Supporting Information for

Preparation of Spiro[imidazolidine-4,3'-indolin]-2'-imines via Copper(I)-Catalyzed Formal [2+2+1] Cycloaddition of 3-Diazoindolin-2-imines and Triazines

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Content

General Information

^{1}H NMR spectra were obtained on 400, or 600 MHz in $CDCl_3$ or DMSO. The chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on 100, or 150 MHz in $CDCl_3$ or DMSO. The chemical shifts were reported in ppm referenced to the internal solvent signals (77.0 ppm for $CDCl_3$ or 42.0 ppm for DMSO). The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. $^{13}C\{^{1}H\}$ for proton-decoupled carbon data was recorded Coupling constants J were reported in hertz unit (Hz). Infrared spectra were obtained on an FTIR spectrometer. High-resolution mass spectra (HRMS) data were obtained by using ESI ionization. Melting points were measured with SGW X-4 micro melting point apparatus. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254.

DCE, DCM and MeCN were dried by distillation over CaH_2. THF and toluene was distilled from Na. $Rh_2(Oct)_4$, $Cu(OTf)_2$, $Cu(OTf)\cdot 1/2C_6H_6$, $Cu(OAc)_2$, CuCl, $Cu(CN)_4PF_6$, AgOTf were used as received from the commercial sources. Triazine, 3-diazoindolin-2-imines and its analogues were prepared according to the published methods.[1-3]

References

1 (a) Kawaguchi, A. W.; Sudo, A.; Endo, T. *J. Poly. Sci. PART A: Poly. Chem*. **2012**, *50*, 1457. (b) Bujnowski, K.; Adamczyk-W, A.; Synoradzki, L. *ARKIVOC* **2008**, *13*, 106.

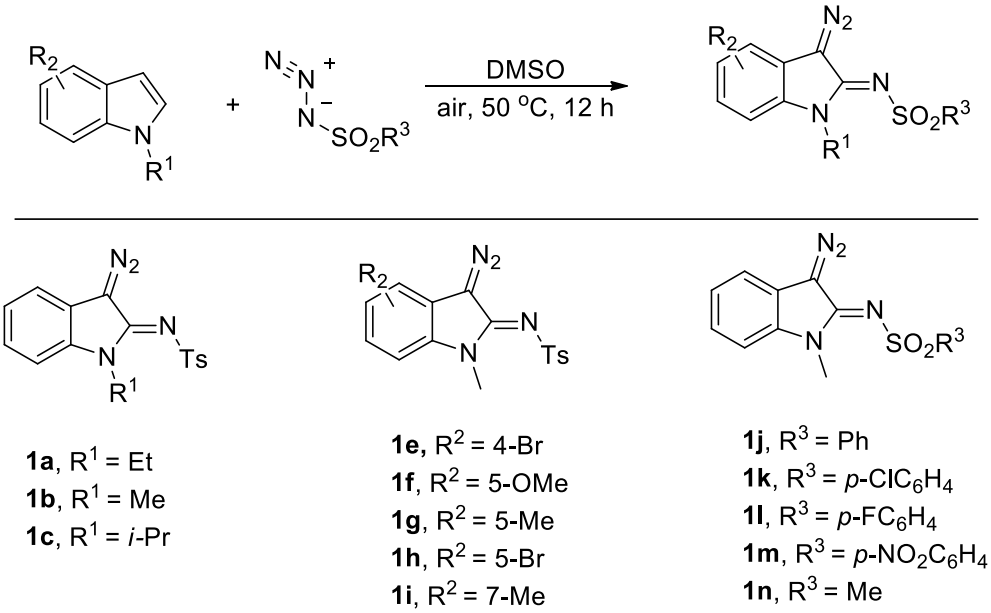
2. Xing, Y. P.; Sheng, G. R.; Wang, J.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 1244.

3. Sheng, G. R.; Huang, K.; Chi, Z. H.; Ding, H. L.; Xing, Y. P.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 5096

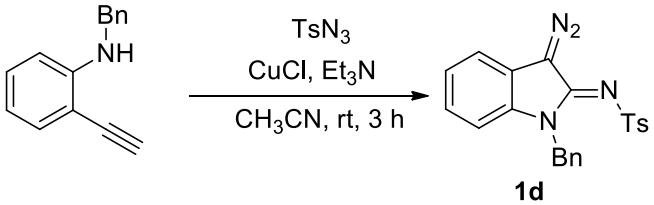
General Procedure for the Synthesis of 1

3-Diazoindolin-2-imines **1a**-**1c** and **1e**-**n** were prepared from indole derivatives and sulfonyl azides according to our published procedure (Scheme S1).[1] 3-Diazoindolin-2-imine **1d** was prepared from N-benzyl-2-ethynylaniline and tolsyl azide through our published method (Scheme S2).[2] The prepared 3-diazoindolin-2-imines were compared with the measured spectroscopic and physical data, and confirmed their identity.

Scheme S1. Preparation of Compounds **1a**-**1c** and **1e**-**n**



Scheme S2. Preparetion of Compound **1d**

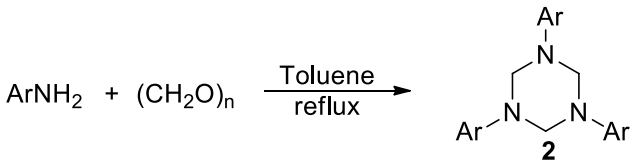


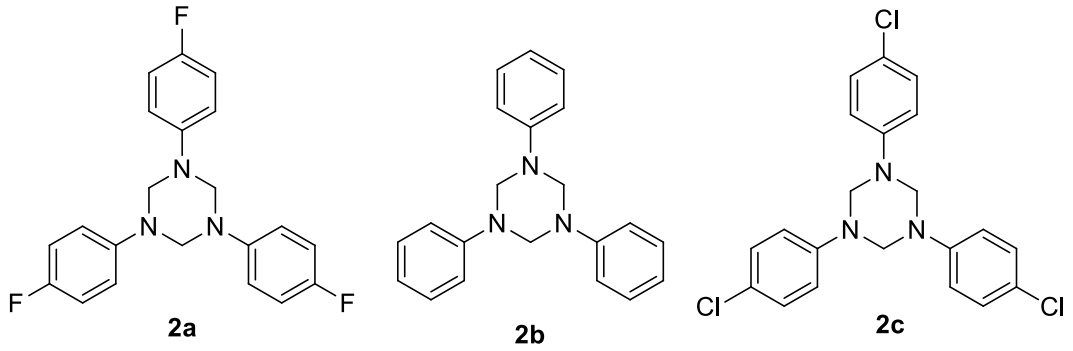
References

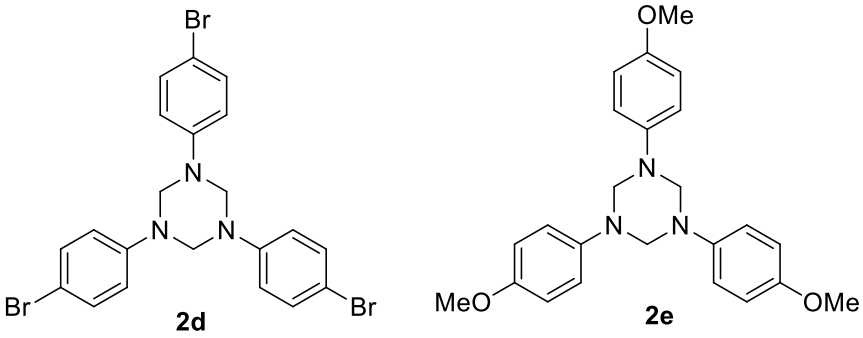
1. Sheng, G. R.; Huang, K.; Chi, Z. H.; Ding, H. L.; Xing, Y. P.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 5096.
2. Xing, Y. P.; Sheng, G. R.; Wang, J.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, *16*, 1244.

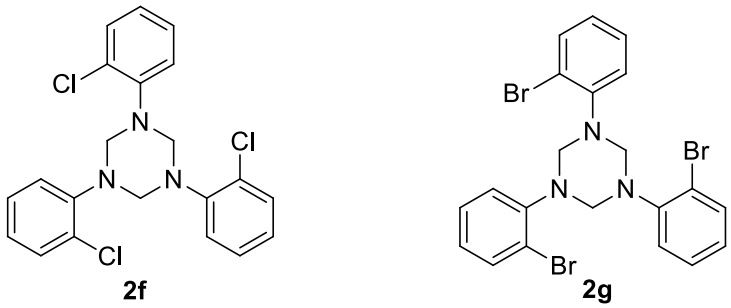
General Procedure for the Synthesis of 2

Triazines **2a-f** were prepared from aromatic amines and paraformadehyde according to the literature.[1] The prepared 3-diazoindolin-2-imines were compared with the measured spectroscopic and physical data, and confirmed their identity.





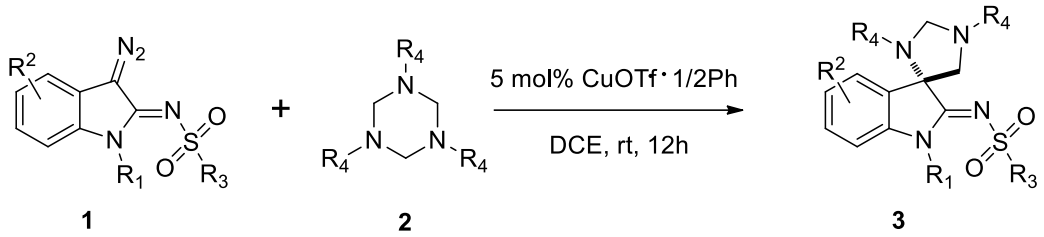




References

1 (a) Kawaguchi, A. W.; Sudo, A.; Endo, T. *J. Poly. Sci. PART A: Poly. Chem*. **2012**, *50*, 1457. (b) Bujnowski, K.; Adamczyk-W, A.; Synoradzki, L. *ARKIVOC* **2008**, *13*, 106.

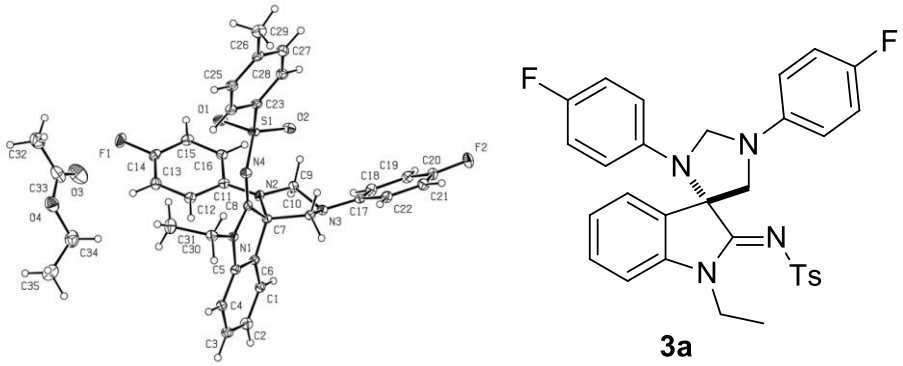
General Procedure for the Synthesis of 3



1 **2** **3**

To an over-dried flask equipped with a magnetic stirrer were added sequentially **1** (0.3 mmol), **2** (0.2 mmol), Cu(OTf)·1/2C_6H_6 (0.01 mmol) and dry DCE (2 mL) under air atmosphere. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1~3:1, v/v) to give product **3**.

The ORTEP and Crystal Parameters of 3a wherein thermal ellipsoids are drawn at 30% probability level



Bond precision: C-C = 0.0071 A Wavelength=0.71073

Cell: a=11.8960(7) b=10.6048(5) c=13.5243(8)
alpha=90 beta=109.984(6) gamma=90
Temperature: 125 K

	Calculated	Reported
Volume	1603.42(17)	1603.44(16)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C31 H28 F2 N4 O2 S, C4 H8 O2	C31 H28 F2 N4 O2 S, C4 H8 O2
Sum formula	C35 H36 F2 N4 O4 S	C35 H36 F2 N4 O4 S
Mr	646.74	646.74
Dx,g cm-3	1.340	1.340
Z	2	2
Mu (mm-1)	0.158	0.158
F000	680.0	680.0
F000'	680.57	
h,k,lmax	14,12,16	14,12,16
Nref	5874[3110]	4376
Tmin,Tmax	0.948,0.961	0.921,1.000
Tmin'	0.934	

Correction method= # Reported T Limits: Tmin=0.921 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.41/0.74 Theta(max)= 25.350

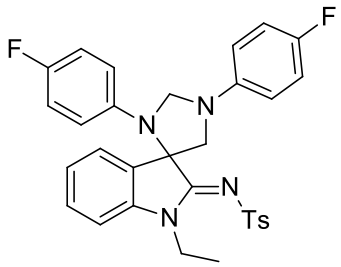
R(reflections)= 0.0518(3903) wR2(reflections)= 0.1349(4376)

S = 1.038 Npar= 419

The crystals of **3a** of suitable quality were obtained from EA/n-hexane, and was analyzed by single crystal diffractometer (Varian, Gemini A Ultra). Atomic coordinates, bond lengths, bond angles, and thermal parameters for compounds **3a** has been deposited at the Cambridge Crystallographic Data Centre. CCDC deposit number for **3a** is 1820074.

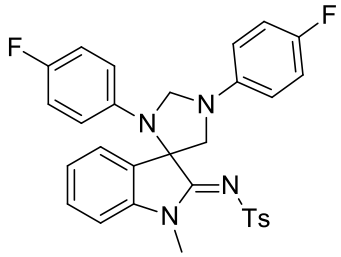
Characterization Data for Products

(*Z*)-N-(1'-Ethyl-1,3-bis(4-fluorophenyl)spiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide (3a)



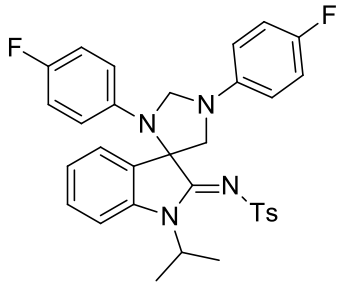
White solid; Yield 63% (70 mg); m.p. 195.0-196.0 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.7, 1.2 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.08 – 6.97 (m, 6H), 6.73 – 6.61 (m, 4H), 6.00 (dd, *J* = 9.2, 4.0 Hz, 2H), 5.20 (s, 1H), 5.14 (s, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.13 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.91 (dq, *J* = 14.1, 7.0 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 156.5 (d, J_{C-F} = 235.7 Hz), 155.9 (d, J_{C-F} = 235.1 Hz),142.5 (d, J_{C-F} = 1.9 Hz), 142.0, 140.03, 139.99, 139.6 (d, J_{C-F} = 1.9 Hz), 132.6, 129.6, 128.8, 125.9, 124.6, 123.2, 115.8 (d, J_{C-F} = 22.3 Hz), 115.7, 115.5 (d, J_{C-F} = 22.2 Hz), 114.4 (d, J_{C-F} = 7.5 Hz), 112.8 (d, J_{C-F} = 7.3 Hz), 109.6, 71.6, 68.9, 60.3, 37.6, 21.3, 11.6; IR(film): 3057, 2979, 2933, 1574, 1515, 1469, 1229, 1151, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 581.1793; found: 581.1797.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-meth ylbenzenesulfonamide (3b)



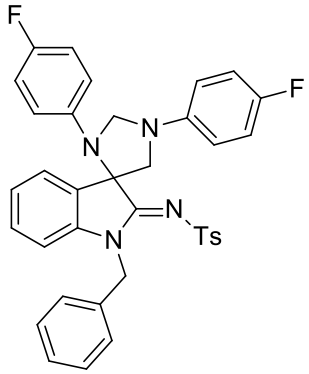
White solid; Yield 55% (60 mg); m.p. 199.0-200.0 °C ; ^{1}H NMR (600 MHz, DMSO) δ 7.51-7.39 (m, 3H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.14-7.09 (m, 5H), 6.85-6.81 (m, 4H), 6.10 (dd, *J* = 6.5, 3.3 Hz, 2H), 5.29 (s, 1H), 4.90 (s, 1H), 4.37 (d, *J* = 8.4 Hz, 1H), 3.81 (d, *J* = 8.4 Hz, 1H), 3.47 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.1, 158.2 (d, J_{C-F} = 233.0 Hz), 157.6 (d, J_{C-F} = 232.0 Hz), 145.4, 144.3, 143.9, 142.9, 142.3, 134.2, 132.2, 131.5, 128.1, 127.0, 124.8, 118.1 (d, J_{C-F} = 21.9 Hz), 117.8 (d, J_{C-F} = 22.0 Hz), 117.1 (d, J_{C-F} = 7.5 Hz), 115.6 (d, J_{C-F} = 7.5 Hz), 113.3, 73.8, 71.5, 62.3, 32.3, 23.4; IR(film): 3259, 3057, 2925, 1732, 1583, 1511, 1470, 1160, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{26}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 567.1637; found: 567.1639.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-isopropylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3c)



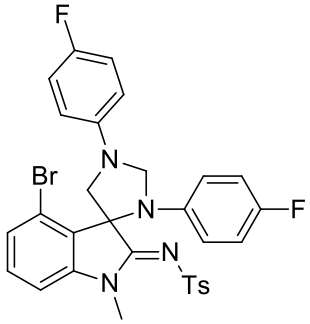
White solid; Yield 46% (53 mg); m.p. 208.0-209.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.26 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.11 – 6.92 (m, 5H), 6.76 – 6.59 (m, 4H), 6.05 – 5.93 (m, 2H), 5.18 (dd, *J* = 17.1, 2.0 Hz, 2H), 5.00-4.93 (m, 1H), 4.66 (d, *J* = 7.9 Hz, 1H), 3.71 (d, *J* = 7.9 Hz, 1H), 2.31 (s, 3H), 1.55 (dd, *J* = 12.6, 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 156.5 (d, J_{C-F} = 235.7 Hz), 155.8 (d, J_{C-F} = 234.9 Hz), 142.6 (d, J_{C-F} = 1.8 Hz), 141.9, 140.3, 139.6 (d, J_{C-F} = 1.8 Hz), 133.1, 129.3, 128.8, 125.9, 124.3, 123.2, 115.8 (d, J_{C-F} = 22.2 Hz), 115.5 (d, J_{C-F} = 22.2 Hz), 114. 4 (d, J_{C-F} = 7.5 Hz), 112. 7 (d, J_{C-F} = 7.4 Hz), 111.4, 71.3, 69.0, 60.2, 46.7, 21.3, 19.0, 18.6; IR(film) :3057, 2975,2876,1574,1511,1397,1229,1183,1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{30}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 595.1950; found: 595.1954.

(*Z*)-N-(1'-Benzyl-1,3-bis(4-fluorophenyl)spiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3d)



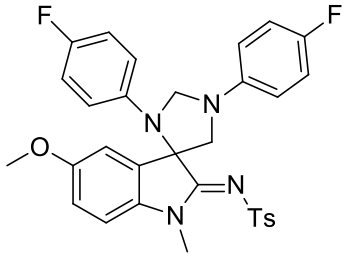
White solid; Yield 54% (67 mg); m.p. 208.0-209.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.25 (m, 7H), 7.09 – 6.97 (m, 6H), 6.69 – 6.63 (m, 2H), 6.62 – 6.52 (m, 2H), 5.98 – 5.91 (m, 2H), 5.33 (d, *J* = 14.9 Hz, 1H), 5.20 (dd, *J* = 10.6, 1.9 Hz, 2H), 4.87 (d, *J* = 14.9 Hz, 1H), 4.66 (d, *J* = 7.9 Hz, 1H), 3.77 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 156.6 (d, J_{C-F} = 235.9 Hz), 155.9 (d, J_{C-F} = 235.0 Hz), 142.5 (d, J_{C-F} = 1.8 Hz), 142.1, 140.2, 139.7, 139.4 (d, J_{C-F} = 1.9 Hz), 134.5, 132.5, 129.5, 128.9, 128.8, 128.3, 126.2, 124.7, 123.1, 115.9 (d, J_{C-F} = 22.3 Hz), 115.5 (d, J_{C-F} = 22.2 Hz), 114.6 (d, J_{C-F} = 7.4 Hz), 112.8 (d, J_{C-F} = 7.3 Hz), 110.3, 71.5, 68.9, 60.5, 46.4, 21.3; IR(film): 3059, 2946, 2834, 1581, 1511, 1395, 1228, 1149, 1087 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{36}H_{30}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 643.1950; found: 643.1934.

(Z)-N-(4'-Bromo-1,3-bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-yliden e)-4-methylbenzenesulfonamide (3e)



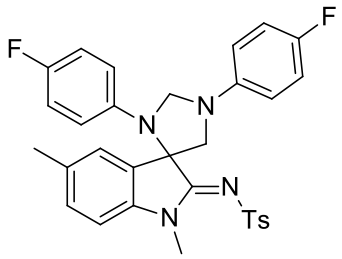
White solid; Yield 69% (86 mg); m.p. 198.0-199.0 ºC ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.19 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.02 – 6.95 (m, 3H), 6.80 – 6.76 (m, 2H), 6.53 – 6.47 (m, 2H), 6.10 – 6.05 (m, 2H), 5.22 – 5.11 (m, 2H), 4.45 (d, *J* = 8.5 Hz, 1H), 3.97 (d, *J* = 8.5 Hz, 1H), 3.51 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 156.2 (d, J_{C-F} = 235.6 Hz), 155.9 (d, J_{C-F} = 234.4 Hz), 143.9, 142.2, 141.3 (d, J_{C-F} = 1.6 Hz), 140.2, 139.0 (d, J_{C-F} = 1.9 Hz), 131.2, 129.0, 128.90, 128.87, 126.1, 117.4, 115.83 (d, J_{C-F} = 22.2 Hz), 115.79 (d, J_{C-F} = 22.2 Hz), 112.8 (d, J_{C-F} = 7.5 Hz), 112.6 (d, J_{C-F} = 7.5 Hz), 108.8, 72.8, 68.8, 58.7, 30.4, 21.4; IR(film): 3054, 2852, 1583, 1514, 1453, 1228, 1151, 1089 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{25}BrF_2N_4NaO_2S^+$ ([M+Na]$^+$): 645.0742; found: 645.0726.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-5'-methoxy-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylid ene)-4-methylbenzenesulfonamide (3f)



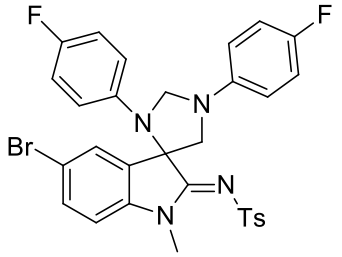
White solid; Yield 78% (90 mg); m.p. 177.0-178.0 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.04 – 6.92 (m, 5H), 6.87 (dd, *J* = 6.5, 2.5 Hz, 2H), 6.78 – 6.71 (m, 2H), 6.65 – 6.58 (m, 2H), 6.07-6.02 (m, 2H), 5.12 (dd, *J* = 37.4, 2.1 Hz, 2H), 4.50 (d, *J* = 8.2 Hz, 1H), 3.73 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H), 3.50 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 156.5 (d, J_{C-F} = 235.7 Hz), 157.6, 156.0 (d, J_{C-F} = 235.3 Hz), 142.5 (d, J_{C-F} = 1.8 Hz), 141.9, 140.3, 139.6 (d, J_{C-F} = 1.8 Hz), 134.6, 133.6, 128.8, 126.0, 115.8 (d, J_{C-F} = 22.2 Hz), 115.7 (d, J_{C-F} = 22.3 Hz), 114.4 (d, J_{C-F} = 7.5 Hz), 114.1, 113.1 (d, J_{C-F} = 7.4 Hz), 110.3, 109.9, 71.9, 69.0, 60.5, 55.7, 30.2, 21.3; IR(film):3057, 2938, 2838, 1583, 1511, 1397, 1229, 1148, 1088 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}F_2N_4NaO_3S^+$ ([M+Na]$^+$): 597.1742; found: 597.1753.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1',5'-dimethylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3g)



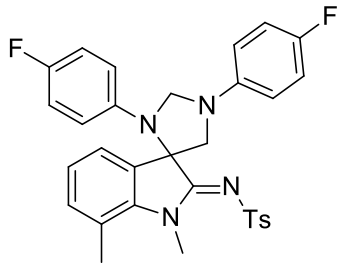
White solid; Yield 63% (70 mg); m.p. 197.0-198.0 ºC ; ^{1}H NMR (400 MHz, DMSO) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.16 – 7.05 (m, 5H), 6.88 – 6.78 (m, 4H), 6.10 (dd, *J* = 9.1, 4.2 Hz, 2H), 5.28 (d, *J* = 3.2 Hz, 1H), 4.89 (d, *J* = 3.1 Hz, 1H), 4.35 (d, *J* = 8.7 Hz, 1H), 3.80 (d, *J* = 8.8 Hz, 1H), 3.45 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.9, 158.2 (d, J_{C-F} = 232.8 Hz), 157.6 (d, J_{C-F} = 232.0 Hz), 145.5, 144.2, 143.0, 142.3, 141.6, 136.5, 134.4, 132.5, 131.5, 128.0, 125.2, 118.2, 118.0, 117.7, 117.1 (d, J_{C-F} = 7.3 Hz), 115.5 (d, J_{C-F} = 7.4 Hz), 113.2, 73.8, 71.5, 62.4, 32.4, 23.3, 23.1; IR(film): 3261, 2924, 2847, 1582, 1511, 1335, 1228, 1161, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 581.1793; found: 581.1803.

(*Z*)-N-(5'-Bromo-1,3-bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3h)



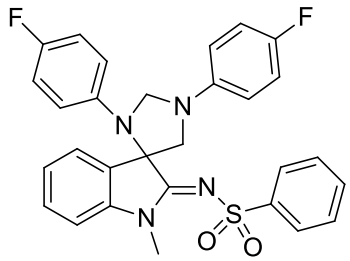
White solid; Yield 36% (45 mg); m.p. 184.0-185.0 ºC ; ^{1}H NMR (400 MHz, DMSO) δ 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 4H), 6.93 – 6.77 (m, 4H), 6.10 (dd, *J* = 8.6, 4.0 Hz, 2H), 5.34 (d, *J* = 3.1 Hz, 1H), 4.87 (d, *J* = 3.0 Hz, 1H), 4.35 (d, *J* = 8.9 Hz, 1H), 3.87 (d, *J* = 8.9 Hz, 1H), 3.43 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.6, 158.3 (d, J_{C-F} = 233.0 Hz), 157.7 (d, J_{C-F} = 233.5 Hz), 145.4, 144.5, 143.2, 142.7, 142.1, 136.6, 135.0, 131.5, 128.1, 127.4, 119.0, 118.1 (d, J_{C-F} = 22.1 Hz), 118.0 (d, J_{C-F} = 22.3 Hz), 117.3 (d, J_{C-F} = 7.4 Hz), 115.6 (d, J_{C-F} = 7.3 Hz), 115.4, 73.6, 71.4, 62.2, 32.3, 23.4; IR(film): 3048, 2929, 2875, 1584, 1512, 1287, 1224, 1143, 1080 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{25}BrF_2N_4NaO_2S^+$ ([M+Na]$^+$): 645.0742; found: 645.0751.

