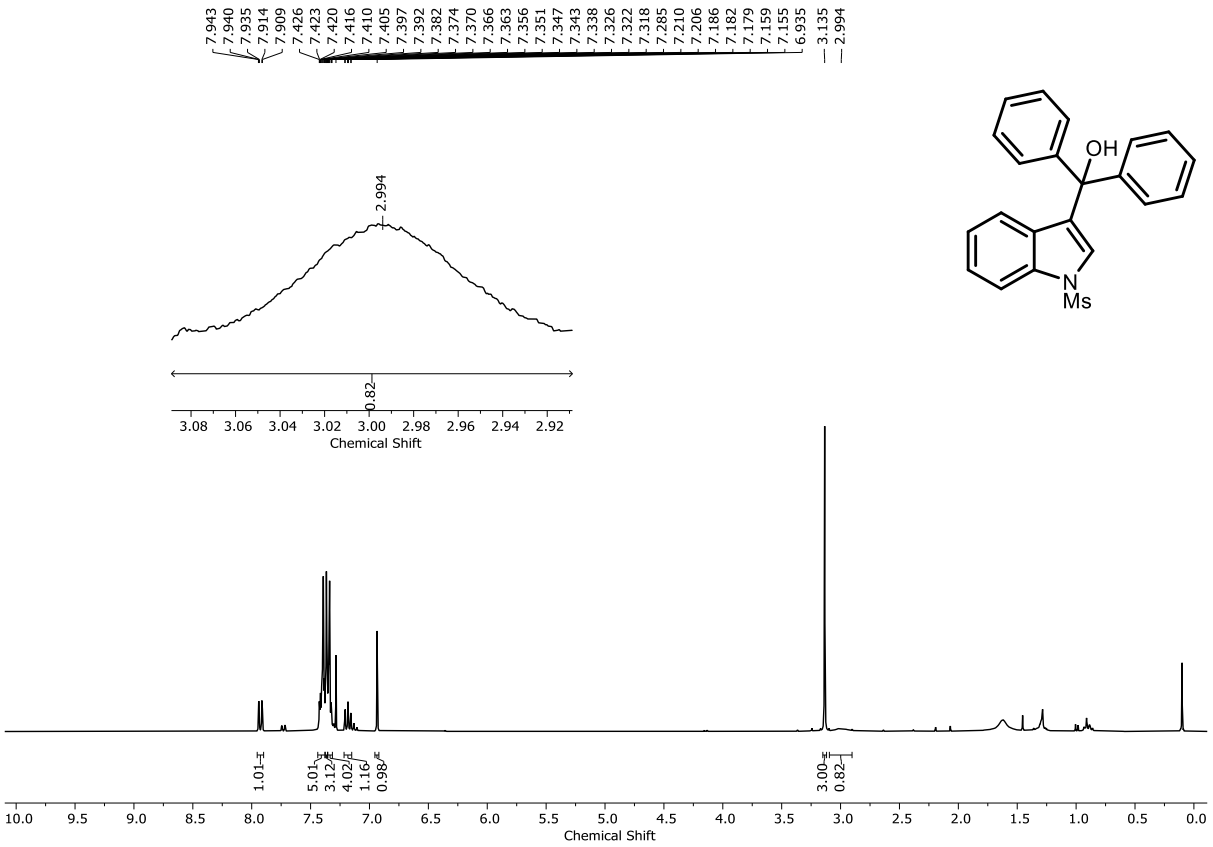
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 5n



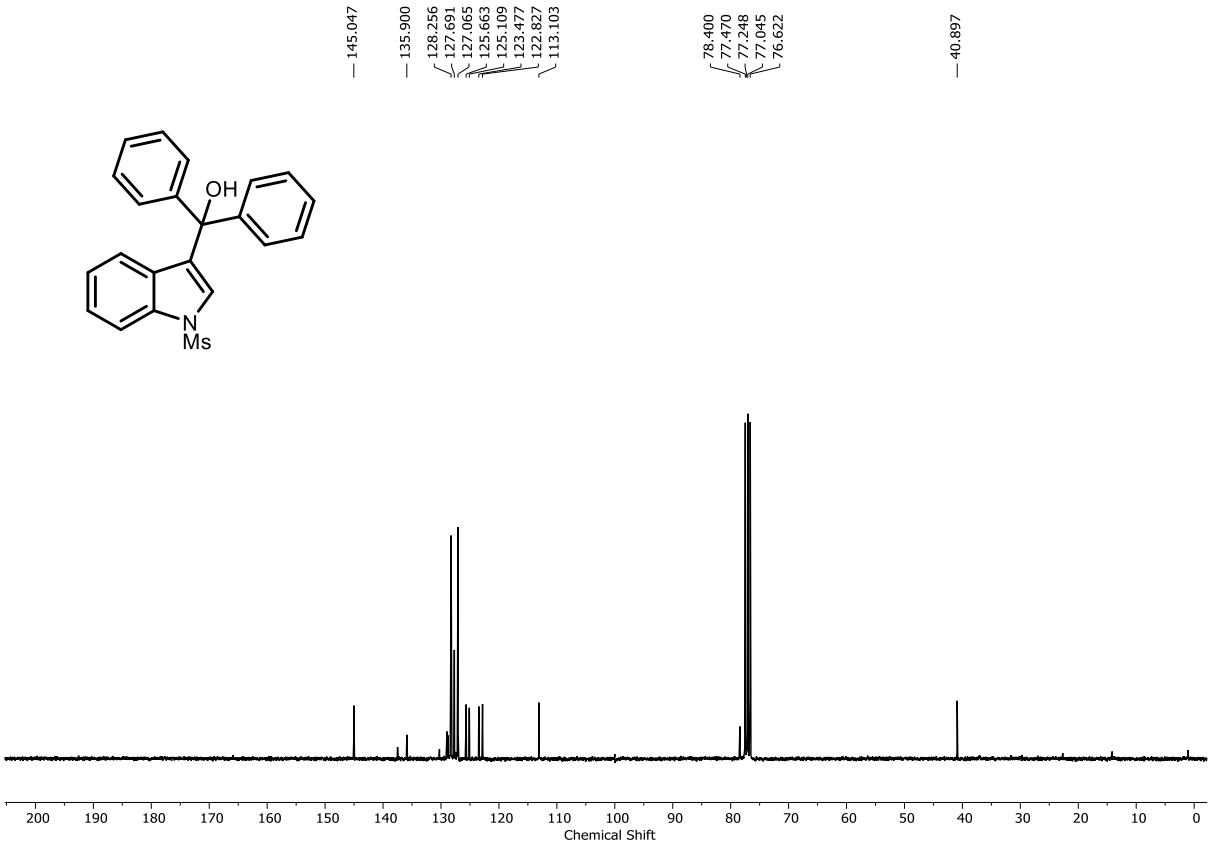
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of 5n



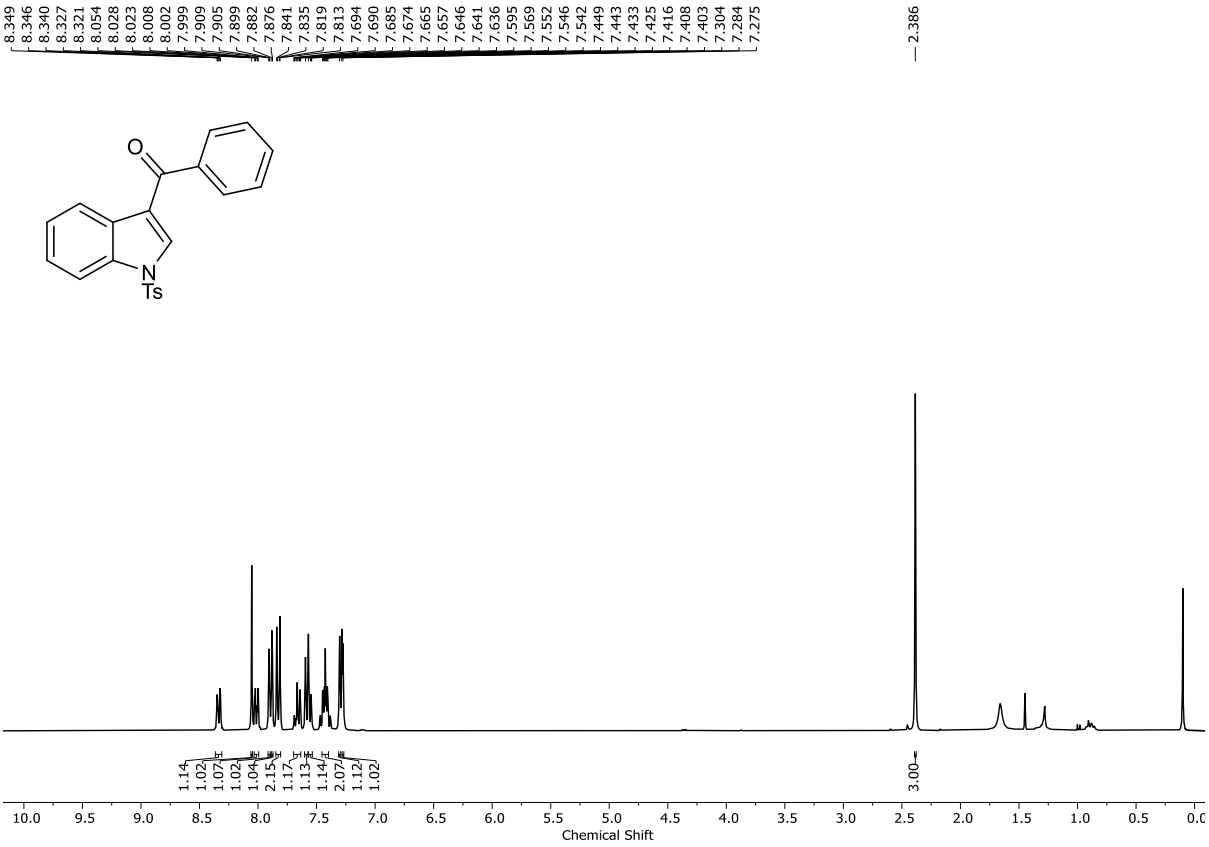
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 5o



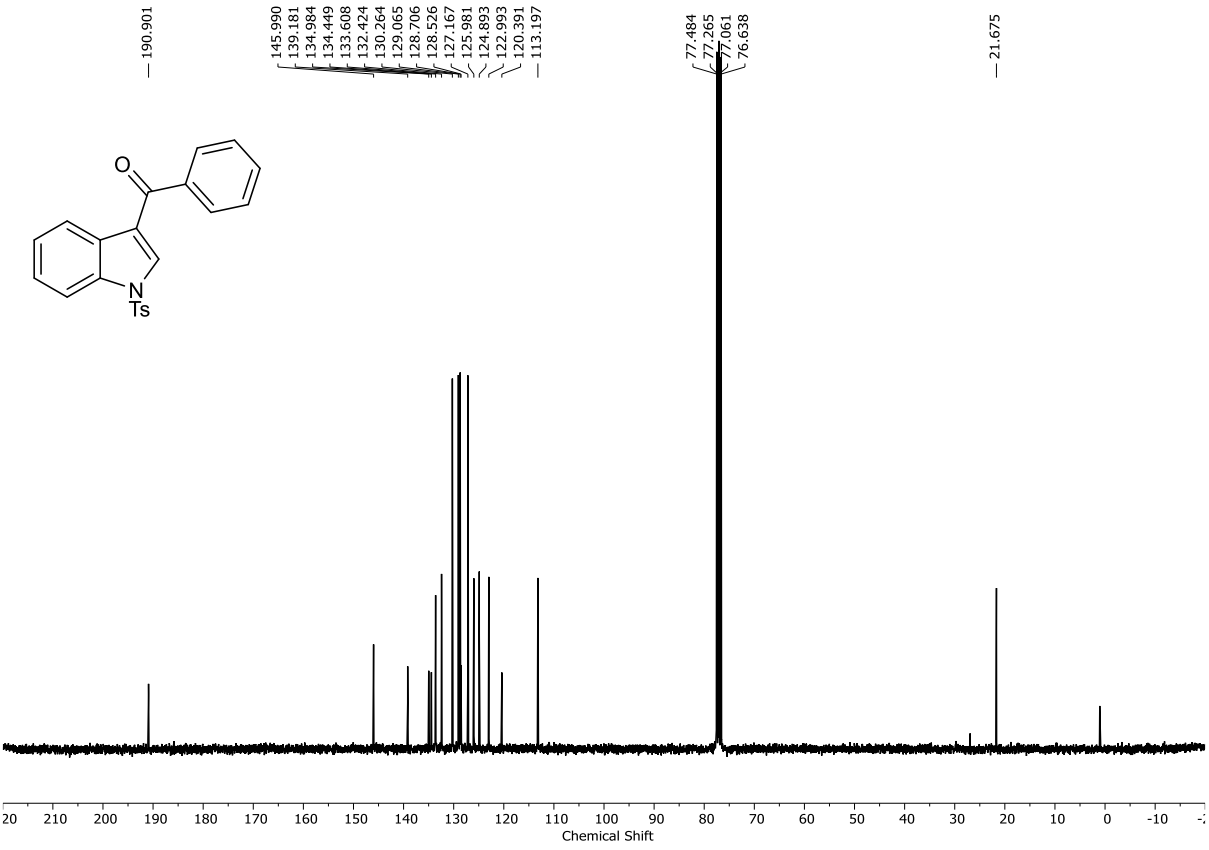
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5o



