Supporting Information

Electrochemical Intramolecular N(sp^2)–H/N(sp^3)–H Coupling for the Synthesis of 1*H*-Indazoles

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Table of Contents

1. General Information

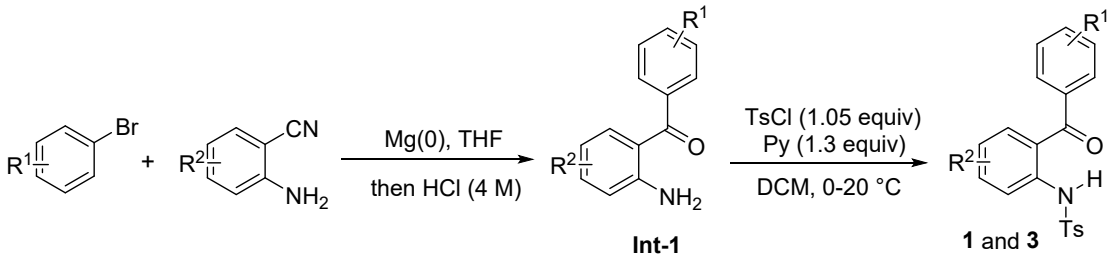
NMR spectra were recorded on Bruker-600 (600 MHz for ^{1}H; 151 MHz for ^{13}C). ^{1}H NMR spectra were referenced relative to internal $Si(Me)_4$ (TMS) at δ 0.00 ppm or $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were recorded at ambient temperature on Bruker-600 (151 MHz) spectrometers and are referenced relative to $CDCl_3$ at δ 77.16 ppm. Data for ^{1}H, ^{13}C NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, quint = quintet, br = broad), integration, and coupling constant (Hz). High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) and Aglient Technologies 7250 GCQTOF using EI-TOF. *n*-Bu_4NBF_4, NH_3 (7 M in MeOH), NH_4I, KOH and MeOH were purchased from Energy Chemical Company in China.

2. General procedure for the synthesis of substrates 1 and 3

Substrates **1a**[1], **1o**, **1p**[2], **1s**[3], **1t**[3], **1u**[3],**1v**, **1w**[4], **1x**, **3b** were synthesized through method A.

Substrates **1b**, **1c**[5], **1d**, **1e**[6], **1f**, **1g**, **1h**[7], **1i**[3], **1j**[4], **1k**[6], **1l**, **1m**, **1n**[8], **1q**, **1r**, **3a**[5], **3c**[5], **3d, 3e**[5], **3f**[9] were synthesized through method B.

Method A[10,11]**:**



Scheme S1 Preparation of the substrate **1** and **3** (Method A)

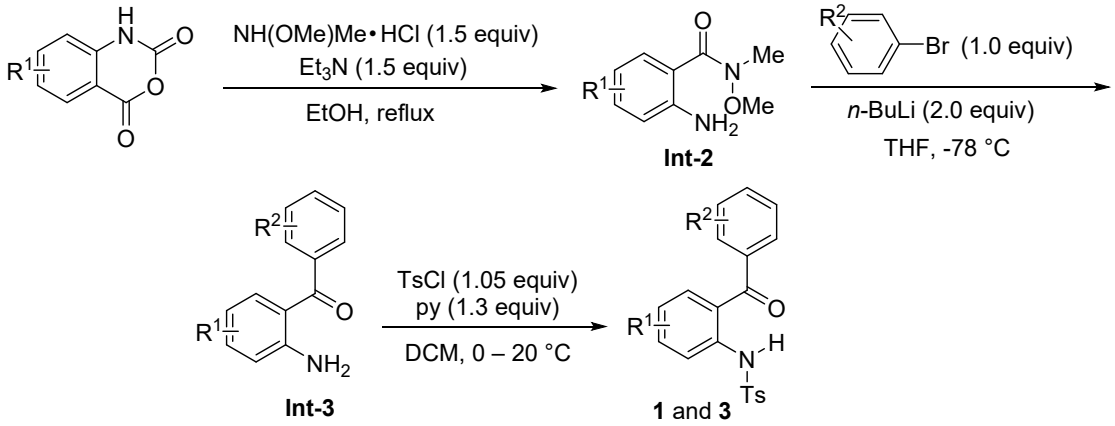
Preparation of Int-1

Magnesium turnings (1.1 equiv.) and dry THF (1M) were added to a flame-dried round-bottom flask under inert atmosphere. After the dropwise addition of aryl bromide (1.0 equiv.) at 0 °C, the reaction mixture was maintained at reflux for 2 hours. Then 2-aminobenzonitrile (0.2 to 0.25 equiv.) was added to this solution at 0 °C. The reaction was warmed to 85 °C and lasts about 12 hours. After the raw materials are consumed (monitored by TLC), the reaction mixture was quenched with 4M hydrochloric acid solution in EtOH at 0 °C and then heated overnight under reflux. The contents were concentrated in vacuum and quenched with saturated $NaHCO_3$ (aq) and extracted with EtOAc (x 3). The organic layers were combined, washed with distilled water (x 3) and brine, dried in $MgSO_4$ and concentrated. Then pass the crude mixture through the silica gel plug and use petroleum ether: EtOAc as an eluent. The material was concentrated in vacuo and subjected to the next step without further purification.

Preparation of substrate 1 and 3

TsCl (1.05 equiv) was added to a solution of **Int-1** (1 equiv), pyridine (1.3 equiv.) in CH_2Cl_2 (0.5 mol/L) at 0 °C. The mixture reacted at room temperature for 12 hours. After concentration, water was added. Then, the mixture was extracted with EtOAc. and washed with 1M HCl solution, H_2O and saturated aqueous NaCl solution in sequence. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Keto-sulfonamides were obtained by chromatographic purification of the crude product.

Method B[11,12]**:**



Scheme S2 Preparation of the substrate **1** and **3** (Method B)

Preparation of substrates Int-2

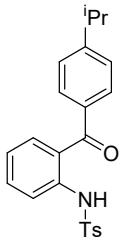
Triethylamine (1.5 equiv.) was added to a solution of *N*, *O*-dimethylhydroxylamine hydrochloride (1.5 equiv.) in 90% aqueous ethanol, and the mixture was stirred at room temperature for 10 minutes. Then, isatoic anhydride (1.0 equiv.) was added and the solution was heated to reflux. 1.5 hours later, the reaction mixture was poured onto an equal volume of ice and saturated $NaHCO_3$ solution. After rotary evaporation to remove the ethanol, extracting with ethyl acetate for three times, washing with water and brine, the organic phase was then dried over anhydrous Na_2SO_4 and activated charcoal and concentrated. The residue was purified by flash column chromatography and distilled to give **Int-2** as a pale yellow oil.

Preparation of substrates Int-3

Under nitrogen atmosphere, *n*-BuLi in hexanes (2.0 equiv.) was added slowly to a mixture of Int-2 (1.0 equiv.), brominated aromatics (1.0 equiv.), and anhydrous tetrahydrofuran (THF) with vigorous stirring at -78 °C. To the reaction solution was added HCl in H_2O (1 M) after 30 min. The mixture was extracted with ethyl acetate (3 × 150 mL) after concentration, washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The compound **Int-3** was separated by flash chromatography on silica gel.

Preparation of substrate 1 and 3

TsCl (1.05 equiv) was added to a solution of **Int-3** (1 equiv), pyridine (1.3 equiv.) in CH_2Cl_2 (0.5 mol/L) at 0 °C. The mixture reacts at room temperature for 12 hours. Then the resulting reaction mixture was concentrated. After adding water and extracting with EtOAc, washing with 1M HCl solution, H_2O and saturated aqueous NaCl solution in sequence, the organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Keto-sulfonamides were obtained by chromatographic purification of the crude product.



1b

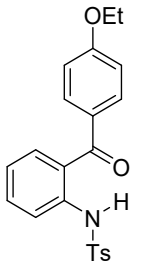
***N*-(2-(4-Isopropylbenzoyl)phenyl)-4-methylbenzenesulfonamide (1b):** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 2.20 g (56% over three steps).

m.p.: 123.5~125.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 3.01– 2.94 (m, 1H), 2.21 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.1, 154.5, 143.7, 138.9, 136.0, 135.3, 133.6, 133.0, 130.4, 129.6, 127.3, 126.9, 126.3, 123.6, 123.4, 34.4, 23.8, 21.5.

HRMS (ESI) calcd. for $C_{23}H_{23}NO_3SNa^+$ ([M+Na]$^+$): 416.1291, found: 416.1293.



1d

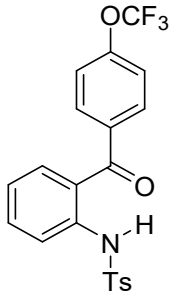
***N*-(2-(4-Ethoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (1d):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 1.86 g (47% over three steps).

m.p.: 123.9~125.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.51–7.47 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.20 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 163.1, 143.6, 138.4, 135.9, 133.1, 132.7, 132.4, 129.8, 129.6, 127.7, 127.3, 124.0, 123.7, 113.9, 64.0, 21.5, 14.8.

HRMS (ESI) calcd. for $C_{22}H_{21}NO_4SNa^+$ ([M+Na]$^+$): 418.1084, found: 418.1083.



1f

4-Methyl-*N*-(2-(4-(trifluoromethoxy)benzoyl)phenyl)benzenesulfonamide (1f): On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 1.78 g (41% over three steps)

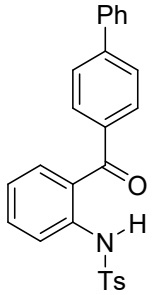
m.p.: 123.4~125.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.35 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 152.4, 143.9, 139.1, 136.0, 135.9, 134.2, 132.8, 132.0, 129.7, 127.4, 126.1, 123.8, 123.5, 120.4 (q, *J* = 259.7 Hz), 120.1, 21.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.57.

HRMS (ESI) calcd. for $C_{21}H_{16}F_3NO_4SNa^+$ ([M+Na]$^+$): 458.0644, found: 458.0650.



1g

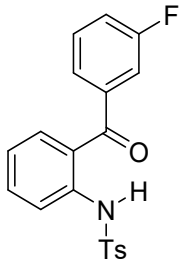
***N*-(2-([1,1'-Biphenyl]-4-carbonyl)phenyl)-4-methylbenzenesulfonamide (1g):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford a White solid, 1.84 g (43% over three steps)

m.p.: 127.7~129.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 4H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 9.0 Hz, 1H), 7.49 (q, *J* = 7.2 Hz, 4H), 7.45–7.42 (m, 2H), 7.13 (t, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.0, 145.6, 143.8, 139.7, 139.0, 136.3, 136.0, 133.8, 133.0, 130.7, 129.7, 129.2, 128.5, 127.4, 127.3, 126.8, 126.7, 123.6, 123.5, 21.5.

HRMS (ESI) calcd. for $C_{26}H_{21}NO_3SNa^+$ ([M+Na]$^+$): 450.1134, found: 450.1137.



1l

***N*-(2-(3-Fluorobenzoyl)phenyl)-4-methylbenzenesulfonamide (1l):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 1.88g (51% over three steps)

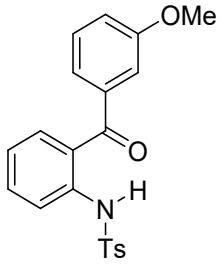
m.p.: 122.8~124.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.55–7.52 (m, 3H), 7.40–7.35 (m, 1H), 7.35 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.26 (td, *J* = 8.4, 2.4 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 1H), 2.24 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 162.1 (d, *J* = 249.2), 144.0, 139.6 (d, *J* = 6.0 Hz), 138.9, 135.7, 134.2, 132.9, 130.0(d, *J* = 7.6 Hz), 129.7, 127.3, 126.2, 125.6 (d, *J* = 3.0 Hz), 123.9, 123.6, 119.7 (d, *J* = 21.1 Hz), 116.6 (d, *J* = 22.7 Hz), 21.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.68.

HRMS (ESI) calcd. for $C_{20}H_{16}FNO_3SNa^+$ ($[M+Na]^+$): 392.0727, found: 392.0726.



1m

***N*-(2-(3-Methoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (1m):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by

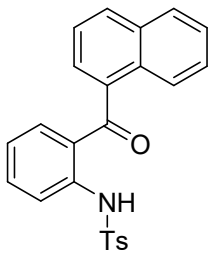
flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford a White solid, 1.98 g (52% over three steps)

m.p.: 123.1~125.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 9.0 Hz, 1H), 7.39 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.11 – 7.18 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (s, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 159.4, 143.9, 139.1, 139.0, 136.0, 133.9, 133.2, 129.7, 129.2, 127.4, 126.5, 123.6, 123.3, 122.6, 118.8, 114.7, 55.6, 21.5.

HRMS (ESI) calcd. for $C_{21}H_{19}NO_4SNa^+$ ([M+Na]$^+$): 404.0927, found: 404.0927.



1o

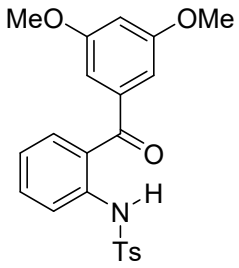
***N*-(2-(1-Naphthoyl)phenyl)-4-methylbenzenesulfonamide (1o):** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford a White solid, 1.96 g (49% over three steps)

m.p.: 123.9~126.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.53–7.49 (m, 2H), 7.44–7.40 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.4, 144.0, 140.3, 136.6, 136.4, 135.0, 134.8, 133.7, 131.6, 130.6, 129.9, 128.6, 127.5, 127.5, 126.7, 125.5, 125.3, 124.3, 123.3, 121.4, 21.7.

HRMS (ESI) calcd. for $C_{24}H_{19}NO_3SNa^+$ ([M+Na]$^+$): 424.0978, found: 424.0977.



1q

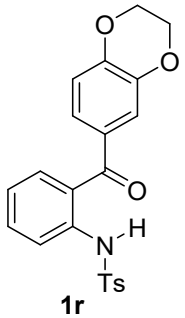
***N*-(2-(3,5-Dimethoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (1q):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 1.97 g (48% over three steps)

m.p.: 124.5~126.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 6.46 (s, 2H), 3.79 (s, 6H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 160.5, 144.0, 139.5, 139.0, 135.9, 133.9, 133.1, 129.7, 127.4, 126.6, 123.7, 123.4, 107.9, 104.7, 55.7, 21.4.

HRMS (ESI) calcd. for $C_{22}H_{21}NO_5SNa^+$ ([M+Na]$^+$): 434.1033, found: 434.1032.



1r

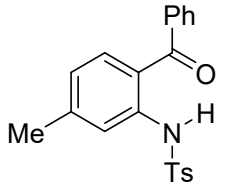
***N*-(2-(2,3-Dihydrobenzo[*b*][1,4]dioxine-6-carbonyl)phenyl)-4-methylbenzenesulfonamide (1r):** On a 10 mmol scale, Prepared following **Method B** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 1.60 g (39% over three steps)

m.p.: 121.1~123.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 3H), 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.93–6.91 (m, 2H), 6.83 (d, *J* = 9.0 Hz, 1H), 4.34 – 4.32 (m, 2H), 4.29–4.28 (m, 2H), 2.22 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.5, 148.1, 143.7, 143.0, 138.5, 135.8, 133.3, 132.5, 130.9, 129.6, 127.6, 127.3, 124.5, 124.0, 123.8, 119.8, 117.0, 64.8, 64.2, 21.5.

HRMS (ESI) calcd. for $C_{22}H_{19}NO_5SNa^+$ ([M+Na]$^+$): 432.0876, found: 432.0878.



1v

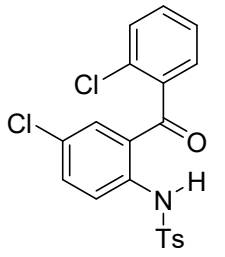
***N*-(2-Benzoyl-5-methylphenyl)-4-methylbenzenesulfonamide (1v):** On a 10 mmol scale, Prepared following **Method A** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 2.38 g (65% over two steps)

m.p.: 123.3~125.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.61 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 6.6 Hz, 1H), 7.40–7.36 (m, 4H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 145.4, 143.7, 139.5, 138.1, 136.2, 133.5, 132.5, 129.83, 129.7, 128.2, 127.4, 124.4, 123.6, 123.4, 22.1, 21.6.

HRMS (ESI) calcd. for $C_{21}H_{19}NO_3SNa^+$ ([M+Na]$^+$): 388.0978, found: 388.0975.



1x

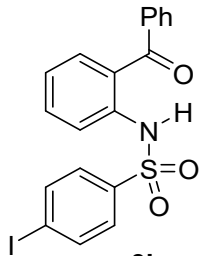
***N*-(4-Chloro-2-(2-chlorobenzoyl)phenyl)-4-methylbenzenesulfonamide (1x):** On a 10 mmol scale, Prepared following **Method A** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford a White solid, 2.90g (69% over two steps)

White solid; m.p.: 123.7~125.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.85 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 9.6 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.14 (dd, *J* = 7.8, 1.2 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197. 8, 144.4, 139.2, 137.5, 136.4, 135.4, 133.6, 132.0, 131.1, 130.4, 130.0, 128.9, 128.5, 127.5, 127.1, 124.2, 121.9, 21.7.

HRMS (ESI) calcd. for $C_{20}H_{15}Cl_2NO_3SNa^+$ ([M+Na]$^+$): 442.0042, found: 442.0043.



3b

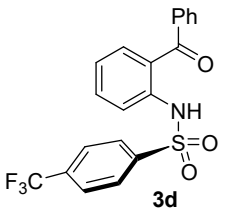
***N*-(2-Benzoylphenyl)-4-iodobenzenesulfonamide (3b):** On a 10 mmol scale, Prepared following **Method A** and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 3.10 g (67% over two steps)

m.p.: 125.8~127.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 9.0 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.39 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.14 (td, *J* = 7.2, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 138.6, 138.5, 138.3, 137.5, 134.0, 133.2, 133.1, 129.9, 128.7, 128.5, 126.9, 124.2, 123.8, 100.7.

HRMS (ESI) calcd. for $C_{19}H_{14}INO_3SNa^+$ ([M+Na]$^+$): 485.9631, found: 485.9633.



3d

***N*-(2-Benzoylphenyl)-4-(trifluoromethyl)benzenesulfonamide (3d):** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the White solid, 2.44 g (60% over two steps)

m.p.: 126.9~128.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.82 – 7.79 (m, 3H), 7.58 – 7.55 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41–7.38 (m, 3H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H).

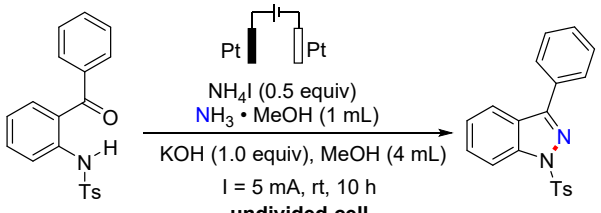
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 142.5, 138.3, 137.4, 134.6 (q, *J* = 31.7 Hz), 134.1, 133.3, 133.2, 129.8, 128.4, 127.9, 126.7, 126.2 (q, *J* = 3.0 Hz), 124.4, 124.0, 123.9 (q, *J* = 273.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.18.

HRMS (ESI) calcd. for $C_{20}H_{14}F_3NO_3SNa^+$ ([M+Na]$^+$): 428.0539, found: 428.0535.

3. Effect of solvent and base on the electrochemical cyclization

Table S1. Optimization of solvent and base



1a **2a**

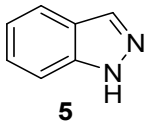
Entry	Solvent	Base	Yield (%)[b]
1	DCE	KOH	29
2	CH_3CN	KOH	21
3	THF	KOH	40
4	DMF	KOH	36

5	DMSO	KOH	65
6	MeOH	DBU	72
7	MeOH	Et_3N	22
8	MeOH	$NaHCO_3$	38
9	MeOH	K_2CO_3	45

[a] Reaction conditions: **1a** (0.3 mmol), NH_3 (7 M in MeOH, 1 mL), solvent (4.0 mL), NH_4I (0.15 mmol), base (0.3 mmol), platinum plate anode (10 mm × 10 mm × 0.3 mm), platinum plate cathode (10 mm × 10 mm × 0.3 mm), r.t. = room temperature, 10 h (Q = 6.22 F mol^{-1}). [b]Isolated yields. n.d. = not detected.

4. General procedure for the transformation 4f into 1*H*-indazole 5 [13]

A mixture of **4f** (0.2 mmol), Mg (2.0 mmol) and dry MeOH (2 mL) was allowed to stir at room temperature under an argon atmosphere. After 3 hours, the reaction mixture was quenched with water, extracted with EtOAc, washed with saturated NH_4Cl solution and brine, and dried over anhydrous $MgSO_4$. Purification by chromatography on silica gel gave the product **5**.



5

1*H*-indazole (5) [13]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 5:1) to afford the product **5** (21.1 mg, 89% yield).

White solid; m.p.: 104.5~106.5 °C.

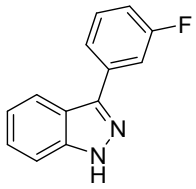
^{1}H NMR (600 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.13 (s, 1H), 7.79 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.2, 134.9, 127.0, 123.3, 121.1, 121.0, 109.9.

5. General procedure for the synthesis of Trys inhibitor 7 [13]

A mixture of **2l** (0.25 mmol), Mg (2.5 mmol) in dry MeOH (3 mL) was allowed to stir at room temperature under an argon atmosphere. After 3 hours, the reaction mixture was quenched with water, extracted with EtOAc, washed with saturated NH_4Cl solution and brine, and dried over anhydrous $MgSO_4$. Purification by chromatography on silica gel gave the product **6**.

To a solution of compound **6** (42.4 mg, 0.2 mmol), 1-bromopinacolone (33 μL, 0.24 mmol) and dry DMF (2 mL), K_2CO_3 (54 mg, 0.4 mmol) was added under an argon atmosphere. After stirring at room temperature for overnight, the reaction mixture was then diluted with ethyl acetate, washed with brine, and dried over anhydrous $MgSO_4$. Purification by chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as an eluent afforded the product **7** (54.2 mg, 87% yield).



6

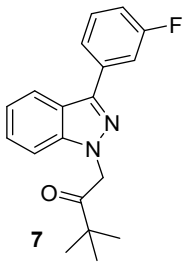
3-(3-Fluorophenyl)-1*H*-indazole (6)[14]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 5:1) to afford the product **6** (48.8 mg, 92% yield).

Colorless oil;

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.94 – 11.73 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 9.6 Hz, 1H), 7.50 (q, *J* = 7.8 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.31 – 7.28 (m, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.3 (d, *J* = 246.1 Hz), 144.6, 141.8, 135.8 (d, *J* = 9.1 Hz), 130.6 (d, *J* = 9.1 Hz), 127.2, 123.4, 121.8, 120.9, 115.2 (d, *J* = 21.1 Hz), 114.7 (d, *J* = 22.7 Hz), 110.5 (d, *J* = 6.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.43.



7

TryS inhibitor Anti-HAT activity (7): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **7** (54.2 mg, 87% yield).

White solid; m.p.: 110.4~112.4 °C.

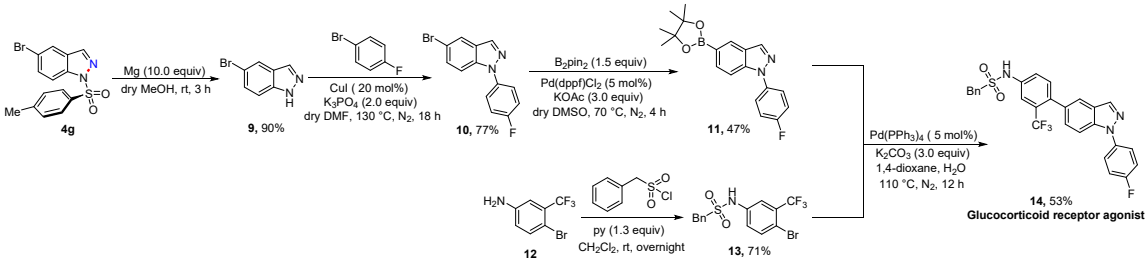
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 10.2 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.09 (td, *J* = 9.0, 3.0 Hz, 1H), 5.41 (d, *J* = 2.4 Hz, 2H), 1.33 (d, *J* = 1.3 Hz, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.9, 163.2 (d, *J* = 261.2 Hz), 143.6, 142.0, 135.8 (d, *J* = 9.1 Hz), 130.3 (d, *J* = 7.6 Hz), 126.9, 123.2 (d, *J* = 1.5 Hz), 122.0, 121.6, 121.3, 114.8 (d, *J* = 21.1 Hz), 114.4 (d, *J* = 21.1 Hz), 109.3, 53.5, 43.6, 26.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.90.

HRMS (ESI) calcd. for $C_{19}H_{19}FN_2ONa^+$ ([M+Na]$^+$): 333.1374, found: 333.1370.

6. General procedure for the synthesis of Glucocorticoid receptor agonist 14[25]



Scheme S3 Synthetic route for Glucocorticoid receptor agonist **14**

Step 1: Under a nitrogen atmosphere, a mixture of **4g** (0.25 mmol), Mg (2.5 mmol) in dry MeOH (3 mL) was added into a flame-dried round-bottom flask and allowed to stir at room temperature. After 3 hours, the reaction mixture was quenched with water, extracted with EtOAc, washed with saturated NH_4Cl solution and brine, and dried over

anhydrous $MgSO_4$. Purification by chromatography on silica gel gave the product **9**. (43.6 g, 90% yield).

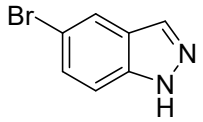
Step 2: Under a nitrogen atmosphere, a solution of compound **9** (985 mg, 5 mmol), 1-bromo-4-fluorobenzene (660 μL, 6 mmol), K_3PO_4 (1.38g, 10 mmol), CuI (190 mg, 1 mmol) and dry DMF (20 mL) were added into a flame-dried round-bottom flask. After stirring at 130 ℃ for 18h, the reaction mixture was then diluted with ethyl acetate, washed with brine, and dried over anhydrous $MgSO_4$. Purification by chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as an eluent afforded the product **10** (1.12 g, 77% yield).

Step 3: Under a nitrogen atmosphere, 5-bromo-1-(4-fluorophenyl)-1*H*-indazole **10** (290.0 mg，1 mmol), [1,10-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (36.3 mg，0.05 mmol) and dry DMSO (15 mL) were added into a flame-dried round-bottom flask. After stirred for 10 min at room temperature, bis- (pinacolato)diboron (380.9 mg, 1.5 mmol) and potassium acetate (414.6 mg, 3.0 mmol) were subsequently added into the reaction system. After stirring at room temperature for 10 min, then heated to 70 °C for 4 h. The mixture was cooled to room temperature, EtOAc and water were added, and the organic phase was collected after three extractions, concentrated under reduced pressure, and eluted with hexane/EtOAc (9:1) to give a white solid **11** (158.9 mg, 47% yield)

Step 4: Under a nitrogen atmosphere, to a flame-dried round-bottom flask, phenylmethanesulfonyl chloride (400.3 mg, 2.1 mmol) was added to a solution of 4-bromo-3-(trifluoromethyl)aniline (480.0 mg, 2.0 mmol), pyridine (2.6 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After stirring at room temperature for 12 hours, the resulting reaction mixture was concentrated under vacuum. After adding water and extracting with EtOAc, washing with 1M HCl solution, H_2O and saturated aqueous NaCl solution in sequence, the organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. and eluted with hexane/EtOAc (5:1) to give a white solid **13** (558.3 mg, 71% yield)

Step 5: Under nitrogen atmosphere, **11** (167.4 mg 0.495 mmol), $Pd(PPh_3)_4$ (29.8 mg, 0.026 mmol), **13** (152.2 mg, 0.450 mmol), 1,4-dioxane (20 mL), K_2CO_3 (2 mmol,)

and water (1 mL) were added into a flame-dried round-bottom flask. The reaction was stirred at 110 °C for 12 h, then cooled to room temperature, added silica gel, concentrated under reduced pressure, and purified by normal phase chromatography, eluting as eluted with PE/EA (3/1) to give a white solid **14** (125.4 mg, 53 % yield)



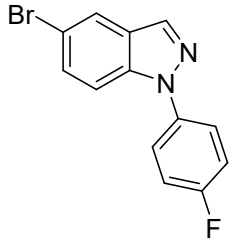
9

5-Bromo-1*H*-indazole (9): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **9** (45.6 mg, 92% yield).

Colorless solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.05 (s, 1H), 7.91 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 134.3, 130.2, 124.9, 123.5, 114.3, 111.4.



10

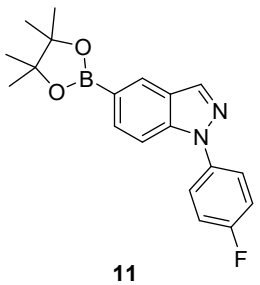
5-Bromo-1-(4-fluorophenyl)-1*H*-indazole (10): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **10**

White solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.93 (s, 1H), 7.65–7.63 (m, 2H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5 (d, *J* = 247.6 Hz), 137.8, 136.0, 134.7, 130.5, 126.8, 124.8 (d, *J* = 9.1 Hz), 123.9, 116.6 (d, *J* = 22.7 Hz), 114.7, 111.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.31.



11

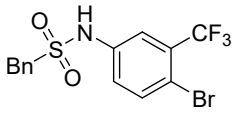
1-(4-Fluorophenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indazole (11): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **11**

White solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.20 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 2H), 1.38 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4 (d, *J* = 246.1Hz), 140.5, 136.4, 136.2, 133.1, 129.8, 125.3, 124.8 (d, *J* = 9.1Hz), 116.5(d, *J* = 22.7Hz), 109.4, 84.0, 25.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.96.



13

***N*-(4-Bromo-3-(trifluoromethyl)phenyl)-1-phenylmethanesulfonamide (13):** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **13**

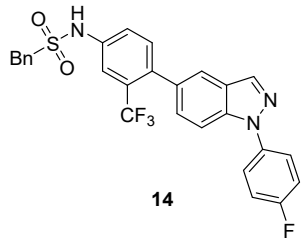
White solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.10 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.98 (s, 1H), 4.35 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 136.1, 131.3 (q, *J* = 30.2 Hz,), 130.9, 129.5, 129.2, 127.8, 123.7, 122.5 (q, *J* = 273.3 Hz), 119.0 (q, *J* = 6.0 Hz), 115.0, 58.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.95.

HRMS (ESI) calcd. for $C_{14}H_{11}BrF_3NO_2Na^+$ ([M+Na]$^+$): 415.9538, found: 415.9533.



14

Glucocorticoid receptor agonist (14): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 3:1) to afford the product **14**

White solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.43 (s, 1H), 7.84 (dd, *J* = 9.0, 4.8 Hz, 3H), 7.79 (s, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.35–7.31 (m, 5H), 4.62 (s, 2H).

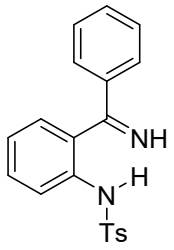
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4 (d, *J* = 243.1Hz), 138.4, 137.6, 135.9, 134.9, 133.6, 132.4, 131.0, 129.2, 128.9, 128.4 (d, *J* = 6.0Hz), 127.7 (q, *J* = 25.7Hz), 123.8 (q, *J* = 274.8Hz), 124.6, 124.4 (d, *J* = 9.1Hz), 121.7, 121.4, 116.5, 116.4, 115.8 (q, *J* = 6.0Hz), 109.7, 57.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.79, -115.37.

HRMS (ESI) calcd. for $C_{27}H_{19}F_4N_3O_2SNa^+$ ([M+Na]$^+$): 548.1026, found: 548.1027.

7. Typical procedure for the synthesis of 8 [15]

N-(2-benzoylphenyl)-4-methylbenzenesulfonamide (**1a**, 1.0 equiv.) and NH_3 (**7 M** in MeOH) (5.0 equiv.) were combined, and the reaction mixture was stirred for 20 h at room temperature. After concentration, the residue was purified by flash silica column chromatography to afford the final product.



8

***N*-(2-(Imino(phenyl)methyl)phenyl)-4-methylbenzenesulfonamide 8:** On a 10 mmol scale, Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product yellow solid, 2.73 g (78%)

m.p.: 114.3~116.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.95 (s, 1H), 9.83 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.36–7.33 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 3H), 6.92 (t, *J* = 7.8 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 180.1, 143.5, 140.5, 140.0, 137.1, 133.3, 132.0, 130.1, 129.6, 128.7, 127.4, 127.2, 123.8, 122.6, 120.8, 21.6.

HRMS (ESI) calcd. for $C_{20}H_{18}N_2O_2SNa^+$ ($[M+Na]^+$): 373.0981, found: 373.0981.

8. General procedure for the electrochemical synthesis of 1*H*-indazoles

8.1 Graphical guide for the set-up

As experimental setup, we used two platinum plate electrodes (10 mm×10 mm×0.3 mm), rubber stoppers, 10 mL columnar round-bottom flask with a 24# mouth, a DC adjustable power supply regulator (HY3005MT) (Made in China) and a magnetic stirrer.

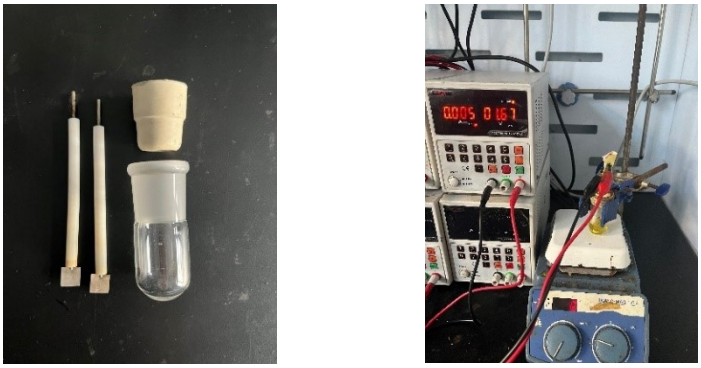
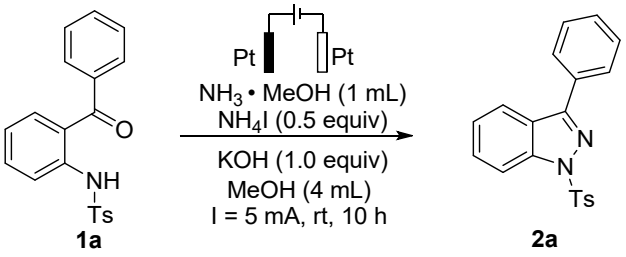


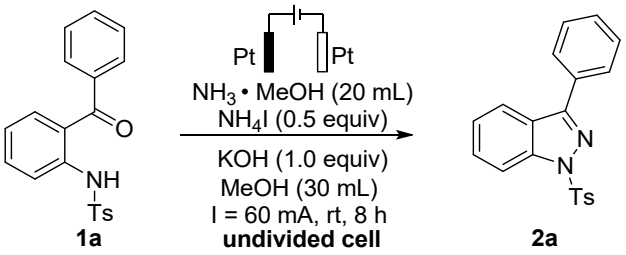
Figure S1 Experiment setup for the electrochemical synthesis of 1*H*-indazoles

8.2 Typical procedure for the synthesis of 2a



After the addition of **1a** (0.3mmol), NH_4I (0.5 equiv.) and KOH (1.0 equiv.) to an undivided cell (10 mL columnar round-bottom flask with a 24# mouth) equipped with two platinum electrodes (10 mm×10 mm×0.3 mm), the liquid reagents NH_3 (7 M in MeOH, 1.0 mL) and MeOH (4 mL) were then added. The resulting mixture was electrolyzed at constant current conditions (5 mA) under room temperature for 10 h. After concentration in vacuum, the residue was purified by column chromatography on silica gel to afford product **2a.**

8.3 Gram-scale synthesis of 2a



After the addition of *N*-(2-Benzoylphenyl)-4-methylbenzenesulfonamide (**1a**, 1.0

g, 2.8 mmol, 1.0 equiv.), NH_4I (0.5 equiv.) and KOH (1.0 equiv.) to a 100 mL oven-dried undivided three neck bottle equipped with two platinum electrodes (10 mm×10 mm×0.3 mm), the liquid reagent NH_3 (7 M in MeOH, 20 mL) and MeOH (30 mL) were then added. The resulting mixture was electrolyzed at constant current conditions (60 mA) under room temperature for 8 h. After concentration in vacuum, the residue was purified by column chromatography on silica gel to afford product **2a** (642.8 mg, 65 % yield).

Figure S2 Experiment Setup for the Gram-scale Synthesis of **2a**.

9. Mechanistic experiments

9.1 Cyclic Voltammetry studies

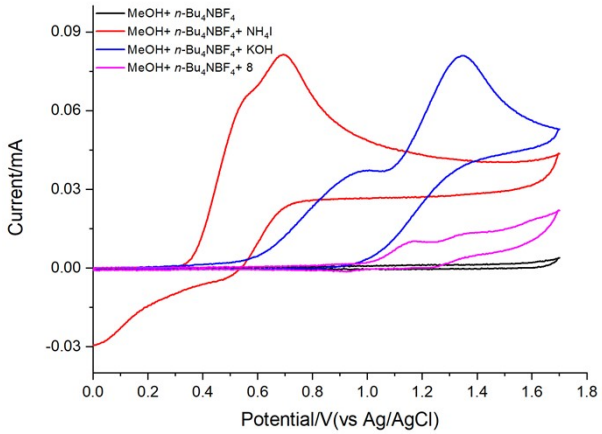
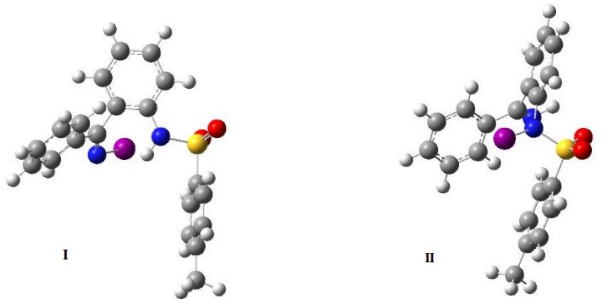


Figure S3 The cyclic voltammograms recorded in MeOH with 0.1 M *n*-Bu_4NBF_4 as

the supporting electrolyte [NH_4I (1 mM), KOH (1 mM), **8** (1 mM)]

Cyclic voltammetry experiments were carried out in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. Ag/AgCl was used as a reference electrode. In all experiments, 10 mL of MeOH was used as a solvent and 0.1 M *n*-Bu_4NBF_4 was used as electrolyte. The scan rate is 0.1 V/s, ranging from 0 V to 1.7 V. The test concentrations of NH_4I, KOH and **8** are all 1 mM.

9.2 DFT calculations

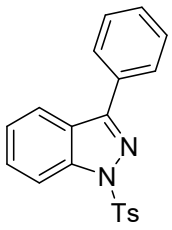


-1727.621563 -1727.653464 ΔG = 20.02 kcal/mol

Figure S4 Density functional theory (DFT) calculations for intermediate **I** and **II**

Density functional theory (DFT) calculations with the empirical dispersion correction D3 developed by Grimme et al.[16-17] using the Minnesota density functional (M062X) [18-19] with the combination of the Def2TZVP basis set for iodine atom and the augmented correlation consistent basis set 6-311+G(d,p) for other atoms,[20] shows that **II** has a lower energy than that of intermediate **I** (ΔG = 20.02kcal/mol). From the above DFT calculations, intermediate **II** is most likely an intermediate generated in this cyclization subsequent reaction.

10. Characterization data for the products



2a

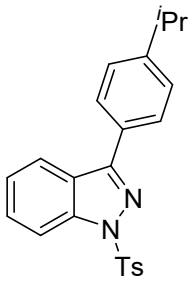
3-Phenyl-1-tosyl-1*H*-indazole (2a) [13]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2a** (89.7 mg, 86% yield).

White solid; m.p.: 107.9~109.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.90 (m, 5H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 145.4, 142.0, 134.8, 131.6, 129.9, 129.7, 129.2, 129.0, 128.4, 127.8, 124.6, 124.5, 121.8, 113.8, 21.8.

HRMS (ESI) calcd. for $C_{20}H_{17}N_2O_2S^+$ ([M+H]$^+$): 349.1005, found: 349.1006.



2b

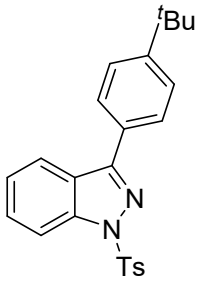
3-(4-Isopropylphenyl)-1-tosyl-1*H*-indazole (2b): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2b** (93.4 mg, 80% yield).

White solid; m.p.: 106.7~108.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.00 – 2.96 (m, 1H), 2.33 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 150.7, 145.3, 142.1, 134.8, 129.9, 129.1, 128.4, 127.7, 127.1, 124.6, 124.5, 121.9, 113.8, 34.2, 24.0, 21.7.

HRMS (ESI) calcd. for $C_{23}H_{22}N_2O_2SNa^+$ ([M+Na]$^+$): 413.1294, found: 413.1292.



2c

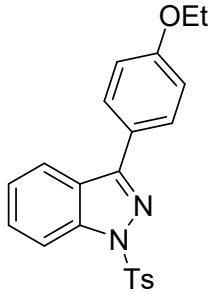
3-(4-(*tert*-Butyl)phenyl)-1-tosyl-1*H*-indazole (2c): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2c** (99.6 mg, 82% yield). m.p.: 107.7~109.5 °C.

Colorless oil;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.0, 151.9, 145.3, 142.1, 134.8, 129.9, 129.1, 128.7, 128.1, 127.7, 125.9, 124.6, 124.5, 121.9, 113.8, 35.0, 31.4, 21.7.

HRMS (ESI) calcd. for $C_{24}H_{24}N_2O_2SNa^+$ ([M+Na]$^+$): 427.1451, found: 427.1451.



2d

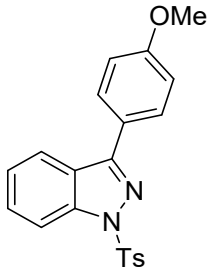
3-(4-Ethoxyphenyl)-1-tosyl-1*H*-indazole (2d): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2d** (104.7 mg, 89% yield).

White solid; m.p.: 107.4~109.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 6.6 Hz, 1H), 7.89 (d, *J* = 6.6 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.09 (q, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.45 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 151.7, 145.2, 142.0, 134.8, 129.9, 129.7, 129.1, 127.7, 124.6, 124.4, 123.9, 121.9, 114.9, 113.7, 63.7, 21.7, 14.9.

HRMS (ESI) calcd. for $C_{22}H_{20}N_2O_3SNa^+$ ($[M+Na]^+$): 415.1087, found: 415.1086.



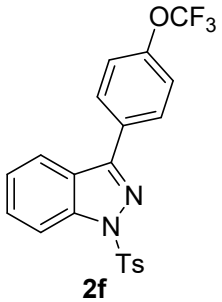
2e

3-(4-Methoxyphenyl)-1-tosyl-1*H*-indazole (2e) [21]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2e** (99.5 mg, 88% yield).

White solid; m.p.: 106.9~108.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.90–7.88(m, 3H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 151.7, 145.3, 142.0, 134.8, 129.9, 129.7, 129.1, 127.7, 124.5, 124.5, 124.1, 121.8, 114.4, 113.7, 55.5, 21.7.



2f

1-Tosyl-3-(4-(trifluoromethoxy)phenyl)-1*H*-indazole (2f): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2f** (102.8 mg, 79% yield).

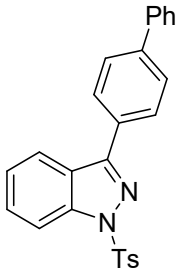
White solid; m.p.: 107.9~109.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 150.2, 145.6, 142.0, 134.7, 130.3, 130.0, 129.9, 129.4, 127.8, 124.8, 124.1, 121.4, 121.4, 120.6 (q, *J* = 274.8 Hz), 113.8, 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.72.

HRMS (ESI) calcd. for $C_{21}H_{15}F_3N_2O_3SNa^+$ ($[M+Na]^+$): 455.0648, found: 455.0645.



2g

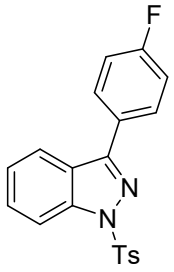
3-([1,1'-Biphenyl]-4-yl)-1-tosyl-1*H*-indazole (2g): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2g** (99.7 mg, 78% yield).

White solid; m.p.: 107.7~109.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41–7.38 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 145.4, 142.5, 142.0, 140.5, 134.8, 130.5, 129.9, 129.2, 129.0, 128.8, 127.9, 127.7, 127.6, 127.2, 124.6, 124.5, 121.8, 113.8, 21.7.

HRMS (ESI) calcd. for $C_{26}H_{20}N_2O_2SNa^+$ ([M+Na]$^+$): 447.1138, found: 447.1141.



2h

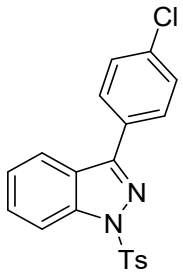
3-(4-Fluorophenyl)-1-tosyl-1*H*-indazole (2h): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2h** (77.1 mg, 70% yield). White solid; m.p.: 107.4~109.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.87 (m, 5H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 9.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7 (d, *J* = 250.7 Hz), 150.8, 145.5, 142.0, 134.8, 130.2 (d, *J* = 7.6 Hz), 130.0, 129.3, 127.7, 124.7, 124.2, 121.5, 116.2, 116.0, 113.8, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.10.

HRMS (ESI) calcd. for $C_{20}H_{15}FN_2O_2SNa^+$ ([M+Na]$^+$): 389.0731, found: 389.0730.



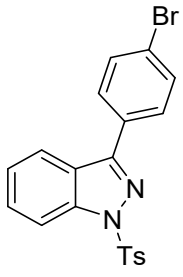
2i

3-(4-Chlorophenyl)-1-tosyl-1*H*-indazole (2i) [22]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2i** (86.7 mg, 75% yield).

White solid; m.p.: 105.9~107.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 145.5, 141.9, 135.7, 134.7, 130.0, 129.9, 129.5, 129.3, 129.2, 127.7, 124.7, 124.1, 121.5, 113.7, 21.7.



2j

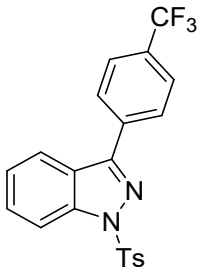
3-(4-Bromophenyl)-1-tosyl-1*H*-indazole (2j): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2j** (93.8 mg, 73% yield).

White solid; m.p.: 107.3~109.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 145.5, 141.9, 134.7, 132.1, 130.5, 130.0, 129.8, 129.3, 127.7, 124.7, 124.0, 121.5, 113.8, 21.7.

HRMS (ESI) calcd. for $C_{20}H_{15}BrN_2O_2SNa^+$ ([M+Na]$^+$): 448.9930, found: 448.9931.



2k

1-Tosyl-3-(4-(trifluoromethyl)phenyl)-1*H*-indazole (2k): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2k** (88.4 mg, 71% yield).

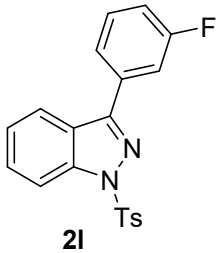
White solid; m.p.: 107.4~109.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.92 (t, *J* = 7.8 Hz, 3H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.7, 142.0, 135.1, 134.7, 131.5 (q, *J* = 31.7 Hz), 130.0, 129.5, 128.6, 127.8, 125.9 (q, *J* = 4.5 Hz), 124.9, 124.1 (q, *J* = 273.3 Hz), 124.0, 121.4, 113.8, 21.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.72.

HRMS (ESI) calcd. for $C_{21}H_{15}F_3N_2O_2SNa^+$ ([M+Na]$^+$): 439.0699, found: 439.0699.



2l

3-(3-Fluorophenyl)-1-tosyl-1*H*-indazole (2l): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2l** (83.2 mg, 76% yield).

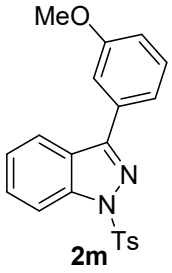
White solid; m.p.: 106.9~108.7 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 9.6 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.46–7.43 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13 (td, *J* = 8.4, 3.0 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0 (d, *J* = 246.1 Hz), 150.3, 145.5, 141.9, 134.6, 133.6 (d, *J* = 9.1 Hz), 130.5 (d, *J* = 9.1 Hz), 130.0, 129.3, 127.7, 124.7, 123.9 (d, *J* = 4.5 Hz), 121.4, 116.5 (d, *J* = 21.1 Hz), 115.2 (d, *J* = 24.2 Hz), 113.7, 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.02.

HRMS (ESI) calcd. for $C_{20}H_{15}FN_2O_2SNa^+$ ([M+Na]$^+$): 389.0731, found: 389.0728.



2m

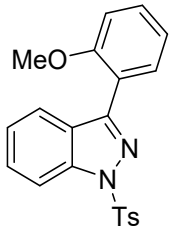
3-(3-Methoxyphenyl)-1-tosyl-1*H*-indazole (2m): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2m** (95.3 mg, 84% yield).

Colorless oil;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.88 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 151.7, 145.4, 142.0, 134.7, 132.8, 130.0, 129.9, 129.2, 127.7, 124.6, 124.4, 121.8, 120.8, 115.4, 113.8, 113.7, 55.5, 21.7.

HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_3SNa^+$ ([M+Na]$^+$): 401.0930, found: 401.0938.



