Supporting Information

Metal-Free Synthesis of Imidazole by $BF_3 \cdot Et_2O$ Promoted Denitrogenative Transannulation of *N*-Sulfonyl-1,2,3-Triazole

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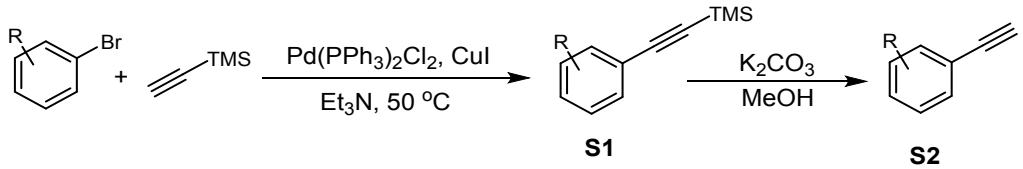
Contents:

General

Analytical thin layer chromatography (TLC) was performed using Silica Gel $HSGF_{254}$ pre-coated plates. Flash column chromatography was performed using 200-300 Mesh Silica Gel. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded using Brucker Avance II DMX 400MHz spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm), $CDCl_3$ (7.26 ppm) or DMSO (2.50 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100MHz. Chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm) or DMSO (40.45 ppm). High resolution mass spectra (HRMS) were obtained by center for instrumental analysis of Zhejiang Sci-Tech University and a waters TOFMS GCT premier instrument for HRMS. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion. Substrates were prepared according to the literature indicated in the following text.

General procedure for preparation of phenylacetylene:

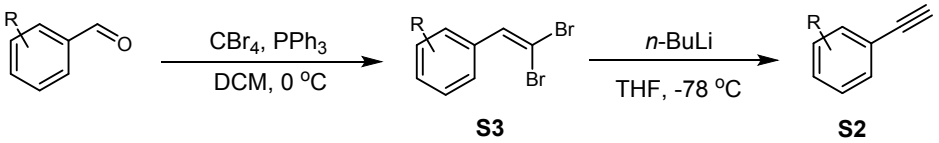
Procedure A[1]:



To a triethylamine solution (10.0 mL) of $Pd(PPh_3)_2Cl_2$ (0.15 mmol) and CuI (0.5 mmol) was added bromobenzene (5.0 mmol) and stirred for 10 min, then added trimethylsilylacetylene (6.0 mmol) dropwise over 30 min. The resulting suspension was allowed to be stirred for 4 h at 50 °C. After completion of the reaction, the mixture was filtered through a short celite bed and the filtrate was concentrated under reduced pressure. The residue was eluted through a silica column (PE) to afford compound **S1** as pale yellow oil.

To trimethyl(phenylethynyl)silane (**S1**), 10.0 mL of MeOH and K_2CO_3 (1.0 mmol) were added and stirred at room temperature, until TLC analysis showed that **S1** was completely consumed. The reaction mixture filtered through a short plug of silica gel. The filtrate was concentrated and then purified by flash column chromatography with PE/EtOAc (10:1) as eluent to give the corresponding product **S2** as colorless oil.

Procedure B[1-3]:

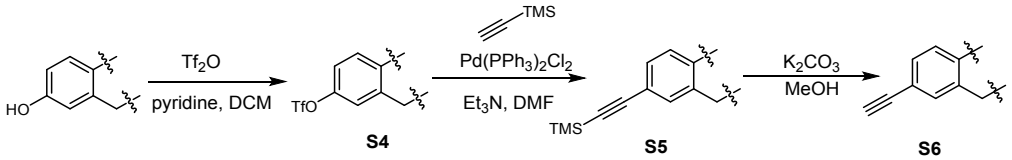


S3 **S2**

To a solution of benzaldehyde (5.0 mmol) and CBr_4 (10.0 mmol) in CH_2Cl_2 (10.0 mL) was added the solution of PPh_3 (20.0 mmol) in CH_2Cl_2 (10.0 mL) via cannula at 0 °C. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S3** as yellow oil.

To a solution of **S3** (4.0 mmol) in THF (10.0 mL) was added *n*-BuLi (8.0 mmol, 2.5 M in hexane) dropwise at -78 °C. After stirring for 2 h, MeOH (4.0 mL) was added and the mixture was stirred for an additional hour, then the reaction was quenched with saturated aqueous NH_4Cl at 0 °C, and the aqueous phase was extracted with Et_2O (10 mL×2). The combined organic phase was dried over Na_2SO_4, after filtration, the filtration was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE) to afford **S2** as yellow oil.

Procedure C[1-3]:



S4 **S5** **S6**

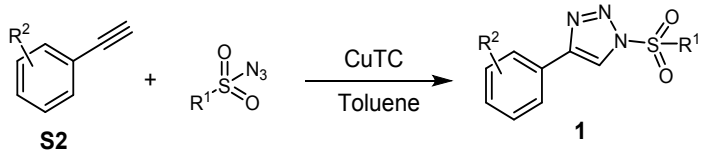
To a solution of estrone (2.7 g, 10.0 mmol) and pyridine (1.62 ml, 20.0 mmol) in 20 mL dry DCM was added Tf_2O (2.0 mL, 12.0 mmol) dropwise at 0 °C. After that, the mixture was warmed to rt, and stirred overnight. The mixture was then quenched with HCl (10%) and extracted with CH_2Cl_2, washed with saturated $NaHCO_3$ and saturated brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to give the corresponding product **S4.**

A mixture of **S4** (1.61 g, 4.0 mmol), ethynyltrimethylsilane (0.79 mL, 5.6 mmol), triethylamine (3.0 mL), and $Pd(PPh_3)_2Cl_2$ (84 mg, 0.12 mmol) in 15 ml DMF was stirred at 90°C for 4 h under nitrogen. The reaction mixture was then diluted with water, extracted with 1: l petroleum ether/ether, washed with water until neutral, and dried (Na_2SO_4), after filtration the filtrate was evaporated. Chromatography of the residue on silica gel provided the corresponding product **S5.**

To **S5** (1.16 g, 3.3 mmol) a solution of K_2CO_3 (0.52 g, 4.95 mmol) in 10 mL MeOH was added and the mixture was stirred at room temperature, until TLC analysis showed that **S5** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The filtration was concentrated and then purified by flash chromatography to give the corresponding product **S6** (726.5 mg, overall 54% yield from estrone)

Synthetic procedure and spectra data of *N*-sulfonyl-1,2,3-triazole (1):

Procedure D[4]:



S2 **1**

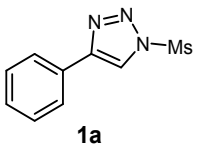
A vial was charged with copper(I) thiophene-2-carboxylate (CuTC, 0.2 mmol, 0.1 equiv in regards to alkyne), toluene (10.0 mL), and the alkyne **S2** (2.0 mmol). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (2.0 mmol) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature. The reaction mixture was stirred until complete consumption of sulfonyl azide monitored by TLC. The reaction was diluted with saturated NH_4Cl (aq.) and extracted with EtOAc (10.0 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered through celite. The filtrate was concentrated in vacuo and the obtained crude product was purified by flash column chromatography on silica gel (PE: EtOAc = 3:1) to give the desired product.

Compounds **1a-e, 1g** were synthesized by using procedure D.

Compounds **1f-i, 1k-o, 1q** and **1r** were synthesized by using procedure B and procedure D.

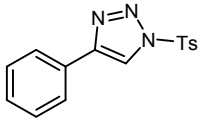
Compounds **1j** and **1p** were synthesized by using procedure A and procedure D.

Compound **1x** was synthesized by using procedure C and procedure D



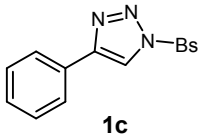
1a

1-(methylsulfonyl)-4-phenyl-1H-1,2,3-triazole (1a)[4]: pale white solid, yield: 75%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 7.86-7.84 (m, 2H), 7.54 – 7.32 (m, 3H), 3.56 (s, 3H).



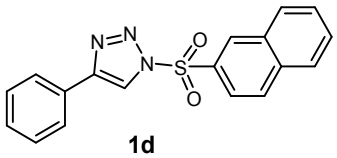
1b

4-phenyl-1-tosyl-1H-1,2,3-triazole (1b)[4]: pale white solid, yield: 80%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.32 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.46-7.31 (m, 5H), 2.44 (s, 3H).



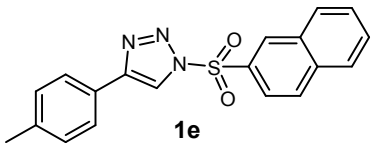
1c

1-((4-bromophenyl)sulfonyl)-4-phenyl-1H-1,2,3-triazole (1c)[4]: pale white solid, yield: 73%;^{1}H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.46-7.38 (m, 3H).



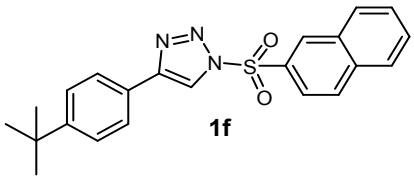
1d

1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-1,2,3-triazole (1d)[5]: pale white solid, yield: 85%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (s, 1H), 8.38 (s, 1H), 8.05-8.00 (m, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.74-7.64 (m, 2H), 7.50 – 7.29 (m, 3H).



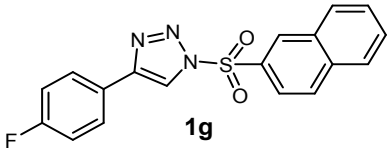
1e

1-(naphthalen-2-ylsulfonyl)-4-(p-tolyl)-1H-1,2,3-triazole (1e): pale white solid, yield: 70%, m.p.: 133.8-135.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.76 (s, 1H), 8.33 (s, 1H), 8.07 – 7.96 (m, 3H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.72-7.63 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.51, 139.11, 135.96, 132.80, 131.85, 131.18, 130.44, 130.26, 129.74, 129.62, 128.25, 128.06, 125.95, 125.90, 122.16, 118.61, 21.30. HRMS (ESI) calcd for $C_{19}H_{16}N_3O_2S^+$ 350.0958, found 350.0970.



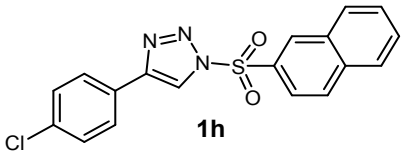
1f

4-(4-(tert-butyl)phenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1f): pale white solid, yield: 77%, m.p.: 124.6-125.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.36 (s, 1H), 8.03-7.92 (m, 3H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.75 (d, *J* = 9.5 Hz, 2H), 7.72-7.65 (m, 2H), 7.54 – 7.36 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 152.34, 147.45, 135.95, 132.81, 131.85, 131.14, 130.44, 130.25, 129.74, 128.24, 128.05, 125.88, 125.81, 122.14, 118.70, 34.71, 31.17. HRMS (ESI) calcd for $C_{22}H_{22}N_3O_2S^+$ 392.1427, found 392.1434.



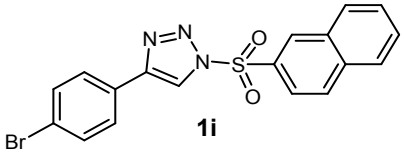
1g

4-(4-fluorophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1g): pale yellow solid, yield: 55%, m.p.: 148.5-150.8 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.46 (s, 1H), 8.99 (s, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.05 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.02 – 7.92 (m, 2H), 7.83 (t, *J* = 7.4 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 8.9 Hz, 2H).^{13}C NMR (100 MHz, DMSO-d6) δ 156.10 (d, J = 241.3 Hz), 145.15, 144.48, 132.91, 132.21, 129.06 (d, J = 8.8 Hz), 128.57, 127.70 (d, J = 7.5 Hz), 127.58, 126.88, 126.68, 126.48, 124.27, 123.90, 116.50 (d, J = 22.1 Hz), 115.94. HRMS (ESI) calcd for $C_{18}H_{13}FN_3O_2S^+$ 354.0707, found 354.0719.



1h

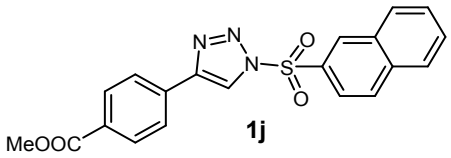
4-(4-chlorophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1h): pale white solid, yield: 60%, m.p.: 154.2-155.9 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.37 (s, 1H), 8.02-8.00 (m, 3H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.76-7.75 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.37, 136.07, 135.02, 132.66, 131.91, 131.34, 130.59, 130.36, 129.80, 129.24, 128.36, 128.12, 127.33, 122.20, 119.09. HRMS (ESI) calcd for $C_{18}H_{13}ClN_3O_2S^+$ 370.0412, found 370.0423.



1i

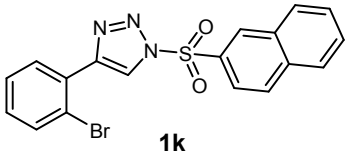
4-(4-bromophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1i): pale white

solid, yield: 60%, m.p.: 146.9-147.7 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.77 (s, 1H), 8.38 (s, 1H), 8.02-8.00 (m, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.60 (m, 4H), 7.54 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.37, 136.01, 132.57, 132.14, 131.85, 131.30, 130.56, 130.34, 129.76, 128.32, 128.08, 127.75, 127.54, 123.16, 122.14, 119.17. HRMS (ESI) calcd for $C_{18}H_{13}BrN_3O_2S^+$ 413.9906, found 413.9911.



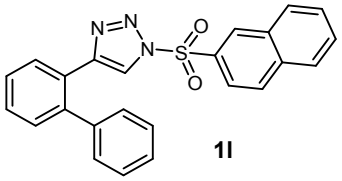
1j

methyl 4-(1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazol-4-yl)benzoate (1j): pale yellow solid, yield: 57%, m.p.: 168.5-169.2 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 9.63 (s, 1H), 9.01 (s, 1H), 8.34-8.26(m, 2H), 8.24-8.09(m, 6H), 7.83-7.78(m, 2H), 3.86 (s, 3H).^{13}C NMR (100 MHz, DMSO-d6) δ 165.83, 145.20, 134.91, 132.73, 132.06, 129.86, 129.80, 128.77, 128.40, 127.40, 127.37, 126.48, 126.30, 125.55, 125.23, 124.08, 123.78, 52.07. HRMS (ESI) calcd for $C_{20}H_{16}N_3O_4S^+$ 394.0856, found 394.0862.



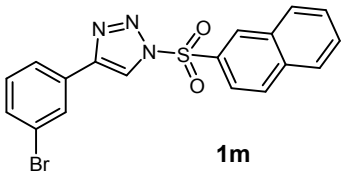
1k

4-(2-bromophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1k): pale yellow solid, yield: 55%, m.p.: 96.9-68.5 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.86 (s, 1H), 8.79 (s, 1H), 8.13–7.98 (m, 4H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.78–7.60 (m, 3H), 7.46 – 7.33 (m, 1H), 7.23-7.19 (m, 1H).^{13}C NMR (100 MHz, Chloroform-d) δ 144.89, 136.00, 133.67, 132.66, 131.86, 131.30, 130.72, 130.52, 130.32, 130.12, 129.78, 129.51, 128.29, 128.07, 127.73, 122.37, 122.16, 121.34. HRMS (ESI) calcd for $C_{18}H_{13}BrN_3O_2S^+$ 413.9906, found 413.9906.



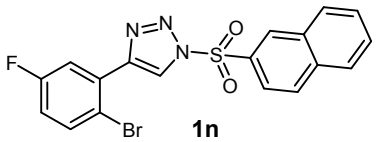
1l

4-([1,1'-biphenyl]-2-yl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1l): light yellow solid, yield: 50%, m.p.: 103.5-105.2 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.58 (s, 1H), 8.11–7.89 (m, 4H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.71 (dd, *J* = 12.5, 8.6 Hz, 2H), 7.44 (dd, *J* = 6.3, 2.7 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 7.03-7.02 (m, 1H).^{13}C NMR (100 MHz, Chloroform-d) δ 146.25, 140.88, 140.72, 135.87, 132.84, 131.79, 130.88, 130.45, 130.16, 130.13, 129.70, 129.06, 128.91, 128.84, 128.55, 128.26, 128.06, 127.89, 127.60, 127.36, 121.99, 121.79. HRMS (ESI) calcd for $C_{24}H_{18}N_3O_2S^+$ 412.1114, found 412.1120.



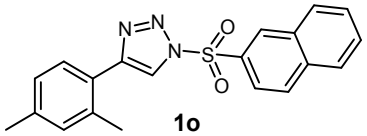
1m

4-(3-bromophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1m): light yellow solid, yield: 55%, m.p.: 102.3-104.2 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.74 (s, 1H), 8.41 (s, 1H), 8.02-7.94 (m, 4H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80–7.54 (m, 3H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.86, 135.89, 132.39, 131.87, 131.71, 131.20, 130.67, 130.48, 130.40, 130.27, 129.66, 128.86, 128.23, 127.98, 124.49, 122.90, 122.00, 119.56. HRMS (ESI) calcd for $C_{18}H_{13}BrN_3O_2S^+$ 413.9906, found 413.9914.



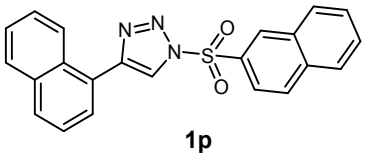
1n

4-(2-bromo-5-fluorophenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1n): yellow solid, yield: 45%, m.p.: 154.2-155.7 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (s, 1H), 8.39 (s, 1H), 8.02-8.00 (m, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.74-7.68 (m, 2H), 7.54-7.53 (m, 2H), 7.41-7.35 (m, 1H), 7.07-7.03 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.05 (d, *J* = 246.6 Hz), 146.30, 136.04, 132.56, 131.86, 131.33, 130.88 (d, *J* = 8.5 Hz), 130.67, 130.58, 130.36, 129.78, 128.34, 128.09, 122.15, 121.69 (d, *J* = 3.1 Hz), 119.49, 115.87, 113.08 (d, *J* = 23.2 Hz). HRMS (ESI) calcd for $C_{18}H_{12}BrFN_3O_2S^+$ 431.9812, found 431.9821.



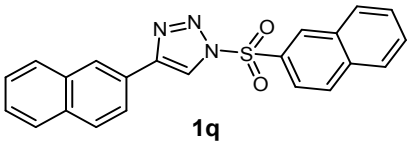
1o

4-(2,4-dimethylphenyl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1o): pale white solid, yield: 65%, m.p.: 137.6-139.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (s, 1H), 8.24 (s, 1H), 8.11 – 7.98 (m, 3H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.83 – 7.56 (m, 3H), 7.07 (d, *J* = 8.9 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.75, 138.89, 135.97, 135.60, 132.82, 131.87, 131.77, 131.19, 130.45, 130.27, 129.76, 128.94, 128.25, 128.07, 126.94, 125.17, 122.19, 120.62, 21.27, 21.11. HRMS (ESI) calcd for $C_{20}H_{18}N_3O_2S^+$ 364.1114, found 364.1118.



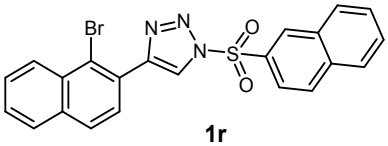
1p

4-(naphthalen-1-yl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1p): yellow solid, yield: 55%, m.p.: 119.2-120.0 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.83 (s, 1H), 8.46 (s, 1H), 8.29 – 8.18 (m, 1H), 8.11-8.04 (m, 1H), 8.04-8.02 (m, 2H), 7.93-7.88 (m, 3H), 7.81 – 7.59 (m, 3H), 7.55 – 7.44 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.50, 136.01, 133.74, 132.65, 131.86, 131.34, 130.79, 130.50, 130.34, 129.76, 129.75, 128.53, 128.28, 128.07, 127.73, 126.97, 126.18, 126.06, 125.18, 124.84, 122.22, 121.92. HRMS (ESI) calcd for $C_{22}H_{16}N_3O_2S^+$ 386.0958, found 386.0966.



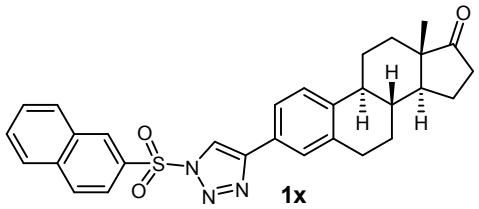
1q

4-(naphthalen-2-yl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1q): pale white solid, yield: 70%, m.p.: 136.9-138.5 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.80 (s, 1H), 8.49 (s, 1H), 8.36 (s, 1H), 8.12 – 7.97 (m, 3H), 7.95 – 7.77 (m, 5H), 7.73-7.64 (m, 2H), 7.50-7.48 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.49, 135.98, 133.45, 133.28, 132.73, 131.85, 131.22, 130.48, 130.30, 129.75, 128.78, 128.26, 128.06, 127.76, 126.65, 126.03, 125.29, 125.29, 123.56, 122.16, 119.29, 119.27. HRMS (ESI) calcd for $C_{22}H_{16}N_3O_2S^+$ 386.0958, found 386.0971.



1r

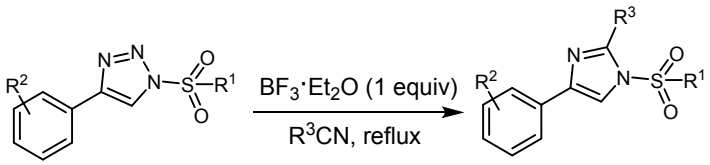
4-(1-bromonaphthalen-2-yl)-1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazole (1r): yellow solid, yield: 60%, m.p.: 142.6-144.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.79 (s, 1H), 8.50 (s, 1H), 8.38-8.35 (m, 1H), 8.12 – 7.96 (m, 2H), 7.93 – 7.77 (m, 5H), 7.71-7.65 (m, 2H), 7.52 – 7.42 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.46, 135.94, 133.41, 133.24, 132.65, 131.81, 131.21, 130.47, 130.30, 129.73, 128.77, 128.25, 128.04, 127.74, 126.64, 125.99, 125.26, 123.54, 122.13, 119.28. HRMS (ESI) calcd for $C_{22}H_{15}BrN_3O_2S^+$ 464.0063, found 464.0069.



1x

(8R,9S,13S,14S)-13-methyl-3-(1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1x): yellow solid, yield: 75%, m.p.: 201.1-202.8 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.76 (s, 1H), 8.35 (s, 1H), 8.03-7.94 (m, 3H), 7.96 – 7.81 (m, 1H), 7.73-7.63 (m, 2H), 7.57-7.54 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 2.94 (d, *J* = 8.8 Hz, 2H), 2.62 – 2.35 (m, 1H), 2.35 – 2.23 (m, 1H), 2.23 – 1.84 (m, 5H), 1.72 – 1.36 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 220.77, 147.38, 140.91, 137.21, 135.93, 132.75, 131.82, 131.12, 130.44, 130.24, 129.72, 128.24, 128.03, 126.54, 126.16, 125.92, 123.40, 122.11, 118.75, 50.41, 47.88, 44.34, 37.91, 35.78, 31.48, 29.24, 26.28, 25.58, 21.51, 13.77. HRMS (ESI) calcd for $C_{30}H_{30}N_3O_3S^+$ 512.2002, found 512.2010.

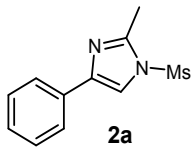
Reaction scope



1 2

General procedure: Under a nitrogen atmosphere, nitrile (1 mL) was added to a reaction flask charged with *N*-sulfonyl-1,2,3-triazole **1** (0.2 mmol) and a stirring bar. The mixture was heated to reflux, and a solution of $BF_3 \cdot Et_2O$ (0.2 mmol) in nitrile (1 mL) was added in one portion. The reaction mixture was stirred at reflux until complete consumption of **1** monitored by TLC. The reaction mixture was filtered through a short plug of silica gel and the filtrate was concentrated and then purified by flash column chromatography (PE: EtOAc=3:1 as eluent) to give the corresponding product **2**.

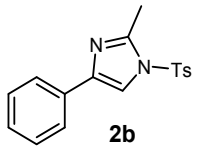
The spectra data of **2b** was the same as that reported in ref. 6.



2a

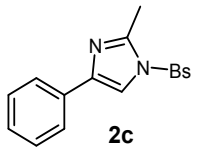
2-methyl-1-(methylsulfonyl)-4-phenyl-1H-imidazole (2a): yellow oil, yield: 58%; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.53 (s, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 3.27 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (100 MHz,

Chloroform-d) δ 145.92, 140.89, 132.03, 128.72, 127.97, 125.21, 113.59, 43.02, 15.18. HRMS (ESI) calcd for $C_{11}H_{13}N_2O_2S^+$ 237.0692, found 237.0694.



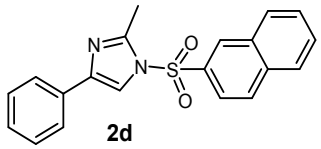
2b

2-methyl-4-phenyl-1-tosyl-1H-imidazole (2b)[6]: yellow oil, yield: 67%; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.67 (s, 1H), 7.41 – 7.32 (m, 4H), 7.29 (d, *J* = 7.4 Hz, 1H), 2.58 (s, 3H), 2.44 (s, 3H).



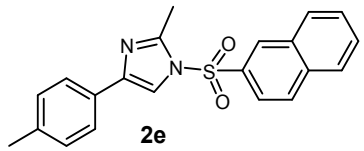
2c

1-((4-bromophenyl)sulfonyl)-2-methyl-4-phenyl-1H-imidazole (2c): yellow oil, yield: 56%; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (d, *J* = 8.7 Hz, 2H), 7.74-7.70 (m, 4H), 7.65 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.08, 140.97, 136.90, 133.17, 132.04, 130.22, 128.73, 128.68, 128.01, 125.22, 113.79, 15.28. HRMS (ESI) calcd for $C_{16}H_{14}BrN_2O_2S^+$ 376.9954, found 376.9962.



2d

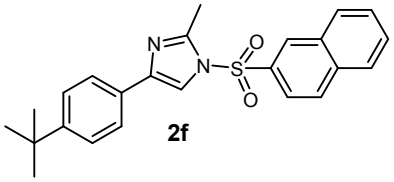
2-methyl-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-imidazole (2d): yellow oil, yield: 84%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 8.04 – 7.92 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.71 (m, 4H), 7.71 – 7.59 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.21 (m, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.07, 140.53, 135.44, 134.47, 132.14, 131.79, 130.31, 130.01, 129.47, 129.27, 128.62, 128.21, 128.01, 127.79, 125.13, 121.37, 114.04, 15.19. HRMS (ESI) calcd for $C_{20}H_{17}N_2O_2S^+$ 349.1005, found 349.1015.



2e

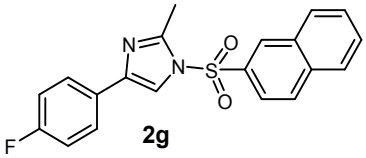
2-methyl-1-(naphthalen-2-ylsulfonyl)-4-(p-tolyl)-1H-imidazole (2e): yellow oil, yield: 61%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (s, 1H), 8.01-7.96 (m, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.81-7.78 (m, 1H), 7.72 (s, 1H), 7.70-7.62 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.61 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.97, 140.65, 137.63, 135.46, 134.60, 131.83, 130.30, 130.00, 129.50, 129.36, 129.33, 129.25, 128.21, 128.03, 125.06, 121.42, 113.55, 21.21, 15.22. HRMS (ESI)

calcd for $C_{21}H_{19}N_2O_2S^+$ 363.1162, found 363.1177.



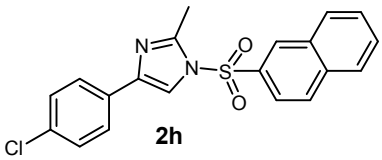
2f

4-(4-(tert-butyl)phenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2f): yellow oil, yield: 85%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 8.00-7.95 (m, 2H), 7.90 (d, J = 7.9 Hz, 1H), 7.79 (dd, J = 8.7, 2.0 Hz, 1H), 7.75 (s, 1H), 7.71-7.63 (m, 4H), 7.41-7.39 (m, 2H), 2.61 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 150.90, 145.97, 140.61, 135.42, 134.60, 131.80, 130.27, 129.97, 129.47, 129.35, 129.19, 128.19, 128.01, 125.54, 124.87, 121.36, 113.66, 34.56, 31.23, 15.22. HRMS (ESI) calcd for $C_{24}H_{25}N_2O_2S^+$ 405.1631, found 405.1635.



