Supporting Information

Radical-Polar Crossover Cyclization: Visible-light-induced Synthesis of γ-alkylated 1,1-disubstituted Cyclopropanes *via* 1,6-Hydrogen Atom Transfer

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1. General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All reactions were carried out in a sealed tube with a magnetic stir bar under an argon atmosphere. Except for the specially mentioned dry solvent, all the solvents were treated according to general methods. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. Product purification was done using silica gel column chromatography. Thin-layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100-200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. ^{1}H NMR spectra were recorded at 400 or 600 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 or 150 MHz (Varian). ^{19}F NMR spectra were recorded at at 376 MHz (Varian). Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ =7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm; H_2O signal was found at δ = 3.34 ppm) for ^{1}H NMR and chemical shifts for ^{13}C NMR spectra are reported in ppm relative to the central $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ = 39.6 ppm). Coupling constants were given in Hz. The following notations were used: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublet, dt-doublet of triplet, td-triplet of doublet. HRMS spectra were recorded a MicrOTOF-QIII (Bruker.Daltonics). The blue light source was provided by shanghai 3S Technology Co., Ltd SSSTECH-LAL1CV 1.0 parallel reactor. High-resolution mass spectra (HRMS) were recorded on a Bruker TOF Premier by the ESI method. The volume of the reaction tube is 10 ml. Photochemical reaction was carried out under visible light irradiation by a blue LED at SSSTECH-LAL1CV 1.0 parallel reactor manufactured by Shanghai 3S Technology Co., Ltd was used in this system. The blue LED's energy peak wavelength is 451 nm, peak width at half-height is 21 nm, irradiance@12 W is 49.2 mW/cm^2. The reaction vessel is a borosilicate glass test tube and the distance between it and the lamp is 0.5 cm, no filter applied. (Figure S1 and S2).

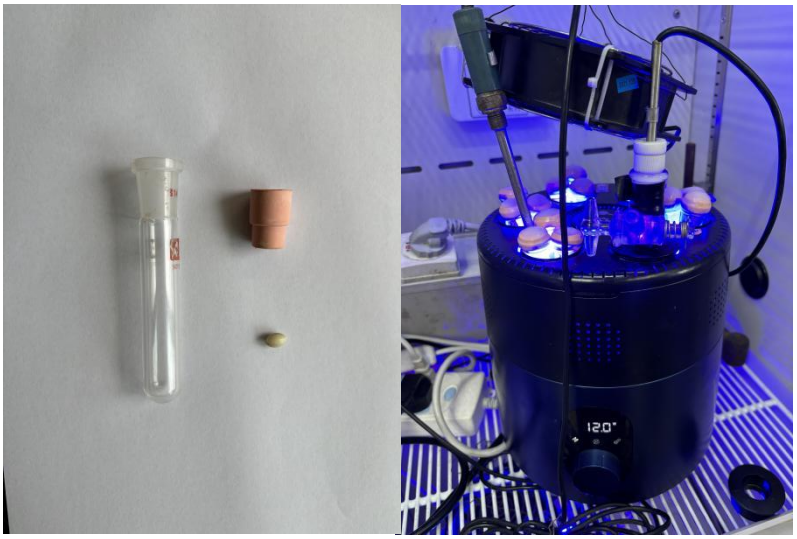


Figure S1. blue LED reactors

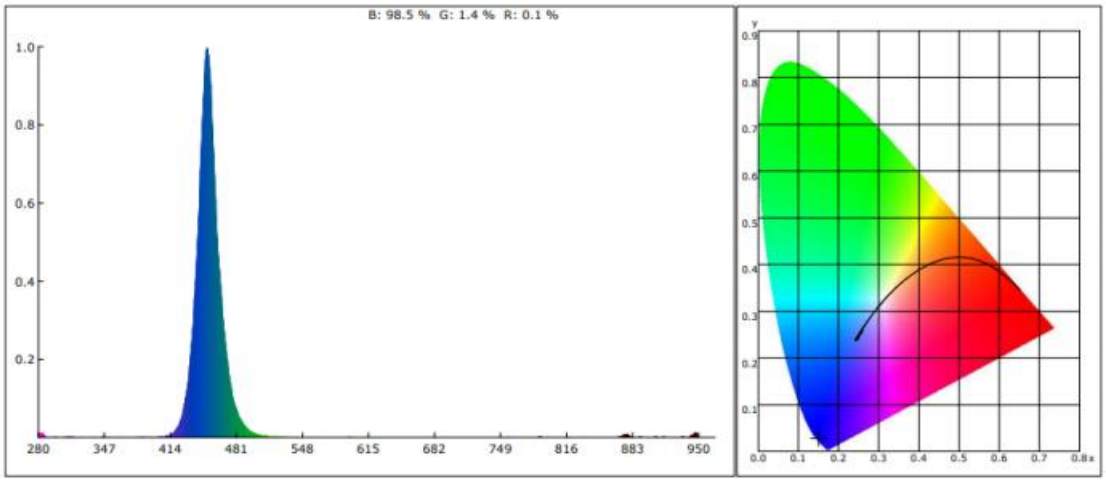
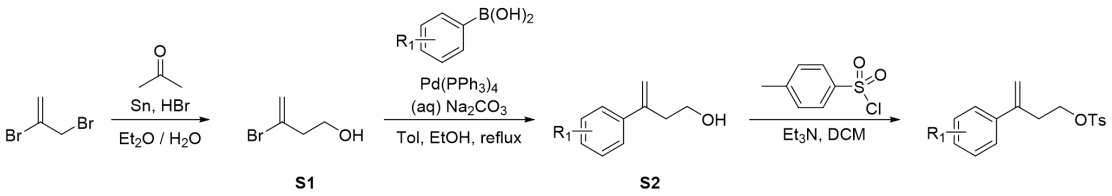


Figure S2. The spectrum of Blue LED

2. Preparation of substrates

2.1 General Procedure for the Synthesis of Cyclopropanation Substrates

General Procedure A:



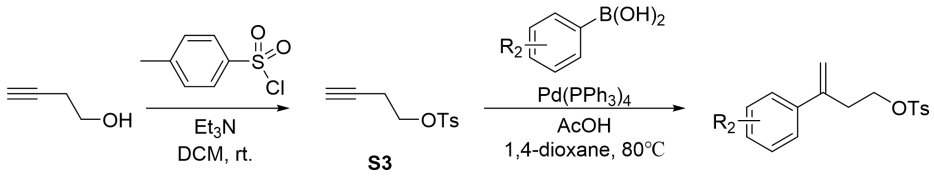
Step 1: To a round bottom flask equipped with a stir bar was added 2,3-dibromopropene (1.3 equiv.) dissolved in Et_2O / H_2O (1:1, 0.4 M) followed by Tin powder (1.3 equiv.), formaldehyde (1.0 equiv.) and HBr (48% aq., several drops) and stirred overnight at room temperature. After the reaction was complete, the reaction mixture was diluted with water and extracted with Et_2O. The combined organic layers were combined, washed with saturated brine solution, dried over anhydrous Na_2SO_4 and and filtered. The filtrate was concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded **S1**.

Step 2: To a double-necked round bottom flask equipped with a stir bar was added tetratriphenylphosphine palladium (0.03 equiv.). After being purged with Ar, 3-Bromo-3-buten-1-ol (1.0 equiv.) dissolved in toluene (0.5 M) was added followed by Na_2CO_3 (aq) (2.0 M, 2.0 equiv.) and Phenylboronic acid (1.01 equiv.) dissolved in EtOH (1.0 M). The reaction mixture was reflux for 10 h (an oil bath). After the reaction was complete, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were combined, washed with saturated brine solution, dried over anhydrous Na_2SO_4 and and filtered. The filtrate was concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded **S2**.

Step 3: To a double-necked flask equipped with a stir bar was purged with Ar three times, and charged with P-toluenesulfonyl chloride (1.3 equiv.) dissolved in DCM (0.8 M), followed by the addition of triethylamine (1.3 equiv.). **S2** dissolved in DCM

(0.8 M), was then added to the reaction mixture and stirred at room temperature overnight. After the reaction was complete, the mixture was washed three times with saturated Na_2CO_3 (aq). The combined organic layers were combined, washed with saturated brine solution, dried over anhydrous Na_2SO_4 and and filtered. The filtrate was concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the desired products.

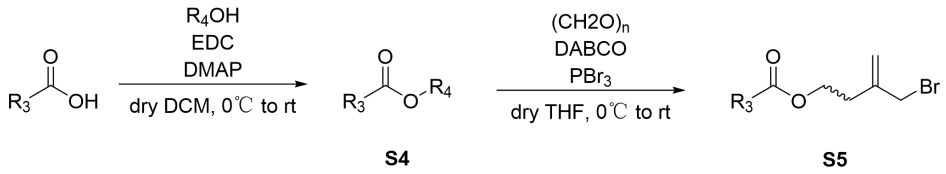
General Procedure B:



S3 was prepared following the General Procedure A with **S2**. Purification by flash column chromatography on silica gel afforded **S3**.

To a double-necked round bottom flask equipped with a stir bar was added **S3** (1.0 equiv.), $Pd(PPh_3)_4$ (5.0 mol%), phenylboronic acid (1.5 equiv.). 1,4-dioxane (0.25 M) and AcOH (15 mol%) were added and the solution was stirred at room temperature for 15 min, then at 80 °C for 22 h (an oil bath). The reaction was cooled to room temperature and the 1,4-dioxane was removed concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the desired products.

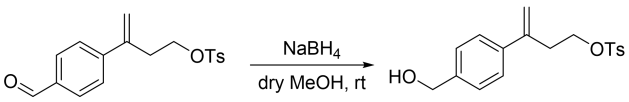
General Procedure C:



Step 1: To a double-necked round bottom flask equipped with a stir bar was added acid (1.0 equiv.), R_4OH (1.5 equiv.), DMAP (0.2 equiv.), EDC (2.0 equiv.) and dry DCM (0.25 M) at 0 °C. Warm the reaction mixture to room temperature and stir overnight. Purification by flash column chromatography on silica gel afforded **S4**.

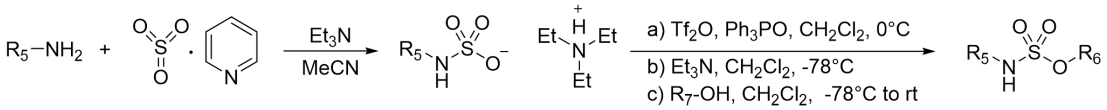
Step 2: To a flask equipped with a stir bar was added$(CH_2O)_n$ (1.3 equiv.), DABCO (1.3 equiv.) and dioxane / H_2O (1:1, 0.5 M) were then added with vigorous stirring, followed by **S4** (1.0 equiv.). The reaction mixture was stirred overnight. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the corresponding compound, which was transfer to a flask equipped with a stir bar with dry THF (0.5 M). Then added PBr_3 (0.35 equiv.) under the condition 0 ℃. The reaction mixture was prestirred for 5 min before warming to room temperature for 4 h. The reaction mixture was quenched with H_2O, extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded **S5**.

General Procedure D:



To a flask equipped with a stir bar was added 3-(4-formylphenyl)but-3-en-1-yl 4-methylbenzenesulfonate (1.0 equiv.). Dry MeOH was then added with vigorous stirring, followed by $NaBH_4$ (1.5 equiv.). The reaction mixture was stirred overnight. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded 3-(4-(hydroxymethyl)phenyl)b-ut-3-en-1-yl 4-methylbenzenesulfonate as colorless oil.

2.2 General Procedure for the Synthesis of Sulfamate Esters

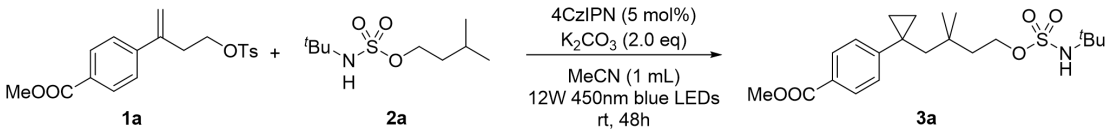


S6

Step 1: A double-necked round bottom flask equipped with a stir bar was charged with sulfur trioxide pyridine complex (SO_3•pyr, 1.0 equiv.). Acetonitrile (0.33 M) was then added. The suspension was stirred at room temperature until all of the SO_3•pyr had dissolved. Upon complete dissolution, the reaction flask was cooled at 0 °C in an ice water bath and purged with Ar for three times. Amine (R_5 –NH_2, 1.0 equiv.) was then added dropwise.. Following complete addition of amine, Et_3N (1.1 equiv.) was added dropwise. The reaction was removed from the ice bath and stirred for 0.5 h. Upon completion, the solvent was concentrated in *vacuo* to give a triethylammonium sulfamate salt **S6**, which was used without further purification.

Step 2: To a double-necked round bottom flask equipped with a stir bar was added triphenylphosphine oxide (1.65 equiv.). The flask was evacuated and backfilled with Ar. Anhydrous CH_2Cl_2 (0.2 M) was added and the flask was cooled at 0 °C. Trifluoromethanesulfonic anhydride (1.5 equiv.) that had been freshly removed from the glovebox was then added to the cooled solution dropwise *via* syringe. The reaction was allowed to stir at 0 °C for 15 minutes. A solution of sulfamate salt **S4** (1.5 equiv.) in CH_2Cl_2 (1.0 M) was added to the activated Ph_3PO. The resulting colorless to pale yellow solution was stirred for 15 minutes at 0 °C. The flask was then charged with Et_3N (3.0 equiv) and CH_2Cl_2 (0.25 M) and the mixture was cooled at -78 °C in a dry ice bath. The sulfamate salt solution was transferred dropwise to the Et_3N solution (during which time a yellow to intense red color often developed). The resultant solution was stirred at –78 °C for 15 minutes. The alcohol (R_7 –OH, 1.0 equiv) was then added as a solution in CH_2Cl_2 (1.0 M) to the triethylamine solution. Without removing the cooling bath, the reaction was then stirred for 18 h, during which time no additional dry ice was added and the mixture warmed to room temperature. After 18 h, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with 1 M HCl and brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the desired products.

3. General procedure for cyclopropanes *via* 1,6-HAT



To an oven-dried 10 mL sealed tube equipped with a stir bar, was charged with methyl 4-(4-(tosyloxy)but-1-en-2-yl)benzoate **1a** (0.1 mmol, 1.0 equiv.), sulfamate ester **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5.0 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv) and MeCN (1.0 mL). The solution was then stirred at room temperature under the irradiation of 12 W 450nm blue LEDs for 48 h using electronic fan to cool the tube. After completion of the reaction, purification by flash column chromatography on silica gel afforded the desired products.

4. Optimization of reaction conditions

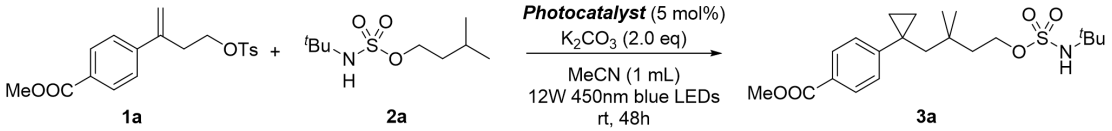


Table S1. Photocatalysts screening[a]

Entry	Photocatalyst (5%)	Yield[b](%)
1	Ph-PTZ	0
2	4CzTPN	76
3	**4CzIPN**	92
4	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	86
5	$[Ir(dtbbpy)(ppy)_2]PF_6$	66
6	*fac*-$Ir(ppy)_3$	48

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), photocatalyst (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, 12 W 450nm blue LEDs, argon, and 24 h. [b] Isolated yield.

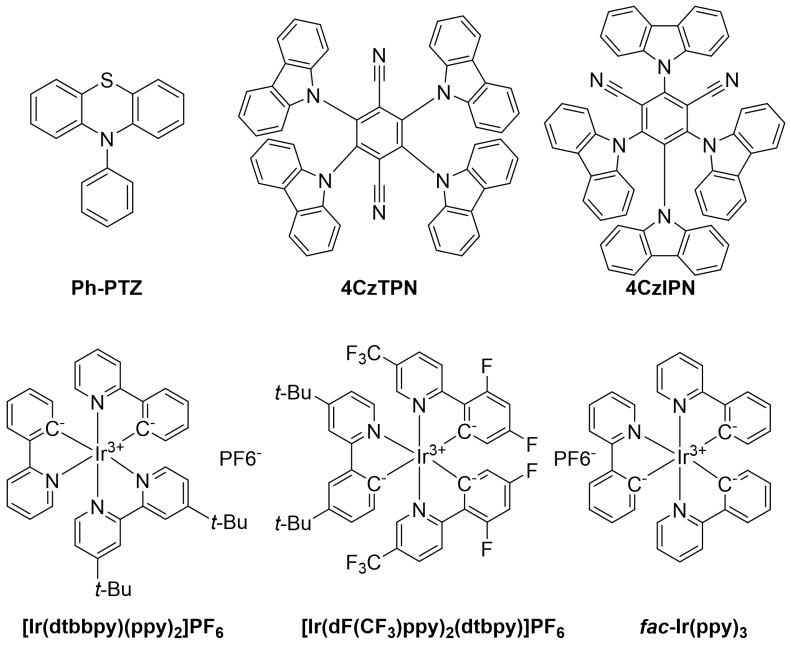
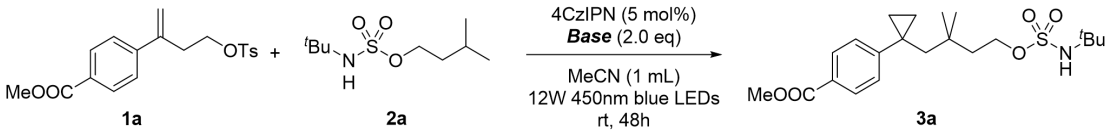


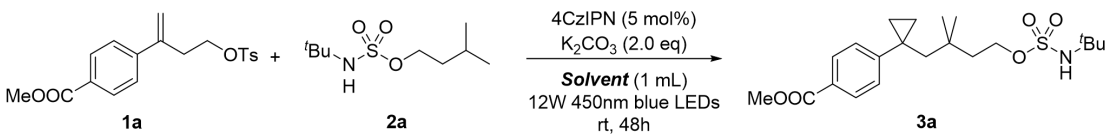
Table S2. Base screening[a]



Entry	Base	Yield[b](%)
1	**K_2CO_3**	92
2	Na_2CO_3	Trace
3	Cs_2CO_3	85
4	$NaHPO_4$	0
5	K_2HPO_4	0
6	DABCO	0
7	DMAP	0

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5 mol%), base (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, 12 W 450nm blue LEDs, argon, and 24 h. [b] Isolated yield.

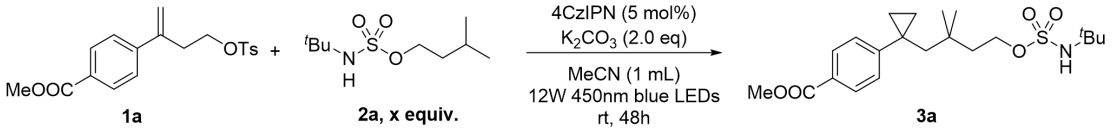
Table S3. Solvents screening[a]



Entry	Solvents	Yield[b](%)
1	**MeCN**	92
2	PhCl	64
3	PhF	58
4	DMSO	Trace
5	Tol	0
6	EA	0

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), solvent (1 mL), RT, 12 W 450nm blue LEDs, argon, and 24 h. [b] Isolated yield.

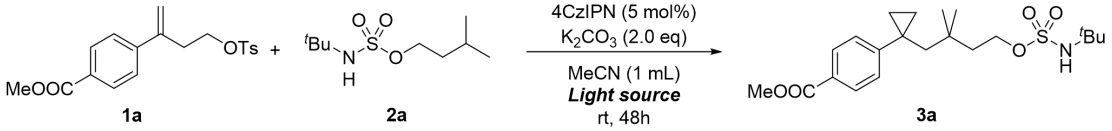
Table S4. Screening the loading of **2a**[a]



Entry	**2a** (x equiv.)	Yield[b](%)
1	1.0	57
2	**2.0**	92
3	3.0	89

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (x mmol, x equiv.), 4CzIPN (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, 12 W 450nm blue LEDs, argon, and 24 h. [b] Isolated yield.

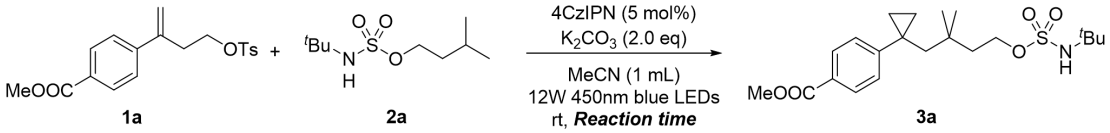
Table S5. Light sources screening[a]



Entry	Light sources	Yield[b](%)
1	12w 7500 k white LEDs	0
2	12w 390 nm purple LEDs	Trace
3	12w 425 nm purple LEDs	77
4	**12w 450 nm blue LEDs**	92
5	12w 525 nm green LEDs	0
6	40w 390nm purple Kessil Lamps	＜10
7	40w 425nm purple Kessil Lamps	61
8	40w 450nm blue Kessil Lamps	88
9	40w 525nm blue Kessil Lamps	0

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, light source, argon, and 24 h. [b] Isolated yield.

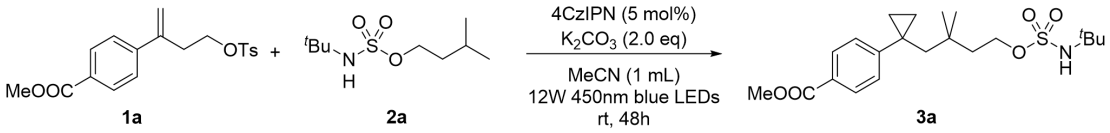
Table S6. Reaction time screening[a]



Entry	Reaction time	Yield[b](%)
1	24h	85
2	**48h**	92
3	72h	88

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, 12 W 450nm blue LEDs, argon, and reaction time. [b] Isolated yield.

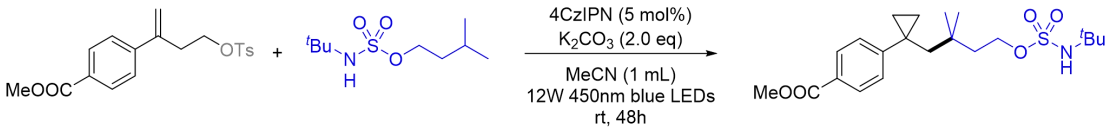
Table S7. Control experiments under the standard conditions[a]



Entry	Changes from the standard conditions	Yield[b](%)
1	**standard conditions**	92
2	in the dark	0
3	without photocatalyst	0
4	without base	0

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), 4CzIPN (5 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv.), MeCN (1 mL), RT, 12 W 450nm blue LEDs, argon, and 48h. [b] Isolated yield.

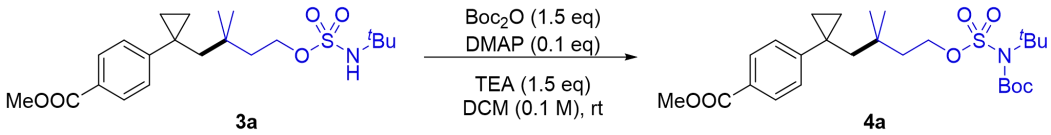
5. 2 mmol-scale reaction



1a, 2 mmol, 720.5 mg **2a**, 4 mmol, 893.3 mg **3a**, 690.4 mg, 84%

A 25 mL Schlenk tube with a magnetic stirring bar was charged with methyl 4-(4-(tosyloxy)but-1-en-2-yl)benzoate **1a** (2 mmol, 1.0 equiv.),sulfamate ester **2a** (4 mmol, 2.0 equiv.), 4CzIPN (5.0 mol%), K_2CO_3 (4 mmol, 2.0 equiv) and MeCN (15 mL). The tube was evacuated and backfilled with argon (three times). The solution was then stirred at room temperature under the irradiation of 12 W 450nm blue LEDs for 48 h using electronic fan to cool the tube. After completion of reaction, purification by flash column chromatography on silica gel afforded the *desired product* (690.4 mg, 84%).

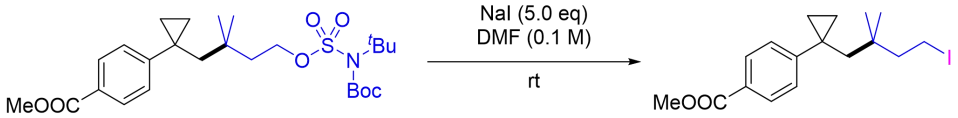
6. Synthetic applications



3a **4a**

To a round flask equipped with a stir bar was added sulfamide ester **3a** (1.0 equiv.), DMAP (0.1 equiv.) and anhydrous DCM (0.1 M). TEA (1.5 equiv.) was added to the flask. Boc_2O (0.15 equiv.) was added dropwisely to the above mixture at 0 °C. Then the mixture was stirred at room temperature for 24 h. After the reaction was complete, the reaction was washed with 1 M HCl, brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

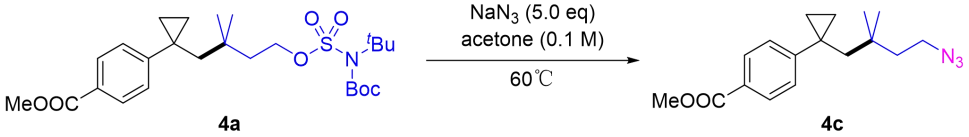
6.1 Synthesis of iodide



4a **4b**

To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), NaI (0.25 mmol, 5.0 equiv.) and anhydrous acetone (0.5 mL, 0.1 M). The mixture was then heated to 60 ℃ and kept stirred overnight. After the reaction was complete, the solvent was removed in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

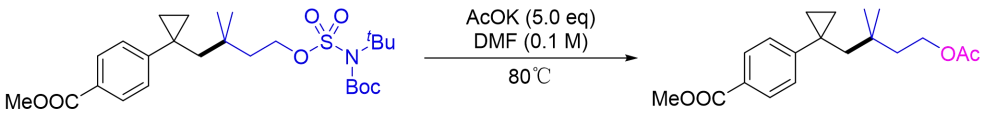
6.2 Synthesis of alkyl azide



4a **4c**

To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), NaN_3 (0.25 mmol, 5.0 equiv.) and DMF (0.5 mL, 0.1 M). The mixture kept stirred at room temperature for 10 h. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

6.3 Synthesis of acetate ester

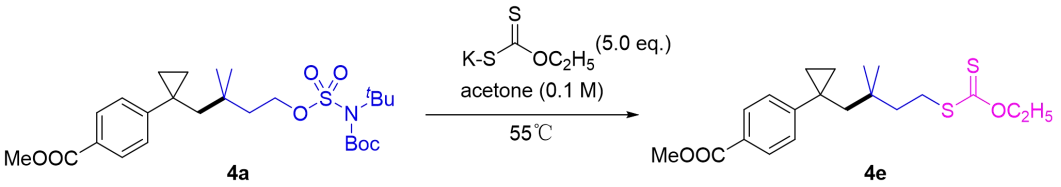


4a **4d**

To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), AcOK (0.25 mmol, 5.0 equiv.) and DMF (0.5 mL, 0.1 M). The mixture was then heated to 80 ℃ and kept stirred for 6 h. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic

layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

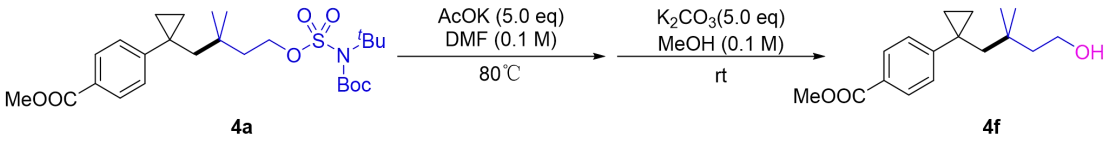
6.4 Synthesis of xanthate



4a **4e**

To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), potassium O-ethyl carbonodithioate (0.25 mmol, 5.0 equiv.) and acetone (0.5 mL, 0.1 M). The mixture was then heated to 55 ℃ and kept stirred for 6 h. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

6.5 Synthesis of alcohol



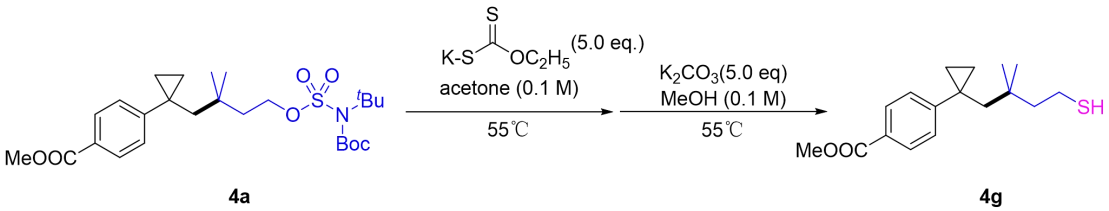
4a **4f**

Step 1: To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), AcOK (0.25 mmol, 5.0 equiv.) and DMF (0.5 mL, 0.1 M). The mixture was then heated to 80 ℃ and kept stirred for 6 h. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. The residue was used directly for the next step.

Step 2: To a 10 mL Schlenk flask charged with a stir bar was added crude methyl 4-(1-(4-acetoxy-2,2-dimethylbutyl)cyclopropyl)benzoate, K_2CO_3 (0.25 mmol, 5.0 equiv.) and MeOH (1.0 mL, 0.05 M). The mixture stirred at room temperature

overnight. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

6.6 Synthesis of thiol

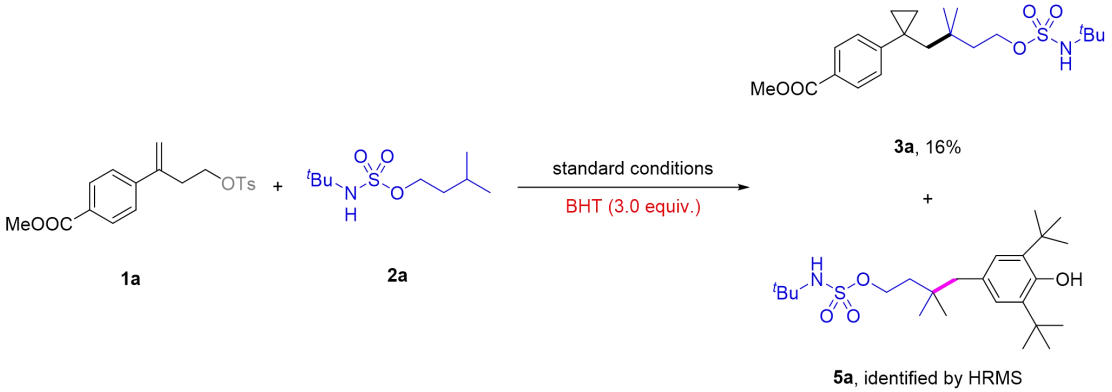


Step 1: To a 10 mL Schlenk flask equipped with a stir bar was added *N*-Boc sulfamate ester (0.05 mmol, 1.0 equiv.), potassium O-ethyl carbonodithioate (0.25 mmol, 5.0 equiv.) and acetone (0.5 mL, 0.1 M). The mixture was then heated to 55 ℃ and kept stirred for 6 h. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. The residue was used directly for the next step.

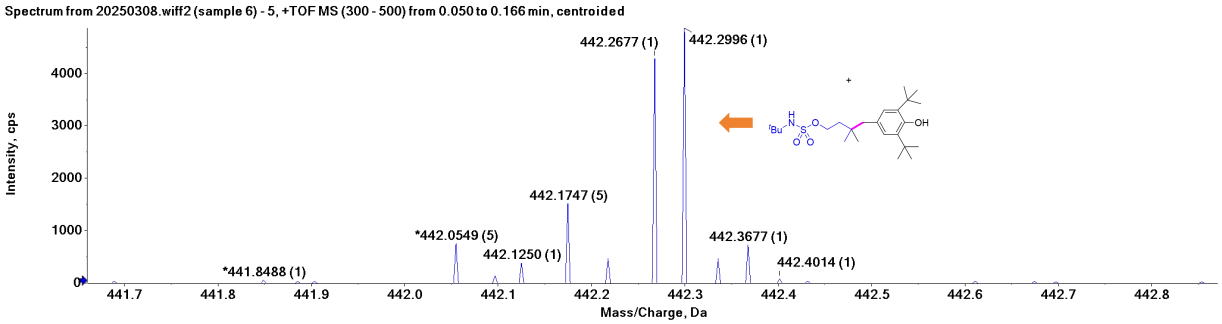
Step 2: To a 10 mL Schlenk flask charged with a stir bar was added crude methyl 4-(1-(4-((ethoxycarbonothioyl)thio)-2,2-dimethylbutyl)cyclopropyl)benzoate, K_2CO_3 (0.25 mmol, 5.0 equiv.) and MeOH (1.0 mL, 0.05 M). The mixture swas then heated to 55 ℃ and kept stirred overnight. After the reaction was complete, the reaction was extracted twice with CH_2Cl_2, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded the *desired product*.

7. Mechanistic Experiments

7.1 Radical trapping experiments



To an oven-dried 10 mL sealed tube equipped with a stir bar, was charged with methyl 4-(4-(tosyloxy)but-1-en-2-yl)benzoate **1a** (36.0 mg, 0.1 mmol, 1.0 equiv.), sulfamate ester **2a** (44.7 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (2.4 mg, 5.0 mol%), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv) and BHT (66.0 mg, 0.3 mmol, 3.0 equiv.). The tube was evacuated and back-filled with argon (three times), then sealed with rubber stopper and parafilm. Then, anhydrous MeCN (1 mL, 0.1 M) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W 450nm blue LEDs for 48 h using electronic fan to cool the tube. After 48 h, the reaction was inhibited as judged by TLC analysis. And the radical adducts with BHT **5a** was indentified by HRMS analysis.



5a HRMS m/z (ESI) calcd for $C_{24}H_{43}NO_4S$ $[M + H]^+$ 442.2986, found 442.2996.

7.2 Stern-Volmer quenching experiments

All fluorescence measurements were recorded by a SHIMADZU RF-5301PC spectrophotometer. First, the emission intensity of 4CzIPN solutions was observed at

552 nm. The solutions were irradiated at 369 nm (Maximum absorption wavelength of 4CzIPN) and fluorescence was measured from 420 nm to 720 nm. Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 10^{-5} M 4CzIPN and varying concentrations of quencher **1a** or **2a** in DMSO at room temperature. In a typical experiment, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 369 nm.

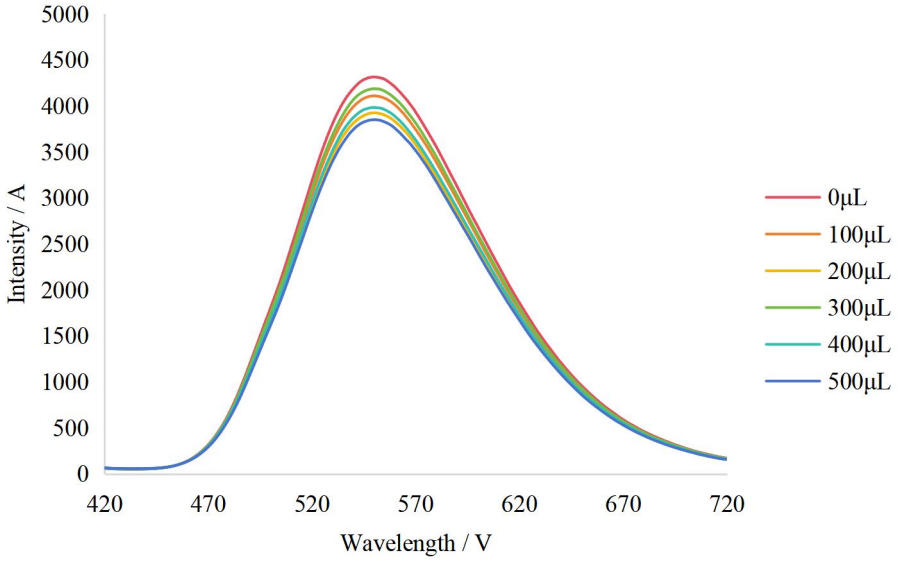


Figure S3. The emission quenching spectrum of 4CzIPN by various concentrations of quencher **1a**

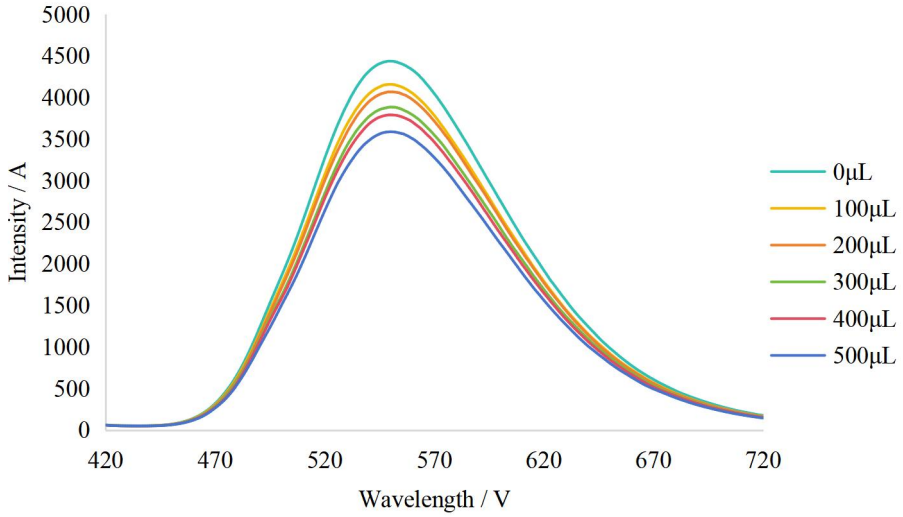


Figure S3. The emission quenching spectrum of 4CzIPN by various concentrations of quencher **2a**

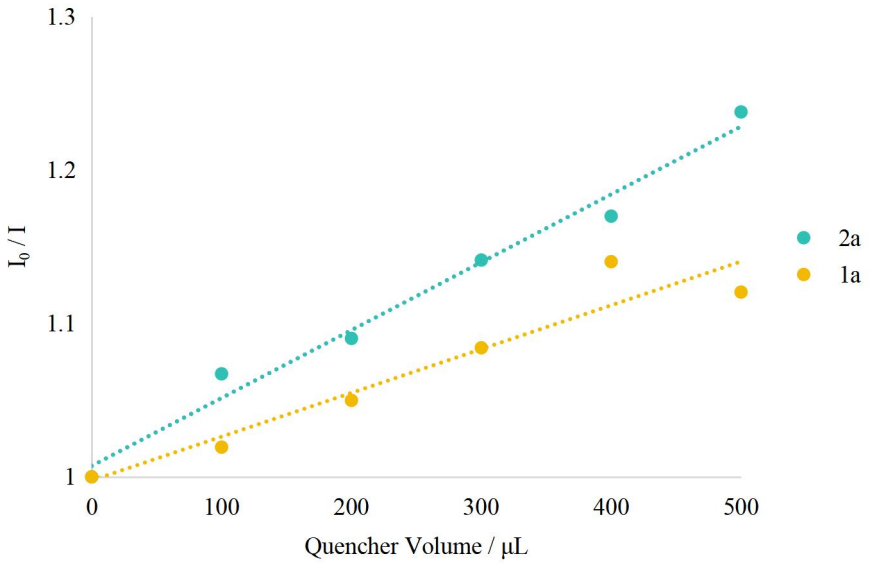


Figure S5. Stern-Volmer plots of 4CzIPN with **1a** and **2a**

The results indicated a faster quenching rate of 4CzIPN* by **2a** than by **1a**.

