

Supporting Information

Transition-Metal- and Oxidant-Free Directed Anodic C-H Sulfonylation of *N,N*-Disubstituted Anilines with Sulfinates

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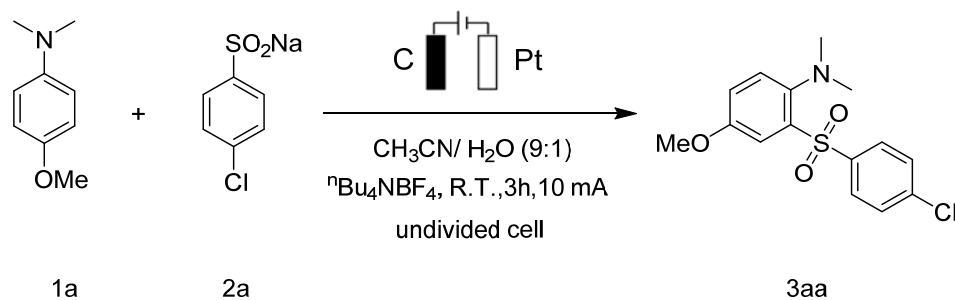
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(A) Typical experimental procedure

(a) General Procedure for the electrochemical C-H sulfonylation of 4-Methoxy-*N,N*-dimethylaniline(1a):

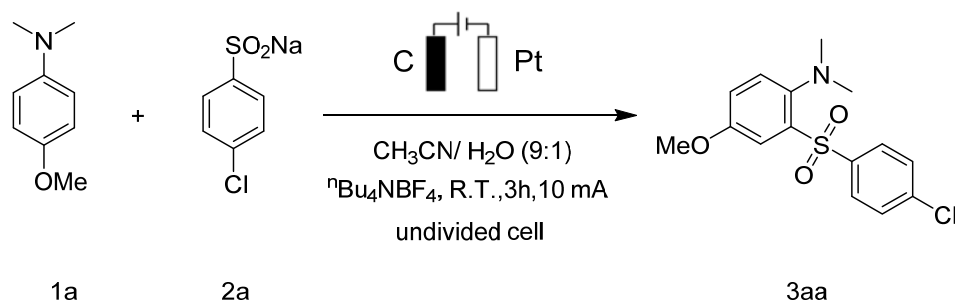
N,N-dimethylaniline(1a):



To an oven-dried undivided three-necked bottle (10mL) were added substrates **1a** aniline (0.3 mmol), Sodium sulfinate (4 equiv), *n*Bu₄NBF₄ (0.1mmol) and CH₃CN/H₂O (9 mL/1 mL), The bottle was equipped graphite rod(ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and pt plate (10 mm×10mm×1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 3h (Figure S1). and stopped until complete consumption of aniline (monitored by TLC). After the reaction was finished, diluted with ethyl acetate (10 mL), and washed with H₂O, extracted with ethyl acetate (3×5 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to afford the desired product **3aa**(88.7mg, 91%).

(b) Typical Experimental Procedure for the electrochemical C-H sulfonylation of 4-Methoxy-*N,N*-dimethylaniline(**1a**) with sodium 4-chlorobenzenesulfinate (**2a**)

up to 1 g Scale:



To an oven-dried undivided three-necked bottle (25mL) were added substrates **1a** 4-Methoxy-*N,N*-dimethylaniline (6.6 mmol), 4-chlorobenzenesulfinate (4 equiv) , $n\text{Bu}_4\text{NBF}_4$ (0.3mmol) and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (18 mL/2 mL), The bottle was equipped graphite rod(ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and pt plate (10 mm \times 10mm \times 1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 18 h, and we stopped the reaction. When we prolong reaction time, the aniline cannot be completed consumption (monitored by TLC). After the reaction was finished, diluted with ethyl acetate (20 mL), and washed with H_2O , extracted with ethyl acetate (3 \times 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10:1) to afford the desired product **3aa**(1.64g, 71%).

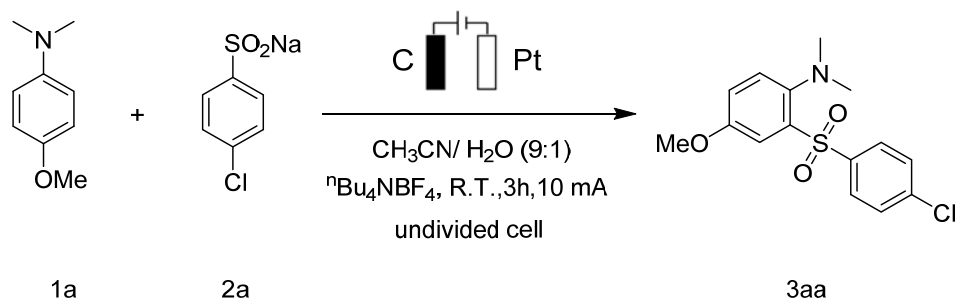


Table S1 Screening of optimal reaction conditions^a

Entry	1a	2a	Electrolyte	Solvent	I (mA)	Yield(%)
1	0.3mmol	1.5equiv	${}^n\text{Bu}_4\text{NBF}_4$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}(9:1)$	10	54
2	0.3mmol	2equiv	${}^n\text{Bu}_4\text{NBF}_4$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}(9:1)$	10	66
3	0.3mmol	3equiv	${}^n\text{Bu}_4\text{NBF}_4$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}(9:1)$	10	82
4	0.3mmol	4equiv	${}^n\text{Bu}_4\text{NBF}_4$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}(9:1)$	10	91

^a Reaction conditions: carbon rod anode, platinum plate cathode, constant current = 10 mA, **1a** (0.3 mmol), ${}^n\text{Bu}_4\text{NBF}_4$ (0.1 mmol), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9.0 mL/1.0 mL), room temperature under air atmosphere for 3 h.

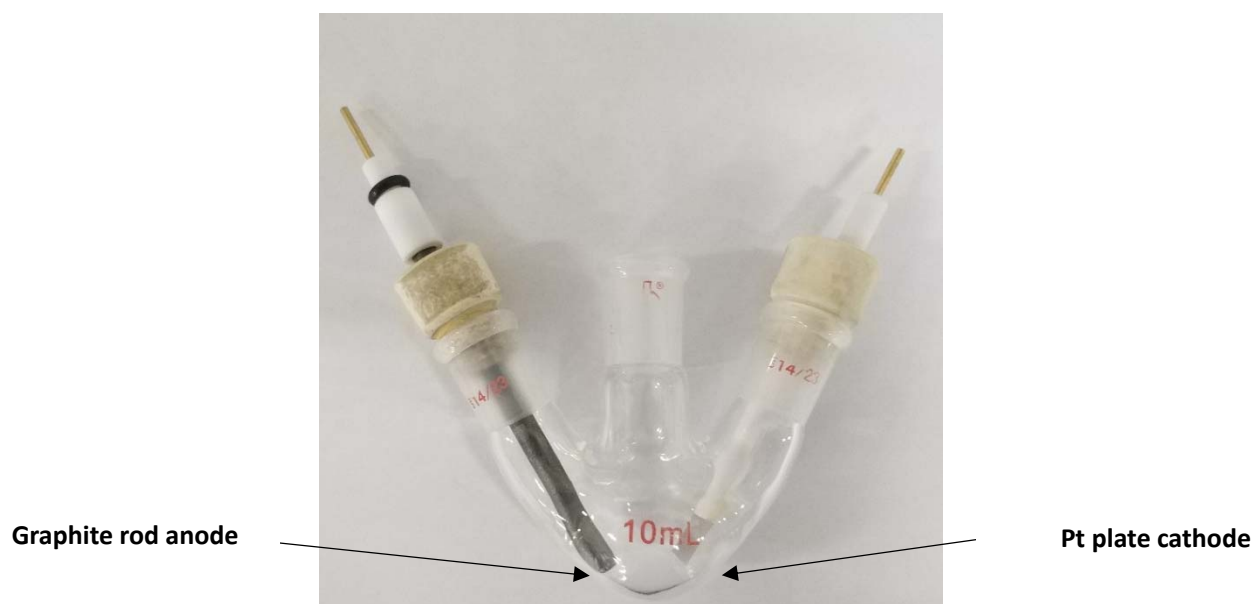


Figure S1. Undivided cell for current controlled electrolysis

Procedure for cyclic voltammetry (CV): Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum plate. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 10 mL solvent containing 0.1 M ${}^n\text{Bu}_4\text{NBF}_4$ were poured into the electrochemical cell in cyclic voltammetry experiments. The CV of all substrates were measured at the concentration of 0.01M. The scan rate was 0.05 V/s, ranging from 0 V to 3.0 V.

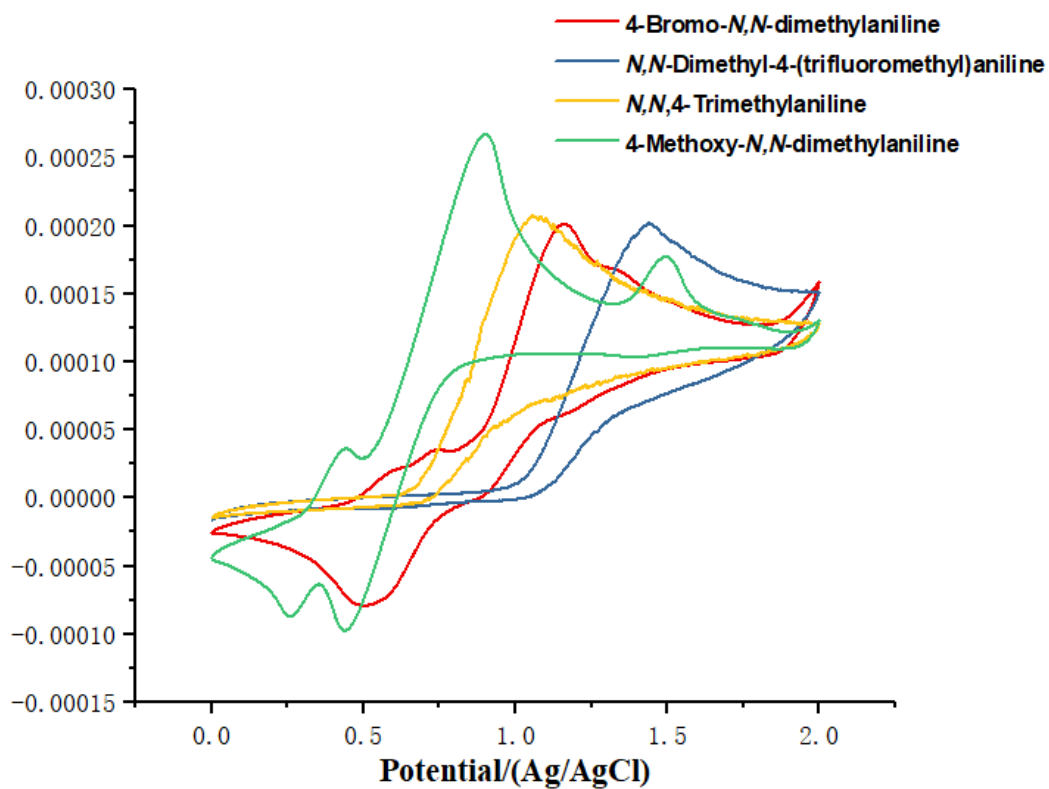


Figure S2. Study of the aniline oxidation potential during electrolysis

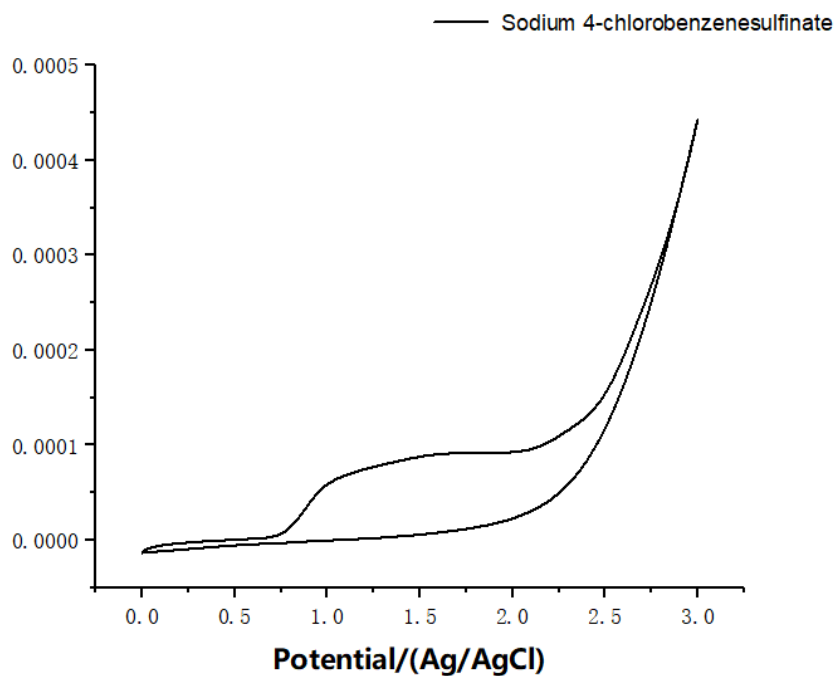


Figure S3. Study of the sodium sulfinate oxidation potential during electrolysis

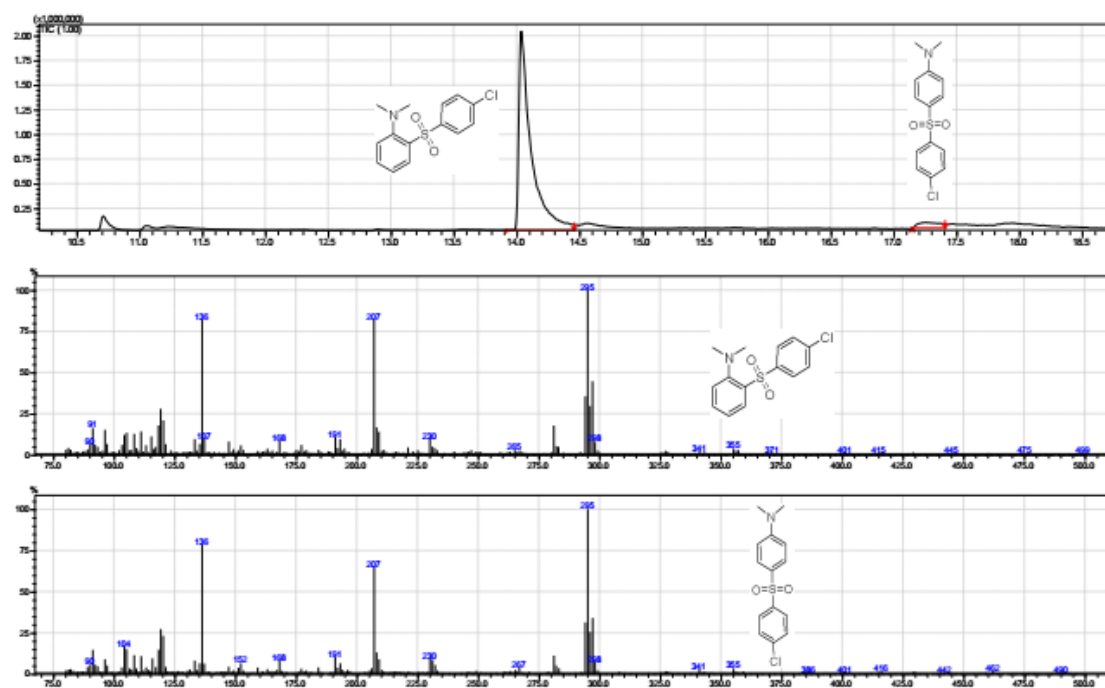


Figure S4. GC-MS of 3ja

Table S2 GC-MS Analytical data of 3ja

Peak#	Ret.Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H
1	14.033	13.965	14.470	TIC	13713109	96.97	2015161	98.17	6.80
2	17.253	17.165	17.420	TIC	427775	3.03	37549	1.83	11.39

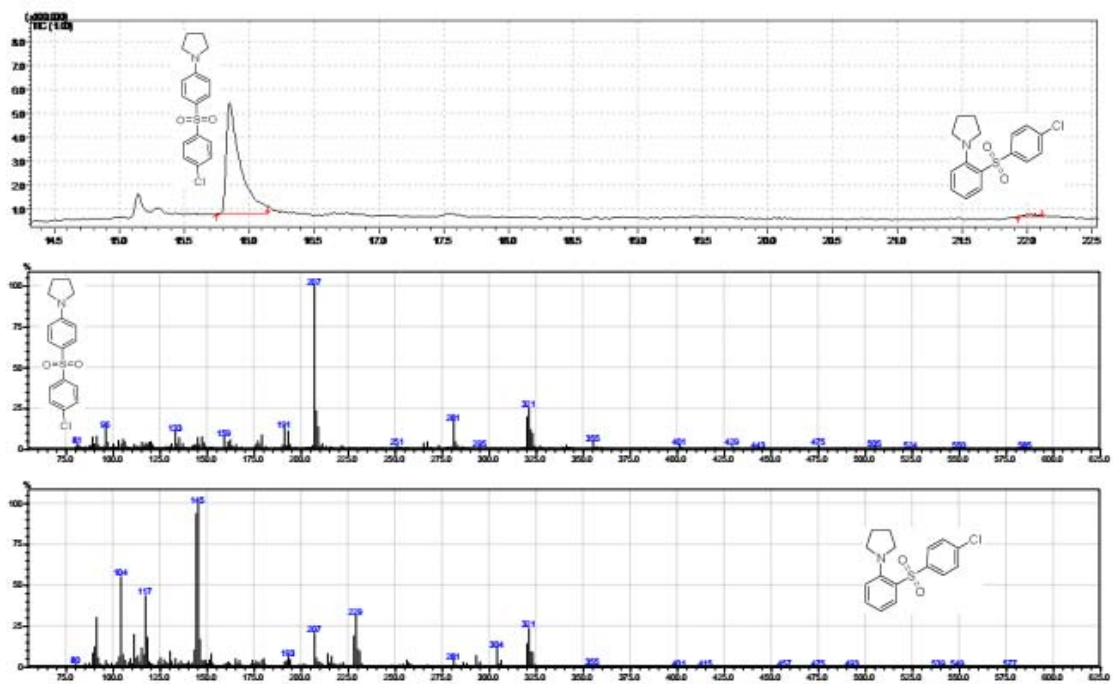


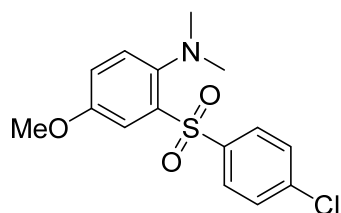
Figure S5. GC-MS of 3ka

Table S3 GC-MS Analytical data of 3ka

Peak#	Ret.Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H
1	15.849	15.760	16.220	TIC	3724040	96.48	468689	96.48	7.95
2	22.060	21.905	22.145	TIC	135767	3.52	17115	3.52	7.93

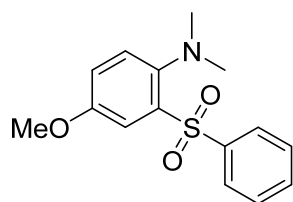
(B) Analytical data ^{a,b}

2-((4-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline(3aa):



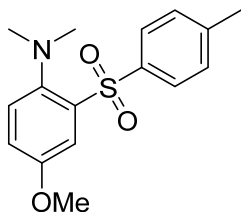
88.7mg, 91% yield; White solid; mp 137.8-139.1 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.85-7.83(m, 2H), 7.73 (d, *J* = 5.0 Hz, 1H), 7.42 (m, 2H), 7.22 (d, *J* = 10 Hz, 1H), 7.12-7.10 (m, 1H), 3.87 (s, 3H), 2.33 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 156.8, 146.1, 140.7, 138.8, 138.5, 129.6, 128.2, 125.7, 121.5, 113.0, 55.8, 45.3; IR (neat, cm⁻¹): 3071, 2948, 2836, 2796, 1902, 1573, 1493, 1291, 1265, 1152, 1082, 868; LRMS (EI, 70eV) *m/z* (%):327 (M⁺+2, 23),325 (M⁺,69), 310 (28), 148 (100), 134 (59); HRMS *m/z* (ESI) calcd for C₁₅H₁₆³⁵ClNO₃S ([M+H]⁺) 326.0612, found 326.0617.

4-Methoxy-*N,N*-dimethyl-2-(phenylsulfonyl)aniline (3ab):



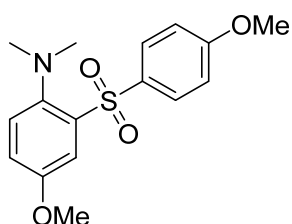
62.0mg, 71% yield; White solid; mp 135.7-137.1 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.89 (d, *J* = 10.0 Hz, 2H), 7.77 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 10.0 Hz, 1H), 7.11-7.09 (m, 1H), 3.88 (s, 3H), 2.30 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 156.7, 146.2, 142.2, 139.0, 132.3, 128.0, 127.9, 125.7, 121.4, 112.9, 55.8, 45.2; IR (neat, cm⁻¹): 3089, 2944, 2854, 2784, 1603, 1496, 1296, 1147, 1045; LRMS (EI, 70eV) *m/z* (%): 291 (M⁺, 82), 226 (28), 148 (100), 134 (67); HRMS *m/z* (ESI) calcd for C₁₅H₁₇NO₃S ([M+H]⁺) 292.1002, found: 292.1013.

4-Methoxy-*N,N*-dimethyl-2-tosylaniline (3ac):



58.6mg, 64% yield; White solid; mp 128.1-129.5 °C (uncorrected); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.78 (d, $J = 10.0$ Hz, 2H), 7.75 (d, $J = 5.0$ Hz, 1H), 7.24 (d, $J = 10.0$ Hz, 2H), 7.20 (d, $J = 10.0$ Hz, 1H), 7.10-7.07 (m, 1H), 3.87 (s, 3H), 2.39 (s, 3H), 2.32 (s, 6H); $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ : 156.7, 146.3, 143.1, 139.3, 139.2, 128.6, 128.2, 125.6, 121.2, 112.9, 55.8, 45.3, 21.5; IR (neat, cm^{-1}): 2947, 2824, 2784, 1594, 1495, 1298, 1264, 1147, 1091, 869; LRMS (EI, 70eV) m/z (%): 305 (M^+ , 84), 240 (39), 148 (100), 134 (66); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 306.1158, found: 306.1162.

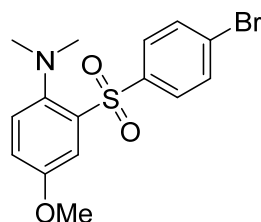
4-Methoxy-2-((4-methoxyphenyl)sulfonyl)-*N,N*-dimethylaniline (3ad):



62.6mg, 65% yield; White solid; mp 132.5-133.5 °C (uncorrected); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.86 (d, $J = 10.0$ Hz, 2H), 7.74 (d, $J = 5.0$ Hz, 1H), 7.21 (d, $J = 10.0$ Hz, 1H), 7.10-7.07 (m, 1H), 6.91 (d, $J = 10.0$ Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 2.35 (s, 6H); $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ : 162.8, 156.6, 146.1, 139.4, 133.6, 130.5, 125.6, 120.9, 113.1, 112.8, 55.8, 55.5, 45.5; IR (neat, cm^{-1}): 3099, 2943, 2833, 2786, 1594, 1487, 1291, 1265, 1145, 1092, 868; LRMS (EI, 70eV) m/z (%): 321 (M^+ , 58), 256 (31), 148 (76), 121 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 322.1108, found: 322.1121.

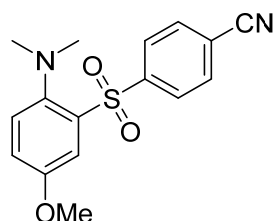
2-((4-Bromophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ae):

90.8mg, 82% yield; White solid; mp 158.6-160.0 °C (uncorrected); $^1\text{H NMR}$ (500 MHz,



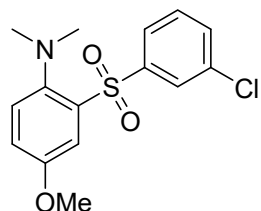
CDCl₃) δ : 7.77 (d, J = 10.0 Hz, 2H), 7.73 (s, 1H), 7.59 (d, J = 10.0 Hz, 2H), 7.23-7.21 (m, 1H), 7.13-7.10 (m, 1H), 3.87 (s, 3H), 2.33 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ : 156.8, 146.1, 141.2, 138.5, 131.2, 129.7, 127.4, 125.7, 121.6, 113.0, 55.9, 45.3; IR (neat, cm⁻¹): 2946, 2838, 2796, 1909, 1572, 1491, 1291, 1263, 1149, 1088, 868; LRMS (EI, 70eV) m/z (%): 371 (M⁺+2, 44), 369 (M⁺, 45), 354 (23), 148 (100), 134 (60); HRMS m/z (ESI) calcd for C₁₅H₁₆⁷⁹BrNO₃S ([M+H]⁺) 370.0107, found: 370.0121.

4-((2-(Dimethylamino)-5-methoxyphenyl)sulfonyl)benzonitrile (3af):



71.1mg, 75% yield; Yellow solid; mp 156.5-157.9 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ : 7.99 (d, J = 10.0 Hz, 2H), 7.75 (d, J = 5.0 Hz, 2H), 7.32 (s, 1H), 7.23 (d, J = 10.0 Hz, 1H), 7.16-7.14 (m, 1H), 3.89 (s, 3H), 2.29 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ : 157.0, 146.6, 146.0, 137.8, 131.8, 128.5, 125.8, 122.0, 117.5, 115.8, 113.1, 55.9, 45.1; IR (neat, cm⁻¹): 3091, 2967, 2864, 2790, 2234, 1606, 1497, 1304, 1226, 1148, 1090; LRMS (EI, 70eV) m/z (%): 316 (M⁺, 87), 251 (27), 148 (100), 134 (59); HRMS m/z (ESI) calcd for C₁₆H₁₆N₂O₃S ([M+H]⁺) 317.0954, found: 317.0963.

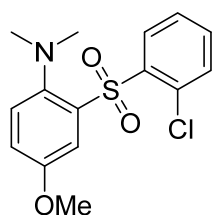
2-((3-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ag):



60.5mg, 62% yield; Yellow solid; mp 136.2-138.0 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ : 7.92 (t, J = 2.5 Hz, 1H), 7.77 (d, J = 10.0 Hz, 1H), 7.73 (d, J = 5.0 Hz, 1H), 7.51-7.49 (m, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 10.0 Hz, 1H), 7.14-7.11 (m, 1H), 3.88 (s, 3H), 2.34 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ : 156.9, 146.2, 143.8, 138.4,

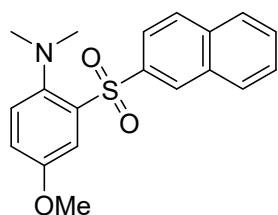
134.1, 132.5, 129.3, 128.4, 126.2, 125.8, 121.7, 113.0, 55.9, 45.3; IR (neat, cm^{-1}): 3087, 2935, 2854, 2824, 1577, 1496, 1292, 1150, 1043, 867, 795; LRMS (EI, 70eV) m/z (%): 327 (M^{+2} , 26), 325 (M^{+} , 78), 310 (31), 148 (100), 134 (58); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}^{35}\text{ClNO}_3\text{S}$ ($[M+H]^+$) 326.0612, found: 326.0626.

2-((2-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ah):



70.2mg, 72% yield; Yellow solid; mp 130.4-131.4 $^{\circ}\text{C}$ (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.32-8.30 (m, 1H), 7.76 (d, $J = 5.0$ Hz, 1H), 7.47-7.45 (m, 2H), 7.36-7.34 (m, 1H), 7.22 (d, $J = 10.0$ Hz, 1H), 7.14-7.12 (m, 1H); 3.88 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.9, 145.9, 139.9, 138.5, 133.3, 131.4, 131.4, 130.9, 126.3, 125.5, 121.7, 113.5, 55.9, 44.8; IR (neat, cm^{-1}): 2976, 2856, 2824, 2783, 1491, 1453, 1305, 1147, 1032, 869, 763; LRMS (EI, 70eV) m/z (%): 327 (M^{+2} , 24), 325 (M^{+} , 71), 310 (16), 148 (100), 134 (62); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}^{35}\text{ClNO}_3\text{S}$ ($[M+H]^+$) 326.0612, found: 326.0623.

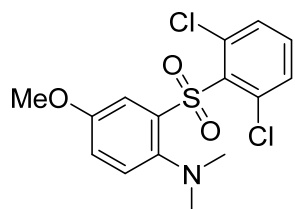
4-Methoxy-*N,N*-dimethyl-2-(naphthalen-2-ylsulfonyl)aniline (3ai):



63.4mg, 62% yield; Yellow solid; mp 136.6-137.6 $^{\circ}\text{C}$ (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.50 (s, 1H), 7.93 (d, $J = 10.0$ Hz, 1H), 7.90-7.87 (m, 3H), 7.83 (d, $J = 5.0$ Hz, 1H), 7.61-7.54 (m, 2H), 7.18 (d, $J = 5.0$ Hz, 1H), 7.10-7.08 (m, 1H), 3.89 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.8, 146.2, 139.2, 139.1, 134.7, 131.9, 129.4, 129.1, 128.5, 127.8, 127.8, 127.1, 125.7, 123.6, 121.4, 113.0, 55.9, 45.3; IR (neat, cm^{-1}): 3069, 2936, 2857, 2786, 1492, 1439, 1220, 1148, 1076, 755; LRMS (EI, 70eV) m/z (%): 341 (M^{+} , 100), 262 (82), 148 (86), 134 (69); HRMS m/z (ESI) calcd

for C₁₉H₁₉NO₃S ([M+H]⁺) 342.1158, found: 342.1171.

2-((2,6-Dichlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3aj):



67.9mg, 63% yield; Yellow solid; mp 149.2-151.1 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.66 (d, *J* = 5.0

Hz, 1H), 7.38 (d, *J* = 10.0 Hz, 2H), 7.29-7.27 (m, 2H), 7.14-

7.12 (m 1H), 3.88 (s, 3H), 2.28 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 157.0, 145.7,

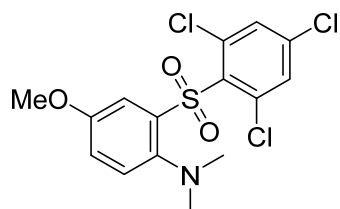
140.4, 137.5, 135.5, 131.9, 131.0, 125.7, 121.8, 112.6, 56.0, 45.3; IR (neat, cm⁻¹):

3077, 2950, 2829, 2789, 1492, 1426, 1314, 1155, 1034, 835, 781; LRMS (EI, 70eV)

m/z (%): 363 (M⁺+4, 28), 359 (M⁺, 84), 183 (30), 148 (94), 121 (100); HRMS *m/z*

(ESI) calcd for C₁₅H₁₅³⁵Cl₂NO₃S ([M+H]⁺) 360.0222, found: 360.0233.