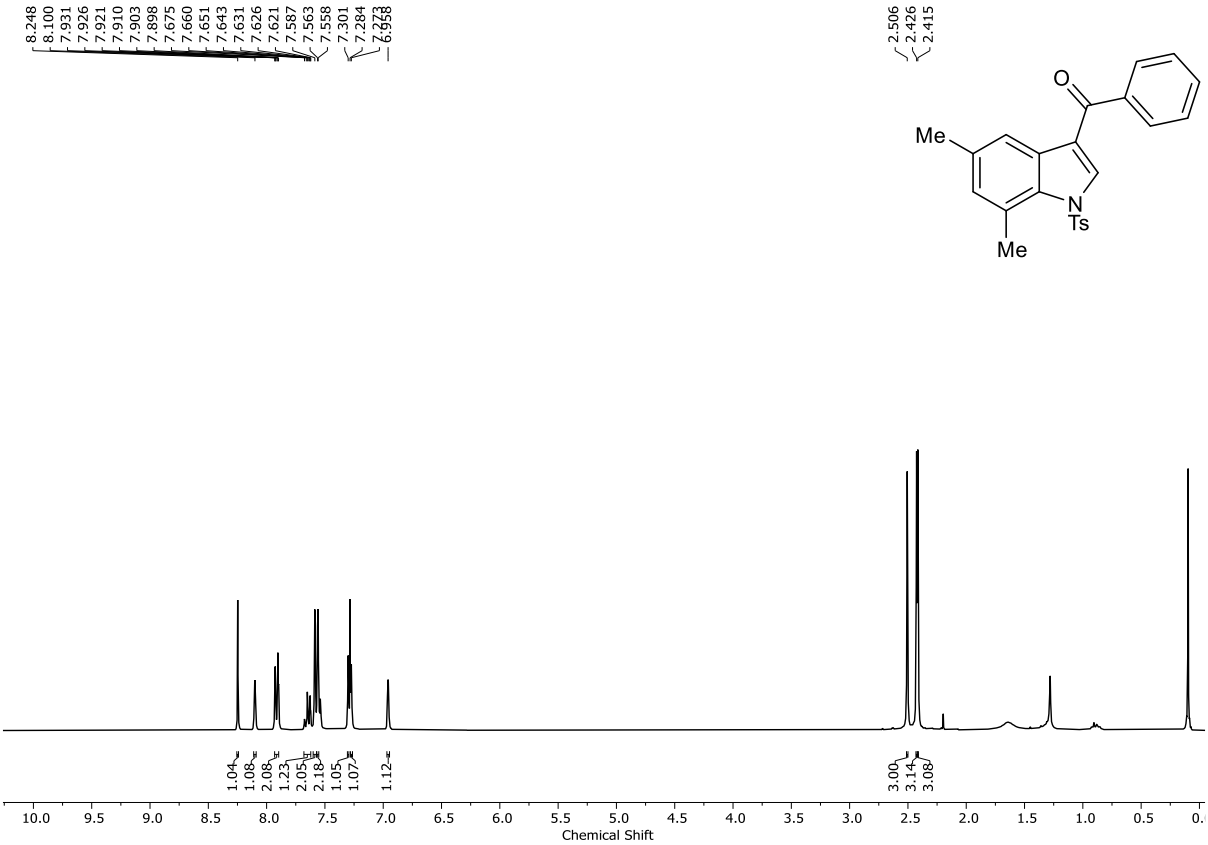
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7a



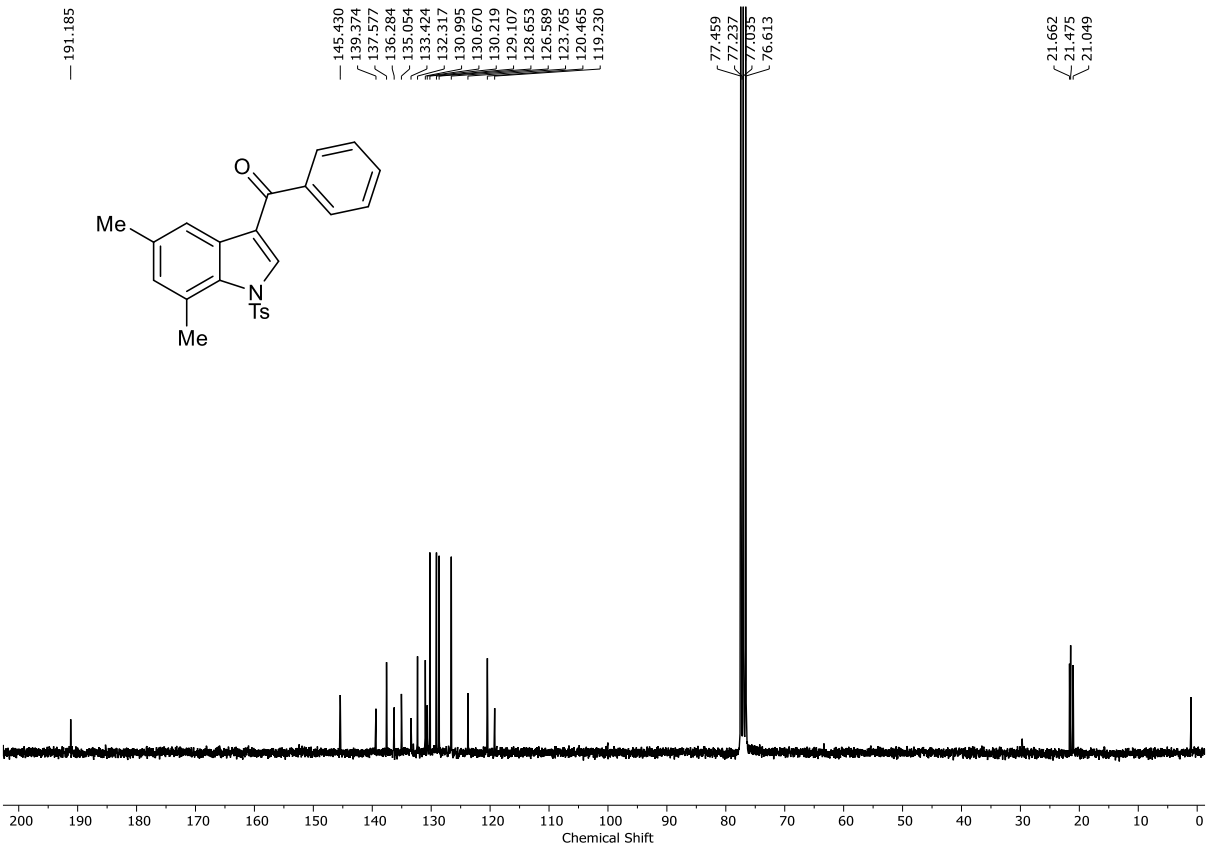
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7a



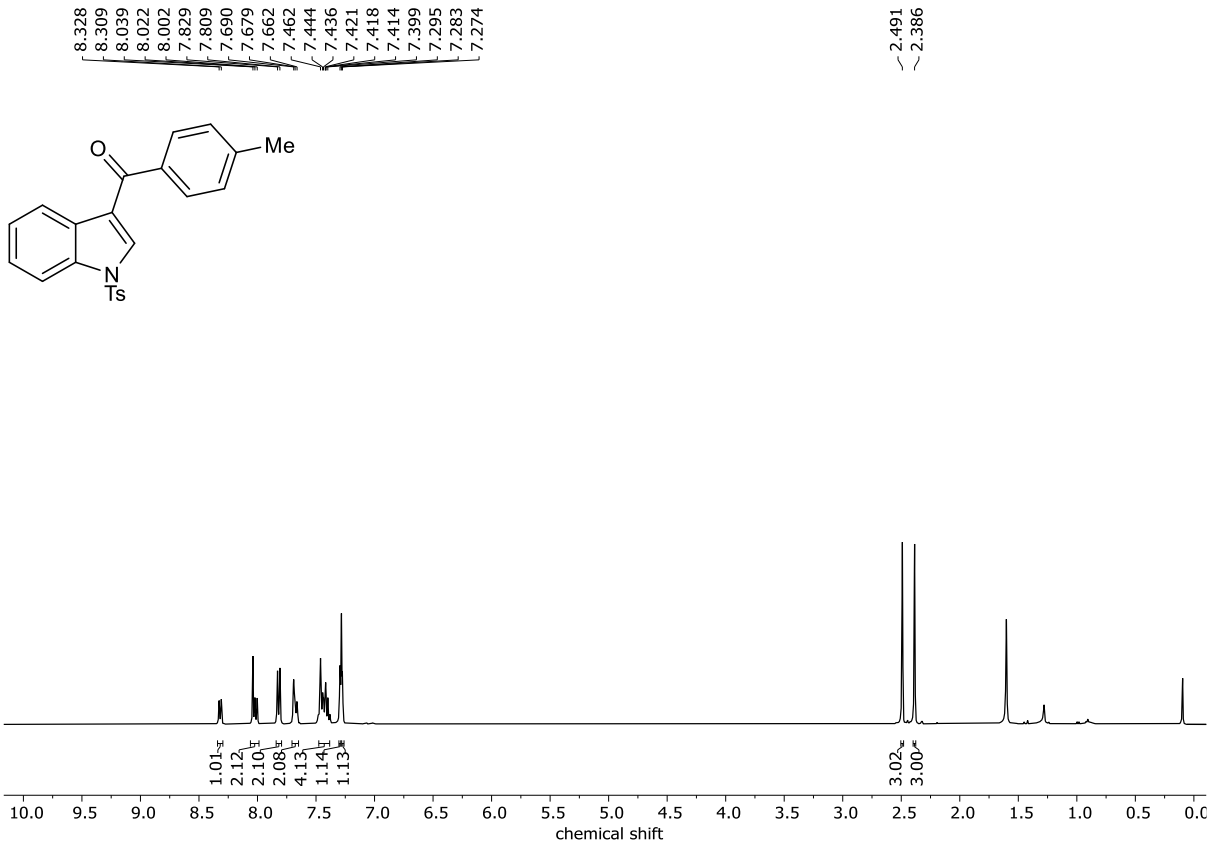
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7b



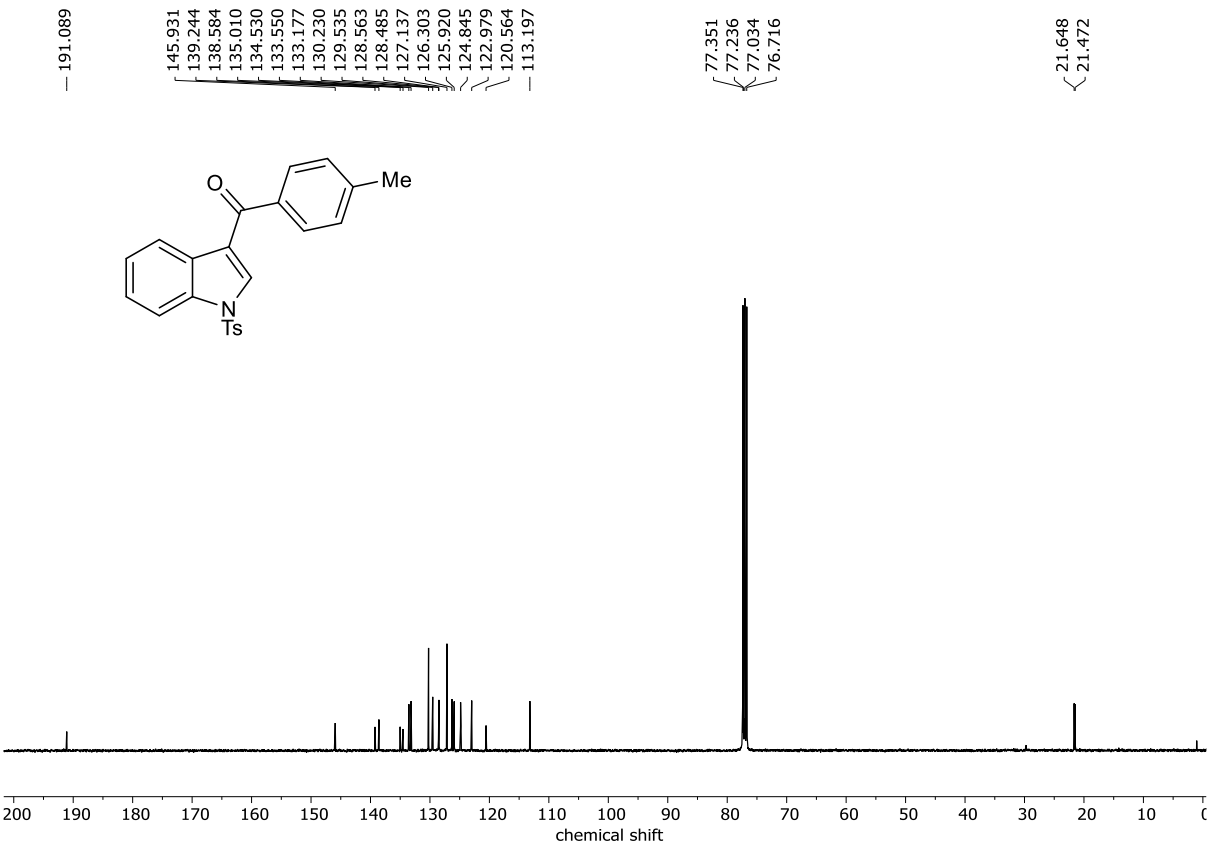
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 7b