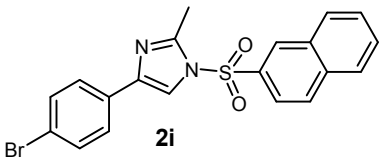
2g

4-(4-fluorophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2g): yellow oil, yield: 82%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (s, 1H), 7.99 (t, *J* = 9.2 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.70-7.65 (m, 5H), 7.05 (t, *J* = 8.4 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 162.44 (d, *J* = 246.6 Hz), 146.13, 139.66, 135.48, 134.43, 131.82, 130.35, 130.07, 129.49, 129.35, 128.38 (d, *J* = 3.2 Hz), 128.25, 128.03, 126.88 (d, *J* = 8.0 Hz), 121.37, 115.56 (d, *J* = 21.7 Hz), 113.67, 15.14. HRMS (ESI) calcd for $C_{20}H_{16}FN_2O_2S^+$ 367.0911, found 367.0923.



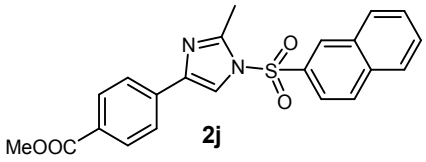
2h

4-(4-chlorophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2h): yellow oil, yield: 80%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (s, 1H), 7.99 (t, *J* = 8.9 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 10.1 Hz, 1H), 7.73 (d, *J* = 9.3 Hz, 1H), 7.72 – 7.56 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.23, 139.39, 135.50, 134.30, 133.49, 131.81, 130.61, 130.39, 130.12, 129.50, 129.41, 128.80, 128.29, 128.04, 126.42, 121.35, 114.20, 15.13. HRMS (ESI) calcd for $C_{20}H_{16}ClN_2O_2S^+$ 383.0616, found 383.0624.



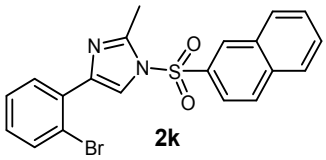
2i

4-(4-bromophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2i): yellow oil, yield: 85%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (s, 1H), 7.99 (t, *J* = 9.1 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.79 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.75 (s, 1H), 7.73 – 7.62 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.21, 139.48, 135.48, 134.33, 131.80, 131.72, 131.16, 130.37, 130.10, 129.49, 129.40, 128.27, 128.03, 126.69, 121.60, 121.35, 114.26, 15.16. HRMS (ESI) calcd for $C_{20}H_{15}BrN_2NaO_2S^+$ 448.9930, found 448.9936.



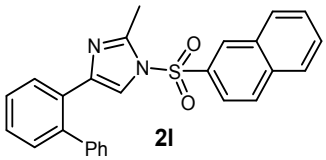
2j

methyl 4-(2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazol-4-yl)benzoate (2j): yellow oil, yield: 49%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.58 (s, 1H), 8.09 – 7.96 (m, 4H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.82-7.80 (m, 3H), 7.75 – 7.61 (m, 2H), 3.91 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.80, 139.48, 136.54, 135.55, 134.27, 131.83, 130.47, 130.44, 130.18, 130.02, 129.53, 129.51, 129.16, 128.33, 128.07, 124.91, 121.37, 115.45, 52.06, 15.18. HRMS (ESI) calcd for $C_{22}H_{19}N_2O_4S^+$ 407.1066, found 407.1071



2k

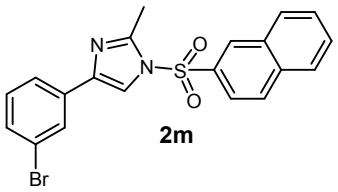
4-(2-bromophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2k): yellow oil, yield: 73%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.58 (s, 1H), 8.24 (s, 1H), 8.06 – 7.97 (m, 2H), 7.92 (t, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.71-7.61 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.04, 137.89, 135.45, 134.51, 133.61, 132.71, 131.80, 130.40, 130.34, 130.02, 129.49, 129.30, 128.74, 128.21, 128.02, 127.39, 121.40, 120.94, 118.22, 15.07. HRMS (ESI) calcd for $C_{20}H_{16}BrN_2O_2S^+$ 427.0110, found 427.0117.



2l

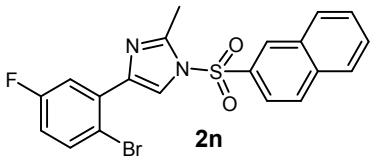
4-([1,1'-biphenyl]-2-yl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2l): yellow oil, yield: 58%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.37 (s, 1H), 8.07 – 7.88 (m, 4H), 7.74-7.67 (m, 2H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 15.1 Hz, 1H), 7.35-7.30 (m, 4H), 7.28 – 7.20 (m, 3H), 6.39 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.81, 142.04, 140.19, 138.84, 135.40, 134.56, 131.74, 130.80, 130.13, 130.08, 129.97, 129.49, 129.21, 129.13, 128.43, 128.31, 128.15, 128.01,

127.63, 127.46, 127.13, 121.49, 117.26, 15.15. HRMS (ESI) calcd for $C_{26}H_{21}N_2O2S^+$ 425.1318, found 425.1327.



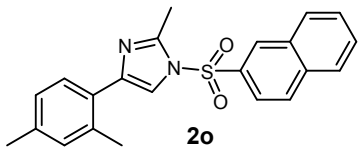
2m

4-(3-bromophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2m): yellow oil, yield: 52%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.57 (s, 1H), 8.06 – 7.94 (m, 3H), 7.91-7.90 (m, 2H), 7.84 – 7.73 (m, 1H), 7.73 – 7.60 (m, 3H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.28, 139.05, 135.49, 134.25, 134.20, 131.79, 130.65, 130.40, 130.15, 130.12, 129.50, 129.43, 128.28, 128.12, 128.03, 123.65, 122.83, 121.33, 114.69, 15.13. HRMS (ESI) calcd for $C_{20}H_{16}BrN_2O_2S^+$ 427.0110, found 427.0124.



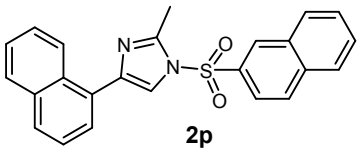
2n

4-(2-bromo-5-fluorophenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2n): yellow oil, yield: 60%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.57 (s, 1H), 8.02-7.98 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.74 (m, 1H), 7.74 – 7.61 (m, 2H), 7.50-7.43 (m, 2H), 7.34-7.29 (m, 1H), 6.98-6.93(m, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.11 (d, *J* = 245.3 Hz), 146.20, 139.40 (d, *J* = 2.9 Hz), 135.52, 134.33, 131.83, 130.41, 130.21, 130.13, 129.48 (d, *J* = 8.7 Hz), 129.26, 128.30, 128.06, 121.37, 120.74, 120.72, 114.65, 114.46, 112.11 (d, *J* = 22.9 Hz), 15.15. HRMS (ESI) calcd for $C_{20}H_{15}BrFN_2O_2S^+$ 445.0016, found 445.0020.



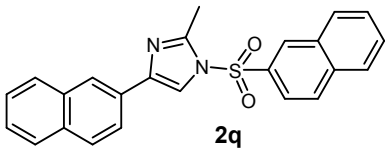
2o

4-(2,4-dimethylphenyl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2o): yellow oil, yield: 64%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.57 (s, 1H), 8.01 (t, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 10.6 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.57 (s, 1H), 7.05-7.03 (m, 2H), 2.62 (s, 3H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.07, 139.86, 137.42, 135.45, 135.00, 134.70, 131.85, 131.58, 130.31, 129.99, 129.50, 129.20, 128.68, 128.50, 128.22, 128.04, 126.70, 121.38, 116.15, 21.61, 21.03, 15.13. HRMS (ESI) calcd for $C_{22}H_{21}N_2O_2S^+$ 377.1318, found 377.1330.



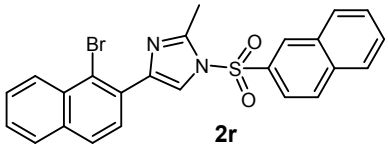
2p

2-methyl-4-(naphthalen-1-yl)-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2p): yellow oil, yield: 71%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.63 (s, 1H), 8.40-8.34 (m, 1H), 8.04-8.01 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.82 (m, 3H), 7.79 (s, 1H), 7.76 – 7.62 (m, 3H), 7.56 – 7.43 (m, 3H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.61, 139.90, 135.51, 134.57, 133.84, 131.87, 130.98, 130.41, 130.08, 129.93, 129.53, 129.42, 128.57, 128.41, 128.27, 128.07, 126.88, 126.44, 125.79, 125.38, 125.26, 121.46, 117.07, 15.25. HRMS (ESI) calcd for $C_{24}H_{19}N_2O_2S^+$ 399.1162, found 399.1175.



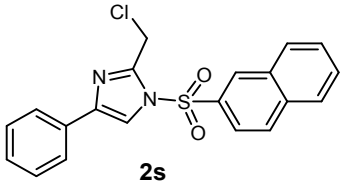
2q

2-methyl-4-(naphthalen-2-yl)-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2q): yellow oil, yield: 95%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.59 (s, 1H), 8.30 (s, 1H), 8.02-7.97 (m, 2H), 7.91-7.80 (m, 7H), 7.71-7.63 (m, 2H), 7.55 – 7.36 (m, 2H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.30, 140.51, 135.49, 134.48, 133.53, 132.97, 131.83, 130.37, 130.05, 129.51, 129.41, 129.36, 128.34, 128.24, 128.17, 128.04, 127.63, 126.30, 125.92, 123.88, 123.25, 121.41, 114.47, 15.25. HRMS (ESI) calcd for $C_{24}H_{18}N_2NaO_2S^+$ 421.0987, found 421.0985



2r

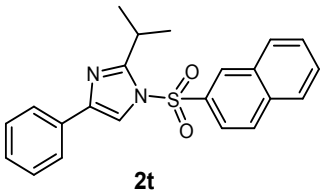
4-(1-bromonaphthalen-2-yl)-2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazole (2r): yellow oil, yield: 99%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.59 (s, 1H), 8.30 (s, 1H), 8.00-7.93 (m, 2H), 7.89-7.79 (m, 6H), 7.63-7.61 (m, 2H), 7.47-7.41 (m, 2H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 146.23, 140.44, 135.40, 134.39, 133.47, 132.91, 131.75, 130.30, 129.98, 129.43, 129.38, 129.30, 128.28, 128.16, 128.11, 127.96, 127.58, 126.25, 125.87, 123.82, 123.21, 121.33, 114.44, 15.18. HRMS (ESI) calcd for $C_{24}H_{18}BrN_2O_2S^+$ 477.0267, found 477.0271.



2s

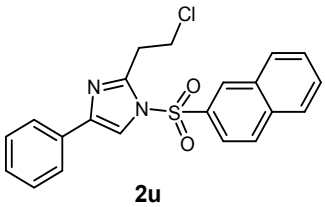
2-(chloromethyl)-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-imidazole (2s): yellow oil, yield: 75%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.71 (s, 1H), 8.10 – 7.83 (m,

5H), 7.80 – 7.53 (m, 4H), 7.44 – 7.25 (m, 3H), 5.03 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.09, 141.73, 135.62, 133.93, 131.75, 131.57, 130.39, 130.20, 129.62, 129.25, 128.67, 128.21, 128.02, 125.30, 122.48, 121.70, 115.34, 36.52. HRMS (ESI) calcd for $C_{20}H_{16}ClN_2O_2S^+$ 383.0616, found 383.0624.



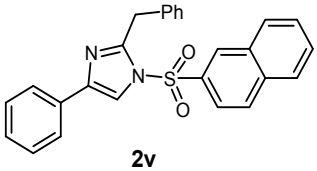
2t

2-isopropyl-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-imidazole (2t): yellow oil, yield: 59%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 8.01-7.96 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.80-7.75 (m, 3H), 7.74 (s, 1H), 7.71-7.63 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 3.68 – 3.44 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 155.14, 140.55, 135.36, 135.23, 132.51, 131.84, 130.22, 129.94, 129.47, 129.00, 128.58, 128.19, 128.03, 127.69, 125.31, 121.28, 113.63, 27.61, 22.07. HRMS (ESI) calcd for $C_{22}H_{20}N_2NaO_2S^+$ 399.1138, found 399.1143.



2u

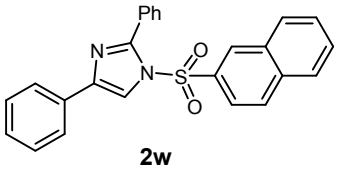
2-(2-chloroethyl)-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-imidazole (2u): yellow oil, yield: 50%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.58 (s, 1H), 8.01-7.99 (m, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.85 – 7.61 (m, 5H), 7.45 – 7.27 (m, 3H), 3.92 (t, *J* = 7.5 Hz, 2H), 3.45 (t, *J* = 7.5 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-d) δ 145.80, 141.00, 135.56, 134.51, 131.92, 131.87, 130.47, 130.19, 129.60, 129.36, 128.67, 128.34, 128.07, 125.25, 122.51, 121.26, 114.23, 40.94, 31.94. HRMS (ESI) calcd for $C_{21}H_{18}ClN_2O_2S^+$ 397.0772, found 397.0786.



2v

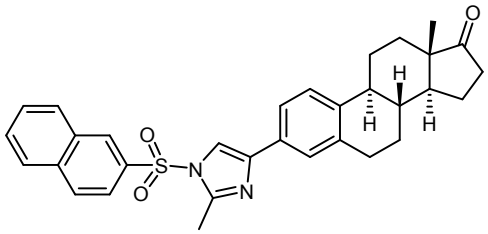
2-benzyl-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1H-imidazole (2v): yellow oil, yield: 39%; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (s, 1H), 7.82 – 7.72 (m, 6H), 7.68 – 7.59 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.34 – 7.26 (m, 2H), 7.10 – 7.01 (m, 4H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.71, 140.97, 135.99, 135.22, 134.33, 132.23, 131.61, 129.80, 129.64, 129.41, 128.66,

128.56, 128.25, 127.90, 127.79, 127.75, 126.57, 125.31, 121.26, 114.54, 114.49, 34.36. HRMS (ESI) calcd for $C_{26}H_{21}N_2O_2S^+$ 425.1318, found 425.1335.



2w

1-(naphthalen-2-ylsulfonyl)-2,4-diphenyl-1H-imidazole (2w): yellow oil, yield: 32%; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (s, 1H), 7.91 – 7.75 (m, 5H), 7.75 – 7.54 (m, 4H), 7.50 – 7.35 (m, 5H), 7.36 – 7.26 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.66, 141.05, 135.31, 133.88, 132.09, 131.43, 130.69, 130.15, 130.06, 129.92, 129.67, 129.49, 129.29, 128.67, 127.98, 127.90, 127.88, 127.69, 125.34, 121.37, 115.38. HRMS (ESI) calcd for $C_{25}H_{19}N_2O_2S^+$ 411.1162, found 411.1175.

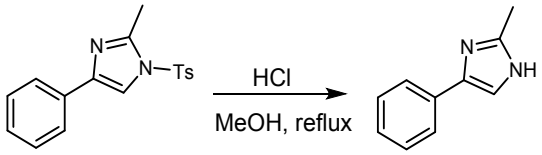


2x

(8R,9S,13S,14S)-13-methyl-3-(2-methyl-1-(naphthalen-2-ylsulfonyl)-1H-imidazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2x): yellow solid, yield: 53%, m.p.: 202.5-204.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 8.07 – 7.87 (m, 3H), 7.80-7.77 (m, 1H), 7.75 – 7.63 (m, 3H), 7.49-7.48 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 1H), 3.13 – 2.75 (m, 2H), 2.61 (s, 3H), 2.53-2.46 (m, 2H), 2.15 – 1.93 (m, 5H), 1.66-1.29 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 220.95, 146.04, 140.47, 139.52, 136.82, 135.45, 134.53, 131.81, 130.30, 130.02, 129.59, 129.49, 129.24, 128.22, 128.02, 125.63, 122.54, 121.36, 113.78, 50.42, 47.92, 44.34, 38.02, 35.79, 31.50, 29.26, 26.39, 25.62, 21.51, 15.19, 13.79. HRMS (ESI) calcd for $C_{32}H_{33}N_2O_3S^+$ 525.2206, found 525.2212.

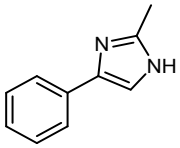
Procedure for the synthesis of 2-methyl-4-phenyl-1H-imidazole (3a):

Procedure E[7]:



2a **3a**, 99 %

Imidazole **2a** (31.2 mg, 0.1 mmol) was dissolved in MeOH (2.0 mL) in a round-bottom flask. HCl (concd, 0.5 mL) was added to this mixture in one portion. The reaction mixture was heated to reflux. After completion of the reaction, MeOH was evaporated and HCl (3M, 5.0 mL) was added. The resulting mixture was extracted with Et_2O (5.0 mL×2), and the organic phase was discarded. The aqueous phase was made alkaline with NaOH (4M, 5 mL) and again extracted with Et_2O (2×5.0 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, after filtration, the filtrate was concentrated under reduced pressure to provide **3a** at high purity (15.6 mg, yellow oil, 99% yield).



3a

2-methyl-4-phenyl-1H-imidazole (3a)[8]: yellow oil, yield: 99%; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.17 (s, 1H), 2.37 (s, 3H).

References

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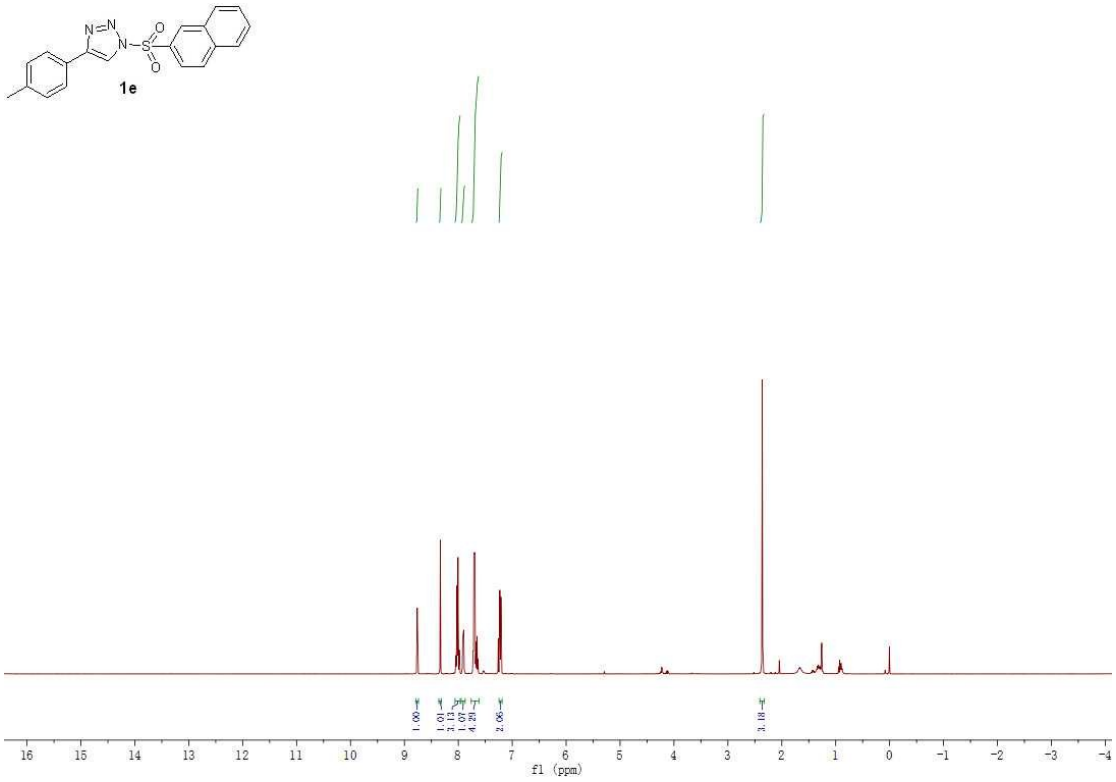
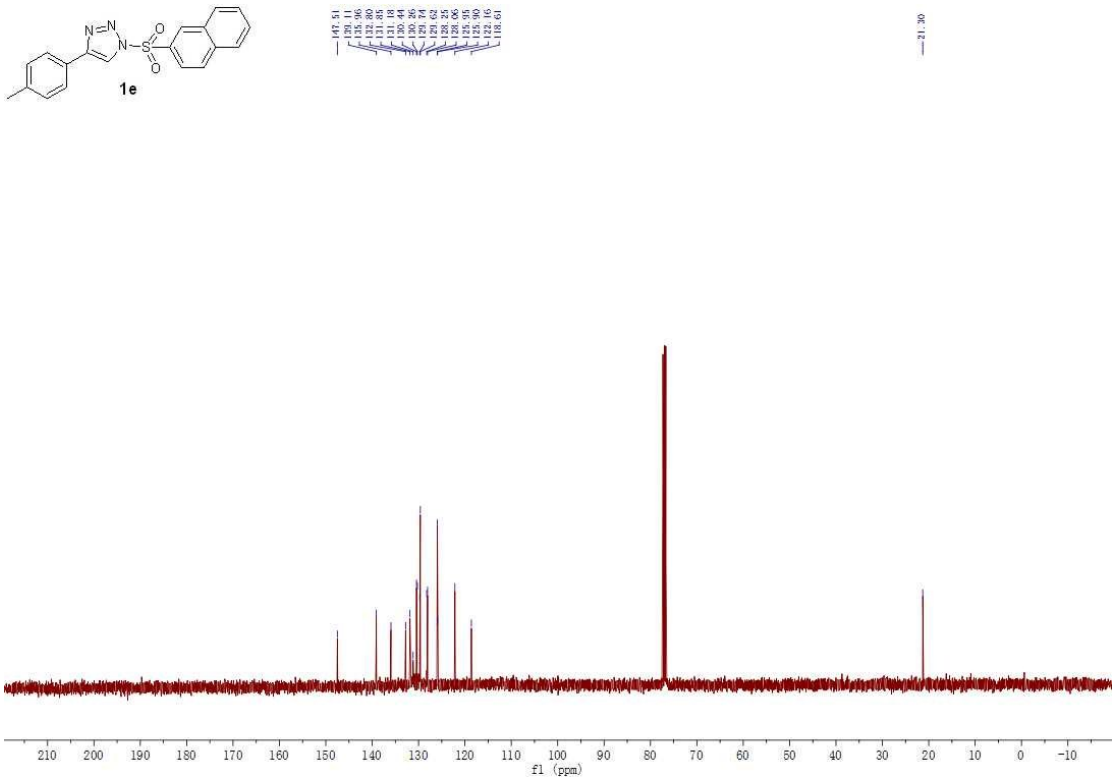
^{1}H and ^{13}C NMR spectra for new compounds