7.3 Cyclic voltammetry measurements

Cyclic voltammograms were taken on a CHI660E electrochemical workstation in MeCN at room temperaturee (25±2℃) using a glass carbon working electrode, saturated calomel electrode (SCE) as reference electrode, Pt wire as the auxiliary electrode, and 10 mM $^{n}Bu_4PF_6$ as supporting electrolyte.

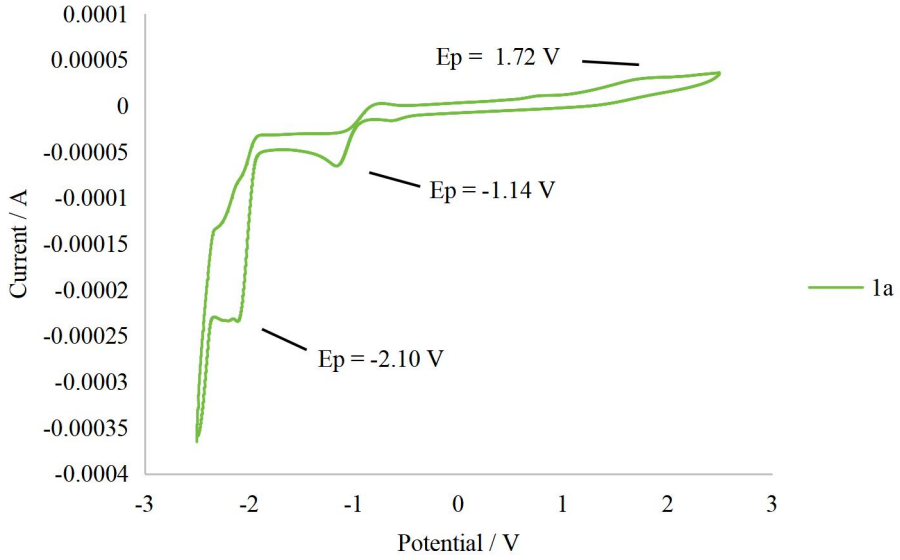


Figure S6. Cyclic voltammogram of **1a** in MeCN Scan direction: from -2.5 V to 2.5 V, then back to -2.5 V

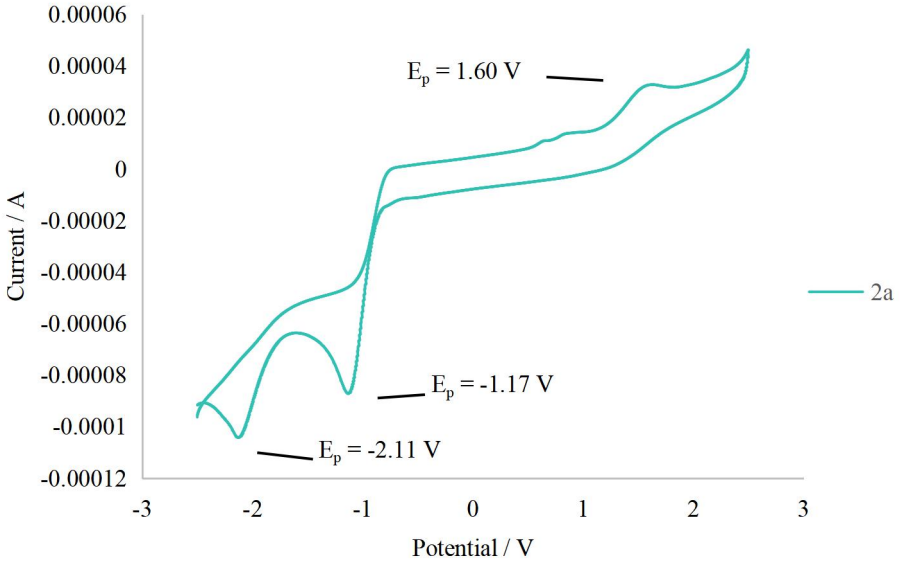


Figure S7. Cyclic voltammogram of **2a** in MeCN Scan direction: from -2.5 V to 2.5 V, then back to -2.5 V

7.4 Light On-Off experiment

A 25 mL Schlenk tube with a magnetic stirring bar was charged with **1a** (2 mmol, 1.0 equiv.), **2a** (4 mmol, 2.0 equiv.), 4CzIPN (5.0 mol%), K_2CO_3 (4 mmol, 2.0 equiv.) and MeCN (15 mL). The tube was evacuated and backfilled with argon (three times). The solution was then stirred at room temperature under the irradiation of 12 W 450nm blue LEDs. After being irradiated for 8 h, a sample (300 μL) of the reaction mixture was pipetted into a nuclear magnetic tube that already contained of $CDCl_3$ (300 μL) of 1,3,5-trimethoxybenzene (0.0083 M). The yield of desired product **3a** was determined by ^1H NMR. Subsequently, the reaction mixture was stirred for 8 h with light off. All of the following yields were analyzed using the same procedure after a 8-hour light on or off.

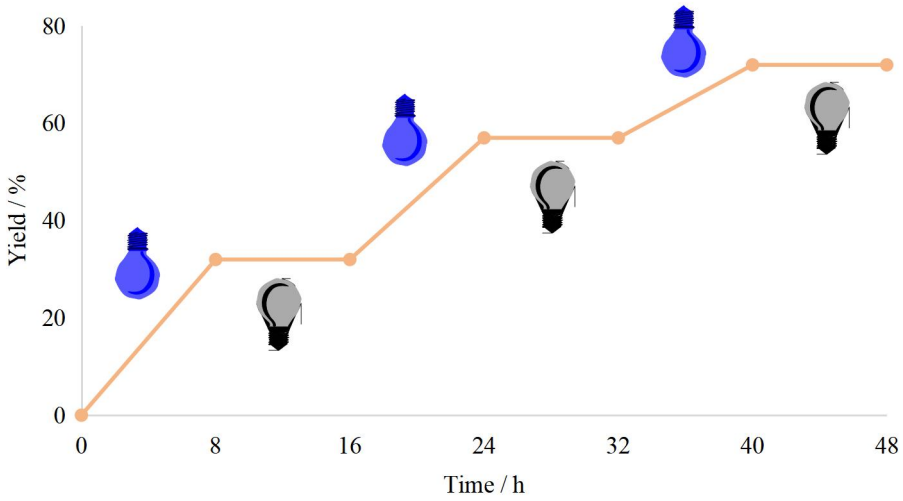
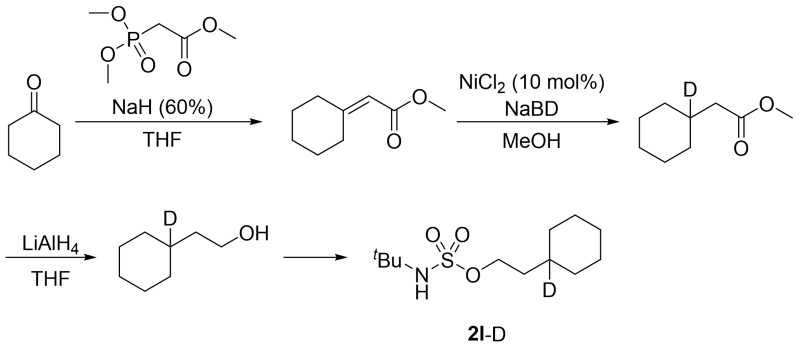


Figure S8. Light on-off study

7.5 *KIE* experiment

Preparation of deuterated alcohol substrate



2l-D

Step 1: To a double-necked round bottom flask equipped with a stir bar was added sodium hydride (1.2 equiv.) in dry THF (0.1 M) followed by trimethyl phosphonoacetate (5.5 mL, 38.2 mmol, 1.2 equiv.) at room temperature. After 5 min, add cyclohexanone (1.0 equiv.) to reaction mixture. Heat the reaction mixture to room temperature overnight (an oil bath). After the reaction was complete, the reaction mixture was diluted with water and extracted with Et_2O. The combined organic layers were combined, washed with saturated brine solution, dried over anhydrous Na_2SO_4 and and filtered. The filtrate was concentrated in *vacuo*. Purification by flash column chromatography on silica gel afforded methyl 2-cyclohexylideneacetate.

Step 2: To a double-necked round bottom flask equipped with a stir bar was added methyl 2-cyclohexylideneacetate (1.0 equiv.), $NiCl_2$ (10 mol%) and MeOH (0.2 M) and the flask was cooled at 0 °C. Add NaBD (3.0 equiv.) to the reaction mixture in three batches. Heat the reaction mixture to room temperature for 6 h (an oil bath). After the reaction was complete, the mixture was cooled to room temperature and filtered by Celite. The combined organic layer was concentrated in *vacuo*. The residue was used directly for the next step.

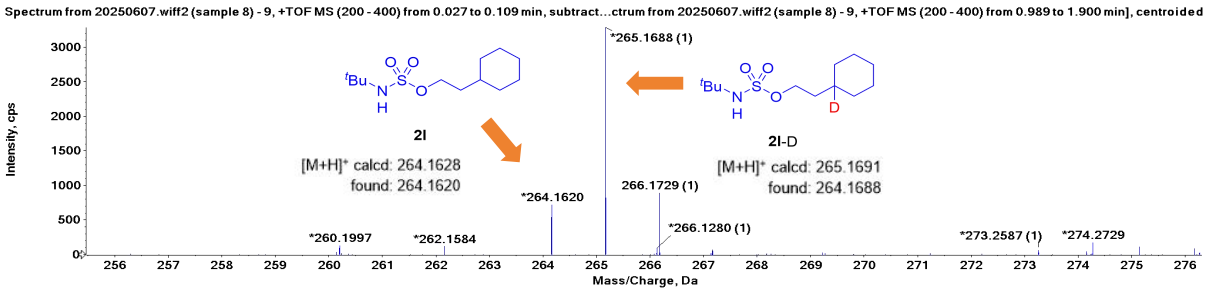
Step 3: To a double-necked round bottom flask equipped with a stir bar was added methyl 2-(cyclohexyl-1-*d*)acetate (1.0 equiv.), $LiAlH_4$ (1.0 M in THF, 3.0 equiv.) and dry THF (0.15 M) at 0 °C. The flask was reflux for 12 h (an oil bath). After the reaction was complete, the mixture was cooled to room temperature and filtered by Celite. The combined organic layer was concentrated in vacuo. Purification by flash column chromatography on silica gel afforded 2-(cyclohexyl-1-*d*)ethan-1-ol.

Step 4: **2l**-D was synthesized according to the method described in **2.2 General Procedure for the Synthesis of Sulfamate Esters**. The deuterium content of sulfamide was mesured by HRMS (83% D-atom) and ^{1}H NMR.

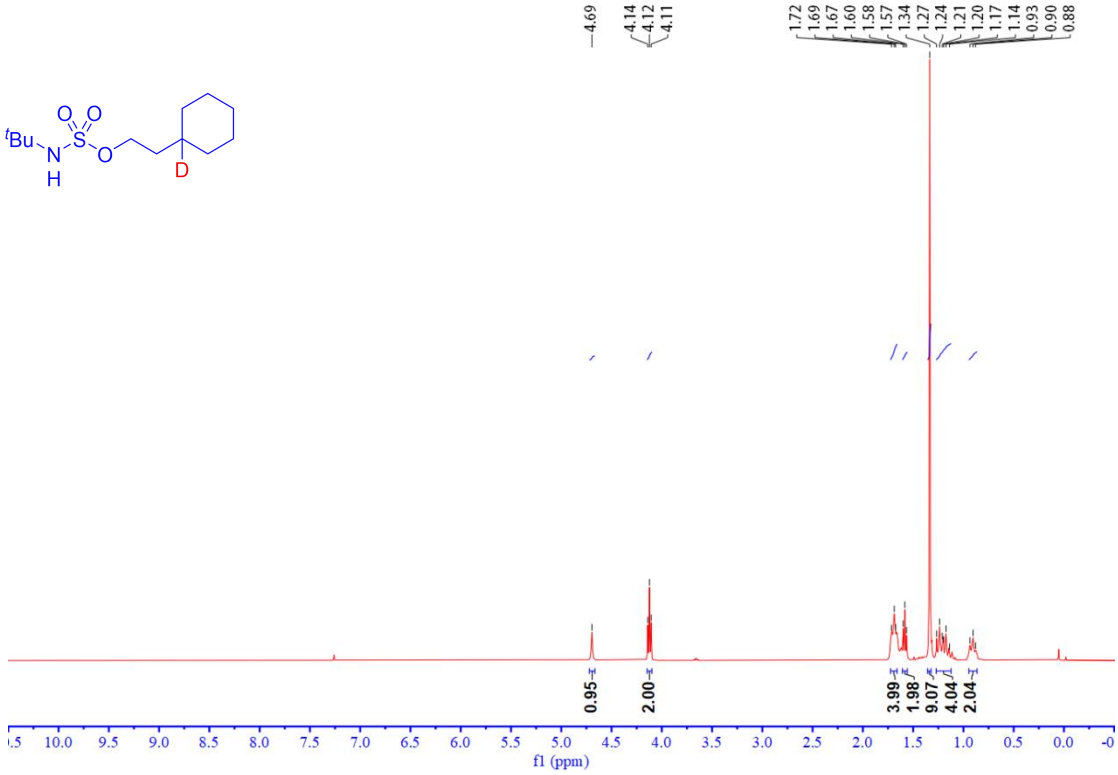
2-(cyclohexyl-1-d)ethyl tert-butylsulfuramidite (2l-D)

Colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.69 (s, 1H), 4.12 (t, *J* = 6.8 Hz, 2H), 1.70 (t, *J* = 11.6 Hz, 4H), 1.58 (t, *J* = 6.8 Hz, 2H), 1.34 (s, 9H), 1.27 – 1.12 (m, 4H), 0.92 (t, *J* = 12.0 Hz, 2H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 68.5, 54.5, 36.1, 36.0, 32.9, 29.6, 26.4, 26.1. **HRMS (ESI-TOF)** m/z: calculated for $C_{12}H_{24}DNO_3S$ $[M + H]^+$: 265.1691, found 265.1688.

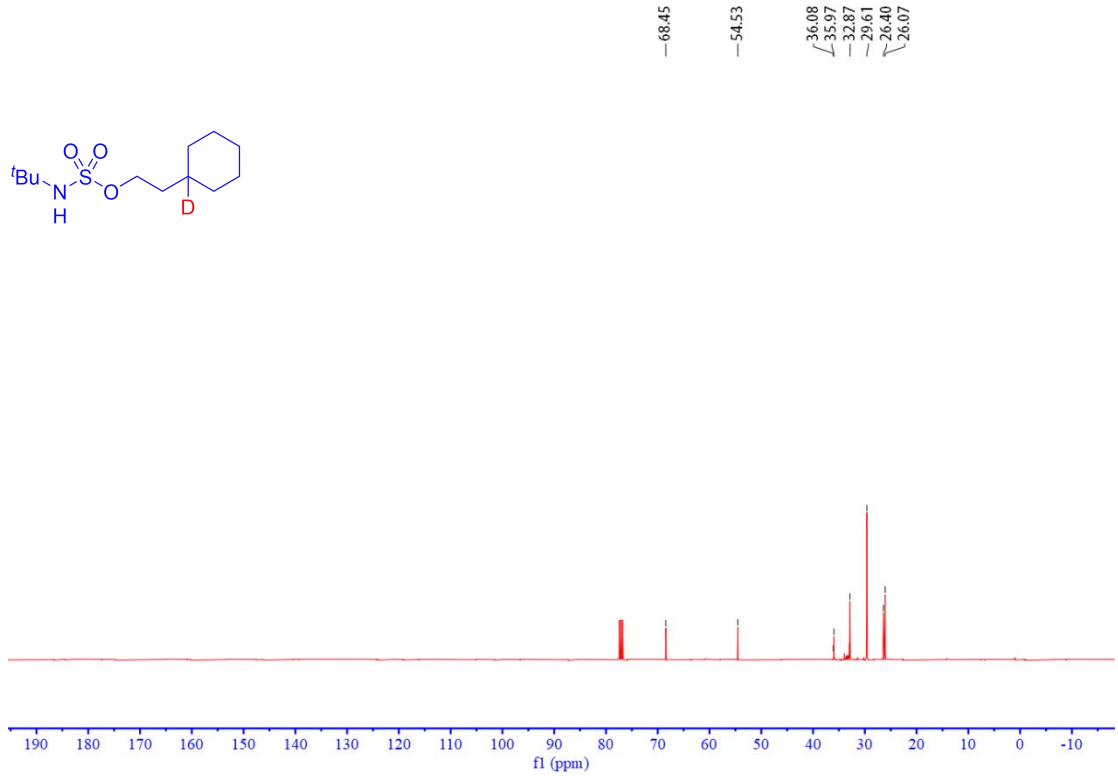
HRMS spectra of compound **2l**-D



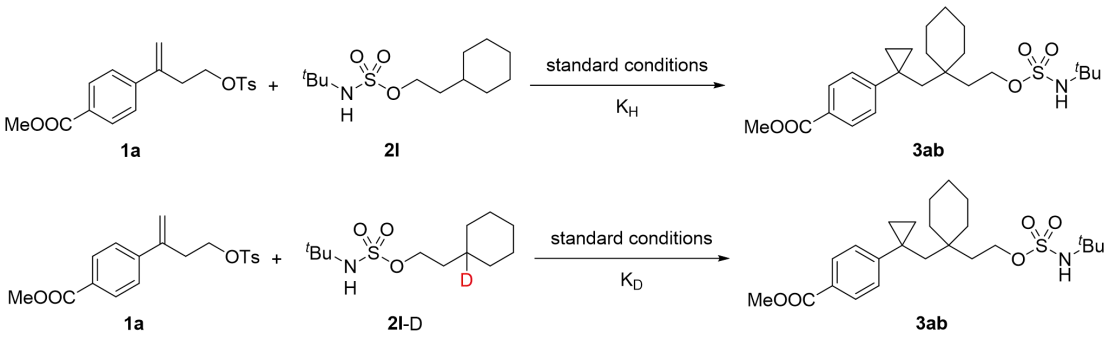
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **2l**-D



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **2l**-D



Procedure for *KIE* experiment



To an oven-dried 10 mL sealed tube equipped with a stir bar, was charged with methyl 4-(4-(tosyloxy)but-1-en-2-yl)benzoate **1a** (0.1 mmol, 1.0 equiv.), sulfamate ester **2l** / **2l**-D (0.2 mmol, 2.0 equiv.), 4CzIPN (5.0 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv) and MeCN (1.0 mL). Six parallel reactions started at the same time, the reaction time was 10 min, 20 min, 30 min, 40 min, 50 min and 60 min. A sample (300 μL) of each reaction mixture was pipetted into a nuclear magnetic tube that already contained of $CDCl_3$ (300 μL) of 1,3,5-trimethoxybenzene (0.0083 M). The yield of desired product **3ab** was determined by ^{1}H NMR.

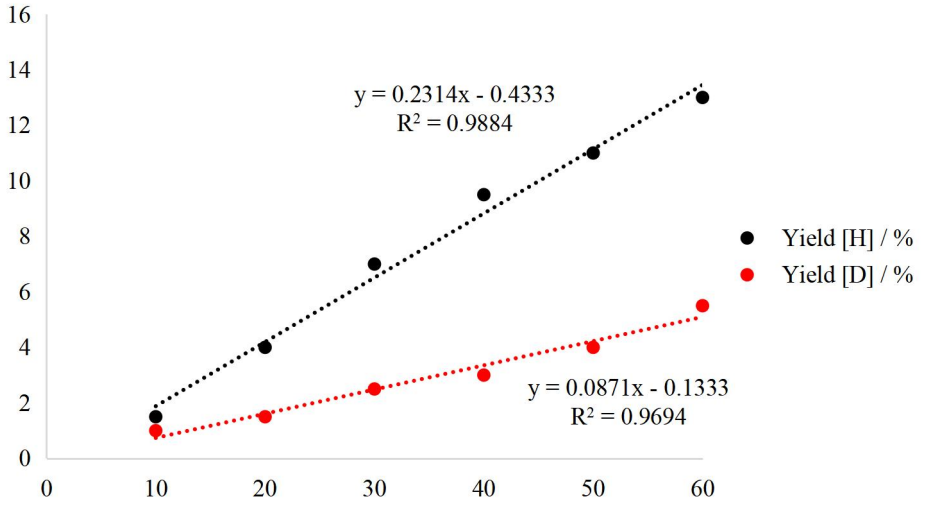


Figure S9. *KIE* experiment

Adjusted intial rate of deutro species

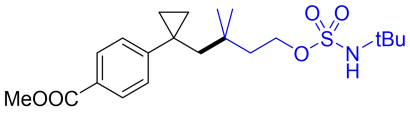
$k_H = 0.2314$

$83\%*k_D + 17\%*k_H = 0.0871$

$k_D = 0.0575$

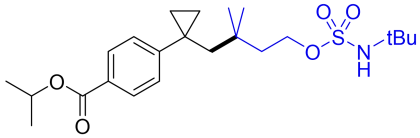
calculation of $KIE = k_H / k_D = 4.02$

8. Characterization of all products



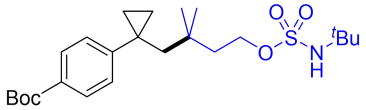
methyl 4-(1-(4-((*N*-(tert-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropyl)benzoate (3a)

Colorless oil (92%, 37.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.35 (s, 1H), 4.04 – 3.99 (m, 2H), 3.89 (s, 3H), 1.70 (s, 2H), 1.51 (t, *J* = 7.7 Hz, 2H), 1.31 (s, 9H), 0.87 – 0.84 (m, 2H), 0.74 (s, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.5, 128.5, 128.1, 126.8, 66.6, 53.6, 51.1, 51.0, 39.9, 33.8, 28.6, 26.8, 22.3, 12.7. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{33}NO_5S$ [M + H]$^+$: 412.2152, found 412.2155.



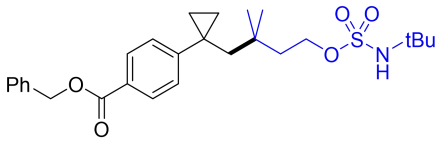
isopropyl 4-(1-(4-((*N*-(*t*ert-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropyl)-benzoate (2b)

Colorless oil (91%, 40.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 5.22 (p, *J* = 6.3 Hz, 1H), 4.46 (s, 1H), 4.04 – 3.99 (m, 2H), 1.70 (s, 2H), 1.52 (t, *J* = 7.6 Hz, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.31 (s, 9H), 0.84 (t, *J* = 5.2 Hz, 2H), 0.74 (s, 8H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 166.0, 151.3, 129.5, 129.1, 128.6, 68.2, 67.6, 54.6, 52.2, 41.0, 34.8, 29.7, 27.9, 23.3, 22.0, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{27}H_{37}NO_5S$ [M + H]$^+$: 488.2465, found 488.2464.



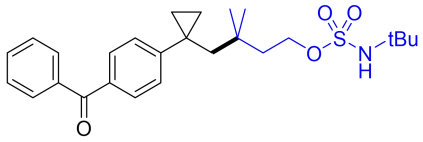
***tert*-butyl 4-(1-(4-((N-(*tert*-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropyl)-benzoate (2c)**

Colorless oil (89%, 40.3 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 1H), 4.02 (t, *J* = 7.6 Hz, 2H), 1.70 (s, 2H), 1.58 (s, 9H), 1.52 (t, *J* = 7.6 Hz, 2H), 1.31 (s, 9H), 0.83 (t, 2H), 0.75 (s, 6H), 0.73 (t, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 165.7, 151.0, 129.7, 129.4, 129.0, 80.8, 67.6, 54.6, 52.2, 41.0, 34.8, 29.7, 28.2, 27.9, 23.3, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{24}H_{39}NO_5S$ [M + H]$^+$: 454.2622, found 454.2623.



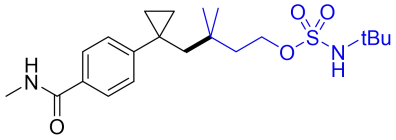
Benzyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropyl)benzoate (3d)

Colorless oil (77%, 37.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.32 (m, 7H), 5.34 (s, 2H), 4.34 (s, 1H), 4.04 – 3.99 (m, 2H), 1.70 (s, 2H), 1.52 (t, *J* = 7.6 Hz, 2H), 1.30 (s, 9H), 0.87 – 0.83 (m, 2H), 0.74 (s, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 165.3, 150.7, 135.1, 128.7, 128.1, 127.6, 127.2, 127.2, 126.7, 66.6, 65.6, 53.6, 51.1, 39.9, 33.7, 28.6, 26.8, 22.3, 12.7. **HRMS (ESI-TOF)** m/z: calculated for $C_{27}H_{37}NO_5S$ [M + H]$^+$: 488.2465, found 488.2462.



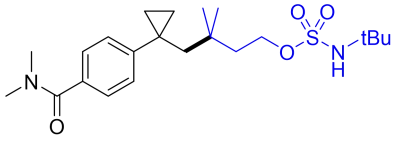
4-(1-(4-benzoylphenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3e)

Colorless oil (89%, 40.7 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 4H), 4.34 (s, 1H), 3.98 – 3.93 (m, 2H), 1.66 (s, 2H), 1.46 (t, *J* = 7.7 Hz, 2H), 1.25 (s, 9H), 0.83 (t, *J* = 5.2 Hz, 2H), 0.72 (s, 6H), 0.70 (t, *J* = 4.2 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 195.4, 150.2, 136.7, 134.3, 131.3, 129.2, 129.0, 128.0, 127.2, 66.5, 53.6, 51.0, 39.8, 33.8, 28.7, 27.0, 22.4, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{26}H_{35}NO_4S$ [M + H]$^+$: 457.2360, found 457.2367.



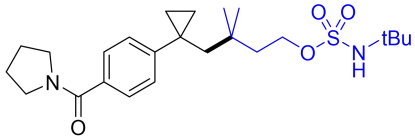
3,3-dimethyl-4-(1-(4-(methylcarbamoyl)phenyl)cyclopropyl)butyl *tert*-butylsulfamate (3f)

Colorless oil (79%, 32.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 4.32 (s, 1H), 3.95 (t, *J* = 7.7 Hz, 2H), 2.99 (d, *J* = 4.7 Hz, 3H), 1.68 (s, 2H), 1.43 (t, *J* = 7.7 Hz, 2H), 1.31 (s, 9H), 0.84 (t, *J* = 4.0 Hz, 2H), 0.77 (s, 6H), 0.72 (t, *J* = 5.3 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.4, 148.5, 131.6, 128.3, 125.9, 66.5, 53.6, 50.7, 39.3, 33.7, 28.7, 28.7, 27.3, 25.8, 22.2, 12.6. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{34}N_2O_4S$ $[M + H]^+$: 411.2312, found 411.2302.



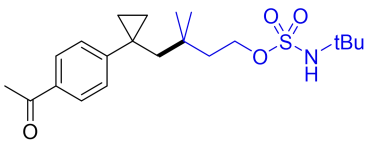
4-(1-(4-(dimethylcarbamoyl)phenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3g)

Colorless oil (80%, 34.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.04 (s, 1H), 3.92 – 3.84 (m, 2H), 3.08 – 2.92 (m, 6H), 1.64 (s, 2H), 1.47 – 1.42 (m, 2H), 1.28 (s, 9H), 0.81 (t, *J* = 5.7 Hz, 2H), 0.77 (s, 6H), 0.69 (t, *J* = 5.2 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 170.7, 146.5, 132.8, 128.1, 126.2, 66.3, 53.4, 50.7, 39.3, 33.7, 28.6, 27.4, 22.2, 12.5. **HRMS (ESI-TOF)** m/z: calculated for $C_{22}H_{36}N_2O_4S$ $[M + H]^+$: 425.2469, found 425.2466.



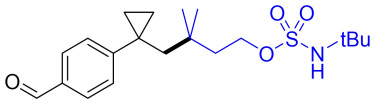
3,3-dimethyl-4-(1-(4-(pyrrolidine-1-carbonyl)phenyl)cyclopropyl)butyl *tert*-butylsulfamate (3h)

Colorless oil (42%, 18.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.30 (m, 4H), 4.93 (s, 1H), 3.88 – 3.83 (m, 2H), 3.56 (t, *J* = 6.9 Hz, 2H), 3.35 (t, *J* = 6.5 Hz, 2H), 1.82 (dt, *J* = 19.4, 7.1 Hz, 4H), 1.60 (s, 2H), 1.43 – 1.37 (m, 2H), 1.24 (s, 9H), 0.77 (t, *J* = 5.2 Hz, 2H), 0.72 (s, 6H), 0.65 – 0.61 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 168.7, 146.8, 133.7, 128.0, 126.2, 66.3, 53.4, 50.7, 48.7, 45.2, 39.4, 33.7, 28.6, 27.3, 25.4, 23.4, 22.2, 12.5. **HRMS (ESI-TOF)** m/z: calculated for $C_{24}H_{38}N_2O_4S$ [M + H]$^+$: 451.2625, found 451.2624.



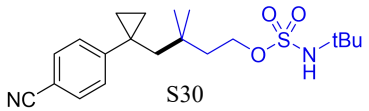
4-(1-(4-acetylphenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3i)

Colorless oil (83%, 32.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 4.30 (s, 1H), 4.01 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 1.71 (s, 2H), 1.52 (t, *J* = 7.6 Hz, 2H), 1.31 (s, 9H), 0.86 (t, *J* = 5.2 Hz, 2H), 0.75 (s, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 196.8, 150.8, 134.0, 128.3, 127.4, 66.6, 53.6, 51.1, 39.9, 33.8, 28.7, 26.9, 25.6, 22.3, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{33}NO_4S$ [M + H]$^+$: 396.2203, found 396.2196.



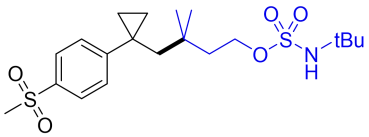
4-(1-(4-formylphenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3j)

Colorless oil (86%, 32.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.96 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 4.31 (s, 1H), 4.05 – 4.00 (m, 2H), 1.73 (s, 2H), 1.52 (t, *J* = 7.6 Hz, 2H), 1.31 (s, 9H), 0.88 (t, 2H), 0.78 – 0.74 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 191.9, 153.6, 134.5, 129.8, 129.8, 67.5, 54.6, 52.2, 41.0, 34.9, 29.7, 27.9, 23.6, 13.9. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{31}NO_4S$ [M + H]$^+$: 382.2047, found 382.2038.



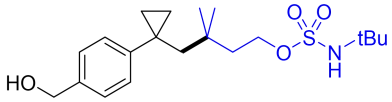
4-(1-(4-cyanophenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3k)

Colorless oil (71%, 26.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 4.37 (s, 1H), 4.04 – 3.99 (m, 2H), 1.70 (s, 2H), 1.51 (t, *J* = 7.6 Hz, 2H), 1.32 (s, 9H), 0.84 (t, 2H), 0.77 (t, 2H), 0.73 (s, 6H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 152.0, 132.2, 130.0, 119.1, 109.8, 67.5, 54.8, 52.1, 41.2, 34.9, 29.8, 28.0, 23.6, 14.0. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{30}N_2O_3S$ [M + H]$^+$: 378.2050, found 378.2051.



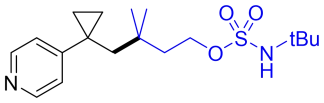
3,3-dimethyl-4-(1-(4-(methylsulfonyl)phenyl)cyclopropyl)butyl *tert*-butylsulfamate (3l)

Colorless oil (78%, 33.7 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.28 (s, 1H), 3.69 (t, 2H), 2.76 (s, 3H), 1.43 (s, 2H), 1.17 (t, *J* = 7.7 Hz, 2H), 1.02 (s, 9H), 0.58 (t, 2H), 0.51 – 0.46 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 151.7, 137.0, 129.0, 126.4, 66.4, 53.6, 50.7, 43.5, 39.6, 33.8, 28.6, 27.2, 22.4, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{33}NO_2S_2$ [M + H]$^+$: 432.1873, found 432.1874.



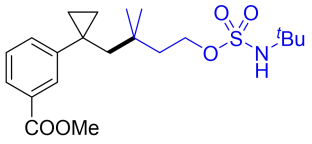
4-(1-(4-(hydroxymethyl)phenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3m)

Colorless oil (48%, 18.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.96 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 4.22 (s, 1H), 4.03 (t, *J* = 7.6 Hz, 2H), 1.73 (s, 2H), 1.53 (t, *J* = 7.6 Hz, 2H), 1.32 (s, 9H), 0.90 (t, *J* = 4.6 Hz, 2H), 0.79 – 0.75 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 191.9, 153.6, 129.8, 129.8, 67.5, 54.7, 52.2, 41.0, 34.9, 29.7, 27.9, 23.6, 13.9. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{33}NO_4S$ [M + H]$^+$: 384.2203, found 384.2200.



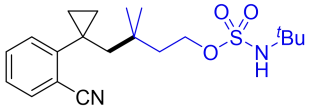
3,3-dimethyl-4-(1-(pyridin-4-yl)cyclopropyl)butyl tert-butylsulfamate (3n)

Colorless oil (34%, 12.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.48 (d, *J* = 5.2 Hz, 2H), 7.30 (d, *J* = 5.7 Hz, 2H), 4.38 (s, 1H), 4.05 (t, *J* = 7.5 Hz, 2H), 1.74 (s, 2H), 1.55 (t, *J* = 7.5 Hz, 2H), 1.33 (s, 9H), 0.87 (d, *J* = 4.0 Hz, 2H), 0.80 – 0.74 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 155.1, 148.1, 123.2, 66.4, 53.7, 50.2, 40.2, 33.9, 28.7, 27.0, 21.6, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{26}H_{35}NO_4S$ $[M + H]^+$: 355.2050, found 355.2040.



methyl 3-(1-(4-((N-(tert-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropyl)benzoate (3o)

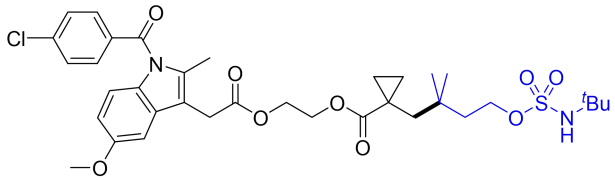
Colorless oil (73%, 30.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 4.55 (s, 1H), 3.94 (t, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 1.63 (s, 2H), 1.43 (t, *J* = 7.7 Hz, 2H), 1.24 (s, 9H), 0.78 (t, 2H), 0.70 – 0.64 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.2, 145.4, 132.9, 129.2, 129.0, 127.3, 126.3, 66.5, 53.5, 51.1, 51.1, 39.9, 33.7, 28.6, 27.0, 22.1, 12.6. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{33}NO_5S$ $[M + H]^+$: 412.2152, found 412.2155.



4-(1-(2-cyanophenyl)cyclopropyl)-3,3-dimethylbutyl *tert*-butylsulfamate (3p)

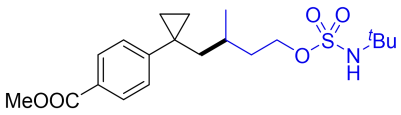
Colorless oil (66%, 25.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, *J* = 8.7 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.22 (d, *J* = 9.8 Hz, 1H), 4.46 (s, 1H), 3.96 (t, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 2H), 1.26 (s, 9H), 0.89 – 0.81 (m, 4H), 0.70 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 148.8, 132.6, 131.5, 130.2, 125.9, 117.5, 113.2, 66.5, 53.6, 50.2, 39.7, 33.5, 28.7, 26.4, 21.6, 13.2. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{30}N_2O_3S$ $[M + H]^+$: 379.2050, found 379.2051.



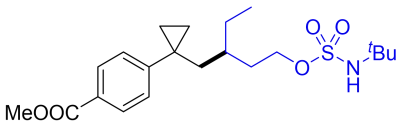
2-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)ethyl 1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2,2-dimethylbutyl)cyclopropane-1-carboxylate (3q)

Yellow oil (61%, 43.0 mg). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.51 (s, 1H), 4.32 – 4.27 (m, 2H), 4.26 – 4.21 (m, 2H), 4.13 (d, *J* = 7.5 Hz, 2H), 3.83 (s, 3H), 3.68 (s, 2H), 2.38 (s, 3H), 1.68 (t, *J* = 7.6 Hz, 2H), 1.61 (s, 2H), 1.34 (s, 9H), 1.11 (q, *J* = 4.2 Hz, 2H), 0.93 (s, 6H), 0.70 (q, 2H). **$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*)** δ 174.8, 170.7, 168.3, 156.1, 139.3, 136.1, 133.9, 131.2, 130.8, 130.6, 129.2, 115.0, 112.3, 111.6, 101.4, 67.6, 62.6, 62.2, 55.7, 54.6, 44.9, 41.2, 34.4, 30.2, 29.7, 27.9, 21.3, 15.1, 13.4. **HRMS (ESI-TOF)** m/z: calculated for $C_{35}H_{45}ClN_2O_9S$ $[M + H]^+$: 705.2607, found 705.2615.