2n

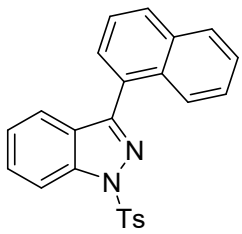
3-(2-Methoxyphenyl)-1-tosyl-1*H*-indazole (2n): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2n** (83.9 mg, 74% yield).

White solid; m.p.: 107.7~109.6 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 9.6 Hz, 2H), 7.44 (t, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 151.1, 145.2, 141.3, 135.0, 131.8, 131.2, 129.8, 128.9, 127.8, 125.9, 123.9, 123.0, 121.0, 120.5, 113.3, 111.4, 55.5, 21.7.

HRMS (ESI) calcd. for $C_{21}H_{18}N_2O_3SNa^+$ ([M+Na]$^+$): 401.0930, found: 401.0933.



2o

3-(Naphthalen-1-yl)-1-tosyl-1*H*-indazole (2o): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2o** (101.9 mg, 85% yield).

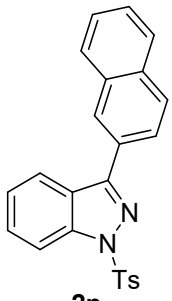
White solid;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 3H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 8.4

Hz, 1H), 7.58 – 7.54 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 145.5, 141.5, 134.9, 134.0, 131.6, 130.1, 129.9, 129.4, 128.6, 128.5, 128.3, 127.9, 126.7, 126.3, 126.3, 125.8, 125.3, 124.5, 122.0, 113.7, 21.8.

HRMS (ESI) calcd. for $C_{24}H_{18}N_2O_2SNa^+$ ($[M+Na]^+$): 421.0981, found: 421.0979.



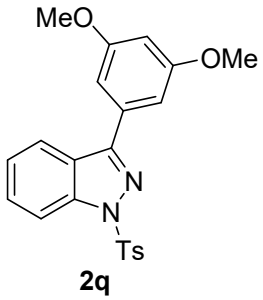
2p

3-(Naphthalen-2-yl)-1-tosyl-1*H*-indazole (2p): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2p** (99.0 mg, 83% yield). White solid; m.p.: 109.3~111.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.06 (t, J = 8.4 Hz, 2H), 7.97 – 7.93(m, 4H), 7.89 – 7.88 (m, 1H), 7.61 (t, J = 8.1 Hz, 1H), 7.55–7.53 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 145.4, 142.0, 134.7, 133.8, 133.3, 129.9, 129.2, 129.0, 128.7, 128.6, 127.9, 127.7, 127.0, 126.7, 125.6, 124.7, 124.6, 121.9, 113.7, 21.7.

HRMS (ESI) calcd. for $C_{24}H_{18}N_2O_2SNa^+$ ($[M+Na]^+$): 421.0981, found: 421.0980.



2q

3-(3,5-Dimethoxyphenyl)-1-tosyl-1*H*-indazole (2q): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with

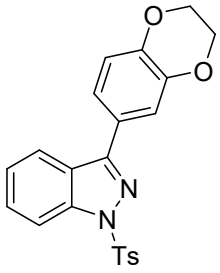
petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2q** (106.4 mg, 87% yield).

White solid; m.p.: 107.1~109.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 2.4 Hz, 2H), 6.57 (t, *J* = 2.4 Hz, 1H), 3.85 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 151.7, 145.4, 141.9, 134.7, 133.2, 129.9, 129.2, 127.7, 124.6, 124.4, 121.8, 113.6, 106.5, 101.7, 55.6, 21.7.

HRMS (ESI) calcd. for $C_{22}H_{20}N_2O_4SNa^+$ ($[M+Na]^+$): 431.1036, found: 431.1036.



2r

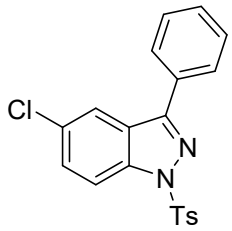
3-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-1-tosyl-1*H*-indazole (2r): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2r** (99.4 mg, 82% yield).

White solid; m.p.: 104.4~106.4 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 3H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.31– 4.29 (m, 4H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 145.3, 145.1, 143.9, 142.0, 134.8, 129.9, 129.1, 127.7, 124.9, 124.5, 124.4, 121.8, 121.7, 117.8, 117.3, 113.7, 64.6, 64.4, 21.7.

HRMS (ESI) calcd. for $C_{22}H_{18}N_2O_4SNa^+$ ($[M+Na]^+$): 429.0880, found: 429.0880.



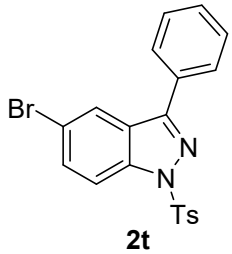
2s

5-Chloro-3-phenyl-1-tosyl-1*H*-indazole (2s) [21]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2s** (78.5 mg, 68% yield).

White solid; m.p.: 107.1~109.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 1H), 8.05 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 6.6 Hz, 2H), 7.66 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0, 145.7, 140.8, 134.5, 132.3, 131.0, 130.1, 130.0, 129.1, 128.3, 127.8, 126.1, 124.4, 118.0, 115.2, 21.8.



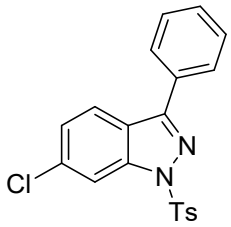
2t

5-Bromo-3-phenyl-1-tosyl-1*H*-indazole (2t) [21]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2t** (88.3 mg, 69% yield).

Colorless oil;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 3H), 7.86 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.55–7.47 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 145.7, 140.4, 134.5, 131.0, 130.5, 130.1, 130.0, 129.7, 129.1, 128.3, 127.8, 125.5, 121.2, 114.8, 21.8.



2u

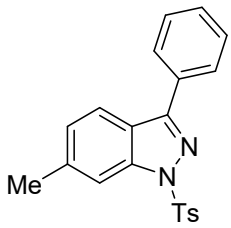
6-Chloro-3-phenyl-1-tosyl-1*H*-indazole (2u): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2u** (82.8 mg, 72% yield).

White solid; m.p.: 106.6~108.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.86 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.51–7.47 (m, 3H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 145.7, 142.3, 135.8, 134.5, 131.0, 130.1, 129.9, 129.0, 128.3, 127.8, 125.5, 122.9, 122.6, 113.7, 21.8.

HRMS (ESI) calcd. for $C_{22}H_{15}ClN_2O_2SNa^+$ ($[M+Na]^+$): 405.0435, found: 405.0435.



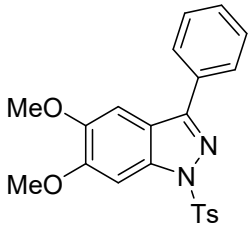
2v

6-Methyl-3-phenyl-1-tosyl-1*H*-indazole (2v) [23]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2v** (83.4 mg, 77% yield).

White solid; m.p.: 107.3~109.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.3 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.8 Hz, 4H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.50–7.44 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 1H), 2.57 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 145.2, 142.6, 140.0, 134.9, 131.7, 129.9, 129.6, 128.9, 128.3, 127.7, 126.5, 122.5, 121.3, 113.4, 22.2, 21.7.



2w

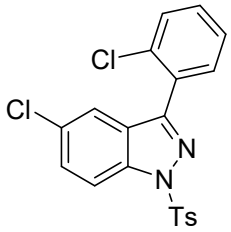
5,6-Dimethoxy-3-phenyl-1-tosyl-1*H*-indazole (2w): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **2w** (92.3 mg, 75% yield).

White solid; m.p.: 105.4~107.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 6.6 Hz, 2H), 7.71 (s, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 4.06 (s, 3H), 3.92 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.1, 151.8, 148.4, 145.3, 137.8, 134.7, 131.8, 129.9, 129.5, 129.0, 128.2, 127.6, 117.4, 101.1, 95.6, 56.6, 56.4, 21.7.

HRMS (ESI) calcd. for $C_{22}H_{20}N_2O_4SNa^+$ ($[M+Na]^+$): 431.1036, found: 431.1036.



2x

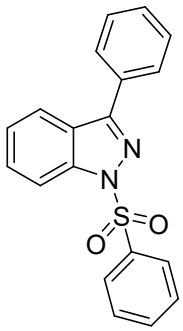
5-Chloro-3-(2-chlorophenyl)-1-tosyl-1*H*-indazole (2x): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **2x** (81.6 mg, 65% yield).

White solid; m.p.: 114.9~116.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.53–7.51 (m, 2H), 7.46–7.42 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.8, 139.7, 134.4, 133.7, 132.1, 131.1, 130.3, 130.3, 130.0, 129.9, 129.8, 127.8, 127.1, 126.4, 121.5, 114.7, 21.8.

HRMS (ESI) calcd. for $C_{22}H_{14}Cl_2N_2O_2SNa^+$ ([M+Na]$^+$): 439.0045, found: 439.0042.



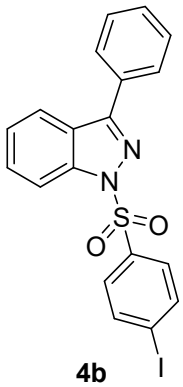
4a

3-Phenyl-1-(phenylsulfonyl)-1*H*-indazole (4a) [22]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **4a** (81.4 mg, 81% yield).

White solid; m.p.: 101.8~103.5 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 6.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.1, 142.0, 137.8, 134.2, 131.5, 129.8, 129.3, 129.0, 128.4, 127.7, 124.7, 124.5, 121.9, 113.7.



4b

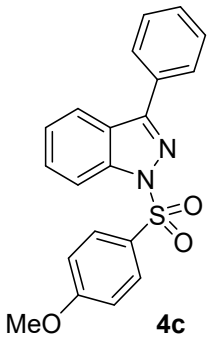
1-((4-Iodophenyl)sulfonyl)-3-phenyl-1*H*-indazole (4b): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **4b** (101.8 mg, 74% yield).

White solid; m.p.: 115.3~117.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.60 (t, *J* = 8.4 Hz, 1H), 7.53–7.48 (m, 3H), 7.40 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 142.0, 138.6, 137.3, 131.3, 129.9, 129.5, 129.0, 128.9, 128.4, 124.9, 124.6, 122.0, 113.7, 102.3.

HRMS (ESI) calcd. for $C_{19}H_{13}IN_2O_2SNa^+$ ([M+Na]$^+$): 482.9635, found: 482.9635.



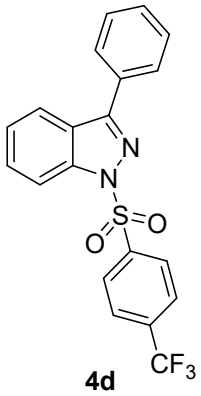
4c

1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-1*H*-indazole (4c) [24]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **4c** (92.5 mg, 85% yield).

White solid; m.p.: 109.8~111.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 7.2 Hz, 3H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 151.6, 141.9, 131.5, 129.9, 129.6, 129.1, 129.0, 128.9, 128.3, 124.5, 124.3, 121.7, 114.4, 113.6, 55.7.



4d

3-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1*H*-indazole (4d): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **4d** (74.8 mg, 62% yield).

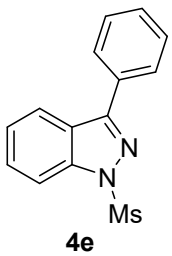
White solid; m.p.: 109.3~110.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 6.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.53–7.50 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 142.0, 135.7 (q, *J* = 33.2 Hz), 131.1, 130.0, 129.6, 129.1, 128.4, 128.3, 126.5 (q, *J* = 3.0 Hz), 125.1, 124.6, 123.0 (q, *J* = 273.3 Hz), 122.1, 113.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.34.

HRMS (ESI) calcd. for $C_{20}H_{13}F_3N_2O_2SNa^+$ ($[M+Na]^+$): 425.0542, found: 425.0540.



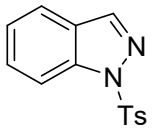
4e

1-(Methylsulfonyl)-3-phenyl-1*H*-indazole (4e) [22]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 20:1) to afford the product **4e** (54.2 mg, 66% yield).

White solid; m.p.: 97.3~99.2 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 6.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 3.30 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 141.9, 131.4, 129.9, 129.4, 129.1, 128.4, 124.7, 124.1, 121.9, 113.6, 41.0.



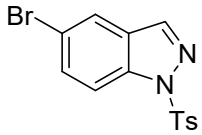
4f

1-Tosyl-1*H*-indazole (4f) [13]**:** Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **4f** (63.8 mg, 78% yield).

White solid; m.p.: 105.5~107.3 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 9.0, 1.2 Hz, 1H), 8.18 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 141.4, 140.4, 134.7, 130.0, 129.3, 127.7, 126.0, 124.3, 121.5, 113.3, 21.7.



4g

5-Bromo-1-tosyl-1*H*-indazole (4g): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethyl acetate (PE/EA = 9:1) to afford the product **4g** (53.2 mg, 51% yield).

Colorless solid;

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 140.1, 139.1, 134.3, 132.3, 130.3, 130.0, 127.4, 123.9, 117.5, 114.6, 21.7.

11. References:

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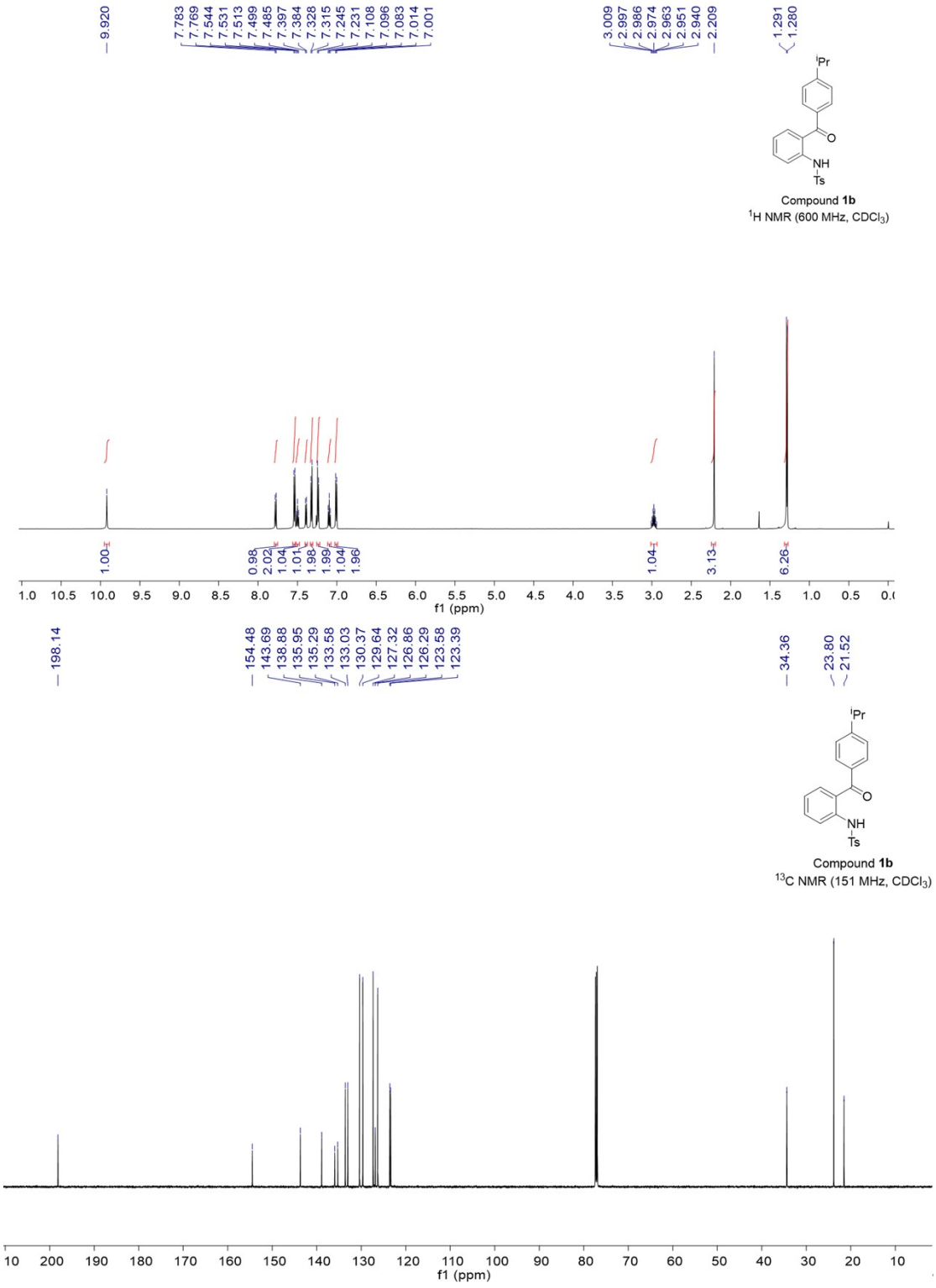
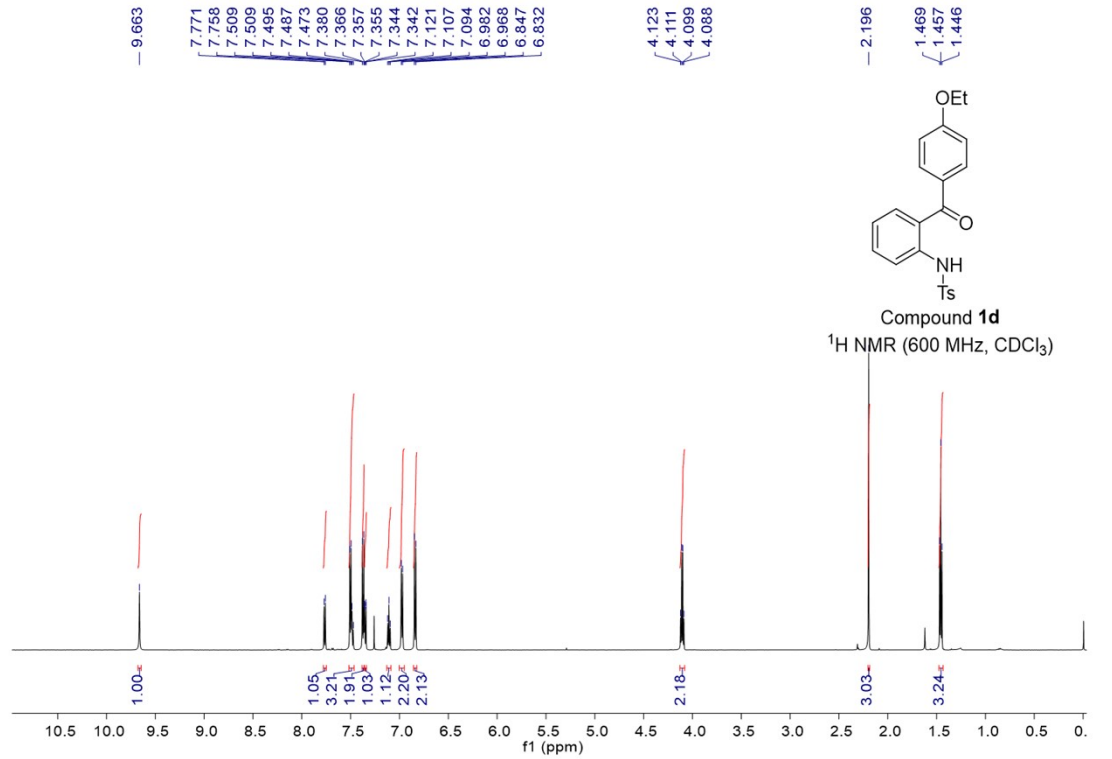
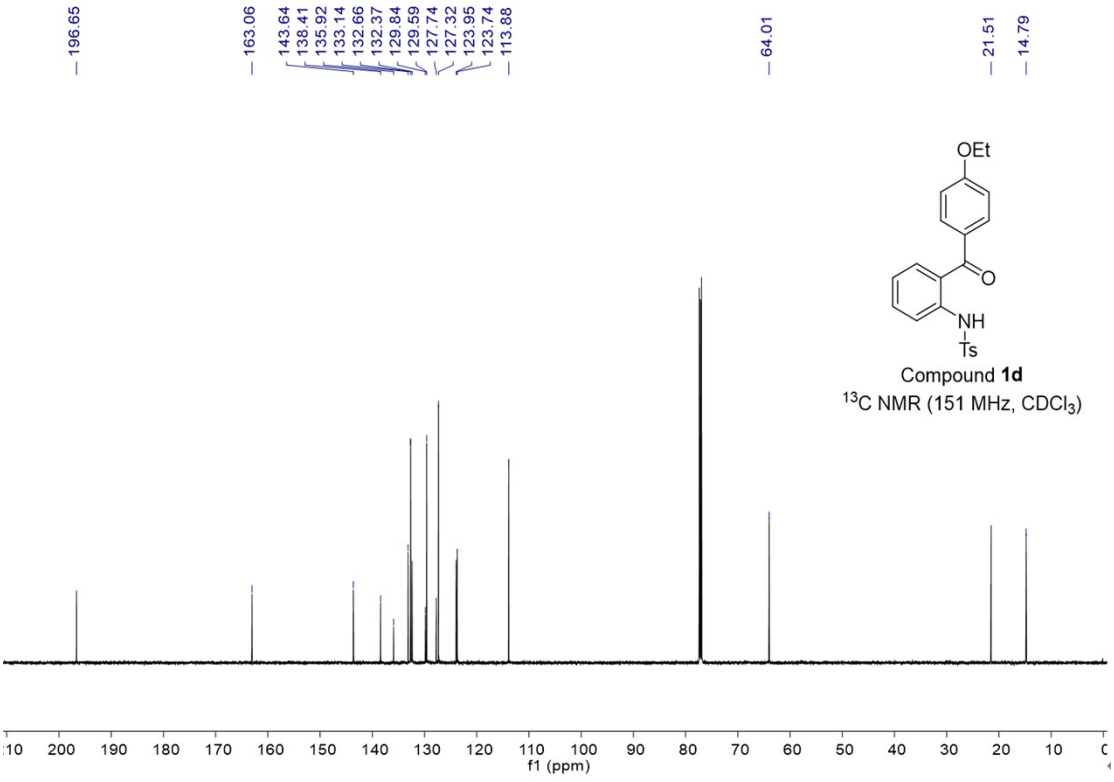
12. NMR spectra of the products

NMR spectra of N-(2-(4-isopropylbenzoyl)phenyl)-4-methylbenzenesulfonamide (**1b**)



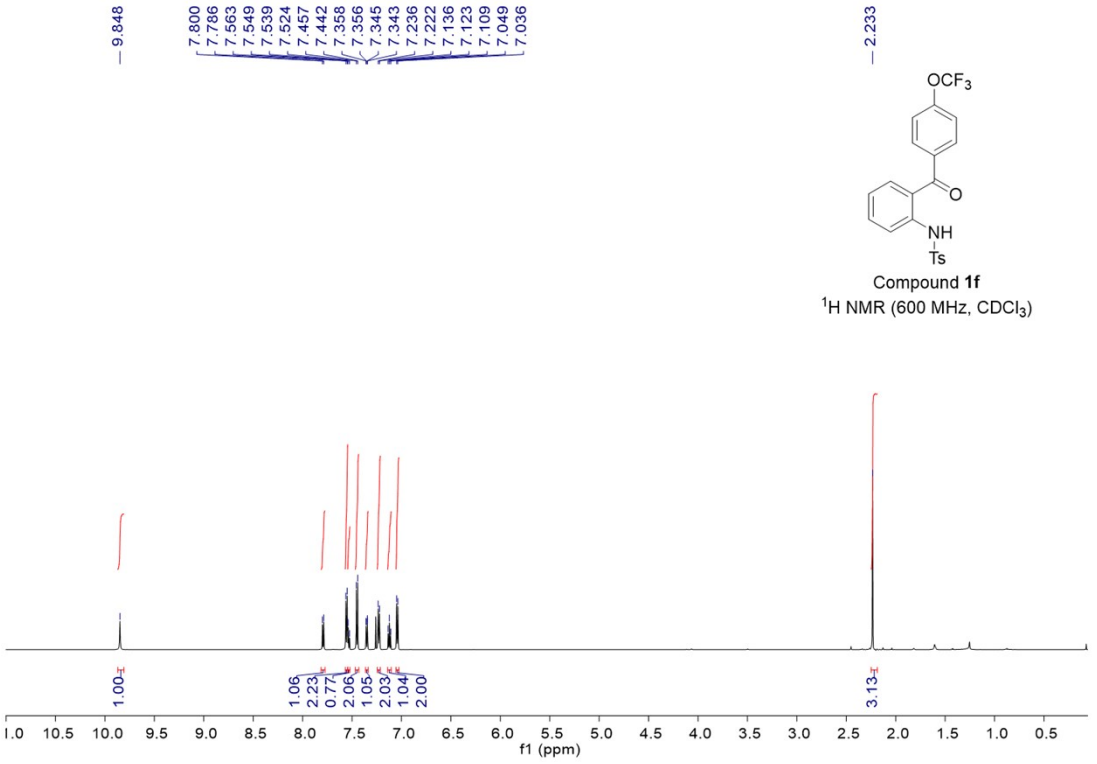
NMR spectra of *N*-(2-(4-ethoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (**1d**)

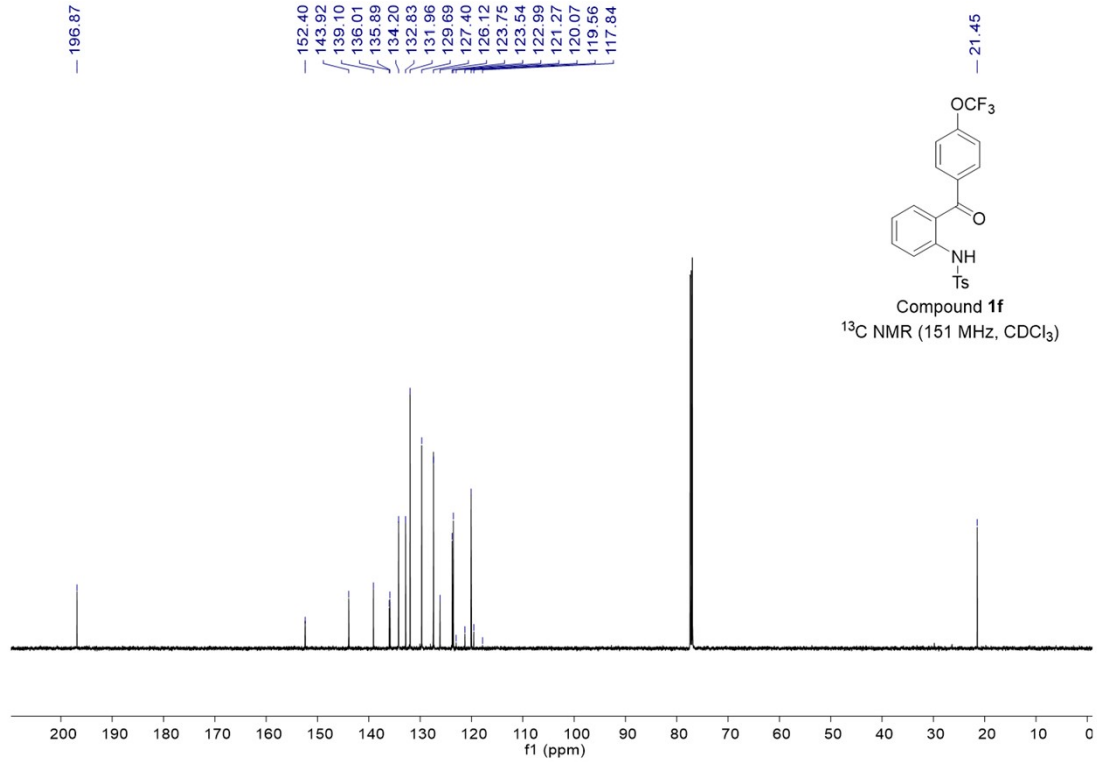


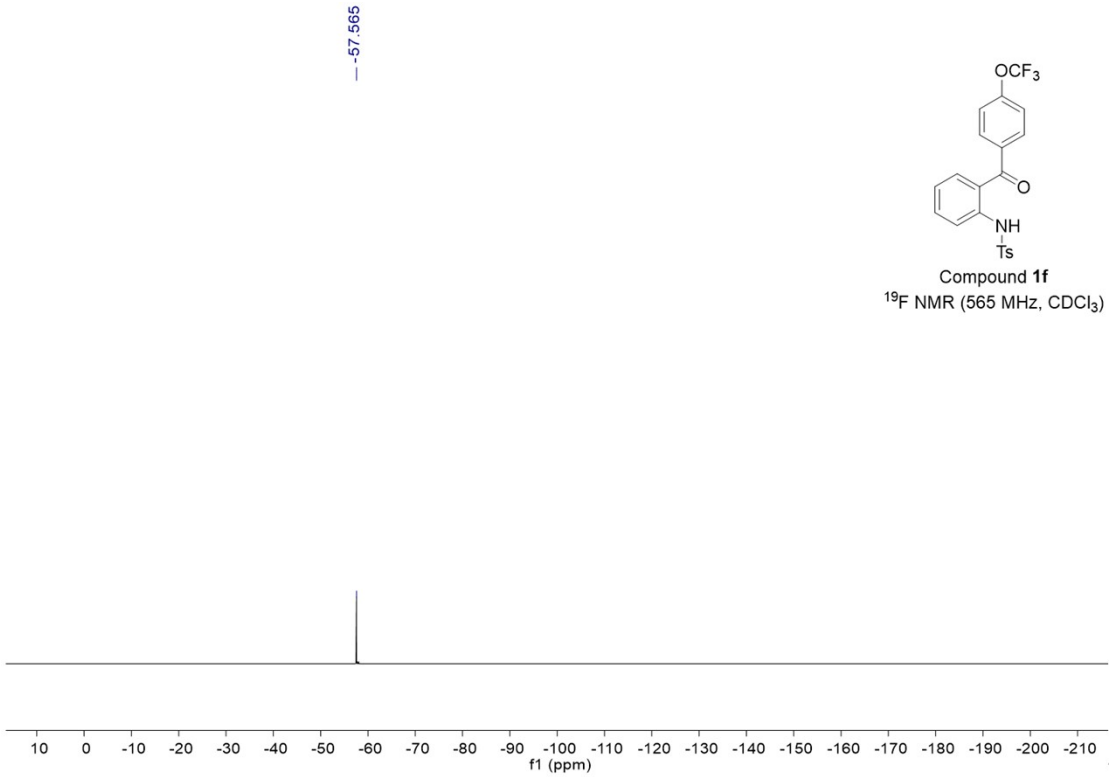


NMR spectra of 4-Methyl-*N*-(2-(4-

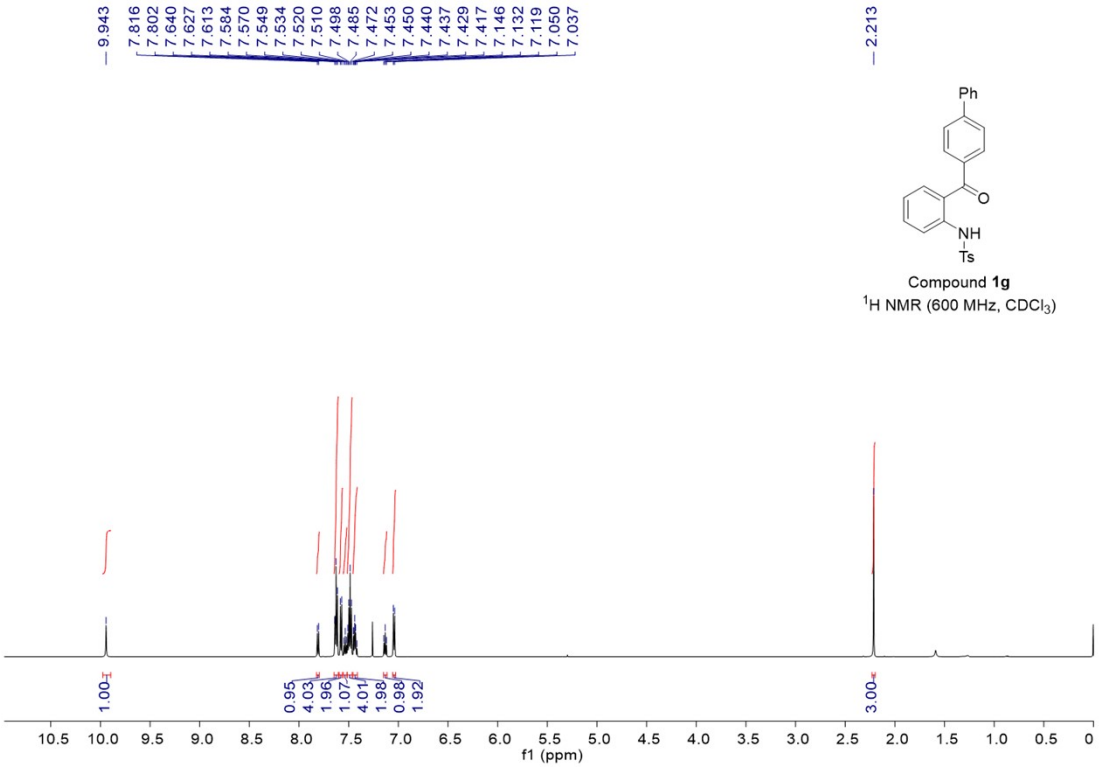
(trifluoromethoxy)benzoyl)phenyl)benzenesulfonamide **(1f)**

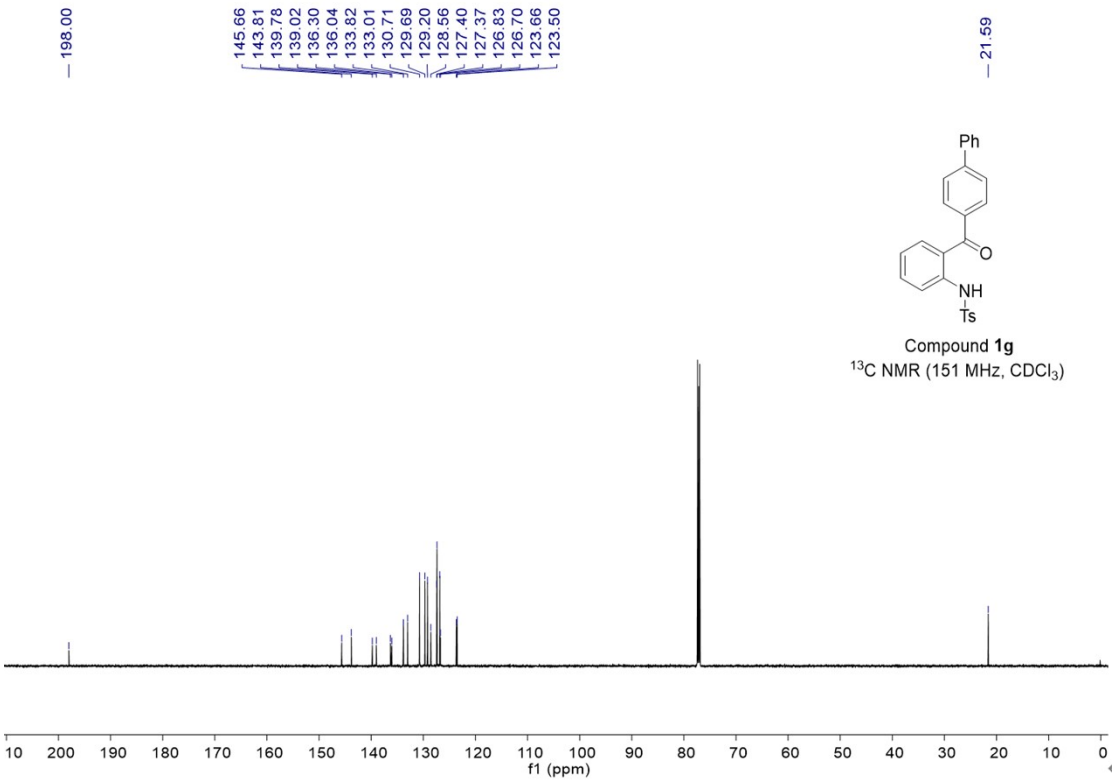




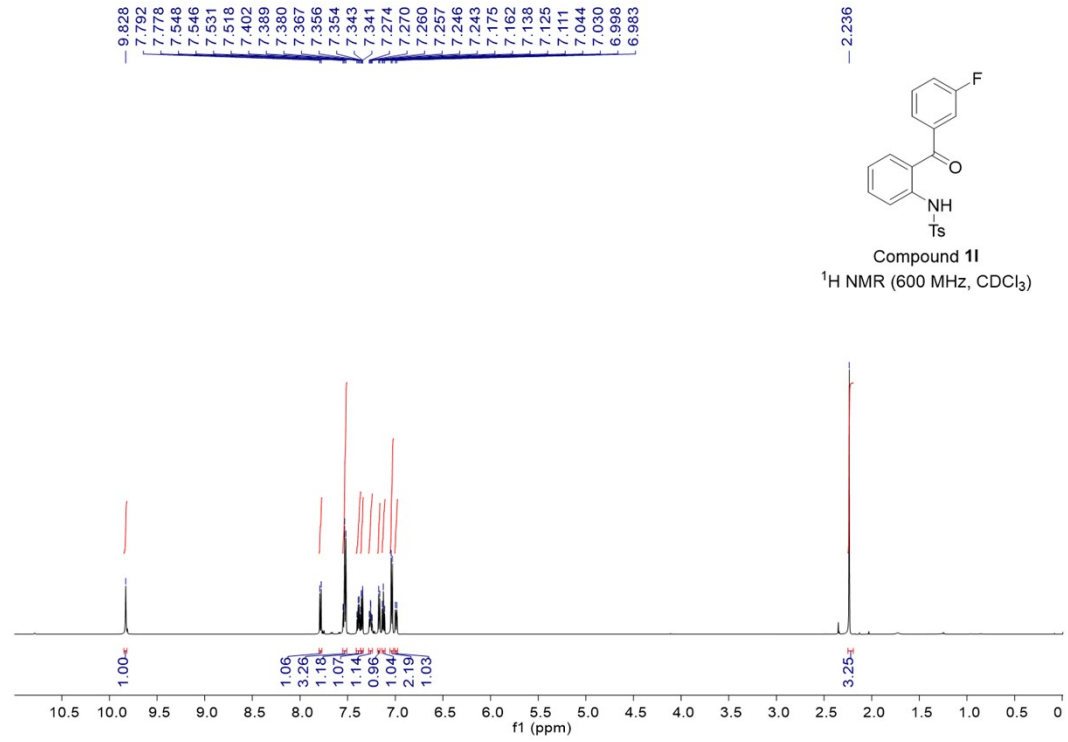


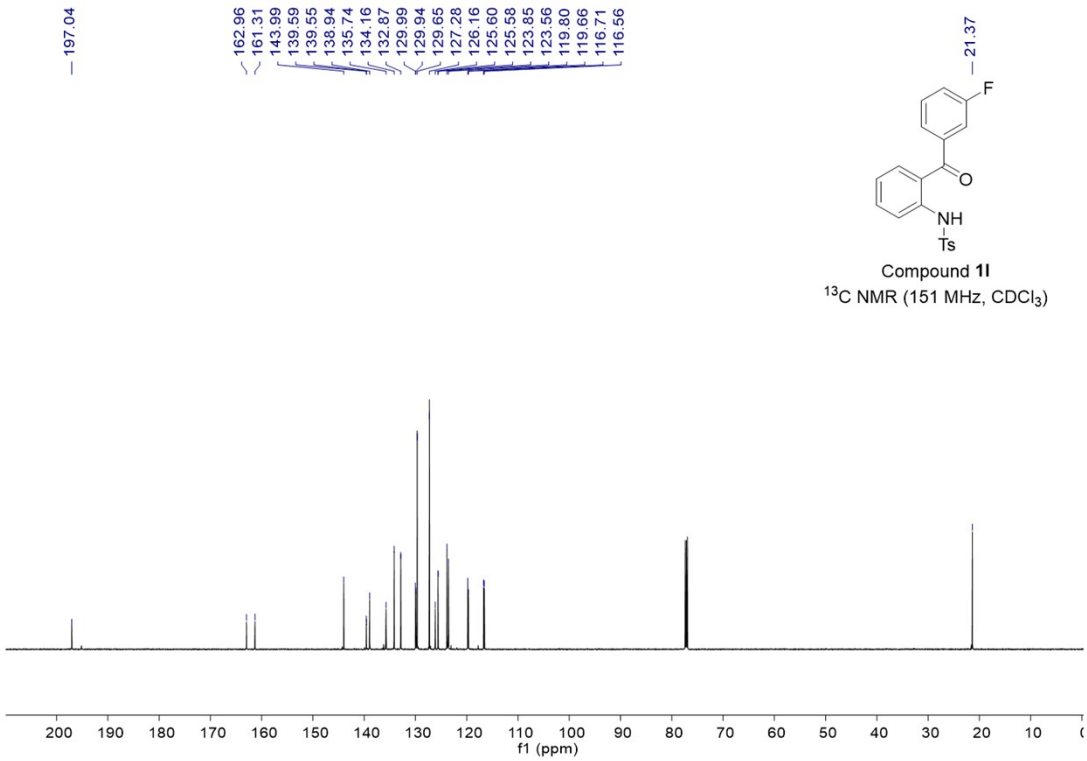
NMR spectra of *N*-(2-([1,1'-biphenyl]-4-carbonyl)phenyl)-4-methylbenzenesulfonamide (**1g**)





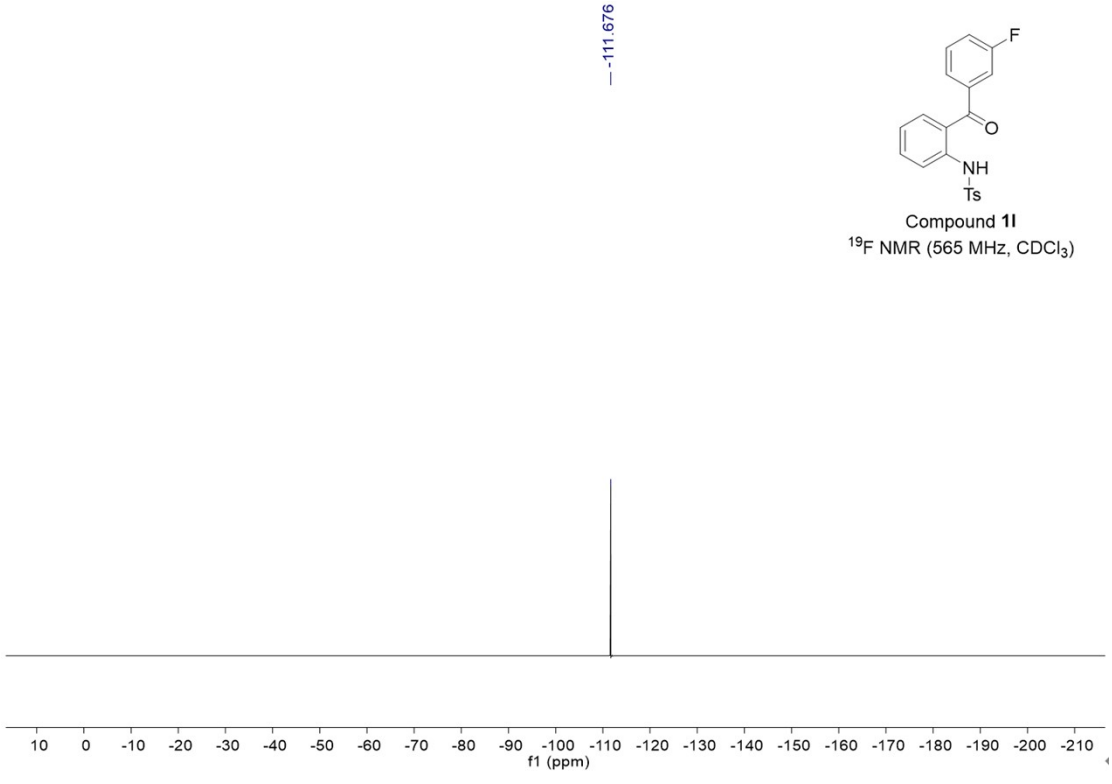
NMR spectra of *N*-(2-(3-Fluorobenzoyl)phenyl)-4-methylbenzenesulfonamide (**1l**)





Compound **1l**

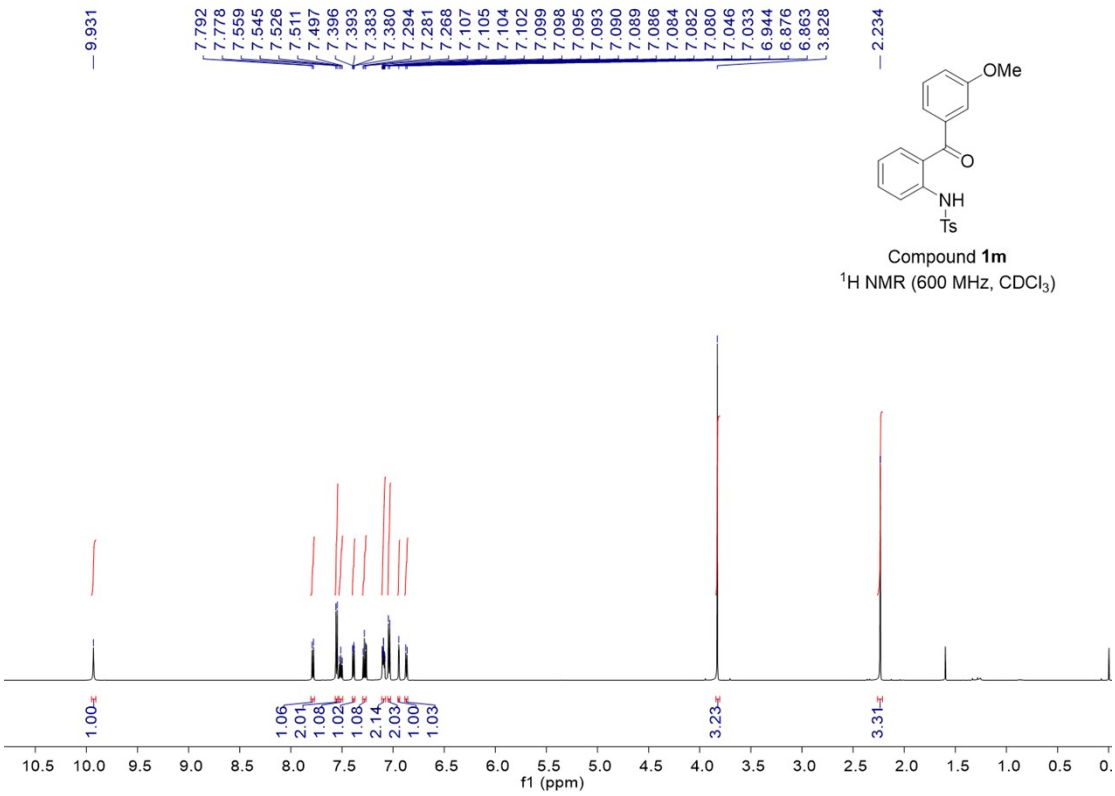
^{13}C NMR (151 MHz, $CDCl_3$)

