

Supporting Information for

Convenient Synthesis of 2-Amino-3-(aryltio)indoles via Rh-Catalyzed Coupling Reaction of 3-Diazoindol-2-imines with Thioesters

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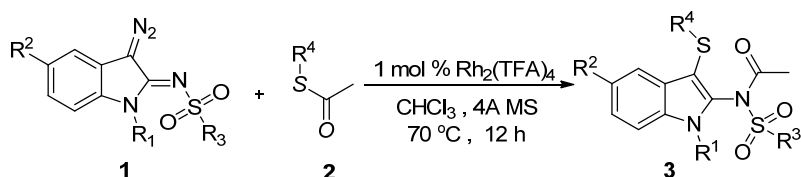
General Information

^1H NMR spectra were obtained on 400 or 600 MHz in CDCl_3 . 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 . The chemical shifts were reported in ppm referenced to the internal solvent signals (77.0 ppm for CDCl_3). The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. 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 EI or 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.

Chloroform was distilled from phosphorous pentoxide. CH_2Cl_2 , MeCN and 1, 2-dichloroethane (DCE) were dried by distillation over CaH_2 . THF, toluene and chlorobenzene was distilled from Na. $\text{Rh}_2(\text{Oct})_4$, $\text{Rh}_2(\text{OAc})_4$, $\text{Rh}_2(\text{TFA})_4$, $\text{Rh}_2(\text{HFB})_4$, S-phenyl ethanethioate, S-ethyl ethanethioate, S-(4-bromophenyl) ethanethioate, m-chloroperbenzoic acid, and samarium (II) iodide solution (0.1 M in THF, contains samarium chips as stabilizer) were used as received from the commercial sources. The (*E*)-1-phenyl-buta-1, 3-diene, 3-diazoindolin-2-imines and its analogues were prepared according to the published methods.¹⁻³ S-(4-Methoxyphenyl)ethanethioate, S-(*p*-tolyl)ethanethioate, 3*H*-benzo[*b*]thiophen-2-one, 3-diazoindolin-2-imines and its analogues were prepared according to the published methods.¹⁻³

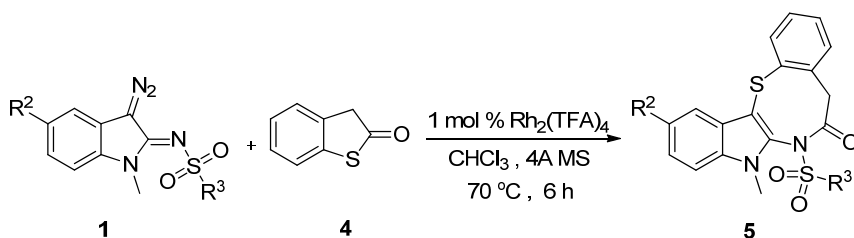
1. (a) Soria-Castro, S.; Peñeñory, A. *Beilstein J. Org. Chem.* **2013**, 9, 467. b) Sawada, N.; Itoh, T.; Yasuda, N. *Tetrahedron Lett.* **2006**, 47, 6595. (c) Chen, S.; Zhao, X.; Chen, J.; Kuznetsova, L.; Wong, S.; Ojima, I. *Bioconjugate Chem.* **2010**, 21, 979.
2. Xing, Y. P.; Sheng, G. R.; Wang, 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 3



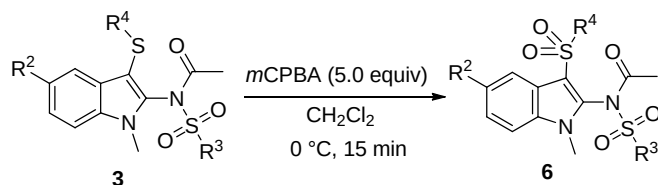
To an oven-dried flask equipped with a magnetic stirring bar were added sequentially **1** (0.2 mmol), **2** (0.3 mmol), $\text{Rh}_2(\text{TFA})_4$ (0.002 mmol), 4 Å MS (40 mg) and dry chloroform (2 ml) under air atmosphere. The reaction vessel was heated to 70 °C in oil bath for 12 hours. Upon completion, the reaction mixture was cooled to room temperature and then the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1, v/v) to give the product **3**.

General Procedure for the Synthesis of 5



To an oven-dried flask equipped with a magnetic stirring bar were added **1** (0.2 mmol), **4** (0.3 mmol), $\text{Rh}_2(\text{TFA})_4$, (0.002 mmol), 4 Å MS (40 mg) and dry chloroform (2 mL) under air atmosphere. Then the mixture was stirred at 70 °C for 6 h. After the reaction completed, the reaction mixture was cooled to room temperature. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1, v/v) to give the product **5**.

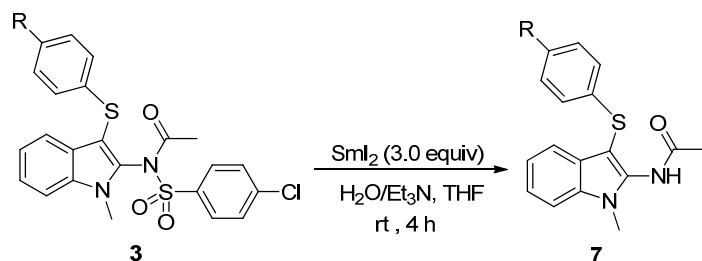
General Procedure for the Synthesis of 6



To an oven-dried flask equipped with a magnetic stirring bar were added **3** (0.1 mmol), *m*CPBA (0.5 mmol), and dry chloroform (2 mL) under air atmosphere. The reaction mixture was stirred at 70 °C for 15min, and then quenched with saturated NaHCO_3 aq. solution and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1, v/v) to give

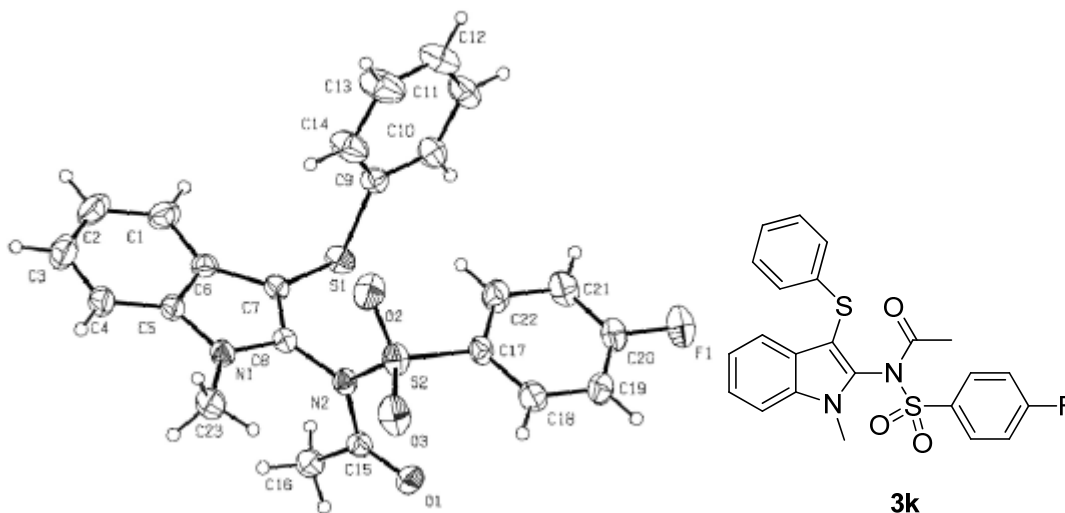
the product **6**.

General Procedure for the Synthesis of **7**



To an oven-dried Schlenk tube equipped with a magnetic stirring bar were added **3** (0.1 mmol). The tube was evacuated and refilled with argon three times, and SmI_2 (3 mL, 0.10 M in THF, 0.30 mmol), H_2O (9 μL , 0.50 mmol), and Et_3N (83 μL , 0.60 mmol) were added sequentially. After stirred at room temperature for 4 h, the resulting mixture was quenched with saturated NaHCO_3 and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by chromatography (petroleum ether /Ethyl acetate = 1.5 : 1, v/v) to give **7**.

The ORTEP and Crystal Parameters of 3k



Bond precision: C-C = 0.0037 Å

Wavelength=0.71073

Cell: a=14.9465 (16) b=9.9560 (8) c=14.9447 (12)

alpha=90

beta=105.076 (10)

gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2147.3 (4)	2147.3 (2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C ₂₃ H ₁₉ F N ₂ O ₃ S ₂	C ₂₃ H ₁₉ F N ₂ O ₃ S ₂
Sum formula	C ₂₃ H ₁₉ F N ₂ O ₃ S ₂	C ₂₃ H ₁₉ F N ₂ O ₃ S ₂
Mr	454.52	454.52
D _x , g cm ⁻³	1.406	1.403
Z	4	4
Mu (mm ⁻¹)	0.285	0.284
F ₀₀₀	944.0	944.0
F ₀₀₀ '	945.41	
h, k, lmax	18, 11, 18	18, 12, 18
Nref	3909	3906
Tmin, Tmax	0.873, 0.903	0.907, 1.000
Tmin'	0.873	

Correction method= # Reported T Limits: Tmin=0.907 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999

Theta(max)= 25.348

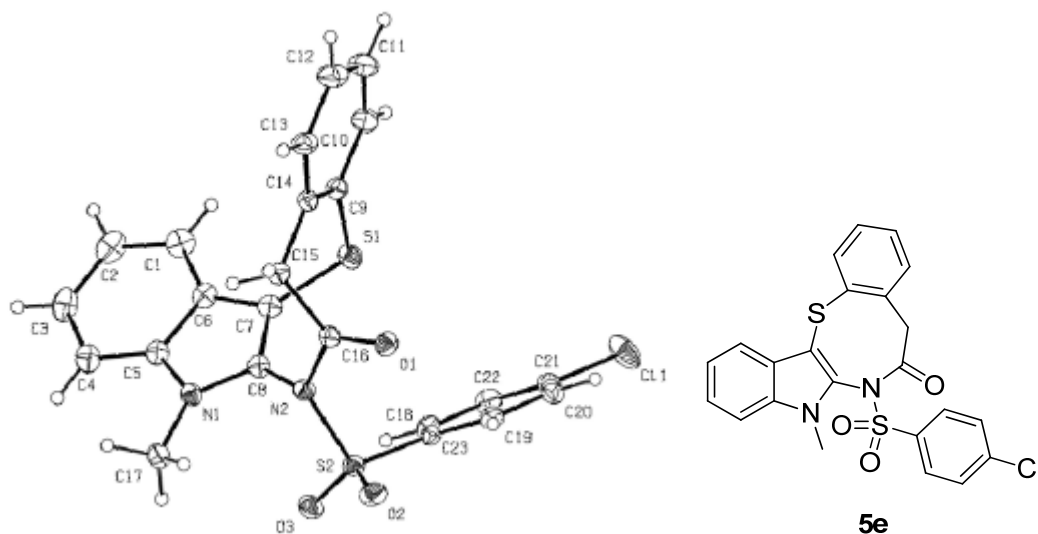
R(reflections)= 0.0441 (3096)

wR2(reflections)= 0.1151 (3906)

S = 1.058

Npar= 282

The ORTEP and Crystal Parameters of 5e



Bond precision: C-C = 0.0039 Å

Wavelength=0.71073

Cell: a=31.8220(18) b=31.8220(18) c=13.3046(5)
 alpha=90 beta=90 gamma=120
 Temperature: 170 K

	Calculated	Reported
Volume	11667.8(16)	11667.7(14)
Space group	R -3	R -3
Hall group	-R 3	-R 3
Moiety formula	C23 H17 Cl N2 O3 S2 [+ solvent]	C23 H17 Cl N2 O3 S2
Sum formula	C23 H17 Cl N2 O3 S2 [+ solvent]	C23 H17 Cl N2 O3 S2
Mr	468.96	468.95
Dx, g cm ⁻³	1.201	1.201
Z	18	18
Mu (mm ⁻¹)	0.332	0.332
F000	4356.0	4356.0
F000'	4364.75	
h, k, lmax	38, 38, 16	37, 36, 15
Nref	4751	4730
Tmin, Tmax	0.880, 0.905	0.804, 1.000
Tmin'	0.853	

Correction method= # Reported T Limits: Tmin=0.804 Tmax=1.000
 AbsCorr = MULTI-SCAN

Data completeness= 0.996

Theta(max)= 25.348

R(reflections)= 0.0515(3650)

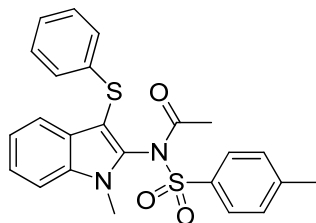
wR2(reflections)= 0.1335(4730)

S = 1.024

Npar= 281

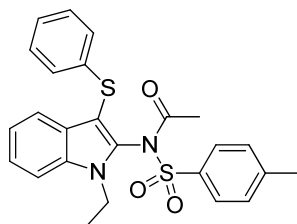
Characterization Data for Products

N-(1-Methyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3a)



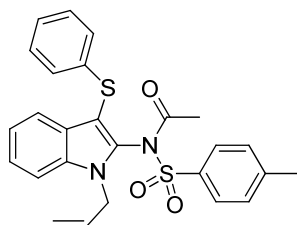
White solid; Yield 54% (49 mg); m.p. 175.5-176.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.44-7.39 (m, 1H), 7.24-7.16 (m, 3H), 7.12-7.07 (m, 3H), 7.03-7.01 (m, 2H), 3.93 (s, 3H), 2.37 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 145.4, 137.1, 136.0, 134.9, 134.4, 130.0, 129.0, 128.9, 127.8, 125.7, 125.2, 124.5, 121.6, 120.7, 110.6, 100.9, 30.3, 23.7, 21.7; IR(film): 3058, 2942, 1723, 1582, 1477, 1363, 1239, 1169 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 473.0964; found: 473.0969.

N-(1-Ethyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3b)



White solid; Yield 70% (65 mg); m.p. 177.5-188.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.8 Hz, 2H), 7.58-7.51 (m, 2H), 7.39 (td, J = 7.2, 1.2 Hz, 1H), 7.22-7.17 (m, 3H), 7.10-7.03 (m, 5H), 4.52-4.33 (m, 2H), 2.37 (s, 3H), 1.77 (m, 3H), 1.59 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 145.3, 137.0, 135.0, 134.8, 133.8, 130.2, 128.9, 128.9, 128.0, 125.7, 125.1, 124.4, 121.5, 120.8, 110.9, 100.7, 38.9, 23.5, 21.6, 14.8; IR(film): 3058, 2991, 1728, 1596, 1479, 1352, 1237, 1169, 1088 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 487.1121; found: 487.1116.

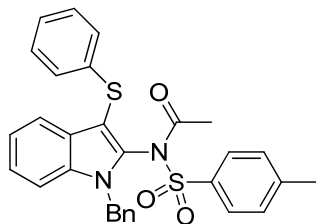
N-(1-Allyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3c)



White solid; Yield 40% (38 mg); m.p. 164.0-165.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.53-7.50 (m, 1H), 7.41-7.37 (m, 1H), 7.23-7.18 (m, 3H), 7.12 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.05-7.03 (m, 2H), 6.09-6.00 (m, 1H), 5.40-5.31 (m, 2H), 5.10-5.04 (m, 1H), 5.00-4.95 (m, 1H), 2.38 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 145.4, 136.9, 135.5, 134.8, 134.0, 132.1, 130.2, 128.9, 127.9, 125.8, 125.2, 124.6, 121.6, 120.8, 118.9, 111.4, 101.5, 46.7, 23.8,

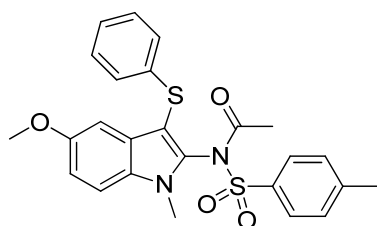
21.7; IR(film): 3058, 2916, 1723, 1596, 1526, 1460, 1362, 1241, 1168 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 499.1121; found: 499.1121.

N-(1-Benzyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3d)



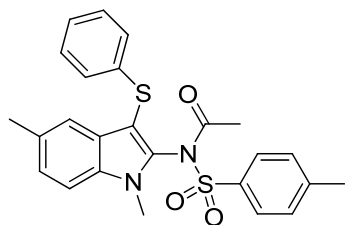
White solid; Yield 45% (45 mg); m.p. 229.0-230.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.4, 7.2 Hz, 1H), 7.39 (d, J = 6.8 Hz, 2H), 7.33-7.28 (m, 3H), 7.25-7.19 (m, 3H), 7.13-7.19 (m, 1H), 7.06-7.02 (m, 4H), 5.66 (d, J = 8.0 Hz, 1H), 5.59 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 145.4, 136.8, 136.4, 135.9, 134.9, 134.3, 130.2, 129.03, 128.97, 128.9, 128.2, 127.9, 127.8, 125.7, 125.2, 124.9, 121.6, 120.8, 111.1, 101.7, 47.5, 22.7, 21.7; IR(film): 3053, 2958, 1713, 1595, 1451, 1356, 1242, 1168, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_3\text{S}_2^+$ ($[\text{M}+\text{H}]^+$): 527.1458; found: 527.1453.

N-(5-Methoxy-1-methyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3e)



White solid; Yield 60% (58 mg); m.p. 151.0-152.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.8 Hz, 1H), 7.26-7.18 (m, 2H), 7.13-7.05 (m, 4H), 7.03-7.01 (m, 2H), 6.97 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 2.38 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 155.6, 145.3, 137.1, 134.9, 134.3, 131.0, 130.0, 129.0, 128.9, 128.6, 125.6, 125.1, 115.4, 111.7, 101.3, 100.0, 55.8, 30.4, 23.7, 21.7; IR(film): 3054, 2935, 1722, 1621, 1487, 1361, 1288, 1170, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_4\text{S}_2^+$ ($[\text{M}+\text{H}]^+$): 481.1250; found: 481.1249.

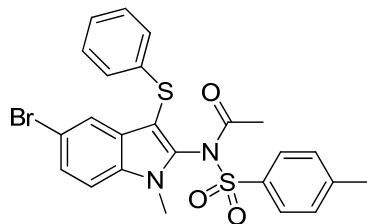
N-(1,5-Dimethyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3f)



White solid; Yield 50% (46 mg); m.p. 187.0-188.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.25-7.18 (m, 3H), 7.13-7.08 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.03-7.01 (m, 2H), 3.91 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 145.3, 137.3, 134.9, 134.4, 134.3, 131.3, 130.0, 128.93, 128.89, 128.1, 126.3, 125.5, 125.0, 112.0, 110.4, 99.9, 30.3, 23.6,

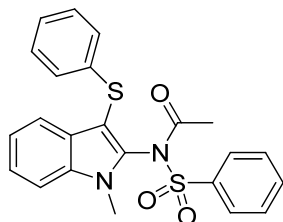
21.7, 21.5; IR(film): 3057, 2923, 1727, 1581, 1479, 1361, 1240, 1186, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 487.1121; found: 487.1111.

N-(5-Bromo-1-methyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3g)



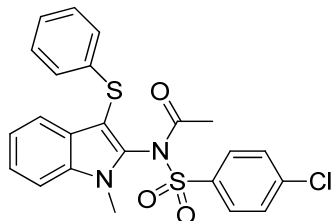
White solid; Yield 35% (40 mg); m.p. 217.0-218.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 2H), 7.72 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 3.6 Hz, 2H), 7.15-7.11 (m, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 3.92 (s, 3H), 2.38 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 145.6, 136.5, 135.4, 134.7, 134.6, 130.0, 129.5, 129.1, 129.0, 127.7, 125.7, 125.4, 123.0, 115.2, 112.3, 100.6, 30.5, 23.6, 21.7; IR(film): 3060, 2946, 1727, 1596, 1521, 1471, 1361, 1238, 1169 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 551.0069; found: 551.0079.

N-(1-Methyl-3-(phenylthio)-1H-indol-2-yl)-N-(phenylsulfonyl)acetamide (3h)



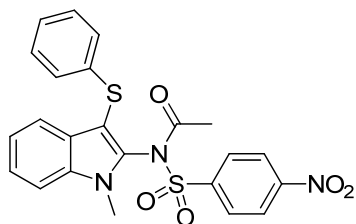
White solid; Yield 58% (51 mg); m.p. 148.0-149.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 8.0 Hz, 2H), 7.59-7.53 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 6.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.12-7.08 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 137.8, 137.0, 136.0, 134.2, 130.0, 128.9, 128.3, 127.8, 125.7, 125.2, 124.6, 121.7, 120.7, 110.6, 101.0, 30.3, 23.7; IR(film): 3061, 2929, 1724, 1582, 1525, 1478, 1363, 1238, 1171 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 459.0808; found: 459.0806.

N-((4-Chlorophenyl)sulfonyl)-N-(1-methyl-3-(phenylthio)-1H-indol-2-yl)acetamide (3i)



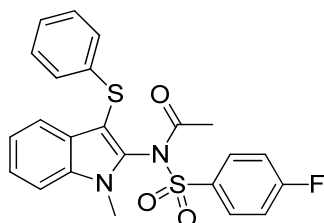
White solid; Yield 80% (75 mg); m.p. 152.0-153.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.25-7.11 (m, 5H), 7.13-7.09 (m, 1H), 7.01-6.99 (m, 1H), 3.93 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 140.9, 137.0, 136.1, 136.0, 134.0, 131.4, 129.0, 128.6, 127.8, 125.5, 125.3, 124.7, 121.8, 120.6, 110.7, 100.8, 30.3, 23.6; IR(film): 3060, 2948, 1727, 1582, 1525, 1475, 1367, 1239, 1170 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 493.0418; found: 493.0424.

N-(1-Methyl-3-(phenylthio)-1H-indol-2-yl)-N-((4-nitrophenyl)sulfonyl)acetamide (3j)



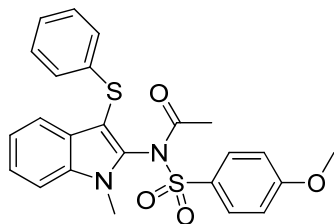
Yellow solid; Yield 54% (52 mg); m.p. 138.0-139.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.8, 2H), 8.02 (d, J = 8.8, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.47-7.44 (m, 1H), 7.28-7.20 (m, 3H), 7.17-7.14 (m, 1H), 6.96 (d, J = 7.6 Hz, 2H), 3.96 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 150.7, 143.1, 136.9, 136.1, 133.4, 131.3, 129.2, 127.8, 125.5, 125.3, 125.0, 123.3, 122.0, 120.7, 110.8, 100.9, 30.4, 23.6; IR(film): 3106, 2924, 1722, 1533, 1477, 1371, 1239, 1174, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 504.0658; found: 504.0658.

N-((4-Fluorophenyl)sulfonyl)-N-(1-methyl-3-(phenylthio)-1H-indol-2-yl)acetamide (3k)



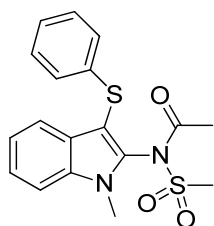
White solid; Yield 67% (61 mg); m.p. 181.0-182.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.95-7.90 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45-7.41 (m, 1H), 7.26-7.24 (m, 1H), 7.22-7.18 (m, 2H), 7.13-7.10 (m, 1H), 7.01-6.99 (m, 2H), 6.94-6.90 (m, 2H), 3.94 (s, 3H), 1.78 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 166.0 (d, $J_{\text{C-F}}$ = 255.8 Hz), 137.0, 136.0, 134.1, 133.6 (d, $J_{\text{C-F}}$ = 3.0 Hz), 133.1 (d, $J_{\text{C-F}}$ = 9.8 Hz), 129.0, 127.8, 125.5, 125.3, 124.7, 121.8, 120.7, 115.6 (d, $J_{\text{C-F}}$ = 22.7 Hz), 110.7, 100.9, 30.3, 23.7; IR(film): 3061, 2933, 1723, 1589, 1525, 1491, 1367, 1240, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{FN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 477.0713; found: 477.0706.

N-((4-Methoxyphenyl)sulfonyl)-N-(1-methyl-3-(phenylthio)-1H-indol-2-yl)acetamide (3l)



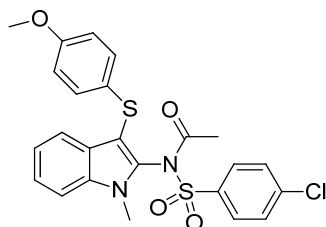
White solid; Yield 72% (64 mg); m.p. 179.0-180.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.83 (m, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.42-7.38 (m, 1H), 7.23-7.16 (m, 3H), 7.09 (t, J = 7.2 Hz, 1H), 7.03-7.01 (m, 2H), 6.73-6.70 (m, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 164.1, 137.1, 135.9, 134.5, 132.4, 129.0, 128.9, 127.7, 125.6, 125.1, 124.5, 121.6, 120.6, 113.4, 110.6, 100.6, 55.5, 30.2, 23.6; IR(film): 3059, 2945, 1722, 1594, 1496, 1362, 1264, 1163, 1024 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}_2^+$ ($[\text{M}+\text{H}]^+$): 467.1094; found: 467.1080.

