

Supporting Information for

Preparation of 3-Aryl-2-aminoindoles, 3-Allyl-3-amino-2-iminoindolines, and
Tetrahydro-[1,4]diazepino[2,3-b]indoles from 3-Diazoindolin-2-imines

Guorong Sheng, Kai Huang, Shicong Ma, Jing Qian, Ping Lu*, and Yanguang Wang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

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General Information

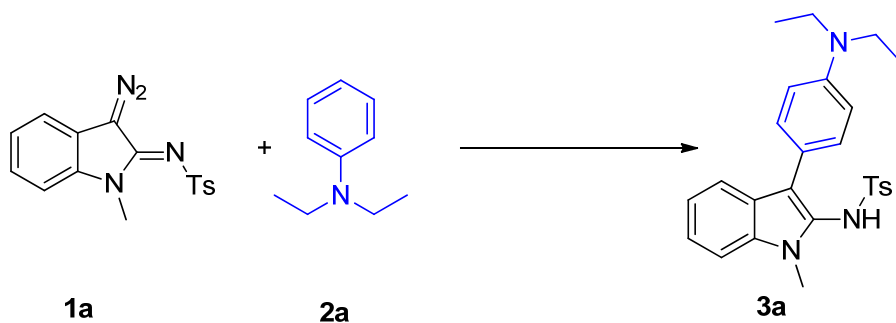
Melting points were recorded on a SGW X-4. NMR spectra were obtained on a Bruker AVANCE DMX400 spectrometer operating at 400 MHz or 500 MHz or 600 MHz for ^1H -NMR, 100 MHz or 125 MHz or 150 MHz for ^{13}C -NMR. Unless otherwise noted, all the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants (J values) were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 and $\text{DMSO}-d_6$ as an internal standard or $\text{CHD}_2\text{COCD}_3$ ($\delta = 2.05$ ppm) in acetone- d_6 as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of CDCl_3 or the center line of a heptet at 39.6 ppm of $\text{DMSO}-d_6$ or the center line of a heptet at 30 ppm of CD_3COCD_3 . High resolution mass spectra (HRMS) were recorded on Waters GCT Premier (EI) and Agilent Technologies 6224 TOF LC/MS apparatus (ESI). IR spectra were run on a Bruker vector 22 spectrometer. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254.

Substrates **1** were prepared according to the published procedures.^{[1][2]} Substrates **2**, **4**, **6** were prepared according to the published procedures.^[3]

References

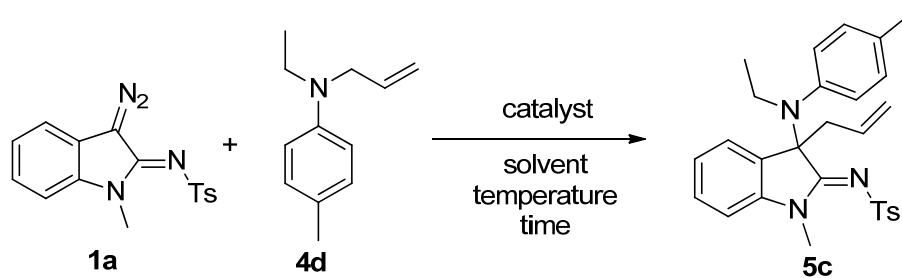
- [1] Y. P. Xing, G. R. Sheng, J. Wang, P. Lu, and Y.G. Wang, *Org. Lett.* **2014**, *16*, 1244–1247.
- [2] G. R. Sheng, K. Huang, Z. H. Chi, H. L. Ding, Y. P. Xing, P. Lu, and Y. G. Wang, *Org. Lett.*, **2014**, *16*, 5096–5099
- [3] Akio Saito, Shoko Oda, Haruhiko Fukaya, and Yuji Hanzawa, *J. Org. Chem.* **2009**, *74*, 1517–1524

Table S1 Screening of the reaction conditions for formation of **3a**^a



Entry	Catalyst	Solvent	T (°C)	1a:2a	Yield (%) ^b
1	Rh₂(Oct)₄	PhCH₃	110	1:1.2	78
2	Rh ₂ (OAc) ₄	PhCH ₃	110	1:1.2	66
3	Rh ₂ (Oct) ₄	CHCl ₃	110	1:1.2	50
4	Rh ₂ (Oct) ₄	DCE	110	1:1.2	45
5	Rh ₂ (Oct) ₄	PhCH ₃	120	1:1.2	67
6	Rh ₂ (Oct) ₄	PhCH ₃	100	1:1.2	74
7	Rh ₂ (Oct) ₄	PhCH ₃	110 ^c	1:1.2	67
8	Rh ₂ (Oct) ₄	PhCH ₃	110 ^d	1:1.2	53
9	Rh ₂ (Oct) ₄	PhCH ₃	110	1:1.5	78
10	Rh ₂ (Oct) ₄	PhCH ₃	110	1:1	56

^a **1a** (0.2 mmol), **2a** (0.24 mmol), cat (2 mol%), solvent (1 mL), N₂, 1 h. ^b Isolated yields after column chromatograph (petroleum : ethyl acetate = 6 : 1). ^c air. ^d oxygen.

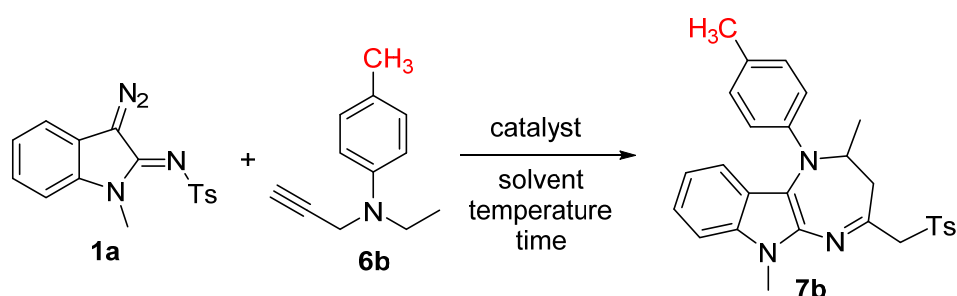
Table S2 Screening of the reaction conditions for the formation of **5c**^a

Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%) ^b
1	Rh ₂ (Oct) ₄	PhCH ₃	100	6	81
2	Rh ₂ (OAc) ₄	PhCH ₃	100	6	76
3	Rh ₂ (S-DOSP) ₄	PhCH ₃	100	6	72
4	Rh ₂ (R-DOSP) ₄	PhCH ₃	100	6	73
5	Rh ₂ (S-PTAD) ₄	PhCH ₃	100	6	34
6	Rh ₂ (Oct) ₄	DCE	100	6	85
7	Rh ₂ (Oct) ₄	CHCl ₃	100	6	60
8	Rh ₂ (Oct) ₄	DCE	80	6	83
9	Rh ₂ (Oct) ₄	DCE	60	6	87
10	Rh ₂ (Oct) ₄	DCE	40	6	72
11	Rh ₂ (Oct) ₄	DCE	60	4	75
12	Rh ₂ (Oct) ₄	DCE	60	8	69
13 ^c	Rh ₂ (Oct) ₄	DCE	60	6	81
14 ^d	Rh ₂ (Oct) ₄	DCE	60	6	87

^a **1a** (0.2 mmol), **4d** (0.24 mmol), cat (2 mol%), solvent (1 mL), N₂, 1h. ^b Isolated yields after column

chromatograph (petroleum : ethyl acetate = 6 : 1). ^c **4d** (0.2 mmol). ^d **4d** (0.3 mmol).

Table S3 Screening of the reaction conditions for electrophilic cyclization of alkyne^a



Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield(%) ^b
1	Rh ₂ (Oct) ₄	PhCH ₃	90	2	43
2	Rh ₂ (Oct) ₄ +AgOTf	PhCH ₃	90	2	13
3	Rh ₂ (Oct) ₄ +CuCl	PhCH ₃	90	2	47
4	Rh ₂ (Oct) ₄ +CuBr	PhCH ₃	90	2	43
5	Rh₂(Oct)₄+CuI	PhCH₃	90	2	64
6	Rh ₂ (Oct) ₄ +Yb(OTf) ₃	PhCH ₃	90	2	52
7	Rh ₂ (Oct) ₄ +In(OTf) ₃	PhCH ₃	90	2	63
8	Rh ₂ (Oct) ₄ +Zn(OTf) ₂	PhCH ₃	90	2	59
9	Rh ₂ (Oct) ₄ +AgOCOCH ₃	PhCH ₃	90	2	41
10	Rh ₂ (Oct) ₄ +Cu(OTf) ₂	PhCH ₃	90	2	38
11	Rh ₂ (Oct) ₄ +CuOTf	PhCH ₃	90	2	40
12	Rh ₂ (Oct) ₄ +Au(PPh ₃) ₃ Cl	PhCH ₃	90	2	64
13	Rh ₂ (Oct) ₄ +CuI ^c	PhCH ₃	90	2	57
14	Rh ₂ (Oct) ₄ +CuI ^d	PhCH ₃	90	2	51
15	Rh ₂ (Oac) ₄ +CuI	PhCH ₃	90	2	55
16	Rh ₂ (S-DOSP) ₄ +CuI	PhCH ₃	90	2	13
17	Rh ₂ (R-DOSP) ₄ +CuI	PhCH ₃	90	2	15
18	Rh ₂ (S-PTAD) ₄ +CuI	PhCH ₃	90	2	trace
19	Rh ₂ (Oct) ₄ +CuI	CH ₃ Cl ₃	90	2	49
20	Rh ₂ (Oct) ₄ +CuI	DCE	90	2	32
21	Rh ₂ (Oct) ₄ +CuI	PhCH ₃	80	2	53
22	Rh ₂ (Oct) ₄ +CuI	PhCH ₃	100	2	60
23	Rh ₂ (Oct) ₄ +CuI	PhCH ₃	90	1	40
24	Rh ₂ (Oct) ₄ +CuI	PhCH ₃	90	3	55

^a **1a** (0.2 mmol), **6b** (0.24 mmol), cat (2 mol%) + additive (2 mol%), solvent (2 mL), N₂. ^b Isolated yields after column chromatograph (petroleum : ethyl acetate = 6 : 1). ^c CuI (5 mol%). ^d CuI (10 mol%).

General Procedures

1. General procedure for the preparation of compounds 3

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1** (0.2 mmol, 1.0 equiv), $\text{Rh}_2(\text{oct})_4$ (0.004 mmol), amine **2** (0.24 mmol) and toluene (2 mL) under N_2 atmosphere. The reaction vessel was placed in an oil bath preheated to 110 °C. The resulting solution was heated at this temperature for 1 hour. After cooled to room temperature, the reaction solution was concentrated in vacuo, and the crude product was purified through silica gel column (petroleum ether / EtOAc = 6:1).

2. General procedure for the preparation of compounds 5

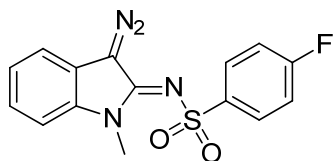
To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1** (0.2 mmol, 1.0 equiv), $\text{Rh}_2(\text{oct})_4$ (0.004 mmol), amine **4** (0.24 mmol) and DCE (2 mL) under N_2 atmosphere. The reaction vessel was placed in an oil bath preheated to 60 °C. The resulting solution was heated at this temperature for 6 hour. After cooled to room temperature, the reaction solution was concentrated in vacuo, and the crude product was purified through silica gel column (petroleum ether / EtOAc = 6:1).

3. General procedure for the preparation of compounds 7

To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added sequentially **1** (0.2 mmol, 1.0 equiv), $\text{Rh}_2(\text{oct})_4$ (0.004 mmol), CuI (0.004 mmol), amine **6** (0.24 mmol) and PhCH_3 (2 mL) under N_2 atmosphere. The reaction vessel was placed in an oil bath preheated to 90 °C. The resulting solution was heated at this temperature for 2 hour. After cooled to room temperature, the reaction solution was concentrated in vacuo, and the crude product was purified through silica gel column (petroleum ether / EtOAc = 6:1).

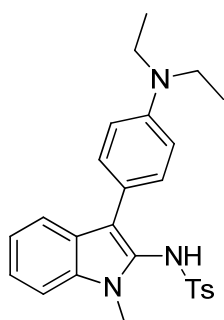
Analysis Data of Products

(Z)-N-(3-diazo-1-methylindolin-2-ylidene)-4-fluorobenzenesulfonamide (1e)



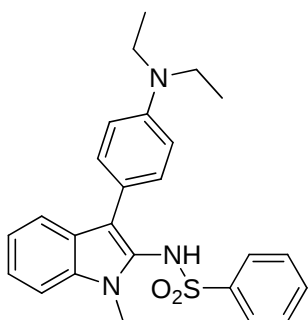
yellow solid; Yield: 56% ; M.p. 141-142⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 7.93 (m, 2H), 7.34 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 3.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5 (d, *J*_{C-F} = 253.0 Hz), 155.2, 139.1 (d, *J*_{C-F} = 3.2 Hz), 134.1, 128.9 (d, *J*_{C-F} = 9.2 Hz), 126.0, 123.1, 118.8, 116.9, 115.8 (d, *J*_{C-F} = 22.4 Hz), 109.8, 29.0; IR (neat, cm⁻¹) 2113, 1534, 1492, 1382, 1270, 1140, 1085, 1010, 793, 741; Elemental Analysis: calcd for C:54.54; H:3.36; N:16.96; Found: C:54.76; H:3.53; N:16.95.

N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (3a)



White solid; Yield: 78% ; M.p. 181-182⁰C ; ¹H NMR (400 MHz, Acetone) δ 8.94 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.08 – 6.99 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.55 – 6.47 (m, 2H), 3.83 (s, 3H), 3.41 (q, *J* = 7.0 Hz, 4H), 2.30 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.1, 143.8, 138.5, 136.1, 130.7, 129.8, 128.0, 127.3, 126.6, 123.4, 121.2, 120.7, 120.5, 114.8, 112.4, 110.7, 45.0, 29.9, 21.8, 13.3; IR (neat, cm⁻¹) 3262, 2970, 1611, 1570, 1516, 1372, 1329, 1159, 1087, 811, 734, 673; HRMS (EI): calcd for: 447.1980, Found: 447.1986.

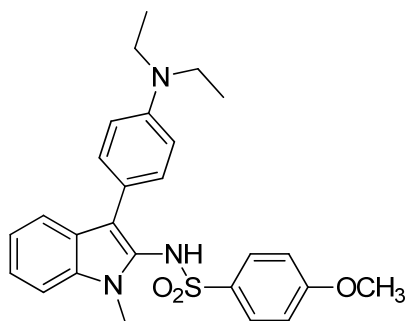
N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)benzenesulfonamide (3b)



White solid; Yield: 89% ; M.p. 84-85⁰C ; ¹H NMR (400 MHz, Acetone) δ 9.04 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.40 – 7.35 (m, 1H), 7.27 – 7.21 (m, 1H), 7.20 – 6.13 (m, 2H), 7.09 – 7.00 (m, 3H), 6.51 – 6.44 (m, 2H), 3.82 (s, 3H), 3.40 (q, *J* = 7.0 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.1, 141.6, 136.1, 133.2, 130.7, 129.3, 127.9, 127.2, 126.6, 123.5, 121.0, 120.7, 120.5, 114.9, 112.6, 110.7, 45.0, 29.9, 13.3; IR (neat, cm⁻¹) 3272, 2970, 1613, 1516, 1372, 1328, 1161, 1091, 820, 734, 686. HRMS (EI): calcd for: 433.1824, Found: 433.1824.

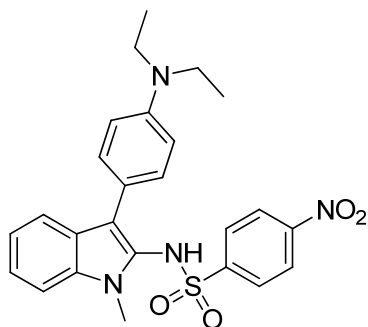
N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-methoxybenzenesulfonamide (3c)

White solid; Yield: 65% ; M.p. 79-80⁰C ; ¹H NMR (400 MHz, Acetone) δ 8.87 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H), 7.09 – 7.00 (m, 3H), 6.67 – 6.59 (m, 2H), 6.55 –



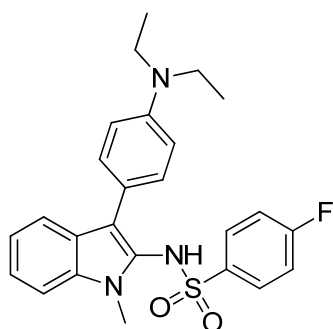
6.47 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.40 (q, $J = 7.0$ Hz, 4H), 1.20 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 163.7, 147.1, 136.1, 132.8, 130.7, 130.0, 127.4, 126.7, 123.4, 121.2, 120.7, 120.5, 114.7, 114.4, 112.5, 110.7, 56.0, 45.0, 29.9, 13.2; IR (neat, cm^{-1}) 3264, 2970, 1573, 1516, 1374, 1328, 1260, 1156, 1090, 827, 678. HRMS (EI): calcd for: 463.1930, Found: 463.1927.

N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-nitrobenzenesulfonamide (3d)



purple solid; Yield: 78% ; M.p. 160-170 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 9.47 (s, 1H), 8.01 – 7.92 (m, 2H), 7.70 – 7.61 (m, 2H), 7.56 (d, $J = 7.3$ Hz, 1H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.27 (s, 1H), 7.15 – 6.95 (m, 3H), 6.40 (d, $J = 8.0$ Hz, 2H), 3.89 (s, 3H), 3.30 (d, $J = 5.8$ Hz, 4H), 1.15 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 150.6, 147.2, 146.9, 136.2, 130.8, 129.5, 126.3, 126.2, 124.5, 123.8, 120.8, 120.7, 120.6, 115.1, 112.1, 110.9, 44.8, 30.2, 13.1; IR (neat, cm^{-1}) 3286, 2971, 1611, 1524, 1348, 1263, 1165, 1089, 850, 818, 738. Elemental Analysis: calcd for C:62.74; H:5.48; N:11.71; Found: C:62.31; H:5.73; N:11.15.

N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-fluorobenzenesulfonamide (3e)

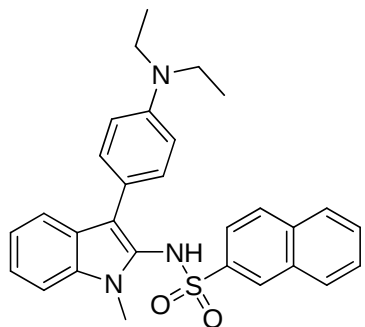


White solid; Yield: 67% ; M.p. 187-188 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 9.12 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.45-7.41 (m, 3H), 7.28 – 7.22 (m, 1H), 7.08 – 7.01 (m, 3H), 6.89 – 6.80 (m, 2H), 6.54 – 6.47 (m, 2H), 3.86 (s, 3H), 3.41 (q, $J = 7.0$ Hz, 4H), 1.21 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 165.7 (d, $J_{\text{C-F}} = 251.3$ Hz), 147.2, 137.4 (d, $J_{\text{C-F}} = 2.9$ Hz), 136.1, 130.8 (d, $J_{\text{C-F}} = 9.7$ Hz), 130.7, 126.9, 126.5, 123.6, 120.9, 120.7, 120.6, 116.3 (d, $J_{\text{C-F}} = 22.8$ Hz), 114.9, 112.3, 110.8, 45.0, 29.9, 13.2; IR (neat, cm^{-1}) 3283, 2973, 1613, 1516, 1264, 1159, 1091, 833, 753, 677. HRMS (EI): calcd for: 451.1730, Found: 451.1733.

N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)naphthalene-2-sulfonamide (3f)

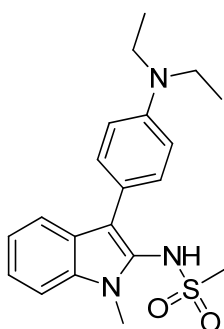
yellow solid; Yield: 72% ; M.p. 94-95 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 9.16 (s, 1H), 8.00 (s, 1H), 7.84 (d, $J = 8.6$ Hz, 2H), 7.65-7.60 (m, 2H), 7.57-7.52 (m, 1H), 7.51 – 7.40 (m, 3H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz,

1H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.09 (d, $J = 8.7$ Hz, 2H), 3.89 (s, 3H), 3.16 (q, $J = 7.0$ Hz, 4H), 1.07 (t, $J = 7.0$ Hz,



6H); ^{13}C NMR (100 MHz, Acetone) δ 146.8, 138.6, 136.1, 135.8, 132.9, 130.4, 130.2, 129.5, 129.3, 129.2, 128.7, 127.9, 127.1, 126.6, 123.51, 123.49, 120.7, 120.6, 120.5, 115.0, 111.9, 110.8, 44.8, 29.9, 13.3; IR (neat, cm^{-1}) 3376, 2970, 1710, 1564, 1517, 1357, 1270, 1154, 1122, 1072, 781, 750, 672. Elemental Analysis: calcd for C: 72.02; H: 6.04; N: 8.69; Found: C: 71.34; H: 6.41; N: 8.07.

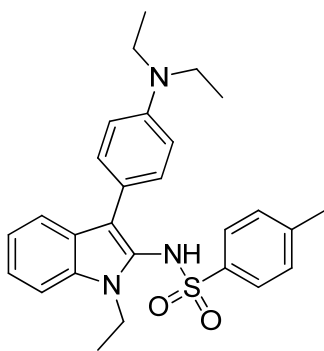
N-(3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)methanesulfonamide(3g)



White solid; Yield: 88% ; M.p. 176-177 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 8.73 (s, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (d, $J = 8.3$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.14 – 7.07 (m, 1H), 6.90 – 6.82 (m, 2H), 3.80 (s, 3H), 3.44 (q, $J = 7.0$ Hz, 4H), 2.46 (s, 3H), 1.18 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 147.7, 136.1, 131.1, 127.6, 126.5, 123.6, 121.5, 120.67, 121.64, 114.6, 113.2, 110.8, 45.0, 41.1, 29.7, 13.1; IR (neat, cm^{-1}) 3263, 2971, 1613, 1516, 1372, 1325, 1263, 1153, 977, 747. HRMS (EI): calcd

for: 371.1667, Found: 371.1673.

N-(3-(4-(diethylamino)phenyl)-1-ethyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3h)



White solid; Yield: 81% ; M.p. 167-168 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 8.93 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.3$ Hz, 1H), 7.31 – 7.26 (m, 2H), 7.26-7.20 (m, 1H), 7.07 – 7.00 (m, 3H), 6.92 (d, $J = 7.9$ Hz, 2H), 6.53 – 6.45 (m, 2H), 4.45 (t, $J = 7.2$ Hz, 2H), 3.40 (q, $J = 7.0$ Hz, 4H), 2.29 (s, 3H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.20 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 147.1, 143.6, 138.6, 135.0, 130.7, 129.8, 128.0, 126.9, 126.5, 123.4, 121.2, 120.8, 120.4, 115.1,

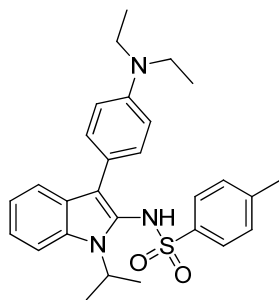
112.4, 111.0, 44.9, 38.2, 21.8, 15.3, 13.3; IR (neat, cm^{-1}) 3262, 2971, 1613, 1515, 1334, 1159, 1092, 811, 743, 674.

HRMS (EI): calcd for: 461.2137, Found: 461.2133.

N-(3-(4-(diethylamino)phenyl)-1-isopropyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3i)

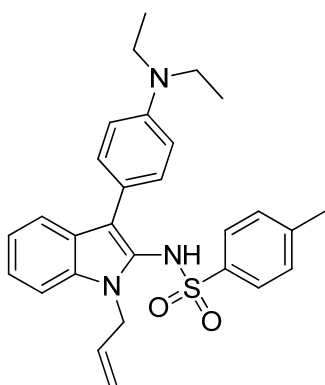
White solid; Yield: 88% ; M.p. 191-192 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 8.92 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 1H), 7.03-6.99 (m, 3H), 6.92 (d, $J = 8.0$ Hz, 2H),

6.51-6.47 (m, 2H), 5.29 – 5.16 (m, 1H), 3.40 (q, $J = 7.0$ Hz, 4H), 2.29 (s, 3H), 1.69 (d, $J = 7.0$ Hz, 6H), 1.20 (t, $J =$



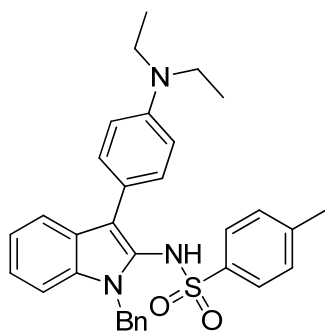
7.0 Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 147.1, 143.6, 138.5, 133.7, 130.8, 129.8, 128.0, 127.6, 126.4, 122.9, 121.2, 121.0, 120.0, 114.8, 113.1, 112.3, 47.2, 44.9, 21.8, 21.4, 13.3; IR (neat, cm^{-1}) 3263, 2972, 1611, 1516, 1457, 1349, 1268, 1160, 1092, 812, 747, 675. HRMS (EI): calcd for: 475.2293, Found: 475.2300.

N-(1-allyl-3-(4-(diethylamino)phenyl)-1H-indol-2-yl)-4-methylbenzenesulfonamide(3j)



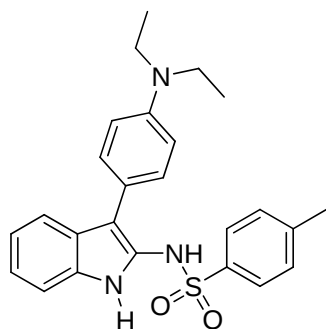
White solid; Yield: 76% ; M.p. 165-166 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 8.90 (s, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.3$ Hz, 1H), 7.28 (d, $J = 8.3$ Hz, 2H), 7.24 – 7.18 (m, 1H), 7.09 – 7.01 (m, 3H), 6.92 (d, $J = 8.0$ Hz, 2H), 6.55 – 6.46 (m, 2H), 6.12-6.01 (m, 1H), 5.19 – 5.17 (m, 2H), 5.07 – 5.00 (m, 2H), 3.41 (q, $J = 7.0$ Hz, 4H), 2.29 (s, 3H), 1.21 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 147.2, 143.7, 138.4, 135.63, 135.55, 130.8, 129.8, 128.0, 126.9, 126.7, 123.5, 121.1, 120.8, 120.6, 116.9, 115.3, 112.4, 111.5, 46.1, 44.9, 21.8, 13.3; IR (neat, cm^{-1}) 3262, 2972, 1613, 1516, 1462, 1330, 1367, 1160, 1015, 812, 750, 676. HRMS (EI): calcd for: 473.2137, Found: 473.2151.

N-(1-benzyl-3-(4-(diethylamino)phenyl)-1H-indol-2-yl)-4-methylbenzenesulfonamide(3k)



White solid; Yield: 73% ; M.p. 106-107 $^{\circ}\text{C}$; ^1H NMR (400 MHz, Acetone) δ 9.09 (s, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 1H), 7.32 – 7.20 (m, 5H), 7.20-7.15 (m, 3H), 7.12 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 2H), 6.52 (d, $J = 8.8$ Hz, 2H), 5.67 (s, 2H), 3.42 (q, $J = 7.0$ Hz, 4H), 2.30 (s, 3H), 1.21 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, Acetone) δ 147.2, 143.8, 139.6, 138.4, 135.7, 130.8, 129.8, 129.4, 128.04, 127.99, 127.8, 127.1, 127.0, 123.6, 121.0, 120.9, 120.7, 115.6, 112.4, 111.6, 47.0, 45.0, 21.8, 13.3; IR (neat, cm^{-1}) 3258, 2926, 1579, 1516, 1461, 1267, 1157, 1087, 810, 735, 676. MS (malditof): calcd for ($\text{C}_{32}\text{H}_{33}\text{N}_3\text{O}_2\text{S}+\text{H}^+$): 524.237, Found 524.237.

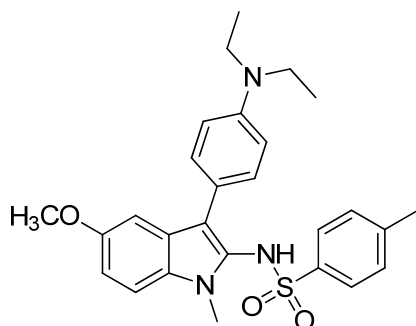
N-(3-(4-(diethylamino)phenyl)-1H-indol-2-yl)-4-methylbenzenesulfonamide(3l)



White solid; Yield: 64% ; M.p. 96-97⁰C ; ¹H NMR (400 MHz, Acetone) δ 10.21 (s, 1H), 8.97 (s, 1H), 7.57 – 7.41 (m, 4H), 7.19 – 6.09 (m, 3H), 7.03 – 6.97 (m, 1H), 6.88 – 6.77 (m, 2H), 6.55 (d, J = 8.8 Hz, 2H), 3.40 (q, J = 7.0 Hz, 4H), 2.35 (s, 3H), 1.17 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.3, 144.4, 138.0, 134.9, 130.9, 130.3, 128.0, 127.8, 127.2, 122.8, 120.9, 120.4, 120.0, 112.6, 112.3, 111.1, 45.0, 21.7, 13.2; IR (neat, cm⁻¹) 3309, 2972, 1608, 1518, 1273, 1141, 1083,

817, 754; HRMS (EI): calcd for: 433.1824, Found: 433.1832.

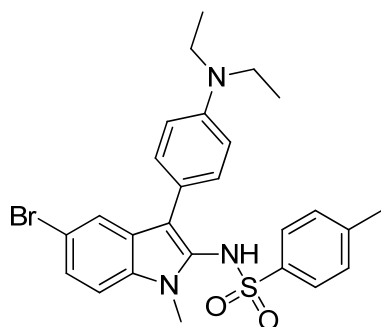
N-(3-(4-(diethylamino)phenyl)-5-methoxy-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3m)



White solid; Yield: 63%; M.p. 138-139⁰C; ¹H NMR (400 MHz, Acetone) δ 8.87 (s, 1H), 7.34 (d, J = 8.9 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.05 – 6.99 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 6.89 (dd, J = 8.9, 2.5 Hz, 1H), 6.54 – 6.48 (m, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.41 (q, J = 7.0 Hz, 4H), 2.30 (s, 3H), 1.21 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 155.5, 147.1, 143.7, 138.5, 131.3, 130.6, 129.8, 128.0, 127.6, 126.7, 121.4, 114.5, 113.8,

112.4, 111.6, 102.1, 56.0, 45.0, 30.0, 21.8, 13.3; IR (neat, cm⁻¹) 3265, 2971, 1515, 1488, 1266, 1160, 1091, 808, 753, 662, HRMS(EI): calcd for: 477.2086, Found: 477.2087.

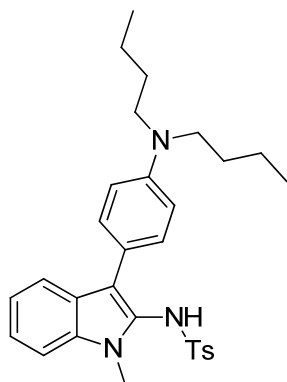
N-(5-bromo-3-(4-(diethylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3n)



White solid; Yield: 76%; M.p. 100-101⁰C ; ¹H NMR (400 MHz, Acetone) δ 9.03 (s, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.34 (dd, J = 8.7, 1.7 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.41 (q, J = 7.0 Hz, 4H), 2.30 (s, 3H), 1.20 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.3, 144.0, 138.3, 134.7, 130.7, 129.9, 128.6, 128.2, 128.0, 126.0, 122.9, 120.2,

114.5, 113.4, 112.9, 112.4, 45.0, 21.8, 13.3; IR (neat, cm⁻¹) 3267, 2970, 1611, 1515, 1471, 1372, 1159, 1091, 865, 811, 662. HRMS (EI): calcd for: 525.1086, Found: 525.1092.

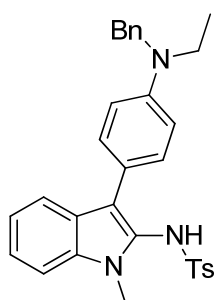
N-(3-(4-(dibutylamino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3o)



White solid; Yield: 76% ; M.p. 61-62⁰C ; ¹H NMR (400 MHz, Acetone) δ 8.99 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23-7.21 (m, 1H), 7.08 – 6.99 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.52 – 6.46 (m, 2H), 3.83 (s, 3H), 3.38 – 3.29 (t, *J* = 8.0 Hz, 4H), 2.30 (s, 3H), 1.69-1.60 (m, 4H), 1.48-1.37 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.5, 143.7, 138.3, 136.1, 130.6, 129.7, 128.0, 127.2, 126.6, 123.4, 121.0, 120.6, 120.4, 114.7, 112.3, 110.7, 51.5, 30.5, 30.0, 21.8, 21.1, 14.5; IR (neat, cm⁻¹) 3375, 2930, 1610, 1570, 1518, 1470, 1284,

1144, 1080, 811, 779, 679 HRMS (EI): calcd for: 503.2606, Found: 503.2610.

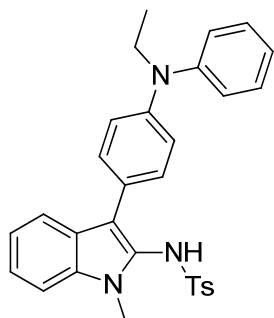
N-(3-(4-(benzyl(ethyl)amino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3p)



White solid; Yield: 74% ; M.p. 84-85⁰C ; ¹H NMR (400 MHz, Acetone) δ 8.93 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 – 7.20 (m, 4H), 7.06-7.01 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.58 (s, 2H), 3.83 (s, 3H), 3.55 (q, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Acetone) δ 147.7, 143.8, 141.0, 138.1, 136.1, 130.6, 129.8, 129.5, 128.0, 127.72, 127.67, 127.3, 126.6, 123.4, 121.9, 120.58, 120.51, 114.6, 112.9, 110.7, 54.7, 46.1, 21.8, 12.9;

IR (neat, cm⁻¹) 3259, 2926, 1577, 1516, 1329, 1294, 1161, 1086, 812, 732, 678. HRMS (EI): calcd for: 509.2137, Found: 509.2134.

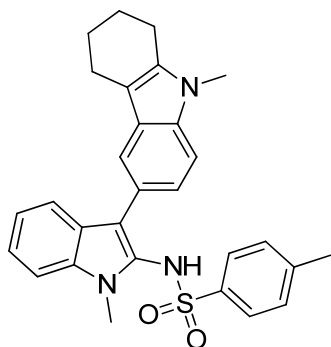
N-(3-(4-(ethyl(phenyl)amino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3q)



White solid; Yield: 81% ; M.p. 84-85⁰C ; ¹H NMR (400 MHz, Acetone) δ 9.03 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 7.14-7.03 (m, 7H), 7.02 – 6.96 (m, 1H), 6.84 – 6.77 (m, 2H), 3.90 – 3.81 (m, 5H), 2.32 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Acetone) δ 148.6, 146.8, 144.1, 138.2, 136.1, 130.7, 130.3, 130.0, 128.1, 127.7, 126.7, 126.5, 123.6, 122.52, 122.47, 120.8, 120.5, 120.4, 114.2, 110.9, 47.1, 30.1, 21.8, 13.3; IR (neat, cm⁻¹) 3264,

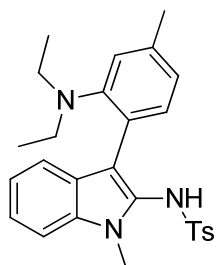
2972, 2928, 1567, 1497, 1373, 1329, 1161, 1090, 812, 736, 675. HRMS (EI): calcd for: 495.1980, Found: 495.1986.

4-methyl-N-(1-methyl-3-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-6-yl)-1H-indol-2-yl)benzenesulfonamide(3r)



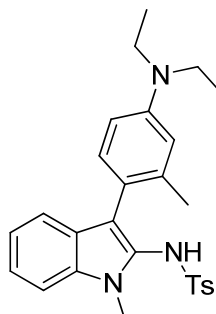
White solid; Yield: 53% ; M.p. 135-136⁰C ; ¹H NMR (400 MHz, Acetone) δ 9.23 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.34 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 1H), 7.18 – 7.13 (m, 1H), 7.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H), 3.65 (s, 3H), 2.87-2.79 (m, 4H), 2.15-2.10 (m, 2H), 2.06 (s, 3H), 1.99 – 1.93 (m, 2H); ¹³C NMR (100 MHz, Acetone) δ 143.3, 138.9, 138.3, 136.5, 136.1, 129.4, 127.8, 127.5, 126.8, 126.7, 126.4, 123.5, 120.9, 120.6, 117.9, 115.9, 110.8, 110.0, 109.4, 32.5, 29.2, 24.28, 24.26, 22.8, 22.1, 21.3; IR (neat, cm⁻¹) 3282, 2930, 1568, 1471, 1377, 1265, 1161, 1089, 810, 753, 677. MS (malditof): calcd for (C₂₉H₂₉N₃O₂S+H⁺): 484.205, Found: 484.205.

N-(3-(2-(diethylamino)-4-methylphenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3s)



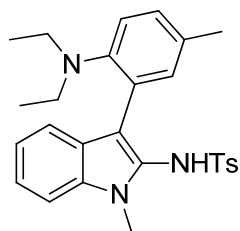
White solid; Yield: 28%; M.p. 146-147⁰C; ¹H NMR (400 MHz, Acetone) δ 10.01 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.27-7.21 (m, 1H), 7.09-7.05 (m, 1H), 7.04 – 7.00 (m, 2H), 6.88 (s, 1H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 0.9 Hz, 2H), 3.93 (s, 3H), 3.00 – 2.72 (m, 4H), 2.36 (s, 3H), 2.27 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.3, 144.5, 137.2, 137.1, 135.7, 132.9, 130.0, 129.7, 127.5, 126.0, 125.8, 124.4, 123.1, 122.3, 120.9, 119.8, 111.0, 109.4, 46.2, 30.5, 21.62, 21.58, 11.7; IR (neat, cm⁻¹) 3384, 2972, 1702, 1567, 1479, 1406, 1332, 1245, 1166, 1090, 743, 674; HRMS (EI): calcd for:461.2137, Found: 461.2138.

N-(3-(4-(diethylamino)-2-methylphenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3t)



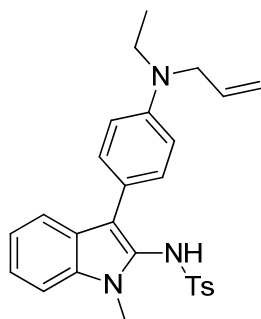
White solid; Yield: 30%; M.p. 111-112⁰C; ¹H NMR (400 MHz, Acetone) δ 8.83 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.23-7.17 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.05 – 6.98 (m, 3H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.42 – 6.36 (m, 2H), 3.83 (s, 3H), 3.48-3.34 (m, 4H), 2.36 (s, 3H), 1.76 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (100 MHz, Acetone) δ 147.4, 144.5, 137.2, 137.1, 135.7, 132.9, 130.0, 129.7, 127.5, 126.0, 125.8, 124.4, 123.1, 122.3, 120.9, 119.8, 111.0, 109.4, 46.2, 30.5, 21.62, 21.58, 11.7; IR (neat, cm⁻¹) 3259, 2969, 1609, 1506, 1373, 1329, 1258, 1157, 1092, 776, 677, 668; HRMS (EI): calcd for:461.2137, Found: 461.2131.

N-(3-(2-(diethylamino)-5-methylphenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3u)



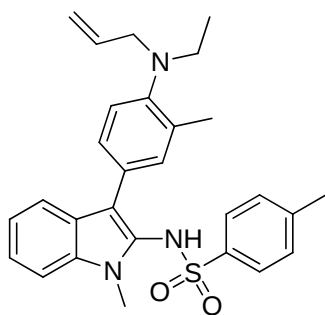
White solid; Yield: 42%; M.p. 141-142⁰C; ¹H NMR (400 MHz, Acetone) δ 10.27 (s, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.28-7.22 (m, 1H), 7.10-7.05 (m, 1H), 7.05 – 7.02 (m, 2H), 6.99 (dd, J = 8.3, 1.6 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 1.8 Hz, 1H), 3.94 (s, 3H), 2.90-2.78 (m, 4H), 2.27 (s, 3H), 2.24 (s, 3H), 1.01 (s, 6H); ¹³C NMR (100 MHz, Acetone) δ 145.0, 144.1, 137.2, 136.0, 133.6, 133.2, 130.2, 129.7, 128.6, 128.1, 127.7, 126.0, 123.1, 121.7, 121.0, 119.8, 111.0, 109.4, 46.3, 30.6, 21.7, 21.0, 11.6; IR (neat, cm⁻¹) 2972, 1701, 1564, 1478, 1407, 1334, 1165, 1089, 747, 678; HRMS (EI): calcd for: 461.2137, Found: 461.2140.

N-(3-(4-(allyl(ethyl)amino)phenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3v)



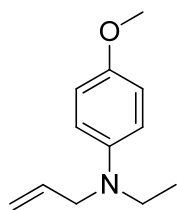
White solid; Yield: 72% ; M.p. 150-151⁰C ; ¹H NMR (400 MHz, Acetone) δ 8.94 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.26-7.21 (m, 1H), 7.07 – 7.04 (m, 1H), 7.04 – 7.00 (m, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.56 – 6.50 (m, 2H), 6.00-5.90 (m, 1H), 5.30-5.10 (m, 2H), 4.00-3.90 (m, 2H), 3.83 (s, 3H), 3.43 (q, J = 7.0 Hz, 2H), 2.30 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Acetone) δ 147.5, 143.8, 138.3, 136.2, 136.1, 130.6, 129.8, 128.0, 127.3, 126.6, 123.4, 121.7, 120.6, 120.5, 116.1, 114.7, 112.7, 110.8, 53.3, 45.4, 30.0, 21.8, 13.0; IR (neat, cm⁻¹) 3264, 2977, 1569, 1516, 1271, 1090, 812, 753, 679; HRMS (EI): calcd for: 459.1980, Found: 459.1977.

N-(3-(4-(allyl(ethyl)amino)-3-methylphenyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide(3w)



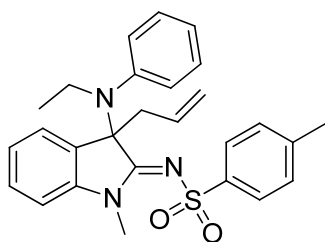
White solid; Yield: 51% ; M.p. 66-67⁰C; ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.01 (s, 1H), 6.87-6.83 (m, 3H), 6.71-6.68 (m, 2H), 5.95-5.83 (m, 1H), 5.26 (dd, J = 17.2, 1.4 Hz, 1H), 5.17 (d, J = 10.2 Hz, 1H), 3.92 (s, 3H), 3.53 (d, J = 6.0 Hz, 2H), 3.01 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 2.18 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.2, 143.4, 135.9, 135.1, 134.8, 134.1, 131.4, 129.0, 127.4, 127.3, 126.4, 126.0, 125.3, 122.8, 121.5, 120.0, 119.8, 116.7, 112.6, 109.8, 56.8, 46.2, 30.2, 21.6, 18.4, 12.5; IR (neat, cm⁻¹) 3373, 2978, 1568, 1494, 1469, 1275, 1142, 1082, 813, 753, 680; HRMS (EI): calcd for: 473.2137, Found: 473.2140.

N-allyl-N-ethyl-4-methoxyaniline(4f)



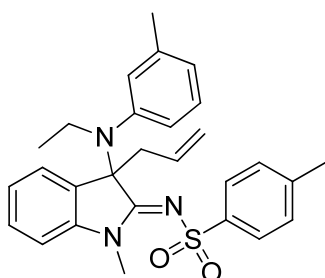
yellow oil; Yield: 86%; ^1H NMR (400 MHz, CDCl_3) δ 6.85 – 6.78 (m, 2H), 6.73 – 6.64 (m, 2H), 5.90-5.80 (m, 1H), 5.21-5.10 (m, 2H), 3.83-3.82 (m, 2H), 3.75 (s, 3H), 3.30 (q, J = 7.1 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 143.1, 135.0, 115.9, 114.7, 114.7, 55.8, 53.6, 45.4, 12.2; HRMS (EI): calcd for: 191.1310, Found: 191.1313.

(Z)-N-(3-allyl-3-(ethyl(phenyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide(5a)



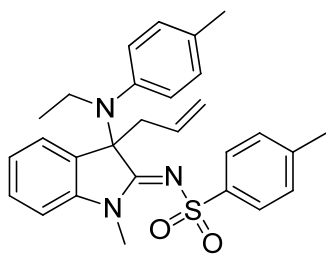
White solid; Yield: 5% ; M.p. 133-134 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.20 (t, J = 7.6 Hz, 2H), 7.15-7.09 (m, 2H), 6.89 (d, J = 7.8 Hz, 1H), 5.09 – 4.94 (m, 1H), 4.89 (dd, J = 17.0, 2.3 Hz, 1H), 4.77 (dd, J = 9.7, 2.3 Hz, 1H), 3.46 (s, 3H), 3.40 (dd, J = 12.5, 7.8 Hz, 1H), 3.00 – 2.74 (m, 2H), 2.44 (s, 3H), 2.29 (dd, J = 12.6, 6.1 Hz, 1H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 144.8, 143.3, 141.9, 141.8, 132.3, 131.0, 129.5, 129.0, 128.8, 128.1, 126.2, 125.2, 124.0, 123.8, 119.8, 109.0, 74.9, 44.0, 42.1, 30.3, 21.5, 13.5; IR (neat, cm^{-1}) 2926, 1582, 1490, 1290, 1146, 1085, 773, 678; HRMS (EI): calcd for: 459.1980, Found: 459.1977

(Z)-N-(3-allyl-3-(ethyl(m-tolyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide(5b)



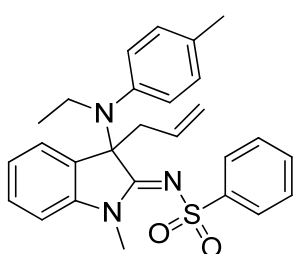
White solid; Yield: 39% ; M.p. 68-69 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.2 Hz, 2H), 7.35-7.24 (m, 5H), 7.18 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 6.93 (d, J = 7.4 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 5.05-4.96 (m, 1H), 4.93 – 4.85 (m, 1H), 4.77 (dd, J = 9.9, 1.8 Hz, 1H), 3.47 (s, 3H), 3.35 (dd, J = 12.5, 8.1 Hz, 1H), 2.85 (q, J = 6.7 Hz, 2H), 2.43 (s, 3H), 2.30 (dd, J = 12.5, 6.4 Hz, 1H), 2.25 (s, 3H), 0.83 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.1, 144.7, 143.3, 141.9, 141.8, 137.7, 132.4, 131.1, 130.4, 129.0, 128.7, 127.7, 126.4, 126.2, 126.0, 124.0, 123.8, 119.7, 109.0, 74.9, 44.0, 42.1, 30.4, 21.4, 21.4, 13.6; IR (neat, cm^{-1}) 2984, 1583, 1486, 1273, 1146, 1086, 918, 755, 679; HRMS (EI): calcd for: 473.2137, Found: 473.2144.

(Z)-N-(3-allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide(5c)



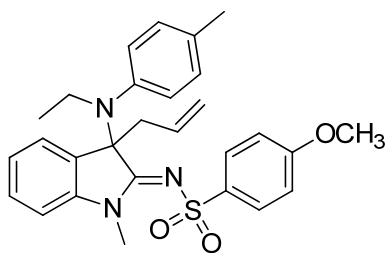
White solid; Yield: 87% ; M.p. 124-125⁰C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.26 (m, 6H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.08 – 4.93 (m, 1H), 4.88 (dd, *J* = 17.0, 2.3 Hz, 1H), 4.76 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.51 – 3.34 (m, 4H), 2.93 – 2.67 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.26 (dd, *J* = 12.6, 6.2 Hz, 1H), 0.82 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 143.3, 141.96, 141.94, 141.7, 134.8, 132.3, 131.1, 129.6, 129.0, 128.7, 128.6, 126.2, 124.0, 123.7, 119.6, 109.0, 75.0, 44.0, 42.0, 30.2, 21.4, 20.9, 13.4; IR (neat, cm⁻¹) 2925, 1597, 1467, 1286, 1145, 1084, 811, 774, 676; HRMS (EI): calcd for: 473.2137, Found: 473.2132.

(Z)-N-(3-allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)benzenesulfonamide(5d)



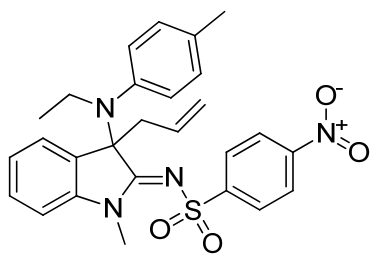
White solid; Yield: 92% ; M.p. 129-130; ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.05 (m, 2H), 7.61 – 7.44 (m, 3H), 7.40 – 7.29 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.09 – 4.94 (m, 1H), 4.89 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.77 (dd, *J* = 9.9, 2.2 Hz, 1H), 3.47 (s, 3H), 3.38 (dd, *J* = 12.5, 7.9 Hz, 1H), 2.90 – 2.67 (m, 2H), 2.31 (s, 3H), 2.26 (dd, *J* = 12.6, 6.2 Hz, 1H), 0.81 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 144.7, 143.3, 141.9, 135.0, 132.4, 131.3, 131.1, 129.7, 128.8, 128.7, 128.4, 126.2, 124.1, 123.8, 119.7, 109.1, 75.1, 44.2, 42.1, 30.3, 21.0, 13.4; IR (neat, cm⁻¹) 3007, 1582, 1468, 1384, 1148, 1087, 813, 753, 679; HRMS (EI): calcd for: 459.1980, Found: 459.1981.

(Z)-N-(3-allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)-4-methoxybenzenesulfonamide(5e)



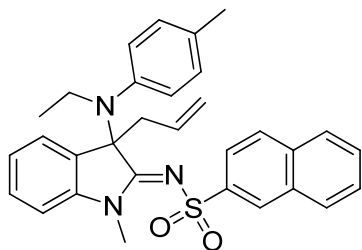
White solid; Yield: 69% ; M.p. 58-59⁰C; ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 7.74 (m, 2H), 7.39 – 7.28 (m, 4H), 7.13 (td, *J* = 7.5, 0.7 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.07 – 4.94 (m, 1H), 4.88 (dd, *J* = 17.0, 2.1 Hz, 1H), 4.76 (dd, *J* = 10.0, 2.2 Hz, 1H), 3.88 (s, 3H), 3.46 (s, 3H), 3.36 (dd, *J* = 12.5, 8.0 Hz, 1H), 2.89 – 2.74 (m, 2H), 2.31 (s, 3H), 2.27 (dd, *J* = 12.6, 6.4 Hz, 1H), 0.81 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.9, 161.8, 143.4, 142.0, 137.0, 134.9, 132.4, 131.1, 129.6, 128.72, 128.69, 128.2, 124.0, 123.7, 119.6, 113.5, 109.0, 75.0, 55.5, 44.1, 42.1, 30.3, 21.0, 13.5; IR (neat, cm⁻¹) 2976, 1577, 1492, 1465, 1257, 1143, 1085, 830, 753, 679; HRMS (EI): calcd for: 489.2086, Found: 489.2084.

(Z)-N-(3-allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)-4-nitrobenzenesulfonamide(5f)



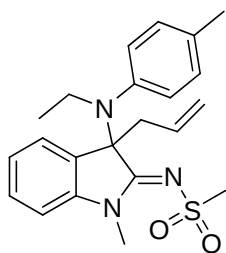
White solid; Yield: 83% ; M.p. 73-74⁰C; ¹H NMR (500 MHz, CDCl₃) δ 8.40 – 8.28 (m, 2H), 8.27 – 8.16 (m, 2H), 7.38-7.33 (m, 4H), 7.21 – 7.15 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.97 – 4.87 (m, 2H), 4.84 – 4.72 (m, 1H), 3.60-3.53 (m, 1H), 3.40 (s, 3H), 2.94-2.86 (m, 1H), 2.76-2.68 (m, 1H), 2.32 (s, 3H), 2.25 (dd, *J* = 12.2, 3.9 Hz, 1H), 0.87 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.8, 150.4, 149.2, 142.7, 141.6, 135.1, 132.2, 130.9, 128.93, 128.89, 127.4, 124.3, 124.1, 123.8, 119.9, 109.4, 75.5, 44.1, 41.8, 29.7, 20.9, 13.2; IR (neat, cm⁻¹) 2982, 1574, 1528, 1349, 1274, 1148, 1087, 988, 753, 650; MS (malditof): calcd for (C₂₇H₂₈N₄O₄S+H⁺): 505.190, Found: 505.190.

(Z)-N-(3-Allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)naphthalene-2-sulfonamide (5g)



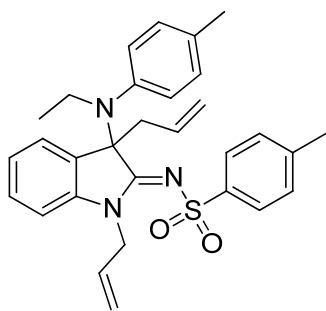
White solid; Yield: 78% ; M.p. 123-124⁰C; ¹H NMR (500 MHz, CDCl₃) δ 8.59 (s, 1H), 8.06 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.96 (t, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.51 (m, 2H), 7.37-7.30 (m, 4H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.09 – 4.96 (m, 1H), 4.92 (dd, *J* = 17.0, 2.2 Hz, 1H), 4.78 (dd, *J* = 9.8, 2.3 Hz, 1H), 3.60 – 3.32 (m, 4H), 3.03 – 2.63 (m, 2H), 2.39 – 2.20 (m, 4H), 0.84 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 143.3, 141.9, 141.7, 134.9, 134.4, 132.4, 132.2, 131.1, 129.5, 129.3, 128.8, 128.7, 128.6, 128.0, 127.7, 127.0, 126.3, 124.1, 123.8, 122.9, 119.8, 109.1, 75.1, 44.1, 42.1, 30.2, 20.9, 13.4; IR (neat, cm⁻¹) 2979, 1578, 1467, 1384, 1274, 1146, 1123, 1073, 752, 672; MS (malditof): calcd for (C₃₁H₃₁N₃O₂S+H⁺): 510.221, Found: 510.221.

(Z)-N-(3-Allyl-3-(ethyl(p-tolyl)amino)-1-methylindolin-2-ylidene)methanesulfonamide (5h)



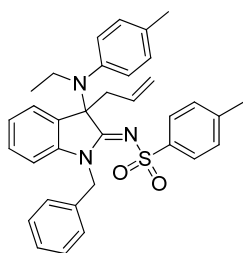
White solid; Yield: 85% ; M.p. 143-144⁰C; ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.28 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.09 – 4.92 (m, 1H), 4.87 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.76 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.44 (s, 3H), 3.35 (dd, *J* = 12.6, 7.9 Hz, 1H), 3.18 (s, 3H), 2.97 – 2.73 (m, 2H), 2.32 (s, 3H), 2.28 (dd, *J* = 12.6, 6.5 Hz, 1H), 0.85 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.2, 143.3, 142.0, 134.9, 132.2, 131.1, 129.3, 128.8, 128.7, 124.1, 123.7, 119.6, 109.0, 74.9, 44.4, 43.8, 42.0, 30.1, 20.9, 13.4; IR (neat, cm⁻¹) 2980, 1585, 1468, 1382, 1279, 1128, 794, 755; HRMS (EI): calcd for: 397.1824, Found: 397.1820.

(Z)-N-(1,3-Diallyl-3-(ethyl(p-tolyl)amino)indolin-2-ylidene)-4-methylbenzenesulfonamide (5i)



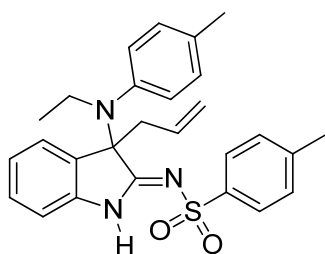
White solid; Yield: 78% ; M.p. 139-140 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.3 Hz, 1H), 7.28-7.25 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 5.83-5.75 (m, 1H), 5.39 – 5.11 (m, 2H), 5.09 – 4.84 (m, 2H), 4.76 (dd, J = 9.4, 2.7 Hz, 1H), 4.56 (dd, J = 16.0, 5.5 Hz, 1H), 4.43 (dd, J = 16.0, 5.6 Hz, 1H), 3.75 (dd, J = 12.5, 7.5 Hz, 1H), 2.94-2.86 (m, 1H), 2.76-2.69 (m, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 2.19 (dd, J = 12.6, 5.7 Hz, 1H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.0, 142.3, 142.1, 141.8, 141.6, 134.8, 132.2, 131.3, 130.6, 129.3, 129.0, 128.8, 128.6, 126.1, 124.1, 123.5, 119.9, 118.5, 109.7, 75.1, 45.3, 44.1, 41.7, 21.4, 21.0, 13.1; IR (neat, cm^{-1}) 2984, 1580, 1467, 1276, 1147, 1089, 919, 754, 697; HRMS (EI): calcd for: 499.2293, Found: 499.2291.

(Z)-N-(3-Allyl-1-benzyl-3-(ethyl(p-tolyl)amino)indolin-2-ylidene)-4-methylbenzenesulfonamide (5j)



White solid; Yield: 69% ; M.p. 61-62 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.29 – 7.18 (m, 8H), 7.17 – 7.04 (m, 3H), 6.85 (d, J = 7.8 Hz, 1H), 5.08 – 4.89 (m, 4H), 4.67 (dd, J = 8.2, 4.0 Hz, 1H), 3.97 (dd, J = 12.2, 6.5 Hz, 1H), 3.00-2.94 (m, 1H), 2.76-2.69 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.17 (dd, J = 12.0, 4.3 Hz, 1H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.7, 142.4, 142.1, 141.7, 141.6, 135.1, 134.8, 132.2, 131.4, 129.1, 129.0, 128.8, 128.6, 127.9, 127.7, 126.1, 124.1, 123.5, 119.9, 109.7, 75.1, 46.3, 44.1, 41.5, 21.4, 21.0, 13.0; IR (neat, cm^{-1}) 3007, 1579, 1466, 1274, 1148, 1089, 753, 703; HRMS(EI): calcd for: 549.2450, Found: 549.2465.

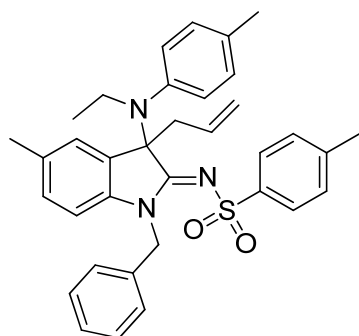
(Z)-N-(3-Allyl-3-(ethyl(p-tolyl)amino)indolin-2-ylidene)-4-methylbenzenesulfonamide (5k)



White solid; Yield: 64% ; M.p. 63-64 °C; ^1H NMR (500 MHz, CDCl_3) δ 9.79 (s, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.26-7.20 (m, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 7.7 Hz, 1H), 5.08 – 4.90 (m, 1H), 4.70 (d, J = 10.1 Hz, 1H), 4.66 (d, J = 17.1 Hz, 1H), 3.06-2.99 (m, 1H), 2.76-2.70 (m, 1H), 2.60 (dd, J = 12.8, 6.2 Hz, 1H), 2.51 – 2.37 (m, 4H), 2.26 (s, 3H), 0.66 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.6, 143.2, 142.6, 140.2, 139.0, 135.4, 131.6, 130.5, 129.4, 128.9, 128.7, 126.6, 124.5, 123.7, 119.9, 110.5, 110.0, 74.6,

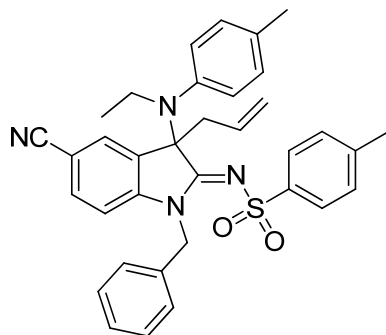
43.8, 42.8, 21.6, 20.9, 14.4; IR (neat, cm^{-1}) 3307, 2982, 1602, 1475, 1272, 1140, 1084, 755, 674; HRMS (EI): calcd for: 459.1980, Found: 459.1987.

(Z)-N-(3-Allyl-1-benzyl-3-(ethyl(p-tolyl)amino)-5-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5l)



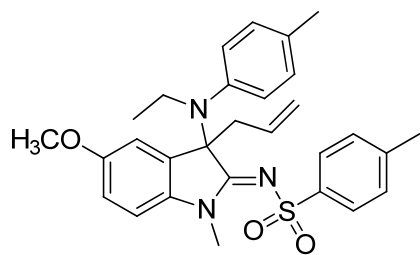
White solid; Yield: 75% ; M.p. 72-73 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.29 – 7.18 (m, 7H), 7.16 – 7.07 (m, 3H), 7.01 (d, $J = 7.9$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 5.11 – 4.79 (m, 4H), 4.68 (dd, $J = 9.5, 2.7$ Hz, 1H), 3.93 (dd, $J = 12.4, 7.8$ Hz, 1H), 3.00-2.94 (m, 1H), 2.77-2.70 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.17 (dd, $J = 12.5, 5.3$ Hz, 1H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 142.2, 141.8, 141.5, 140.1, 135.2, 134.6, 133.2, 132.3, 131.5, 128.93, 128.91, 128.8, 128.5, 127.9, 127.7, 126.1, 124.8, 119.8, 109.5, 75.1, 46.4, 44.0, 41.6, 21.4, 21.3, 21.0, 13.0; IR (neat, cm^{-1}) 2982, 1576, 1493, 1442, 1276, 1148, 1088, 753, 674; HRMS(EI): calcd for: 563.2606, Found: 563.2606.

