Photochemical Chloro-Sulfoximidation of Bicyclo[1.1.1]pentane with Sulfonimidoyl Chlorides

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General Information

Unless otherwise stated, all reagents were purchased from Bide Chemical, TCI, J&K Scientific Ltd, Adamas-beta®, Aladdin or other commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. All kinds of amides, thiophenol, 1,1-dibromo-2,2 bis(chloromethyl)cyclopropane phenyllithium are commercially available. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. The heating reaction condition was performed under oil bath with magnetic stirrer DF-101T. The cooling reaction condition was performed with Chang Cheng cooler DFY-5L. Reactions were monitored by thin layer chromatography using 0.25 mm Merck silica gel precoated plates (60F-254). Visualization was accomplished by irradiation with UV light at 254 nm. Column chromatography was performed using Macherey-Nagel silica gel 60 M (particle size 0.040–0.063 mm). Chemical yields refer to pure isolated substances. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 25 °C on Bruker spectrometers at 400 or 500 MHz respectively, using $CDCl_3$ as the solvent and TMS as the internal reference. The description of the signals includes the following: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Gas chromatographic (GC) analyses are performed on a GC equipped with a flameionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μm df) column. GC-MS analyses are performed on a GC-MS with an EI mode. Crystallographic data were obtained at 223.00 K on a Bruker APEX-II diffractometer, radiation: MoKα (λ = 0.71073). High-resolution mass spectra (HRMS) were recorded on an Agilent UHPLC TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF). The IR spectrum is recorded on a Brucker Alpha FT/IR instrument. The blue LEDs (45 W, λ = 370-550 nm, λ_{max} = 456 nm) is purchased from Kessil.

Starting Materials Preparation

Sulfonimidoyl chlorides

Substrates 1-(a-z, aa-ab)[1], were prepared according to the procedures reported in the literature (Fig. S1).

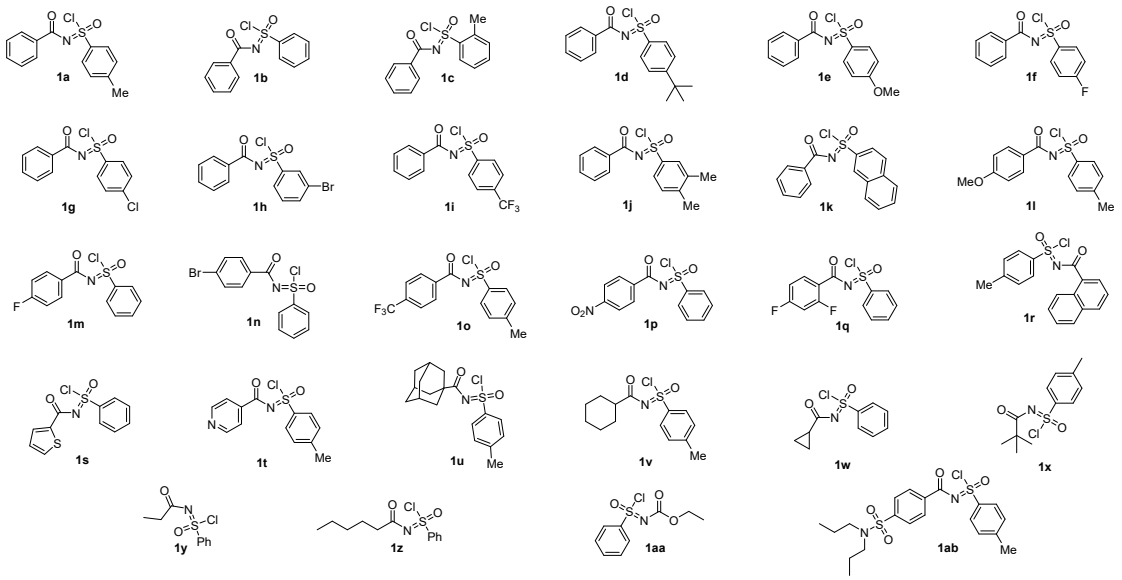
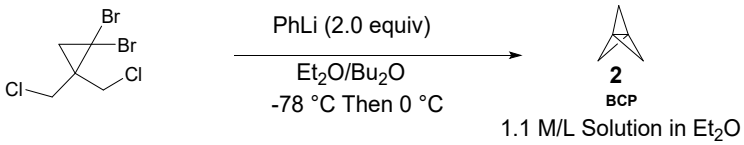


Figure S1. Sulfonimidoyl chlorides used in the reaction.

Preparation of **BCP**



A flame-dried flask equipped with a stir bar was charged with 1,1-dibromo-2,2 bis(chloromethyl)cyclopropane (5.0 g, 16.8 mmol). To this was added 10 mL of Et_2O. The solution was cooled to -78 ºC (a white suspension formed), 20 mL of PhLi (20 mL, 38 mmol, 2.3 equiv, 1.9 M in n-Bu_2O) was added slowly dropwise. The mixture was stirred at -78 ºC for 15 min, then warmed to 0 ºC and stirred for another 2 h. The reaction flask was fitted with a flask-to-flask vacuum distillation piece attached to a receiving flask cooled to -78 ºC. A pump was used to evacuate the system down slowly to ~10 Torr, and the solution was held at this pressure for 10 min. This resulted in the distillation of the Et_2O/propellane solution. The concentration was checked by NMR by taking a 100 µL aliquot of the stock solution and determining the ratio of propellane to an added standard, such as 1,3,5-trimethoxybenzene (35%-45% yield) (Fig. S2). This solution should be kept in a -20 °C freezer, and the propellane is stable for at least several months under these conditions[2].

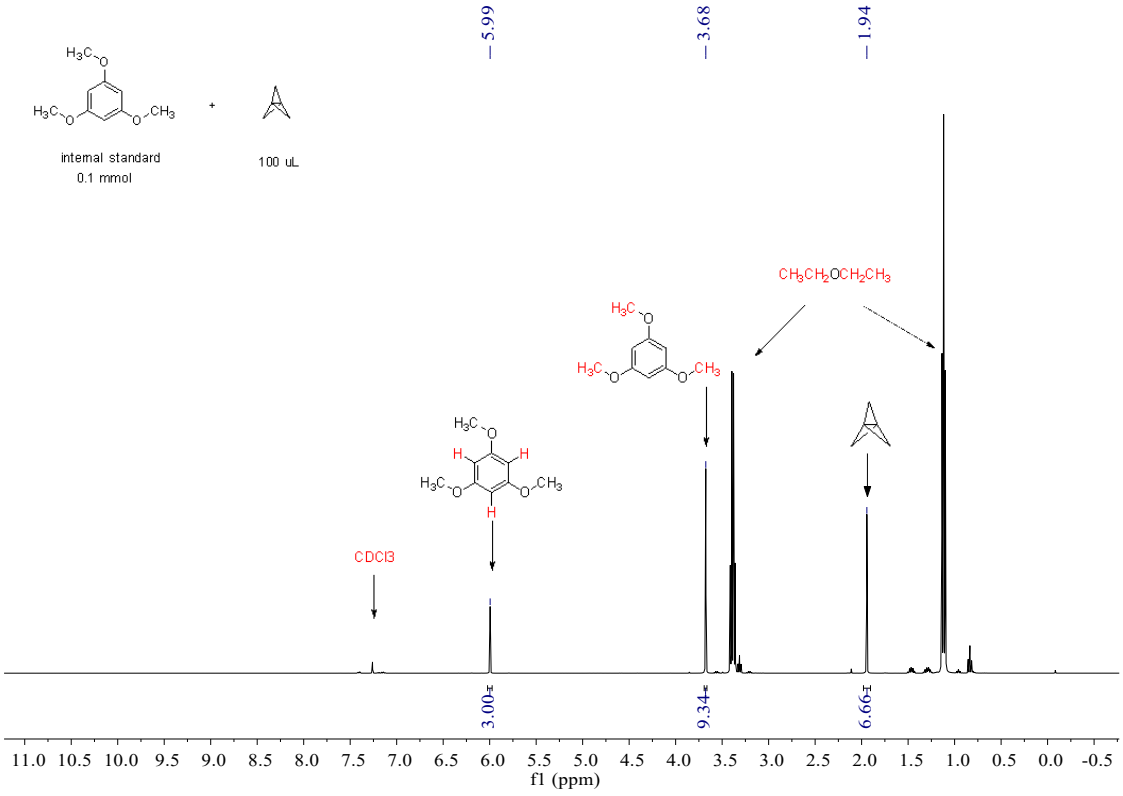


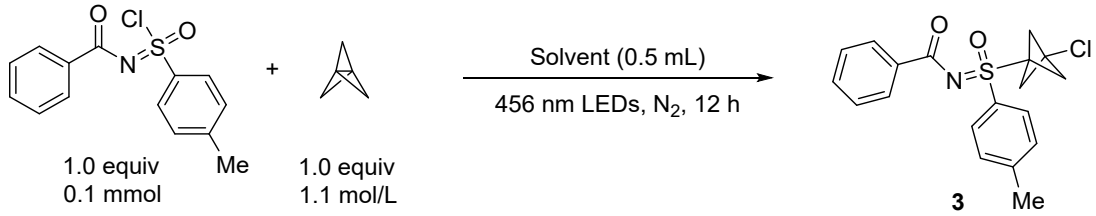
Figure S2. Preparation of BCP.

Optimization of the Reaction Conditions

General Procedure:

In a N_2-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with sulfonimidoyl chlorides (0.1 mmol, 1.0 equiv.), solvent (0.5 mL) and BCP (0.1 mmol, 1.1M, 1.0 equiv.) was added. Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb) for 12 h. After the reaction finished, the solvent is removed under vacuum, and the resulting residue is purified by flash column chromatography to afford the corresponding products.

Table S1. Screening of solvent.

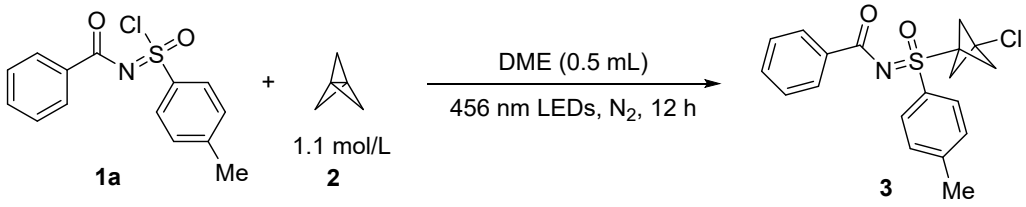


Entry[a]	Solvent	Yield (%)[b]
1	DME	79(76)
2	DME	70[c]
3	DME	63[d]
4	DCM	58
5	DCE	51
6	CH_3CN	43
7	$CHCl_3$	40
8	EA	47
9	DMAC	20
10	DMF	6
11	THF	7
12	DMSO	Trace
13	MeOH	Trace
14	EtOH	8
15	Acetone	49
16	*n*-hexane	24
17	Anisole	57
18	1,4-Dioxane	Trace

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv.), **2** (0.1 mmol, 1.0 equiv, 1.1M), solvent (0.5 mL), blue LEDs, 45 °C, 12 h; [b]GC yield with biphenyl as internal standard is shown and isolated yield is shown in

parenthesis; [c]DME was 1.0 mL; [d]DME was 1.5 mL.

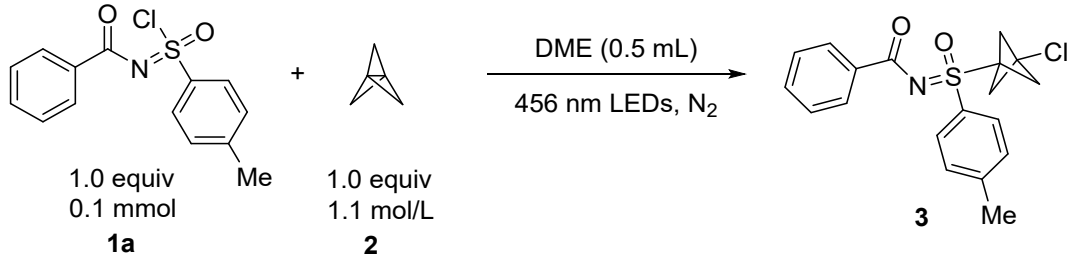
Table S2. Screening of the amount of **1a** and **2**.



Entry[a]	**1a** (equiv.)	**2** (x equiv.)	Yield (%)[b]
1	1.0	1.0	79(76)
2	1.0	1.3	79
3	1.0	1.5	78

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv.), **2** (x equiv, 1.1M), DME (0.5 mL), blue LEDs, 45 ℃, 12 h; [b]GC yield with biphenyl as internal standard is shown and isolated yield is shown in parenthesis.

Table S3. Screening of reaction time.



Entry[a]	Reaction time	Yield (%)[b]
1	1 h	5
2	2 h	18
3	4 h	53
4	6 h	70
5	8 h	72
6	10 h	76
7	11 h	78
8	12 h	79(76)
9	13 h	79
10	18 h	79

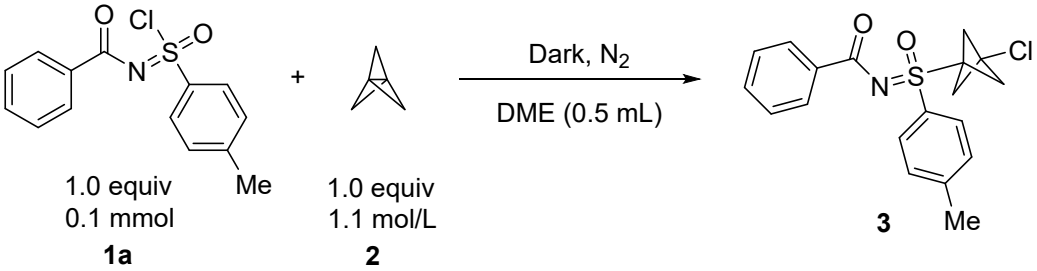
[a]Conditions: **1a** (0.1 mmol, 1.0 equiv.), **2** (0.1 mmol, 1.0 equiv, 1.1M), DME (0.5 mL), blue LEDs, 45 ℃; [b]GC yield with biphenyl as internal standard is shown and isolated yield is shown in parenthesis.

Table S4. Control experiments.

Entry[a]	Variation of conditions	Yield (%)[b]
1	None	79(76)
2	370 nm LED instead of 456 nm LED	47
3	390 nm LED instead of 456 nm LED	29
4	440 nm LED instead of 456 nm LED	74
5	In 25 ℃ Without light	35
6	In 40 ℃ Without light	45
7	In 80 ℃ Without light	52

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv.), **2** (0.1 mmol, 1.0 equiv, 1.1M), DME (0.5 mL), LEDs source, 45 ℃, 12 h; [b]GC yield with biphenyl as internal standard is shown and isolated yield is shown in parenthesis.

Table S5. Investigation of the background reaction in the absence of light.

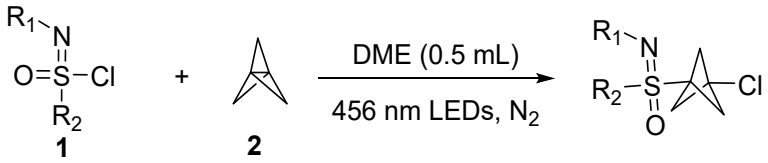


Entry[a]	Temperature (℃)	Reaction time	Yield (%)[b]
1	25	12 h	35
2	25	24 h	50
3	25	36 h	61
4	40	12 h	45
5	40	24 h	56
6	40	36 h	68
7	50	12 h	48
8	50	24 h	58
9	50	36 h	66
10	60	12 h	49
11	60	24 h	60
12	60	36 h	70

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv.), **2** (0.1 mmol, 1.0 equiv, 1.1M), DME (0.5 mL), in dark; [b]GC yield with biphenyl as internal standard is shown and isolated yield is shown in parenthesis.

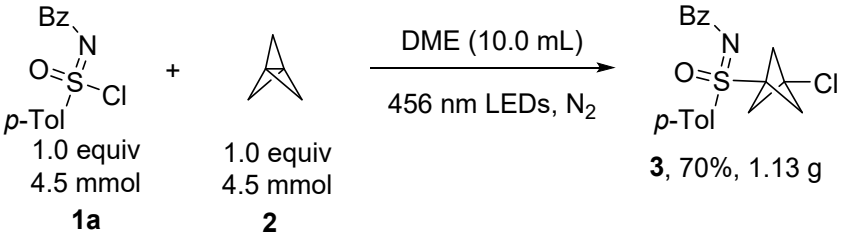
General Procedure for the Reaction

General Procedure



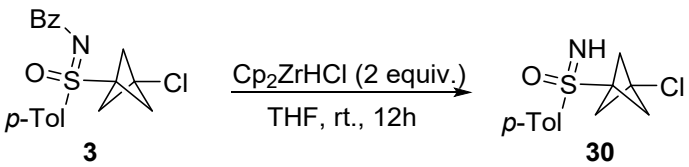
In a N_2-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with sulfonimidoyl chlorides **1** (0.1 mmol, 1.0 equiv.), DME (0.5 mL), and BCP **2** (0.1 mmol, 1.0 equiv, 1.1M). Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb, cooled with a fan, reaction temperature: approximately 45 °C. see reaction set-up below) for 12 h. After the reaction finished, the solvent is removed under vacuum, and the resulting residue is purified by flash column chromatography to afford the corresponding products.

Gram scale synthesis of 3



In a N_2-filled glove-box, an oven-dried vial (25 mL) equipped with a magnetic stir bar was charged with **1a** (4.5 mmol, 1.0 equiv.), DME (10.0 mL), and **2** (4.5 mmol, 1.0 equiv, 1.1M). Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb) for 30 h. After the reaction finished, the solvent is removed under vacuum, and the resulting residue is purified by flash column chromatography to afford the corresponding product **3** (70%, 1.13g).

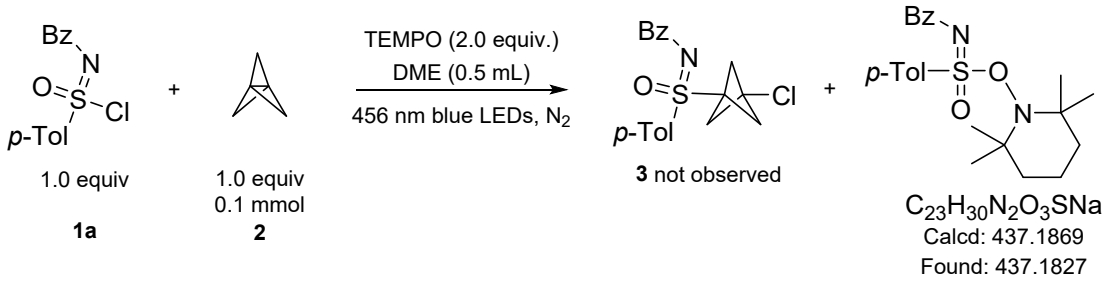
The synthesis of 30



According to the procedures reported in the literature.[3] A 10 mL screw-cap reaction tube equipped with a stirring bar was charged with **3** (0.20 mmol) and 2.0 mL THF. Then Schwartz's reagent (0.4 mmol, 2.0 equiv. cas: 37342-97-5), was added and the mixture was stirred at room temperature for 12h. After completion, the reaction was quenched by adding H_2O and was neutralized by adding 5 mL NaOH (1.0 M) solution. Then the reaction mixture was extracted with ethyl acetate (10 x 2 mL). After concentration under reduced pressure, and the resulting residue is purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 2:1) to afford a colorless oil **30** (71%).

Mechanism studies

Radical-Trapping Experiments



In a N_2-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with sulfonimidoyl chlorides **1a** (0.1 mmol, 1.0 equiv.), TEMPO (0.2 mmol, 2.0 equiv.), DME (0.5 mL), and BCP **2** (0.1 mmol, 1.0 equiv, 1.1M). Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb) for 12 h. After the reaction finished, the reaction mixture is analyzed by GC and HRMS (Fig. S4). No desired product **3** is detected. These results indicated that a radical mechanism might be operative.

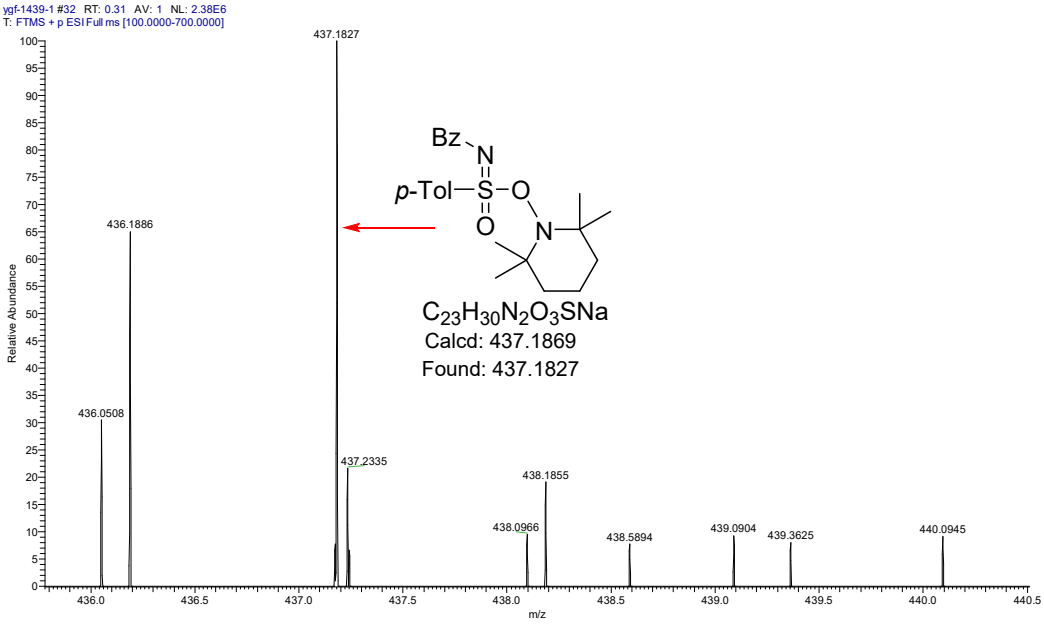
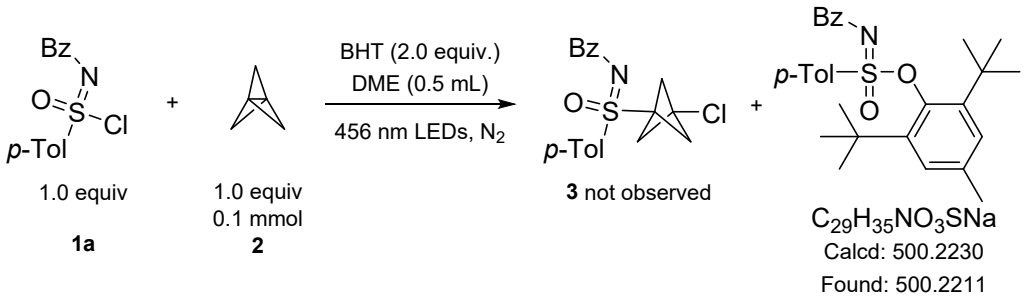


Figure S3. The HRMS result for radical trapping with TEMPO.



In a N_2-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with sulfonimidoyl chlorides **1a** (0.1 mmol, 1.0 equiv.), BHT (0.2 mmol, 2.0 equiv.), DME (0.5 mL), and BCP **2** (0.1 mmol, 1.0 equiv, 1.1M). Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb) for 12 h. After the reaction finished, the reaction mixture is analyzed by GC and HRMS (Fig. S5). No desired product **3** is detected. These results indicated that a radical mechanism might be operative.

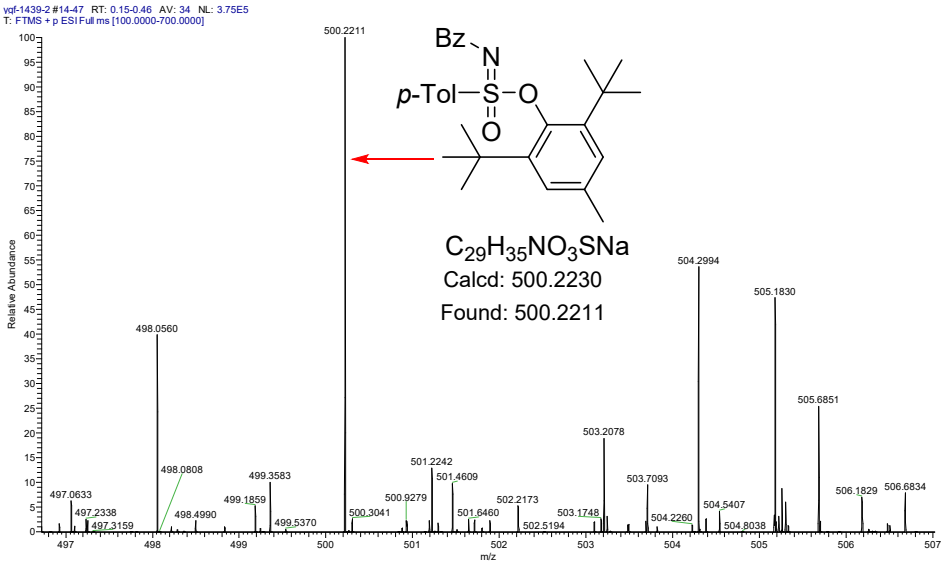
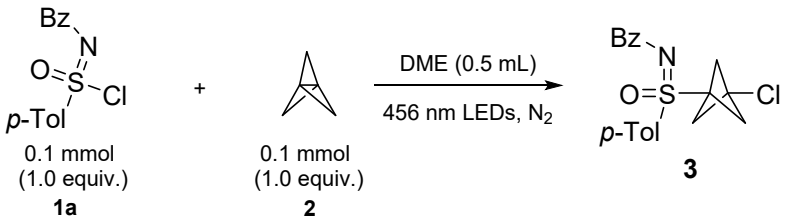


Figure S4. The HRMS result for radical trapping with BHT.

Turn on/off profile experiment



In a N_2-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with sulfonimidoyl chlorides **1a** (0.1 mmol, 1.0 equiv.), DME (0.5 mL), and BCP **2** (0.1 mmol, 1.0 equiv, 1.1M). Then the vial was sealed with a rubber cap, removed from the glove-box. The resulting reaction mixture is vigorously stirred under the irradiation of blue LEDs (distance app. 4.0 cm from the bulb). The process of photocatalytic reaction with and without light was monitored by GC, the yields were detected using biphenyl as internal standard (Fig. S6). Given the presence of a measurable background reaction, light on/off experiments indicated that the reaction proceeds slowly even in the absence of irradiation.

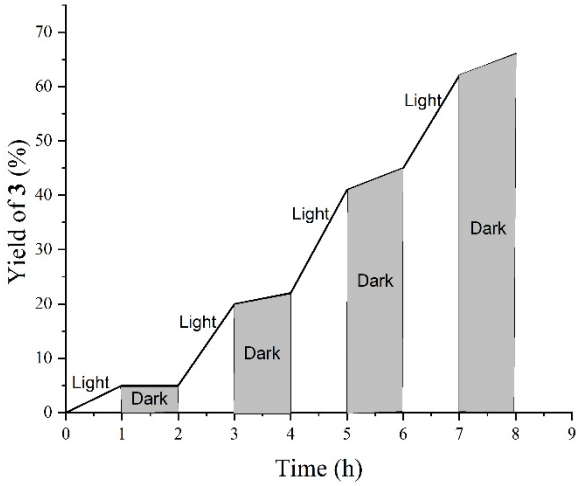


Figure S5. Light on/off experiment.

Quantum yield measurement

The quantum yield (Φ) is determined by the known ferrioxalate actinometry method. A ferrioxalate actinometry solution is prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry. The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm (Fig. S7).

The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The solutions are prepared and stored in a dark laboratory:

1. Potassium ferrioxalate solution: 59 mg of potassium ferrioxalate and 27.8 μL of sulfuric acid (96%) are added to a 10 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. Phenantroline solution: 0.2% by weight of 1,10-phenanthroline in water (20 mg in 10 mL volumetric flask).
3. Buffer solution: to a 10 mL volumetric flask, 494 mg of NaOAc and 100 μL of sulfuric acid (96%)

are added and filled to the mark with water (HPLC grade). To determine the photon flux of the spectrophotometer, 1.0 mL of the ferrioxalate solution is placed in a flame-dried tube and irradiated with blue LEDs for specified time intervals (5 s, 15 s, 30 s, 45 s, and 60 s). After irradiation, the actinometer solution is removed and placed in a 10 mL volumetric flask containing 0.18 mL of 1,10-phenanthroline solution and 1 mL of buffer solution. This flask is filled to the mark with water (HPLC grade). The flask is then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution is measured at 510 nm.

Based on the data, we get the graph between the number of moles of Fe(II) product (y axis) and time (x axis). Then, the irradiated light intensity is estimated to 1.20 x 10^{-8} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.

For five clean tubes, according to the general procedure, the 0.1 mmol scale model reaction solution is irradiated with Blue LEDs for specified time intervals (30 min, 60 min, 90 min, 120 min and 150 min). The moles of products formed are determined by GC, and the yields are detected using

biphenyl as reference standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity). The slope gives the quantum yield (Φ) of the photoreaction, 0.34259 (34.3%). Thus, a radical chain pathway is less likely.

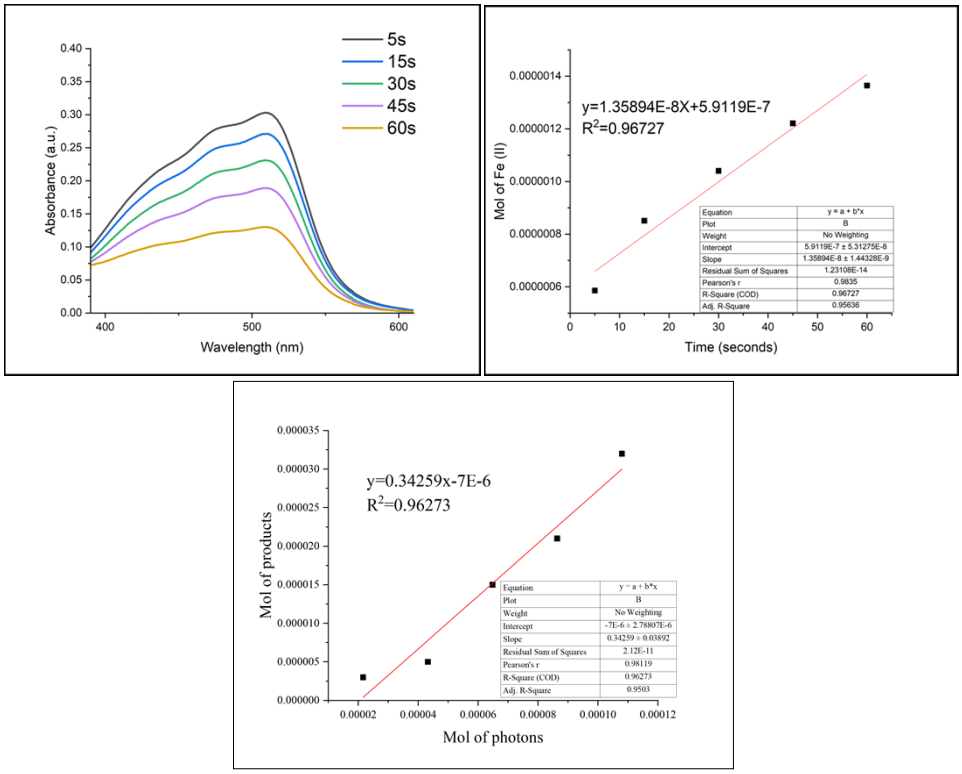


Figure S6. Quantum yield measurement.