N-(1-Methyl-3-(phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3m)



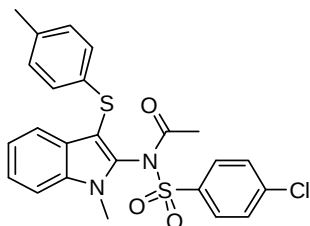
White solid; Yield 53% (40 mg); m.p. 183.0-184.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43-7.39 (m, 1H), 7.25-7.22 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.09-7.07 (m, 3H), 3.85 (s, 3H), 3.29 (s, 3H), 1.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 136.8, 135.9, 134.4, 129.1, 127.9, 126.0, 125.5, 124.6, 121.8, 120.4, 110.6, 100.8, 41.9, 30.1, 23.7; IR(film): 3014, 2931, 1727, 1582, 1478, 1360, 1241, 1168, 1022 cm⁻¹; HRMS (ESI) calcd for C₁₈H₁₈N₂NaO₃S₂⁺ ([M+Na]⁺): 397.0651; found: 397.0653.

N-((4-Chlorophenyl)sulfonyl)-N-(3-((4-methoxyphenyl)thio)-1-methyl-1H-indol-2-yl)acetamide (3n)



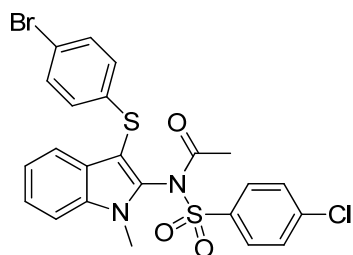
White solid; Yield 85% (81 mg); m.p. 140.0-141.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.40 (m, 1H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.99-6.95 (m, 2H), 6.77-6.73 (m, 2H), 3.90 (s, 3H), 3.72 (s, 3H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 157.9, 140.9, 136.3, 135.9, 133.5, 131.5, 128.6, 127.9, 127.7, 127.2, 124.6, 121.6, 120.6, 114.7, 110.6, 102.4, 55.2, 30.1, 23.5; IR(film): 3064, 2941, 1780, 1712, 1574, 1489, 1361, 1286, 1170 cm⁻¹; HRMS (ESI) calcd for C₂₄H₂₂ClN₂O₃S₂⁺ ([M+H]⁺): 501.0704; found: 501.0704.

N-((4-Chlorophenyl)sulfonyl)-N-(1-methyl-3-(p-tolylthio)-1H-indol-2-yl)acetamide (3o)



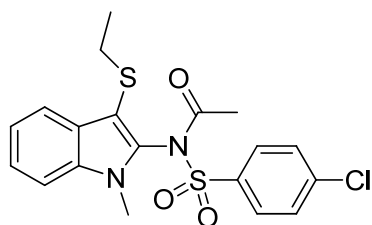
White solid; Yield 72% (70 mg); m.p. 178.0-179.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.43-7.40 (m, 1H), 7.25-7.21 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 2.73 (s, 3H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 140.9, 136.2, 136.0, 135.1, 133.8, 133.2, 131.5, 129.8, 128.6, 127.8, 125.7, 124.6, 121.7, 120.7, 110.6, 101.5, 30.2, 23.6, 20.8; IR(film): 3060, 2946, 1727, 1596, 1521, 1471, 1361, 1238, 1169 cm⁻¹; IR(film): 3067, 2923, 1727, 1582, 1525, 1474, 1366, 1239, 1170 cm⁻¹; HRMS (ESI) calcd for C₂₄H₂₁ClN₂NaO₃S₂⁺ ([M+Na]⁺): 507.0574; found: 507.0555.

N-((4-Bromophenyl)thio)-1-methyl-1H-indol-2-yl)-N-((4-chlorophenyl)sulfonyl)acetamide (3p)



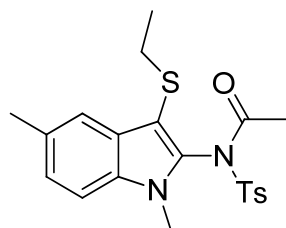
White solid; Yield 73% (80 mg); m.p. 161.0-162.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.86-7.84 (m, 2H), 7.53-7.49 (m, 2H), 7.45-7.41 (m, 1H), 7.32-7.22 (m, 5H), 6.88-7.86 (m, 2H), 3.93 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 141.0, 136.2, 136.04, 136.00, 134.0, 131.9, 131.3, 128.6, 127.3, 127.0, 124.8, 121.9, 120.4, 118.8, 110.8, 100.2, 30.3, 23.6; IR(film): 3062, 2938, 1726, 1582, 1473, 1366, 1239, 1170, 1083 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{BrClN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 570.9523; found: 570.9523.

N-((4-Chlorophenyl)sulfonyl)-N-(3-(ethylthio)-1-methyl-1H-indol-2-yl)acetamide (3q)



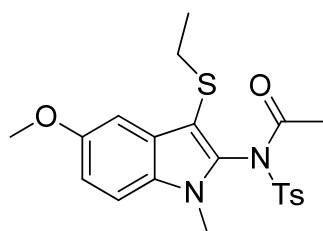
Colorless oil; Yield 70% (59 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.42-7.36 (m, 2H), 7.28-7.24 (m, 1H), 3.81 (s, 3H), 2.88-2.74 (m, 2H), 1.87 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 141.0, 136.6, 135.8, 132.1, 131.3, 128.9, 128.1, 124.3, 121.1, 120.5, 110.4, 105.7, 30.01, 29.91, 23.6, 15.1; IR(film): 3061, 2929, 1727, 1583, 1525, 1472, 1367, 1238, 1170 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 445.0418; found: 445.0413.

N-(3-(Ethylthio)-1,5-dimethyl-1H-indol-2-yl)-N-tosylacetamide (3r)



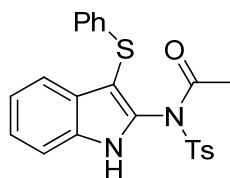
Colorless oil; Yield 78% (65 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 2H), 7.56 (s, 1H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 3.78 (s, 3H), 2.90-2.74 (m, 2H), 2.50 (s, 3H), 2.46 (s, 3H), 1.85 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.0, 145.4, 135.5, 134.2, 132.6, 130.5, 129.9, 129.2, 128.4, 125.9, 119.9, 110.1, 105.0, 30.1, 30.0, 23.7, 21.7, 21.5, 15.1; IR(film): 3033, 2925, 1722, 1596, 1525, 1486, 1362, 1239, 1169 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{ClN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 439.1121; found: 439.1116.

N-(3-(Ethylthio)-5-methoxy-1-methyl-1H-indol-2-yl)-N-tosylacetamide (3s)



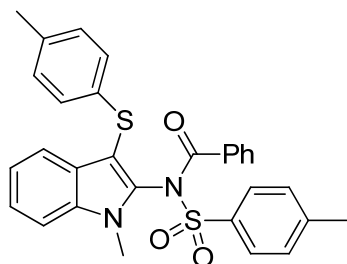
Colorless oil; Yield 65% (56 mg); ^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 9.0, 2.4$ Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.88-2.72 (m, 2H), 2.47 (s, 3H), 1.86 (s, 3H), 1.24 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.0, 155.2, 145.4, 135.5, 132.9, 130.9, 129.9, 129.2, 129.0, 114.9, 111.4, 105.0, 101.6, 55.9, 30.2, 30.1, 23.7, 21.7, 15.1; IR(film): 2962, 2928, 1720, 1623, 1575, 1487, 1362, 1237, 1168 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{ClN}_2\text{NaO}_4\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 455.1071; found: 455.1073.

N-(3-(Phenylthio)-1H-indol-2-yl)-N-tosylacetamide (3t)



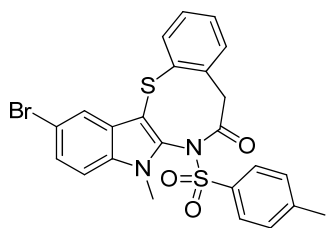
White solid; Yield 52% (45 mg); m.p. 226.0-227.0 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.64 (s, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 2.8$ Hz, 1H), 7.52 (d, $J = 3.2$ Hz, 1H), 7.38-7.34 (m, 1H), 7.22-7.17 (m, 3H), 7.12-7.09 (m, 3H), 7.06-7.03 (m, 2H), 2.38 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 145.4, 136.7, 134.7, 134.6, 132.3, 129.6, 129.1, 128.9, 128.3, 125.8, 125.2, 124.7, 121.5, 120.5, 112.4, 102.1, 23.8, 21.7; IR(film): 3059, 2951, 1704, 1595, 1478, 1416, 1365, 1231, 1168 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 459.0808; found: 459.0796.

N-(1-Methyl-3-(p-tolylthio)-1H-indol-2-yl)-N-tosylbenzamide (3u)



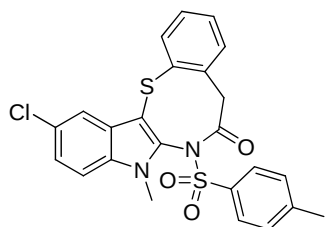
Yellow oil; Yield 19% (20 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.36-7.32 (m, 1H), 7.21-7.17 (m, 6H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.99-6.97 (m, 2H), 6.71 (d, $J = 7.8$ Hz, 2H), 6.30 (d, $J = 7.8$ Hz, 2H), 4.13 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.7, 145.4, 136.1, 134.5, 134.18, 134.16, 133.0, 132.7, 131.6, 130.3, 129.2, 129.1, 128.05, 127.98, 127.1, 125.4, 124.2, 121.1, 120.7, 110.5, 101.5, 31.2, 21.8, 20.8; IR (film): 3058, 2922, 1702, 1597, 1492, 1474, 1365, 1261, 1171 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_3\text{S}_2^+$ ($[\text{M}+\text{H}]^+$): 527.1458; found: 527.1444.

11-Bromo-8-methyl-7-tosyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5a)



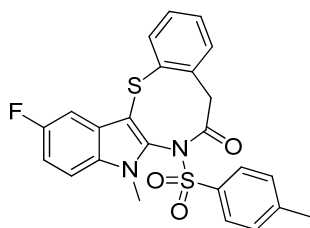
White solid; Yield 63% (69 mg); m.p. 238.0-239.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.79 (m, 3H), 7.44-7.40 (m, 2H), 7.32-7.24 (m, 3H), 7.12-7.03 (m, 2H), 6.95 (d, $J = 7.6$ Hz, 1H), 3.98 (s, 3H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.14 (d, $J = 14.4$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 145.9, 138.2, 135.5, 135.0, 132.7, 132.5, 131.3, 131.2, 130.1, 129.3, 128.4, 128.3, 127.6, 127.3, 122.5, 115.1, 112.0, 97.9, 43.5, 31.5, 21.8; IR(film): 3054, 2925, 1727, 1595, 1520, 1471, 1368, 1173, 1116 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 548.9913; found: 548.9912.

11-Chloro-8-methyl-7-tosyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5b)



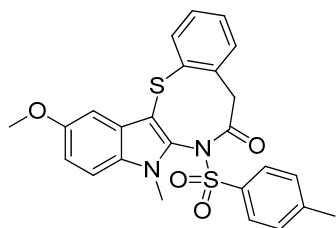
White solid; Yield 74% (71 mg); m.p. 220.0-221.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 1.6$ Hz, 1H), 7.41 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 1H), 7.31-7.25 (m, 3H), 7.11 (dd, $J_1 = J_2 = 7.2$ Hz, 1H), 7.08-7.04 (m, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 3.99 (s, 3H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.15 (d, $J = 14.4$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 145.9, 138.3, 135.2, 135.0, 132.7, 132.5, 131.3, 130.2, 129.3, 128.3, 127.8, 127.7, 127.6, 124.8, 119.39, 111.6, 98.0, 43.5, 31.6, 21.8; IR(film): 3060, 2950, 1728, 1596, 1520, 1471, 1367, 1173, 1086 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{ClN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 505.0418; found: 505.0419.

11-Fluoro-8-methyl-7-tosyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5c)



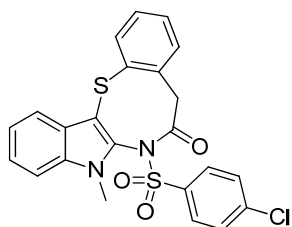
White solid; Yield 89% (83 mg); m.p. 173.0-174.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.41-7.32 (m, 3H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.11-7.06 (m, 2H), 7.05-7.01 (m, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 3.98 (s, 3H), 3.56 (d, $J = 14.4$ Hz, 1H), 3.15 (d, $J = 14.4$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 158.8 (d, $J_{\text{C-F}} = 237.3$ Hz), 145.9, 138.4, 135.0, 133.3, 132.7, 132.5, 131.4, 131.2, 130.1, 129.2, 128.2, 127.6, 127.4 (d, $J_{\text{C-F}} = 10.2$ Hz), 113.0 (d, $J_{\text{C-F}} = 26.4$ Hz), 111.5 (d, $J_{\text{C-F}} = 9.4$ Hz), 104.9 (d, $J_{\text{C-F}} = 24.2$ Hz), 98.3 (d, $J_{\text{C-F}} = 4.9$ Hz), 43.4, 31.6, 21.7; IR(film): 3057, 2961, 1729, 1596, 1524, 1486, 1363, 1173, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{FN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 489.0713; found: 489.0717.

11-Methoxy-8-methyl-7-tosyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5d)



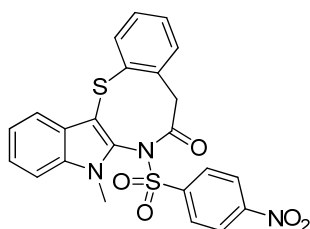
White solid; Yield 67% (67 mg); m.p. 227.0-228.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.34 (d, J = 9.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.11-7.08 (m, 2H), 7.08-7.04 (m, 1H), 7.02-6.99 (m, 1H), 6.95 (d, J = 7.2 Hz, 1H), 3.97 (s, 3H), 3.84 (s, 3H), 3.56 (d, J = 14.4 Hz, 1H), 3.19 (d, J = 14.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 155.5, 145.7, 137.2, 135.2, 132.9, 132.5, 132.0, 131.9, 131.2, 130.2, 129.2, 128.1, 127.45, 127.43, 115.0, 111.4, 100.9, 97.7, 55.8, 43.5, 31.4, 21.8; IR(film): 3058, 2947, 1726, 1623, 1487, 1367, 1288, 1172, 1116 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 501.0913; found: 501.0925.

7-((4-Chlorophenyl)sulfonyl)-8-methyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5e)



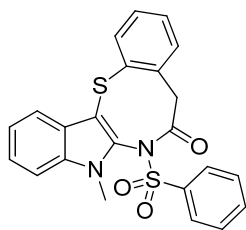
White solid; Yield 78% (73 mg); m.p. 166.0-167.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.86 (m, 2H), 7.71-7.70 (m, 1H), 7.45-7.36 (m, 5H), 7.23 (s, 1H), 7.09-7.03 (m, 2H), 6.93 (s, 1H), 3.99 (s, 3H), 3.59-3.55 (m, 1H), 3.18-3.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 141.3, 136.9, 136.8, 135.0, 134.1, 132.4, 131.6, 131.4, 131.3, 128.9, 128.3, 127.6, 126.7, 124.5, 121.7, 120.0, 110.4, 98.4, 43.3, 31.3; IR(film): 3061, 2951, 1728, 1583, 1474, 1398, 1283, 1182, 1115 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{ClN}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 491.0261; found: 491.0260.

8-Methyl-7-((4-nitrophenyl)sulfonyl)-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5f)



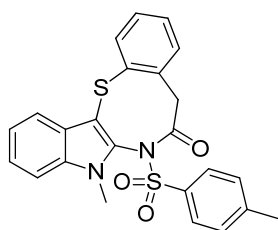
White solid; Yield 84% (84 mg); m.p. 154.0-155.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.28-8.25 (m, 2H), 8.11-8.08 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.42-7.36 (m, 2H), 7.26-7.22 (m, 1H), 7.11-7.07 (m, 1H), 7.05-7.01 (m, 1H), 6.93 (d, J = 7.6 Hz, 1H), 4.01 (s, 3H), 3.58 (d, J = 14.4 Hz, 1H), 3.18 (d, J = 14.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 150.9, 141.0, 136.9, 136.3, 134.7, 132.4, 131.6, 131.3, 131.0, 128.4, 127.7, 126.6, 124.7, 123.6, 121.9, 120.0, 110.5, 98.5, 43.2, 31.3; IR(film): 3064, 2952, 1732, 1607, 1538, 1475, 1373, 1285, 1181 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 502.0502; found: 502.0546.

8-Methyl-7-(phenylsulfonyl)-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5g)



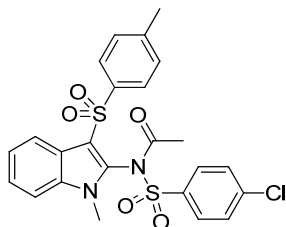
White solid; Yield 87% (76 mg); m.p. 134.0-135.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.96-7.94 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 1H), 7.41-7.35 (m, 2H), 7.25-7.21 (m, 1H), 7.10-7.07 (m, 1H), 7.05-7.01 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 4.01 (s, 3H), 3.58 (d, J = 14.4 Hz, 1H), 3.16 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 137.1, 136.9, 135.7, 135.1, 134.5, 132.4, 131.6, 131.3, 130.2, 128.6, 128.2, 127.5, 126.8, 124.4, 121.6, 120.0, 110.4, 98.4, 43.5, 31.4; IR(film): 3061, 2950, 1728, 1585, 1523, 1474, 1368, 1174, 1115 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 457.0651; found: 457.0647.

8-Methyl-7-tosyl-7,8-dihydrobenzo[7,8][1,4]thiazocino[3,2-b]indol-6(5H)-one (5h)



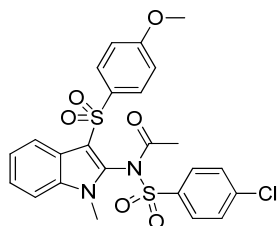
White solid; Yield 73% (65 mg); m.p. 224.0-225.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.25-7.21 (m, 1H), 7.11-7.07 (m, 1H), 7.05-7.02 (m, 1H), 6.94 (d, J = 7.2 Hz, 1H), 4.01 (s, 3H), 3.57 (d, J = 14.0 Hz, 1H), 3.17 (d, J = 14.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 145.8, 137.3, 136.9, 135.2, 132.8, 132.4, 131.7, 131.3, 130.2, 129.2, 128.2, 127.5, 126.8, 124.3, 121.5, 120.0, 110.4, 98.3, 43.5, 31.4, 21.8; IR(film): 3058, 2951, 1727, 1596, 1523, 1474, 1367, 1173, 1085 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 471.0808; found: 471.0821.

N-(5-Bromo-1-methyl-3-(phenylsulfonyl)-1H-indol-2-yl)-N-tosylacetamide (6a)



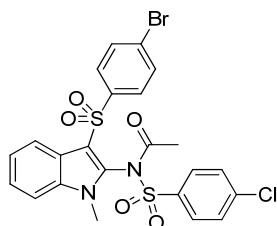
White solid; Yield 98% (101 mg); m.p. 146.5-147.5 °C; ^1H NMR (400 MHz, DMSO) δ 8.14-8.11 (m, 2H), 7.88-7.83 (m, 3H), 7.78-7.74 (m, 3H), 7.49-7.45 (m, 1H), 7.41-7.34 (m, 3H), 3.74 (s, 3H), 2.35 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.8, 144.7, 140.7, 139.8, 136.6, 134.9, 132.5, 131.6, 130.4, 129.7, 127.1, 125.6, 123.9, 123.0, 120.2, 112.7, 111.6, 30.8, 24.2, 21.5; IR(film): 3071, 2924, 1698, 1575, 1474, 1366, 1304, 1262, 1145 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 539.0473; found: 539.0465.

N-((4-Chlorophenyl)sulfonyl)-N-(3-((4-methoxyphenyl)sulfonyl)-1-methyl-1H-indol-2-yl)acetamide (6b)



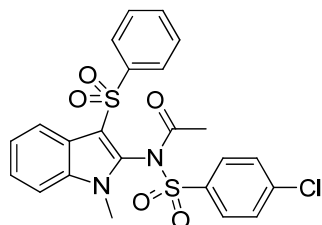
White solid; Yield 98% (104 mg); m.p. 126.0-127.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 8.8 Hz, 2H), 8.60 (d, J = 8.8 Hz, 3H), 7.50-7.40 (m, 4H), 7.33-7.28 (m, 1H), 6.92 (d, J = 9.2 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 163.1, 141.4, 135.9, 134.7, 134.5, 132.0, 131.6, 128.84, 128.79, 125.3, 123.4, 123.3, 120.6, 114.1, 111.5, 110.8, 55.5, 30.2, 24.0; IR(film): 3098, 2925, 1731, 1594, 1498, 1474, 1366, 1262, 1143 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{NaO}_6\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 555.0422; found: 555.0417.

N-(3-((4-Bromophenyl)sulfonyl)-1-methyl-1H-indol-2-yl)-N-((4-chlorophenyl)sulfonyl)acetamide (6c)



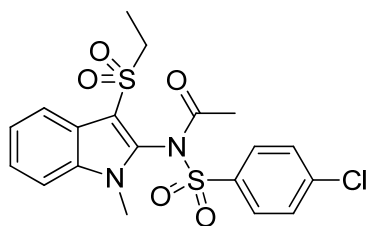
White solid; Yield 89% (103 mg); m.p. 144.0-145.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.06-8.03 (m, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.81-7.78 (m, 2H), 7.61-7.58 (m, 2H), 7.51-7.15 (m, 4H), 7.36-7.32 (m, 1H), 3.85 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 141.8, 141.6, 135.7, 134.8, 132.3, 131.8, 129.0, 128.1, 125.5, 123.8, 123.4, 120.4, 110.9, 110.1, 30.3, 24.0; IR(film): 3095, 2946, 1730, 1574, 1516, 1474, 1388, 1239, 1170 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{BrClN}_2\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 602.9421; found: 602.9407.

N-((4-Chlorophenyl)sulfonyl)-N-(1-methyl-3-(phenylsulfonyl)-1H-indol-2-yl)acetamide (6d)



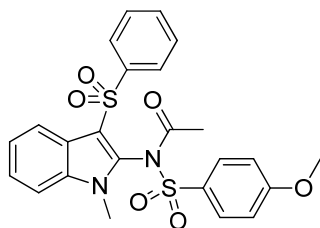
White solid; Yield 98% (99 mg); m.p. 155.0-156.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.05-7.02 (m, 2H), 7.90-7.88 (m, 3H), 7.56-7.51 (m, 1H), 7.47-7.41 (m, 6H), 7.34-7.30 (m, 1H), 3.86 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 142.9, 141.4, 135.7, 134.7, 133.0, 132.2, 131.9, 129.0, 128.8, 126.3, 125.4, 123.6, 120.6, 110.8, 110.5, 30.2, 23.9; IR(film): 3098, 2925, 1731, 1519, 1475, 1367, 1307, 1240, 1170 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 525.0316; found: 525.0308.

N-((4-Chlorophenyl)sulfonyl)-N-(3-(ethylsulfonyl)-1-methyl-1H-indol-2-yl)acetamide (6e)



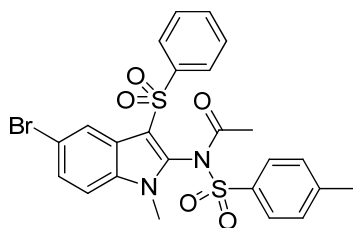
White solid; Yield 97% (88 mg); m.p. 188.0-189.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.16-8.13 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.57-7.55 (m, 2H), 7.50-7.45 (m, 2H), 7.43-7.37 (m, 1H), 3.83 (s, 3H), 3.40-3.22 (m, 2H), 2.03 (s, 3H), 1.37 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 141.5, 136.0, 134.6, 131.50, 131.45, 129.1, 125.4, 123.9, 123.5, 120.7, 110.8, 110.2, 51.5, 30.1, 23.9, 6.62; IR(film): 3097, 2941, 1731, 1520, 1518, 1475, 1366, 1308, 1170 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 477.0316; found: 477.0315.

N-((4-Methoxyphenyl)sulfonyl)-N-(1-methyl-3-(phenylsulfonyl)-1H-indol-2-yl)acetamide (6f)



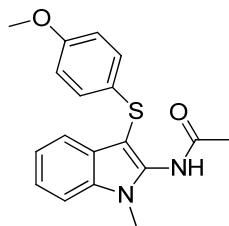
White solid; Yield 98% (98 mg); m.p. 177.0-178.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.47-7.40 (m, 4H), 7.33-7.29 (m, 1H), 6.94 (d, J = 9.2 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 164.5, 142.9, 134.7, 132.92, 132.90, 132.8, 128.9, 128.5, 126.6, 125.1, 123.6, 123.4, 120.6, 113.7, 110.8, 110.5, 55.7, 30.2, 24.0; IR(film): 3067, 2945, 1726, 1593, 1518, 1474, 1364, 1266, 1163 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_6\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 521.0811; found: 521.0791.

N-(5-Bromo-1-methyl-3-(phenylsulfonyl)-1H-indol-2-yl)-N-tosylacetamide (6g)



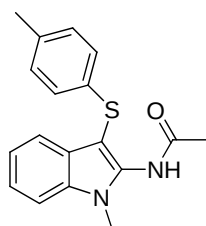
White solid; Yield 98% (110 mg); m.p. 147.0-148.0 °C; ^1H NMR (600 MHz, DMSO) δ 8.00-7.97 (m, 5H), 7.76 (d, J = 9.0 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.65-7.62 (m, 3H), 7.46 (d, J = 7.8 Hz, 2H), 3.71 (s, 3H), 2.44 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 169.4, 146.6, 142.4, 134.8, 134.2, 133.7, 133.3, 130.5, 130.03, 130.01, 128.4, 127.0, 124.7, 122.1, 116.7, 115.2, 110.9, 31.1, 24.1, 21.7; IR(film): 3075, 2959, 1695, 1597, 1576, 1428, 1305, 1264, 1145 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{NaO}_5\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$): 582.9967; found: 582.9957.