(Z)-N-(3-Allyl-1-benzyl-5-cyano-3-(ethyl(p-tolyl)amino)indolin-2-ylidene)-4-methylbenzenesulfonamide (5m)



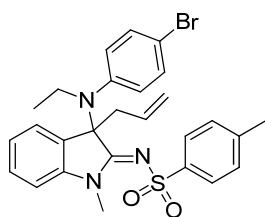
White solid; Yield: 32% ; M.p. 84-85 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.56 (s, 1H), 7.56 – 7.50 (m, 1H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.28-7.23 (m, 5H), 7.18 (d, $J = 6.3$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 1H), 5.05 – 4.87 (m, 4H), 4.77 – 4.66 (m, 1H), 4.10 – 3.89 (m, 1H), 2.99-2.92 (m, 1H), 2.75-2.68 (m, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.24 – 2.07 (m, 1H), 0.93 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.3, 146.1, 142.2, 141.3, 141.0, 135.5, 134.2, 133.8, 133.5, 130.4, 129.2, 129.1, 128.9, 128.8, 128.1, 127.7, 127.3, 126.2, 120.7, 118.9, 110.1, 106.5, 74.9, 46.5, 44.3, 41.5, 21.5, 21.0, 13.0; IR (neat, cm^{-1}) 2984, 1579, 1488, 1274, 1150, 1088, 817, 752, 673; HRMS (EI): calcd for: 574.2402, Found: 574.2416.

(Z)-N-(3-Allyl-3-(ethyl(p-tolyl)amino)-5-methoxy-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5n)



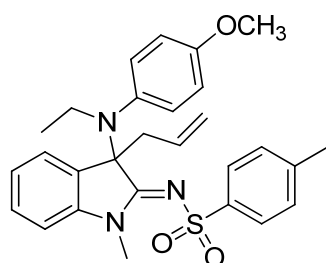
White solid; Yield: 69% ; M.p. 66-67 °C ; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.31-7.25 (m, 4H), 6.98 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 2.2$ Hz, 1H), 6.84-6.78 (m, 2H), 5.11 – 4.97 (m, 1H), 4.91 (dd, $J = 16.9$, 1.7 Hz, 1H), 4.79 (dd, $J = 9.9$, 2.0 Hz, 1H), 3.81 (s, 3H), 3.47 (s, 3H), 3.28 (dd, $J = 12.5$, 8.0 Hz, 1H), 2.81 (q, $J = 7.0$ Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H), 2.25 (dd, $J = 12.6$, 6.3 Hz, 1H), 0.80 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 156.9, 142.0, 141.9, 141.6, 136.9, 134.9, 134.0, 131.0, 129.6, 129.0, 128.7, 126.2, 119.7, 112.9, 111.1, 109.4, 75.1, 55.8, 44.1, 42.3, 30.6, 21.4, 20.9, 13.5; IR (neat, cm^{-1}) 2927, 1580, 1491, 1276, 1145, 1087, 810, 753, 672; HRMS (EI): calcd for: 503.2243, Found: 503.2258.

(Z)-N-(3-Allyl-3-((4-bromophenyl)(ethyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5o)



White solid; Yield: 78% ; M.p. 60-61 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.2$ Hz, 2H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.30 – 7.25 (m, 5H), 7.23 (d, $J = 8.7$ Hz, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 5.06 – 4.93 (m, 1H), 4.90 (dd, $J = 17.0$, 2.2 Hz, 1H), 4.79 (dd, $J = 9.6$, 2.2 Hz, 1H), 3.46 (s, 3H), 3.36 (dd, $J = 12.3$, 7.7 Hz, 1H), 2.99 – 2.73 (m, 2H), 2.44 (s, 3H), 2.30 (dd, $J = 12.4$, 6.0 Hz, 1H), 0.85 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 144.0, 143.2, 142.0, 141.6, 132.0, 131.1, 130.6, 130.5, 129.1, 129.0, 126.2, 123.9, 123.7, 120.1, 118.2, 109.2, 74.6, 43.8, 42.1, 30.2, 21.5, 13.5; IR (neat, cm^{-1}) 2980, 1579, 1485, 1276, 1145, 1084, 808, 752, 676; HRMS (EI): calcd for: 537.1086, Found: 537.1069.

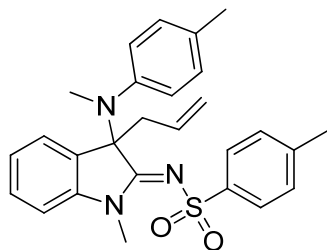
(Z)-N-(3-Allyl-3-(ethyl(4-methoxyphenyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5p)



White solid; Yield: 80% ; M.p. 135-136 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.40-7.35 (m, 3H), 7.34 – 7.28 (m, 3H), 7.15 (t, $J = 7.3$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.73 (d, $J = 8.9$ Hz, 2H), 5.10 – 4.94 (m, 1H), 4.88 (d, $J = 16.8$ Hz, 1H), 4.77 (dd, $J = 10.0$, 1.9 Hz, 1H), 3.78 (s, 3H), 3.47 (s, 3H), 3.29 (dd, $J = 12.5$, 8.1 Hz, 1H), 2.76 (q, $J = 7.0$ Hz, 2H), 2.44 (s, 3H), 2.25 (dd, $J = 12.6$, 6.4 Hz, 1H), 0.79 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.0, 157.3, 143.4, 142.0, 141.8, 137.5, 132.4, 131.3, 131.1, 129.1, 128.8, 126.2, 124.1, 123.7, 119.6, 113.1, 109.0, 75.1, 55.2, 44.4, 42.1, 30.4, 21.5,

13.4; IR (neat, cm^{-1}) 2982, 1579, 1506, 1466, 1277, 1144, 1084, 810, 753, 675; HRMS (EI): calcd for: 489.2086, Found: 489.2067.

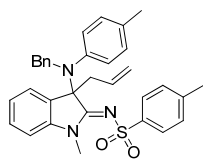
(Z)-N-(3-Allyl-1-methyl-3-(methyl(p-tolyl)amino)indolin-2-ylidene)-4-methylbenzenesulfonamide (5q)



White solid; Yield: 89% ; M.p. 57-58 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 4H), 7.19 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 5.11 – 4.98 (m, 1H), 4.98 – 4.89 (m, 1H), 4.80 (dd, J = 9.8, 2.0 Hz, 1H), 3.69 (dd, J = 12.4, 7.8 Hz, 1H), 3.41 (s, 3H), 2.46 (s, 3H), 2.42 – 2.35 (m, 4H), 2.30 (s, 3H);

^{13}C NMR (125 MHz, CDCl_3) δ 169.8, 145.5, 143.1, 141.7, 141.6, 134.0, 131.6, 131.1, 128.9, 128.9, 128.8, 126.7, 126.4, 123.8, 123.7, 119.9, 109.0, 74.6, 42.3, 38.0, 29.8, 21.4, 20.8; IR (neat, cm^{-1}) 2985, 1579, 1467, 1276, 1147, 1085, 925, 812, 754, 678; HRMS (EI): calcd for: 459.1980, Found: 459.1972.

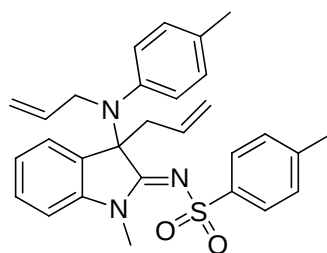
(Z)-N-(3-Allyl-3-(benzyl(p-tolyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5r)



White solid; Yield: 36% ; M.p. 62-63 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 7.3 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.21 – 7.13 (m, 3H), 7.08 (t, J = 7.3 Hz, 2H), 7.06 – 6.98 (m, 3H), 6.90 (d, J = 7.9 Hz, 1H), 6.75 (d, J = 8.1 Hz, 2H), 5.09-5.02 (m, 1H),

4.88 (d, J = 16.7 Hz, 1H), 4.80 (dd, J = 10.1, 1.6 Hz, 1H), 4.28 (d, J = 14.3 Hz, 1H), 3.93 (d, J = 14.3 Hz, 1H), 3.63 (s, 3H), 2.98 (dd, J = 12.5, 8.0 Hz, 1H), 2.51 (dd, J = 12.5, 6.6 Hz, 1H), 2.45 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.6, 143.7, 142.7, 142.0, 141.5, 138.9, 134.3, 132.2, 130.7, 129.1, 129.0, 128.8, 128.6, 128.4, 127.7, 126.4, 126.3, 124.2, 124.1, 120.1, 109.3, 74.4, 54.1, 43.0, 31.7, 21.5, 20.8; IR (neat, cm^{-1}) 3008, 1587, 1467, 1275, 1146, 1086, 917, 814, 753, 678; MS (malditof): calcd for ($\text{C}_{33}\text{H}_{33}\text{N}_3\text{O}_2\text{S}+\text{H}^+$): 536.237, Found: 536.237.

(Z)-N-(3-Allyl-3-(allyl(p-tolyl)amino)-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (5s)

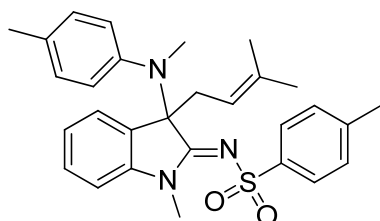


White solid; Yield: 71% ; M.p. 65-66 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, J = 8.2 Hz, 2H), 7.38 – 7.19 (m, 6H), 7.14 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.8 Hz, 1H), 5.83 – 5.59 (m, 1H), 5.08 – 4.94 (m, 1H), 4.94 – 4.73 (m, 4H), 3.55 (dd, J = 14.2, 5.2 Hz, 1H), 3.50 – 3.37 (m, 5H), 2.43 (s, 3H), 2.33 (dd, J = 12.5, 6.3 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.9,

143.3, 142.6, 141.85, 14.78, 136.4, 134.5, 132.0, 131.0, 129.0, 128.87, 128.85, 128.6, 126.2, 124.1, 123.8, 119.9,

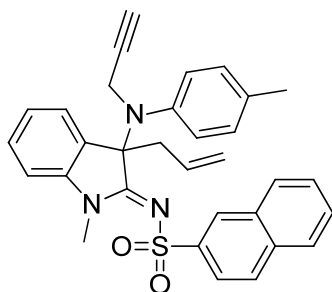
116.3, 109.1, 74.6, 53.5, 42.2, 30.2, 21.5, 20.9; IR (neat, cm^{-1}) 2983, 1578, 1467, 1276, 1145, 1085, 920, 812, 753, 678; HRMS (EI): calcd for: 485.2137, Found: 485.2134.

(Z)-4-Methyl-N-(1-methyl-3-(methyl(p-tolyl)amino)-3-(3-methylbut-2-en-1-yl)indolin-2-ylidene)benzenesulfonamide (5ua)



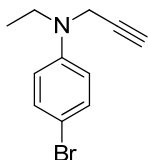
White solid; Yield: 68% ; M.p. 57-58 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.26 (m, 1H), 7.24 – 7.12 (m, 5H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.97 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 7.8$ Hz, 1H), 4.41 (t, $J = 7.4$ Hz, 1H), 3.52 (dd, $J = 12.9, 8.4$ Hz, 1H), 3.44 (s, 3H), 2.51 (s, 3H), 2.39-2.36 (m, 4H), 2.28 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.4, 145.8, 143.2, 141.7, 141.6, 136.3, 133.5, 132.2, 128.9, 128.7, 128.6, 126.5, 126.1, 123.8, 123.6, 116.3, 108.8, 74.7, 38.0, 37.3, 30.1, 25.8, 21.4, 20.8, 18.1; IR (neat, cm^{-1}) 2984, 1577, 1467, 1276, 1147, 1085, 931, 810, 794, 676; HRMS (EI): calcd for: 487.2293, Found: 487.2279.

(Z)-N-(3-Allyl-1-methyl-3-(prop-2-yn-1-yl(p-tolyl)amino)indolin-2-ylidene)naphthalene-2-sulfonamide (5x)



White solid; Yield: 62%; M.p. 115-116 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 1.3$ Hz, 1H), 7.95 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.84 (d, $J = 8.7$ Hz, 3H), 7.63 – 7.49 (m, 2H), 7.37 (d, $J = 7.4$ Hz, 1H), 7.30 – 7.21 (m, 1H), 7.07 (td, $J = 7.5, 0.7$ Hz, 1H), 6.87-6.82 (m, 3H), 6.71 (d, $J = 8.3$ Hz, 2H), 5.13 – 4.96 (m, 2H), 4.88 (dd, $J = 7.8, 4.4$ Hz, 1H), 4.42 (dd, $J = 18.4, 2.0$ Hz, 1H), 3.91 (dd, $J = 18.4, 2.3$ Hz, 1H), 3.63 (dd, $J = 11.2, 5.6$ Hz, 1H), 3.46 (s, 3H), 2.93 (dd, $J = 11.5, 3.7$ Hz, 1H), 2.23 (t, $J = 2.3$ Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 143.8, 142.7, 140.8, 134.3, 132.0, 131.9, 130.4, 129.2, 128.9, 128.8, 128.5, 127.9, 127.6, 126.8, 126.5, 124.25, 124.21, 122.6, 120.6, 109.0, 82.9, 73.7, 72.2, 42.3, 39.1, 29.9, 20.5; IR (neat, cm^{-1}) 3056, 2921, 1622, 1574, 1518, 1488, 1469, 1384, 1493, 1148, 1126, 1072, 778, 750, 674; HRMS (ESI): calcd for ($\text{C}_{32}\text{H}_{29}\text{N}_3\text{O}_2\text{S} + \text{H}^+$): 520.2053, Found: 520.2066.

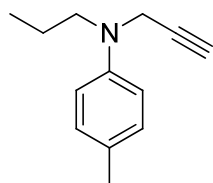
4-Bromo-N-ethyl-N-(prop-2-yn-1-yl)aniline (6d)



Yellow oil; Yield: 80%; ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 2H), 6.73 – 6.66 (m, 2H), 3.98 (d, $J = 2.4$ Hz, 2H), 3.41 (q, $J = 7.1$ Hz, 2H), 2.19 (t, $J = 2.4$ Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 131.8, 115.3, 109.6, 79.8, 71.9, 45.7, 39.6, 12.2; HRMS (EI): calcd for: 237.0153, Found:237.0158.

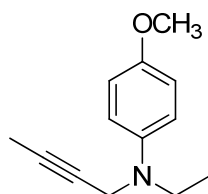
4-Methyl-N-(prop-2-yn-1-yl)-N-propylaniline (6f)



Yellow oil; Yield: 83%; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.99 (d, J = 2.3 Hz, 2H), 3.31 – 3.20 (m, 2H), 2.26 (s, 3H), 2.16 (t, J = 2.3 Hz, 1H), 1.71 – 1.60 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 129.6, 127.0, 114.3, 80.3, 71.6, 53.4, 40.4, 20.6, 20.3, 11.5; HRMS (EI): calcd for: 187.1361,

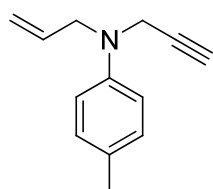
Found:187.1361.

N-(But-2-yn-1-yl)-N-ethyl-4-methoxyaniline (6j)



Yellow oil; Yield: 88%; ^1H NMR (400 MHz, CDCl_3) δ 6.92 – 6.77 (m, 4H), 3.88 (q, J = 2.3 Hz, 2H), 3.76 (s, 3H), 3.32 (q, J = 7.1 Hz, 2H), 1.78 (t, J = 2.3 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 143.1, 117.2, 114.5, 79.5, 75.2, 55.6, 46.0, 41.0, 12.4, 3.6; HRMS (EI): calcd for: 203.1310, Found:203.1308.

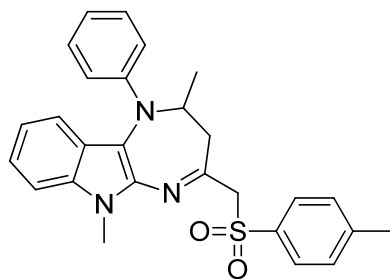
N-Allyl-4-methyl-N-(prop-2-yn-1-yl)aniline (6k)



Yellow oil; Yield: 84%; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (d, J = 8.5 Hz, 2H), 6.85 – 6.74 (m, 2H), 5.94-5.84 (m, 1H), 5.30-5.24 (m, 1H), 5.20-5.16 (m, 1H), 3.99 (d, J = 2.3 Hz, 2H), 3.92 (d, J = 5.4 Hz, 2H), 2.26 (s, 3H), 2.17 (t, J = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 134.3, 129.6, 127.6, 116.8, 114.7, 80.0, 71.8, 54.0, 39.9, 20.3; HRMS (EI): calcd for:

185.1204, Found:185.1207.

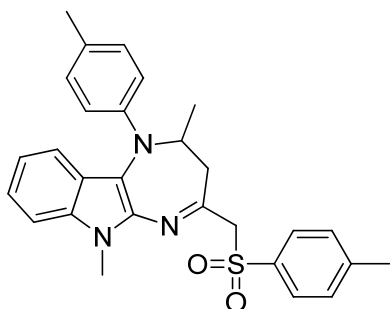
2,6-Dimethyl-1-phenyl-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7a)



Yellow solid; Yield: 31%; M.p. 227-228 $^{\circ}\text{C}$; ^1H NMR (400 MHz, acetone) δ 7.75 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 8.3 Hz, 1H), 7.26-7.20 (m, 2H), 7.15-7.09 (m, 1H), 6.96 – 6.90 (m, 3H), 6.86 – 6.77 (m, 2H), 4.67 – 4.59 (m, 1H), 4.51 – 4.41 (m, 2H), 3.38 (s, 3H), 3.25 (dd, J = 16.8, 5.2 Hz, 1H), 2.52 (dd, J = 16.7, 3.4 Hz, 1H), 2.43 (s, 3H), 1.00 (d, J =

6.9 Hz, 3H); ^{13}C NMR (100 MHz, Acetone) δ 156.3, 151.0, 145.6, 137.6, 136.4, 134.6, 130.6, 130.1, 129.6, 123.9, 122.6, 122.4, 122.1, 121.2, 119.4, 113.8, 110.6, 69.1, 55.1, 44.3, 28.3, 21.6, 18.8; IR (neat, cm^{-1}) 2929, 1702, 1597, 1495, 1317, 1251, 1151, 1086, 817, 750, 681; HRMS (EI): calcd for: 457.1824, Found: 457.1831.

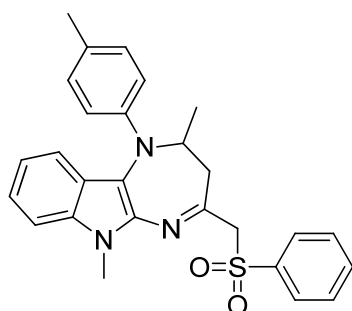
2,6-Dimethyl-1-(p-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7b)



Yellow solid; Yield: 64% ; M.p. 224-225 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.22 – 7.11 (m, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.88 – 6.77 (m, 3H), 4.50 – 4.39 (m, 1H), 4.36 (d, J = 13.1 Hz, 1H), 4.22 (d, J = 13.0 Hz, 1H), 3.33 (s, 3H), 3.19 (dd, J = 16.7, 5.0 Hz, 1H), 2.46 (dd, J = 16.7, 2.8 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 0.97 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ

152.2, 147.7, 144.6, 135.7, 135.3, 132.7, 131.5, 129.7, 129.5, 128.6, 123.1, 122.1, 121.2, 121.0, 118.3, 114.2, 109.1, 68.8, 54.1, 43.6, 27.7, 21.6, 20.7, 18.3; IR (neat, cm^{-1}) 3053, 2925, 1605, 1466, 1317, 1262, 1151, 1084, 816, 739, 678; HRMS (EI): calcd for: 471.1980, Found: 471.1985.

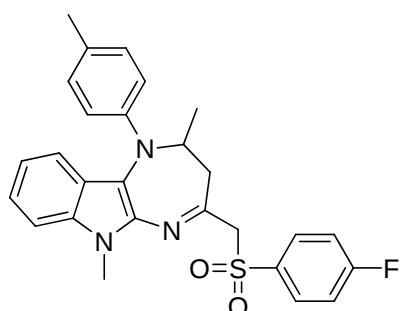
2,6-Dimethyl-4-((phenylsulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7c)



Yellow solid; Yield: 55% ; M.p. 199-200 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.81 (m, 2H), 7.70 – 7.57 (m, 1H), 7.52-7.47 (m, 2H), 7.20 – 7.12 (m, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.85-6.79 (m, 3H), 4.48 – 4.41 (m, 1H), 4.39 (d, J = 13.2 Hz, 1H), 4.25 (d, J = 13.1 Hz, 1H), 3.30 (s, 3H), 3.20 (dd, J = 16.7, 5.0 Hz, 1H), 2.48 (dd, J = 16.7, 2.9 Hz, 1H), 2.29 (s, 3H), 0.98 (d, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.9, 147.7, 138.7, 135.3,

133.6, 132.6, 131.6, 129.7, 128.9, 128.6, 123.2, 122.1, 121.2, 121.0, 118.3, 114.3, 109.1, 68.8, 54.1, 43.6, 27.9, 20.7, 18.3; IR (neat, cm^{-1}) 2925, 1610, 1509, 1310, 1263, 1154, 817, 742, 690; HRMS (EI): calcd for: 457.1824, Found: 457.1818.

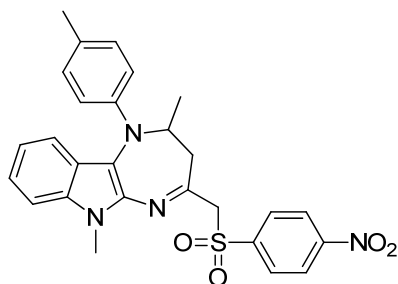
4-(((4-Fluorophenyl)sulfonyl)methyl)-2,6-dimethyl-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7d)



Yellow solid; Yield: 57% ; M.p. 225-226 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.88-7.83 (m, 2H), 7.24 – 7.11 (m, 4H), 7.03 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.85-6.81 (m, 3H), 4.54 – 4.41 (m, 1H), 4.37 (d, J = 13.2 Hz,

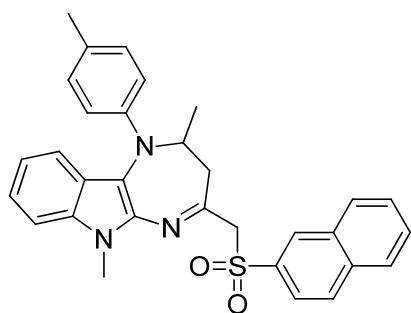
1H), 4.24 (d, $J = 13.2$ Hz, 1H), 3.36 (s, 3H), 3.17 (dd, $J = 16.6, 5.1$ Hz, 1H), 2.48 (dd, $J = 16.5, 2.9$ Hz, 1H), 2.29 (s, 3H), 0.99 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.8 (d, $J_{\text{C-F}} = 256.4$ Hz), 151.9, 147.6, 135.3, 134.6 (d, $J_{\text{C-F}} = 3.1$ Hz), 132.6, 131.53, 131.46 (d, $J_{\text{C-F}} = 9.6$ Hz), 129.8, 123.3, 121.9, 121.2, 121.0, 118.4, 116.2 (d, $J_{\text{C-F}} = 22.6$ Hz), 114.3, 109.2, 68.8, 54.4, 43.7, 27.8, 20.6, 18.4; IR (neat, cm^{-1}) 3056, 2927, 1591, 1507, 1324, 1262, 1150, 1084, 839, 818, 742; HRMS (EI): calcd for: 475.1730, Found: 475.1737.

2,6-Dimethyl-4-(((4-nitrophenyl)sulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7e)



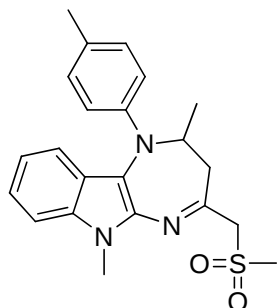
Yellow solid; Yield: 40% ; M.p. 204-205 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.42 – 8.25 (m, 2H), 8.15 – 7.98 (m, 2H), 7.20 (d, $J = 3.4$ Hz, 2H), 7.07 (d, $J = 8.2$ Hz, 2H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.88-6.82 (m, 3H), 4.58-4.50 (m, 1H), 4.48 (d, $J = 13.4$ Hz, 1H), 4.35 (d, $J = 13.4$ Hz, 1H), 3.33 (s, 3H), 3.19 (dd, $J = 16.4, 5.4$ Hz, 1H), 2.52 (dd, $J = 16.4, 3.0$ Hz, 1H), 2.33 (s, 3H), 1.02 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 151.2, 150.7, 147.3, 144.2, 135.4, 132.6, 131.6, 130.1, 129.8, 124.0, 123.6, 121.7, 121.1, 121.0, 118.6, 114.5, 109.2, 68.5, 55.2, 43.8, 27.8, 20.6, 18.4; IR (neat, cm^{-1}) 2924, 1568, 1530, 1468, 1347, 1156, 1087, 1015, 854, 745, 686; HRMS (ESI): calcd for ($\text{C}_{27}\text{H}_{26}\text{N}_4\text{O}_4\text{S}+\text{H}^+$): 503.1748, Found: 503.1728.

2,6-Dimethyl-4-((naphthalen-2-ylsulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7f)



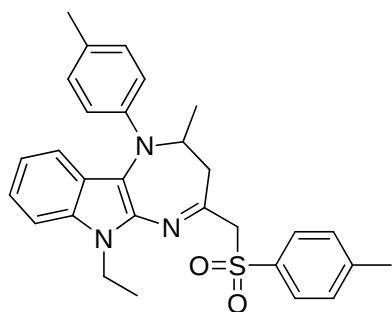
Yellow solid; Yield: 59% ; M.p. 94-95 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1H), 7.95-7.83 (m, 4H), 7.72 – 7.63 (m, 1H), 7.62 – 7.55 (m, 1H), 7.15 – 7.07 (m, 1H), 7.08 – 6.97 (m, 3H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.86 – 6.74 (m, 3H), 4.55 – 4.37 (m, 2H), 4.32 (d, $J = 13.1$ Hz, 1H), 3.23 (dd, $J = 16.7, 5.0$ Hz, 1H), 2.97 (s, 3H), 2.52 (dd, $J = 16.7, 2.8$ Hz, 1H), 2.29 (s, 3H), 0.99 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 147.7, 135.5, 135.25, 135.22, 132.5, 132.0, 131.5, 130.4, 129.7, 129.4, 129.3, 129.1, 127.8, 127.6, 123.2, 123.1, 122.12, 121.09, 120.9, 118.2, 114.2, 109.1, 68.7, 54.0, 43.7, 27.4, 20.7, 18.3; IR (neat, cm^{-1}) 3055, 2927, 1611, 1509, 1316, 1263, 1152, 818, 744, 676; HRMS (ESI): calcd for ($\text{C}_{31}\text{H}_{29}\text{N}_3\text{O}_2\text{S}+\text{H}^+$): 508.2053, Found: 508.2049.

2,6-Dimethyl-4-((methylsulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7g)



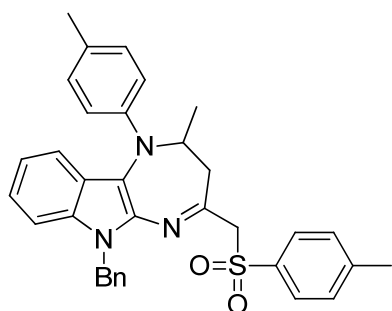
Yellow solid; Yield: 32% ; M.p. 70-71⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.88 – 6.82 (m, 1H), 4.68 – 4.39 (m, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 4.11 (d, *J* = 13.5 Hz, 1H), 3.81 (s, 3H), 3.20 (dd, *J* = 16.6, 5.0 Hz, 1H), 3.03 (s, 3H), 2.46 (dd, *J* = 16.6, 2.6 Hz, 1H), 2.29 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 147.8, 135.6, 132.3, 132.0, 129.8, 123.6, 122.6, 121.2, 121.1, 118.4, 115.1, 109.2, 67.4, 54.0, 43.8, 40.0, 28.4, 20.7, 18.1; IR (neat, cm⁻¹) 2927, 1610, 1509, 1467, 1309, 1260, 1153, 1118, 911, 817, 736; HRMS (EI): calcd for: 395.1667, Found: 395.1664.

6-Ethyl-2-methyl-1-(p-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7h)



Yellow solid; Yield: 60%; M.p. 191-192⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.77 (m, 3H), 4.51 – 4.40 (m, 1H), 4.37 (d, *J* = 13.1 Hz, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.20 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.47 (dd, *J* = 16.7, 3.0 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 147.7, 144.7, 135.8, 134.2, 132.1, 131.4, 129.7, 129.6, 128.5, 123.0, 122.0, 121.4, 121.1, 118.1, 114.1, 109.1, 69.1, 54.1, 43.4, 36.2, 21.6, 20.7, 18.3, 14.8; IR (neat, cm⁻¹) 2976, 2930, 1526, 1507, 1317, 1230, 1154, 1084, 909, 816, 738; HRMS (EI): calcd for: 485.2137, Found: 485.2132.

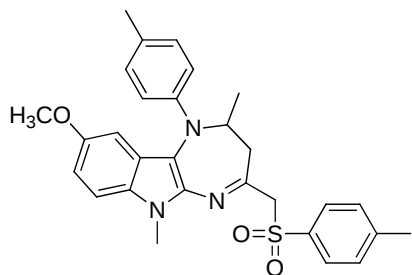
6-Benzyl-2-methyl-1-(p-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7i)



Yellow solid; Yield: 44%; M.p. 85-86⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.16 (m, 5H), 7.07 – 7.03 (m, 4H), 6.99 (d, *J* = 6.7 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.83 – 6.78 (m,

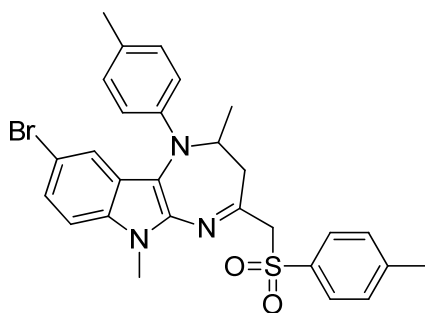
1H), 5.12 – 4.95 (m, 2H), 4.53 – 4.38 (m, 1H), 4.33 (d, $J = 13.2$ Hz, 1H), 4.18 (d, $J = 13.1$ Hz, 1H), 3.22 (dd, $J = 16.7, 5.0$ Hz, 1H), 2.50 (dd, $J = 16.8, 2.8$ Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H), 1.02 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 147.6, 144.6, 138.9, 135.9, 134.8, 132.4, 131.6, 129.8, 129.6, 128.44, 128.38, 126.9, 126.5, 123.4, 122.1, 121.6, 121.0, 118.6, 114.4, 109.9, 68.8, 54.1, 44.8, 43.7, 21.6, 20.7, 18.4; IR (neat, cm^{-1}) 2925, 1597, 1508, 1454, 1317, 1152, 1084, 909, 816, 737; HRMS (EI): calcd for: 547.2293, Found: 547.2300.

9-methoxy-2,6-dimethyl-1-(p-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7j)



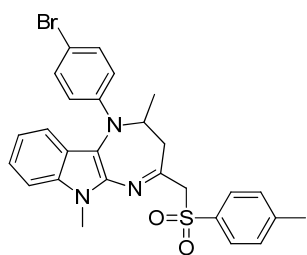
Yellow solid; Yield: 56%; M.p. 76-77 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.10 (d, $J = 8.9$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 2H), 6.89 – 6.75 (m, 3H), 6.35 (d, $J = 2.4$ Hz, 1H), 4.48 – 4.40 (m, 1H), 4.34 (d, $J = 13.1$ Hz, 1H), 4.21 (d, $J = 13.0$ Hz, 1H), 3.58 (s, 3H), 3.30 (s, 3H), 3.17 (dd, $J = 16.8, 5.0$ Hz, 1H), 2.50 (dd, $J = 16.8, 3.1$ Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H), 0.99 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 152.3, 147.2, 144.6, 135.7, 133.6, 131.1, 130.7, 129.7, 129.5, 128.6, 121.5, 121.4, 113.7, 113.7, 110.0, 102.3, 68.7, 55.7, 53.8, 43.5, 27.8, 21.6, 20.6, 18.4; IR (neat, cm^{-1}) 2929, 1614, 1511, 1383, 1317, 1297, 1265, 1155, 1086, 806, 744; HRMS (EI): calcd for: 501.2086, Found: 501.2072.

9-bromo-2,6-dimethyl-1-(p-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7k)



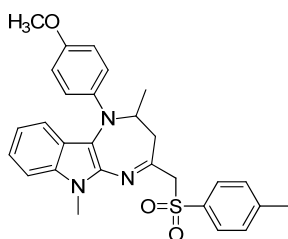
Yellow solid; Yield: 40%; M.p. 98-99 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.23 (dd, $J = 8.8, 1.9$ Hz, 1H), 7.10 – 6.98 (m, 4H), 6.79 (d, $J = 8.4$ Hz, 2H), 4.50 – 4.37 (m, 1H), 4.35 (d, $J = 13.0$ Hz, 1H), 4.21 (d, $J = 13.0$ Hz, 1H), 3.32 (s, 3H), 3.17 (dd, $J = 16.8, 4.9$ Hz, 1H), 2.47 (dd, $J = 16.8, 3.1$ Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 0.96 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 147.4, 144.6, 135.7, 133.8, 133.5, 131.8, 129.9, 129.6, 128.5, 126.0, 123.0, 122.9, 121.8, 113.5, 111.3, 110.7, 68.7, 54.0, 43.6, 27.9, 21.6, 20.7, 18.3; IR (neat, cm^{-1}) 2924, 1610, 1508, 1465, 1378, 1263, 1153, 1087, 820, 752; HRMS (EI): calcd for: 549.1086, Found: 549.1081.

1-(4-bromophenyl)-2,6-dimethyl-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole(7l)



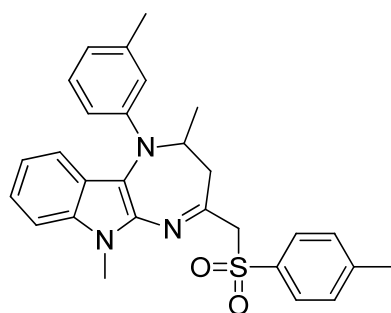
yellow solid; Yield: 56%; M.p. 202-203⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.26 – 7.15 (m, 4H), 6.99 – 6.92 (m, 1H), 6.91 – 6.86 (m, 1H), 6.79 – 6.70 (m, 2H), 4.62 – 4.47 (m, 1H), 4.35 (d, *J* = 13.1 Hz, 1H), 4.23 (d, *J* = 13.0 Hz, 1H), 3.35 (s, 3H), 3.16 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.55 (dd, *J* = 16.6, 3.5 Hz, 1H), 2.41 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.5, 148.1, 144.7, 135.5, 135.1, 133.8, 132.0, 129.6, 128.5, 123.2, 122.0, 121.2, 120.5, 118.8, 113.6, 112.3, 109.3, 68.6, 54.7, 43.7, 27.9, 21.6, 18.4; IR (neat, cm⁻¹) 2929, 1586, 1528, 1486, 1317, 1302, 1153, 1083, 909, 814, 736; HRMS (EI): calcd for: 535.0929, Found: 535.0922.

1-(4-methoxyphenyl)-2,6-dimethyl-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7m)



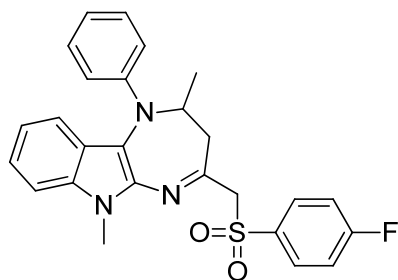
Yellow solid; Yield: 65%; M.p. 91-92⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.09 (m, 2H), 6.92 – 6.86 (m, 3H), 6.84 – 6.73 (m, 3H), 4.38 (d, *J* = 13.1 Hz, 1H), 4.31 – 4.25 (m, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 3.77 (s, 3H), 3.32 (s, 3H), 3.19 (dd, *J* = 16.6, 5.0 Hz, 1H), 2.48 – 2.33 (m, 4H), 0.94 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 151.3, 144.6, 144.3, 135.8, 135.4, 132.1, 129.5, 128.6, 124.4, 123.2, 121.1, 121.0, 118.2, 115.0, 114.4, 109.0, 68.9, 55.4, 54.7, 43.3, 27.7, 21.6, 18.3; IR (neat, cm⁻¹) 2931, 1597, 1526, 1505, 1467, 1381, 1316, 1243, 1153, 1084, 1036, 910, 827, 737; HRMS (EI): calcd for: 487.1930, Found: 487.1940.

2,6-dimethyl-1-(*m*-tolyl)-4-(tosylmethyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7n)



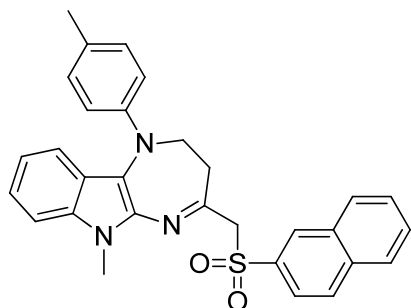
Yellow solid; Yield: 43%; M.p. 220-221⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.13 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.78 – 6.75 (m, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.62 – 4.45 (m, 1H), 4.36 (d, *J* = 13.1 Hz, 1H), 4.24 (d, *J* = 13.1 Hz, 1H), 3.33 (s, 3H), 3.18 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.53 (dd, *J* = 16.7, 3.1 Hz, 1H), 2.41 (s, 3H), 2.26 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 149.6, 144.6, 138.9, 135.6, 135.2, 133.1, 129.5, 128.9, 128.6, 123.1, 122.6, 121.9, 121.4, 120.9, 118.8, 118.4, 113.6, 109.1, 68.6, 54.2, 43.8, 27.8, 21.59, 21.58, 18.4; IR (neat, cm⁻¹) 2926, 1600, 1526, 1488, 1382, 1317, 1153, 1084, 909, 737; HRMS (EI): calcd for: 471.1980, Found: 471.1978.

4-(((4-fluorophenyl)sulfonyl)methyl)-2,6-dimethyl-1-phenyl-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7o)



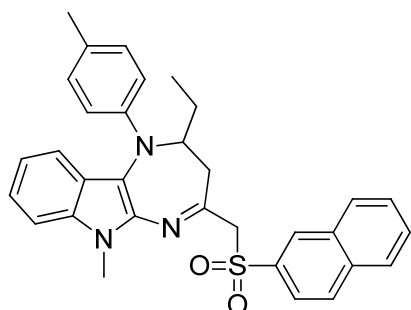
Yellow solid; Yield: 52%; M.p. 223-224⁰C ; ¹H NMR (600 MHz, CDCl₃) δ 7.85 – 7.82 (m, 2H), 7.25 – 7.16 (m, 4H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.99 – 6.88 (m, 4H), 6.85 (t, *J* = 7.2 Hz, 1H), 4.64 – 4.57 (m, 1H), 4.36 (d, *J* = 13.2 Hz, 1H), 4.24 (d, *J* = 13.2 Hz, 1H), 3.38 (s, 3H), 3.17 (dd, *J* = 16.6, 5.3 Hz, 1H), 2.56 (dd, *J* = 16.4, 2.4 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.8 (d, *J*_{C-F} = 256.5 Hz), 153.2, 149.4, 135.3, 134.5 (d, *J*_{C-F} = 3.1 Hz), 133.3, 131.5 (d, *J*_{C-F} = 9.5 Hz), 129.2, 123.3, 121.6, 121.3, 121.0, 120.8, 118.6, 116.2 (d, *J*_{C-F} = 22.6 Hz), 113.5, 109.2, 68.8, 54.8, 43.9, 27.9, 18.5; IR (neat, cm⁻¹) 3061, 2926, 2854, 1704, 1613, 1590, 1526, 1493, 1470, 1319, 1290, 1149, 1083, 909, 839, 740; HRMS (EI): calcd for: 461.1573, Found: 461.1567.

6-methyl-4-((naphthalen-2-ylsulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole (7p)



Yellow solid; Yield: 25%; M.p. 76-77⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 1.2 Hz, 1H), 7.93 – 7.86 (m, 3H), 7.78 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.61 – 7.53 (m, 1H), 7.10 – 7.16 (m, 1H), 7.06 (d, *J* = 9.2 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.88 – 6.81 (m, 3H), 4.35 (s, 2H), 3.77 – 3.65 (m, 2H), 3.01 – 2.96 (m, 2H), 2.95 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 146.0, 135.4, 135.3, 134.8, 132.3, 132.0, 131.0, 130.4, 129.8, 129.4, 129.3, 129.1, 127.8, 127.6, 123.3, 123.1, 120.7, 120.6, 120.4, 118.5, 116.7, 109.2, 68.4, 47.5, 39.7, 27.3, 20.6; IR (neat, cm⁻¹) 2925, 1612, 1508, 1372, 1313, 1151, 1128, 1071, 909, 863, 737; HRMS (ESI): calcd for (C₃₀H₂₇N₃O₂S+H⁺): 494.1897, Found: 494.1862.

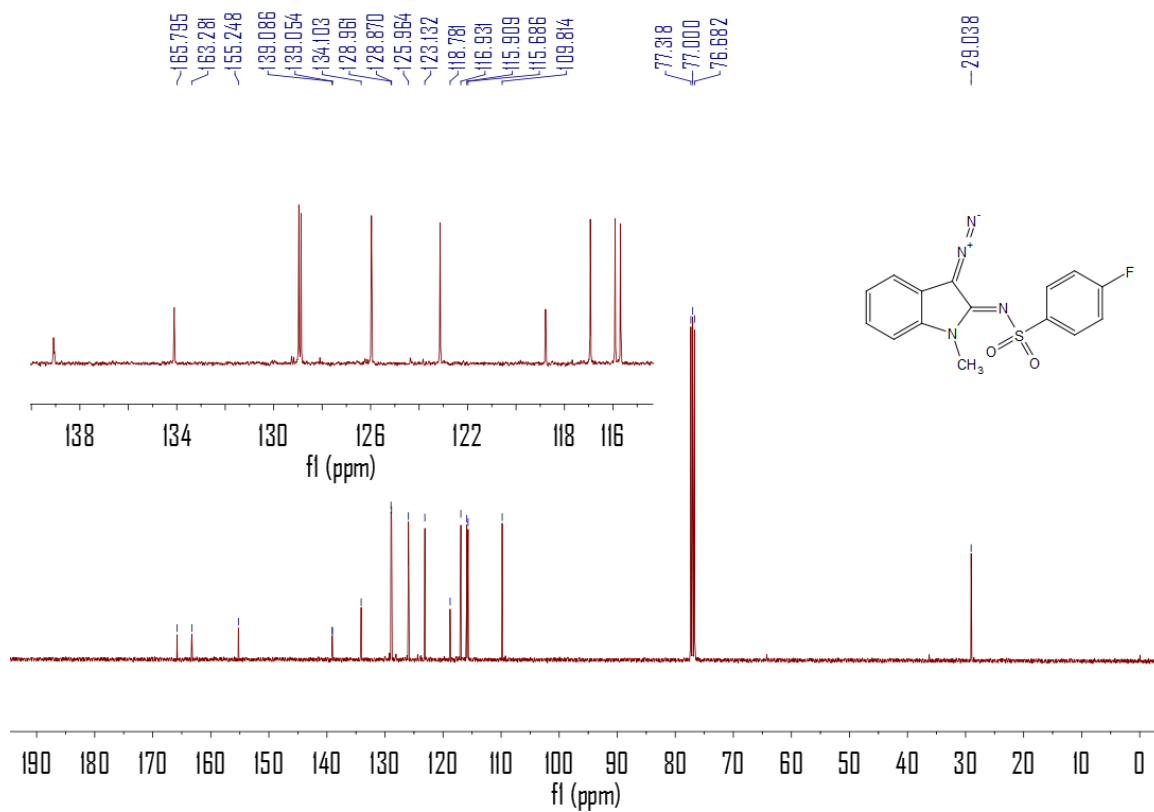
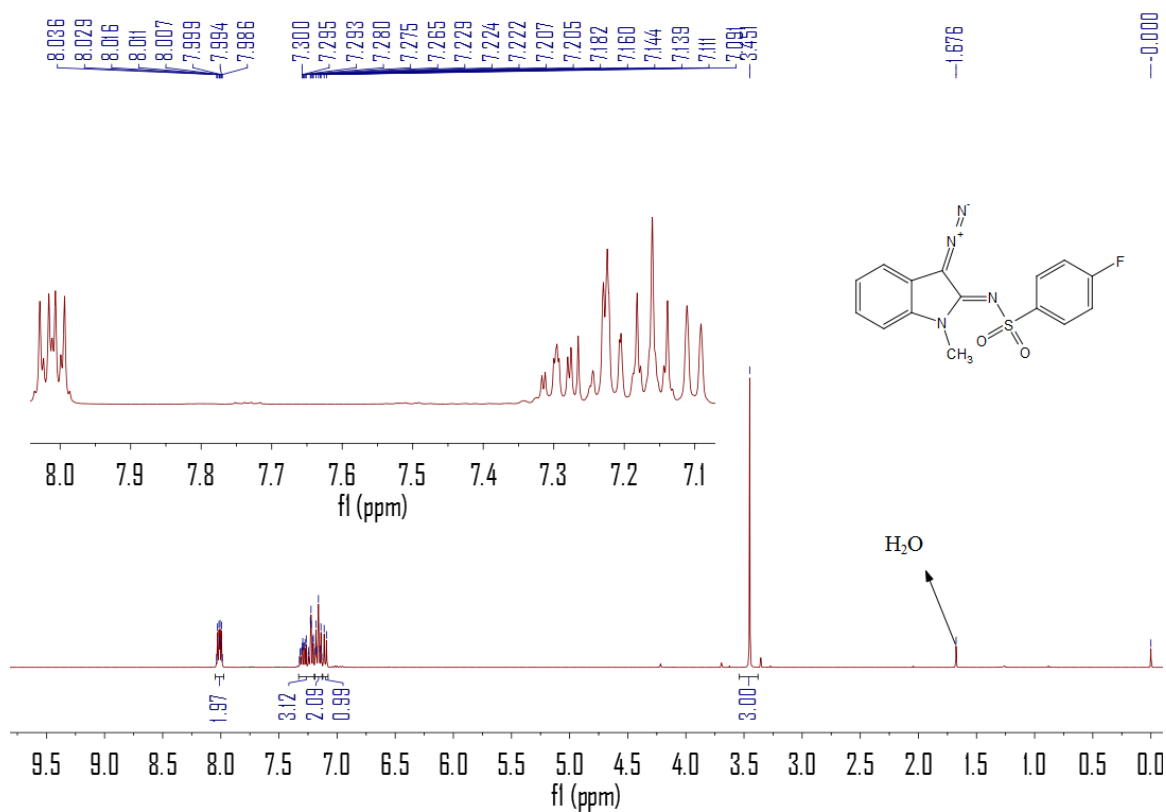
2-ethyl-6-methyl-4-((naphthalen-2-ylsulfonyl)methyl)-1-(p-tolyl)-1,2,3,6-tetrahydro-[1,4]diazepino[2,3-b]indole(7q)

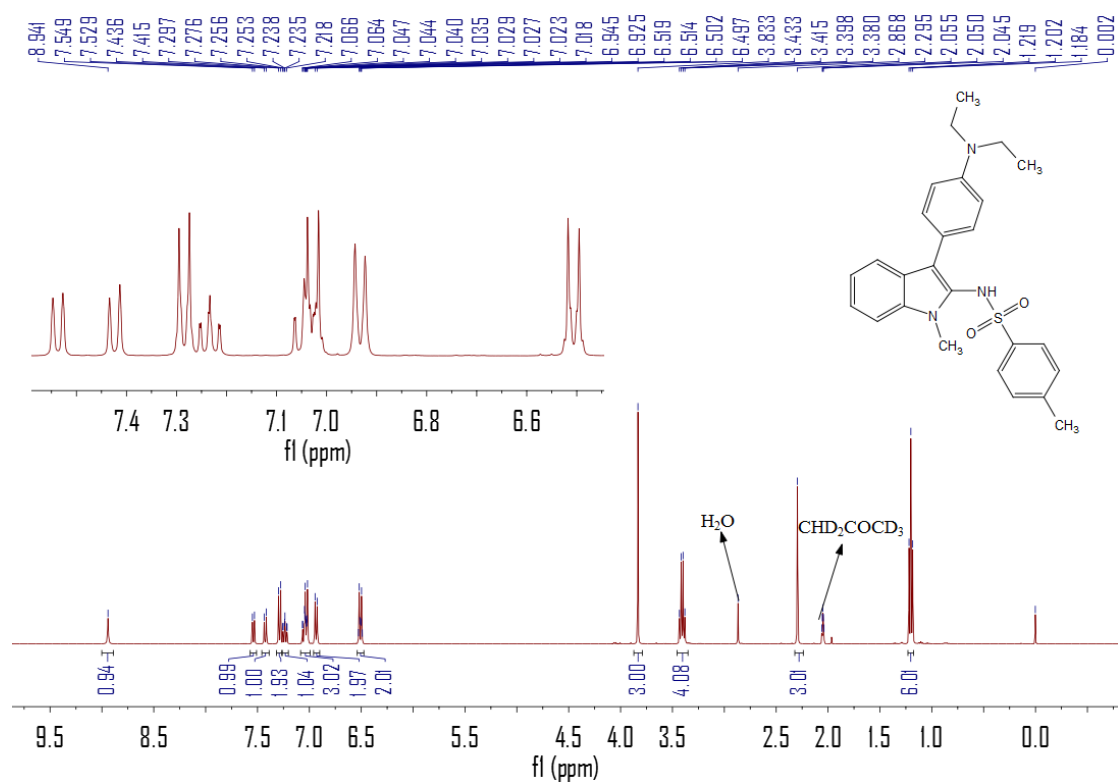


Yellow solid; Yield: 63%; M.p. 97-98 ⁰C ; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 1.0 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.90 (t, *J* = 7.4 Hz, 2H),

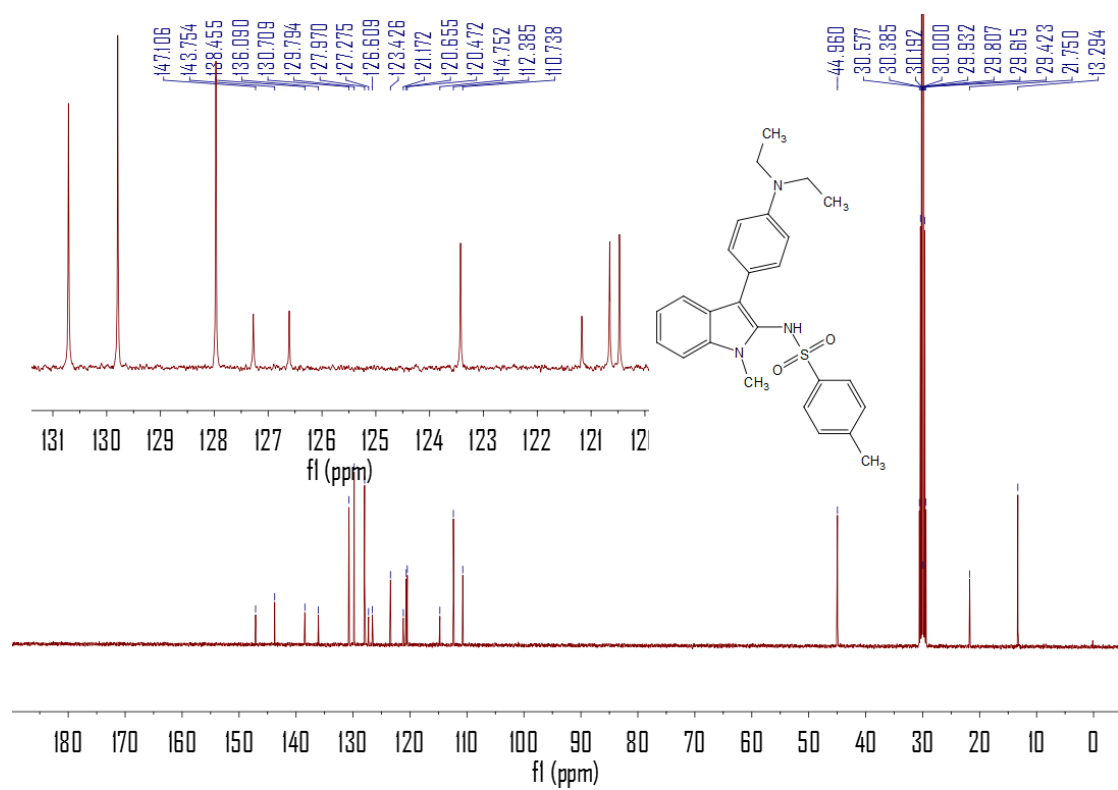
7.84 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.69 – 7.63 (m, 1H), 7.61 – 7.56 (m, 1H), 7.13 – 7.08 (m, 1H), 7.05 – 7.00 (m, 3H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.84 (d, $J = 8.3$ Hz, 2H), 6.81– 6.75(m, 1H), 4.45 (d, $J = 13.1$ Hz, 1H), 4.29 (d, $J = 13.1$ Hz, 1H), 4.18 – 4.07 (m, 1H), 3.31 (dd, $J = 16.9, 4.5$ Hz, 1H), 2.96 (s, 3H), 2.53 (dd, $J = 16.9, 3.1$ Hz, 1H), 2.29 (s, 3H), 1.37 – 1.28 (m, 1H), 0.99 – 0.95 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 148.1, 135.5, 135.2, 132.4, 132.0, 131.4, 130.4, 129.7, 129.33, 129.28, 129.0, 127.8, 127.7, 123.2, 123.1, 122.3, 121.0, 120.9, 118.2, 114.0, 109.0, 68.8, 59.9, 43.1, 27.3, 24.4, 20.6, 11.5; IR (neat, cm^{-1}) 2961, 2929, 1608, 1527, 1509, 1310, 1251, 1152, 1069, 861, 813, 739; HRMS (ESI): calcd for ($\text{C}_{32}\text{H}_{31}\text{N}_3\text{O}_2\text{S}+\text{H}^+$): 522.2210, Found: 522.2236.