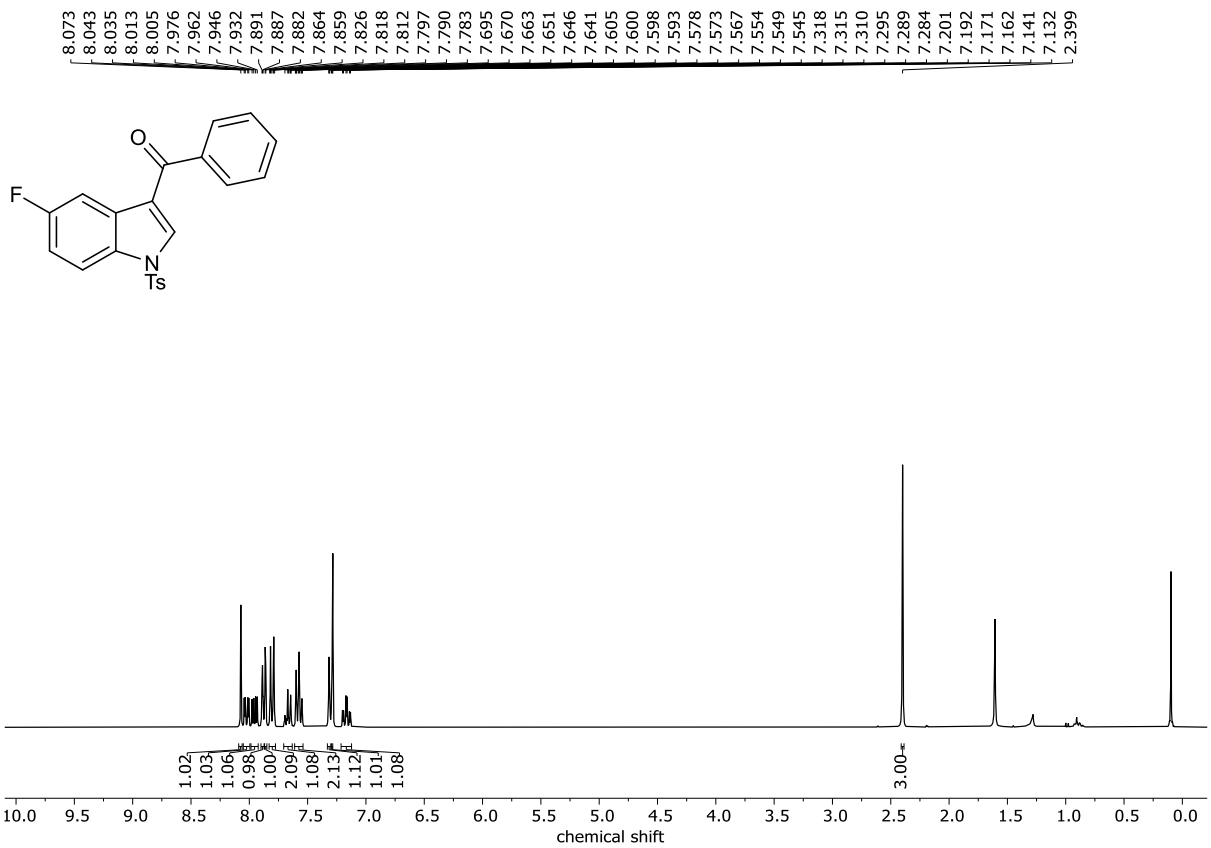
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 7c



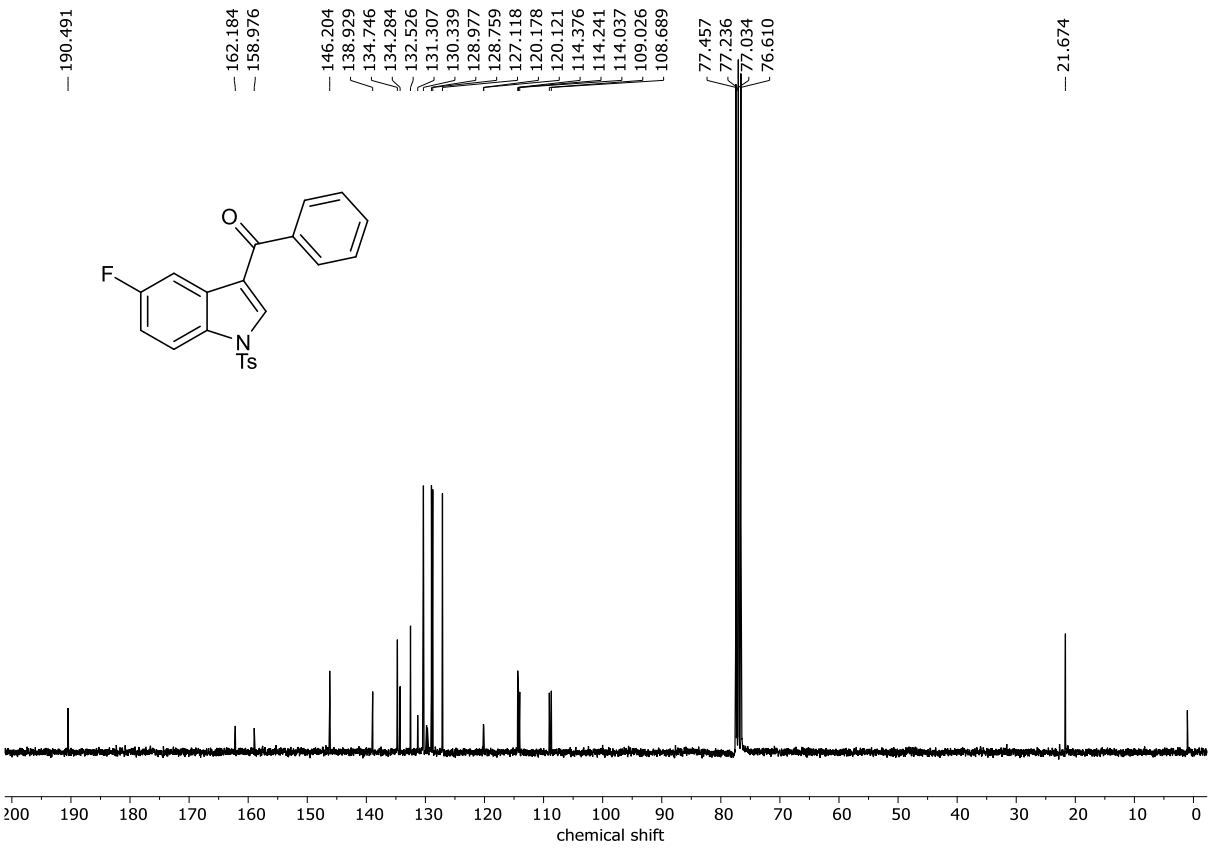
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 7c



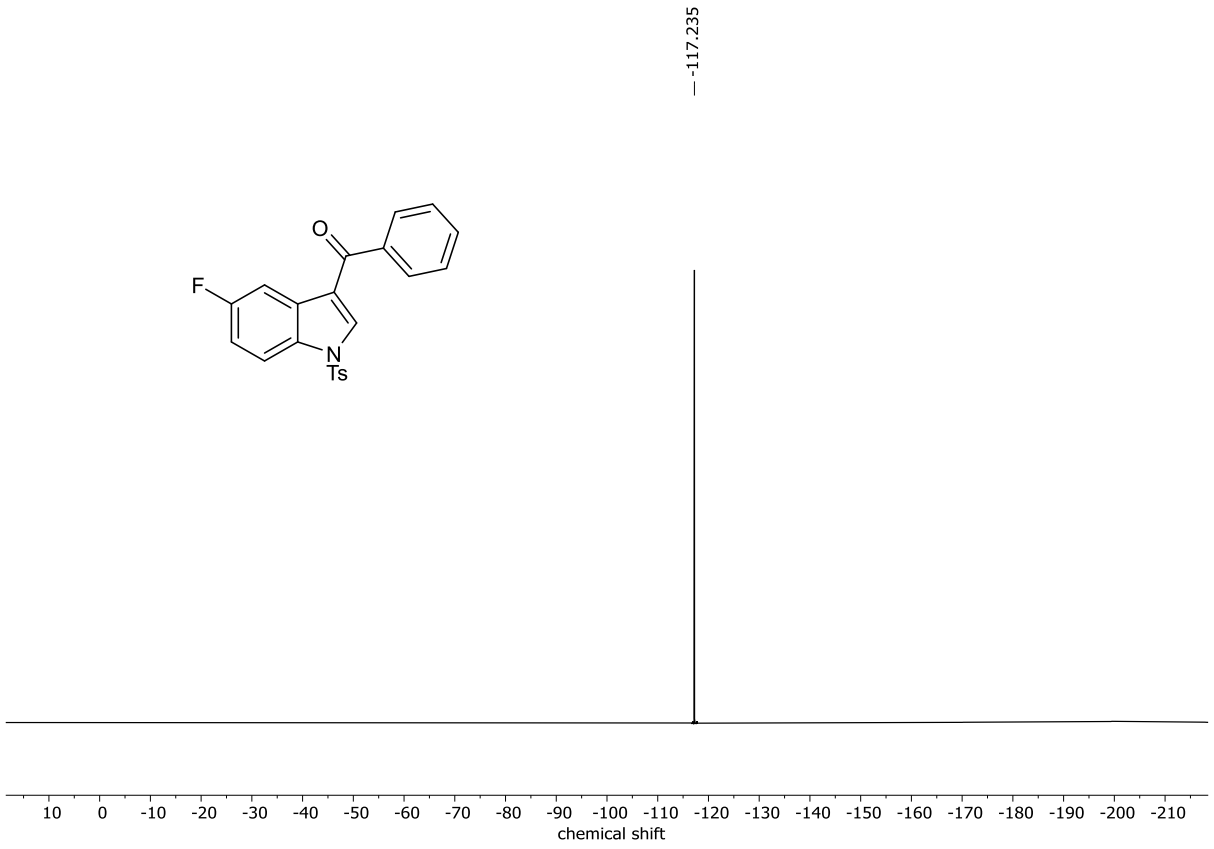
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7d



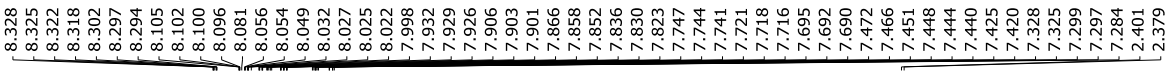
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7d

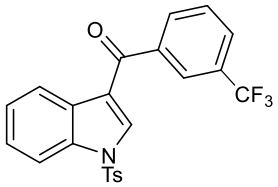


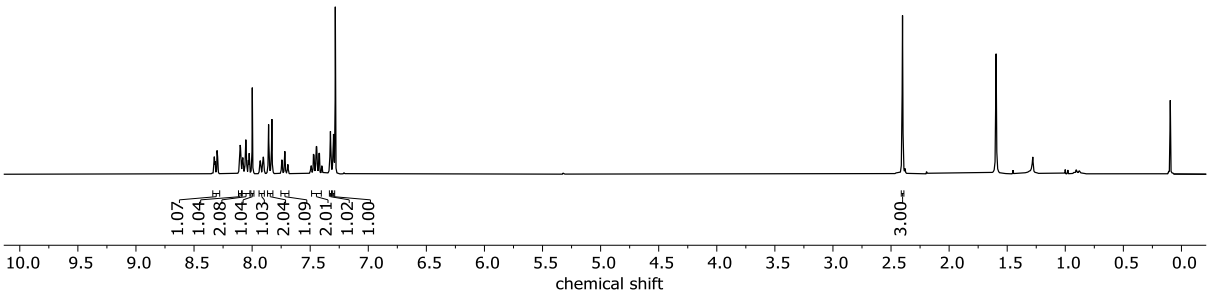
^{19}F NMR (282 MHz, $CDCl_3$) spectra of 7d



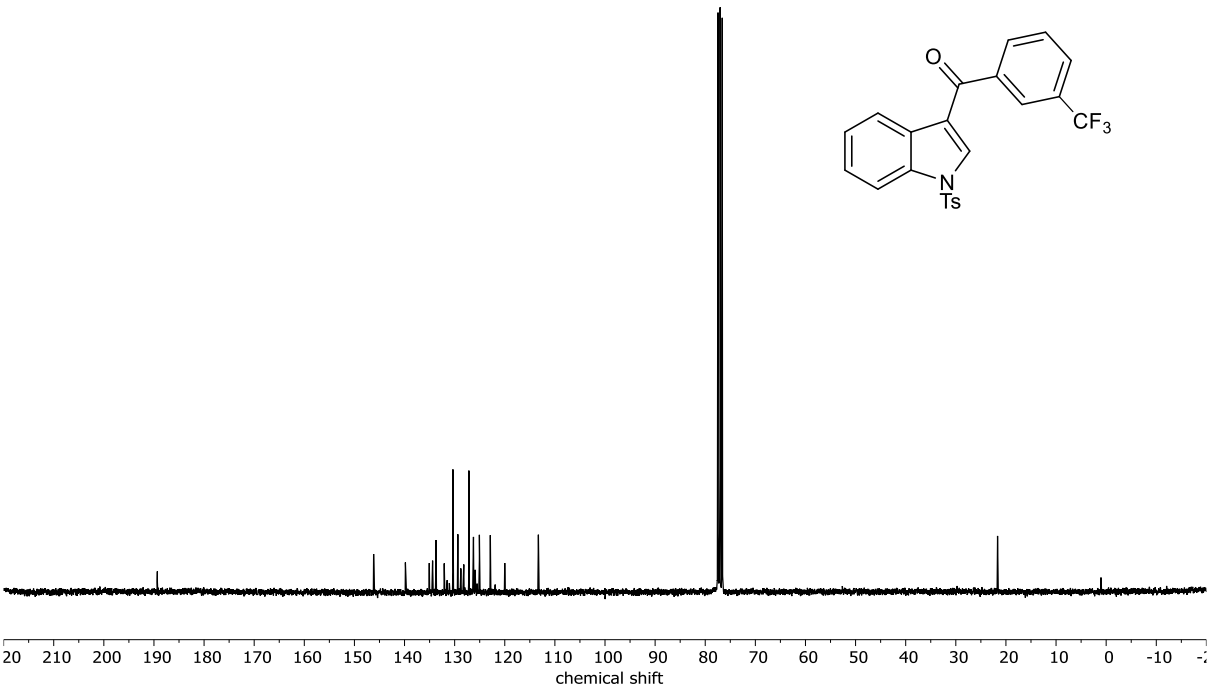
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7e



