Supporting Information

Irodium-catalyzed regioselective C−H sulfonamidation of 1,2,4-thiadiazoles with sulfonyl azides in water

Xian-Ting Cao[a,*], Su-Ning Wei [a], Hao-Tian Sun[a], Meng Li[a], Zuo-Ling Zheng[a], Guannan Wang[a, *]

[a]*College of Medical Engineering& the Key Laboratory for Medical Functional Nanomaterials, Jining Medical University, Jining, 272067, China.*
E-mail address: cchem1234@163.com (X. T. Cao), chemwangguannan@gmail.com (Pro. G.N. Wang)

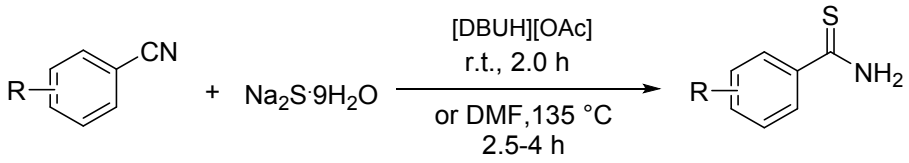
Table of Contents

1. General Information

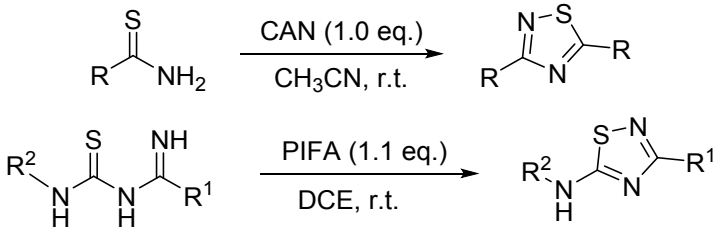
All the reagents were obtained commercially and used without any prior purification. ^{1}H NMR spectra were recorded on a BrukerAvanceII 500 spectrometer. All products were isolated by column chromatography on a silica gel (200–300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd).

2. Experimental Information

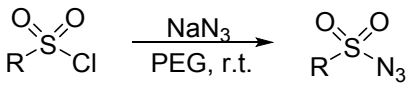
Preparation of the materials starting materials (Thioamides) were prepared according to our previous work. [1-2]



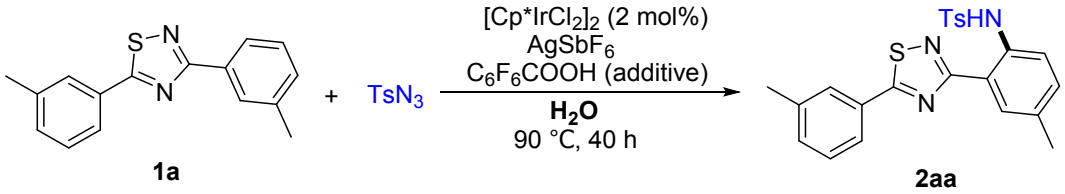
Preparation of the materials starting materials (1,2,4-Thiadiazoles) were prepared according to literature procedures. [3-4]



Preparation of the materials starting materials (sulfonyl azides) were prepared according to literature procedures. [5]



General procedure for the synthesis of product 2aa-2bi and 4a-4m (compound 2aa as the example).



3,5-di-*m*-tolyl-1,2,4-thiadiazole (**1a**, 0.2 mmol), 4--methylbenzenesulfonyl azide (0.3 mmol), $[Cp^*IrCl_2]_2$ (2.0 mol %), $AgSbF_6$ (8 mol %), C_6F_5COOH (40 mol %) were dissolved in H_2O (1 mL) in a pressure tube. The mixture was stirred at 90 °C for 40 hours. After that, the solvent was removed under vacuum and the residue was purified by silica gel chromatography to afford product (**2aa**).

[1] X.-T. Cao, L. Qiao, H. Zheng, H.-Y. Yang, P.-F. Zhang, *RSC Adv.,* 2018, **8**, 170-175.

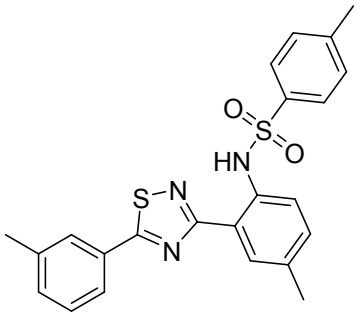
[2] X.-T. Cao, H.-Y. Yang, H. Zheng, P.-F, Zhang. *Heterocycles,* 2018, **96**, 509-517.

[3] G. Vanajatha, V. P. Reddy, *Tetrahedron Lett.,* 2016, **57**, 2356-2359.

[4] A. Mariappan, K. Rajaguru, N. M. Chola, S. Muthusubramanian, N. Bhuvanesh. *J. Org. Chem.,* 2016, **81**, 6573-6579.

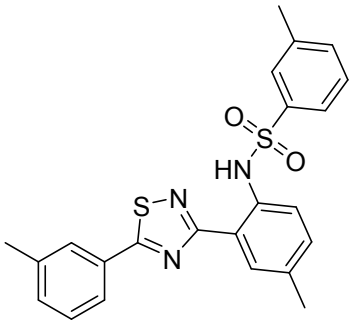
[5] H. Zeng, H. Shao, *Green Chem. Lett. Rev.,* 2013, **6**, 222-227.

3. Characterization data of the products.

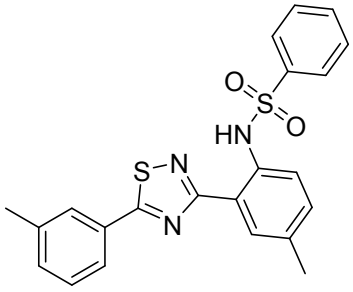


2aa:

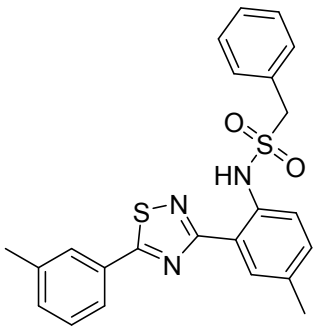
White solid, ^1H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 8.07 (s, 1H), 7.78-7.72 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 7.40-7.30 (m, 2H), 7.14 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 2.16 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.68, 171.97, 143.37, 139.56, 136.29, 134.47, 133.96, 133.45, 132.36, 130.93, 129.71, 129.49, 129.27, 128.04, 127.06, 124.71, 121.63, 121.34, 21.39, 21.36, 20.77 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1128.

2ab: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.13 (s, 1H), 7.83-7.57 (m, 3H), 7.49-7.32 (m, 4H), 7.23-7.02 (m, 3H), 2.47 (s, 3H), 2.34 (s, 3H), 2.16 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.65, 171.89, 139.56, 139.04, 138.86, 134.39, 134.08, 133.50, 132.37, 130.93, 129.63, 129.50, 128.49, 128.01, 127.36, 124.70, 124.19, 121.79, 121.44, 21.38, 21.18, 20.79 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1128.

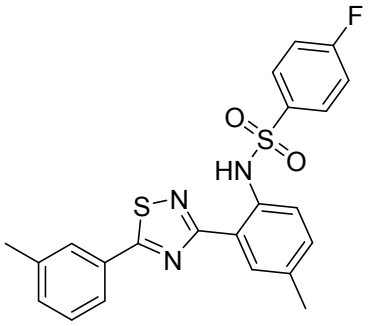
2ac: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.14 (s, 1H), 7.85-7.77 (m, 2H), 7.65 (d, J = 8.5 Hz, 3H), 7.45-7.33 (m, 3H), 7.27-7.33 (m, 2H), 7.21 (dd, J = 8.4, 1.8 Hz, 1H), 2.47 (s, 3H), 2.34 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.68, 171.86, 139.57, 139.17, 134.32, 134.12, 133.50, 132.63, 132.40, 130.97, 129.63, 129.50, 128.65, 128.04, 127.02, 124.71, 121.63, 121.32, 21.38, 20.79 ppm. HRMS (ESI): Calculated for $C_{22}H_{19}N_3O_2S_2$: $[M+H]^+$ 422.0992, Found 422.0969.

2ad: 

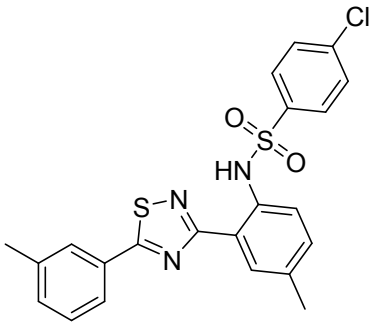
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.01 (s, 1H), 8.24 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.55-7.48 (m, 2H), 7.32-7.27 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 6.6 Hz, 1H), 6.84-6.79 (m, 2H), 4.22 (s, 2H), 2.37 (s, 3H), 2.35 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.34, 171.38, 139.34, 135.04, 133.46, 133.32, 132.80, 131.10, 130.47, 129.43, 129.30, 128.42, 128.27, 128.12, 128.06, 124.71, 119.95, 119.08, 56.97, 21.34, 20.80 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1125.

2ae:



White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 8.15 (s, 1H), 7.86-7.76 (m, 2H), 7.70-7.57 (m, 3H), 7.48-7.35 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.91 (t, *J* = 8.5 Hz, 2H), 2.47 (s, 3H), 2.36 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.80, 171.80, 164.94 (d, *J* = 254.9 Hz), 139.60, 135.17 (d, *J* = 3.1 Hz), 134.41, 134.08, 133.56, 132.45, 131.08, 129.75 (d, *J* = 9.4 Hz), 129.56, 129.52, 128.03, 124.69, 121.76, 121.45, 115.88 (d, *J* = 22.6 Hz), 21.36, 20.79 ppm. HRMS (ESI): Calculated for $C_{22}H_{18}FN_3O_2S_2$: $[M+H]^+$ 440.0897, Found 440.0877.

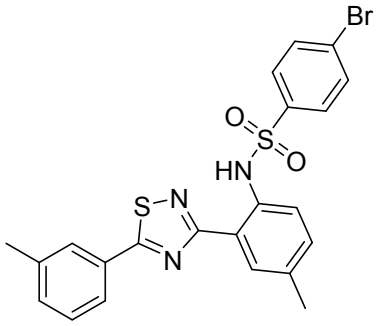
2af:



White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.07 (s, 1H), 7.78-7.68 (d, *J* = 9.2 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.52-7.43 (m, 2H), 7.38-7.28 (m, 2H), 7.16-7.04 (m, 3H), 2.39 (s, 3H), 2.28 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.83, 171.79, 139.60, 139.13, 137.64, 134.50, 133.96, 133.57, 132.47, 131.12, 129.57,

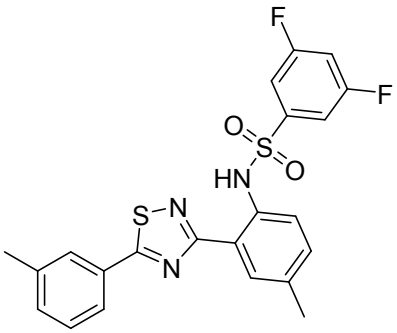
129.52, 128.94, 128.47, 128.05, 124.72, 121.78, 121.50, 21.38, 20.81 ppm. HRMS (ESI): Calculated for $C_{22}H_{18}ClN_3O_2S_2$: $[M+H]^+$ 456.0602, Found 456.0576.

2ag:



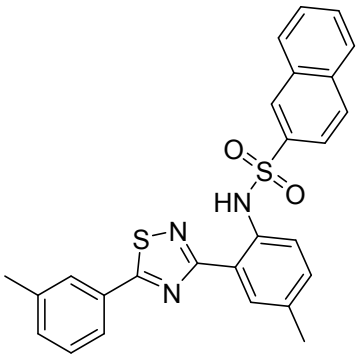
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.09 (s, 1H), 8.17 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.51-7.47 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 3H), 7.25-7.22 (m, 1H), 2.49 (s, 3H), 2.38 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.87, 171.81, 139.61, 138.15, 134.56, 133.92, 133.56, 132.49, 131.92, 131.12, 129.60, 129.53, 128.54, 128.08, 127.67, 124.73, 121.89, 121.58, 21.38, 20.81 ppm. HRMS (ESI): Calculated for $C_{22}H_{18}BrN_3O_2S_2$: $[M+H]^+$ 500.0097, Found 500.0092.

2ah:

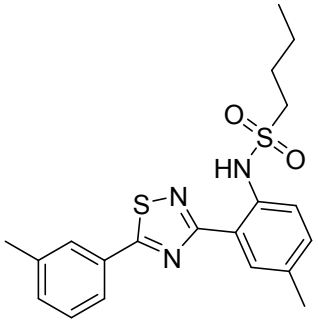


White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.19 (s, 1H), 8.17 (s, 1H), 7.91-7.76 (m, 2H), 7.63 (t, *J* = 9.0 Hz, 1H), 7.48-7.36 (m, 2H), 7.28-7.13 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H), 2.36 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.03, 171.71, 162.45 (d, *J* = 256.0 Hz), 162.36 (d, *J* = 256.4 Hz), 161.43, 161.34, 142.42, 139.62, 134.87, 133.63, 133.50, 132.59, 131.22, 129.53, 128.06, 124.73, 121.67, 121.55, 110.68 (d, *J* = 28.4 Hz), 108.31 (t, *J* = 25.0 Hz), 21.37, 20.82 ppm. HRMS (ESI): Calculated for $C_{22}H_{17}F_2N_3O_2S_2$: $[M+H]^+$ 458.0803, Found 458.0782.

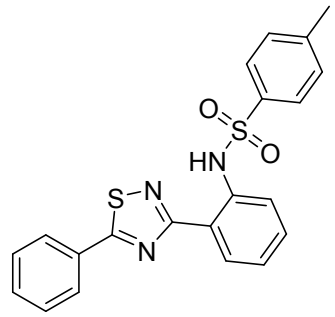
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.45 (d, *J* = 256.0 Hz), 162.36 (d, *J* = 256.4 Hz).

2ai: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.28 (s, 1H), 8.06 (s, 1H), 7.74-7.62 (m, 6H), 7.59-7.56 (m, 1H), 7.48-7.34 (m, 4H), 7.19 (d, *J* = 8.4, 1H), 2.44 (s, 3H), 2.29 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.63, 171.82, 139.46, 136.20, 134.70, 134.29, 134.10, 133.45, 132.40, 131.86, 130.99, 129.57, 129.42, 129.12, 128.97, 128.65, 128.03, 127.77, 127.28, 124.70, 122.11, 121.58, 121.35, 21.37, 20.76 ppm. HRMS (ESI): Calculated for $C_{26}H_{21}N_3O_2S_2$: $[M+H]^+$ 472.1148, Found 472.1123.

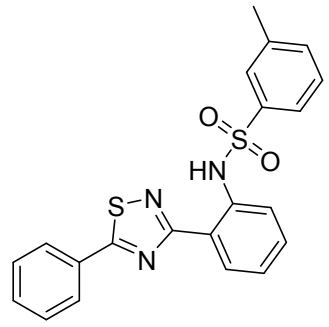
2aj: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.05 (s, 1H), 8.36 (d, *J* = 1.4 Hz, 1H), 7.87-7.80 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.44-7.36 (m, 2H), 7.29-7.26 (m, 1H), 3.14-3.05 (m, 2H), 2.47 (s, 3H), 2.41 (s, 3H), 1.73-1.66 (m, 2H), 1.36-1.27 (m, 2H), 0.77 ppm (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.81, 172.12, 139.52, 135.13, 133.50, 133.20, 132.73, 131.47, 129.65, 129.45, 128.09, 124.77, 119.74, 119.06, 51.22, 25.31, 21.36, 21.33, 20.74, 13.47 ppm. HRMS (ESI): Calculated for $C_{20}H_{23}N_3O_2S_2$: $[M+H]^+$ 402.1305, Found 402.1283.



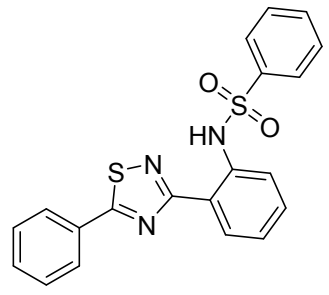
2ak:

White solid, ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.39 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.05-8.02 (m, 2H), 7.75 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.62-7.55 (m, 5H), 7.42-7.38 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.26 ppm (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.51, 171.93, 143.58, 137.04, 136.32, 132.67, 131.61, 130.85, 129.76, 129.60, 129.39, 127.54, 127.11, 123.98, 120.91, 120.72, 21.44 ppm. HRMS (ESI): Calculated for $C_{21}H_{17}N_3O_2S_2$: $[M+H]^+$ 408.0835, Found 408.0821.



2al:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 6.4 Hz, 2H), 7.78-7.32 (m, 7H), 7.23-7.06 (m, 3H), 2.20 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.52, 171.88, 139.10, 138.99, 136.97, 133.58, 132.70, 131.61, 130.83, 129.72, 129.62, 128.59, 127.53, 127.41, 124.20, 124.14, 121.12, 121.03, 21.19 ppm. HRMS (ESI): $C_{21}H_{17}N_3O_2S_2$: $[M+H]^+$ 408.0835, Found 408.0821.

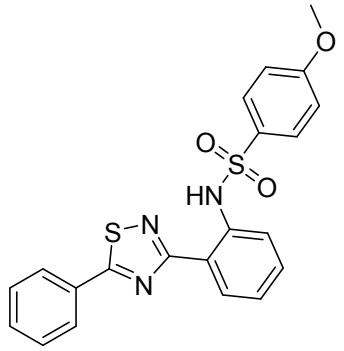


2am:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.39 (s, 1H), 8.38 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.12-7.91 (m, 2H), 7.81-7.64 (m, 3H), 7.62-7.50 (m, 3H), 7.46-7.36 (m, 2H),

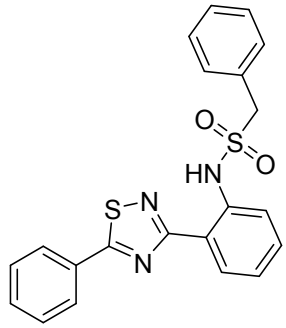
7.29 (t, J = 7.8 Hz, 2H), 7.17 ppm (t, J = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.55, 171.86, 139.25, 136.91, 132.78, 132.70, 131.64, 130.89, 129.72, 129.62, 128.77, 127.55, 127.07, 124.13, 120.96, 120.79 ppm. HRMS (ESI): Calculated for $C_{20}H_{15}N_3O_2S_2$: $[M+H]^+$ 394.0679, Found 394.0666.

2an:

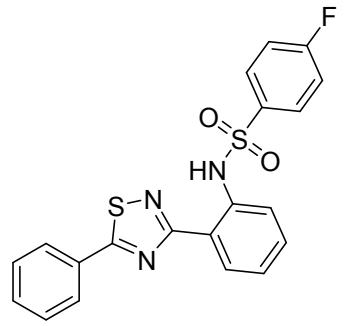


White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.39 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 6.6 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.68-7.62 (m, 2H), 7.60-7.53 (m, 3H), 7.40 (t, J = 8.5 Hz, 1H), 7.16 (t, J = 8.1 Hz, 1H), 6.74 (d, J = 9.0 Hz, 2H), 3.70 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.51, 171.96, 162.90, 137.13, 132.68, 131.60, 130.89, 130.88, 129.75, 129.61, 129.25, 127.55, 123.96, 120.94, 120.73, 113.95, 55.47 ppm. HRMS (ESI): Calculated for $C_{21}H_{17}N_3O_3S_2$: $[M+H]^+$ 424.0784, Found 424.0768.

2ao:

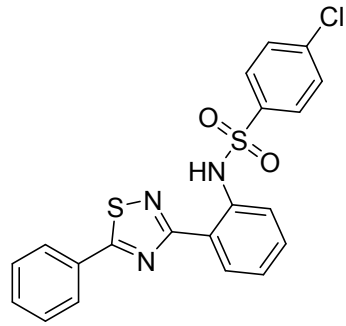


White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.54 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 7.0 Hz, 2H), 7.62-7.42 (m, 4H), 7.28 (s, 1H), 7.13-6.79 (m, 5H), 4.35 ppm (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.24, 171.37, 137.51, 132.54, 132.05, 130.98, 130.48, 129.54, 129.45, 128.34, 128.18, 127.54, 123.77, 119.98, 118.84, 57.29 ppm. HRMS (ESI): Calculated for $C_{21}H_{17}N_3O_2S_2$: $[M+H]^+$ 408.0835, Found 408.0821.



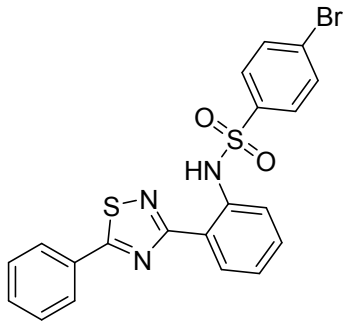
2ap:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.40 (d, *J* = 7.9, 1H), 8.02 (d, *J* = 6.7 Hz, 2H), 7.80-7.68 (m, 3H), 7.62-7.53 (m, 3H), 7.42 (t, *J* = 8.5 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.95 ppm (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.66, 171.80, 165.04 (d, *J* = 255.2 Hz), 136.70, 135.27 (d, *J* = 3.2 Hz), 132.77, 131.71, 131.00, 129.83 (d, *J* = 9.4 Hz), 129.64, 127.55, 124.38, 121.09, 120.90, 116.02 ppm (d, *J* = 22.7 Hz). HRMS (ESI): Calculated for $C_{20}H_{14}FN_3O_2S_2$: $[M+H]^+$ 412.0584, Found 412.0564.

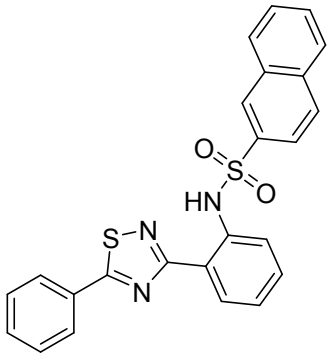


2aq:

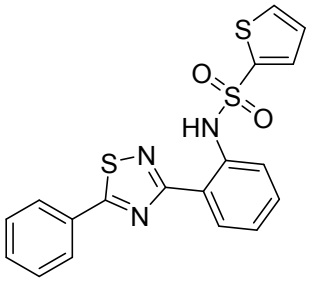
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 6.7 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 8.3 Hz, 2H), 7.53-7.45 (m, 3H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.12 ppm (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.68, 171.78, 139.30, 137.73, 136.58, 132.77, 131.72, 131.03, 129.64, 129.07, 128.52, 127.56, 124.46, 121.13, 120.92 ppm. HRMS (ESI): Calculated for $C_{20}H_{14}ClN_3O_2S_2$: $[M+H]^+$ 428.0289, Found 428.0265.

2ar: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.56-7.44 (m, 5H), 7.38-7.29 (m, 3H), 7.16-7.11 ppm (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.69, 171.79, 138.26, 136.55, 132.77, 132.05, 131.73, 131.03, 129.64, 128.58, 127.83, 127.57, 124.49, 121.17, 120.97 ppm. HRMS (ESI): Calculated for $C_{20}H_{14}BrN_3O_2S_2$: $[M+H]^+$ 471.9784, Found 471.9776.

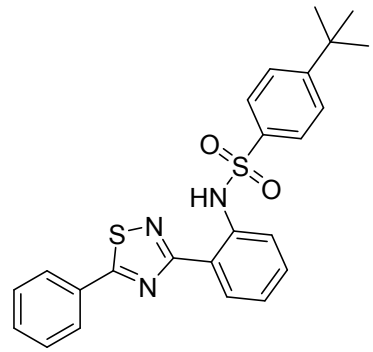
2as: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.38-8.27 (m, 2H), 7.99-7.91 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.73-7.67 (m, 2H), 7.66-7.63 (m, 1H), 7.59-7.44 (m, 5H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.13 ppm (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.50, 171.82, 136.88, 136.22, 134.77, 132.67, 131.89, 131.65, 130.90, 129.67, 129.56, 129.15, 129.13, 128.76, 128.75, 127.80, 127.54, 127.39, 124.15, 122.09, 121.03, 120.81 ppm. HRMS (ESI): Calculated for $C_{24}H_{17}N_3O_2S_2$: $[M+H]^+$ 444.0835, Found 444.0809.

2at: 

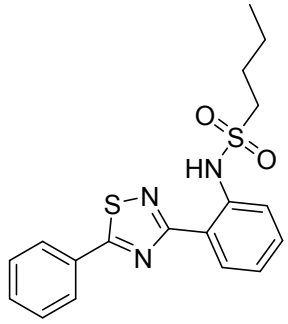
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.52 (s, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.67-7.52 (m, 3H), 7.50-7.30 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.85 ppm (t, *J* = 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.68, 171.76, 139.94, 136.66, 132.72, 132.51, 132.19, 131.69, 130.86, 129.69, 129.62, 127.58, 127.06, 124.54, 121.29, 121.17 ppm. HRMS (ESI): Calculated for $C_{18}H_{13}N_3O_2S_3$: $[M+H]^+$ 400.0243, Found 400.0220.

2au:



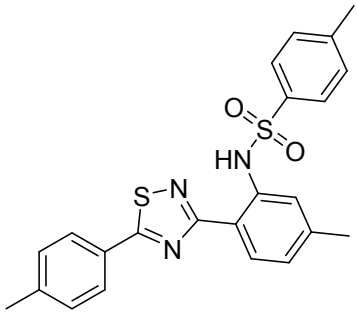
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.32 (d, *J* = 7.9, 1H), 7.95 (d, *J* = 7.9, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.57-7.55 (m, 2H), 7.52-7.46 (m, 3H), 7.34 (t, *J* = 8.6 Hz, 1H), 7.23-7.19 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 1.12 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.45, 171.94, 156.49, 137.09, 136.32, 132.67, 131.63, 130.84, 129.76, 129.60, 127.54, 126.89, 125.74, 123.96, 120.97, 120.84, 35.02, 30.94 ppm. HRMS (ESI): Calculated for $C_{24}H_{23}N_3O_2S_3$: $[M+H]^+$ 450.1305, Found 450.1284.

2av:

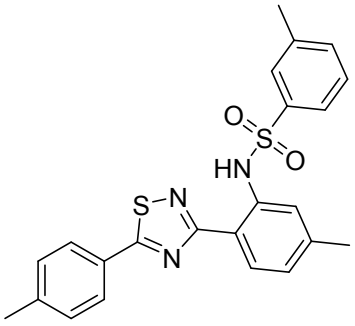


White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.50 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.54-7.44 (m, 3H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.12-2.98 (m, 2H), 1.68-1.61 (m, 2H), 1.30-1.21 (m, 2H), 0.71 ppm (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.65, 172.10, 137.63, 132.70, 132.00, 131.41, 129.74, 129.58, 127.59, 123.41, 119.60, 118.52, 51.51, 25.33, 21.32, 13.46 ppm. HRMS (ESI): Calculated for $C_{18}H_{19}N_3O_2S_3$: $[M+H]^+$

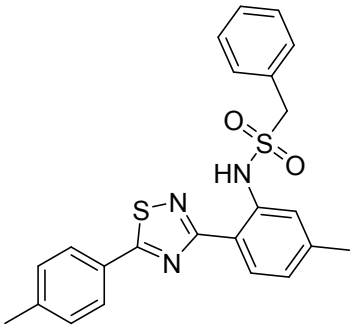
374.0992, Found 374.0975.

2aw: 

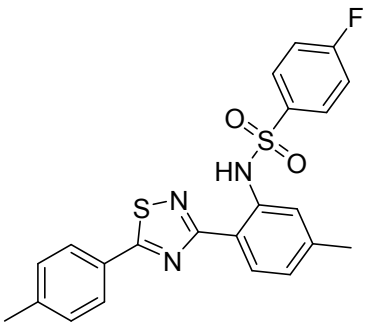
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.25 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.54-7.47 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.18 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.33, 171.87, 143.47, 143.39, 142.19, 136.88, 136.38, 130.61, 130.23, 129.33, 127.46, 127.19, 127.09, 125.02, 121.23, 118.57, 21.75, 21.73, 21.44 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1126.

2ax: 

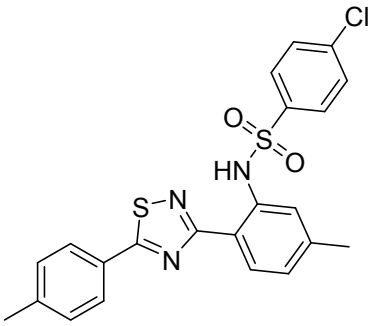
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 19.3 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19-7.12 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 2.19 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.33, 171.82, 143.41, 142.18, 139.12, 138.89, 136.79, 133.48, 130.58, 130.24, 128.51, 127.45, 127.41, 127.16, 125.18, 124.20, 121.59, 118.81, 21.73, 21.18 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1128.

2ay: 

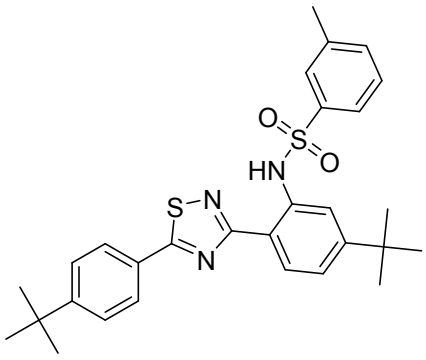
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 7.67-7.58 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.00-6.92 (m, 3H), 6.92-6.82 (m, 3H), 4.26 (s, 2H), 2.36 ppm (d, *J* = 2.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.05, 171.33, 143.22, 142.71, 137.38, 130.77, 130.53, 130.06, 128.37, 128.31, 128.15, 127.47, 126.98, 124.76, 119.16, 117.59, 57.26, 21.87, 21.72 ppm. HRMS (ESI): Calculated for $C_{23}H_{21}N_3O_2S_2$: $[M+H]^+$ 436.1148, Found 436.1125.

2az: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.78-7.63 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.07-6.84 (m, 3H), 2.44 (s, 3H), 2.38 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.47, 171.72, 164.99 (d, *J* = 254.9 Hz), 143.52, 142.33, 136.52, 135.32, 130.74, 130.26, 129.78 (d, *J* = 9.4 Hz), 127.46, 127.08, 125.42, 121.47, 118.77, 115.94 (d, *J* = 22.6 Hz), 21.74 ppm. HRMS (ESI): Calculated for $C_{22}H_{18}N_3FO_2S_2$: $[M+H]^+$ 440.0897, Found 440.0874.

2ba: 

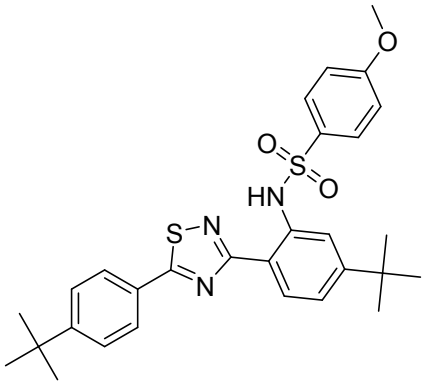
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.61-7.40 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19-7.14 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 2.37 (s, 3H), 2.31 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.51, 171.71, 143.52, 142.36, 139.19, 137.77, 136.41, 130.76, 130.26, 129.00, 128.49, 127.47, 127.09, 125.50, 121.47, 118.80, 21.75, 21.74 ppm. HRMS (ESI): Calculated for $C_{22}H_{18}N_3ClO_2S_2$: $[M+H]^+$ 456.0602, Found 456.0573.

2bb: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.92-7.86 (m, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.53-7.48 (m, 3H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.12-703 (m, 3H), 2.13 (s, 3H), 1.30 (s, 9H), 1.25 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.33, 171.74, 156.47, 155.20, 139.05, 138.78, 136.71, 133.50, 130.32, 128.53, 127.83, 127.38, 127.13, 126.57, 124.39, 121.07, 118.36, 117.75, 35.25, 35.12, 31.11, 31.01, 21.14 ppm. HRMS (ESI): Calculated for $C_{29}H_{33}N_3O_2S_2$: $[M+H]^+$ 520.2087, Found 520.2070.

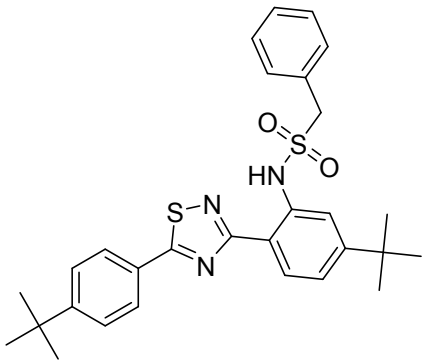
138.78, 136.71, 133.50, 130.32, 128.53, 127.83, 127.38, 127.13, 126.57, 124.39,

136.62, 134.85, 132.73, 130.37, 129.73, 128.67, 127.48, 127.39, 127.29, 127.12, 126.58,



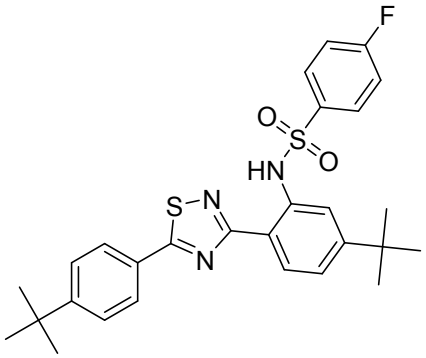
2bc:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.09-7.92 (m, 2H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.69-7.64 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.16 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.77-6.69 (m, 2H), 3.71 (s, 3H), 1.38 (s, 9H), 1.33 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.32, 171.78, 162.84, 156.44, 155.19, 136.81, 130.88, 130.32, 129.42, 127.37, 127.14, 126.55, 120.98, 118.29, 117.69, 113.81, 55.45, 35.23, 35.10, 31.10, 31.01 ppm. HRMS (ESI): Calculated for $C_{29}H_{33}N_3O_3S_2$: $[M+H]^+$ 536.2036, Found 536.2015.



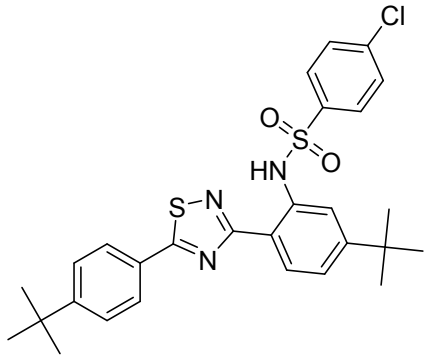
2bd:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.05-6.88 (m, 5H), 4.32 (s, 2H), 1.39 ppm (d, *J* = 9.0 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.03, 171.32, 156.30, 155.87, 137.29, 130.49, 128.34, 128.31, 128.17, 127.38, 126.95, 126.38, 121.03, 117.65, 116.06, 57.30, 35.26, 35.22, 31.14, 31.33 ppm. HRMS (ESI): Calculated for $C_{29}H_{33}N_3O_2S_2$: $[M+H]^+$ 520.2087, Found 520.2070.



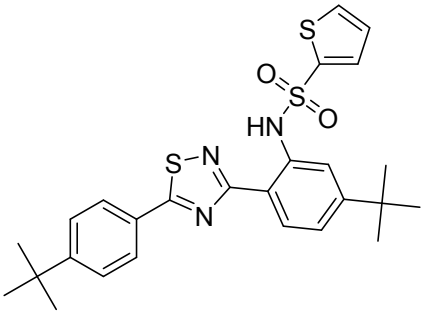
2be:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.42 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.77-7.68 (m, 3H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.19 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.95 (t, *J* = 8.6 Hz, 2H), 1.38 (s, 9H), 1.33 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.49, 171.63, 165.01 (d, *J* = 255.0 Hz), 155.98 (d, *J* = 151.2 Hz), 136.40, 135.27, 135.24, 130.47, 129.98 (d, *J* = 9.4 Hz), 127.38, 127.05, 126.61, 121.42, 118.50, 117.91, 115.90 (d, *J* = 22.6 Hz), 35.26, 35.14, 31.11, 31.01 ppm. HRMS (ESI): Calculated for $C_{28}H_{30}FN_3O_2S_2$: $[M+H]^+$ 524.1836, Found 524.1839.



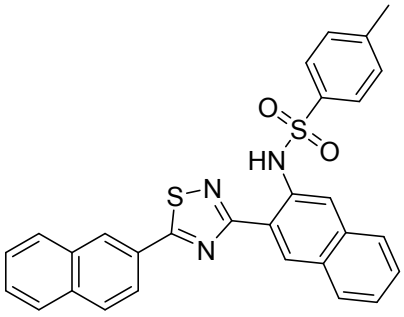
2bf:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.27-7.24(m, 2H), 7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 1.38 (s, 9H), 1.33 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.51, 171.60, 156.59, 155.41, 139.22, 137.73, 136.27, 130.50, 130.08, 128.95, 128.68, 127.38, 127.04, 126.61, 121.52, 118.53, 117.93, 35.26, 35.15, 31.11, 31.02 ppm. HRMS (ESI): Calculated for $C_{28}H_{30}ClN_3O_2S_2$: $[M+H]^+$ 540.1541, Found 540.1533.



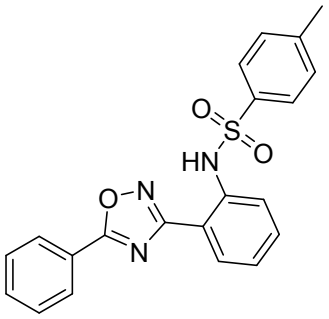
2bg:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.50 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 1.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.29 (d, *J* = 4.9 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.81-6.75 (m, 1H), 1.30 (s, 9H), 1.28 ppm (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.48, 171.60, 156.51, 155.39, 140.02, 136.40, 132.45, 132.11, 130.34, 127.41, 127.09, 126.97, 126.58, 121.56, 118.67, 118.13, 35.25, 35.19, 31.11, 31.05 ppm. HRMS (ESI): Calculated for $C_{26}H_{29}N_3O_2S_2$: $[M+H]^+$ 512.1495, Found 512.1470.

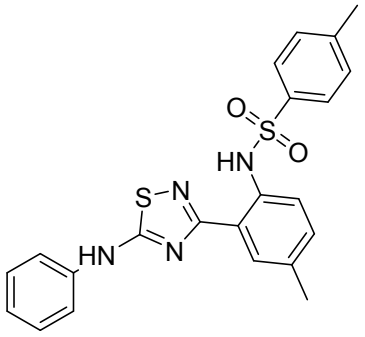


2bh:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.93 (s, 1H), 8.57 (s, 1H), 8.15 (s, 1H), 8.06 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.01 (t, *J* = 8.1 Hz, 2H), 7.92-7.85 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.65-7.58 (m, 4H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.19 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.48, 172.08, 143.51, 136.24, 135.26, 134.61, 133.45, 133.03, 132.00, 129.88, 129.58, 129.35, 129.15, 128.62, 128.44, 128.16, 128.08, 128.04, 127.44, 127.14, 126.96, 125.75, 123.83, 121.12, 118.51, 21.38 ppm. HRMS (ESI): Calculated for $C_{29}H_{21}N_3O_2S_2$: $[M+H]^+$ 508.1148, Found 508.1123.

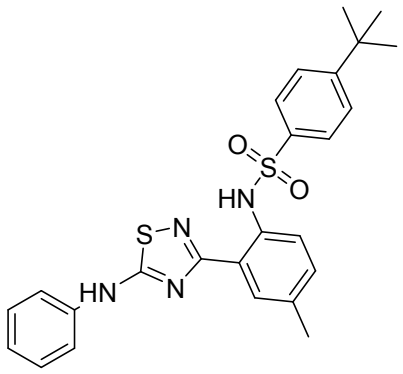
2bi: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.26-8.20 (m, 2H), 8.15 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.66 (m, 5H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.29 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.96, 167.43, 143.85, 136.88, 136.13, 133.46, 132.31, 129.52, 129.48, 129.39, 128.32, 127.22, 124.34, 123.38, 121.22, 115.73, 21.46 ppm. HRMS (ESI): Calculated for $C_{21}H_{17}N_3O_3S$: $[M+H]^+$ 392.1064, Found 392.1053.

4a: 

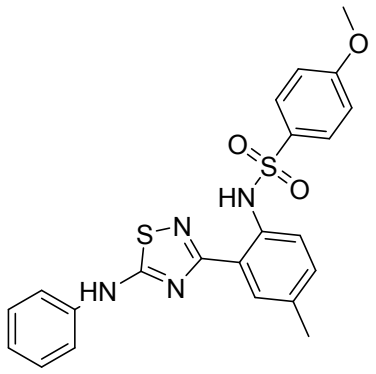
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.91 (s, 1H), 7.94 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 2.25 (s, 3H), 2.23 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.48, 167.61, 143.53, 138.84, 136.17, 134.29, 133.64, 131.97, 130.58, 129.88, 129.38, 127.12, 124.62, 120.96, 120.87, 118.51, 21.43, 20.65 ppm. HRMS (ESI): Calculated for $C_{22}H_{20}N_4O_2S_2$: $[M+H]^+$ 437.1101, Found 437.1083.

4b:

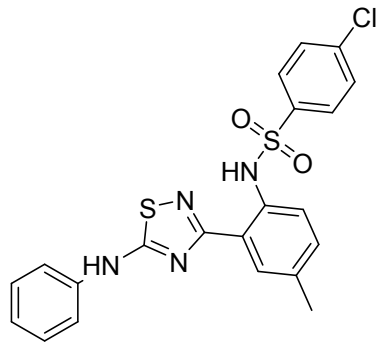


White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.23 (s, 1H), 11.21 (s, 1H), 7.95 (s, 1H), 7.56 (d, J = 8.5 Hz, 4H), 7.52 (d, J = 8.4 Hz, 1H), 7.47-7.40 (m, 4H), 7.25 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 1.14 ppm (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.71, 167.61, 156.63, 139.84, 136.29, 134.29, 133.82, 132.36, 131.01, 130.01, 126.95, 126.42, 123.99, 121.39, 121.04, 118.58, 35.21, 31.02, 20.80 ppm. HRMS (ESI): Calculated for $C_{25}H_{26}N_4O_2S_2$: $[M+H]^+$ 479.1570, Found 479.1553.

4c:

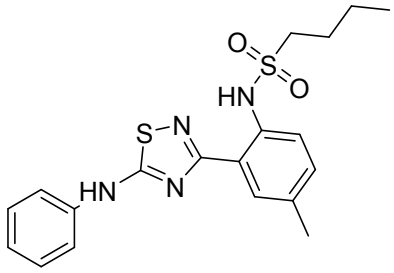


White solid,; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.77 (s, 1H), 7.87 (s, 1H), 7.62-7.55 (m, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.38-7.32 (m, 2H), 7.19-7.17 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (dd, J = 8.4, 1.9 Hz, 1H), 6.72-6.63 (m, 2H), 3.64 (s, 3H), 2.18 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.50, 167.53, 162.85, 138.81, 134.41, 133.65, 132.04, 130.77, 130.57, 129.97, 129.27, 124.74, 120.97, 120.94, 118.56, 113.94, 55.48, 20.70 ppm. HRMS (ESI): Calculated for $C_{22}H_{20}N_4O_3S_2$: $[M+H]^+$ 453.1050, Found 453.1030.