UV/Vis absorption spectroscopy Studies

Dichloromethane degassed with a stream of Ar for 1 h. First, we prepare **1a** (0.0005 mol/L, 50 mL), **2** (0.0005 mol/L, 50 mL). Pure dichloromethane solution absorption is subtracted as background. We measure the UV–vis absorption of **1a**, **2**, and **1a** + **2** mixture, which ranging from 250 nm to 800 nm and all results are showed below (Fig. S7). UV-visible absorption spectroscopy indicated that neither (**1a**) nor (**2**) exhibits significant absorption under the reaction conditions.

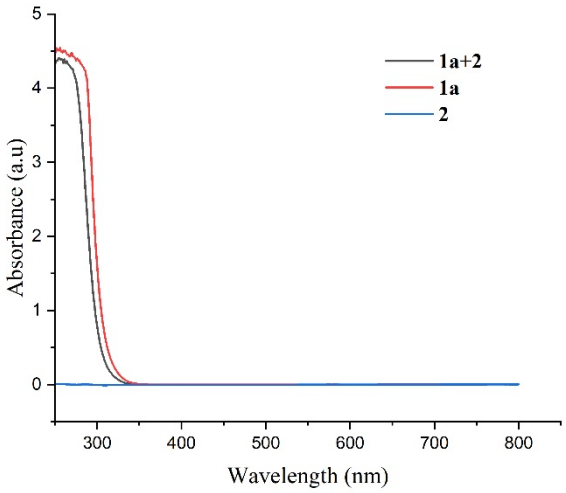


Figure S7. UV/Vis absorption spectroscopy.

Failed examples

Under standard conditions, we attempted several S-alkyl-, S-heteroaryl-substituted, and drug-derived sulfonimidoyl chlorides, but all were ineffective (Fig. S8).

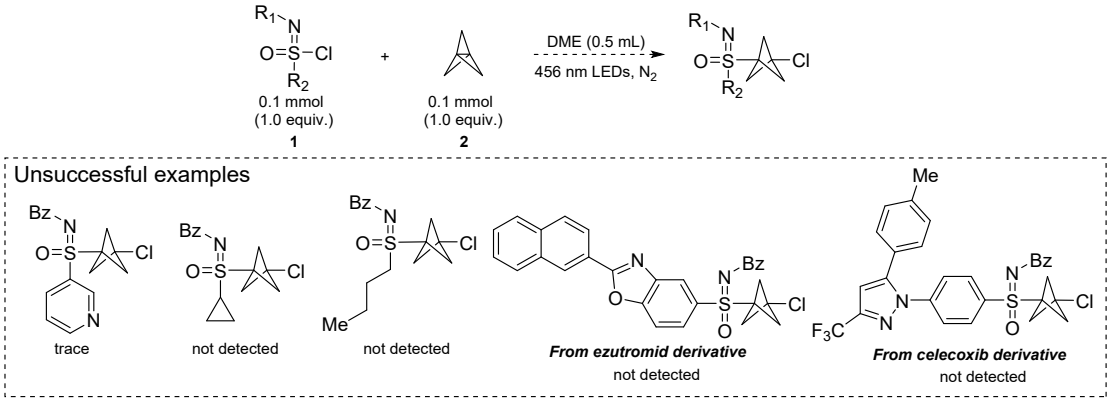


Figure S8. Failed examples.

Evaluation of In Situ Generated Sulfonimidoyl Bromides in Reactions with BCP

In the first step, DBDMH (3.5 equiv), cesium carbonate (2.0 equiv), amide (0.1 mmol), and thiophenol (2.5 equiv) were sequentially added to a reaction tube. DCM (1.5 mL) was then added, and the mixture was stirred at 25 °C for 6 hours. The reaction mixture was then concentrated under reduced pressure. Subsequently, in a N_2-filled glovebox, DME (0.5 mL) and BCP 2 (0.1 mmol, 1.0 equiv, 1.1 M) were sequentially added. The tube was then sealed with a rubber cap and removed from the glovebox. The resulting reaction mixture was vigorously stirred under irradiation from blue LEDs (distance ca. 4.0 cm from the bulb) for 12 hours. No formation of the desired product was observed (Fig. S9).

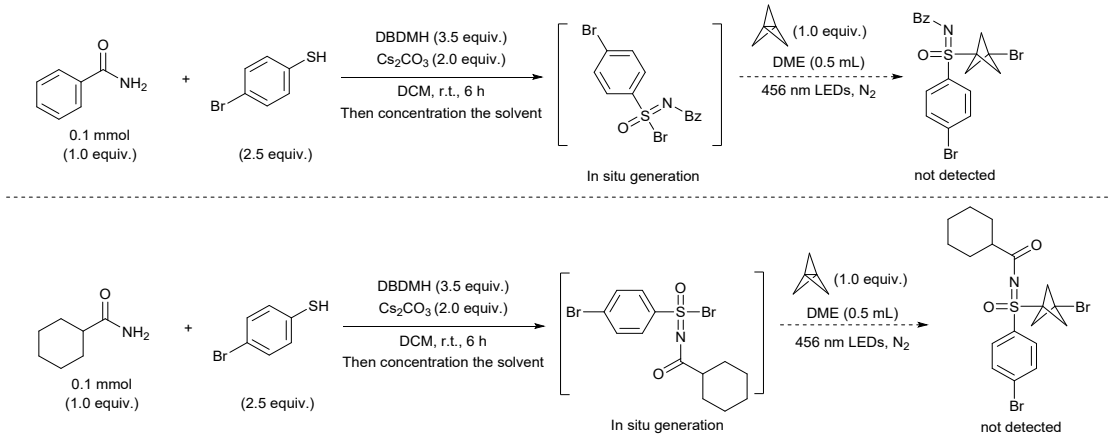
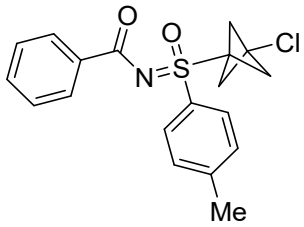


Figure S9. Attempted reaction of sulfonimidoyl bromides with BCP.

Characterization of products



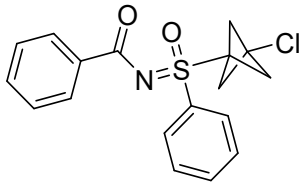
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ⁶-sulfaneylidene)benzamide (3): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (27.3 mg, 76%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 – 8.14 (m, 2H), 7.81 – 7.78 (m, 2H), 7.53 – 7.50 (m, 1H), 7.43 – 7.38 (m, 4H), 2.53 – 2.46 (m, 6H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 174.0, 145.4, 135.6, 132.4, 132.3, 130.5, 129.6, 128.2, 128.16, 57.8, 50.9, 48.5, 21.8.

IR v (neat, cm^{-1}): 2925, 1635, 1579, 1449, 1311, 1276, 1228, 1171, 714, 568.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{19}ClNO_2S$: 360.0820; Found 360.0818.



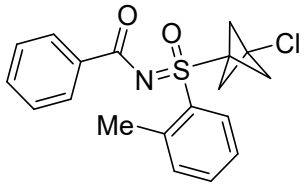
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene)benzamide (4): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (27.6 mg, 80%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.15 (m, 2H), 7.95 – 7.92 (m, 2H), 7.72 – 7.67 (m, 1H), 7.63 – 7.59 (m, 2H), 7.55 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 2.57 – 2.43 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 135.5, 135.47, 134.2, 132.4, 129.8, 129.7, 128.2, 128.19, 57.9, 50.7, 48.4.

IR v (neat, cm^{-1}): 2926, 1635, 1579, 1448, 1311, 1277, 1229, 1202, 1130, 714.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{17}ClNO_2S$: 346.0663; Found 346.0659.

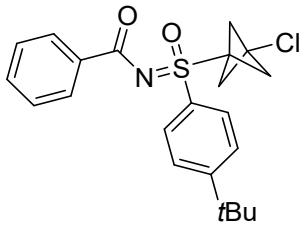


N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(o-tolyl)-λ⁶-sulfaneylidene)benzamide (5): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (26.9 mg, 75%).

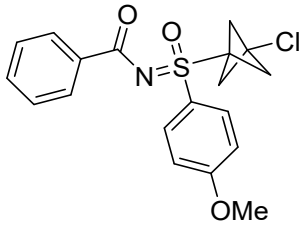
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.13 (m, 2H), 8.01 – 7.98 (m, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.38 (m, 3H), 7.36 – 7.34 (m, 1H), 2.62 (s, 3H), 2.54 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 138.6, 135.4, 134.0, 133.7, 133.6, 132.4, 130.5, 129.7, 128.2, 127.4, 57.7, 50.9, 48.3, 21.2.

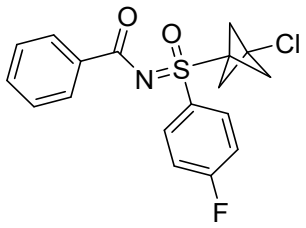
IR v (neat, cm^{-1}): 2923, 1634, 1579, 1449, 1311, 1274, 1227, 1201, 1129, 714.
HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{19}ClNO_2S$: 360.0820; Found 360.0816.



N-((4-(tert-butyl)phenyl)(3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)-λ^6-sulfaneylidene)benzamide (6): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (26.5 mg, 66%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.15 (m, 2H), 7.85 – 7.82 (m, 2H), 7.61 – 7.58 (m, 2H), 7.54 – 7.50 (m, 1H), 7.44 – 7.39 (m, 2H), 2.55 – 2.47 (m, 6H), 1.35 (s, 9H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 158.2, 135.6, 132.4, 132.2, 129.6, 128.2, 128.1, 126.9, 57.9, 51.0, 48.5, 35.5, 31.2.
IR v (neat, cm^{-1}): 2926, 1636, 1449, 1399, 1311, 1278, 1134, 923, 827, 713.
HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{25}ClNO_2S$: 402.1289; Found 402.1281.



N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)benzamide (7): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (25.9 mg, 69%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.14 (m, 2H), 7.86 – 7.82 (m, 2H), 7.53 – 7.49 (m, 1H), 7.43 – 7.39 (m, 2H), 7.07 – 7.03 (m, 2H), 3.88 (s, 3H), 2.54 – 2.46 (m, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.9, 164.3, 135.7, 132.3, 130.4, 129.6, 128.2, 126.2, 115.2, 57.8, 55.9, 51.1, 48.5.
IR v (neat, cm^{-1}): 2923, 1634, 1593, 1495, 1449, 1311, 1280, 833, 714, 570.
HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{19}ClNO_3S$: 376.0769; Found 376.0763.



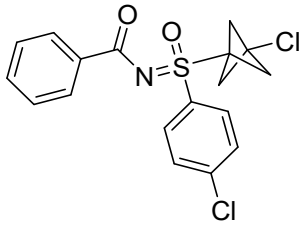
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(4-fluorophenyl)(oxo)-λ^6-sulfaneylidene)benzamide (8): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (25.3 mg, 70%).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.07 (m, 2H), 7.96 – 7.92 (m, 2H), 7.57 – 7.49 (m, 1H), 7.43 – 7.40 (m, 2H), 7.34 – 7.26 (m, 2H), 2.61 – 2.43 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.9, 166.2 (d, *J* = 258.3 Hz), 135.3, 132.6, 131.3 (d, *J* = 3.8 Hz), 131.1 (d, *J* = 10.1 Hz), 129.6, 128.2, 117.3 (d, *J* = 23.9 Hz), 57.8, 50.9, 48.4.

^{19}F{^{1}H} NMR (471 MHz, Chloroform-*d*) δ -102.67.

IR v (neat, cm^{-1}): 2926, 1635, 1587, 1490, 1449, 1311, 1277, 714, 568, 522.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}ClFNO_2S$: 364.0569; Found 364.0562.



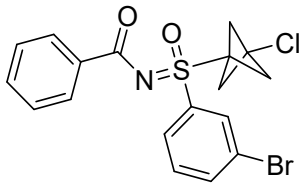
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)(oxo)-λ^6-sulfaneylidene)benzamide (9): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (27.4 mg, 72%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.09 (m, 2H), 7.89 – 7.81 (m, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 2.57 – 2.45 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.9, 141.1, 135.2, 134.0, 132.6, 130.2, 129.7, 128.2, 57.8, 50.8, 48.4.

IR v (neat, cm^{-1}): 2925, 1635, 1579, 1475, 1449, 1311, 1275, 1230, 749, 598.9.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}Cl_2NO_2S$: 380.0273; Found 380.0266.



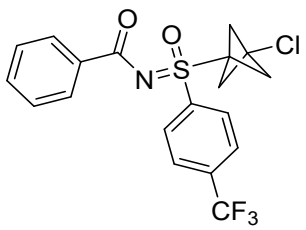
N-((3-bromophenyl)(3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)-λ^6-sulfaneylidene)benzamide (10): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (30.9 mg, 73%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 – 8.10 (m, 2H), 8.06 – 8.06 (m, 1H), 7.86 – 7.78 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.44 – 7.41 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.45 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.9, 137.6, 137.3, 135.1, 132.7, 131.3, 131.0, 129.7, 128.3, 126.7, 124.0, 57.9, 50.8, 48.4.

IR v (neat, cm^{-1}): 1635, 1449, 1311, 1277, 1230, 1201, 713, 582, 560, 453

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}BrClNO_2S$: 423.9768; Found 423.9747.



N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)benzamide (11): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a

colorless oil (26.8 mg, 65%).

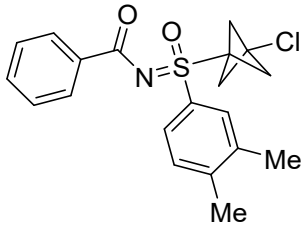
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.11 (m, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.44 – 7.41 (m, 2H), 2.61 – 2.46 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 174.0, 139.6, 136.0 (d, *J* = 34.0 Hz), 135.0, 132.8, 129.7, 128.9, 128.3, 127.0 (q, *J* = 3.8 Hz), 123.1 (d, *J* = 273.4 Hz), 57.8, 50.6, 48.4.

^{19}F{^{1}H} NMR (471 MHz, Chloroform-*d*) δ -63.22.

IR v (neat, cm^{-1}): 2926, 1636, 1579, 1449, 1403, 1322, 1276, 1232, 1173, 1062.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{16}ClF_3NO_2S$: 414.0537; Found 414.0528.



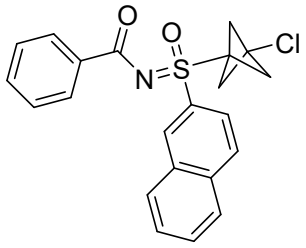
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(3,4-dimethylphenyl)(oxo)-λ^6-sulfaneylidene)benzamide (12): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (29.1 mg, 78%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.15 (m, 2H), 7.67 – 7.65 (m, 1H), 7.63 – 7.60 (m, 1H), 7.53 – 7.49 (m, 1H), 7.43 – 7.39 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 2.54 – 2.46 (m, 6H), 2.34 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.9, 144.0, 138.7, 135.6, 132.3, 132.2, 130.9, 129.6, 128.7, 128.1, 125.64 57.7, 50.8, 48.4, 20.1, 20.08.

IR v (neat, cm^{-1}): 2926, 1635, 1578, 1311, 1276, 1200, 1127, 1025, 714, 584.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{21}ClNO_2S$: 374.0976; Found 374.0970.



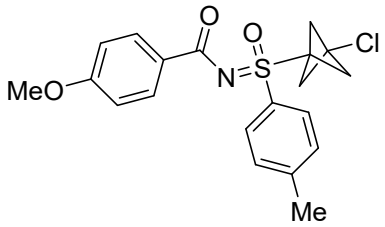
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(naphthalen-2-yl)(oxo)-λ^6-sulfaneylidene)benzamide (13): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (26.8 mg, 68%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 1.6 Hz, 1H), 8.20 – 8.17 (m, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.80 (m, 1H), 7.72 – 7.63 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.41 (m, 2H), 2.58 – 2.50 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 135.6, 135.5, 132.6, 132.5, 132.4, 130.4, 130.1, 129.8, 129.7, 129.6, 128.21, 128.2, 128.1, 122.5, 58.0, 51.0, 48.5.

IR v (neat, cm^{-1}): 2922, 1634, 1449, 1311, 1279, 1227, 1126, 921, 714, 565.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{19}ClNO_2S$: 396.0820; Found 396.0810.



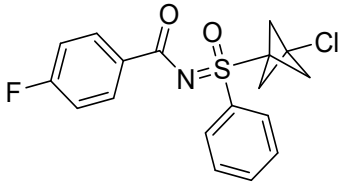
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)-4-methoxybenzamide (14): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (23.3 mg, 60%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 8.07 (m, 2H), 7.80 – 7.77 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.92 – 6.87 (m, 2H), 3.86 (s, 3H), 2.55 – 2.43 (m, 9H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 173.5, 163.1, 145.2, 132.5, 131.7, 130.5, 128.3, 113.4, 57.8, 55.5, 50.9, 48.5, 21.8.

IR v (neat, cm^{-1}): 2923, 1631, 1602, 1508, 1278, 1253, 1200, 847, 771, 950.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{21}ClNO_3S$: 390.0925; Found 390.0919.



N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-fluorobenzamide (15): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (28.9 mg, 79%).

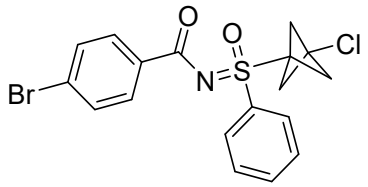
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.11 (m, 2H), 7.96 – 7.86 (m, 2H), 7.75 – 7.66 (m, 1H), 7.61 (m, 2H), 7.13 – 7.02 (m, 2H), 2.56 – 2.43 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 165.6 (d, *J* = 253.5 Hz), 135.4, 134.2, 132.1 (d, *J* = 9.1 Hz), 131.7 (d, *J* = 3.0 Hz), 129.9, 128.2, 115.1 (d, *J* = 22.2 Hz), 57.8, 50.8, 48.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.25 (m).

IR v (neat, cm^{-1}): 2923, 1635, 1600, 1504, 1504, 1447, 1272, 1223, 1130, 686.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}ClFNO_2S$: 364.0569; Found 364.0564.



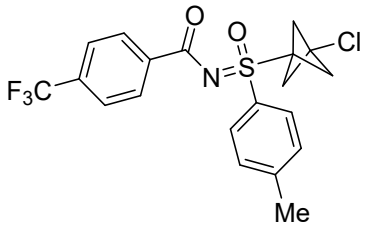
4-bromo-N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)benzamide (16): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (30.9 mg, 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.99 (m, 2H), 7.92 – 7.89 (m, 2H), 7.73 – 7.68 (m, 1H), 7.64 – 7.59 (m, 2H), 7.56 – 7.53 (m, 2H), 2.54 – 2.45 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 135.3, 134.4, 134.3, 131.5, 131.3, 129.9, 128.2, 127.4, 57.9, 50.9, 48.4.

IR v (neat, cm^{-1}): 2925, 1636, 1449, 1311, 1277, 1232, 1129, 925, 712, 584.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}BrClNO_2S$: 423.9768; Found 423.9745.



N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)-4-(trifluoromethyl)benzamide (17): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (31.2 mg, 73%).

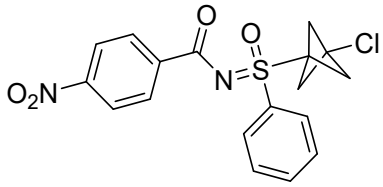
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.24 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.78 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.66 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.40 (d, *J* = 8.0 Hz, 2H), 2.55 – 2.49 (m, 6H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.6, 145.7, 138.8, 133.7 (d, *J* = 32.3 Hz), 131.8, 130.6, 129.9, 128.2, 125.2 (q, *J* = 4.0 Hz), 124.0 (d, *J* = 272.7 Hz), 57.8, 50.9, 48.4, 21.8.

^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ -62.87.

IR v (neat, cm^{-1}): 2928, 1636, 1581, 1409, 1326, 1231, 1179, 921, 864, 705.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{18}ClF_3NO_2S$: 428.0693; Found 428.0679.



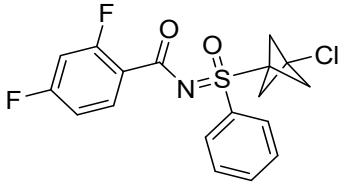
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-nitrobenzamide (18): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (24.6 mg, 63%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.23 (m, 4H), 7.94 – 7.91 (m, 2H), 7.76 – 7.72 (m, 1H), 7.66 – 7.62 (m, 2H), 2.57 – 2.48 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.3, 150.7, 141.3, 135.3, 135.0, 131.1, 130.5, 128.6, 123.8, 58.3, 51.3, 48.8.

IR v (neat, cm^{-1}): 2925, 1639, 1602, 1523, 1448, 1276, 1230, 1202, 721, 583.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{16}ClN_2O_4S$: 391.0514; Found 391.0507.



N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-2,4-difluorobenzamide (19): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (32.5 mg, 82%).

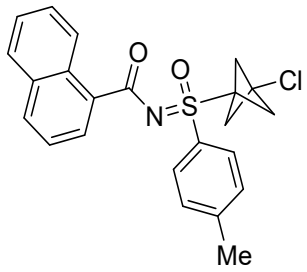
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.98 (m, 1H), 7.94 – 7.92 (m, 2H), 7.71 – 7.67 (m, 1H), 7.63 – 7.59 (m, 2H), 6.91 – 6.80 (m, 2H), 2.52 – 2.44 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6 (d, *J* = 4.0 Hz), 165.2 (d, *J* = 259.6 Hz), 162.6 (d, *J* = 259.6 Hz), 135.0, 134.3, 134.0 (dd, *J* = 11.1, 3.0 Hz), 129.9, 128.2, 120.7 (dd, *J* = 10.1, 4.0 Hz), 111.3 (dd, *J* = 21.2, 4.0 Hz), 105.0 (dd, *J* = 27.3, 25.3 Hz), 57.9, 50.8, 48.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.85 – 103.9 (m), -104.35 – -104.50 (m).

IR v (neat, cm^{-1}): 2927, 1635, 1612, 1499, 1447, 1227, 1131, 916, 686, 548.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{15}ClF_2NO_2S$: 382.0475; Found 382.0471.



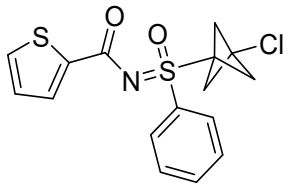
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)-1-naphthamide (20): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (29.9 mg, 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.03 (d, *J* = 8.4 Hz, 1H), 8.36 – 8.35 (m, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.84 (m, 3H), 7.59 – 7.46 (m, 3H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.53 (m, 6H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.3, 145.4, 134.1, 132.7, 132.3, 131.5, 130.6, 130.2, 128.4, 128.3, 127.4, 126.7, 126.0, 124.6, 57.9, 51.0, 48.5, 21.8.

IR v (neat, cm^{-1}): 2924, 1632, 1591, 1508, 1279, 1243, 1199, 813, 782, 649.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{21}ClNO_2S$: 410.0976; Found 410.0970.



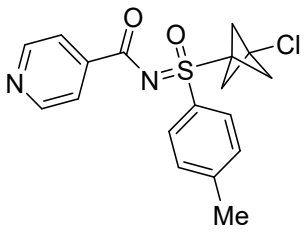
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)thiophene-2-carboxamide (21): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (22.8 mg, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.80 – 7.78 (m, 1H), 7.72 – 7.68 (m, 1H), 7.63 – 7.59 (m, 2H), 7.50 – 7.48 (m, 1H), 7.09 – 7.06 (m, 1H), 2.56 – 2.41 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 141.0, 135.3, 134.3, 132.5, 131.9, 129.9, 128.3, 127.9, 57.9, 50.9, 48.4.

IR v (neat, cm^{-1}): 2924, 1623, 1521, 1447, 1416, 1359, 1266, 1227, 1120, 751.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{15}ClNO_2S_2$: 352.0227; Found 352.0218.



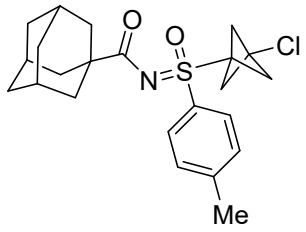
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)isonicotinamide (22): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (26.6 mg, 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 – 8.73 (m, 2H), 7.94 – 7.93 (m, 2H), 7.80 – 7.77 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.57 – 2.44 (m, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.3, 150.4, 145.9, 142.7, 131.6, 130.7, 128.2, 123.0, 57.9, 50.9, 48.4, 21.8.

IR v (neat, cm^{-1}): 2923, 1639, 1594, 1557, 1408, 1322, 1285, 1231, 1141, 568.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{18}ClN_2O_2S$: 361.0772; Found 361.0768.



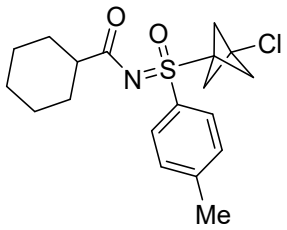
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)-1-naphthamide (23): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (17.5 mg, 42%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.46 – 2.35 (m, 9H), 2.05 – 1.97 (m, 3H), 1.93 – 1.90 (m, 6H), 1.74 – 1.68 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.3, 145.0, 132.7, 130.4, 128.2, 57.9, 50.7, 48.4, 43.5, 39.7, 36.9, 28.5, 21.7.

IR v (neat, cm^{-1}): 2903, 2849, 1635, 1451, 1324, 1231, 1111, 941, 856, 578.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{29}ClNO_2S$: 418.1602; Found 418.1592.



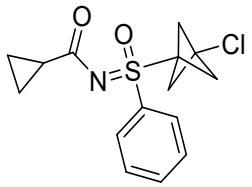
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ^6-sulfaneylidene)cyclohexanecarboxamide (24): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (18.3 mg, 50%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.70 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.48 – 2.35 (m, 9H), 2.03 – 1.87 (m, 2H), 1.82 – 1.70 (m, 2H), 1.67 – 1.62 (m, 2H), 1.51 – 1.36 (m, 2H), 1.35 – 1.17 (m, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.5, 145.1, 132.5, 130.4, 128.1, 57.9, 50.7, 48.3, 47.8, 29.9, 26.1, 25.9, 21.7.

IR v (neat, cm^{-1}): 2927, 2853, 1644, 1449, 1309, 1275, 1247, 1227, 1199, 575.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{25}ClNO_2S$: 366.1289; Found 366.1282.



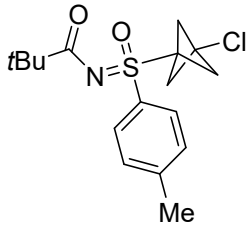
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene)cyclopropanecarboxamide (25): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (12.4 mg, 40%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.69 – 7.65 (m, 1H), 7.61 – 7.56 (m, 2H), 2.45 – 2.37 (m, 6H), 1.79 – 1.73 (m, 1H), 1.03 – 0.96 (m, 2H), 0.85 – 0.78 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.9, 135.5, 133.9, 129.6, 128.0, 57.7, 50.6, 48.2, 17.9, 9.2, 9.1.

IR v (neat, cm^{-1}): 2923, 1635, 1447, 1382, 1347, 1274, 1228, 1201, 867, 687.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{17}ClNO_2S$: 310.0663; Found 310.0655.



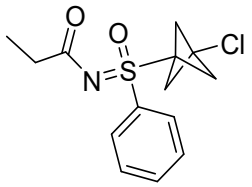
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-λ⁶-sulfaneylidene)pivalamide (26): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (20.7 mg, 61%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.42 – 2.36 (m, 6H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.2, 145.1, 132.6, 130.4, 128.1, 57.8, 50.7, 48.3, 41.7, 27.9, 21.7.

IR v (neat, cm^{-1}): 2971, 1644, 1478, 1391, 1284, 1228, 1172, 1097, 845, 656.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{17}H_{23}ClNO_2S$: 340.1133; Found 340.1131.



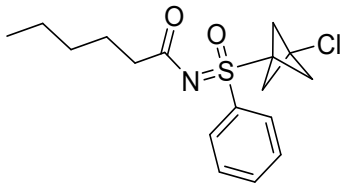
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene)propionamide (27): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (11.9 mg, 40%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.70 – 7.65 (m, 1H), 7.61 – 7.57 (m, 2H), 2.46 – 2.38 (m, 8H), 1.15 –1.11 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.5, 135.6, 134.0, 129.7, 128.1, 57.9, 50.7, 48.4, 32.9, 10.0.

IR v (neat, cm^{-1}): 2924, 1649, 1448, 1349, 1274, 1201, 1098, 836, 754, 568.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{17}ClNO_2S$: 298.0663; Found 298.0654.



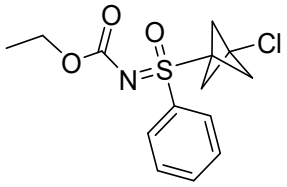
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene)hexanamide (28): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (11.2 mg, 33%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.70 – 7.65 (m, 1H), 7.61 – 7.57 (m, 2H), 2.46 – 2.38 (m, 8H), 1.68 – 1.62 (m, 2H), 1.34 – 1.30 (m, 4H), 0.91 – 0.88 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.0, 135.6, 134.0, 129.7, 128.2, 57.9, 50.7, 48.4, 39.7, 31.6, 25.5, 22.6, 14.1.

IR v (neat, cm^{-1}): 2956, 2927, 2857, 1649, 1448, 1227, 1201, 1184, 1099, 687.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{17}H_{23}ClNO_2S$: 340.1133; Found 340.1126.



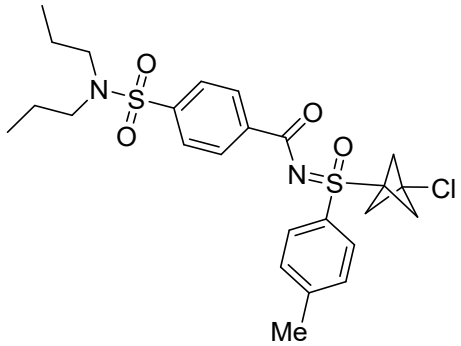
ethyl ((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene)carbamate (29): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (13.1 mg, 42%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 2H), 7.72 – 7.68 (m, 1H), 7.63 – 7.58 (m, 2H), 4.15 – 4.02 (m, 2H), 2.48 – 2.41 (m, 6H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 135.3, 134.3, 129.8, 128.4, 62.4, 57.6, 50.5, 48.4, 14.4.

IR v (neat, cm^{-1}): 2981, 2925, 1671, 1448, 1367, 1241, 1202, 1147, 1019, 734.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{17}ClNO_3S$: 314.0612; Found 314.0605.



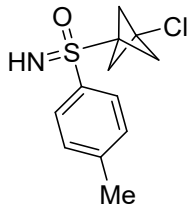
N-((3-chlorobicyclo[1.1.1]pentan-1-yl)(oxo)(p-tolyl)-l6-sulfaneylidene)-4-(N,N-dipropylsulfamoyl)benzamide (30): Prepared according to **condition A**, and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 4:1) to afford a colorless oil (33.9 mg, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.21 (m, 2H), 7.89 – 7.82 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.16 – 3.03 (m, 4H), 2.59 – 2.44 (m, 9H), 1.60 – 1.50 (m, *J* = 7.4 Hz, 4H), 0.87 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.4, 145.7, 143.4, 138.9, 131.8, 130.6, 130.1, 128.1, 126.8, 57.8, 50.9, 50.1, 48.4, 22.1, 21.8, 11.3.