Copies of ^1H & ^{13}C NMR Spectra

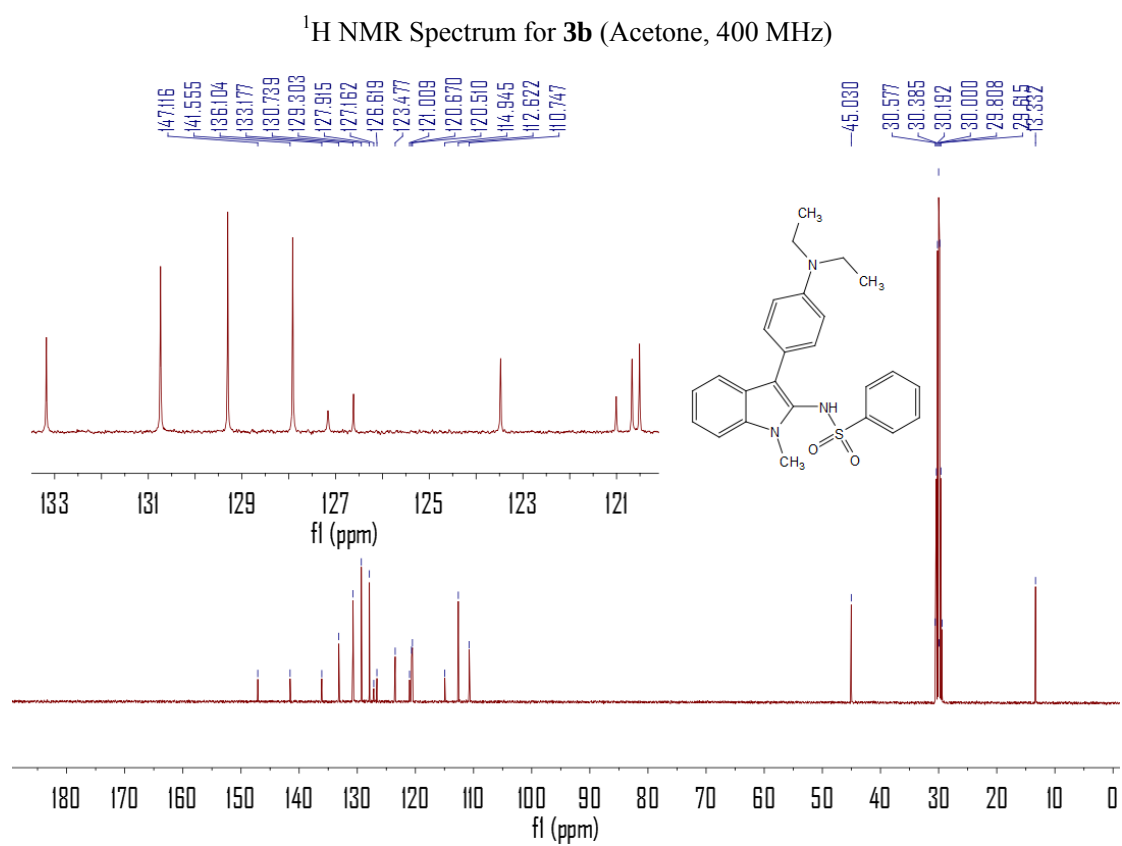
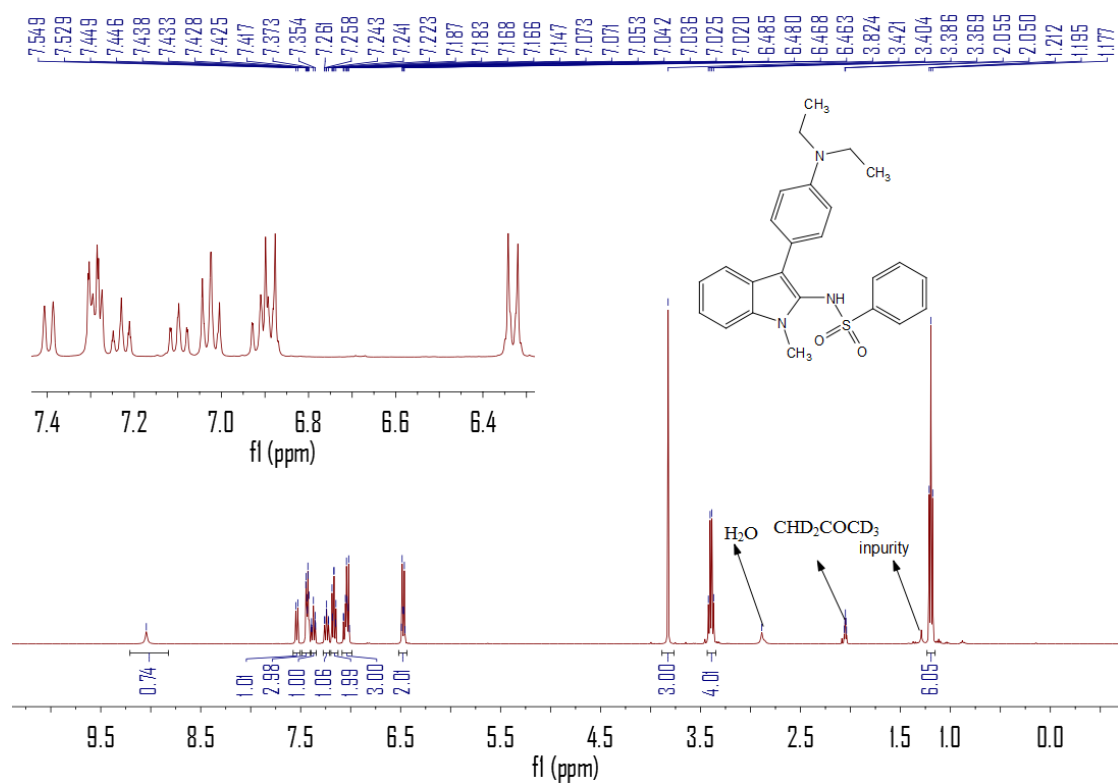


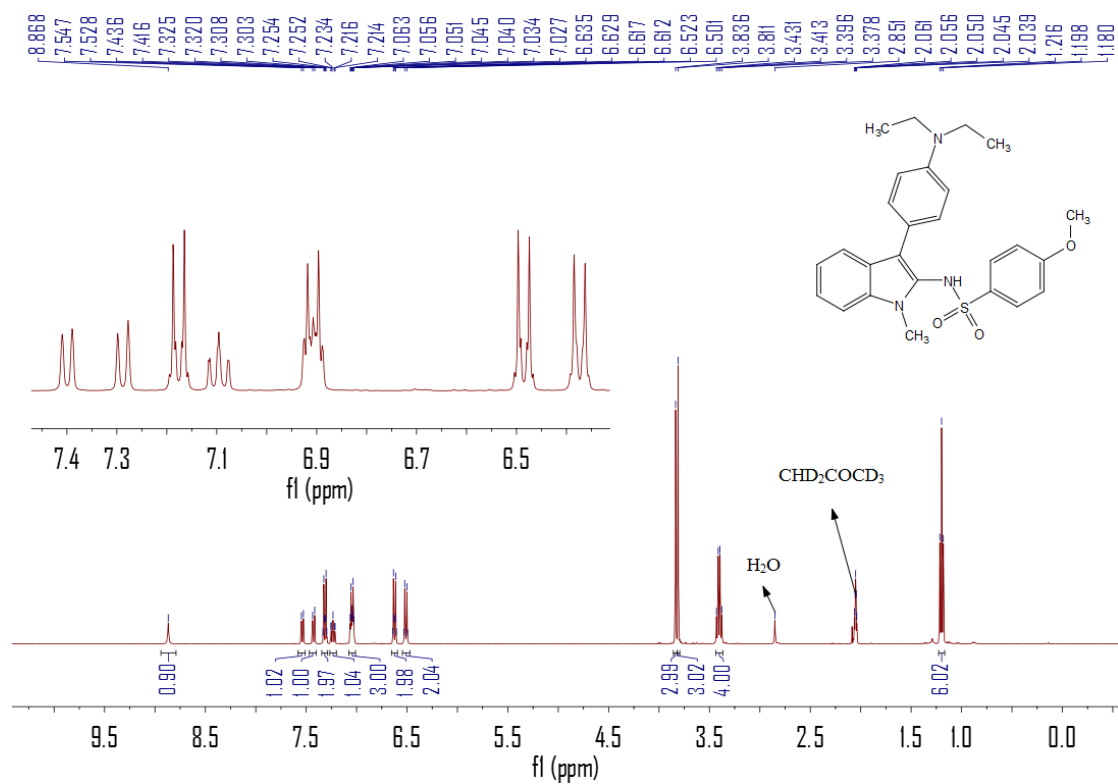


¹H NMR Spectrum for **3a** (Acetone, 400 MHz)

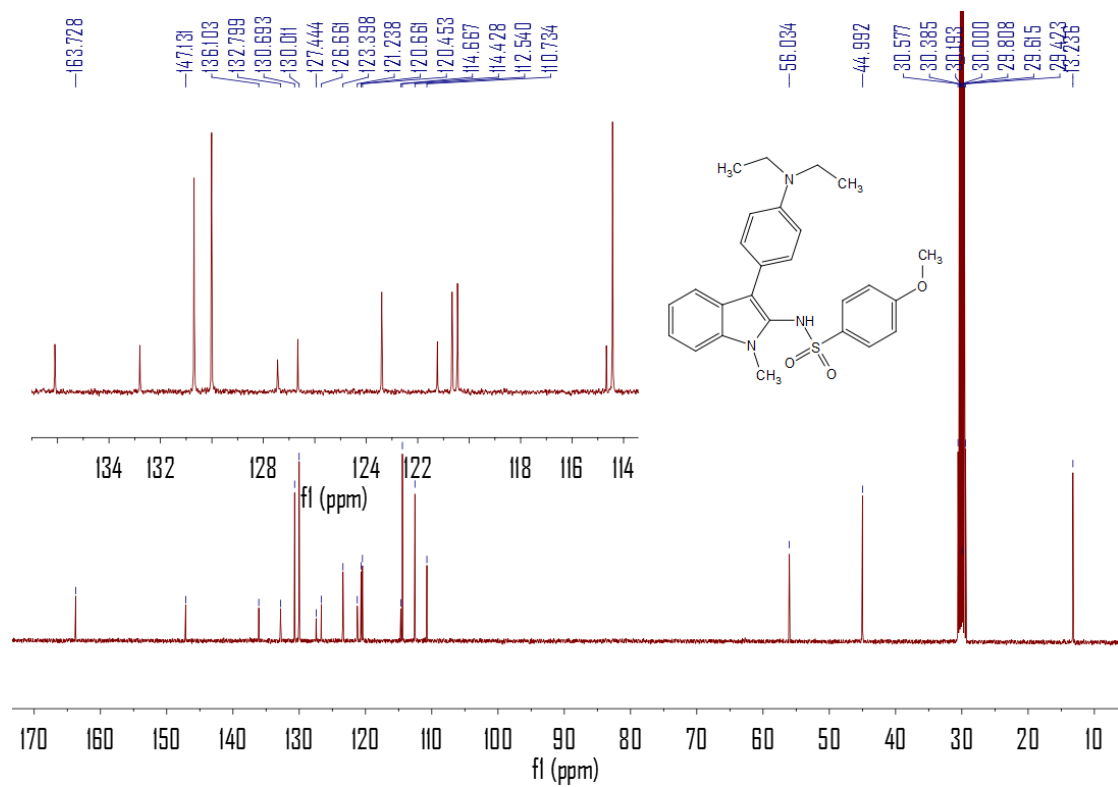


¹³C NMR Spectrum for **3a** (Acetone, 100 MHz)

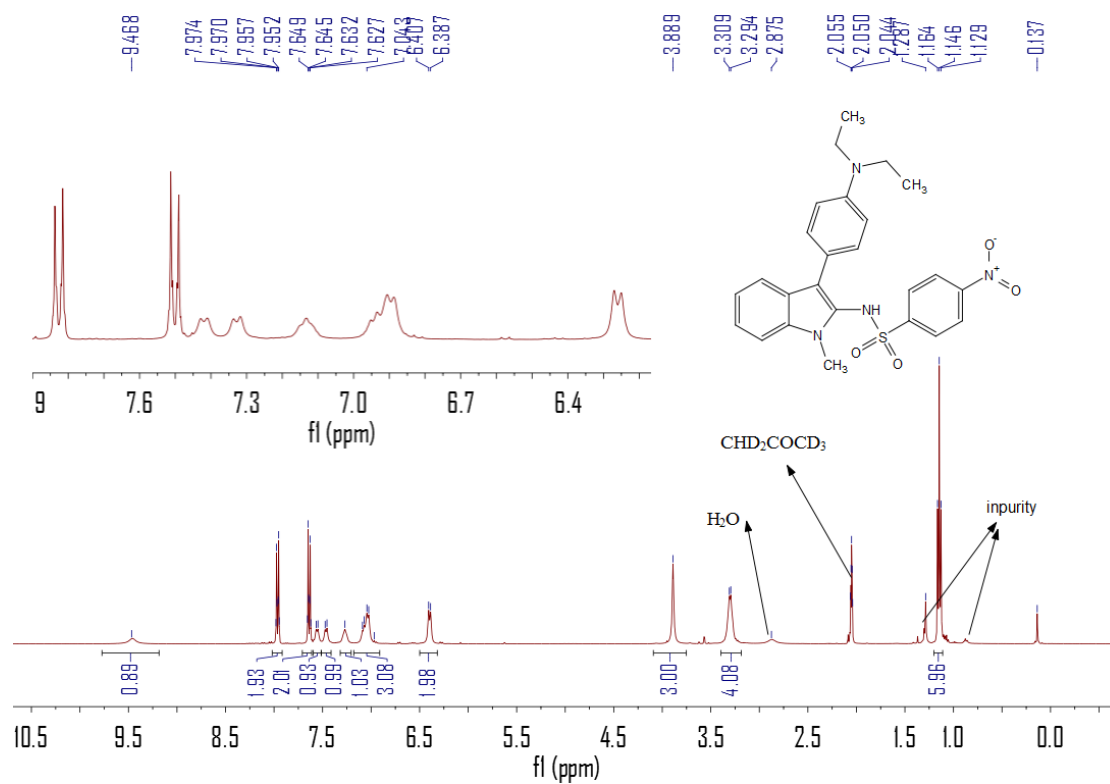




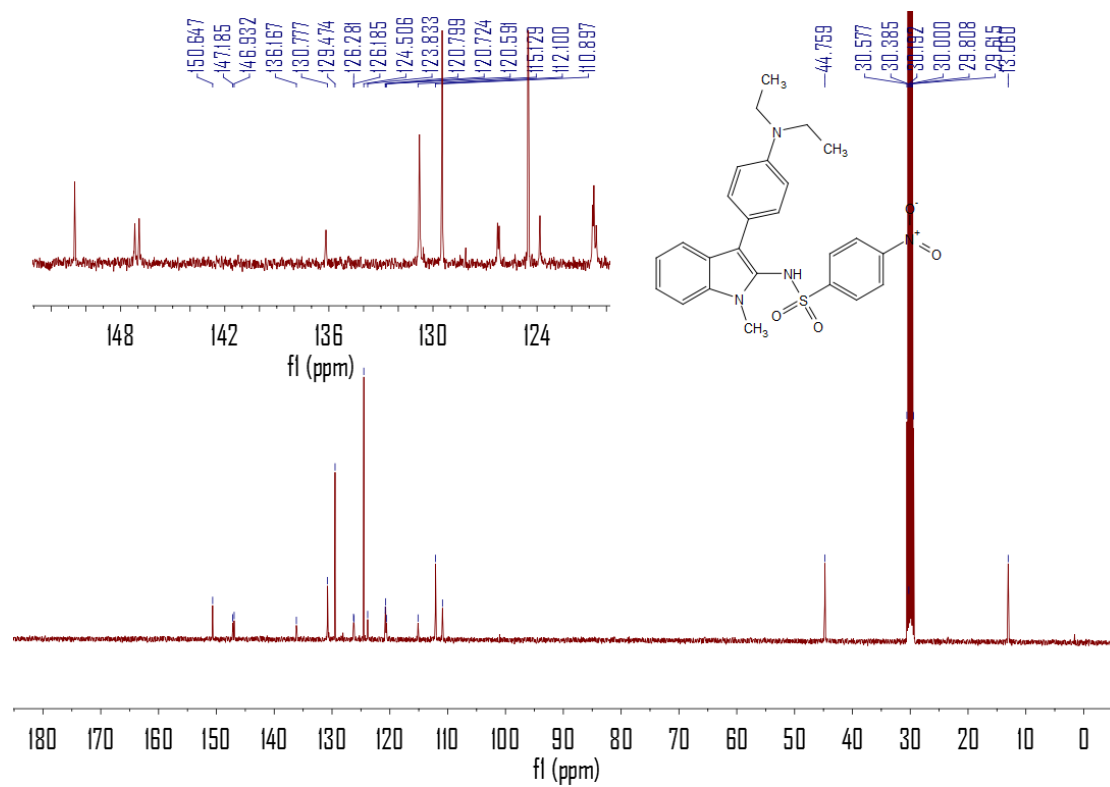
¹H NMR Spectrum for **3c** (Acetone, 400 MHz)



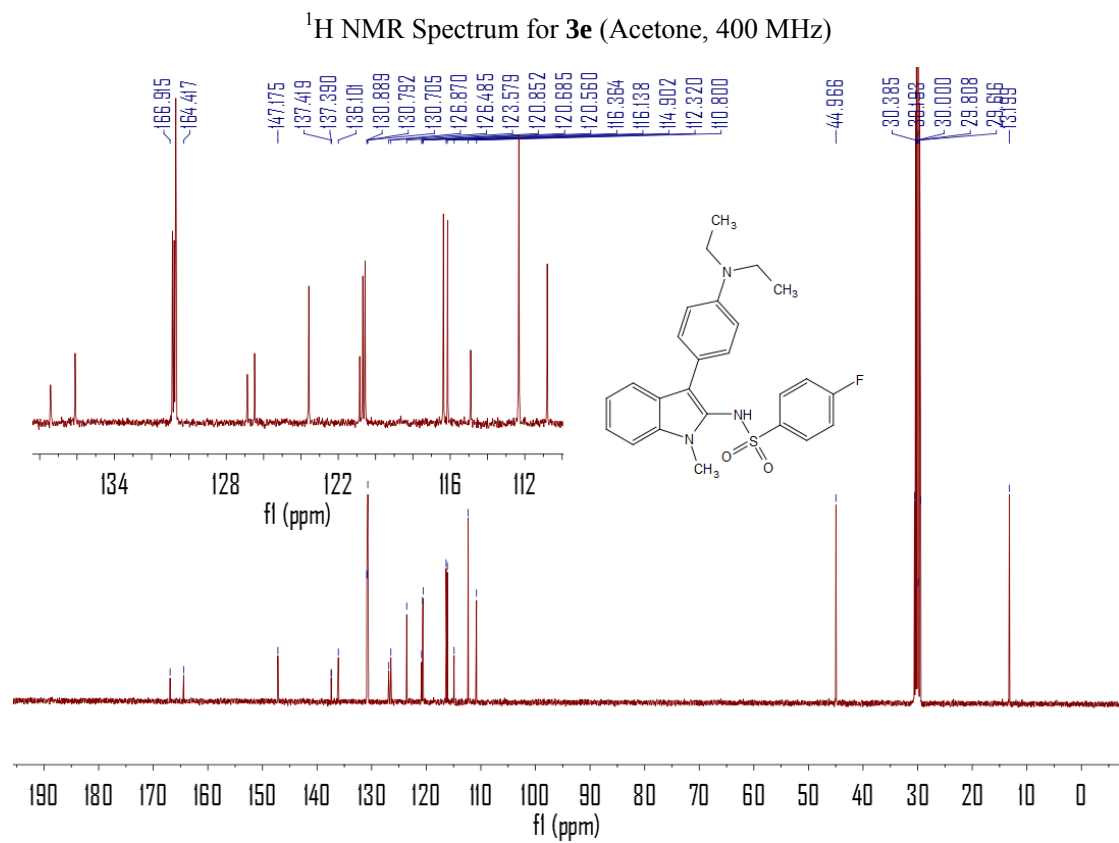
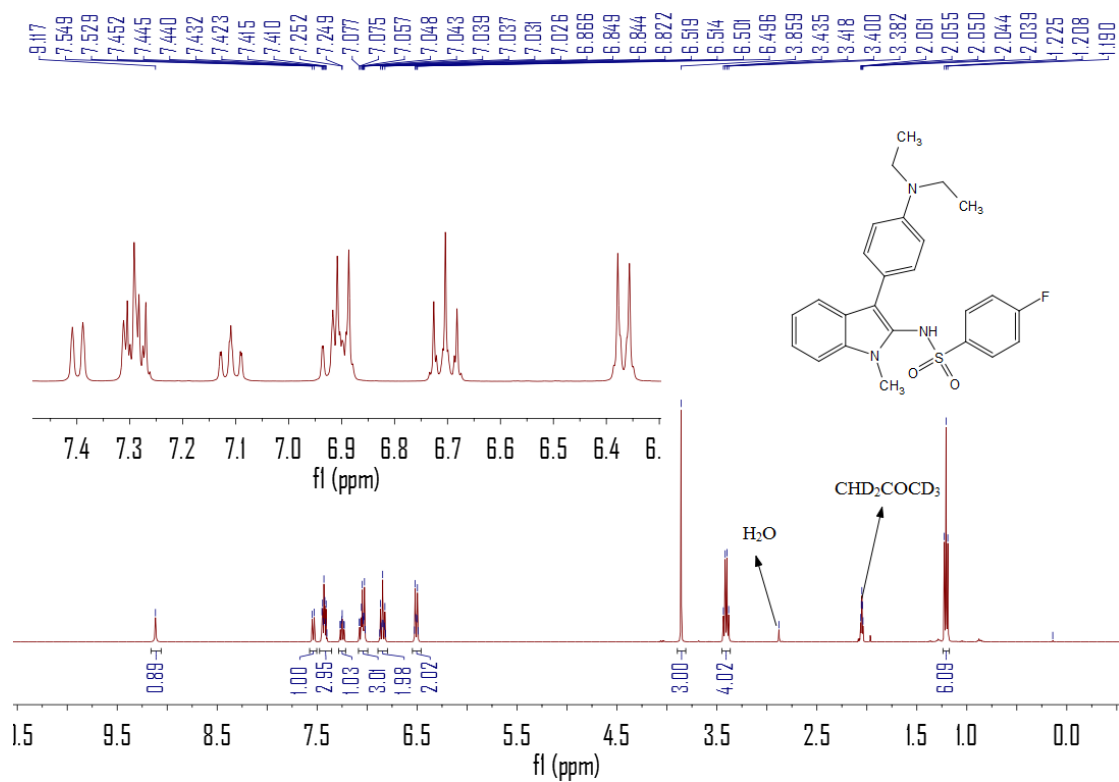
¹³C NMR Spectrum for **3c** (Acetone, 100 MHz)

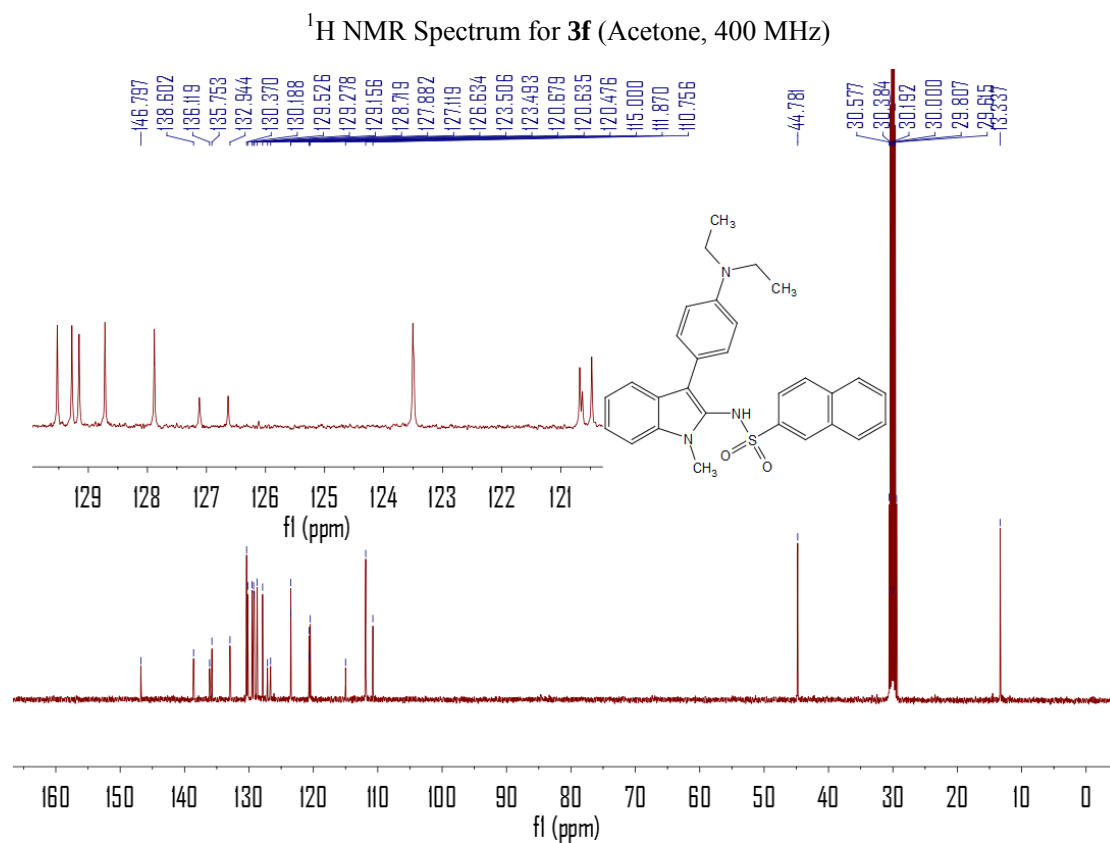
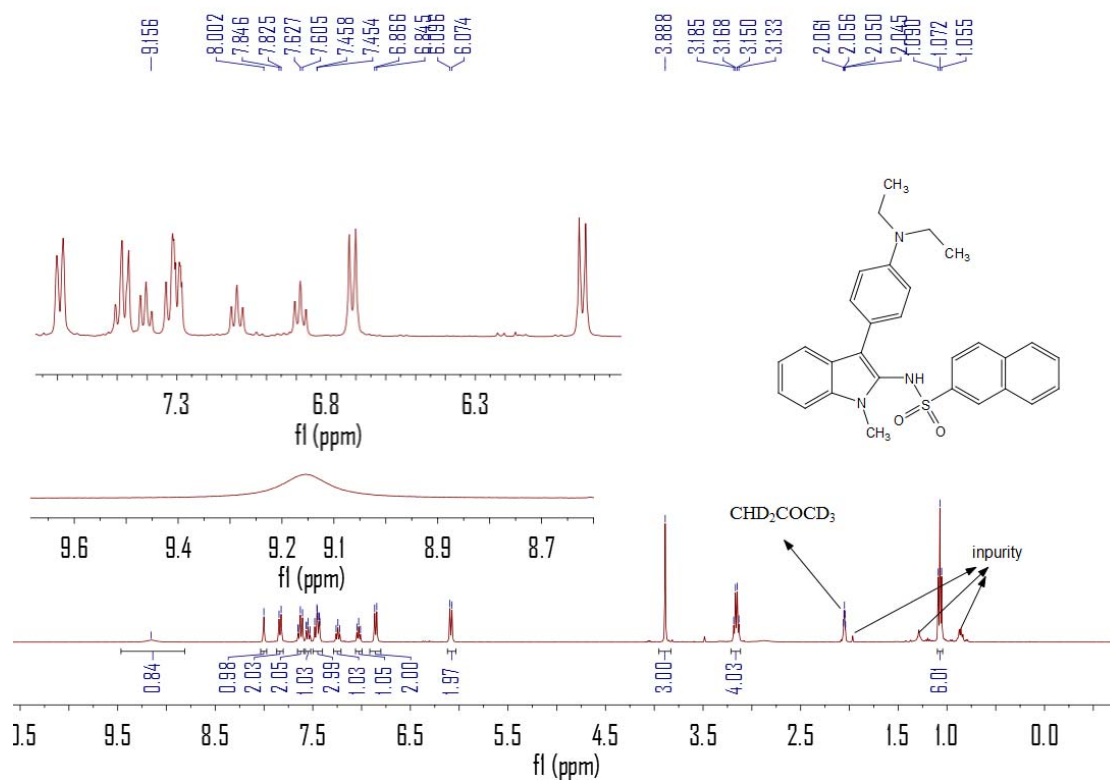


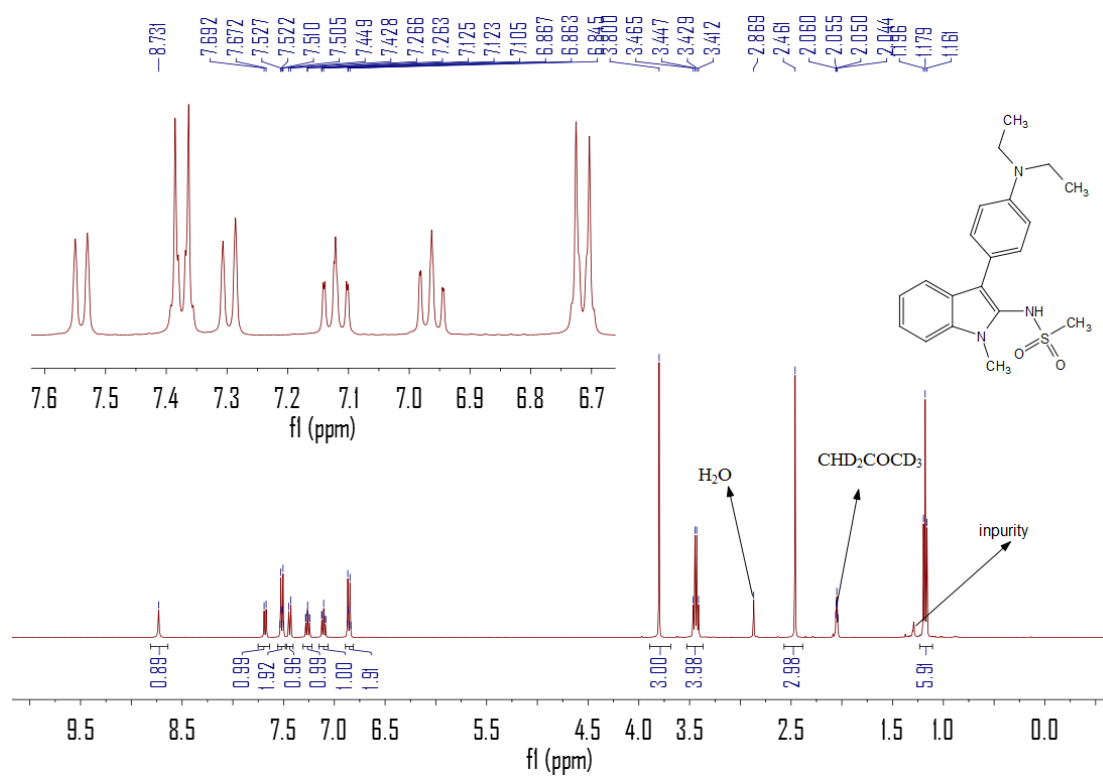
¹H NMR Spectrum for **3d** (Acetone, 400 MHz)



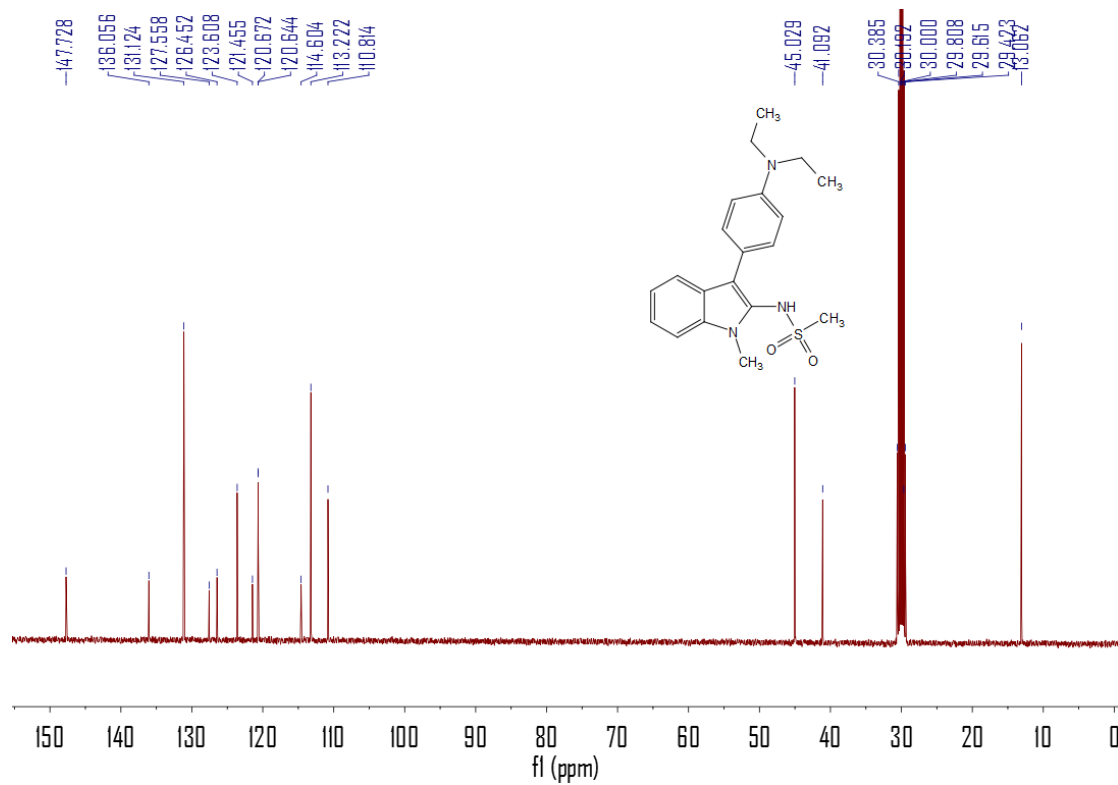
¹³C NMR Spectrum for **3d** (Acetone, 100 MHz)



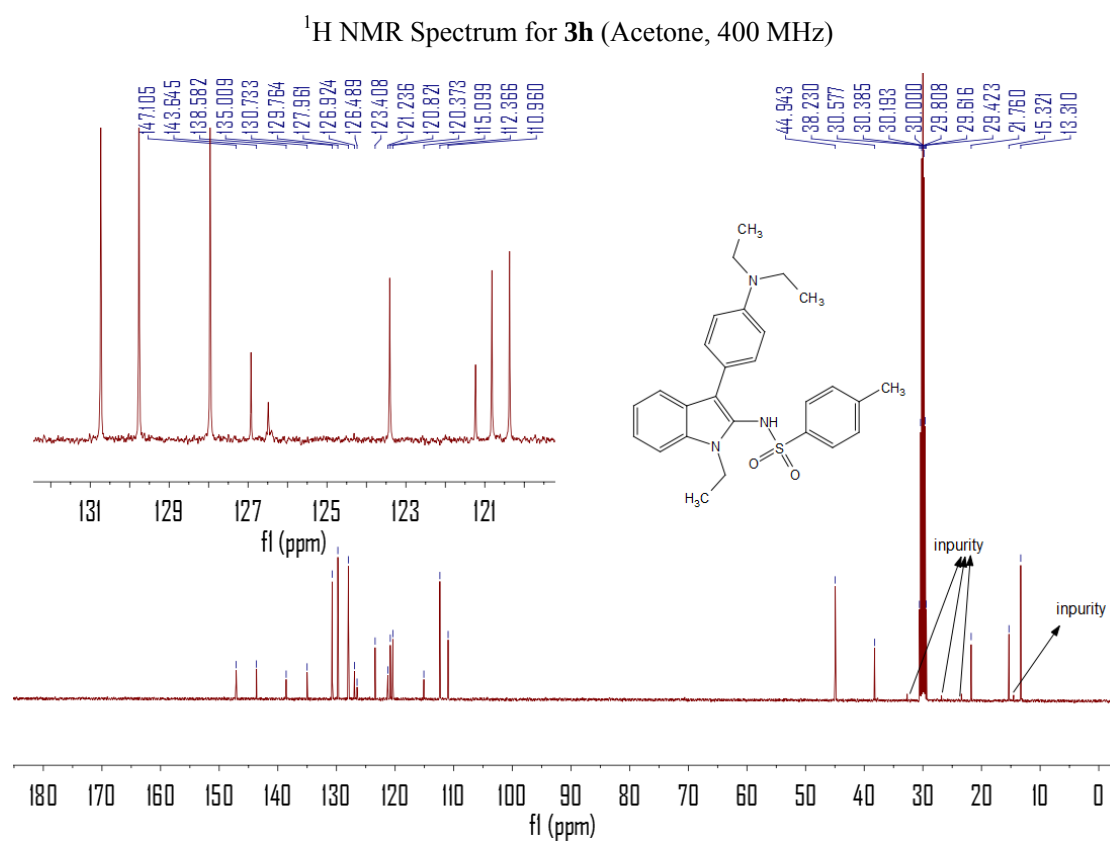
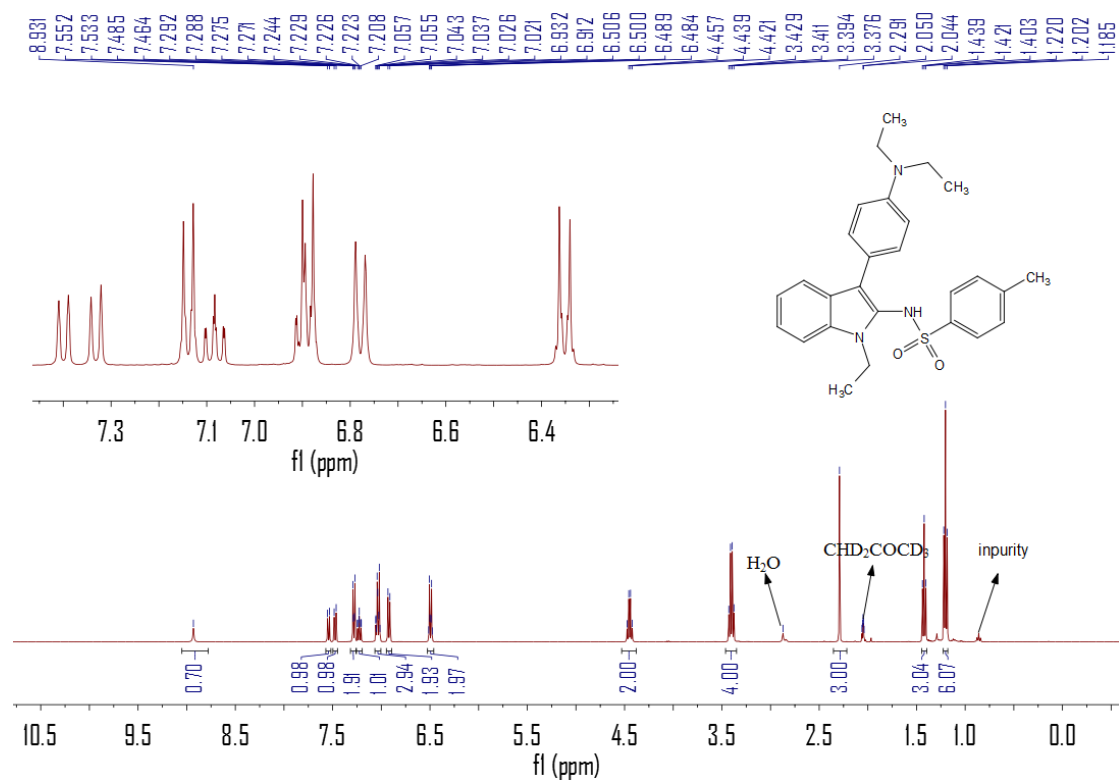


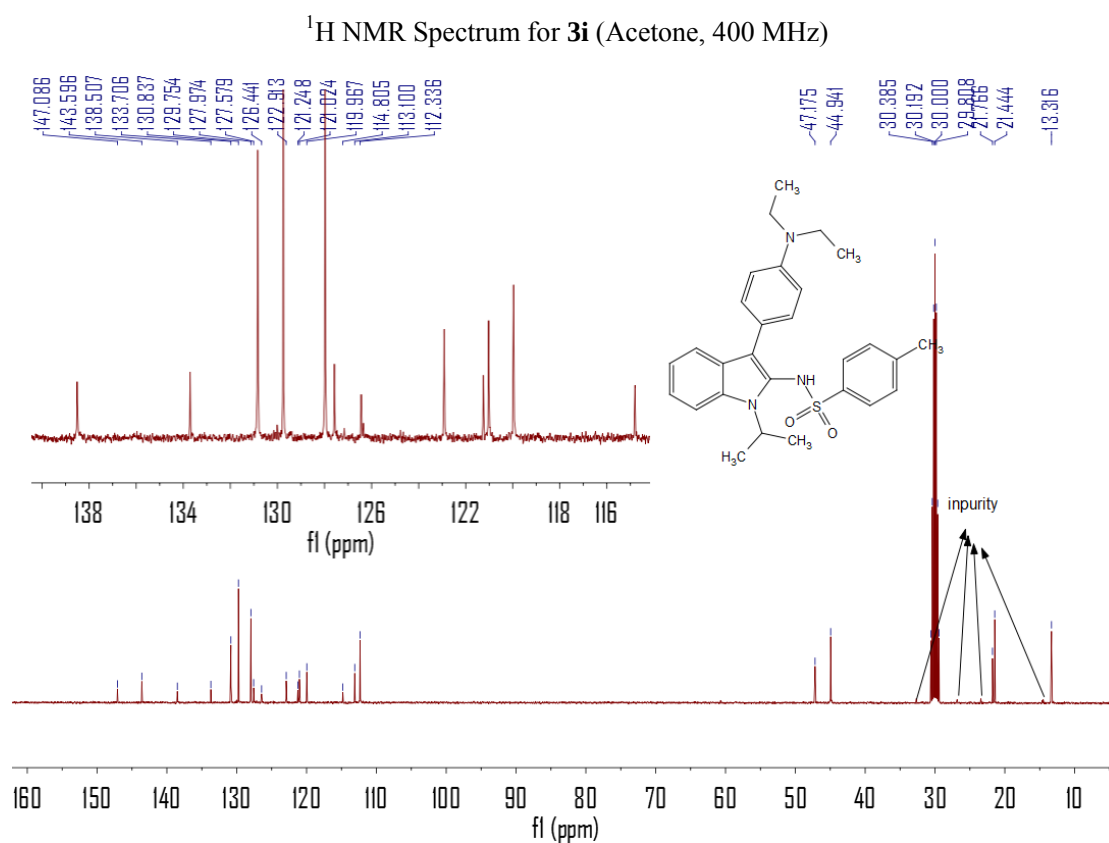
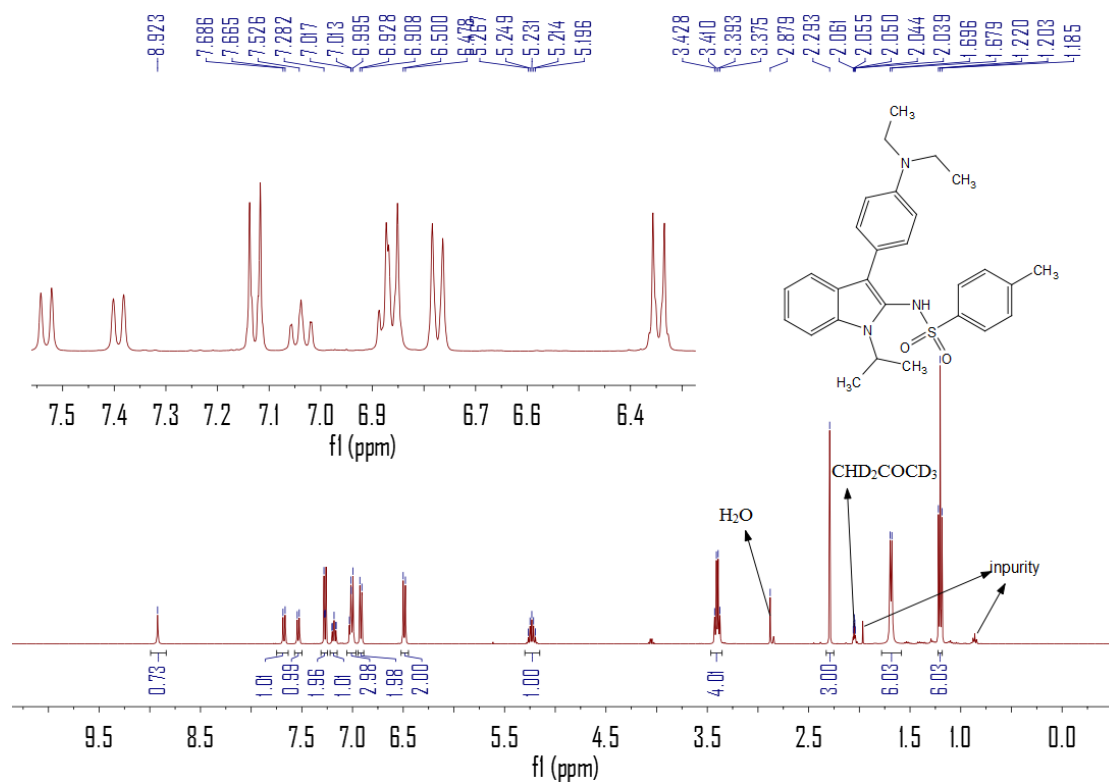


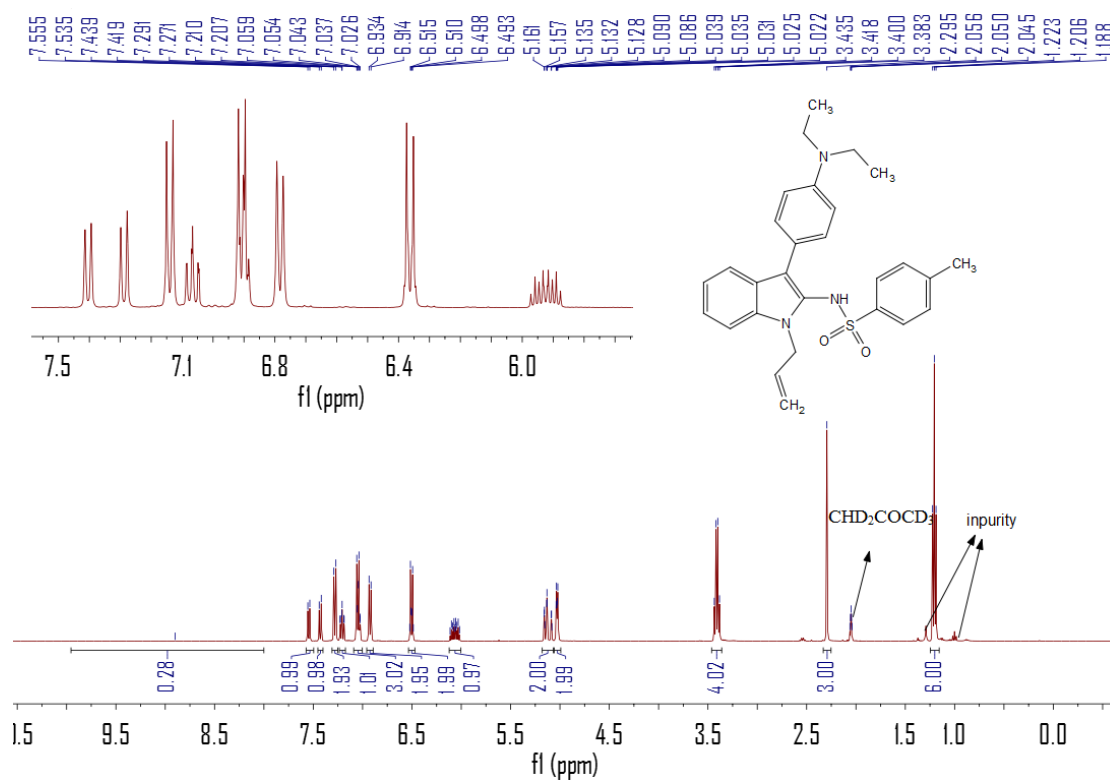
¹H NMR Spectrum for **3g** (Acetone, 400 MHz)



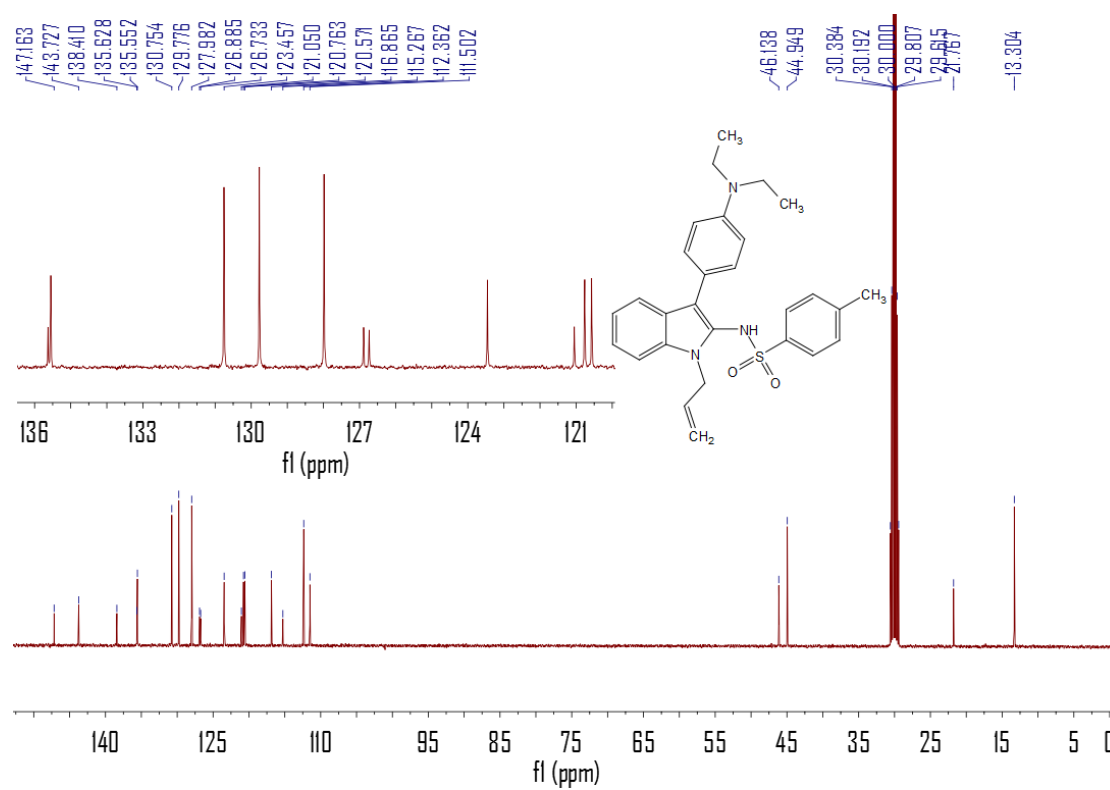
¹³C NMR Spectrum for **3g** (Acetone, 100 MHz)



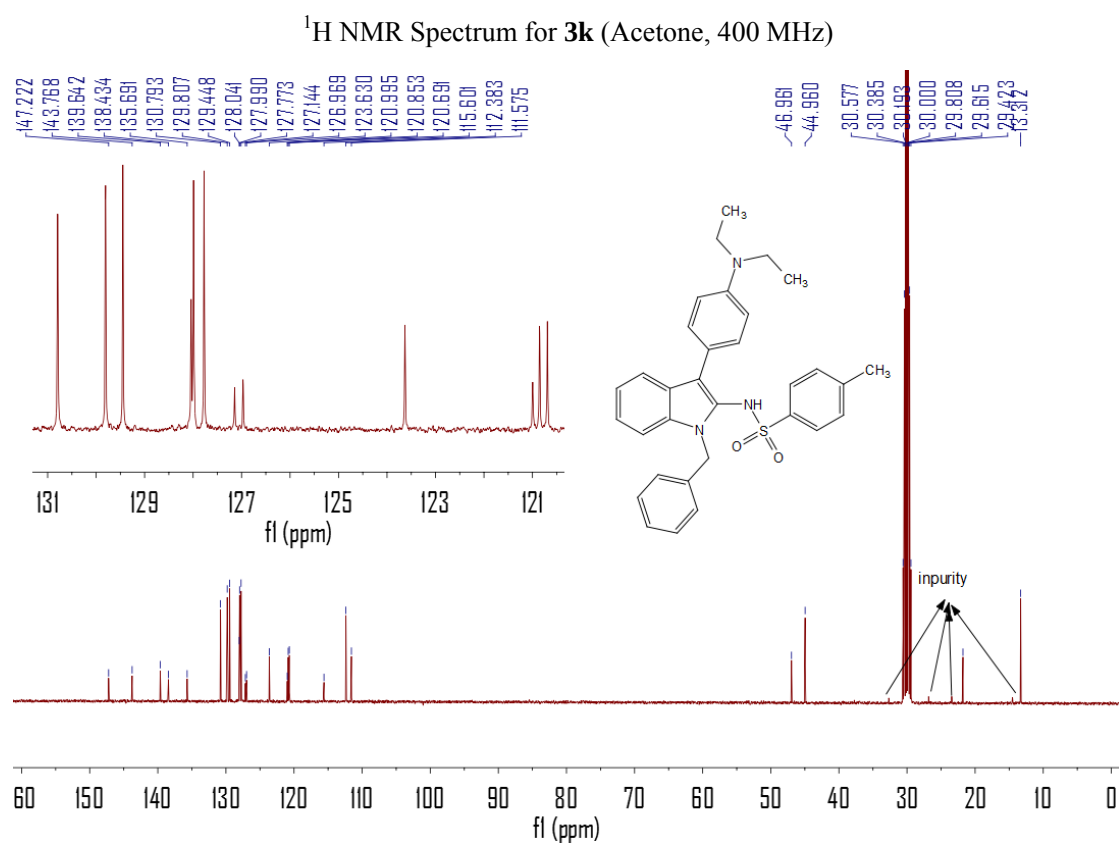
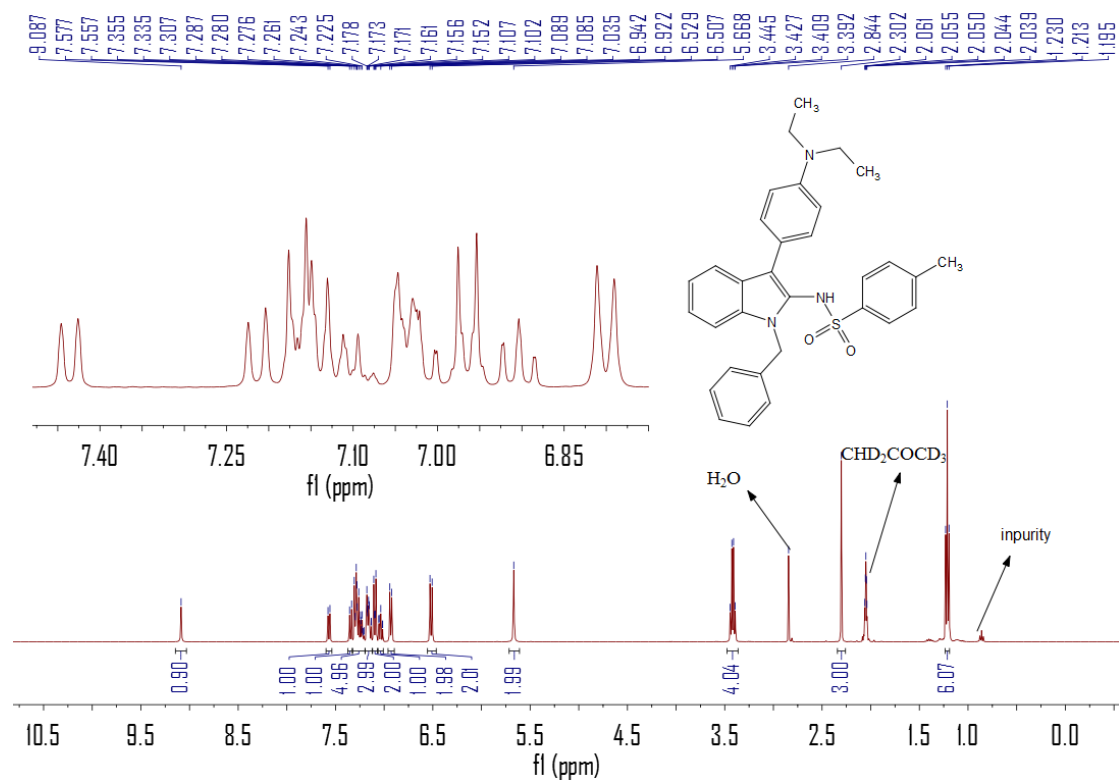


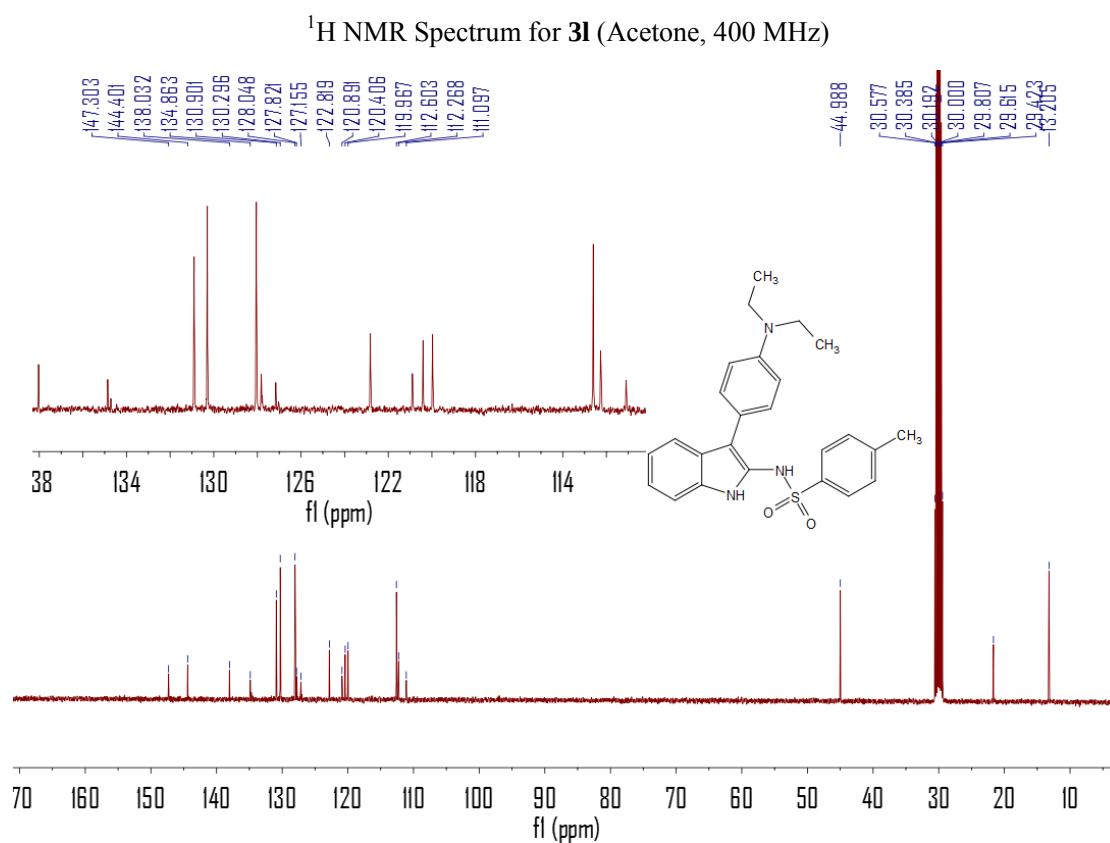
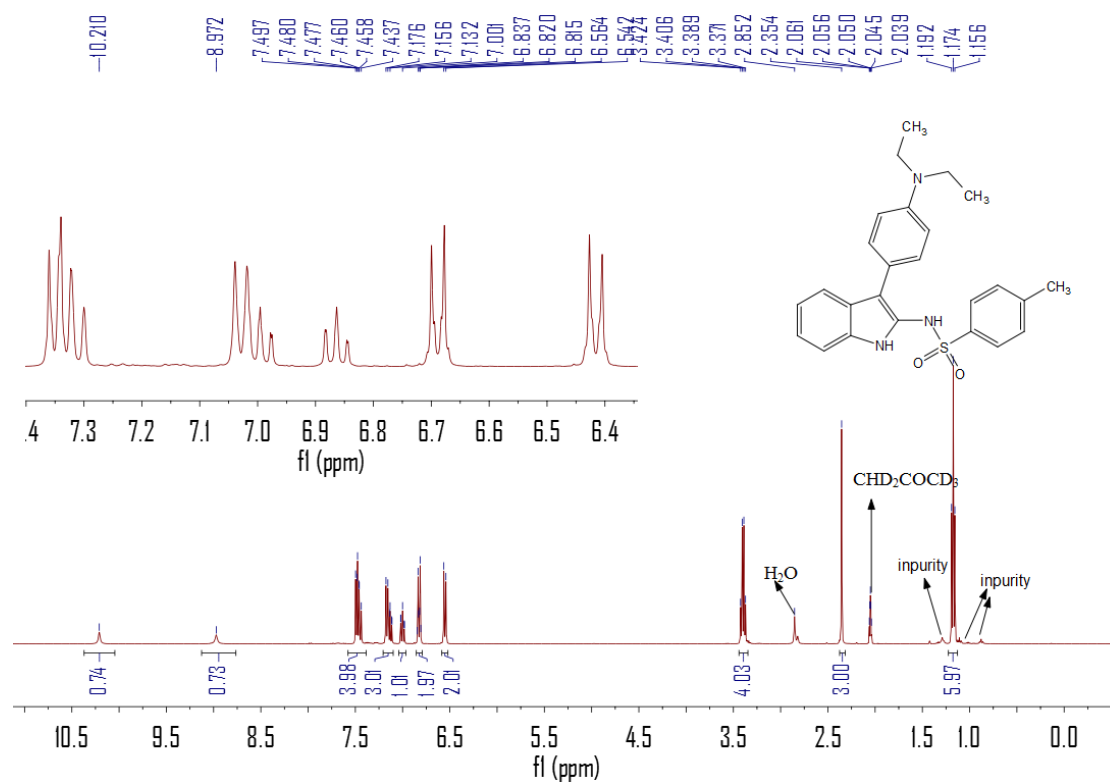


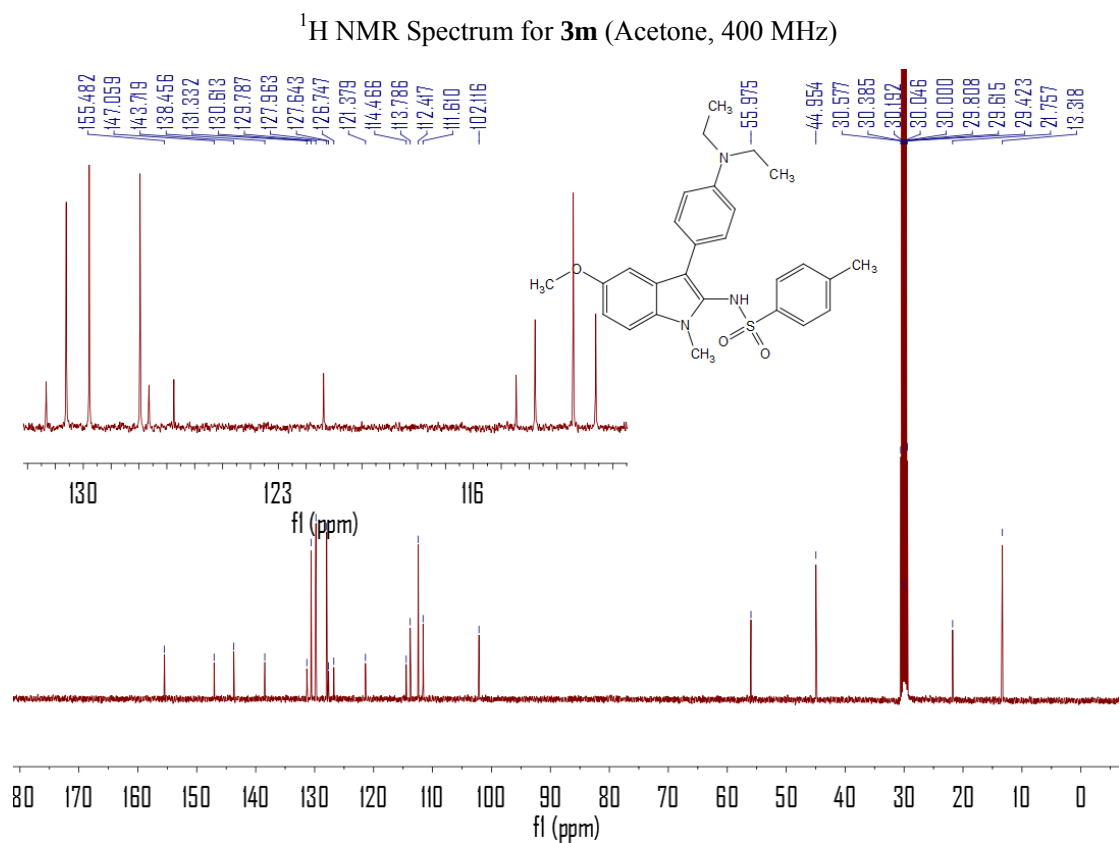
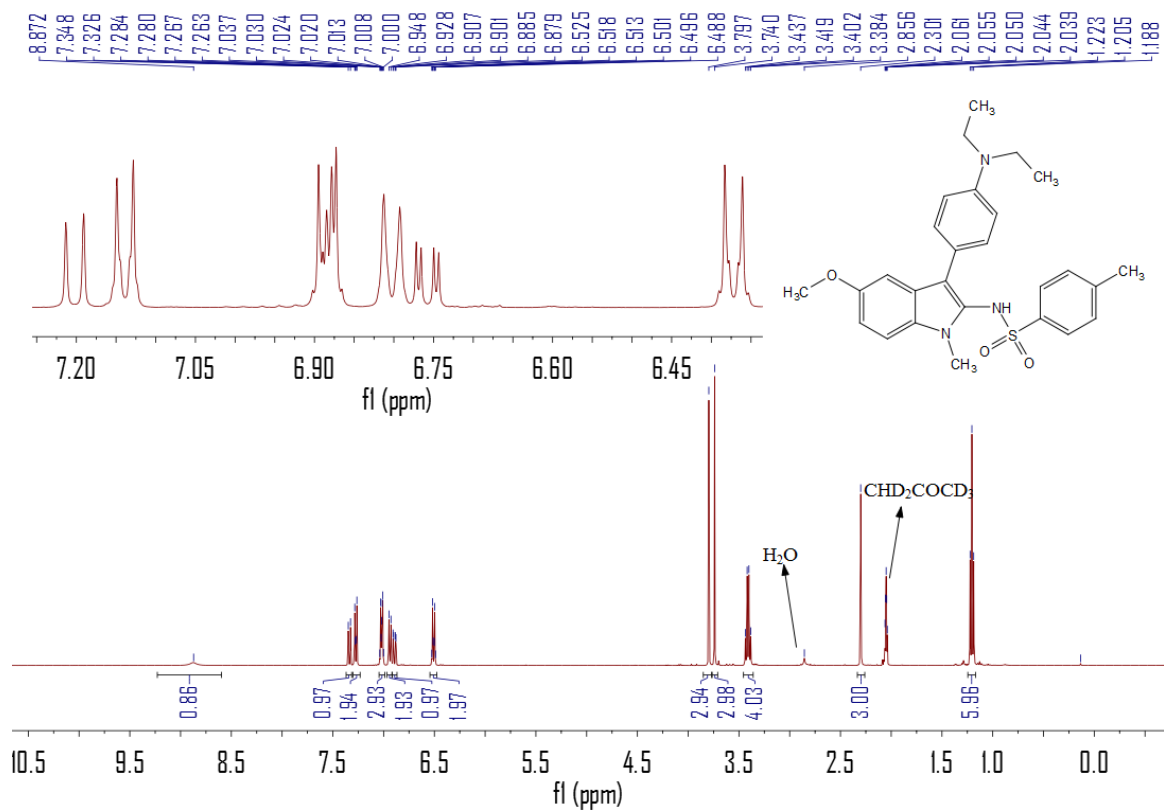
¹H NMR Spectrum for **3j** (Acetone, 400 MHz)

