

# Supporting Information

## Direct Aminosulfonylation of Electron-rich (hetero)Arenes Utilizing tert-Butyl Chlorosulfonylcarbamate with Diisopropylethylamine

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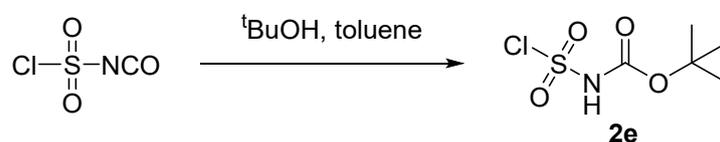
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## 1. General methods

Unless otherwise noted, all the reagents were purchased from commercial suppliers including J&K chemical, Accela, Bidepharm, Adamas and used without further purification. The progress of all the reactions was monitored by thin layer chromatography with standard TLC silica gel plates, and the developed plates were visualized under UV light. All the compounds were purified by column chromatography. Chromatography was performed on silica gel (100–200 mesh). Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400/500/600 NMR spectrometer. Chemical shifts were reported in parts per million (ppm,  $\delta$ ). Proton coupling multiplicity are described as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Tetramethylsilane (TMS) was used as internal standard ( $^1\text{H}$  NMR: TMS at 0.00 ppm;  $\text{CHCl}_3$  at 7.26 ppm, DMSO at 2.50 ppm;  $^{13}\text{C}$  NMR:  $\text{CHCl}_3$  at 77.16 ppm, DMSO at 39.52 ppm). Low-resolution mass spectra (LRMS) were recorded using an Agilent HPLC-MS (1200-6110). High-resolution mass spectra (HRMS) were recorded on an Agilent 1290-6545 UHPLC-QTOF (ESI) mass spectrometer.

## 2. Experimental procedures

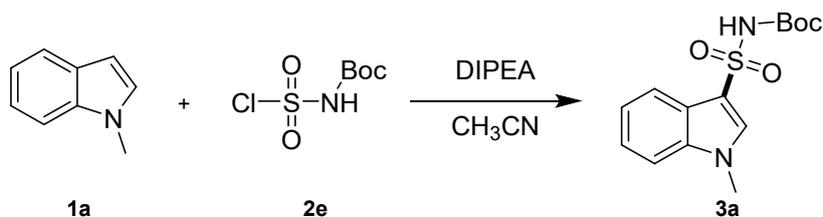
### 2.1 General synthetic procedure of *tert*-butyl chlorosulfonylcarbamate (**2e**)



Add a solution of chlorosulfonyl isocyanate (1.928 g, 13.62 mmol, 1.0 equiv.) in 5.4 mL of toluene dropwise to a solution of anhydrous *tert*-butanol (1.106 g, 14.92 mmol, 1.1 equiv.) in 0.8 mL of anhydrous toluene under argon at 0 °C. Stir the reaction mixture vigorously for 1 hour at 0 °C. Add 14.0 mL of petroleum ether and stir the resulting reaction mixture for an additional 30 minutes at rt. Filter the product, wash with 3 x 10 mL of petroleum ether and dry under vacuum for several minutes to yield 2.3 g *tert*-butyl (chlorosulfonyl)carbamate, white solid, yield = 78%. Store the product under argon at -18°C until use.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.46 (s, 1H), 1.57 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  147.63, 87.21, 28.01. The data were consistent with the reference.<sup>1</sup>

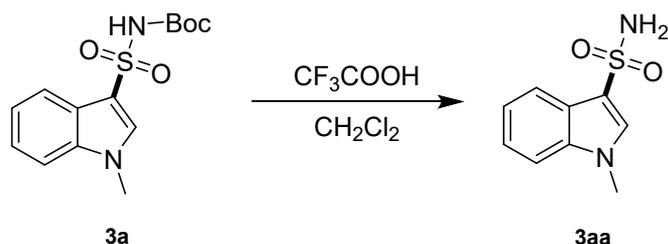


### 2.2 General synthetic procedure of aminosulfonylation of electron-rich (hetero)arenes



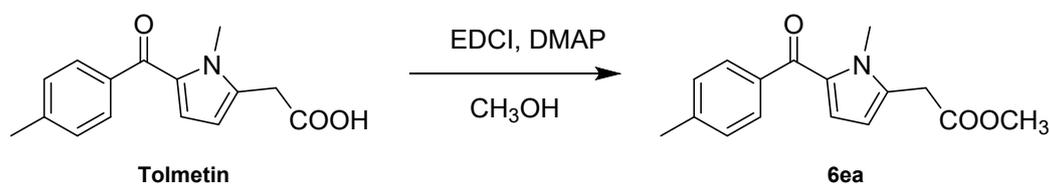
To an oven dried 8 mL vial with a magnetic stir bar was added 1-methyl-1*H*-indole **1a** (52.5 mg, 0.4 mmol), fresh prepared *tert*-butyl (chlorosulfonyl)carbamate **2e** (172.5 mg, 0.8 mmol) and anhydrous  $\text{CH}_3\text{CN}$  (4.0 mL, 0.1 M). Then, *N,N*-diisopropylethylamine (103.4 mg, 0.8 mmol) was added. After that, the vial was capped and stirred under room temperature for 1 hours. The mixture was transferred to a 25 mL round-bottom flask and the solvent was removed under reduced pressure. The residue was purified by flash silica column chromatography eluting with 30-60% ethyl acetate/petroleum ether to afford the desired product **3a**.

## 2.3 General synthetic procedure for one-pot deprotection of -Boc

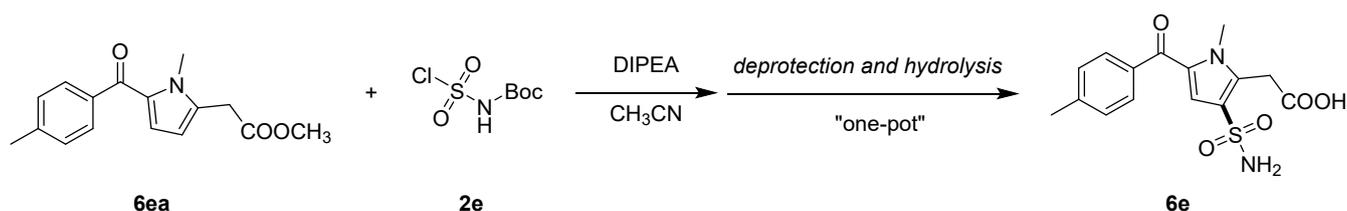


After the aminosulfonylation reaction (see section 2.2) was completed, the mixture was transferred to a 25 mL round-bottom flask and the solvent was removed under reduced pressure. Without purification, 10 mL  $\text{CH}_2\text{Cl}_2$  and 2 mL  $\text{CF}_3\text{COOH}$  were added. The mixture was stirred at room temperature for 2 hours and the solvent was evaporated in vacuo. Then, 15 mL aqueous saturated  $\text{NaHCO}_3$  solution was added. The aqueous layer was extracted three times with ethyl acetate (5 mL  $\times$  3). The combined organic phase was washed with saturated brine (15 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by flash silica column chromatography eluting with 2-5%  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  to afford the desired product 1-methyl-1*H*-indole-3-sulfonamide. (**3aa**, pink solid, 89% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.89 – 7.85 (m, 2H), 7.54 (d,  $J = 8.3$  Hz, 1H), 7.32 – 7.27 (m, 1H), 7.22 (t,  $J = 7.5$  Hz, 1H), 7.14 (s, 2H), 3.84 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  136.59, 131.85, 123.32, 122.62, 120.86, 119.66, 117.32, 110.68, 32.82. **LRMS** (ESI) ( $m/z$ ): 211.1  $[\text{M}+\text{H}]^+$ .

## 2.4 The scale-up reaction

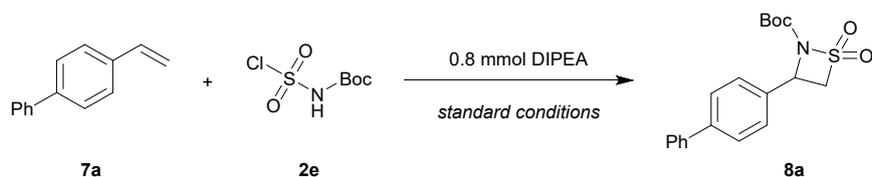


To a 50 mL round-bottom flask with a magnetic stir bar was added Tolmetin (1 g, 3.89 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 1.49 g, 7.77 mmol), 4-dimethylaminopyridine (DMAP, 95 mg, 0.78 mmol) and  $\text{CH}_3\text{OH}$  (25 mL). The reaction was heated to reflux for 16 hours and the solvent was removed under reduced pressure. Then, 30 mL of water was added and the aqueous layer was extracted three times with ethyl acetate (15 mL  $\times$  3). The combined organic phase was washed with saturated brine (15 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by flash silica column chromatography eluting with 20-30% ethyl acetate/petroleum ether to afford the desired white solid product (**6ea**, 1.01 g, 95%).  $^1\text{H NMR}$  (400 MHz,  $\text{Chloroform}-d$ )  $\delta$  7.71 (d,  $J = 8.2$  Hz, 2H), 7.24 (d,  $J = 8.0$  Hz, 2H), 6.67 (d,  $J = 4.0$  Hz, 1H), 6.10 (d,  $J = 4.0$  Hz, 1H), 3.94 (s, 3H), 3.75 (s, 3H), 3.72 (s, 2H), 2.42 (s, 3H); **LRMS** (ESI) ( $m/z$ ): 272.2  $[\text{M}+\text{H}]^+$



To a 100 mL round-bottom flask with a magnetic stir bar was added **6ea** (1.01 g, 3.72 mmol), fresh prepared *tert*-butyl (chlorosulfonyl)carbamate **2e** (1.61 g, 7.45 mmol) and anhydrous  $\text{CH}_3\text{CN}$  (37 mL, 0.1 M). Then, *N,N*-diisopropylethylamine (0.96 g, 7.45 mmol) was added. After that, the vial was capped and stirred under room temperature for 1 hour. The mixture was removed under reduced pressure. Subsequently, 50 mL of 4M aqueous HCl was added to the flask, the solvent was stirred for 4 hours at 90 °C. Then, the aqueous layer was extracted three times with ethyl acetate (25 mL  $\times$  3). The combined organic phase was washed with saturated brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The solvent was removed under reduced pressure then the residue was purified by flash silica column chromatography eluting with 2-5%  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  to afford the desired white solid product. (**6e**, 1.14 g, 91%).  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  12.76 (br, 1H), 7.66 (d,  $J = 7.7$  Hz, 2H), 7.36 (d,  $J = 7.7$  Hz, 2H), 7.18 (s, 2H), 6.81 (s, 1H), 4.12 (s, 2H), 3.84 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  184.87, 169.89, 142.46, 136.02, 135.02, 129.00, 128.97, 128.87, 125.46, 119.96, 33.25, 30.29, 21.10. **HRMS** (ESI) calculated for  $[\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_5\text{S}]^+$   $[\text{M}+\text{H}]^+$ : 337.0853, found  $m/z$  337.0853.

## 2.5 The intermediate trapping experiment

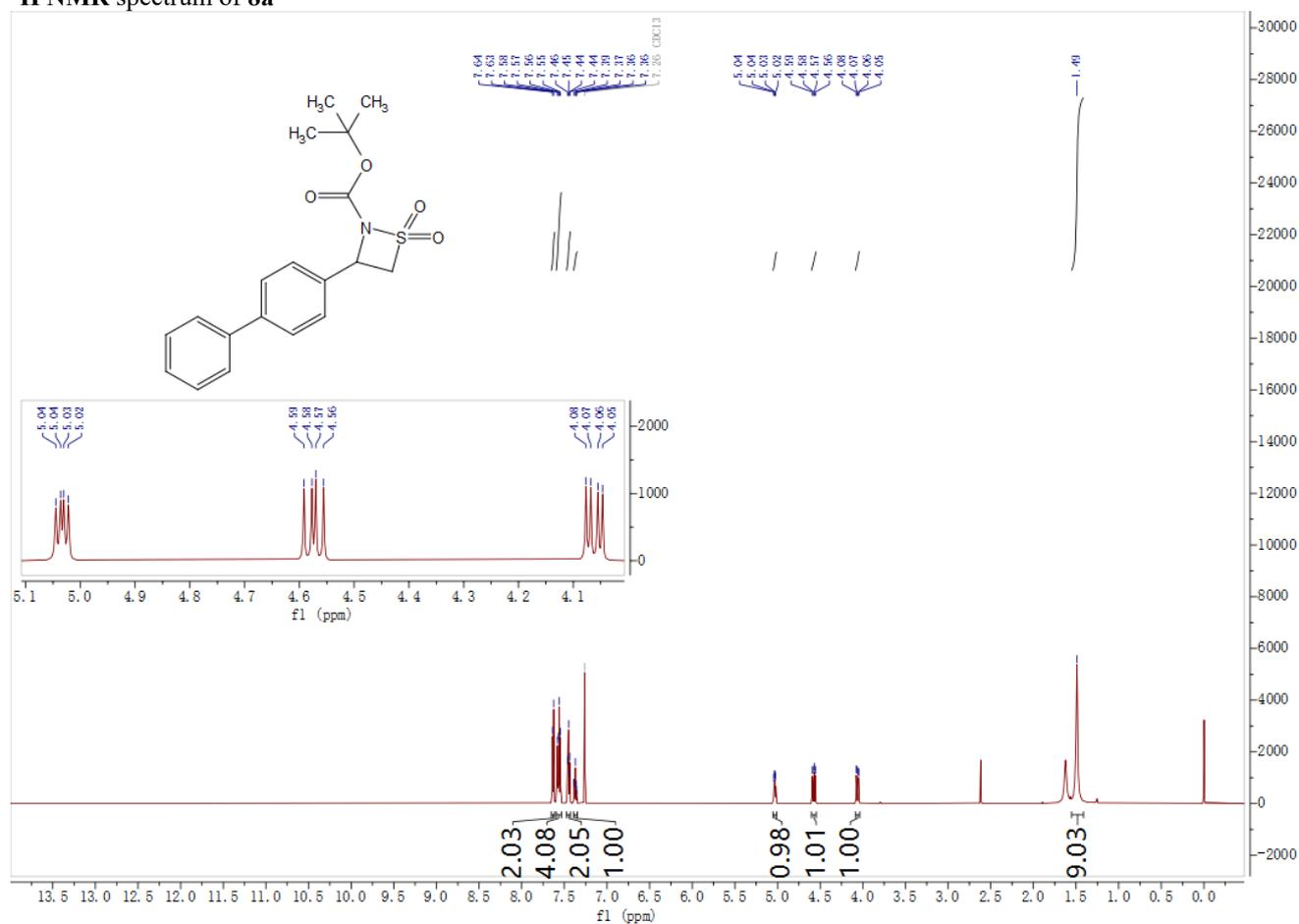


To an oven dried 8 mL vial with a magnetic stir bar was added 4-vinyl-1,1'-biphenyl **7a** (72 mg, 0.4 mmol), fresh prepared *tert*-butyl (chlorosulfonyl)carbamate **2e** (172.5 mg, 0.8 mmol) and anhydrous  $\text{CH}_3\text{CN}$  (4.0 mL, 0.1 M). Then, *N,N*-diisopropylethylamine (103.4 mg, 0.8 mmol) was added. After that, the vial was capped and stirred under room temperature for 1 hour. The mixture was transferred to a 25 mL round-bottom flask and the solvent was removed under reduced pressure. The residue was purified by flash silica column chromatography eluting with 15-30% ethyl acetate/petroleum ether to afford the desired product **8a**.

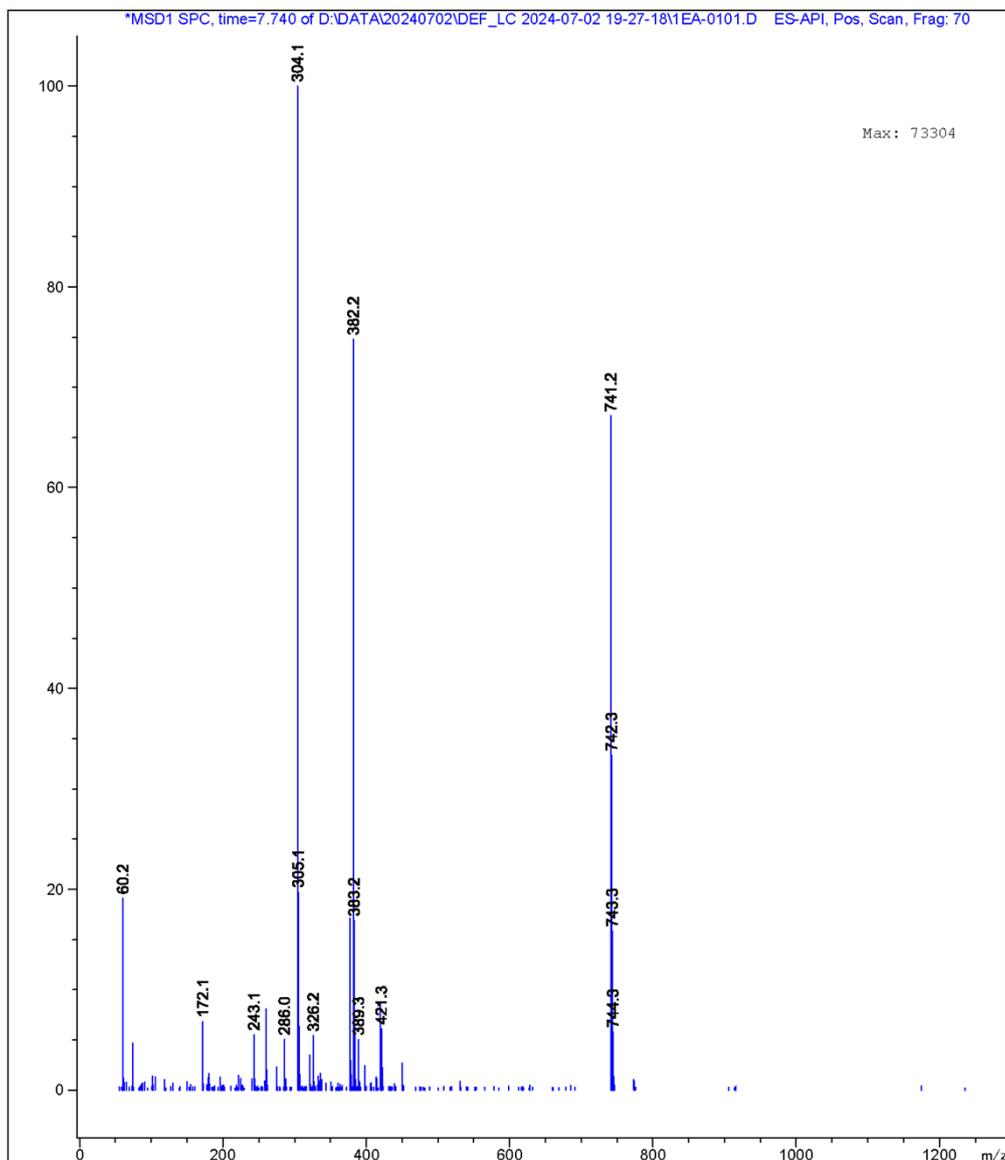
$^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  7.65 – 7.61 (m, 2H), 7.60 – 7.53 (m, 4H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 5.03 (dd,  $J = 8.6, 5.2$  Hz, 1H), 4.57 (dd,  $J = 12.9, 8.6$  Hz, 1H), 4.06 (dd,  $J = 12.9, 5.2$  Hz, 1H), 1.49 (s, 9H).

LRMS (ESI) ( $m/z$ ): 382.2 [ $\text{M}+\text{Na}$ ] $^+$ , 741.2 [ $2\text{M}+\text{Na}$ ] $^+$

$^1\text{H NMR}$  spectrum of **8a**

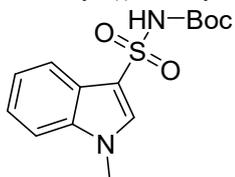


LRMS data of **8a**



### 3. Characterization data of products

*tert*-butyl ((1-methyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3a**)



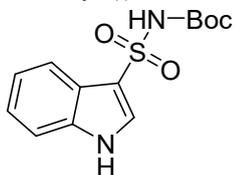
General procedure was followed to obtain **3a** (114 mg, 92%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.94 (d,  $J = 9.2$  Hz, 1H), 7.87 (s, 1H), 7.69 (br, 1H), 7.43 – 7.27 (m, 3H), 3.85 (s, 3H), 1.36 (s, 9H);

$^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  149.50, 137.01, 135.93, 124.08, 123.85, 123.74, 122.62, 119.96, 111.56, 110.46, 83.45, 33.84, 28.07, 27.98.

**HRMS** (ESI) calculated for  $[\text{C}_{14}\text{H}_{18}\text{N}_2\text{NaO}_4\text{S}]^+$   $[\text{M}+\text{Na}]^+$ : 333.0879, found  $m/z$  333.0878.

*tert*-butyl ((1*H*-indol-3-yl)sulfonyl)carbamate (**3b**)



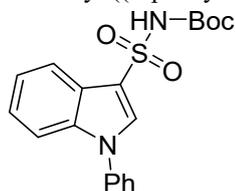
General procedure was followed to obtain **3b** (100 mg, 84%) as a light yellow solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.10 (s, 1H), 11.33 (s, 1H), 8.02 (d, *J* = 3.1 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.18 (m, 2H), 1.24 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 150.02, 135.92, 132.31, 122.99, 122.96, 121.40, 118.89, 112.74, 112.68, 81.34, 27.57.

**HRMS** (ESI) calculated for [C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 319.0723, found *m/z* 319.0725.

*tert*-butyl ((1-phenyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3c**)



General procedure was followed to obtain **3c** (142 mg, 95%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 8.07 – 8.03 (m, 1H), 7.62 – 7.54 (m, 2H), 7.52 – 7.45 (m, 4H), 7.39 – 7.29 (m, 2H), 1.37 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 149.54, 137.81, 136.56, 134.78, 130.10, 128.52, 125.01, 124.36, 124.24, 123.19, 120.20, 114.22, 111.61, 83.65, 28.04.

**HRMS** calculated for [C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 395.1036, found *m/z* 395.1035.

*tert*-butyl ((1-benzyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3d**)



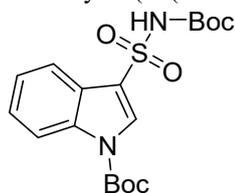
General procedure was followed to obtain **3d** (125 mg, 81%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.47 (br, 1H), 7.39 – 7.28 (m, 6H), 7.16 (dd, *J* = 7.3, 2.4 Hz, 2H), 5.36 (s, 2H), 1.34 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*) δ 149.41, 136.51, 135.52, 135.34, 129.22, 128.54, 127.25, 124.31, 123.93, 122.79, 120.11, 112.17, 111.04, 83.54, 51.17, 28.01.

**HRMS** (ESI) calculated for [C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 409.1192, found *m/z* 409.1194.

*tert*-butyl 3-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1*H*-indole-1-carboxylate (**3e**)



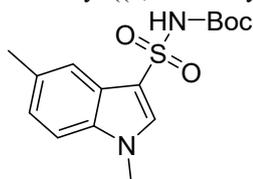
General procedure was followed to obtain **3e** (84 mg, 53%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.71 (br, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.34 (m, 1H), 1.68 (s, 9H), 1.39 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 149.21, 148.47, 135.52, 132.90, 126.12, 124.64, 124.58, 119.98, 118.29, 115.78, 86.13, 84.23, 28.17, 28.01.

**HRMS** (ESI) calculated for [C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>6</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 419.1247, found *m/z* 419.1244.

*tert*-butyl ((1,5-dimethyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3f**)



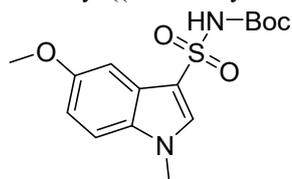
General procedure was followed to obtain **3f** (114 mg, 88%) as a pink solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.29 (s, 1H), 8.03 (s, 1H), 7.61 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H), 1.26 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 150.03, 135.58, 135.01, 130.67, 124.52, 123.60, 118.65, 110.92, 110.90, 81.38, 33.14, 27.63, 21.25.

**HRMS** (ESI) calculated for [C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 347.1036, found *m/z* 347.1036.

tert-butyl ((5-methoxy-1-methyl-1H-indol-3-yl)sulfonyl)carbamate (**3g**)



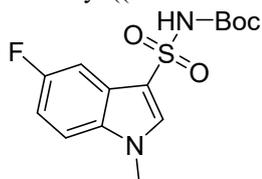
General procedure was followed to obtain **3g** (102 mg, 75%) as a pink solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.78 (s, 1H), 7.49 (br, 1H), 7.34 (d,  $J = 2.4$  Hz, 1H), 7.24 (s, 1H), 6.96 (dd,  $J = 9.0, 2.5$  Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 1.35 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*)  $\delta$  156.31, 149.47, 135.84, 132.02, 124.89, 114.36, 111.39, 110.84, 101.28, 83.45, 56.00, 34.02, 28.11.

**HRMS** (ESI) calculated for  $[C_{15}H_{20}N_2NaO_5S]^+$   $[M+Na]^+$ : 363.0985, found  $m/z$  363.0984.

tert-butyl ((5-fluoro-1-methyl-1H-indol-3-yl)sulfonyl)carbamate (**3h**)



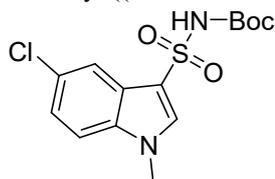
General procedure was followed to obtain **3h** (121 mg, 92%) as a light yellow solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.88 (s, 1H), 7.66 (br, 1H), 7.59 (dd,  $J = 9.2, 2.5$  Hz, 1H), 7.31 (dd,  $J = 9.0, 4.1$  Hz, 1H), 7.09 (t,  $J = 10.2$  Hz, 1H), 3.85 (s, 3H), 1.37 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*)  $\delta$  159.45 (d,  $J = 239.3$  Hz), 149.49 (d,  $J = 6.8$  Hz), 136.98, 133.51, 124.74 (d,  $J = 11.1$  Hz), 112.41 (d,  $J = 26.1$  Hz), 111.59, 111.51, 105.51 (d,  $J = 25.9$  Hz), 83.66, 34.14, 28.07.

**HRMS** (ESI) calculated for  $[C_{14}H_{17}FN_2NaO_4S]^+$   $[M+Na]^+$ : 351.0785, found  $m/z$  351.0784.

tert-butyl ((5-chloro-1-methyl-1H-indol-3-yl)sulfonyl)carbamate (**3i**)



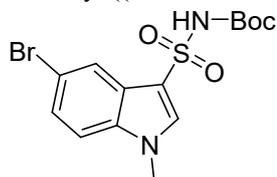
General procedure was followed to obtain **3i** (131 mg, 95%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.91 (t,  $J = 1.3$  Hz, 1H), 7.87 (s, 1H), 7.48 (br, 1H), 7.33 – 7.29 (m, 2H), 3.85 (s, 3H), 1.38 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*)  $\delta$  149.37, 136.86, 135.41, 128.79, 125.03, 124.31, 119.60, 111.63, 111.43, 83.76, 34.09, 28.10.

**HRMS** (ESI) calculated for  $[C_{14}H_{17}ClN_2NaO_4S]^+$   $[M+Na]^+$ : 367.049, found  $m/z$  367.0493.

tert-butyl ((5-bromo-1-methyl-1H-indol-3-yl)sulfonyl)carbamate (**3j**)



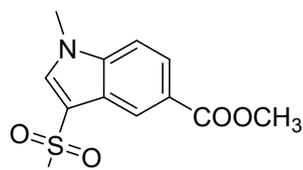
General procedure was followed to obtain **3j** (139 mg, 89%) as a pink solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.07 (d,  $J = 1.9$  Hz, 1H), 7.85 (s, 1H), 7.48 – 7.41 (m, 2H), 7.28 – 7.23 (m, 1H), 3.85 (s, 3H), 1.38 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*)  $\delta$  149.34, 136.75, 135.72, 126.91, 125.55, 122.63, 116.36, 112.00, 111.34, 83.78, 34.08, 28.11.

**HRMS** (ESI) calculated for  $[C_{14}H_{17}BrN_2NaO_4S]^+$   $[M+Na]^+$ : 410.9985, found  $m/z$  410.9986.

methyl 3-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1-methyl-1H-indole-5-carboxylate (**3k**)



Boc-NH

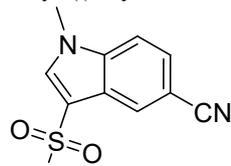
General procedure was followed to obtain **3k** (125 mg, 85%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 1.7 Hz, 1H), 8.07 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.94 (s, 1H), 7.58 (br, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 1.36 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 167.47, 149.32, 139.43, 137.43, 125.14, 124.75, 123.60, 122.51, 113.21, 110.40, 83.72, 52.32, 34.10, 28.08.

HRMS (ESI) calculated for [C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>6</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 391.0934, found *m/z* 391.0938.

tert-butyl ((5-cyano-1-methyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3l**)



Boc-NH

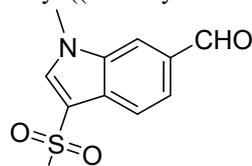
General procedure was followed to obtain **3l** (102 mg, 76%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.17 – 7.62 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.44 (m, 1H), 3.92 (s, 3H), 1.38 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 149.52, 138.43, 137.82, 126.60, 125.51, 123.80, 119.52, 113.17, 111.65, 105.92, 84.03, 34.19, 28.06.

HRMS (ESI) calculated for [C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>S]<sup>+</sup> [M+H]<sup>+</sup>: 336.1013, found *m/z* 336.1015.

tert-butyl ((6-formyl-1-methyl-1*H*-indol-3-yl)sulfonyl)carbamate (**3m**)



Boc-NH

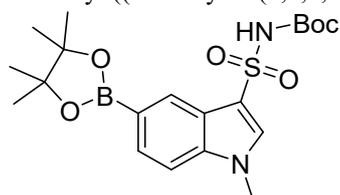
General procedure was followed to obtain **3m** (88 mg, 65%) as a white solid.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.12 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 8.05 (s, 1H), 7.98 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.49 (br, 1H), 3.97 (s, 3H), 1.37 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 192.02, 149.29, 139.24, 136.87, 132.42, 128.85, 124.22, 120.60, 112.74, 112.44, 83.89, 34.24, 28.10.

HRMS (ESI) calculated for [C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 337.0864, found *m/z* 337.0864.

tert-butyl ((1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)sulfonyl)carbamate (**3n**)



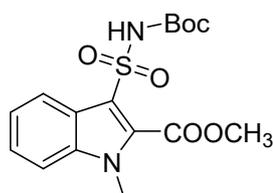
General procedure was followed to obtain **3n** (161 mg, 92%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.87 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.46 (br, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 1.37 (s, 12H), 1.36 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 149.34, 139.01, 136.41, 129.86, 127.17, 123.61, 112.07, 109.83, 84.02, 83.49, 33.88, 28.10, 25.05.

HRMS (ESI) calculated for [C<sub>20</sub>H<sub>29</sub>BN<sub>2</sub>NaO<sub>6</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 459.1732, found *m/z* 459.1737.

methyl 3-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1-methyl-1*H*-indole-2-carboxylate (**3o**)



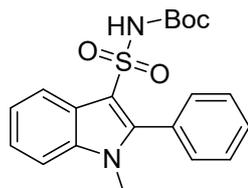
General procedure was followed to obtain **3o** (118 mg, 80%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.89 (br, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 4.06 (s, 3H), 3.96 (s, 3H), 1.29 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 160.98, 149.77, 136.48, 130.60, 125.96, 124.92, 123.73, 122.73, 116.47, 110.59, 83.81, 53.47, 32.68, 28.00.

HRMS (ESI) calculated for [C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>6</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 391.0934, found *m/z* 391.0934.

tert-butyl ((1-methyl-2-phenyl-1H-indol-3-yl)sulfonyl)carbamate (**3p**)



General procedure was followed to obtain **3p** (133 mg, 86%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.15 (m, 1H), 7.62 – 7.46 (m, 5H), 7.45 – 7.30 (m, 3H), 7.12 (br, 1H), 3.57 (s, 3H), 1.25 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 149.43 (d, *J* = 6.7 Hz), 144.29, 135.94, 130.62, 130.10, 129.01, 128.59, 125.51, 123.68, 122.84, 121.00, 110.89, 110.12, 83.20, 31.22, 27.98.

HRMS (ESI) calculated for [C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 409.1192, found *m/z* 409.1196.

tert-butyl ((5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)sulfonyl)carbamate (**3q**)



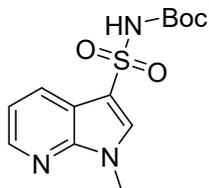
General procedure was followed to obtain **3q** (123 mg, 91%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.57 (br, 1H), 7.24 – 7.18 (m, 1H), 7.09 – 7.03 (m, 1H), 4.25 – 4.19 (m, 2H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.27 (p, *J* = 6.5, 6.0 Hz, 2H), 1.37 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 149.49, 134.29, 133.06, 123.00, 122.24, 120.85, 117.36, 111.57, 83.36, 45.12, 28.11, 24.36, 22.68.

HRMS (ESI) calculated for [C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>4</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 359.1036, found *m/z* 359.1037.

tert-butyl ((1-methyl-1H-pyrrolo[2,3-*b*]pyridin-3-yl)sulfonyl)carbamate (**3r**)



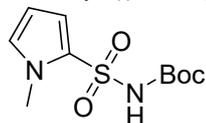
General procedure was followed to obtain **3r** (113 mg, 91%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.45 – 8.40 (m, 1H), 8.25 (dt, *J* = 8.0, 1.7 Hz, 1H), 8.02 (s, 1H), 7.26 – 7.19 (m, 1H), 3.95 (s, 3H), 1.33 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 149.66, 147.25, 144.89, 135.55, 128.76, 118.42, 116.93, 110.71, 83.59, 32.28, 28.00.

HRMS (ESI) calculated for [C<sub>13</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>S]<sup>+</sup> [M+H]<sup>+</sup>: 312.1013, found *m/z* 312.1016.

tert-butyl ((1-methyl-1H-pyrrol-2-yl)sulfonyl)carbamate (**5a**)



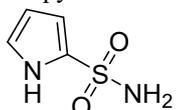
General procedure was followed to obtain **5a** (80 mg, 77%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (br, 1H), 7.00 (dd, *J* = 4.1, 1.9 Hz, 1H), 6.82 (t, *J* = 2.3 Hz, 1H), 6.16 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.88 (s, 3H), 1.40 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 149.56, 129.74, 125.17, 120.42, 108.09, 84.22, 36.05, 27.97.

**HRMS** (ESI) calculated for [C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 259.0758, found *m/z* 259.0760.

1*H*-pyrrole-2-sulfonamide (**5b**)



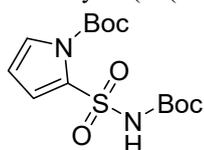
General procedure was followed and deprotected to obtain **5b** (38 mg, 65%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.70 (s, 1H), 7.15 (s, 2H), 6.93 – 6.87 (m, 1H), 6.56 – 6.50 (m, 1H), 6.14 – 6.08 (m, 1H);

**<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 131.42, 121.46, 110.92, 108.11.

**HRMS** (ESI) calculated for [C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 145.0077, found *m/z* 145.0077.

*tert*-butyl 2-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1*H*-pyrrole-1-carboxylate (**5c**)



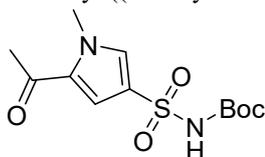
General procedure was followed to obtain **5c** (85 mg, 61%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (br, 1H), 7.39 (dd, *J* = 3.3, 1.9 Hz, 1H), 7.23 (dd, *J* = 3.7, 1.9 Hz, 1H), 6.25 (t, *J* = 3.5 Hz, 1H), 1.62 (s, 9H), 1.40 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 149.10, 147.14, 128.52, 127.72, 126.08, 110.42, 86.67, 83.88, 27.99, 27.95.

**HPLC-MS** (ESI) calculated for [C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>SNa]<sup>+</sup> [M+Na]<sup>+</sup>: 369.1091, found *m/z* 369.1095.

*tert*-butyl ((5-acetyl-1-methyl-1*H*-pyrrol-3-yl)sulfonyl)carbamate (**5d**)



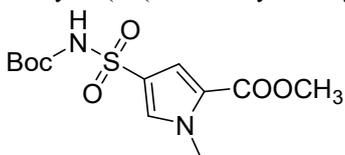
General procedure was followed to obtain **5d** (115 mg, 95%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (br, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 3.96 (s, 3H), 2.45 (s, 3H), 1.43 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*) δ 189.20, 149.49, 133.14, 131.44, 120.91, 118.72, 84.00, 38.66, 28.11, 27.33.

**HRMS** (ESI) calculated for [C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>5</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 325.0829, found *m/z* 325.0832.

methyl 4-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1-methyl-1*H*-pyrrole-2-carboxylate (**5e**)



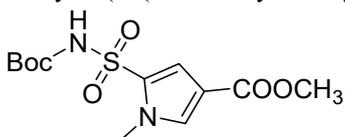
General procedure was followed to obtain **5e** (115 mg, 90%) as a white solid.

**<sup>1</sup>H NMR** (600 MHz, DMSO-*d*<sub>6</sub>) δ 11.36 (s, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 1.35 (s, 9H);

**<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 160.04, 150.03, 132.10, 122.92, 121.52, 116.04, 81.81, 51.62, 37.01, 27.63.

**HRMS** (ESI) calculated for [C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 317.0813, found *m/z* 317.0816.

methyl 5-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-1-methyl-1*H*-pyrrole-3-carboxylate (**5f**)



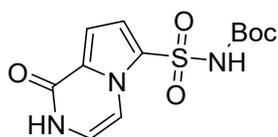
General procedure was followed to obtain **5f** (96 mg, 75%) as a white solid.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (br, 1H), 7.41 (s, 1H), 7.38 (s, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 1.41 (s, 9H);

**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*) δ 163.84, 149.34, 132.92, 127.28, 120.76, 115.30, 84.68, 51.68, 36.85, 27.98.

**HRMS** (ESI) calculated for [C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 317.0813, found *m/z* 317.0814.

*tert*-butyl ((1-oxo-1,2-dihydropyrrolo[1,2-*a*]pyrazin-6-yl)sulfonyl)carbamate (**5g**)



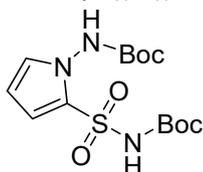
General procedure was followed to obtain **5g** (114 mg, 91%) as a white solid.

$^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.03 (br, 1H), 11.17 (s, 1H), 7.55 (d,  $J = 6.0$  Hz, 1H), 7.14 (d,  $J = 4.3$  Hz, 1H), 7.00 (d,  $J = 4.4$  Hz, 1H), 6.95 (t,  $J = 5.9$  Hz, 1H), 1.29 (s, 9H);

$^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$  155.21, 149.79, 128.29, 124.19, 118.75, 116.93, 108.32, 105.62, 82.43, 27.49.

**HRMS** (ESI) calculated for  $[\text{C}_{12}\text{H}_{16}\text{N}_3\text{O}_5\text{S}]^+ [\text{M}+\text{H}]^+$ : 314.0805, found  $m/z$  314.0806.

*tert*-butyl ((1-((tert-butoxycarbonyl)amino)-1*H*-pyrrol-2-yl)sulfonyl)carbamate (**5h**)



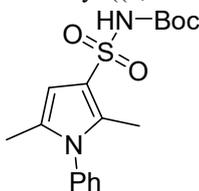
General procedure was followed to obtain **5h** (111 mg, 77%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.46 (br, 1H), 6.99 – 6.92 (m, 2H), 6.19 (t,  $J = 3.7$  Hz, 1H), 1.49 (s, 9H), 1.42 (s, 9H);

$^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  155.23, 150.05, 149.69, 130.29, 118.37, 106.85, 84.65, 83.18, 28.16, 28.01.

**HRMS** calculated for  $[\text{C}_{14}\text{H}_{23}\text{N}_3\text{NaO}_6\text{S}]^+ [\text{M}+\text{Na}]^+$ : 384.1200, found  $m/z$  384.1199.

*tert*-butyl ((2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)sulfonyl)carbamate (**5i**)



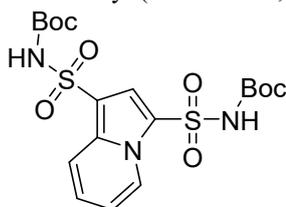
General procedure was followed to obtain **5i** (130 mg, 93%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.60 (br, 1H), 7.53 – 7.44 (m, 3H), 7.20 – 7.14 (m, 2H), 6.36 (s, 1H), 2.26 (s, 3H), 1.95 (s, 3H), 1.44 (s, 9H);

$^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  149.89, 137.04, 134.71, 129.72, 129.51, 129.18, 128.19, 116.56, 107.19, 83.20, 28.14, 12.77, 11.89.

**HRMS** calculated for  $[\text{C}_{17}\text{H}_{22}\text{N}_2\text{NaO}_4\text{S}]^+ [\text{M}+\text{Na}]^+$ : 373.1192, found  $m/z$  373.1193.

di-*tert*-butyl (indolizine-1,3-disulfonyl)dicarbamate (**5j**)



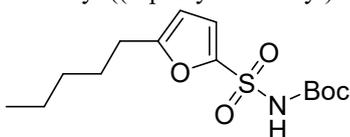
General procedure was followed to obtain **5j** (139 mg, 73%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.92 (d,  $J = 7.1$  Hz, 1H), 8.24 (d,  $J = 9.1$  Hz, 1H), 7.98 (s, 1H), 7.65 (br, 2H), 7.50 – 7.39 (m, 1H), 7.11 (t,  $J = 7.0$  Hz, 1H), 1.39 (s, 18H);

$^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  149.46, 149.40, 136.99, 127.29, 127.12, 125.18, 119.11, 118.39, 115.54, 110.28, 85.12, 84.28, 28.09, 28.00.

**HRMS** (ESI) calculated for  $[\text{C}_{18}\text{H}_{25}\text{N}_3\text{NaO}_8\text{S}_2]^+ [\text{M}+\text{Na}]^+$ : 498.0975, found  $m/z$  498.0980.

*tert*-butyl ((5-pentylfuran-2-yl)sulfonyl)carbamate (**5k**)



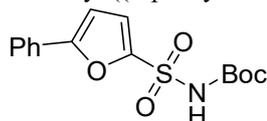
General procedure was followed to obtain **5k** (105 mg, 83%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.42 (br, 1H), 7.18 (d,  $J = 3.4$  Hz, 1H), 6.18 (d,  $J = 3.4$  Hz, 1H), 2.71 (t,  $J = 7.6$  Hz, 2H), 1.75 – 1.63 (m, 2H), 1.44 (s, 9H), 1.37 – 1.32 (m, 4H), 0.94 – 0.89 (m, 3H);

$^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  162.71, 148.77, 144.06, 121.01, 107.34, 84.47, 31.30, 28.33, 27.94, 27.33, 22.40, 14.05.

**HRMS** (ESI) calculated for  $[\text{C}_{14}\text{H}_{23}\text{NNaO}_5\text{S}]^+ [\text{M}+\text{Na}]^+$ : 340.1189, found  $m/z$  340.1188.

*tert*-butyl ((5-phenylfuran-2-yl)sulfonyl)carbamate (**5l**)



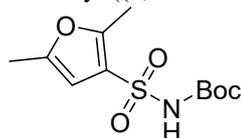
General procedure was followed to obtain **5l** (116 mg, 90%) as a white solid.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.53 (br, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.37 (m, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 1.42 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 158.65, 148.69, 145.12, 129.67, 129.09, 128.87, 125.07, 121.71, 106.36, 84.75, 27.98.

HRMS (ESI) calculated for [C<sub>15</sub>H<sub>15</sub>NO<sub>5</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 322.0755, found *m/z* 322.0757.