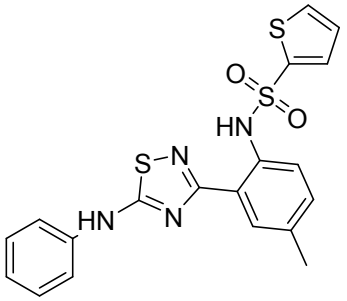
4d:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.69 (s, 1H), 7.87 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.19-7.15 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 2.18 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.68, 167.50, 139.21, 138.74, 137.56, 134.28, 133.82, 132.12, 130.75, 130.01, 129.03, 128.56, 124.93, 121.37, 121.29, 118.71, 20.73 ppm. HRMS (ESI): Calculated for $C_{21}H_{17}ClN_4O_2S_2$: $[M+H]^+$ 457.0554, Found 457.0531.



4e:

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.76 (s, 1H), 8.05 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.14-7.05 (m, 2H), 3.07-2.95 (m, 2H), 2.23 (s, 3H), 1.67-1.58 (m, 2H), 1.26-1.17 (m, 2H), 0.71 ppm (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.58, 167.85, 138.83, 134.88, 133.21, 132.34, 131.11, 129.91, 124.72, 119.90, 119.09, 118.65, 51.26, 25.25, 21.35, 20.69, 13.50 ppm. HRMS (ESI): Calculated for $C_{19}H_{22}N_4O_2S_2$: $[M+H]^+$ 403.1257, Found 403.1233.

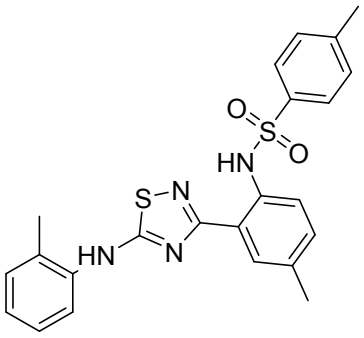


4f:

White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.45 (s, 1H), 11.24 (s, 1H), 8.01 (s,

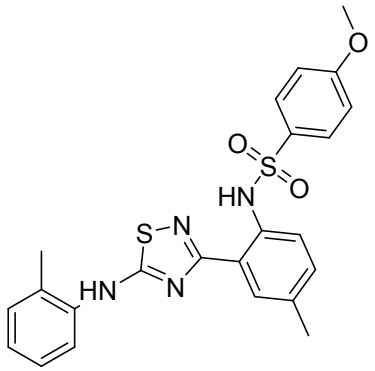
1H), 7.84 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 3H), 7.52-7.43 (m, 3H), 7.32 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.08-6.98 (m, 1H), 2.32 ppm (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.77, 167.54, 139.78, 139.30, 134.56, 134.32, 133.99, 133.44, 132.38, 131.05, 130.04, 128.06, 124.04, 121.63, 121.17, 118.65, 20.84 ppm. HRMS (ESI): Calculated for $C_{19}H_{16}N_4O_2S_3$: $[M+H]^+$ 429.0508, Found 429.0489.

4g:



White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 7.89 (s, 1H), 7.85 (s, 1H), 7.55-7.47 (m, 3H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.28-7.22 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.06 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 2.19 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.48, 167.18, 142.35, 136.22, 135.38, 133.44, 132.53, 130.91, 130.63, 129.63, 129.60, 128.30, 126.70, 126.09, 125.60, 120.08, 119.93, 20.45, 19.66, 16.67 ppm. HRMS (ESI): Calculated for $C_{23}H_{22}N_4O_2S_2$: $[M+H]^+$ 451.1257, Found 451.1234.

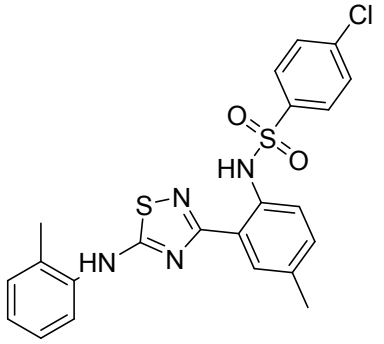
4h:



White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.08 (s, 1H), 8.01 (s, 1H), 7.83 (s, 1H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.25-7.18 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.64 (s, 3H), 2.25 (s, 3H), 2.16 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

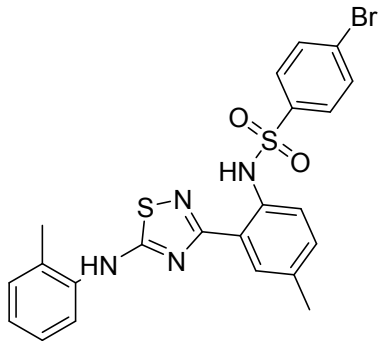
180.50, 167.22, 161.76, 136.27, 133.47, 132.52, 130.86, 130.58, 129.89, 129.66, 129.64, 128.19, 126.64, 125.54, 120.16, 120.02, 119.97, 112.84, 54.43, 19.64, 16.65 ppm. HRMS (ESI): Calculated for $C_{23}H_{22}N_4O_3S_2$: $[M+H]^+$ 467.1206, Found 467.1194.

4i:

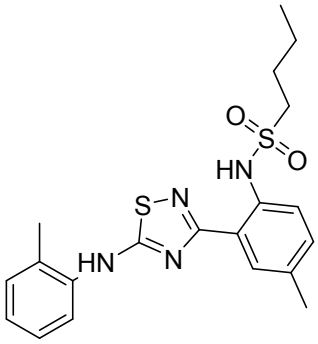


White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.88 (s, 1H), 7.85 (s, 1H), 7.54-7.49 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27-7.22 (m, 2H), 7.19-7.17 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 2.27 (s, 3H), 2.21 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.59, 167.07, 138.04, 136.69, 136.12, 133.21, 132.91, 131.01, 130.68, 129.80, 129.76, 127.91, 127.50, 126.74, 125.78, 120.51, 120.33, 120.19, 19.70, 16.66 ppm. HRMS (ESI): Calculated for $C_{22}H_{19}ClN_4O_2S_2$: $[M+H]^+$ 471.0711, Found 471.0692.

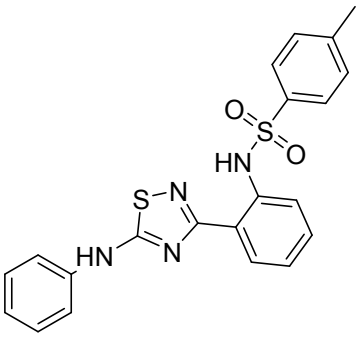
4j:



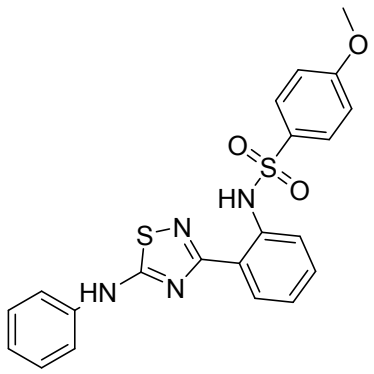
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.07 (s, 1H), 7.86 (s, 1H), 7.77 (s, 1H), 7.52-7.41 (m, 3H), 7.37-7.30 (m, 3H), 7.29-7.20 (m, 2H), 7.16-7.11 (m, 1H), 7.10-7.05 (m, 1H), 2.28 (s, 3H), 2.22 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.65, 167.25, 137.26, 136.15, 133.20, 132.90, 130.98, 130.89, 130.68, 129.80, 129.77, 127.58, 126.76, 126.57, 125.76, 120.51, 120.43, 120.21, 19.71, 16.67 ppm. HRMS (ESI): Calculated for $C_{22}H_{19}BrN_4O_2S_2$: $[M+H]^+$ 515.0206, Found 515.0193.

4k: 

White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.04 (s, 1H), 8.00 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.27-7.19 (m, 2H), 7.14-7.09 (m, 2H), 3.02-2.94 (m, 2H), 2.27 (s, 3H), 2.25 (s, 3H), 1.66-1.55 (m, 2H), 1.29-1.20 (m, 2H), 0.72 ppm (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.71, 167.40, 136.24, 133.97, 132.07, 131.23, 130.61, 130.07, 129.77, 126.68, 125.65, 120.30, 118.90, 118.11, 50.15, 24.22, 20.32, 19.63, 16.66, 12.48 ppm. HRMS (ESI): Calculated for $C_{20}H_{24}N_4O_2S_2$: $[M+H]^+$ 417.1414, Found 451.1401.

4l: 

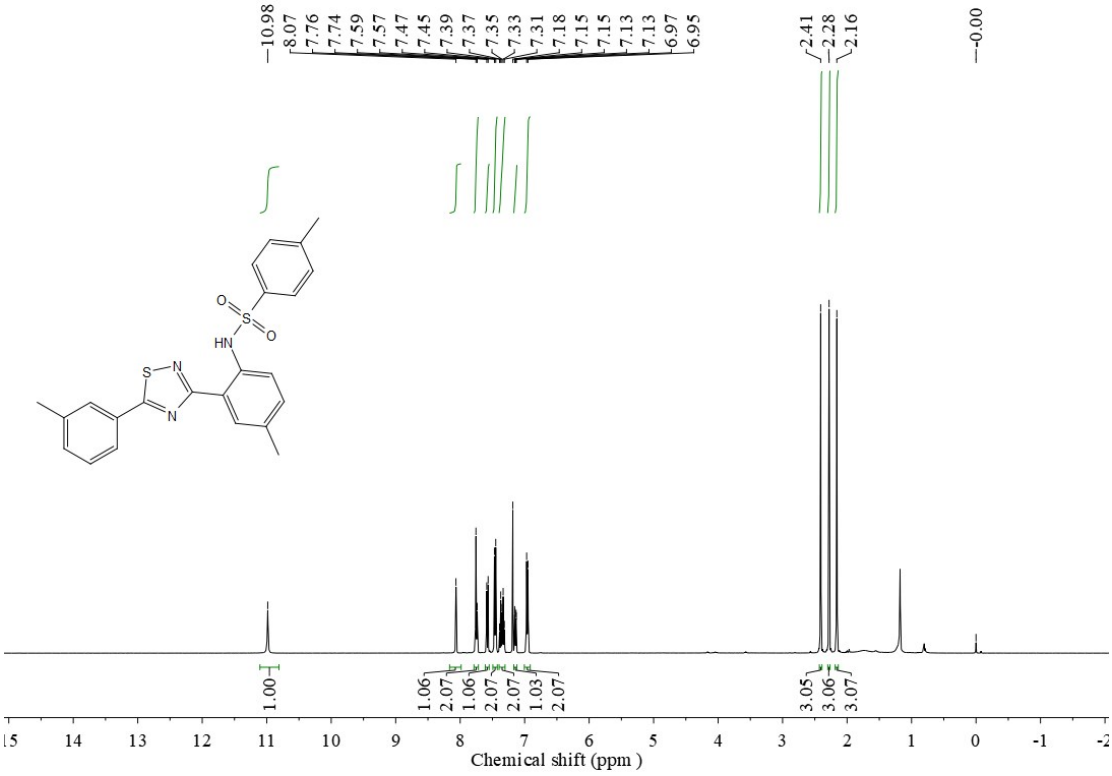
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.47 (s, 1H), 8.62 (s, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 3H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 2.29 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.36, 167.53, 143.66, 138.70, 137.01, 136.33, 131.30, 130.52, 130.00, 129.49, 127.18, 124.89, 123.72, 120.50, 120.15, 118.66, 21.49 ppm. HRMS (ESI): Calculated for $C_{21}H_{18}N_4O_2S_2$: $[M+H]^+$ 423.0944, Found 423.0919.

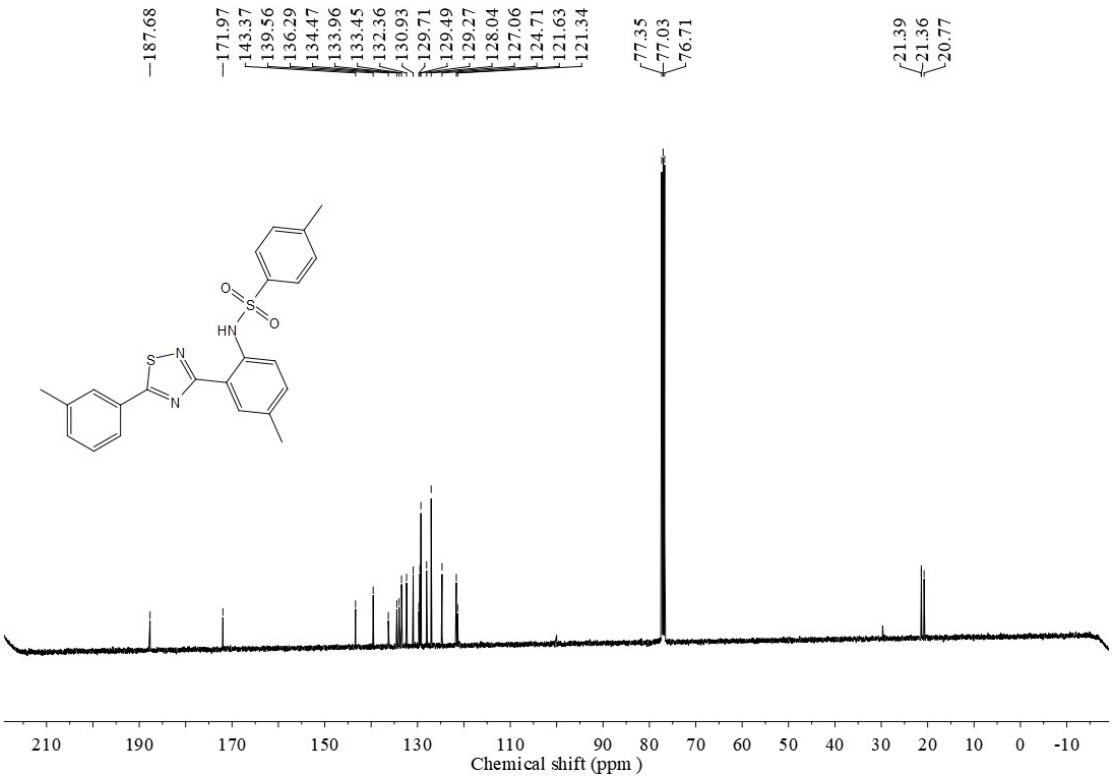


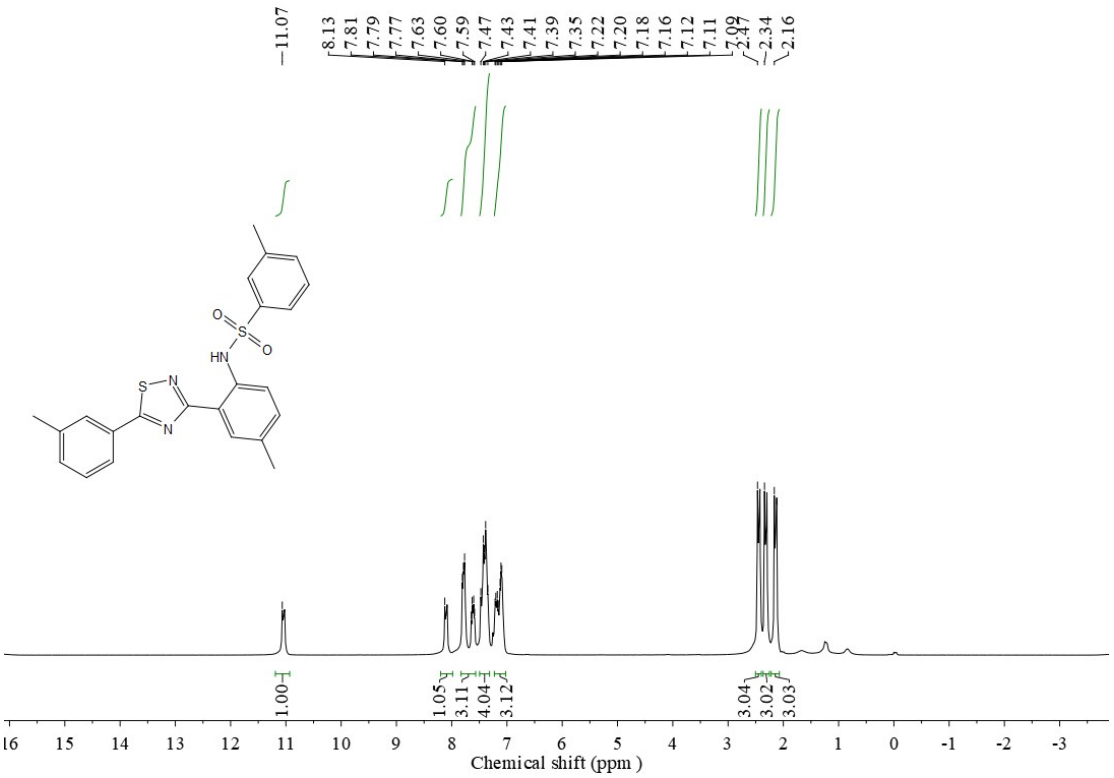
4m:

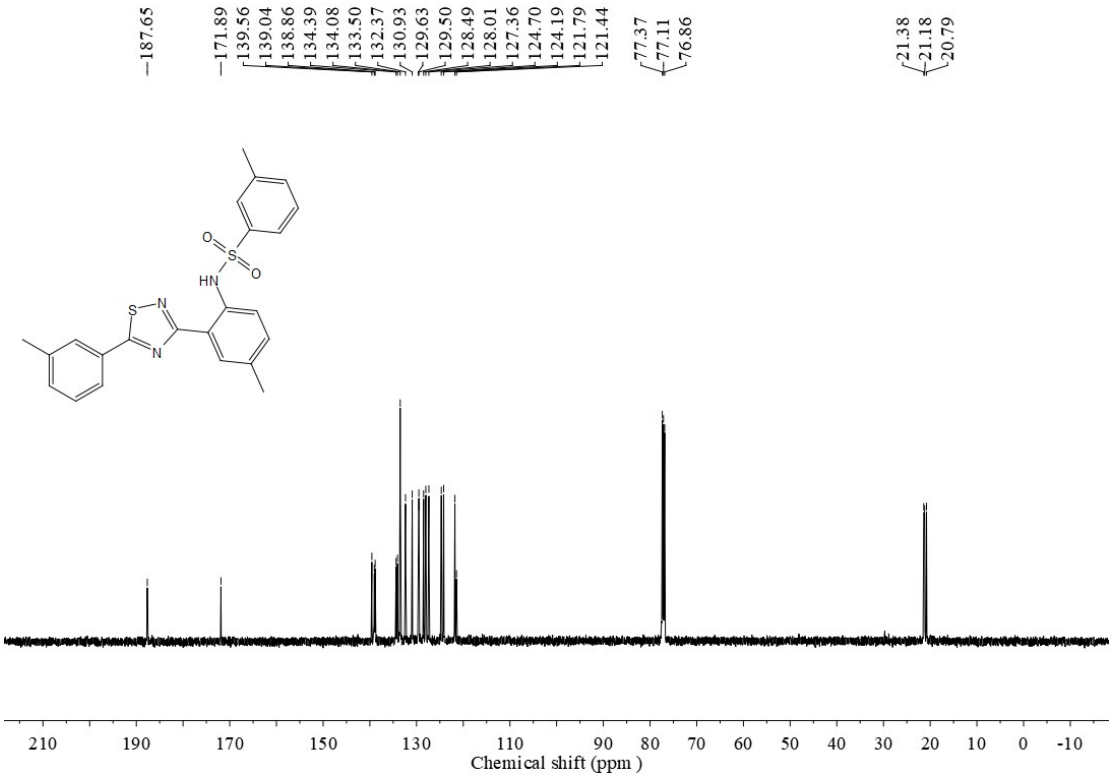
White solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.46 (s, 1H), 8.66 (s, 1H), 8.18 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.34-7.27 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.38, 167.68, 162.95, 138.78, 137.05, 131.24, 130.83, 130.57, 129.96, 129.32, 124.78, 123.72, 120.67, 120.22, 118.65, 114.04, 55.51. HRMS (ESI): Calculated for $C_{21}H_{18}N_4O_3S_2$: $[M+H]^+$ 439.0893, Found 439.0875.

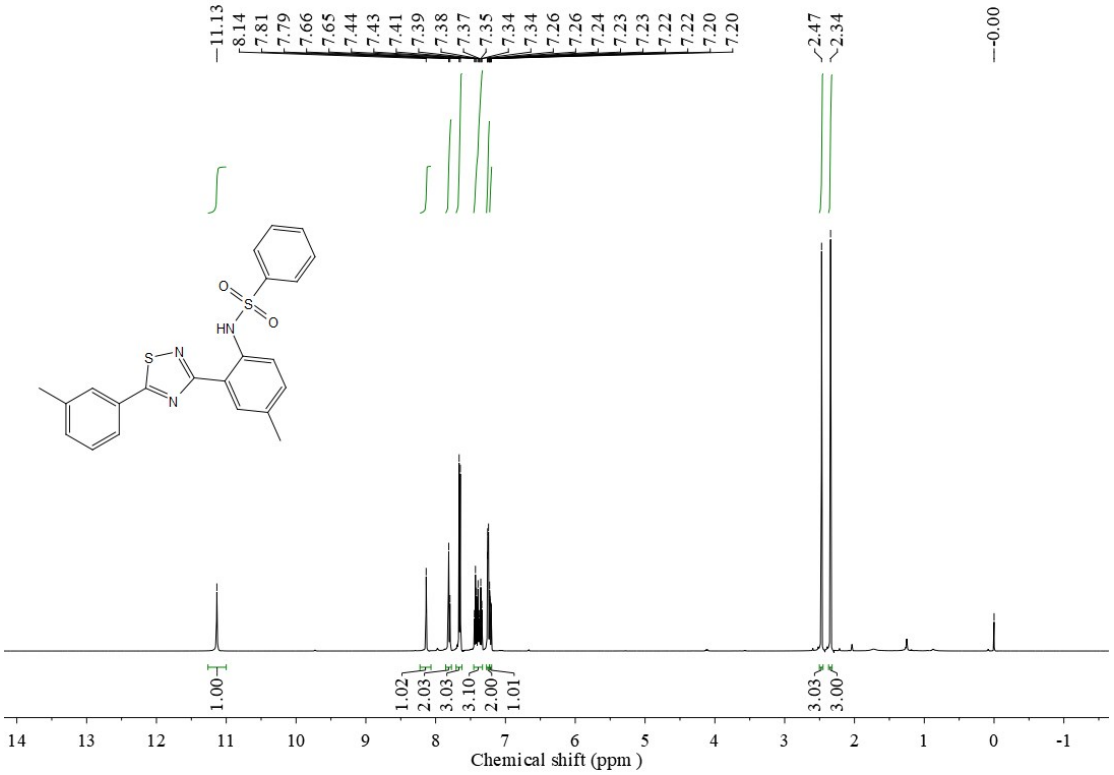
4. ^{1}H and ^{13}C NMR spectra of the products

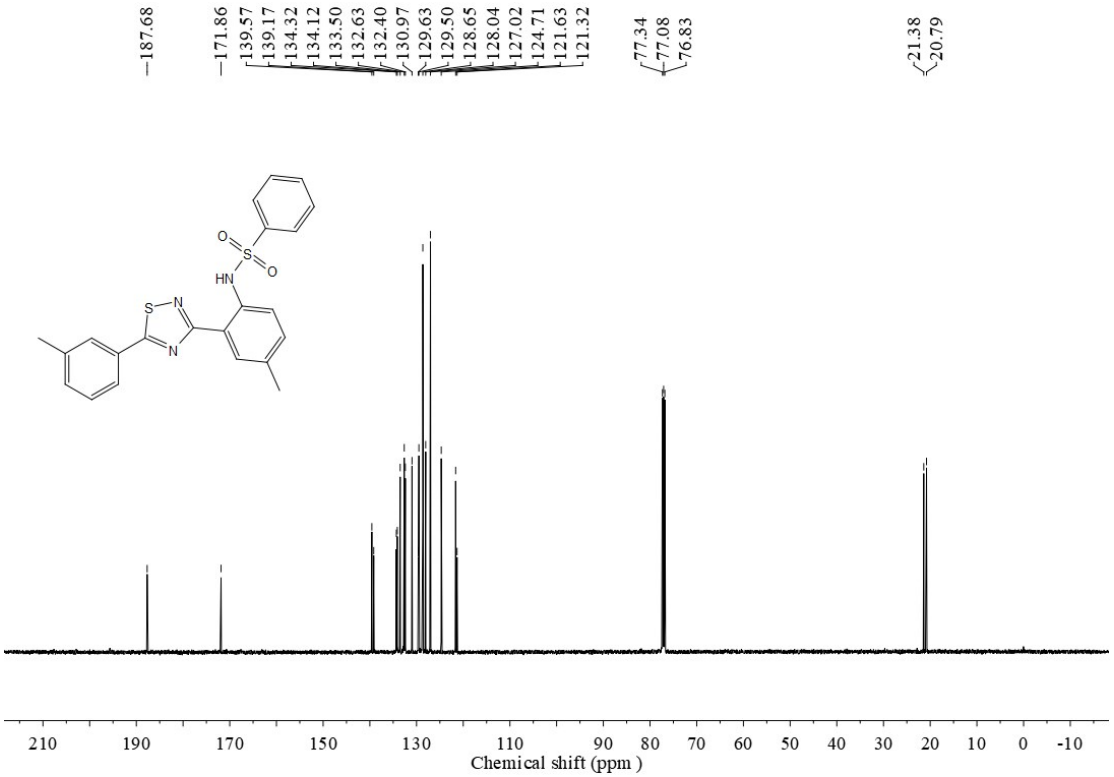


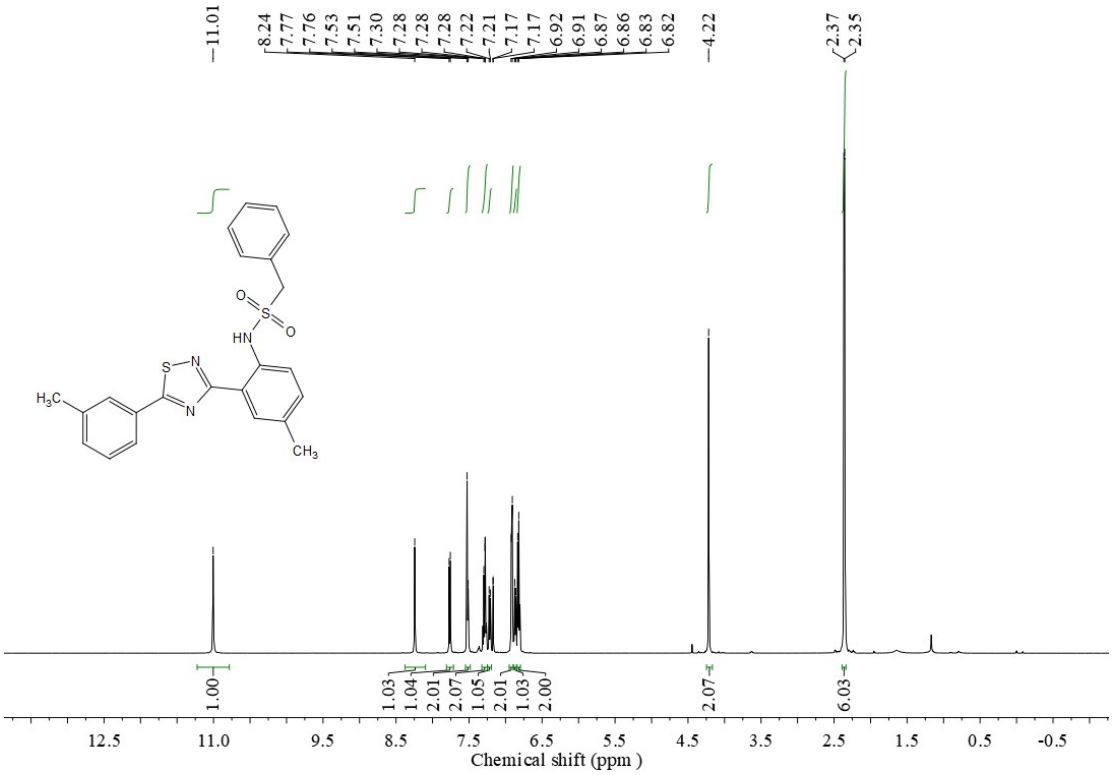


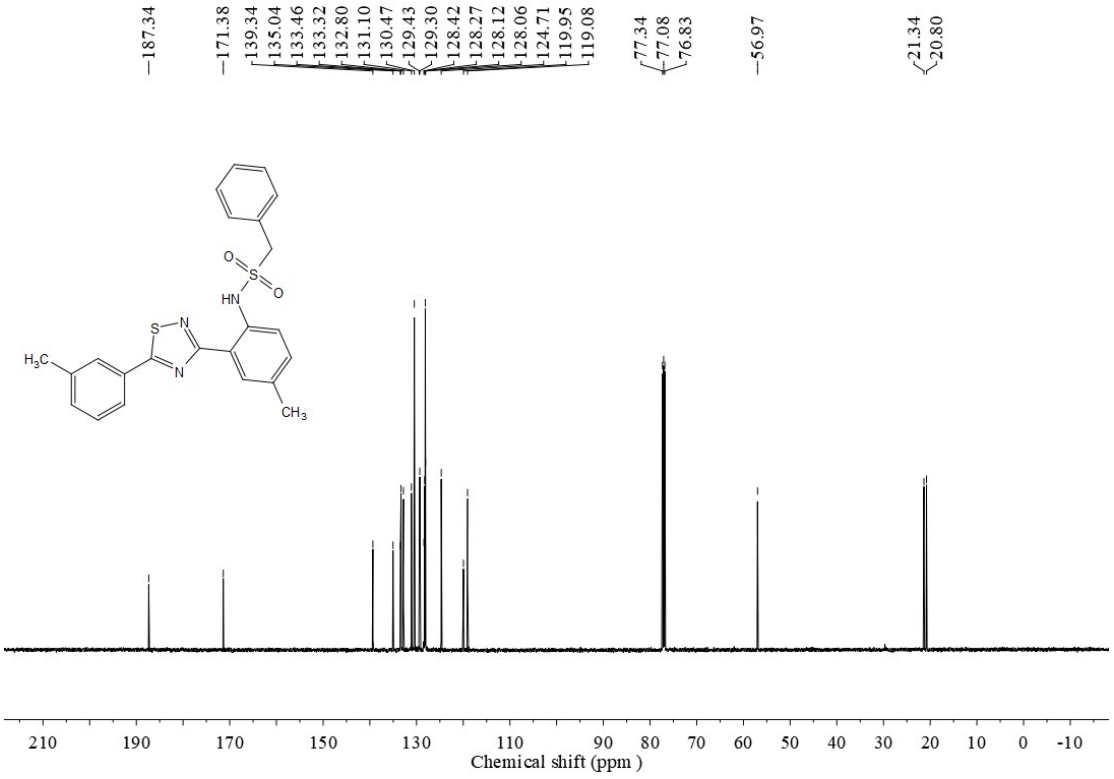

11.07
8.13
7.81
7.79
7.77
7.63
7.60
7.59
7.47
7.43
7.41
7.39
7.35
7.22
7.20
7.18
7.16
7.12
7.11
2.47
2.34
2.16
1.00
1.05
3.11
4.04
3.12
3.04
3.02
3.03
Chemical shift (ppm)

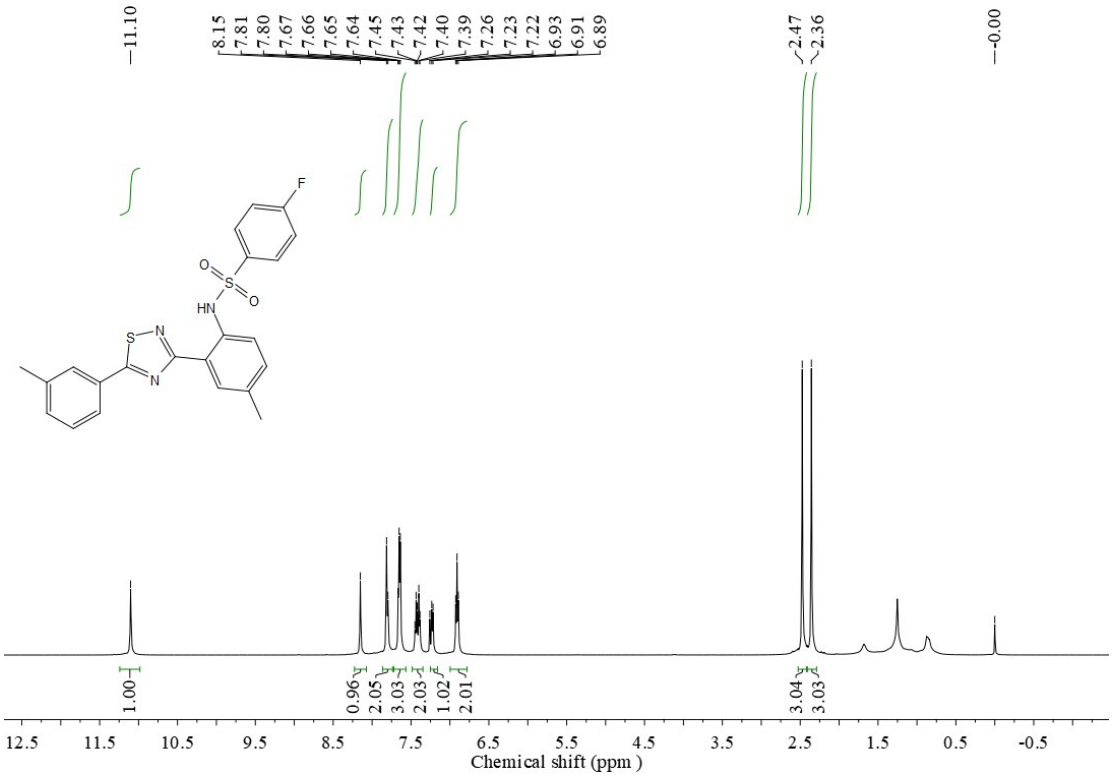

187.65
171.89
139.56
139.04
138.86
134.39
134.08
133.50
132.37
130.93
129.63
129.50
128.49
128.01
127.36
124.70
124.19
121.79
121.44
77.37
77.11
76.86
21.38
21.18
20.79
Chemical shift (ppm)

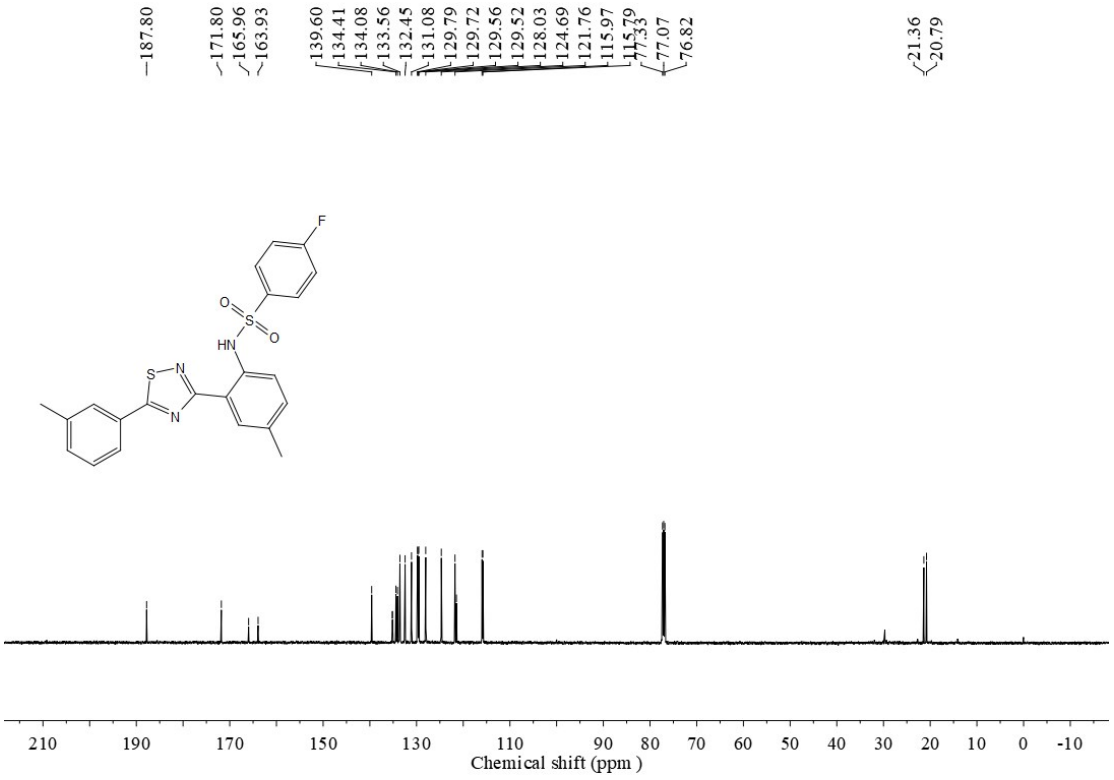

11.13
8.14
7.81
7.79
7.66
7.65
7.44
7.43
7.41
7.39
7.38
7.37
7.35
7.34
7.34
7.26
7.26
7.24
7.23
7.23
7.22
7.22
7.20
7.20
2.47
2.34
0.00
1.00
1.02
2.03
3.03
3.10
2.00
1.01
3.03
3.00
Chemical shift (ppm)

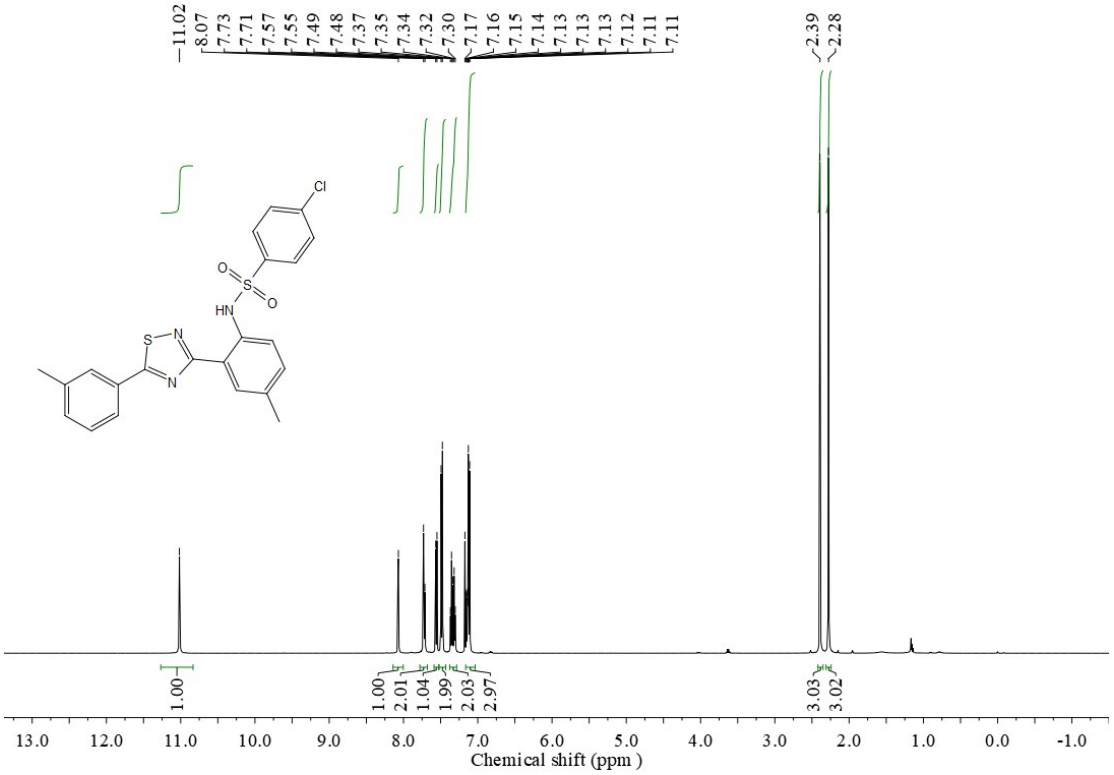

187.68
171.86
139.57
139.17
134.32
134.12
133.50
132.63
132.40
130.97
129.63
129.50
128.65
128.04
127.02
124.71
121.63
121.32
77.34
77.08
76.83
21.38
20.79
Chemical shift (ppm)

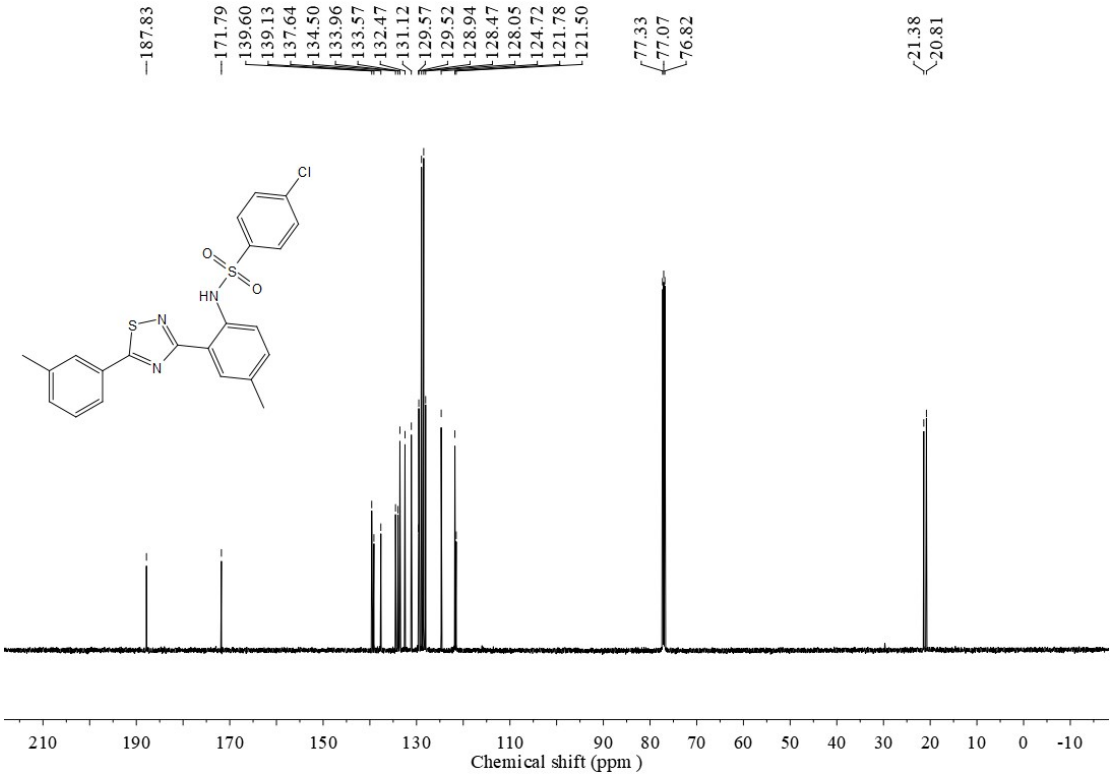

11.01
8.24
7.77
7.76
7.53
7.51
7.30
7.28
7.28
7.28
7.22
7.21
7.17
7.17
6.92
6.91
6.87
6.86
6.83
6.82
4.22
2.37
2.35
1.00
1.03
1.04
2.01
2.07
1.05
2.01
1.03
2.00
2.07
6.03
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