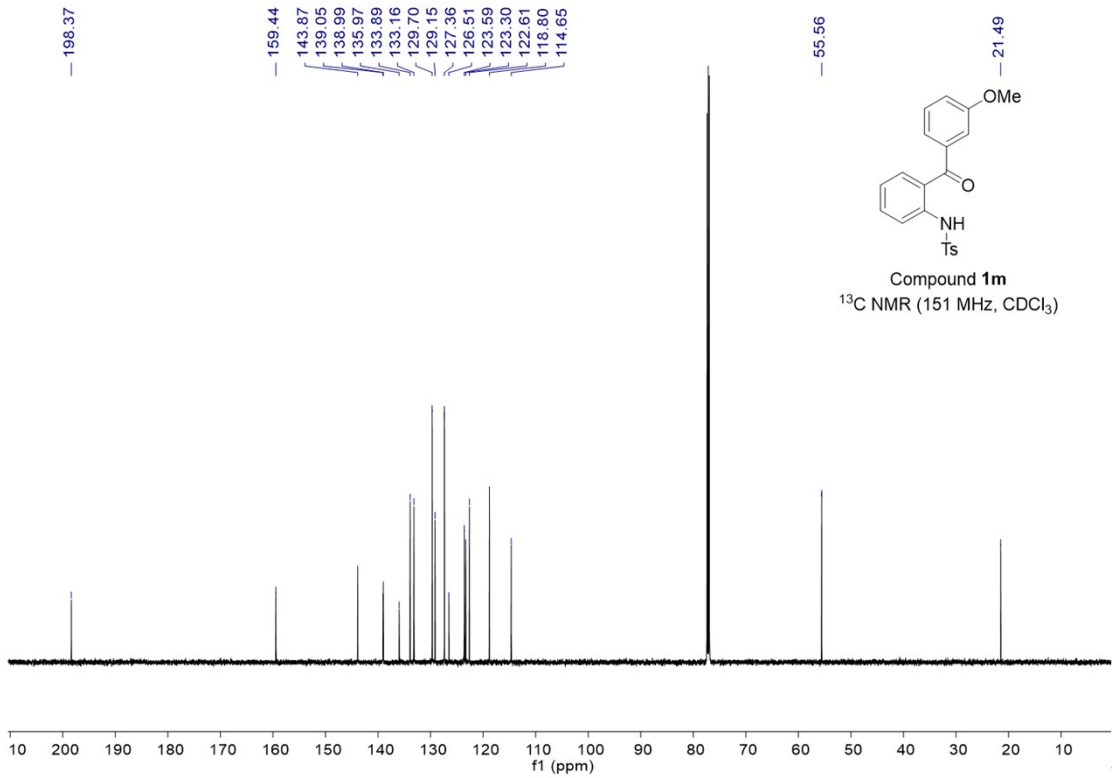


Compound **1l**

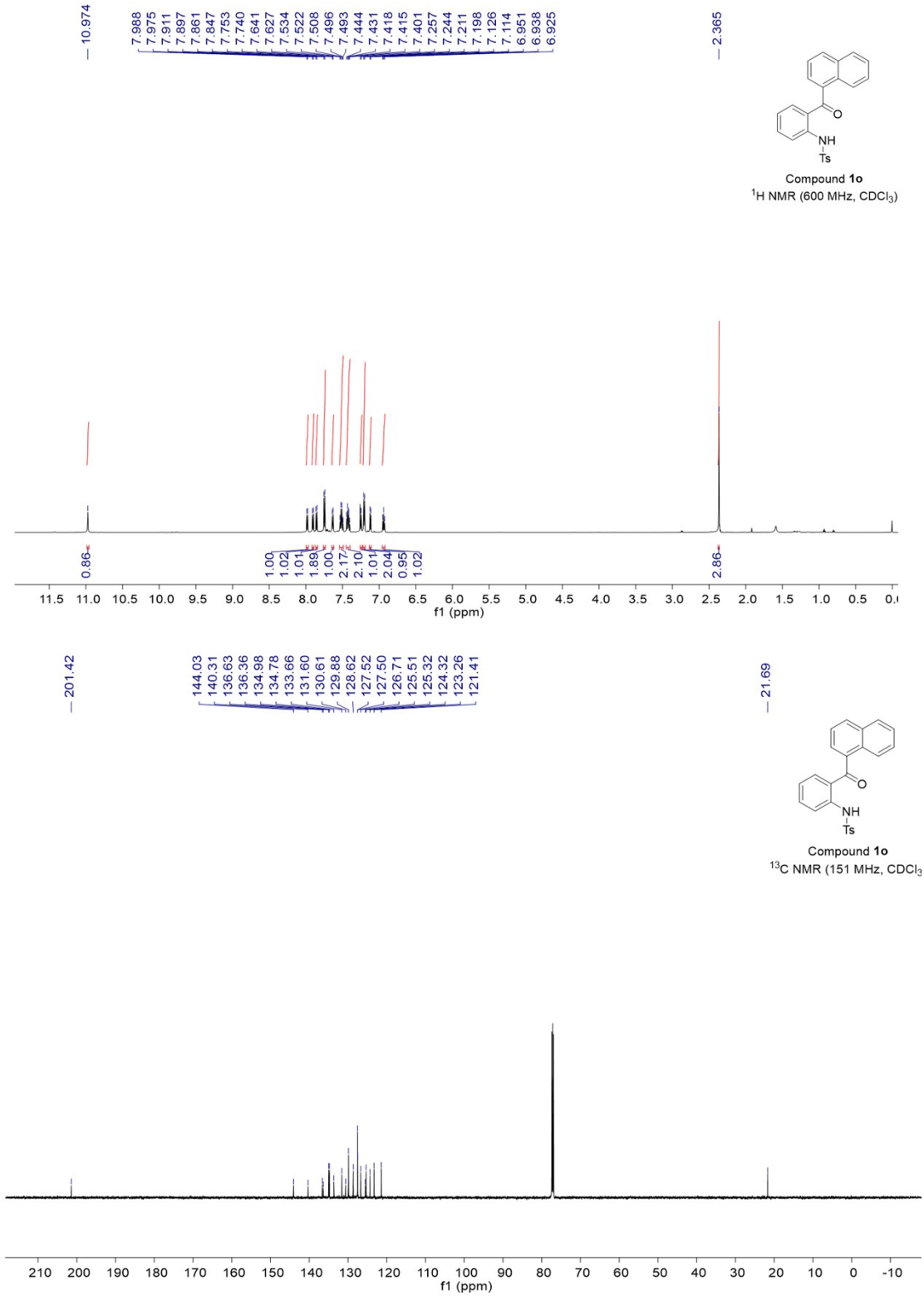
^{19}F NMR (565 MHz, $CDCl_3$)

NMR spectra of *N*-(2-(3-Methoxybenzoyl)phenyl)-4-methylbenzenesulfonamide (**1m**)



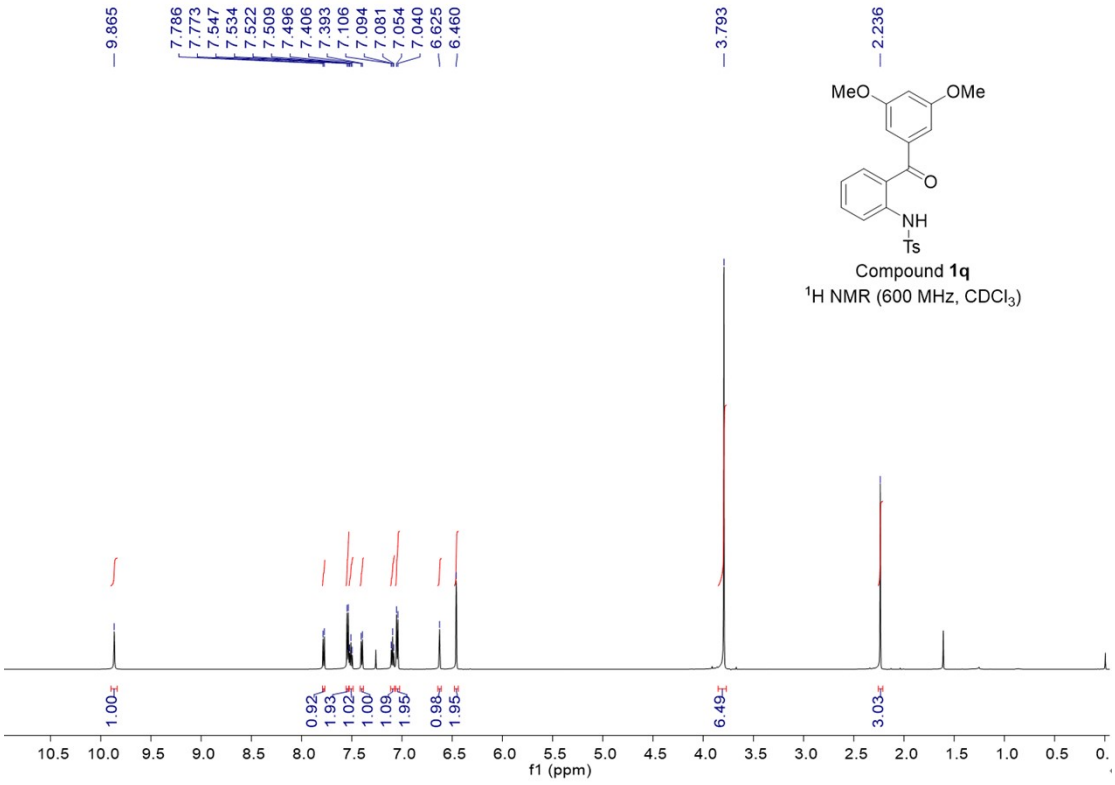


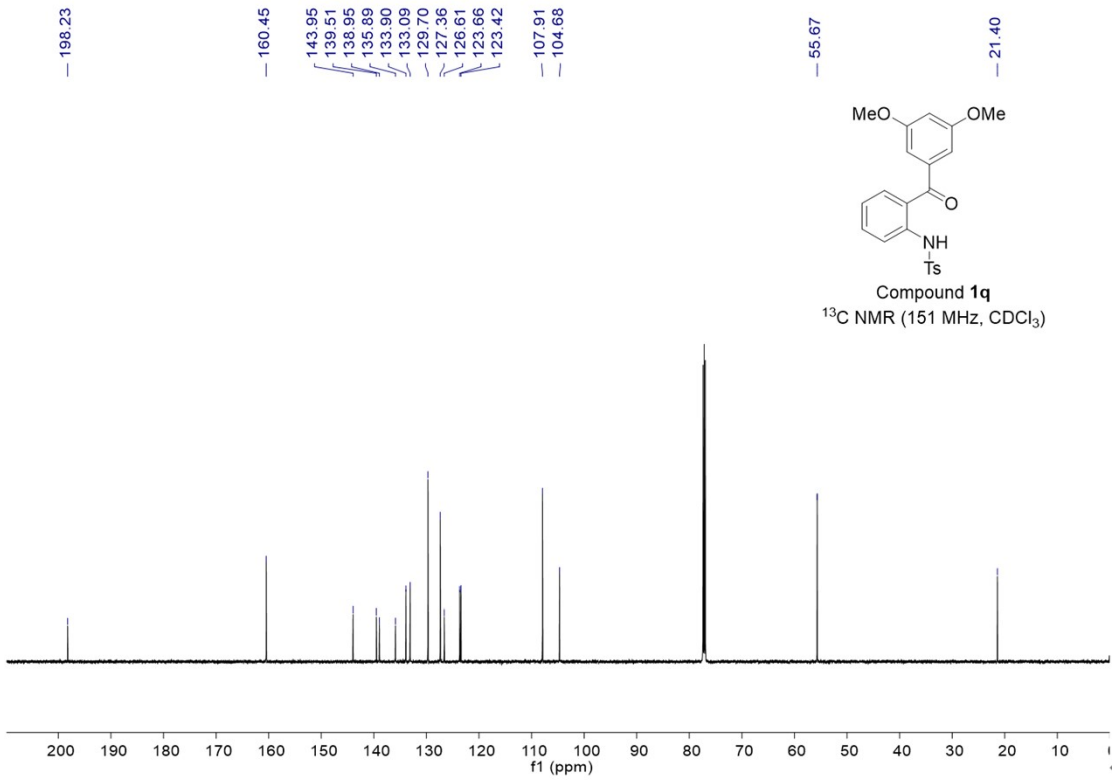
NMR spectra of N-(2-(1-naphthoyl)phenyl)-4-methylbenzenesulfonamide **(1o)**



NMR spectra of *N*-(2-(3,5-Dimethoxybenzoyl)phenyl)-4-methylbenzenesulfonamide

(1q)


9.865
7.786
7.773
7.547
7.534
7.522
7.509
7.496
7.406
7.393
7.106
7.094
7.081
7.054
7.040
6.625
6.460
3.793
2.236
MeO
OMe
O
NH
Ts
Compound 1q
1H NMR (600 MHz, CDCl3)
1.00
0.92
1.93
1.02
1.00
1.09
1.95
0.98
1.95
6.49
3.03
f1 (ppm)


198.23
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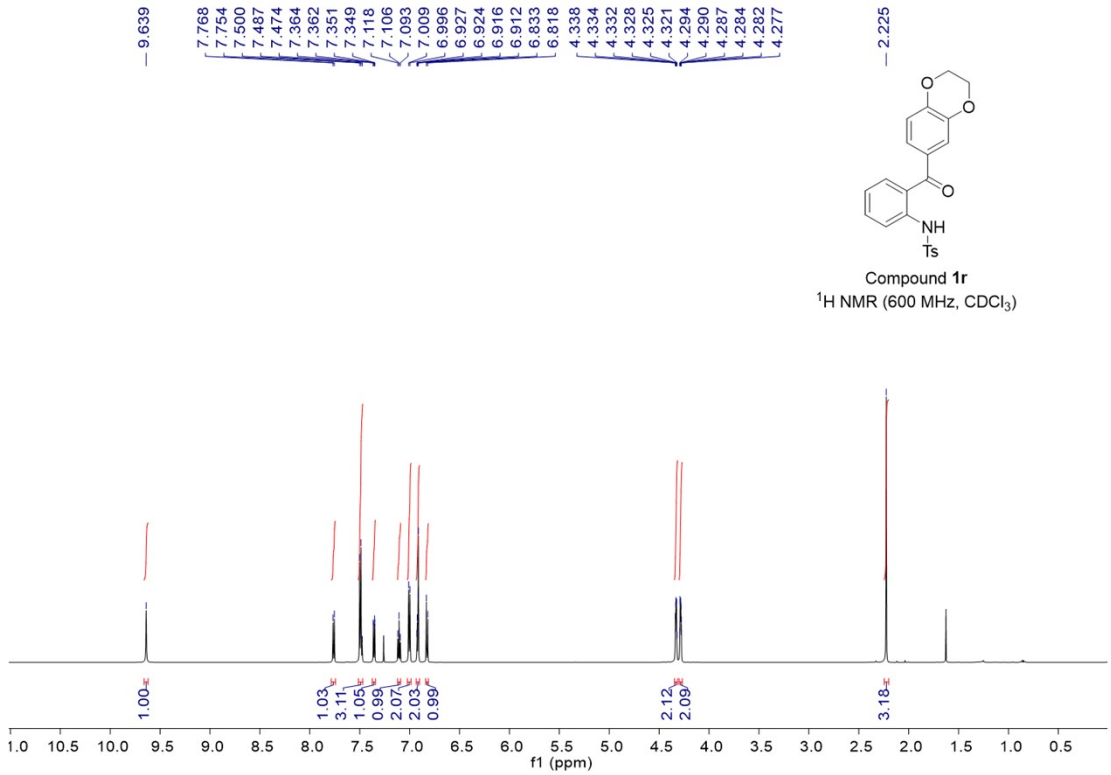
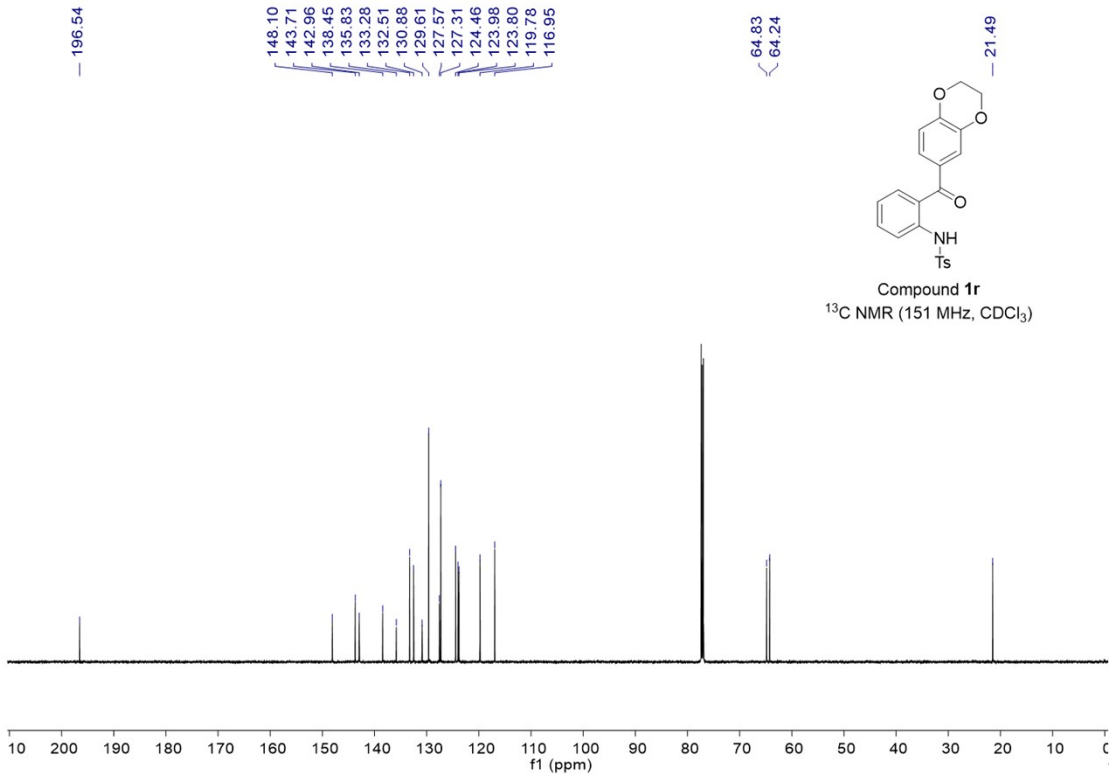
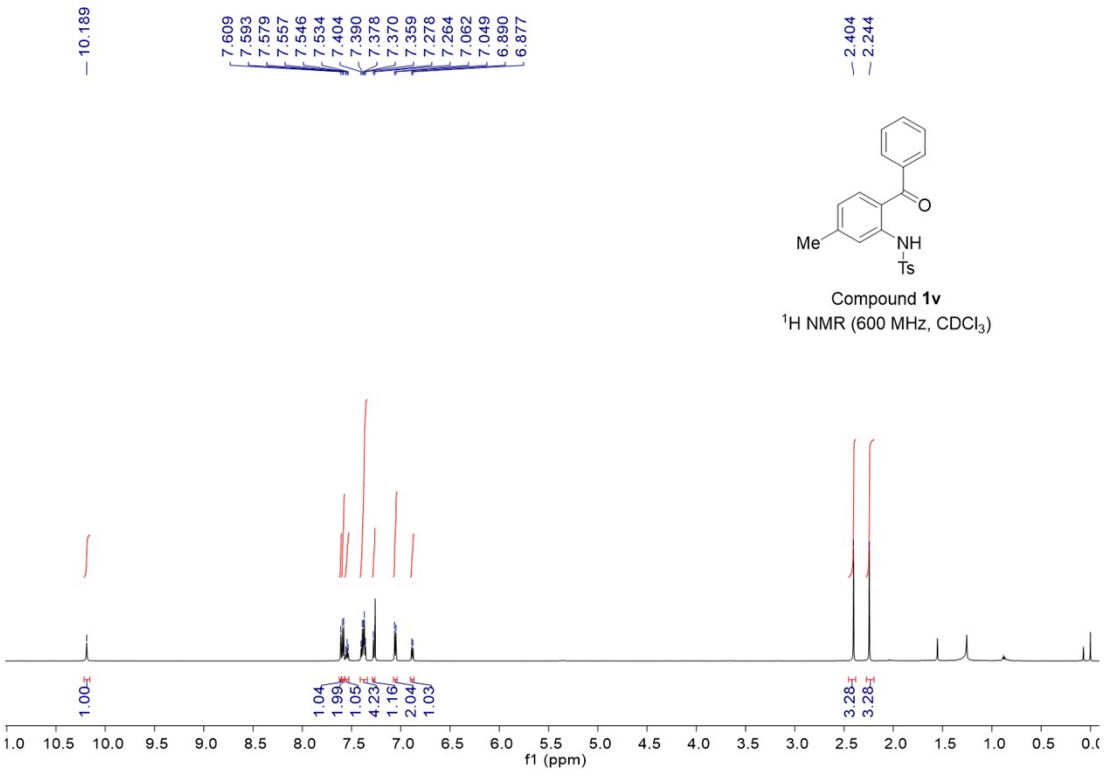
143.95
139.51
138.95
135.89
133.90
133.09
129.70
127.36
126.61
123.66
123.42
107.91
104.68
55.67
21.40
MeO
OMe
O
NH
Ts
Compound 1q
13C NMR (151 MHz, CDCl3)
f1 (ppm)

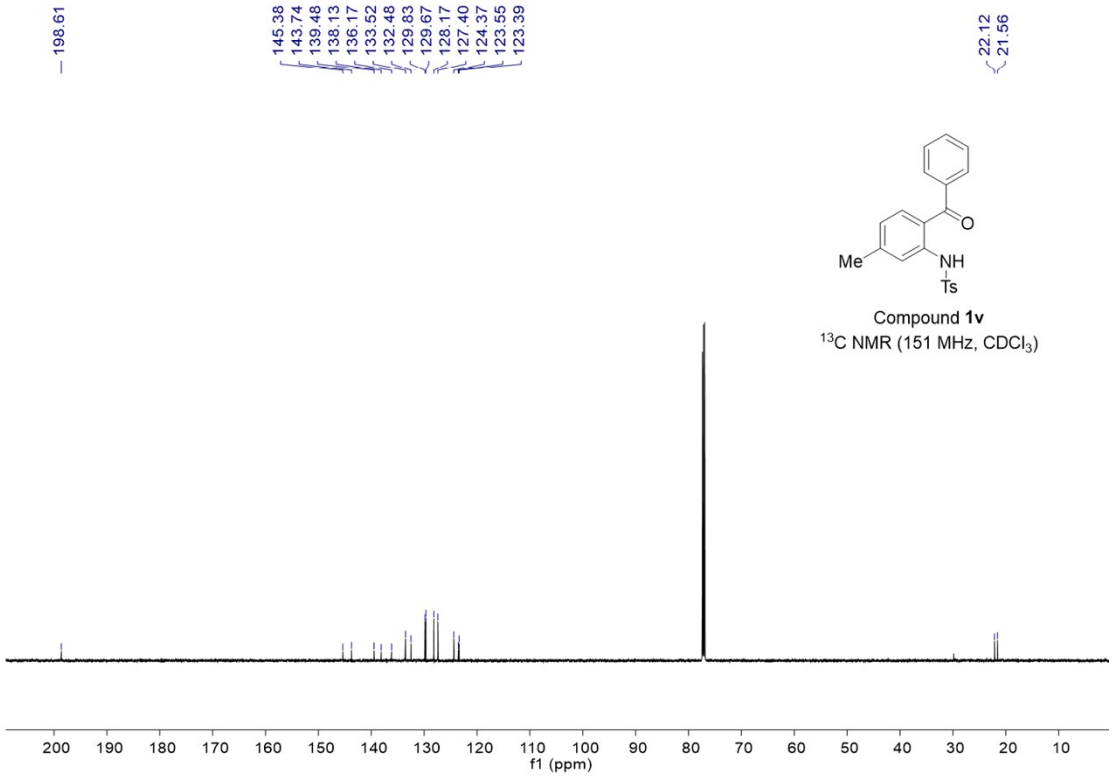
NMR spectra of *N*-(2-(2,3-Dihydrobenzo[*b*][1,4]dioxine-6-carbonyl)phenyl)-4-methylbenzenesulfonamide (**1r**)



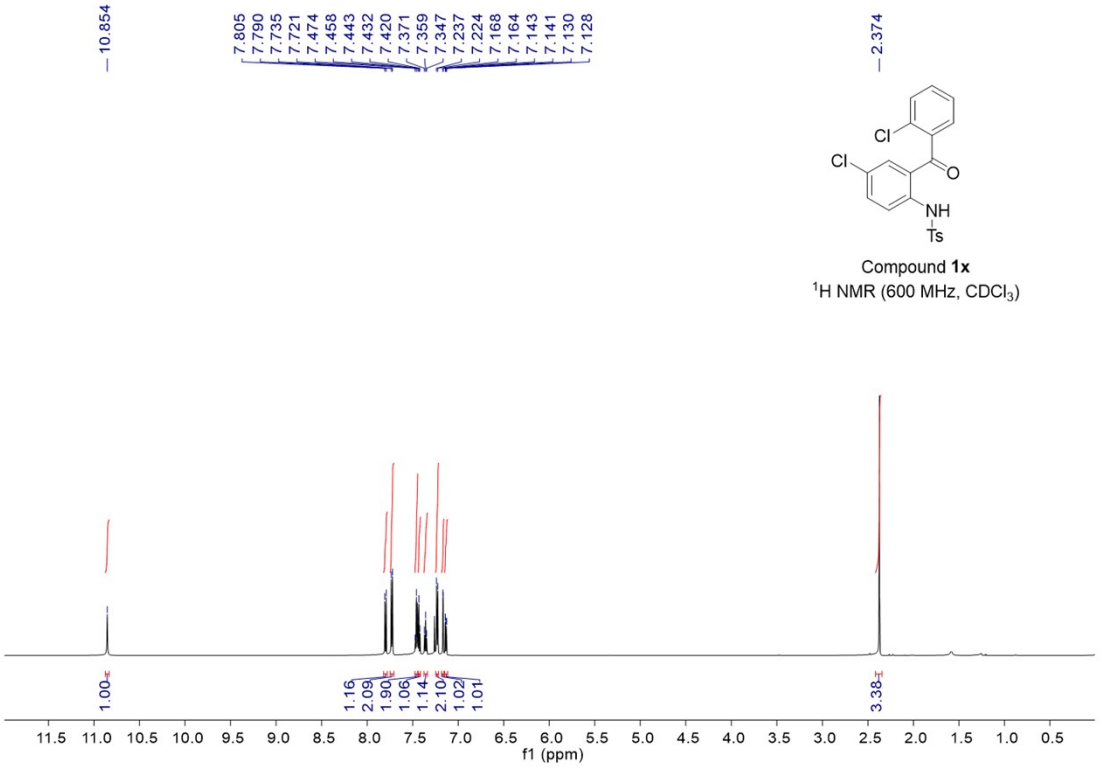


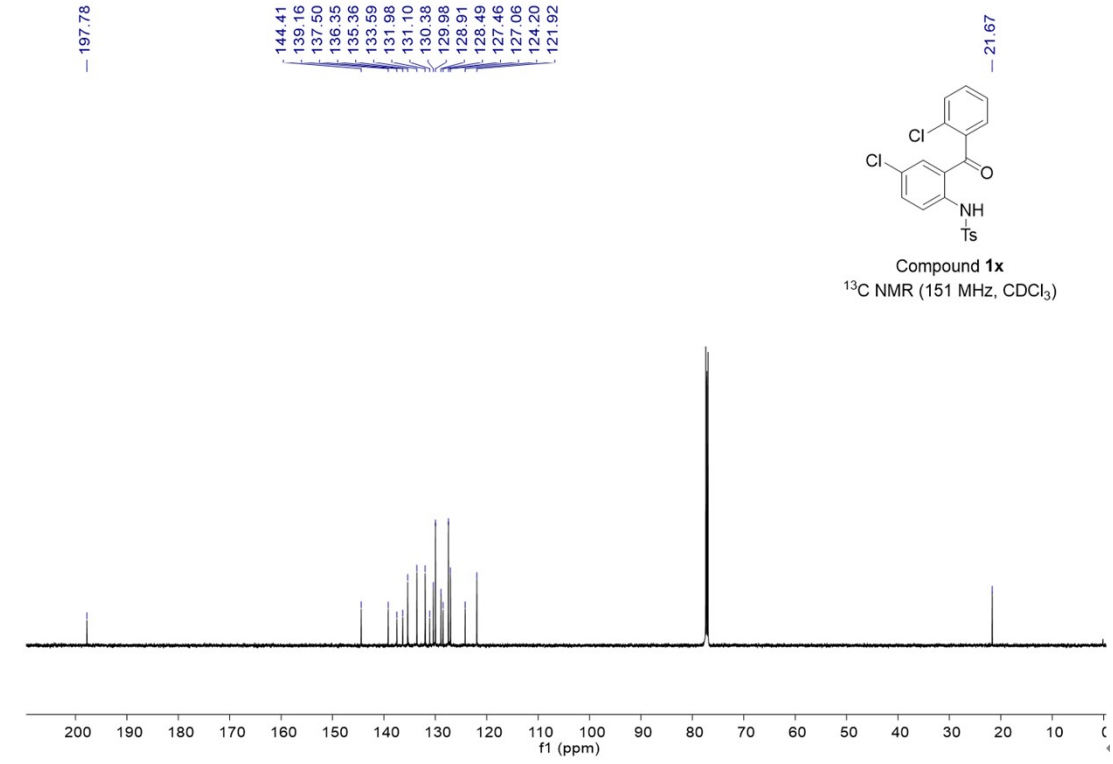
NMR spectra of *N*-(2-Benzoyl-5-methylphenyl)-4-methylbenzenesulfonamide (**1v**)



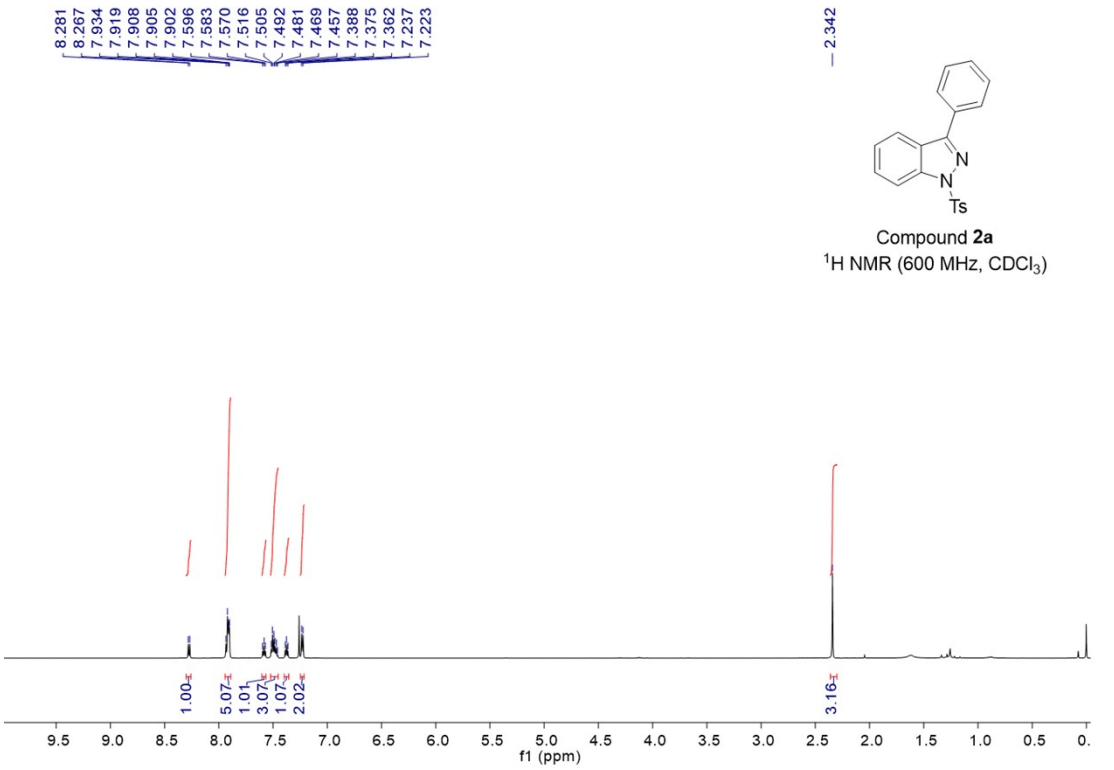


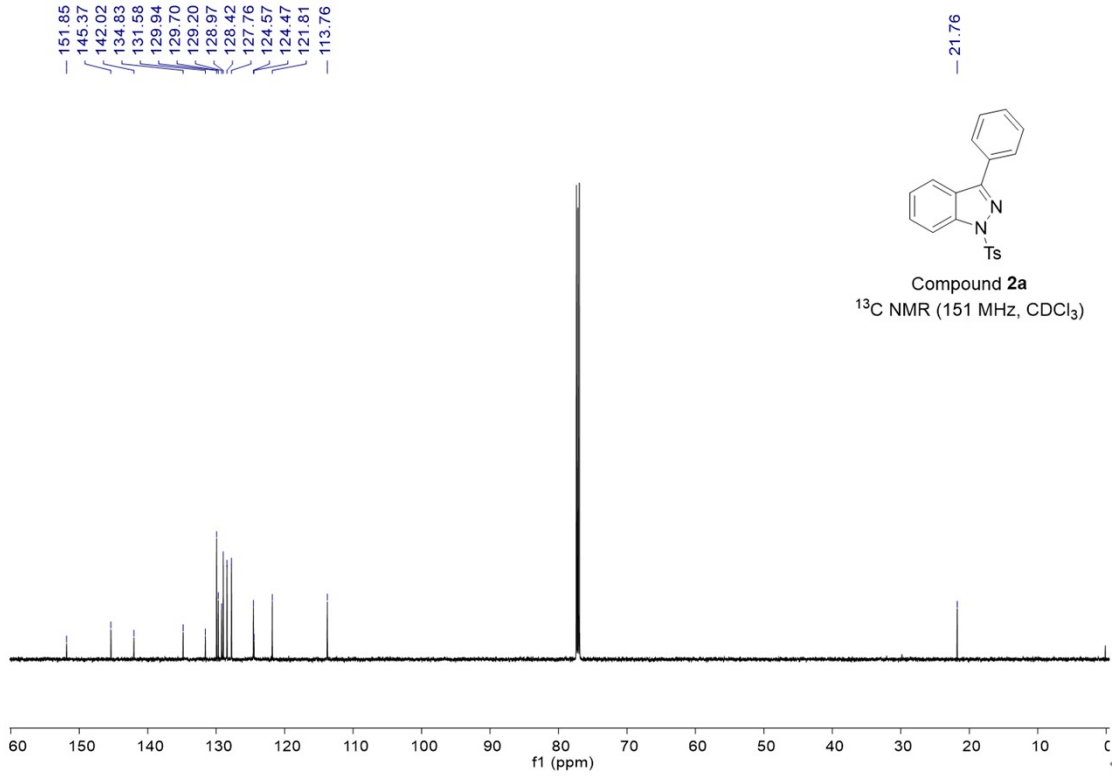
NMR spectra of *N*-(4-Chloro-2-(2-chlorobenzoyl)phenyl)-4-methylbenzenesulfonamide (**1x**)



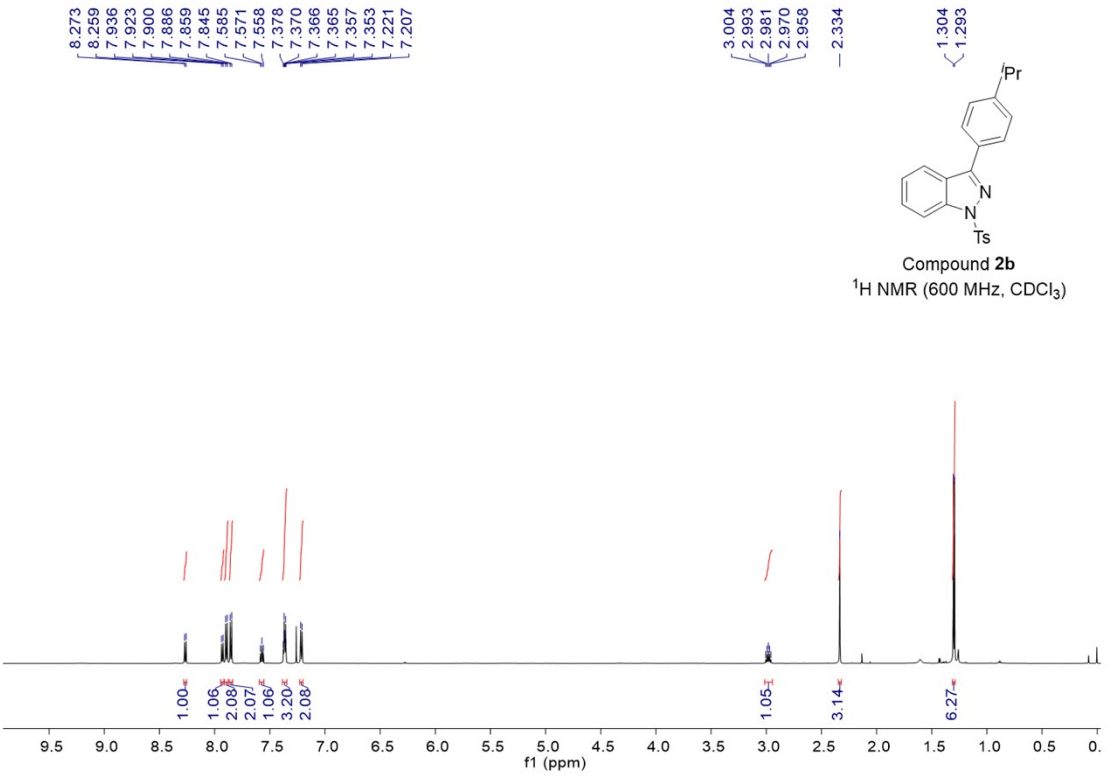


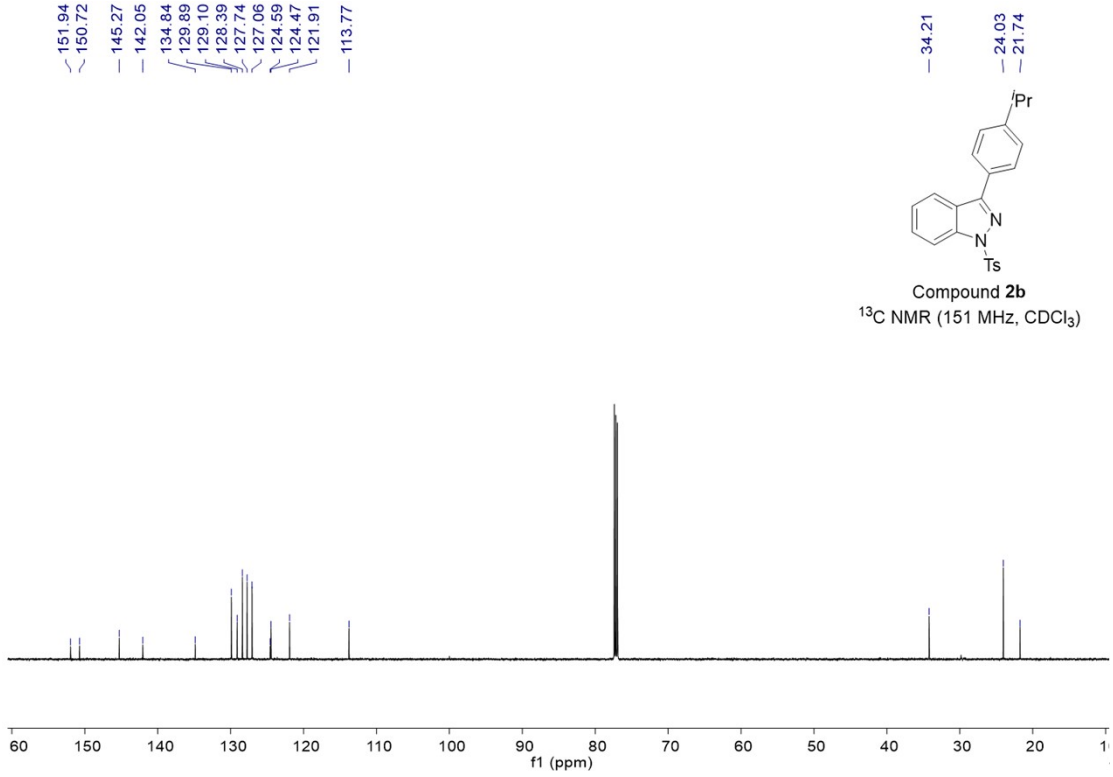
NMR spectra of 3-Phenyl-1-tosyl-1*H*-indazole (**2a**)



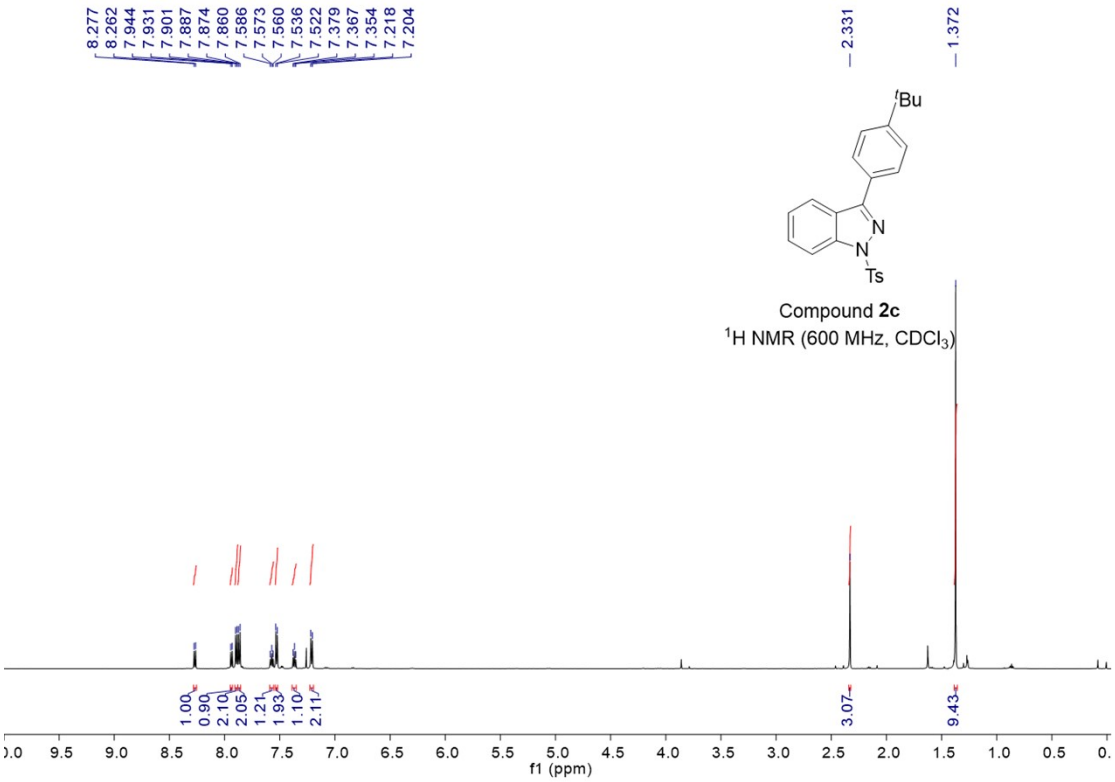


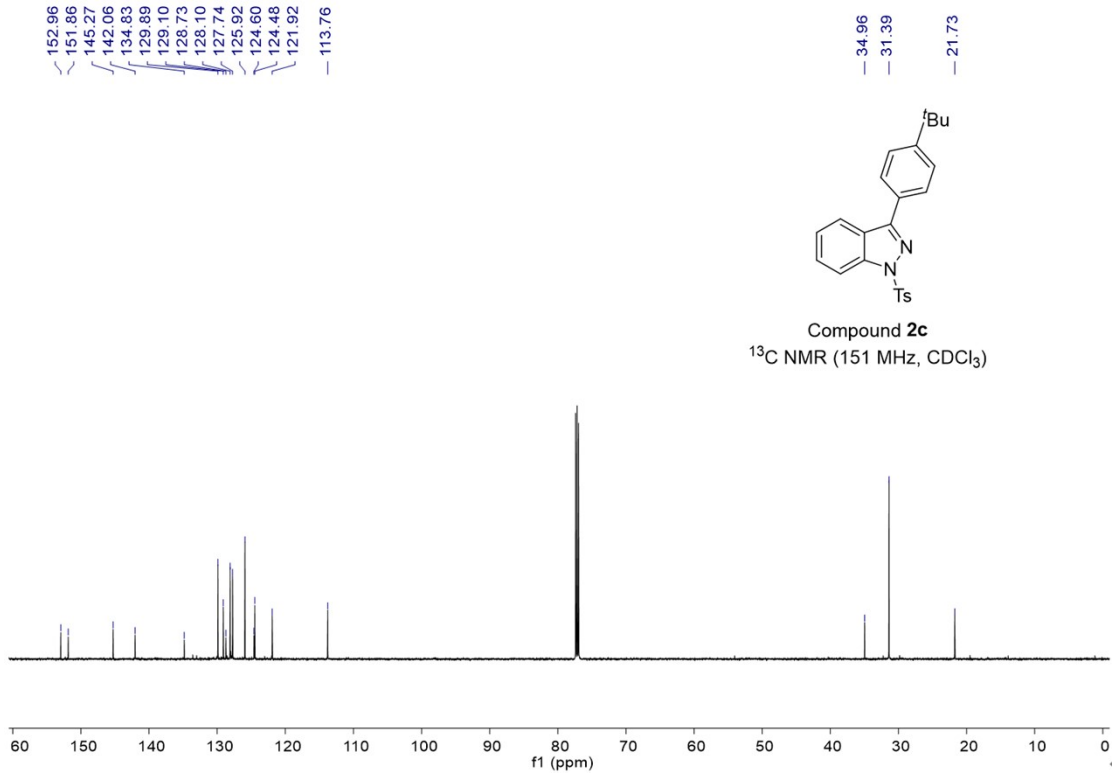
NMR spectra of 3-(4-isopropylphenyl)-1-tosyl-1*H*-indazole (**2b**)



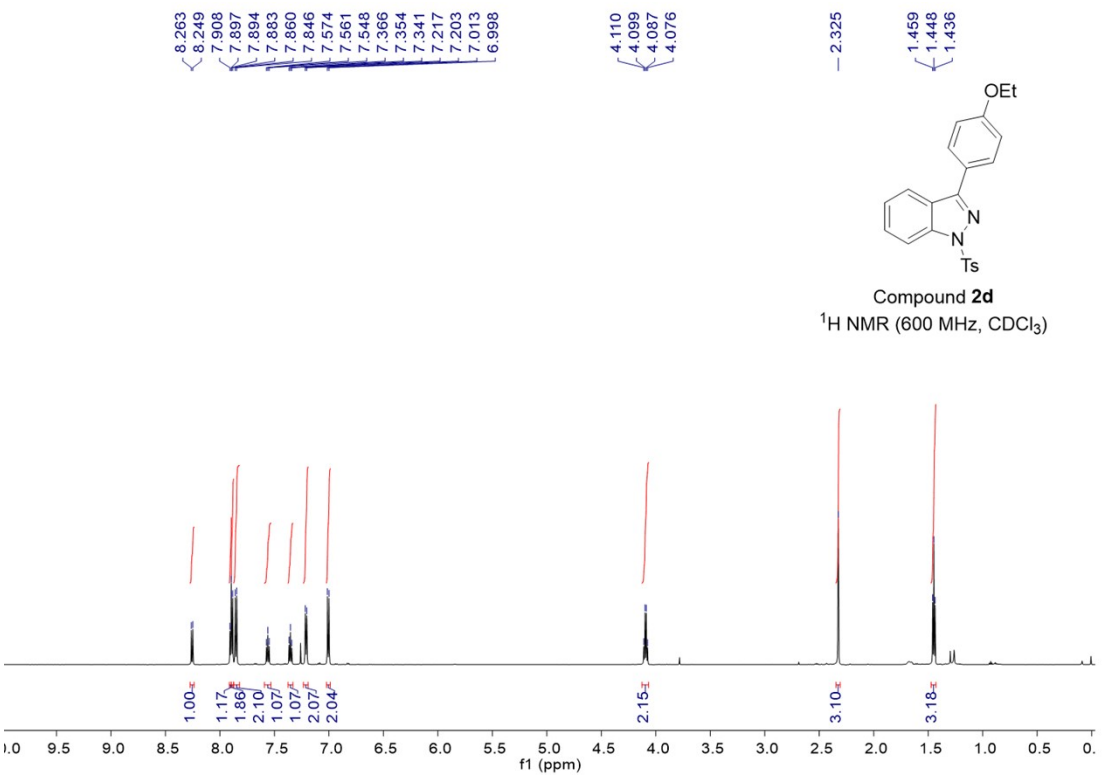


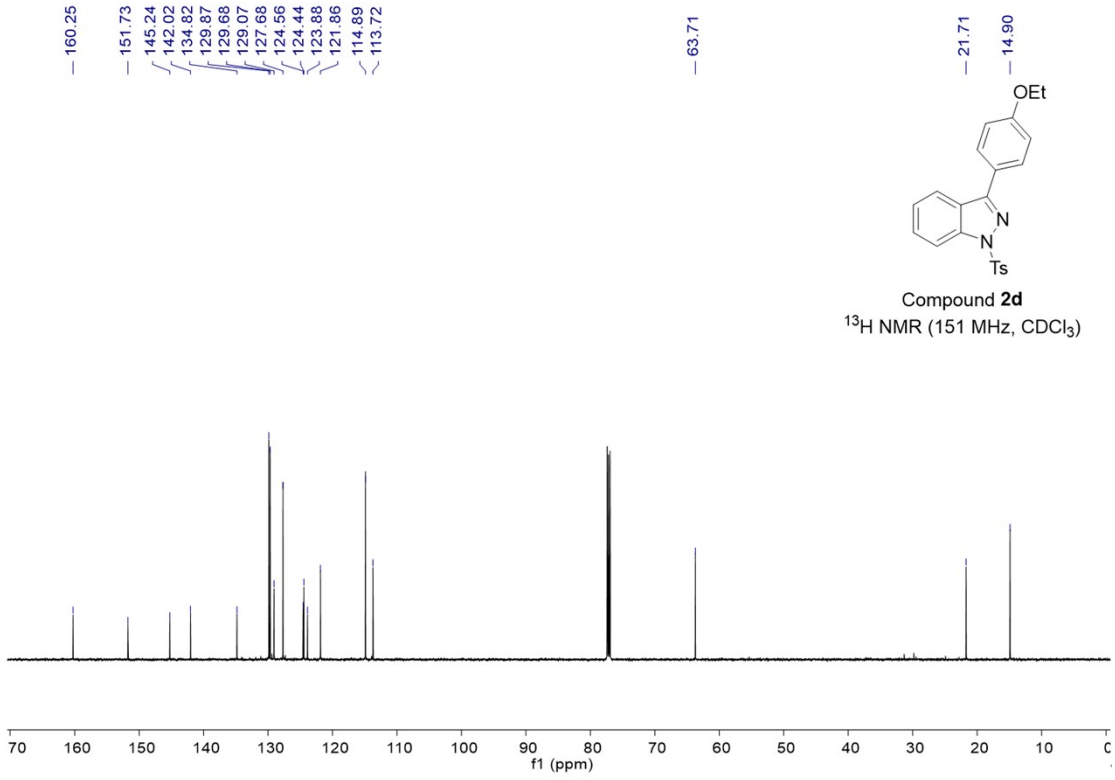
NMR spectra of 3-(4-(*tert*-Butyl)phenyl)-1-tosyl-1*H*-indazole (**2c**)