IR v (neat, cm^{-1}): 2949, 2911, 1660, 1533, 1421, 1301, 1273, 1150, 1111, 898.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{32}ClN_2O_4S_2$: 523.1487; Found 523.1468.



(3-chlorobicyclo[1.1.1]pentan-1-yl)(imino)(p-tolyl)-λ^6-sulfanone (31): Purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 2:1) to afford a colorless oil (36.2 mg, 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 1H), 2.44 (s, 3H), 2.38 – 2.31 (m, 6H).

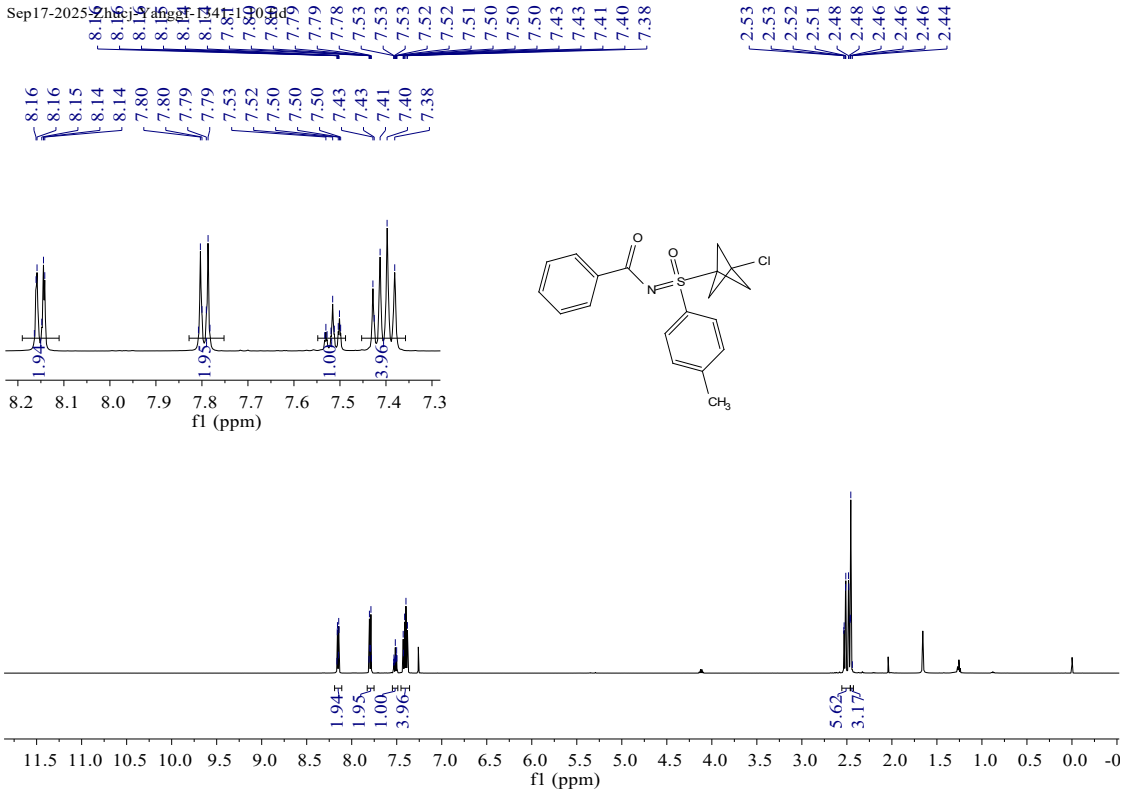
^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 136.1, 130.0, 128.9, 57.1, 51.3, 48.4, 21.7.

IR v (neat, cm^{-1}): 2922, 1533, 1463, 1388, 1260, 1222, 1108, 1005, 955, 814.

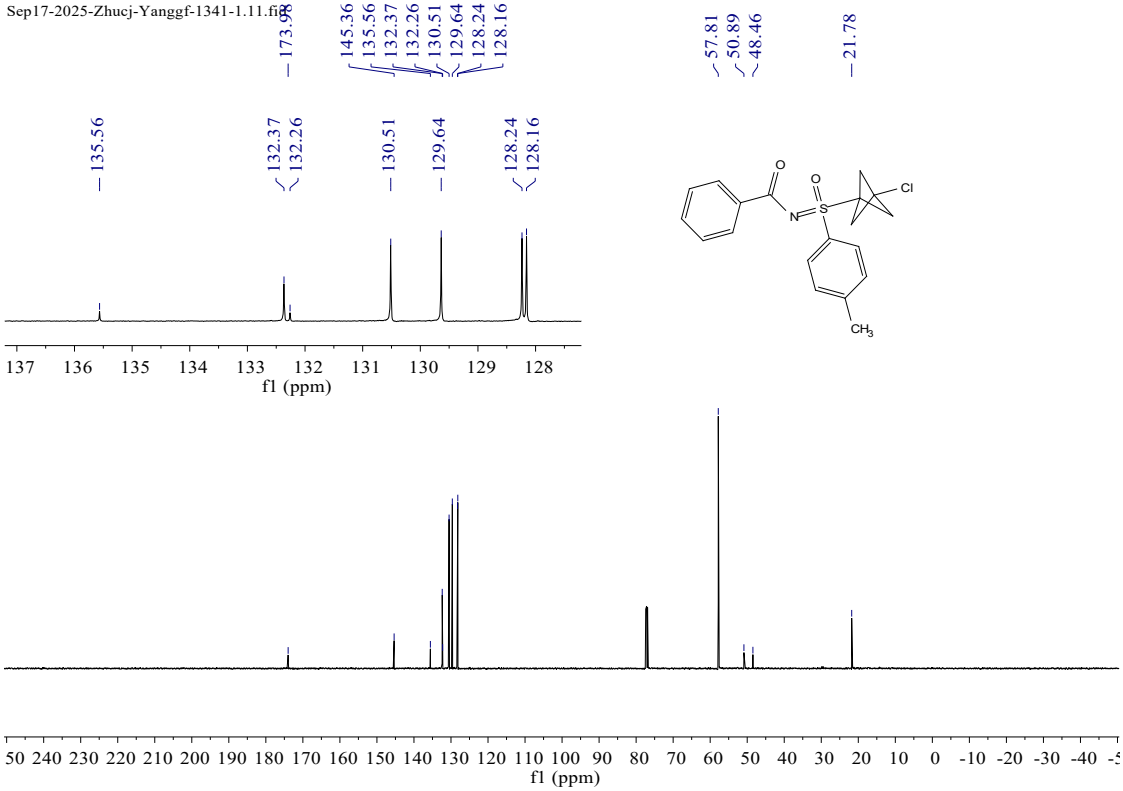
HRMS (ESI): $[M+H]^+$ calcd. for $C_{12}H_{15}ClNOS$: 256.0557; Found 256.0555.

NMR Spectrums

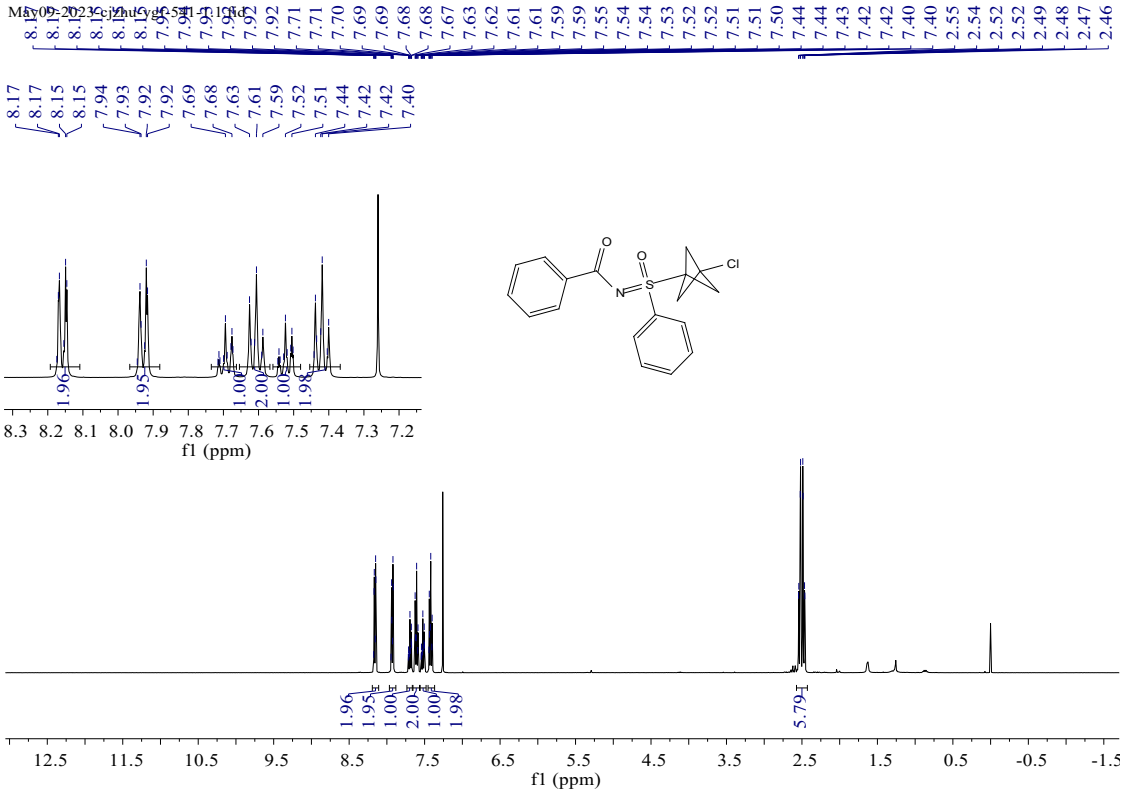
Product (3), ^{1}H NMR (500 MHz, Chloroform-*d*)



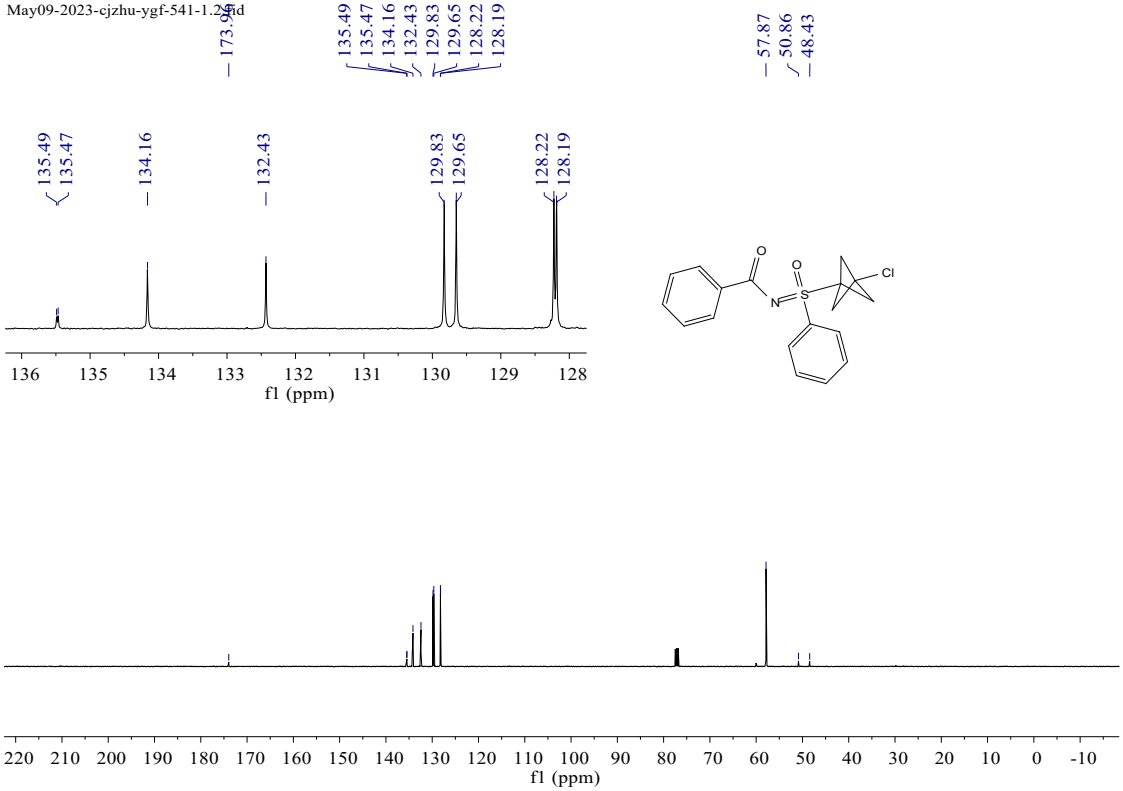
Product (3), ^{13}C NMR (125 MHz, Chloroform-*d*)



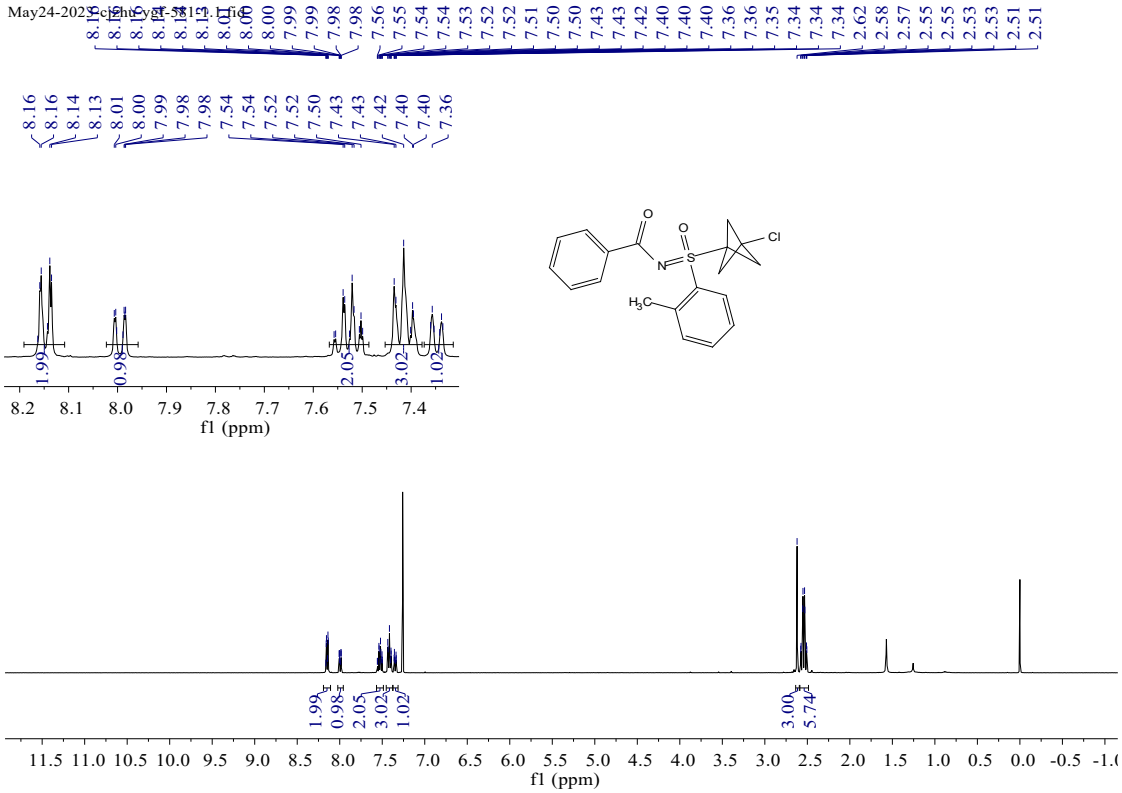
Product (4), ^{1}H NMR (400 MHz, Chloroform-*d*)



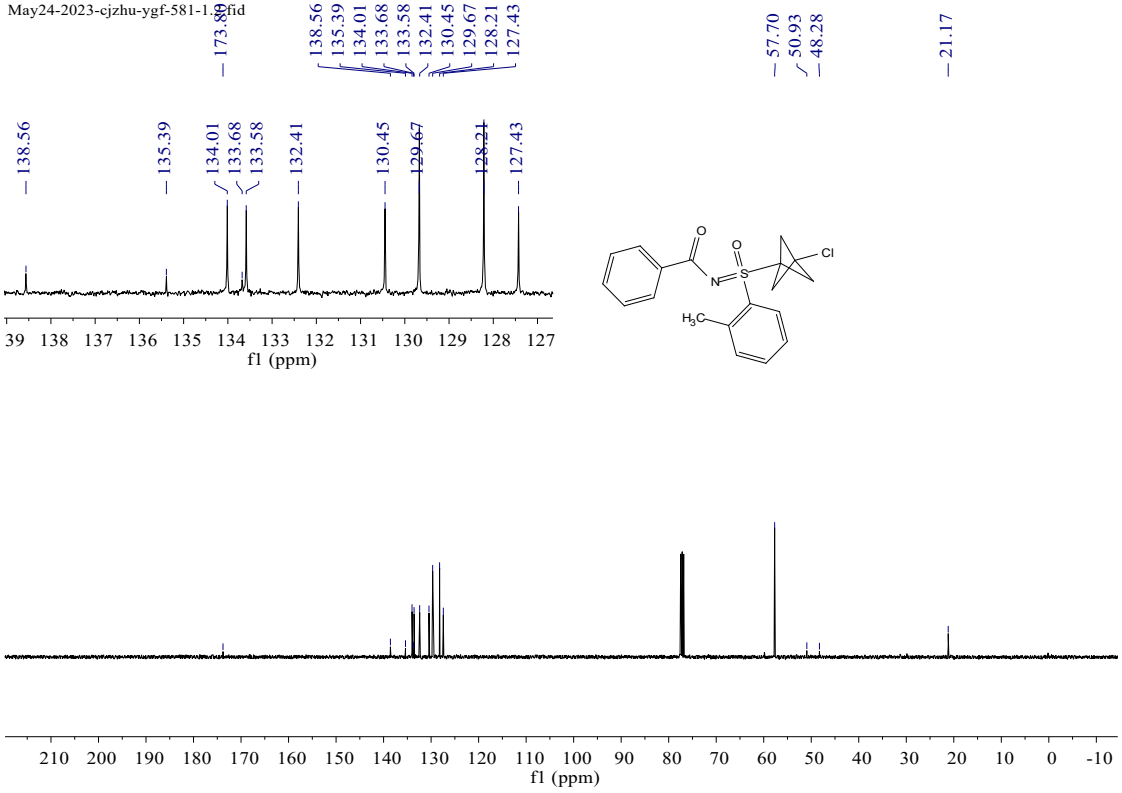
Product (4), ^{13}C NMR (100 MHz, Chloroform-*d*)



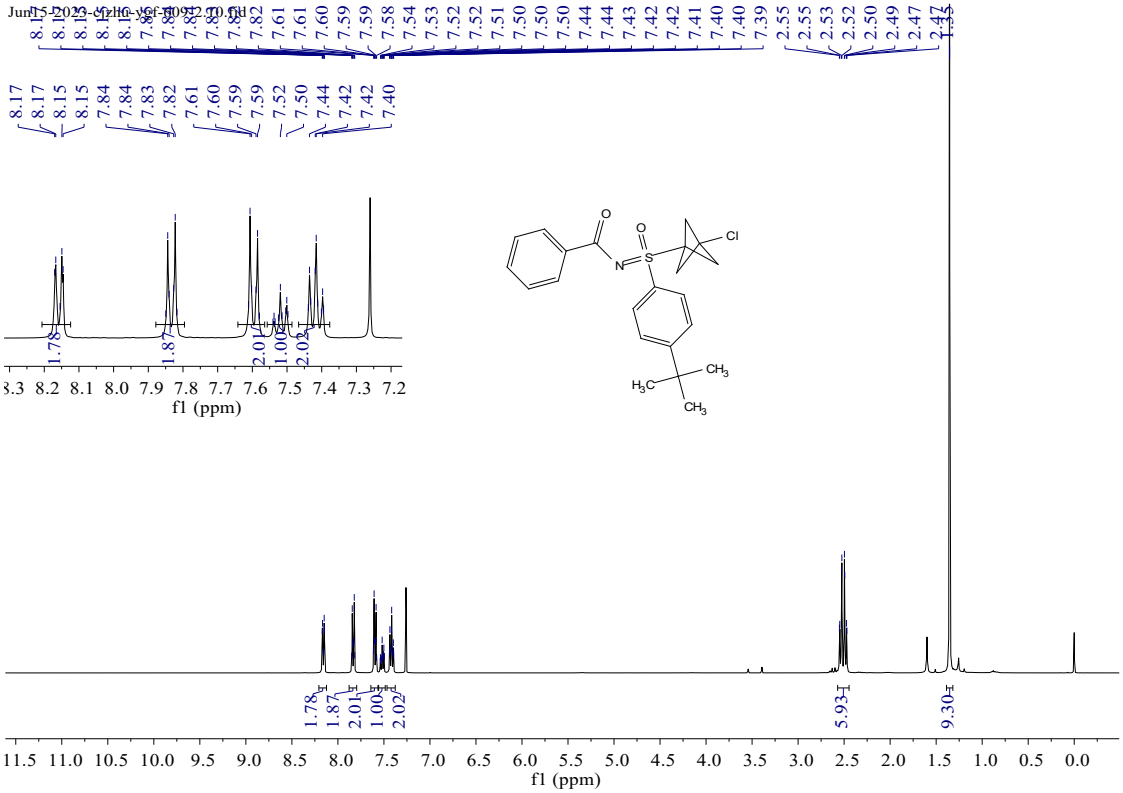
Product (5), ^{1}H NMR (400 MHz, Chloroform-*d*)



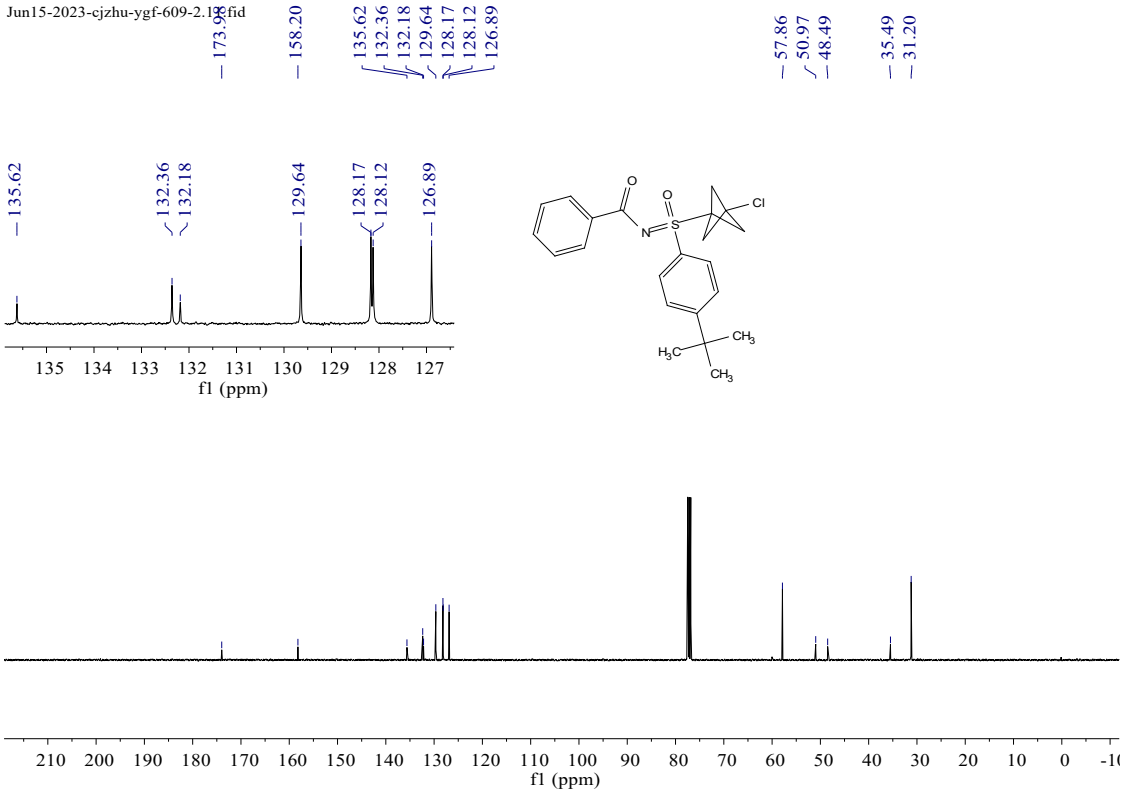
Product (5), ^{13}C NMR (100 MHz, Chloroform-*d*)



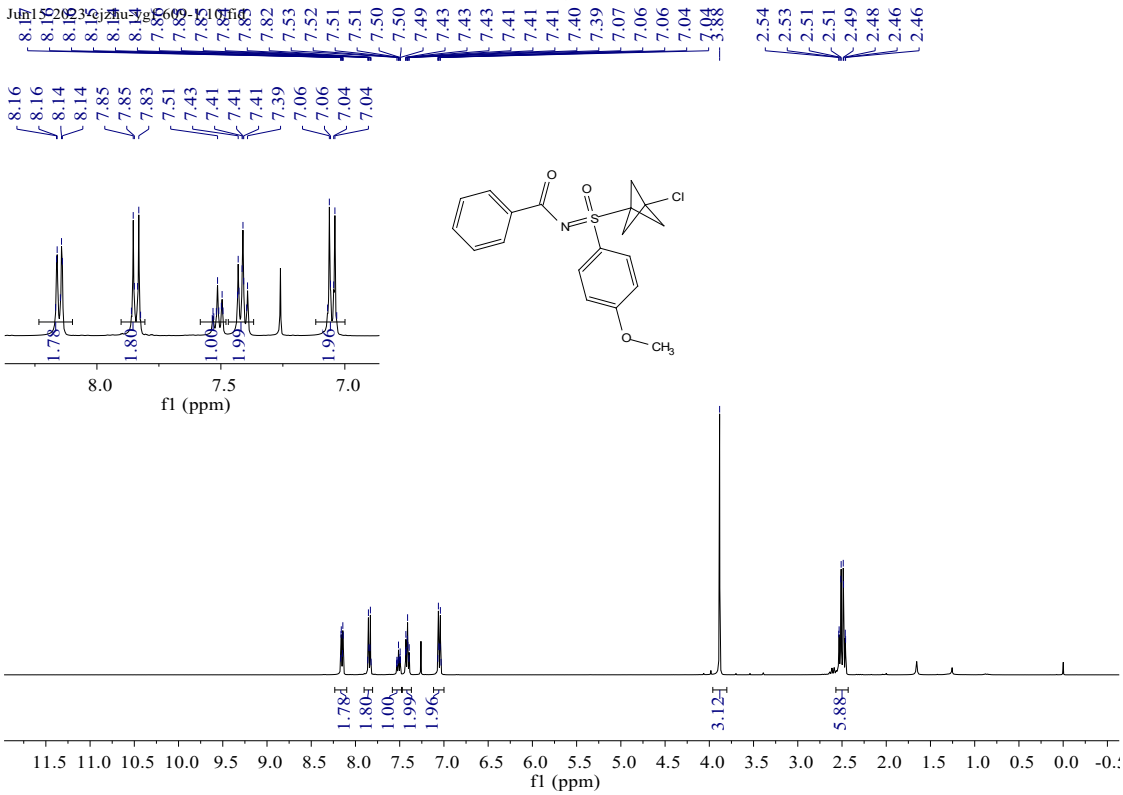
Product (6), ^{1}H NMR (400 MHz, Chloroform-*d*)



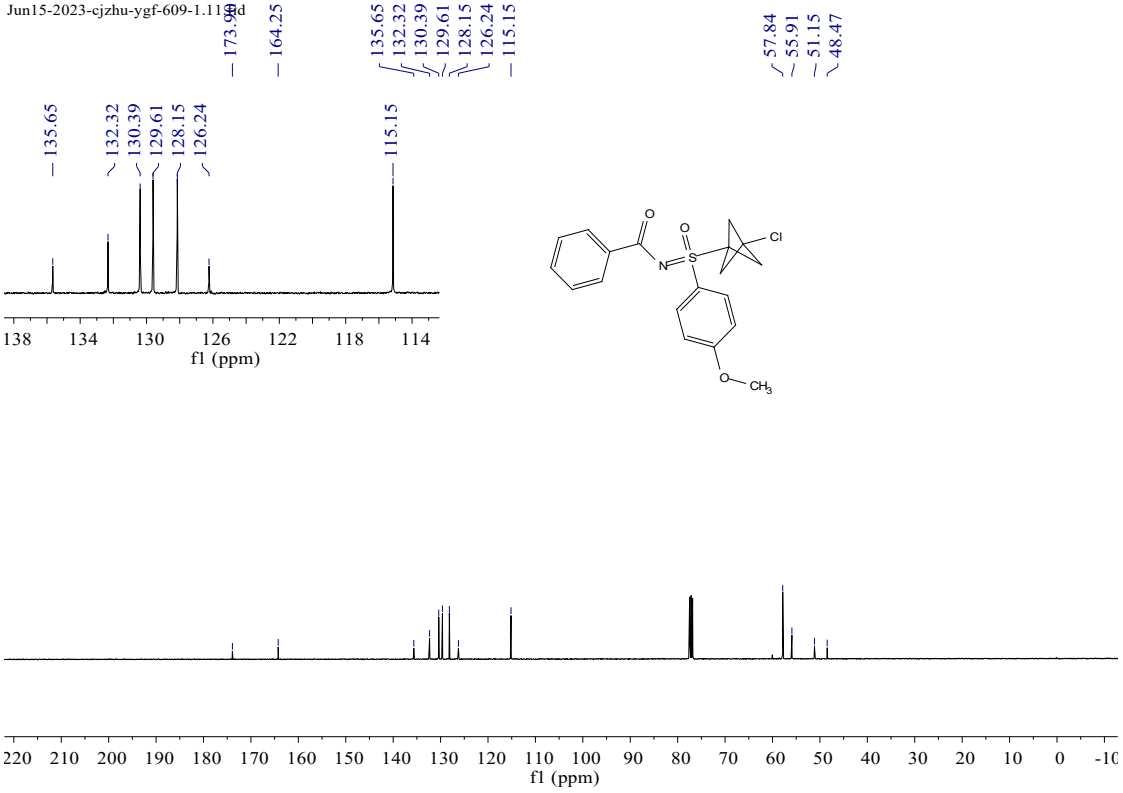
Product (6), ^{13}C NMR (100 MHz, Chloroform-*d*)