(Z)-N-(1,3-bis(4-Fluorophenyl)-1',7'-dimethylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3i)



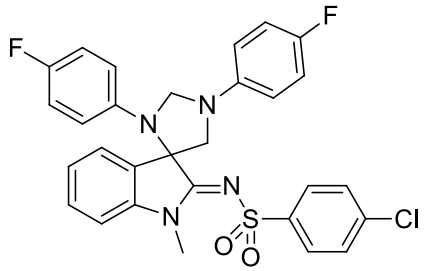
White solid; Yield 82% (92 mg); m.p. 191.0-192.0 ºC ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.97 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.76 – 6.73 (m, 2H), 6.62 – 6.60 (m, 2H), 6.06 – 6.00 (m, 2H), 5.16 (dd, *J* = 32.7, 2.1 Hz, 2H), 4.55 (d, *J* = 7.9 Hz, 1H), 3.74 (s, 3H), 3.67 (d, *J* = 8.0 Hz, 1H), 2.65 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 156.5 (d, J_{C-F} = 235.6 Hz), 155.9 (d, J_{C-F} = 235.5 Hz), 142.5 (d, J_{C-F} = 2.1 Hz), 142.0, 140.3, 139.7 (d, J_{C-F} = 1.8 Hz), 138.9, 133.6, 133.3, 128.8, 126.0, 124.7, 121.3, 120.9, 115.8 (d, J_{C-F} = 22.6 Hz), 115.7 (d, J_{C-F} = 22.9 Hz), 114.3 (d, J_{C-F} = 7.5 Hz), 112.9 (d, J_{C-F} = 7.4 Hz), 71.1, 69.0, 60.6, 33.4, 21.3, 19.5; IR(film): 3056, 2869, 1581, 1511, 1397, 1229, 1150, 1091 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 581.1793; found: 581.1792.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzene sulfonamide (3j)



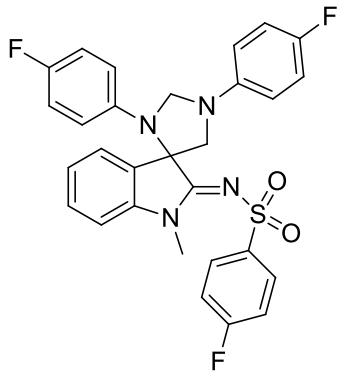
White solid; Yield 89% (94 mg); m.p. 207.0-208.0 ºC ; ^{1}H NMR (400 MHz, DMSO) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.33 (m, 5H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.07 (m, 3H), 6.89 – 6.80 (m, 4H), 6.14 (dd, *J* = 9.2, 4.2 Hz, 2H), 5.31 (d, *J* = 3.3 Hz, 1H), 4.93 (d, *J* = 3.2 Hz, 1H), 4.38 (d, *J* = 8.8 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 170.3, 158.2 (d, J_{C-F} = 232.9 Hz), 157.6 (d, J_{C-F} = 232.2 Hz), 145.7, 145.4, 143.8, 142.3, 134.20, 134.17, 132.2, 131.1, 128.0, 127.1, 124.9, 118.2, 118.0, 117.8, 117.1 (d, J_{C-F} = 7.4 Hz), 115.6 (d, J_{C-F} = 7.4 Hz), 113.4, 73.8, 71.5, 62.3, 32.3; IR(film):3055,2929,2864,1586,1511,1397,1226,1151,1088 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 643.1950; found: 643.1934.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-chlorobenzenesulfonamide (3k)



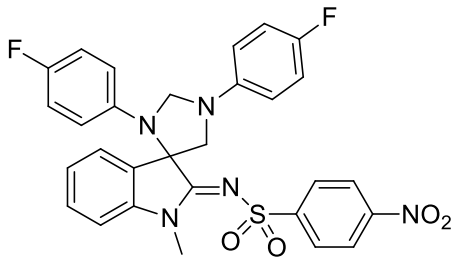
White solid; Yield 61% (69 mg); m.p. 206.0-207.0 °C ; ^{1}H NMR (600 MHz, DMSO) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.33 (m, 4H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.13 – 7.07 (m, 3H), 6.82 – 6.77 (m, 4H), 6.04 (dd, *J* = 9.2, 4.1 Hz, 2H), 5.27 (d, *J* = 3.2 Hz, 1H), 4.87 (d, *J* = 3.1 Hz, 1H), 4.37 (d, *J* = 8.7 Hz, 1H), 3.78 (d, *J* = 8.7 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.8, 158.2 (d, J_{C-F} = 232.8Hz), 157.6 (d, J_{C-F} = 232.5 Hz), 145.4, 144.5, 143.7, 142.3, 138.9, 134.3, 132.2, 131.2, 129.9, 127.3, 124.8, 118.1 (d, J_{C-F} = 22.0 Hz), 117.8 (d, J_{C-F} = 22.0 Hz), 117.1 (d, J_{C-F} = 7.5 Hz), 115.7 (d, J_{C-F} = 7.4 Hz), 113.6, 73.9, 71.5, 62.3, 32.4; IR(film): 3045, 2856, 1584, 1511, 1470, 1394, 1228, 1151, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{23}ClF_2N_4NaO_2S^+$ ([M+Na]$^+$): 587.1091; found: 587.1091.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-fluorobenzenesulfonamide (3l)



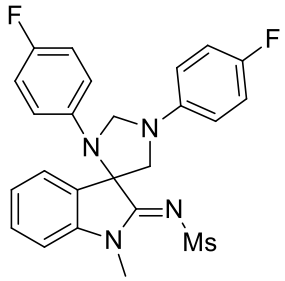
White solid; Yield 63% (69 mg); m.p. 193.0-194.0 °C ; ^{1}H NMR (400 MHz, DMSO) δ 7.66 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.47 – 7.35 (m, 2H), 7.23-7.08 (m, 6H), 6.90 – 6.75 (m, 4H), 6.09 (dd, *J* = 9.0, 3.8 Hz, 2H), 5.30 (d, *J* = 3.3 Hz, 1H), 4.90 (d, *J* = 3.2 Hz, 1H), 4.38 (d, *J* = 8.8 Hz, 1H), 3.80 (d, *J* = 8.8 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 170.6, 166.0 (d, J_{C-F} = 248.2 Hz), 158.2 (d, J_{C-F} = 232.7 Hz), 157.6 (d, J_{C-F} = 232.7 Hz), 145.4 (d, J_{C-F} = 1.0 Hz), 143.8, 142.3 (d, J_{C-F} = 0.9 Hz), 142.1 (d, J_{C-F} = 2.9 Hz), 134.2, 132.2, 131.0 (d, J_{C-F} = 9.3 Hz), 127.2, 124.8, 118.10 (d, J_{C-F} = 22.2 Hz), 118.08 (d, J_{C-F} = 21.5 Hz), 117.8 (d, J_{C-F} = 22.1 Hz), 117.1 (d, J_{C-F} = 7.3 Hz), 115.6 (d, J_{C-F} = 7.3 Hz), 113.5, 73.9, 71.5, 62.3, 32.3; IR(film): 3062, 2925, 2856, 1580,1510,1392,1228,1149,1085 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{23}F_3N_4NaO_2S^+$ ([M+Na]$^+$): 571.1386; found: 571.1407.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-nitro benzenesulfonamide (3m)



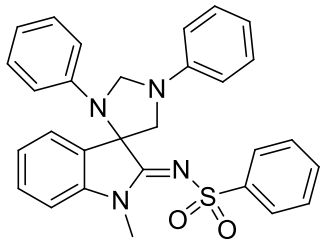
White solid; Yield 45% (52 mg); m.p. 210.0-211.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.43 (t, *J* = 8 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.09 (m, 2H), 7.06 – 6.97 (m, 2H), 6.83 – 6.73 (m, 2H), 6.68 – 6.58 (m, 2H), 6.12 – 5.98 (m, 2H), 5.20 (d, *J* = 2.3 Hz, 1H), 5.07 (d, *J* = 2.2 Hz, 1H), 4.50 (d, *J* = 8.2 Hz, 1H), 3.75 (d, *J* = 8.2 Hz, 1H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 156.7 (d, J_{C-F} = 236.5 Hz), 156.1 (d, J_{C-F} = 236.7 Hz), 149.2, 148.5, 142.3, 140.9, 139.5, 132.0, 130.0, 127.4, 125.5, 123.6, 123.2, 116.0 (d, J_{C-F} = 22.2 Hz), 115.9 (d, J_{C-F} = 22.5 Hz), 114.4 (d, J_{C-F} = 7.5 Hz), 113.1 (d, J_{C-F} = 7.5 Hz), 110.1, 72.1, 69.1, 60.3, 30.3; IR(film):3105, 3054, 2867, 1567, 1510, 1349, 1229, 1152, 1087 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{23}F_2N_5NaO_2S^+$ ([M+Na]$^+$): 598.1331; found: 598.1346.

(*Z*)-N-(1,3-Bis(4-fluorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)methan esulfonamide (3n)



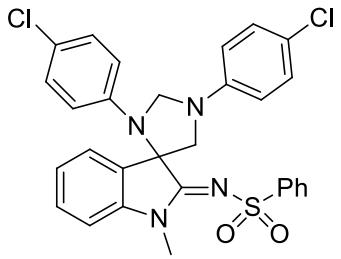
White solid; Yield 65% (61 mg); m.p. 145.0-146.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.13 – 7.03 (m, 2H), 7.02 – 6.94 (m, 2H), 6.86 – 6.77 (m, 2H), 6.67 – 6.55 (m, 2H), 6.15 – 6.05 (m, 2H), 5.20 (d, *J* = 2.2 Hz, 1H), 5.09 (d, *J* = 2.1 Hz, 1H), 4.48 (d, *J* = 8.1 Hz, 1H), 3.69 (d, *J* = 8.1 Hz, 1H), 3.50 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 156.5 (d, J_{C-F} = 235.9 Hz), 155.9 (d, J_{C-F} = 235.6 Hz), 142.6, 142.5, 141.2, 139.58, 139.56, 132.1, 129.7, 124.8, 122.9, 116.2, 115.83 (d, J_{C-F} = 22.2 Hz), 115.80 (d, J_{C-F} = 22.1 Hz), 114.3 (d, J_{C-F} = 7.6 Hz), 112.9 (d, J_{C-F} = 7.2 Hz), 109.7, 71.7, 69.0, 60.3, 43.3, 29.6; IR(film): 3057, 2935, 2875, 1588, 1511, 1396, 1229, 1128, 1098 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{22}F_2N_4NaO_2S^+$ ([M+Na]$^+$): 491.1324; found: 491.1330.

(*Z*)-N-(1'-Methyl-1,3-diphenylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzenesulfonamide (3o)



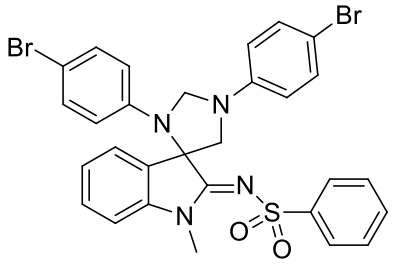
White solid; Yield 81% (80 mg); m.p. 138.0-139.0 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.27 (m, 5H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.11 – 7.04 (m, 4H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.68 (m, 3H), 6.15 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 1H), 5.16 (s, 1H), 4.52 (d, *J* = 8.3 Hz, 1H), 3.82 (d, *J* = 8.3 Hz, 1H), 3.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 145.9, 143.2, 142.9, 141.3, 132.5, 131.4, 129.6, 129.4, 129.2, 128.2, 126.2, 124.9, 123.1, 118.7, 118.1, 113.4, 112.2, 109.6, 71.5, 68.2, 60.0, 30.2; IR(film):3062, 2912, 2843, 1597, 1573, 1502, 1301, 1150, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{26}N_4NaO_2S^+$ ([M+Na]$^+$): 517.1669; found: 517.1675.

(*Z*)-N-(1,3-Bis(4-chlorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzene sulfonamide (3p)



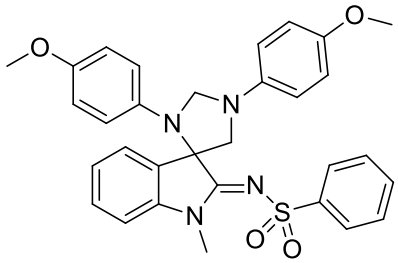
White solid; Yield 81% (91 mg); m.p. 210.0-211.0 ºC; ^{1}H NMR (600 MHz, DMSO) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.15 (d, *J* = 8.6 Hz, 2H), 5.32 (d, *J* = 3.5 Hz, 1H), 4.94 (d, *J* = 3.4 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 3.85 (d, *J* = 9.0 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.0, 147.3, 145.6, 144.3, 143.8, 134.2, 134.0, 132.4, 131.3, 131.1, 128.1, 127.2, 124.8, 124.5, 123.9, 117.5, 116.3, 113.5, 73.5, 70.9, 61.8, 32.3; IR(film): 3052, 2924, 2881, 1589, 1495, 1345, 1303, 1151, 1087 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}Cl_2N_4NaO_2S^+$ ([M+Na]$^+$): 585.0889; found: 585.0899.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzen esulfonamide (3q)



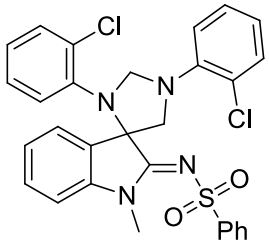
White solid; Yield 72% (94 mg); m.p. 226.0-227.0 °C; ^{1}H NMR (600 MHz, DMSO) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.32 (m, 6H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.16 - 7.10 (m, 3H), 6.77 (d, *J* = 7.8 Hz, 2H), 6.11 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 1H), 4.92 (s, 1H), 4.38 (d, *J* = 8.8 Hz, 1H), 3.84 (d, *J* = 9.4 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.0, 147.6, 145.6, 144.7, 143.8, 134.3, 134.2, 134.0, 133.9, 132.4, 131.2, 128.1, 127.2, 124.8, 118.0, 116.9, 113.5, 112.0, 111.5, 73.5, 70.8, 61.7, 32.3; IR(film):3069,2926,2834, 1589,1493,1346,1303,1150,1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}Br_2N_4NaO_2S^+$ ([M+Na]$^+$): 672.9879; found: 672.9864.

(*Z*)-N-(1,3-Bis(4-methoxyphenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzenesulfonamide (3r)



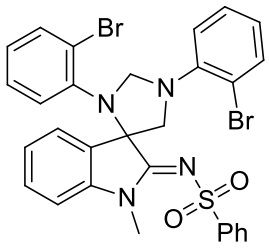
White solid; Yield 41% (45 mg); m.p. 153.0-154.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.28 (m, 3H), 7.26 – 7.21 (m, 2H), 7.11 – 7.03 (m, 2H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.67 – 6.62 (m, 4H), 6.09 (d, *J* = 6.8 Hz, 2H), 5.18 (s, 1H), 5.07 (s, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 152.8, 152.2, 143.1, 141.4, 140.6, 137.7, 132.6, 131.3, 129.5, 128.2, 126.2, 124.8, 123.4, 114.9, 114.8, 114.6, 113.4, 109.5, 72.0, 69.2, 60.7, 55.8, 55.5, 30.3; IR(film): 3058, 2946, 2833, 1588, 1511, 1287, 1243, 1150, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{30}N_4NaO_4S^+$ ([M+Na]$^+$): 577.1880; found: 577.1891.

(Z)-N-(1,3-bis(2-Chlorophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzenesulfonamide (3s)



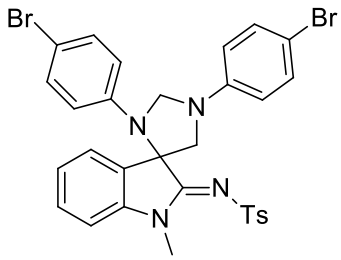
White solid; Yield 53% (60 mg); m.p. 149.9-155.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.34 (m, 2H), 7.30 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.02 – 6.96 (m, 3H), 6.63 (td, *J* = 7.8, 1.6 Hz, 1H), 6.60 – 6.51 (m, 2H), 5.79 (s, 1H), 5.48 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.49 (dd, *J* = 12.2, 7.5 Hz, 1H), 4.35 – 4.26 (m, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.6, 142.5, 142.1, 140.8, 131.5, 130.0, 129.7, 129.3, 129.0, 128.3, 127.8, 127.2, 126.1, 124.7, 123.4, 121.2, 119.2, 119.0, 118.1, 112.4, 112.4, 110.0, 69.1, 51.7, 29.3; IR(film): 3063, 2927, 1595, 1516, 1469, 1289, 1149, 1085 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}Cl_2N_4NaO_2S^+$ ([M+Na]$^+$): 585.0889; found: 585.0886.

(Z)-N-(1,3-bis(2-Bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)benzenesulfonamide (3t)



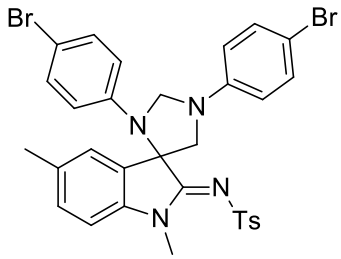
White solid; Yield 62% (80 mg); m.p. 73.4-74.5 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.43 – 7.29 (m, 5H), 7.29 – 7.22 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.95 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.67 (td, *J* = 7.8, 1.5 Hz, 1H), 6.54 – 6.44 (m, 2H), 5.77 (s, 1H), 5.46 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.45 (dd, *J* = 12.5, 8.2 Hz, 1H), 4.38 (dd, *J* = 8.3, 5.3 Hz, 1H), 4.27 (dd, *J* = 12.5, 5.3 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 143.4, 142.5, 142.1, 141.7, 132.6, 132.3, 131.5, 130.0, 129.5, 128.5, 128.2, 127.9, 126.1, 124.7, 123.4, 119.6, 118.6, 112.5, 112.4, 111.8, 110.1, 109.6, 69.1, 51.7, 29.4; IR(film): 3058, 2925, 1591, 1515, 1465, 1287, 1148, 1085 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}Br_2N_4NaO_2S^+$ ([M+Na]$^+$): 672.9879; found: 672.9874.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3u)



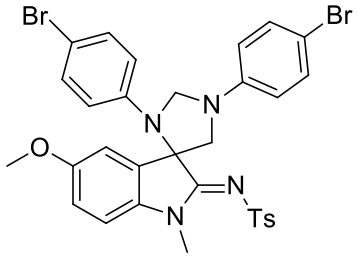
White solid; Yield 45% (60 mg); m.p. 224.0-225.0 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.26 – 7.23 (m, 1H), 7.16 – 7.00 (m, 6H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.97 (d, *J* = 8.8 Hz, 2H), 5.19 (d, *J* = 2.3 Hz, 1H), 5.11 (d, *J* = 2.3 Hz, 1H), 4.55 (d, *J* = 8.3 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 3.51 (s, 3H), 2.34 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 144.7, 142.3, 142.0, 141.2, 139.8, 132.1, 131.9, 131.8, 129.9, 128.9, 126.1, 125.0, 122.9, 115.0, 113.8, 111.0, 110.4, 109.7, 71.4, 68.2, 59.9, 29.9, 21.5; IR(film): 3050, 2923, 2865, 1592, 1495, 1344, 1283, 1162, 1085 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{26}Br_2N_4NaO_2S^+$ ([M+Na]$^+$): 687.0035; found: 687.0009.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1',5'-dimethylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3v)



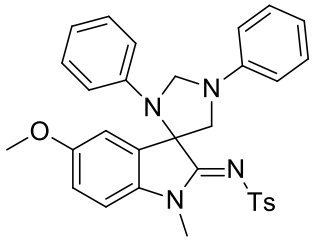
White solid; Yield 63% (85 mg); m.p. 216.0-217.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.96 (d, *J* = 8.9 Hz, 2H), 5.18 (d, *J* = 2.4 Hz, 1H), 5.10 (d, *J* = 2.3 Hz, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 3.74 (d, *J* = 8.3 Hz, 1H), 3.49 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.7, 142.2, 142.0, 139.9, 138.8, 135.0, 132.0, 131.9, 131.8, 130.2, 128.9, 126.0, 123.5, 115.0, 113.7, 110.9, 110.3, 109.5, 71.3, 68.2, 59.9, 30.0, 21.4, 21.1; IR(film): 2920, 2847, 1589, 1494, 1392, 1338, 1283, 1148, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}Br_2N_4NaO_2S^+$ ([M+Na]$^+$): 701.0192; found: 701.0172.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-5'-methoxy-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3w)



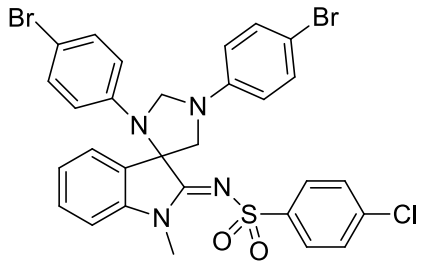
White solid; Yield 67% (93 mg); m.p. 221.0-222.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.41 – 7.33 (m, 2H), 7.14 – 7.08 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.57 – 6.54 (m, 2H), 5.98 – 5.96 (m, 2H), 5.17 (d, *J* = 2.4 Hz, 1H), 5.08 (d, *J* = 2.4 Hz, 1H), 4.52 (d, *J* = 8.4 Hz+ , 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 3.50 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 157.7, 144.8, 142.1, 142.0, 140.0, 134.5, 133.3, 132.1, 131.9, 128.9, 126.0, 115.0, 114.2, 113.8, 111.0, 110.45, 110.36, 109.7, 71.5, 68.2, 60.0, 55.8, 30.2, 21.4; IR(film):3045, 2929, 2837, 1589, 1494, 1337, 1285, 1148, 1087 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}Br_2N_4NaO_3S^+$ ([M+Na]$^+$): 717.0141; found: 717.0123.

(*Z*)-N-(5'-Methoxy-1'-methyl-1,3-diphenylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3x)



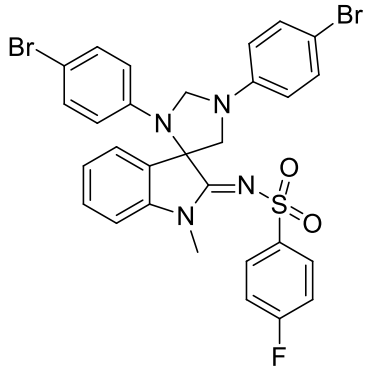
White solid; Yield 70% (75 mg); m.p. 134.0-135.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.99 – 6.95 (m, 3H), 6.90 – 6.81 (m, 3H), 6.70 (d, *J* = 7.6 Hz, 3H), 6.16 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 1H), 5.12 (s, 1H), 4.49 (d, *J* = 8.3 Hz, 1H), 3.81 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H), 3.53 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 157.7, 146.0, 143.3, 141.7, 140.3, 134.7, 134.0, 129.3, 129.2, 128.8, 126.1, 118.7, 118.0, 114.3, 113.5, 112.3, 110.2, 109.7, 71.7, 68.2, 60.1, 55.8, 30.5, 21.4; IR(film): 3041, 2834, 1598, 1502, 1393, 1332, 1285, 1147, 1087 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{30}N_4NaO_3S^+$ ([M+Na]$^+$): 561.1931; found: 561.1925.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-chlorobenzenesulfonamide (3y)



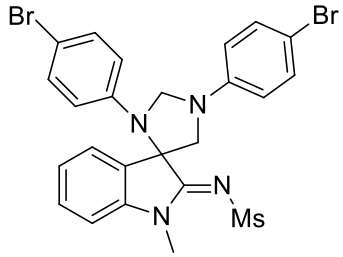
White solid; Yield 68% (93 mg); m.p. 169.0-170.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.44 – 7.33 (m, 3H), 7.28 – 7.24 (m, 1H), 7.24 – 7.19 (m, 2H), 7.18 – 7.02 (m, 4H), 6.55 (d, *J* = 8.9 Hz, 2H), 5.97 (d, *J* = 9.0 Hz, 2H), 5.18 (d, *J* = 2.5 Hz, 1H), 5.07 (d, *J* = 2.4 Hz, 1H), 4.50 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 144.6, 142.0, 141.3, 141.0, 138.0, 132.1, 132.0, 131.7, 130.0, 128.5, 127.5, 125.2, 122.9, 114.9, 113.8, 111.1, 110.6, 109.9, 71.5, 68.2, 59.8, 30.0; IR(film): 3067, 2925, 2854, 1609, 1585, 1490, 1286, 1165, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{23}Br_2ClN_4NaO_2S^+$ ([M+Na]$^+$): 706.9489; found: 706.9476.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-fluorobenzenesulfonamide (3z)



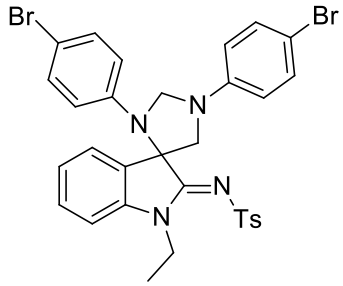
White solid; Yield 53% (71 mg); m.p. 203.0-204.0 ºC; ^{1}H NMR (600 MHz, DMSO) δ 7.70 – 7.62 (m, 2H), 7.48 – 7.36 (m, 4H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.04 (m, 5H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.07 (d, *J* = 8.9 Hz, 2H), 5.30 (d, *J* = 3.5 Hz, 1H), 4.91 (d, *J* = 3.4 Hz, 1H), 4.38 (d, *J* = 8.9 Hz, 1H), 3.83 (d, *J* = 9.0 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.2, 166.1 (d, $J_{C\text{-}F}$ = 248.9 Hz), 147.6, 144.6, 143.7, 142.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 134.1, 134.0, 133.9, 132.3, 131.0 (d, $J_{C\text{-}F}$ = 9.3 Hz), 127.3, 124.7, 118.2, 118.0, 117.9, 116.8, 113.5, 111.8 (d, $J_{C\text{-}F}$ = 77.0 Hz), 104.0, 73.5, 70.8, 61.8, 32.3; IR(film): 3362, 3261, 2924, 1587, 1493, 1400, 1340, 1148, 1086 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{23}Br_2FN_4NaO_2S^+$ ([M+Na]$^+$): 690.9785; found: 690.9776.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)methanesulfonamide (3A)



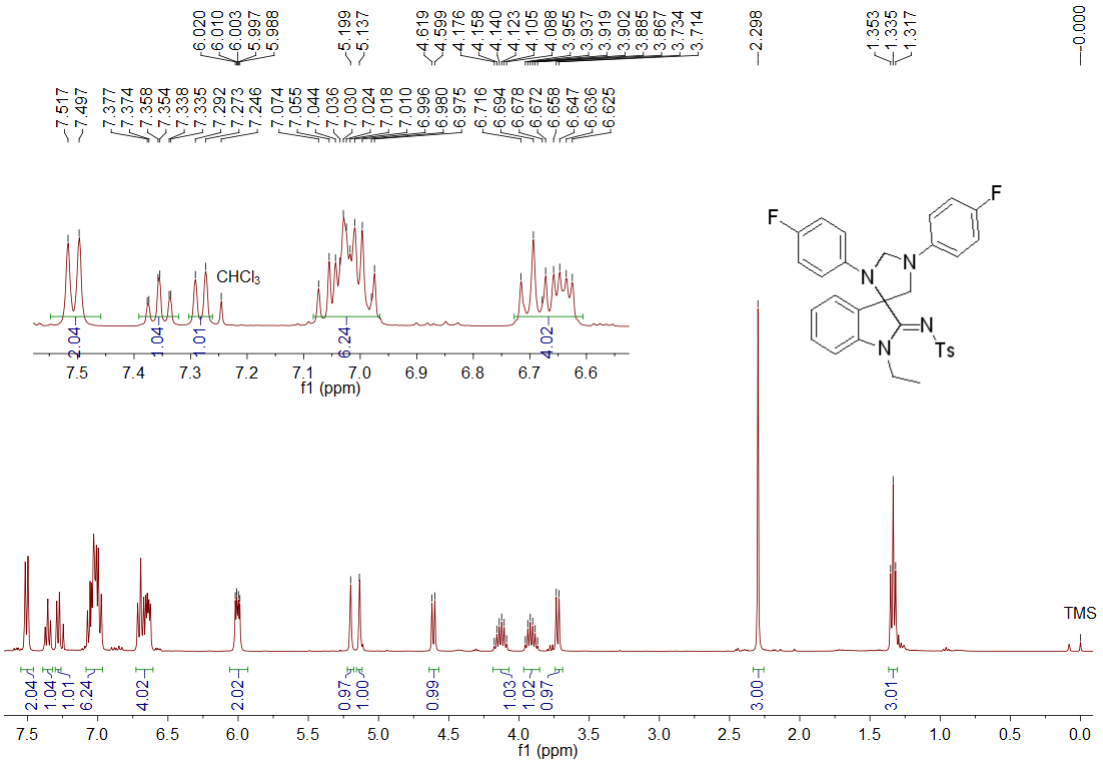
White solid; Yield 73% (86 mg); m.p. 202.0-203.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.12 – 7.03 (m, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 6.04 (d, *J* = 8.9 Hz, 2H), 5.19 (d, *J* = 2.4 Hz, 1H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.48 (d, *J* = 8.2 Hz, 1H), 3.71 (d, *J* = 8.3 Hz, 1H), 3.50 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 144.7, 142.0, 141.1, 132.04, 132.02, 131.7, 129.9, 124.9, 122.7, 114.9, 113.8, 111.0, 110.5, 109.7, 71.4, 68.2, 59.6, 43.4, 29.6; IR(film): 3044, 2934, 2845, 1590, 1495, 1337, 1295, 1128, 1098 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{22}Br_2FN_4NaO_2S^+$ ([M+Na]$^+$): 610.9722; found: 610.9726.