4-Methoxy-*N,N*-dimethyl-2-((2,4,6-trichlorophenyl)sulfonyl)aniline (3ak):



78.8mg, 67% yield; Yellow solid; mp 153.6-154.4 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.64 (d, *J* =

5.0 Hz, 1H), 7.41 (s, 2H), 7.28 (d, *J* = 10.0 Hz, 1H), 7.16-

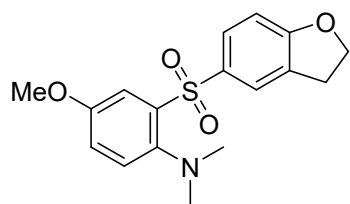
7.13 (m, 1H), 3.87 (s, 3H), 2.32 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 157.1, 145.6,

139.9, 137.3, 136.3, 136.2, 130.6, 125.7, 121.9, 112.7, 55.9, 45.4; IR (neat, cm⁻¹):

3091, 2942, 2825, 2783, 1537, 1498, 1363, 1318, 1159, 1032, 831, 799; HRMS *m/z*

(ESI) calcd for C₁₅H₁₄³⁵Cl₃NO₃S ([M+H]⁺) 393.9833, found: 393.9842.

2-((2,3-Dihydrobenzofuran-5-yl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3al):



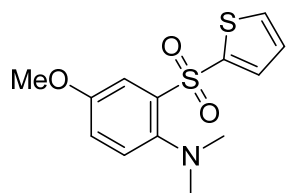
60.9mg, 61% yield; Yellow solid; mp 131.2-133.5 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.76-7.73

(m, 3H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.09-7.04 (m, 1H),

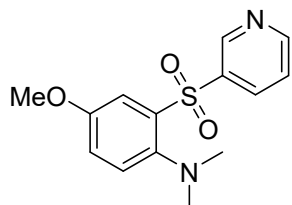
6.79 (d, $J = 10.0$ Hz, 1H), 4.64 (t, $J = 7.5$ Hz, 2H), 3.86 (s, 3H), 3.22 (t, $J = 10.0$ Hz, 2H), 2.38 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 163.7, 156.6, 146.2, 139.6, 133.6, 130.2, 127.0, 125.6, 125.6, 120.9, 112.9, 108.5, 55.8, 45.6, 28.9; IR (neat, cm^{-1}): 2959, 2831, 2783, 1601, 1483, 1291, 1266, 1135, 1164, 716; LRMS (EI, 70eV) m/z (%): 333 (M^+ , 82), 268 (54), 148 (100), 121 (88); IR (KBr, cm^{-1}): 2959, 2831, HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 334.1008, found: 334.1012.

4-Methoxy-*N,N*-dimethyl-2-(thiophen-2-ylsulfonyl)aniline (3am):



66.8mg, 75% yield; Yellow solid; mp 122.1-122.4 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 7.73-7.72 (m, 1H), 7.70 (d, $J = 3.0$ Hz, 1H), 7.61-7.60 (m, 1H), 7.28 (d, $J = 10.0$ Hz, 1H), 7.12-7.09 (m, 1H), 7.04-7.02 (m, 1H), 3.85 (s, 3H), 2.54 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.6, 146.7, 143.0, 139.0, 133.8, 133.2, 126.4, 125.4, 121.2, 112.9, 55.8, 46.0; IR (neat, cm^{-1}): 3101, 2939, 2833, 2791, 1601, 1497, 1399, 1308, 1146, 1033, 857, 740; LRMS (EI, 70eV) m/z (%): 297 (M^+ , 100), 218 (58), 148 (90), 121 (97); HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}_2$ ($[\text{M}+\text{H}]^+$) 298.0566, found: 298.0572.

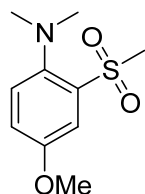
4-Methoxy-*N,N*-dimethyl-2-(pyridin-3-ylsulfonyl)aniline(3an):



72.7mg, 83% yield; Yellow solid; mp 80.9-90.0 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 9.05 (s, 1H), 8.70-8.69 (m, 1H), 8.14-8.12 (m, 1H), 7.69 (d, $J = 3.0$ Hz, 1H), 7.37-7.34 (m, 1H), 7.18 (d, $J = 8.5$ Hz, 1H), 7.10-7.07 (m, 1H), 3.83 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.9, 152.7, 149.4, 145.9, 138.4, 138.1, 135.8,

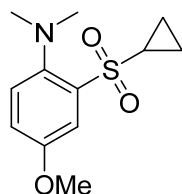
125.7, 122.6, 121.8, 112.9, 55.8, 45.3; IR (neat, cm^{-1}): 2980, 1674, 1484, 1296, 1269, 1148, 1126, 1024, 953, 752; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 293.0954, found: 293.0959.

4-Methoxy-*N,N*-dimethyl-2-(methylsulfonyl)aniline(3ao):



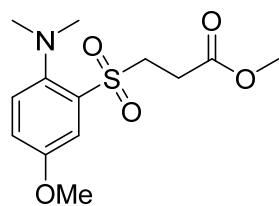
35.0mg, 51% yield; Yellow solid; mp 75.1-76.5 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 7.50 (d, $J = 5.0$ Hz, 1H), 7.40 (d, $J = 10.0$ Hz, 1H), 7.15-7.13 (m, 1H), 3.84 (s, 3H), 3.35 (s, 3H), 2.73 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.5, 146.4, 137.5, 124.9, 120.9, 112.7, 55.7, 46.2, 42.5; IR (neat, cm^{-1}): 3032, 2958, 2824, 2779, 1603, 1488, 1296, 1145, 1023, 825, 769, 527; LRMS (EI, 70eV) m/z (%): 213 (M- CH_3 , 49), 198 (44), 132 (100), 105 (74); HRMS m/z (ESI) calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 230.0845, found: 230.0862.

2-(Cyclopropylsulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ap):



50.5mg, 66% yield; White solid; mp 131.4-131.9 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 7.43-7.30 (m, 2H), 7.11 (d, $J = 10.0$ Hz, 1H), 3.83 (s, 3H), 3.44-3.39 (m, 1H), 2.74 (s, 6H), 1.27-1.25 (m, 2H), 0.97-0.95 (m, 2H); ^{13}C NMR (125MHz, CDCl_3) δ : 156.7, 146.6, 138.2, 125.2, 120.6, 112.7, 55.8, 46.3, 31.3, 5.4; IR (neat, cm^{-1}): 3088, 2947, 2830, 2791, 1603, 1489, 1306, 1286, 1133, 1034, 883; LRMS (EI, 70eV) m/z (%): 255 (M^+ , 69), 240 (37), 148 (100), 134 (55); HRMS m/z (ESI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 256.1002, found: 256.1020.

Methyl 3-((2-(dimethylamino)-5-methoxyphenyl)sulfonyl)propanoate (3aq):



44.2mg, 49% yield; Yellow liquid; ^1H NMR (500 MHz, CDCl_3)

δ : 7.51 (d, $J = 3.0$ Hz, 1H), 7.38 (d, $J = 10.0$ Hz, 1H), 7.16-7.14

(m, 1H), 3.90 (t, $J = 7.5$ Hz, 2H), 3.84 (s, 3H), 3.65 (s, 3H), 2.72

(s, 6H), 2.69 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (125MHz, CDCl_3) δ : 170.7, 156.7, 146.8,

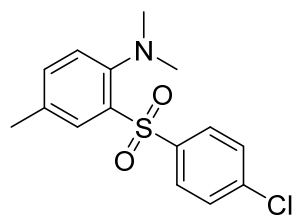
135.4, 124.8, 121.3, 113.8, 55.8, 52.1, 49.2, 46.3, 27.7; IR (neat, cm^{-1}): 3310, 2963,

2858, 1610, 1497, 1301, 1243, 1136, 833; LRMS (EI, 70eV) m/z (%): 301 (M^+ , 100),

242 (39), 148 (91), 120 (58); HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$)

302.1057, found: 302.1062.

2-((4-Chlorophenyl)sulfonyl)-N,N,4-trimethylaniline(3ba):



53.8mg, 58% yield; Yellow solid; mp 125.1-126.5 $^{\circ}\text{C}$

(uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.03 (d, $J = 5.0$

Hz, 1H), 7.84-7.82 (m, 2H), 7.42-7.40 (m, 2H), 7.39-7.37 (m,

1H), 7.17 (d, $J = 10$ Hz, 1H), 2.41 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ :

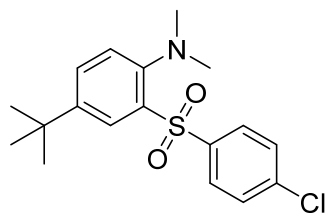
151.0, 140.9, 138.8, 137.1, 135.6, 135.5, 129.7, 129.6, 128.2, 124.3, 45.3, 20.9; IR

(neat, cm^{-1}): 2950, 2866, 2839, 1911, 1573, 1490, 1304, 1265, 1149, 825; LRMS (EI,

70eV) m/z (%): 311 (M^++2 , 12), 309 (M^+ , 37), 244 (36), 132 (100), 105 (75); HRMS

m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}^{35}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 310.0663, found: 310.0672.

4-(Tert-butyl)-2-((4-chlorophenyl)sulfonyl)-N,N-dimethylaniline (3ca):



42.1mg, 40% yield; White solid; mp 126.1-127.2 $^{\circ}\text{C}$

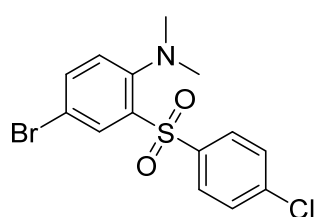
(uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.23 (d, $J =$

5.0 Hz, 1H), 7.84 (d, $J = 5.0$ Hz, 2H), 7.60-7.58 (m, 1H),

7.41 (d, $J = 10.0$ Hz, 2H), 7.21 (d, $J = 10.0$ Hz, 1H), 2.38 (s, 6H), 1.36 (s, 9H); ^{13}C

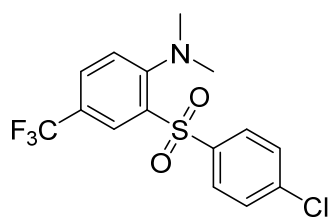
NMR (125MHz, CDCl₃) δ : 150.9, 148.8, 141.0, 138.7, 136.9, 132.0, 129.6, 128.2, 126.2, 124.0, 45.3, 34.9, 31.2; IR(neat, cm⁻¹): 3092, 2969, 2863, 2830, 1576, 1491, 1303, 1153, 1088, 833, 758, 603; LRMS (EI, 70eV) m/z (%): 338 (M⁺+2, 11), 351 (M⁺, 33), 336 (67), 286 (25), 160 (100); HRMS m/z (ESI) calcd for C₁₈H₂₂³⁵ClNO₂S ([M+H]⁺) 352.1133, found: 352.1142.

4-Bromo-2-((4-chlorophenyl)sulfonyl)-*N,N*-dimethylaniline(3da):



45.9mg, 41% yield; White solid; mp 128.0-128.9 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ : 8.36 (d, J = 5.0 Hz, 1H), 7.83 (d, J = 10.0 Hz, 2H), 7.68-7.65 (m, 1H), 7.44 (d, J = 5.0 Hz, 2H), 7.16-7.14 (m, 1H), 2.42 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ : 152.6, 140.0, 139.4, 139.1, 137.9, 132.5, 129.7, 128.4, 126.1, 118.2, 45.3; LRMS (EI, 70eV) m/z (%): 377 (M⁺+4, 33), 373 (M⁺, 49), 310 (48), 198 (100), 169 (88); IR (neat, cm⁻¹): 3084, 2945, 2842, 2800, 1576, 1476, 1308, 1151, 1089, 838, 757; HRMS m/z (ESI) calcd for C₁₄H₁₃⁷⁹Br³⁵ClNO₂S ([M+H]⁺) 373.9612, found: 374.1021.

2-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethyl-4-(trifluoromethyl)aniline(3ea):

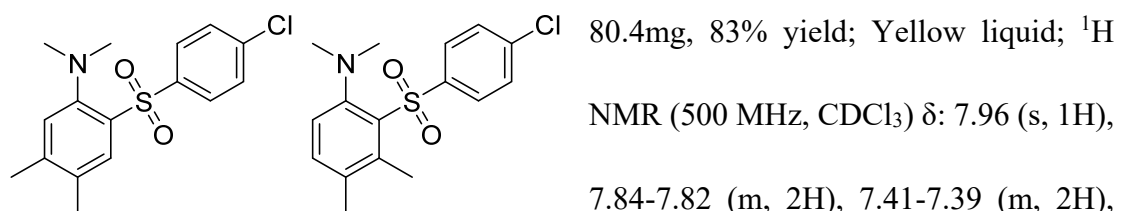


54.5mg, 50% yield; Yellow solid; mp 134.2-135.2 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ : 8.51 (s, 1H), 7.83 (d, J = 10.0 Hz, 2H), 7.81-7.79 (m, 1H), 7.45 (d, J = 10.0 Hz, 2H), 7.34 (d, J = 10.0 Hz, 1H), 2.54 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ : 156.7, 139.7, 139.6, 137.5, 131.6 (q, J = 10.4 Hz), 129.7, 128.5, 127.6 (q, J = 5.7 Hz), 124.5, 45.3; ¹⁹F NMR (471 MHz, CDCl₃) δ : -62.26; IR (neat, cm⁻¹): 3097, 2841, 2799, 1927, 1610, 1498, 1329, 1131, 830, 759; LRMS (EI, 70eV) m/z (%): 300 (M⁺+2, 8),

363 (M^+ , 24), 298 (29), 186 (73), 159 (100); HRMS m/z (ESI) calcd for $C_{15}H_{13}^{35}ClF_3NO_2S$ ($[M+H]^+$) 364.0380, found: 364.0401.

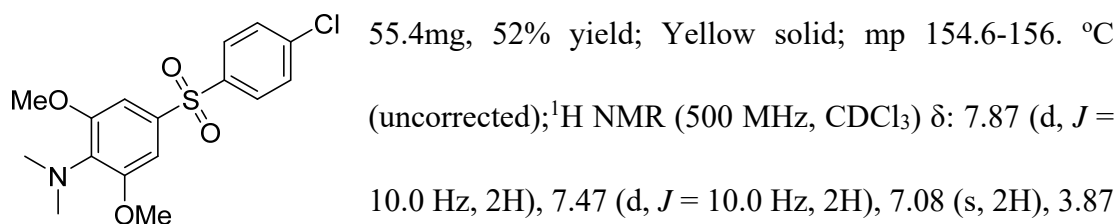
2-((4-Chlorophenyl)sulfonyl)-*N,N*,4,5-tetramethylaniline and 2-((4-

Chlorophenyl)sulfonyl)-*N,N*,3,4-tetramethylaniline (3fa):



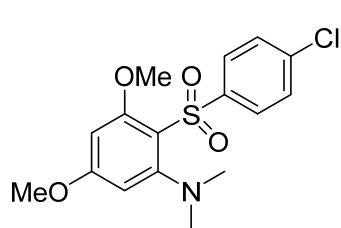
7.02 (s, 1H), 2.39 (s, 6H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ : 151.2, 144.6, 141.2, 138.6, 134.5, 134.1, 130.2, 129.5, 128.2, 128.0, 127.3, 125.4, 45.4, 20.0, 19.3; LRMS (EI, 70eV) m/z (%): 325 ($M^+ + 2$, 16), 323 (M^+ , 49), 258 (38), 146 (87), 132 (100); HRMS m/z (ESI) calcd for $C_{16}H_{18}^{35}ClNO_2S$ ($[M+H]^+$) 324.0820, found: 324.0878. 1H NMR (500 MHz, $CDCl_3$) δ : 7.40-7.38 (m, 4H), 7.31 (d, $J = 10.0$ Hz, 1H), 6.96 (d, $J = 10.0$ Hz, 1H), 2.74 (s, 3H), 2.27 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (125MHz, $CDCl_3$) δ : 151.7, 144.9, 139.5, 138.6, 137.3, 136.4, 135.8, 135.3, 134.1, 130.1, 128.0, 127.9, 121.0, 44.6, 20.7, 17.2; LRMS (EI, 70eV) m/z (%): 325 ($M^+ + 2$, 4), 323 (M^+ , 13), 244 (27), 146 (39), 132 (100); HRMS m/z (ESI) calcd for $C_{16}H_{18}^{35}ClNO_2S$ ($[M+H]^+$) 324.0820, found: 324.0824.

4-((4-Chlorophenyl)sulfonyl)-2,6-dimethoxy-*N,N*-dimethylaniline (3ga):



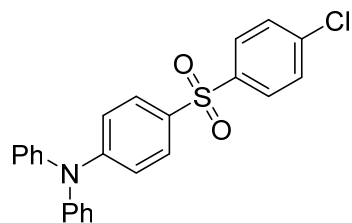
129.5, 128.7, 104.6, 56.2, 42.9; LRMS (EI, 70eV) m/z (%):357 (M⁺+2, 33), 355 (M⁺, 100), 340 (42), 207 (19), 147 (31); IR (neat, cm⁻¹): 3085, 2932, 2862, 2834, 1947, 1580, 1455, 1310, 1120, 1084, 833, 753; HRMS m/z (ESI) calcd for C₁₆H₁₈³⁵ClNO₄S ([M+H]⁺) 356.0718, found: 356.0648.

4-((4-Chlorophenyl)sulfonyl)-3,5-dimethoxy-N,N-dimethylaniline (3ha):



68.2mg, 64% yield; Yellow solid; mp 131.6-133.0 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.67 (d, *J* = 10.0 Hz, 2H), 7.37 (d, *J* = 10.0 Hz, 2H), 6.12 (d, *J* = 2.5 Hz, 1H), 5.83 (d, *J* = 2.5 Hz, 1H), 3.80 (s, 3H), 3.35 (s, 3H), 2.98 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 164.5, 160.7, 156.3, 144.7, 137.6, 128.1, 128.0, 109.2, 95.6, 90.6, 55.3, 55.3, 45.5; LRMS (EI, 70eV) m/z (%):357 (M⁺+2, 10), 355(M⁺, 30), 290 (81), 178 (100), 150 (29); IR (neat, cm⁻¹): 3089, 2974, 2843, 1589, 1474, 1303, 1145, 1089, 815, 754; HRMS m/z (ESI) calcd for C₁₆H₁₈³⁵ClNO₄S ([M+H]⁺) 356.0718, found: 356.0792.

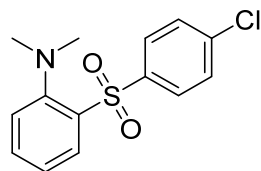
4-((4-Chlorophenyl)sulfonyl)-N,N-diphenylaniline (3ia):



80.4mg, 64% yield; Yellow solid; mp 164.7-166.4 °C (uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.85 (d, *J* = 10.0 Hz, 2H), 7.66 (d, *J* = 10.0 Hz, 2H), 7.45 (d, *J* = 10.0 Hz, 2H), 7.33-7.30 (m, 4H), 7.17-7.11 (m, 6H), 6.96 (d, *J* = 10.0 Hz, 2H); ¹³C NMR (125MHz, CDCl₃) δ: 152.3, 145.9, 141.1, 139.2, 131.0, 129.8, 129.4, 129.0, 128.8, 128.7, 126.2, 125.2, 122.3, 119.3; IR (neat, cm⁻¹): 3066, 1579, 1489, 1306, 1147, 1106,

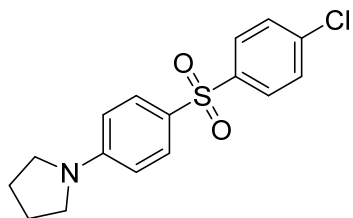
831, 761; HRMS m/z (ESI) calcd for $C_{24}H_{18}^{35}ClNO_2S$ ($[M+H]^+$) 420.0820, found:420.0873.

2-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylaniline (3ja):



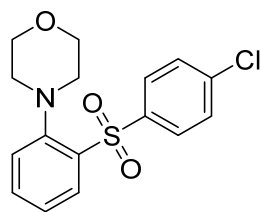
55.8mg, 63% yield; Yellow solid; mp 131.3-132.5 °C (uncorrected); 1H NMR (500 MHz, $CDCl_3$) δ : 8.24-8.22 (m, 1H), 7.82 (d, $J = 10.0$ Hz, 2H), 7.60-7.56 (m, 1H), 7.41 (d, $J = 10.0$ Hz, 2H), 7.35-7.31 (m, 1H), 7.28-7.27 (m, 1H), 2.43 (s, 6H); ^{13}C NMR (125MHz, $CDCl_3$) δ : 153.7, 140.8, 138.9, 137.5, 135.0, 129.8, 129.6, 128.3, 125.27, 124.4, 45.4; LRMS (EI, 70eV) m/z (%): 297 (M^++2 , 6) 295 (M^+ , 19), 230 (34), 118 (97), 91 (100); IR (neat, cm^{-1}): 3089, 2829, 1589, 1476, 1307, 1151, 1087; HRMS m/z (ESI) calcd for $C_{14}H_{14}^{35}ClNO_2S$ ($[M+H]^+$) 296.0507, found: 296.0621.

1-(4-((4-Chlorophenyl)sulfonyl)phenyl)pyrrolidine (3ka):



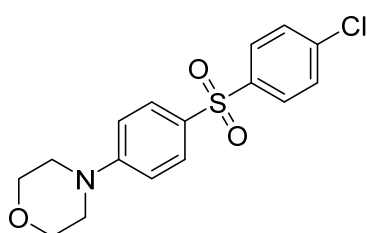
29.9mg, 31% yield; Yellow solid; mp 131.6-132.5 °C (uncorrected); 1H NMR (500 MHz, $CDCl_3$) δ : 7.81 (d, $J = 10.0$ Hz, 2H), 7.71 (d, $J = 10.0$ Hz, 2H), 7.40 (d, $J = 10.0$ Hz, 2H), 6.52 (d, $J = 10.0$ Hz, 2H), 3.33-3.30 (m, 4H), 2.03-2.00 (m, 4H); ^{13}C NMR (125MHz, $CDCl_3$) δ : 150.8, 142.2, 138.6, 129.6, 129.2, 128.3, 125.0, 111.2, 47.6, 25.4; LRMS (EI, 70eV) m/z (%): 323 (M^++2 , 33), 321 (M^+ , 100), 320 (82), 162 (12), 159 (22); IR (neat, cm^{-1}): 3087, 1579, 1489, 1306, 1147, 1106, 831, 761; HRMS m/z (ESI) calcd for $C_{16}H_{16}^{35}ClNO_2S$ ($[M+H]^+$) 322.0663, found: 322.0721.

4-(2-((4-Chlorophenyl)sulfonyl)phenyl)morpholine (3la):



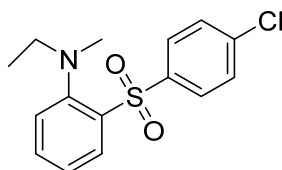
27.9mg, 27% yield; White solid; mp 128.8-131.3 °C (uncorrected); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 8.31-8.29 (m, 1H), 7.82 (d, $J = 10.0$ Hz, 2H), 7.65-7.63 (m, 1H), 7.44 (d, $J = 10.0$ Hz, 2H), 7.42-7.39 (m, 1H), 7.32-7.30 (m, 1H), 3.63 (t, $J = 5.0$ Hz, 4H), 2.75 (t, $J = 5.0$ Hz, 4H); $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ : 152.3, 141.1, 139.0, 136.7, 135.3, 130.7, 129.0, 128.6, 125.8, 124.4, 66.7, 53.6; LRMS (EI, 70eV) m/z (%): 339 ($\text{M}^+ + 2$, 11), 337 (M^+ , 33), 242 (59), 214 (79), 180 (100); IR (neat, cm^{-1}): 3063, 2935, 2852, 2834, 1573, 1472, 1282, 1249, 1157, 1083, 917, 833; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{16}^{35}\text{ClNO}_3\text{S}$ ($[\text{M} + \text{H}]^+$) 338.0612, found: 338.0687.

4-(4-((4-Chlorophenyl)sulfonyl)phenyl)morpholine (3la):



19.2mg, 19% yield; White solid; mp 127.2-128.7 °C (uncorrected); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.83 (d, $J = 10.0$ Hz, 2H), 7.77 (d, $J = 10.0$ Hz, 2H), 7.43 (d, $J = 10.0$ Hz, 2H), 6.88 (d, $J = 10.0$ Hz, 2H), 3.83 (t, $J = 5.0$ Hz, 4H), 3.27 (t, $J = 5.0$ Hz, 4H); $^{13}\text{C NMR}$ (125MHz, CDCl_3) δ : 154.2, 141.3, 139.1, 129.5, 129.4, 129.3, 128.6, 113.8, 66.4, 47.2; IR (neat, cm^{-1}): 3083, 2961, 2835, 1589, 1505, 1304, 1248, 1153, 1106, 828; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{16}^{35}\text{ClNO}_3\text{S}$ ($[\text{M} + \text{H}]^+$) 338.0612, found: 338.0693.

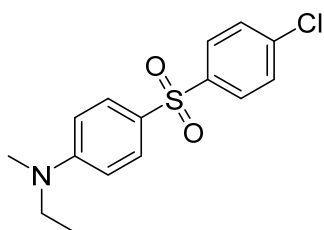
2-((4-Chlorophenyl)sulfonyl)-*N*-ethyl-*N*-methylaniline (3ma):



27.8mg, 30% yield; Yellow liquid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 8.28-8.26 (m, 1H), 7.81 (d, $J = 10.0$ Hz, 2H), 7.60-7.56 (m, 1H), 7.41 (d, $J = 10.0$ Hz, 2H), 7.36-7.32 (m, 1H), 7.24-7.22 (m,

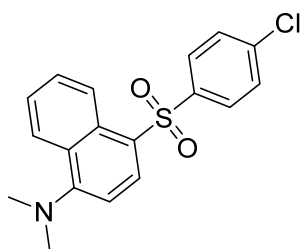
1H), 2.82-2.78 (m, 2H), 2.38 (s, 3H), 0.68 (d, $J = 10.0$ Hz, 3H); ^{13}C NMR (125MHz, CDCl_3) δ : 153.0, 140.8, 138.9, 137.6, 134.8, 130.1, 129.8, 128.3, 125.1, 125.0, 51.6, 42.8, 11.8; IR (neat, cm^{-1}): 2983, 1590, 1520, 1472, 1393, 1314, 1153, 1109, 824, 767; LRMS (EI, 70eV) m/z (%): HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}^{35}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 310.0063, found: 310.0098.

4-((4-Chlorophenyl)sulfonyl)-*N*-ethyl-*N*-methylaniline (3ma):



26.0mg, 28% yield; Yellow solid; mp 141.1-142.3 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 7.82 (d, $J = 10.0$ Hz, 2H), 7.71 (d, $J = 10.0$ Hz, 2H), 7.41 (d, $J = 10.0$ Hz, 2H), 6.64 (d, $J = 10.0$ Hz, 2H), 3.44-3.40 (m, 2H), 2.96 (s, 3H), 1.13 (t, $J = 5.0$ Hz, 3H); ^{13}C NMR (125MHz, CDCl_3) δ : 152.1, 142.0, 138.6, 129.8, 129.6, 129.2, 128.4, 128.3, 125.3, 110.9, 46.6, 37.5, 11.3; LRMS (EI, 70eV) m/z (%): 309 (M- CH_3 , 35), 294 (100), 119 (33), 104 (5); IR (neat, cm^{-1}): 2981, 1589, 1518, 1472, 1391, 1314, 1150, 1105, 827, 767; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}^{35}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 310.0063, found: 310.0102.

4-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylnaphthalen-1-amine (3na):

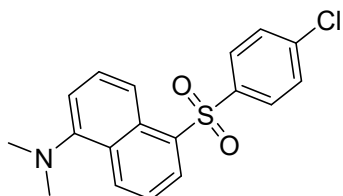


44.2mg, 43% yield; Yellow solid; mp 120.8-122.1 °C (uncorrected); ^1H NMR (500 MHz, CDCl_3) δ : 8.50 (d, $J = 10.0$ Hz, 1H), 8.41 (d, $J = 10.0$ Hz, 1H), 8.18 (d, $J = 10.0$ Hz, 1H), 7.86 (d, $J = 10.0$ Hz, 2H), 7.54-7.46 (m, 2H), 7.39 (d, $J = 10.0$ Hz, 2H), 7.03 (d, $J = 10.0$ Hz, 1H), 2.98 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ : 157.2, 141.0, 139.1, 131.4, 130.1, 129.2, 128.5, 128.2, 128.0, 127.0, 125.7, 125.4, 124.4, 111.2, 44.6; IR (neat, cm^{-1}): 2928, 2797, 1580, 1476, 1307, 1148, 1089, 825, 753;

LRMS (EI, 70eV) m/z (%):347 (M⁺+2, 33), 345 (M⁺, 100), 186 (41), 169 (38), 115 (19);

HRMS m/z (ESI) calcd for C₁₈H₁₆³⁵ClNO₂S ([M+H]⁺) 346.0663, found: 346.0762.

5-((4-Chlorophenyl)sulfonyl)-N,N-dimethylnaphthalen-1-amine (3na)



14.5mg, 14% yield; Yellow solid; mp 122.8-124.1 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 8.29 (d, *J* =

10.0 Hz, 1H), 7.96 (d, *J* = 10.0 Hz, 2H), 7.89 (d, *J* = 10.0 Hz,

1H), 7.81 (d, *J* = 10.0 Hz, 2H), 7.62-7.59 (m, 1H), 7.56-7.52 (m, 1H), 7.47 (d, *J* = 10.0

Hz, 2H), 2.59 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 149.7, 141.6, 138.6, 138.2, 137.8,

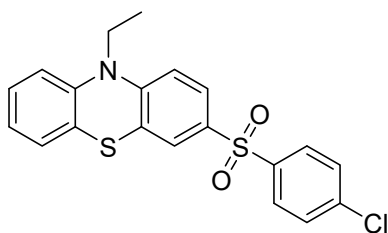
132.8, 129.5, 129.4, 128.8, 128.7, 128.4, 127.1, 126.6, 125.2, 124.1, 43.6; LRMS (EI,

70eV) m/z (%):347 (M⁺+2, 10), 345 (M⁺, 30), 330 (5), 168 (100), 141 (28); IR (neat, cm⁻¹):

2920, 2791, 1577, 1475, 1307, 1145, 1086, 821, 756; HRMS m/z (ESI) calcd for

C₁₈H₁₆³⁵ClNO₂S ([M+H]⁺) 346.0663, found: 346.0771.

3-((4-Chlorophenyl)sulfonyl)-10-ethyl-10H-phenothiazine (3oa):



92.6mg, 77% yield; Yellow solid; mp 161.2-162.5 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.82 (d, *J*

= 10.0 Hz, 2H), 7.67-7.65 (m, 1H), 7.56 (d, *J* = 2.0 Hz,

1H), 7.42 (d, *J* = 10.0 Hz, 2H), 7.16-7.12 (m, 1H), 7.06-7.04 (m, 1H), 6.95-6.92 (m, 1H),

6.86-6.83 (m, 2H), 3.92-3.88 (m, 2H), 1.38 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125MHz,

CDCl₃) δ: 149.5, 142.9, 140.6, 139.4, 133.7, 129.5, 128.7, 127.7, 127.4, 127.4, 126.2,

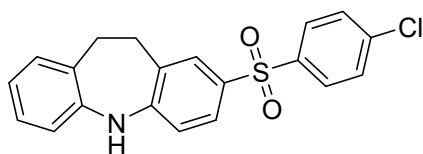
125.2, 123.6, 122.8, 115.6, 114.5, 42.3, 12.7; LRMS (EI, 70eV) m/z (%):303 (M⁺+2, 1),

401 (M⁺, 3), 345 (100), 168 (58), 153 (22); IR (neat, cm⁻¹): 3058, 2976, 1732, 1564, 1461,

1319, 1157, 1475, 1307, 1145, 1086, 821, 756; HRMS m/z (ESI) calcd for

$C_{20}H_{16}^{35}ClNO_2S_2$ ($[M+H]^+$) 402.0384, found: 402.0392.