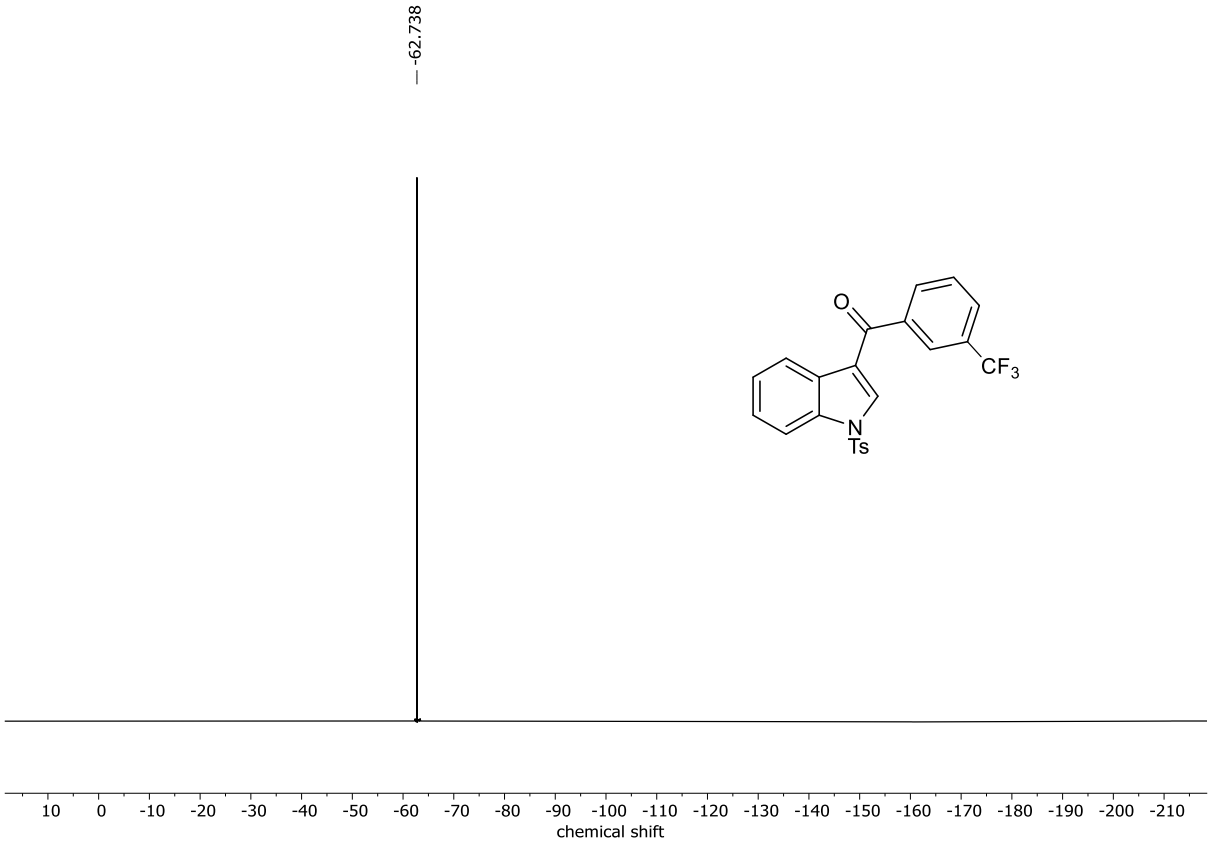




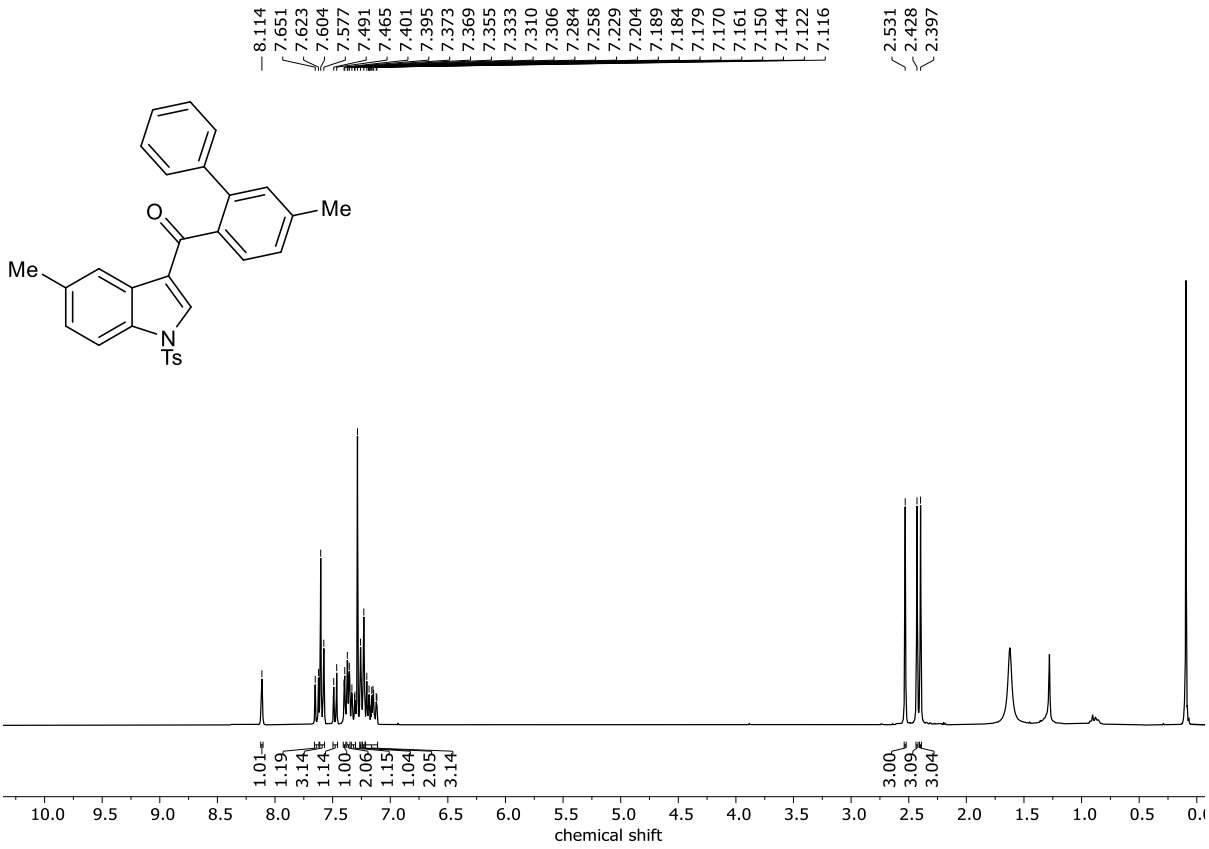
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 7e



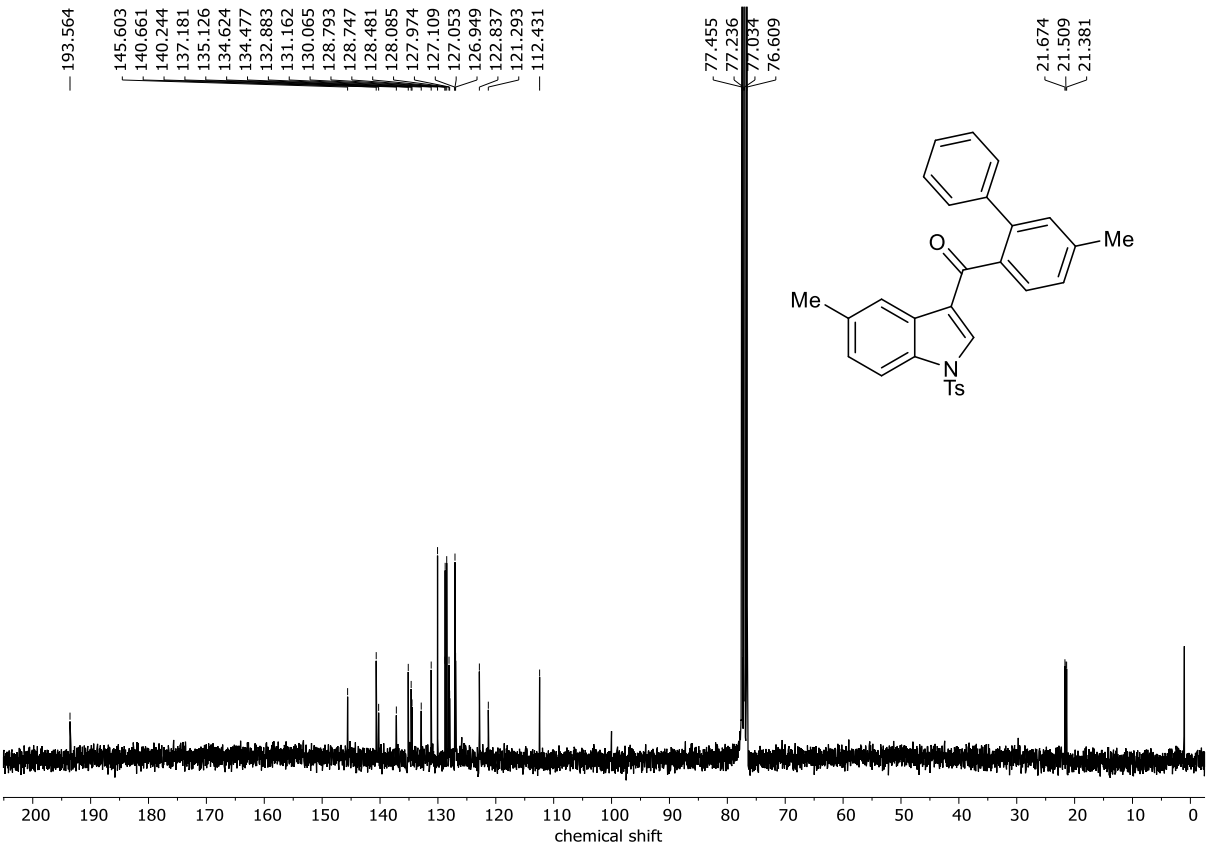
^{19}F NMR (282 MHz, $CDCl_3$) spectra of 7e



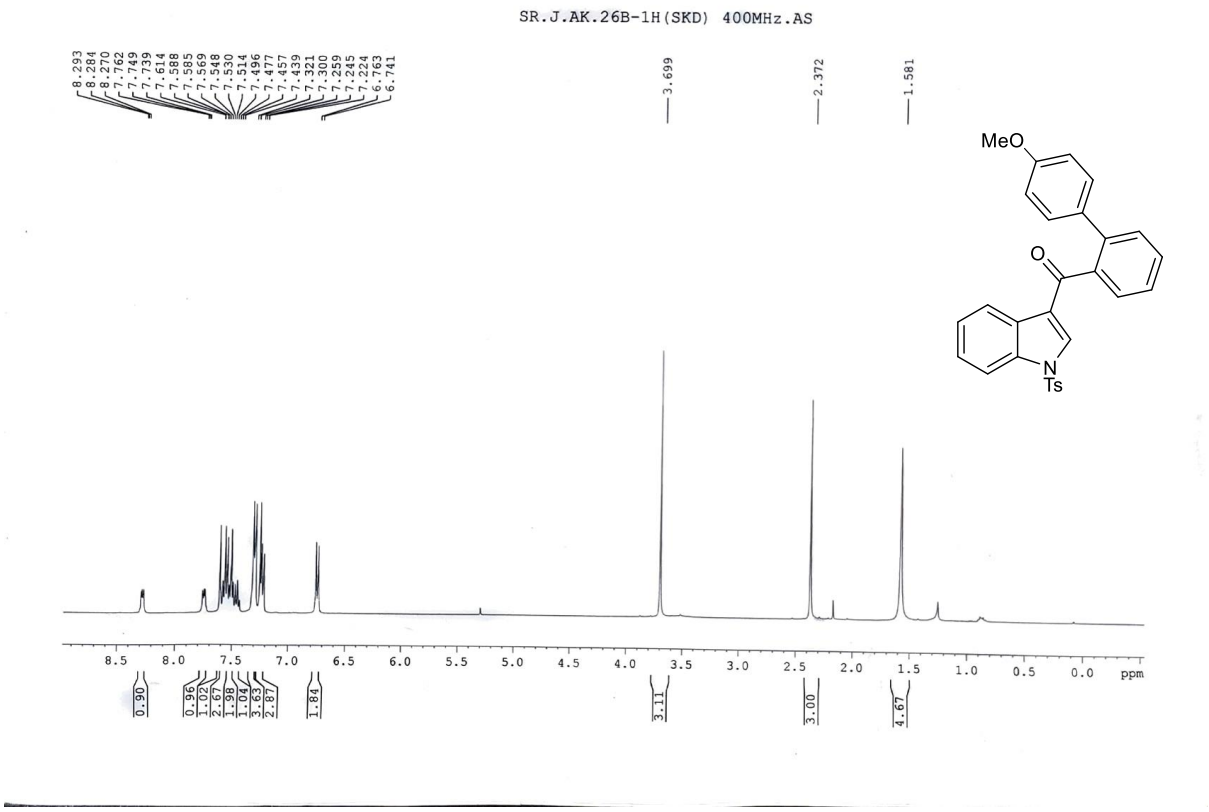
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7f



