Supporting Information

for

Rhodium-Catalyzed Intramolecular Cyclization for Synthesizing Thiodihydropyrans

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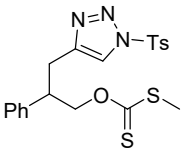
Content

1. General information

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry nitrogen unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. All solvents were freshly distilled prior to use in synthesis unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using silica gel HSGF254 pre-coated plates. Flash column chromatography was performed using silica gel (200-300 mesh). ^{1}H, ^{13}C NMR spectra were measured on Brucker Avance IIDMX 400MHz spectrometers (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR). Chemical shifts are reported as δ values relative to internal tetramethylsilane (TMS: 0.00 ppm) or deuterated solvent (Chloroform-d: 7.26 ppm, 77.16 ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) were taken from the spectra directly and are uncorrected. Melting points are uncorrected. High resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization.

2. Preparation of triazoles

Substrates involved in the manuscript:



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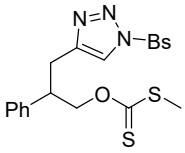

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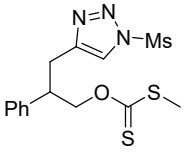

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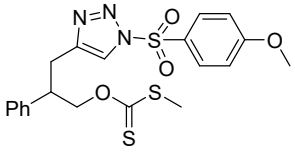

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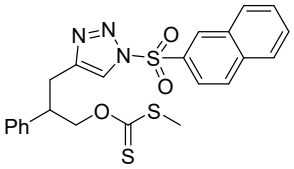

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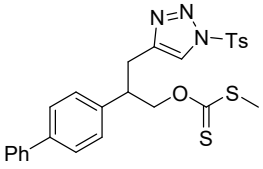

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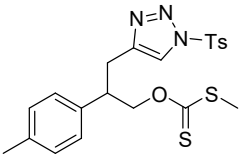

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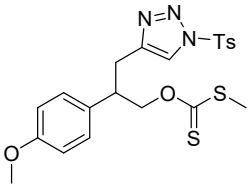

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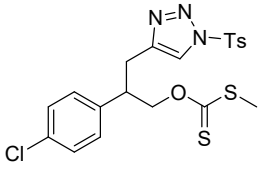

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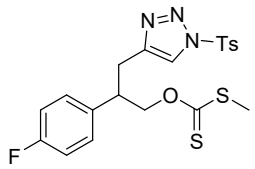

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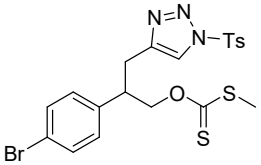

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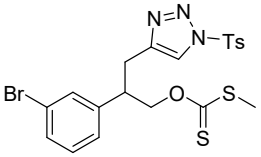

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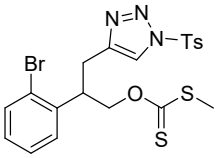

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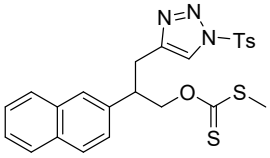

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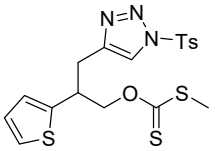

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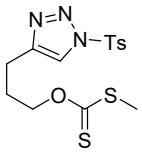

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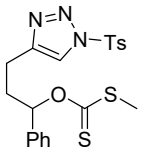

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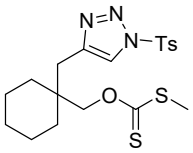

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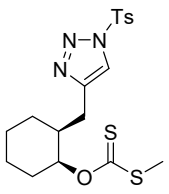
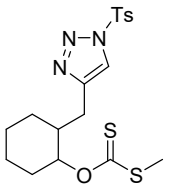
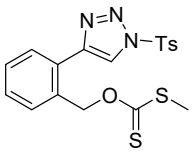


1s



1s'



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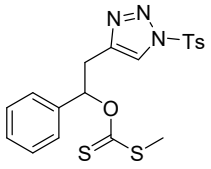

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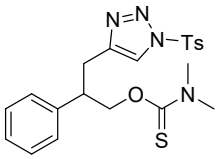
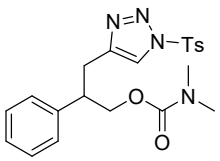
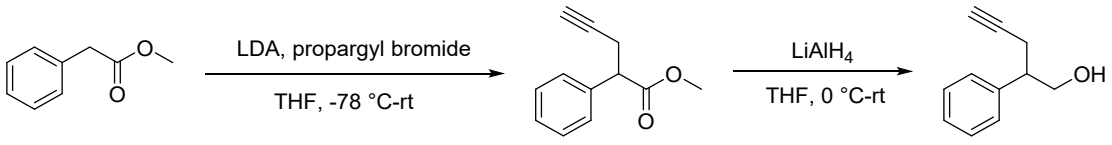


1v



1w

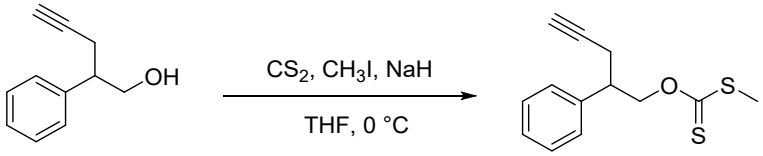
Typical procedure (1a):



S1 **S2** **S3**

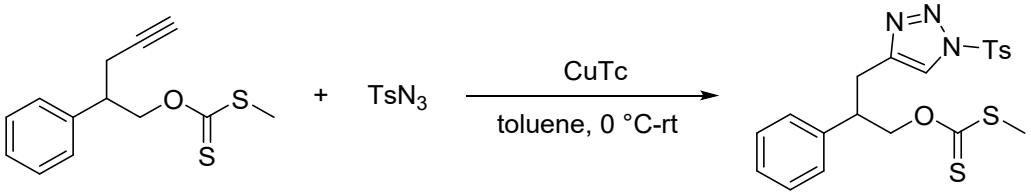
Step A: To a THF (20 mL) solution of *i*-Pr_2NH (1.6 mL, 11 mmol) was added *n*-BuLi (1 M in hexane, 4.4 mL, 11 mmol) dropwise at 0 °C. After being stirred for 30 min, the mixture was cooled to -78 °C. A solution of **S1** (10.0 mmol) in THF (3 mL) was added dropwise over 30 min. After 30 min, a solution of 3-bromo-1-propyne (0.95 mL, 11 mmol) in THF (1 mL) was added dropwise. The mixture was warmed to rt, stirred for another 30 min, and poured into saturated ammonium chloride (10 mL). After extraction with EtOAc, the combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by distillation gave **S2**.

Step B: A solution of **S2** (10 mmol) in THF (5 mL) was added dropwise to a suspension of $LiAlH_4$ (0.3 g, 8 mmol) in THF (15 mL) over 60 min at 0 °C. After the starting material disappeared, NaOH (2 M, 10 mL) were slowly added to the reaction mixture. The reaction mixture filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography with PE/EtOAc (10:1) as eluent to give the corresponding product **S3**.[1]



S3 **S4**

Step C: NaH (0.68 g, 17 mmol) was added to the reaction flask, and then THF (15 mL) was added. The reaction was placed in an ice bath, and **S3** was added at 0 °C. After 30 min of reaction, CS_2 (0.6 mL, 10.2 mmol) was added. After 30 min of reaction, CH_3I (0.6 mL, 10.2 mmol) was added, and then the room temperature reaction was restored and detected by TLC. After the reaction was completed, it was quenched with saturated ammonium chloride solution (15 mL), extracted with ethyl acetate, washed with saturated sodium chloride, dried with anhydrous sodium sulfate, filtered, concentrated, and then purified by flash chromatography with PE/EtOAc (30:1) as eluent to give the corresponding product **S4**.[2]



S4 **S5**

Step D: Under a nitrogen atmosphere, dry toluene (6 mL) was added to reaction flask charged with copper (I) thiophene-2-carboxylate (CuTc, 0.057 g, 0.3 mmol) and the alkyne (3.0 mmol). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (3.6 mmol) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature and stirred until TLC analysis showed that alkyne was completely consumed. The reaction mixture filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography with PE/EtOAc (5:1) as eluent to give the corresponding product **S5**.[3]

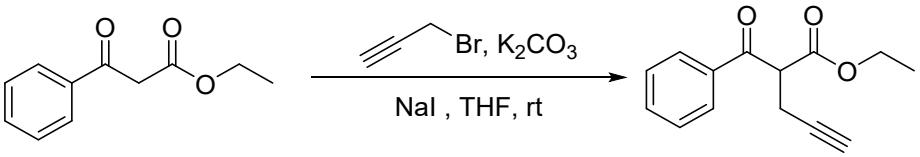
2.1 For 1a-1o and 1r:

The synthetic procedures of **1a-1o** were similar with the typical procedure (**1a**) except that different substituents of ethyl formate in step A and azides in step C were used.

2.2 For 1p:

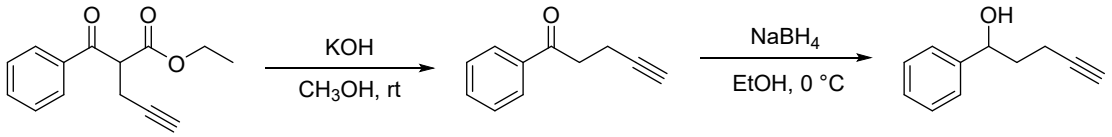
The synthesis step of **1p** is similar to the typical process step (**1a**), only **steps C** and **D** are used.

Typical procedure for synthesis of alkynol (1q):



S6 **S7**

Step E: K_2CO_3 (2.1 g, 15 mmol) and NaI (0.59 g, 4 mmol) were added to the 100 mL round bottom bottle. THF (20 mL) was added as solvent, and then benzoyl ethyl acetate **S6** (1.7 mL, 10 mmol) was slowly added. After 2 hours, propargyl bromide (0.86 mL, 10 mmol) was added. After 12 hours, the reaction was completed and the saturated ammonium chloride solution was quenched. The organic phase was extracted with ethyl acetate, washed with saturated NaCl solution, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. Directly cast the next step.[4]



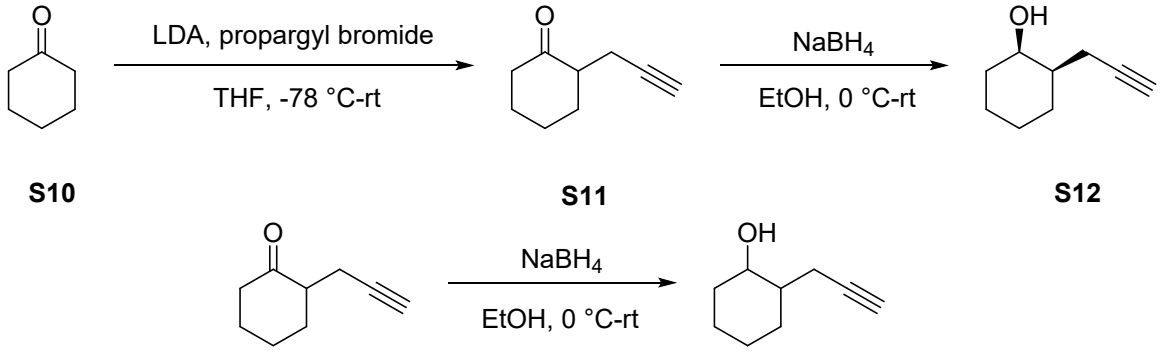
S7 **S8** **S9**

Step F: KOH (0.45 g, 8 mmol) was added to the reaction flask, and CH_3OH (10 mL) was added as the solvent. Then **S7** was dissolved in CH_3OH (5 mL) and slowly added to the reaction, reacted at room temperature and detected by TLC. After the raw material was completely reacted, the raw material was directly concentrated under reduced pressure, then quenched with saturated ammonium chloride, extracted with ethyl acetate, washed with saturated NaCl, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and recrystallized to obtain **S8**.

Step G: MeOH (6 mL) was added to the 100 mL round bottom bottle as a solvent, and the raw material that previous step prepared dissolved with MeOH (4 mL) was added. Then $NaBH_4$ (0.11 g, 3 mmol) was added, and TLC detection was performed until the raw material was completely reacted. After the reaction was completed, it was quenched with water, extracted with ethyl acetate, washed with saturated NaCl, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and then purified by flash chromatography with PE/EtOAc (5:1) as eluent to give the corresponding product **S9**.

The method of synthesizing **1q** from **S9** is the same as **step B** and **step C**.

Typical procedure for synthesis of alkynol (1s and 1s'):



S10 **S11** **S12**

S11 **S13** (R / S mixed products)

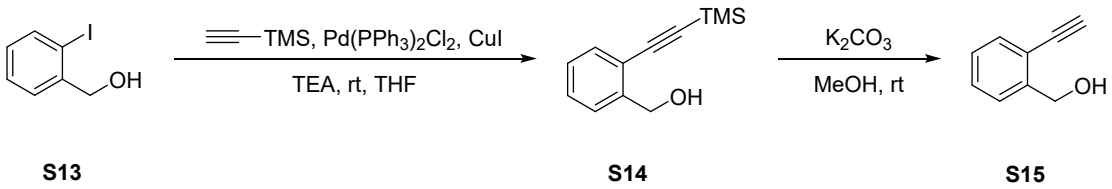
Step H: To a THF (20 mL) solution of *i*-Pr_2NH (1.6 mL, 11 mmol) was added *n*-BuLi (1 M in hexane, 4.4 mL, 11 mmol) dropwise at 0 °C. After being stirred for 30 min, the mixture was cooled to -78 °C. A solution of **S10** (10.0 mmol) in THF (3 mL) was added dropwise over 30 min. After 30 min, a solution of 3-bromo-1-propyne

(0.95 mL, 11 mmol) in THF (1 mL) was added dropwise. The mixture was warmed to rt, stirred for another 30 min, and poured into saturated ammonium chloride (10 mL). After extraction with AcOEt (2×50 mL), the combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by distillation gave **S11**.[5]

Step I: MeOH (10 mL) was added to the 100 mL round bottom bottle as a solvent, and **S11** dissolved with MeOH (5 mL) was added. Then $NaBH_4$ (0.38 g, 10 mmol) was added to restore the reaction at room temperature and detected by TLC. After the reaction was completed, it was quenched with water, extracted with ethyl acetate, washed with saturated NaCl, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and then purified by flash chromatography with PE/EtOAc (5:1) as eluent to give the corresponding product **S12** and **S13**.[5]

The method of synthesizing **1s** from **S12** is the same as **step B** and **step C**. The synthesis of **1s'** is the same as that of **1s**.

Typical procedure for synthesis of alkynol (1t):



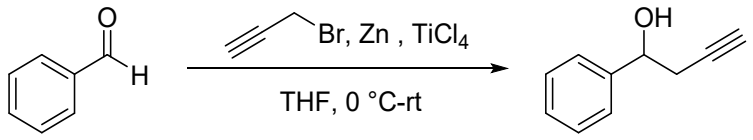
S13 **S14** **S15**

Step J: THF (15 mL) and triethylamine (3 equiv) were added to the reaction flask containing $Pd(PPh_3)_2Cl_2$ (0.28 g, 0.3 mmol), CuI (0.19 g, 1 mmol), **S13** (2.34 g 10 mmol) and stirred for 10 min, then trimethylsilylacetylene (1.2 m L, 12 mmol) was added slowly, and the reaction was detected by TLC at room temperature. After completion of the reaction, silica gel short column, washed with ethyl acetate, concentrated and then purified by flash chromatography with PE/EtOAc (8:1) as eluent to give the corresponding product **S14**.

Step K: **S14** dissolved in methanol (10 mL) was added to the reaction flask at room temperature under air conditions, and then K_2CO_3 (1.32 g, 9.6 mmol) was added. After the raw materials was consumed completely, the reaction mixture was passed through a silica gel column, rinsed with ethyl acetate and concentrated. Then purified by flash chromatography with PE/EtOAc (5:1) as eluent to give the corresponding product **S15**.

The method of synthesizing **1t** from **S15** is the same as **step B** and **step C**.

Typical procedure for synthesis of alkynol (1u):

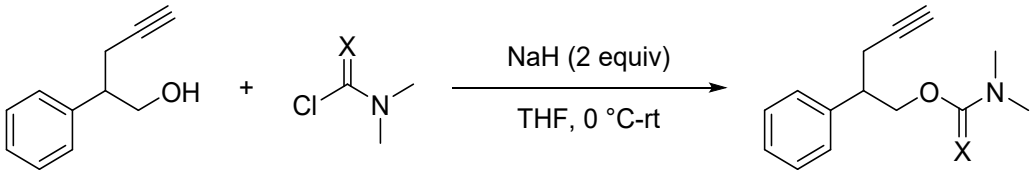


S16 **S17**

Step L: The magnesium powder (0.66 g, 10 mmol) was added to the reaction bottle, and the ultra-dry THF (6 mL) was added to the system. The reaction was placed in an ice bath and cooled to 0 ℃. The propargyl bromide (1.0 mL, 10 mmol) was slowly added to the reaction, and then the $TiCl_4$ solution (1 M in CH_2Cl_2, 1.0 mL) was added dropwise. The reaction was carried out in an ice bath for 10 minutes, followed by a slow dropwise addition of benzaldehyde (0.5 mL, 5 mmol). The reaction was restored to room temperature after 10 minutes, and the reaction was detected by TLC. At the end of the reaction, the reaction was quenched with saturated ammonium chloride, extracted with ethyl acetate, washed with saturated NaCl, and dried with anhydrous sodium sulfate. Then purified by flash chromatography with PE/EtOAc (5:1) as eluent to give the corresponding product **S17**.[6]

The method of synthesizing **1u** from **S17** is the same as **step B** and **step C**.

Typical procedure for synthesis of alkynol (1v and 1w):

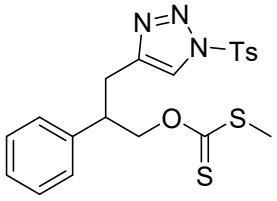


S3 **S18** **S19**

Step M: NaH (0.24 g, 6 mmol) was added to the reaction flask, and then THF (5 mL) was added. **S3** (3 mmol) dissolved in THF (3 mL) was added at 0 ° C for 40 minutes, and then **S18** (0.42 g, 3.3 mmol) was added. At the end of the reaction, the reaction was quenched with saturated ammonium chloride, extracted with ethyl acetate, washed with saturated NaCl, and dried with anhydrous sodium sulfate. Then purified by flash chromatography with PE/EtOAc (15:1) as eluent to give the corresponding product **S19**.

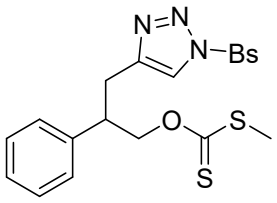
The method of synthesizing **1v** and **1w** from **S19** is the same as **step C**.

The spectral data of compounds **1a**-**1w** were shown below.



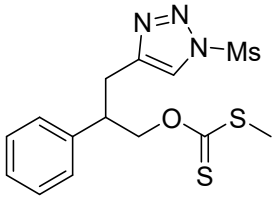
1a

S-methyl O-(2-phenyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1a**): white solid, m.p.: 93.2-95.6 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.18 (dd, *J* = 7.6, 1.9 Hz, 2H), 4.78 (d, *J* = 6.6 Hz, 2H), 3.66 – 3.50 (m, 1H), 3.34 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.12 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.52 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.66, 147.13, 145.18, 139.66, 133.25, 130.40, 128.83, 128.53, 127.86, 127.52, 121.47, 76.17, 44.23, 28.79, 21.89, 18.98; ESI-HRMS *m/z* calcd for $C_{20}H_{22}N_3O_3S_3^+$ $[M + H]^+$ 448.0818, found 448.0824.



1b

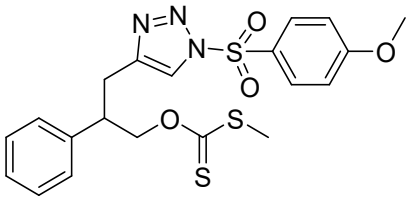
O-(3-(1-((4-bromophenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-2-phenylpropyl) S-methyl carbonodithioate (**1b**): white solid, m.p.: 88.6-90.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 1H), 7.33 – 7.27 (m, 4H), 7.21 – 7.14 (m, 2H), 4.79 (d, *J* = 6.6 Hz, 2H), 3.64 – 3.54 (m, 2H), 3.35 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.12 (dd, *J* = 14.9, 9.1 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.68, 145.51, 139.54, 135.22, 133.18, 131.32, 129.80, 128.84, 127.84, 127.56, 121.53, 76.16, 44.21, 28.75, 19.01; ESI-HRMS *m/z* calcd for $C_{19}H_{19}BrN_3O_3S_3^+$ $[M + H]^+$ 511.9766, found 511.9771.



1c

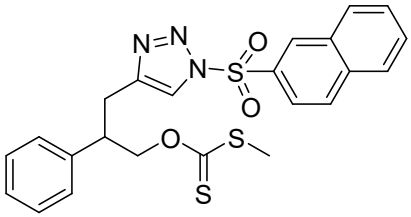
S-methyl O-(3-(1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)-2-phenylpropyl) carbonodithioate (**1c**): white solid, m.p.: 63.2-65.8 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (s, 1H), 7.39 – 7.22 (m, 5H), 4.83 (d, *J* = 6.7 Hz, 2H), 3.71 –

3.62 (m, 1H), 3.44 (s, 3H), 3.42 – 3.36 (m, 1H), 3.20 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.69, 145.35, 139.59, 128.95, 127.88, 127.68, 121.32, 76.30, 44.22, 42.63, 28.72, 19.03; ESI-HRMS *m/z* calcd for $C_{14}H_{18}N_3O_3S_3^+$ $[M + H]^+$ 372.0505, found 372.0512.



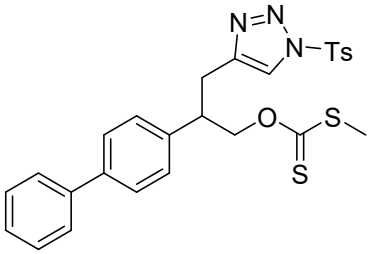
1d

O-(3-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-2-phenylpropyl) S-methyl carbonodithioate (**1d**): white solid, m.p.: 93.1-95.2 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.53 (s, 1H), 7.35 – 7.25 (m, 3H), 7.18 (m, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.78 (d, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 3.65 – 3.53 (m, 1H), 3.34 (dd, *J* = 14.9, 6.3 Hz, 1H), 3.12 (dd, *J* = 14.9, 8.9 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.63, 165.27, 145.09, 139.70, 131.04, 128.83, 127.87, 127.52, 127.16, 121.34, 115.05, 76.20, 56.00, 44.24, 28.79, 18.97; ESI-HRMS *m/z* calcd for $C_{20}H_{22}N_3O_4S_3^+$ $[M + H]^+$ 464.0767, found 464.0779.



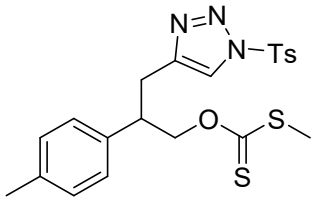
1e

S-methyl O-(3-(1-(naphthalen-2-ylsulfonyl)-1H-1,2,3-triazol-4-yl)-2-phenylpropyl) carbonodithioate (**1e**): white solid, m.p.: 92.5-95.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.65 (d, *J* = 8.5 Hz, 1H), 8.55 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.63 (s, 1H), 7.25 – 7.23 (m, 3H), 7.12 (dd, *J* = 6.5, 3.0 Hz, 2H), 4.75 (d, *J* = 6.7 Hz, 2H), 3.61 – 3.49 (m, 1H), 3.32 (dd, *J* = 14.9, 6.1 Hz, 1H), 3.10 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.62, 145.09, 139.55, 137.57, 134.22, 132.21, 131.24, 129.68, 129.34, 128.78, 128.24, 127.79, 127.68, 127.50, 124.30, 123.79, 121.55, 76.13, 44.17, 28.79, 18.96; ESI-HRMS *m/z* calcd for $C_{23}H_{22}N_3O_3S_3$ $[M + H]^+$ 484.0818, found 484.0822.



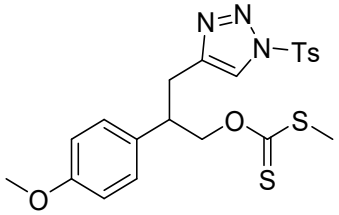
1f

O-(2-([1,1'-biphenyl]-4-yl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1f**): white solid, m.p.: 110.3-112.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 3H), 7.55 – 7.46 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 6.6 Hz, 2H), 3.71 – 3.60 (m, 1H), 3.38 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.15 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.54 (s, 3H), 2.41 (s, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 215.70, 147.12, 145.21, 140.56, 140.32, 138.66, 133.20, 130.39, 128.91, 128.46, 128.29, 127.50, 127.45, 127.06, 121.57, 76.14, 43.90, 28.77, 21.83, 19.05; ESI-HRMS *m/z* calcd for $C_{26}H_{26}N_3O_3S_3^+$ $[M + H]^+$ 524.1131, found 524.1140.



1g

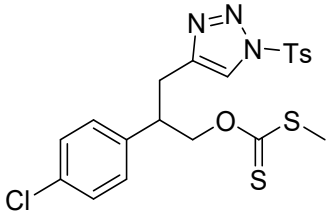
S-methyl O-(2-(p-tolyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1g**): clear oil; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.75 (d, *J* = 6.6 Hz, 2H), 3.62 – 3.45 (m, 1H), 3.32 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.09 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.52 (s, 3H), 2.48 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.65, 147.10, 145.32, 137.10, 136.54, 133.31, 130.37, 129.50, 128.53, 127.69, 121.46, 76.35, 43.82, 28.81, 21.87, 21.12, 18.96; ESI-HRMS *m/z* calcd for $C_{21}H_{24}N_3O_3S_3^+$ $[M + H]^+$ 462.0974, found 462.0974



1h

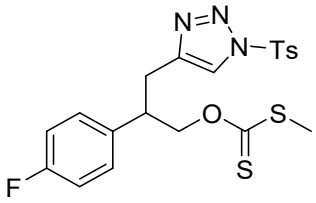
O-(2-(4-methoxyphenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl

carbonodithioate (**1h**): white solid, m.p.: 91.4-93.5 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.74 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.58 – 3.47 (m, 1H), 3.31 (dd, *J* = 14.9, 6.1 Hz, 1H), 3.07 (dd, *J* = 14.9, 9.1 Hz, 1H), 2.52 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.66, 158.87, 147.13, 145.33, 133.28, 131.53, 130.39, 128.84, 128.50, 121.48, 114.22, 76.44, 55.30, 43.42, 28.89, 21.86, 18.97; ESI-HRMS *m/z* calcd for $C_{21}H_{24}N_3O_4S_3^+$ [M + H]$^+$478.0923, found 478.0930



1i

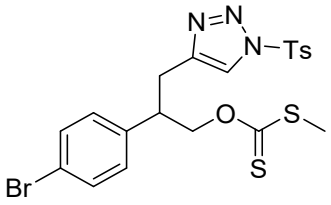
O-(2-(4-chlorophenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1i**): white solid, m.p.: 102.4-104.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 2.9 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 4.75 (d, *J* = 6.1 Hz, 2H), 3.67 – 3.52 (m, 1H), 3.30 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.06 (dd, *J* = 14.9, 9.1 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.68, 147.28, 144.87, 138.17, 133.18, 133.12, 130.46, 129.19, 128.92, 128.48, 121.52, 75.74, 43.68, 28.61, 21.92, 19.09; ESI-HRMS *m/z* calcd for $C_{20}H_{21}ClN_3O_3S_3^+$ [M + H]$^+$482.0428, found 482.0436



1j

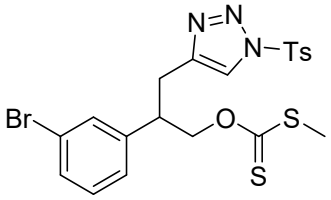
O-(2-(4-fluorophenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1j**): white solid, m.p.: 85.3-88.2 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.59 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.08 (m, 2H), 7.05 – 6.87 (m, 2H), 4.76 (d, *J* = 6.5 Hz, 2H), 3.74 – 3.50 (m, 1H), 3.31 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.07 (dd, *J* = 14.9, 9.1 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.68, 161.96 (d, *J* = 245.9 Hz), 147.26,

145.02, 135.39 (d, *J* = 3.3 Hz), 133.17, 130.44, 129.37 (d, *J* = 8.0 Hz), 128.49, 121.49, 115.65 (d, *J* = 21.3 Hz), 75.99, 43.54, 28.80, 21.88, 19.04. ^{19}F NMR (376 MHz, Chloroform-d) δ -114.76; ESI-HRMS *m/z* calcd for $C_{20}H_{21}FN_3O_3S_3^+$ $[M + H]^+$ 466.0724, found 466.0730.



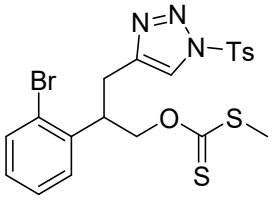
1k

O-(2-(4-bromophenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1k**): white solid, m.p.: 100.7-103.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.61 (s, 1H), 7.43 – 7.36 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.75 (d, *J* = 6.5 Hz, 2H), 3.67 – 3.49 (m, 1H), 3.30 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.07 (dd, *J* = 14.9, 9.0 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.67, 147.28, 144.84, 138.72, 133.13, 131.87, 130.48, 129.56, 128.49, 121.53, 121.29, 75.66, 43.75, 28.56, 21.94, 19.10; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrN_3O_3S_3^+$ $[M + H]^+$ 525.9923, found 525.9926



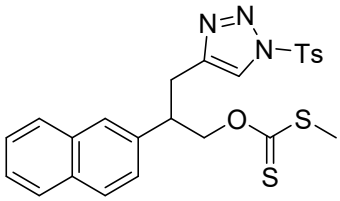
1l

O-(2-(3-bromophenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1l**): white solid, m.p.: 103.1–104.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.44 – 7.37 (m, 3H), 7.34 (s, 1H), 7.22 – 7.10 (m, 2H), 4.75 (d, *J* = 6.5 Hz, 2H), 3.64 – 3.51 (m, 1H), 3.31 (dd, *J* = 15.0, 6.5 Hz, 1H), 3.10 (dd, *J* = 15.0, 8.7 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.61, 147.25, 144.70, 142.16, 133.13, 130.99, 130.65, 130.49, 130.38, 128.53, 126.54, 122.82, 121.47, 75.61, 43.95, 28.53, 21.91, 19.05; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrN_3O_3S_3^+$ $[M + H]^+$ 525.9923, found 525.9933.



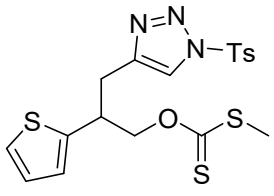
1m

O-(2-(2-bromophenyl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) S-methyl carbonodithioate (**1m**): clear oil; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.65 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.20 – 7.09 (m, 1H), 4.89 – 4.70 (m, 2H), 4.25 – 4.04 (m, 1H), 3.34 (dd, *J* = 15.0, 6.6 Hz, 1H), 3.18 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.52 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.55, 147.17, 144.78, 138.71, 133.30, 133.24, 130.42, 128.94, 128.58, 128.30, 127.95, 125.23, 121.45, 74.86, 42.63, 28.05, 21.89, 19.00; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrN_3O_3S_3^+$ $[M + H]^+$ 525.9923, found 525.9923.



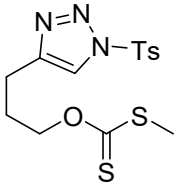
1n

S-methyl O-(2-(naphthalen-2-yl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1n**): white solid, m.p.: 108.4-110.7 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.84 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.74 (m, 3H), 7.62 (s, 1H), 7.58 (s, 1H), 7.53 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.87 (d, *J* = 6.6 Hz, 2H), 3.85 – 3.70 (m, 1H), 3.43 (dd, *J* = 15.0, 6.1 Hz, 1H), 3.25 (dd, *J* = 15.0, 9.1 Hz, 1H), 2.51 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.71, 147.05, 145.19, 137.00, 133.41, 133.09, 132.72, 130.35, 128.63, 128.35, 127.80, 127.75, 126.95, 126.37, 126.07, 125.61, 121.58, 76.22, 44.35, 28.65, 21.88, 19.03; ESI-HRMS *m/z* calcd for $C_{24}H_{24}N_3O_3S_3^+$ $[M + H]^+$ 498.0974, found 498.0977.



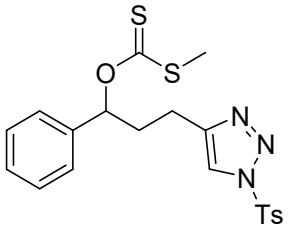
1o

S-methyl O-(2-(thiophen-2-yl)-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1o**): clear oil; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 5.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.81 (d, *J* = 3.4 Hz, 1H), 4.77 (d, *J* = 6.0 Hz, 2H), 3.95 – 3.81 (m, 1H), 3.35 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.13 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.57 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.55, 147.22, 144.73, 142.54, 133.20, 130.44, 128.58, 126.90, 125.48, 124.49, 121.68, 75.94, 39.89, 30.10, 21.91, 19.11; ESI-HRMS *m/z* calcd for $C_{18}H_{20}N_3O_3S_4^+$ $[M + H]^+$ 454.0382, found 454.0377.



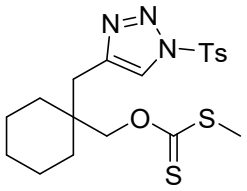
1p

S-methyl O-(3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1p**): white solid; m.p.: 78.6-80.2 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.94 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 4.64 (t, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.47 (s, 3H), 2.26 – 2.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.96, 147.29, 146.64, 133.19, 130.50, 128.66, 120.80, 72.63, 27.55, 22.07, 21.90, 19.11; ESI-HRMS *m/z* calcd for $C_{14}H_{18}N_3O_3S_3^+$ $[M + H]^+$ 372.0505, found 372.0507.



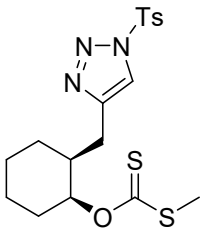
1q

S-methyl O-(1-phenyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1q**): white solid, m.p.: 68.9-70.1 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.90 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.25 (m, 5H), 6.63 – 6.45 (m, 1H), 2.94 – 2.73 (m, 2H), 2.56 (s, 3H), 2.55 – 2.48 (m, 1H), 2.48 (s, 3H), 2.43 – 2.27 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.11, 147.25, 146.64, 138.72, 133.24, 130.48, 128.67, 128.46, 126.78, 120.85, 83.83, 35.31, 21.91, 21.62, 19.17; ESI-HRMS *m/z* calcd for $C_{20}H_{22}N_3O_3S_3^+$ $[M + H]^+$ 448.0818, found 448.0820.



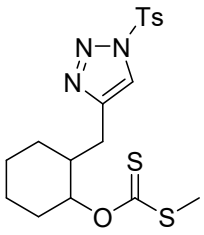
1r

S-methyl O-((1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)cyclohexyl)methyl) carbonodithioate (**1r**): white solid, m.p.: 98.5-100.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (d, *J* = 8.3 Hz 2H), 7.86 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.29 (s, 2H), 2.87 (s, 2H), 2.61 (s, 3H), 2.48 (s, 3H), 1.68 – 1.41 (m, 10H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.79, 147.18, 143.91, 133.22, 130.45, 128.67, 122.13, 77.97, 37.41, 32.66, 31.85, 25.90, 21.90, 21.41, 19.07; ESI-HRMS *m/z* calcd for $C_{19}H_{26}N_3O_3S_3^+$ $[M + H]^+$ 440.1131, found 440.1135



1s

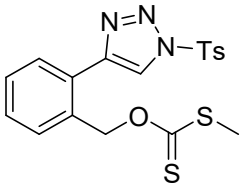
S-methylO-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)cyclohexyl) carbonodithioate (**1s**): clear oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.64 – 5.51 (m, 1H), 2.70 (d, *J* = 7.6 Hz, 2H), 2.61 (s, 3H), 2.48 (s, 3H), 2.22 – 2.08 (m, 2H), 1.85 – 1.76 (m, 1H), 1.72 – 1.64 (m, 1H), 1.61 – 1.32 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.23, 147.18, 145.36, 133.20, 130.44, 128.72, 121.72, 81.17, 40.59, 29.02, 28.22, 27.87, 24.95, 21.91, 20.76, 18.90; ESI-HRMS *m/z* calcd for $C_{18}H_{24}N_3O_3S_3^+$ $[M + H]^+$ 426.0974, found 426.0974.



1s' (d.r.=1.61:1)

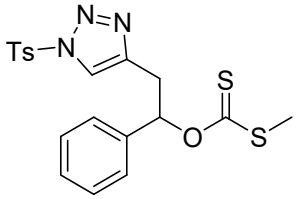
S-methyl O-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)cyclohexyl) carbonodithioate (**1s'**): clear oil; major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.42

– 5.28 (m, 1H), 2.93 (dd, *J* = 14.8, 4.7 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.52 (s, 3H), 2.48 (s, 3H), 2.27 – 2.19 (m, 2H), 1.89 – 1.82 (m, 1H), 1.41 – 1.12 (m, 6H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.64 – 5.51 (m, 1H), 2.70 (d, *J* = 7.6 Hz, 2H), 2.61 (s, 3H), 2.48 (s, 3H), 2.22 – 2.08 (m, 2H), 1.85 – 1.76 (m, 1H), 1.72 – 1.64 (m, 1H), 1.61 – 1.32 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.65, 215.23, 147.17, 147.15, 145.52, 145.36, 133.28, 133.21, 130.44, 130.41, 128.73, 121.72, 121.32, 86.11, 81.18, 41.95, 40.59, 30.74, 30.59, 29.02, 28.47, 28.21, 27.87, 24.95, 24.85, 24.29, 21.89, 20.77, 18.89. ESI-HRMS *m/z* calcd for $C_{18}H_{24}N_3O_3S_3^+$ $[M + H]^+$ 426.0974, found 426.0974.



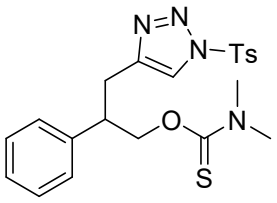
1t

S-methyl O-(2-(1-tosyl-1H-1,2,3-triazol-4-yl)benzyl) carbonodithioate (**1t**): white solid, m.p.: 78.8-80.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.27 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.69 (m, 1H), 7.57 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.73 (s, 2H), 2.58 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.11, 147.51, 145.62, 133.01, 132.54, 130.87, 130.61, 129.87, 129.39, 129.10, 128.82, 121.54, 73.58, 21.96, 19.28; ESI-HRMS *m/z* calcd for $C_{18}H_{18}N_3O_3S_3^+$ $[M + H]^+$ 420.0505, found 420.0497.



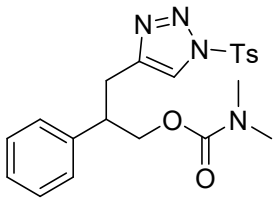
1u

S-methyl O-(1-phenyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) carbonodithioate (**1u**): white solid, m.p.: 67.9-70.1 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.90 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.25 (m, 5H), 6.63 – 6.45 (m, 1H), 2.94 – 2.73 (m, 2H), 2.56 (s, 3H), 2.55 – 2.48 (m, 1H), 2.48 (s, 3H), 2.43 – 2.27 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 215.11, 147.25, 146.64, 138.72, 133.24, 130.48, 128.67, 128.46, 126.78, 120.85, 83.83, 35.31, 21.91, 21.62, 19.17; ESI-HRMS *m/z* calcd for $C_{19}H_{20}N_3O_3S_3^+$ $[M + H]^+$ 434.0661, found 434.0659.



1v

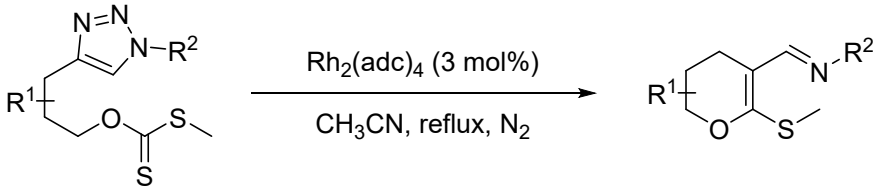
O-(2-phenyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl) dimethylcarbamothioate (**1v**): clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.19 – 7.14 (m, 2H), 4.75 – 4.56 (m, 2H), 3.60 – 3.46 (m, 1H), 3.34 (s, 3H), 3.29 (dd, *J* = 15.0, 6.2 Hz, 1H), 3.08 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.97 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.78, 147.11, 145.44, 140.23, 133.25, 130.41, 128.70, 128.50, 127.83, 127.28, 121.44, 74.20, 44.58, 42.77, 37.72, 28.76, 21.86. ESI-HRMS *m/z* calcd for $C_{21}H_{25}N_4O_3S_2^+$ [M + H]$^+$ 445.1363 , found 445.1363.



1w

2-phenyl-3-(1-tosyl-1H-1,2,3-triazol-4-yl)propyl dimethylcarbamate (**1w**): clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.15 (dd, *J* = 7.5, 1.6 Hz, 2H), 4.28 (d, *J* = 6.7 Hz, 2H), 3.43 – 3.34 (m, 1H), 3.29 (dd, *J* = 14.9, 5.9 Hz, 1H), 3.05 (dd, *J* = 14.9, 9.2 Hz, 3H), 2.90 (s, 3H), 2.81 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.32, 147.07, 145.66, 140.39, 133.28, 130.37, 128.63, 128.49, 127.87, 127.20, 121.36, 68.44, 44.81, 36.46, 35.80, 28.70, 21.85. ESI-HRMS *m/z* calcd for $C_{21}H_{25}N_4O_4S^+$ [M + H]$^+$ 429.1591, found 429.1612.

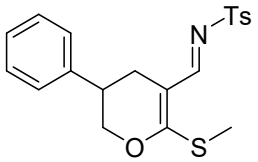
3. General procedure for synthesis of 3,4-dihydro-2H-pyran



1 **2**

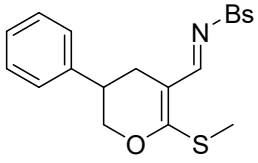
3.1 Typical procedure (2a):

1a (89.5 mg, 0.20 mmol) and $Rh_2(adc)_4$ (5.5 mg, 3 mol%) were added to a 25 mL glass reaction tube. Ultra-dry acetonitrile (2 mL) was added under N_2 conditions. Put the reaction tube into a preheated oil pan in advance and the mixture changes from purple to brown. The reaction was detected by TLC. At the end of the reaction, the reaction was cooled to room temperature, the solvent was evaporated under reduced pressure, and purified by silica gel column chromatography (PE:EtOAc = 5:1) to obtain **2a**.



2a

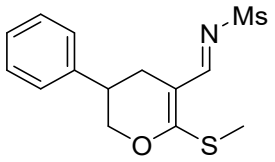
(E)-4-methyl-N-((6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2a**): white solid, m.p.: 140.2-142.3 ºC; 92.5 mg, 99% yield; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.21 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.31 (m, 5H), 7.21 (d, *J* = 7.3 Hz, 2H), 4.70 – 4.44 (m, 1H), 4.14 (t, *J* = 10.6 Hz, 1H), 3.24 – 2.99 (m, 1H), 2.94 – 2.79 (m, 1H), 2.53 – 2.47 (m, 1H), 2.47 – 2.43 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.81, 166.27, 143.50, 139.43, 137.07, 129.55, 128.96, 127.60, 127.57, 127.35, 111.11, 74.38, 37.75, 28.15, 21.62, 13.56; ESI-HRMS *m/z* calcd for $C_{20}H_{22}NO_3S_2^+$ $[M + H]^+$ 388.1036, found 388.1036.



2b

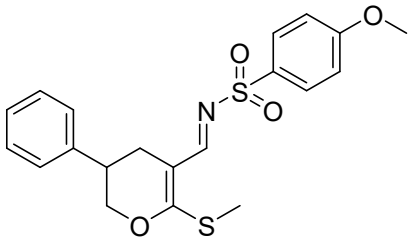
(E)-4-bromo-N-((6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2b**): white solid, m.p.: 133.5-135.8 ºC; 76.5 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J*

= 8.6 Hz, 2H), 7.43 – 7.27 (m, 3H), 7.21 (d, *J* = 7.1 Hz, 2H), 4.69 – 4.46 (m, 1H), 4.15 (t, *J* = 10.6 Hz, 1H), 3.28 – 2.99 (m, 1H), 2.95 – 2.80 (m, 1H), 2.52 – 2.43 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 174.08, 166.66, 139.26, 139.24, 132.18, 129.10, 129.01, 127.70, 127.65, 127.34, 111.01, 74.54, 37.70, 28.11, 13.52; ESI-HRMS *m/z* calcd for $C_{19}H_{19}BrNO_3S_2^+$ $[M + H]^+$ 451.9984, found 451.9987.



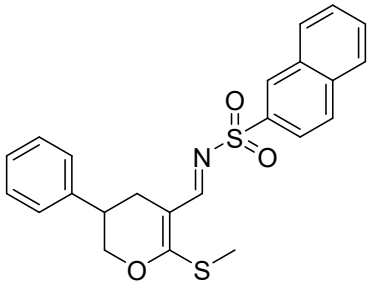
2c

(E)-N-((6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)methanesulfonamide (**2c**): white solid, m.p.: 141.6-143.5 ºC; 57.0 mg; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.19 (s, 1H), 7.43 – 7.28 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 2H), 4.70 – 4.43 (m, 1H), 4.18 (t, *J* = 10.5 Hz, 1H), 3.29 – 3.11 (m, 1H), 3.03 (s, 3H), 2.90 (dd, *J* = 18.1, 4.1 Hz, 1H), 2.54 (dd, *J* = 16.6, 11.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 173.43, 167.11, 139.40, 129.02, 127.63, 127.35, 110.63, 74.44, 40.74, 37.71, 28.09, 13.55; ESI-HRMS *m/z* calcd for $C_{14}H_{18}NO_3S_2^+$ $[M + H]^+$ 312.0723, found 312.0722.