N-(3-((4-Methoxyphenyl)thio)-1-methyl-1H-indol-2-yl)acetamide (7a)



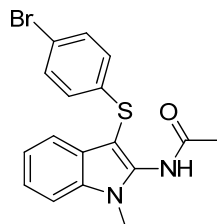
Colorless oil; Yield 85% (55 mg); ^1H NMR (600 MHz, DMSO) δ 10.17 (s, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 7.8$ Hz, 1H), 7.21 (m, 1H), 7.08-7.05 (m, 3H), 6.78 (d, $J = 7.8$ Hz, 2H), 3.66 (s, 3H), 3.60 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 170.8, 158.0, 138.5, 135.2, 129.1, 128.9, 127.8, 122.5, 120.8, 118.8, 115.0, 110.9, 96.0, 55.6, 30.2, 23.1; IR(film): 3054, 2939, 1673, 1556, 1492, 1464, 1392, 1242, 1174 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: 326.1089; found: 326.1091.

N-(1-Methyl-3-(p-tolylthio)-1H-indol-2-yl)acetamide (7b)



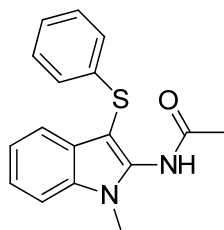
White solid; Yield 98% (61 mg); m.p. 130.0-131.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, DMSO) δ 10.17 (s, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.24-7.20 (m, 1H), 7.07 (dd, $J_1 = J_2 = 7.6$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 3.61 (s, 3H), 2.18 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 170.8, 138.9, 135.3, 135.2, 134.7, 129.9, 127.8, 126.6, 122.6, 120.9, 118.8, 110.9, 94.7, 30.3, 23.0, 20.9; IR(film): 3049, 2941, 1673, 1556, 1491, 1467, 1393, 1265, 1107 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{18}\text{BrN}_2\text{OS}$: 310.1140; found: 310.1142.

N-(3-((4-Bromophenyl)thio)-1-methyl-1H-indol-2-yl)acetamide (7c)



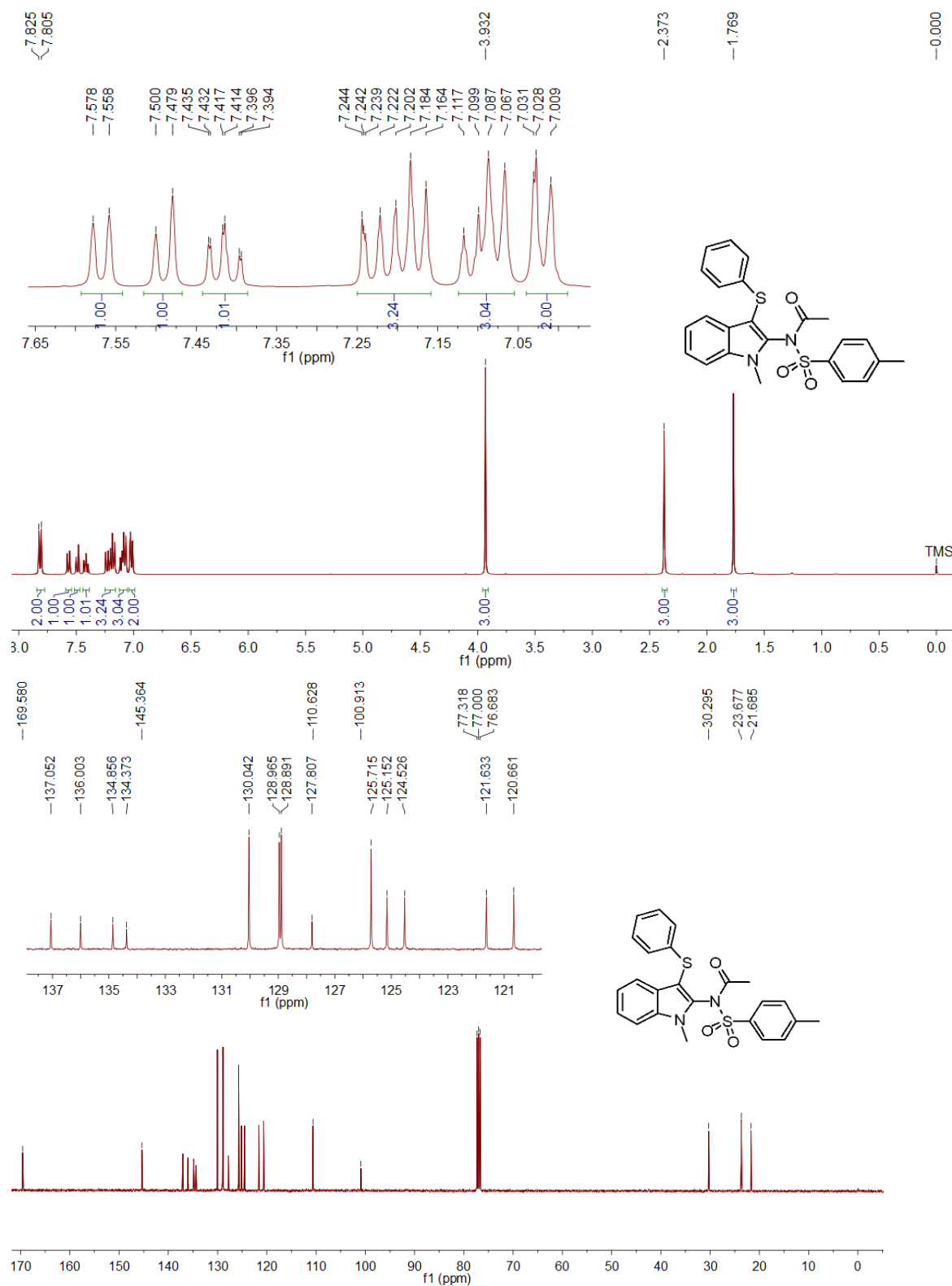
White solid; Yield 86% (64 mg); m.p. 117.0-118.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.25 (dd, $J_1 = J_2 = 7.6$ Hz, 1H), 7.12-7.08 (m, 1H), 6.97-6.94 (m, 2H), 3.63 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 170.2, 138.7, 138.1, 134.9, 131.5, 127.5, 127.0, 122.3, 120.7, 118.1, 117.5, 110.6, 92.8, 29.8, 22.5; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{BrN}_2\text{OS}$: 374.0088; found: 374.0089.

N-(1-Methyl-3-(phenylthio)-1H-indol-2-yl)acetamide (7d)

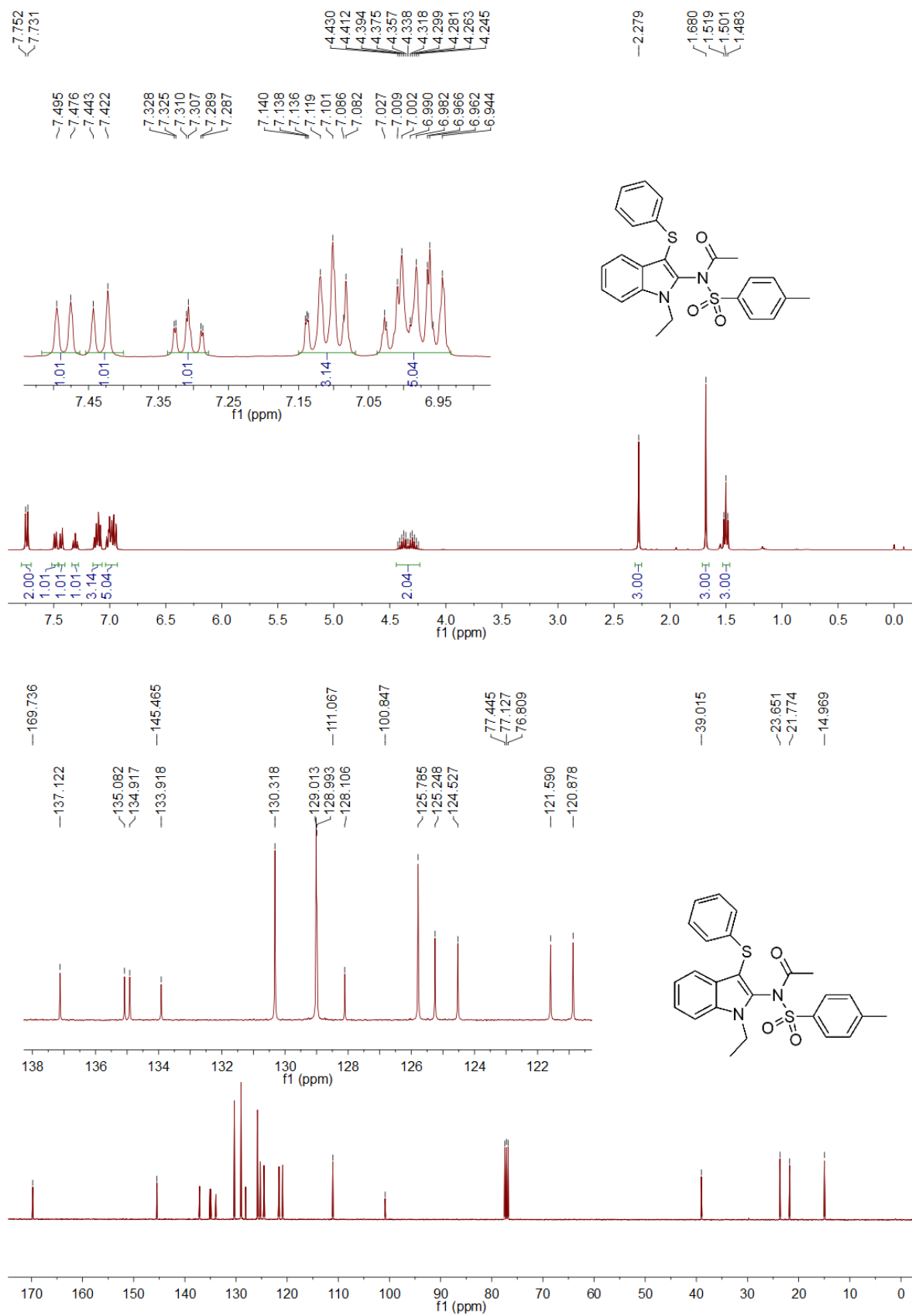


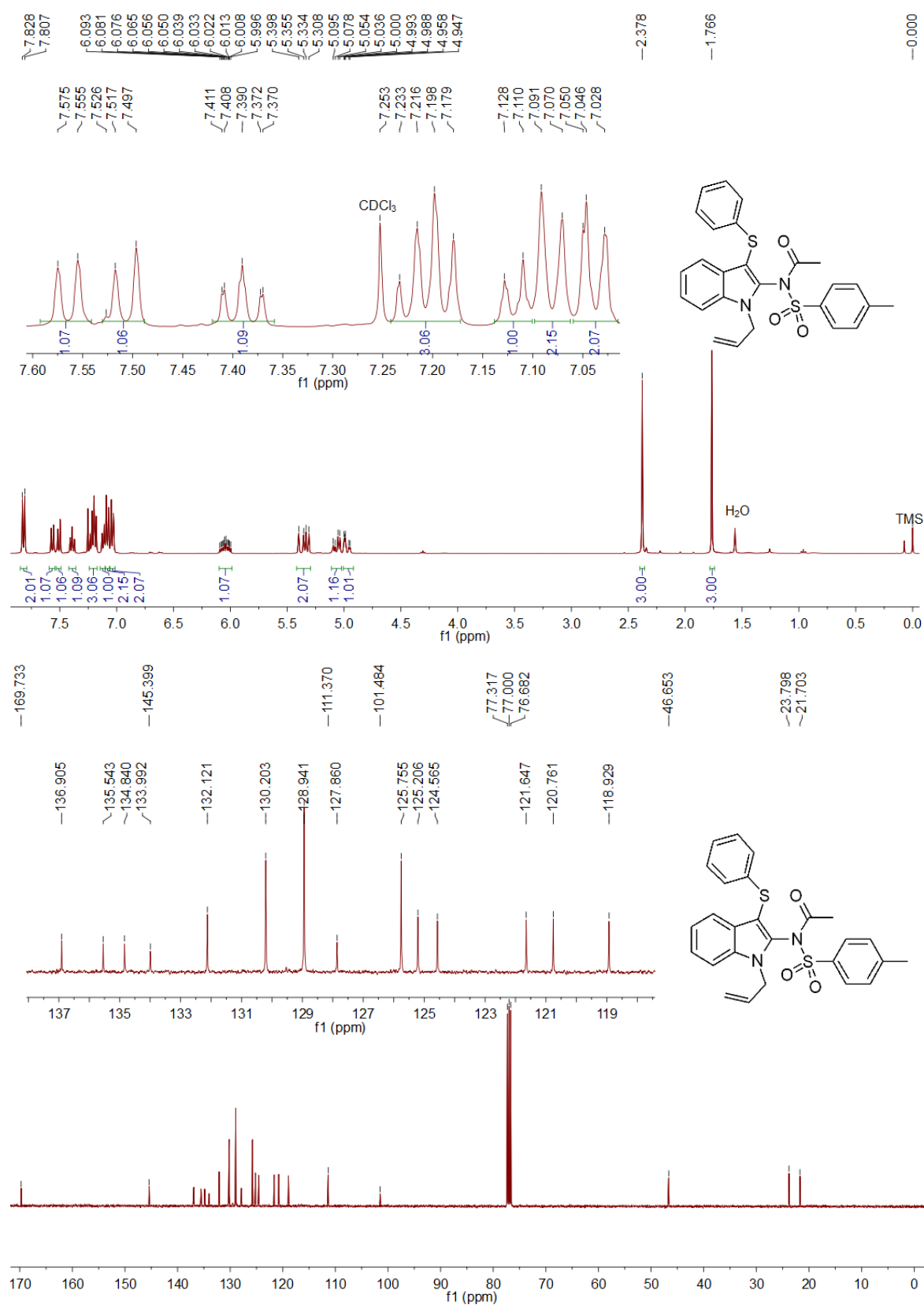
Fellow yellow solid; Yield 95% (56 mg); m.p. 113.0-114.0 °C; ^1H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.25-7.22 (m, 1H), 7.18 (dd, $J_1 = J_2 = 7.6$ Hz, 1H), 7.10-7.01 (m, 4H), 3.63 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 170.8, 139.1, 138.9, 135.3, 129.3, 127.8, 126.1, 125.3, 122.7, 121.0, 118.8, 111.0, 94.0, 30.4, 23.0; IR(film): 3054, 2942, 1673, 1557, 1478, 1439, 1393, 1269, 1024 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{OS}$: 296.0983; found: 296.0980.