*tert*-butyl ((2,5-dimethylfuran-3-yl)sulfonyl)carbamate (**5m**)



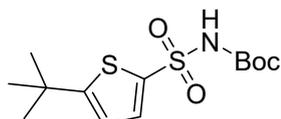
General procedure was followed to obtain **5m** (66 mg, 60%) as a white solid.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.52 (br, 1H), 6.22 (s, 1H), 2.54 (s, 3H), 2.25 (s, 3H), 1.43 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 156.84, 151.02, 149.48, 120.13, 105.48, 83.91, 28.09, 13.34, 13.26.

HRMS (ESI) calculated for [C<sub>11</sub>H<sub>16</sub>NO<sub>5</sub>S]<sup>-</sup> [M-H]<sup>-</sup>: 274.0755, found *m/z* 274.0756.

*tert*-butyl ((5-(*tert*-butyl)thiophen-2-yl)sulfonyl)carbamate (**5n**)



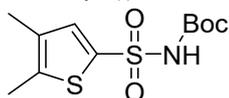
General procedure was followed to obtain **5n** (92 mg, 72%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 3.9 Hz, 1H), 7.44 (br, 1H), 6.84 (d, *J* = 3.9 Hz, 1H), 1.44 (s, 9H), 1.40 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 166.76, 148.64, 134.55, 134.39, 121.49, 83.86, 34.94, 31.79, 27.50.

HRMS (ESI) calculated for [C<sub>13</sub>H<sub>21</sub>NNaO<sub>4</sub>S<sub>2</sub>]<sup>+</sup> [M+Na]<sup>+</sup>: 342.0804, found *m/z* 342.0804.

*tert*-butyl ((4,5-dimethylthiophen-2-yl)sulfonyl)carbamate (**5o**)



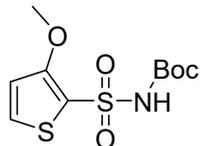
General procedure was followed to obtain **5o** (99 mg, 85%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.34 (br, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 1.45 (s, 9H);

<sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 149.11, 143.46, 137.51, 134.18, 133.03, 84.29, 28.09, 13.81, 13.70.

HRMS (ESI) calculated for [C<sub>11</sub>H<sub>16</sub>NO<sub>4</sub>S<sub>2</sub>]<sup>-</sup> [M-H]<sup>-</sup>: 290.0526, found *m/z* 290.053.

*tert*-butyl ((3-methoxythiophen-2-yl)sulfonyl)carbamate (**5p**)



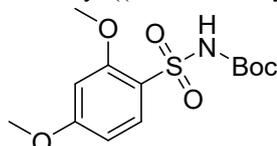
General procedure was followed to obtain **5p** (108 mg, 92%) as a white solid.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.60 (br, 1H), 7.56 (d, *J* = 5.5 Hz, 1H), 6.85 (d, *J* = 5.5 Hz, 1H), 3.99 (s, 3H), 1.40 (s, 9H);

<sup>13</sup>C NMR (125 MHz, Chloroform-*d*) δ 159.25, 149.27, 131.82, 115.48, 114.73, 84.16, 59.50, 28.00.

HRMS (ESI) calculated for [C<sub>10</sub>H<sub>14</sub>NO<sub>5</sub>S<sub>2</sub>]<sup>-</sup> [M-H]<sup>-</sup>: 292.0319, found *m/z* 292.0318.

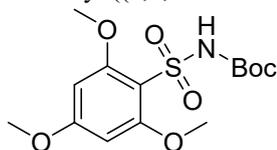
*tert*-butyl ((2,4-dimethoxyphenyl)sulfonyl)carbamate (**5q**)



General procedure was followed to obtain **5q** (96 mg, 76%) as a white solid.

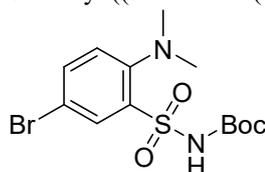
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.67 (br, 1H), 6.56 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 1.32 (s, 9H);  
**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.73, 158.45, 149.65, 133.74, 118.63, 104.44, 99.39, 83.64, 56.48, 55.91, 27.91.  
**HRMS** (ESI) calculated for [C<sub>13</sub>H<sub>19</sub>NNaO<sub>6</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 340.0825, found *m/z* 340.0825.

*tert*-butyl ((2,4,6-trimethoxyphenyl)sulfonyl)carbamate (**5r**)



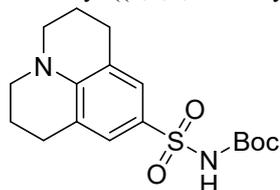
General procedure was followed to obtain **5r** (131 mg, 94%) as a white solid.  
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (br, 1H), 6.12 (s, 2H), 3.89 (s, 6H), 3.84 (s, 3H), 1.33 (s, 9H);  
**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 165.03, 160.83, 150.18, 108.80, 91.34, 83.12, 56.75, 55.69, 27.92.  
**HRMS** (ESI) calculated for [C<sub>14</sub>H<sub>21</sub>NNaO<sub>7</sub>S]<sup>+</sup> [M+Na]<sup>+</sup>: 370.0931, found *m/z* 370.0932.

*tert*-butyl ((5-bromo-2-(dimethylamino)phenyl)sulfonyl)carbamate (**5s**)



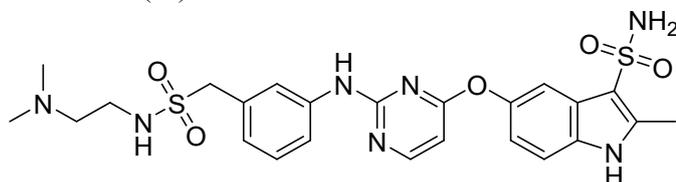
General procedure was followed to obtain **5s** (93 mg, 61%) as a white solid.  
**<sup>1</sup>H NMR** (500 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 2.4 Hz, 1H), 7.70 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 2.73 (s, 6H), 1.30 (s, 9H);  
**<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*) δ 152.44, 149.79, 137.66, 137.16, 133.95, 125.65, 118.16, 83.95, 46.37, 27.85.  
**HRMS** (ESI) calculated for [C<sub>13</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>4</sub>S]<sup>+</sup> [M+H]<sup>+</sup>: 379.0322, found *m/z* 379.0325.

*tert*-butyl ((2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)sulfonyl)carbamate (**5t**)



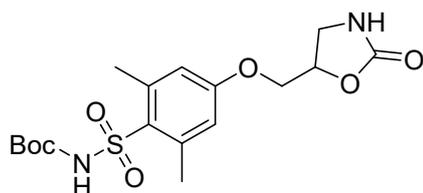
General procedure was followed to obtain **5t** (113 mg, 80%) as a white solid.  
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (br, 1H), 7.34 (s, 2H), 3.25 (t, *J* = 5.8 Hz, 4H), 2.73 (t, *J* = 6.3 Hz, 4H), 1.93 (dt, *J* = 11.6, 6.1 Hz, 4H), 1.40 (s, 9H);  
**<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 149.76, 146.84, 127.28, 121.90, 120.09, 83.35, 49.91, 28.07, 27.79, 21.21.  
**HRMS** (ESI) calculated for [C<sub>17</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S]<sup>+</sup> [M+H]<sup>+</sup>: 353.1530, found *m/z* 353.1530.

5-((2-((3-((N-(2-(dimethylamino)ethyl)sulfamoyl)methyl)phenyl)amino)pyrimidin-4-yl)oxy)-2-methyl-1*H*-indole-3-sulfonamide (**6a**)



General procedure was followed and typical deprotected to obtain **6a** (125 mg, 56%) as a white solid.  
**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.89 (s, 1H), 9.63 (s, 1H), 8.33 (d, *J* = 5.6 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.11 – 6.95 (m, 5H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 5.6 Hz, 1H), 4.13 (s, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.60 (s, 3H), 2.47 – 2.40 (m, 2H), 2.24 (s, 6H);  
**<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 170.23, 159.83, 159.75, 146.53, 140.24, 140.01, 131.74, 130.26, 128.16, 125.38, 123.84, 121.03, 118.64, 116.45, 113.99, 112.01, 111.54, 98.13, 58.30, 57.42, 44.50, 12.70.  
**HRMS** (ESI) calculated for [C<sub>24</sub>H<sub>28</sub>N<sub>7</sub>O<sub>5</sub>S<sub>2</sub>]<sup>-</sup> [M-H]<sup>-</sup>: 558.1599, found *m/z* 558.1599.

*tert*-butyl ((2,6-dimethyl-4-((2-oxooxazolidin-5-yl)methoxy)phenyl)sulfonyl)carbamate (**6b**)



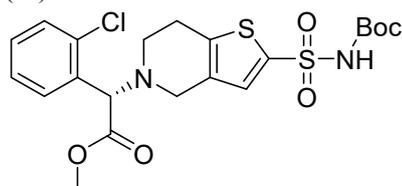
General procedure was followed to obtain **6b** (151 mg, 94%) as a white solid.

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  6.64 (s, 1H), 6.53 (s, 2H), 5.27 (br, 1H), 4.99 – 4.88 (m, 1H), 4.36 (t,  $J$  = 9.0 Hz, 1H), 4.29 – 4.22 (m, 1H), 4.18 – 4.06 (m, 2H), 2.24 (s, 6H), 1.48 (s, 9H);

$^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  158.01, 152.12, 151.02, 139.54, 123.73, 112.60, 84.48, 72.73, 67.43, 48.09, 28.02, 21.48.

**HRMS** (ESI) calculated for  $[\text{C}_{17}\text{H}_{24}\text{N}_2\text{NaO}_7\text{S}]^+ [\text{M}+\text{Na}]^+$ : 423.1196, found  $m/z$  423.1197.

methyl (*S*)-2-(2-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)-6,7-dihydrothieno[3,2-*c*]pyridin-5(4H)-yl)-2-(2-chlorophenyl)acetate (**6c**)



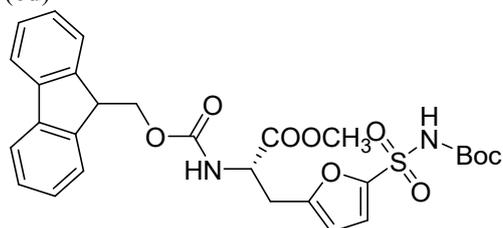
General procedure was followed to obtain **6c** (134 mg, 67%) as a white solid.

$^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.62 – 7.57 (m, 1H), 7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 4.94 (s, 1H), 3.78 – 3.62 (m, 5H), 2.98 – 2.87 (m, 4H), 1.45 (s, 9H);

$^{13}\text{C NMR}$  (125 MHz, Chloroform-*d*)  $\delta$  171.34, 148.96, 143.52, 135.79, 134.98, 134.16, 133.39, 133.15, 130.16, 129.94, 129.85, 127.37, 84.41, 67.59, 52.43, 49.99, 47.56, 28.19, 28.13, 26.15.

**HRMS** (ESI) calculated for  $[\text{C}_{21}\text{H}_{24}\text{ClN}_2\text{O}_6\text{S}_2]^- [\text{M}-\text{H}]^-$ : 499.0770, found  $m/z$  499.0771.

methyl (*S*)-2-(((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-3-(5-(*N*-(*tert*-butoxycarbonyl)sulfamoyl)furan-2-yl)propanoate (**6d**)



General procedure was followed to obtain **6d** (132 mg, 58%) as a white solid.

$^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  7.76 (d,  $J$  = 7.5 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.14 (br, 1H), 6.23 (s, 1H), 5.57 (d,  $J$  = 7.9 Hz, 1H), 4.68 (q,  $J$  = 6.2 Hz, 1H), 4.41 (dq,  $J$  = 17.5, 10.5, 9.2 Hz, 2H), 4.21 (t,  $J$  = 6.8 Hz, 1H), 3.77 (s, 3H), 3.27 (qd,  $J$  = 15.4, 5.6 Hz, 2H), 1.41 (s, 9H);

$^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  171.10, 156.16, 155.70, 145.83, 143.88, 143.75, 141.47, 127.92, 127.28, 125.20, 120.42, 120.16, 110.18, 84.54, 67.30, 53.07, 52.78, 47.22, 31.43, 27.96.

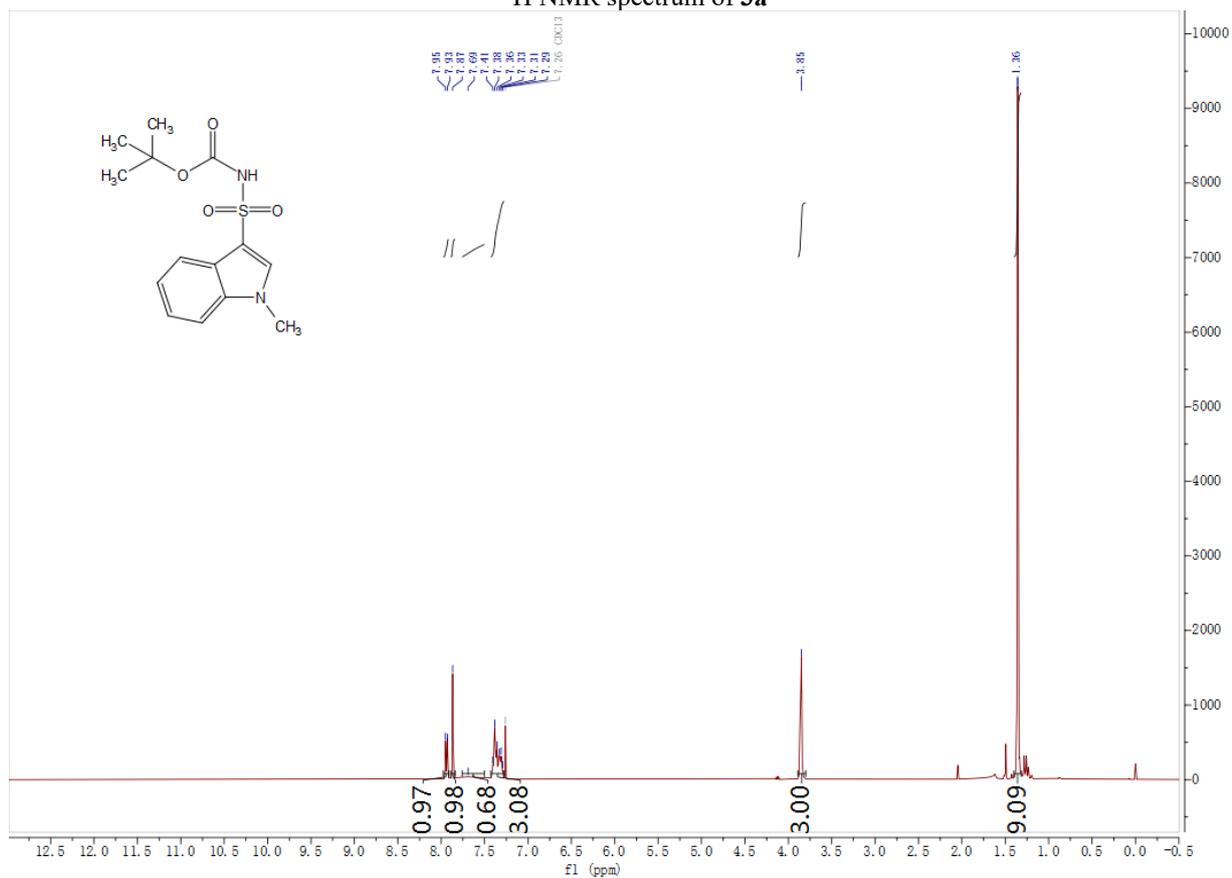
**HRMS** (ESI) calculated for  $[\text{C}_{28}\text{H}_{30}\text{N}_2\text{NaO}_9\text{S}]^+ [\text{M}+\text{Na}]^+$ : 593.1564, found  $m/z$  593.1566.

#### 4. Reference

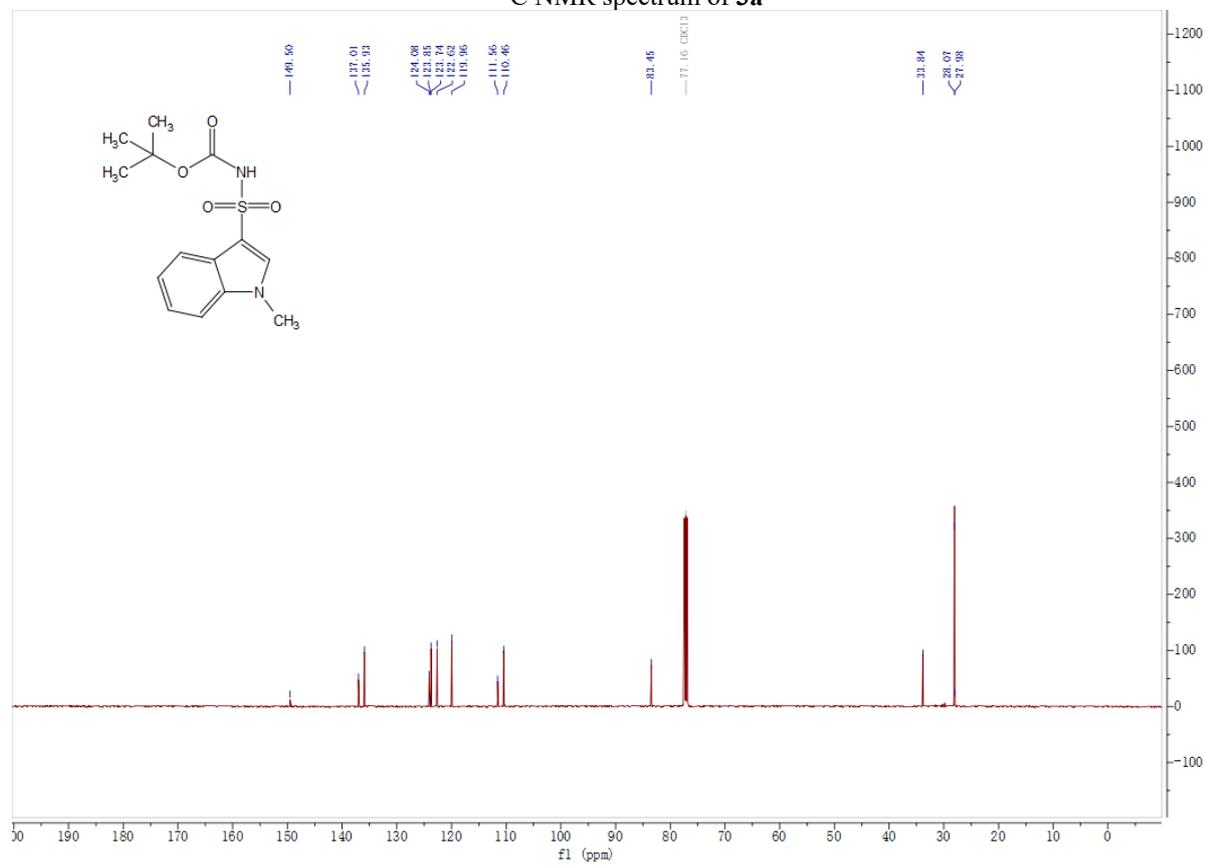
- Gorelik, D. J.; Turner, J. A.; Taylor, M. S., Catalyst-Controlled, Site-Selective Sulfamoylation of Carbohydrate Derivatives. *Org. Lett.* **2022**, *24* (29), 5249-5253.