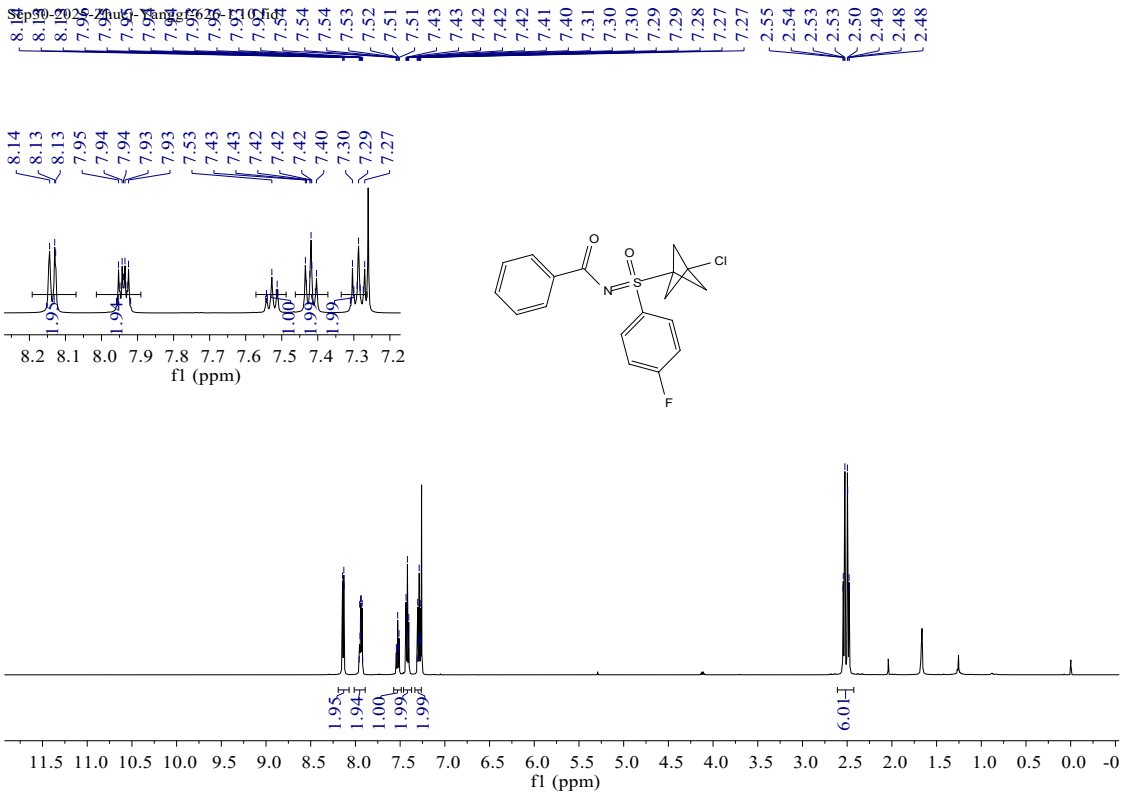
Product (7), ^{1}H NMR (400 MHz, Chloroform-*d*)



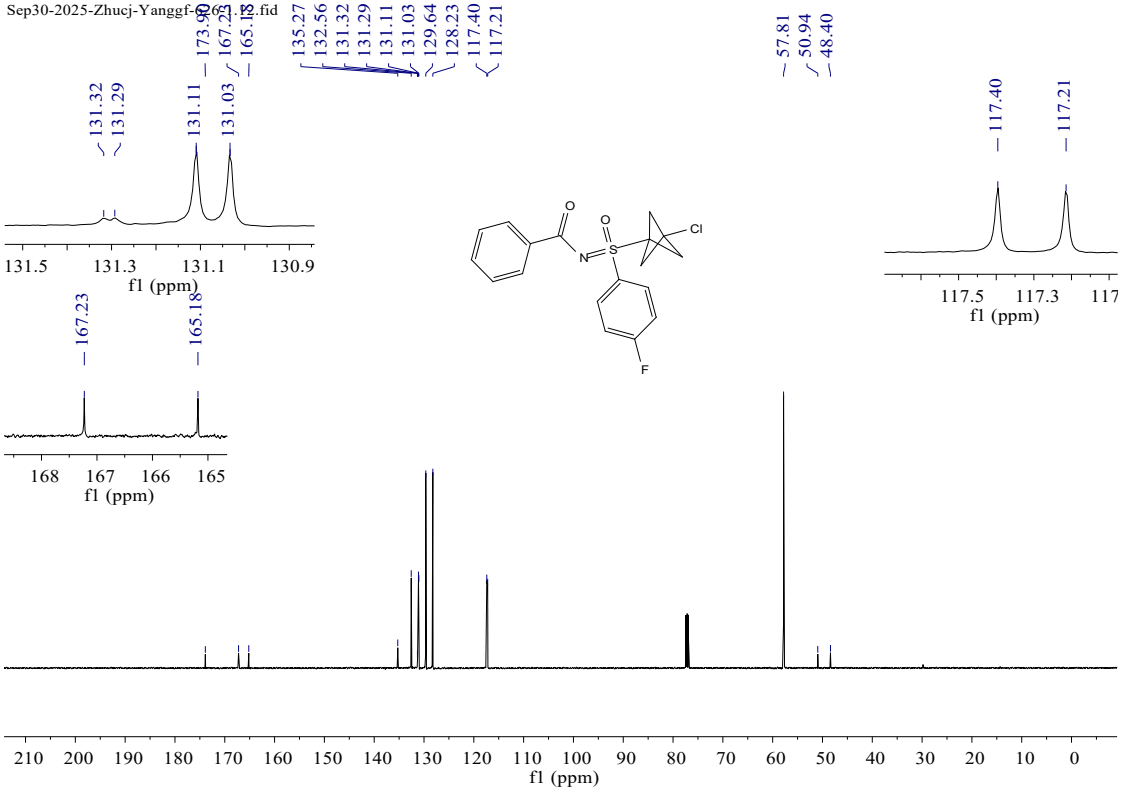
Product (7), ^{13}C NMR (100 MHz, Chloroform-*d*)



Product (8), ^{1}H NMR (500 MHz, Chloroform-*d*)

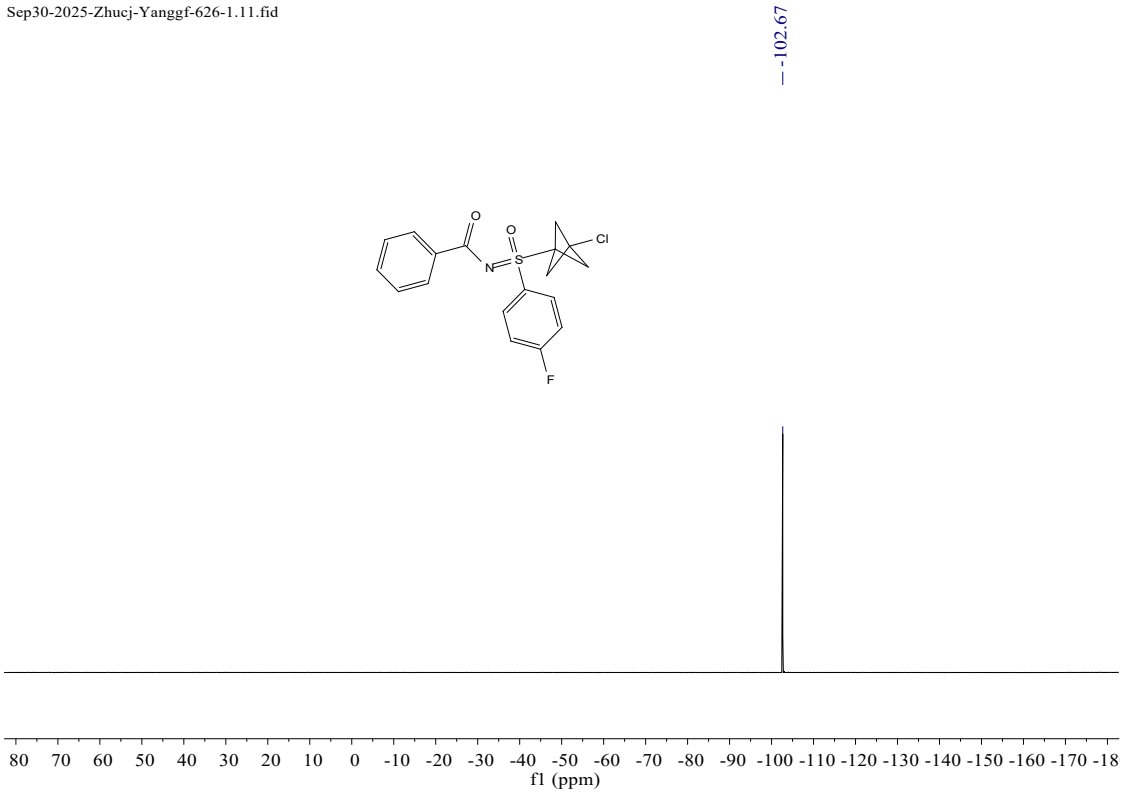


Product (8), ^{13}C NMR (125 MHz, Chloroform-*d*)



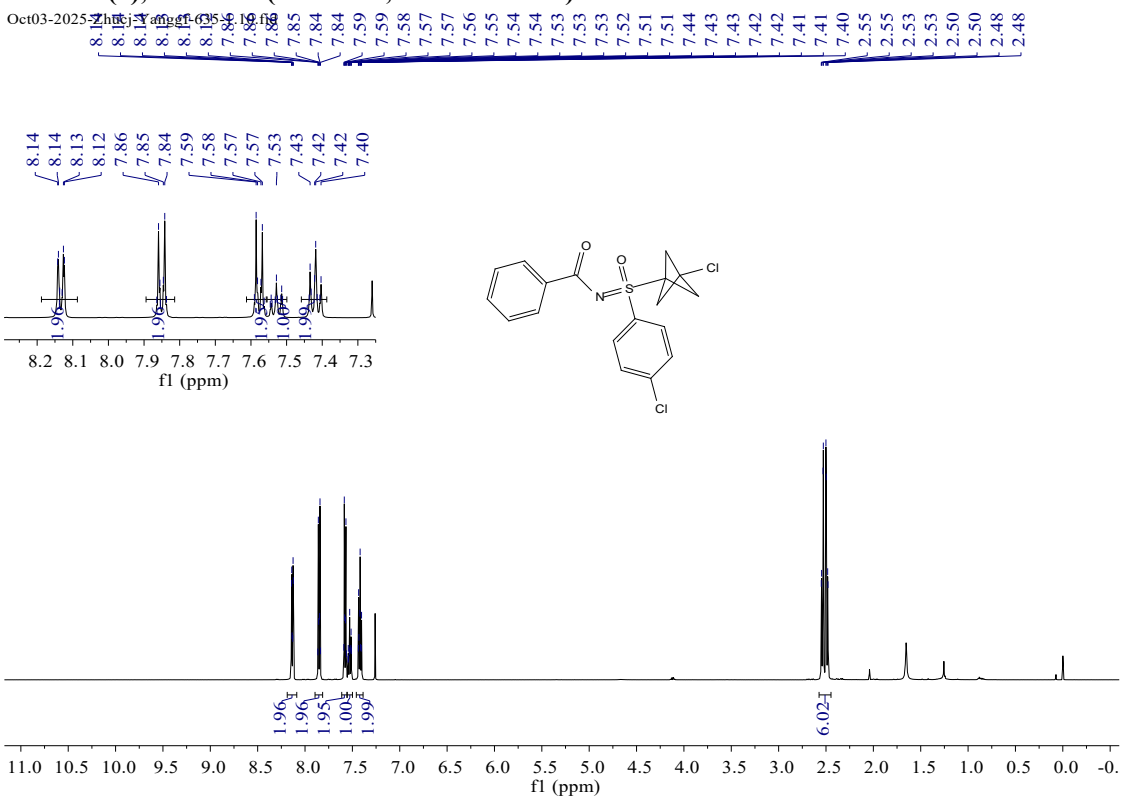
Product (8), $^{19}F\{^{1}H\}$ NMR (471 MHz, Chloroform-*d*)

Sep30-2025-Zhucj-Yanggf-626-1.11.fid

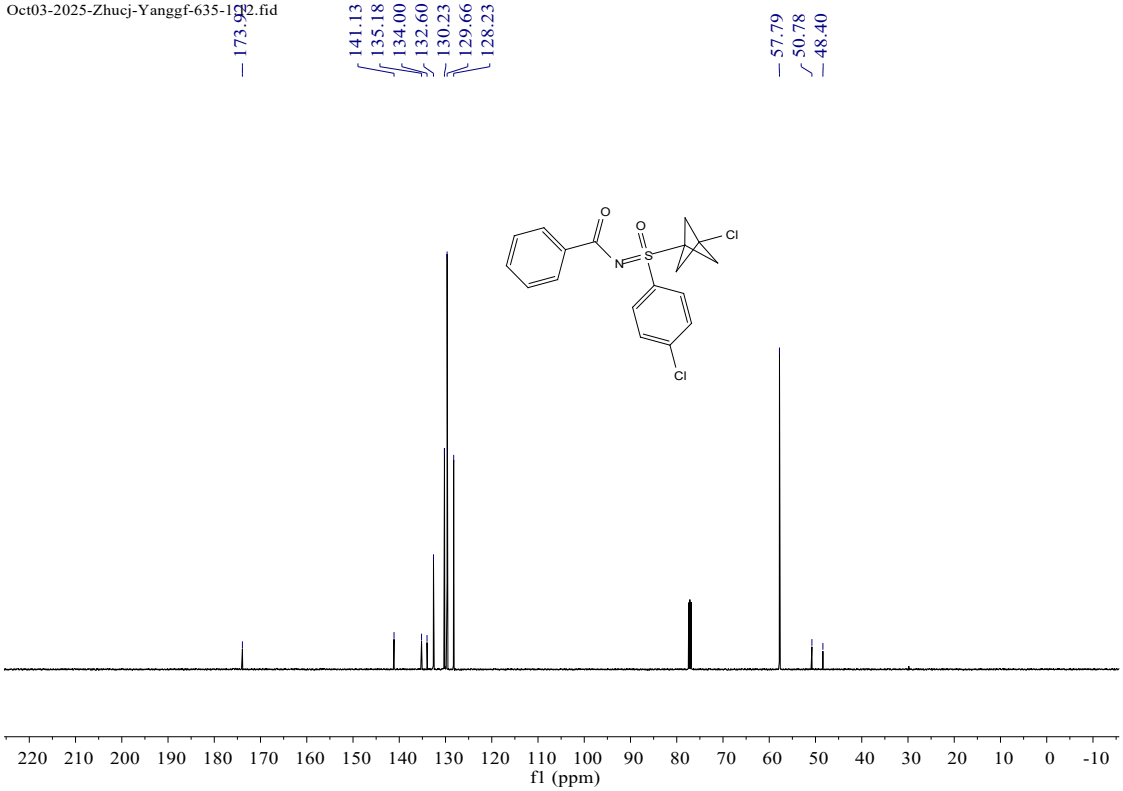


Product (9), ^{1}H NMR (500 MHz, Chloroform-*d*)

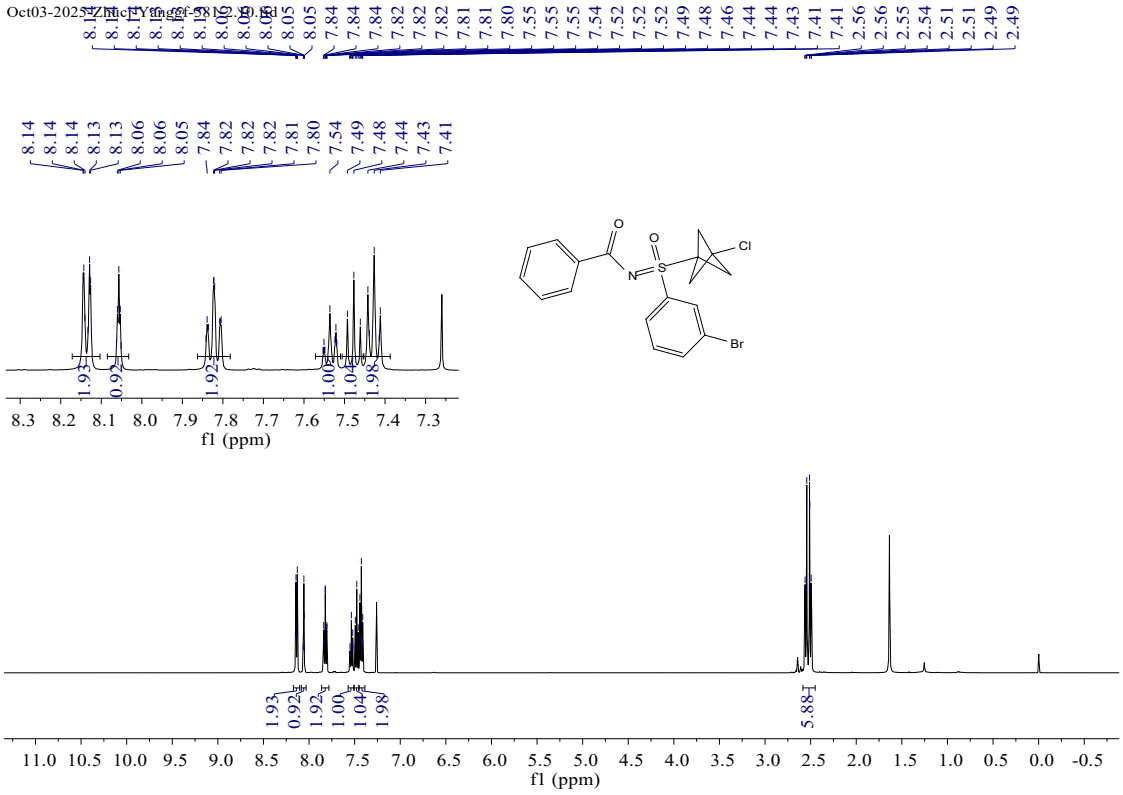
Oct03-2025-Zhucj-Yanggf-635-1.9.fid



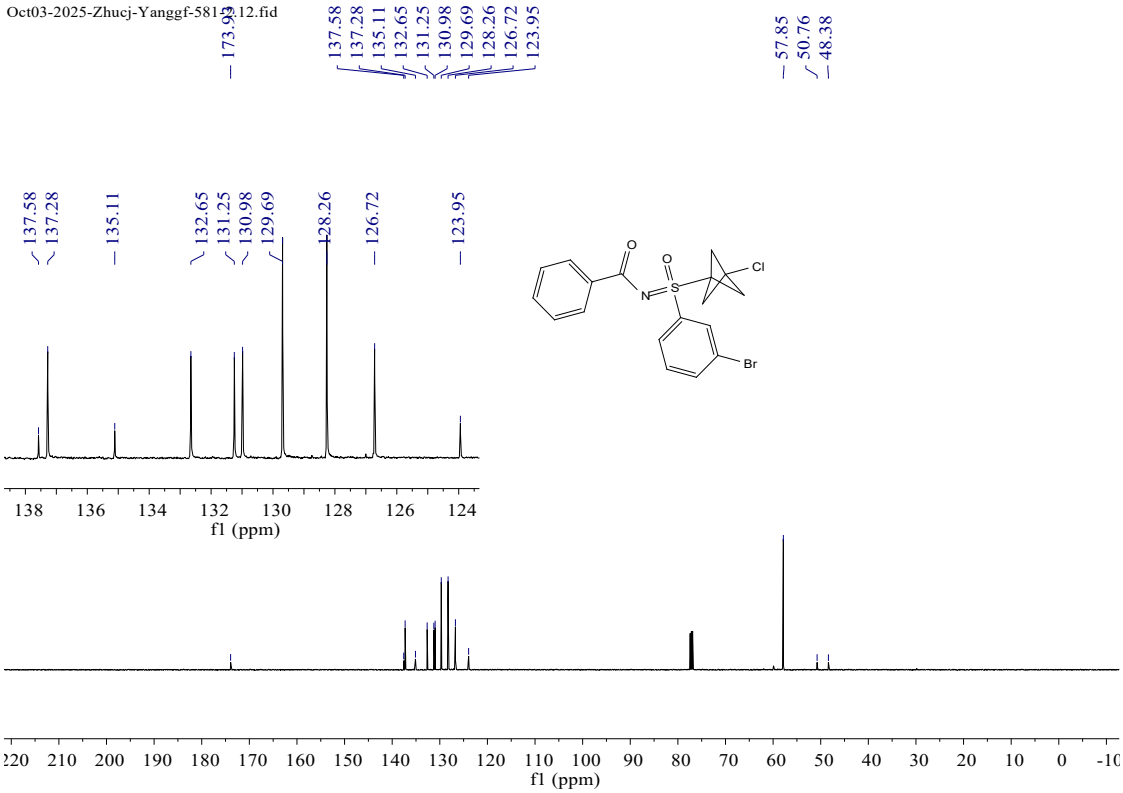
Product (9), ^{13}C NMR (125 MHz, Chloroform-*d*)



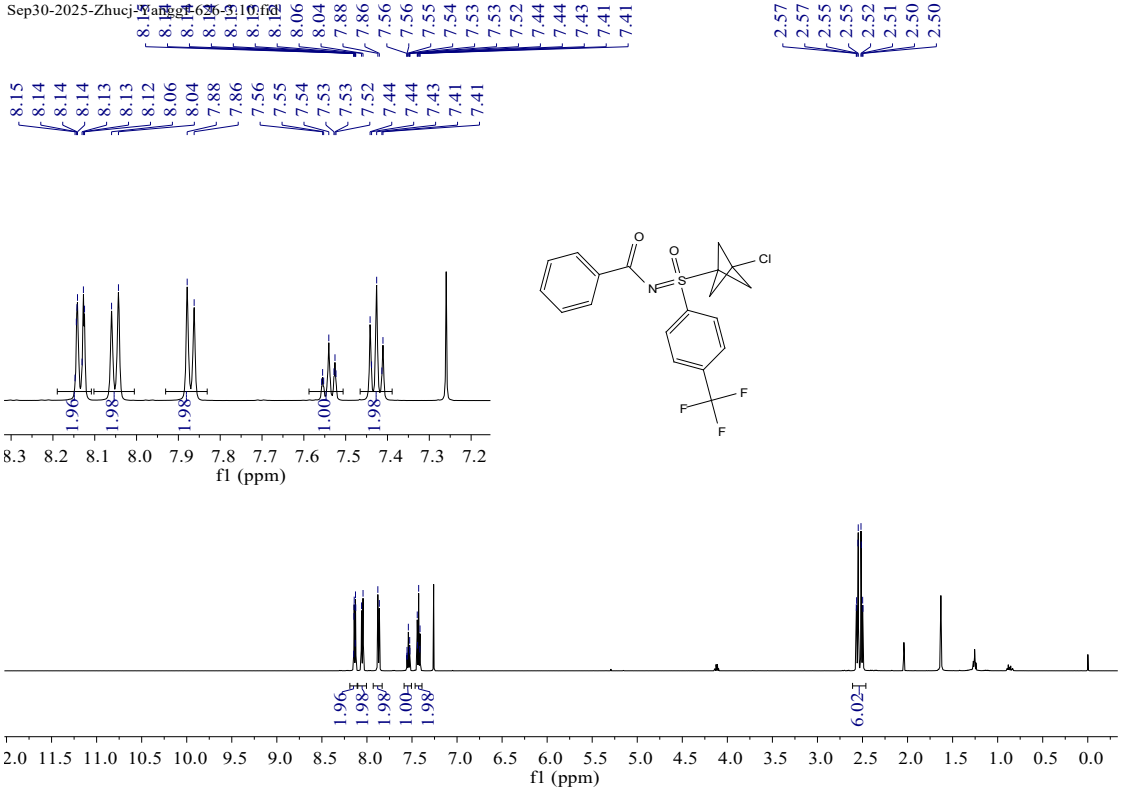
Product (10), ^{1}H NMR (500 MHz, Chloroform-*d*)



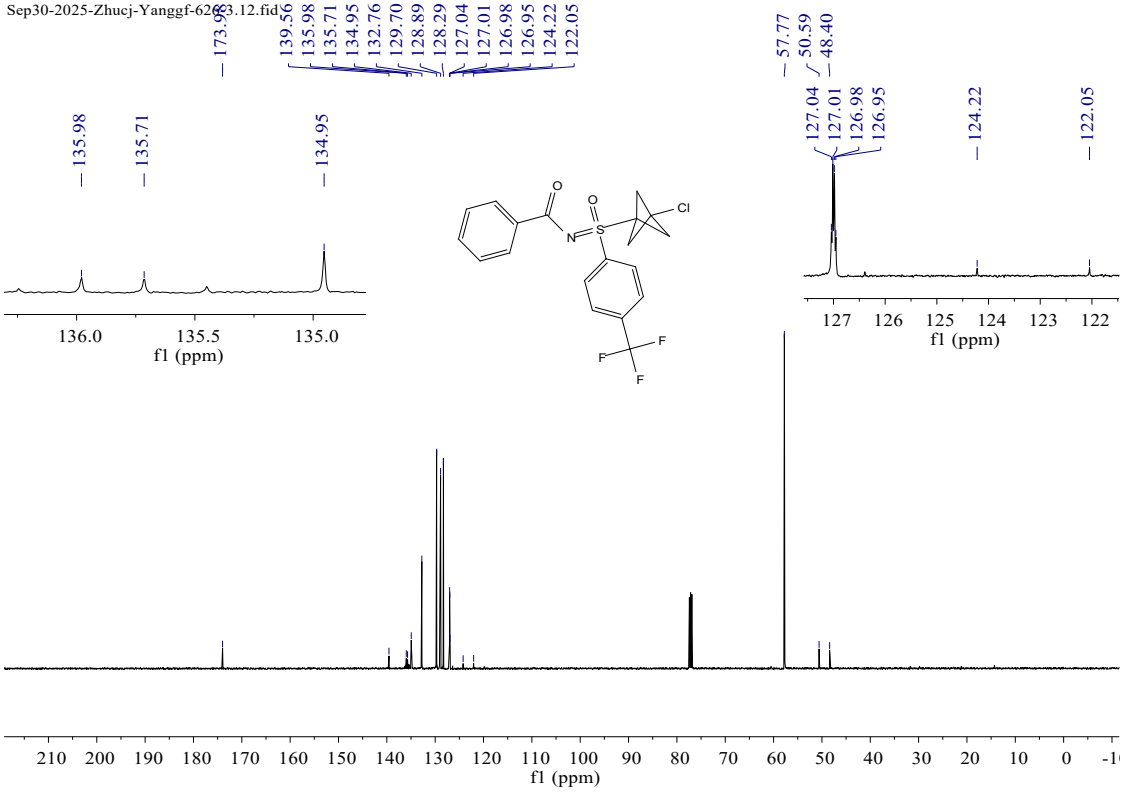
Product (10), ^{13}C NMR (125 MHz, Chloroform-*d*)



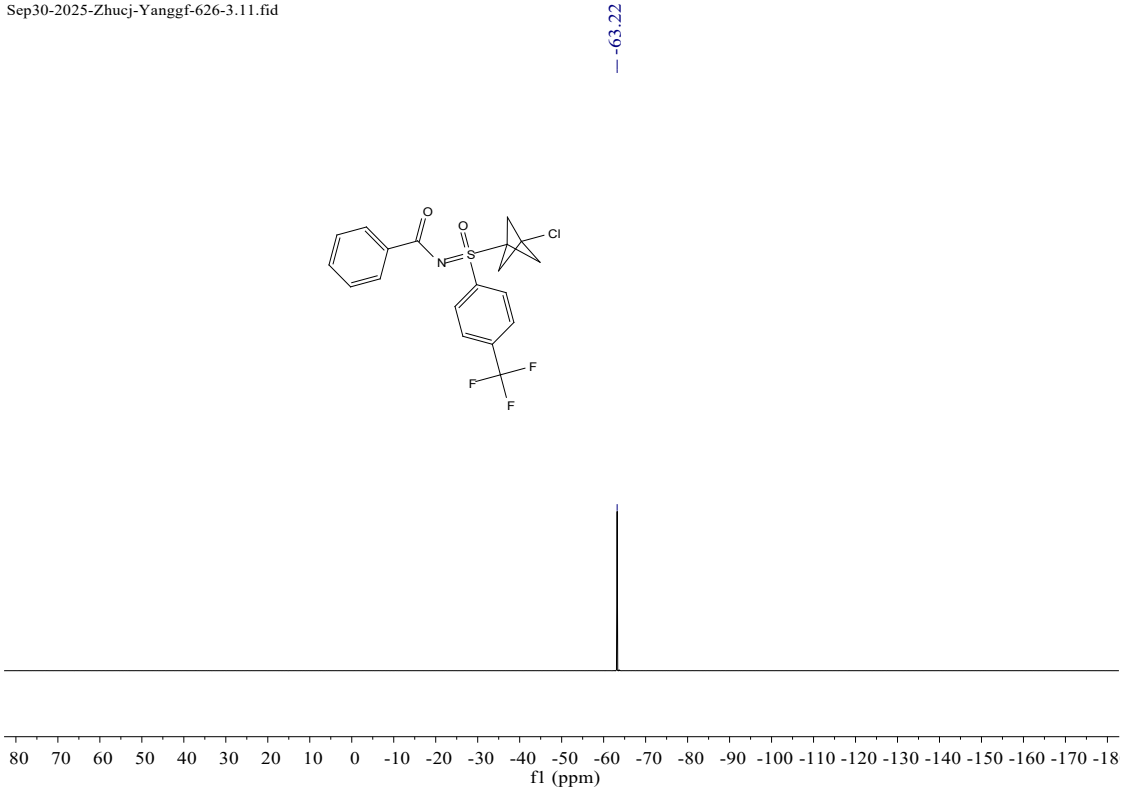
Product (11), ^{1}H NMR (500 MHz, Chloroform-*d*)



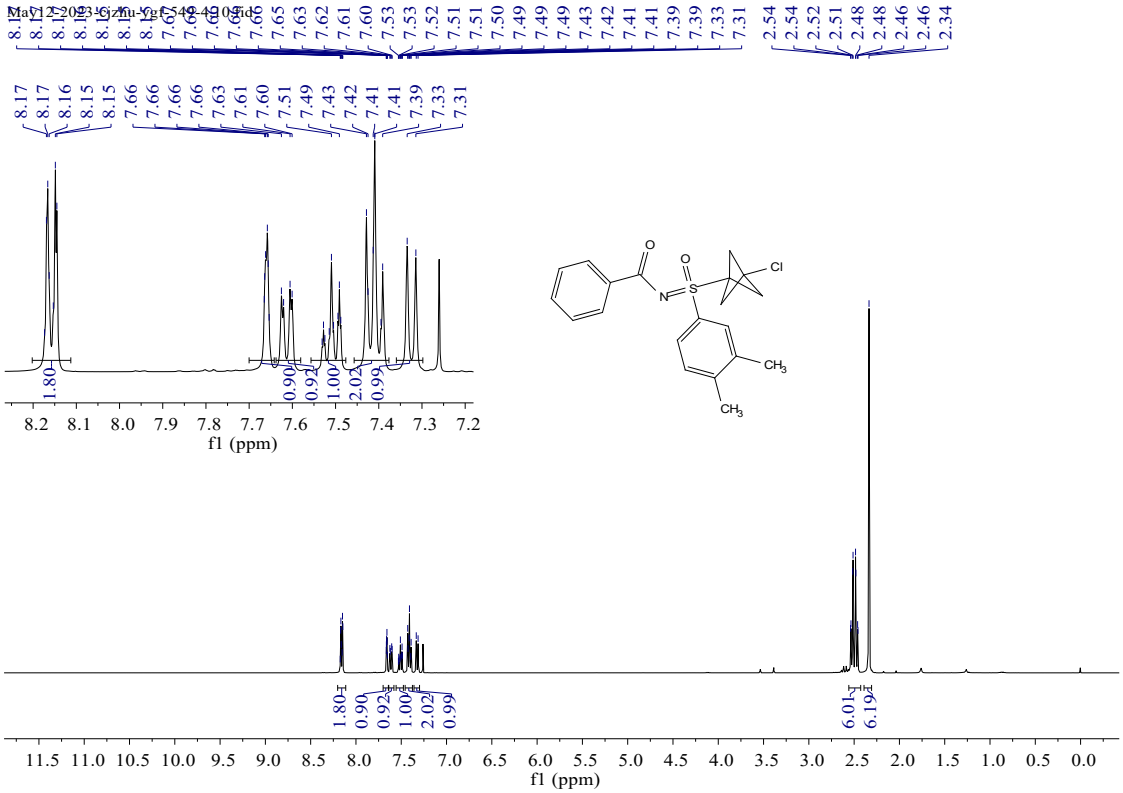
Product (11), ^{13}C NMR (125 MHz, Chloroform-*d*)