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125.90
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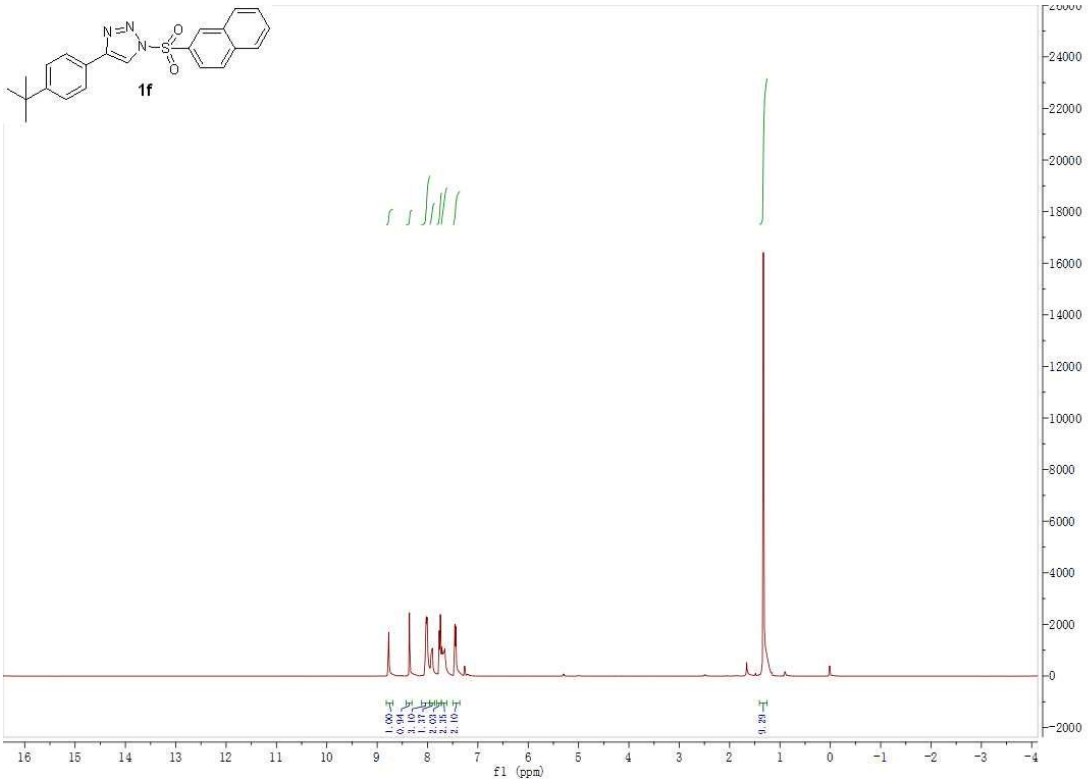
21.30
f1 (ppm)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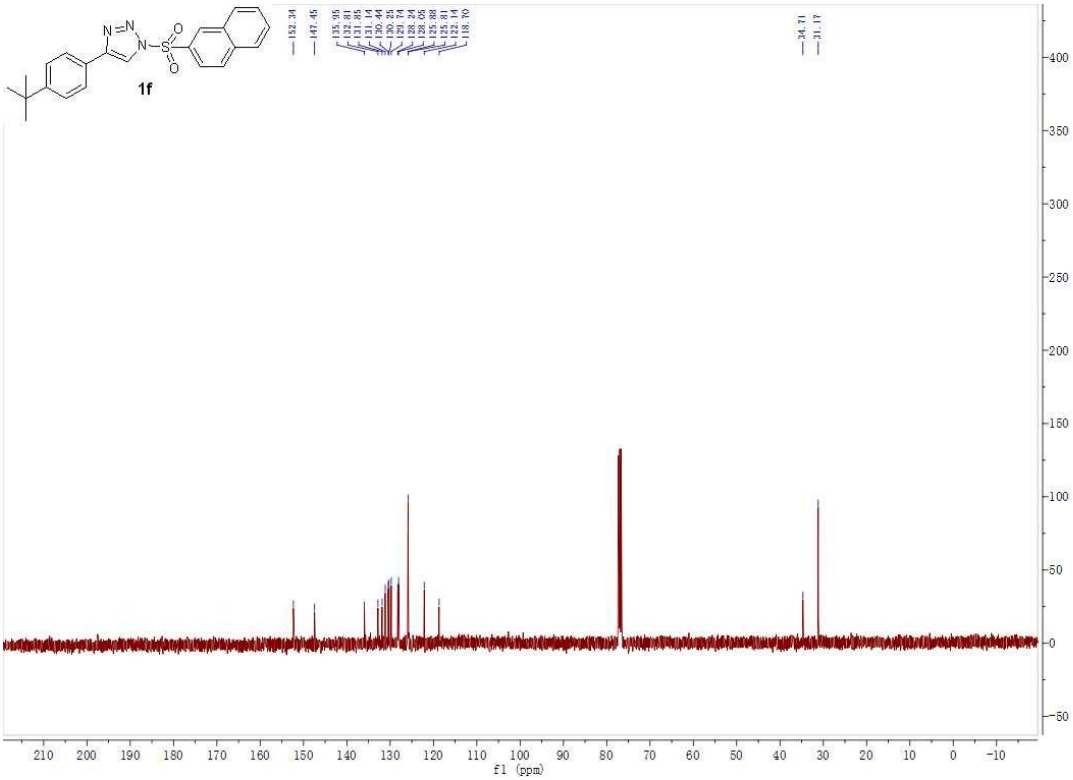
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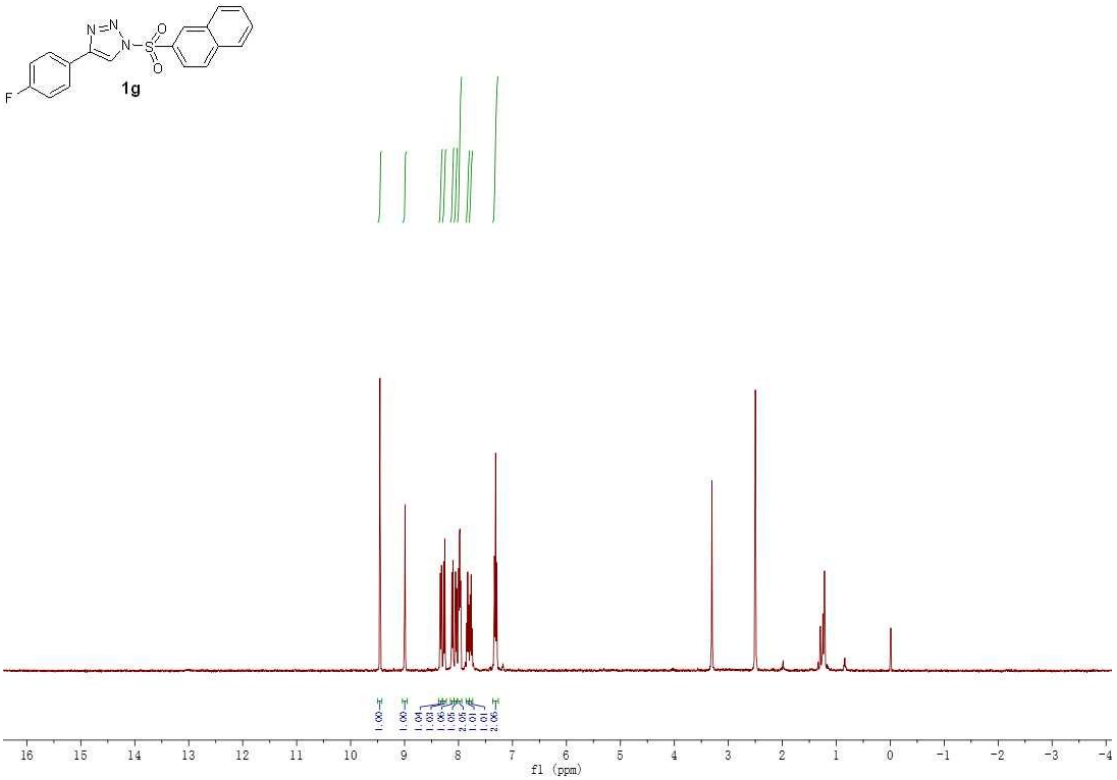
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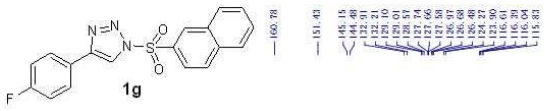
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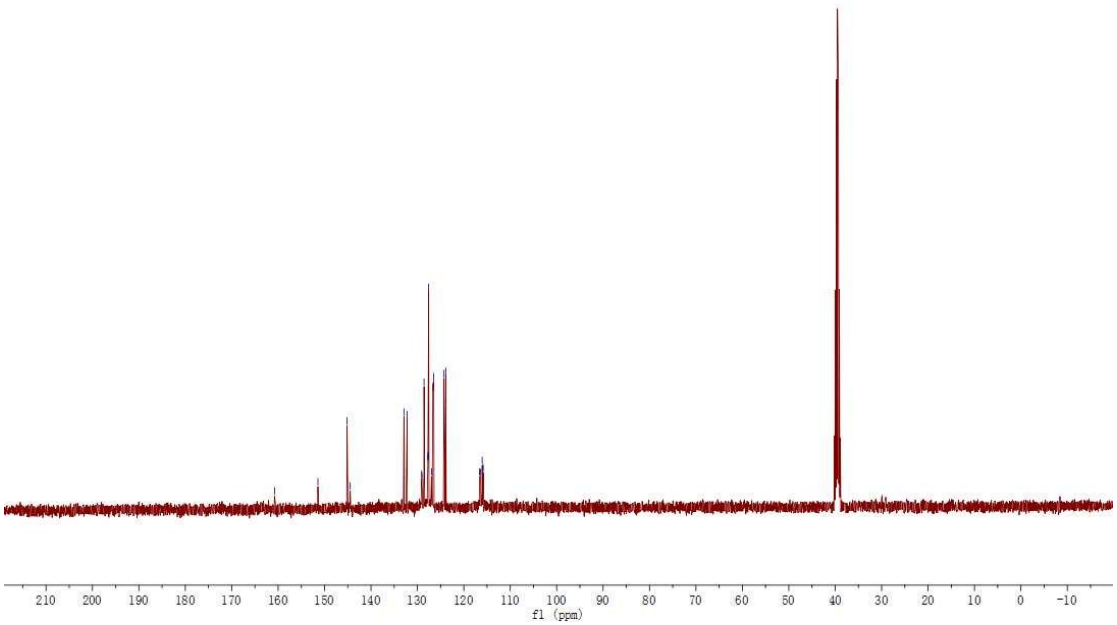
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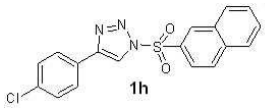
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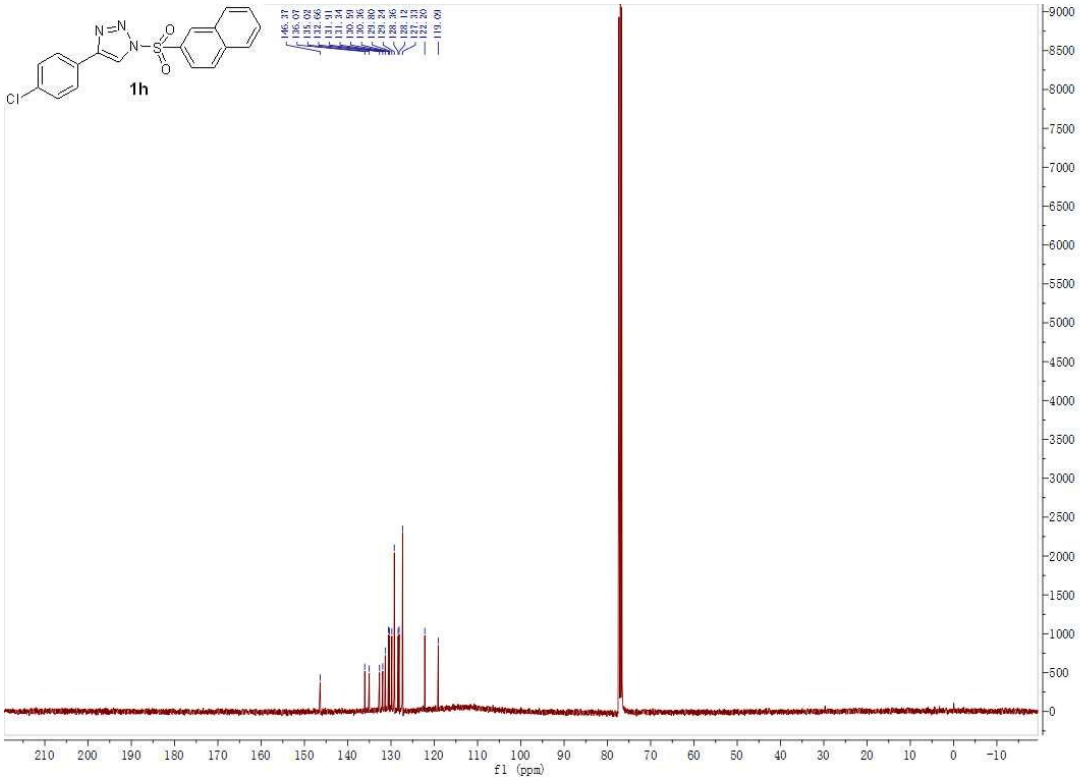
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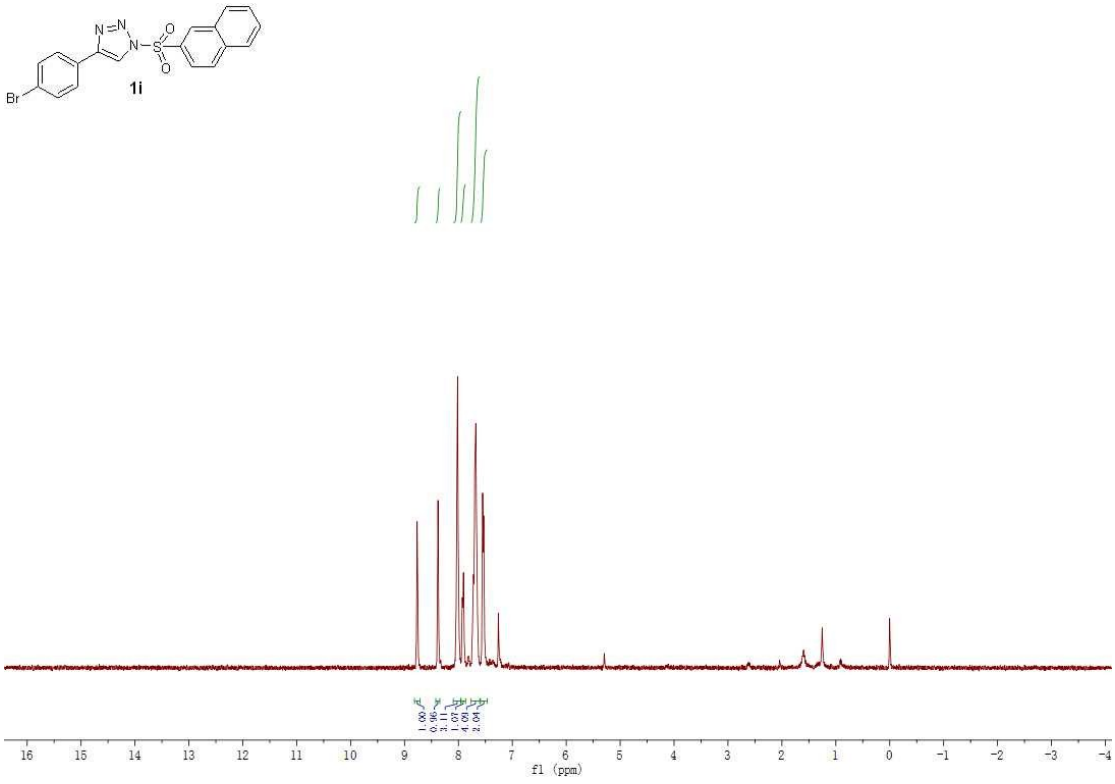
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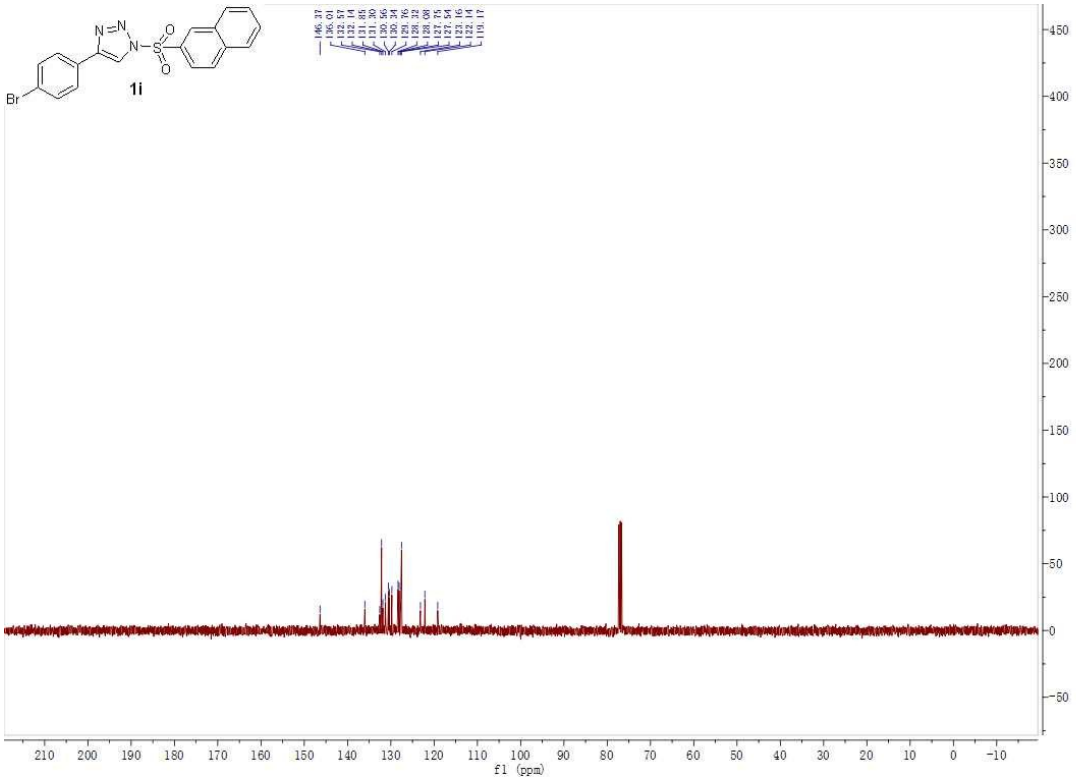
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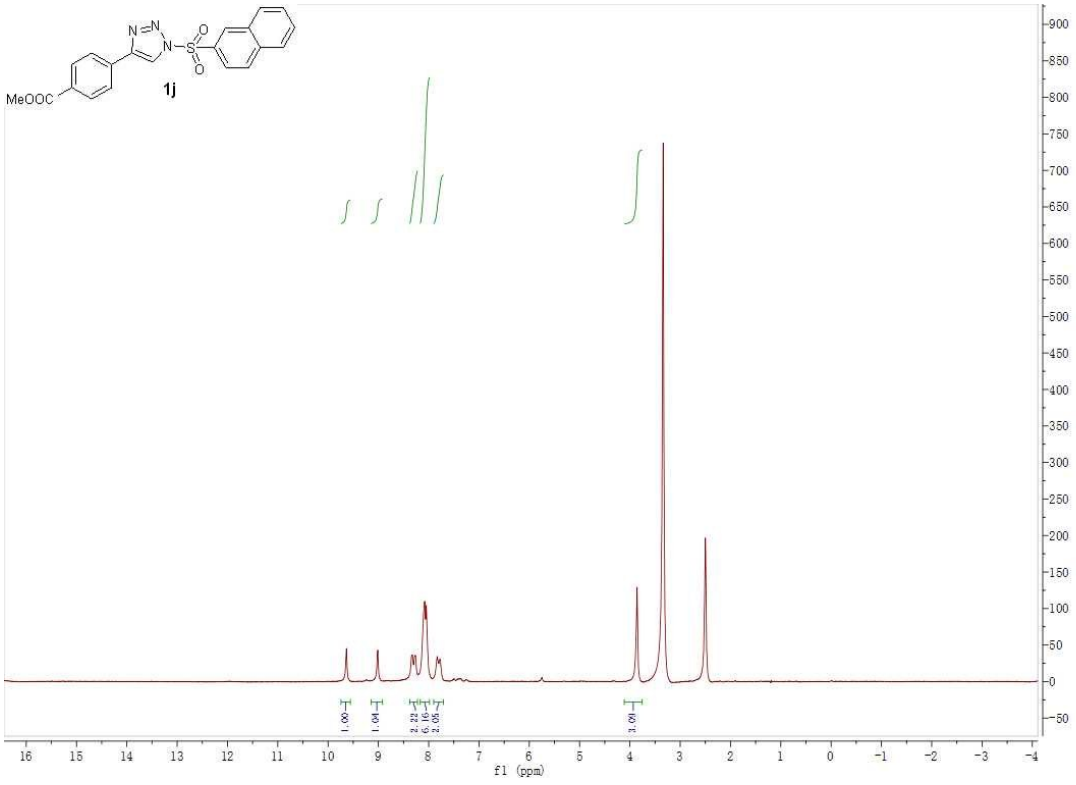
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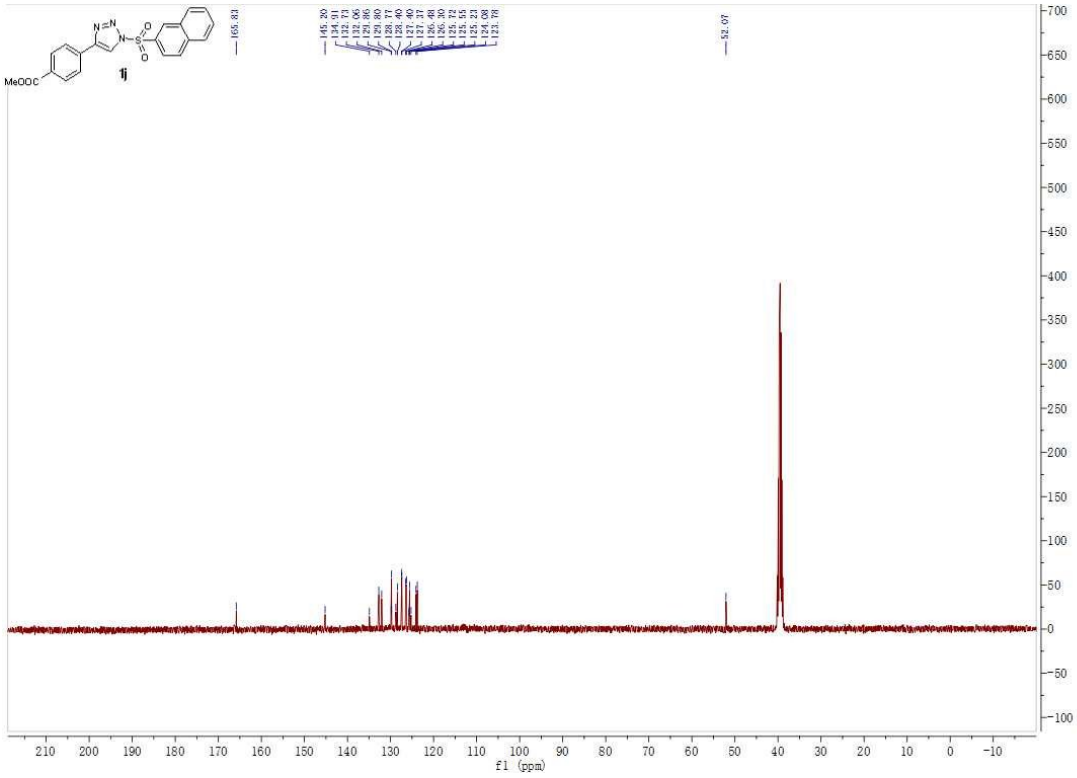
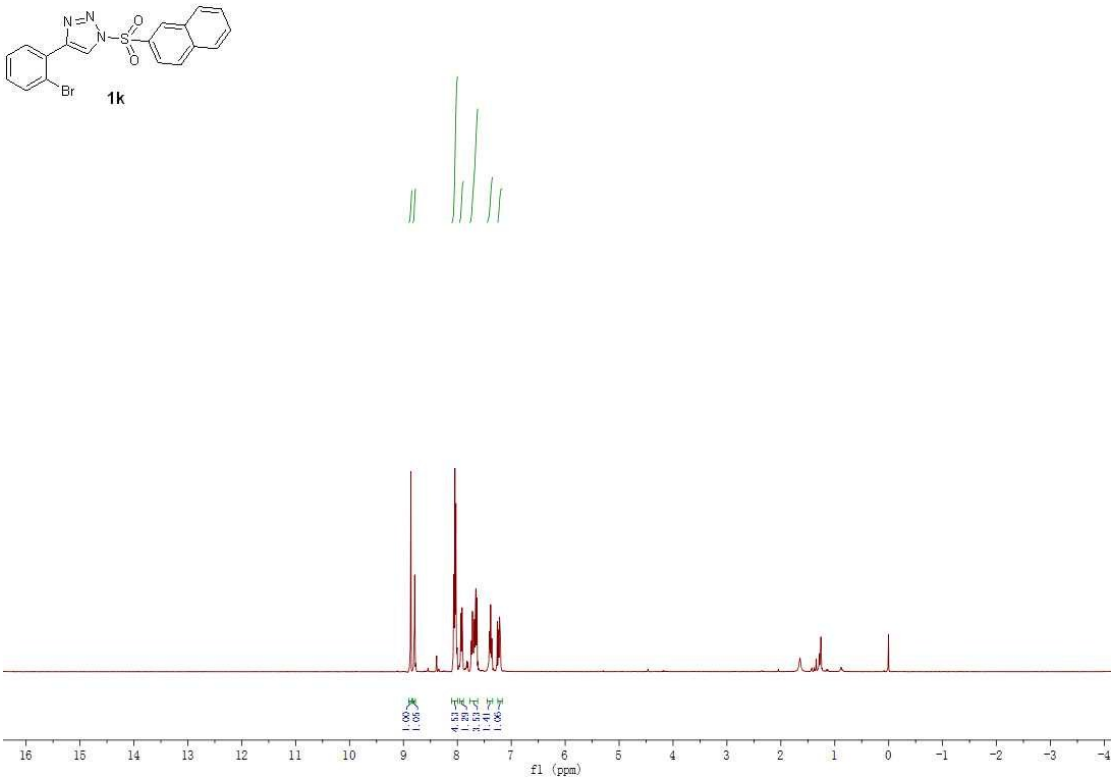
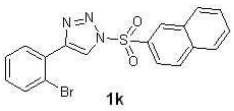
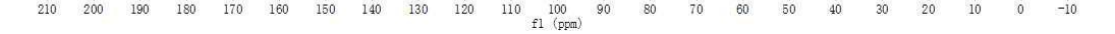
1j
f1 (ppm)

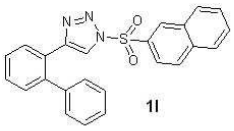

MeOOC
1j
165.83
145.20
134.31
132.73
132.06
129.86
129.60
128.77
128.40
127.40
127.23
126.49
126.30
125.72
125.15
125.23
124.08
123.78
52.07
f1 (ppm)


Br
1k
1.00
1.05
4.53
1.29
3.13
3.41
1.06
f1 (ppm)

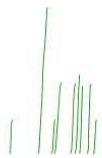

Br

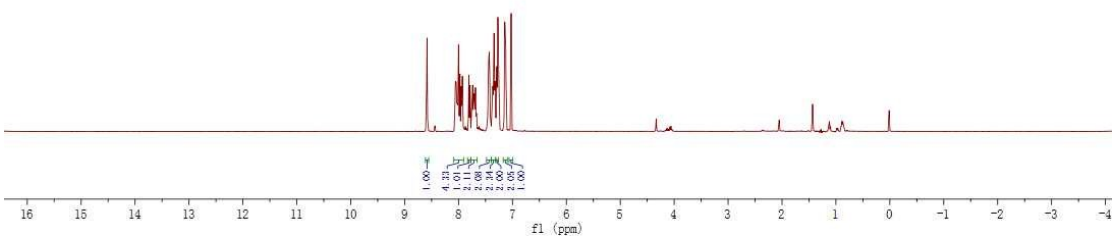
1k

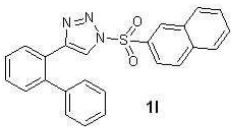

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



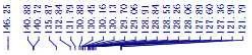
1l

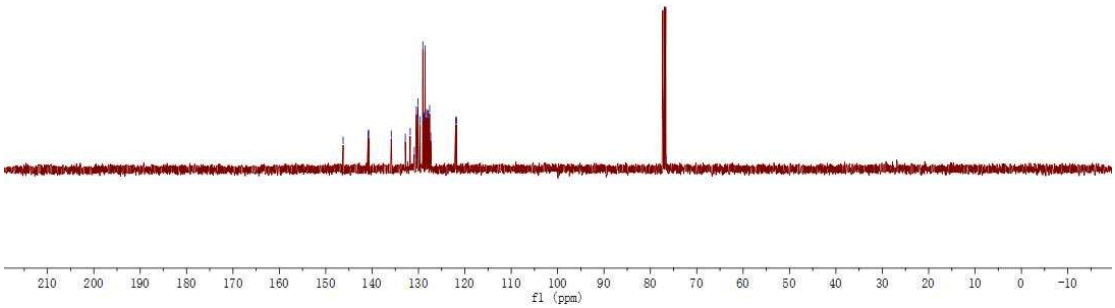


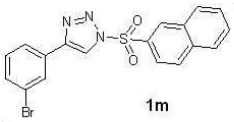

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)