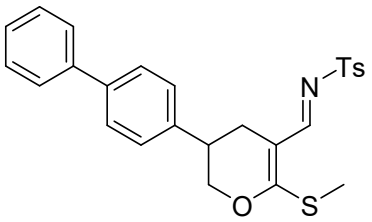
2d

(E)-4-methoxy-N-((6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2d**): clear oil; 80.5 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.44 – 7.27 (m, 3H), 7.20 (d, *J* = 7.1 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 4.60 – 4.50 (m, 1H), 4.13 (t, *J* = 10.6 Hz, 1H), 3.88 (s, 3H), 3.21 – 3.08 (m, 1H), 2.92 – 2.80 (m, 1H), 2.53 – 2.46 (m, 1H), 2.45 (s, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 172.48, 165.89, 163.04, 139.45, 131.58, 129.72, 128.96, 127.56, 127.36, 114.15, 111.07, 74.33, 55.64, 37.76, 28.17, 13.58; ESI-HRMS *m/z* calcd for $C_{20}H_{22}NO_4S_2^+$ $[M + H]^+$ 404.0985, found 404.0984.



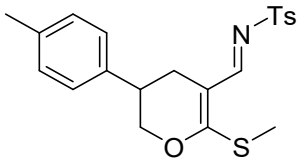
2e

(E)-N-((6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)naphthalene-2-sulfonamide (**2e**): clear oil; 89.9 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 8.82 (d, *J* = 8.7 Hz, 1H), 8.39 (d, *J* = 7.3 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.62 – 7.53 (m, 2H), 7.37 – 7.27 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.51 (d, *J* = 10.2 Hz, 1H), 4.10 (t, *J* = 10.5 Hz, 1H), 3.18 – 2.99 (m, 1H), 2.82 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.50 – 2.41 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 173.40, 166.72, 139.38, 135.54, 134.31, 134.17, 128.97, 128.68, 128.03, 127.58, 127.38, 126.75, 125.84, 124.33, 111.19, 74.46, 37.71, 27.96, 13.56; ESI-HRMS *m/z* calcd for $C_{23}H_{22}NO_3S_2^+$ $[M + H]^+$ 457.1468, found 457.1491.



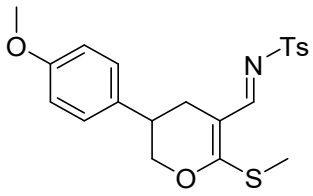
2f

(E)-N-((3-([1,1'-biphenyl]-4-yl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2f**): white solid, m.p. 142.3-145.8 °C; 90.4 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.63 – 7.55 (m, 4H), 7.47 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.26 (m, 2H), 4.75 – 4.49 (m, 1H), 4.17 (t, *J* = 10.5 Hz, 1H), 3.29 – 3.10 (m, 1H), 3.00 – 2.82 (m, 1H), 2.52 (dd, *J* = 16.8, 11.0 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.88, 166.25, 143.54, 140.54, 138.42, 137.02, 129.57, 128.88, 127.79, 127.65, 127.61, 127.49, 127.08, 111.03, 74.35, 37.42, 28.12, 21.65, 13.59; ESI-HRMS *m/z* calcd for $C_{26}H_{26}NO_3S_2^+$ $[M + H]^+$ 464.1349, found 464.1349.



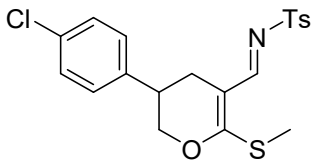
2g

(E)-4-methyl-N-((6-(methylthio)-3-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2g**): white solid, m.p. 138.1-140.8 °C; 72.5 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 4.69 – 4.37 (m, 1H), 4.10 (t, *J* = 10.5 Hz, 1H), 3.28 – 2.99 (m, 1H), 2.84 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.51 – 2.40 (m, 7H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.86, 166.28, 143.48, 137.24, 137.08, 136.33, 129.61, 129.54, 127.58, 127.21, 111.13, 74.54, 37.31, 28.13, 21.63, 21.07, 13.56; ESI-HRMS *m/z* calcd for $C_{21}H_{24}NO_3S_2^+$ $[M + H]^+$ 402.1192, found 402.1201.



2h

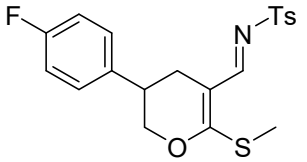
(E)-N-((3-(4-methoxyphenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2h**): white solid, m.p. 140.7-143.2 °C; 88.0 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.85 (d, *J* = 6.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.19 – 7.06 (m, 2H), 6.96 – 6.83 (m, 2H), 4.62 – 4.43 (m, 1H), 4.18 – 4.01 (m, 1H), 3.83 (s, 3H), 3.17 – 3.02 (m, 1H), 2.84 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.53 – 2.37 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.91, 166.29, 158.97, 143.50, 137.08, 131.34, 129.55, 128.35, 127.59, 114.36, 111.10, 74.62, 55.36, 36.90, 28.21, 21.63, 13.55; ESI-HRMS *m/z* calcd for $C_{21}H_{24}NO_4S_2^+$ $[M + H]^+$ 418.1141, found 418.1143.



2i

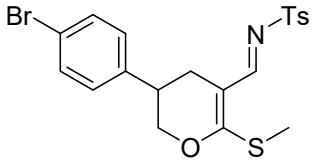
(E)-N-((3-(4-chlorophenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2i**): white solid, m.p. 142.8-145.2 °C; 71.2 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.24

(m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.62 – 4.43 (m, 1H), 4.10 (t, *J* = 10.4 Hz, 1H), 3.24 – 3.04 (m, 1H), 2.93 – 2.75 (m, 1H), 2.50 – 2.38 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.85, 166.18, 143.61, 137.90, 136.90, 133.40, 129.59, 129.13, 128.70, 127.62, 110.72, 74.04, 37.15, 27.98, 21.66, 13.56; ESI-HRMS *m/z* calcd for $C_{20}H_{21}ClNO_3S_2^{++}$ $[M + H]^+$ 422.0646, found 422.0650.



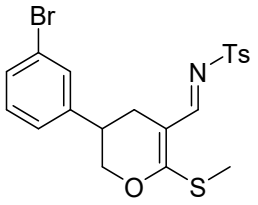
2j

(E)-N-((3-(4-fluorophenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2j**): white solid, m.p. 123.4-126.8 °C; 78.1 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.65 – 4.37 (m, 1H), 4.09 (t, *J* = 10.5 Hz, 1H), 3.25 – 2.95 (m, 1H), 2.95 – 2.70 (m, 1H), 2.55 – 2.32 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.84, 162.11 (d, *J* = 246.2 Hz), 160.89, 143.58, 136.96, 135.15 (d, *J* = 3.2 Hz), 129.57, 128.87 (d, *J* = 7.9 Hz), 127.61, 115.85 (d, *J* = 21.3 Hz), 110.84, 74.25, 37.03, 28.20, 21.63, 13.54. ^{19}F NMR (376 MHz, Chloroform-d) δ -114.78; ESI-HRMS *m/z* calcd for $C_{20}H_{21}FNO_3S_2^+$ $[M + H]^+$ 406.0941, found 406.0942.



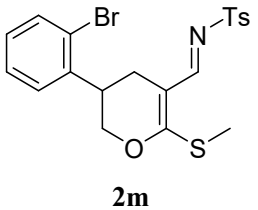
2k

(E)-N-((3-(4-bromophenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2k**): white solid, m.p. 144.9-146.7 °C; 81.2 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.62 – 4.38 (m, 1H), 4.09 (t, *J* = 10.5 Hz, 1H), 3.23 – 3.01 (m, 1H), 2.91 – 2.75 (m, 1H), 2.52 – 2.34 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.89, 166.17, 143.63, 138.43, 136.87, 132.08, 129.60, 129.07, 127.61, 121.45, 110.68, 73.95, 37.21, 27.91, 21.67, 13.57; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrNO_3S_2^+$ $[M + H]^+$ 466.0141, found 466.0141.



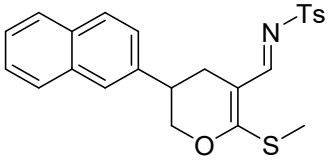
2l

(E)-N-((3-(3-bromophenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2l**): white solid, m.p. 117.4-119.3 °C; 51.3 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 4.67 – 4.39 (m, 1H), 4.10 (t, *J* = 10.5 Hz, 1H), 3.24 – 3.00 (m, 1H), 2.95 – 2.74 (m, 1H), 2.51 – 2.38 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.74, 166.16, 143.61, 141.73, 136.89, 130.74, 130.53, 130.50, 129.59, 127.63, 126.05, 123.01, 110.70, 73.88, 37.47, 27.97, 21.65, 13.58; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrNO_3S_2^+$ $[M + H]^+$ 466.0141, found 466.0148.



2m

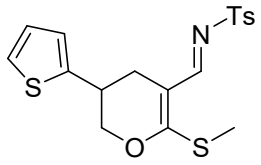
(E)-N-((3-(2-bromophenyl)-6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2m**): white solid, m.p. 143.5-146.7 °C; 56.9 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.55 (m, 1H), 7.42 – 7.27 (m, 3H), 7.21 – 7.10 (m, 2H), 4.64 – 4.41 (m, 1H), 4.13 (t, *J* = 10.0 Hz, 1H), 3.77 – 3.55 (m, 1H), 2.97 – 2.75 (m, 1H), 2.50 (dd, *J* = 16.9, 10.3 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.98, 166.23, 143.59, 138.43, 136.91, 133.40, 129.58, 129.02, 128.12, 127.71, 127.62, 124.86, 110.83, 73.05, 36.71, 26.99, 21.65, 13.58; ESI-HRMS *m/z* calcd for $C_{20}H_{21}BrNO_3S_2^+$ $[M + H]^+$ 466.0141, found 466.0150.



2n

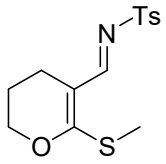
(E)-4-methyl-N-((6-(methylthio)-3-(naphthalen-2-yl)-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2n**): white solid, m.p. 142.3-145.2 °C; 86.7 mg;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 7.91 – 7.79 (m, 5H), 7.69 – 7.61 (m, 1H), 7.57 – 7.44 (m, 2H), 7.37 – 7.24 (m, 3H), 4.74 – 4.52 (m, 1H), 4.21 (t, *J* = 10.5 Hz, 1H), 3.40 – 3.17 (m, 1H), 3.06 – 2.82 (m, 1H), 2.62 (dd, *J* = 16.8, 11.0 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 173.01, 166.32, 143.56, 136.99, 136.68, 133.48, 132.71, 129.59, 128.71, 127.76, 127.71, 127.62, 126.50, 126.12, 125.98, 125.58, 111.03, 74.43, 37.79, 27.94, 21.66, 13.61; ESI-HRMS *m/z* calcd for $C_{24}H_{24}NO_3S_2^+$ [M + H]$^+$ 438.1192, found 438.1195.



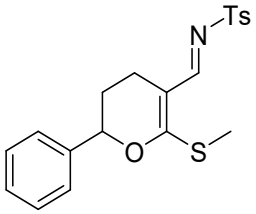
2o

(E)-4-methyl-N-((6-(methylthio)-3-(thiophen-2-yl)-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2o**): white solid, m.p. 138.4-140.2 °C; 66.1 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.92 (d, *J* = 3.5 Hz, 1H), 4.71 – 4.40 (m, 1H), 4.13 (t, *J* = 10.2 Hz, 1H), 3.60 – 3.34 (m, 1H), 3.06 – 2.79 (m, 1H), 2.51 (dd, *J* = 16.7, 10.4 Hz, 1H), 2.47 – 2.42 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.79, 166.22, 143.59, 142.22, 136.91, 129.59, 127.63, 127.10, 124.49, 124.35, 110.36, 74.37, 33.35, 29.10, 21.66, 13.55; ESI-HRMS *m/z* calcd for $C_{18}H_{20}NO_3S_3^+$ [M + H]$^+$ 394.0600, found 394.0597.



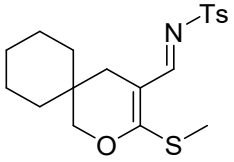
2p

(E)-4-methyl-N-((6-(methylthio)-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2p**): yellow solid, m.p. 128.1-130.0 °C; 57.6 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.36 – 4.28 (m, 2H), 2.44 (s, 3H), 2.42 – 2.35 (m, 5H), 2.02 – 1.84 (m, 2H).^{13}C NMR (101 MHz, Chloroform-d) δ 173.66, 166.55, 143.43, 137.15, 129.54, 127.55, 111.16, 70.87, 21.63, 21.16, 20.62, 13.46; ESI-HRMS *m/z* calcd for $C_{14}H_{18}NO_3S_2^+$ [M + H]$^+$ 312.0723, found 312.0719.



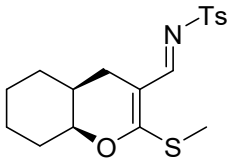
2q

(E)-4-methyl-N-((6-(methylthio)-2-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)benzenesulfonamide (**2q**): clear oil; 62.6 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.20 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.39 – 7.28 (m, 4H), 5.14 (dd, *J* = 10.5, 2.3 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.48 – 2.38 (m, 7H), 2.33 – 2.17 (m, 1H), 2.05 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 173.25, 166.33, 143.50, 138.87, 137.07, 129.58, 128.84, 128.74, 127.60, 125.97, 110.96, 82.79, 28.82, 21.67, 21.16, 13.56; ESI-HRMS *m/z* calcd for $C_{20}H_{22}NO_3S_2^+$ [M + H]$^+$ 388.1036, found 388.1034.



2r

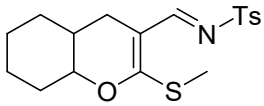
(E)-4-methyl-N-((3-(methylthio)-2-oxaspiro[5.5]undec-3-en-4-yl)methylene)benzenesulfonamide (**2r**): white solid, m.p.: 125.2-127.8 ºC; 62.0 mg, 83% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 2.22 (s, 2H), 1.59 – 1.21 (m, 10H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.69, 167.10, 143.41, 137.13, 129.54, 127.61, 110.26, 78.02, 33.14, 32.08, 31.41, 26.19, 21.64, 21.38, 13.51; ESI-HRMS *m/z* calcd for $C_{19}H_{26}NO_3S_2^+$ [M + H]$^+$ 380.1349, found 380.1349.



2s

(E)-4-methyl-N-((2-(methylthio)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)methylene)benzenesulfonamide (**2s**): white solid, m.p.: 173.1-175.6 ºC; 71.5 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.39 – 4.31 (m, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.38 (d, *J* = 6.7 Hz, 1H),

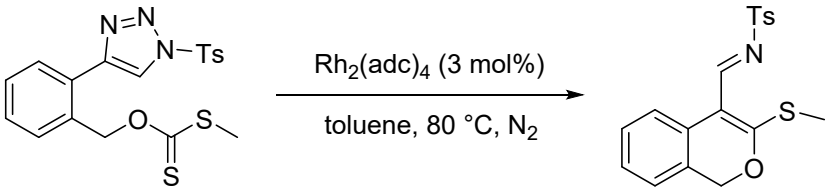
2.28 (dd, *J* = 17.0, 2.7 Hz, 1H), 2.13 – 1.98 (m, 2H), 1.77 – 1.69 (m, 1H), 1.66 – 1.24 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.68, 166.74, 143.33, 137.26, 129.52, 127.56, 109.11, 79.91, 31.91, 29.71, 26.71, 26.51, 24.19, 21.63, 20.45, 13.31; ESI-HRMS *m/z* calcd for $C_{18}H_{24}NO_3S_2^+$ [M + H]$^+$ 366.1192, found 366.1195.



2s'(d.r.=1.61:1)

(E)-4-methyl-N-((2-(methylthio)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)methylene)benzenesulfonamide (**2s'**): clear oil, 70.5 mg; major isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 7.84 (d, *J* = 6.8 Hz, 2H), 7.31 (d, *J* = 10.0 Hz, 2H), 3.77 – 3.68 (m, 1H), 2.58 (dd, *J* = 16.6, 5.4 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.27 – 2.19 (m, 1H), 2.12 – 1.68 (m, 8H). minor isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.39 – 4.31 (m, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.38 (d, *J* = 6.7 Hz, 1H), 2.28 (dd, *J* = 17.0, 2.7 Hz, 1H), 2.13 – 1.98 (m, 2H), 1.77 – 1.69 (m, 1H), 1.66 – 1.24 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.26, 172.66, 166.73, 166.46, 143.33, 137.28, 129.51, 127.55, 111.02, 109.11, 84.21, 79.92, 38.73, 36.48, 36.38, 31.91, 31.31, 31.23, 29.70, 28.01, 27.90, 26.71, 26.52, 25.05, 24.35, 24.19, 21.61, 20.45, 13.42, 13.29. ESI-HRMS *m/z* calcd for $C_{18}H_{24}NO_3S_2^+$ [M + H]$^+$ 366.1192, found 366.1195.

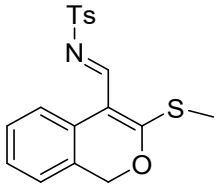
3.2 General procedure for synthesis of 2t and 2u



1t **2t**

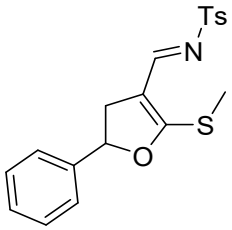
1t (83.9 mg, 0.20 mmol) and $Rh_2(adc)_4$ (5.5 mg, 3 mol%) were added to a 25 mL glass reaction tube. Ultra-dry toluene (2 mL) was added under N_2 conditions, and then the reaction tube was placed in an oil pan at 80 °C. The mixture gradually changed from green to brown. The reaction was detected by TLC. After the reaction, it was

cooled to room temperature, and the solvent was evaporated under reduced pressure. It was purified by silica gel column chromatography PE/EtOAc (4:1) to obtain **2t**. **2u** operation mode is the same as **2t**.



2t

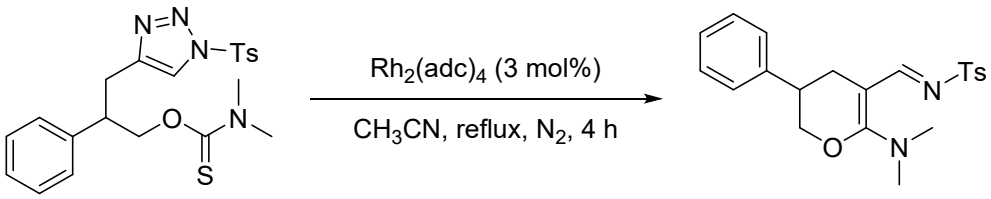
(E)-4-methyl-N-((3-(methylthio)-1H-isochromen-4-yl)methylene)benzenesulfonamide (**2t**): clear oil, 30.6 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 8.35 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 5.23 (s, 2H), 2.54 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 178.56, 163.87, 143.60, 137.06, 129.64, 129.09, 128.10, 127.57, 127.22, 126.09, 124.44, 123.85, 110.95, 72.35, 21.64, 14.71; ESI-HRMS *m/z* calcd for $C_{18}H_{18}NO_3S_2^+$ $[M + H]^+$ 360.0723, found 360.0718.



2u

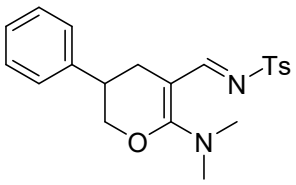
(E)-4-methyl-N-((2-(methylthio)-5-phenyl-4,5-dihydrofuran-3-yl)methylene)benzenesulfonamide (**2u**): clear oil, 52.3 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.36 – 7.29 (m, 4H), 5.88 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.44 (dd, *J* = 14.9, 10.2 Hz, 1H), 3.05 (dd, *J* = 14.9, 8.1 Hz, 1H), 2.56 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 175.94, 160.89, 143.38, 139.32, 137.34, 129.53, 129.05, 128.97, 127.50, 126.01, 110.86, 88.34, 36.33, 21.60, 13.17; ESI-HRMS *m/z* calcd for $C_{19}H_{20}NO_3S_2^+$ $[M + H]^+$ 374.0879, found 374.0883.

3.3 Control experiment



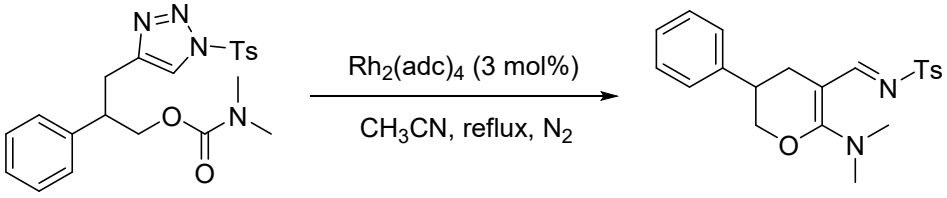
1V **2V**

1v (88.9 mg, 0.20 mmol) and $Rh_2(adc)_4$ (5.5 mg, 3 mol%) were added to a 25 mL glass reaction tube. Ultra-dry acetonitrile (2 mL) was added under N_2 conditions. Put the reaction tube into a preheated oil pan in advance and the mixture changes from purple to brown. The reaction was detected by TLC, At the end of reaction, the reaction was cooled to room temperature, the solvent was evaporated under reduced pressure, and purified by silica gel column chromatography (PE:EtOAc = 1:1) to obtain **2v.**



2v

(E)-N-((6-(dimethylamino)-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**2v**): clear oil, 70.8 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.24 (m, 5H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.43 – 4.37 (m, 1H), 4.09 – 4.03 (m, 1H), 3.18 (s, 6H), 3.15 – 3.08 (m, 1H), 2.79 (dd, *J* = 15.9, 6.5 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 163.87, 141.99, 139.88, 139.82, 129.26, 128.80, 127.38, 127.32, 126.77, 89.28, 72.87, 41.92, 39.45, 28.54, 21.50. ESI-HRMS *m/z* calcd for $C_{21}H_{25}N_2O_3S^+$ $[M + H]^+$ 385.1580, found 385.1578.



1w N.D.

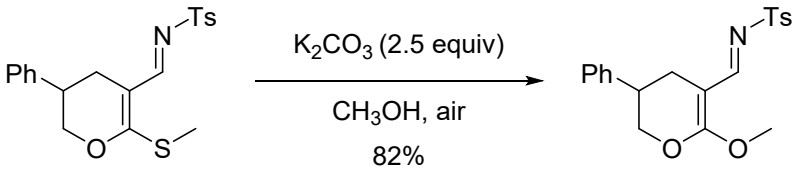
1w (85.7 mg, 0.20 mmol) and $Rh_2(adc)_4$ (5.5 mg, 3 mol%) were added to a 25 mL glass reaction tube. Ultra-dry acetonitrile (2 mL) was added under N_2 conditions. Put the reaction tube into a preheated oil pan in advance and the mixture changes from purple to brown. The reaction was detected by TLC, but no desired product was detected.

4. The large scale reaction and further transformation

4.1 Large scale reaction.

To a 50 mL glass pressure seal tube was added **1a** (895.2 mg, 2.0 mmol), $Rh_2(adc)_4$ (55.0 mg, 3 mol%) and Ultra-dry acetonitrile (20 mL) was added under N_2 conditions. Put the reaction tube into a preheated oil pan in advance and the mixture changes from purple to brown. The reaction was detected by TLC. At the end of the reaction, the reaction was cooled to room temperature, the solvent was evaporated under reduced pressure, and purified by silica gel column chromatography PE/EtOAc (5:1) to obtain **2a** (98%) as a white solid.

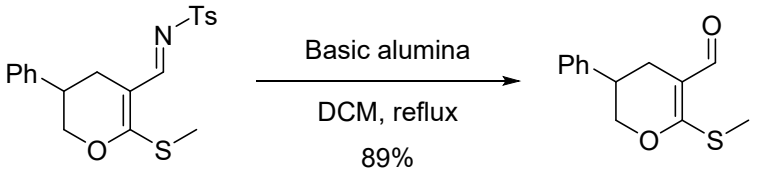
4.2 Further transformation.



2a **3**

Under air conditions, K_2CO_3 (345.5 mg, 0.5 mmol), **2a** (77.5 mg, 0.2 mmol) and stirrer were added to a 10 mL reaction flask, and then 2 mL methanol was added to the reaction flask. The reaction was carried out at room temperature for 4 h. The raw materials disappeared under TLC monitoring. After the reaction, the product was passed through a silica gel short column, concentrated under reduced pressure. Then the mixture was evaporated and the residue was purified by silica gel column PE/EtOAc (2:1) to give **3**. The yield of the product was 82%.

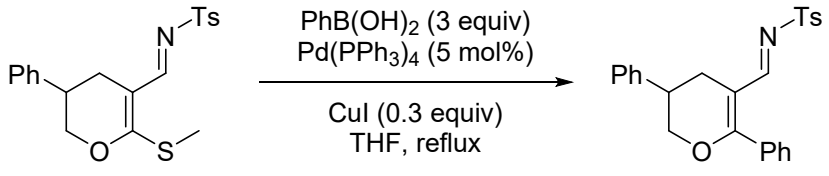
(E)-N-((6-methoxy-3-phenyl-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**3**): clear oil, ^{1}H NMR (400 MHz, Chloroform-d) δ 9.08 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.26 (m, 5H), 7.23 – 7.18 (m, 2H), 4.60 – 4.54 (m, 1H), 4.24 (t, *J* = 10.7 Hz, 1H), 3.93 (s, 3H), 3.18 – 3.07 (m, 1H), 2.90 – 2.80 (m, 1H), 2.50 (dd, *J* = 15.7, 11.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.72, 165.73, 142.87, 138.85, 138.20, 129.40, 128.95, 127.63, 127.38, 127.23, 89.37, 74.23, 55.50, 37.74, 26.08, 21.58; ESI-HRMS *m/z* calcd for $C_{20}H_{22}NO_4S^+$ $[M + H]^+$ 372.1264, found 372.1264.



2a **4**

Under air conditions, **2a** (58.1 mg, 0.15 mmol) and stirrer were added to a 10 mL reaction flask, and then 2 mL DCM was added to the flask as a solvent, and then alkaline silica gel (1g) and a small amount of potassium carbonate were added. The reaction was carried out at reflux temperature, and TLC detection was carried out until the reaction raw material disappeared. After the completion of the reaction, the hydrolysate PE/EtOAc (6:1) was obtained by silica gel short column, vacuum concentration, and column chromatography purification.[6]

6-(methylthio)-3-phenyl-3,4-dihydro-2H-pyran-5-carbaldehyde (**4**): clear oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 7.43 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.19 (m, 2H), 4.55 – 4.47 (m, 1H), 4.07 (t, *J* = 10.5 Hz, 1H), 3.20 – 3.08 (m, 1H), 2.86 – 2.74 (m, 1H), 2.50 – 2.36 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 188.34, 170.45, 139.89, 128.94, 127.35, 115.48, 73.88, 37.67, 26.64, 13.33; ESI-HRMS *m/z* calcd for $C_{13}H_{15}O_2S^+$ $[M + H]^+$ 235.0787, found 235.0790.

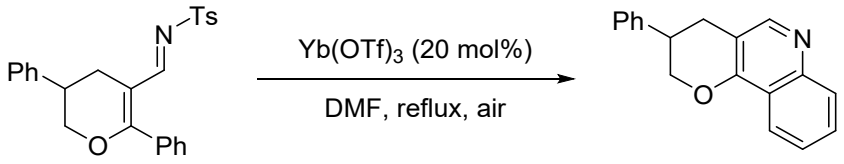


2a **5**

$Pd(PPh_3)_4$ (9 mg, 5 mol%), CuTc (8.6 mg, 0.075 mmol), **2a** (0.15 mmol, 58.1 mg), phenylboronic acid (55 mg, 0.45 mmol) and THF (2 mL) were added to the 25 mL reaction tube. The reaction was carried out at reflux temperature and detected by TLC until the raw material disappeared. After the reaction, the product was transferred, concentrated by silica gel short column under reduced pressure, and finally obtained **6** by column chromatography PE/EtOAc (6:1).[7]

(E)-N-((3,6-diphenyl-3,4-dihydro-2H-pyran-5-yl)methylene)-4-methylbenzenesulfonamide (**5**): white solid, m.p.: 83.3-85.4 ºC; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.72 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.53 – 7.44 (m, 4H), 7.42 – 7.36 (m, 2H), 7.35 – 7.25 (m, 5H), 4.68 – 4.55 (m, 1H), 4.21 (t, *J* = 10.6 Hz, 1H), 3.30 – 3.13 (m, 1H), 3.07 – 2.97 (m, 1H), 2.59 (dd, *J* = 17.2, 11.1 Hz,

1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.53, 170.01, 143.67, 139.91, 136.64, 132.54, 131.35, 130.08, 129.60, 128.96, 128.67, 127.64, 127.50, 127.41, 111.13, 72.70, 37.70, 27.64, 21.64; ESI-HRMS *m/z* calcd for $C_{25}H_{24}NO_3S^+$ $[M + H]^+$ 418.1471, found 418.1486.



5 **6**

5 (42 mg, 0.1 mmol), $Yb(OTf)_3$ (12 mg, 20 mol%) and DMF (2 mL) were added to the 25 mL reaction tube, and the reaction was carried out at reflux temperature under air conditions. TLC monitoring was performed until the raw material disappeared. After the reaction was completed, ethyl acetate was extracted, washed several times with water, washed with saturated sodium chloride, dried with anhydrous sodium sulfate, and then subjected to column chromatography to obtain the final product **6** with a yield of 60%.

3-phenyl-3,4-dihydro-2H-pyrano[3,2-c]quinoline (**6**): clear oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.56 (s, 1H), 7.57 – 7.52 (m, 5H), 7.52 – 7.46 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 4.67 – 4.47 (m, 1H), 4.16 (t, *J* = 10.5 Hz, 1H), 3.34 – 3.14 (m, 1H), 3.04 – 2.86 (m, 1H), 2.54 (dd, *J* = 17.1, 10.9 Hz, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 191.66, 171.66, 140.35, 132.69, 130.78, 130.24, 128.93, 128.36, 127.40, 127.38, 115.44, 72.37, 37.68, 25.94. ESI-HRMS *m/z* calcd for $C_{18}H_{16}NO^+$ $[M + H]^+$ 262.1226, found 262.1233.

5. References

[1] Z.-M. Man, H.-C. Dai, Y.-P. Shi, D.-D. Yang and C.-Y. Li. *Org. Lett.,* **2016**, *18*, 4962−4965.

[2] L.-J. Cheng, J.-H. Xie, L.-X. Wang and Q.-L. Zhou. *Adv. Synth. Catal.,* **2012**, *354*, 1105-1113.

[3] J. Raushel and V. V. Fokin. *Org. Lett.,* **2010**, *12*, 4952-4955.

[4] D. M. Wanner, P. M. Becker, S. Suhr, N. Wannenmacher, S. Ziegler, J. Herrmann, F. Willig, J. Gabler, K. Jangid, J. Schmid, A. C. Hans, W. Frey, B. Sarkar, J. Kästner, R. Peters. *Angew. Chem. Int. Ed.,* **2023**, *62,* e202307317.

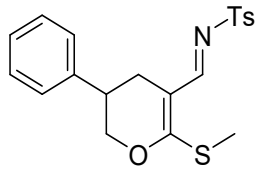
[5] A. K. Nakate, M. S. Pratapure and Kontham, R. *Org. Biomol. Chem.*, **2018**, *16*, 3229-3240.

[6] T. Chen, Z.-X. Yan, S.-G. Duan, Z.-F. Xu and C.-Y. Li. *Org. Chem. Front.,* **2021**, *8*, 6371-6376.

[7] A. Elagamy, L. K. Elghoneimy, R. K. Arafa and R. Pratap. *Tetrahedron Lett.,* **2022**, *100,* 153882.

6. X-ray data of compounds 2a

2a:



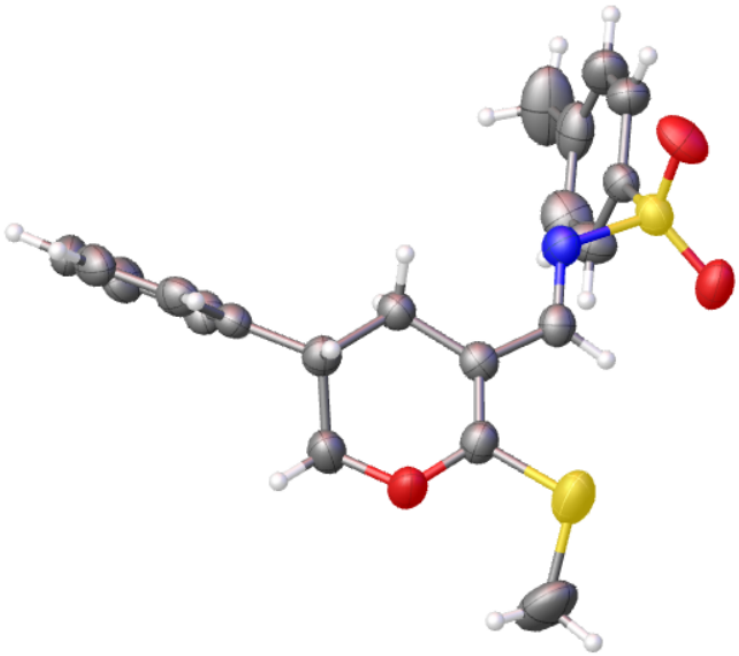


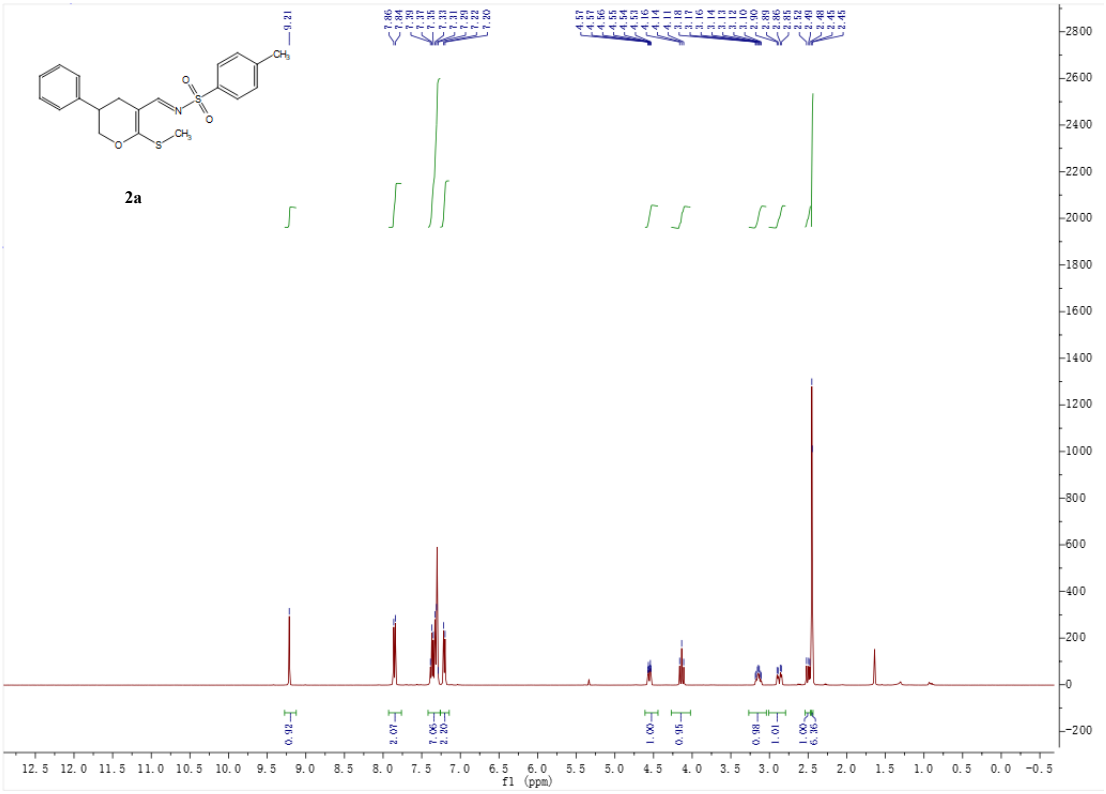
Table 1 Crystal data and structure refinement for WYX3136_0m_a.

Identification code	WYX3136_0m_a
Empirical formula	$C_{40}H_{42}N_2O_6S_4$
Formula weight	774.99
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.111(3)
b/Å	11.691(4)
c/Å	20.374(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1931.9(12)
Z	2
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	0.295
F(000)	816.0
Crystal size/mm^3	0.22 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)

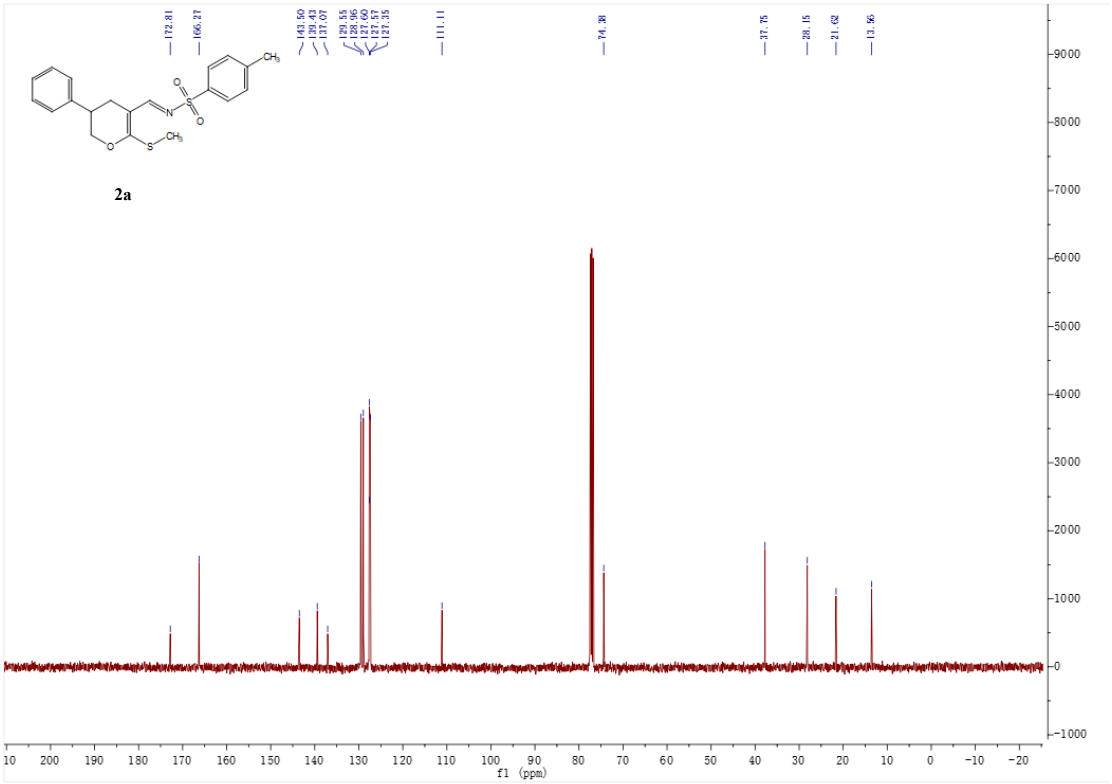
2Θ range for data collection/°	1.998 to 55.122
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-26 \leq l \leq 16$
Reflections collected	8271
Independent reflections	6120 [R_{int}= 0.0262, R_{sigma}= 0.0984]
Data/restraints/parameters	6120/0/473
Goodness-of-fit on F^2	0.919
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0998, wR_2 = 0.1027
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.26

7. Copies of NMR spectra

^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



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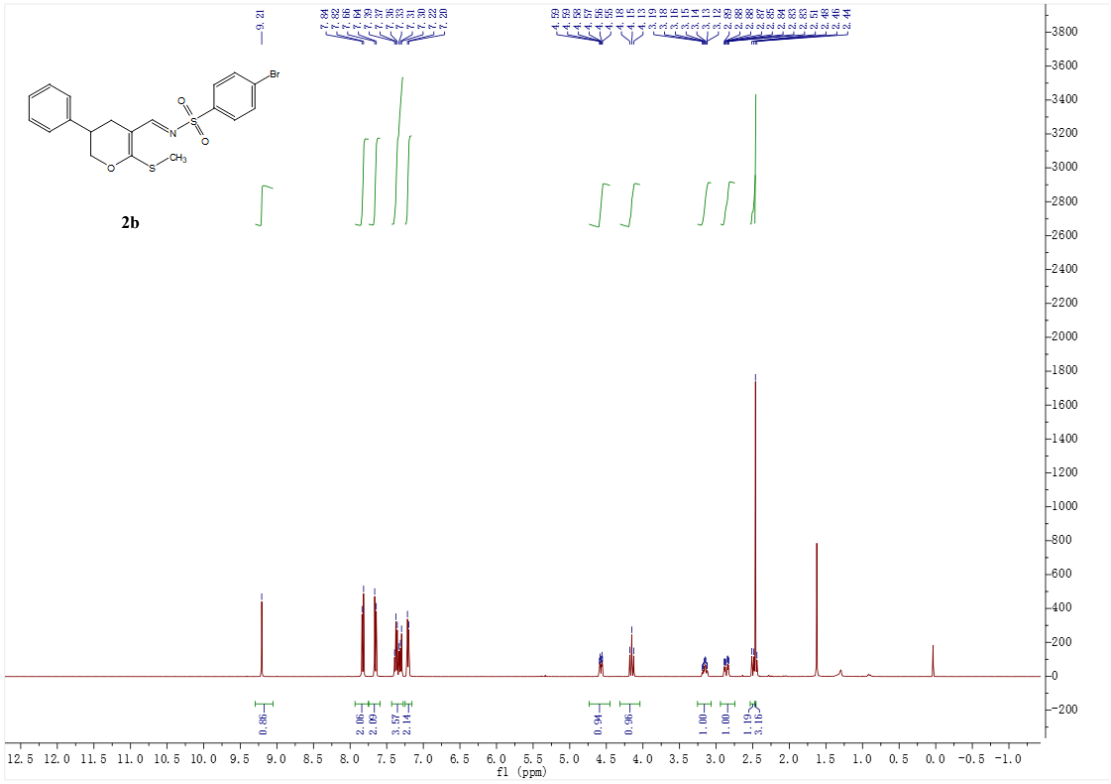

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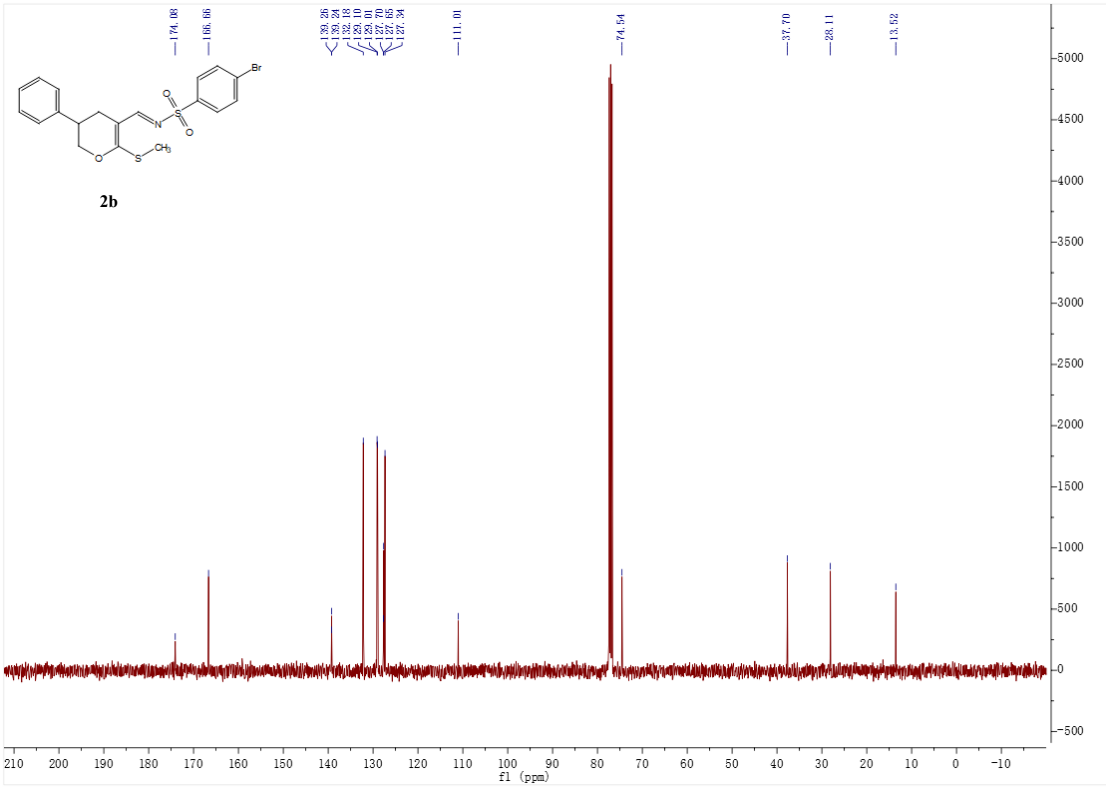

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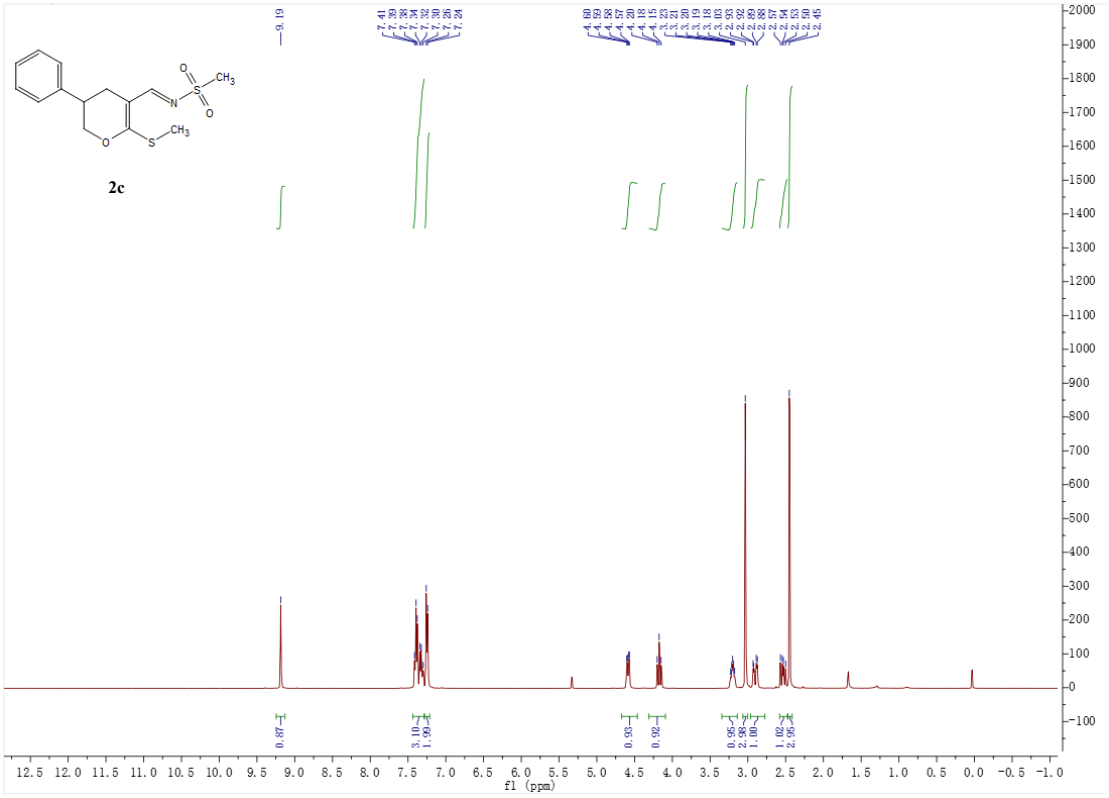