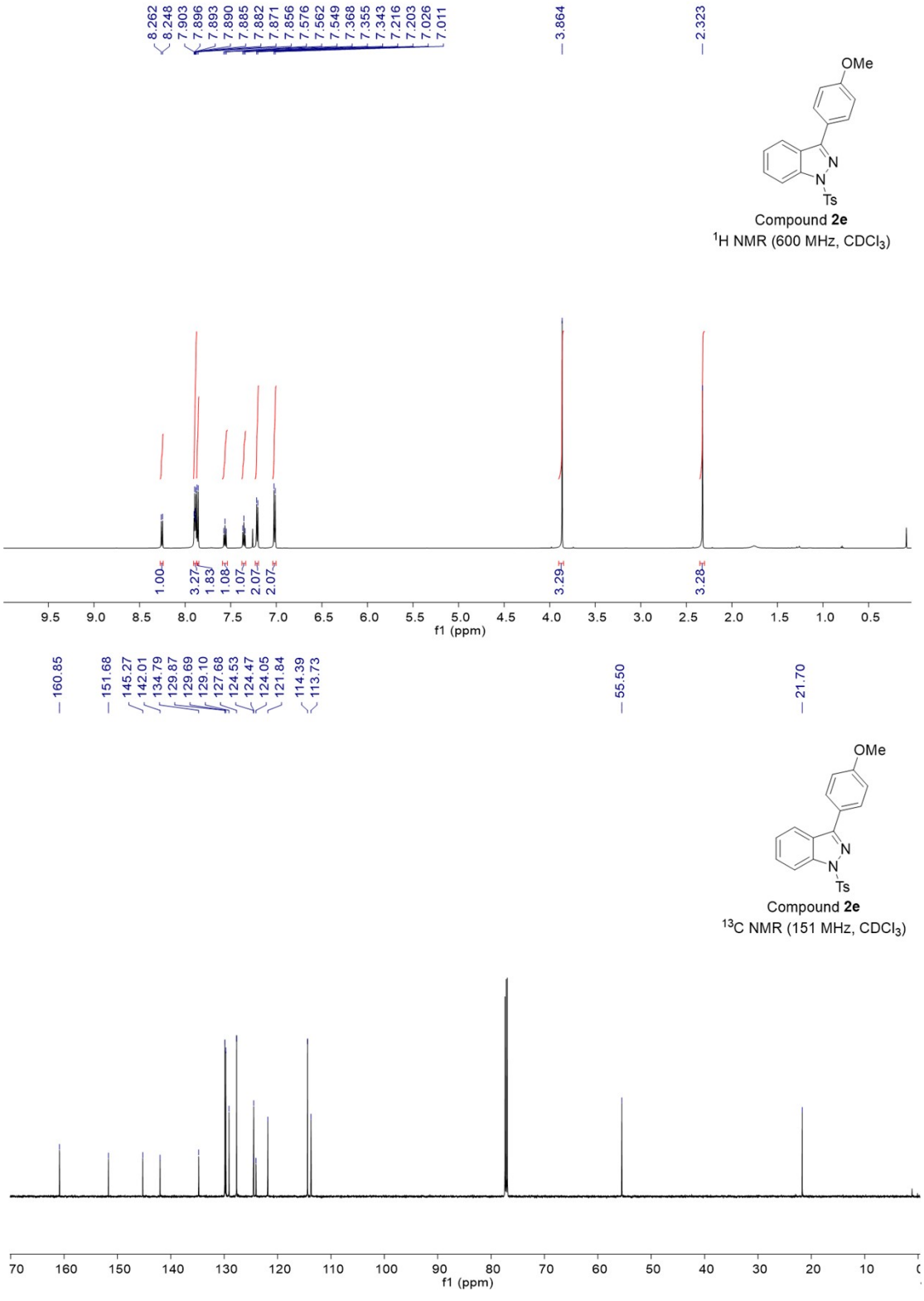


NMR spectra of 3-(4-Ethoxyphenyl)-1-tosyl-1*H*-indazole (**2d**)

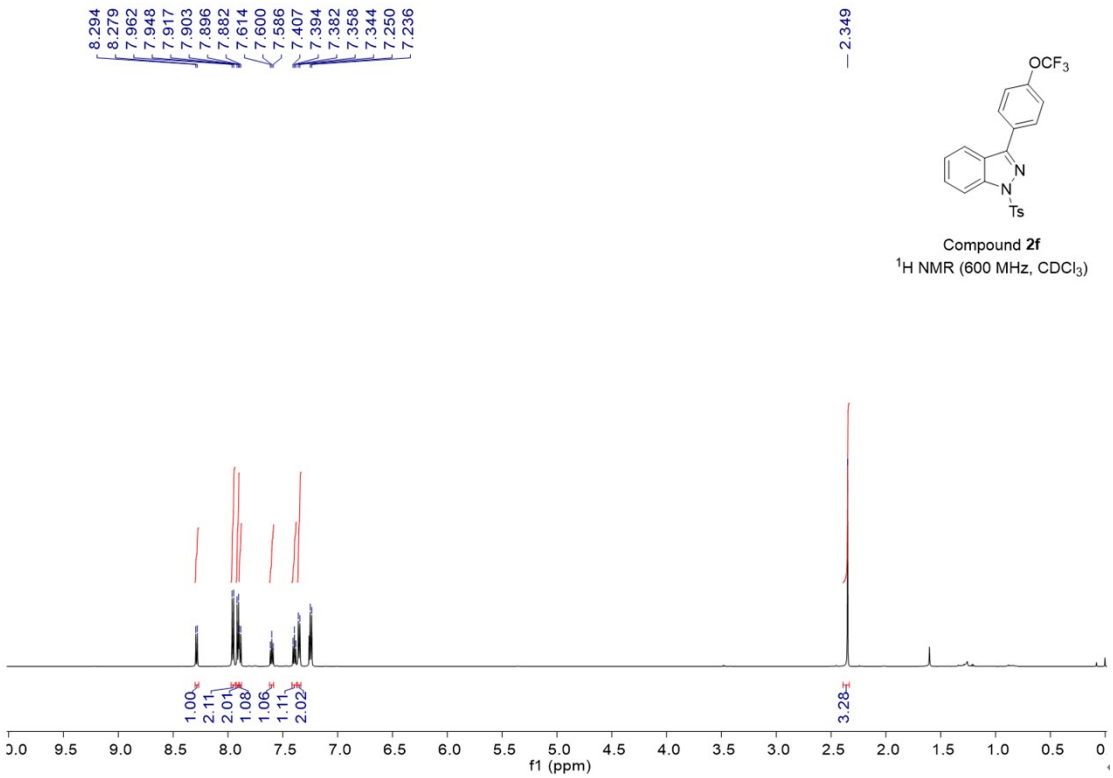




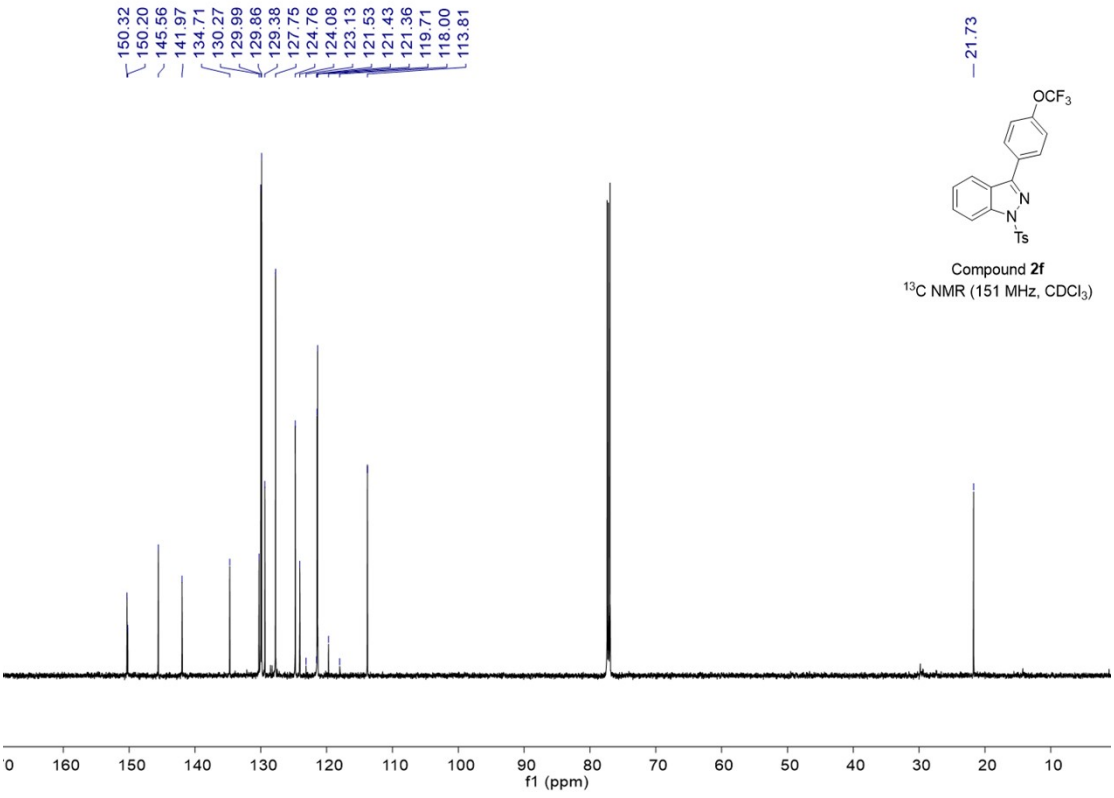
NMR spectra of 3-(4-Methoxyphenyl)-1-tosyl-1*H*-indazole (**2e**)



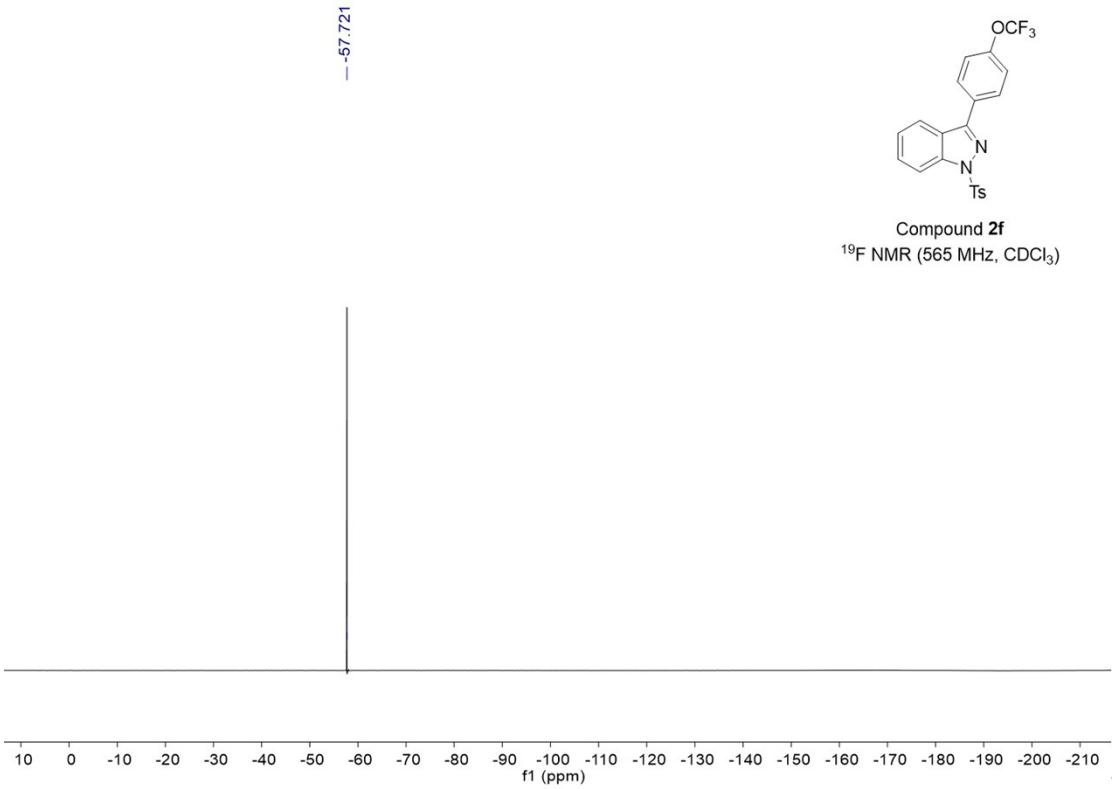
NMR spectra of 1-tosyl-3-(4-(Trifluoromethoxy)phenyl)-1*H*-indazole (**2f**)



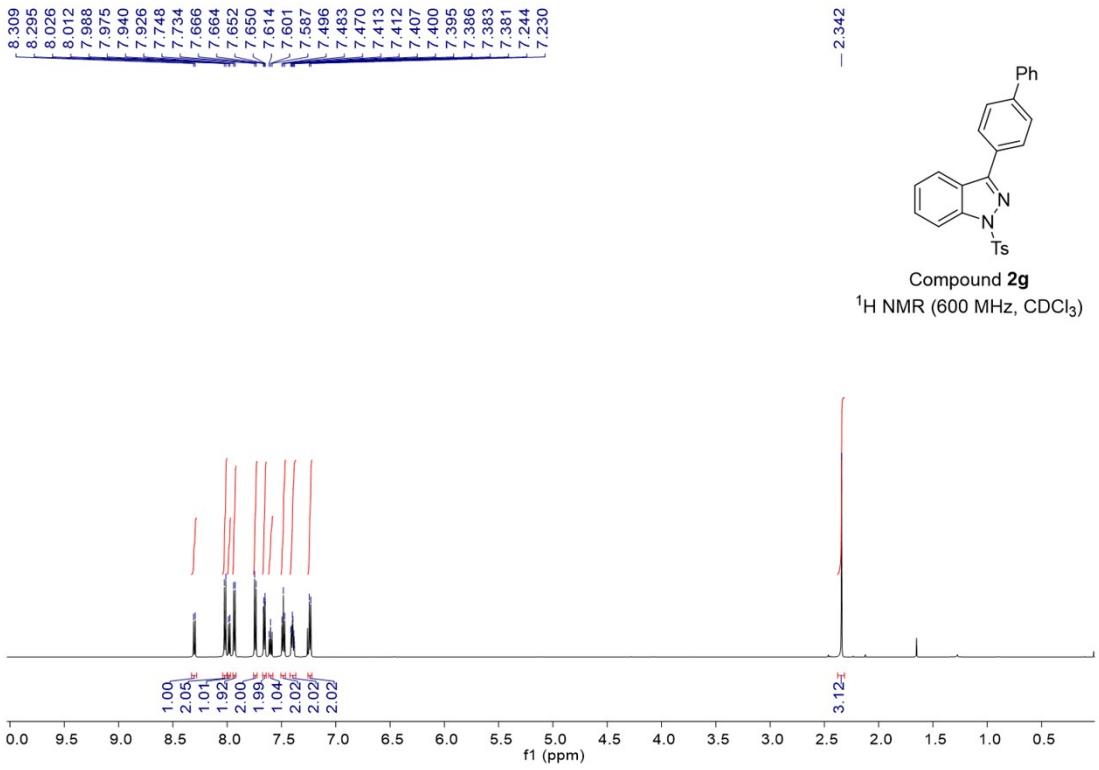
Compound **2f**
^{1}H NMR (600 MHz, $CDCl_3$)

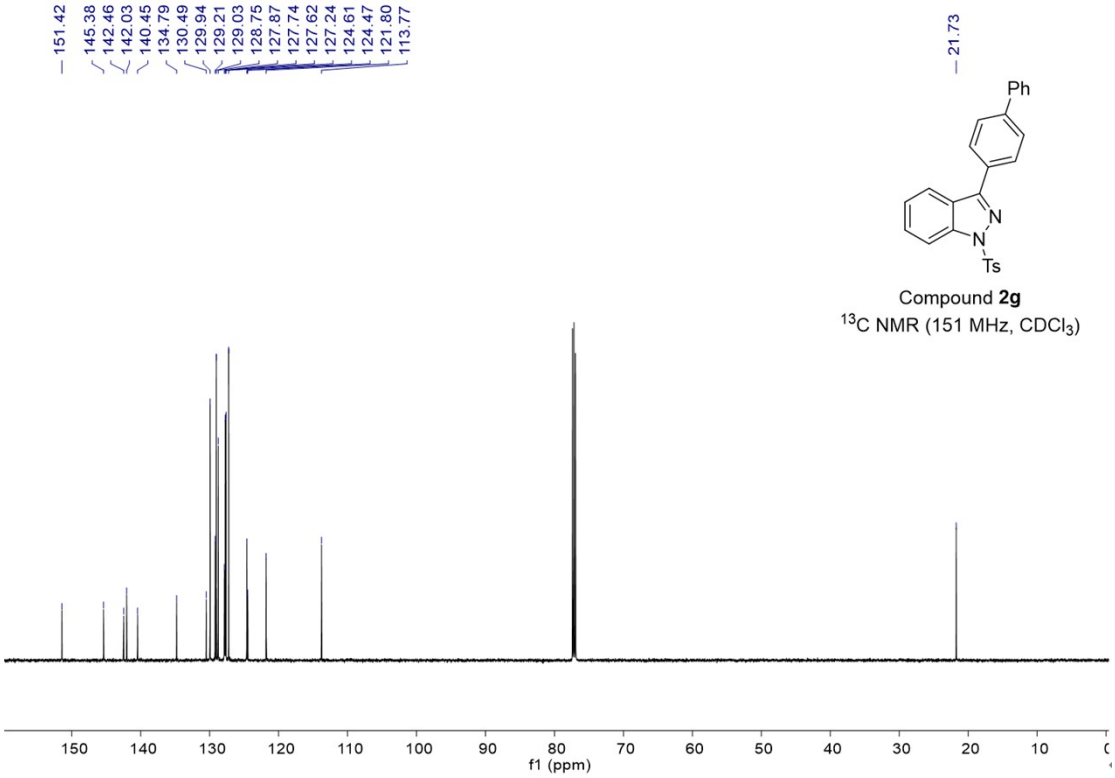


Compound **2f**
^{13}C NMR (151 MHz, $CDCl_3$)

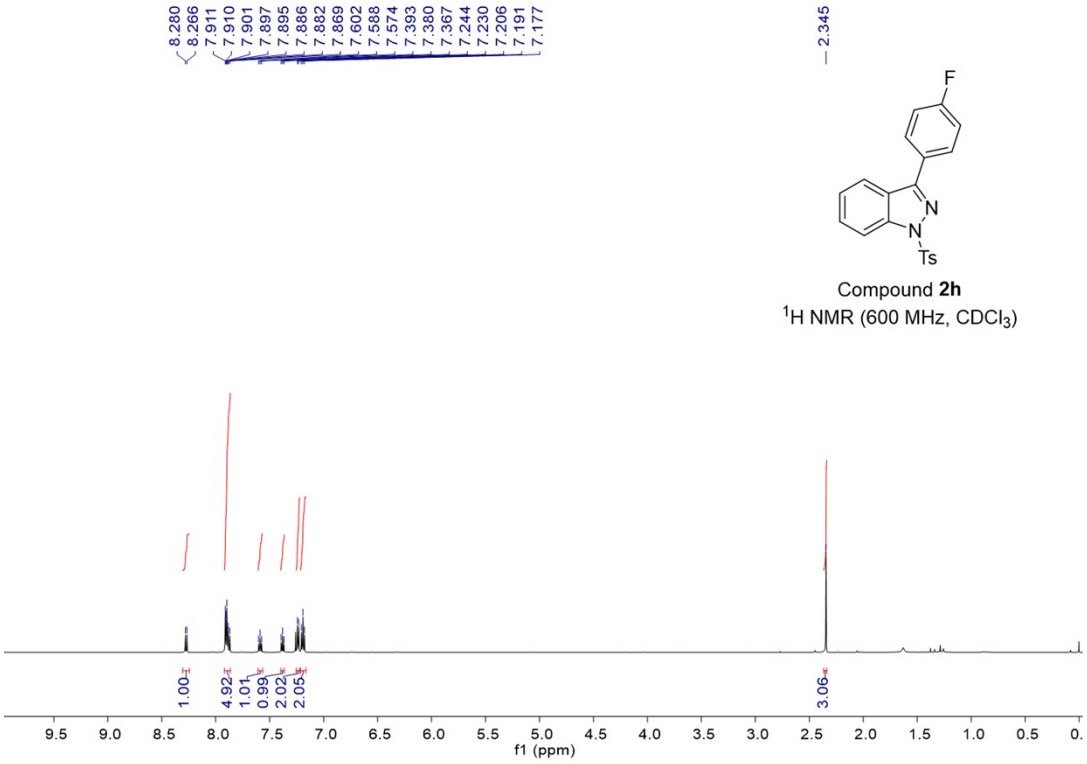


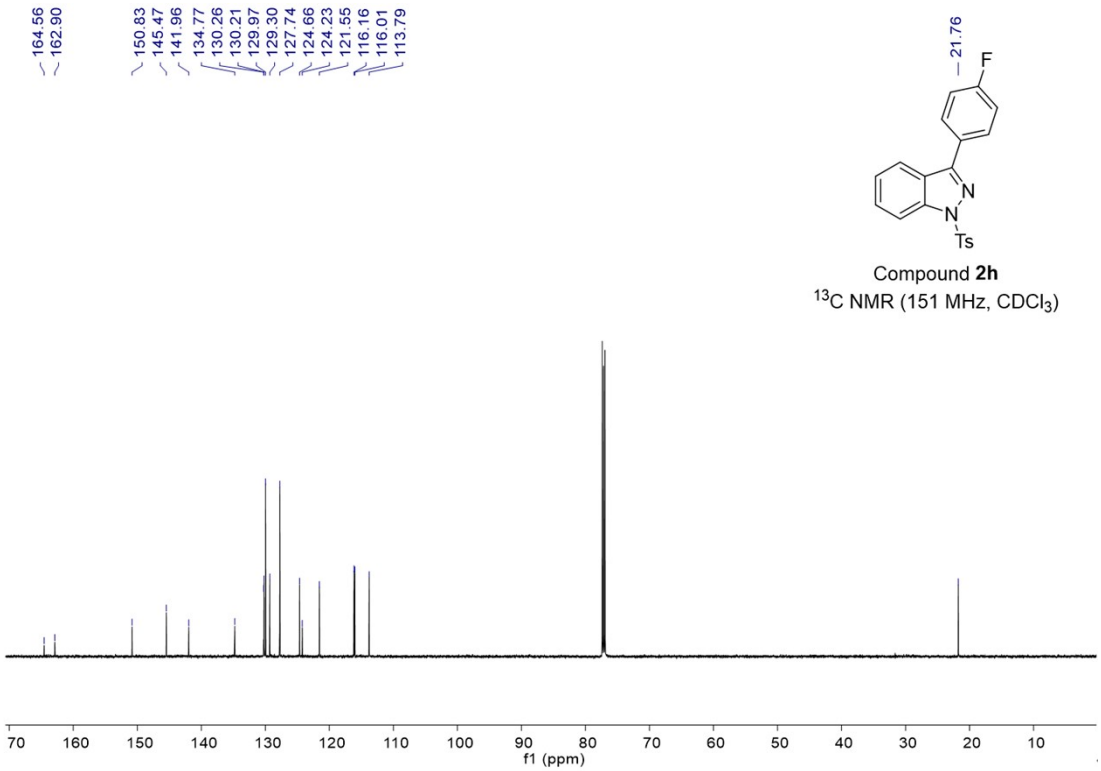
NMR spectra of 3-([1,1'-biphenyl]-4-yl)-1-tosyl-1*H*-indazole (**2g**)





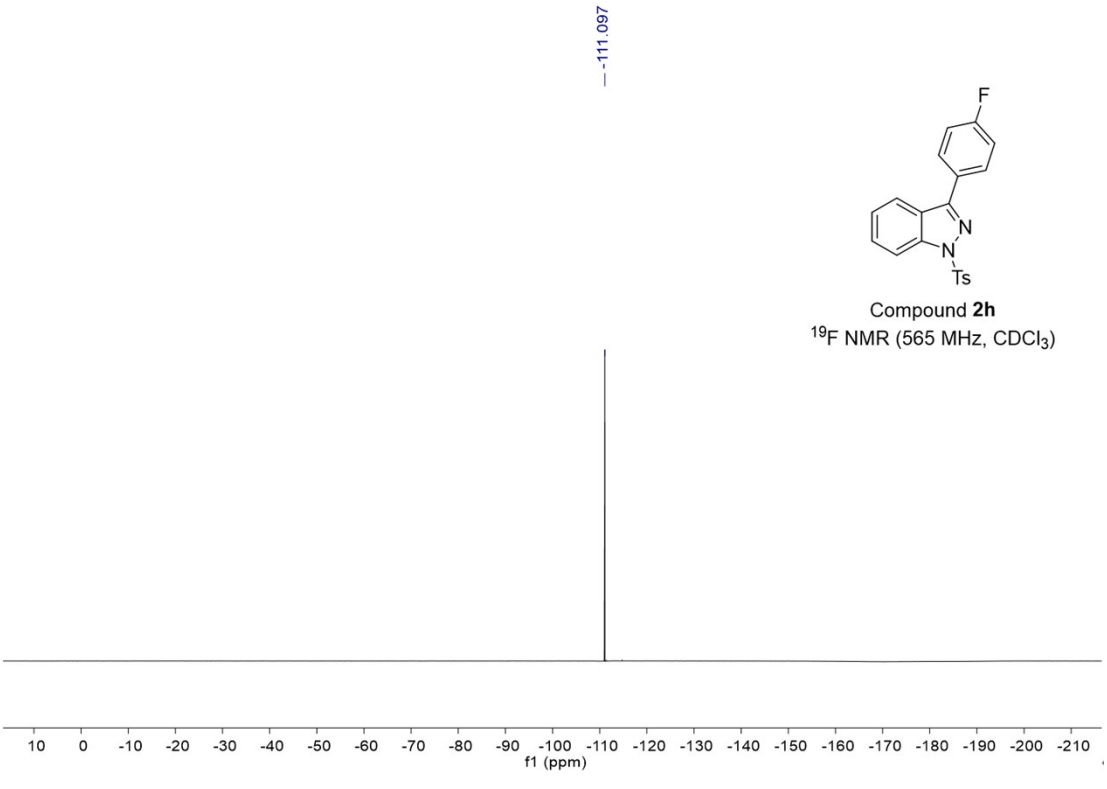
NMR spectra of 3-(4-Fluorophenyl)-1-tosyl-1*H*-indazole (**2h**)





Compound **2h**

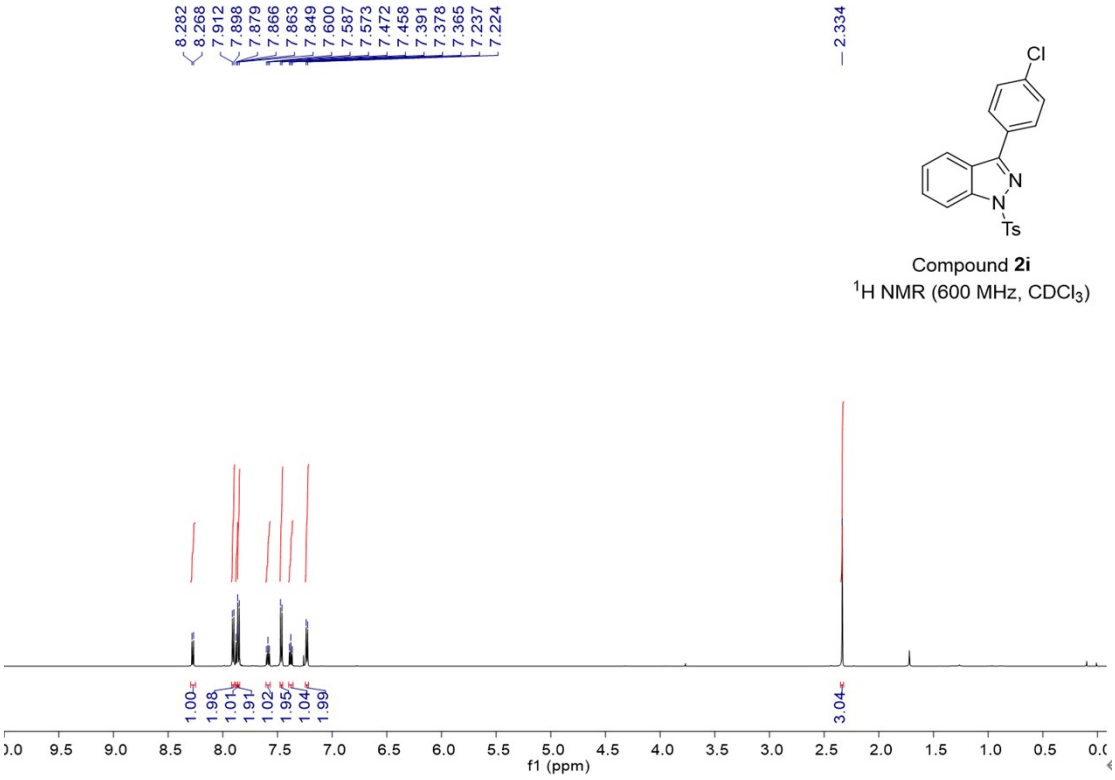
^{13}C NMR (151 MHz, $CDCl_3$)



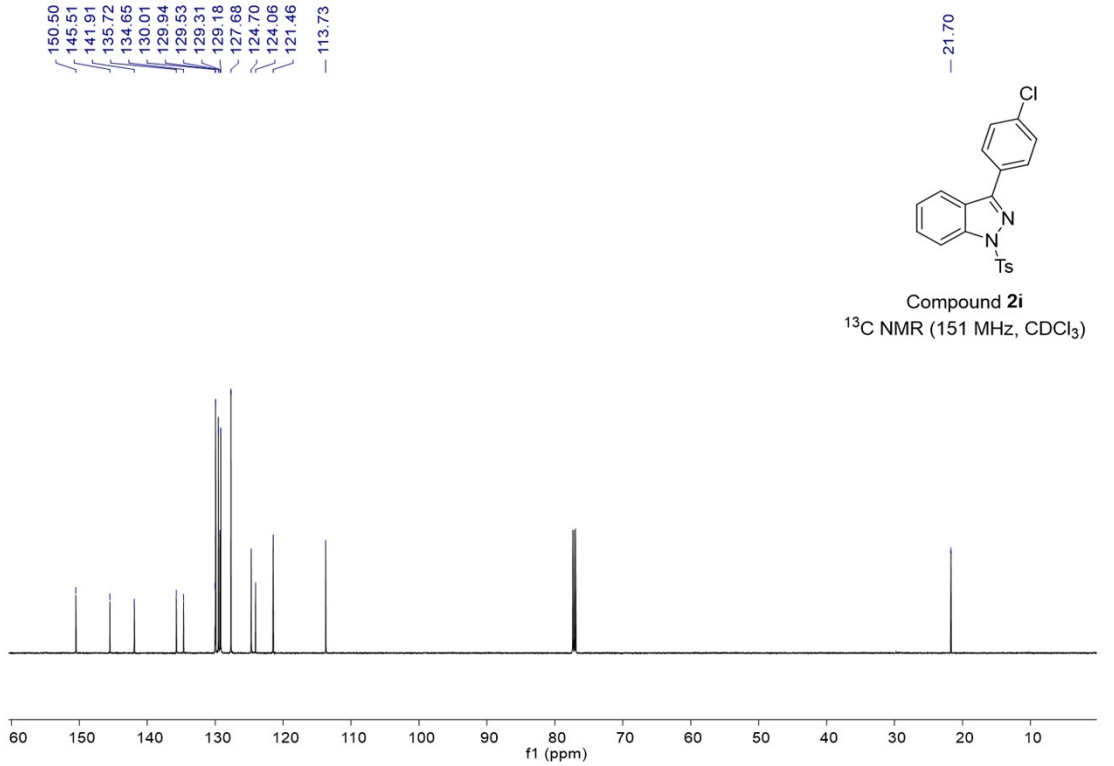
Compound **2h**

^{19}F NMR (565 MHz, $CDCl_3$)

NMR spectra of 3-(4-Chlorophenyl)-1-tosyl-1*H*-indazole (**2i**)

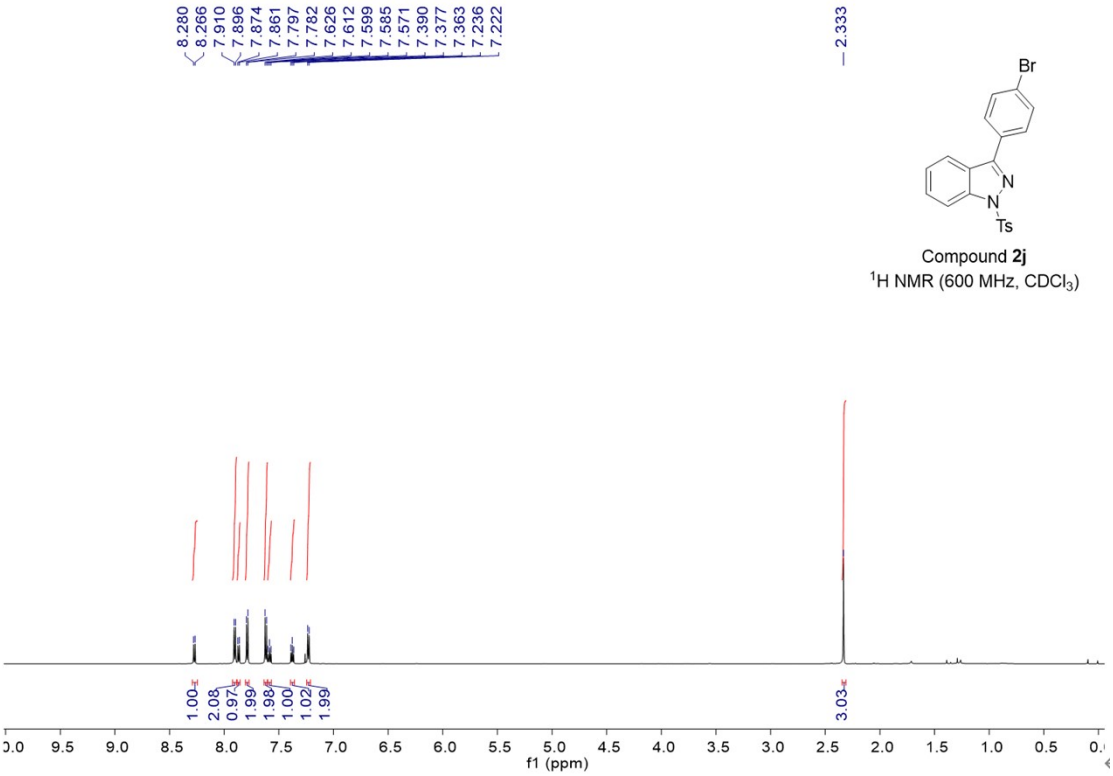


Compound **2i**
^{1}H NMR (600 MHz, $CDCl_3$)

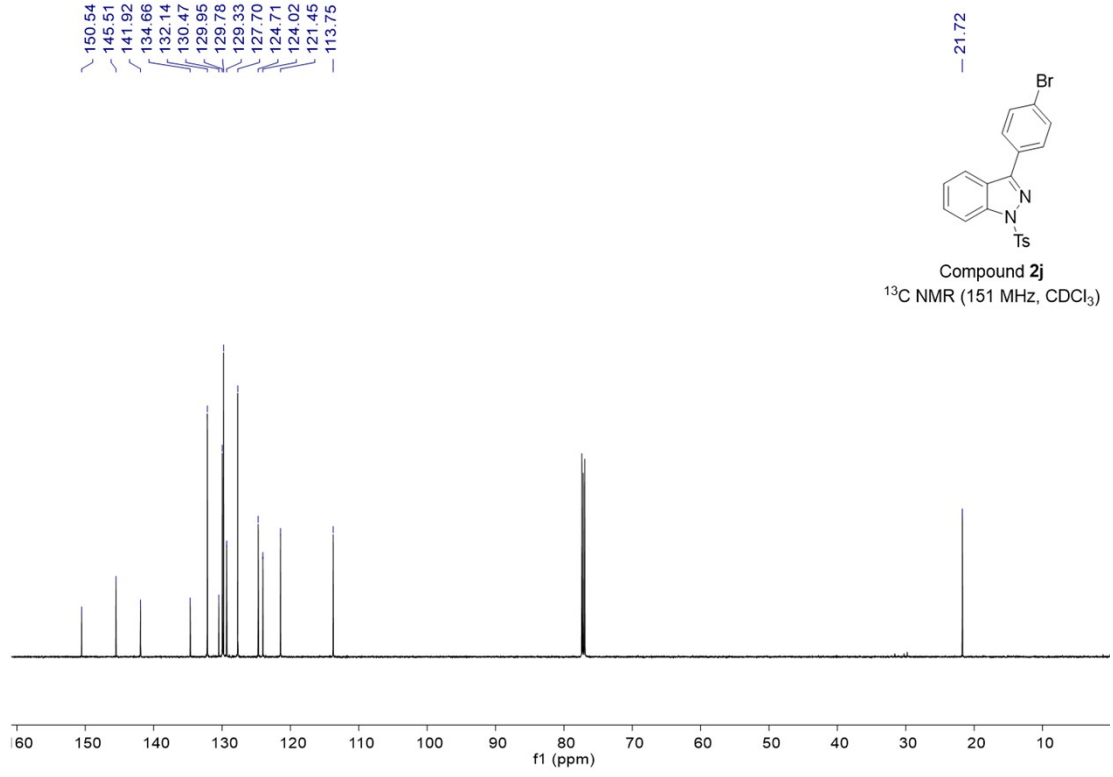


Compound **2i**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 3-(4-Bromophenyl)-1-tosyl-1*H*-indazole (**2j**)

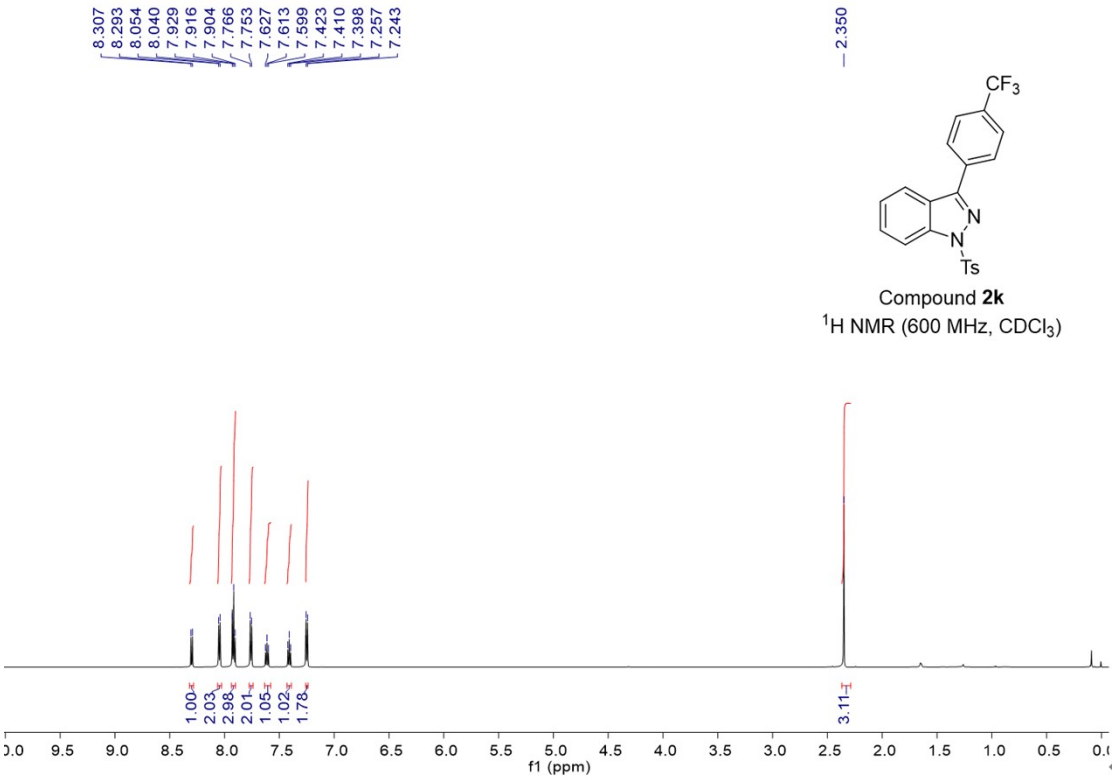


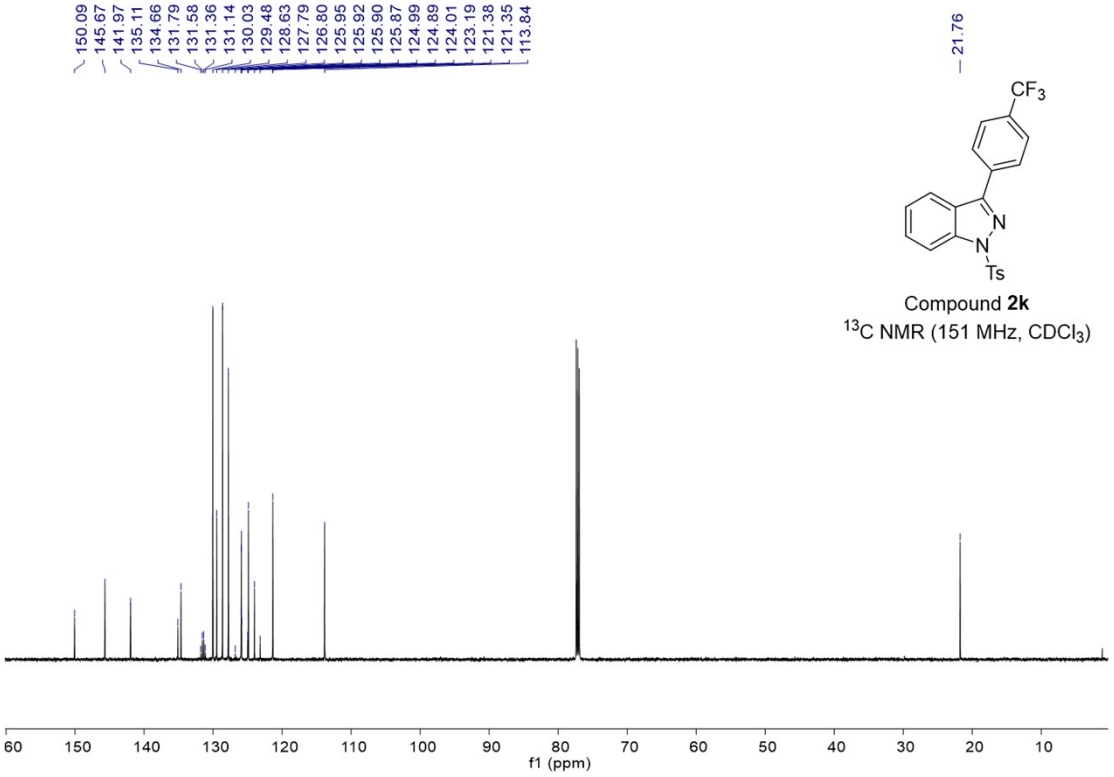
Compound **2j**
^{1}H NMR (600 MHz, $CDCl_3$)

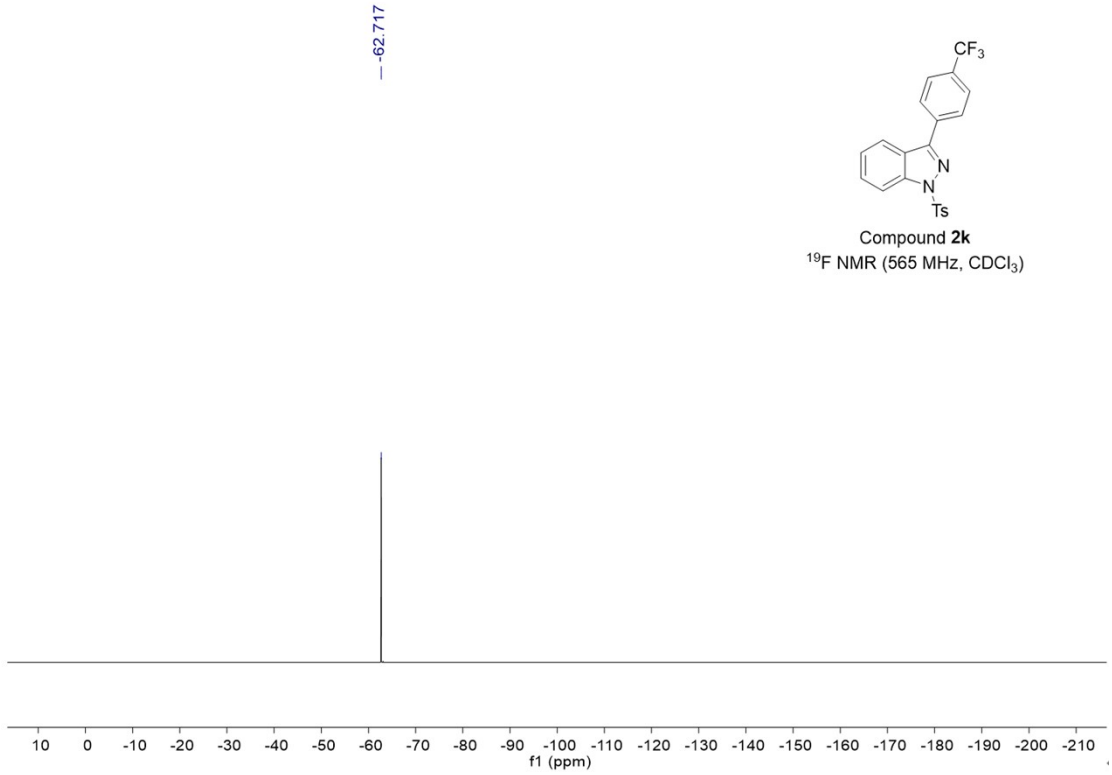


Compound **2j**
^{13}C NMR (151 MHz, $CDCl_3$)

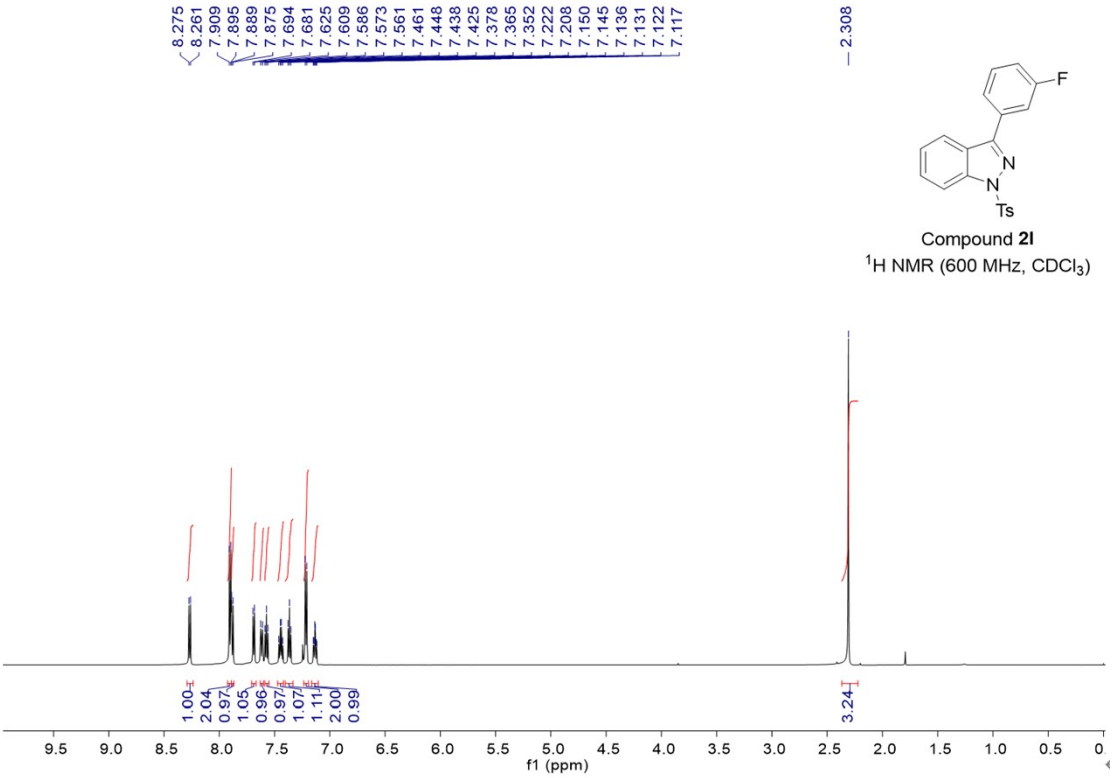
NMR spectra of 1-tosyl-3-(4-(trifluoromethyl)phenyl)-1*H*-indazole (**2k**)