(*Z*)-N-(1,3-Bis(4-bromophenyl)-1'-ethylspiro[imidazolidine-4,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide (3B)

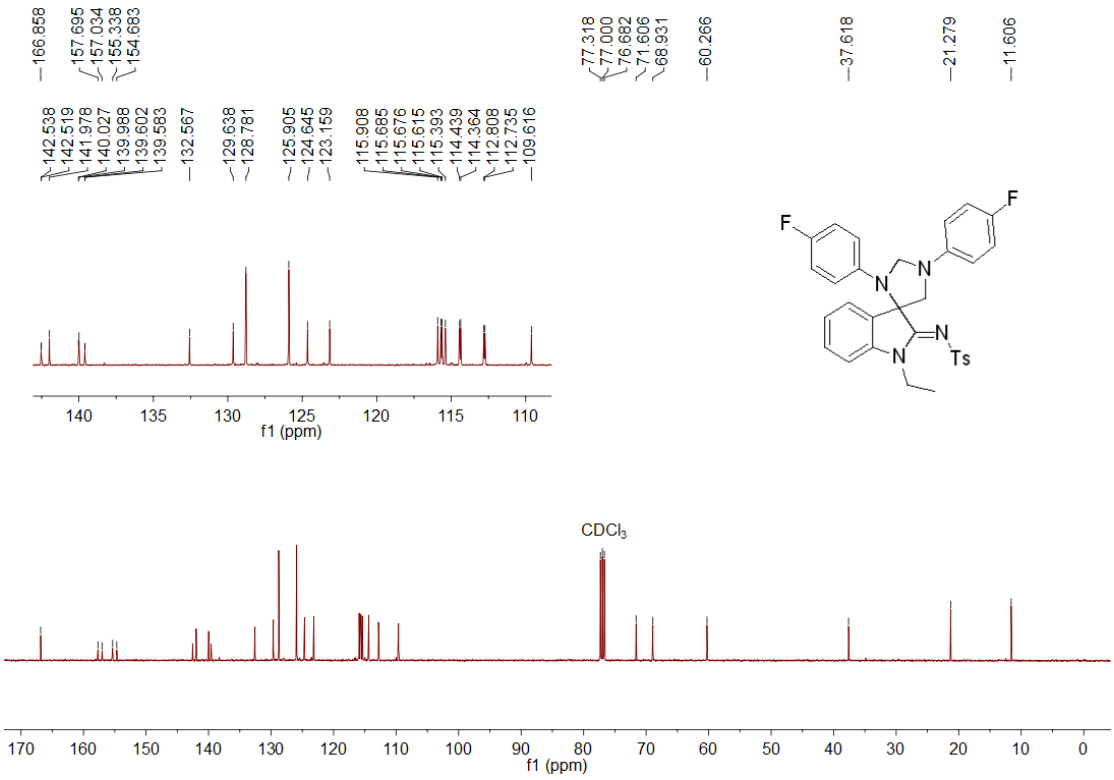


White solid; Yield 45% (75 mg); m.p. 221.0-222.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.10 – 6.98 (m, 6H), 6.57 (d, *J* = 8.9 Hz, 2H), 5.93 (d, *J* = 9.0 Hz, 2H), 5.19 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 2.4 Hz, 1H), 4.61 (d, *J* = 8.1 Hz, 1H), 4.19 – 4.10 (m, 1H), 3.95- 3.86 (m, 1H), 3.75 (d, *J* = 8.2 Hz, 1H), 2.33 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 144.7, 142.2, 142.0, 139.9, 139.7, 132.3, 132.1, 131.7, 129.8, 128.9, 125.9, 124.8, 123.0, 115.0, 113.6, 111.0, 110.2, 109.7, 71.2, 68.2, 59.9, 37.6, 21.4, 11.6; IR(film): 2976, 2925, 2873, 1582, 1494, 1394, 1342, 1151, 1085 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{28}Br_2N_4NaO_2S^+$ ([M+Na]$^+$): 701.0192; found: 701.0163.