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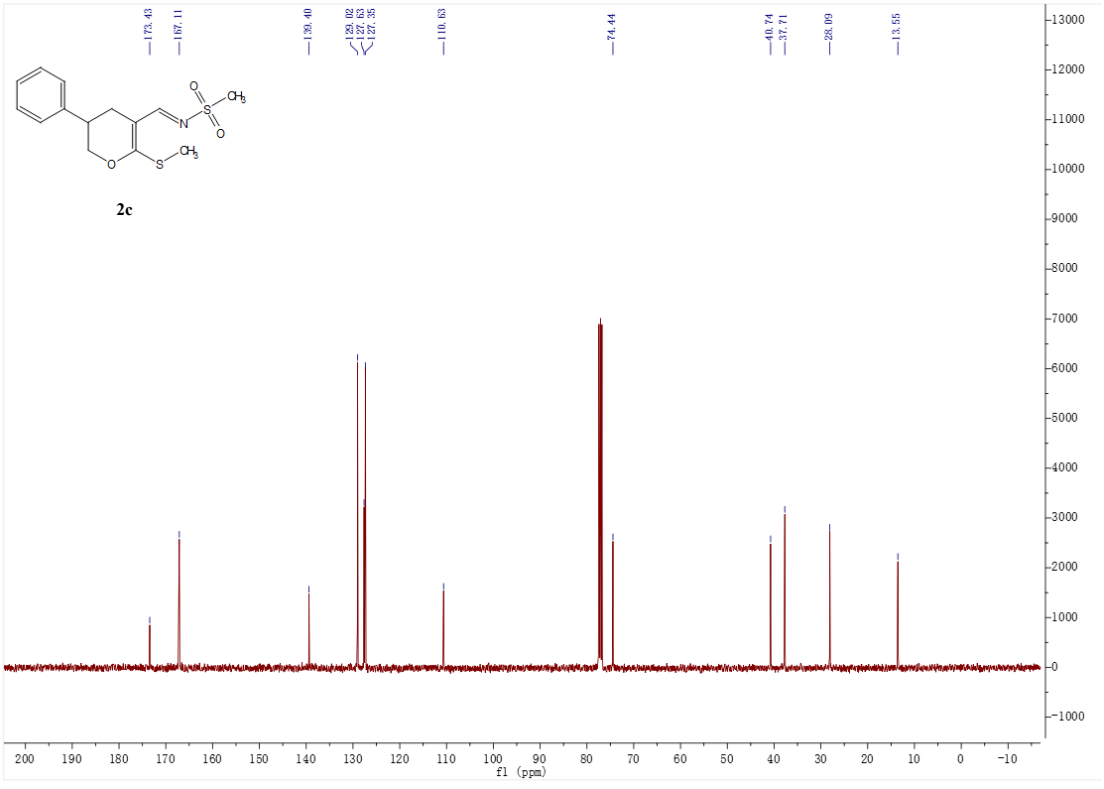

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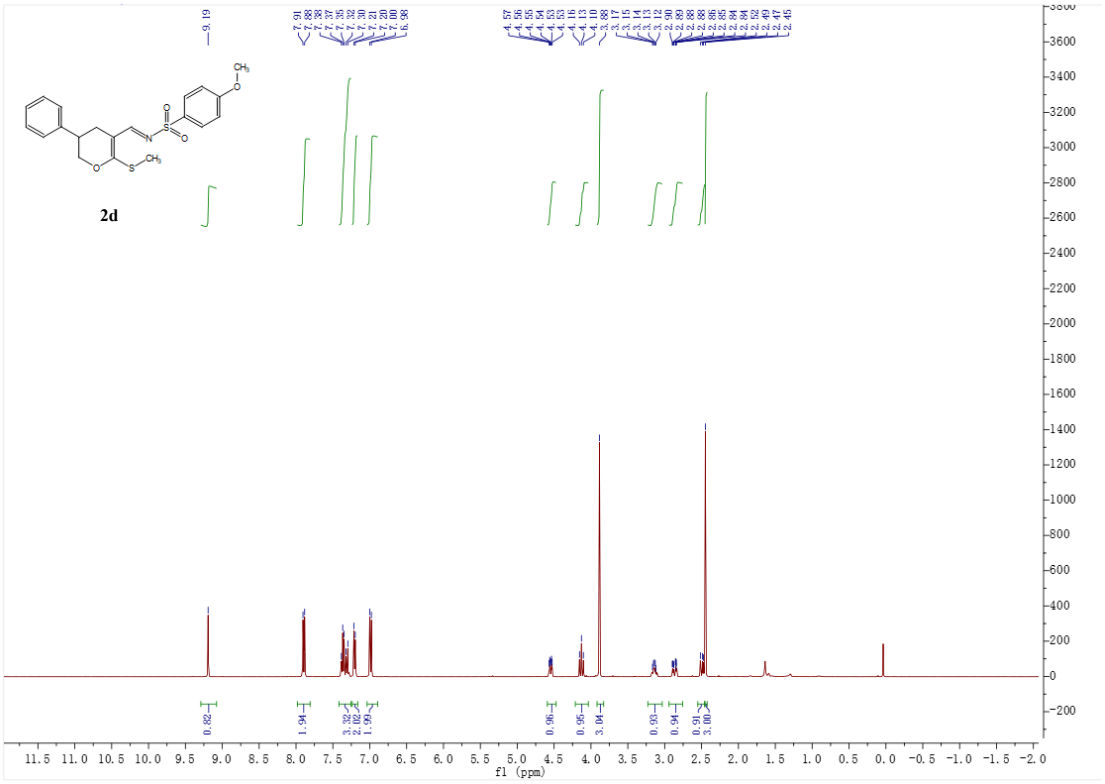

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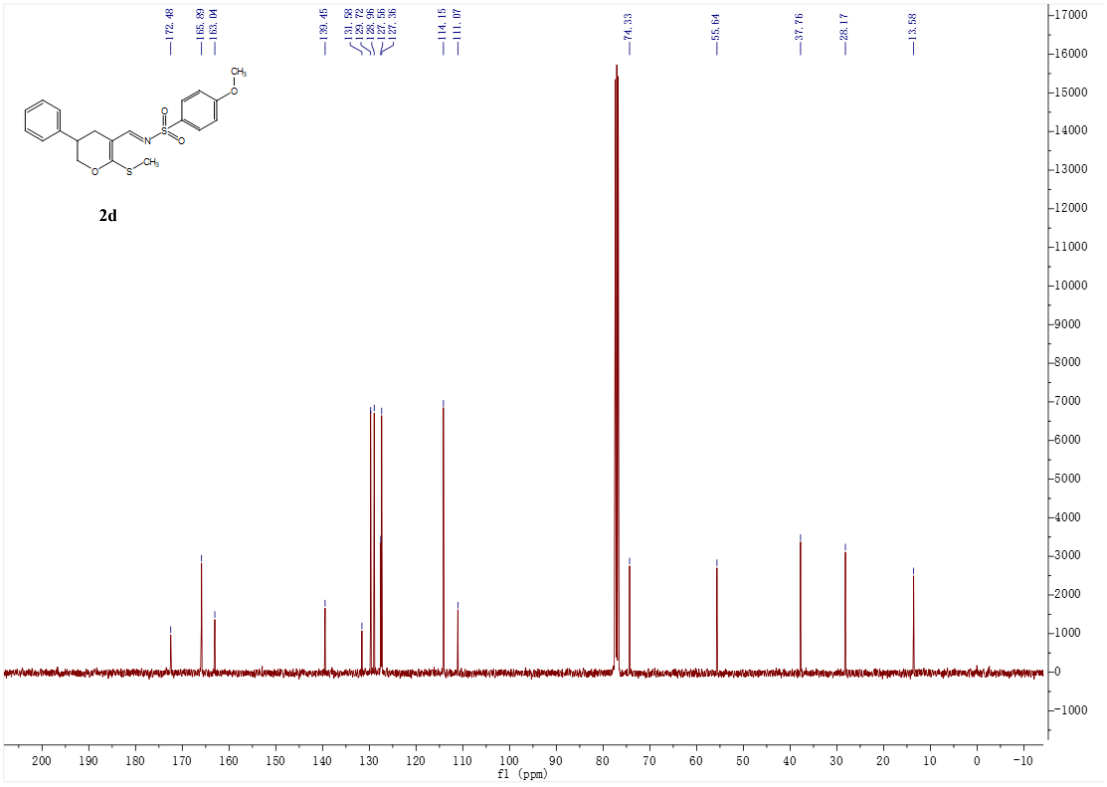

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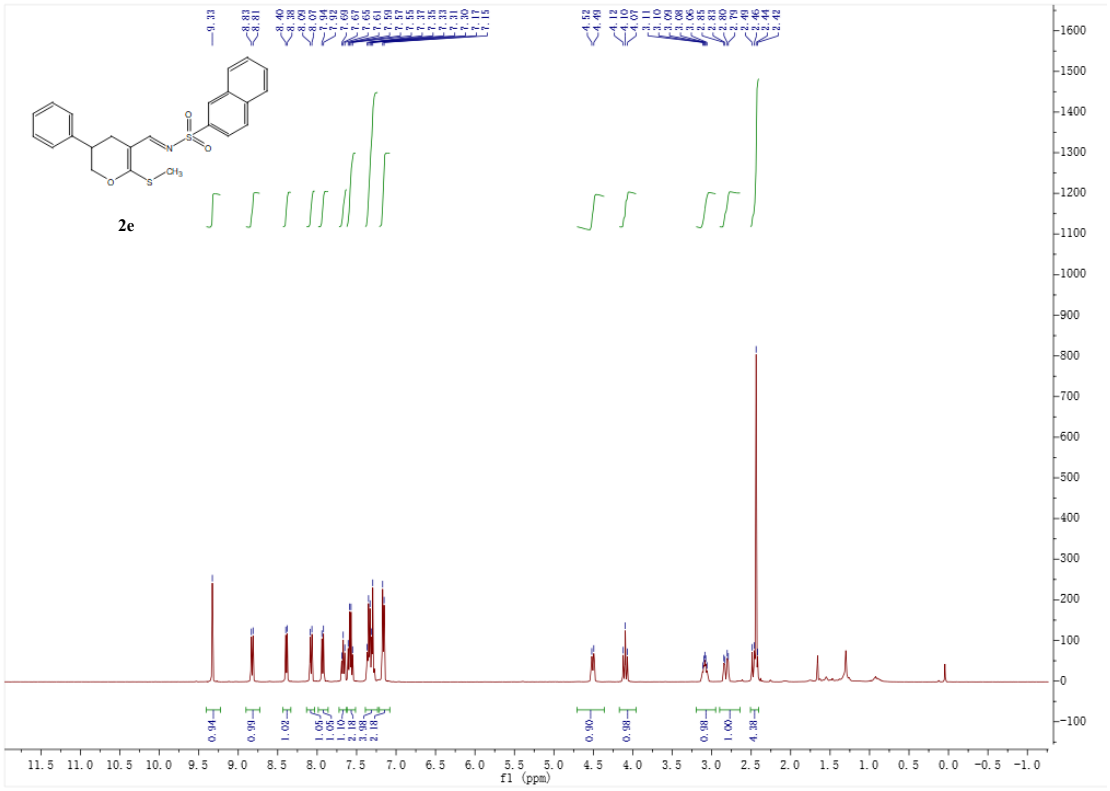

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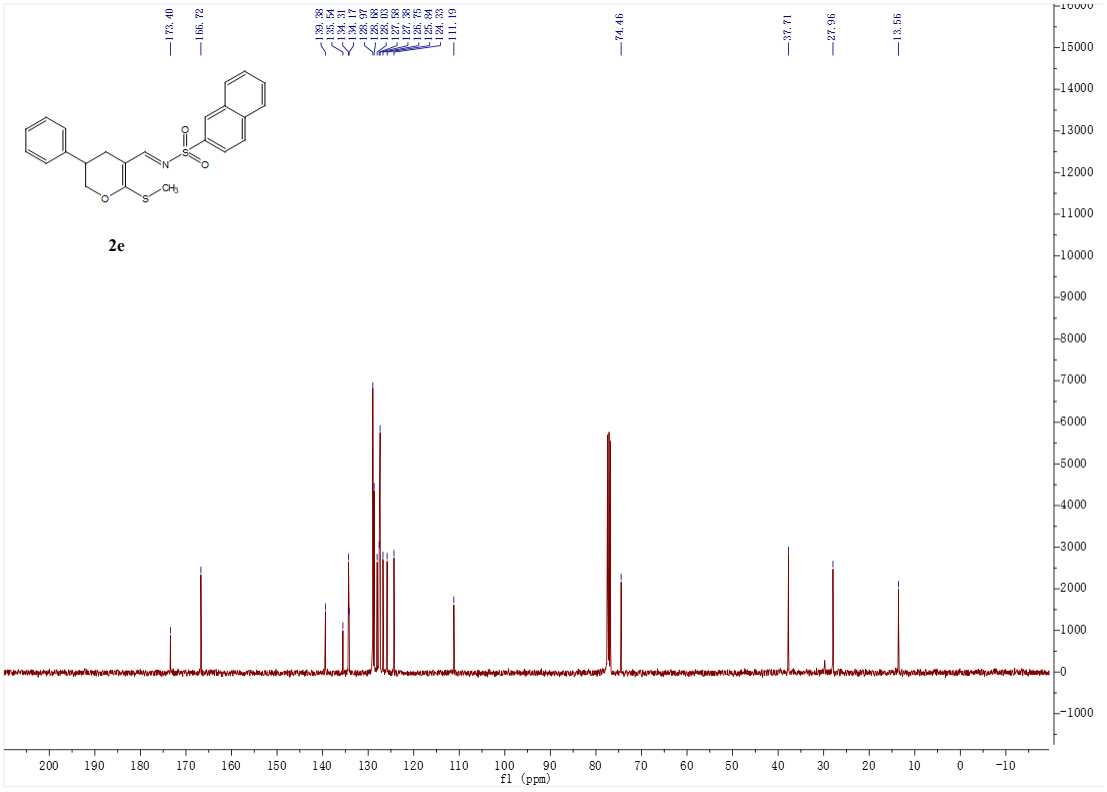

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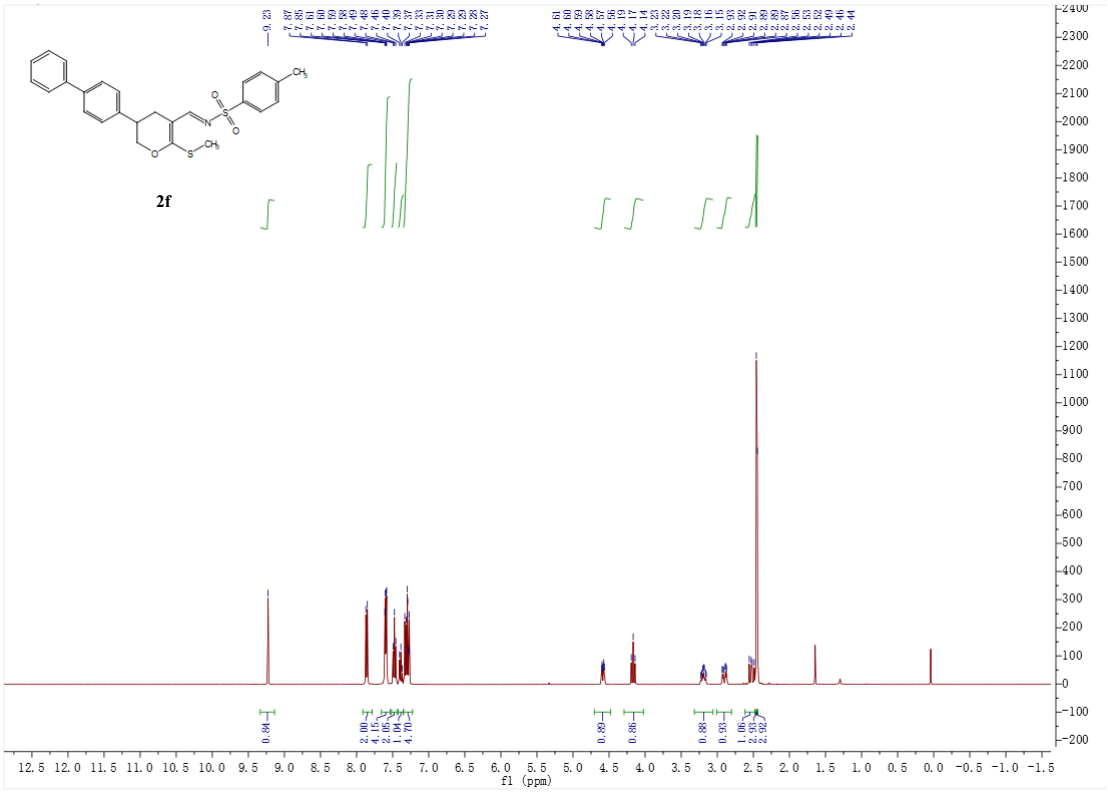

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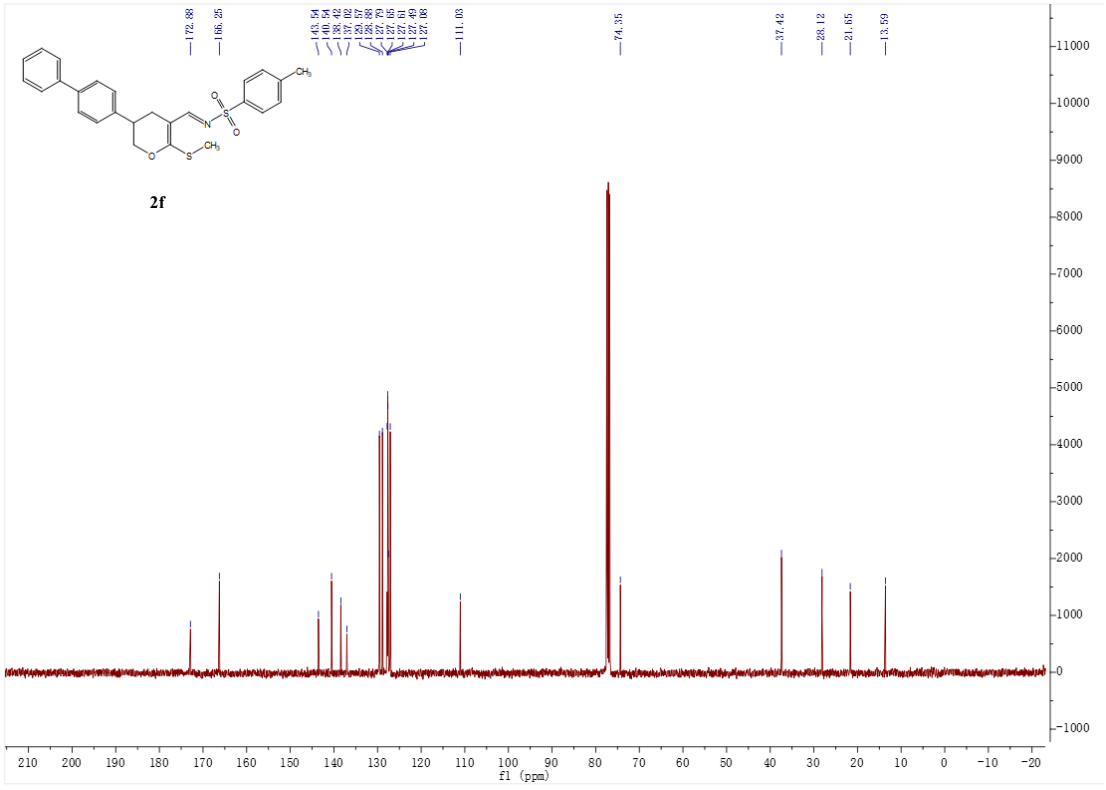

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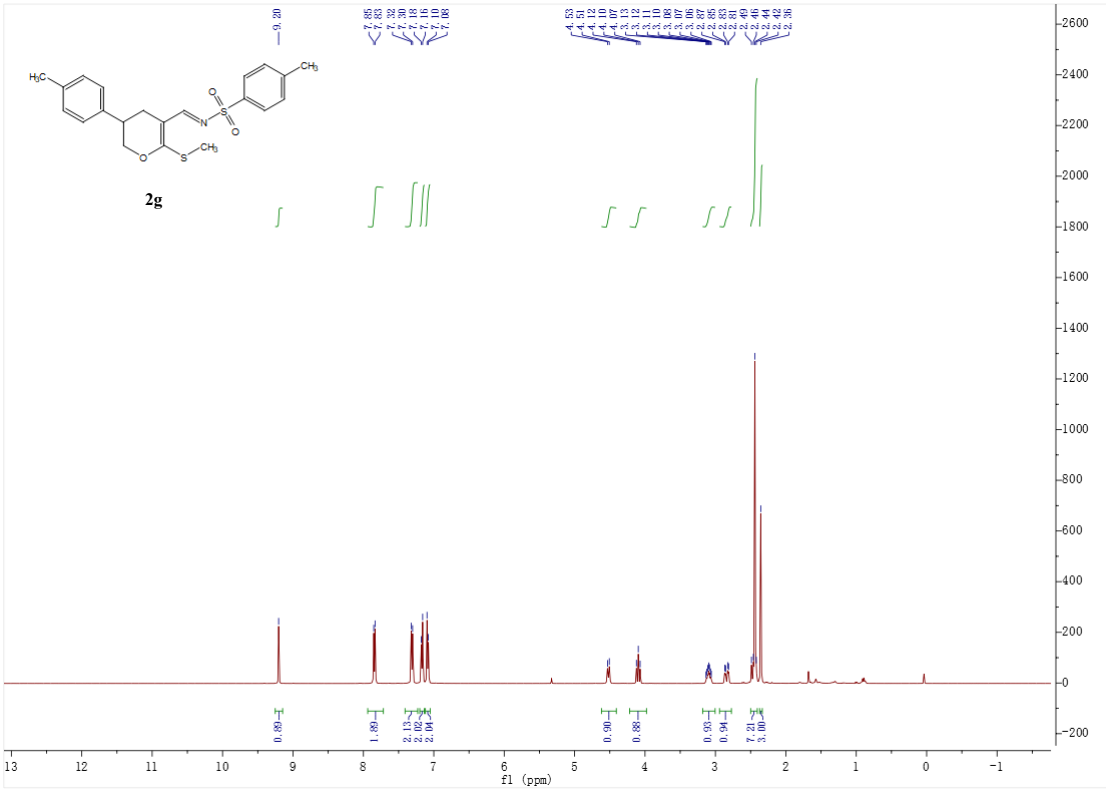

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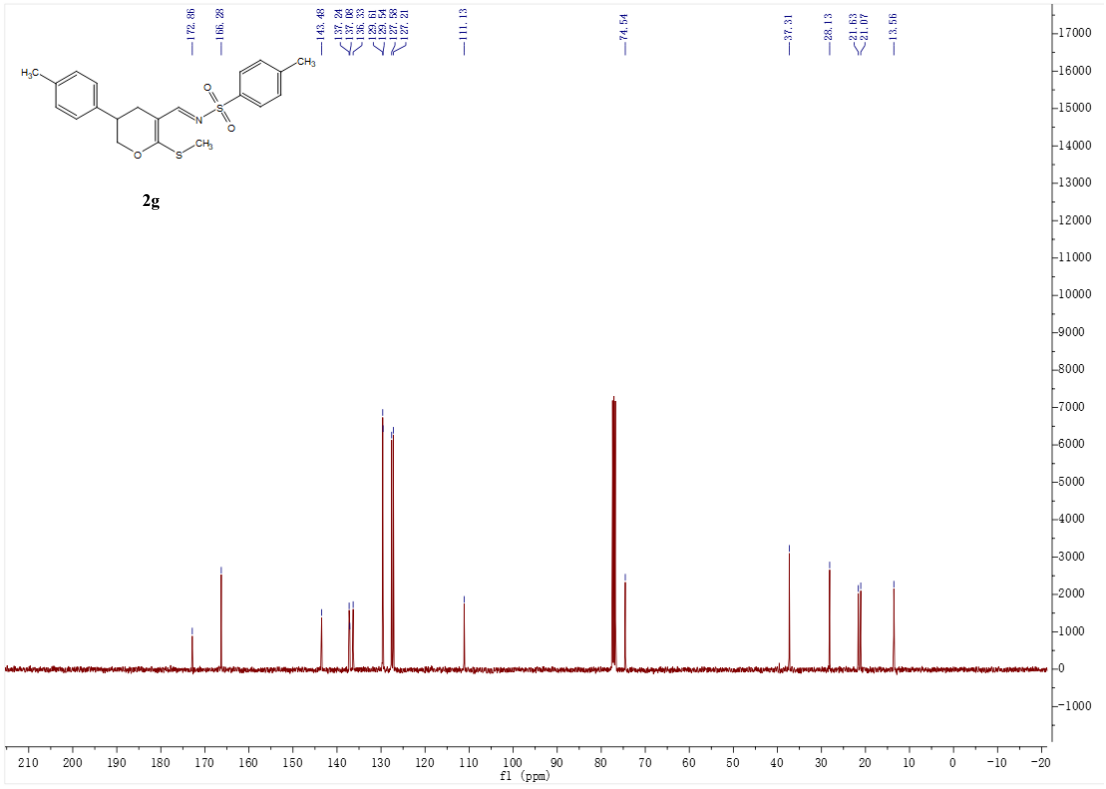

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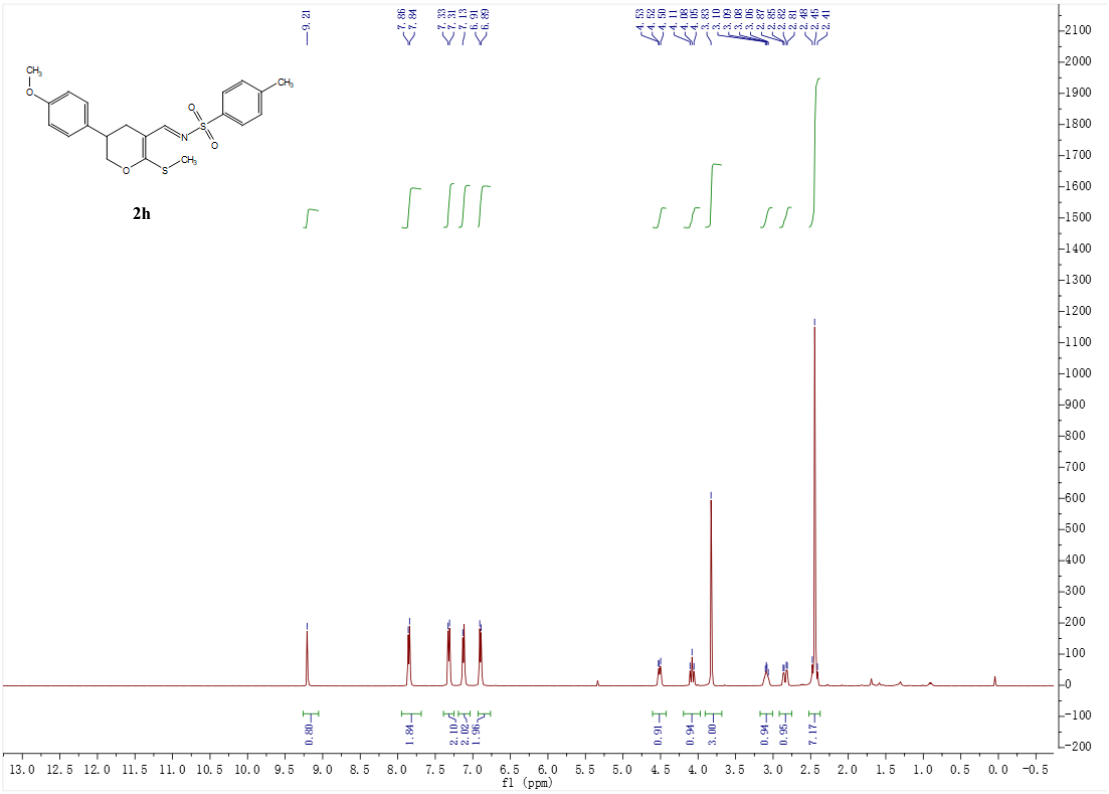

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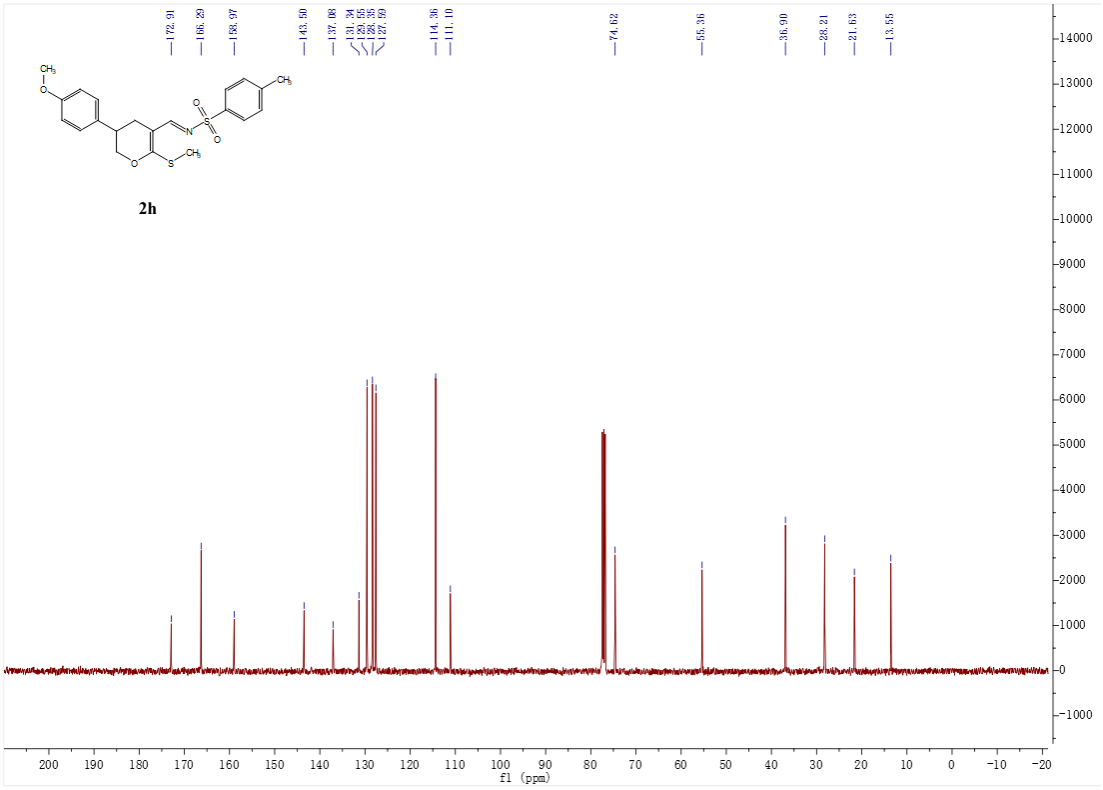

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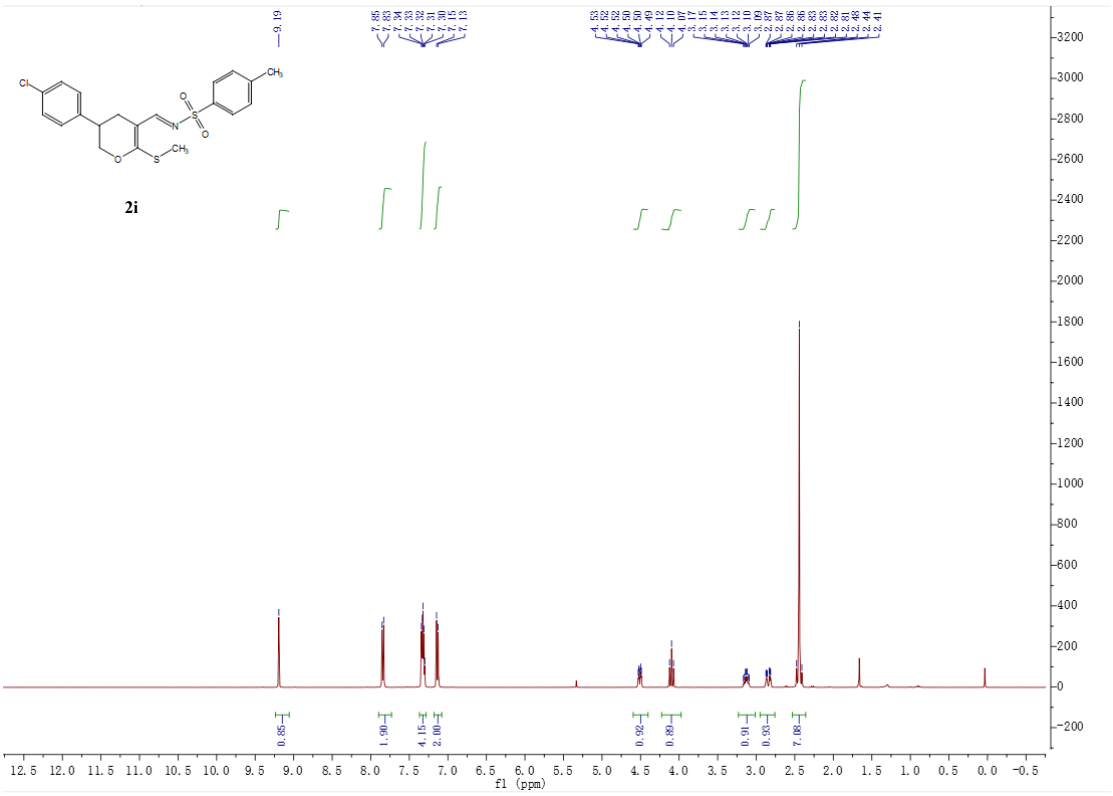

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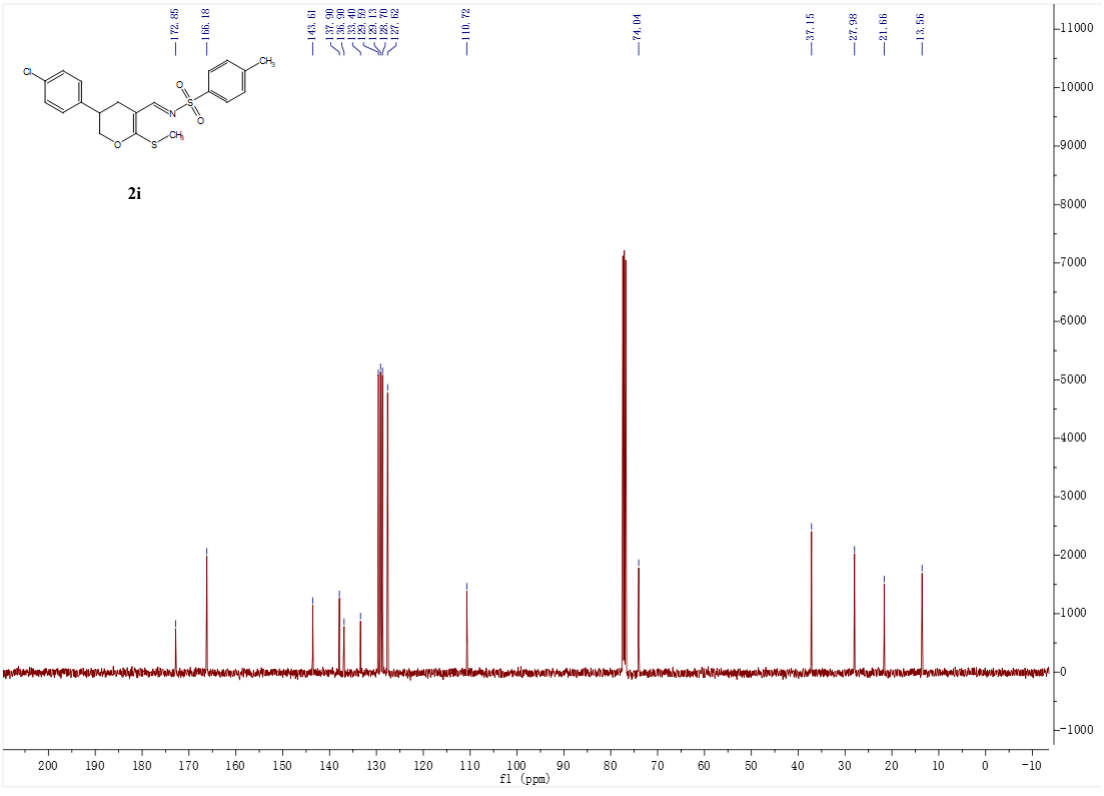

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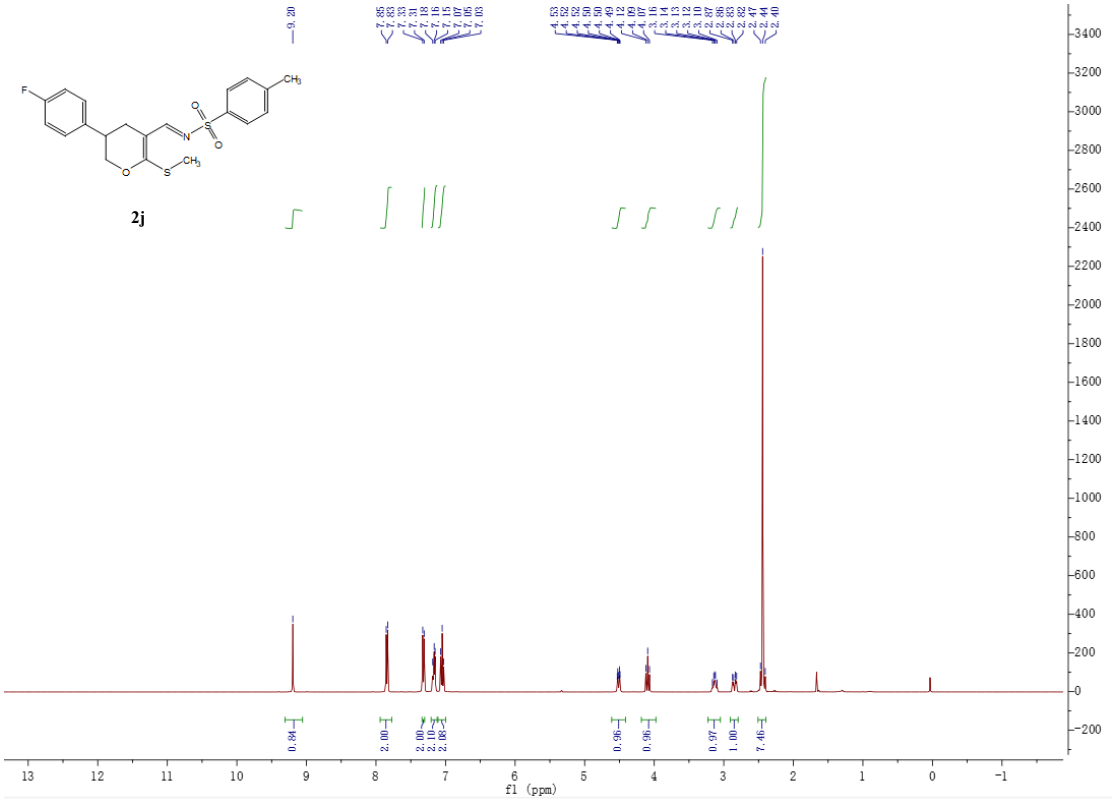

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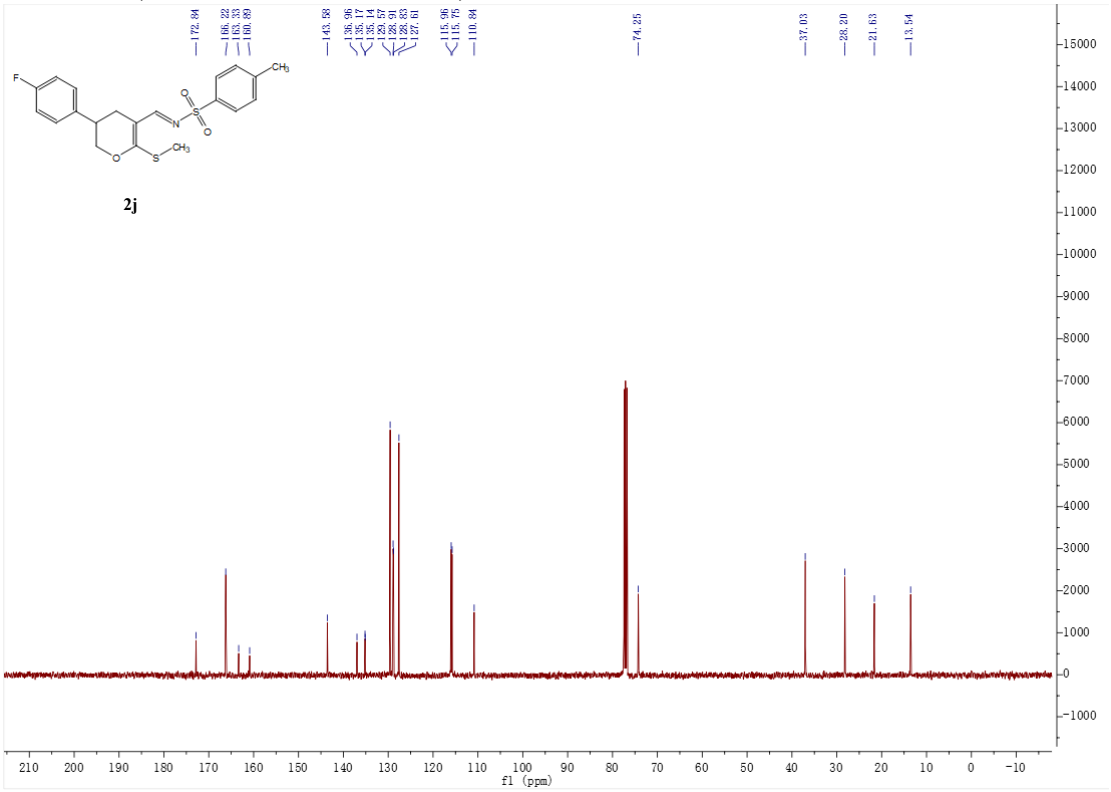
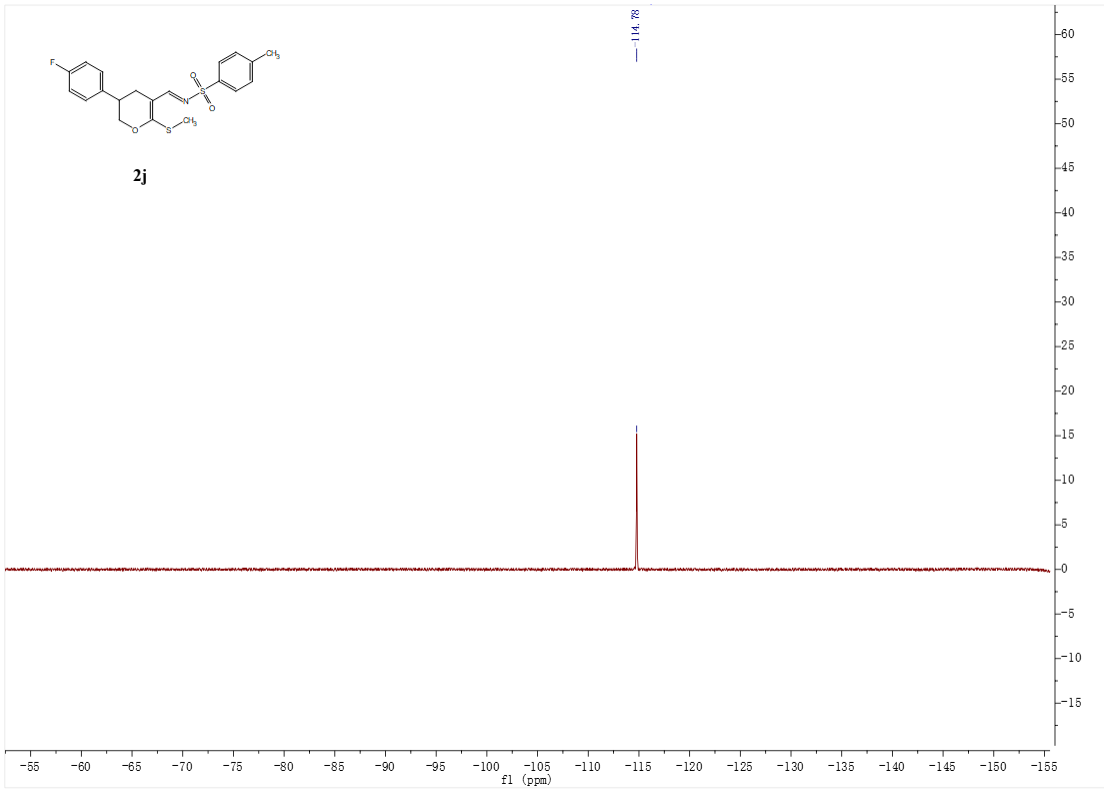