2-((4-Chlorophenyl)sulfonyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (3pa):



34.7mg, 32% yield; Yellow solid; mp 156.5-158.1 °C

(uncorrected); 1H NMR (500 MHz, $CDCl_3$) δ : 8.95 (s,

1H), 7.88-7.86 (m, 1H), 7.80 (d, $J = 10.0$ Hz, 2H), 7.39 (d, $J = 10.0$ Hz, 2H), 7.24-7.22

(m, 1H), 7.16-7.12 (m, 1H), 7.02-7.00 (m, 1H), 6.92-6.90 (m, 1H), 6.86-6.81 (m, 2H),

3.07 (t, $J = 5.0$ Hz, 2H), 2.97 (t, $J = 5.0$ Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ : 142.2,

140.6, 140.3, 139.8, 136.5, 132.8, 130.7, 129.5, 128.6, 128.4, 128.2, 127.1, 124.5, 120.4,

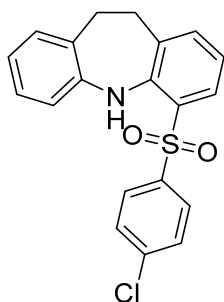
119.2, 118.9, 35.4, 34.7; LRMS (EI, 70eV) m/z (%): 371 ($M^+ + 2$, 33), 369 (M^+ , 100), 193

(34), 165 (13), 89 (7); IR (neat, cm^{-1}): 3355, 3015, 2921, 2851, 1581, 1464, 1340, 1282,

1088, 866, 754; HRMS m/z (ESI) calcd for $C_{20}H_{16}^{35}ClNO_2S$ ($[M+H]^+$) 370.0663, found:

370.0674.

4-((4-Chlorophenyl)sulfonyl)-10,11-dihydro-5H-dibenzo[b,f]azepine(3pa):



16.6 mg, 15% yield; Yellow solid; mp 153.2-155.1 °C (uncorrected);

1H NMR (500 MHz, $CDCl_3$) δ : 7.84 (d, $J = 10.0$ Hz, 2H), 7.59-7.53

(m, 2H), 7.42 (d, $J = 10.0$ Hz, 2H), 7.11-7.04 (m, 2H), 6.85 (t, $J =$

7.5 Hz, 1H), 6.80-6.76 (m, 2H), 6.58 (s, 1H), 3.05-3.01 (m, 4H);

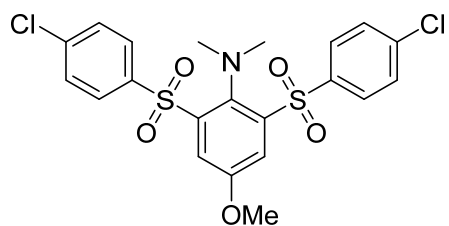
^{13}C NMR (125MHz, $CDCl_3$) δ : 146.8, 141.2, 140.4, 139.1, 130.8, 130.4, 129.7, 129.4,

129.1, 128.6, 127.5, 127.1, 126.8, 121.2, 118.8, 118.1, 35.5, 34.5; IR (neat, cm^{-1}):

3344, 3081, 2904, 2846, 1582, 1491, 1352, 1135, 1098, 826, 752; HRMS m/z (ESI)

calcd for $C_{20}H_{16}^{35}ClNO_2S$ ($[M+H]^+$) 370.0663, found: 370.0672.

2,6-bis((4-chlorophenyl)sulfonyl)-4-methoxy-N,N-dimethylaniline(4aa):



18.0mg, 12%; White solid; mp 157.2-158.1 °C

(uncorrected); ¹H NMR (500 MHz, CDCl₃) δ: 7.78

(s, 2H), 7.74 (d, *J* = 8.5 Hz, 4H), 7.59 (d, *J* = 8.5

Hz, 4H), 3.90 (s, 3H), 2.25 (s, 6H); ¹³C NMR (125MHz, CDCl₃) δ: 156.7, 144.9, 142.6,

139.9, 139.8, 129.4, 128.7, 121.1, 56.4, 43.1; IR (neat, cm⁻¹): 3075, 2945, 2831, 2794,

1906, 1578, 1492, 1291, 1265, 1158, 1081, 864; HRMS *m/z* (ESI) calcd for

C₂₁H₁₉³⁵Cl₂NO₅S₂ ([M+H]⁺) 500.0160, found 500.0167.

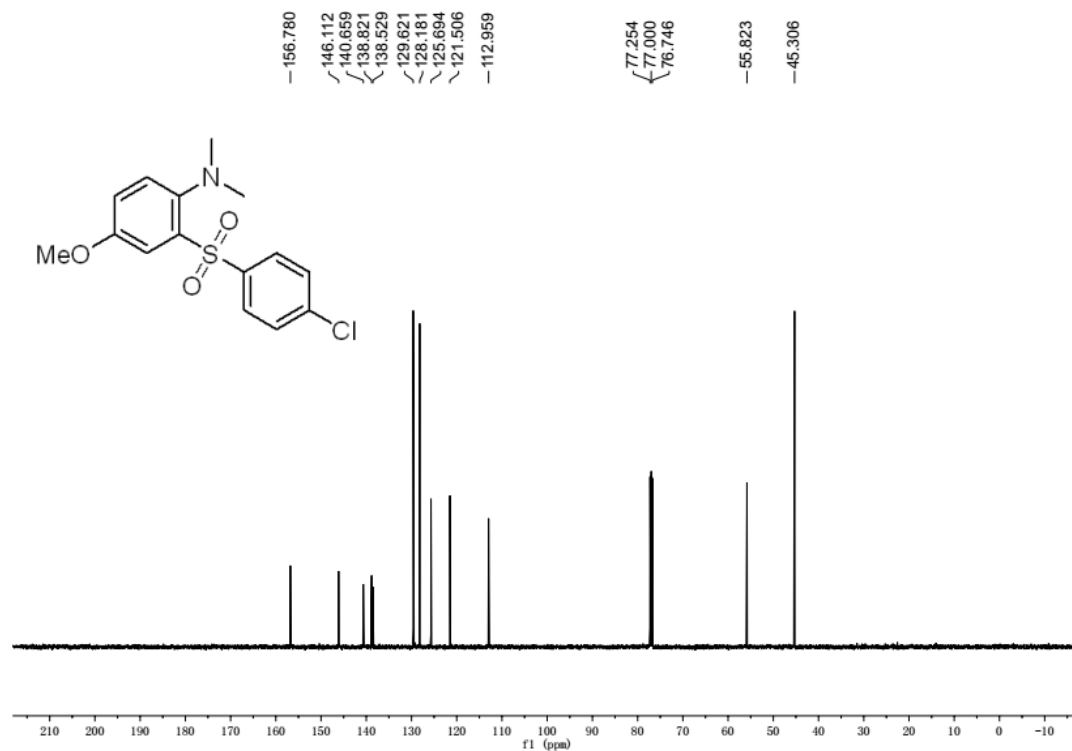
Notes and references:

(a) T. C. Johnson, Bryony L. Elbert, A. J. M. Farley, T. W. Gorman, C. Genicot, B. Lallemand, P. Pasau, J. Flasz, J. L. Castro, M. MacCoss, D. J. Dixon, R. S. Paton, C. J. Schofield, M. D. Smith and M. C. Willis, *Chem. Sci.*, 2018, **9**, 629;

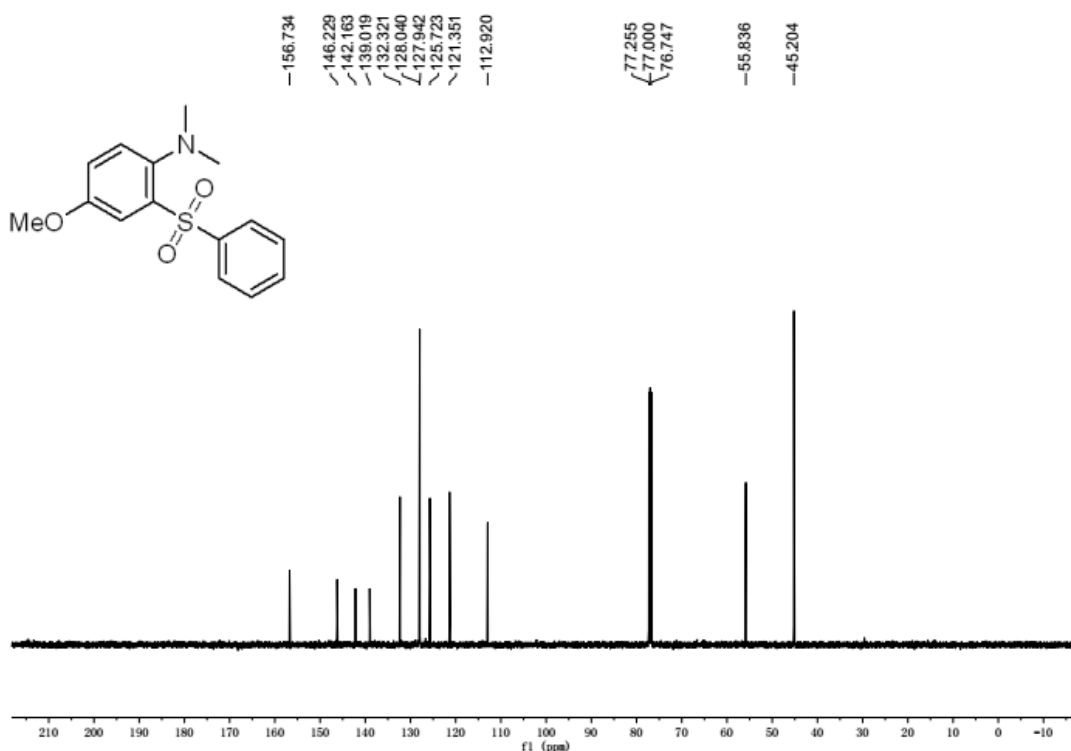
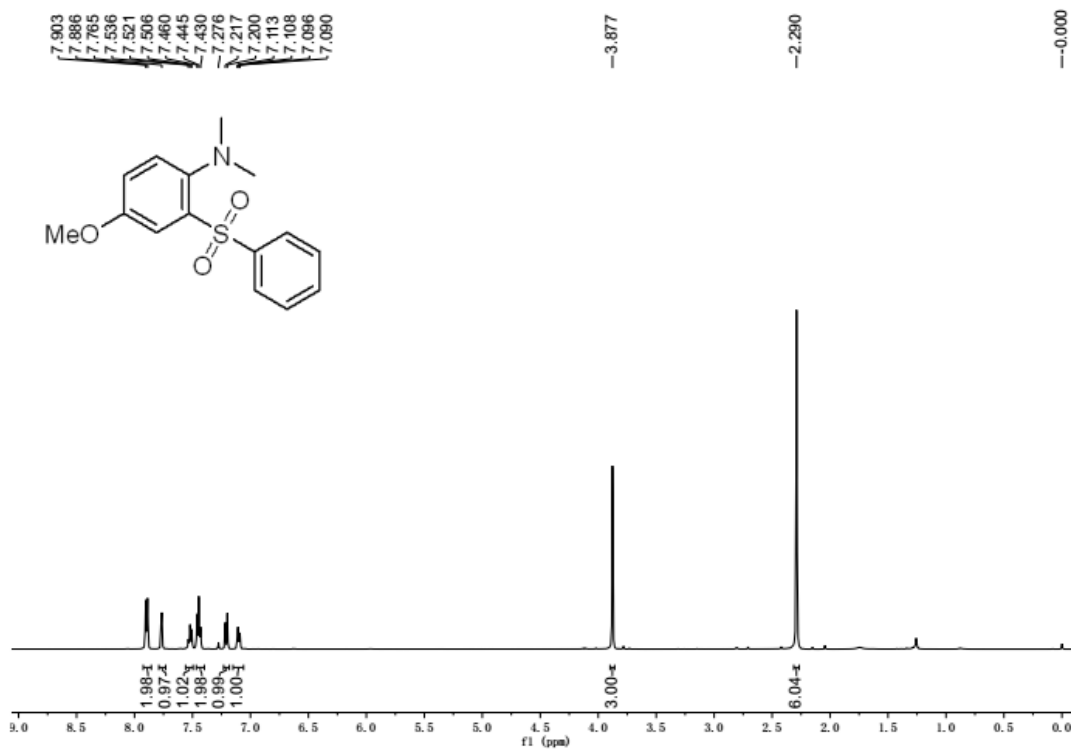
(b) K. Zhou, J. Zhang, L. Lai, J. Cheng, J. Sun and J. Wu, *Chem. Commun.*, 2018, **54**, 7459.

(C) Spectra

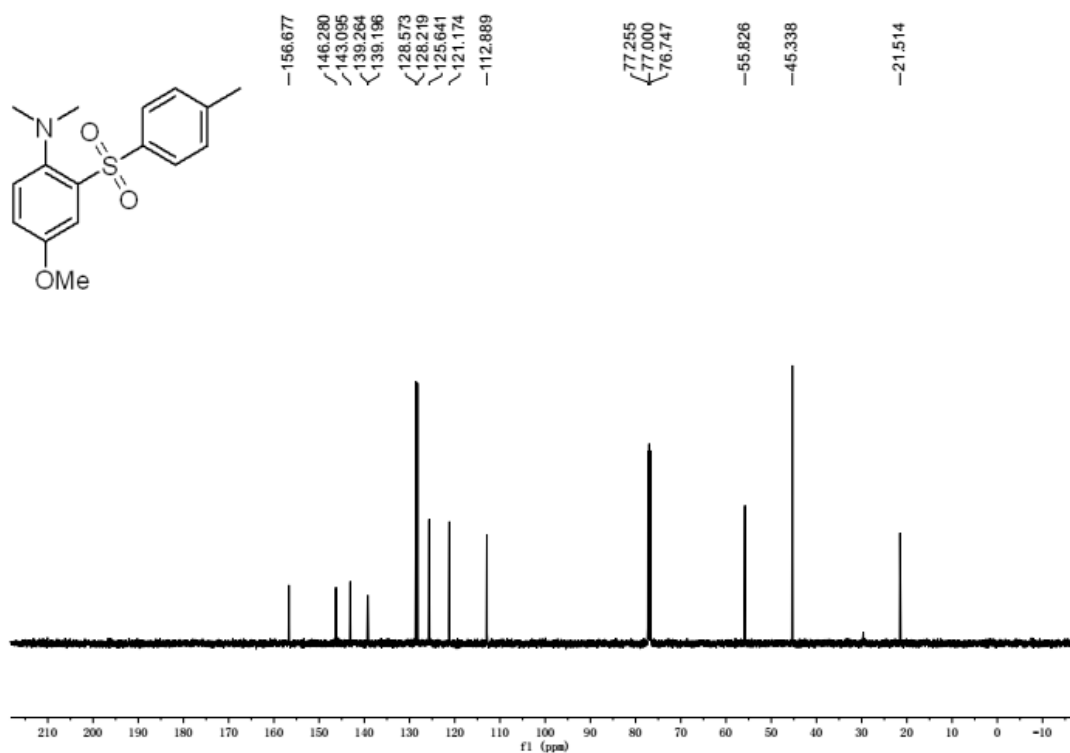
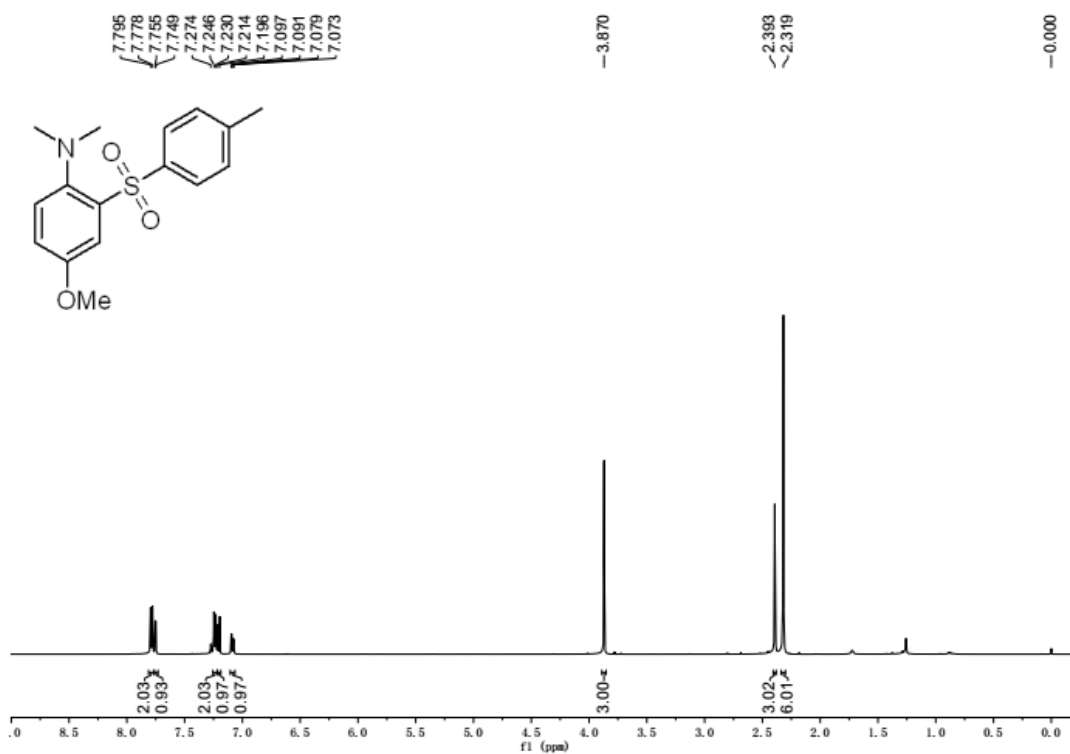
2-((4-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline(3aa):



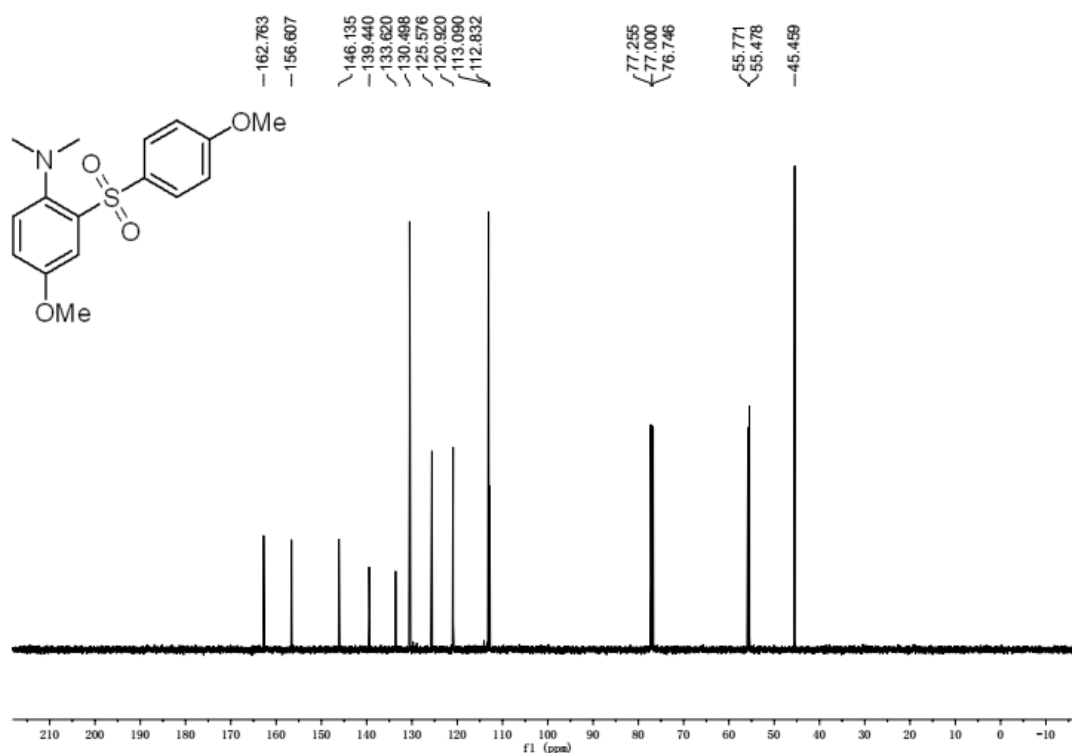
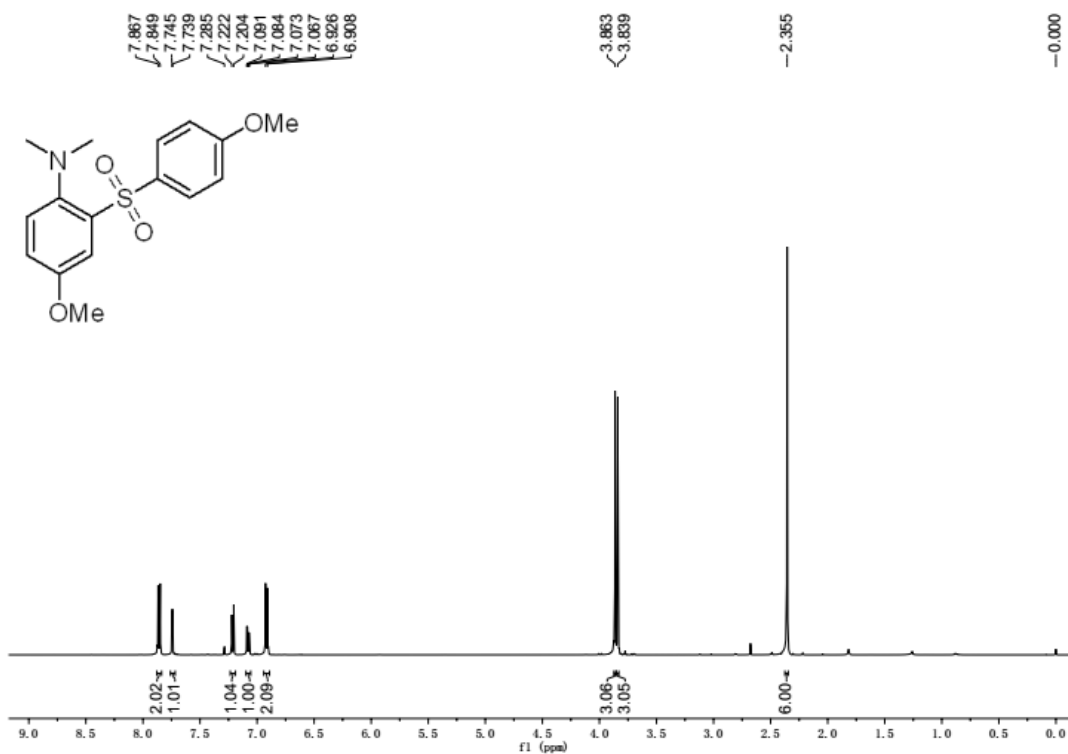
4-Methoxy-*N,N*-dimethyl-2-(phenylsulfonyl)aniline (3ab):



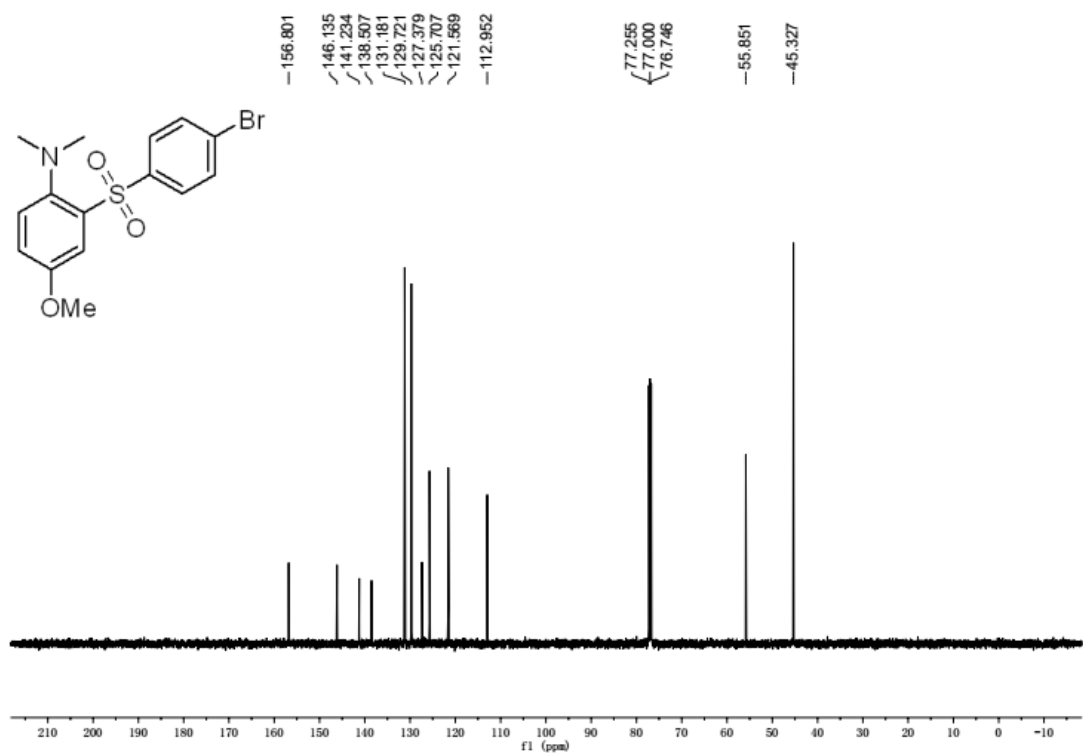
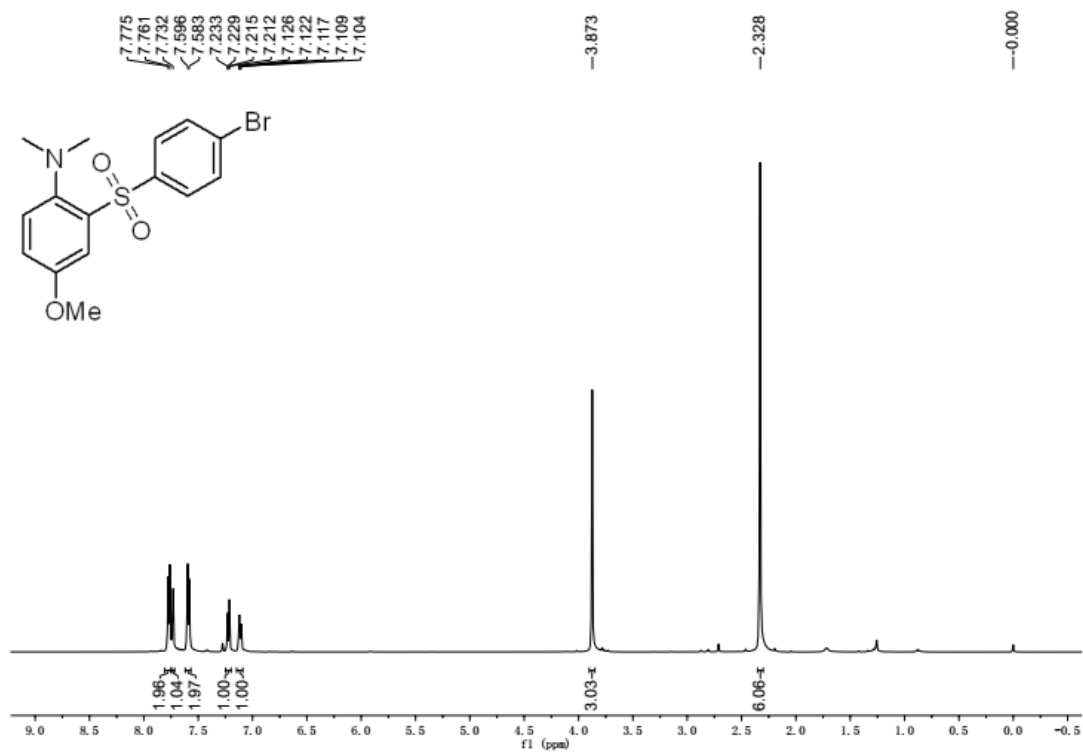
4-Methoxy-N,N-dimethyl-2-tosylaniline (3ac):



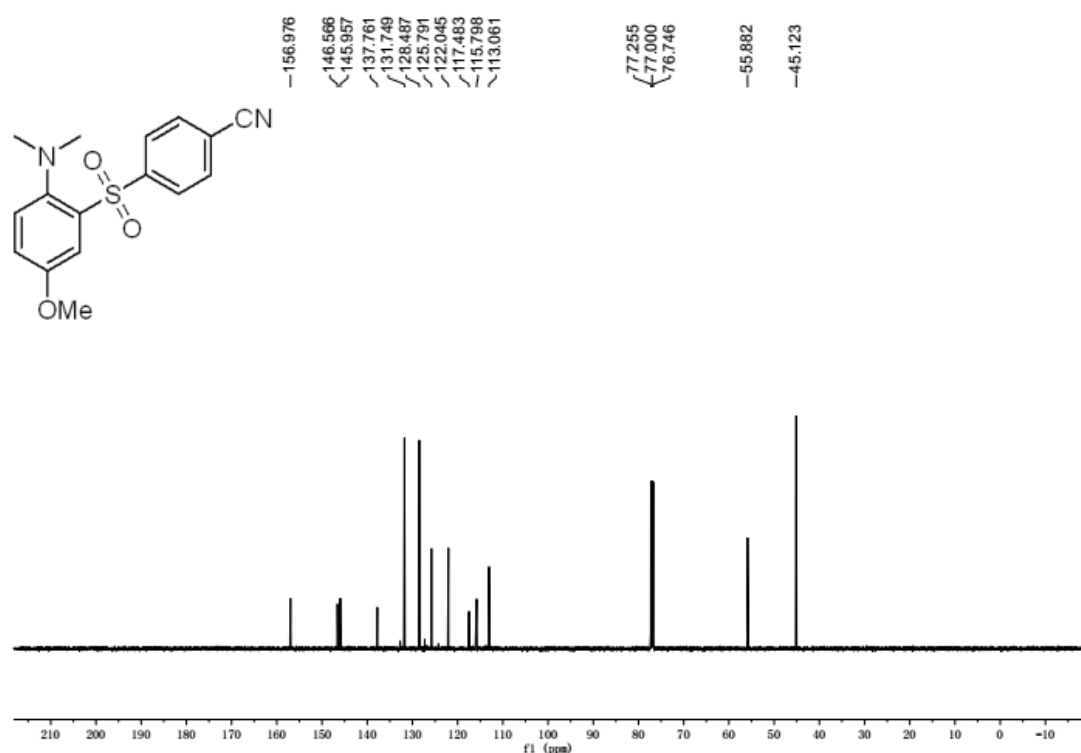
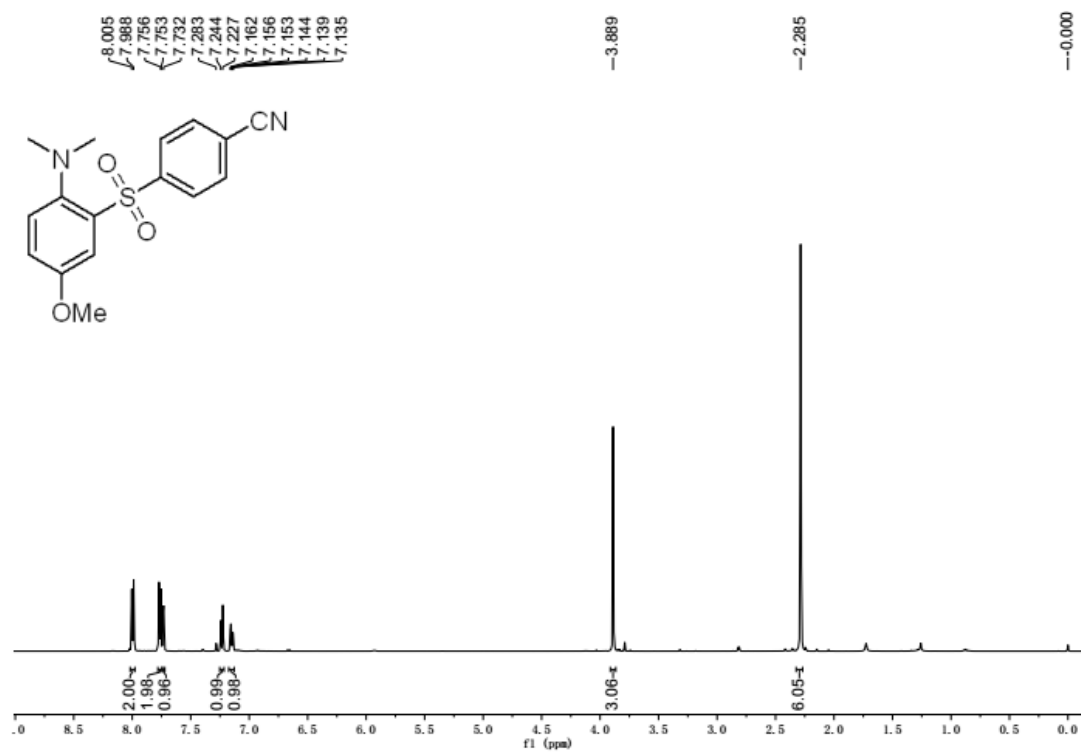
4-Methoxy-2-((4-methoxyphenyl)sulfonyl)-*N,N*-dimethylaniline (3ad):