## 5. NMR spectrum

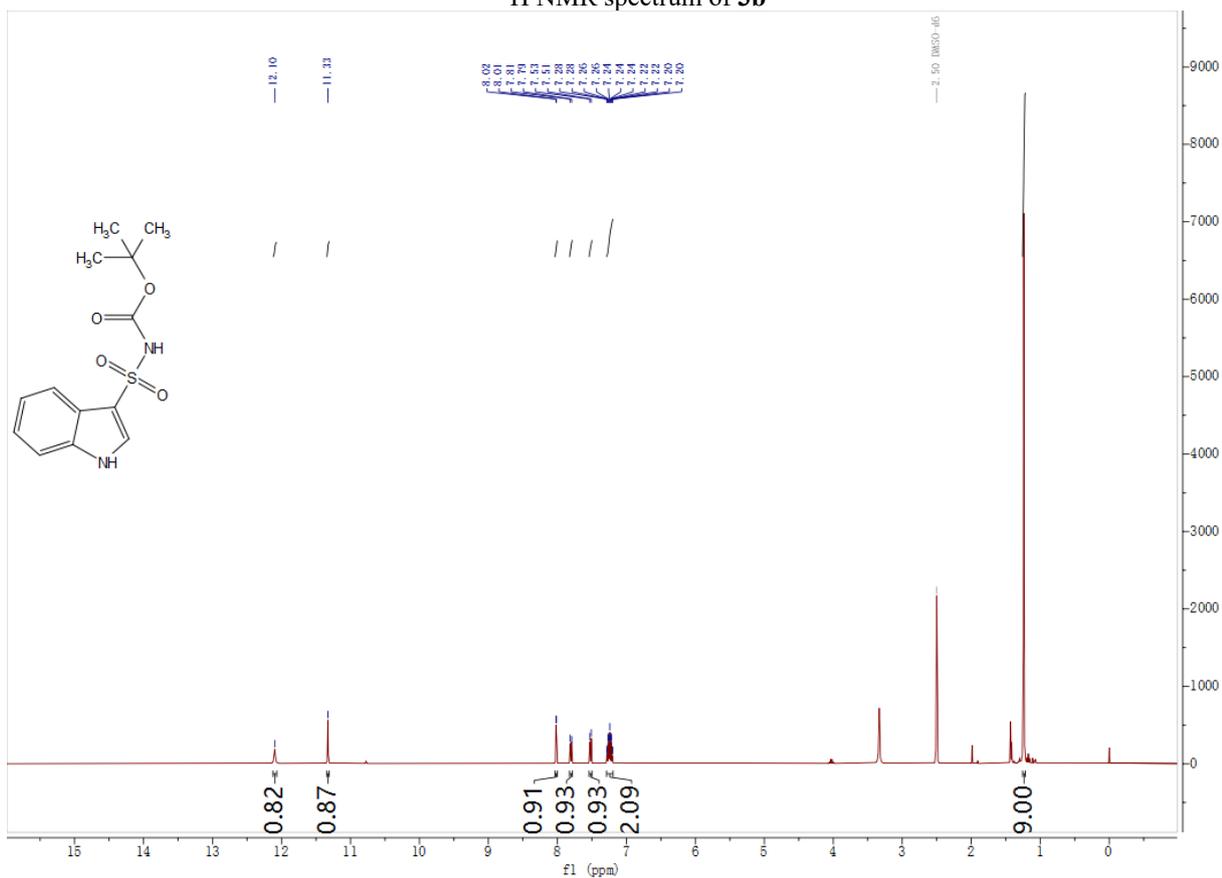
<sup>1</sup>H NMR spectrum of 3a



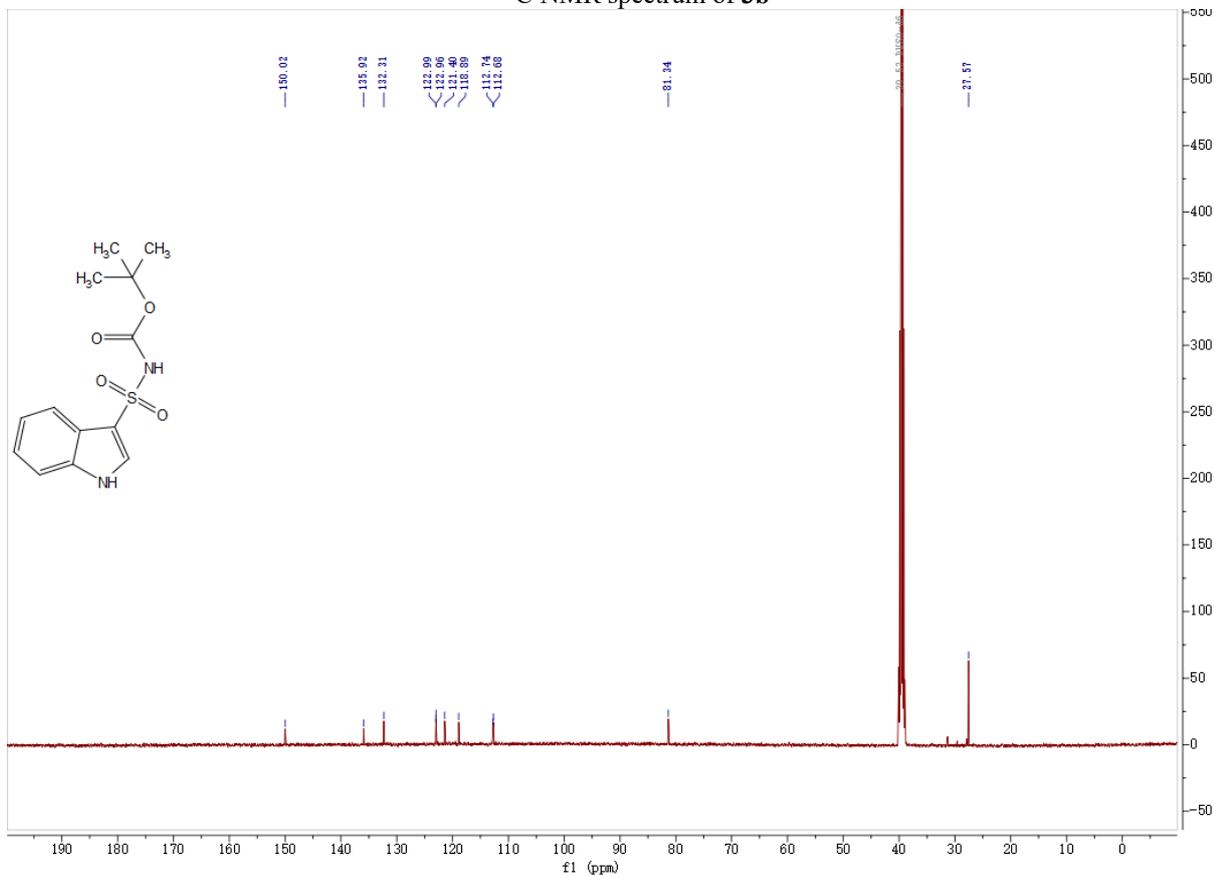
<sup>13</sup>C NMR spectrum of 3a



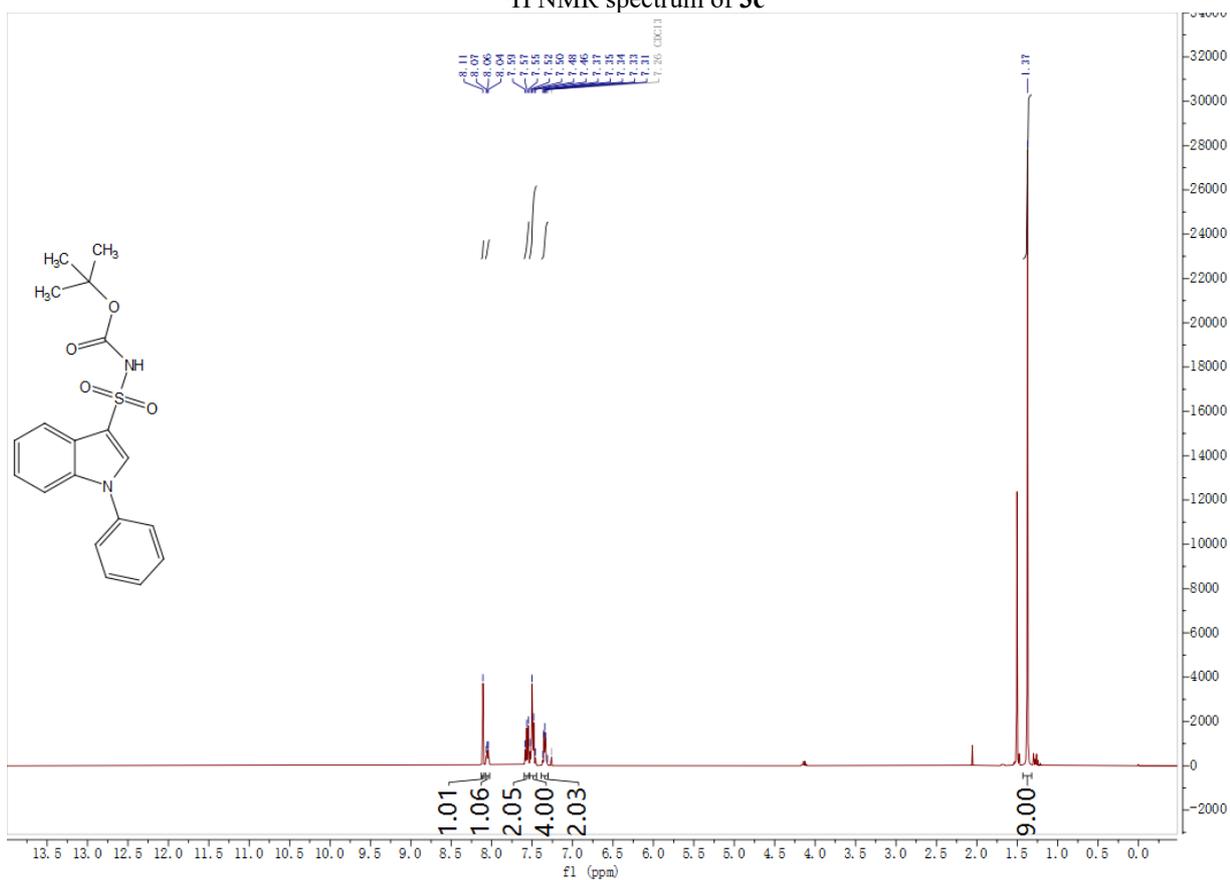
<sup>1</sup>H NMR spectrum of **3b**



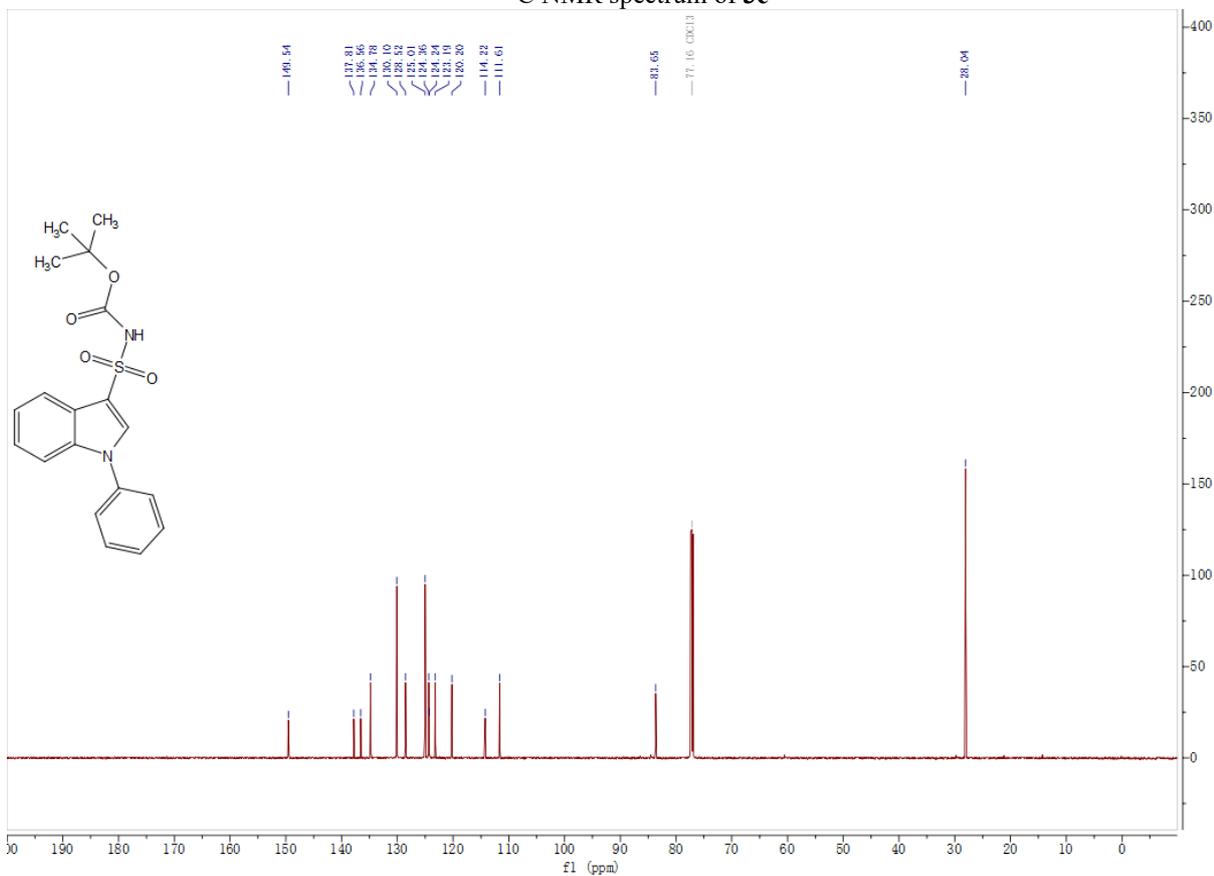
<sup>13</sup>C NMR spectrum of **3b**



<sup>1</sup>H NMR spectrum of 3c

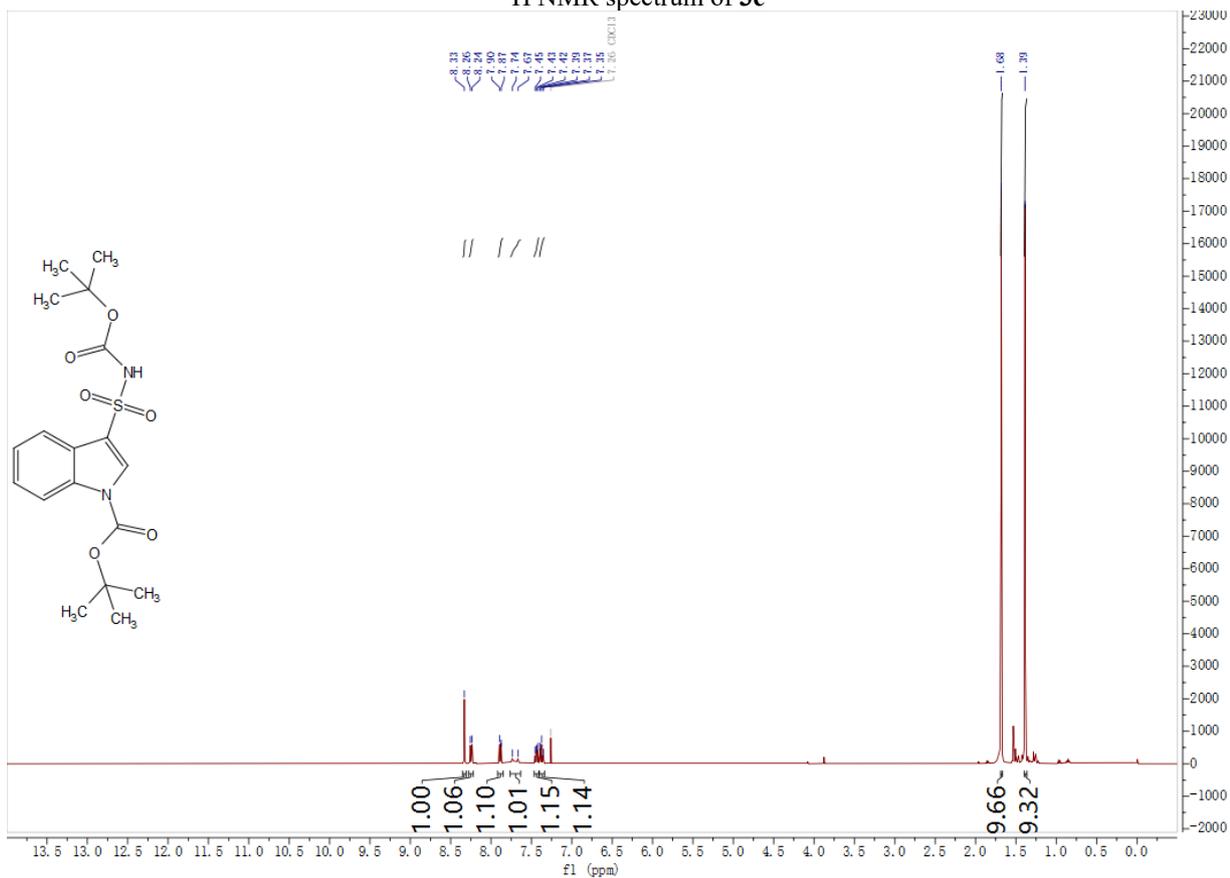


<sup>13</sup>C NMR spectrum of 3c

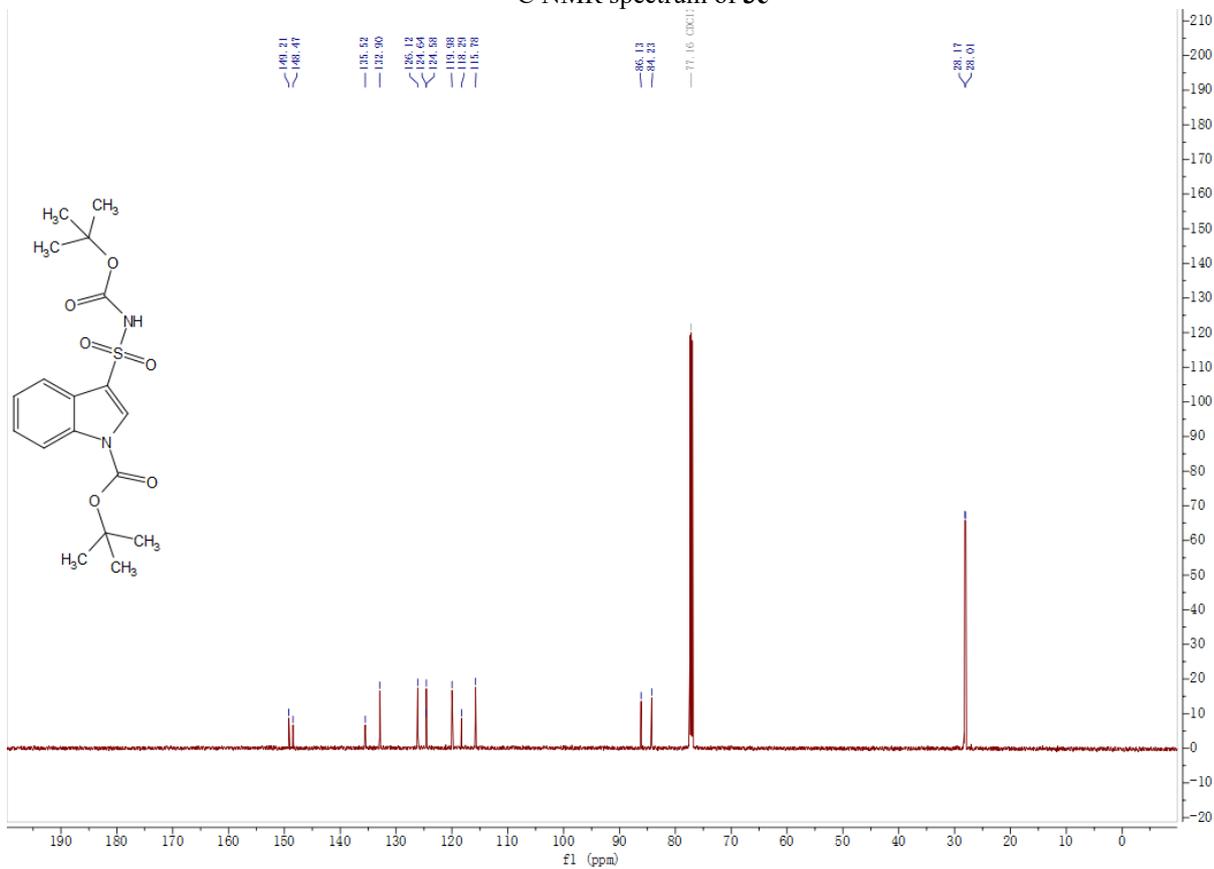




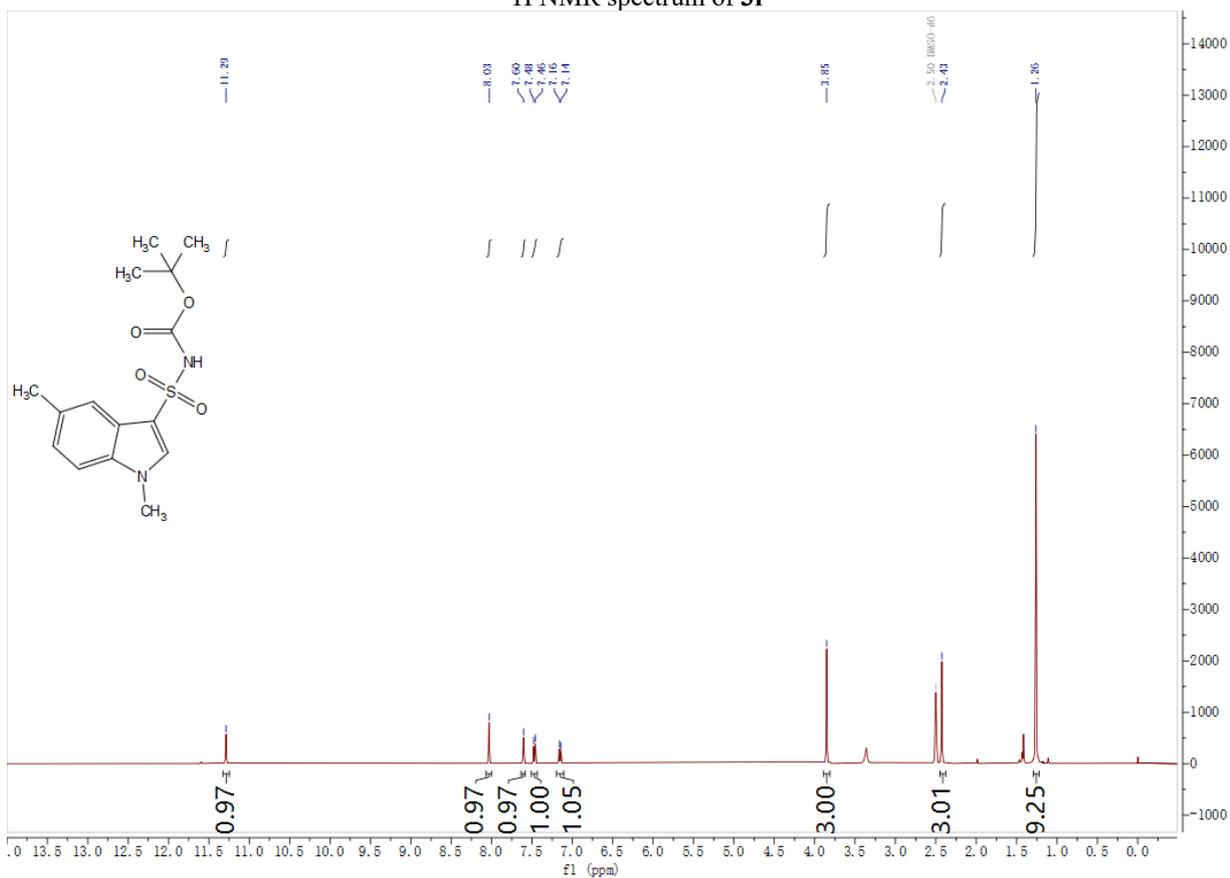
<sup>1</sup>H NMR spectrum of 3e



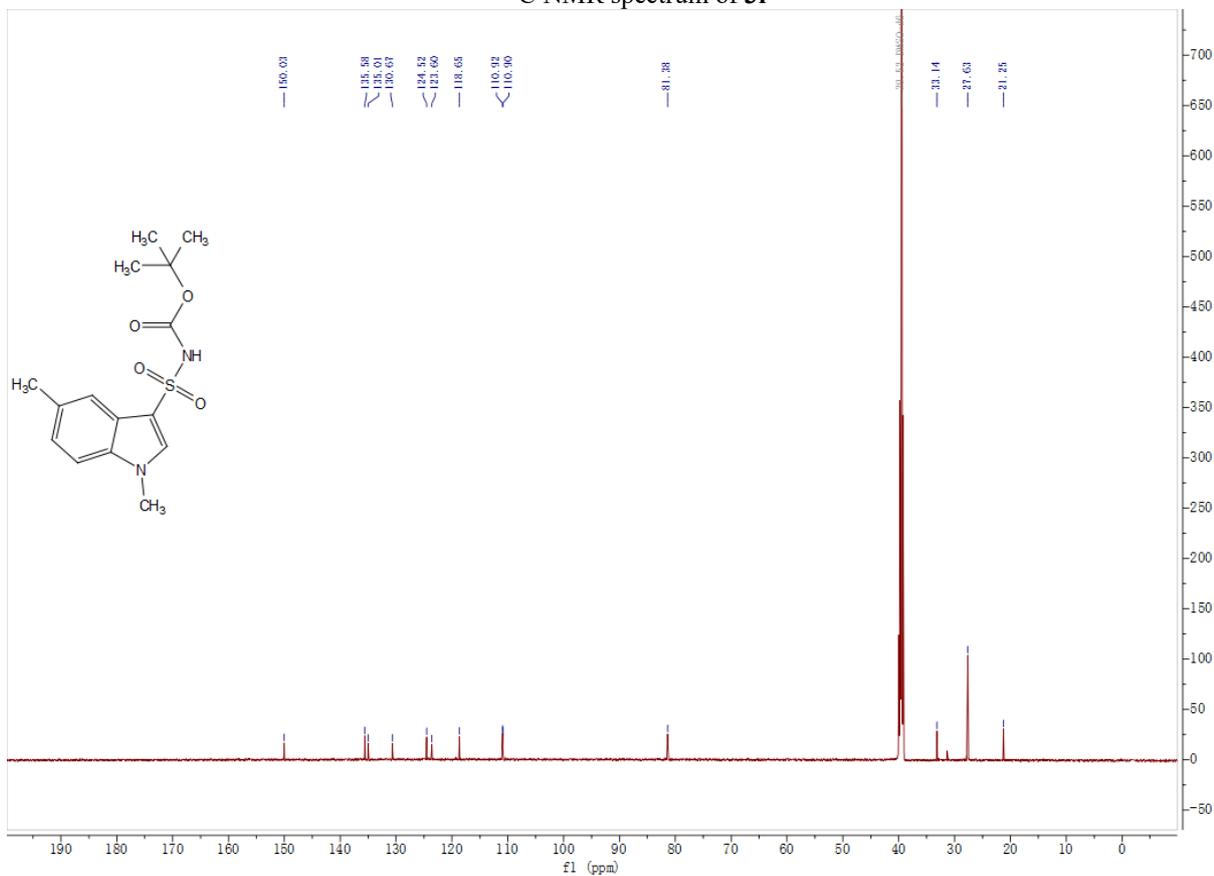
<sup>13</sup>C NMR spectrum of 3e



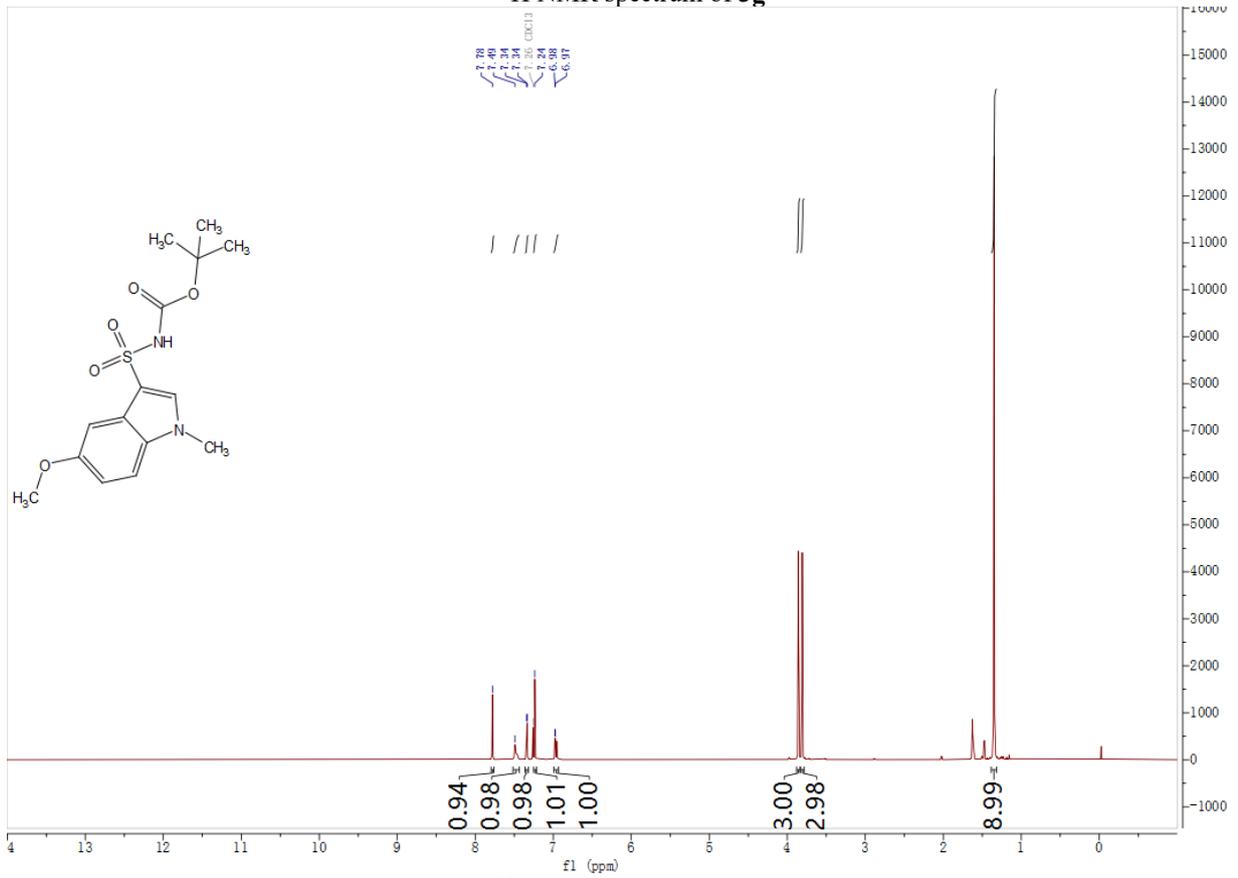
<sup>1</sup>H NMR spectrum of 3f



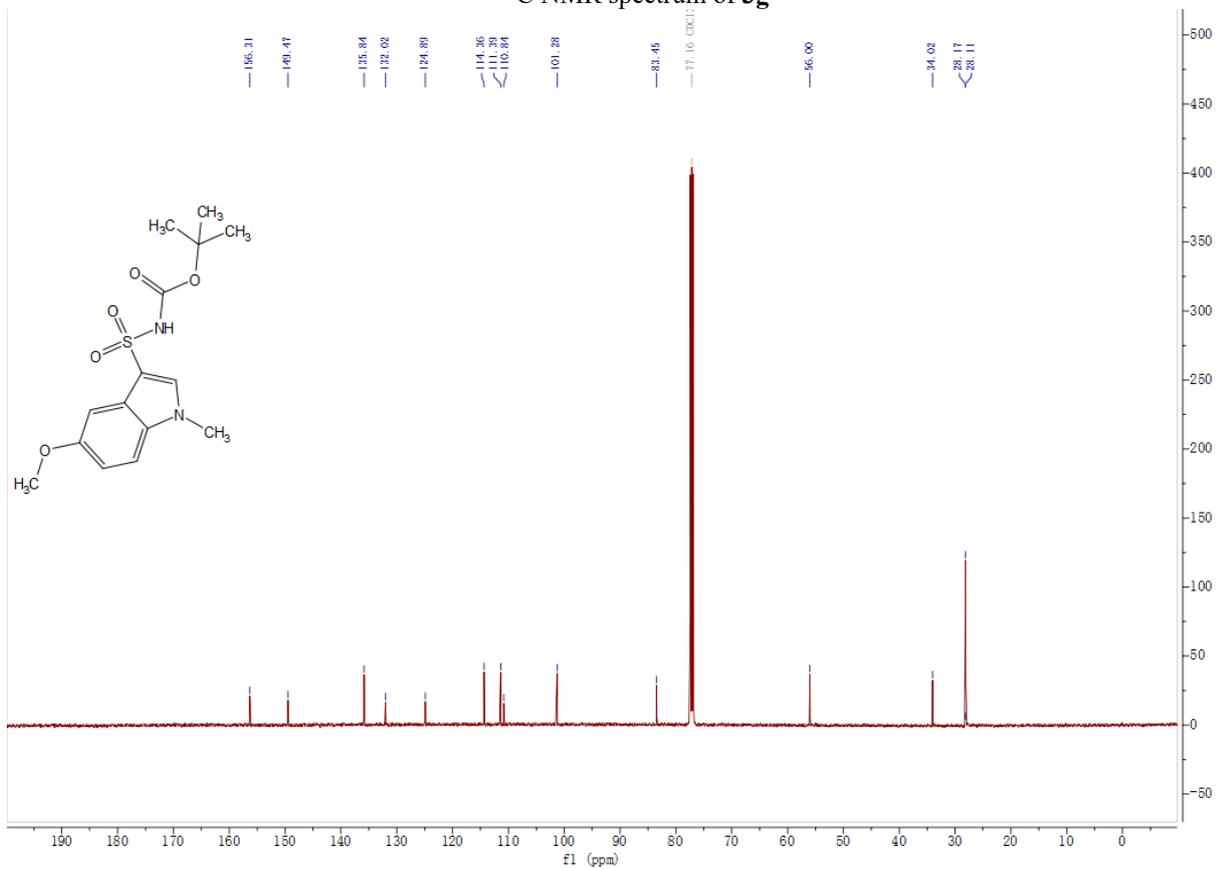
<sup>13</sup>C NMR spectrum of 3f



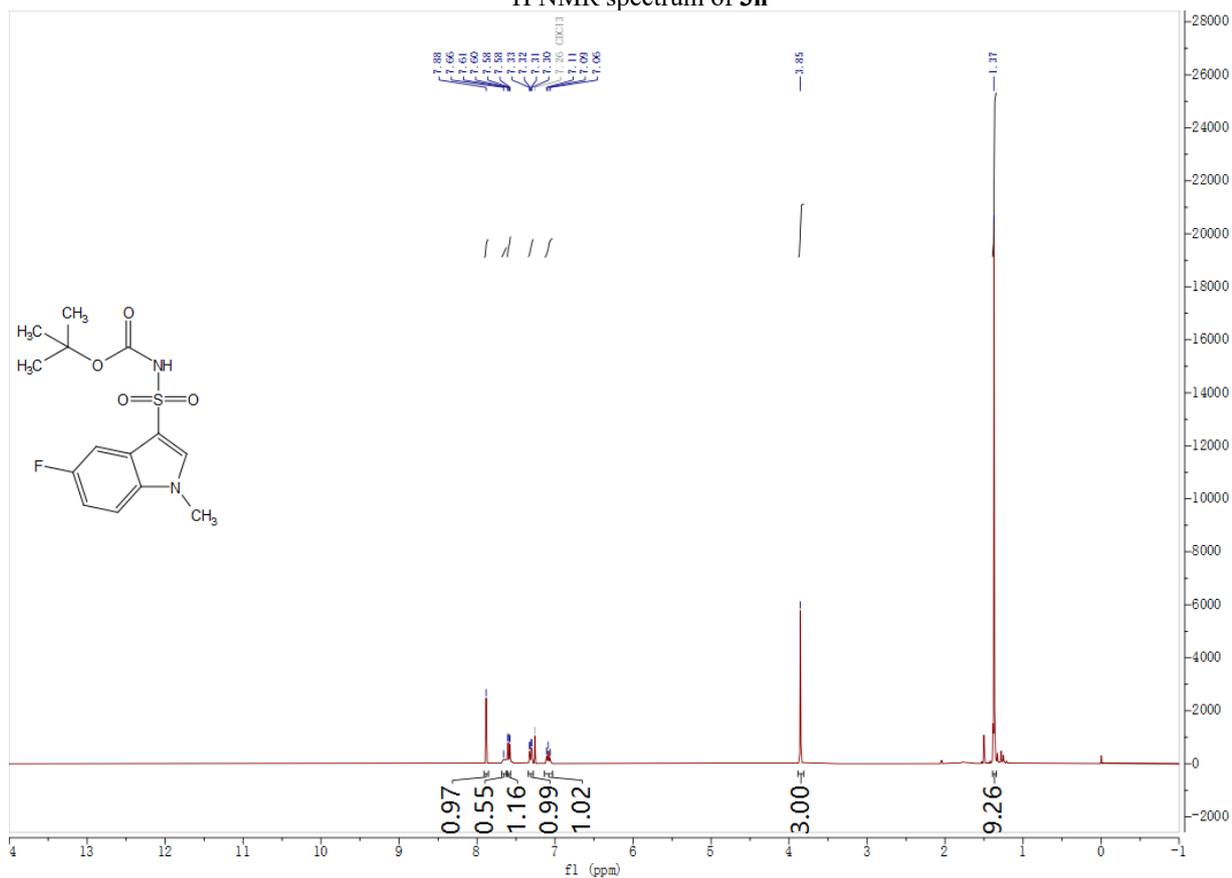
<sup>1</sup>H NMR spectrum of 3g



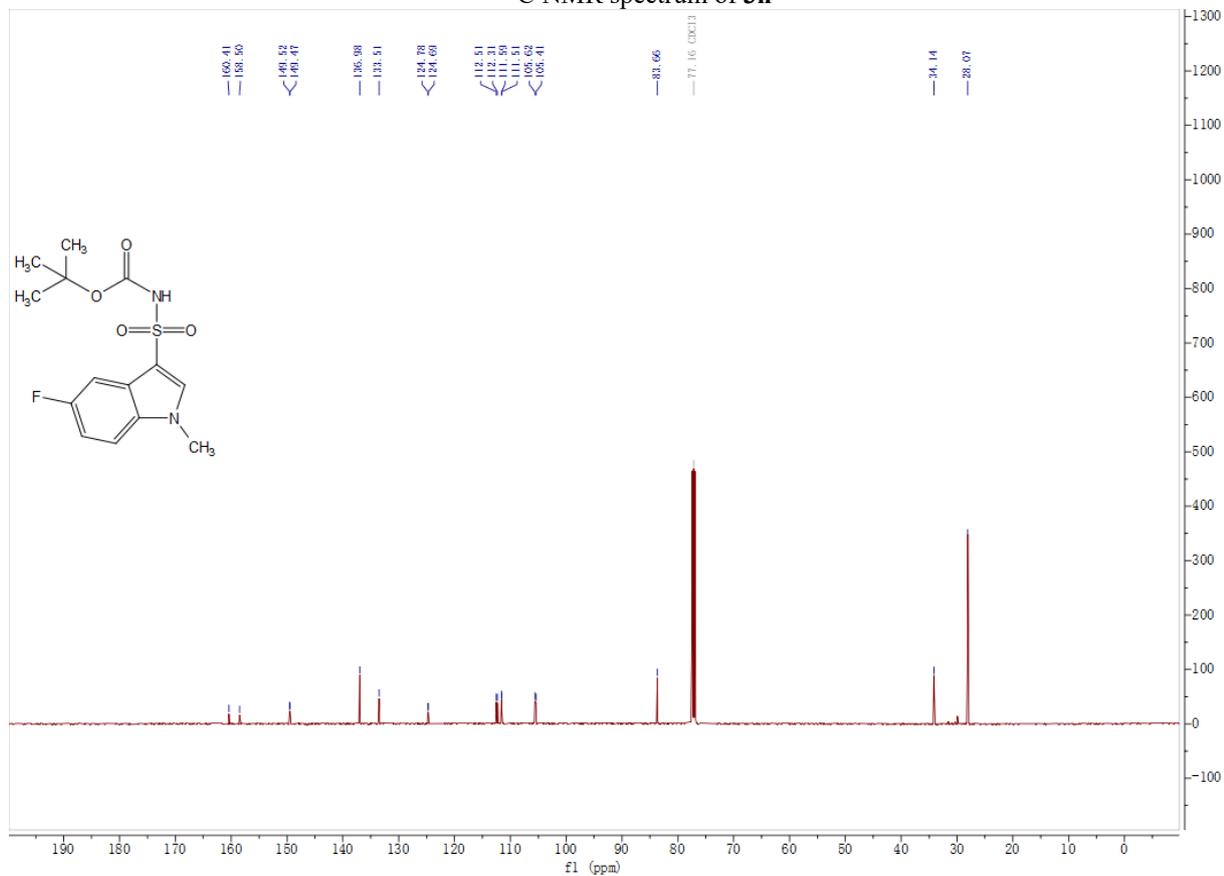
<sup>13</sup>C NMR spectrum of 3g



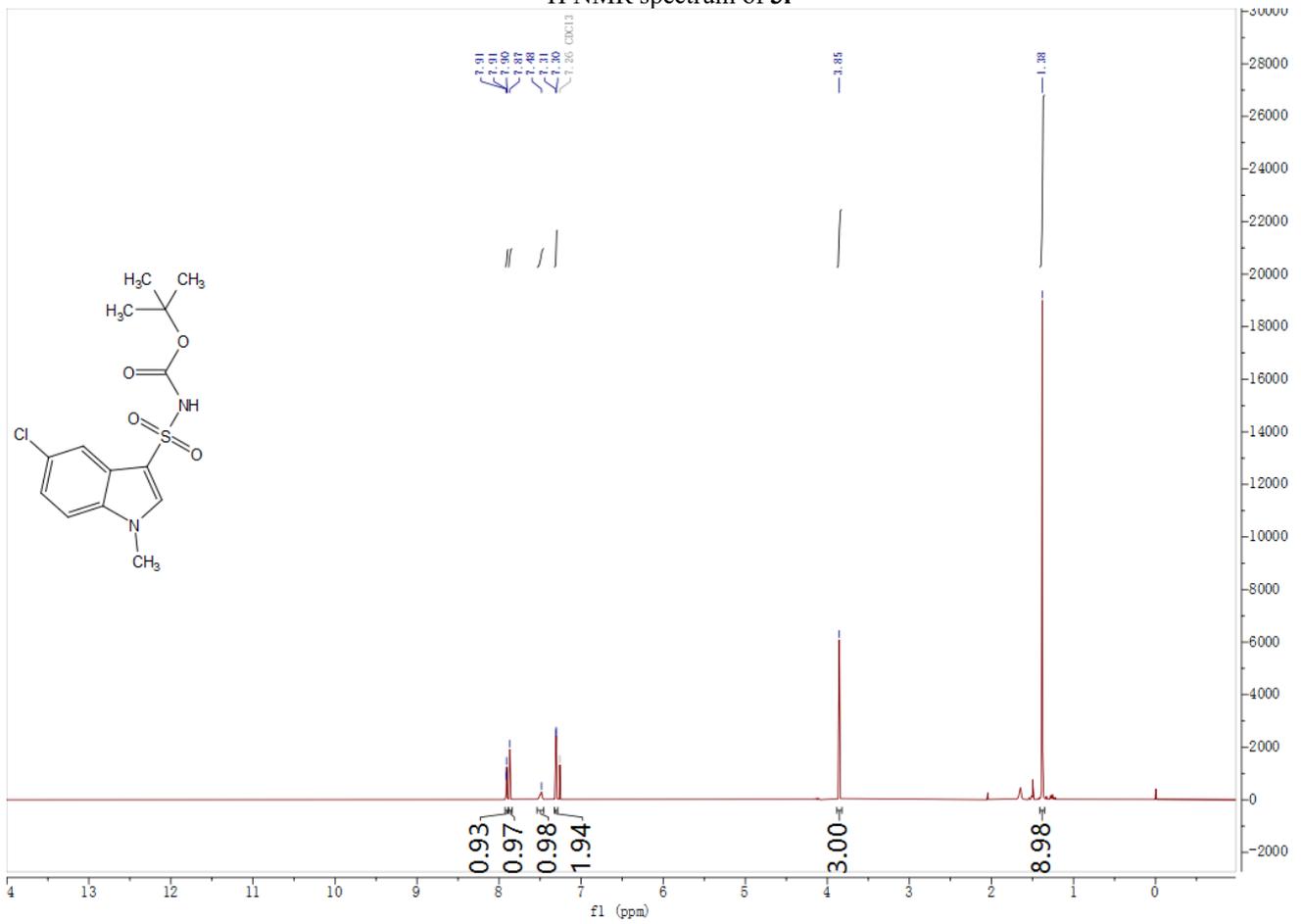
<sup>1</sup>H NMR spectrum of **3h**



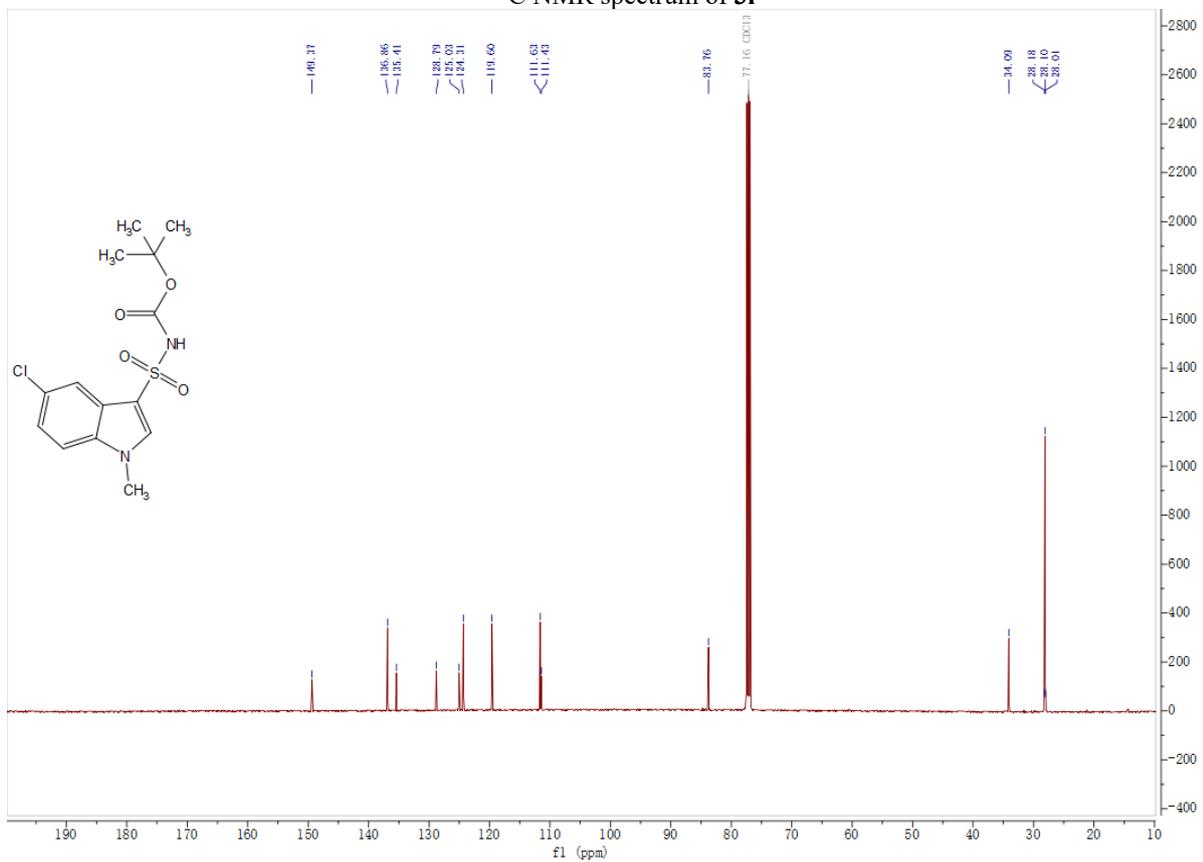
<sup>13</sup>C NMR spectrum of **3h**