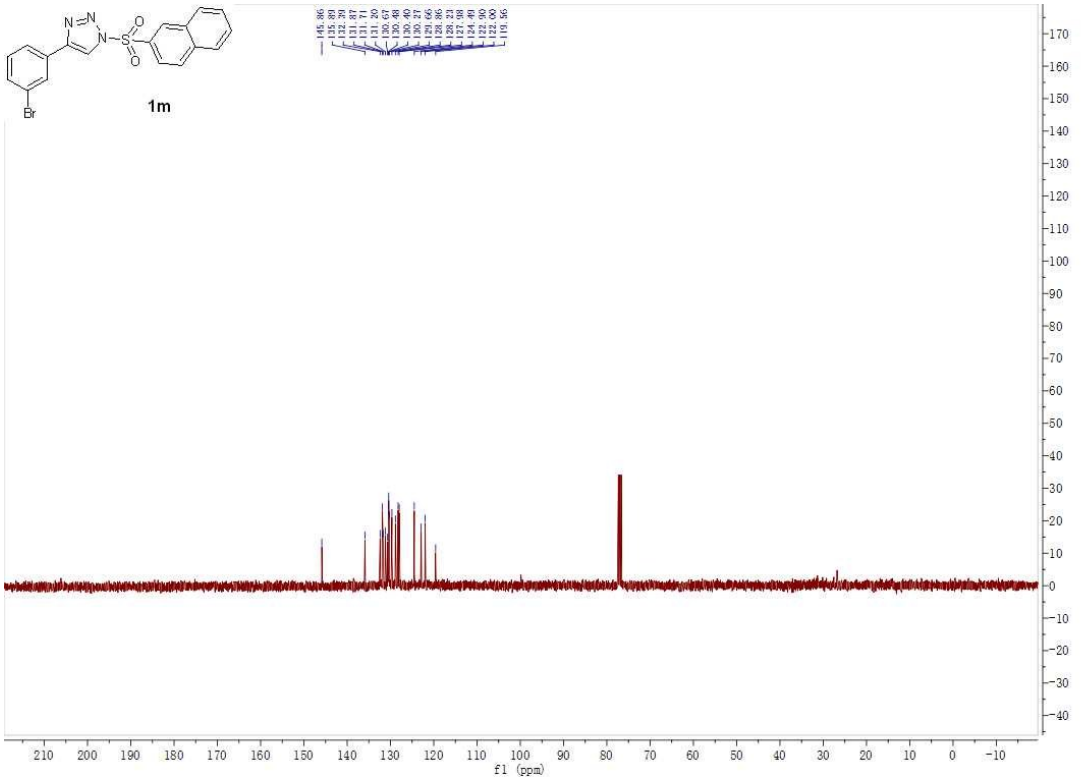
1l

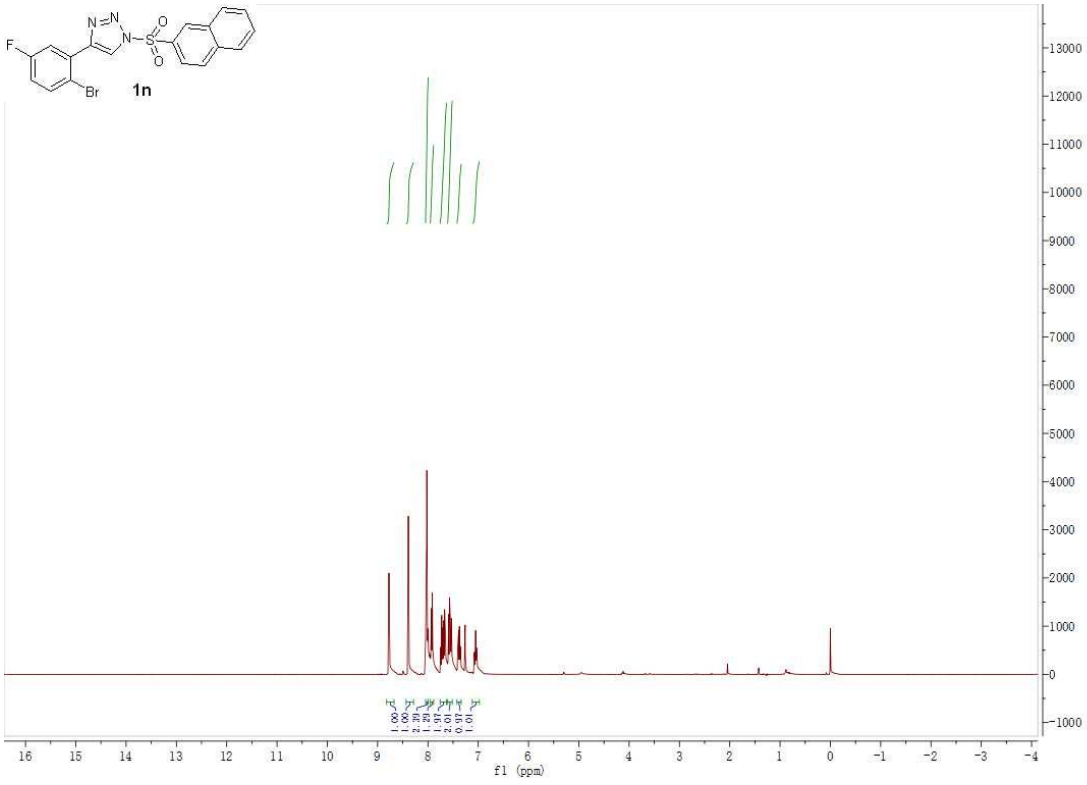


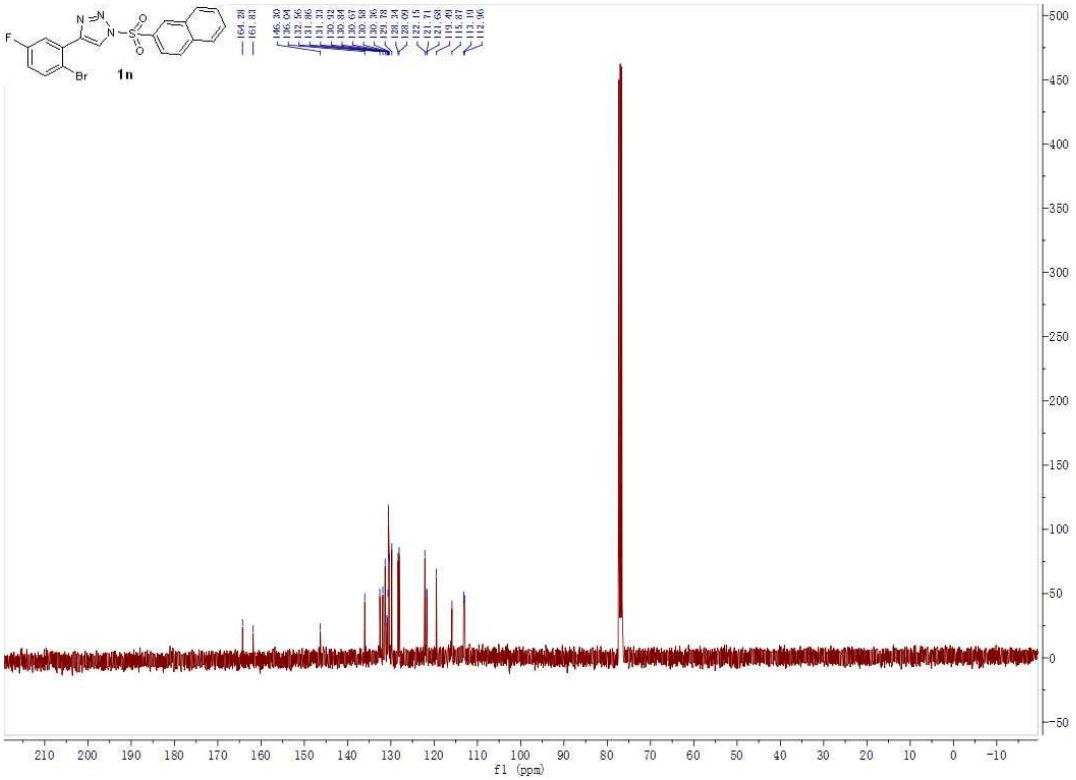


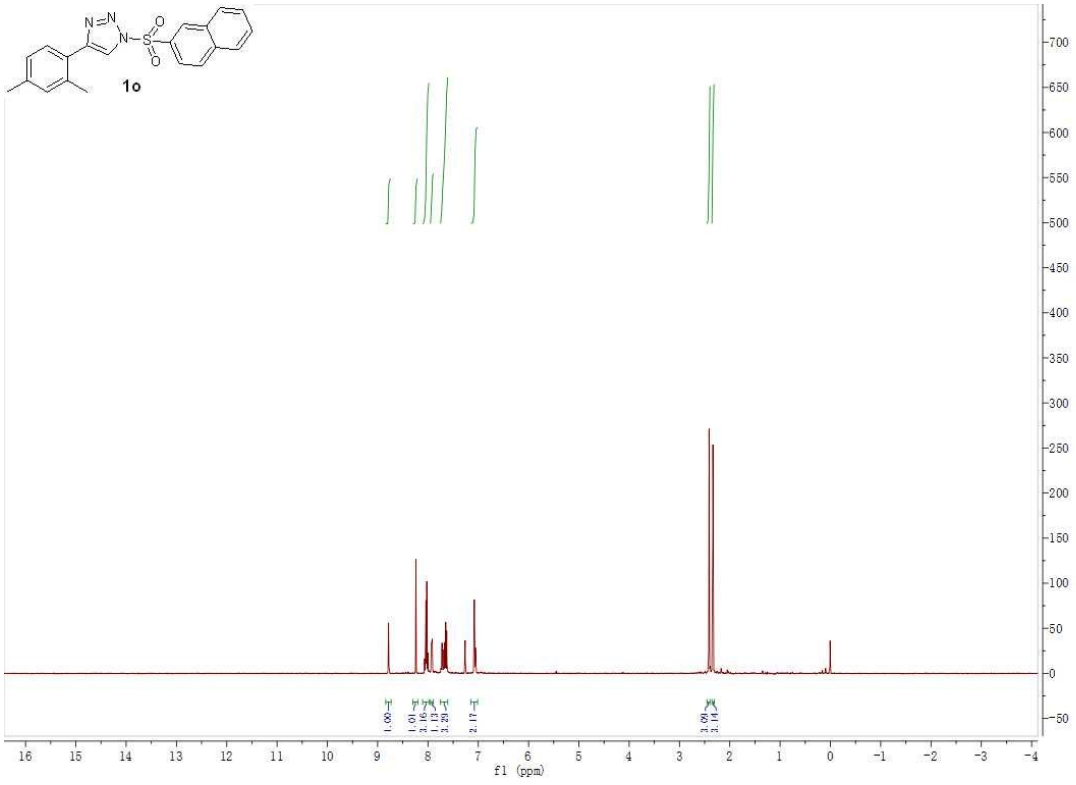


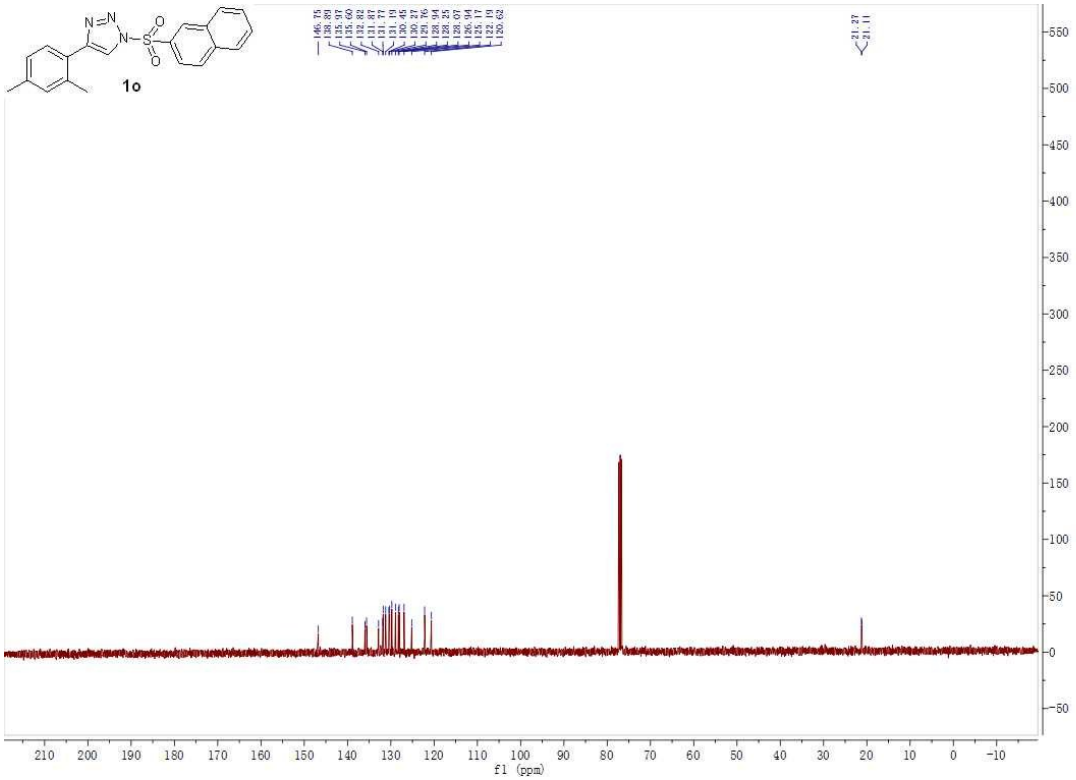
1m

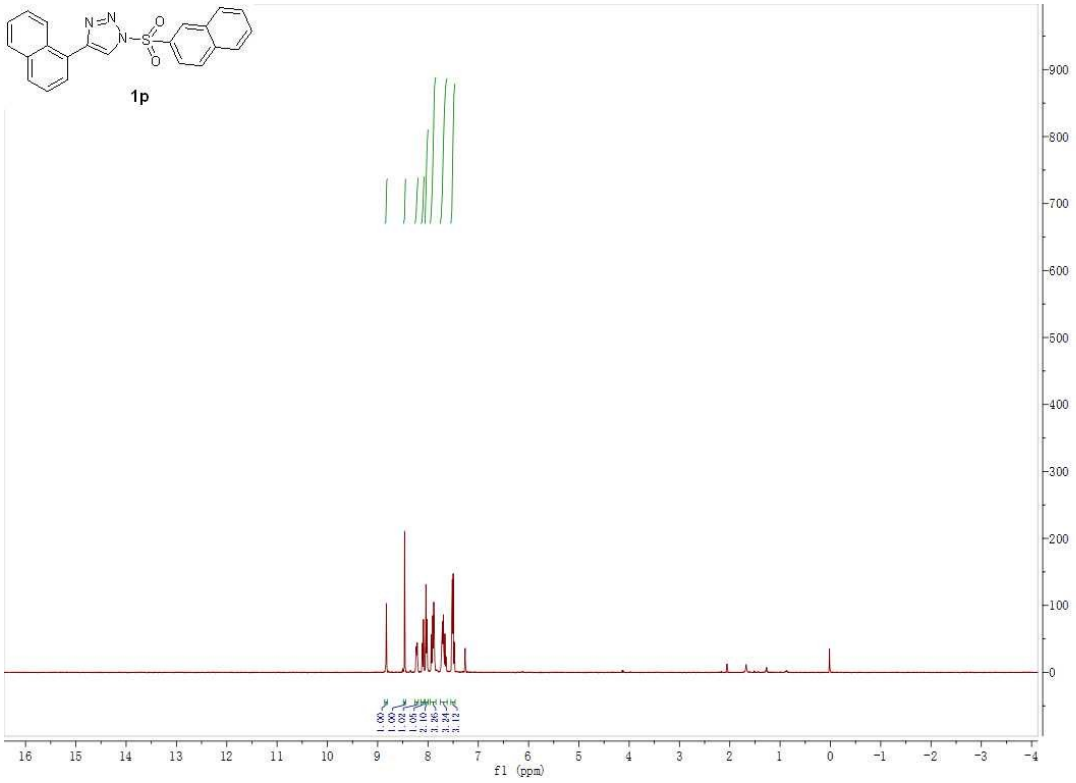

1m
f1 (ppm)

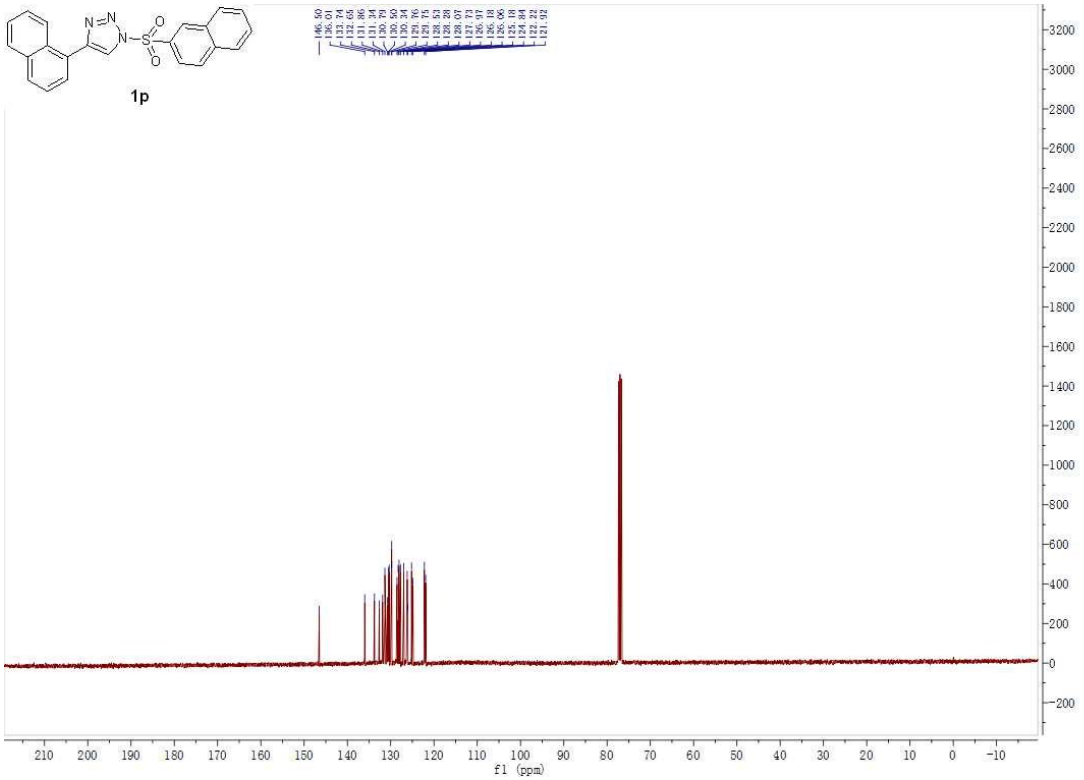

1n
f1 (ppm)

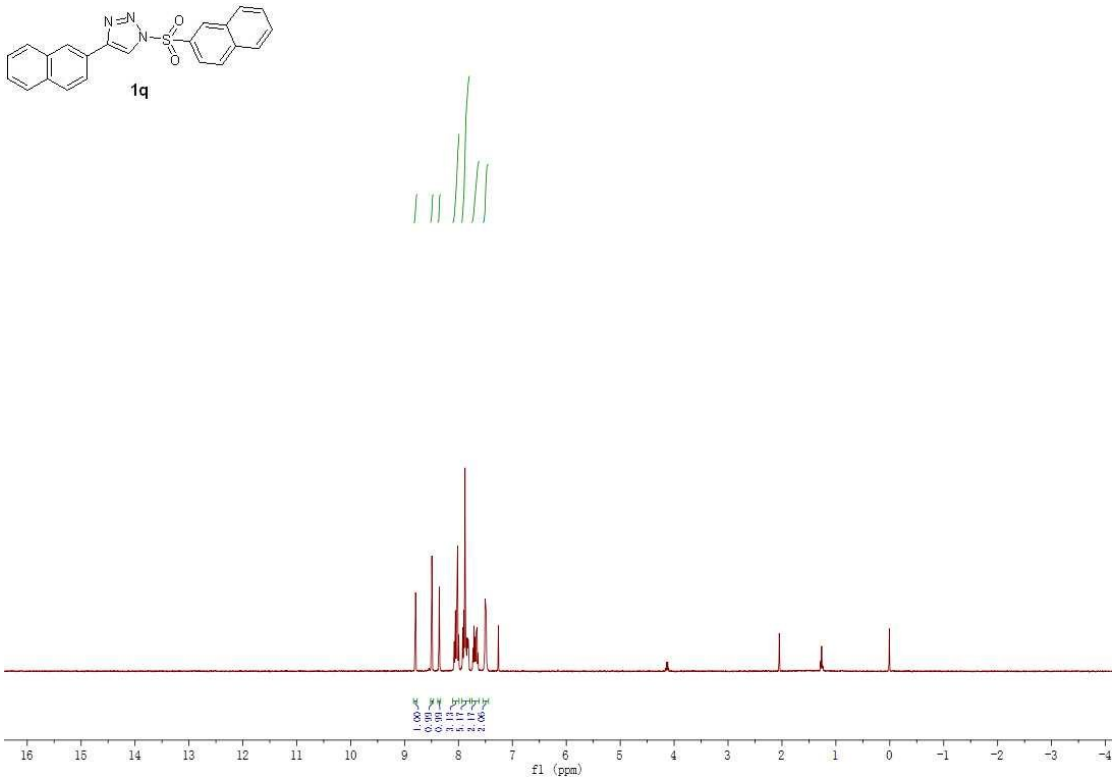

1n
F
Br
N
N
S
O
O
164.28
161.83
146.30
136.04
132.95
132.66
131.31
130.92
130.84
130.63
130.58
130.36
129.78
128.24
128.05
122.15
121.71
121.68
119.40
115.87
113.19
112.96
f1 (ppm)

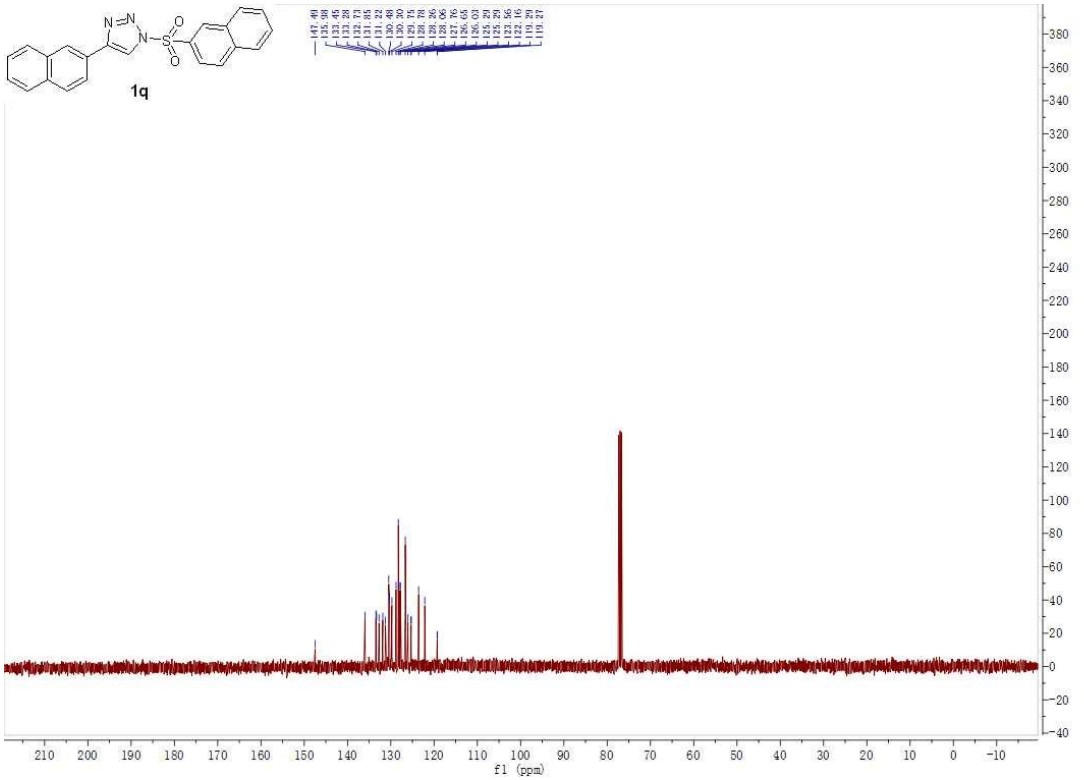

1o
N
N
S
O
O
1.00
1.01
3.16
1.15
2.29
2.17
3.09
3.14
f1 (ppm)

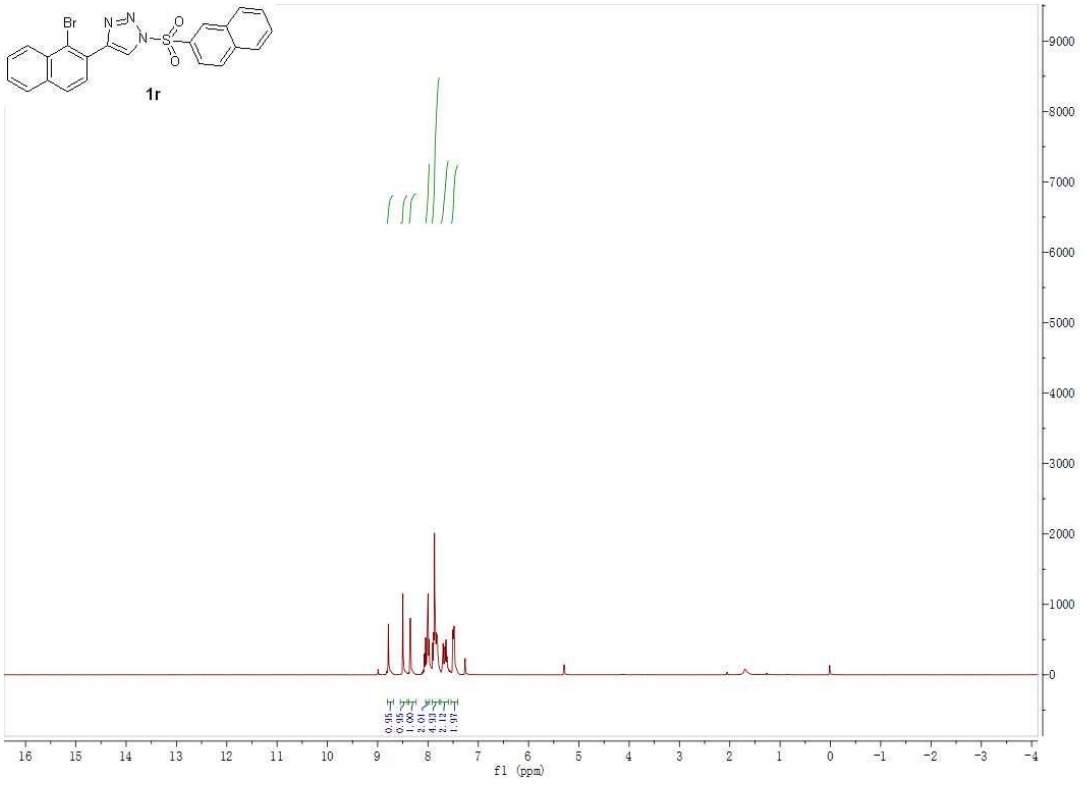

1o
146.75
138.89
135.97
135.60
132.82
131.87
131.77
131.13
130.45
130.27
129.76
129.54
128.25
128.07
126.94
125.17
122.19
120.62
21.27
21.11
f1 (ppm)

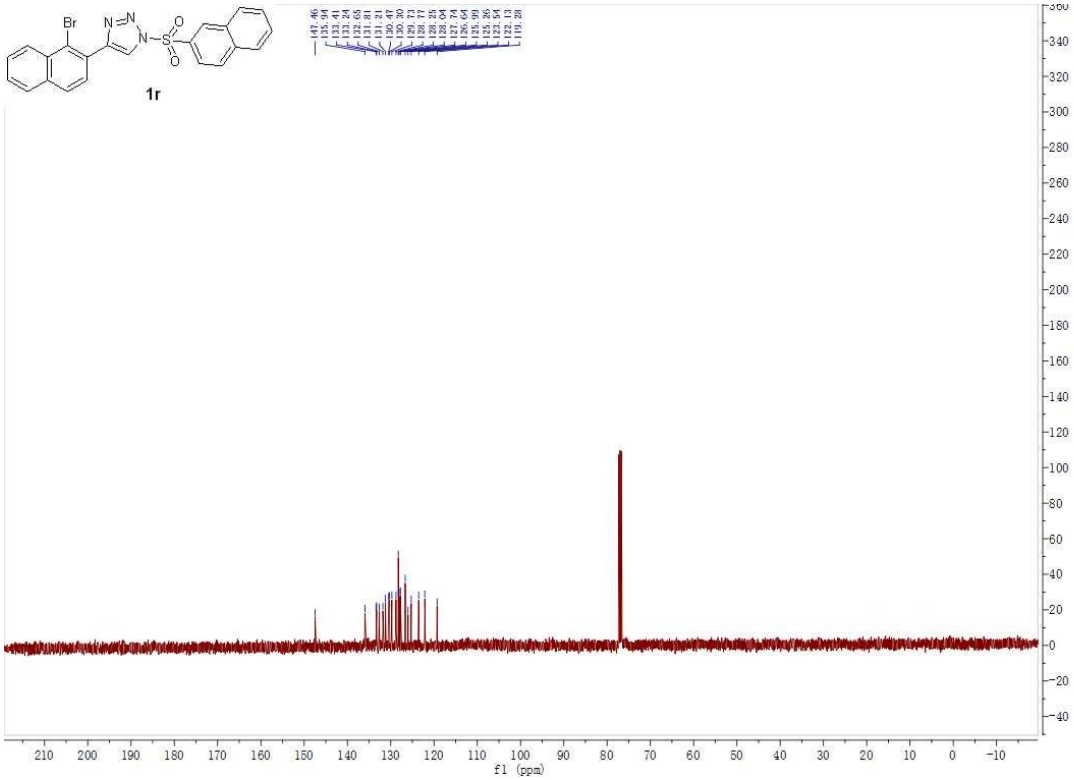

1p
1.00
1.00
1.02
1.05
2.10
2.36
2.24
3.12
f1 (ppm)

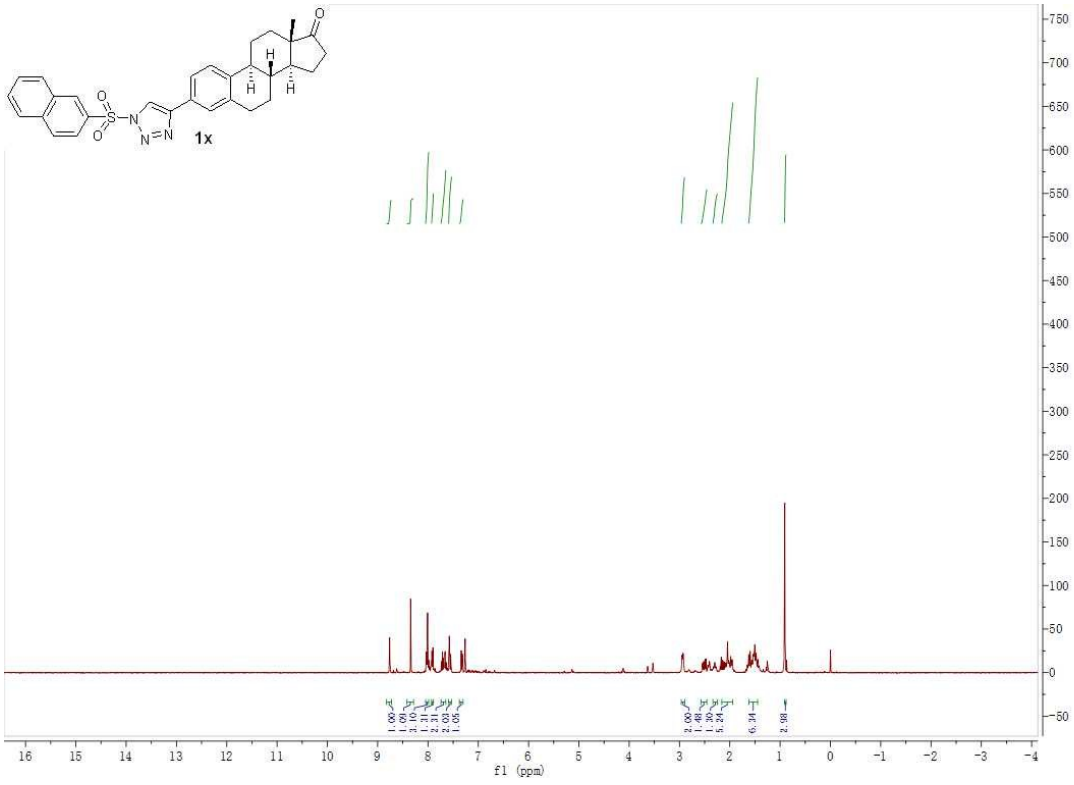

1p
f1 (ppm)