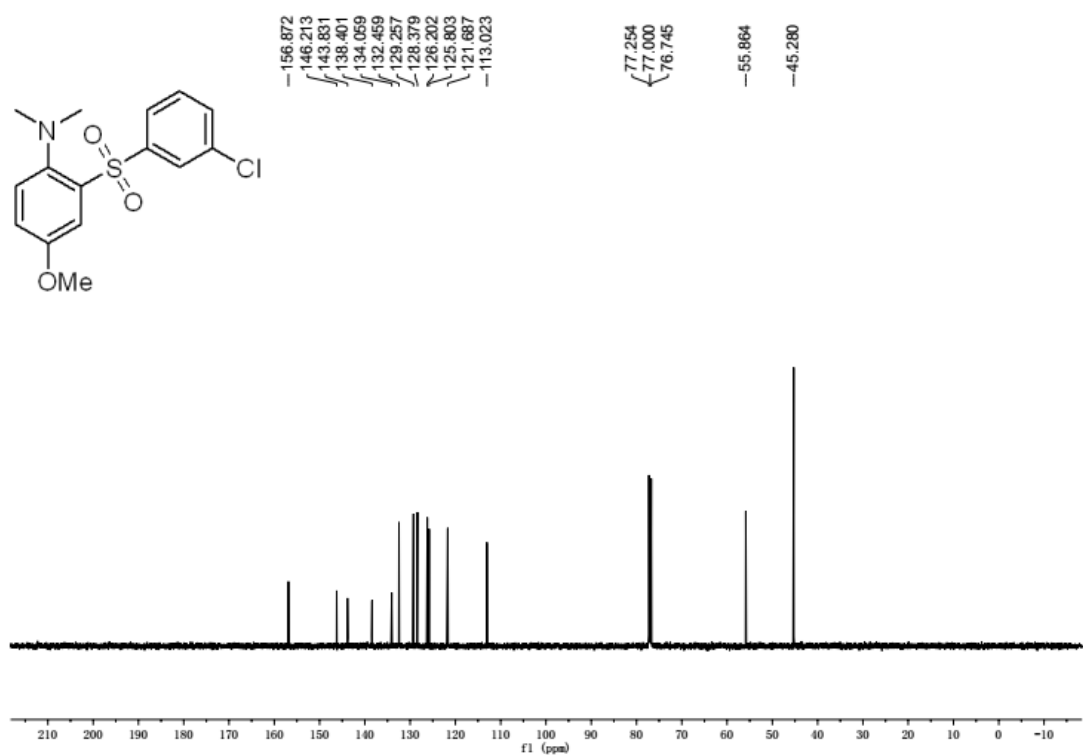
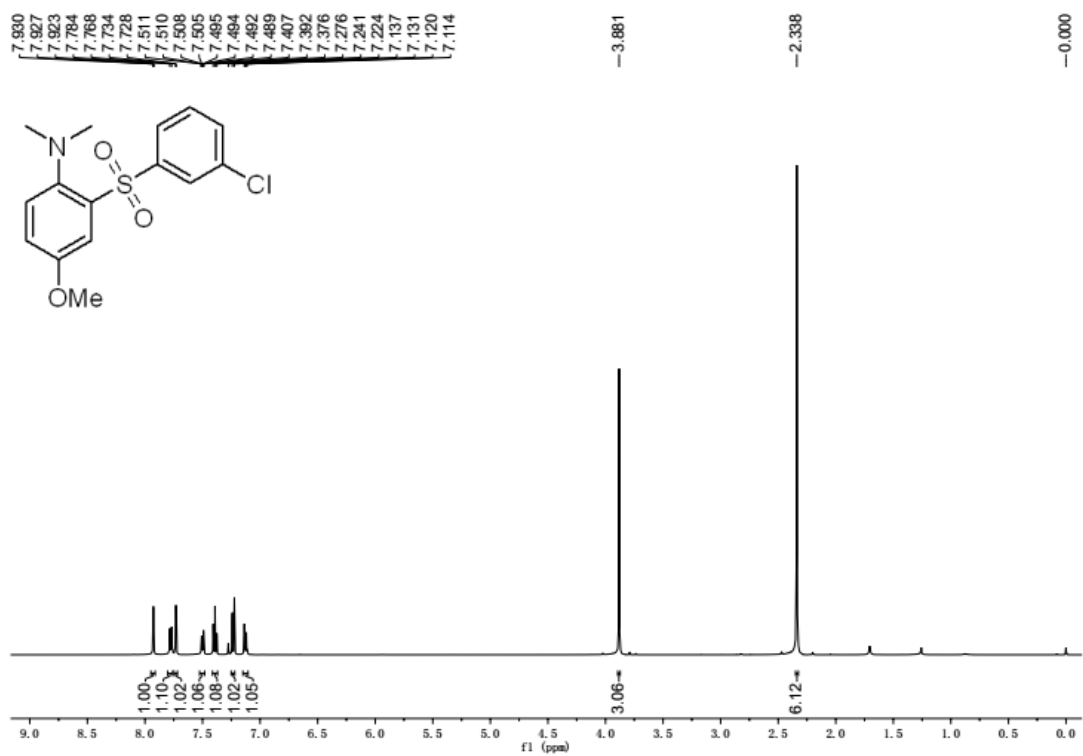
2-((4-Bromophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ae):



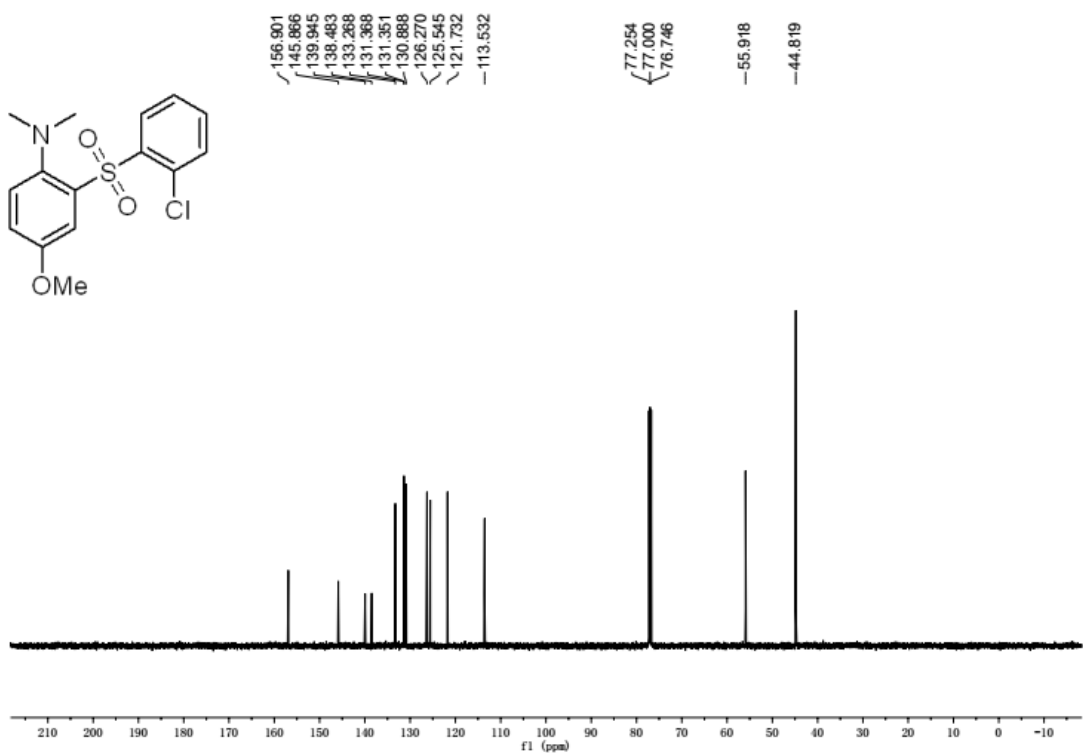
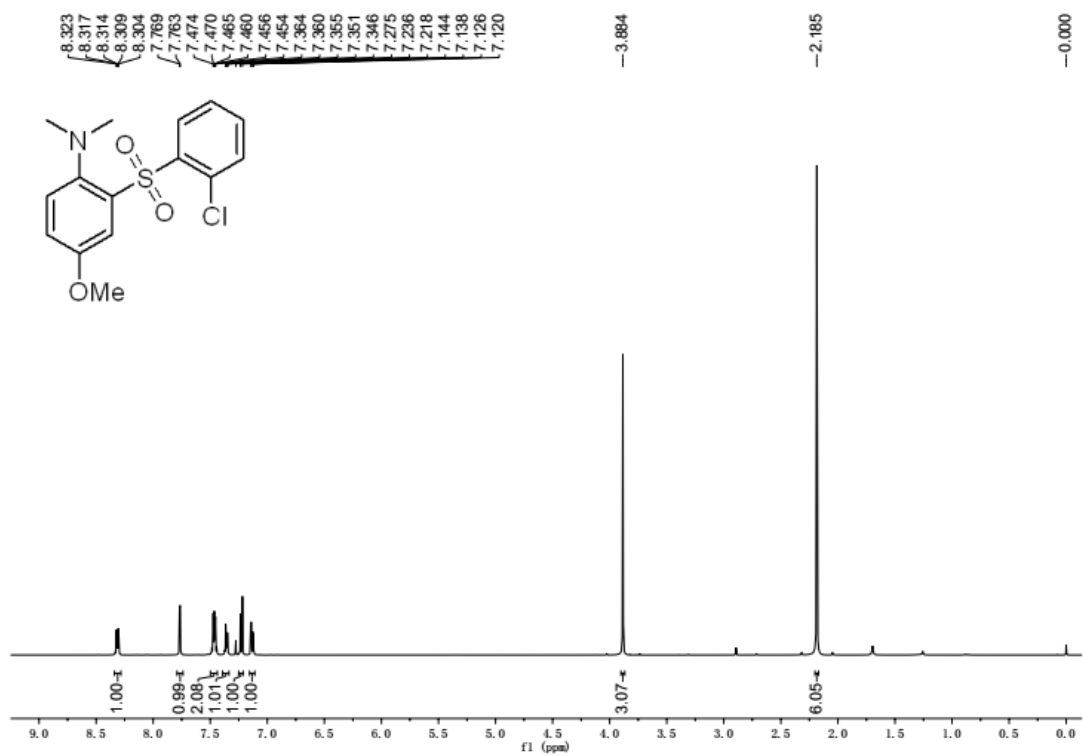
4-((2-(Dimethylamino)-5-methoxyphenyl)sulfonyl)benzonitrile (3af):



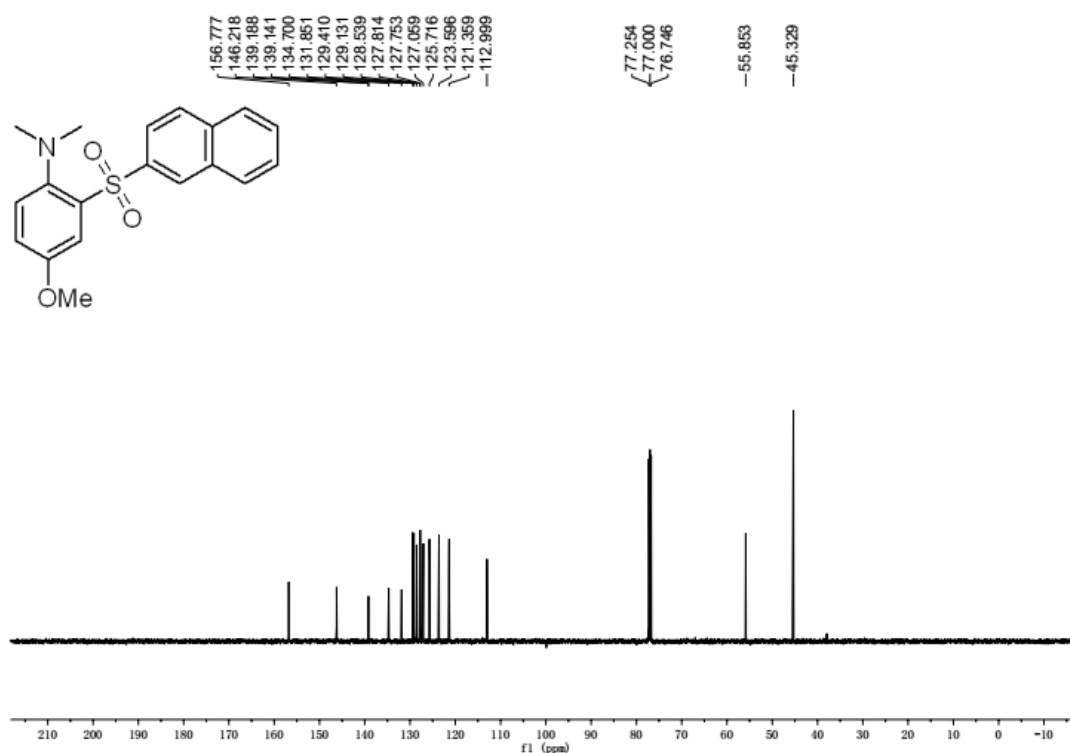
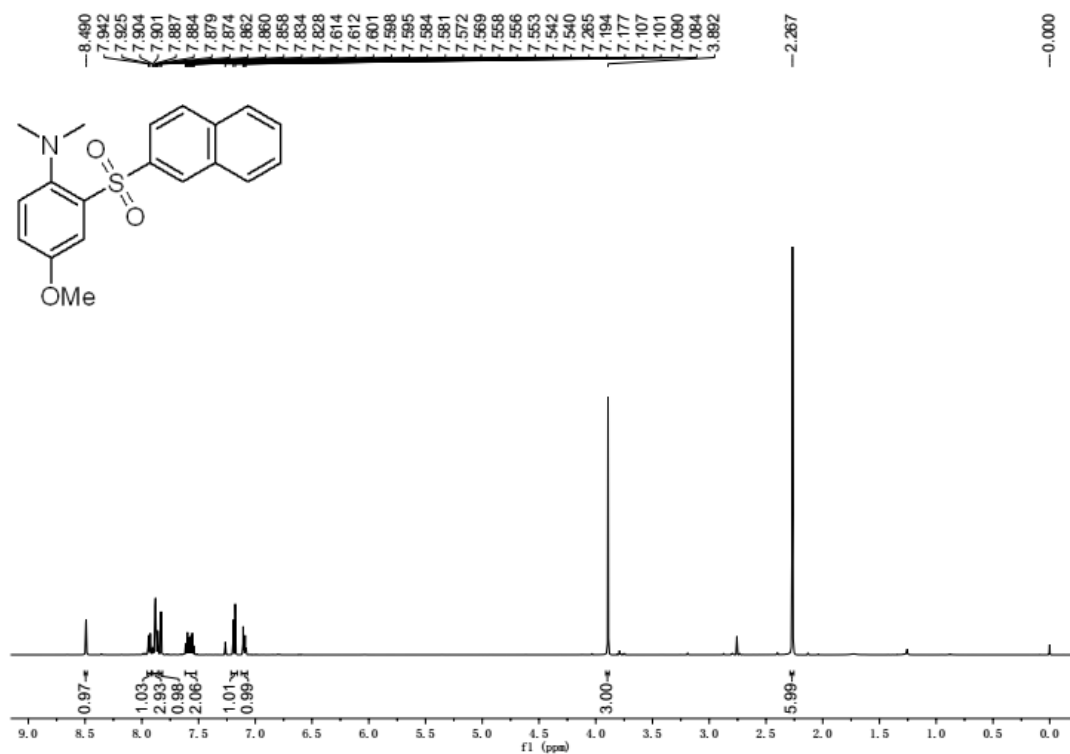
2-((3-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ag):



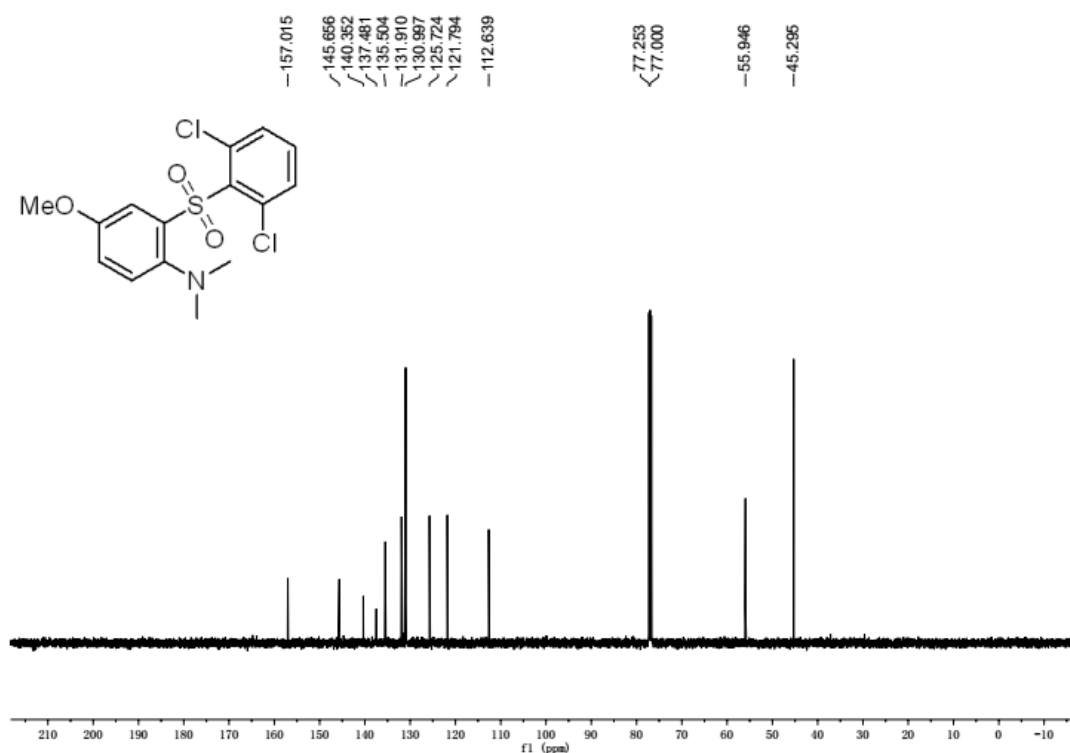
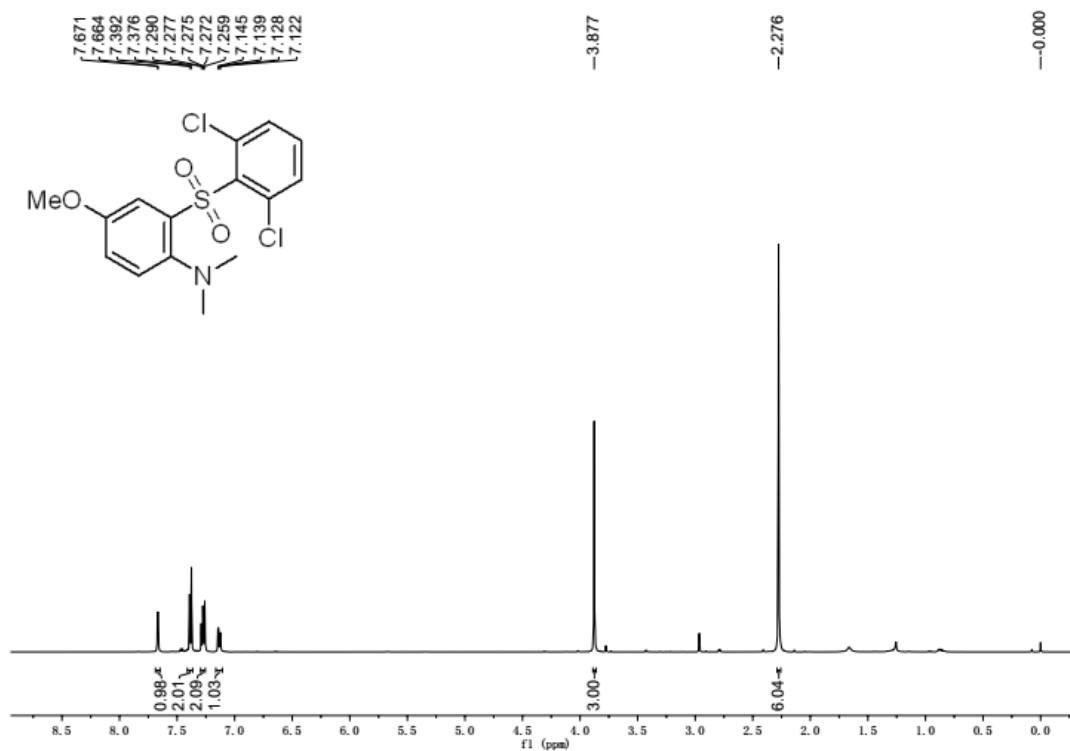
2-((2-Chlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ah):



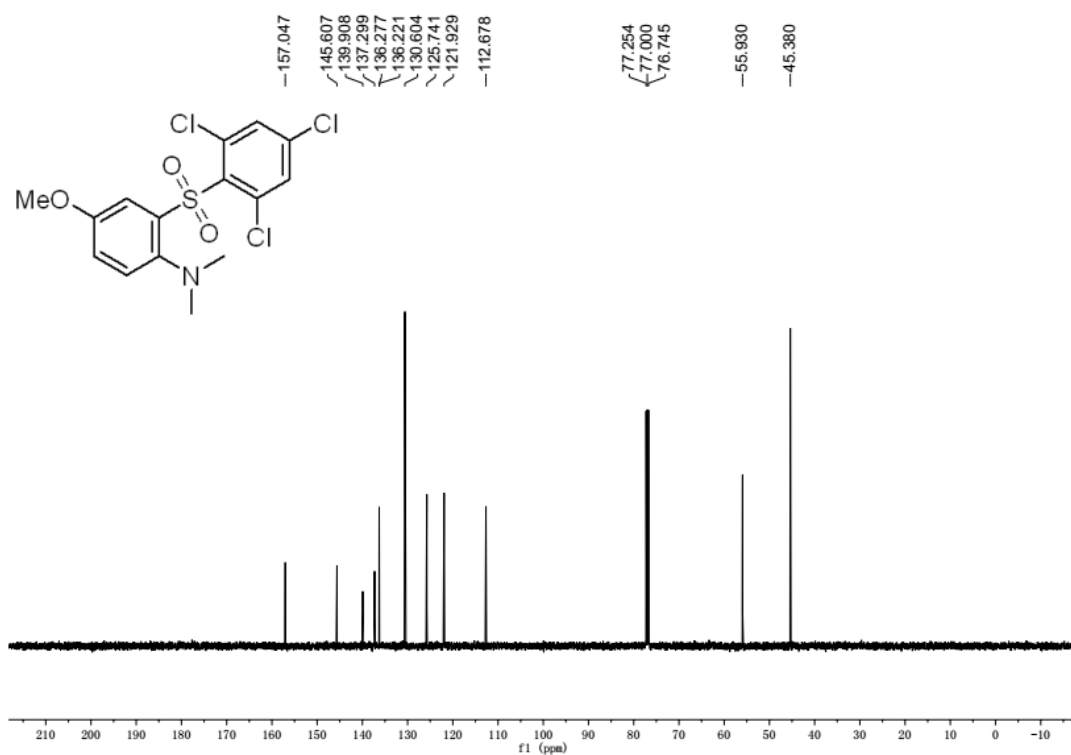
4-Methoxy-*N,N*-dimethyl-2-(naphthalen-2-ylsulfonyl)aniline (3ai):



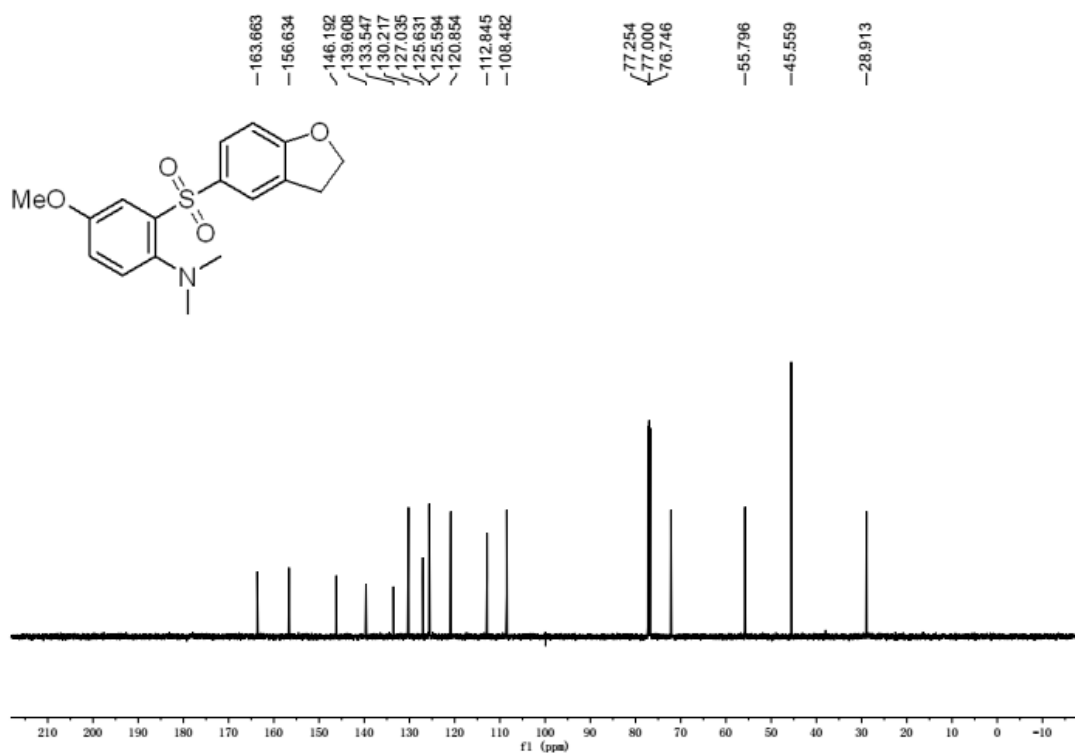
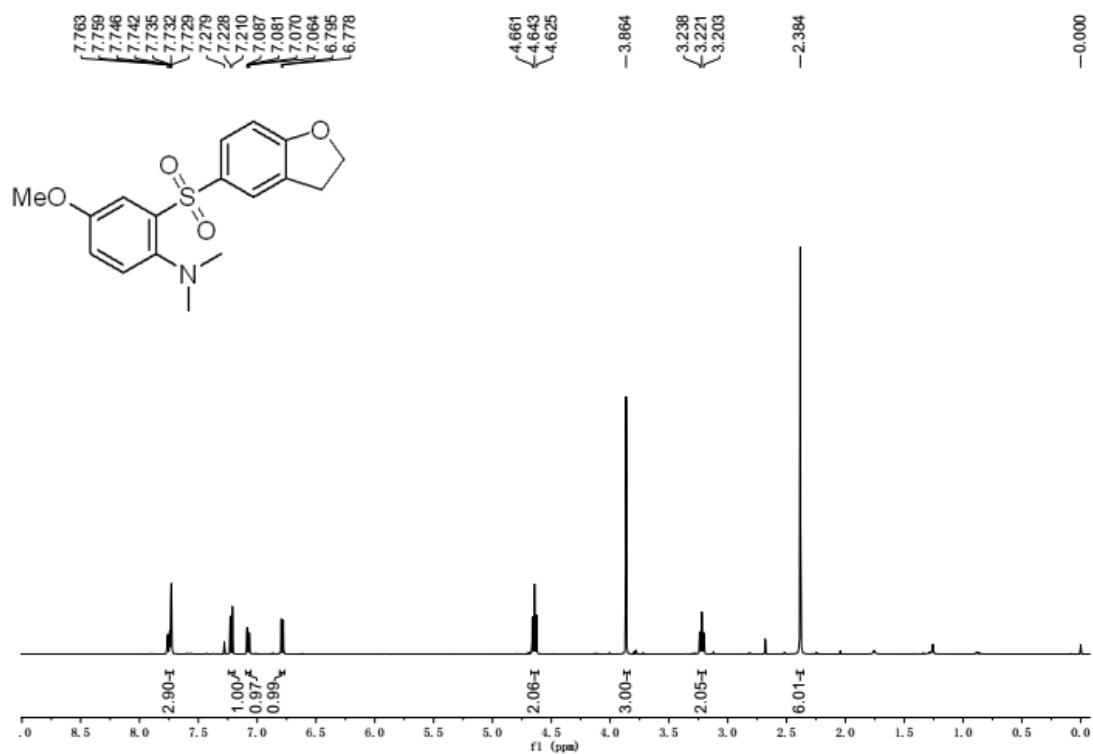
2-((2,6-Dichlorophenyl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3aj):