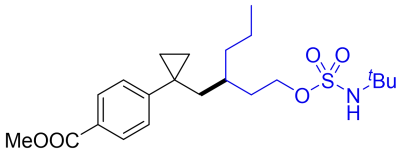
methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-methylbutyl)cyclopropyl)-benzoate (3r)

Colorless oil (74%, 29.4 mg). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.47 (s, 1H), 4.07 – 3.96 (m, 2H), 3.88 (s, 3H), 1.85 – 1.75 (m, 2H), 1.47 – 1.34 (m, 3H), 1.27 (s, 9H), 0.95 – 0.87 (m, 4H), 0.81 – 0.67 (m, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*)** δ 166.0, 149.4, 128.6, 127.7, 126.9, 67.4, 53.5, 51.0, 46.0, 34.7, 28.6, 27.4, 22.9, 18.5, 12.4, 12.3. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{31}NO_5S$ $[M + H]^+$: 398.5373, found 398.5381.



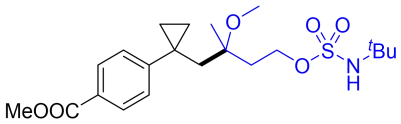
methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-ethylbutyl)cyclopropyl)benzoate (3s)

Colorless oil (64%, 26.3 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 1H), 4.03 – 3.95 (m, 2H), 3.89 (s, 3H), 1.76 – 1.65 (m, 2H), 1.60 – 1.52 (m, 2H), 1.28 (s, 12H), 0.85 (t, *J* = 9.0 Hz, 2H), 0.78 – 0.68 (m, 5H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.2, 150.6, 129.8, 128.9, 128.0, 68.6, 54.6, 52.1, 43.6, 34.3, 31.9, 29.7, 25.5, 24.2, 13.4, 13.3, 10.3. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{33}NO_5S$ [M + H]$^{+}$: 412.2152, found 412.2141.



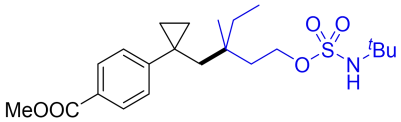
methyl 4-(1-(2-(2-((*N*-(*tert*-butyl)sulfamoyl)oxy)ethyl)pentyl)cyclopropyl)benzo-ate (3t)

Colorless oil (53%, 22.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 1H), 4.00 (q, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 1.80 – 1.68 (m, 2H), 1.61 – 1.51 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 2H), 1.29 (s, 9H), 1.22 – 1.17 (m, 2H), 0.87 (t, 2H), 0.79 (t, *J* = 6.9 Hz, 3H), 0.70 (t, *J* = 4.1 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.1, 150.5, 129.6, 128.8, 127.9, 68.5, 54.6, 52.0, 43.9, 35.4, 32.7, 32.3, 29.6, 24.1, 19.1, 14.3, 13.3, 13.3. **HRMS (ESI-TOF)** m/z: calculated for $C_{22}H_{35}NO_5S$ [M + H]$^{+}$: 426.2309, found 426.2310.



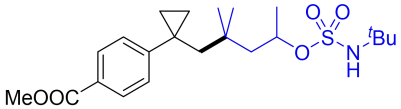
methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-methoxy-2-methylbutyl)cyclopr-opyl)benzoate (3u)

Colorless oil (90%, 38.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.31 (s, 1H), 4.07 (t, *J* = 7.5 Hz, 2H), 3.89 (s, 3H), 2.86 (s, 3H), 1.91 (d, *J* = 5.3 Hz, 2H), 1.88 – 1.83 (m, 1H), 1.78 – 1.71 (m, 1H), 1.32 (s, 9H), 1.04 (s, 3H), 0.89 (d, *J* = 2.7 Hz, 3H), 0.80 (t, *J* = 6.5 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.1, 128.4, 128.3, 126.8, 65.8, 53.6, 51.0, 47.6, 46.5, 36.0, 28.7, 28.6, 22.4, 21.6, 12.7, 12.5. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{31}NO_6S$ $[M + H]^+$: 414.1945, found 414.1955.



methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-ethyl-2-methylbutyl)cyclopropyl) benzoate (3v)

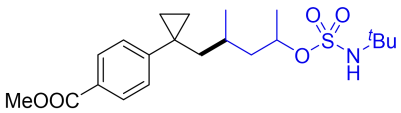
Colorless oil (72%, 30.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 4.35 (s, 1H), 3.97 (t, *J* = 7.8 Hz, 2H), 3.89 (s, 3H), 1.69 (s, 2H), 1.55 – 1.49 (m, 2H), 1.31 (s, 11H), 1.14 – 1.07 (m, 2H), 0.86 (d, *J* = 16.1 Hz, 2H), 0.74 – 0.65 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.7, 128.5, 128.2, 126.8, 66.4, 53.6, 51.0, 48.2, 36.3, 36.2, 31.2, 28.6, 24.2, 22.1, 12.8, 12.8, 6.9. **HRMS (ESI-TOF)** m/z: calculated for $C_{22}H_{35}NO_5S$ $[M + H]^+$: 425.2236, found 425.2243.



methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2,2-dimethylpentyl)cyclopropyl)benzoate (3w)

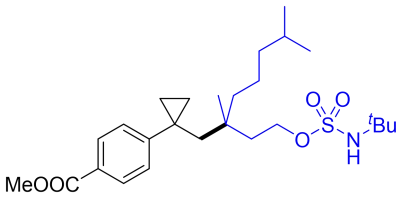
Colorless oil (72%, 22.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.69 – 4.63 (m, 1H), 4.39 (s, 1H), 3.88 (s, 3H), 1.85 (d, *J* = 13.6 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.32 (s, 9H), 1.25 (q, *J* = 6.2 Hz, 3H), 0.87 (t, *J* = 5.8 Hz, 1H), 0.81 – 0.71 (m, 9H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.9, 128.5, 128.2, 126.7, 76.7, 53.8, 51.1, 51.0, 48.8, 34.2, 28.8, 27.2, 27.0,

22.4, 21.9, 12.9, 12.7. **HRMS (ESI-TOF)** m/z: calculated for $C_{22}H_{35}NO_5S$ $[M + H]^+$: 426.2309, found 426.2317.



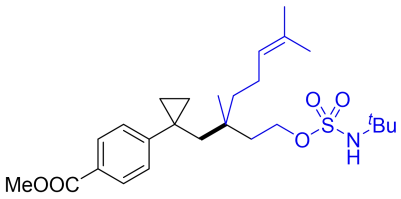
methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-methylpentyl)cyclopropyl)benzoate (3x)

Colorless oil (65%, 26.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.67 – 4.60 (m, 1H), 4.08 (s, 1H), 3.89 (s, 3H), 1.85 – 1.75 (m, 2H), 1.58 (s, 2H), 1.53 – 1.47 (m, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.22 (s, 9H), 0.93 (d, *J* = 6.5 Hz, 4H), 0.76 – 0.68 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.2, 150.7, 129.8, 128.9, 128.0, 78.0, 54.8, 52.1, 47.3, 44.5, 29.8, 28.1, 24.1, 21.5, 19.9, 13.5, 13.4. **HRMS (ESI-TOF)** m/z: calculated for $C_{21}H_{33}NO_5S$ $[M + H]^+$: 412.2152, found 412.2148.



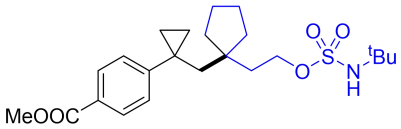
methyl 4-(1-(2-(2-((*N*-(*tert*-butyl)sulfamoyl)oxy)ethyl)-2,6-dimethylheptyl)cyclopropyl)benzoate (3y)

Colorless oil (73%, 35.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.42 (s, 1H), 3.98 (t, *J* = 7.8 Hz, 2H), 3.88 (s, 3H), 1.70 (q, *J* = 14.7 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.43 – 1.37 (m, 1H), 1.31 (s, 9H), 1.06 – 0.95 (m, 4H), 0.90 – 0.82 (m, 4H), 0.80 (d, *J* = 6.6 Hz, 6H), 0.74 – 0.68 (m, 5H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.0, 151.7, 129.5, 129.3, 127.8, 67.5, 54.6, 52.0, 49.5, 40.1, 39.6, 38.1, 37.2, 29.7, 27.9, 25.8, 23.2, 22.7, 22.6, 21.2, 13.9, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{26}H_{43}NO_5S$ $[M + H]^+$: 482.2935, found 482.2938.



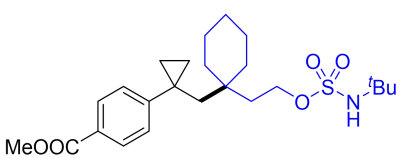
methyl 4-(1-(2-(2-((*N*-(*tert*-butyl)sulfamoyl)oxy)ethyl)-2,6-dimethylhept-5-en-1-yl)cyclopropyl)benzoate (3z)

Colorless oil (42%, 20.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 4.84 (t, *J* = 7.1 Hz, 1H), 4.25 (s, 1H), 3.99 (t, *J* = 7.7 Hz, 2H), 3.89 (s, 3H), 1.80 – 1.71 (m, 4H), 1.63 (s, 3H), 1.58 – 1.52 (m, 5H), 1.31 (s, 9H), 1.11 – 1.06 (m, 2H), 0.87 (d, *J* = 6.2 Hz, 2H), 0.76 – 0.71 (m, 5H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.6, 130.3, 128.6, 128.2, 126.8, 123.3, 66.4, 53.6, 52.0, 48.5, 39.0, 36.8, 36.2, 28.6, 24.6, 24.6, 22.2, 21.1, 16.6, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{26}H_{41}NO_5S$ [M + H]$^+$: 480.2778, found 480.2779.



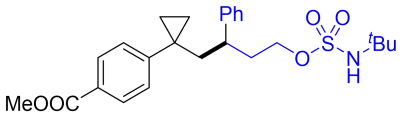
methyl 4-(1-((1-(2-((*N*-(*tert*-butyl)sulfamoyl)oxy)ethyl)cyclopentyl)methyl)cyclopropyl)benzoate (3aa)

Colorless oil (63%, 27.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 4.35 (s, 1H), 3.99 (t, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 1.76 (s, 2H), 1.65 (t, *J* = 7.6 Hz, 2H), 1.49 – 1.44 (m, 4H), 1.33 (s, 9H), 1.23 – 1.15 (m, 4H), 0.87 – 0.83 (m, 2H), 0.74 (t, *J* = 5.2 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.5, 128.5, 128.5, 127.0, 67.0, 53.6, 51.0, 47.2, 44.8, 36.8, 34.9, 28.7, 22.9, 22.6, 12.5. **HRMS (ESI-TOF)** m/z: calculated for $C_{23}H_{35}NO_5S$ [M + H]$^+$: 438.2309, found 438.2310.



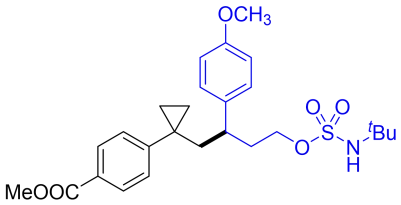
methyl 4-(1-((1-(2-((*N*-(*tert*-butyl)sulfamoyl)oxy)ethyl)cyclohexyl)methyl)cyclopropyl)benzoate (3ab)

Colorless oil (42%, 21.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 10.3 Hz, 2H), 4.34 (s, 1H), 3.96 (t, *J* = 7.7 Hz, 2H), 3.89 (s, 3H), 1.74 (s, 2H), 1.65 (t, *J* = 7.8 Hz, 2H), 1.37 – 1.33 (m, 3H), 1.32 (s, 9H), 1.30 – 1.26 (m, 2H), 1.18 – 1.08 (m, 5H), 0.84 (t, *J* = 4.0 Hz, 2H), 0.75 (t, *J* = 5.3 Hz, 2H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.9, 128.5, 128.2, 126.8, 66.2, 53.6, 51.0, 47.7, 36.2, 35.1, 33.1, 28.7, 24.9, 22.0, 20.5, 12.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{24}H_{37}NO_5S$ [M + H]$^+$: 452.2465, found 452.2462.



methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-phenylbutyl)cyclopropyl)benzoate (3ac)

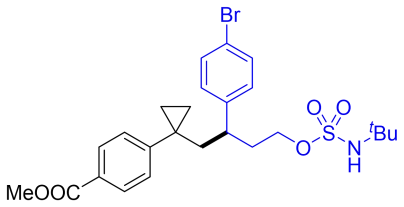
Colorless oil (68%, 31.3 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.23 (dt, 2H), 7.17 (t, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 2H), 4.10 (s, 1H), 3.84 (s, 3H), 3.79 – 3.72 (m, 1H), 3.68 – 3.62 (m, 1H), 2.53 – 2.46 (m, 1H), 2.10 – 2.01 (m, 2H), 1.84 – 1.75 (m, 2H), 1.15 (s, 9H), 0.81 – 0.56 (m, 4H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 149.2, 142.6, 128.6, 127.8, 127.5, 126.9, 126.7, 125.6, 67.3, 53.5, 51.0, 46.0, 39.4, 34.2, 28.5, 23.1, 12.6, 11.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{25}H_{33}NO_5S$ [M + H]$^+$: 460.2152, found 460.2144.



methyl 4-(1-(4-((*N*-(*tert*-butyl)sulfamoyl)oxy)-2-(4-methoxyphenyl)butyl)cyclopropyl)benzoate (3ad)

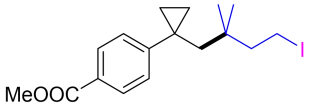
Colorless oil (59%, 28.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (s, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.09 (s,

1H), 3.91 (s, 3H), 3.83 – 3.73 (m, 5H), 2.50 (s, 1H), 2.13 – 2.07 (m, 2H), 1.86 – 1.79 (m, 2H), 1.23 (s, 9H), 0.75 – 0.66 (m, 3H), 0.39 – 0.33 (m, 1H). **$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*)** δ 166.0, 157.2, 149.3, 134.5, 128.6, 127.8, 127.6, 126.8, 112.9, 67.4, 54.2, 53.5, 51.0, 46.2, 38.5, 34.4, 28.6, 23.0, 12.6, 11.9. **HRMS (ESI-TOF)** m/z: calculated for $C_{26}H_{35}NO_6S$ $[M + H]^+$: 490.6343, found 490.6345.



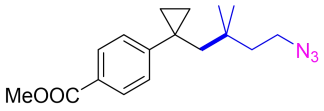
methyl 4-(1-(2-(4-bromophenyl)-4-((*N*-(*tert*-butyl)sulfamoyl)oxy)butyl)cyclopropyl)benzoate (XX)

Colorless oil (71%, 38.2 mg). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 4.07 (s, 1H), 3.84 (s, 3H), 3.79 – 3.74 (m, 1H), 3.67 – 3.60 (m, 1H), 2.49 (s, 1H), 2.06 (dd, *J* = 14.1, 5.7 Hz, 2H), 1.75 (dd, *J* = 14.3, 9.0 Hz, 2H), 1.16 (s, 9H), 0.70 – 0.60 (m, 3H), 0.31 – 0.25 (m, 1H). **$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*)** δ 167.0, 149.9, 142.6, 131.6, 129.7, 129.6, 128.8, 128.0, 120.3, 67.9, 54.6, 52.0, 46.8, 40.0, 35.3, 29.6, 24.0, 13.6, 13.0. **HRMS (ESI-TOF)** m/z: calculated for $C_{25}H_{32}BrNO_5S$ $[M + H]^+$: 539.5043, found 539.5033.



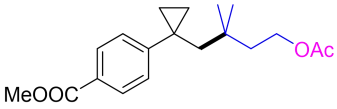
methyl 4-(1-(4-iodo-2,2-dimethylbutyl)cyclopropyl)benzoate (4b)

Colorless oil (98%, 18.9 mg). **^1H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.02 – 2.98 (m, 2H), 1.77 – 1.72 (m, 2H), 1.67 (s, 2H), 0.87 (t, *J* = 6.3 Hz, 2H), 0.74 – 0.70 (m, 8H). **$^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.5, 128.6, 128.0, 126.8, 51.0, 50.0, 47.3, 37.2, 26.3, 22.3, 12.7, 0.0. **HRMS (ESI-TOF)** m/z: calculated for $C_{17}H_{23}IO_2$ $[M + H]^+$: 387.0816, found 387.0818.



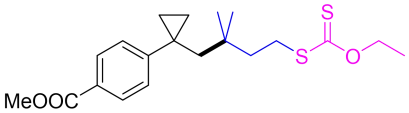
methyl 4-(1-(4-azido-2,2-dimethylbutyl)cyclopropyl)benzoate (4c)

Colorless oil (92%, 13.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 3.10 (t, 2H), 1.69 (s, 2H), 1.39 (t, *J* = 6.9 Hz, 2H), 0.87 (t, 2H), 0.75 – 0.71 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 166.0, 150.6, 128.5, 128.1, 126.9, 51.0, 50.9, 46.5, 39.9, 33.9, 26.8, 22.4, 12.7. **HRMS (ESI-TOF)** m/z: calculated for $C_{17}H_{23}N_3O_2$ [M + H]$^+$: 302.1863, found 302.1854.



methyl 4-(1-(4-acetoxy-2,2-dimethylbutyl)cyclopropyl)benzoate (4d)

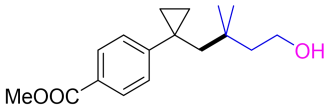
Colorless oil (81%, 12.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 3.96 (t, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 1.98 (s, 3H), 1.70 (s, 2H), 1.41 (t, 2H), 0.84 (t, 2H), 0.74 – 0.71 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 171.2, 167.1, 151.8, 129.5, 129.2, 127.7, 61.7, 52.0, 52.0, 40.8, 34.8, 28.0, 23.4, 21.1, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{19}H_{26}O_4$ [M + H]$^+$: 319.1904, found 319.1905.



methyl 4-(1-(4-((ethoxycarbonothioyl)thio)-2,2-dimethylbutyl)cyclopropyl)benzoate (4e)

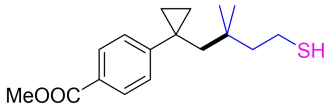
Colorless oil (77%, 14.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.89 – 2.83 (m, 2H), 1.65 (s, 2H), 1.39 – 1.31 (m, 5H), 0.78 (t, 2H), 0.70 – 0.65 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 215.1, 167.0, 151.7, 129.5, 129.2, 127.8, 69.8,

52.0, 51.7, 41.6, 36.0, 31.4, 27.5, 23.4, 13.8, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{20}H_{28}O_3S_2$ $[M + H]^+$: 381.1553, found 381.1549.



methyl 4-(1-(4-hydroxy-2,2-dimethylbutyl)cyclopropyl)benzoate (4f)

Colorless oil (63%, 9.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.56 (t, 2H), 1.70 (s, 2H), 1.38 (t, *J* = 7.6 Hz, 2H), 0.84 (t, *J* = 4.0 Hz, 2H), 0.75 – 0.71 (m, 8H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.1, 152.0, 129.5, 129.2, 127.7, 59.7, 52.3, 52.0, 45.6, 34.9, 29.7, 28.2, 23.5, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{17}H_{24}O_3$ $[M + H]^+$: 277.3833, found 277.3834.

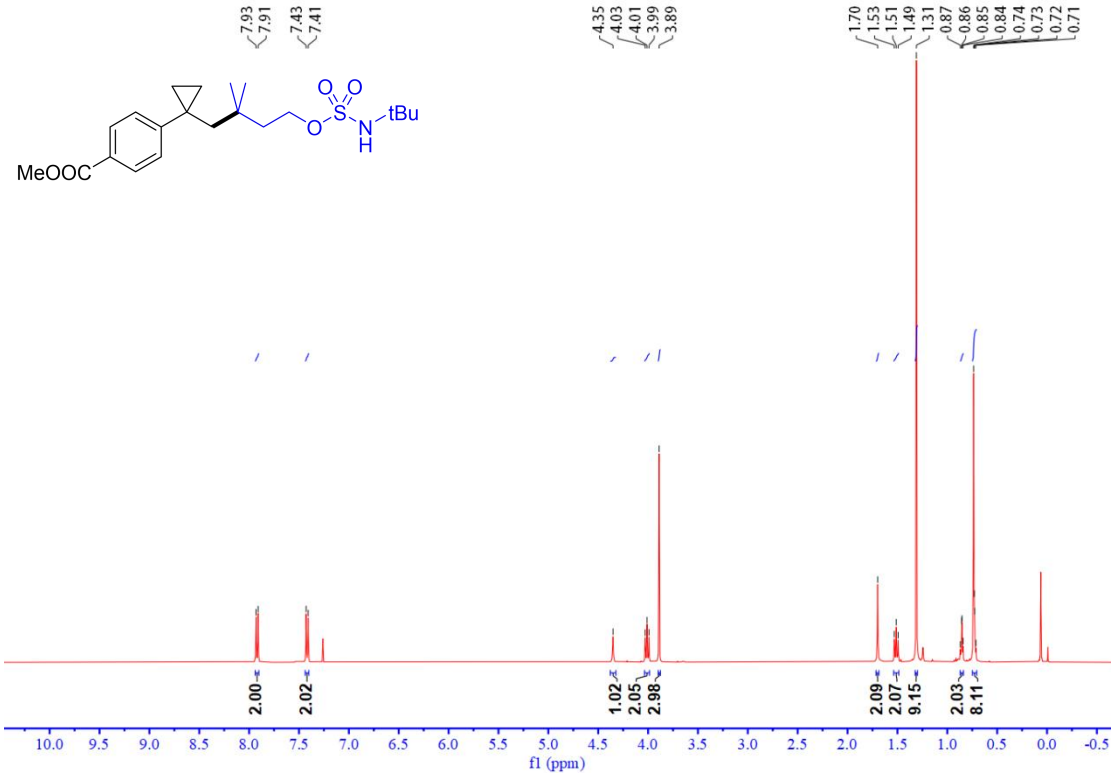


methyl 4-(1-(4-mercapto-2,2-dimethylbutyl)cyclopropyl)benzoate (4g)

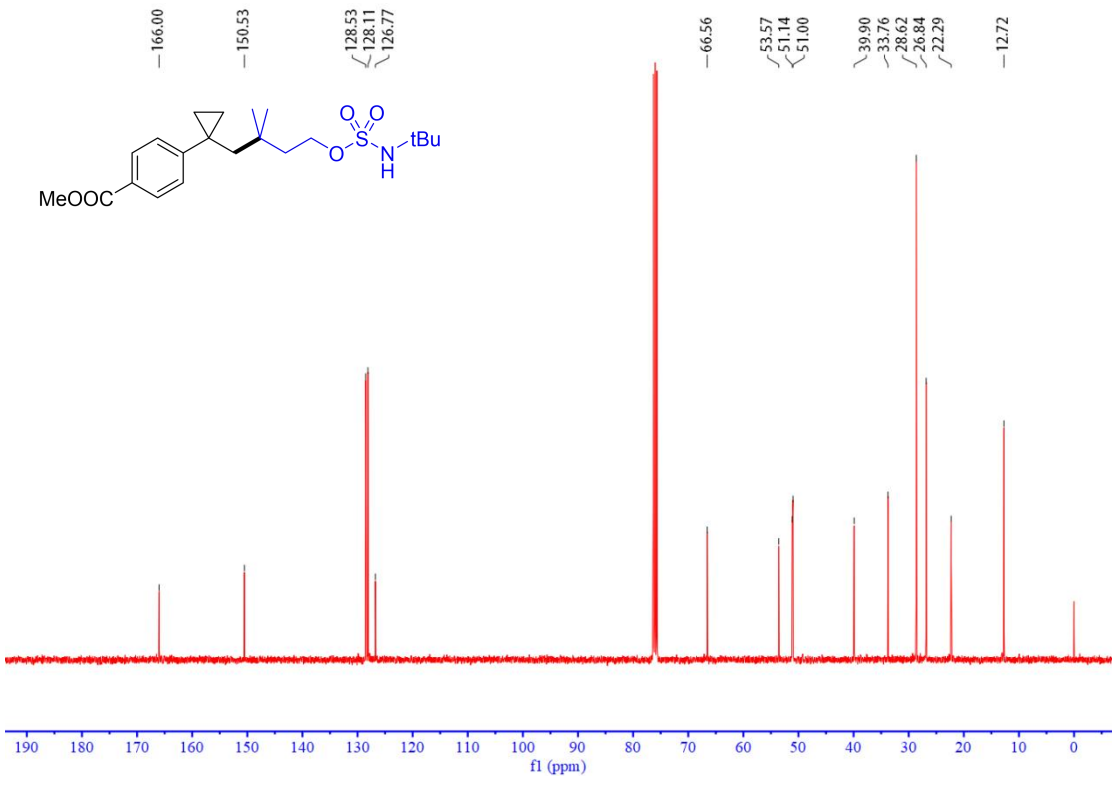
Colorless oil (63%, 6,8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 2.50 – 2.45 (m, 2H), 1.67 (s, 2H), 1.46 – 1.41 (m, 2H), 0.86 (t, *J* = 6.4 Hz, 2H), 0.72 (t, *J* = 4.6 Hz, 2H), 0.68 (s, 6H). **^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*)** δ 167.1, 151.8, 129.5, 129.2, 127.7, 52.0, 51.8, 43.0, 35.8, 34.4, 29.7, 27.7, 23.4, 13.8. **HRMS (ESI-TOF)** m/z: calculated for $C_{17}H_{24}O_2S$ $[M + H]^+$: 293.1570, found 293.1571.

9. NMR spectra

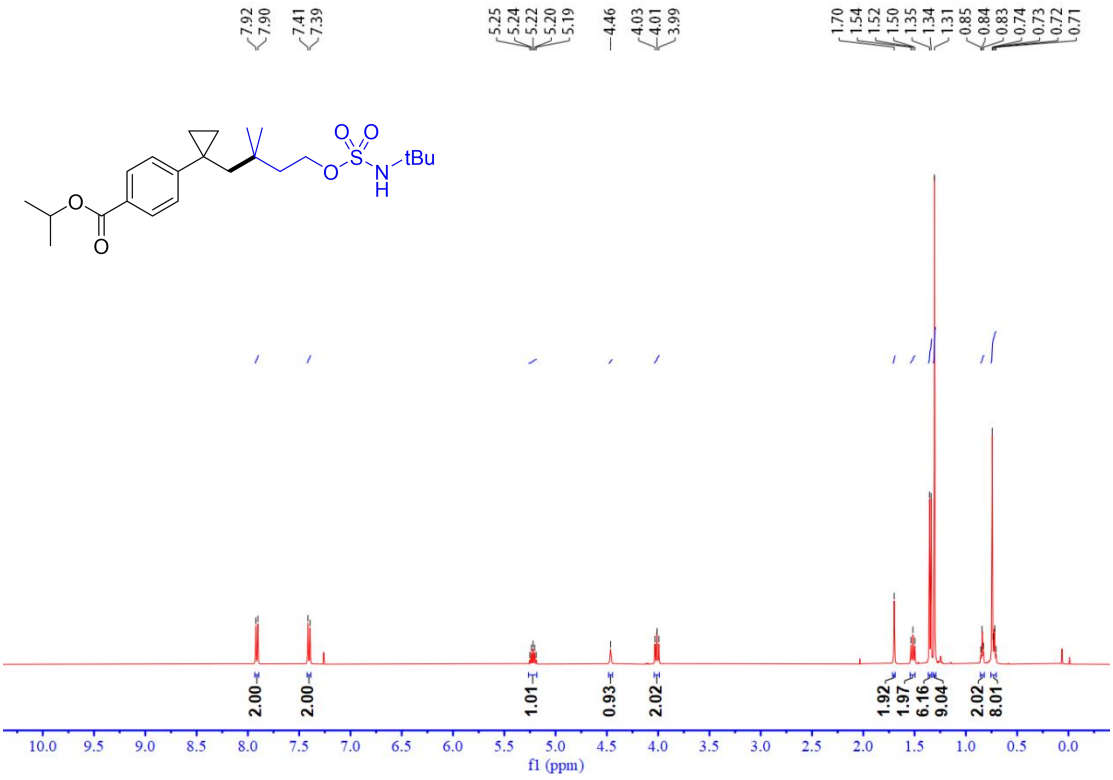
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3a**



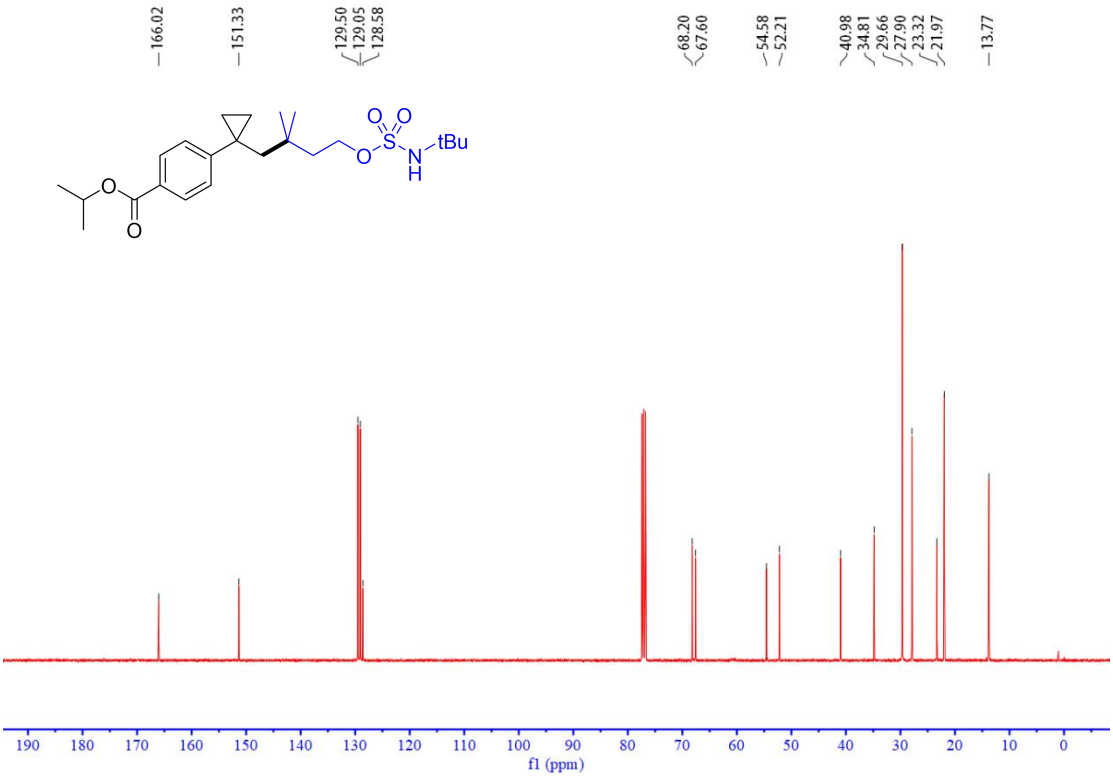
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3a**



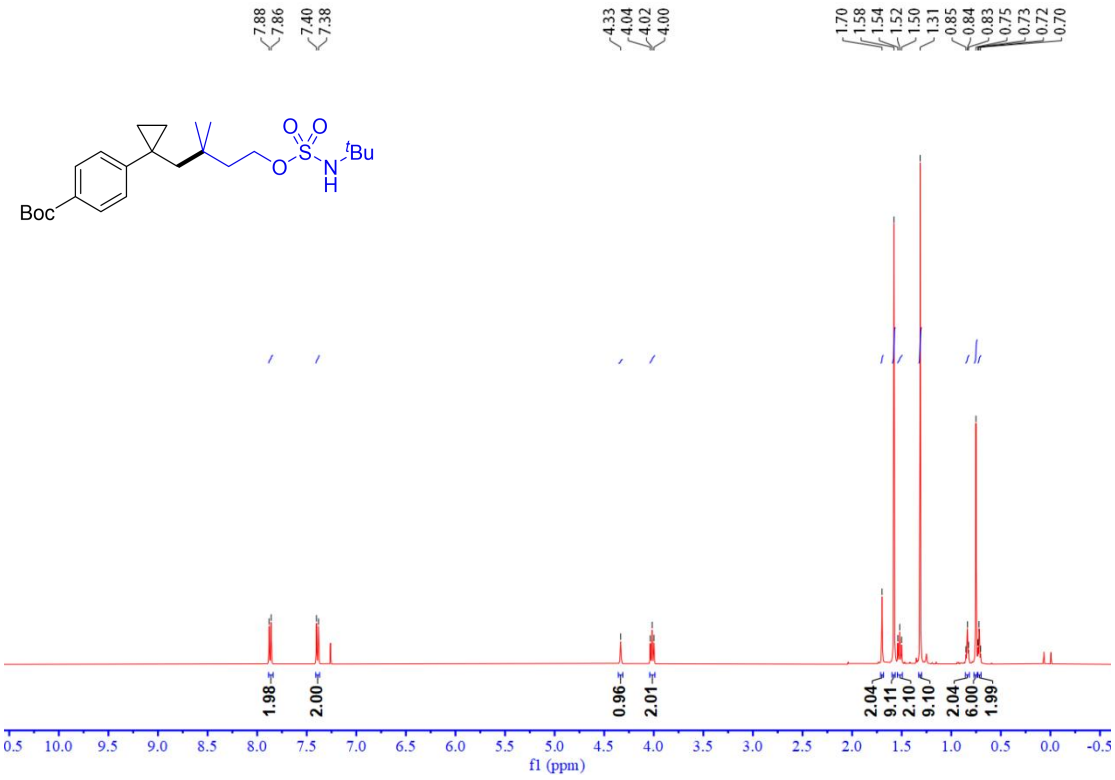
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **2b**



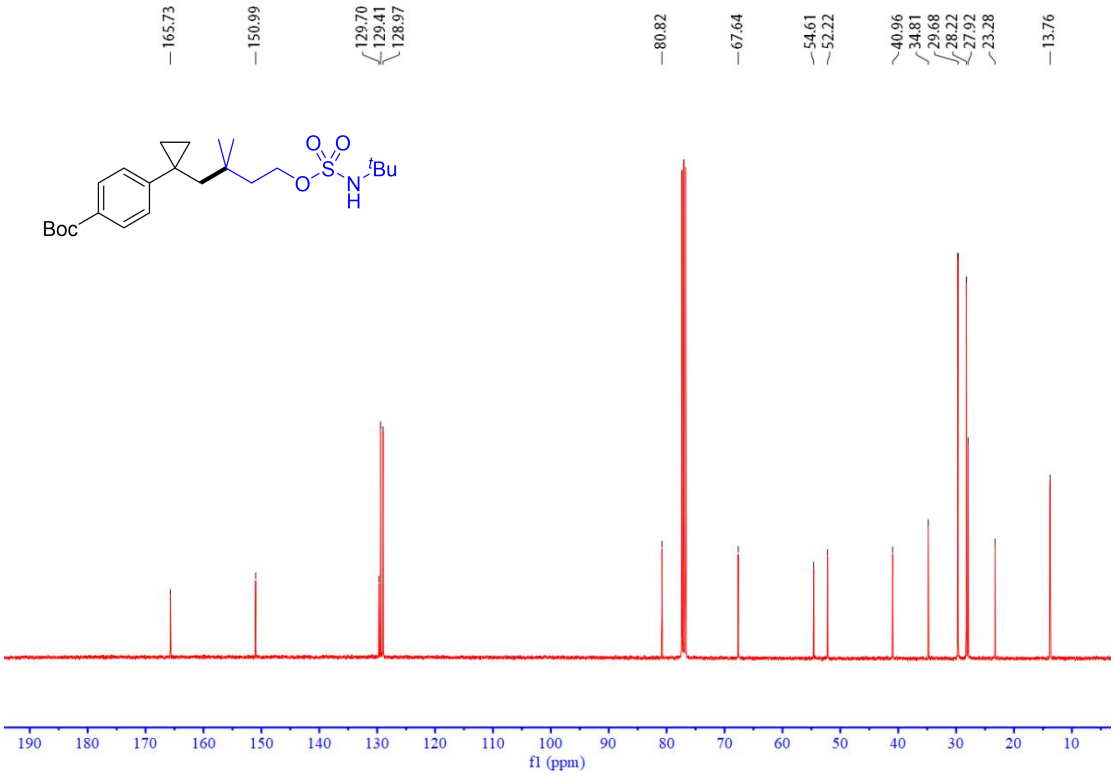
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **2b**