^{19}F NMR (376 MHz, Chloroform-d)



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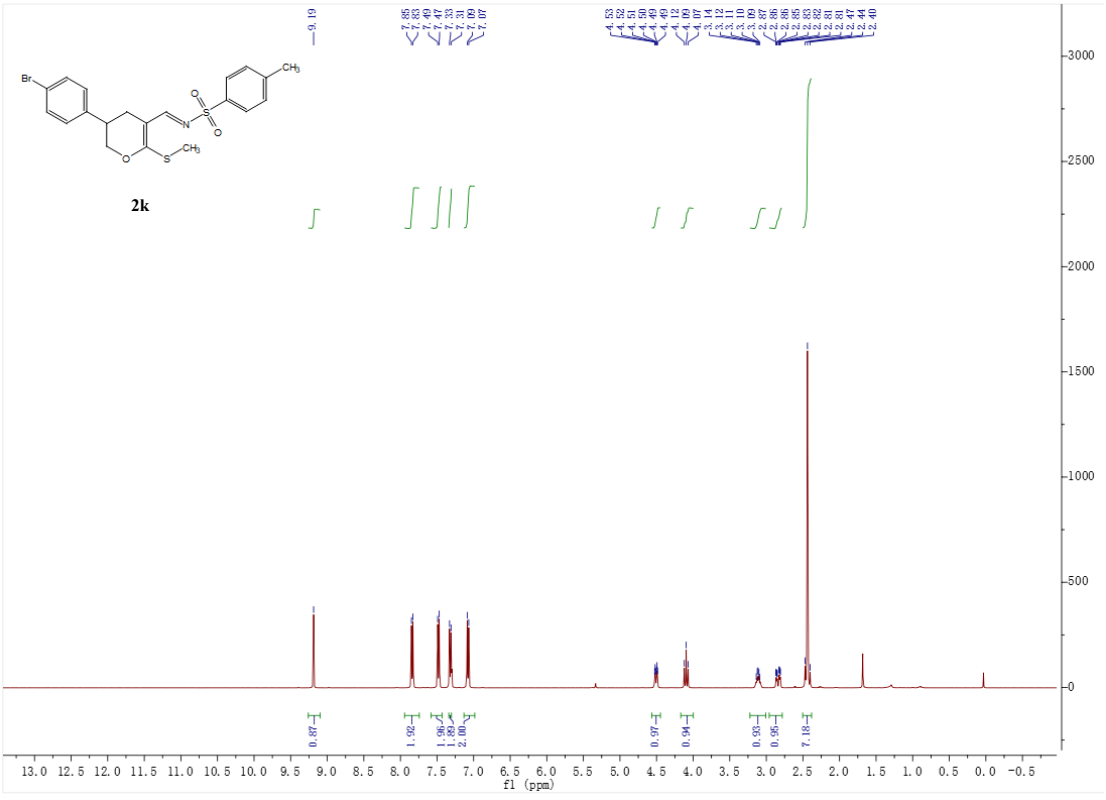

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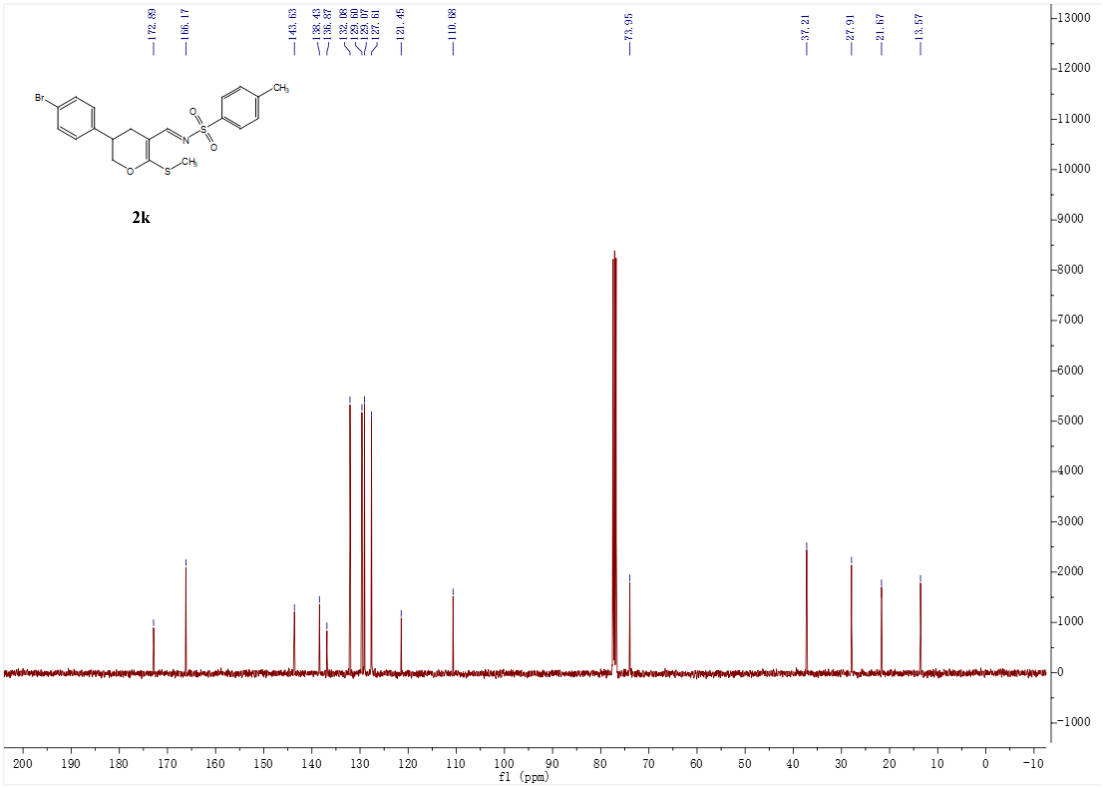
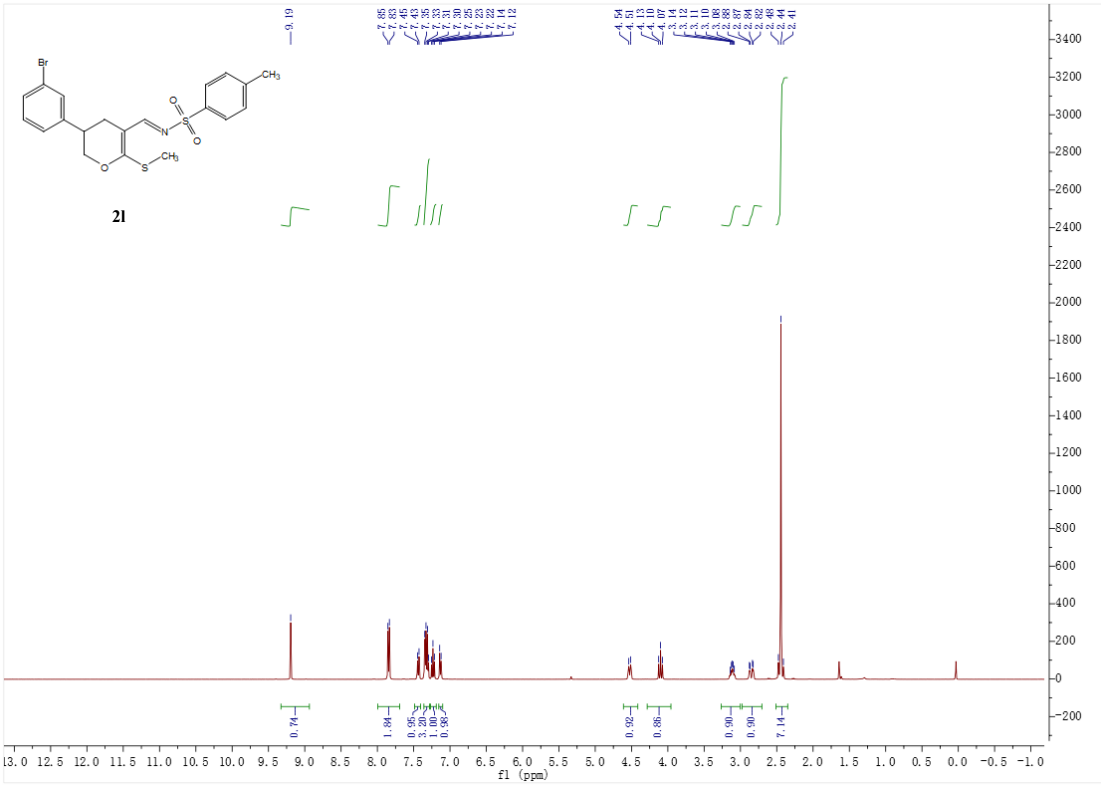
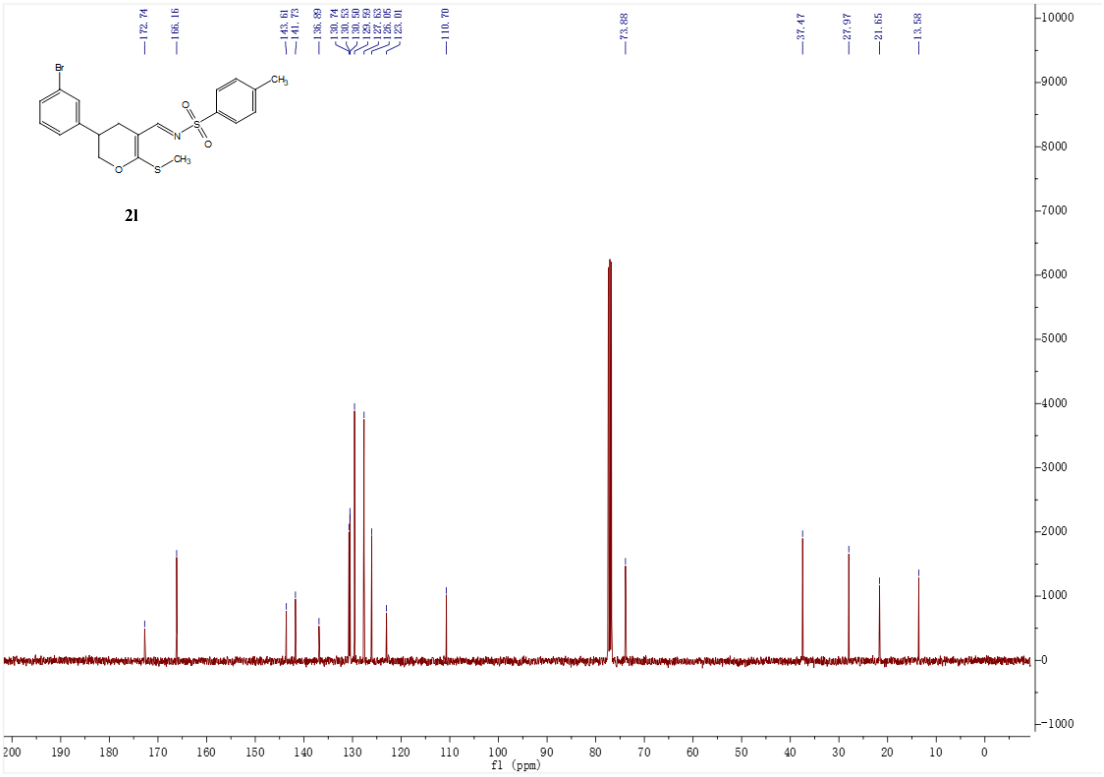


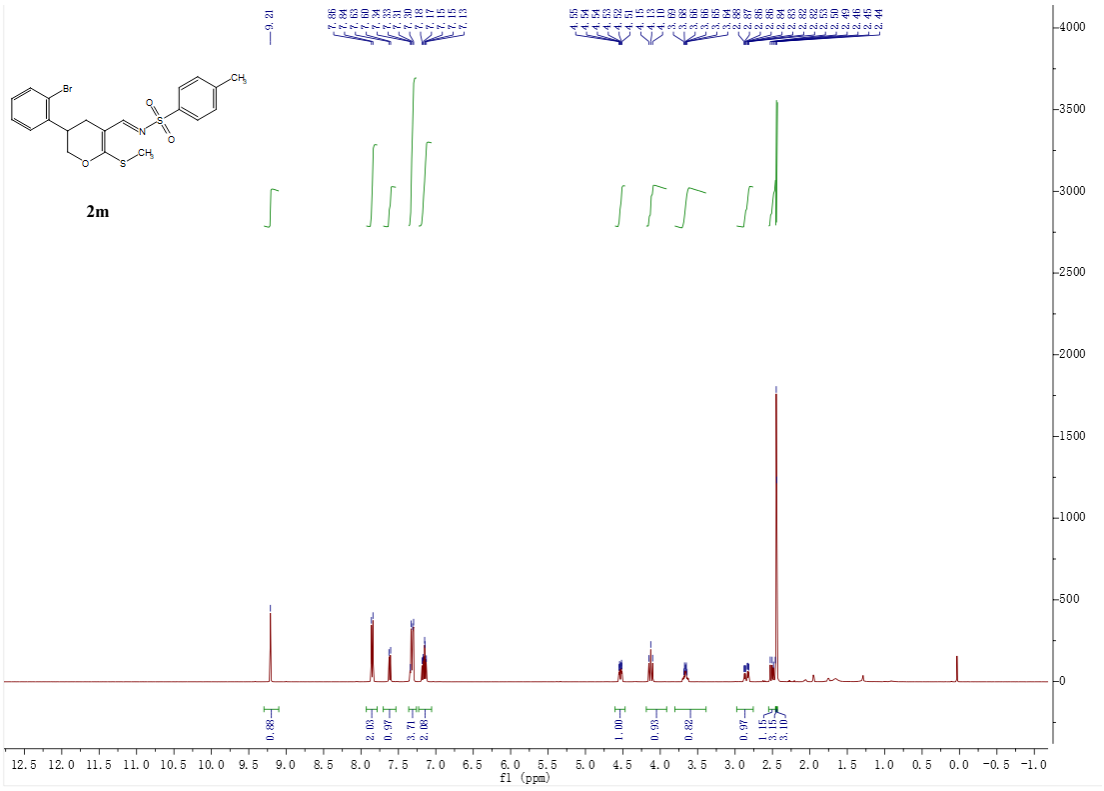
^{1}H NMR (400 MHz, Chloroform-d)



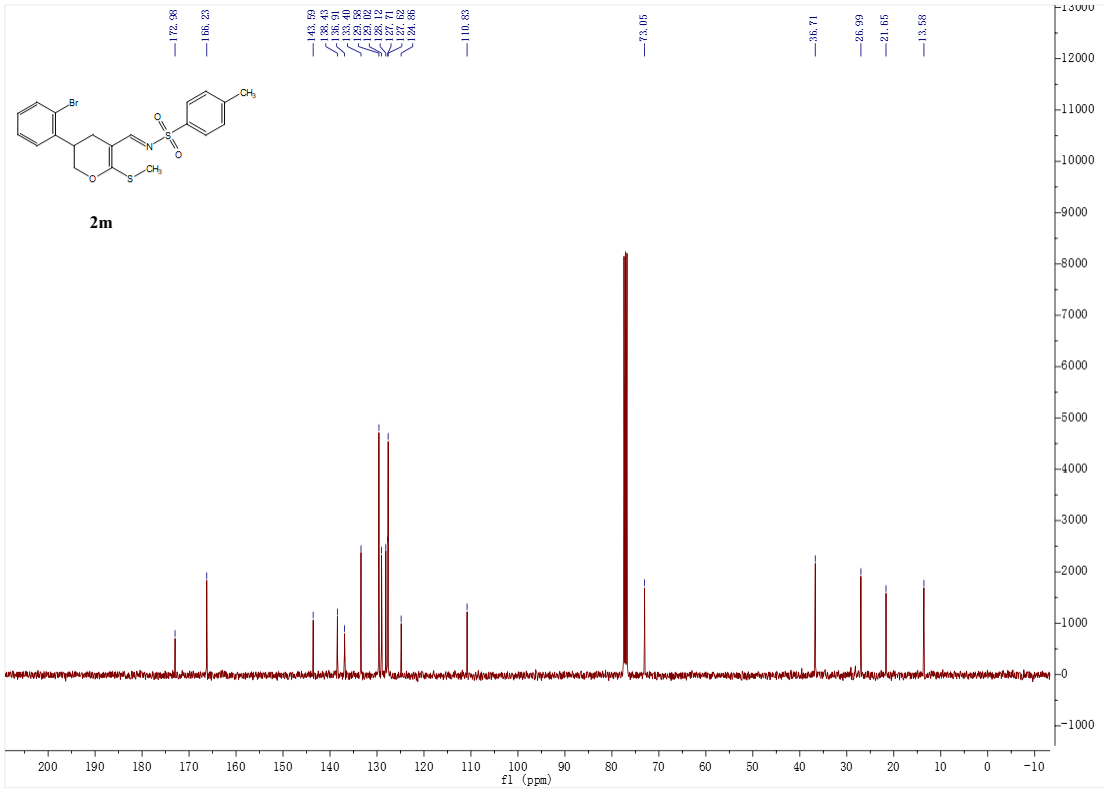
^{13}C NMR (101 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



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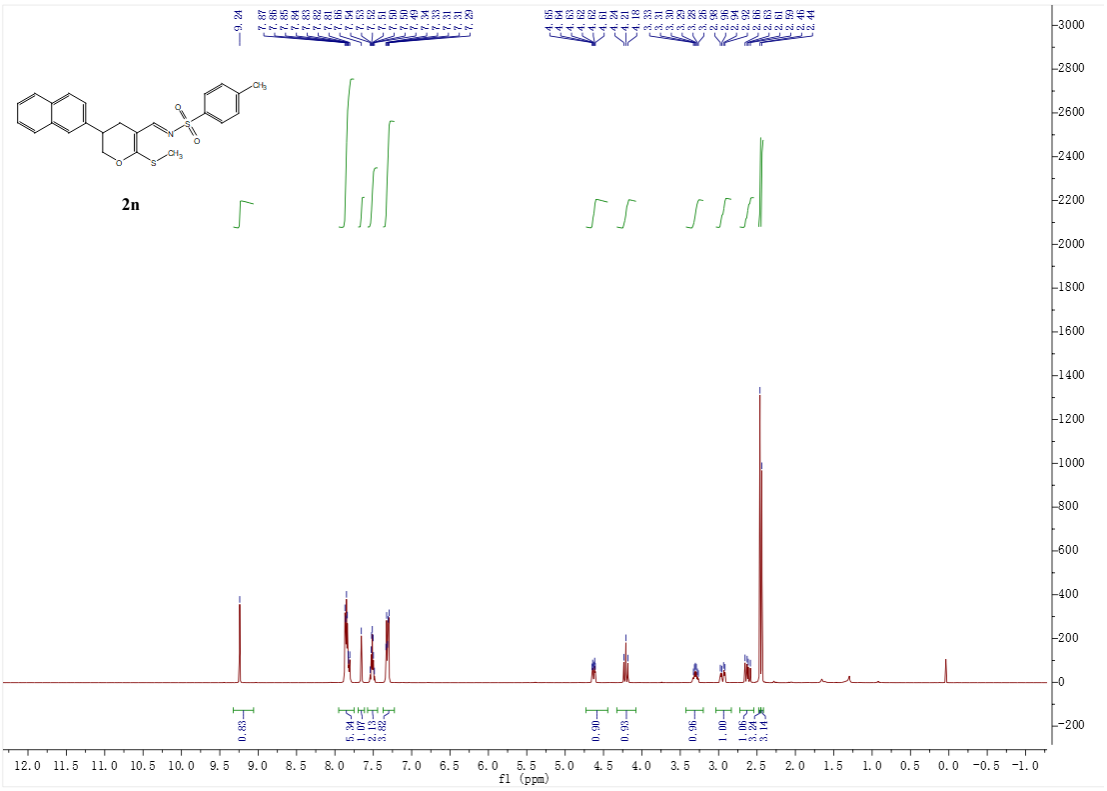
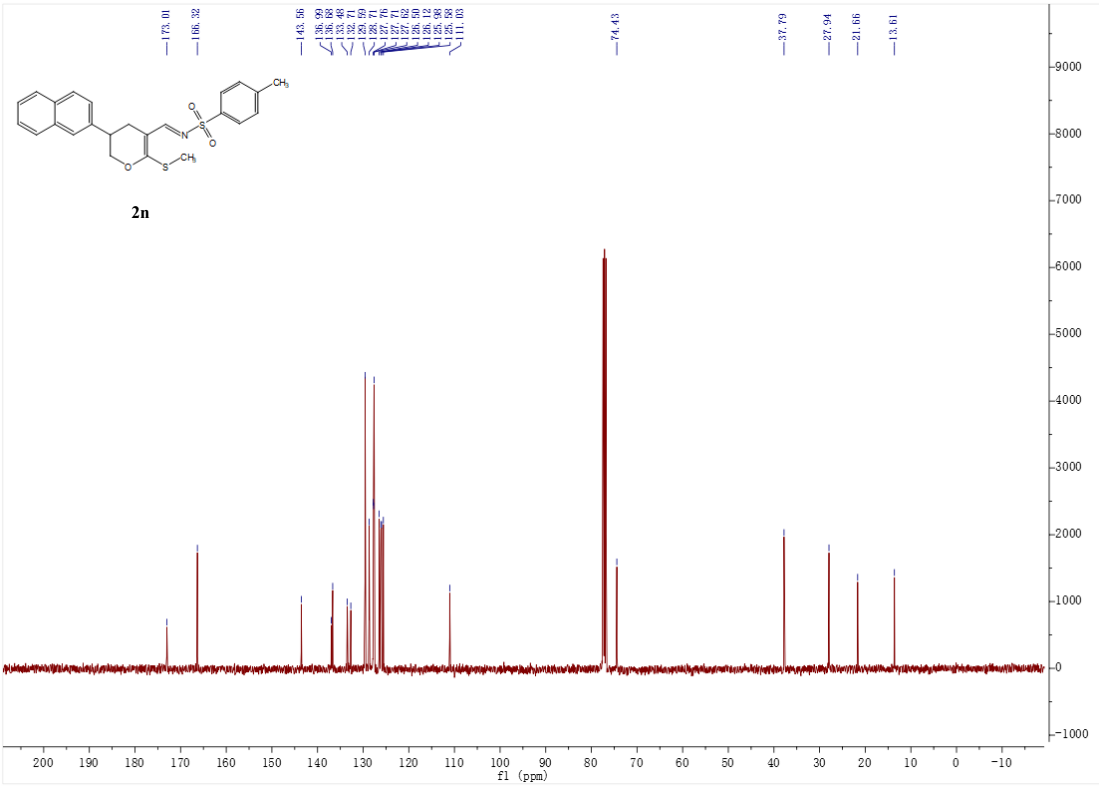
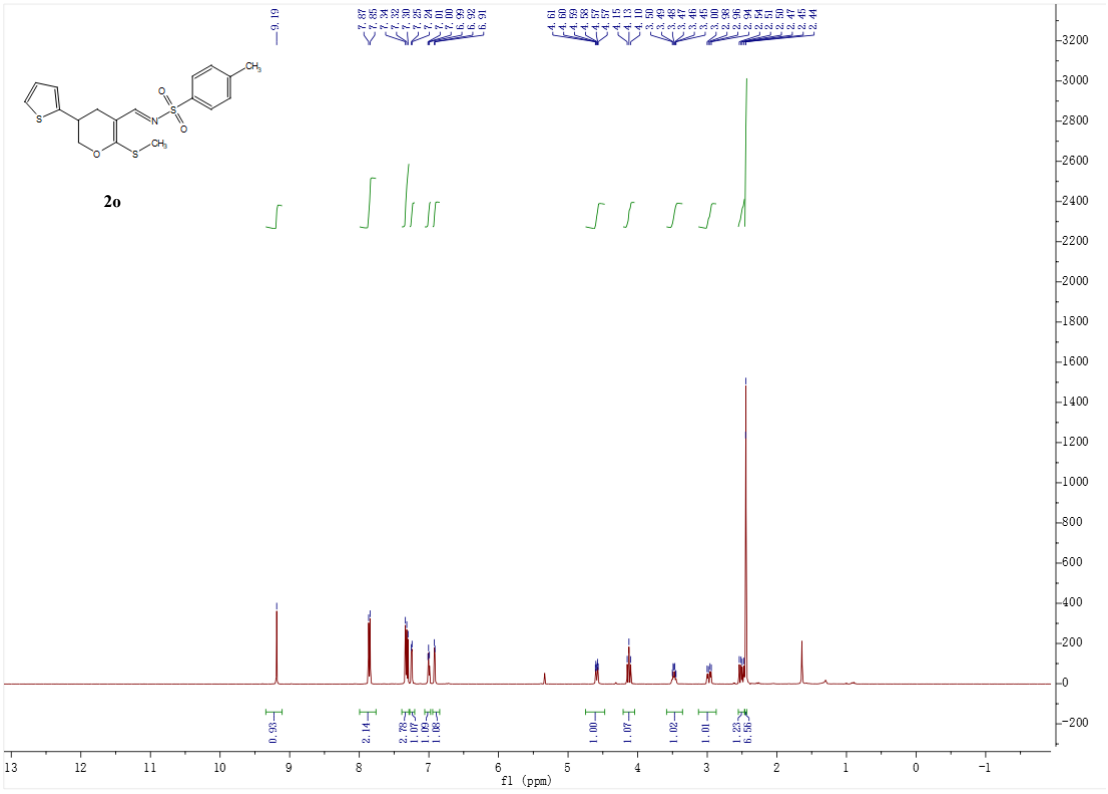


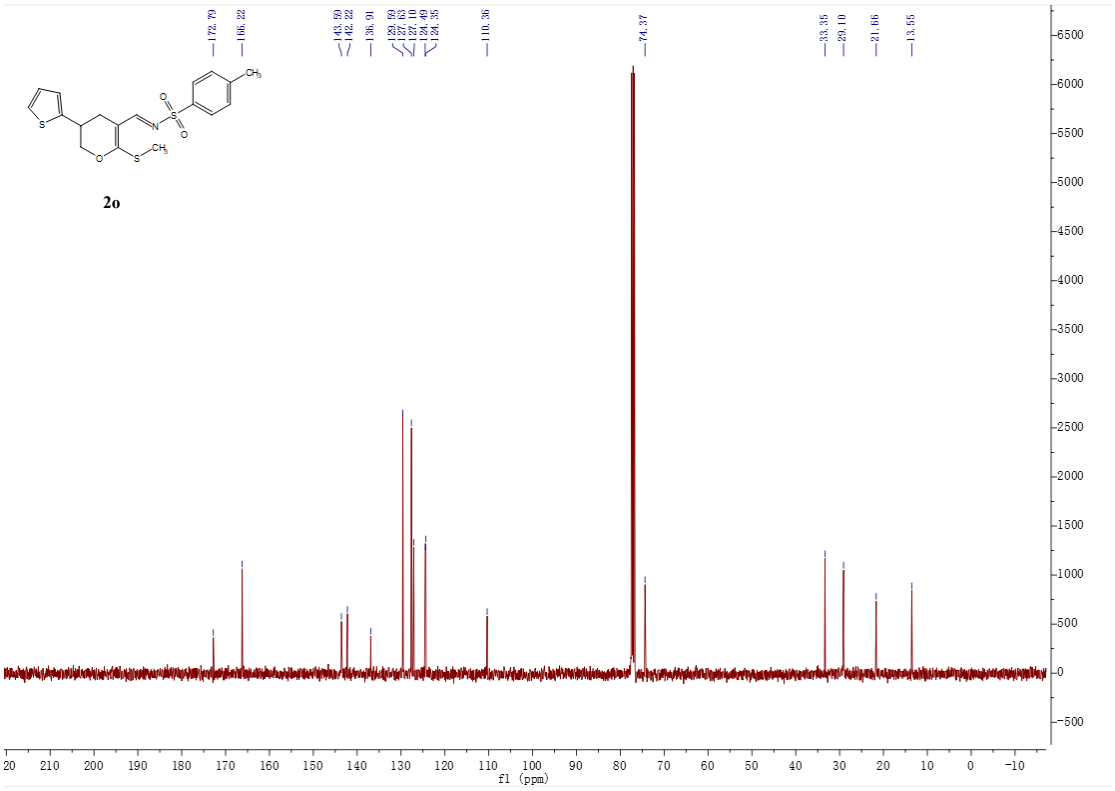
^{13}C NMR (101 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



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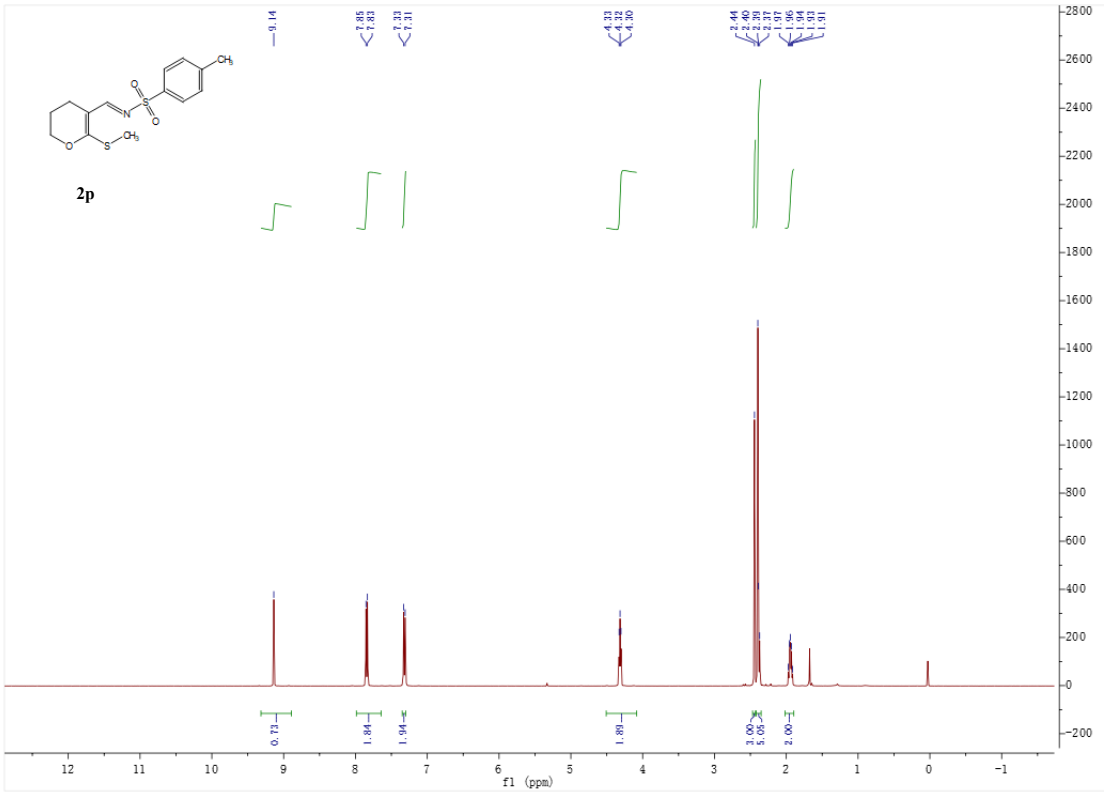

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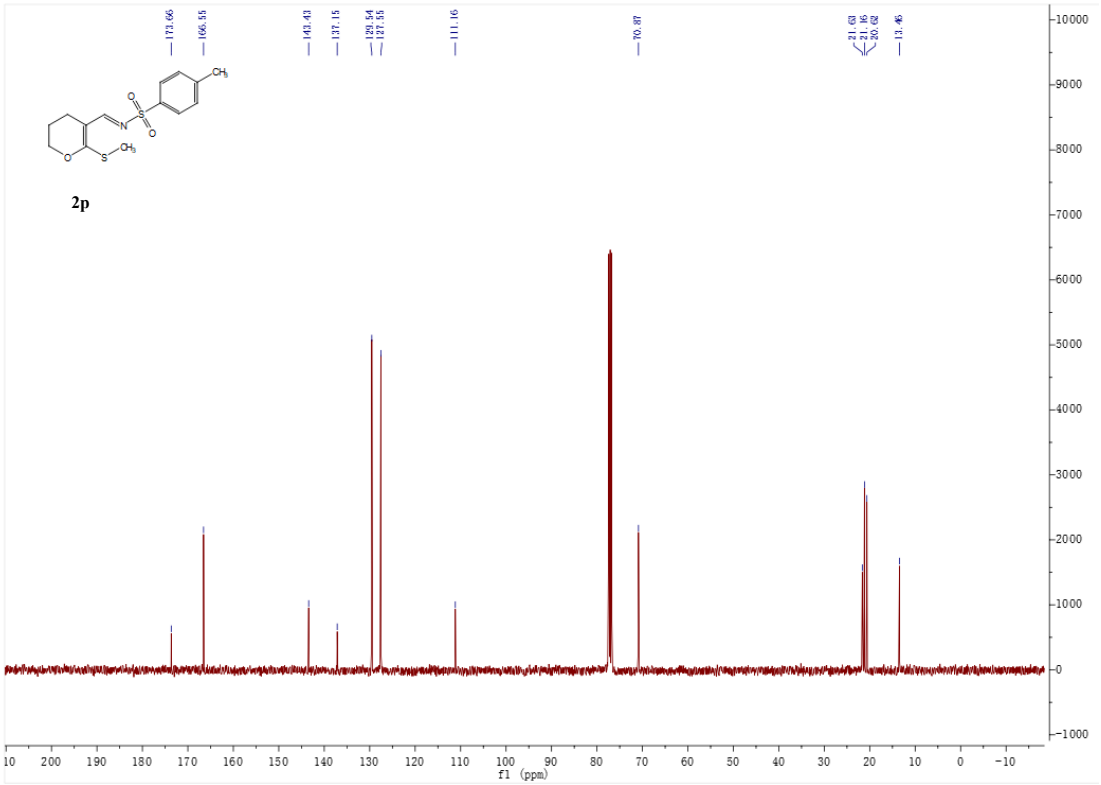

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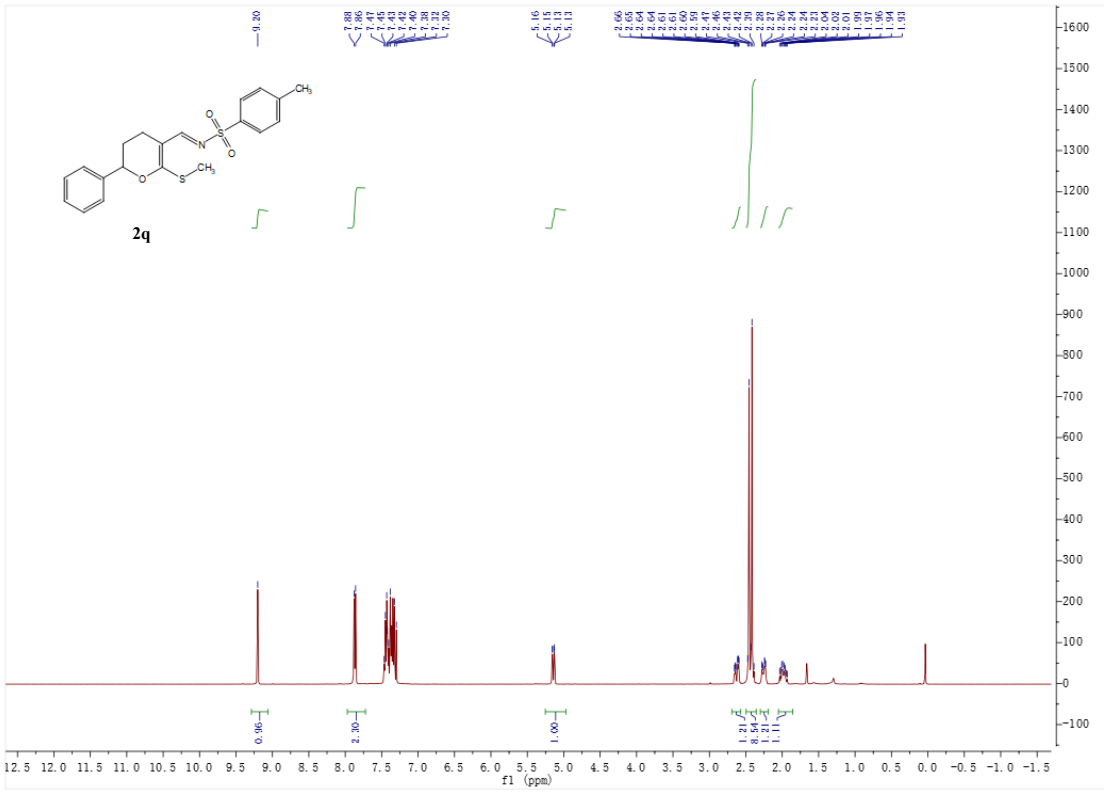

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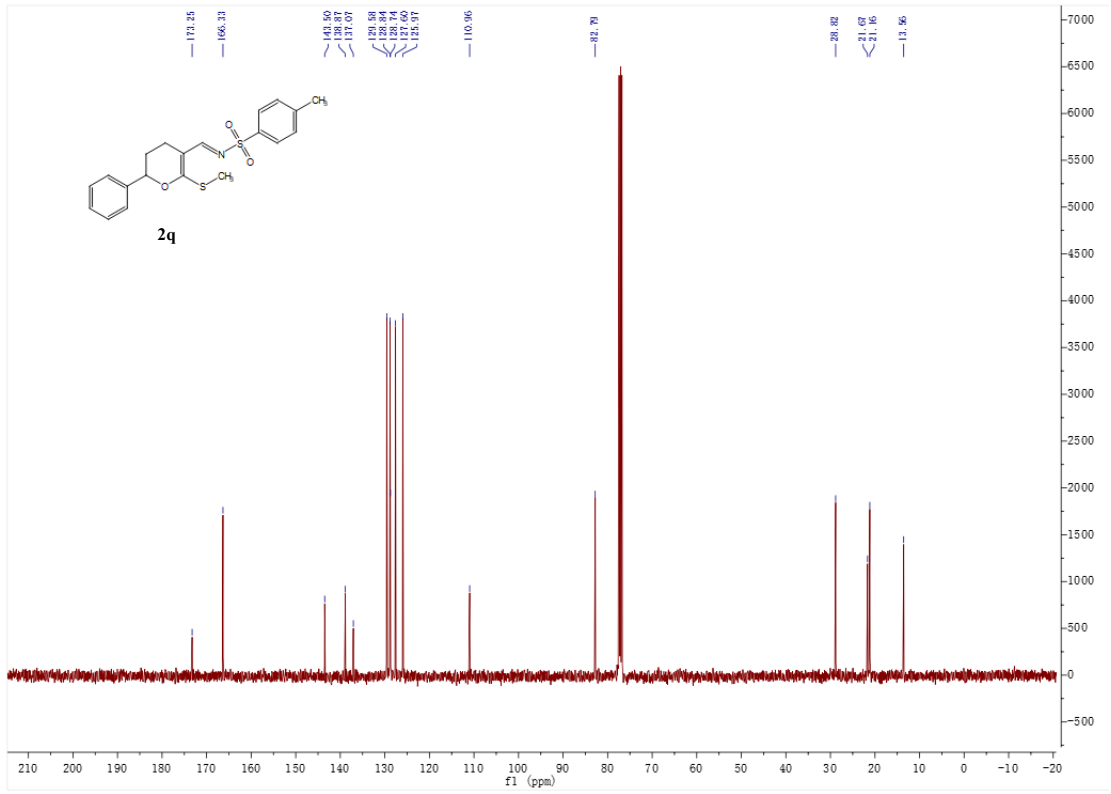

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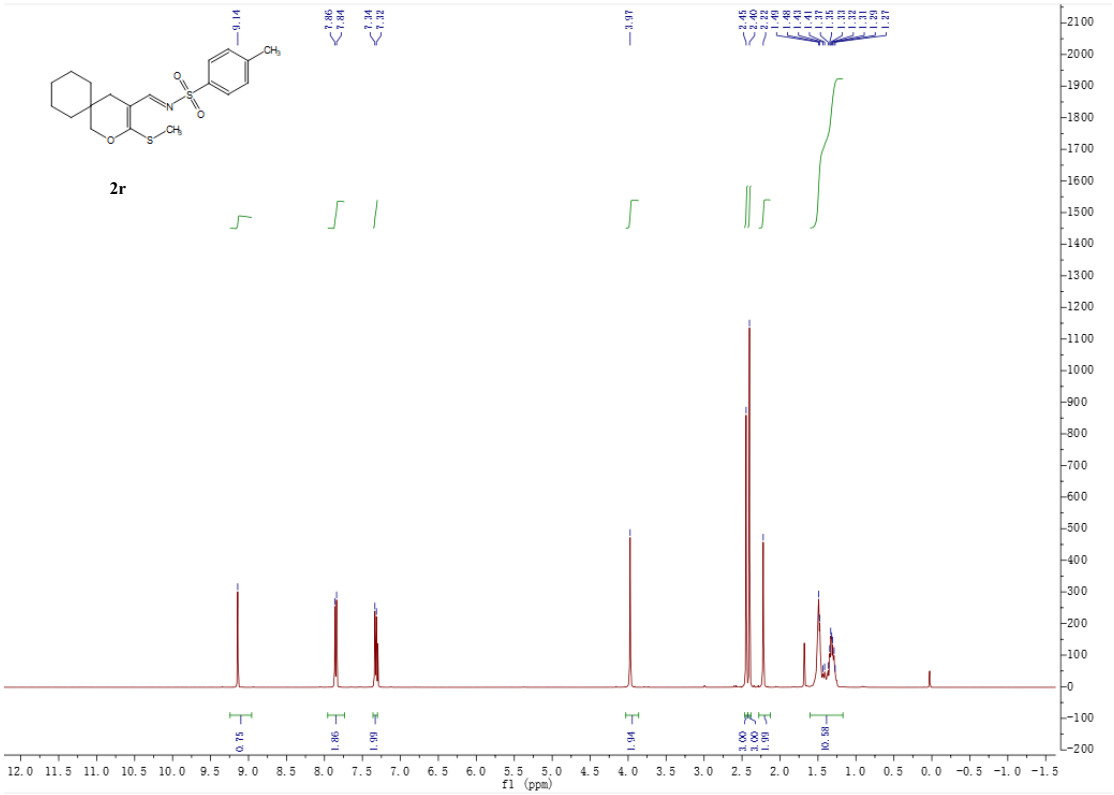

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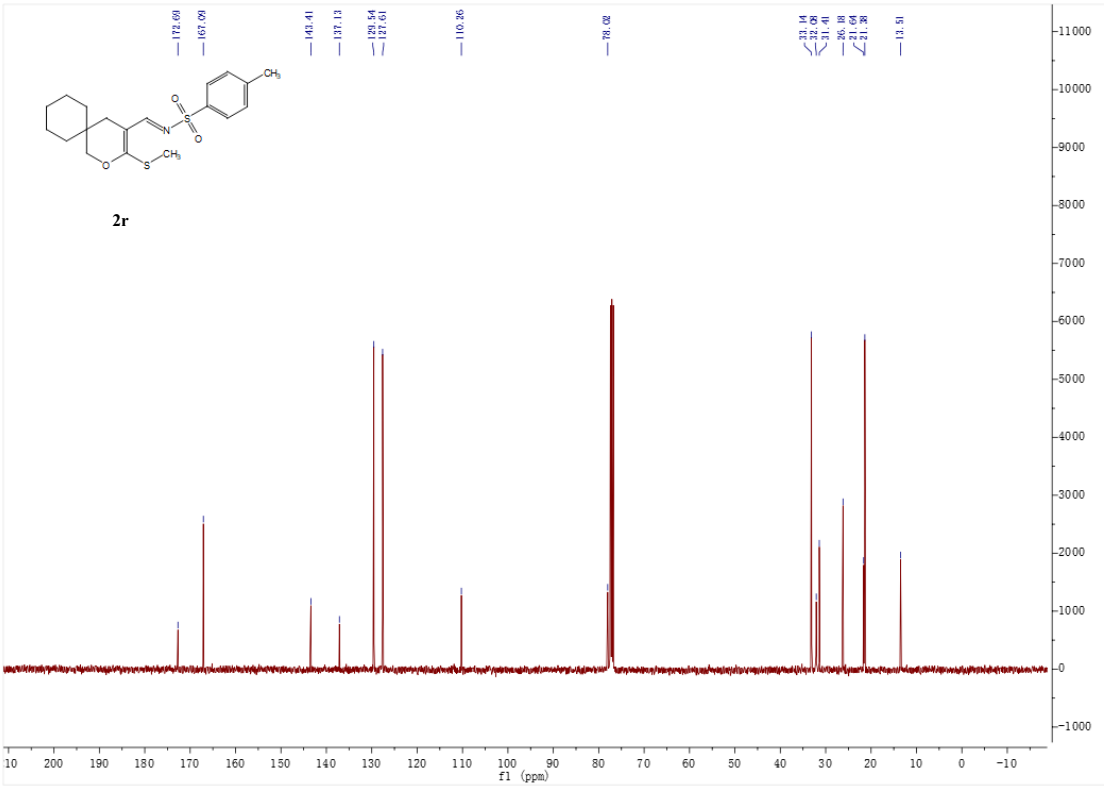