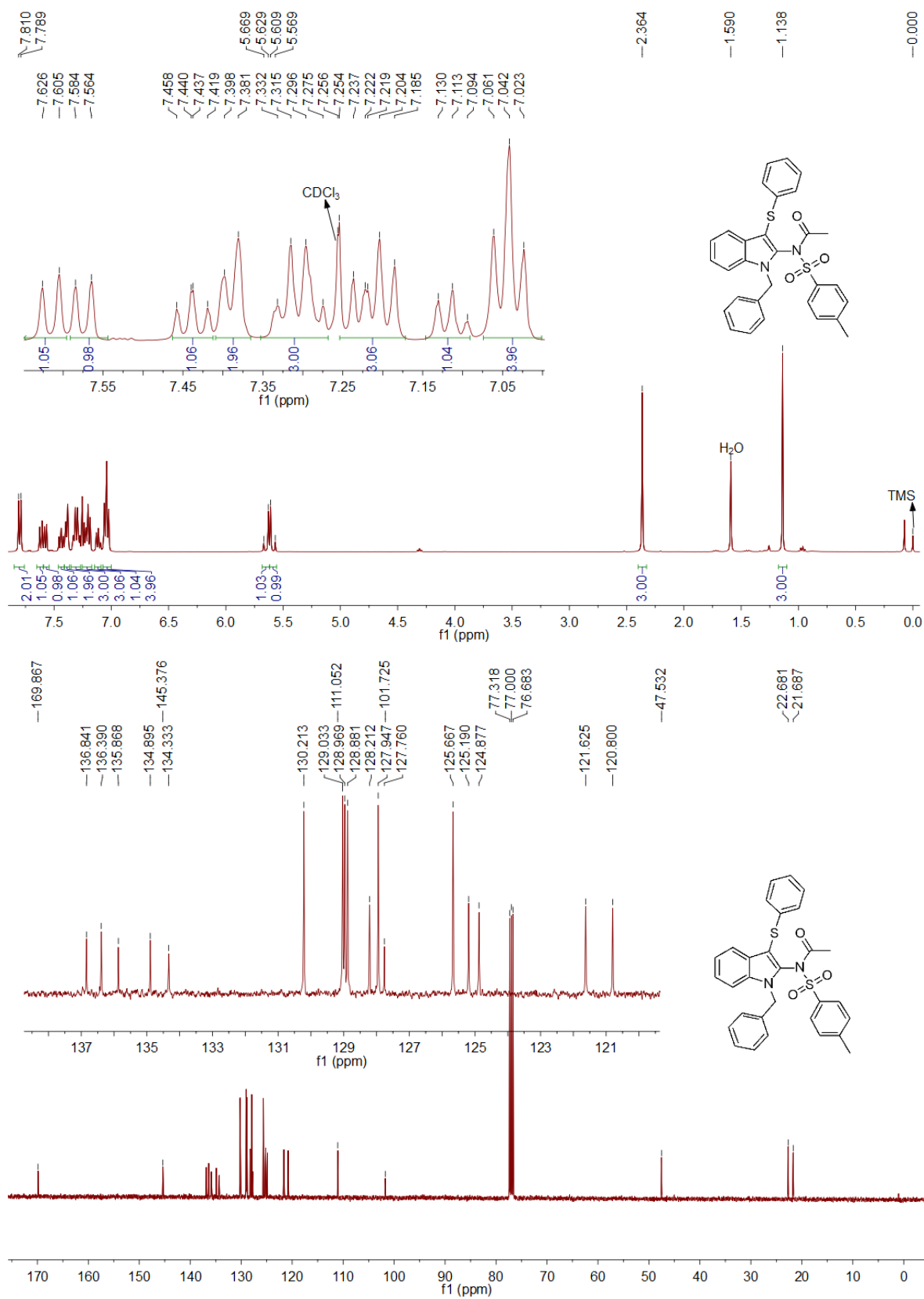
Copies of NMR Spectra



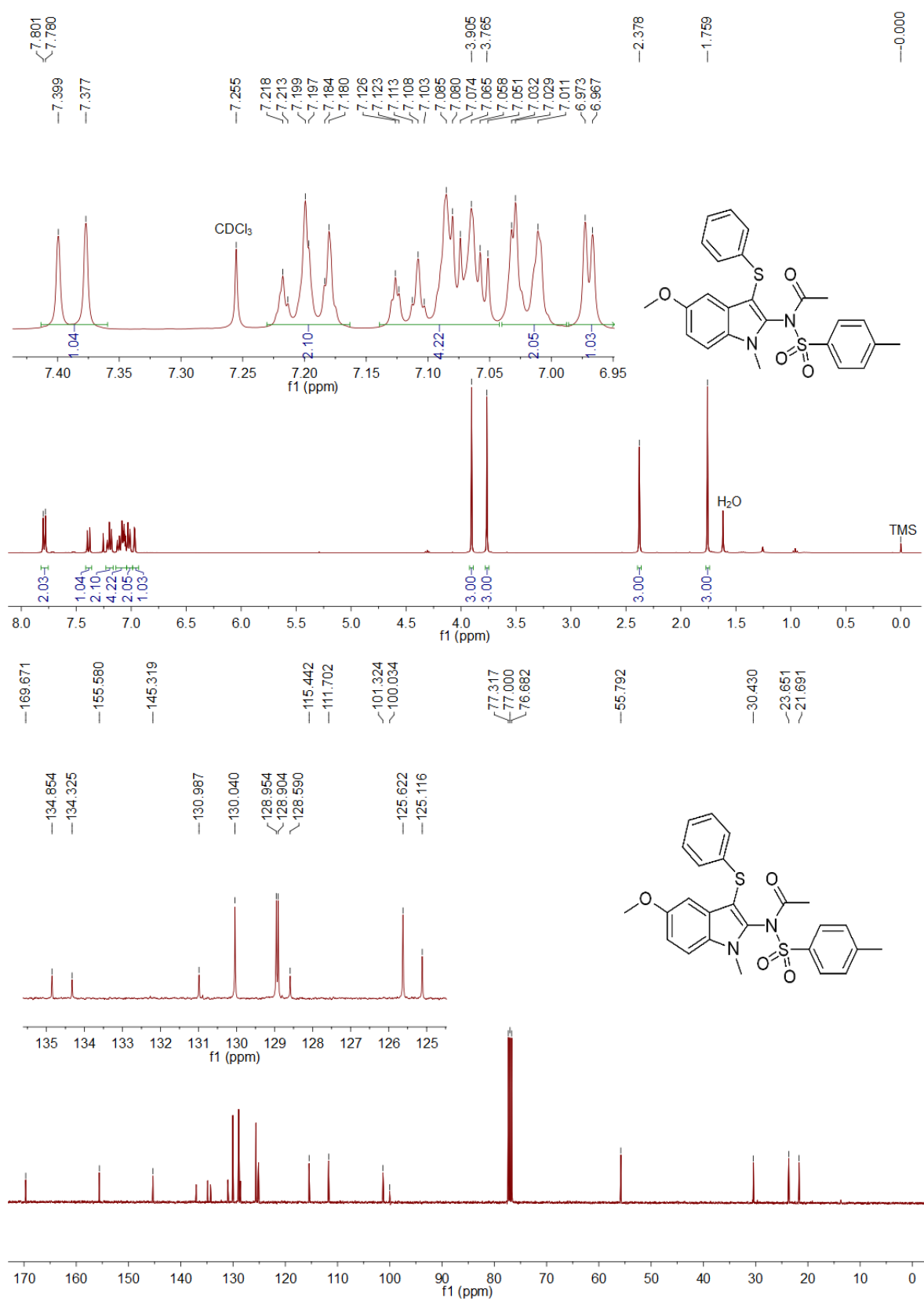
¹H and ¹³C NMR of Compound 3a



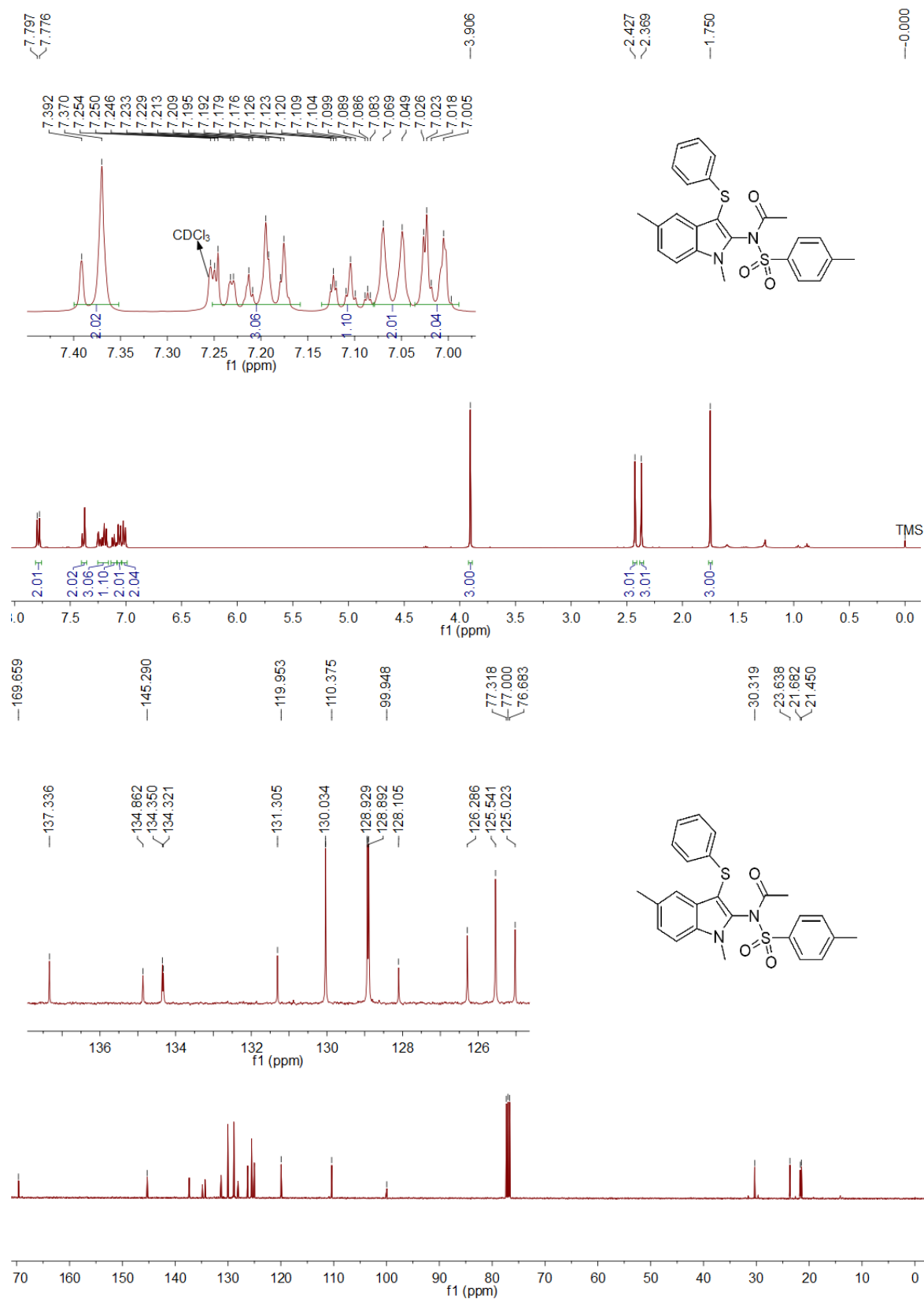


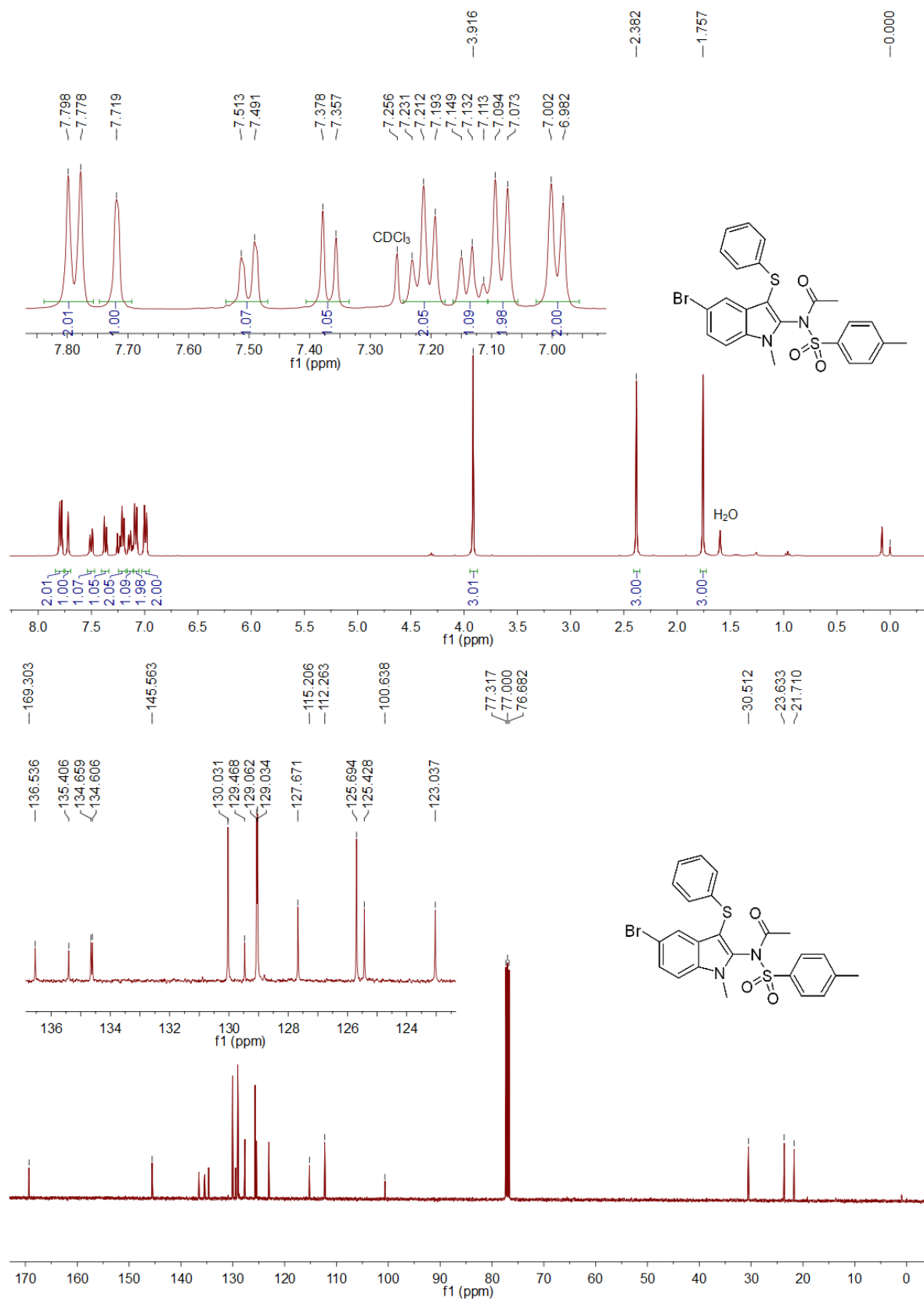


¹H and ¹³C NMR of Compound 3d

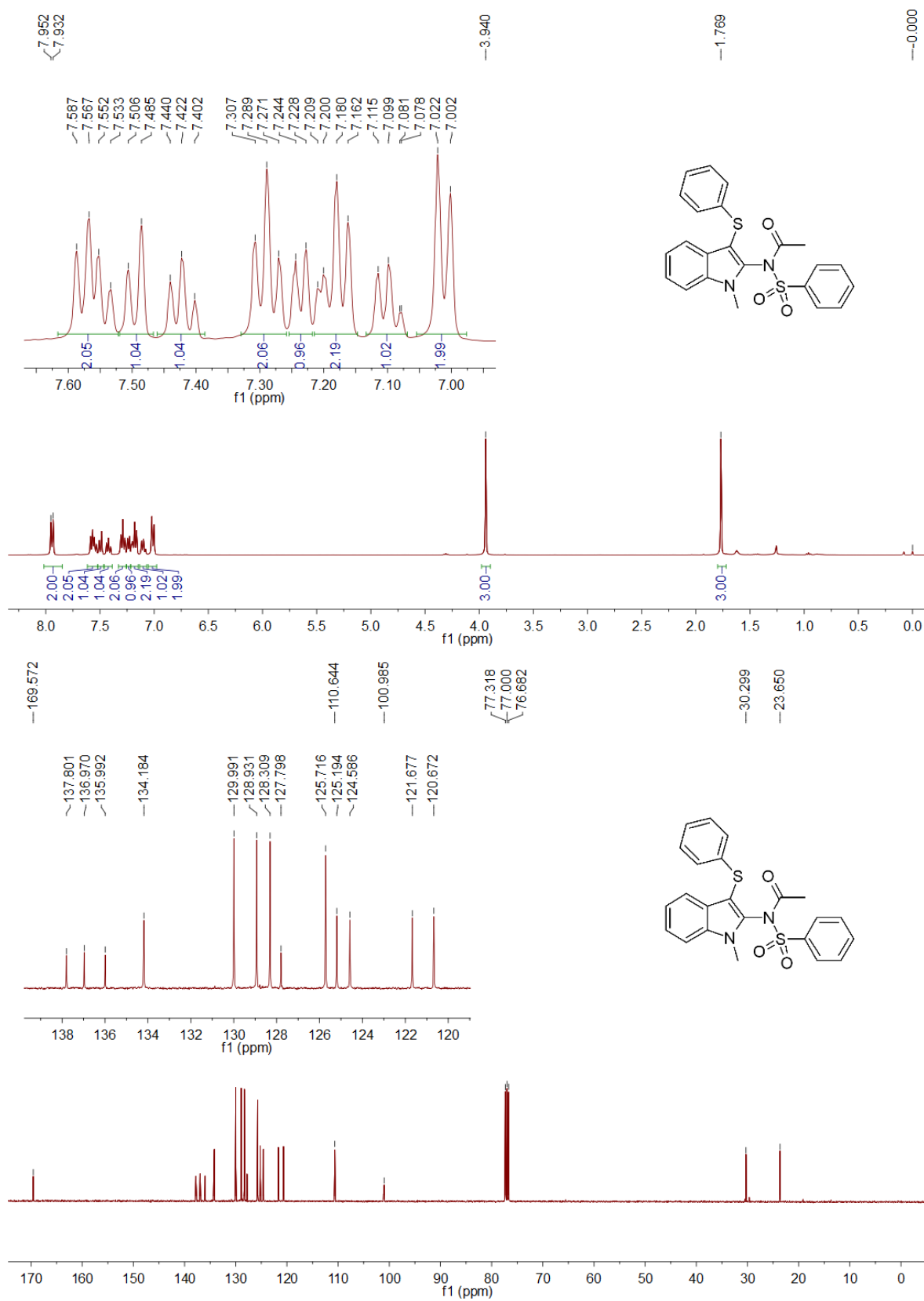


¹H and ¹³C NMR of Compound 3e

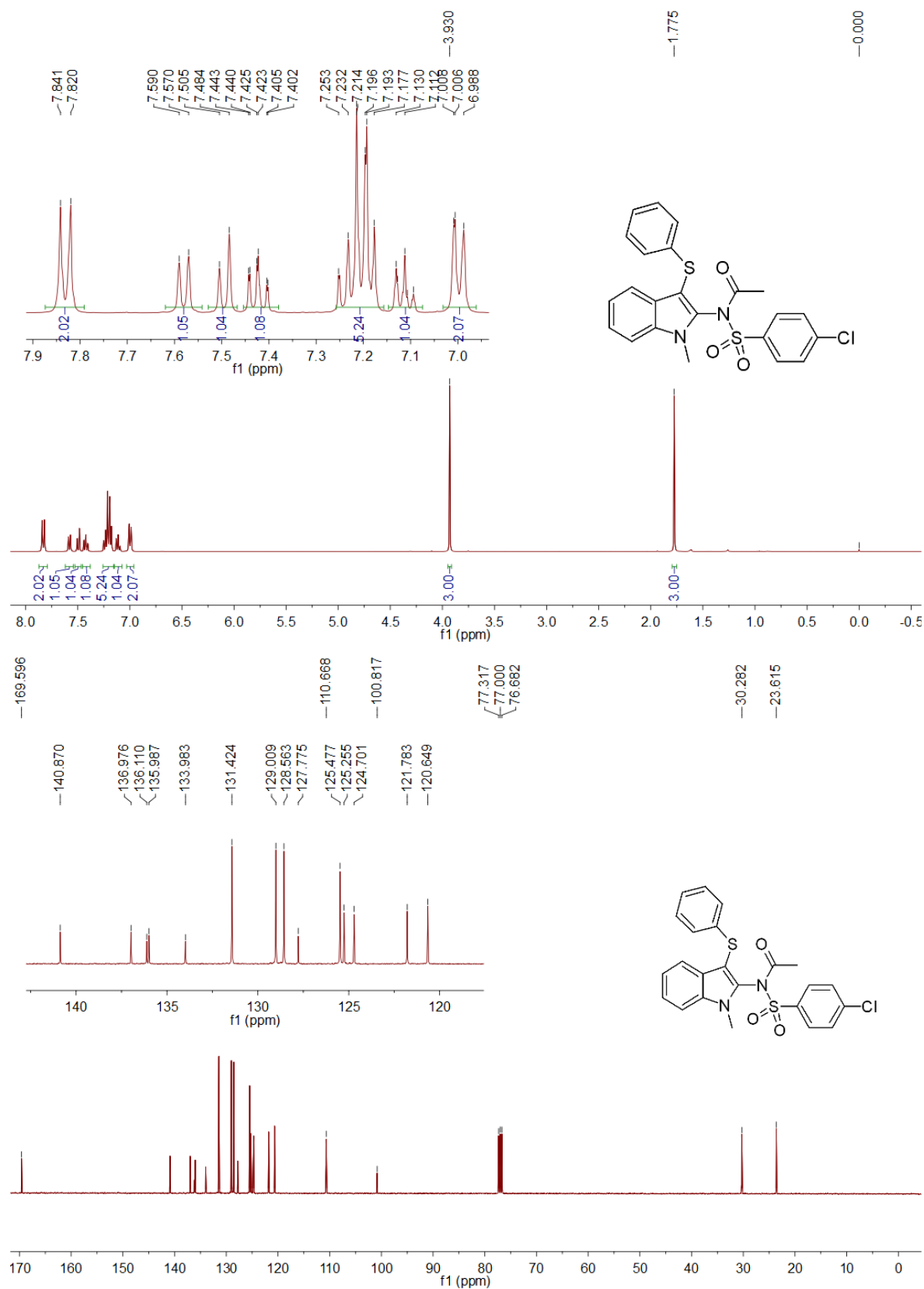