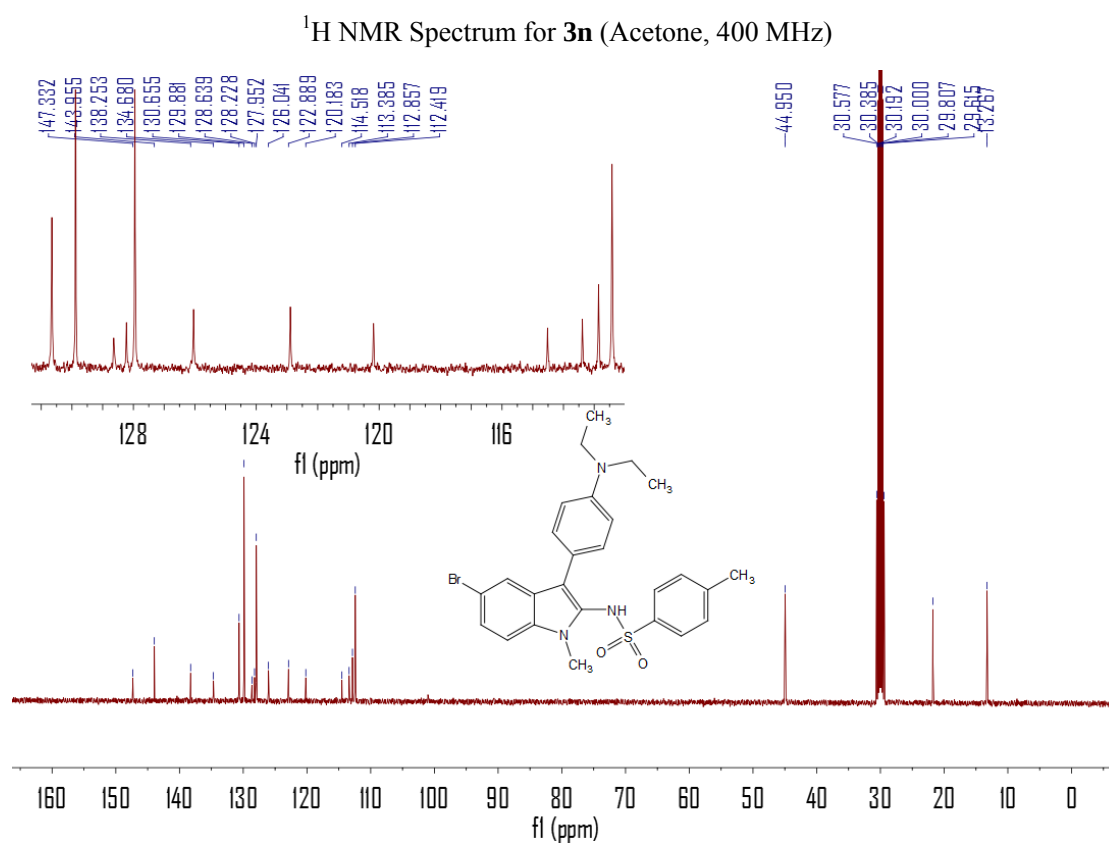
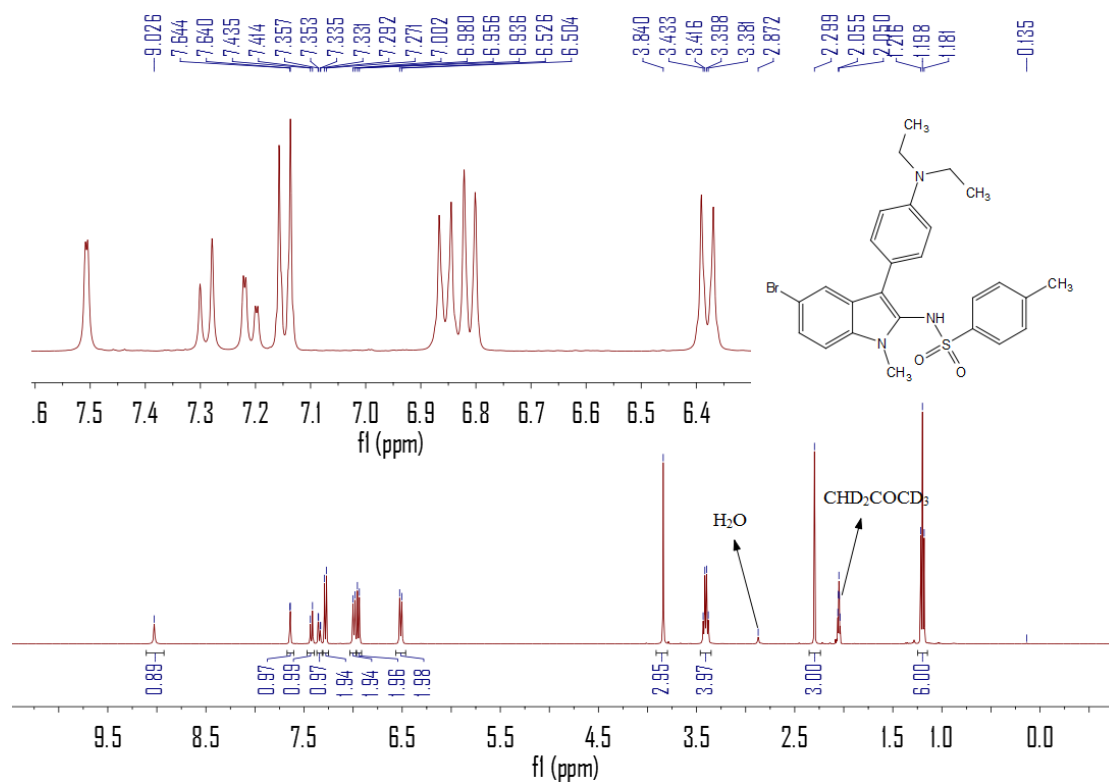


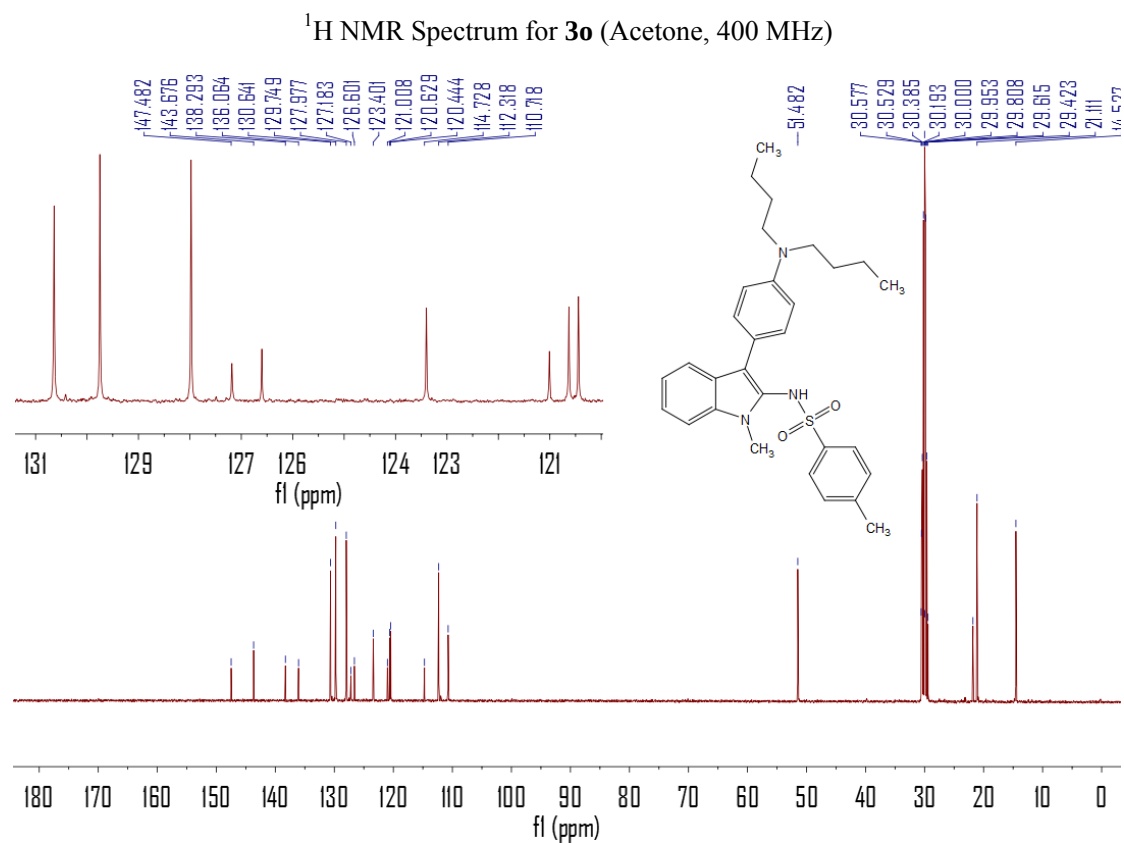
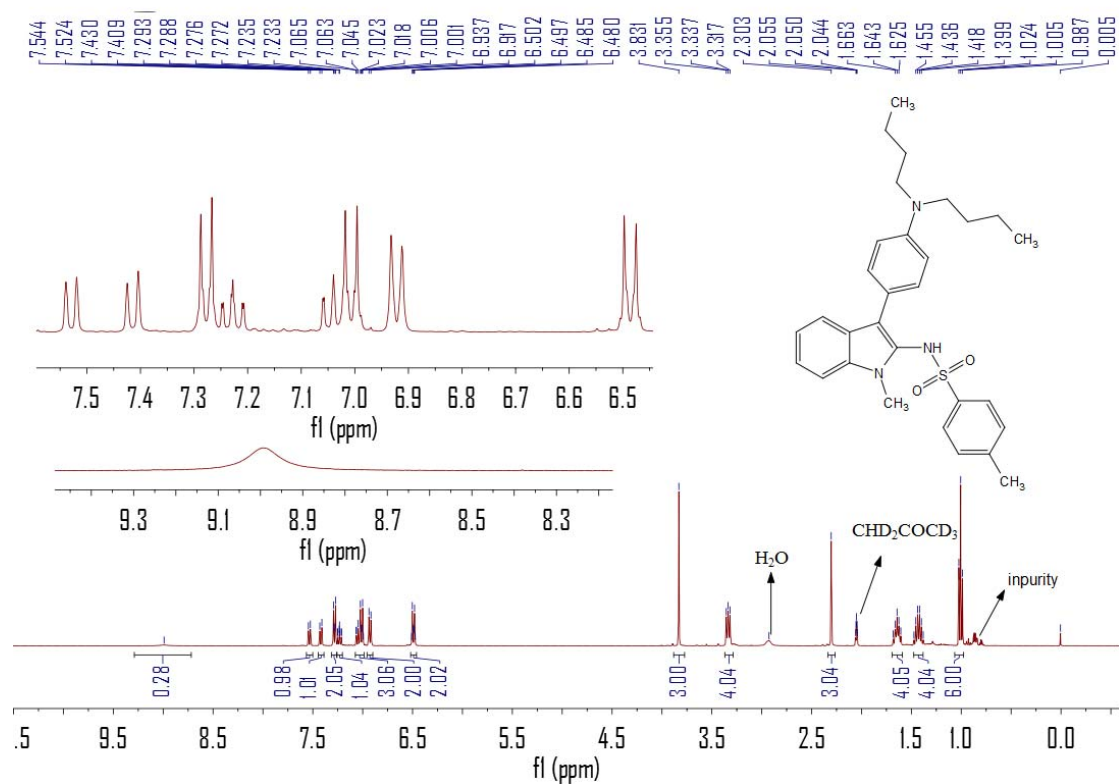
¹³C NMR Spectrum for **3j** (Acetone, 100 MHz)

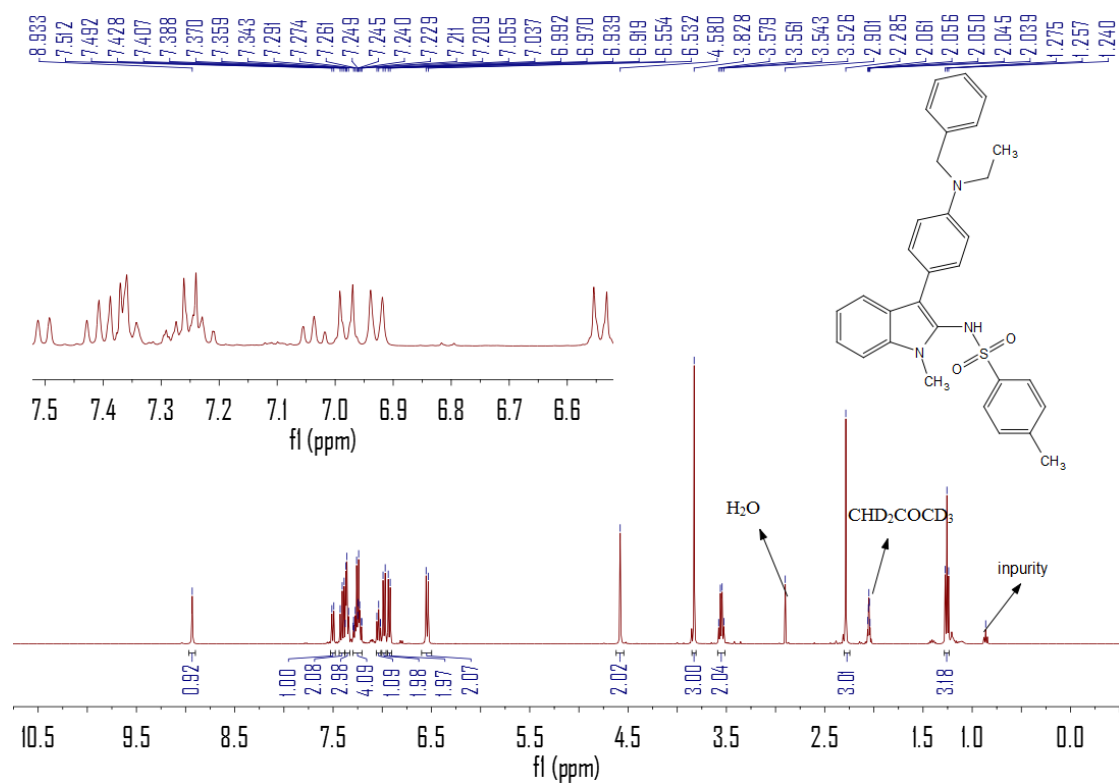




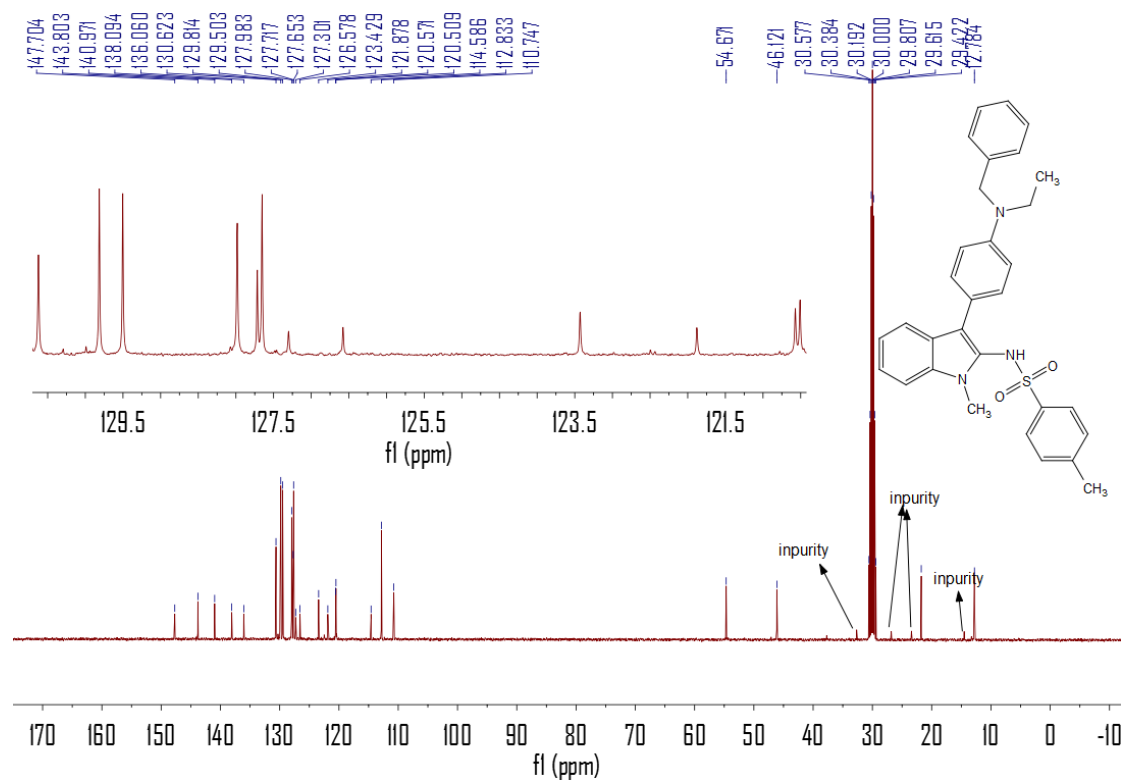




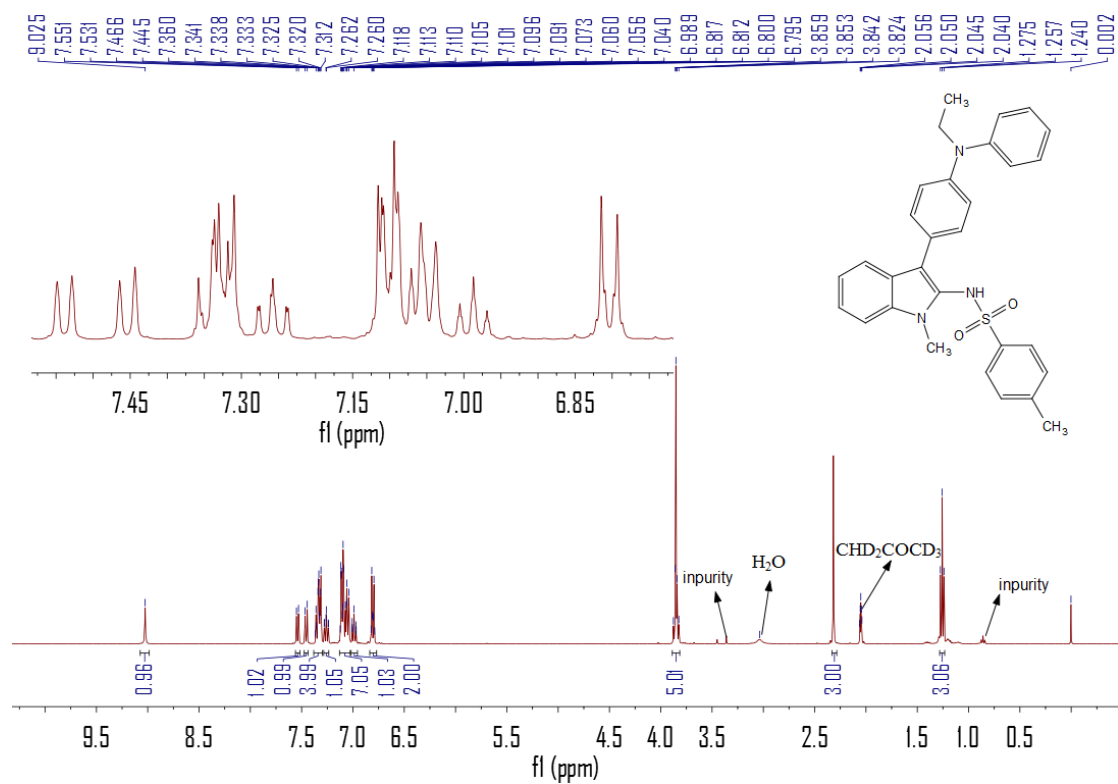




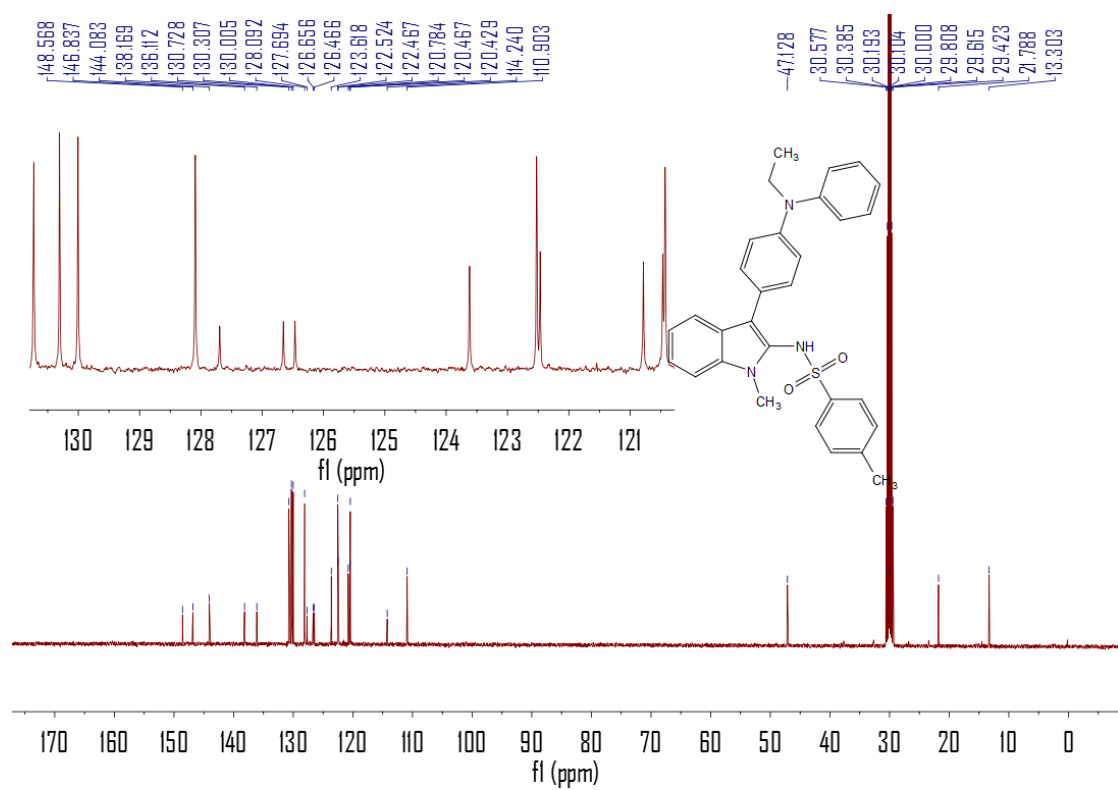
¹H NMR Spectrum for **3p** (Acetone, 400 MHz)



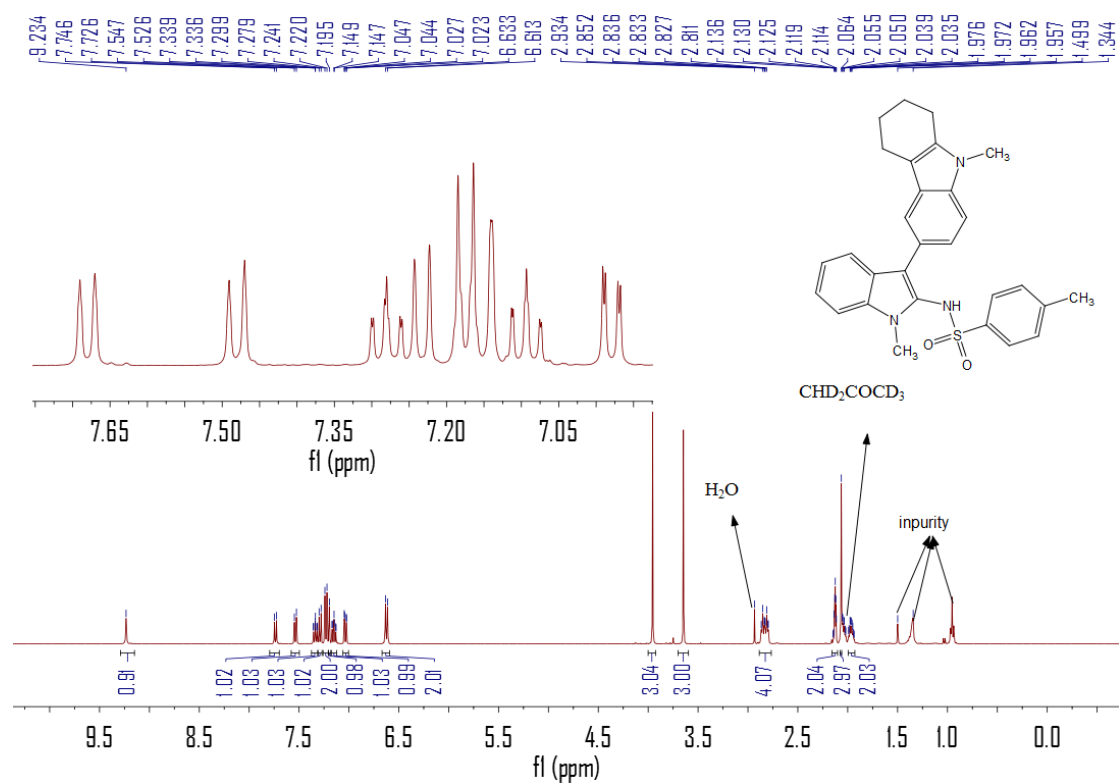
¹³C NMR Spectrum for **3p** (Acetone, 100 MHz)



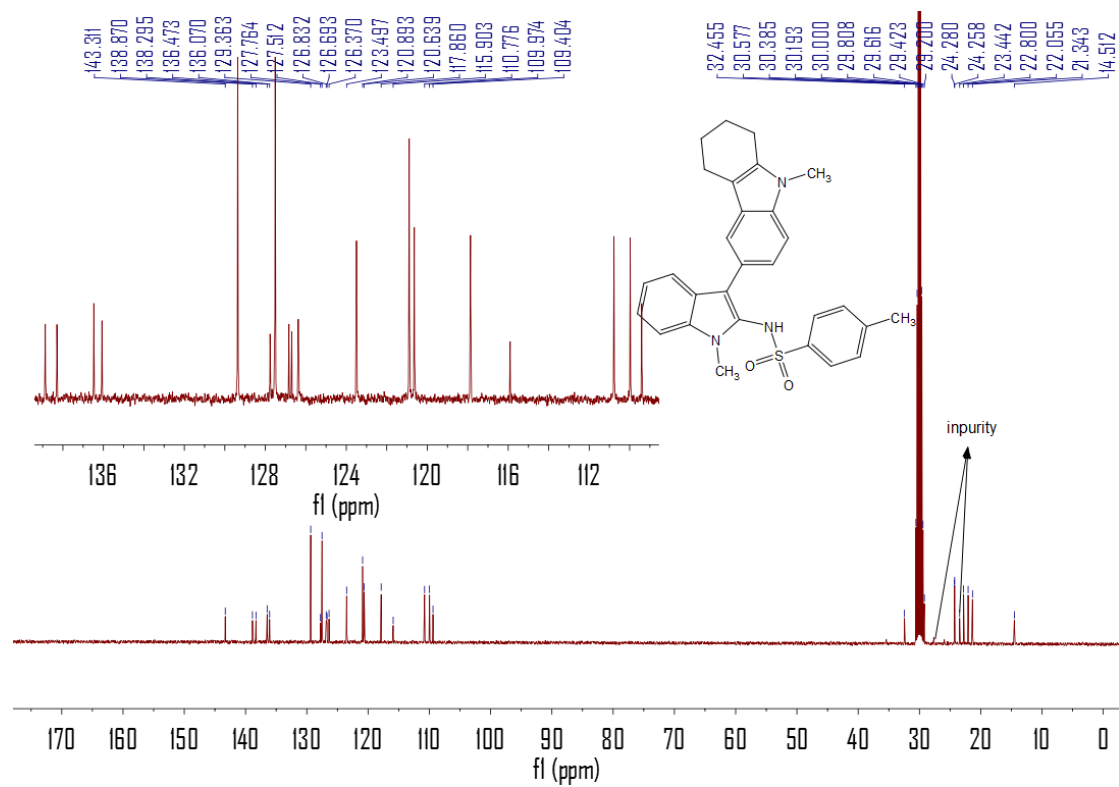
¹H NMR Spectrum for **3q** (Acetone, 400 MHz)



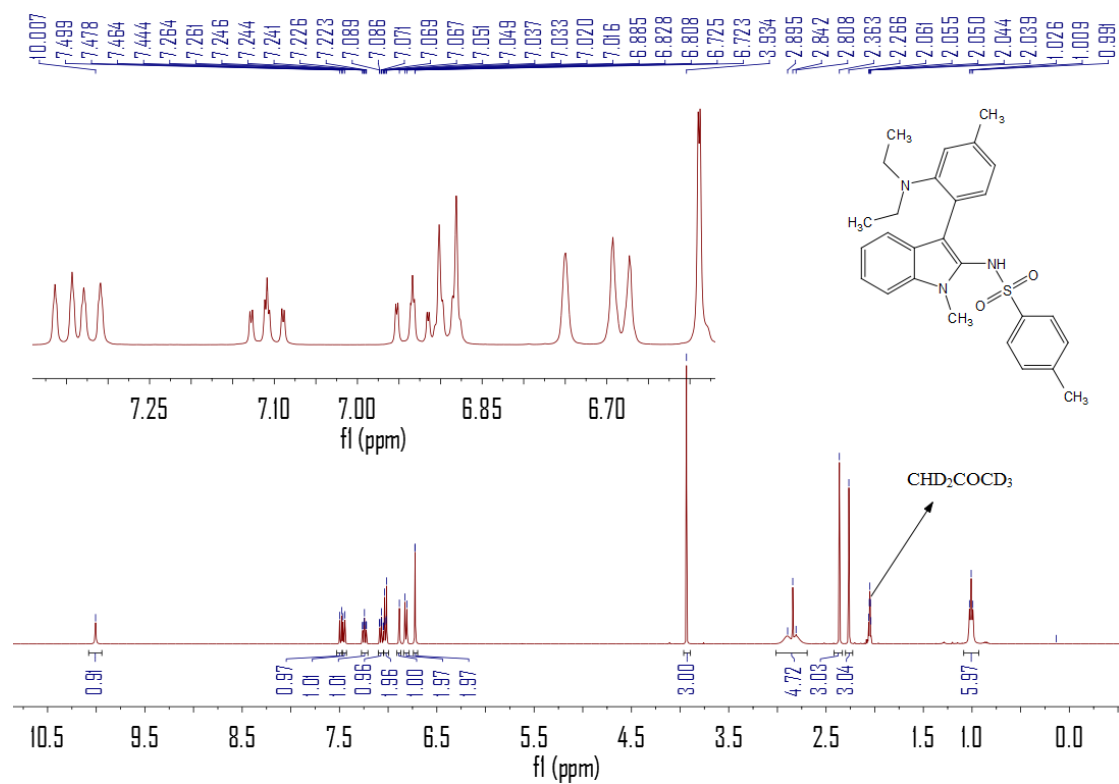
¹³C NMR Spectrum for **3q** (Acetone, 100 MHz)



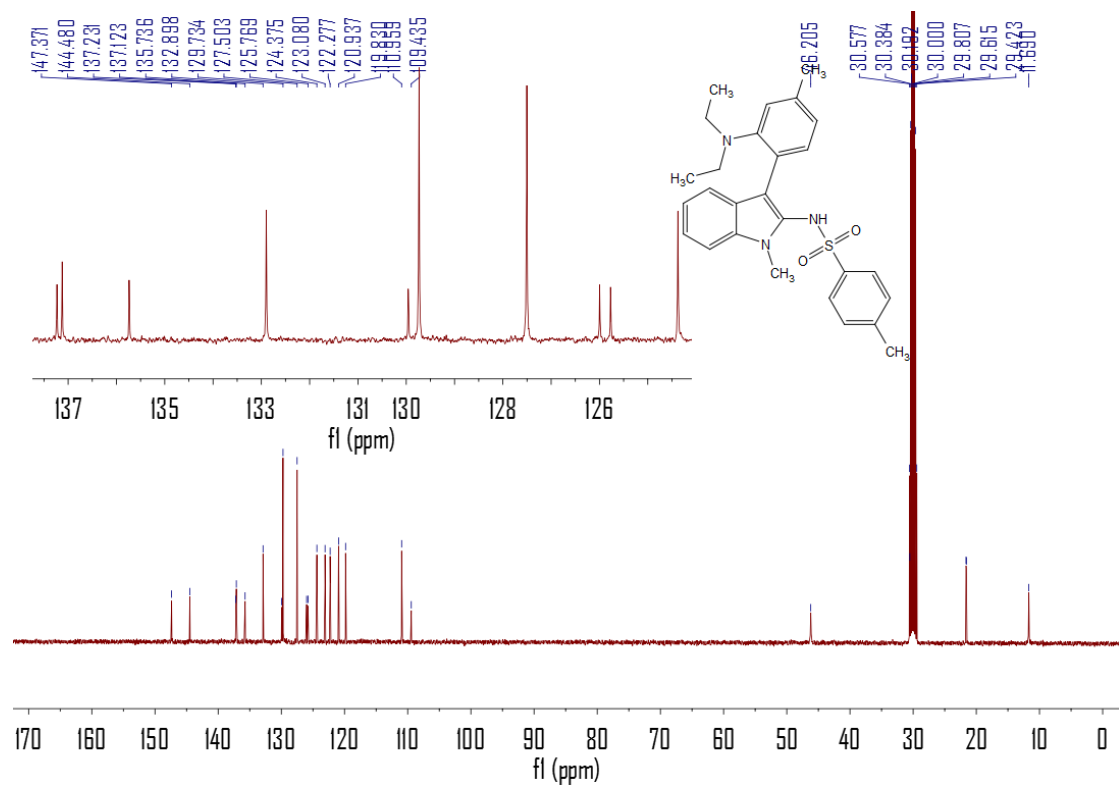
¹H NMR Spectrum for **3r** (Acetone, 400 MHz)



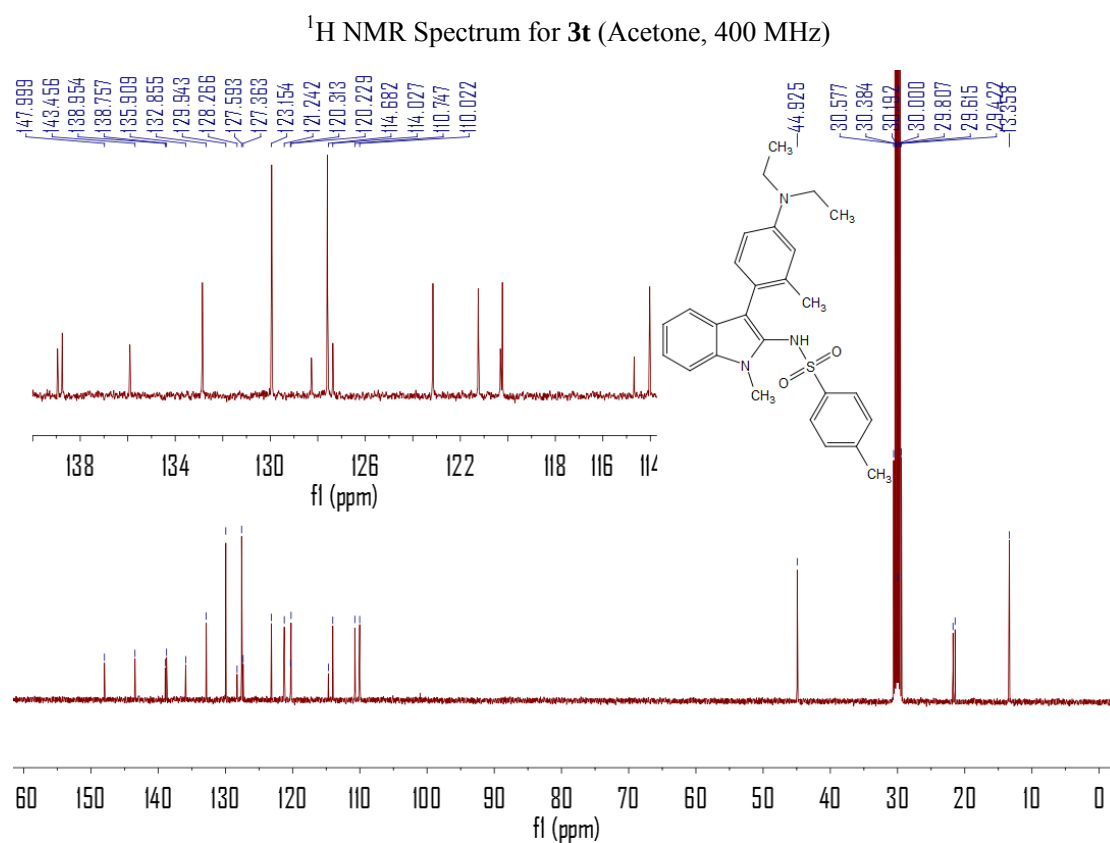
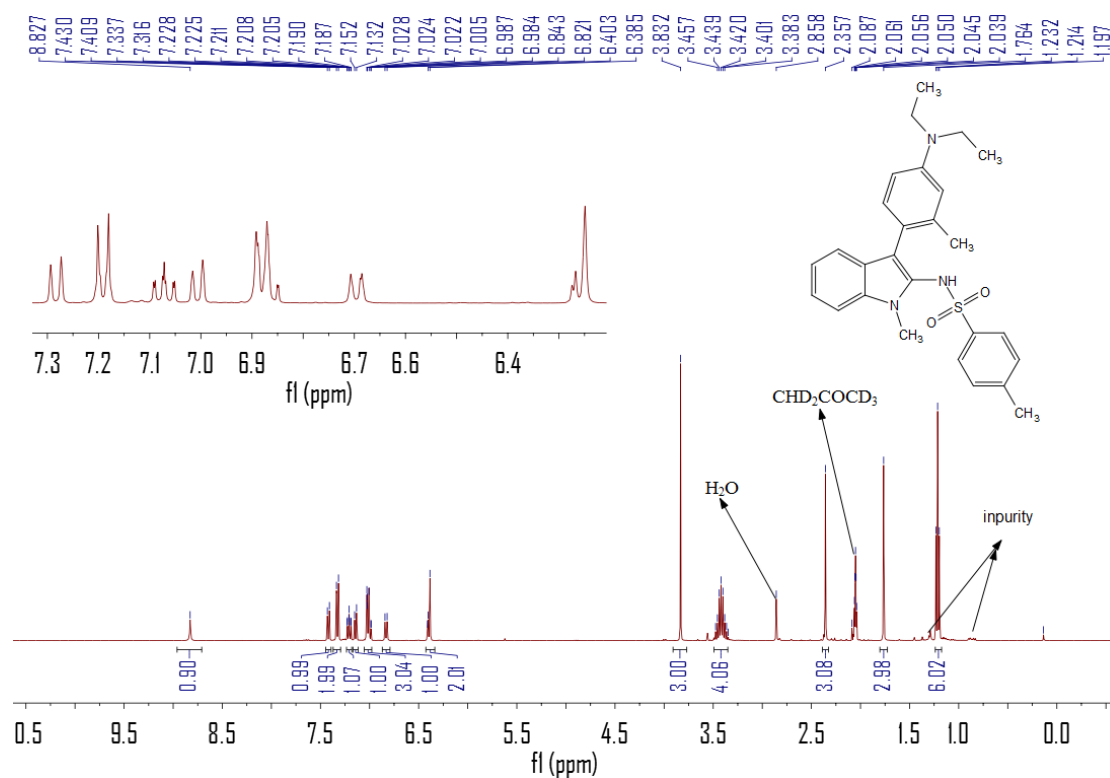
¹³C NMR Spectrum for **3r** (Acetone, 100 MHz)

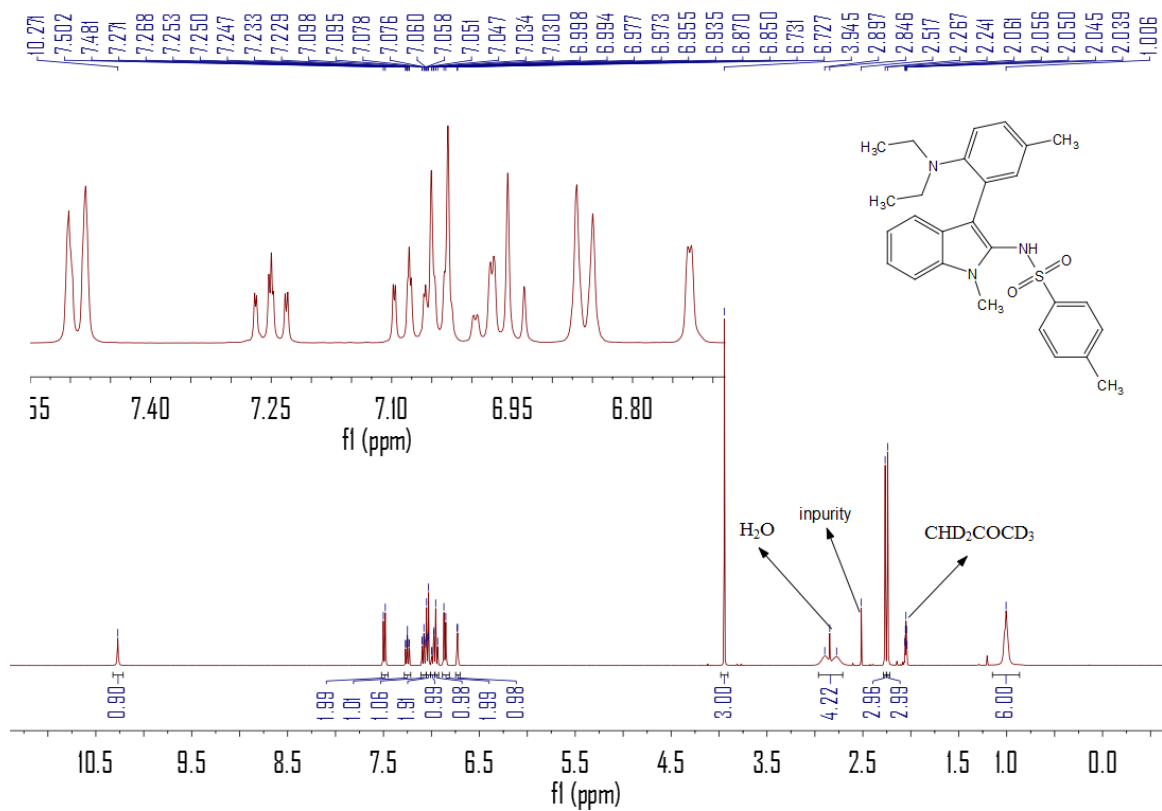


¹H NMR Spectrum for **3s** (Acetone, 400 MHz)

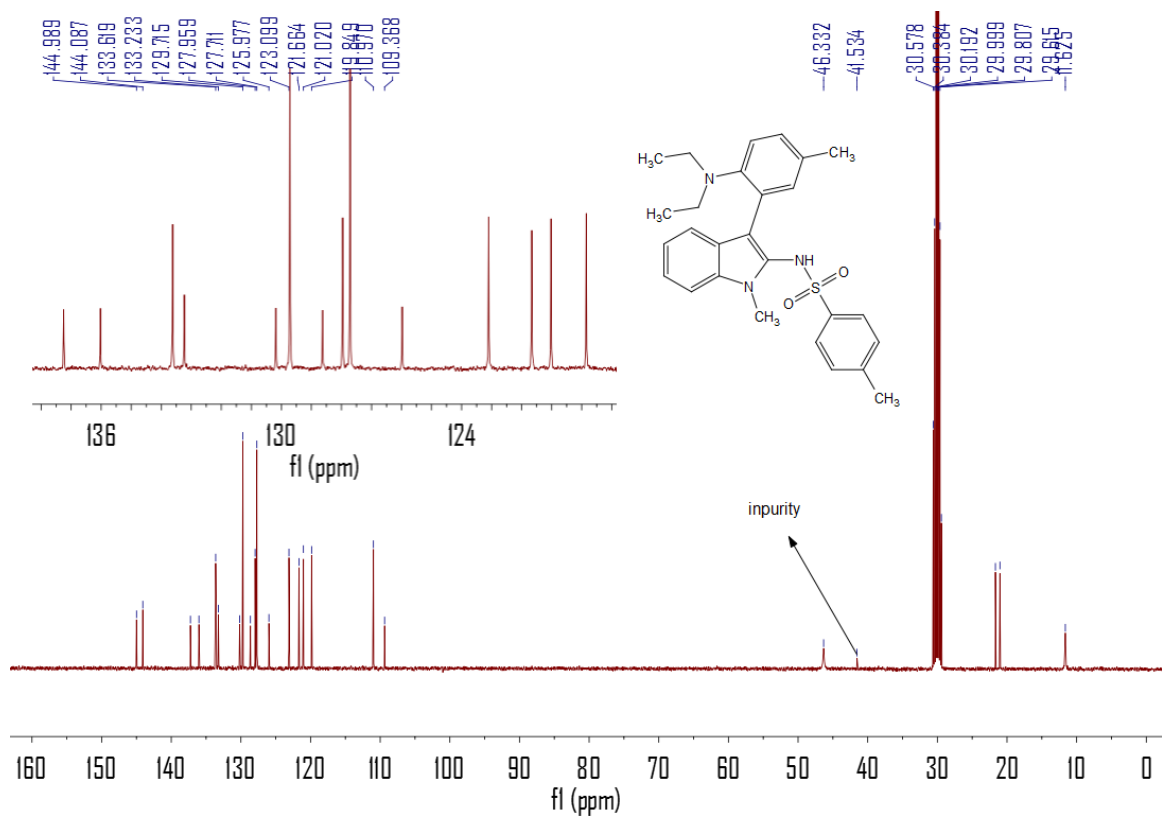


¹³C NMR Spectrum for **3s** (Acetone, 100 MHz)

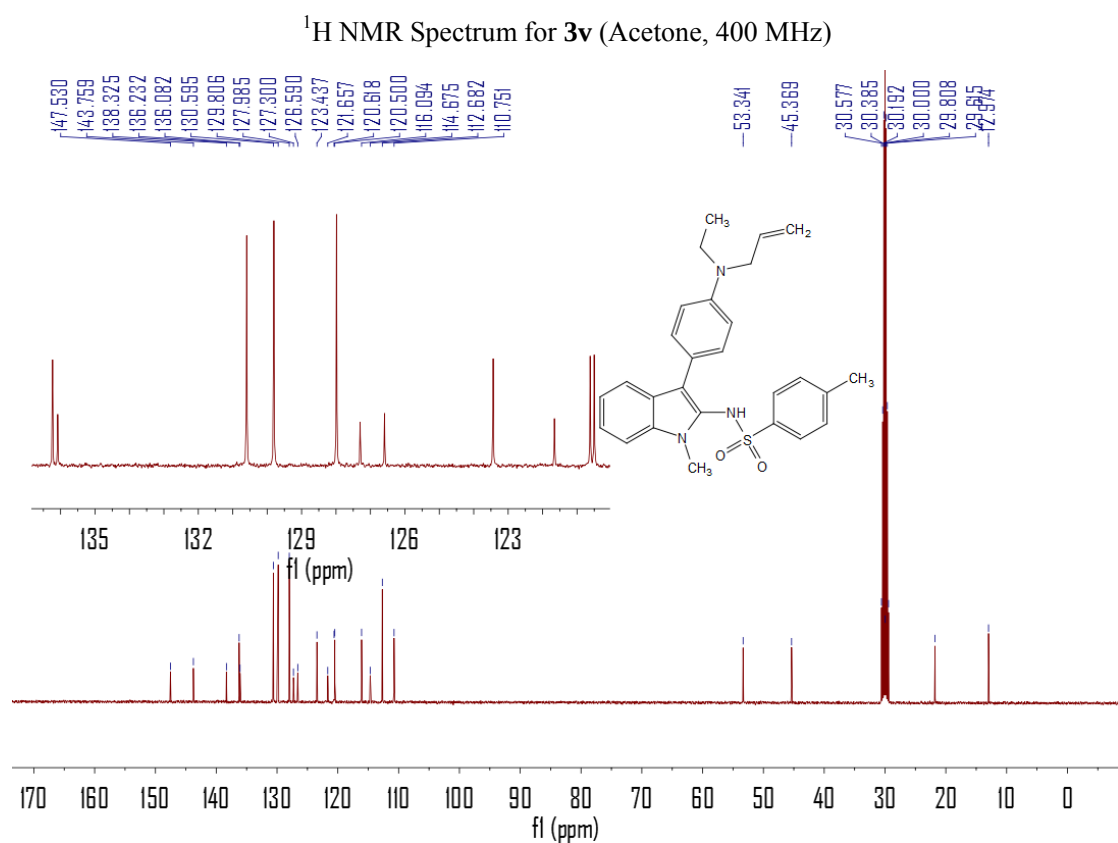
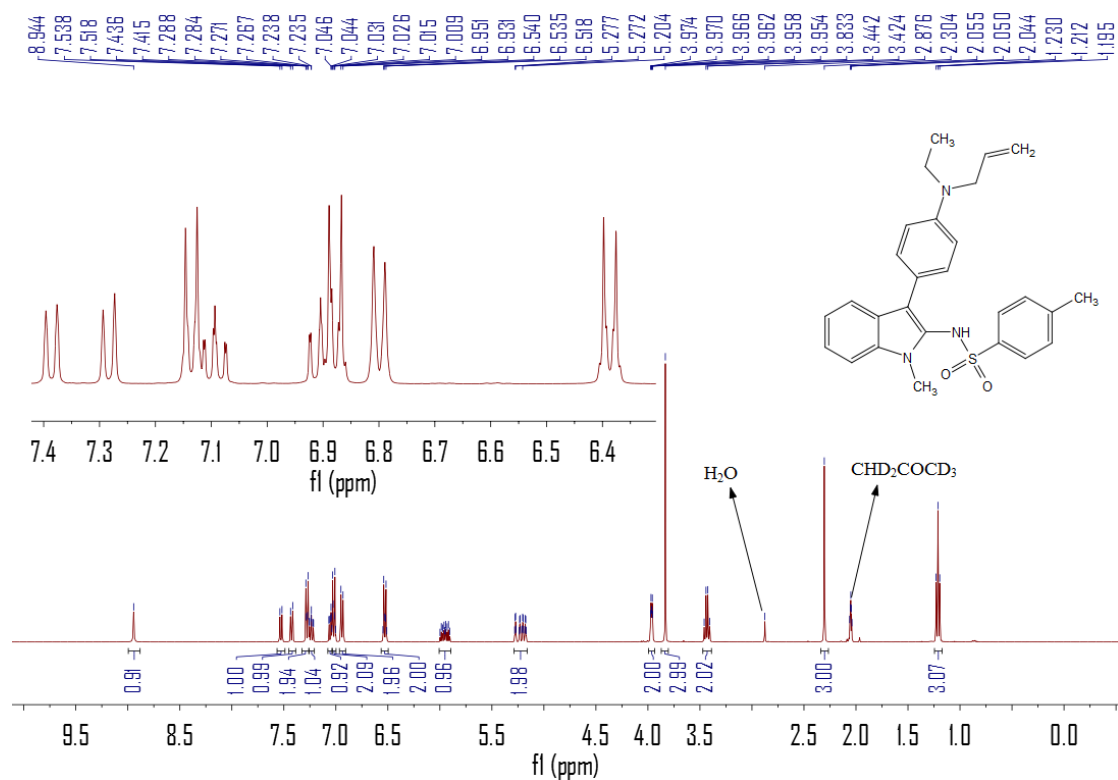


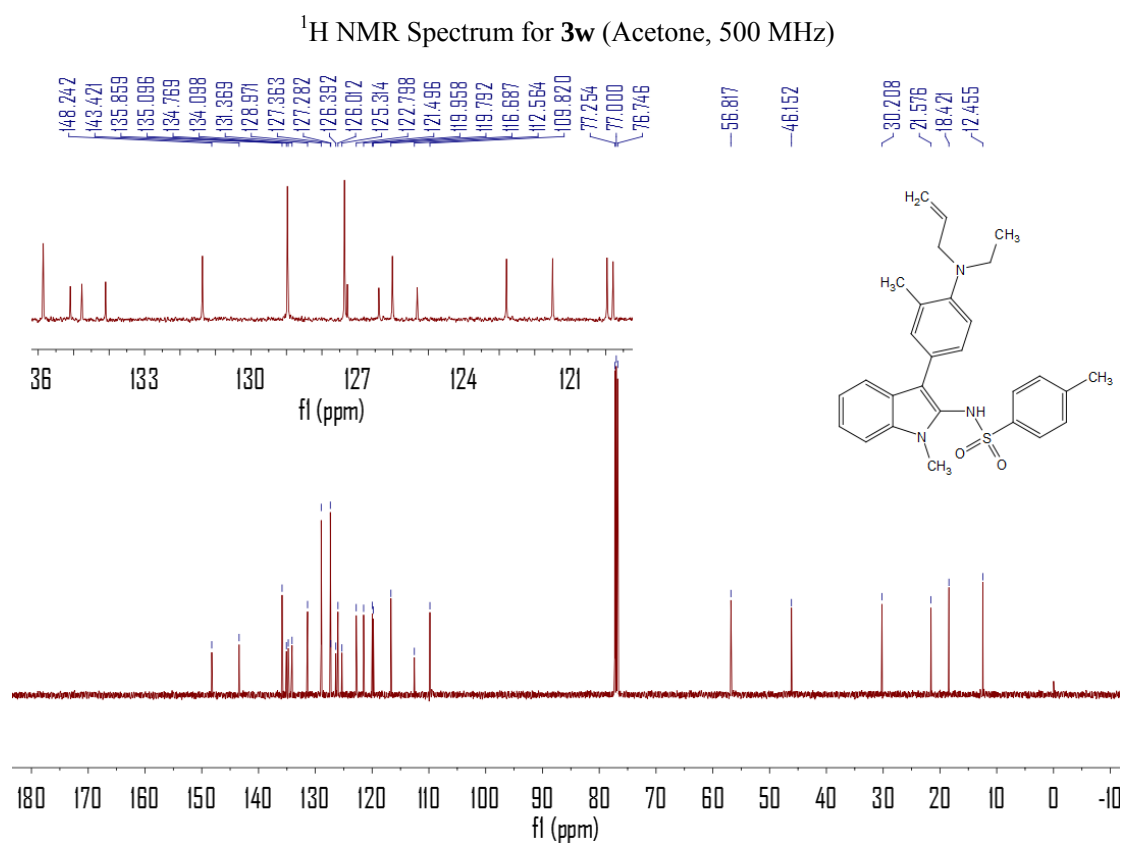
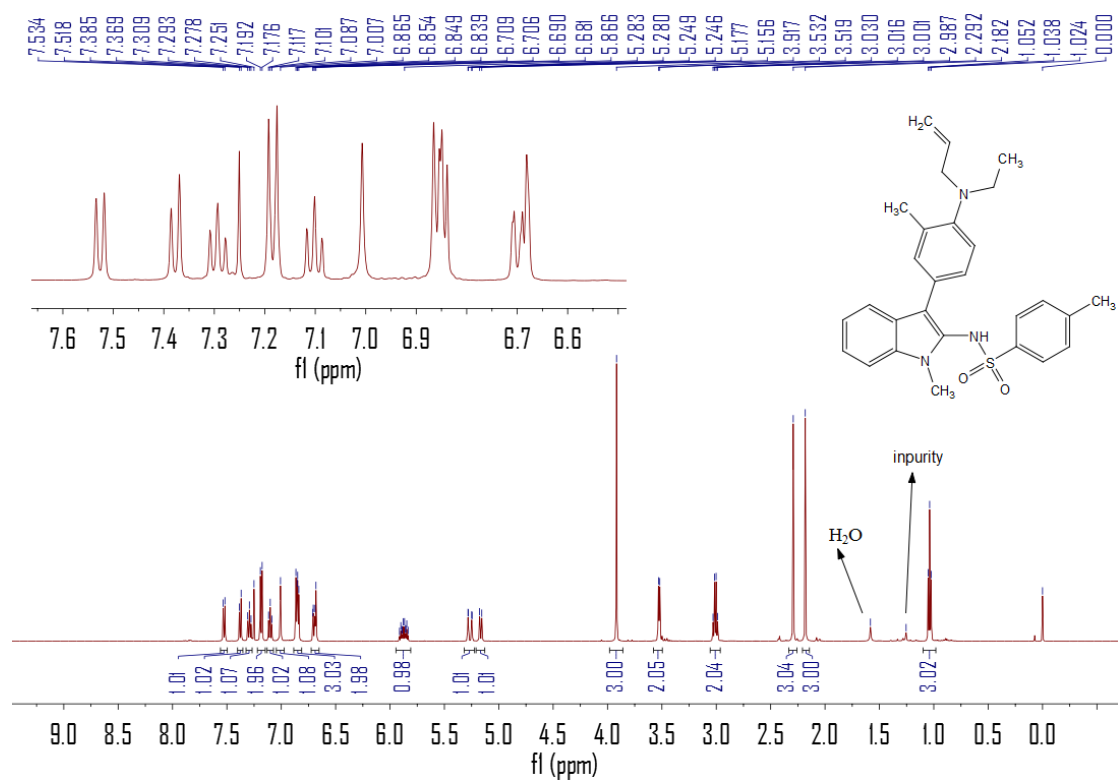


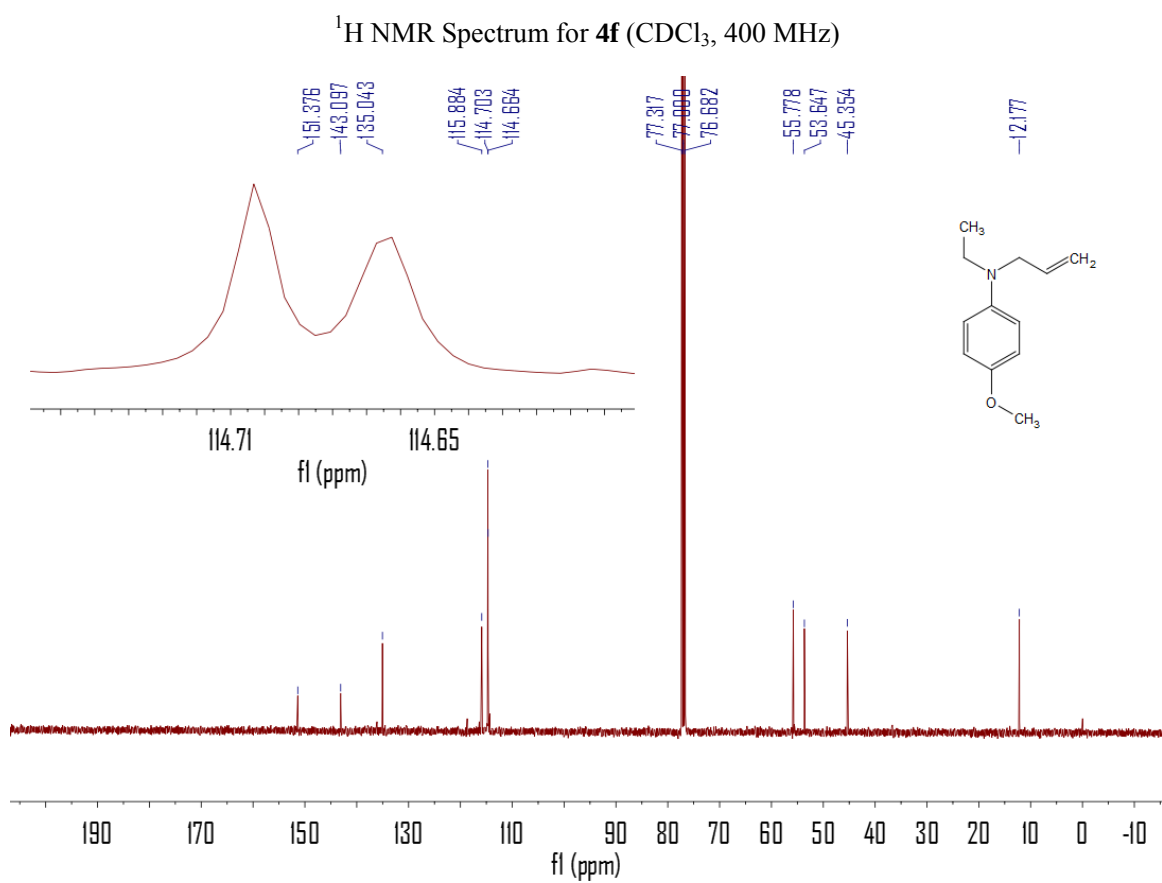
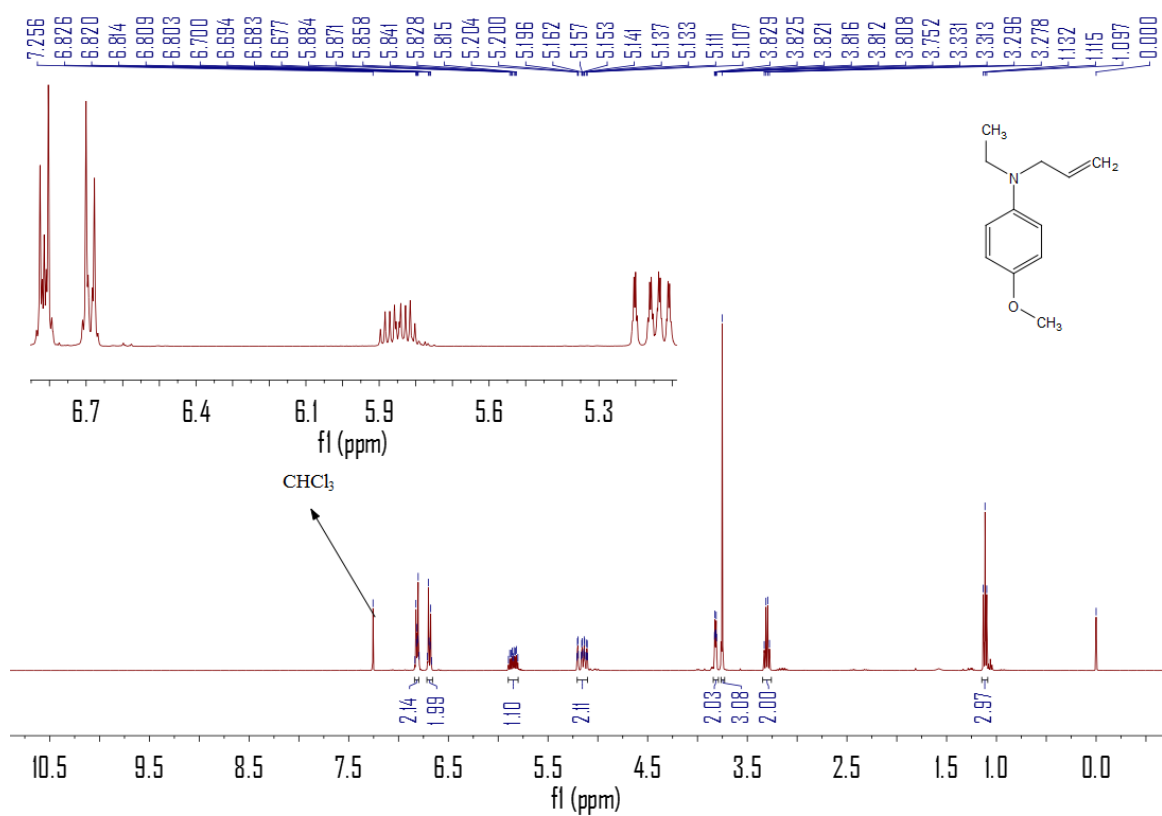
¹H NMR Spectrum for **3u** (Acetone, 400 MHz)