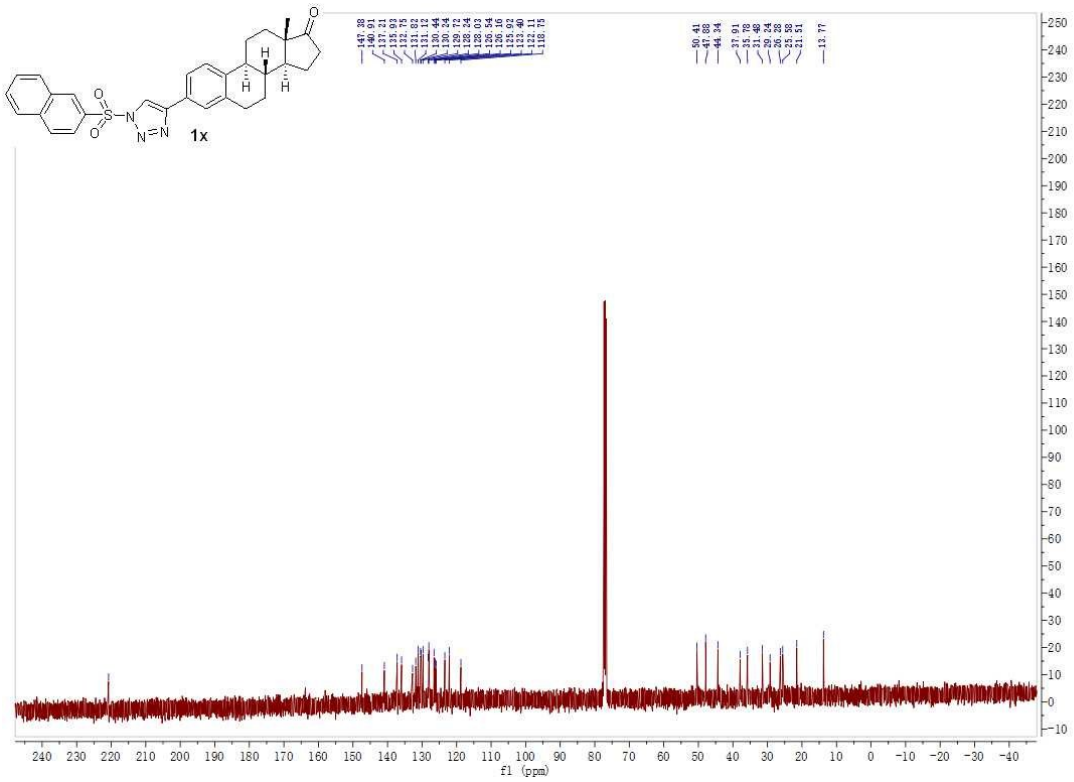

1q
f1 (ppm)


1q
f1 (ppm)


Br
1r
f1 (ppm)


Br
N
N
S
O
O
1r
f1 (ppm)


O
H
H
H
O
S
O
N
N
N
1x
f1 (ppm)


1x
147.38
140.91
137.21
135.03
133.70
131.82
131.12
130.44
130.34
129.72
128.54
128.03
126.54
126.16
125.62
123.40
123.11
118.75
50.41
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37.91
35.78
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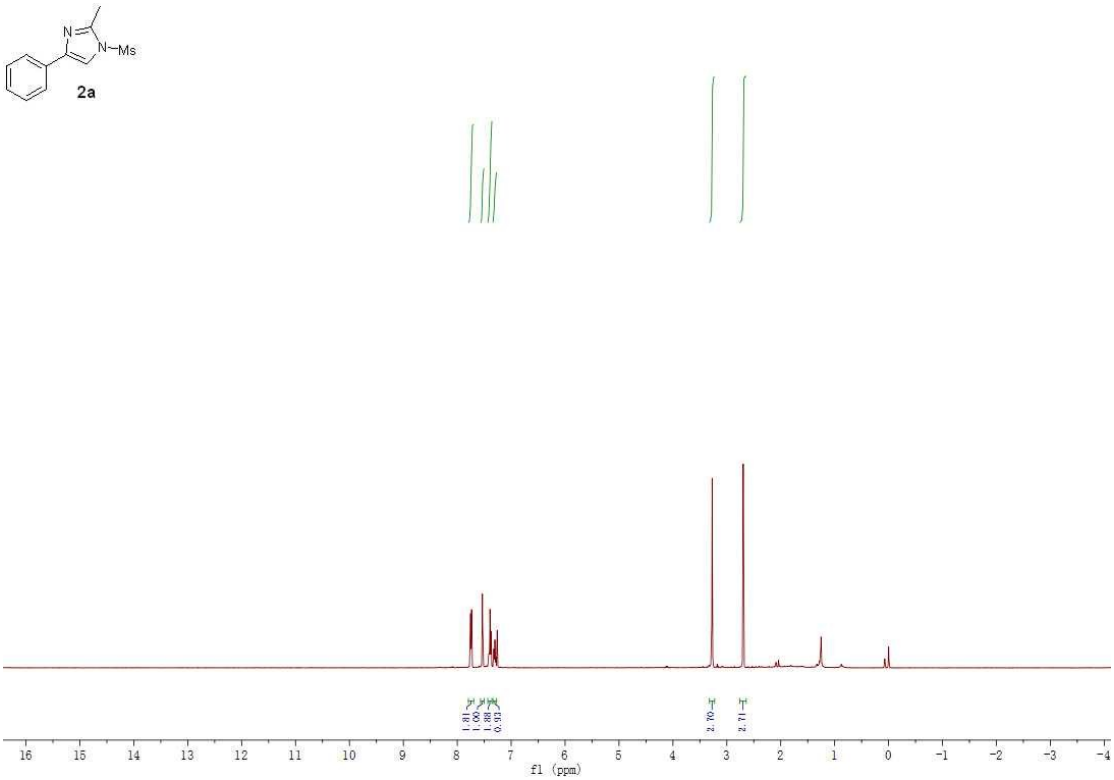
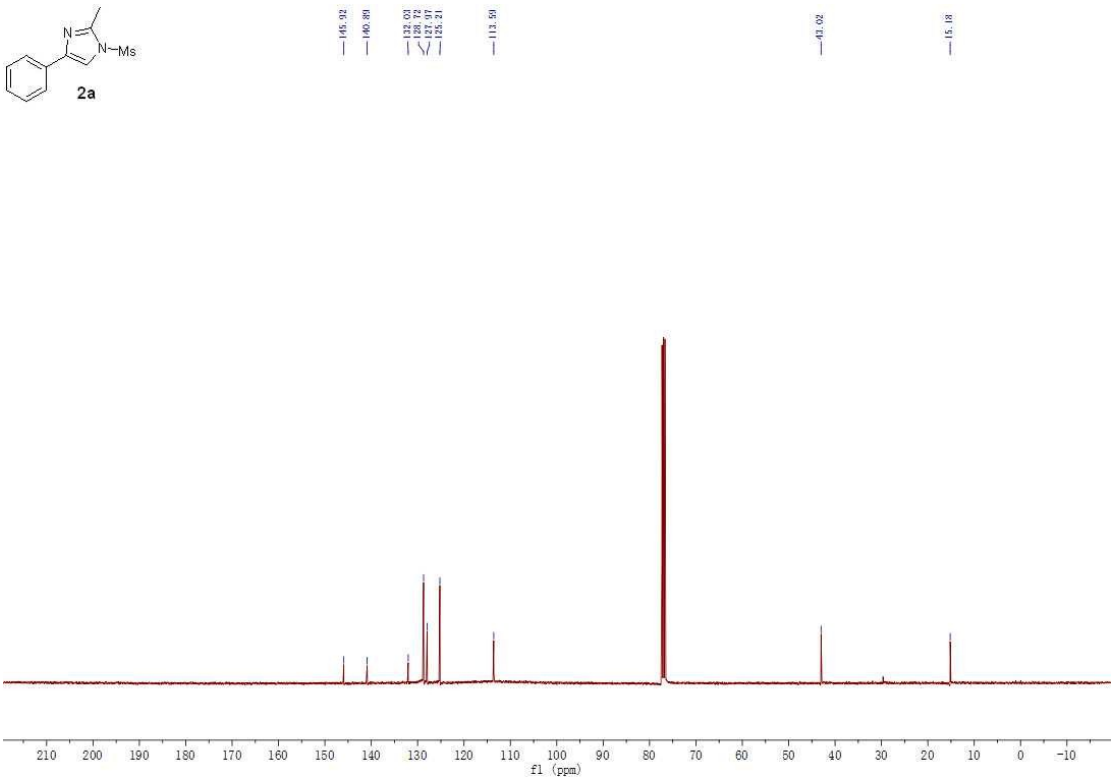
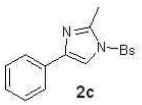
30.24
26.28
25.58
21.51
13.77
f1 (ppm)

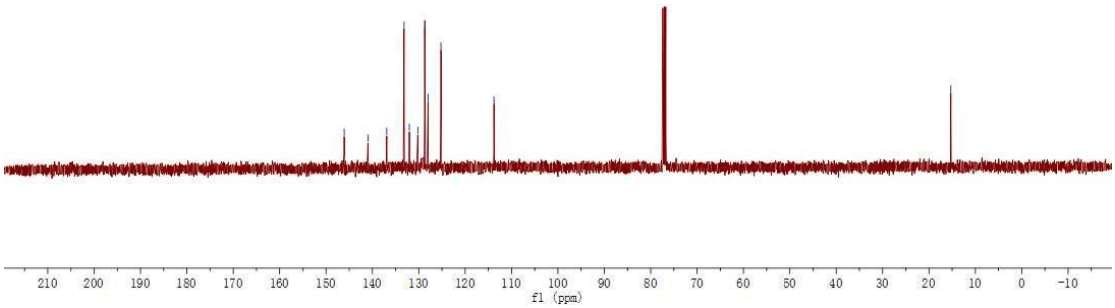

2a
1.01
1.00
1.88
0.93
2.70
2.71
f1 (ppm)

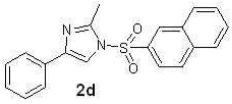

N
N
Ms
2a
145.92
140.80
133.93
128.72
127.97
125.21
113.59
43.02
15.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N
N
Bs
2c
1.98
4.00
1.00
2.02
1.03
2.91
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


N
N
Bs

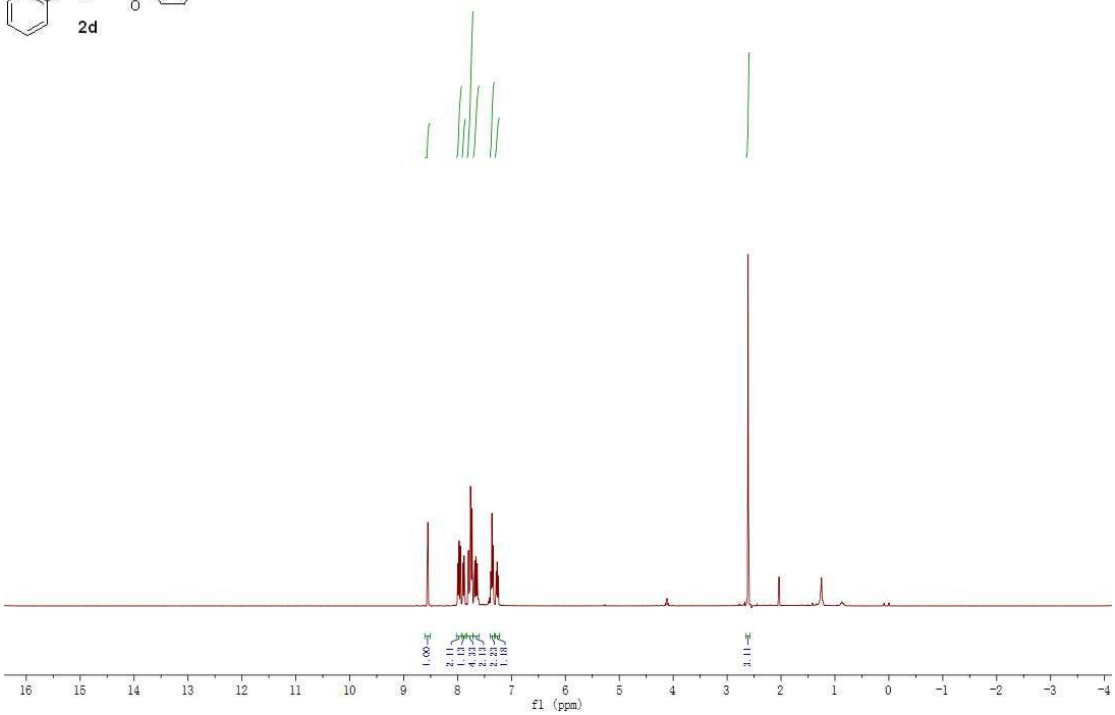
2c

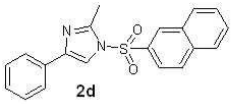

146.08
140.97
136.90
133.17
132.04
130.22
128.73
128.68
128.01
125.22
113.70
15.28


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

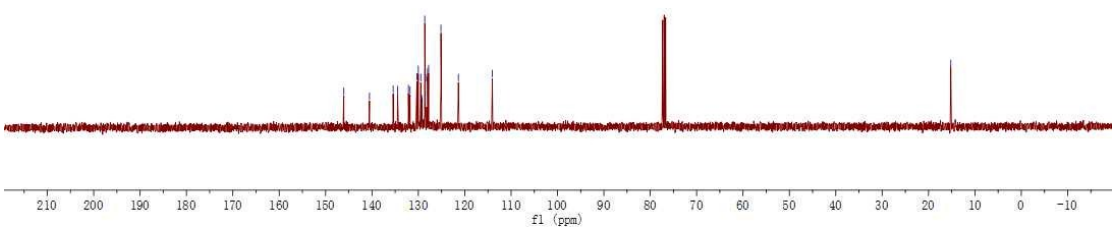

N
N
S
O
O

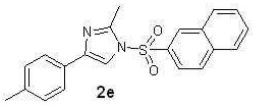
2d


1.00
2.11
4.23
2.13
2.23
1.38
3.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

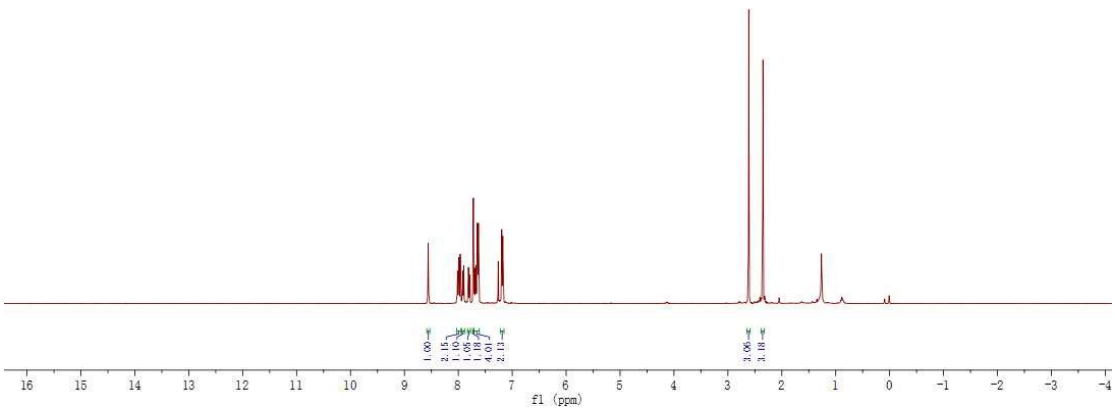


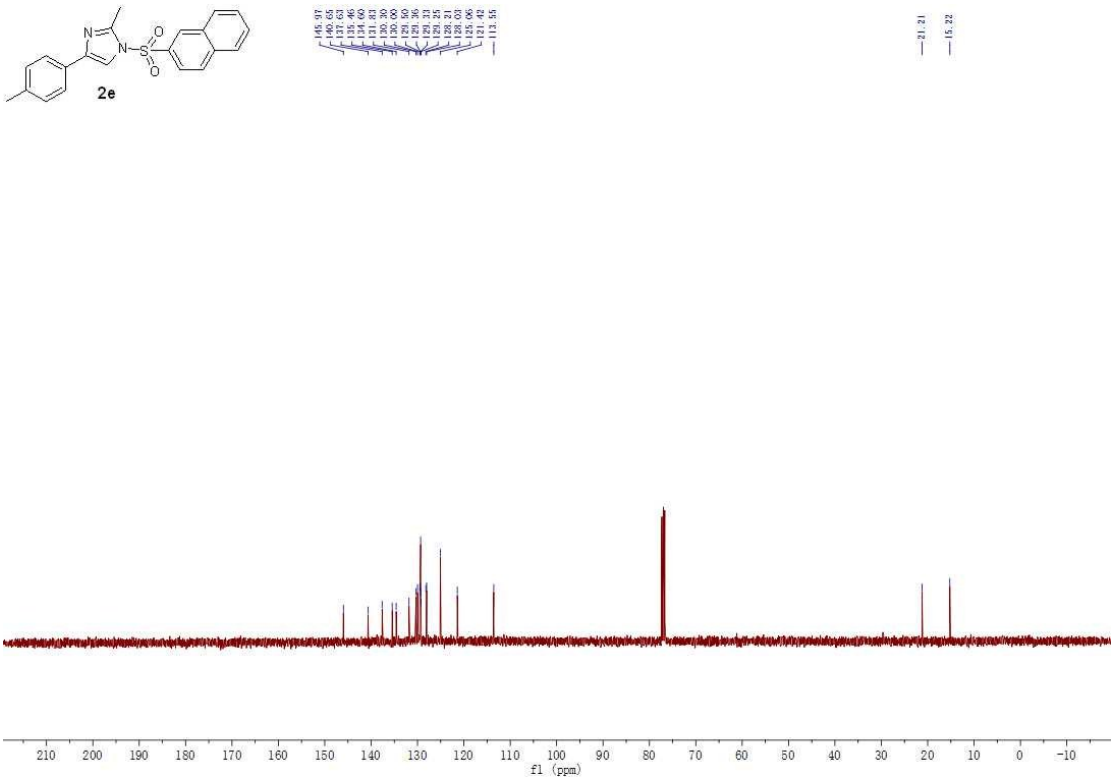
2d

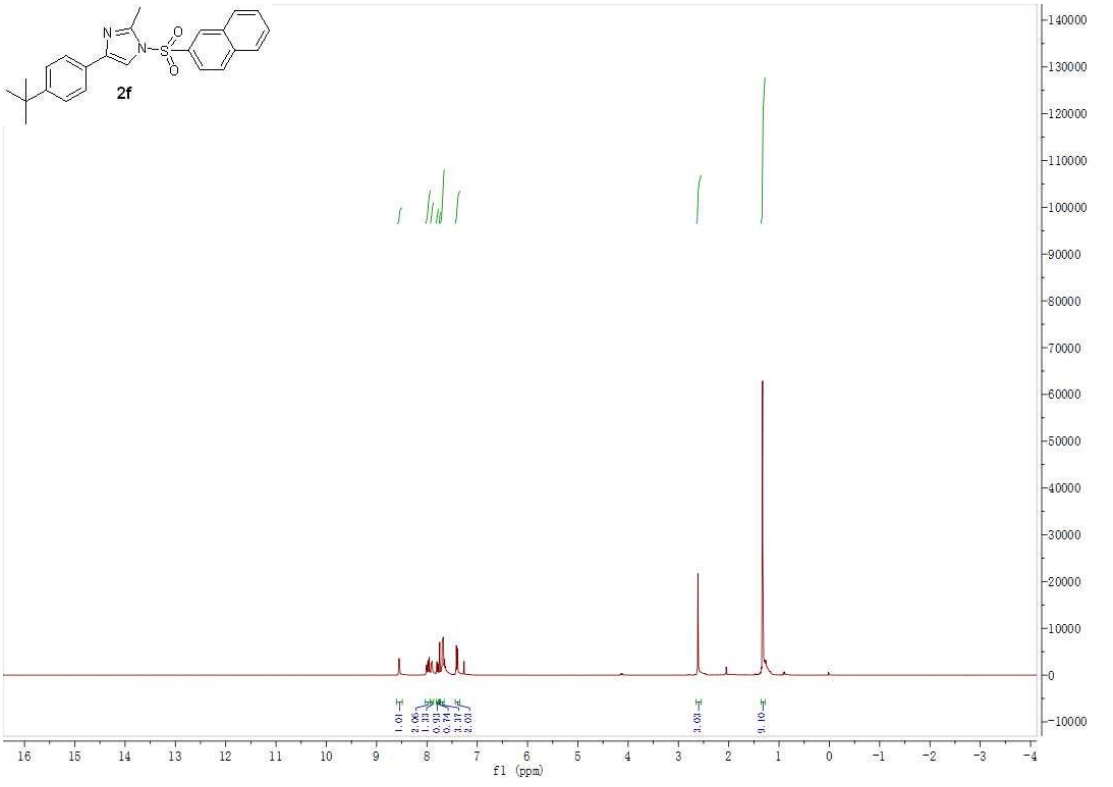

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

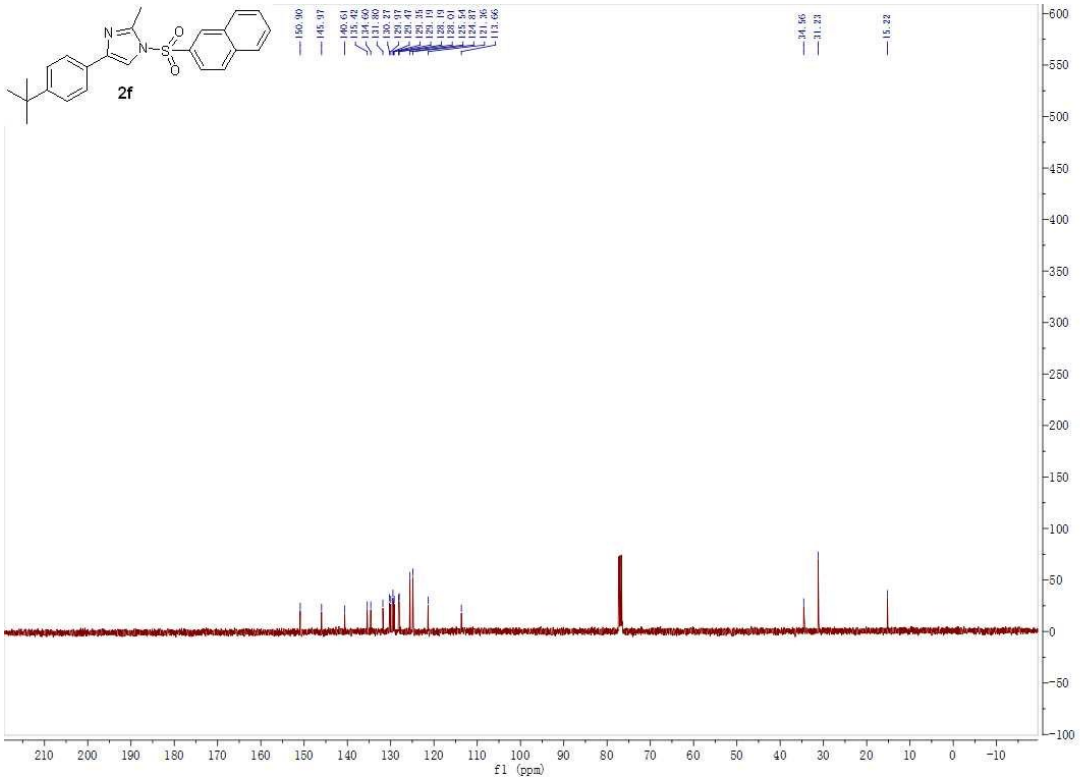


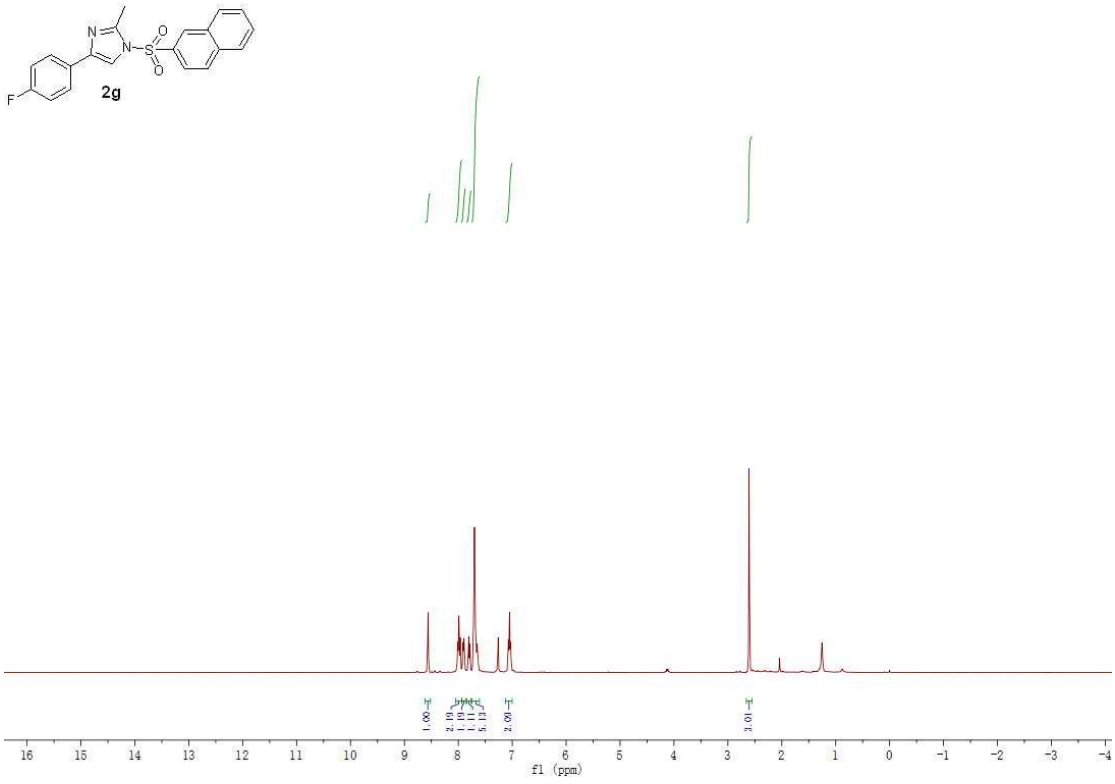
2e

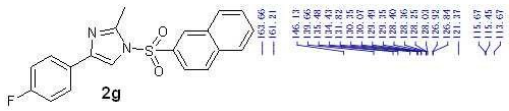

1.00
2.15
1.10
1.05
1.18
4.01
2.13
3.00
3.18
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

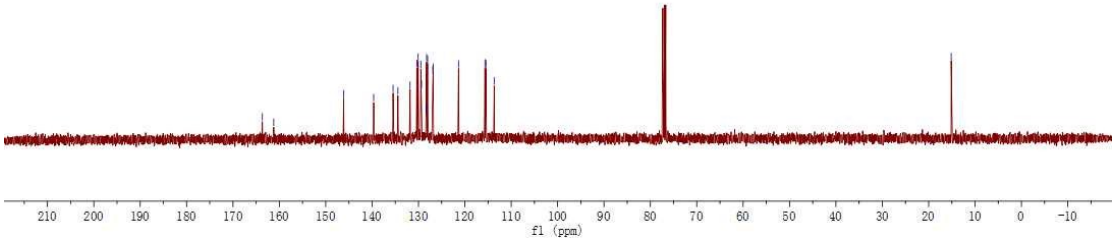

2e
145.97
140.65
137.63
134.46
134.06
131.83
130.30
130.00
129.60
129.36
129.33
129.25
129.21
128.03
125.06
121.42
113.55
21.21
15.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

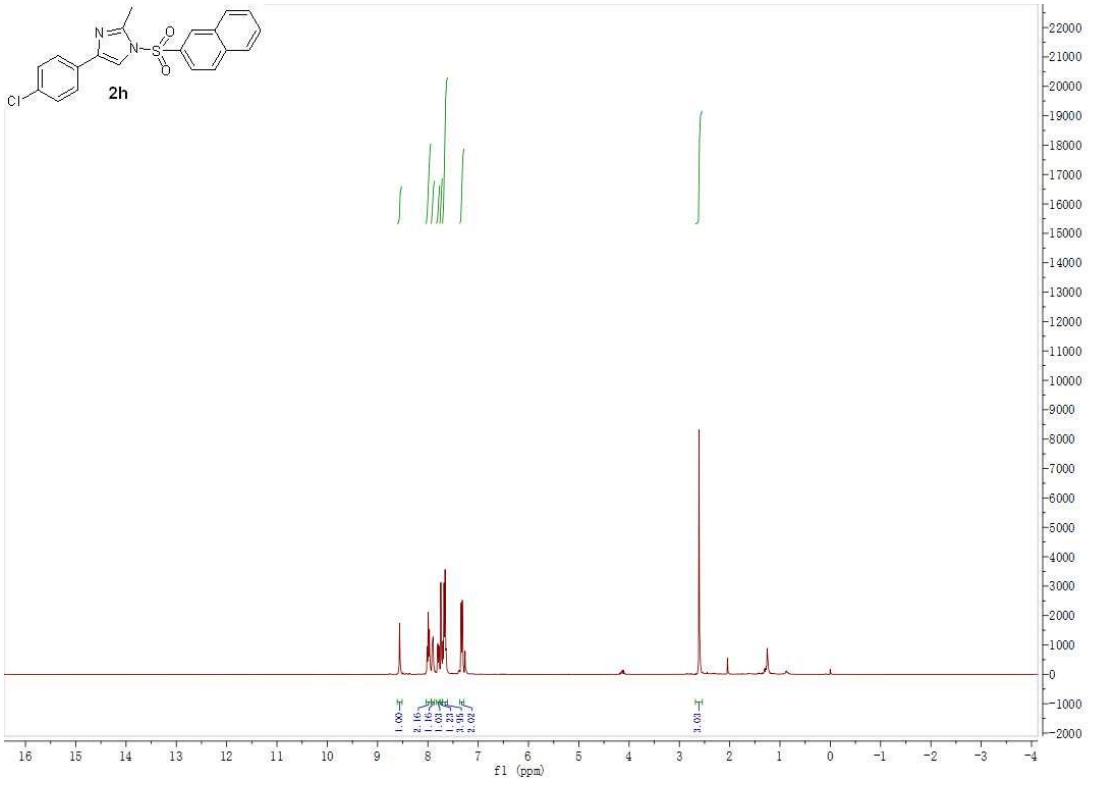

2f
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
1.01
2.06
1.33
0.31
0.34
2.17
2.03
3.03
9.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