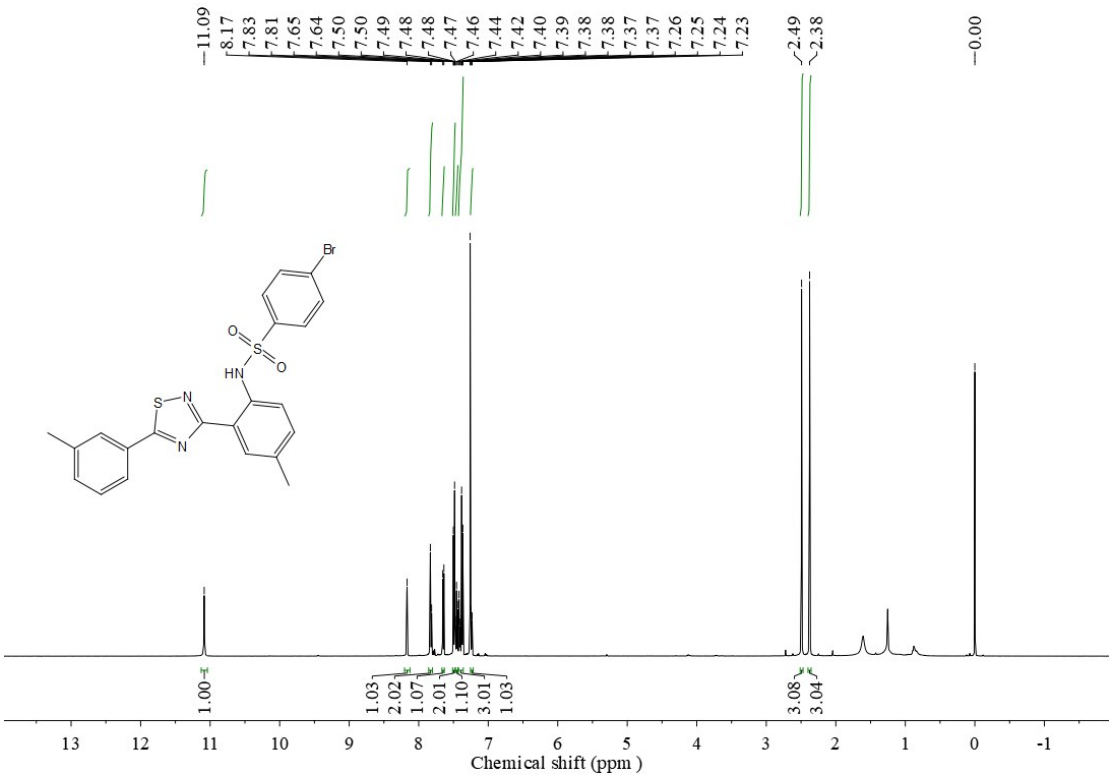

187.34
171.38
139.34
135.04
133.46
133.32
132.80
131.10
130.47
129.43
129.30
128.42
128.27
128.12
128.06
124.71
119.95
119.08
77.34
77.08
76.83
56.97
21.34
20.80
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

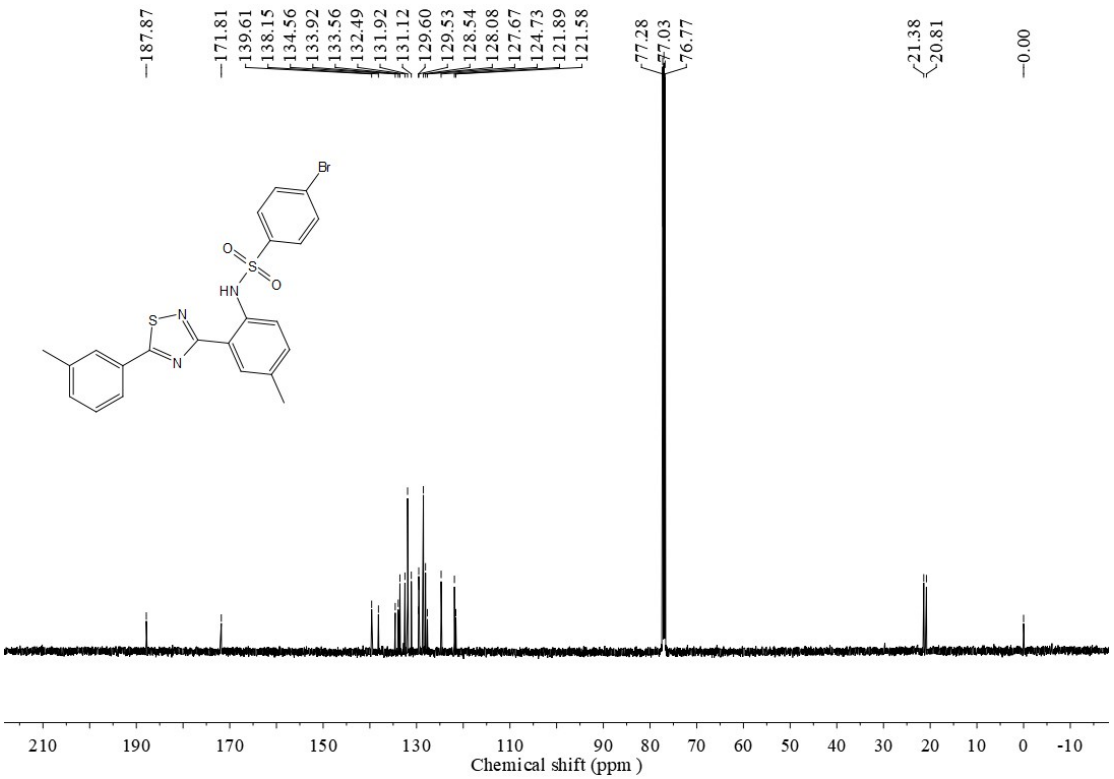

11.10
8.15
7.81
7.80
7.67
7.66
7.65
7.64
7.45
7.43
7.42
7.40
7.39
7.26
7.23
7.22
6.93
6.91
6.89
2.47
2.36
0.00
F
O
S
O
HN
S
N
N
1.00
0.96
2.05
3.03
2.03
1.02
2.01
3.04
3.03
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

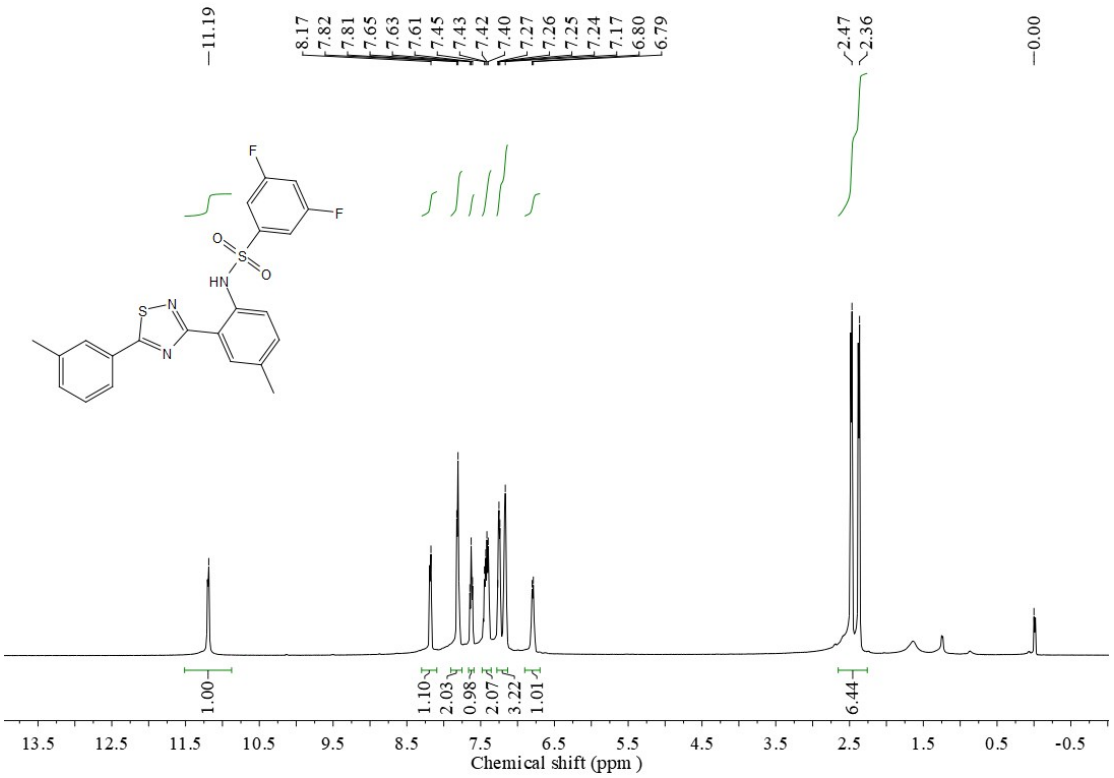

187.80
171.80
165.96
163.93
139.60
134.41
134.08
133.56
132.45
131.08
129.79
129.72
129.56
129.52
128.03
124.69
121.76
115.97
115.79
77.33
77.07
76.82
21.36
20.79
F
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

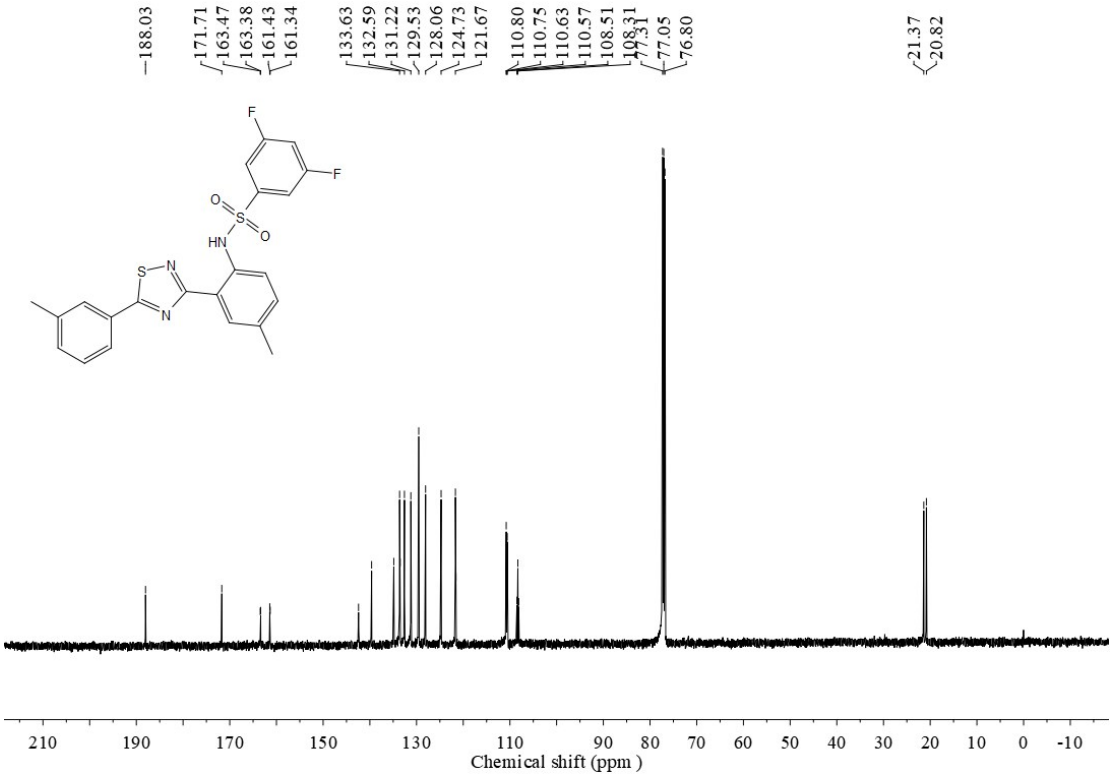

11.02
8.07
7.73
7.71
7.57
7.55
7.49
7.48
7.37
7.35
7.34
7.32
7.30
7.17
7.16
7.15
7.14
7.13
7.13
7.13
7.12
7.11
7.11
2.39
2.28
Cl
O
S
O
HN
S
N
N
1.00
1.00
2.01
1.04
1.99
2.03
2.97
3.03
3.02
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical shift (ppm)

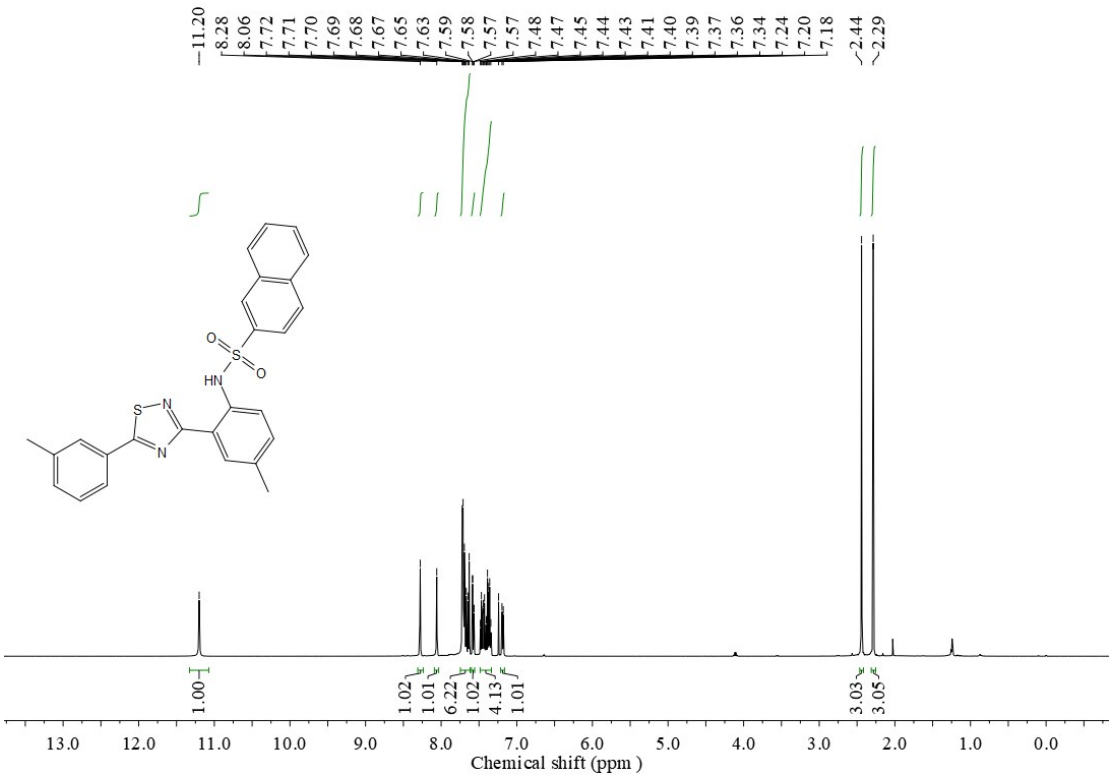

187.83
171.79
139.60
139.13
137.64
134.50
133.96
133.57
132.47
131.12
129.57
129.52
128.94
128.47
128.05
124.72
121.78
121.50
77.33
77.07
76.82
21.38
20.81
Cl
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

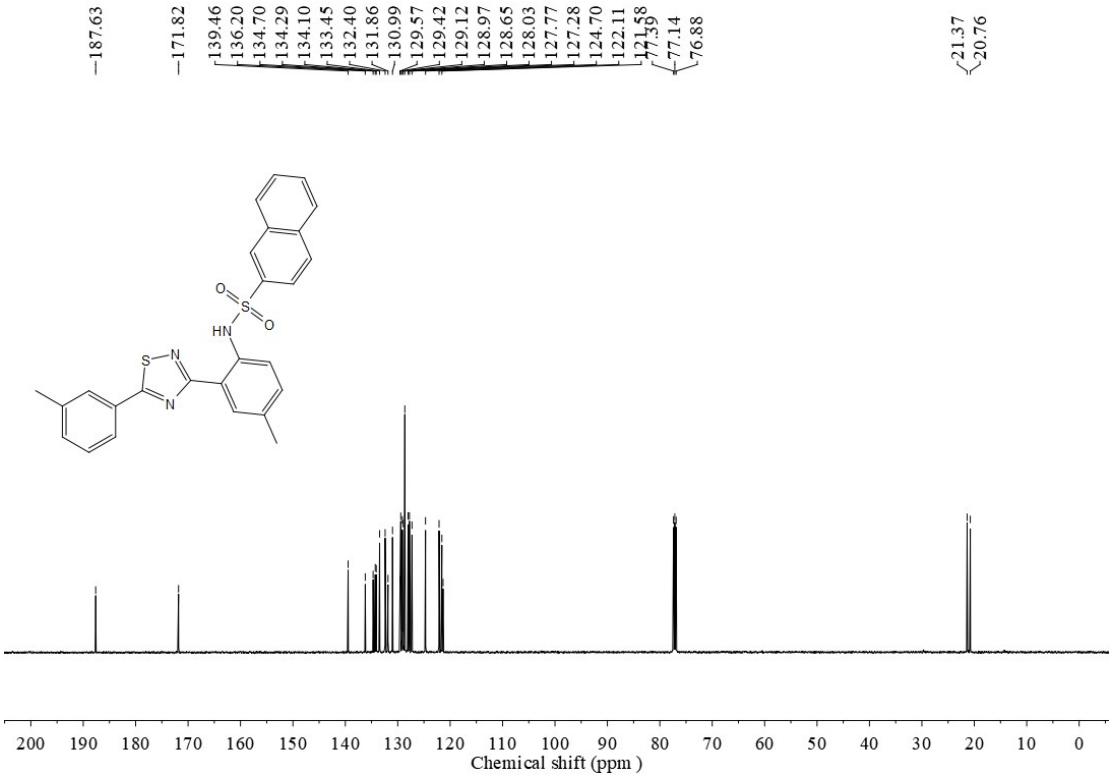

11.09
8.17
7.83
7.81
7.65
7.64
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.44
7.42
7.40
7.39
7.38
7.38
7.37
7.37
7.26
7.25
7.24
7.23
2.49
2.38
0.00
Br
O
S
O
HN
S
N
N
1.00
1.03
2.02
1.07
2.01
1.10
3.01
1.03
3.08
3.04
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical shift (ppm)

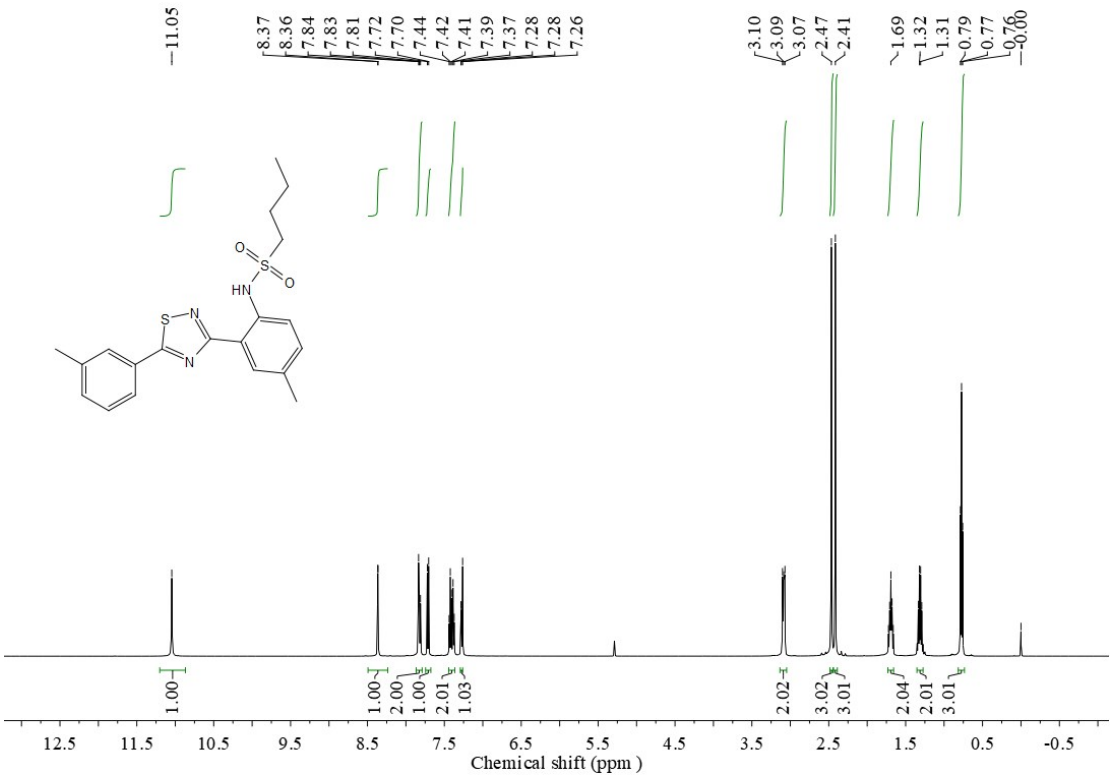

187.87
171.81
139.61
138.15
134.56
133.92
133.56
132.49
131.92
131.12
129.60
129.53
128.54
128.08
127.67
124.73
121.89
121.58
77.28
77.03
76.77
21.38
20.81
0.00
Br
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

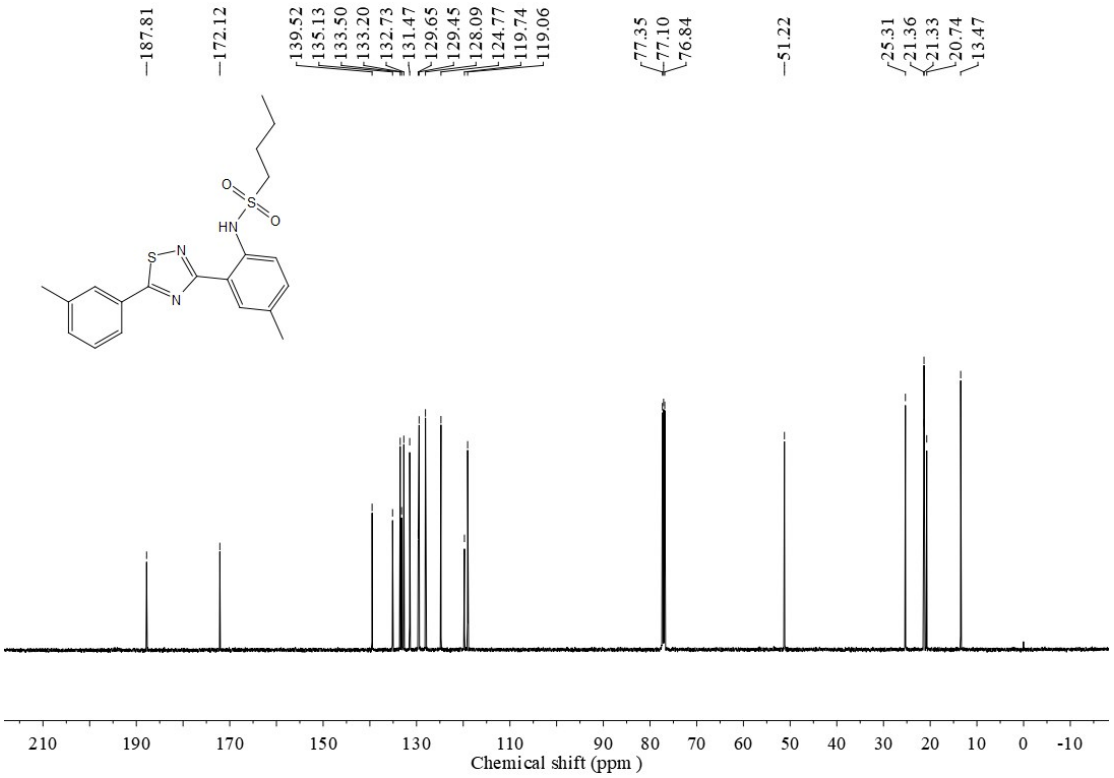

11.19
8.17
7.82
7.81
7.65
7.63
7.61
7.45
7.43
7.42
7.40
7.27
7.26
7.25
7.24
7.17
6.80
6.79
2.47
2.36
0.00
F
F
O
S
O
HN
S
N
N
1.00
1.10
2.03
0.98
2.07
3.22
1.01
6.44
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

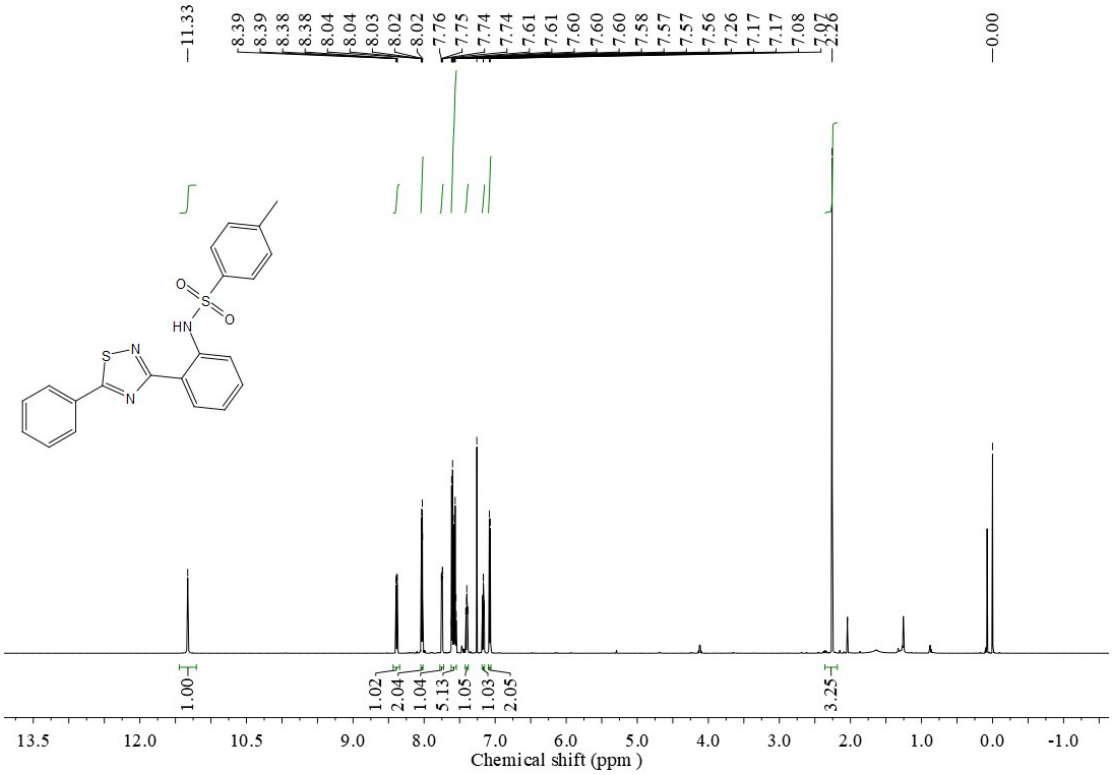

188.03
171.71
163.47
163.38
161.43
161.34
133.63
132.59
131.22
129.53
128.06
124.73
121.67
110.80
110.75
110.63
110.57
108.51
108.31
77.31
77.05
76.80
21.37
20.82
F
F
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

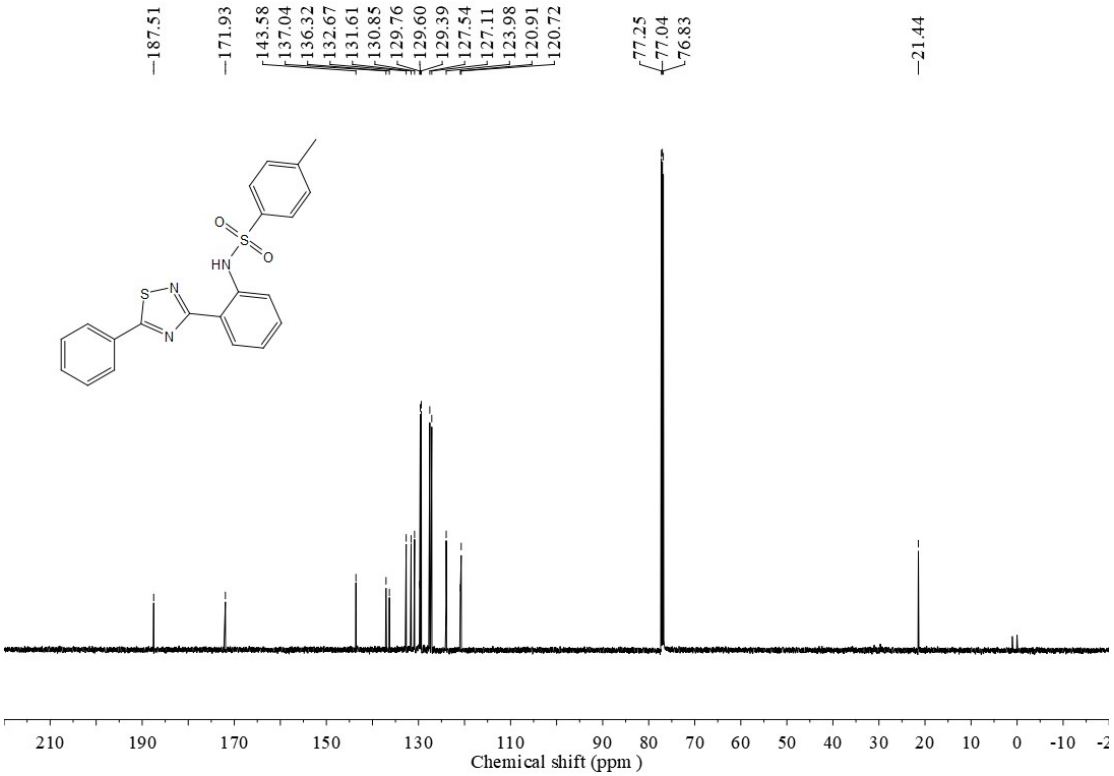

11.20
8.28
8.06
7.72
7.71
7.70
7.69
7.68
7.67
7.65
7.63
7.59
7.58
7.57
7.57
7.48
7.47
7.45
7.44
7.43
7.41
7.40
7.39
7.37
7.36
7.34
7.24
7.20
7.18
2.44
2.29
1.00
1.02
1.01
6.22
1.02
4.13
1.01
3.03
3.05
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

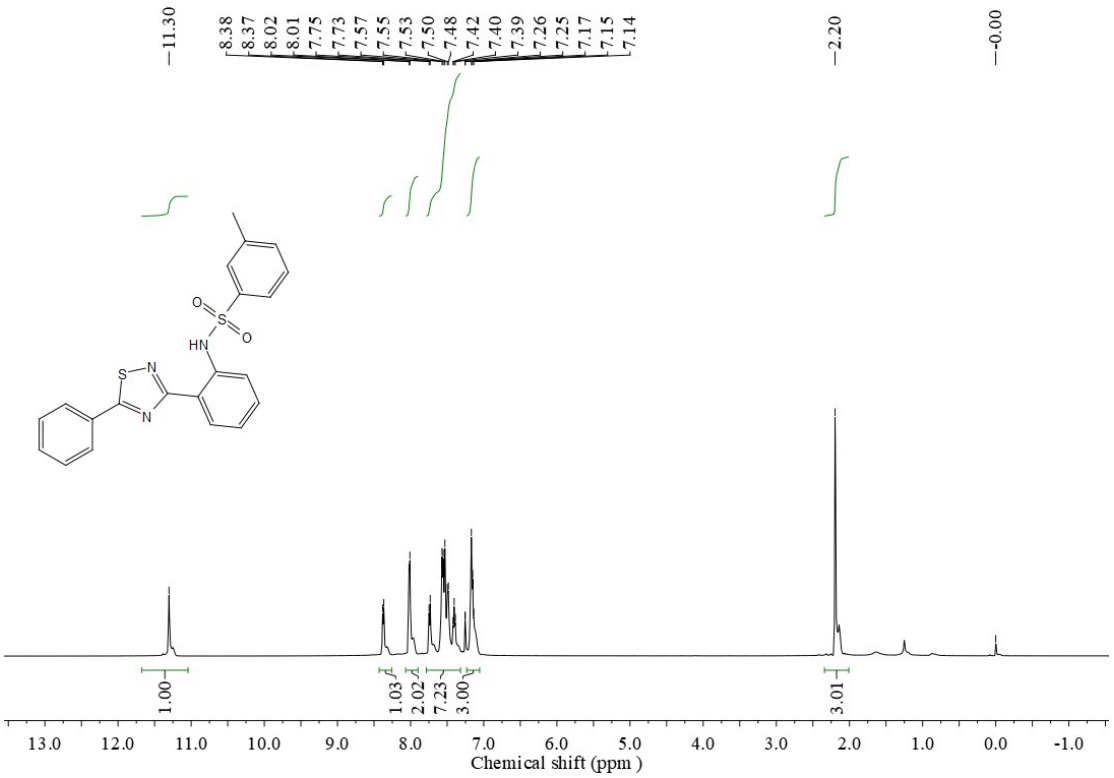

187.63
171.82
139.46
136.20
134.70
134.29
134.10
133.45
132.40
131.86
130.99
129.57
129.42
129.12
128.97
128.65
128.03
127.77
127.28
124.70
122.11
121.58
77.39
77.14
76.88
21.37
20.76
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

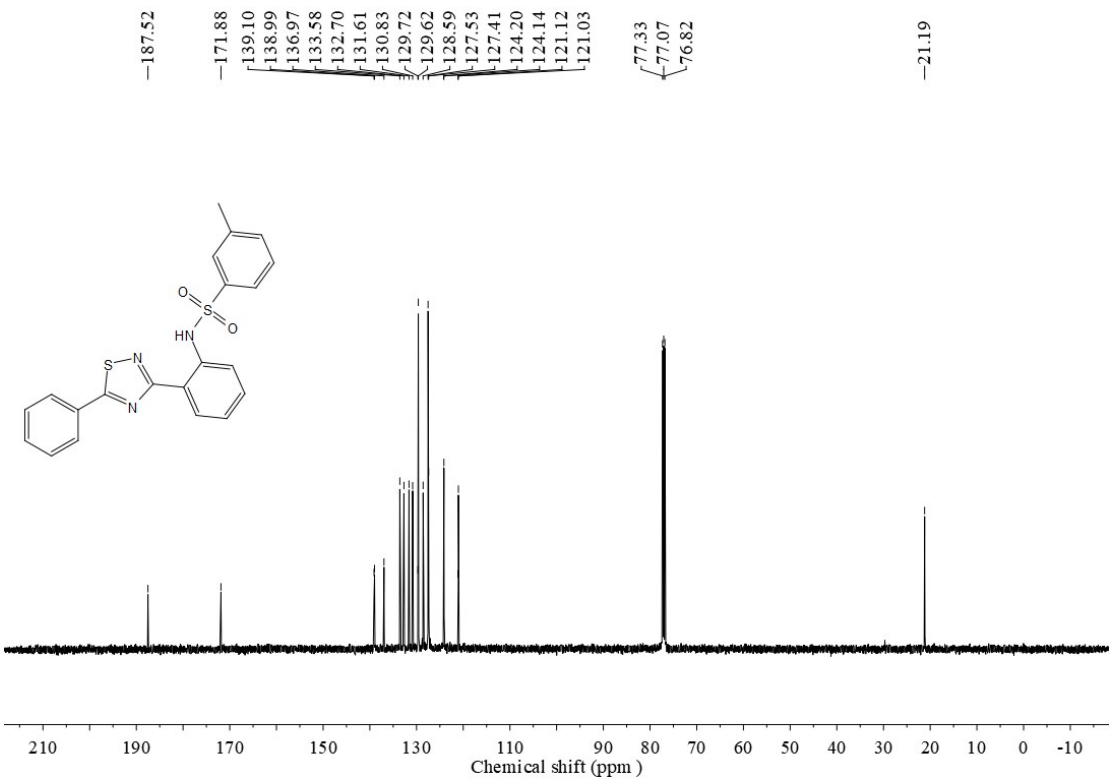

11.05
8.37
8.36
7.84
7.83
7.81
7.72
7.70
7.44
7.42
7.41
7.39
7.37
7.28
7.28
7.26
3.10
3.09
3.07
2.47
2.41
1.69
1.32
1.31
0.79
0.77
0.76
0.00
1.00
1.00
2.00
1.00
2.01
1.03
2.02
3.02
3.01
2.04
2.01
3.01
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

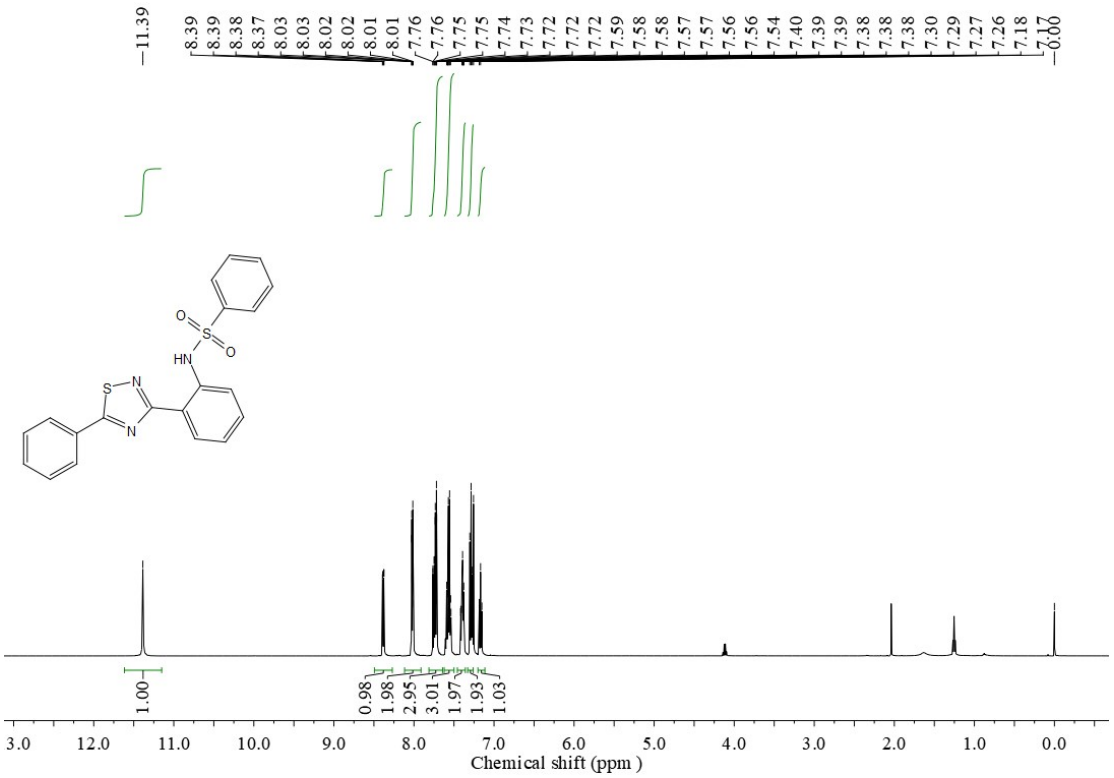

187.81
172.12
139.52
135.13
133.50
133.20
132.73
131.47
129.65
129.45
128.09
124.77
119.74
119.06
77.35
77.10
76.84
51.22
25.31
21.36
21.33
20.74
13.47
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

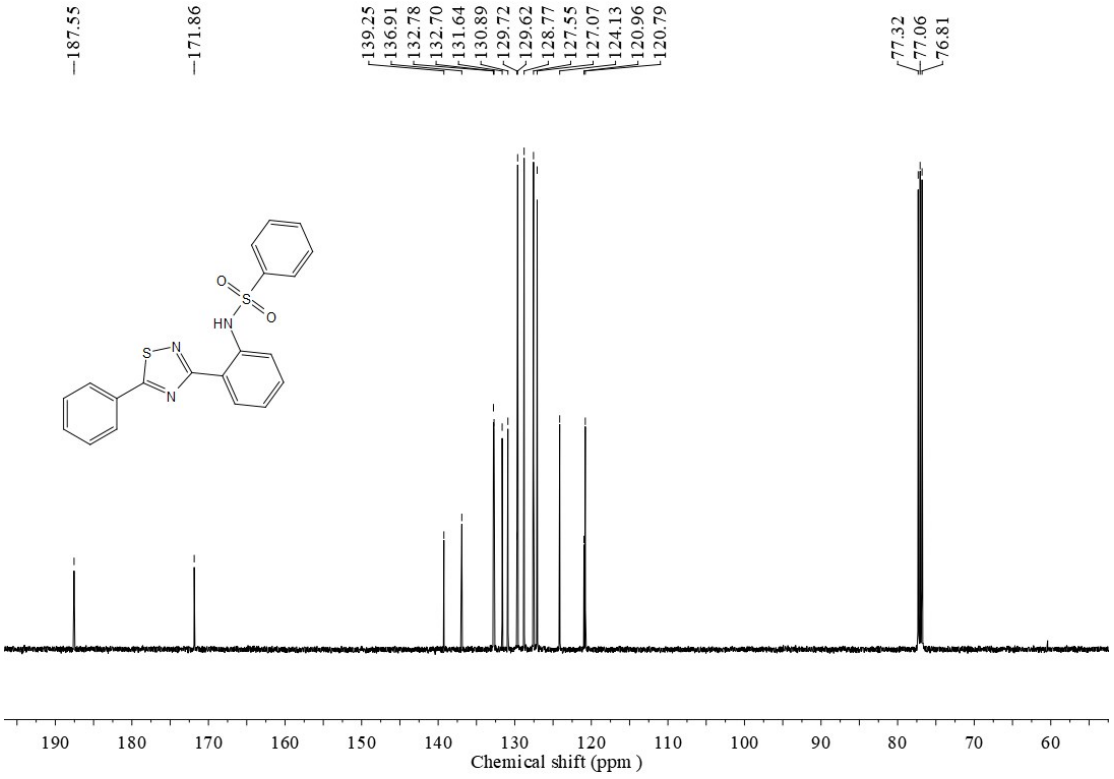

11.33
8.39
8.39
8.38
8.38
8.04
8.04
8.03
8.02
8.02
7.76
7.75
7.74
7.74
7.61
7.61
7.60
7.60
7.60
7.58
7.57
7.57
7.56
7.26
7.17
7.17
7.08
2.26
0.00
1.00
1.02
2.04
1.04
5.13
1.05
1.03
2.05
3.25
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical shift (ppm)