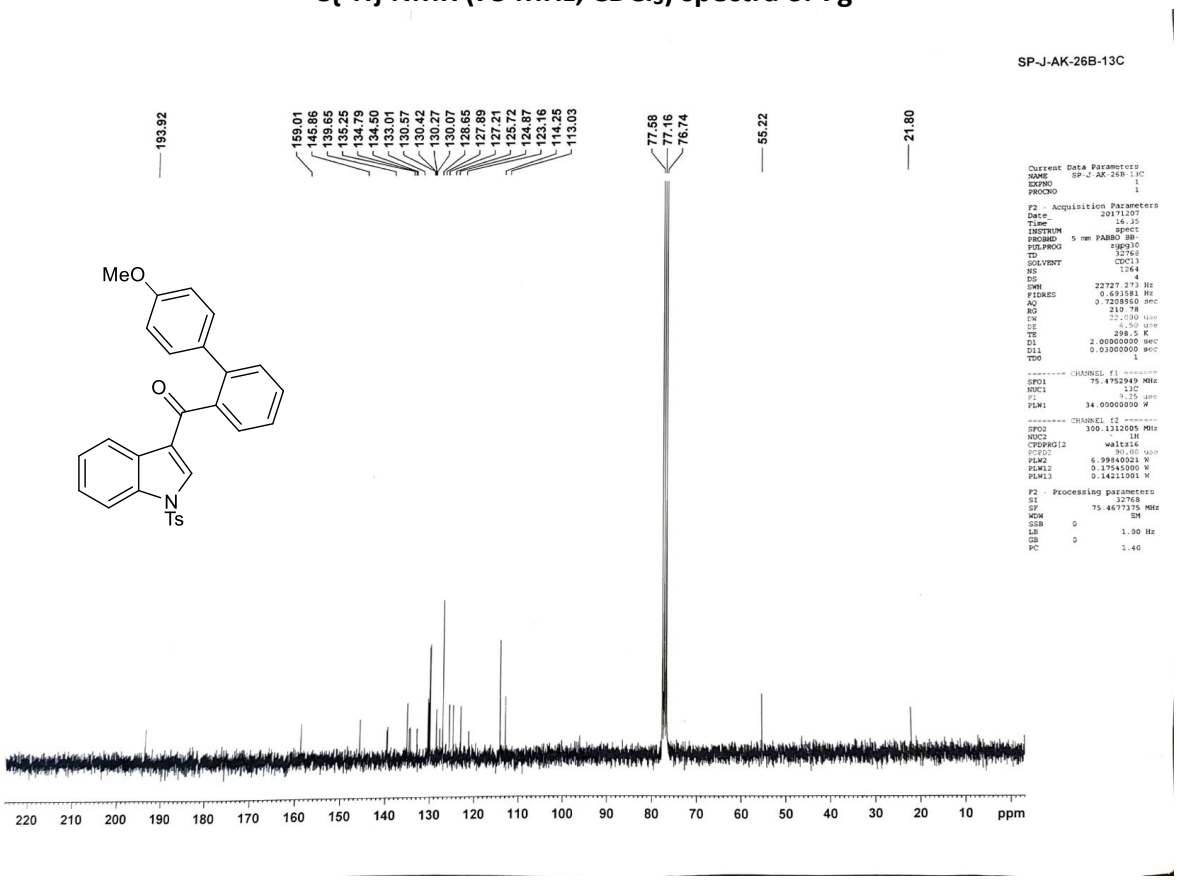
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7f



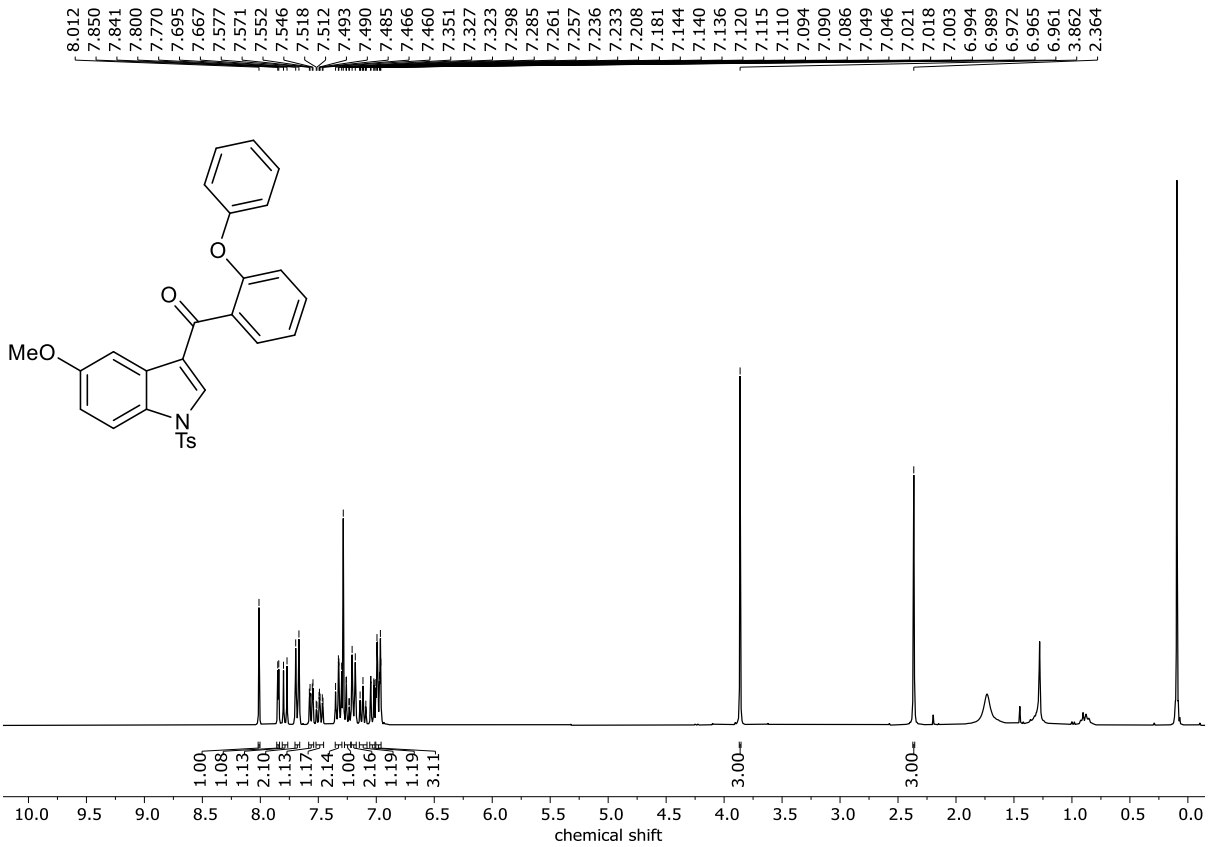
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 7g



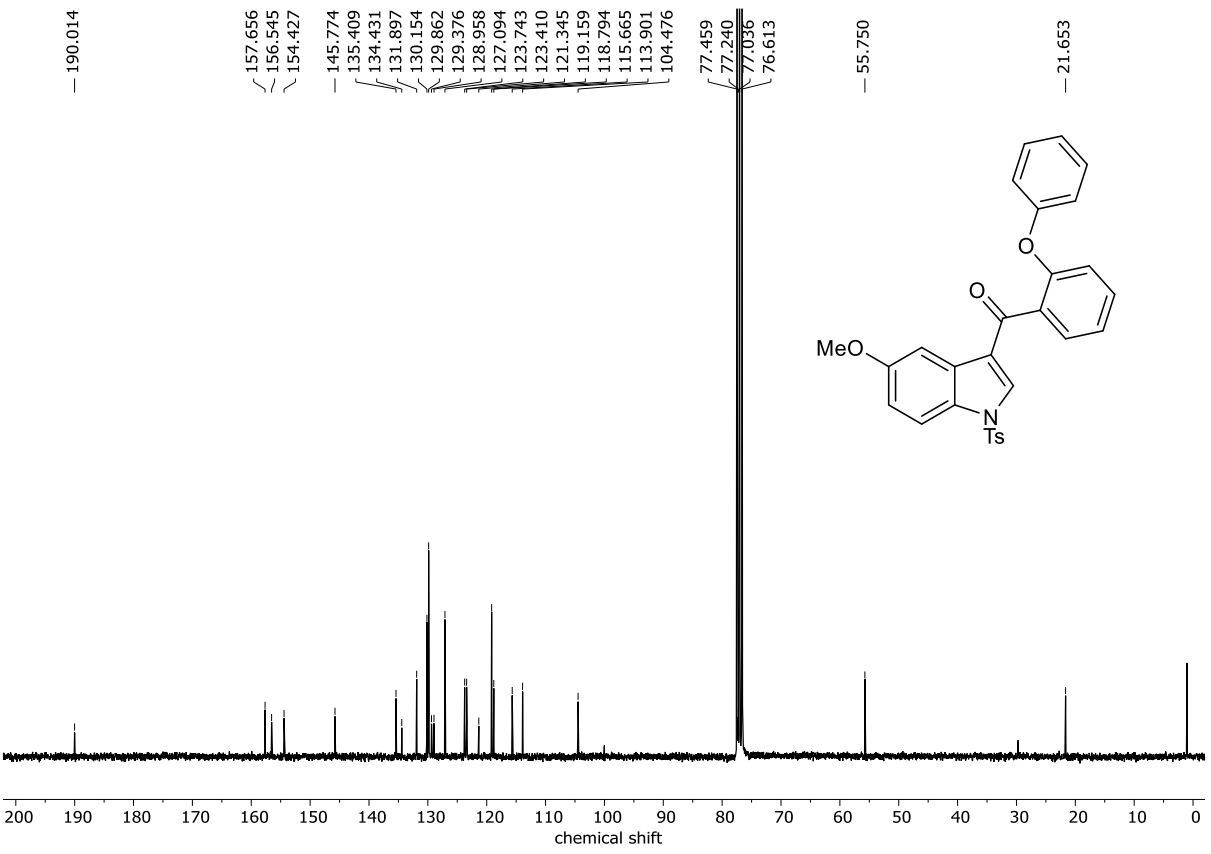
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7g



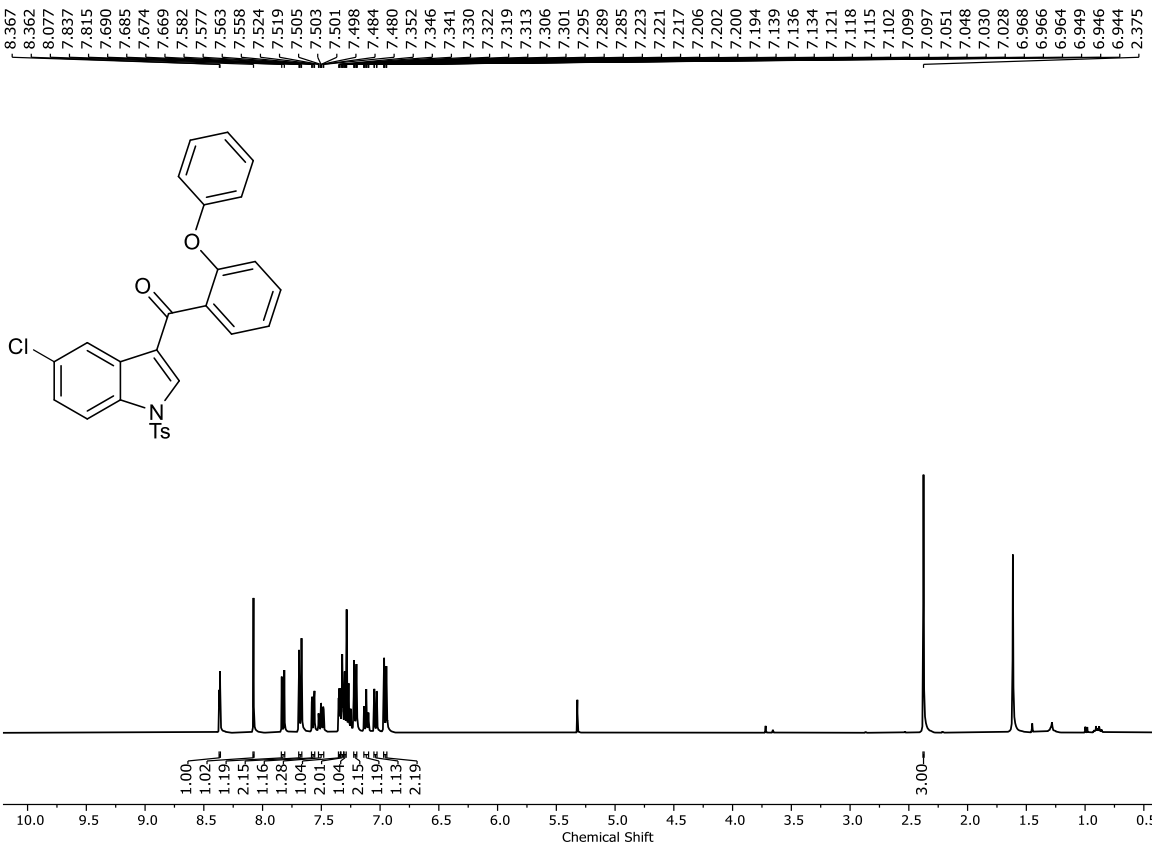
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7h