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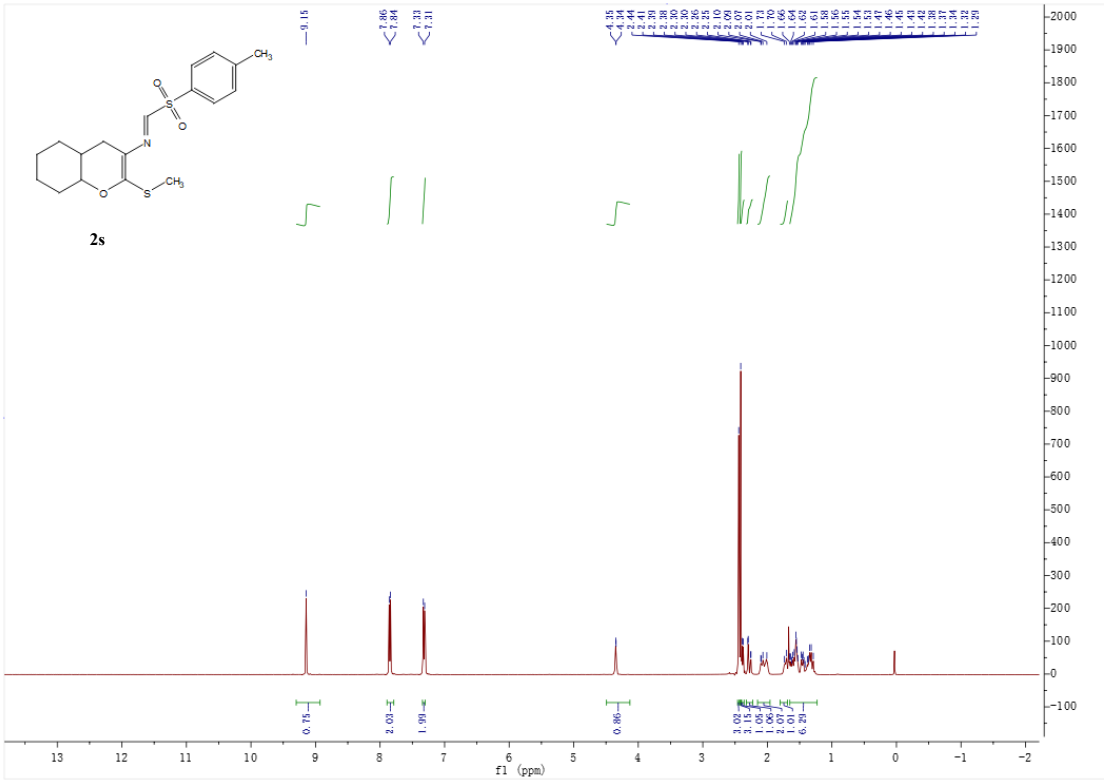
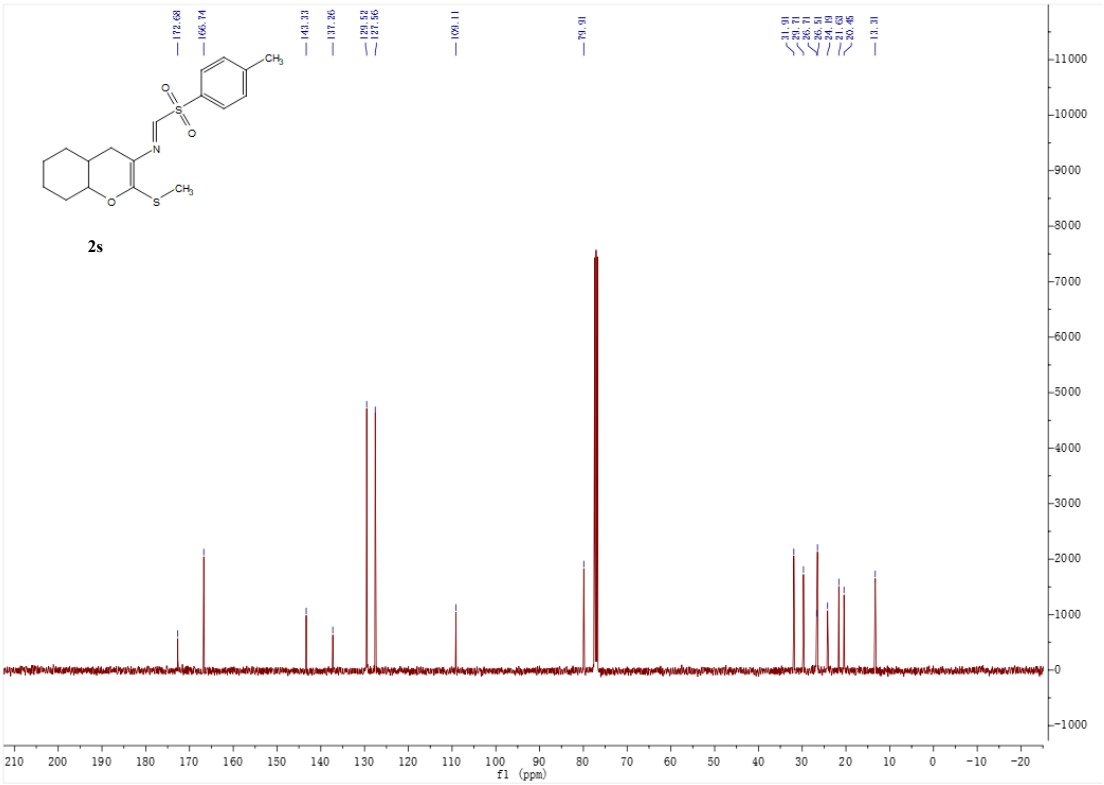


^{13}C NMR (101 MHz, Chloroform-d)



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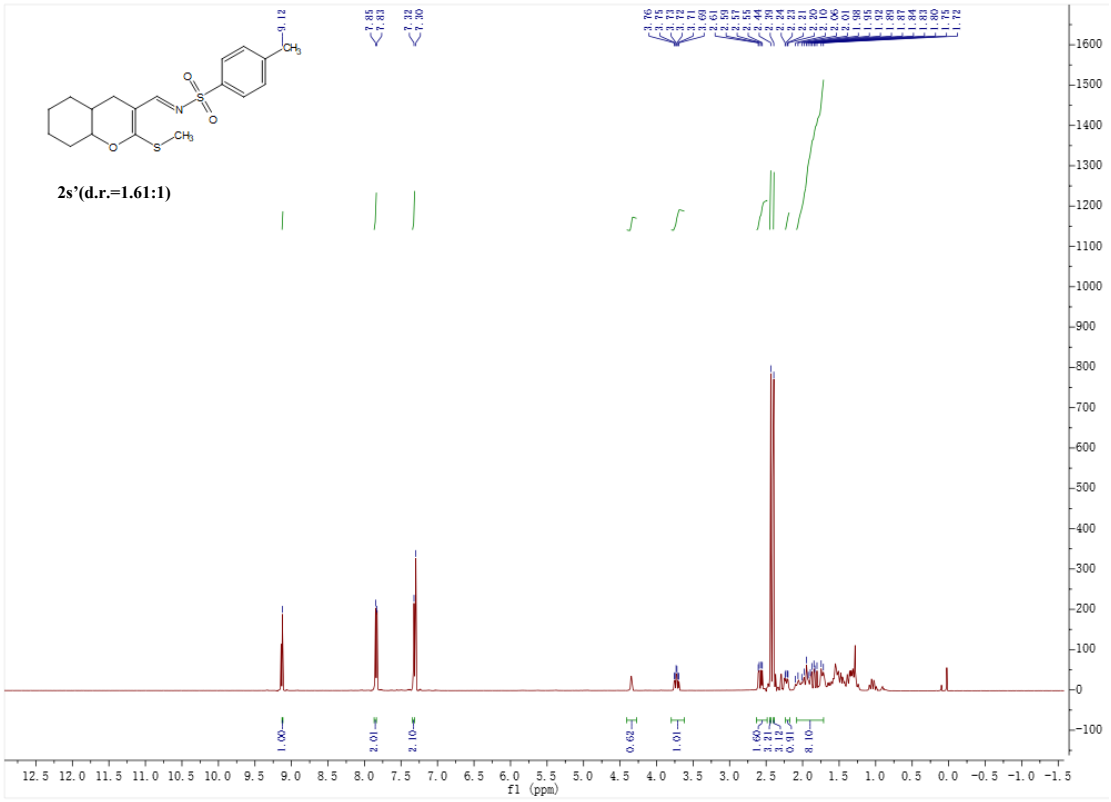

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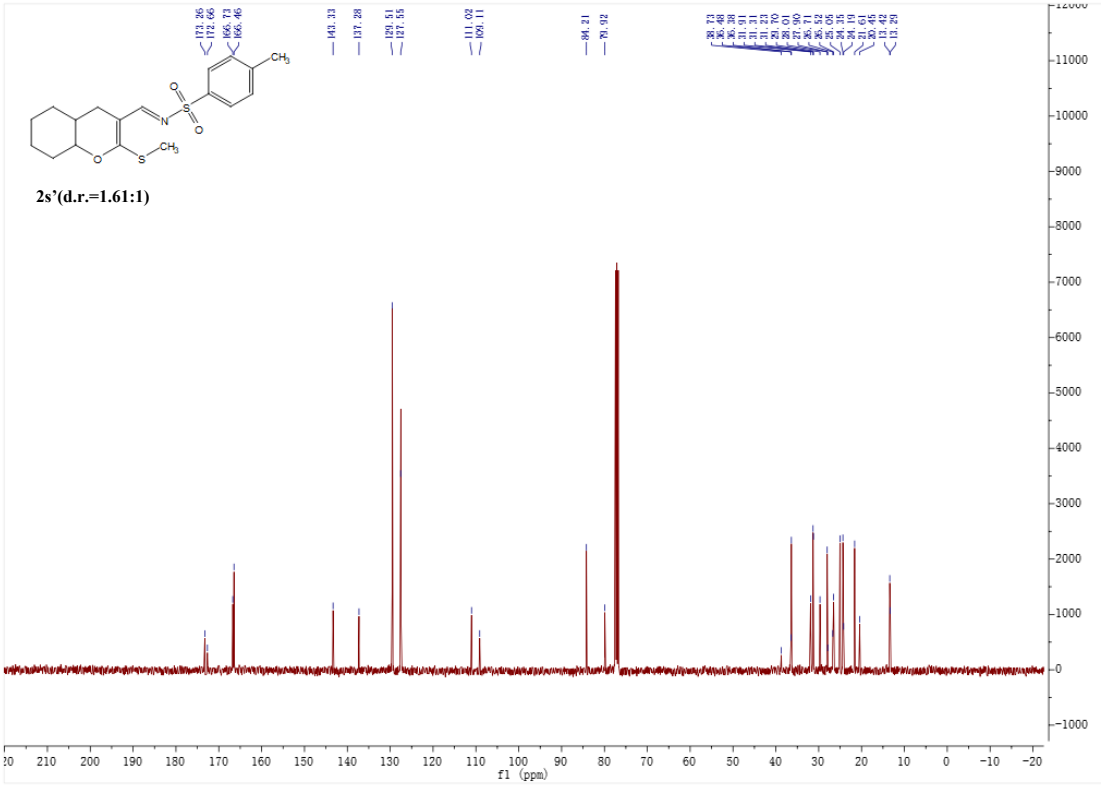

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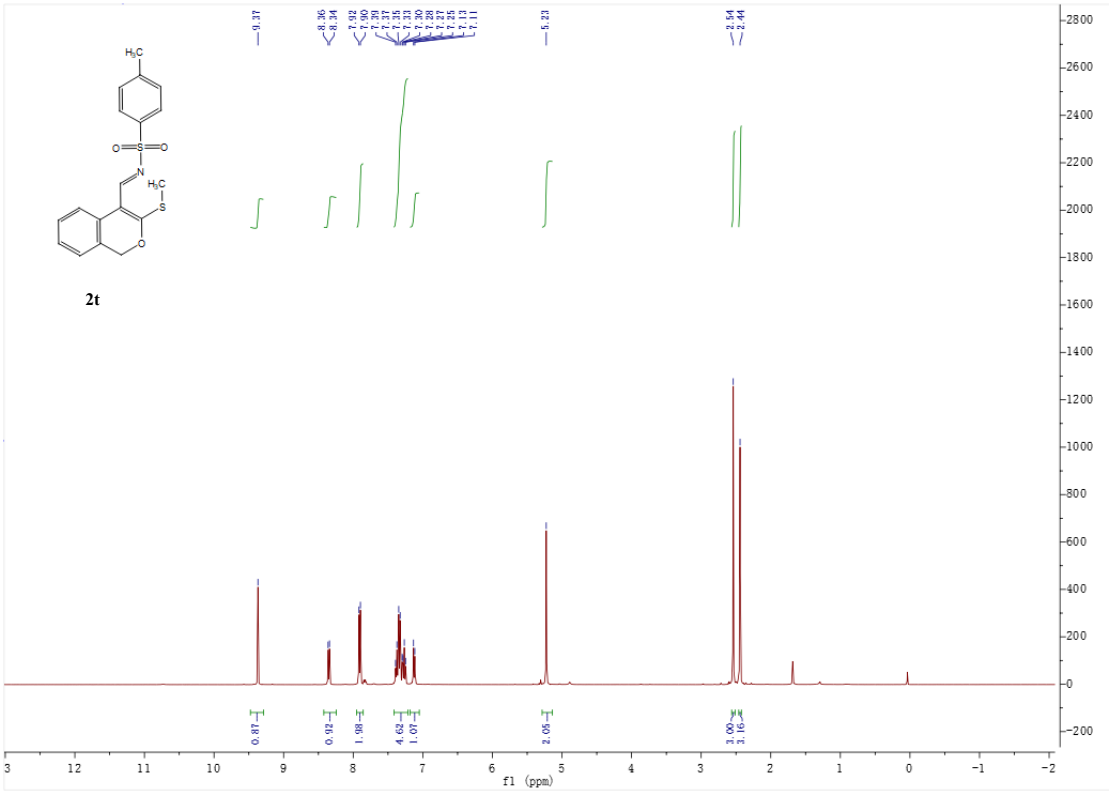

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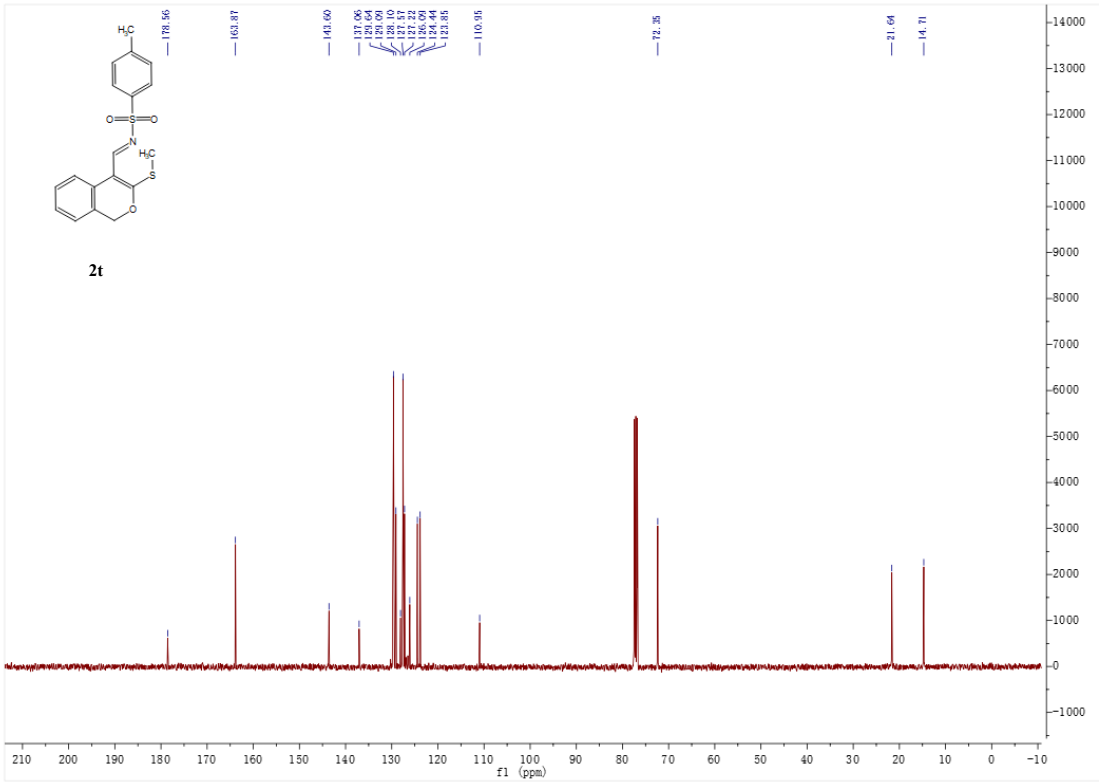

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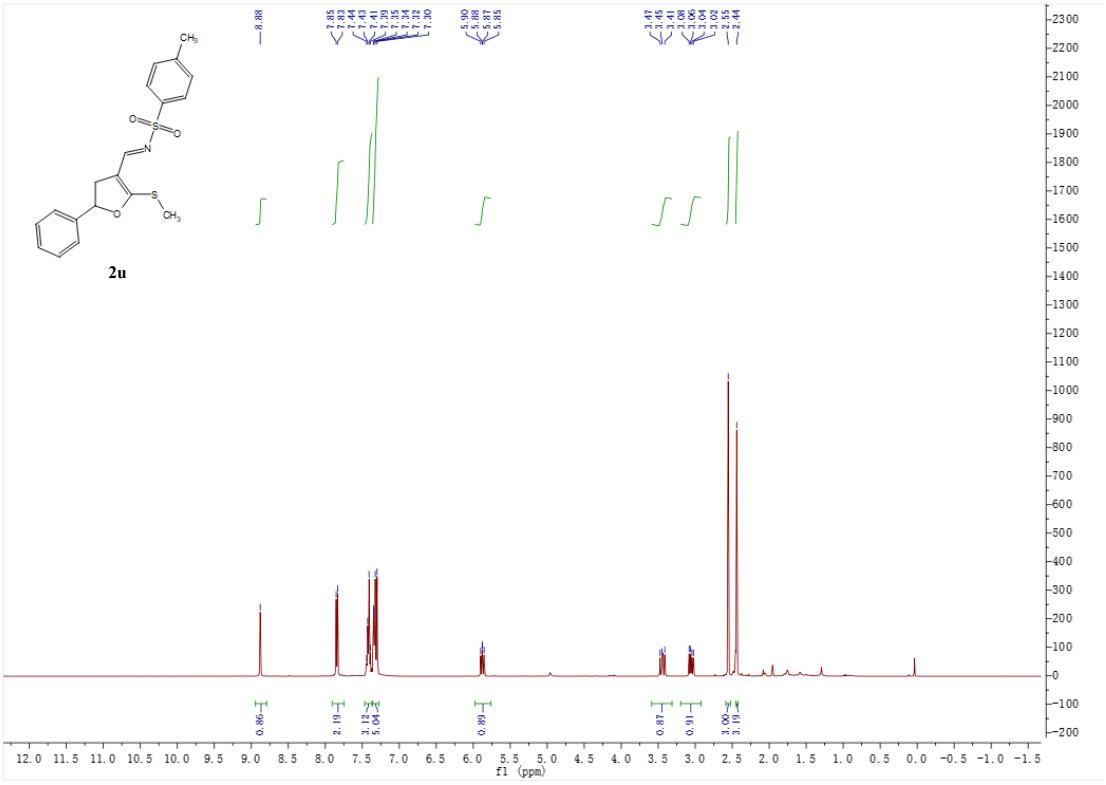

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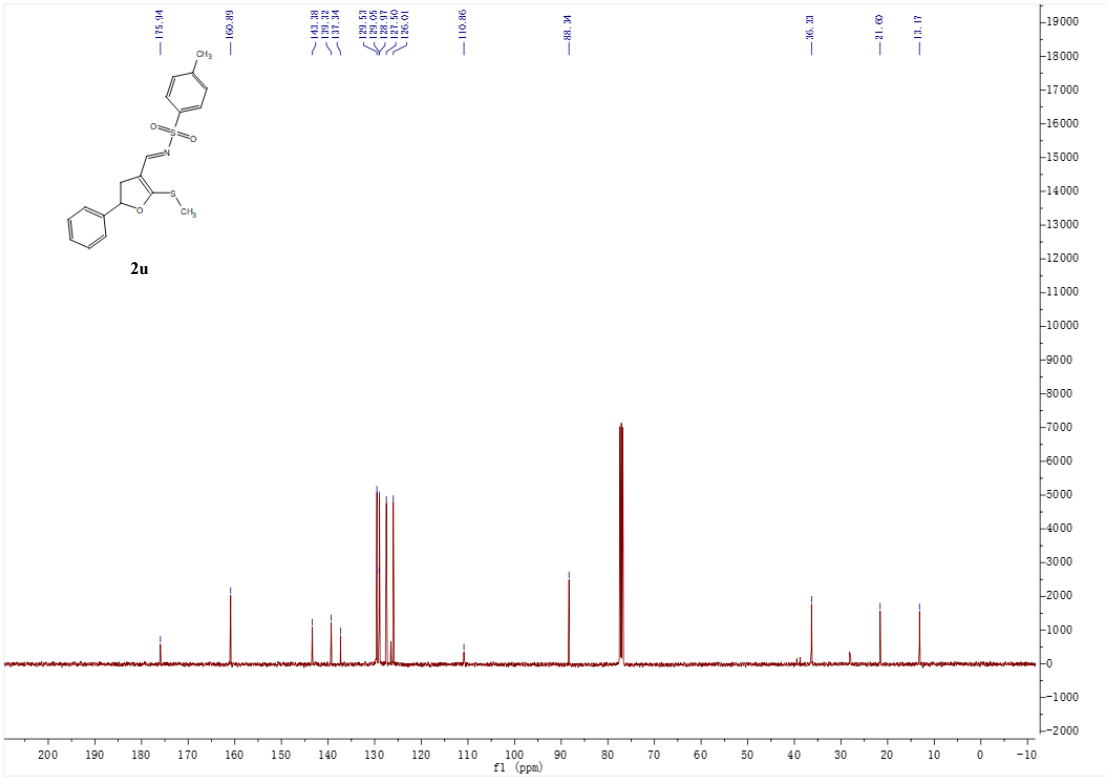

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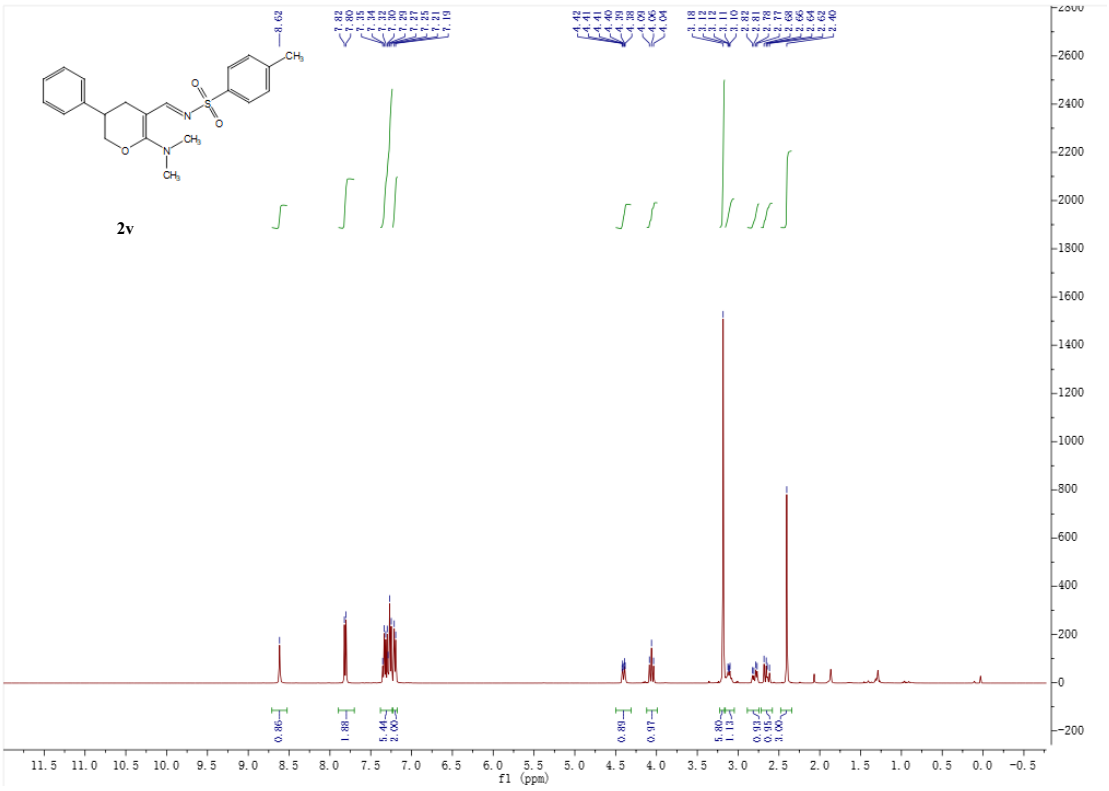

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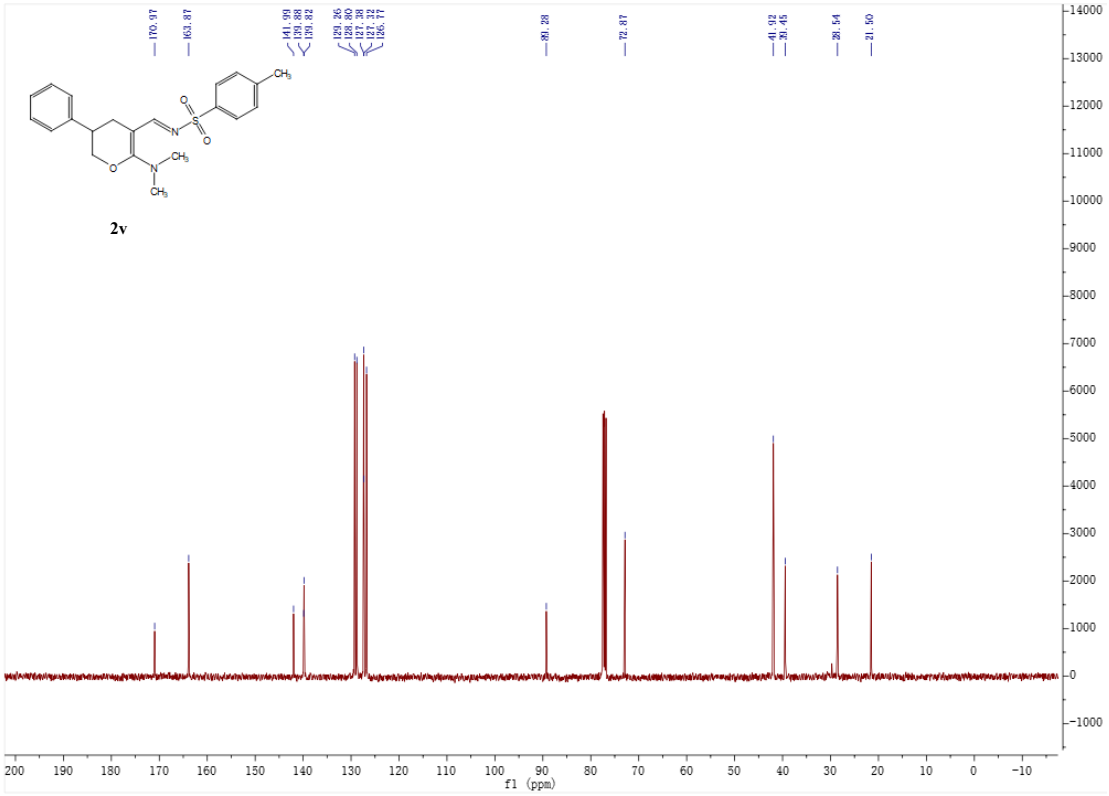

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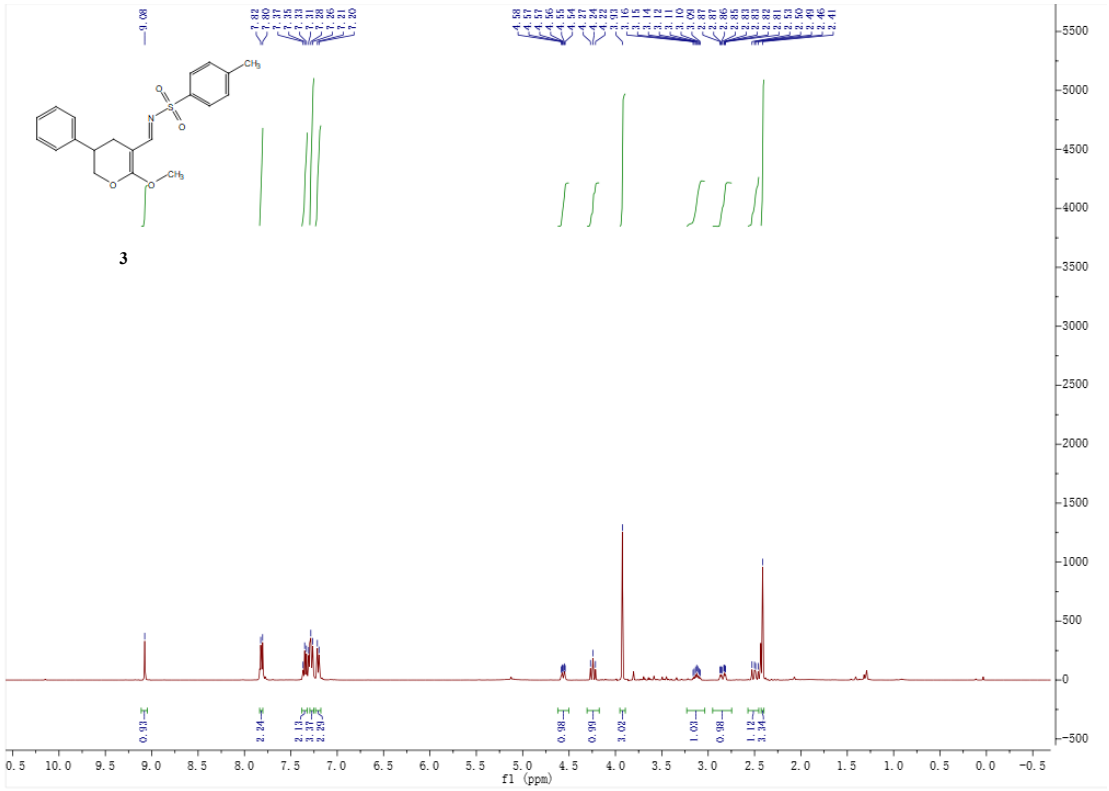

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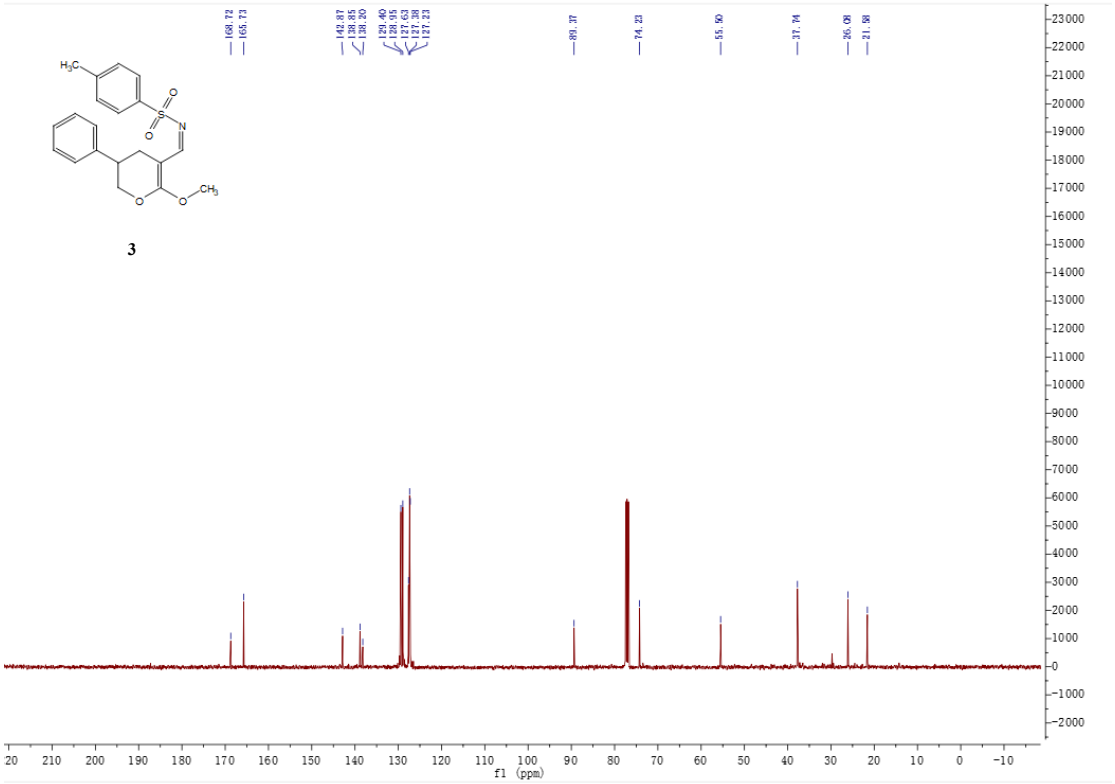

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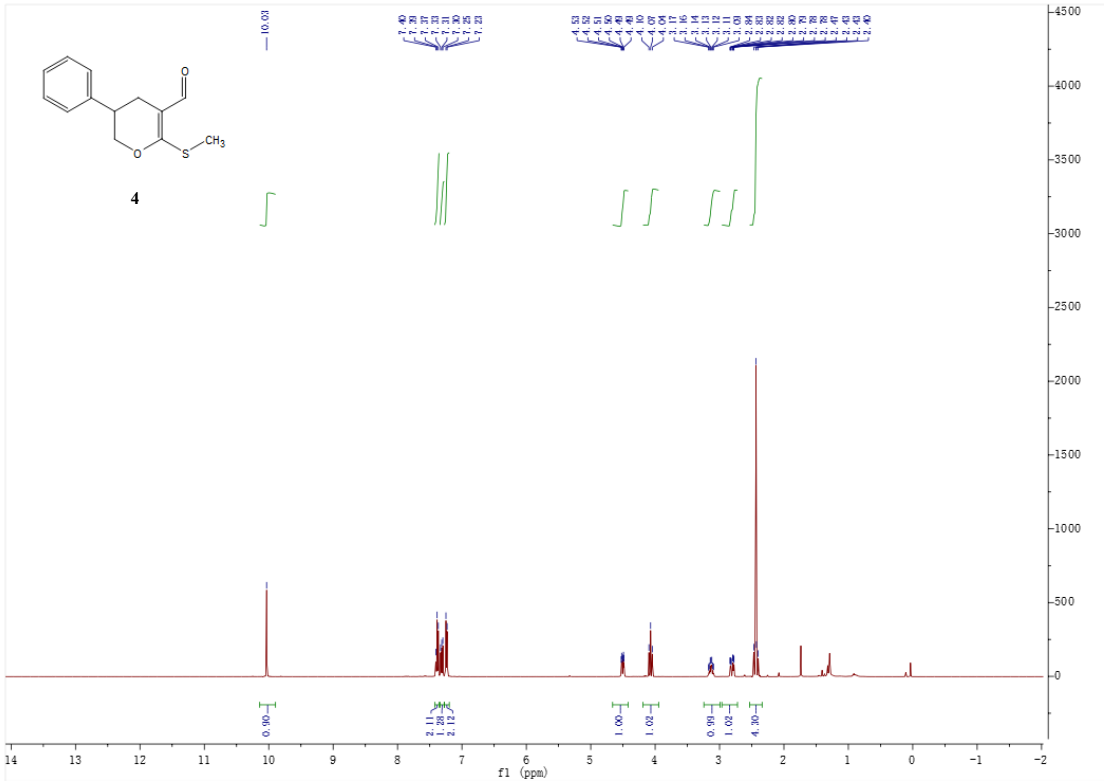

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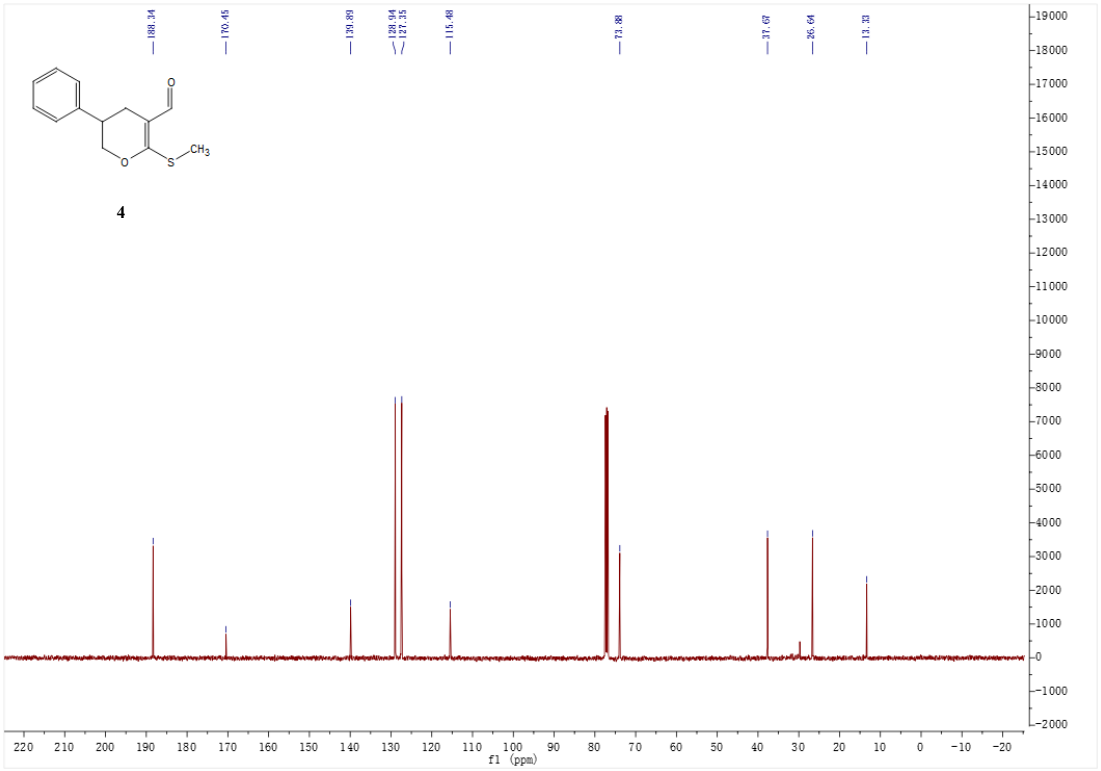

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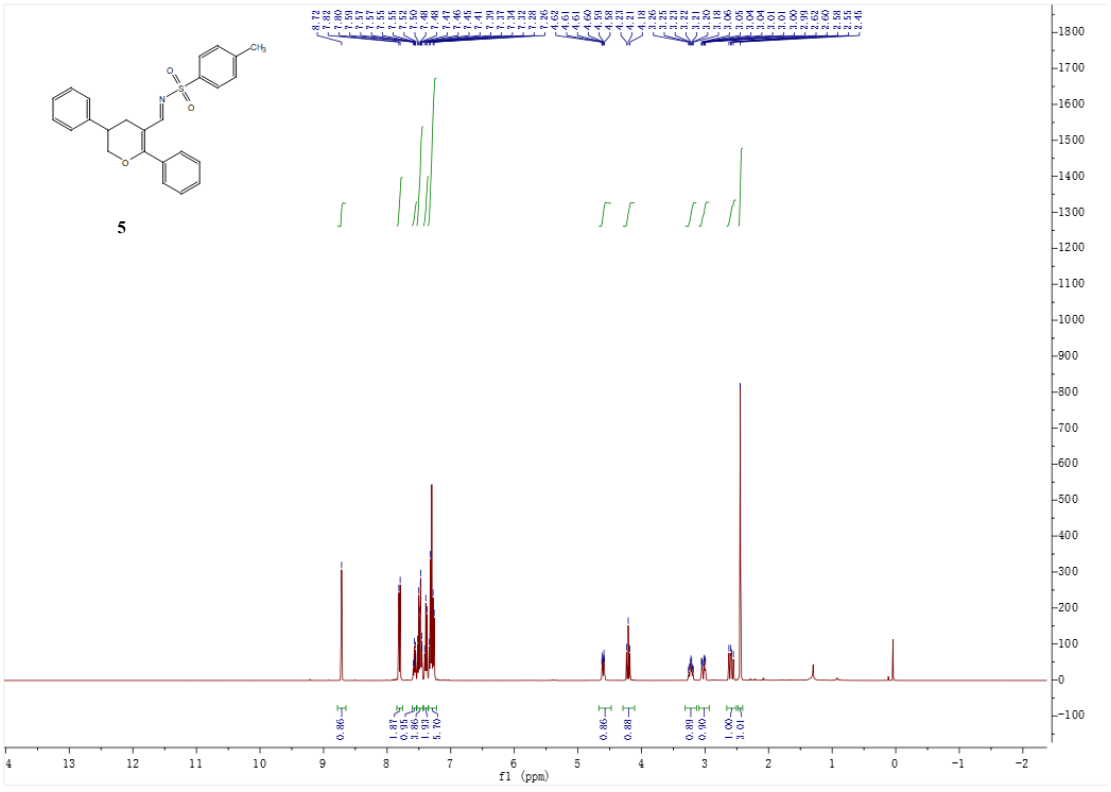

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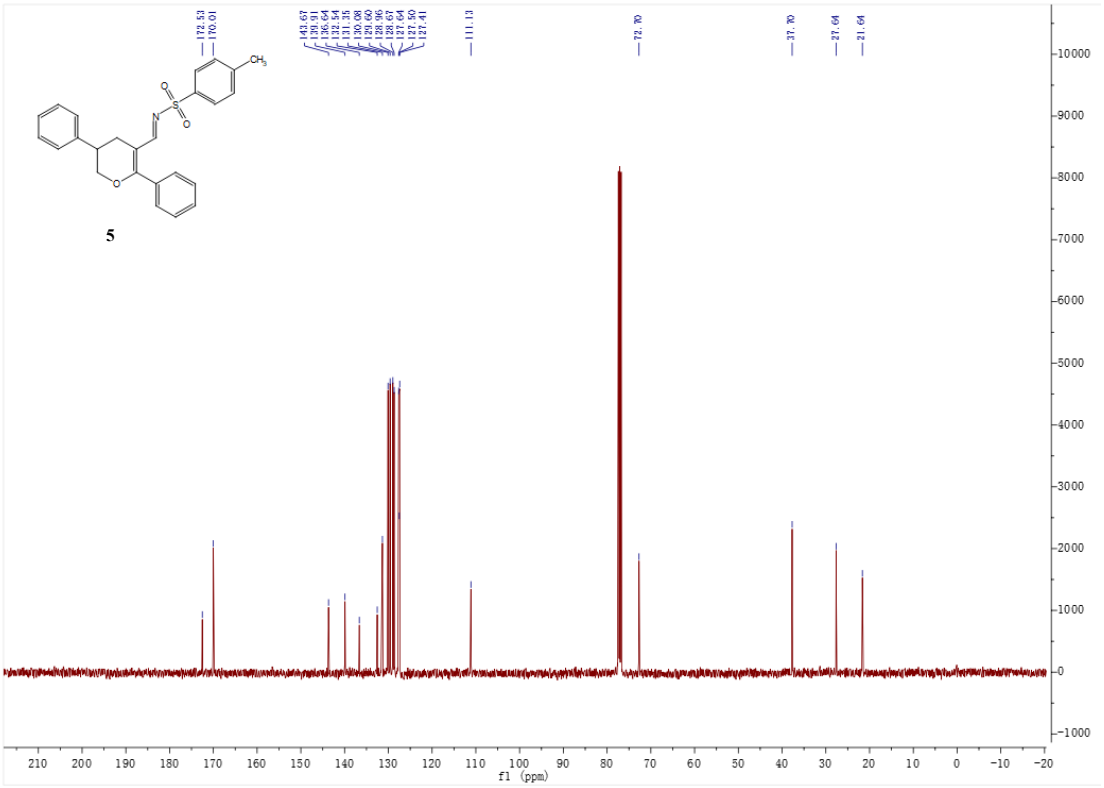

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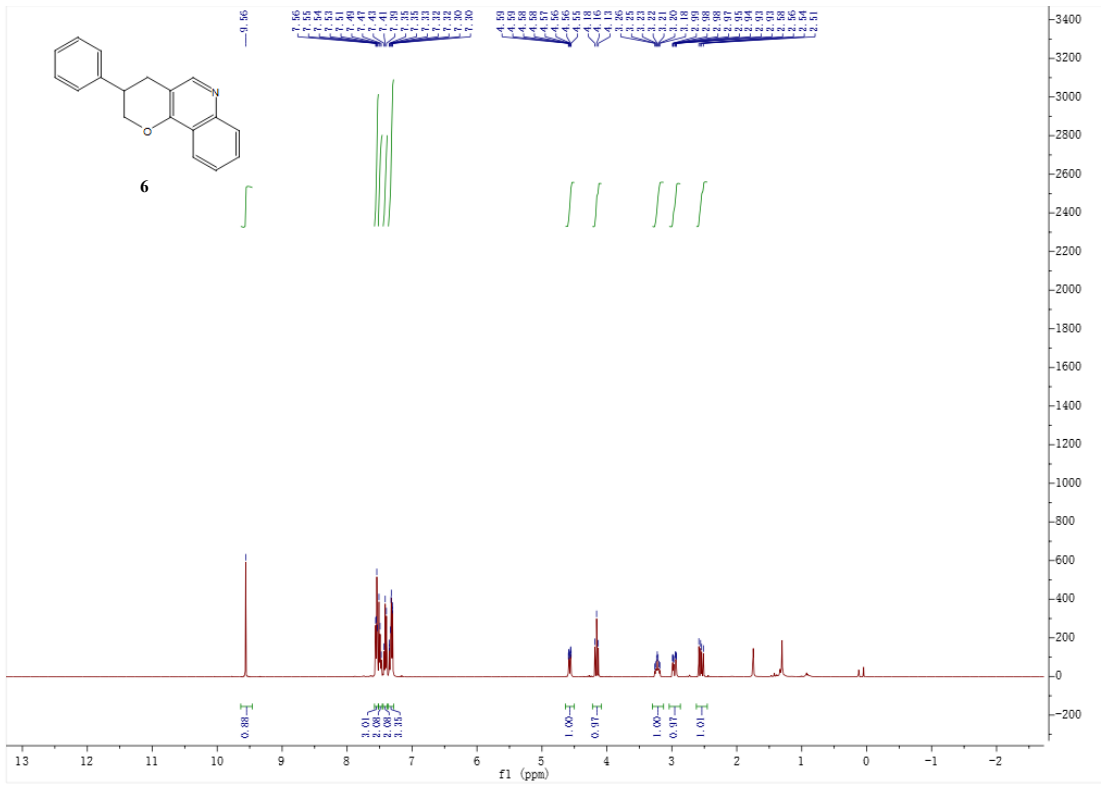