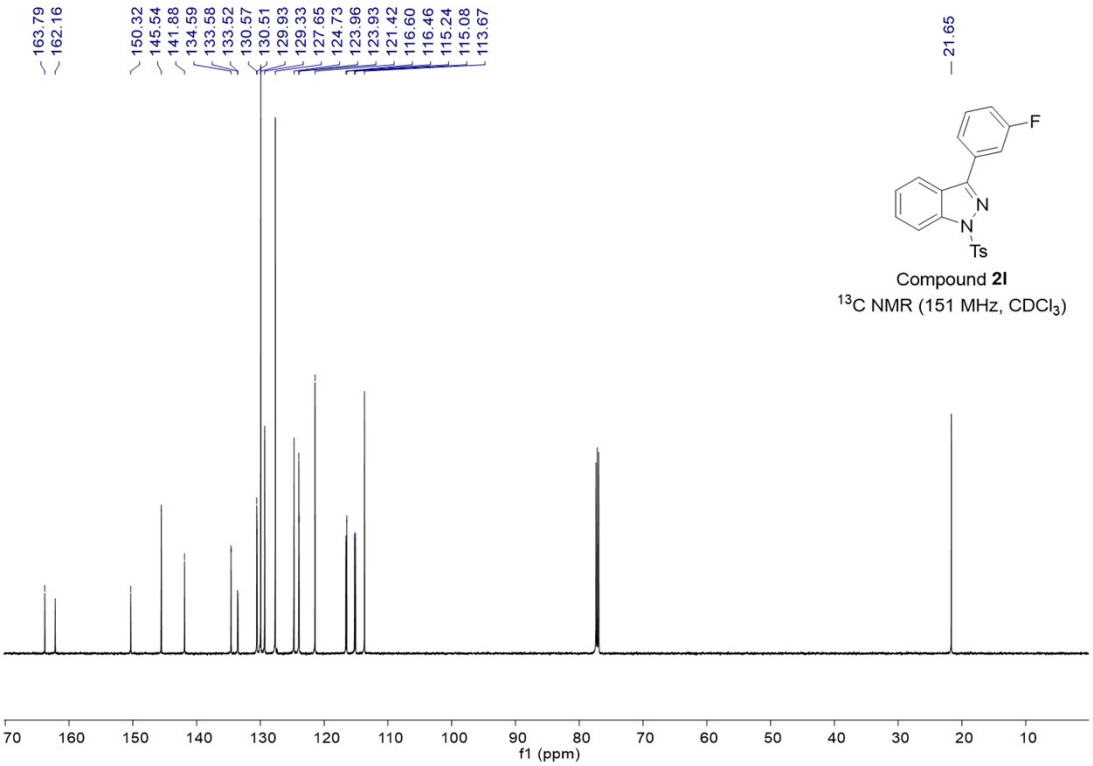






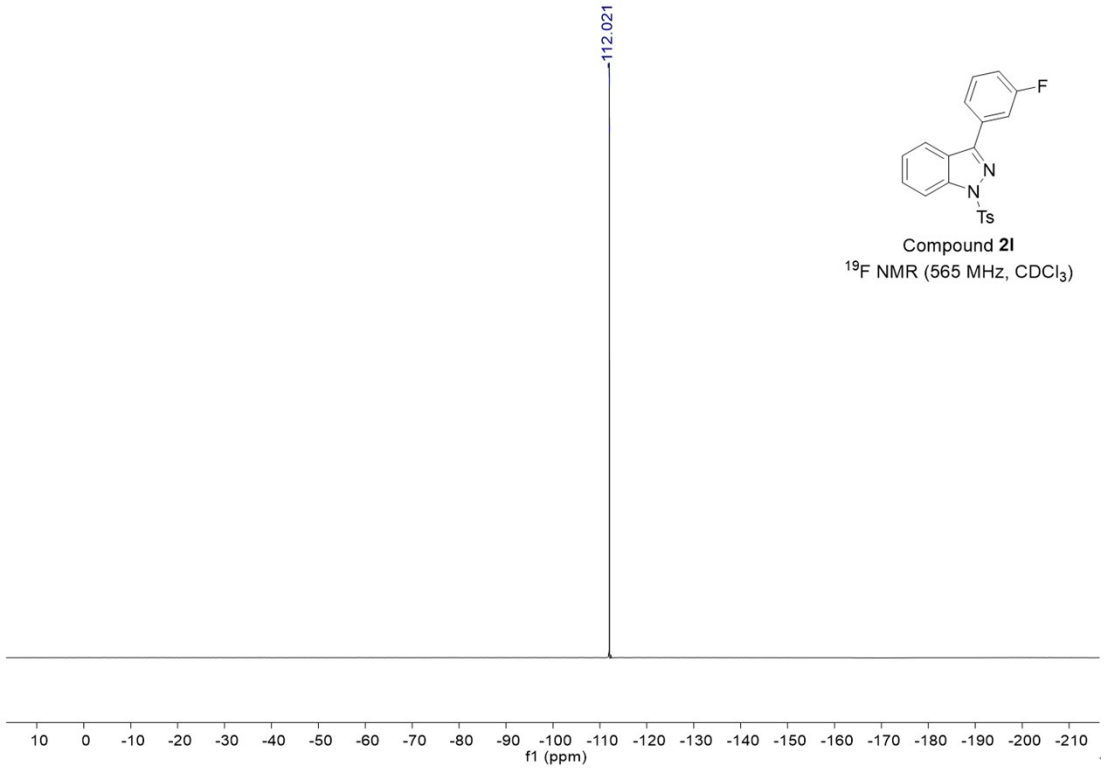
NMR spectra of 3-(3-Fluorophenyl)-1-tosyl-1*H*-indazole (**2l**)





Compound **2l**

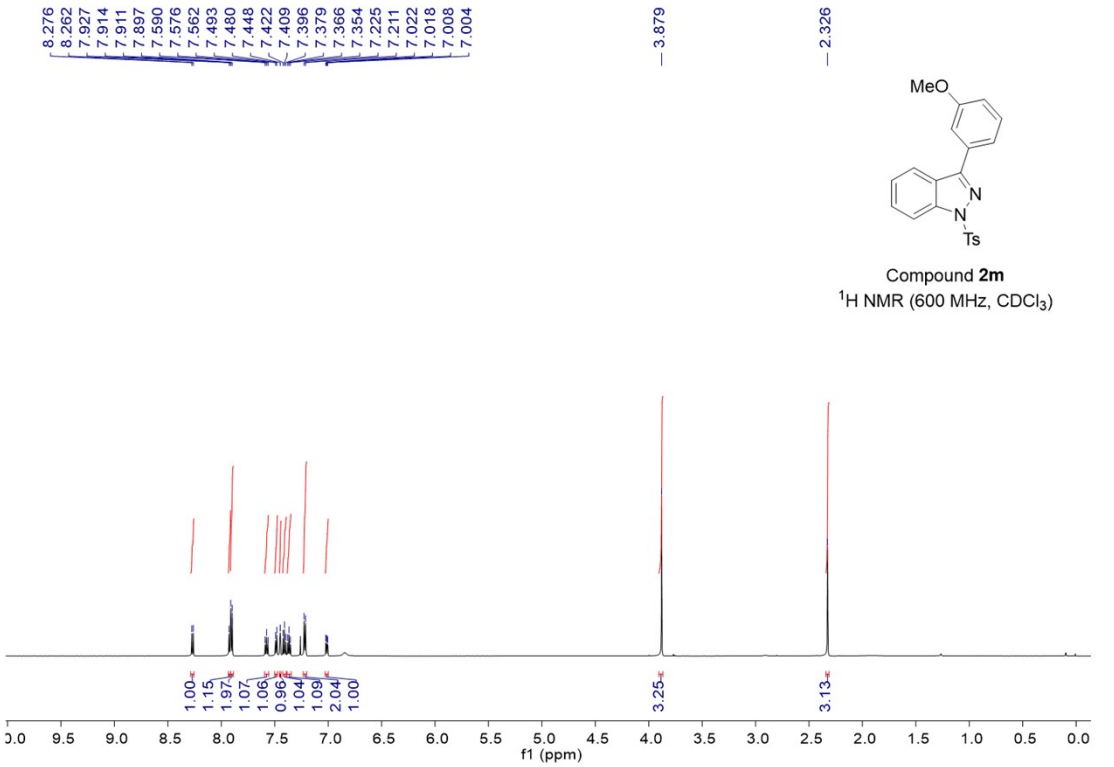
^{13}C NMR (151 MHz, $CDCl_3$)



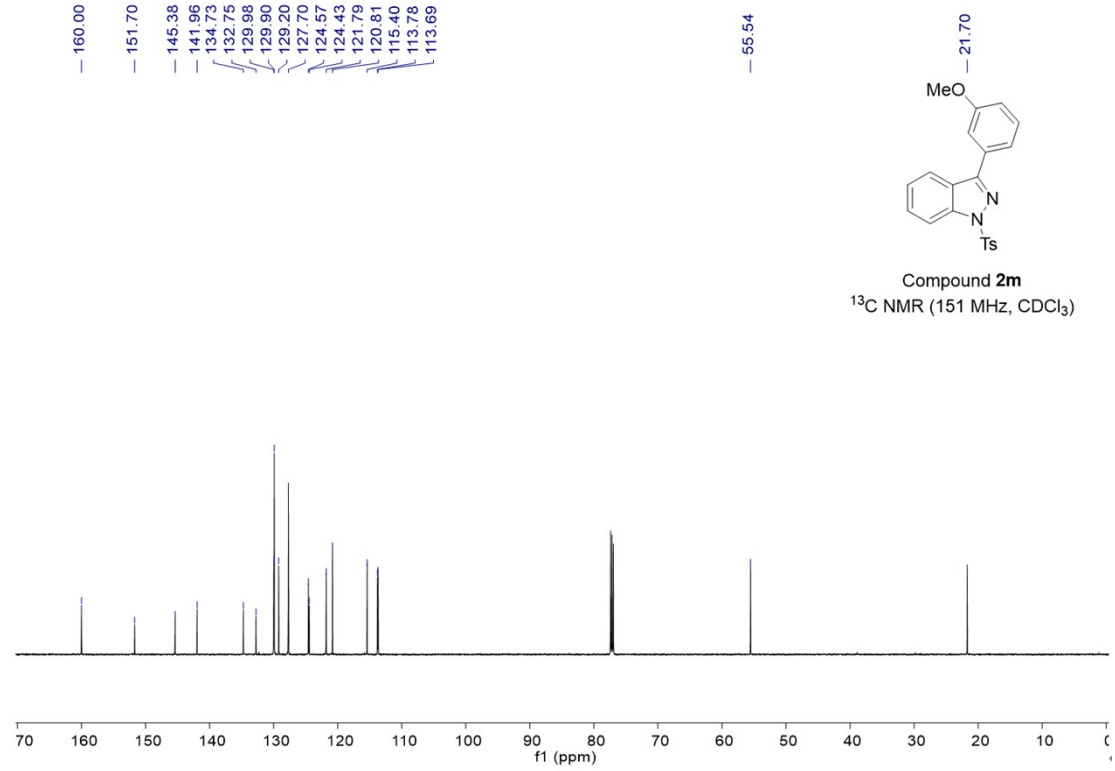
Compound **2l**

^{19}F NMR (565 MHz, $CDCl_3$)

NMR spectra of 3-(3-Methoxyphenyl)-1-tosyl-1*H*-indazole (**2m**)

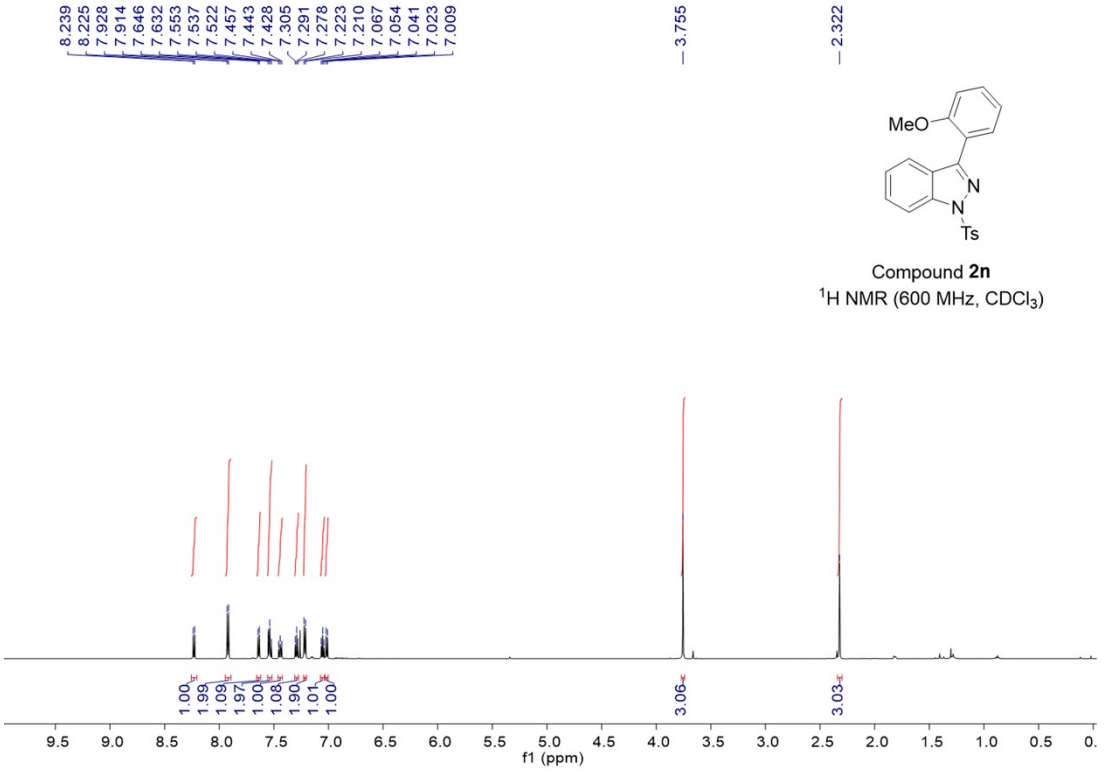


Compound **2m**
^{1}H NMR (600 MHz, $CDCl_3$)

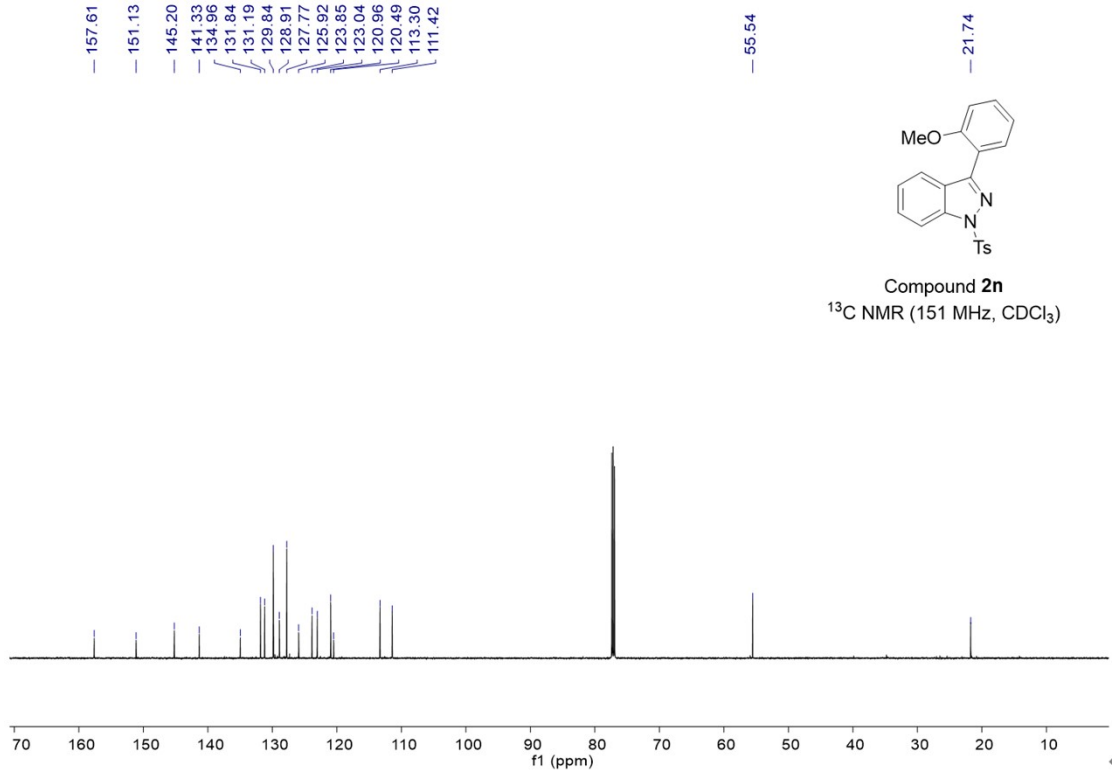


Compound **2m**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 3-(2-Methoxyphenyl)-1-tosyl-1*H*-indazole (**2n**)

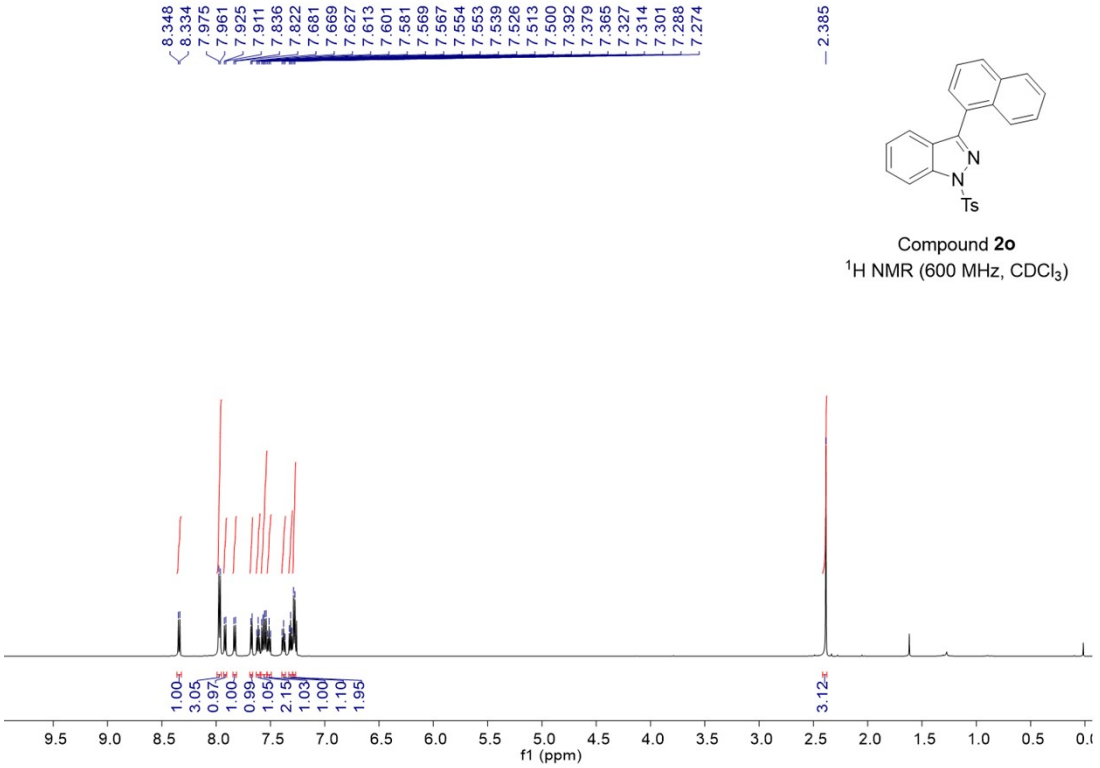


Compound **2n**
^{1}H NMR (600 MHz, $CDCl_3$)

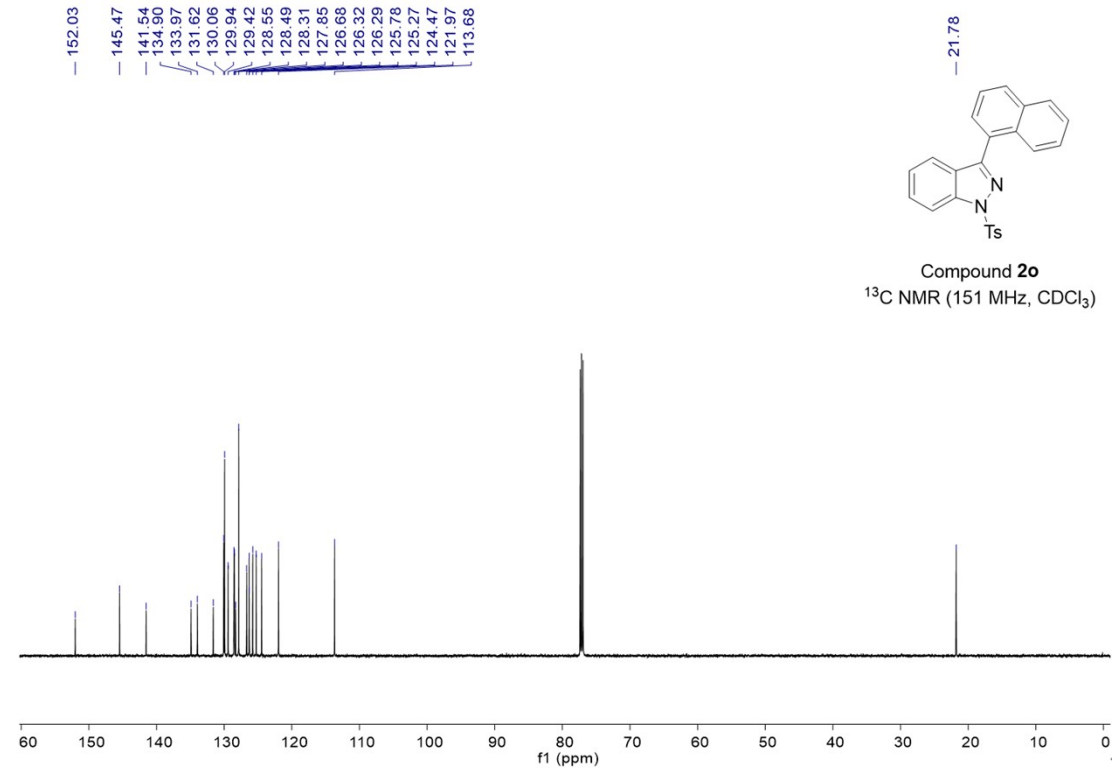


Compound **2n**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 3-(Naphthalen-1-yl)-1-tosyl-1*H*-indazole (**2o**)

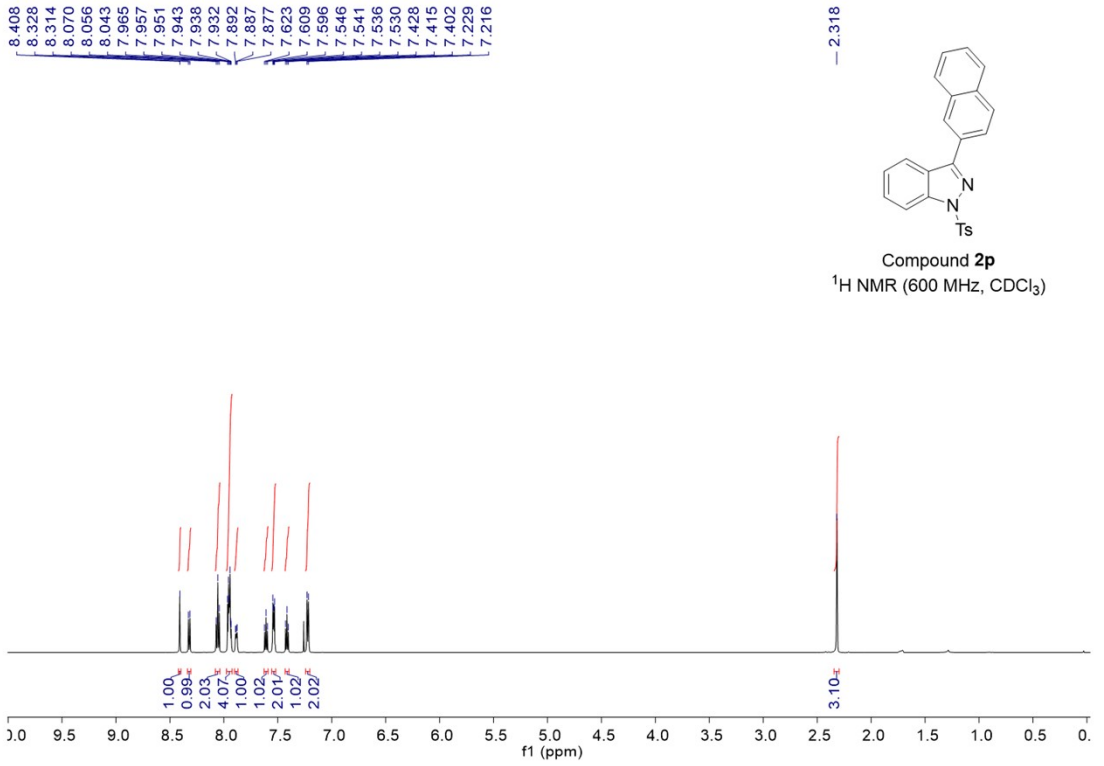


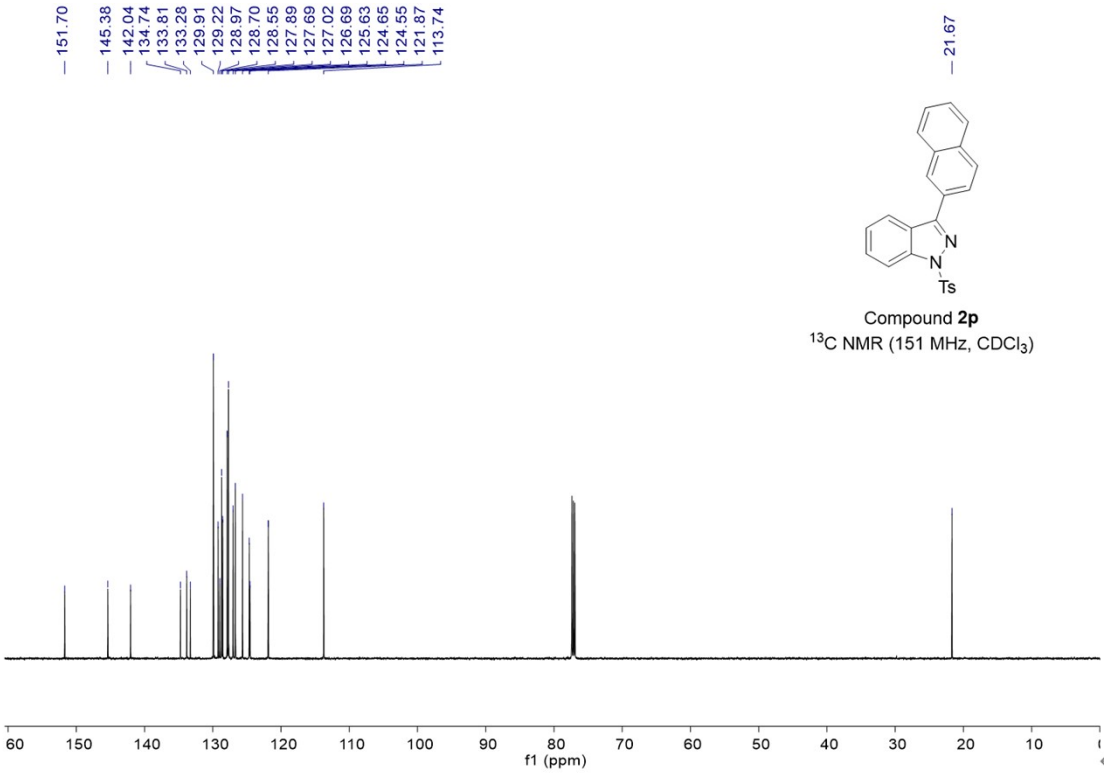
Compound **2o**
^{1}H NMR (600 MHz, $CDCl_3$)



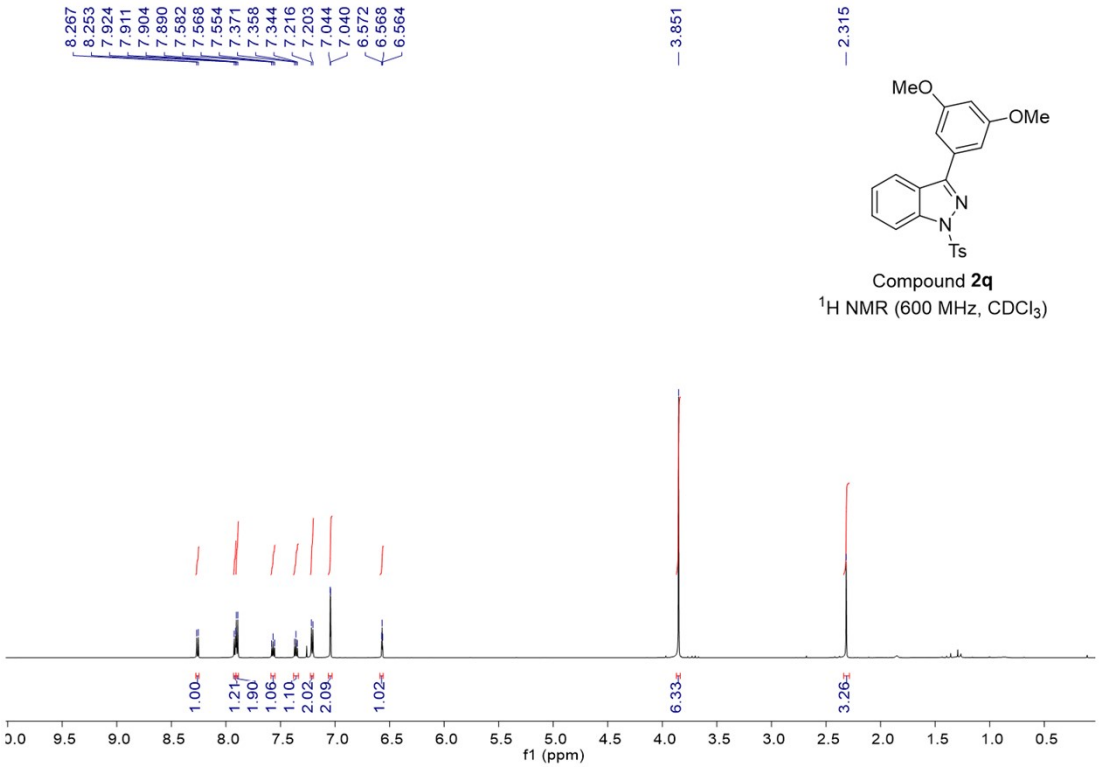
Compound **2o**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 3-(Naphthalen-2-yl)-1-tosyl-1*H*-indazole (**2p**)



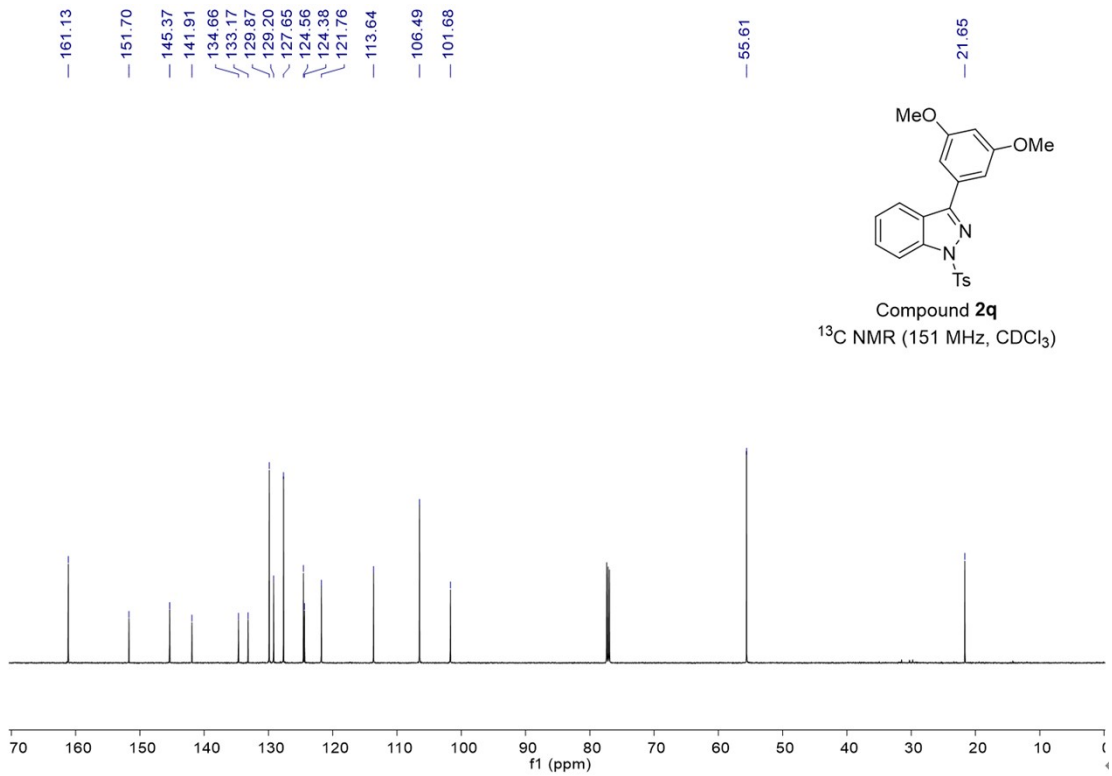


NMR spectra of 3-(3,5-Dimethoxyphenyl)-1-tosyl-1*H*-indazole (**2q**)



Compound **2q**

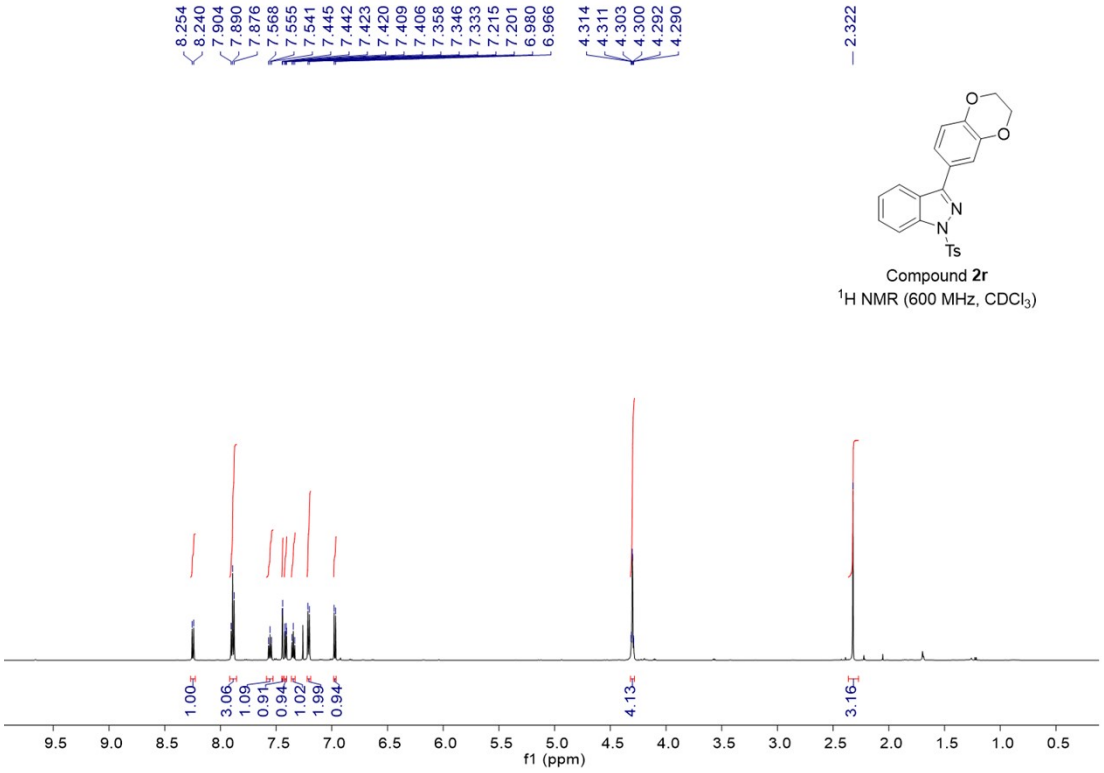
^{1}H NMR (600 MHz, $CDCl_3$)

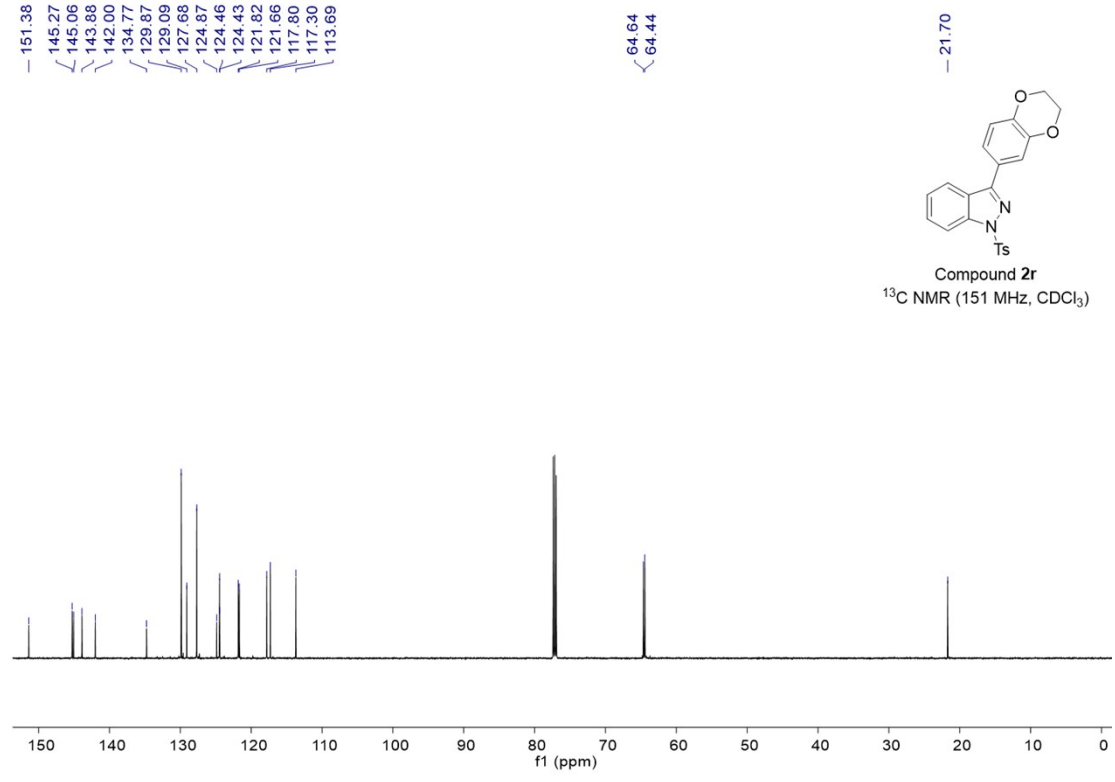


Compound **2q**

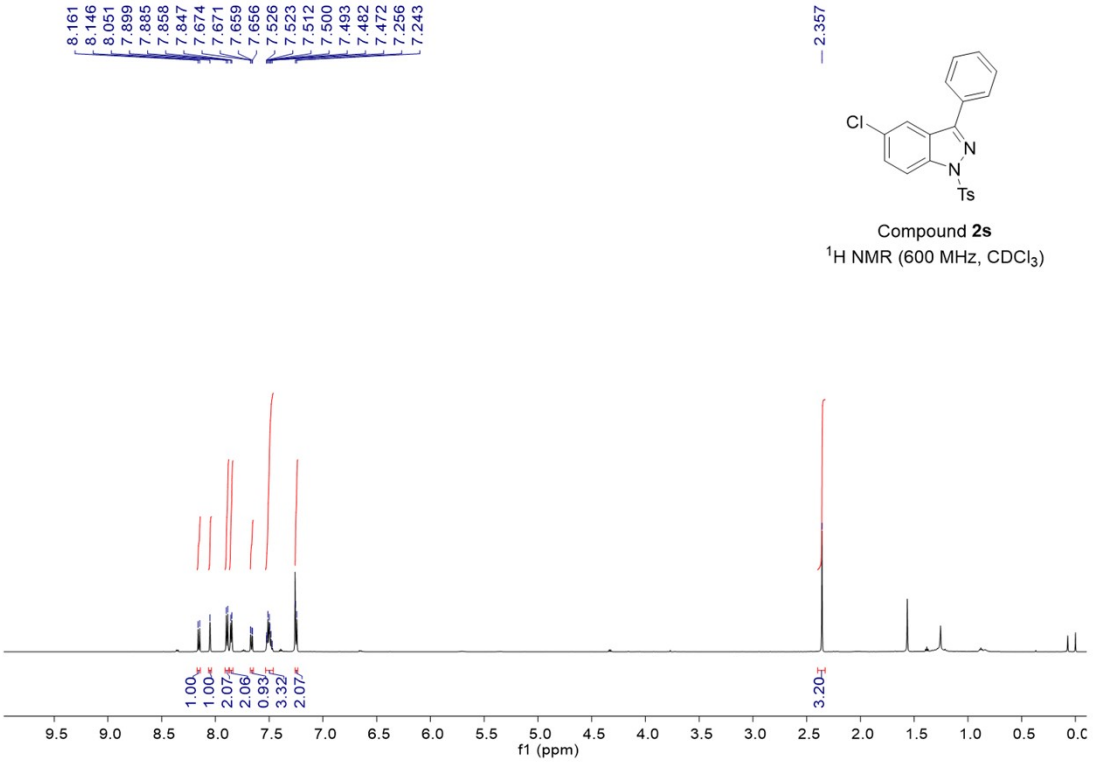
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-tosyl-1*H*-indazole (**2r**)

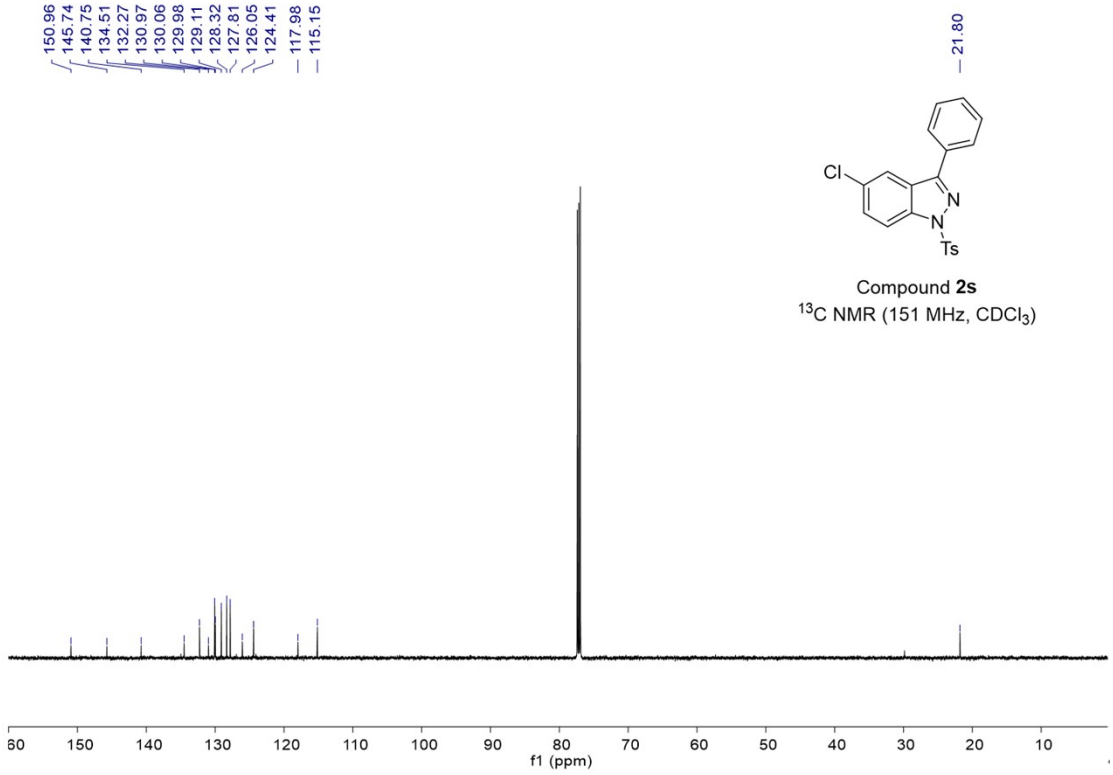




NMR spectra of 5-Chloro-3-phenyl-1-tosyl-1*H*-indazole (**2s**)

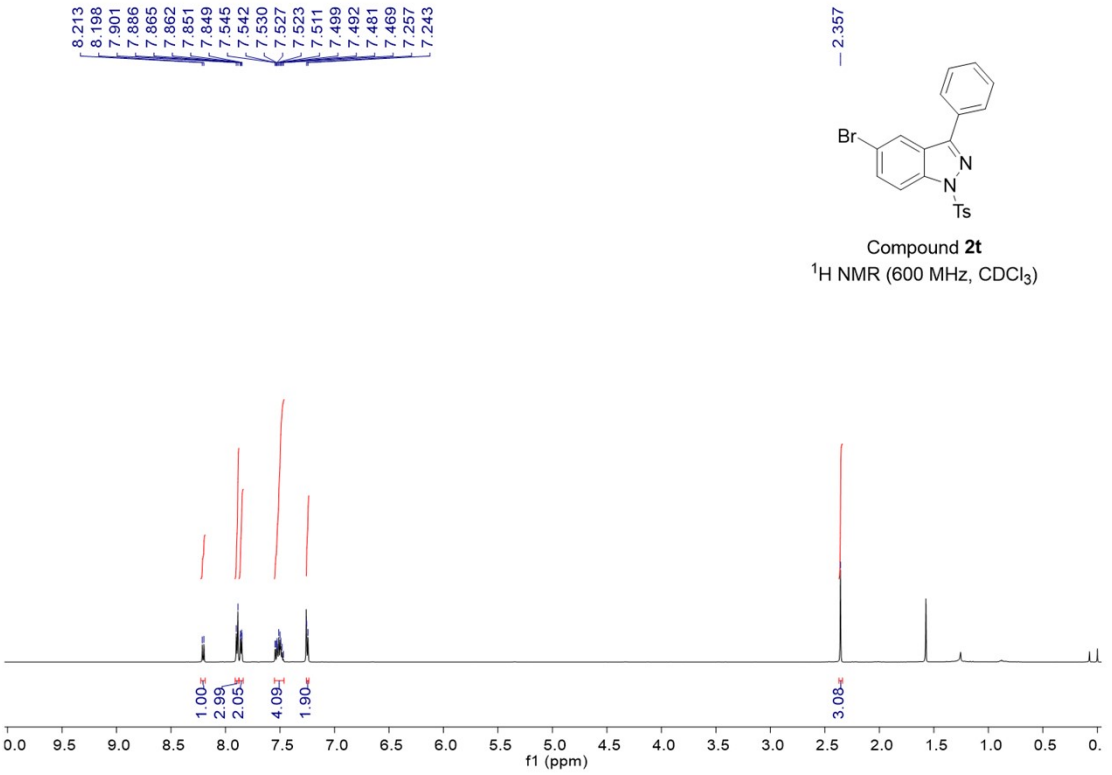


Compound **2s**
^{1}H NMR (600 MHz, $CDCl_3$)

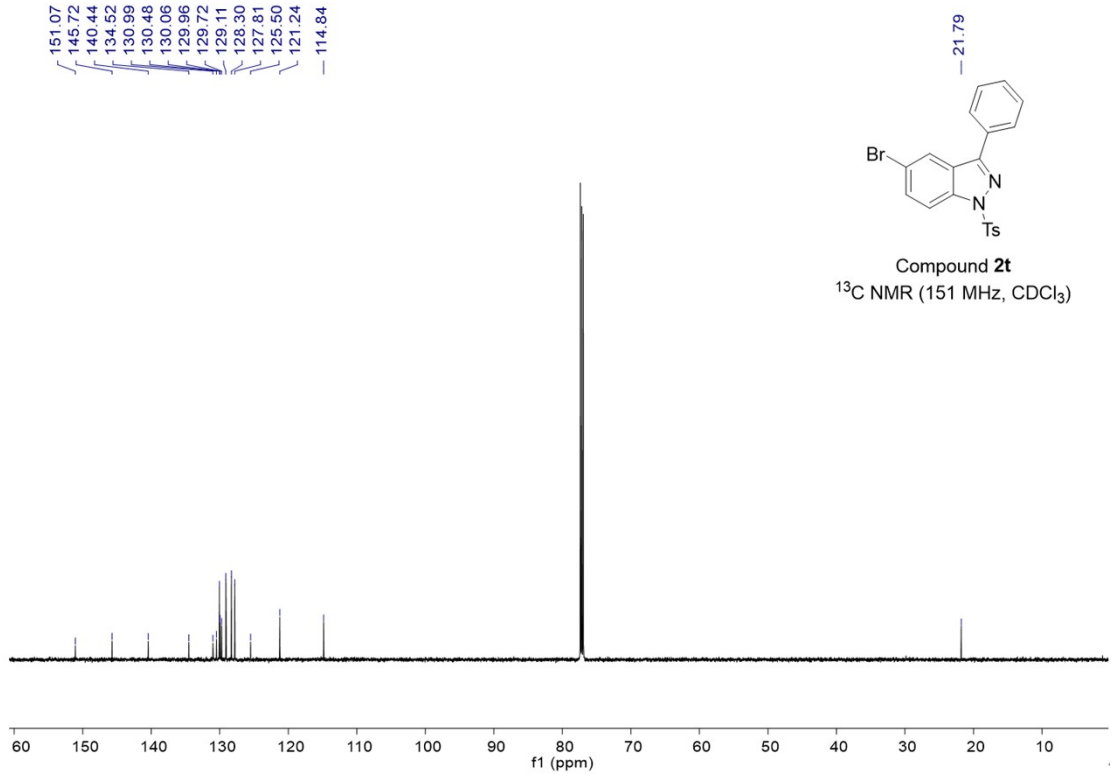


Compound **2s**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 5-Bromo-3-phenyl-1-tosyl-1*H*-indazole (**2t**)