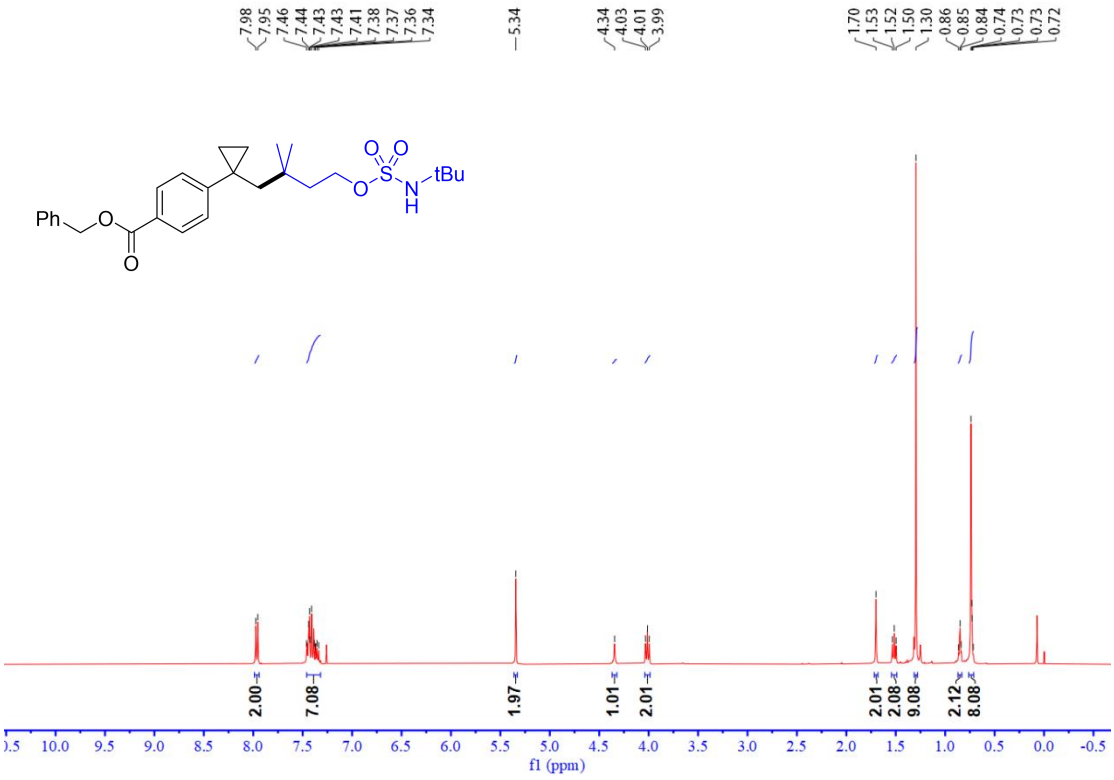
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3c**



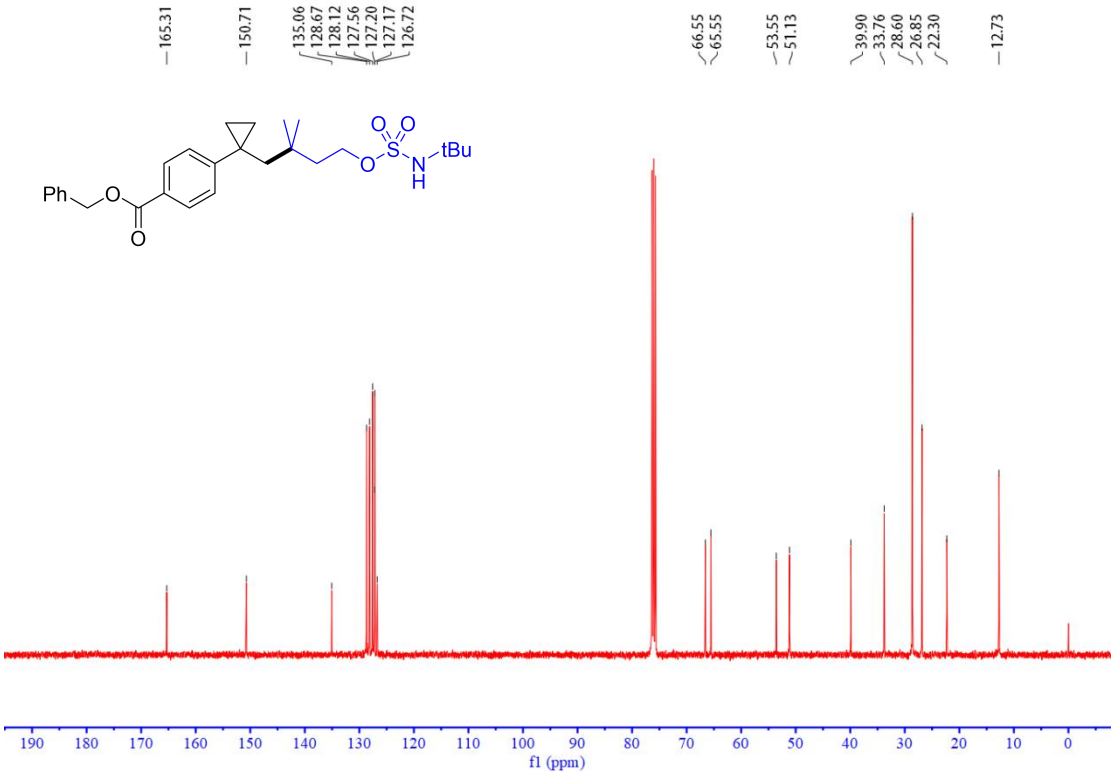
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3c**



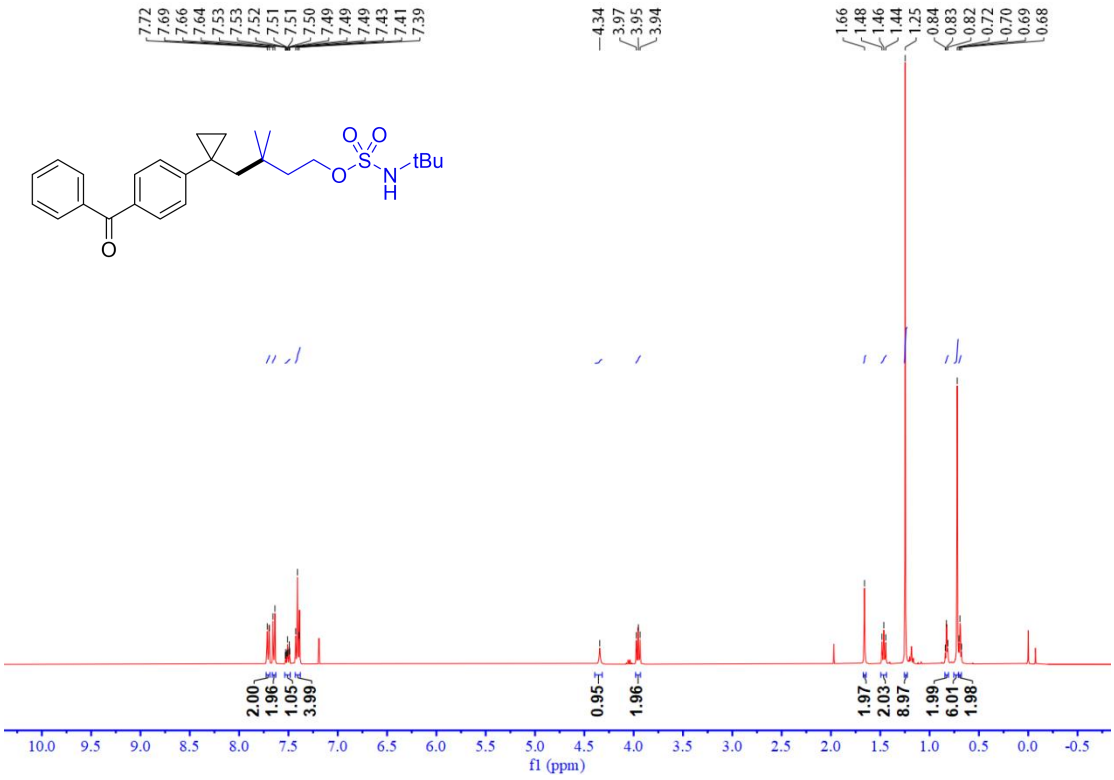
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3d**



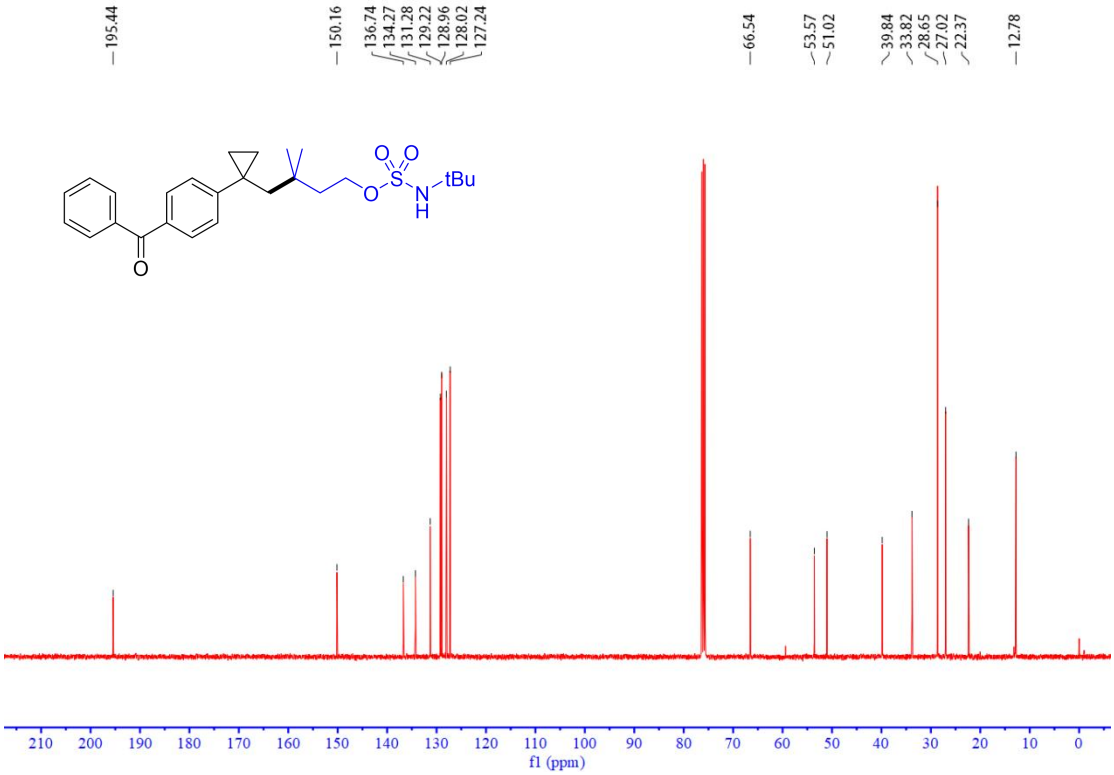
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3d**



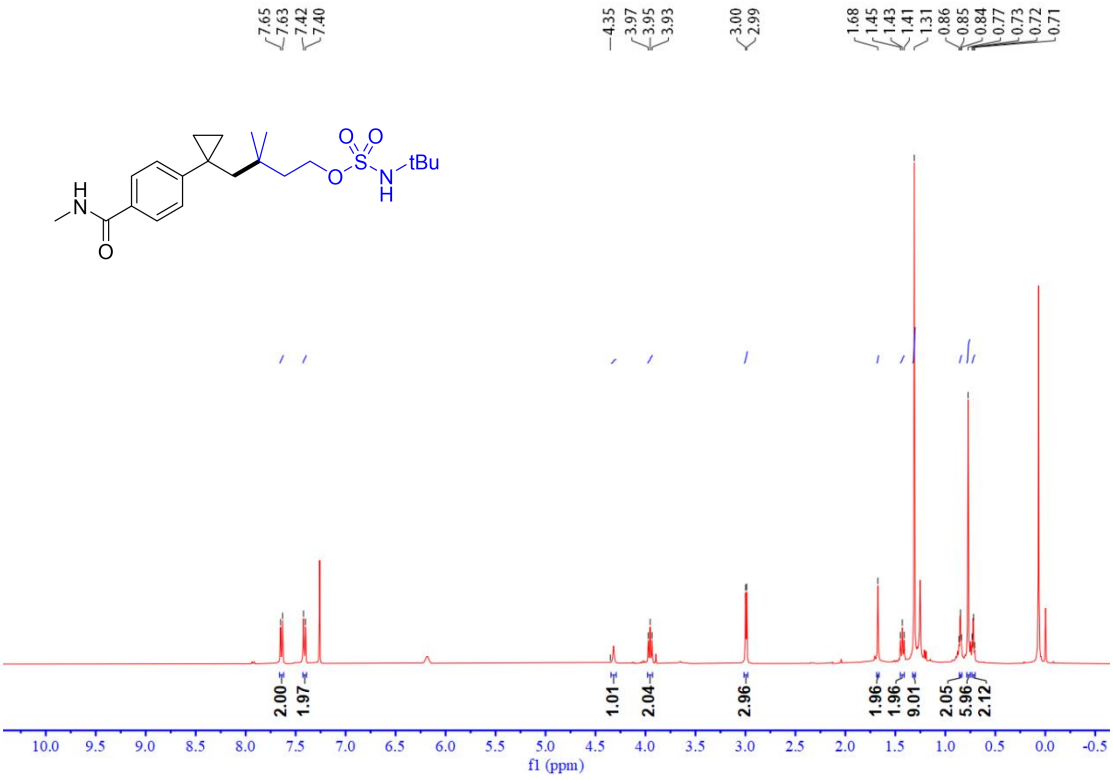
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3e**



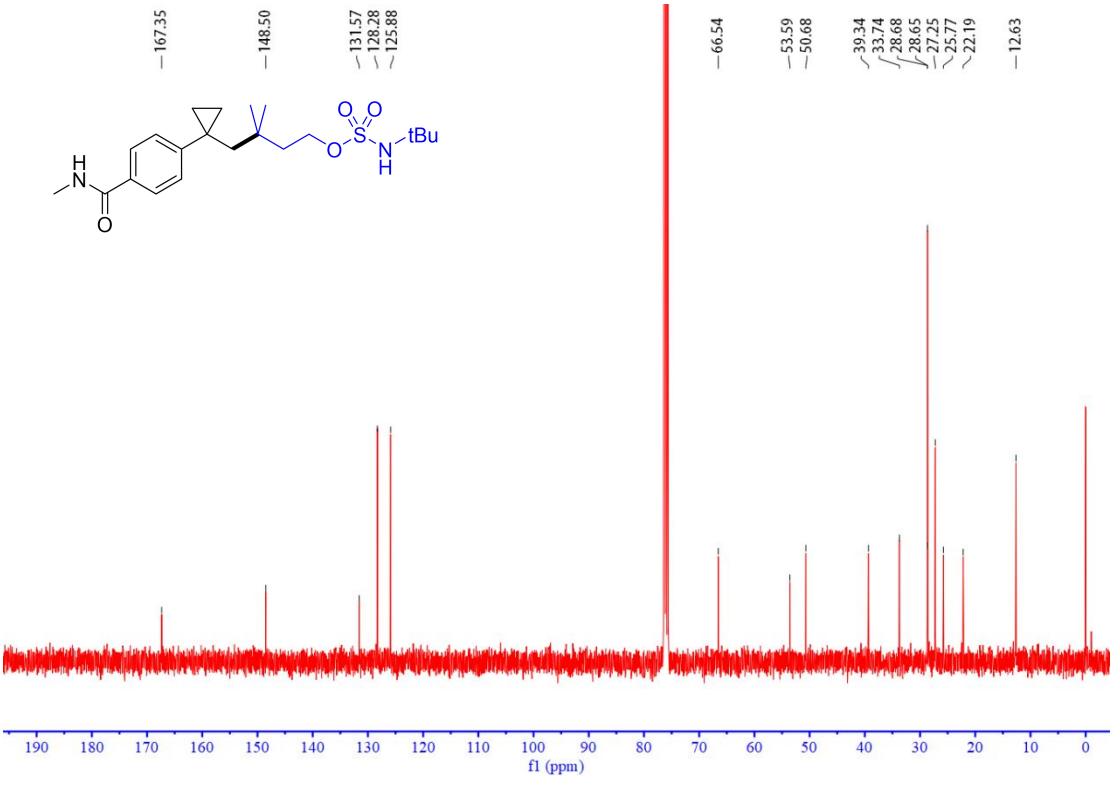
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3e**



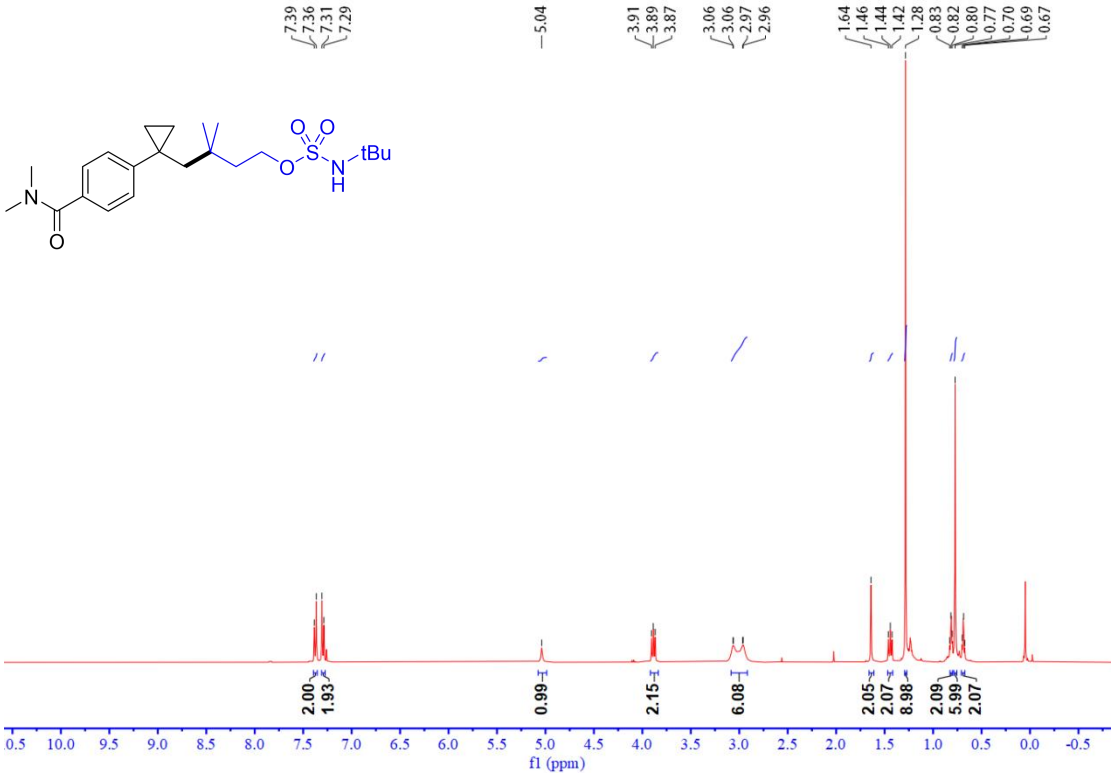
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3f**



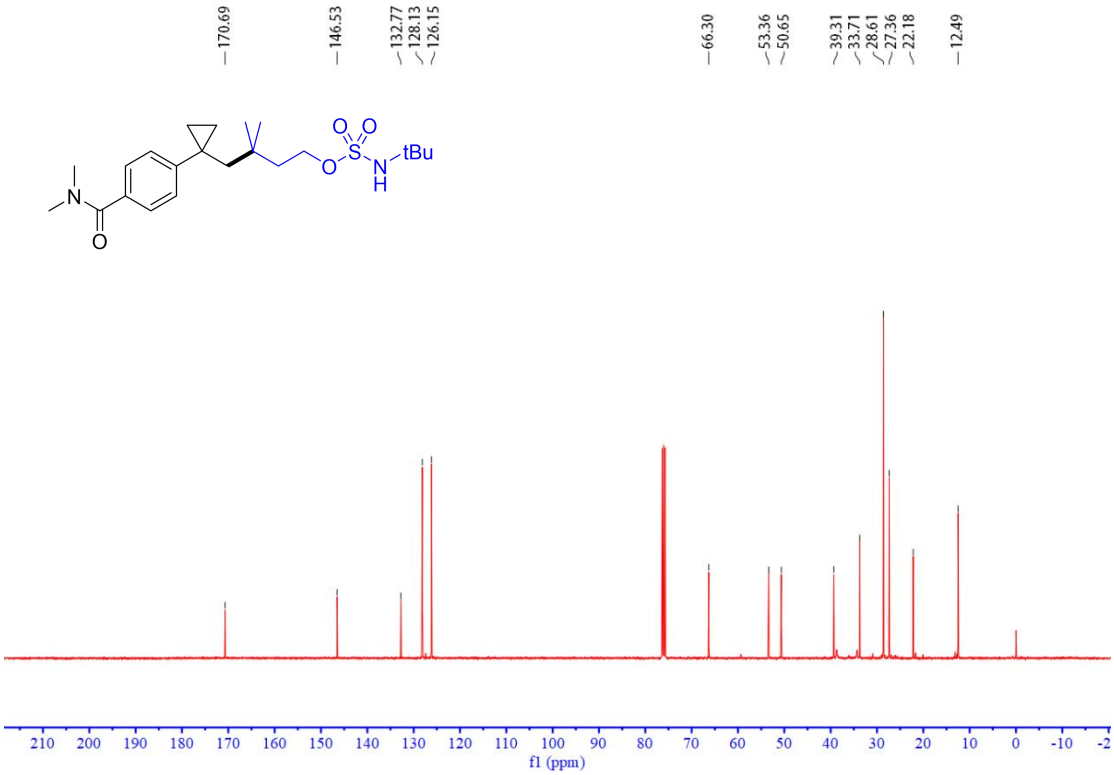
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3f**



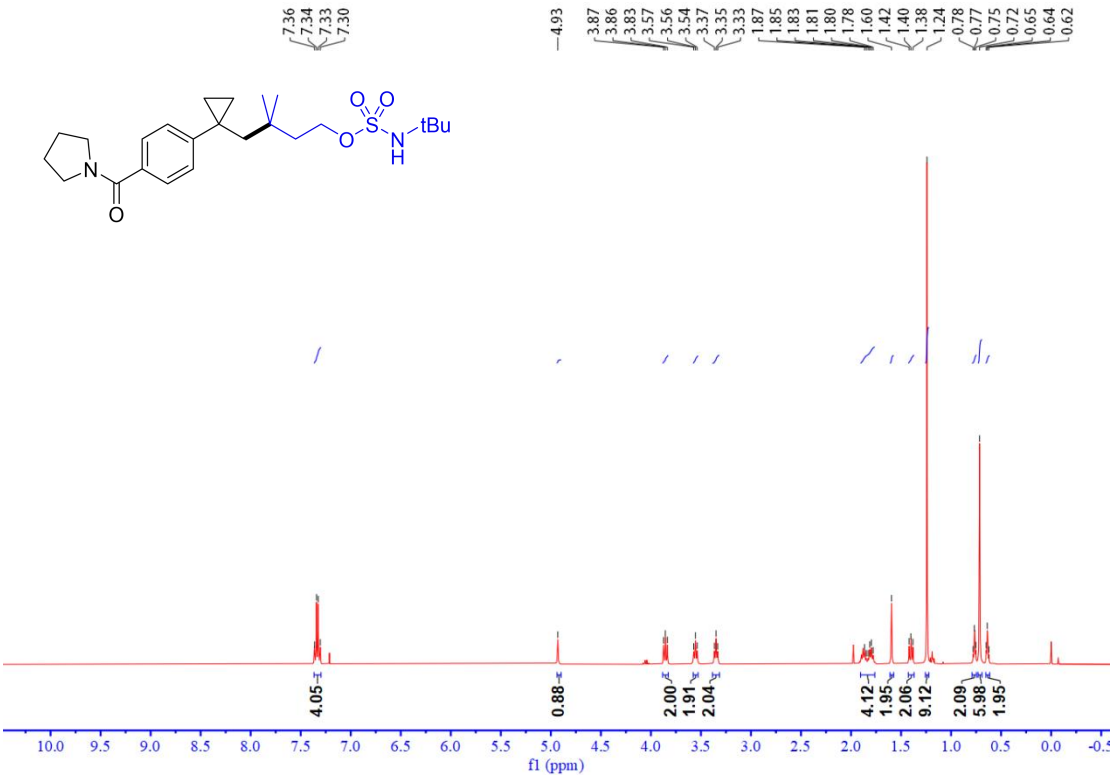
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3g**



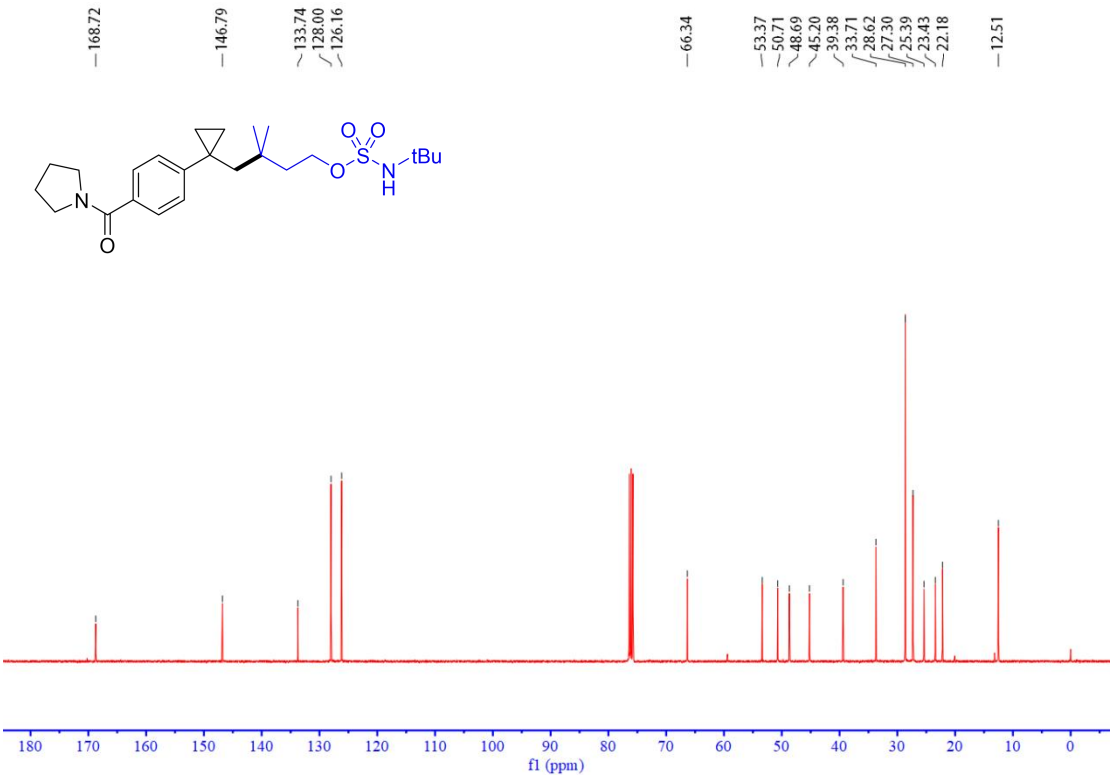
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3g**



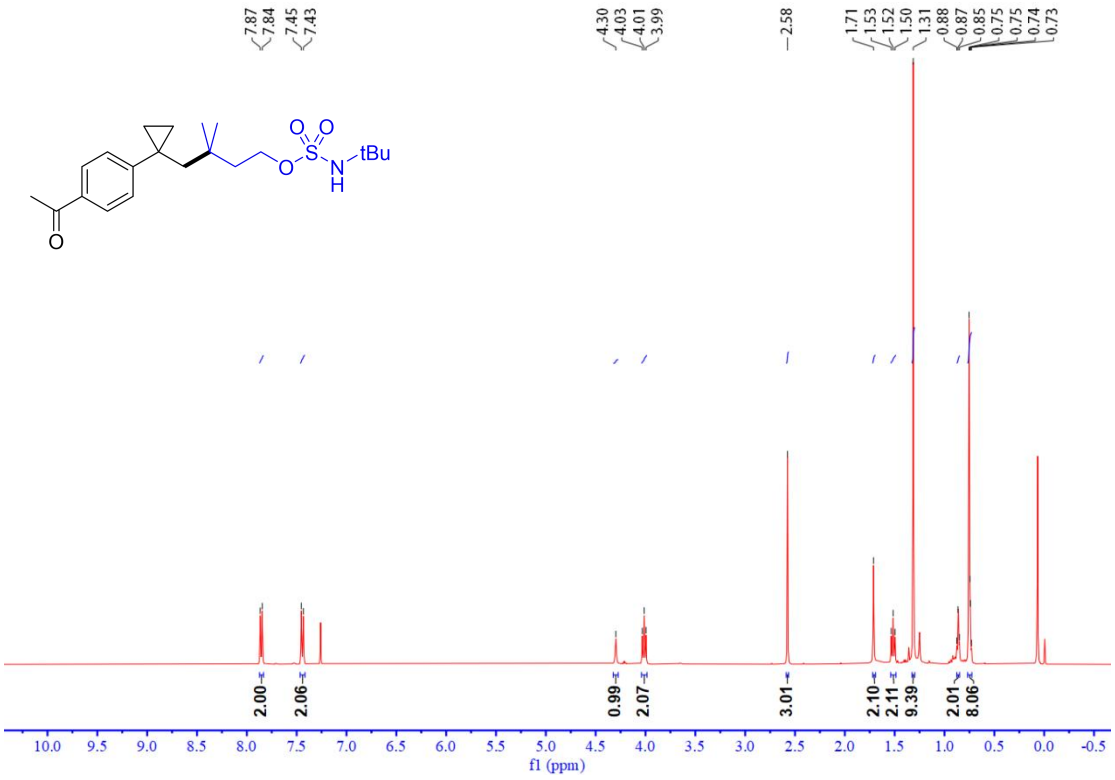
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3h**



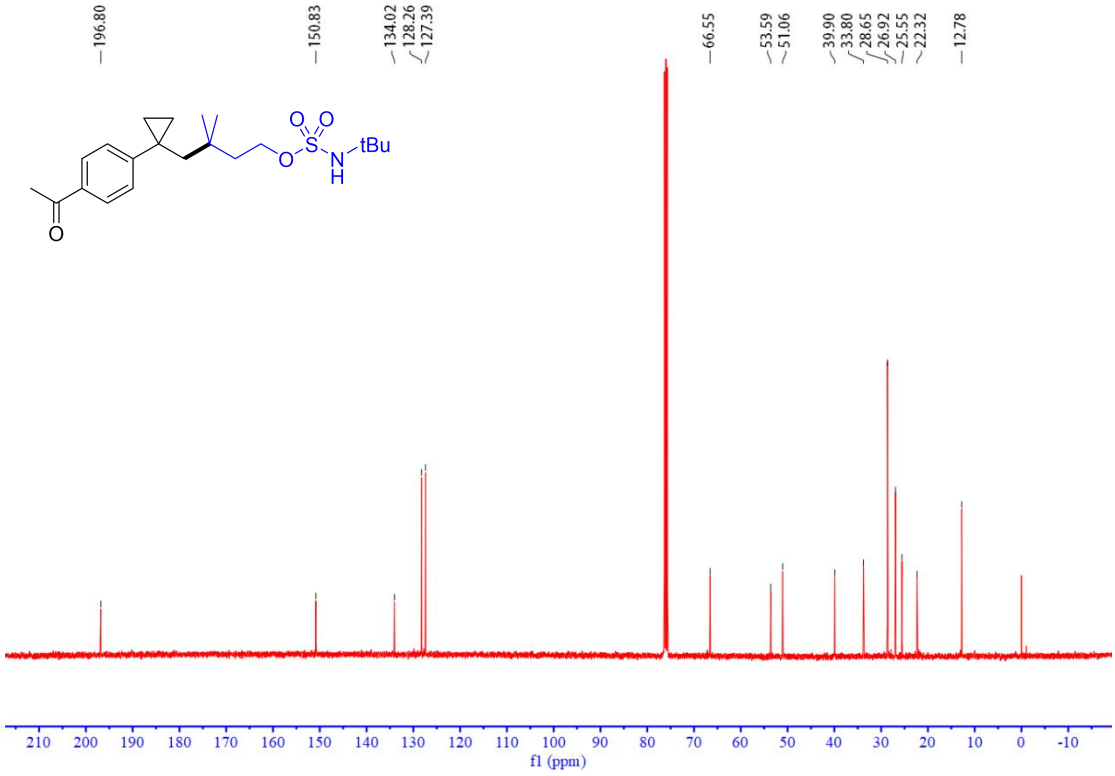
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3h**



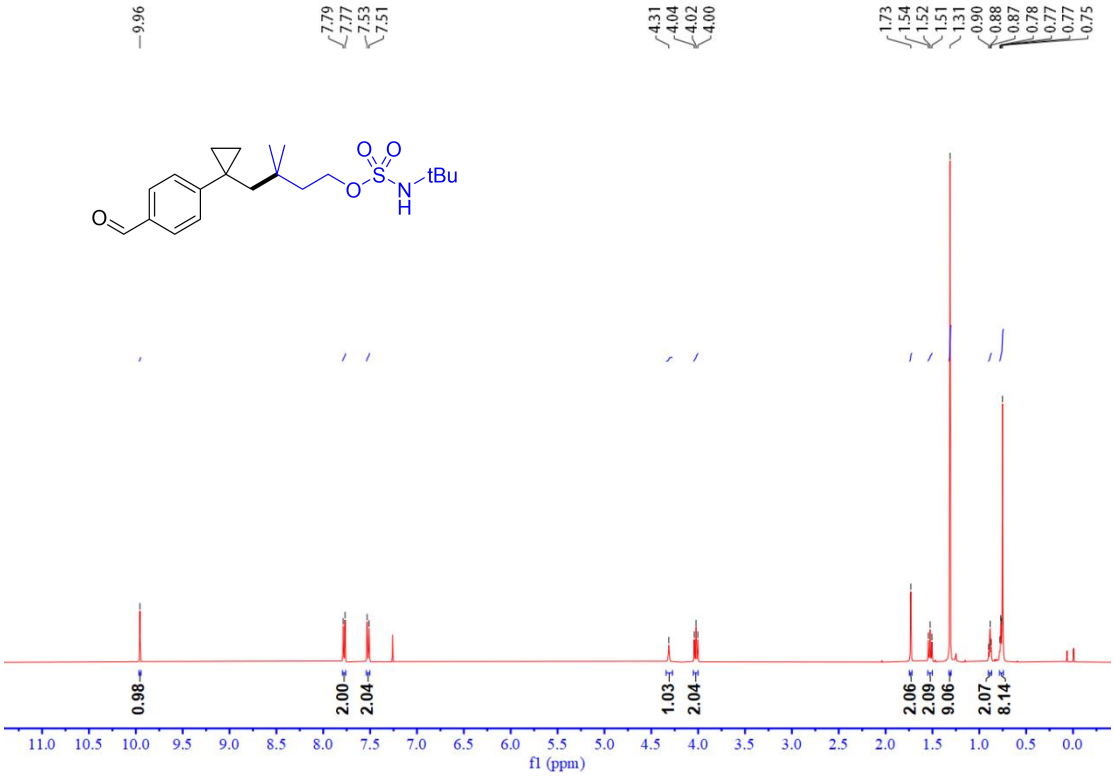
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound**3i**



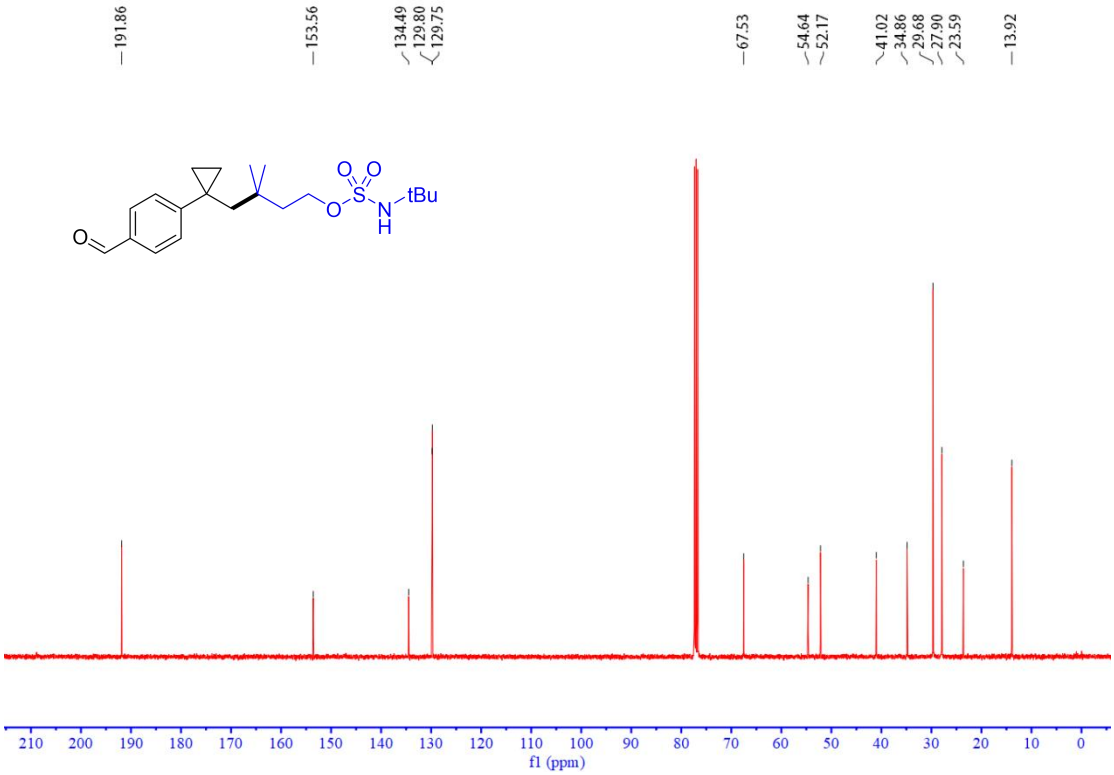
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3i**