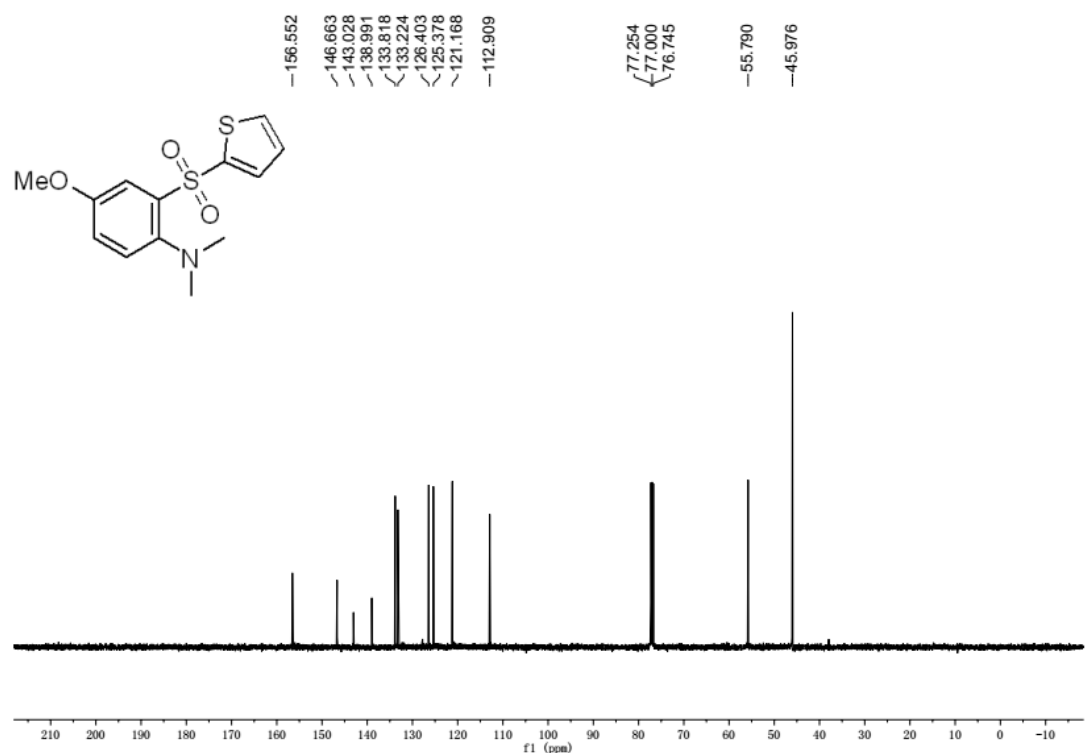
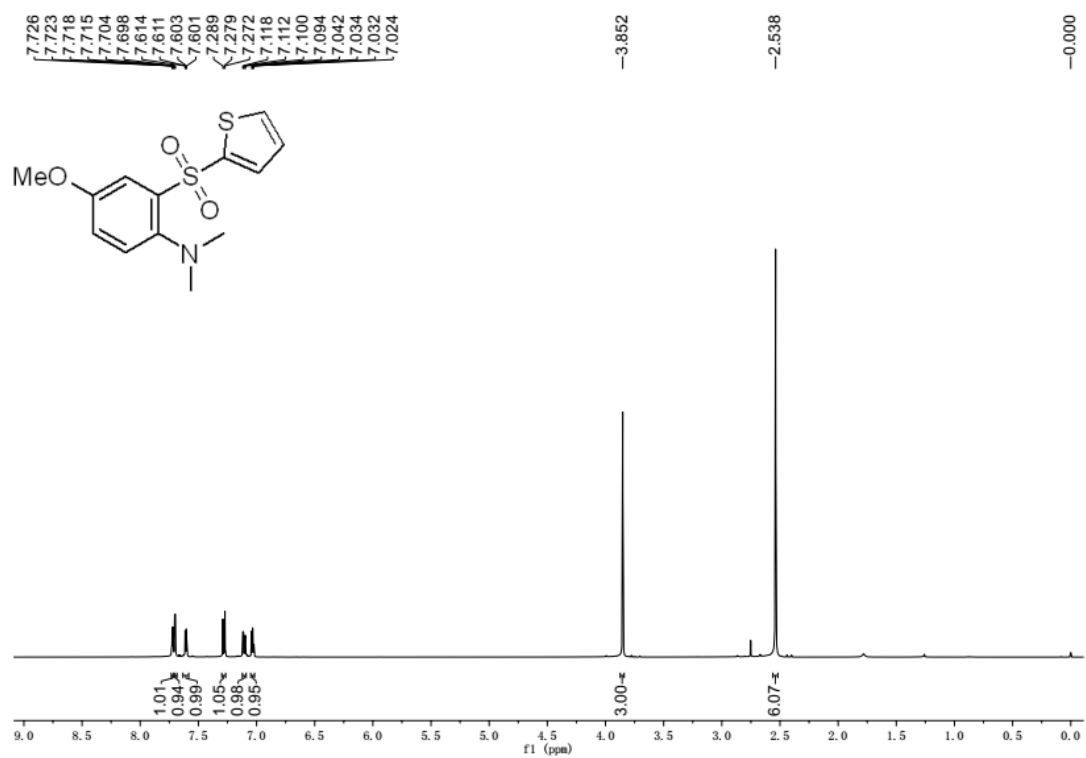
4-Methoxy-*N,N*-dimethyl-2-((2,4,6-trichlorophenyl)sulfonyl)aniline (3ak):



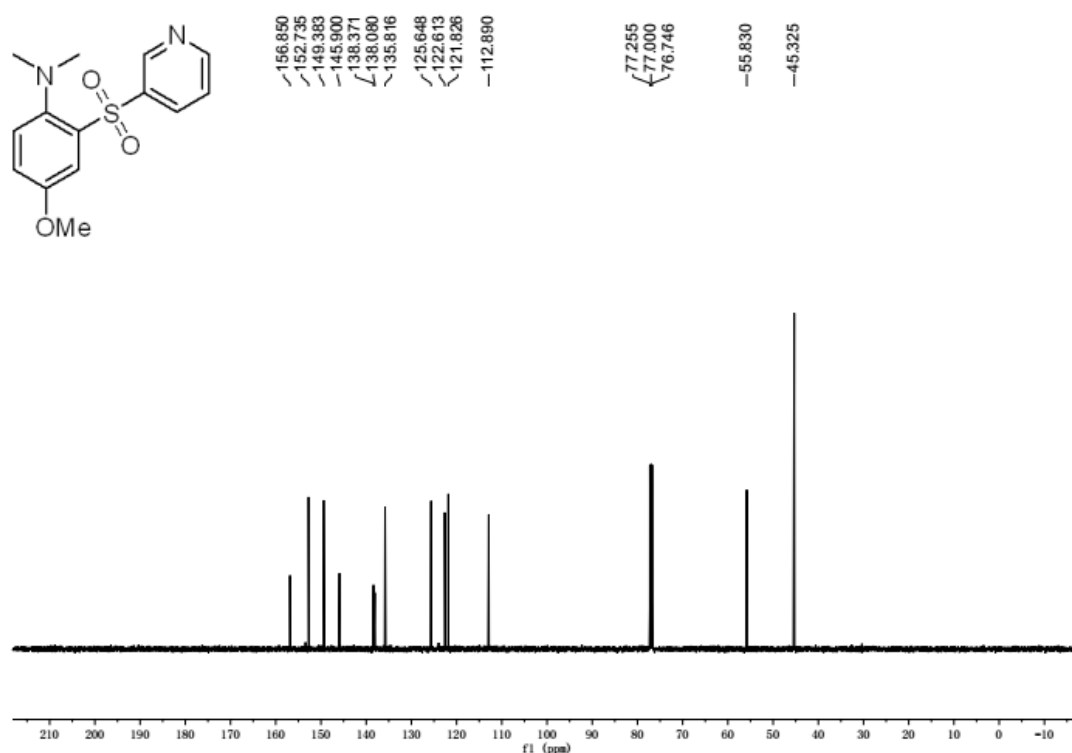
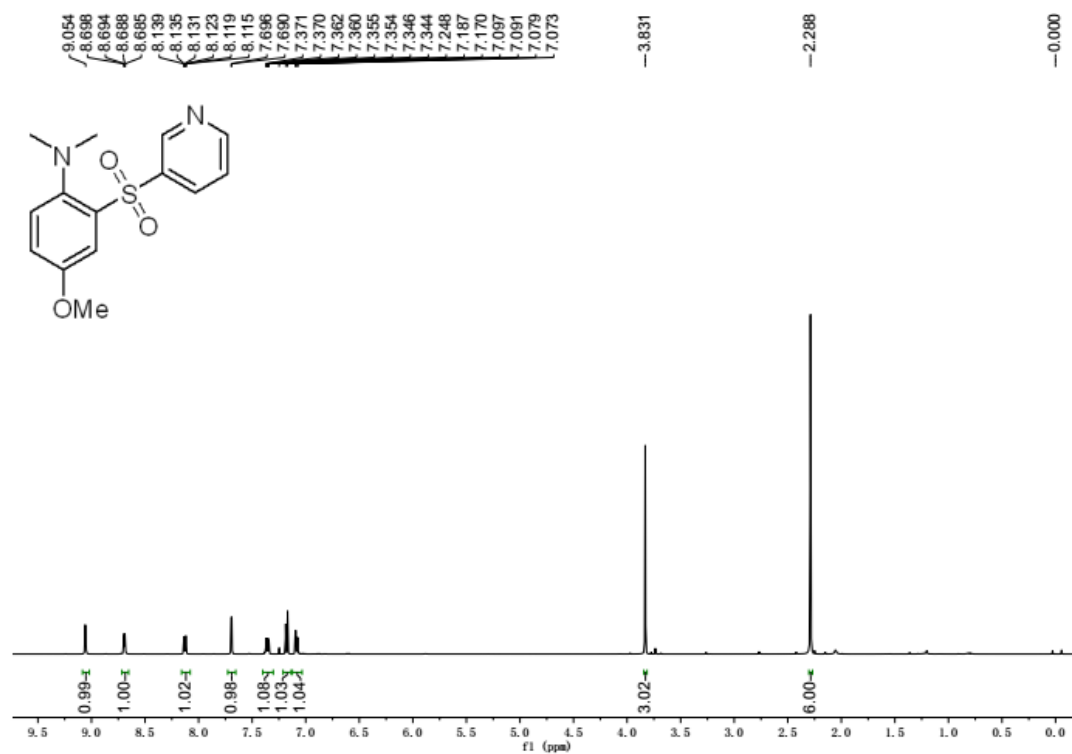
2-((2,3-Dihydrobenzofuran-5-yl)sulfonyl)-4-methoxy-*N,N*-dimethylaniline (3a):



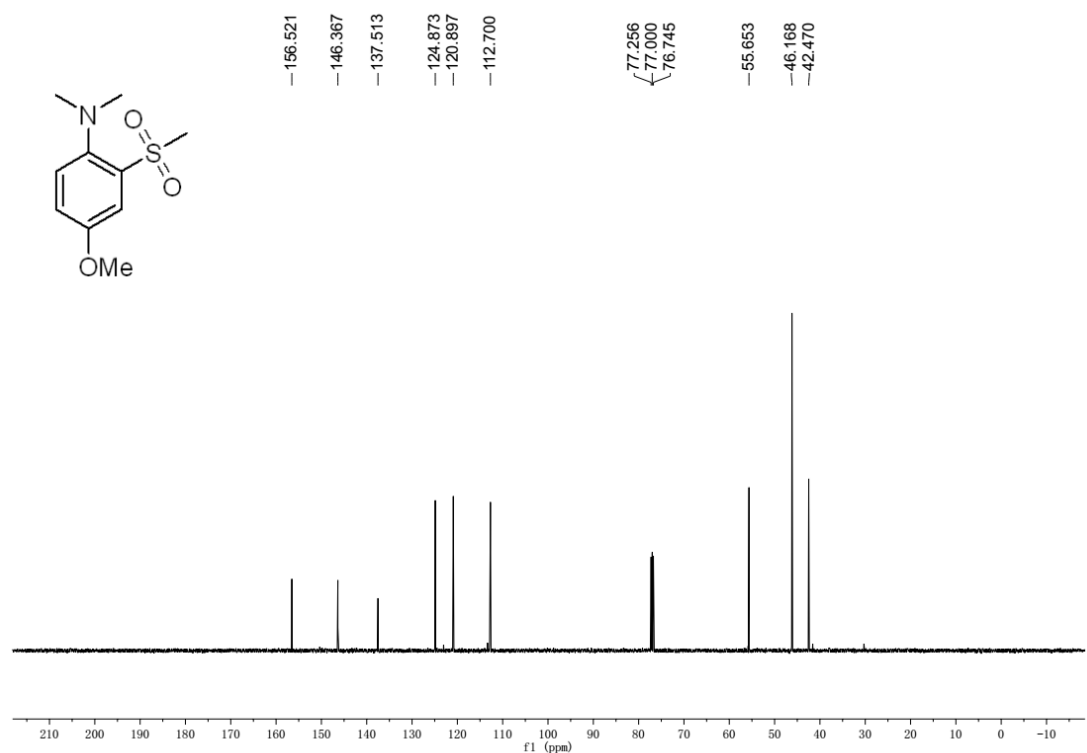
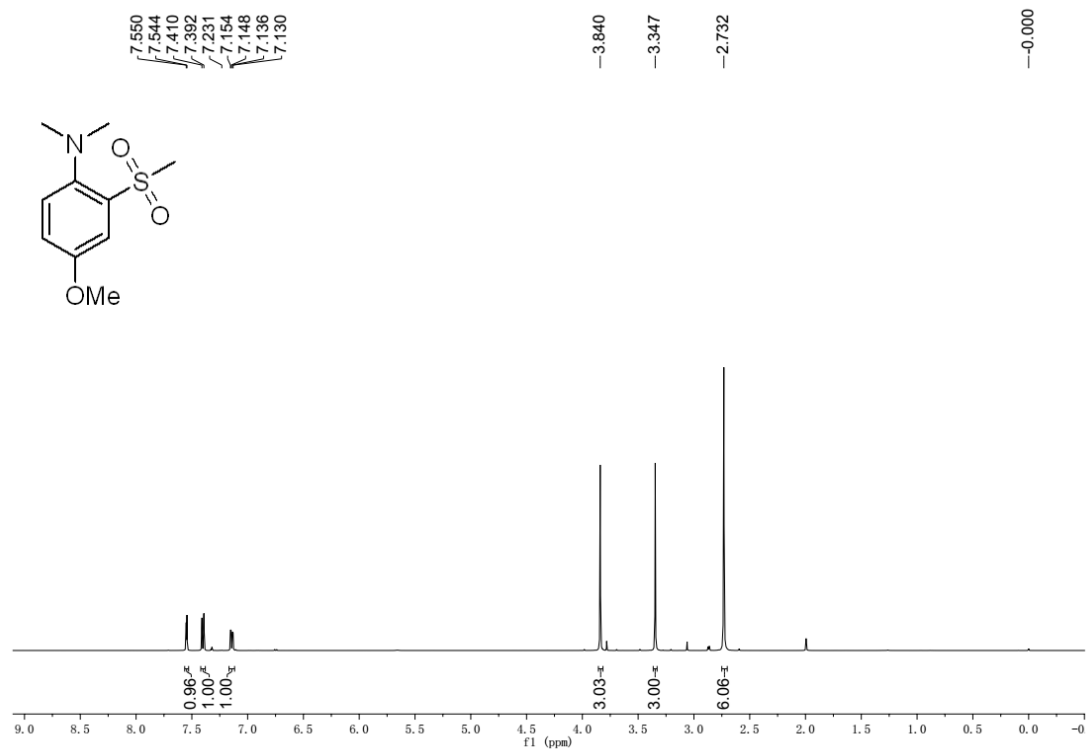
4-Methoxy-*N,N*-dimethyl-2-(thiophen-2-ylsulfonyl)aniline(3am):



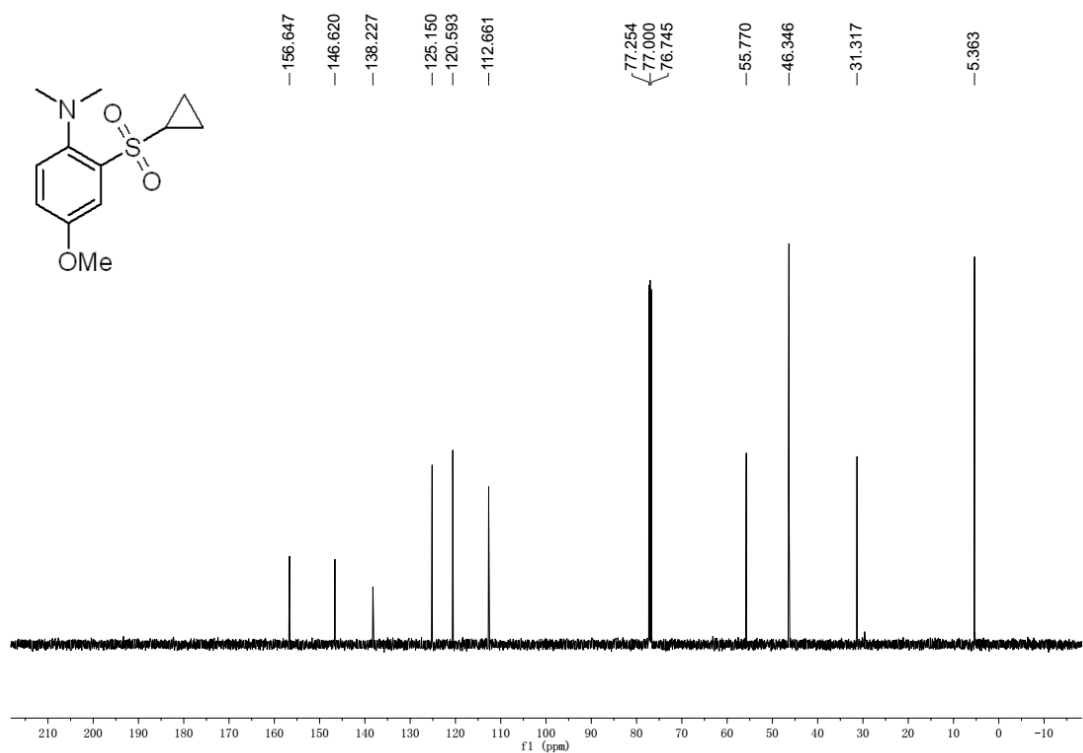
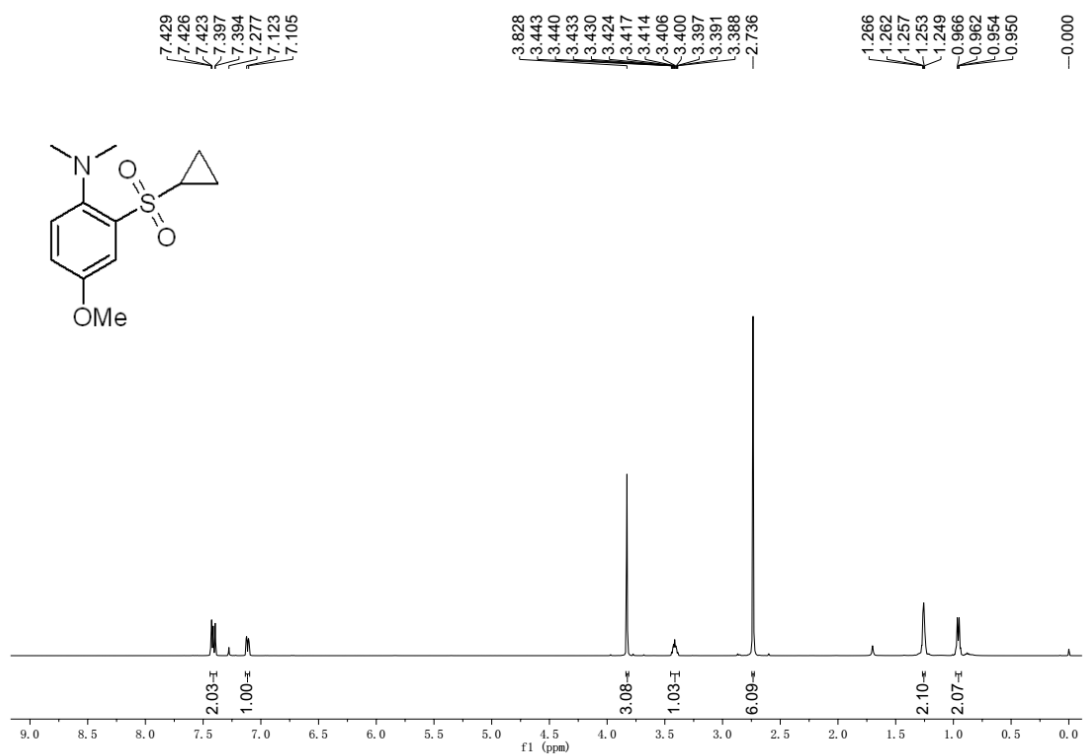
4-Methoxy-N,N-dimethyl-2-(pyridin-3-ylsulfonyl)aniline(3an):



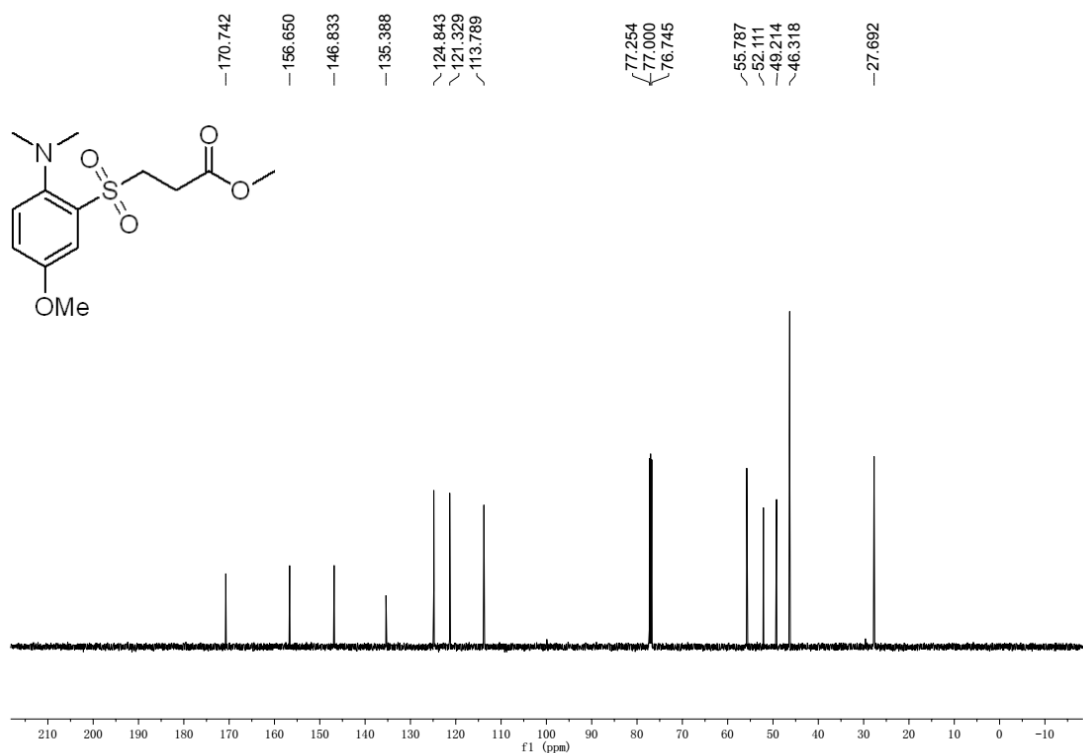
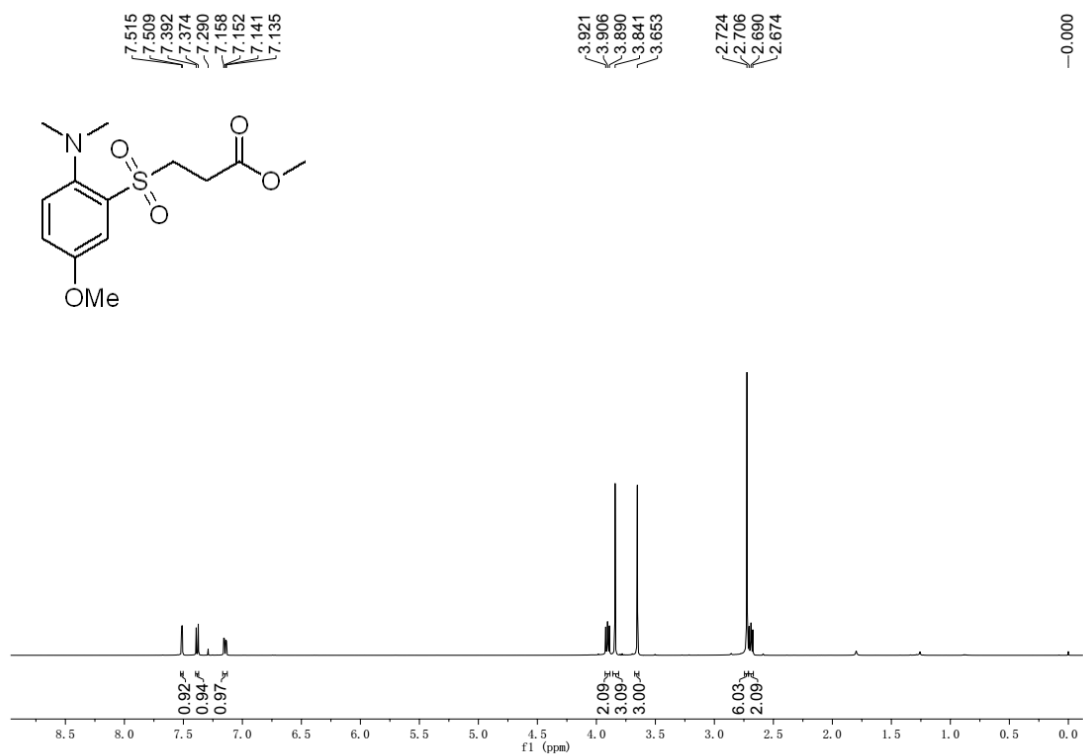
4-Methoxy-N,N-dimethyl-2-(methylsulfonyl)aniline(3ao):



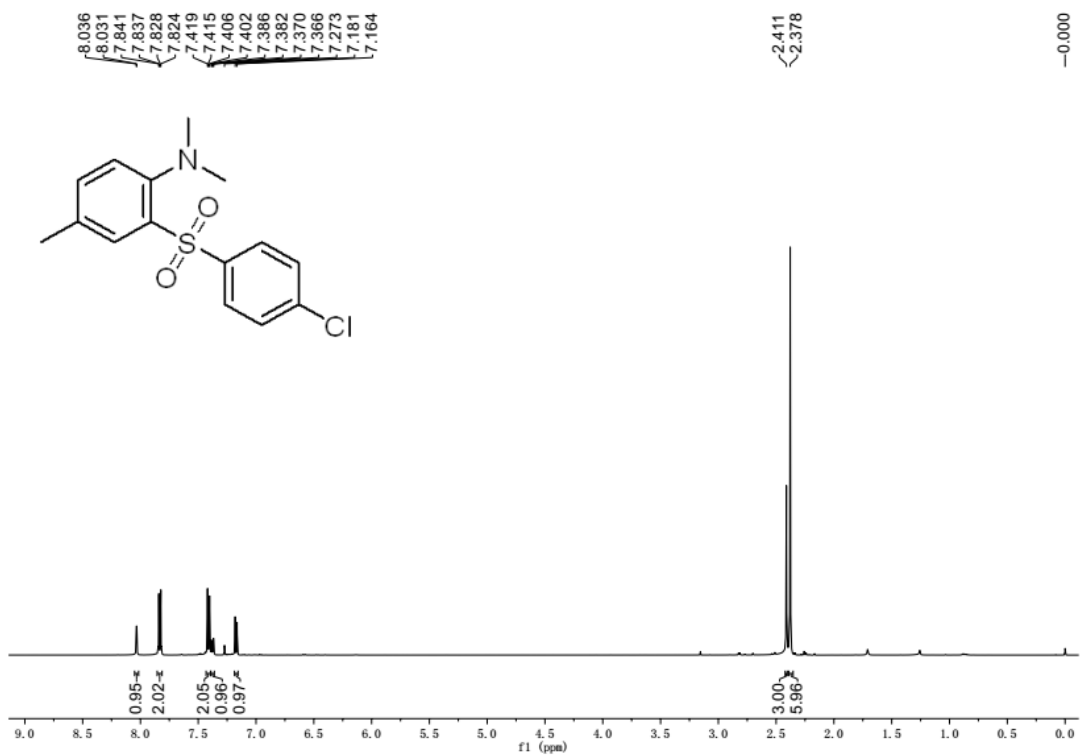
2-(Cyclopropylsulfonyl)-4-methoxy-*N,N*-dimethylaniline (3ap):



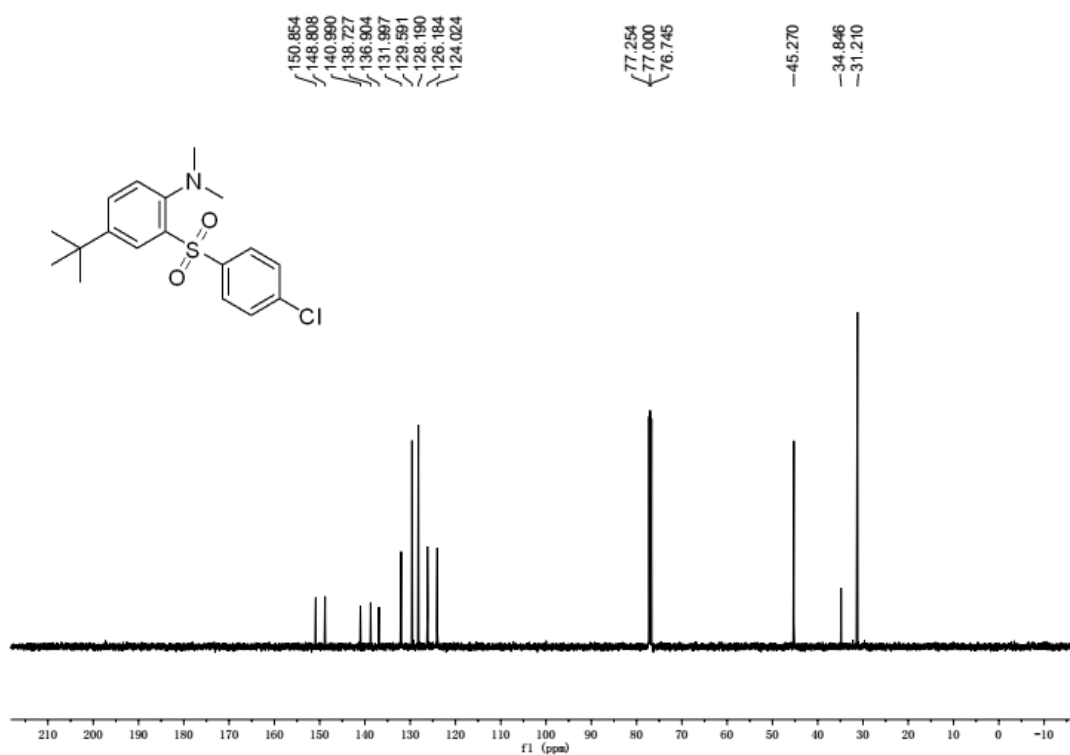
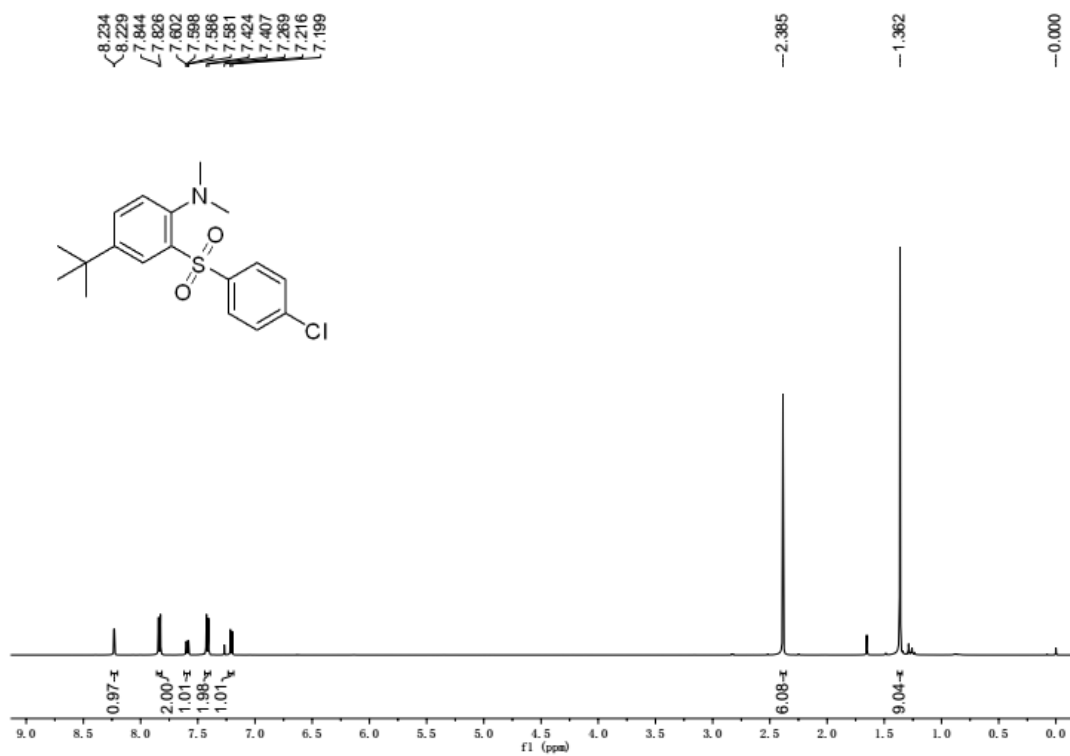
Methyl 3-((2-(dimethylamino)-5-methoxyphenyl)sulfonyl)propanoate (3aq):