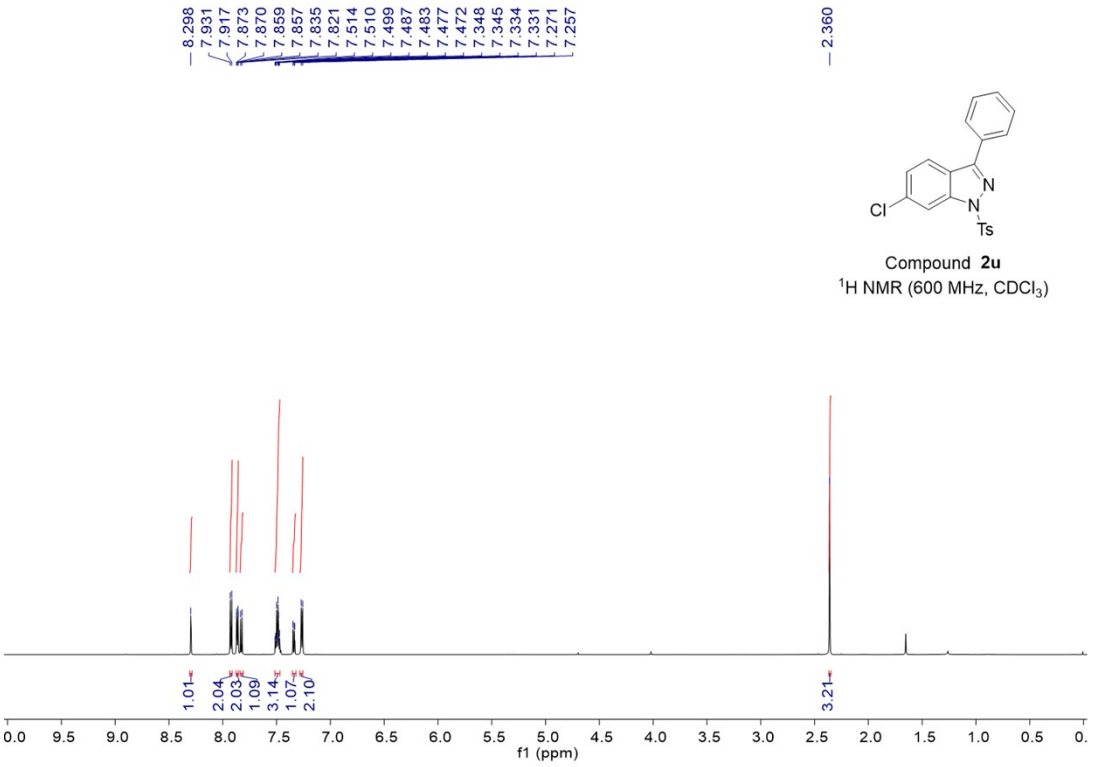


Compound **2t**
^{1}H NMR (600 MHz, $CDCl_3$)

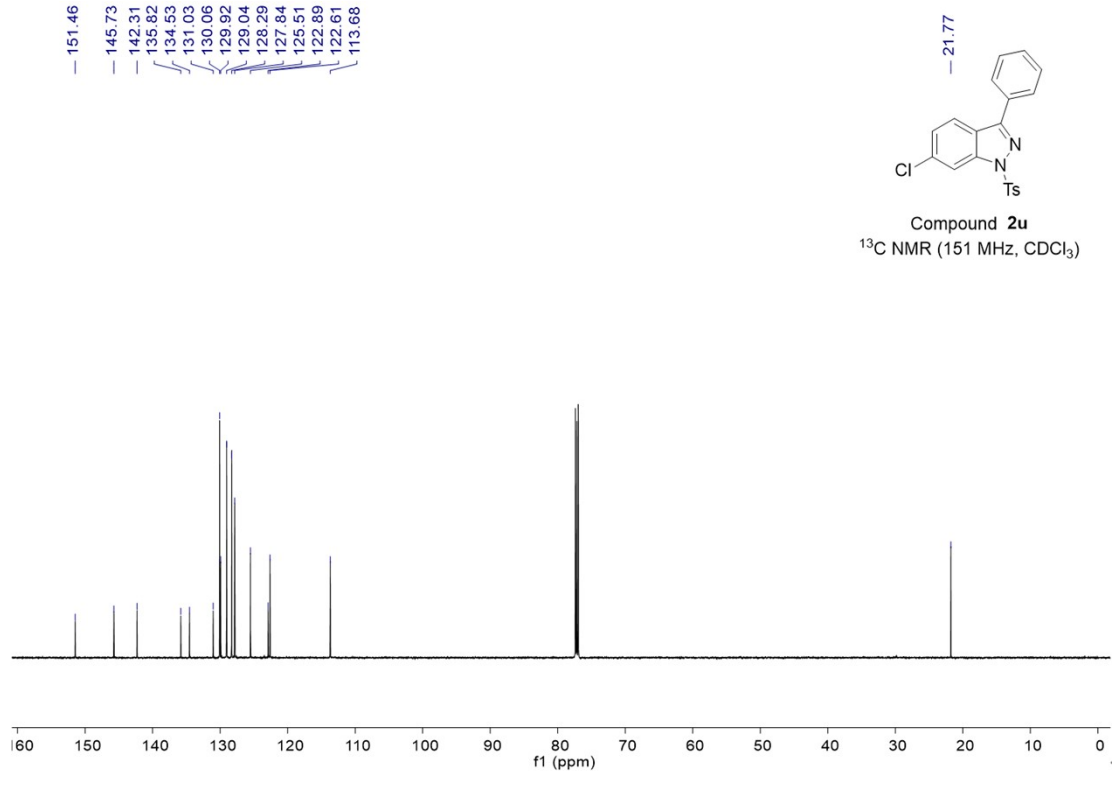


Compound **2t**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 6-Chloro-3-phenyl-1-tosyl-1*H*-indazole (**2u**)

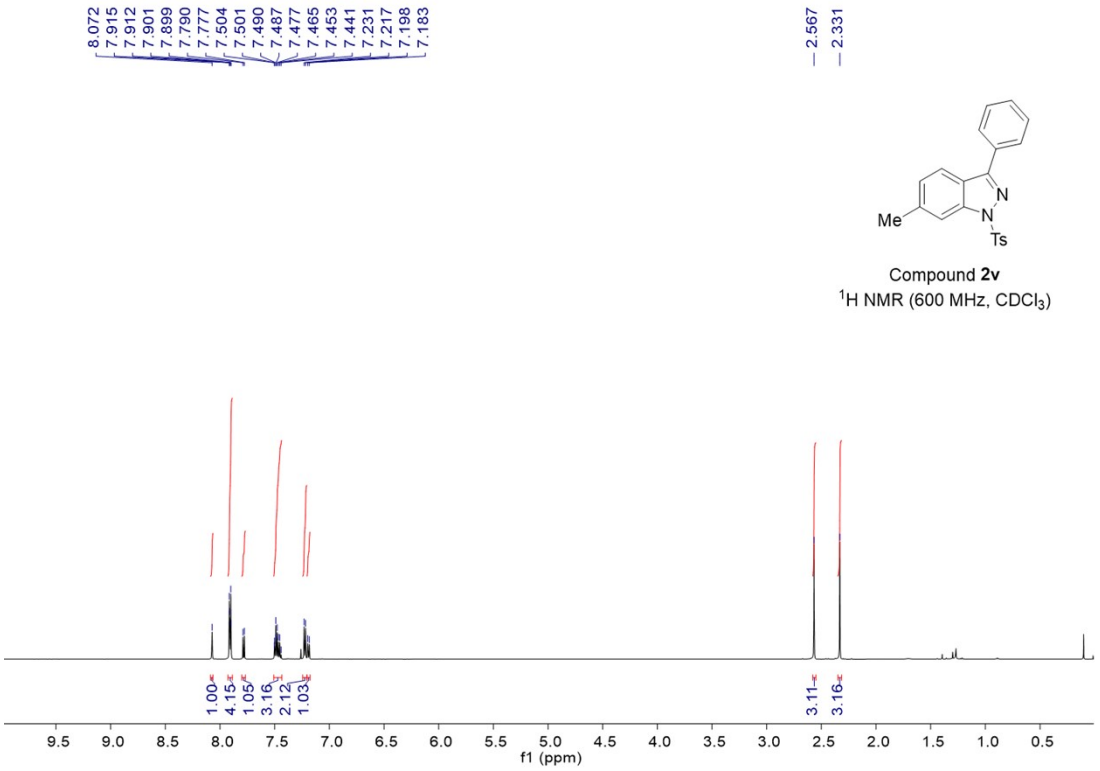


Compound **2u**
^{1}H NMR (600 MHz, $CDCl_3$)

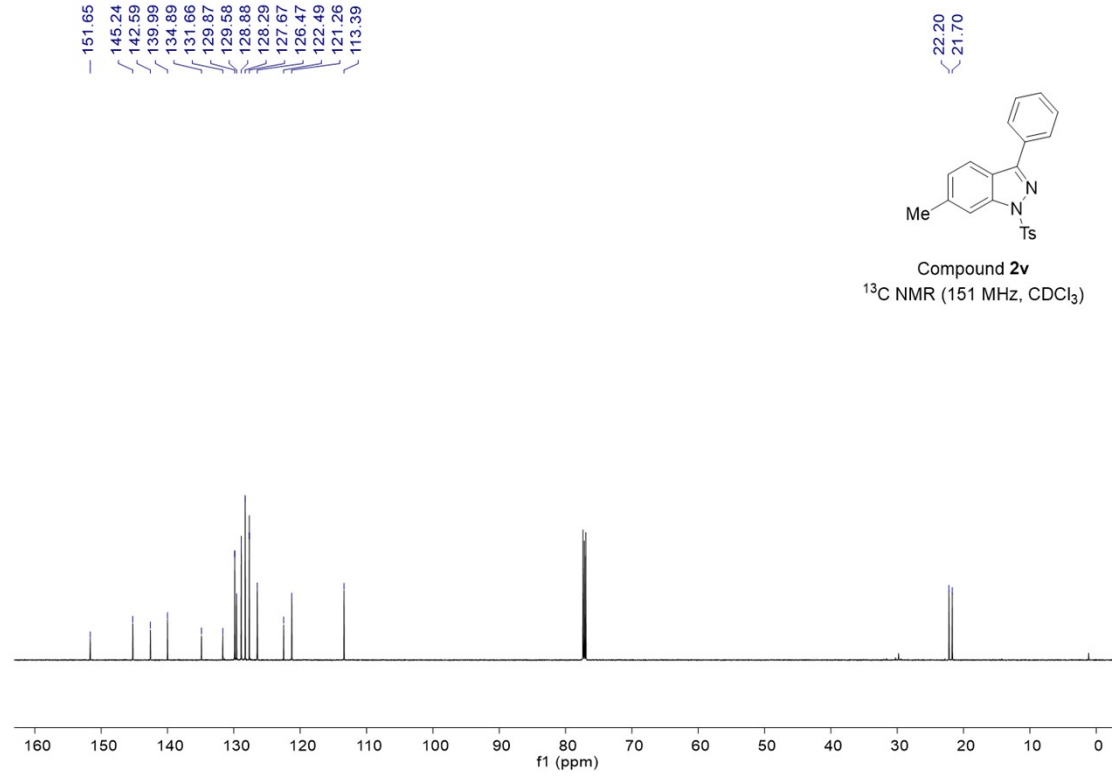


Compound **2u**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 6-Methyl-3-phenyl-1-tosyl-1*H*-indazole (**2v**)

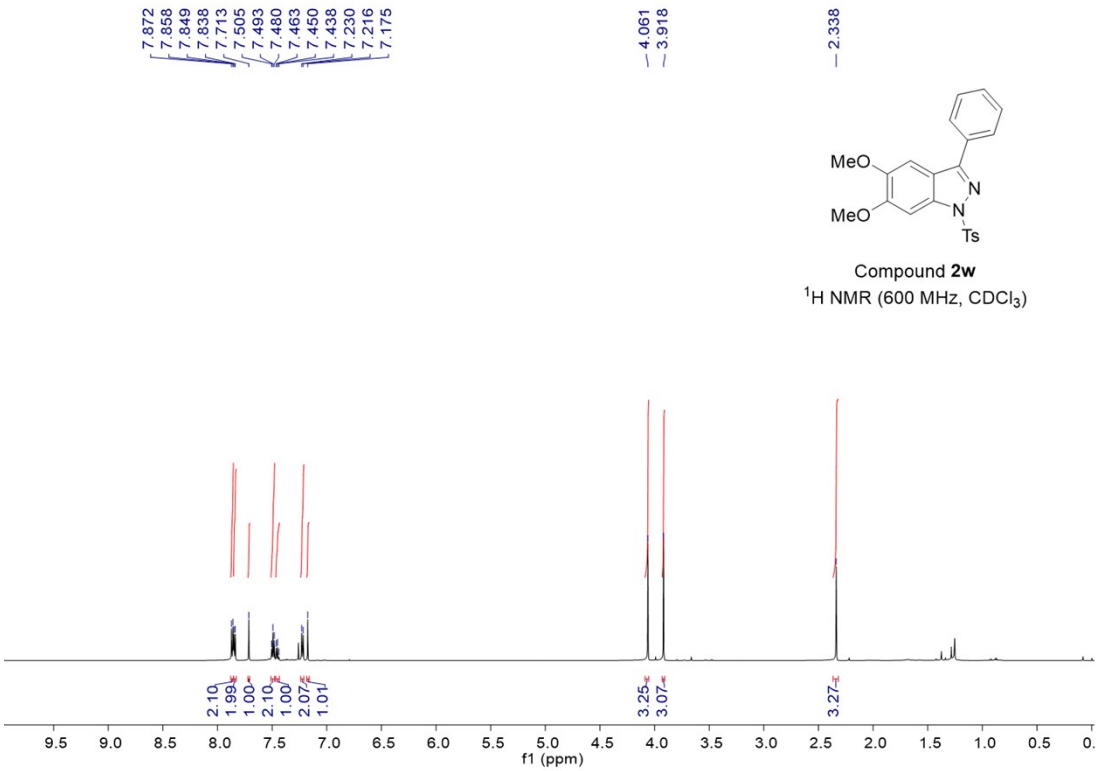


Compound **2v**
^{1}H NMR (600 MHz, $CDCl_3$)

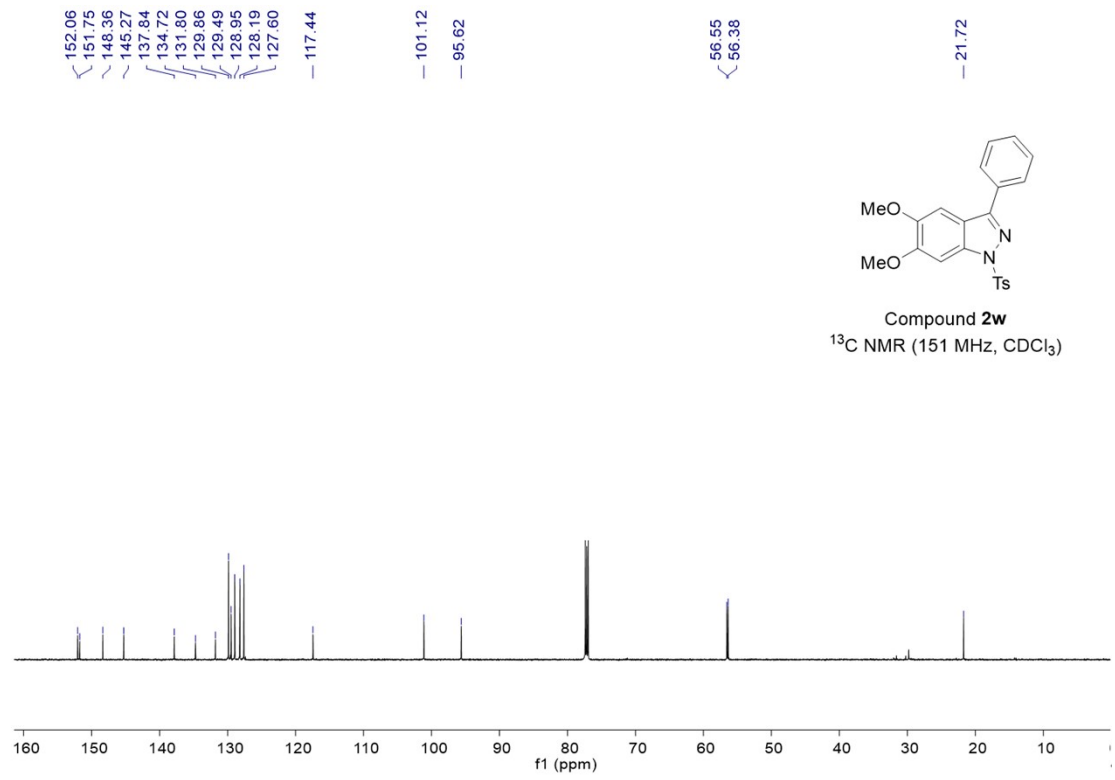


Compound **2v**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 5,6-Dimethoxy-3-phenyl-1-tosyl-1*H*-indazole (**2w**)

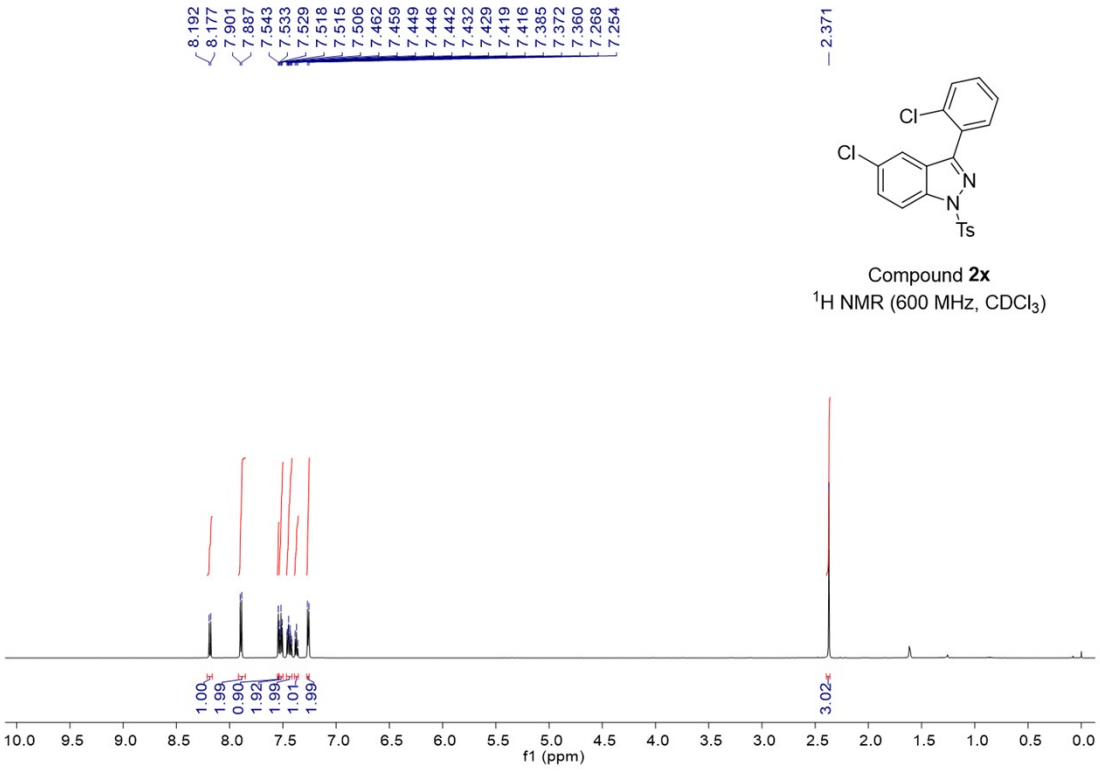


Compound **2w**
^{1}H NMR (600 MHz, $CDCl_3$)

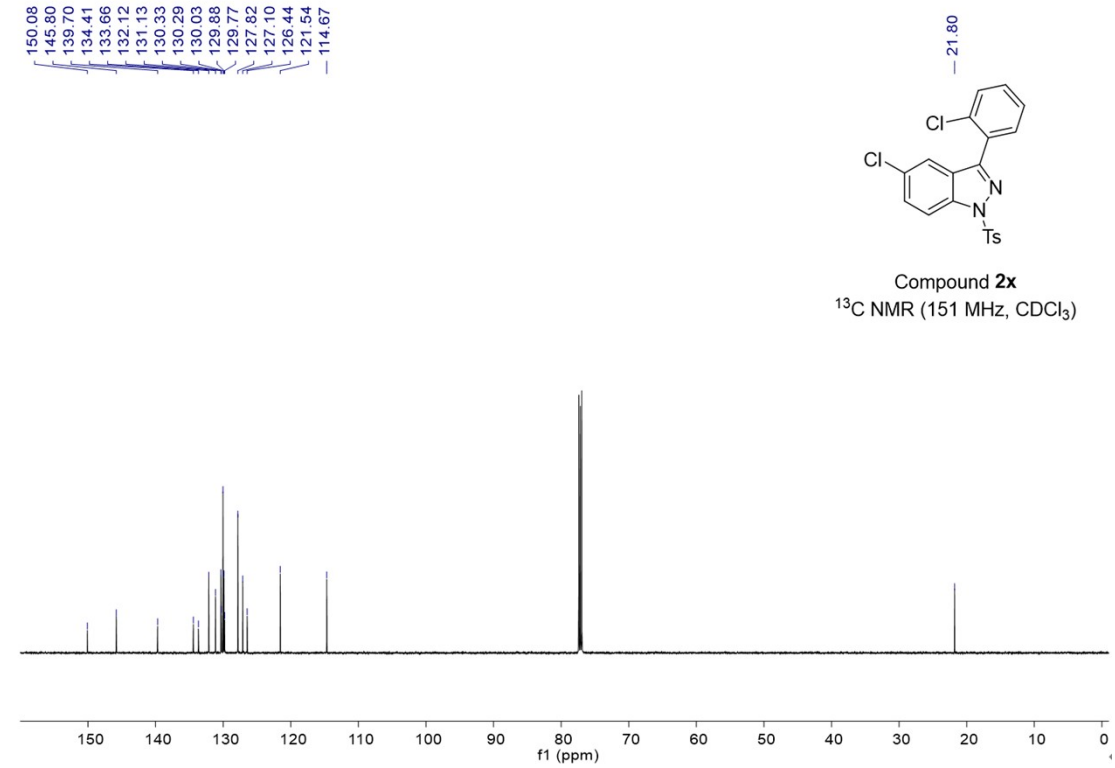


Compound **2w**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 5-Chloro-3-(2-chlorophenyl)-1-tosyl-1*H*-indazole (**2x**)

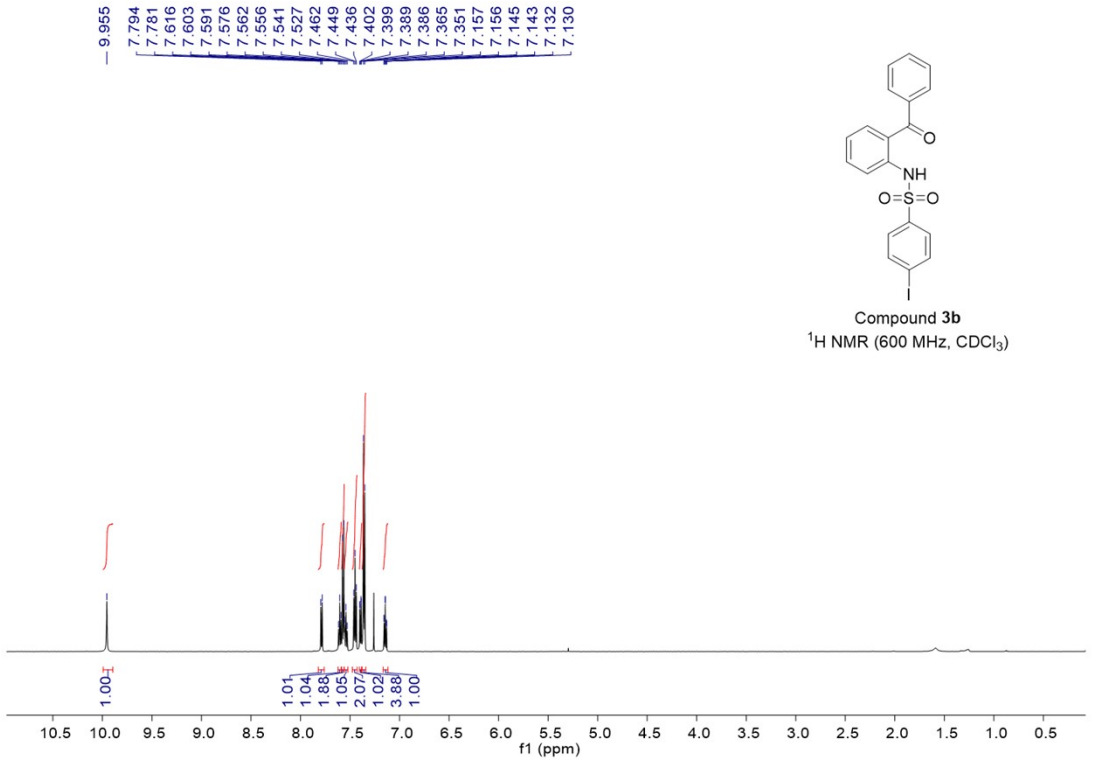


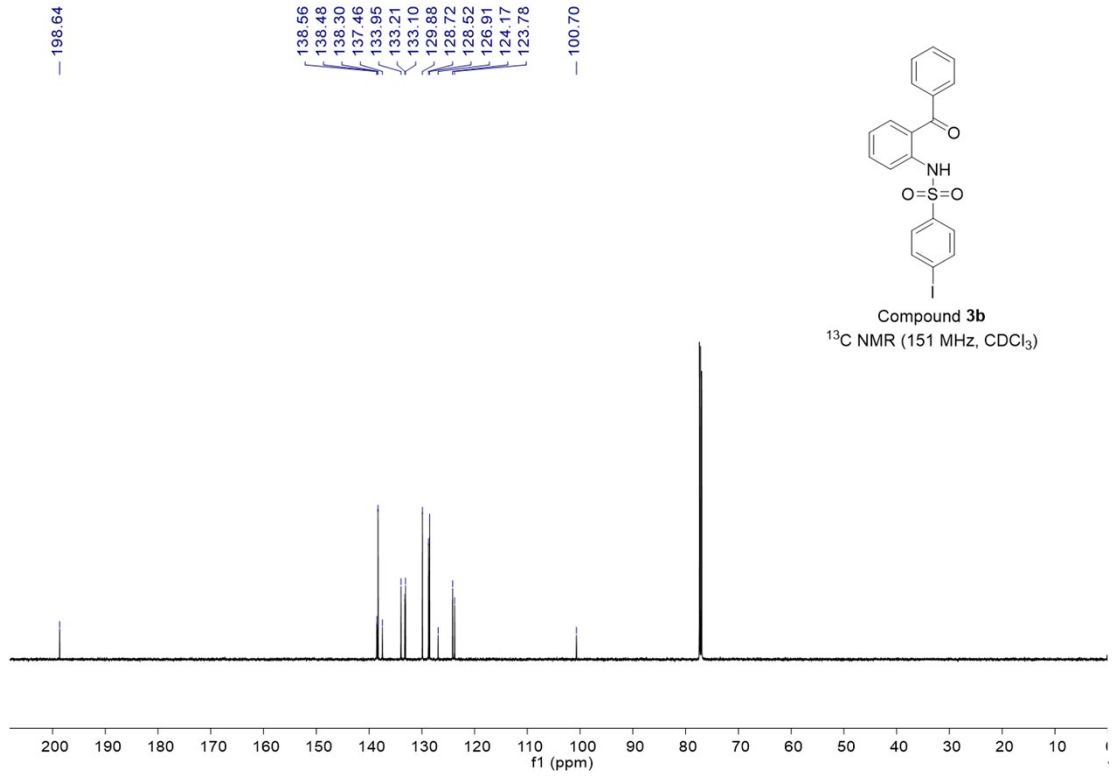
Compound **2x**
^{1}H NMR (600 MHz, $CDCl_3$)



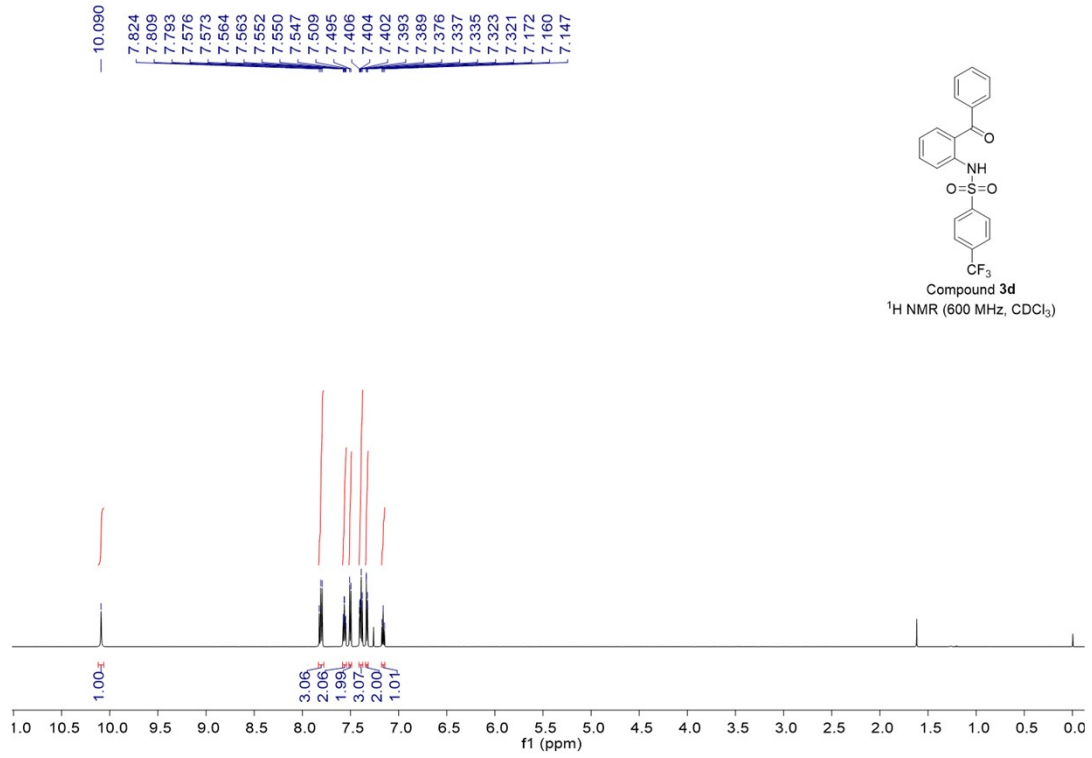
Compound **2x**
^{13}C NMR (151 MHz, $CDCl_3$)

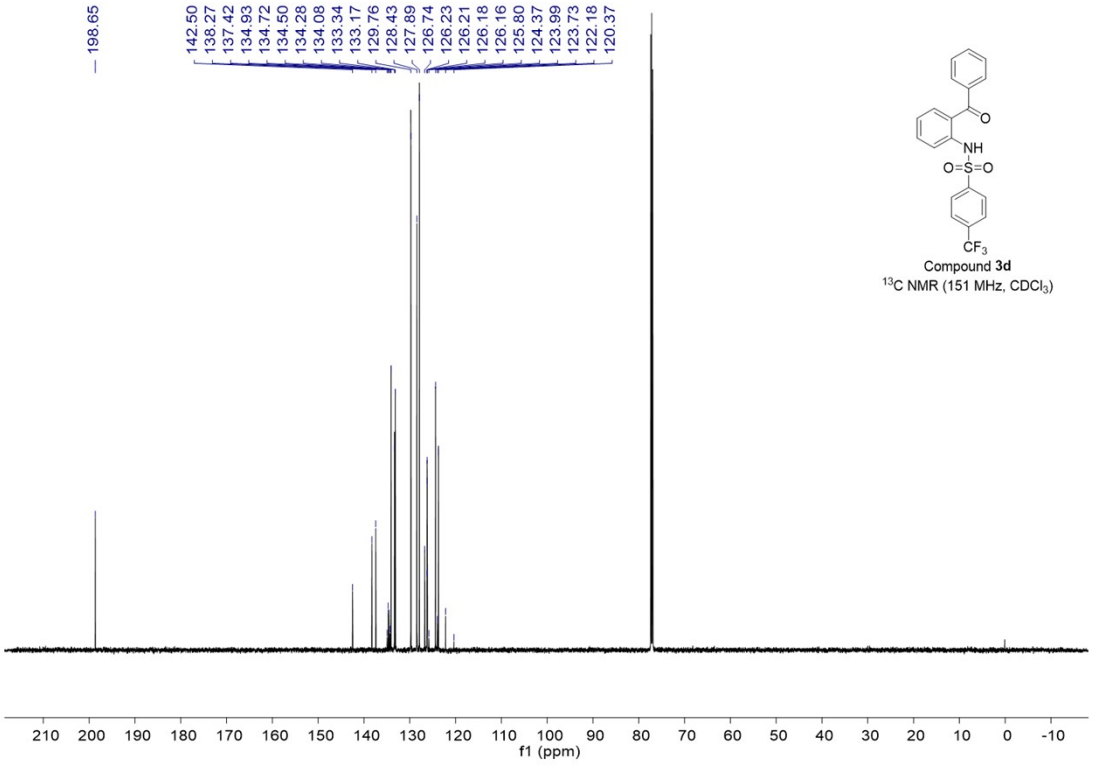
NMR spectra of *N*-(2-Benzoylphenyl)-4-iodobenzenesulfonamide (**3b**)

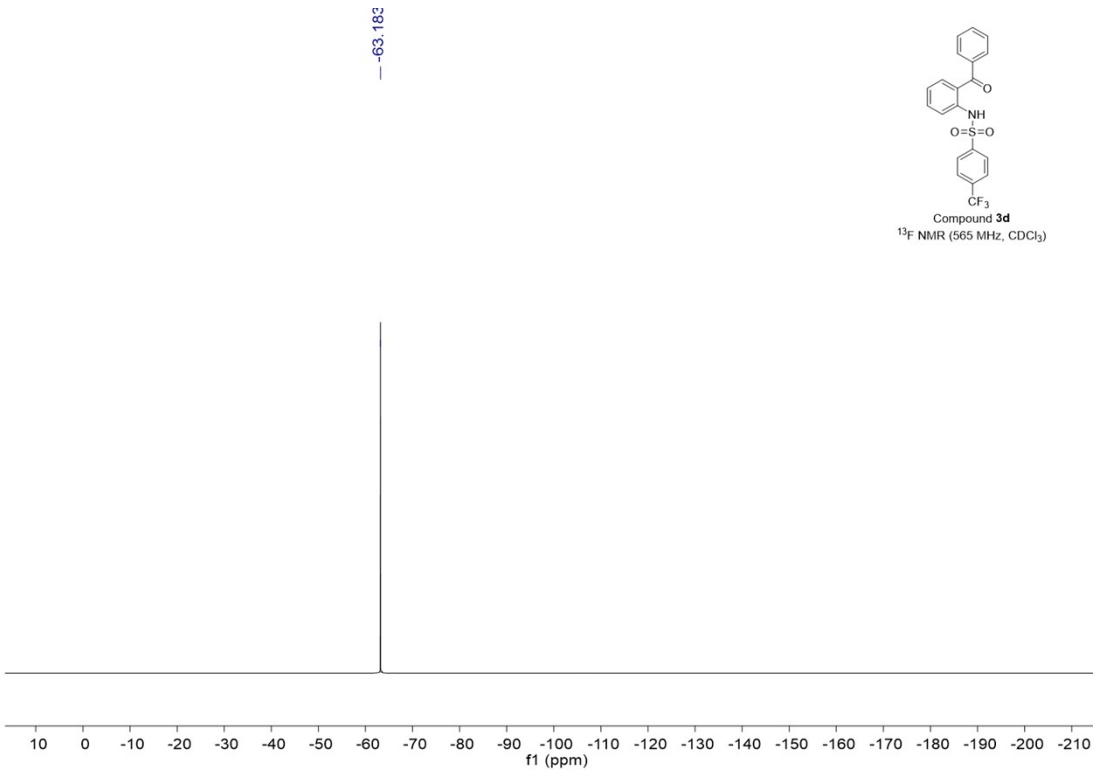




NMR spectra of N-(2-benzoylphenyl)-4-(trifluoromethyl)benzenesulfonamide (**3d**)



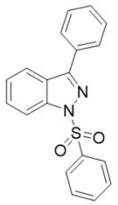




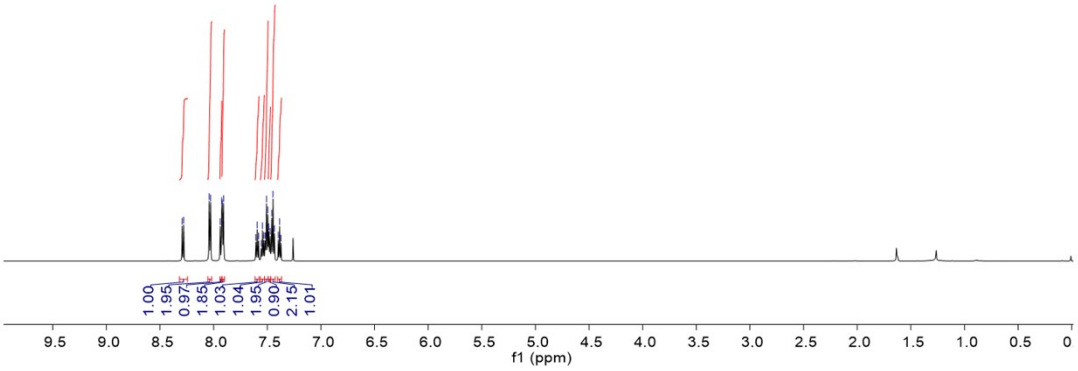
Compound **3d**

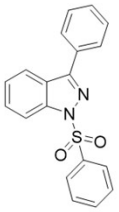
^{13}F NMR (565 MHz, $CDCl_3$)

NMR spectra of 3-Phenyl-1-(phenylsulfonyl)-1*H*-indazole (**4a**)

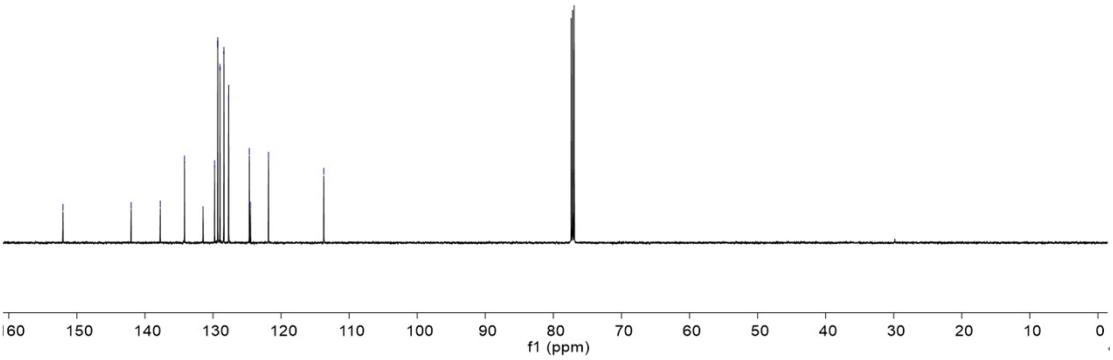


Compound **4a**
^{1}H NMR (600 MHz, $CDCl_3$)

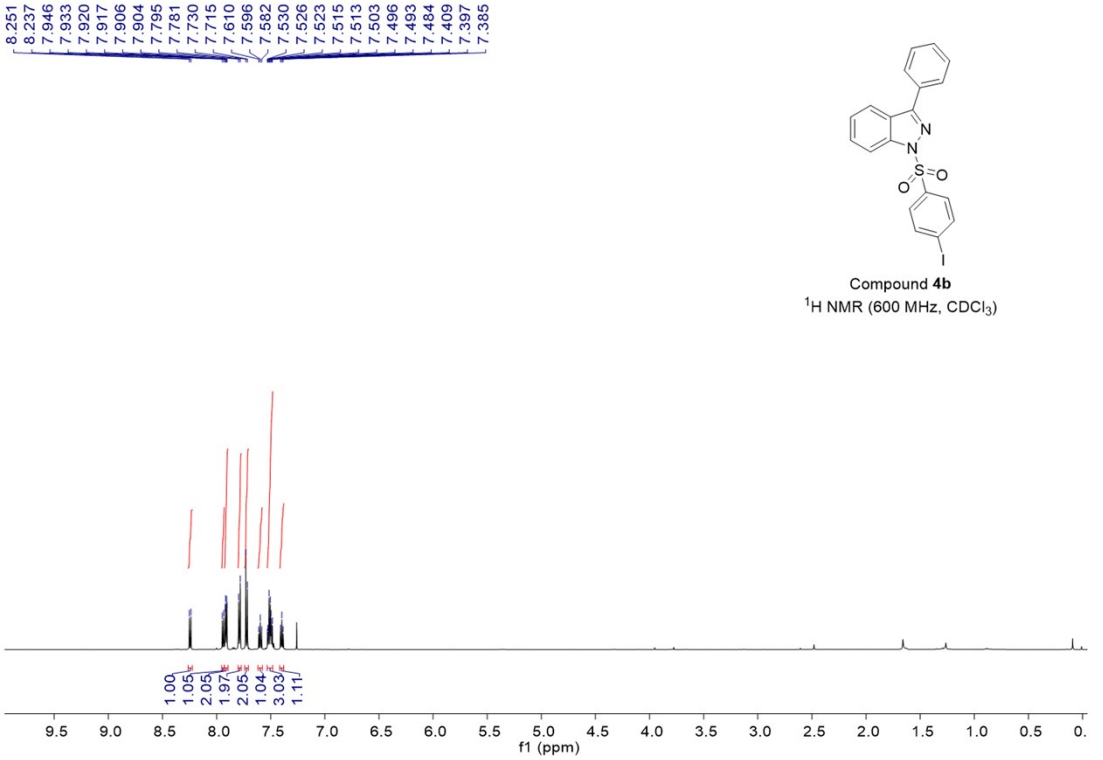


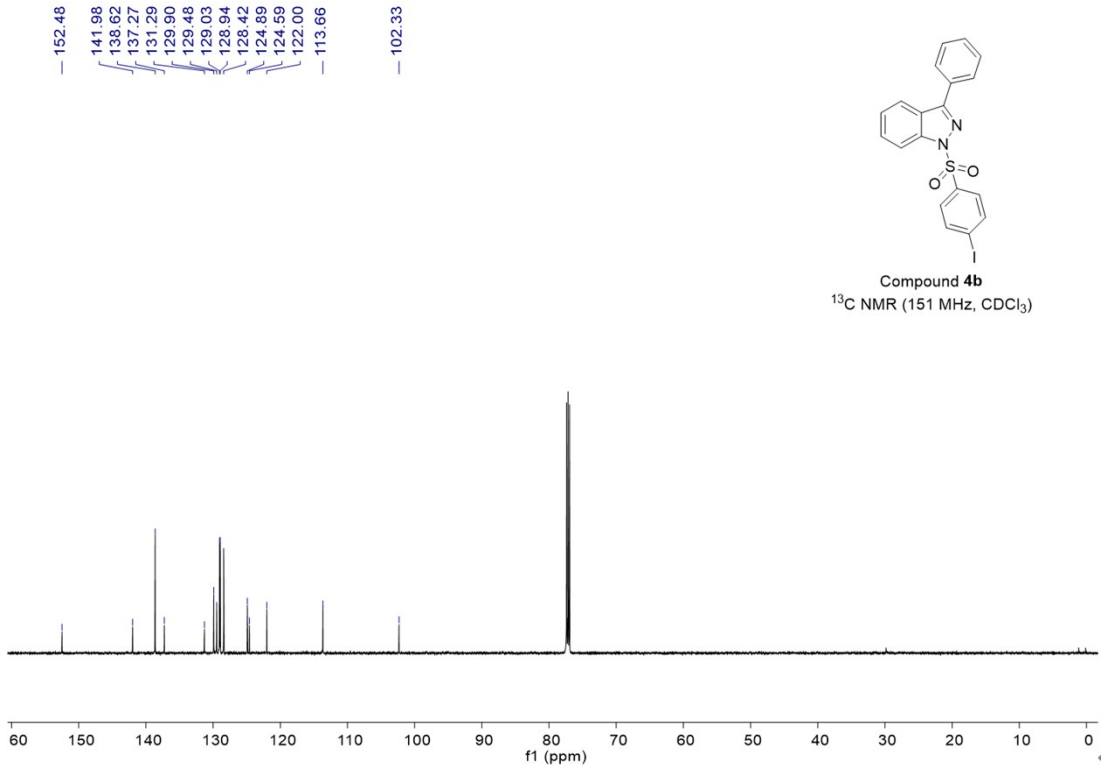


Compound **4a**
^{13}C NMR (151 MHz, $CDCl_3$)

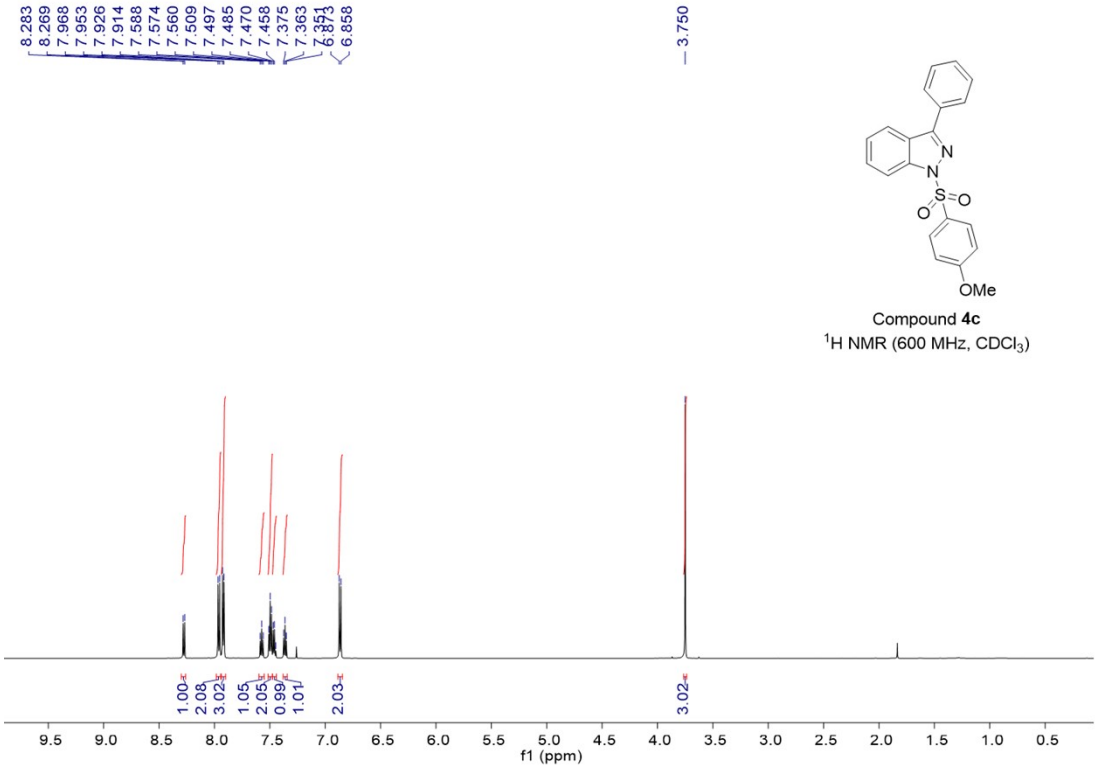


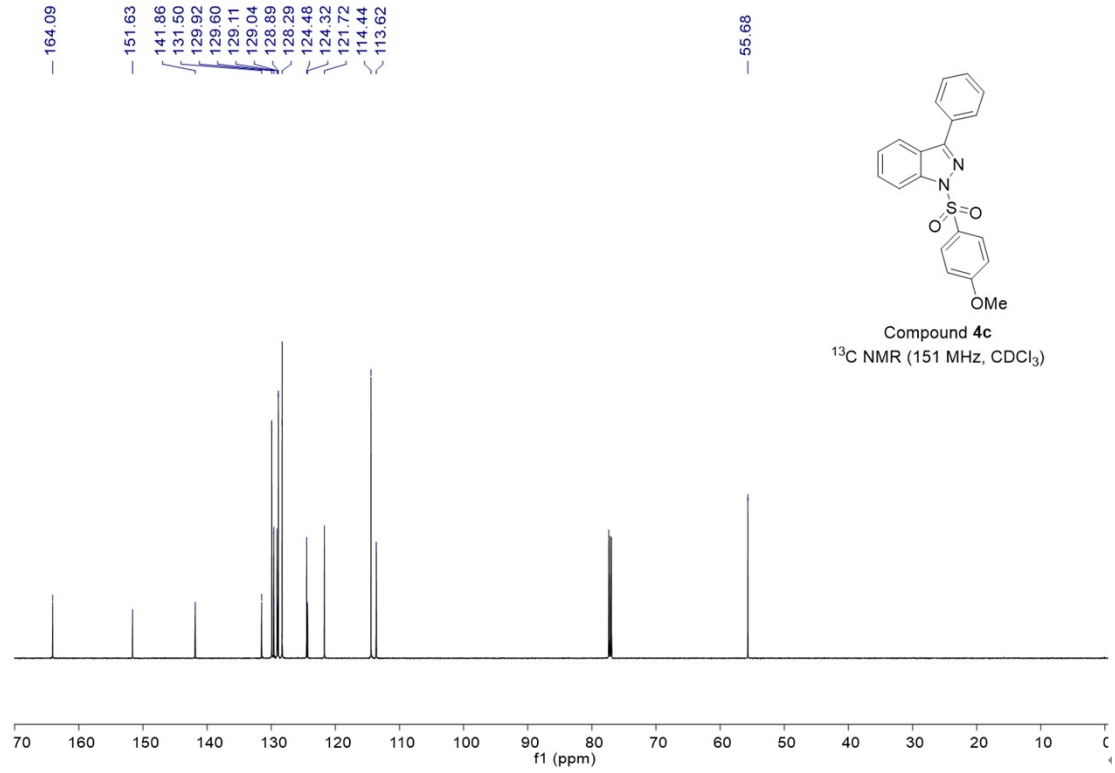
NMR spectra of 1-((4-Iodophenyl)sulfonyl)-3-phenyl-1*H*-indazole (**4b**)