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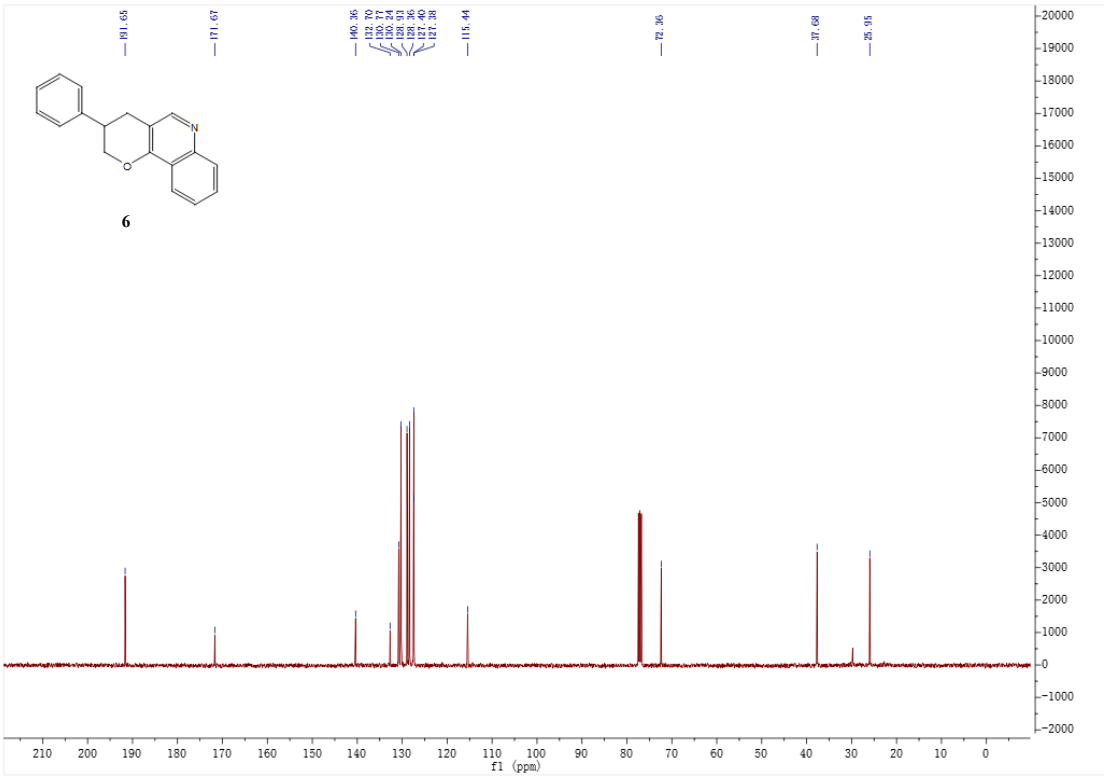

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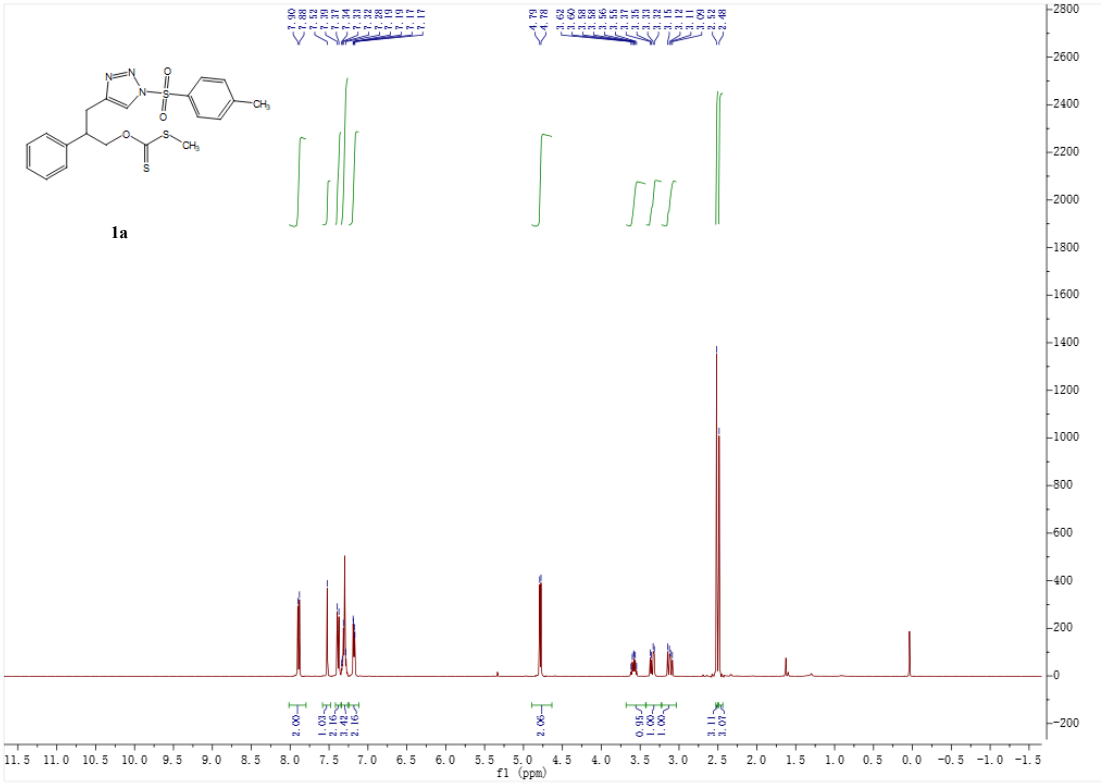

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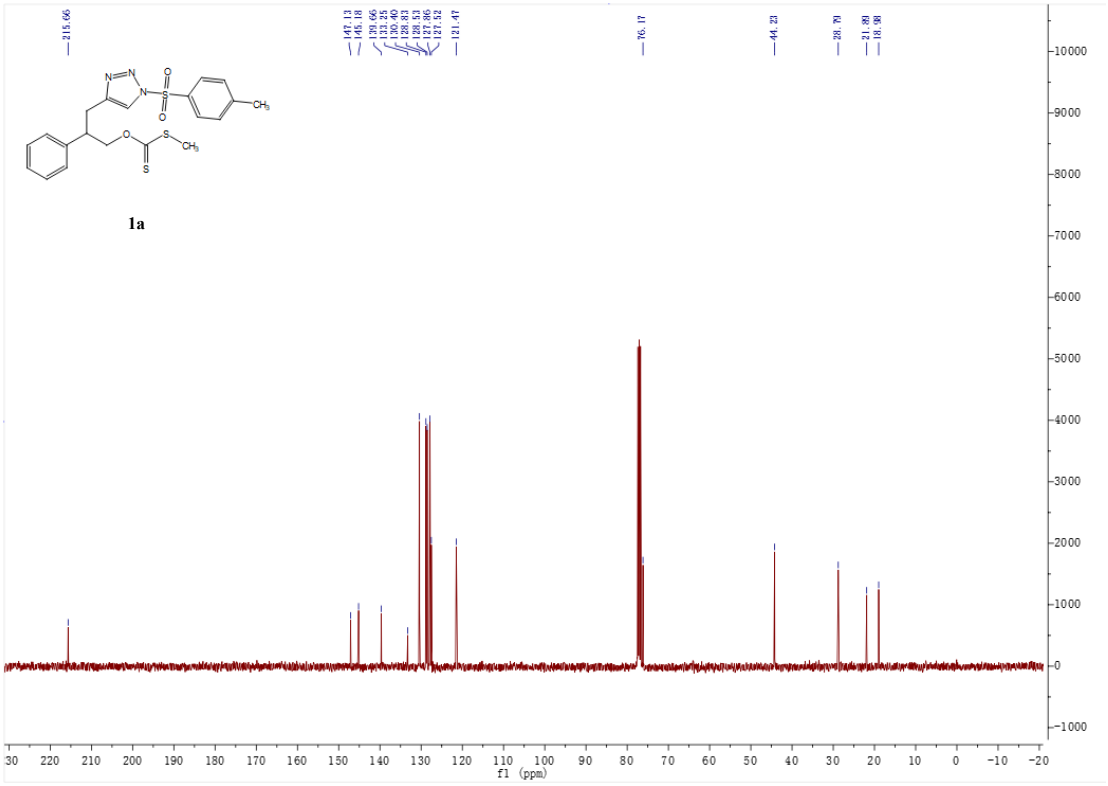

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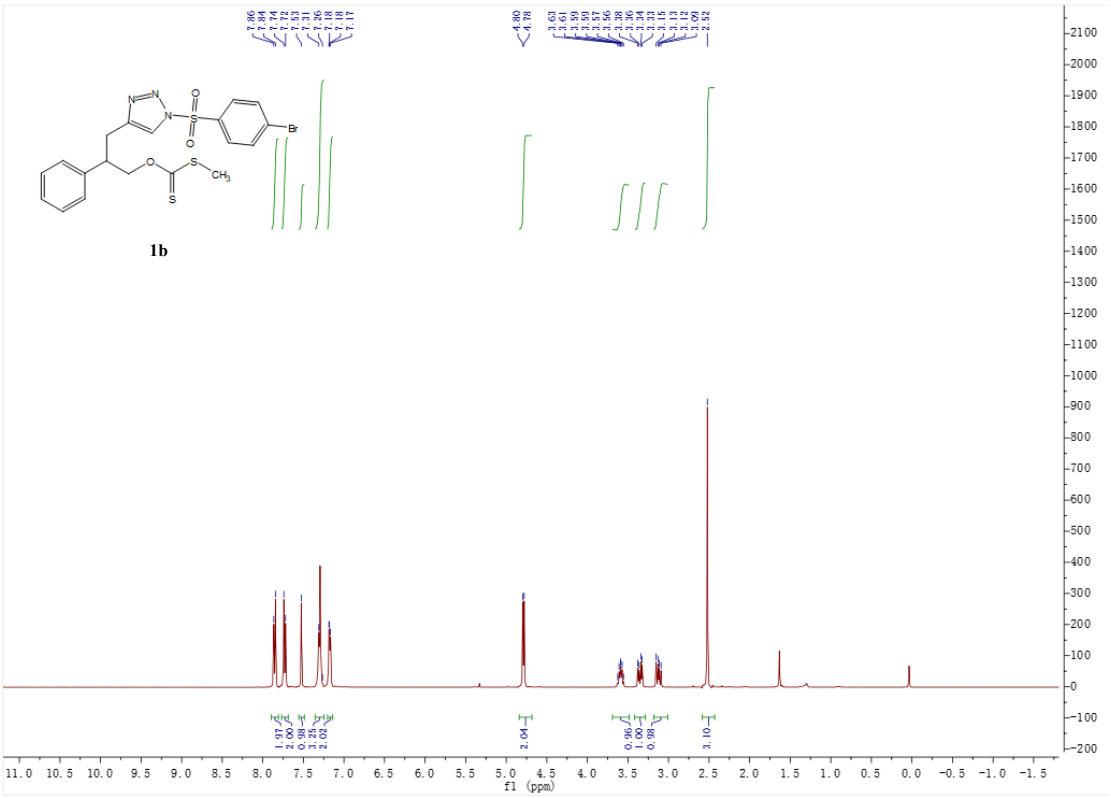

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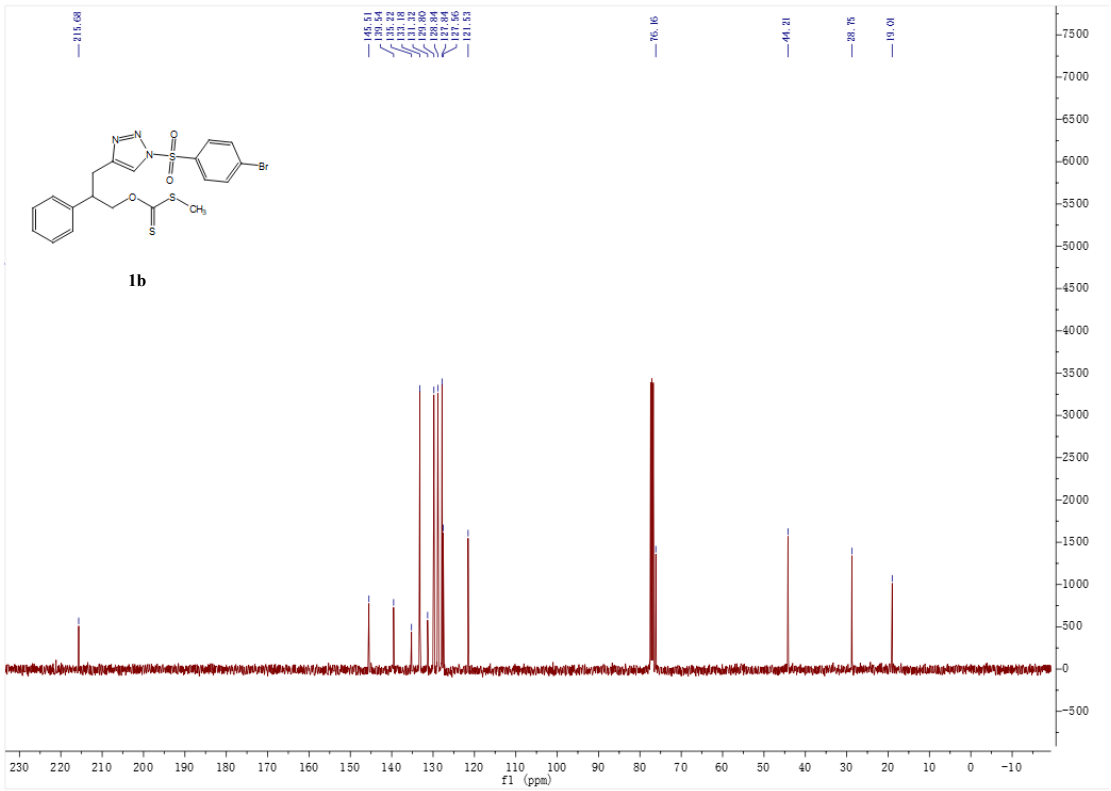

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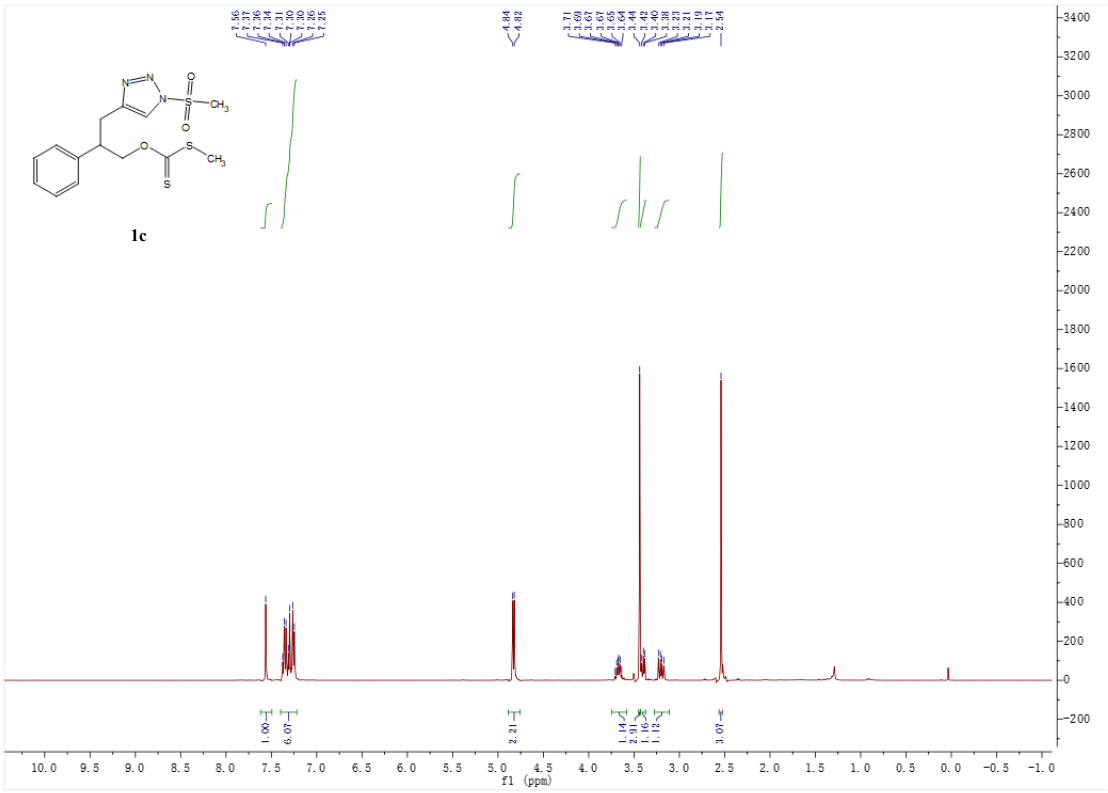

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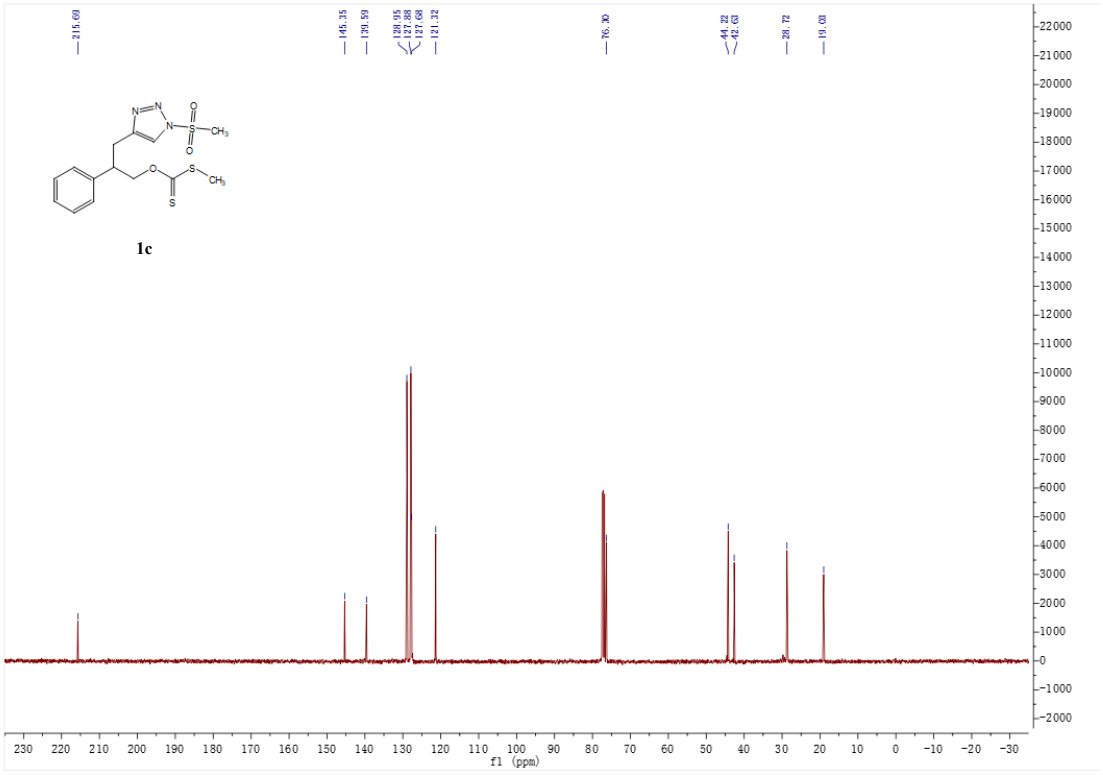

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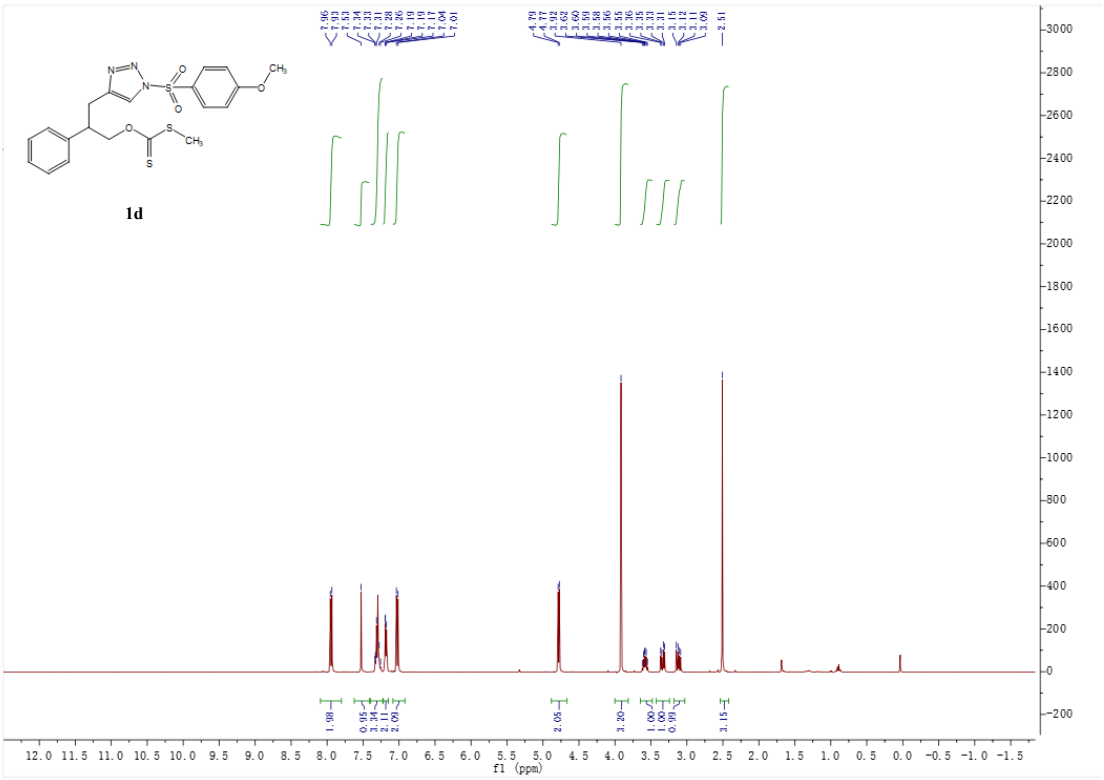

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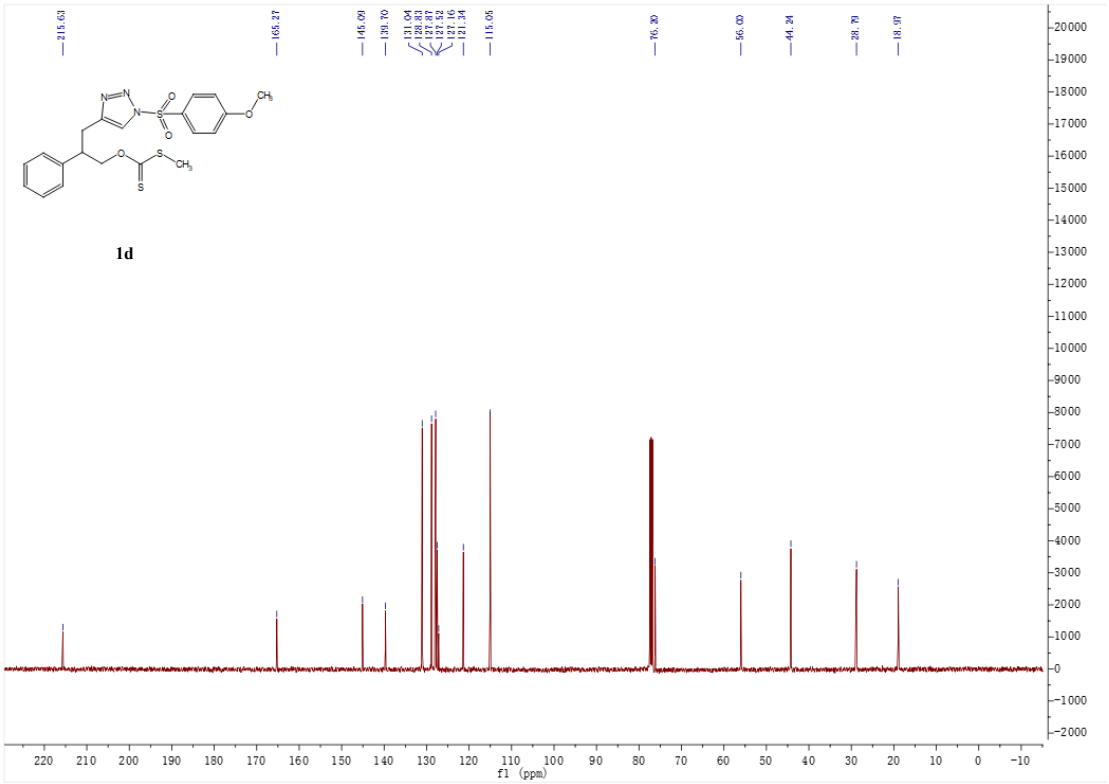

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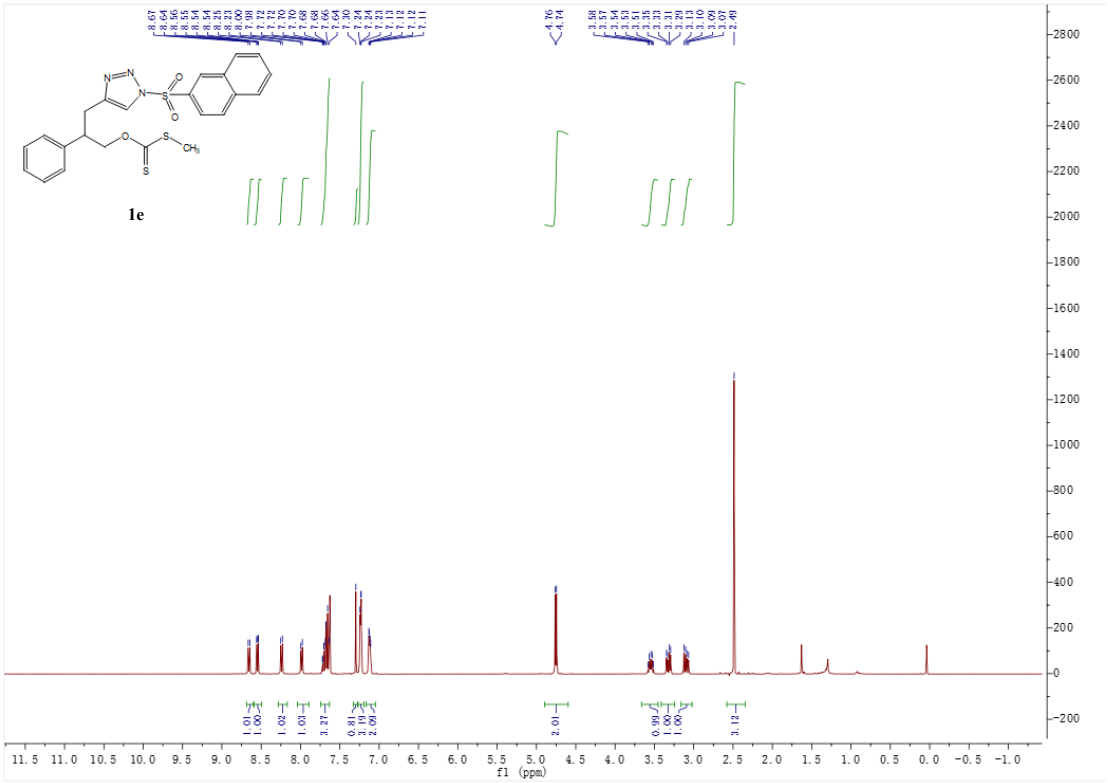

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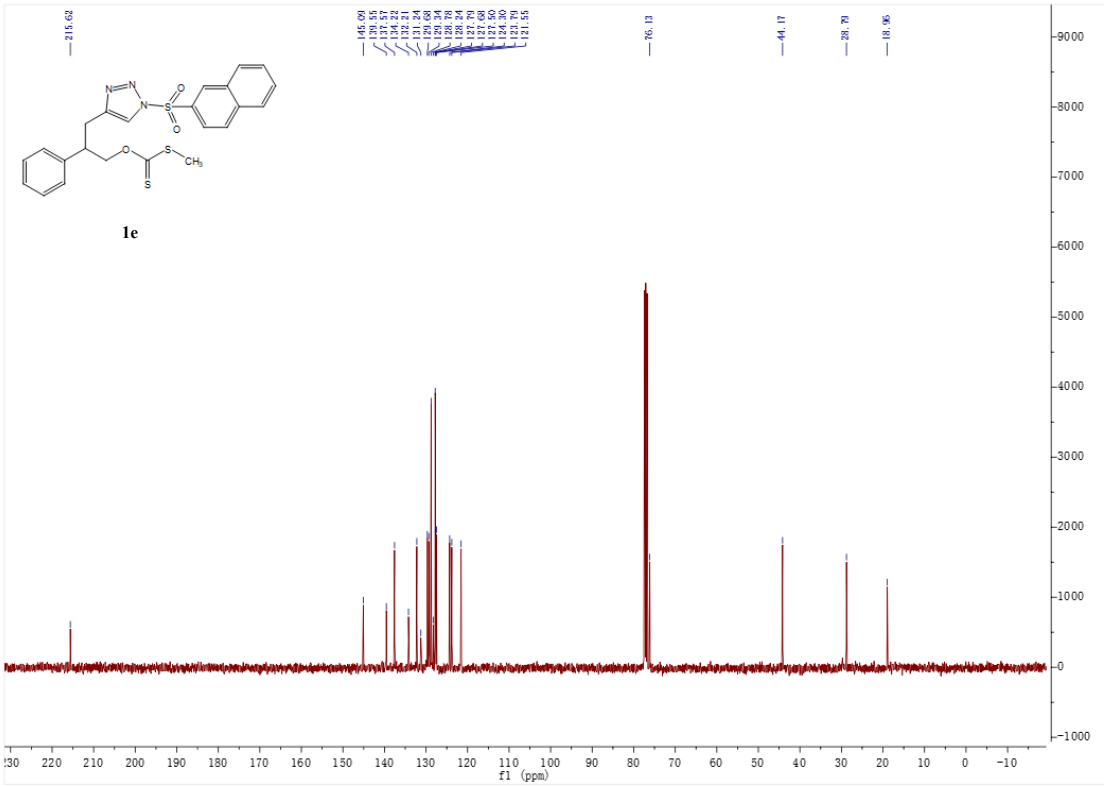

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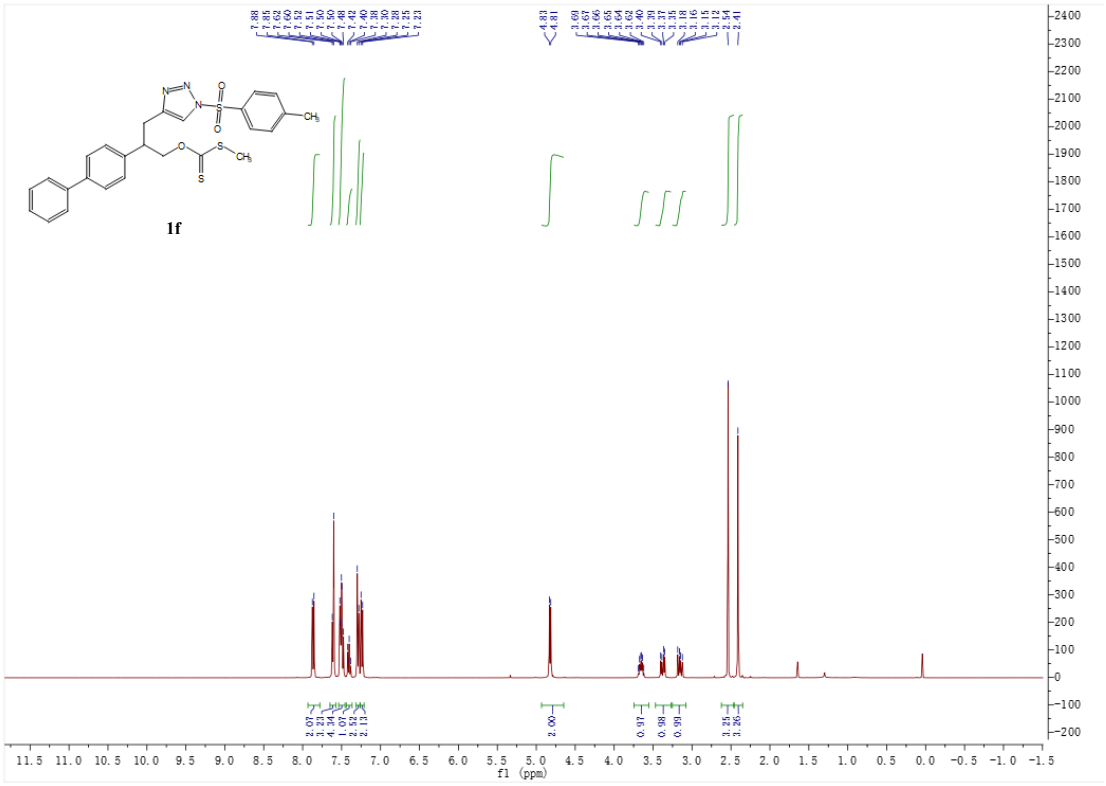

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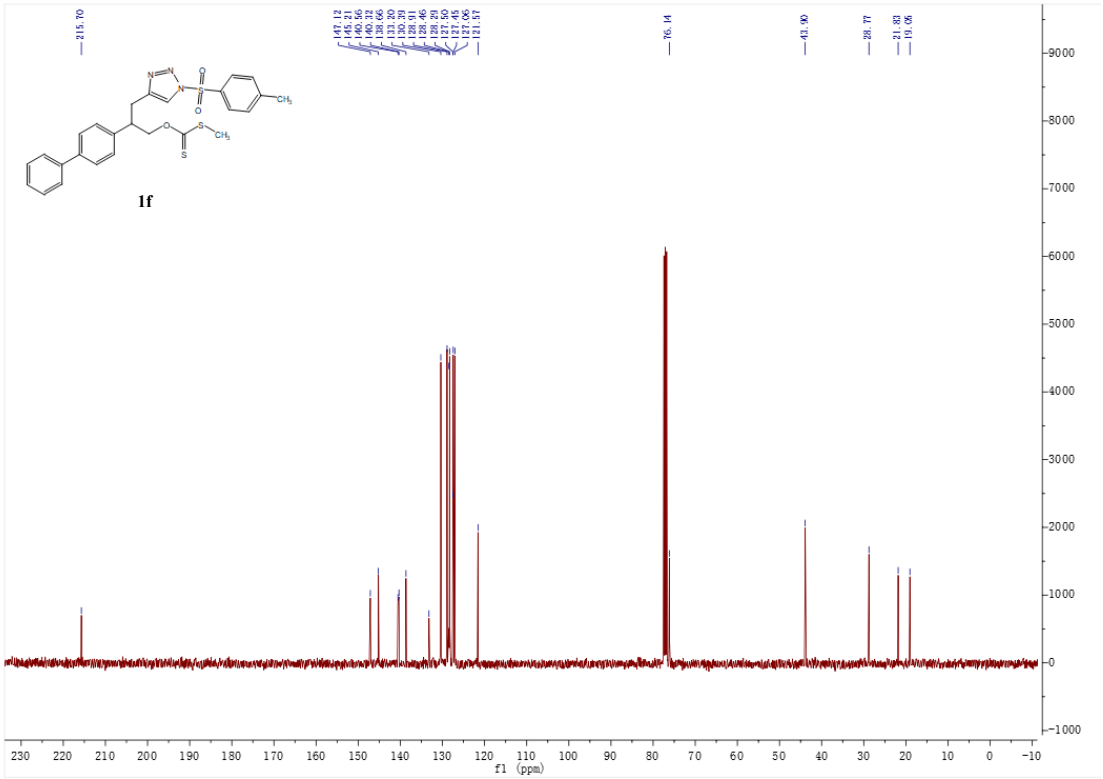

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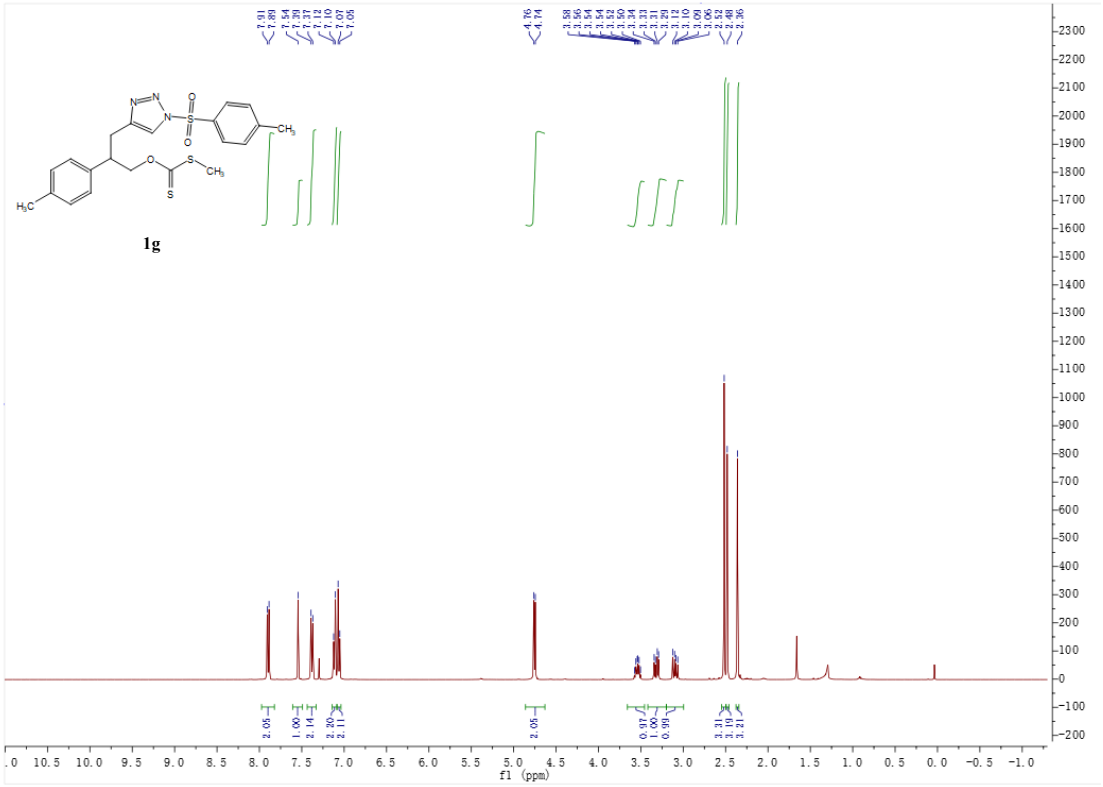

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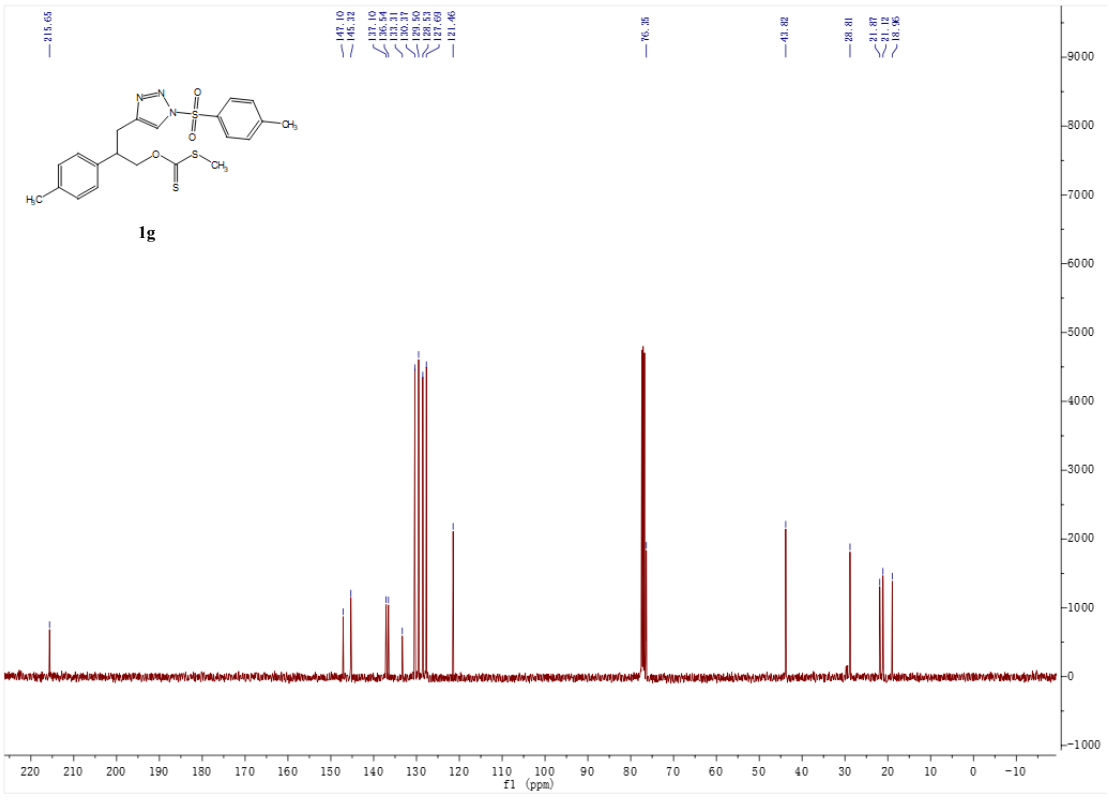

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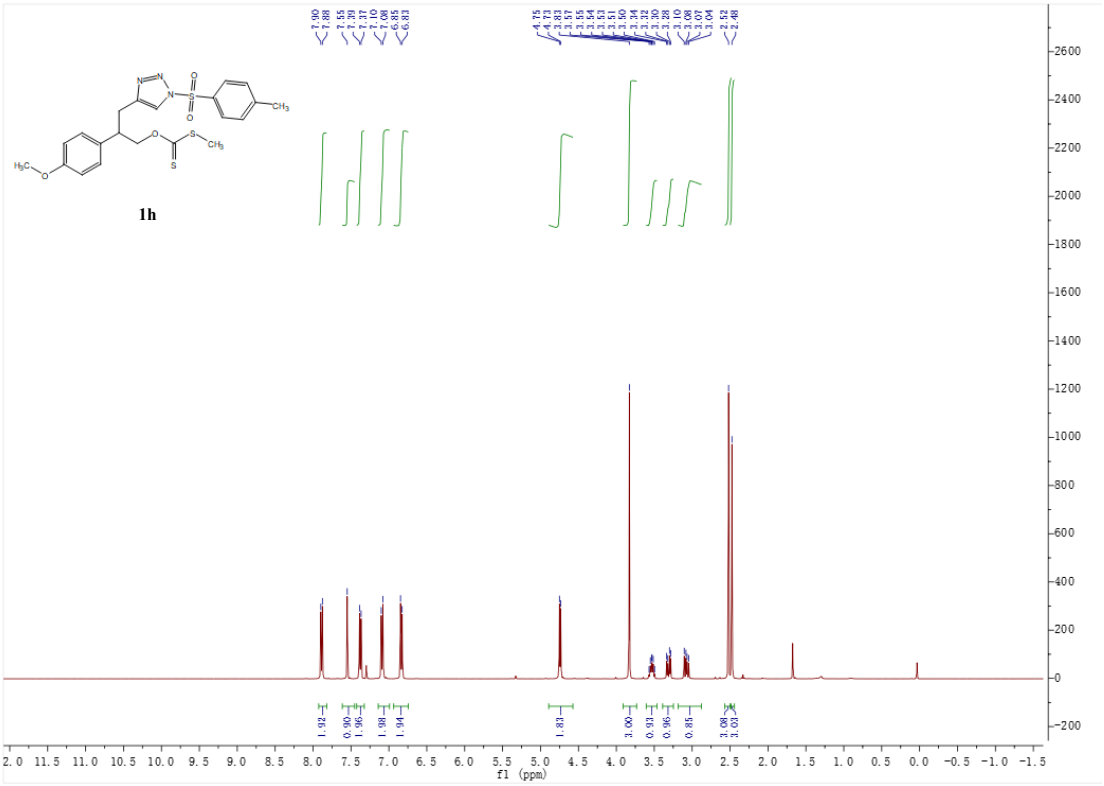

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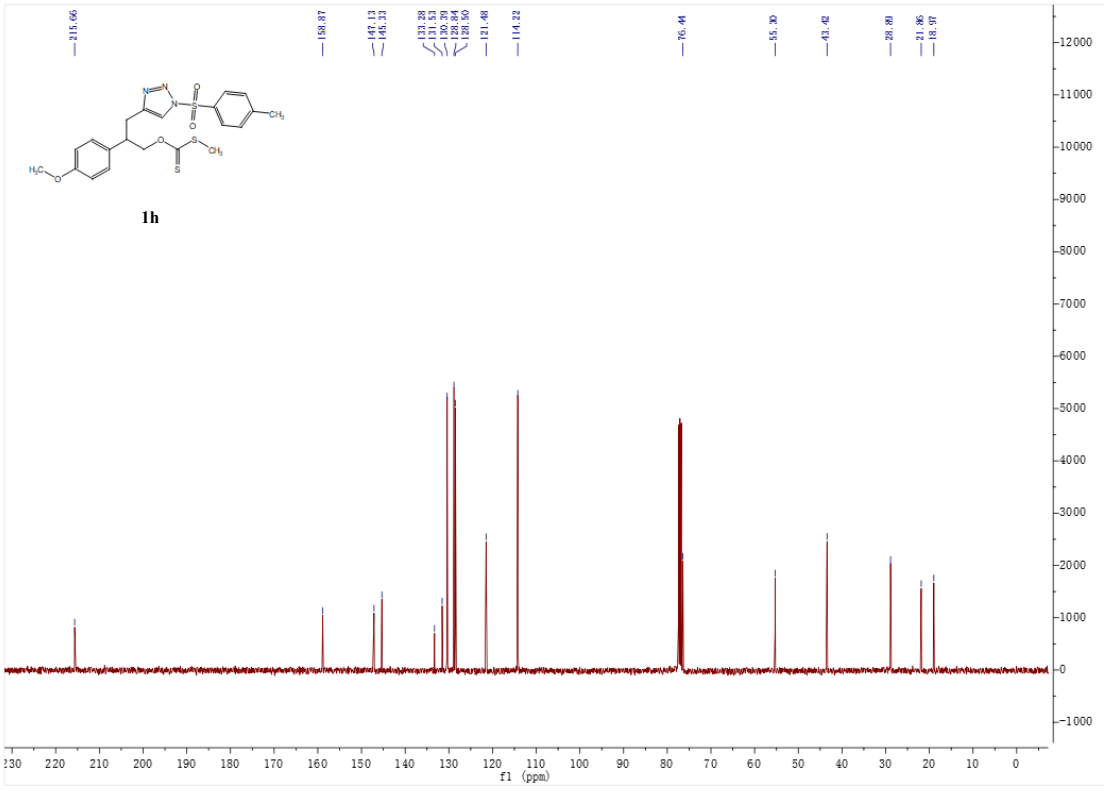