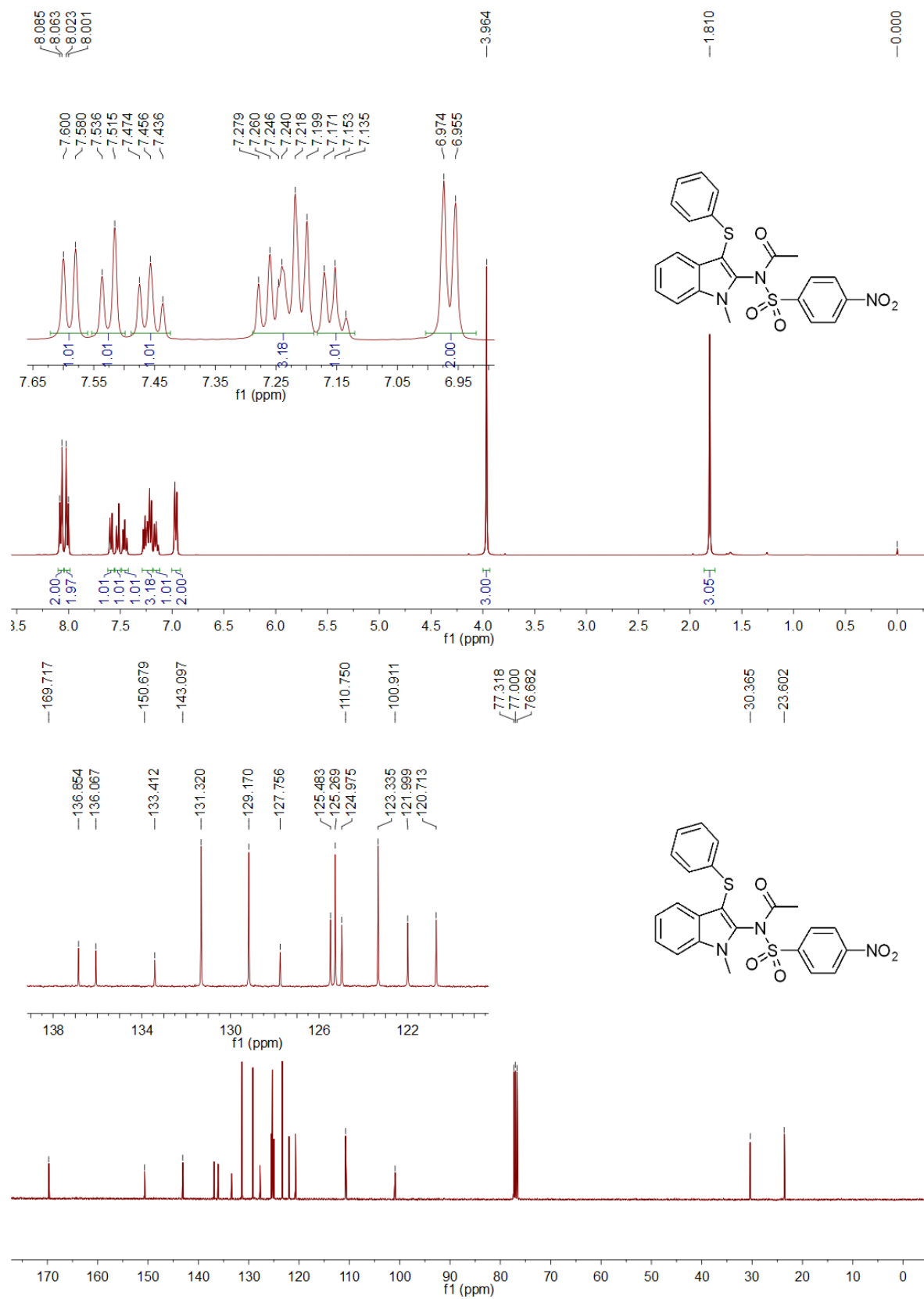
¹H and ¹³C NMR of Compound 3g



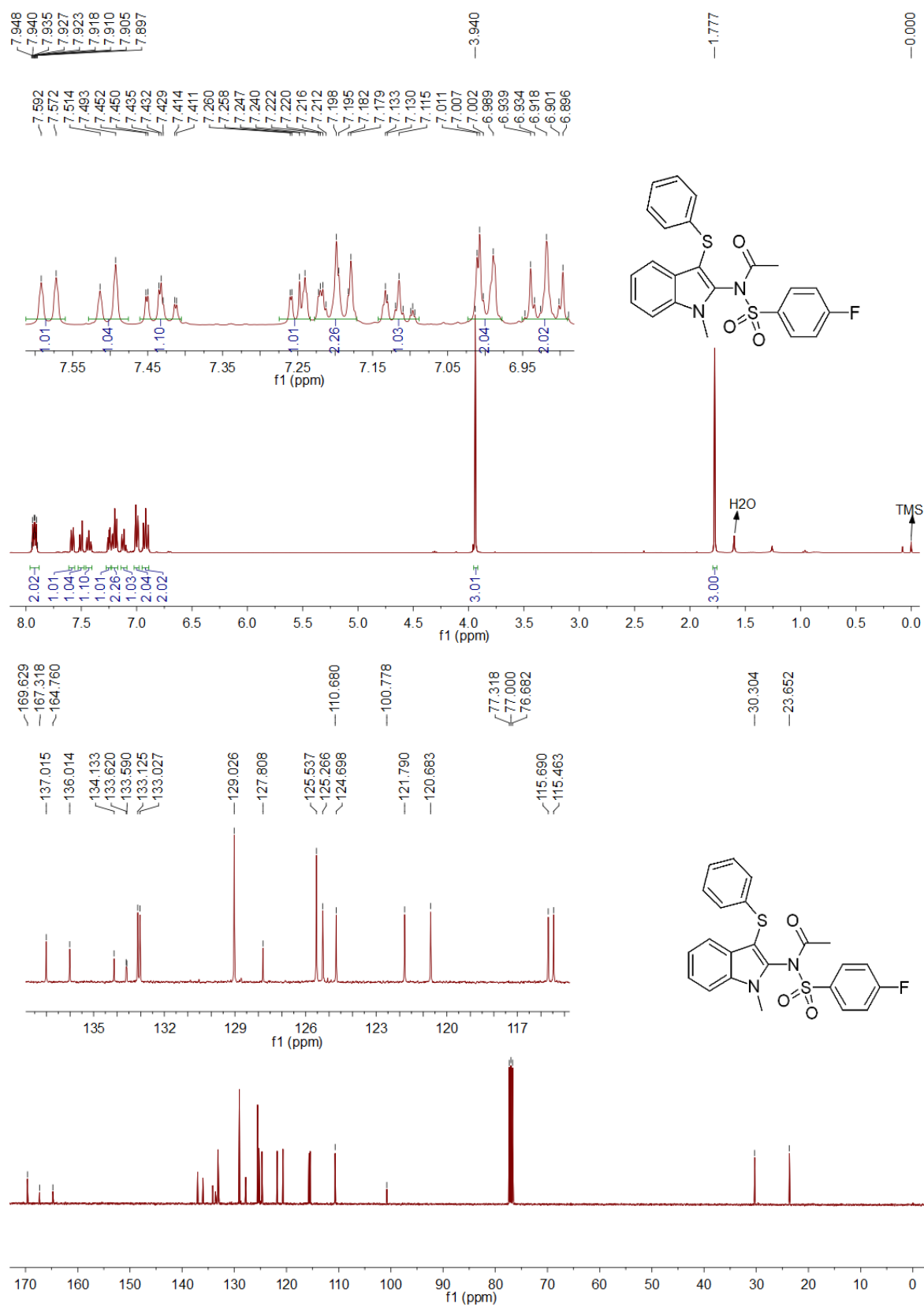
¹H and ¹³C NMR of Compound 3h



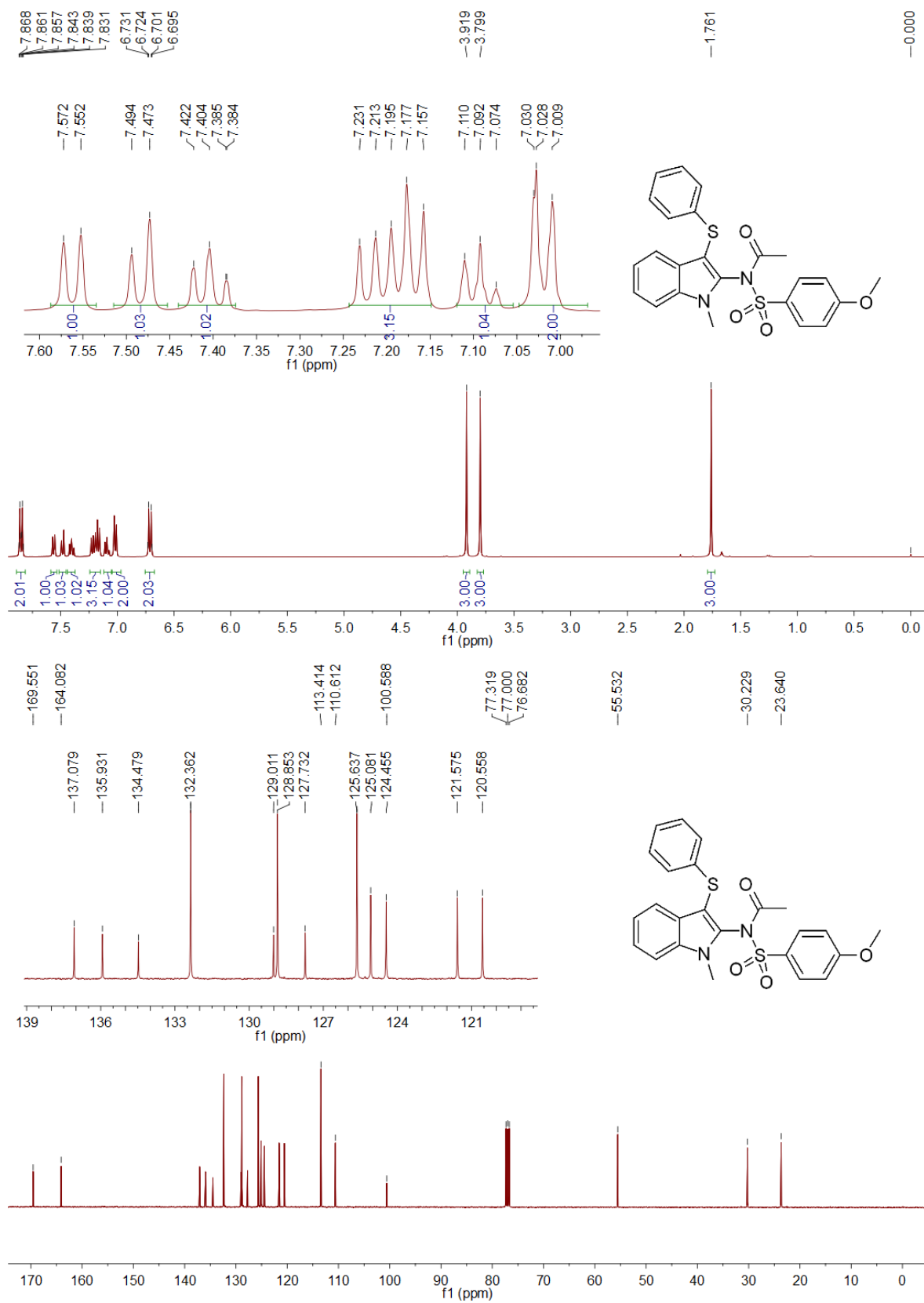
¹H and ¹³C NMR of Compound 3i



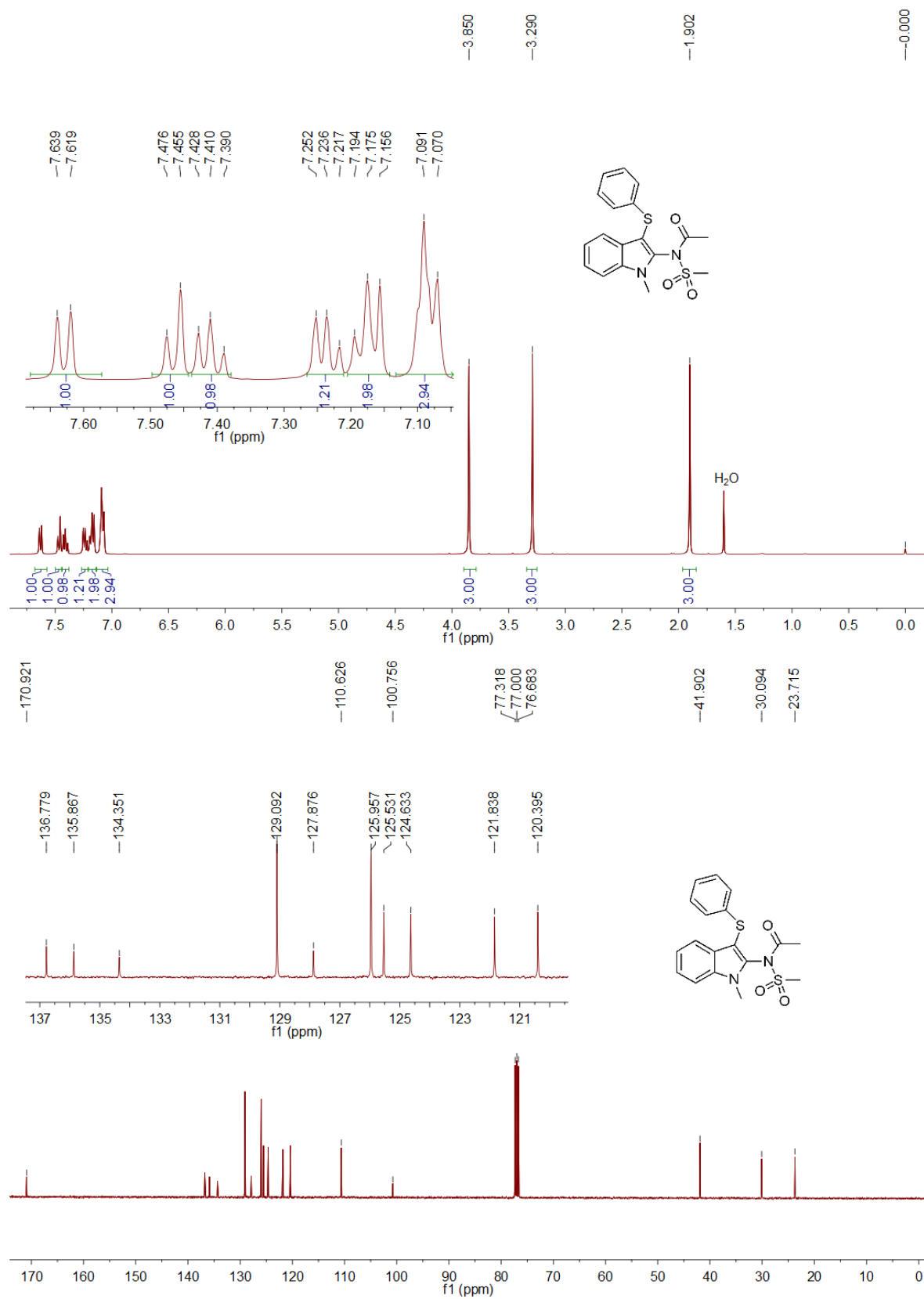
¹H and ¹³C NMR of Compound 3j

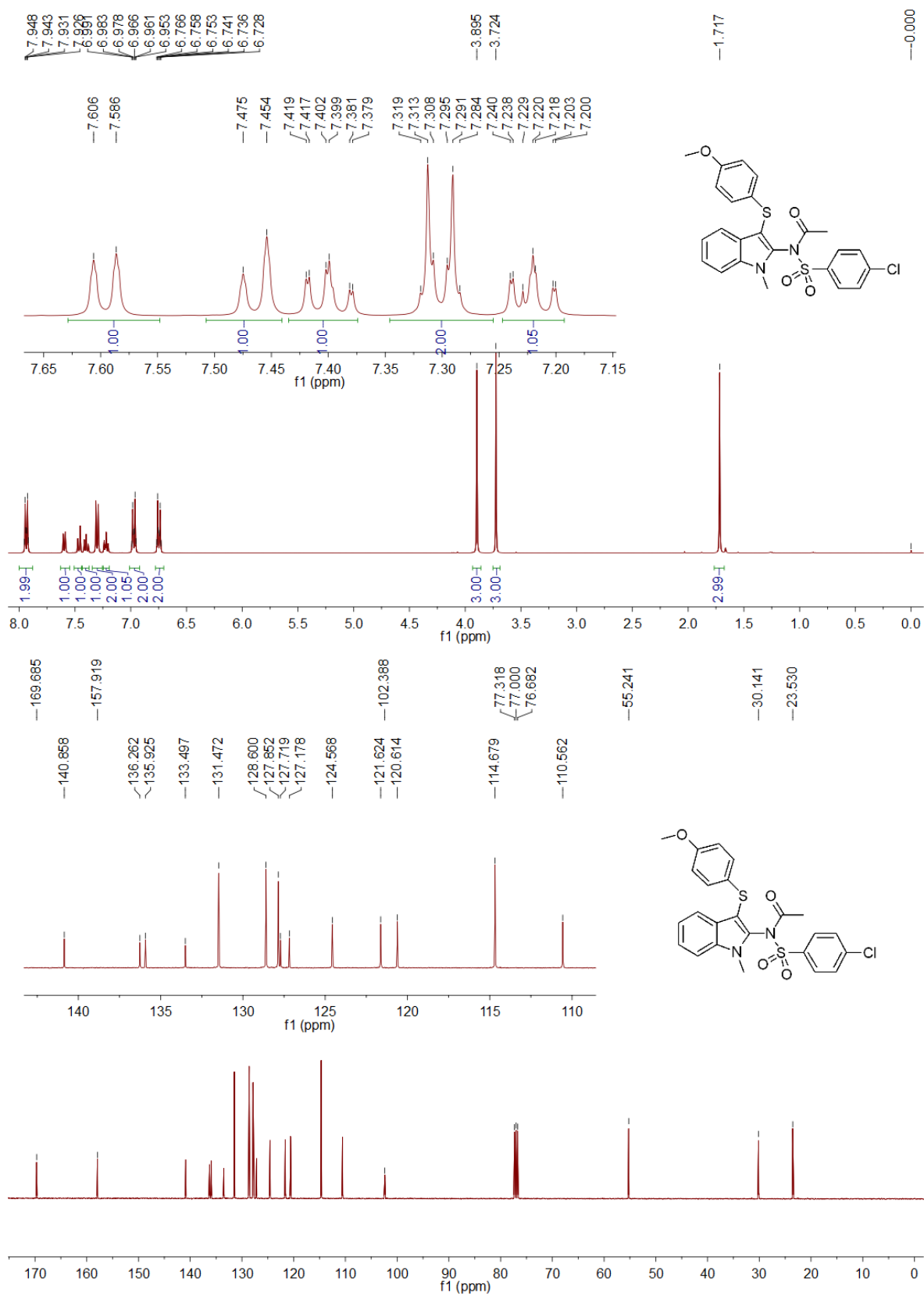


¹H and ¹³C NMR of Compound 3k

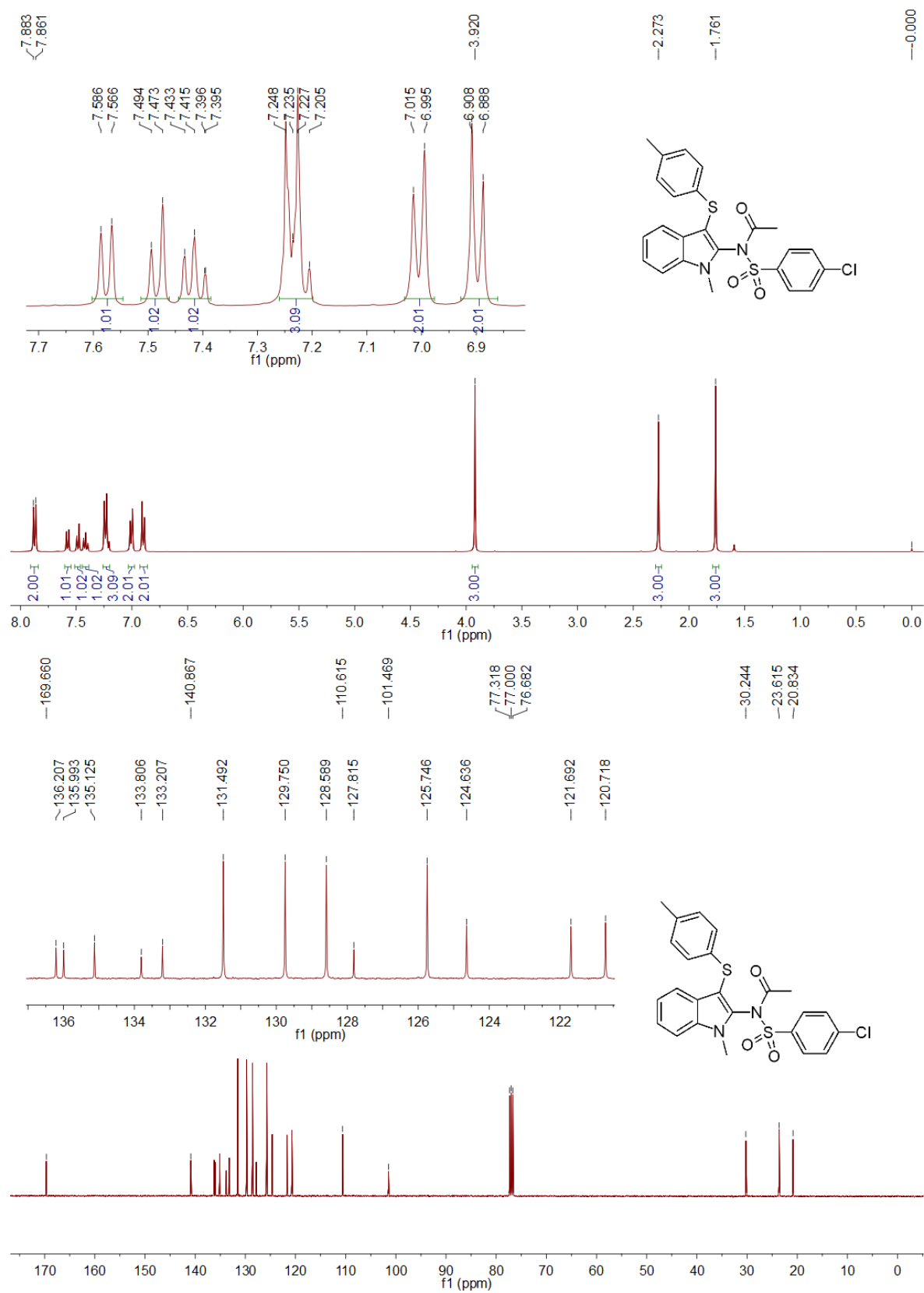