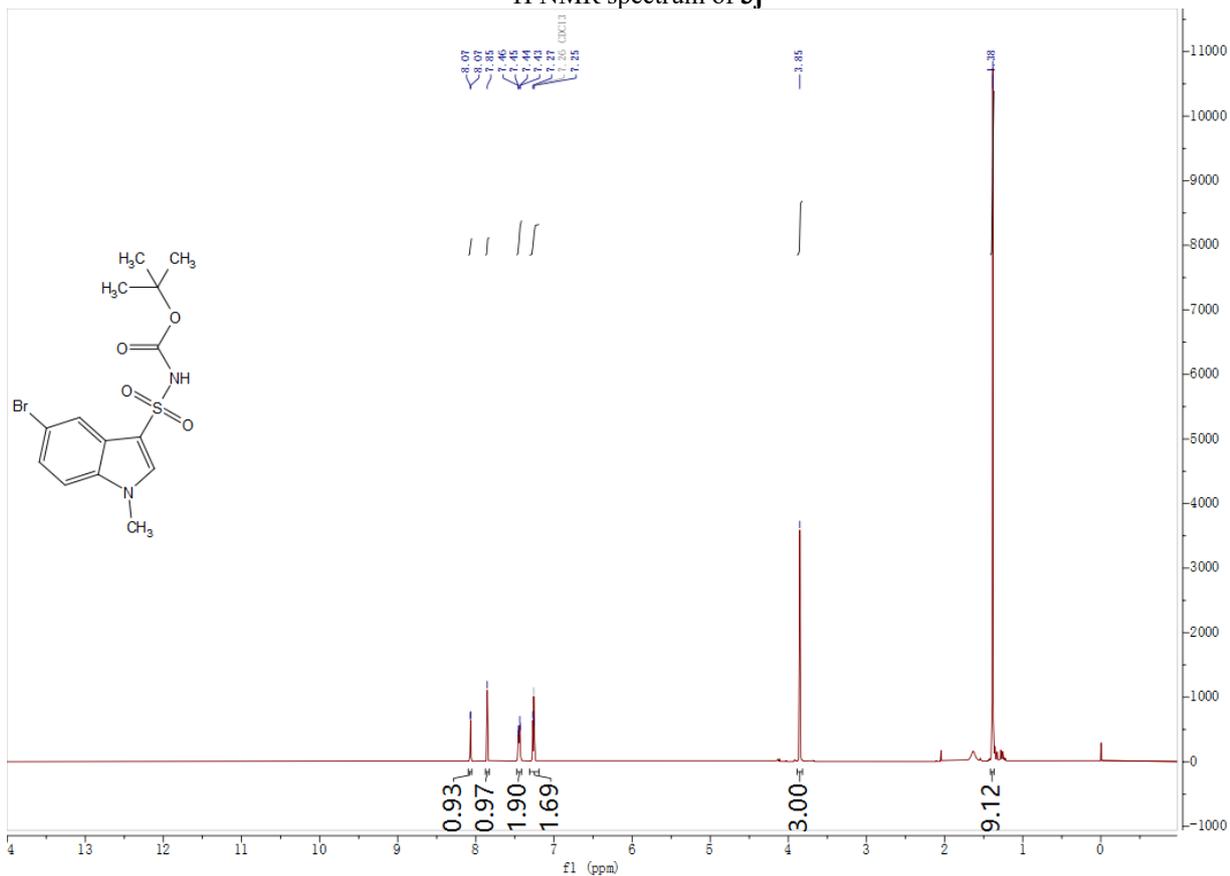
<sup>1</sup>H NMR spectrum of **3i**



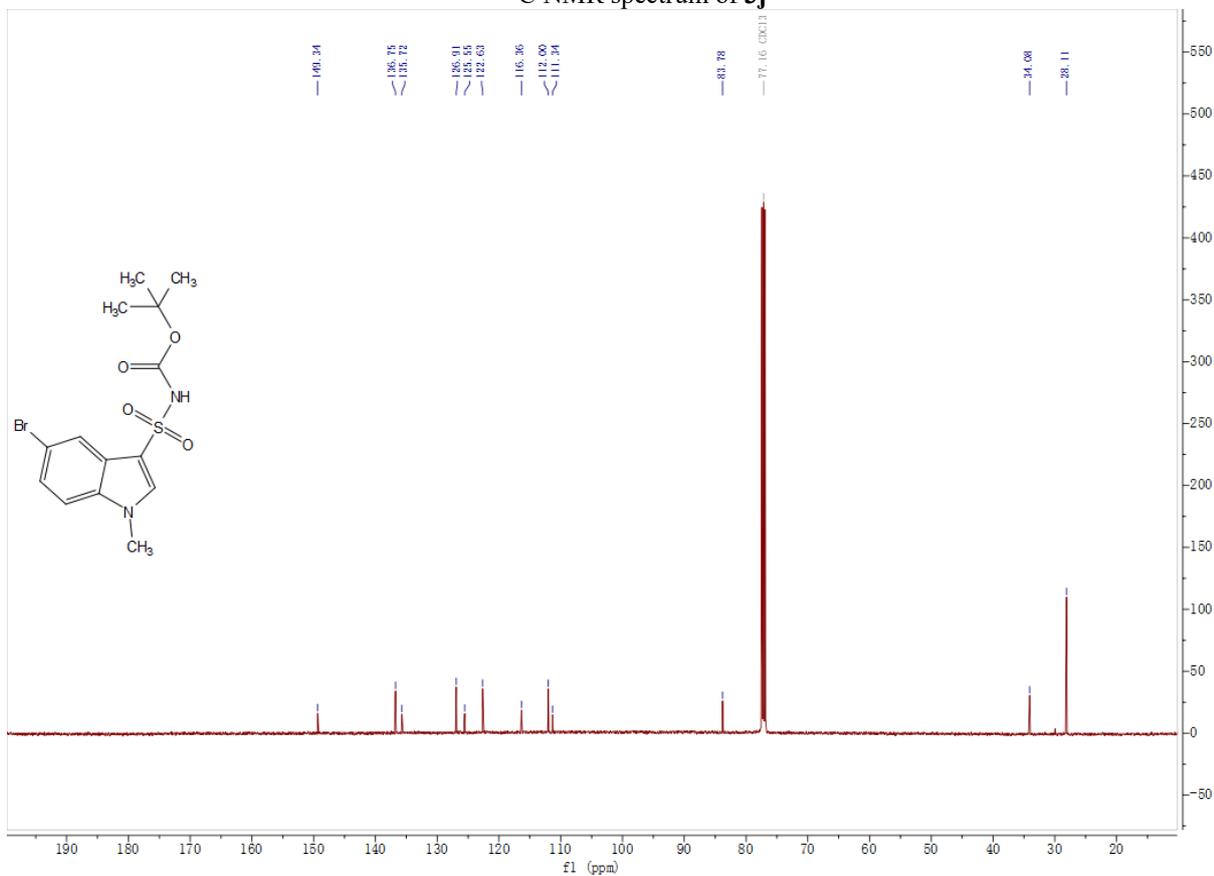
<sup>13</sup>C NMR spectrum of **3i**



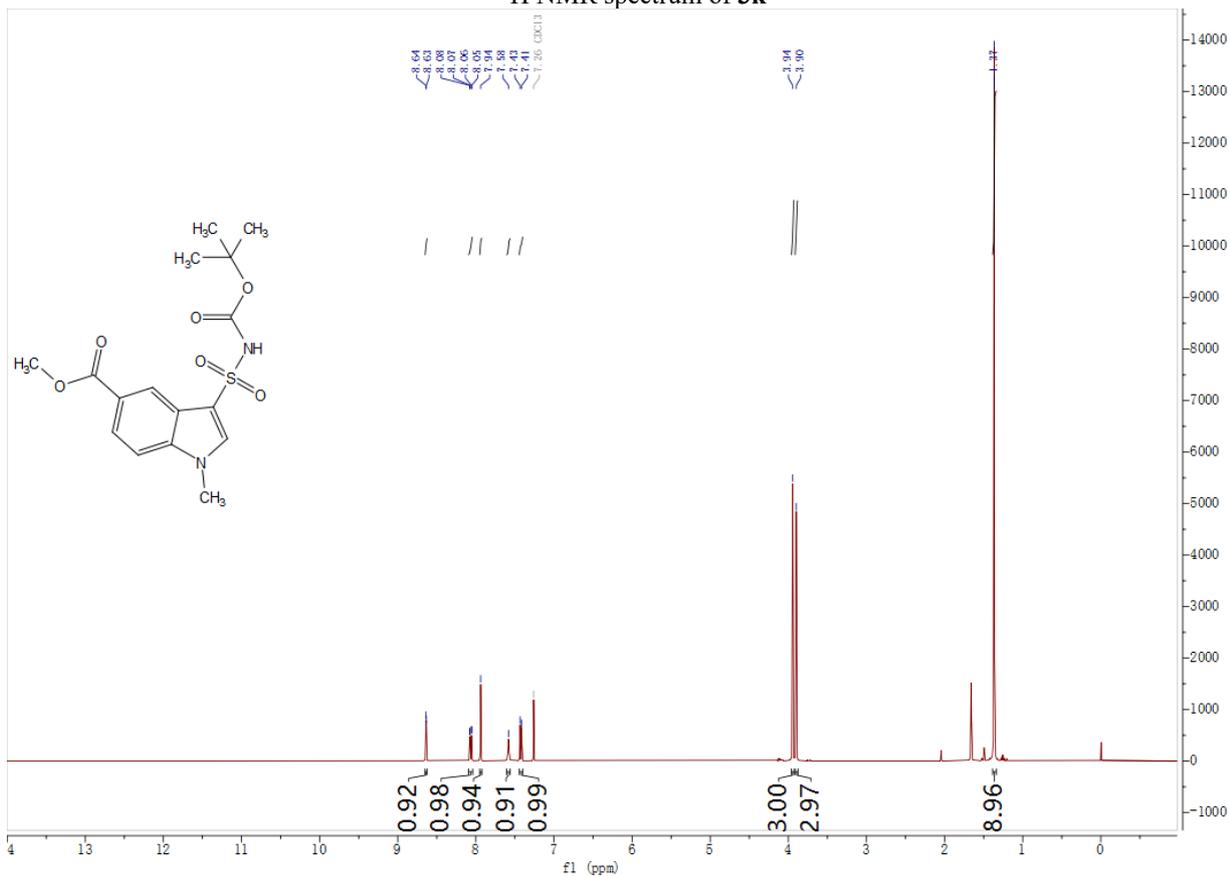
<sup>1</sup>H NMR spectrum of **3j**



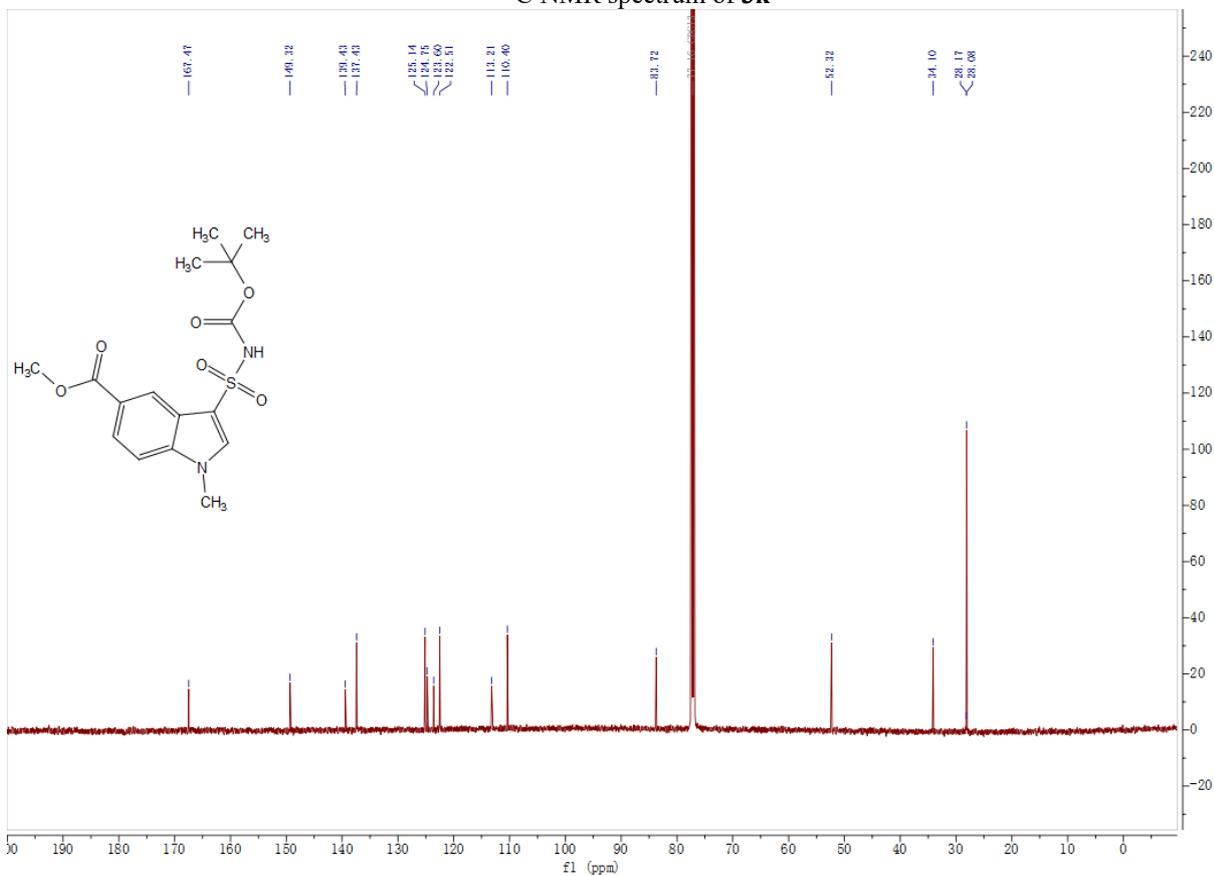
<sup>13</sup>C NMR spectrum of **3j**



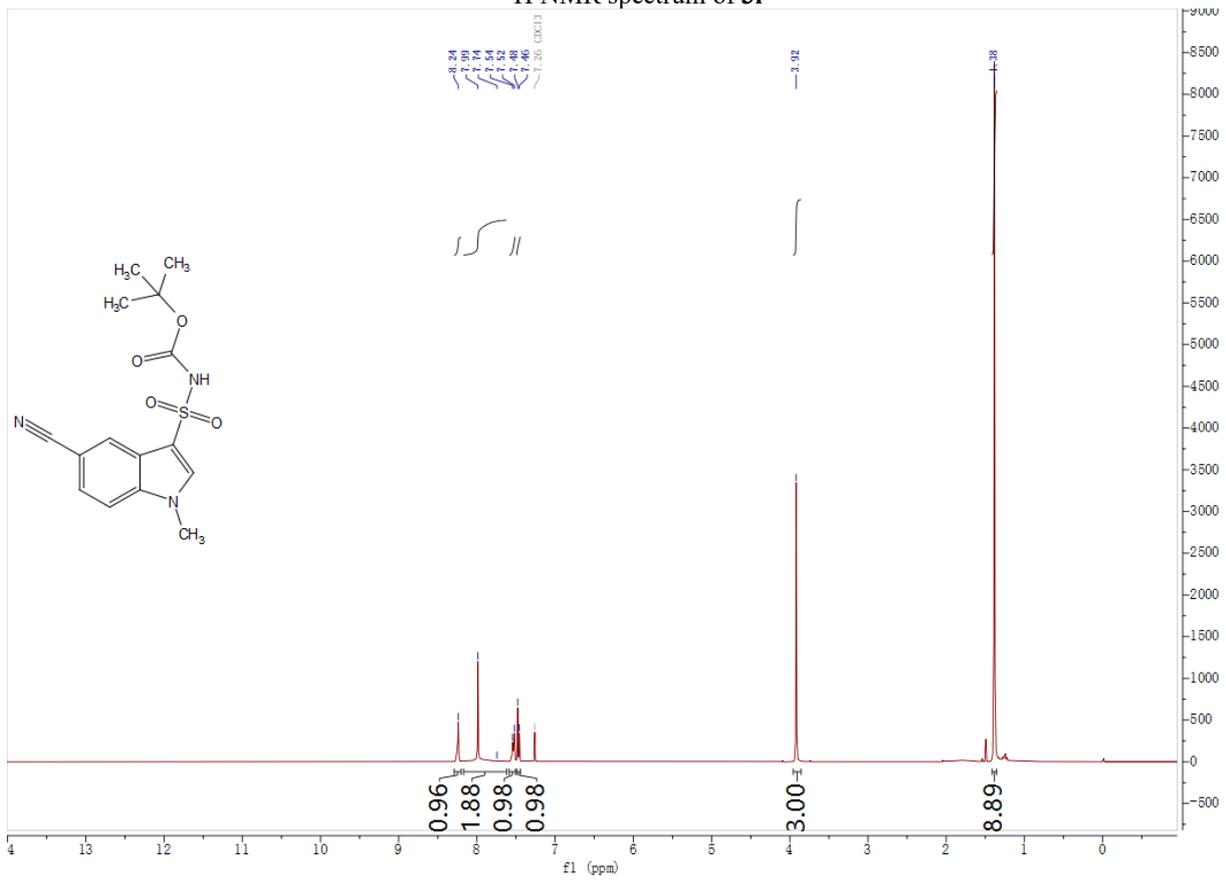
<sup>1</sup>H NMR spectrum of 3k



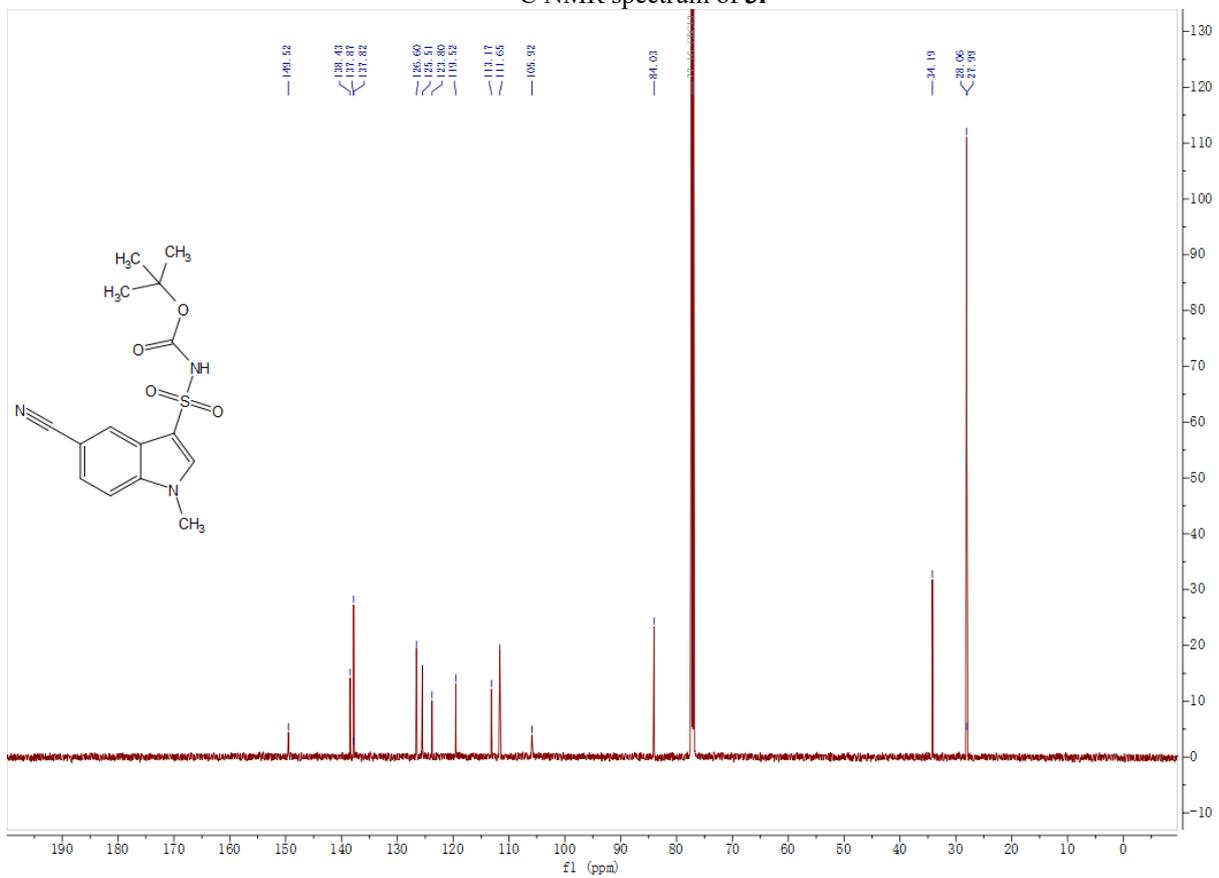
<sup>13</sup>C NMR spectrum of 3k



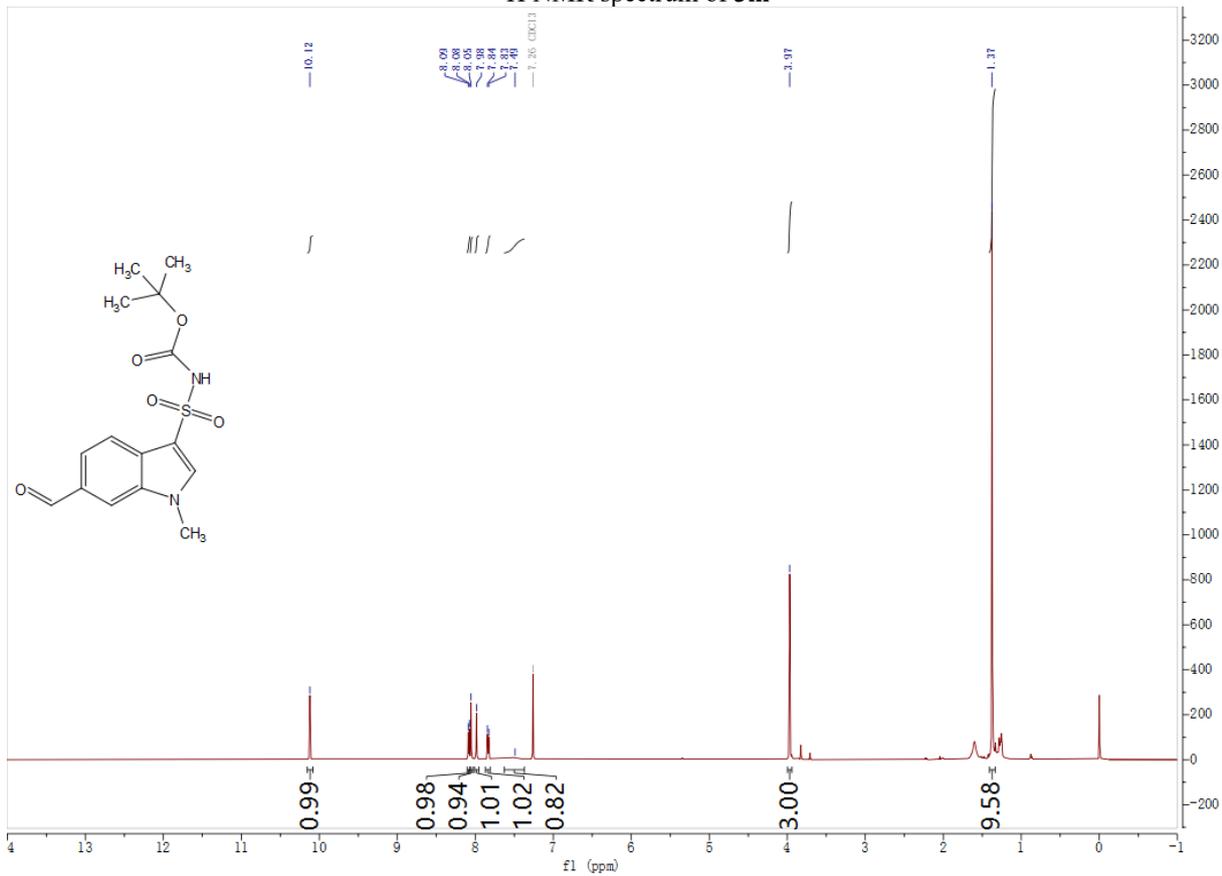
<sup>1</sup>H NMR spectrum of **31**



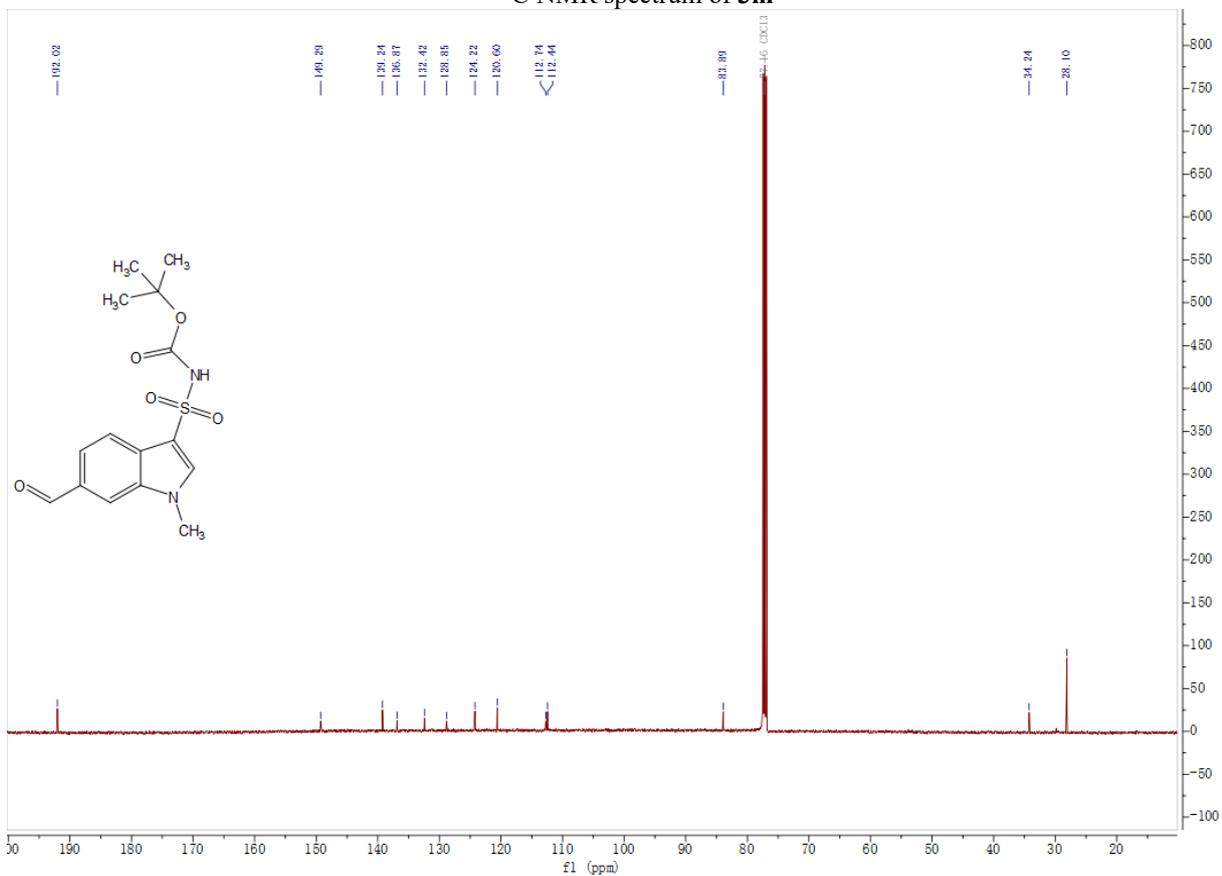
<sup>13</sup>C NMR spectrum of **31**



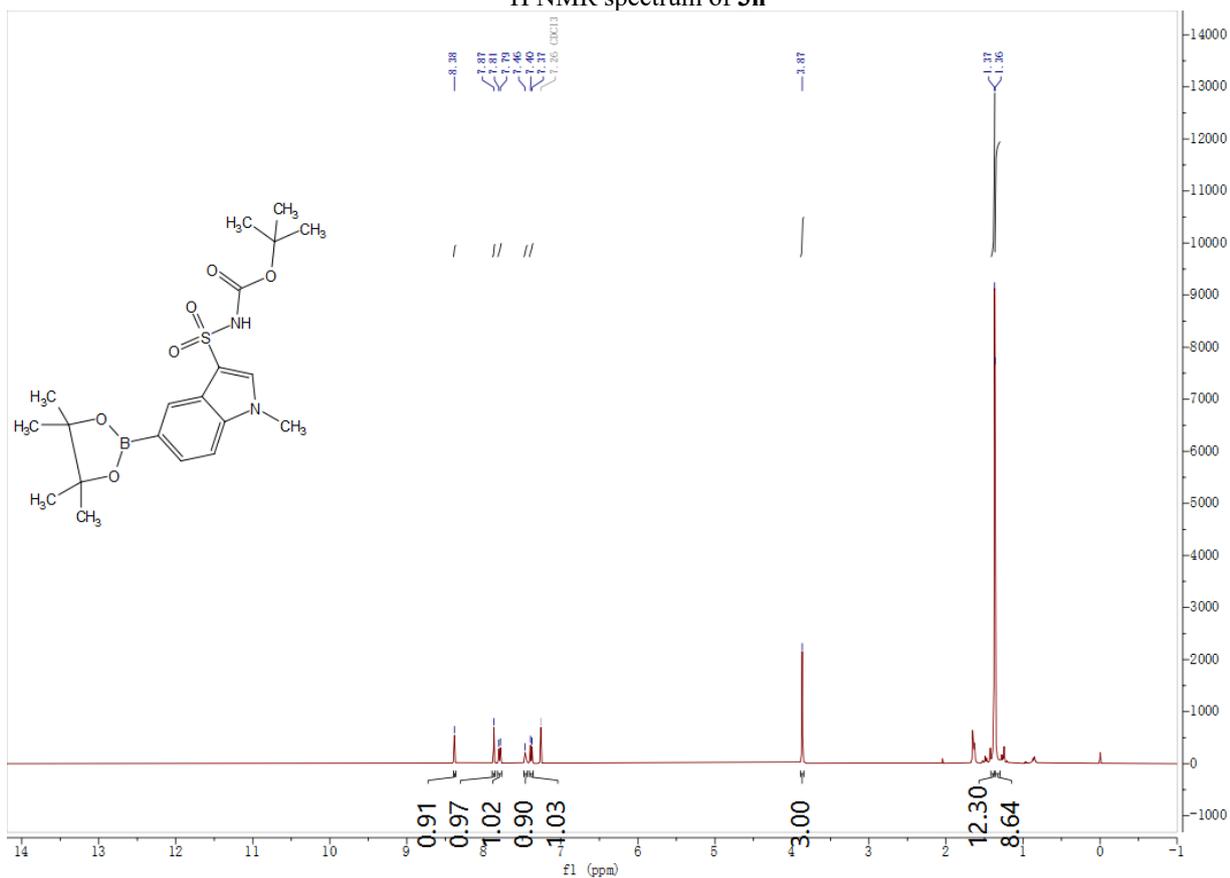
<sup>1</sup>H NMR spectrum of **3m**



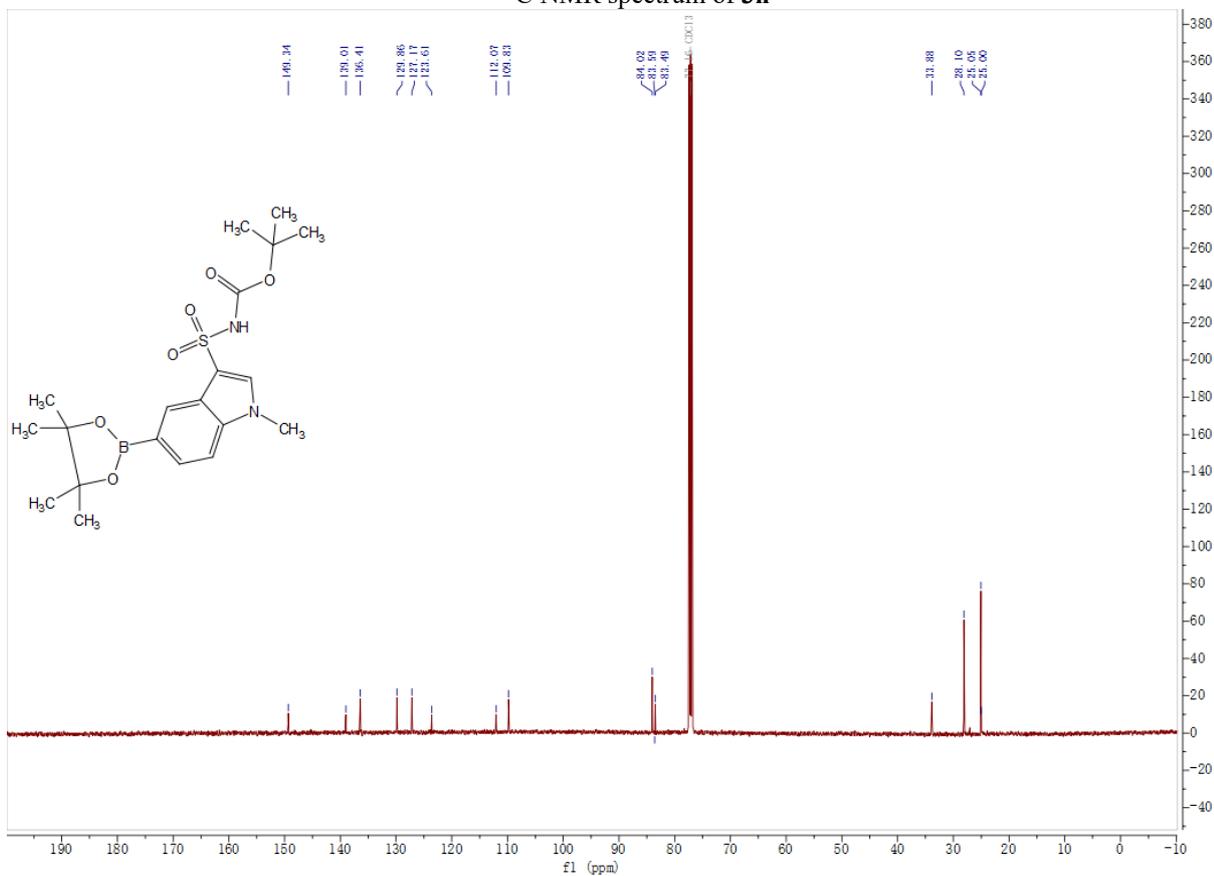
<sup>13</sup>C NMR spectrum of **3m**



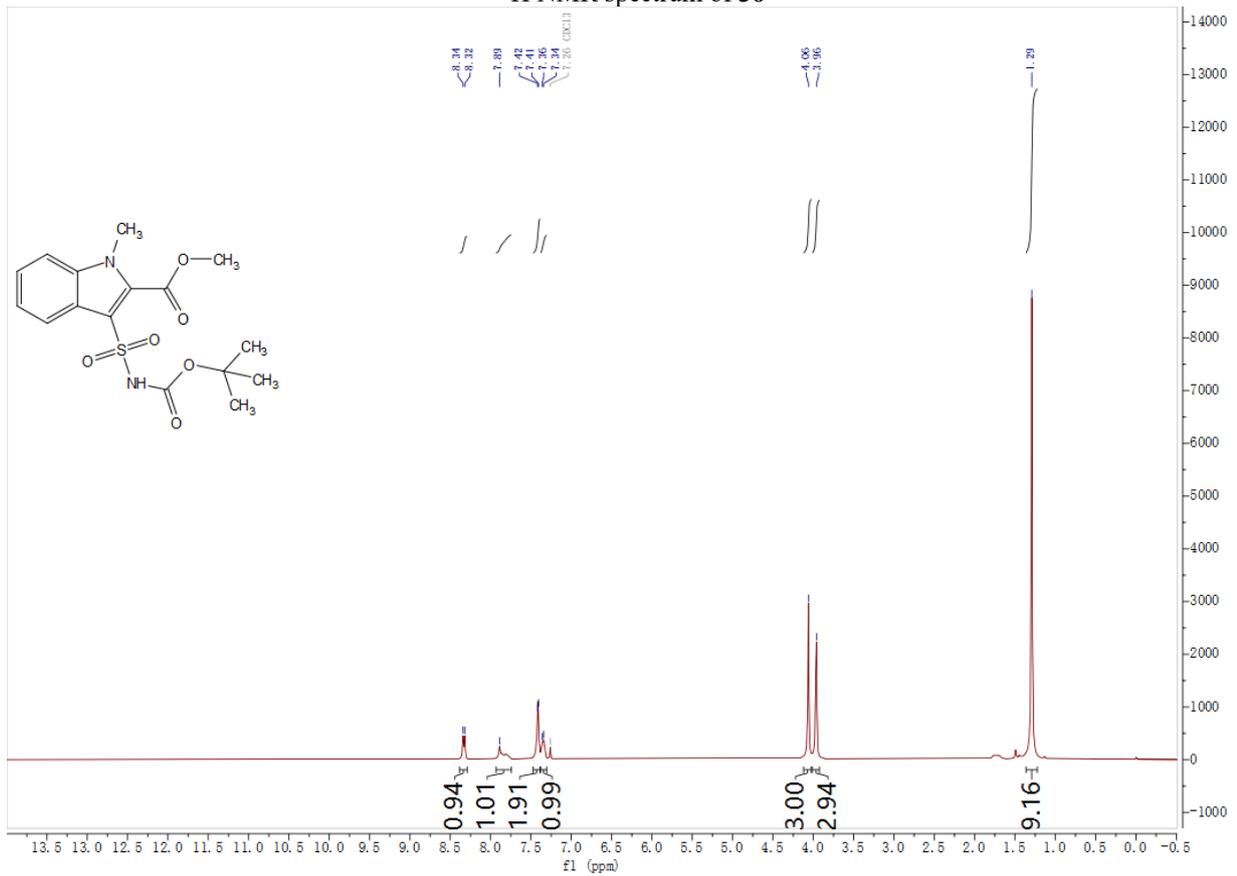
<sup>1</sup>H NMR spectrum of **3n**



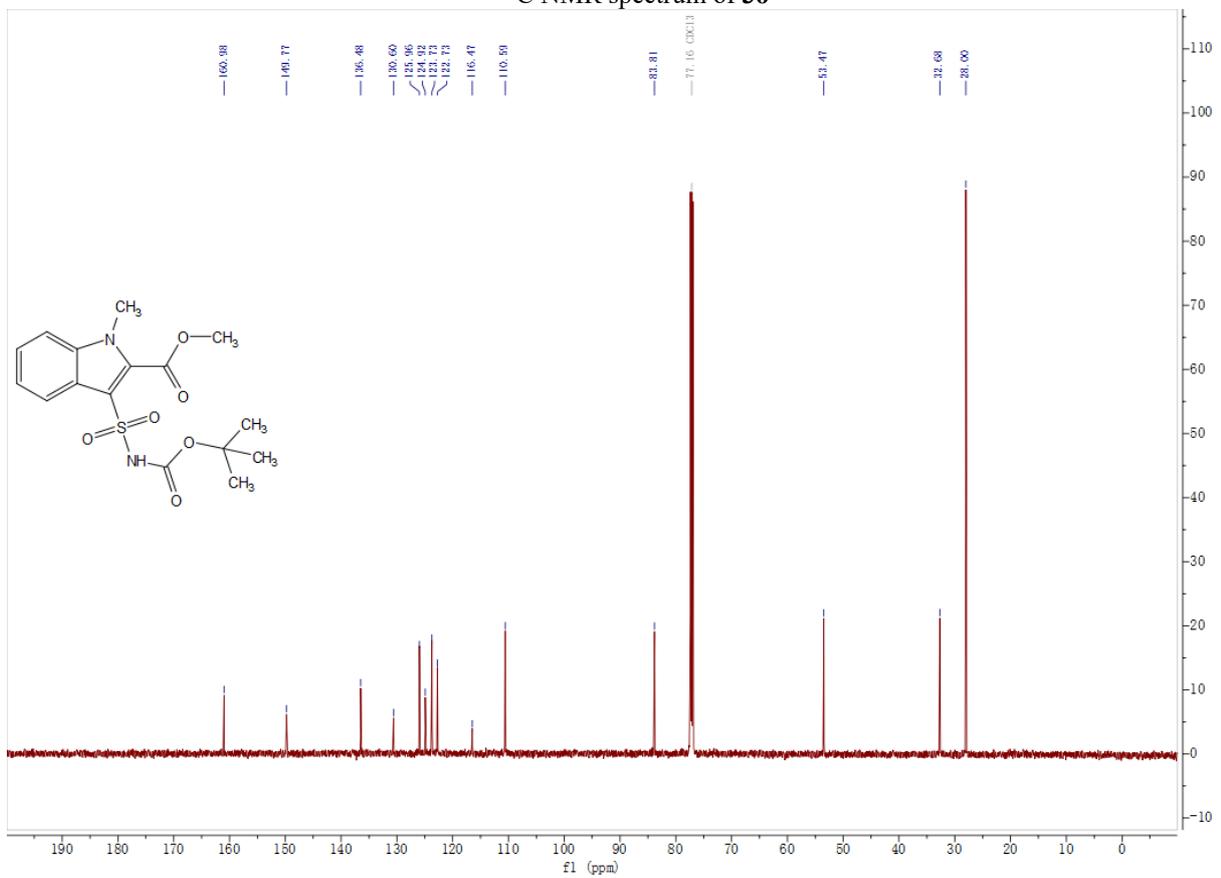
<sup>13</sup>C NMR spectrum of **3n**



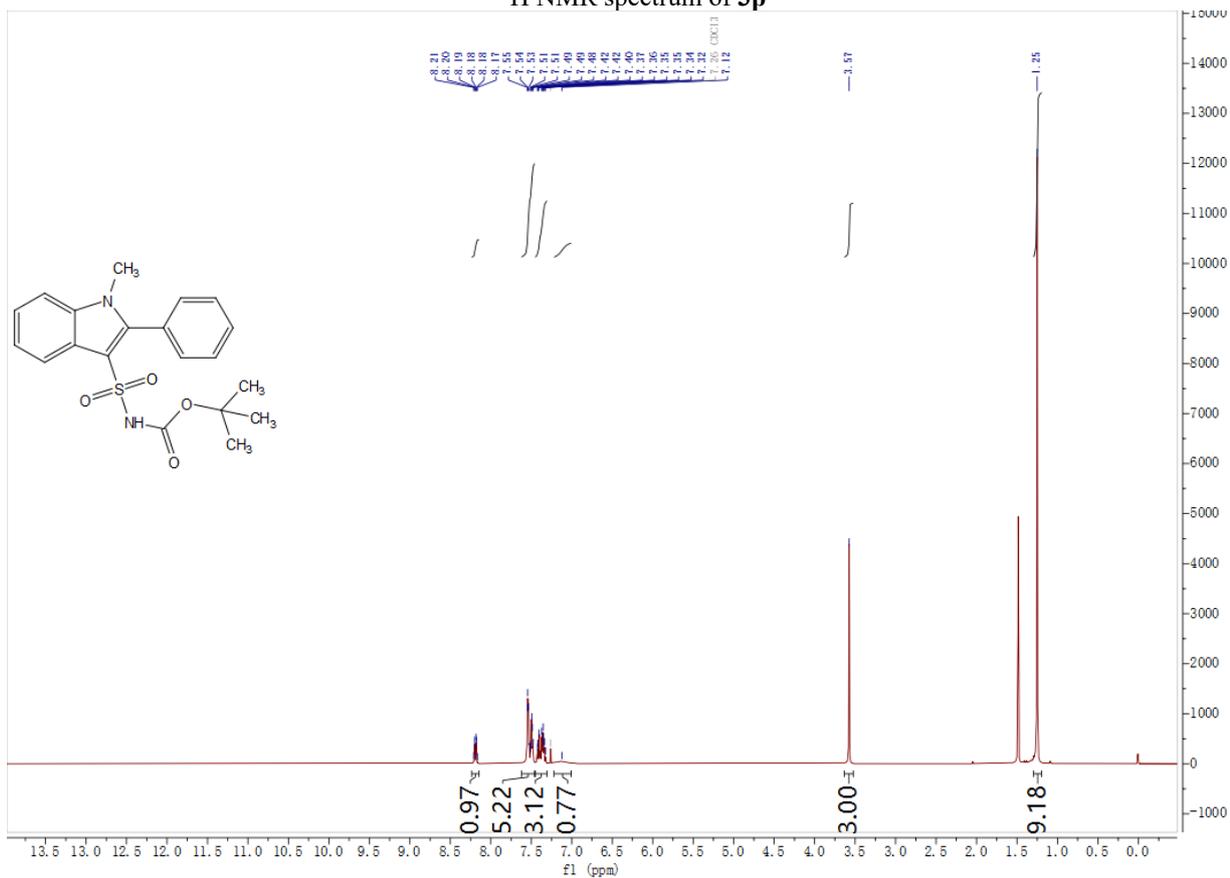
<sup>1</sup>H NMR spectrum of **30**



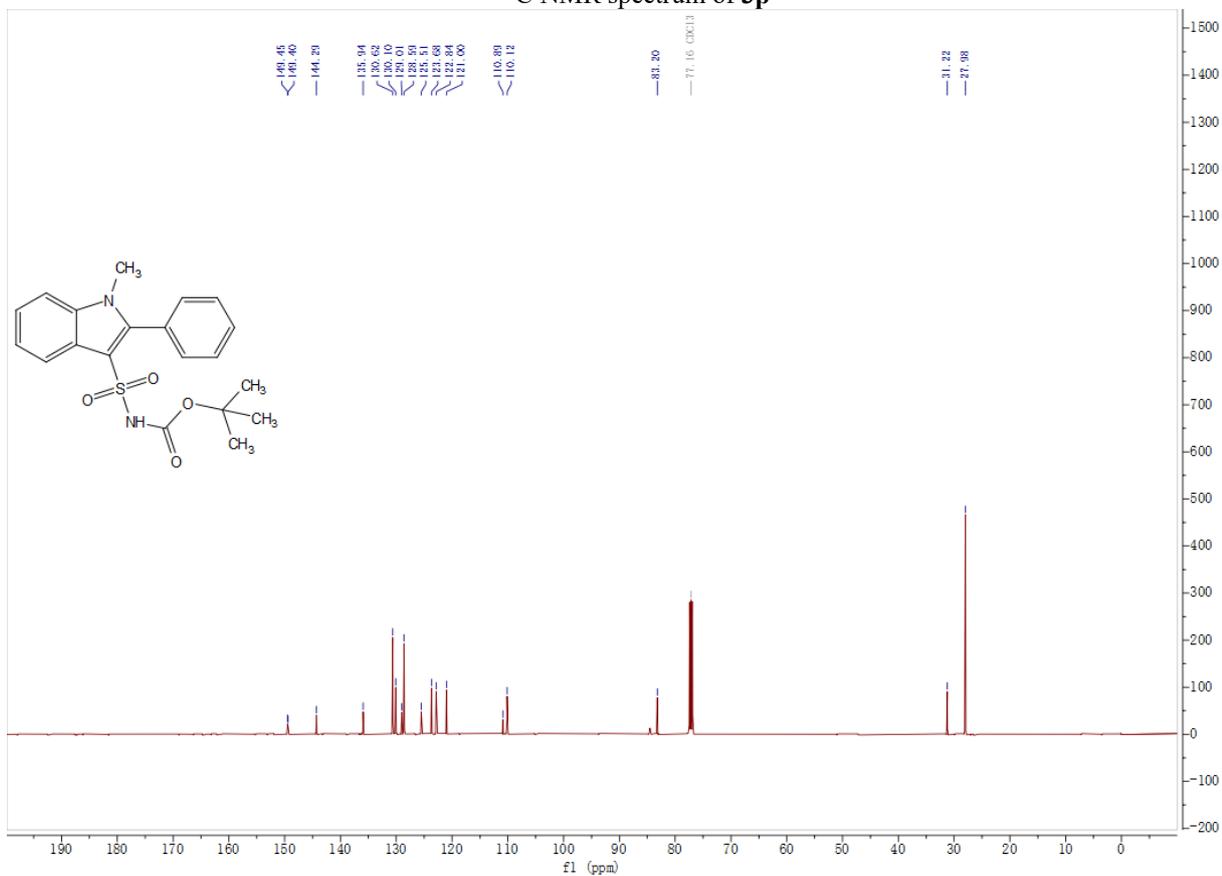
<sup>13</sup>C NMR spectrum of **30**