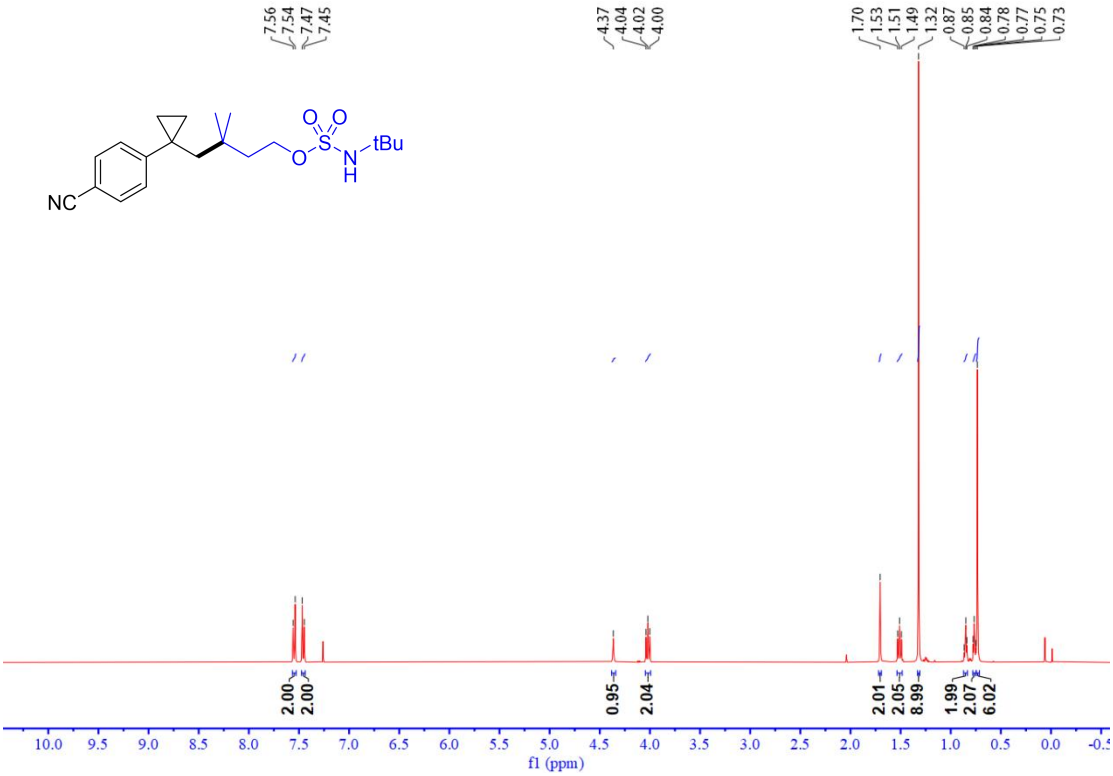
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3j**



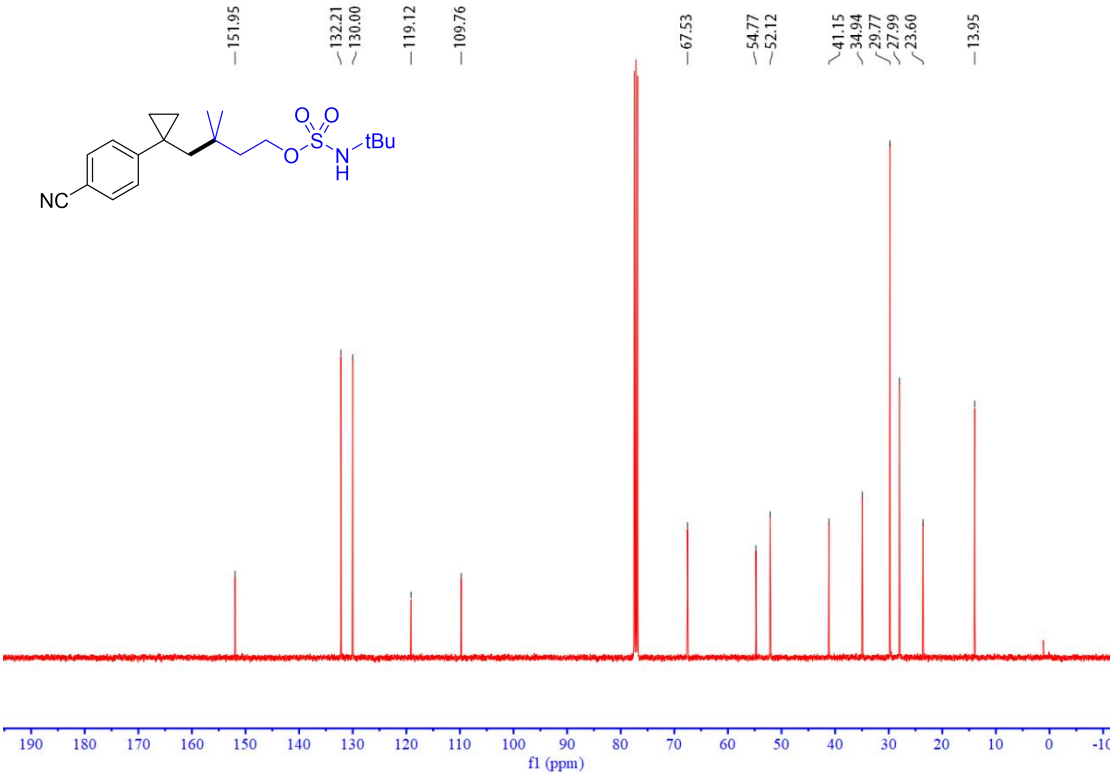
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3j**



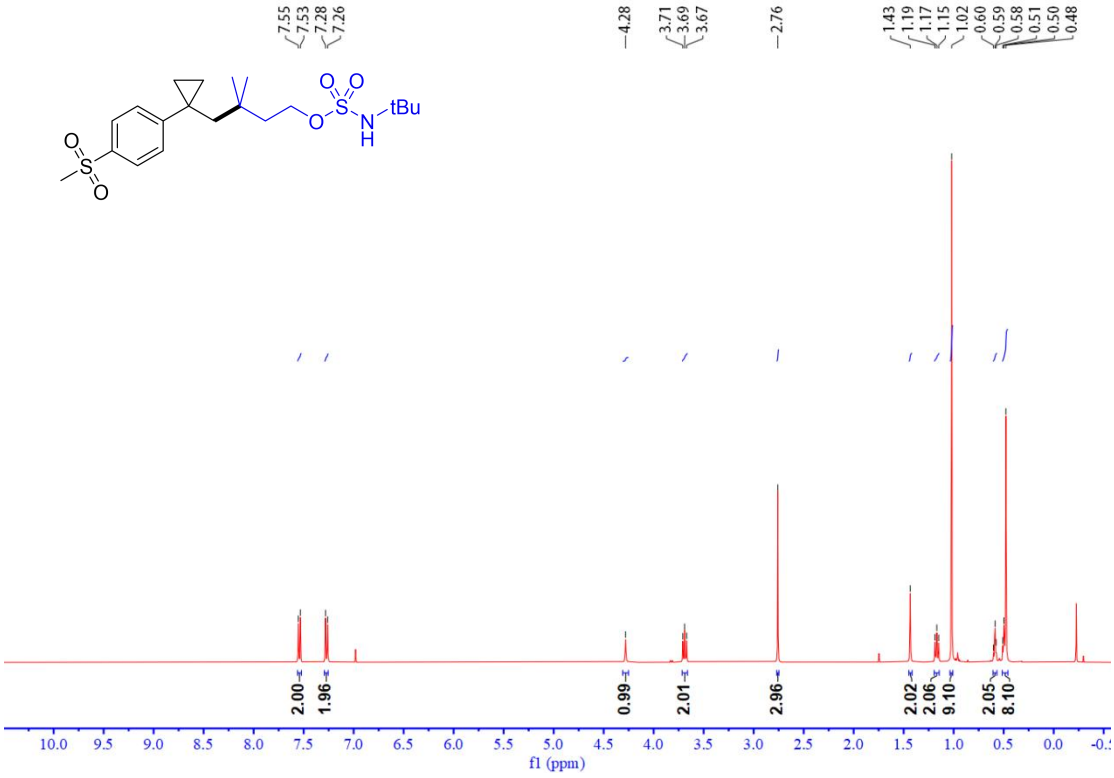
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3k**



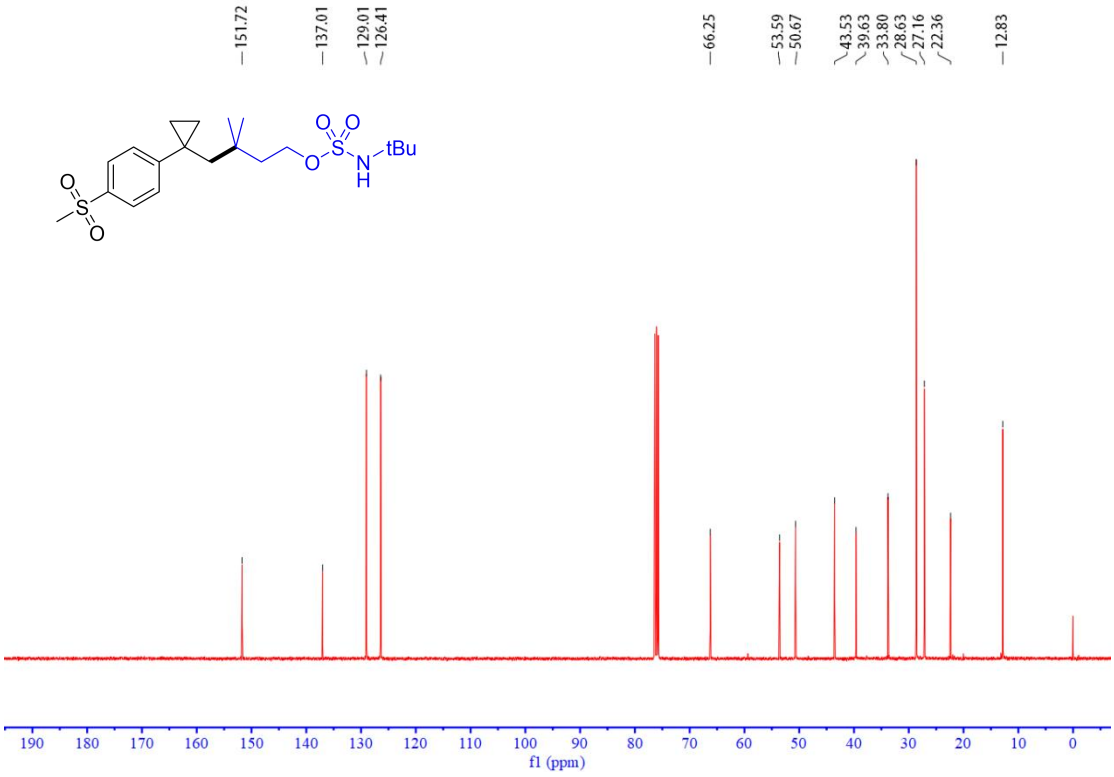
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3k**



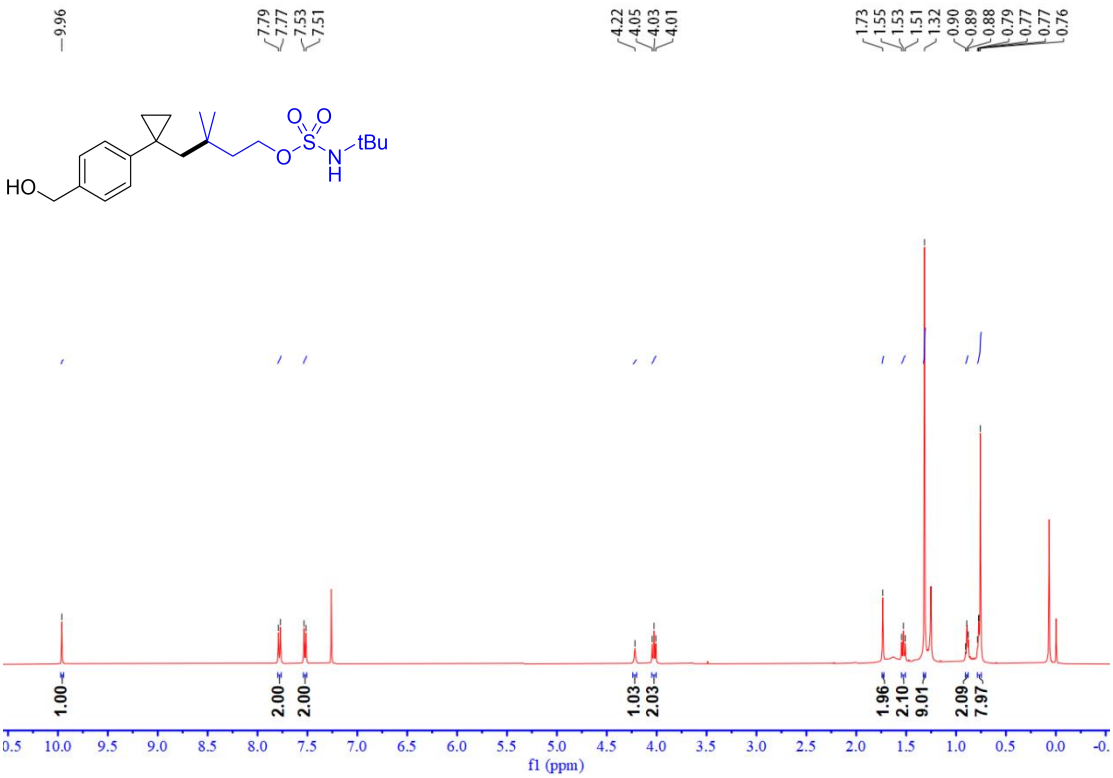
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3l**



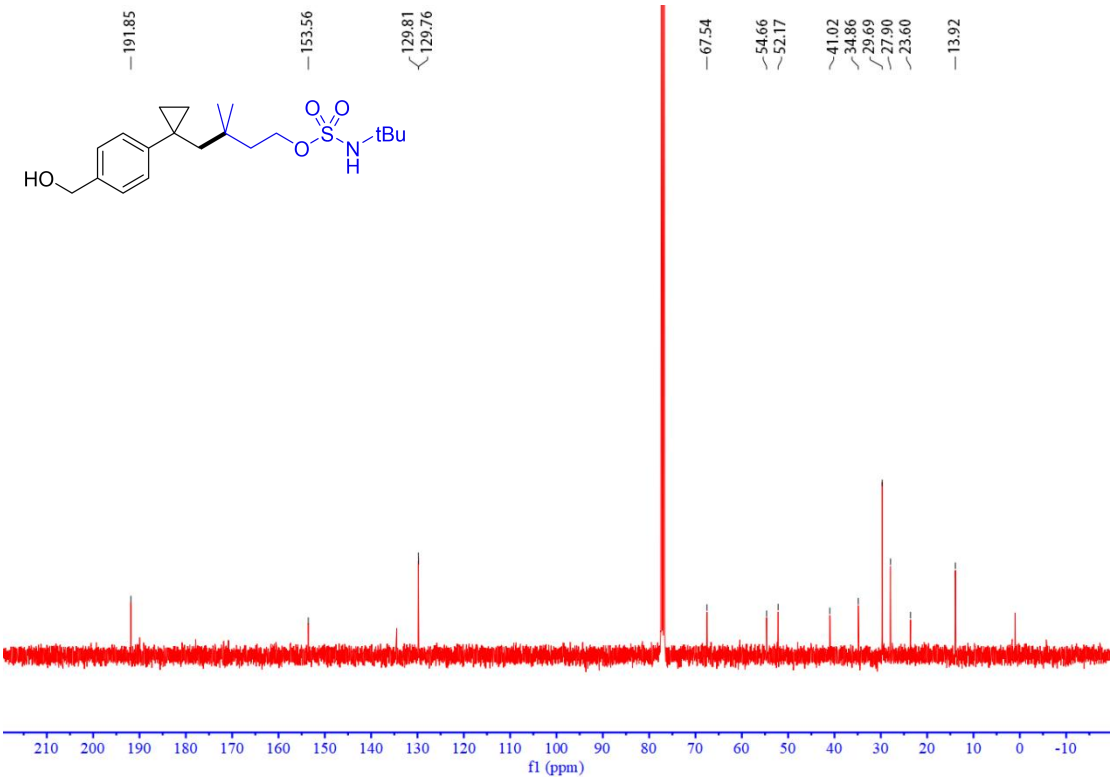
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3l**



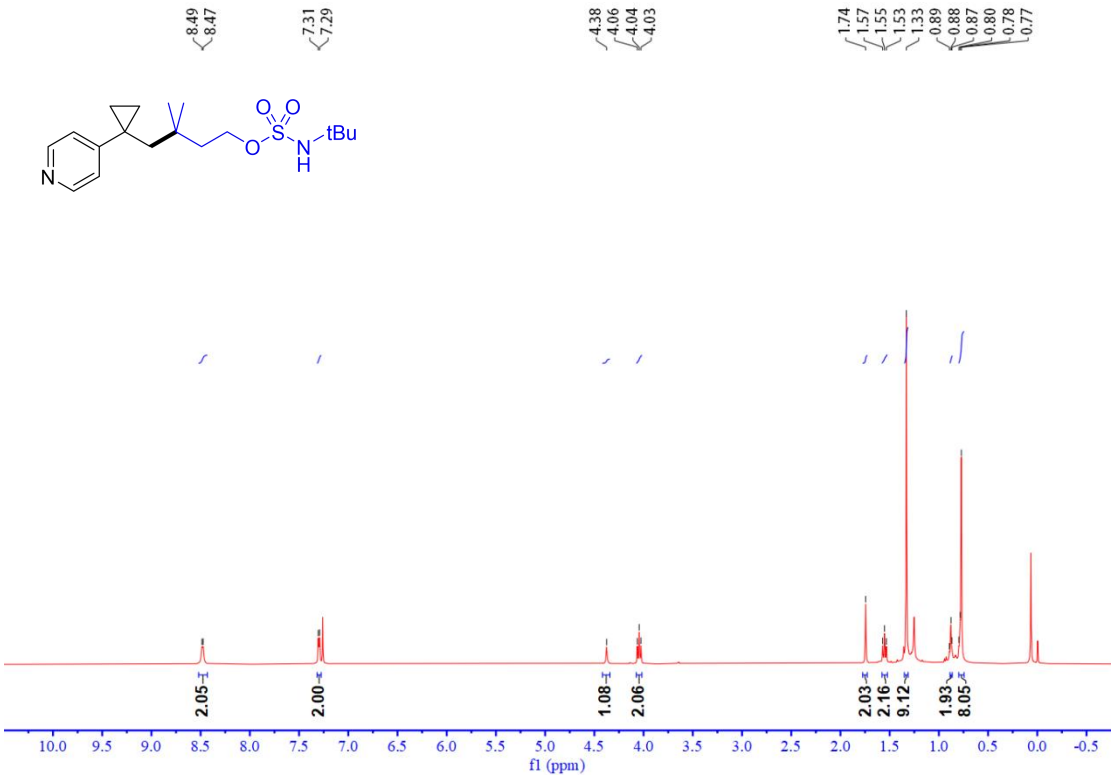
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3m**



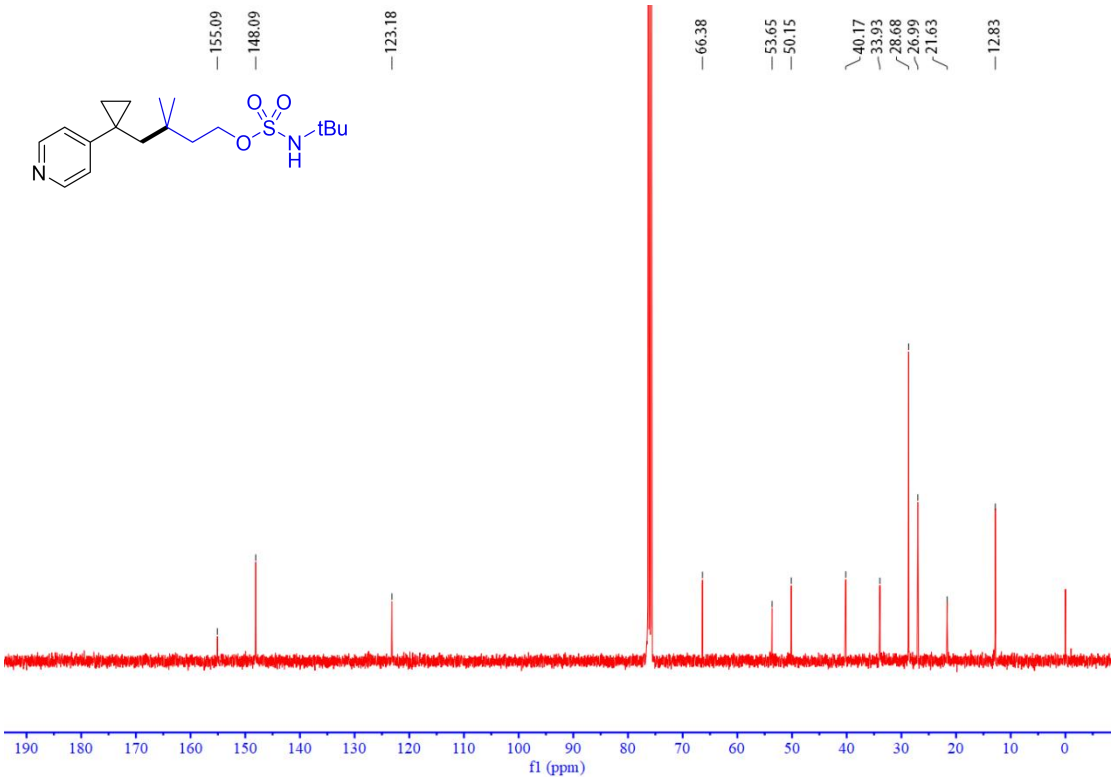
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3m**



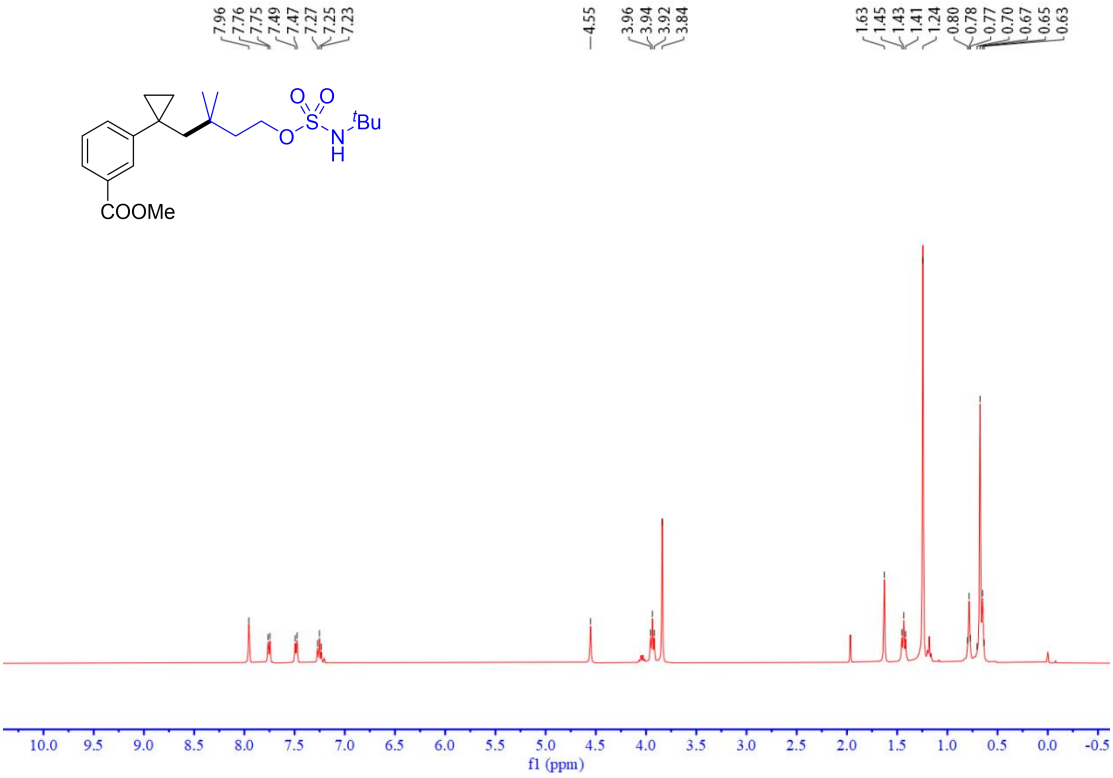
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3n**



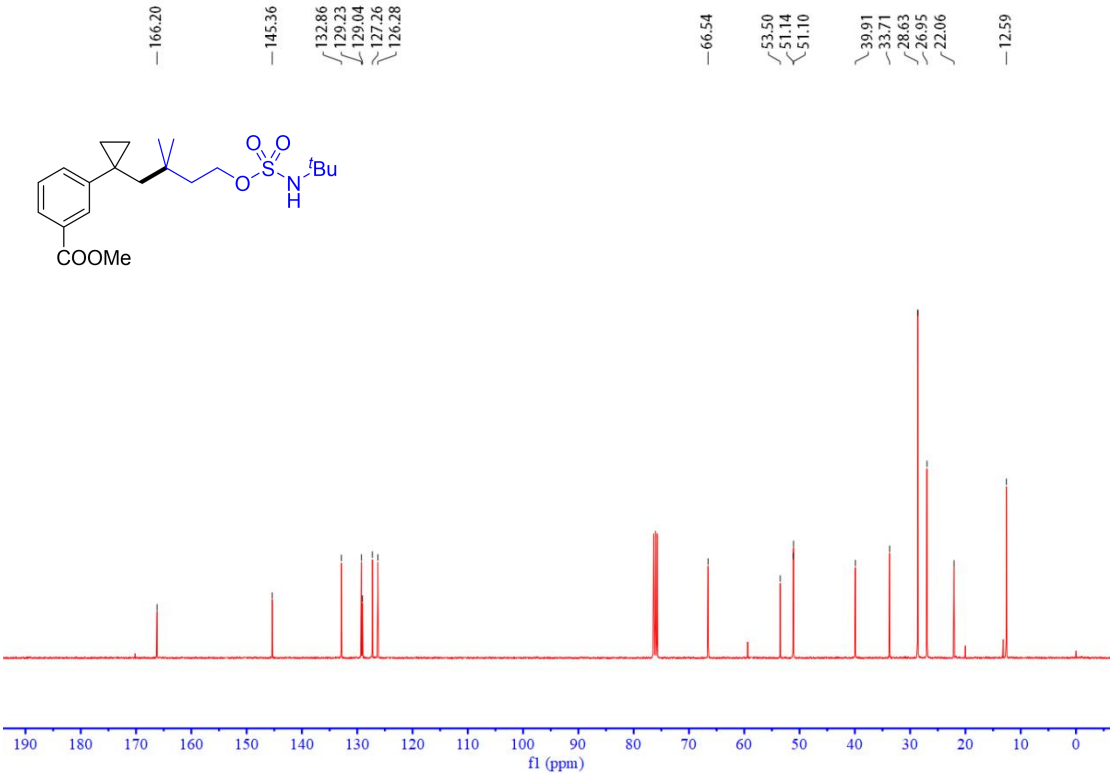
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3n**



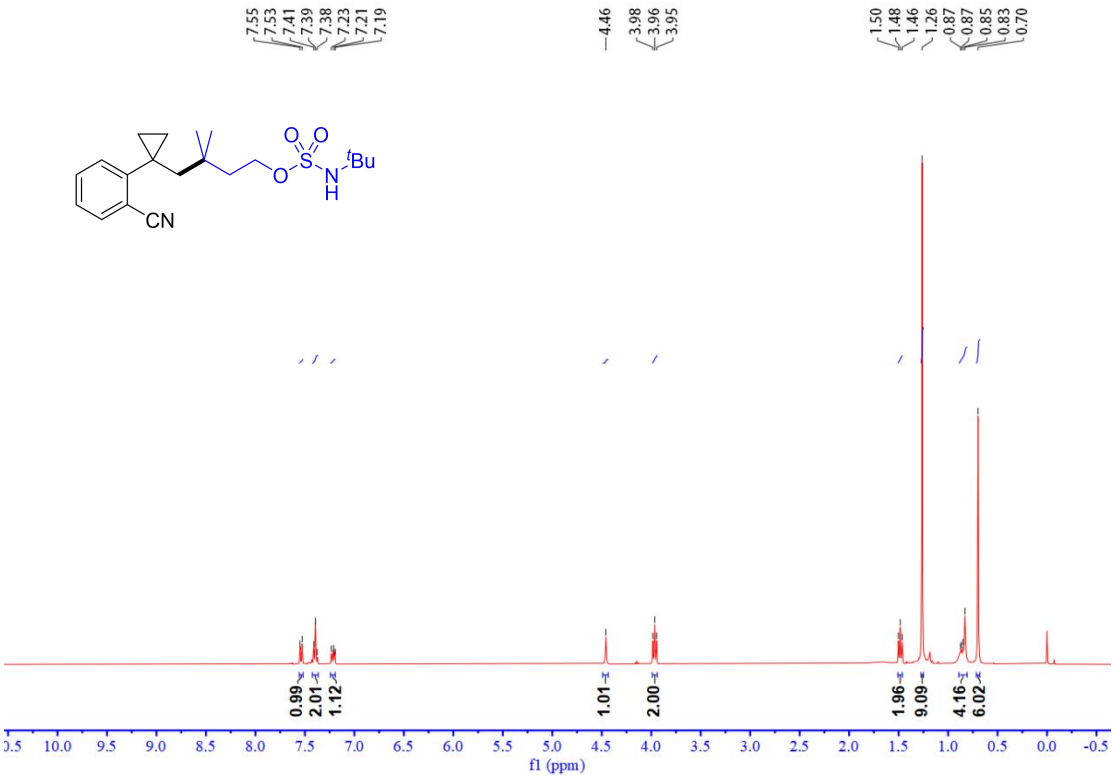
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3o**



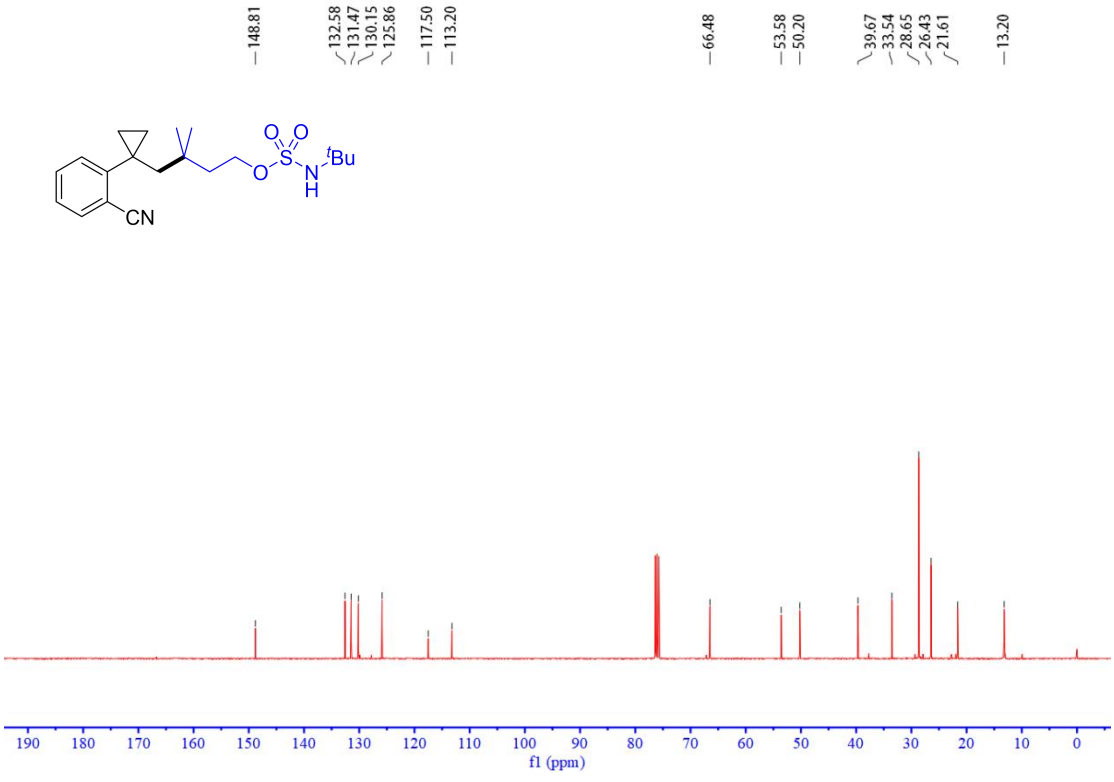
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3o**



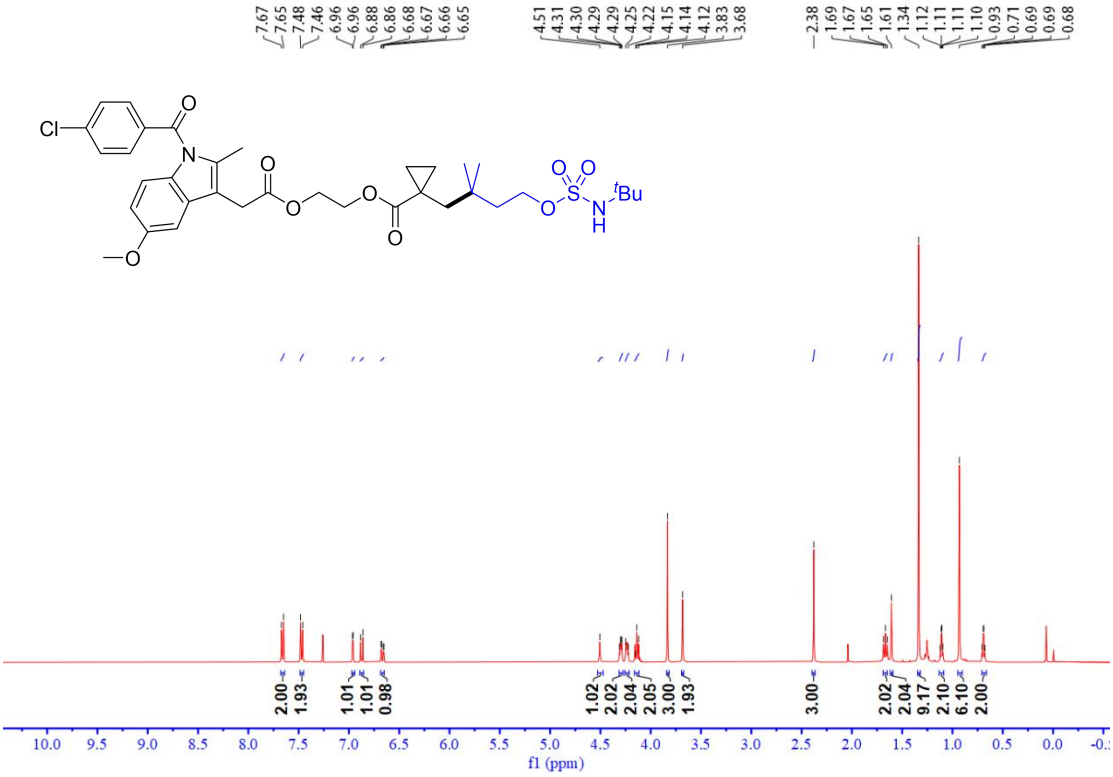
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3p**



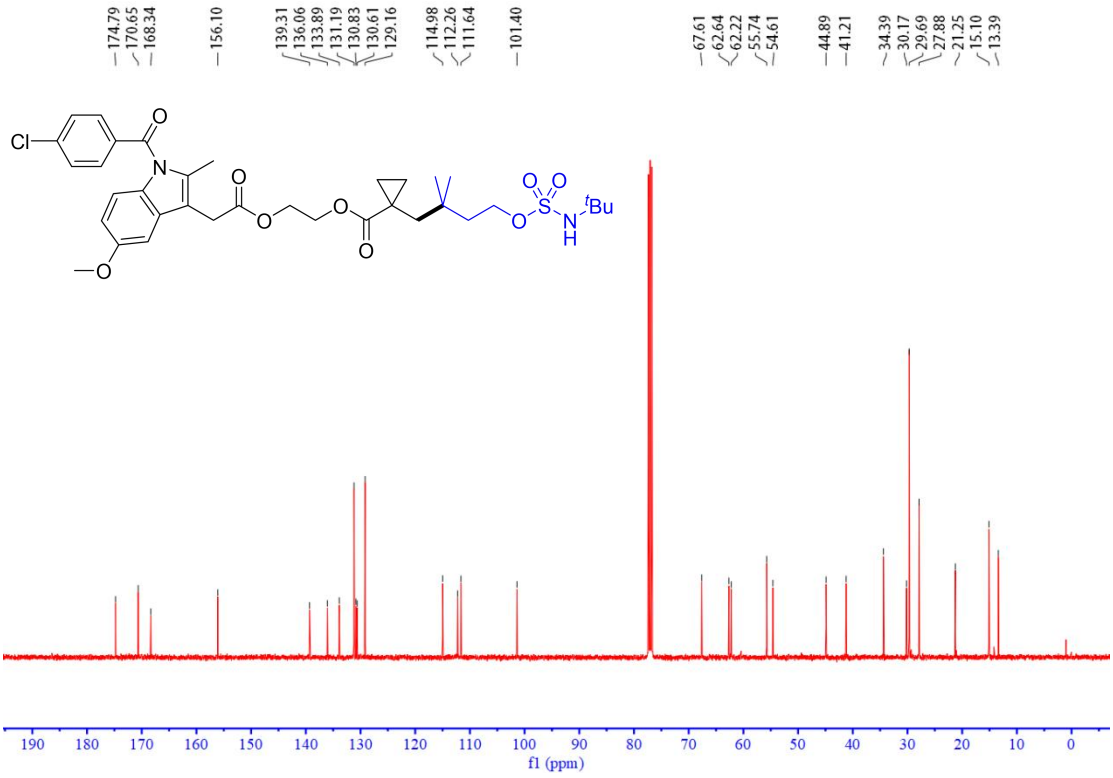
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3p**