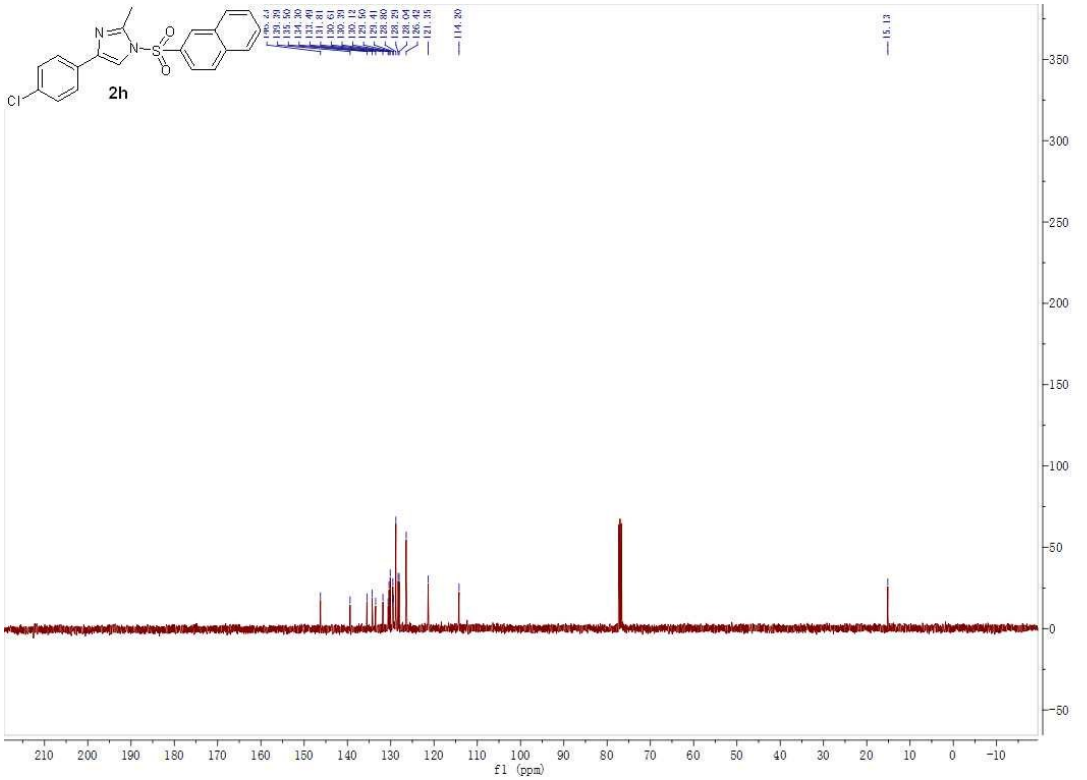

2f
150.90
145.97
140.61
135.42
134.60
131.80
130.27
129.97
129.47
129.35
129.19
128.19
125.91
125.54
124.87
121.36
113.66
34.96
31.23
15.22
f1 (ppm)

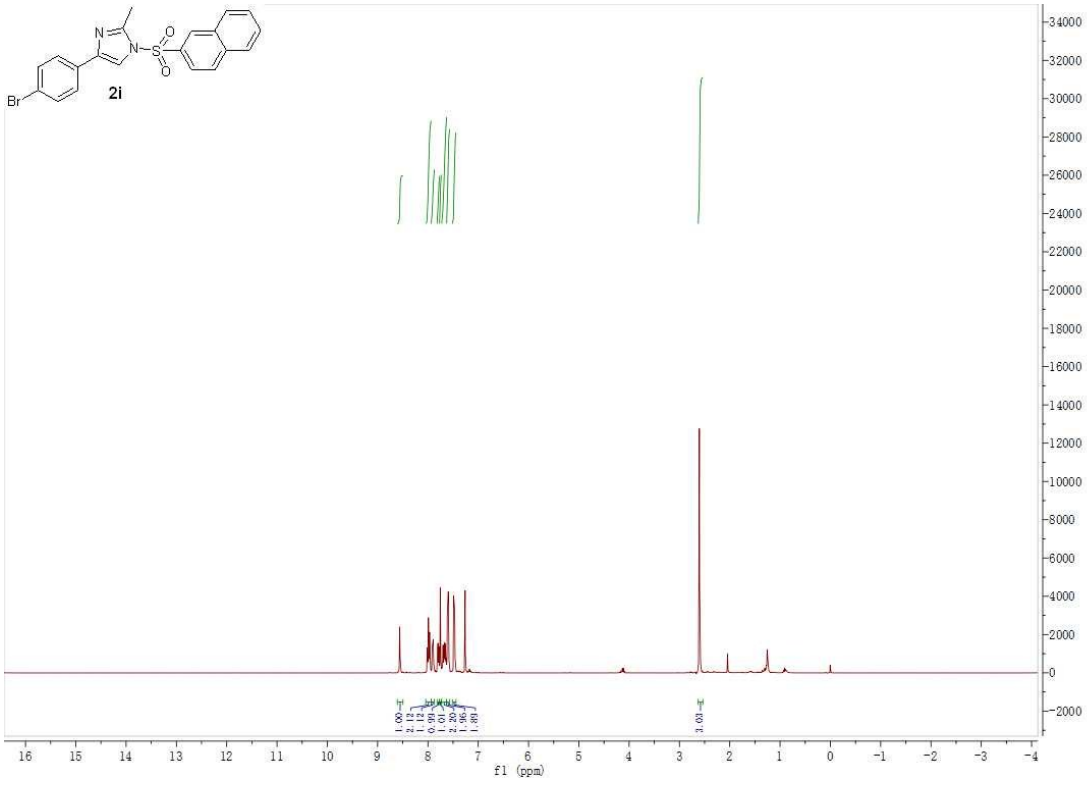

2g
1.00
2.19
2.19
1.11
5.13
2.09
3.01
f1 (ppm)

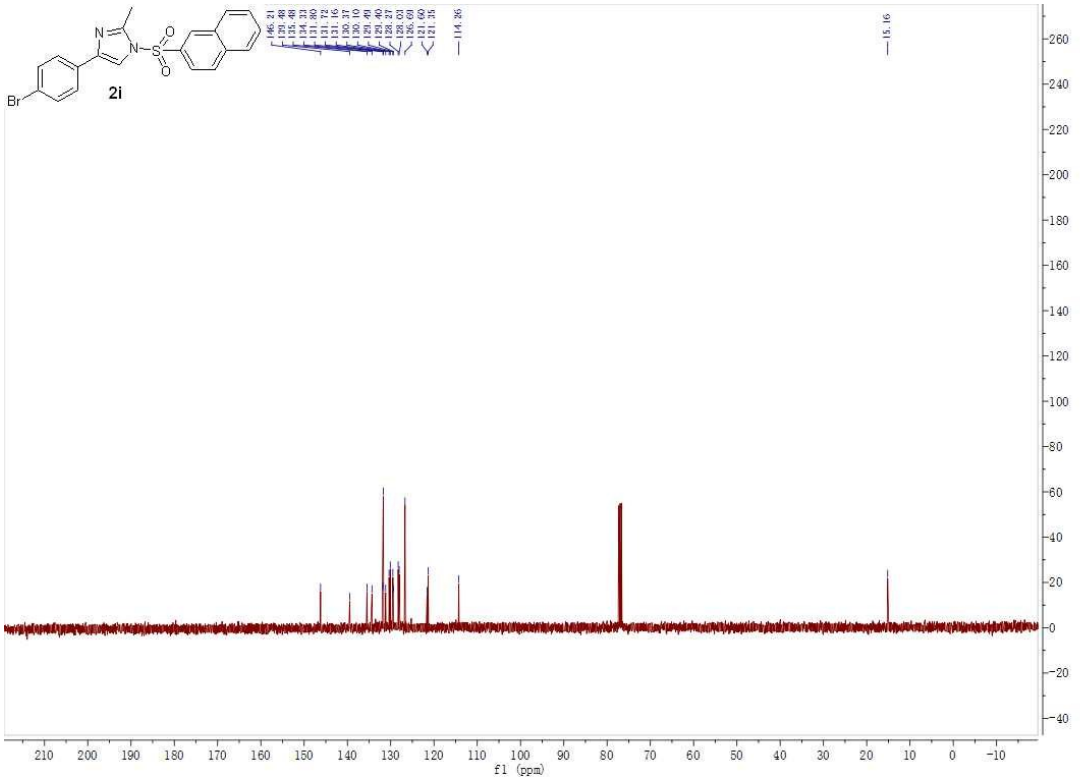

2g

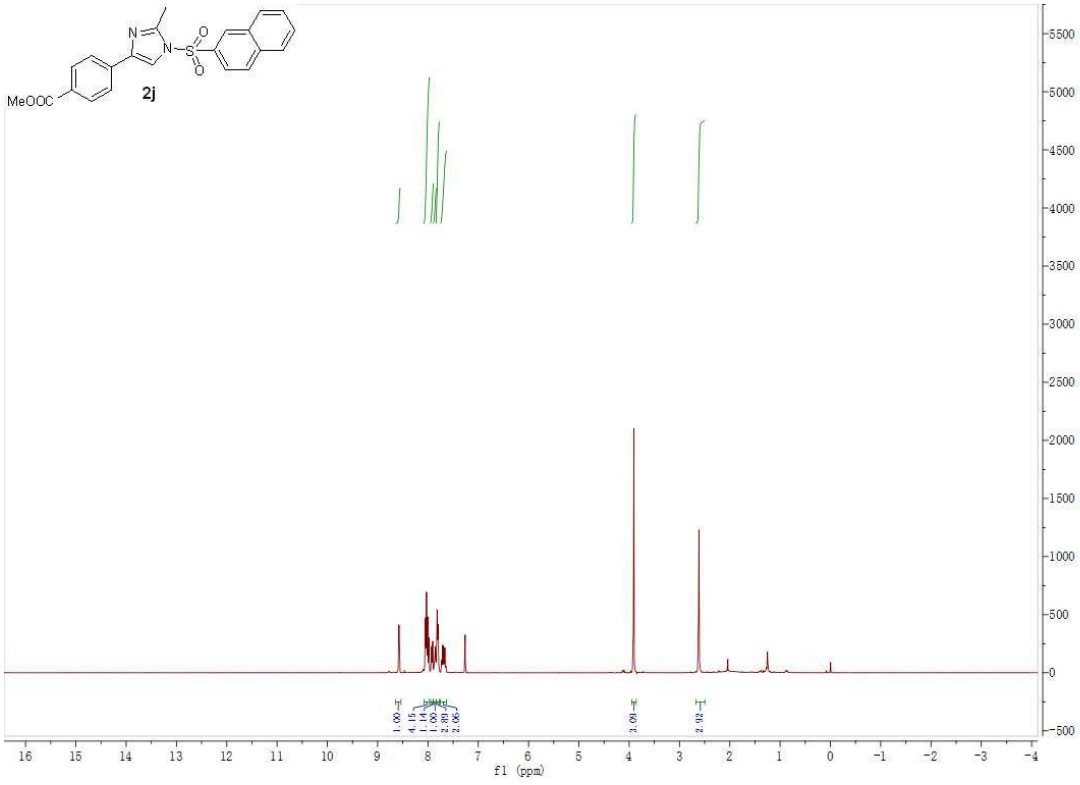

f1 (ppm)

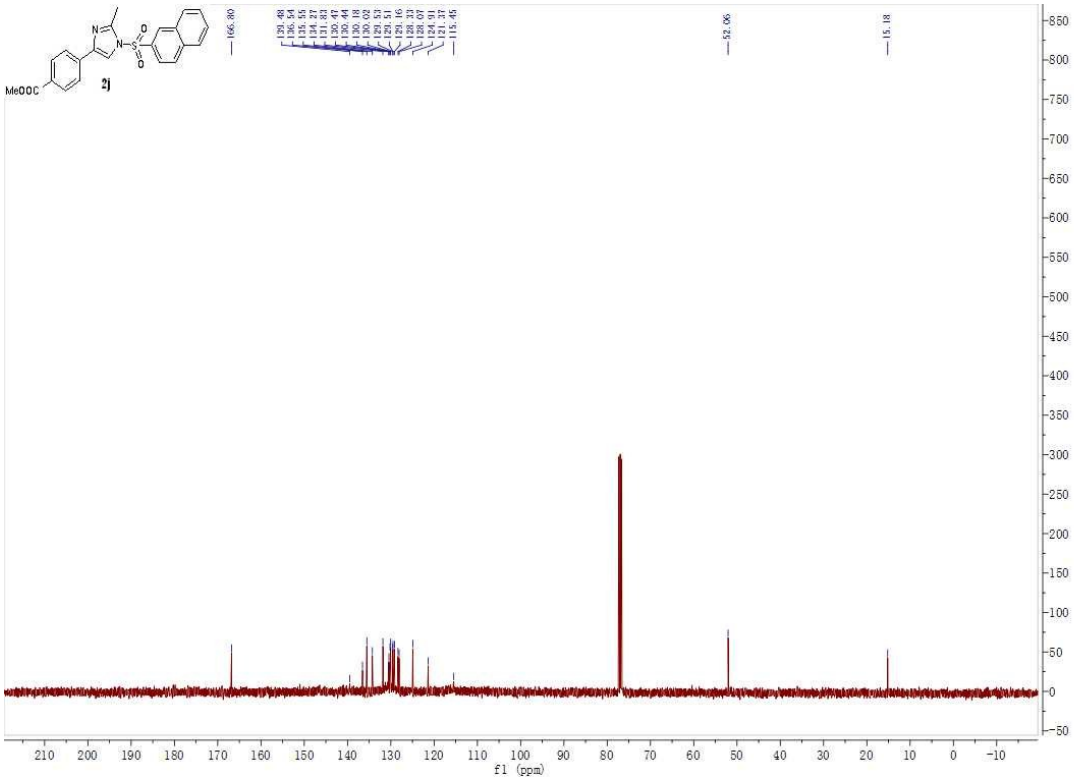

2h
f1 (ppm)

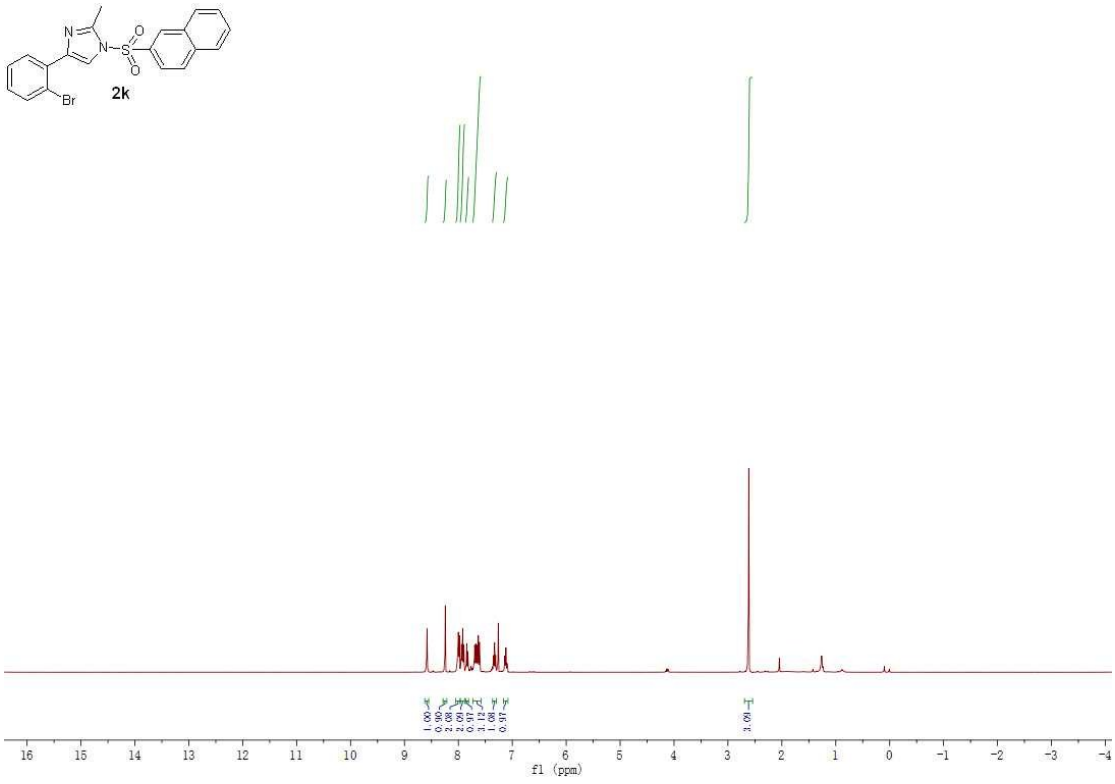

2h
Cl
f1 (ppm)

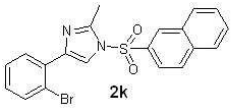

2i
Br
f1 (ppm)

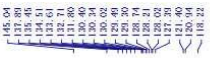

Br
2i
f1 (ppm)

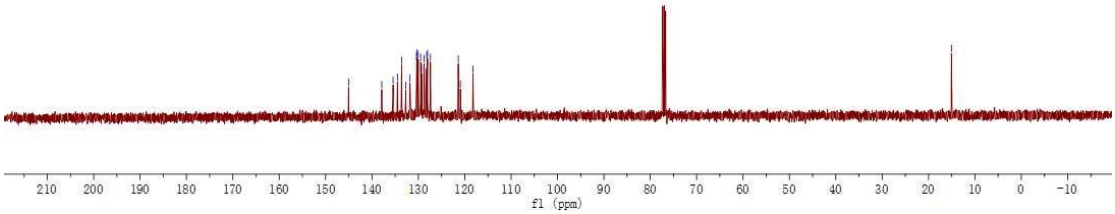

MeOOC
2j
f1 (ppm)

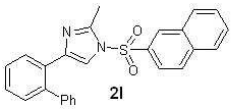

MeOOC
2j
166.80
139.48
136.54
135.55
134.27
131.93
130.47
130.44
130.18
130.02
129.53
129.51
129.16
128.33
128.07
124.91
121.37
115.45
52.06
15.18
f1 (ppm)

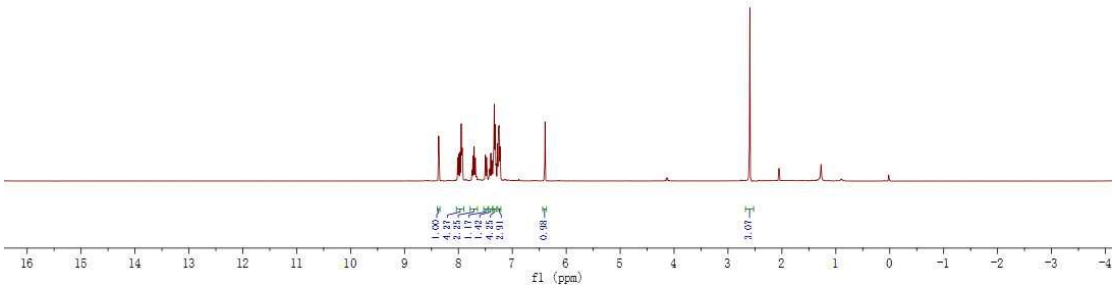

Br
2k
1.00
0.90
2.08
2.09
0.97
3.12
1.08
0.97
3.09
f1 (ppm)