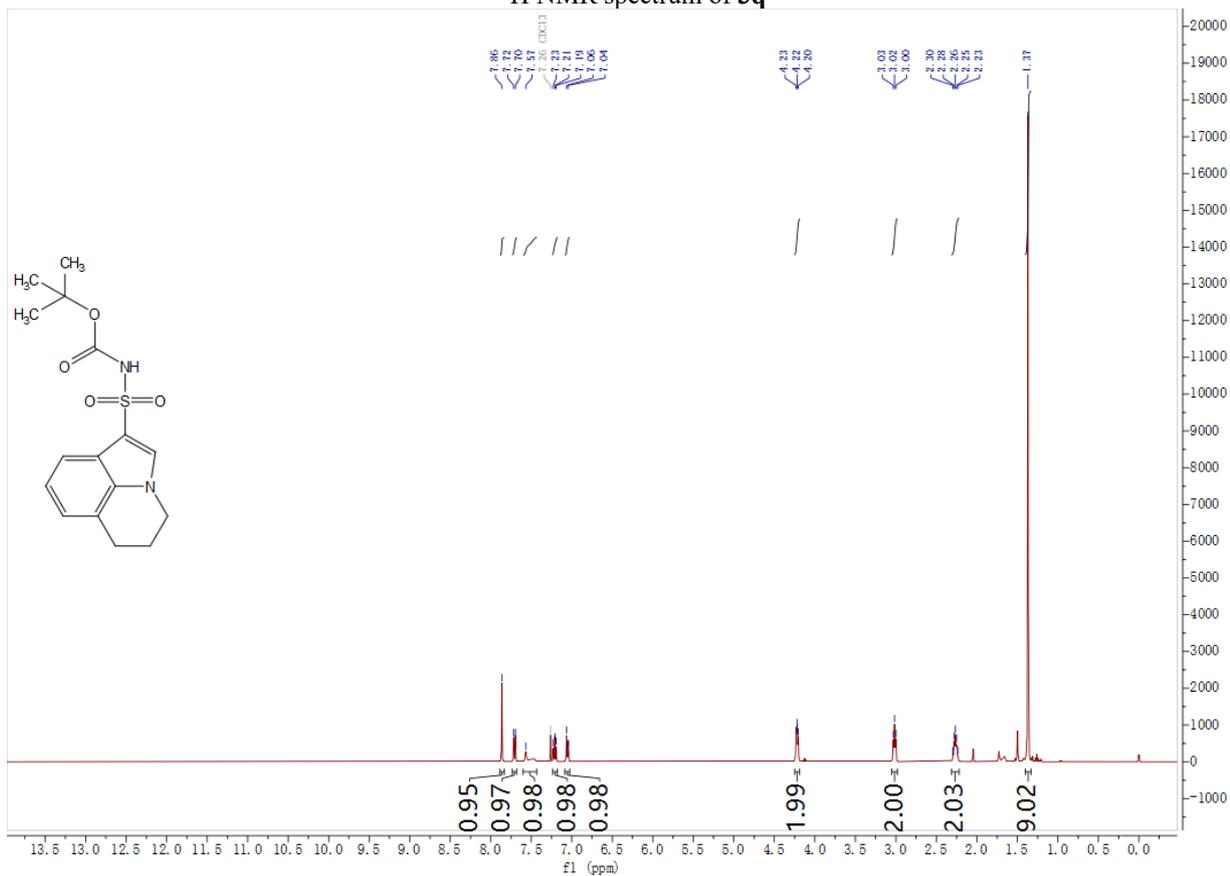
<sup>1</sup>H NMR spectrum of **3p**



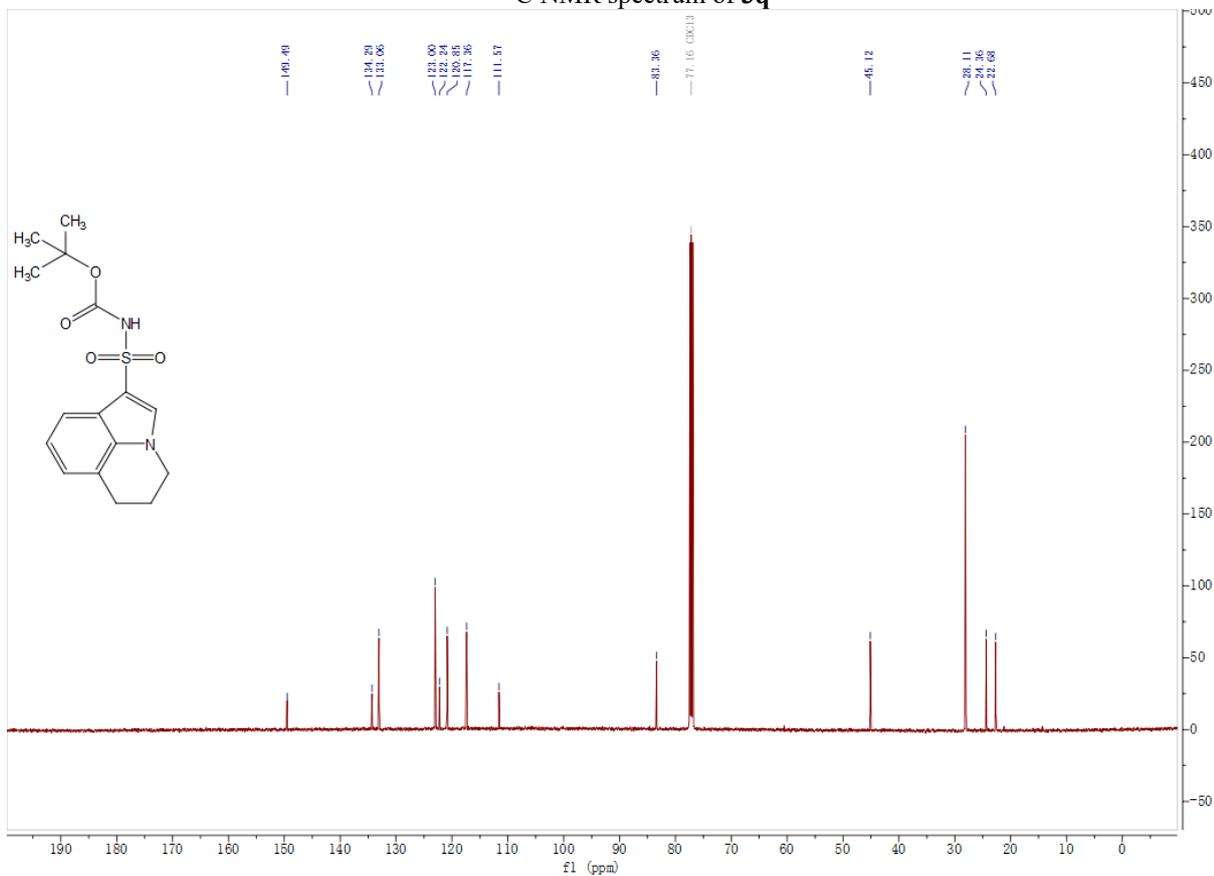
<sup>13</sup>C NMR spectrum of **3p**



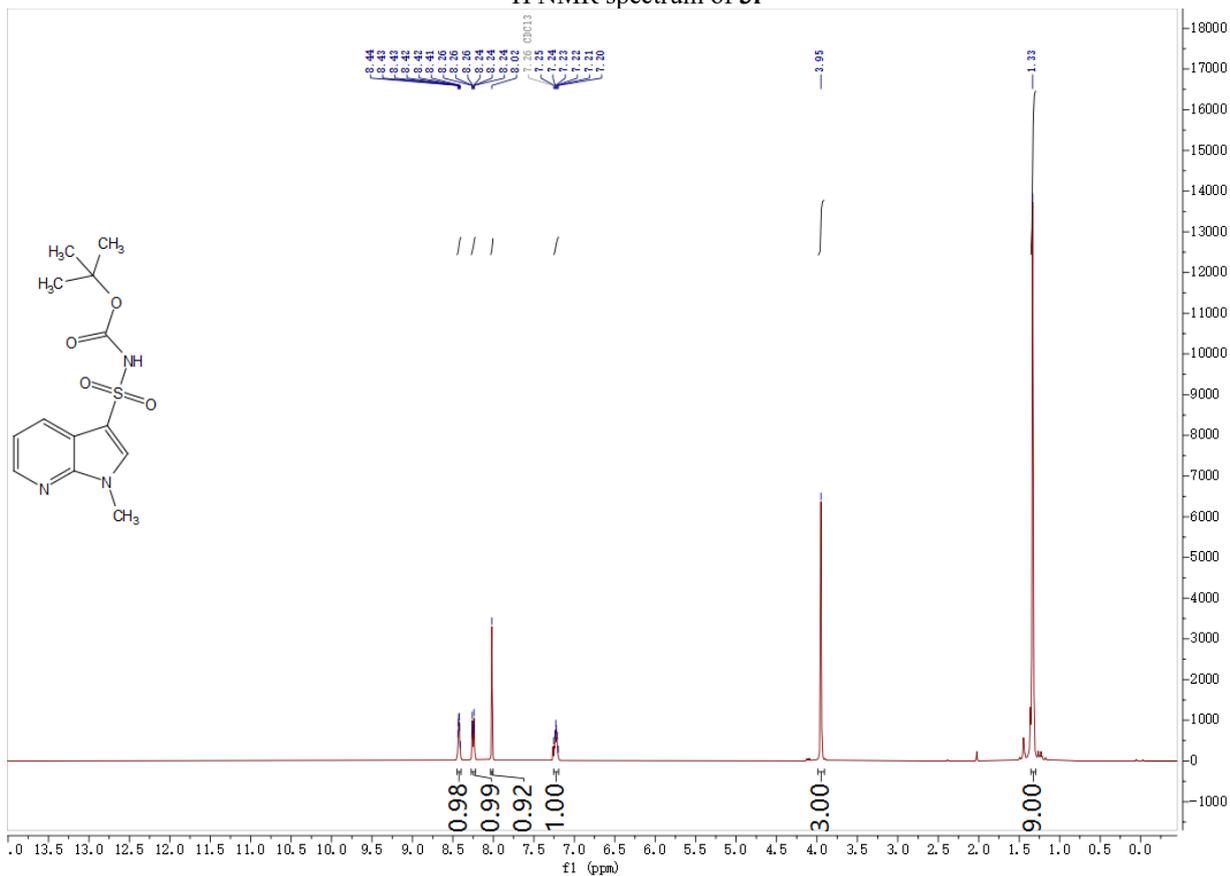
<sup>1</sup>H NMR spectrum of **3q**



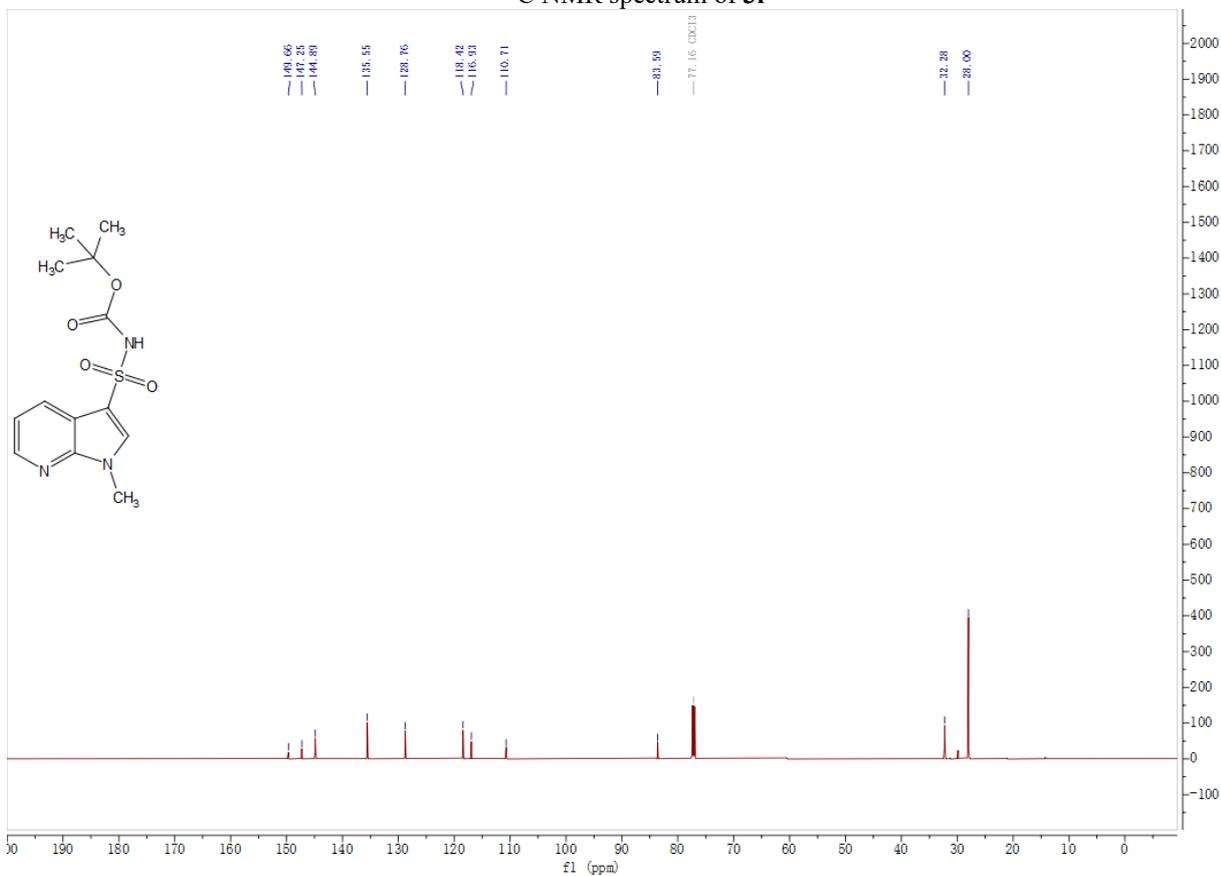
<sup>13</sup>C NMR spectrum of **3q**



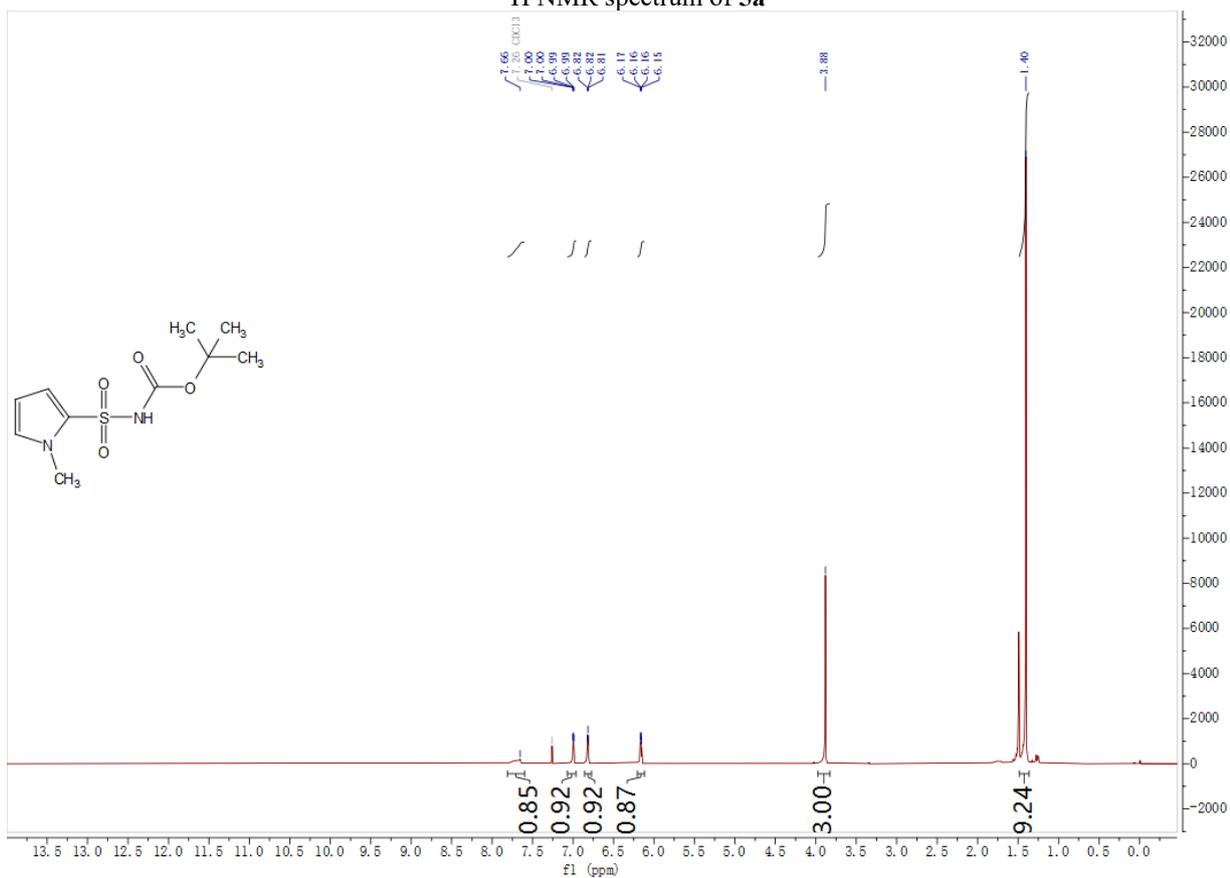
<sup>1</sup>H NMR spectrum of 3r



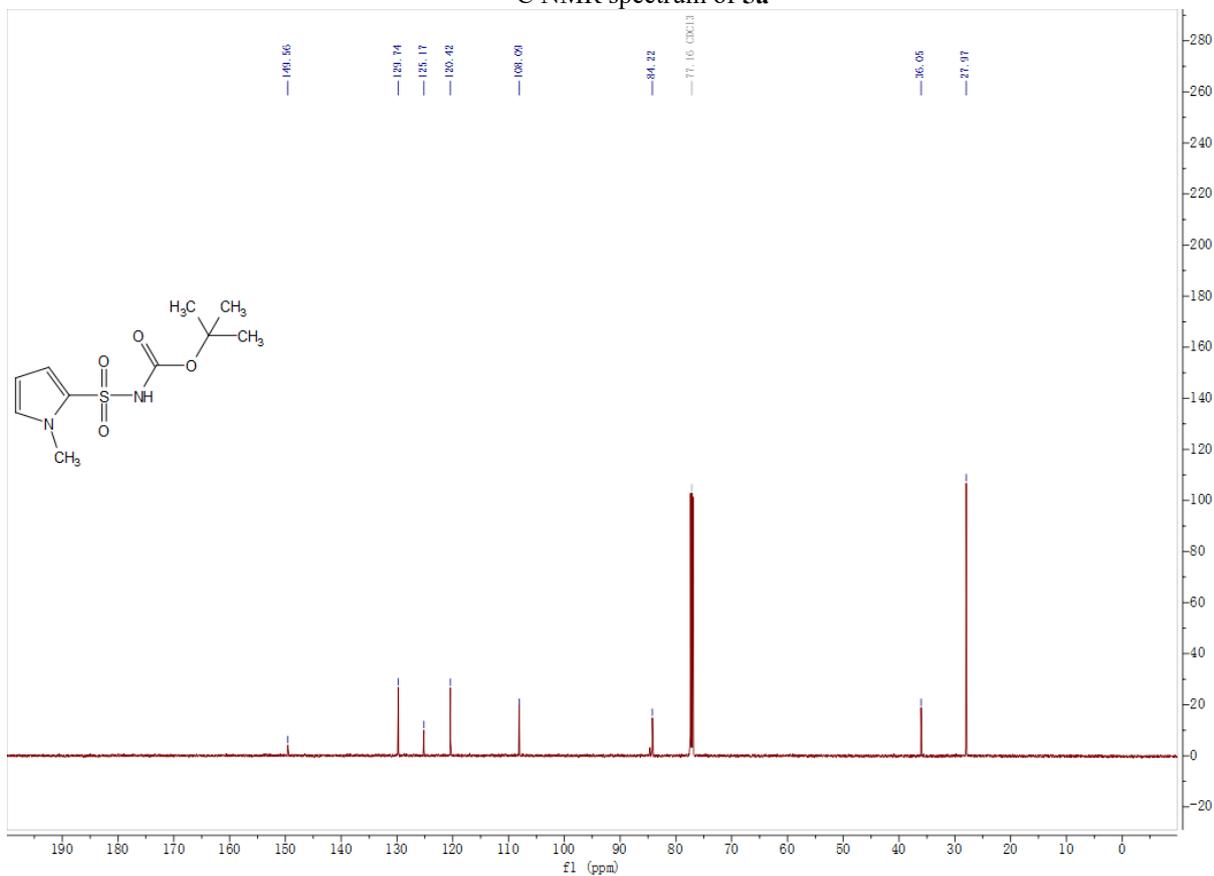
<sup>13</sup>C NMR spectrum of 3r



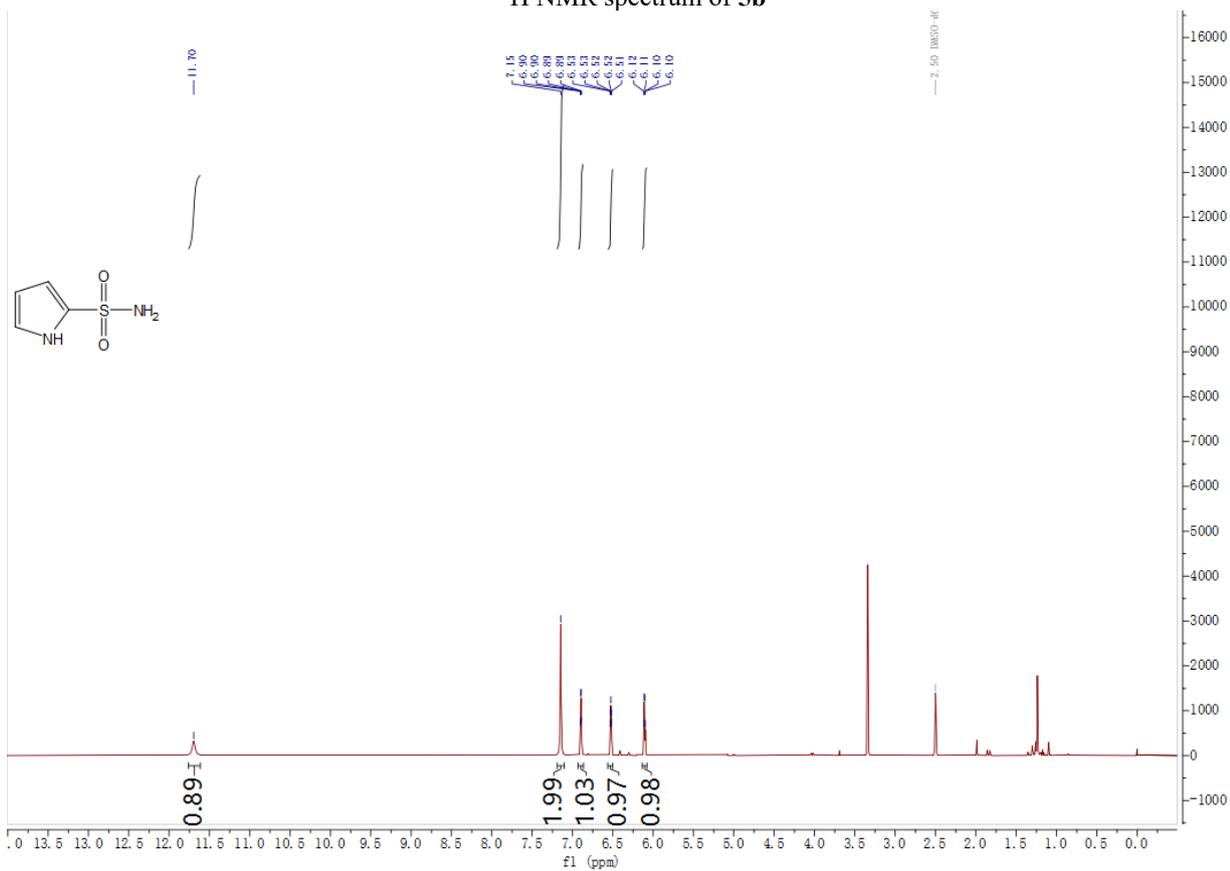
<sup>1</sup>H NMR spectrum of 5a



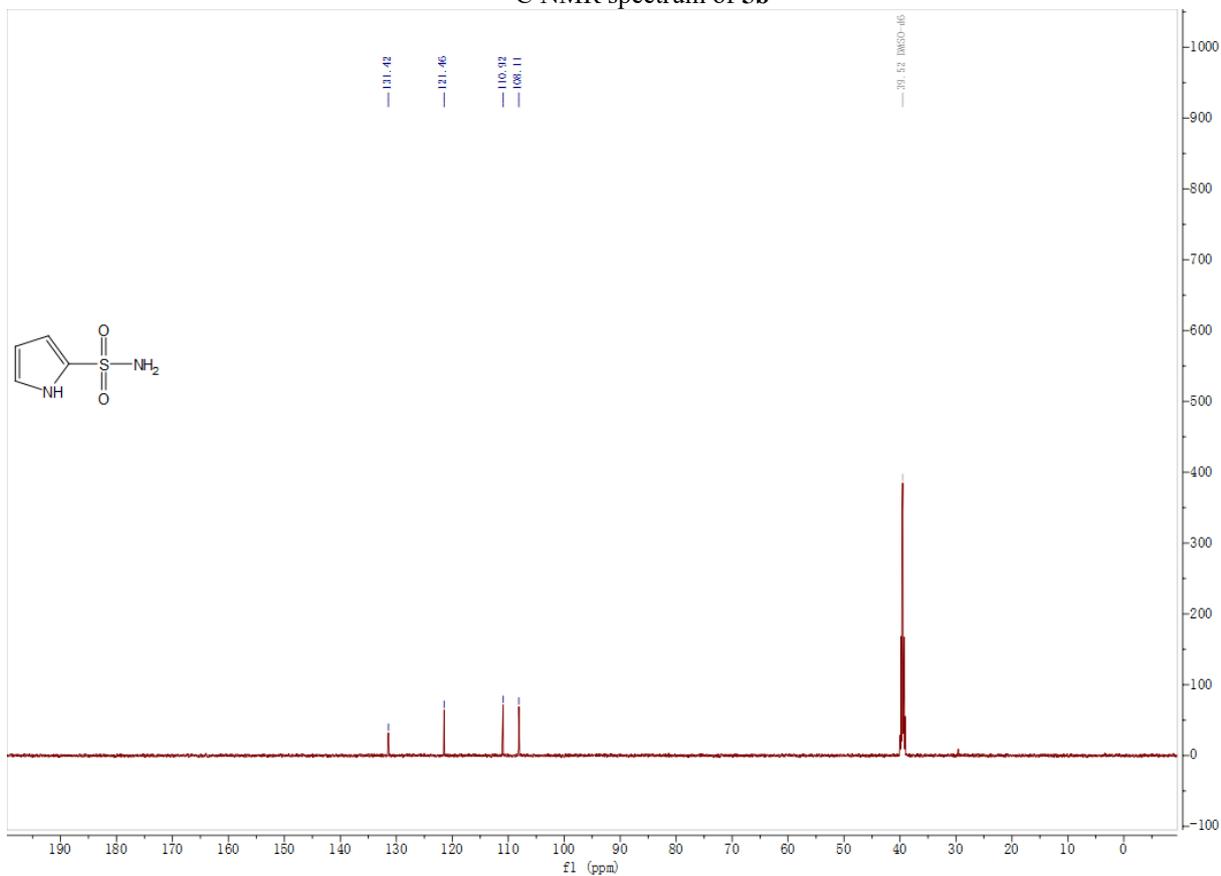
<sup>13</sup>C NMR spectrum of 5a



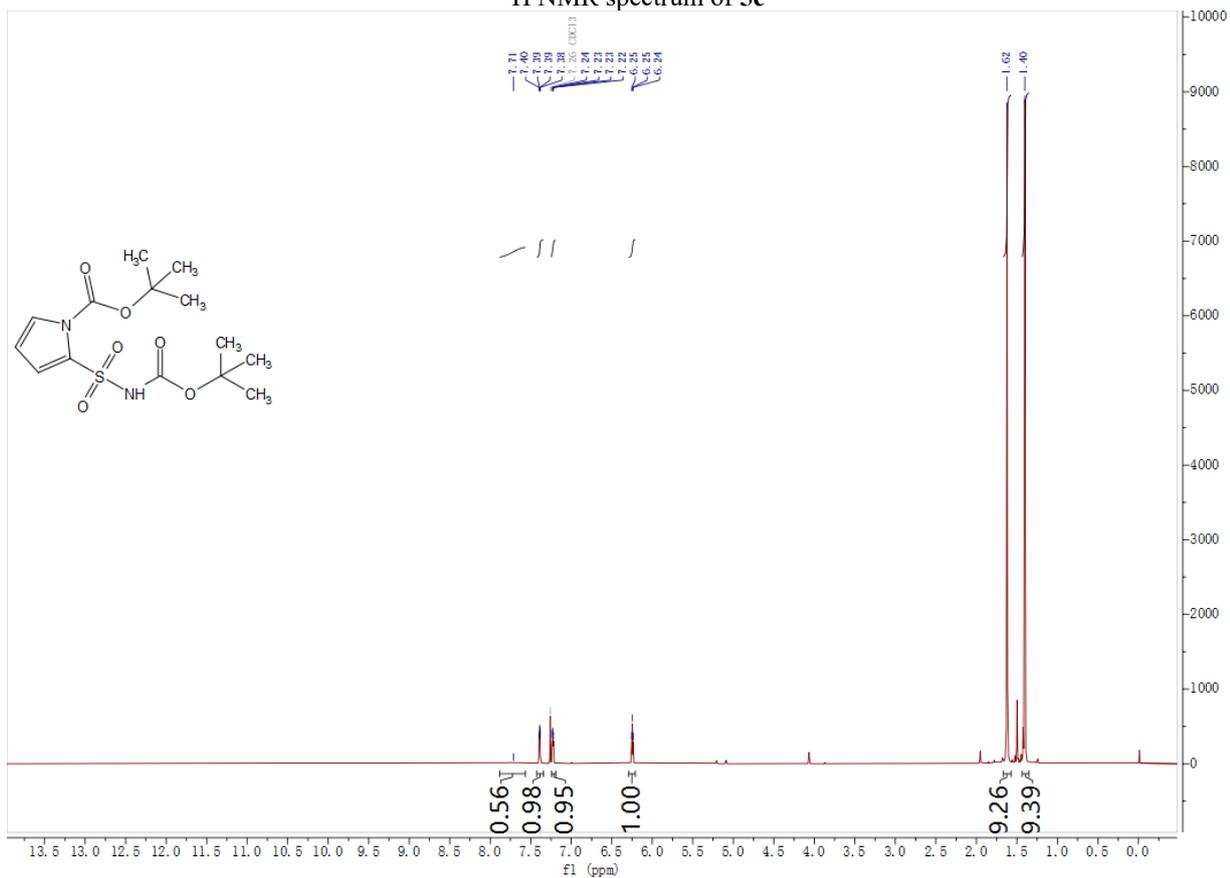
<sup>1</sup>H NMR spectrum of **5b**



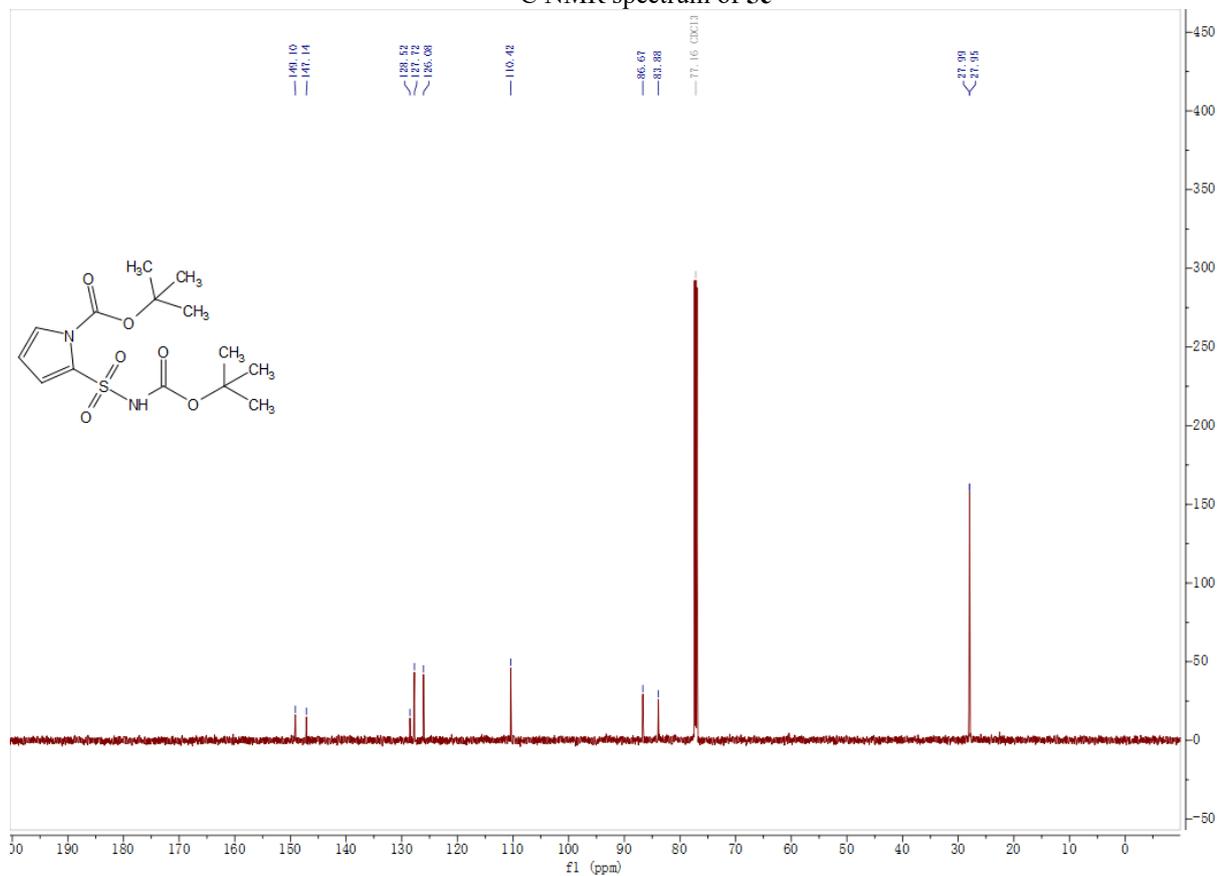
<sup>13</sup>C NMR spectrum of **5b**



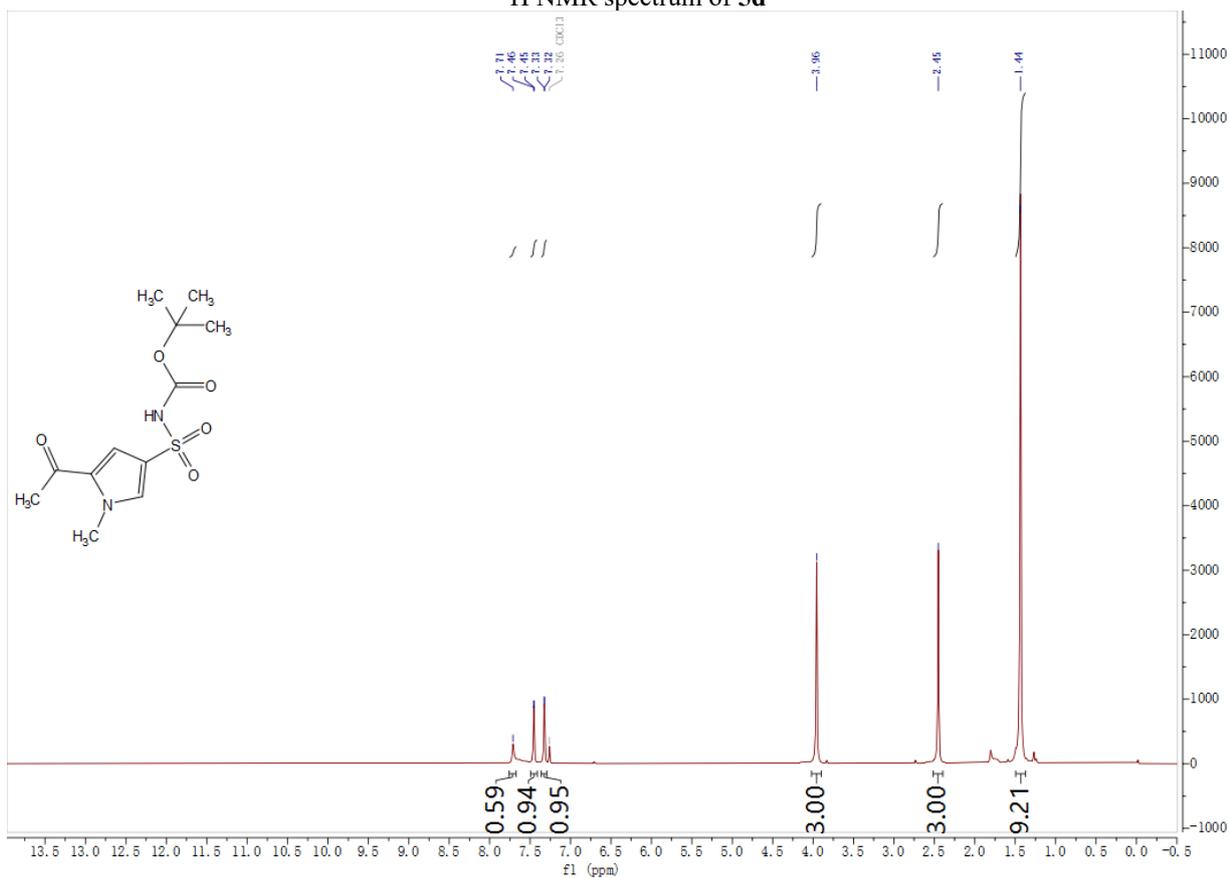
<sup>1</sup>H NMR spectrum of **5c**



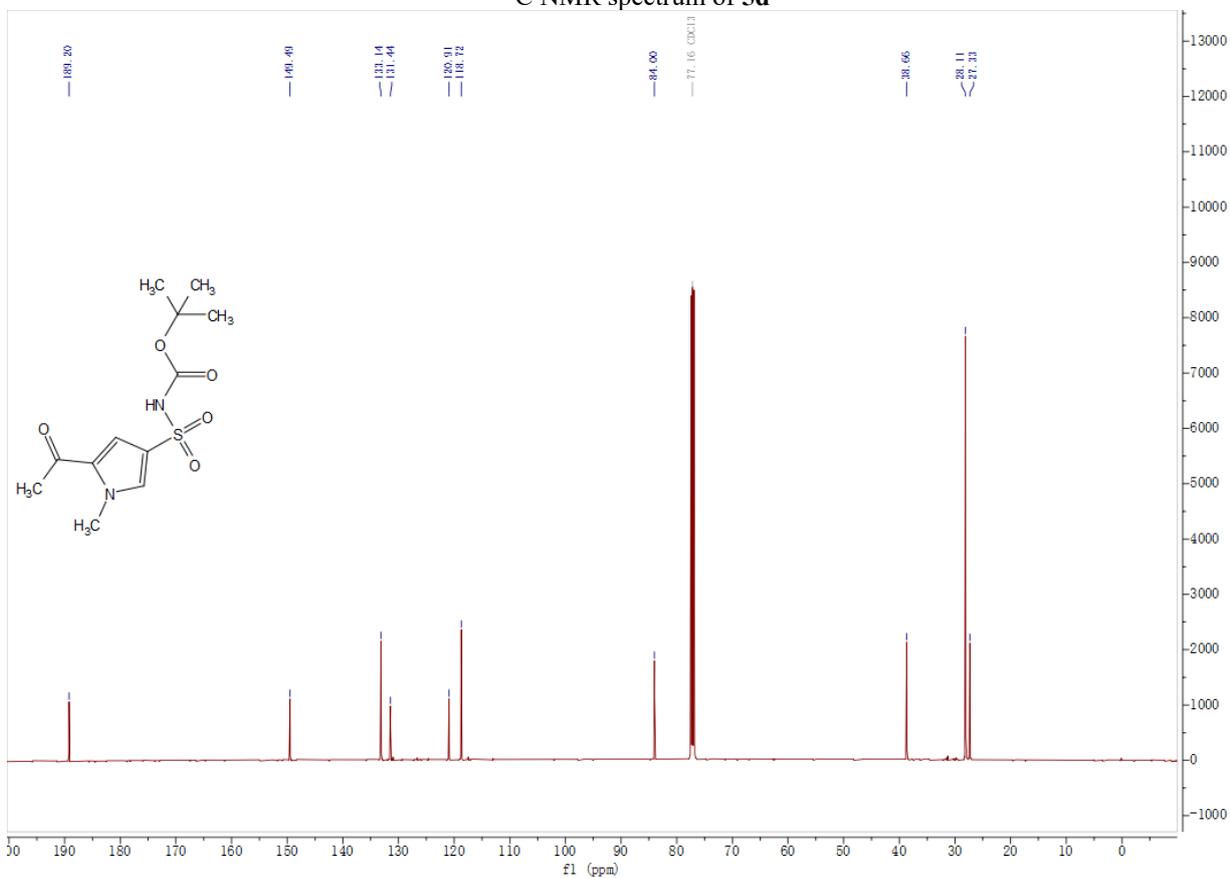
<sup>13</sup>C NMR spectrum of **5c**



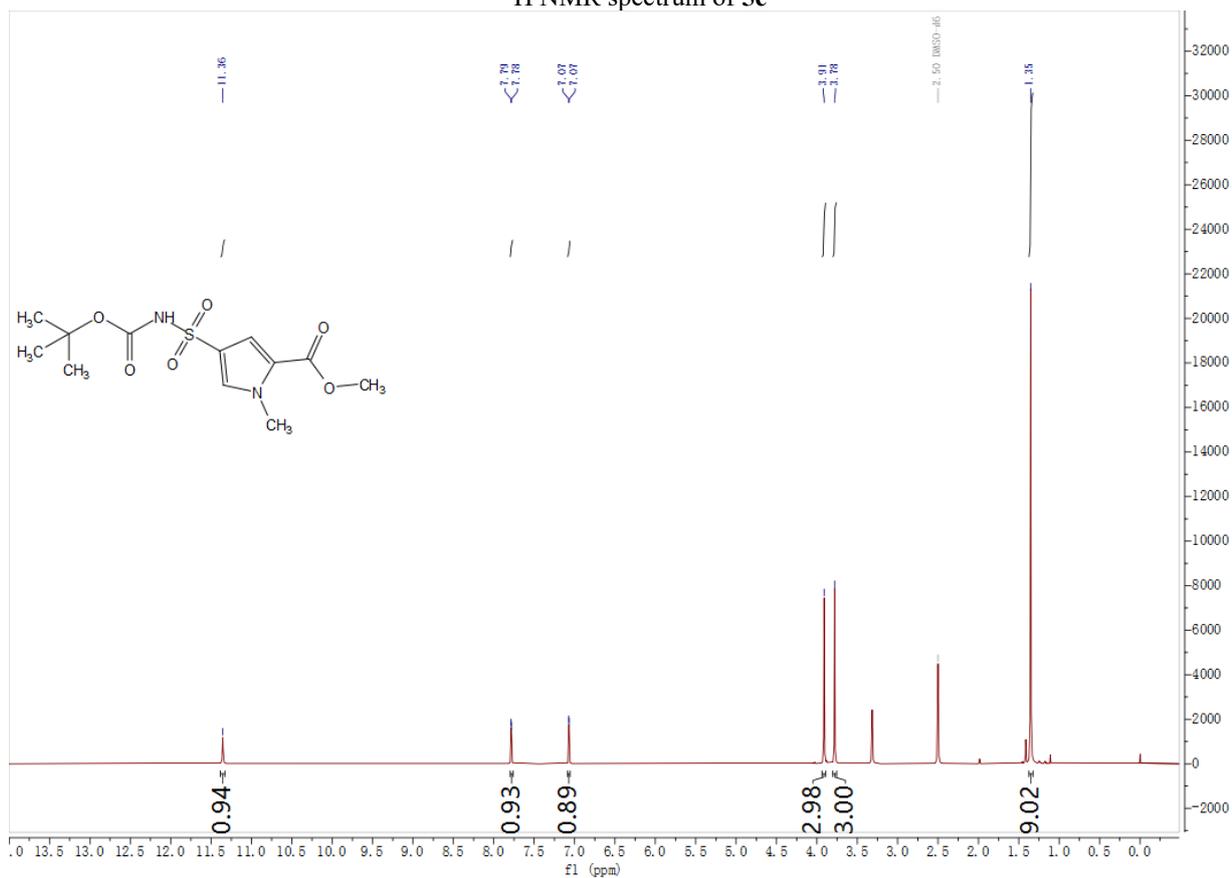
<sup>1</sup>H NMR spectrum of **5d**



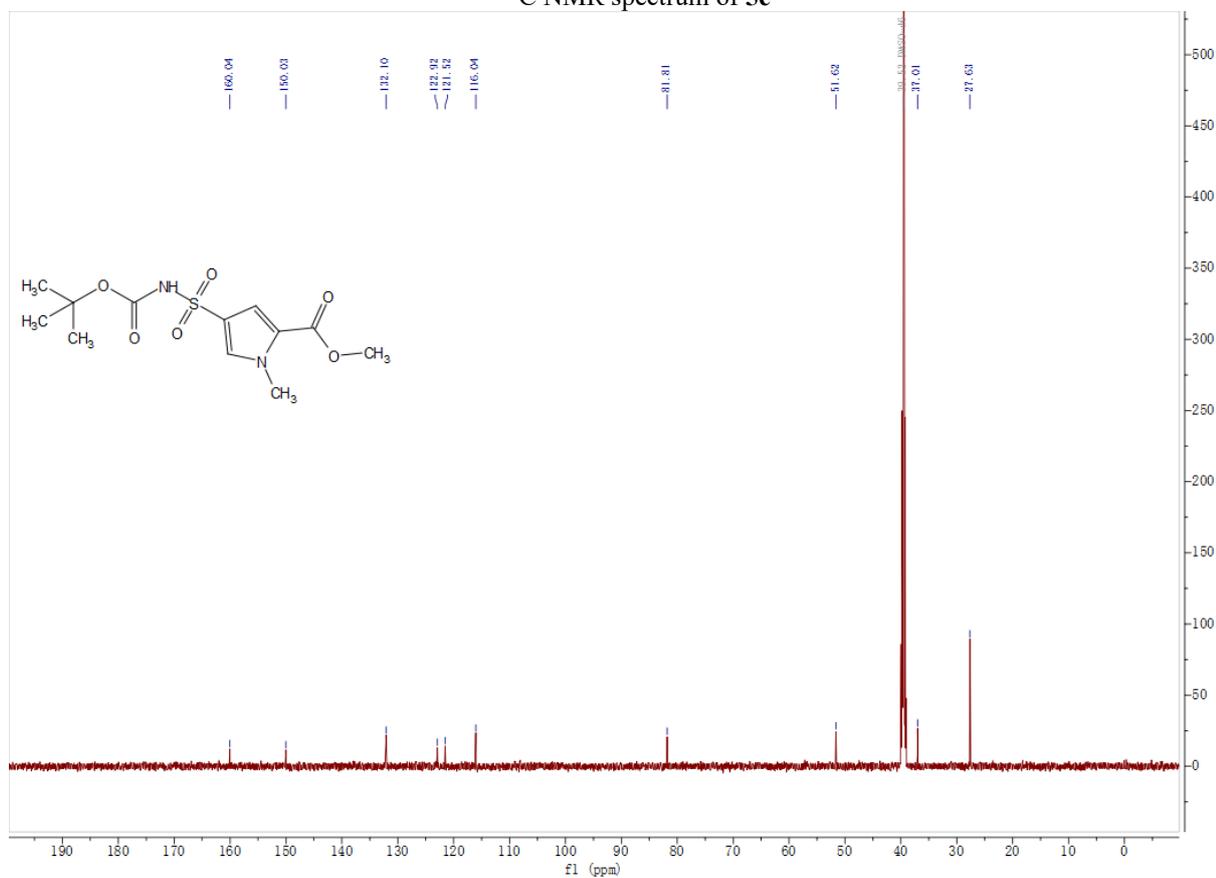
<sup>13</sup>C NMR spectrum of **5d**



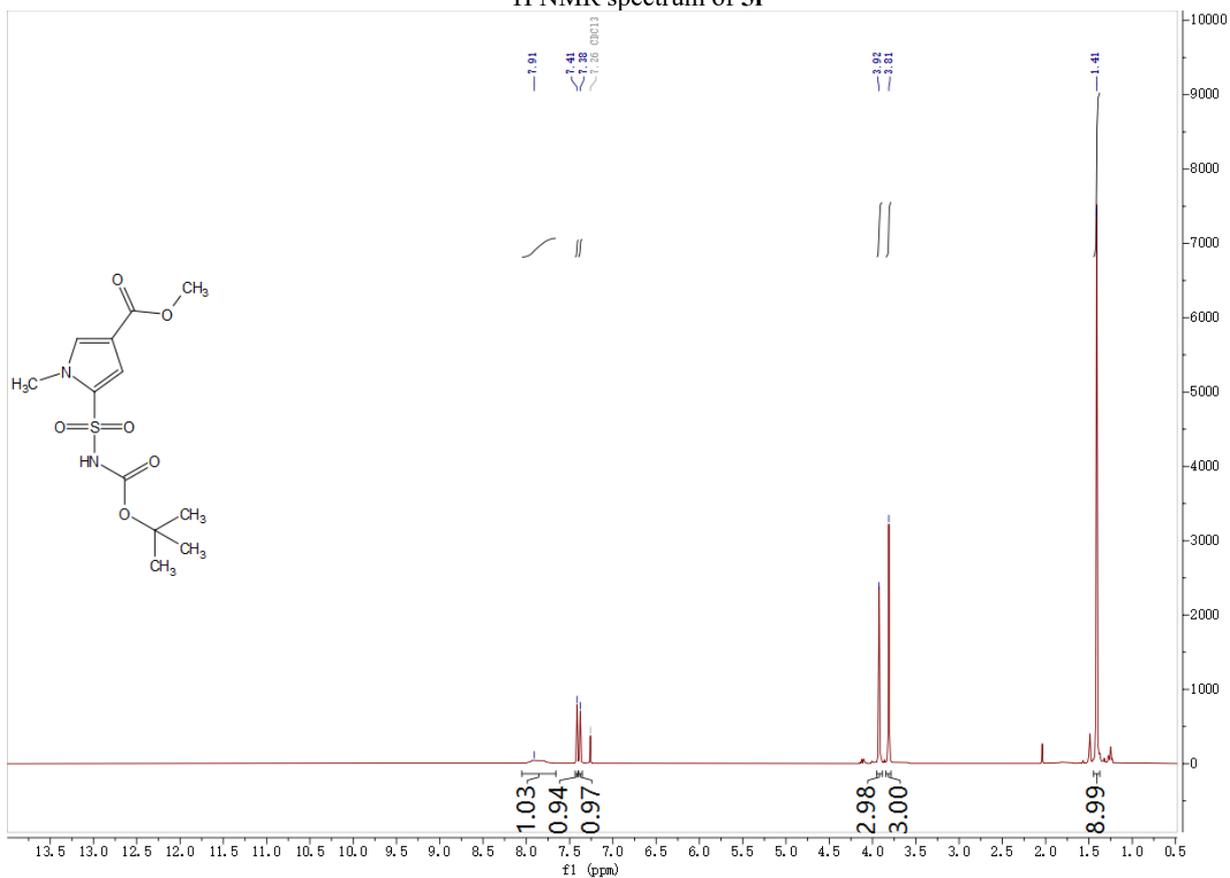