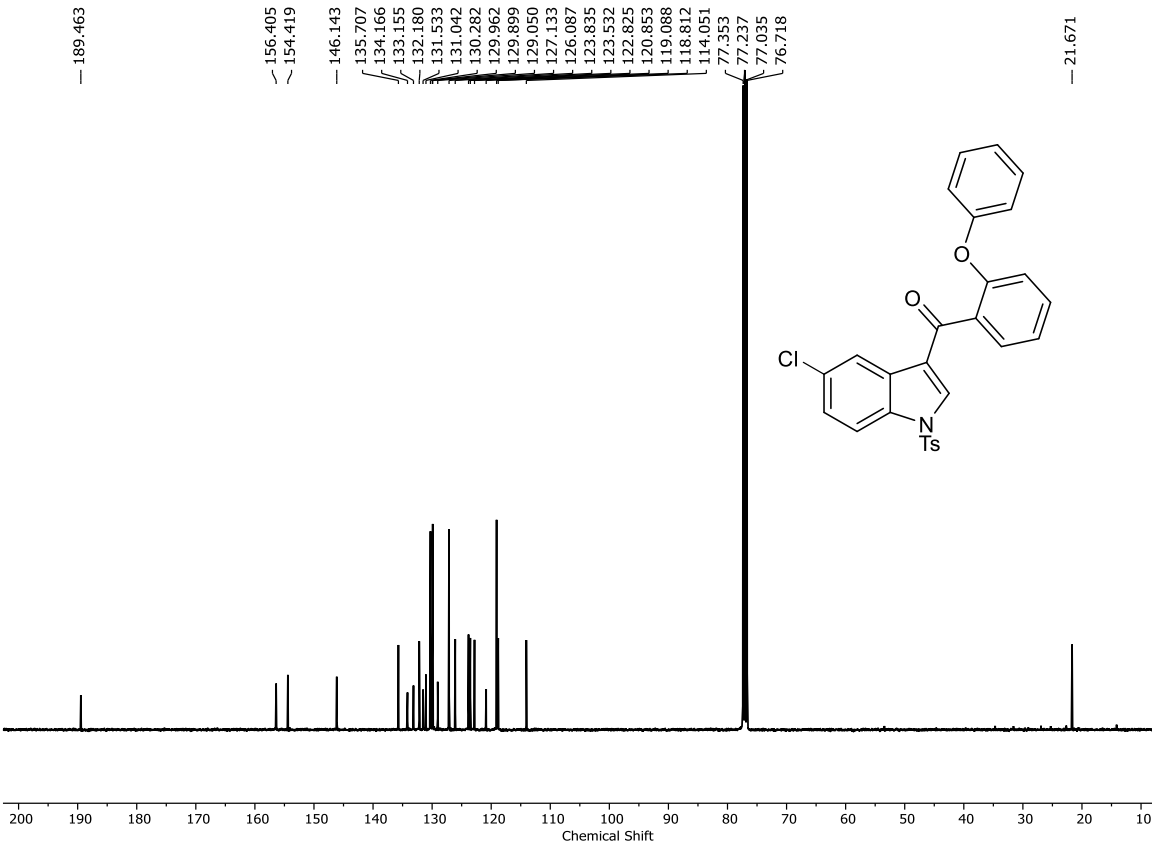
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7h



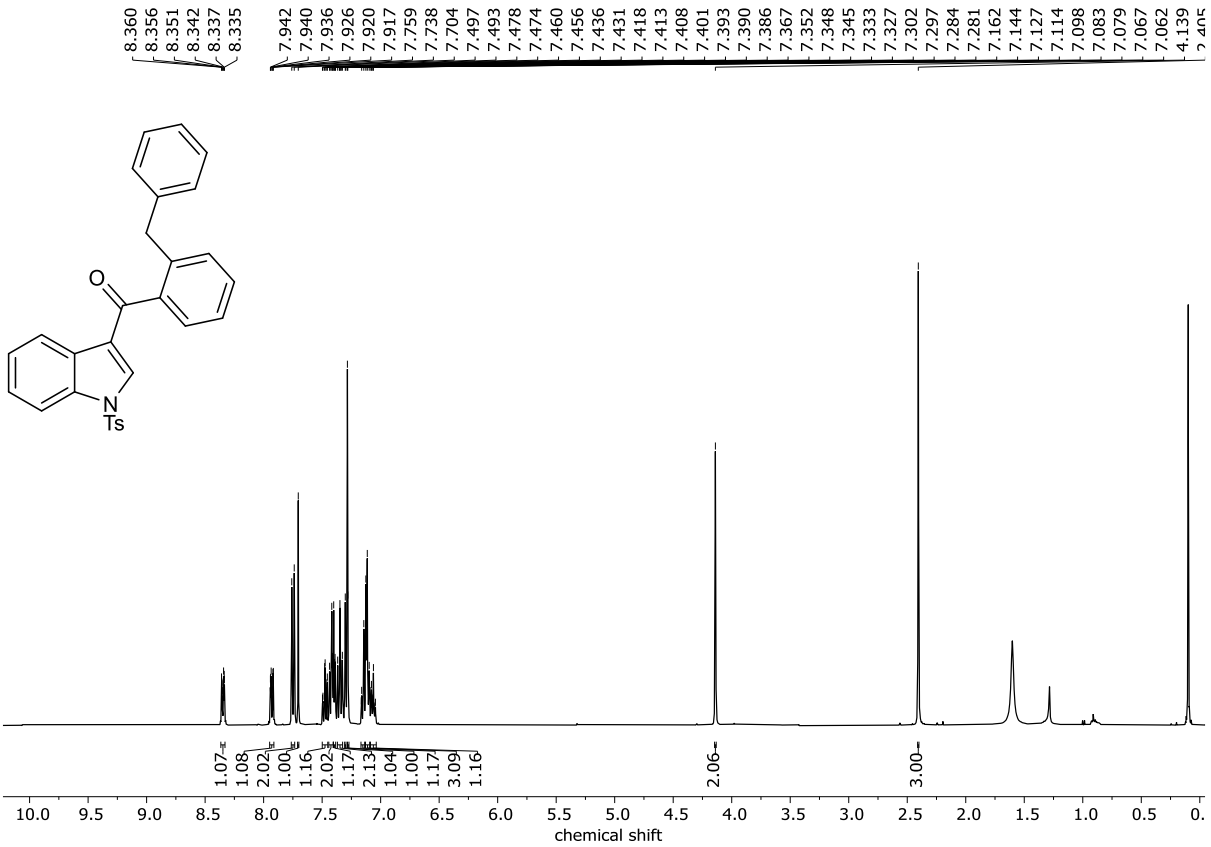
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 7i



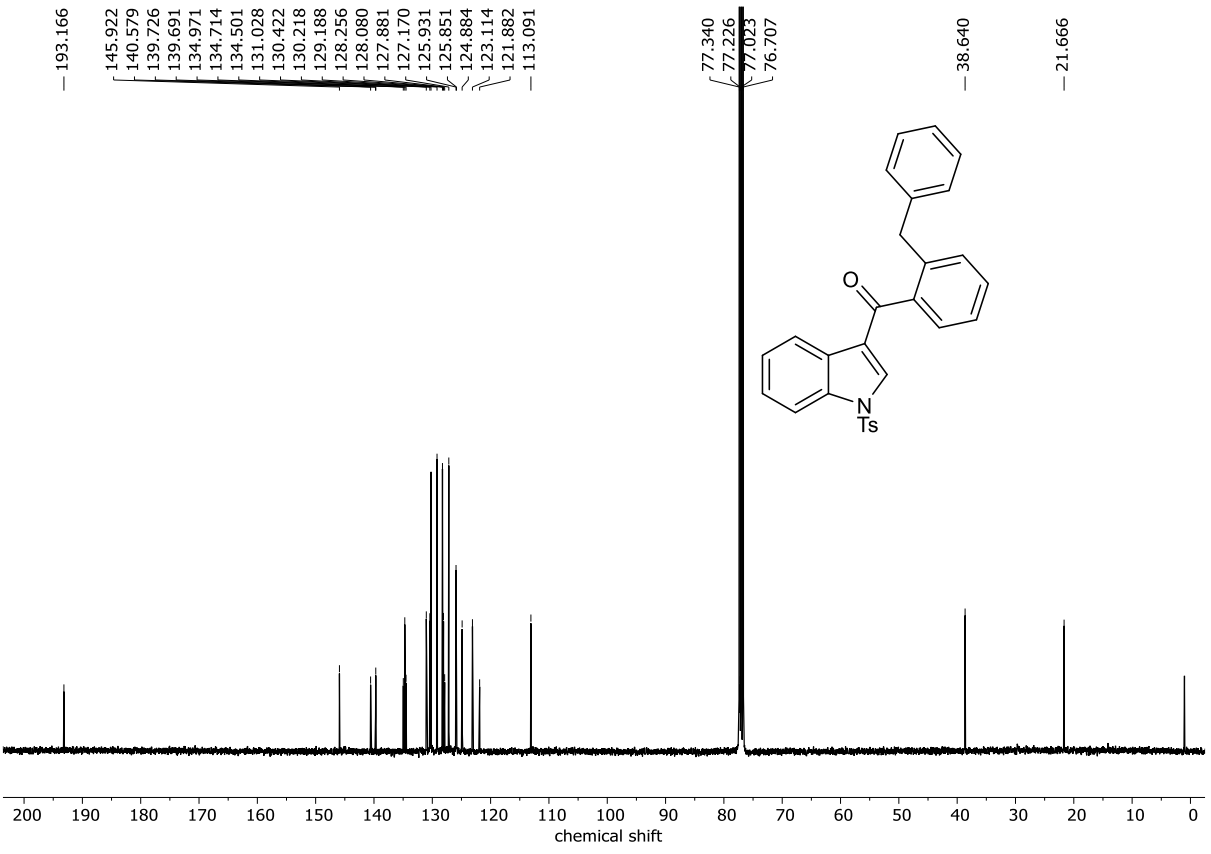
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 7i



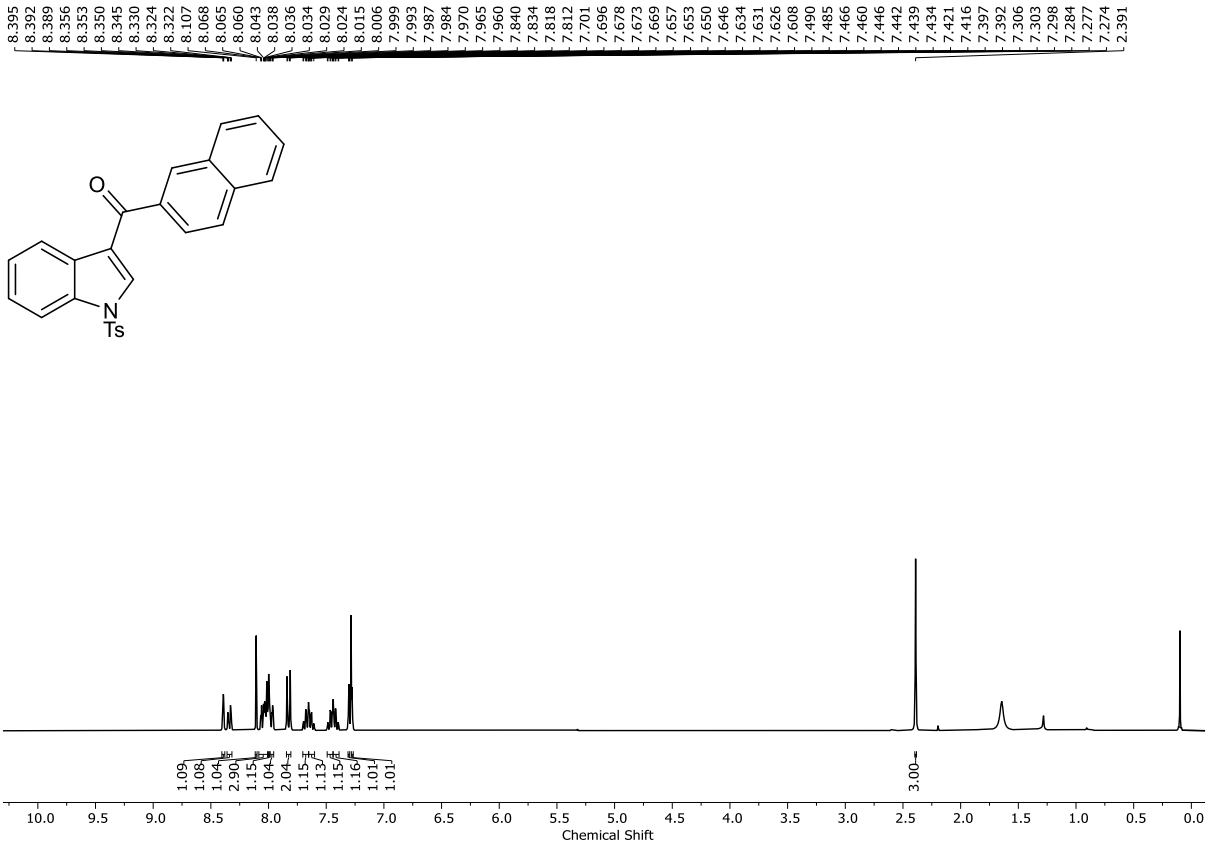
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 7j