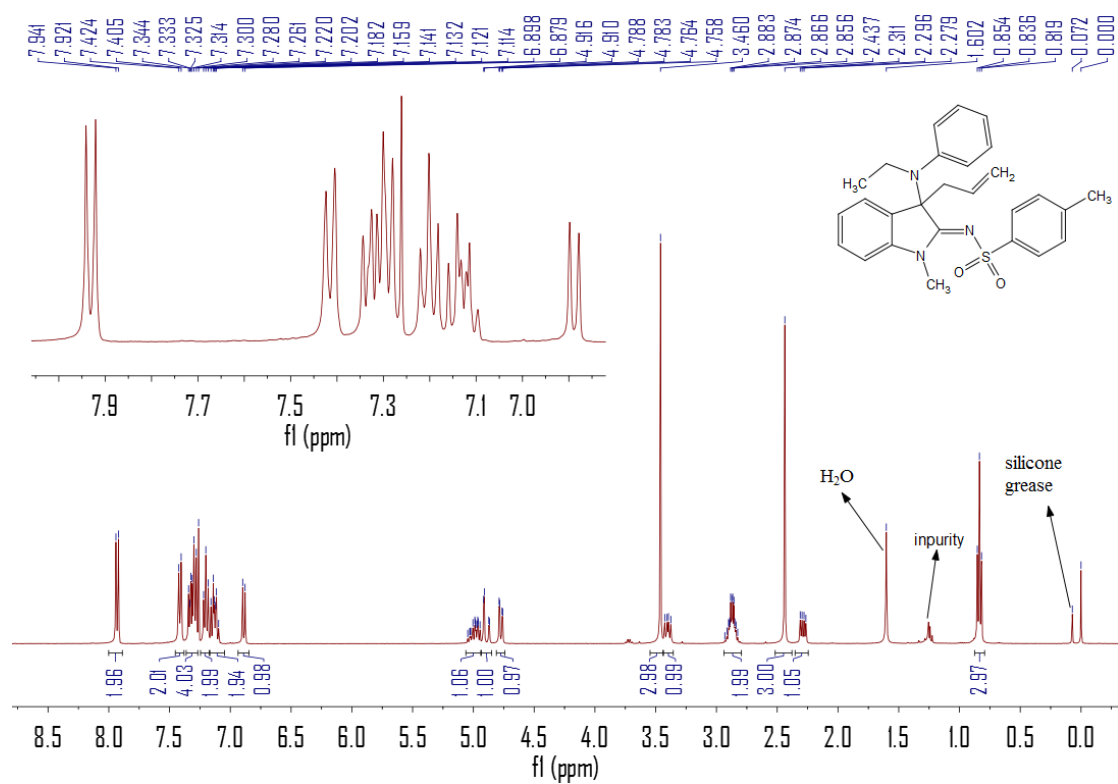


¹³C NMR Spectrum for **3u** (Acetone, 100 MHz)

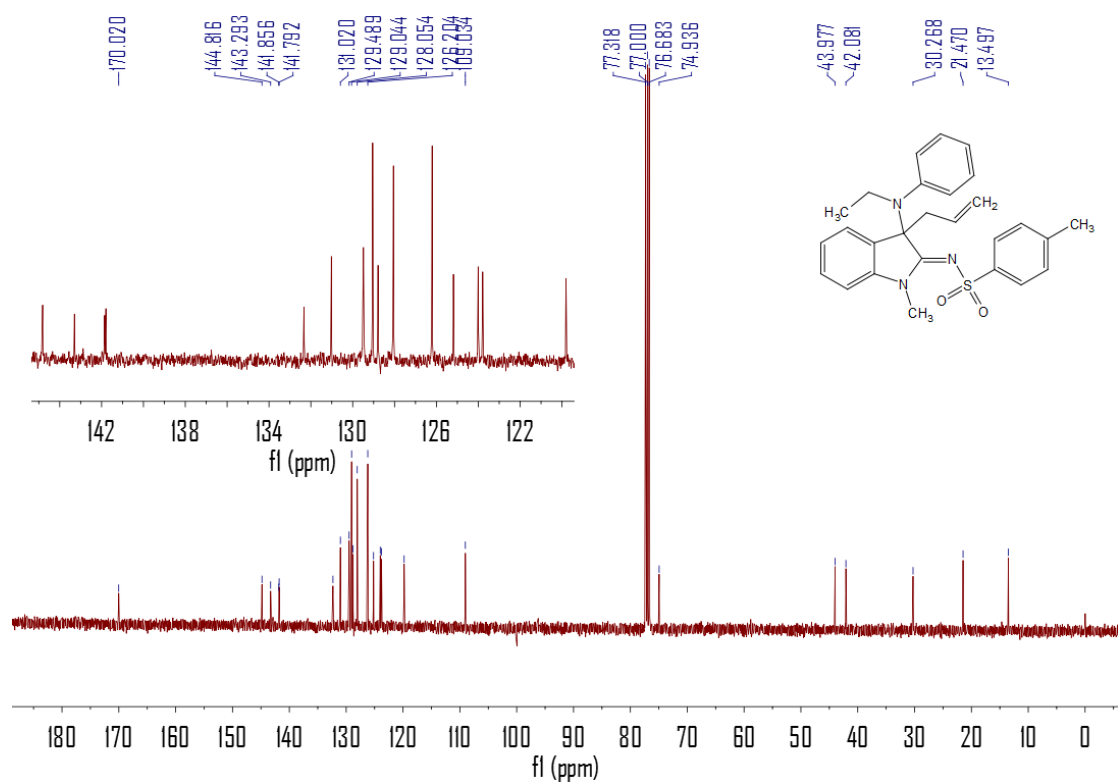




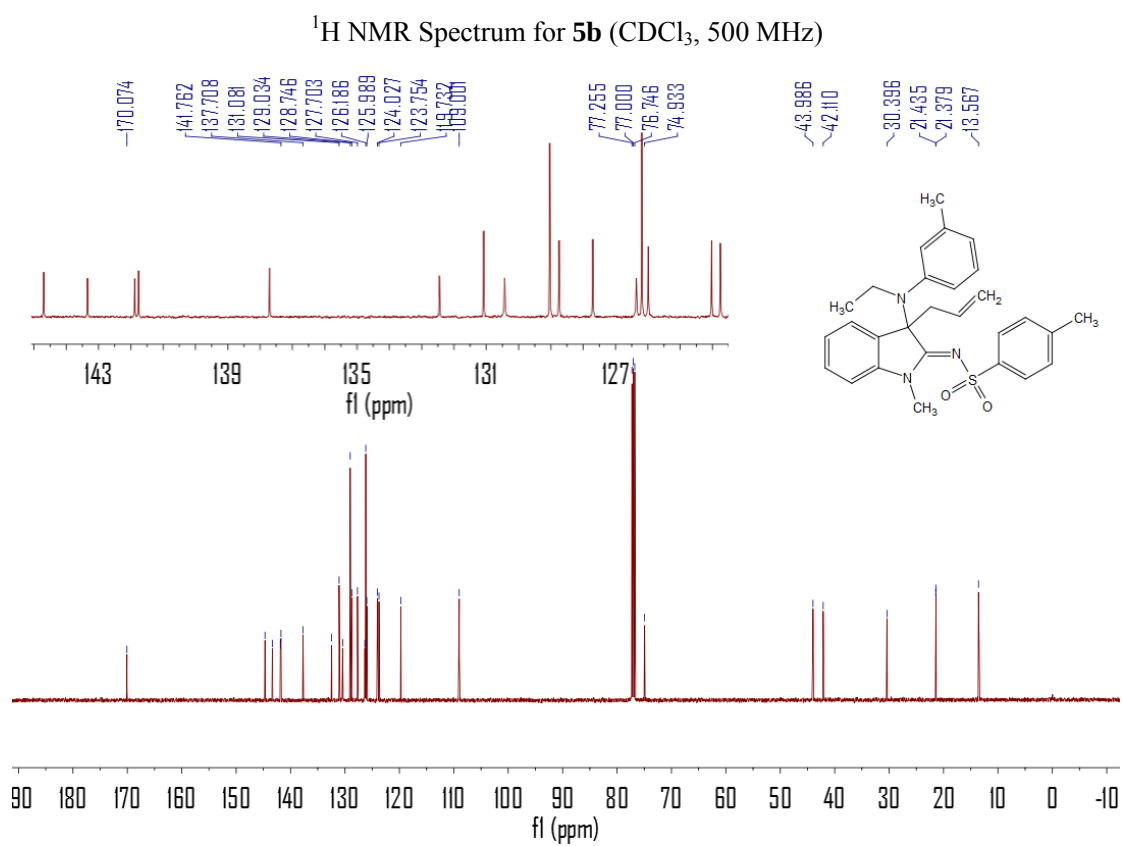
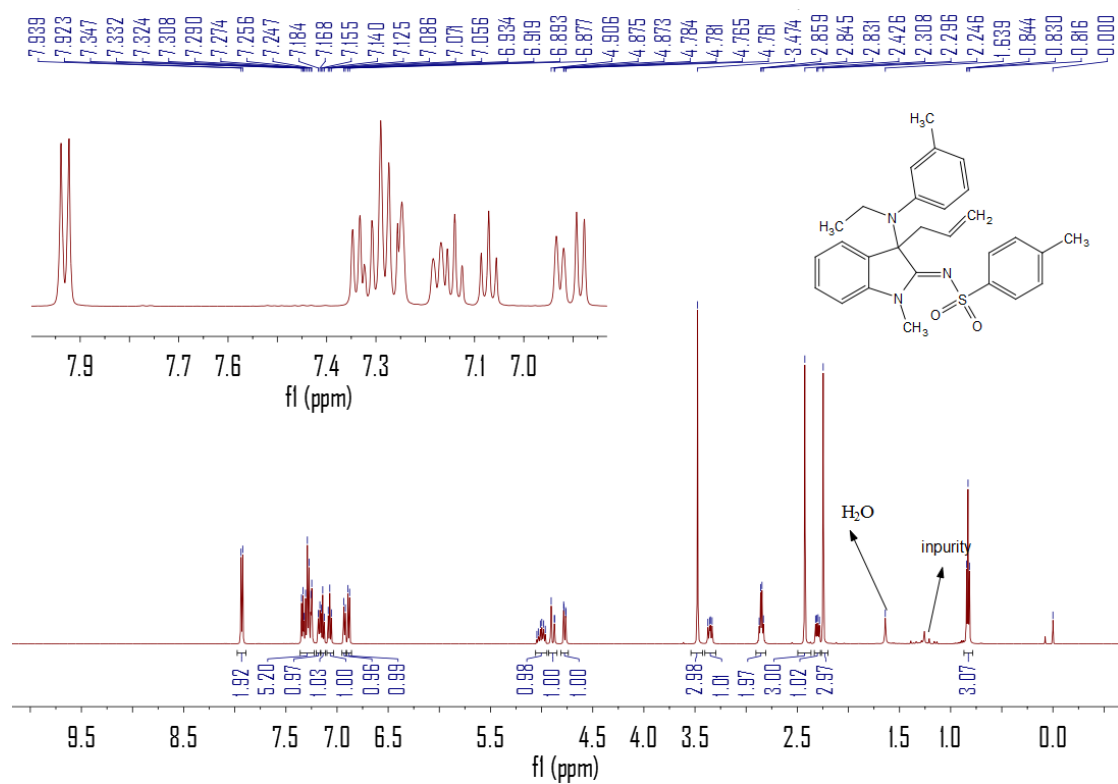


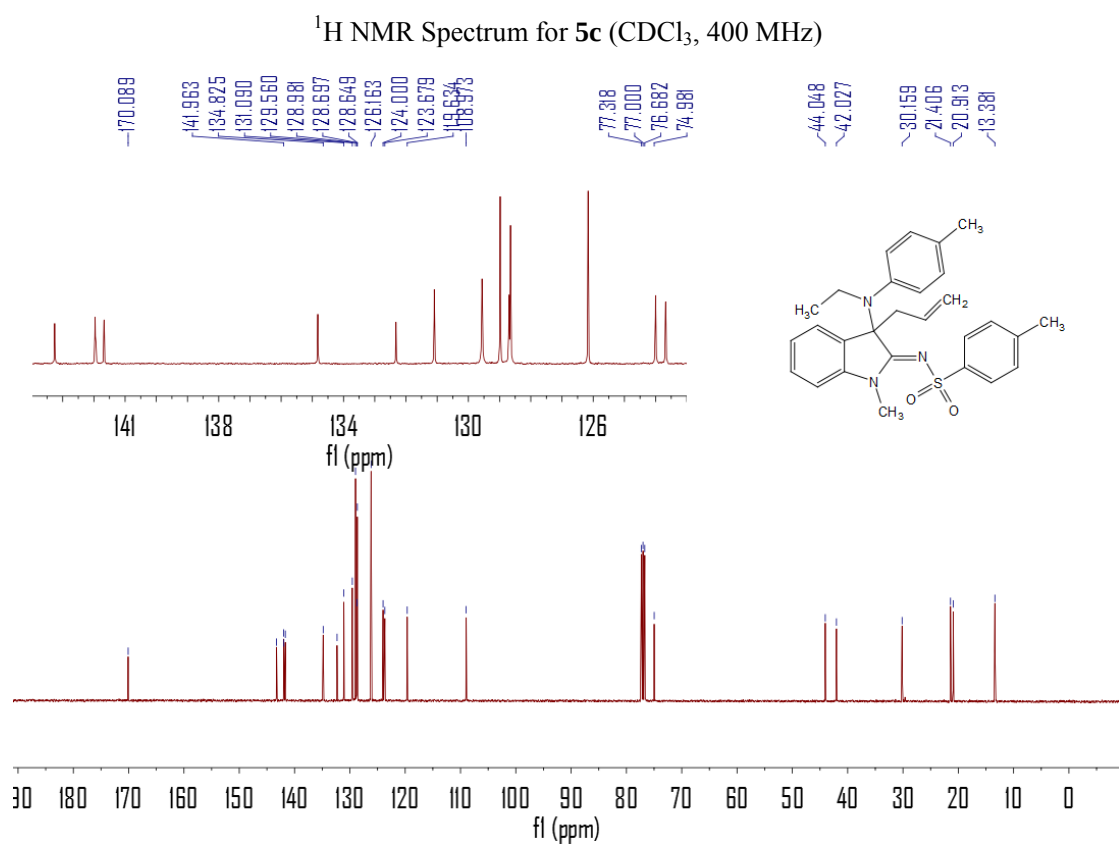
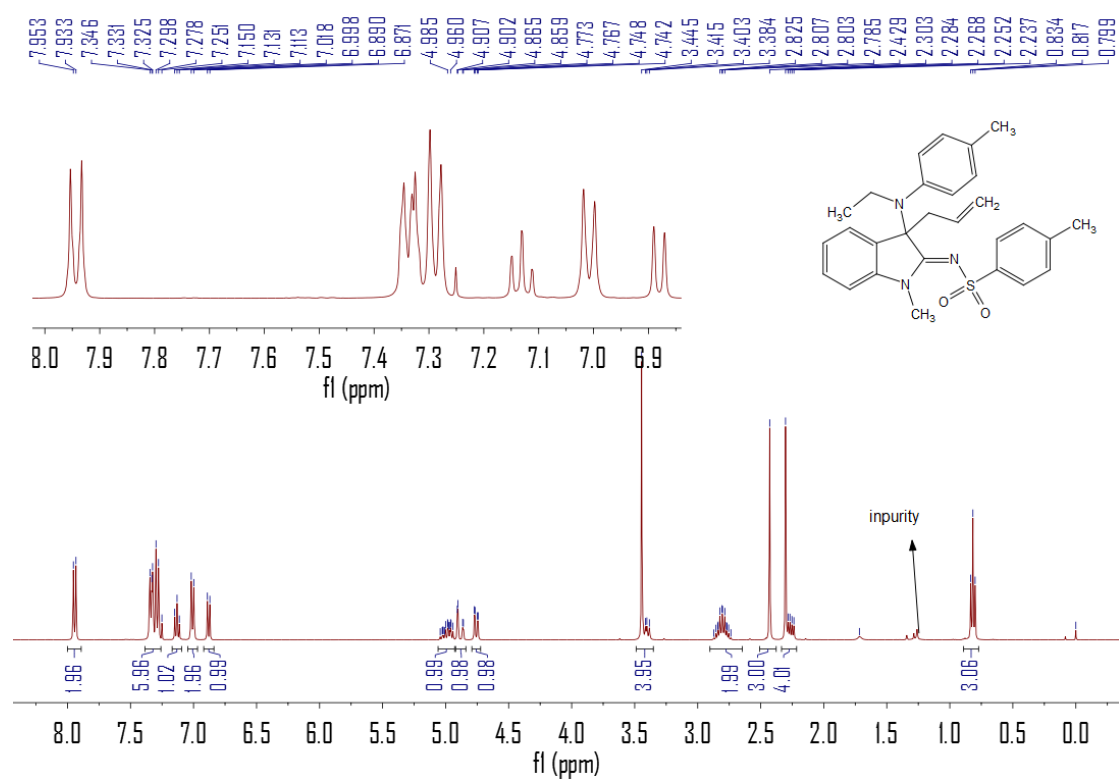


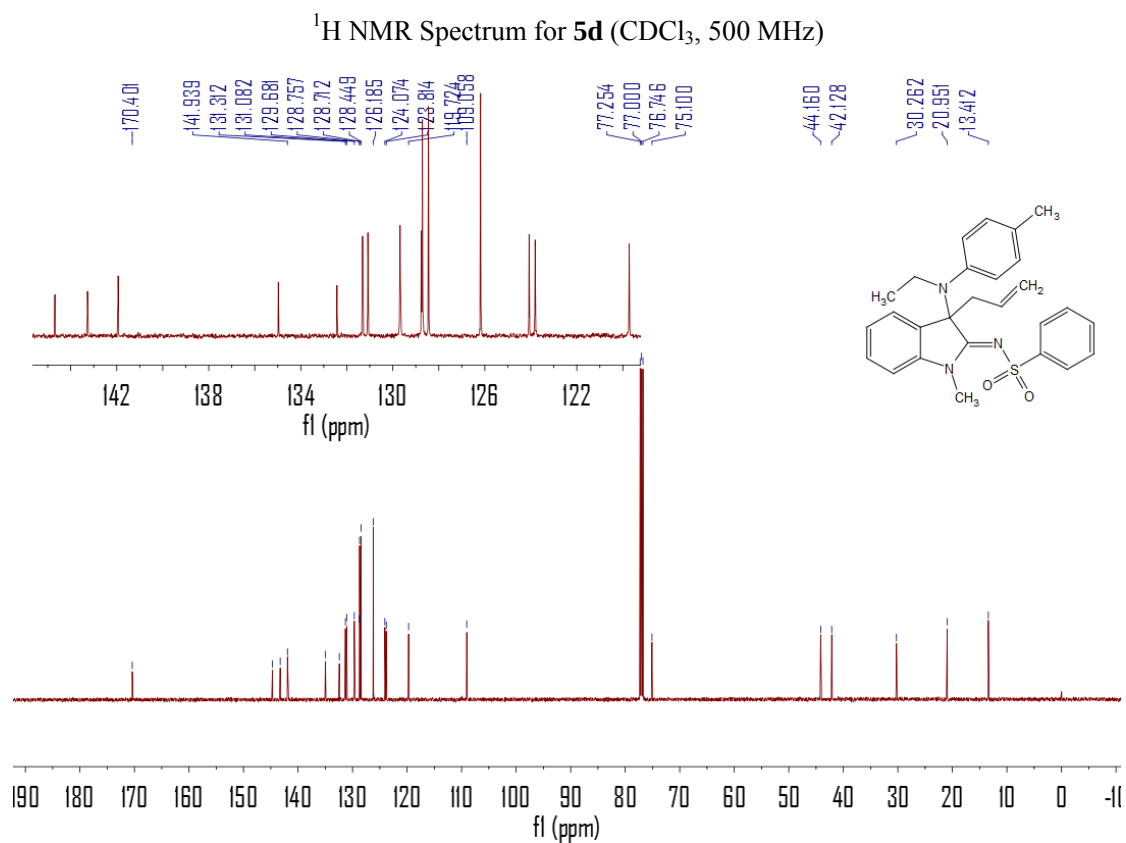
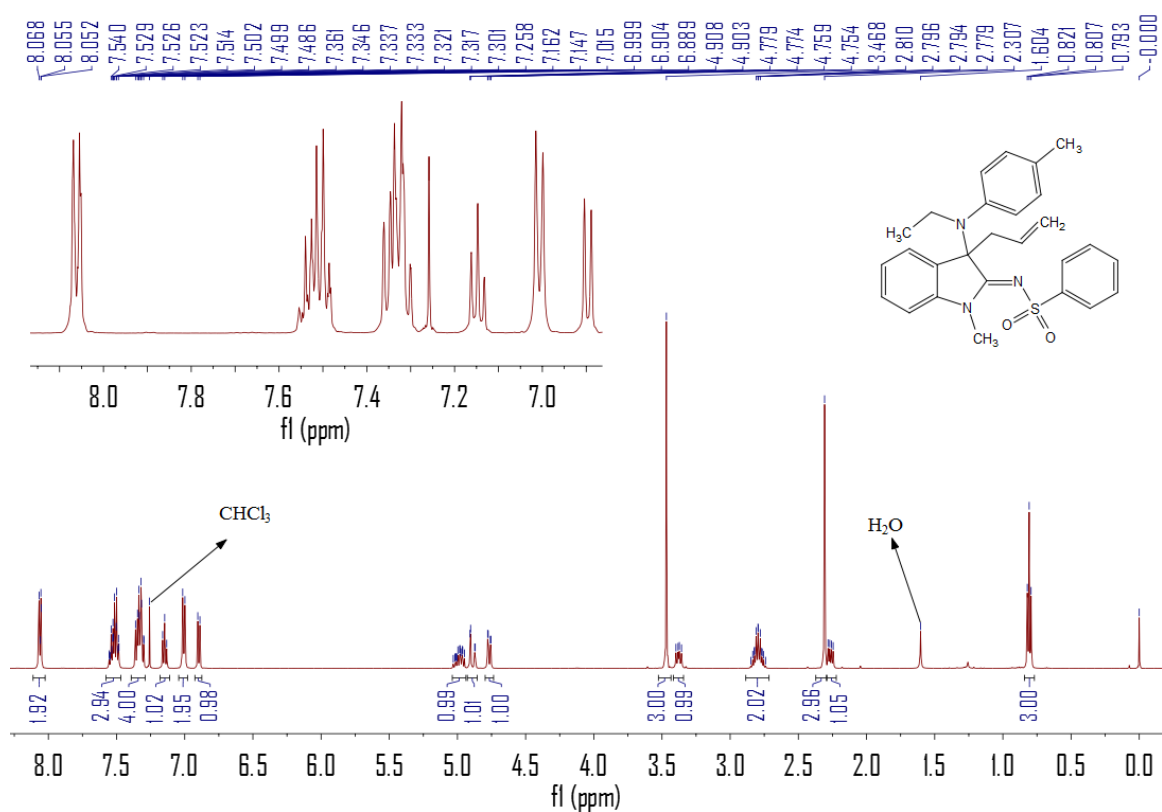
¹H NMR Spectrum for **5a** (CDCl₃, 400 MHz)

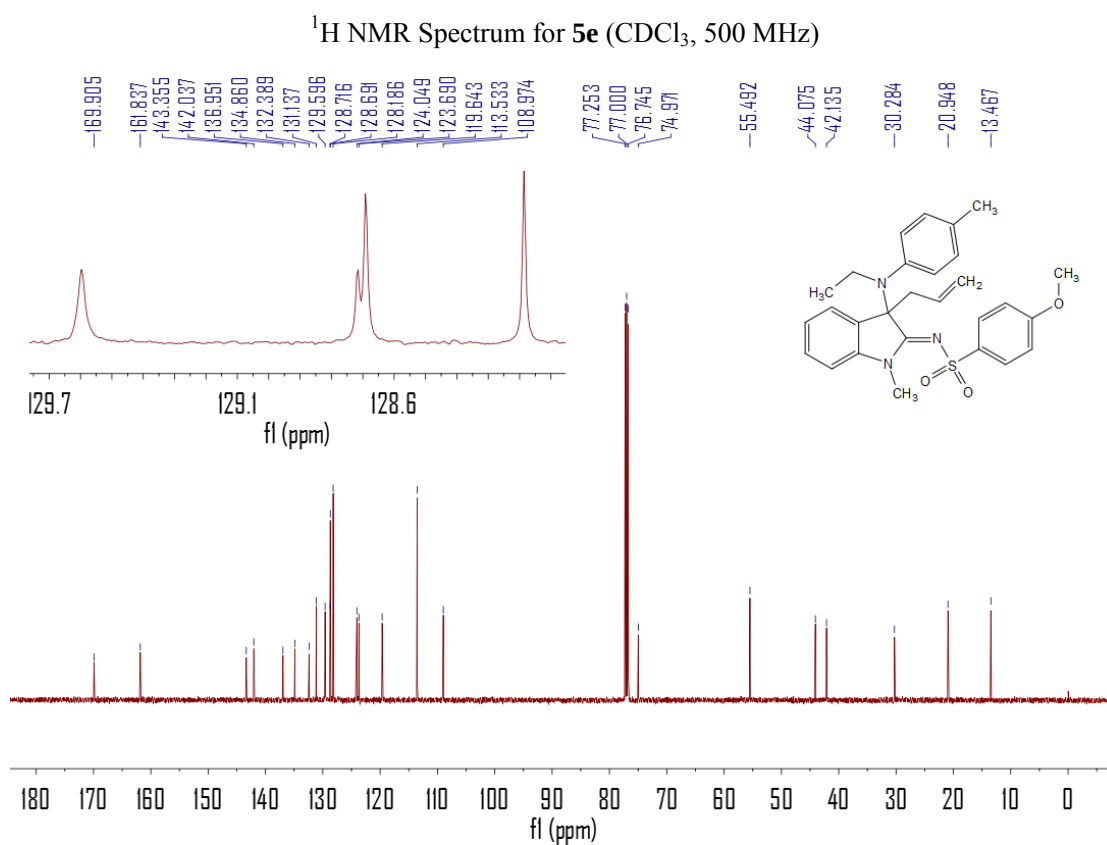
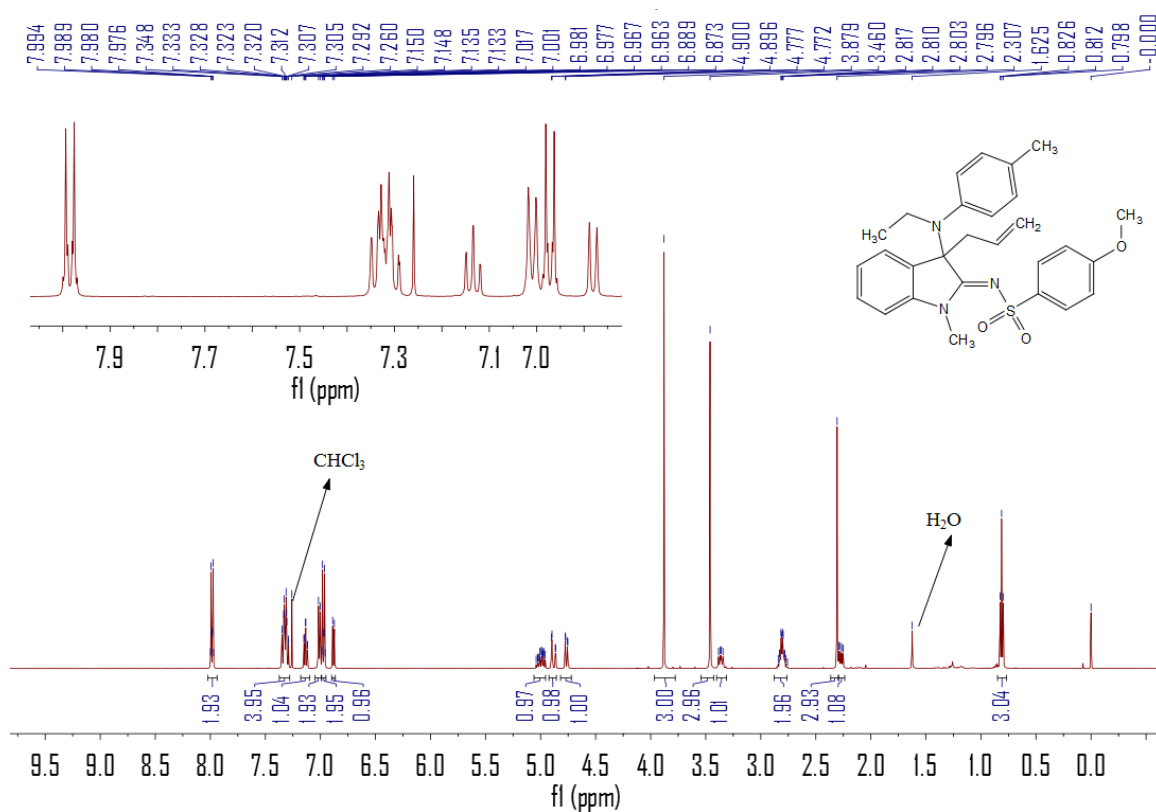


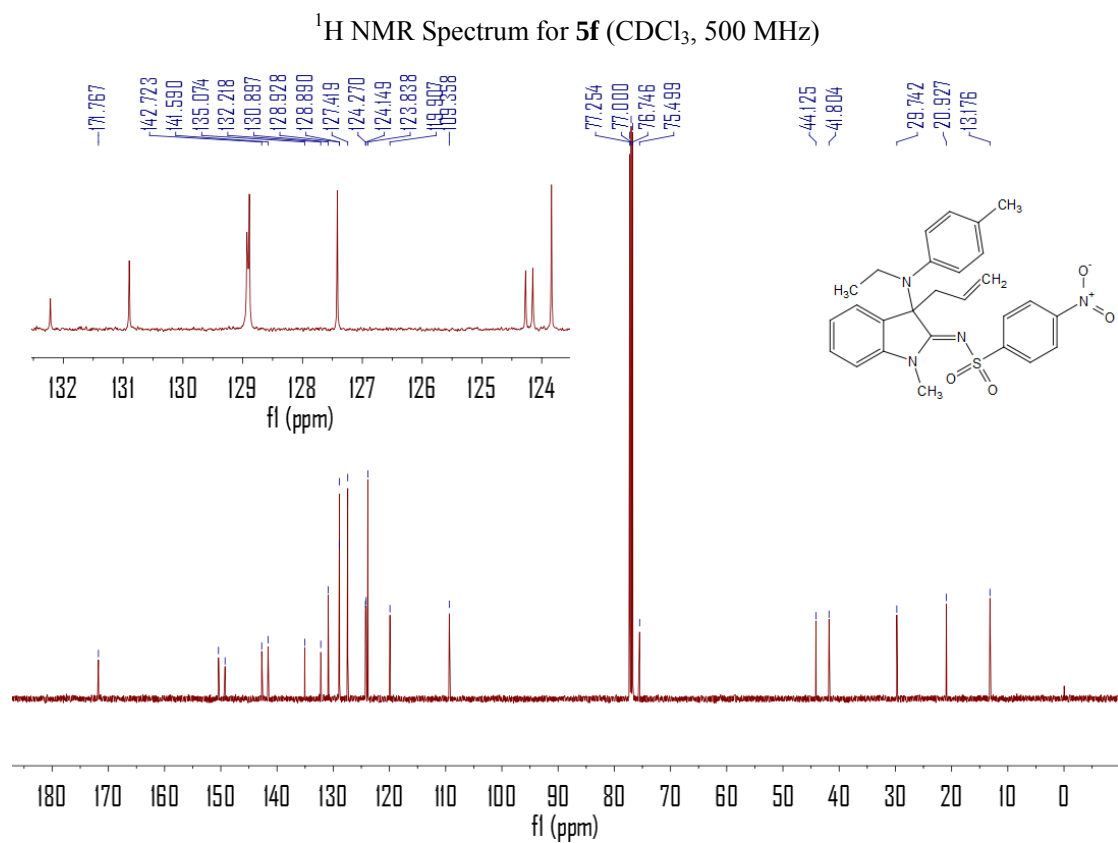
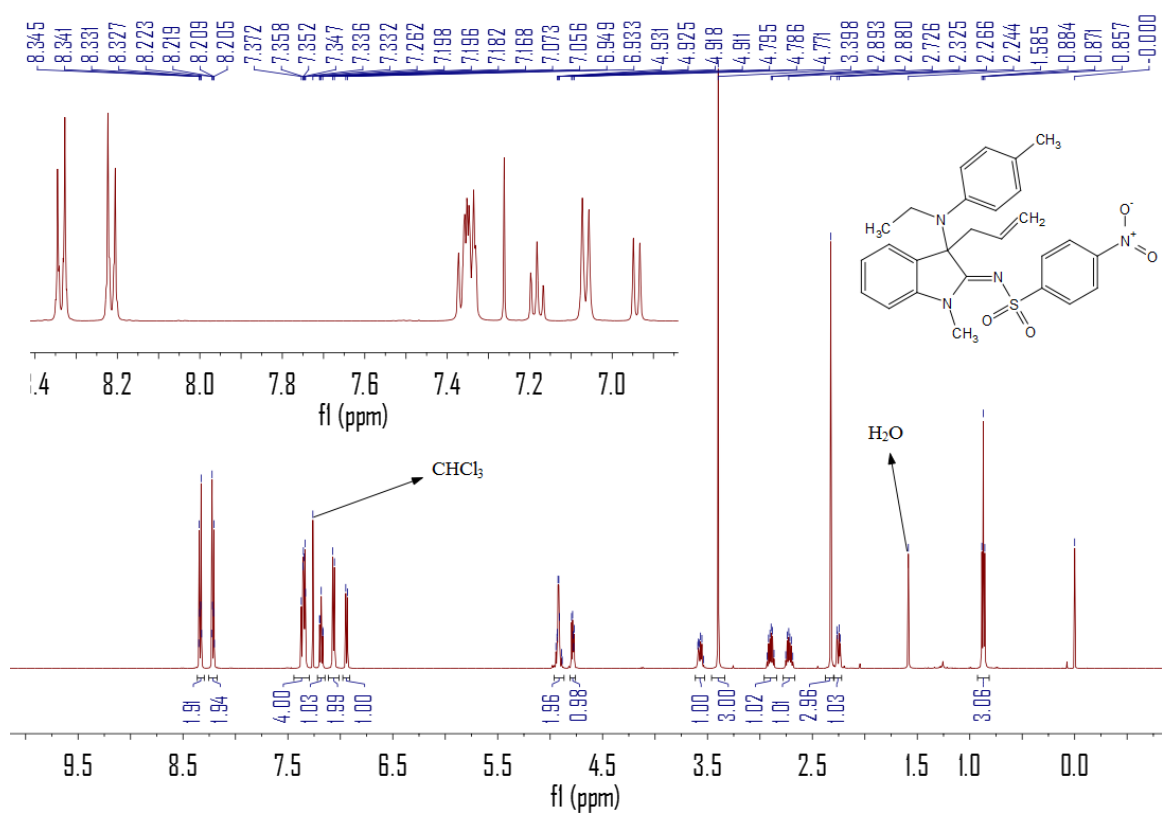
¹³C NMR Spectrum for **5a** (CDCl₃, 100 MHz)

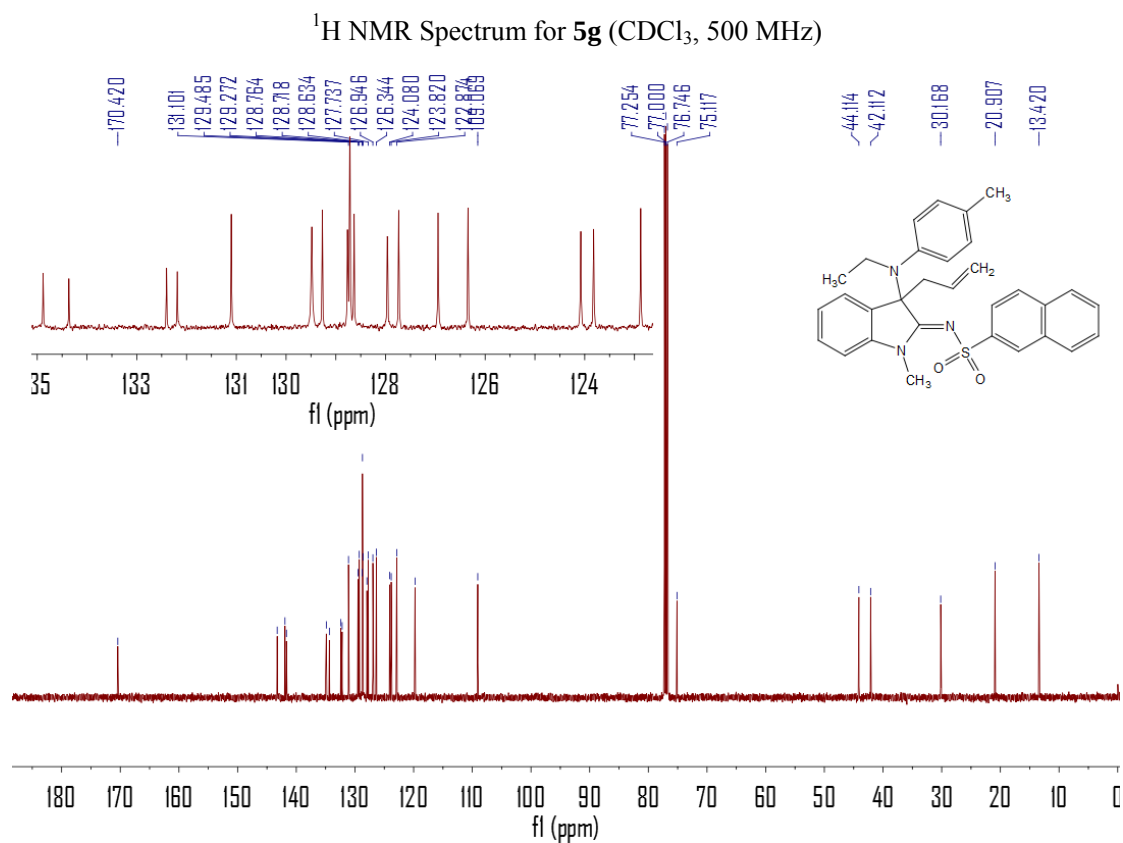
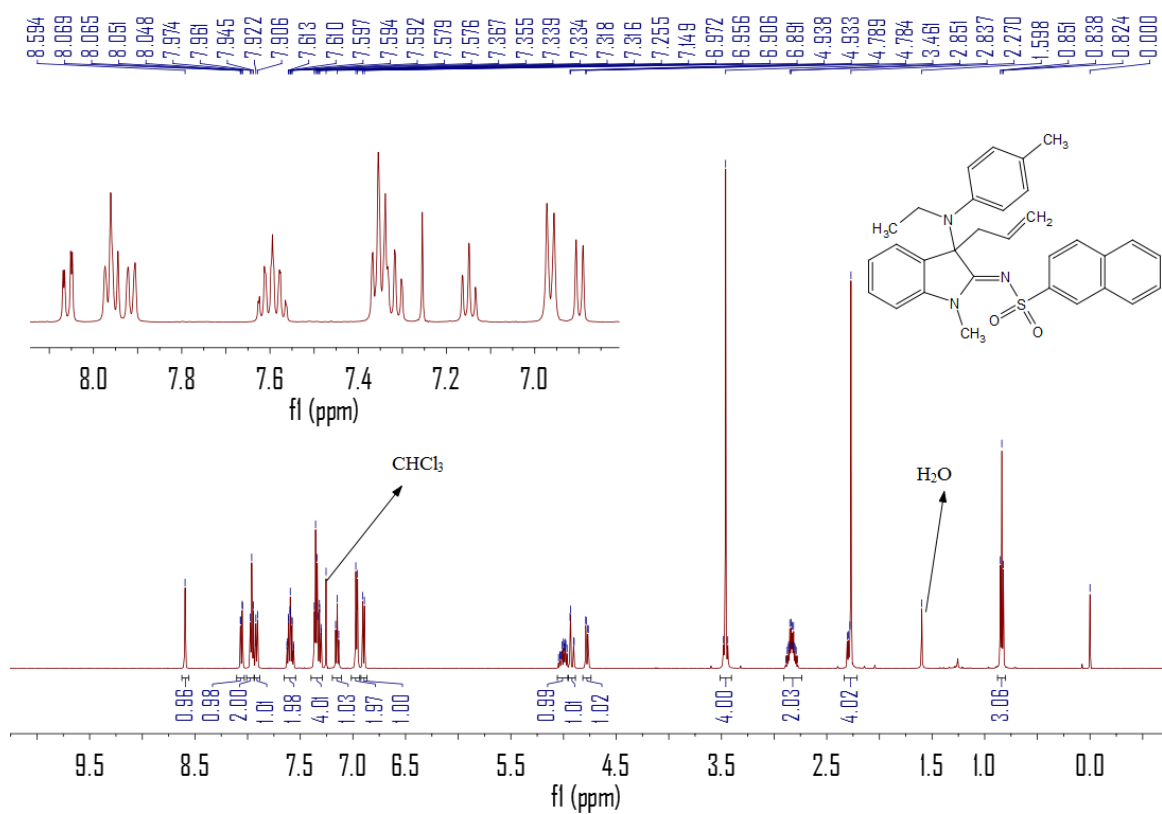


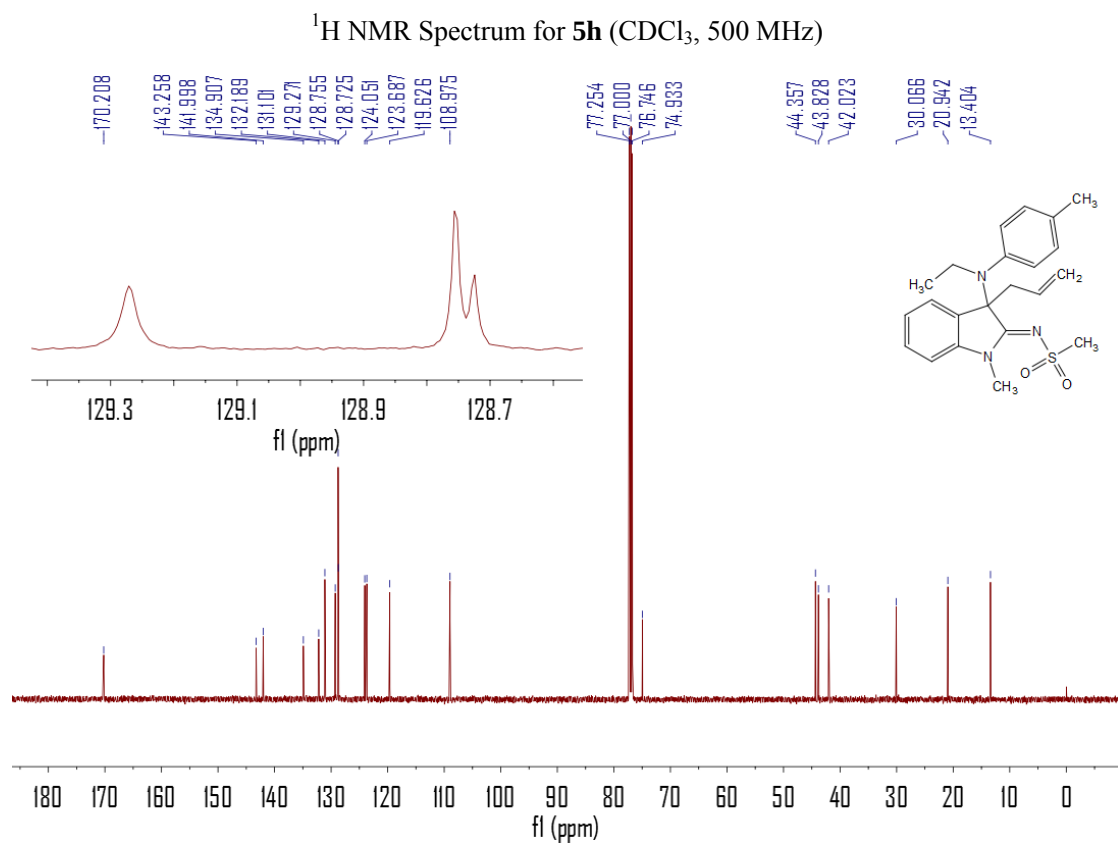
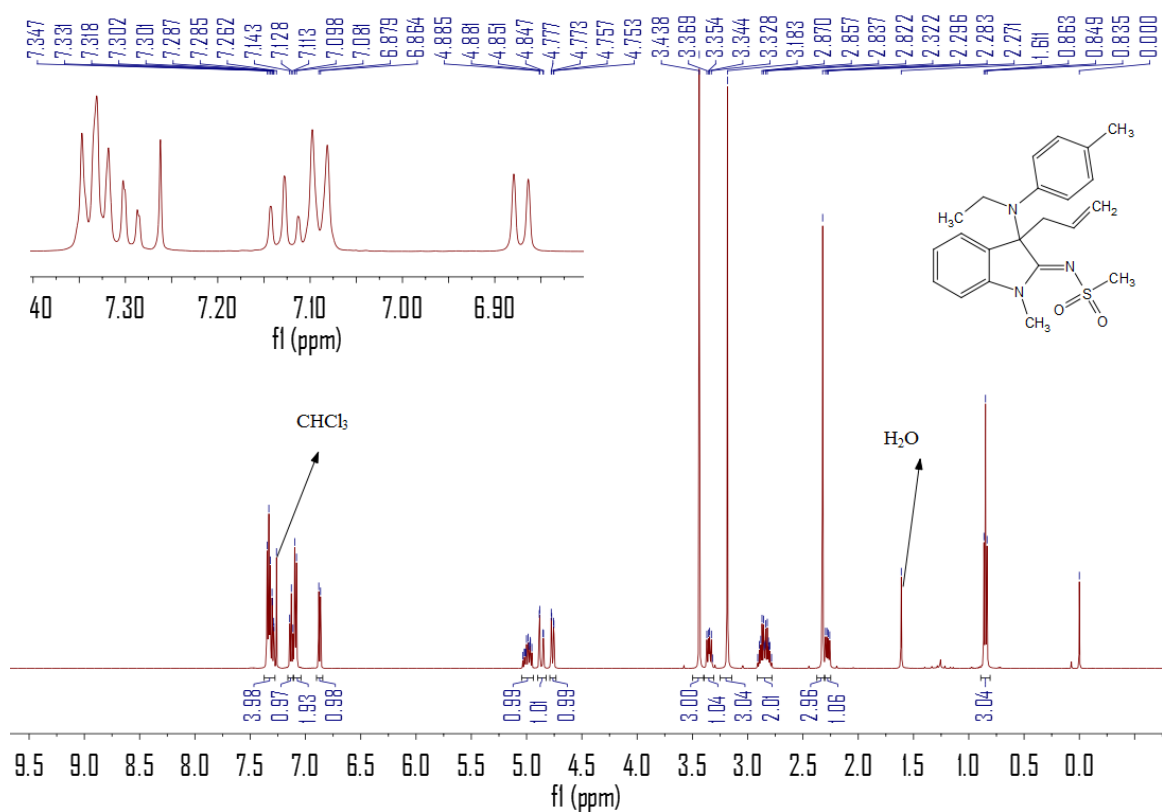


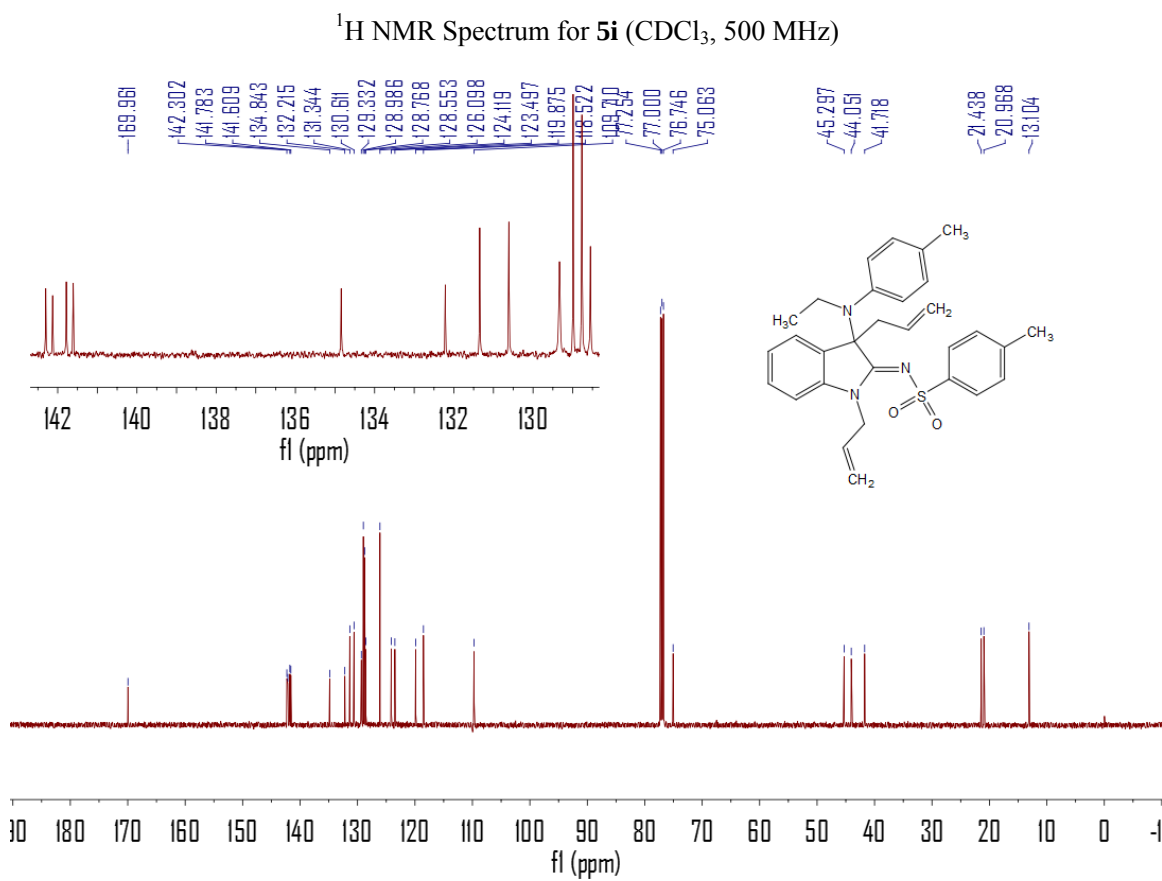
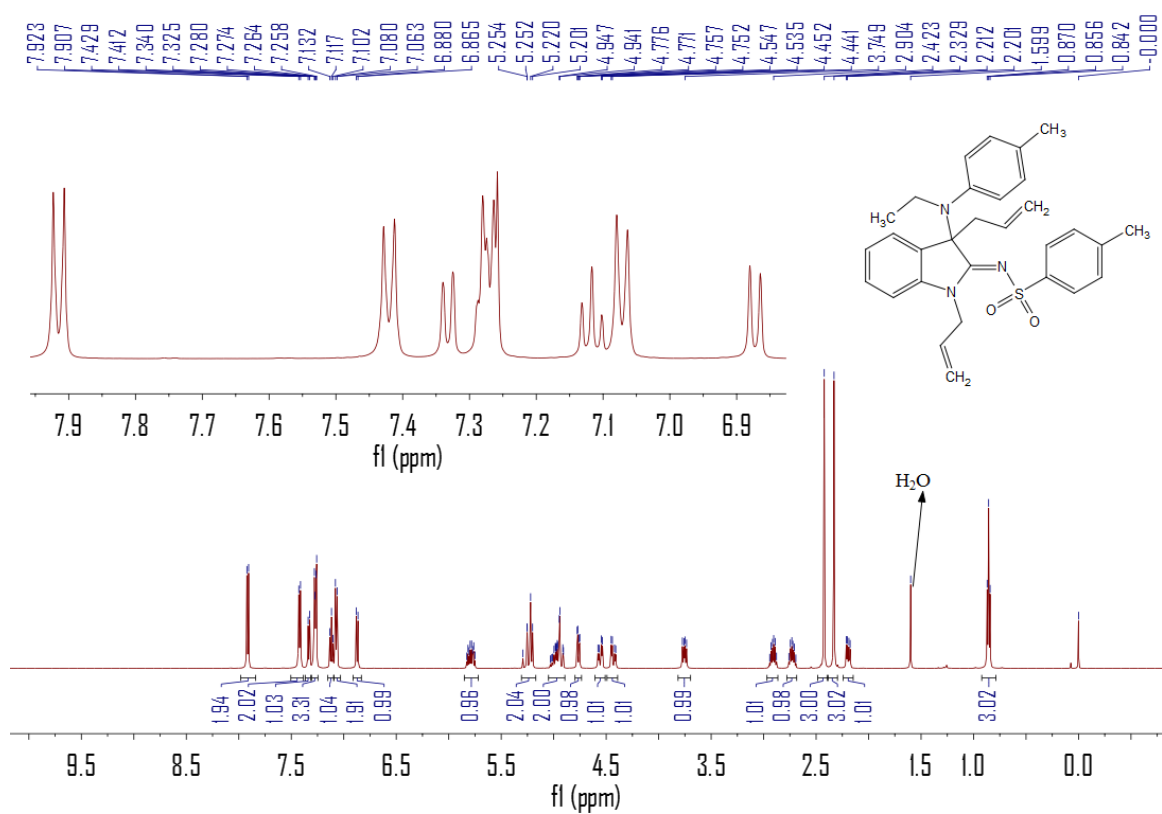


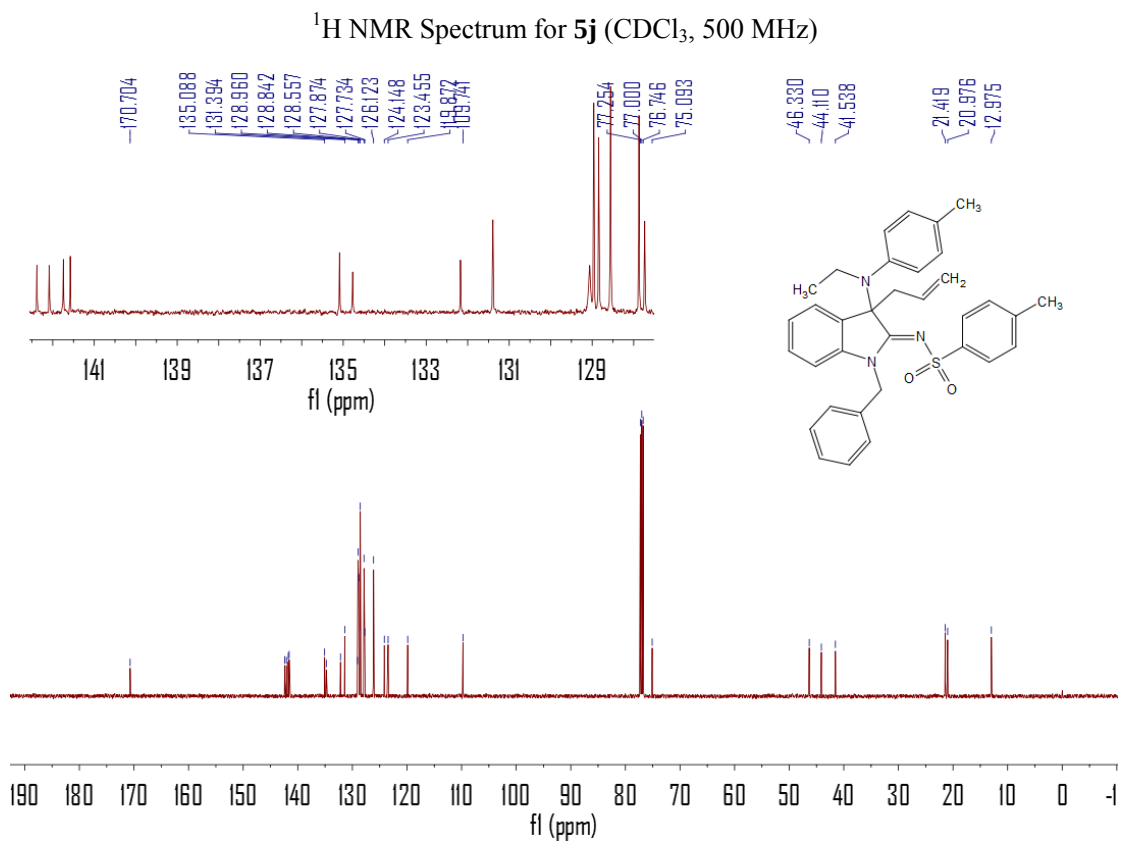
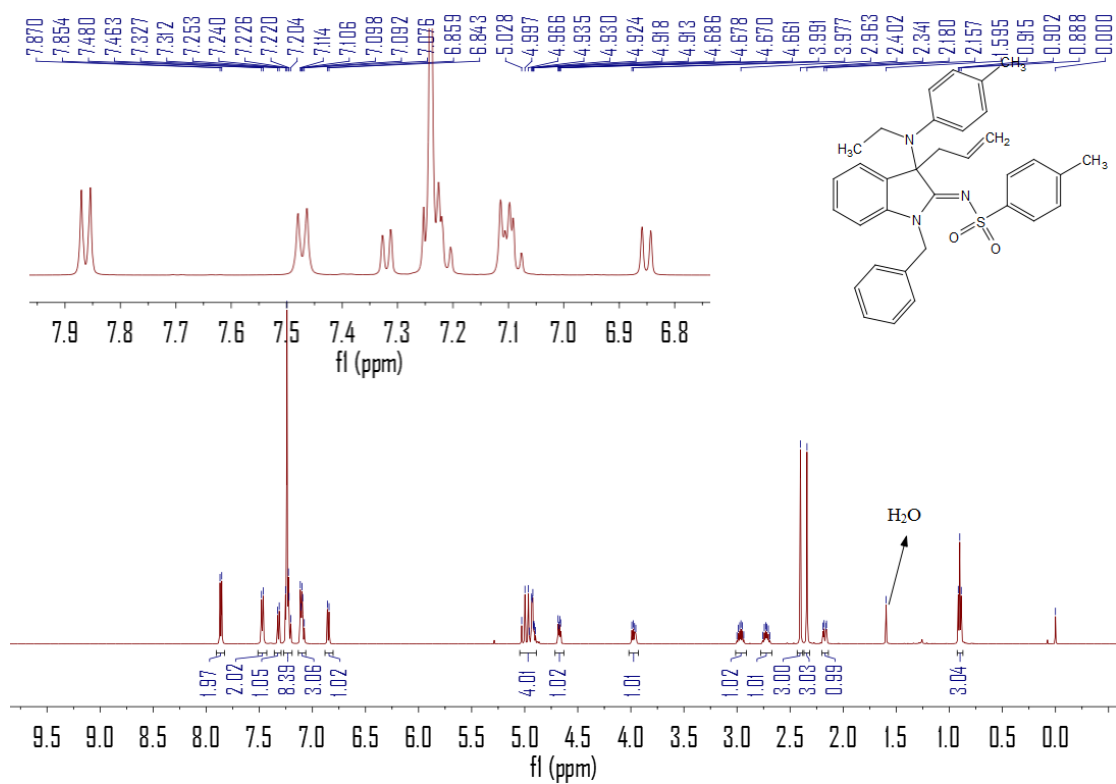