<sup>1</sup>H NMR spectrum of **5e**



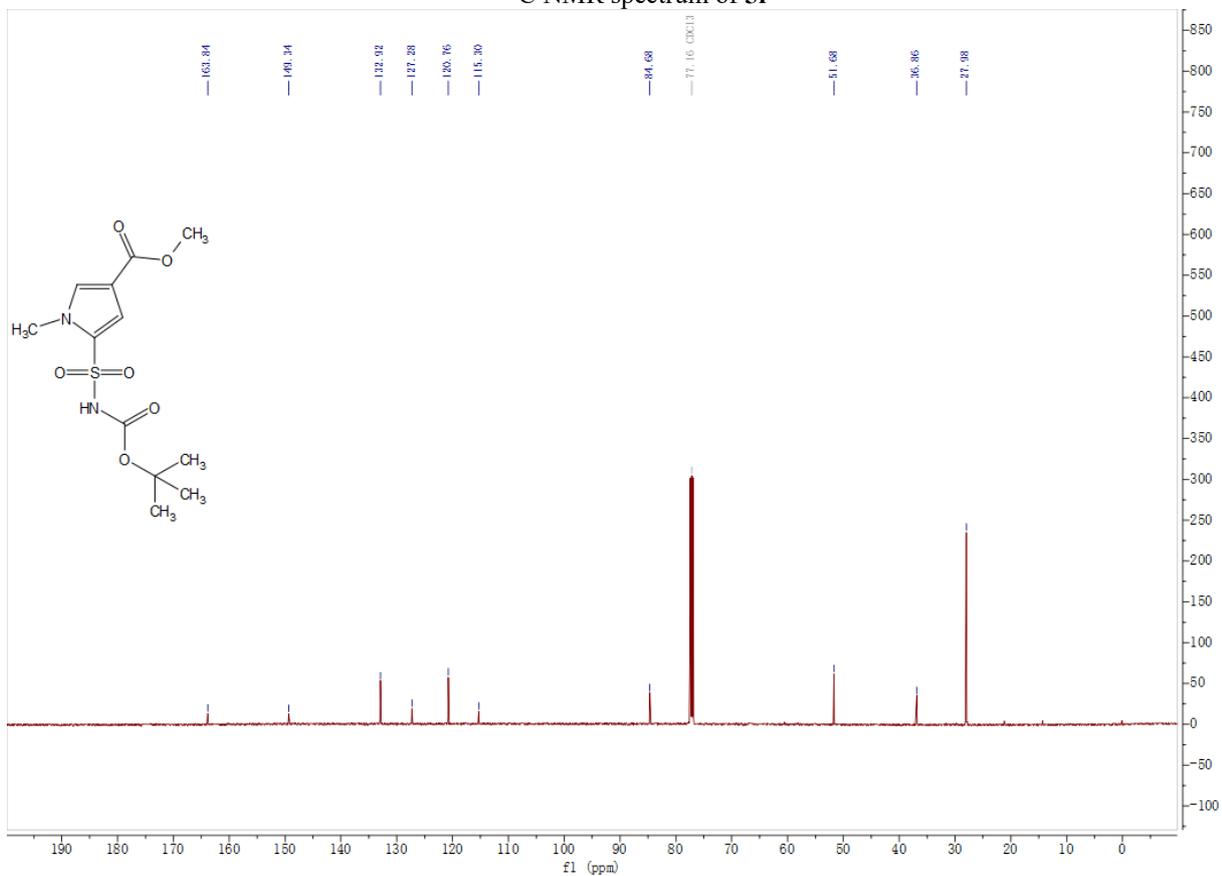
<sup>13</sup>C NMR spectrum of **5e**



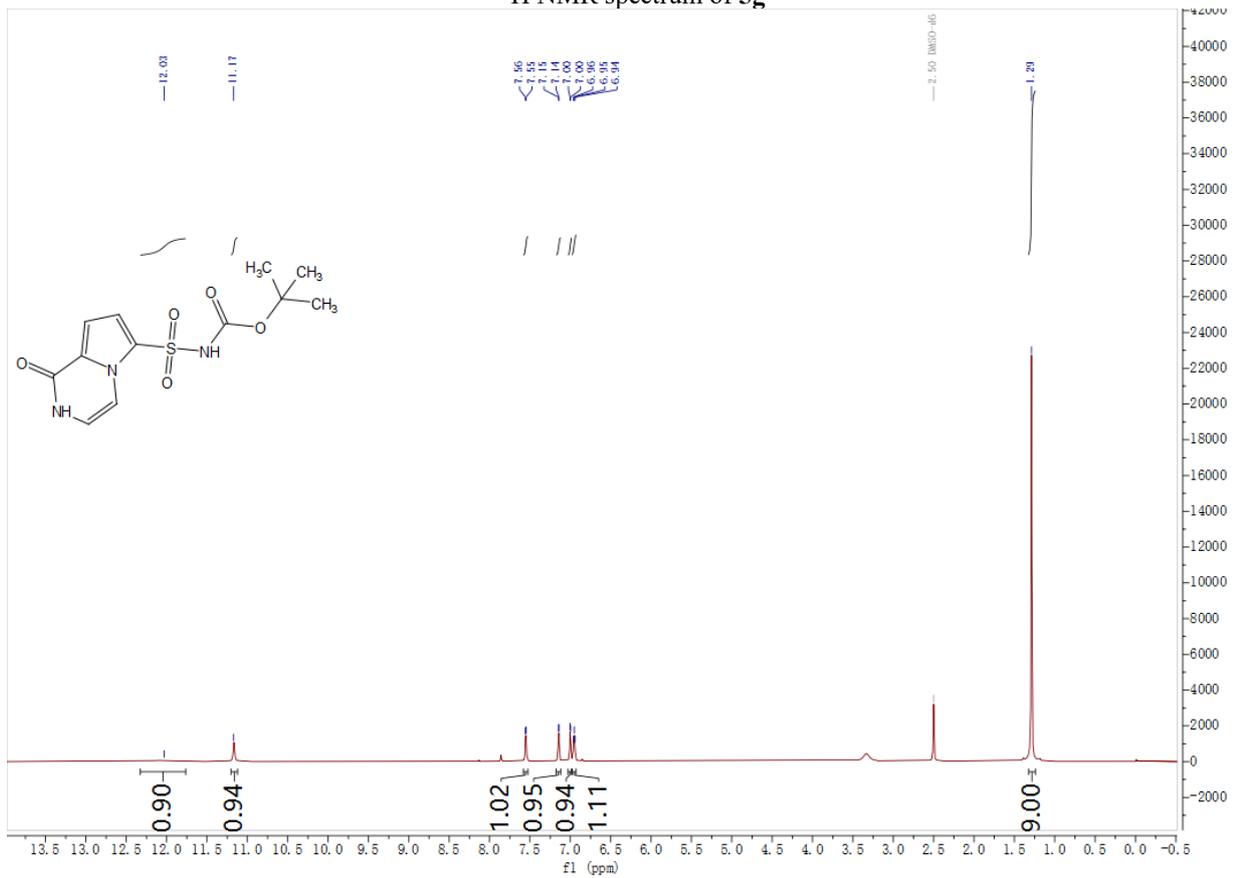
<sup>1</sup>H NMR spectrum of **5f**



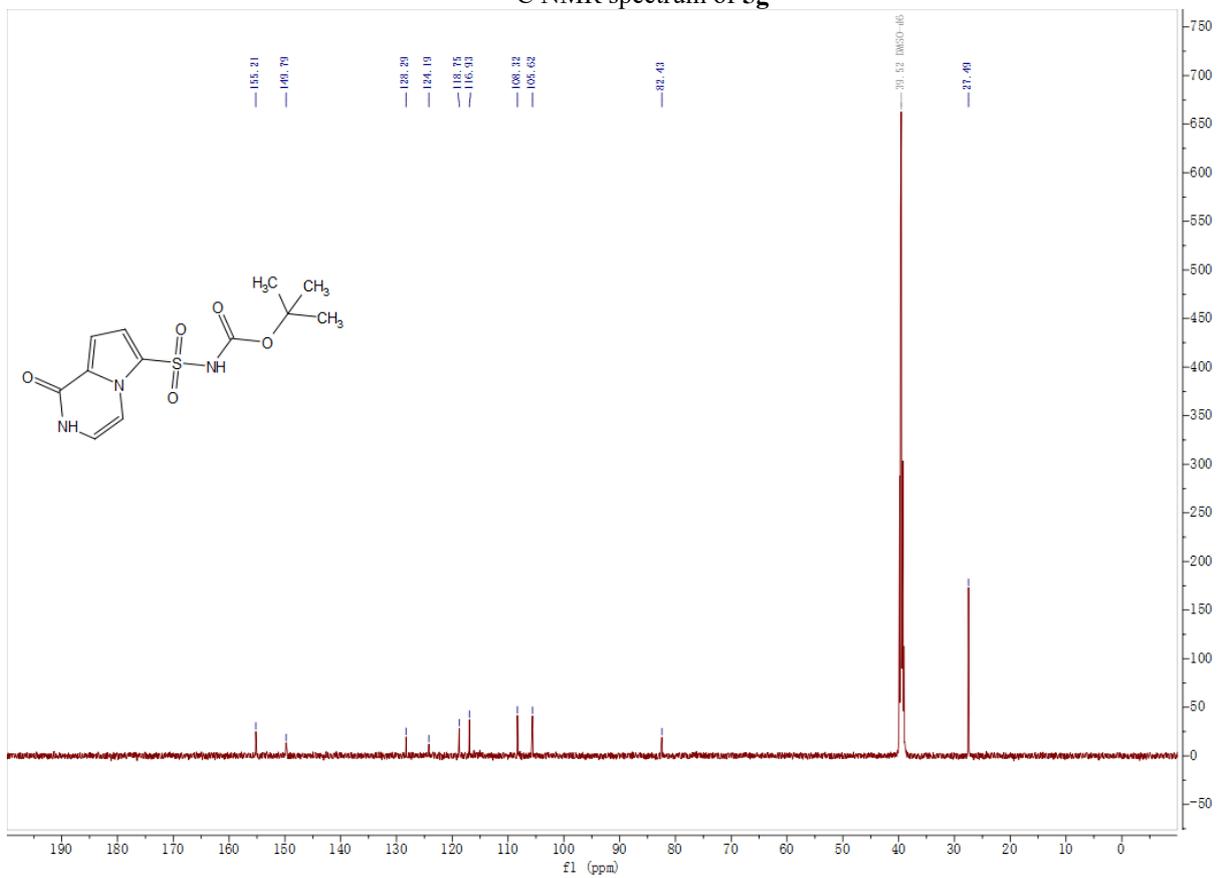
<sup>13</sup>C NMR spectrum of **5f**



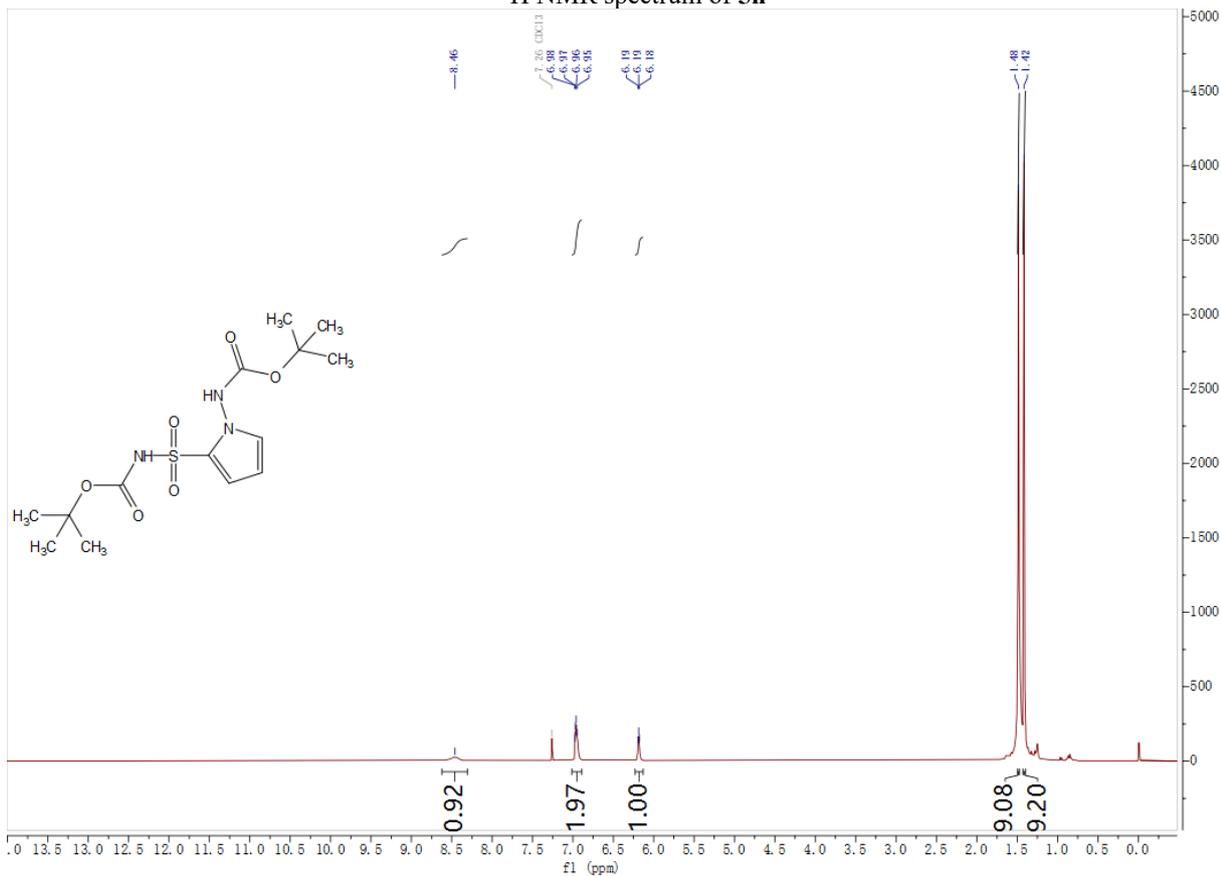
<sup>1</sup>H NMR spectrum of **5g**



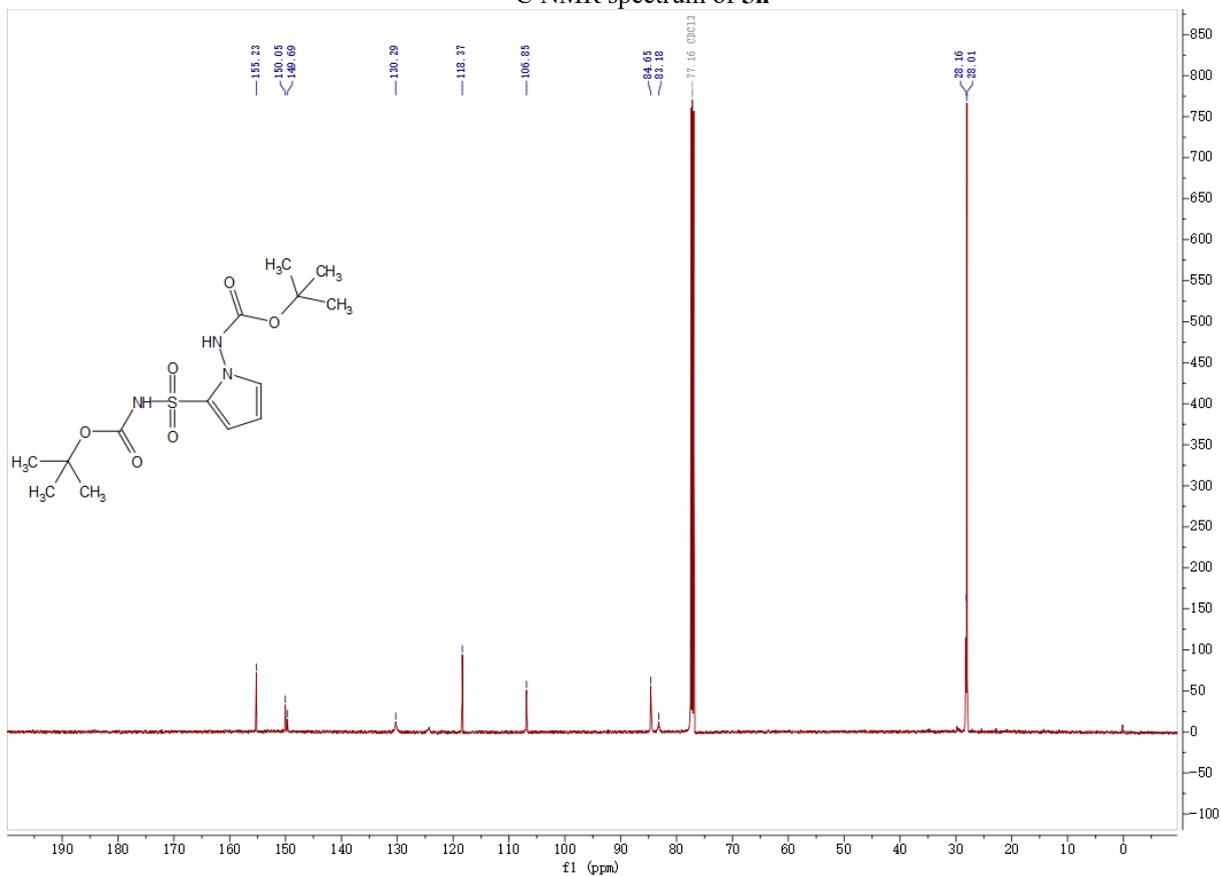
<sup>13</sup>C NMR spectrum of **5g**



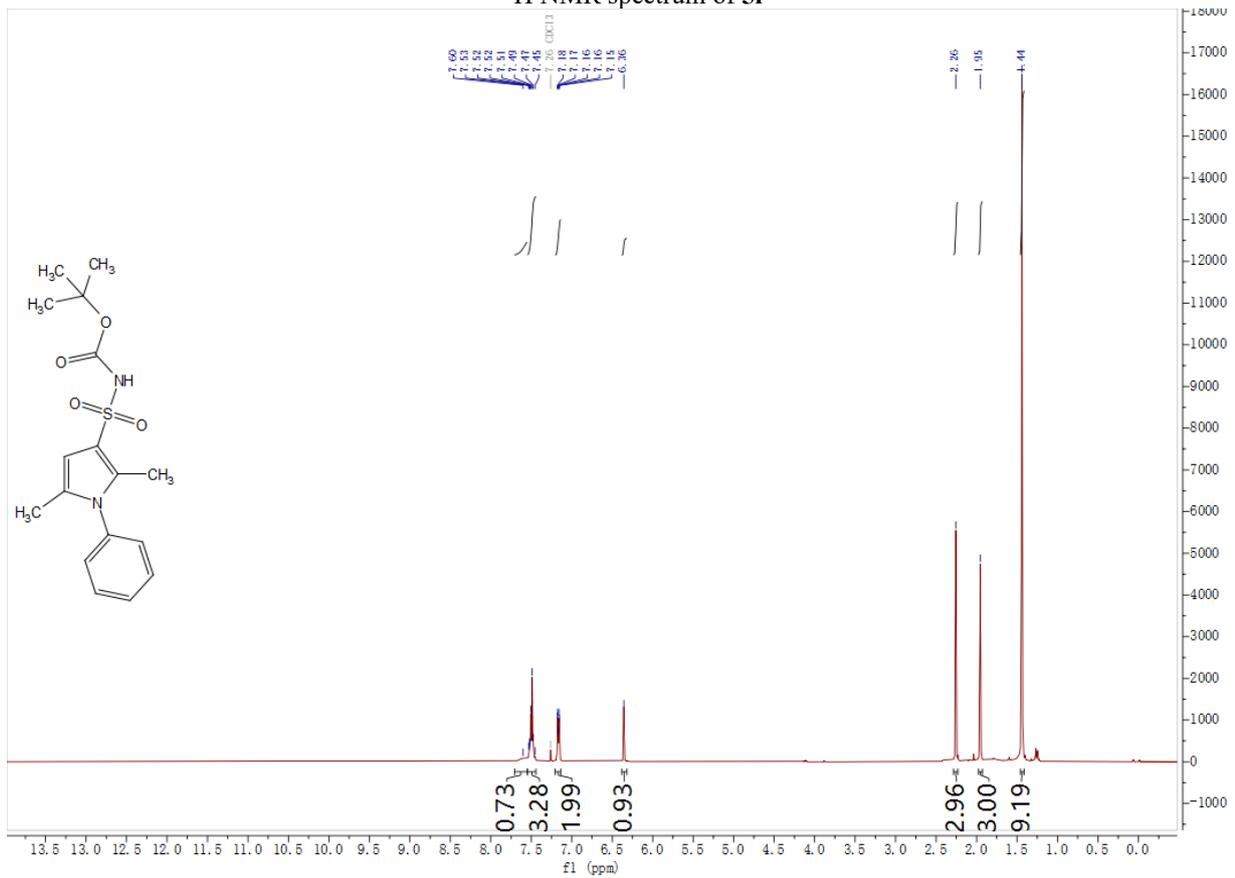
<sup>1</sup>H NMR spectrum of **5h**



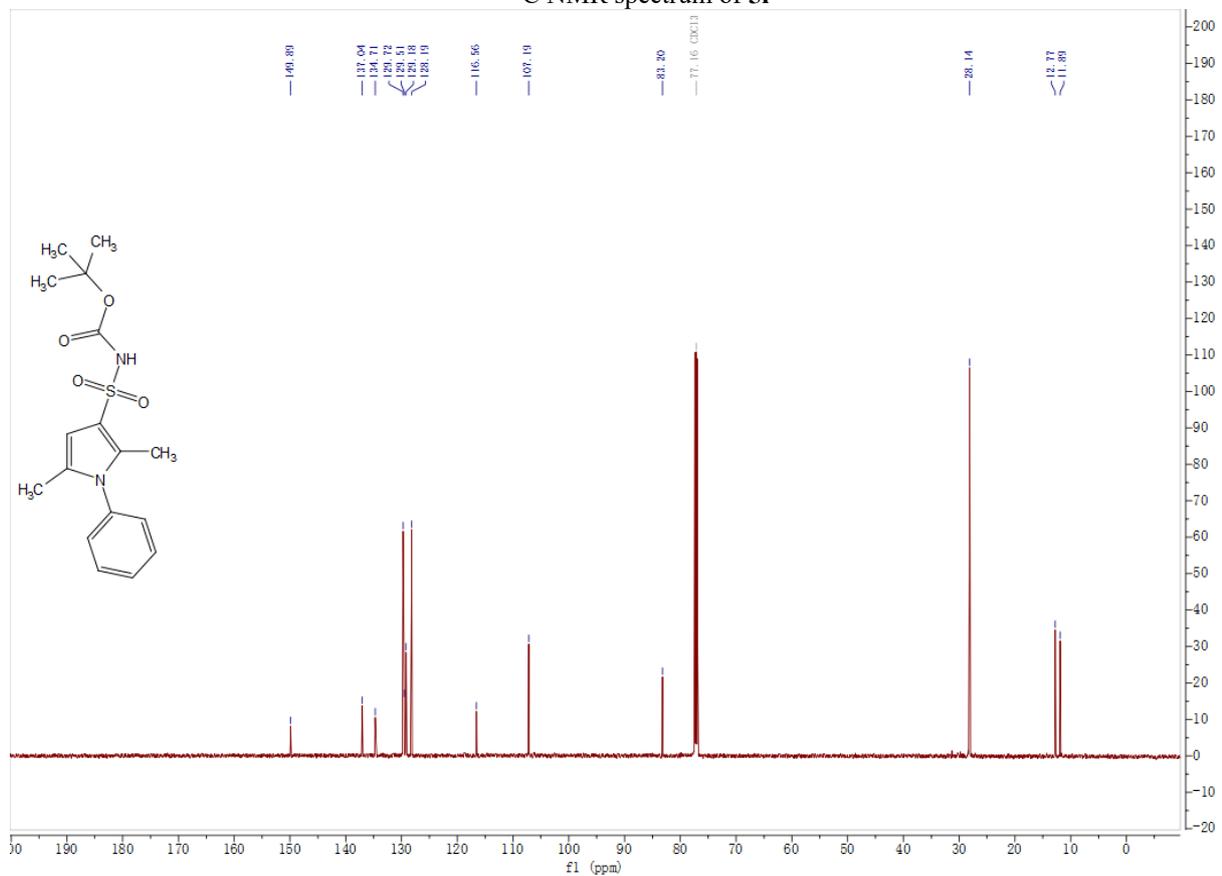
<sup>13</sup>C NMR spectrum of **5h**



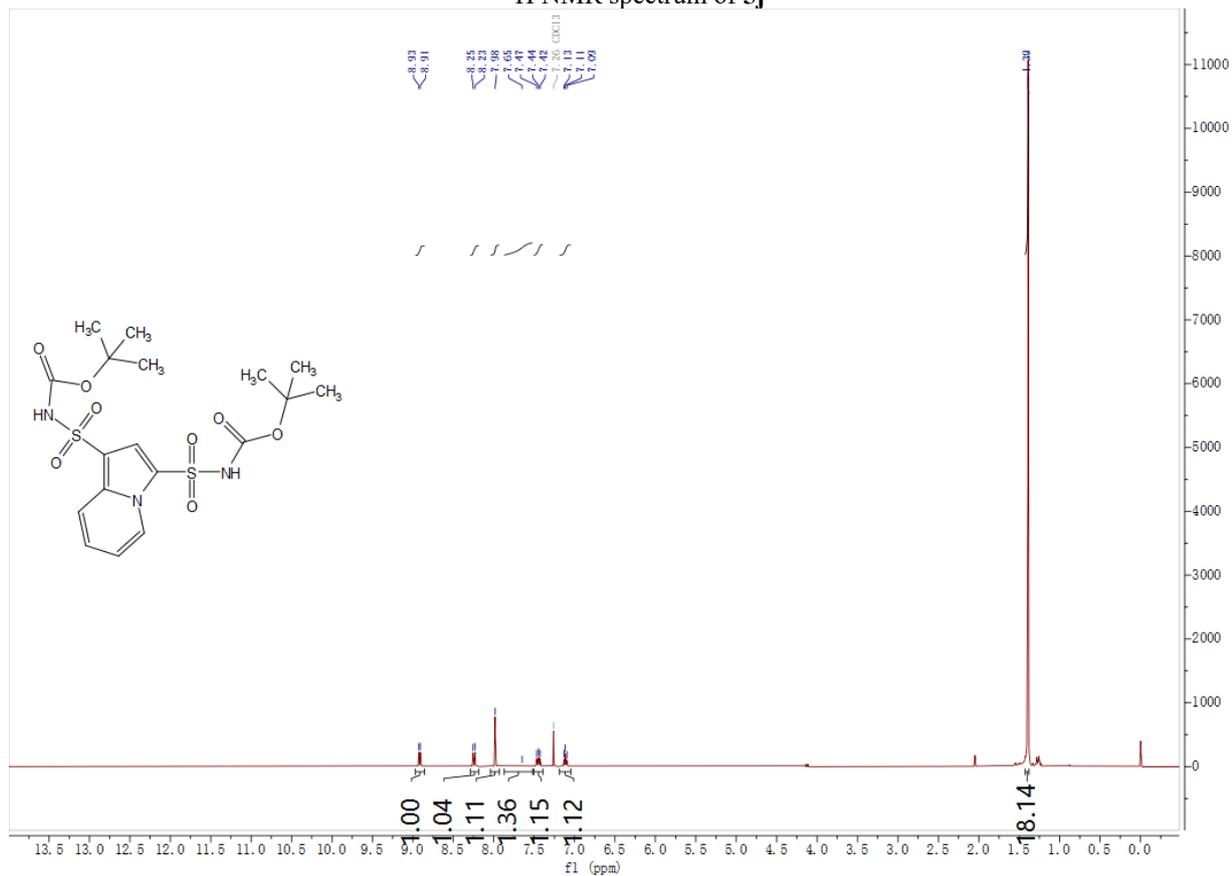
<sup>1</sup>H NMR spectrum of **5i**



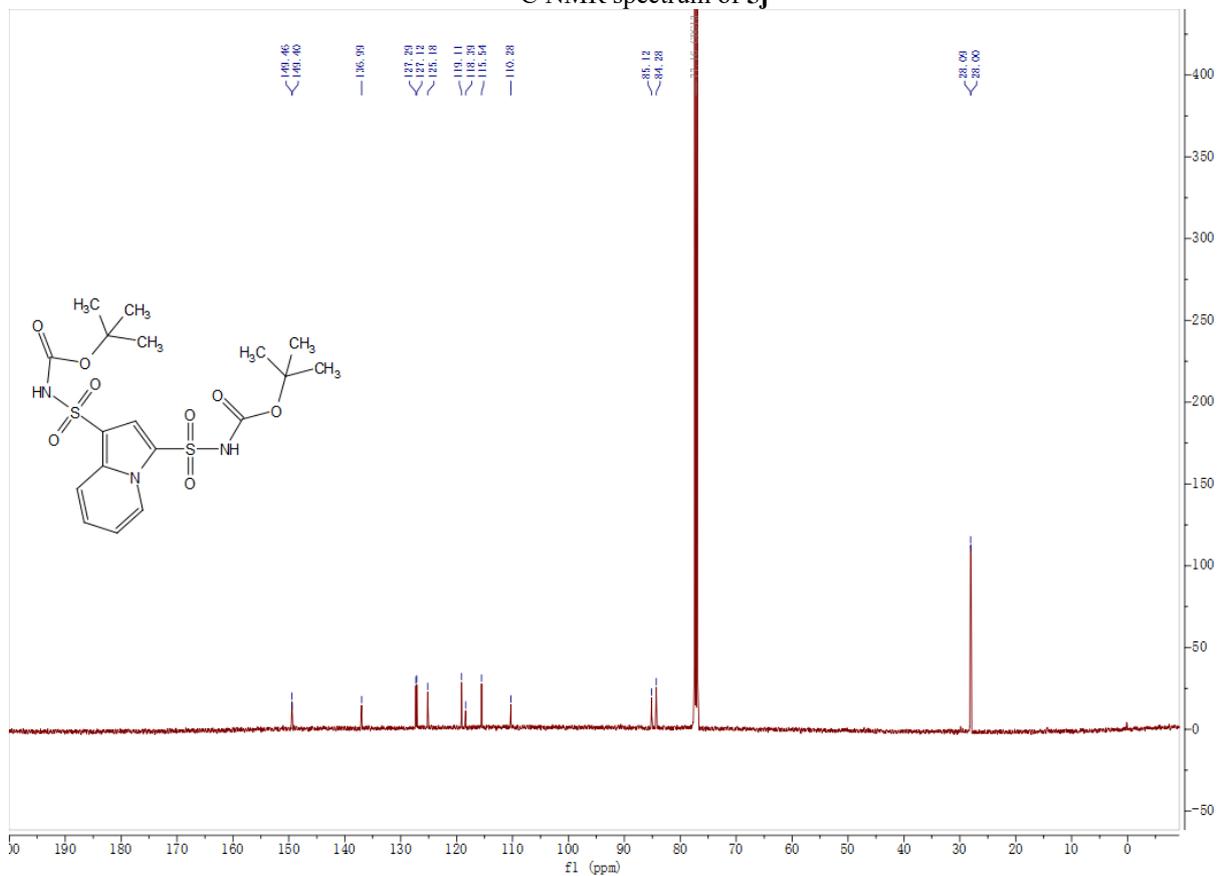
<sup>13</sup>C NMR spectrum of **5i**



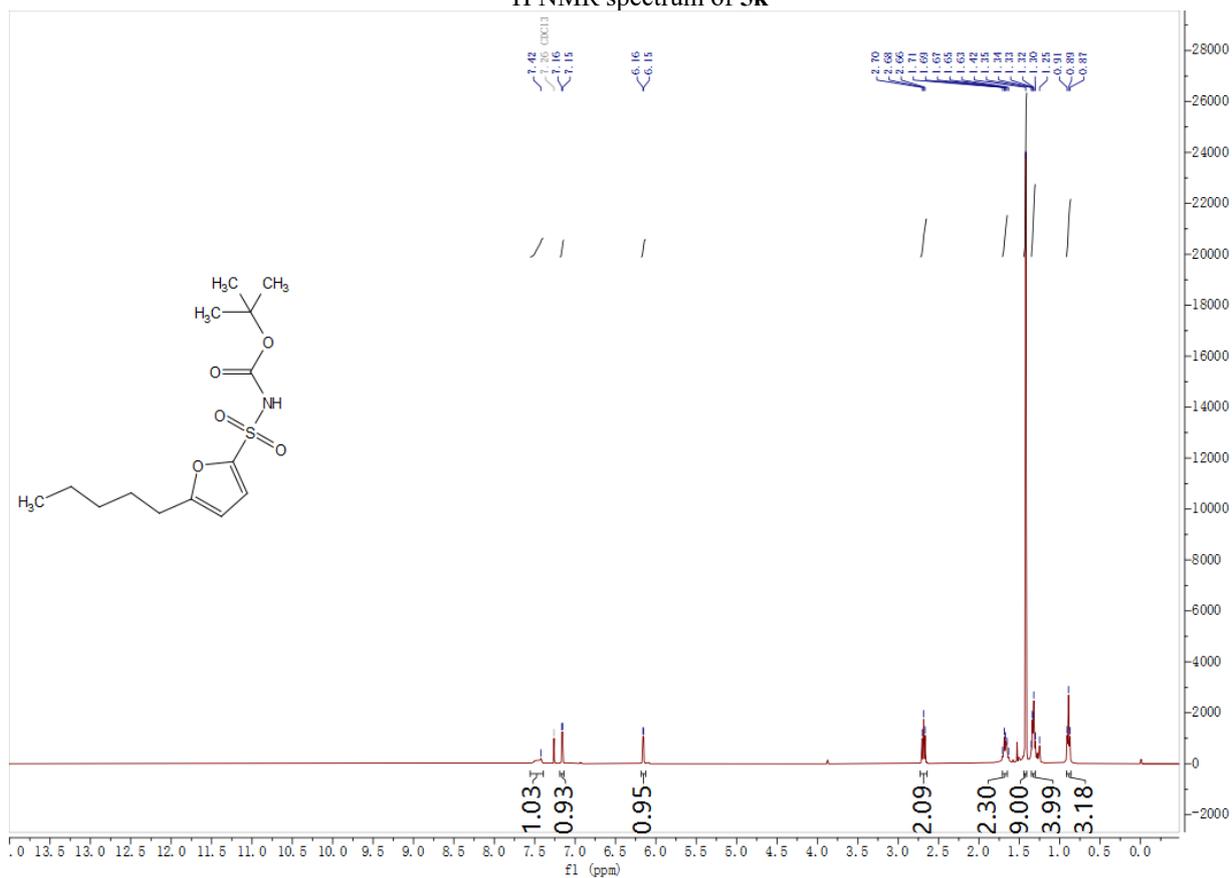
<sup>1</sup>H NMR spectrum of **5j**



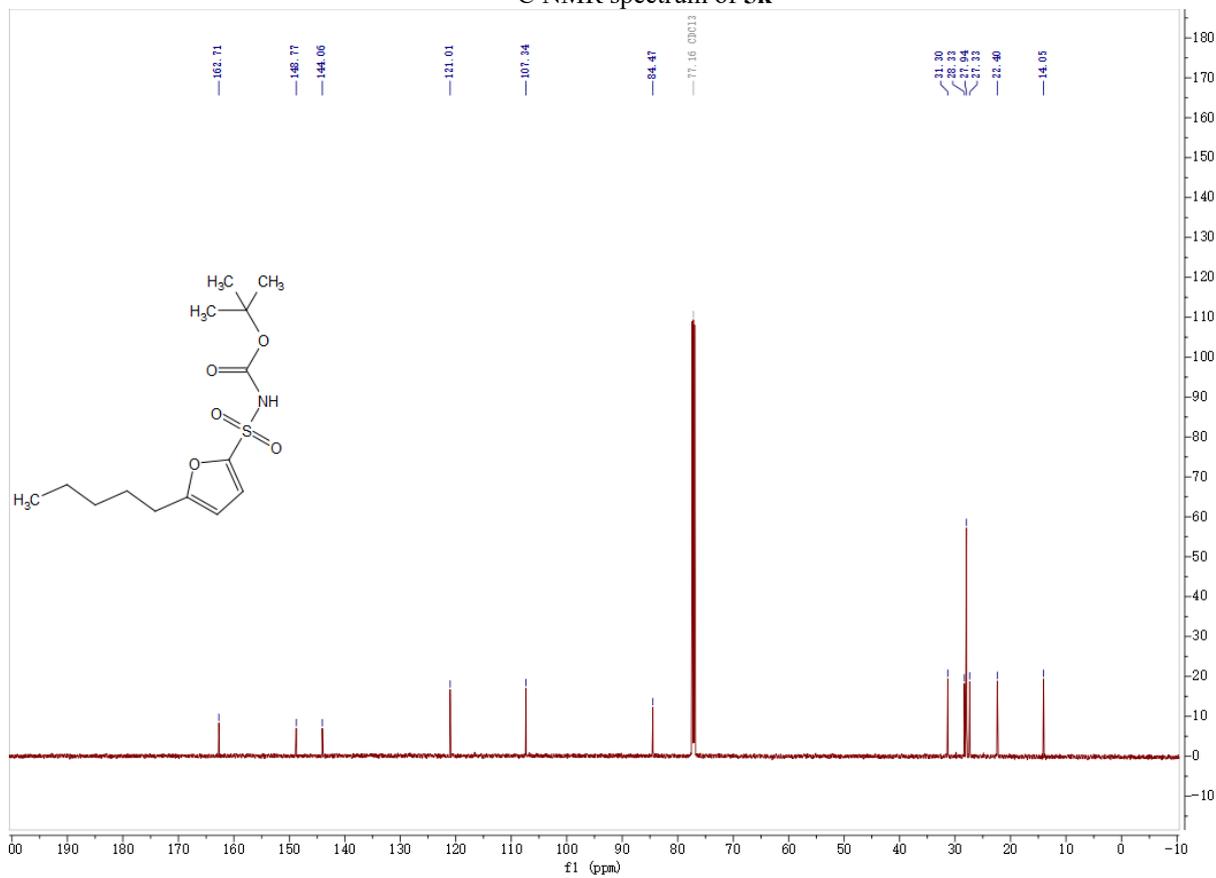
<sup>13</sup>C NMR spectrum of **5j**



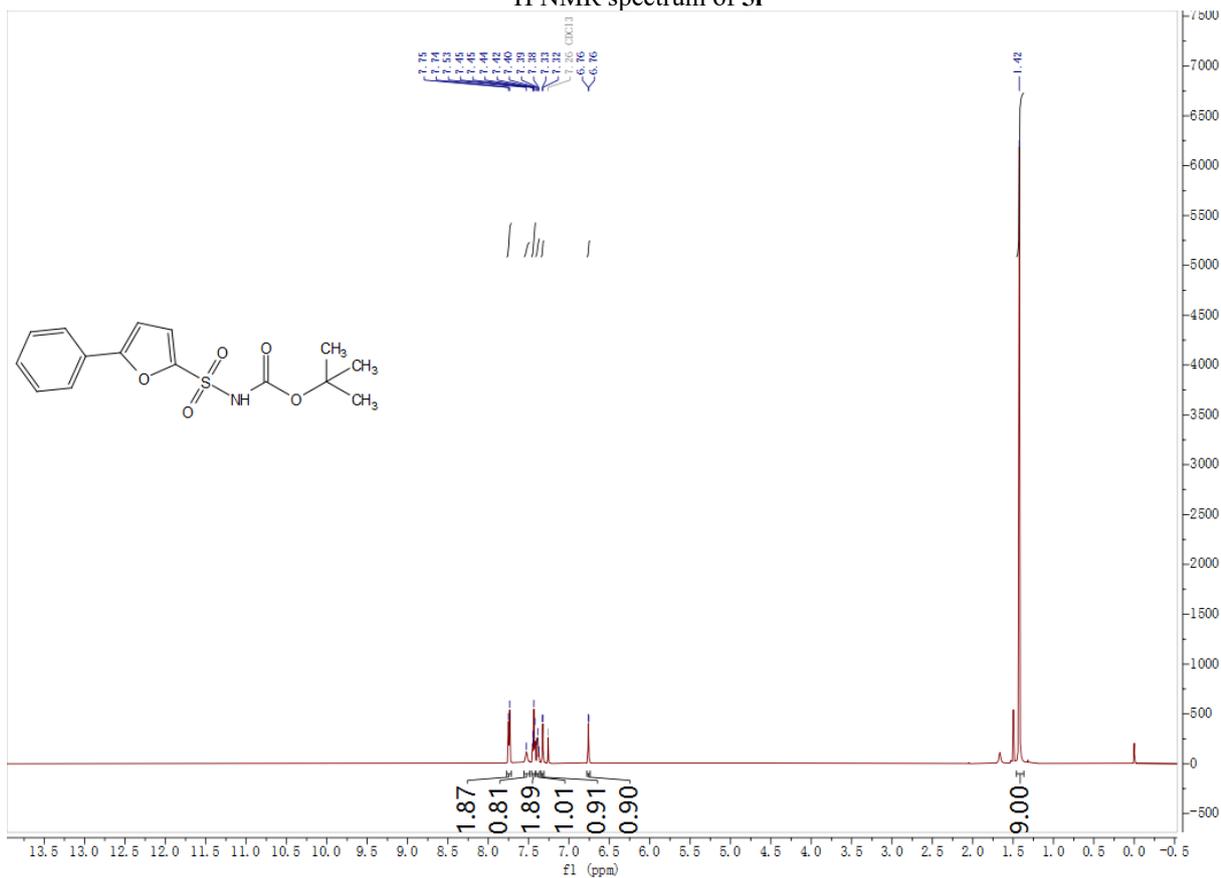
<sup>1</sup>H NMR spectrum of **5k**



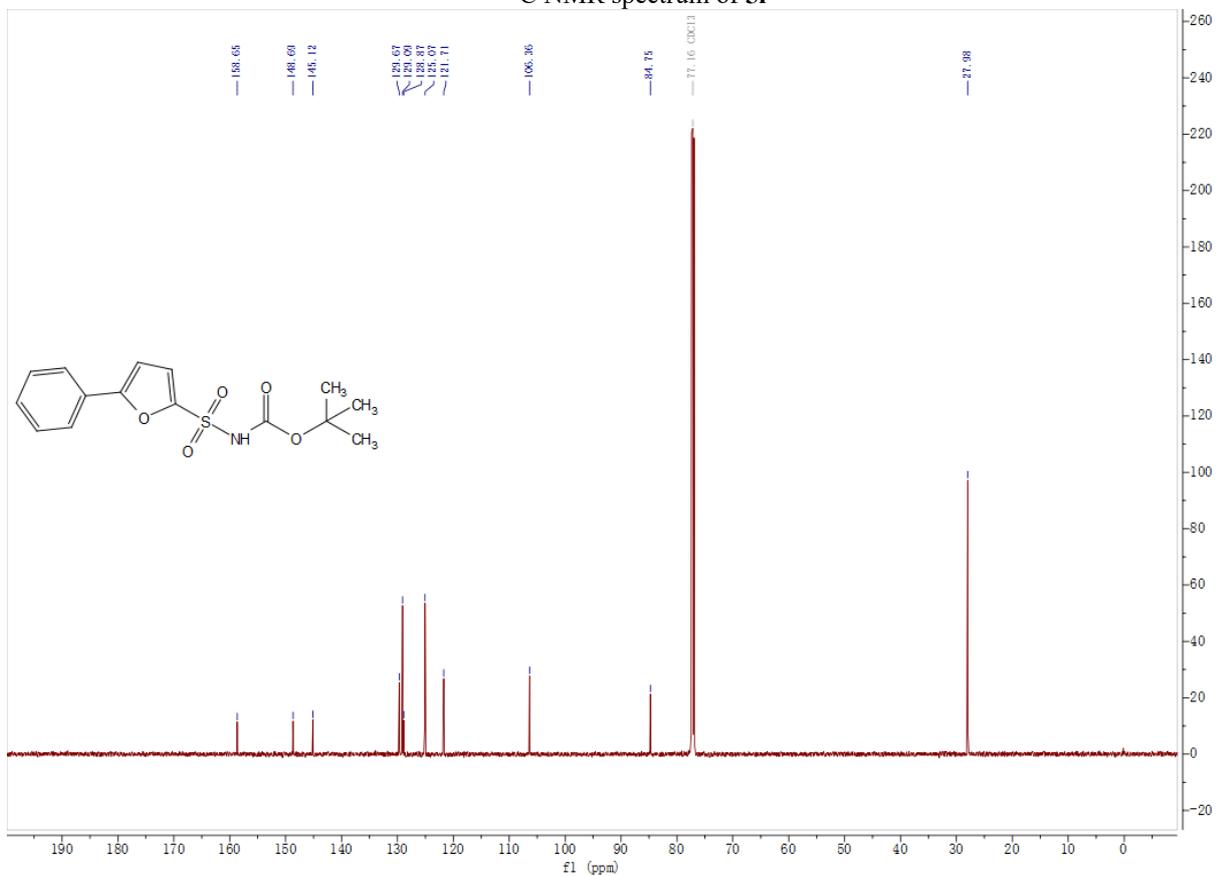
<sup>13</sup>C NMR spectrum of **5k**