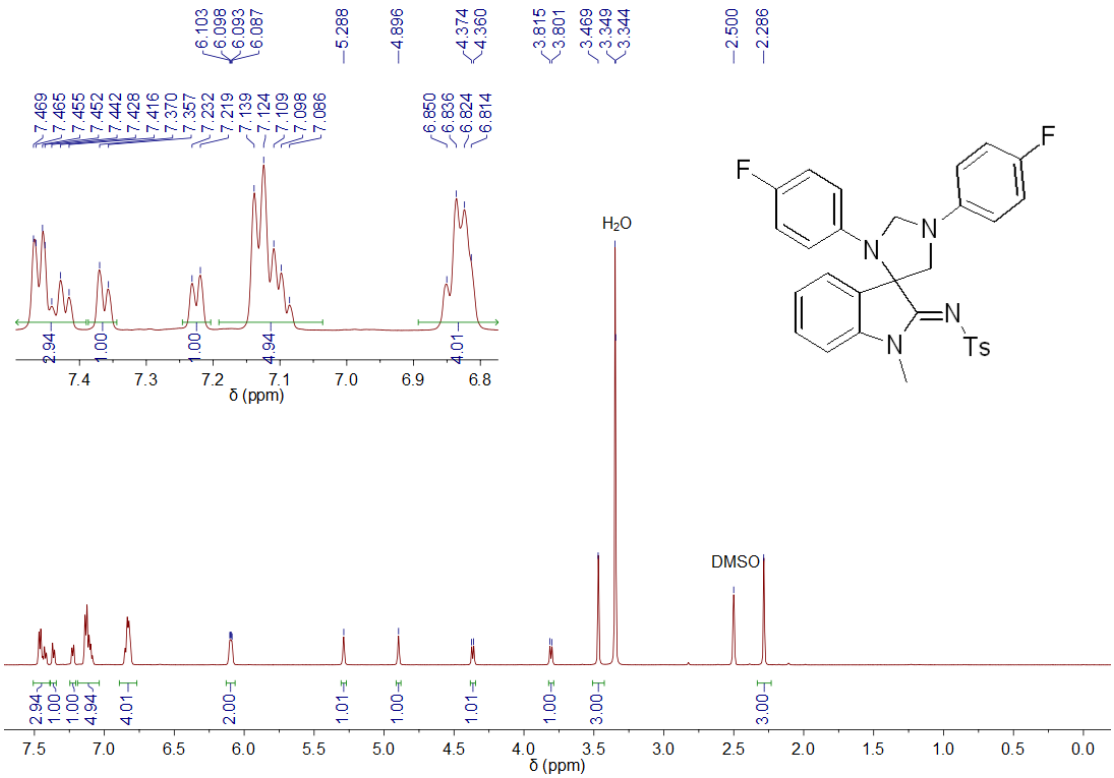
Copies of NMR Spectra



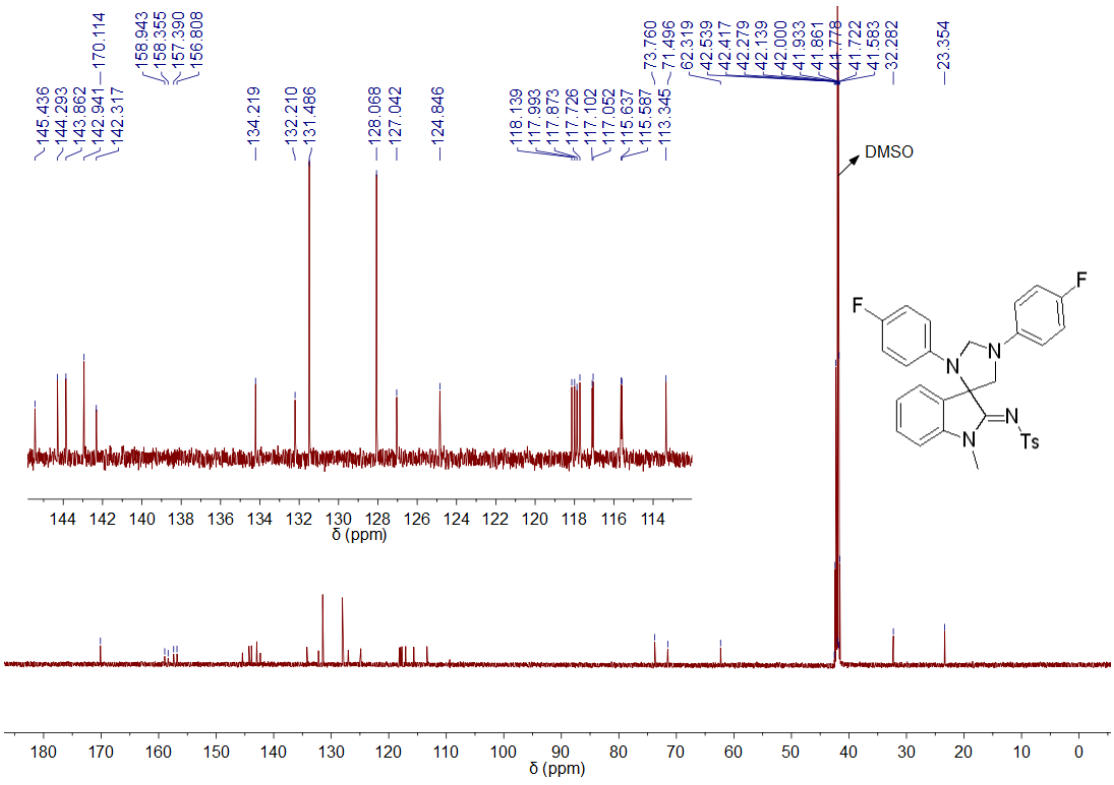
^{1}H NMR of Compoud 3a



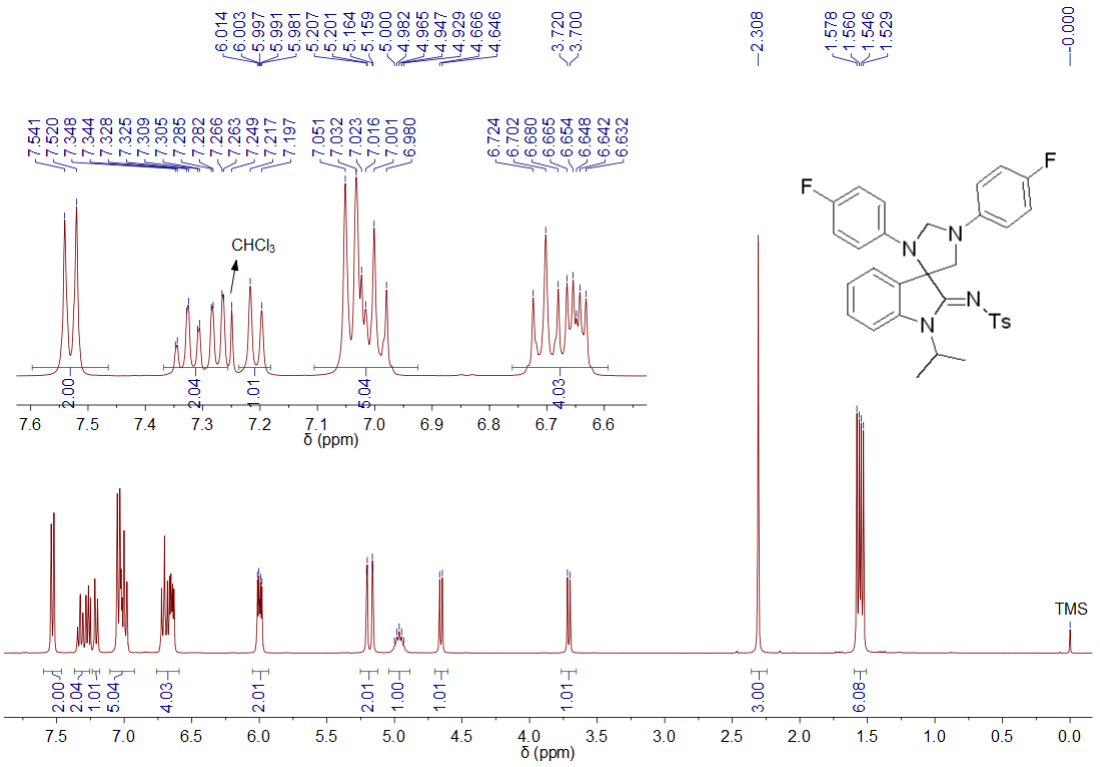
^{13}C NMR of Compoud 3a



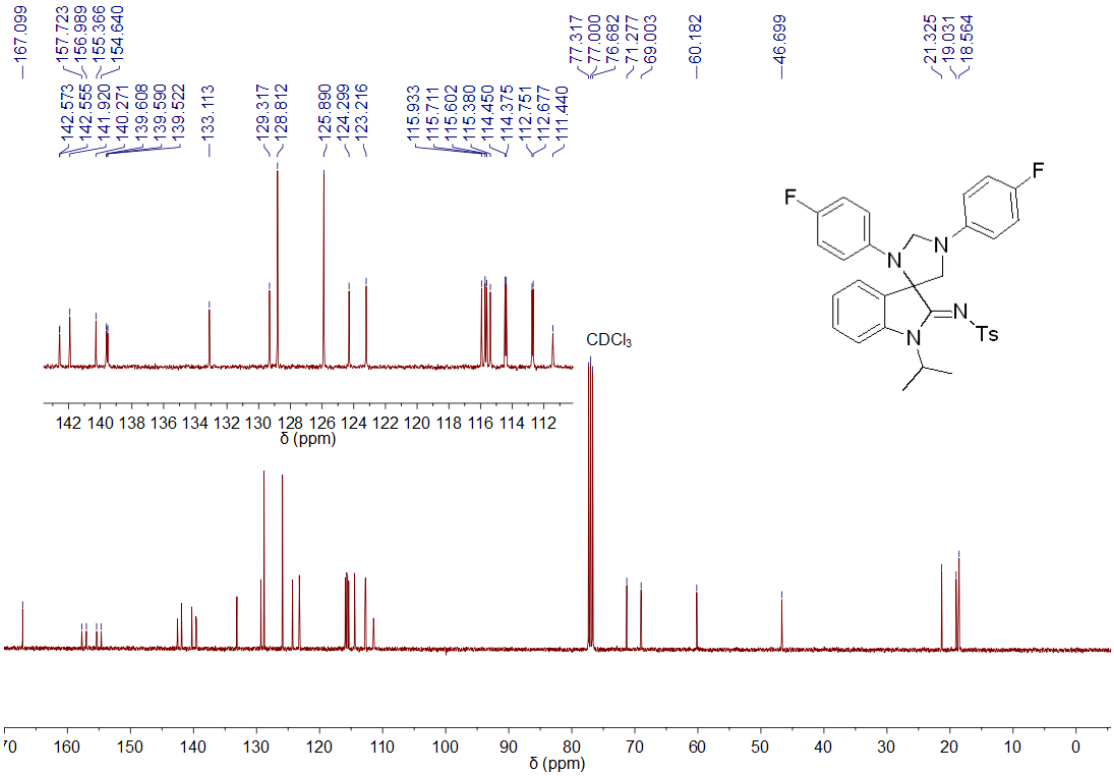
^{1}H NMR of Compoud 3b



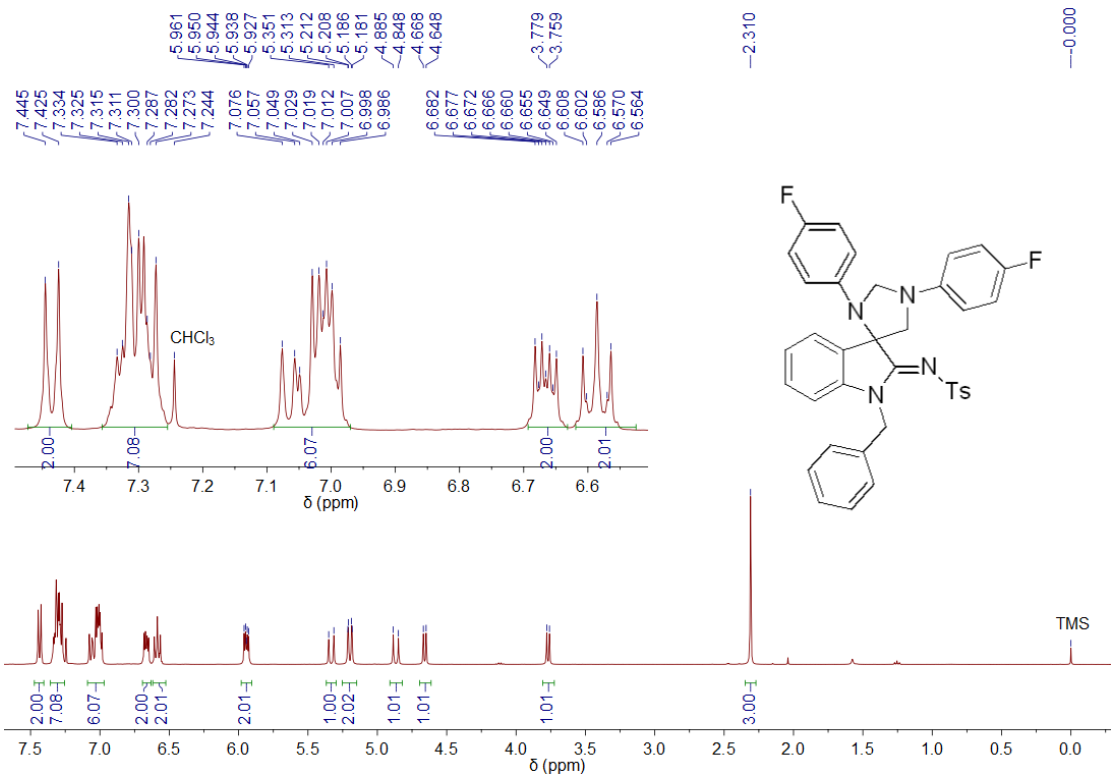
^{13}C NMR of Compoud 3b



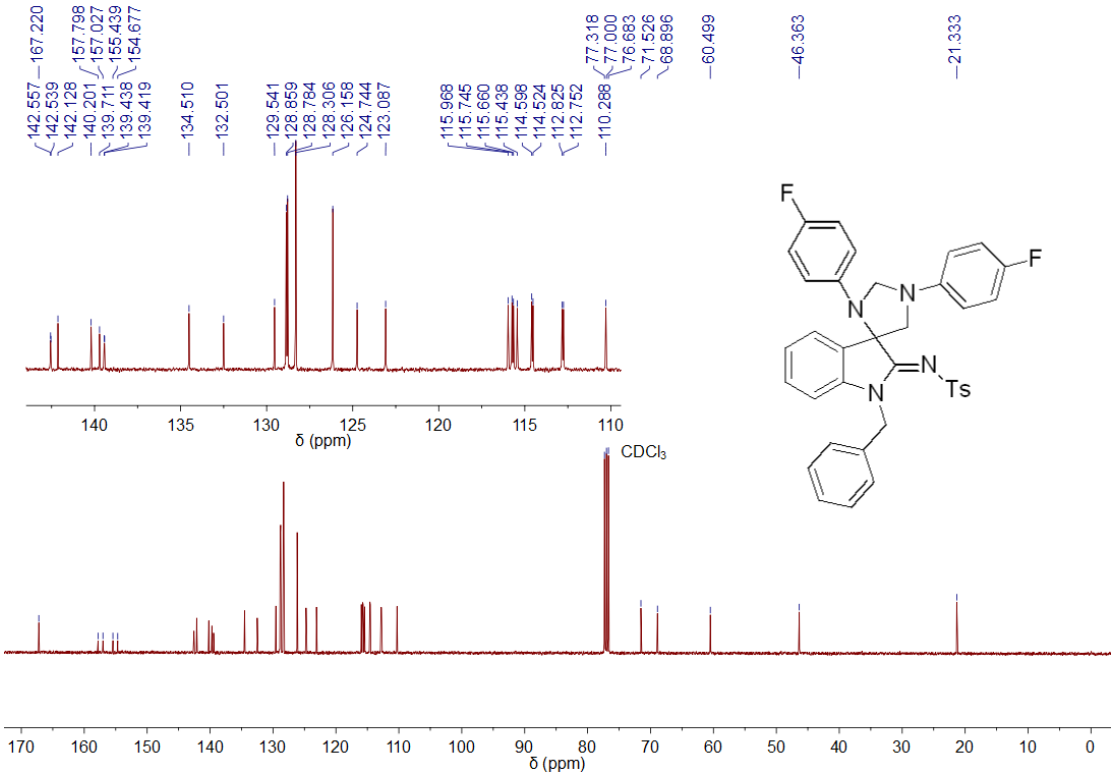
^{1}H NMR of Compoud 3c



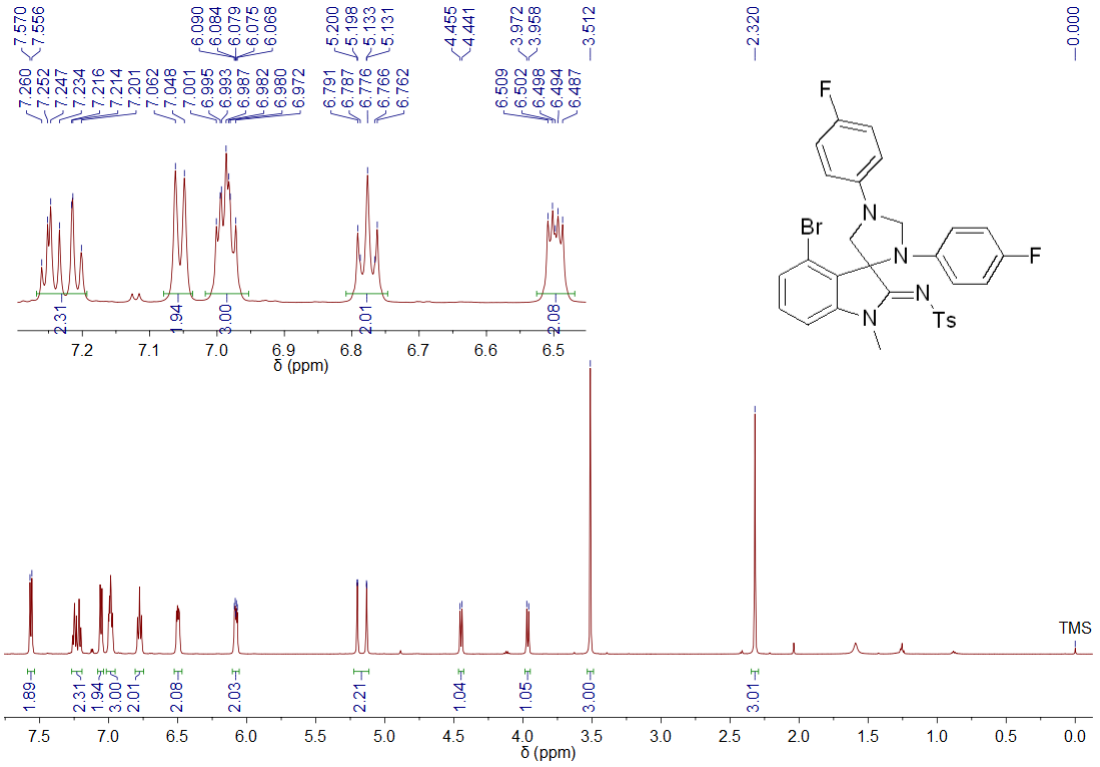
^{13}C NMR of Compoud 3c



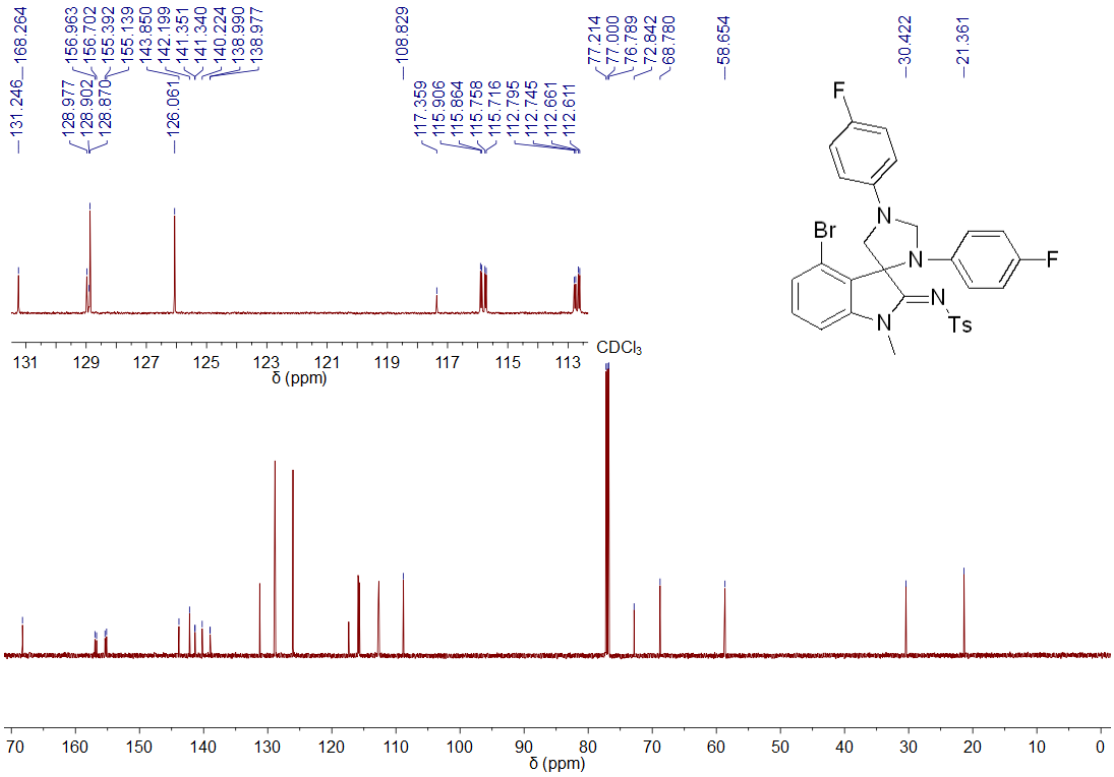
^{1}H NMR of Compoud 3d



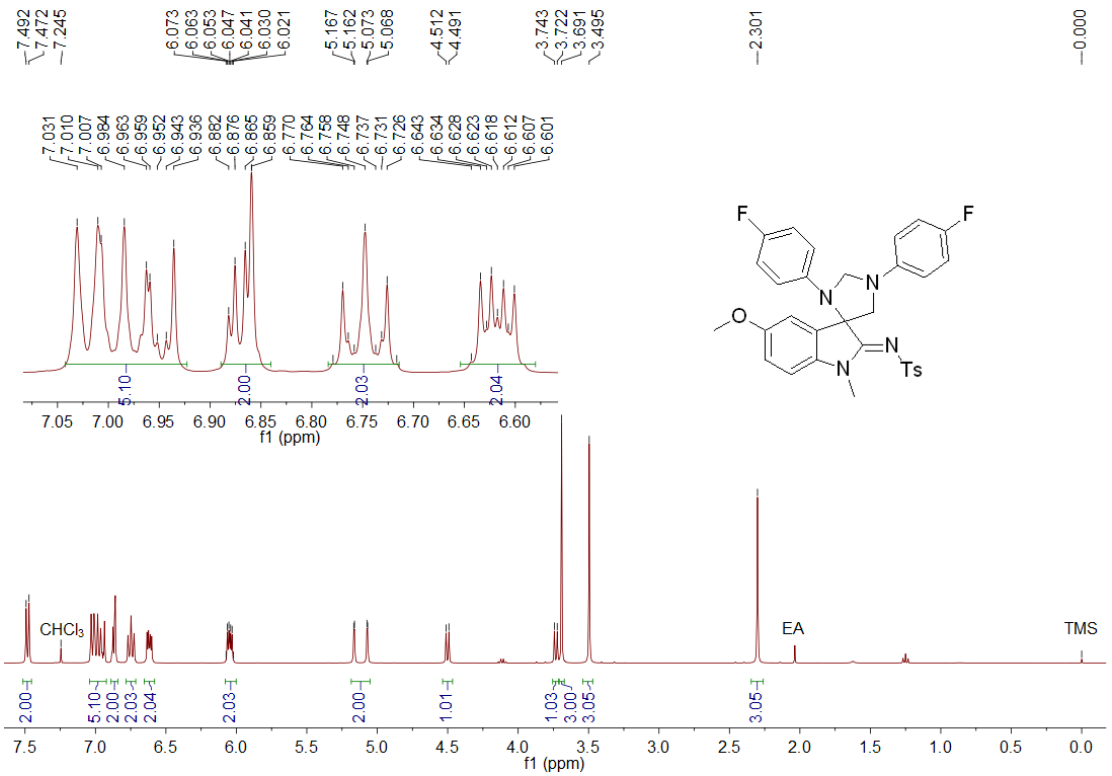
^{13}C NMR of Compoud 3d



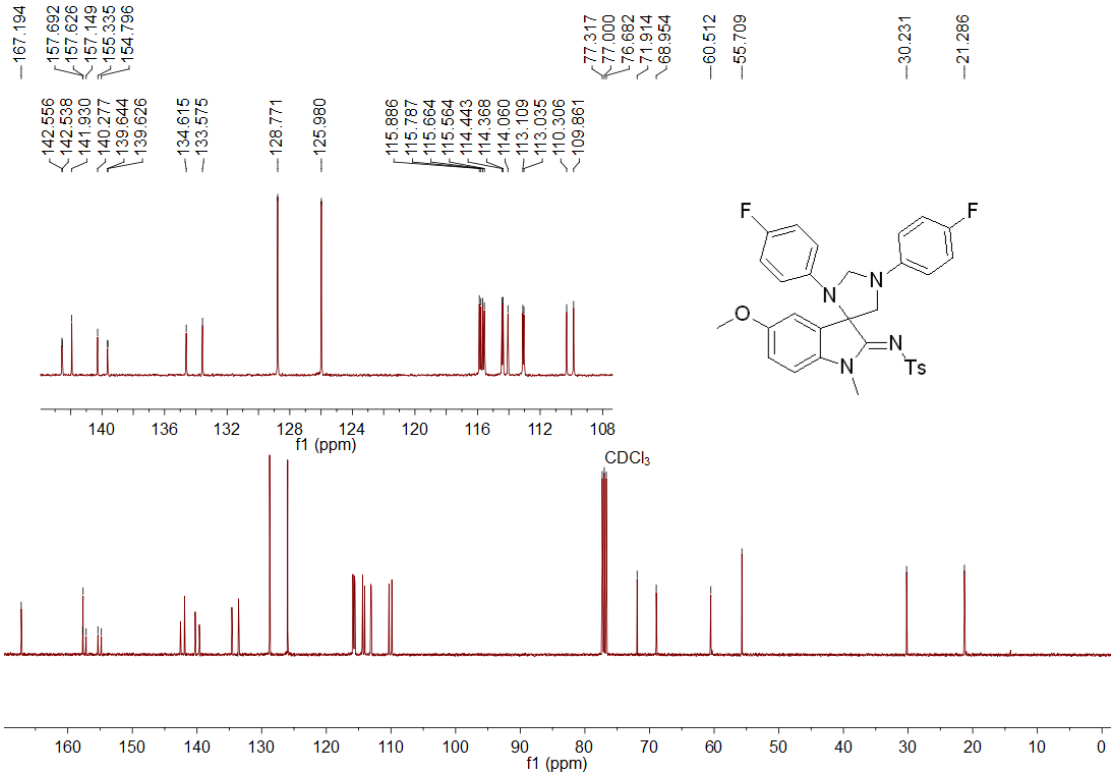
^{1}H NMR of Compoud 3e



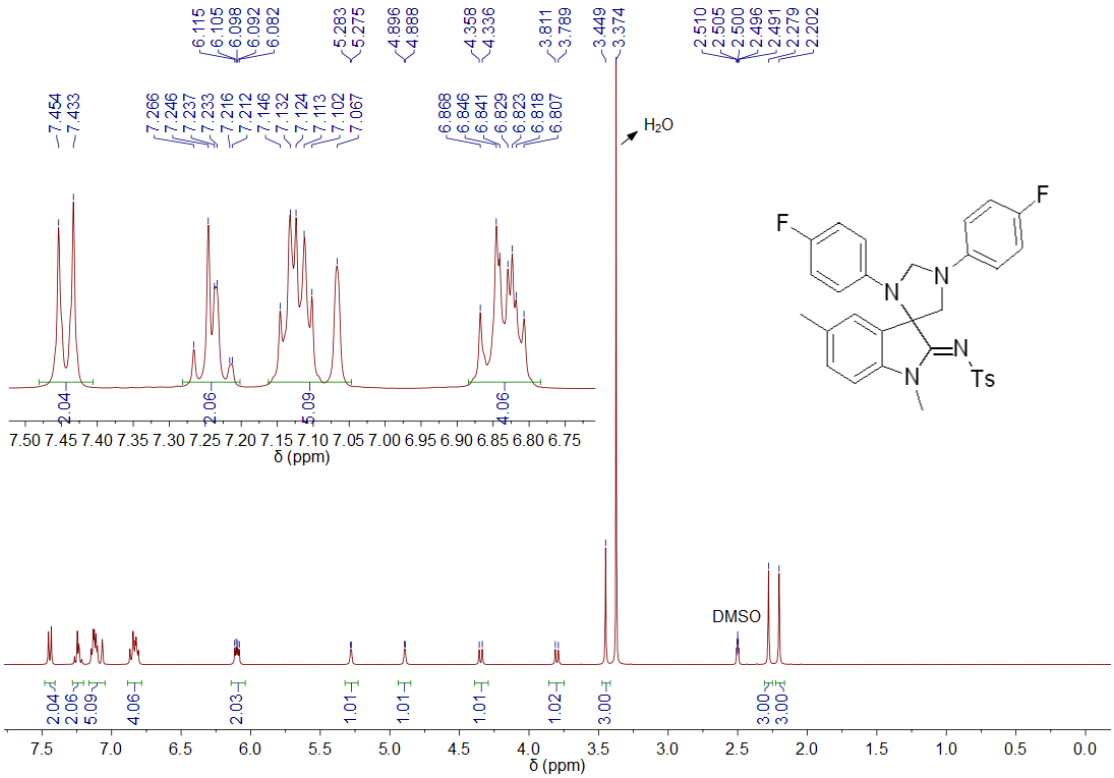
^{13}C NMR of Compoud 3e



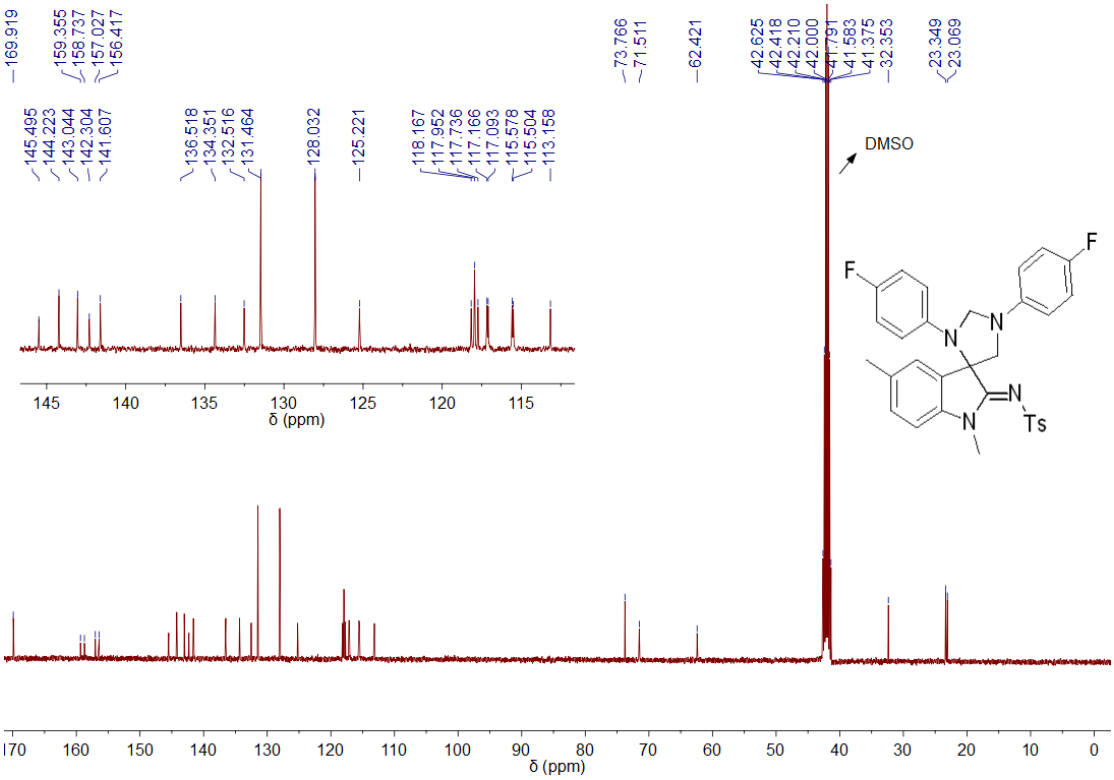
^{1}H NMR of Compoud 3f



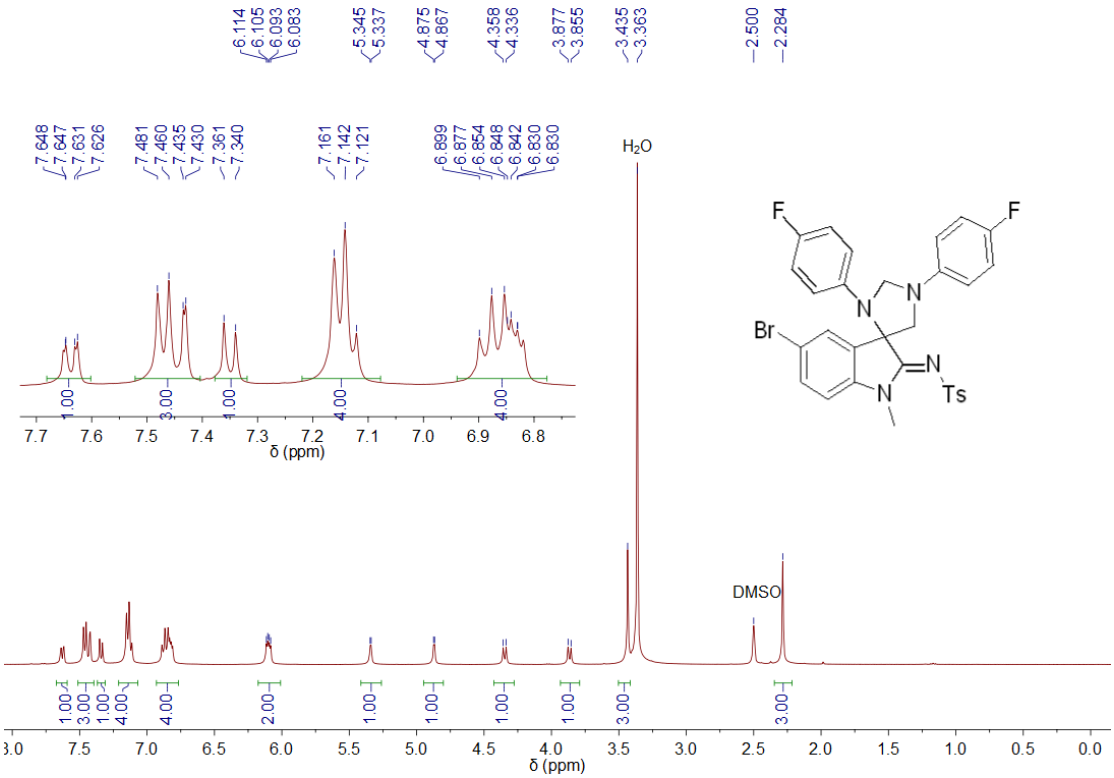