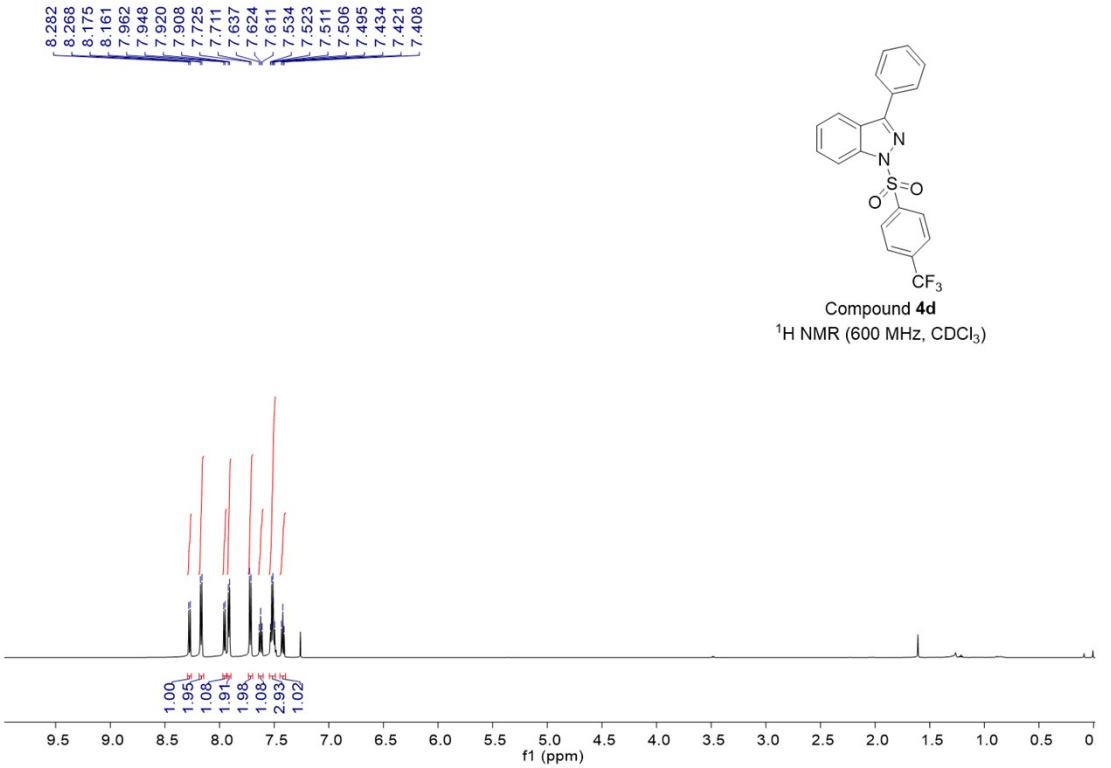


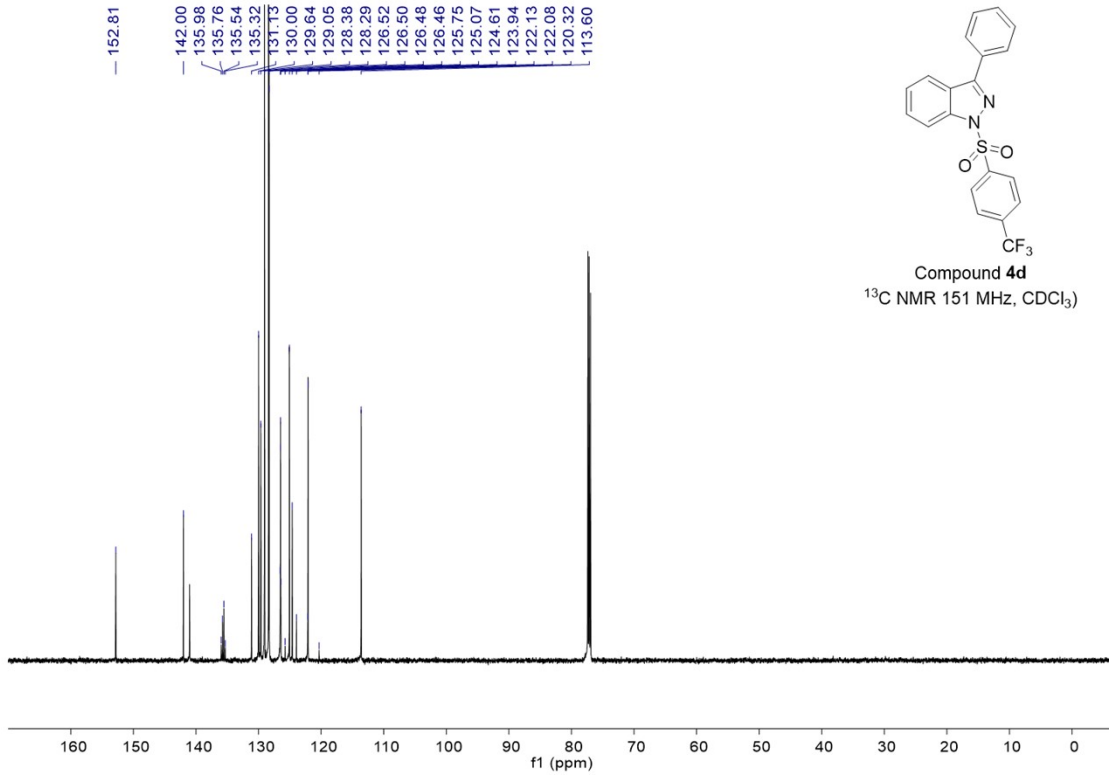
NMR spectra of 1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-1*H*-indazole (**4c**)

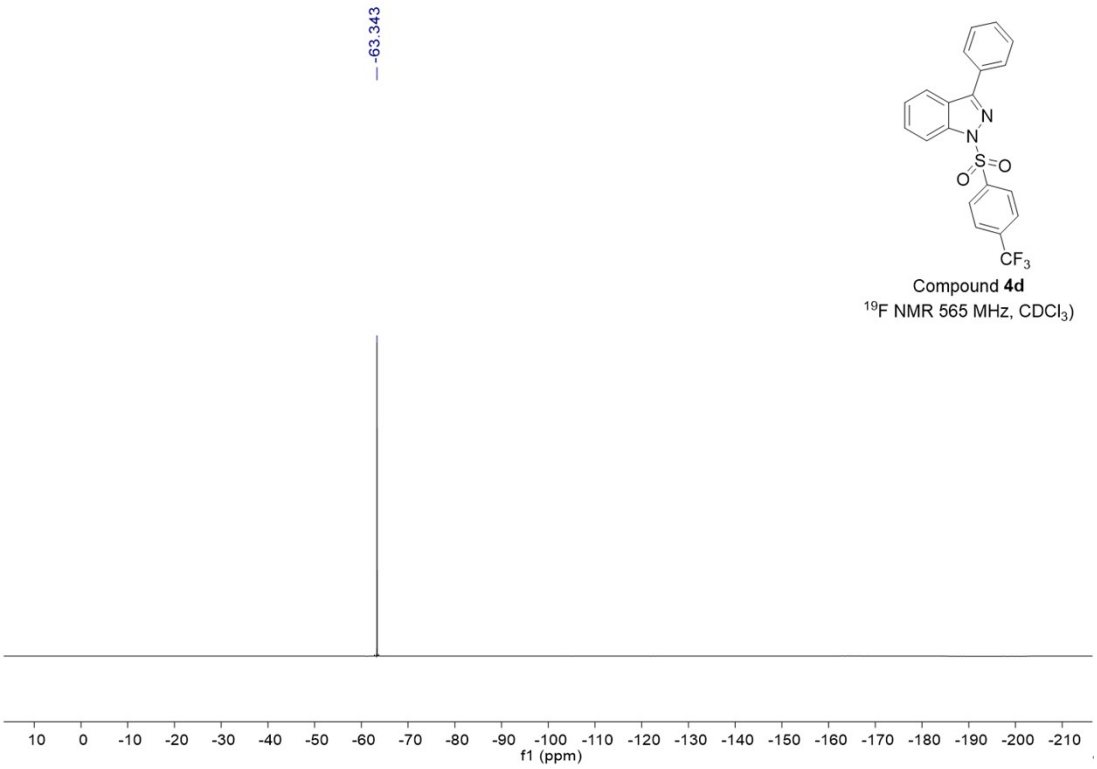




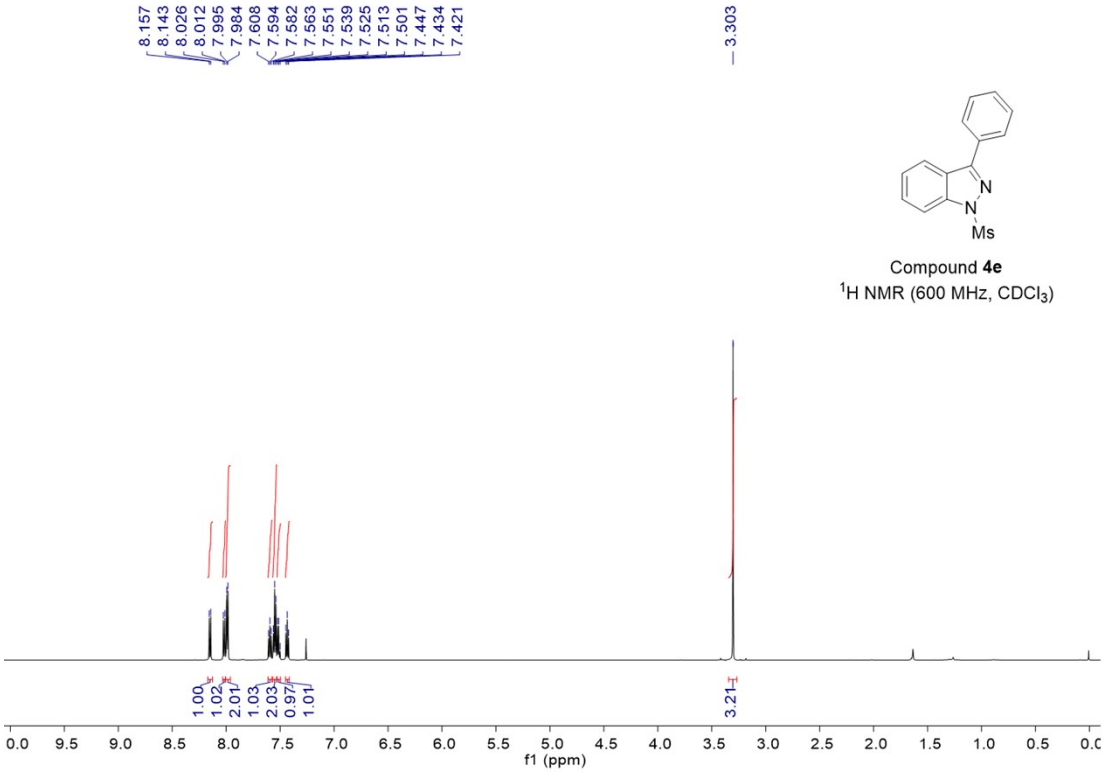
NMR spectra of 3-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1*H*-indazole (**4d**)

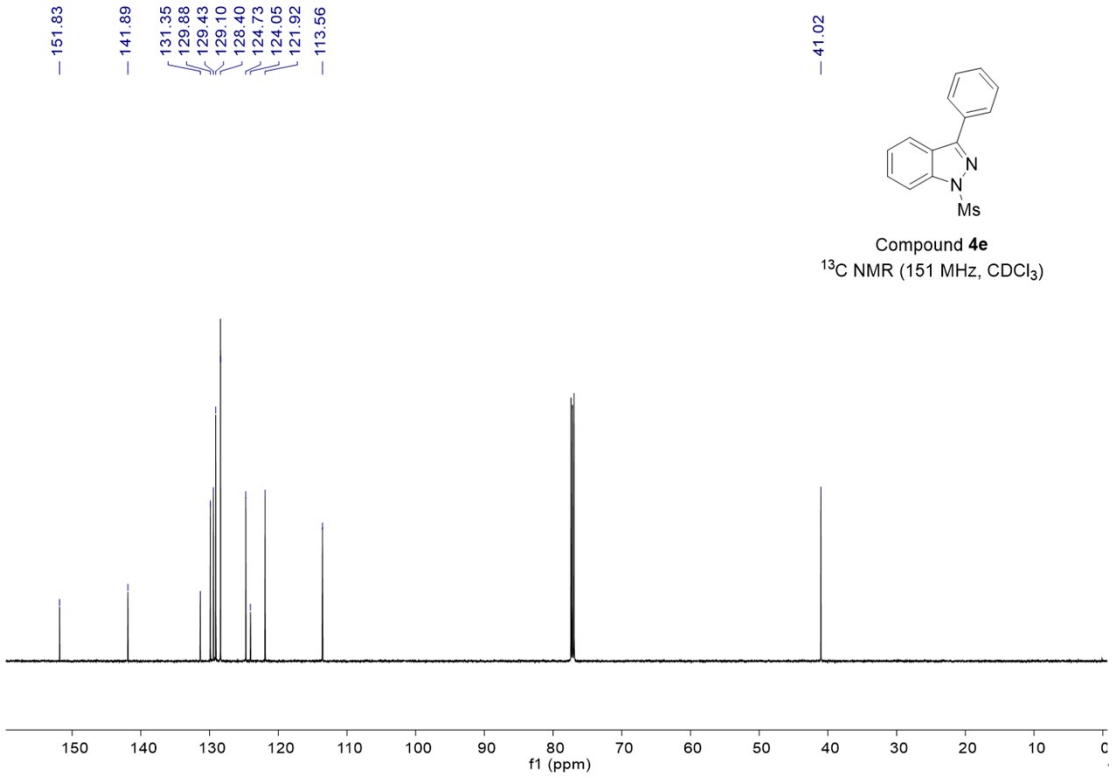






NMR spectra of 1-(Methylsulfonyl)-3-phenyl-1*H*-indazole (**4e**)

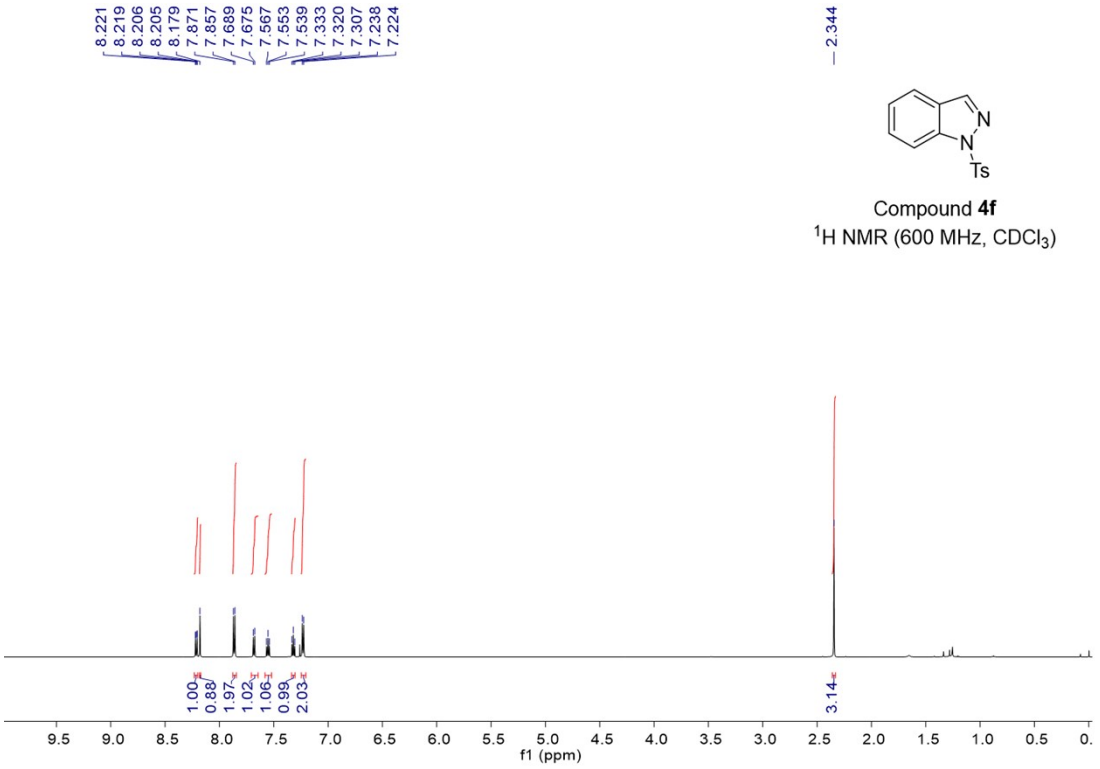




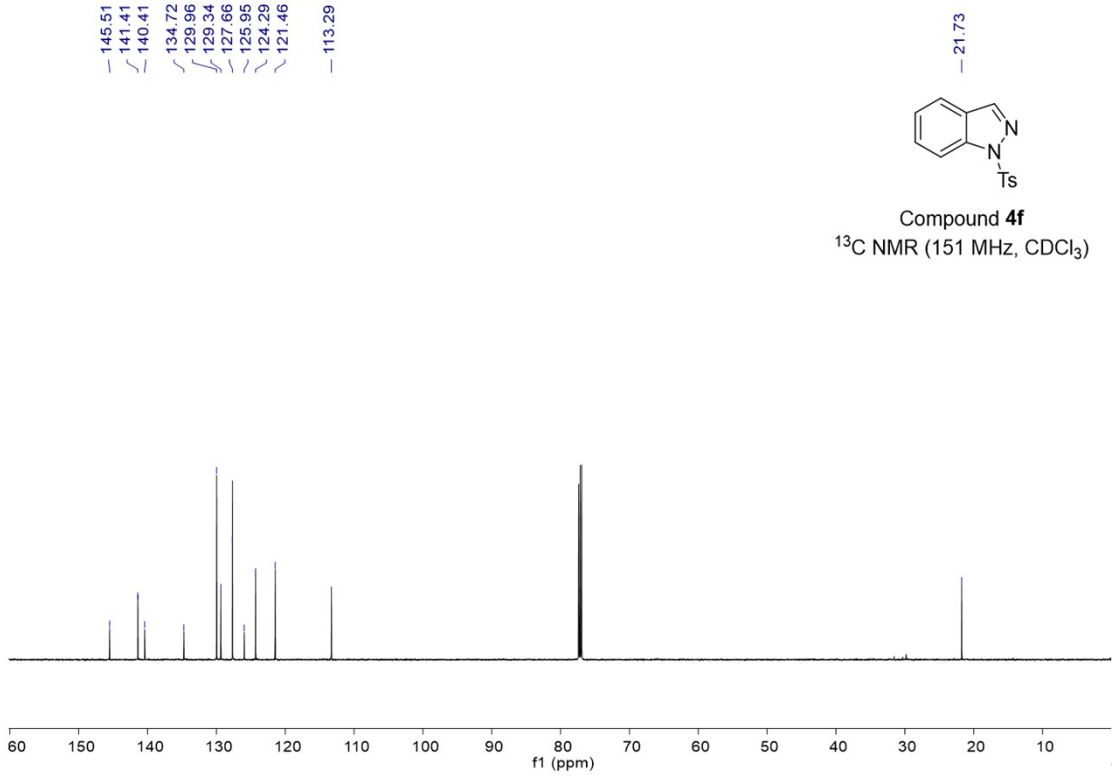
Compound **4e**

^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 1-Tosyl-1*H*-indazole (**4f**)

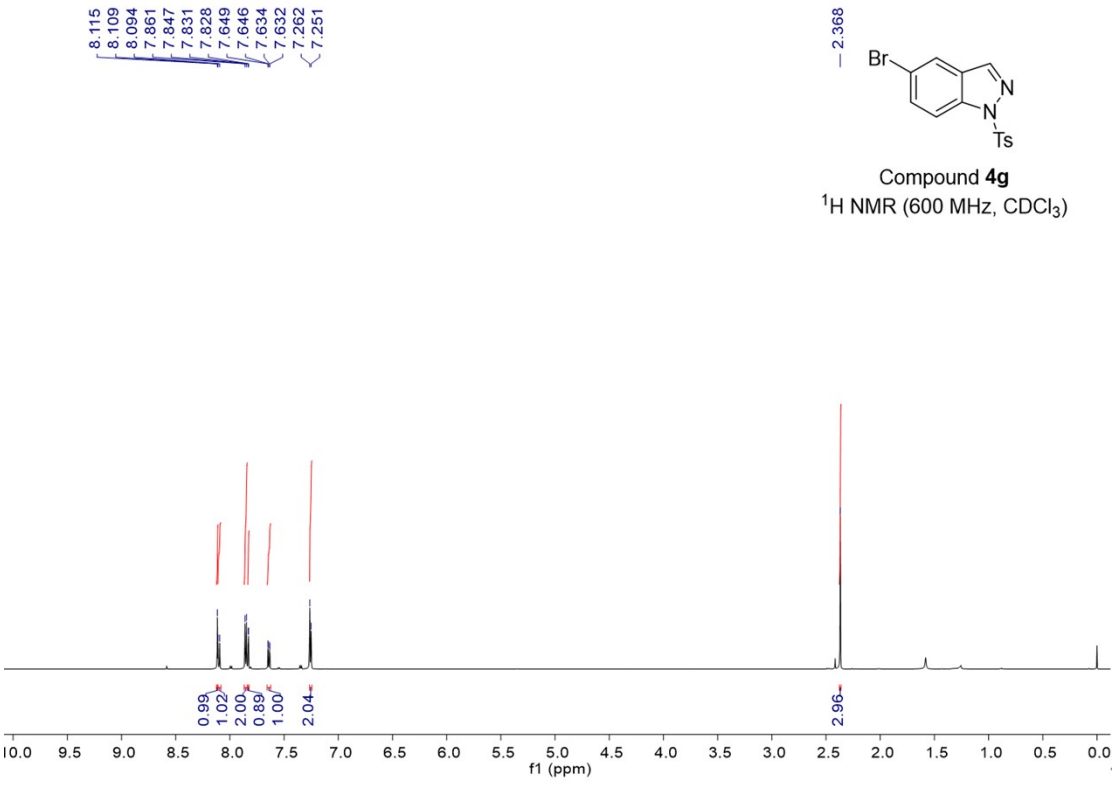


Compound **4f**
^{1}H NMR (600 MHz, $CDCl_3$)

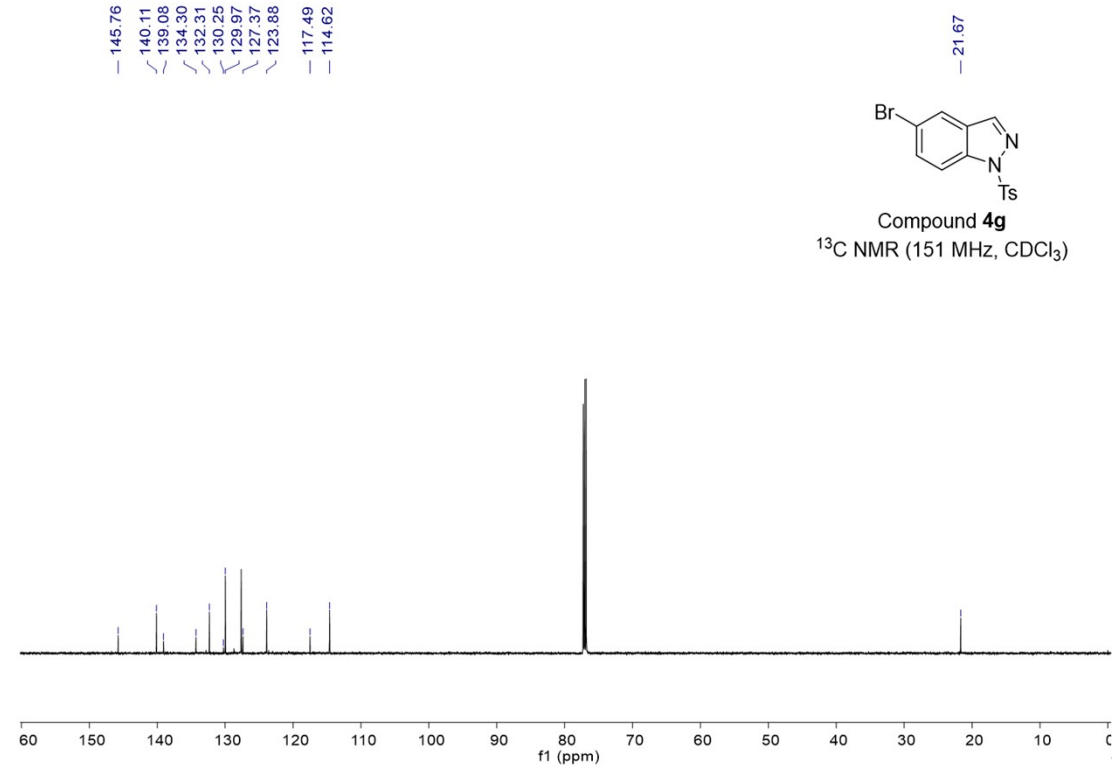


Compound **4f**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 5-bromo-1-tosyl-1H-indazole **(4g)**

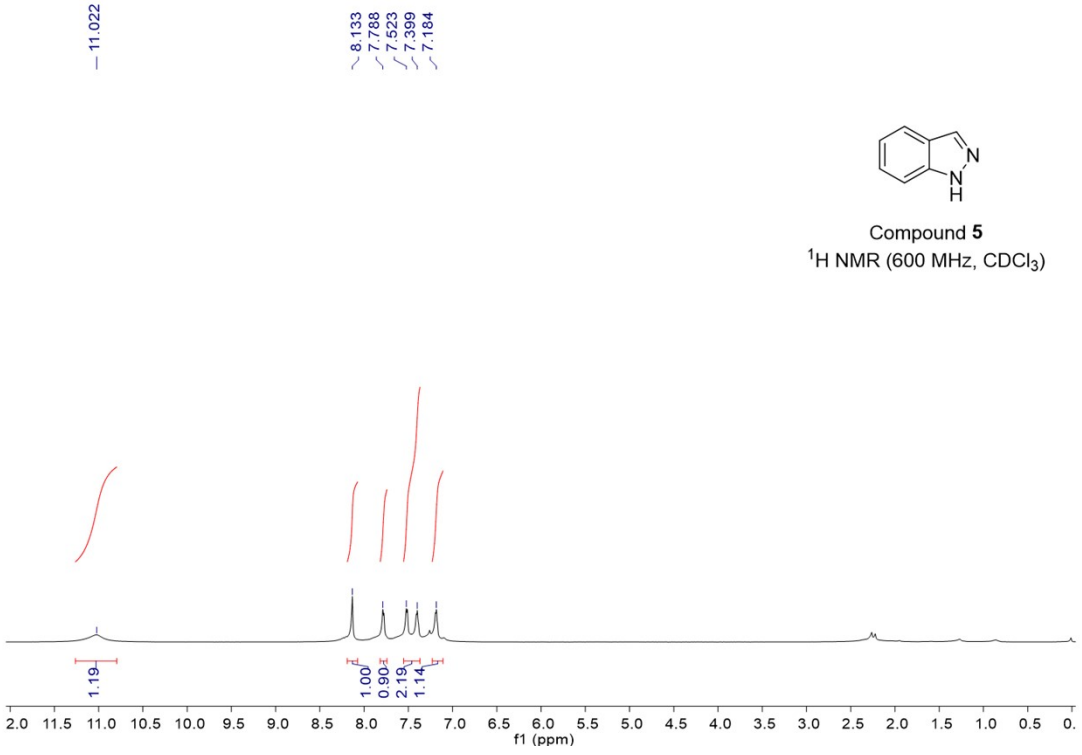


Compound **4g**
^{1}H NMR (600 MHz, $CDCl_3$)

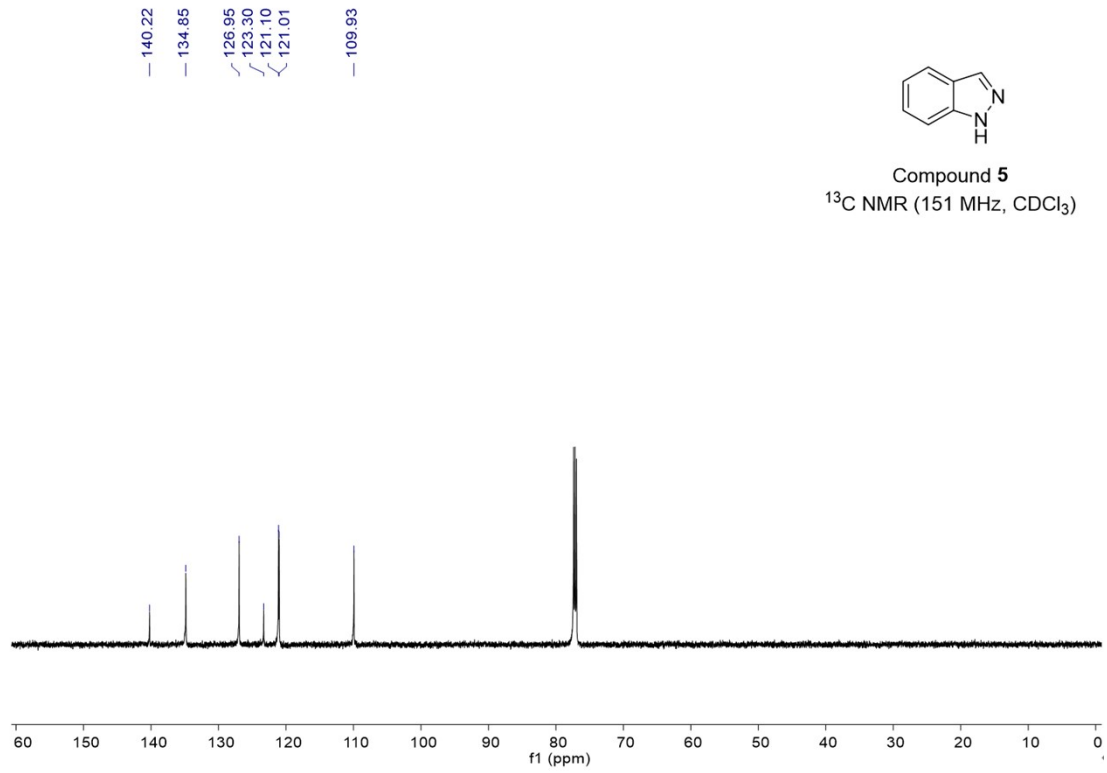


Compound **4g**
^{13}C NMR (151 MHz, $CDCl_3$)

NMR spectra of 1*H*-indazole (**5**)

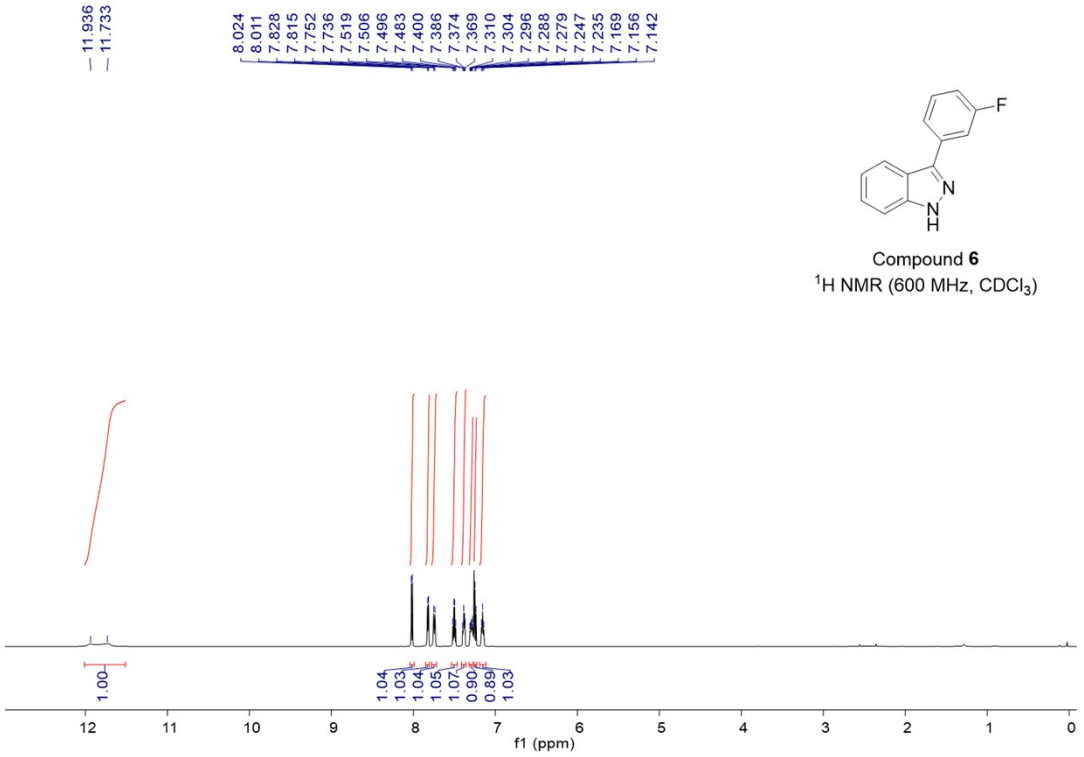


Compound **5**
^{1}H NMR (600 MHz, $CDCl_3$)

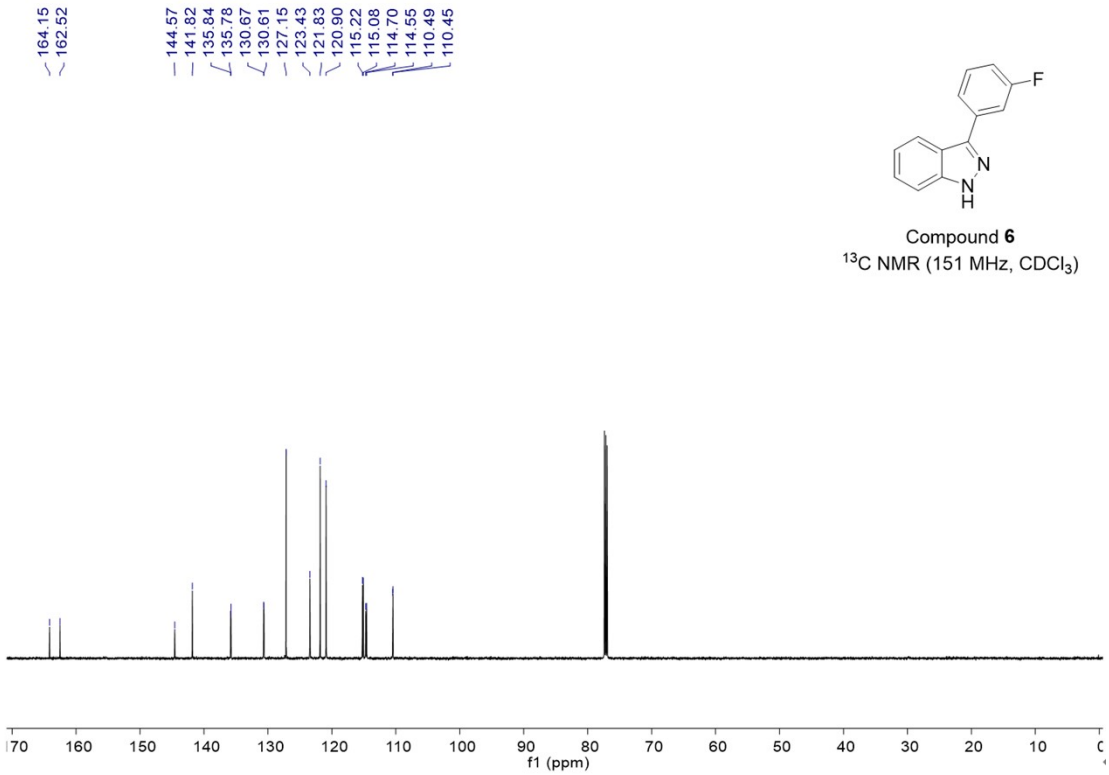


Compound **5**
^{13}C NMR (151 MHz, $CDCl_3$)

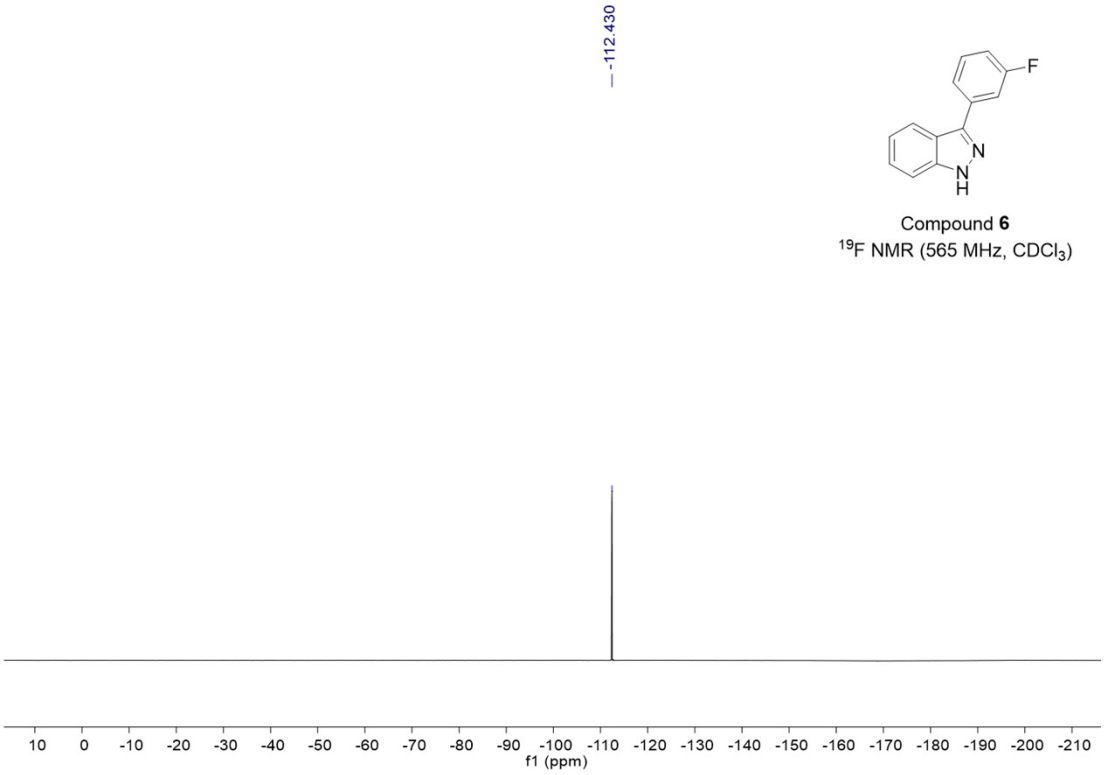
NMR spectra of 3-(3-Fluorophenyl)-1*H*-indazole (**6**)



Compound **6**
^{1}H NMR (600 MHz, $CDCl_3$)



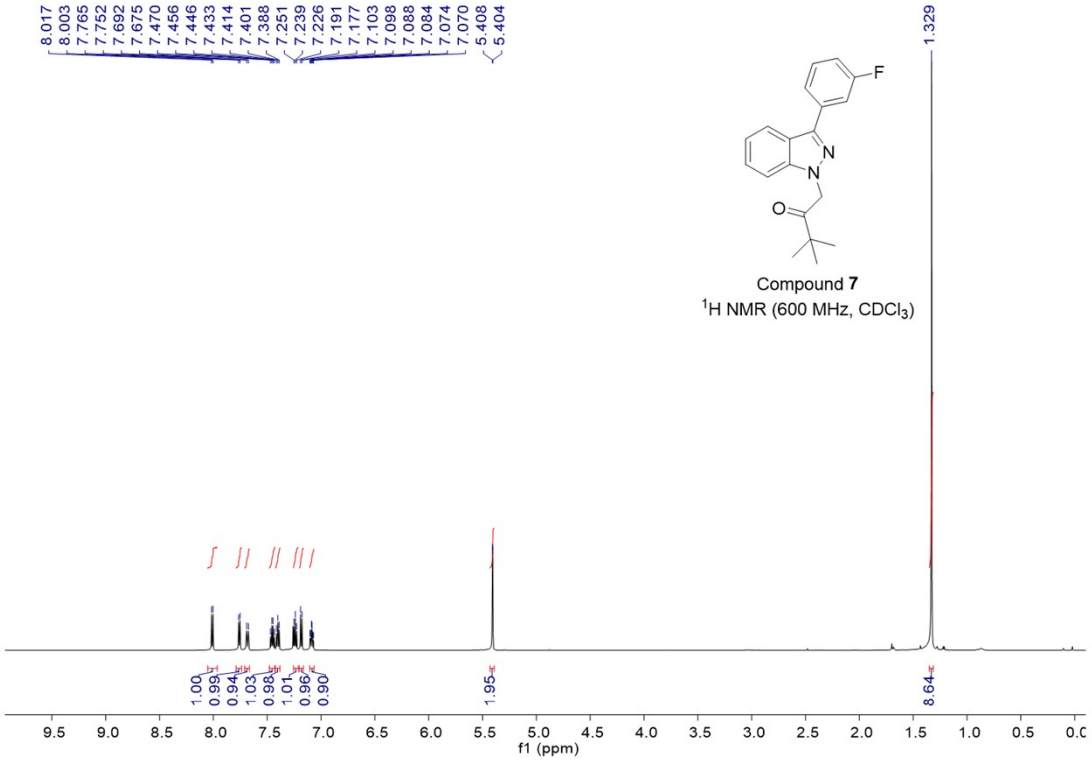
Compound **6**
^{13}C NMR (151 MHz, $CDCl_3$)

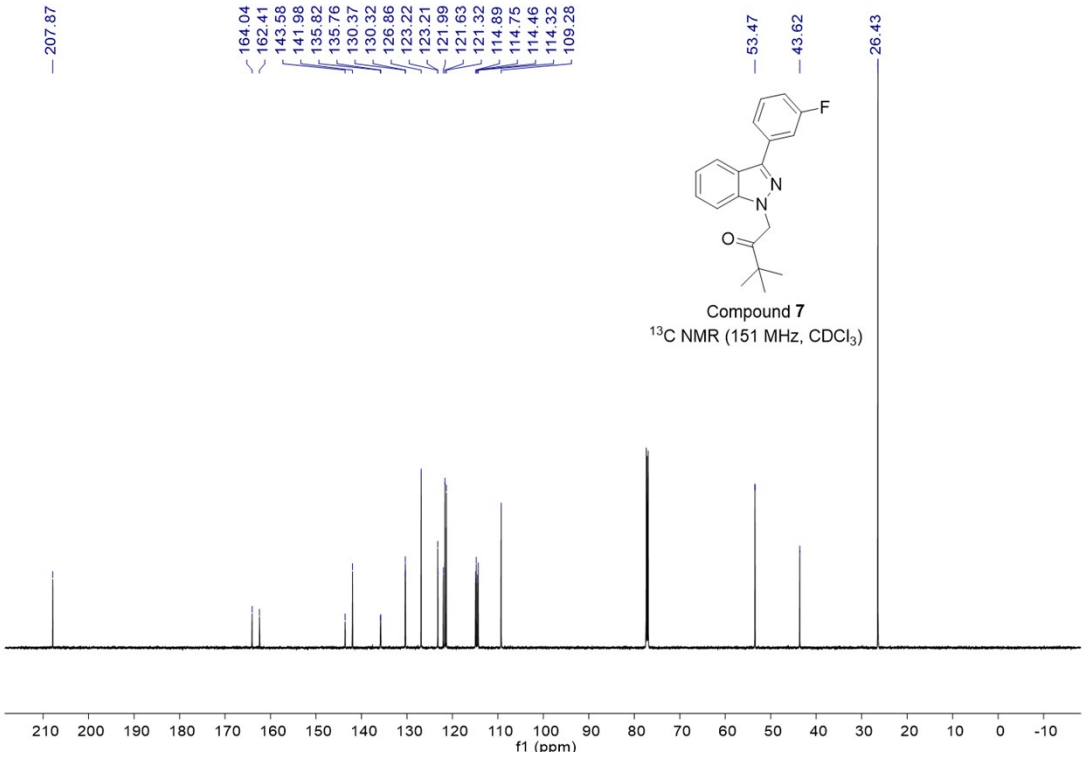


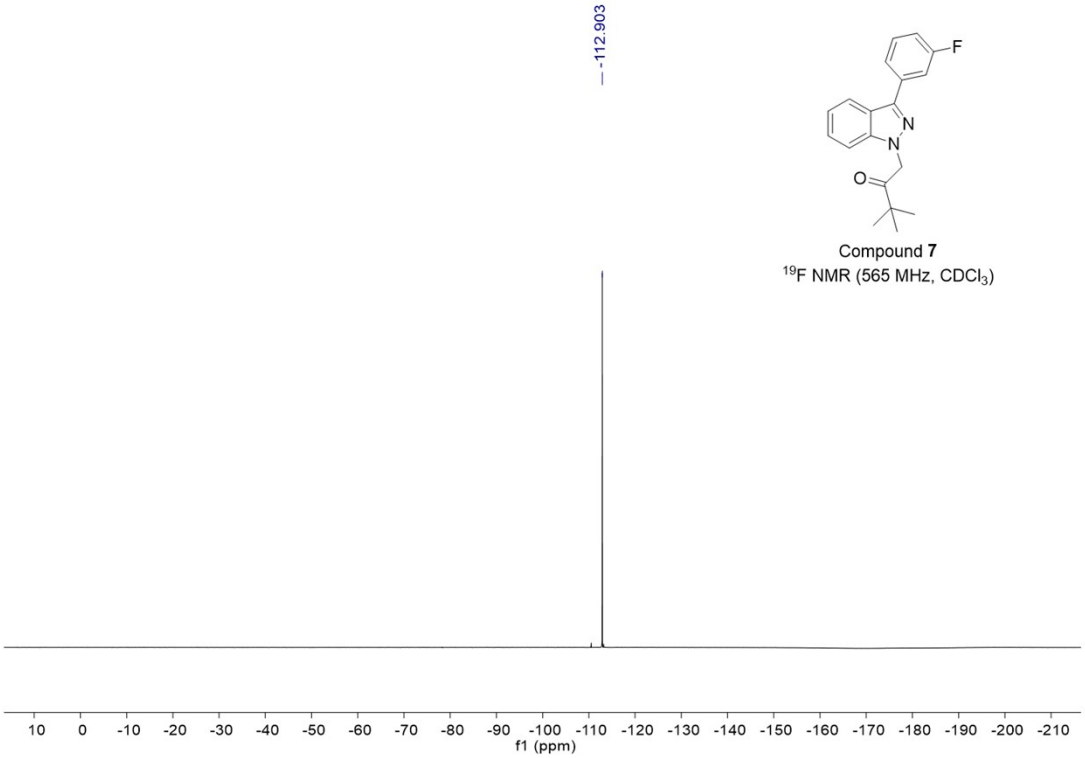
Compound **6**

^{19}F NMR (565 MHz, $CDCl_3$)