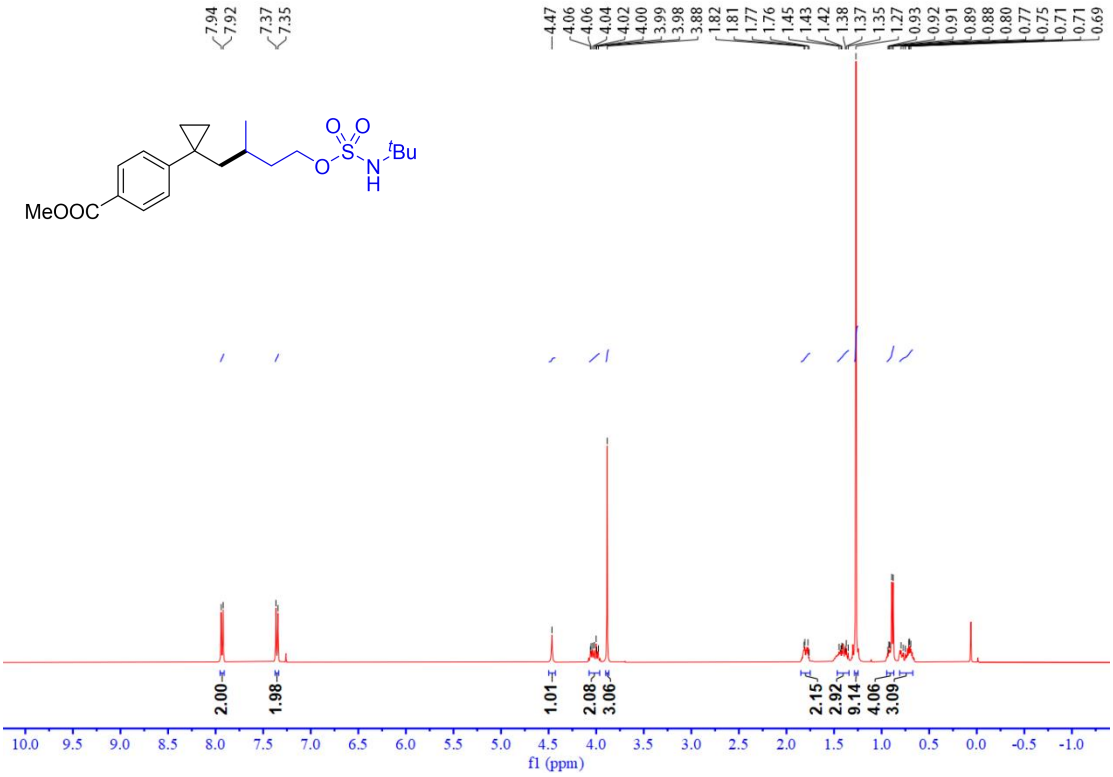
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3q**



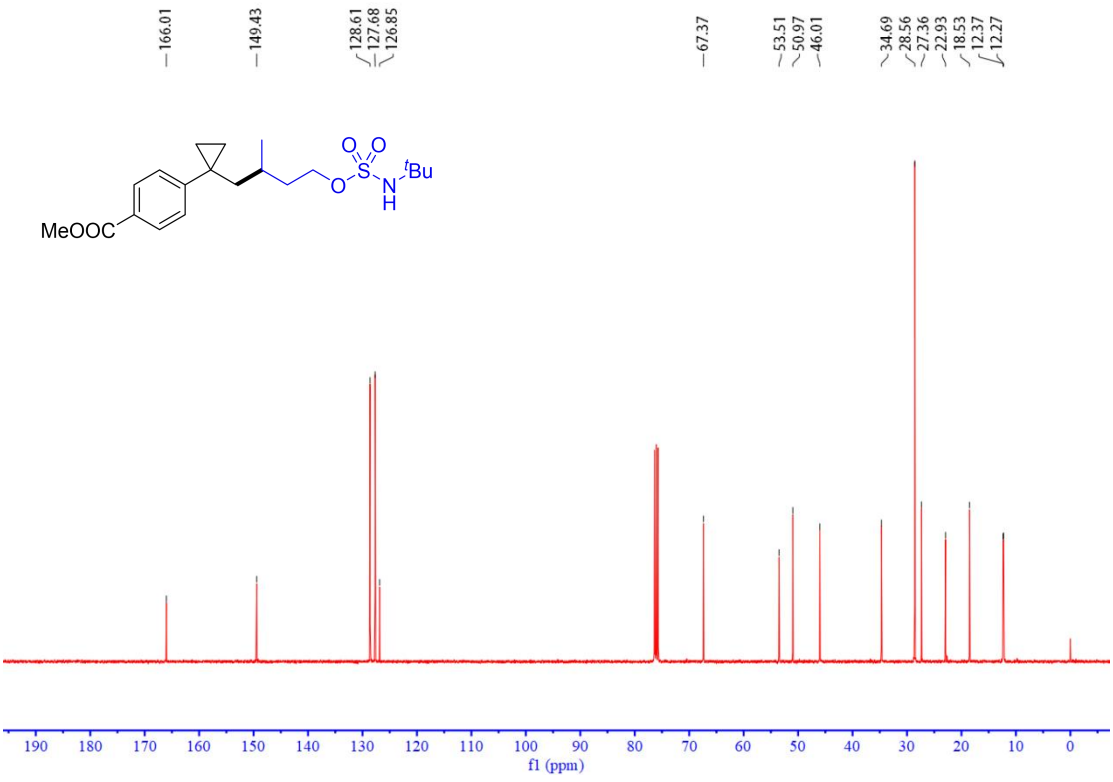
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3q**



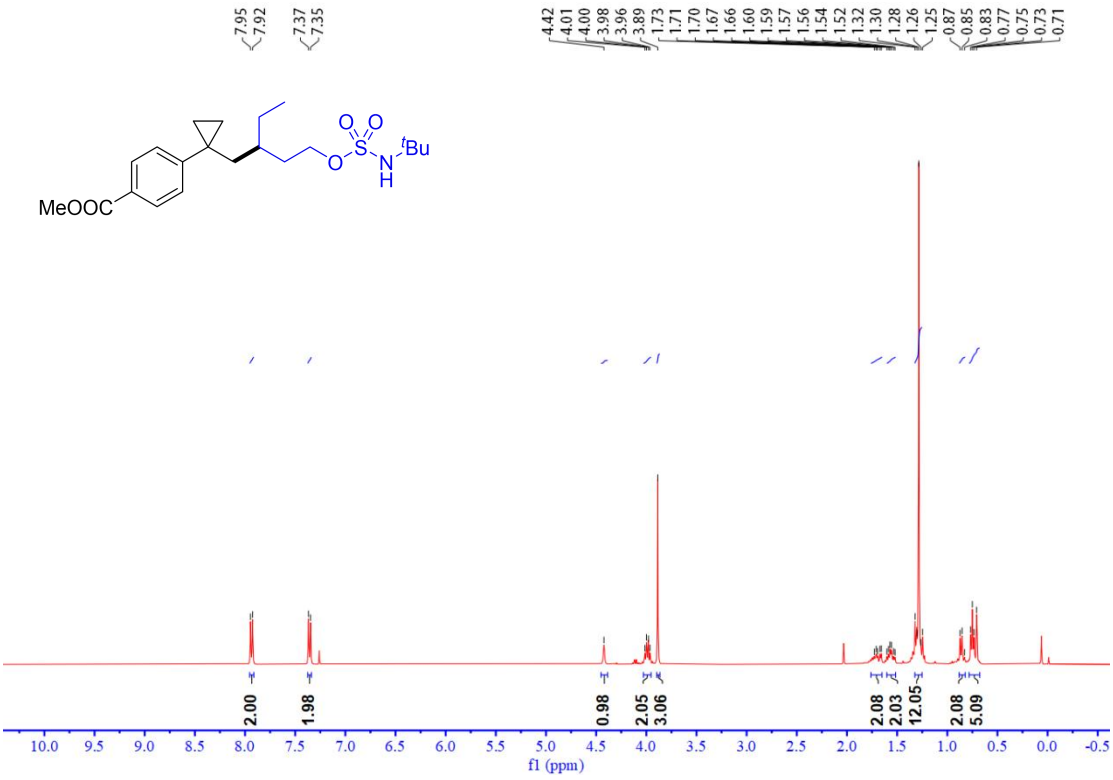
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3r**



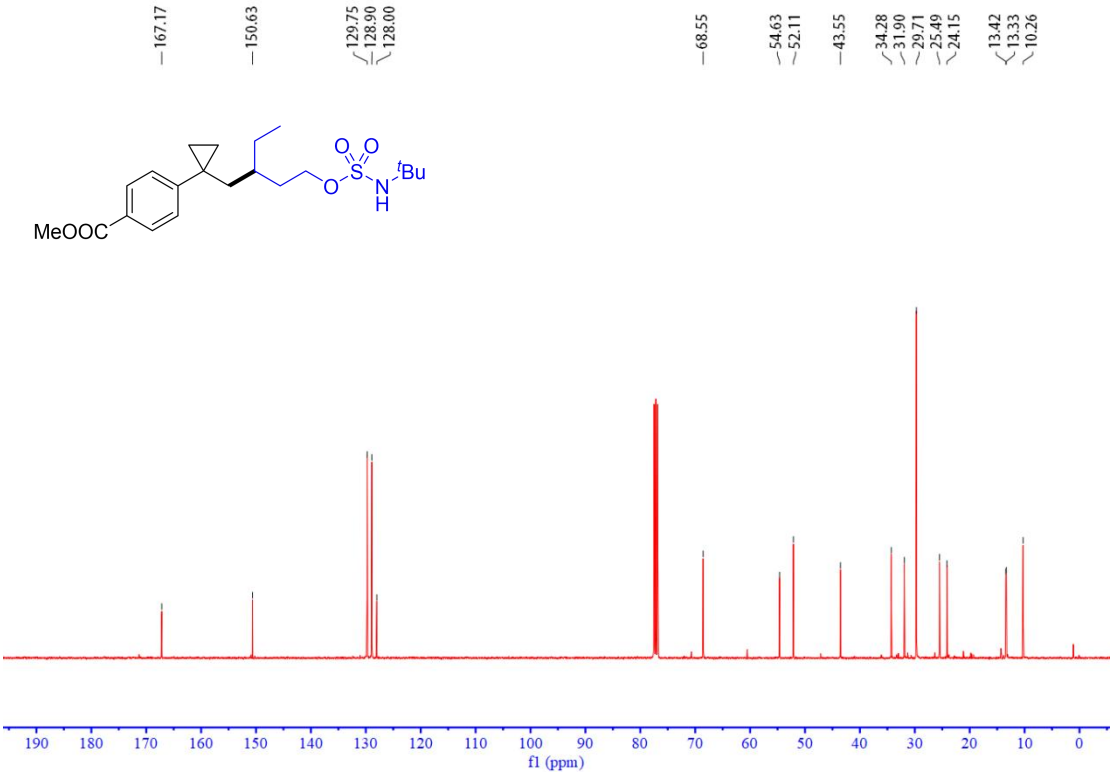
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3r**



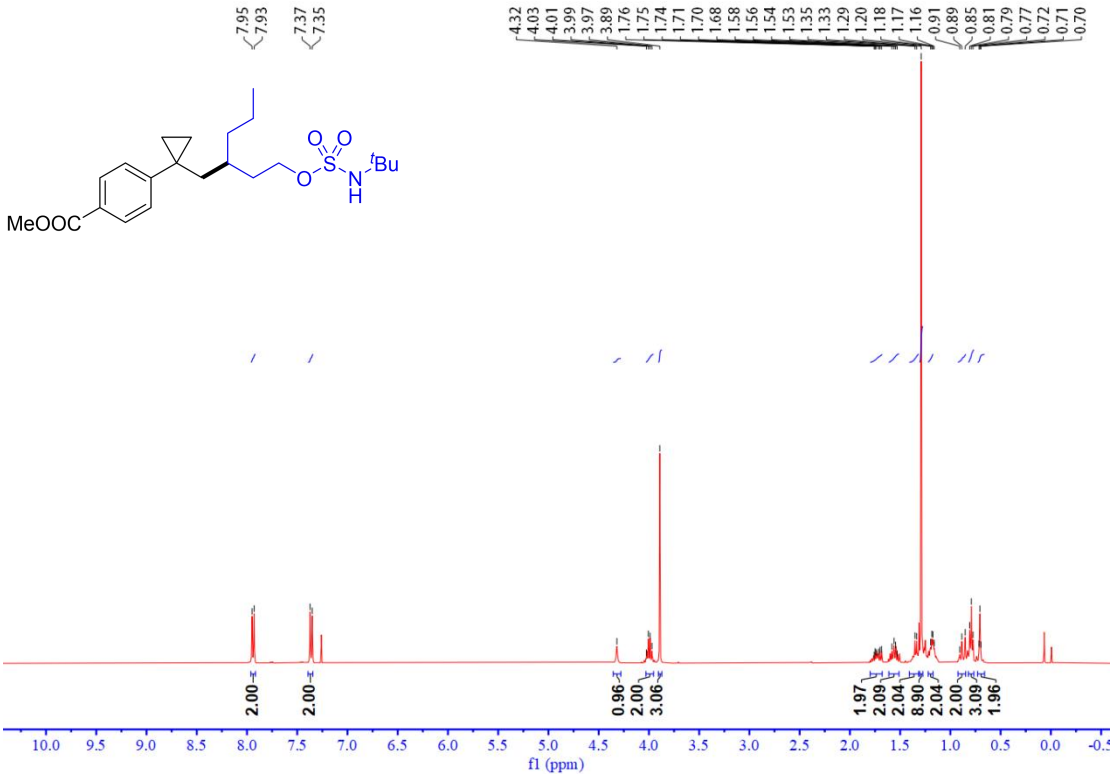
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3s**



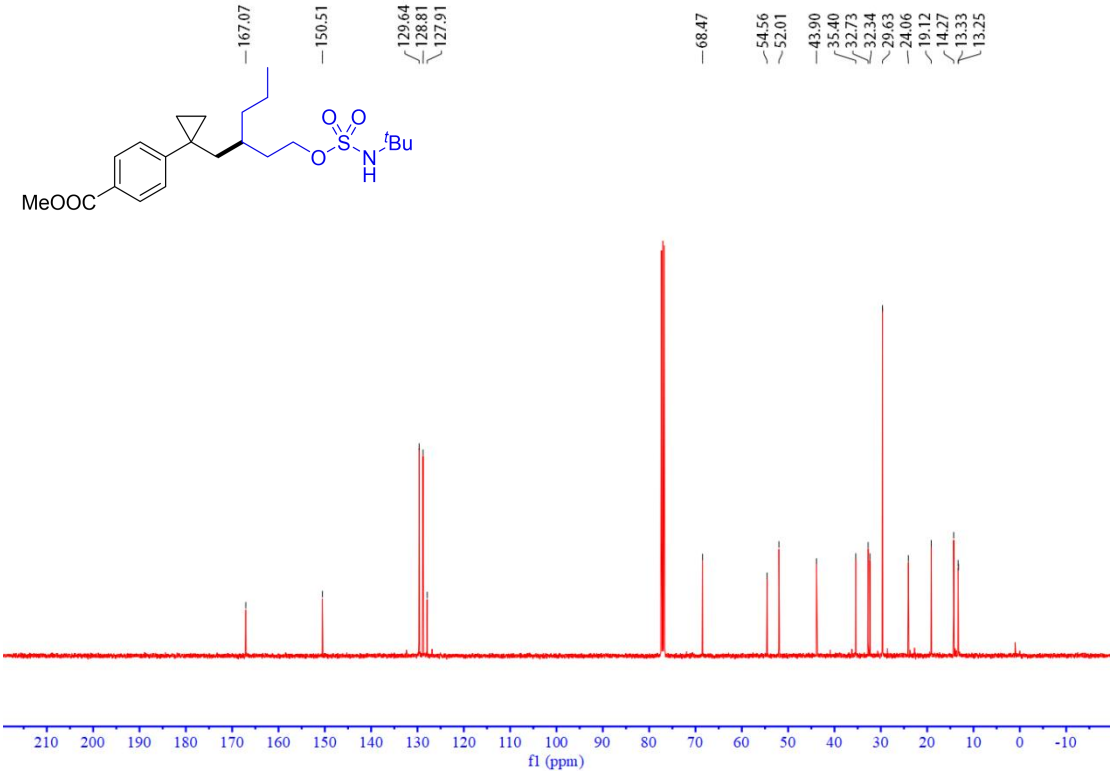
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3s**



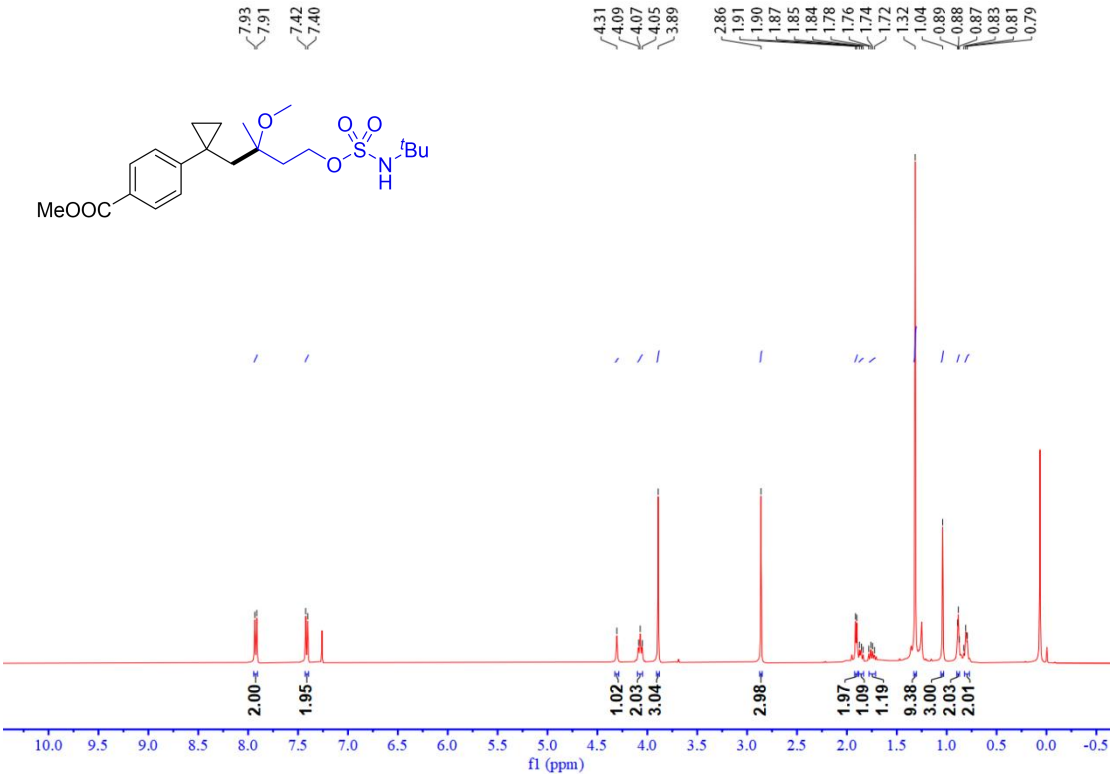
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3t**



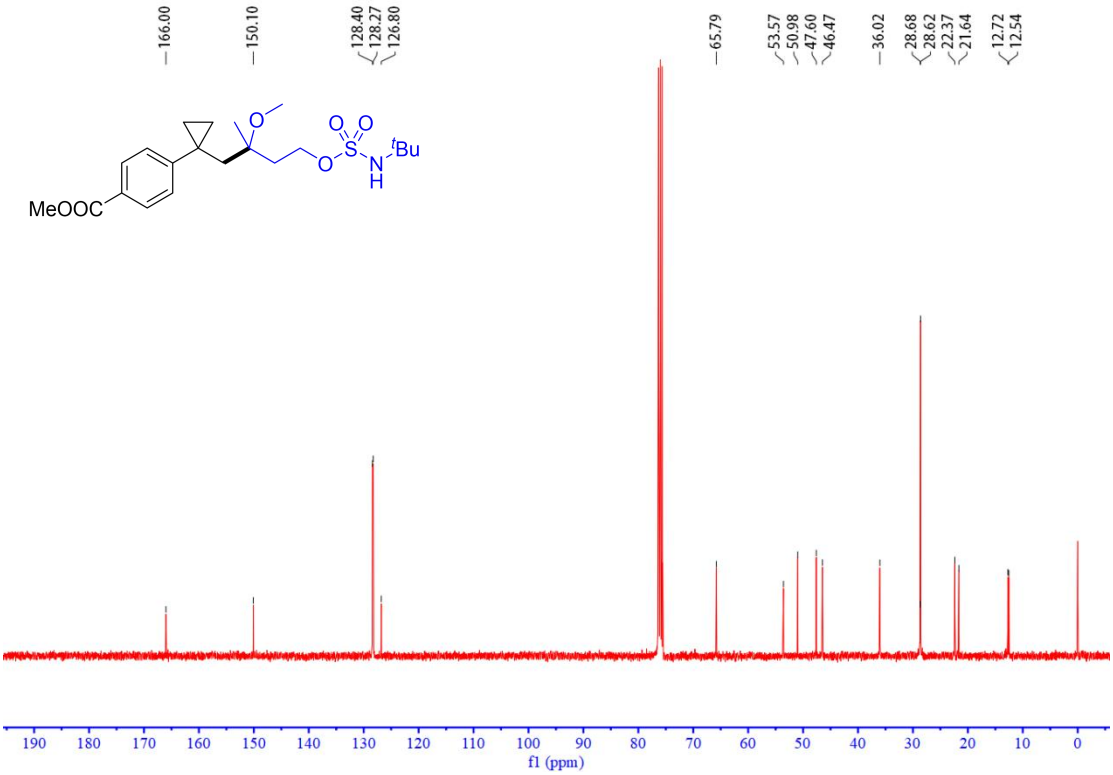
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3t**



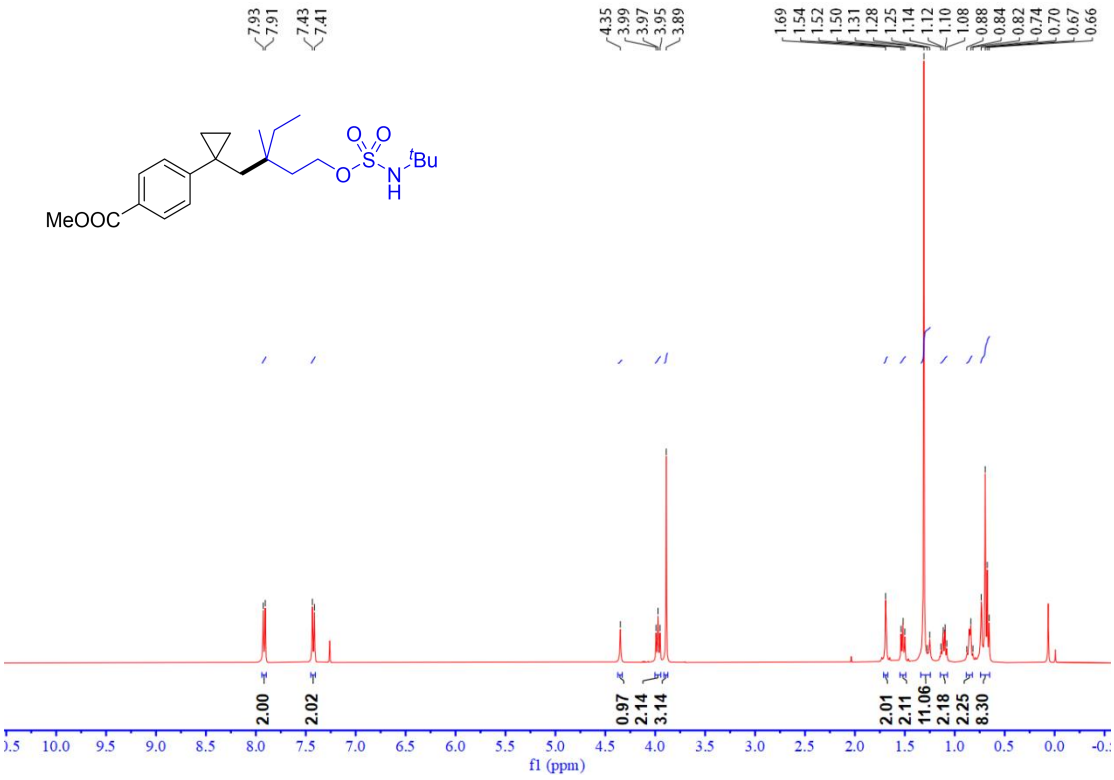
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3u**



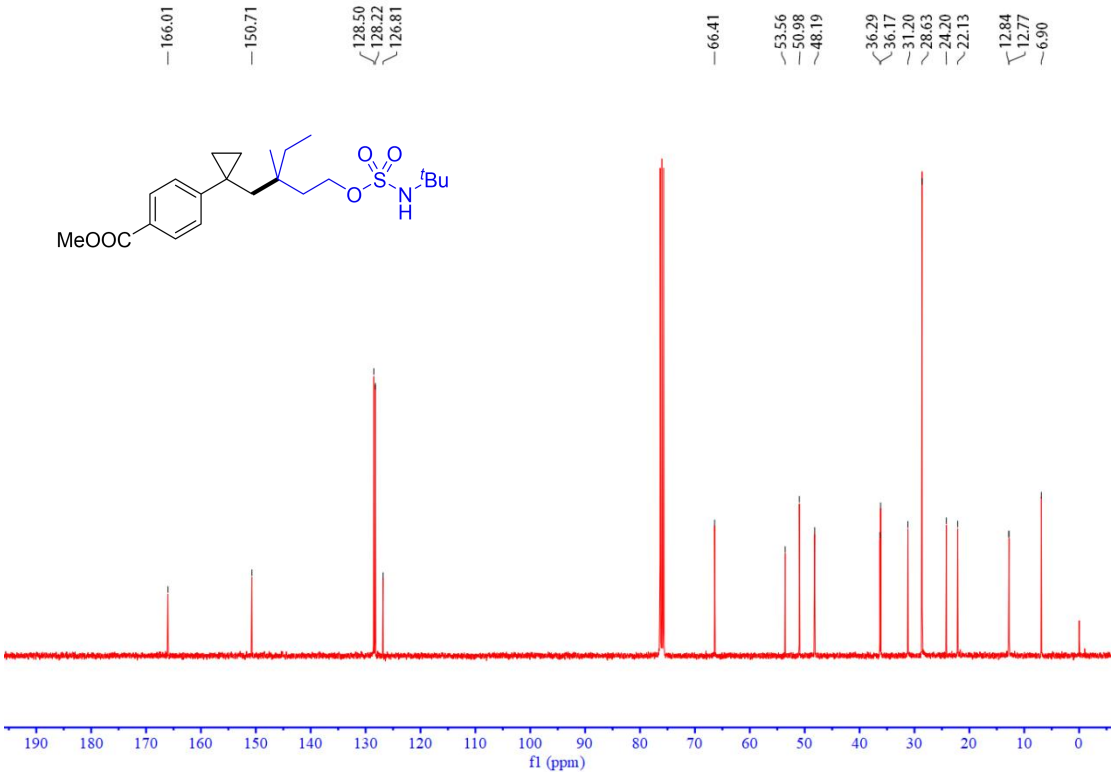
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3u**



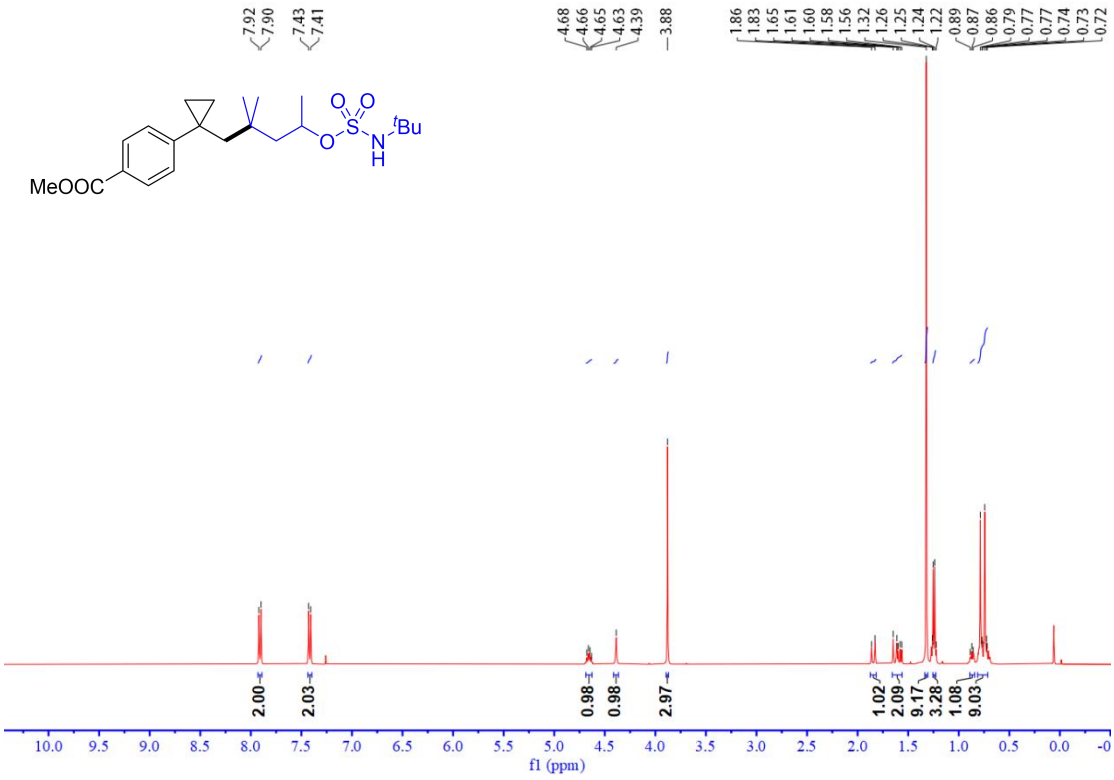
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3v**



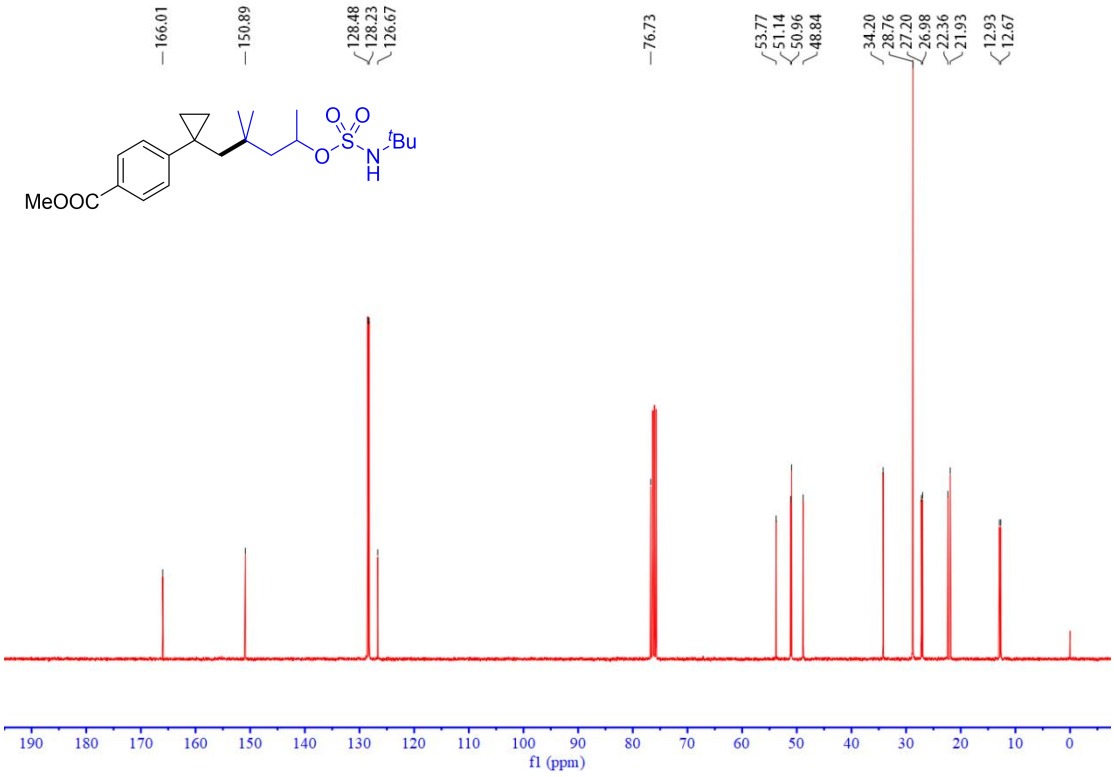
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3v**



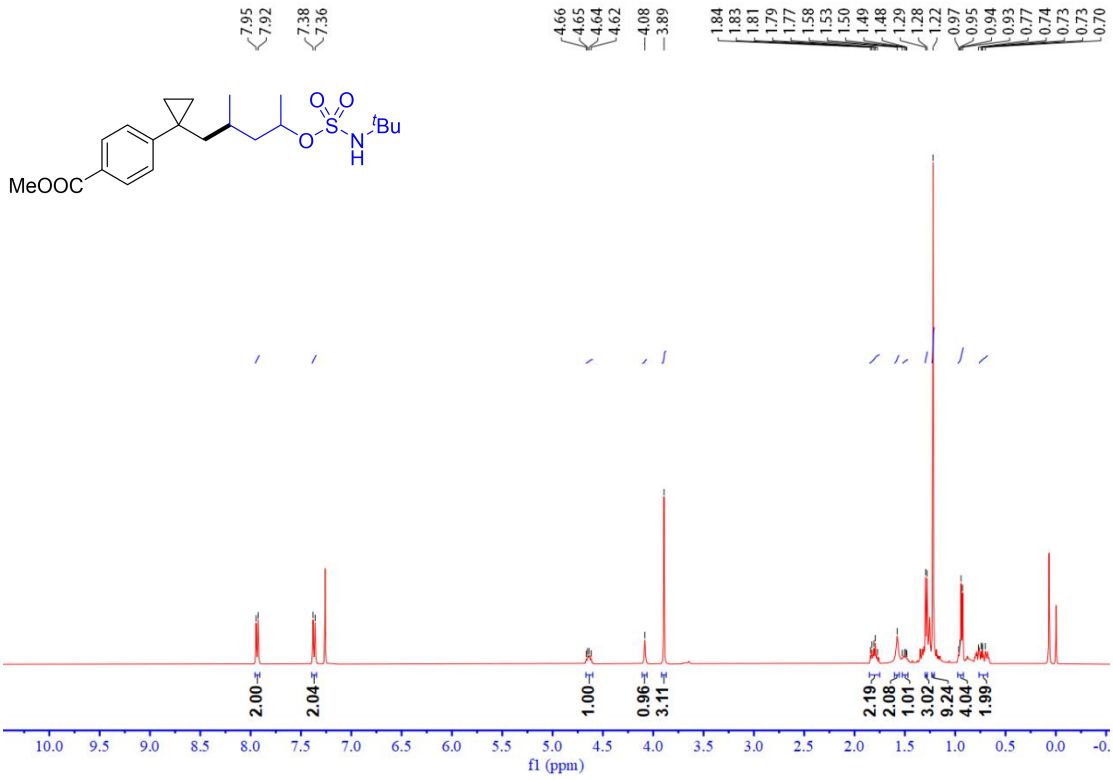
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3w**



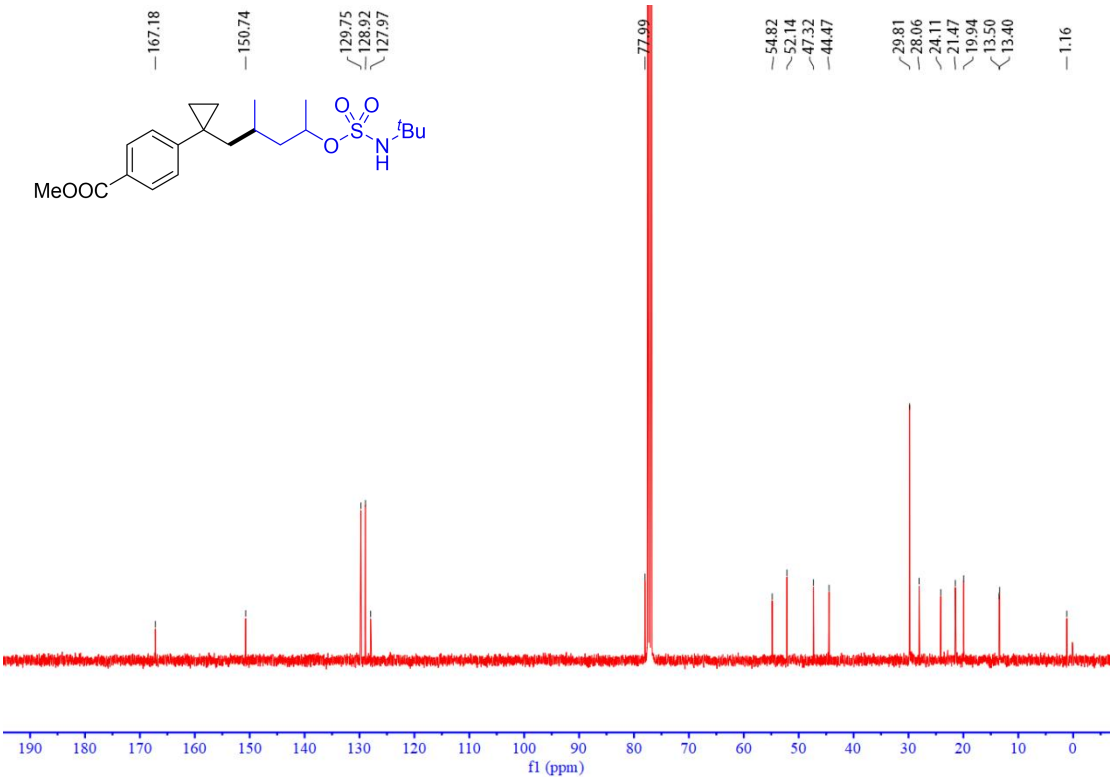
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3w**