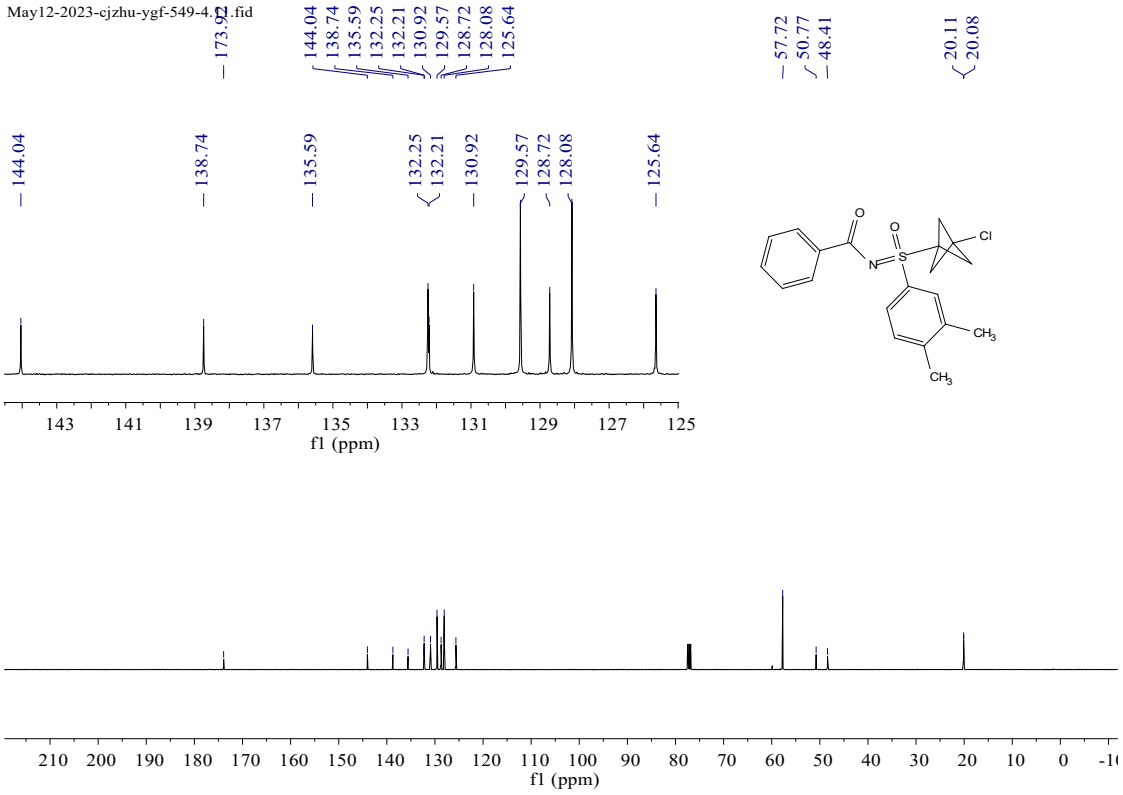
Product (11), ^{19}F{^{1}H} NMR (471 MHz, Chloroform-*d*)



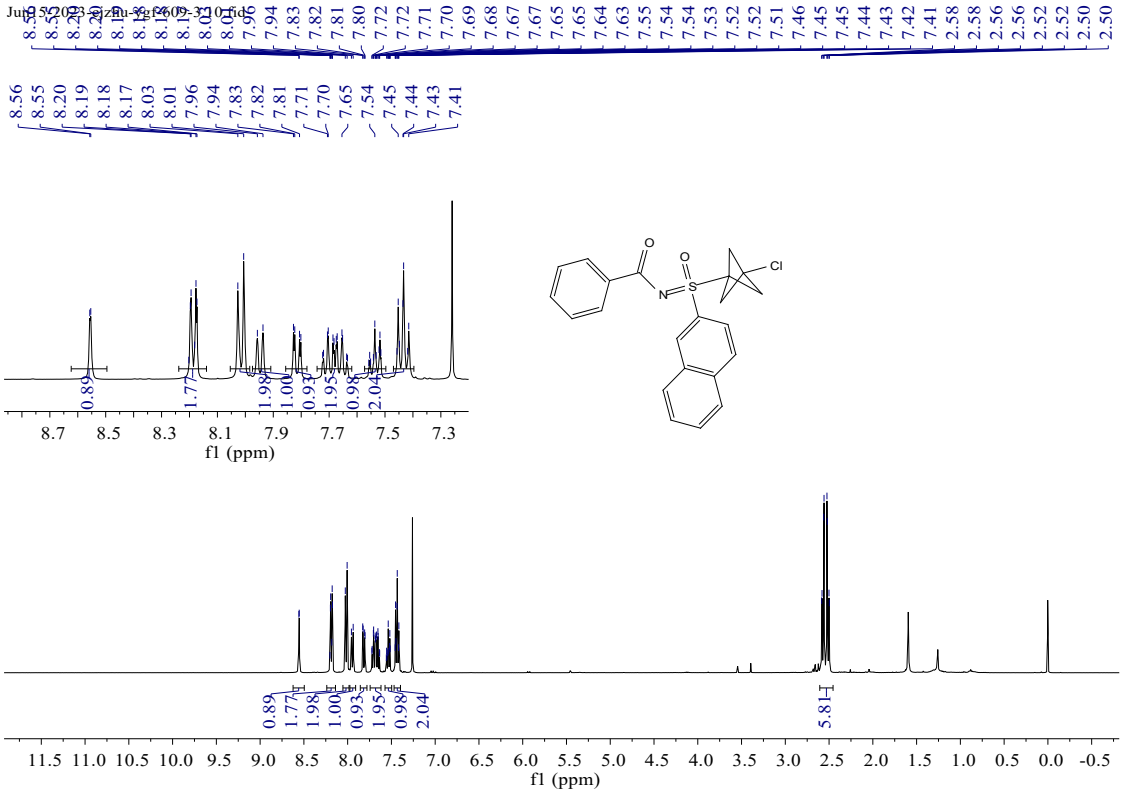
Product (12), ^{1}H NMR (400 MHz, Chloroform-*d*)



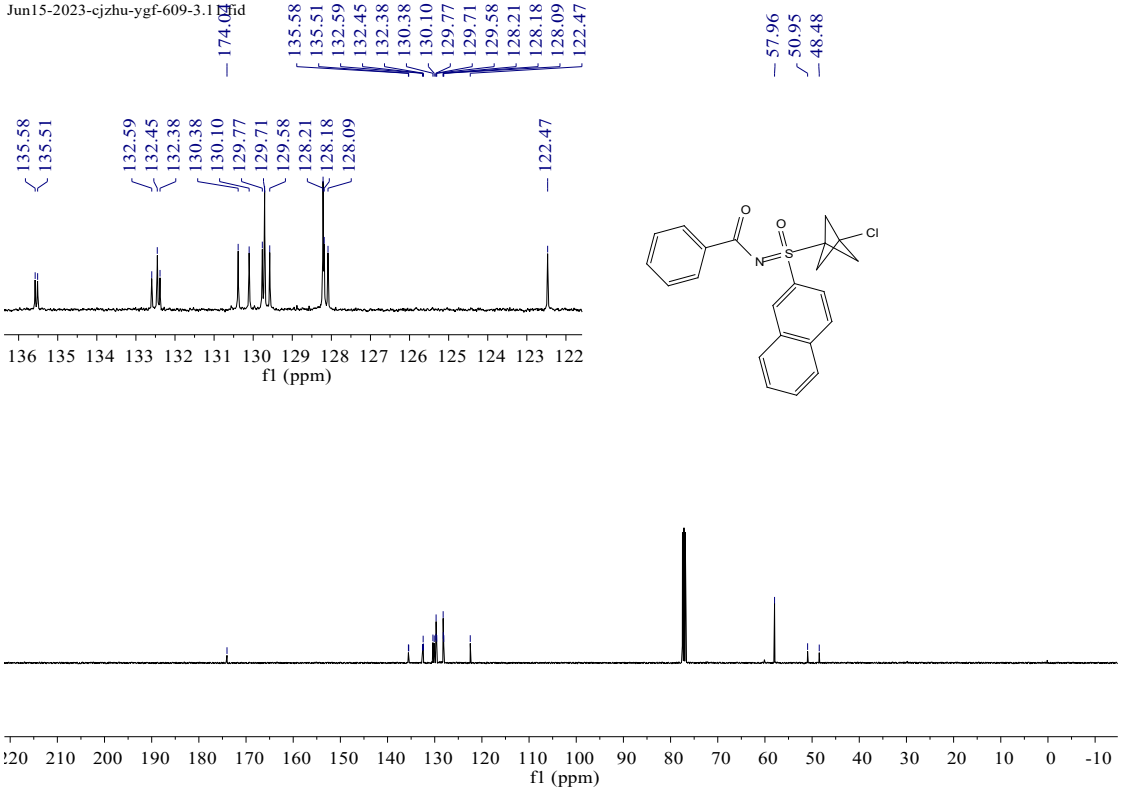
Product (12), ^{13}C NMR (100 MHz, Chloroform-*d*)



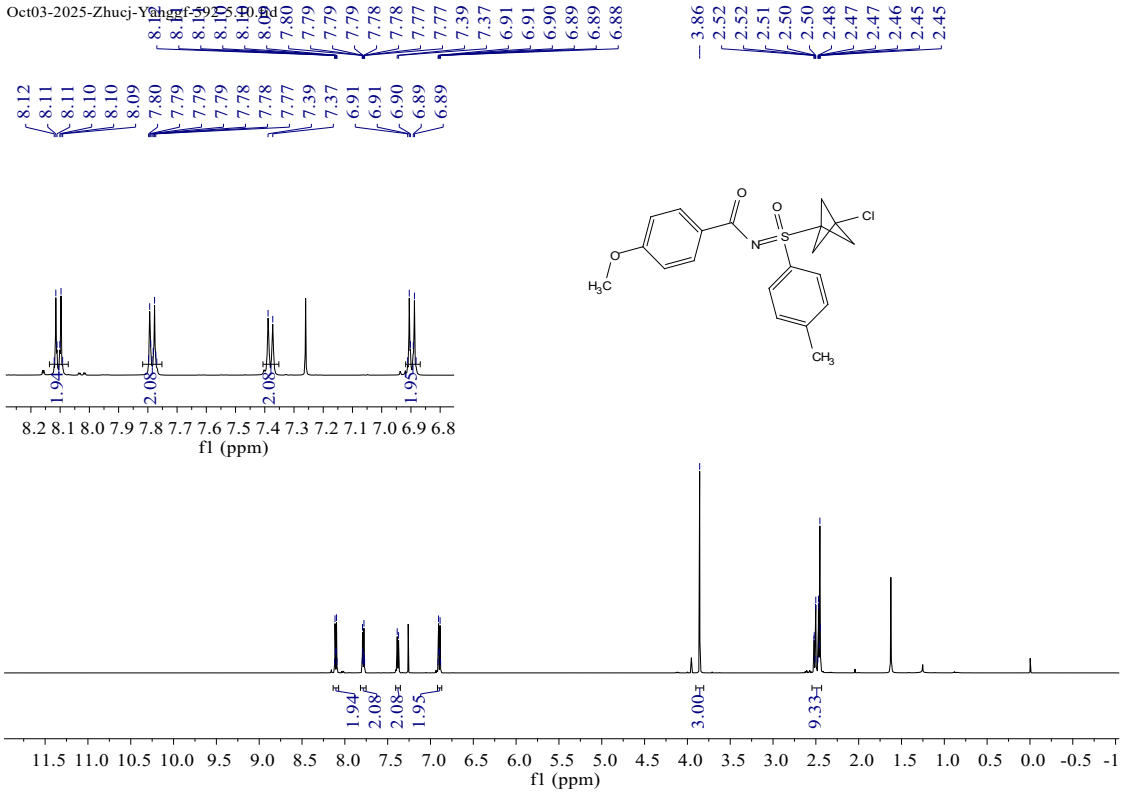
Product (13), ^{1}H NMR (400 MHz, Chloroform-*d*)



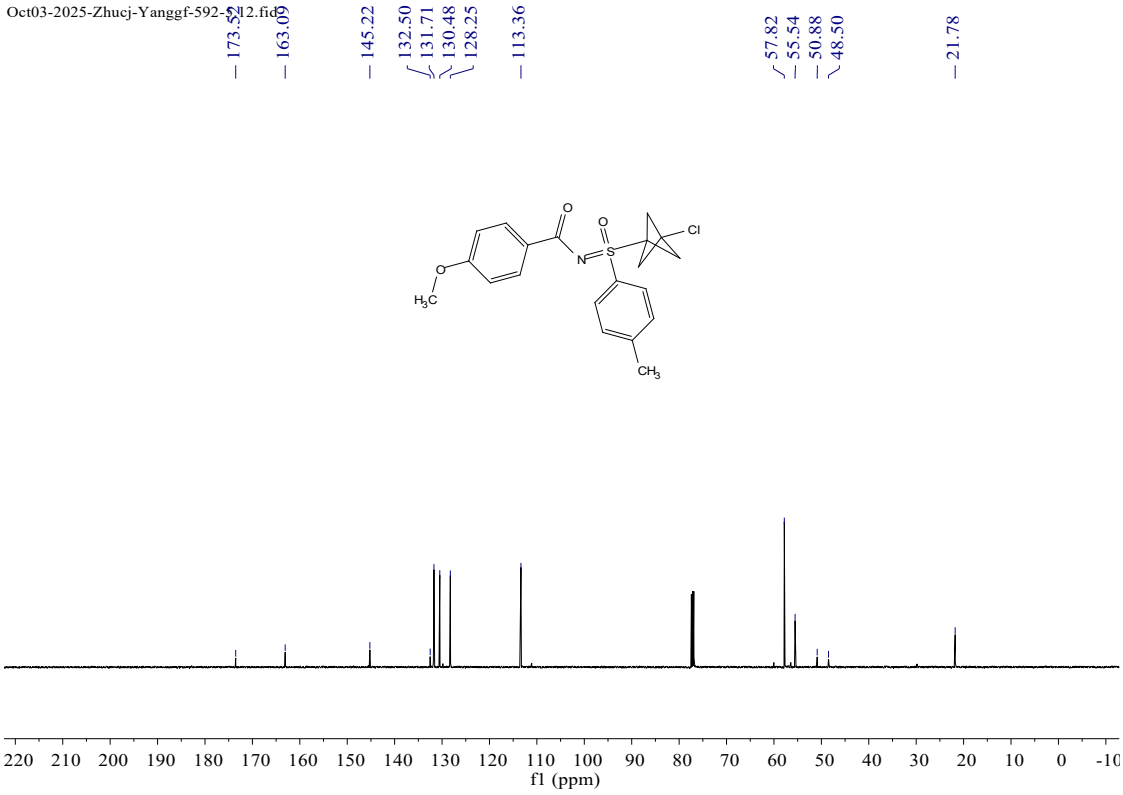
Product (13), ^{13}C NMR (100 MHz, Chloroform-*d*)



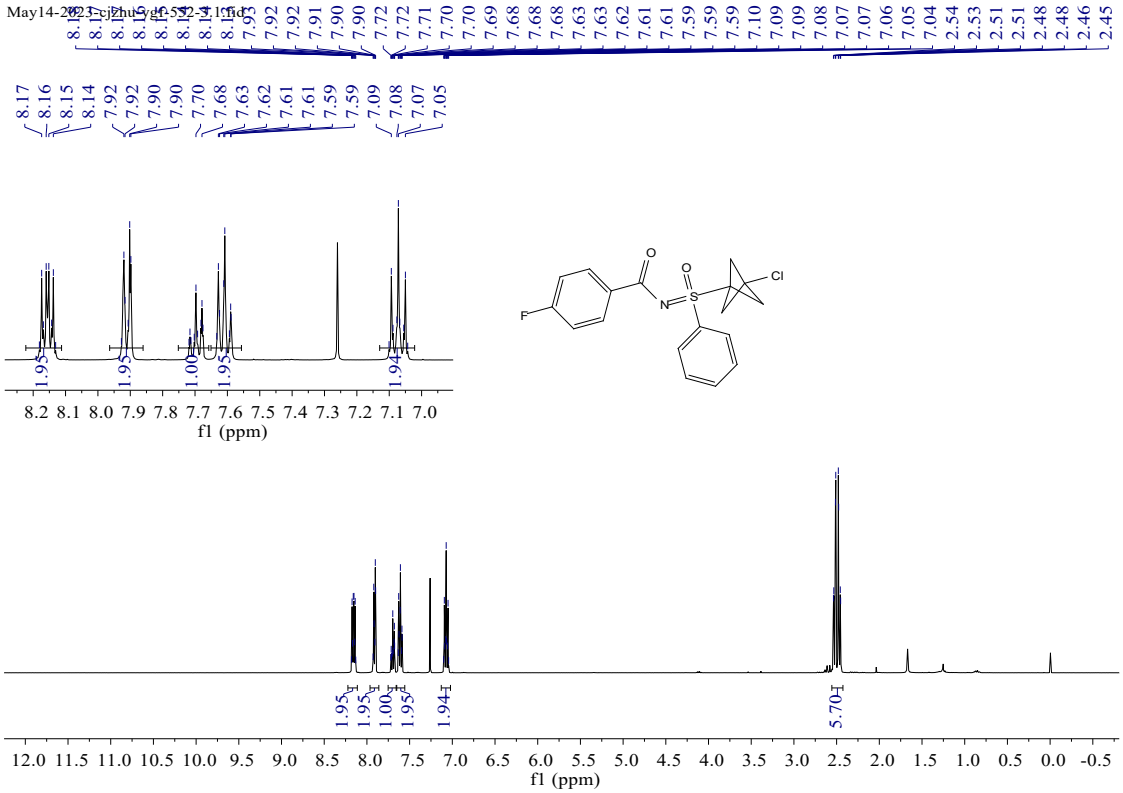
Product (14), ^{1}H NMR (500 MHz, Chloroform-*d*)



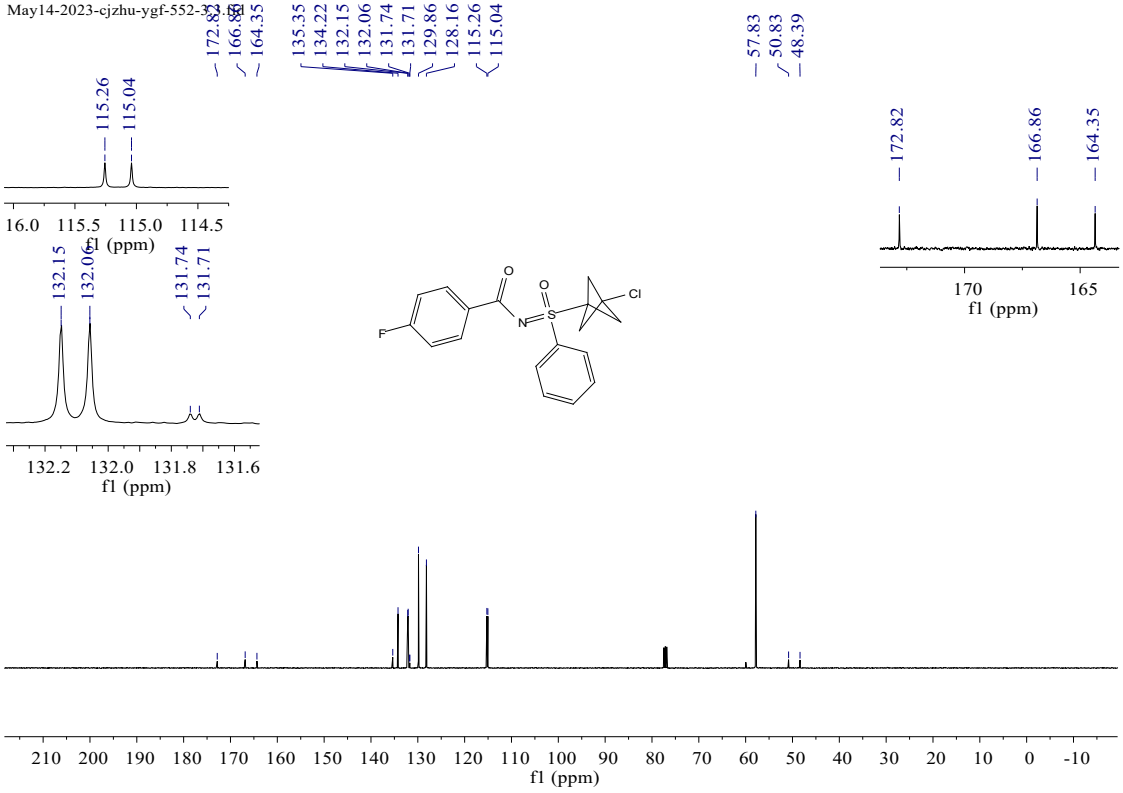
Product (14), ^{13}C NMR (125 MHz, Chloroform-*d*)



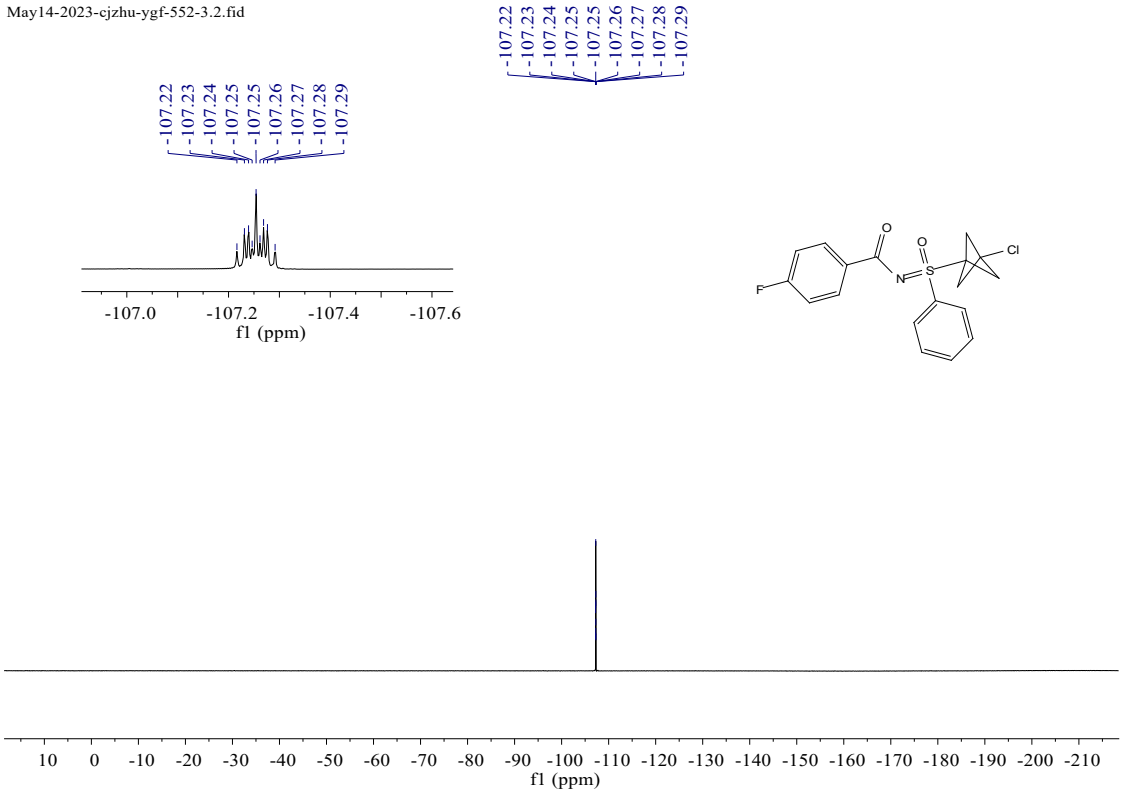
Product (15), ^{1}H NMR (400 MHz, Chloroform-*d*)



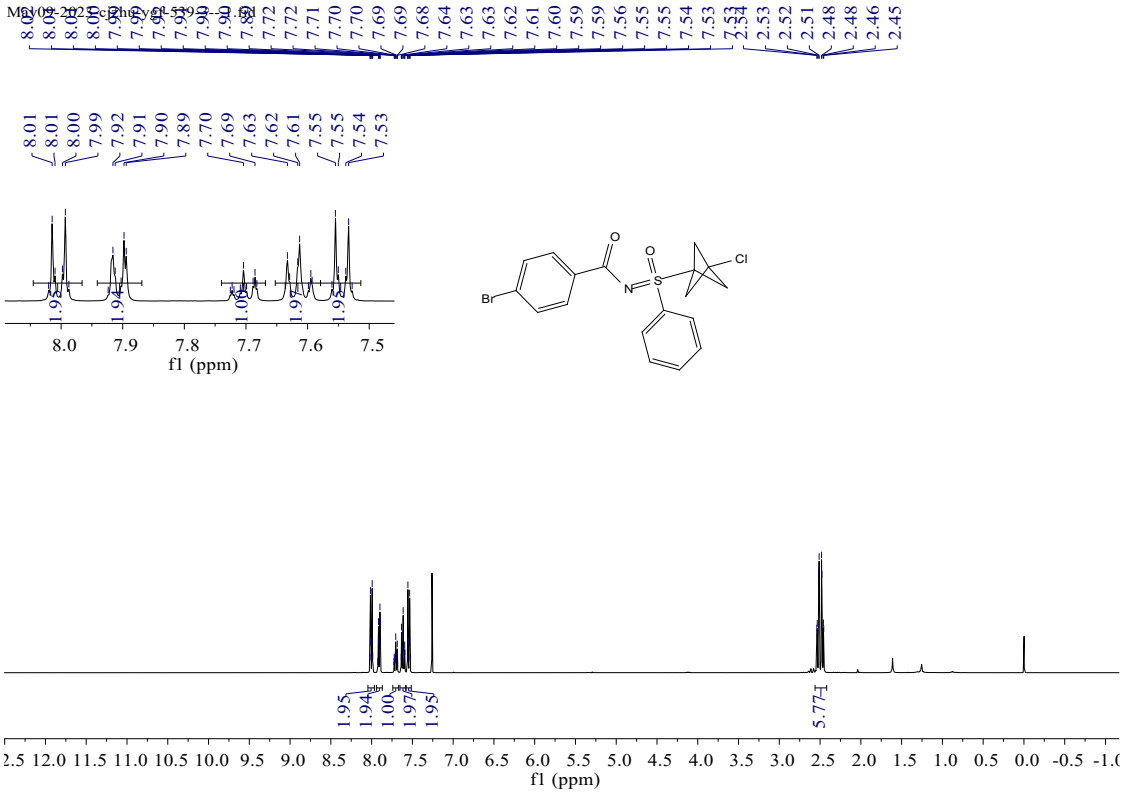
Product (15), ^{13}C NMR (100 MHz, Chloroform-*d*)



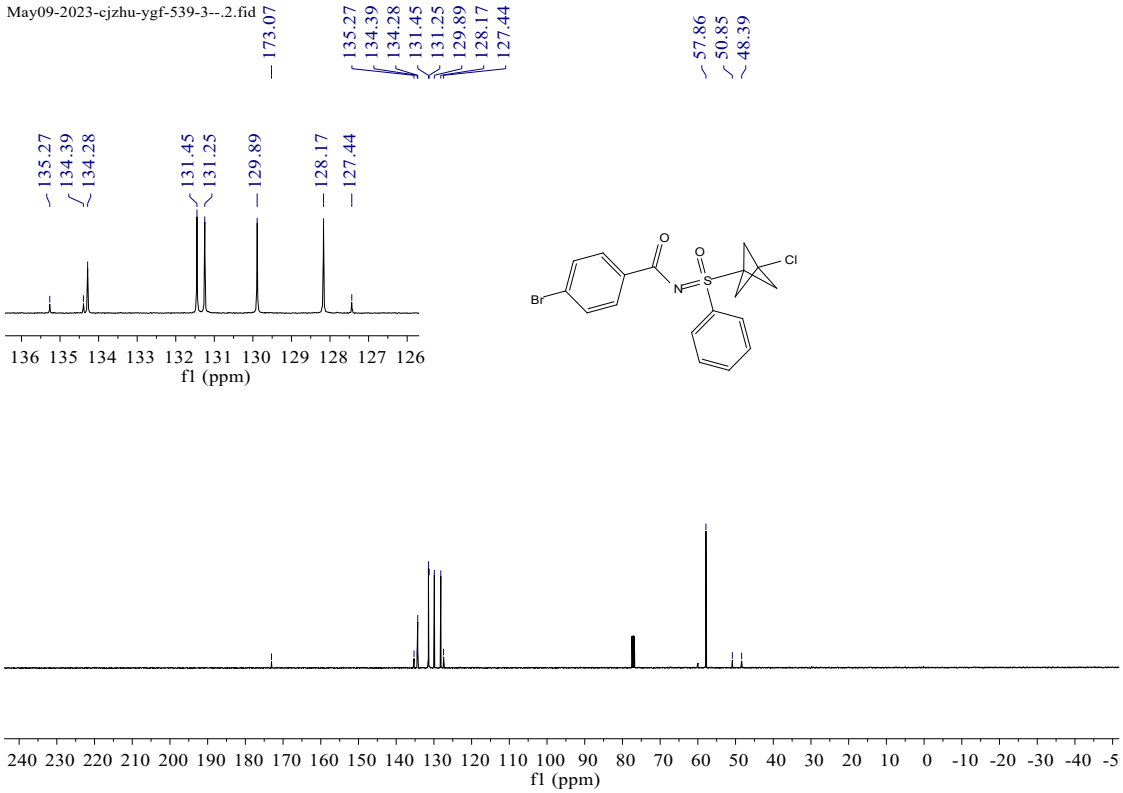
Product (15), $^{19}F\{^{1}H\}$ NMR (376 MHz, Chloroform-*d*)