¹H and ¹³C NMR of Compound 3l

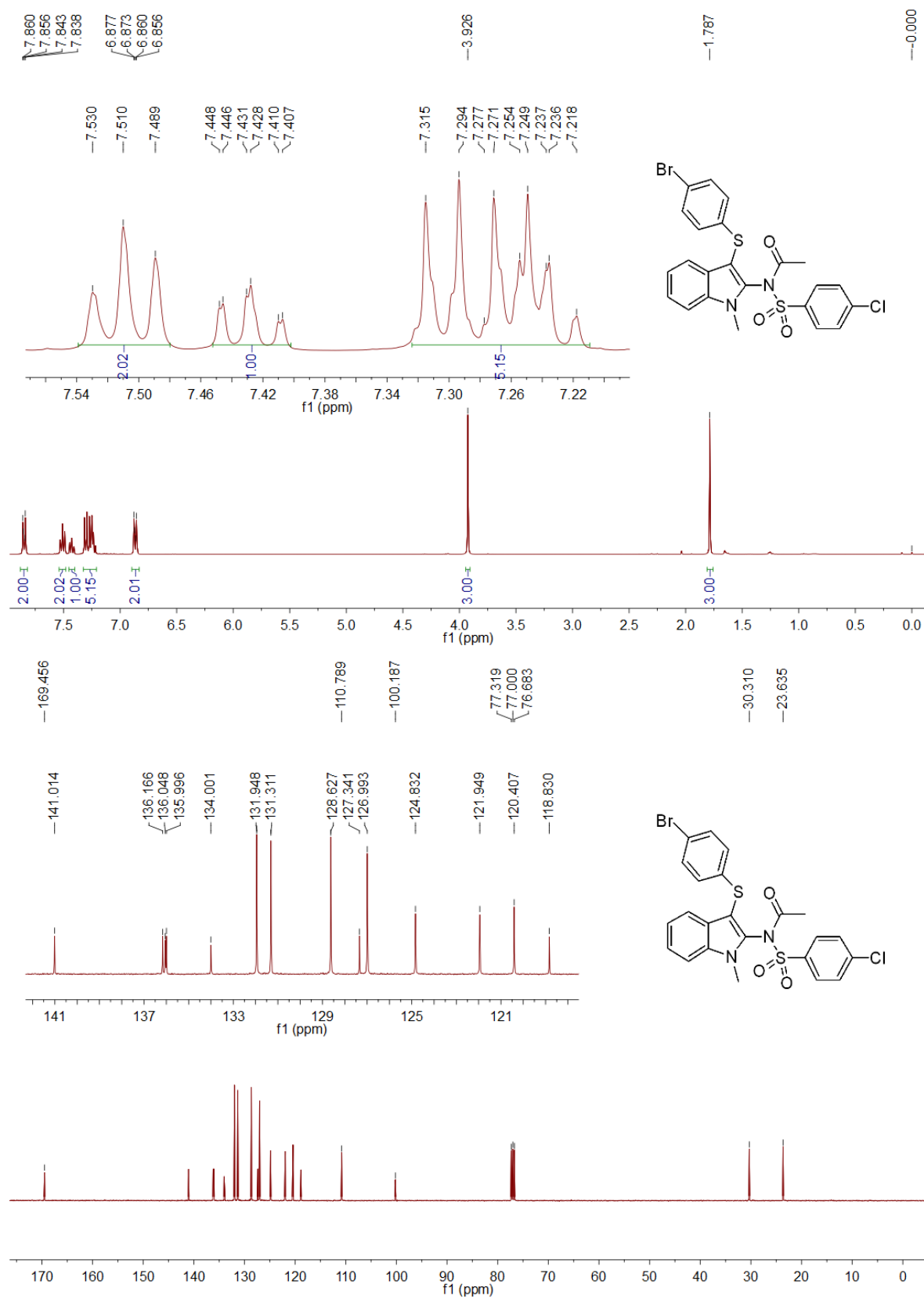




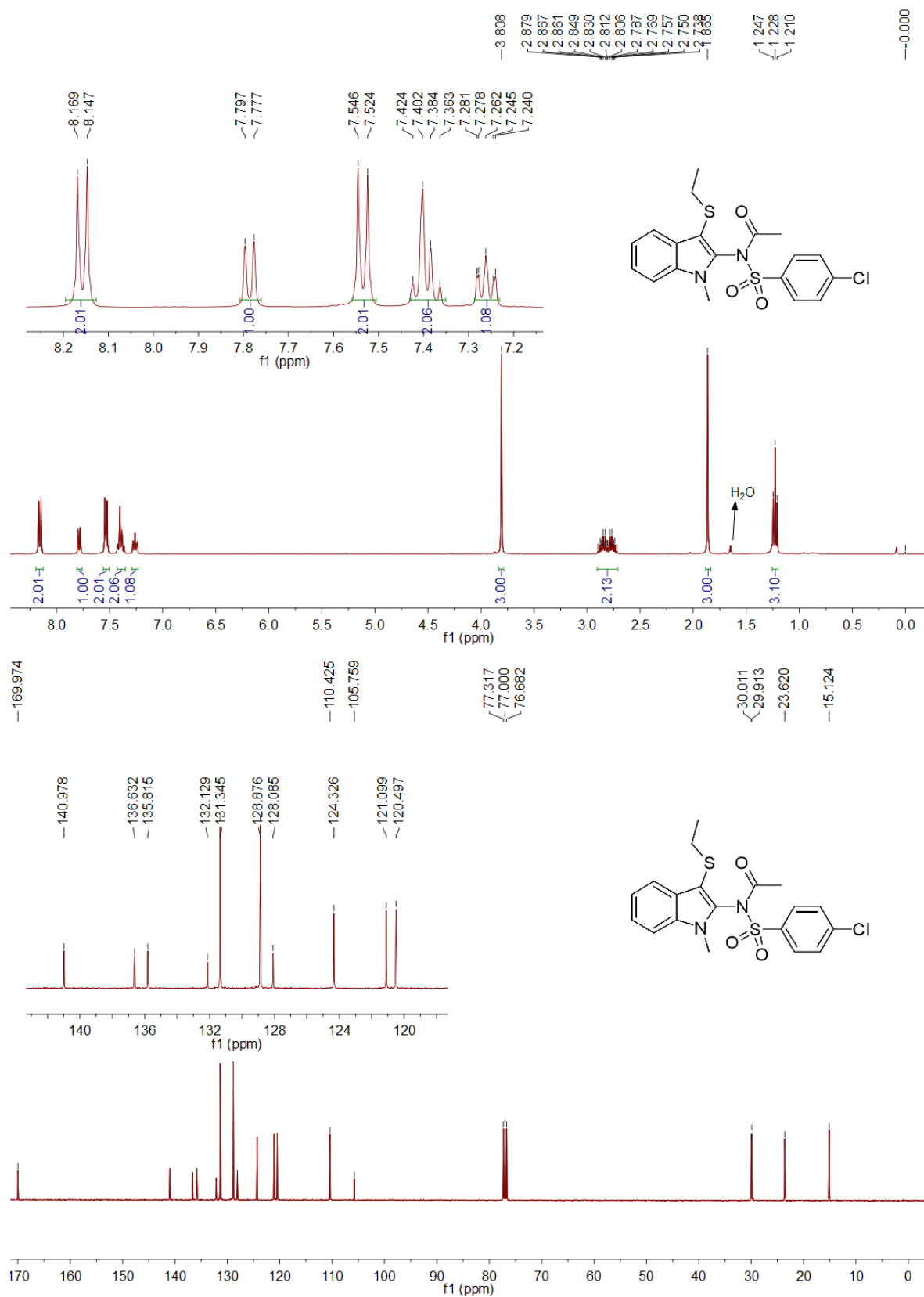
¹H and ¹³C NMR of Compound 3n

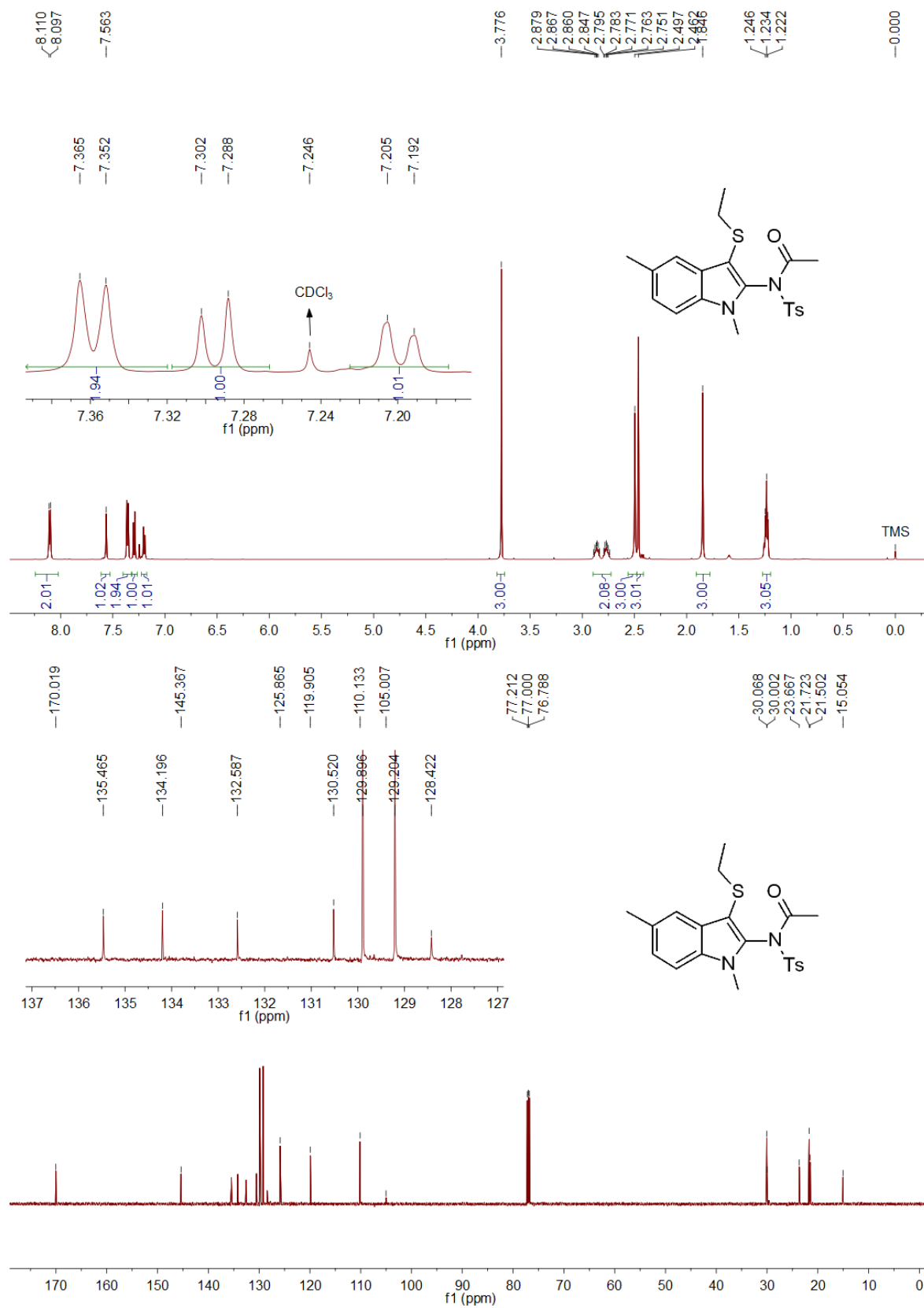


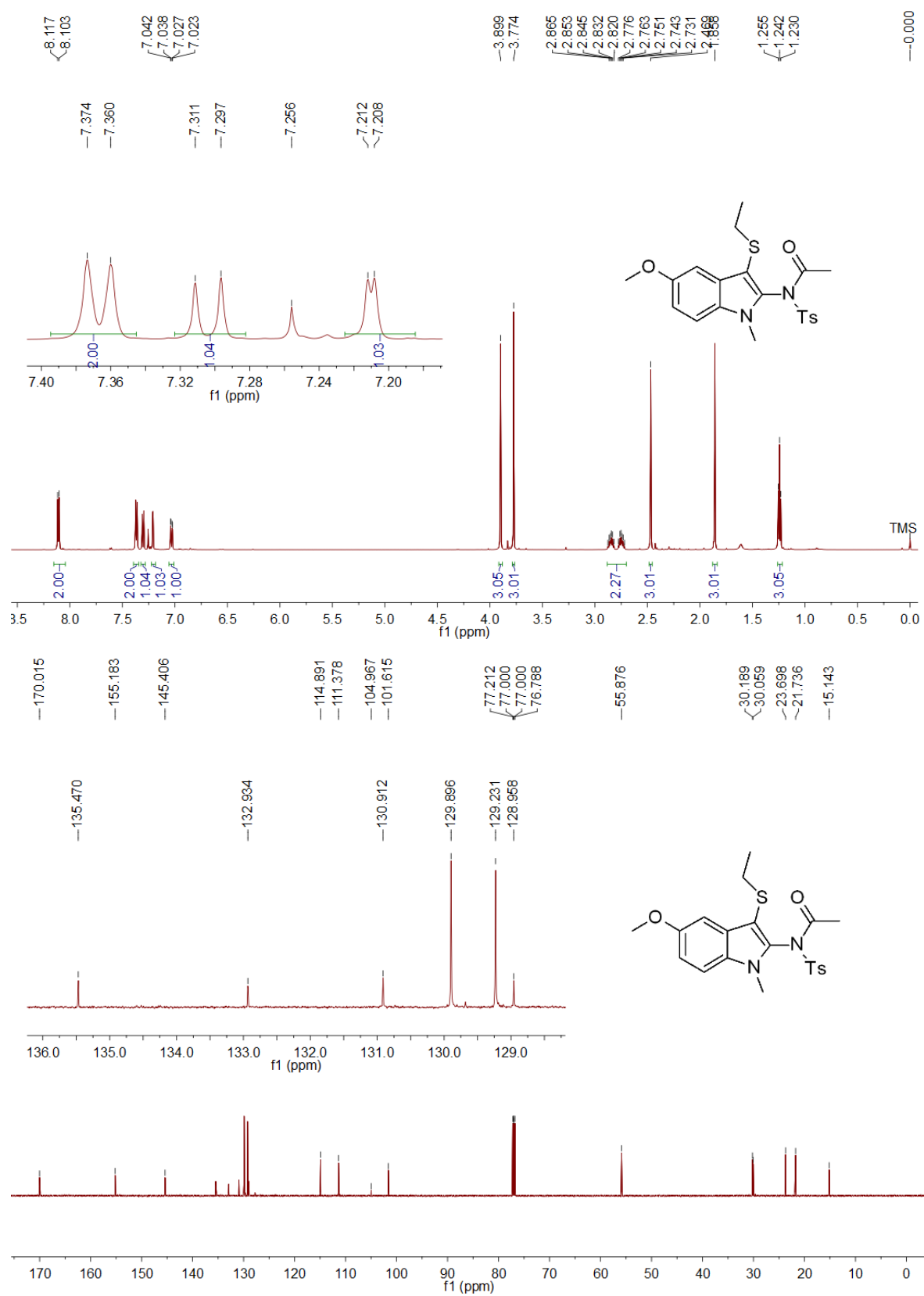
¹H and ¹³C NMR of Compound 3o



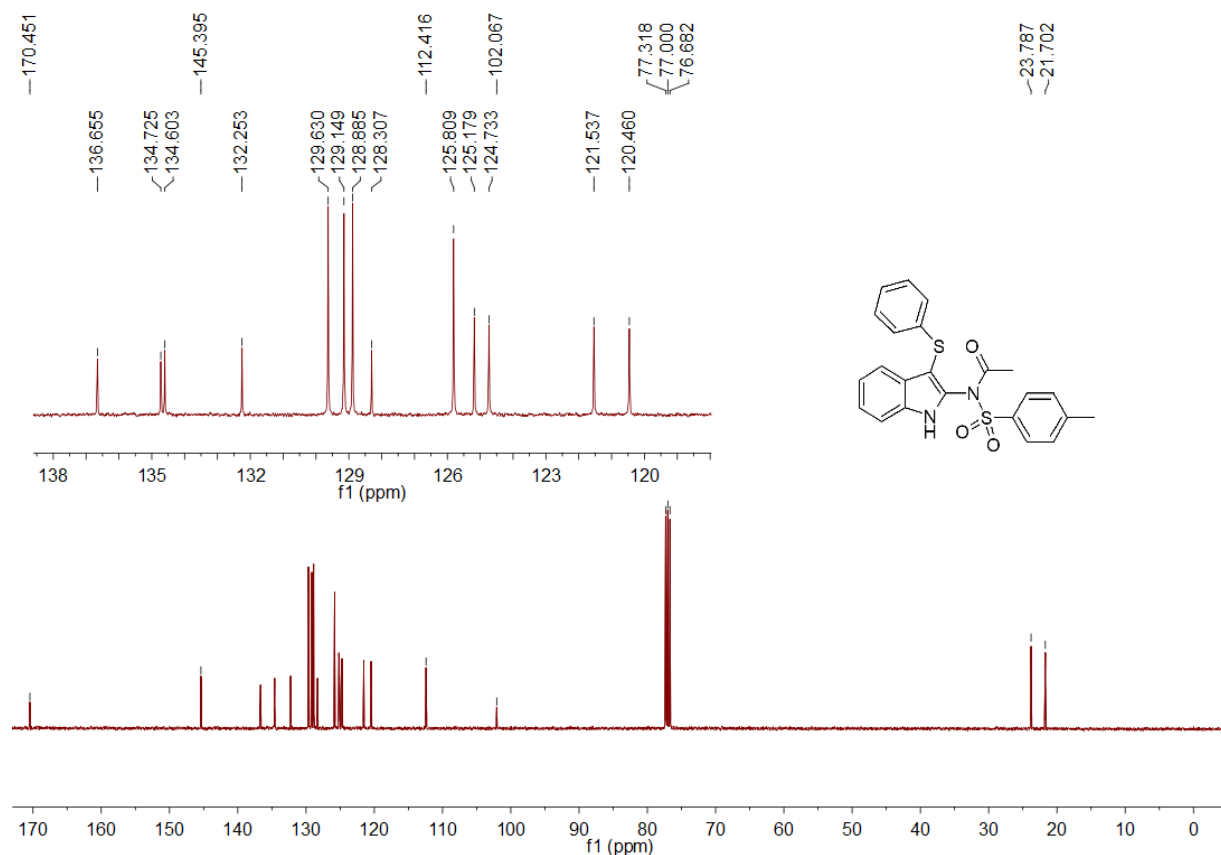
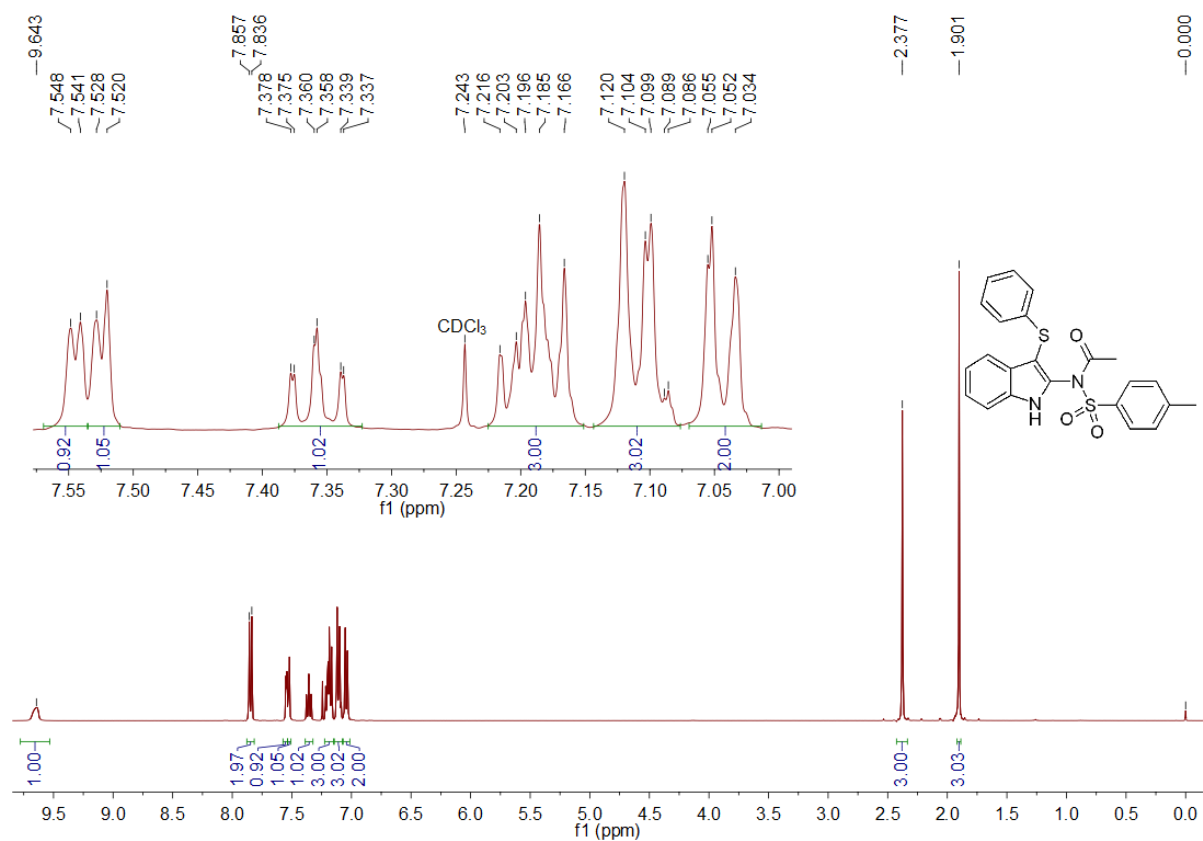
¹H and ¹³C NMR of Compound 3p