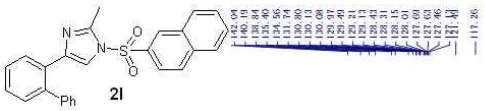

Br
2k

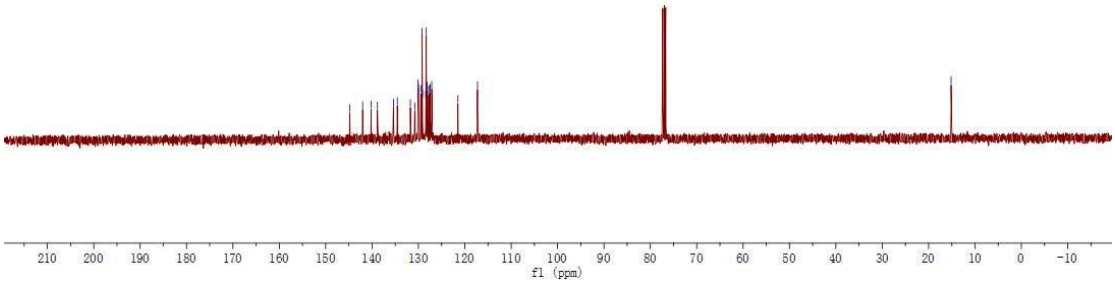


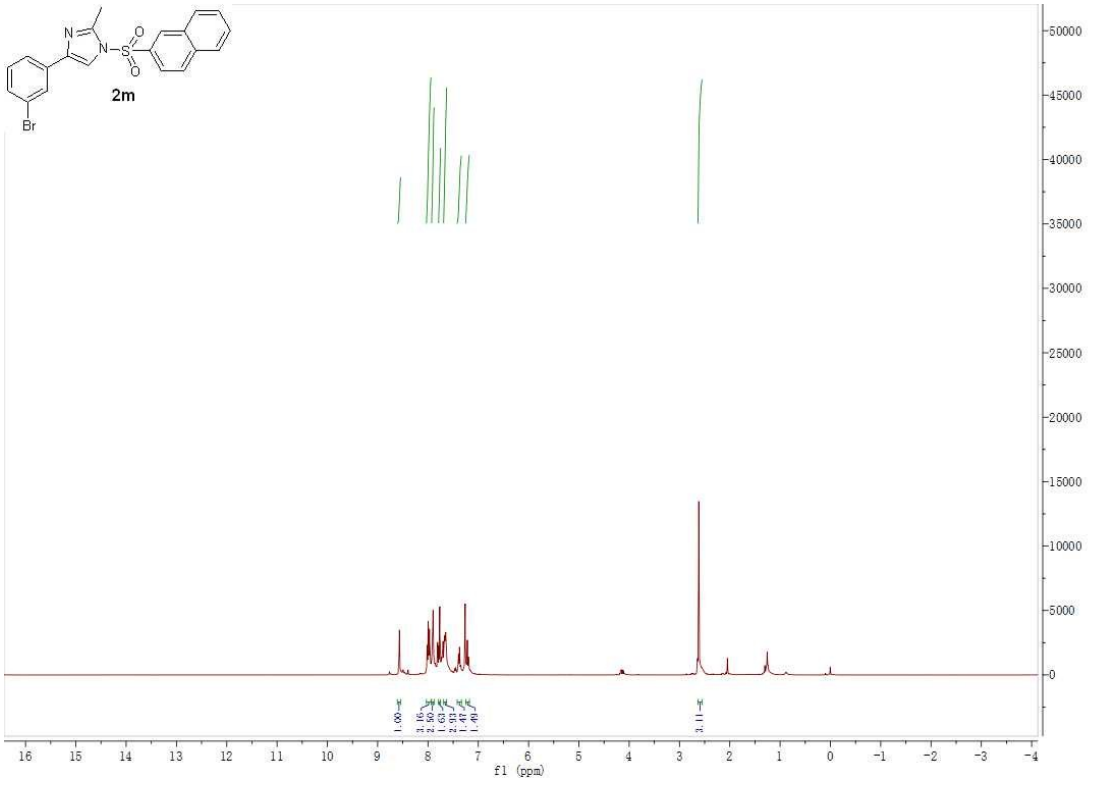

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

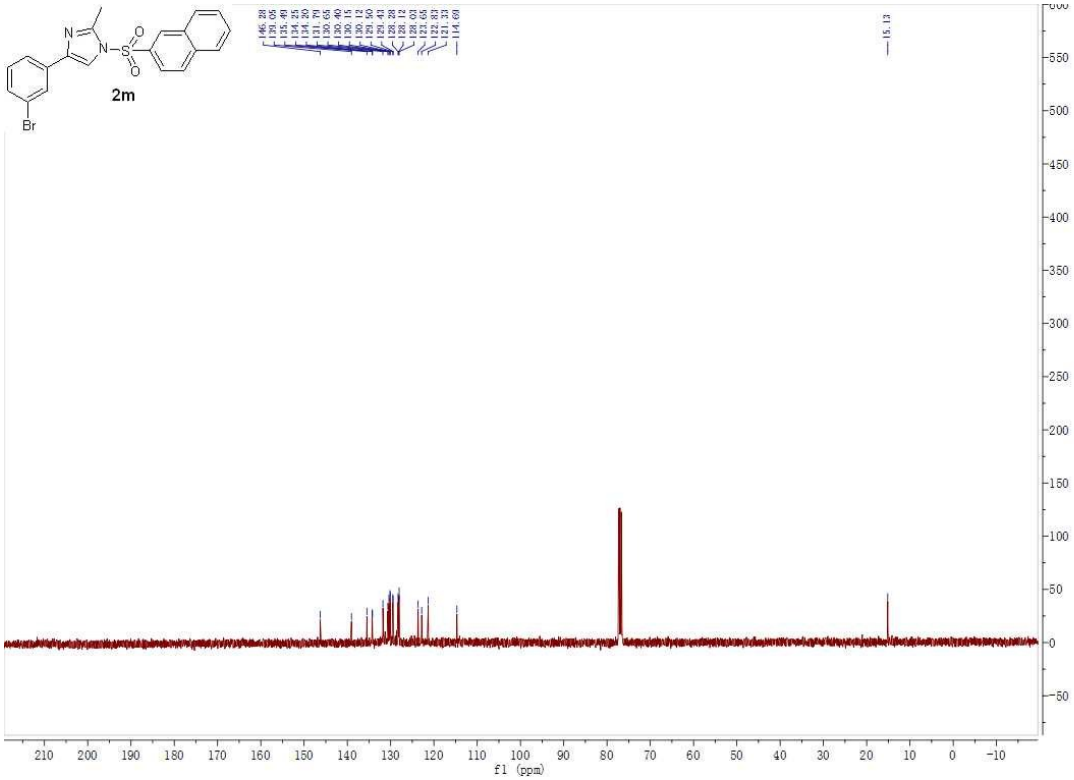

Ph
2l

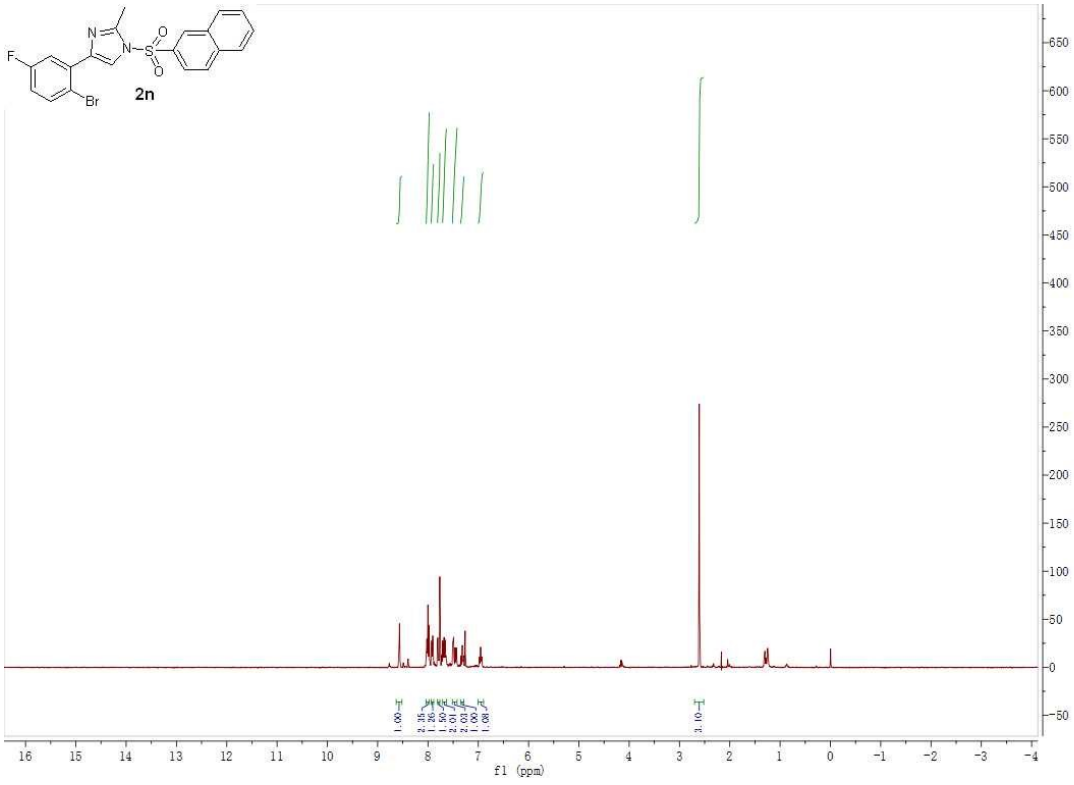

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

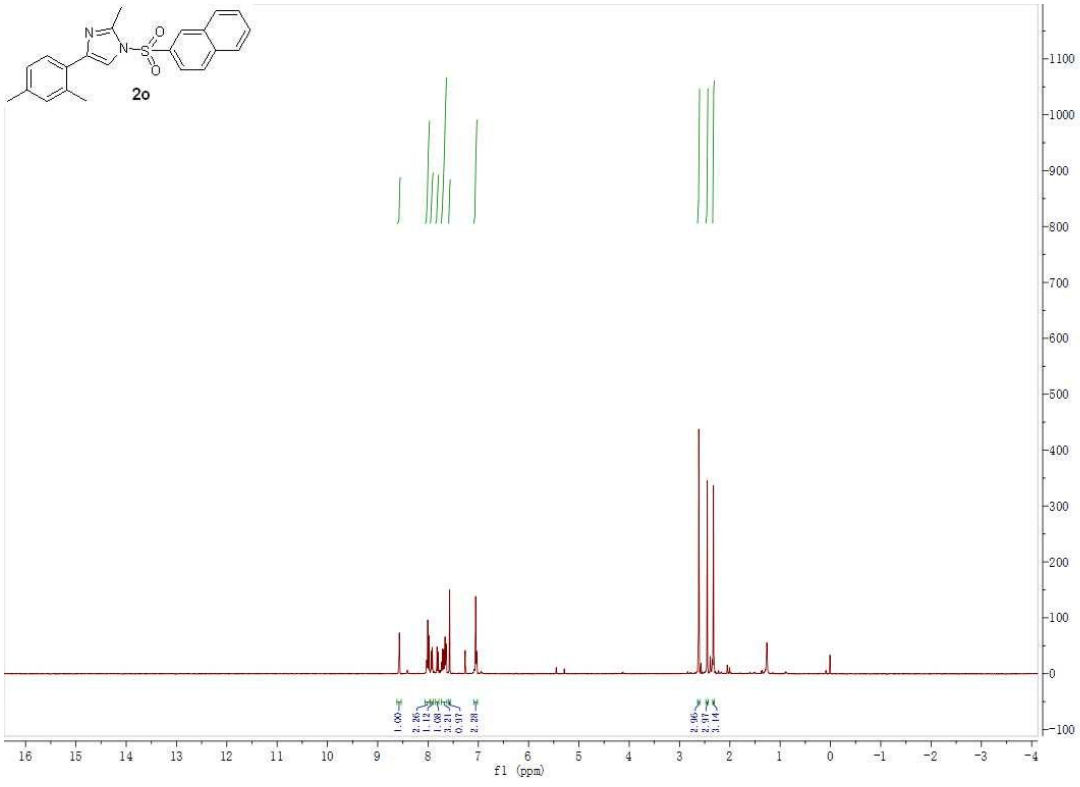

Ph
2l

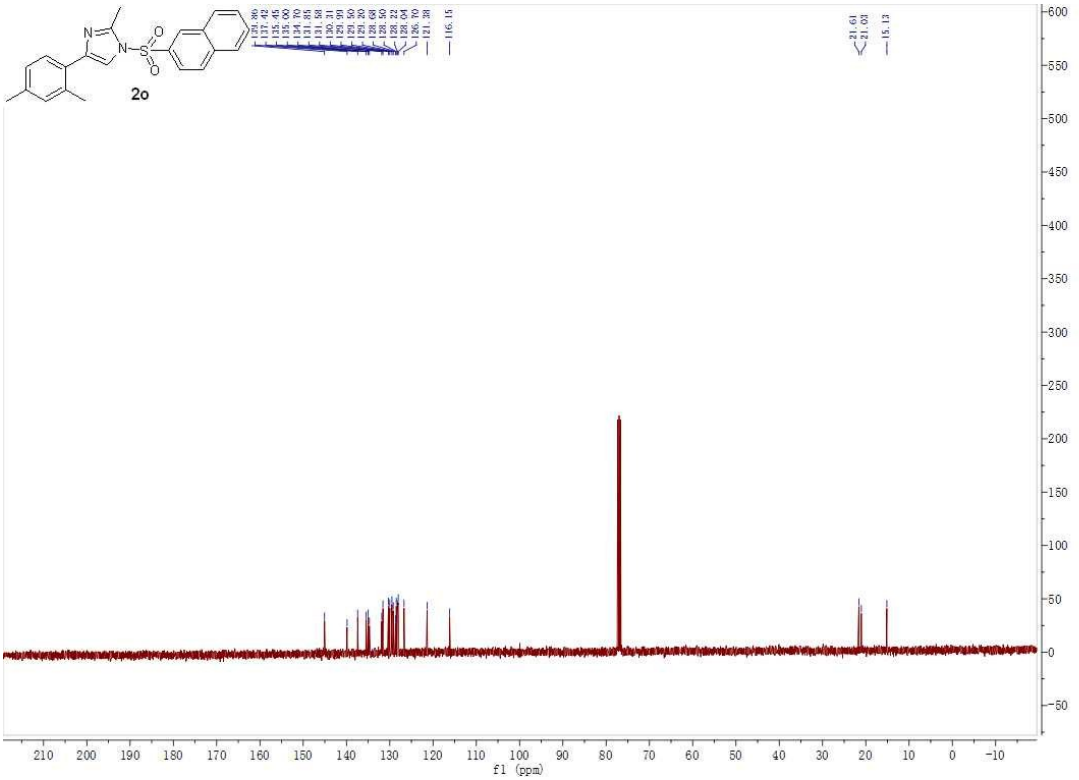

f1 (ppm)

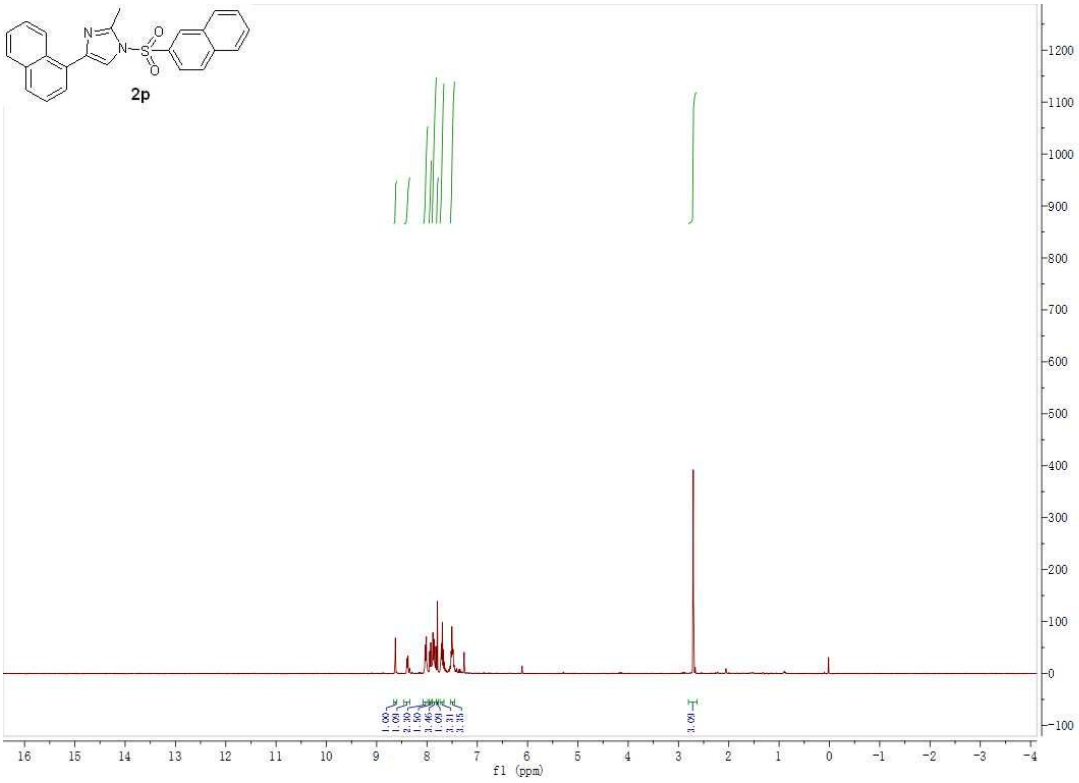

Br
2m
f1 (ppm)

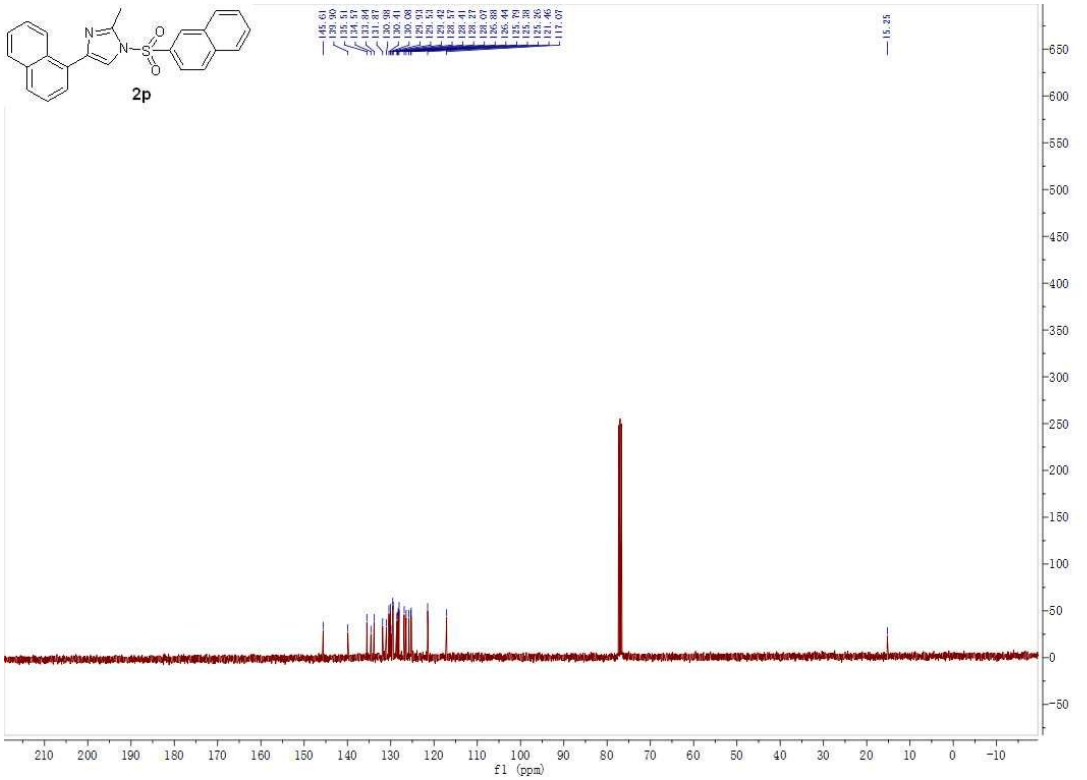

2m
Br
f1 (ppm)

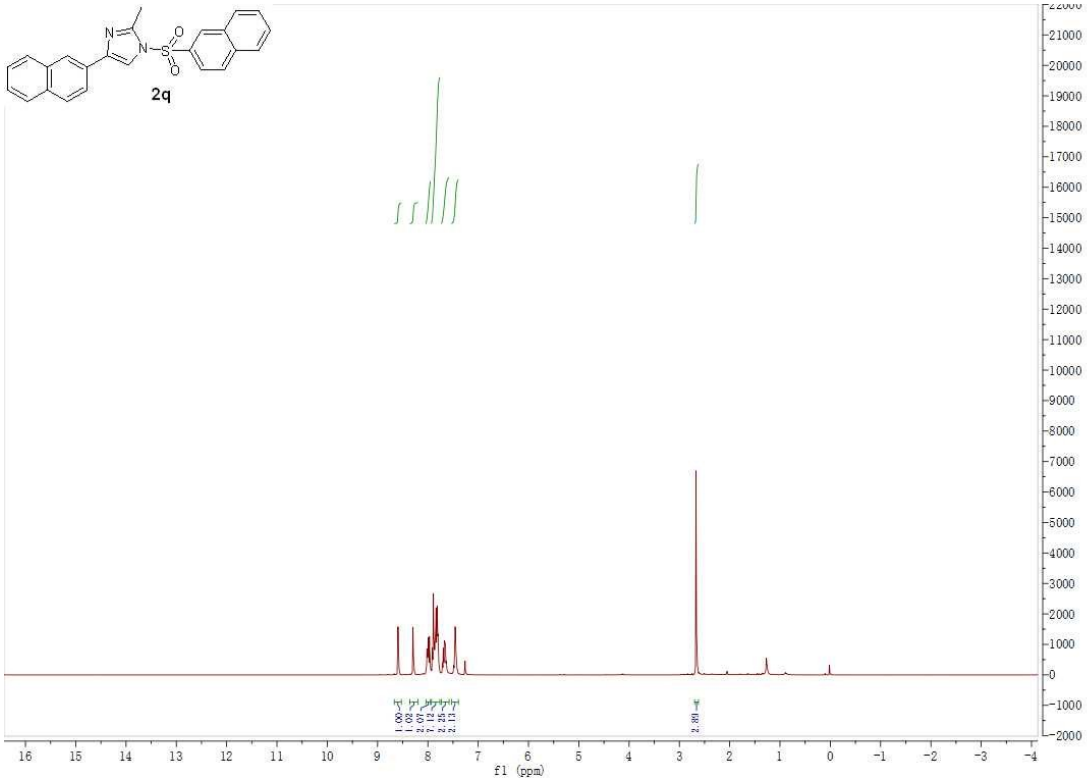

2n
F
Br
f1 (ppm)

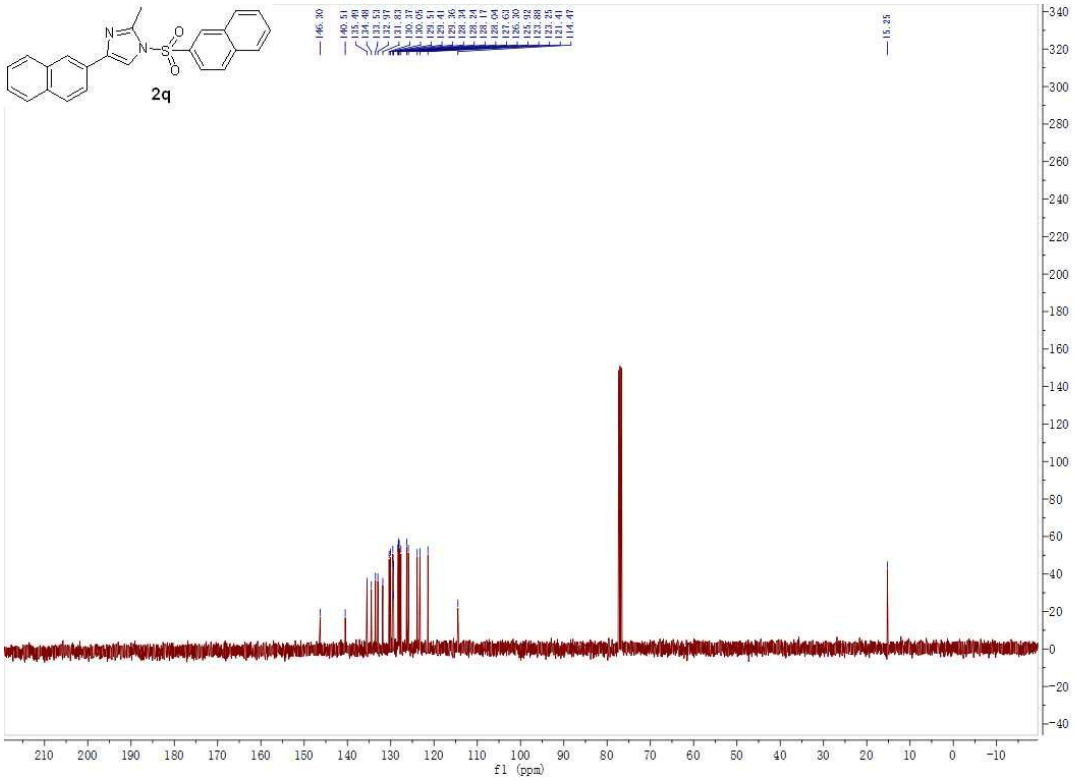

2o
1.00
2.26
2.12
1.08
2.17
0.97
2.28
2.96
2.07
3.14
f1 (ppm)

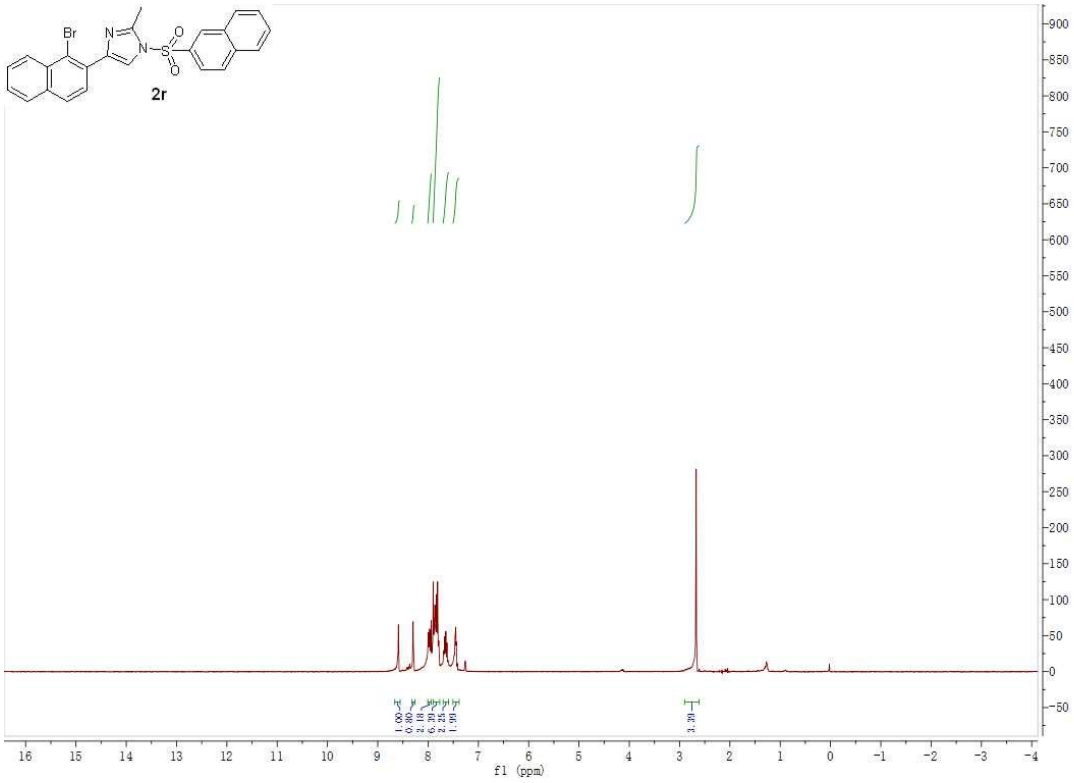

2o
21.61
21.03
15.13
f1 (ppm)

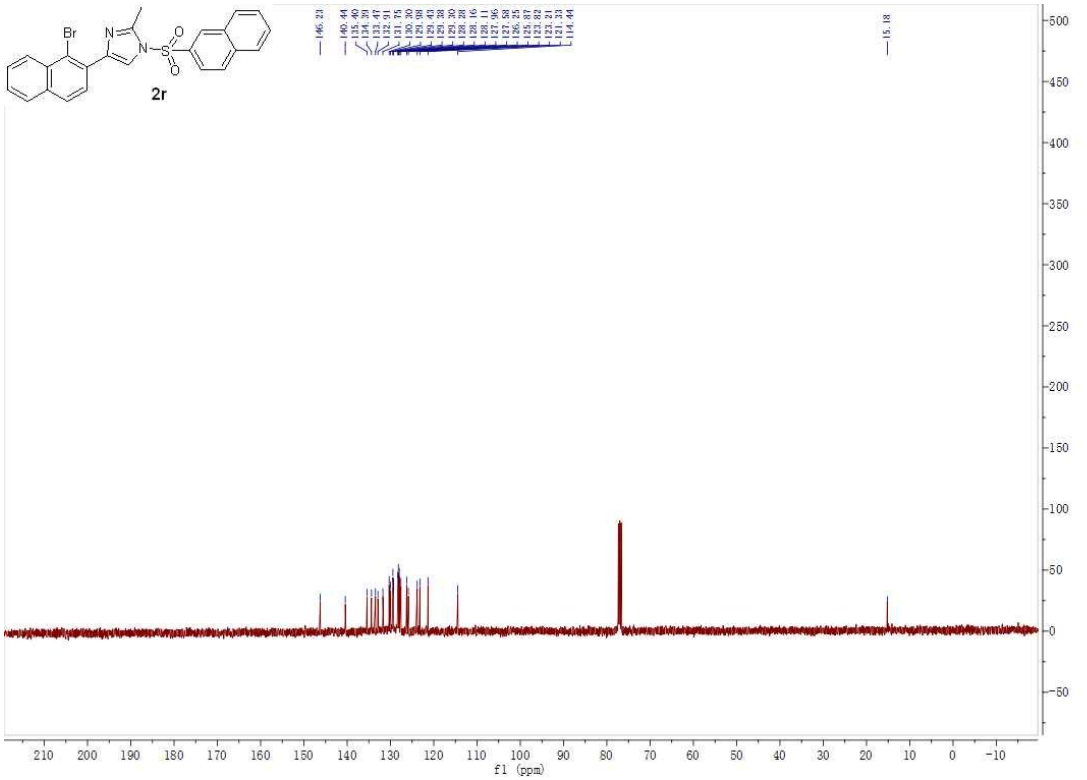

2p
f1 (ppm)

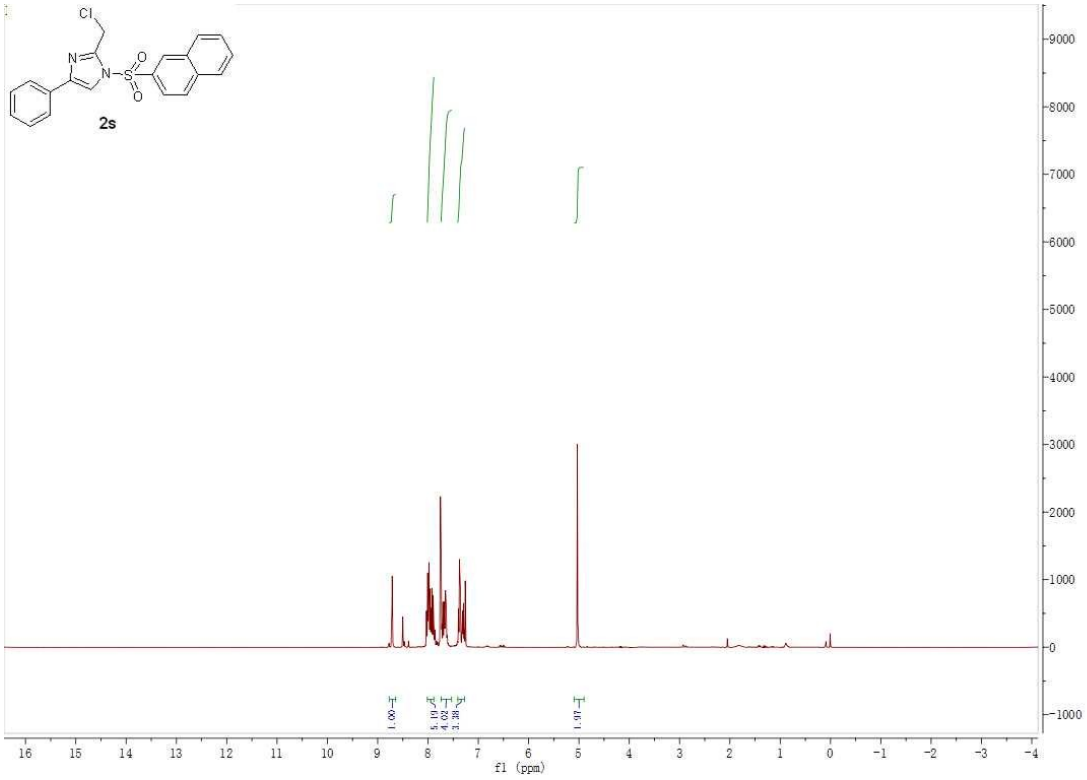

2p
f1 (ppm)

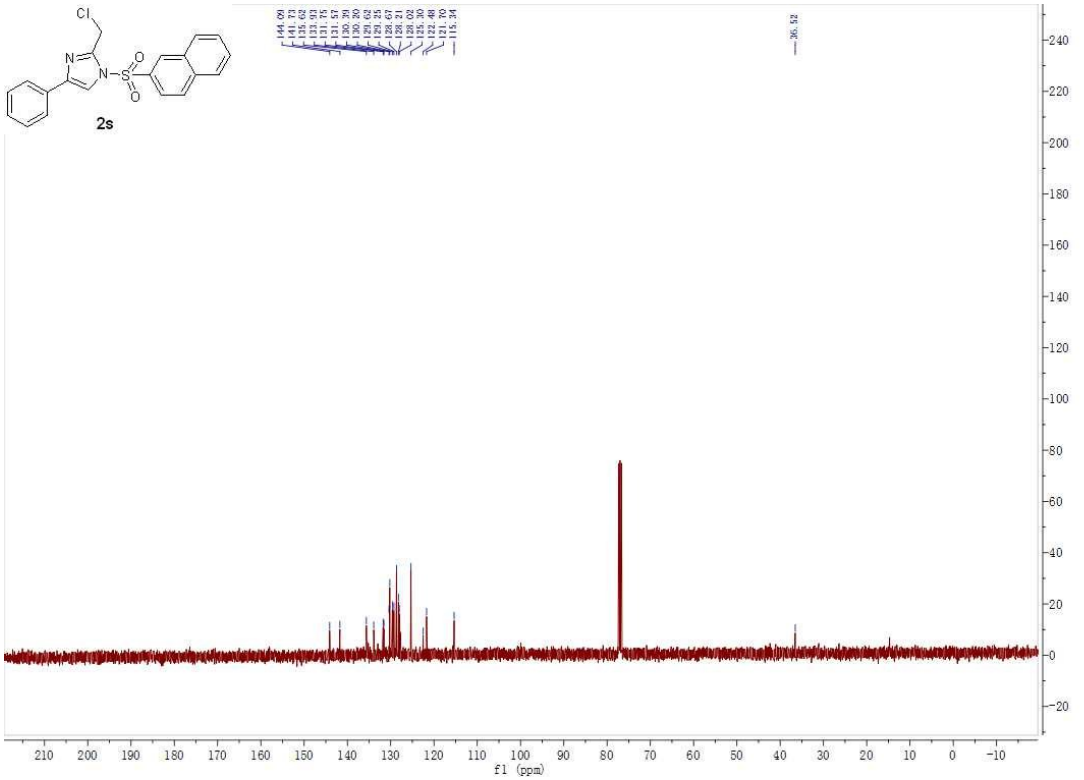

2q
f1 (ppm)