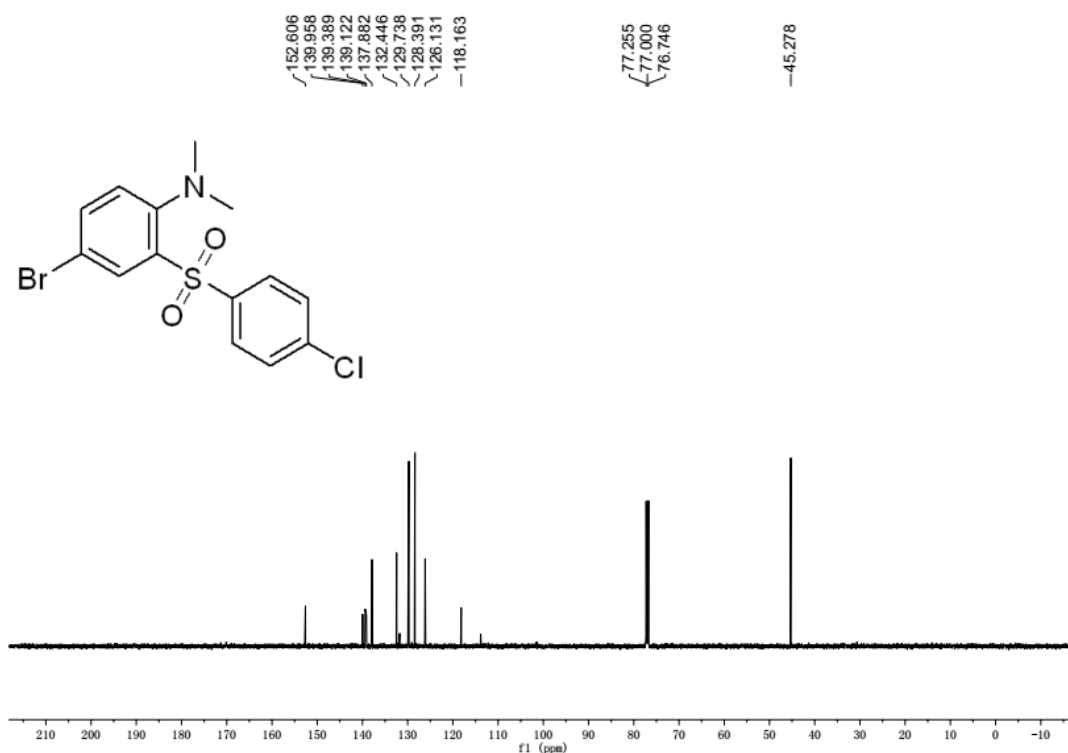
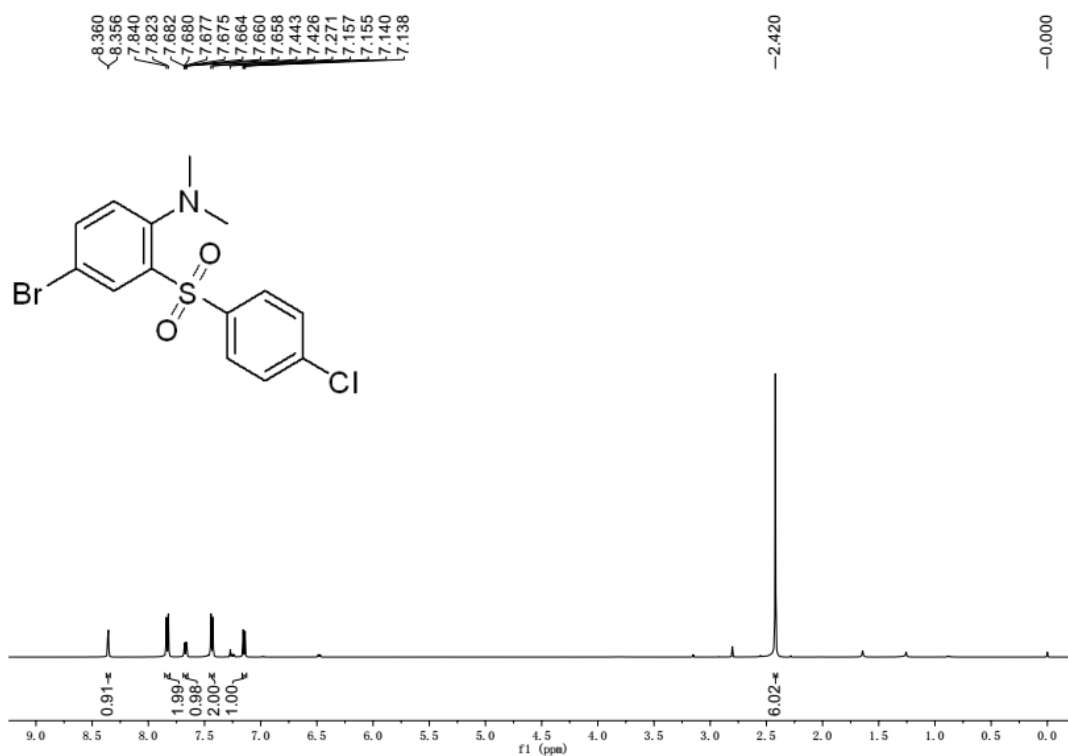
2-((4-Chlorophenyl)sulfonyl)-*N,N*,4-trimethylaniline(3ba):



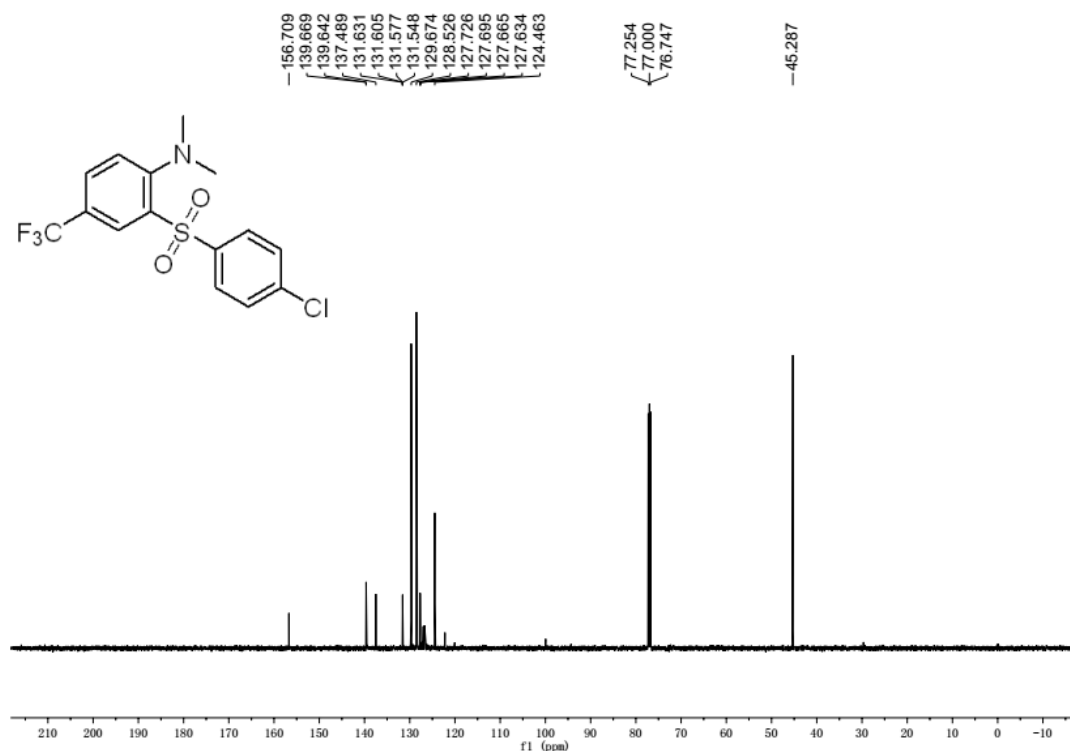
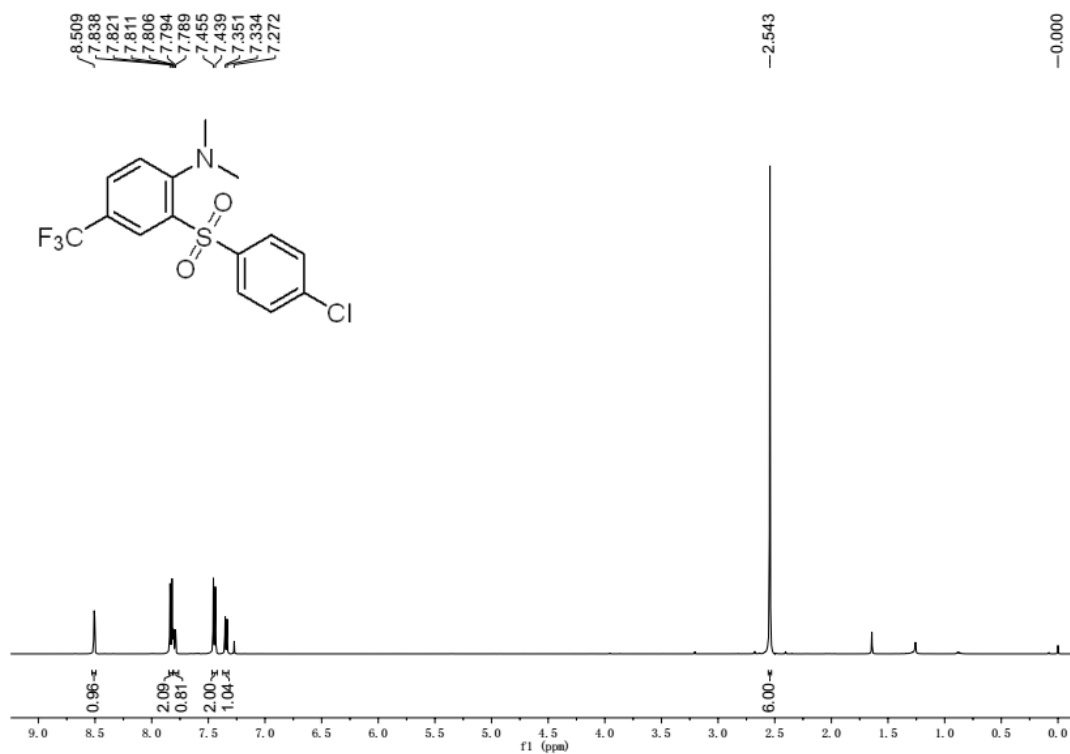
4-(Tert-butyl)-2-((4-chlorophenyl)sulfonyl)-*N,N*-dimethylaniline (3ca):

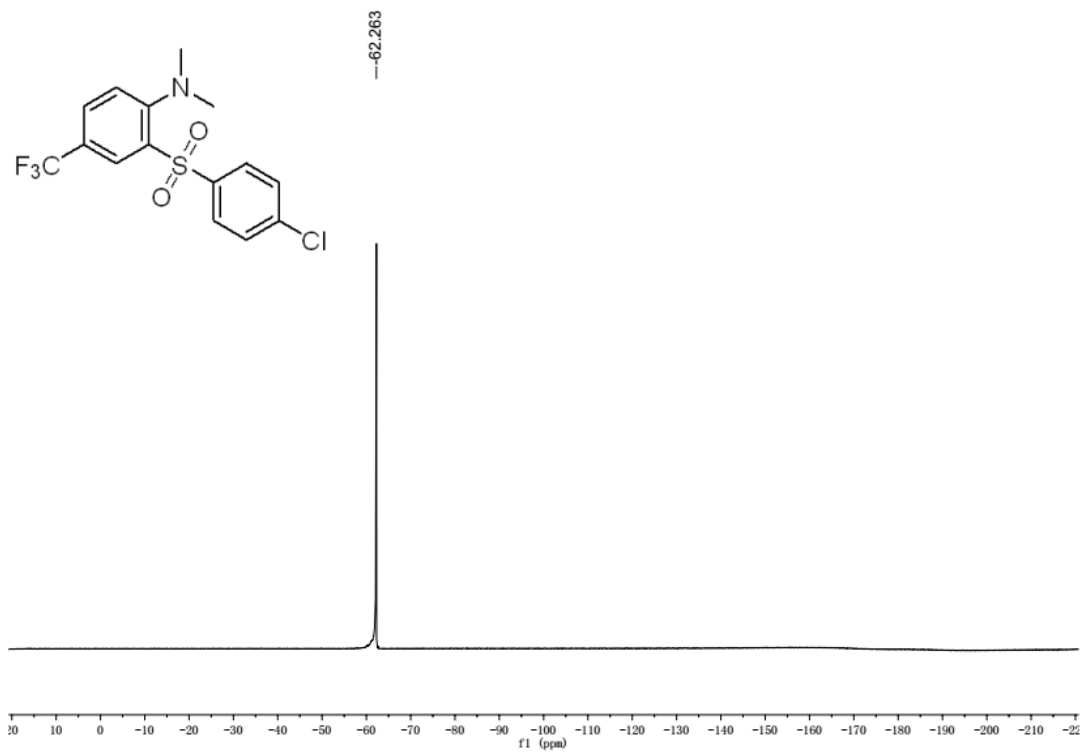


4-Bromo-2-((4-chlorophenyl)sulfonyl)-*N,N*-dimethylaniline(3da):



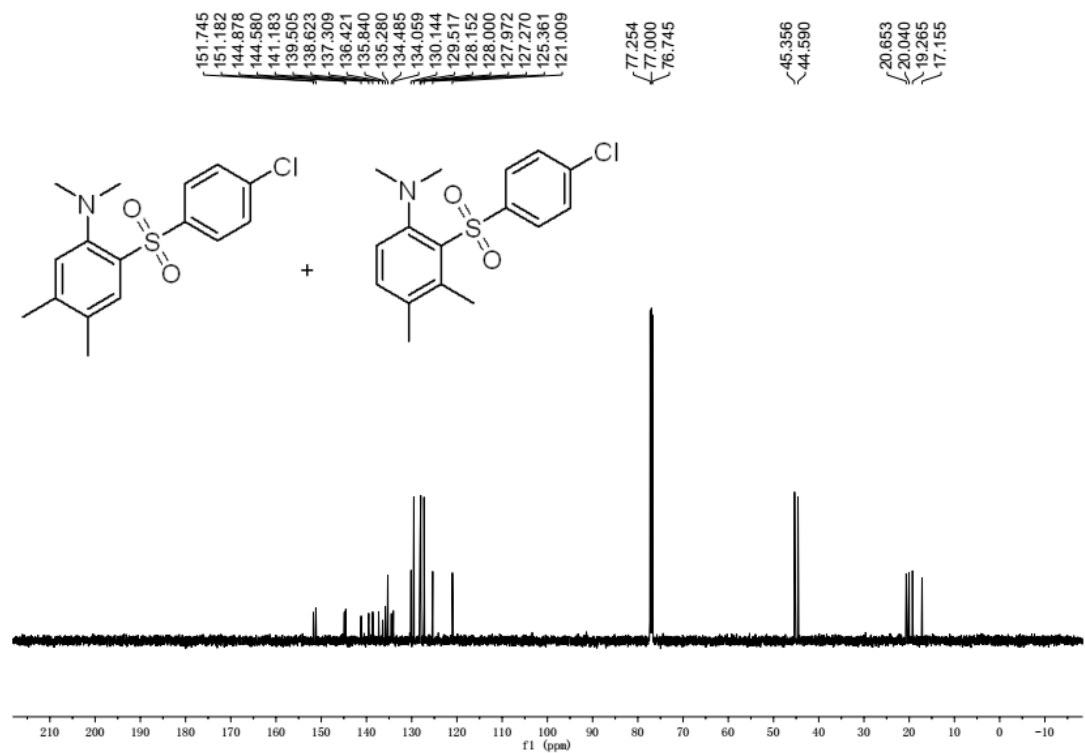
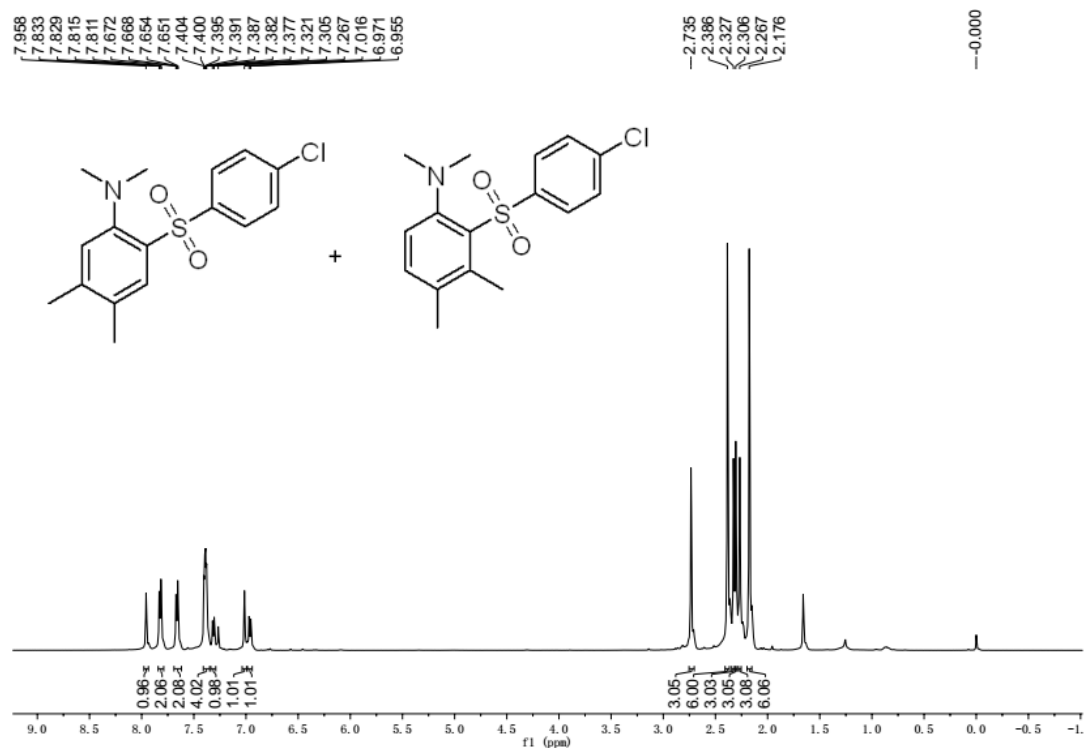
2-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethyl-4-(trifluoromethyl)aniline: (3ea) :



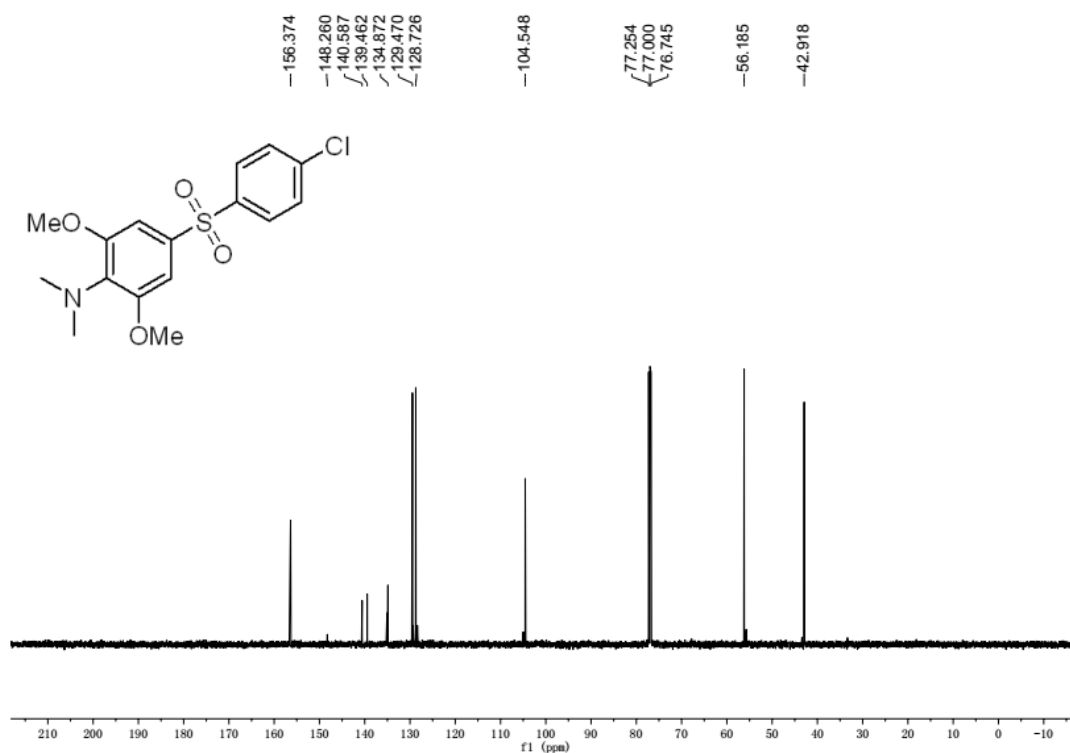
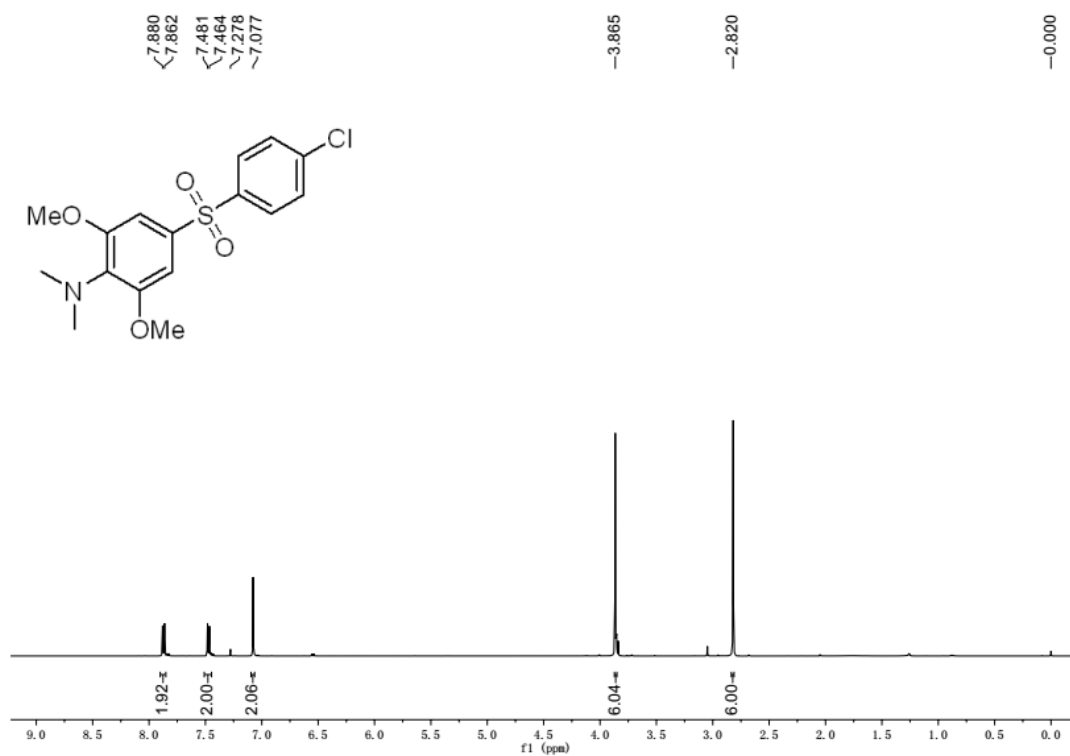


2-((4-Chlorophenyl)sulfonyl)-*N,N*,4,5-tetramethylaniline and 2-((4-

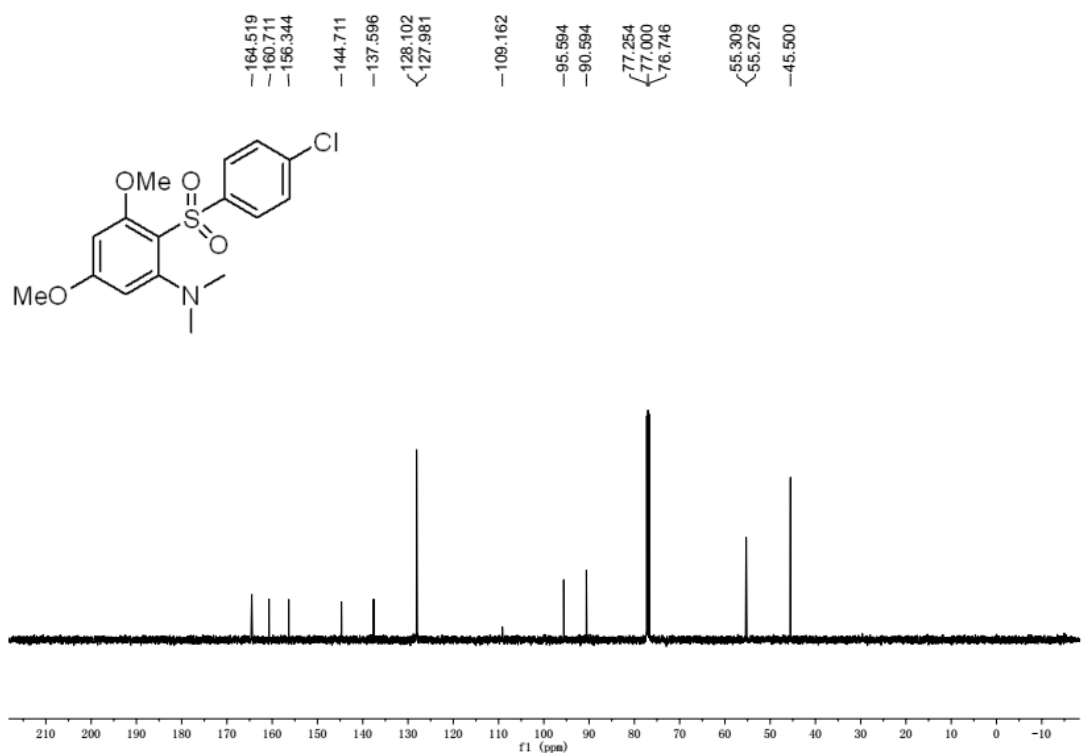
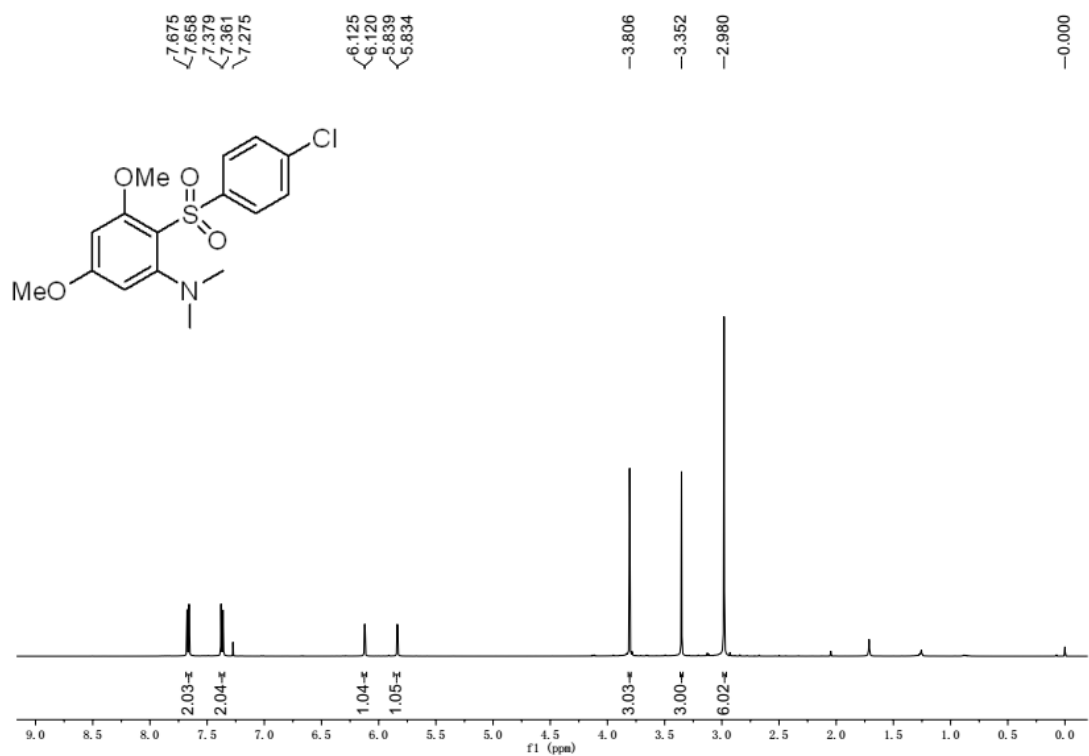
Chlorophenyl)sulfonyl)-*N,N*,3,4-tetramethylaniline (3fa):