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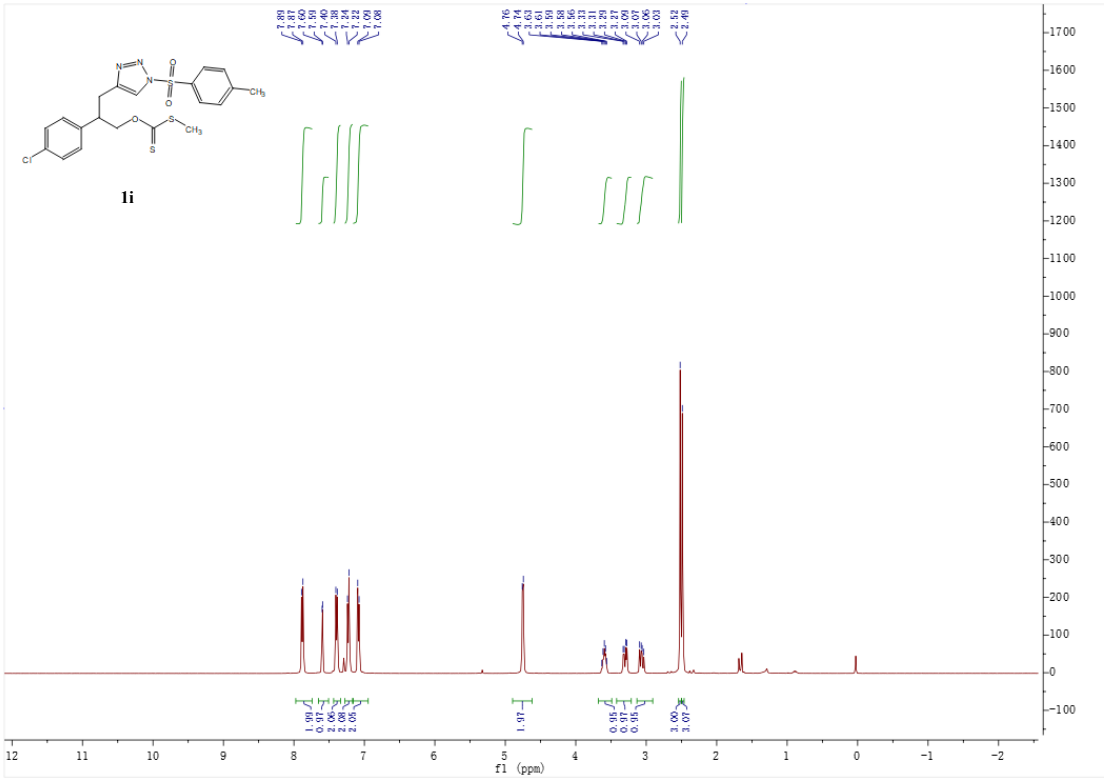

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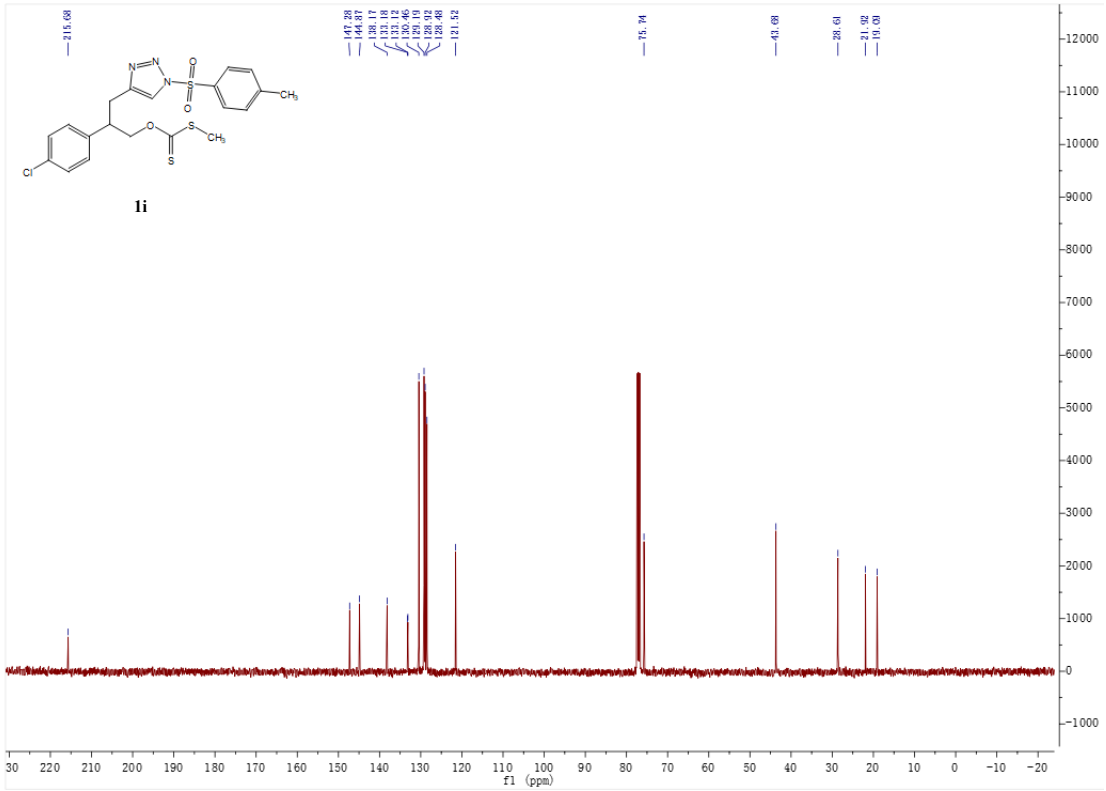

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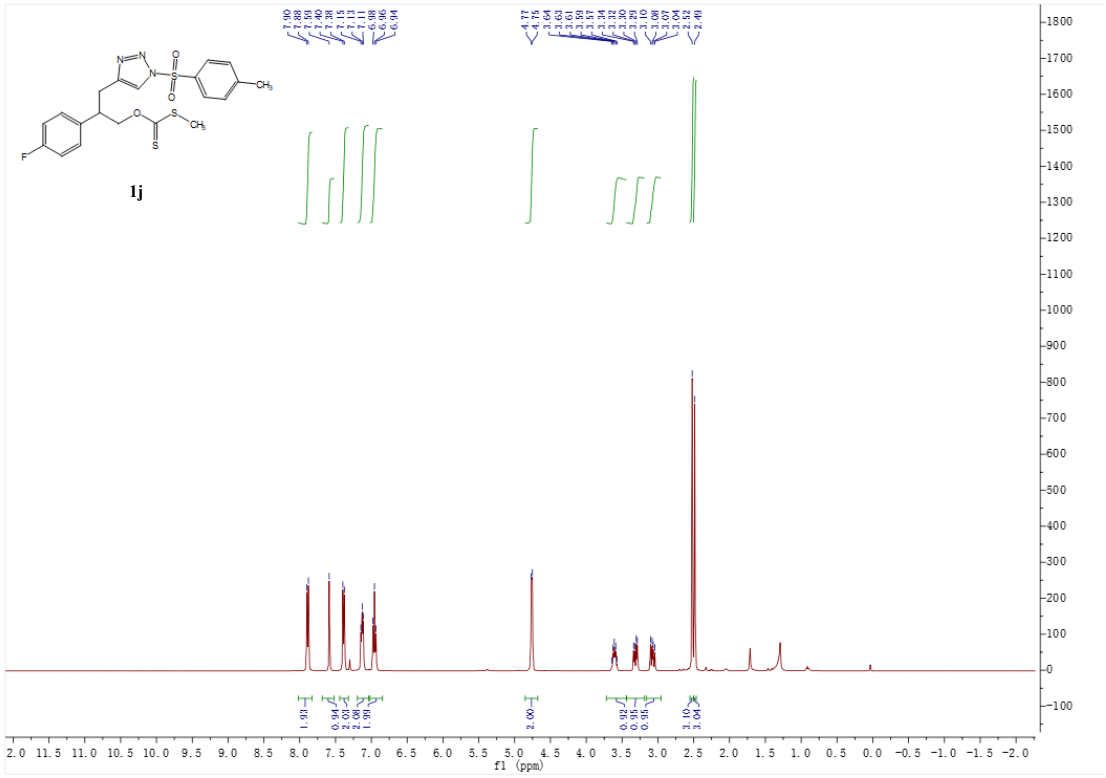
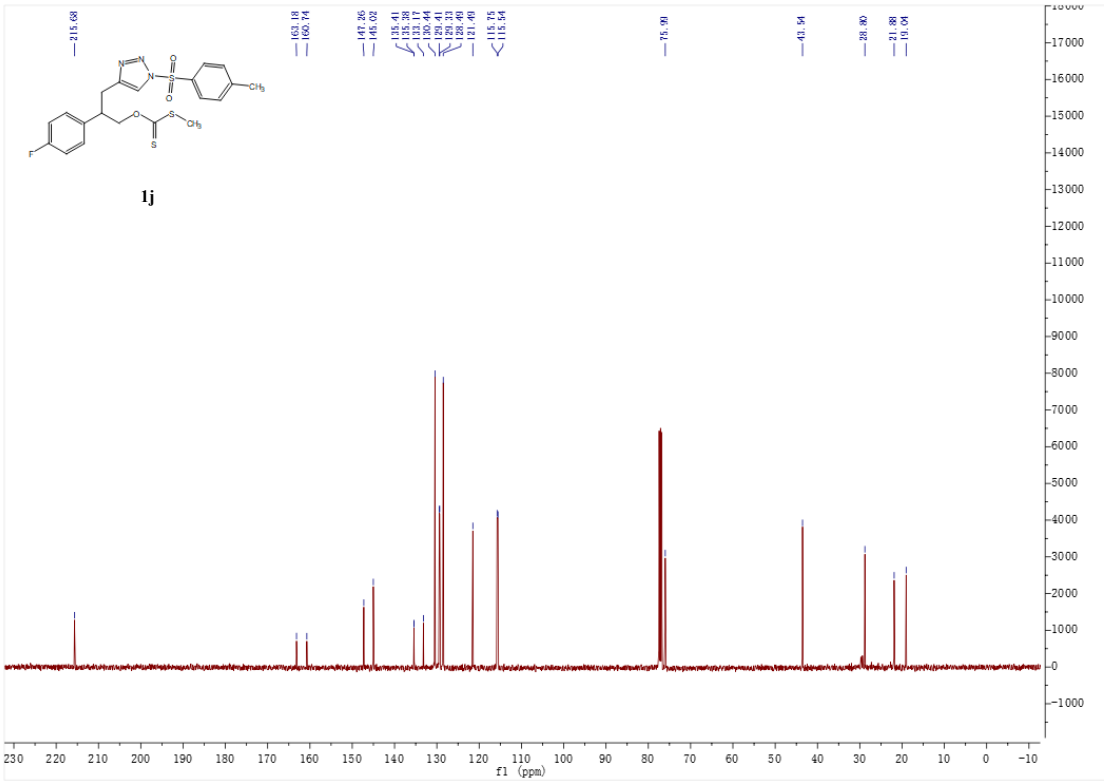
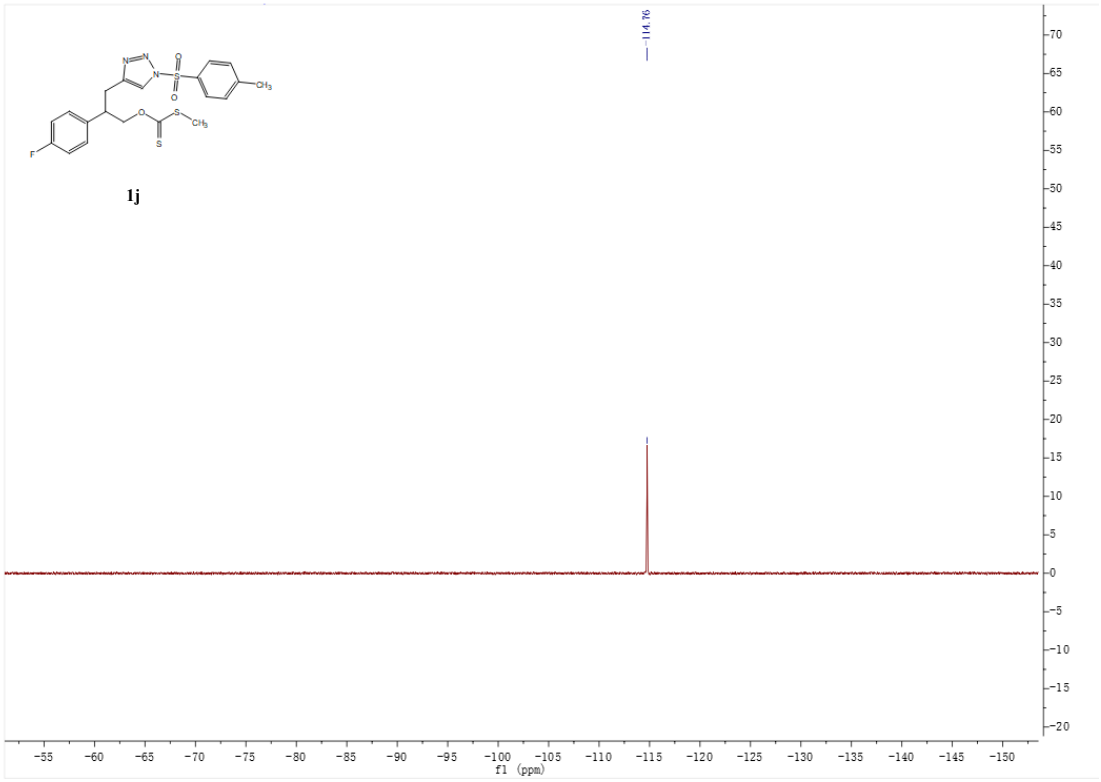


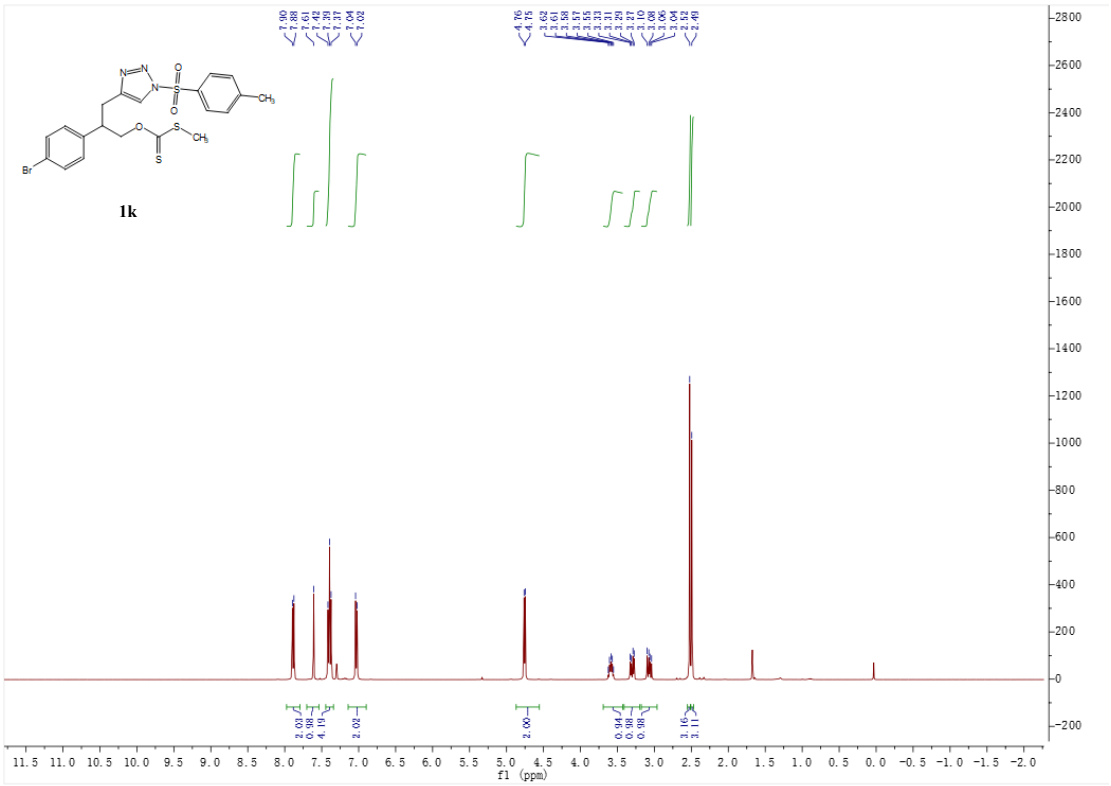
^{13}C NMR (101 MHz, Chloroform-d)



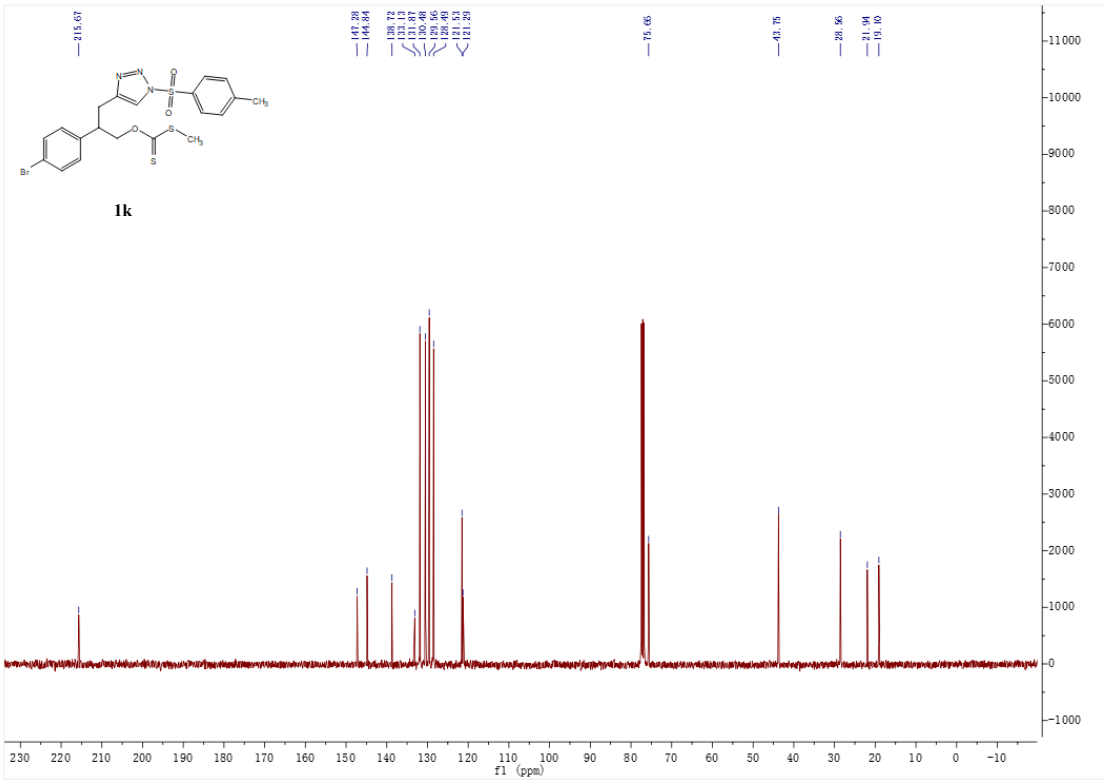
^{19}F NMR (376 MHz, Chloroform-d)



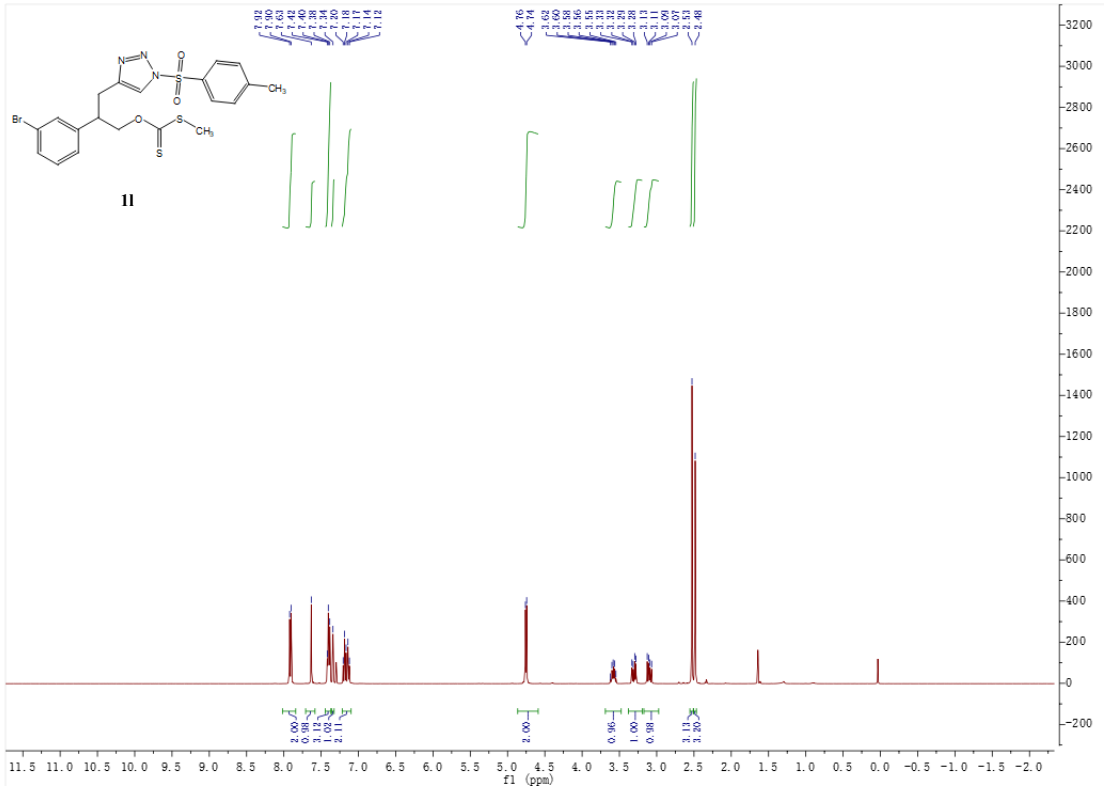
^{1}H NMR (400 MHz, Chloroform-d)



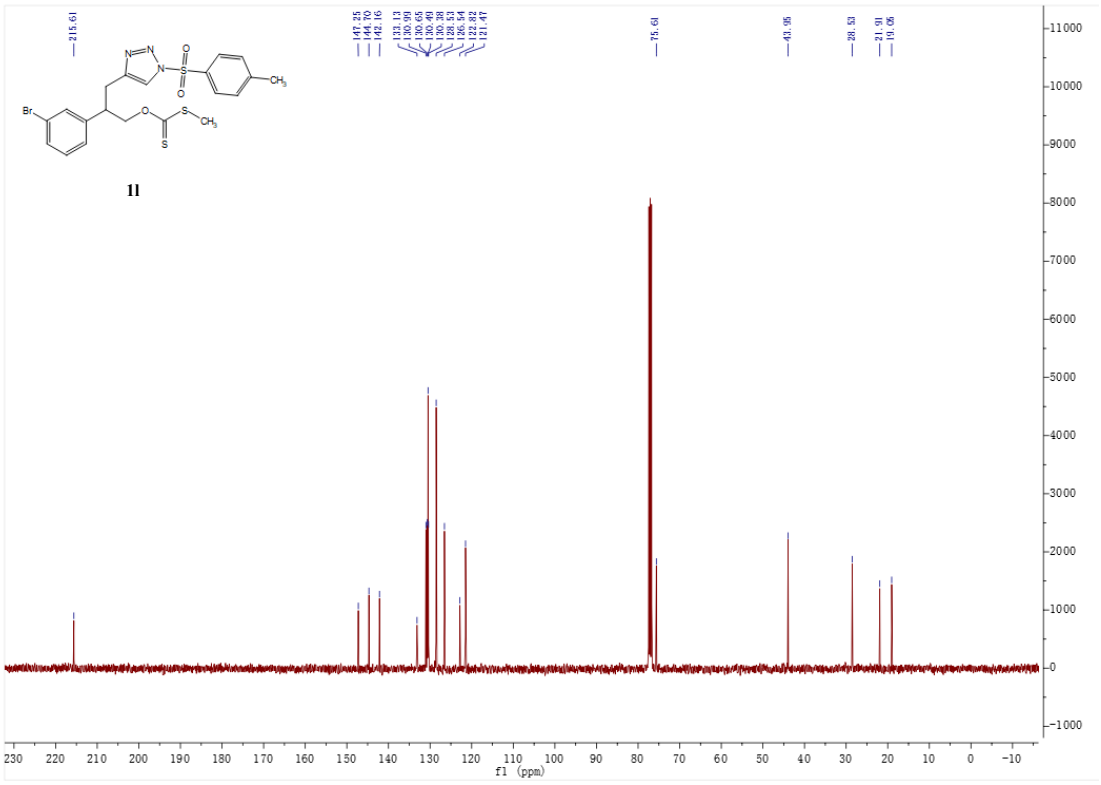
^{13}C NMR (101 MHz, Chloroform-d)



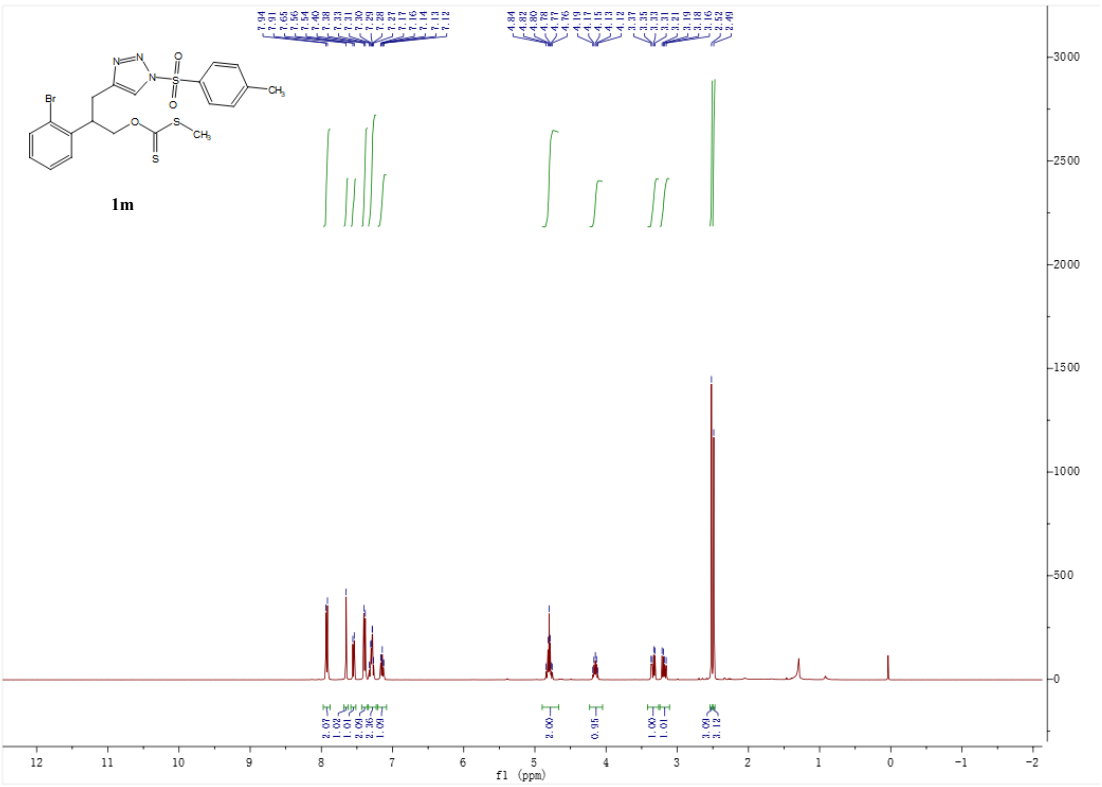
^{1}H NMR (400 MHz, Chloroform-d)



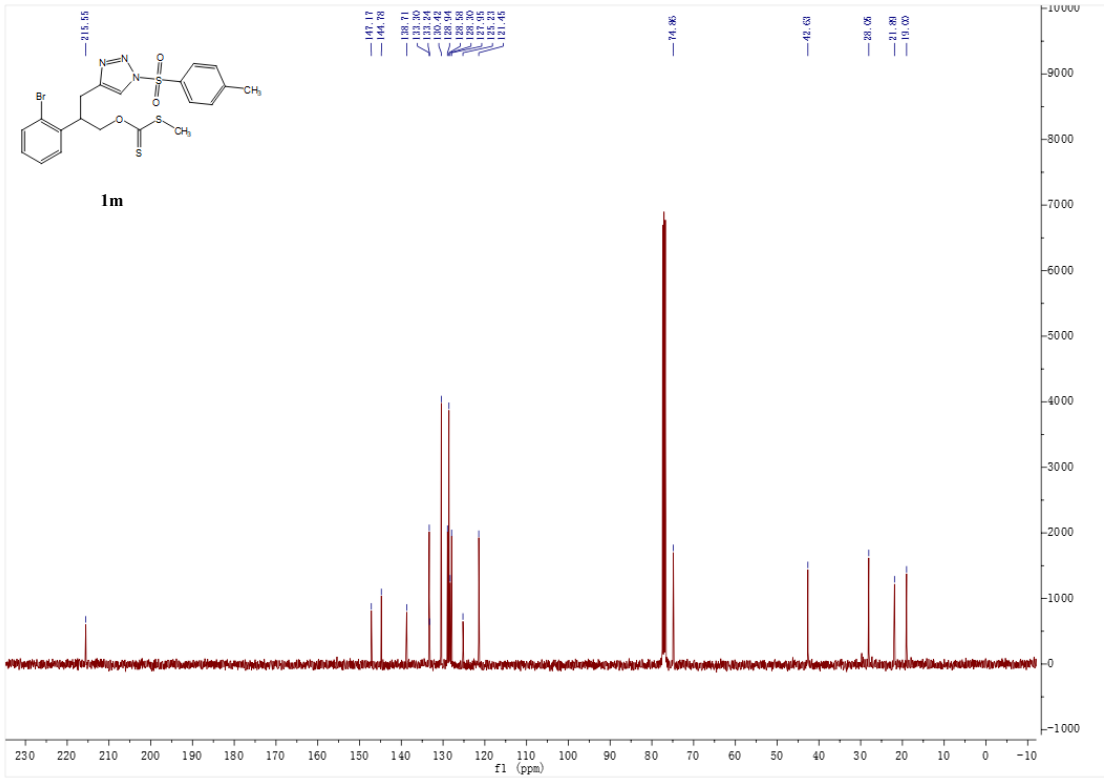
^{13}C NMR (101 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



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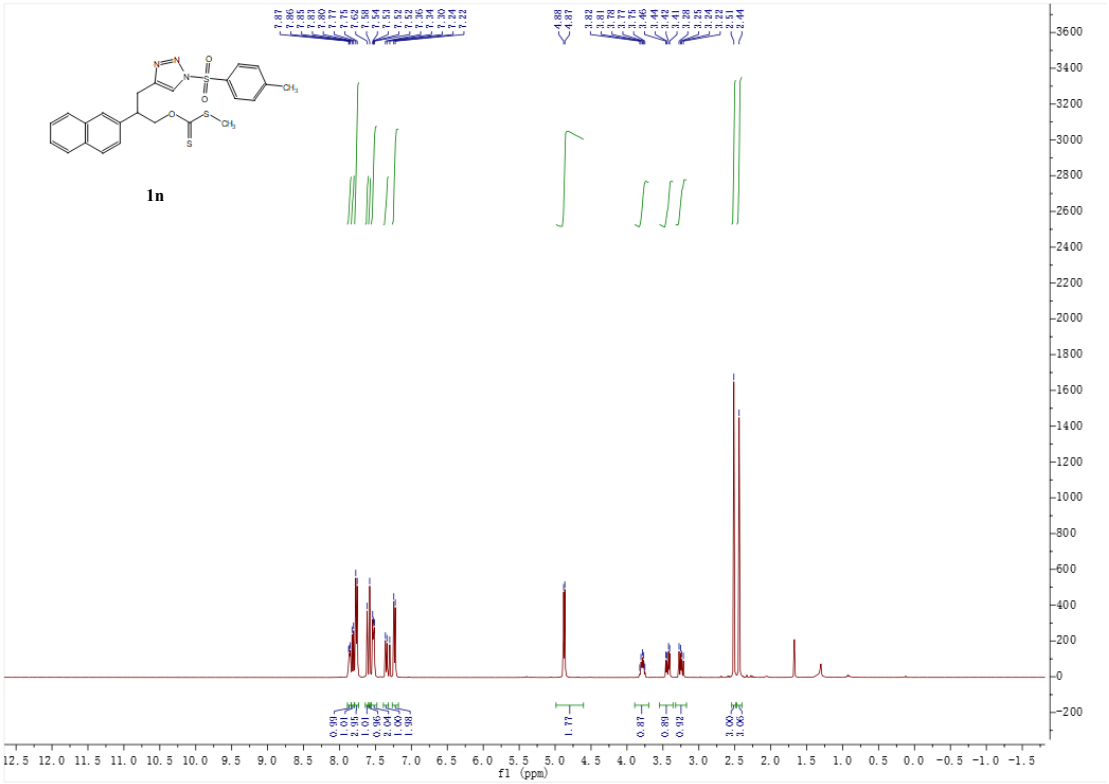

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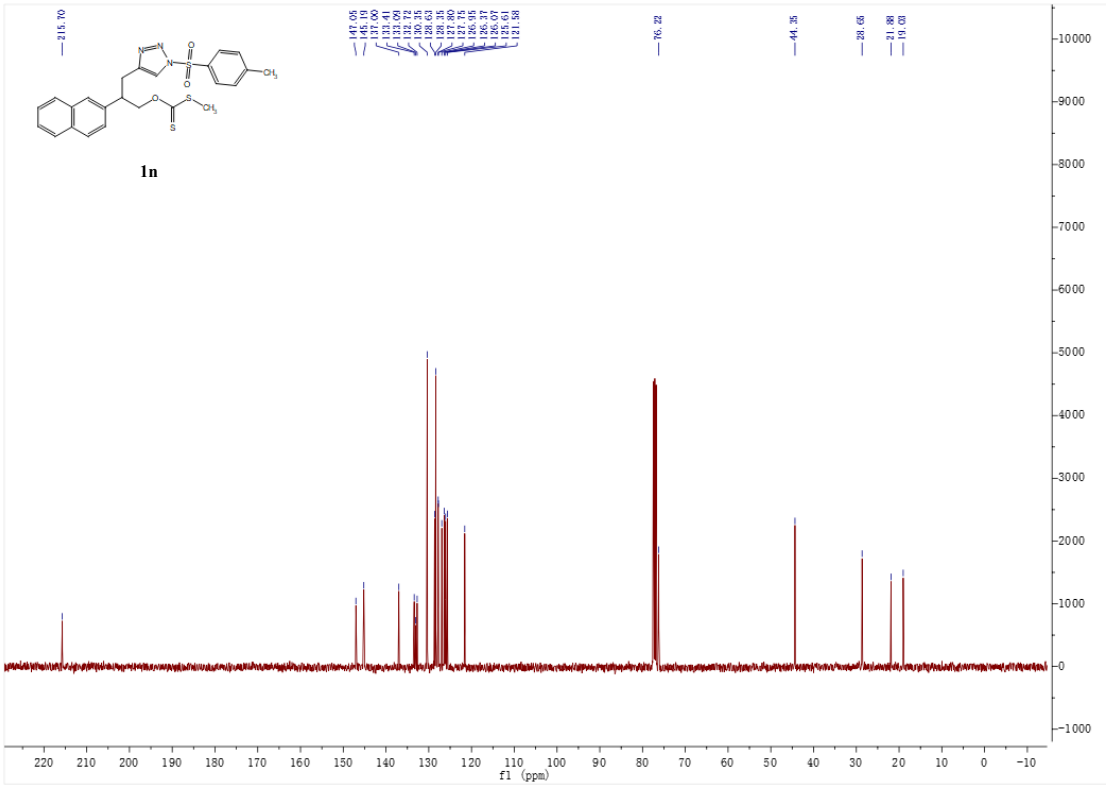

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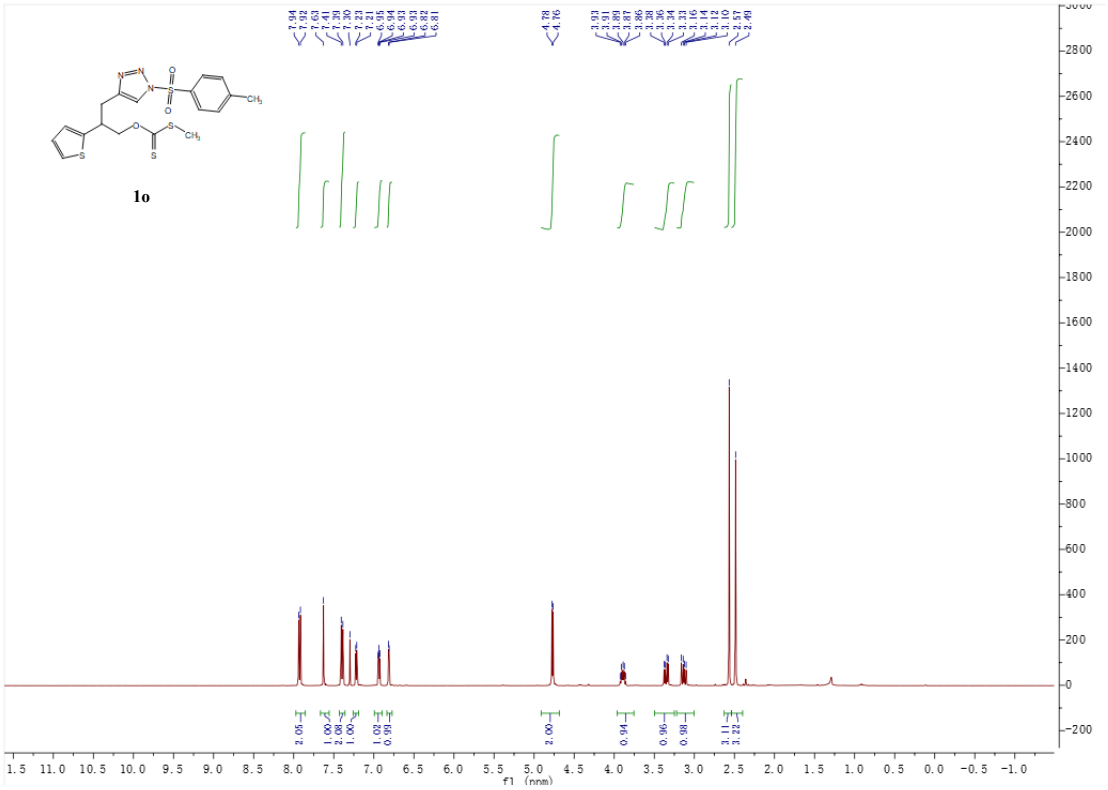

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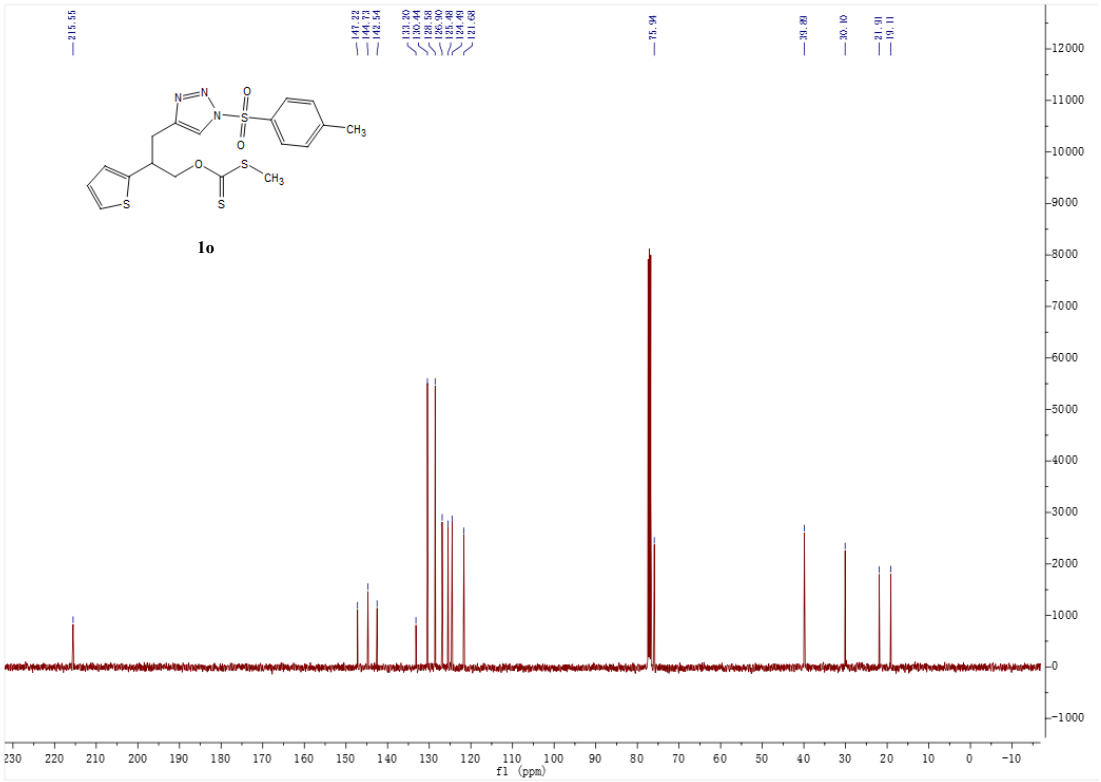

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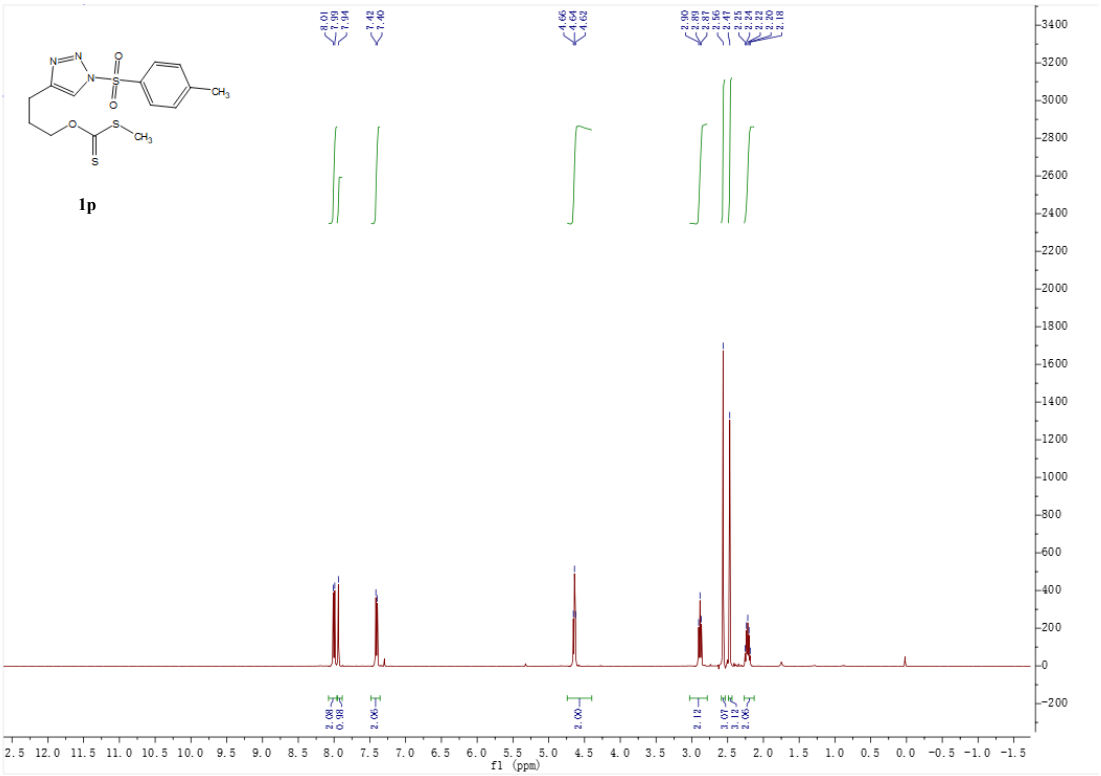
^{1}H NMR (400 MHz, Chloroform-d)