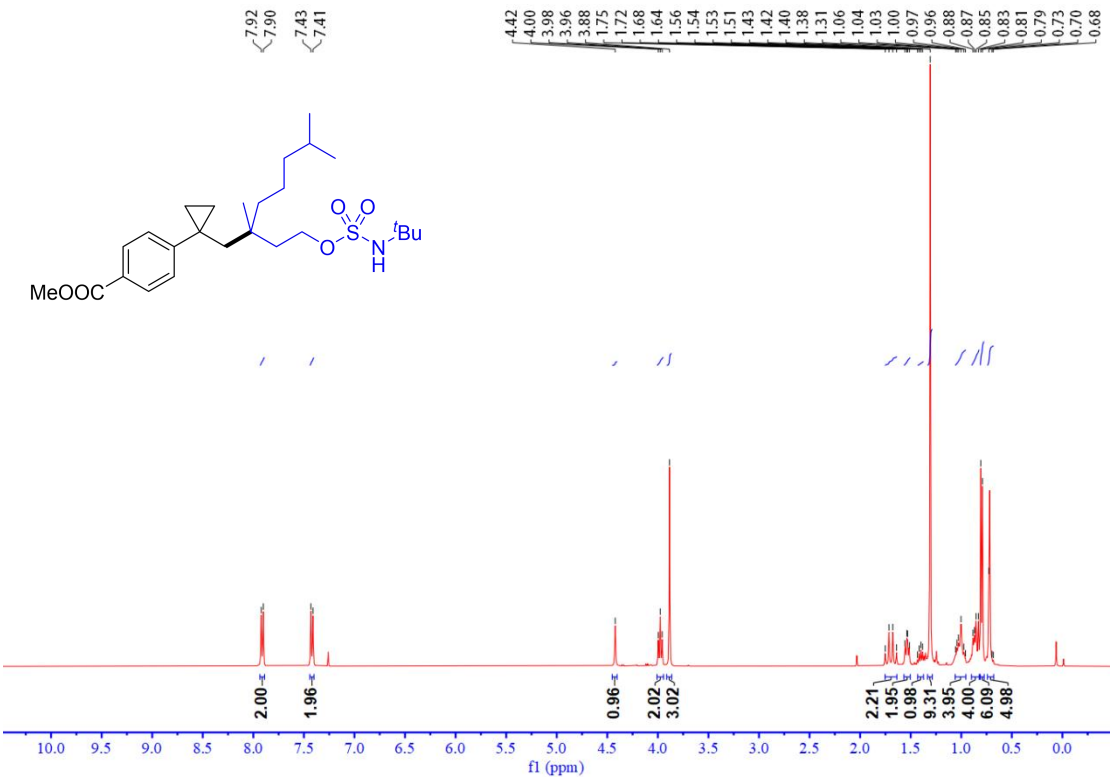
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3x**



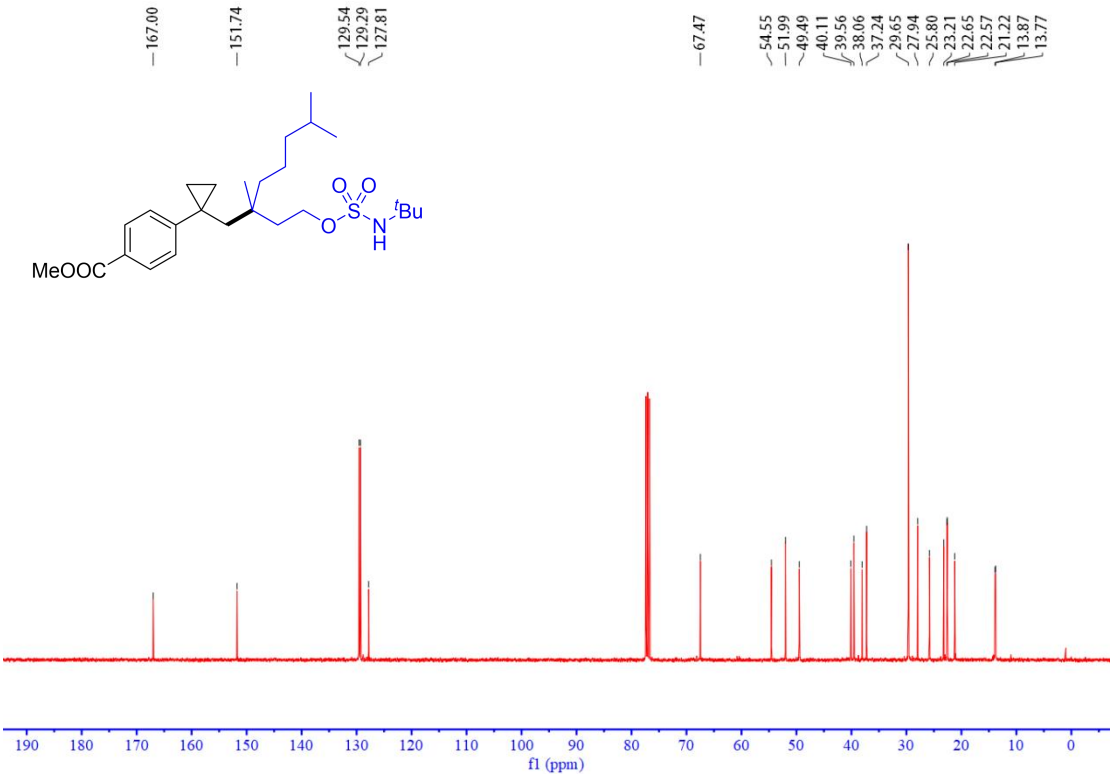
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3x**



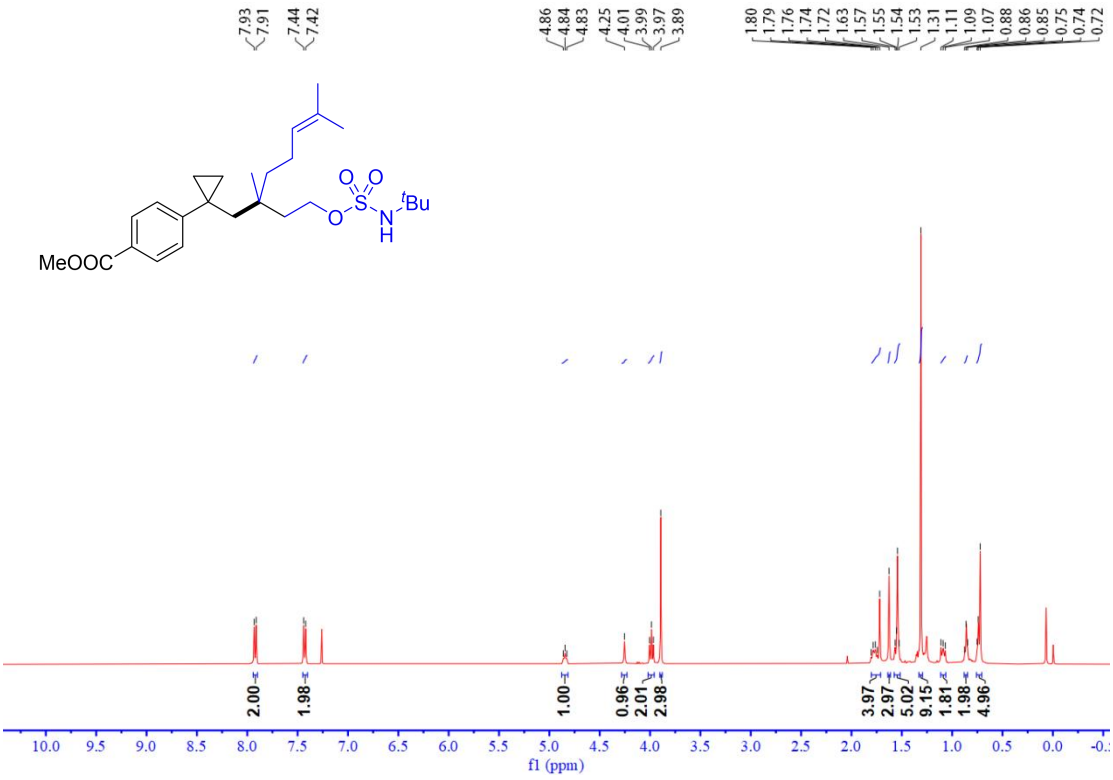
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3y**



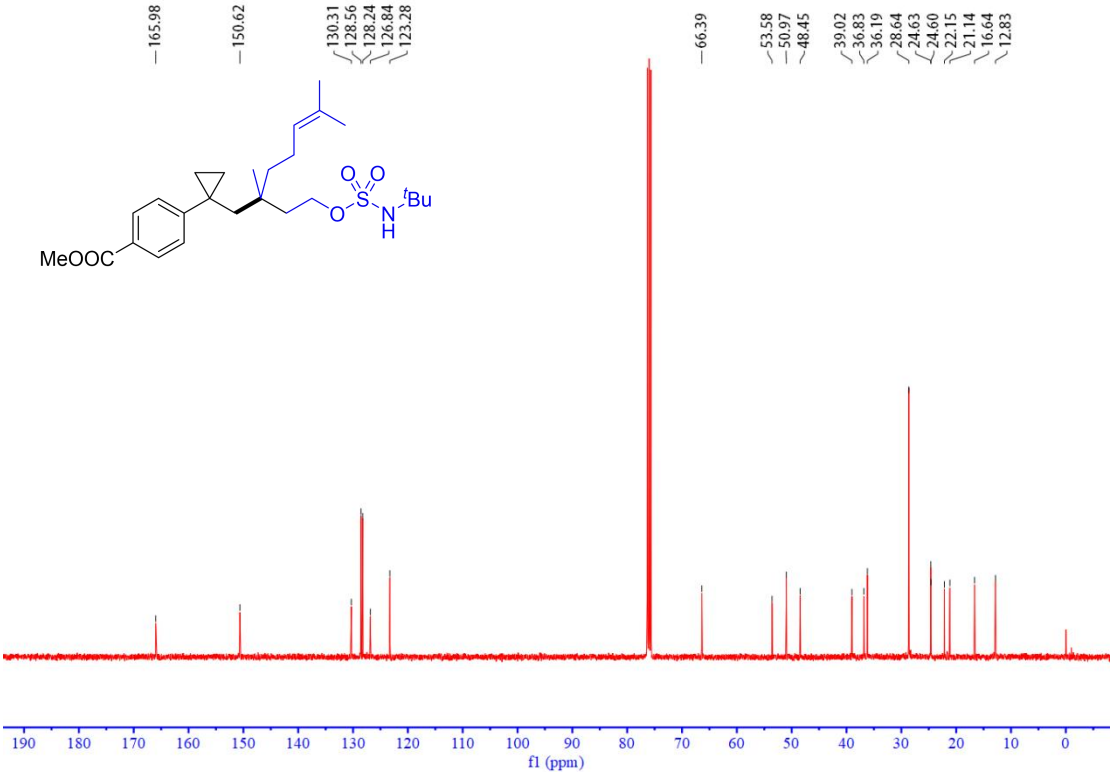
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3y**



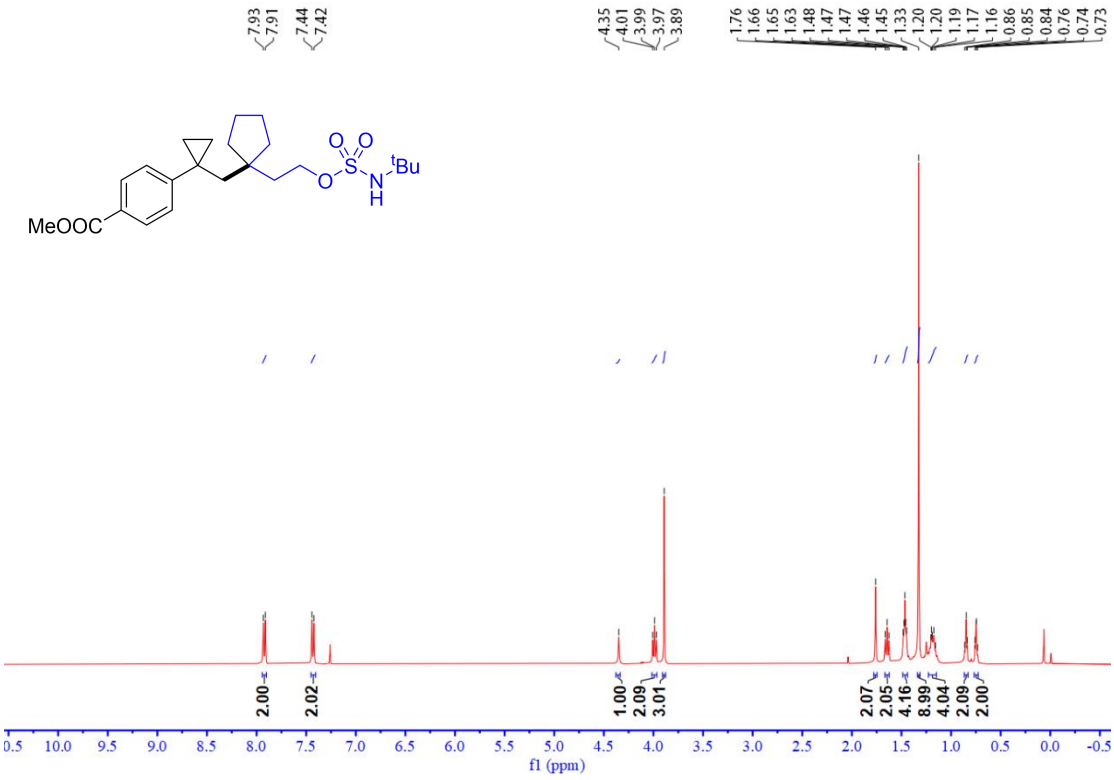
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3z**



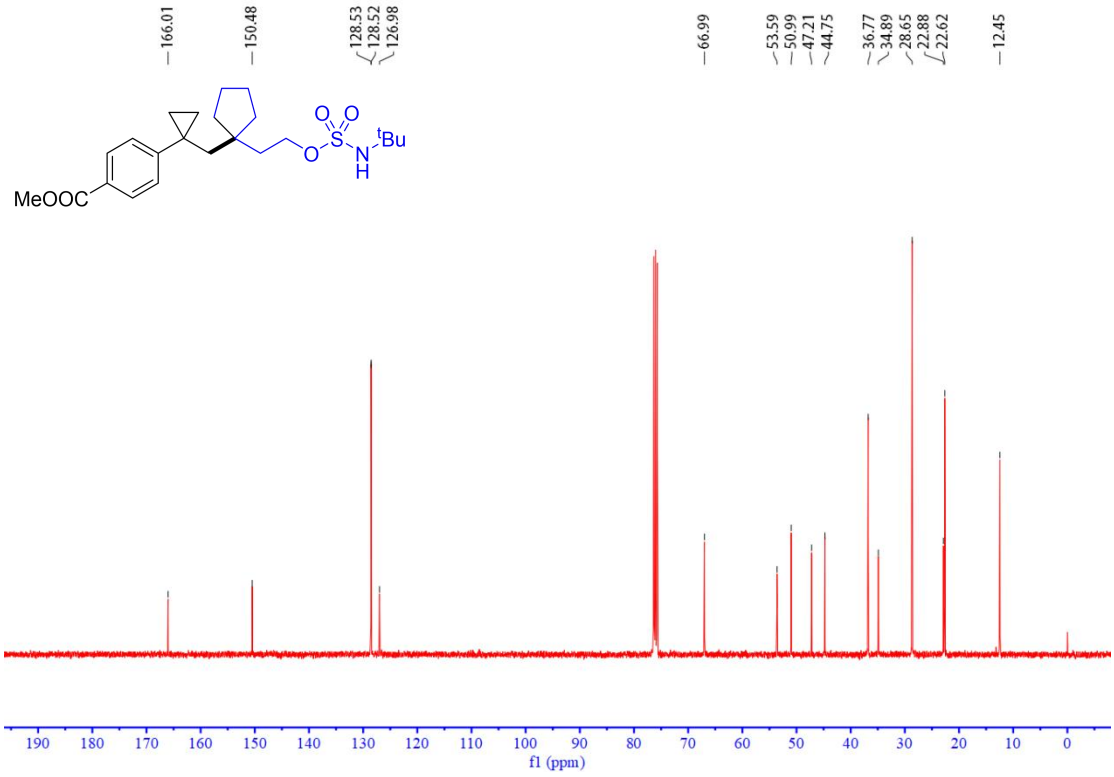
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3z**



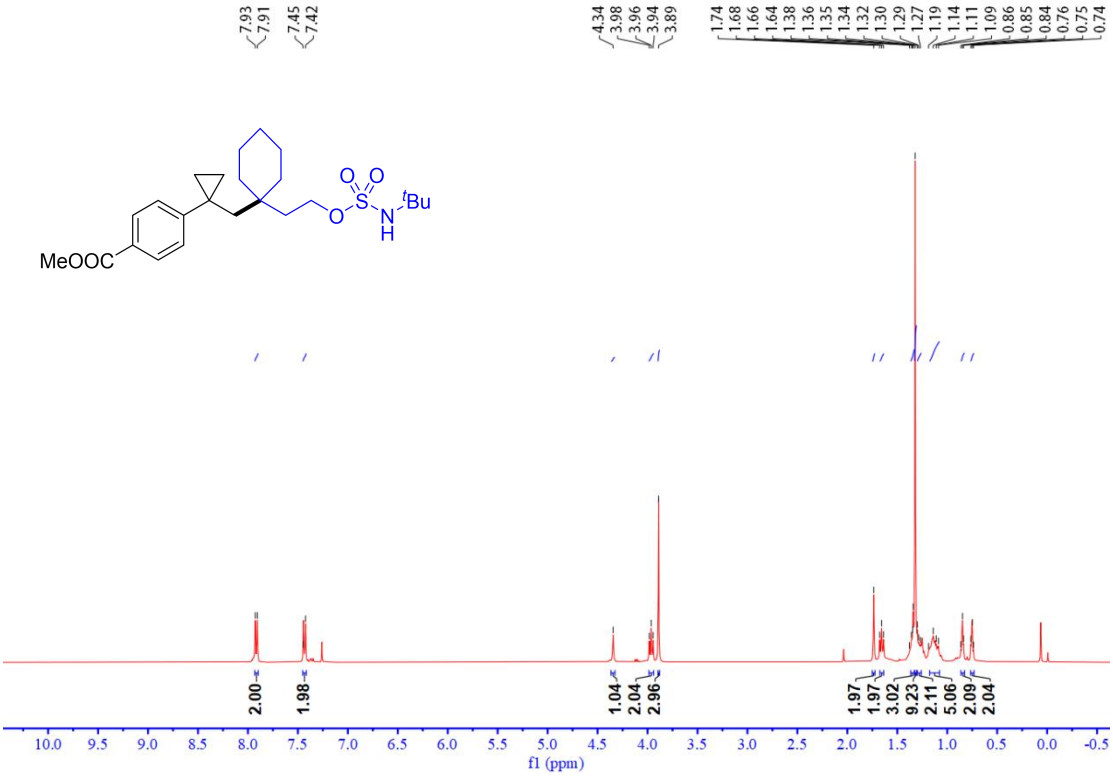
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3aa**



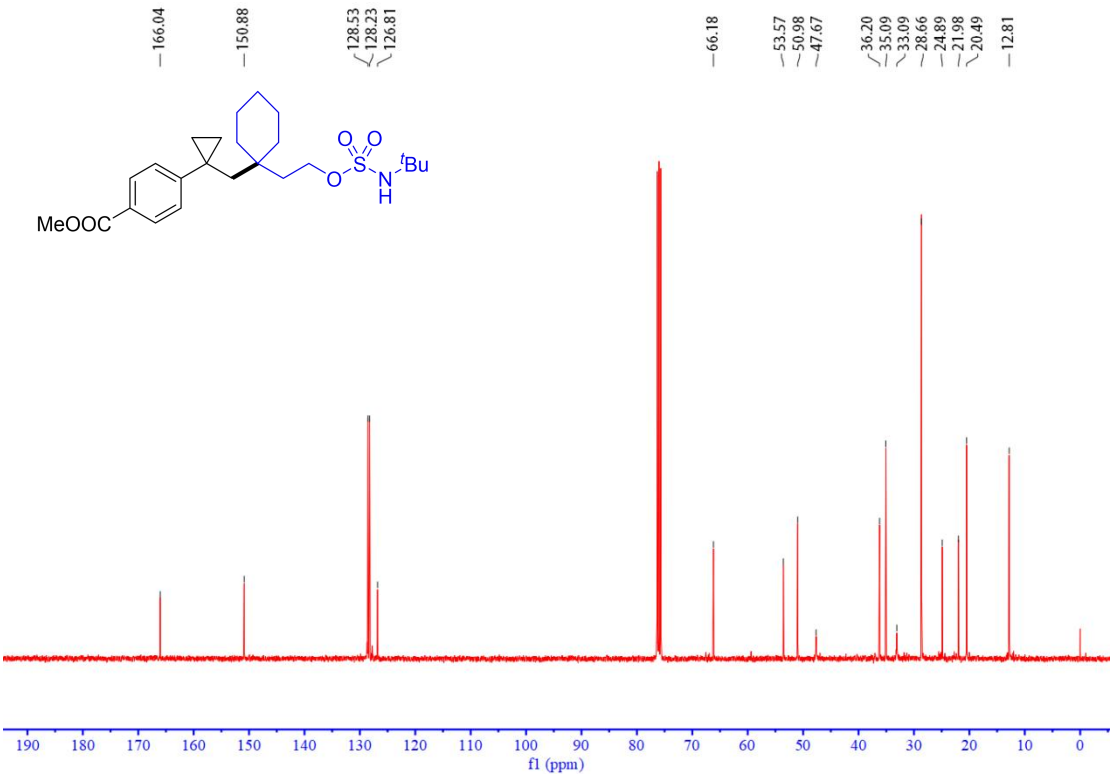
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3aa**



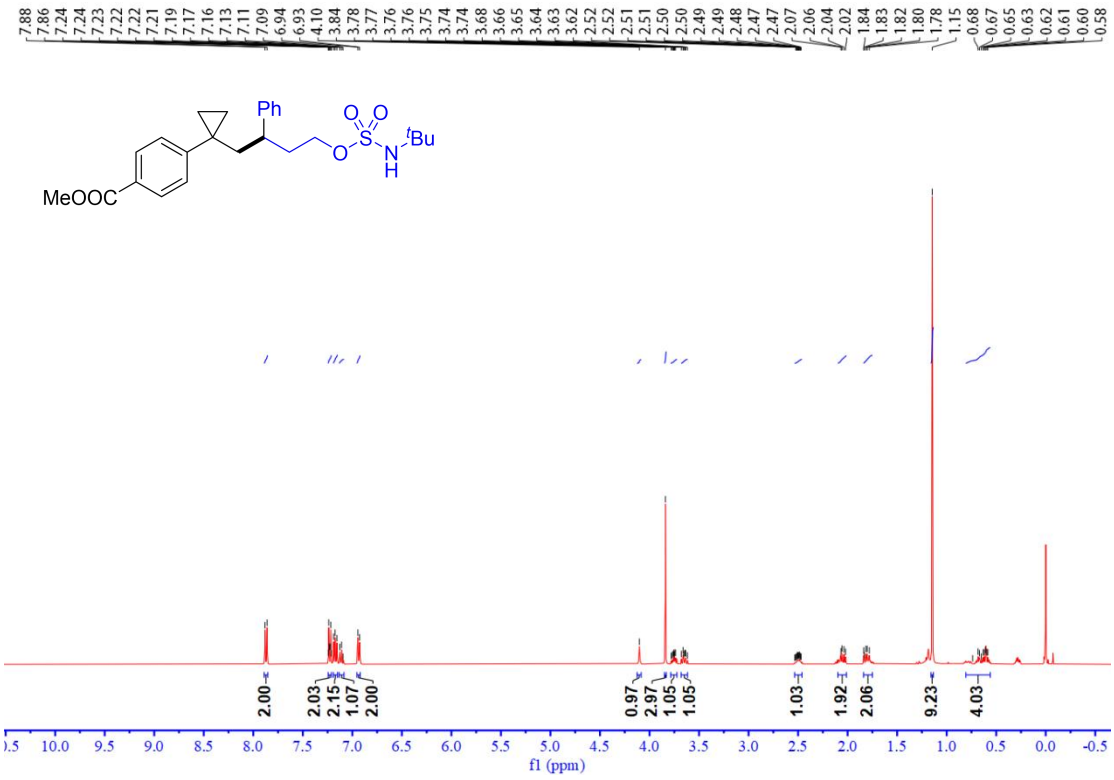
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ab**



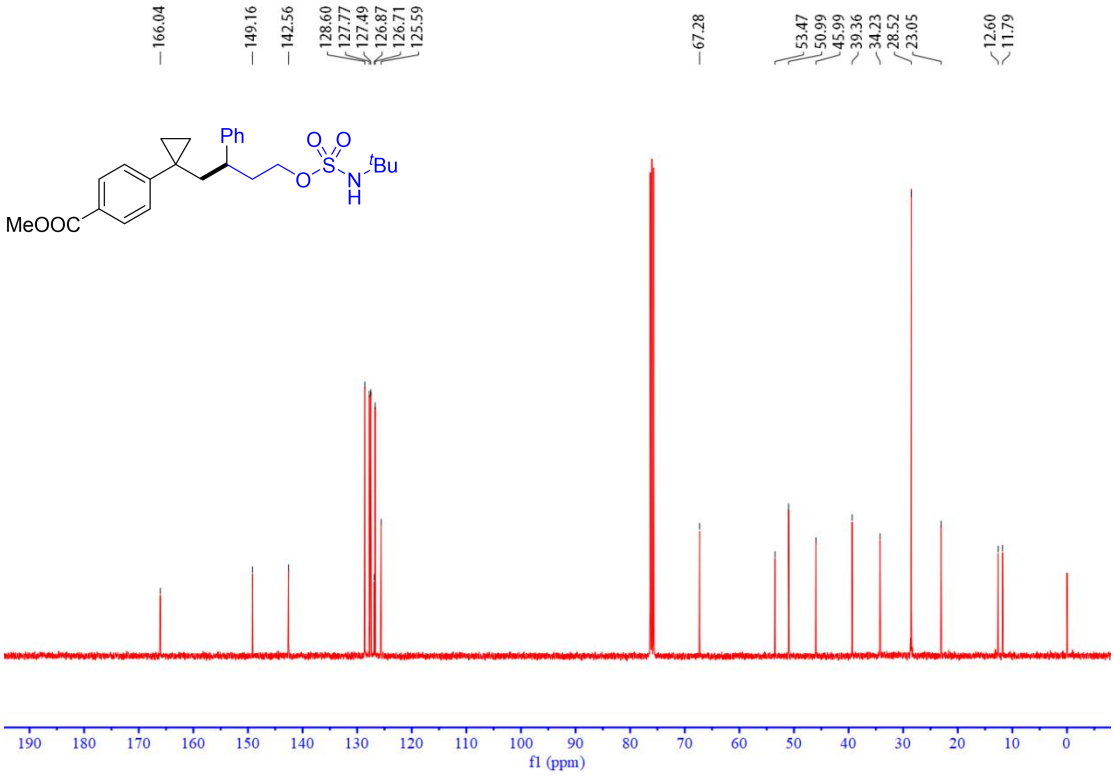
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ab**



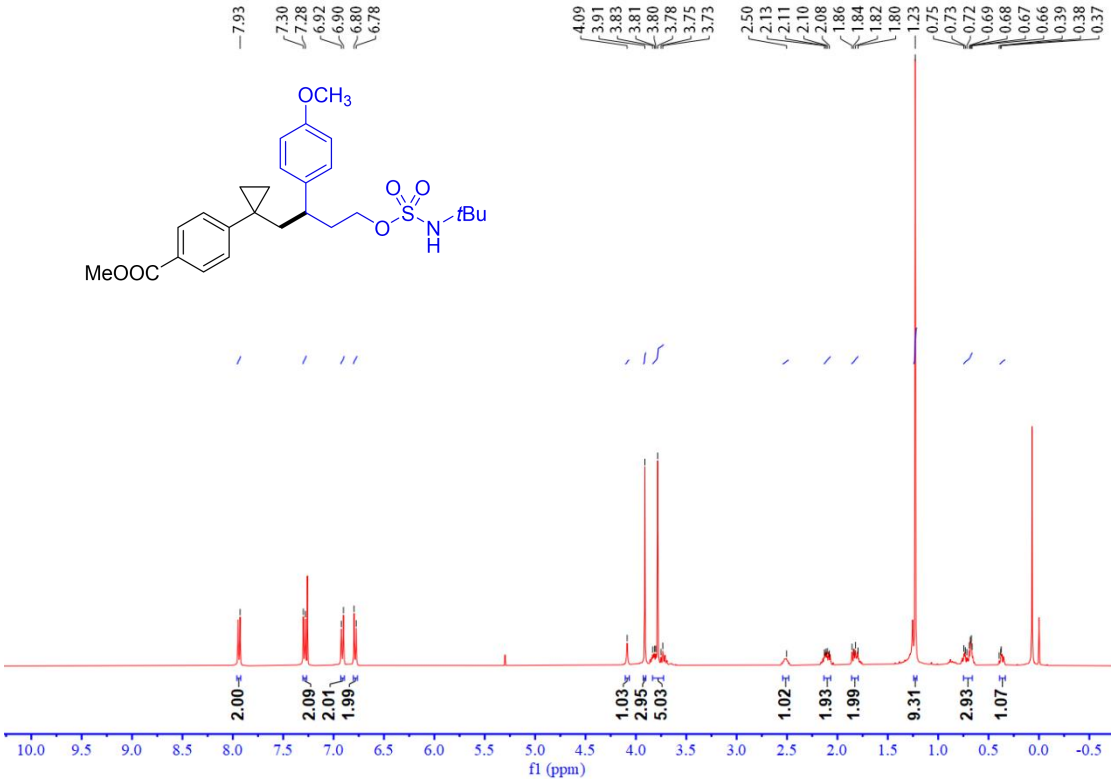
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ac**



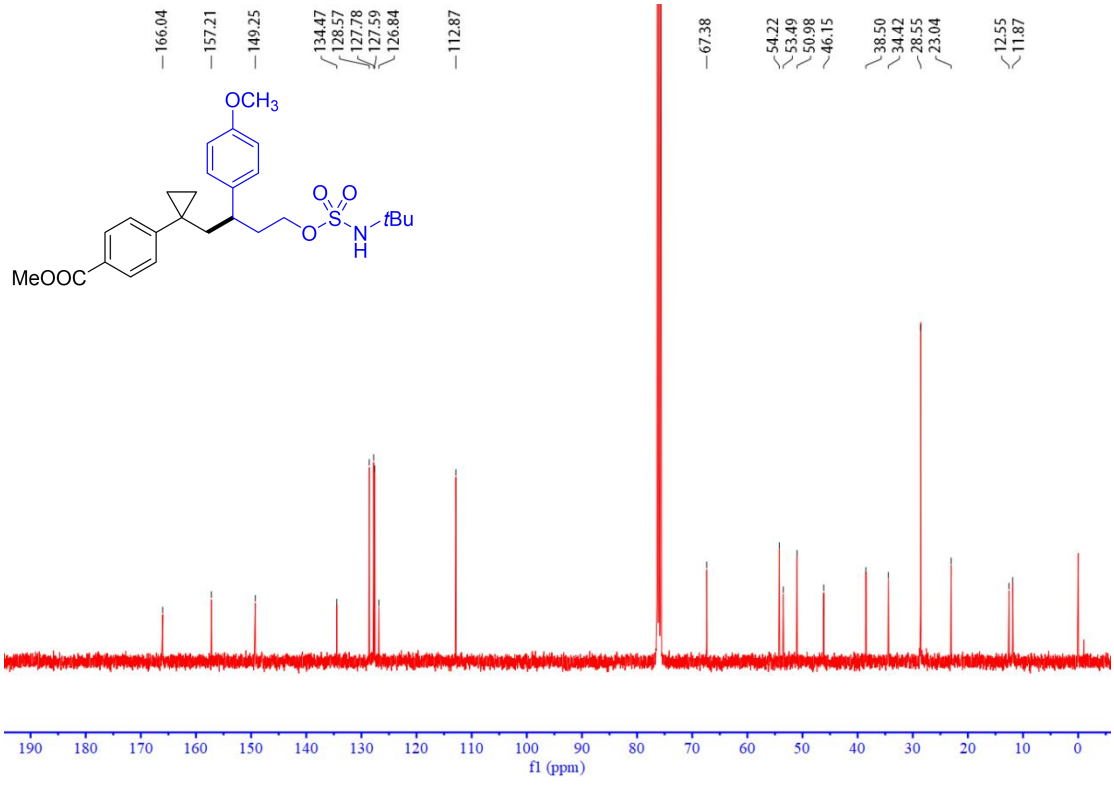
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ac**



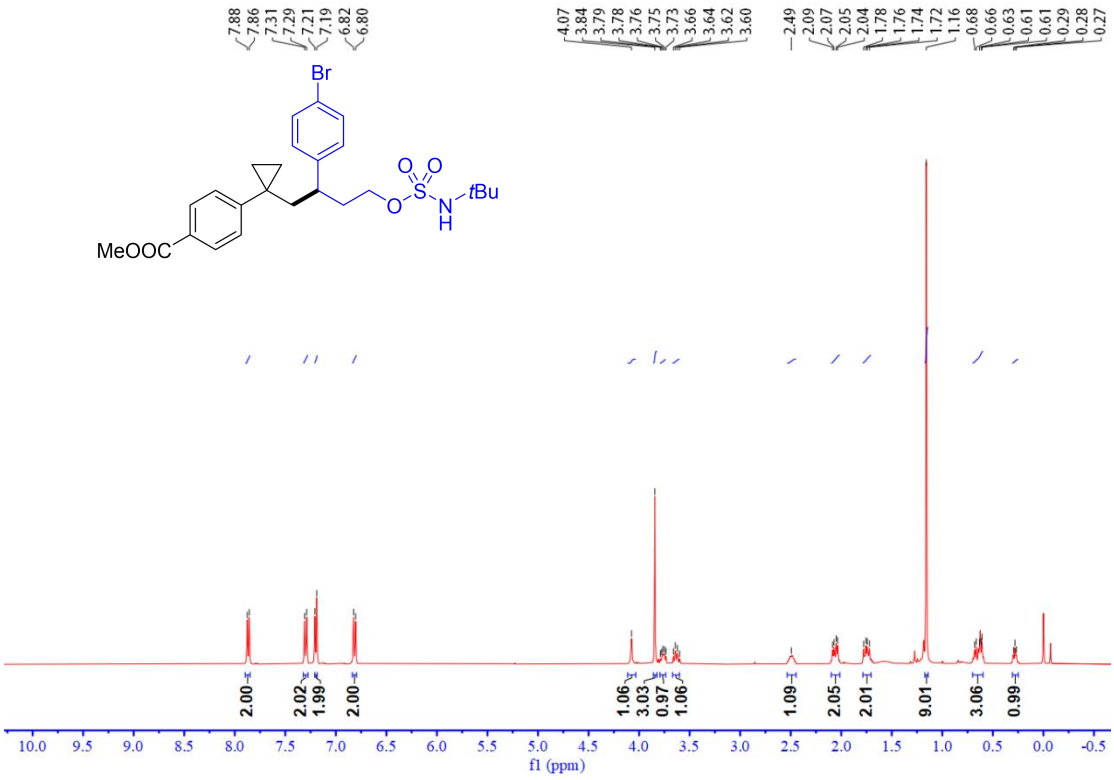
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ad**



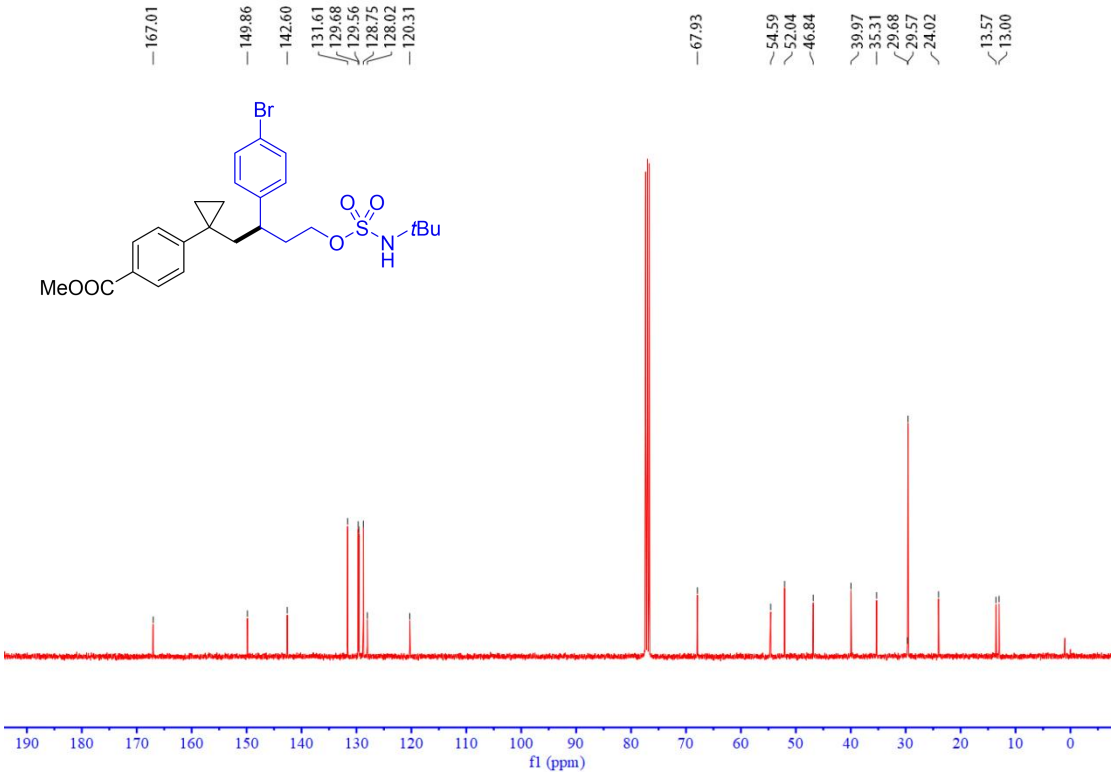
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ad**