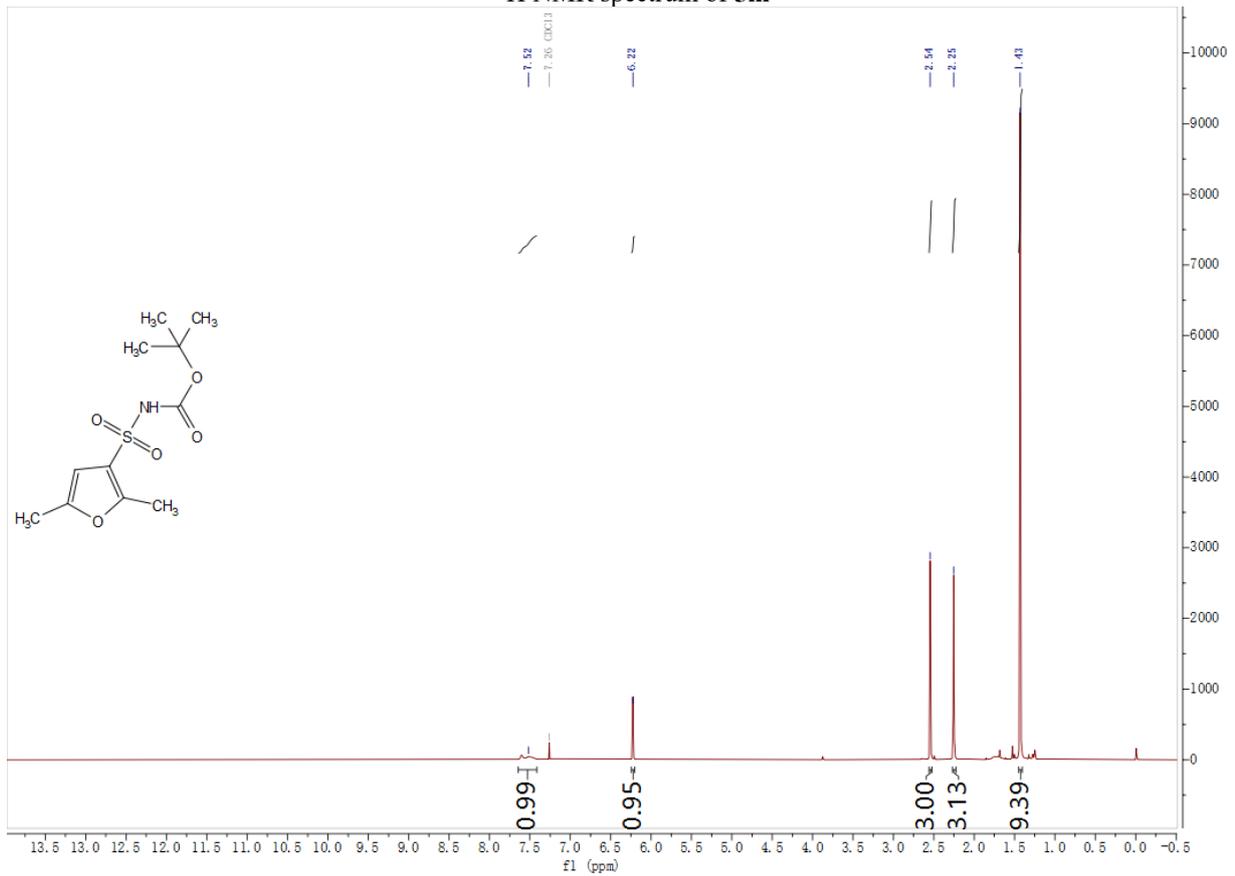
<sup>1</sup>H NMR spectrum of **51**



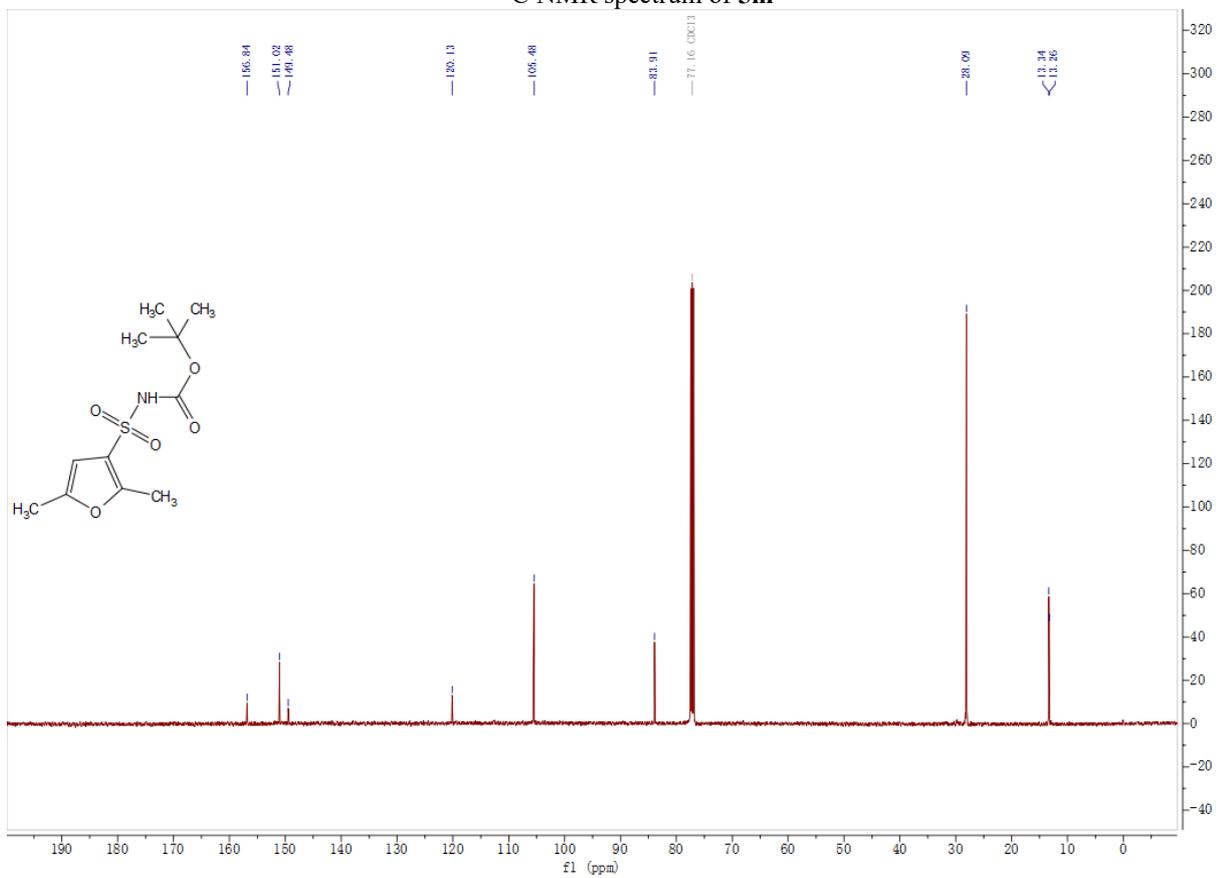
<sup>13</sup>C NMR spectrum of **51**



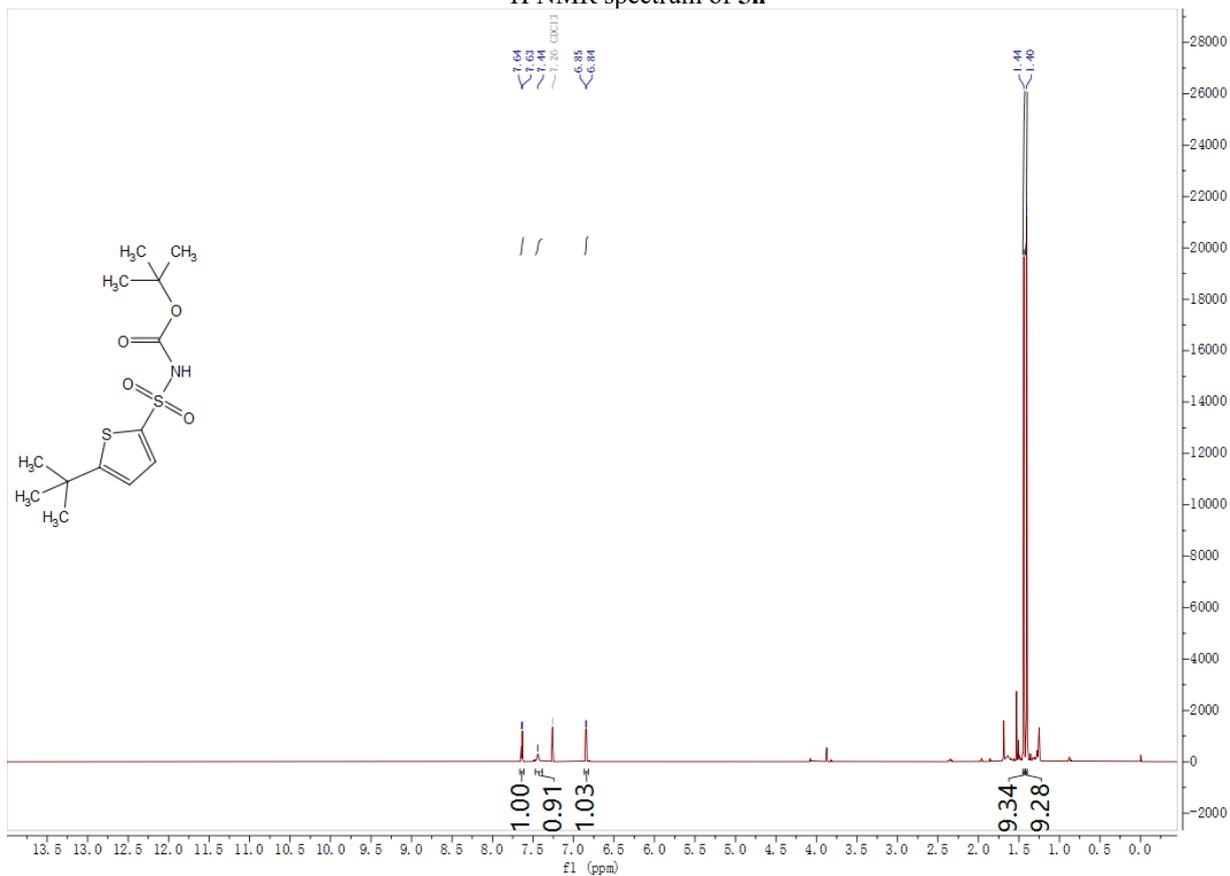
<sup>1</sup>H NMR spectrum of **5m**



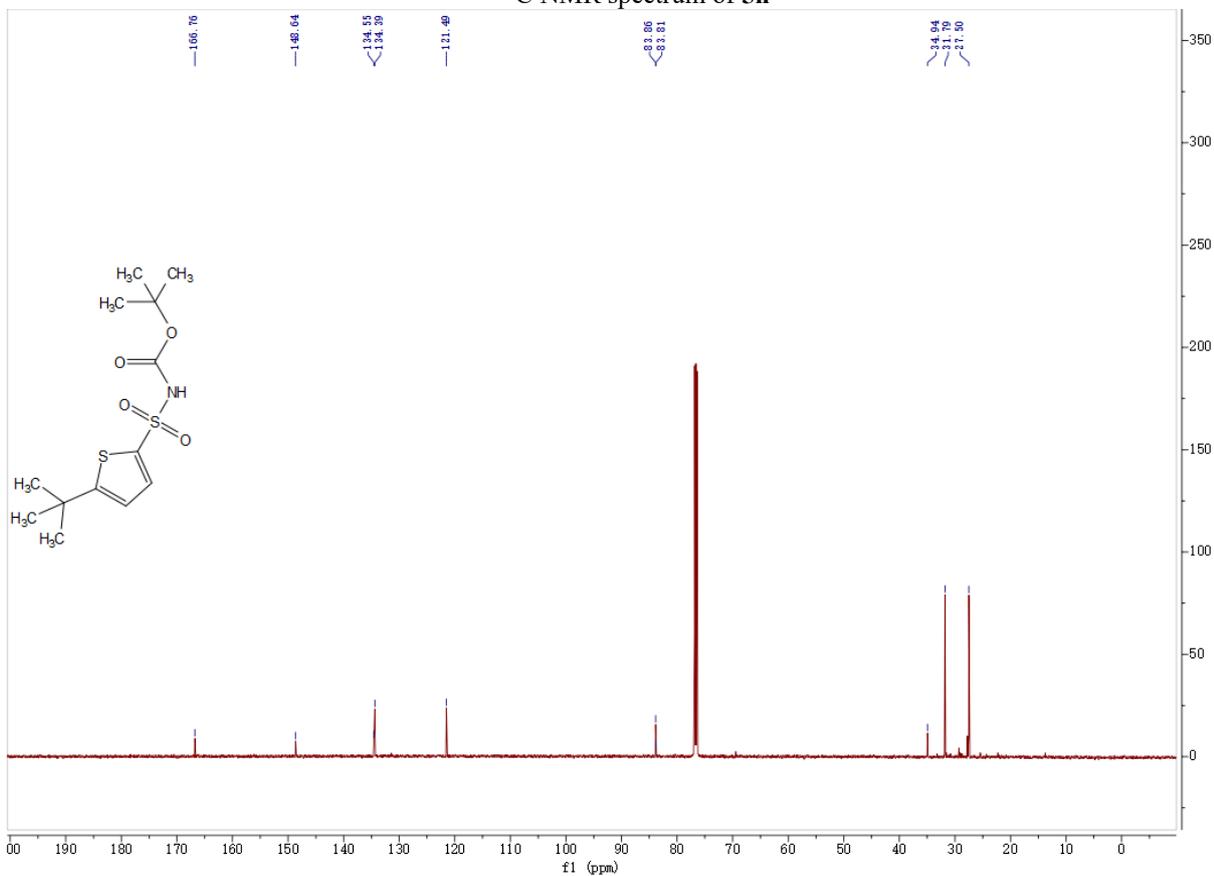
<sup>13</sup>C NMR spectrum of **5m**



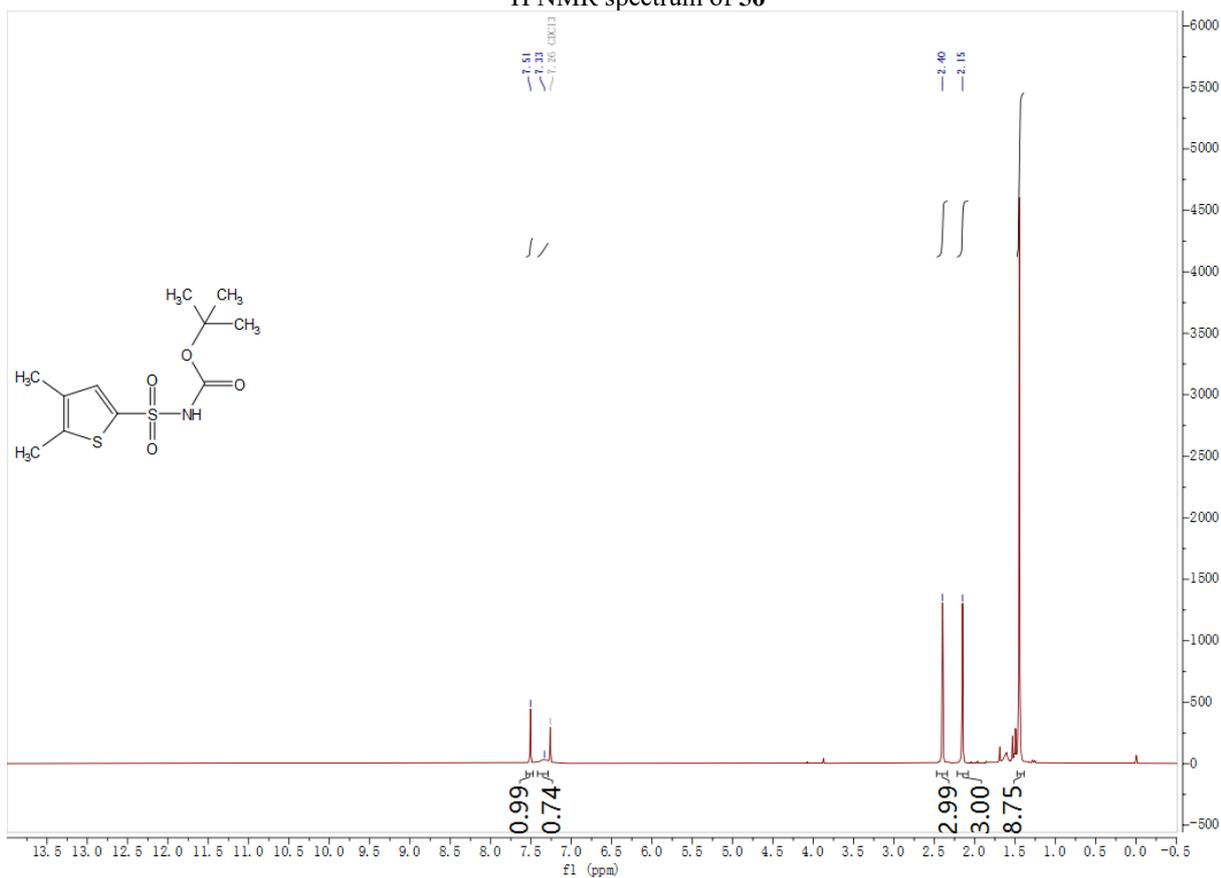
<sup>1</sup>H NMR spectrum of **5n**



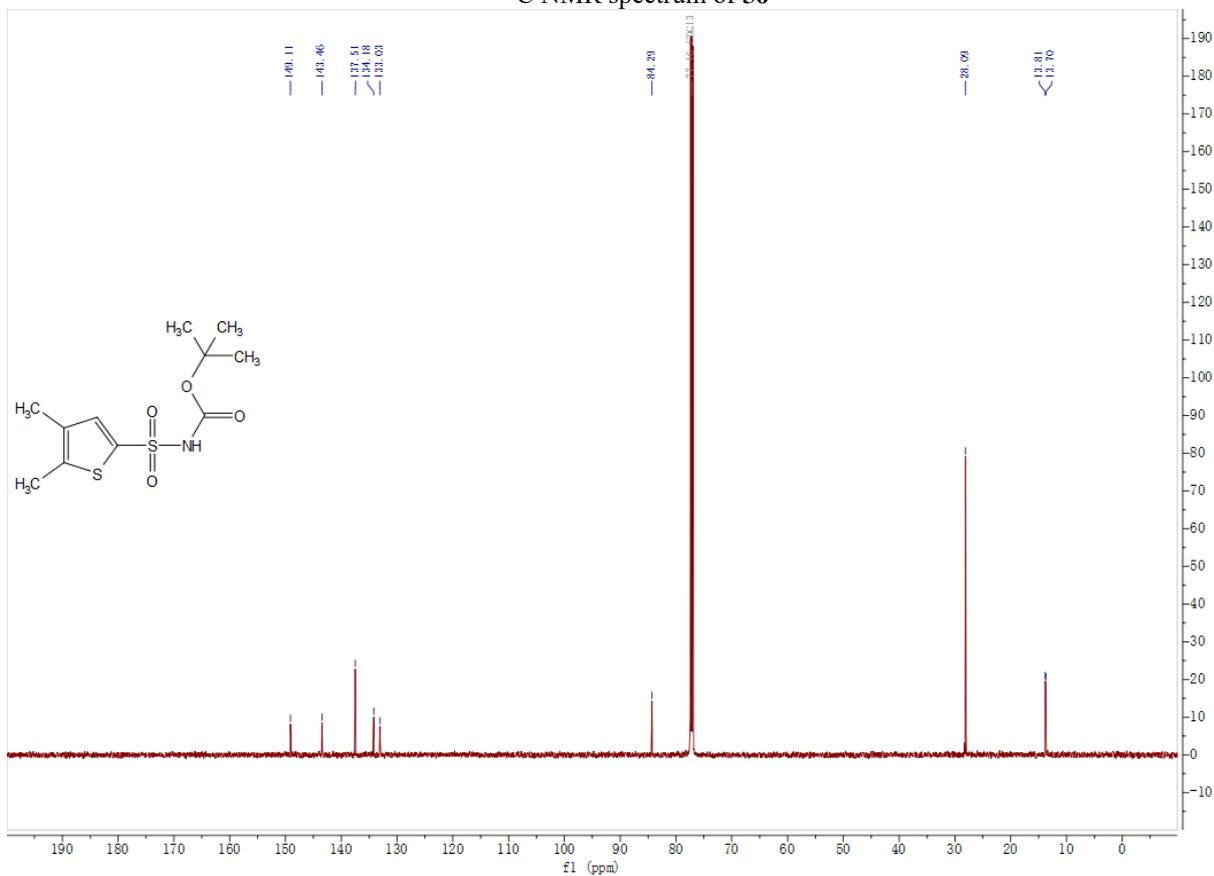
<sup>13</sup>C NMR spectrum of **5n**



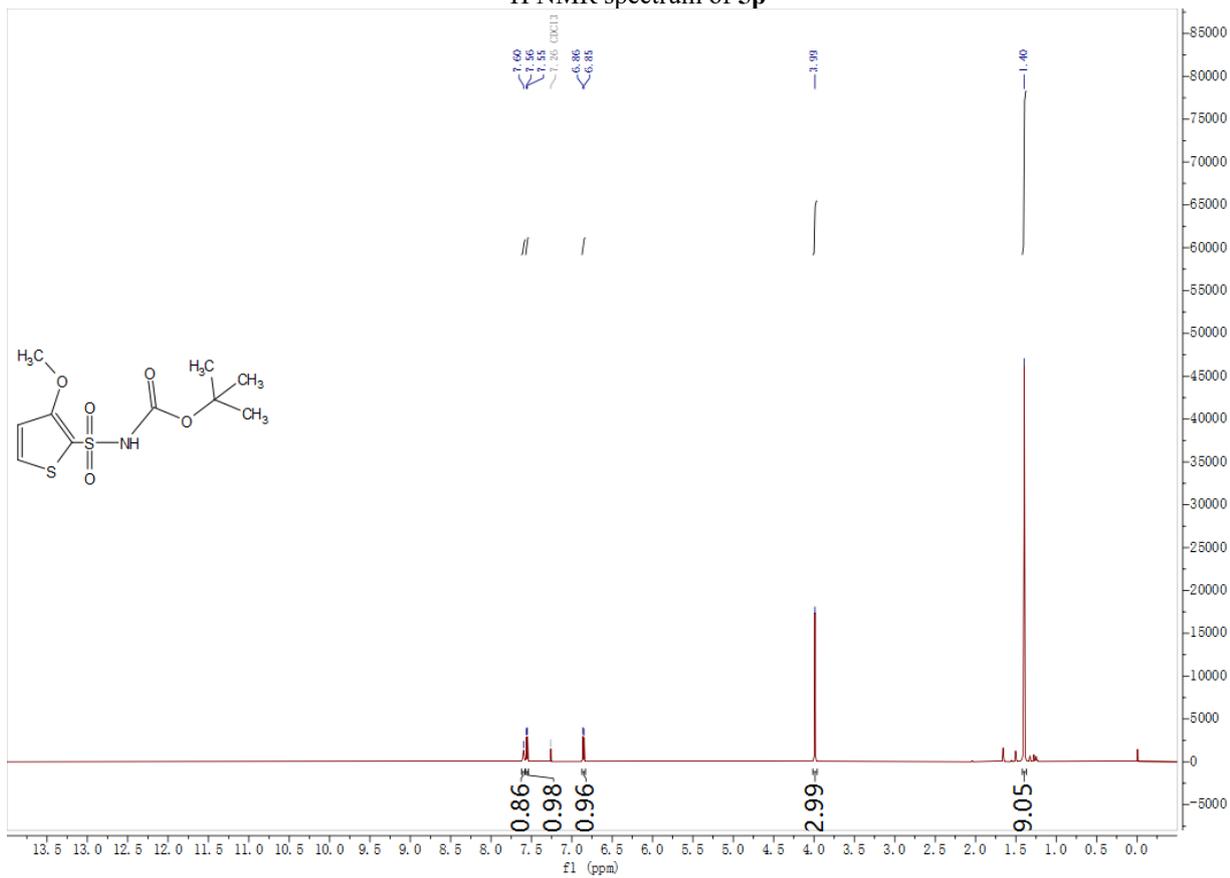
<sup>1</sup>H NMR spectrum of **50**



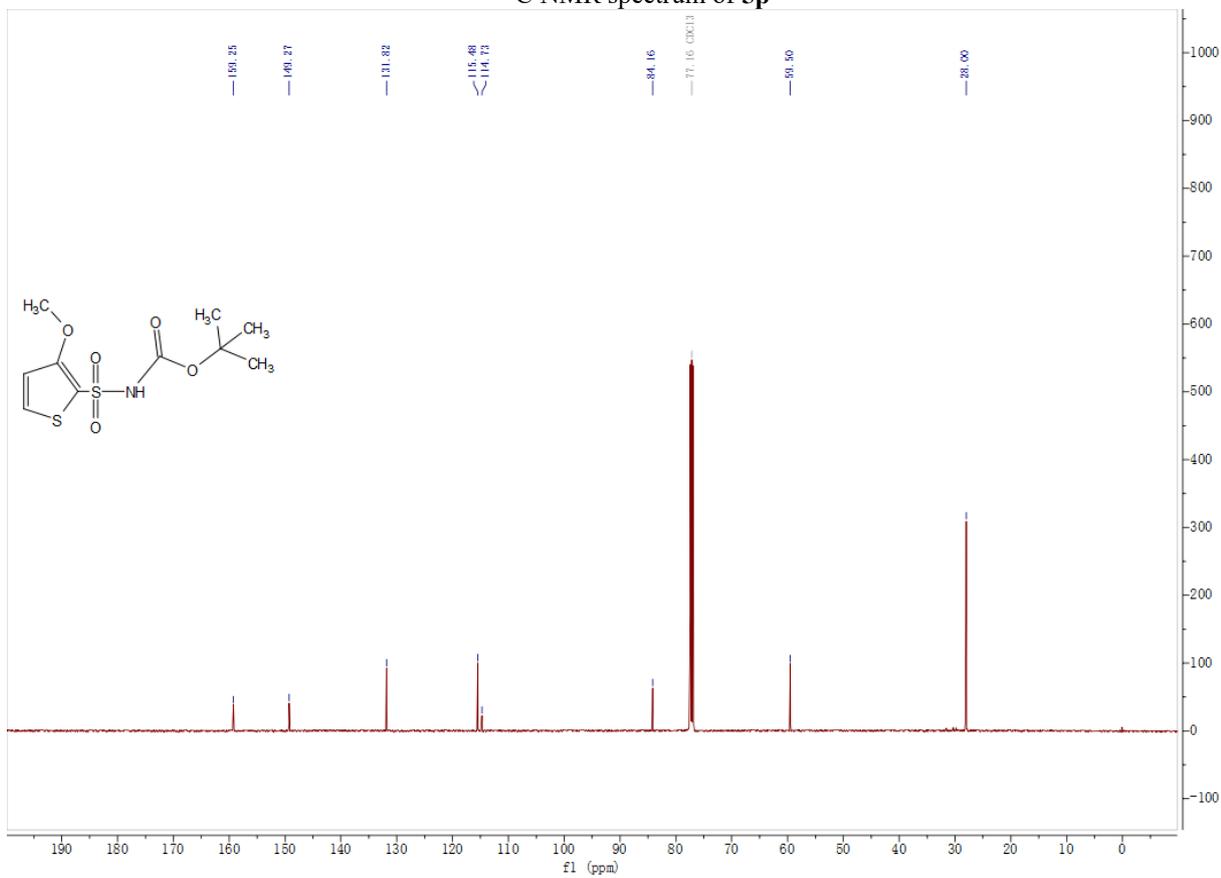
<sup>13</sup>C NMR spectrum of **50**



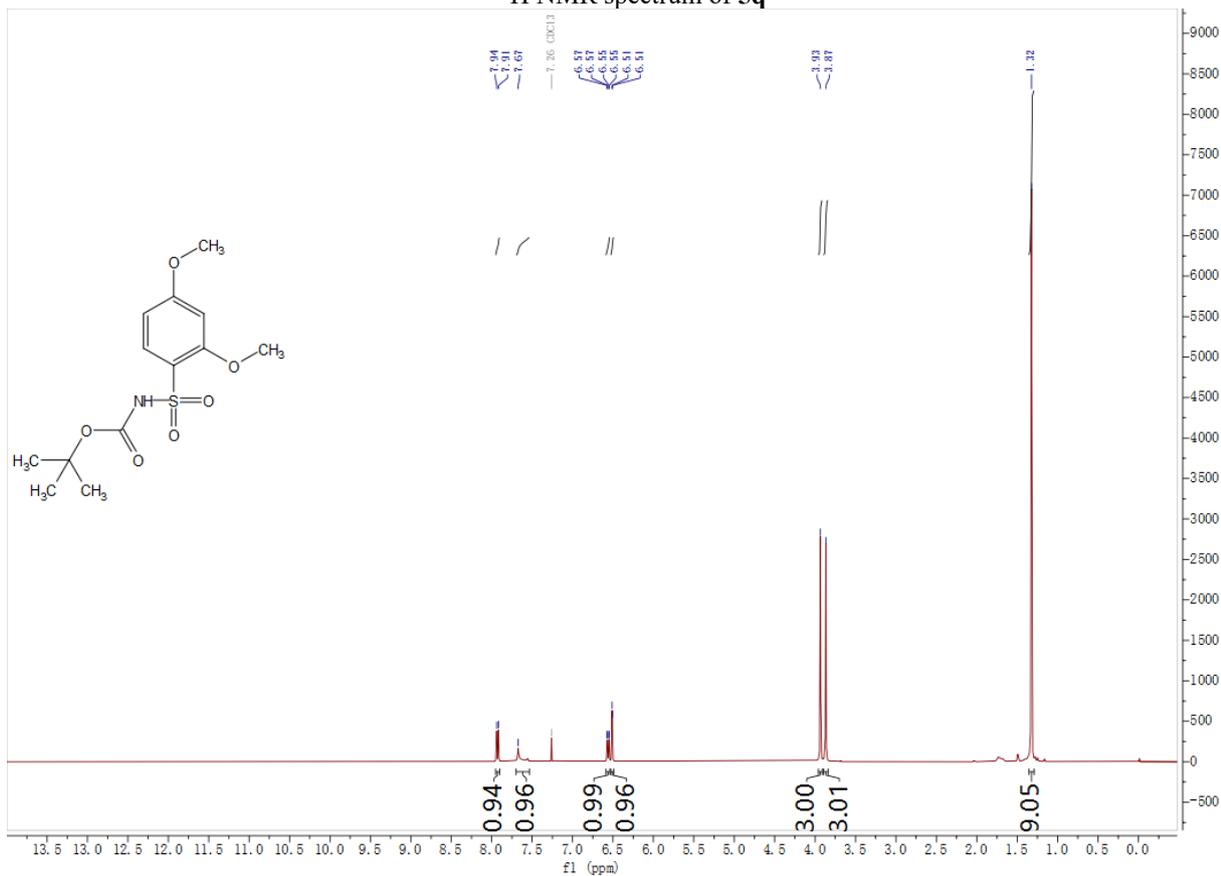
<sup>1</sup>H NMR spectrum of **5p**



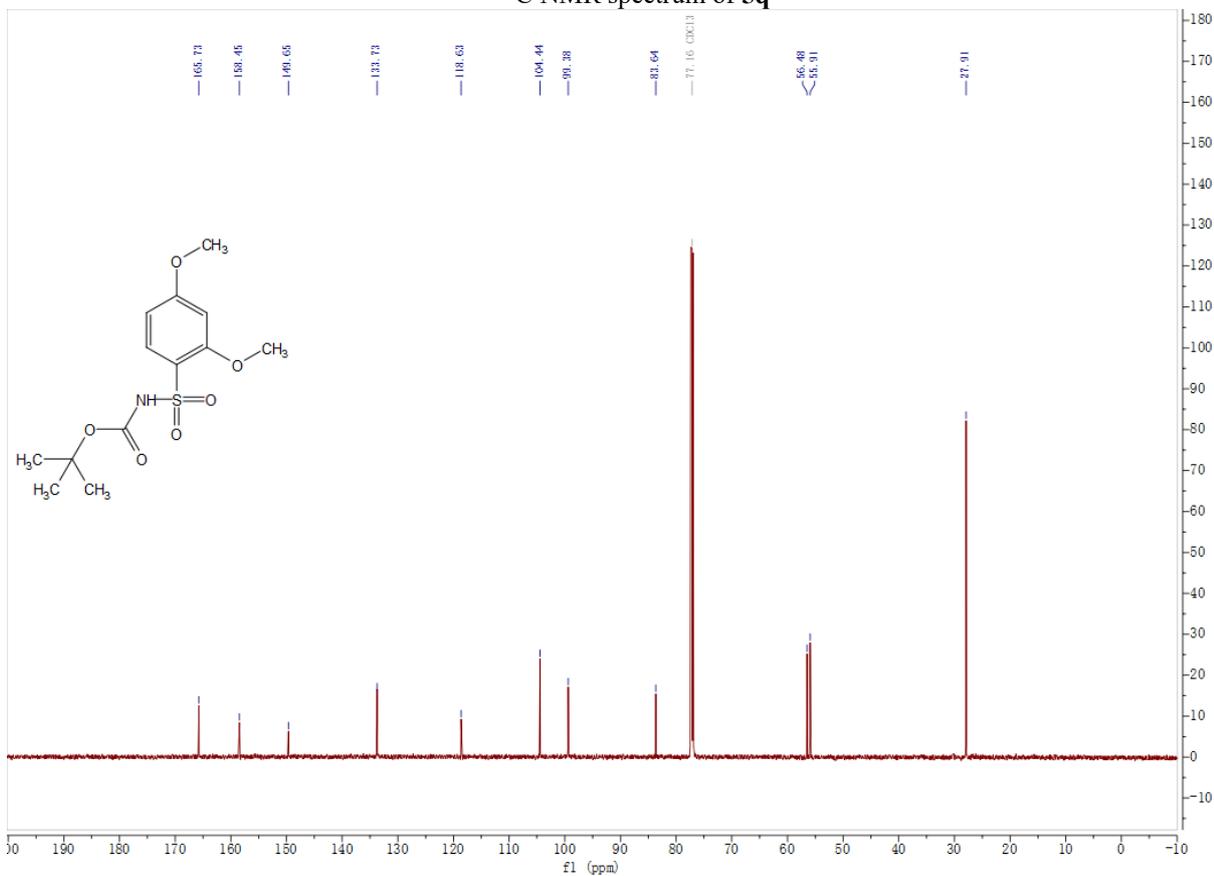
<sup>13</sup>C NMR spectrum of **5p**



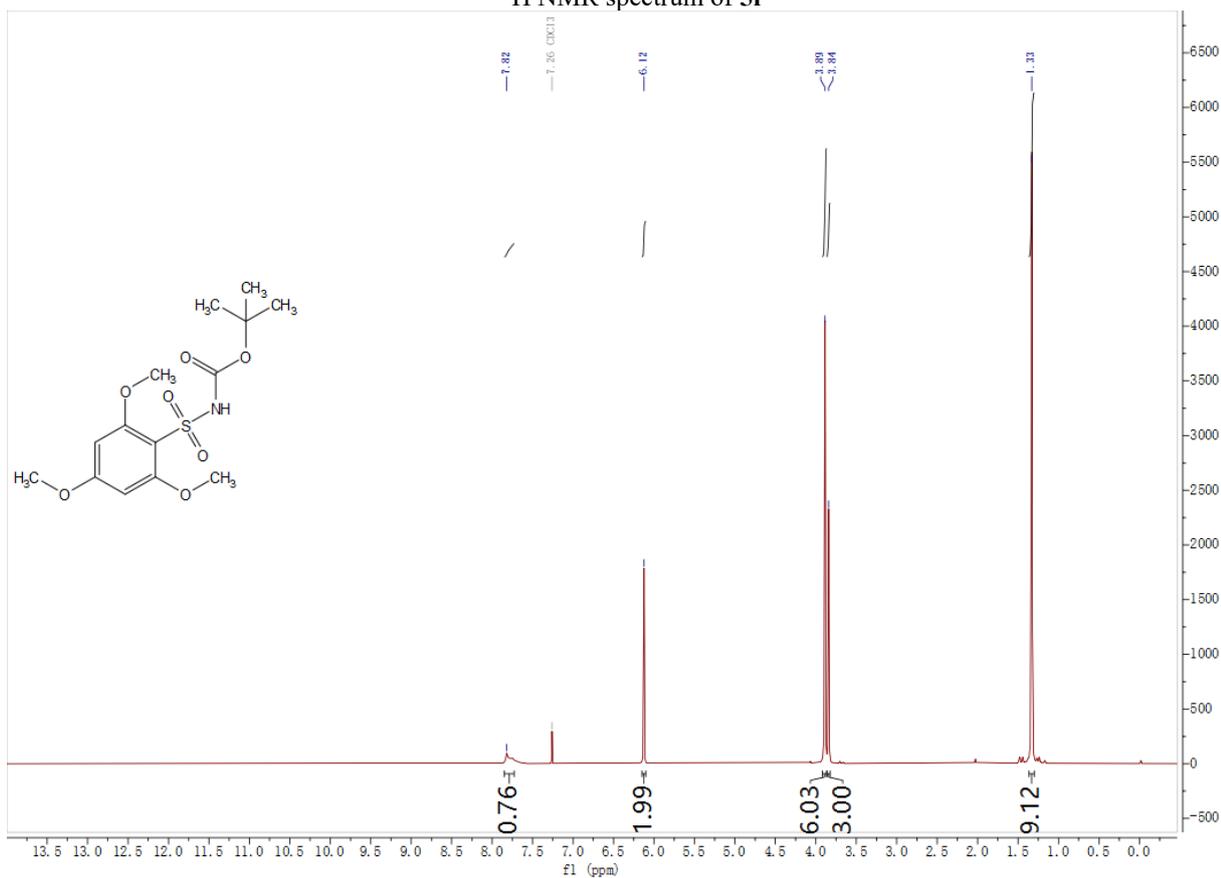
<sup>1</sup>H NMR spectrum of **5q**



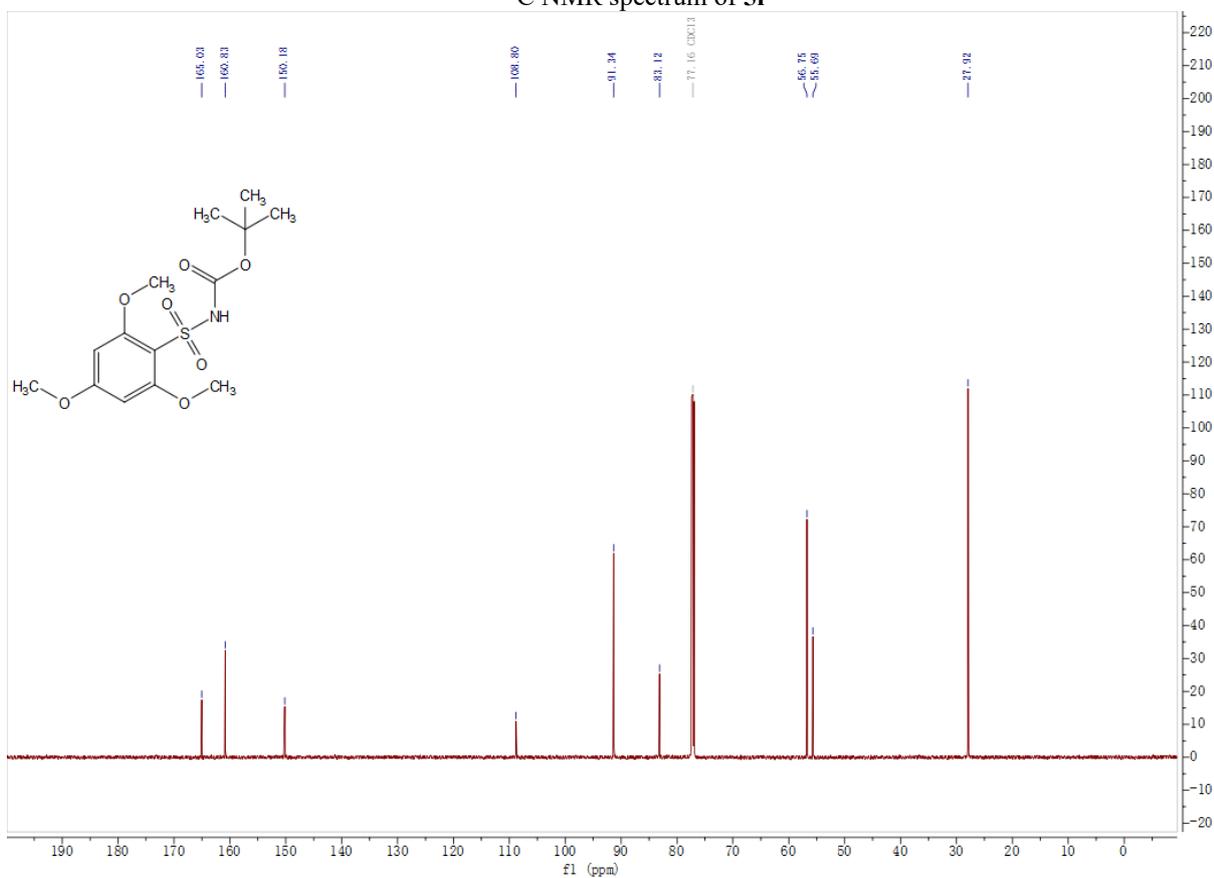
<sup>13</sup>C NMR spectrum of **5q**



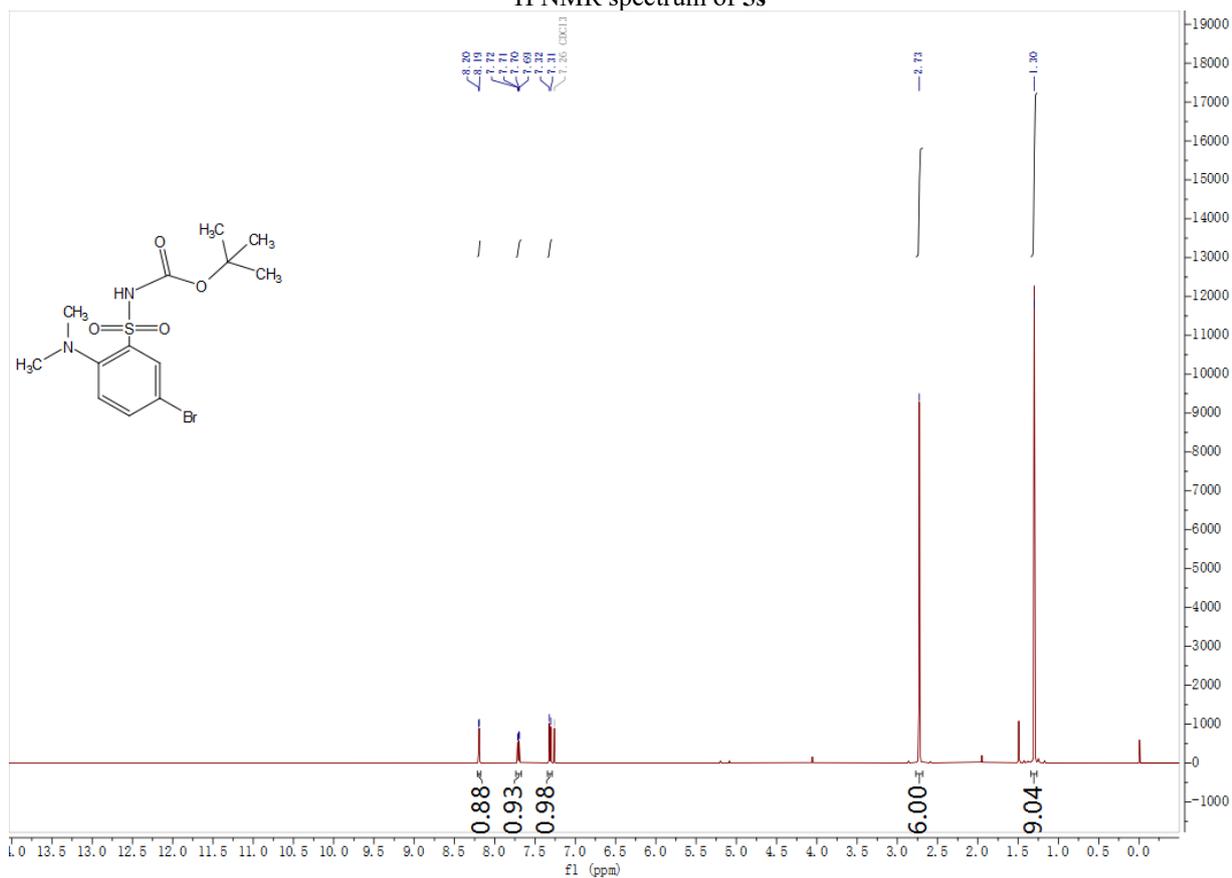
<sup>1</sup>H NMR spectrum of **5r**



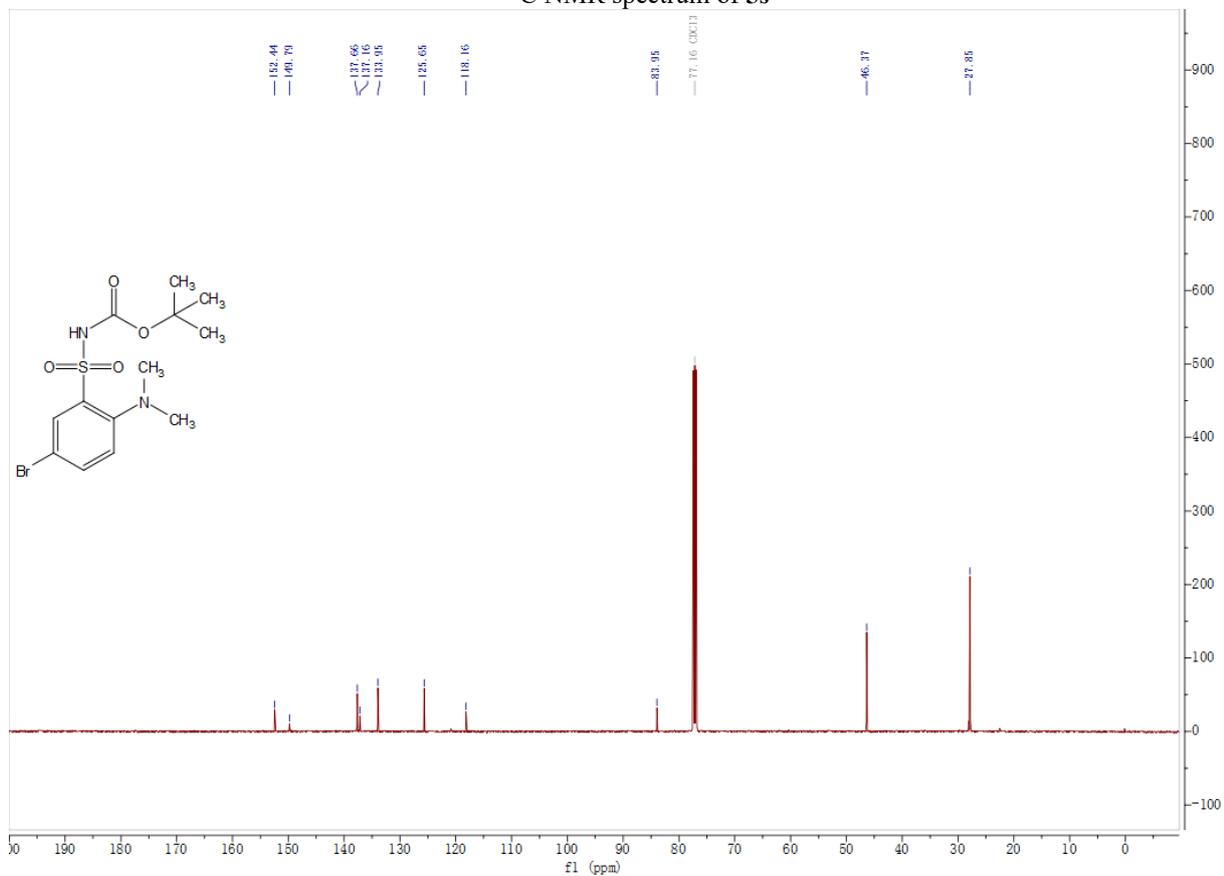
<sup>13</sup>C NMR spectrum of **5r**