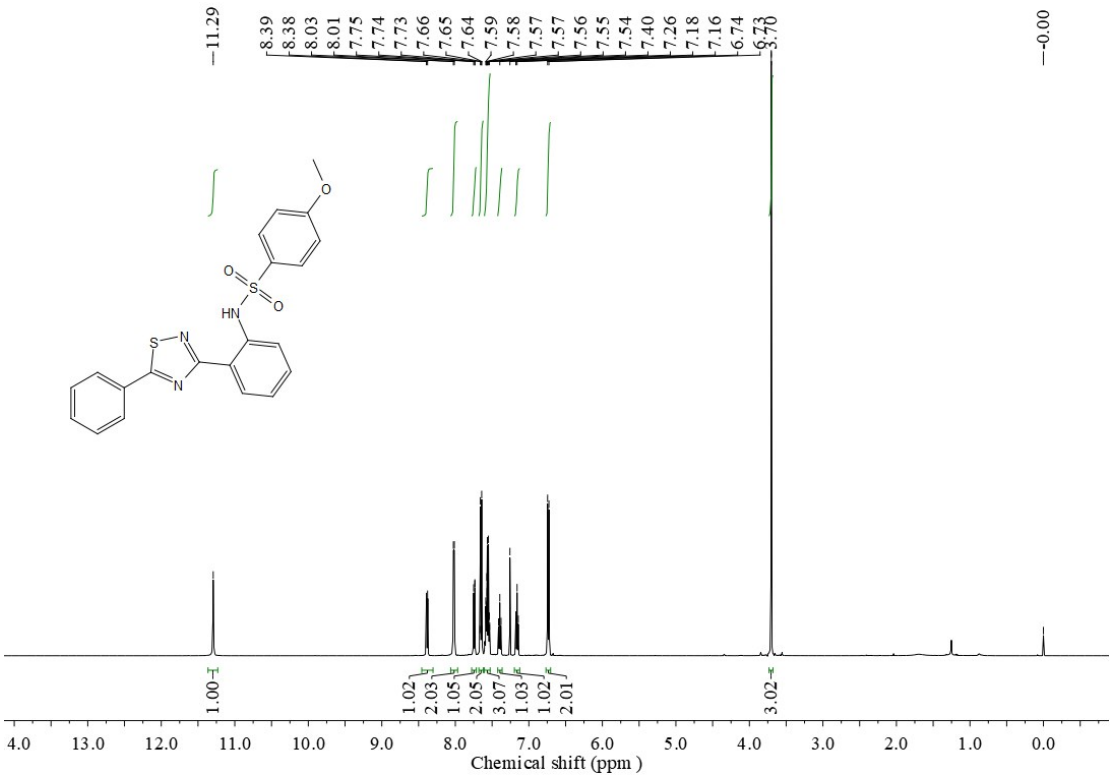

187.51
171.93
143.58
137.04
136.32
132.67
131.61
130.85
129.76
129.60
129.39
127.54
127.11
123.98
120.91
120.72
77.25
77.04
76.83
21.44
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

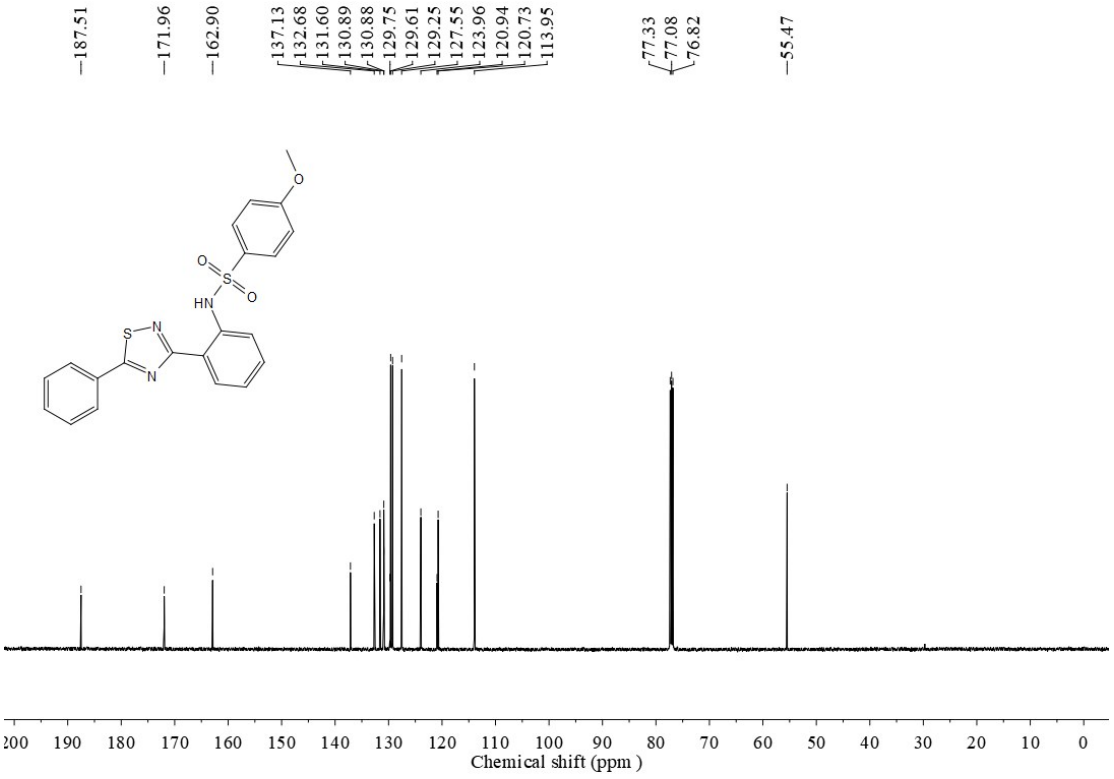

11.30
8.38
8.37
8.02
8.01
7.75
7.73
7.57
7.55
7.53
7.50
7.48
7.42
7.40
7.39
7.26
7.25
7.17
7.15
7.14
2.20
0.00
1.00
1.03
2.02
2.23
3.00
3.01
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
Chemical shift (ppm)

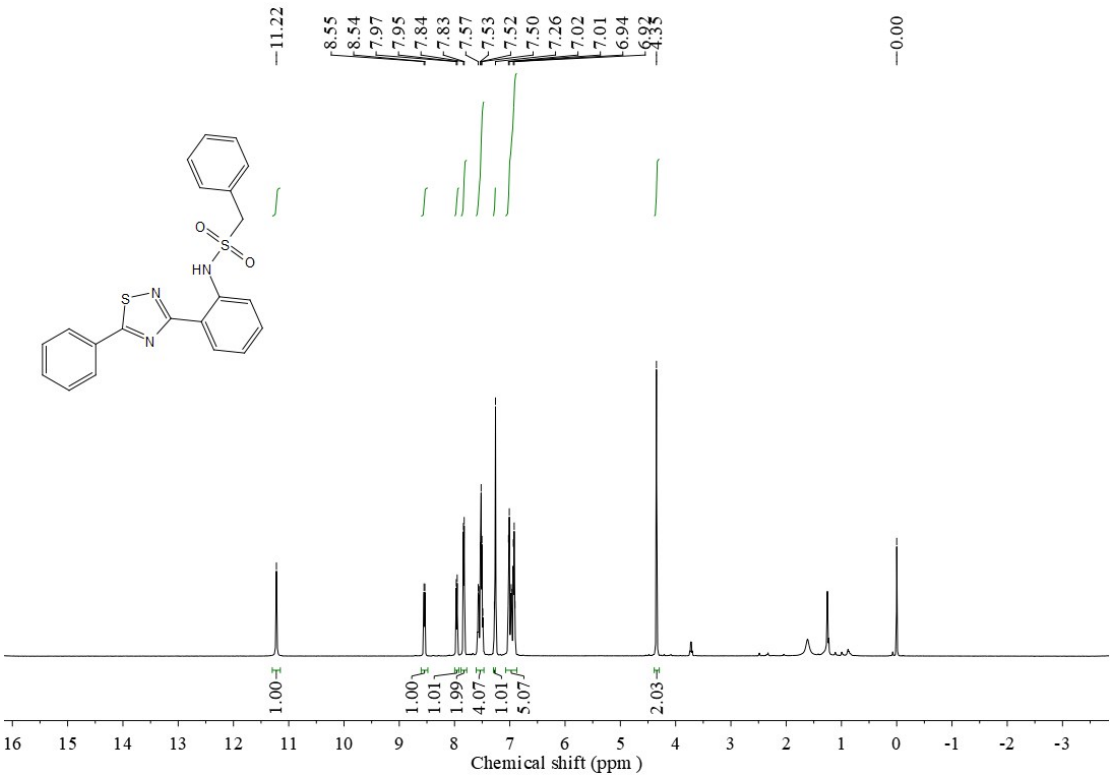

187.52
171.88
139.10
138.99
136.97
133.58
132.70
131.61
130.83
129.72
129.62
128.59
127.53
127.41
124.20
124.14
121.12
121.03
77.33
77.07
76.82
21.19
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift (ppm)

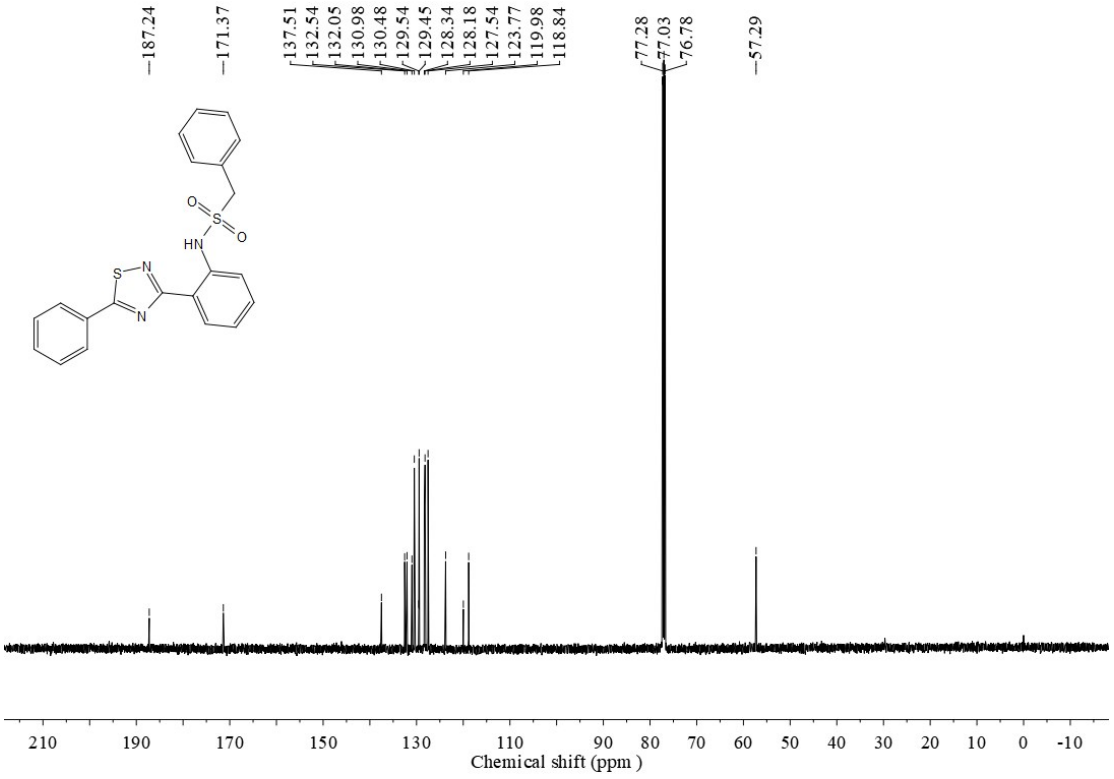

11.39
8.39
8.39
8.38
8.37
8.03
8.03
8.02
8.02
8.01
8.01
7.76
7.76
7.75
7.75
7.74
7.73
7.72
7.72
7.72
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.54
7.40
7.39
7.39
7.38
7.38
7.38
7.30
7.29
7.27
7.26
7.18
7.17
0.00
O
S
O
HN
S
N
N
1.00
0.98
1.98
2.95
3.01
1.97
1.93
1.03
3.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

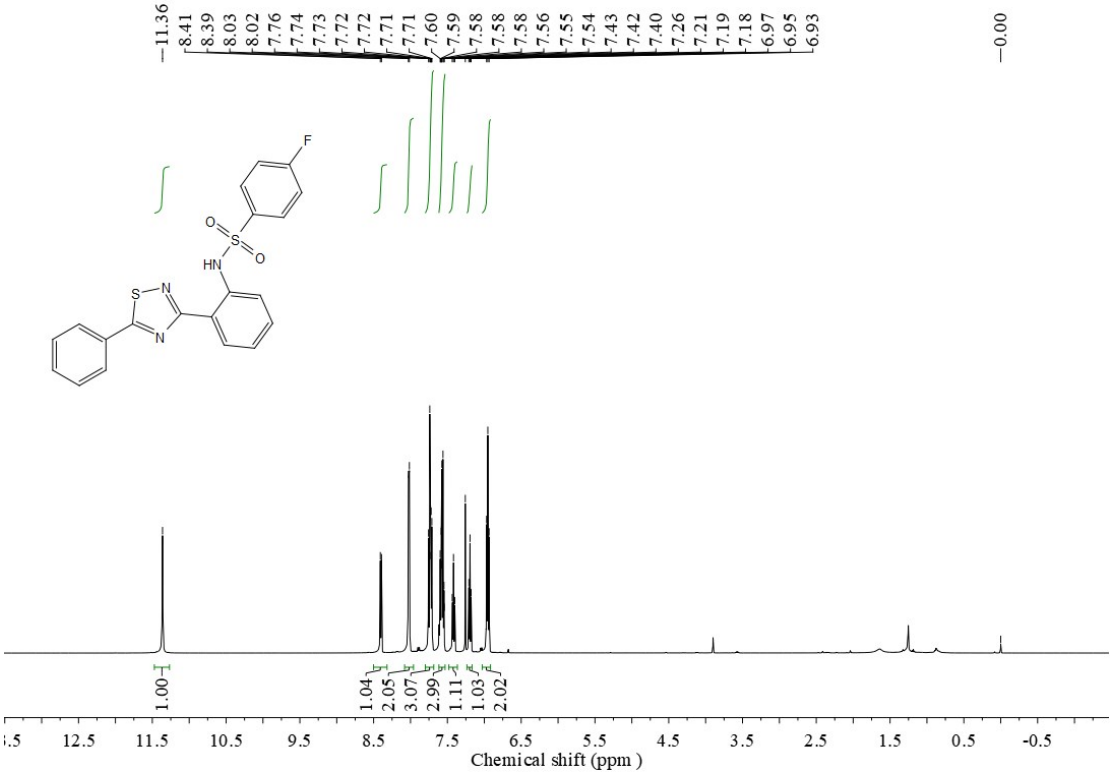

187.55
171.86
139.25
136.91
132.78
132.70
131.64
130.89
129.72
129.62
128.77
127.55
127.07
124.13
120.96
120.79
77.32
77.06
76.81
O
S
O
HN
S
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
Chemical shift (ppm)

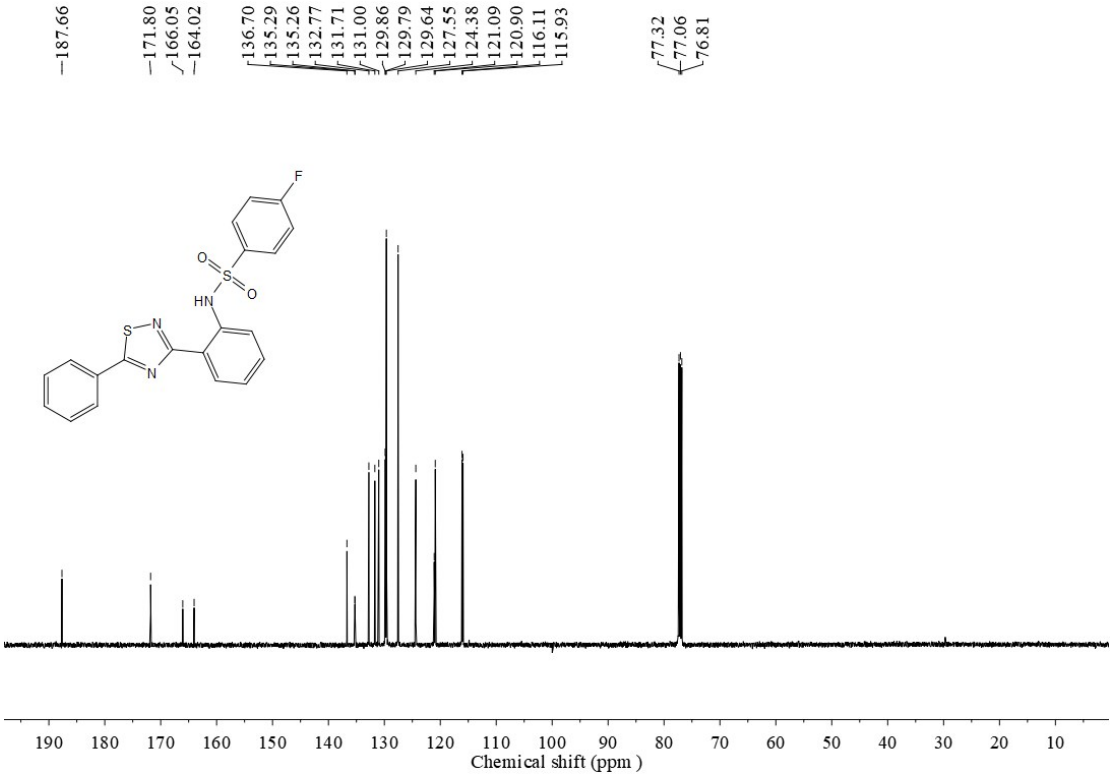

11.29
8.39
8.38
8.03
8.01
7.75
7.74
7.73
7.66
7.65
7.64
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.40
7.26
7.18
7.16
6.74
6.73
3.70
0.00
1.00
1.02
2.03
1.05
2.05
3.07
1.03
1.02
2.01
3.02
Chemical shift (ppm)

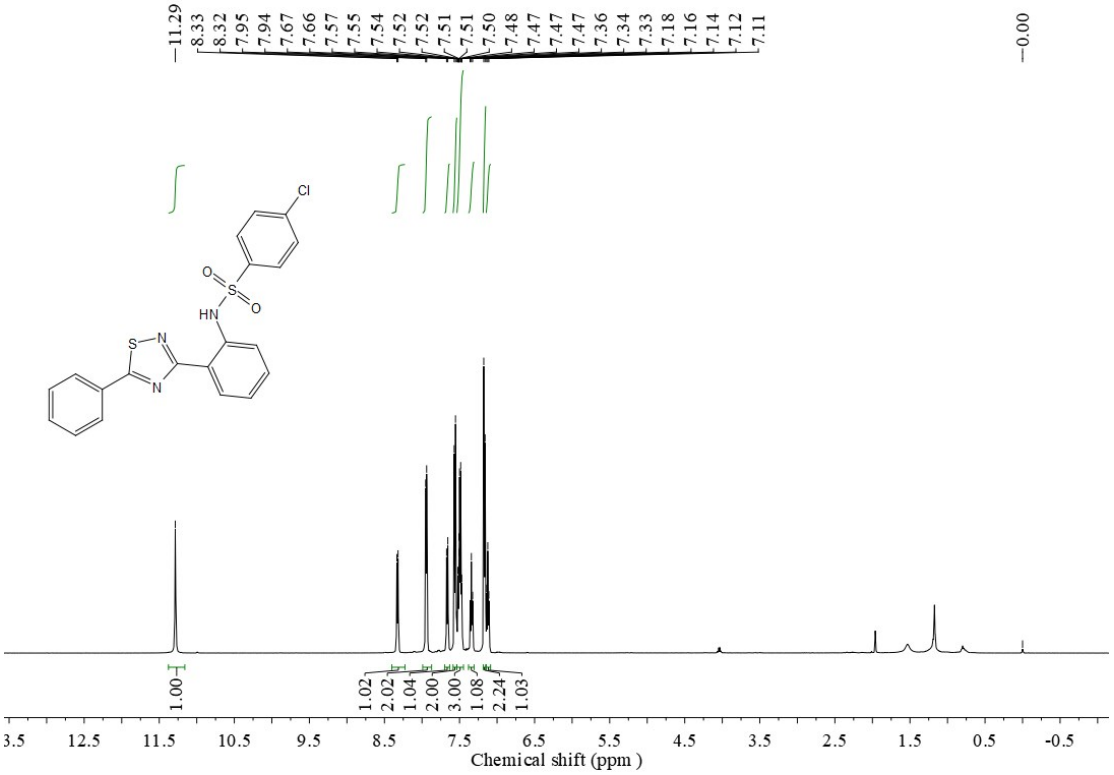

187.51
171.96
162.90
137.13
132.68
131.60
130.89
130.88
129.75
129.61
129.25
127.55
123.96
120.94
120.73
113.95
77.33
77.08
76.82
55.47
Chemical shift (ppm)

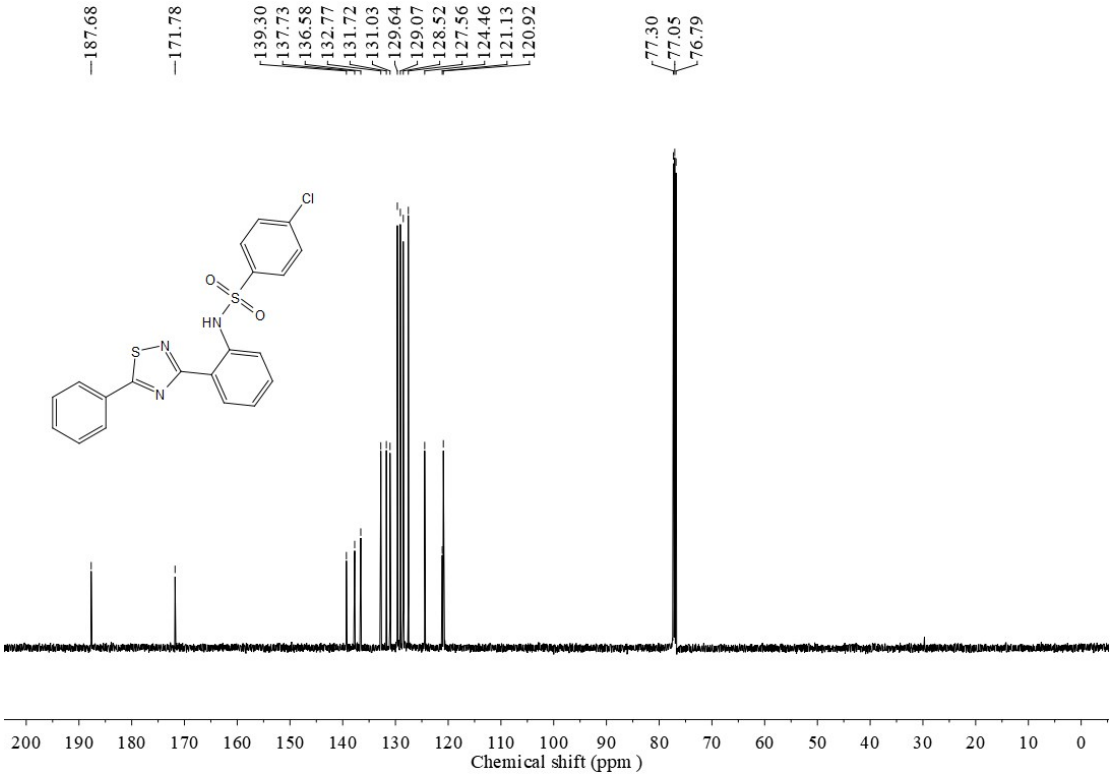

11.22
8.55
8.54
7.97
7.95
7.84
7.83
7.57
7.53
7.52
7.50
7.26
7.02
7.01
6.94
6.92
4.35
0.00
1.00
1.00
1.01
1.99
4.07
1.01
5.07
2.03
Chemical shift (ppm)

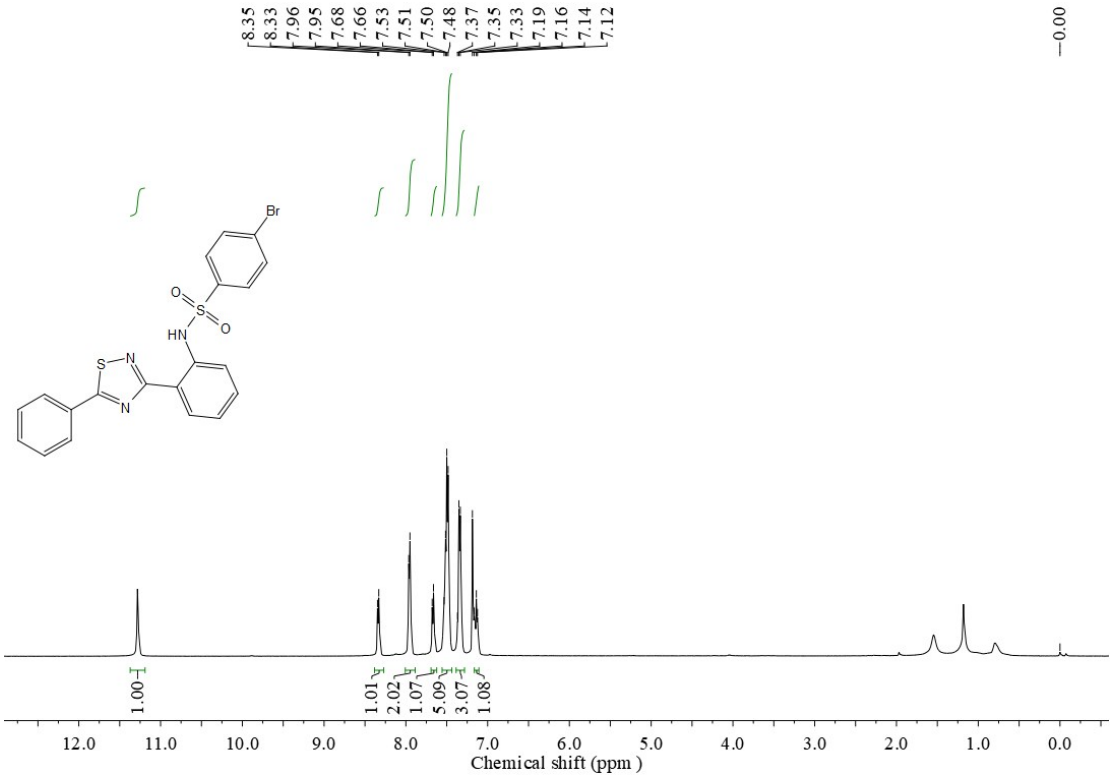

187.24
171.37
137.51
132.54
132.05
130.98
130.48
129.54
129.45
128.34
128.18
127.54
123.77
119.98
118.84
77.28
77.03
76.78
57.29
Chemical shift (ppm)

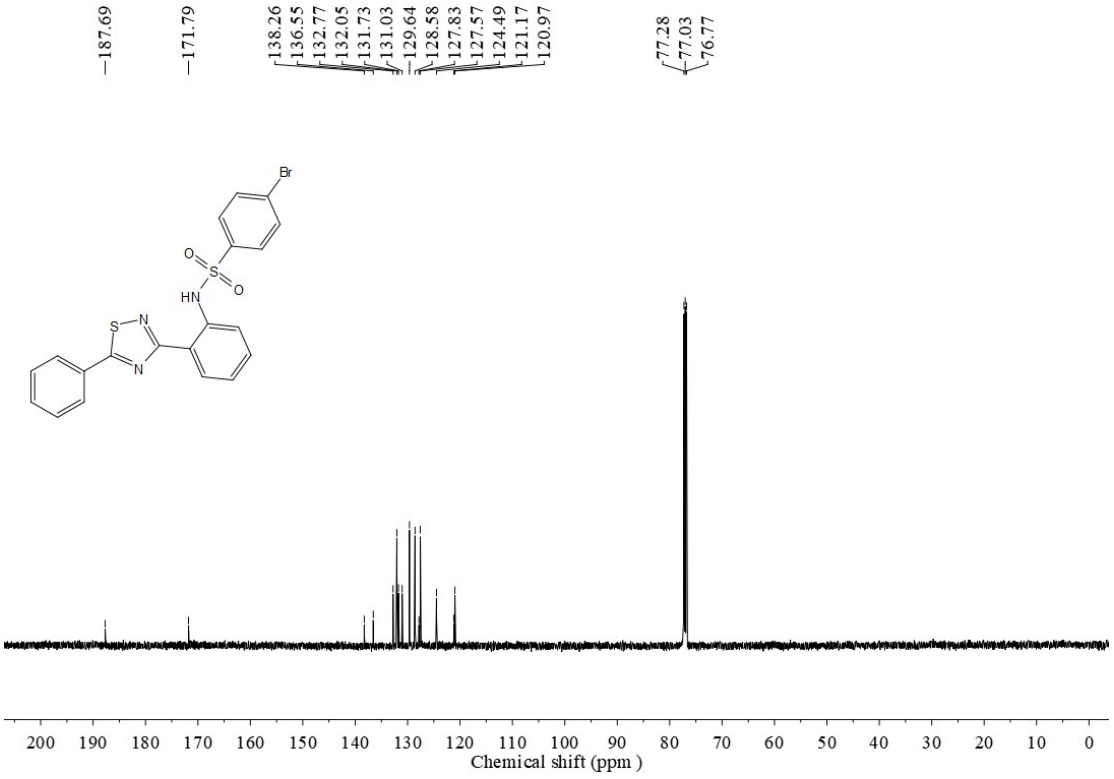

11.36
8.41
8.39
8.03
8.02
7.76
7.74
7.73
7.72
7.72
7.71
7.71
7.60
7.59
7.58
7.58
7.58
7.56
7.55
7.54
7.43
7.42
7.40
7.26
7.21
7.19
7.18
6.97
6.95
6.93
0.00
F
O
S
O
HN
S
N
N
1.00
1.04
2.05
3.07
2.99
1.11
1.03
2.02
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

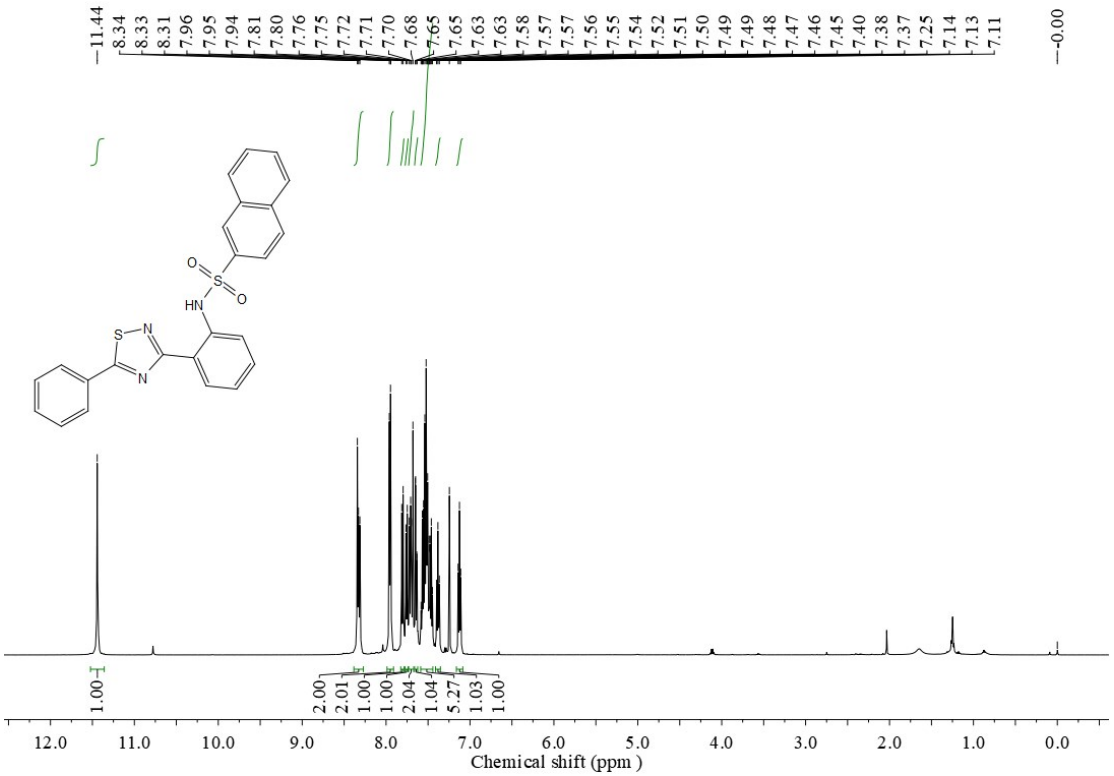

187.66
171.80
166.05
164.02
136.70
135.29
135.26
132.77
131.71
131.00
129.86
129.79
129.64
127.55
124.38
121.09
120.90
116.11
115.93
77.32
77.06
76.81
F
O
S
O
HN
S
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical shift (ppm)

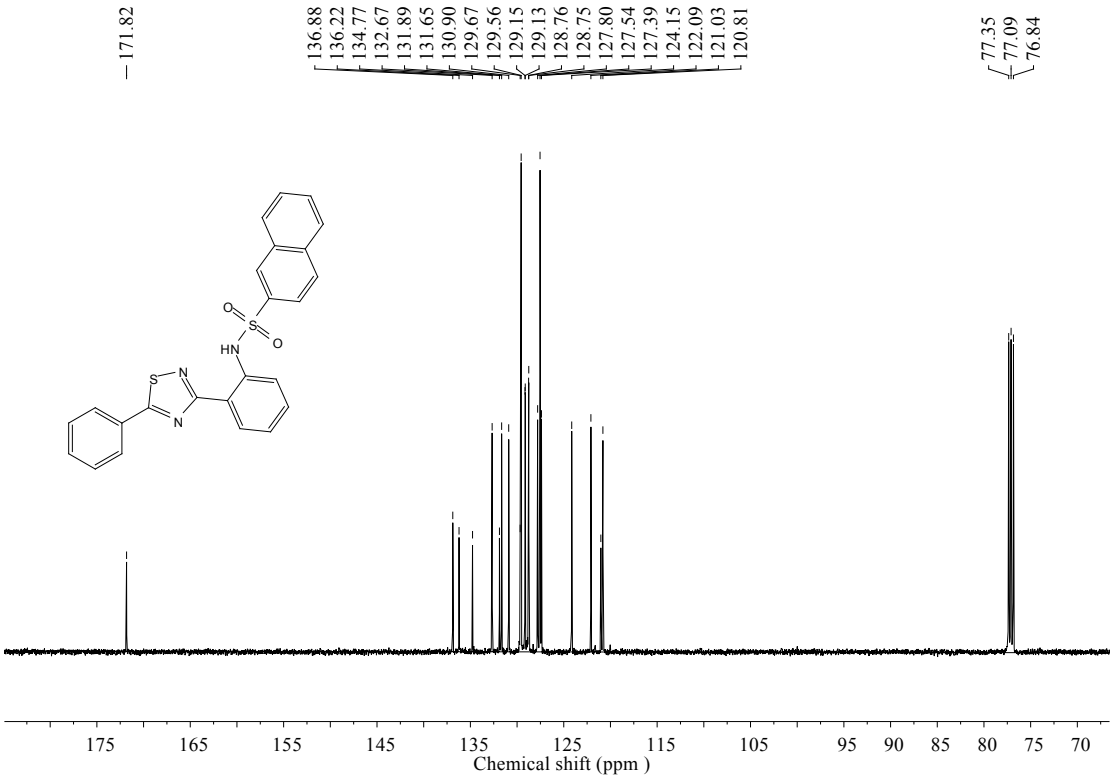

11.29
8.33
8.32
7.95
7.94
7.67
7.66
7.57
7.55
7.54
7.52
7.52
7.51
7.51
7.50
7.48
7.47
7.47
7.47
7.36
7.34
7.33
7.18
7.16
7.14
7.12
7.11
0.00
Cl
O
S
O
HN
S
N
N
1.00
1.02
2.02
1.04
2.00
3.00
1.08
2.24
1.03
Chemical shift (ppm)

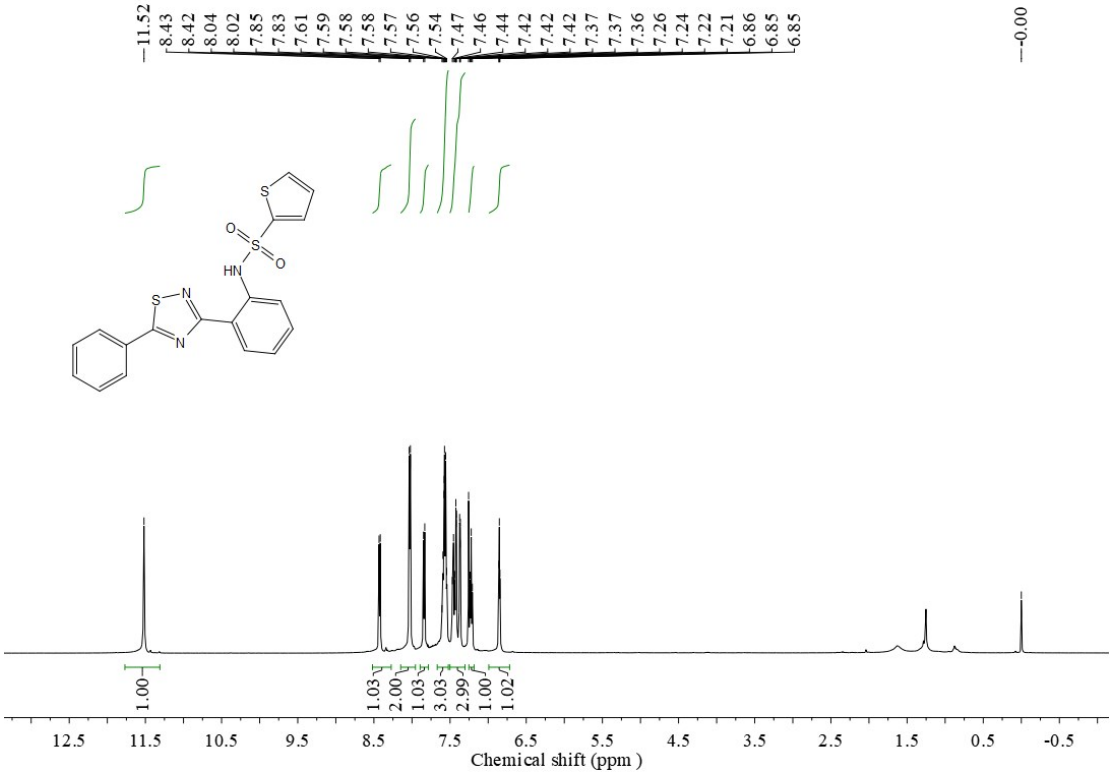

187.68
171.78
139.30
137.73
136.58
132.77
131.72
131.03
129.64
129.07
128.52
127.56
124.46
121.13
120.92
77.30
77.05
76.79
Cl
O
S
O
HN
S
N
N
Chemical shift (ppm)

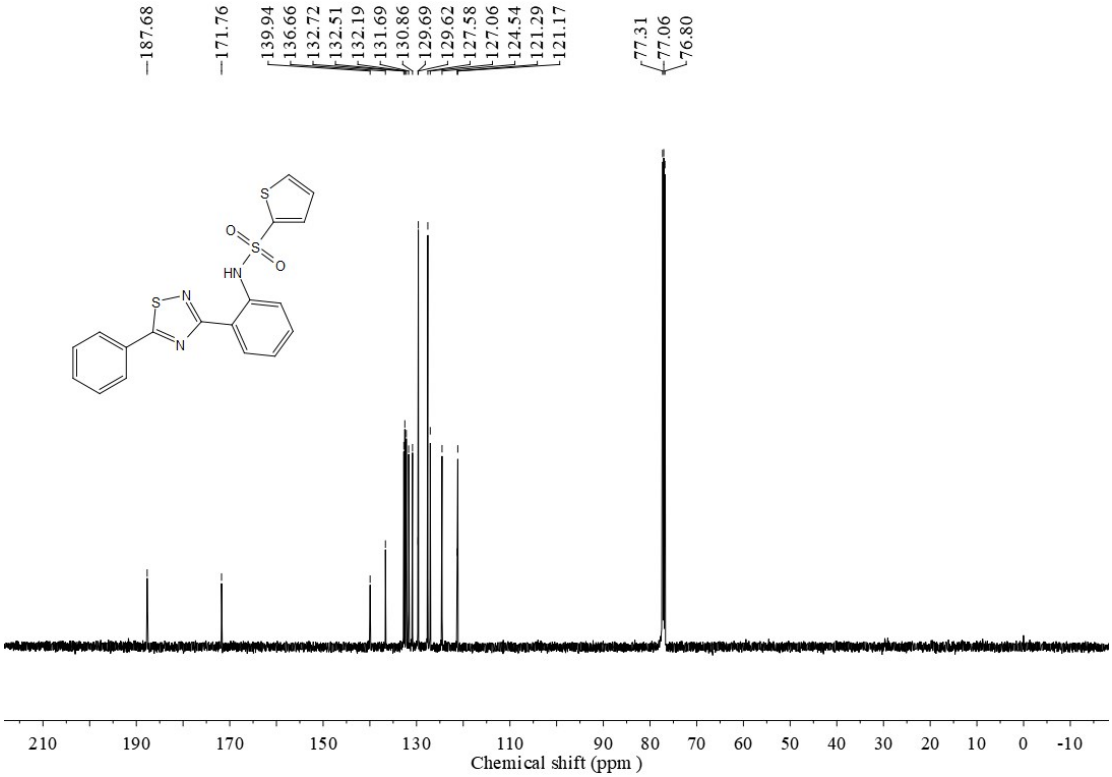

8.35
8.33
7.96
7.95
7.68
7.66
7.53
7.51
7.50
7.48
7.37
7.35
7.33
7.19
7.16
7.14
7.12
0.00
Br
O
S
O
HN
S
N
N
1.00
1.01
2.02
1.07
5.09
3.07
1.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