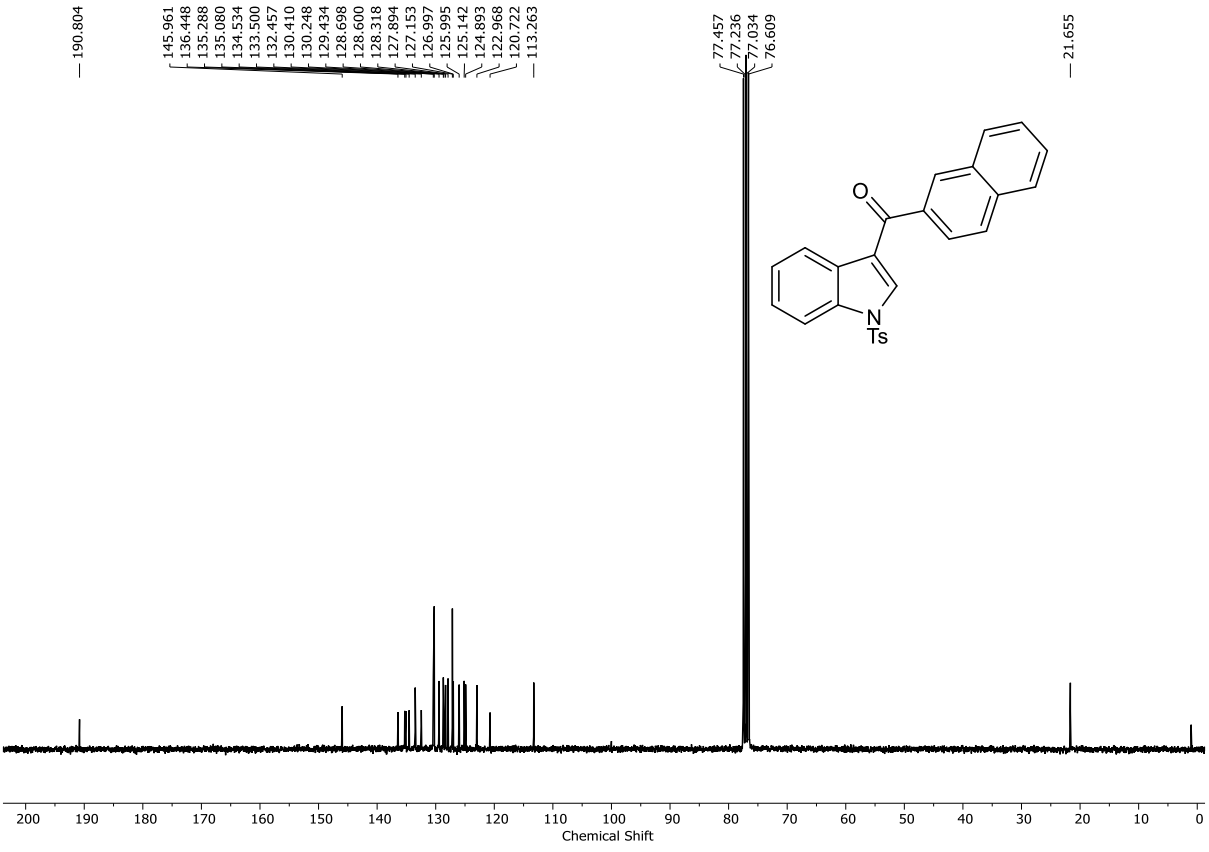
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 7j



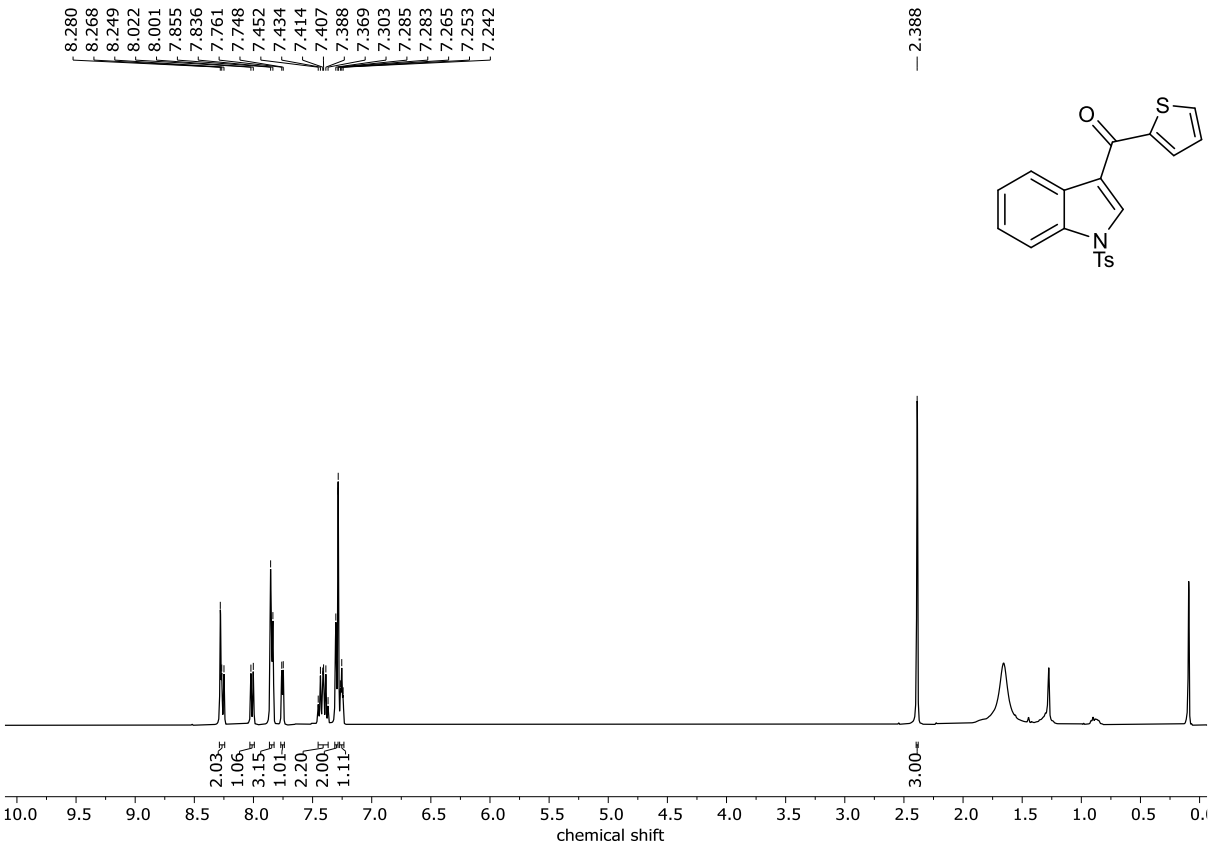
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7k



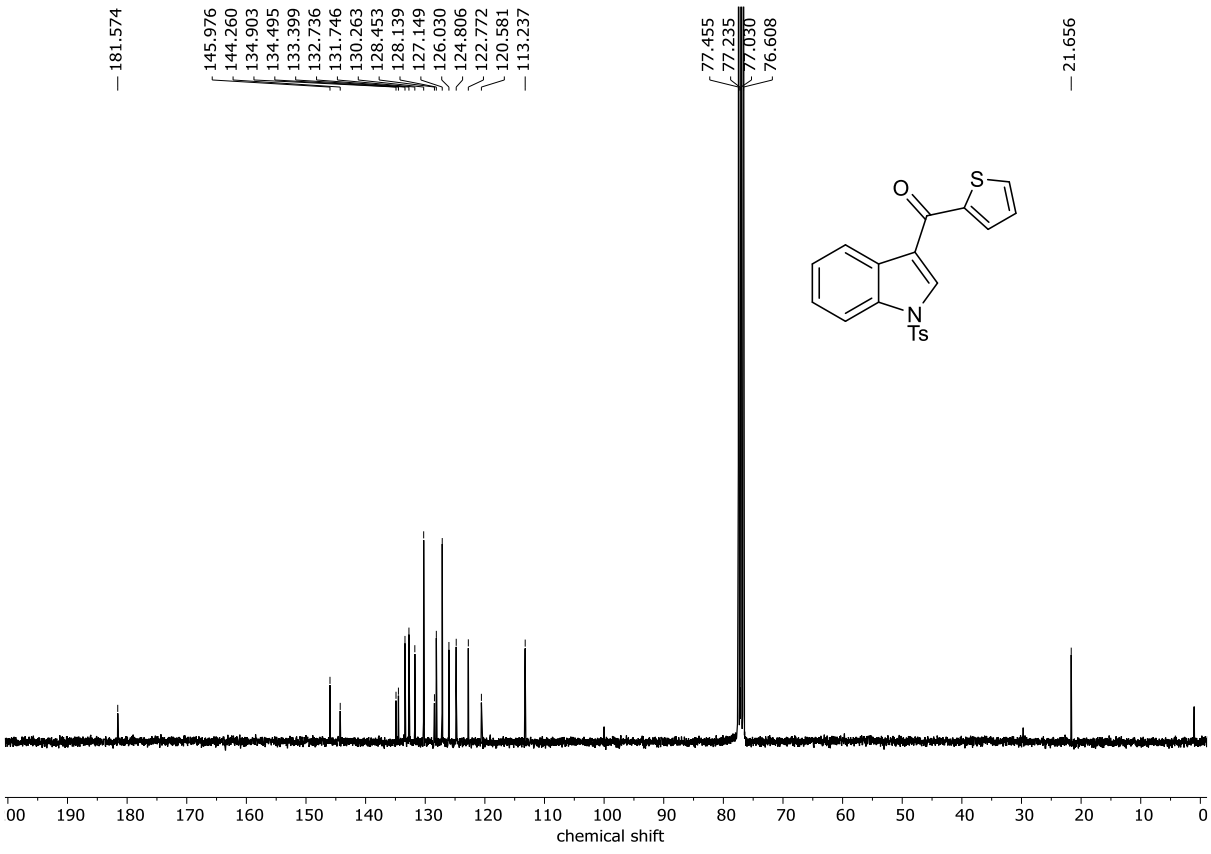
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 7k



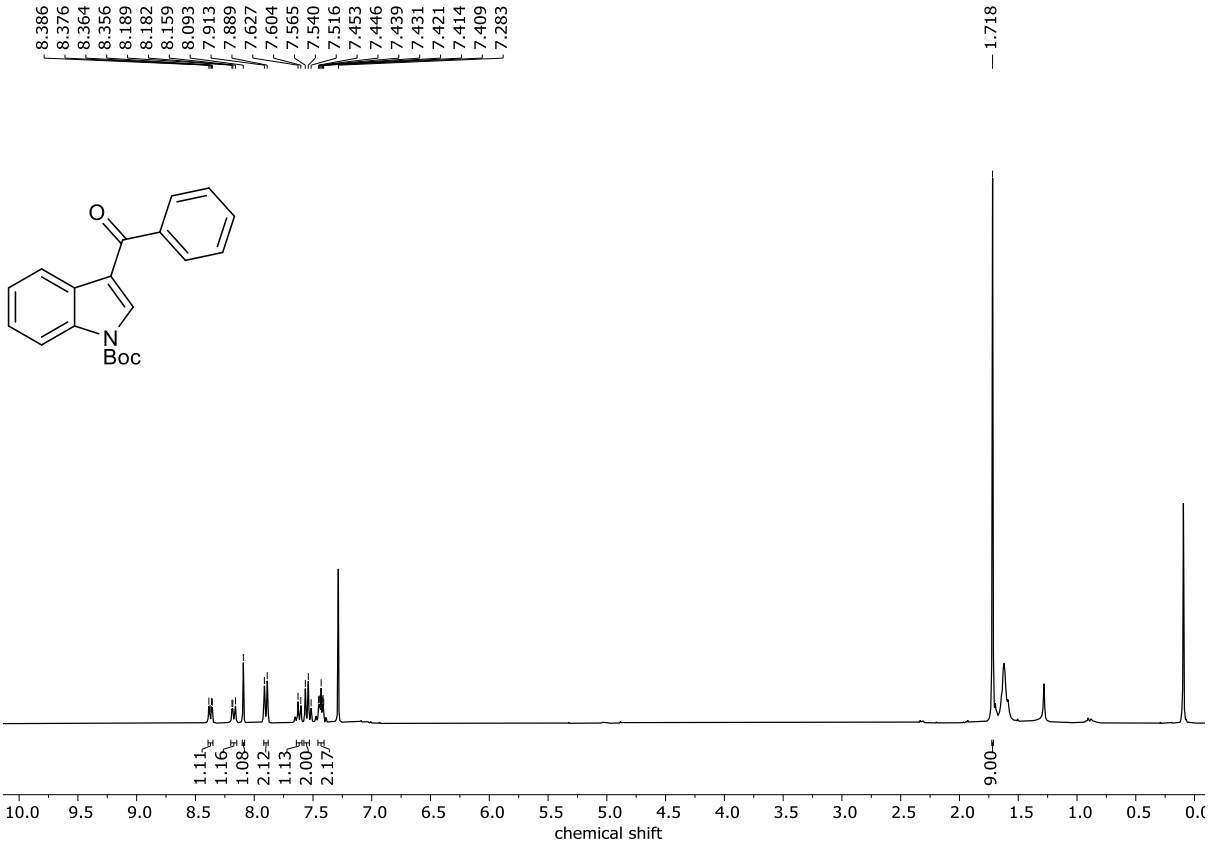
^{1}H NMR (400 MHz, $CDCl_3$) spectra of 7l