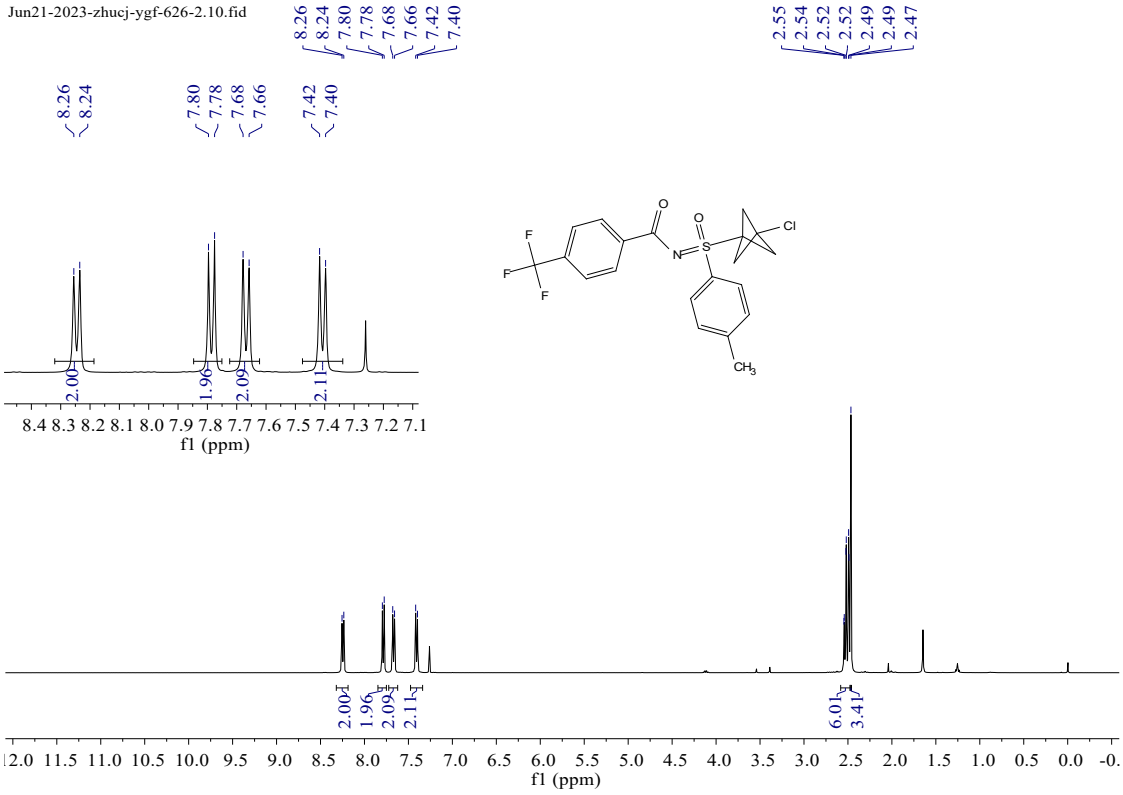
Product (16), ^{1}H NMR (400 MHz, Chloroform-*d*)



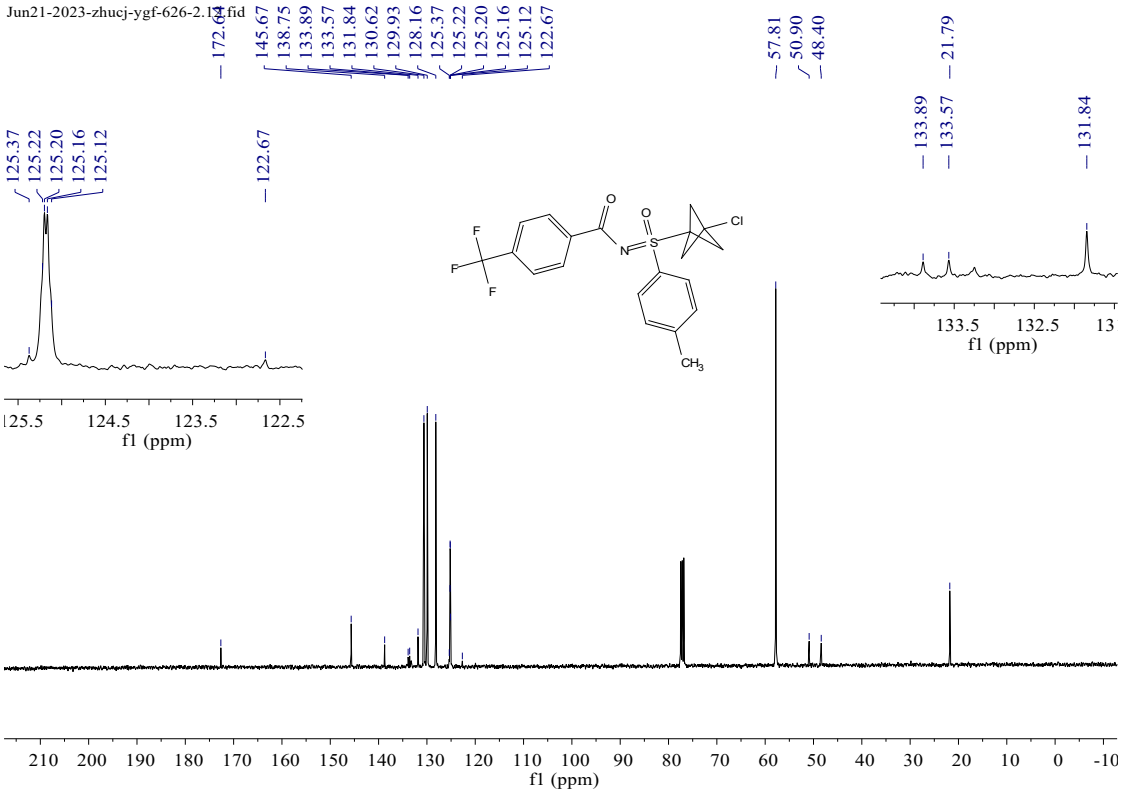
Product (16), ^{13}C NMR (100 MHz, Chloroform-*d*)



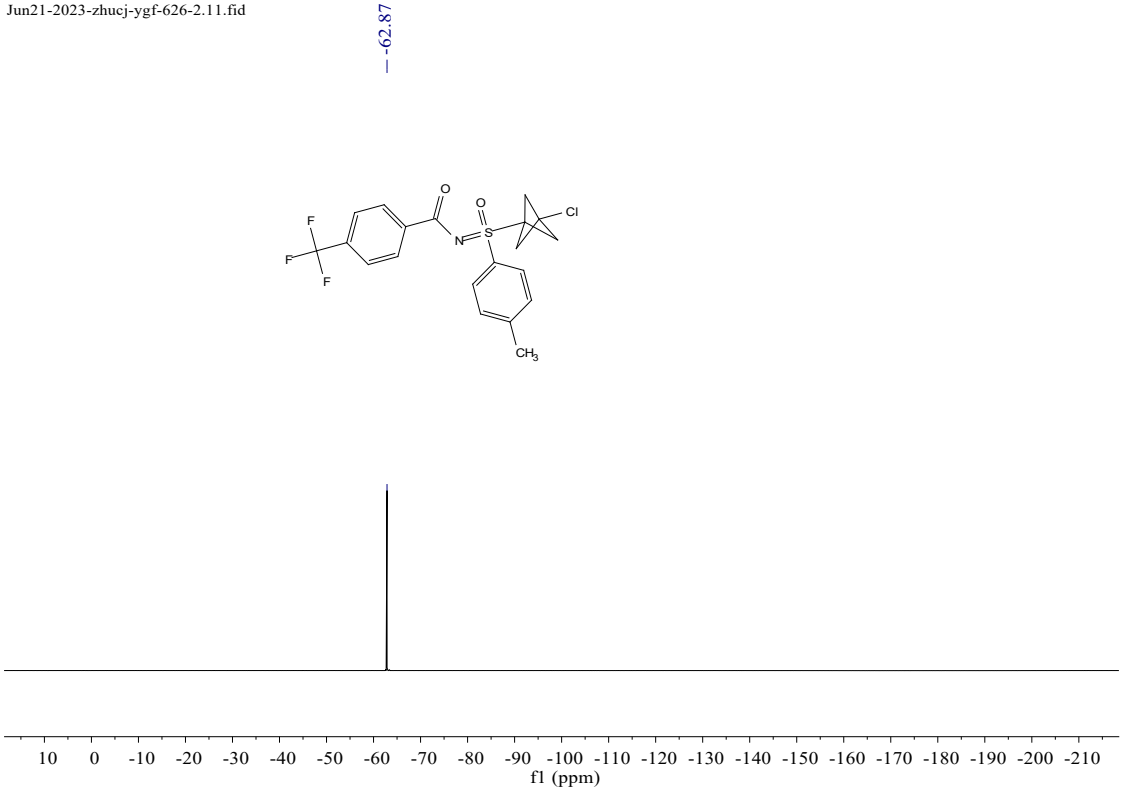
Product (17), ^{1}H NMR (400 MHz, Chloroform-*d*)



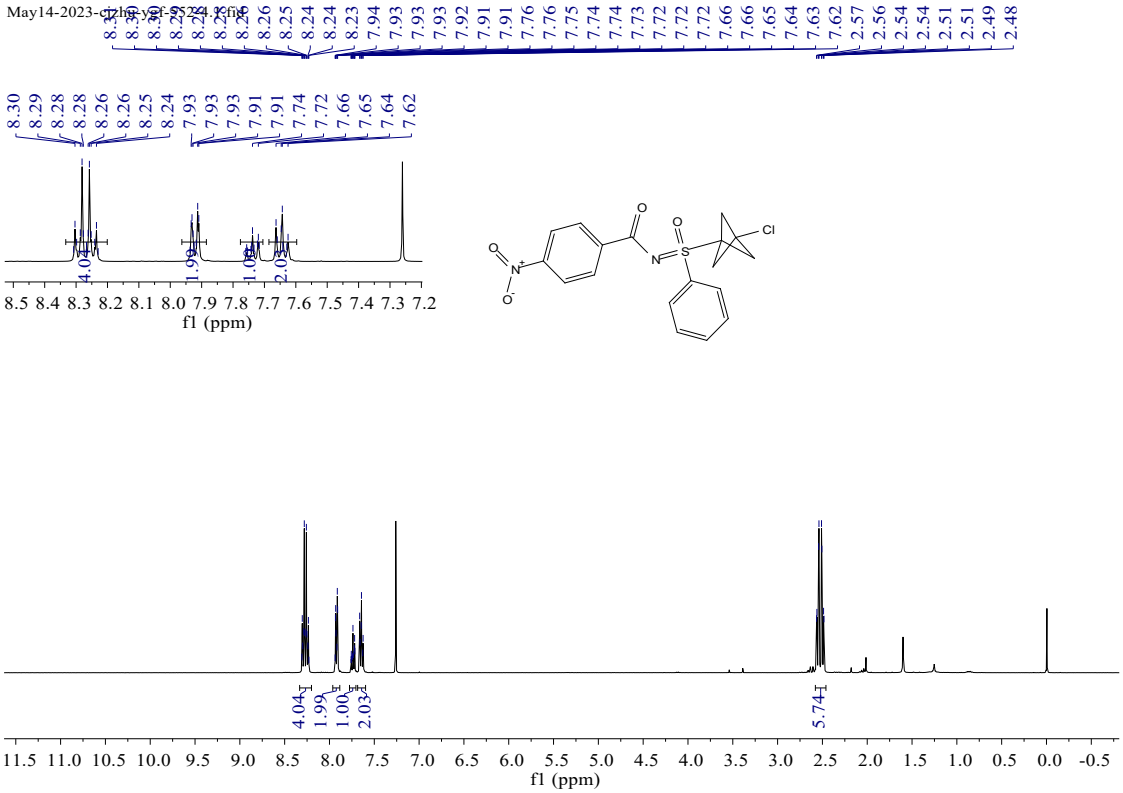
Product (17), ^{13}C NMR (100 MHz, Chloroform-*d*)



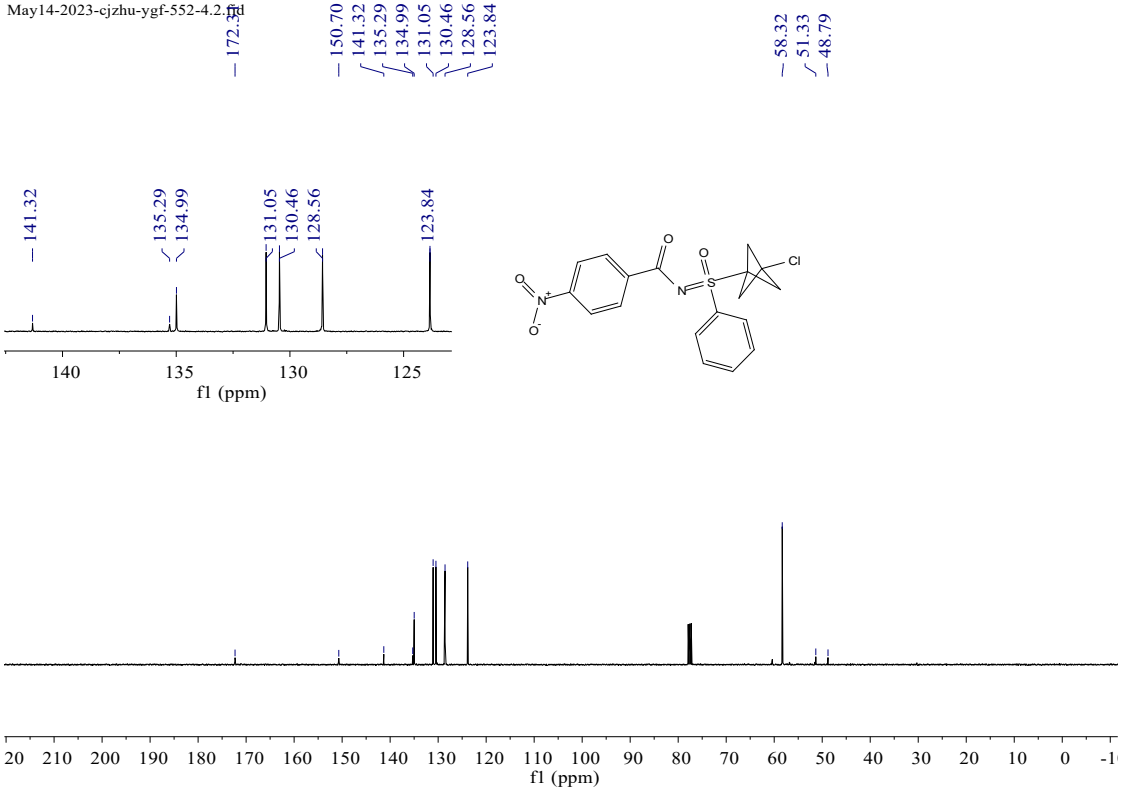
Product (17), ^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*)



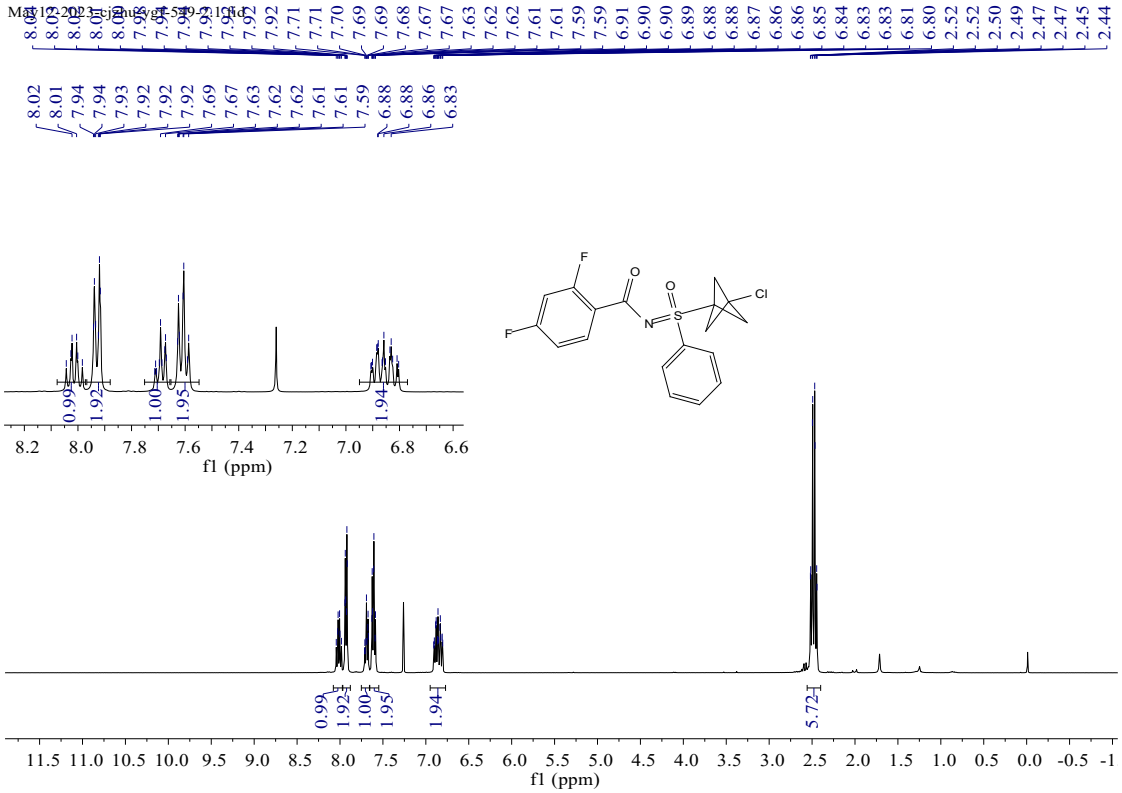
Product (18), ^{1}H NMR (400 MHz, Chloroform-*d*)



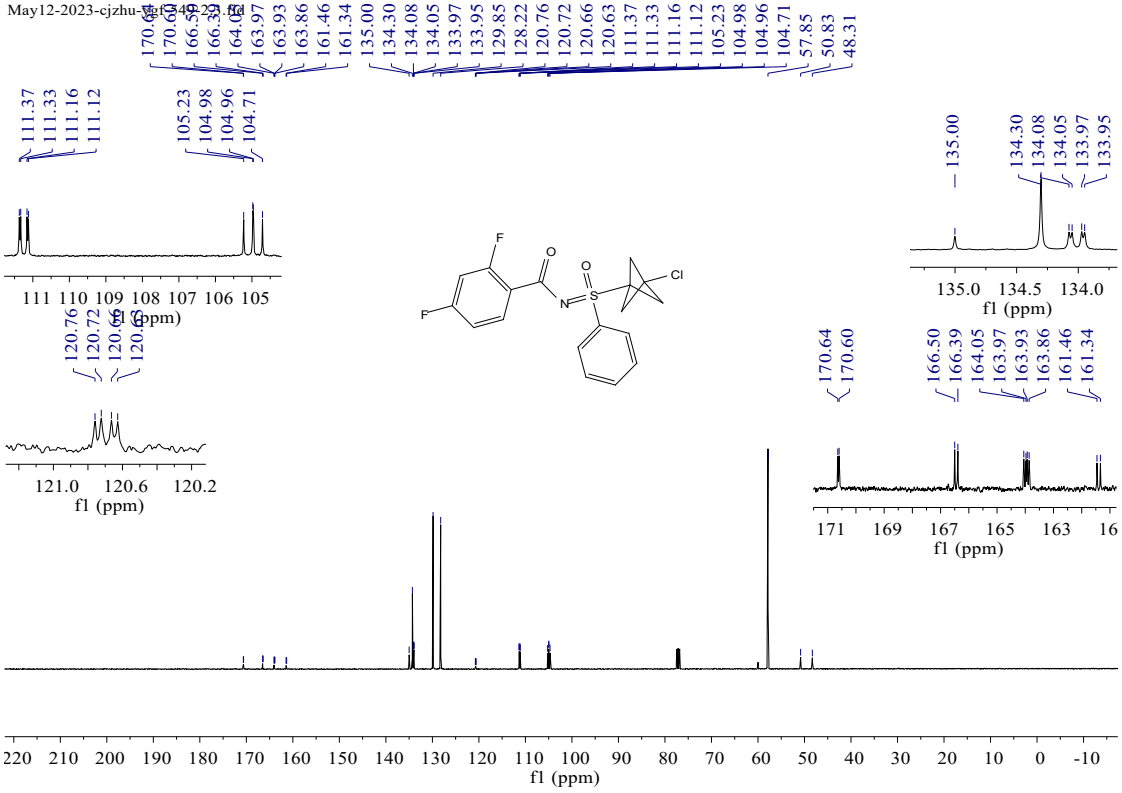
Product (18), ^{13}C NMR (100 MHz, Chloroform-*d*)



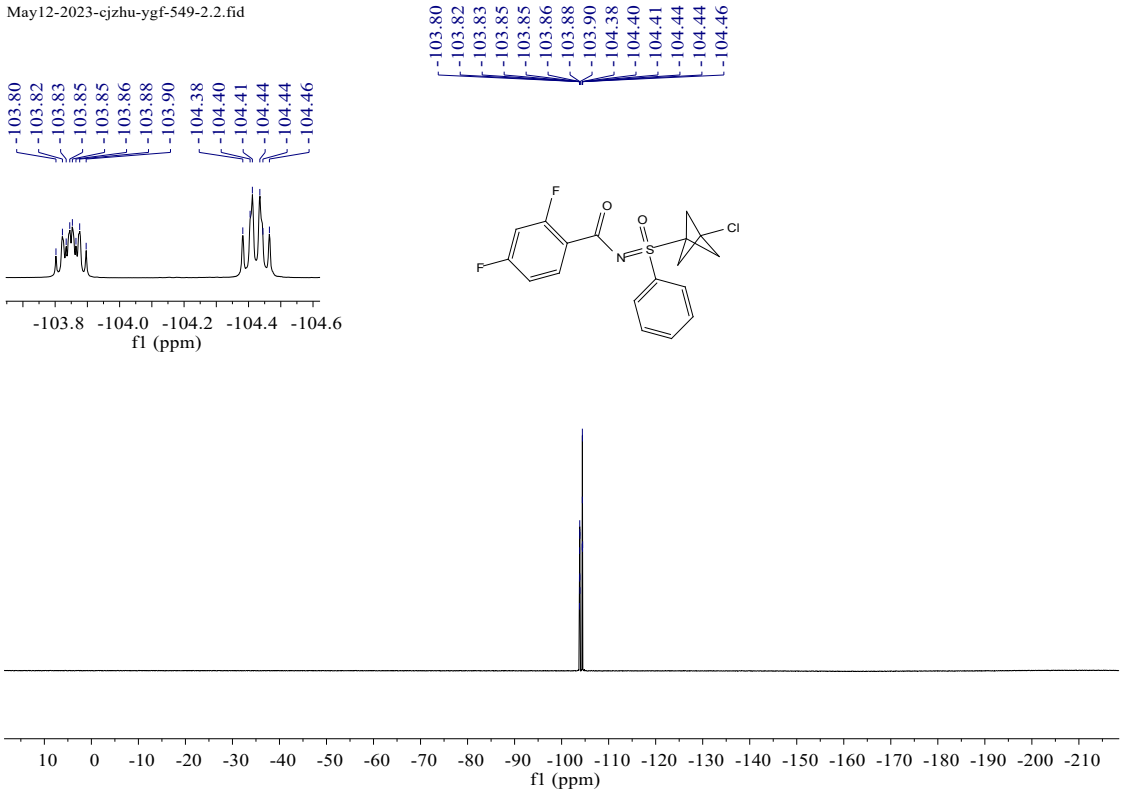
Product (19), ^{1}H NMR (400 MHz, Chloroform-*d*)



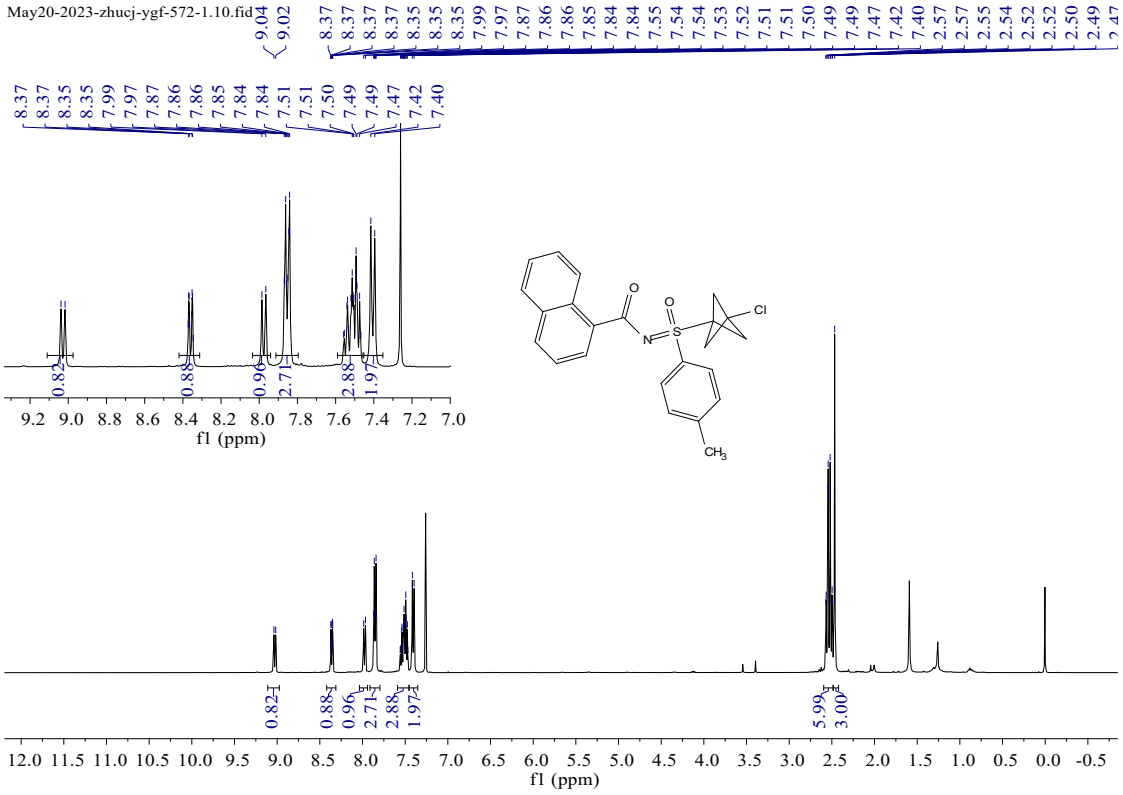
Product (19), ^{13}C NMR (100 MHz, Chloroform-*d*)



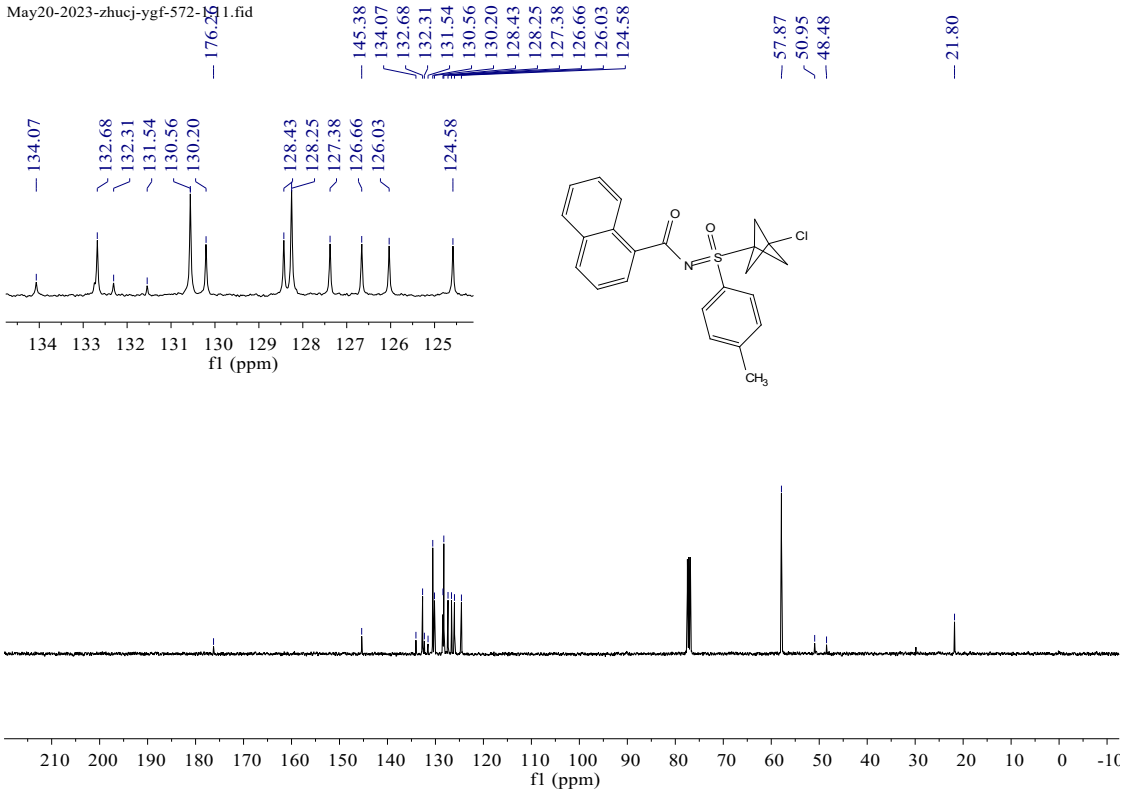
Product (19), $^{19}F\{^{1}H\}$ NMR (376 MHz, Chloroform-*d*)



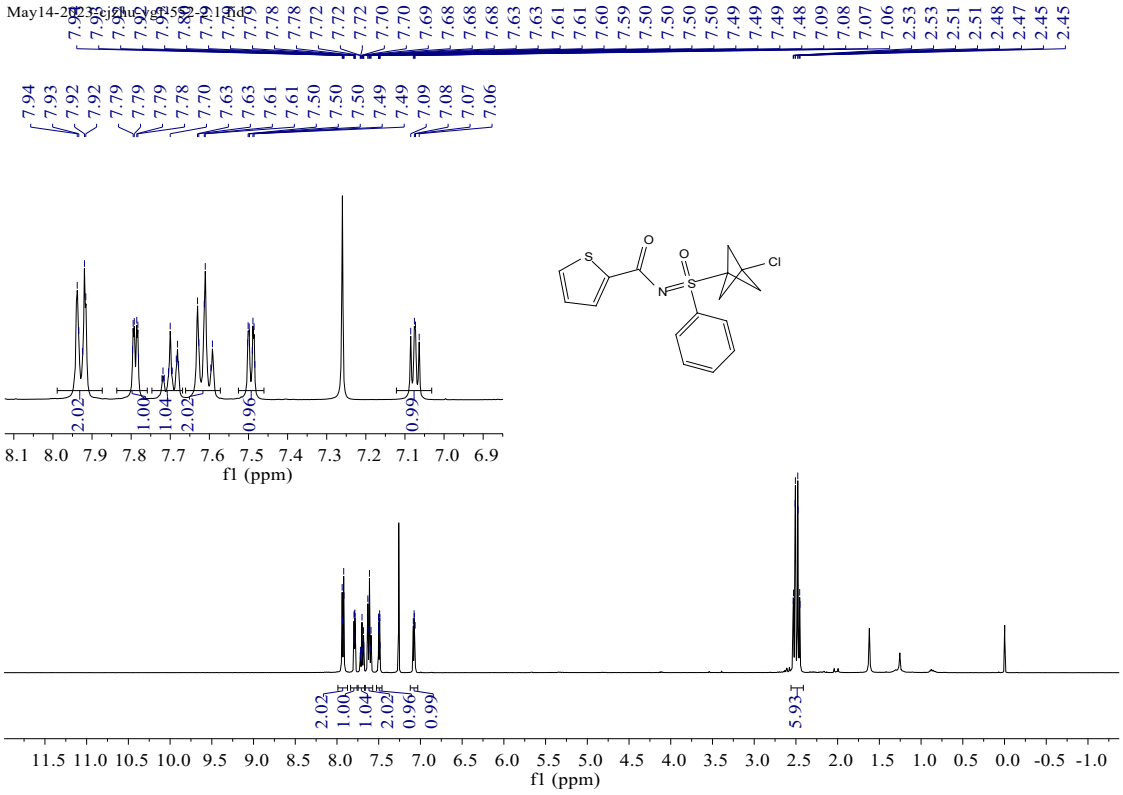
Product (20), ^{1}H NMR (400 MHz, Chloroform-*d*)