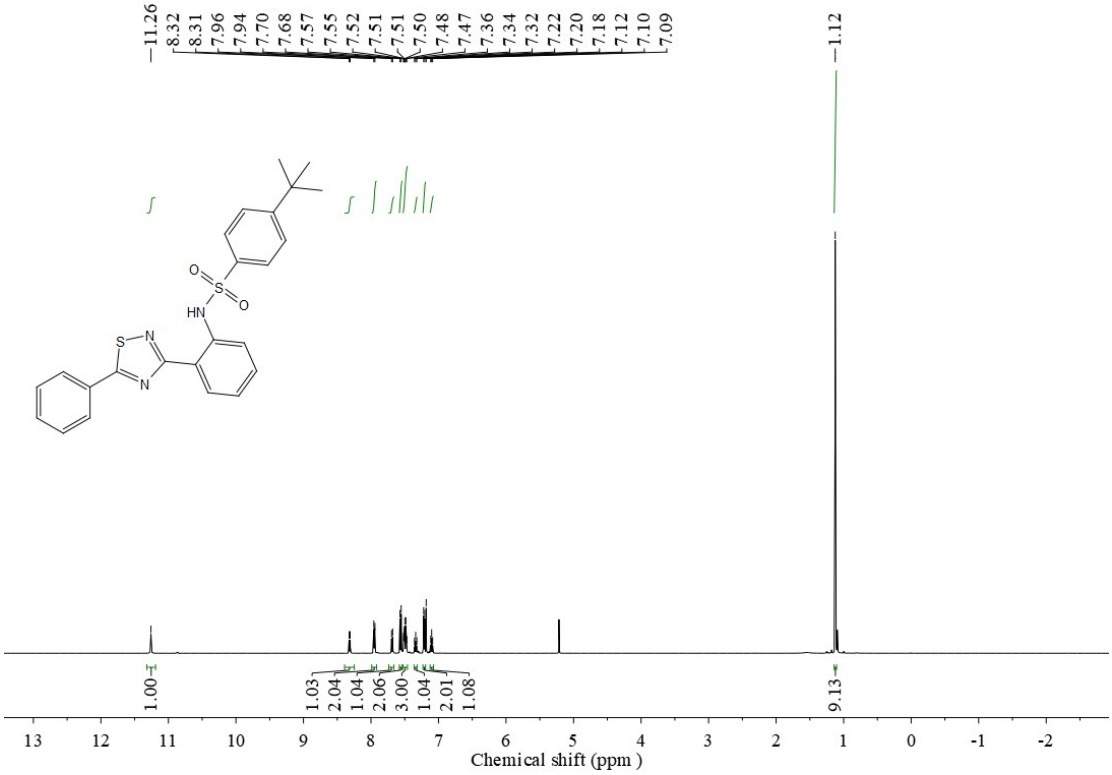

187.69
171.79
138.26
136.55
132.77
132.05
131.73
131.03
129.64
128.58
127.83
127.57
124.49
121.17
120.97
77.28
77.03
76.77
Br
O
S
O
HN
S
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

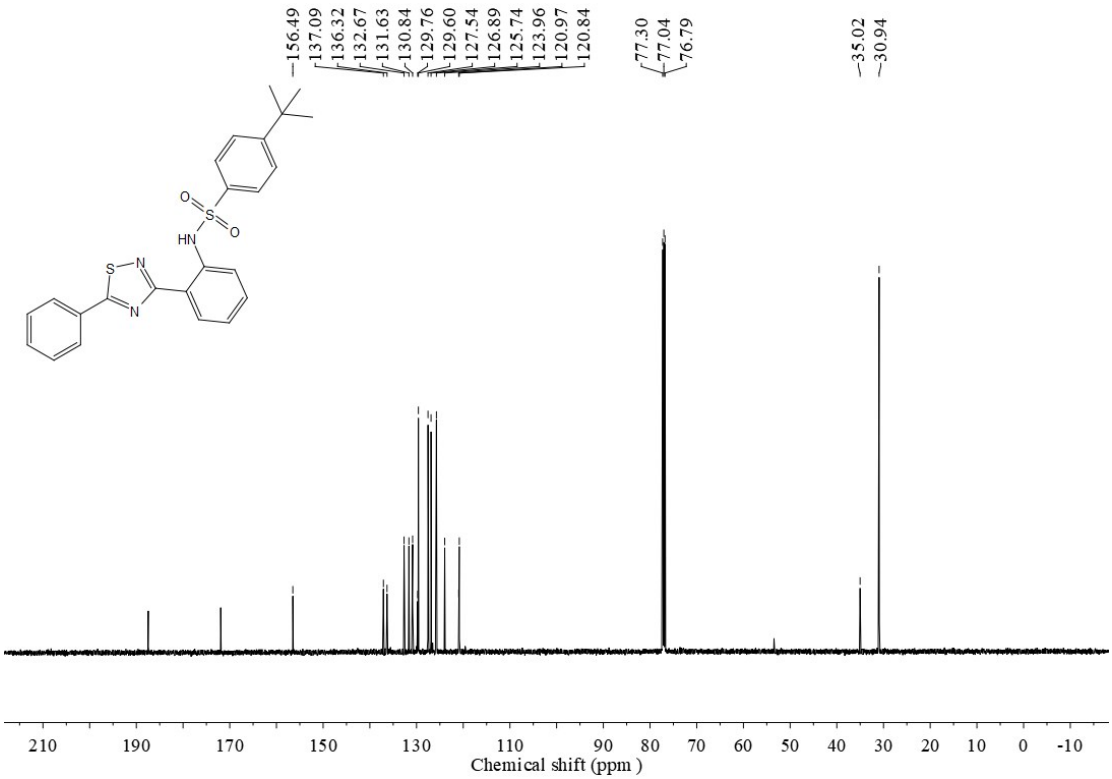

11.44
8.34
8.33
8.31
7.96
7.95
7.94
7.81
7.80
7.76
7.75
7.72
7.71
7.70
7.68
7.65
7.65
7.63
7.63
7.58
7.57
7.57
7.56
7.55
7.54
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.40
7.38
7.37
7.25
7.14
7.13
7.11
0.00
1.00
2.00
2.01
1.00
1.00
2.04
1.04
5.27
1.03
1.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

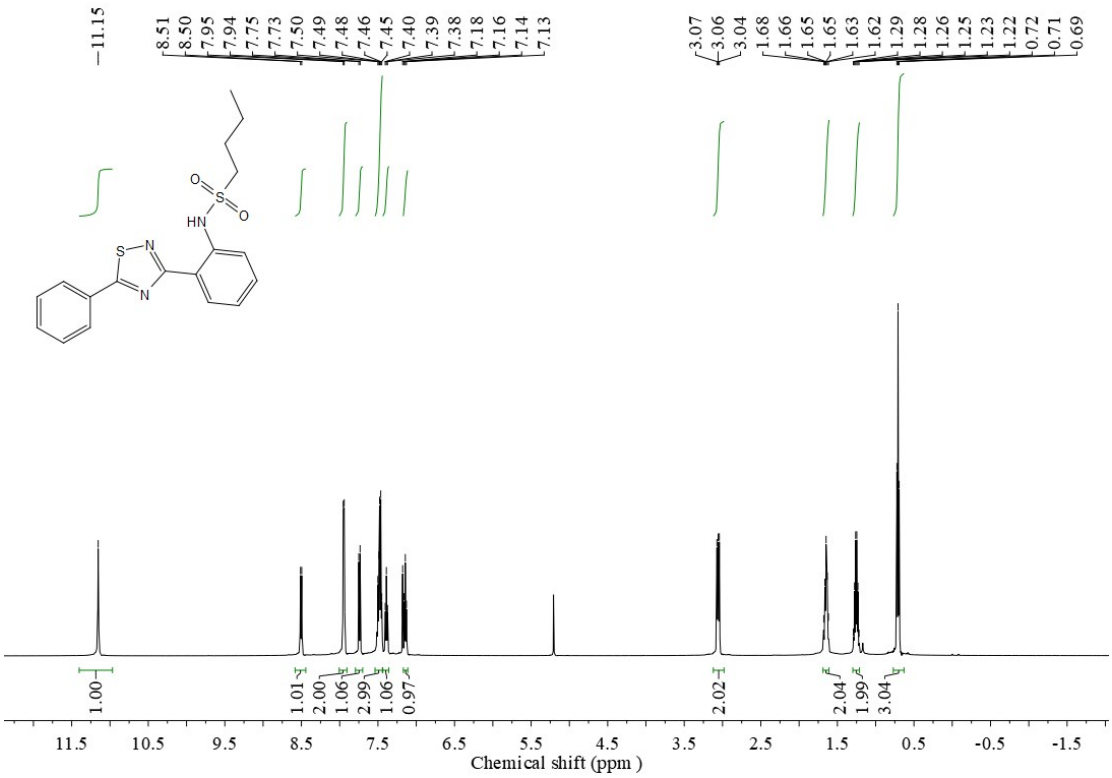

171.82
136.88
136.22
134.77
132.67
131.89
131.65
130.90
129.67
129.56
129.15
129.13
128.76
128.75
127.80
127.54
127.39
124.15
122.09
121.03
120.81
77.35
77.09
76.84
175
165
155
145
135
125
115
105
95
90
85
80
75
70
Chemical shift (ppm)

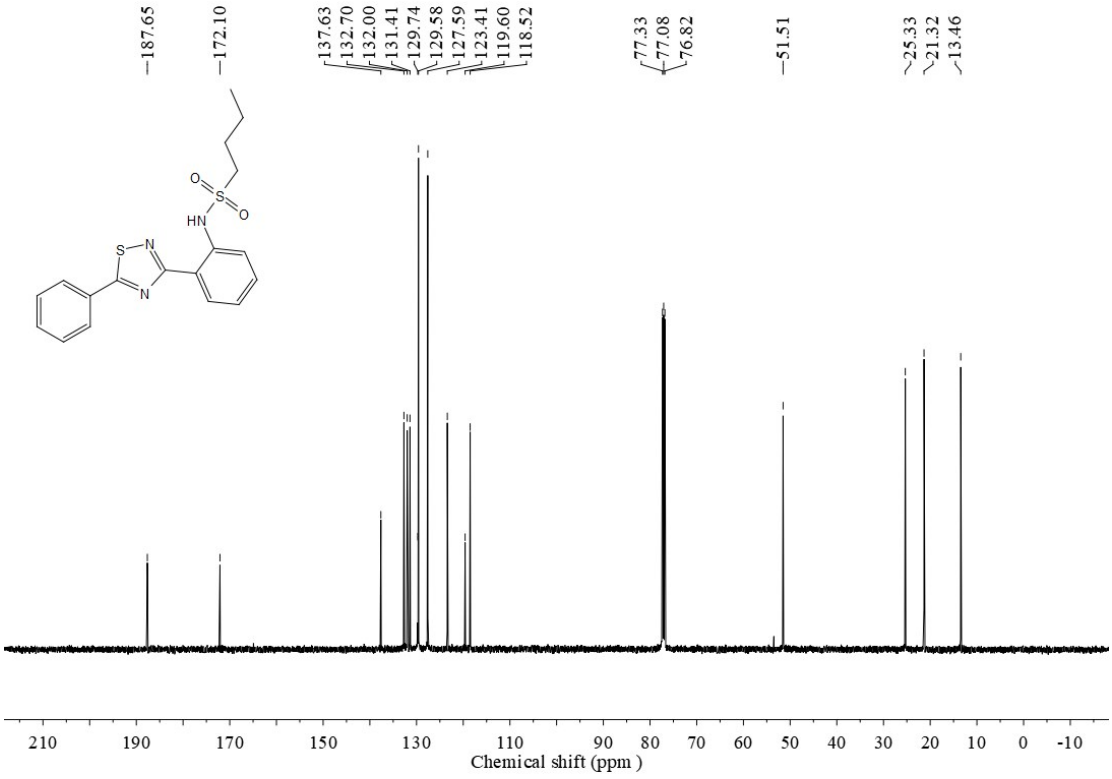

11.52
8.43
8.42
8.04
8.02
7.85
7.83
7.61
7.59
7.58
7.58
7.57
7.56
7.54
7.47
7.46
7.44
7.42
7.42
7.42
7.37
7.37
7.36
7.26
7.24
7.22
7.21
6.86
6.85
6.85
0.00
1.00
1.03
2.00
1.03
3.03
2.99
1.00
1.02
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

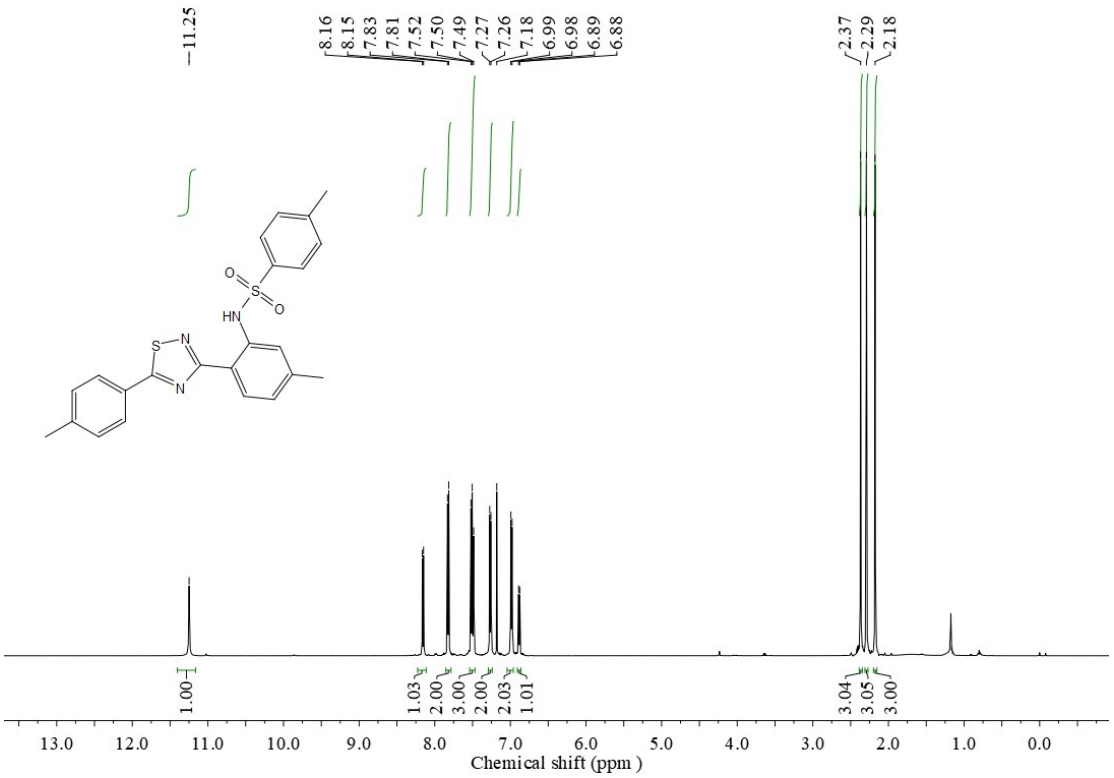

187.68
171.76
139.94
136.66
132.72
132.51
132.19
131.69
130.86
129.69
129.62
127.58
127.06
124.54
121.29
121.17
77.31
77.06
76.80
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

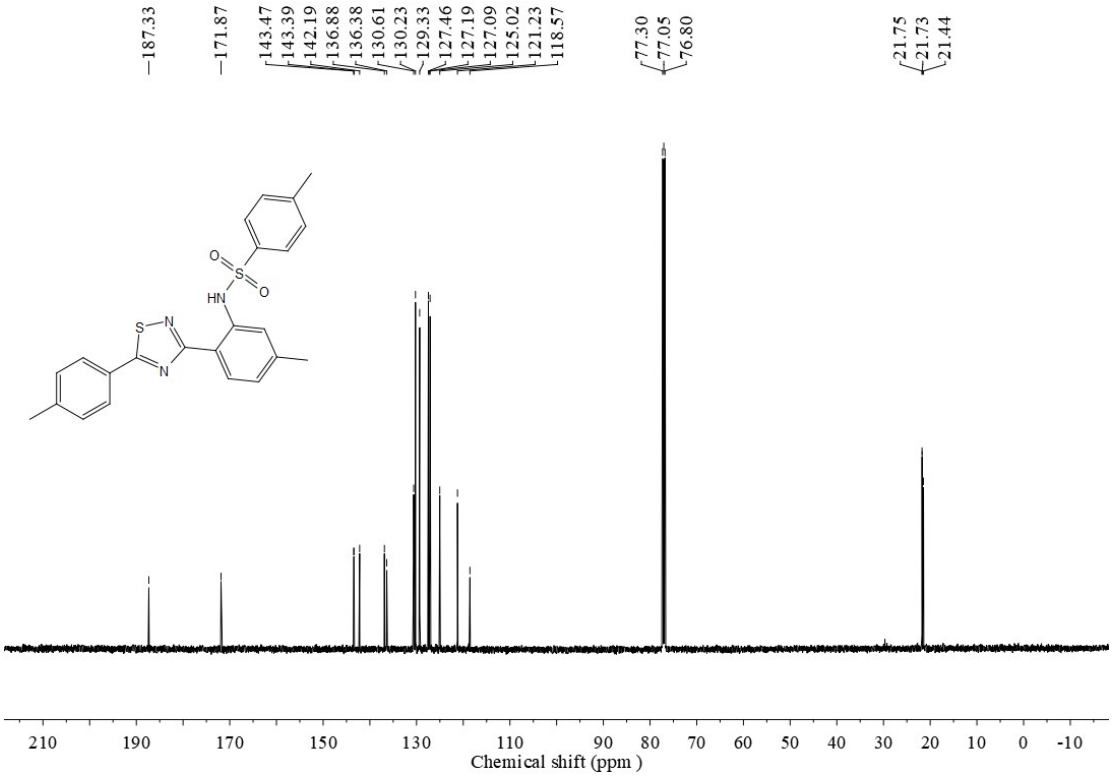

11.26
8.32
8.31
7.96
7.94
7.70
7.68
7.57
7.55
7.52
7.51
7.51
7.50
7.48
7.47
7.36
7.34
7.32
7.22
7.20
7.18
7.12
7.10
7.09
1.12
1.00
1.03
2.04
1.04
2.06
3.00
1.04
2.01
1.08
9.13
Chemical shift (ppm)

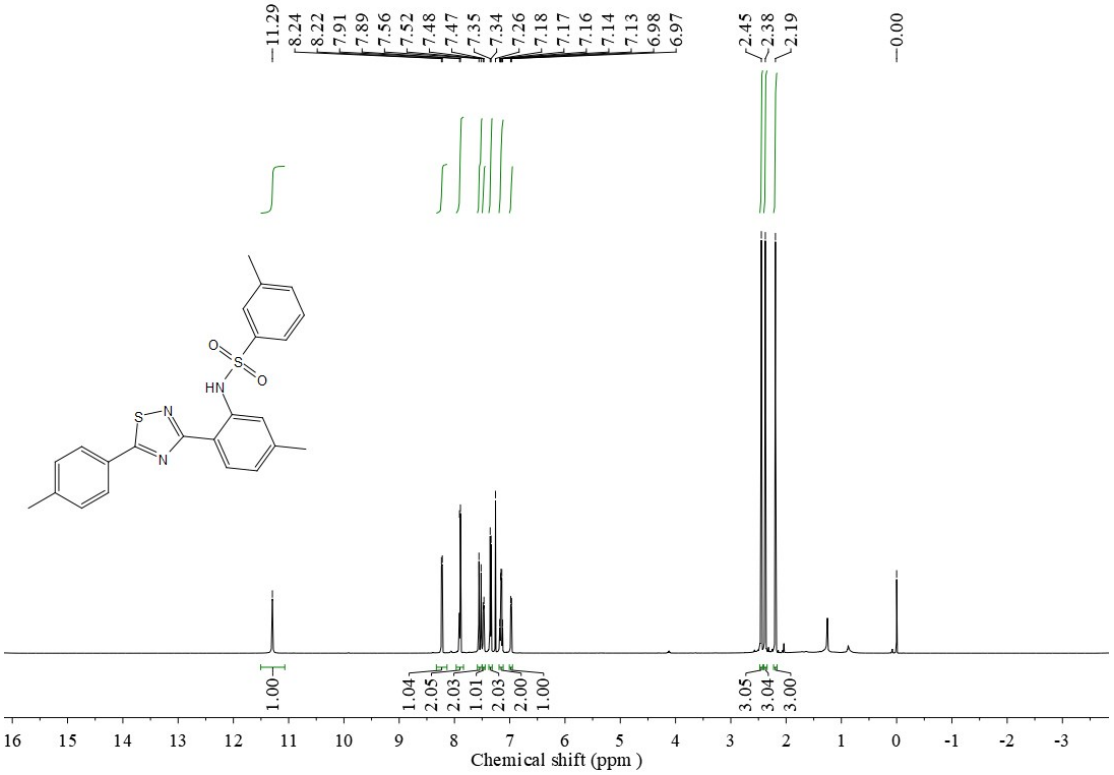

156.49
137.09
136.32
132.67
131.63
130.84
129.76
129.60
127.54
126.89
125.74
123.96
120.97
120.84
77.30
77.04
76.79
35.02
30.94
Chemical shift (ppm)

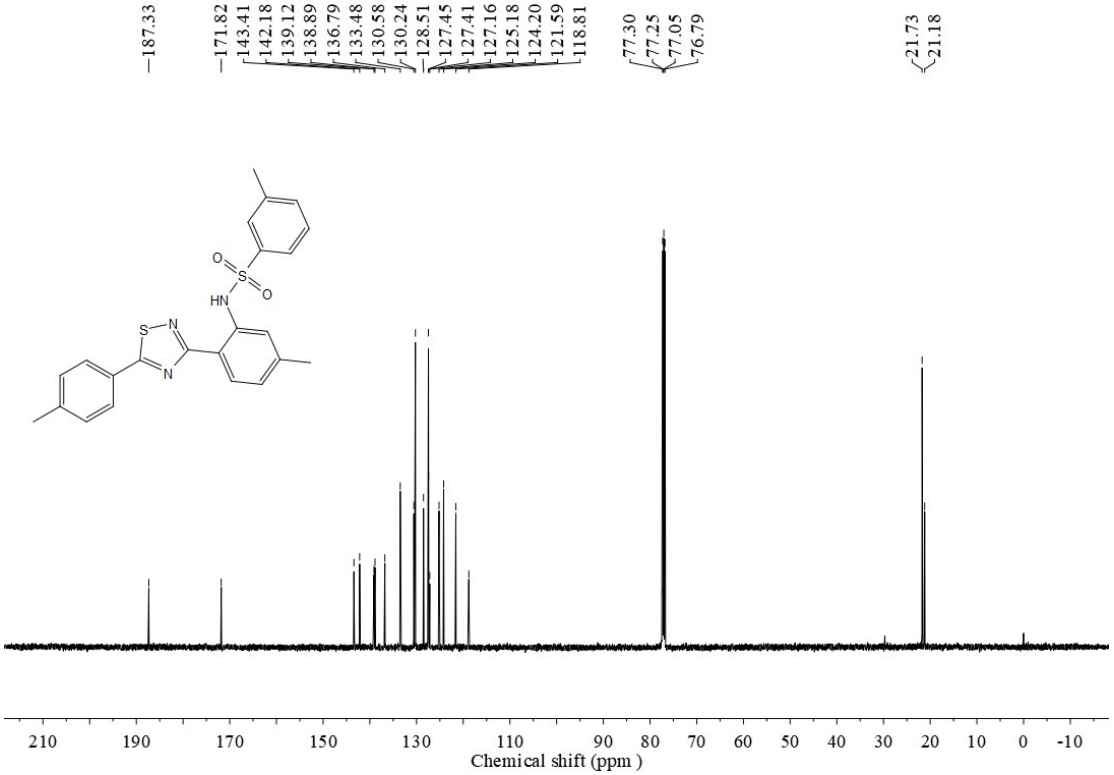

11.15
8.51
8.50
7.95
7.94
7.75
7.73
7.50
7.49
7.48
7.46
7.45
7.40
7.39
7.38
7.18
7.16
7.14
7.13
3.07
3.06
3.04
1.68
1.66
1.65
1.65
1.63
1.62
1.29
1.28
1.26
1.25
1.23
1.22
0.72
0.71
0.69
1.00
1.01
2.00
1.06
2.99
1.06
0.97
2.02
2.04
1.99
3.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
Chemical shift (ppm)

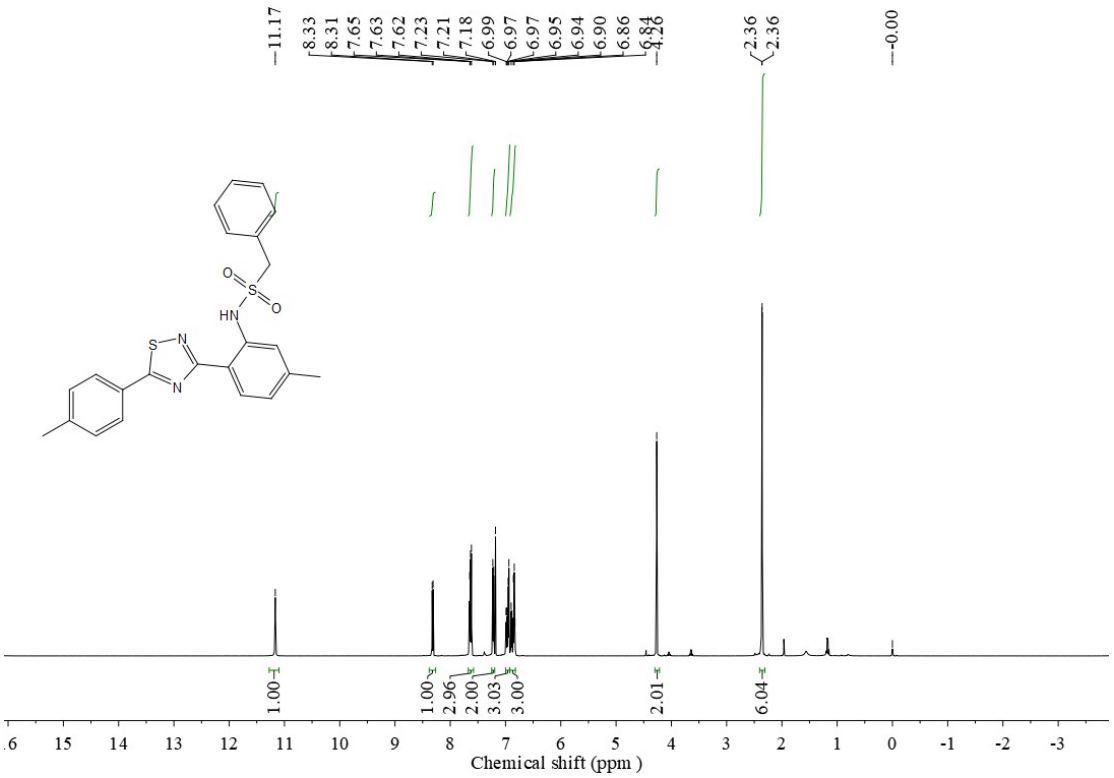

187.65
172.10
137.63
132.70
132.00
131.41
129.74
129.58
127.59
123.41
119.60
118.52
77.33
77.08
76.82
51.51
25.33
21.32
13.46
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

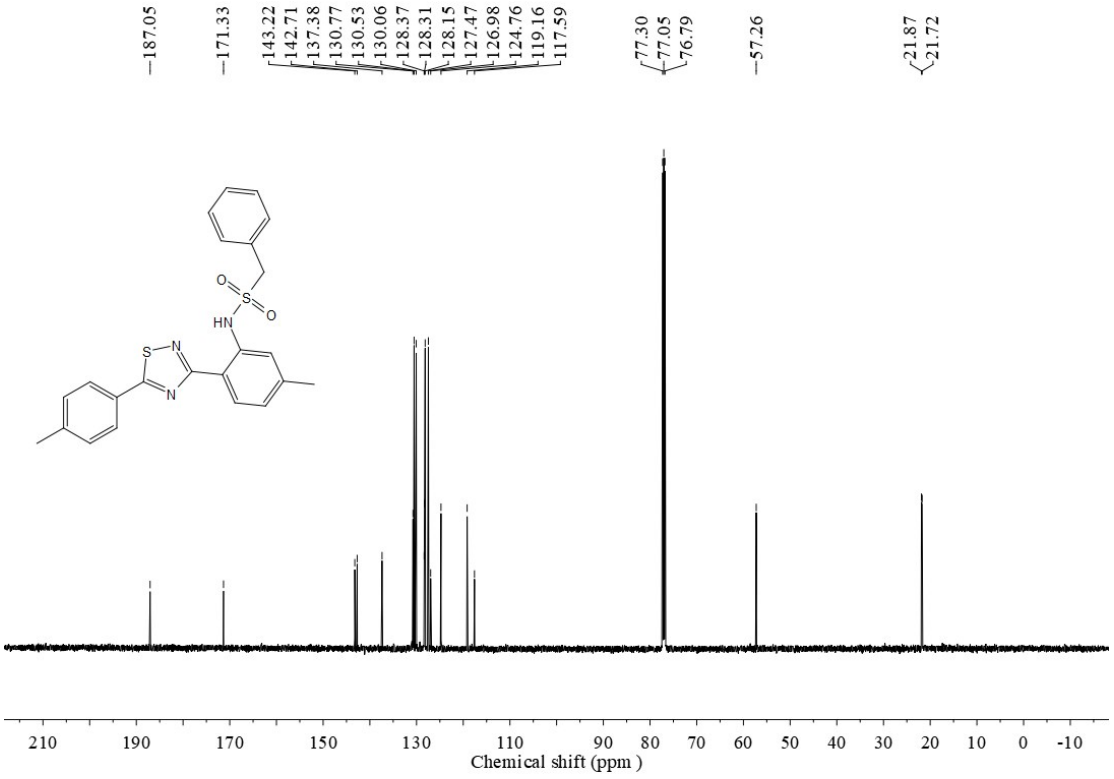

11.25
8.16
8.15
7.83
7.81
7.52
7.50
7.49
7.27
7.26
7.18
6.99
6.98
6.89
6.88
2.37
2.29
2.18
1.00
1.03
2.00
3.00
2.00
2.03
1.01
3.04
3.05
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

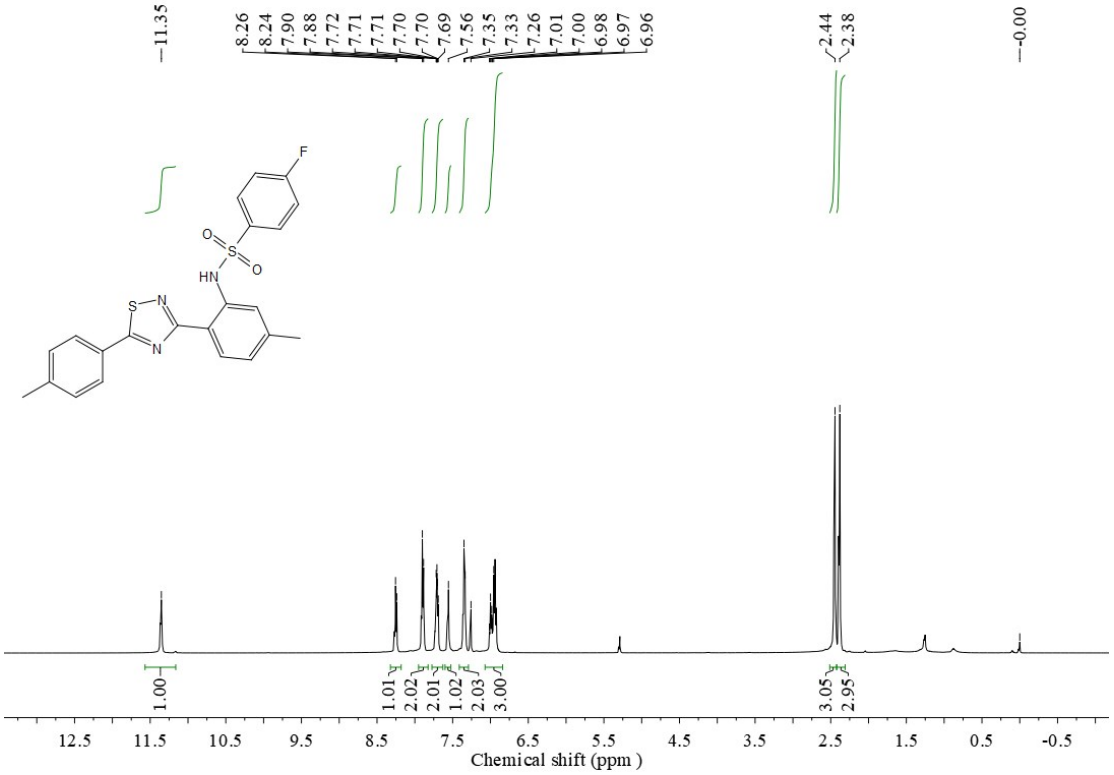

187.33
171.87
143.47
143.39
142.19
136.88
136.38
130.61
130.23
129.33
127.46
127.19
127.09
125.02
121.23
118.57
77.30
77.05
76.80
21.75
21.73
21.44
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

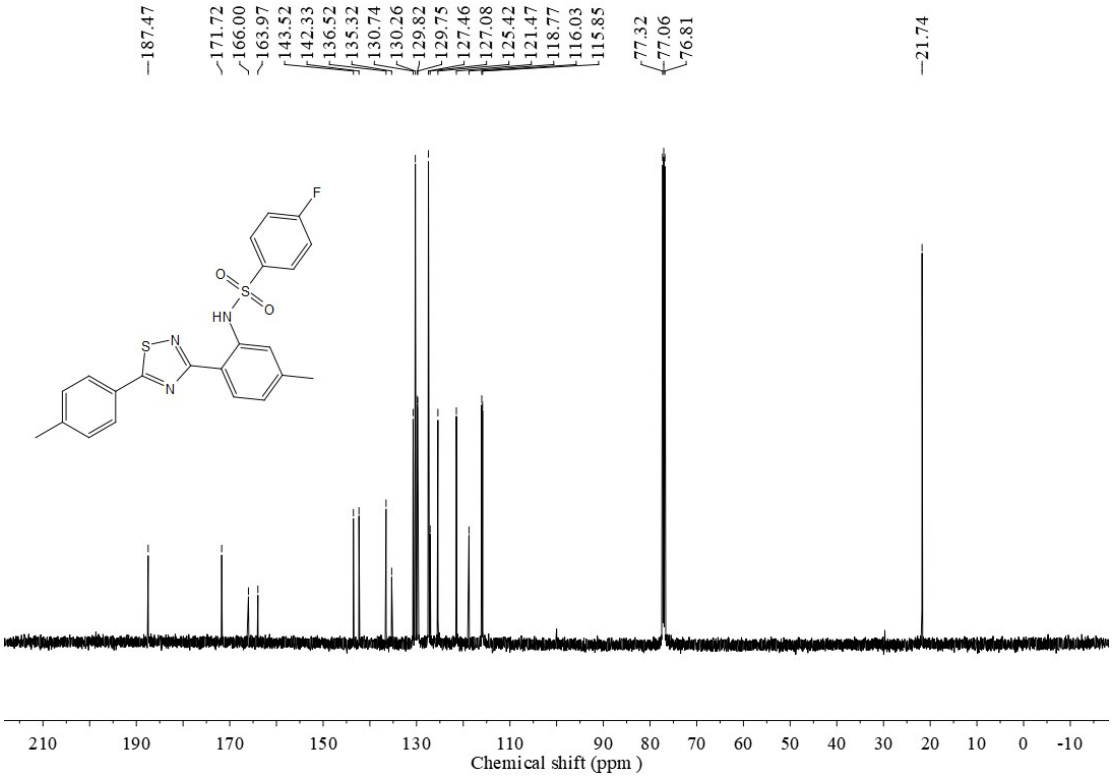

11.29
8.24
8.22
7.91
7.89
7.56
7.52
7.48
7.47
7.35
7.34
7.26
7.18
7.17
7.16
7.14
7.13
6.98
6.97
2.45
2.38
2.19
0.00
1.00
1.04
2.05
2.03
1.01
2.03
2.00
1.00
3.05
3.04
3.00
Chemical shift (ppm)

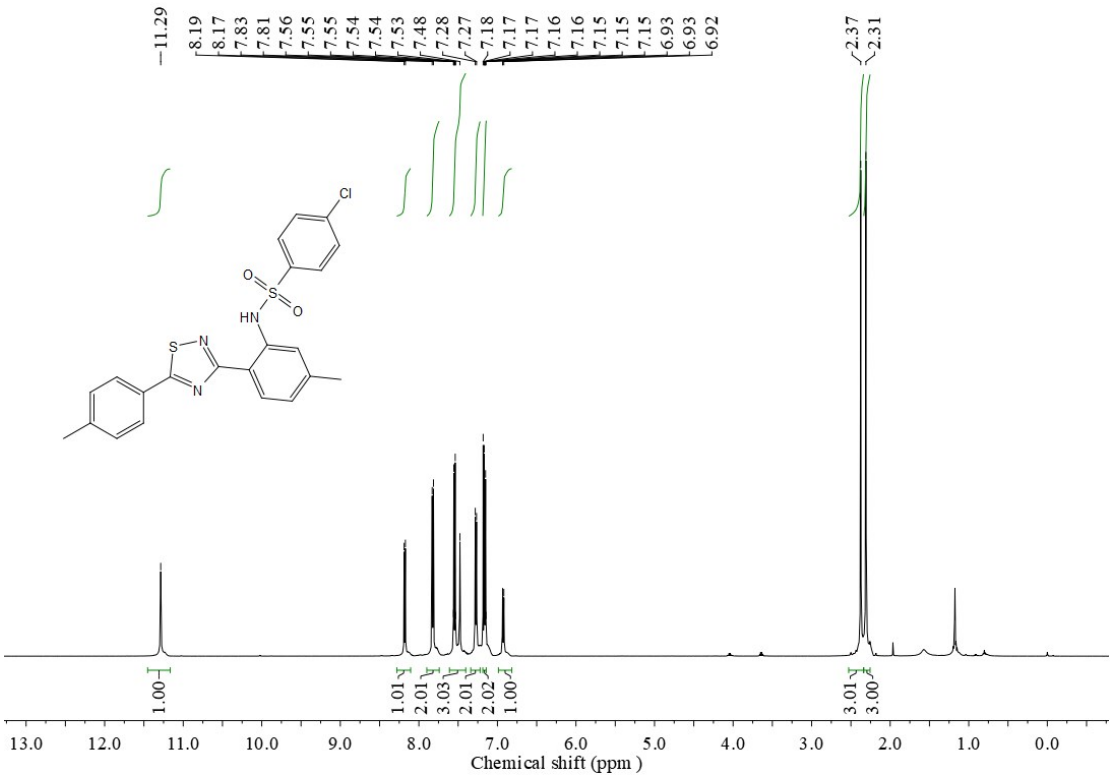

187.33
171.82
143.41
142.18
139.12
138.89
136.79
133.48
130.58
130.24
128.51
127.45
127.41
127.16
125.18
124.20
121.59
118.81
77.30
77.25
77.05
76.79
21.73
21.18
Chemical shift (ppm)

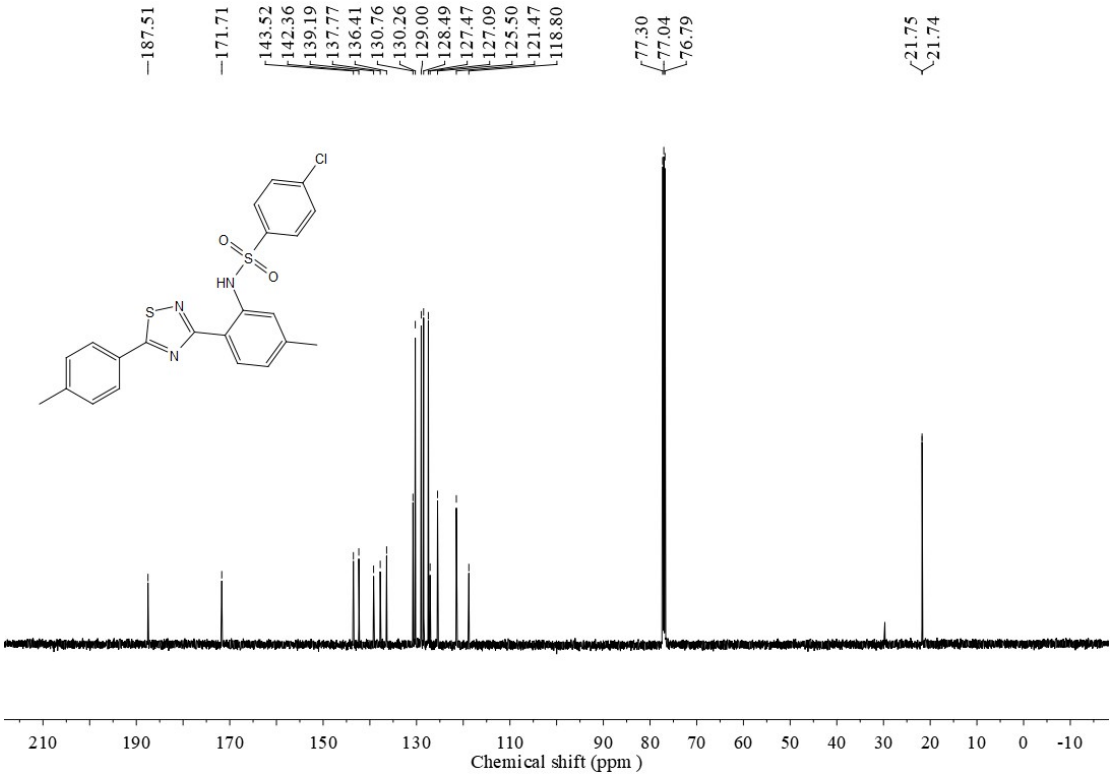

11.17
8.33
8.31
7.65
7.63
7.62
7.23
7.21
7.18
6.99
6.97
6.97
6.95
6.94
6.90
6.86
6.84
4.26
2.36
2.36
0.00
1.00
1.00
2.96
2.00
3.03
3.00
2.01
6.04
Chemical shift (ppm)