^{13}C NMR of Compoud 3f



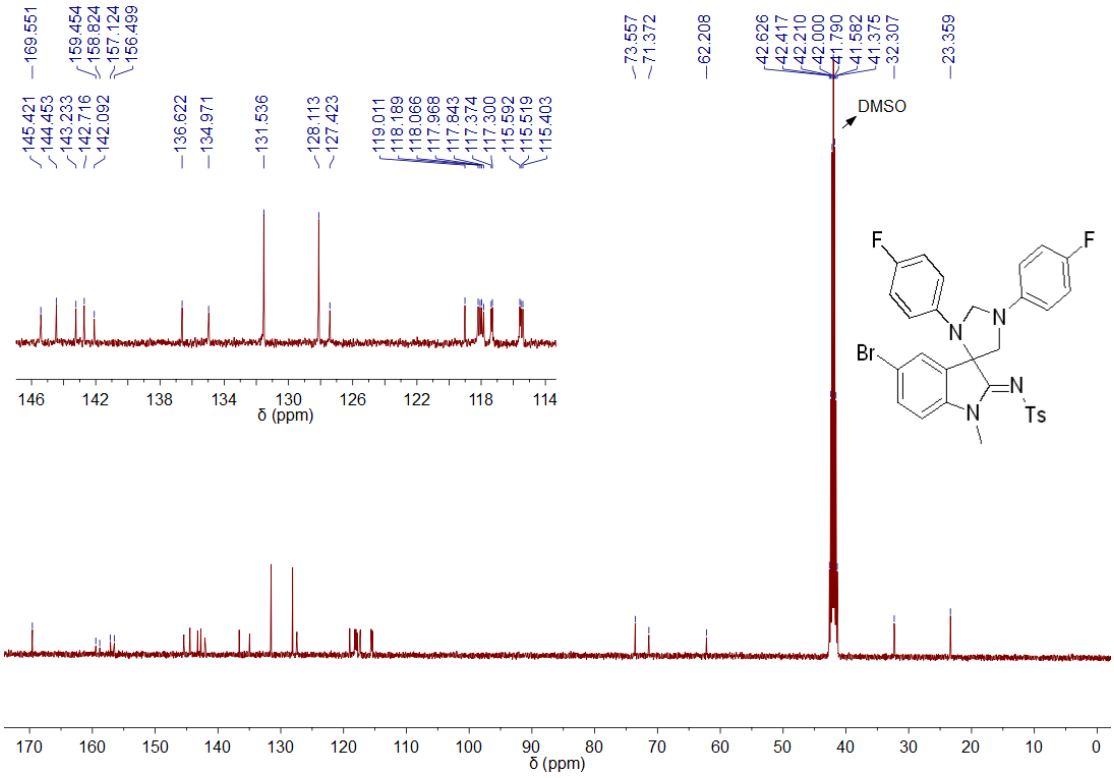
^{1}H NMR of Compoud 3g



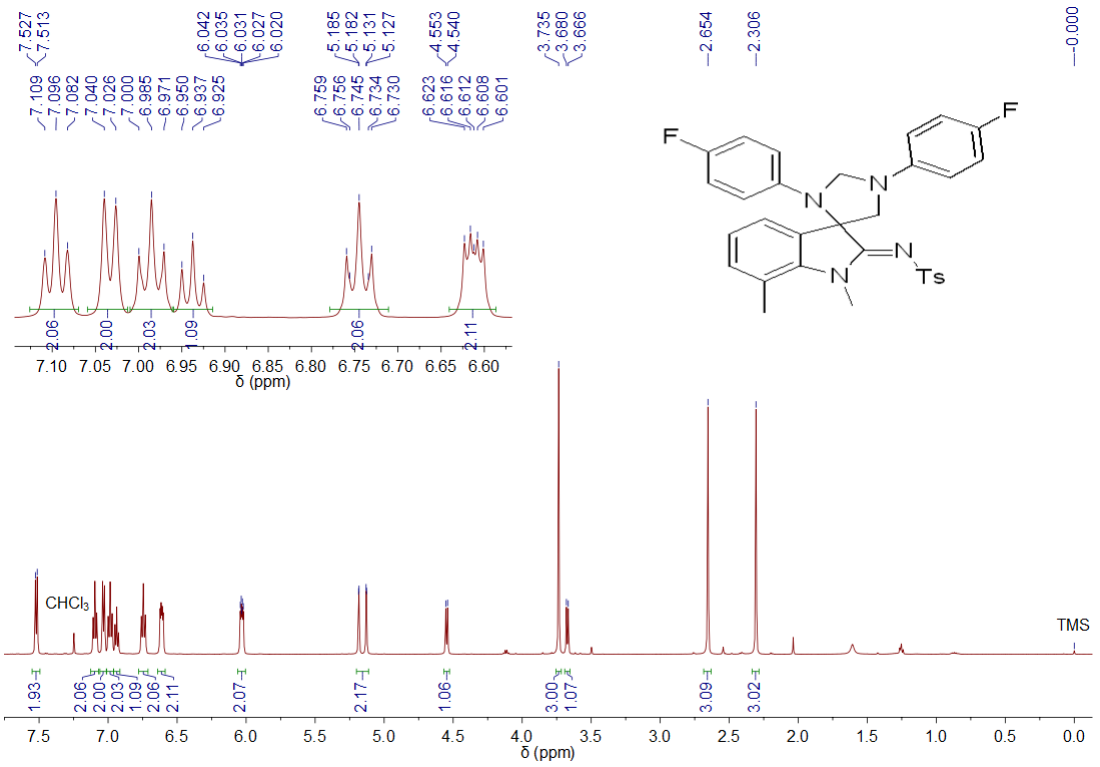
^{13}C NMR of Compoud 3g



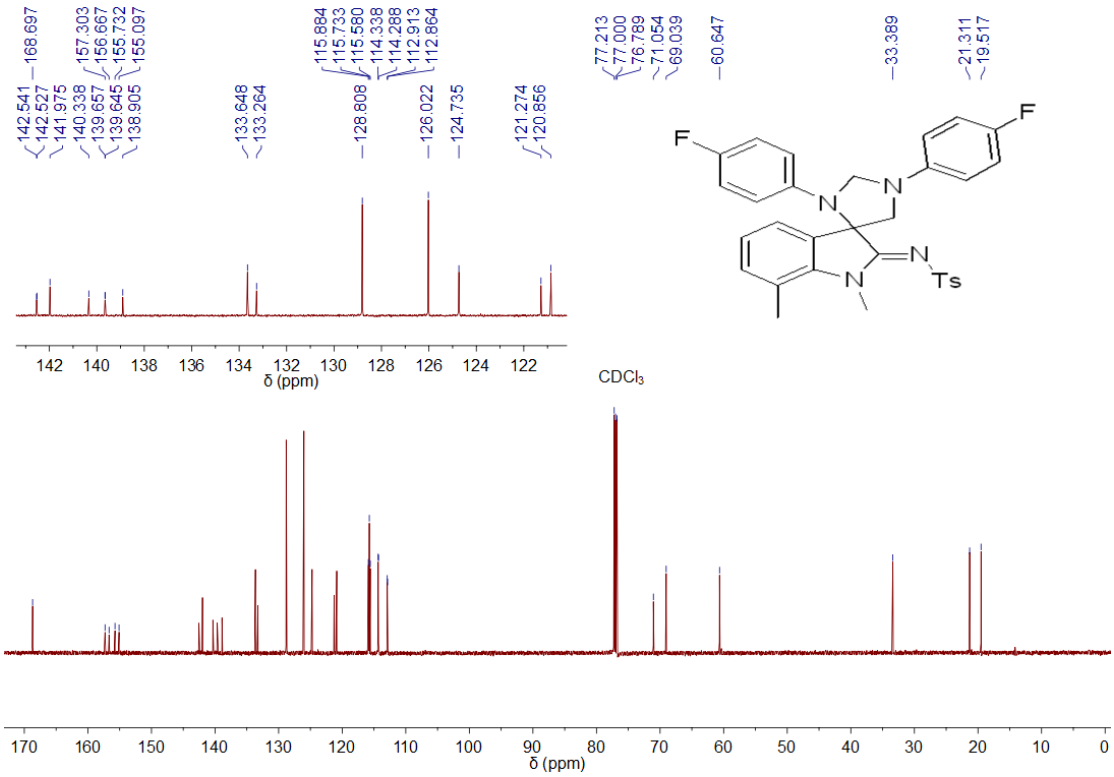
^{1}H NMR of Compoud 3h



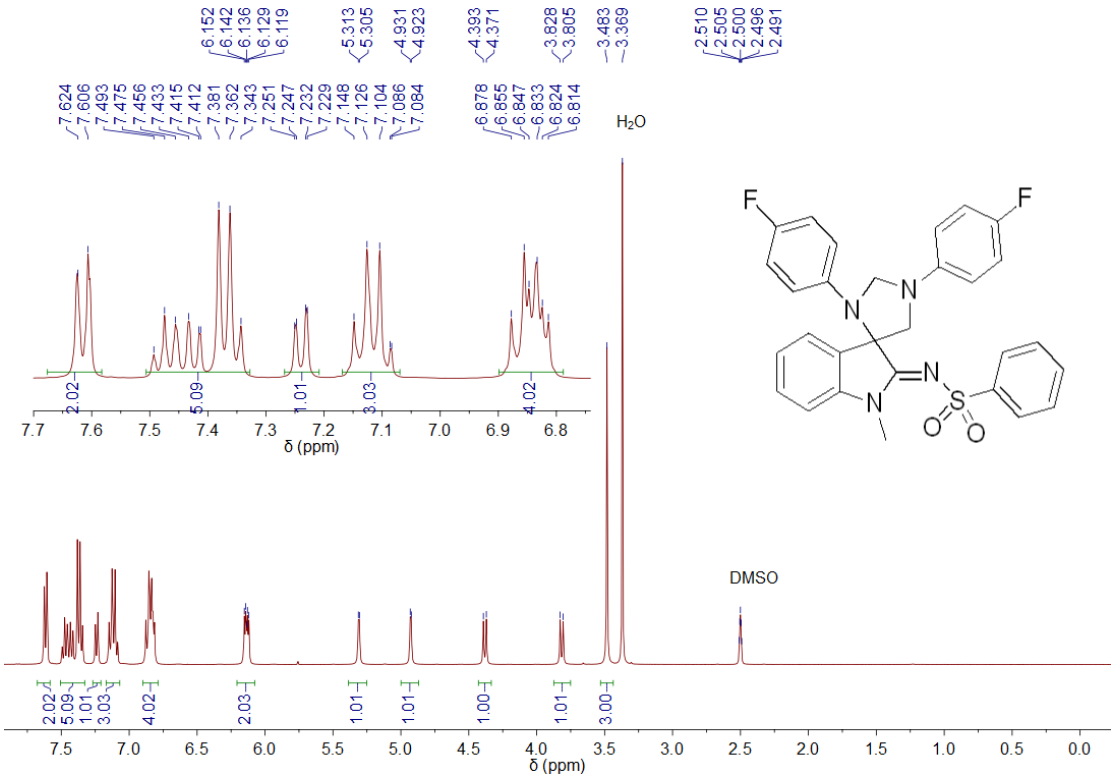
^{13}C NMR of Compoud 3h



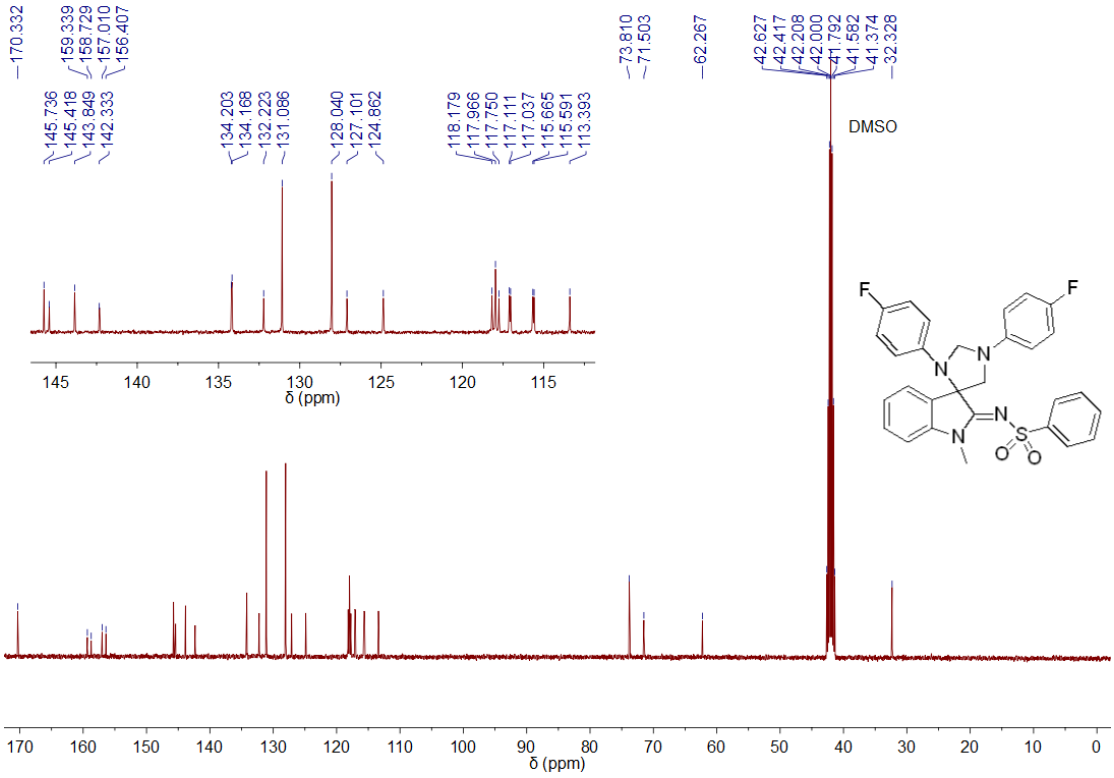
^{1}H NMR of Compoud 3i



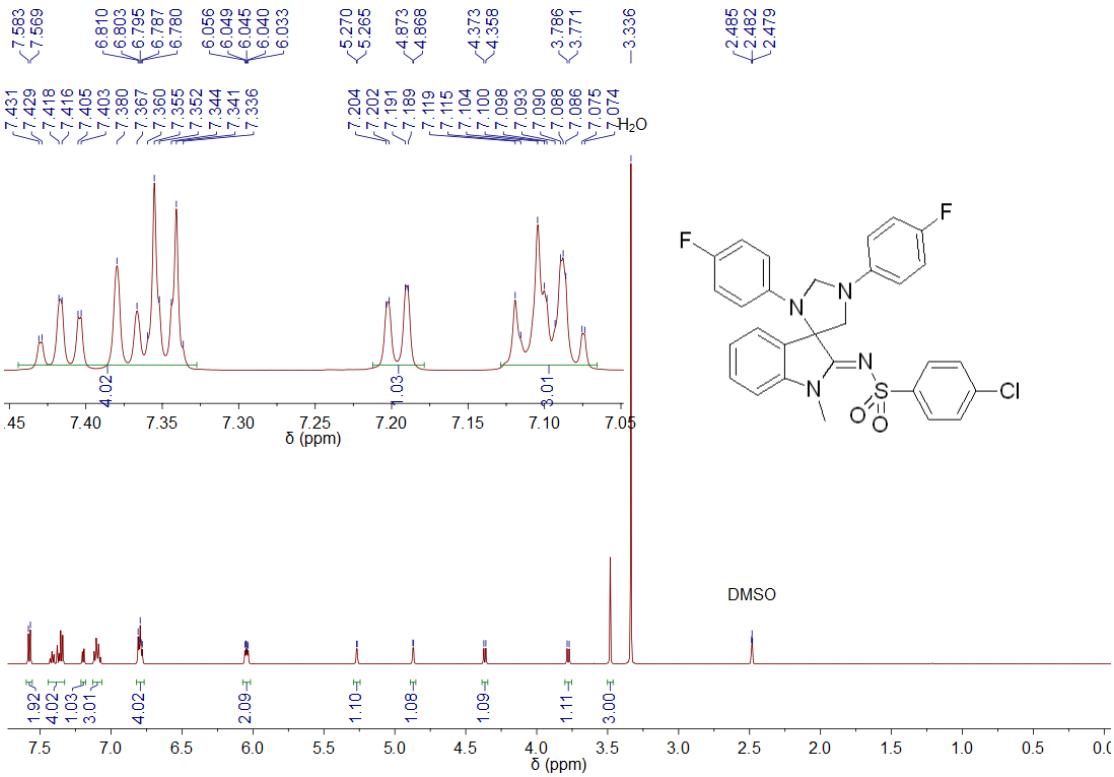
^{13}C NMR of Compoud 3i



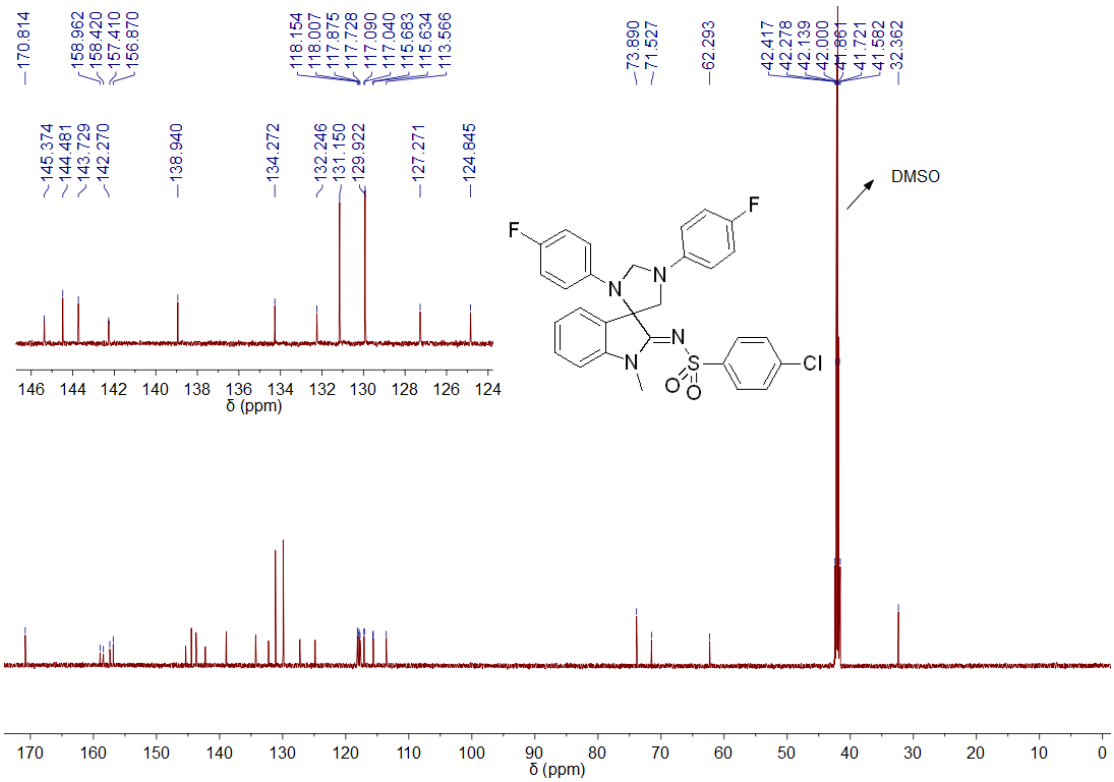
^{1}H NMR of Compoud 3j



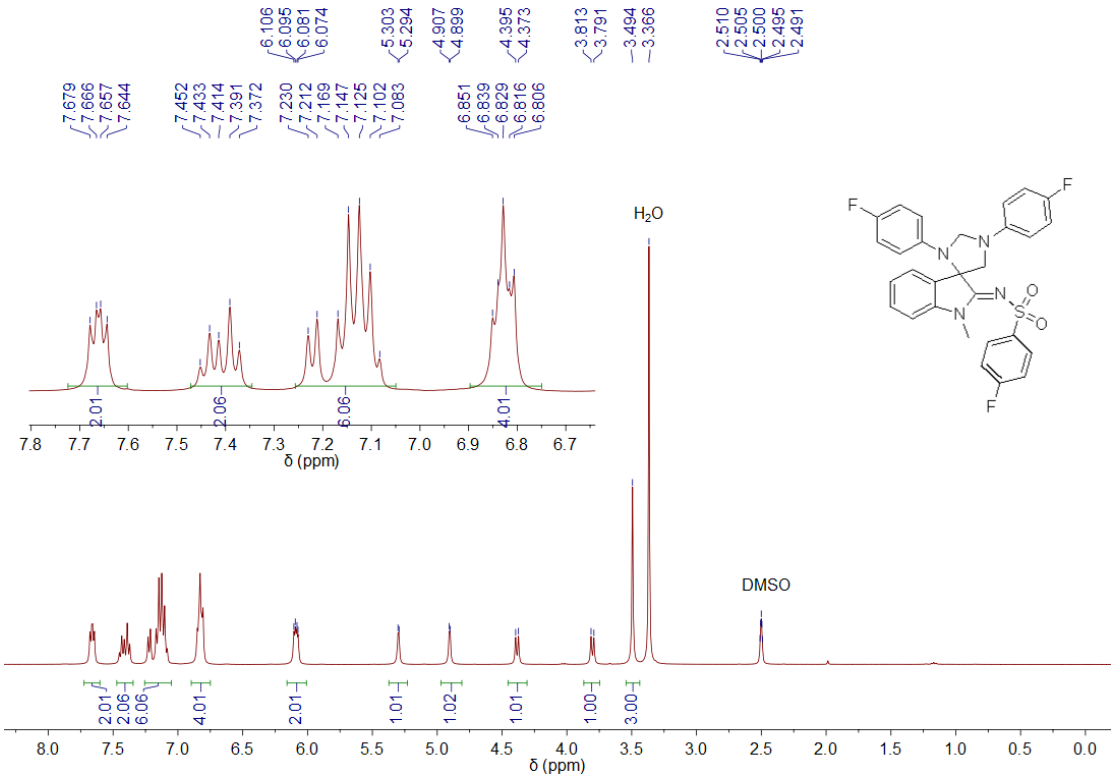
^{13}C NMR of Compoud 3j



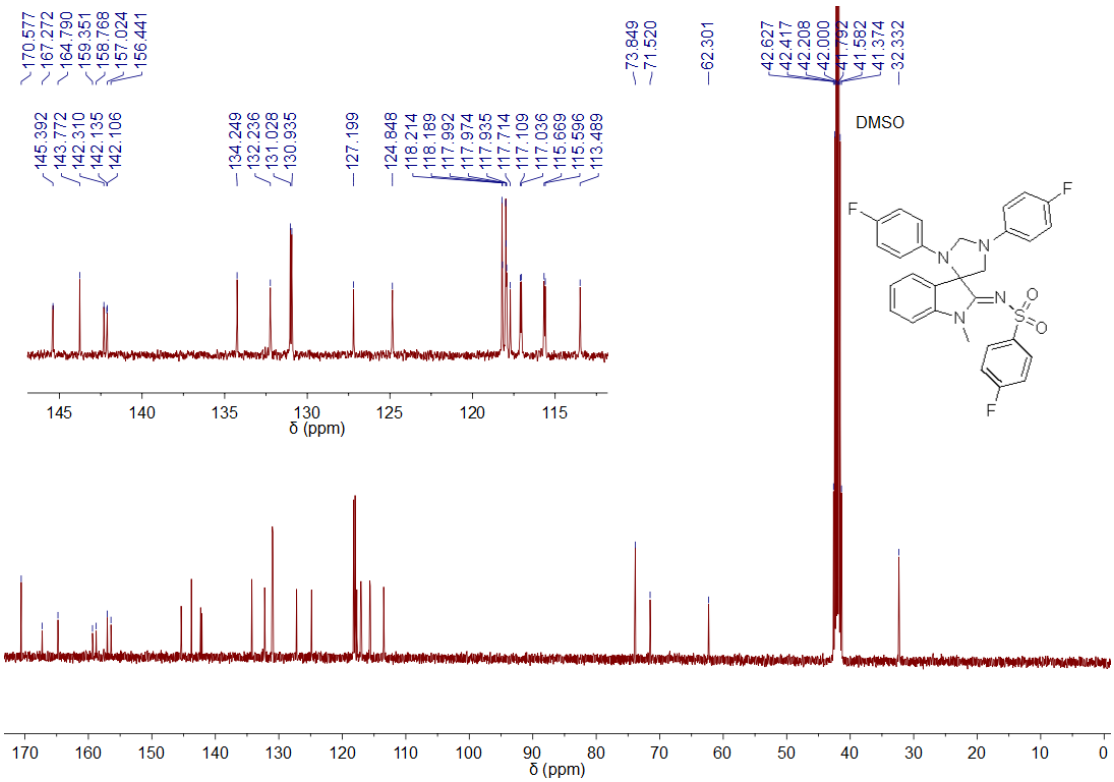
^{1}H NMR of Compoud 3k



^{13}C NMR of Compoud 3k



^{1}H NMR of Compoud 3l



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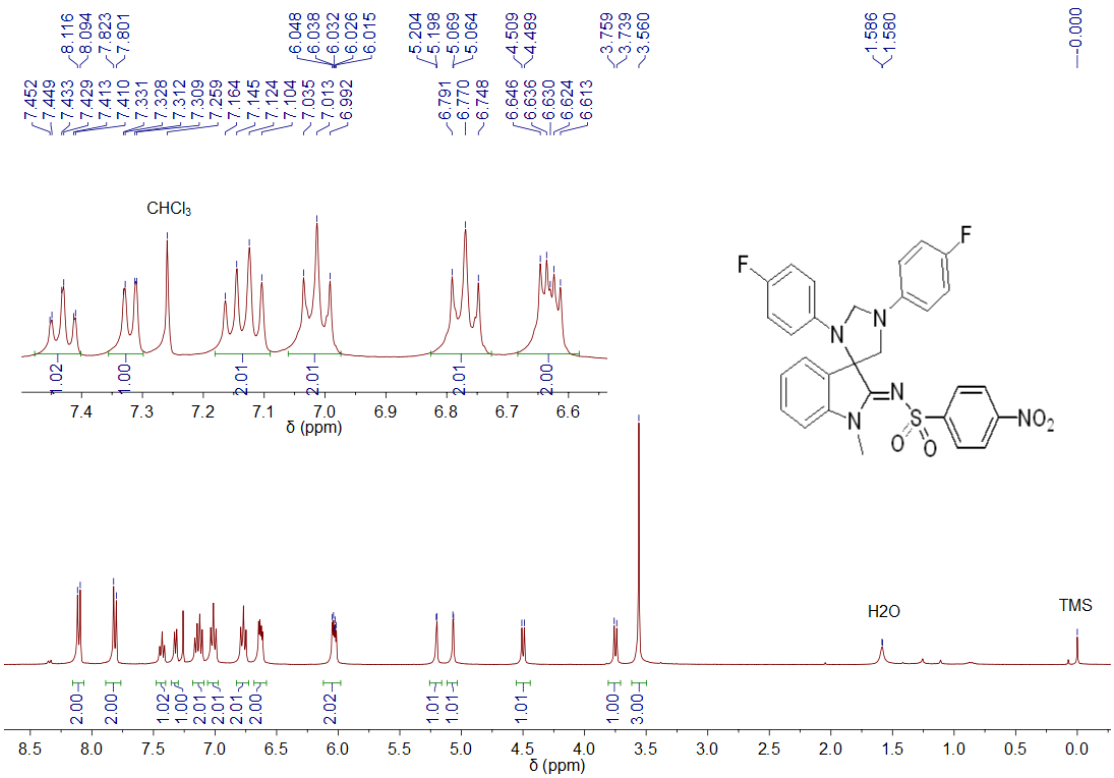
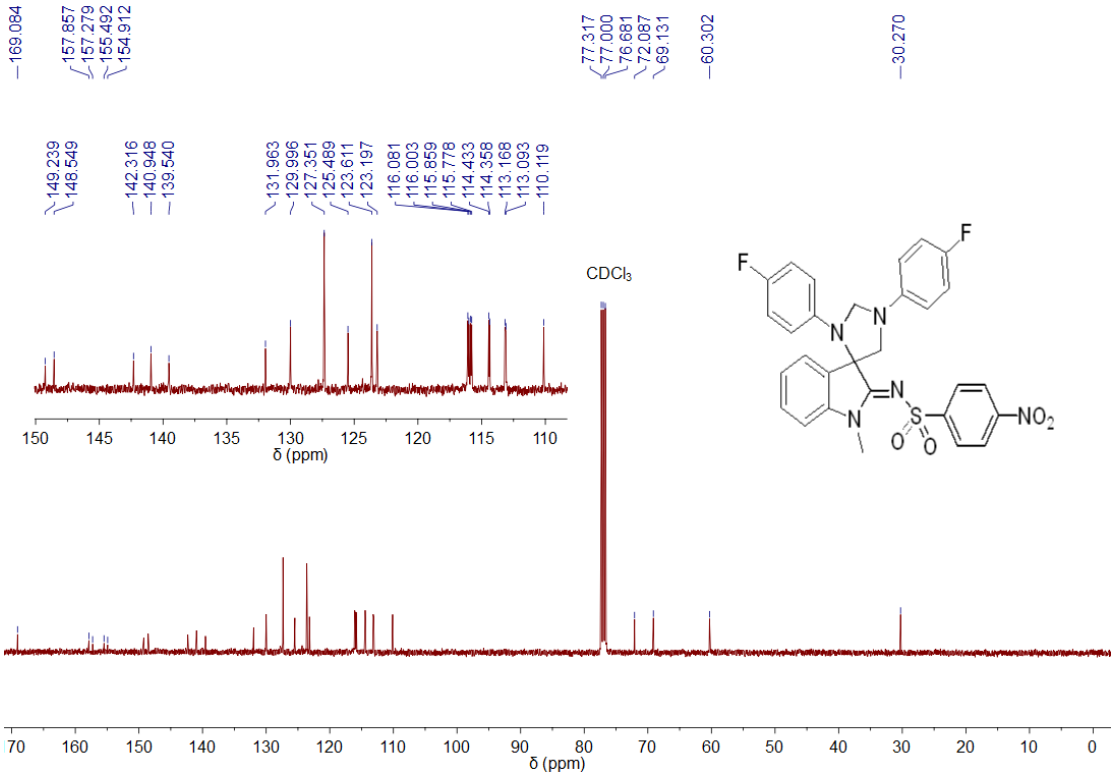
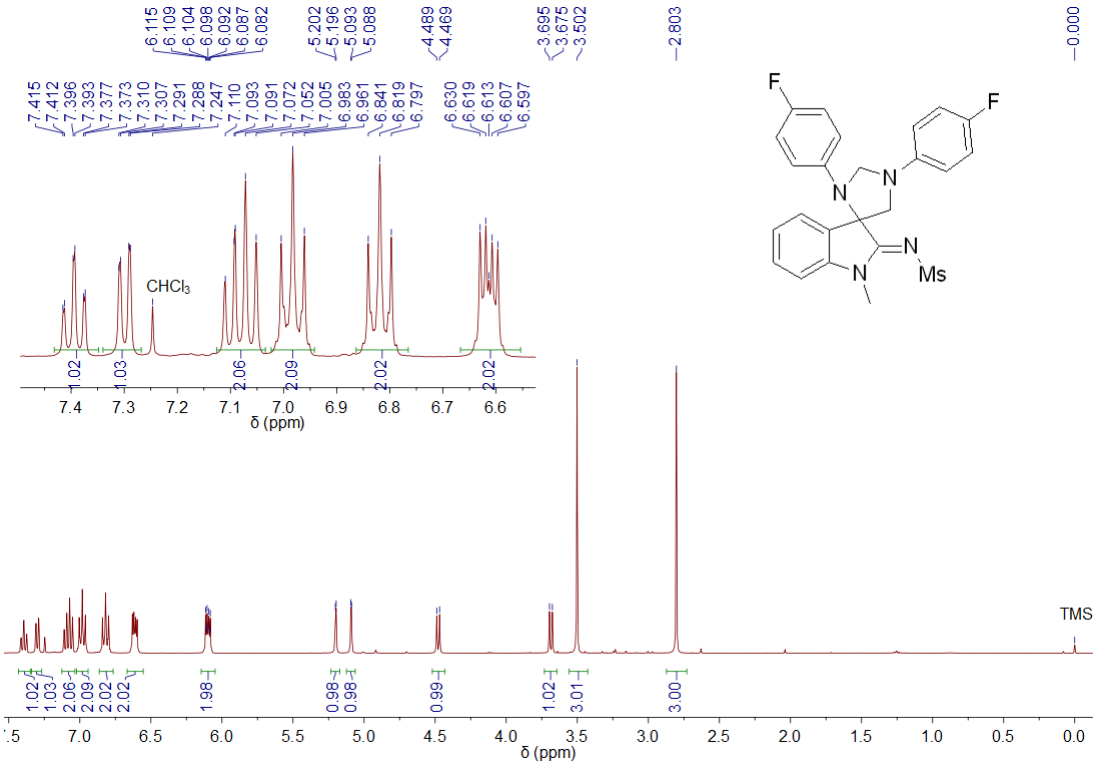