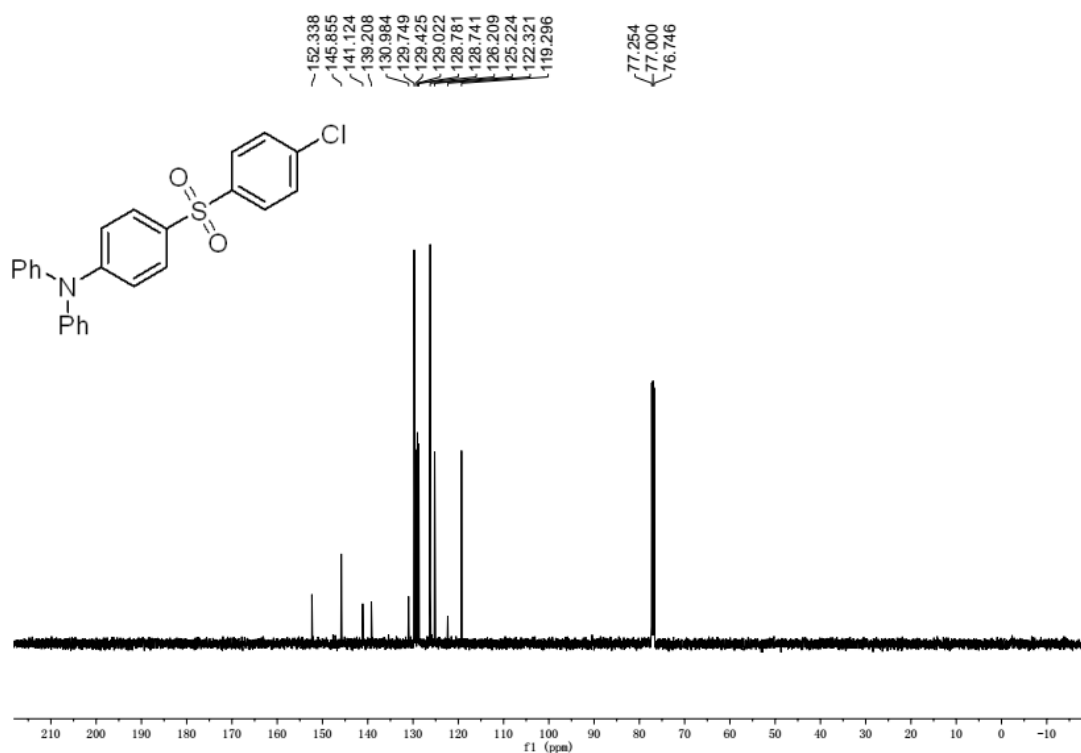
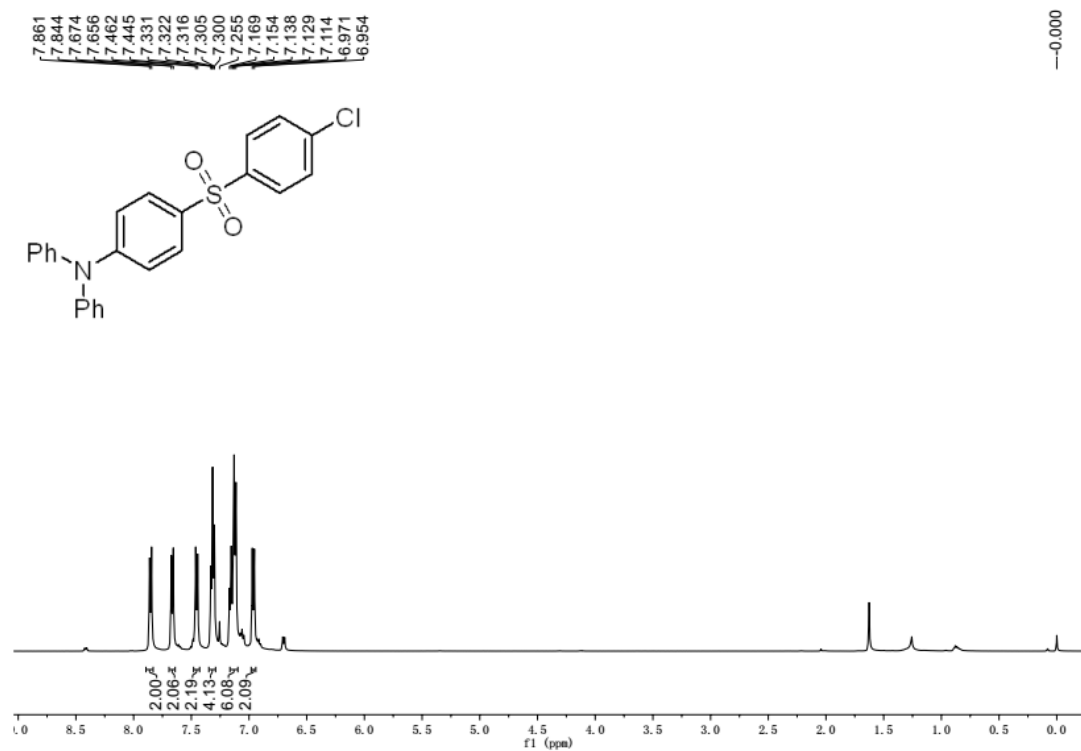
4-((4-Chlorophenyl)sulfonyl)-2,6-dimethoxy-N,N-dimethylaniline (3ga):



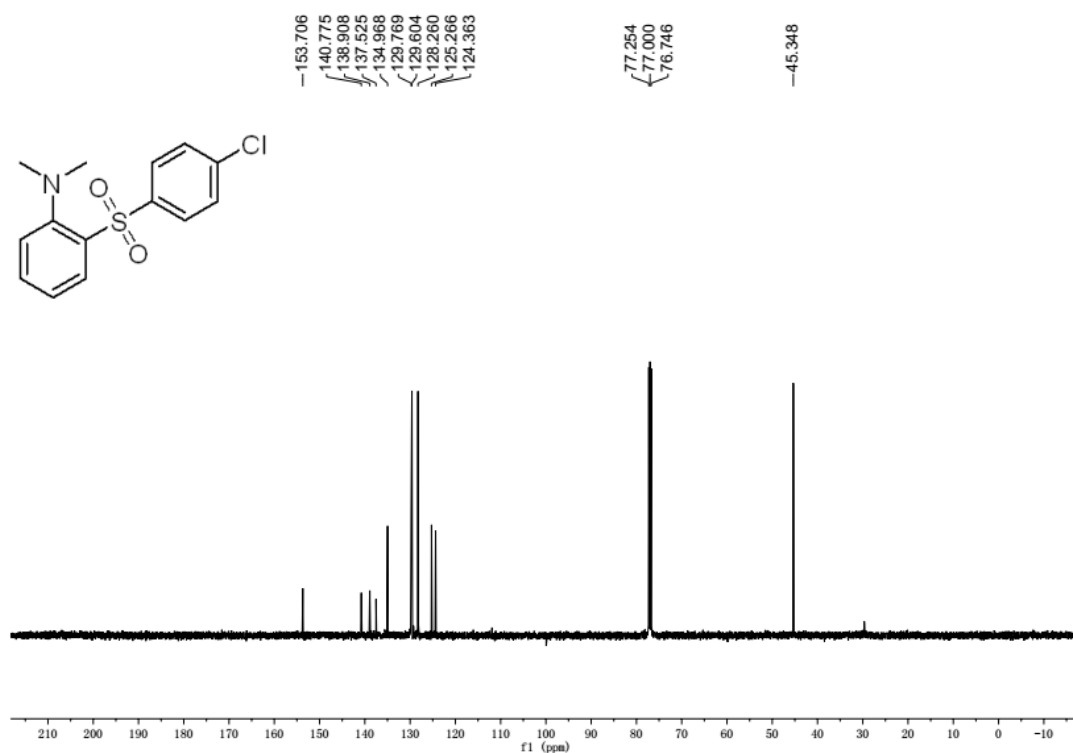
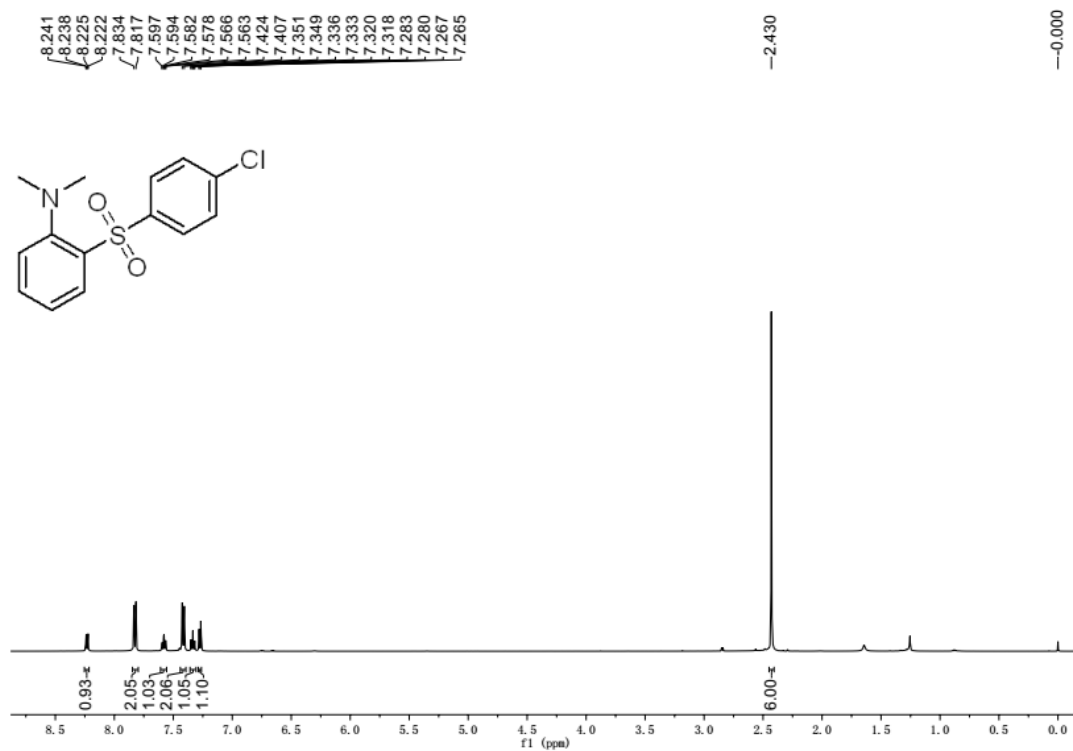
4-((4-Chlorophenyl)sulfonyl)-3,5-dimethoxy-N,N-dimethylaniline (3ha)



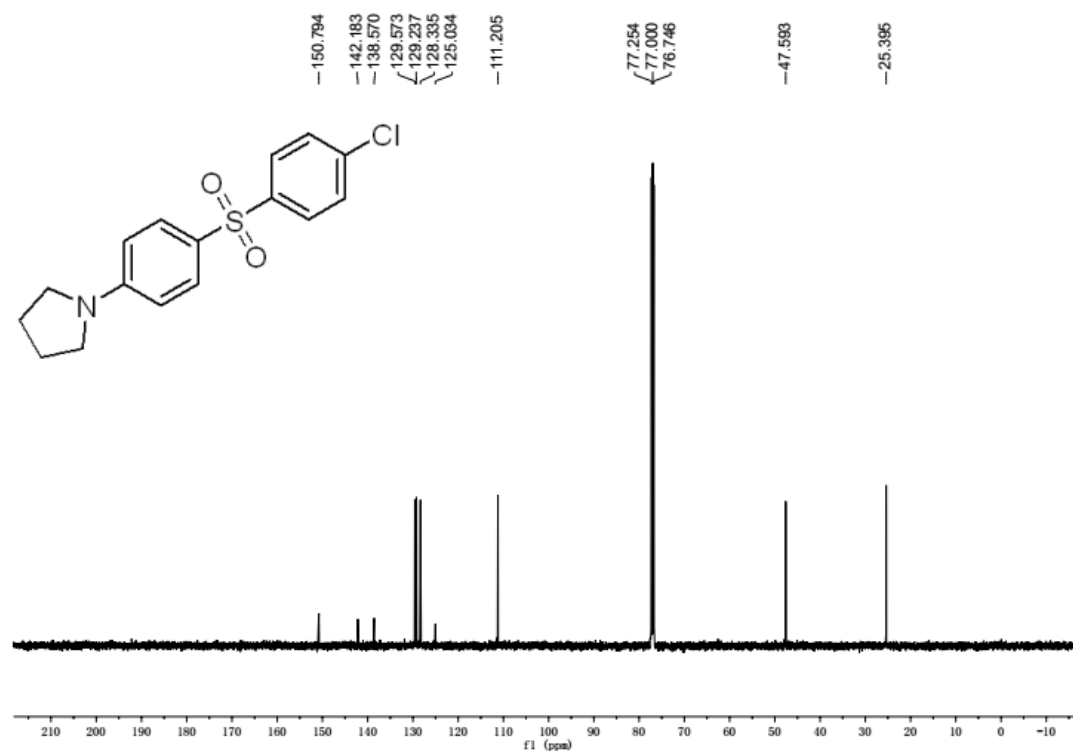
4-((4-Chlorophenyl)sulfonyl)-*N,N*-diphenylaniline (3ia):



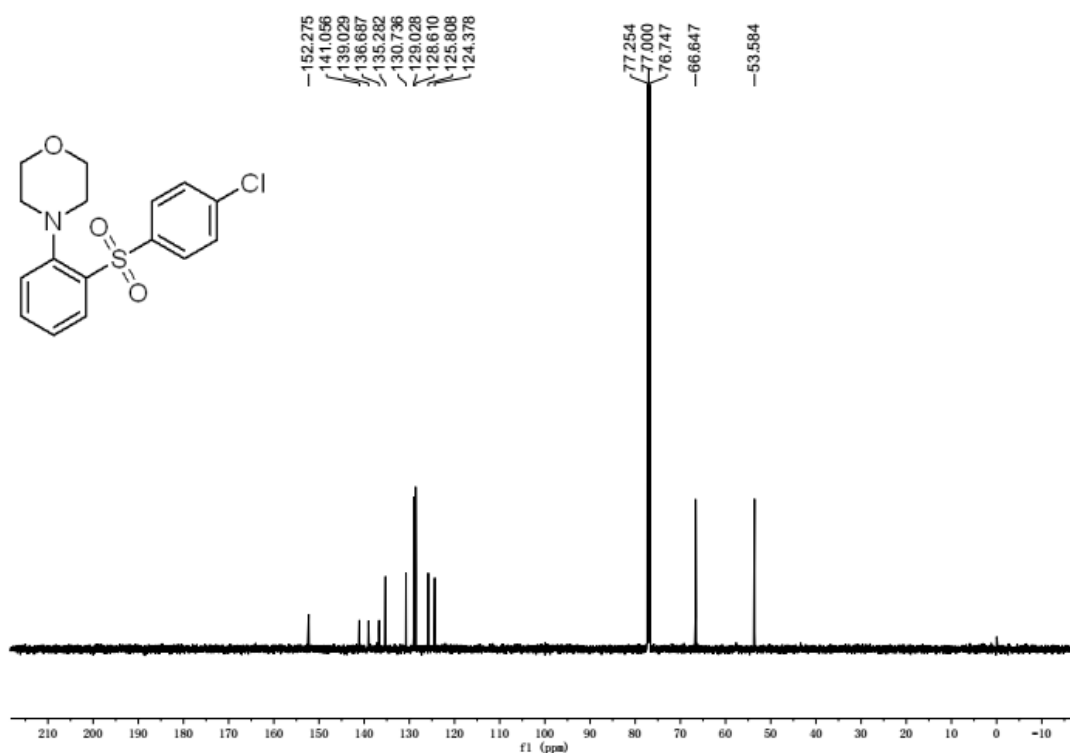
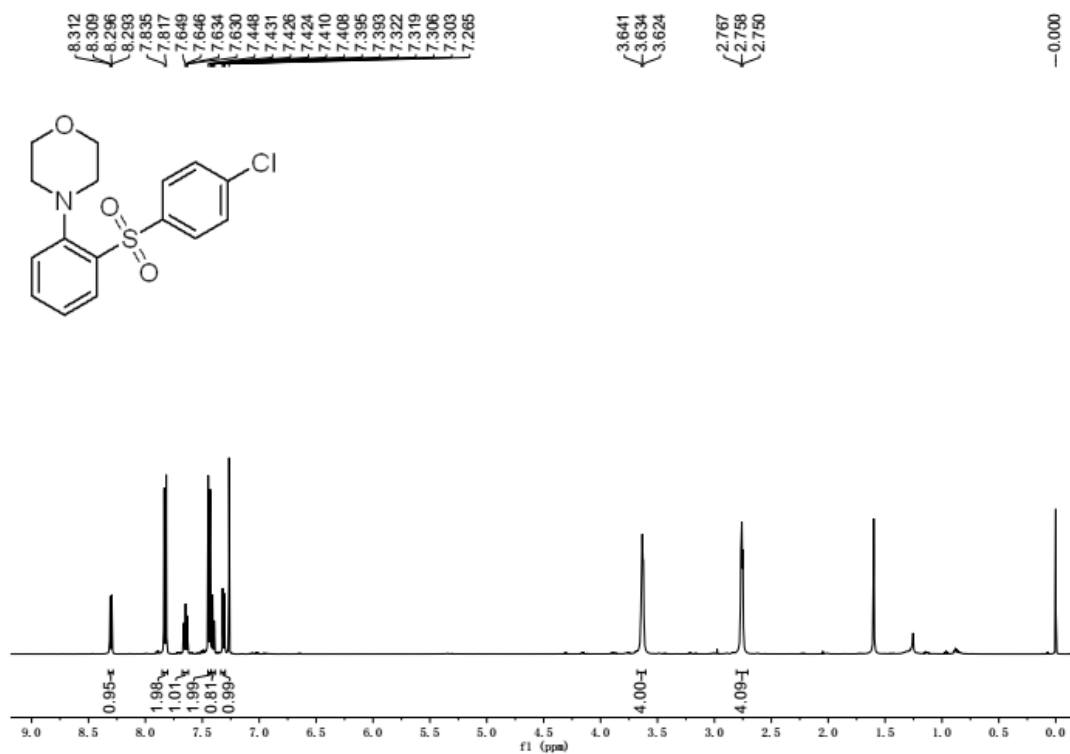
2-((4-chlorophenyl)sulfonyl)-*N,N*-dimethylaniline (3ja)



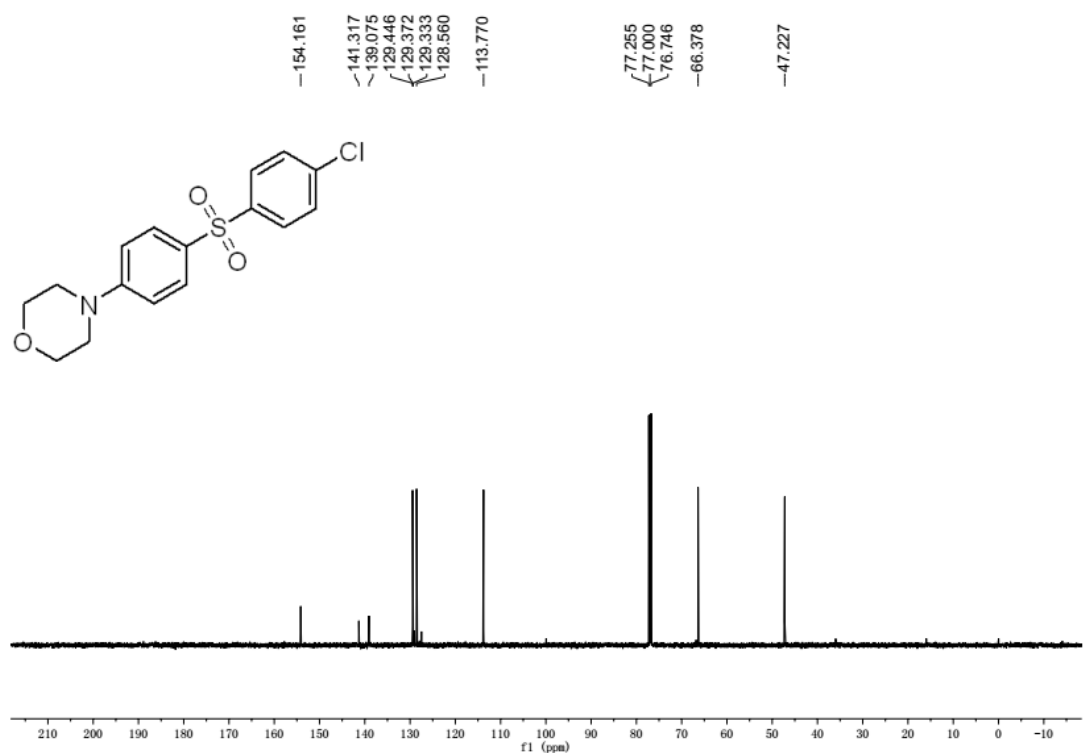
1-(4-((4-Chlorophenyl)sulfonyl)phenyl)pyrrolidine (3ka):



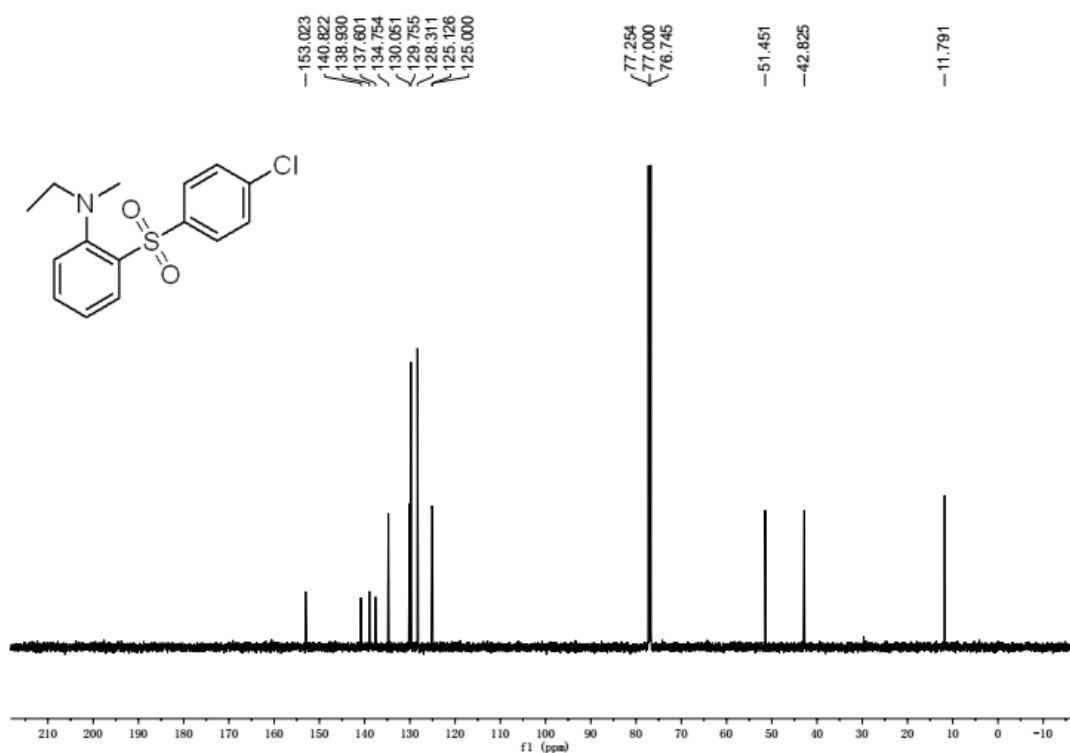
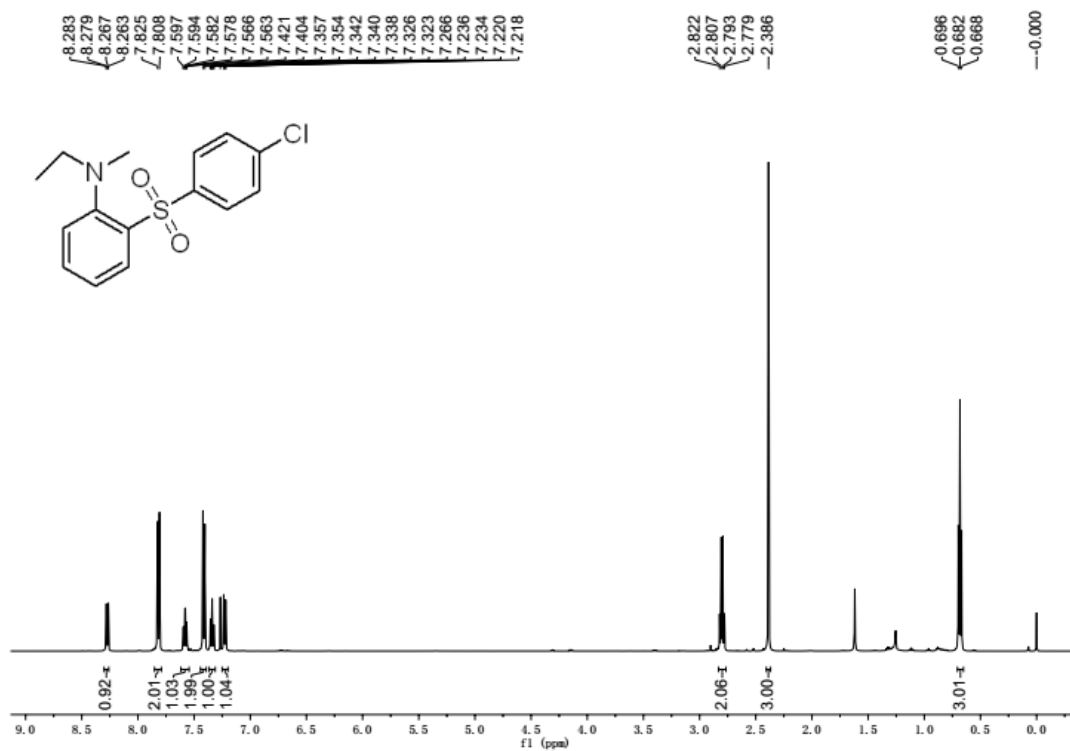
4-(2-((4-Chlorophenyl)sulfonyl)phenyl)morpholine (3la):



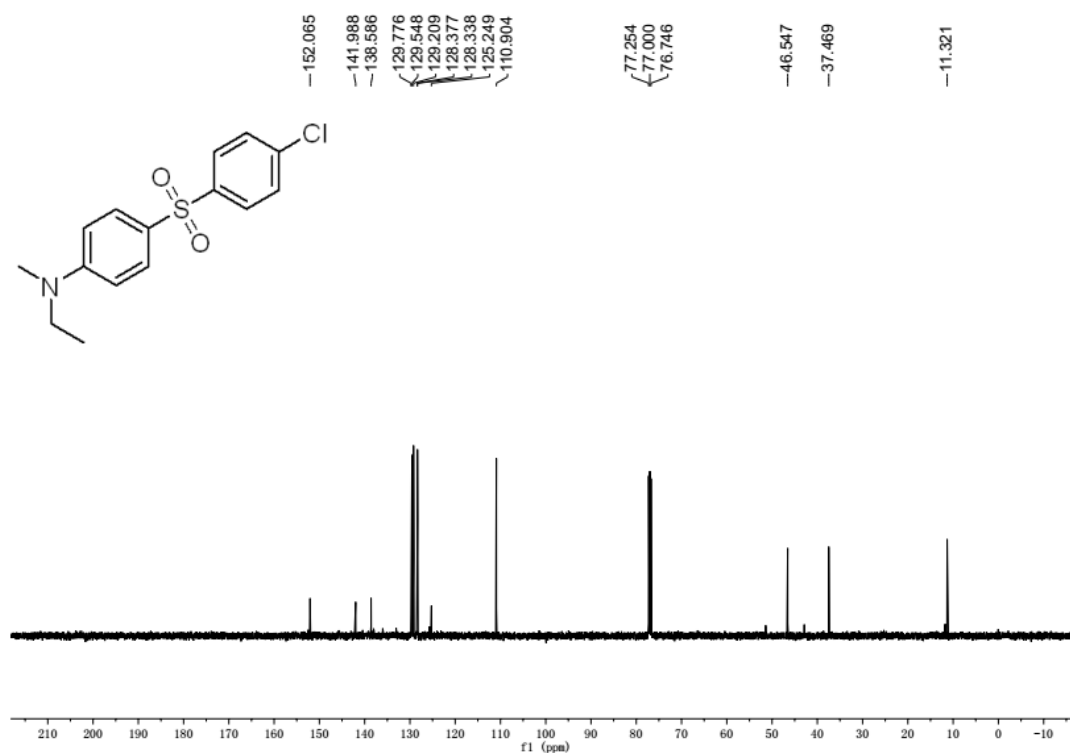
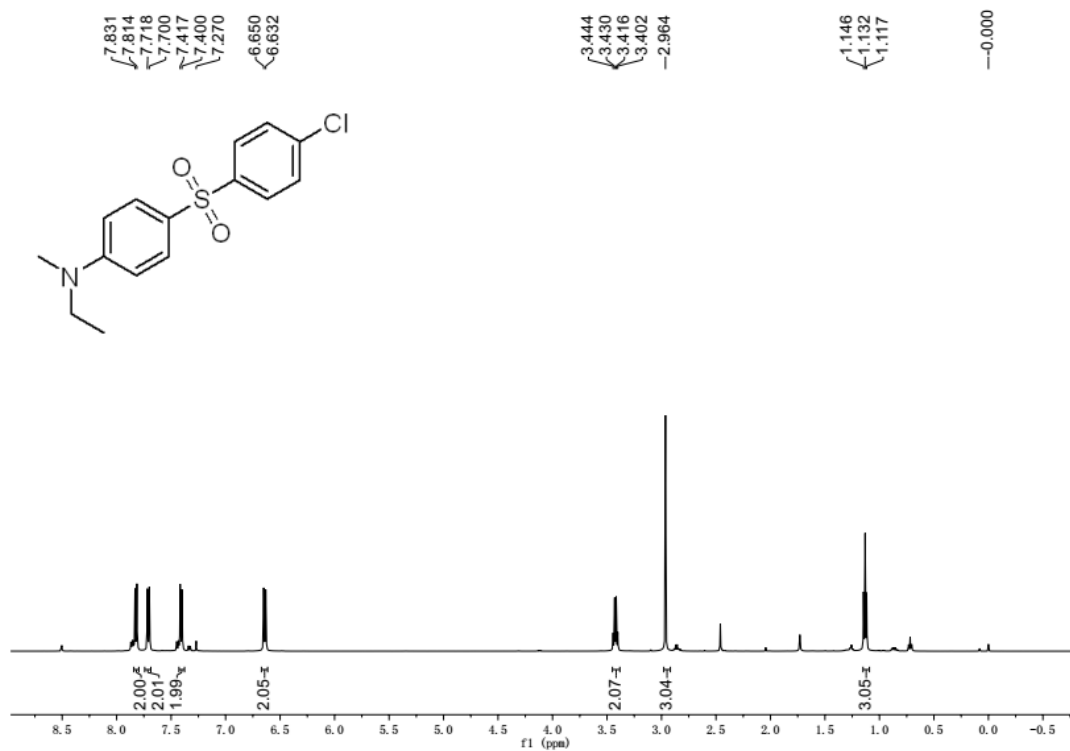
4-(4-((4-Chlorophenyl)sulfonyl)phenyl)morpholine (3la):