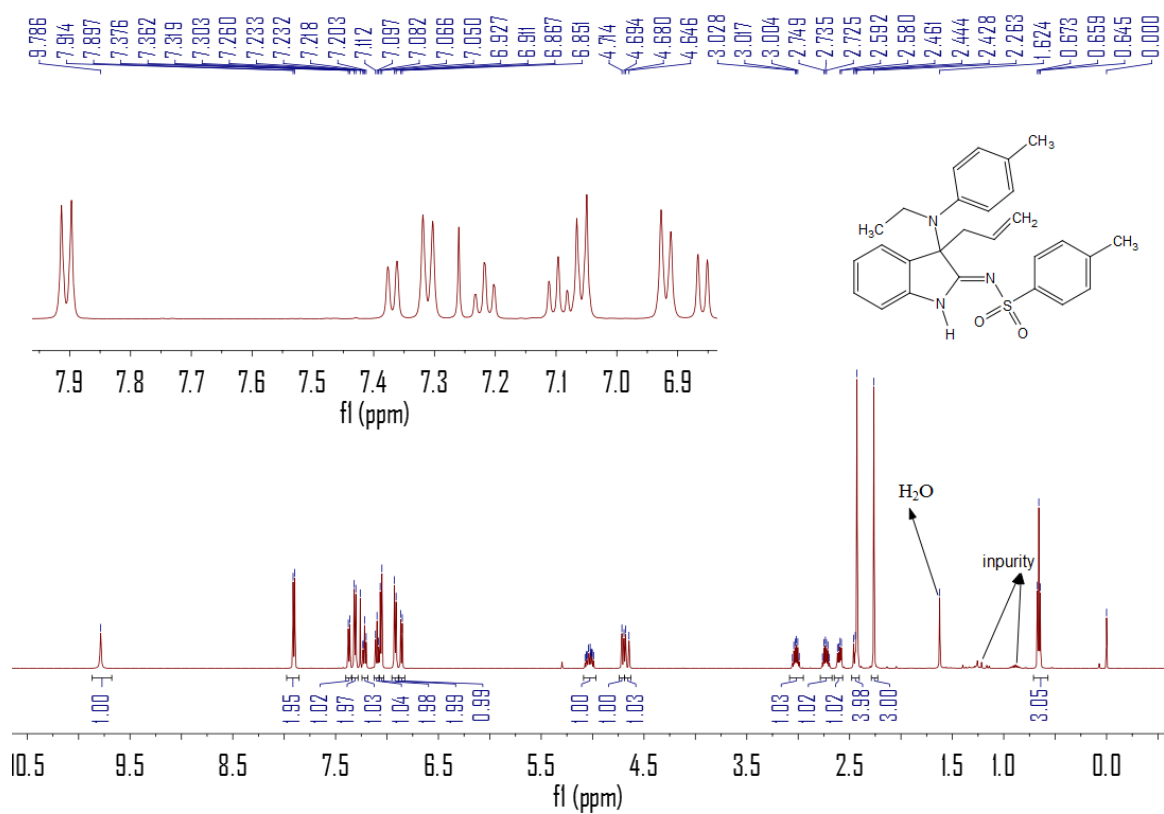




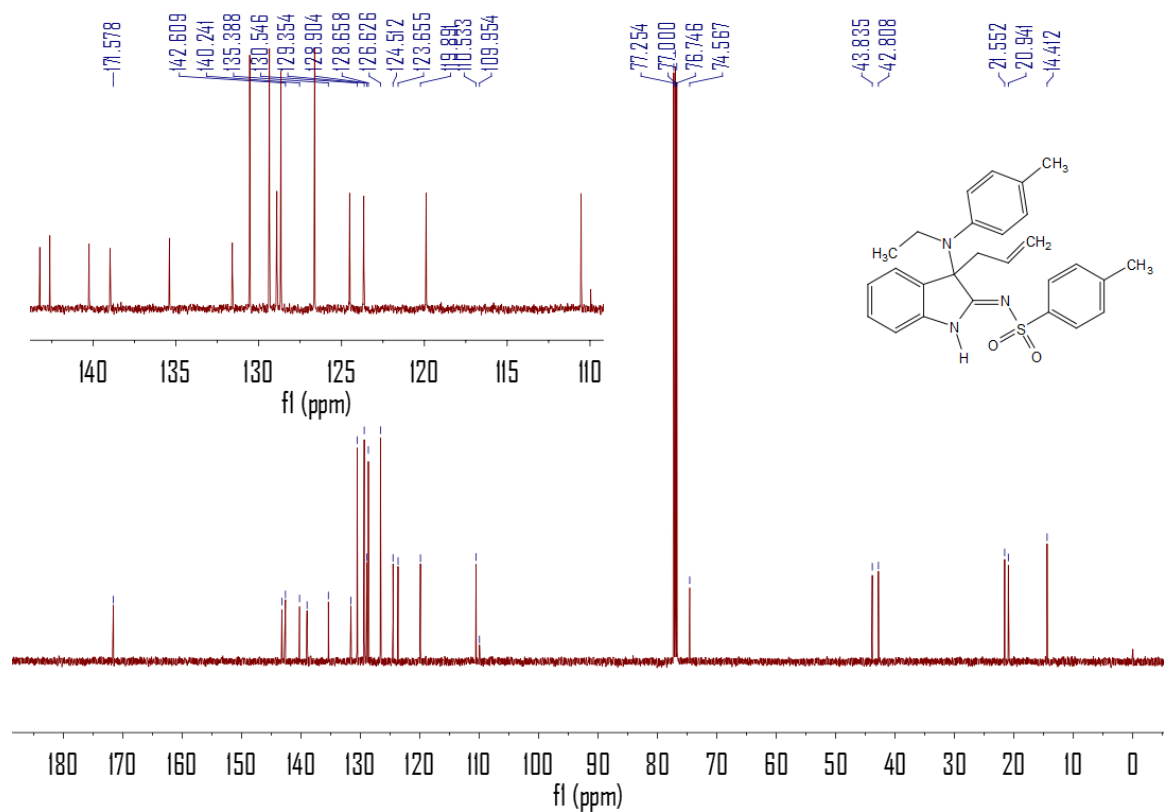




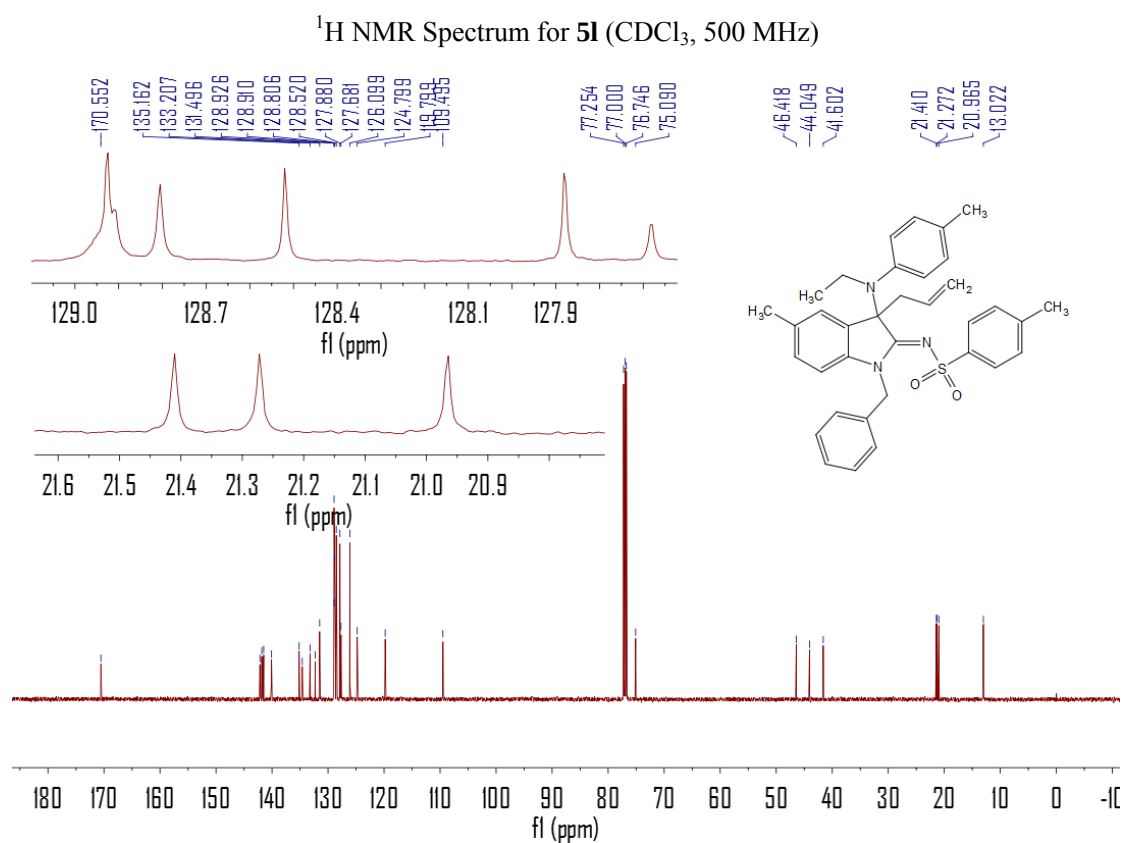
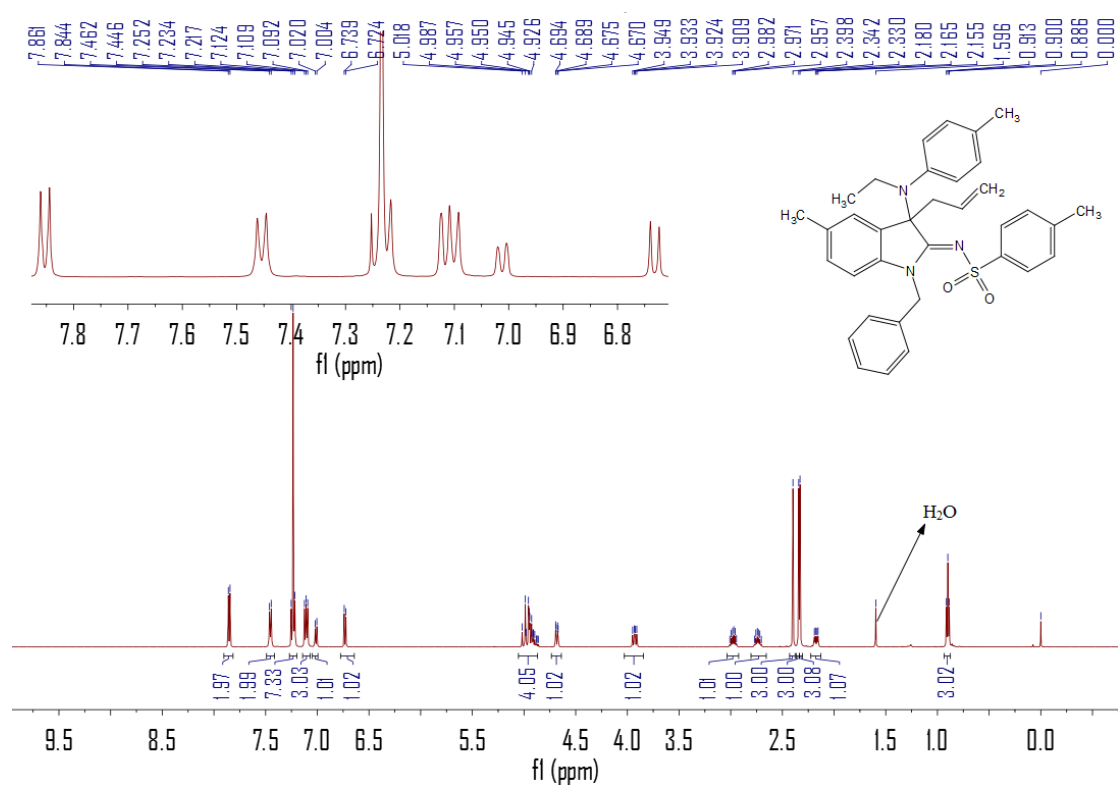


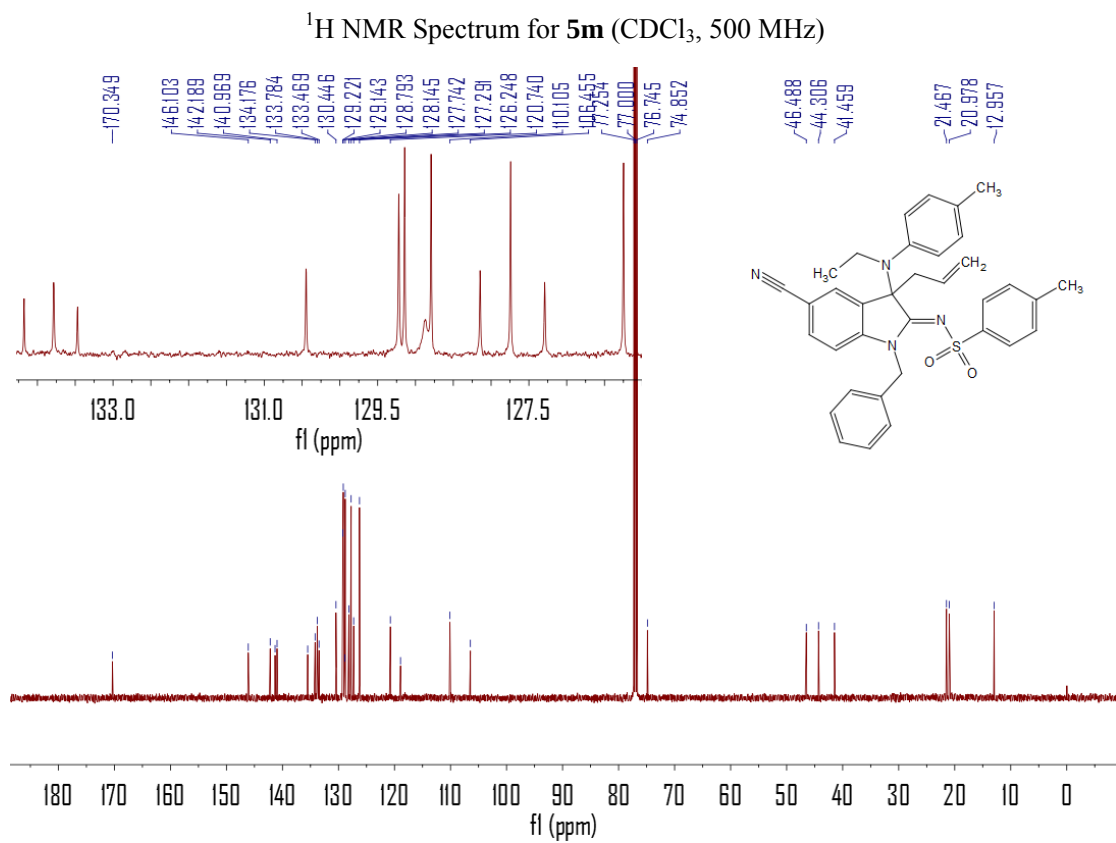
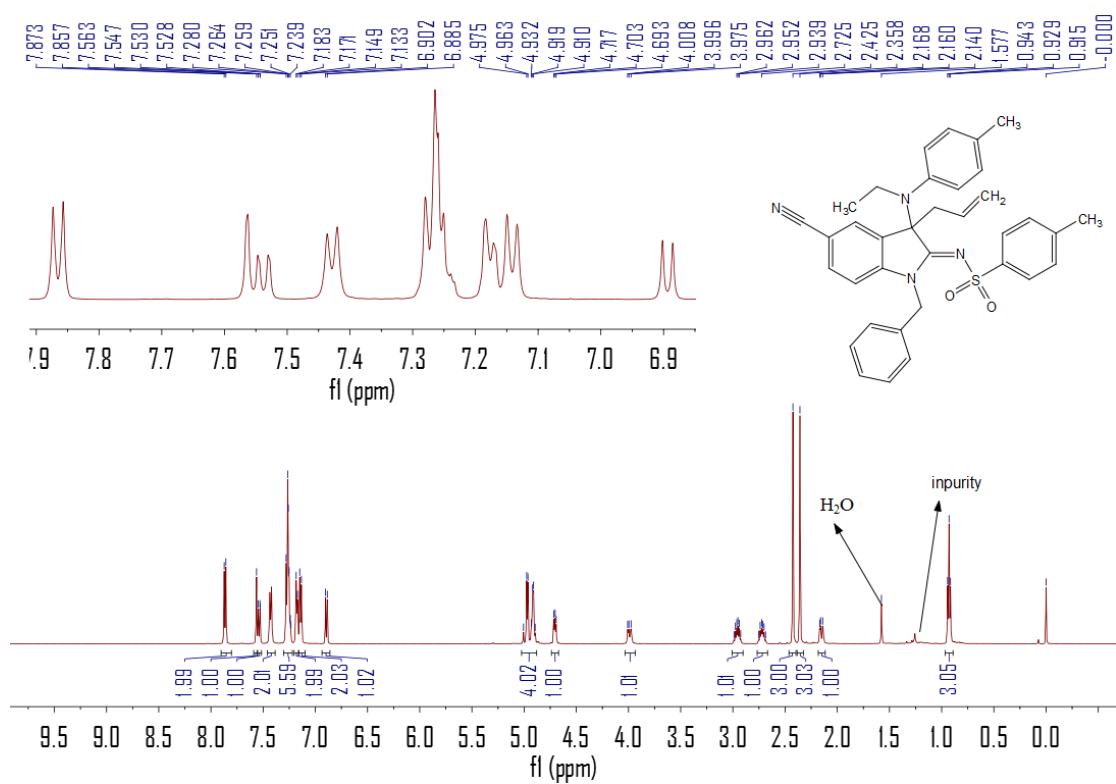


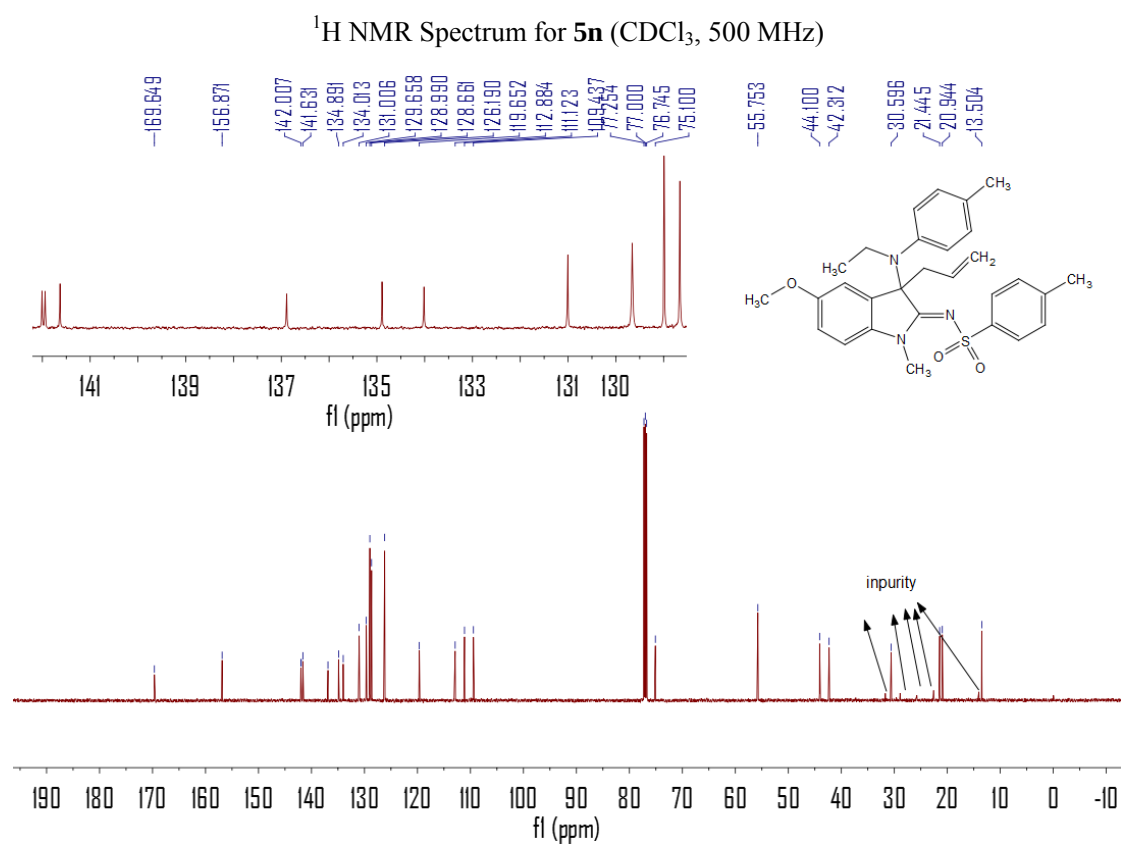
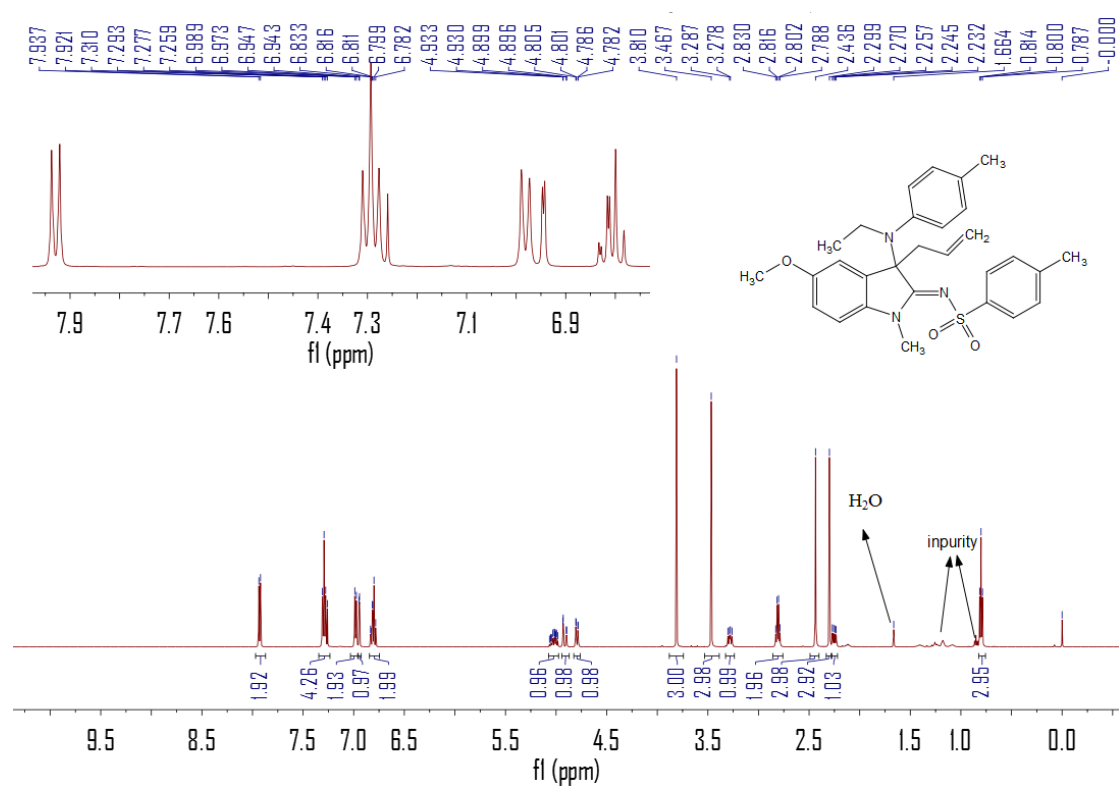
¹H NMR Spectrum for 5k (CDCl₃, 500 MHz)

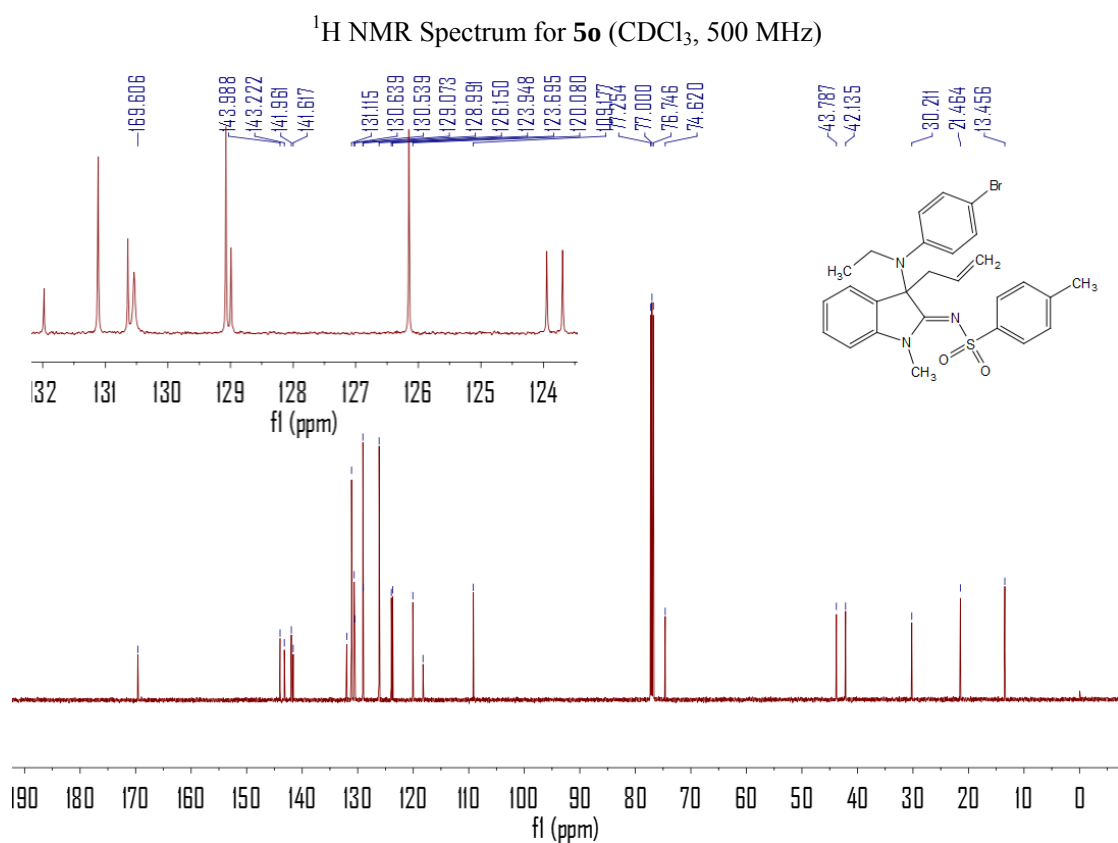
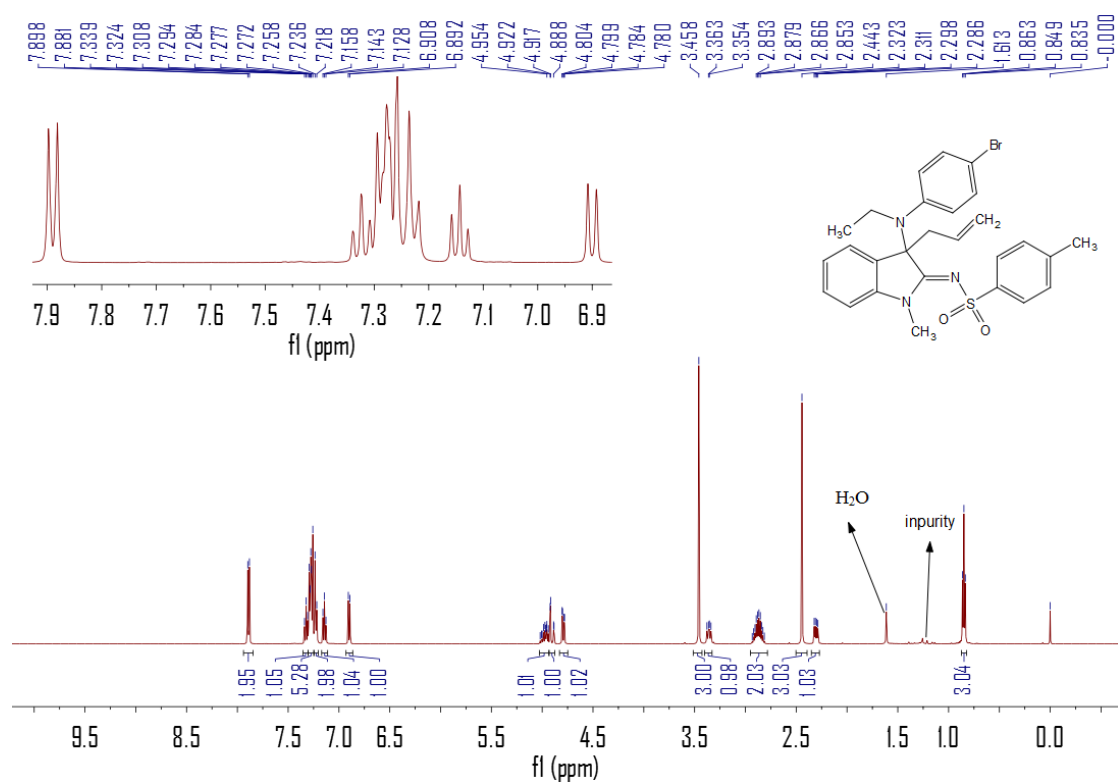


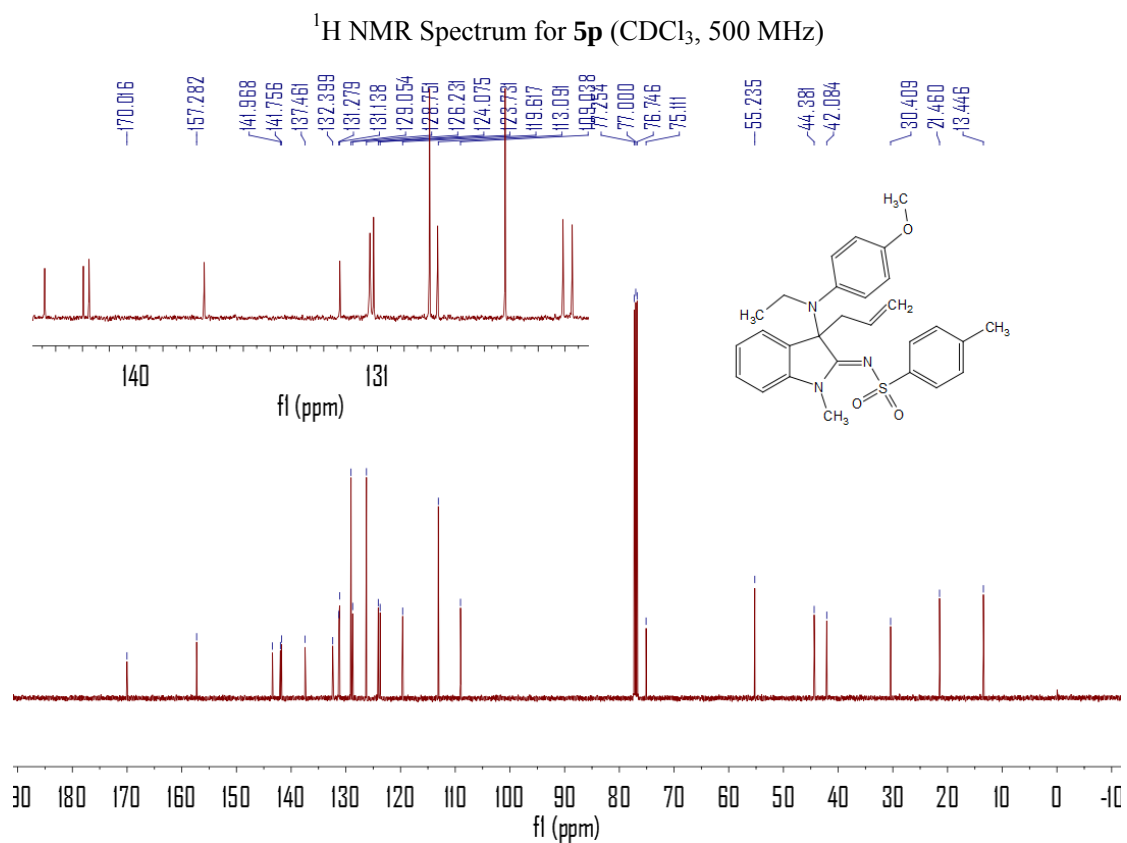
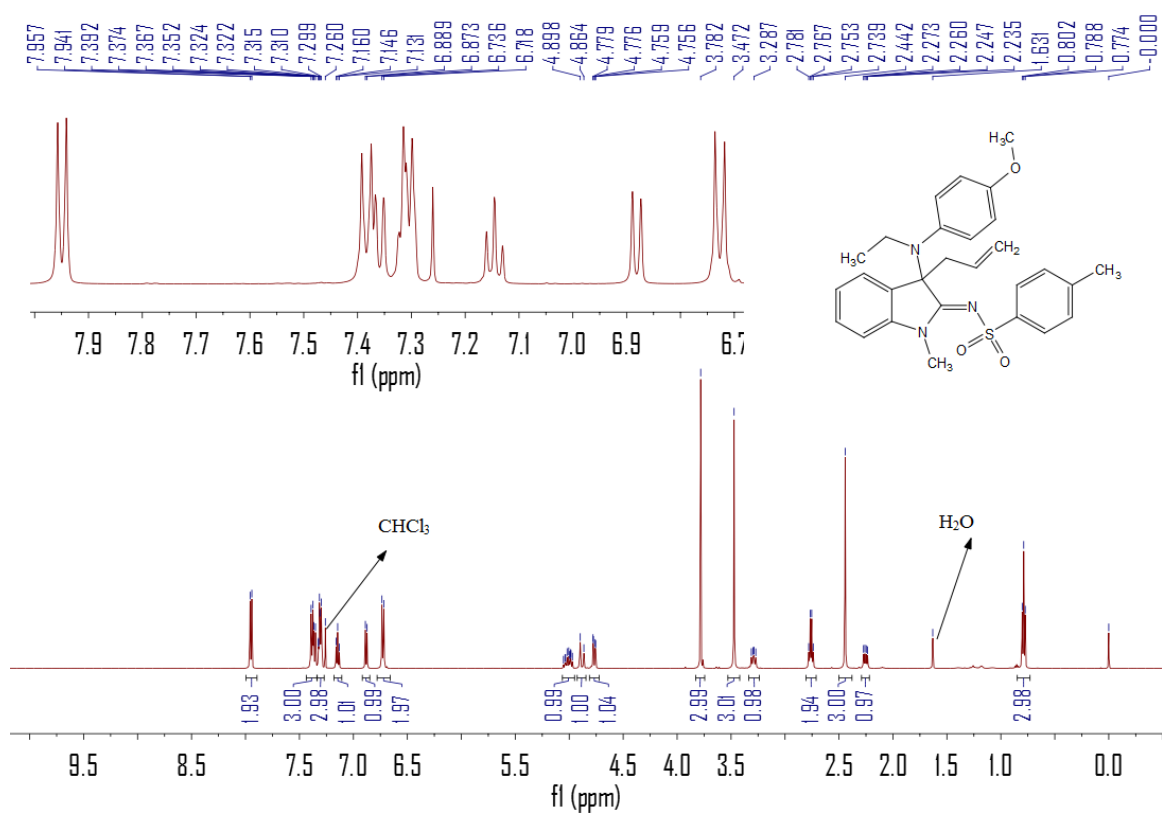
¹³C NMR Spectrum for 5k (CDCl₃, 125 MHz)

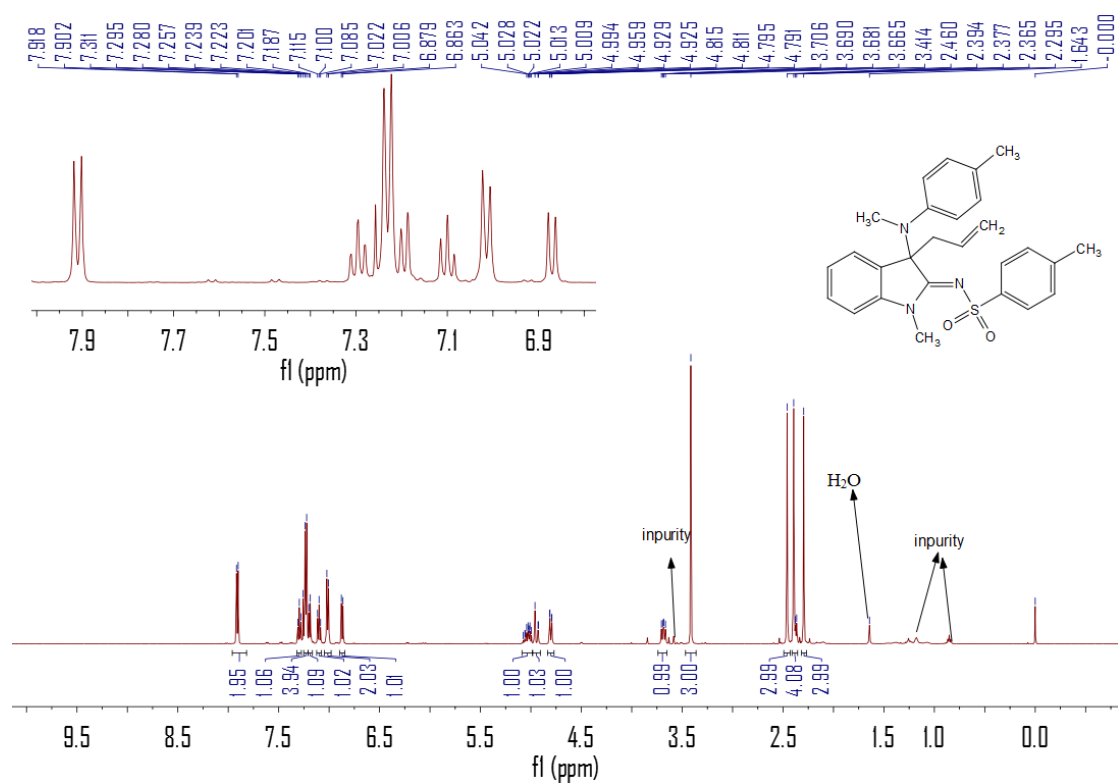




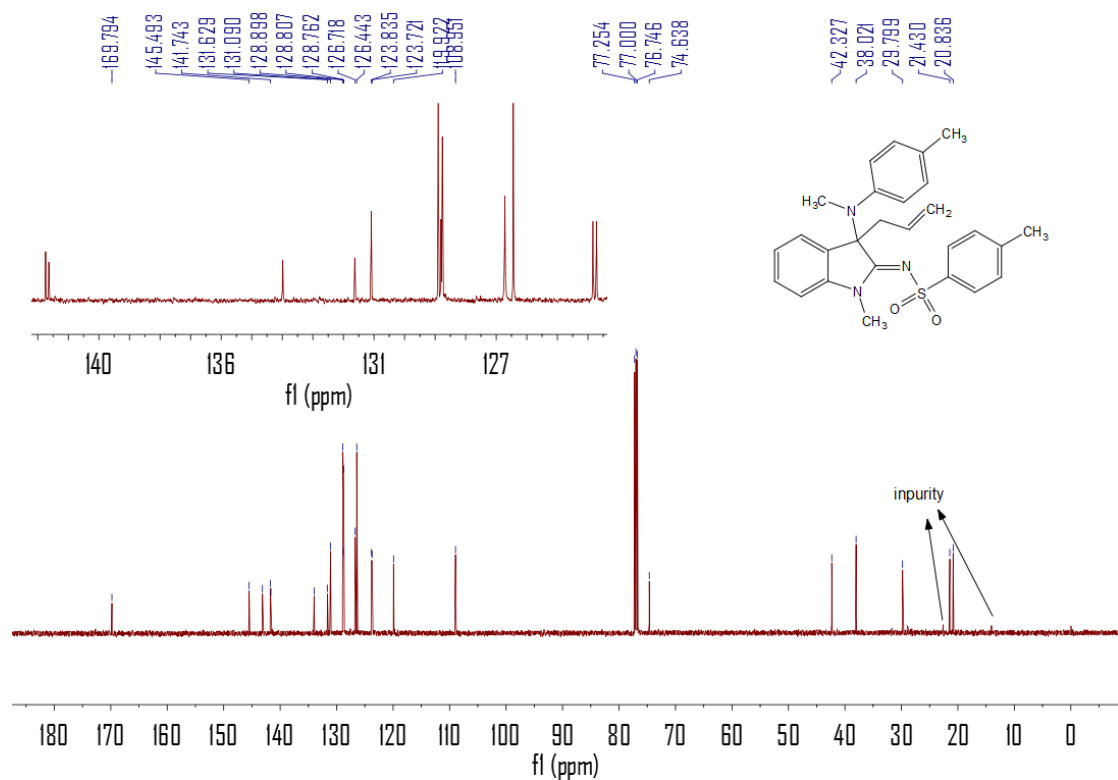




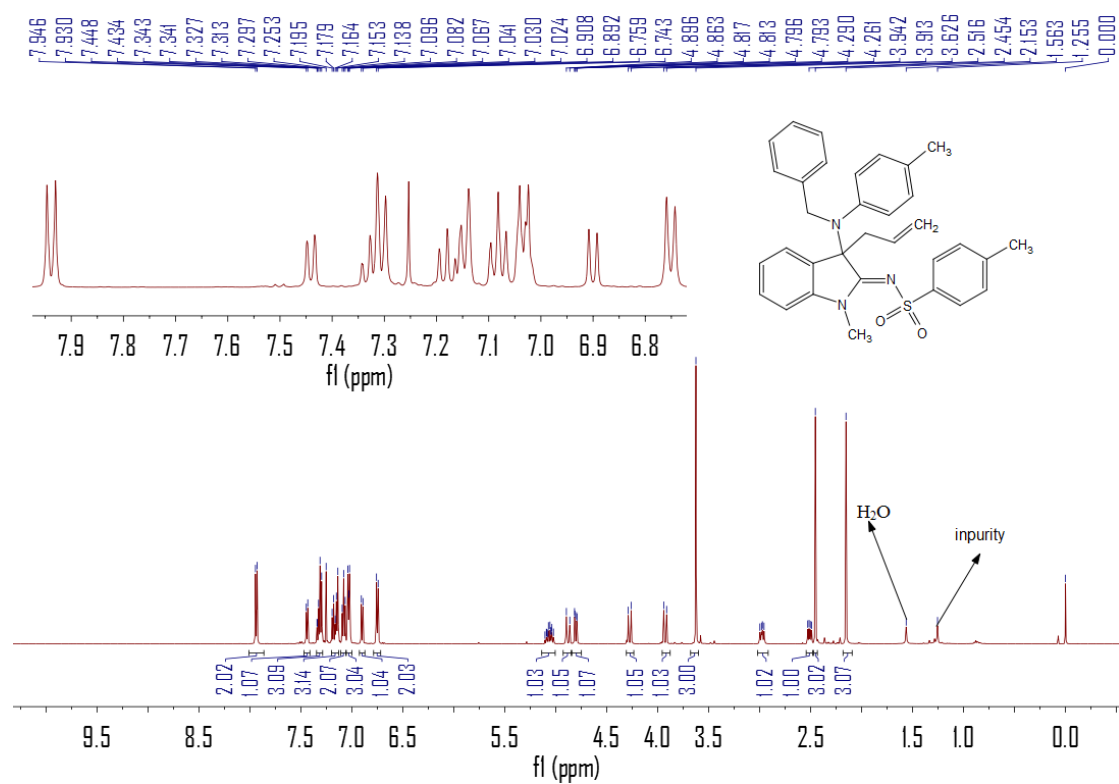




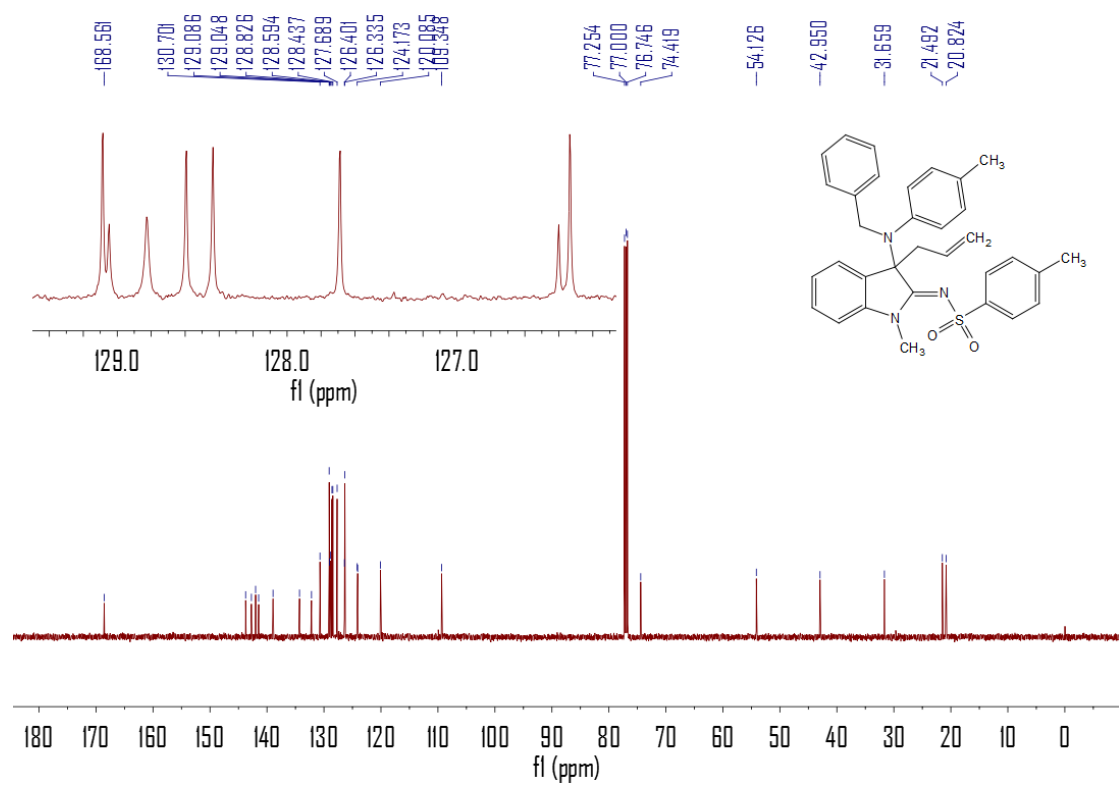
¹H NMR Spectrum for **5q** (CDCl₃, 500 MHz)



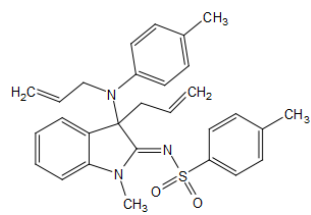
¹³C NMR Spectrum for **5q** (CDCl₃, 125 MHz)

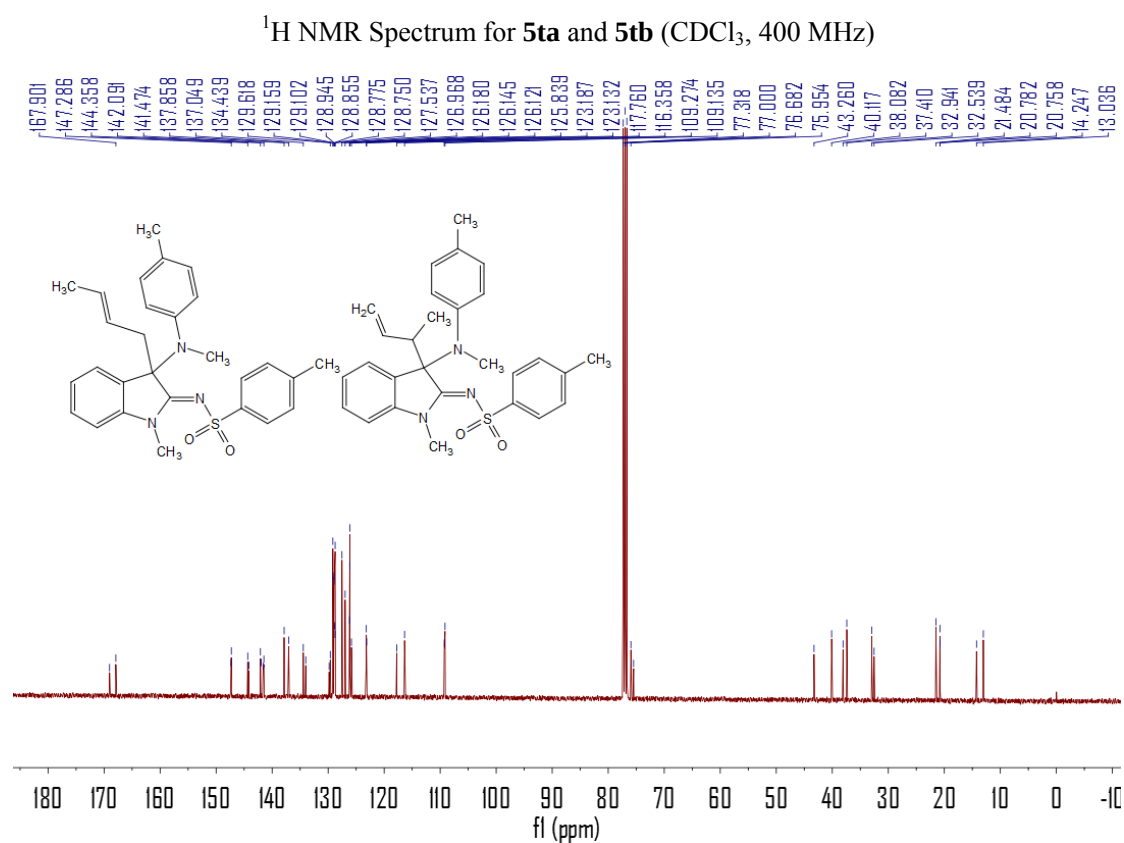
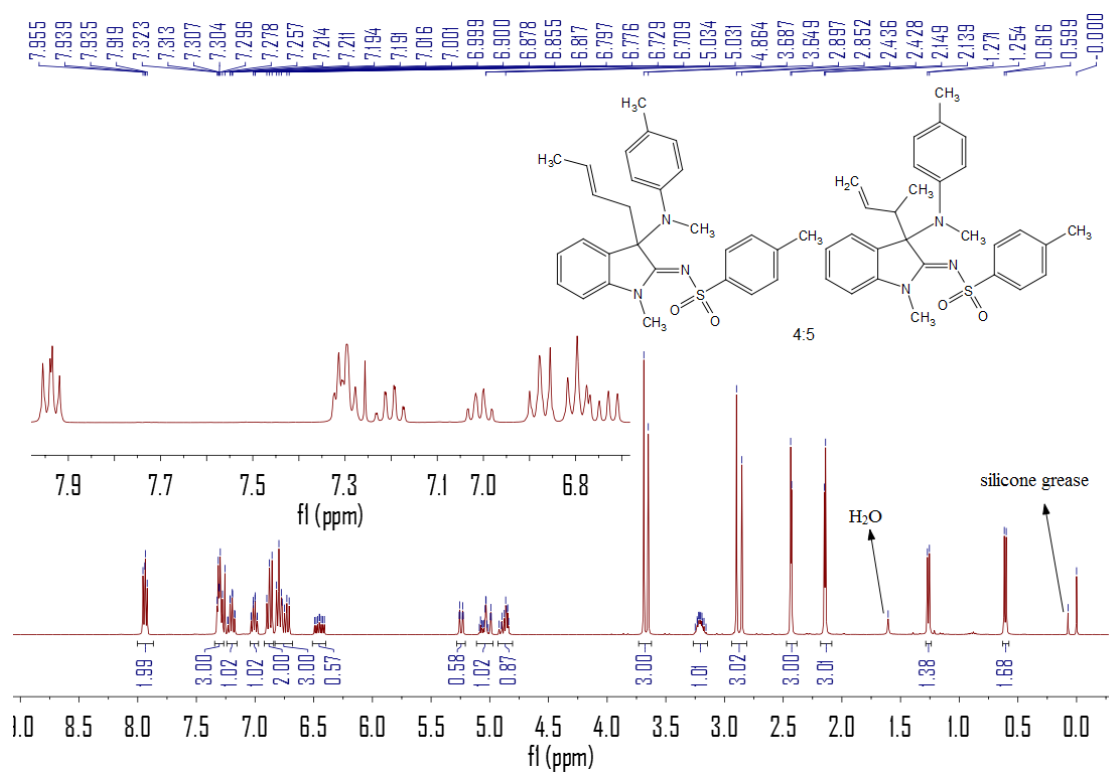


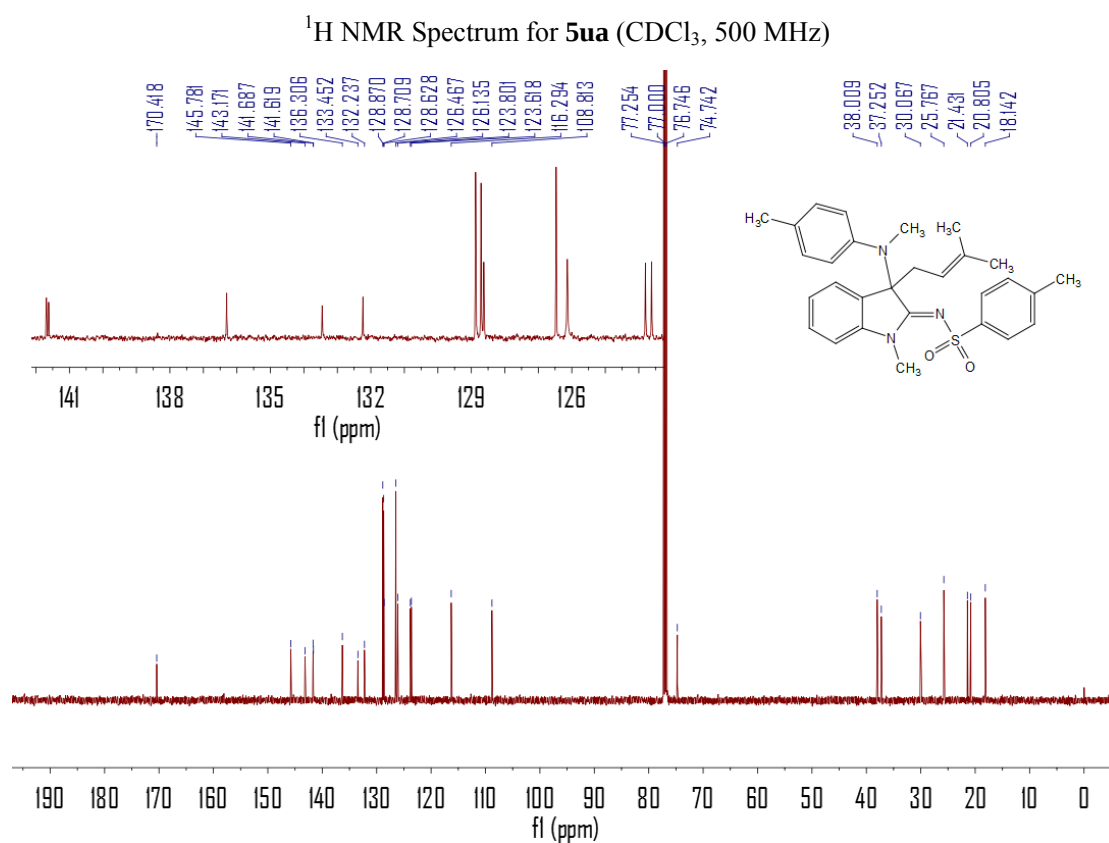
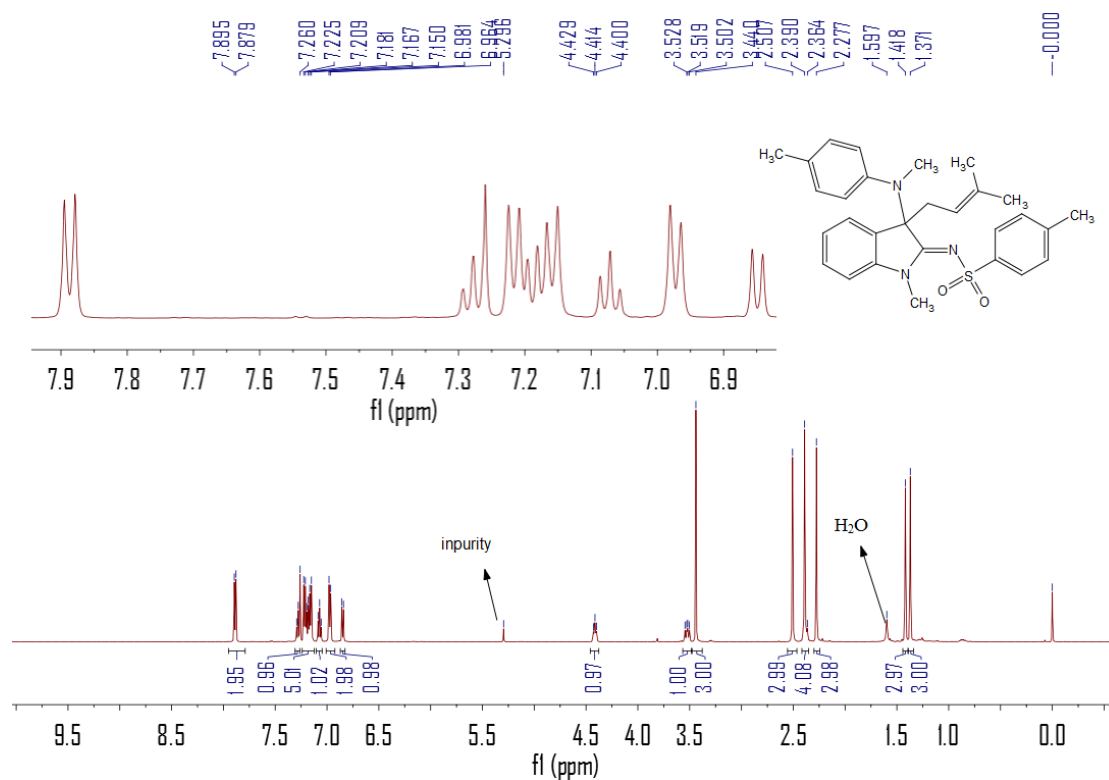
¹H NMR Spectrum for **5r** (CDCl₃, 500 MHz)

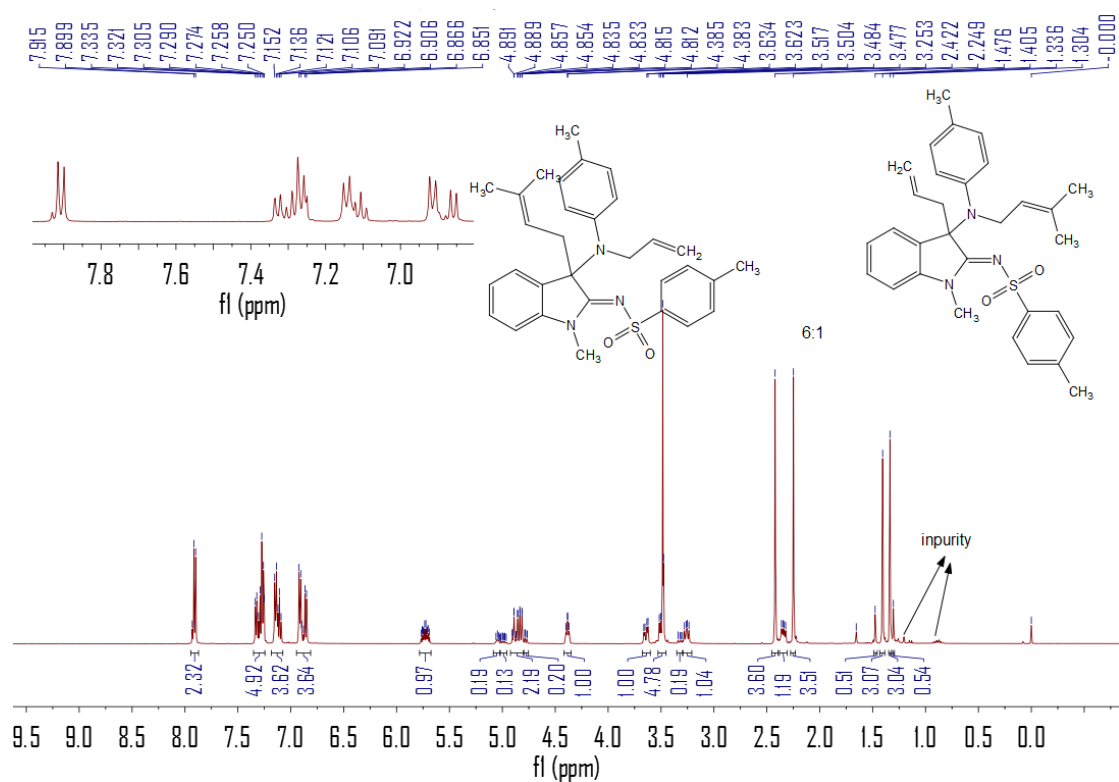


¹³C NMR Spectrum for **5r** (CDCl₃, 125 MHz)