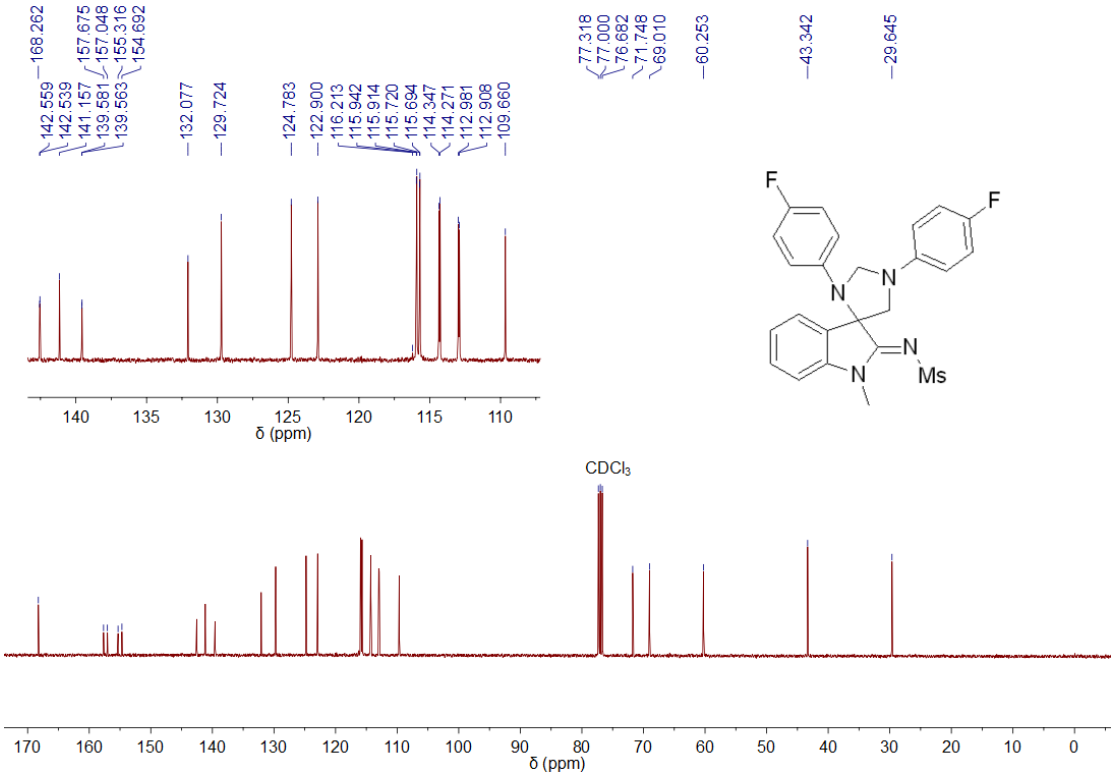
^{1}H NMR of Compoud 3m



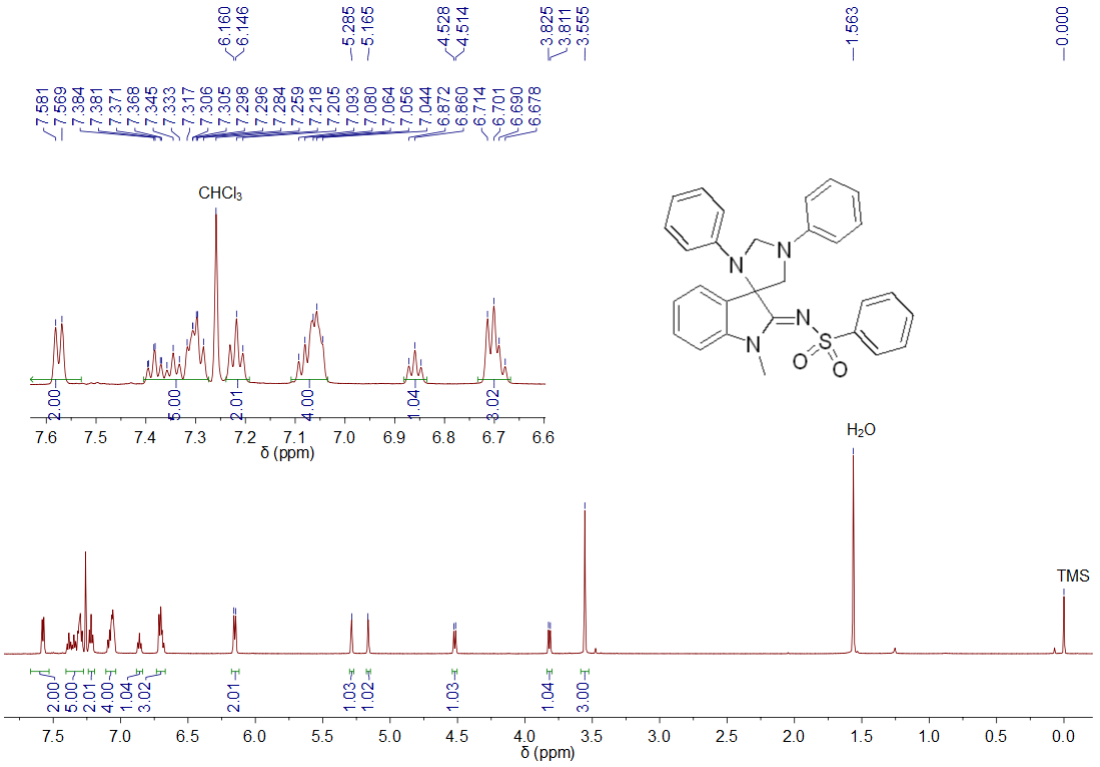
^{13}C NMR of Compoud 3m



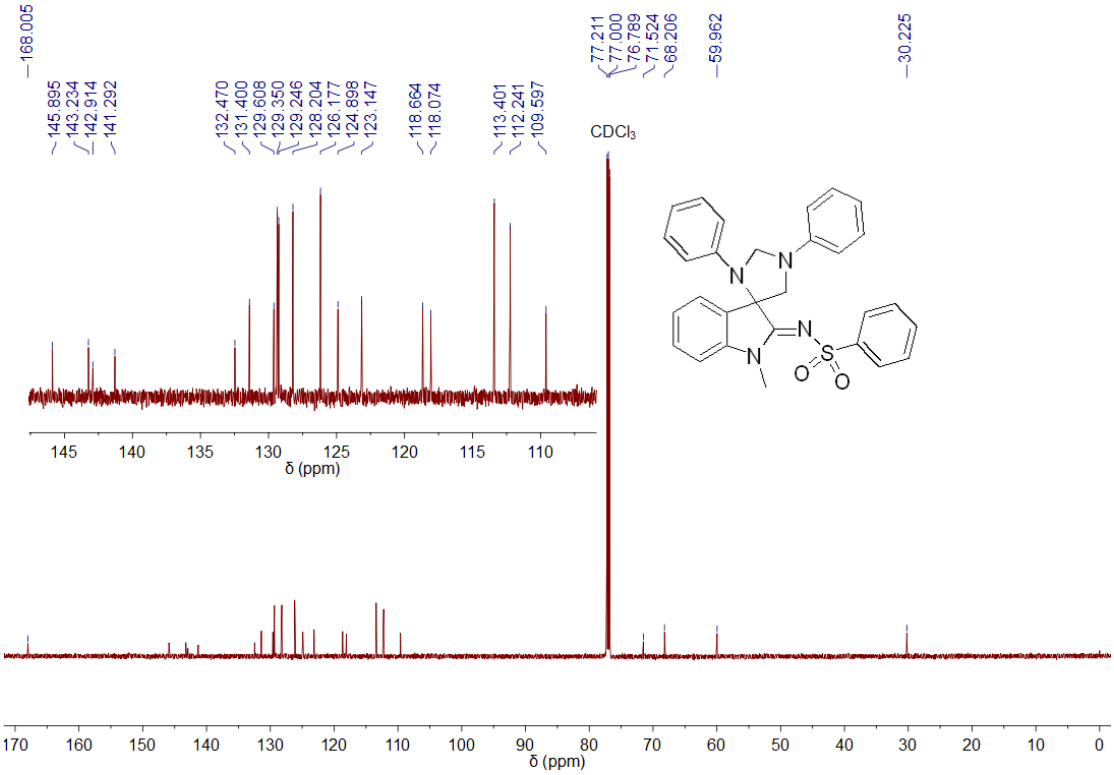
^{1}H NMR of Compoud 3n



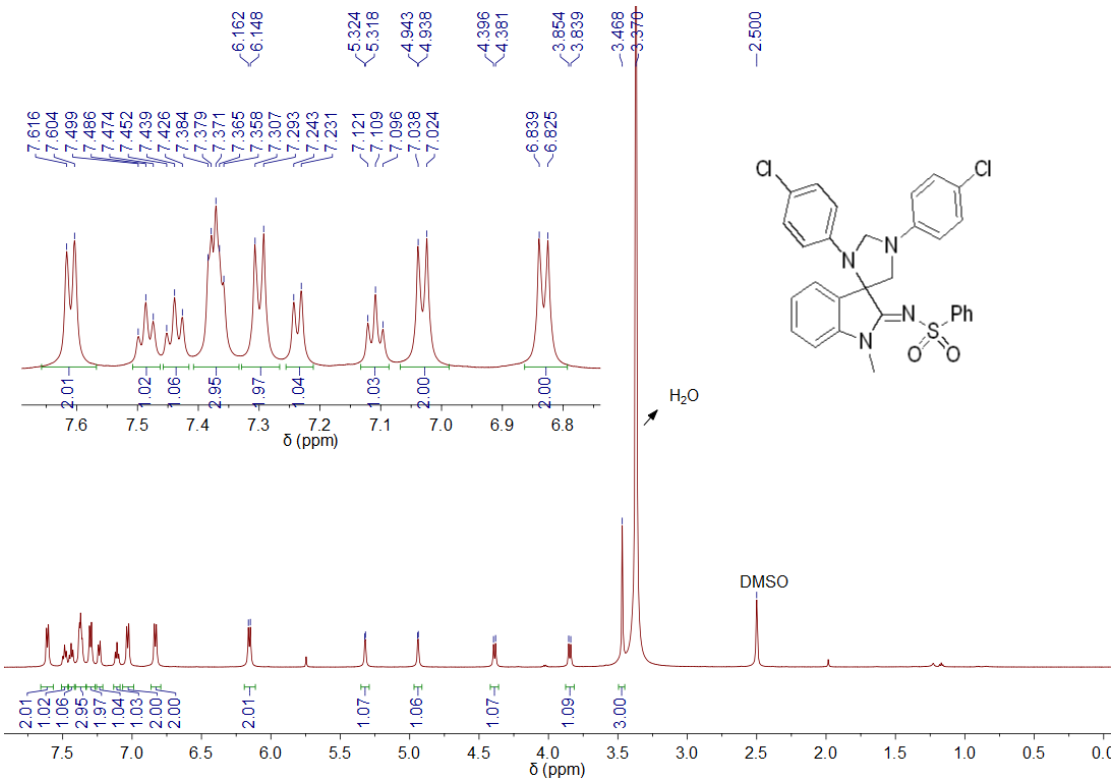
^{13}C NMR of Compoud 3n



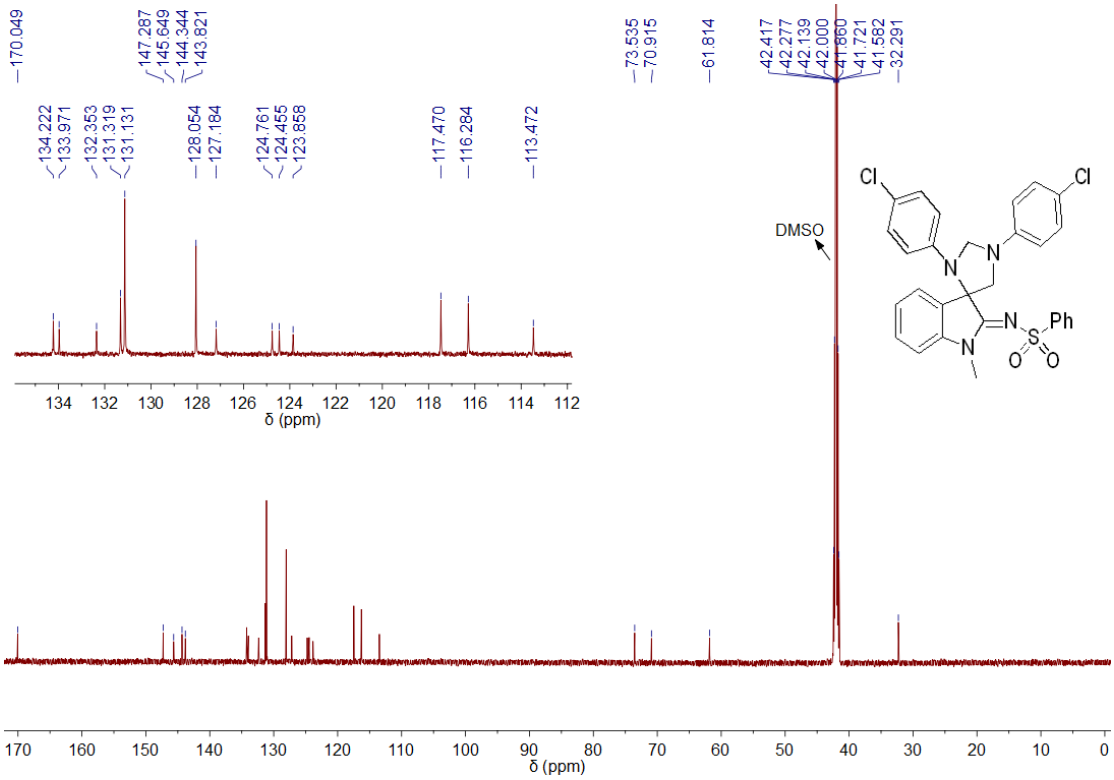
^{1}H NMR of Compoud 3o



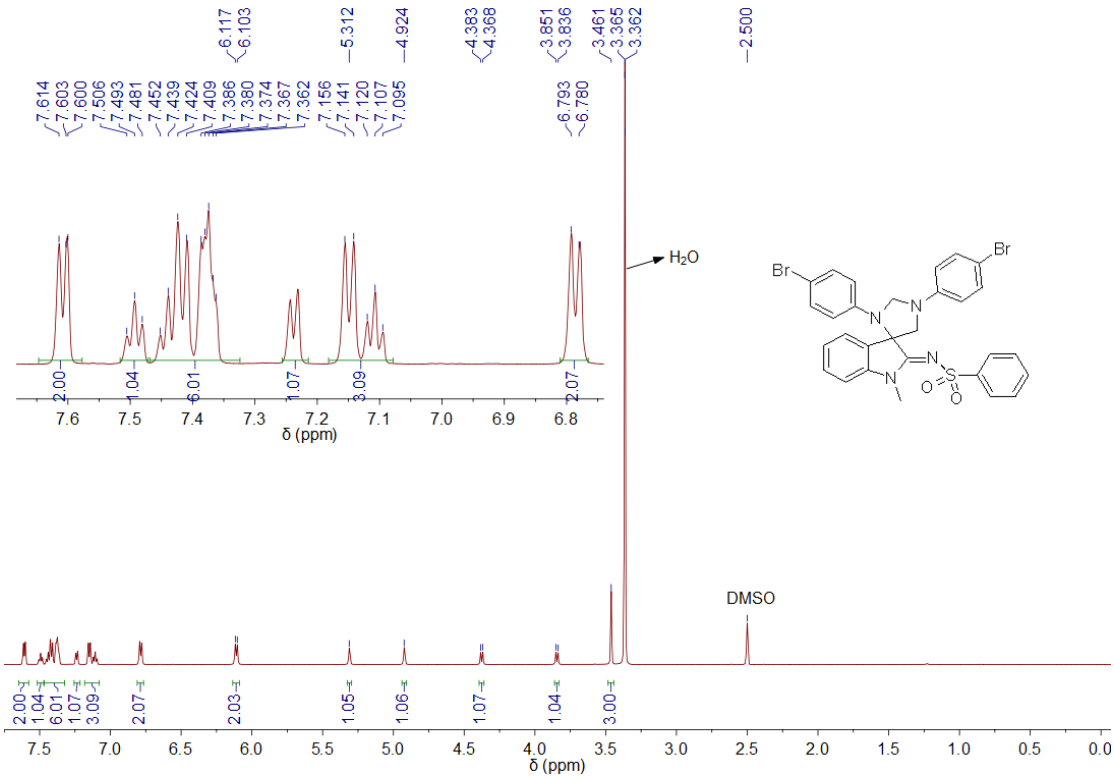
^{13}C NMR of Compoud 3o



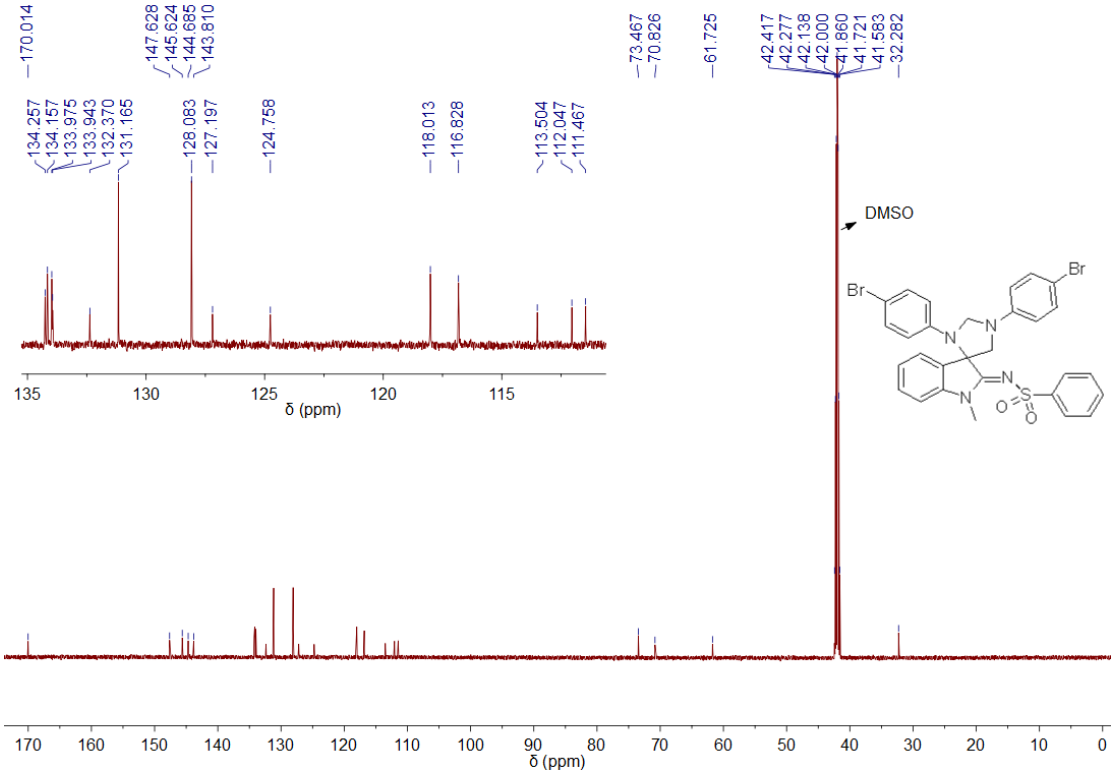
^{1}H NMR of Compoud 3p



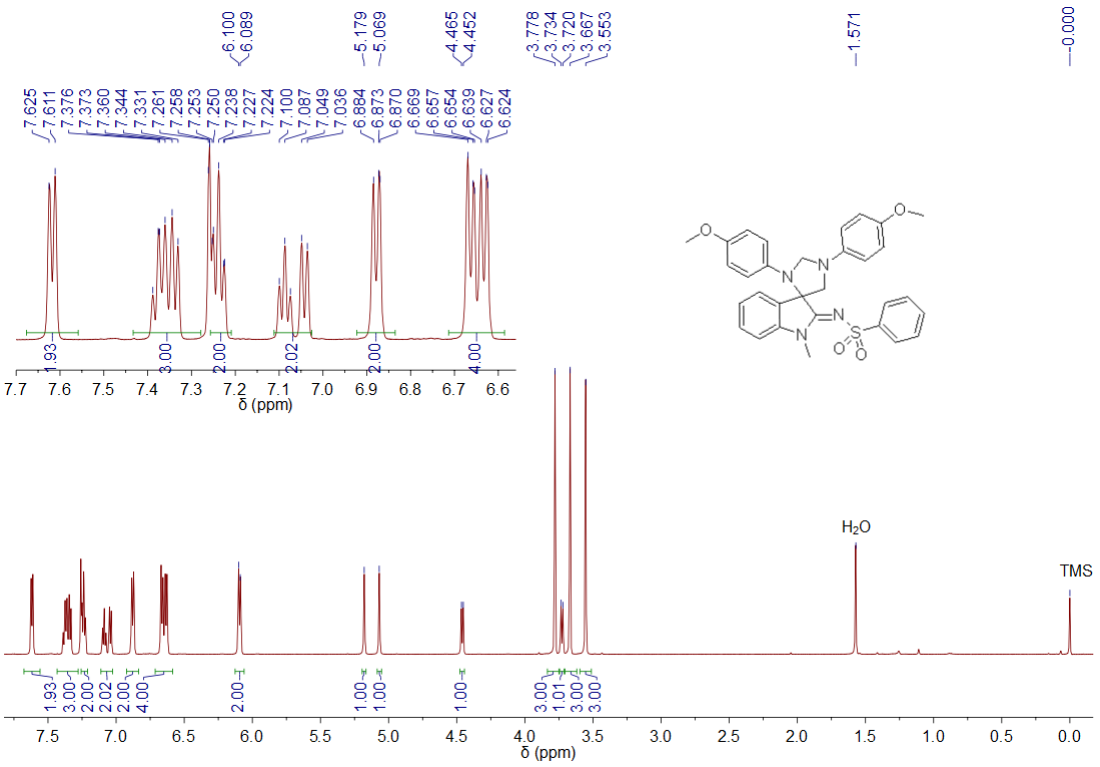
^{13}C NMR of Compoud 3p



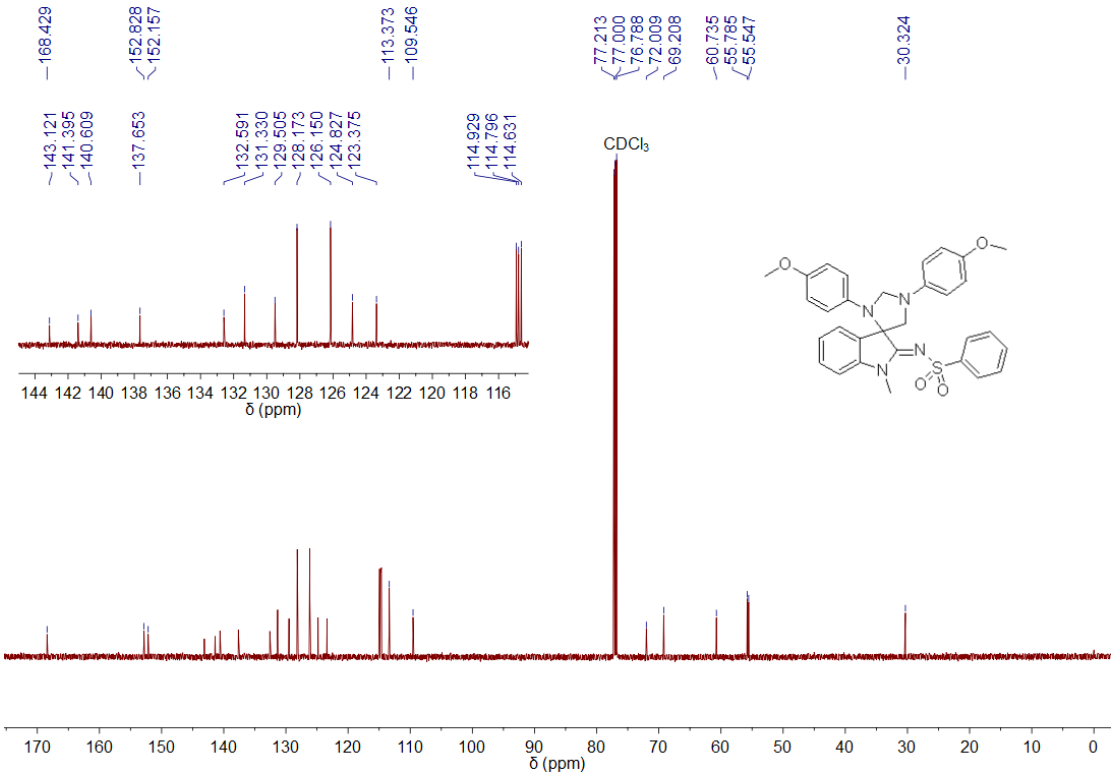
^{1}H NMR of Compoud 3q



^{13}C NMR of Compoud 3q



^{1}H NMR of Compoud 3r



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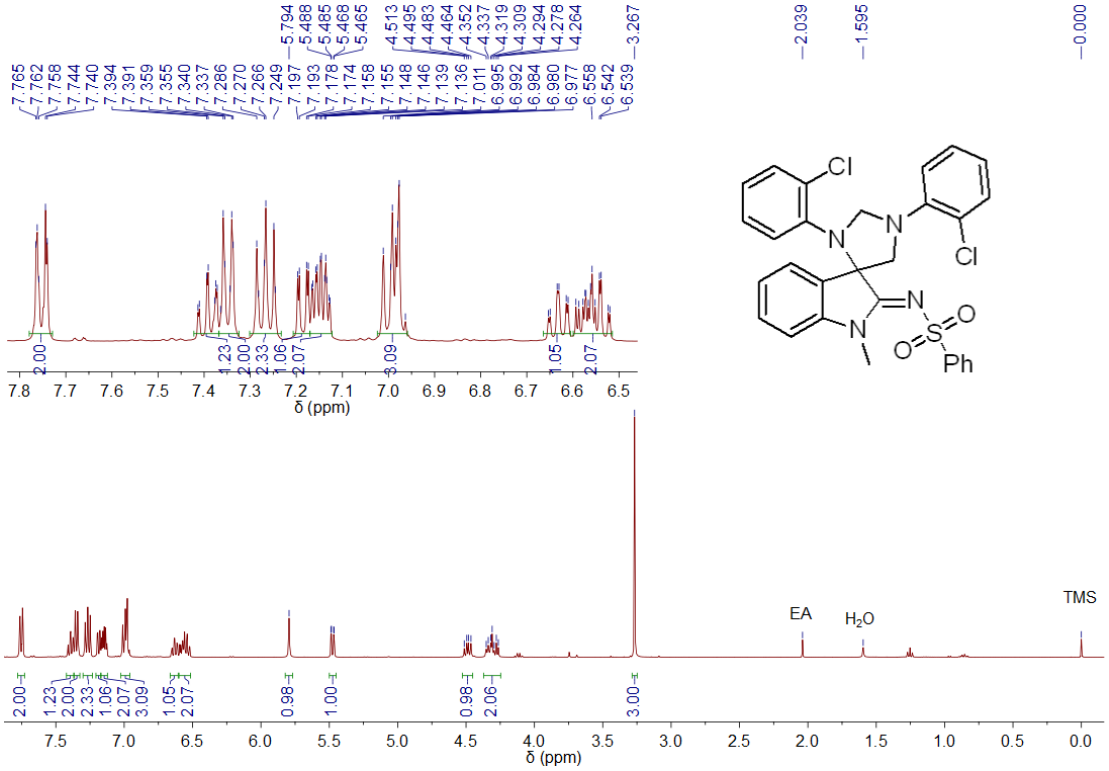
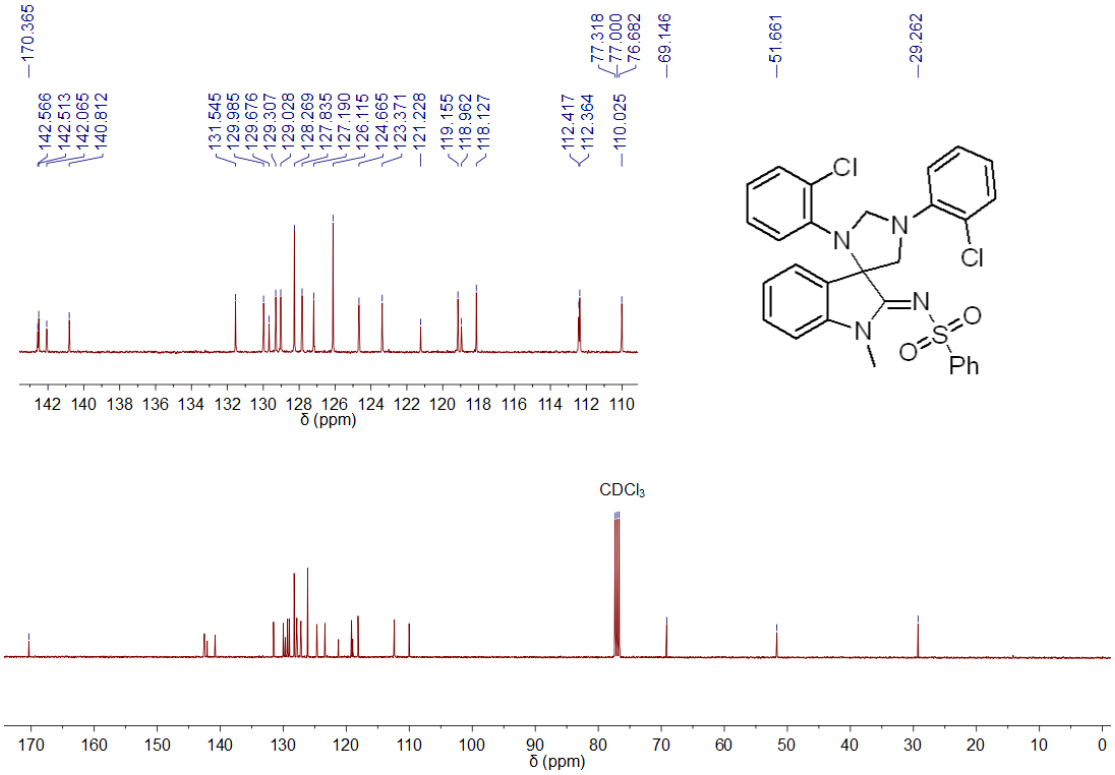
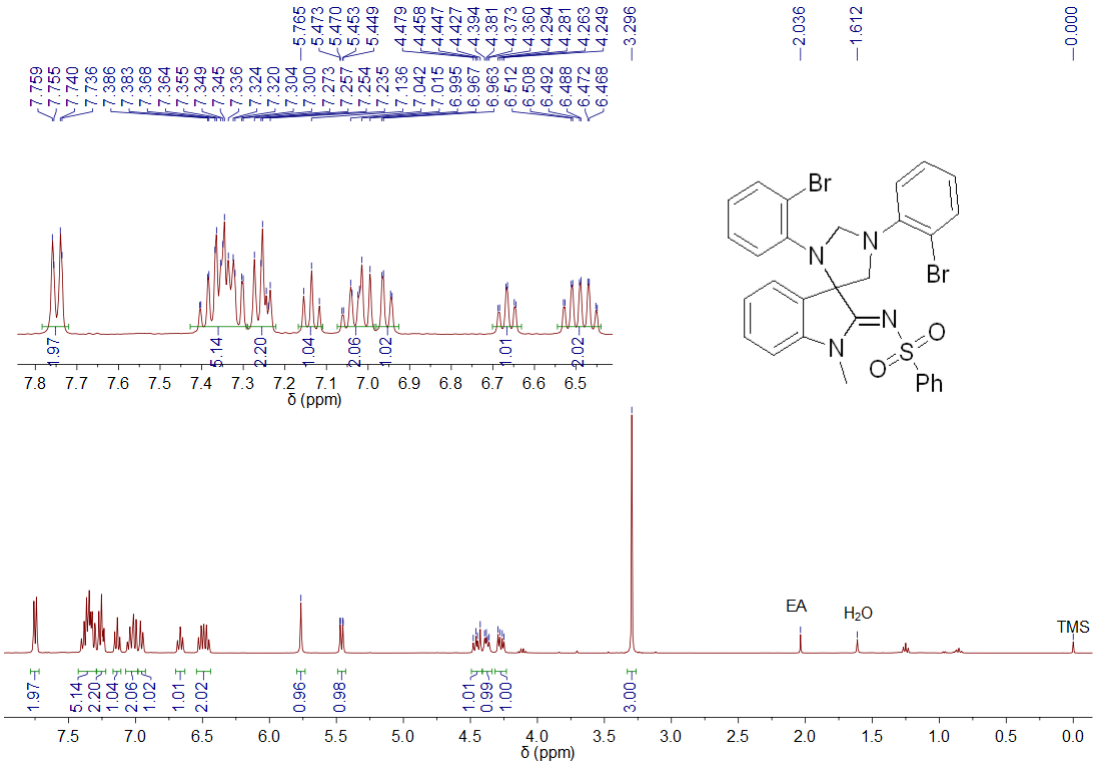