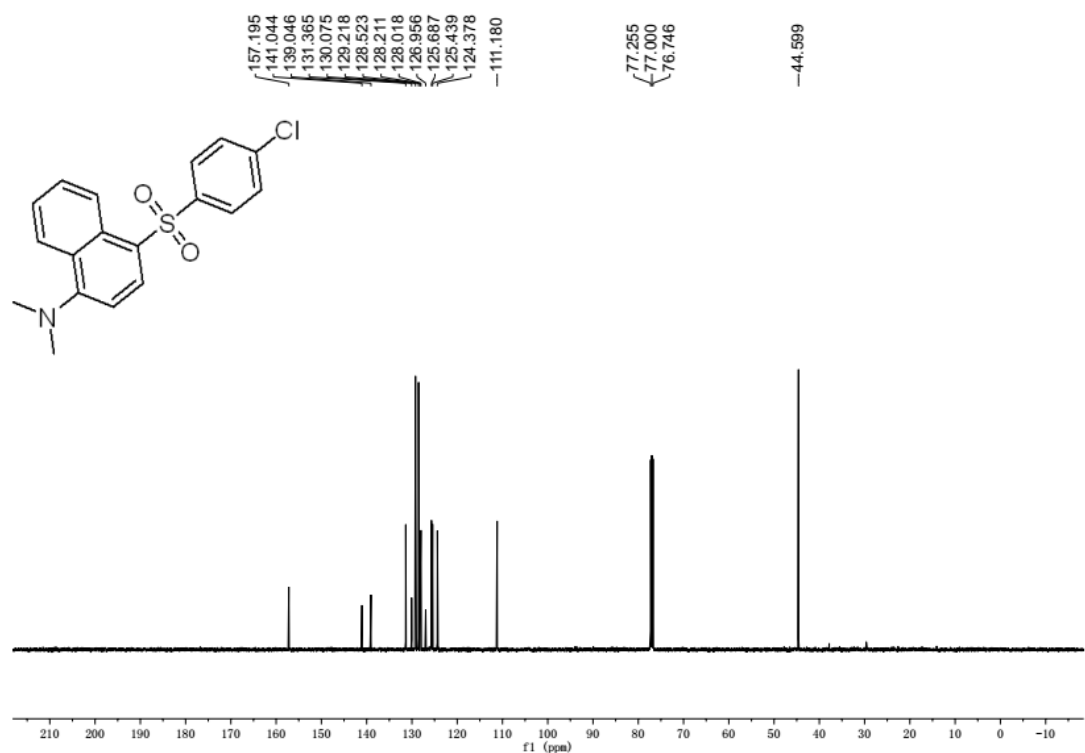
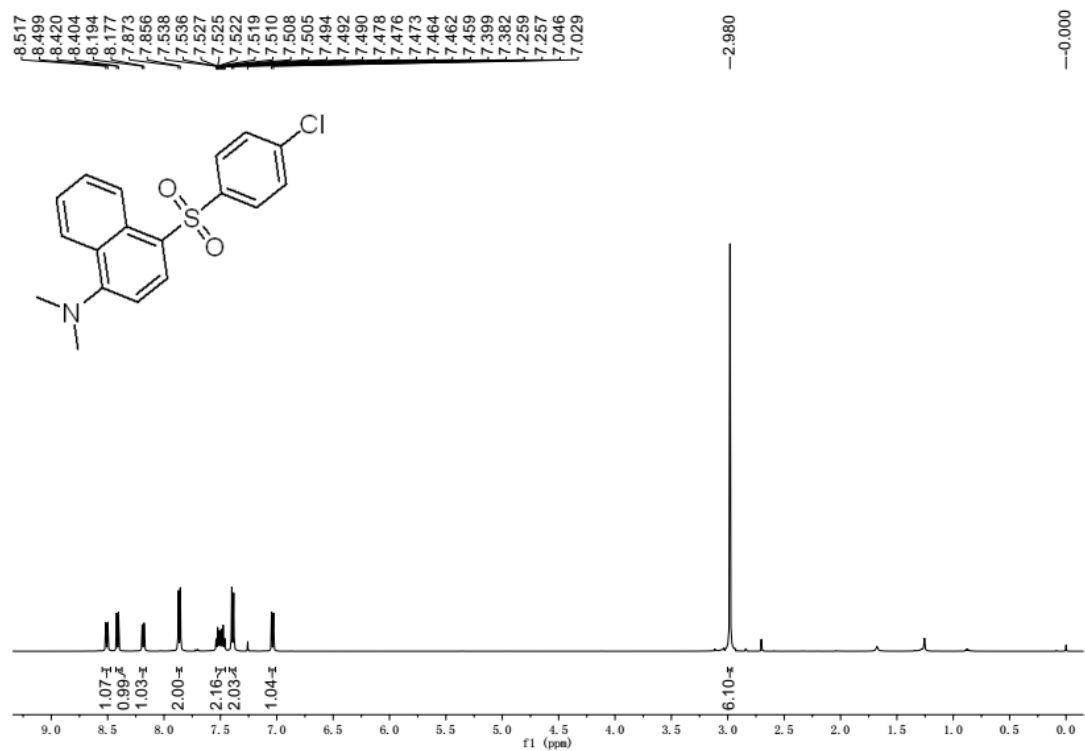
2-((4-Chlorophenyl)sulfonyl)-*N*-ethyl-*N*-methylaniline (3ma):



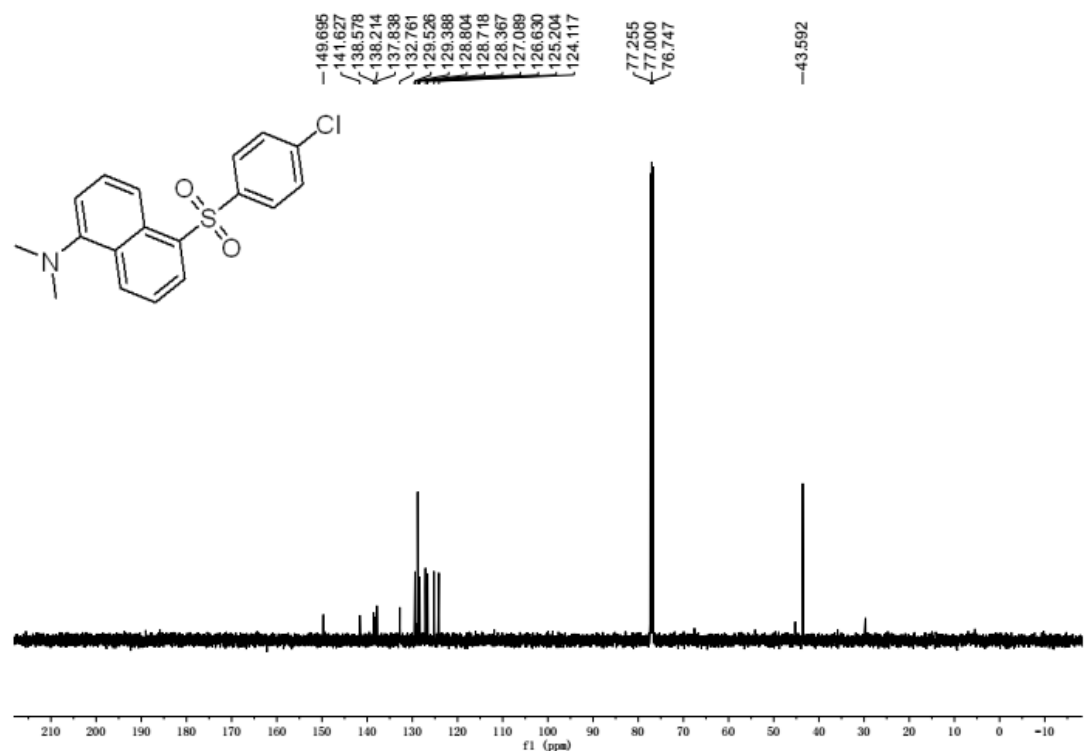
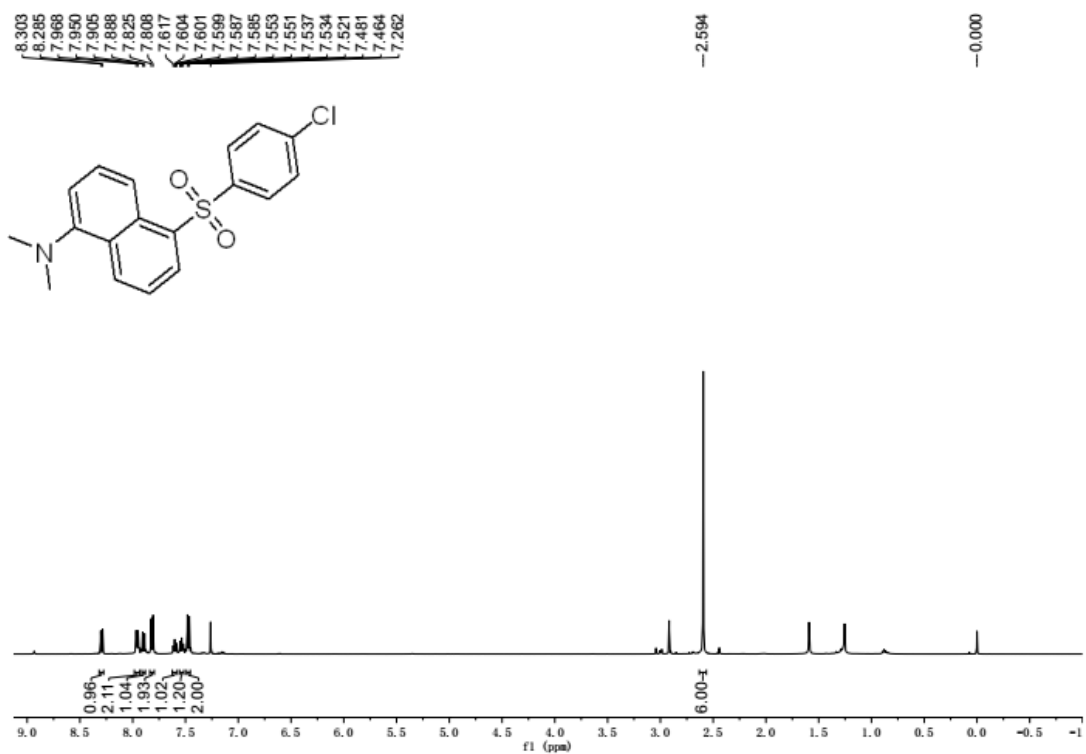
4-((4-Chlorophenyl)sulfonyl)-N-ethyl-N-methylaniline (3ma):



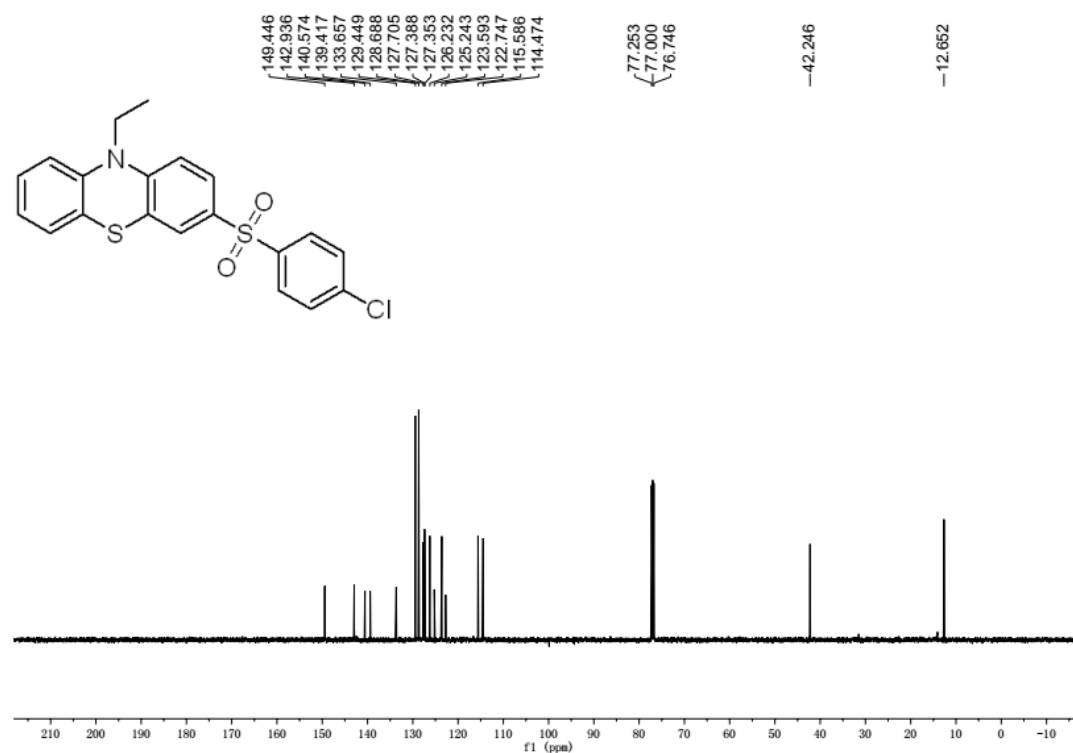
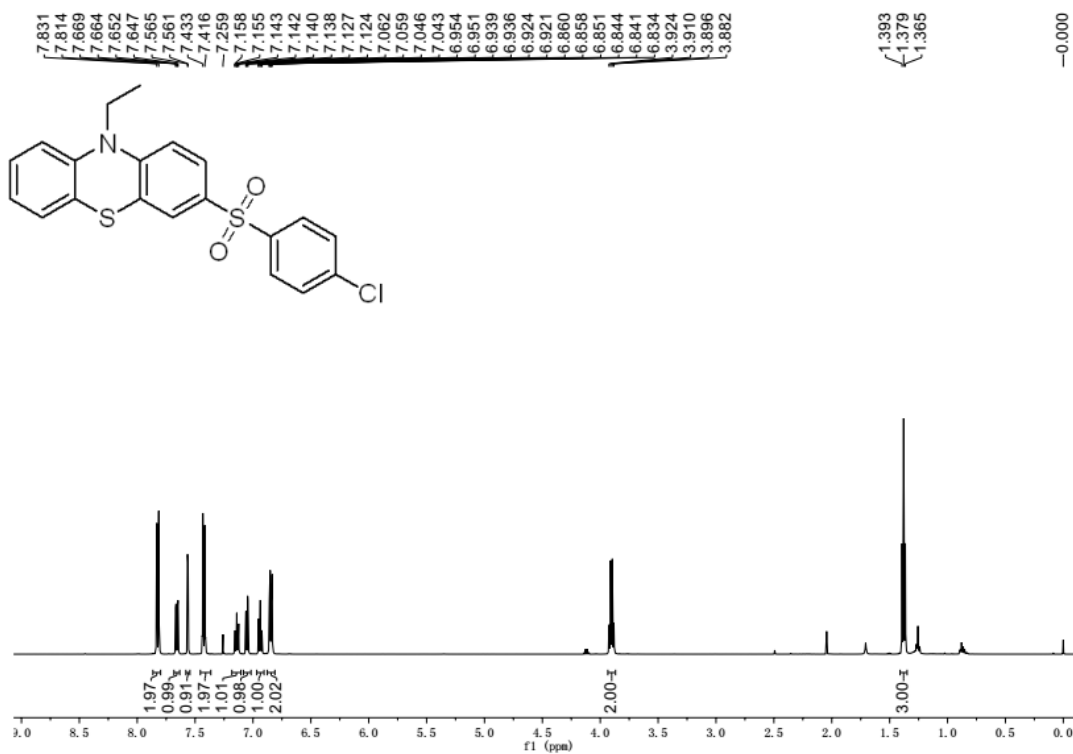
4-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylnaphthalen-1-amine (3na):



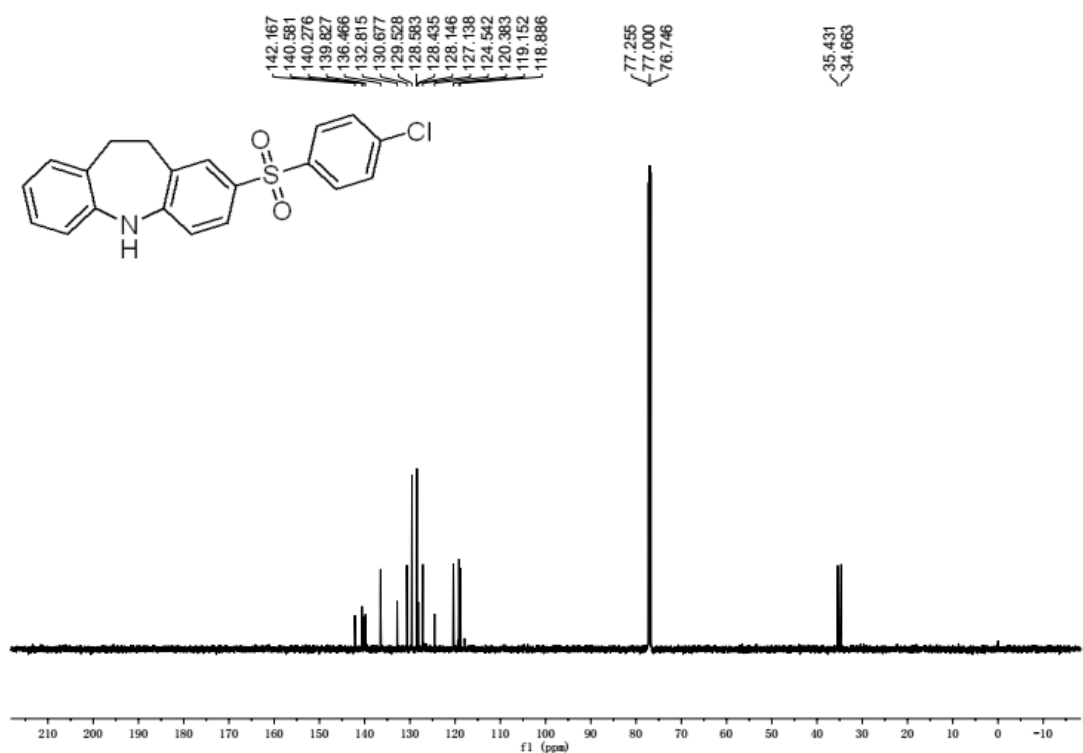
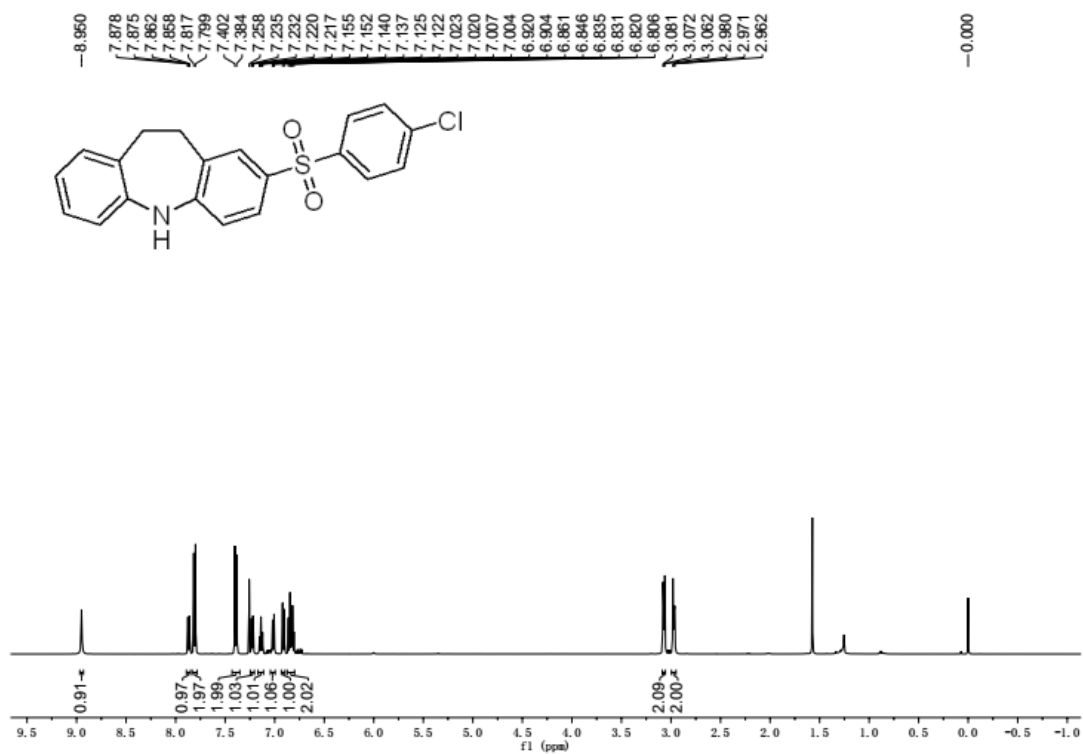
5-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylnaphthalen-1-amine (3na):



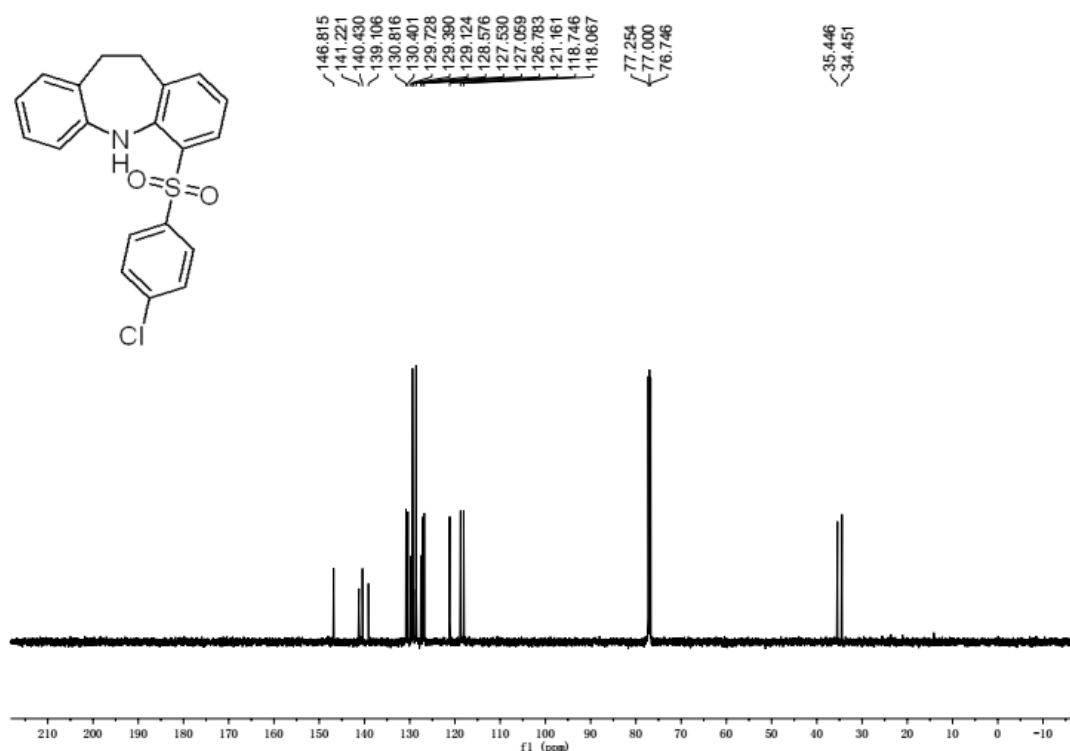
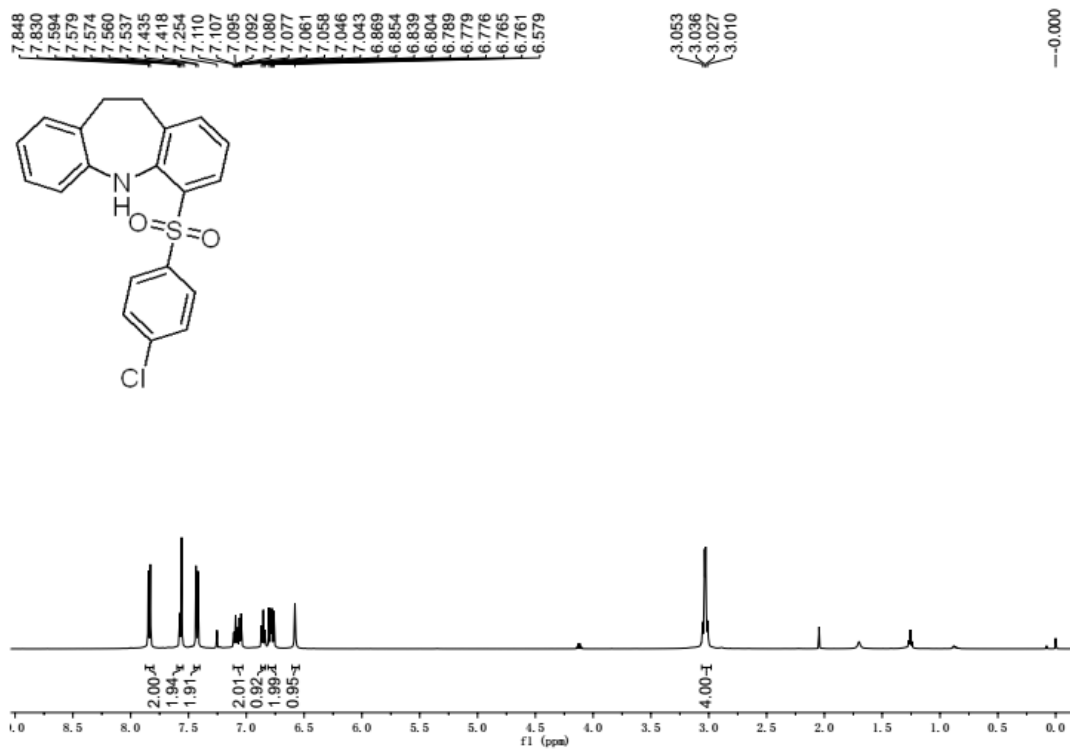
3-((4-Chlorophenyl)sulfonyl)-10-ethyl-10H-phenothiazine (30a):



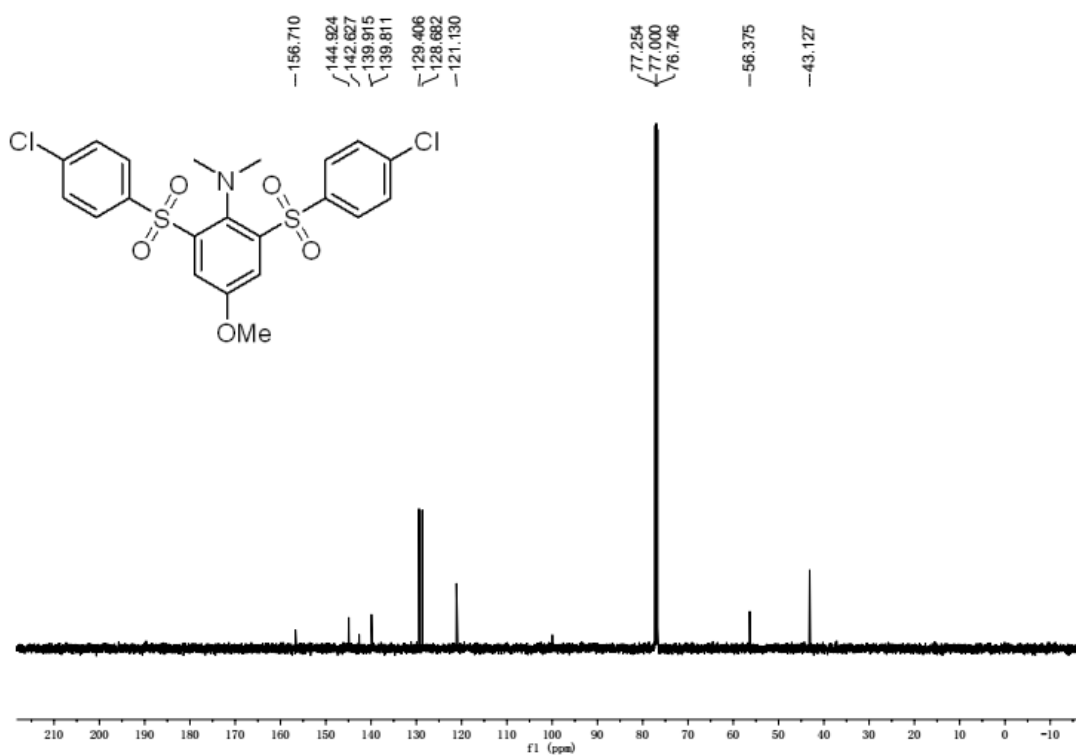
2-((4-Chlorophenyl)sulfonyl)-10,11-dihydro-5H-dibenzo[b,f]azepine(3pa):



4-((4-Chlorophenyl)sulfonyl)-10,11-dihydro-5H-dibenzo[b,f]azepine(3pa):

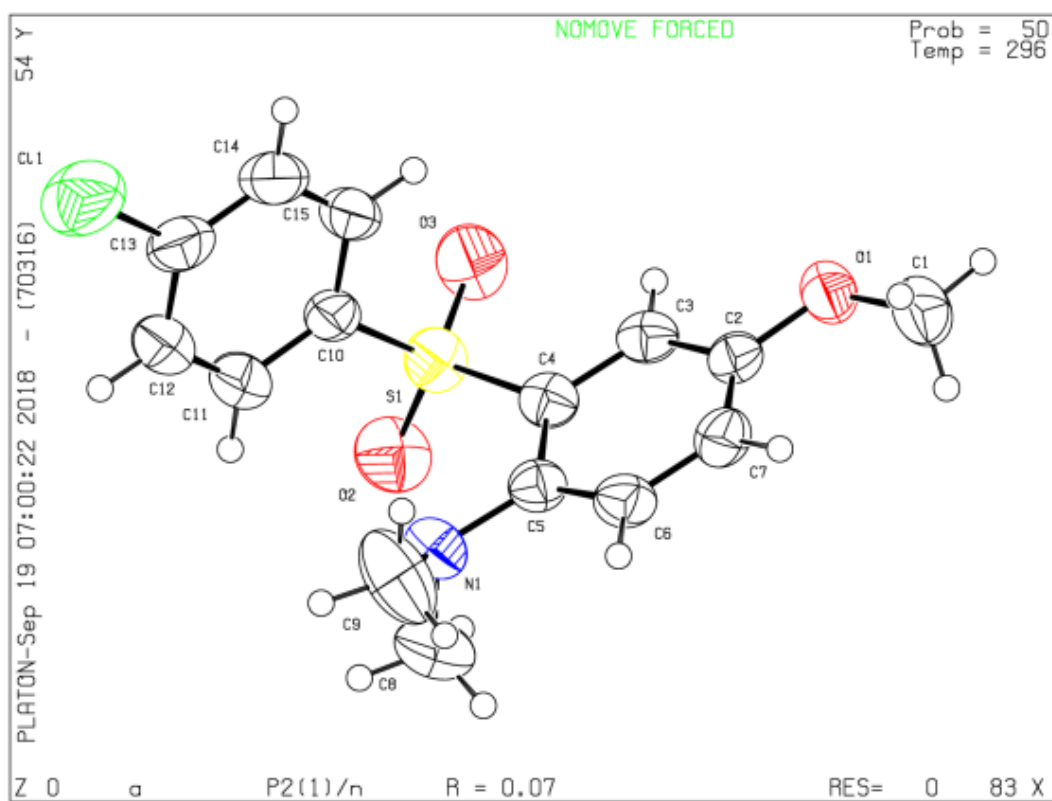
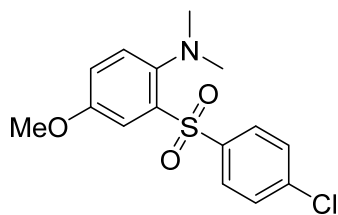


2,6-bis((4-chlorophenyl)sulfonyl)-4-methoxy-N,N-dimethylaniline(4aa):



(D) The X-ray single-crystal diffraction analysis of 3aa

(CCDC 1903203)



The X-ray single-crystal diffraction analysis of 3na

(CCDC 1923102)