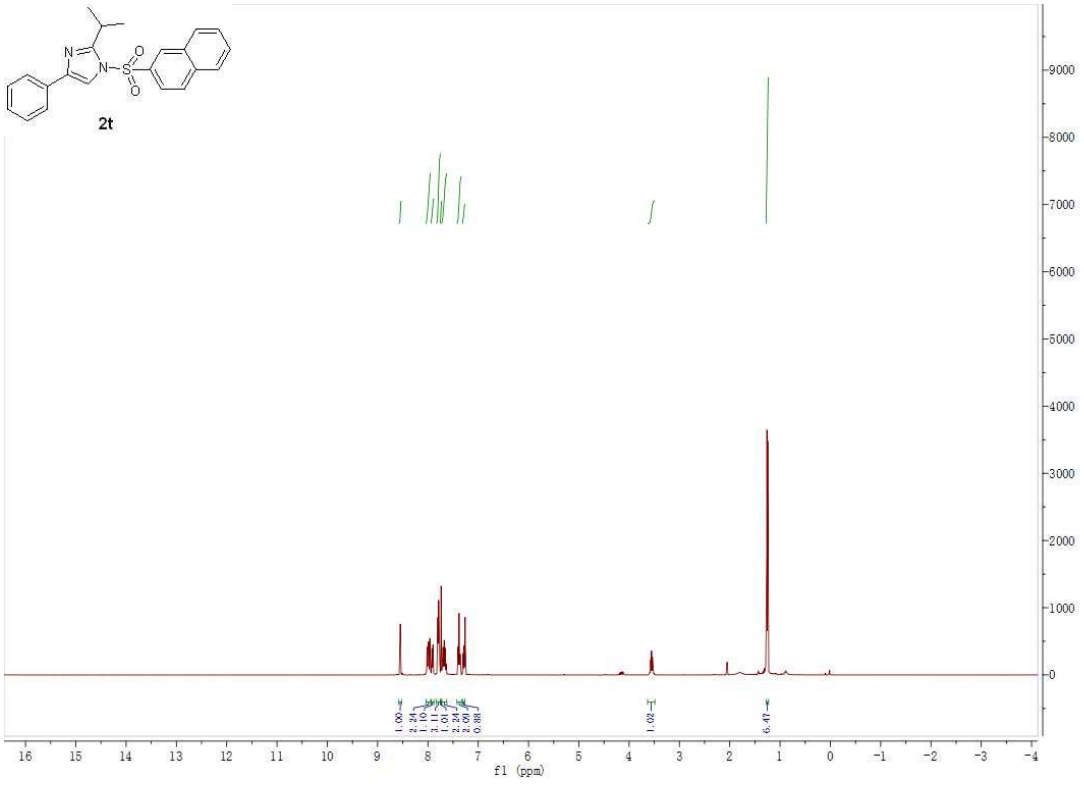

2q
f1 (ppm)

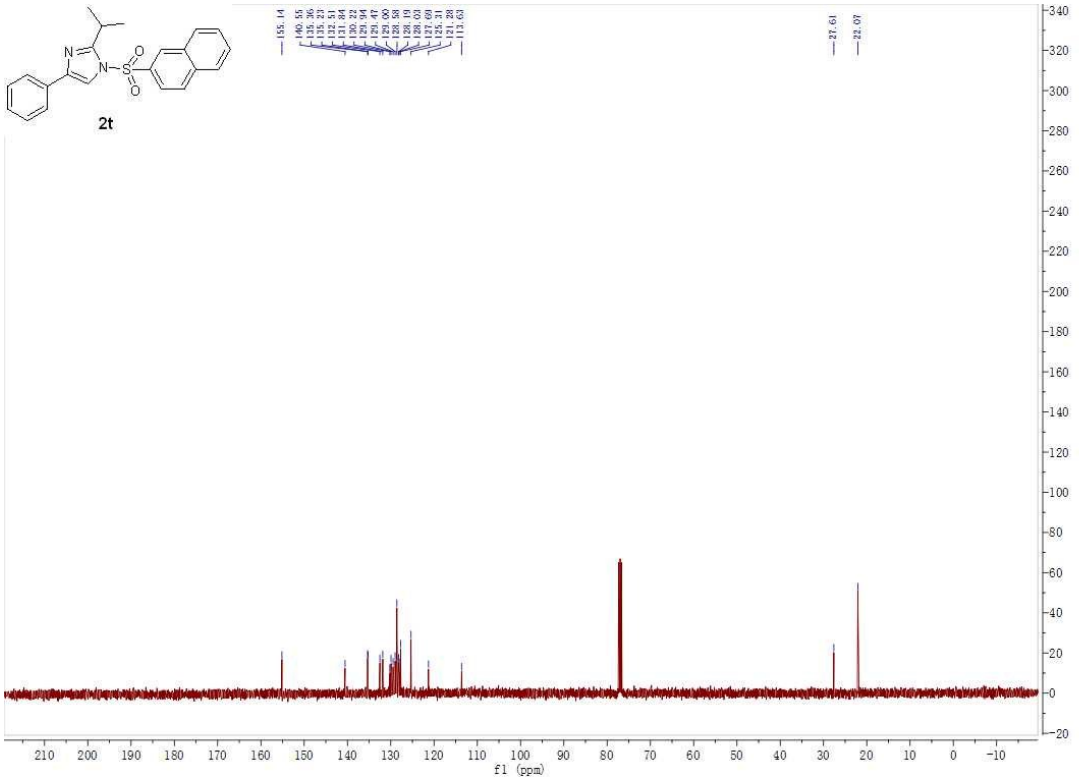

Br
2r
f1 (ppm)

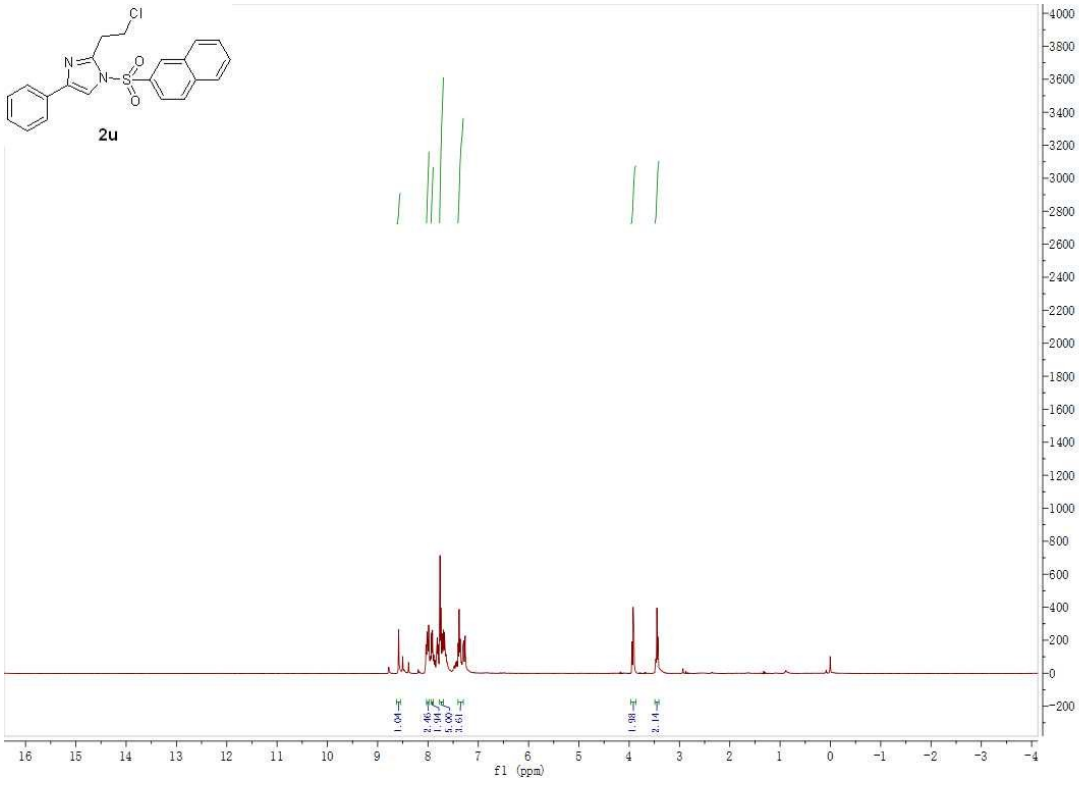

Br
N
N
S
O
O
2r
146.23
140.44
135.40
134.70
133.47
132.91
131.75
130.30
130.08
129.43
129.38
129.20
128.36
128.16
128.11
127.96
127.55
126.25
125.87
123.82
121.31
114.44
15.18
f1 (ppm)

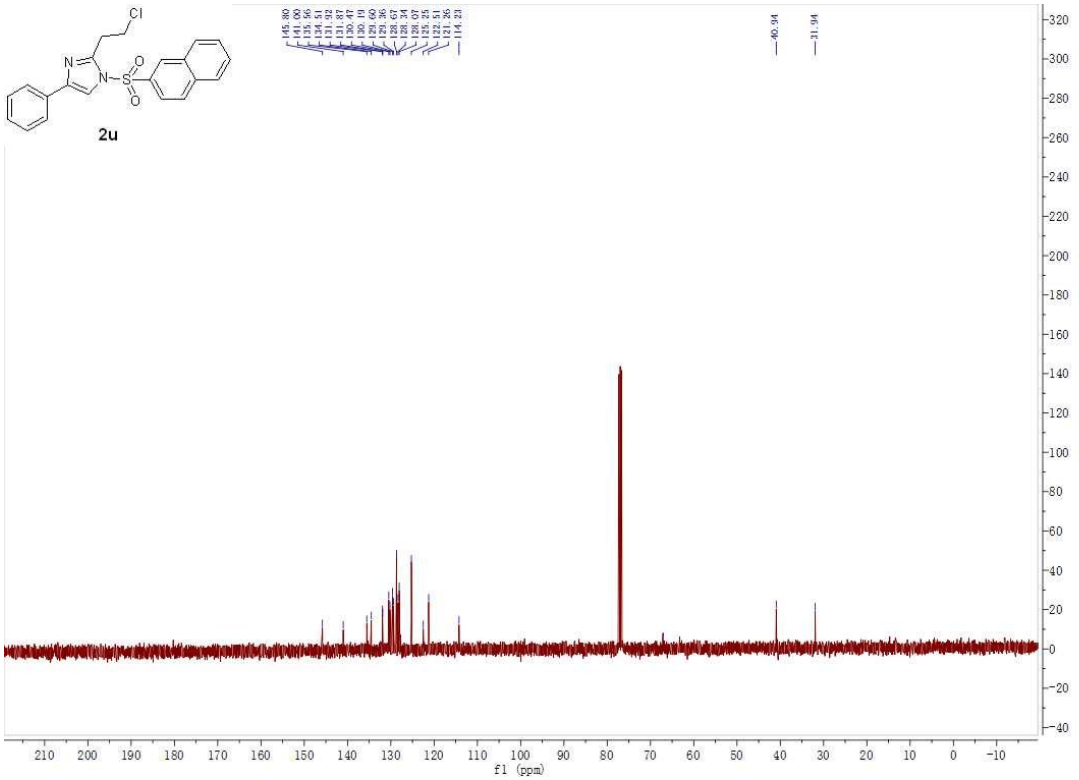

Cl
N
N
S
O
O
2s
1.00
5.19
4.02
3.38
1.97
f1 (ppm)

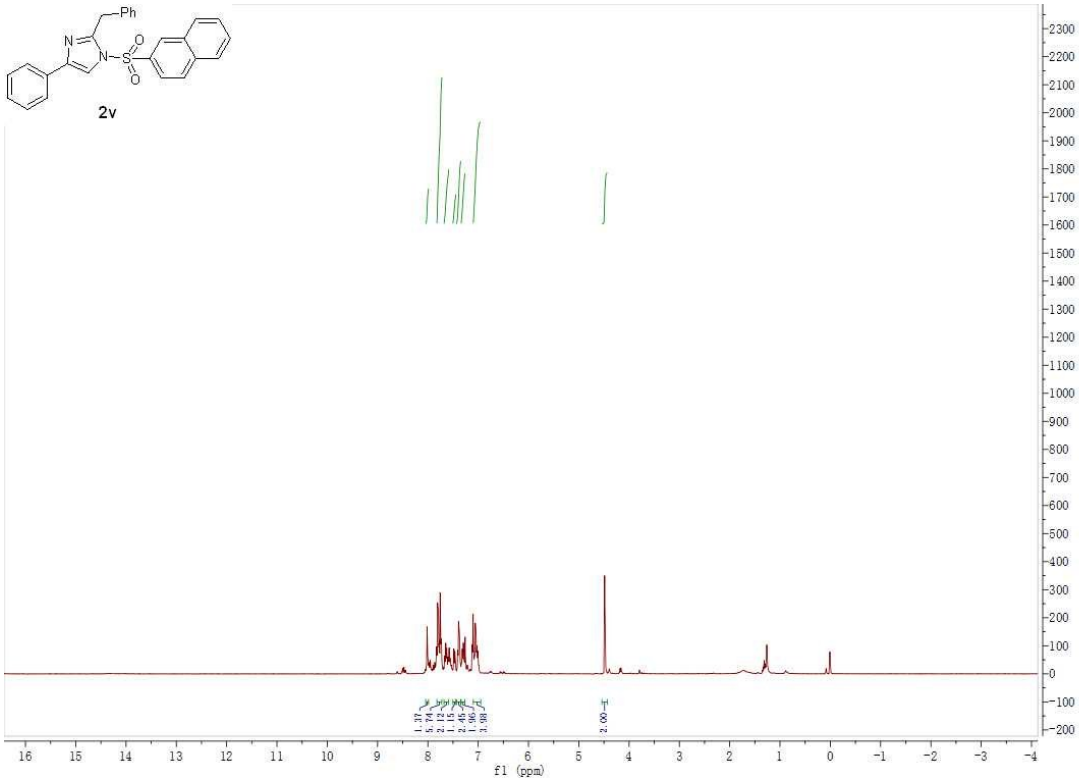

2s
144.09
141.73
135.62
133.93
131.75
131.57
130.39
130.20
129.62
129.21
128.67
128.21
126.02
125.50
123.48
121.70
115.34
36.52
f1 (ppm)

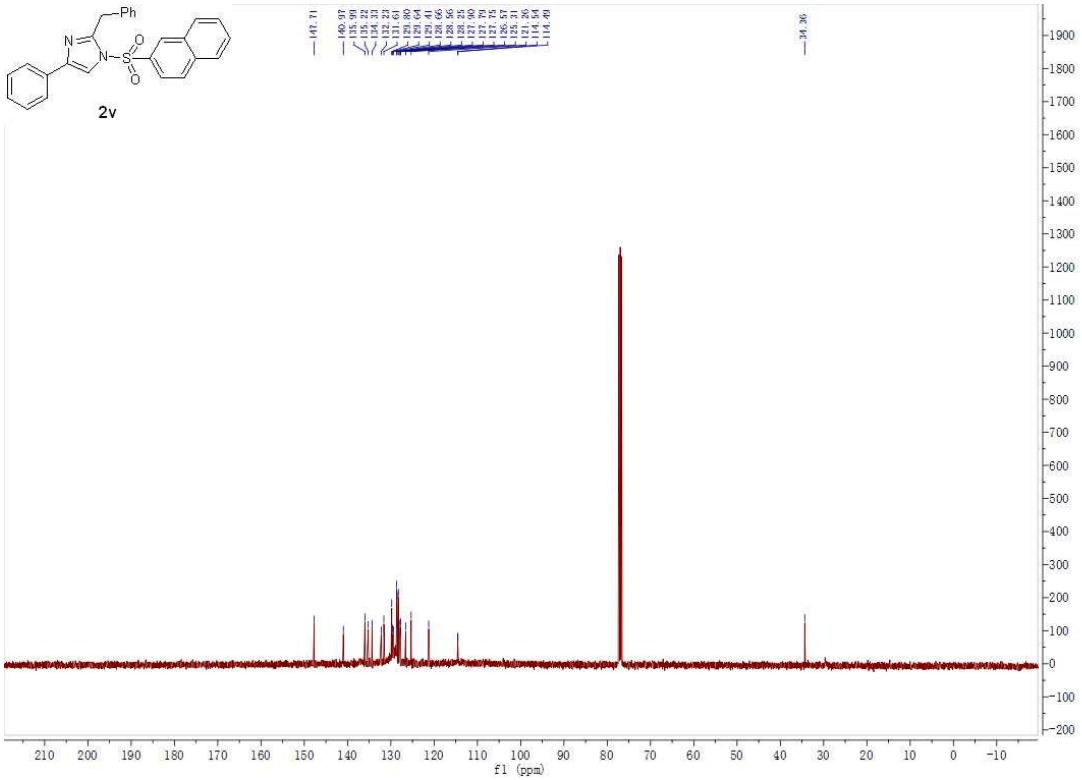

2t
1.00
2.24
1.10
1.11
1.01
2.24
2.09
0.88
1.02
6.47
f1 (ppm)

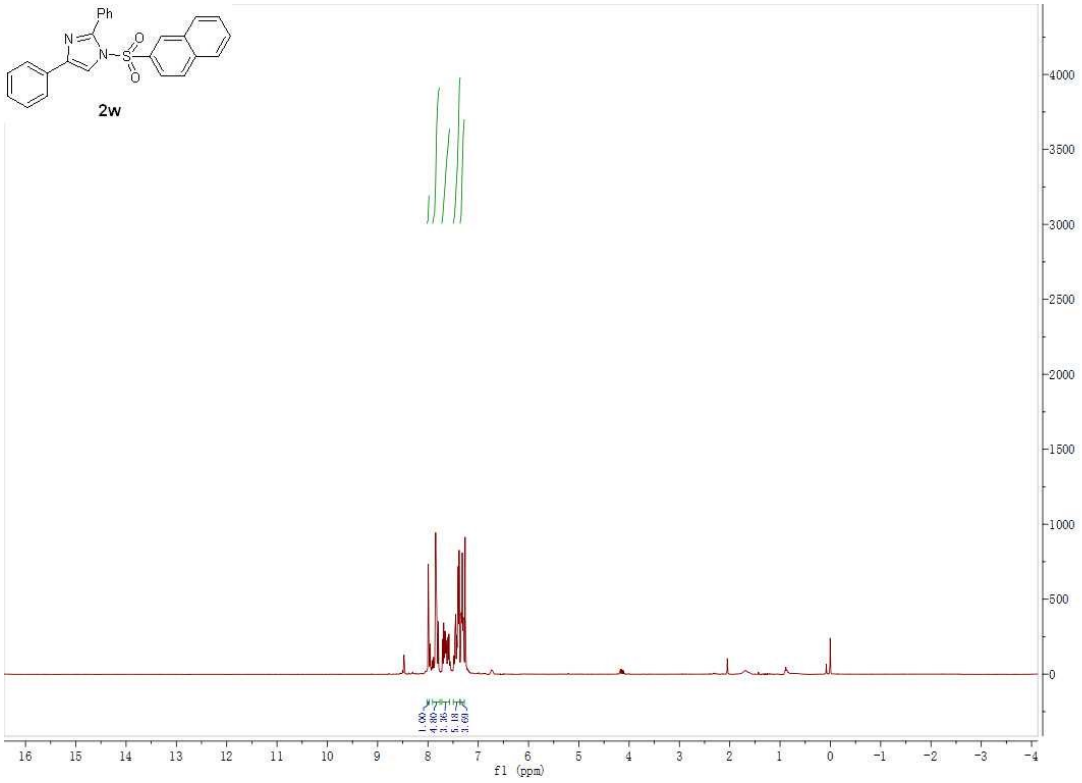

2t
155.14
140.55
135.21
132.51
131.84
129.47
129.00
128.58
128.03
127.69
125.31
121.28
113.63
27.61
22.07
f1 (ppm)

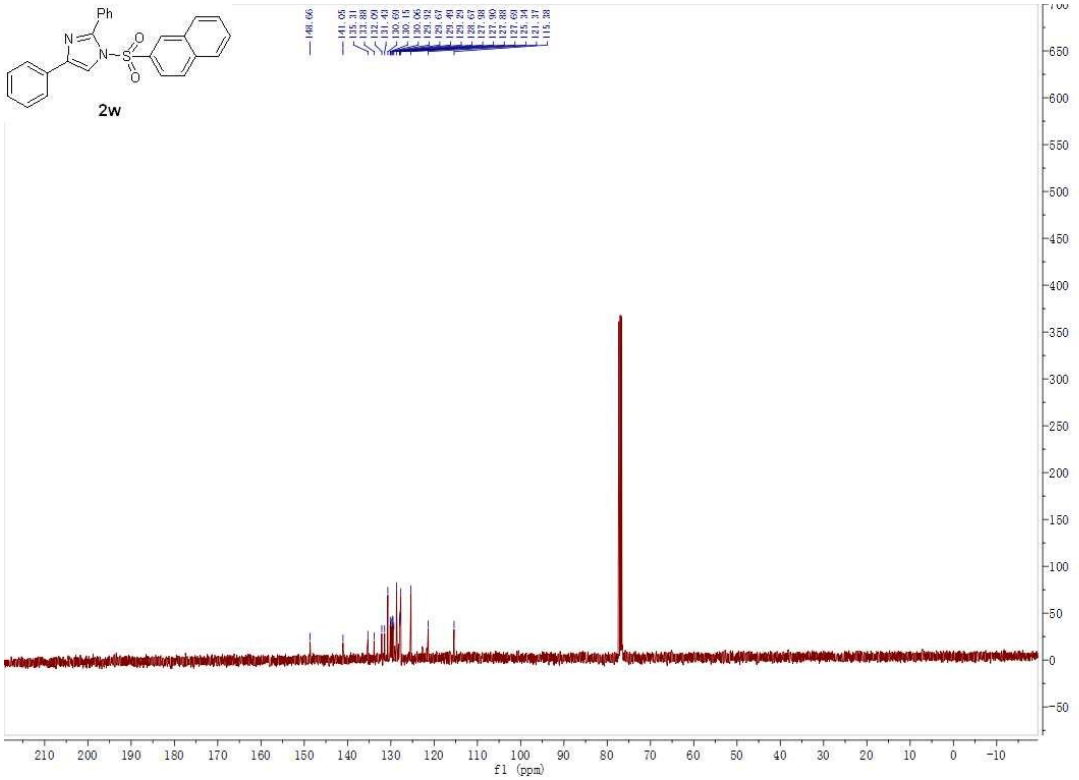

Cl
2u
1.04
2.46
1.00
1.61
1.98
2.14
f1 (ppm)

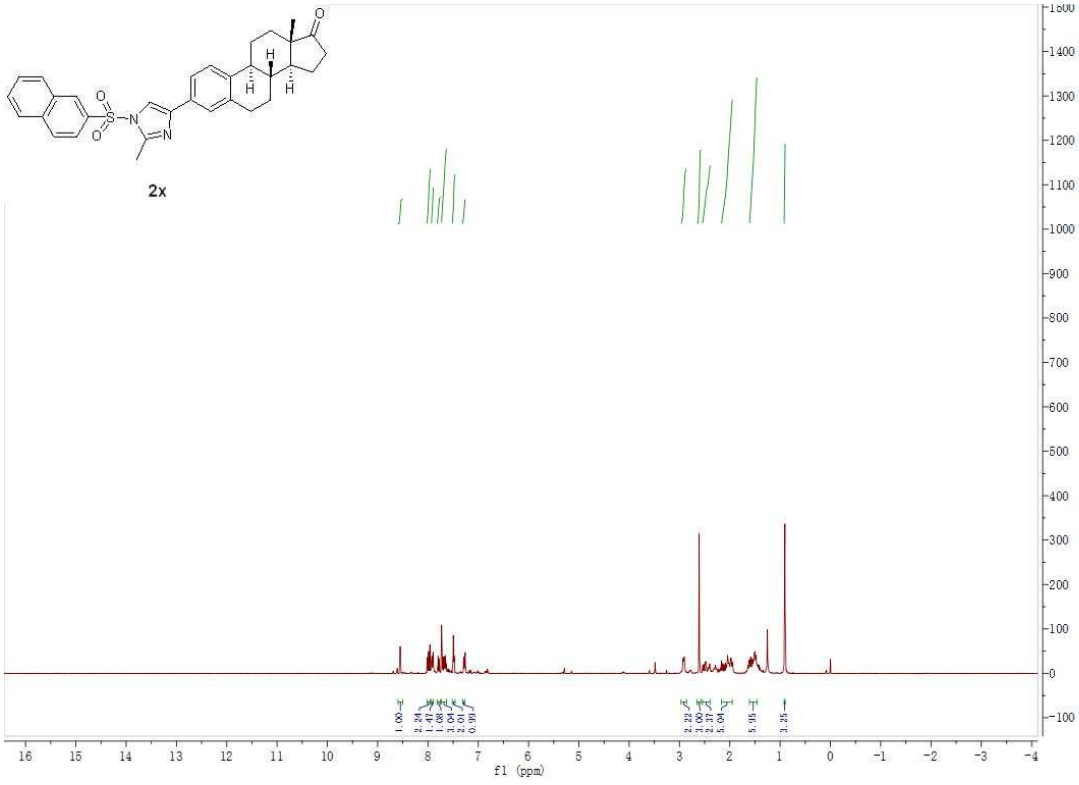

Cl
N
N
S
O
O
2u
145.80
141.60
141.56
134.51
131.92
131.87
131.47
130.19
129.60
129.36
128.67
128.34
126.07
125.25
122.51
121.26
114.23
40.94
31.94
f1 (ppm)

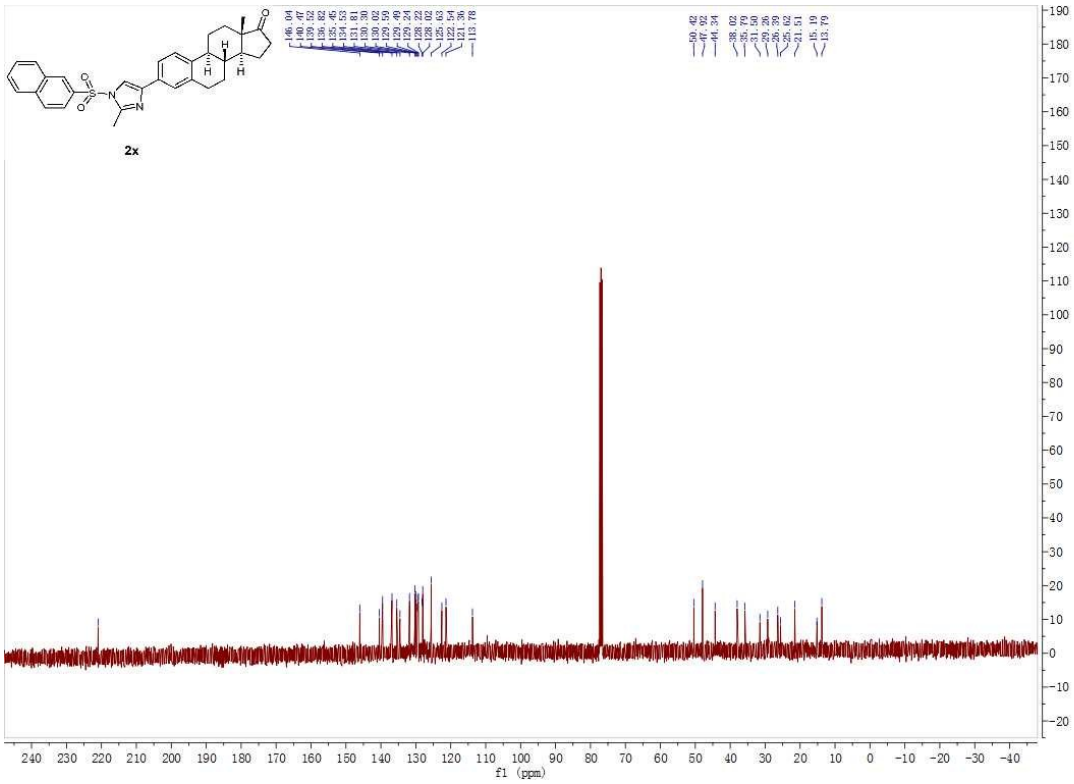

Ph
N
N
S
O
O
2v
1.17
5.74
2.12
2.15
2.04
1.16
3.98
2.00
f1 (ppm)


Ph
N
N
S
O
O
2v
147.71
140.97
135.99
135.22
134.33
132.23
131.61
131.00
129.64
129.41
128.66
128.55
128.24
127.90
127.79
127.75
126.57
125.31
121.26
114.54
114.40
34.36
f1 (ppm)


Ph
N
N
S
O
O
2w
1.00
4.80
3.36
5.18
3.69
f1 (ppm)


Ph
N
N
S
O
O
2w
f1 (ppm)


O
H
H
H
O
O
S
N
N
2x
f1 (ppm)


2x
146.04
140.47
139.52
138.82
135.45
134.53
131.81
130.30
130.02
129.59
129.49
129.23
128.22
128.02
125.63
122.54
121.36
113.78
60.42
47.92
44.54
38.02
35.79
31.50
29.26
26.39
25.62
23.51
15.19
13.79
f1 (ppm)