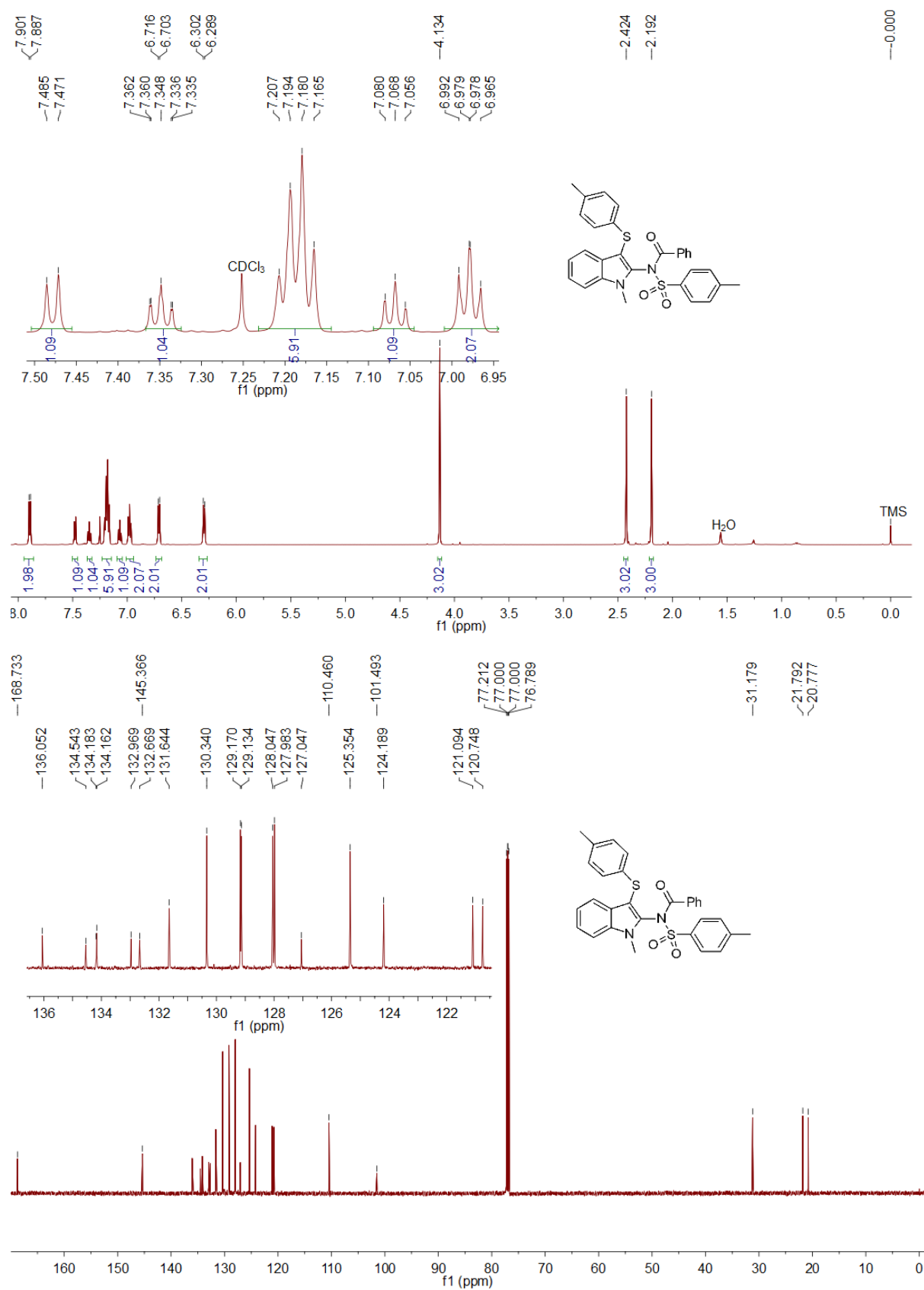


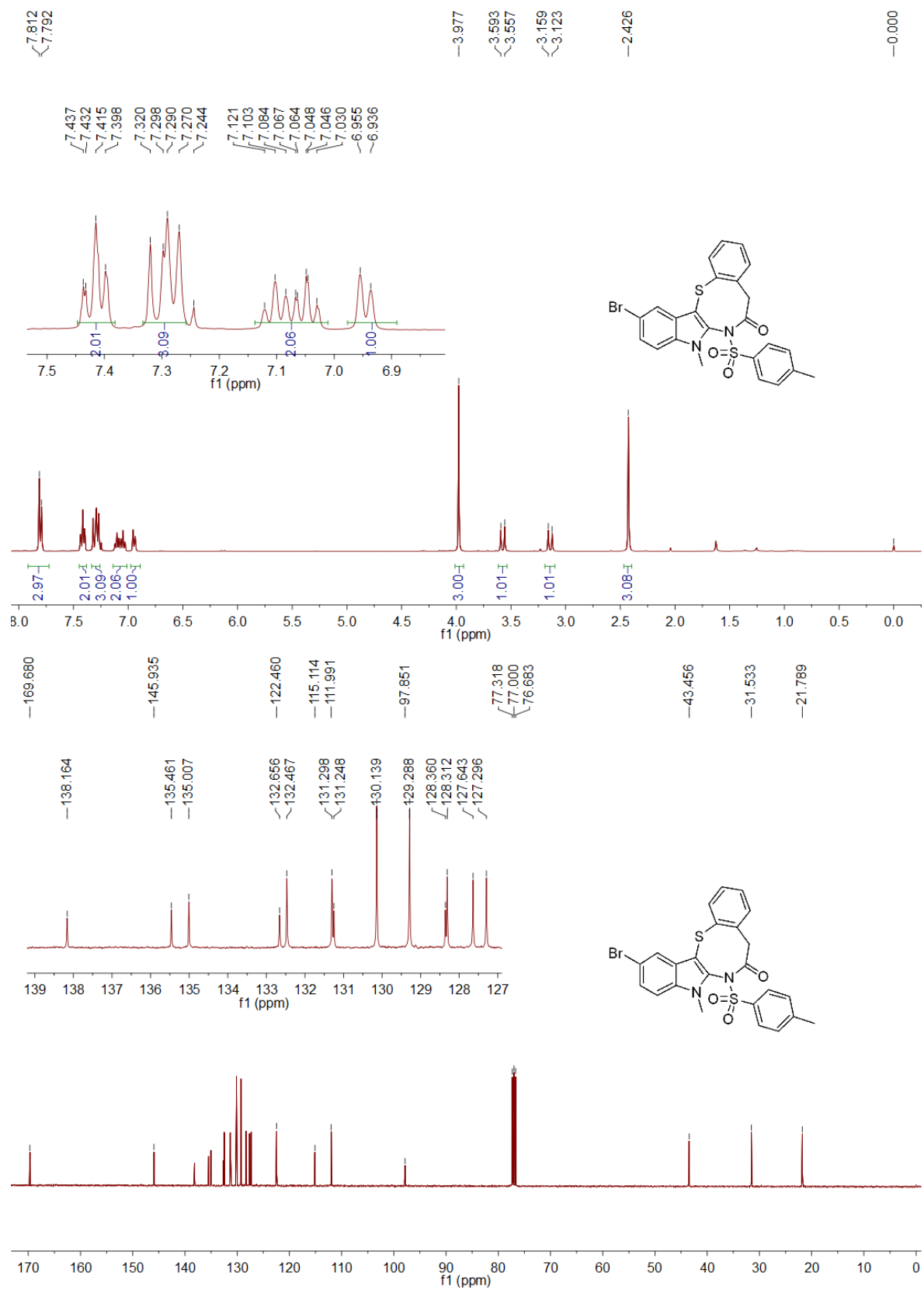


¹H and ¹³C NMR of Compound 3s

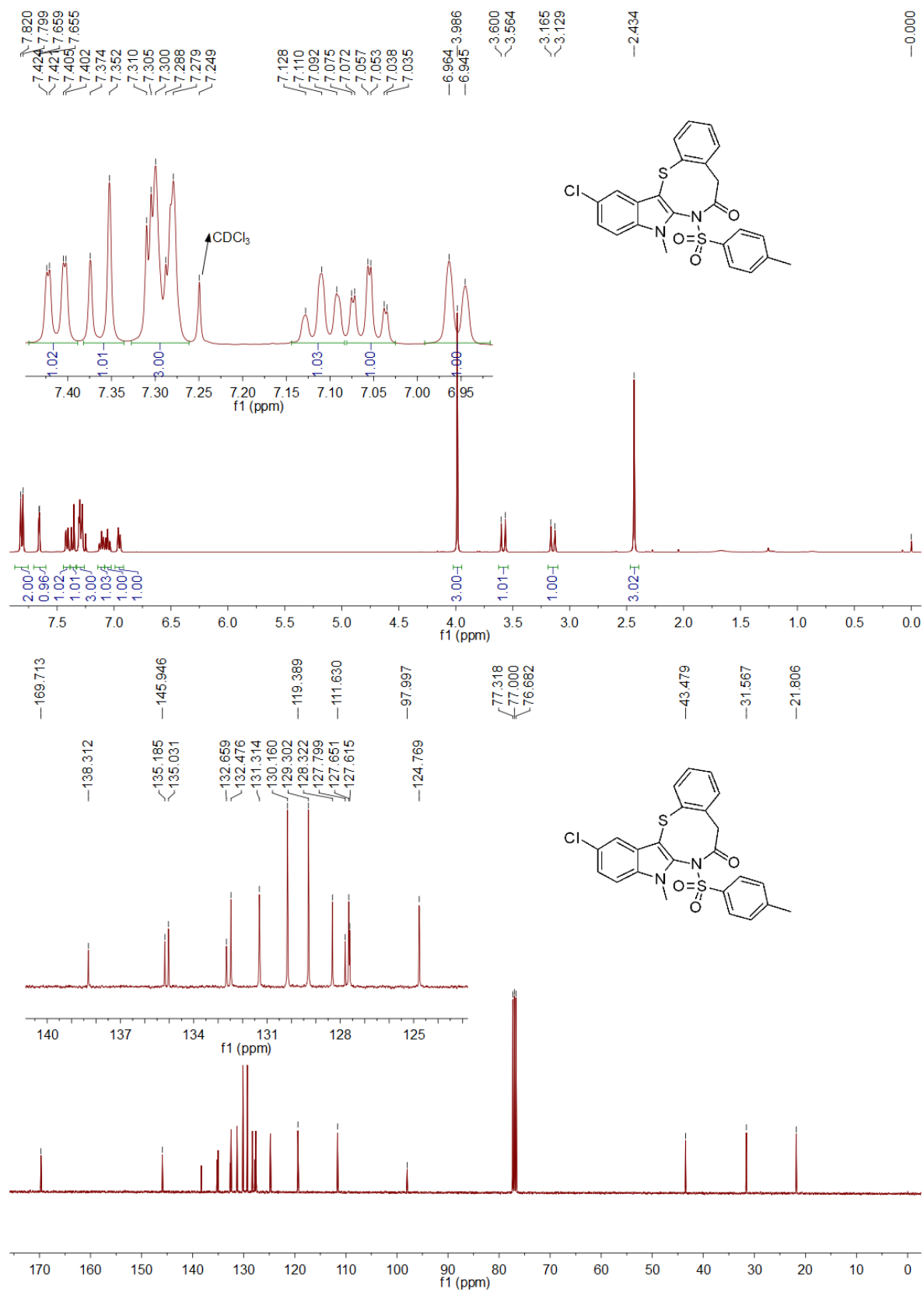


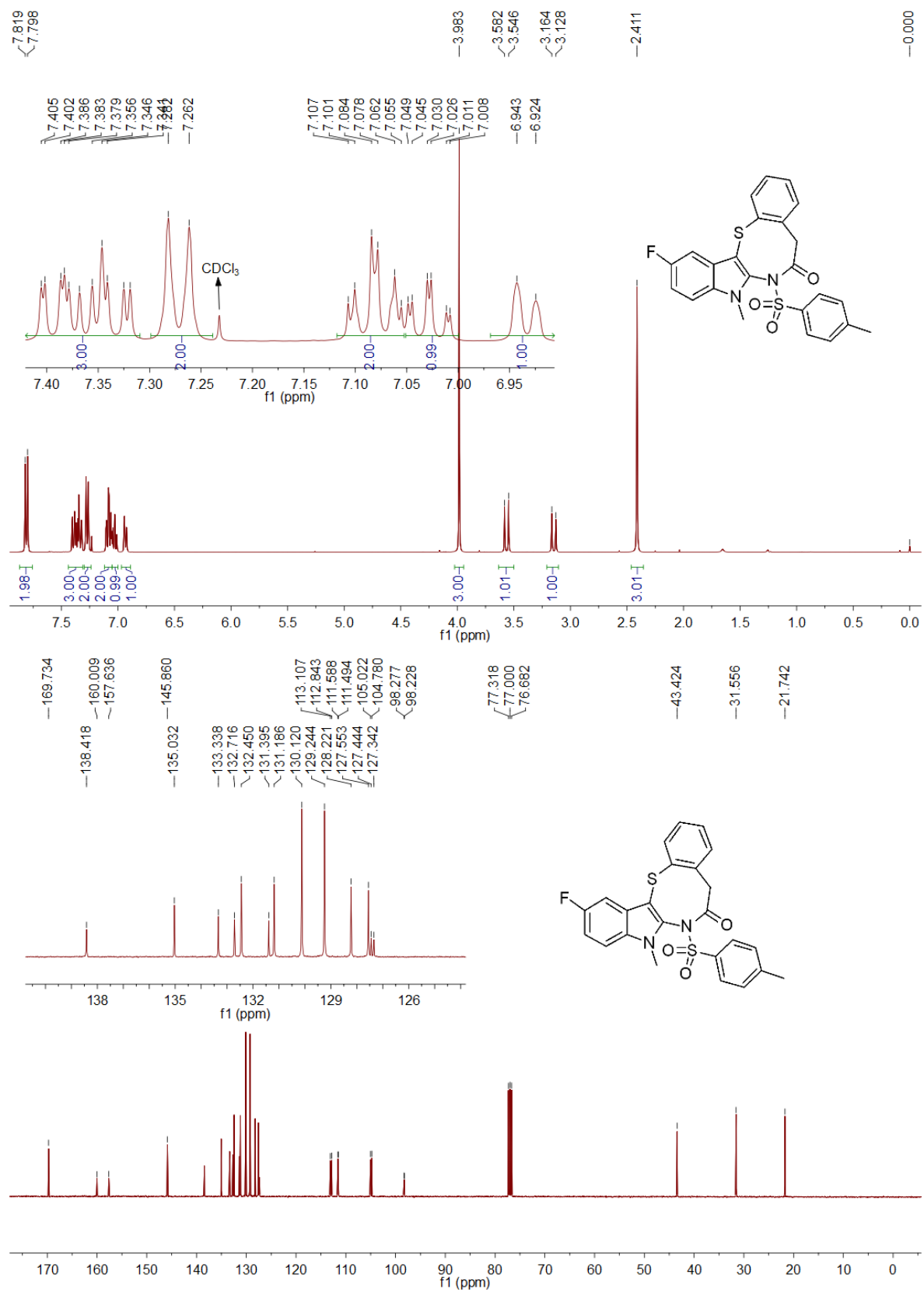
¹H and ¹³C NMR of Compound 3t

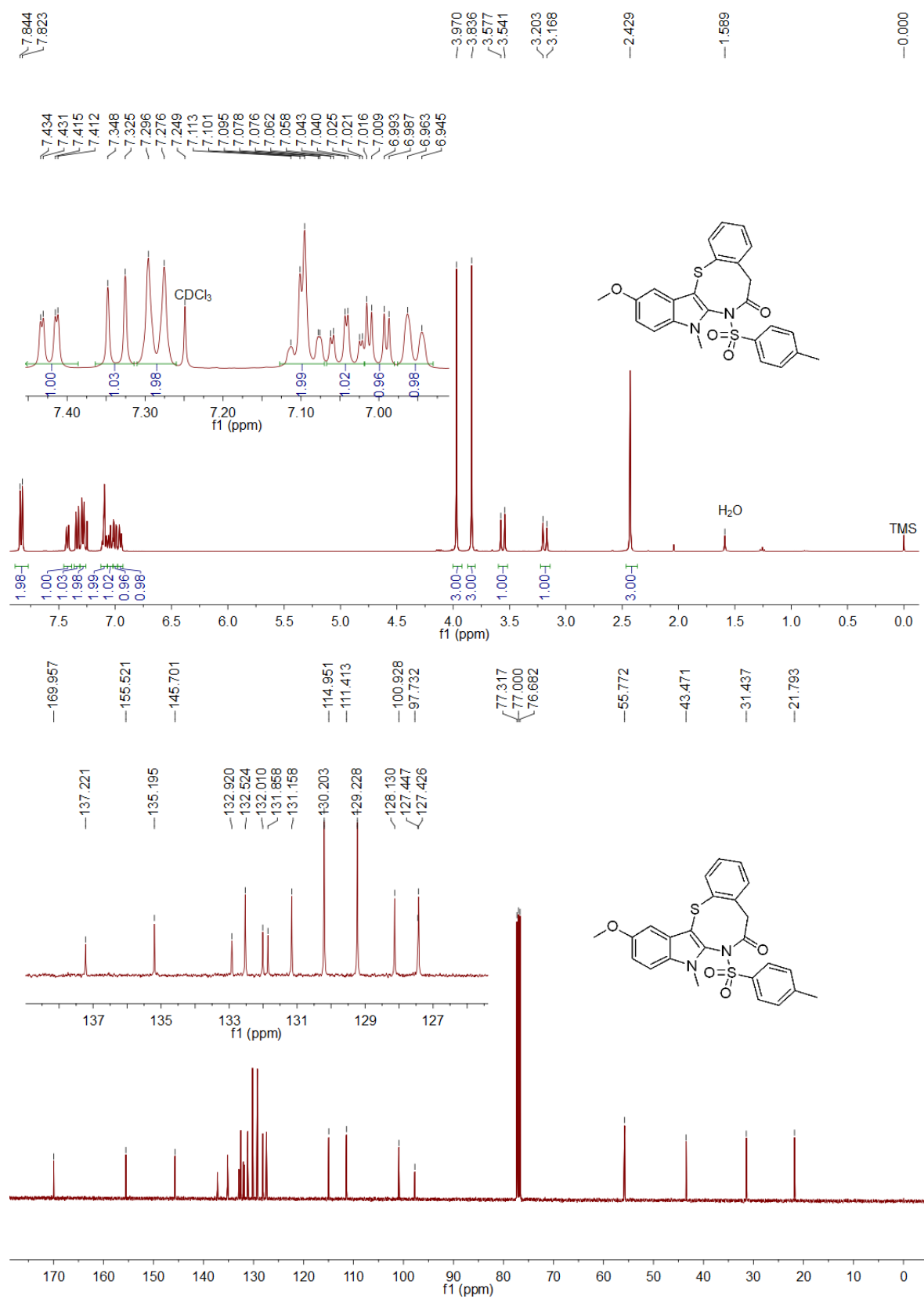




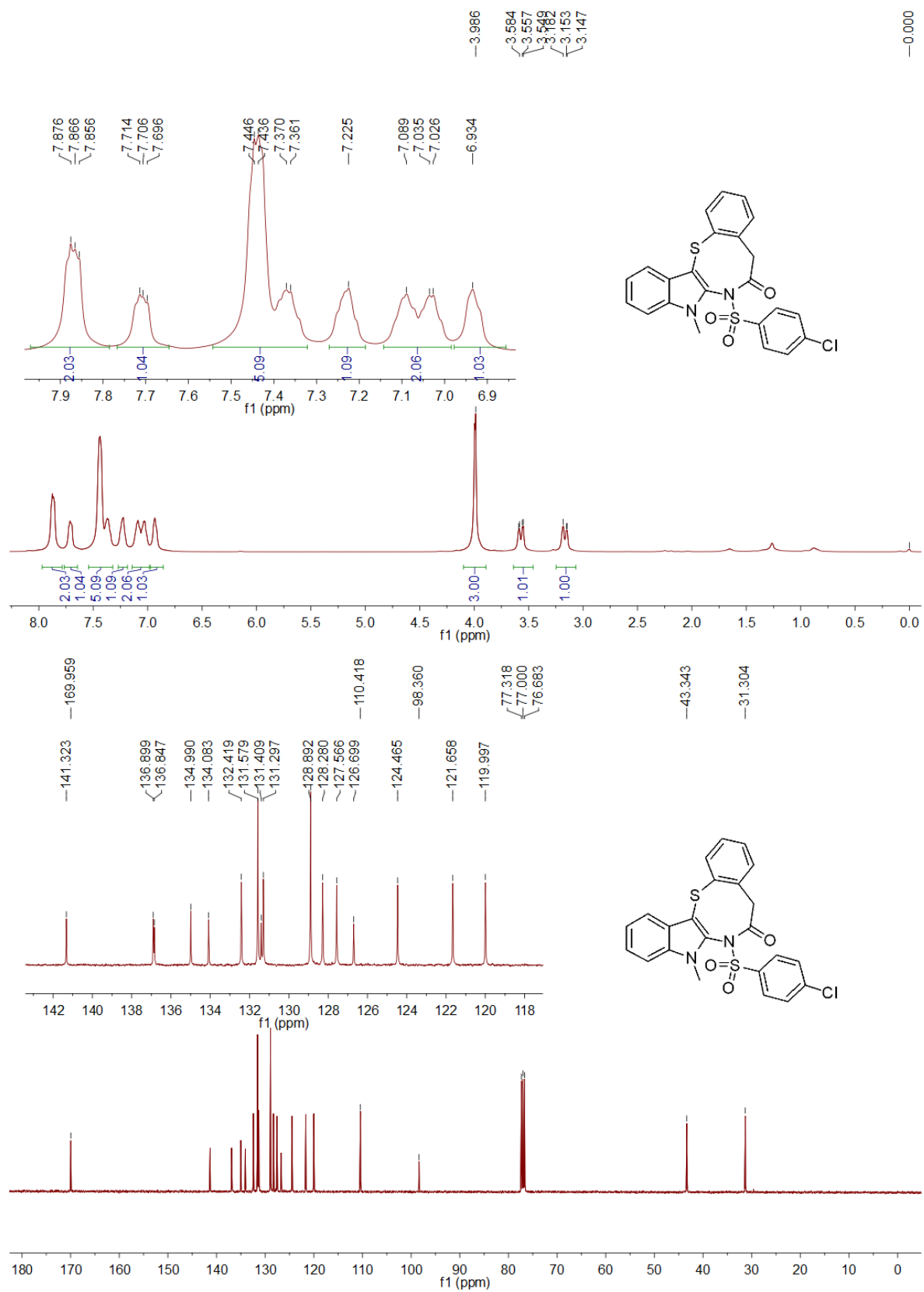
¹H and ¹³C NMR of Compound 5a



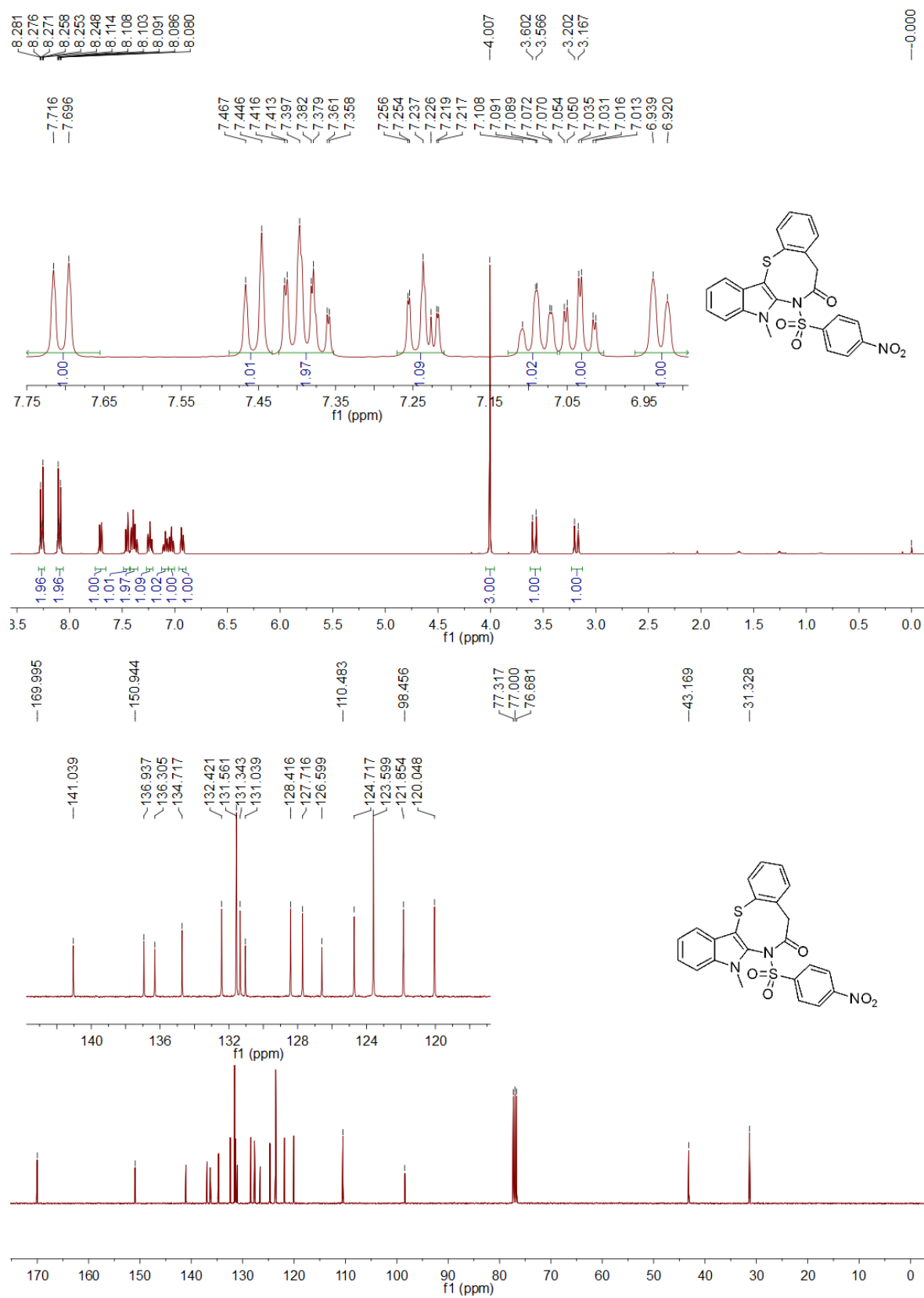




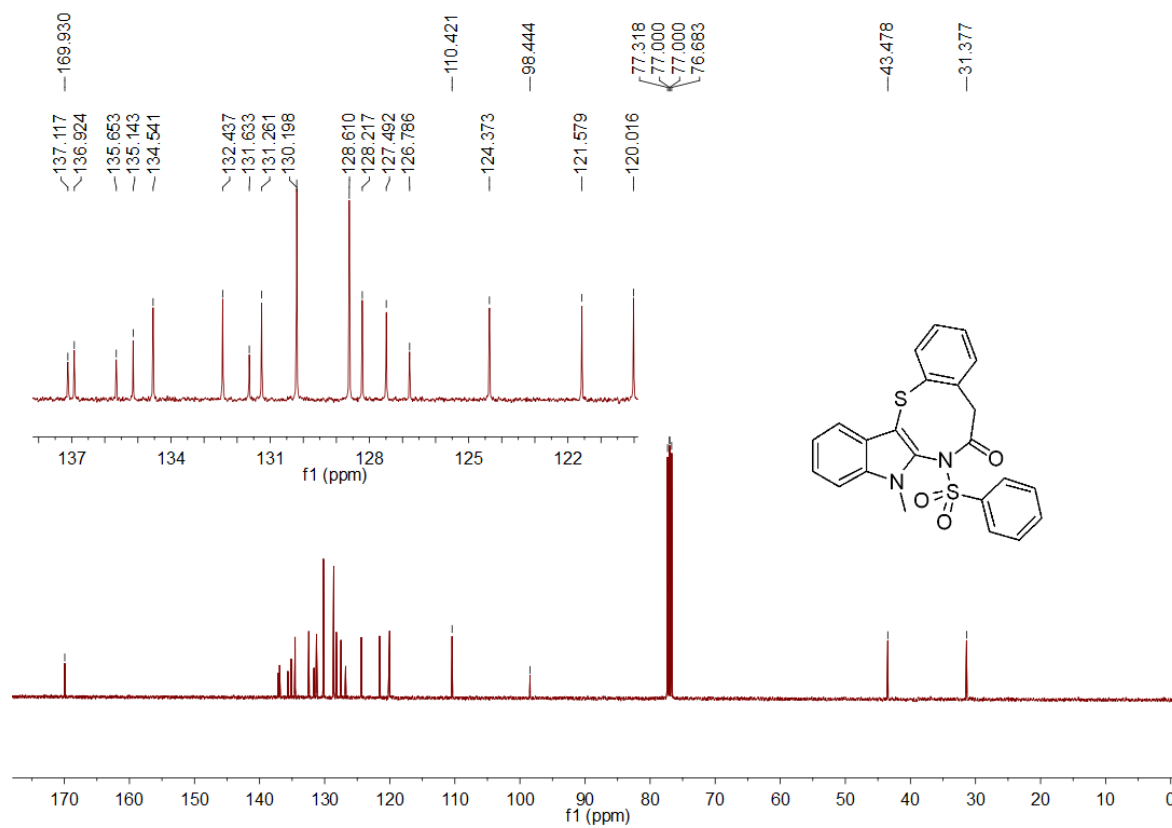
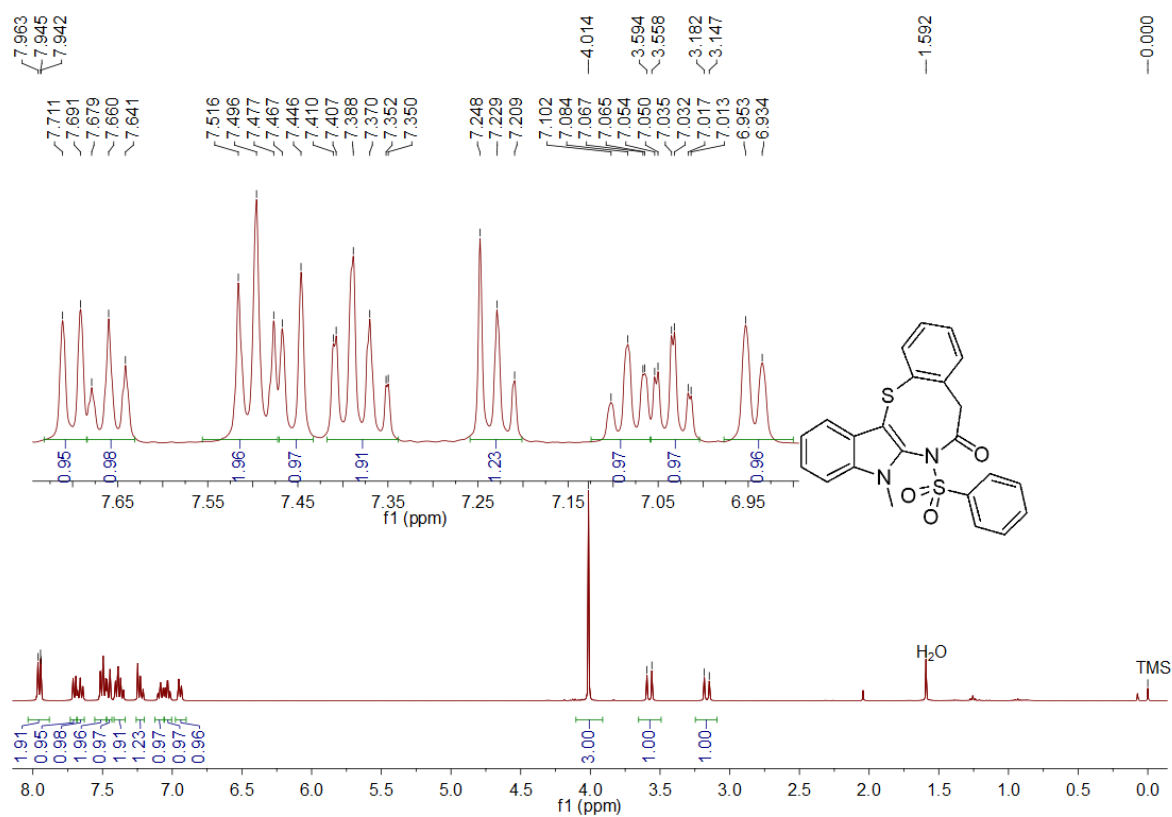
¹H and ¹³C NMR of Compound 5d



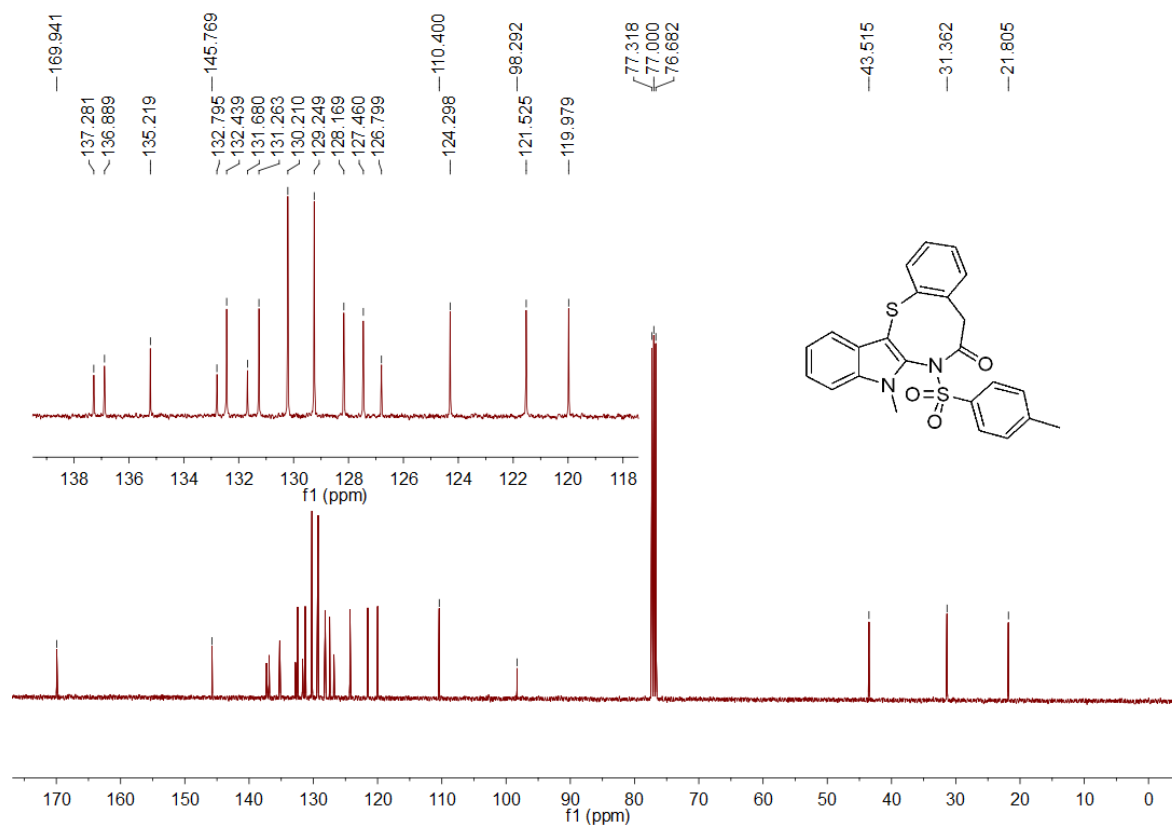
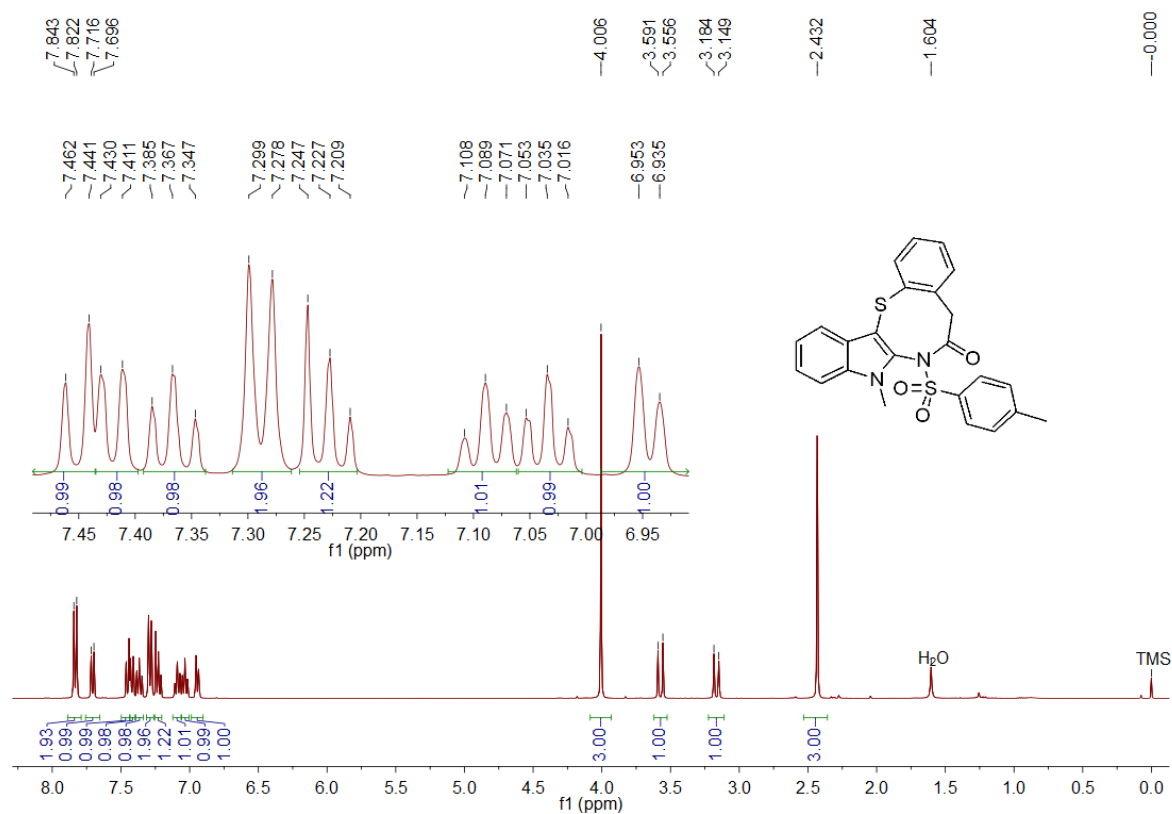
¹H and ¹³C NMR of Compound 5e