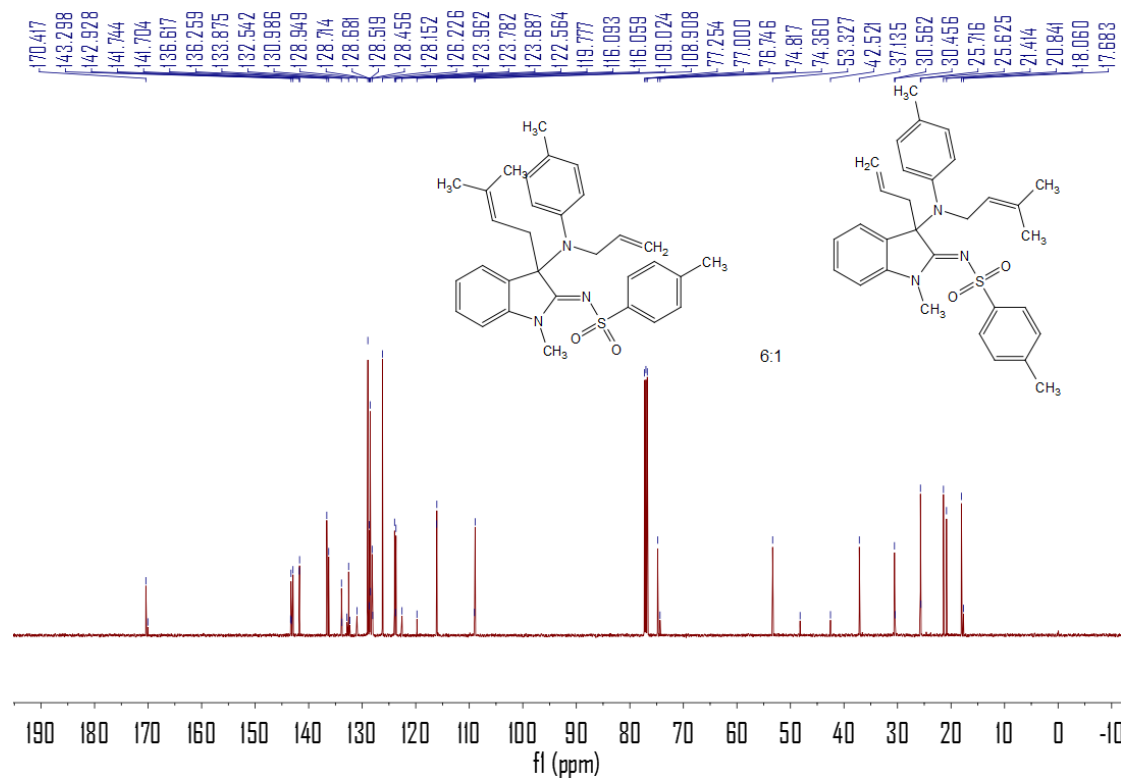
Cc1ccc(cc1)S(=O)(=O)N2C(=N2)c3ccccc3N(C2/C=C/C4=CC=C(C)C4)C#CC5=CC=CC=C5



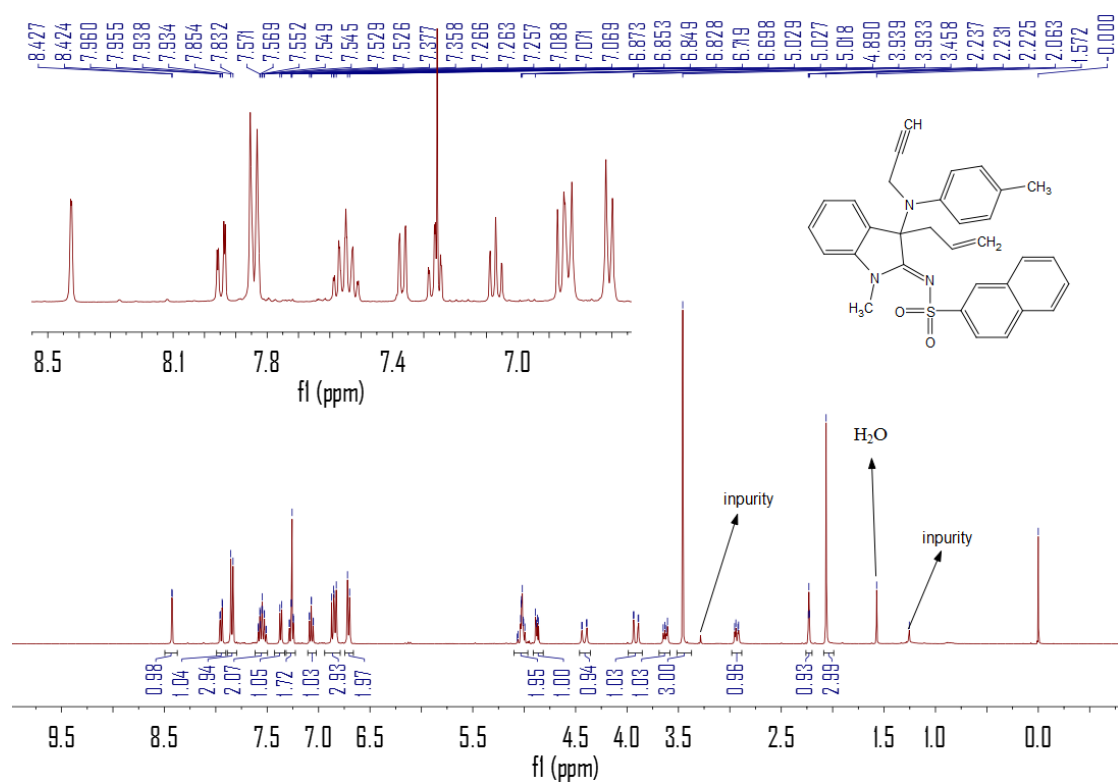




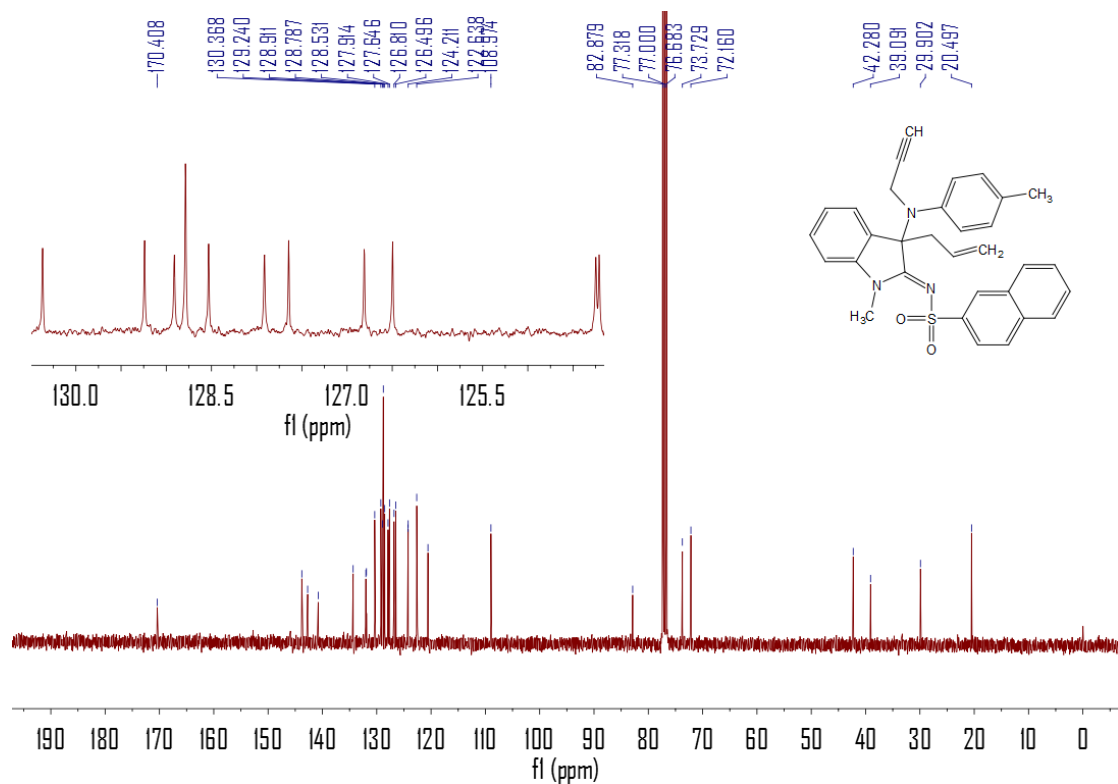
¹H NMR Spectrum for 5v and 5w (CDCl₃, 500 MHz)



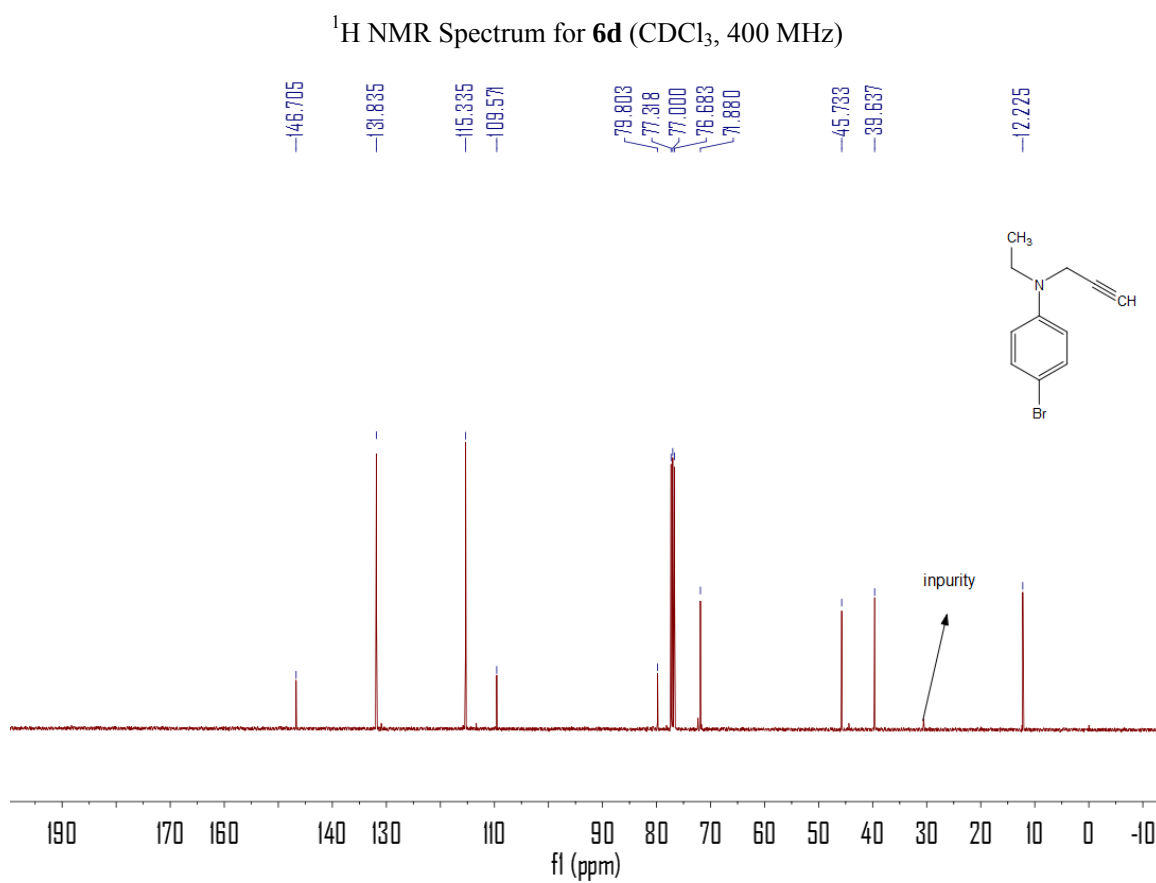
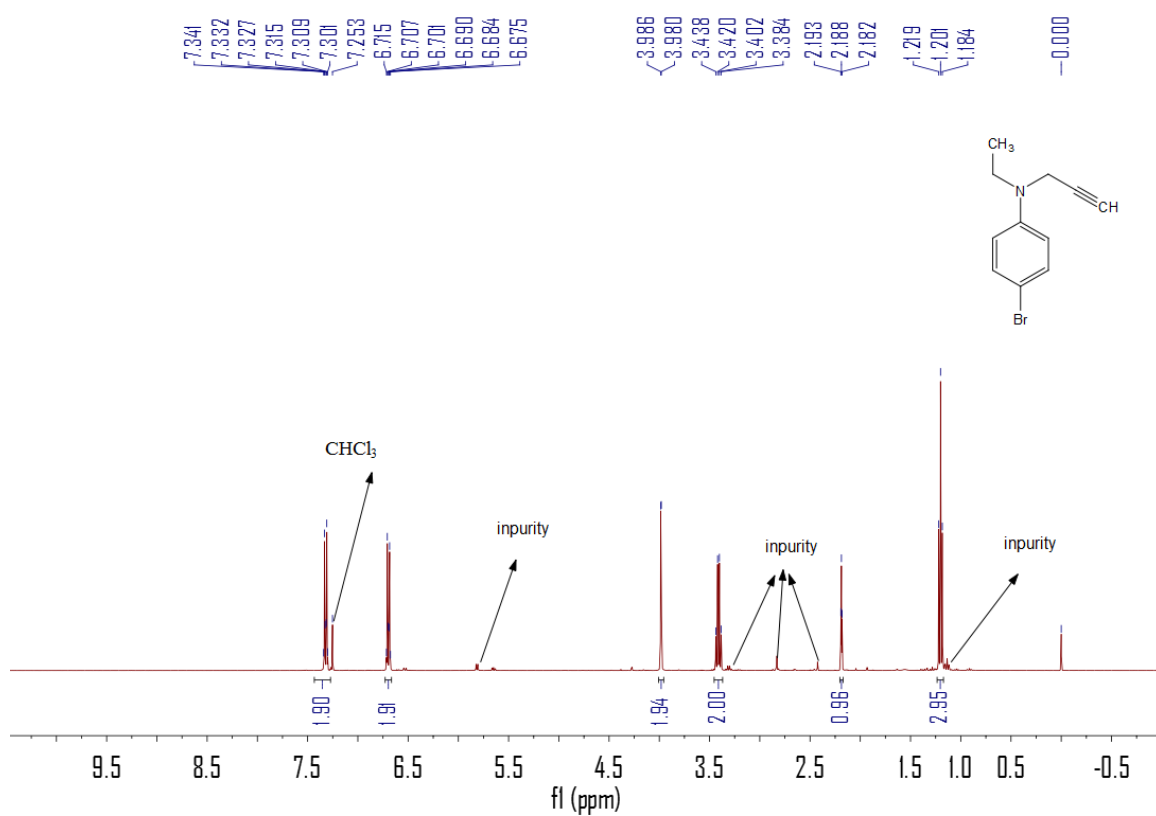
¹³C NMR Spectrum for 5v and 5w (CDCl₃, 125 MHz)

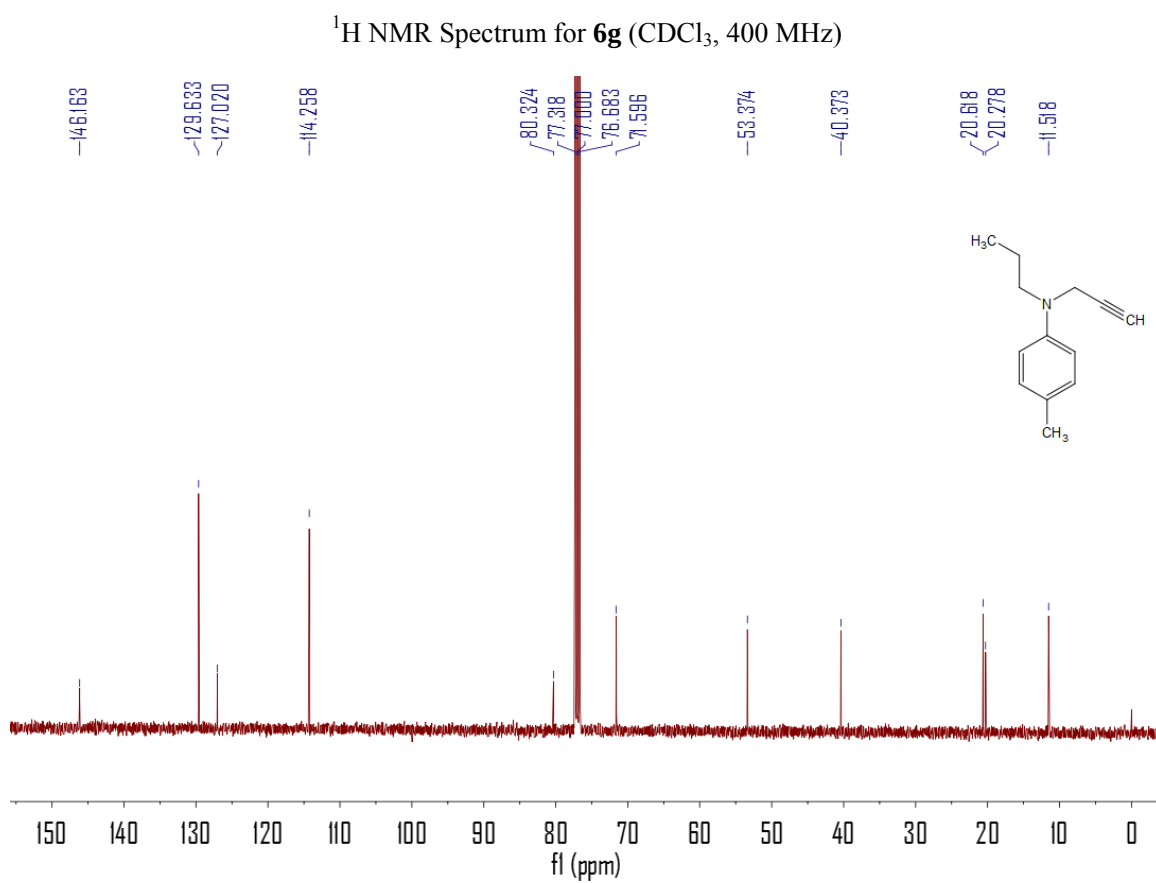
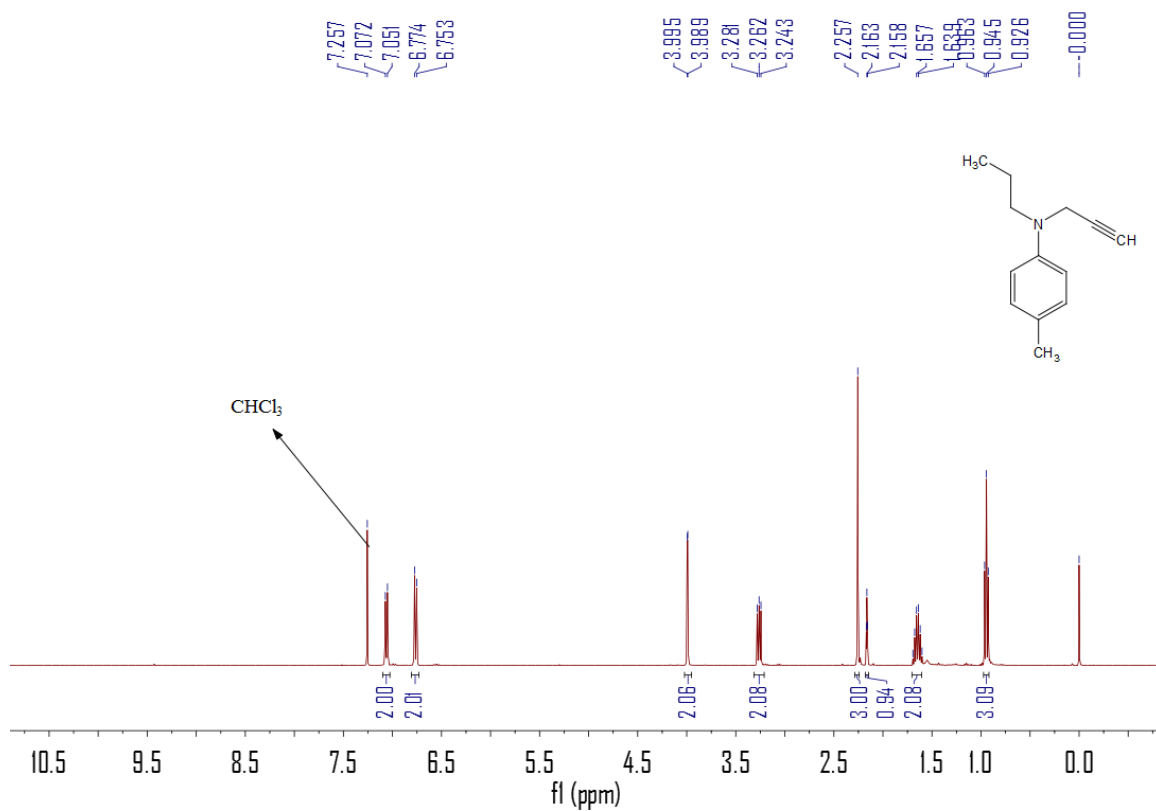


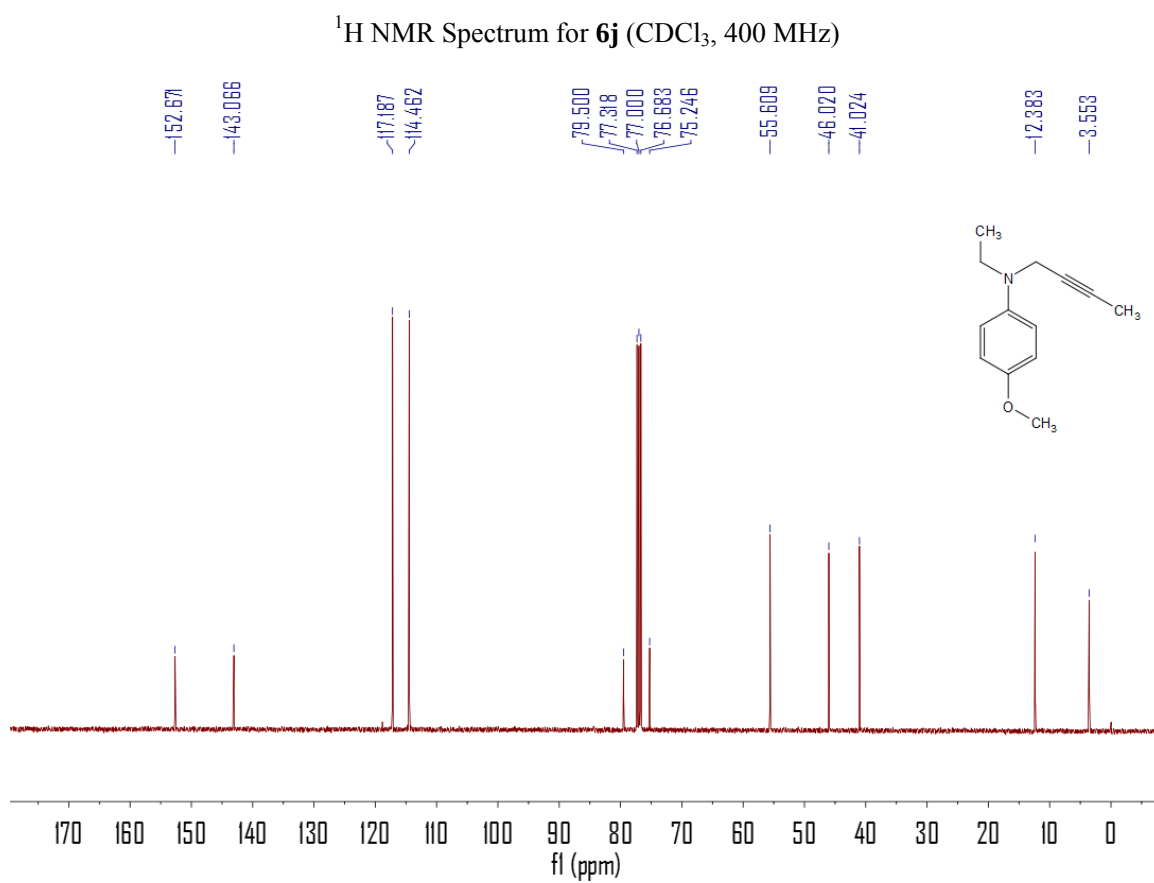
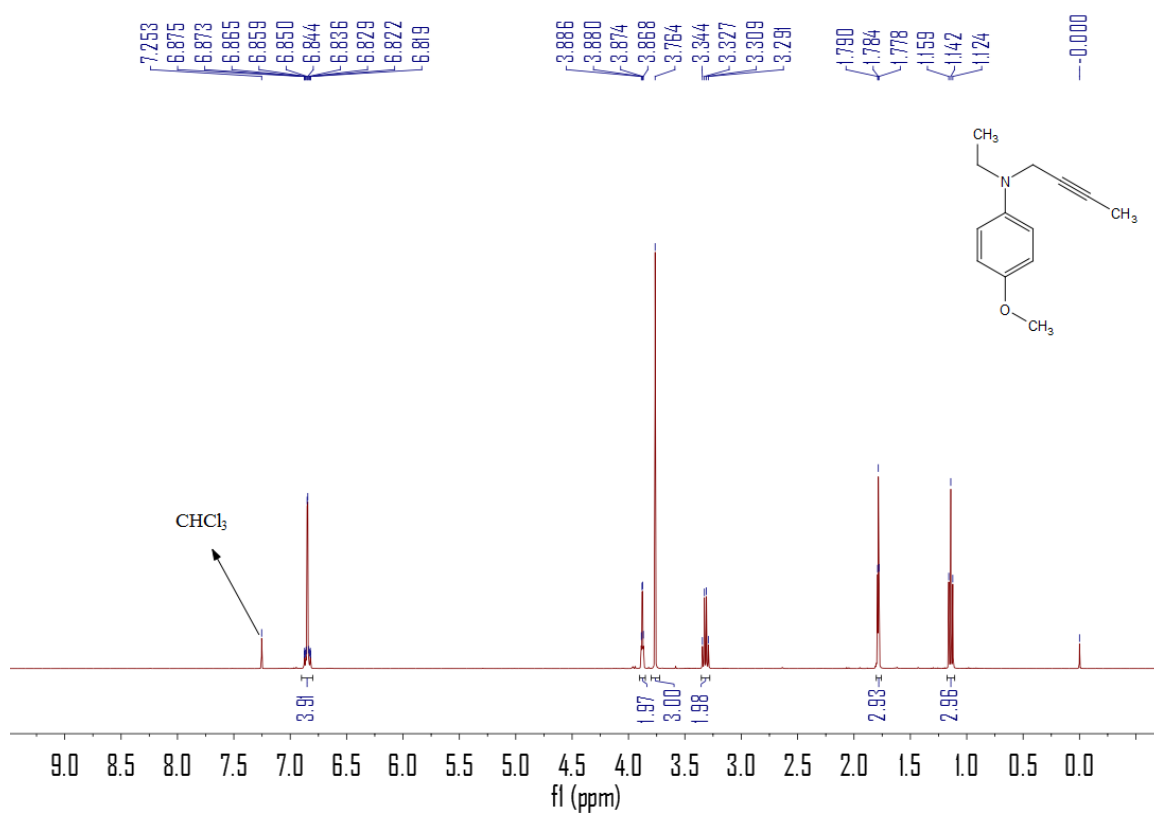
¹H NMR Spectrum for 5x (CDCl₃, 400 MHz)

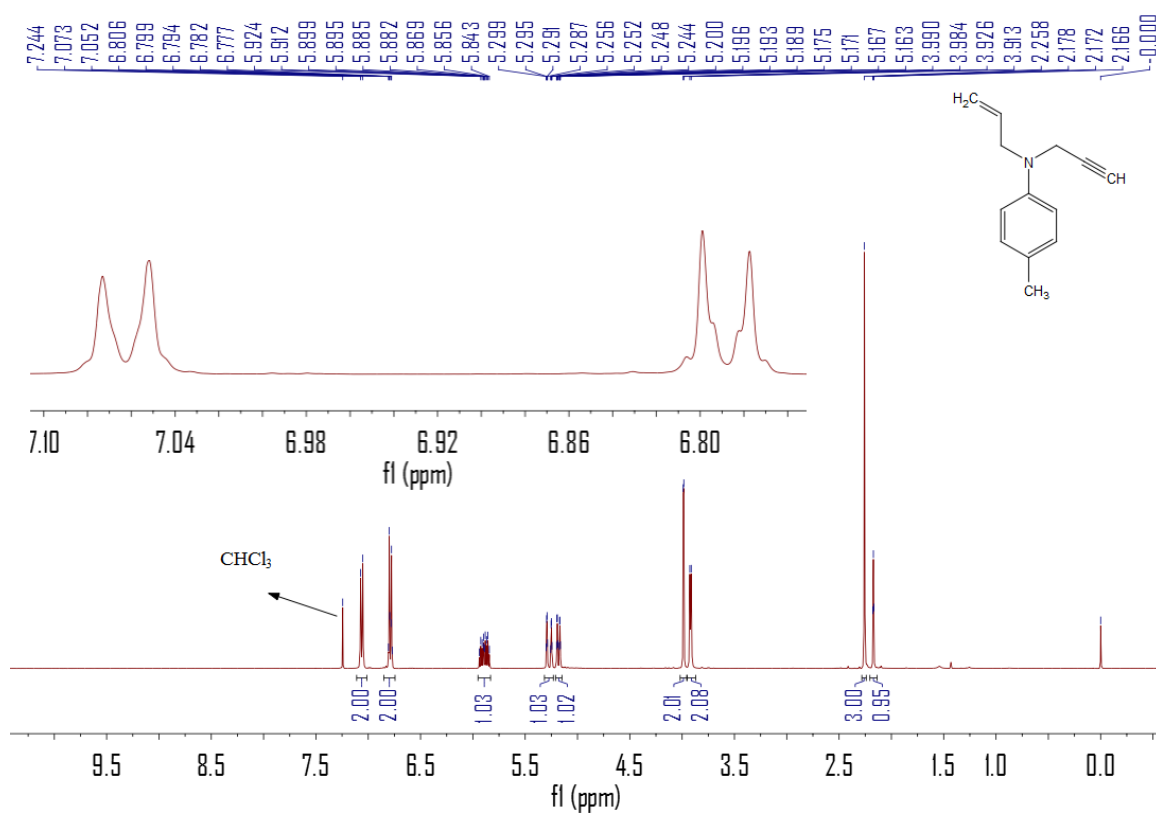


¹³C NMR Spectrum for 5x (CDCl₃, 100 MHz)

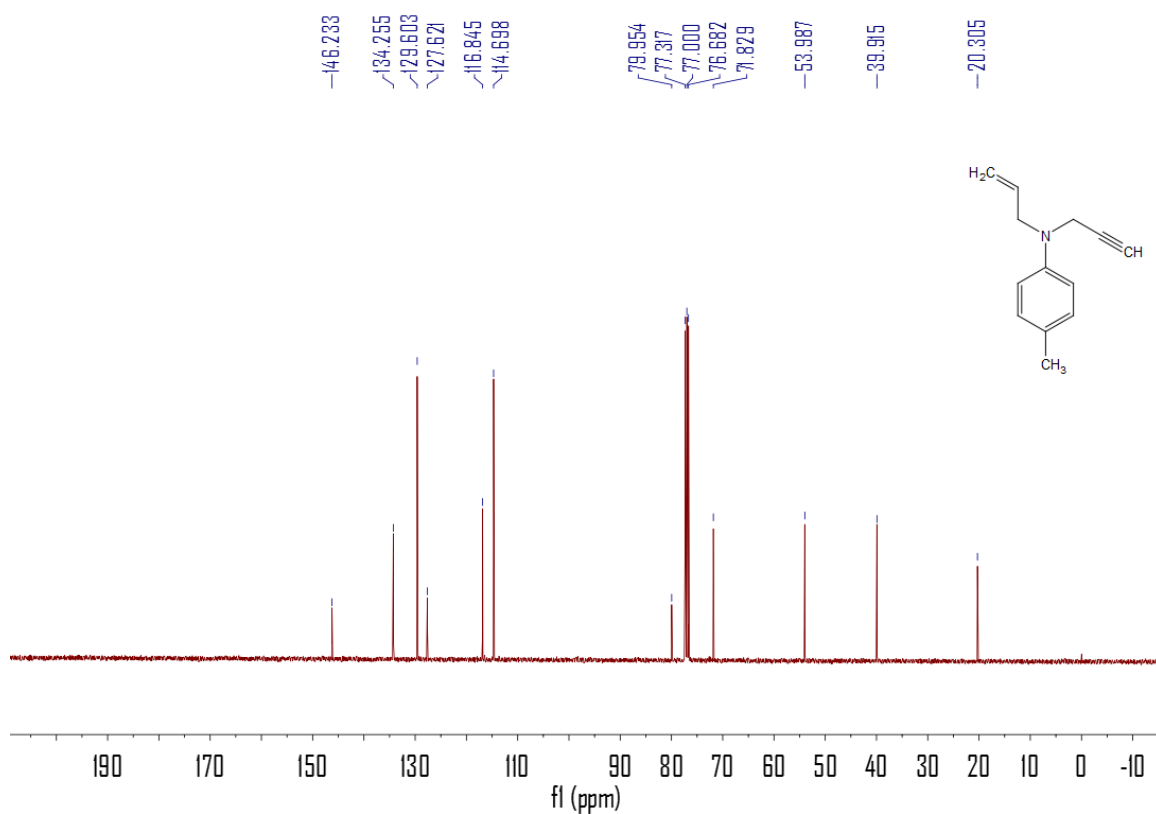




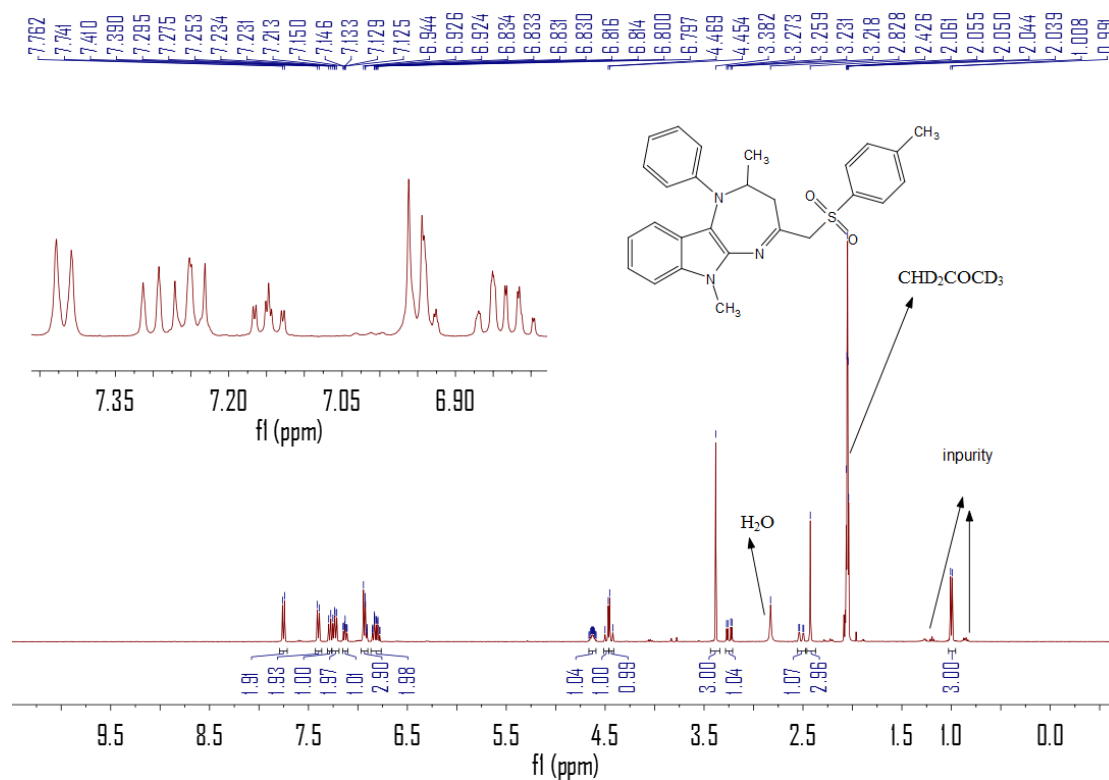




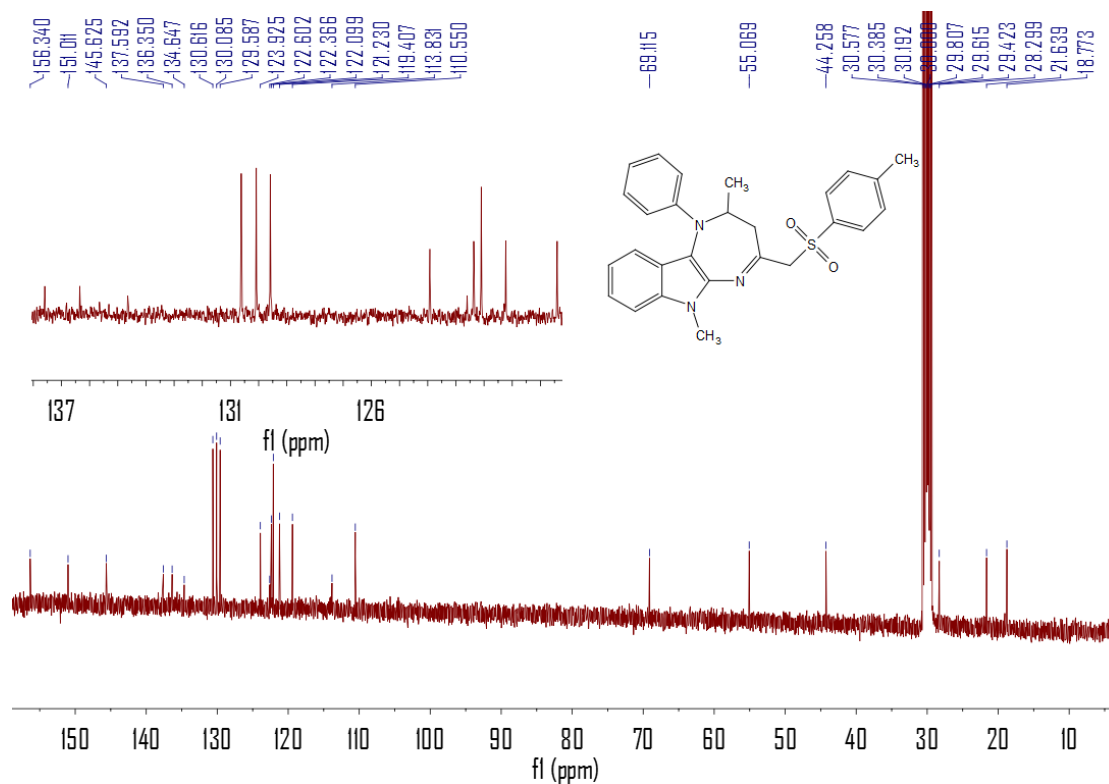
¹H NMR Spectrum for **6k** (CDCl₃, 400 MHz)



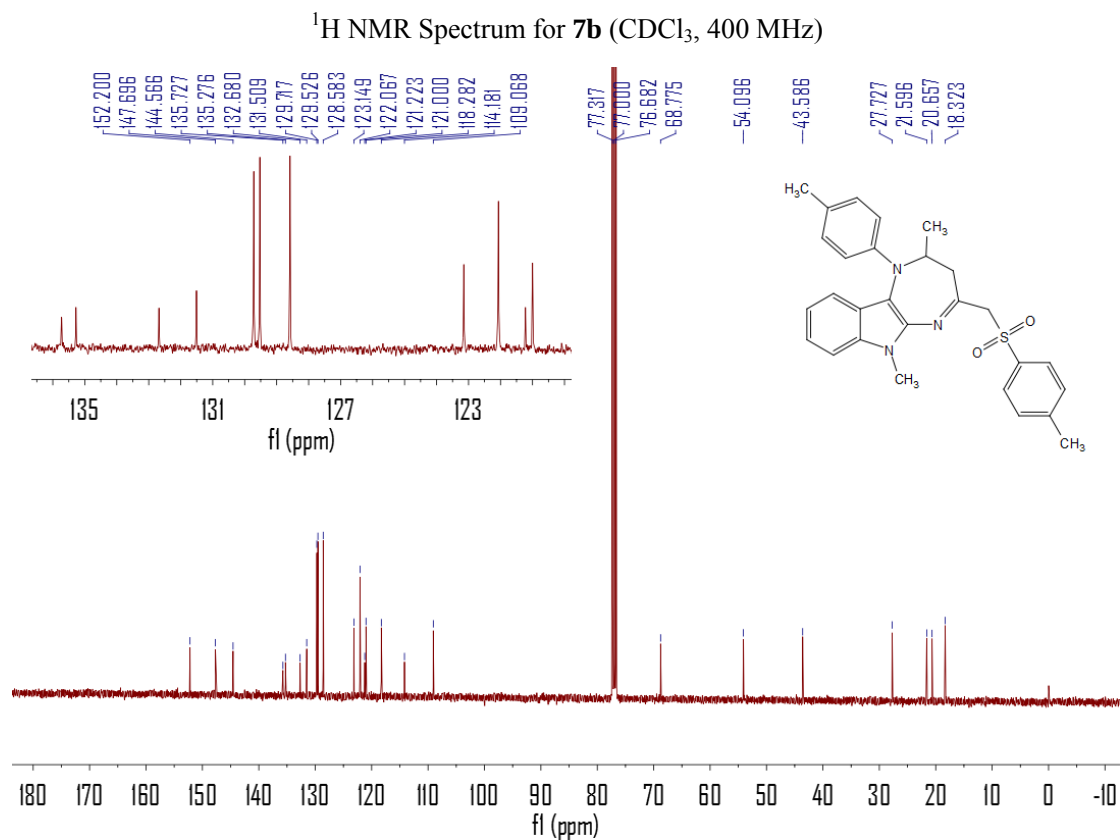
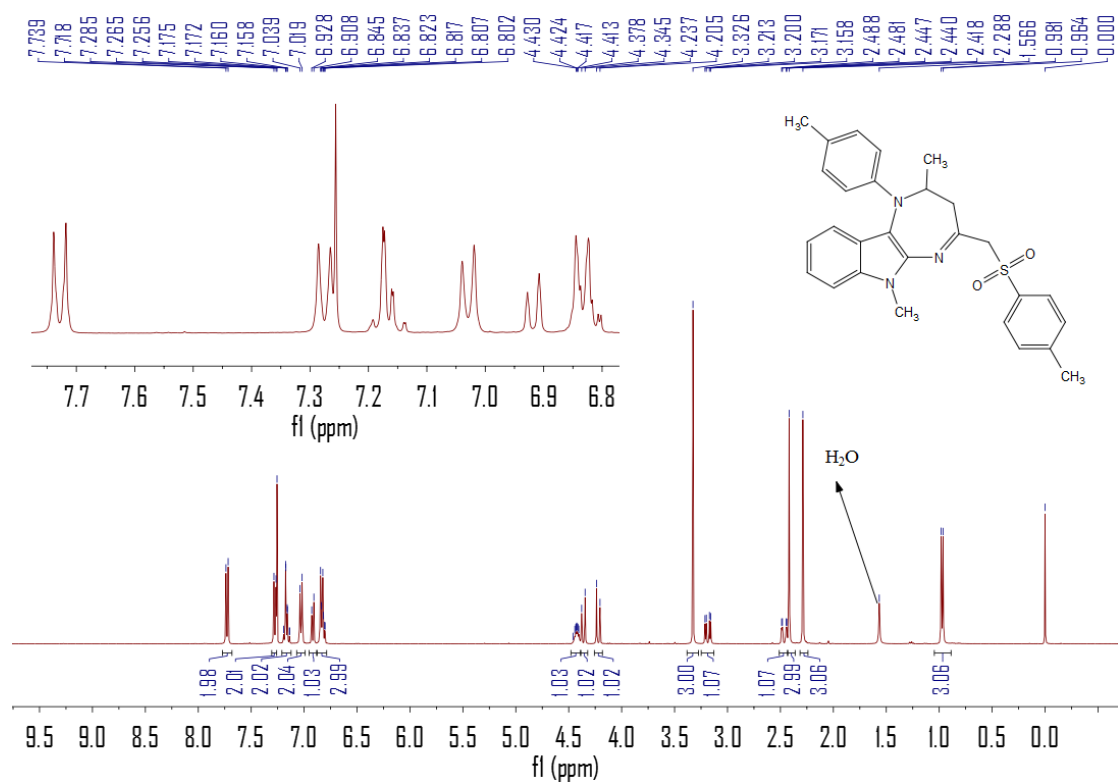
¹³C NMR Spectrum for **6k** (CDCl₃, 100 MHz)

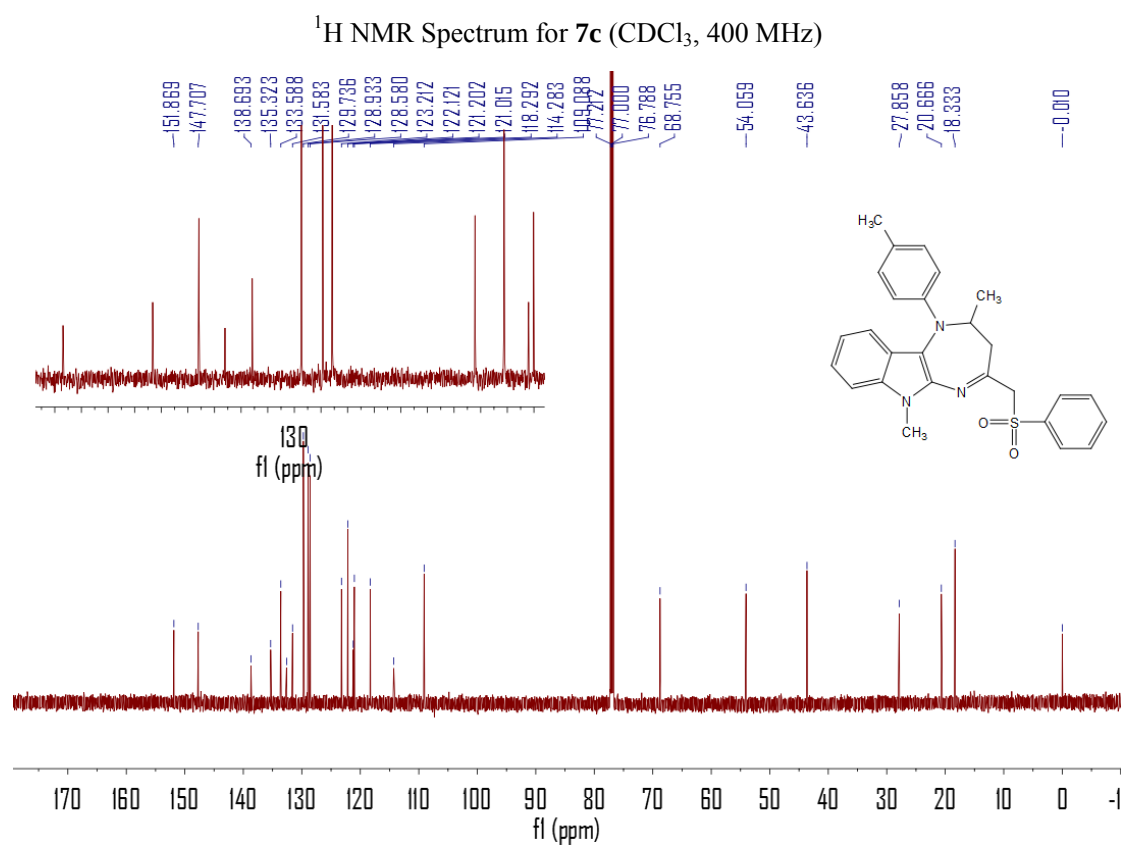
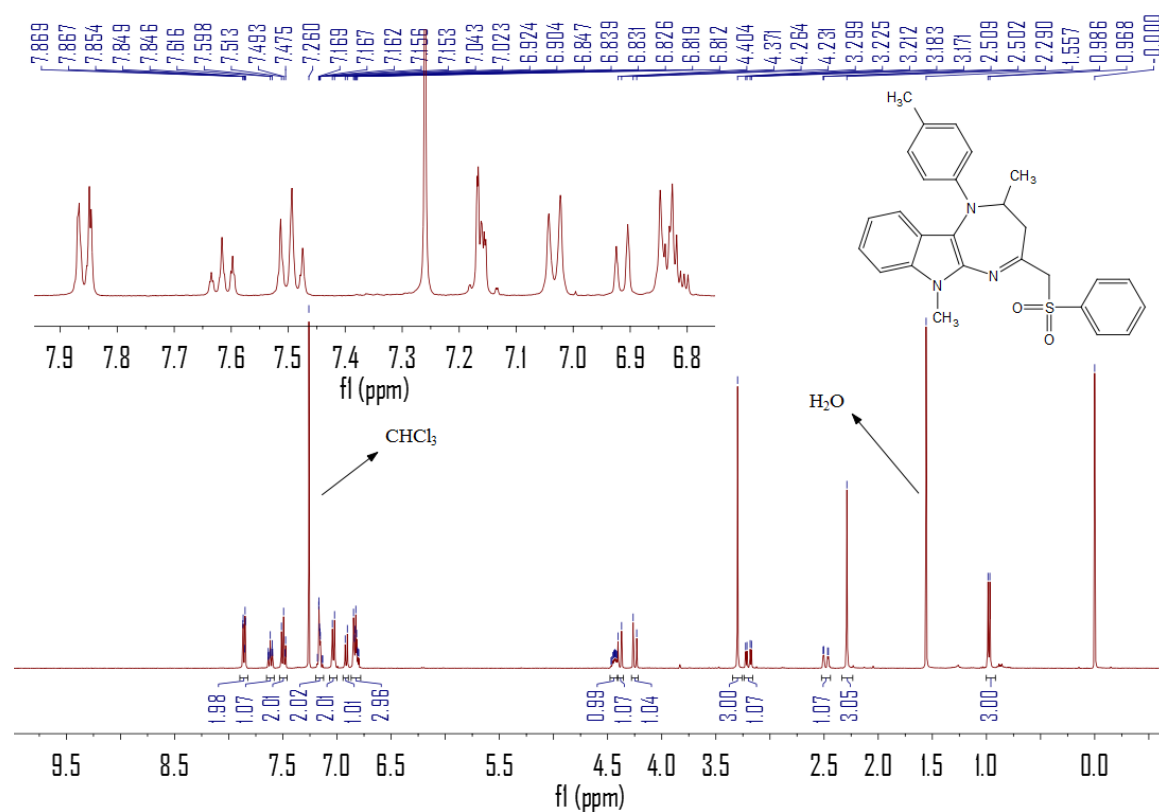


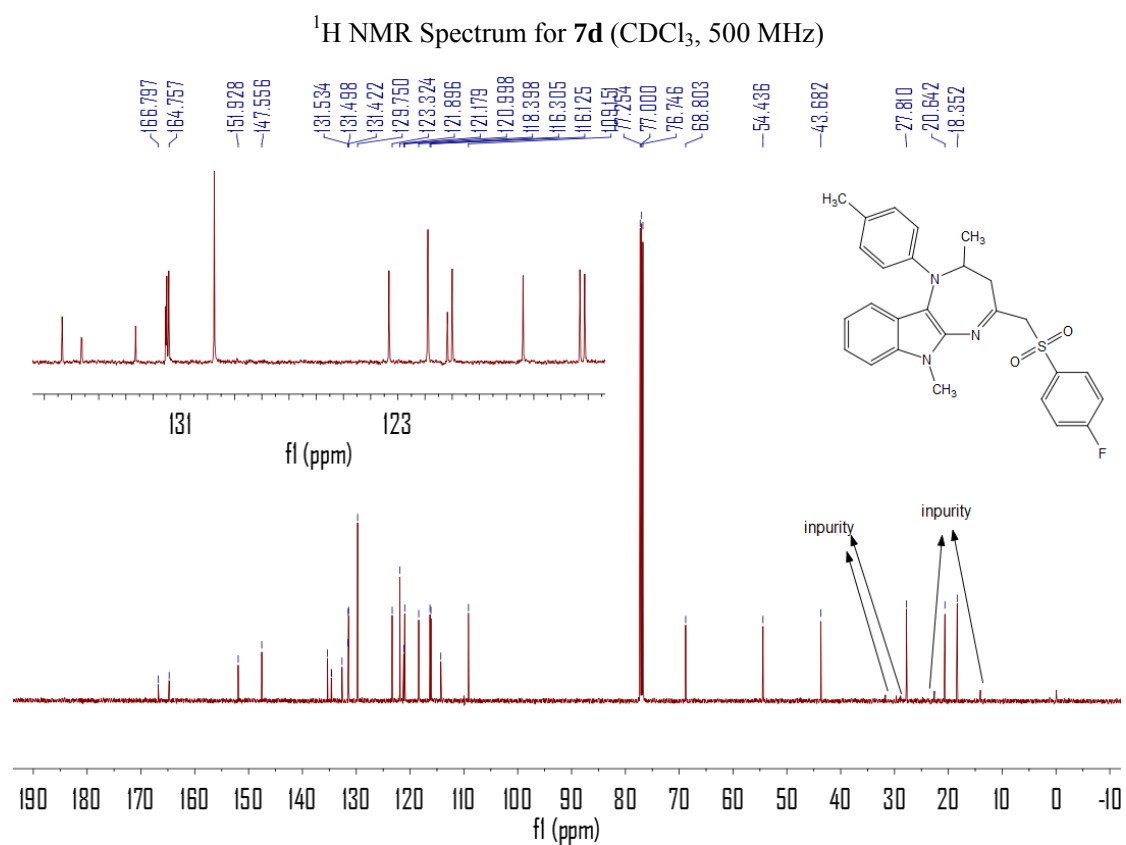
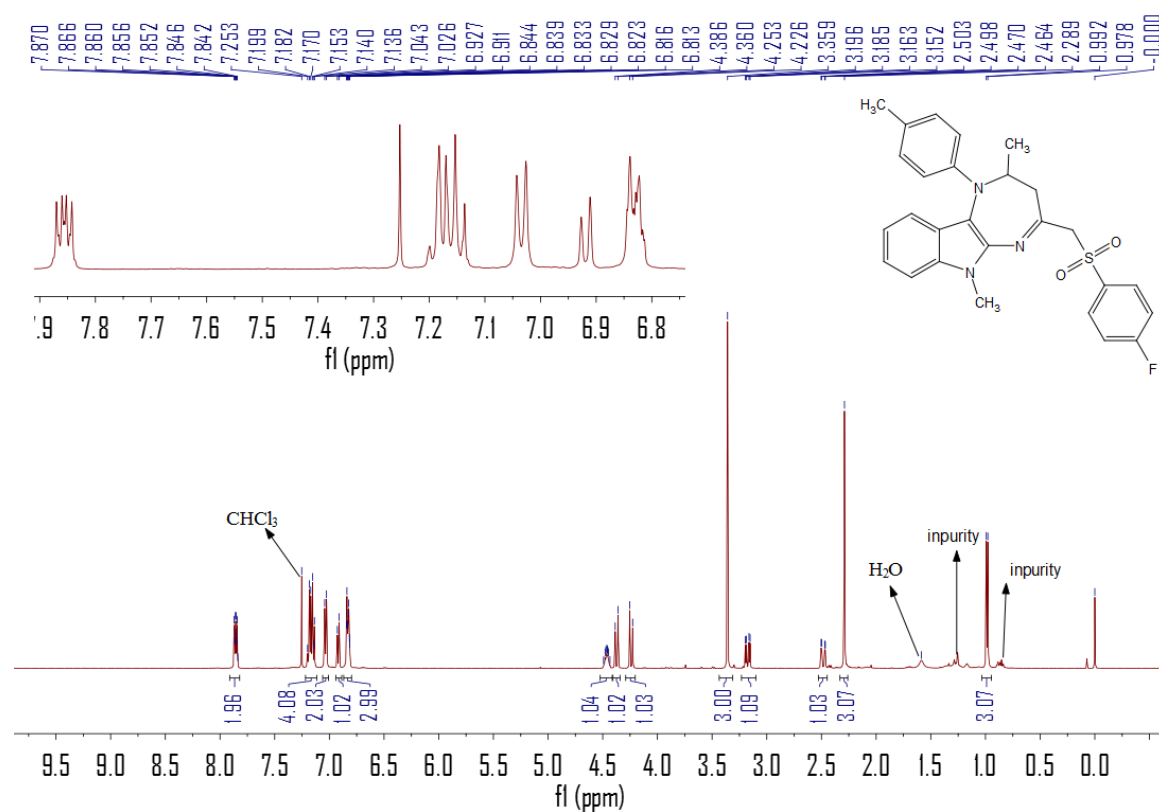
¹H NMR Spectrum for **7a** (Actone, 400 MHz)

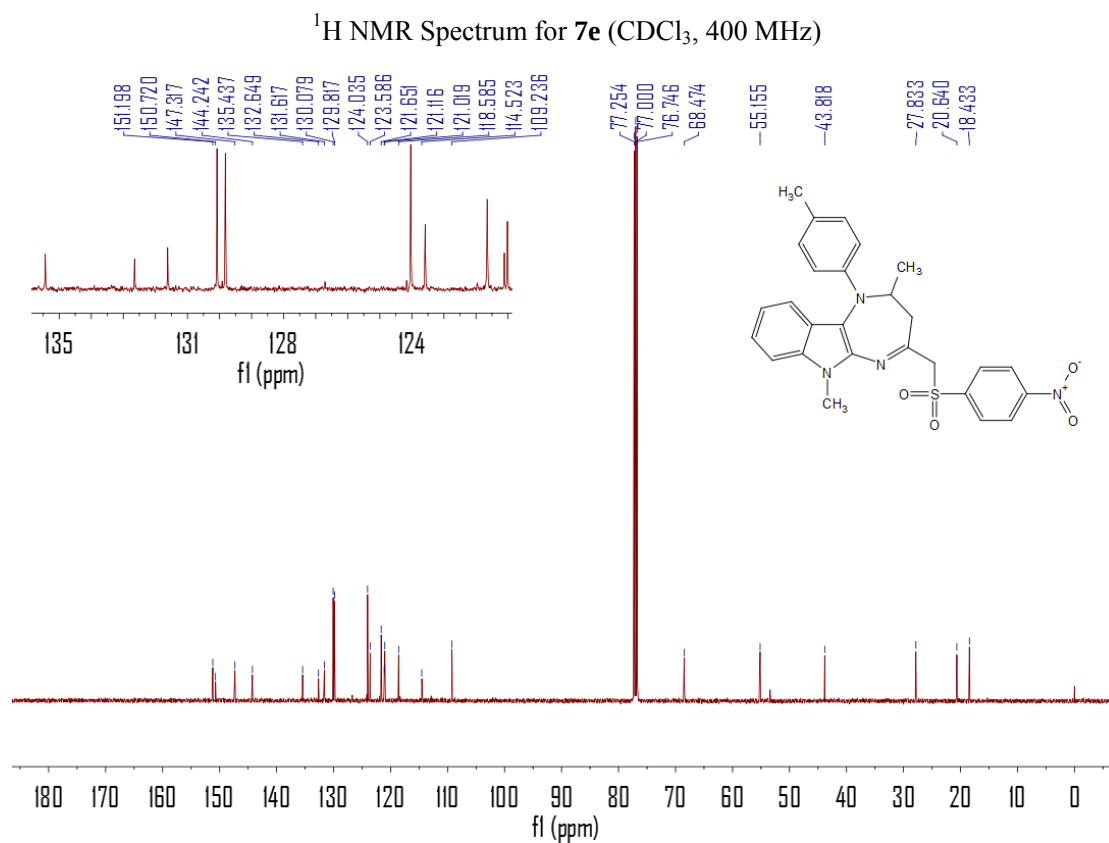
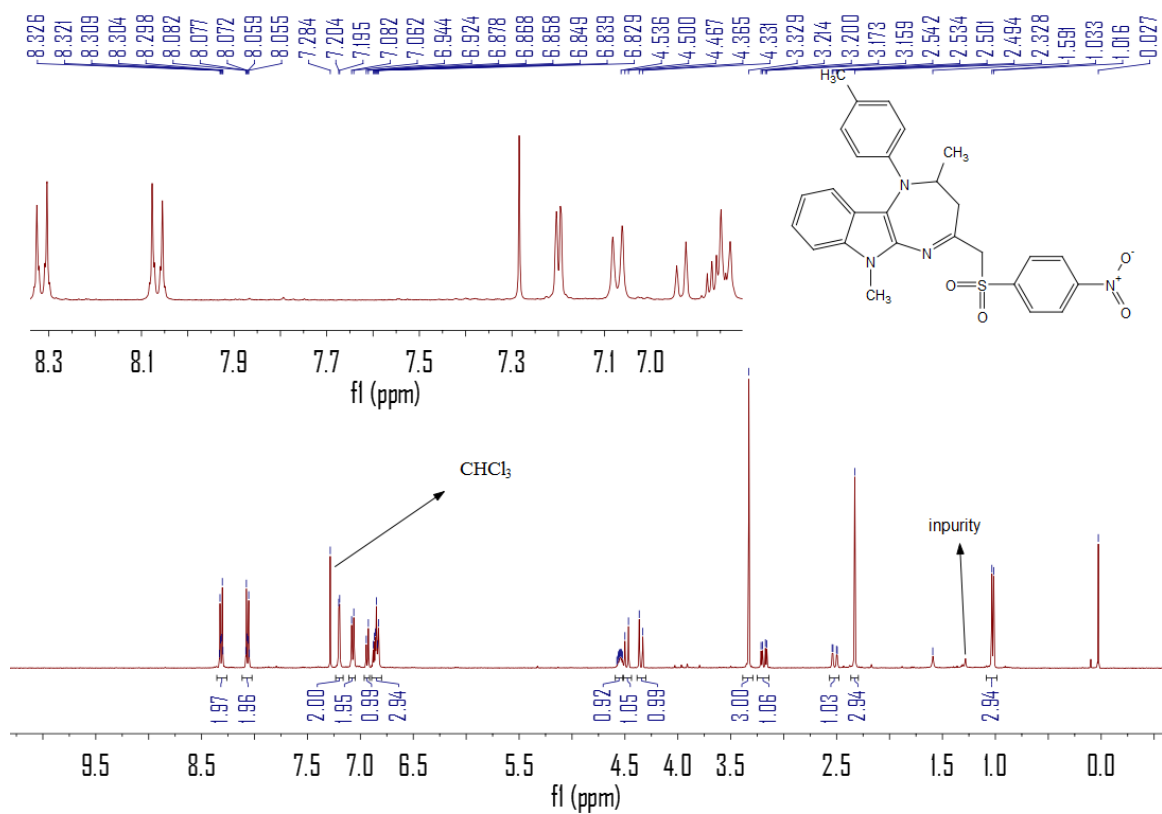