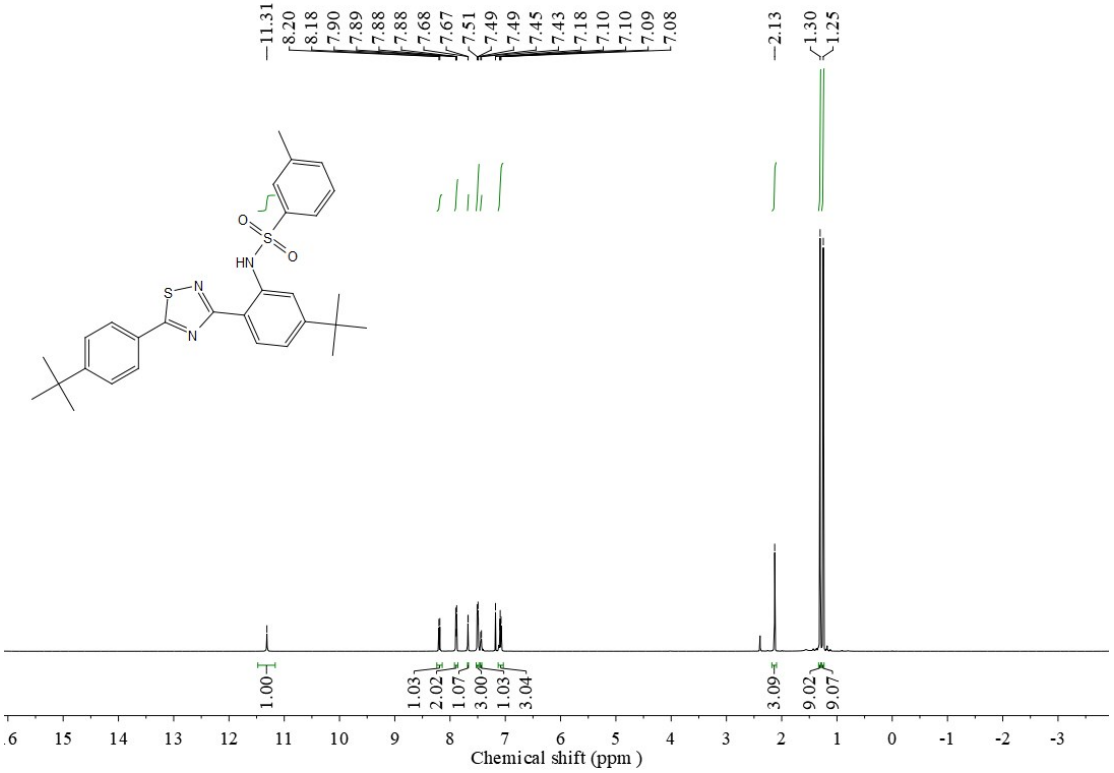

187.05
171.33
143.22
142.71
137.38
130.77
130.53
130.06
128.37
128.31
128.15
127.47
126.98
124.76
119.16
117.59
77.30
77.05
76.79
57.26
21.87
21.72
Chemical shift (ppm)

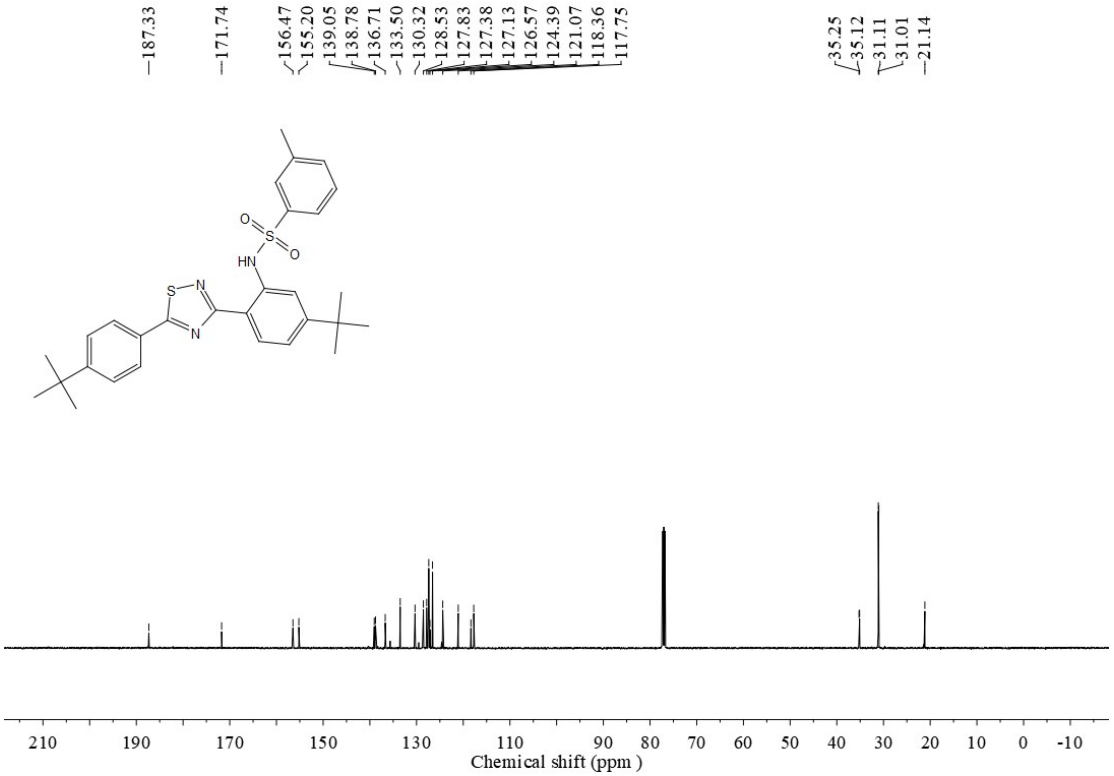

11.35
8.26
8.24
7.90
7.88
7.72
7.71
7.71
7.70
7.70
7.69
7.56
7.35
7.33
7.26
7.01
7.00
6.98
6.97
6.96
2.44
2.38
0.00
F
O
S
O
HN
S
N
N
1.00
1.01
2.02
2.01
1.02
2.03
3.00
3.05
2.95
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

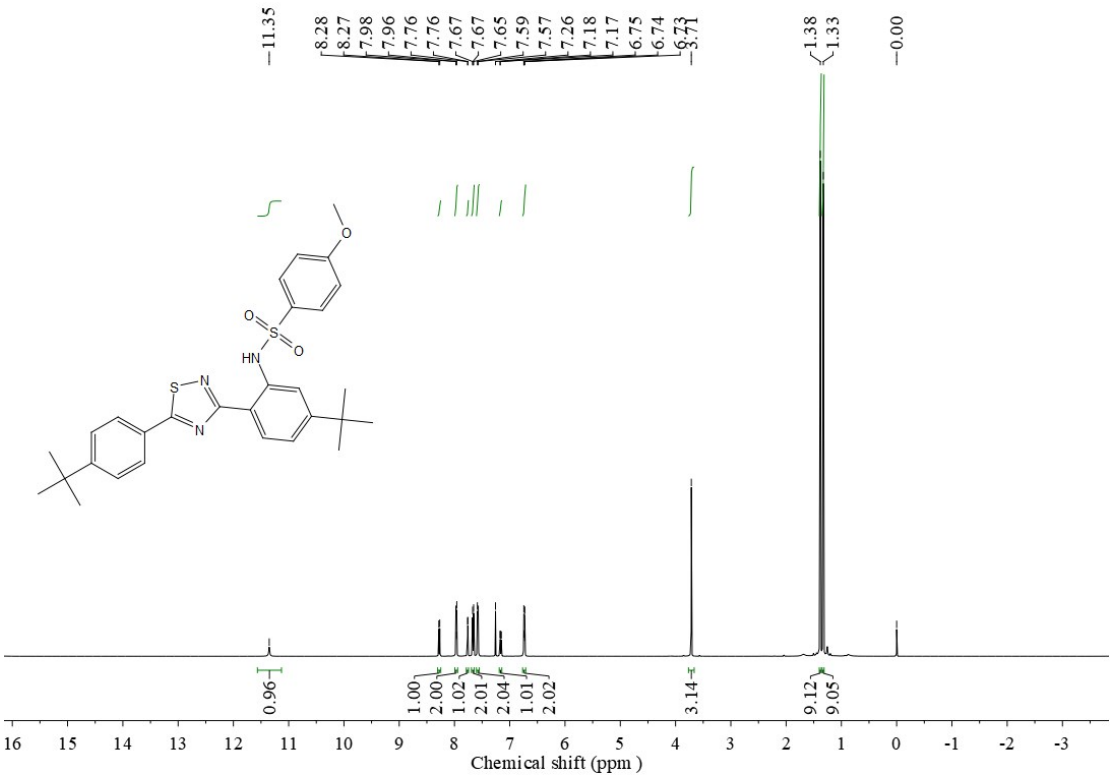

187.47
171.72
166.00
163.97
143.52
142.33
136.52
135.32
130.74
130.26
129.82
129.75
127.46
127.08
125.42
121.47
118.77
116.03
115.85
77.32
77.06
76.81
21.74
F
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

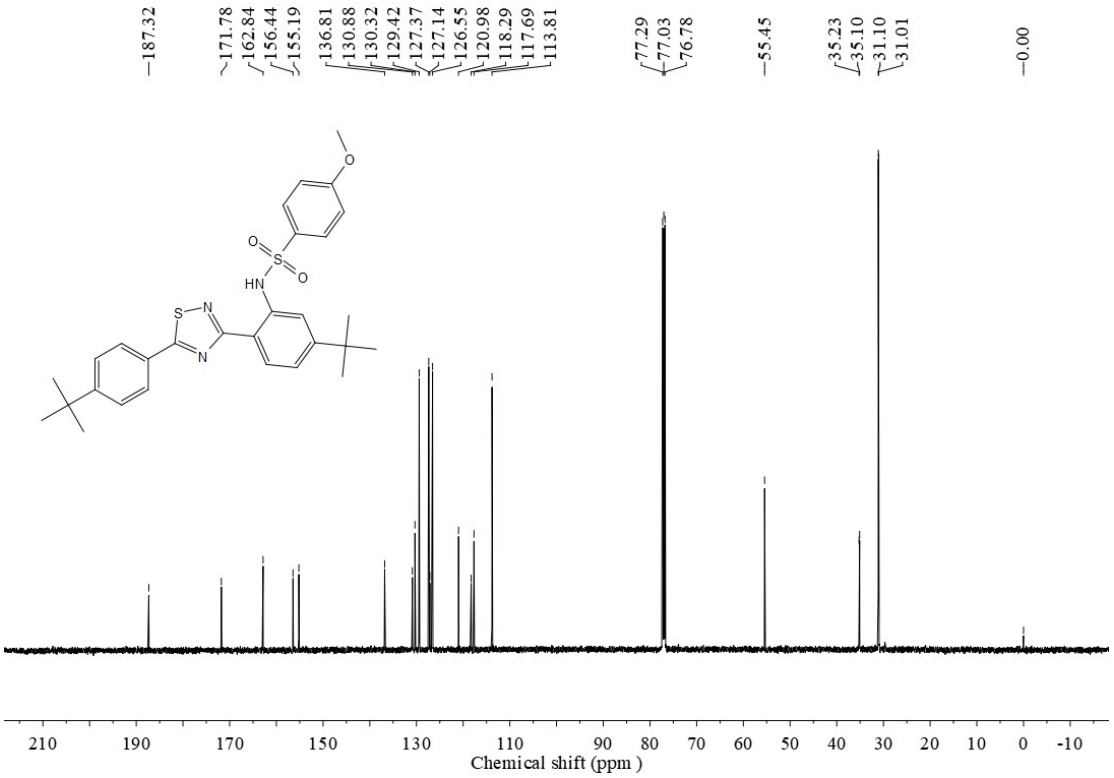

11.29
8.19
8.17
7.83
7.81
7.56
7.55
7.55
7.54
7.54
7.53
7.48
7.28
7.27
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.15
6.93
6.93
6.92
2.37
2.31
Cl
O
S
O
HN
S
N
N
1.00
1.01
2.01
3.03
2.01
2.02
1.00
3.01
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

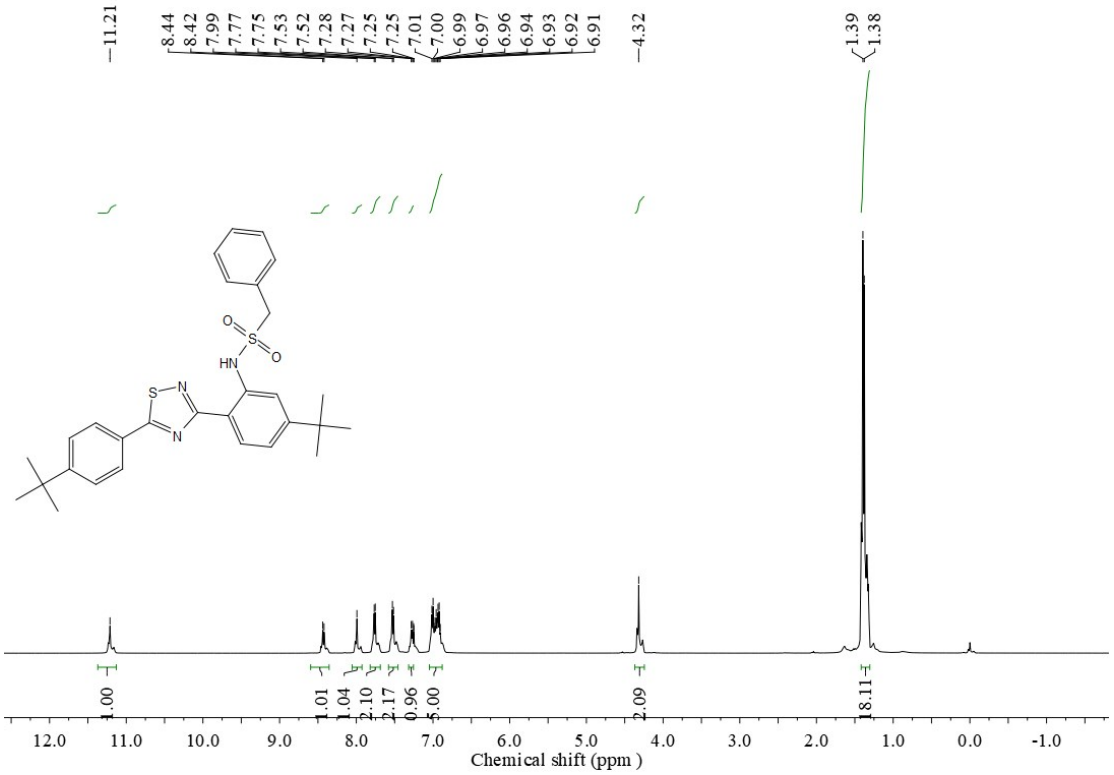

187.51
171.71
143.52
142.36
139.19
137.77
136.41
130.76
130.26
129.00
128.49
127.47
127.09
125.50
121.47
118.80
77.30
77.04
76.79
21.75
21.74
Cl
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

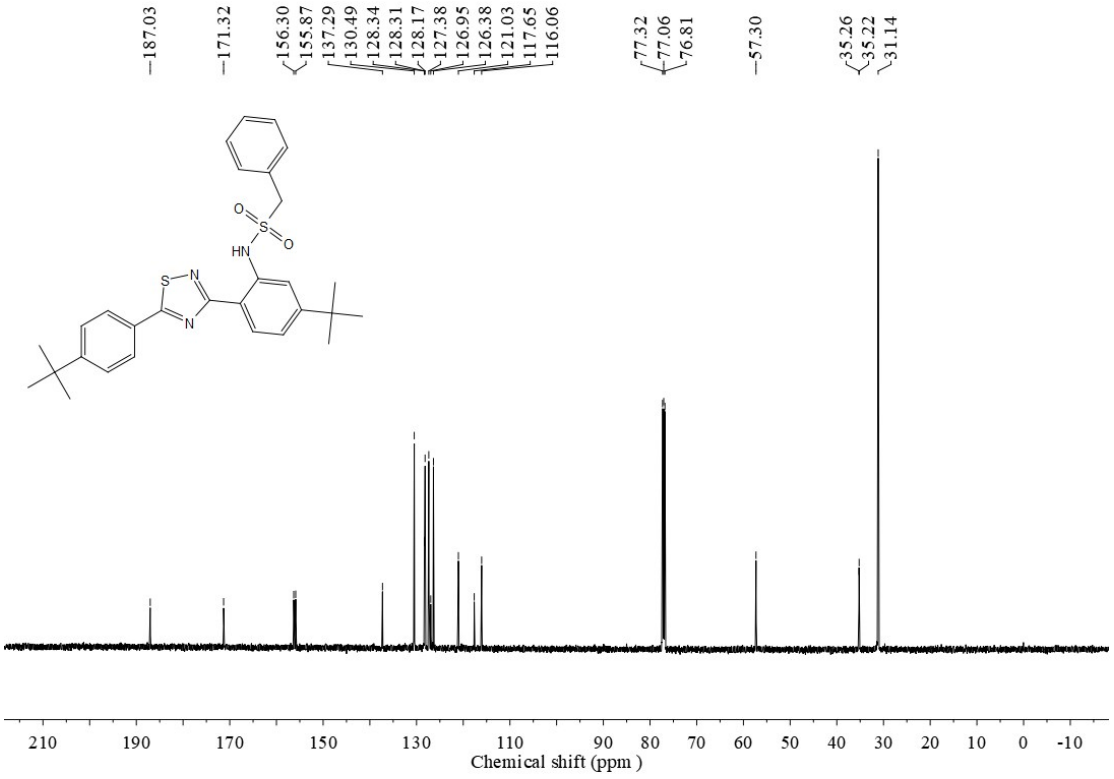

11.31
8.20
8.18
7.90
7.89
7.88
7.88
7.68
7.67
7.51
7.49
7.49
7.45
7.43
7.18
7.10
7.10
7.09
7.08
2.13
1.30
1.25
1.00
1.03
2.02
1.07
3.00
1.03
3.04
3.09
9.02
9.07
Chemical shift (ppm)

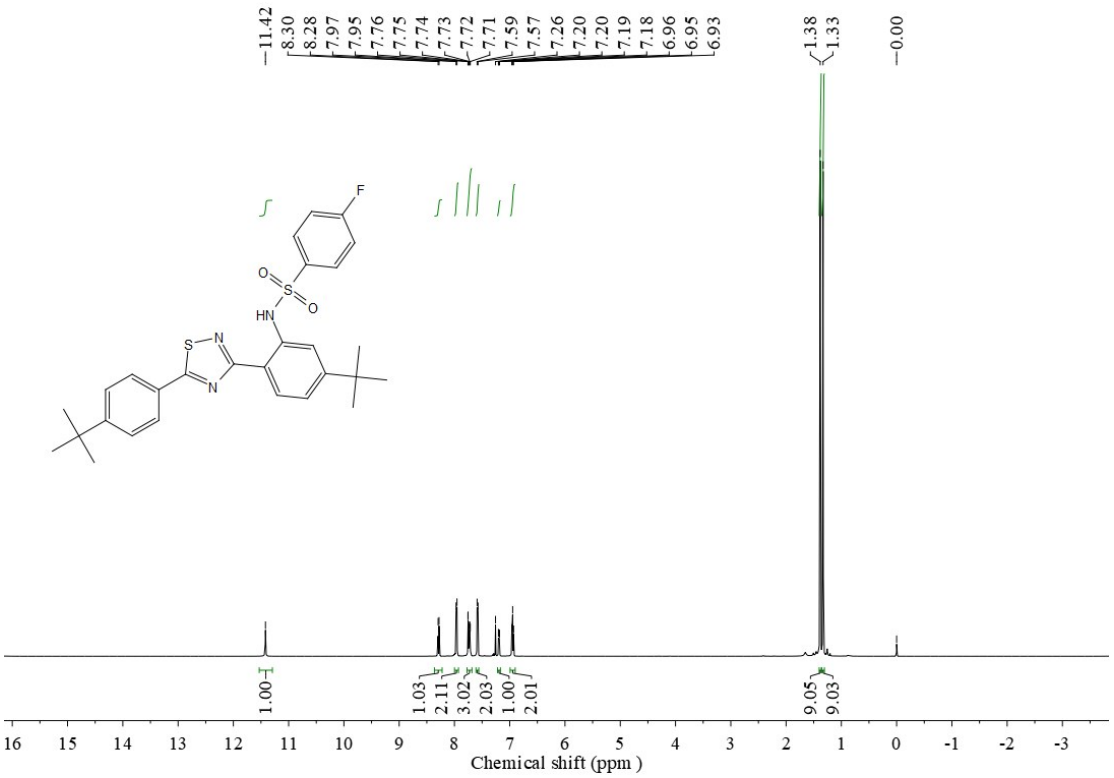

187.33
171.74
156.47
155.20
139.05
138.78
136.71
133.50
130.32
128.53
127.83
127.38
127.13
126.57
124.39
121.07
118.36
117.75
35.25
35.12
31.11
31.01
21.14
Chemical shift (ppm)

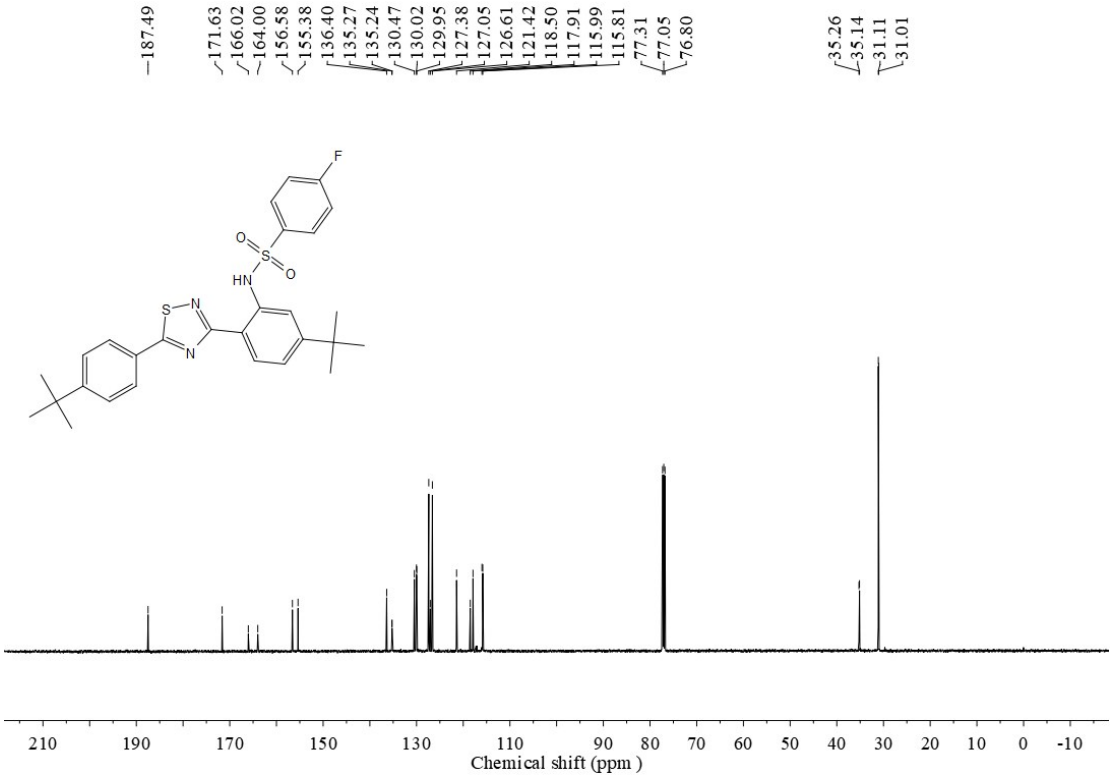

11.35
8.28
8.27
7.98
7.96
7.76
7.76
7.67
7.67
7.65
7.59
7.57
7.26
7.18
7.17
6.75
6.74
6.73
6.71
1.38
1.33
0.00
0.96
1.00
2.00
1.02
2.01
2.04
1.01
2.02
3.14
9.12
9.05
Chemical shift (ppm)

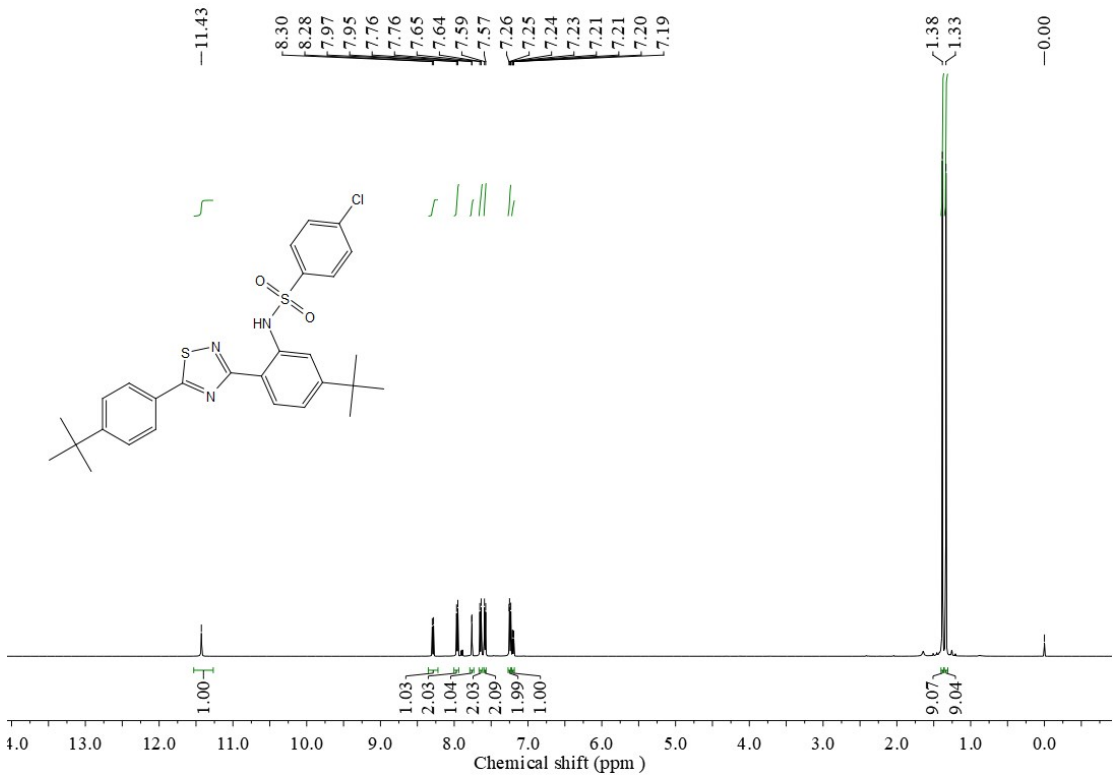

187.32
171.78
162.84
156.44
155.19
136.81
130.88
130.32
129.42
127.37
127.14
126.55
120.98
118.29
117.69
113.81
77.29
77.03
76.78
55.45
35.23
35.10
31.10
31.01
0.00
Chemical shift (ppm)

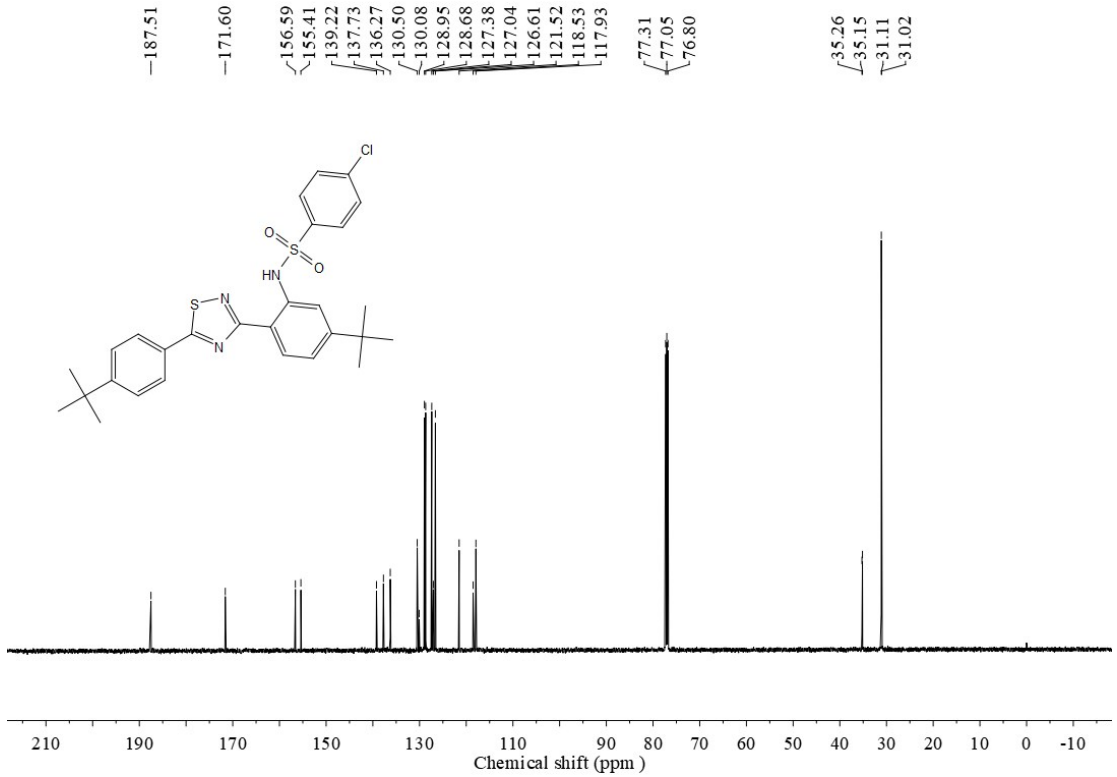

11.21
8.44
8.42
7.99
7.77
7.75
7.53
7.52
7.28
7.27
7.25
7.25
7.01
7.00
6.99
6.97
6.96
6.94
6.93
6.92
6.91
4.32
1.39
1.38
1.00
1.01
1.04
2.10
2.17
0.96
5.00
2.09
18.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical shift (ppm)

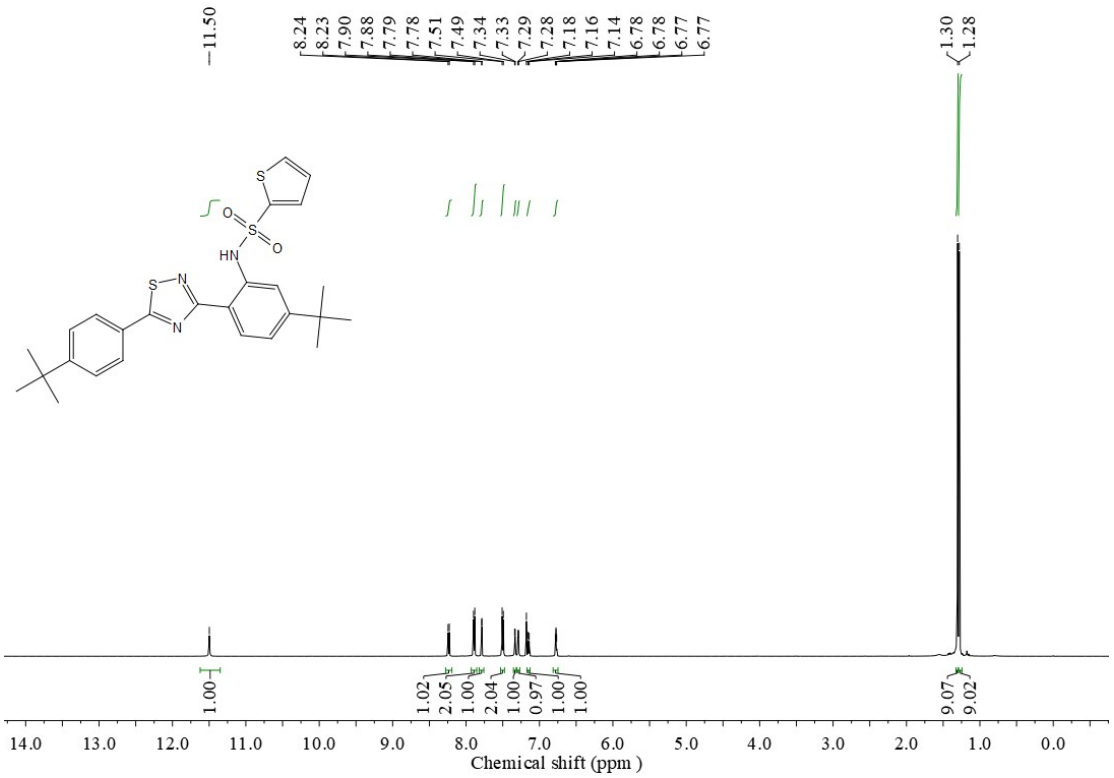

187.03
171.32
156.30
155.87
137.29
130.49
128.34
128.31
128.17
127.38
126.95
126.38
121.03
117.65
116.06
77.32
77.06
76.81
57.30
35.26
35.22
31.14
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

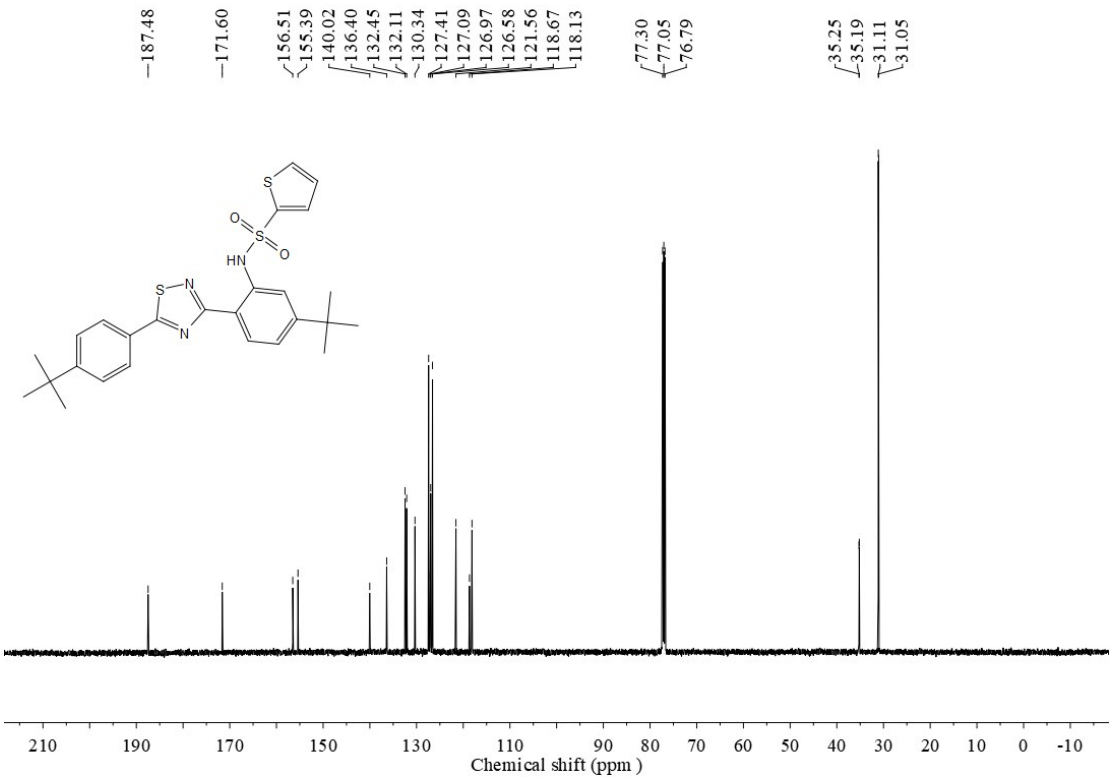

11.42
8.30
8.28
7.97
7.95
7.76
7.75
7.74
7.73
7.72
7.71
7.59
7.57
7.26
7.20
7.20
7.19
7.18
6.96
6.95
6.93
1.38
1.33
0.00
F
O
S
O
HN
S
N
N
1.00
1.03
2.11
3.02
2.03
1.00
2.01
9.05
9.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
Chemical shift (ppm)

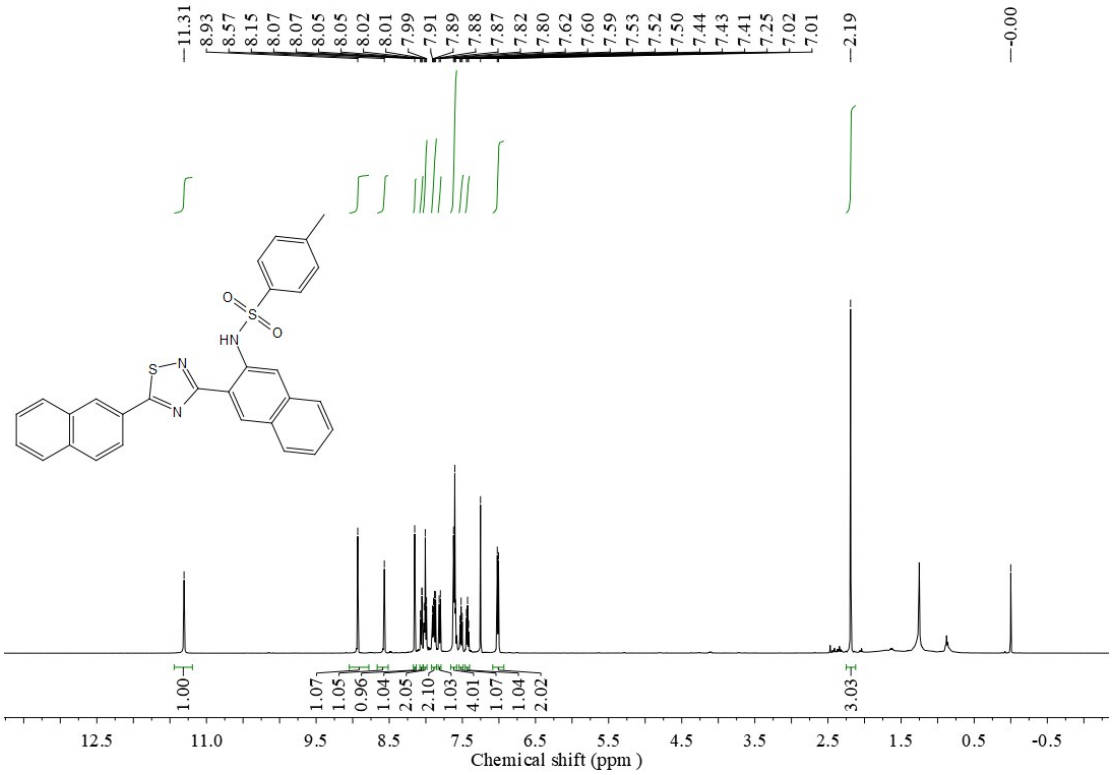

187.49
171.63
166.02
164.00
156.58
155.38
136.40
135.27
135.24
130.47
130.02
129.95
127.38
127.05
126.61
121.42
118.50
117.91
115.99
115.81
77.31
77.05
76.80
35.26
35.14
31.11
31.01
F
O
S
O
HN
S
N
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift (ppm)

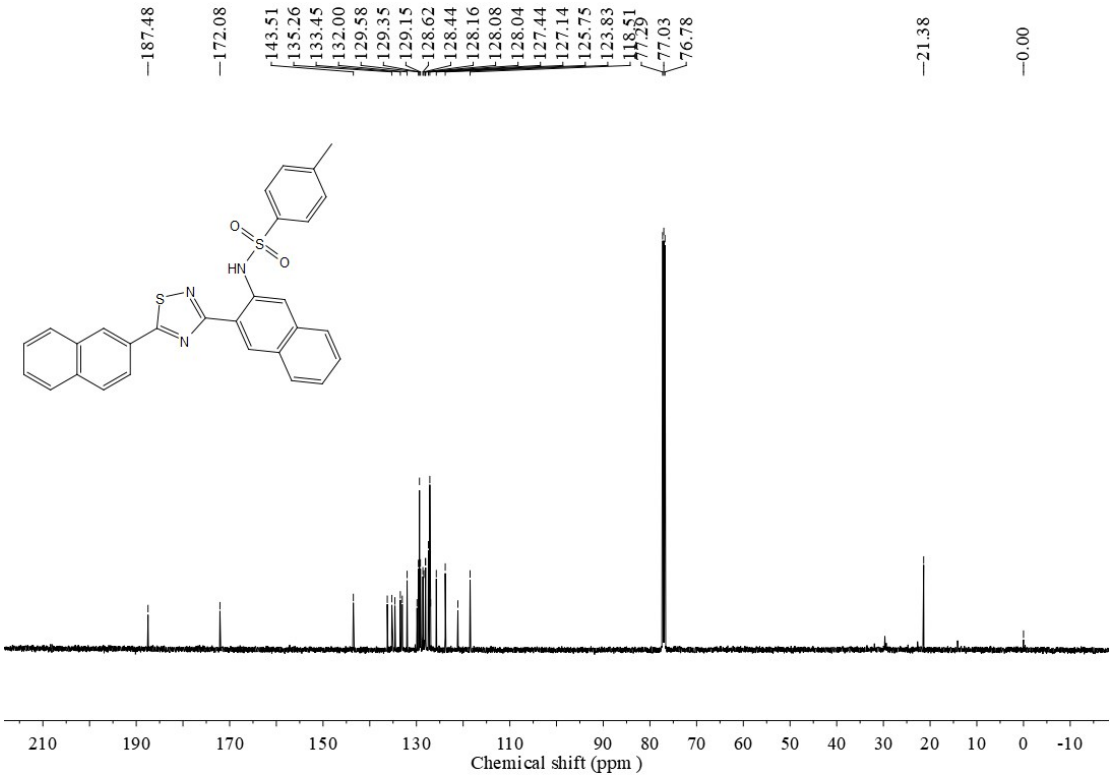

11.43
8.30
8.28
7.97
7.95
7.76
7.76
7.65
7.64
7.59
7.57
7.26
7.25
7.24
7.23
7.21
7.21
7.20
7.19
1.38
1.33
0.00
Cl
O
S
O
HN
S
N
N
1.00
1.03
2.03
1.04
2.03
2.09
1.99
1.00
9.07
9.04
4.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)