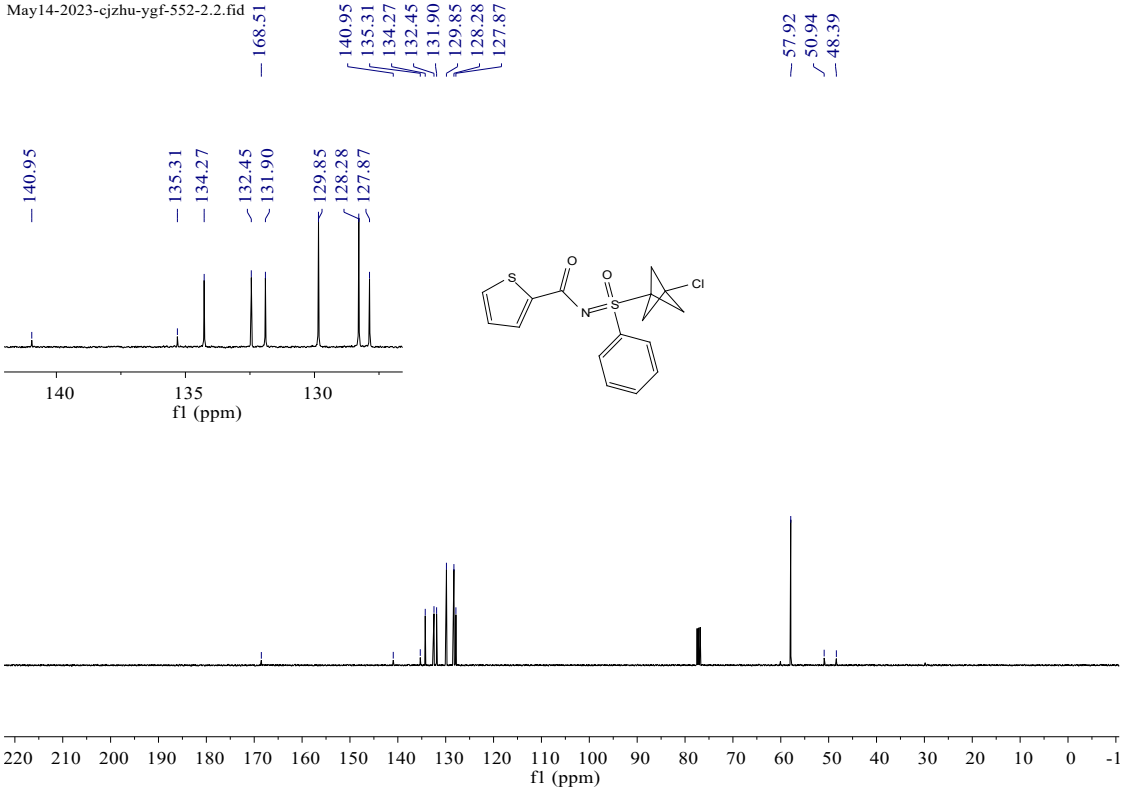
Product (20), ^{13}C NMR (100 MHz, Chloroform-*d*)



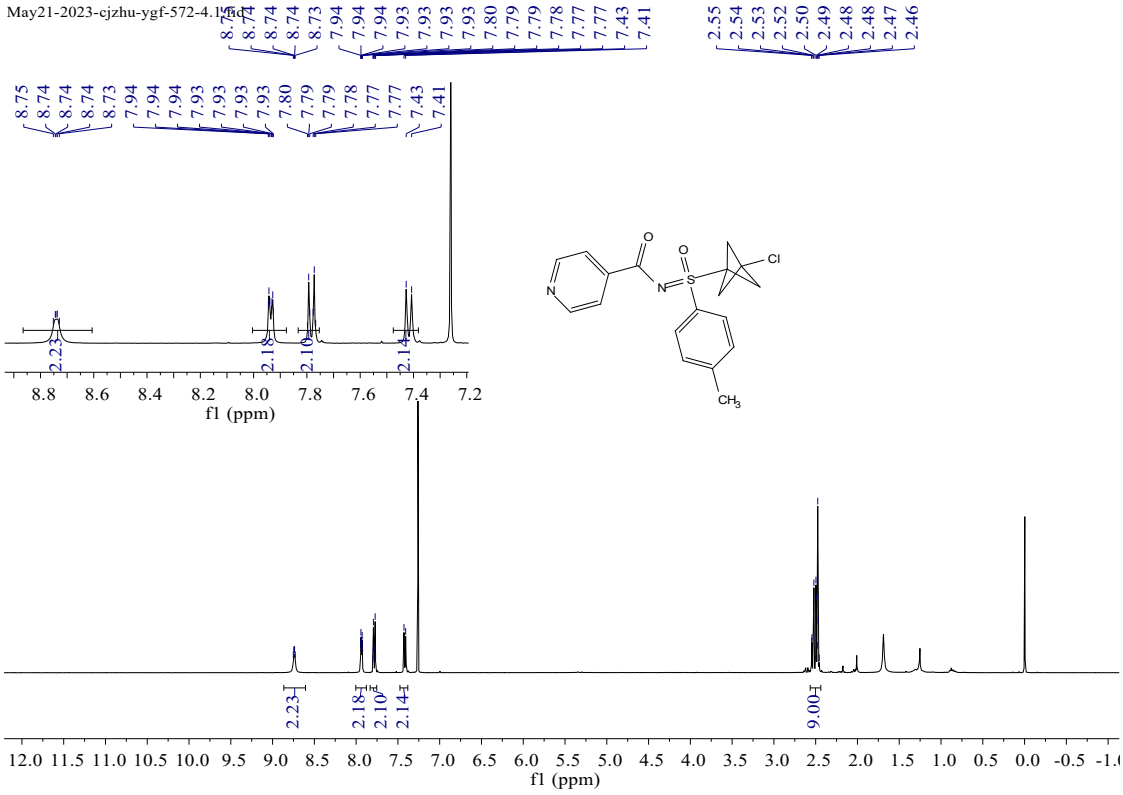
Product (21), ^{1}H NMR (400 MHz, Chloroform-*d*)



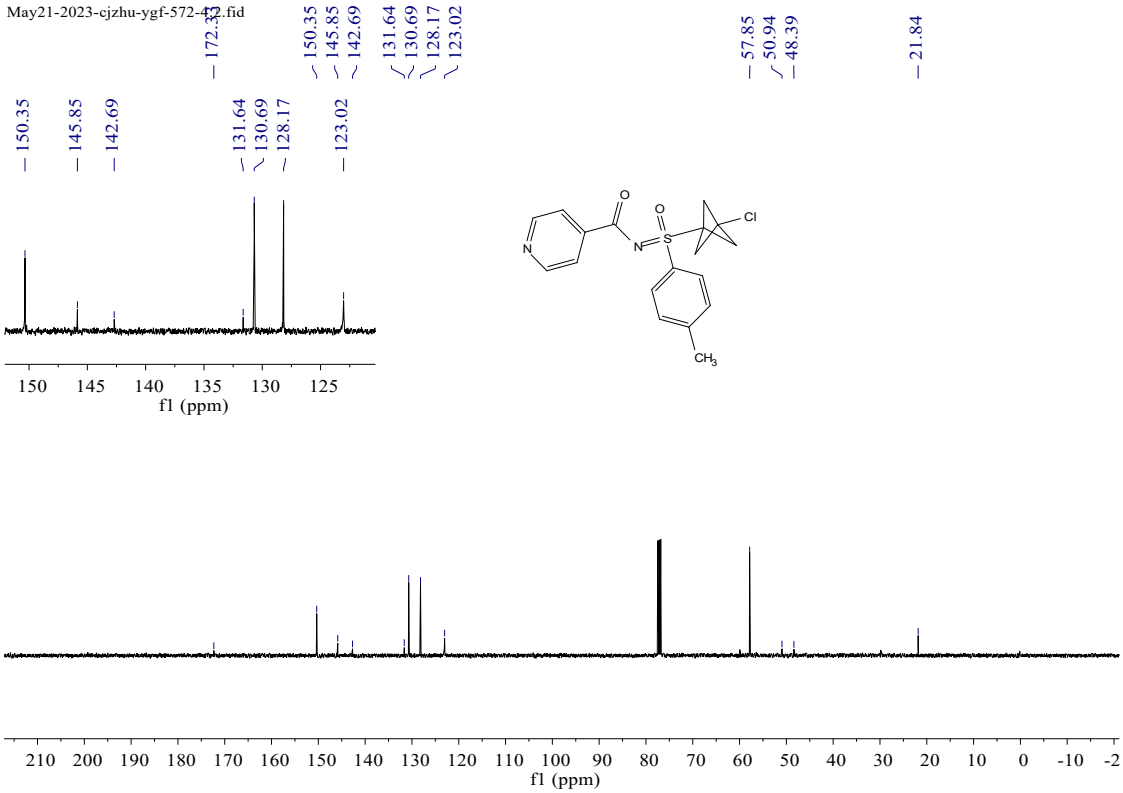
Product (21), ^{13}C NMR (100 MHz, Chloroform-*d*)



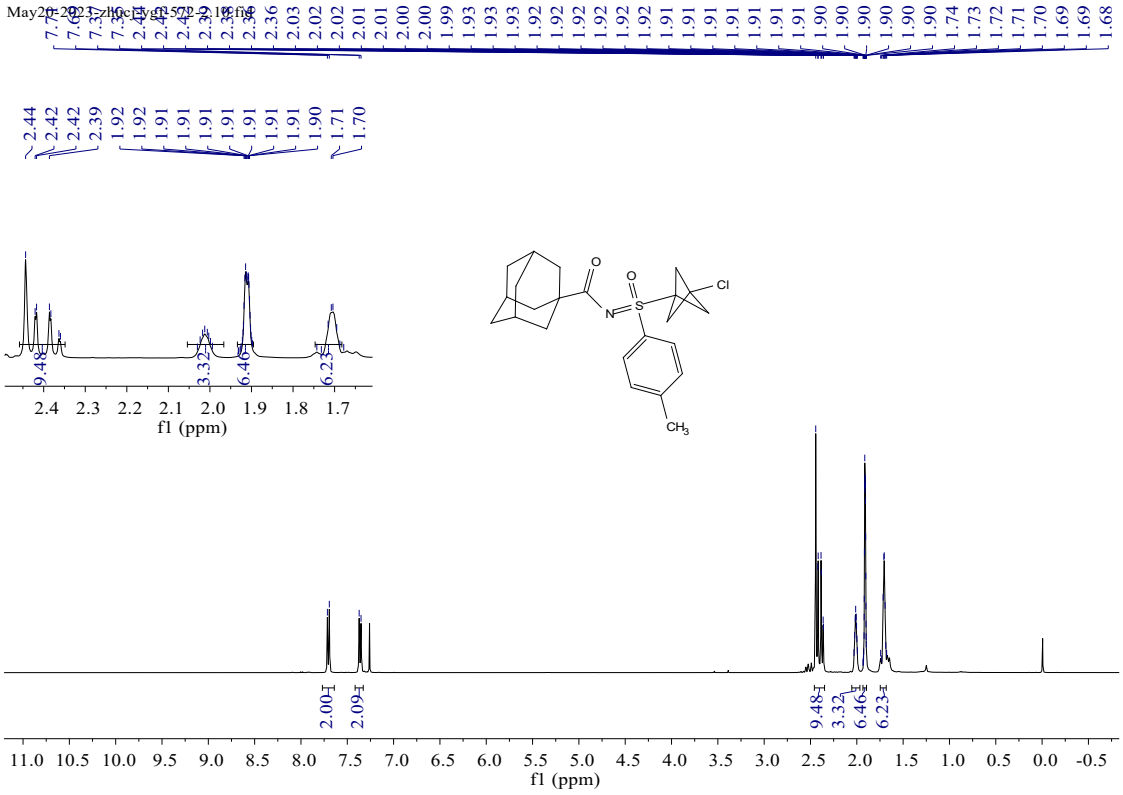
Product (22), ^{1}H NMR (400 MHz, Chloroform-*d*)



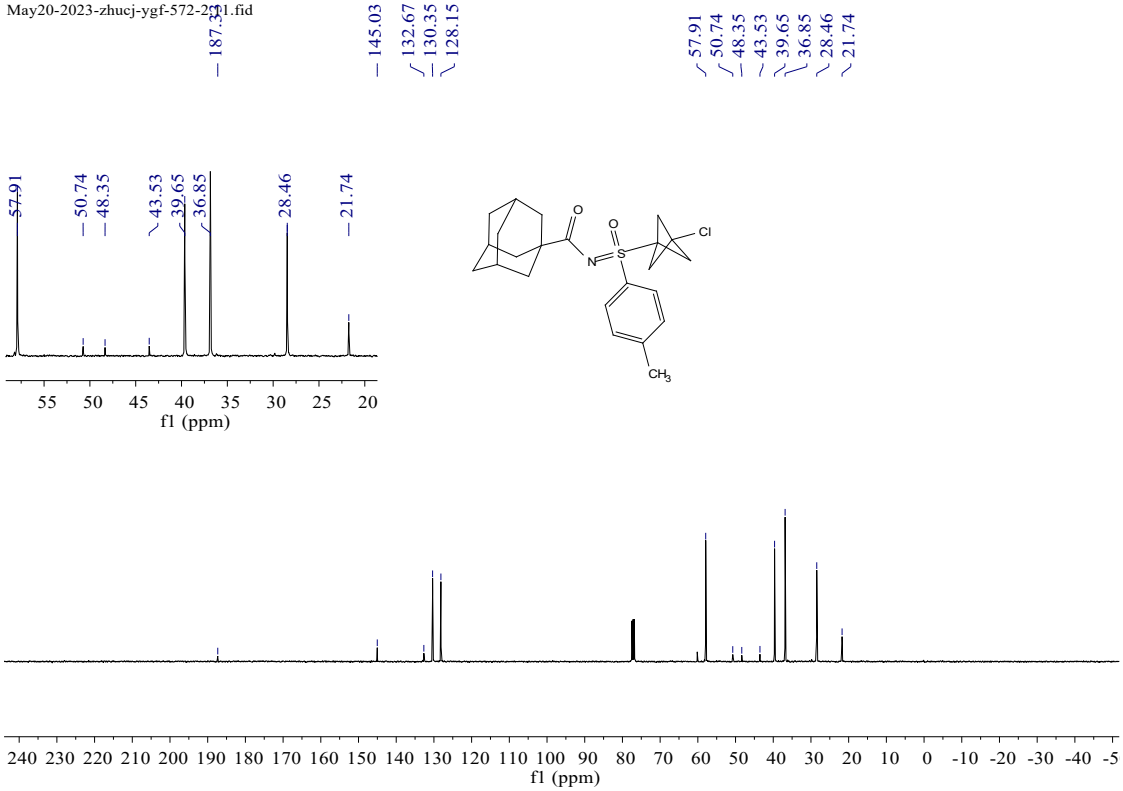
Product (22), ^{13}C NMR (100 MHz, Chloroform-*d*)



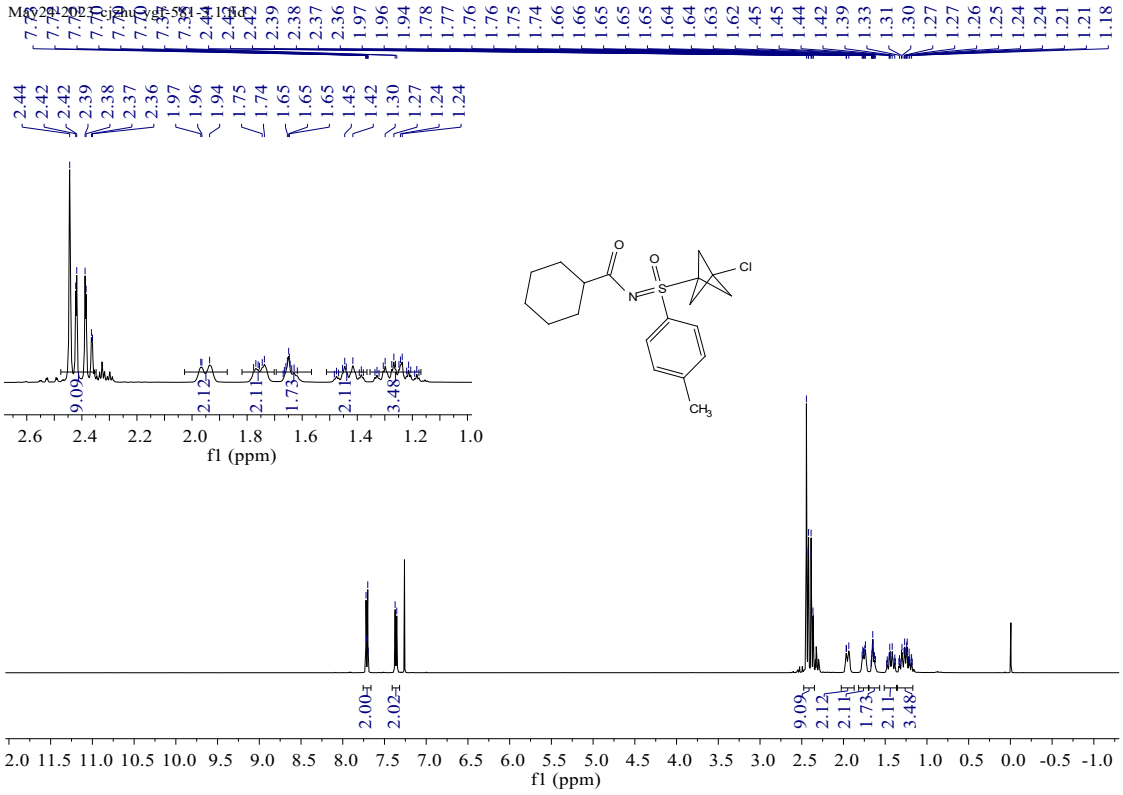
Product (23), ^{1}H NMR (400 MHz, Chloroform-*d*)



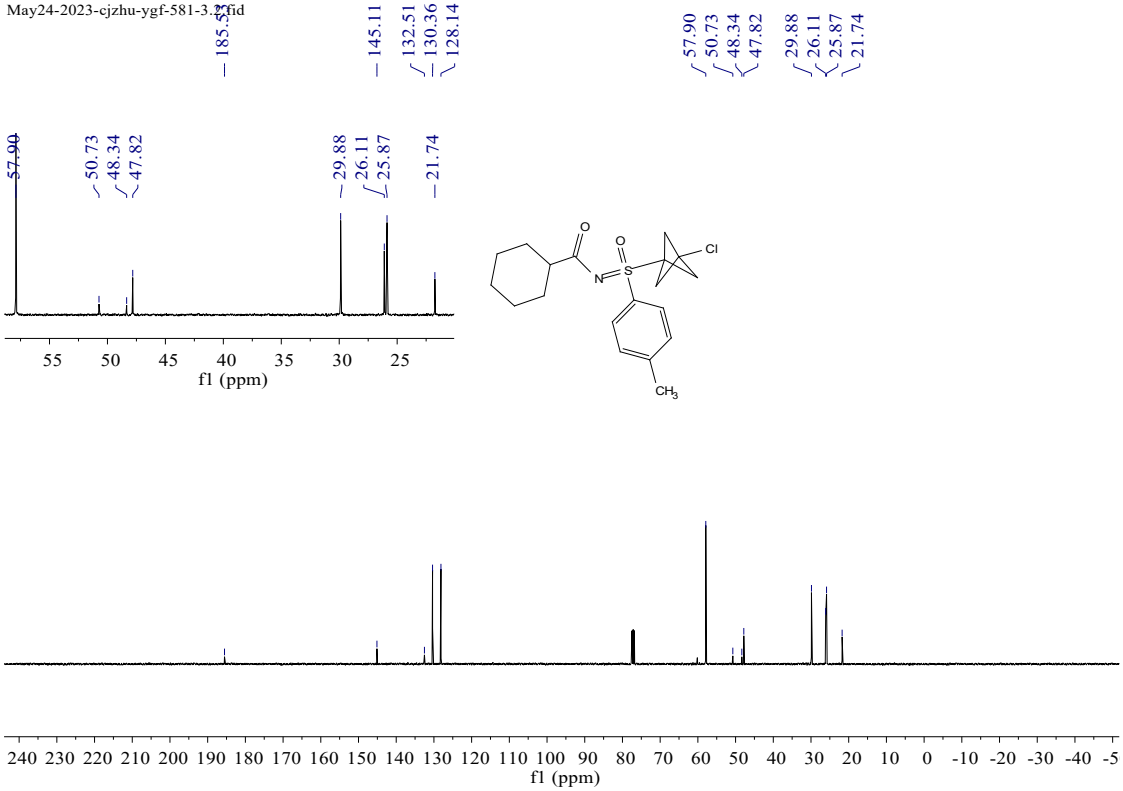
Product (23), ^{13}C NMR (100 MHz, Chloroform-*d*)



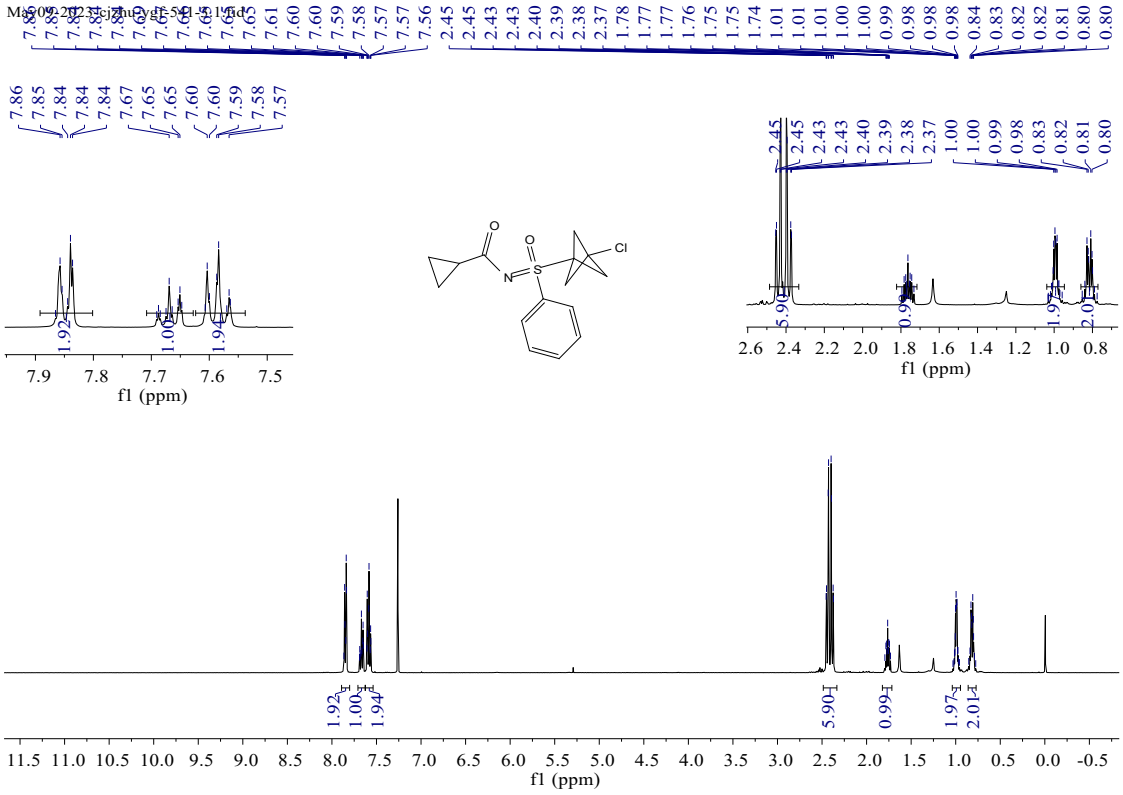
Product (24), ^{1}H NMR (400 MHz, Chloroform-*d*)



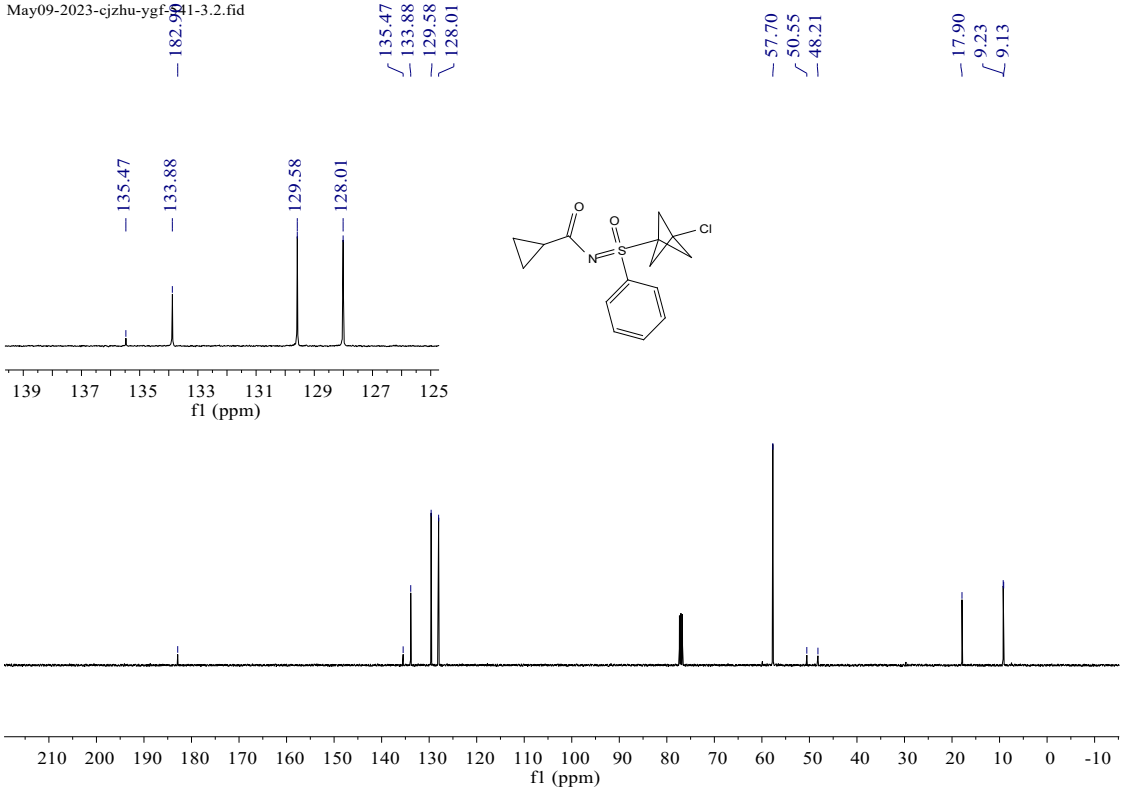
Product (24), ^{13}C NMR (100 MHz, Chloroform-*d*)



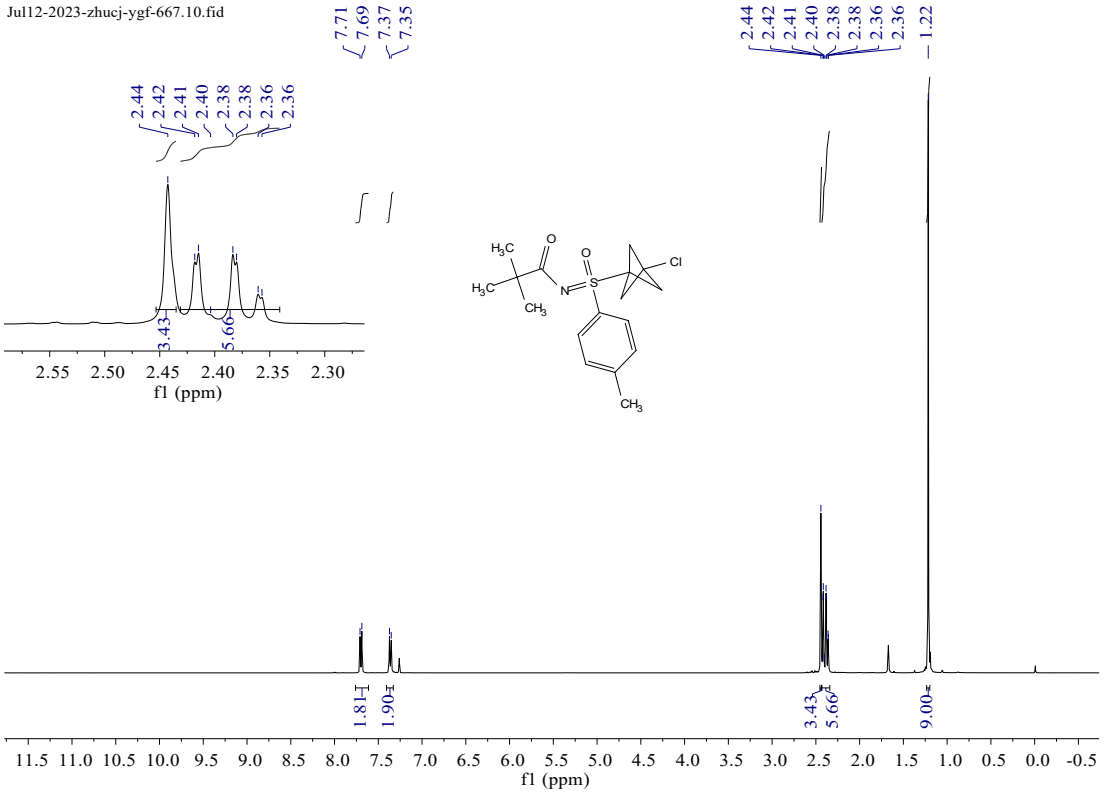
Product (25), ^{1}H NMR (400 MHz, Chloroform-*d*)



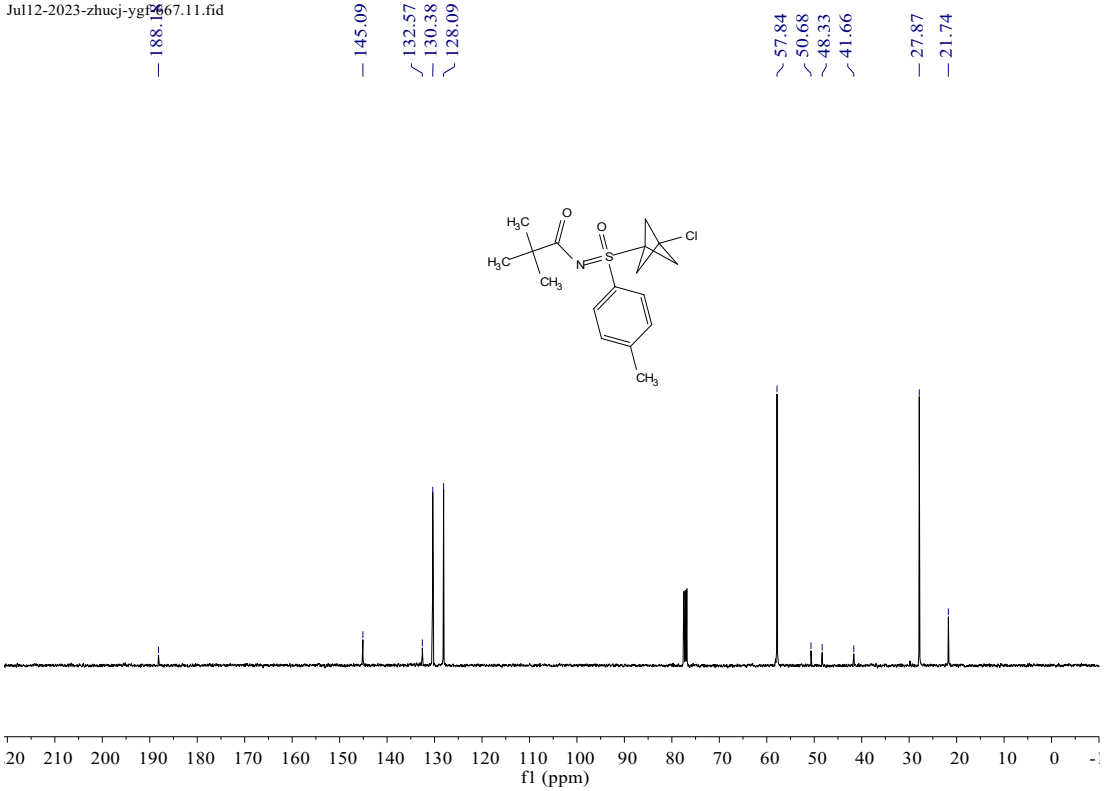
Product (25), ^{13}C NMR (100 MHz, Chloroform-*d*)