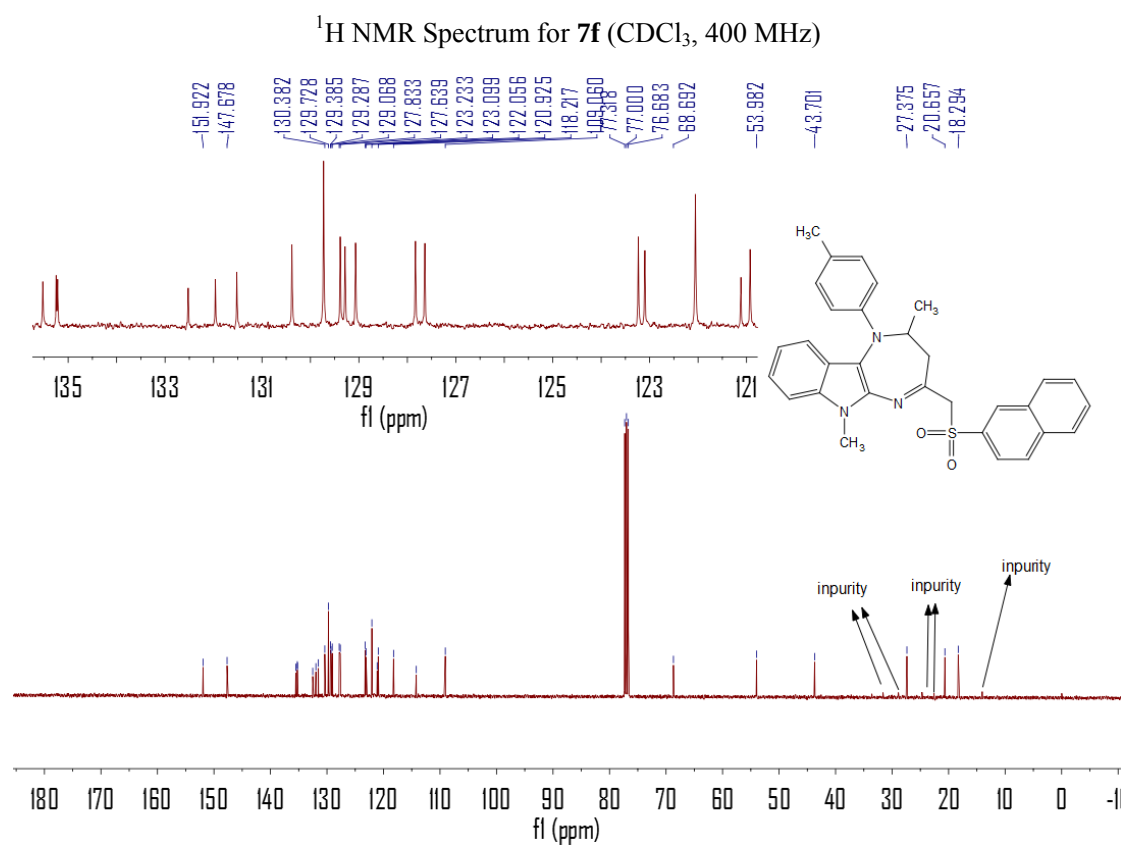
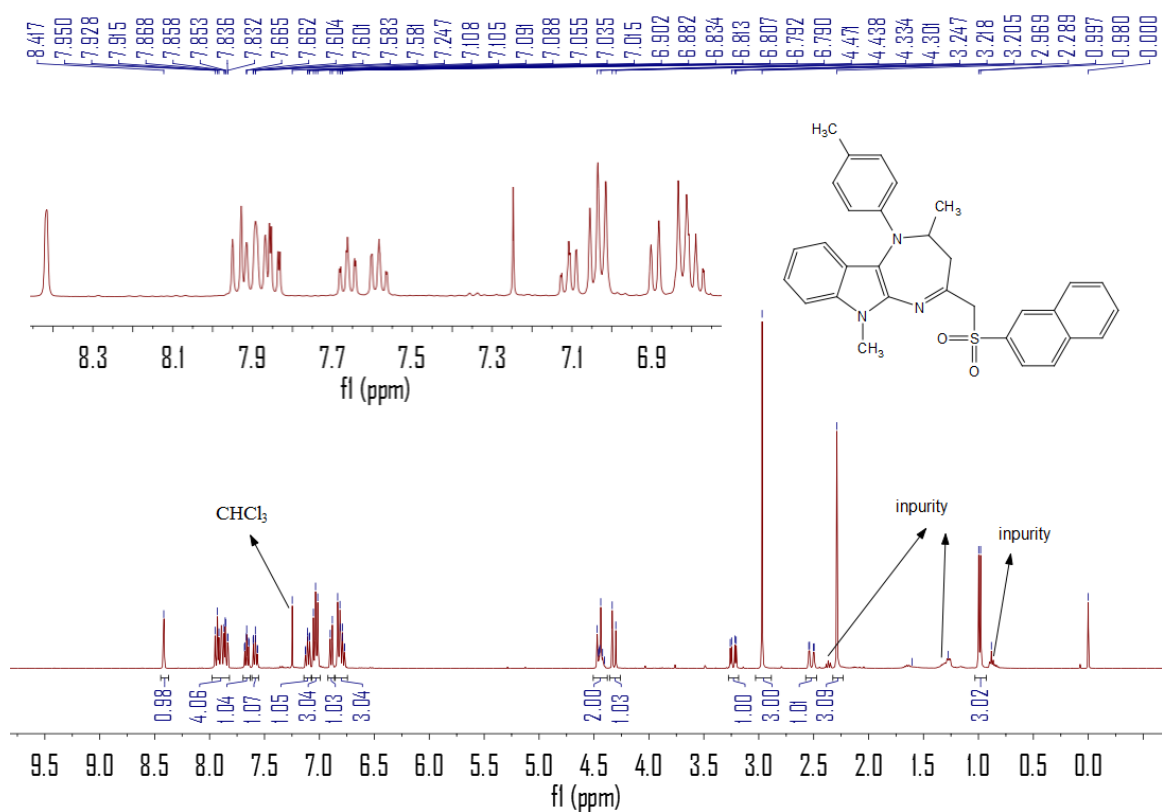
¹³C NMR Spectrum for **7a** (Actone, 100 MHz)

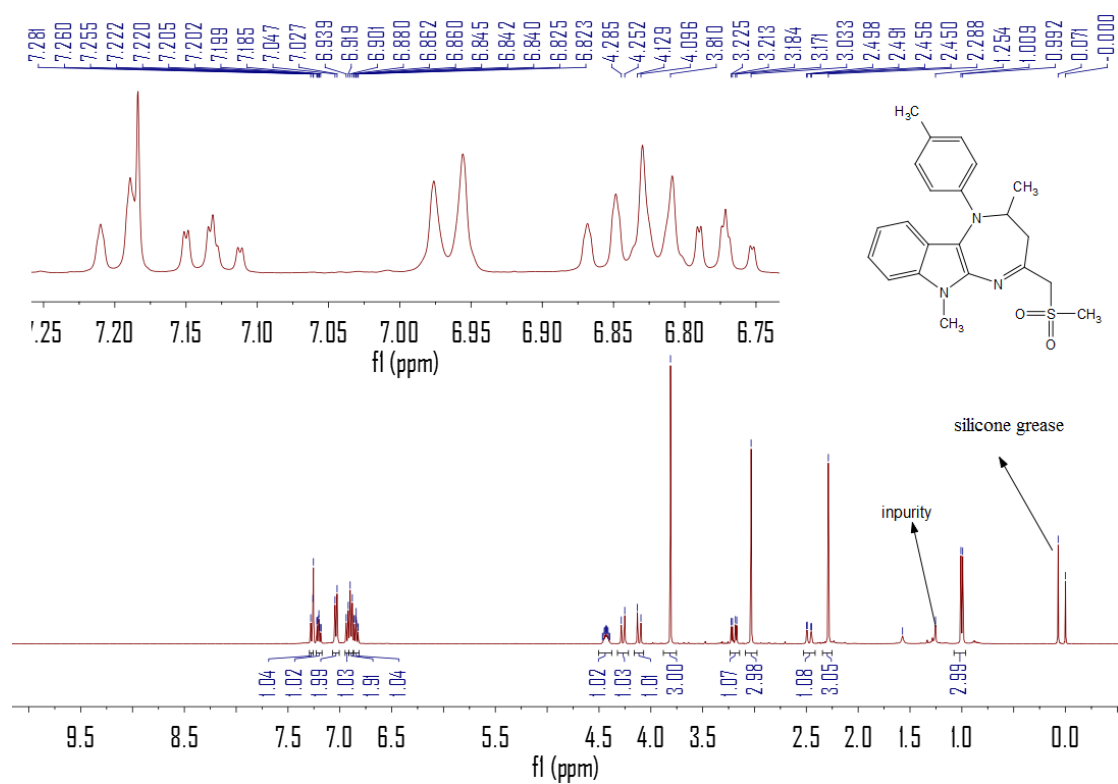




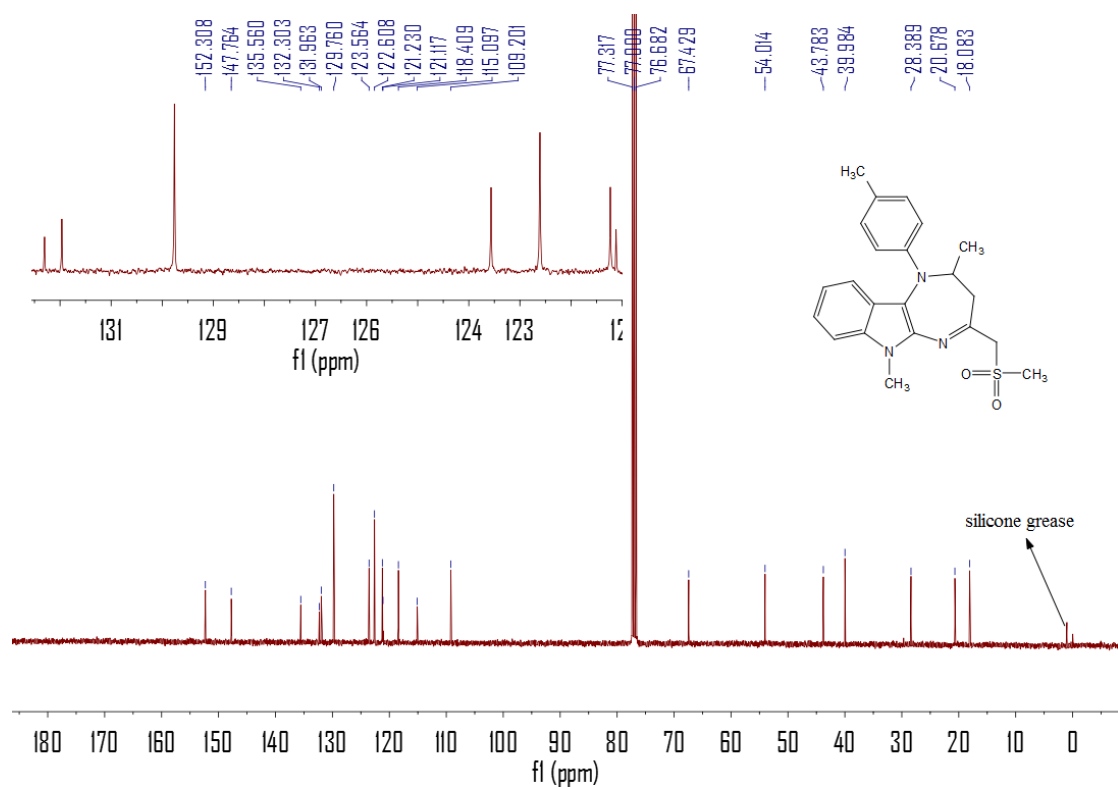




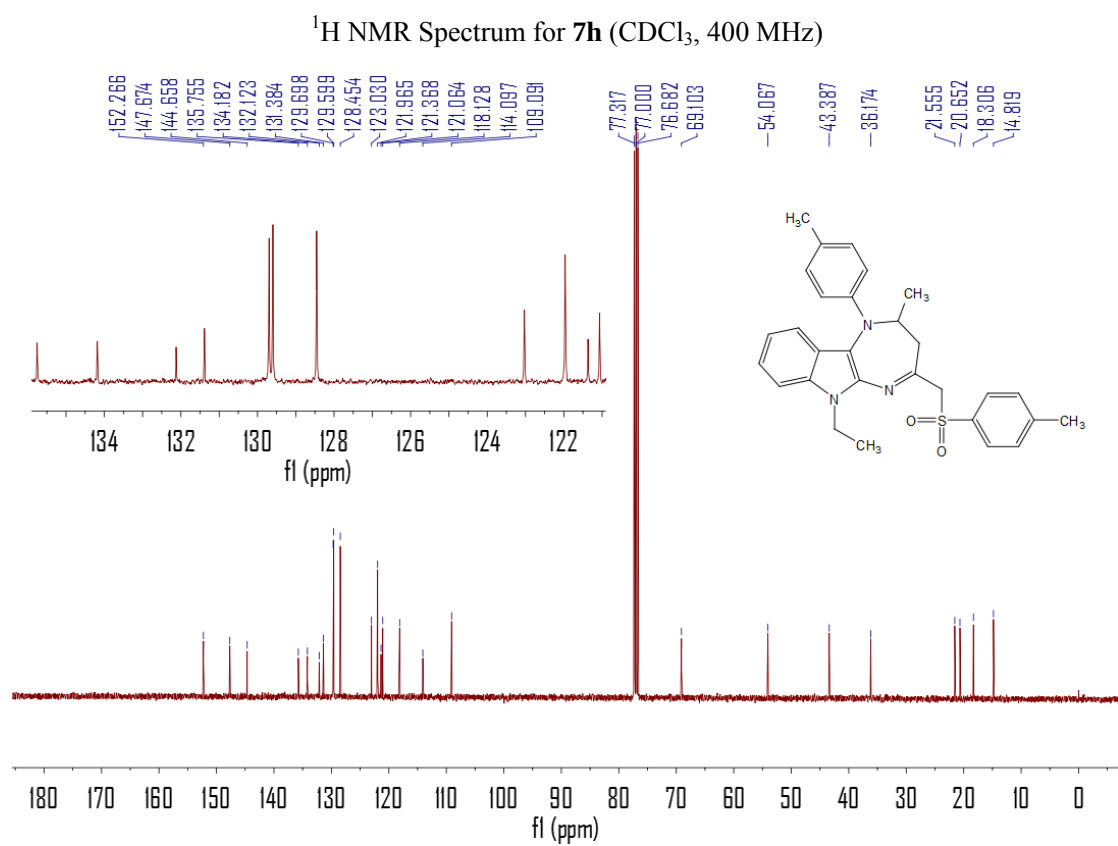
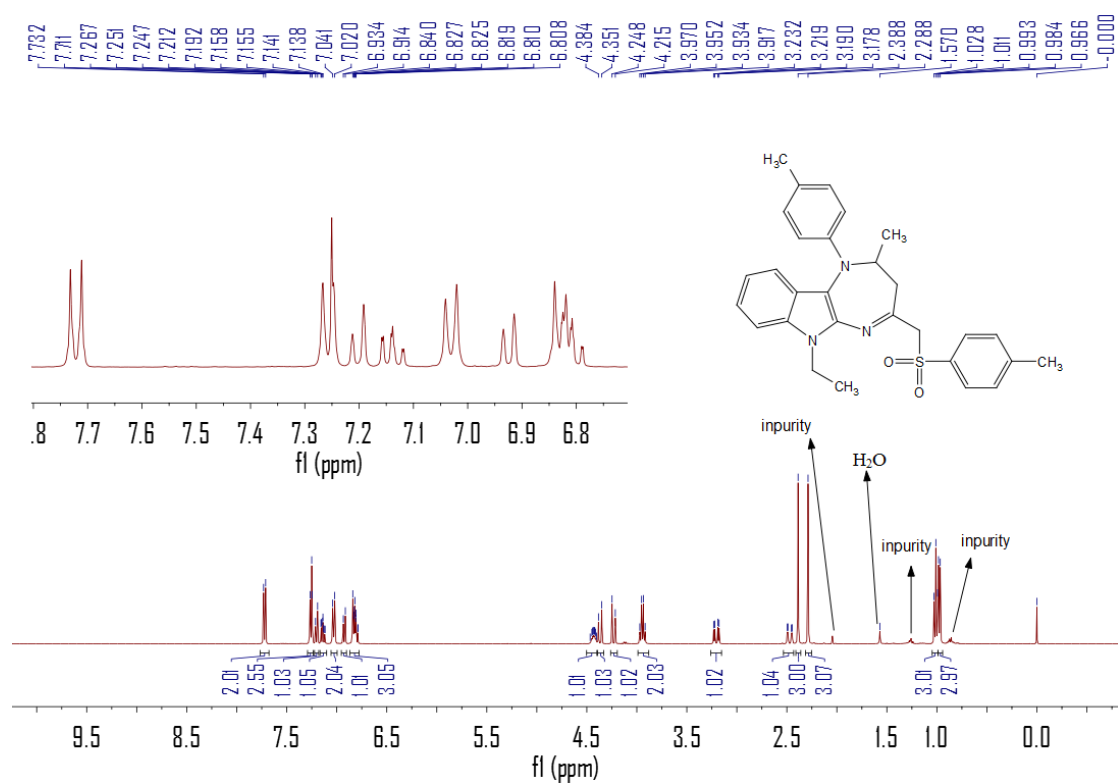


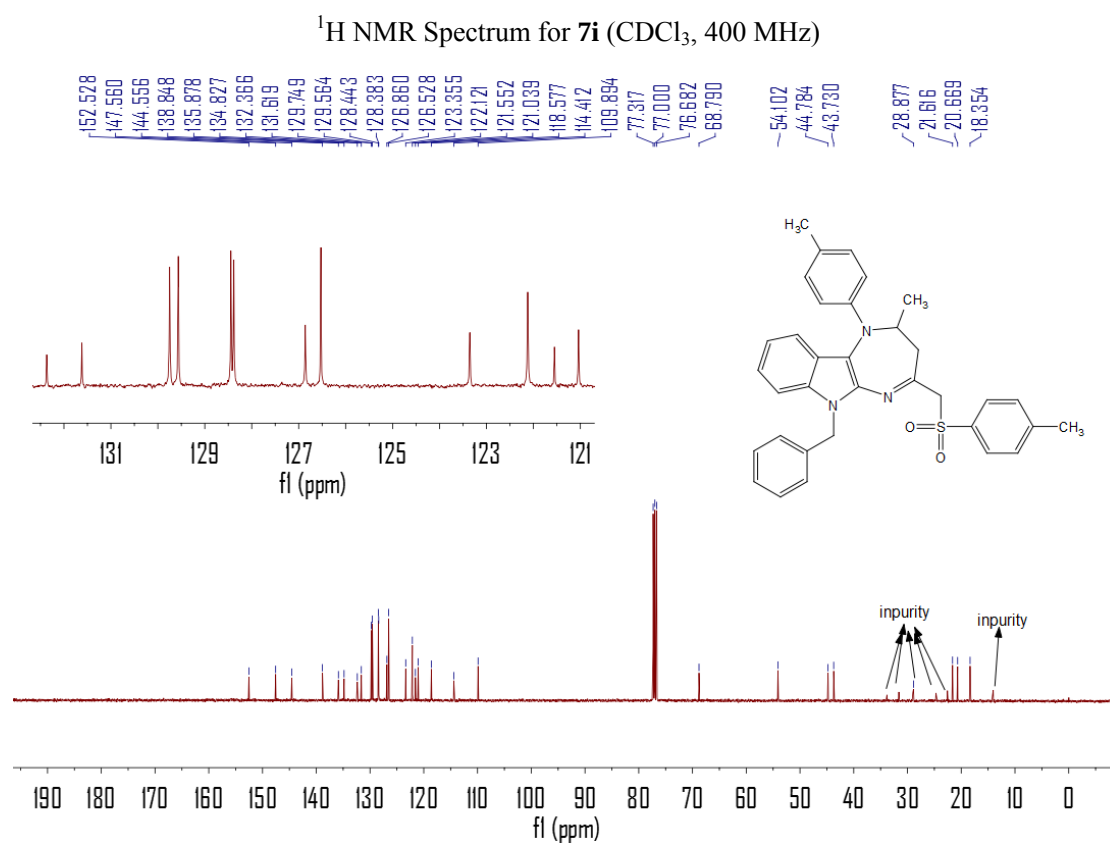
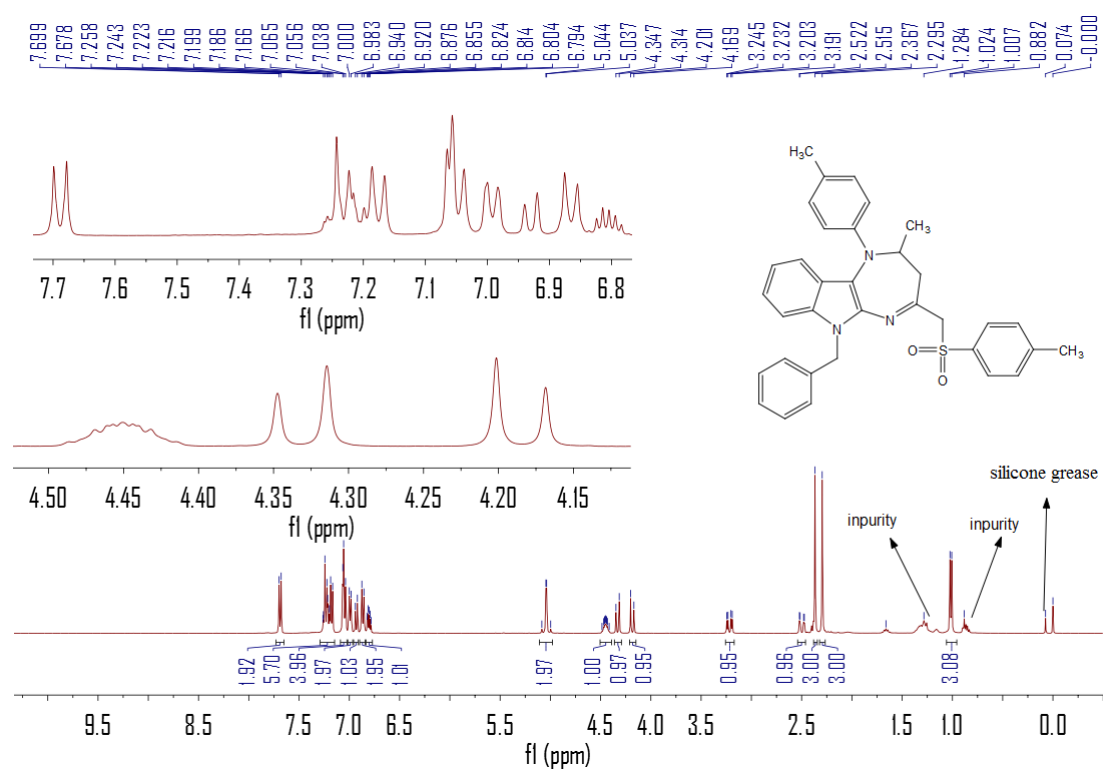


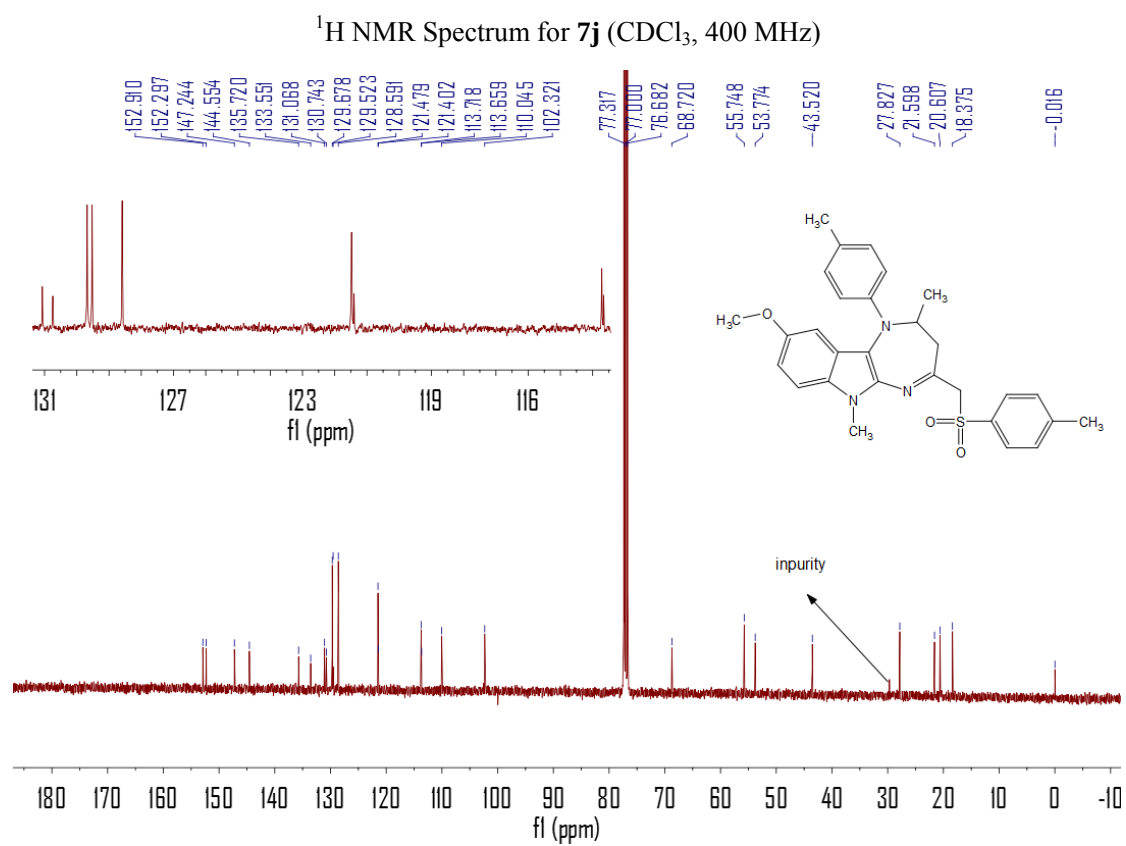
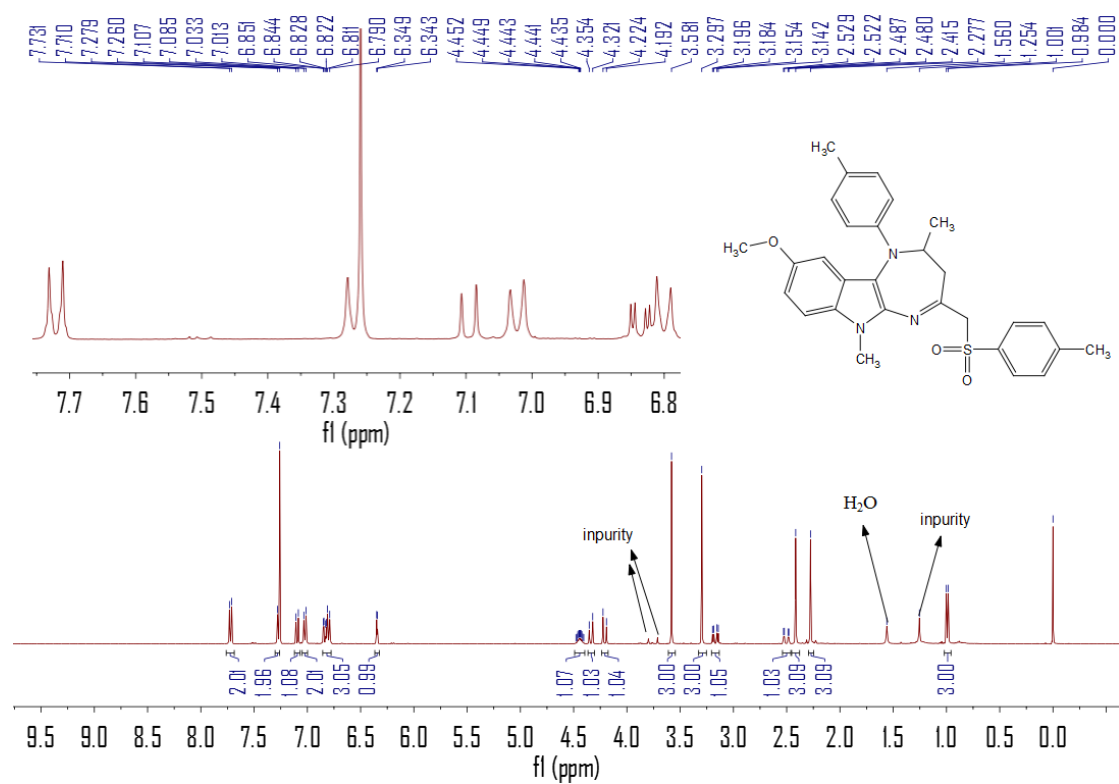
¹H NMR Spectrum for **7g** (CDCl₃, 400 MHz)

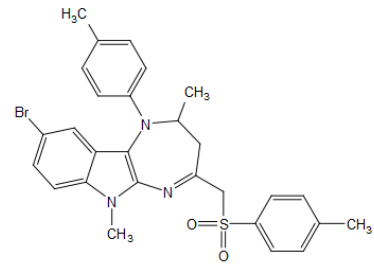


¹³C NMR Spectrum for **7g** (CDCl₃, 100 MHz)



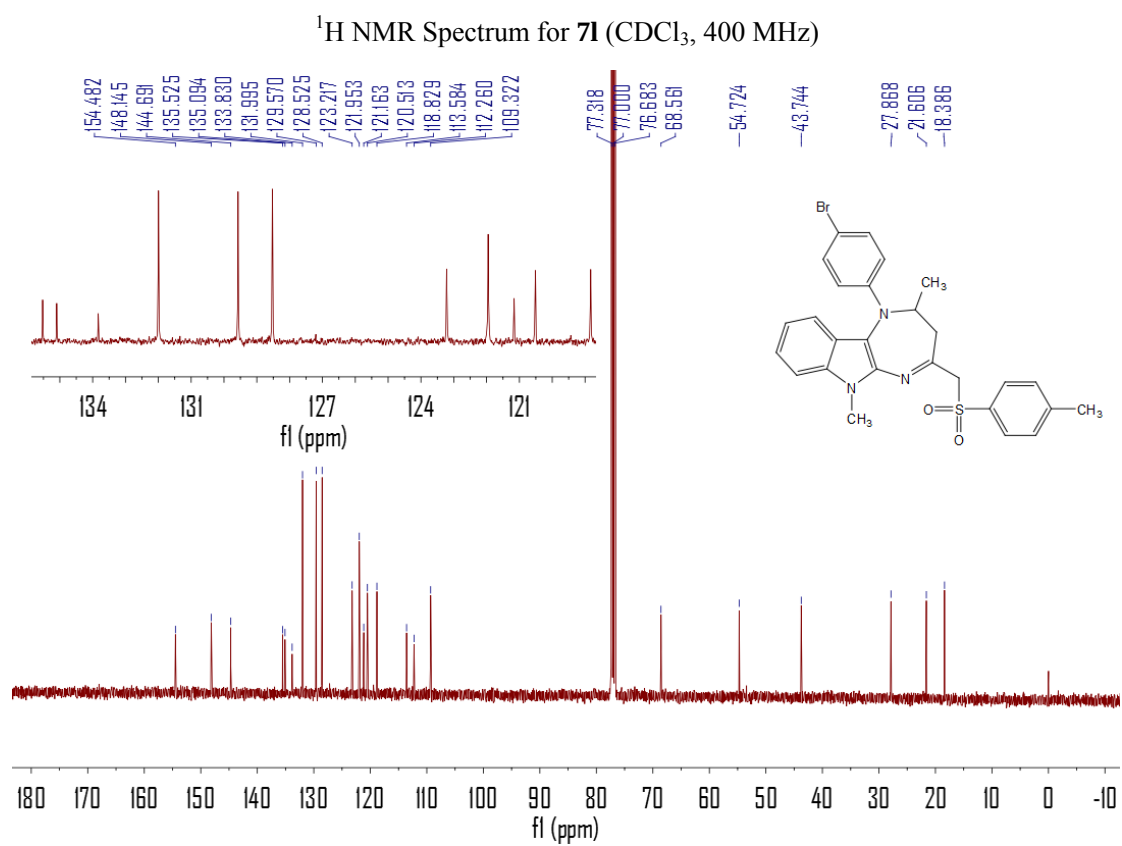
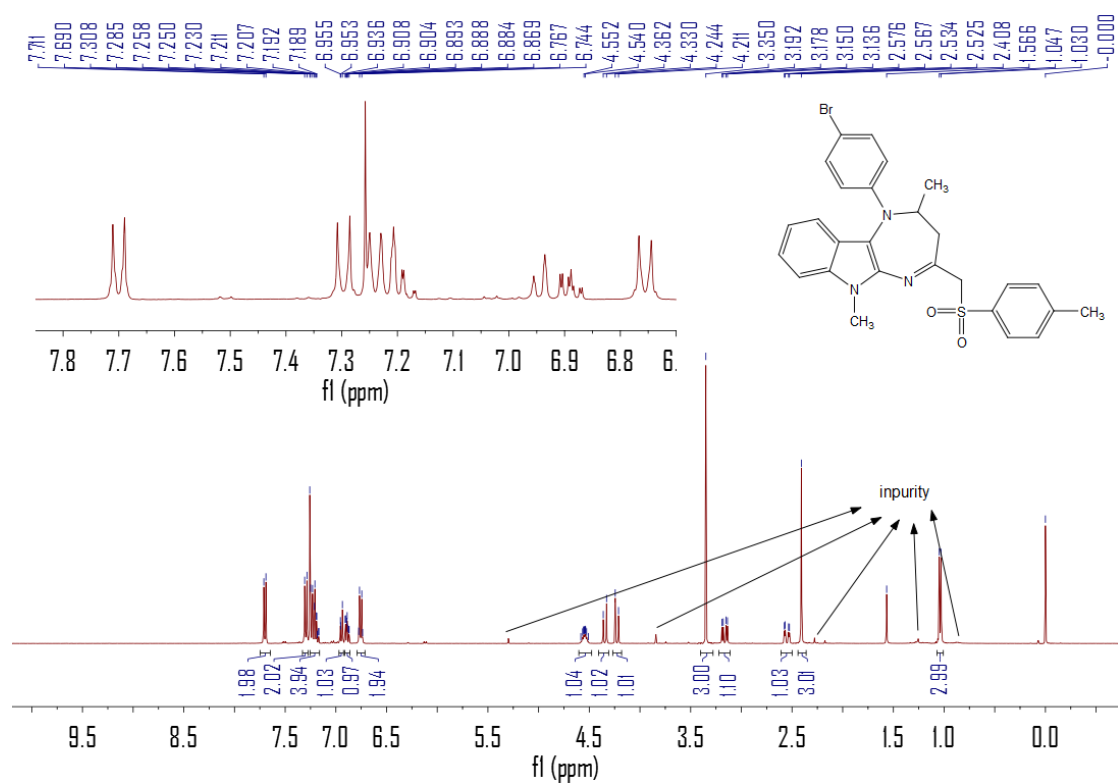


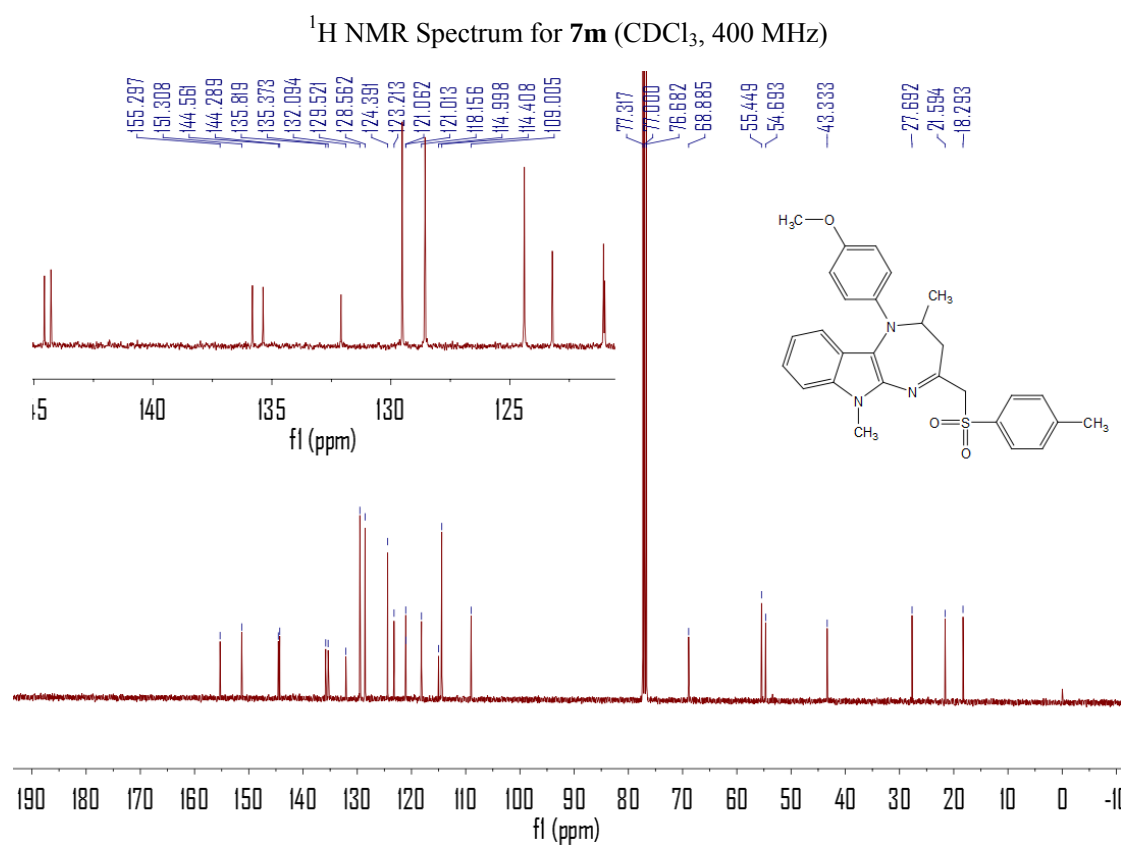
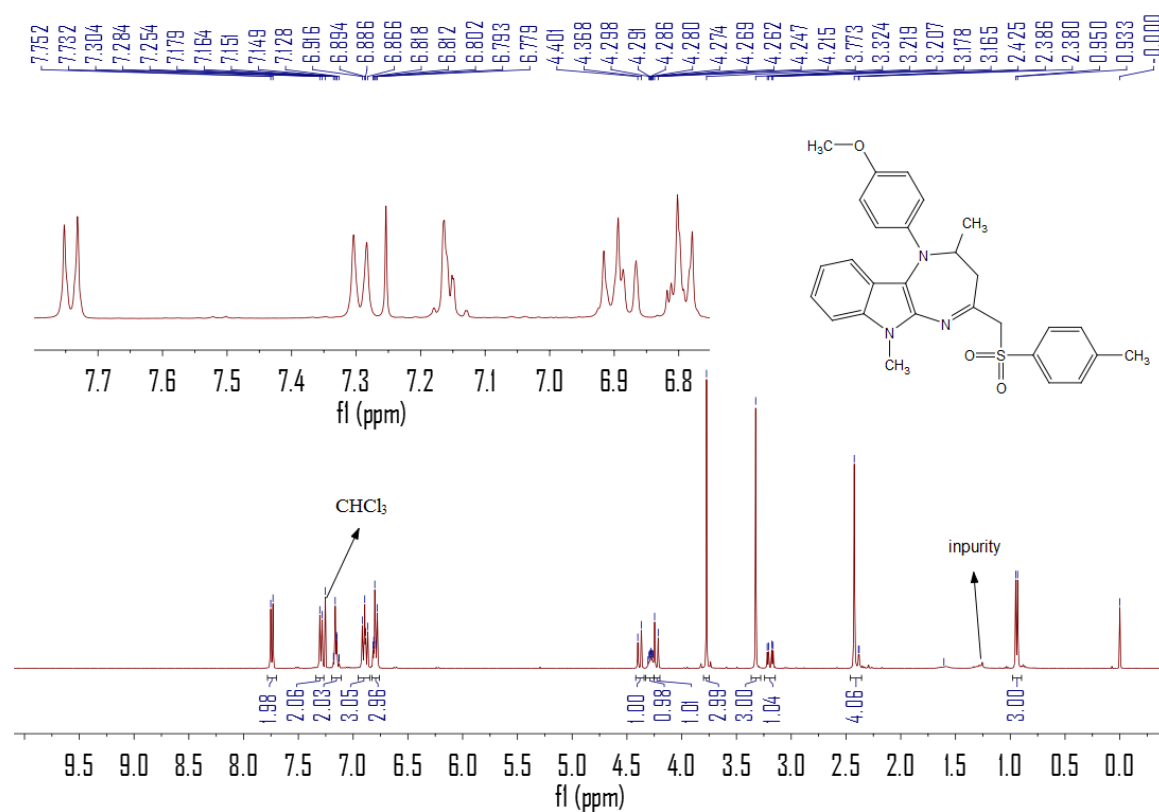


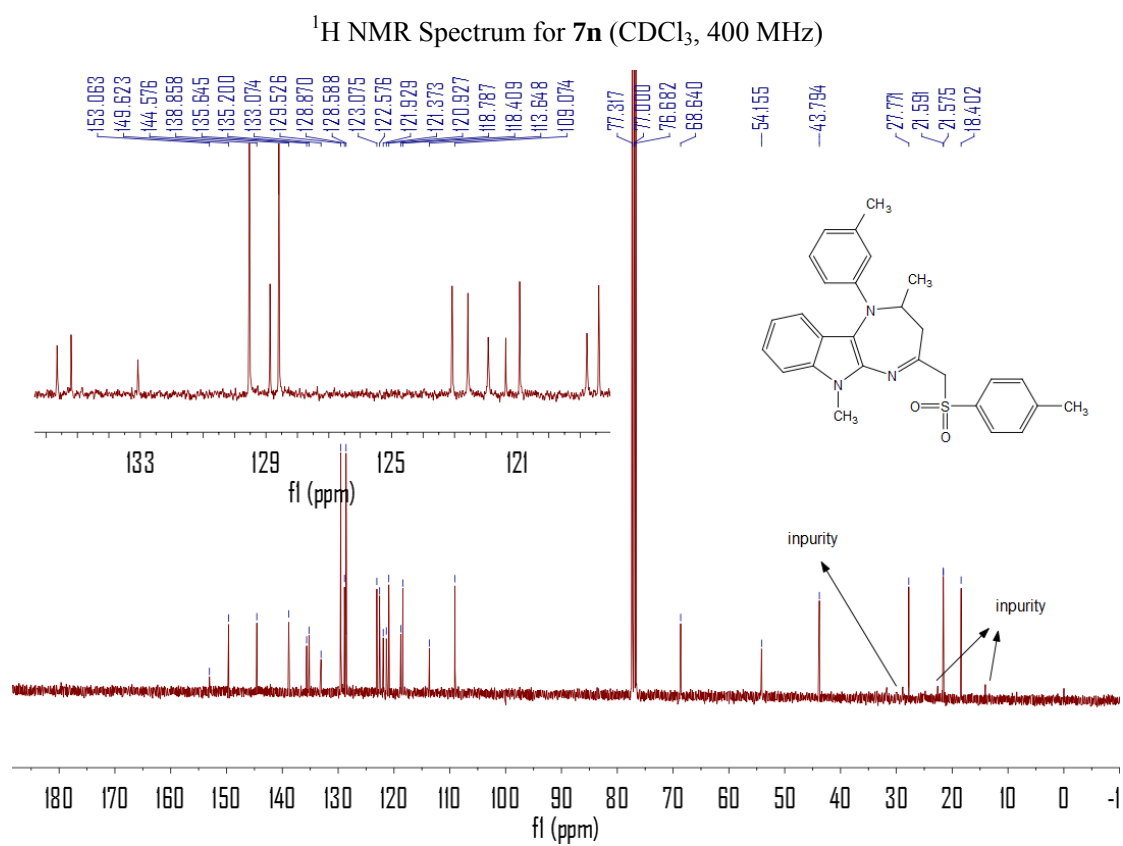
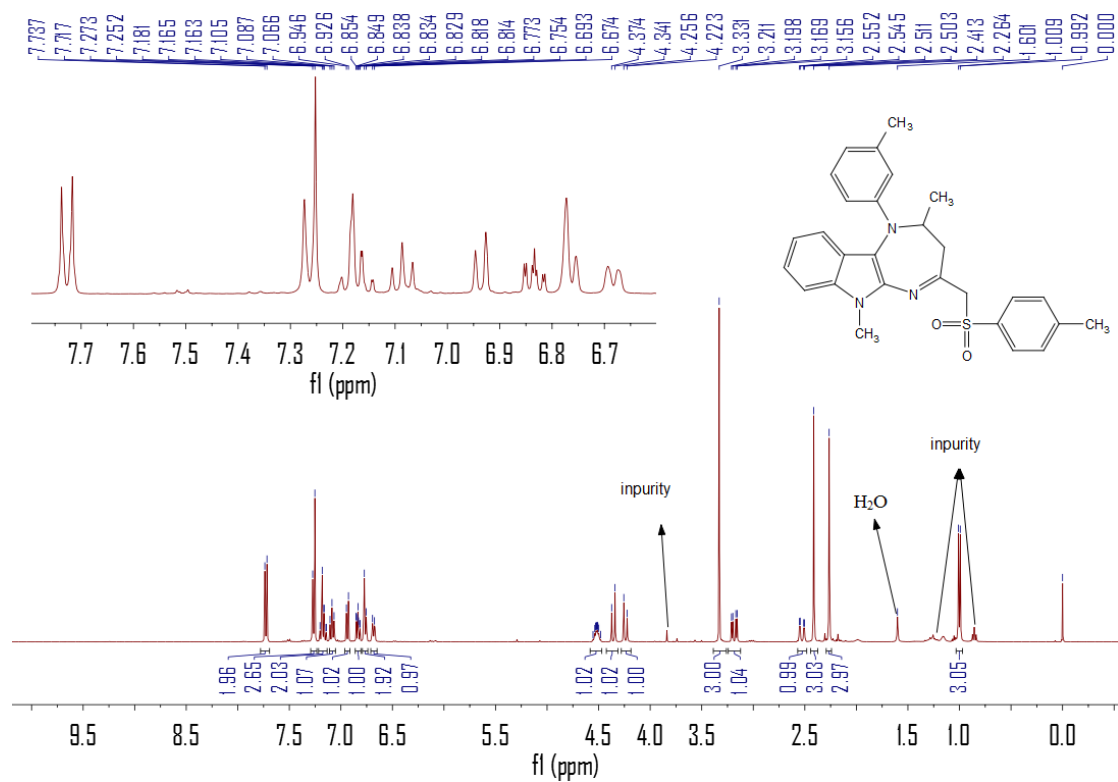


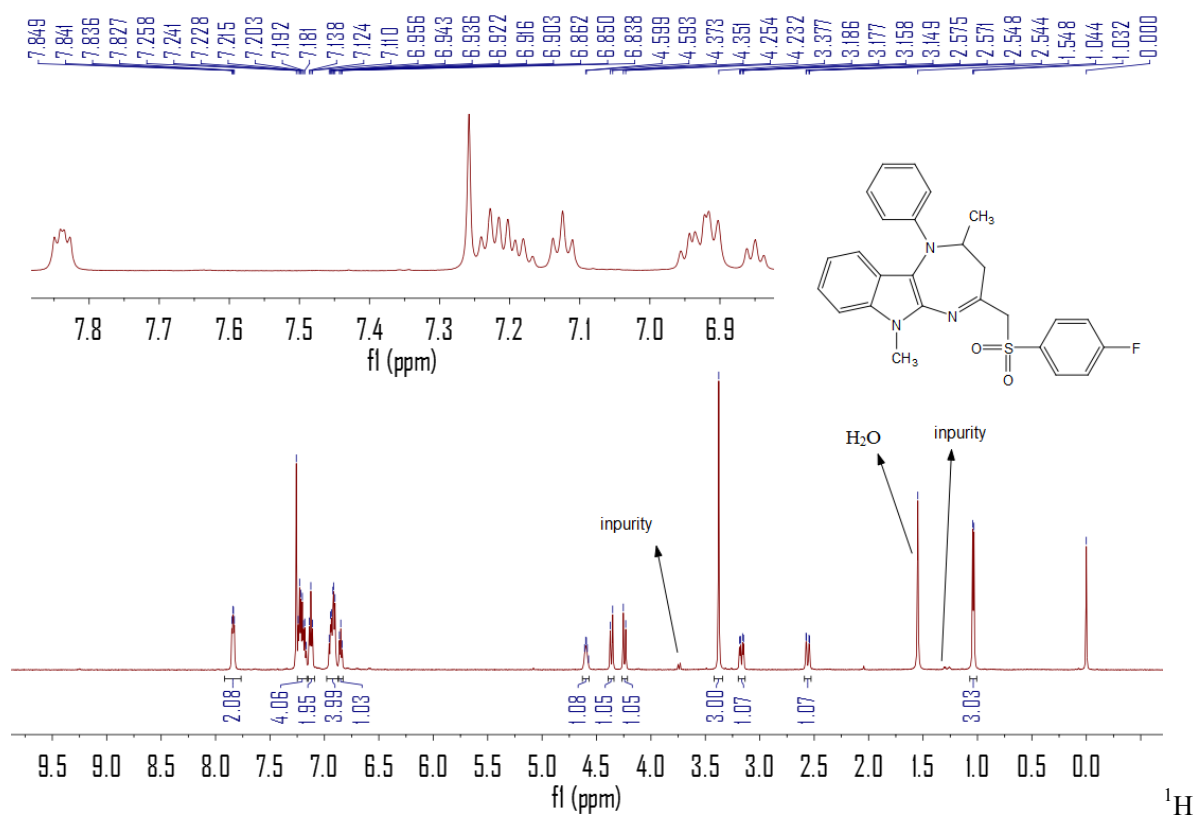
Chemical structure of compound 10b is shown on the right. The structure is a complex molecule with a central indole-like core, a bromophenyl group, a 4-methylphenyl group, and a 4-methylphenyl group.

Cc1ccc(cc1)S(=O)(=O)CC2=C3N(C)C(=N2)c4c(c3)c5ccccc5N(C)C4Br

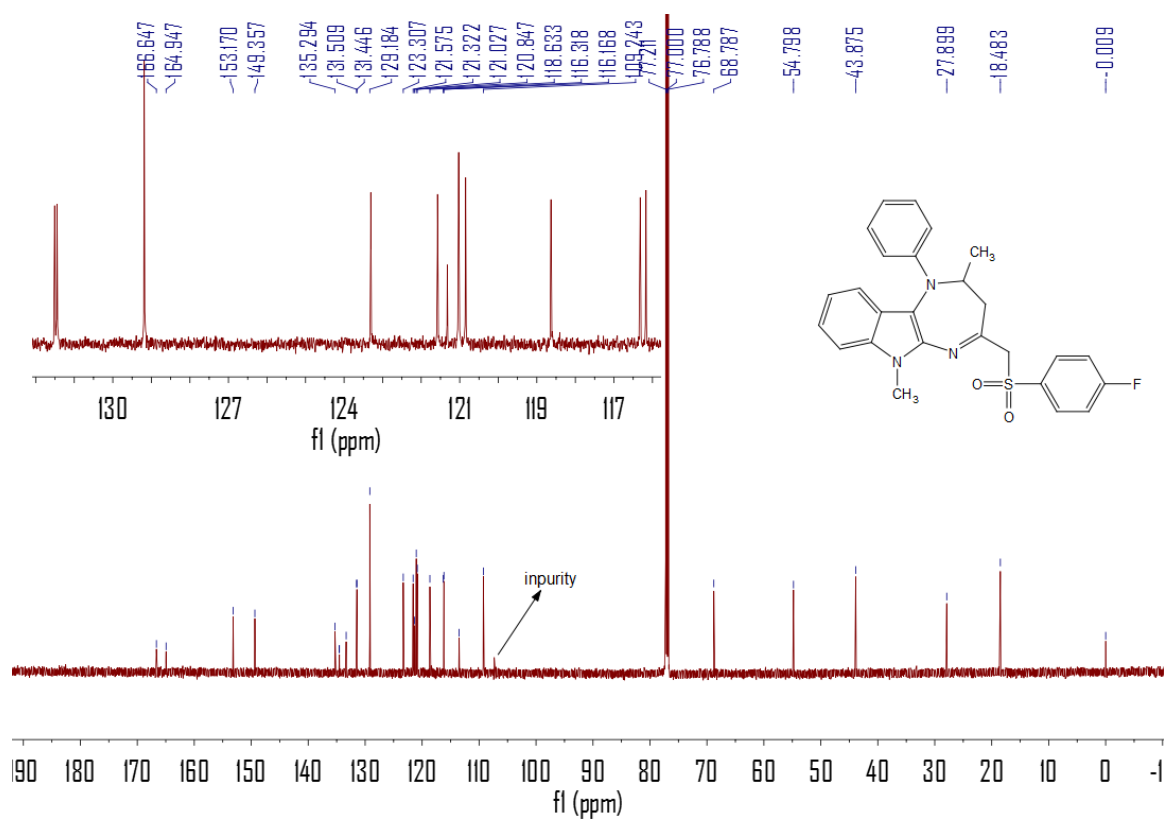




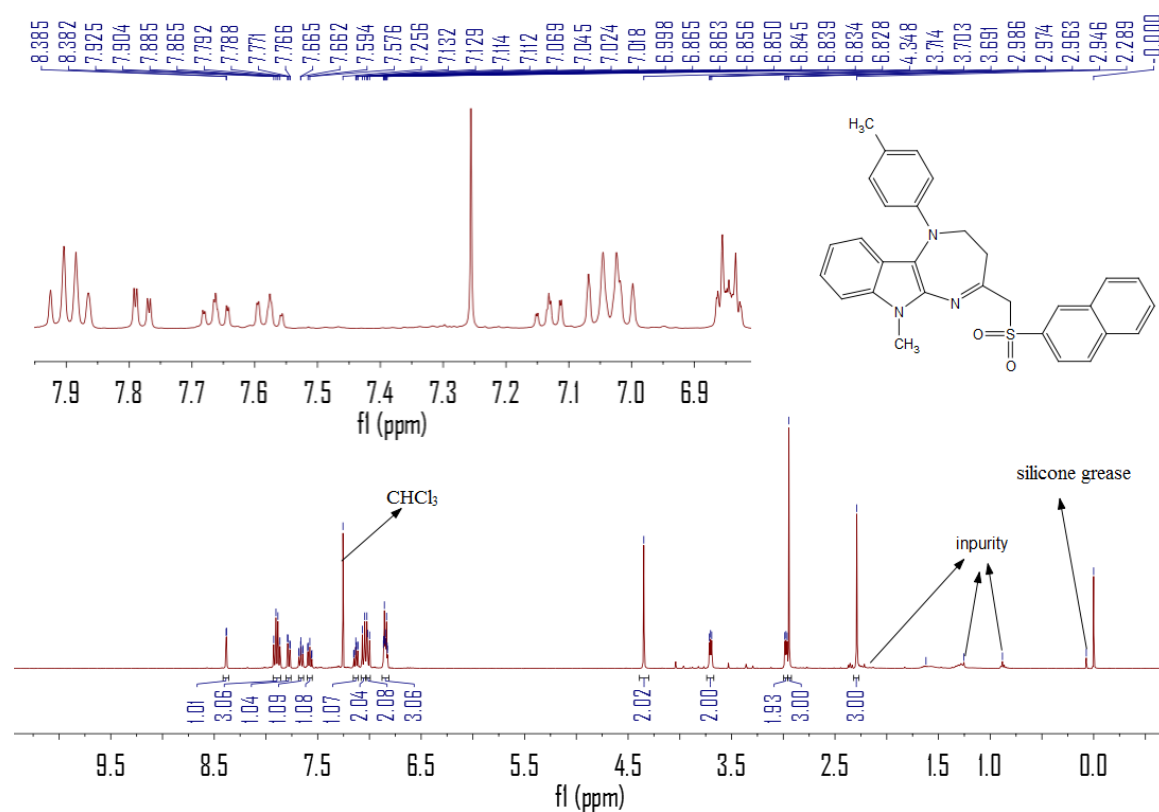




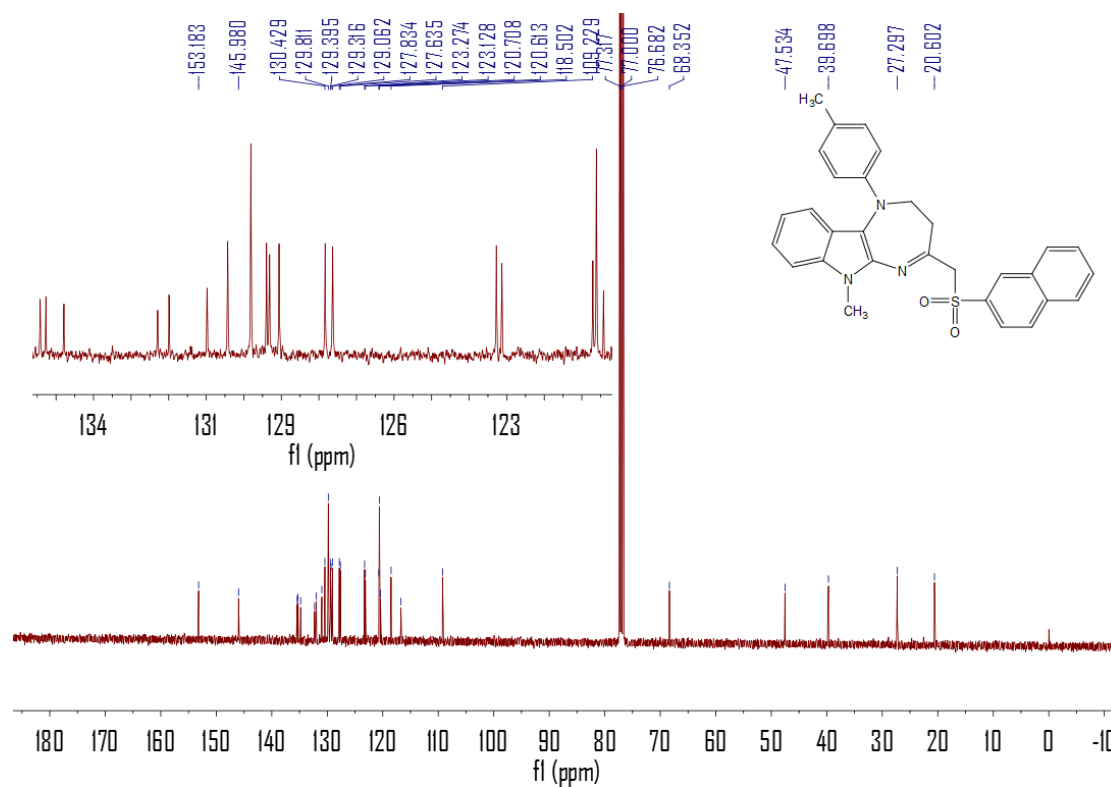
NMR Spectrum for **7o** (CDCl₃, 600 MHz)



¹³C NMR Spectrum for **7o** (CDCl₃, 150 MHz)



¹H NMR Spectrum for **7p** (CDCl₃, 400 MHz)



¹³C NMR Spectrum for **7p** (CDCl₃, 100 MHz)

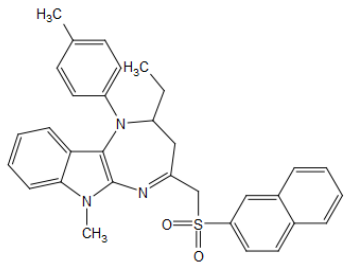


Figure 1 displays the ^{13}C NMR spectra of compound **1**. The top spectrum is the ^{13}C NMR spectrum in CDCl_3 , showing peaks from 135 to 121 ppm. The bottom spectrum is the ^{13}C NMR spectrum in $\text{DMSO}-d_6$, showing peaks from 180 to -1 ppm. The chemical structure of compound **1** is shown on the right.

Cc1ccc(cc1)C2=CN3C(=N2)C(=C4C=CC=C5C4=CC=C(C=C5)S(=O)(=O)C6=CC=CC=C6)CC3C

Crystal Structures of **7a**