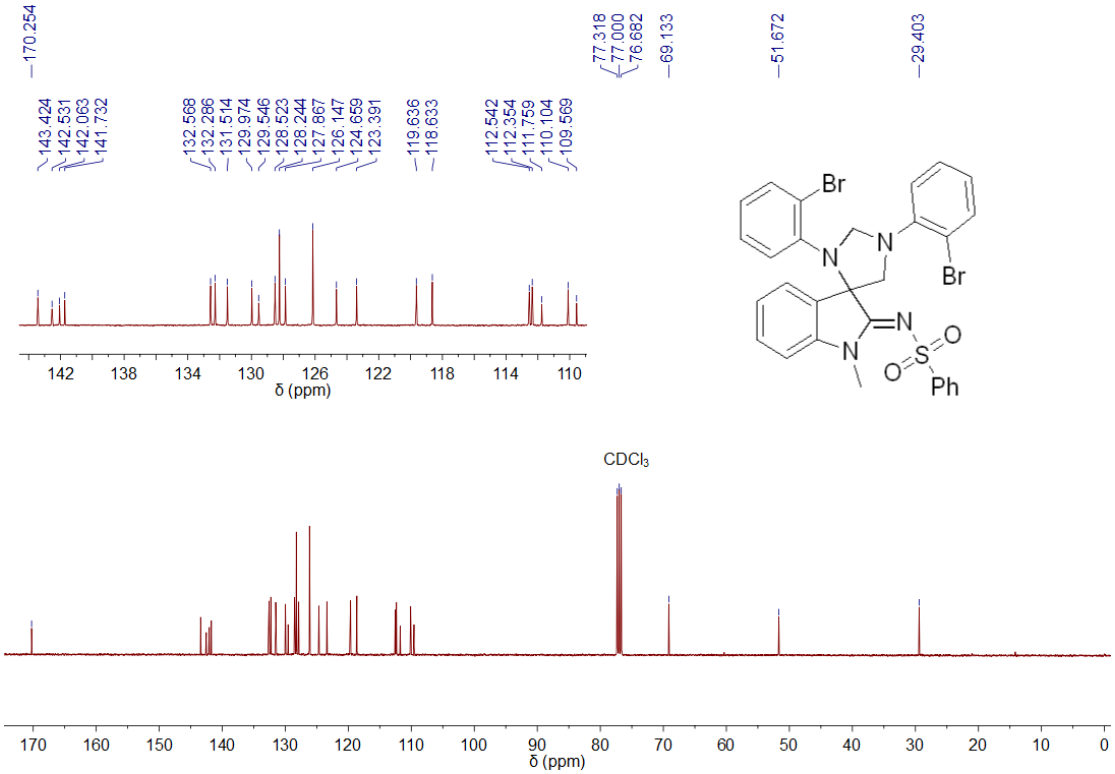
^{1}H NMR of Compoud 3s



^{13}C NMR of Compoud 3s



^{1}H NMR of Compoud 3t



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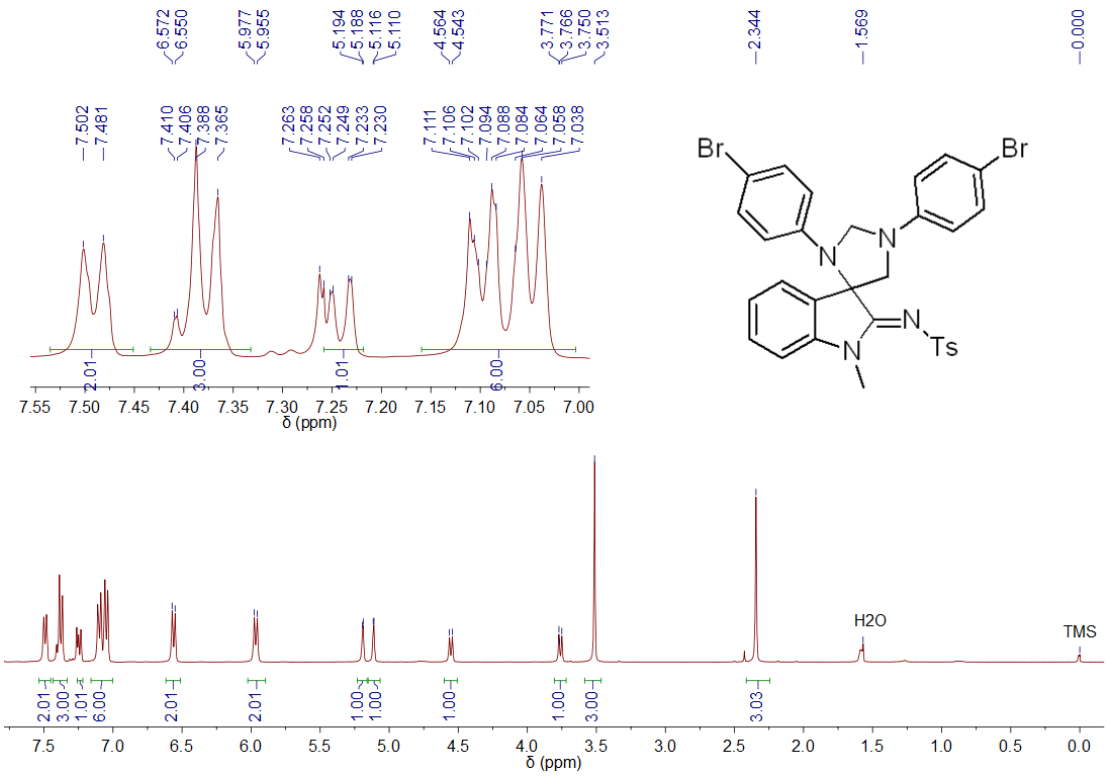
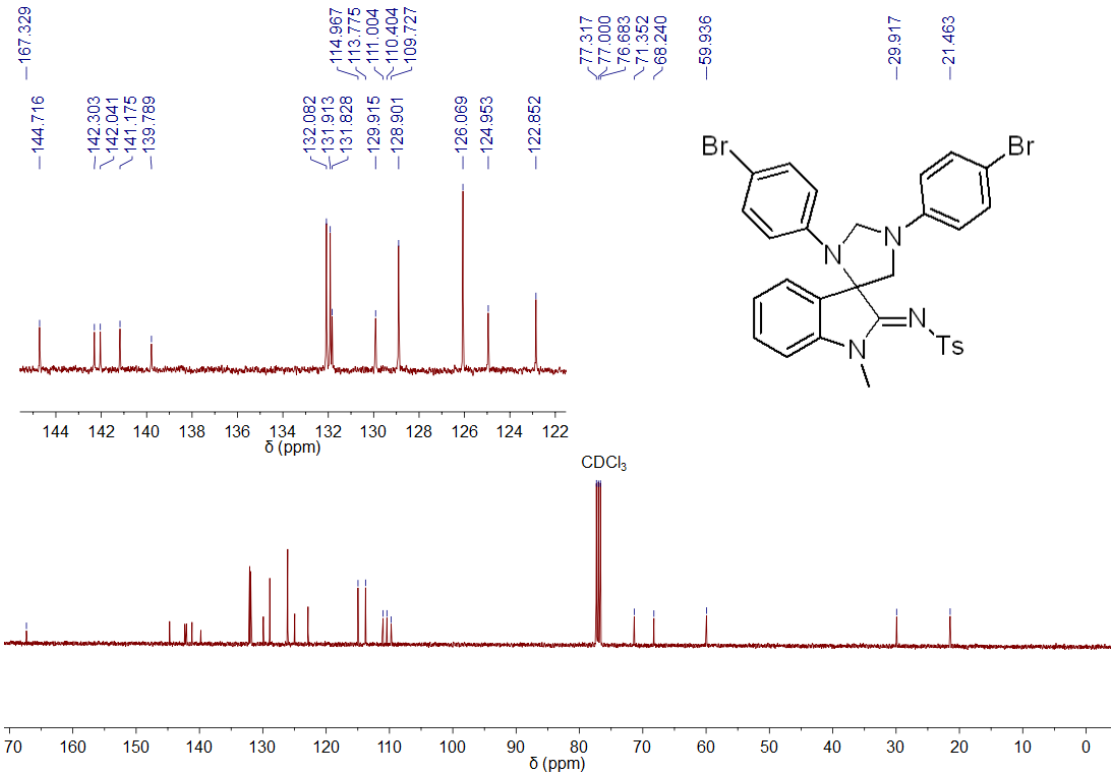
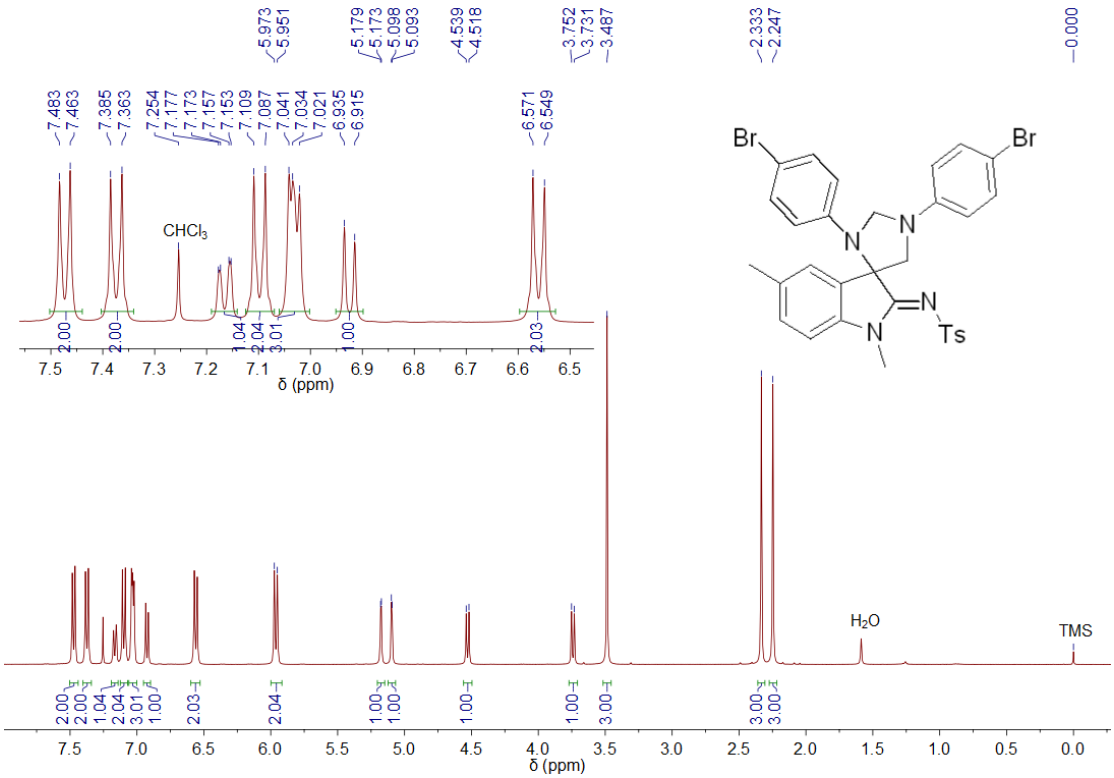