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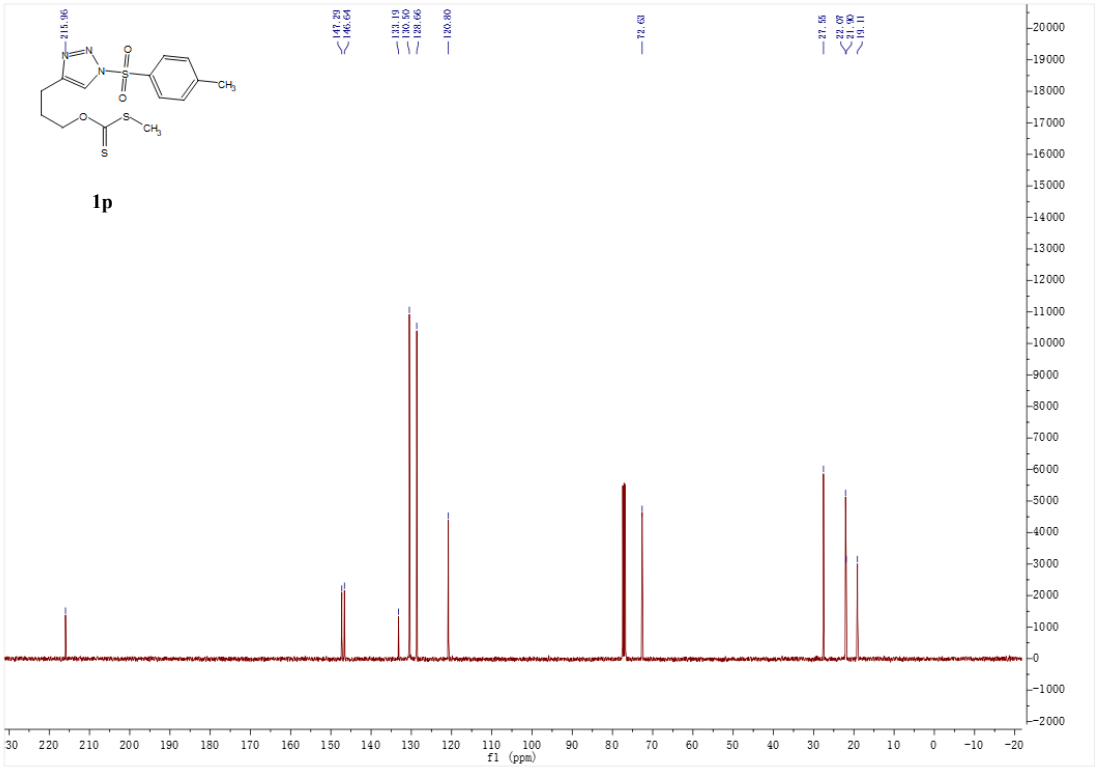
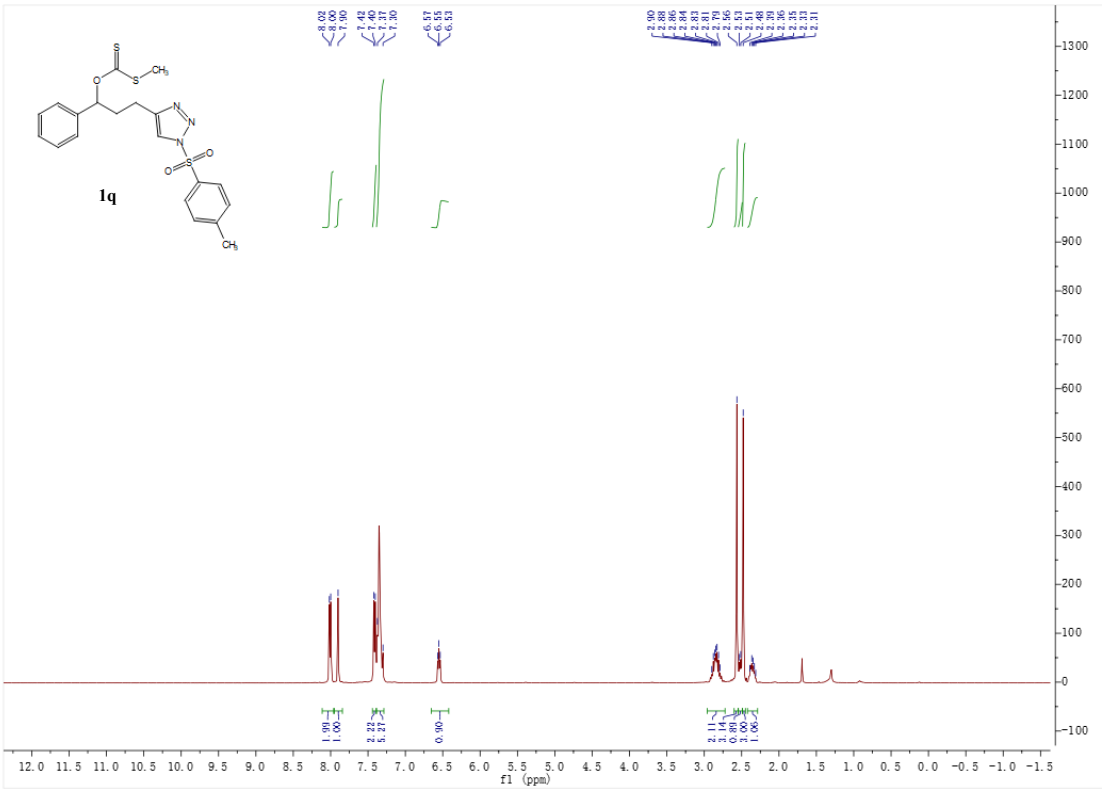
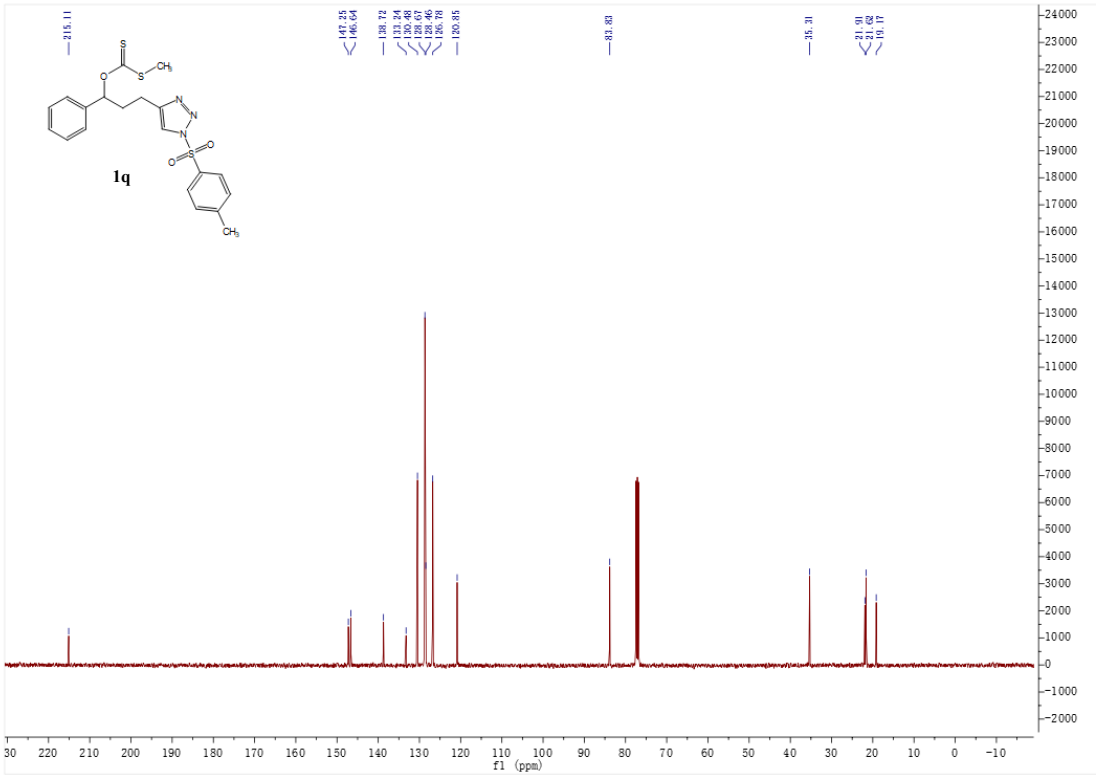
^{13}C NMR (101 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



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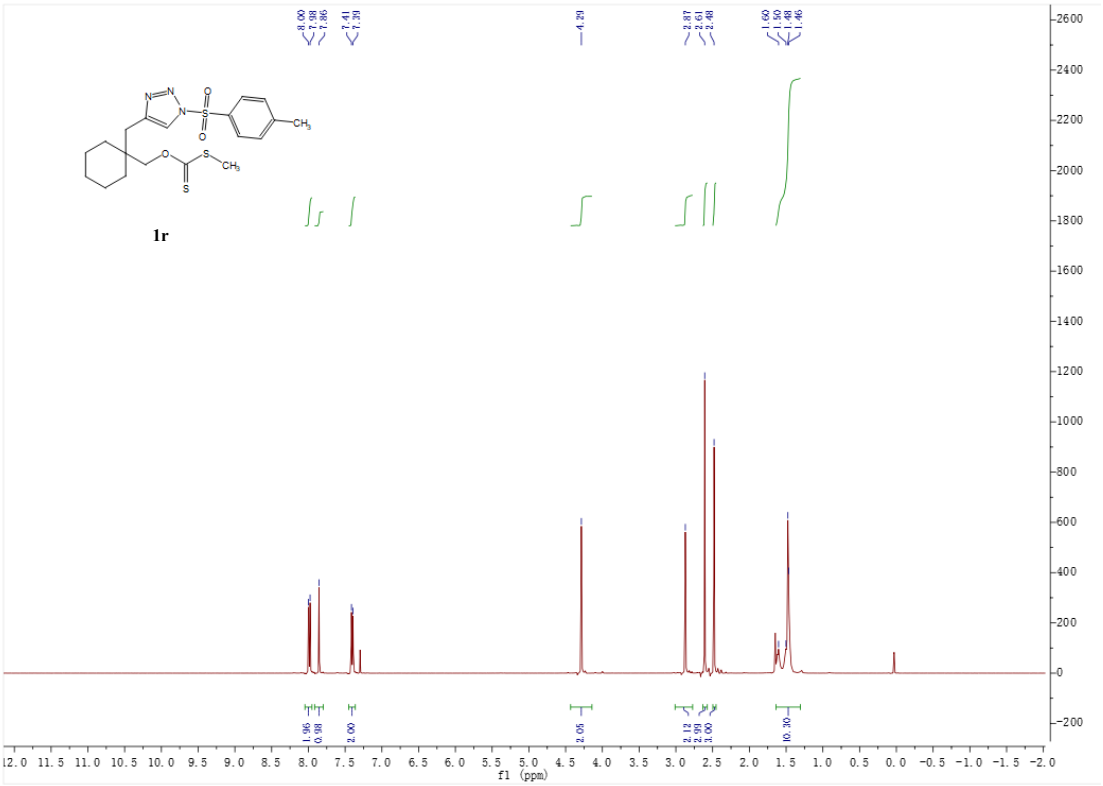

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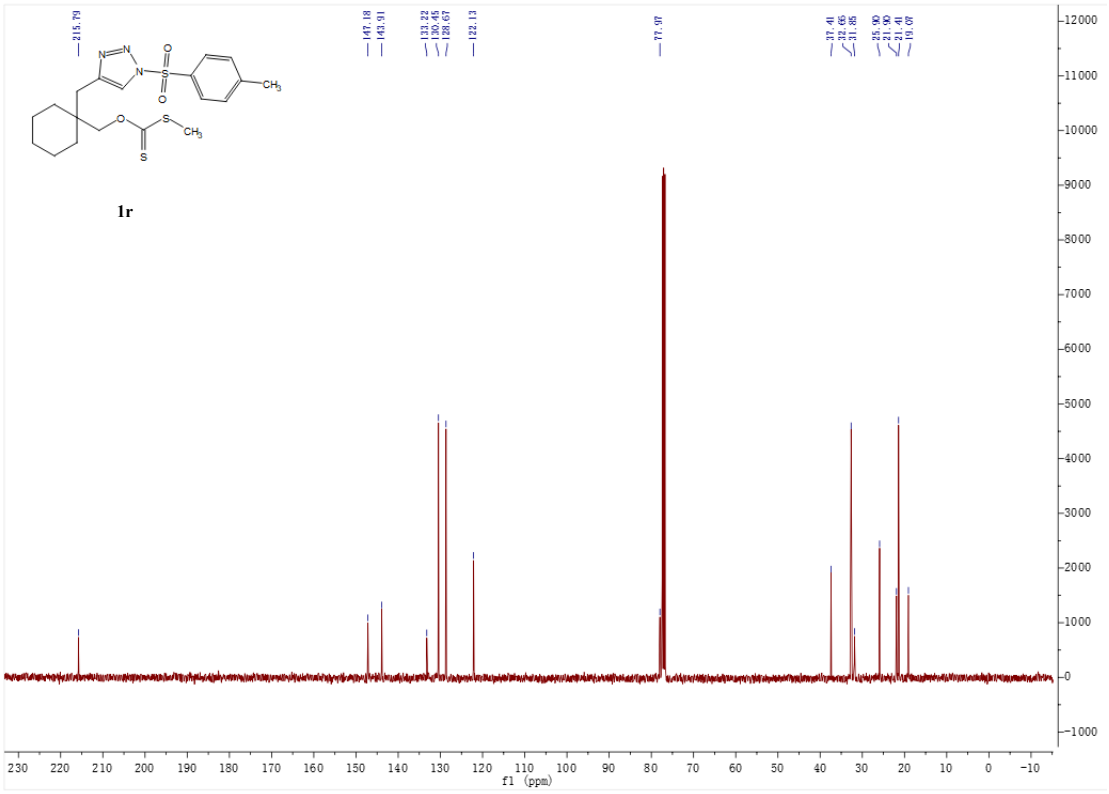

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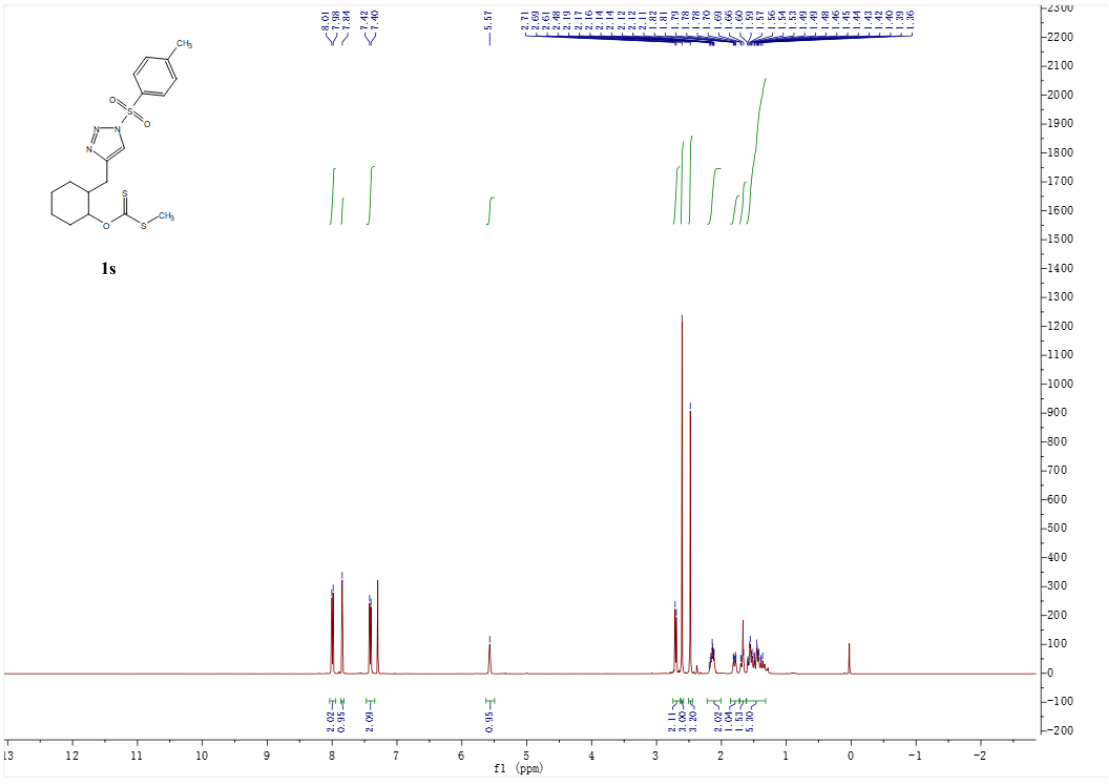
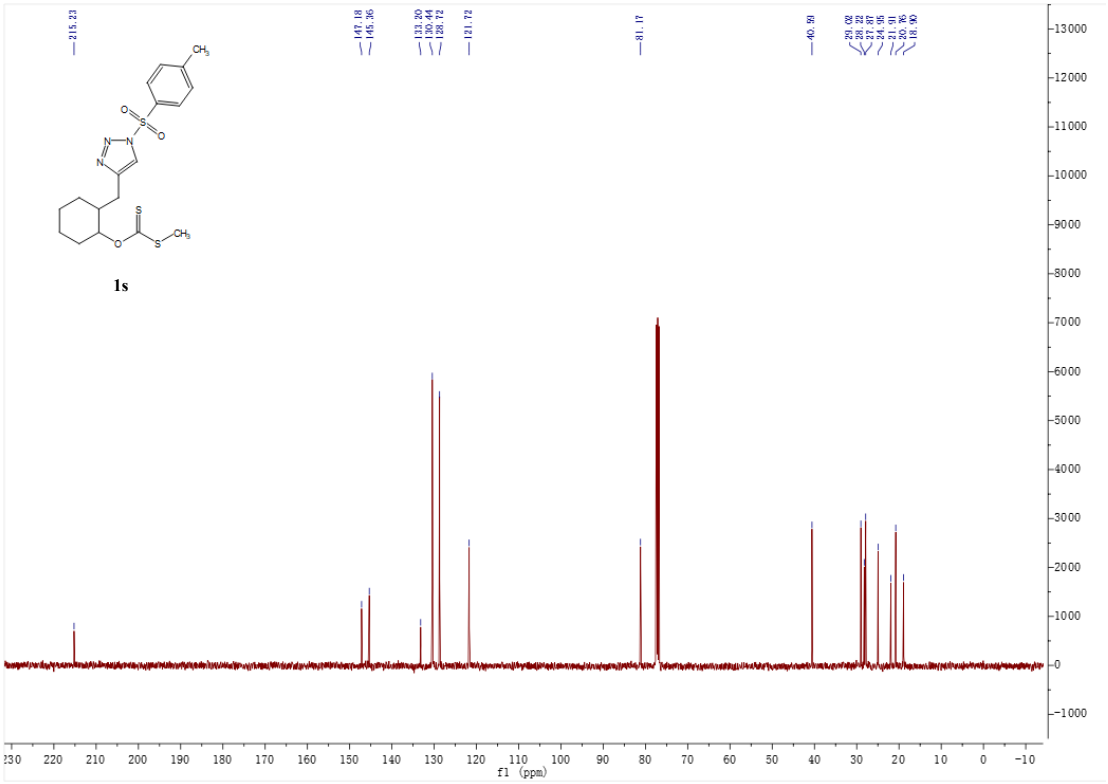


^{13}C NMR (101 MHz, Chloroform-d)



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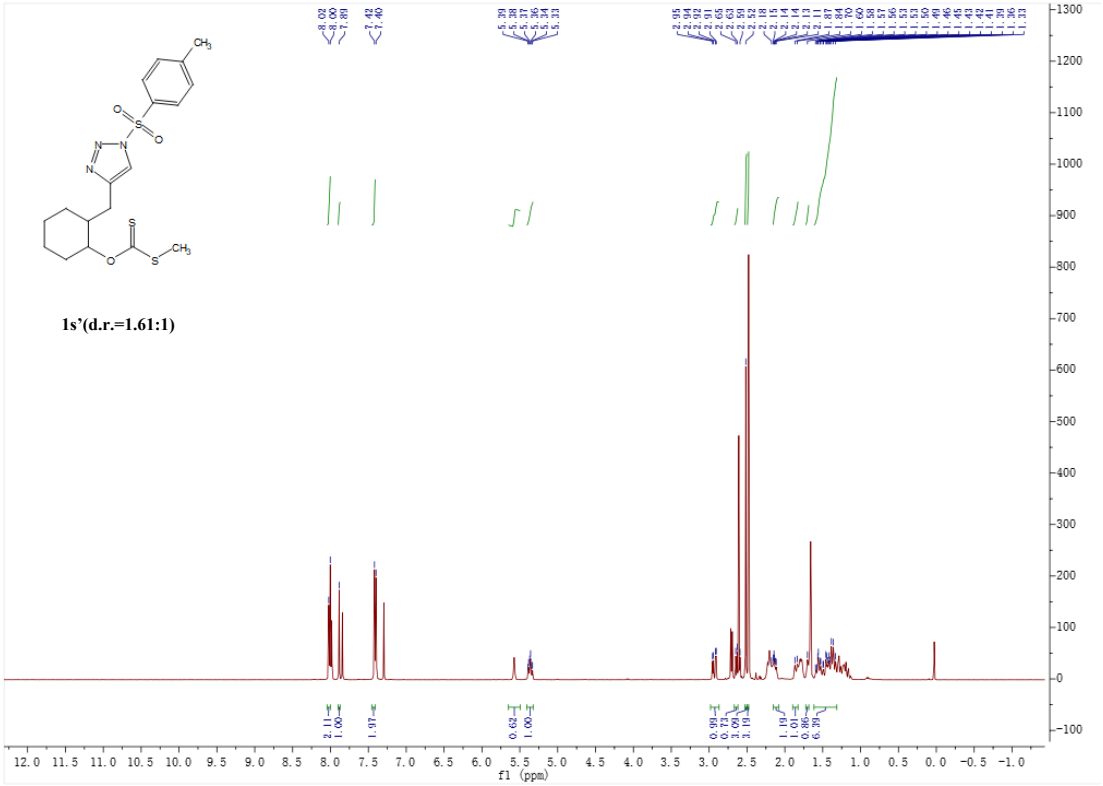

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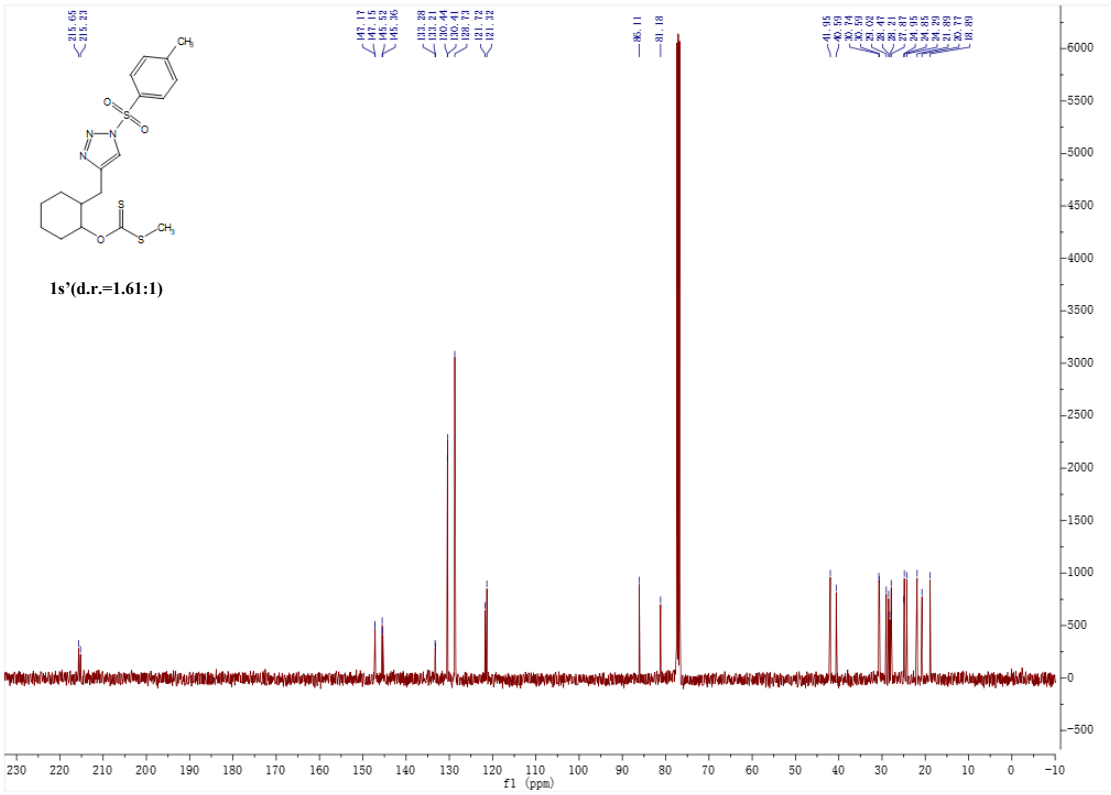

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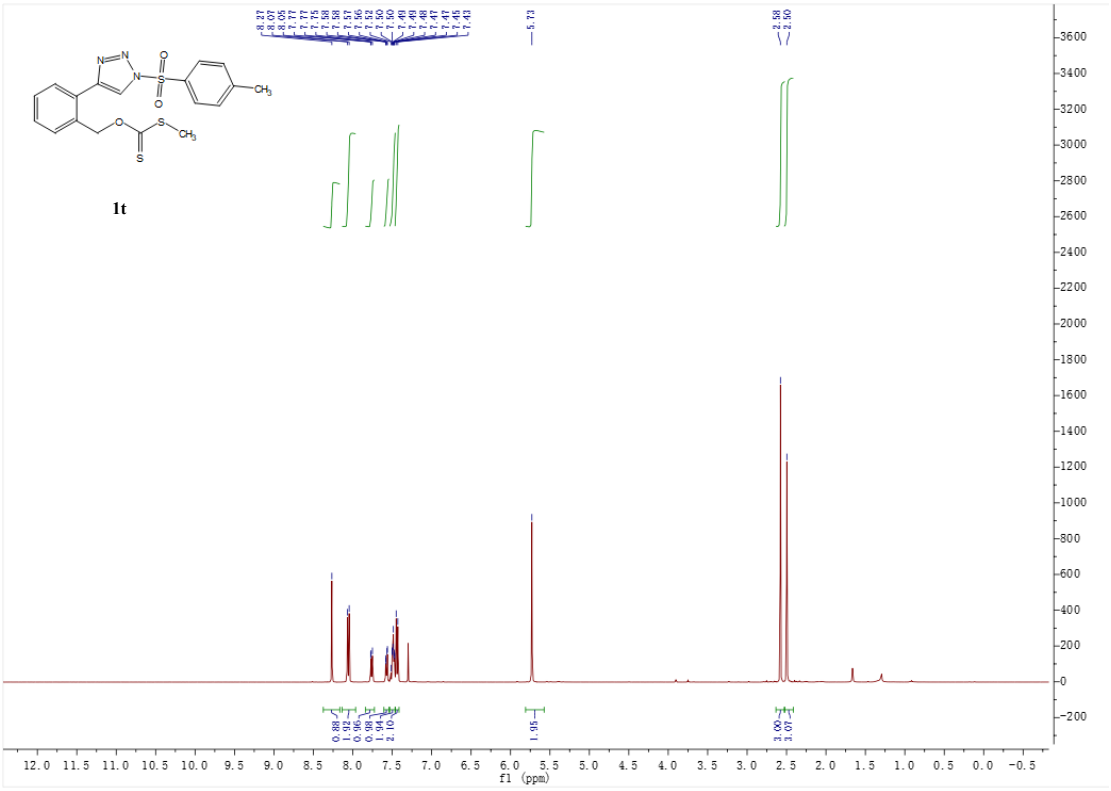

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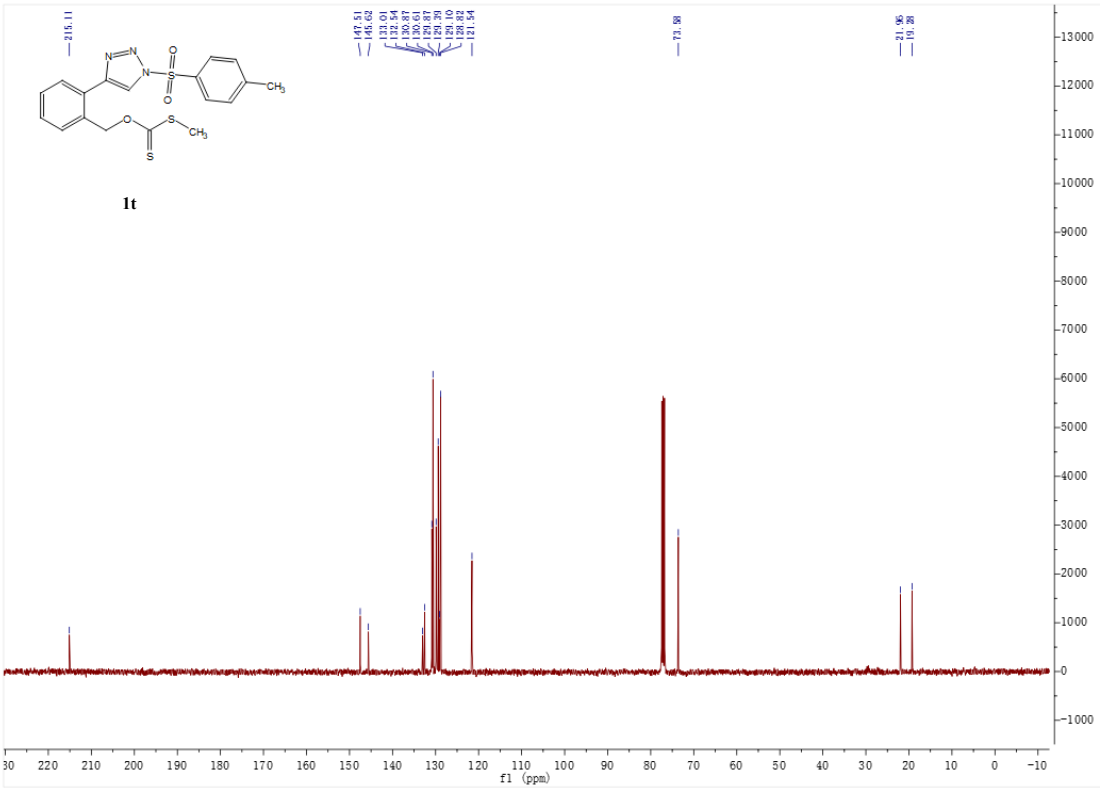

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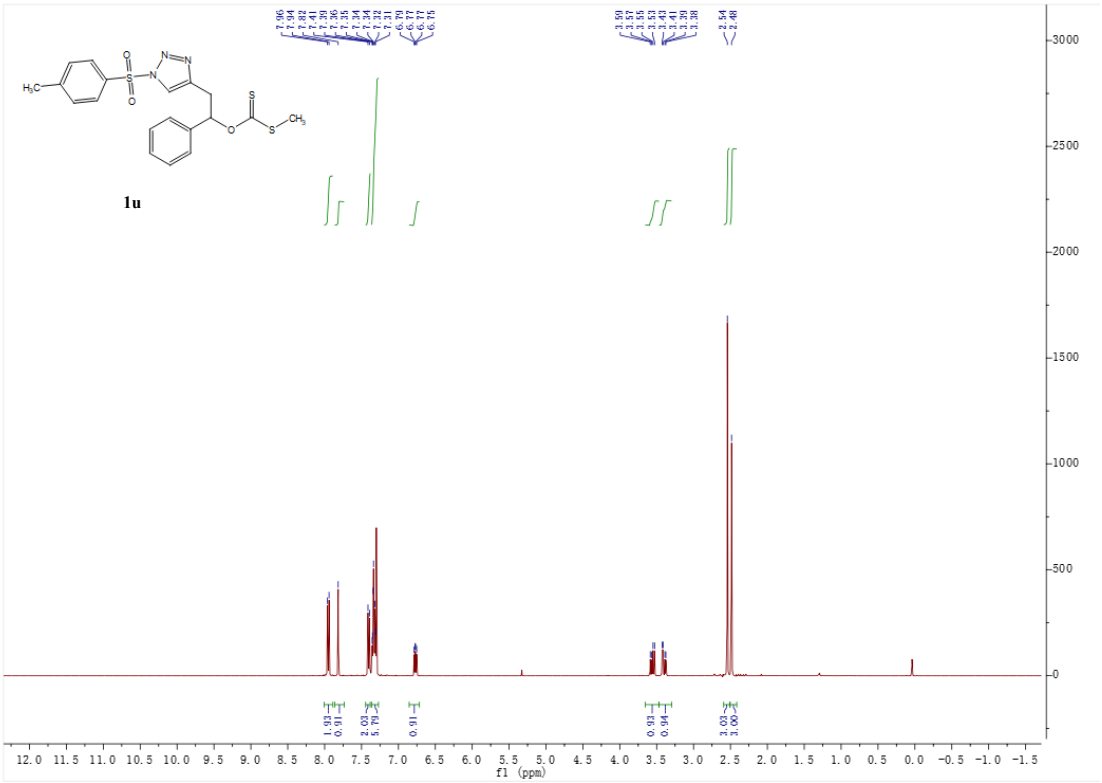

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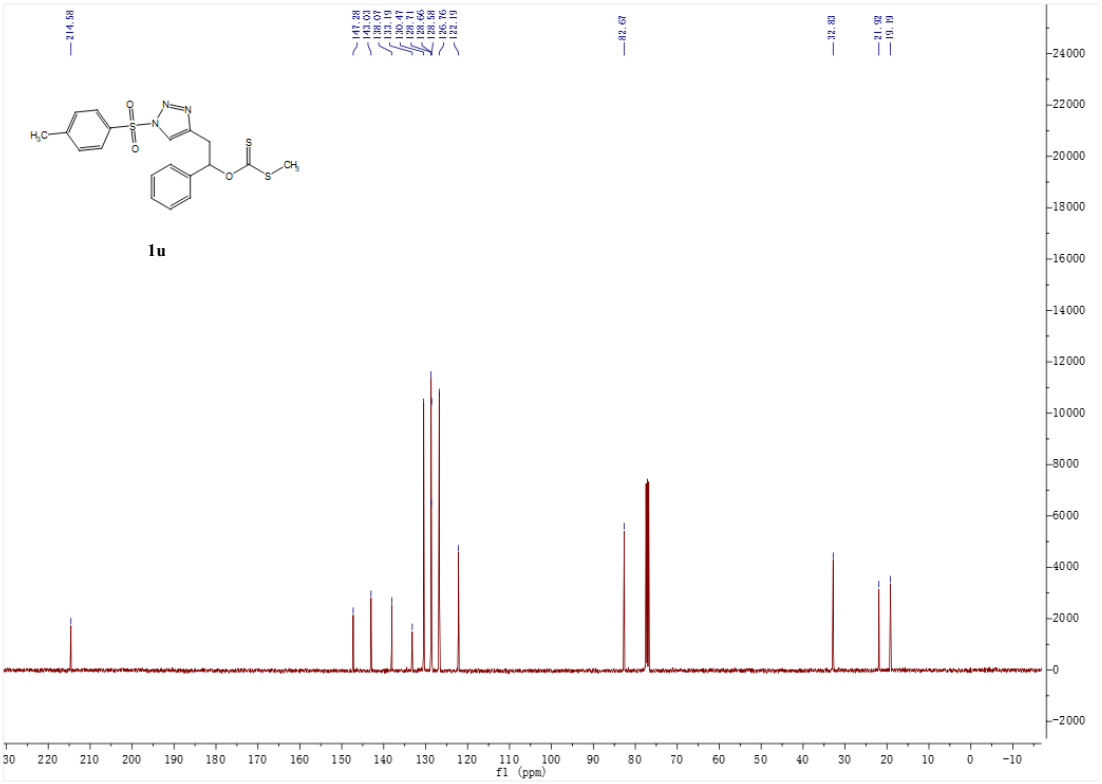

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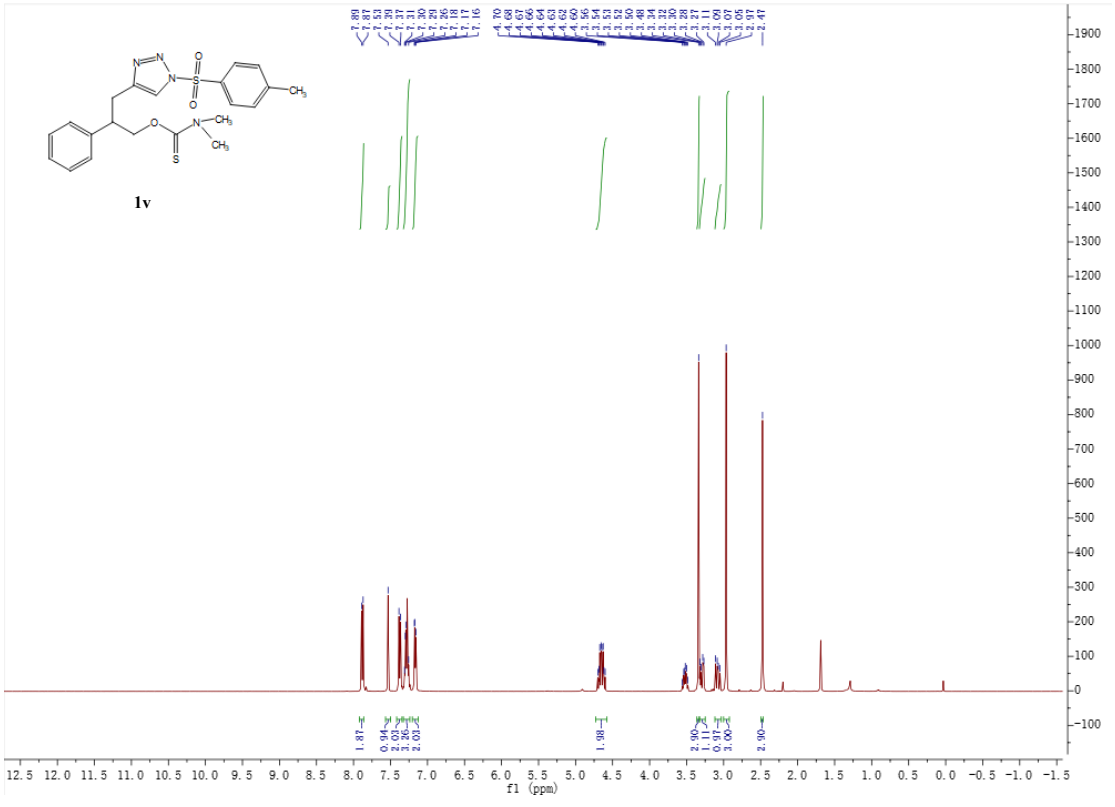

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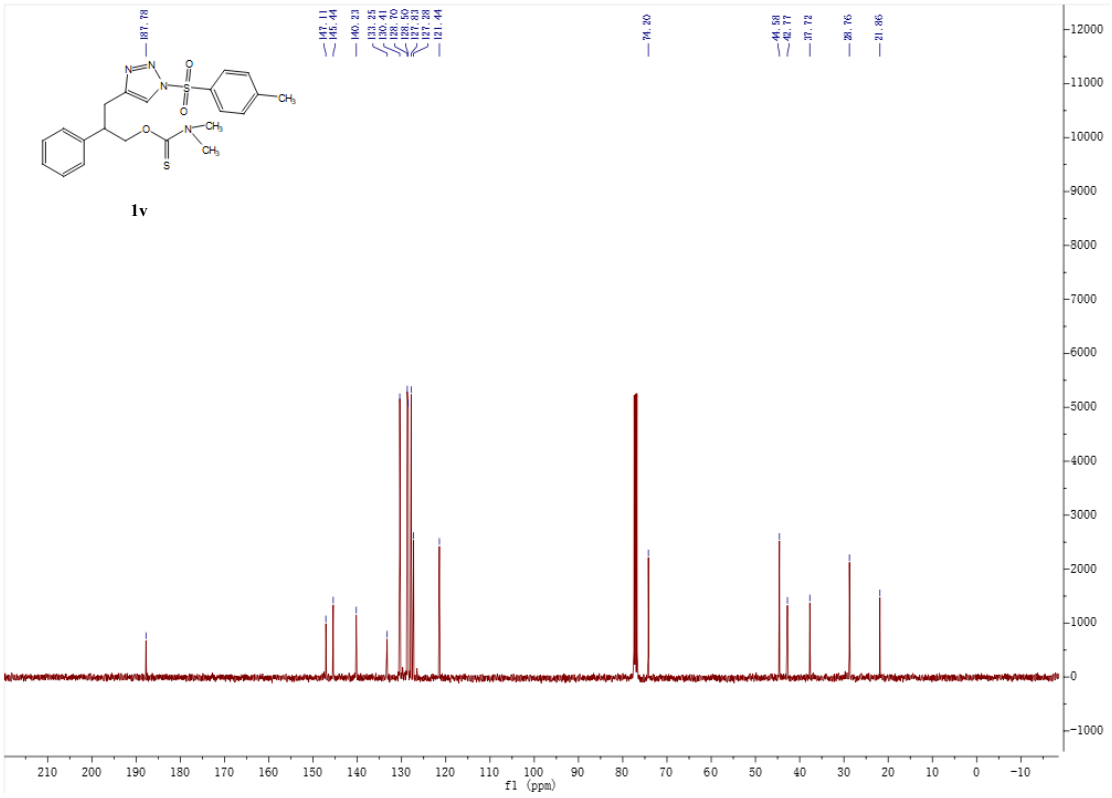

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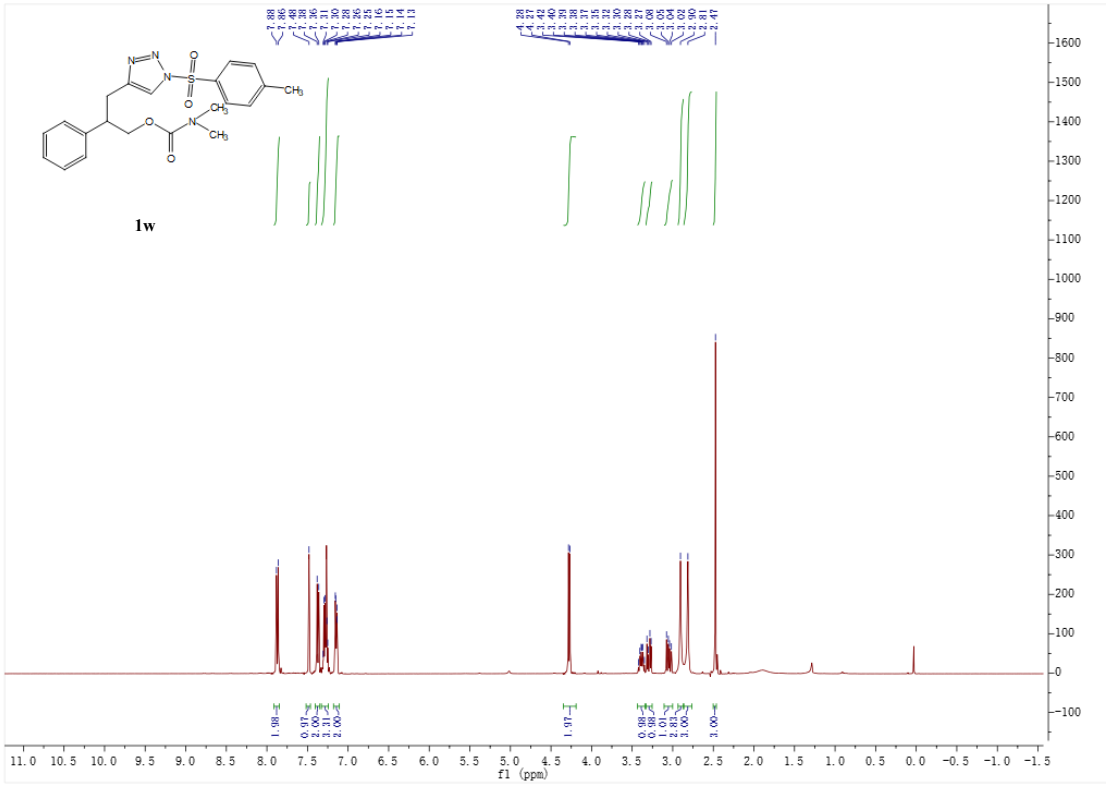

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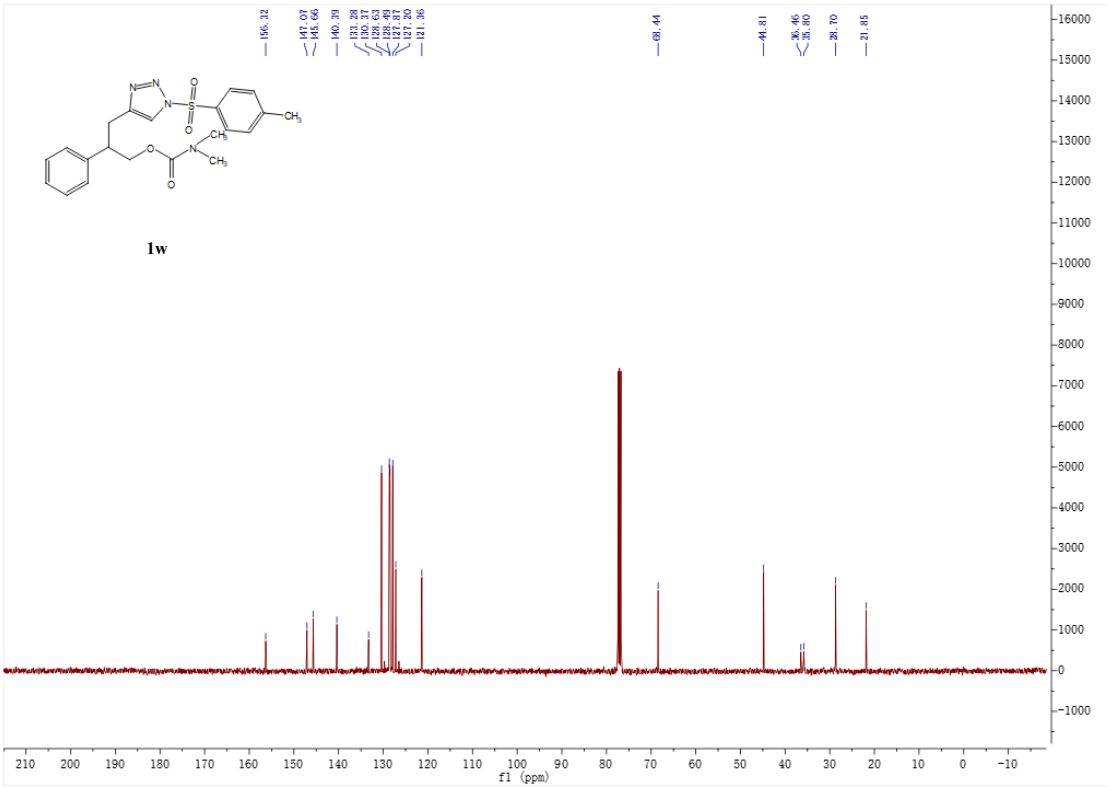
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140.39
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127.20
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69.44
44.81
36.46
35.80
28.70
21.85
f1 (ppm)

1w