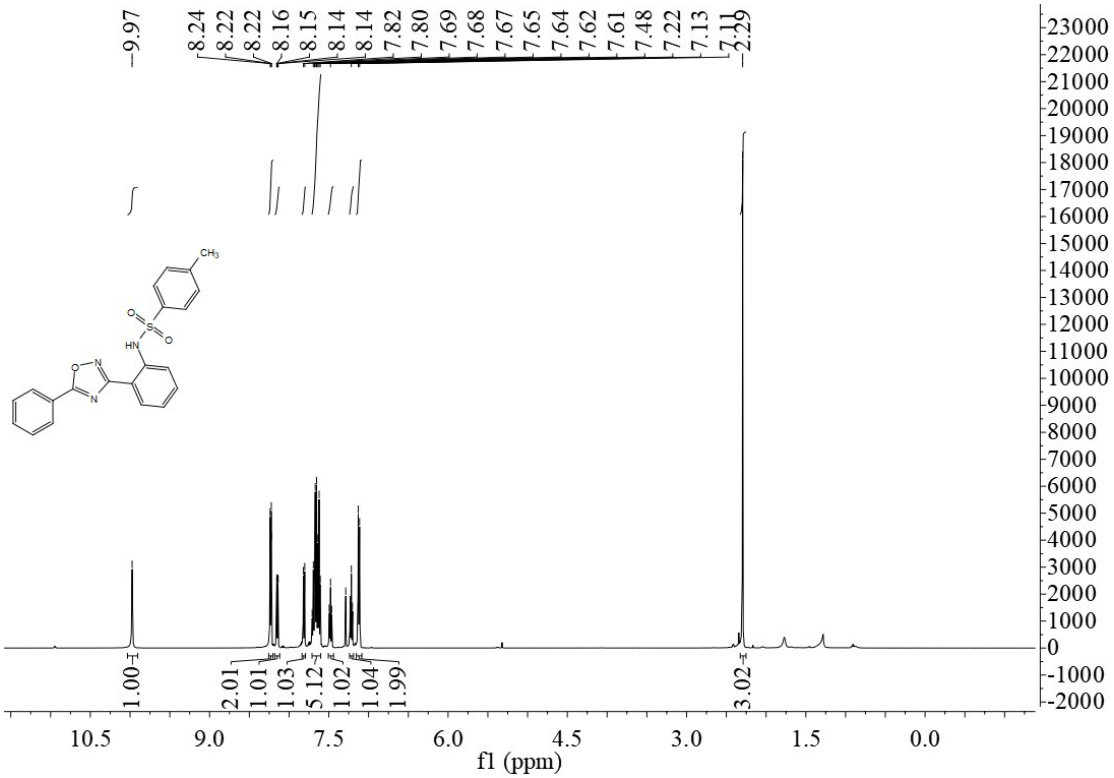

187.51
171.60
156.59
155.41
139.22
137.73
136.27
130.50
130.08
128.95
128.68
127.38
127.04
126.61
121.52
118.53
117.93
77.31
77.05
76.80
35.26
35.15
31.11
31.02
Cl
O
S
O
HN
S
N
N
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

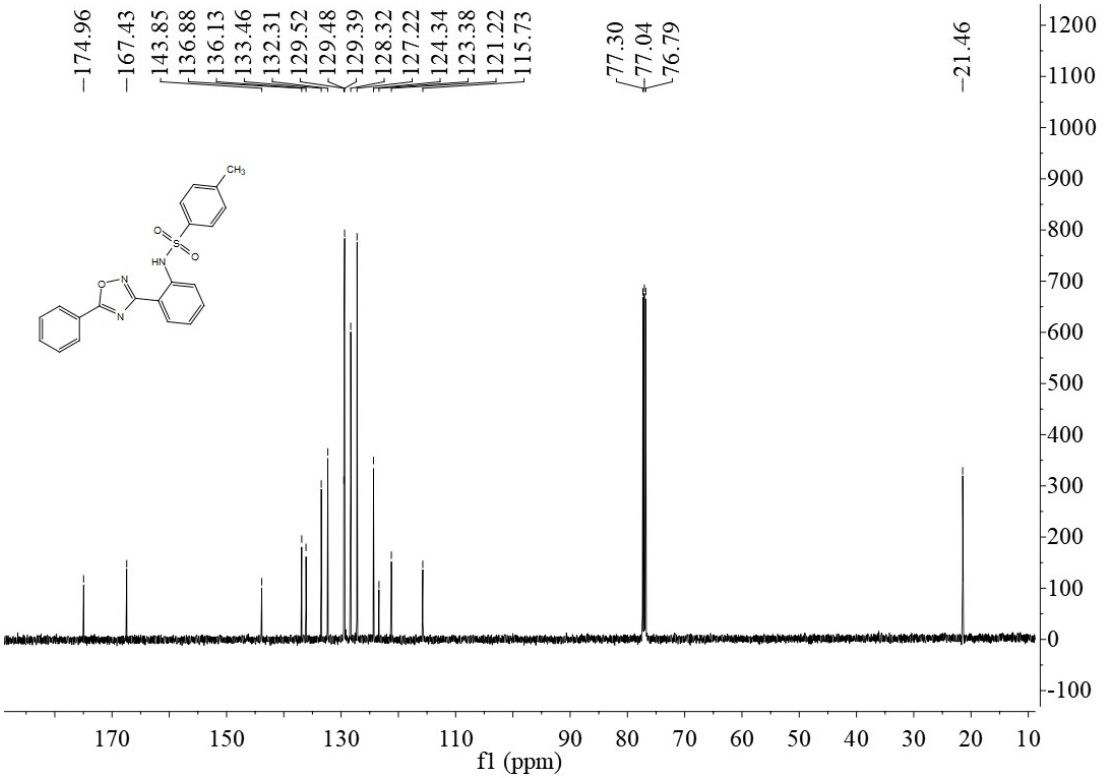

11.50
8.24
8.23
7.90
7.88
7.79
7.78
7.51
7.49
7.34
7.33
7.29
7.28
7.18
7.16
7.14
6.78
6.78
6.77
6.77
1.30
1.28
1.00
1.02
2.05
1.00
2.04
1.00
0.97
1.00
1.00
9.07
9.02
Chemical shift (ppm)

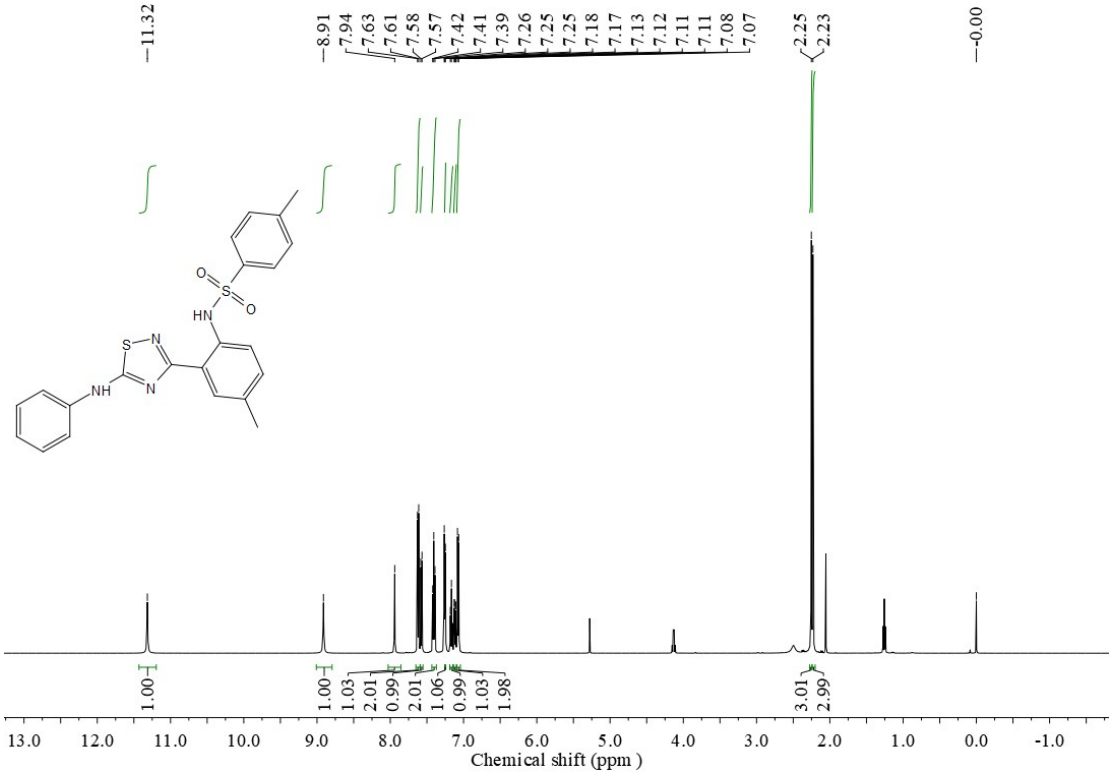

187.48
171.60
156.51
155.39
140.02
136.40
132.45
132.11
130.34
127.41
127.09
126.97
126.58
121.56
118.67
118.13
77.30
77.05
76.79
35.25
35.19
31.11
31.05
Chemical shift (ppm)

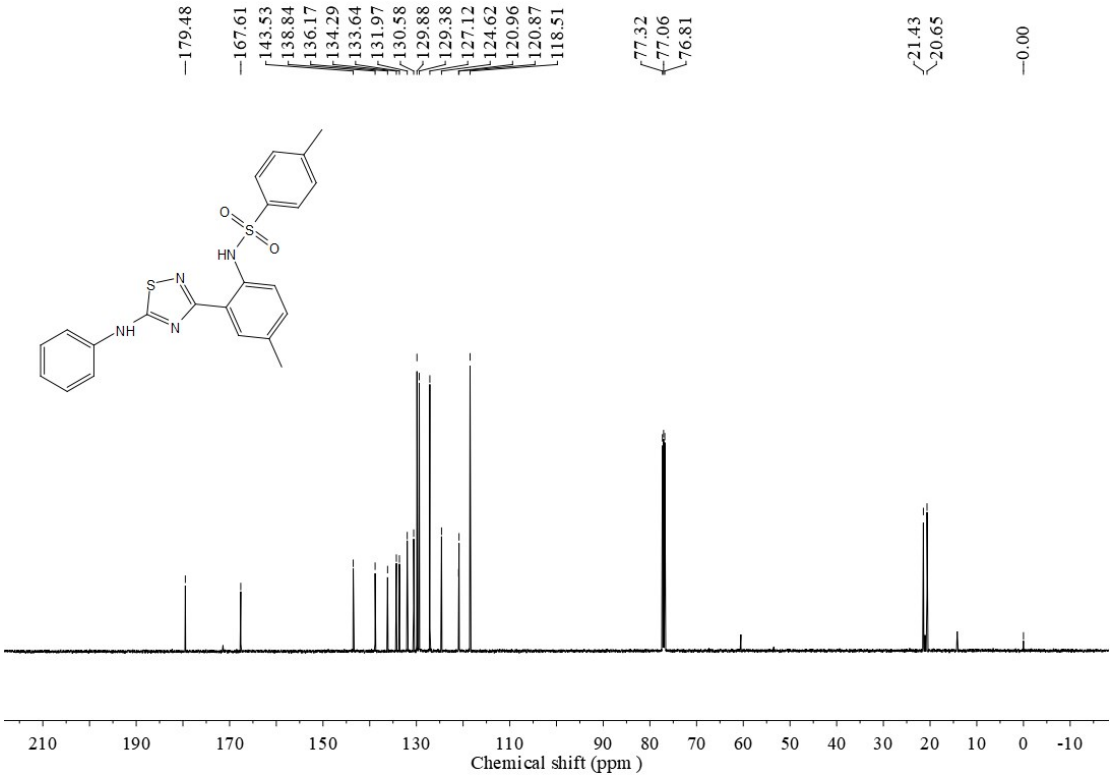

11.31
8.93
8.57
8.15
8.07
8.07
8.05
8.05
8.02
8.01
7.99
7.91
7.89
7.88
7.87
7.82
7.80
7.62
7.60
7.59
7.53
7.52
7.50
7.44
7.43
7.41
7.25
7.02
7.01
2.19
0.00
1.00
1.07
1.05
0.96
1.04
2.05
2.10
1.03
4.01
1.07
1.04
2.02
3.03
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
Chemical shift (ppm)

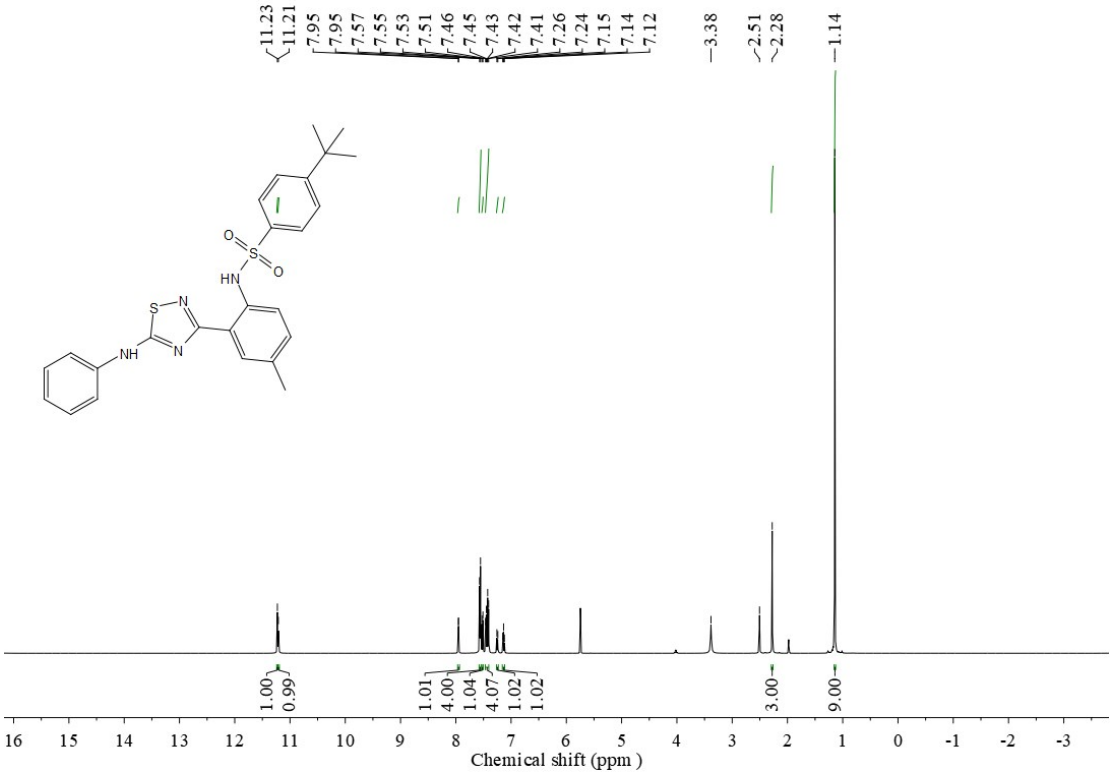

187.48
172.08
143.51
135.26
133.45
132.00
129.58
129.35
129.15
128.62
128.44
128.16
128.08
128.04
127.44
127.14
125.75
123.83
118.51
77.29
77.03
76.78
21.38
0.00
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

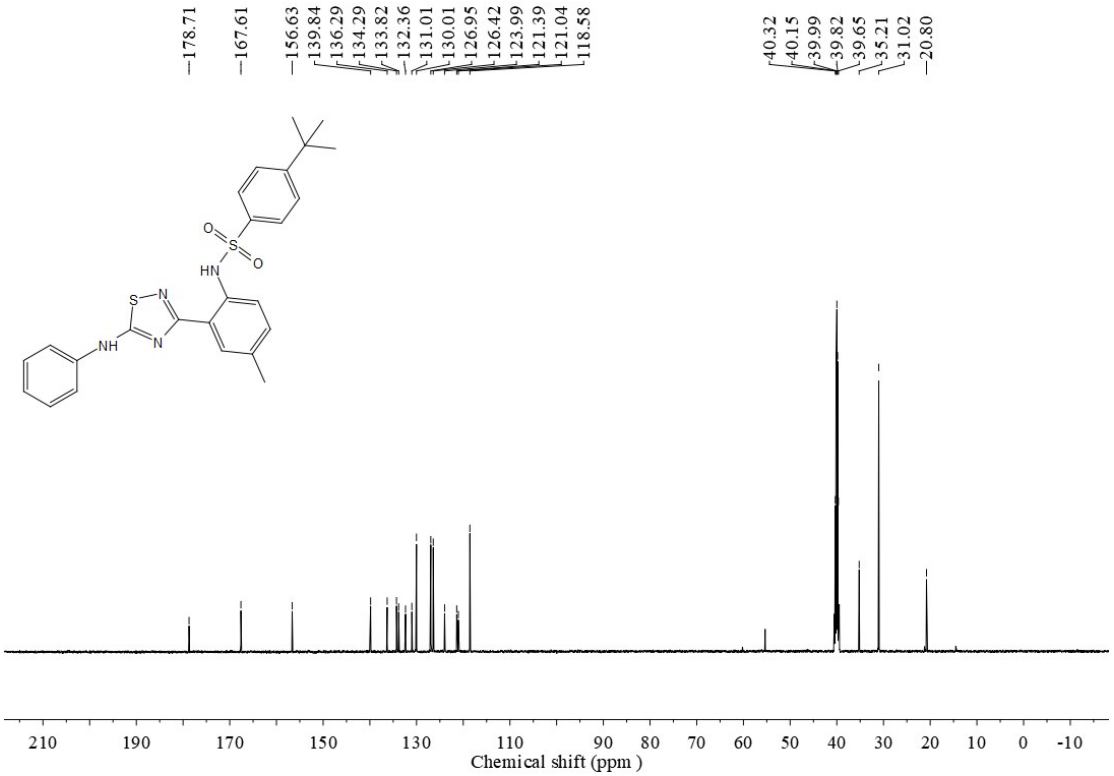

9.97
8.24
8.22
8.22
8.16
8.15
8.14
8.14
7.82
7.80
7.69
7.68
7.67
7.65
7.64
7.62
7.61
7.48
7.22
7.13
7.11
2.29
1.00
2.01
1.01
1.03
5.12
1.02
1.04
1.99
3.02
f1 (ppm)

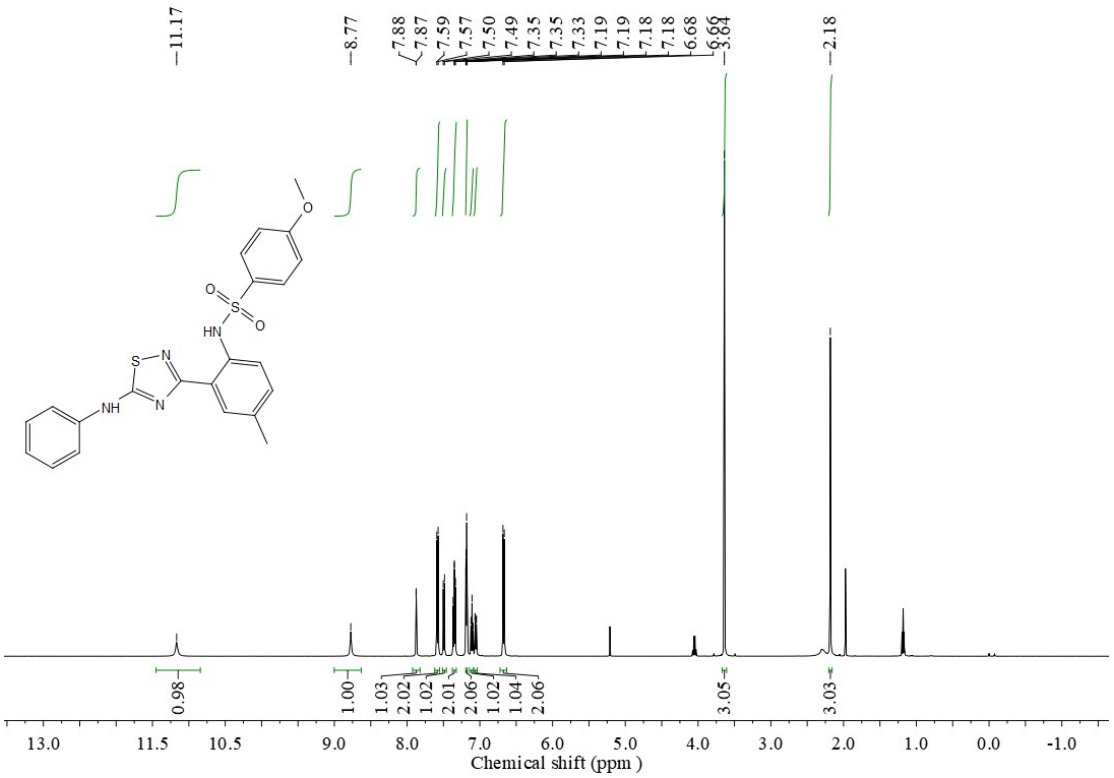

174.96
167.43
143.85
136.88
136.13
133.46
132.31
129.52
129.48
129.39
128.32
127.22
124.34
123.38
121.22
115.73
77.30
77.04
76.79
21.46
f1 (ppm)

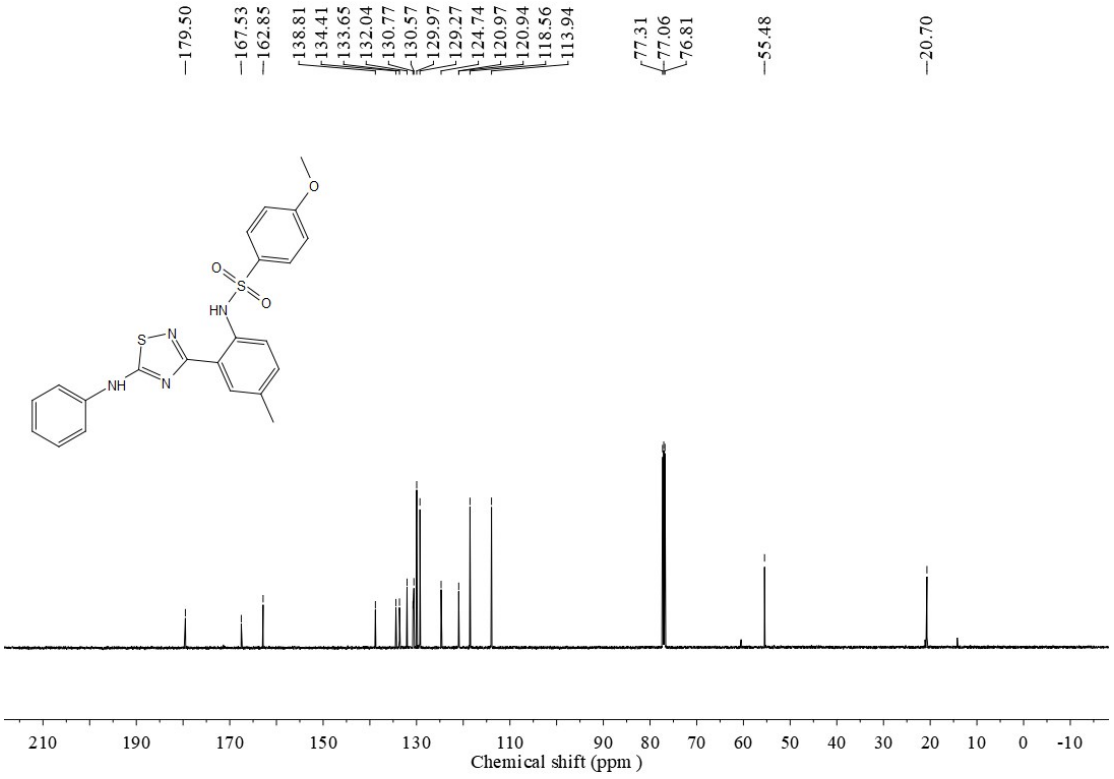

11.32
8.91
7.94
7.63
7.61
7.58
7.57
7.42
7.41
7.39
7.26
7.25
7.25
7.18
7.17
7.13
7.12
7.11
7.11
7.08
7.07
2.25
2.23
0.00
1.00
1.00
1.03
2.01
0.99
2.01
1.06
0.99
1.03
1.98
3.01
2.99
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical shift (ppm)

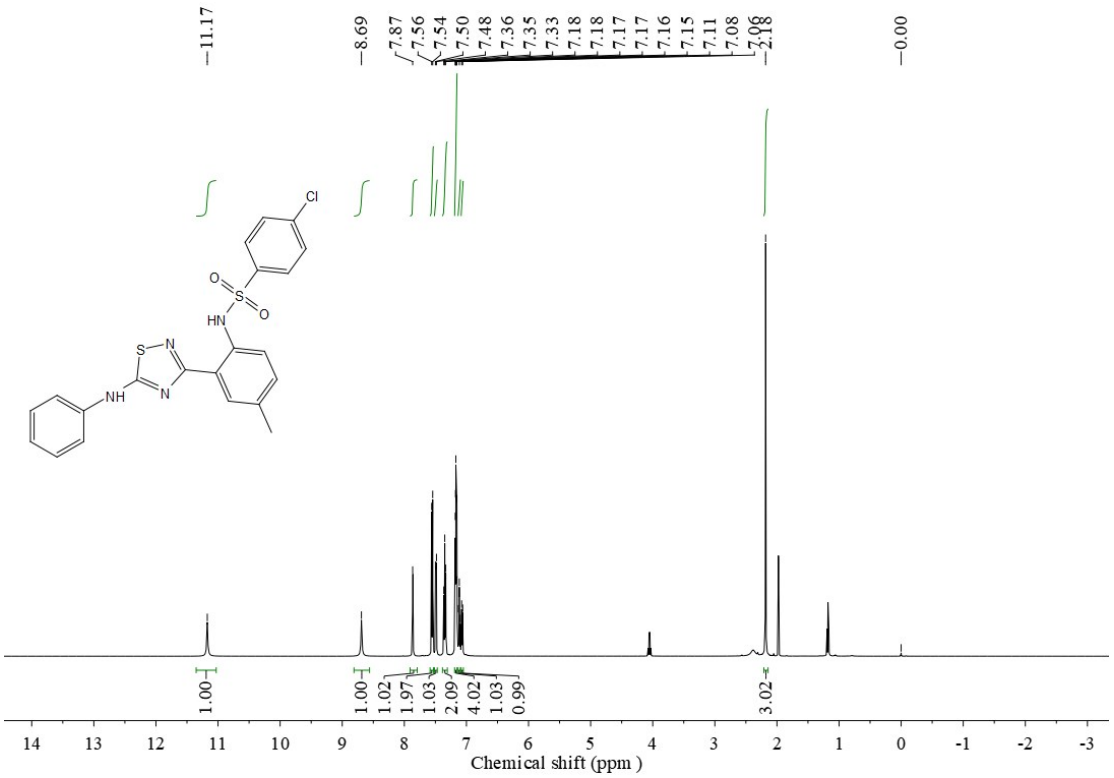

179.48
167.61
143.53
138.84
136.17
134.29
133.64
131.97
130.58
129.88
129.38
127.12
124.62
120.96
120.87
118.51
77.32
77.06
76.81
21.43
20.65
0.00
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

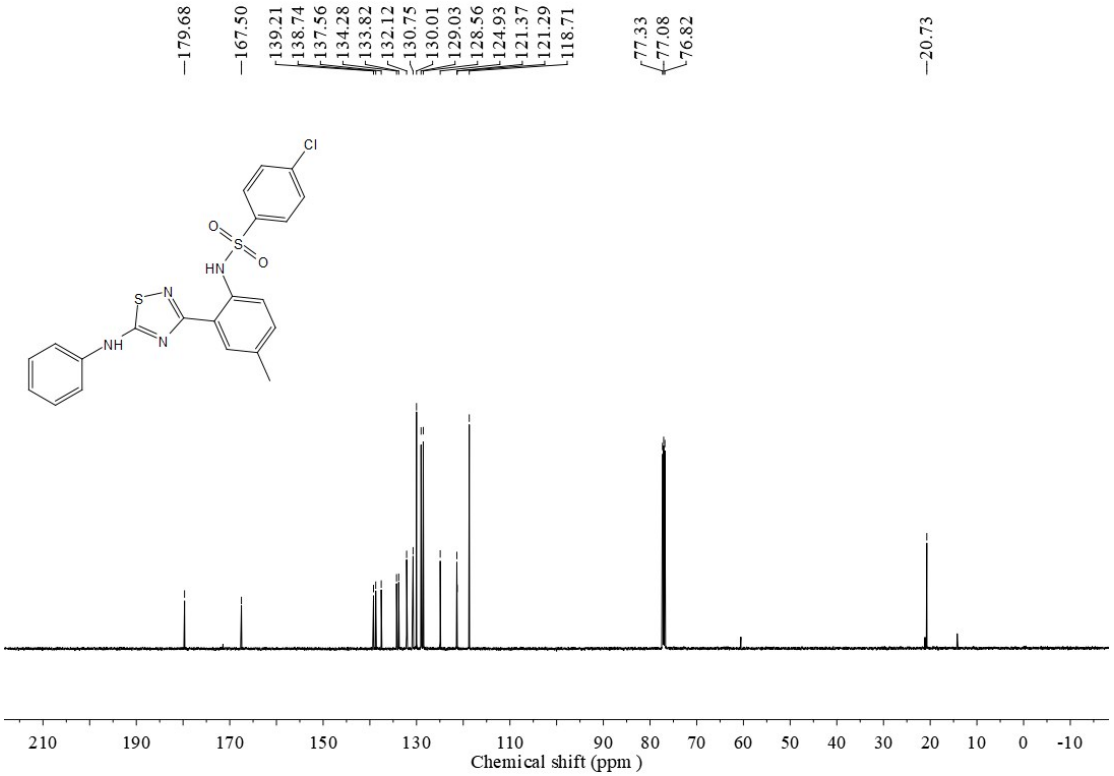

11.23
11.21
7.95
7.95
7.57
7.55
7.53
7.51
7.46
7.45
7.43
7.42
7.41
7.26
7.24
7.15
7.14
7.12
3.38
2.51
2.28
1.14
1.00
0.99
1.01
4.00
1.04
4.07
1.02
1.02
3.00
9.00
Chemical shift (ppm)

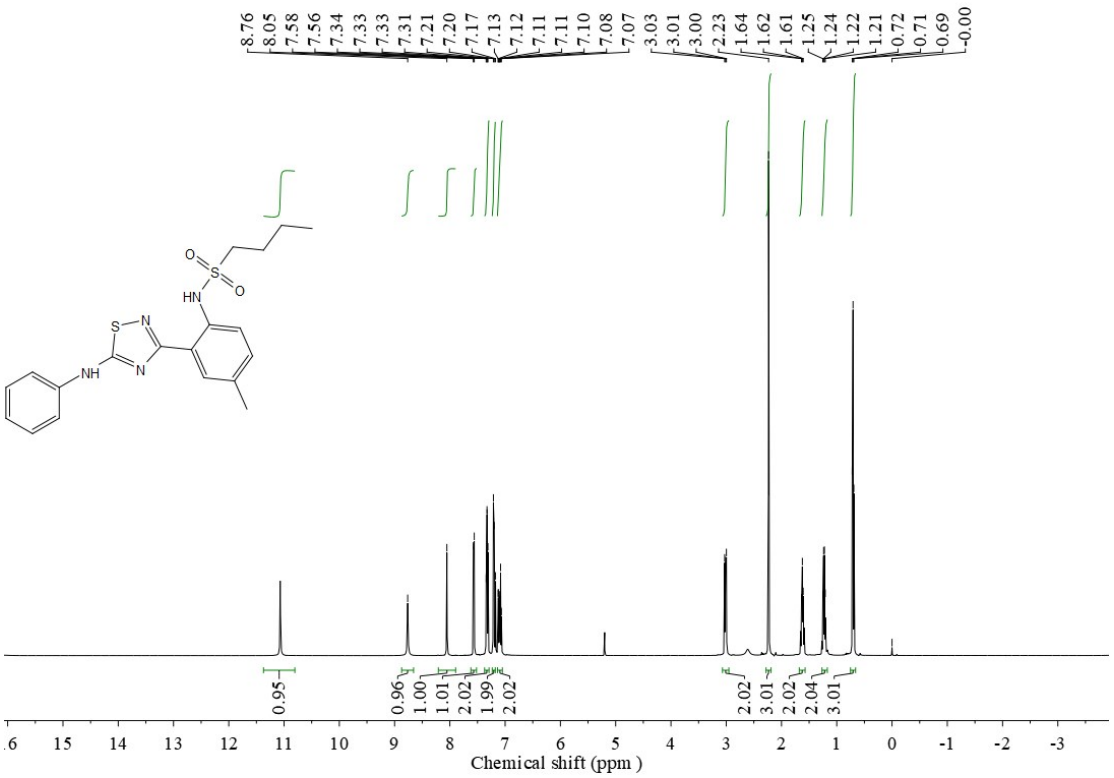

178.71
167.61
156.63
139.84
136.29
134.29
133.82
132.36
131.01
130.01
126.95
126.42
123.99
121.39
121.04
118.58
40.32
40.15
39.99
39.82
39.65
35.21
31.02
20.80
Chemical shift (ppm)

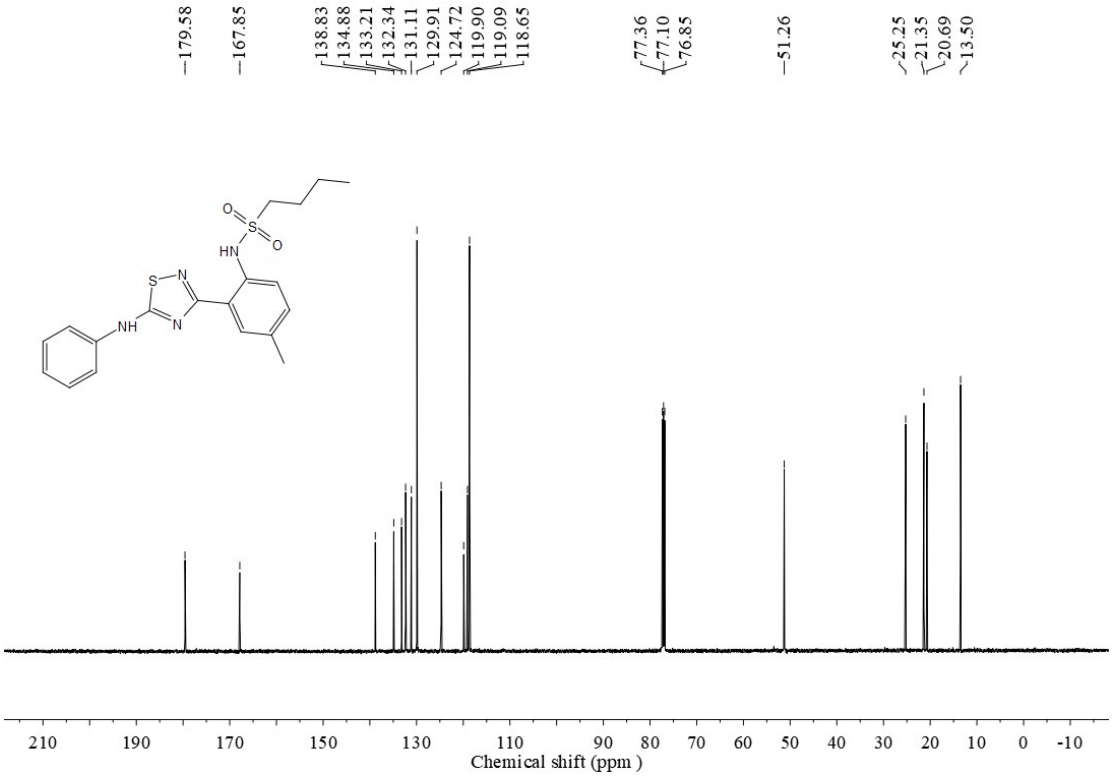

11.17
8.77
7.88
7.87
7.59
7.57
7.50
7.49
7.35
7.35
7.33
7.19
7.19
7.18
7.18
6.68
6.66
3.84
2.18
0.98
1.00
1.03
2.02
1.02
2.01
2.06
1.02
1.04
2.06
3.05
3.03
13.0
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
Chemical shift (ppm)

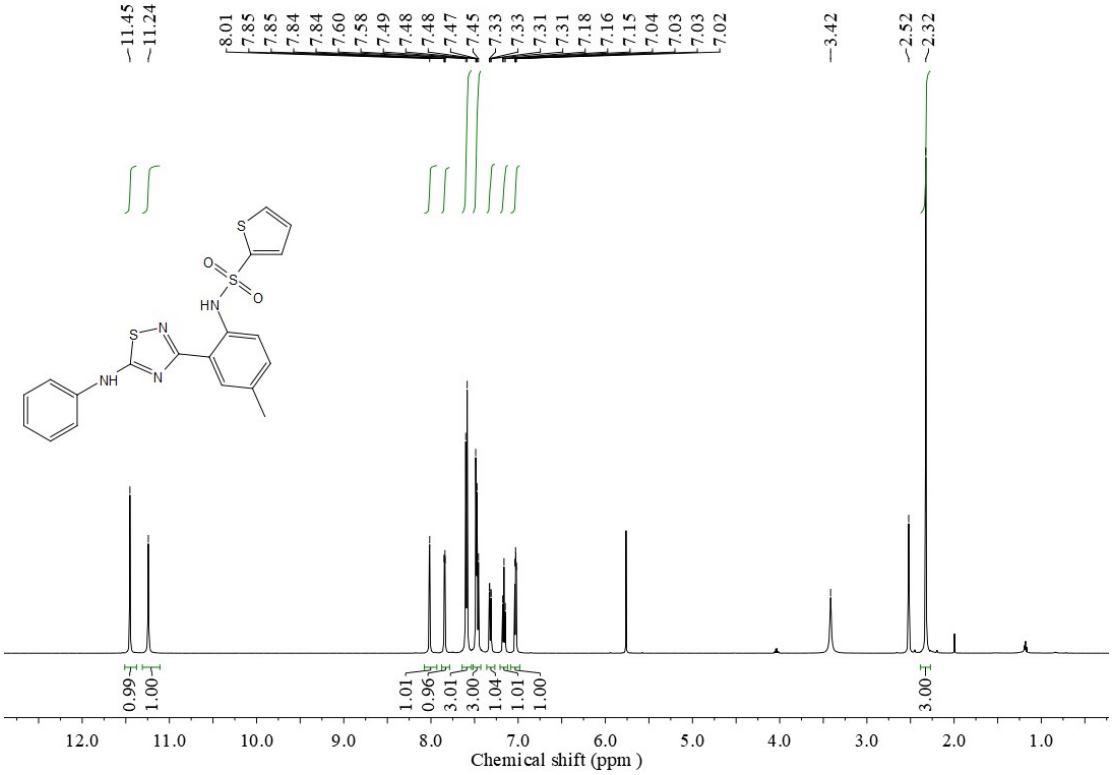

179.50
167.53
162.85
138.81
134.41
133.65
132.04
130.77
130.57
129.97
129.27
124.74
120.97
120.94
118.56
113.94
77.31
77.06
76.81
55.48
20.70
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

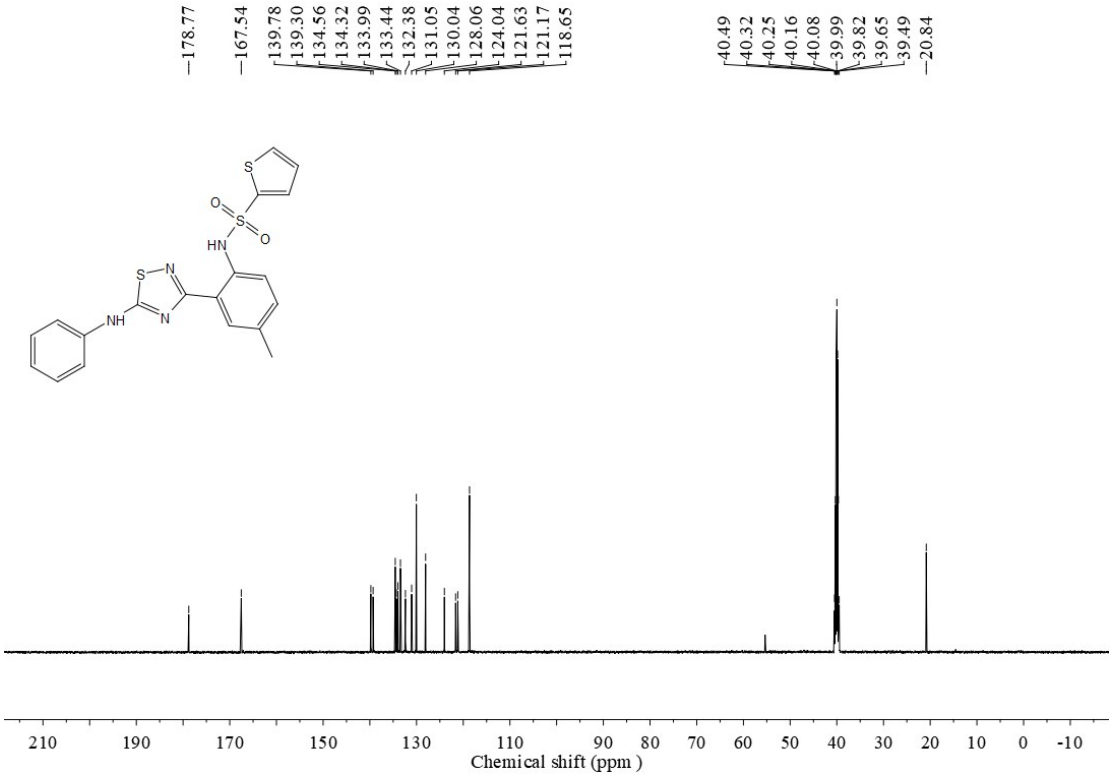

11.17
8.69
7.87
7.56
7.54
7.50
7.48
7.36
7.35
7.33
7.18
7.18
7.17
7.17
7.16
7.15
7.11
7.08
7.06
2.18
0.00
Cl
O
S
O
HN
S
N
N
NH
1.00
1.00
1.02
1.97
1.03
2.09
4.02
1.03
0.99
3.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
Chemical shift (ppm)