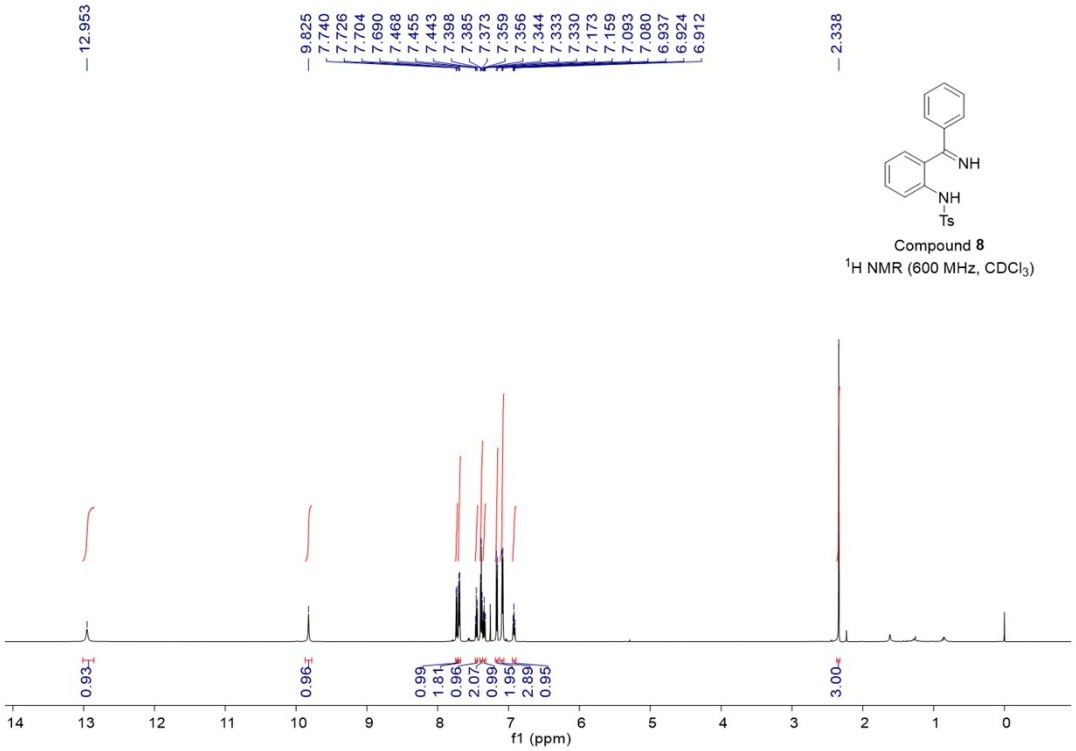
NMR spectra of TryS inhibitor Anti-HAT activity (**7**)

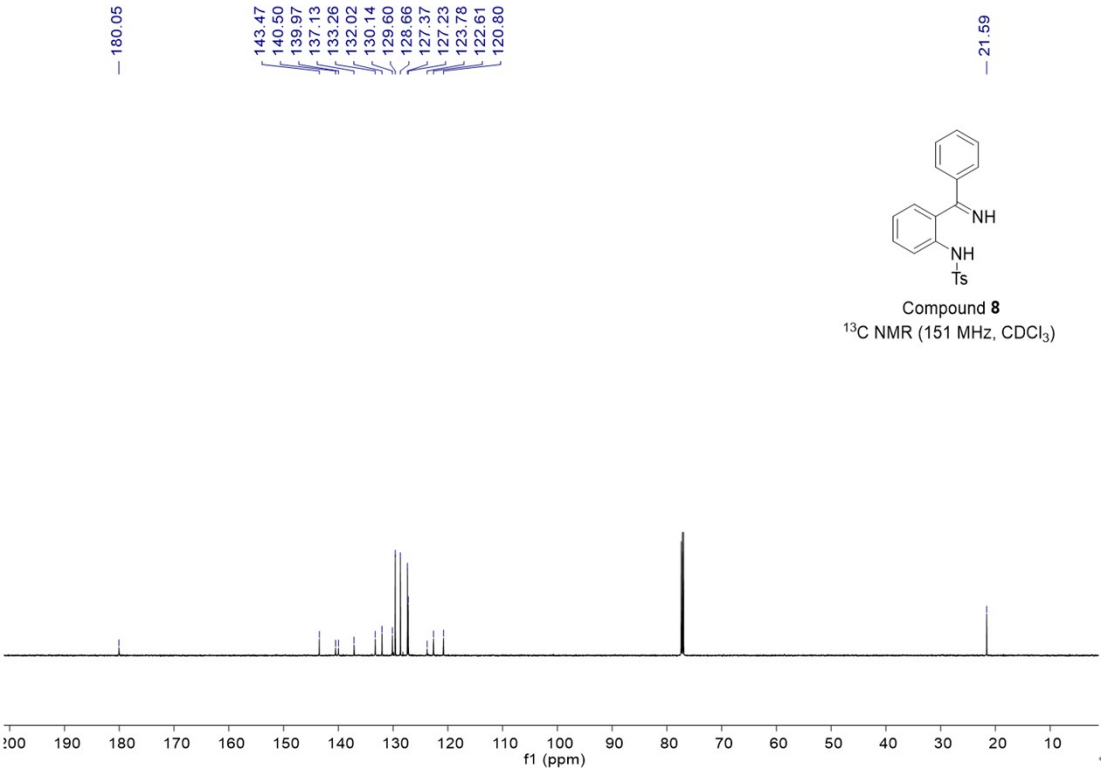






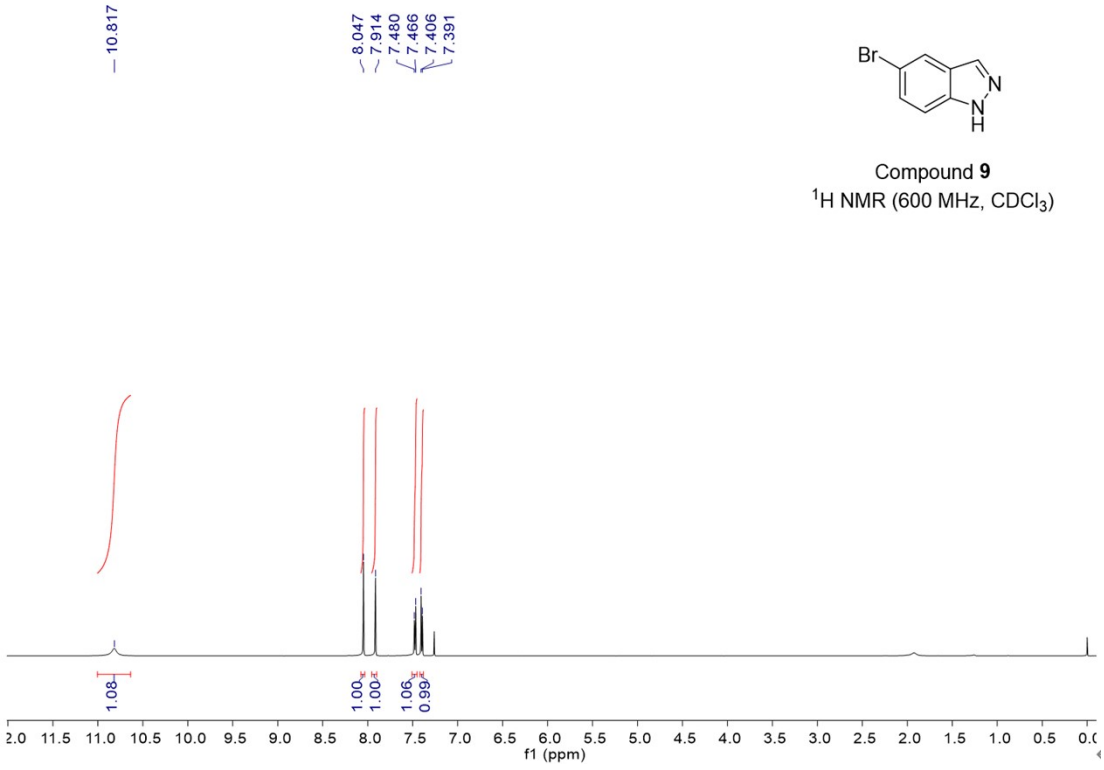
NMR spectra of *N*-(2-(Imino(phenyl)methyl)phenyl)-4-methylbenzenesulfonamide (**8**)



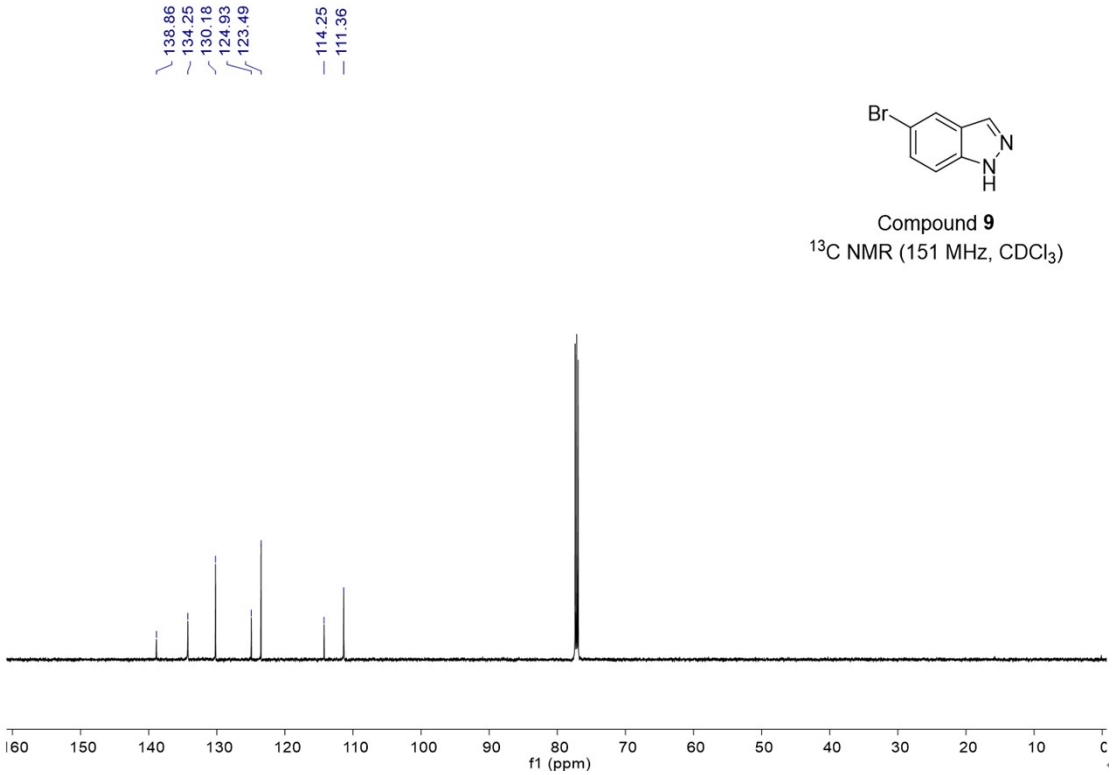


Compound **8**
^{13}C NMR (151 MHz, $CDCl_3$)

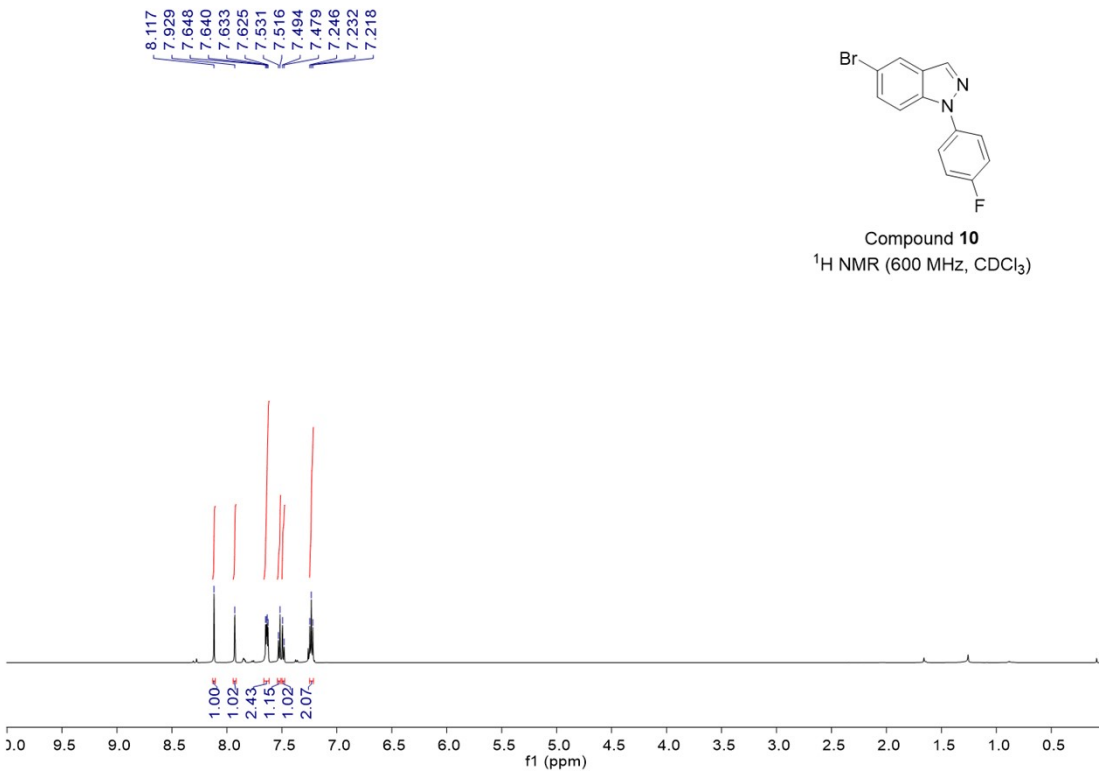
NMR spectra of 5-bromo-1H-indazole **(9)**

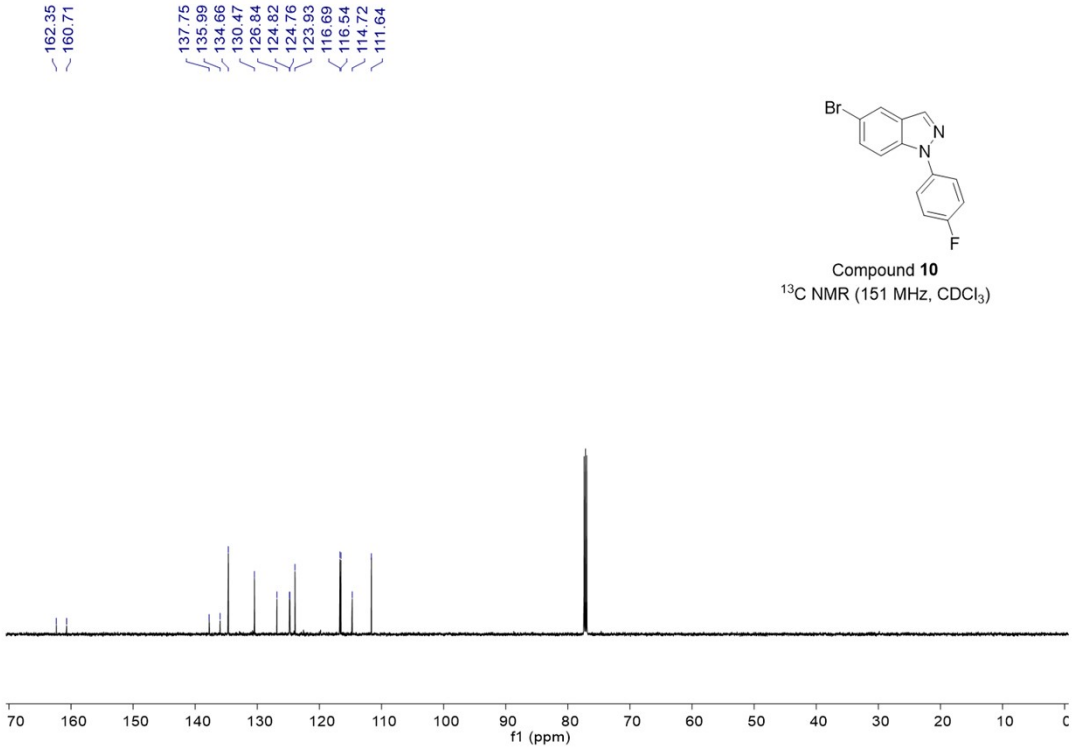


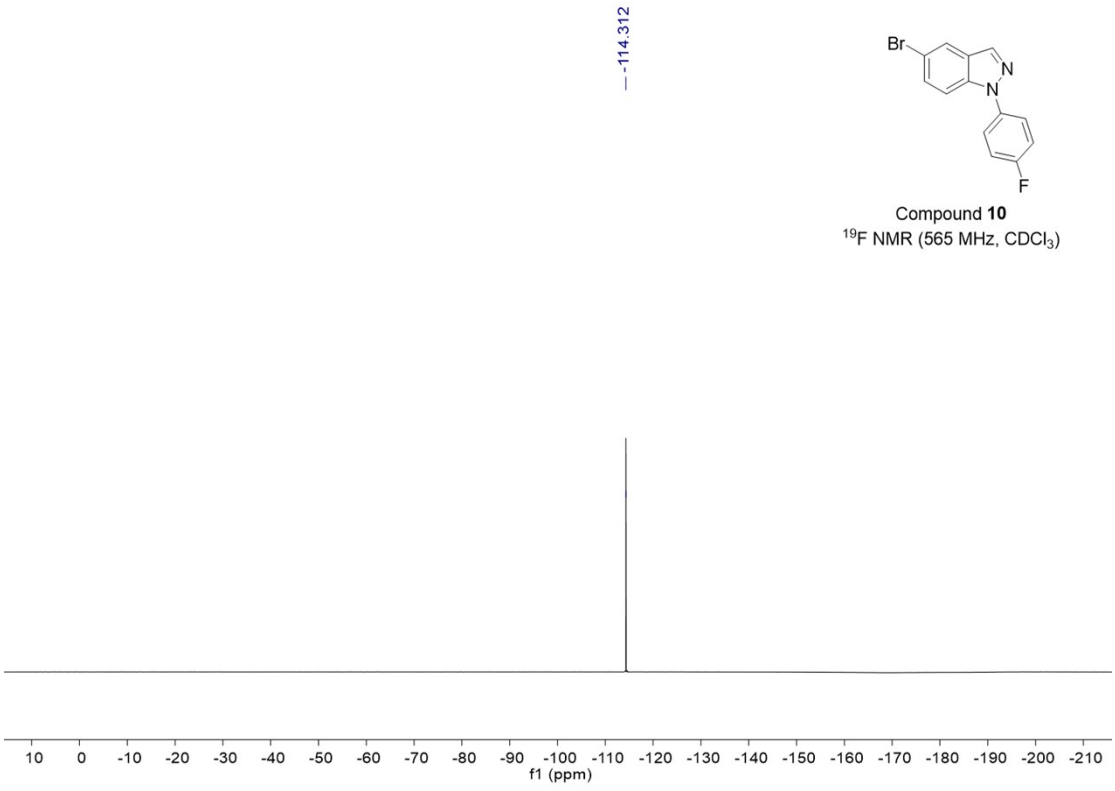
Compound **9**
^{1}H NMR (600 MHz, $CDCl_3$)



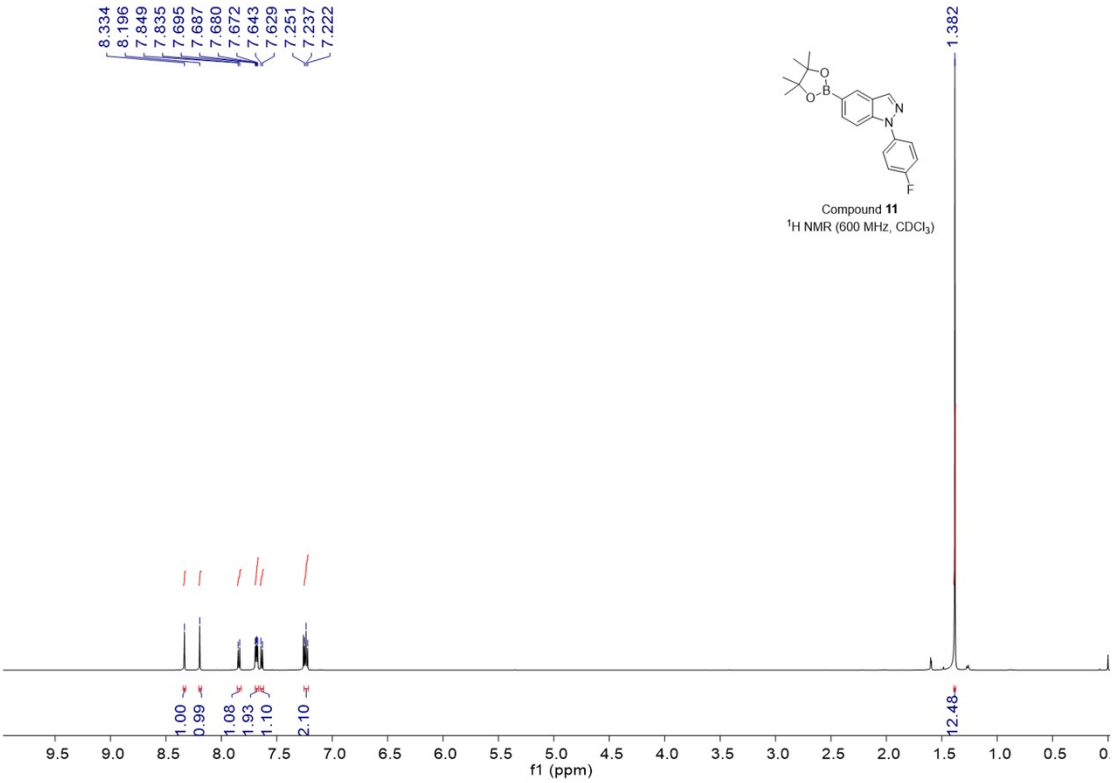
NMR spectra of 5-bromo-1-(4-fluorophenyl)-1H-indazole **(10)**

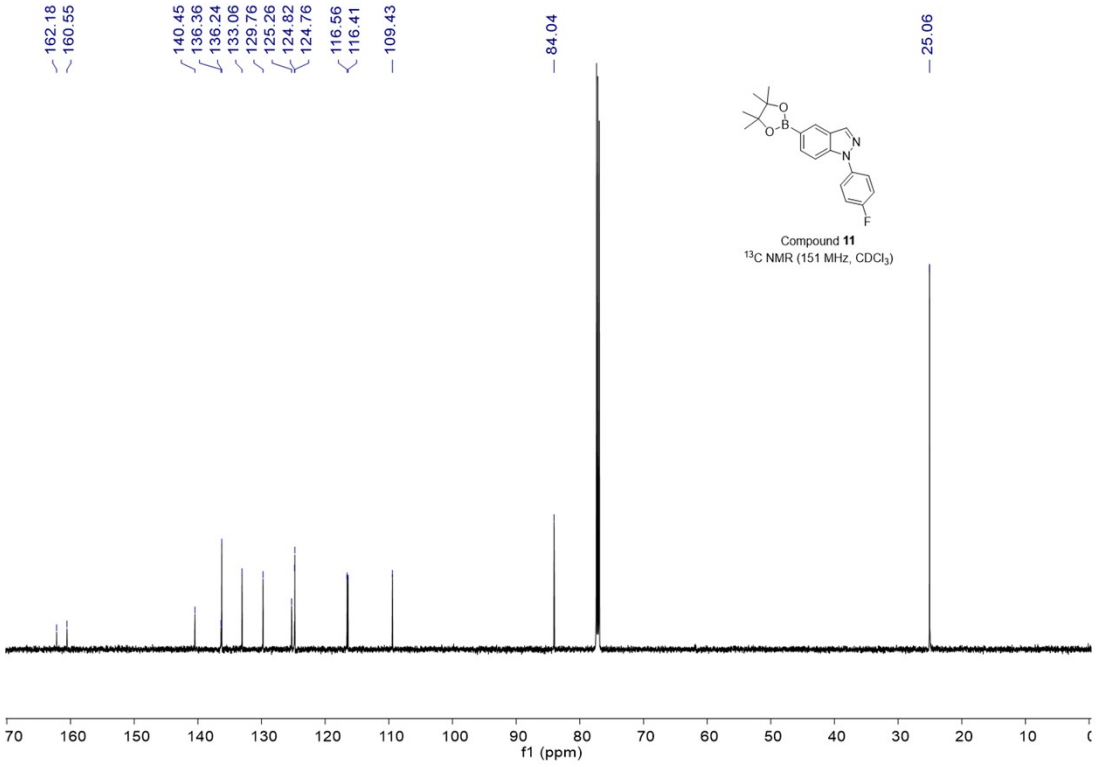


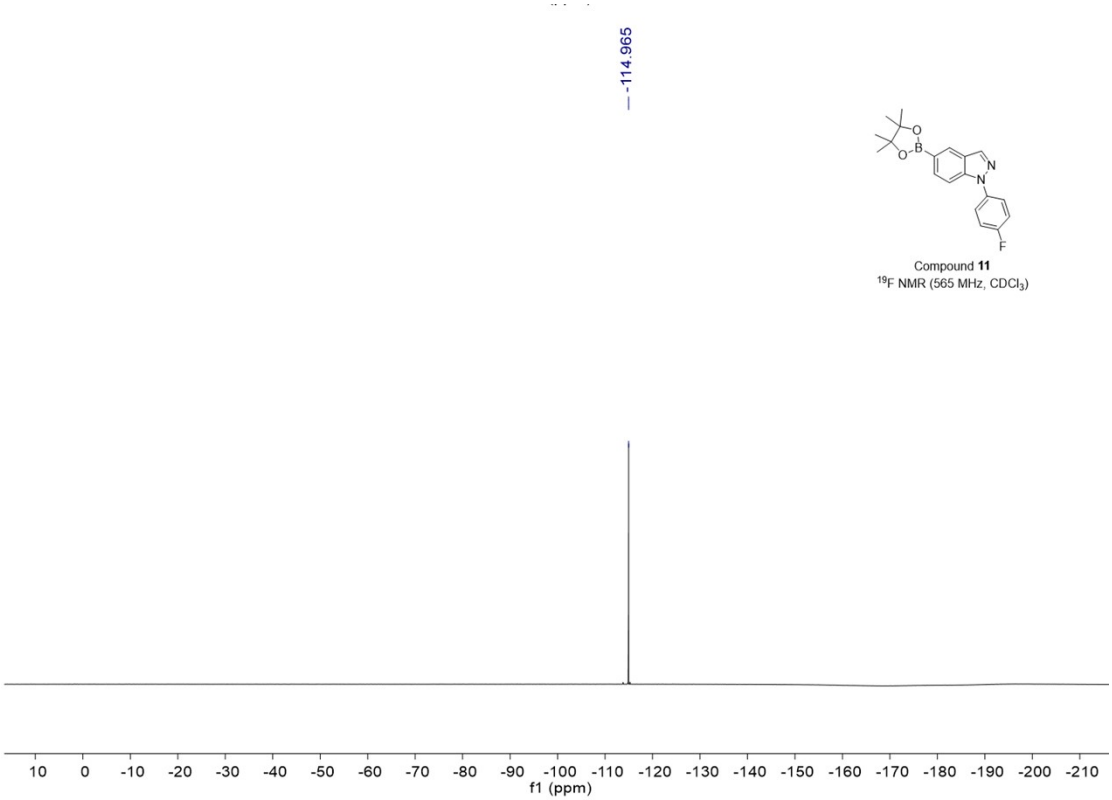




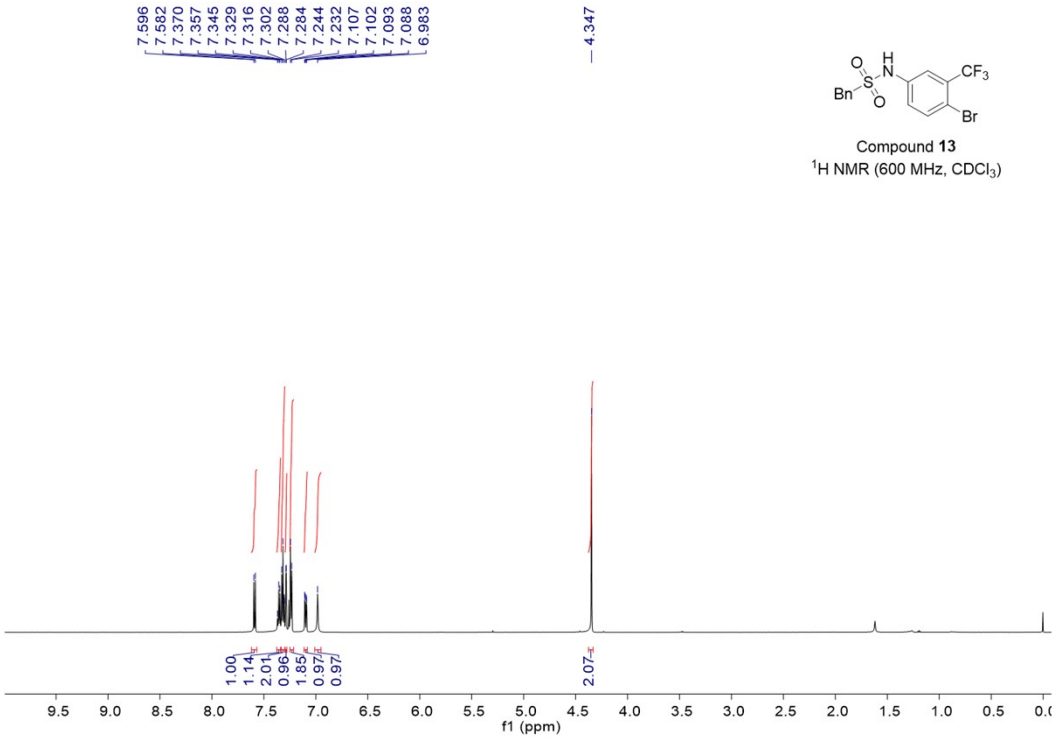
NMR spectra of 1-(4-fluorophenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indazole **(11)**

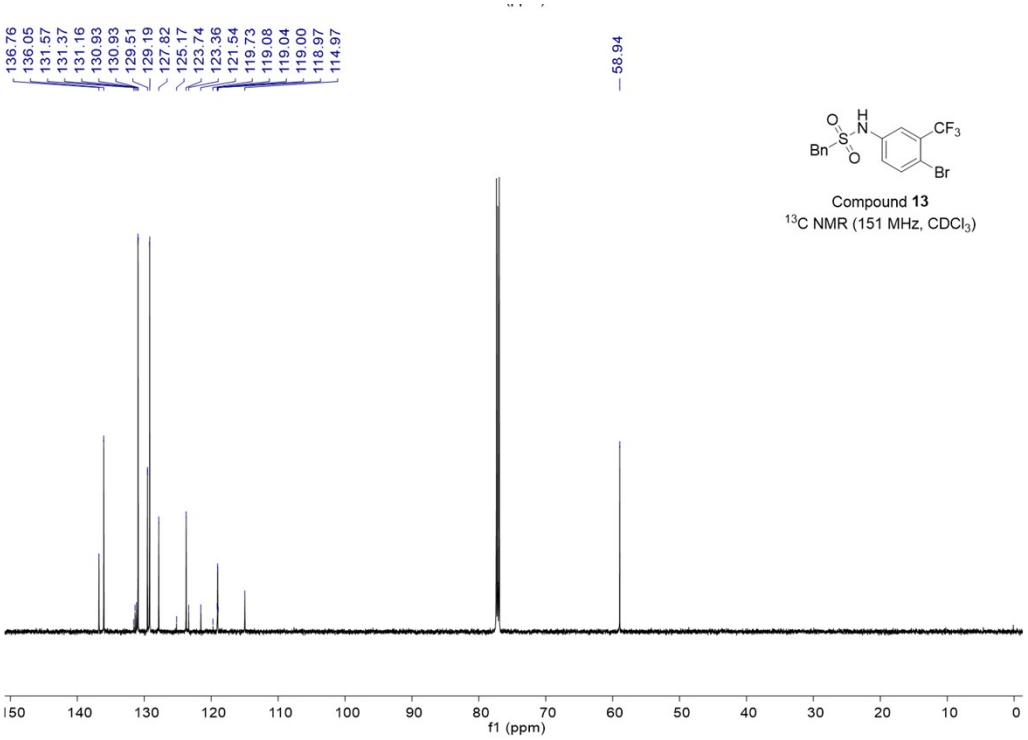

8.334
8.196
7.849
7.835
7.695
7.687
7.680
7.672
7.643
7.629
7.251
7.237
7.222
1.382
Compound 11
1H NMR (600 MHz, CDCl3)
1.00
0.99
1.08
1.93
1.10
2.10
12.48
f1 (ppm)


162.18
160.55
140.45
136.36
136.24
133.06
129.76
125.26
124.82
124.76
116.56
116.41
109.43
84.04
25.06
Compound 11
13C NMR (151 MHz, CDCl3)
f1 (ppm)



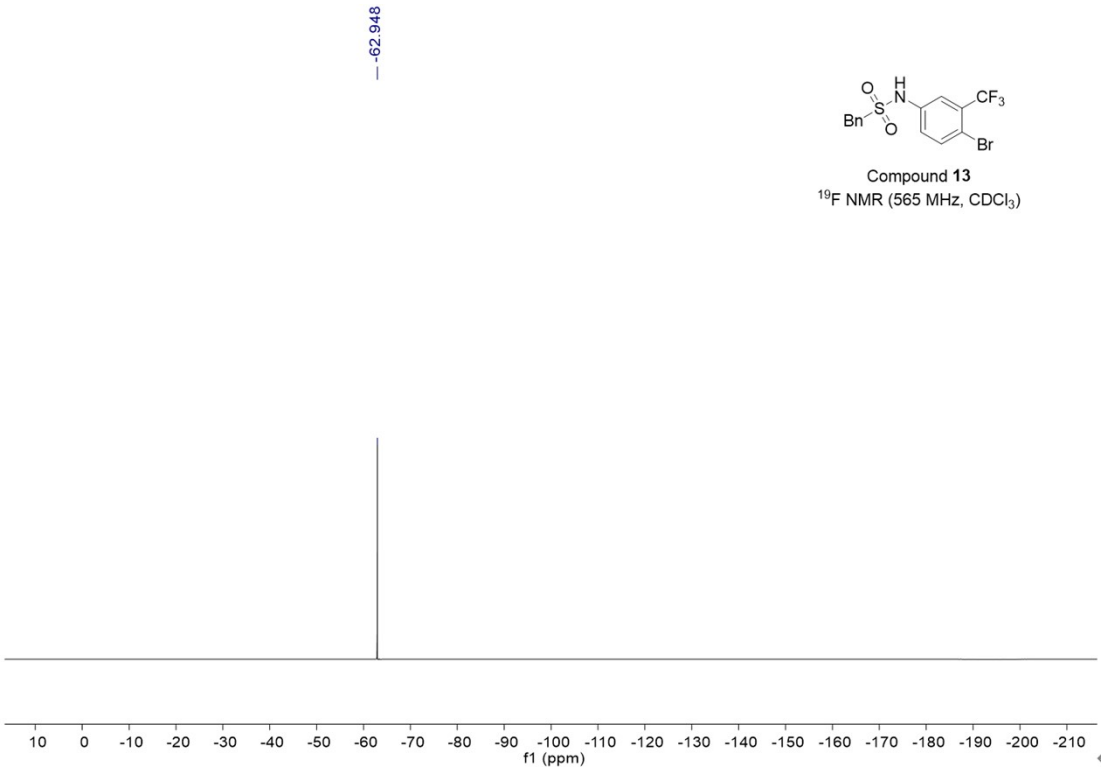
NMR spectra of N-(4-bromo-3-(trifluoromethyl)phenyl)-1-phenylmethanesulfonamide **(13)**





Compound **13**

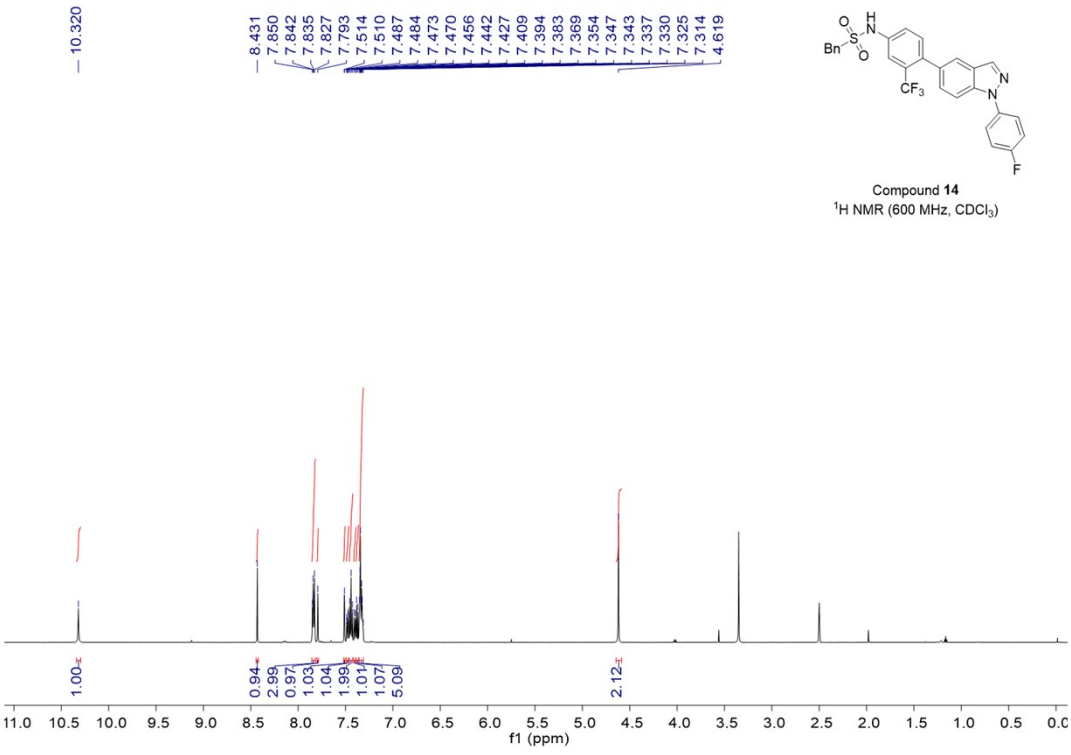
^{13}C NMR (151 MHz, $CDCl_3$)

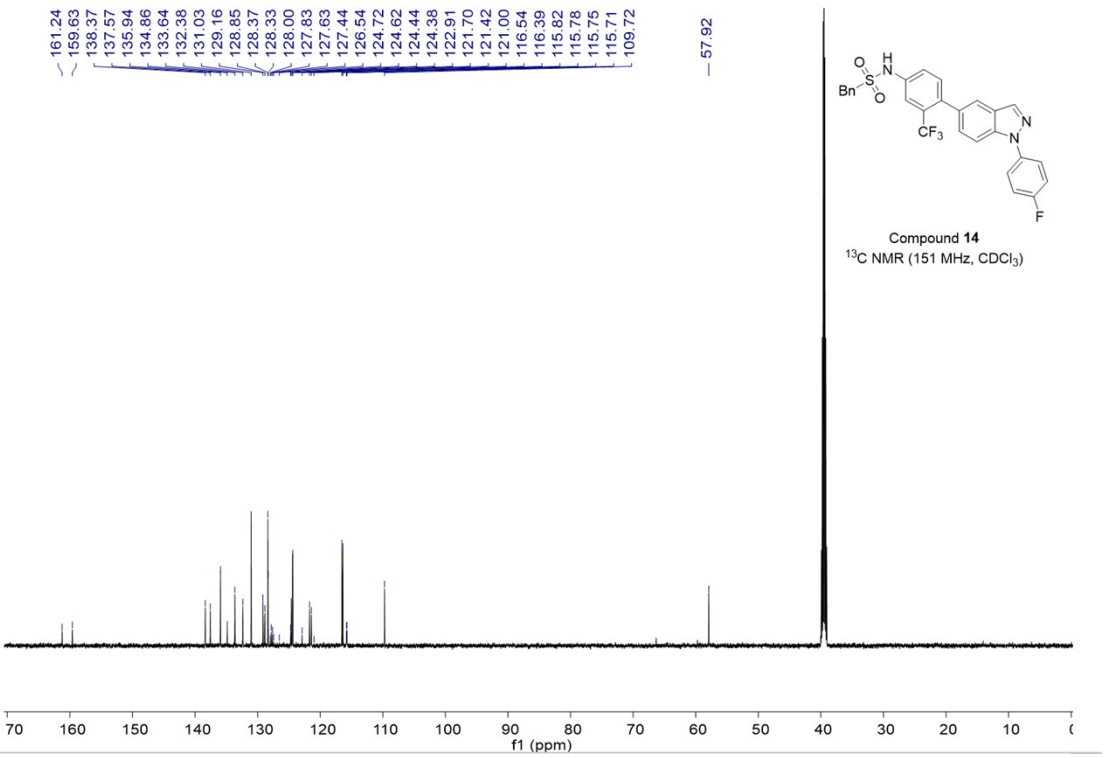


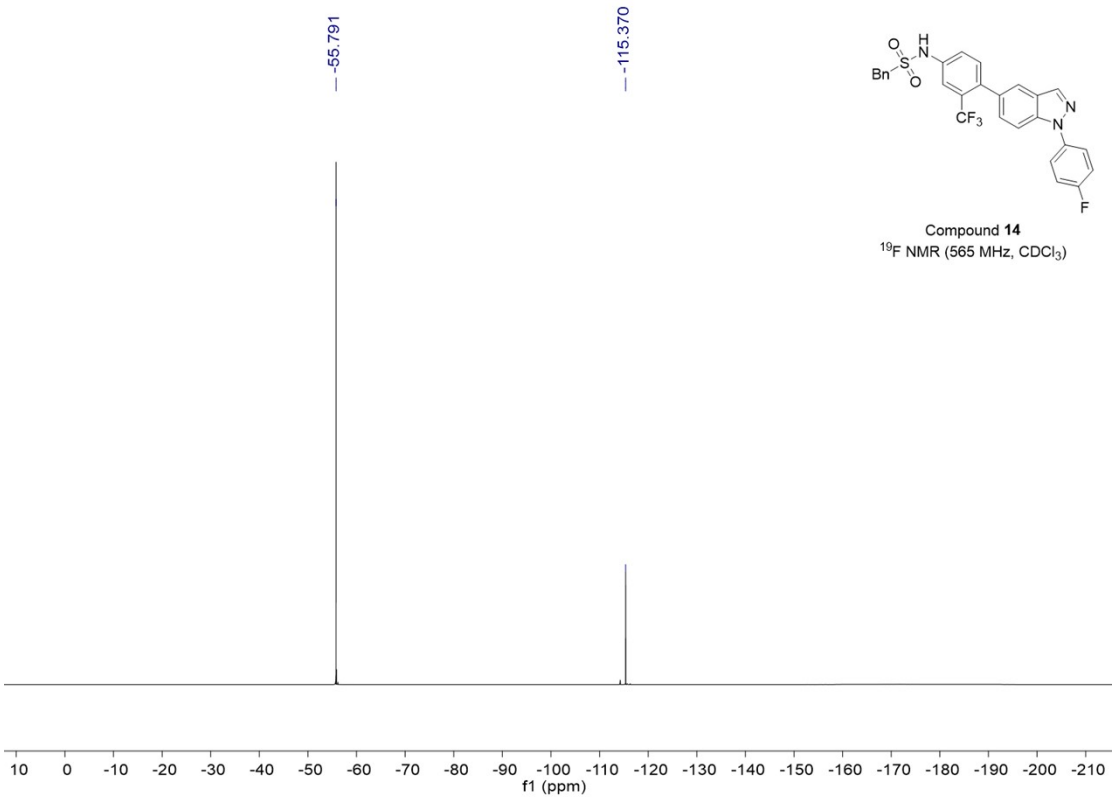
Compound **13**

^{19}F NMR (565 MHz, $CDCl_3$)

NMR spectra of Glucocorticoid receptor agonist **(14)**







13. Crystallographic data for 2e and 8.

The compound **2e** was crystalized over a solution of **2e** (50 mg) in CH_2Cl_2/petroleum (1 mL/1 mL) at room temperature. The mixed solvent spontaneously evaporates in open air to obtain the crystals of **2e**. Then the crystals were carefully collected and used for X-ray diffraction analysis. The crystal structure was further determined by Bruker D8 QUEST X-ray single crystal diffractometer. The CCDC number of **2e** is **2191796**.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

Bond precision: C-C = 0.0032 A Wavelength=0.71073

Cell: a=14.2948(8) b=8.5708(4) c=15.3612(8)
alpha=90 beta=95.345(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1873.84(17)	1873.84(17)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H18 N2 O3 S	C21 H18 N2 O3 S
Sum formula	C21 H18 N2 O3 S	C21 H19 N2 O3 S
Mr	378.43	379.44
Dx,g cm-3	1.341	1.345
Z	4	4
Mu (mm-1)	0.197	0.197
F000	792.0	796.0
F000'	792.83	
h,k,lmax	20,12,22	20,11,21
Nref	5788	4789
Tmin,Tmax	0.977,0.980	0.743,1.000
Tmin'	0.971	

Correction method= # Reported T Limits: Tmin=0.743 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.827 Theta(max)= 30.645

R(reflections)= 0.0517(3013) wR2(reflections)= 0.1746(4789)

S = 1.026 Npar= 246

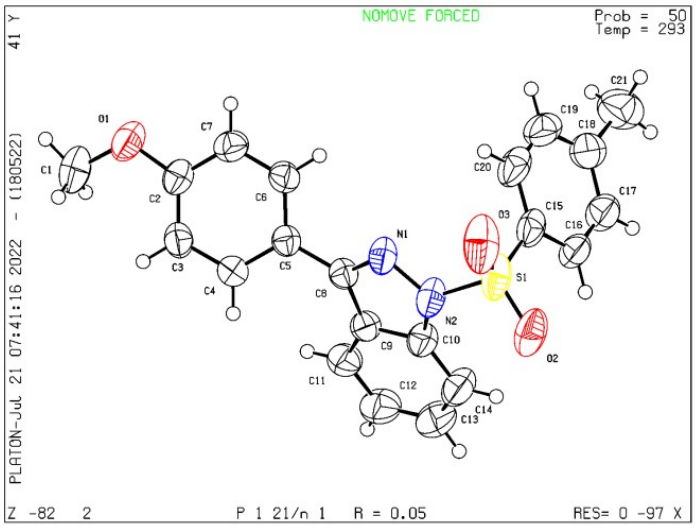


Figure S5 X-ray structure of **2e** (ORTEP diagram with ellipsoid contour 50% probability)

The compound **8** was crystalized over a solution of **8** (50 mg) in CH_2Cl_2/petroleum (1 mL/1 mL) at room temperature. The mixed solvent spontaneously evaporates in open air to obtain the crystals of **8**. Then the crystals were carefully collected and used for X-ray diffraction analysis. The crystal structure was further determined by Bruker D8 QUEST X-ray single crystal diffractometer. The CCDC number of **8** is **2222403**.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 2

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 2

Bond precision: C-C = 0.0028 A Wavelength=0.71073

Cell: a=11.349(8) b=10.096(7) c=15.893(11)
alpha=90 beta=97.84(4) gamma=90
Temperature: 273 K

	Calculated	Reported
Volume	1804(2)	1804(2)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C20 H18 N2 O2 S	C20 H18 N2 O2 S
Sum formula	C20 H18 N2 O2 S	C19 H19 N3 O2 S
Mr	350.42	353.43
Dx,g cm-3	1.290	1.301
Z	4	4
Mu (mm-1)	0.195	0.196
F000	736.0	744.0
F000'	736.78	
h,k,lmax	14,13,20	14,13,20
Nref	4126	4089
Tmin,Tmax	0.977,0.981	0.682,0.746
Tmin'	0.962	

Correction method= # Reported T Limits: Tmin=0.682 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 27.468

R(reflections)= 0.0418(3506) wR2(reflections)= 0.1207(4089)

S = 1.025 Npar= 234

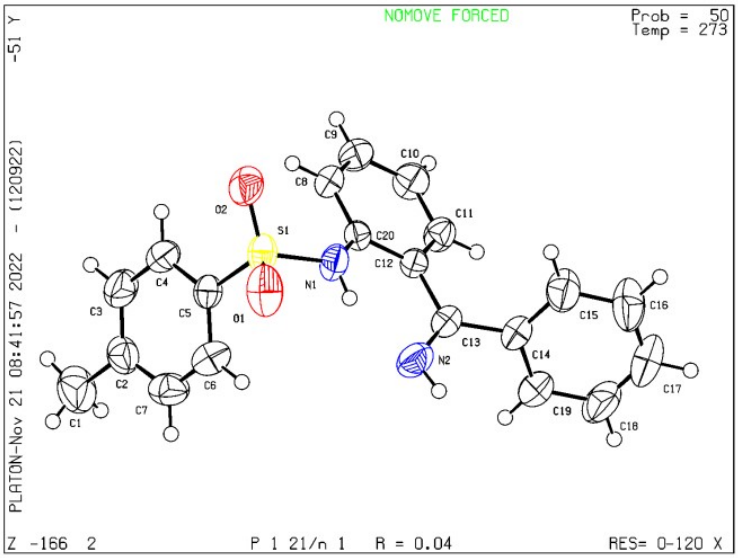


Figure S6 X-ray structure of **8** (ORTEP diagram with ellipsoid contour 50% probability)

14. Determination of the Faradaic Efficiency

$$\text{F.E.}(\%) = \frac{\text{n x F x mol of product or intermediate formed}}{\text{acculumated charge (C)}} \times 100\ \%$$

$$= \frac{2 \times 96485\ \text{C mol}^{-1} \times 0.3\ \text{mmol} \times 10^{-3} \times 86\ \%}{5\ \text{mA} \times 10^{-3} \times 10\ \text{h} \times 3600} \times 100\ \%$$

$$= 27.7\%$$

The F.E. (%) of the product **2a** was calculated by (1). The F.E. is the proportion of electrons consumed in each electrochemical reaction of the total applied charge and represents the selectivity of the electrochemical system for each reaction. In Eq (1), F is the Faradaic constant (96485 C mol^{-1}), and n is the number of electrons required for the production of products. The yield is the proportion of reactant converted to target product.