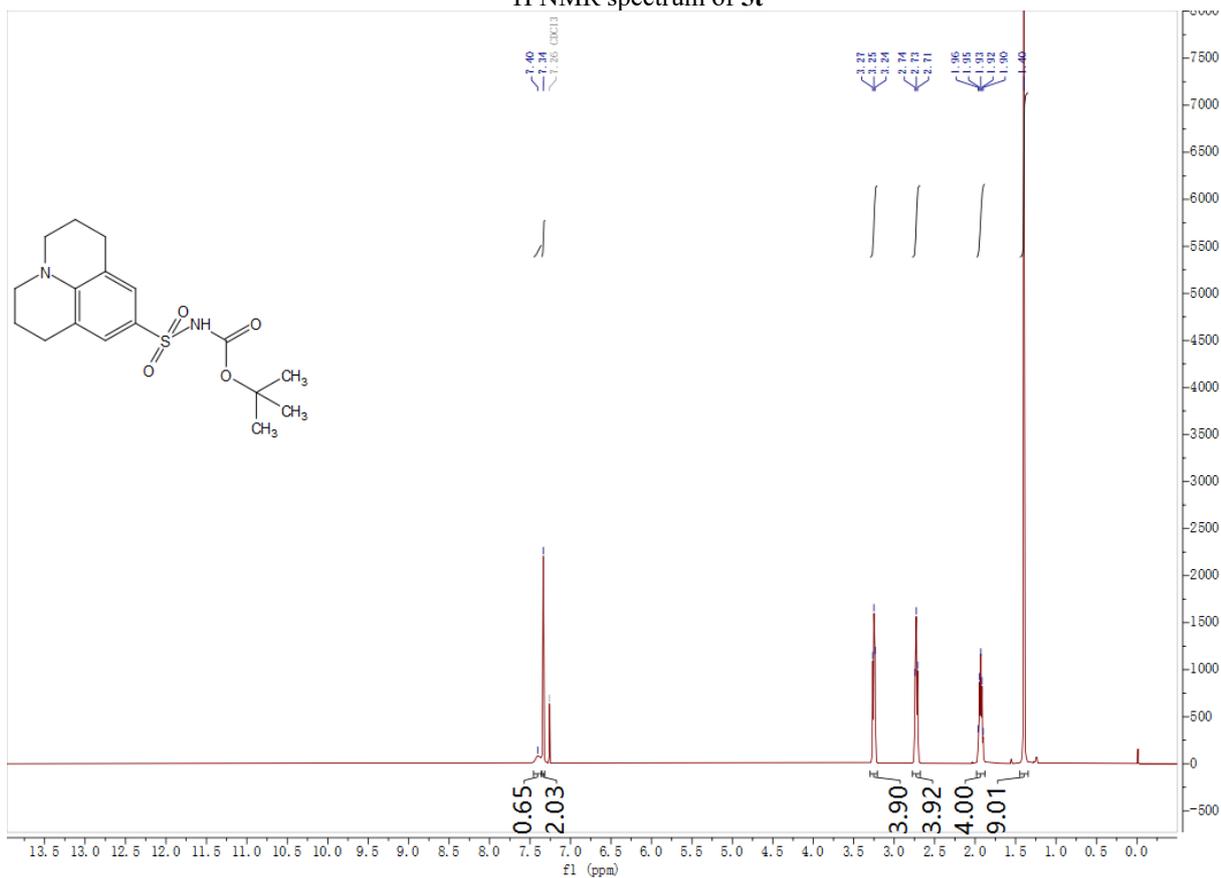
<sup>1</sup>H NMR spectrum of **5s**



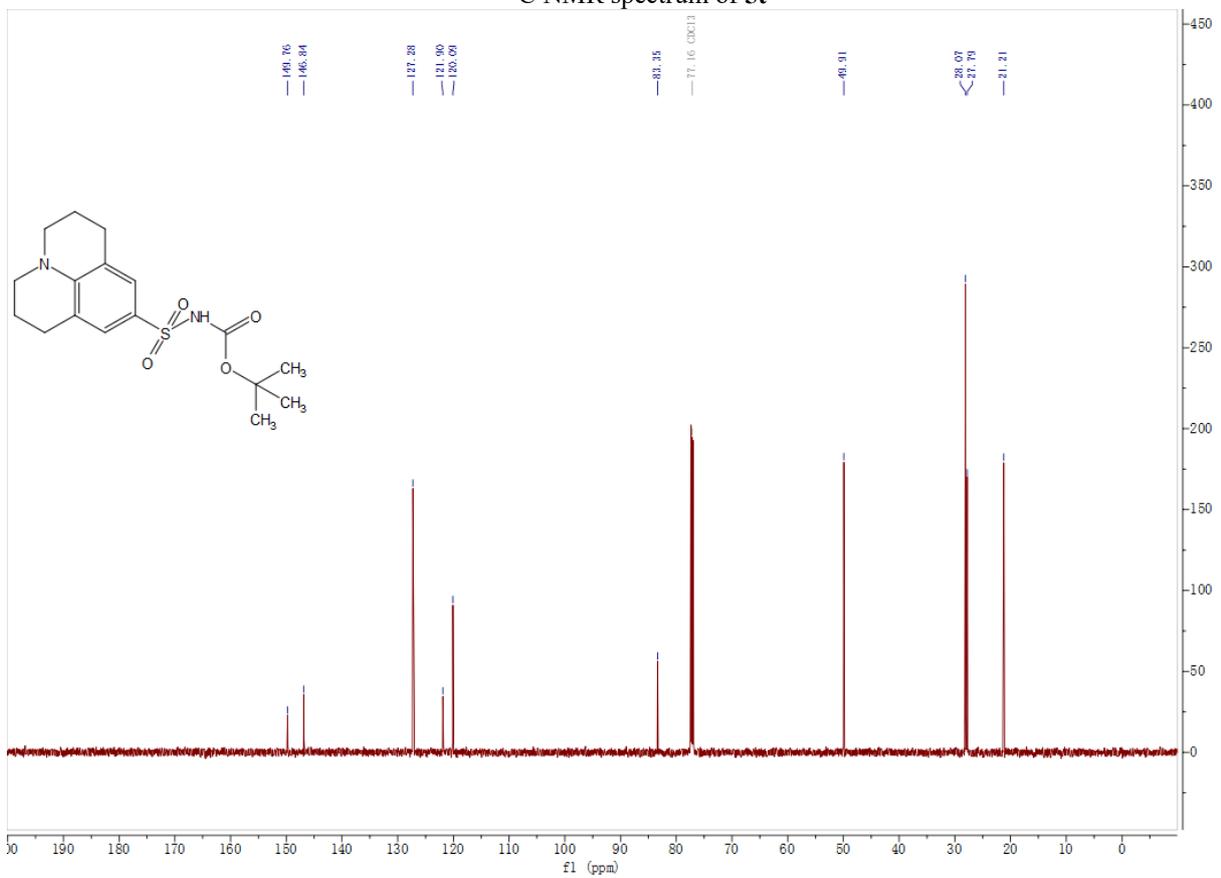
<sup>13</sup>C NMR spectrum of **5s**



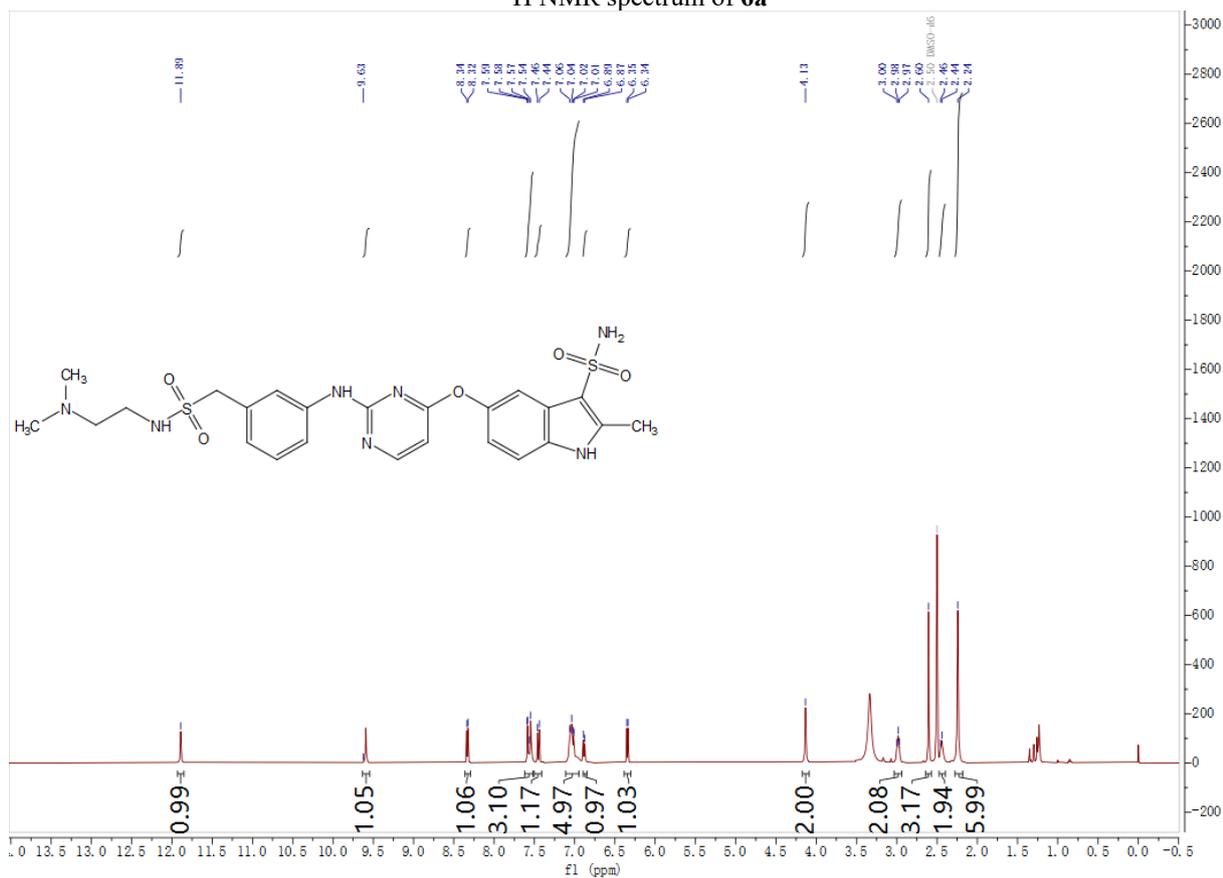
<sup>1</sup>H NMR spectrum of **5t**



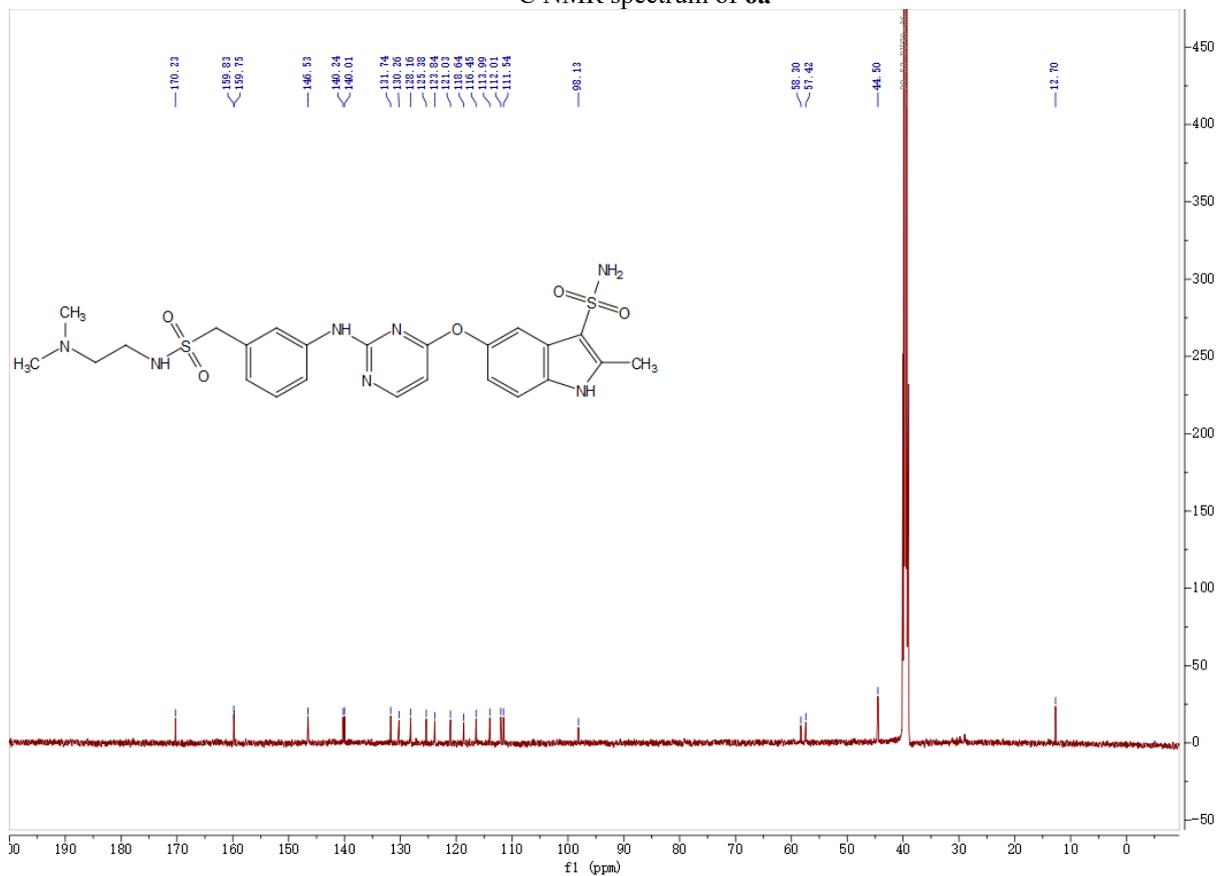
<sup>13</sup>C NMR spectrum of **5t**



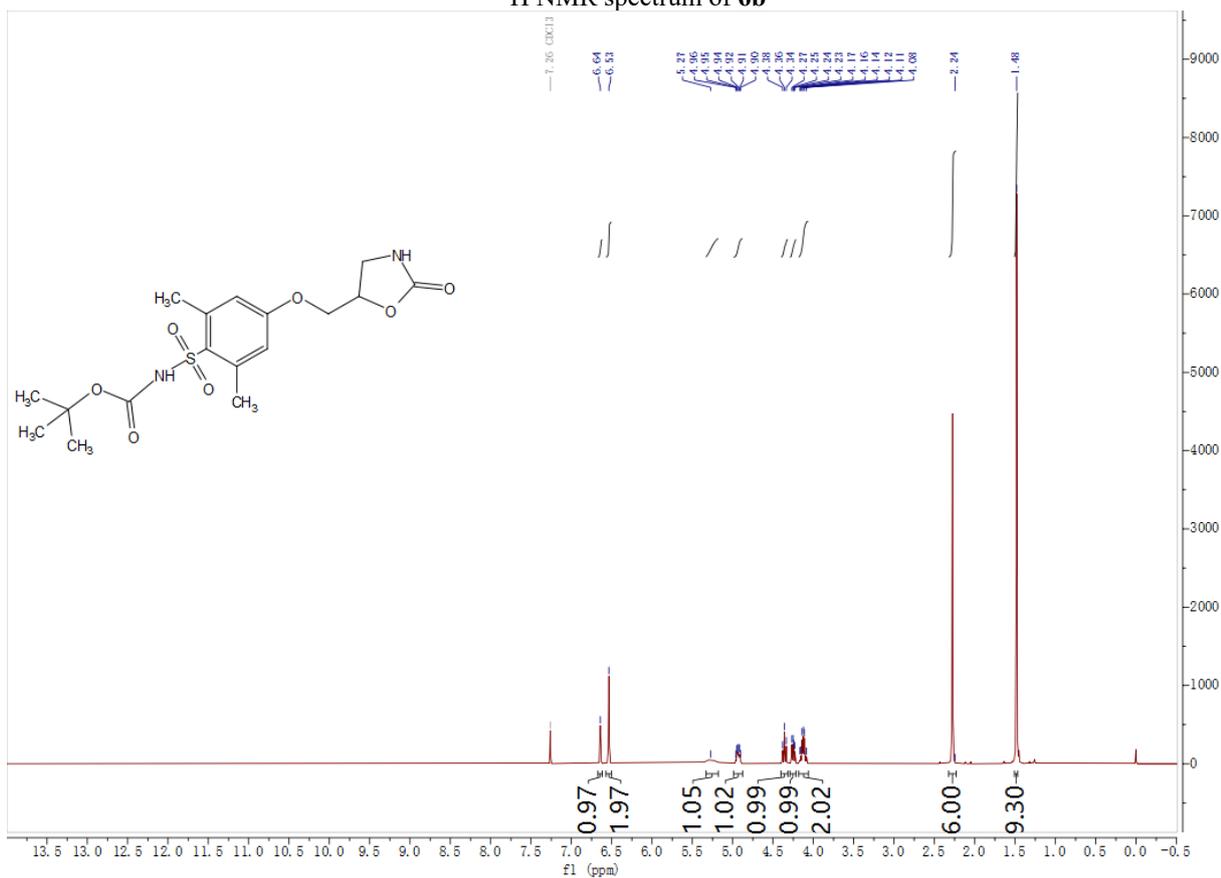
<sup>1</sup>H NMR spectrum of 6a



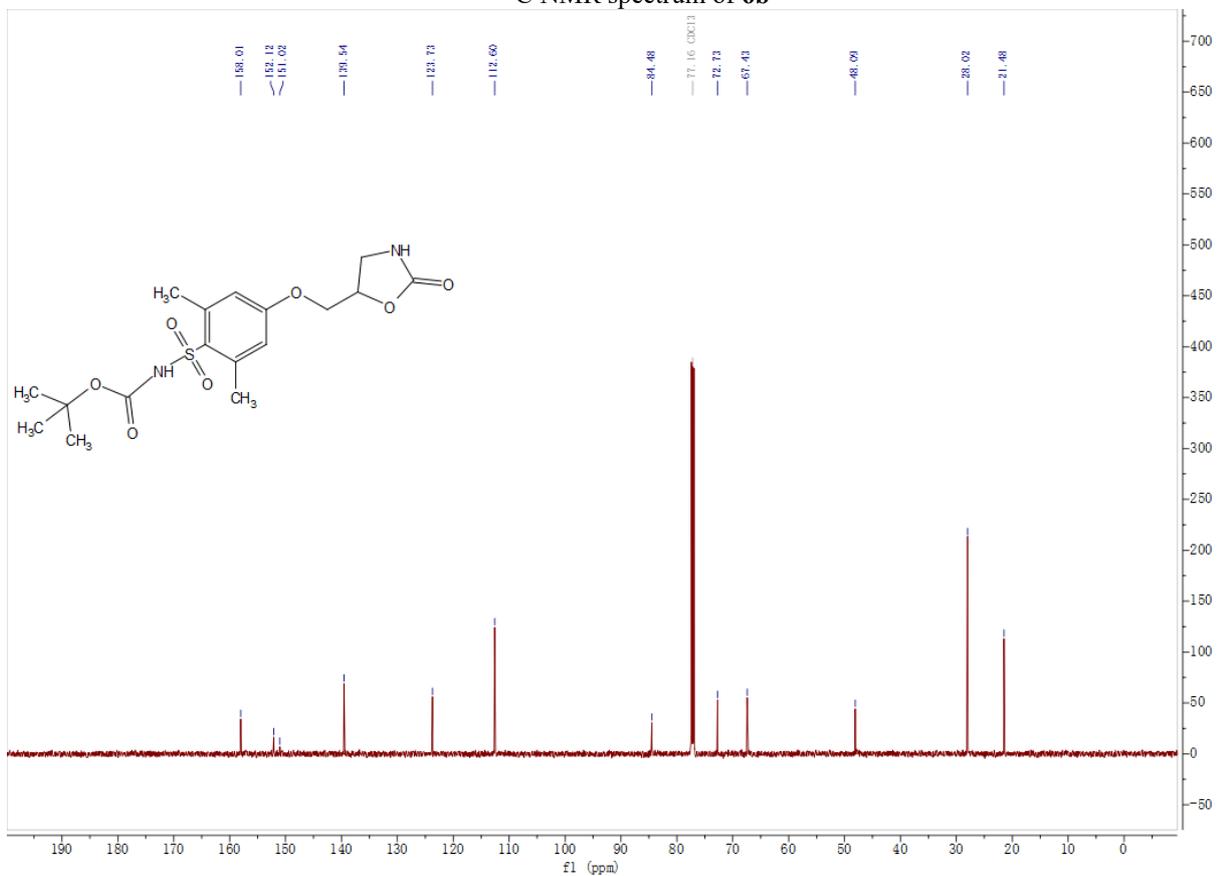
<sup>13</sup>C NMR spectrum of 6a



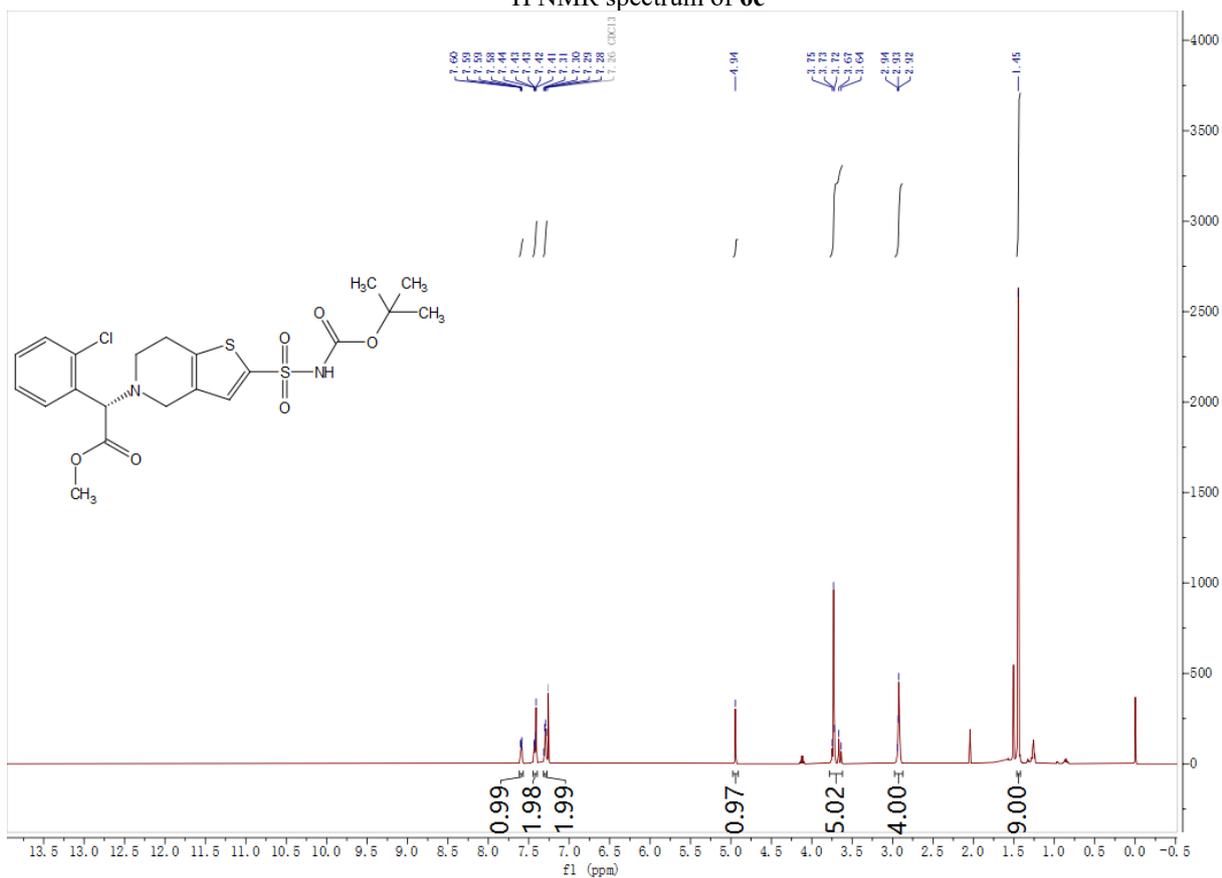
<sup>1</sup>H NMR spectrum of **6b**



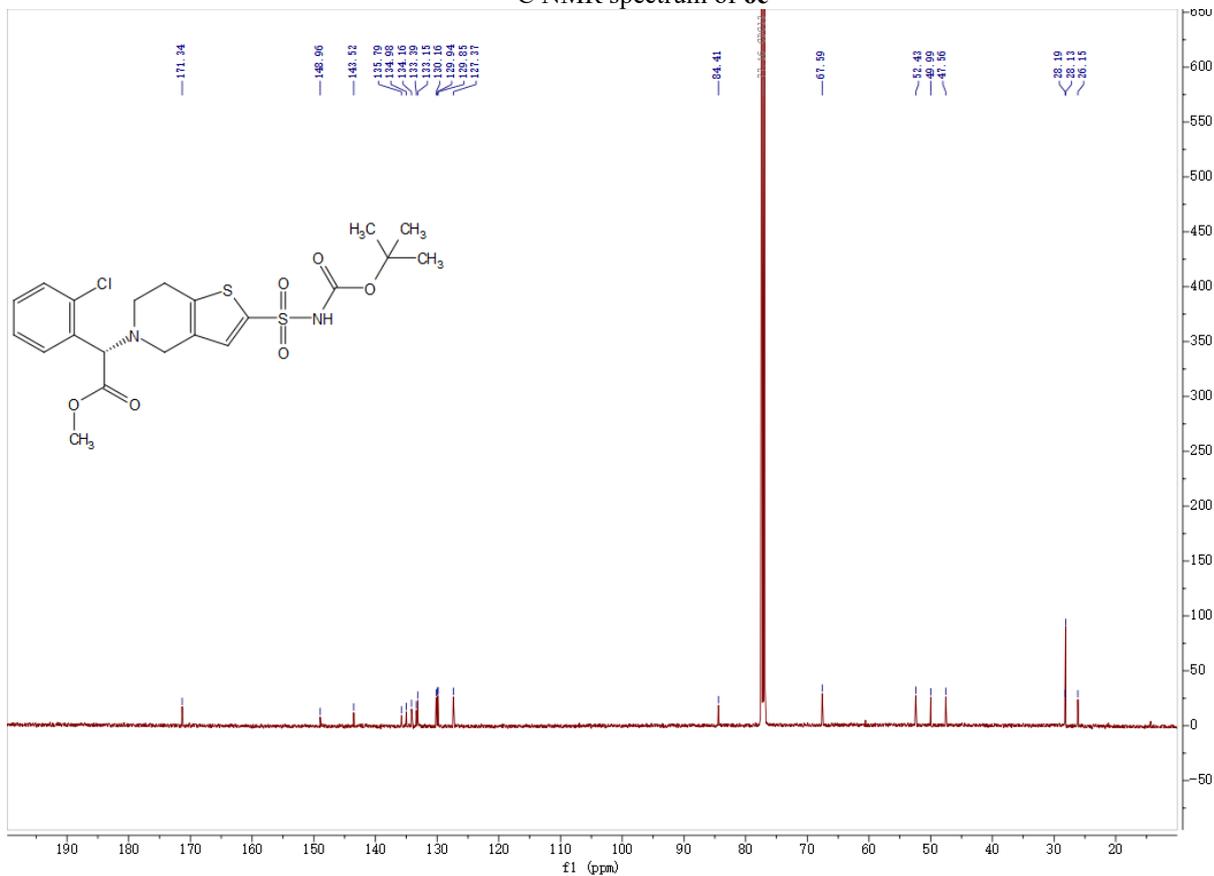
<sup>13</sup>C NMR spectrum of **6b**



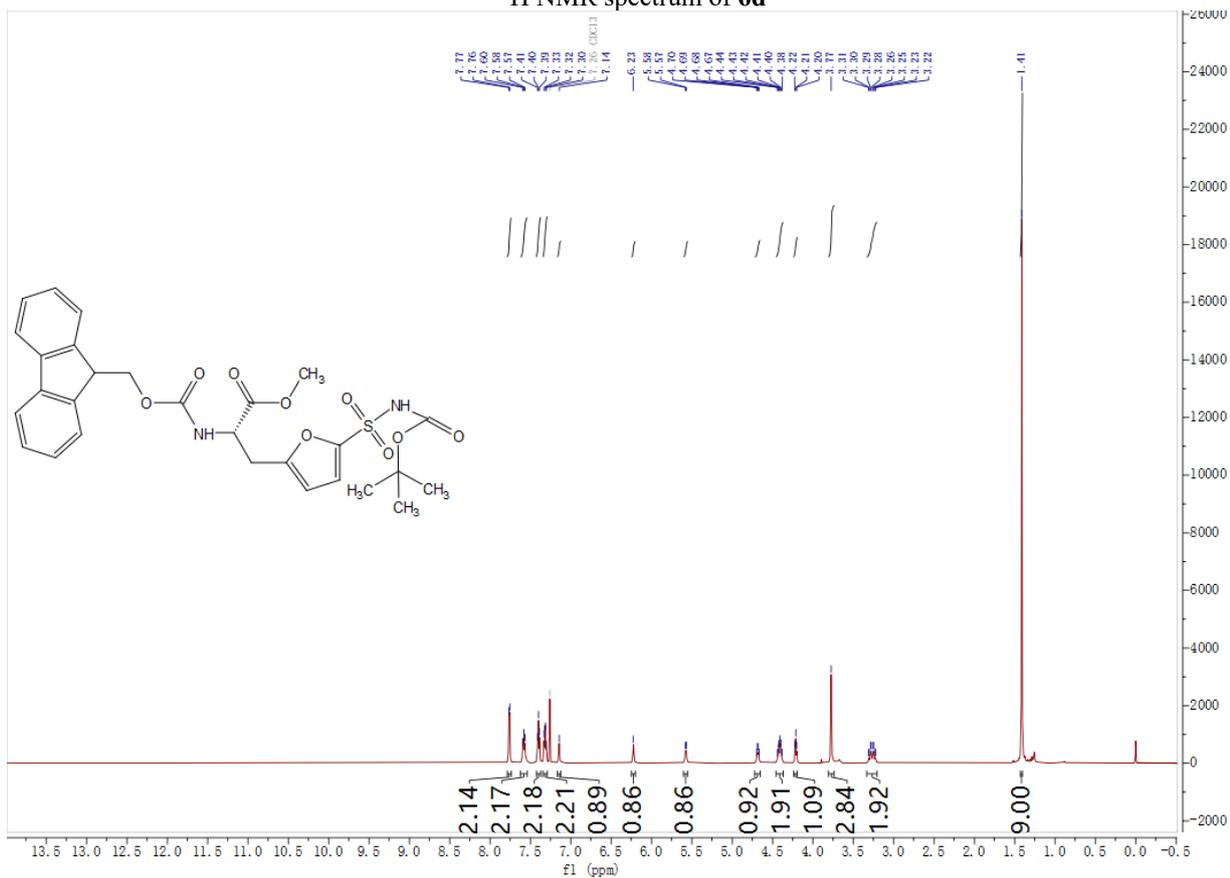
<sup>1</sup>H NMR spectrum of 6c



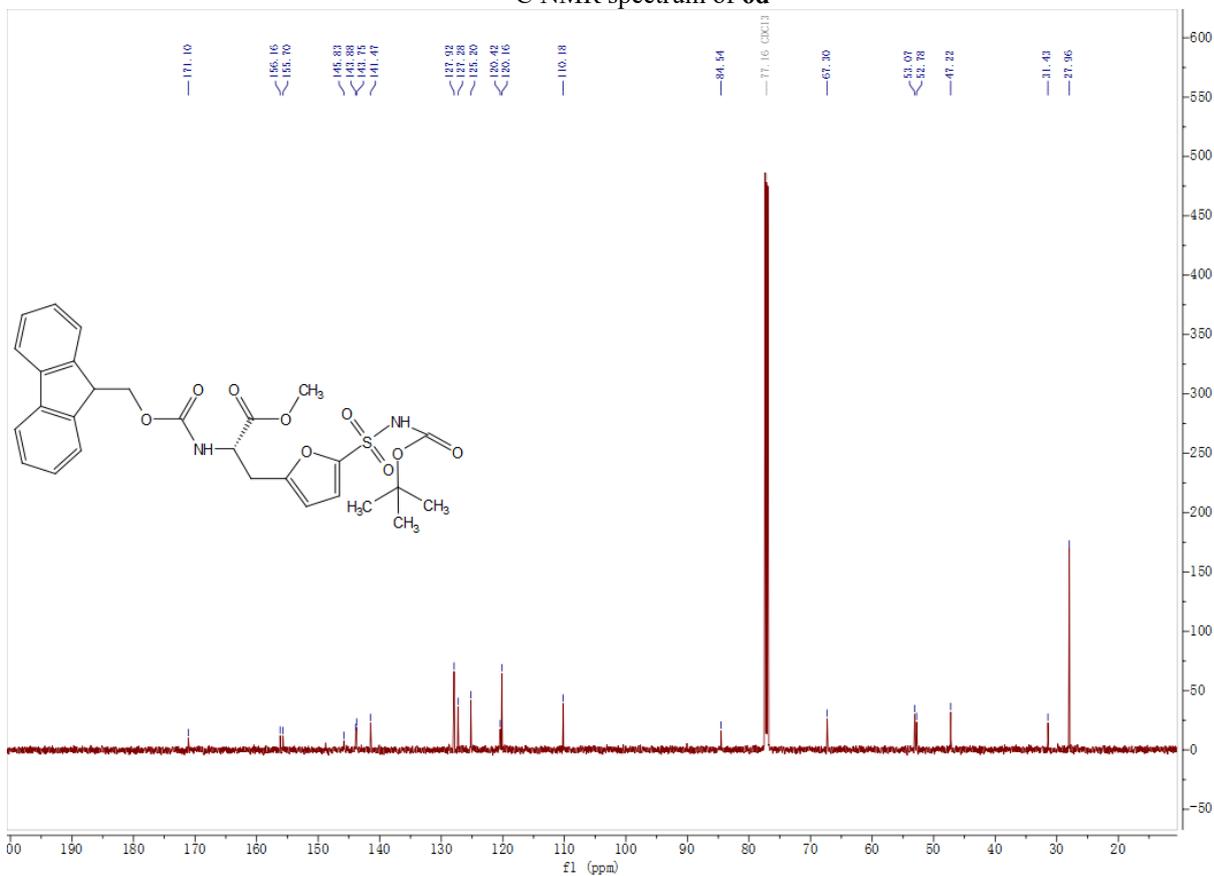
<sup>13</sup>C NMR spectrum of 6c



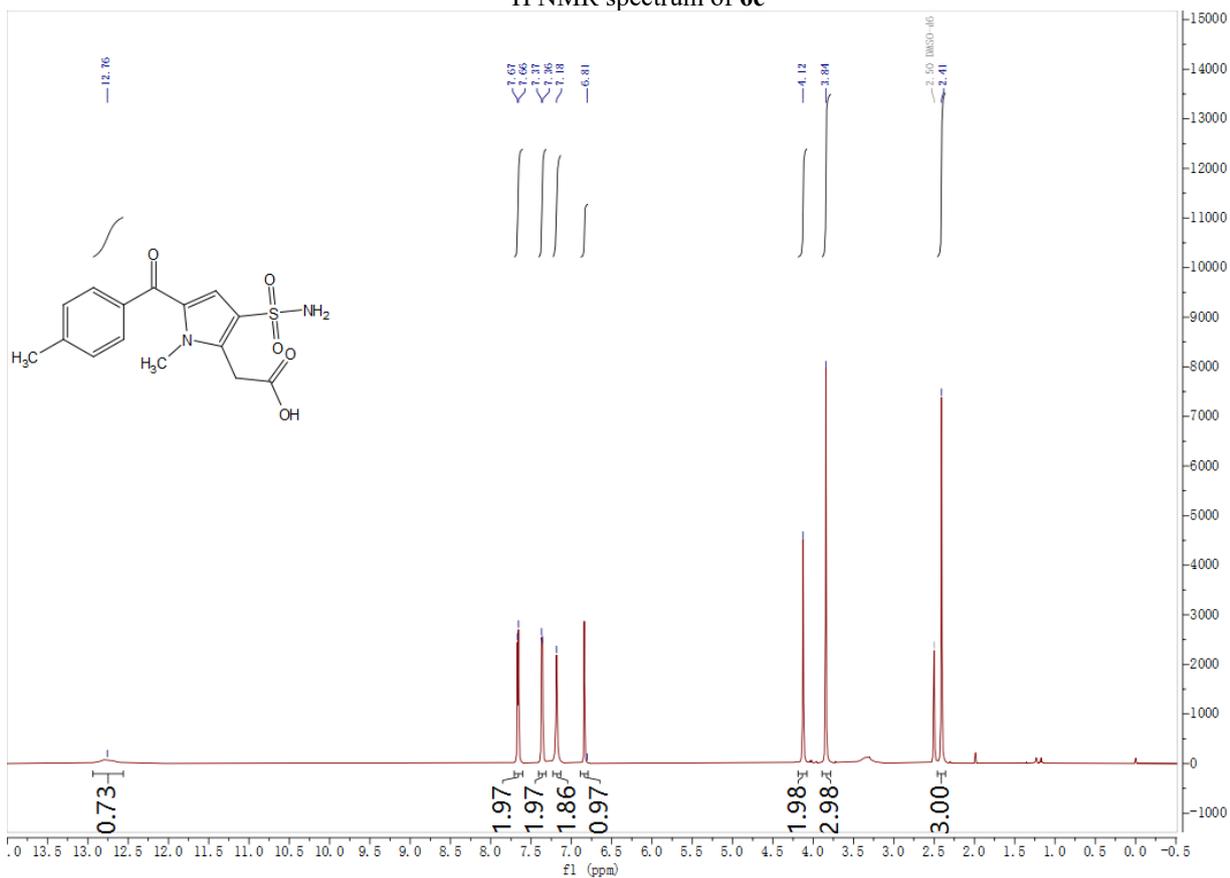
<sup>1</sup>H NMR spectrum of 6d



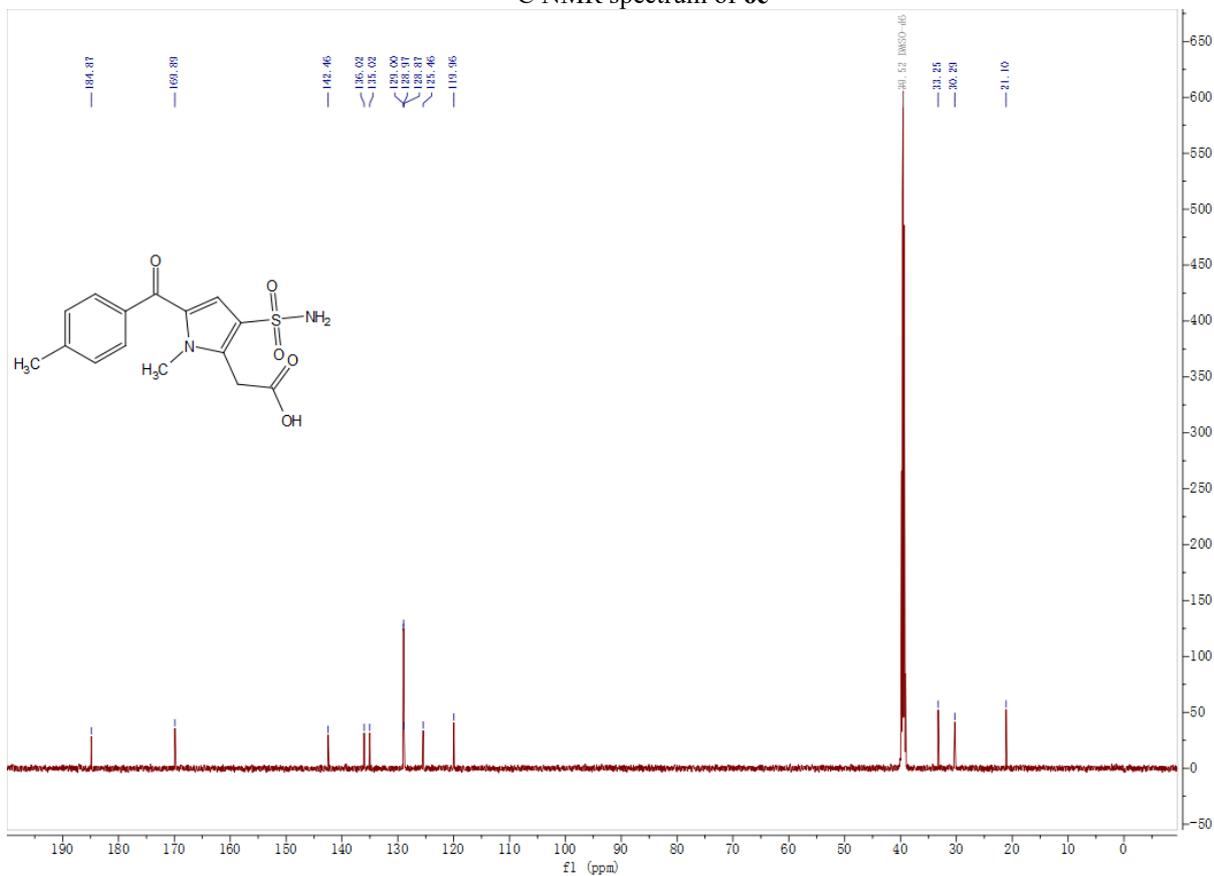
<sup>13</sup>C NMR spectrum of 6d



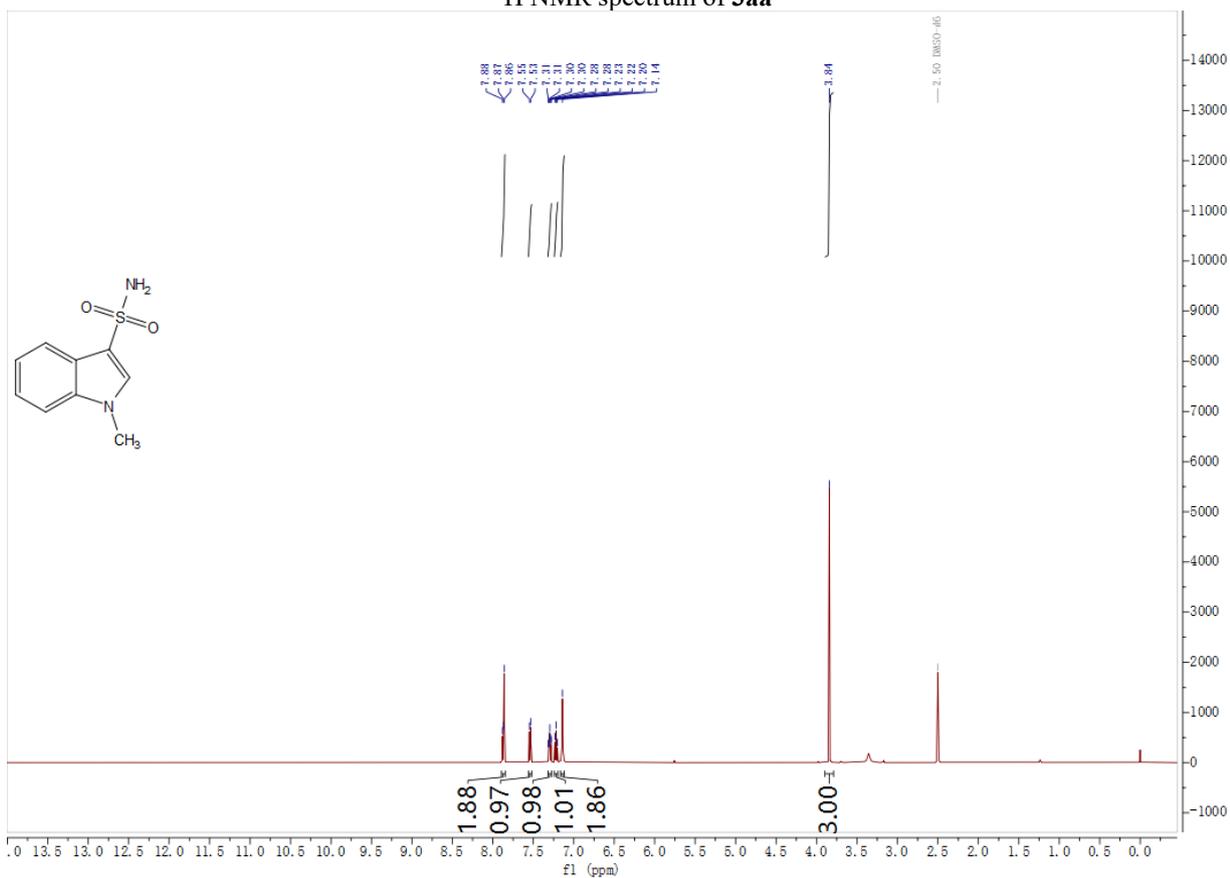
<sup>1</sup>H NMR spectrum of 6e



<sup>13</sup>C NMR spectrum of 6e



<sup>1</sup>H NMR spectrum of **3aa**



<sup>13</sup>C NMR spectrum of **3aa**