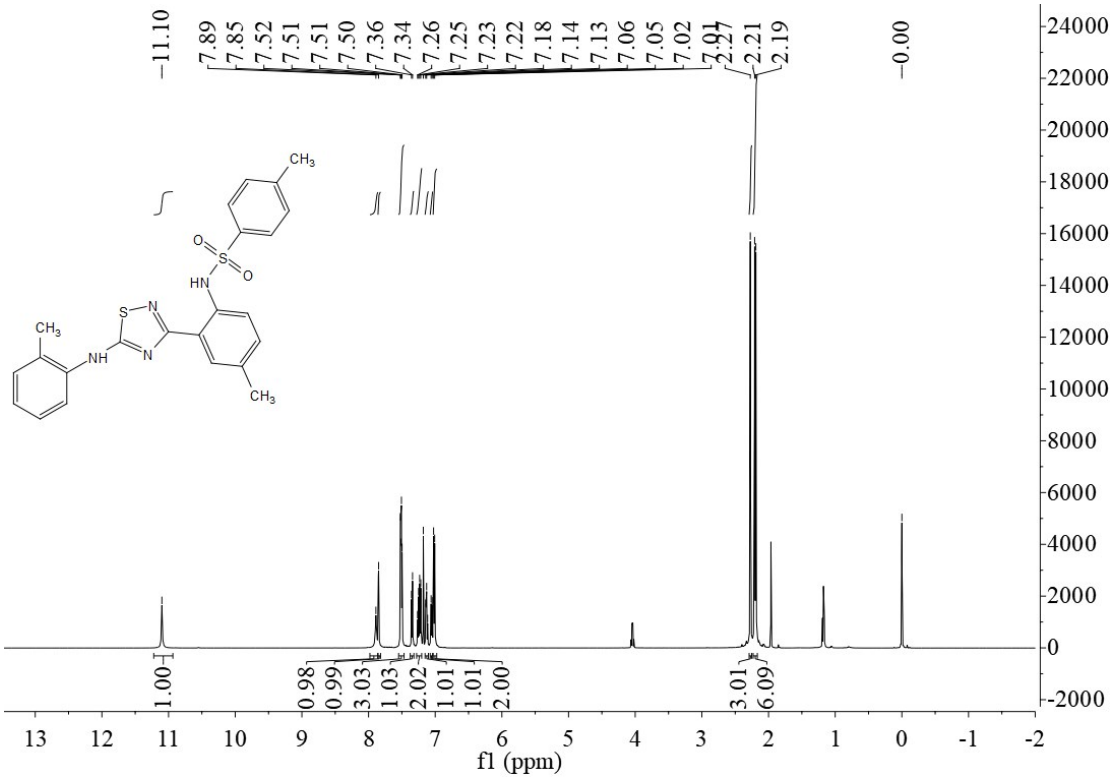

179.68
167.50
139.21
138.74
137.56
134.28
133.82
132.12
130.75
130.01
129.03
128.56
124.93
121.37
121.29
118.71
77.33
77.08
76.82
20.73
Cl
O
S
O
HN
S
N
N
NH
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift (ppm)

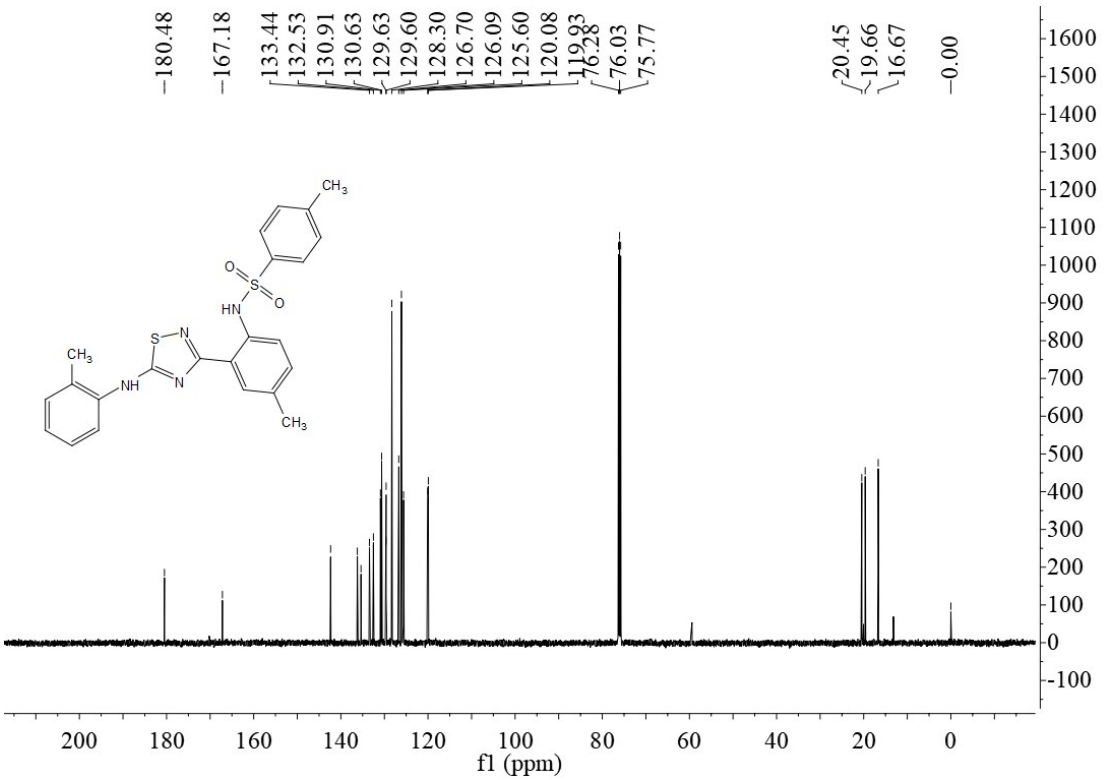

8.76
8.05
7.58
7.56
7.34
7.33
7.33
7.31
7.21
7.20
7.17
7.13
7.12
7.11
7.11
7.10
7.08
7.07
3.03
3.01
3.00
2.23
1.64
1.62
1.61
1.25
1.24
1.22
1.21
0.72
0.71
0.69
-0.00
0.95
0.96
1.00
1.01
2.02
1.99
2.02
2.02
3.01
2.02
2.04
3.01
Chemical shift (ppm)

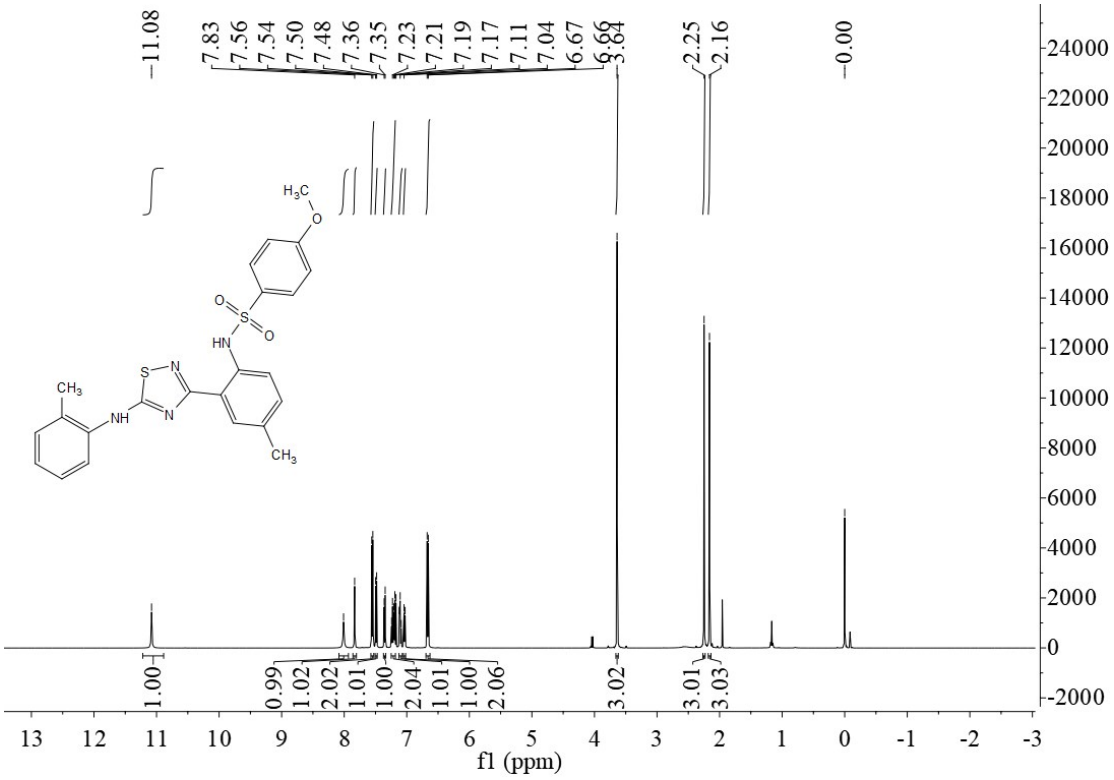

179.58
167.85
138.83
134.88
133.21
132.34
131.11
129.91
124.72
119.90
119.09
118.65
77.36
77.10
76.85
51.26
25.25
21.35
20.69
13.50
Chemical shift (ppm)

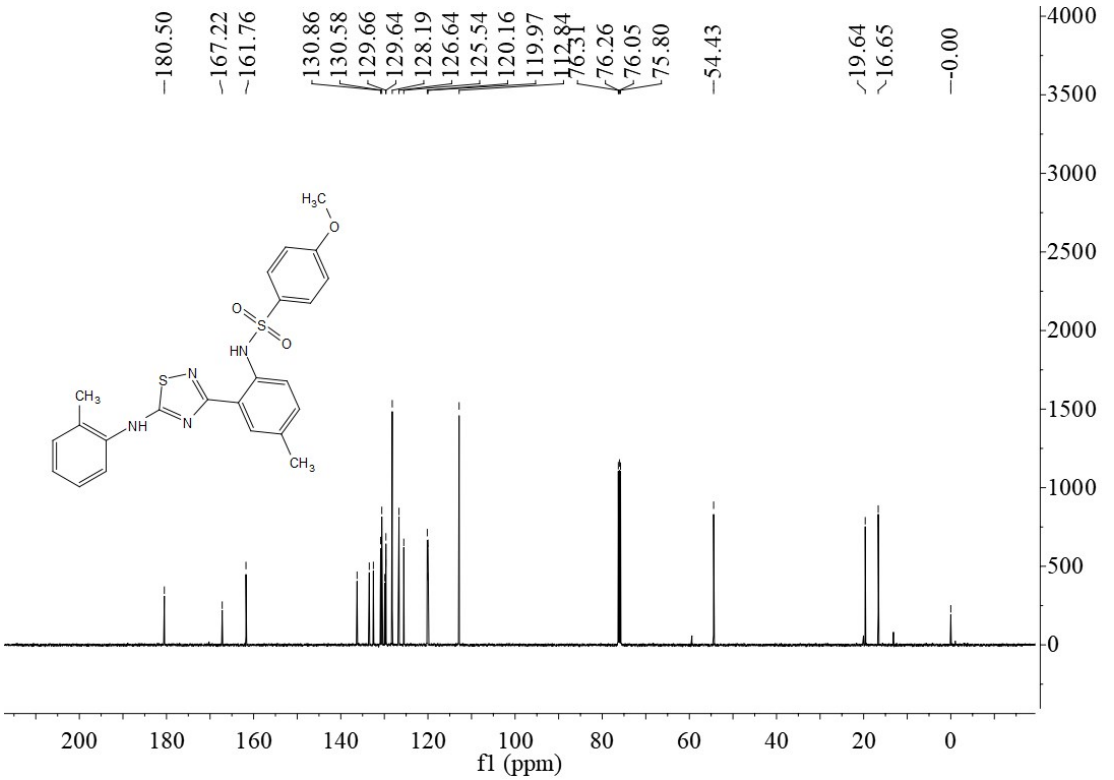

11.45
11.24
8.01
7.85
7.85
7.84
7.84
7.60
7.58
7.49
7.48
7.48
7.47
7.45
7.33
7.33
7.31
7.31
7.18
7.16
7.15
7.04
7.03
7.03
7.02
3.42
2.52
2.32
0.99
1.00
1.01
0.96
3.01
3.00
1.04
1.01
1.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical shift (ppm)

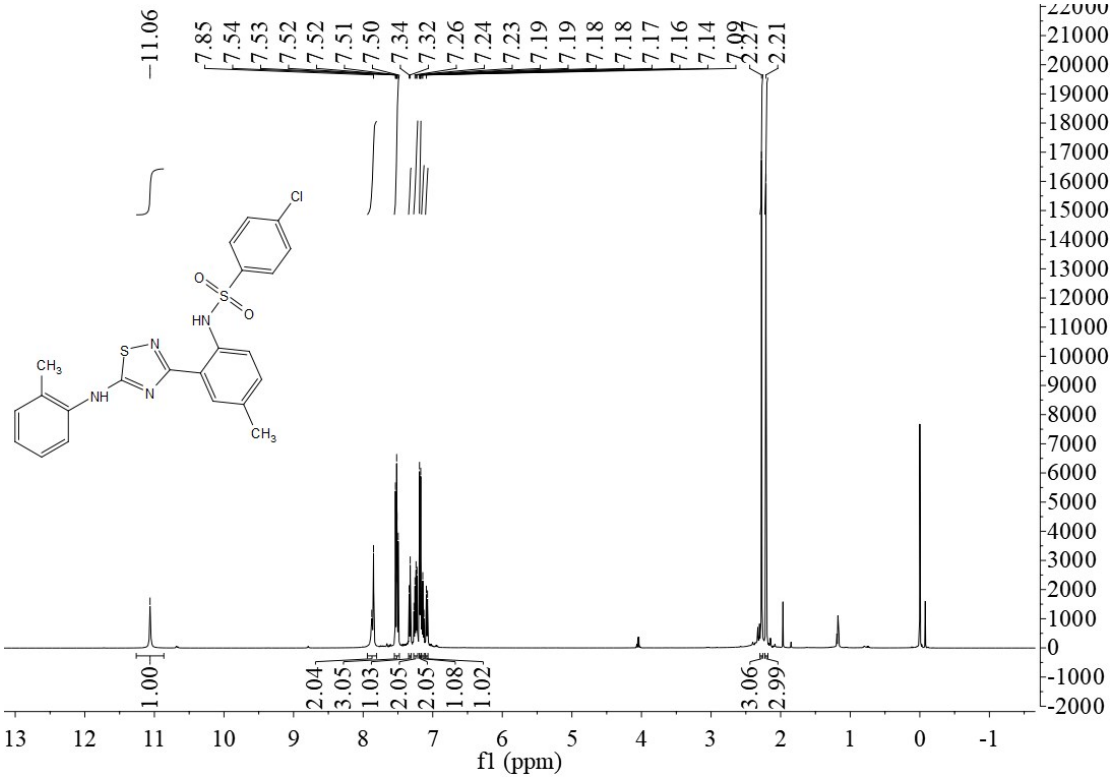

178.77
167.54
139.78
139.30
134.56
134.32
133.99
133.44
132.38
131.05
130.04
128.06
124.04
121.63
121.17
118.65
40.49
40.32
40.25
40.16
40.08
39.99
39.82
39.65
39.49
20.84
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)

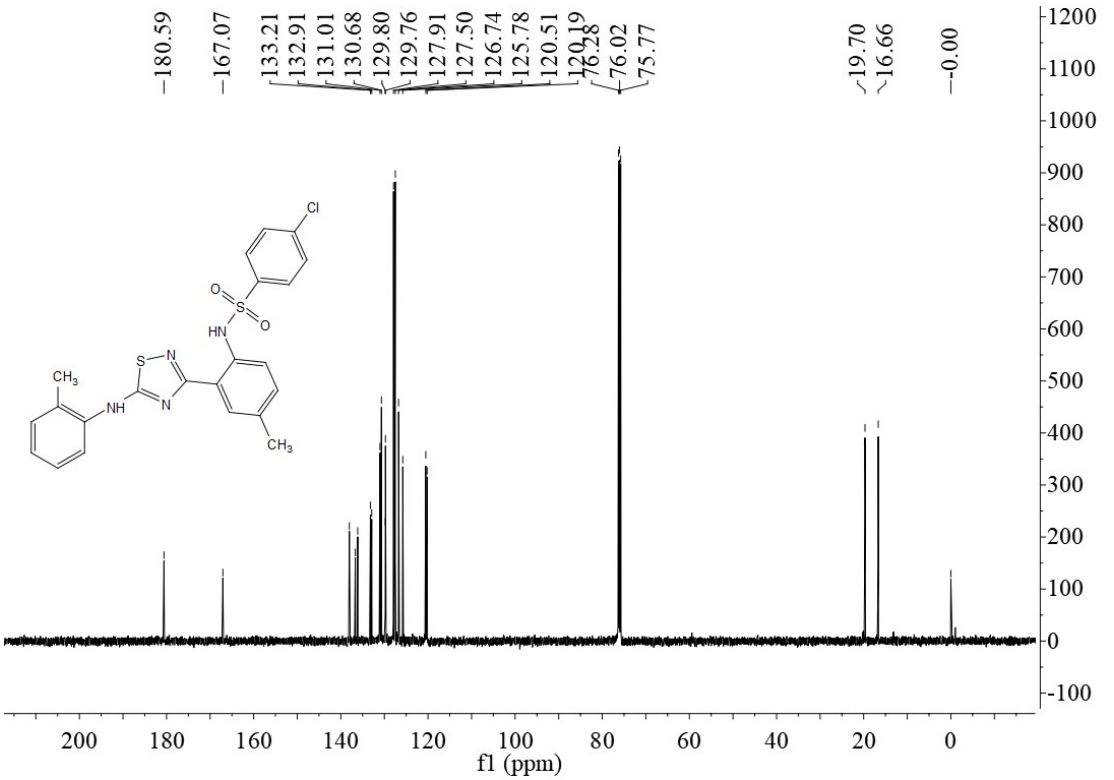

11.10
7.89
7.85
7.52
7.51
7.51
7.50
7.36
7.34
7.26
7.25
7.23
7.22
7.18
7.14
7.13
7.06
7.05
7.02
2.27
2.21
2.19
0.00
1.00
0.98
0.99
3.03
1.03
2.02
1.01
1.01
2.00
3.01
6.09
f1 (ppm)

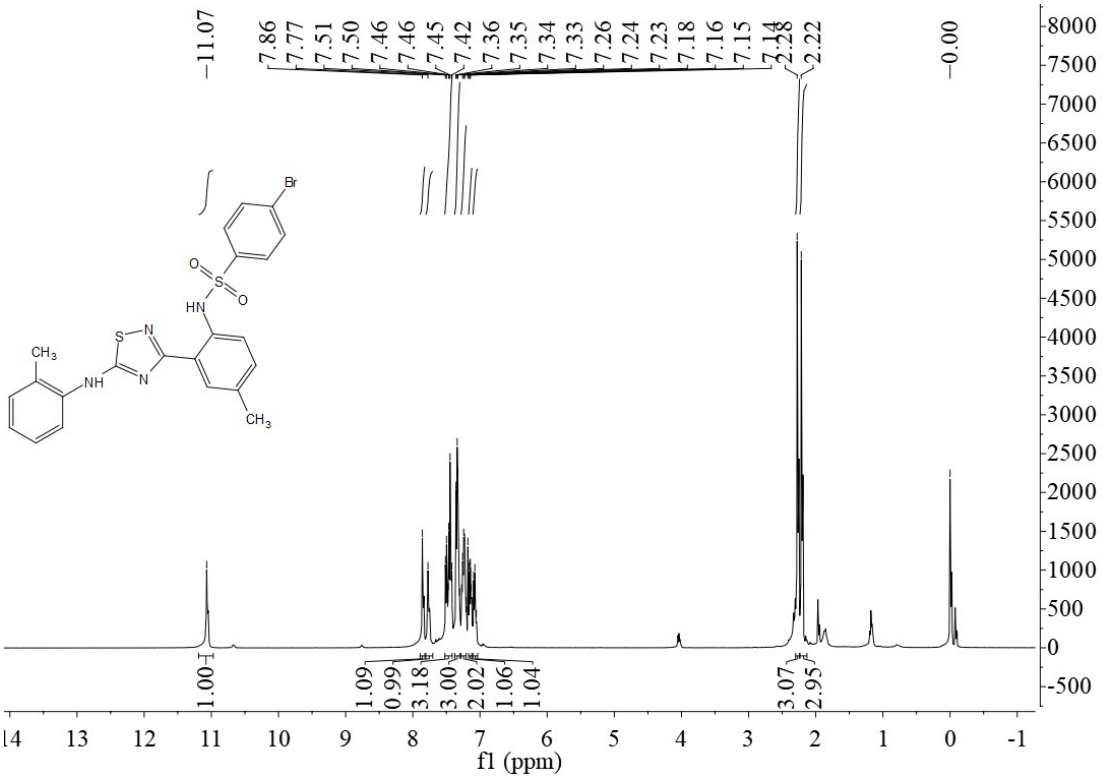

180.48
167.18
133.44
132.53
130.91
130.63
129.63
129.60
128.30
126.70
126.09
125.60
120.08
119.93
76.28
76.03
75.77
20.45
19.66
16.67
0.00
f1 (ppm)

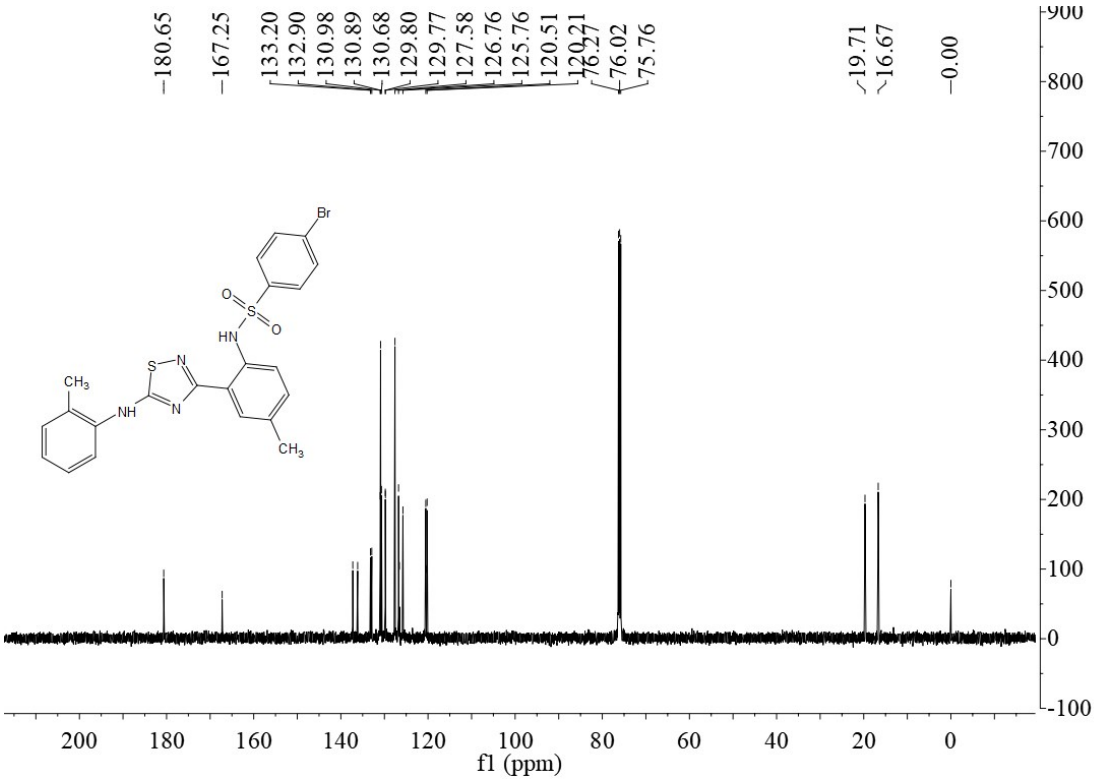

11.08
7.83
7.56
7.54
7.50
7.48
7.36
7.35
7.23
7.21
7.19
7.17
7.11
7.04
6.67
6.66
3.64
2.25
2.16
0.00
1.00
0.99
1.02
2.02
1.01
1.00
2.04
1.01
1.00
2.06
3.02
3.01
3.03
f1 (ppm)

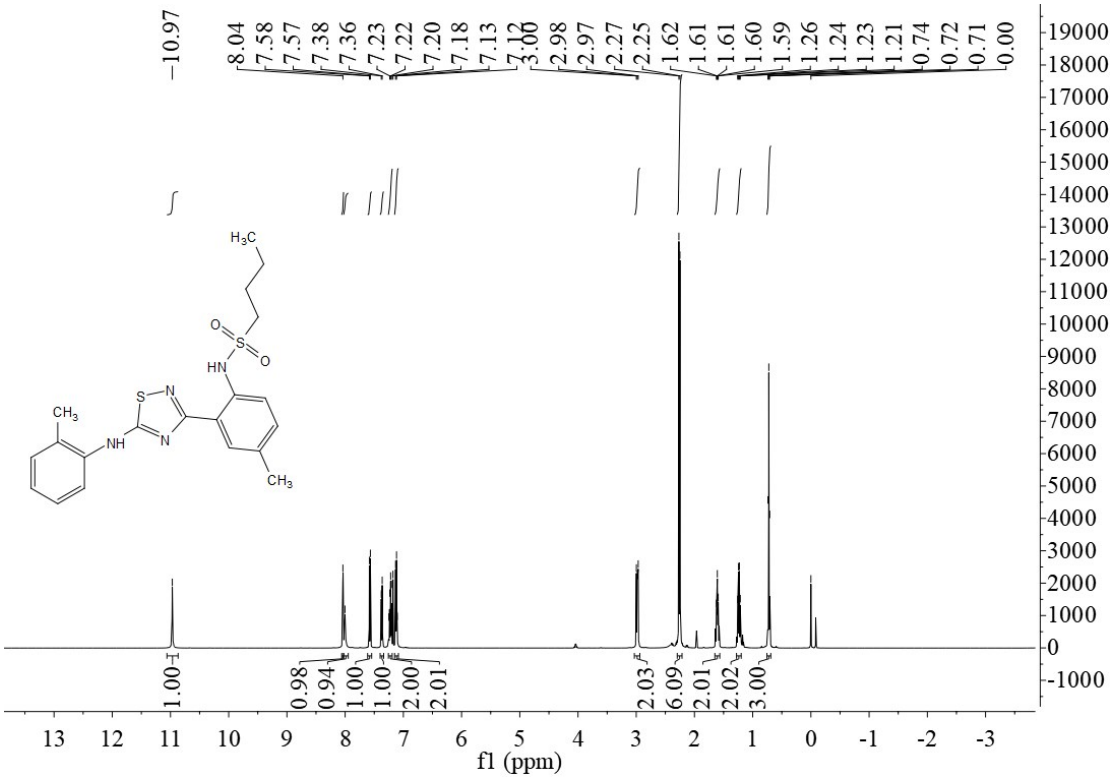

180.50
167.22
161.76
130.86
130.58
129.66
129.64
128.19
126.64
125.54
120.16
119.97
112.84
76.31
76.26
76.05
75.80
54.43
19.64
16.65
0.00
f1 (ppm)

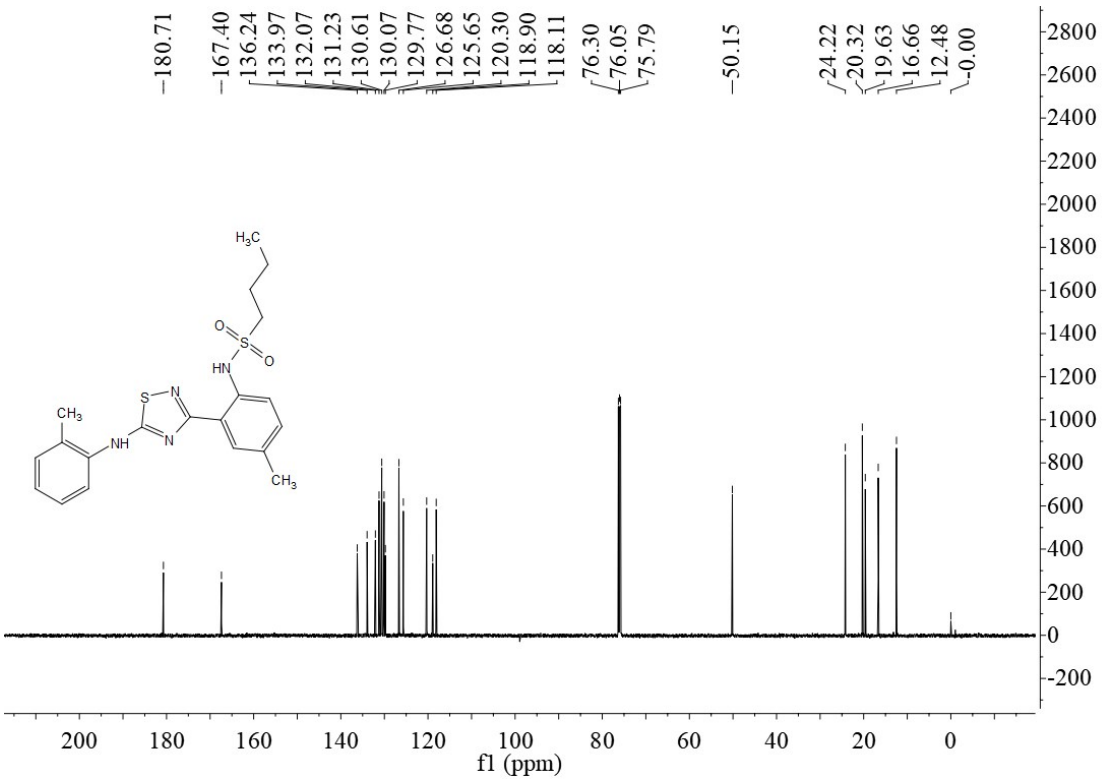

11.06
7.85
7.54
7.53
7.52
7.52
7.51
7.50
7.34
7.32
7.26
7.24
7.23
7.19
7.19
7.18
7.18
7.17
7.16
7.14
7.09
2.27
2.21
1.00
2.04
3.05
1.03
2.05
2.05
1.08
1.02
3.06
2.99
f1 (ppm)

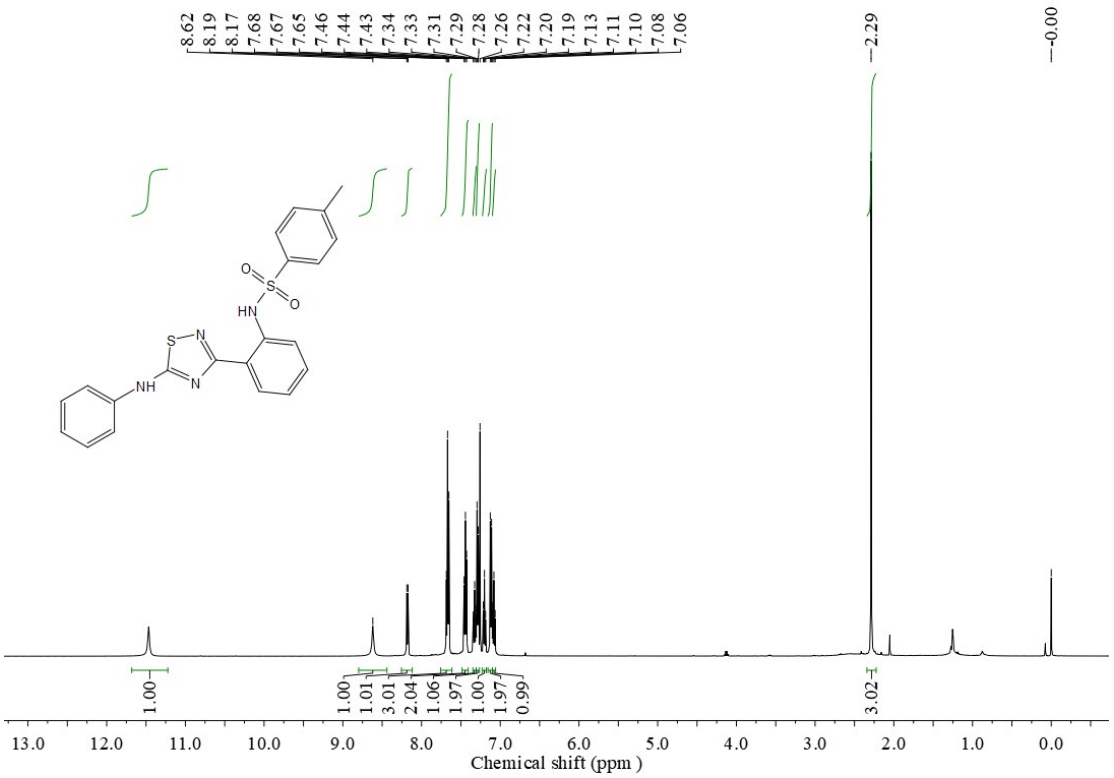

180.59
167.07
133.21
132.91
131.01
130.68
129.80
129.76
127.91
127.50
126.74
125.78
120.51
120.19
76.28
76.02
75.77
19.70
16.66
0.00
f1 (ppm)

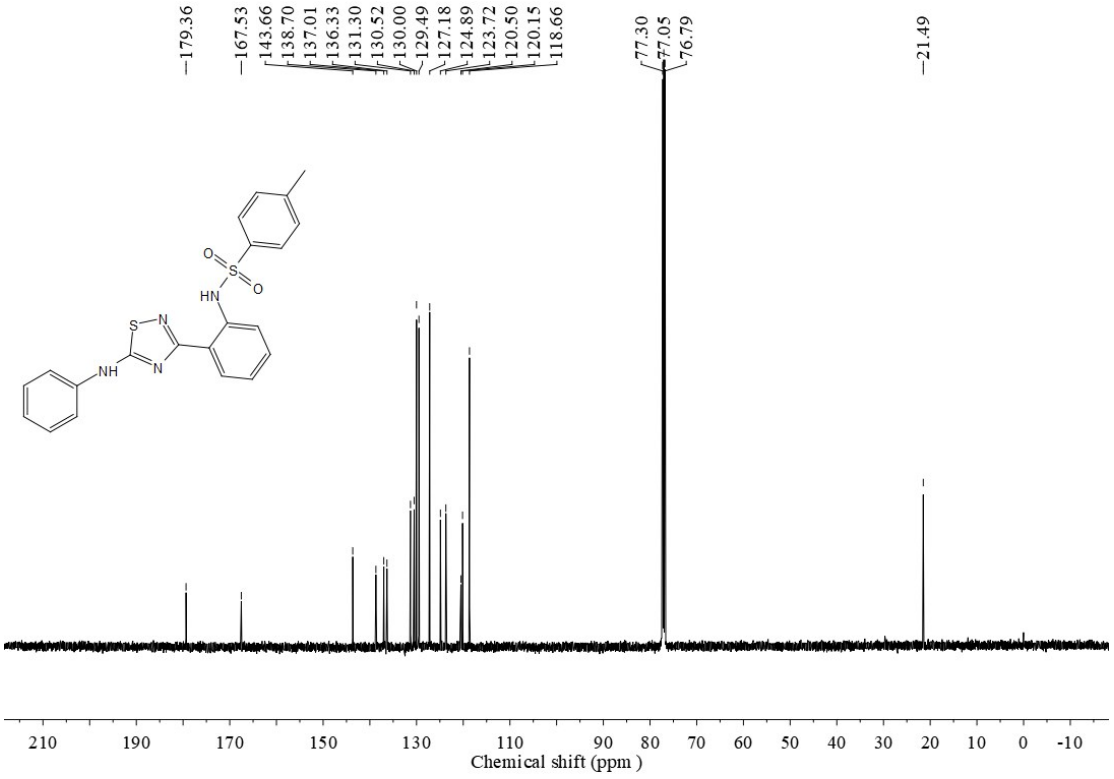

11.07
7.86
7.77
7.51
7.50
7.46
7.46
7.45
7.42
7.36
7.35
7.34
7.33
7.26
7.24
7.23
7.18
7.16
7.15
7.14
2.28
2.22
0.00
1.00
1.09
0.99
3.18
3.00
2.02
1.06
1.04
3.07
2.95
f1 (ppm)

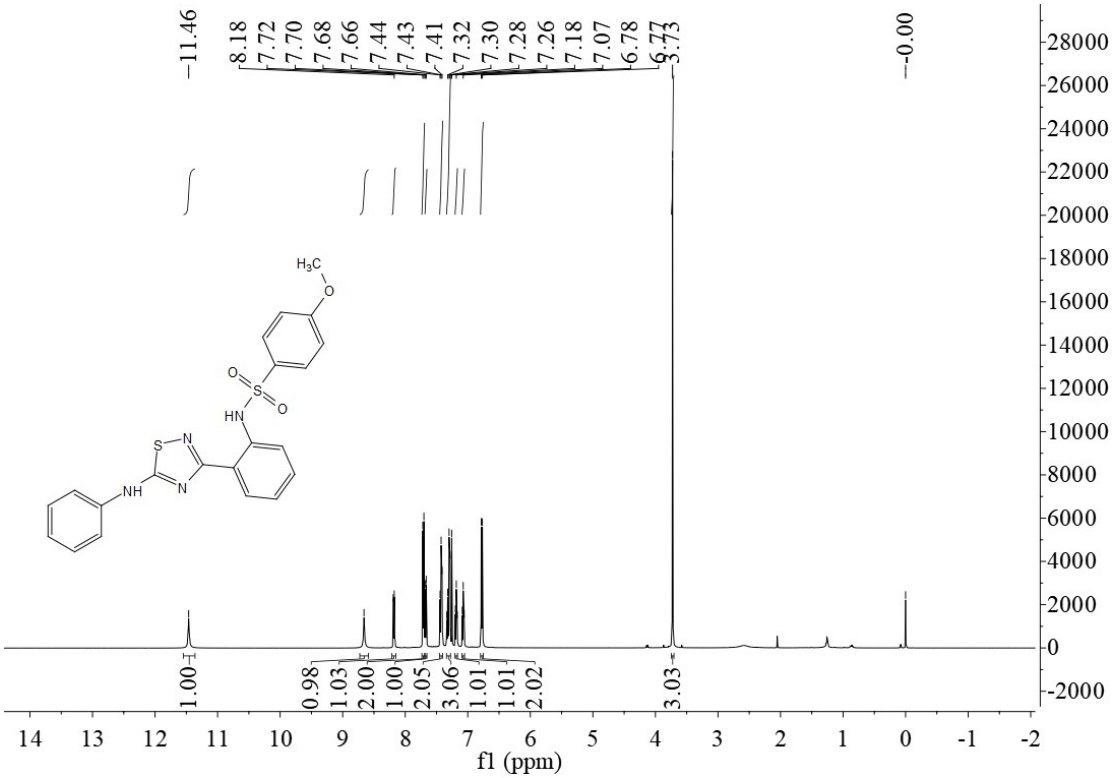

180.65
167.25
133.20
132.90
130.98
130.89
130.68
129.80
129.77
127.58
126.76
125.76
120.51
120.21
76.27
76.02
75.76
19.71
16.67
0.00
f1 (ppm)

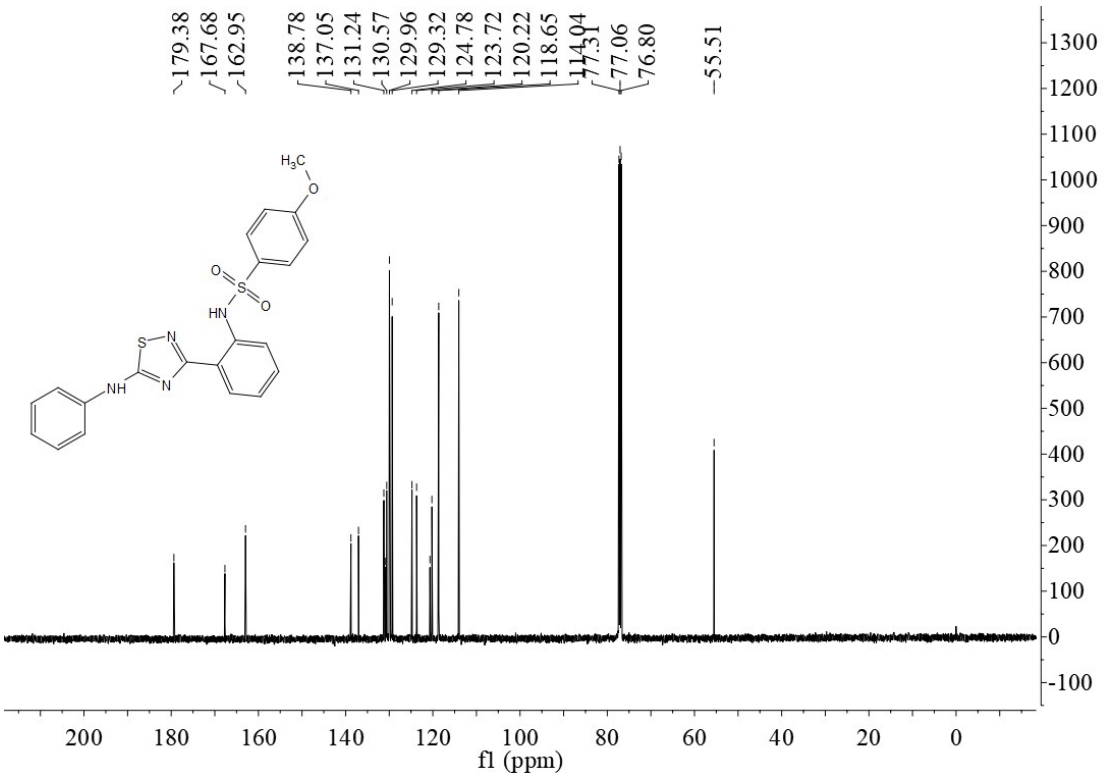

10.97
8.04
7.58
7.57
7.38
7.36
7.23
7.22
7.20
7.18
7.13
7.12
3.00
2.98
2.97
2.27
2.25
1.62
1.61
1.61
1.60
1.59
1.26
1.24
1.23
1.21
0.74
0.72
0.71
0.00
1.00
0.98
0.94
1.00
1.00
2.00
2.01
2.03
6.09
2.01
2.02
3.00
f1 (ppm)


180.71
167.40
136.24
133.97
132.07
131.23
130.61
130.07
129.77
126.68
125.65
120.30
118.90
118.11
76.30
76.05
75.79
50.15
24.22
20.32
19.63
16.66
12.48
0.00
f1 (ppm)


8.62
8.19
8.17
7.68
7.67
7.65
7.46
7.44
7.43
7.34
7.33
7.31
7.29
7.28
7.26
7.22
7.20
7.19
7.13
7.11
7.10
7.08
7.06
2.29
0.00
1.00
1.00
1.01
3.01
2.04
1.06
1.97
1.00
1.97
0.99
3.02
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift (ppm)


179.36
167.53
143.66
138.70
137.01
136.33
131.30
130.52
130.00
129.49
127.18
124.89
123.72
120.50
120.15
118.66
77.30
77.05
76.79
21.49
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical shift (ppm)


11.46
8.18
7.72
7.70
7.68
7.66
7.44
7.43
7.41
7.32
7.30
7.28
7.26
7.18
7.07
6.78
6.77
3.73
0.00
1.00
0.98
1.03
2.00
1.00
2.05
3.06
1.01
1.01
2.02
3.03
f1 (ppm)


179.38
167.68
162.95
138.78
137.05
131.24
130.57
129.96
129.32
124.78
123.72
120.22
118.65
114.04
77.31
77.06
76.80
55.51
f1 (ppm)