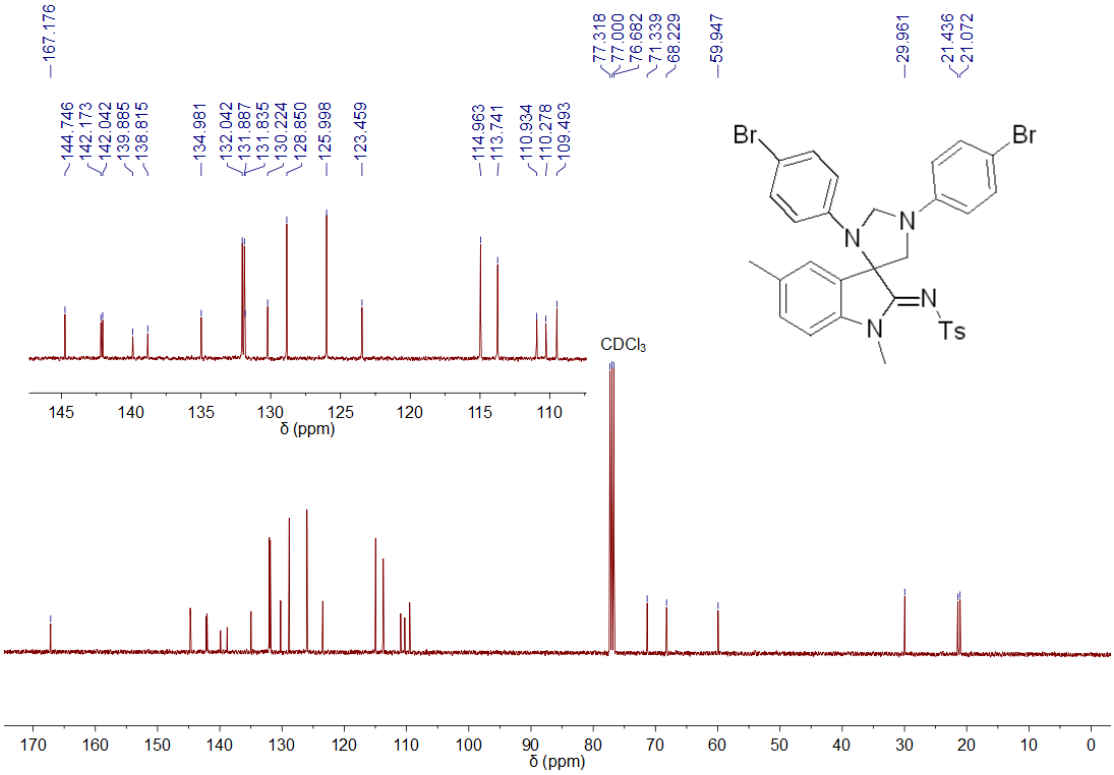
^{1}H NMR of Compoud 3u



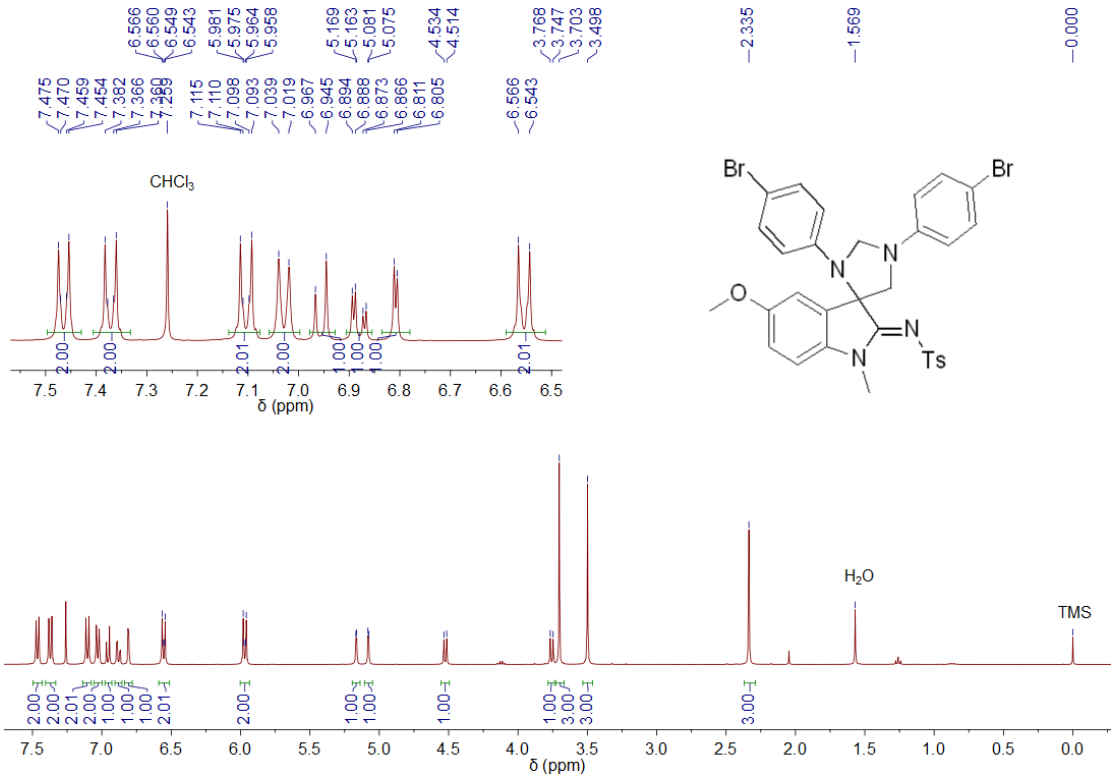
^{13}C NMR of Compoud 3u



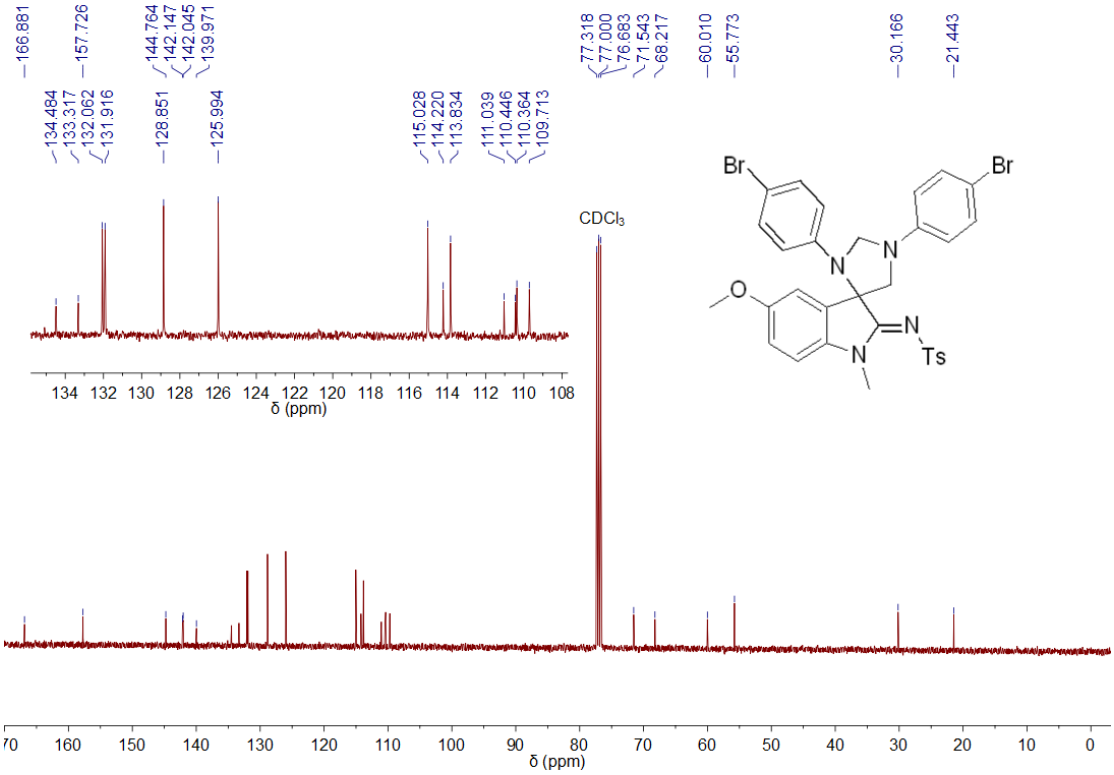
^{1}H NMR of Compoud 3v



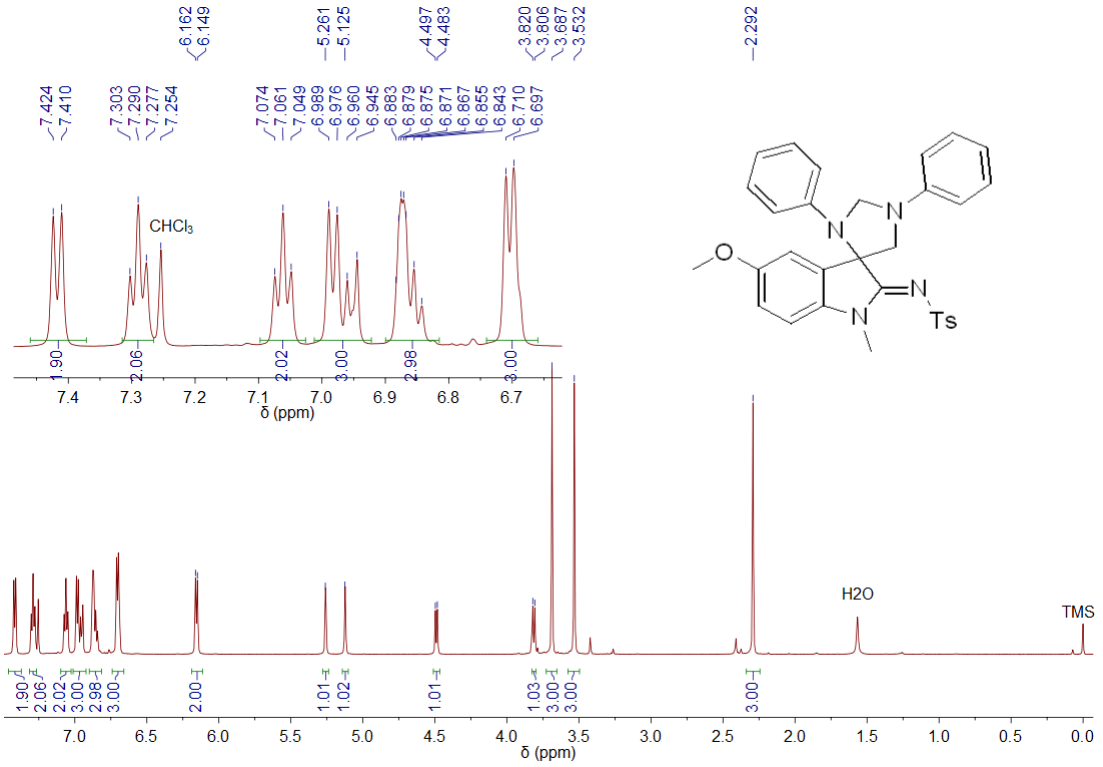
^{13}C NMR of Compoud 3v



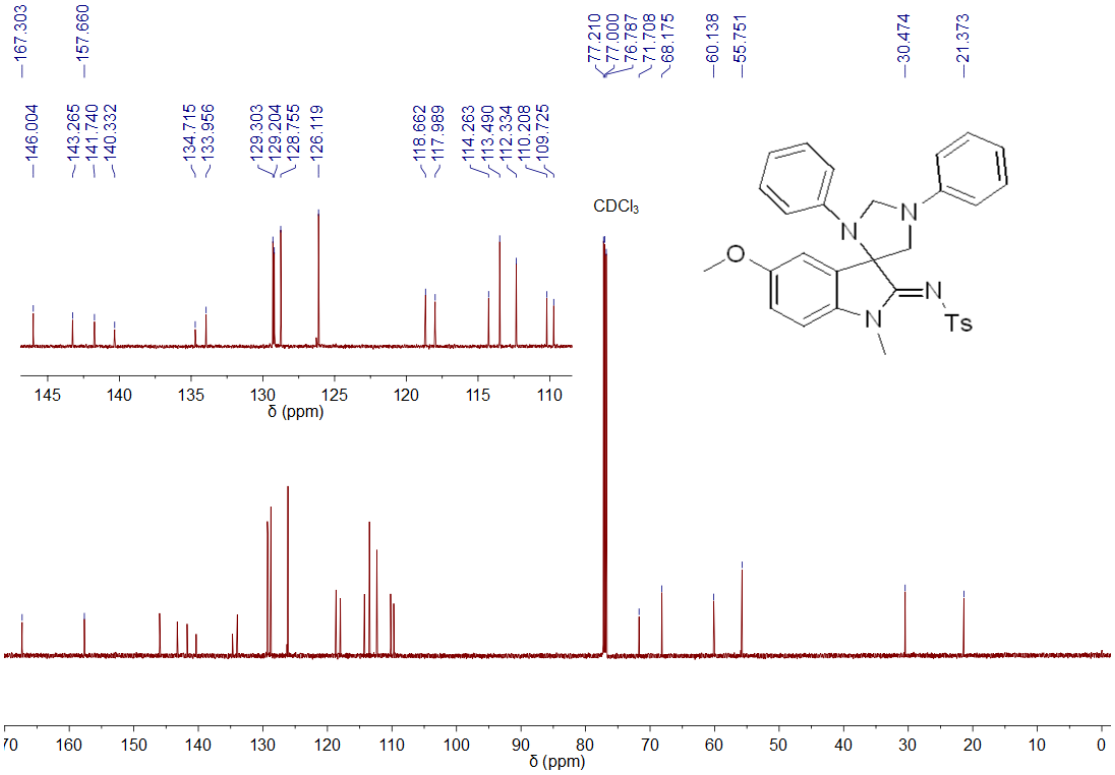
^{1}H NMR of Compoud 3w



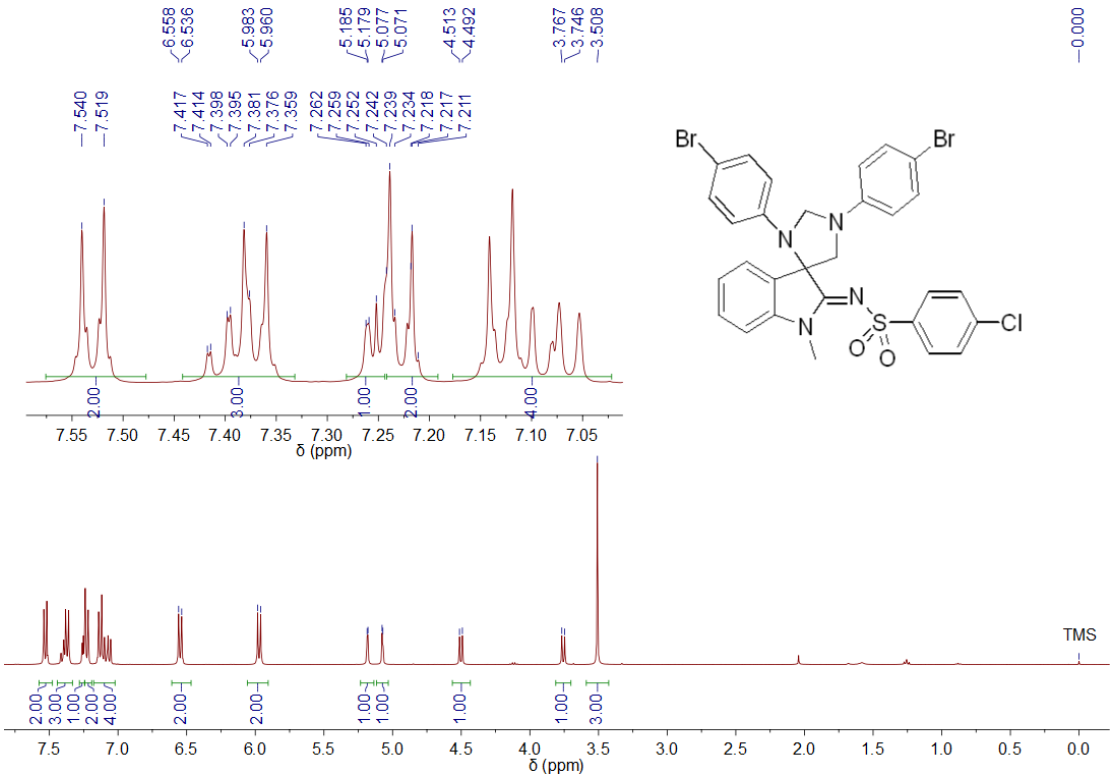
^{13}C NMR of Compoud 3w



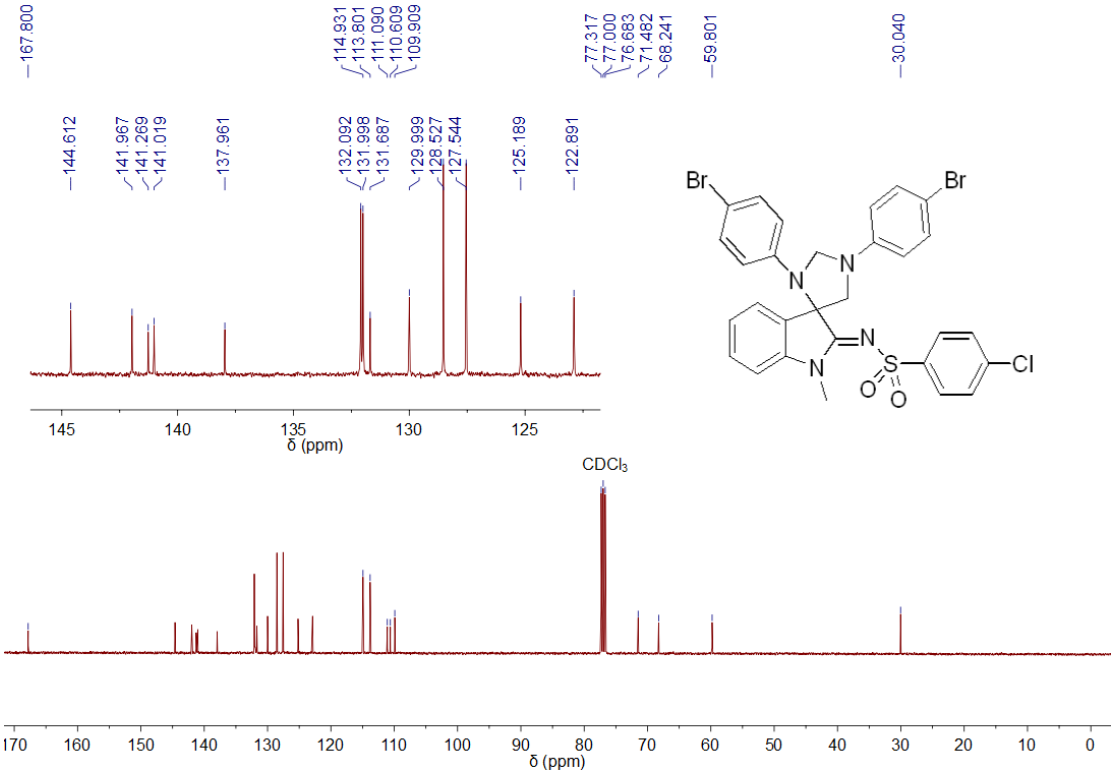
^{1}H NMR of Compoud 3x



^{13}C NMR of Compoud 3x



^{1}H NMR of Compoud 3y



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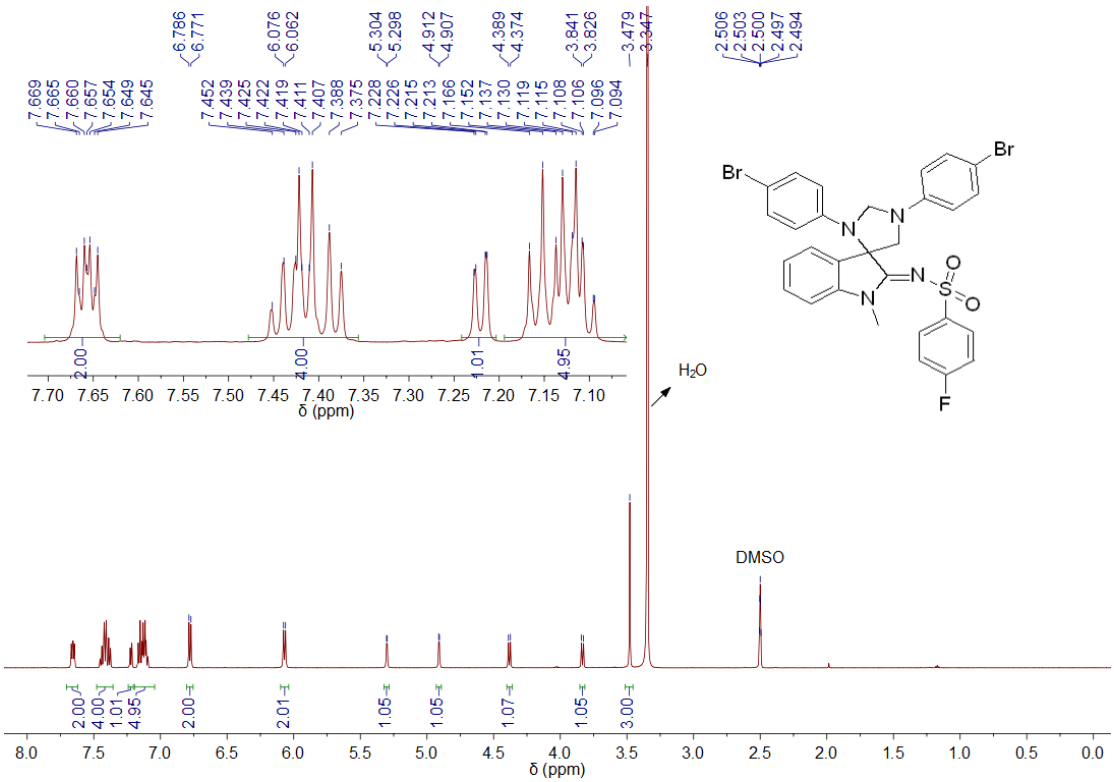
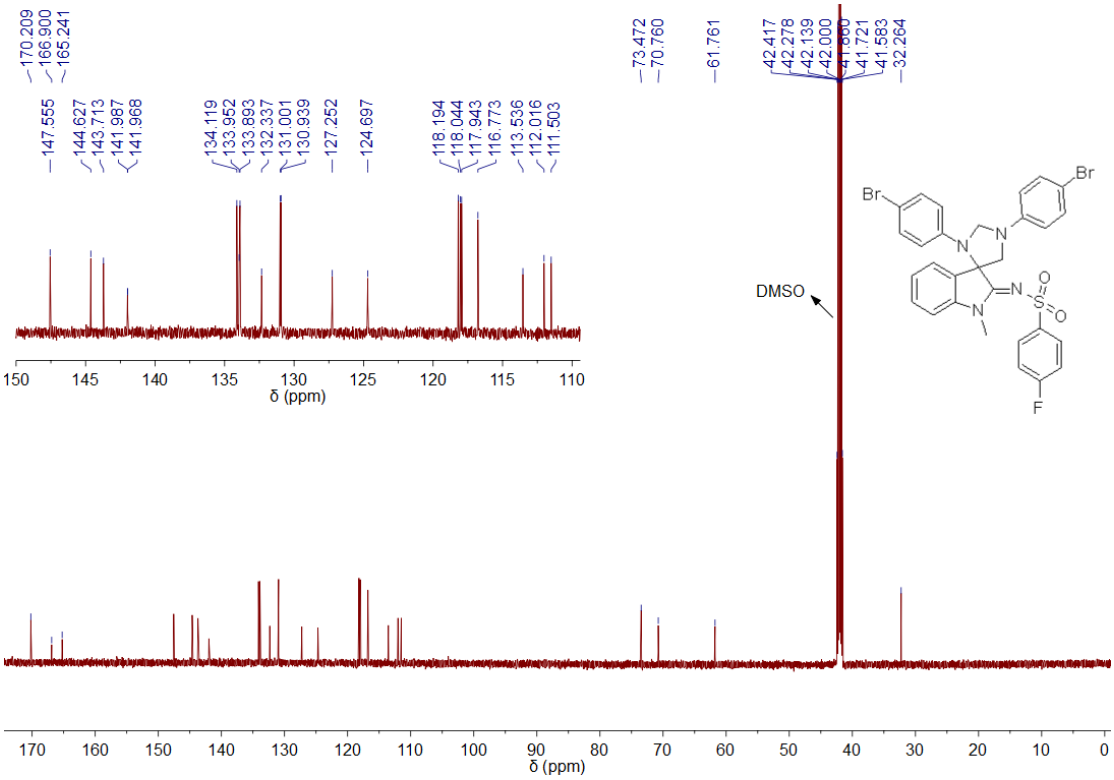


^{1}H NMR of Compoud 3z



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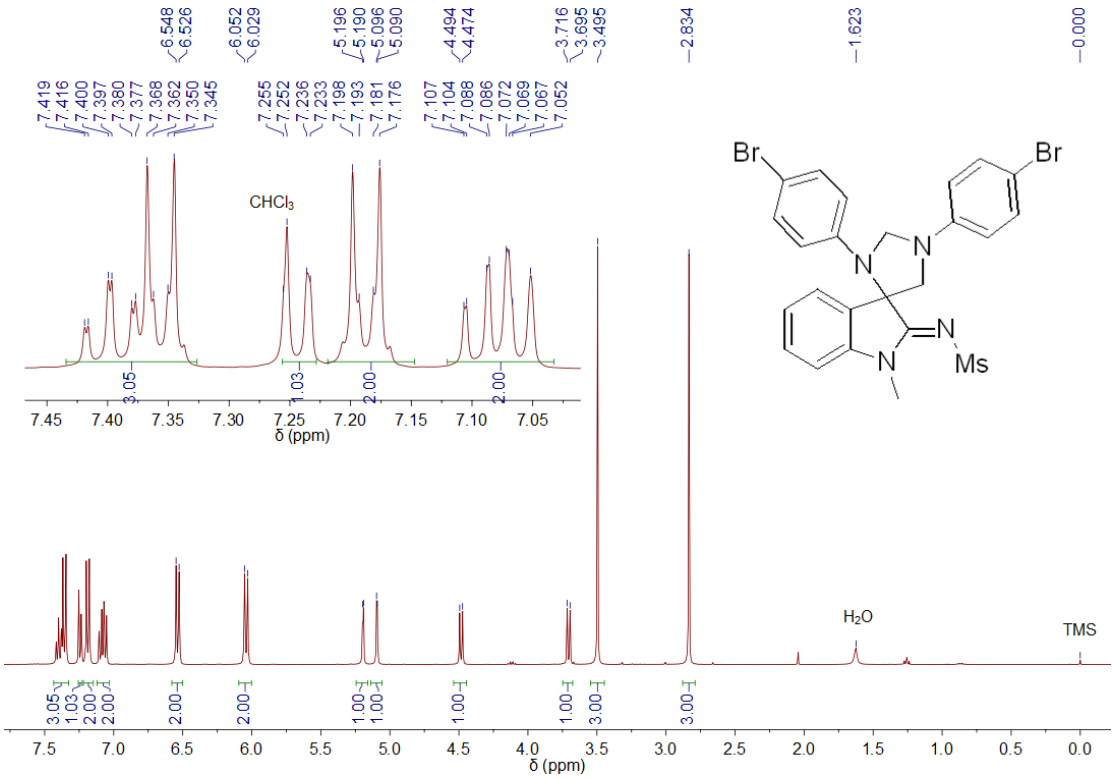
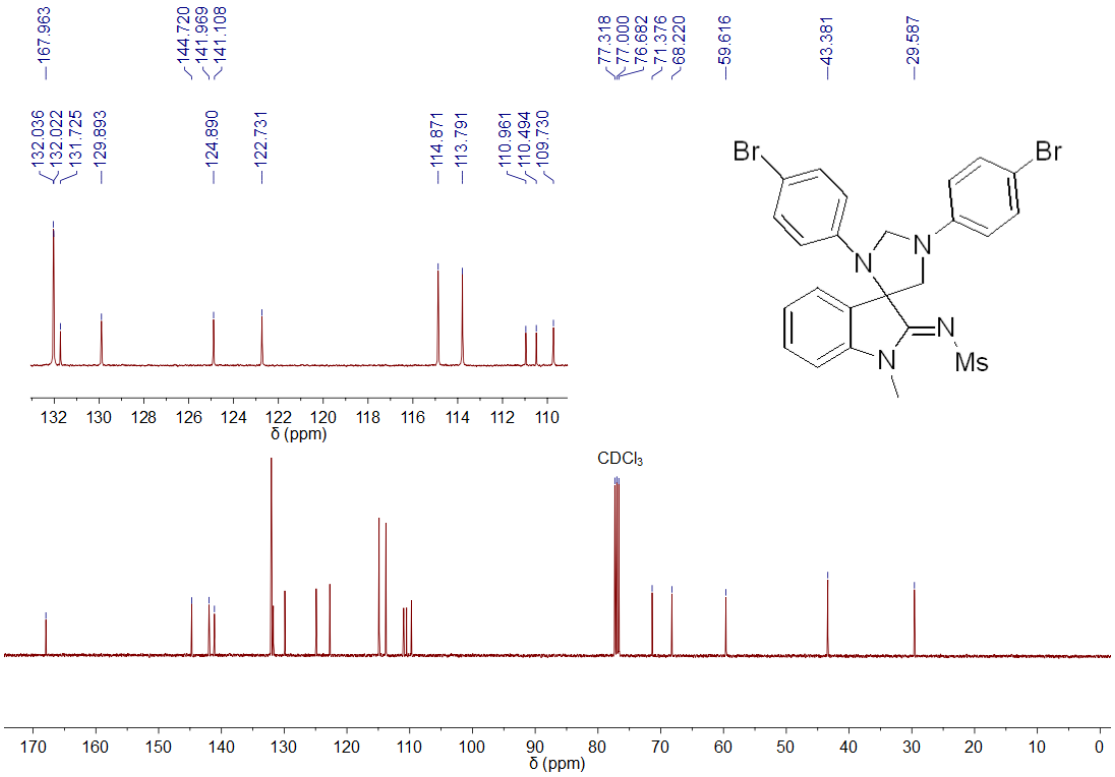
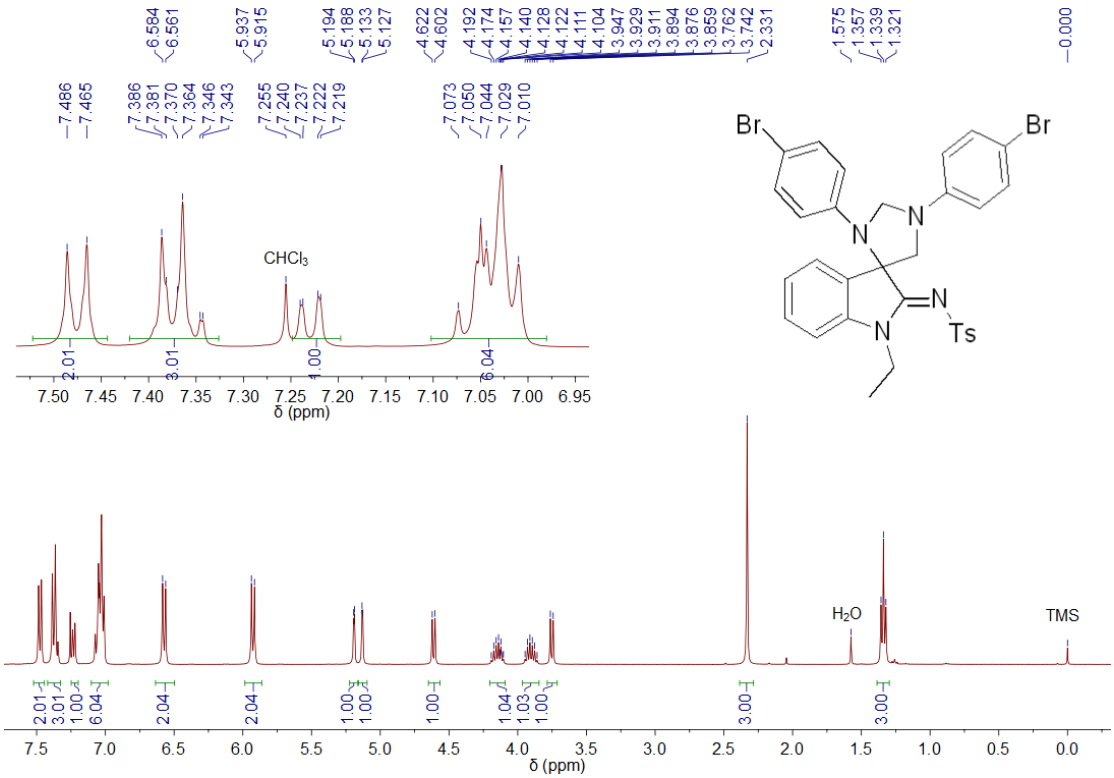


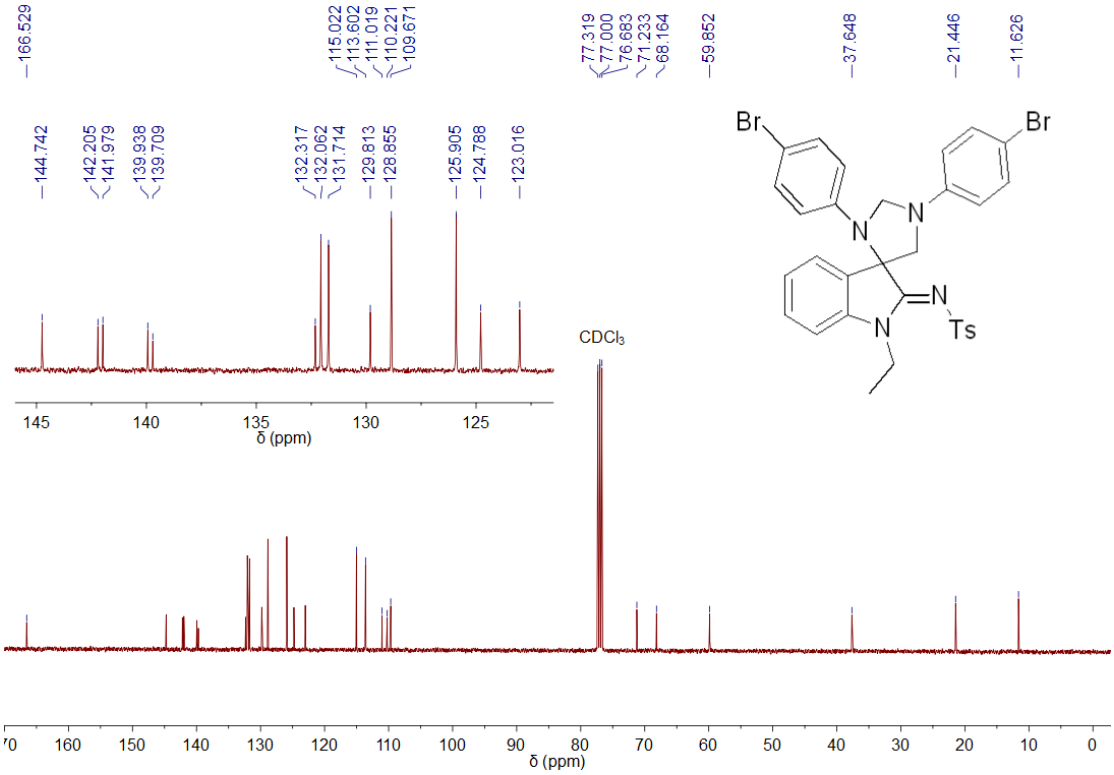
[1]H NMR of Compoud 3A



[13]C NMR of Compoud 3A

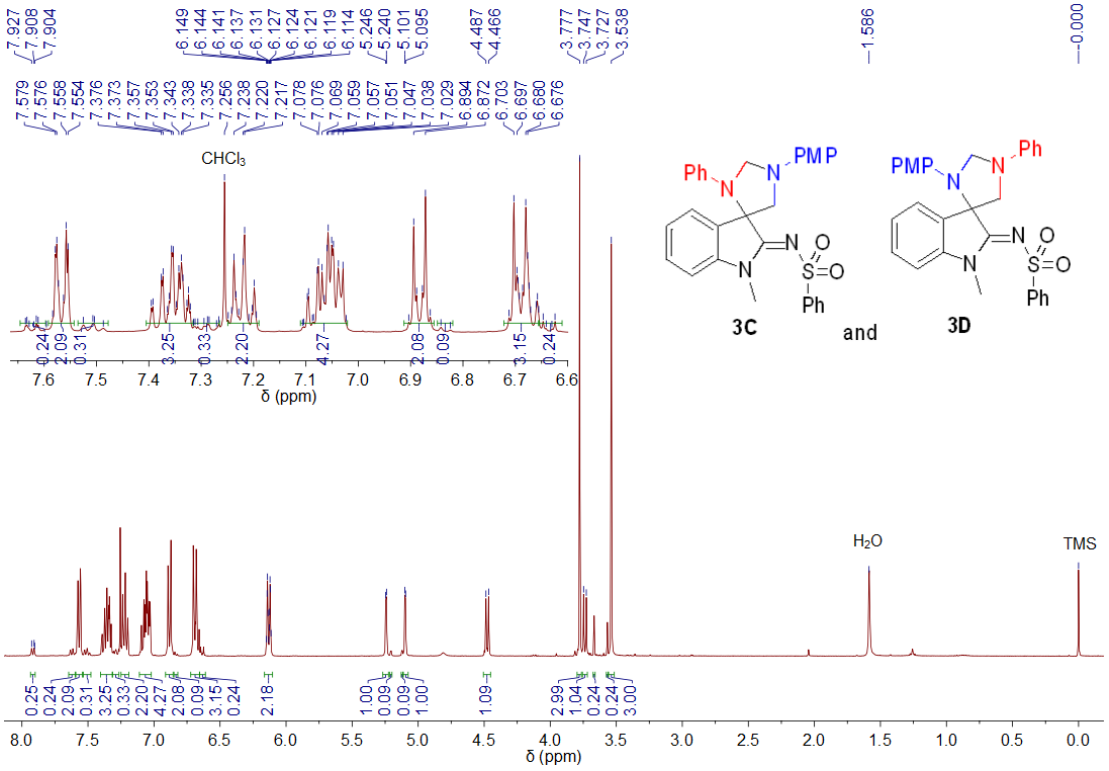


^{1}H NMR of Compoud 3B

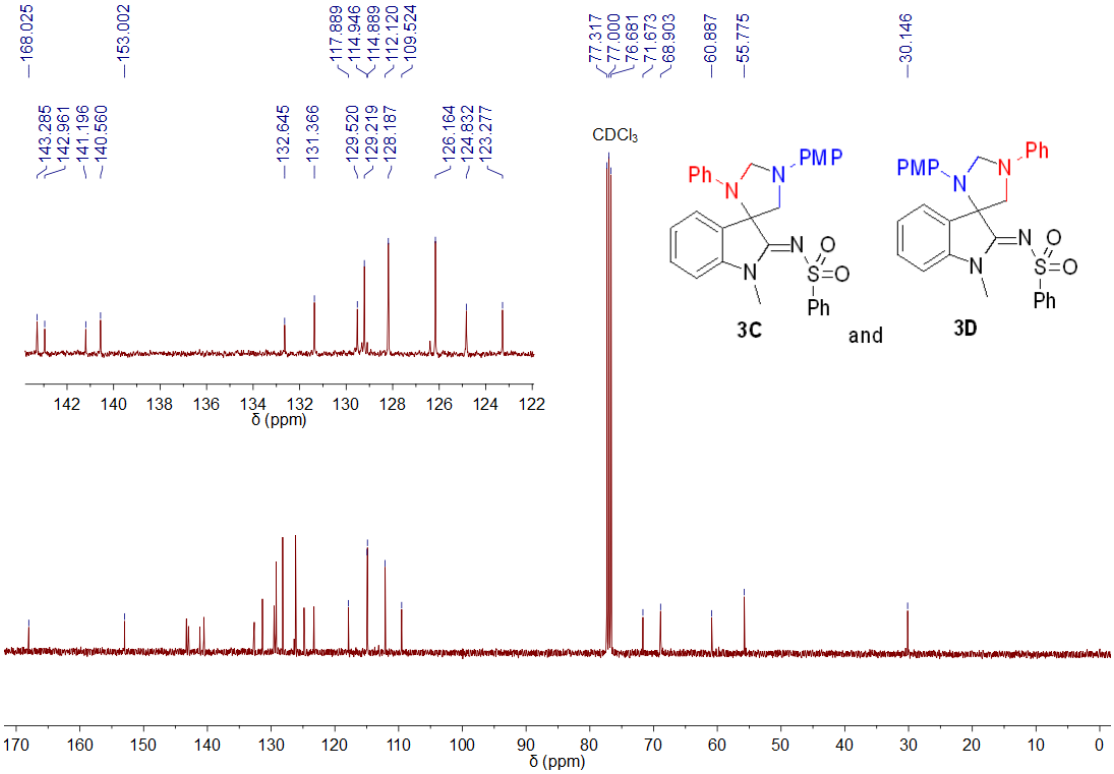


^{13}C NMR of Compoud 3B

NMR Spectra for Compounds 3C and 3D

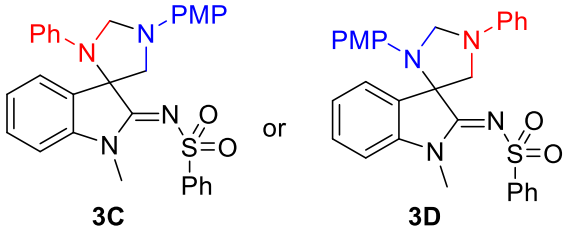


^{1}H NMR of Compounds 3C and 3D



^{13}C NMR of Compounds 3C and 3D

HRMS Spectra for Compounds 3C and 3D



3C **3D**

Caculated for $C_{30}H_{28}N_4NaO_3S^+$ [M + Na^+]: 547.1774