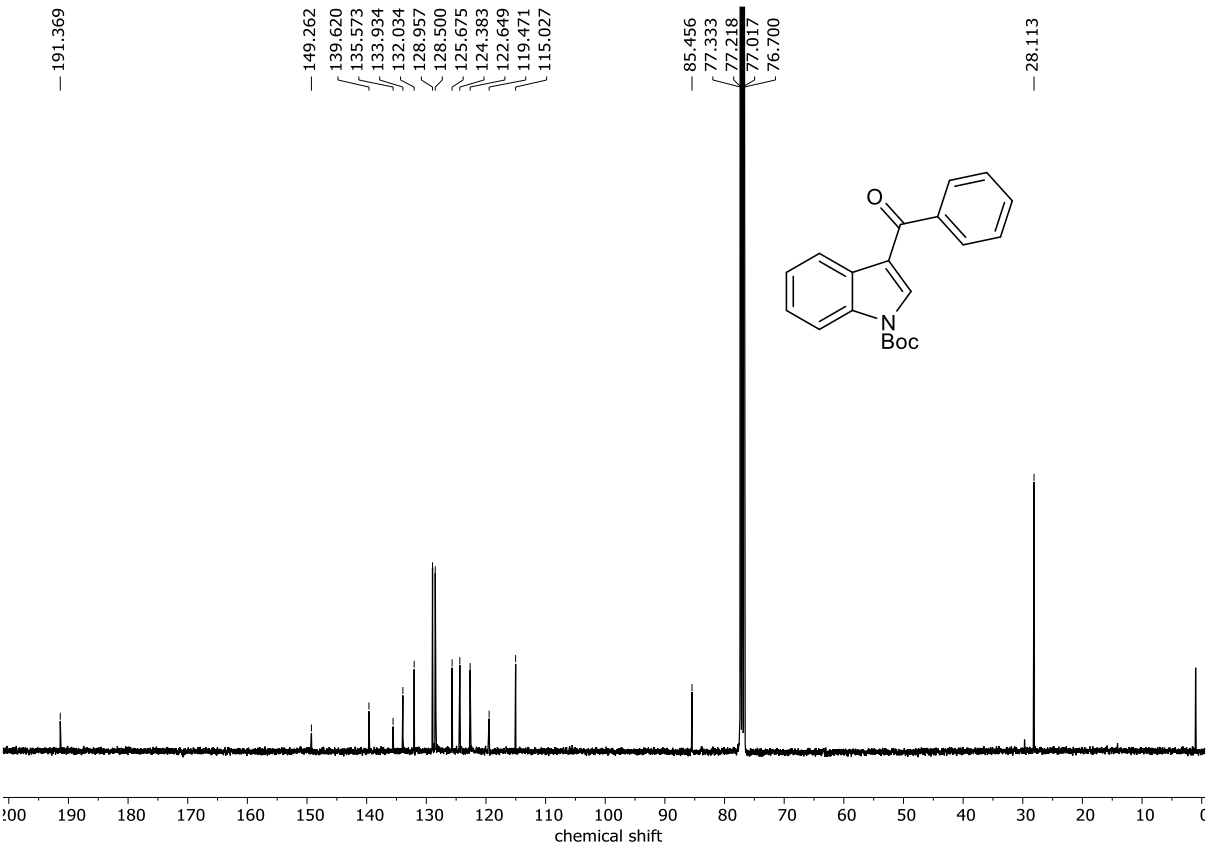
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of 7l



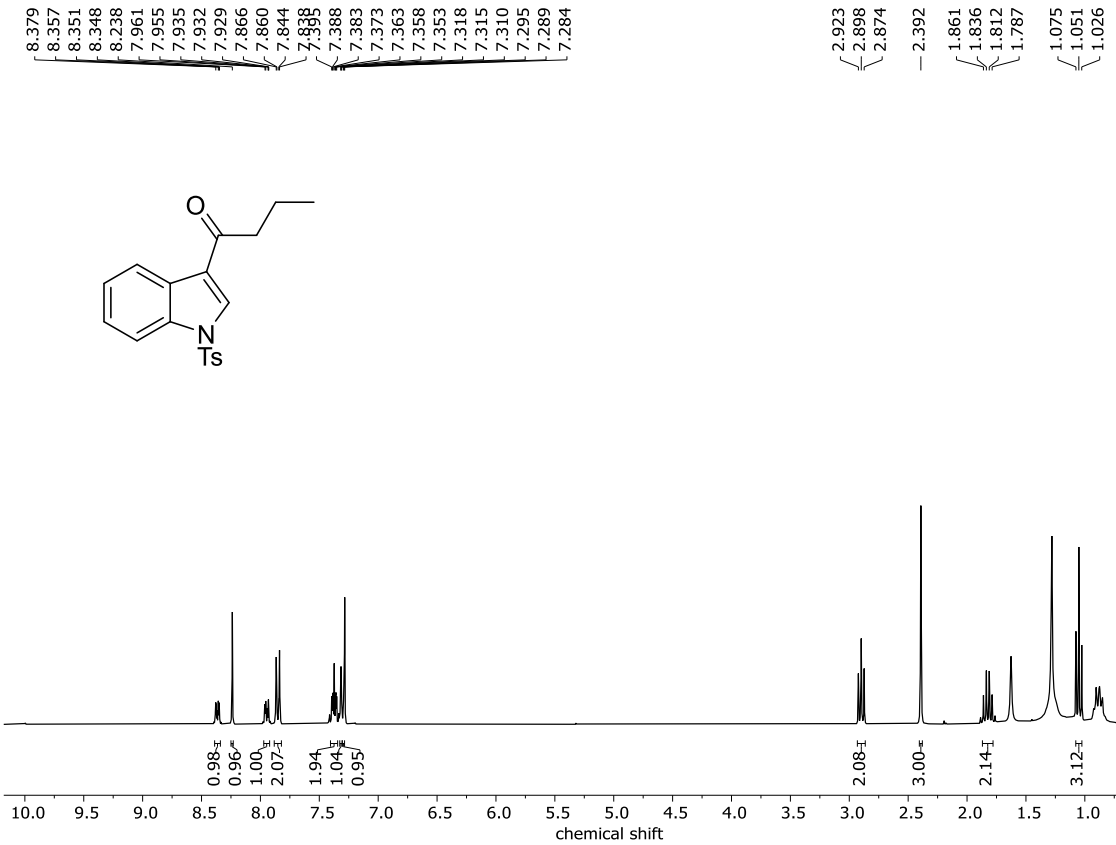
^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7m



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 7m



^{1}H NMR (300 MHz, $CDCl_3$) spectra of 7n



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of 7n

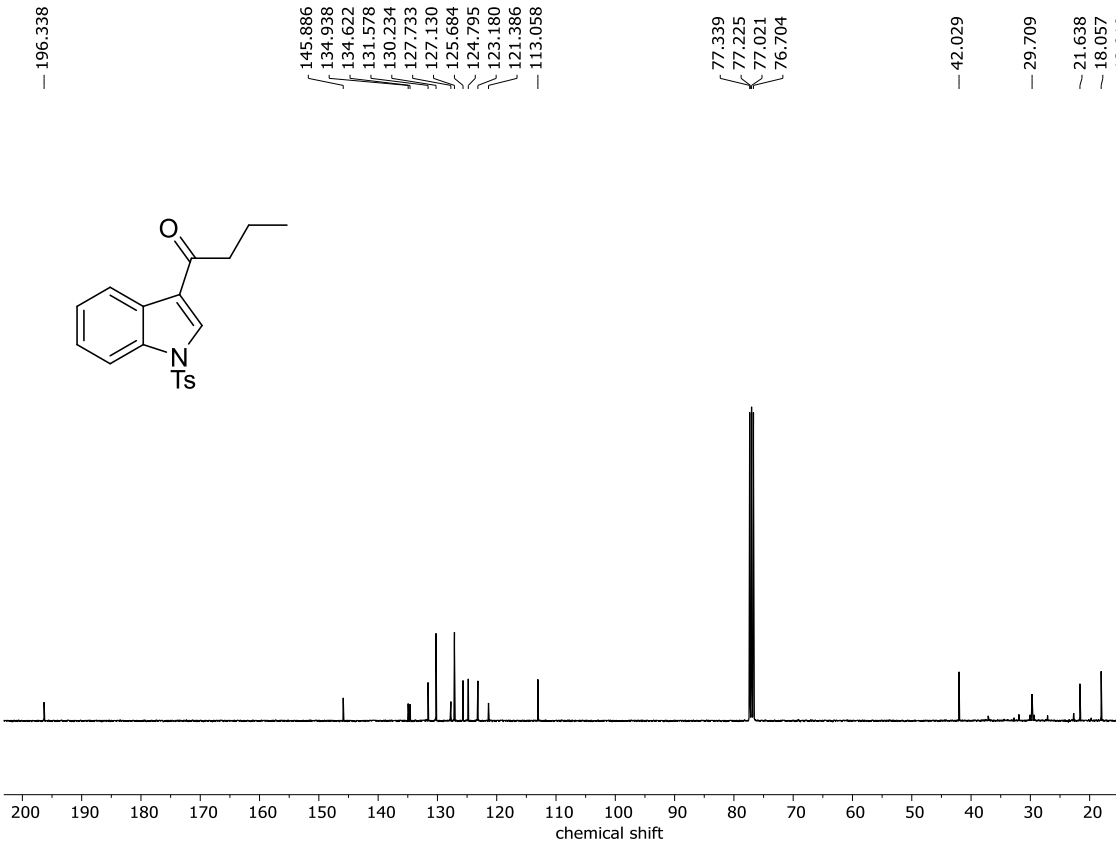
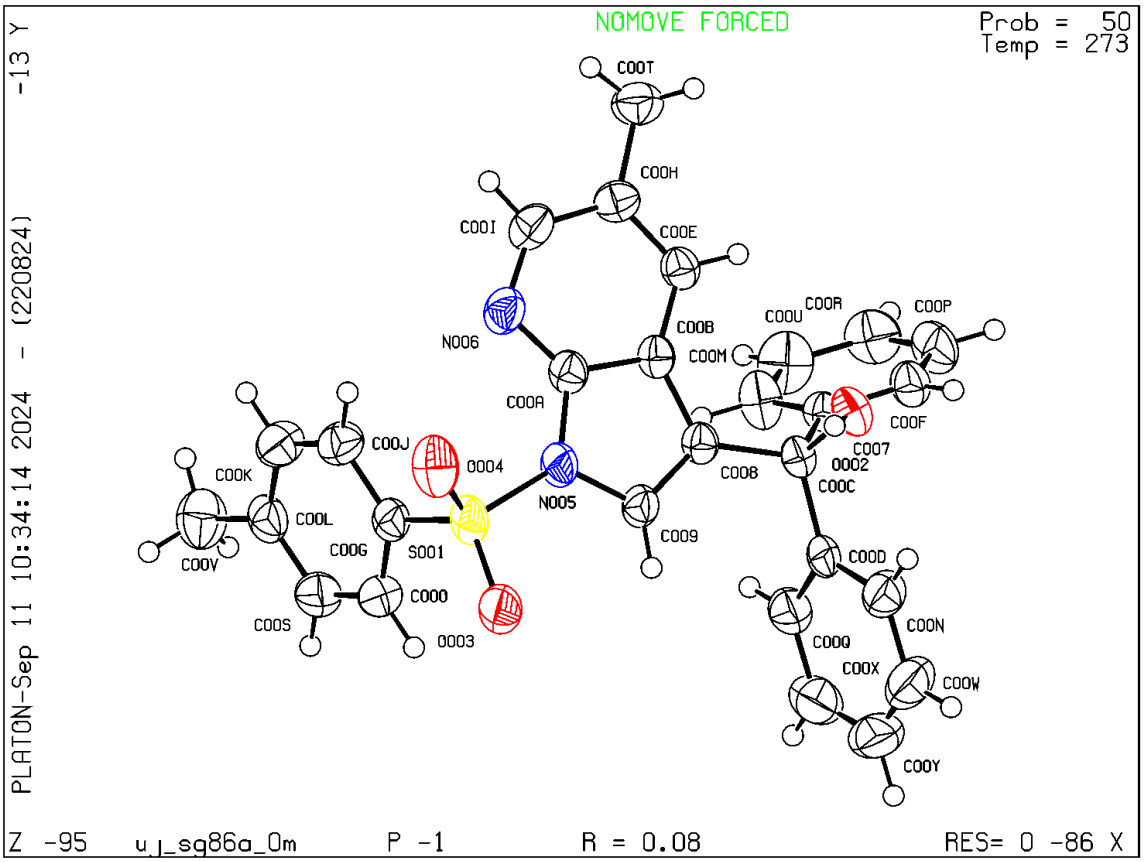


Table – S1. Crystallographic data of 5m (CCDC No. 2379103):

Formula	$C_{28}H_{24}N_2O_3S$
M_r	468.55
Crystal system	Triclinic
Space group	P -1
a / Å	9.5972(5)
b / Å	11.4600(5)
c / Å	12.1476(6)
α /°	64.713(1)
β /°	76.619(2)
γ /°	82.311(2)
V /Å^3	1174.30(10)
Z	2
D_{calcd} /mg m^{-3}	1.325
μ /mm^{-1}	0.171
θ/°	27.550
T /K	273



References:

1. (a) Kundal, S.; Jalal, S.; Paul, K.; Jana, U. *Eur. J. Org. Chem*., **2015**, 5513. (b) Chanda, R.; Chakraborty, B.; Rana, G.; Jana, U. *Eur. J. Org. Chem.*, **2020**, 61. (c) Jalal, S.; Paul, K.; Jana, U. *Org. Lett.*, **2016**, 18, 6512–6515. (d) Paul, K.; Jalal, S.; Kundal, S.; Jana, U. *J. Org. Chem.*, **2016**, 81,1164.