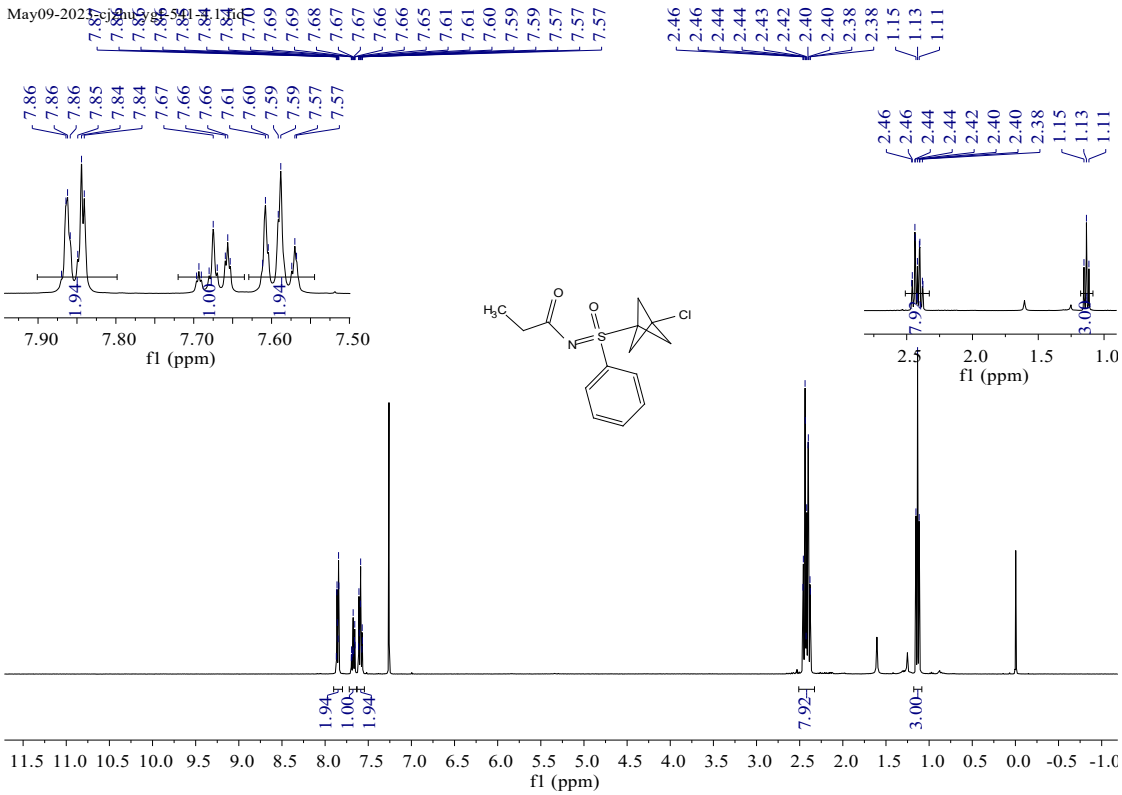
Product (26), ^{1}H NMR (400 MHz, Chloroform-*d*)



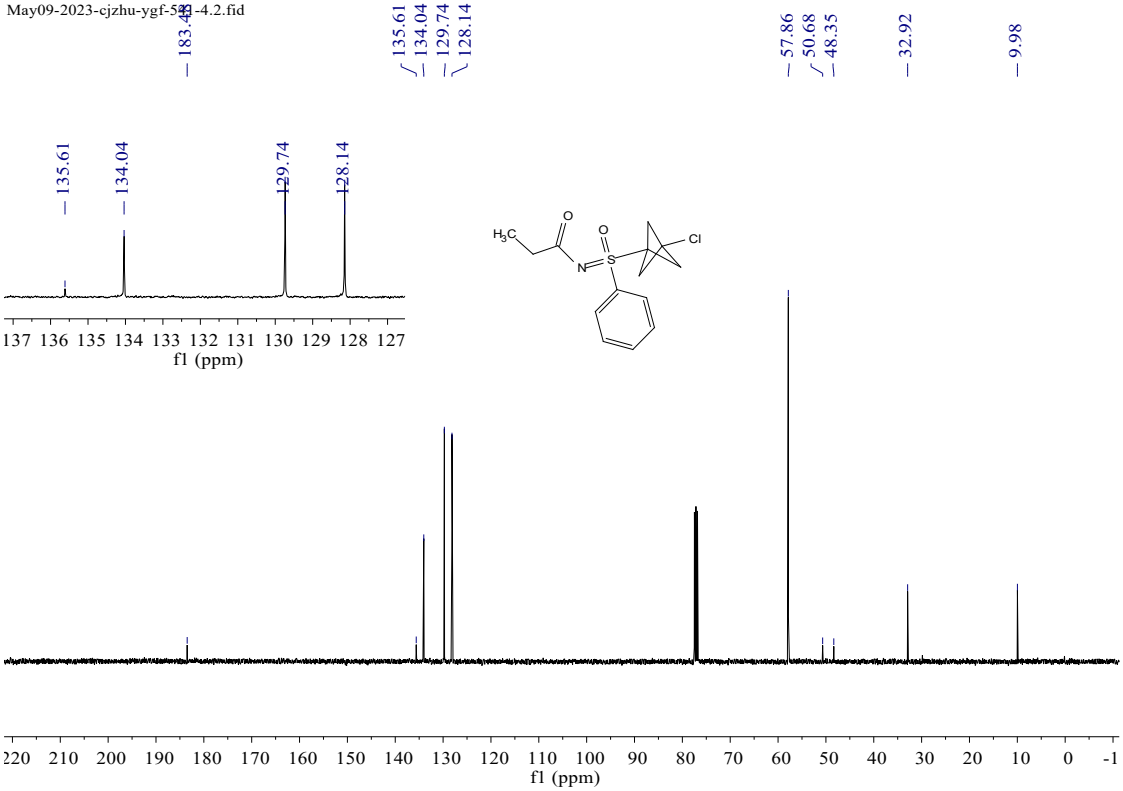
Product (26), ^{13}C NMR (100 MHz, Chloroform-*d*)



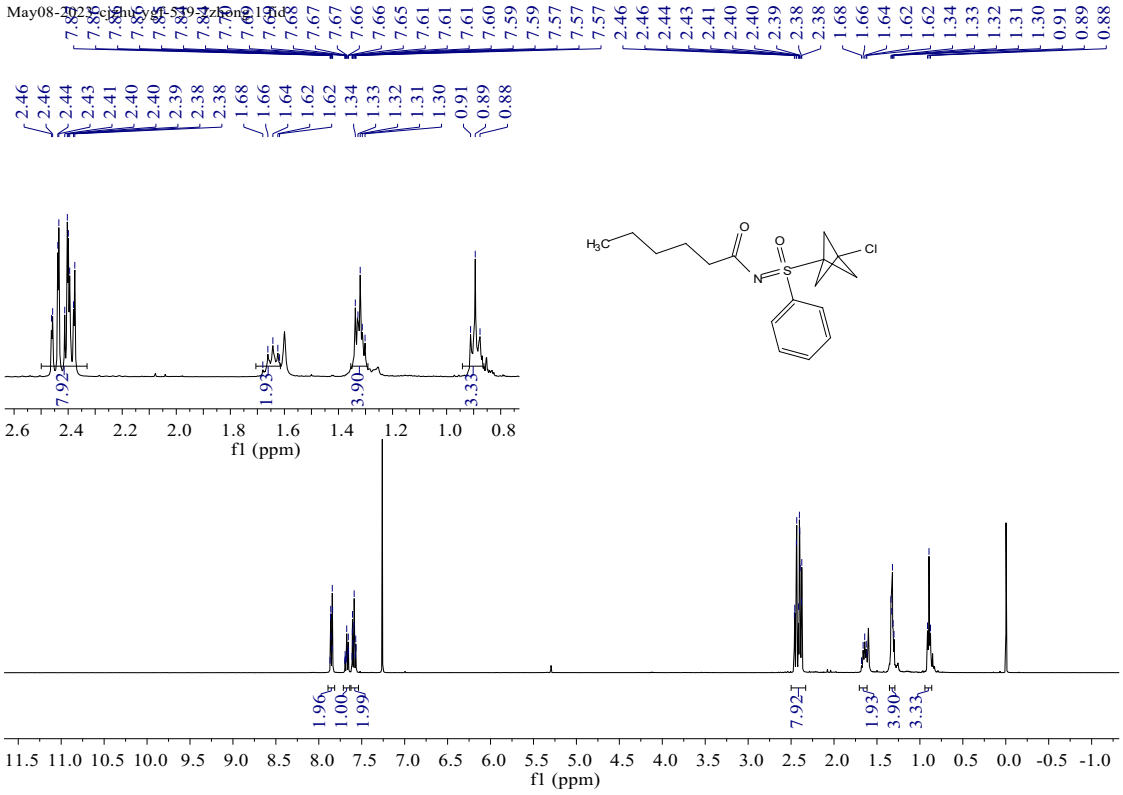
Product (27), ^{1}H NMR (400 MHz, Chloroform-*d*)



Product (27), ^{13}C NMR (100 MHz, Chloroform-*d*)



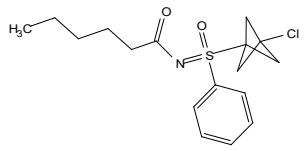
Product (28), ^{1}H NMR (400 MHz, Chloroform-*d*)

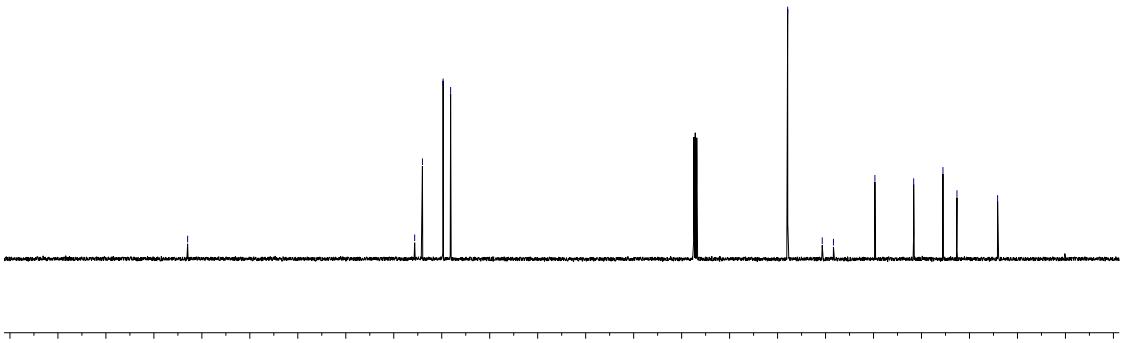


Product (28), ^{13}C NMR (100 MHz, Chloroform-*d*)

May09-2023-cjzhu-ygf-589-2zhong-c.1.fid

182.95
135.64
134.03
129.72
128.15
57.90
50.69
48.36
39.71
31.63
25.53
22.61
14.14



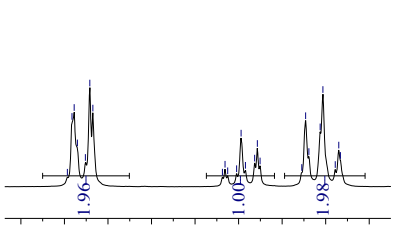


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

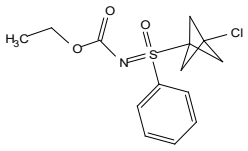
Product (29), ^{1}H NMR (400 MHz, Chloroform-*d*)

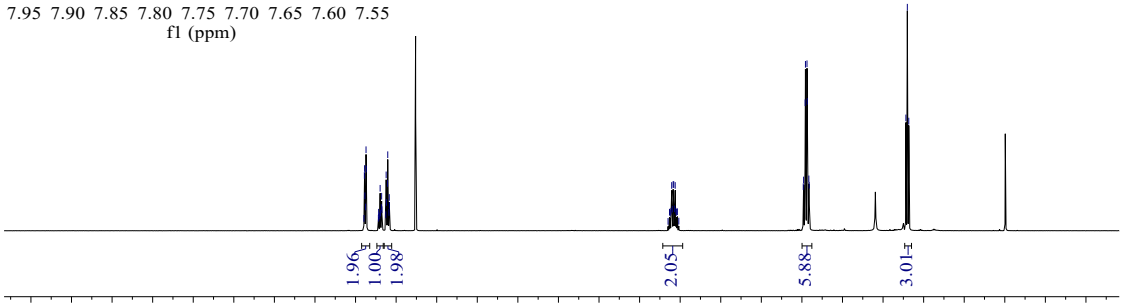
May08-2023-cjzhu-ygf-589-1 zhong-1.fid

7.89 7.89 7.89 7.88 7.87 7.87 7.72 7.70 7.68 7.68 7.68 7.62 7.62 7.61 7.60 7.58 7.58
4.15 4.13 4.12 4.11 4.10 4.10 4.09 4.08 4.07 4.06 4.05 4.04 4.03 4.02 2.48 2.48 2.46 2.46 2.44 2.43 2.41 2.41 1.22 1.20 1.18



7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55
f1 (ppm)





12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

Product (29), ^{13}C NMR (100 MHz, Chloroform-*d*)

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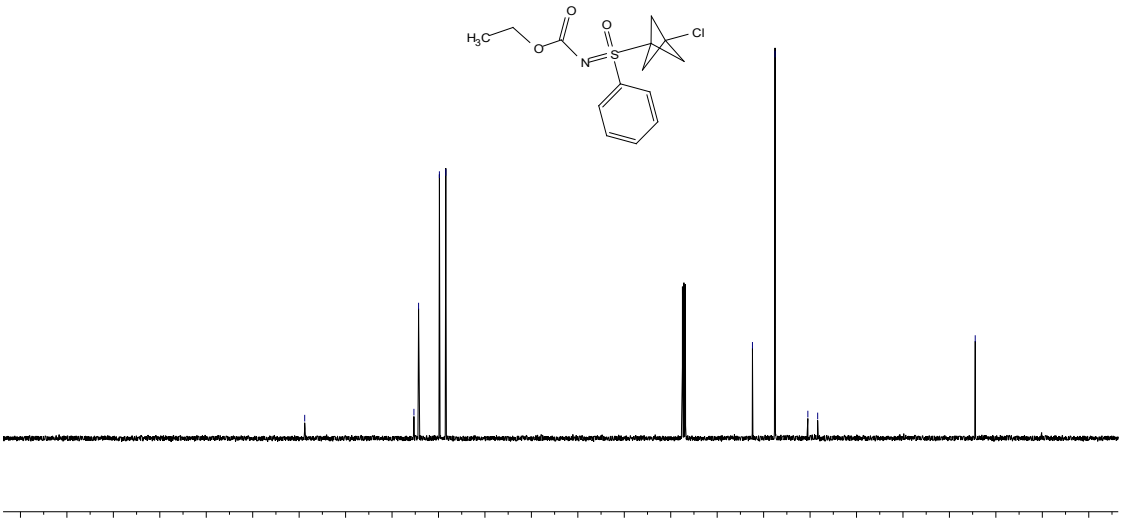
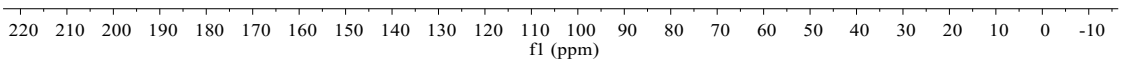
158.88
135.29
134.29
129.80
128.43
62.41
57.55
50.48
48.36
14.44

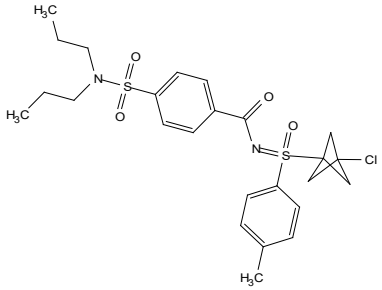




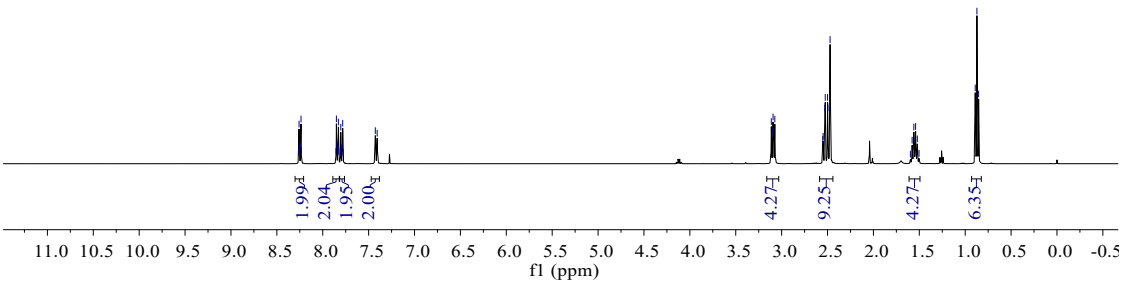
Product (30), ^{1}H NMR (400 MHz, Chloroform-*d*)

Apr15-2026-cjzhu-YGF-1441-10f1.fid

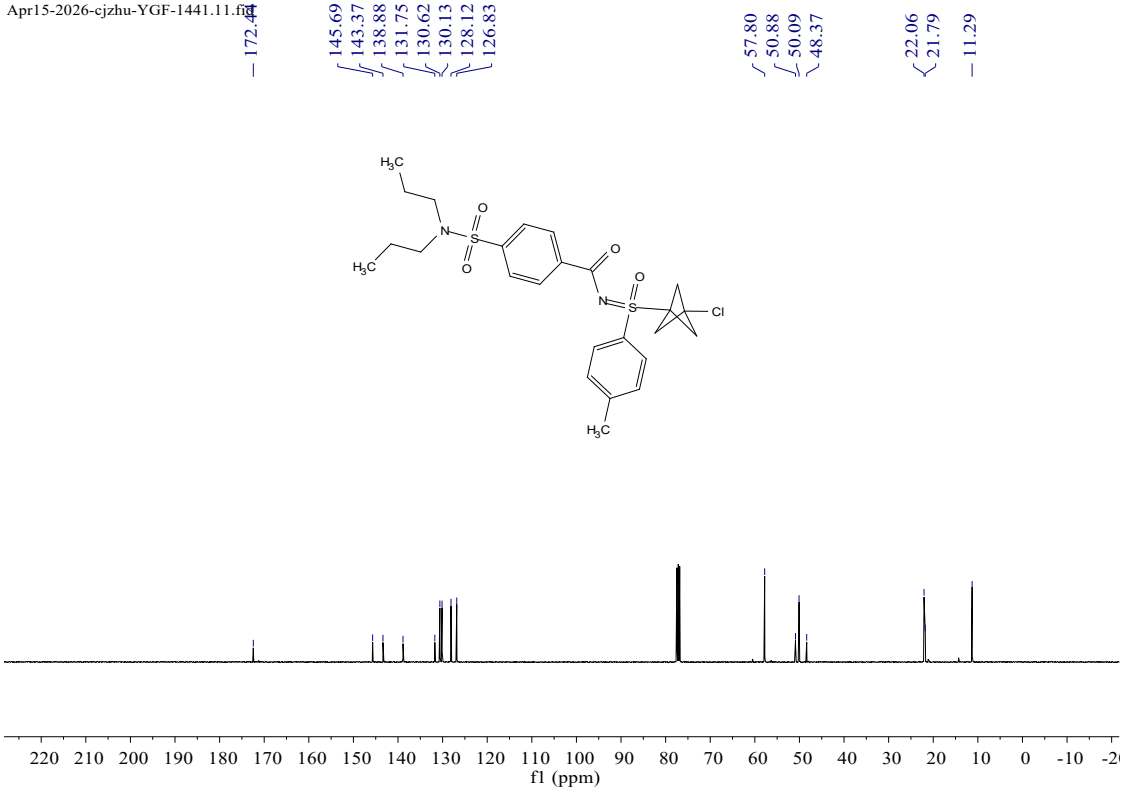
8.26
8.25
8.24
8.23
8.22
7.86
7.85
7.85
7.83
7.83
7.83
7.81
7.80
7.80
7.79
7.78
7.78
7.43
7.41
3.11
3.10
3.09
3.09
3.07
2.55
2.55
2.53
2.52
2.50
2.50
2.47
1.60
1.58
1.56
1.54
1.52
1.50
0.89
0.87
0.85



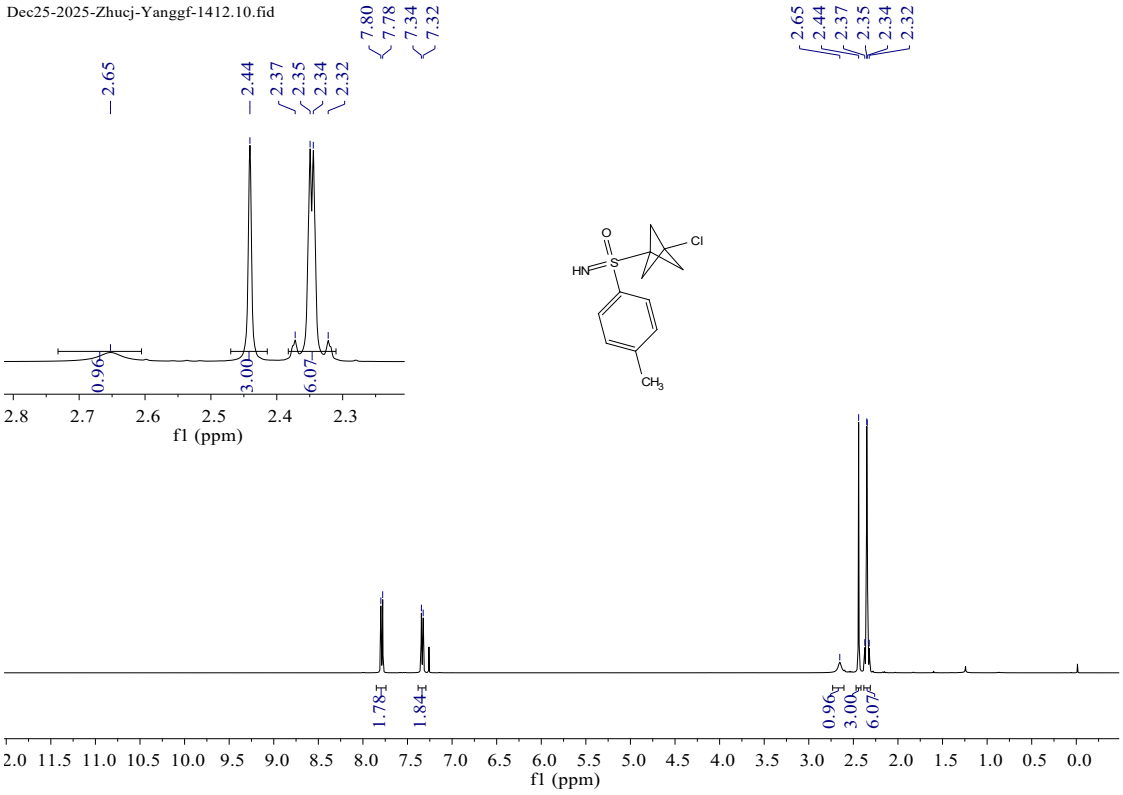
1.99
2.04
1.95
2.00
4.27
9.25
4.27
6.35



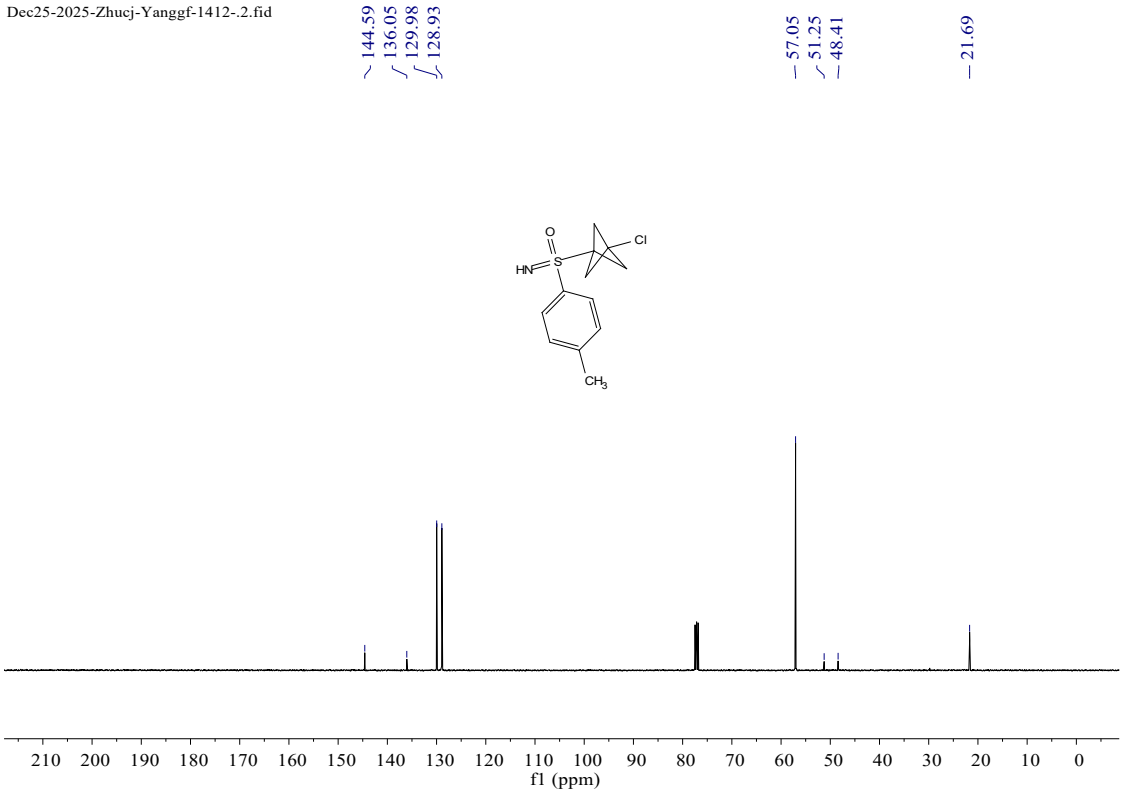
Product (30), ^{13}C NMR (100 MHz, Chloroform-*d*)



Product (31), ^{1}H NMR (400 MHz, Chloroform-*d*)

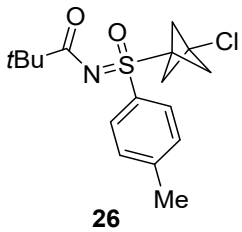


Product (31), ^{13}C NMR (100 MHz, Chloroform-*d*)

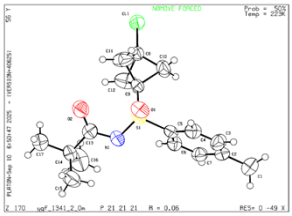


X-ray Single Crystal Data

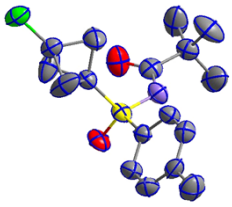
A single crystal of product **(26)** suitable for *X*-ray crystallography was obtained by crystallization via evaporation from *n*-hexane/dichloromethane solution.



26



26



26

CCDC number **Identification code**	**2487148** **26**
Empirical formula	$C_{17}H_{22}ClNO_2S$
Formula weight	339.86
Temperature/K	223.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.1820(7)
b/Å	10.2582(12)
c/Å	28.320(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1796.0(4)
Z	4
ρ_{calc}g/cm^3	1.257
μ/mm^{-1}	0.335
F(000)	720.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.224 to 50.69
Index ranges	$-7 \le h \le 7$, $-12 \le k \le 8$, $-34 \le l \le 34$
Reflections collected	11689
Independent reflections	3300 [R_{int} = 0.0473, R_{sigma} = 0.0496]
Data/restraints/parameters	3300/0/203
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.1315
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1458
Largest diff. peak/hole / e Å^{-3}	0.45/-0.21
Flack parameter	0.04(5)

Figure S11. The X-ray Structure of **26**

References

(1) (a) Li, B.; Hu, J.; Xu, Z.; Liao, M.; Chi, Y. R.; Wu, X. Control Over S(VI) Stereogenicity for the Asymmetric Synthesis of Sulfonimidoyl Derivatives by Isothiourea-Catalyzed Covalent Activation of Sulfur(VI) Atoms. *Angew. Chem. Int. Ed.* **2025**, *64,* e202510595. (b) Zeng, D.; Zhang, X.; Zheng, H.; Wang, M.; Jiang, X. Construction of a Chiral Click Chemistry Platform via Enantioselective F/Cl Exchange at S(VI) Centers. *J. Am. Chem. Soc.* **2025**, *147,* 30380-30389. (c) Yang, G.-f.; Yuan, Y.; Tian, Y.; Zhang, S.-q.; Cui, X.; Xia, B.; Li, G.-x.; Tang, Z. Synthesis of Chiral Sulfonimidoyl Chloride via Desymmetrizing Enantioselective Hydrolysis. *J. Am. Chem. Soc.* **2023**, *145,* 5439-5446.

(2) (a) Pickford, H. D.; Ripenko, V.; McNamee, R. E.; Holovchuk, S.; Thompson, A. L.; Smith, R. C.; Mykhailiuk, P. K.; Anderson, E. A. Rapid and Scalable Halosulfonylation of Strain-Release Reagents**. *Angew. Chem. Int. Ed.* **2023**, *62,* e202213508. (b) Cuadros, S.; Goti, G.; Barison, G.; Raulli, A.; Bortolato, T.; Pelosi, G.; Costa, P.; Dell'Amico, L. A General Organophotoredox Strategy to Difluoroalkyl Bicycloalkane (CF2-BCA) Hybrid Bioisosteres. *Angew. Chem. Int. Ed.* **2023**, *62,* e202303585.

(3) Dai, L.; Chen, Y.-Y.; Xiao, L.-J.; Zhou, Q.-L. Intermolecular Enantioselective Benzylic C(sp3)−H Amination by Cationic Copper Catalysis. *Angew. Chem. Int. Ed.* **2023**, *62,* e202304427.