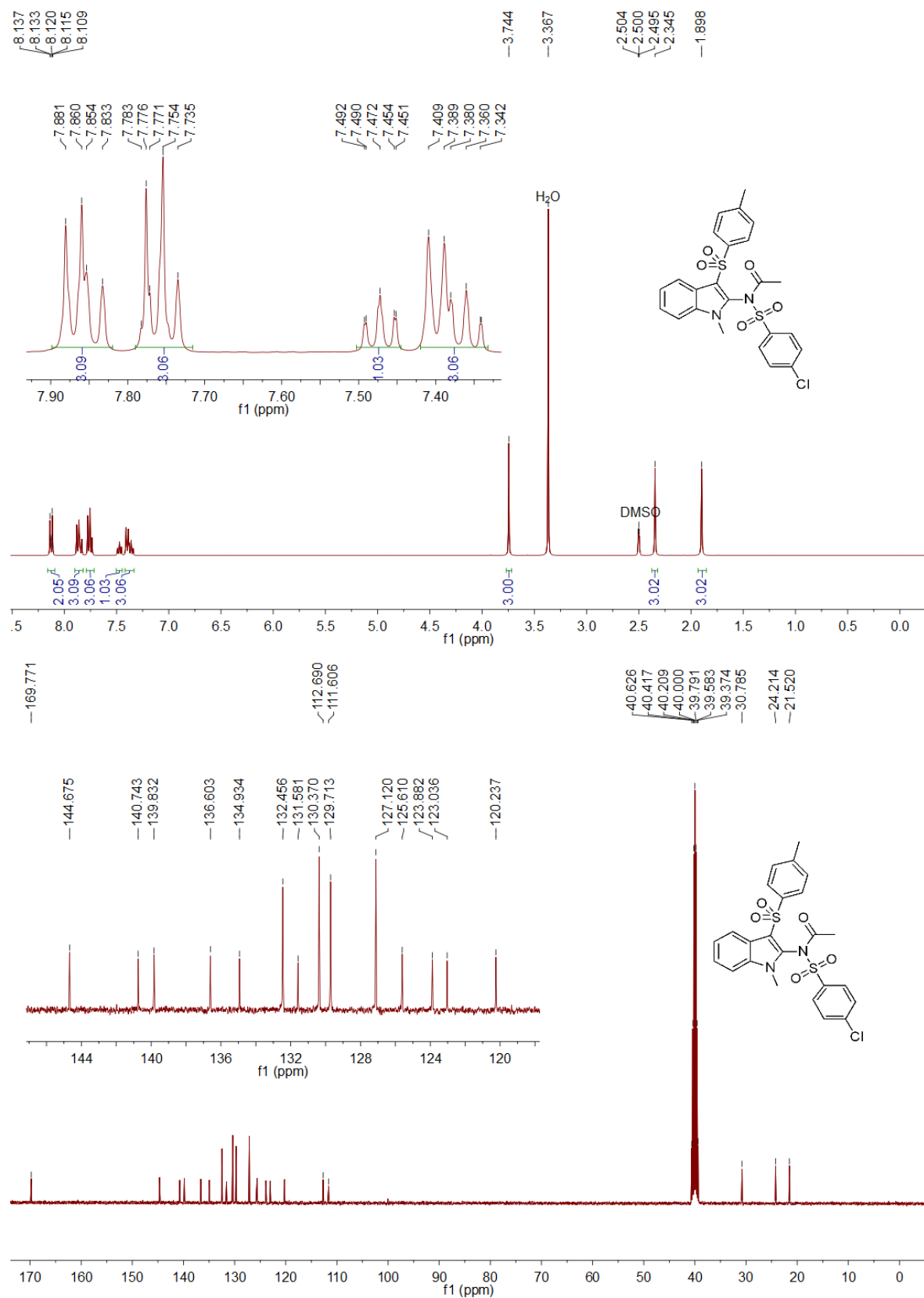
¹H and ¹³C NMR of Compound 5f

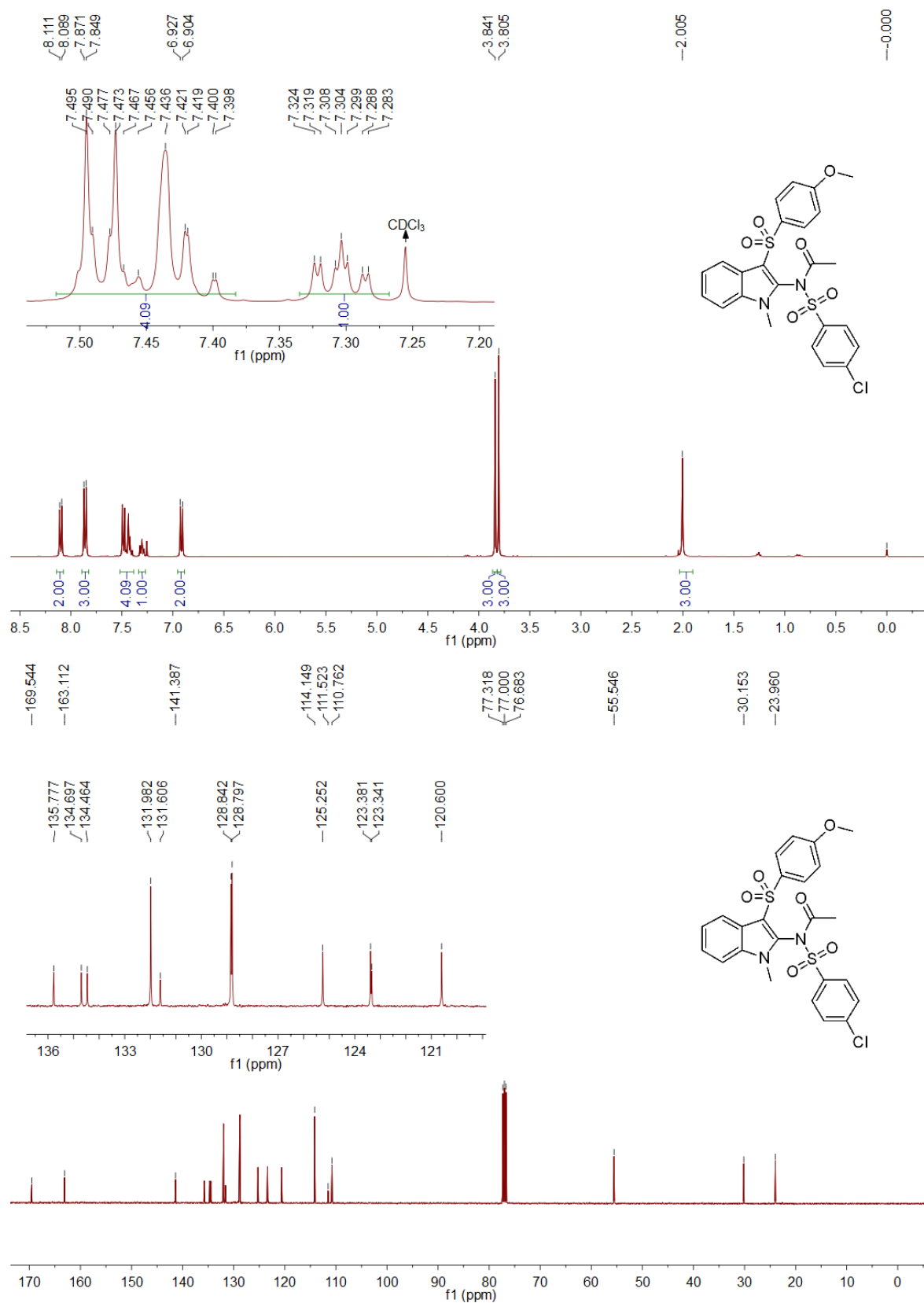


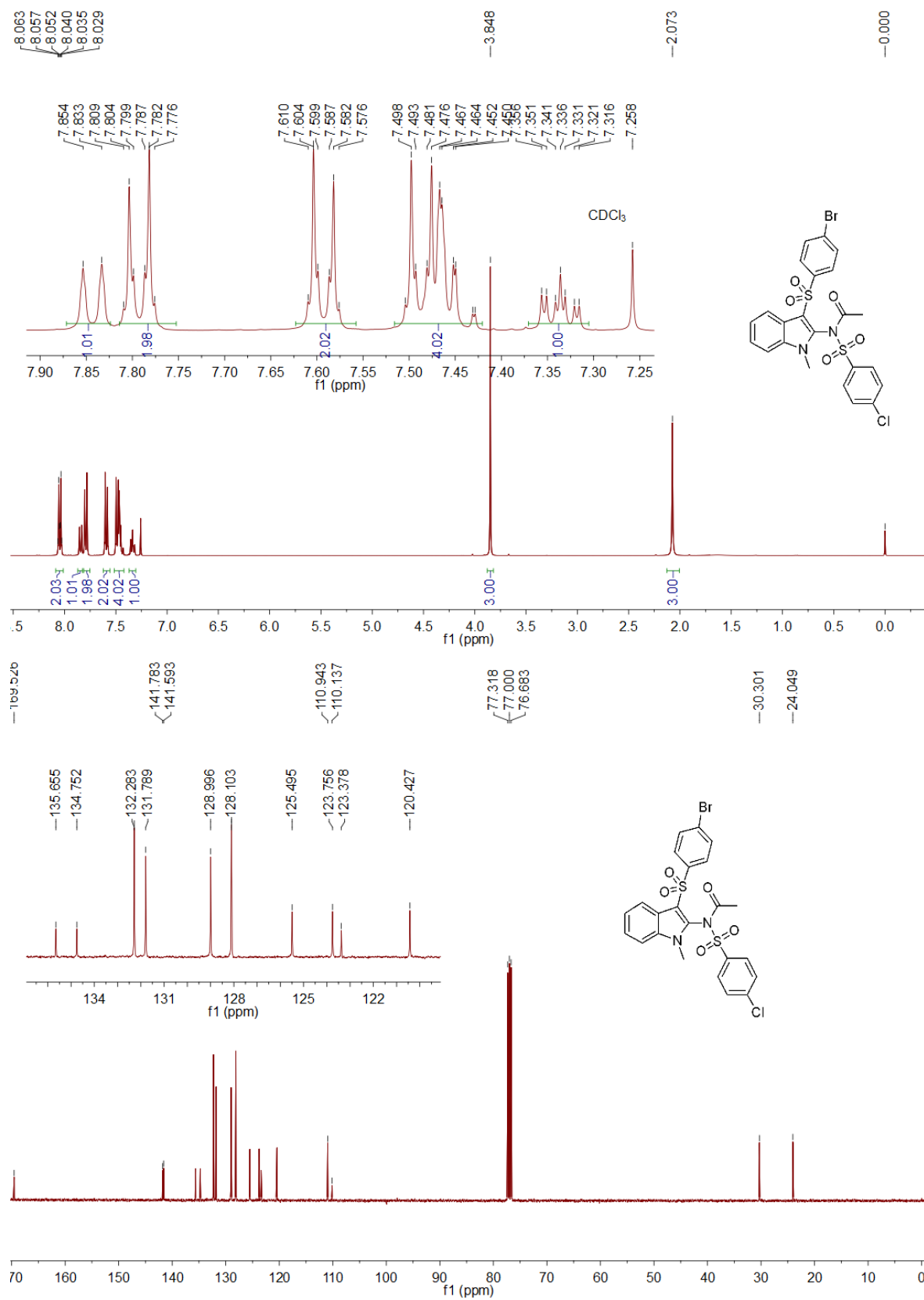
¹H and ¹³C NMR of Compound 5g



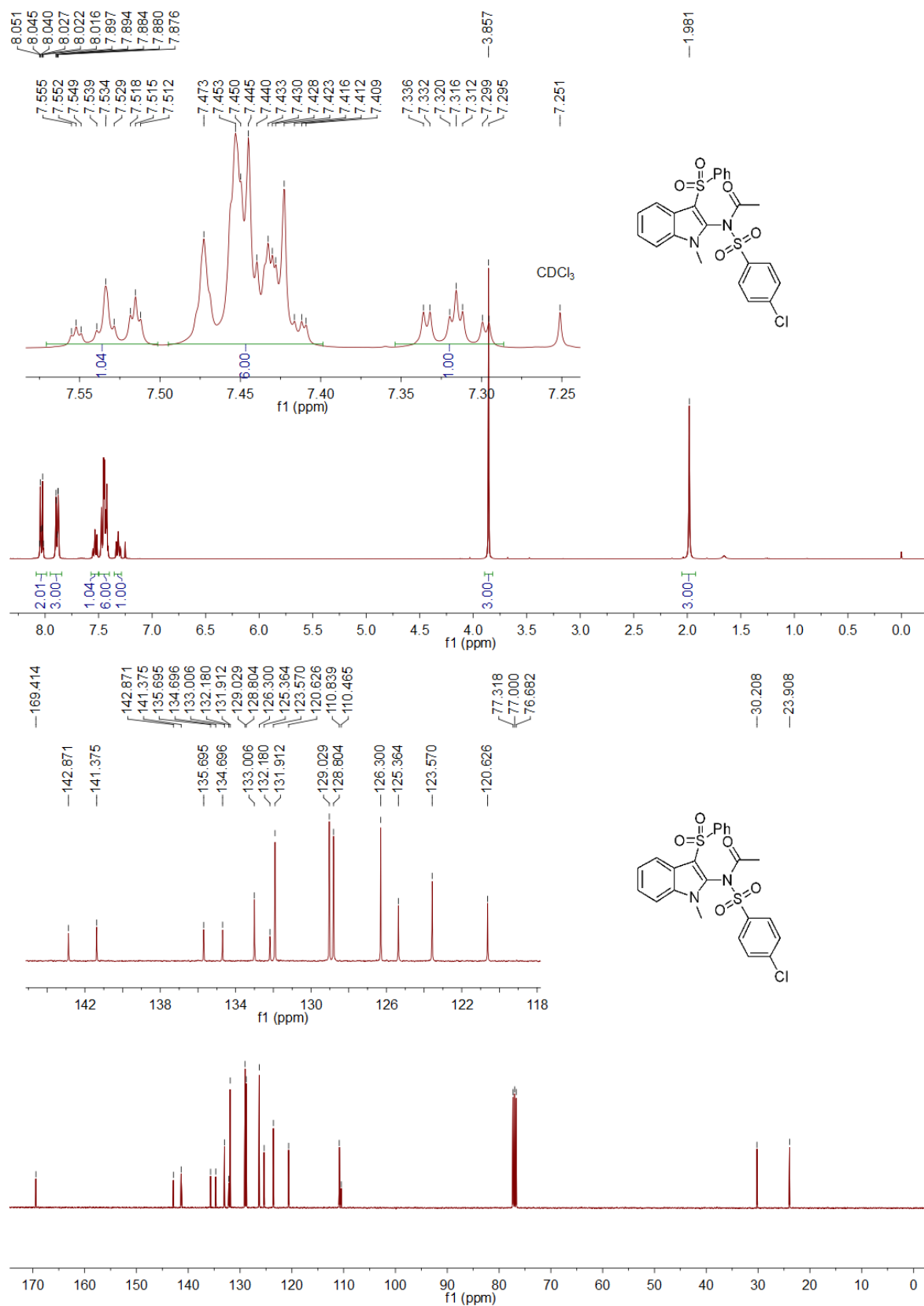
¹H and ¹³C NMR of Compound 5h



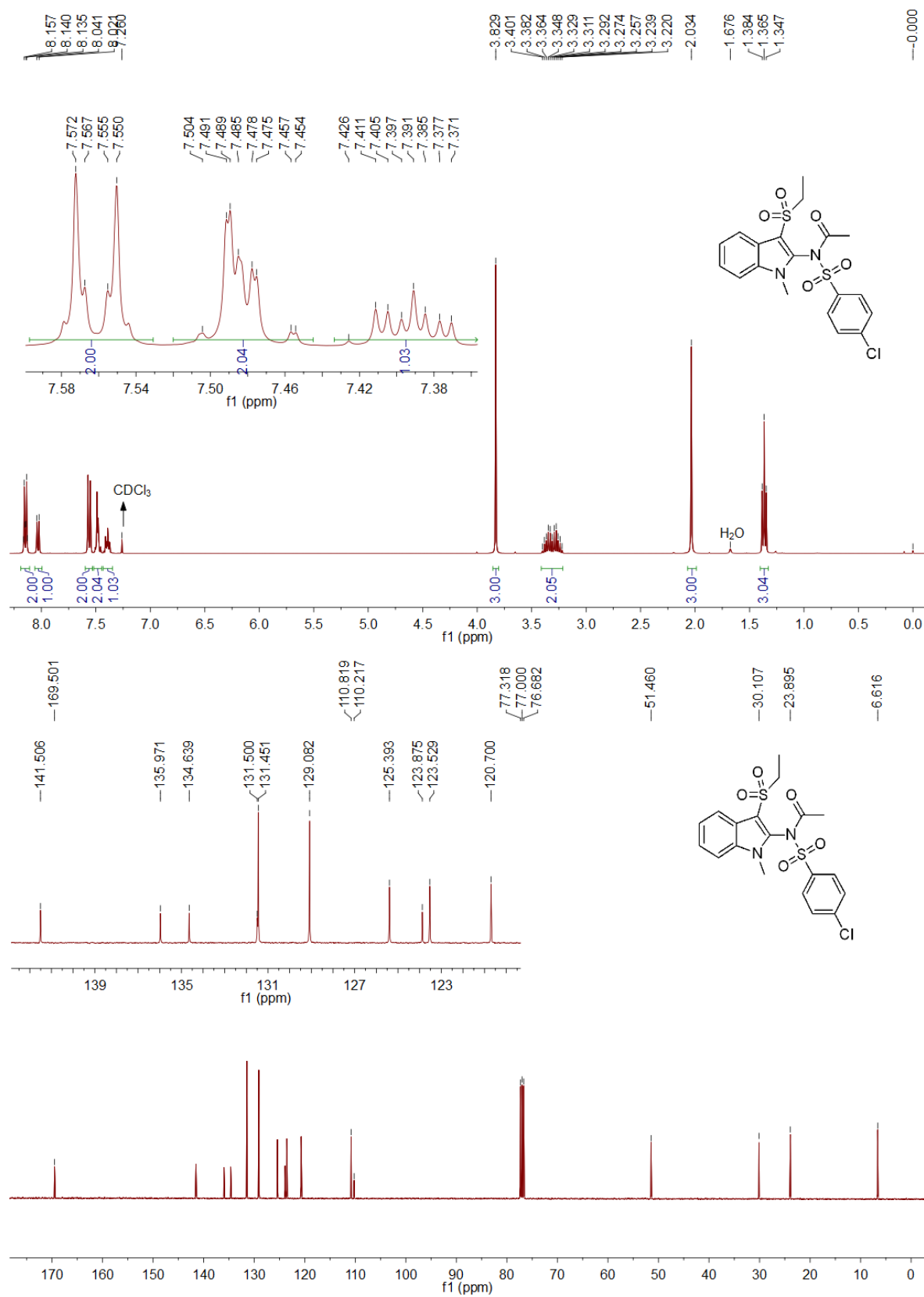




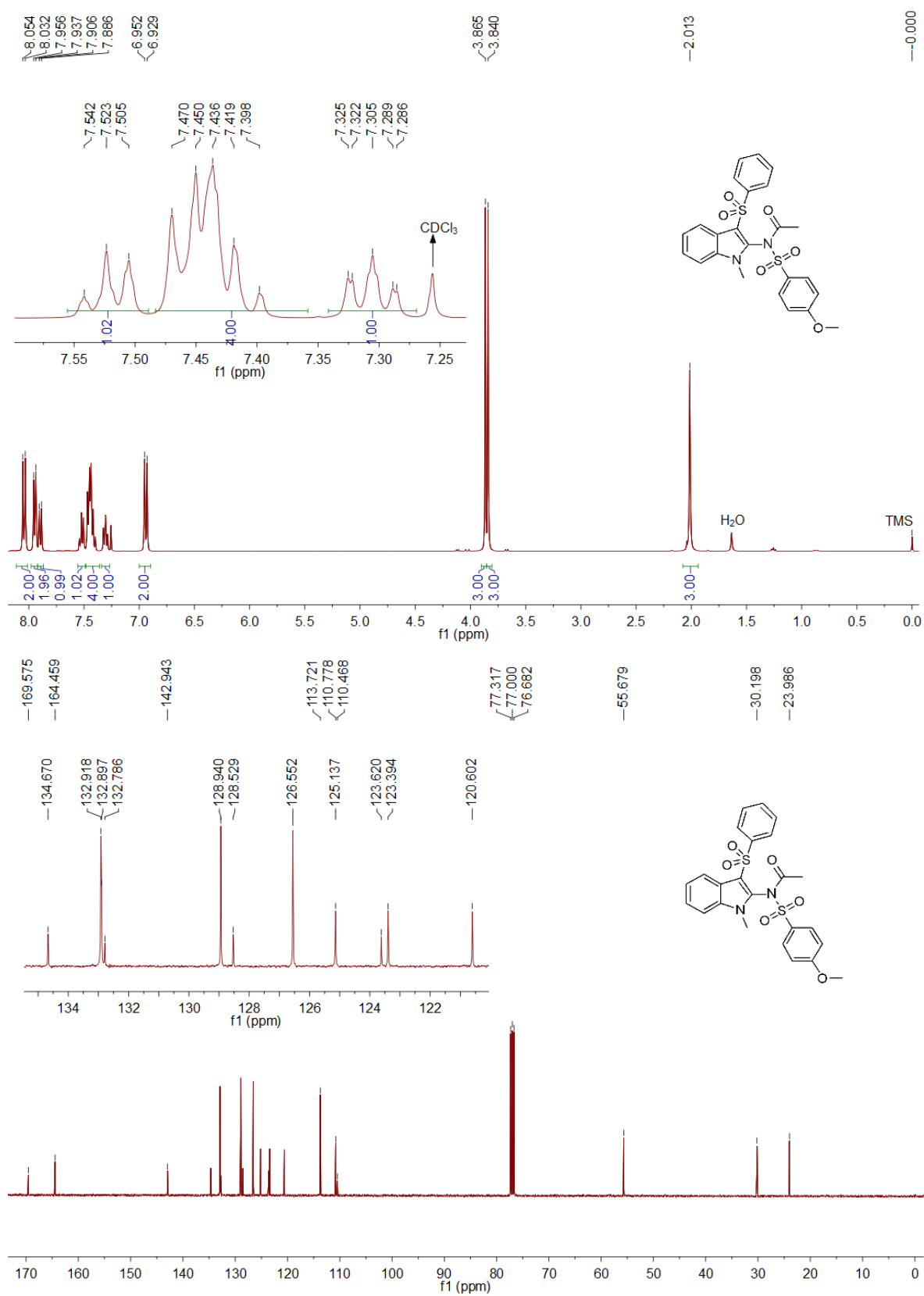
¹H and ¹³C NMR of Compound 6c



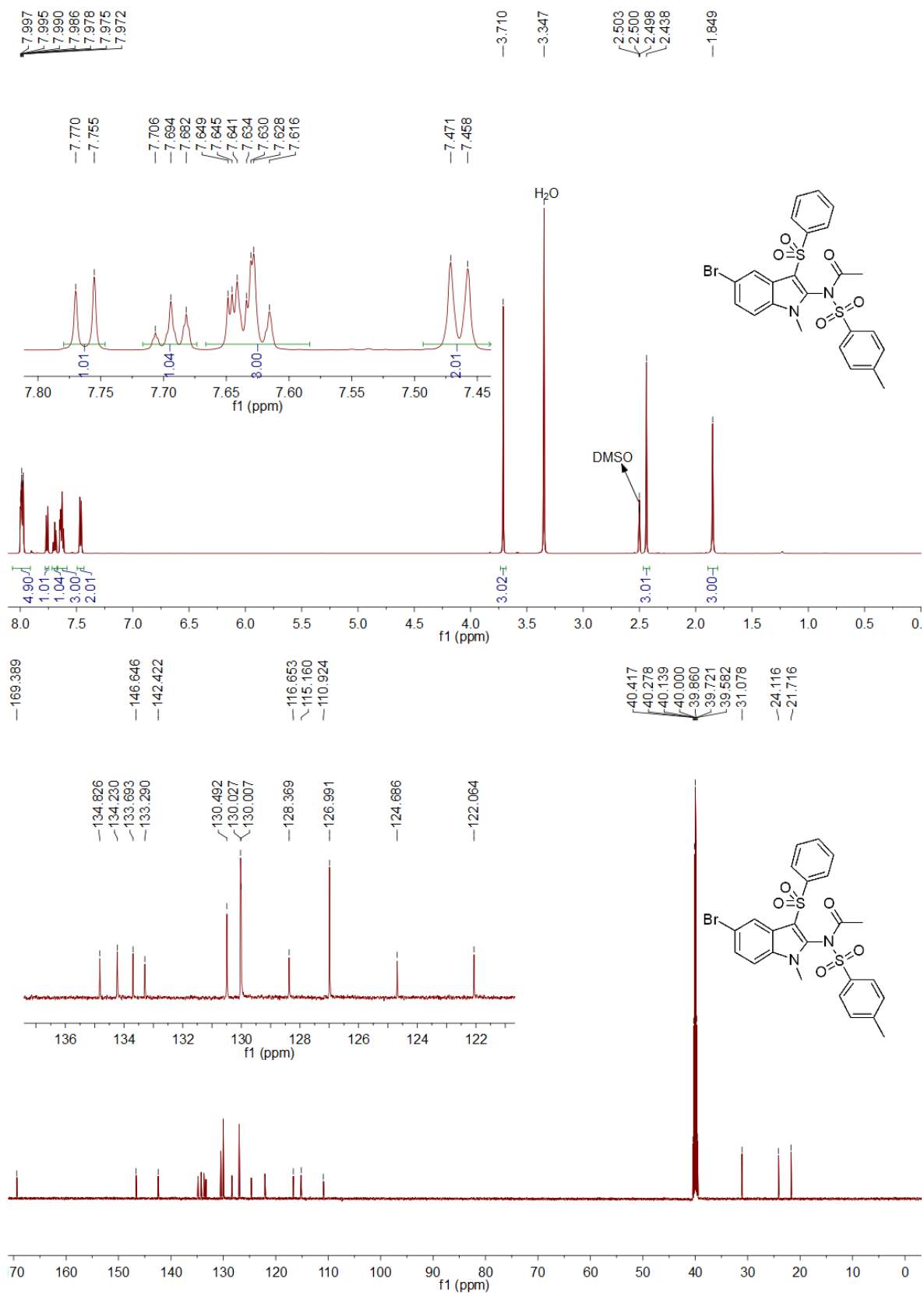
¹H and ¹³C NMR of Compound 6d



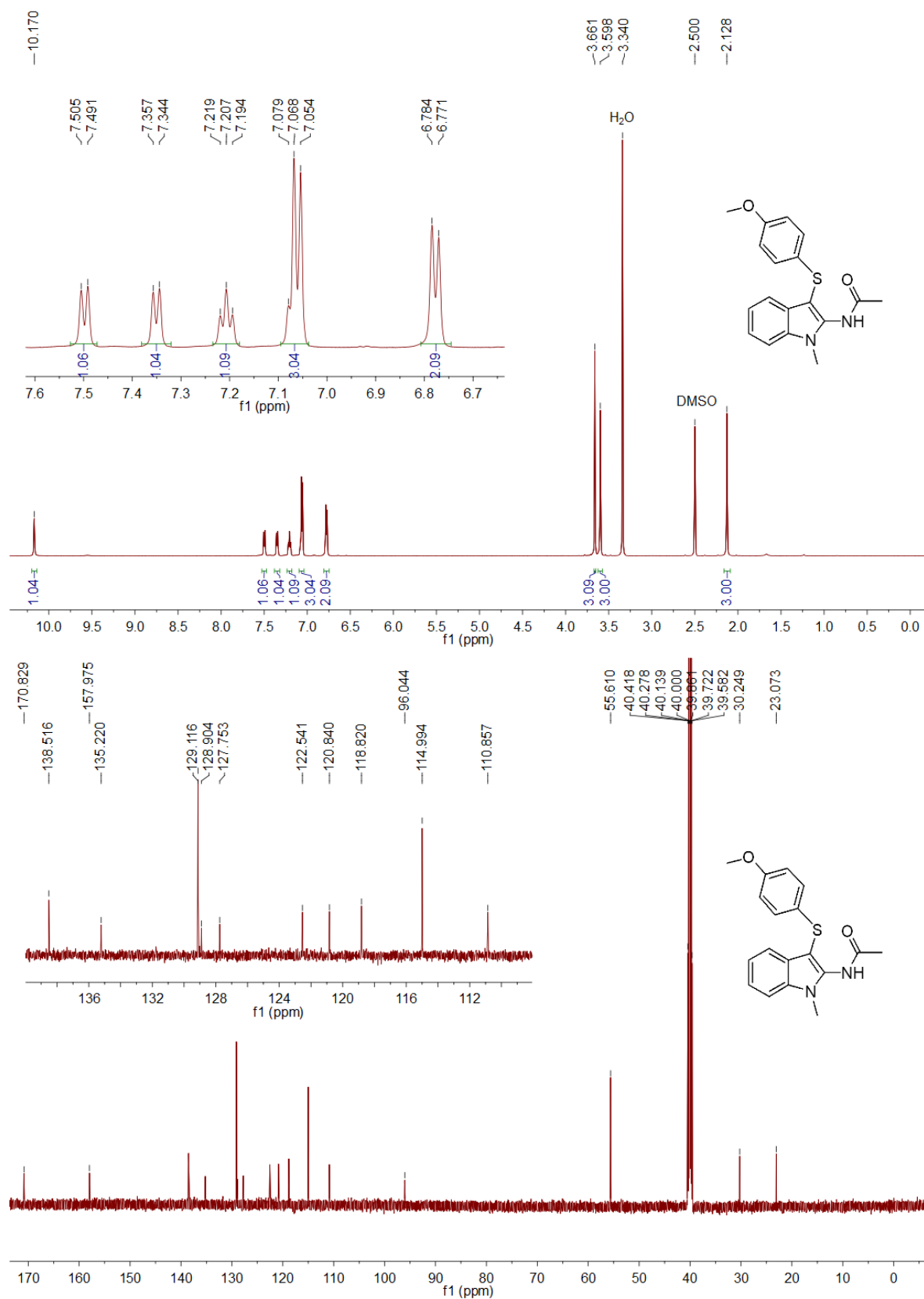
¹H and ¹³C NMR of Compound 6e



¹H and ¹³C NMR of Compound 6f



¹H and ¹³C NMR of Compound 6g



¹H and ¹³C NMR of Compound 7a