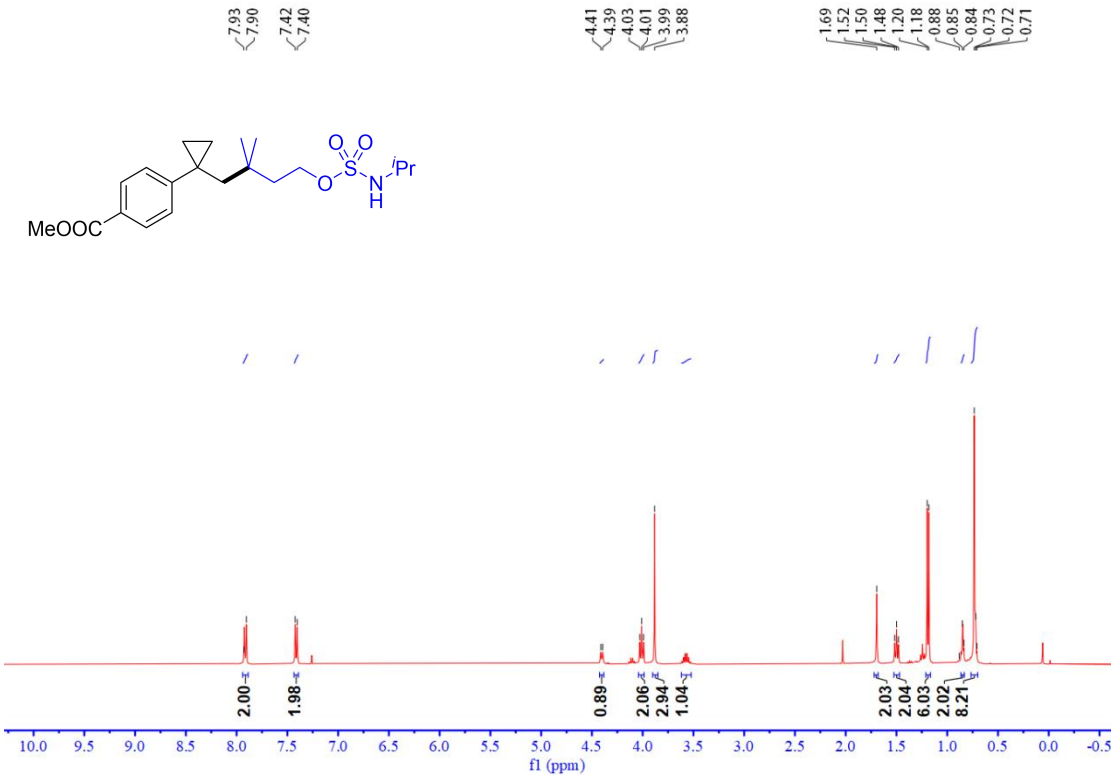
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ae**



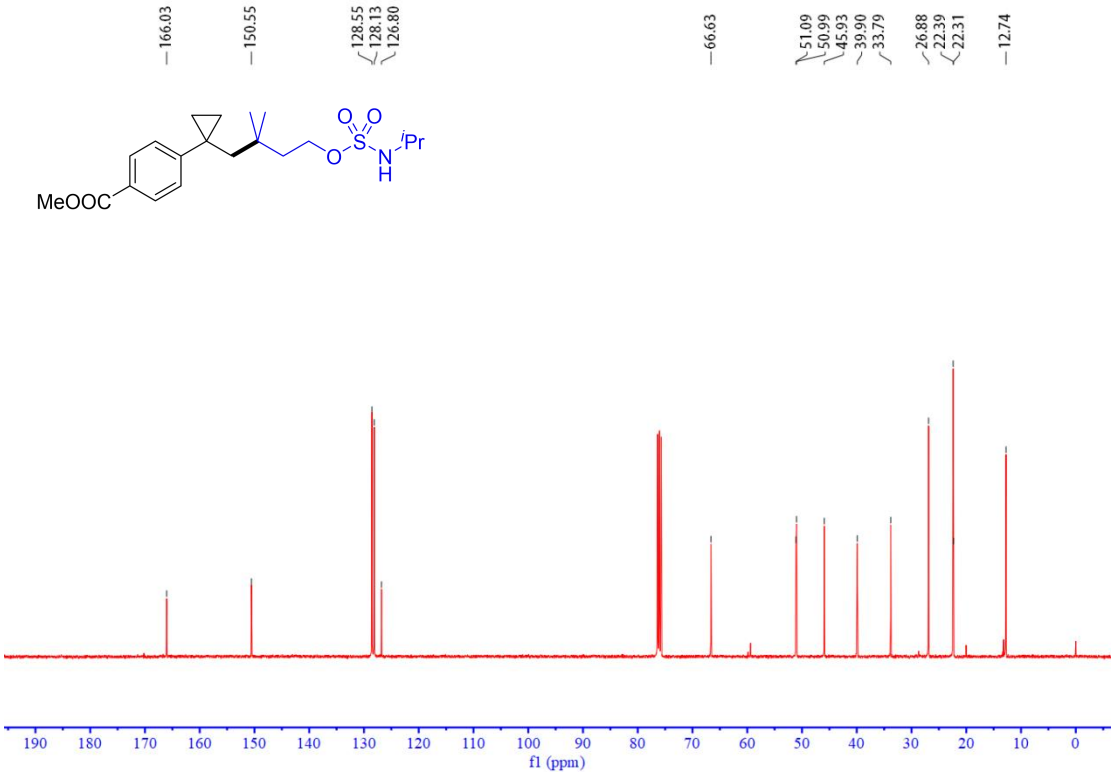
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ae**



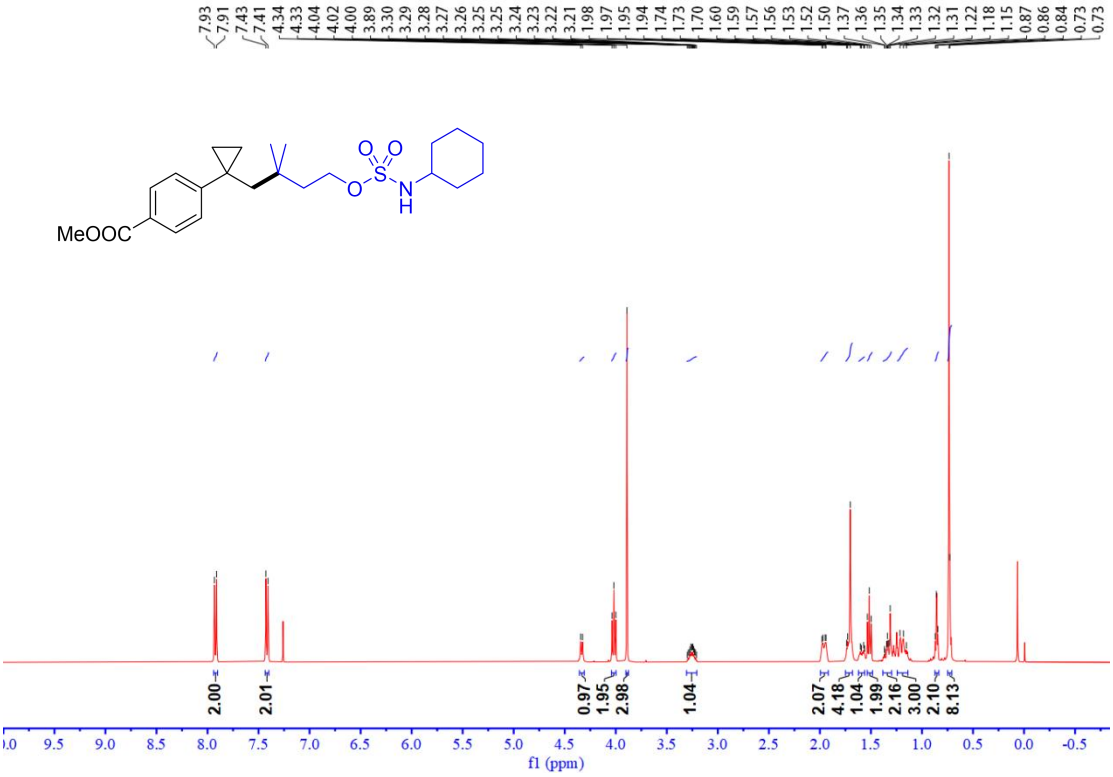
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3af**



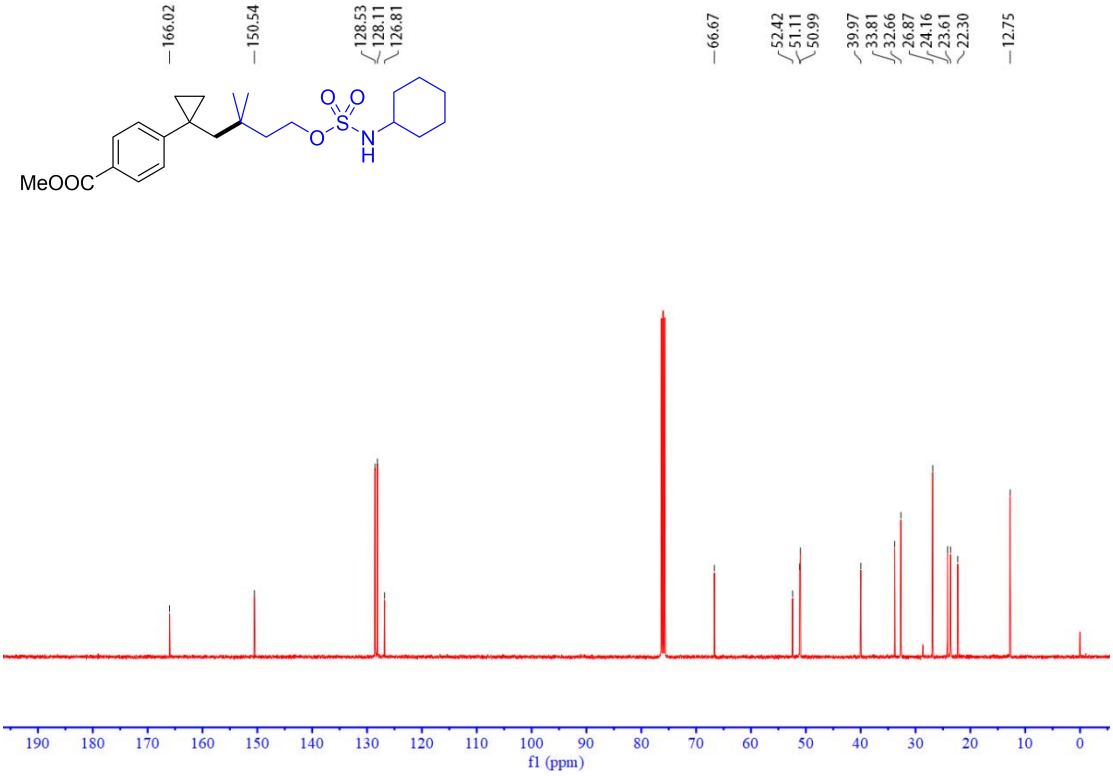
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3af**



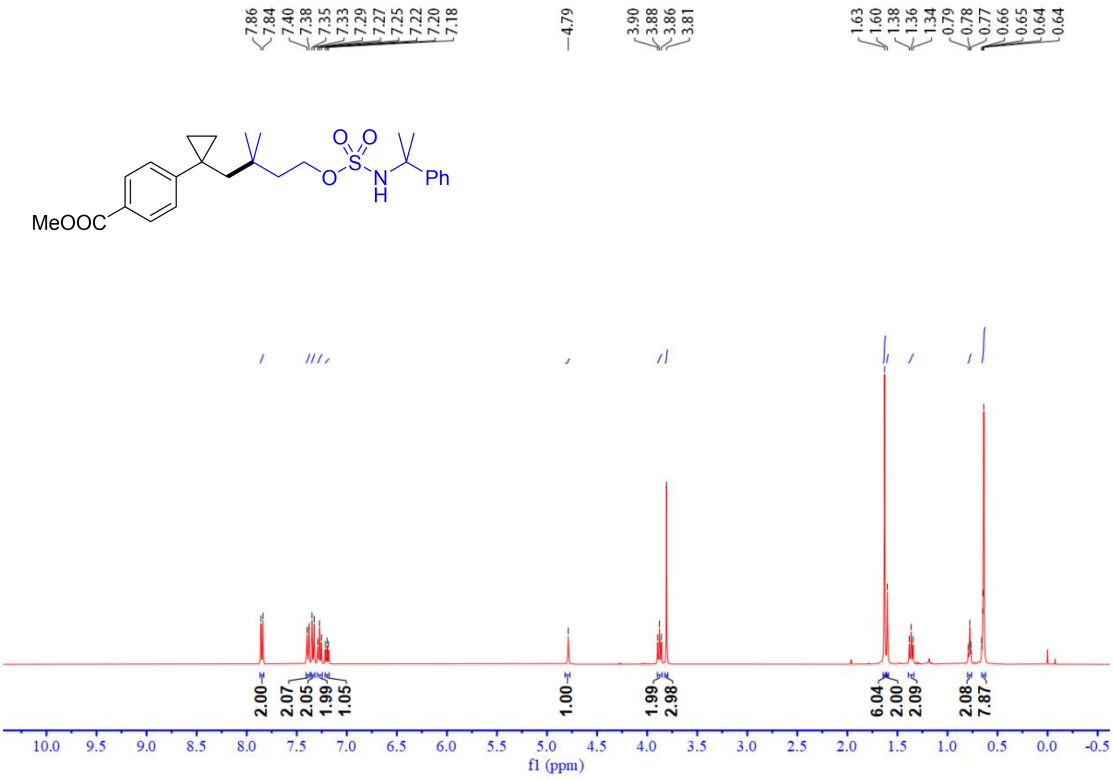
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ag**



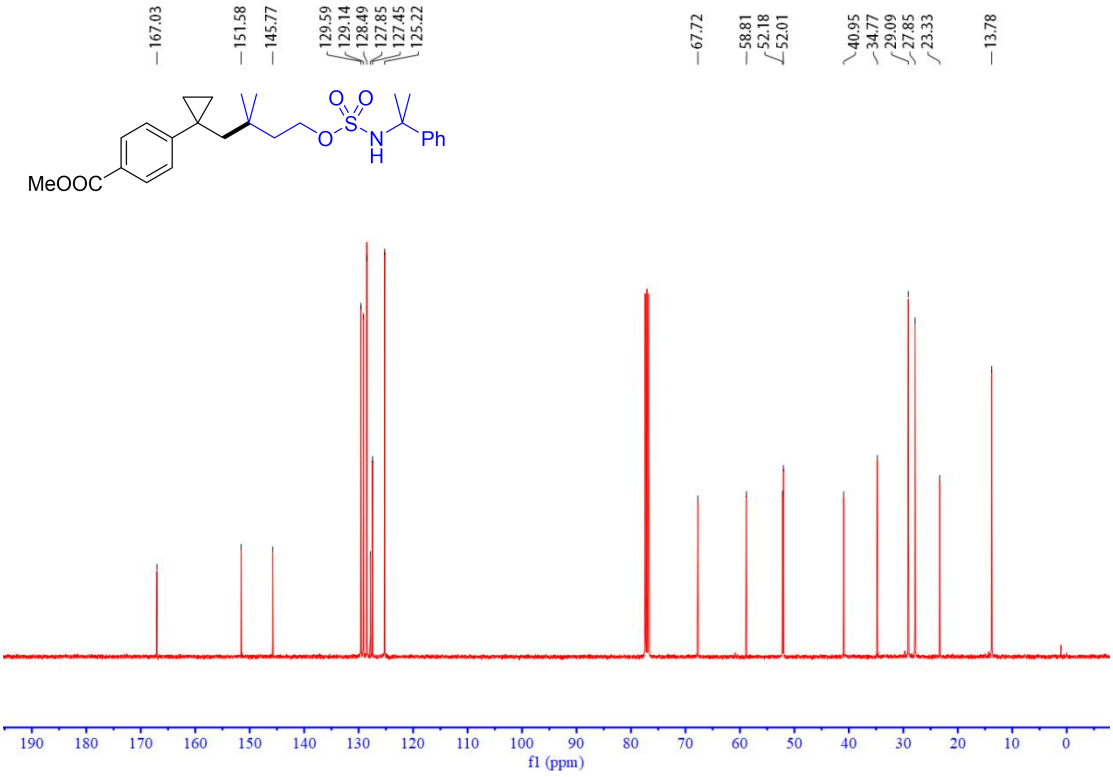
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ag**



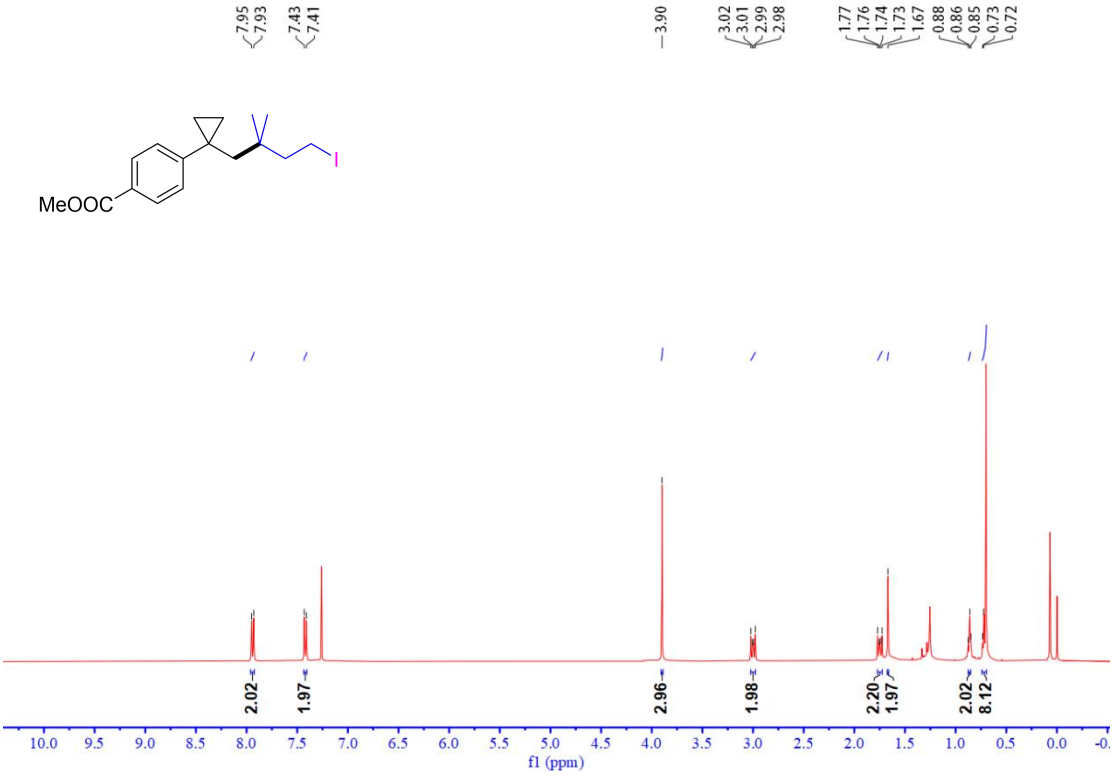
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **3ah**



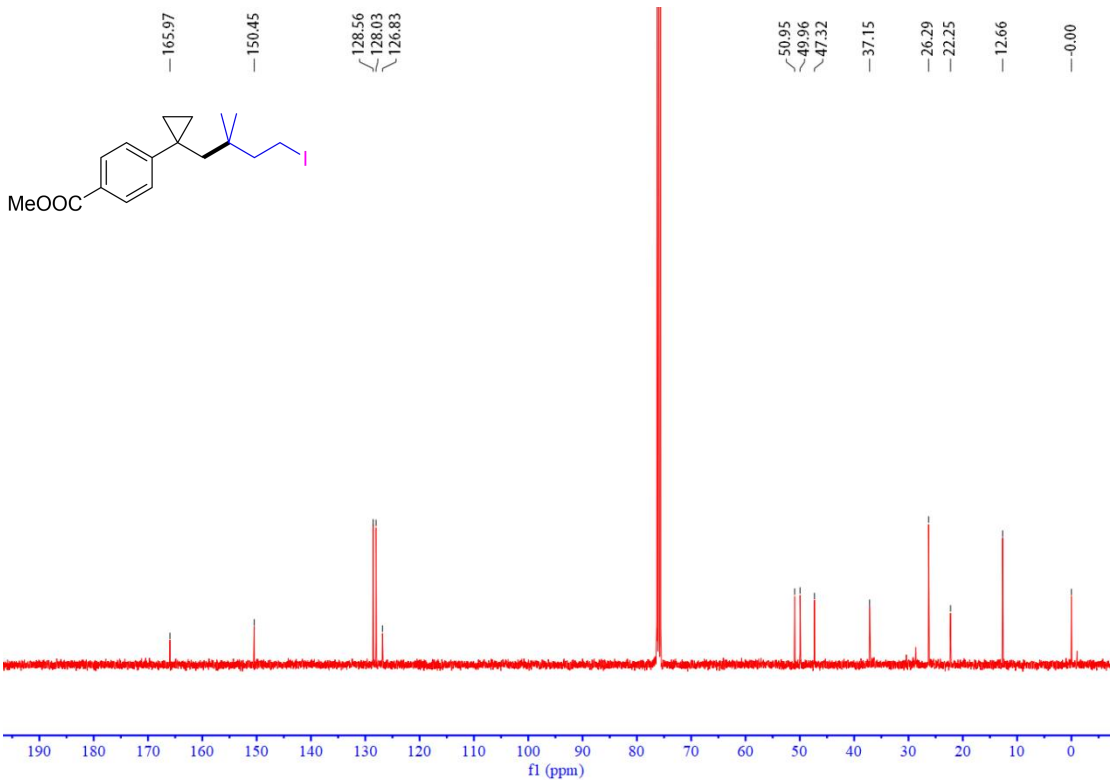
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **3ah**



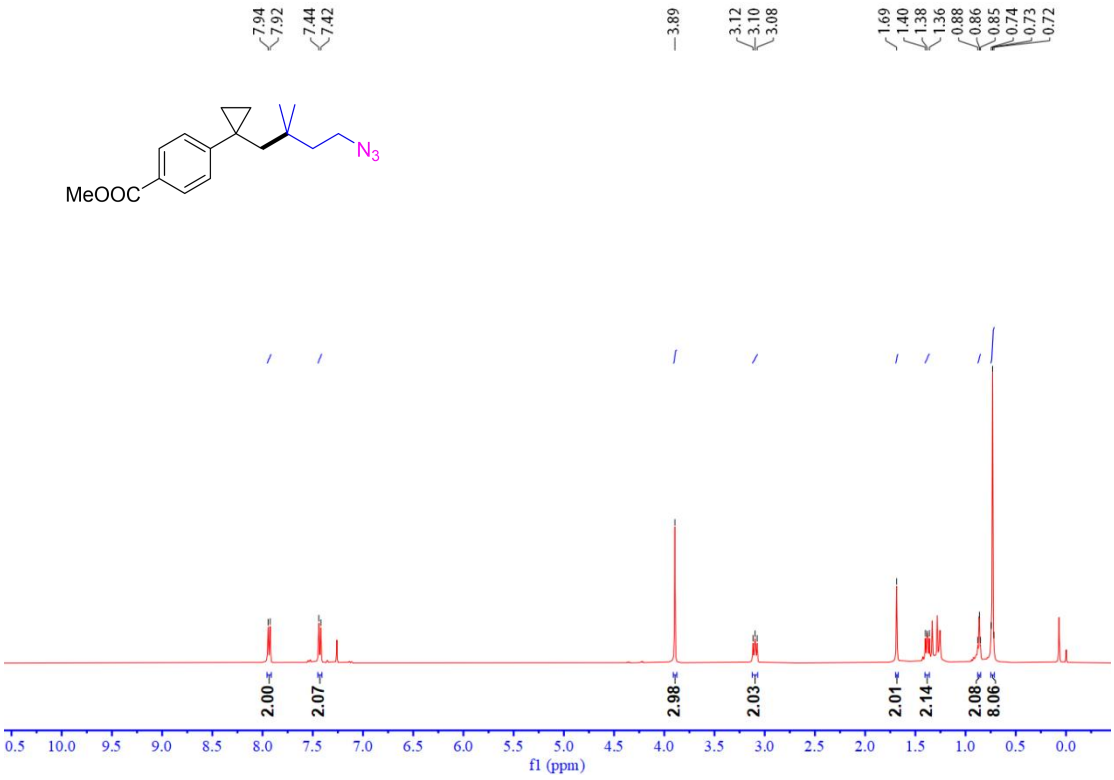
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4b**



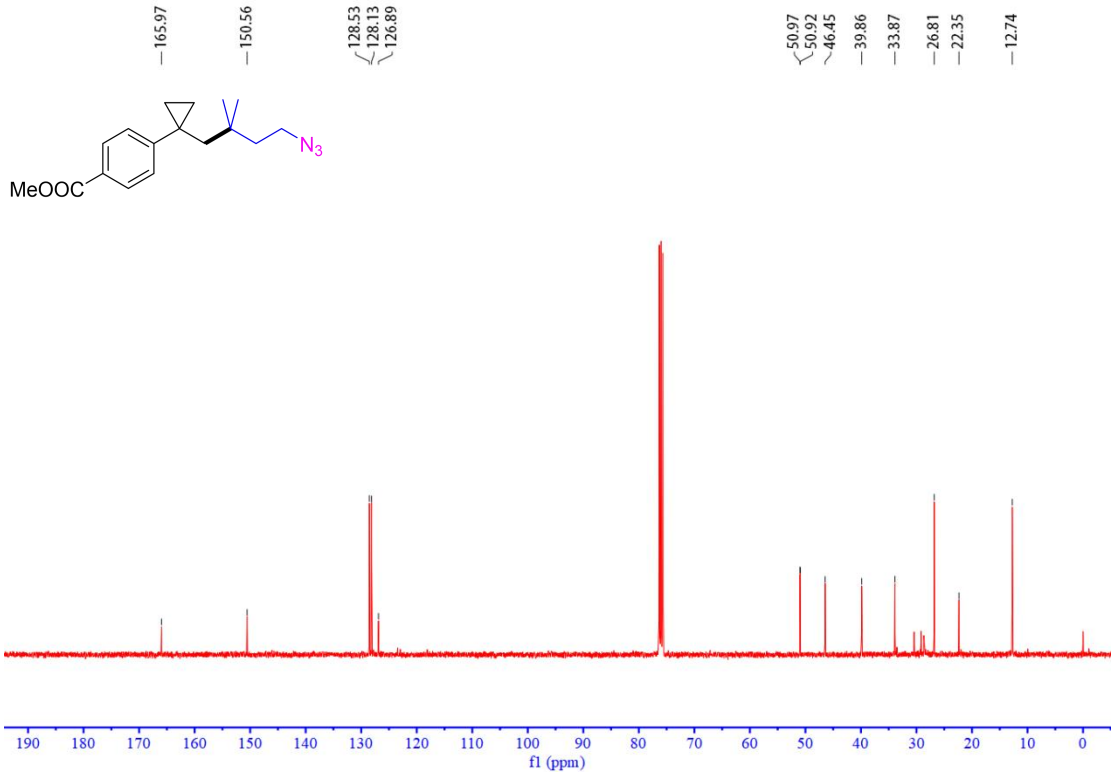
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4b**



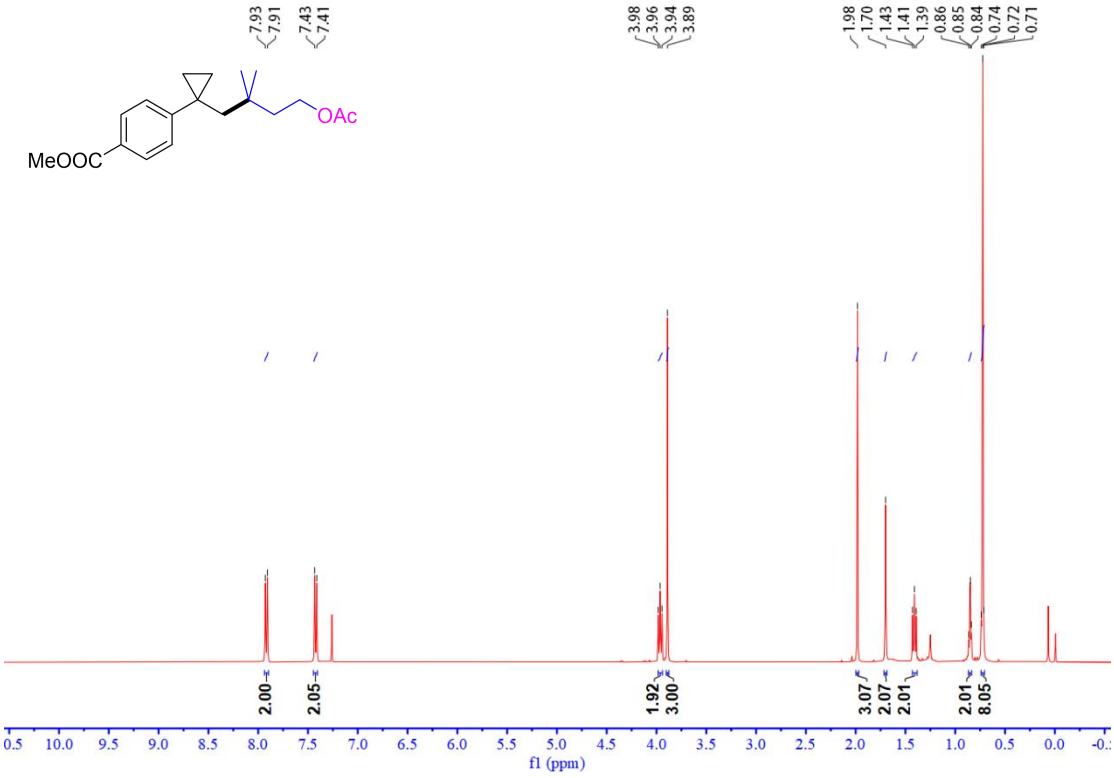
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4c**



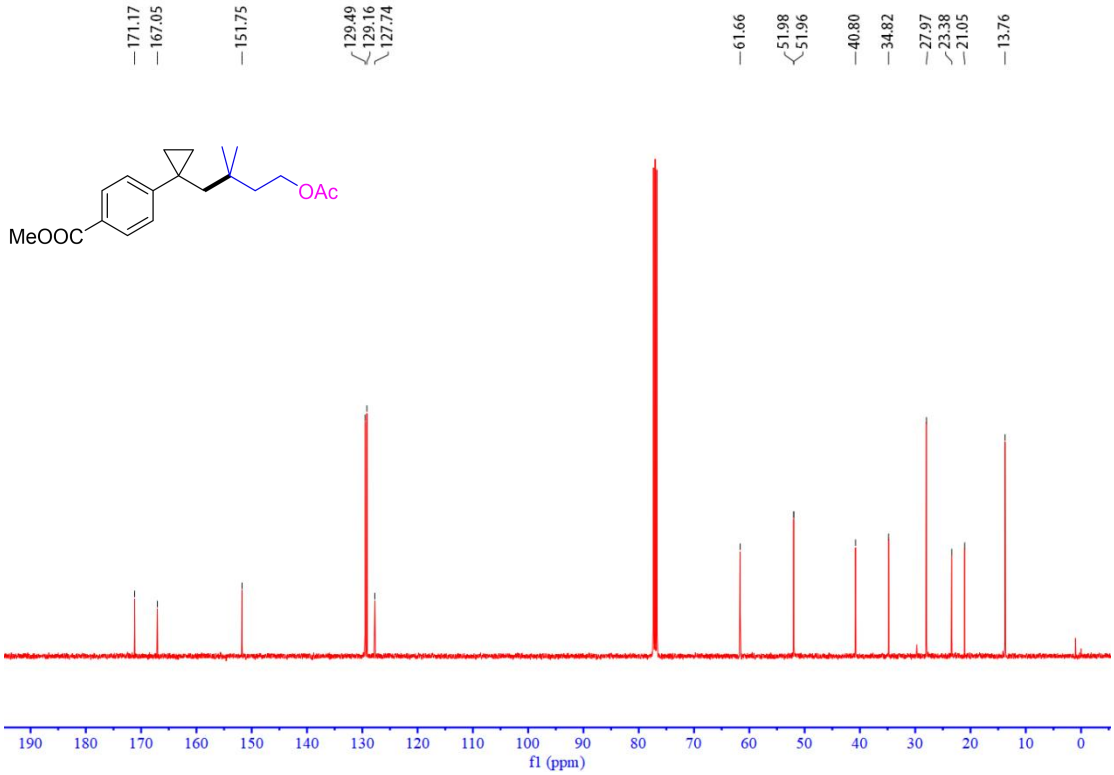
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4c**



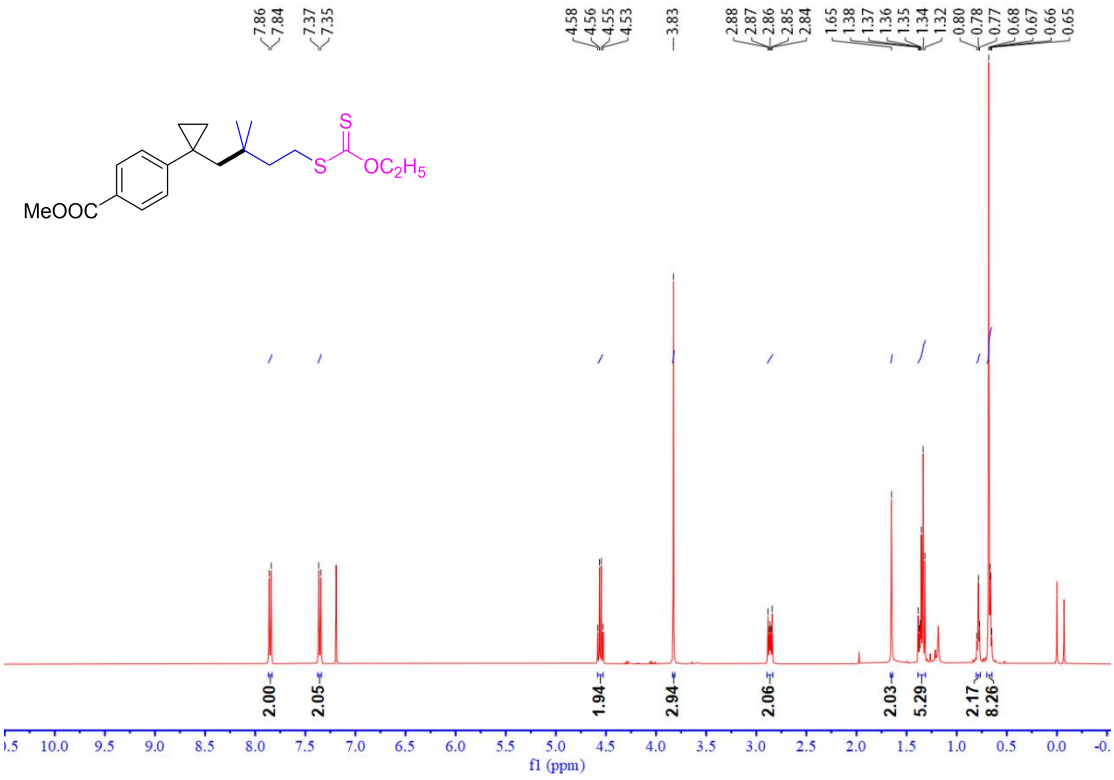
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4d**



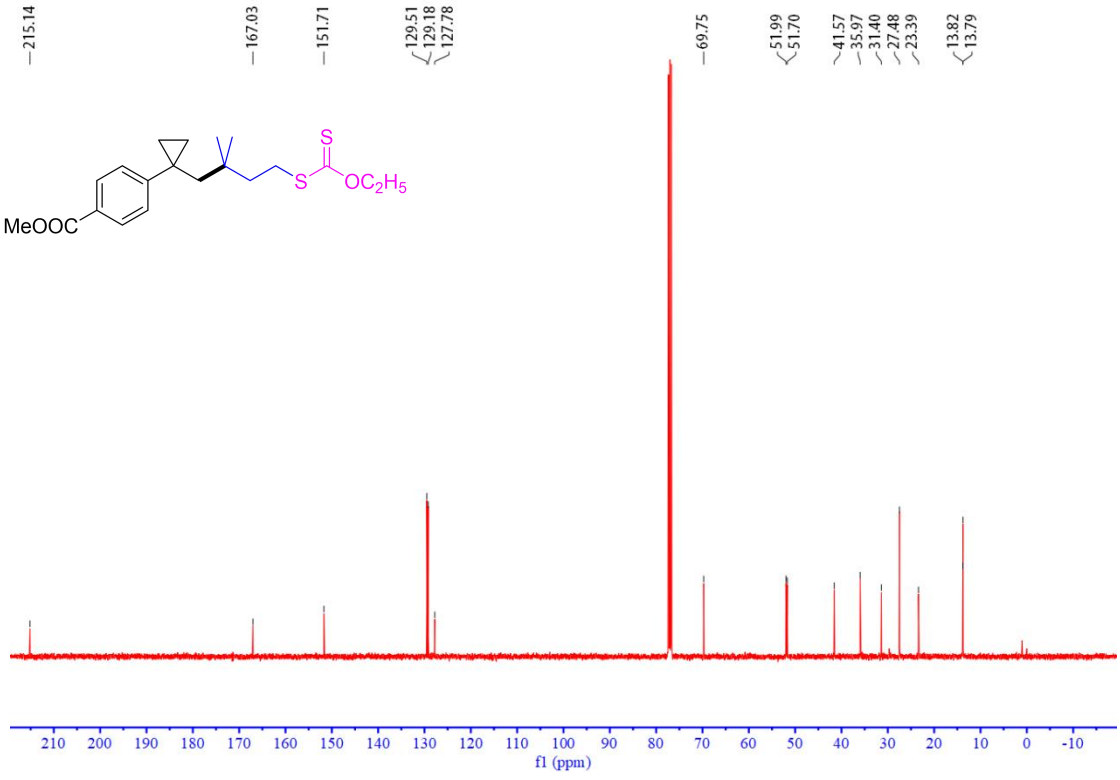
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4d**



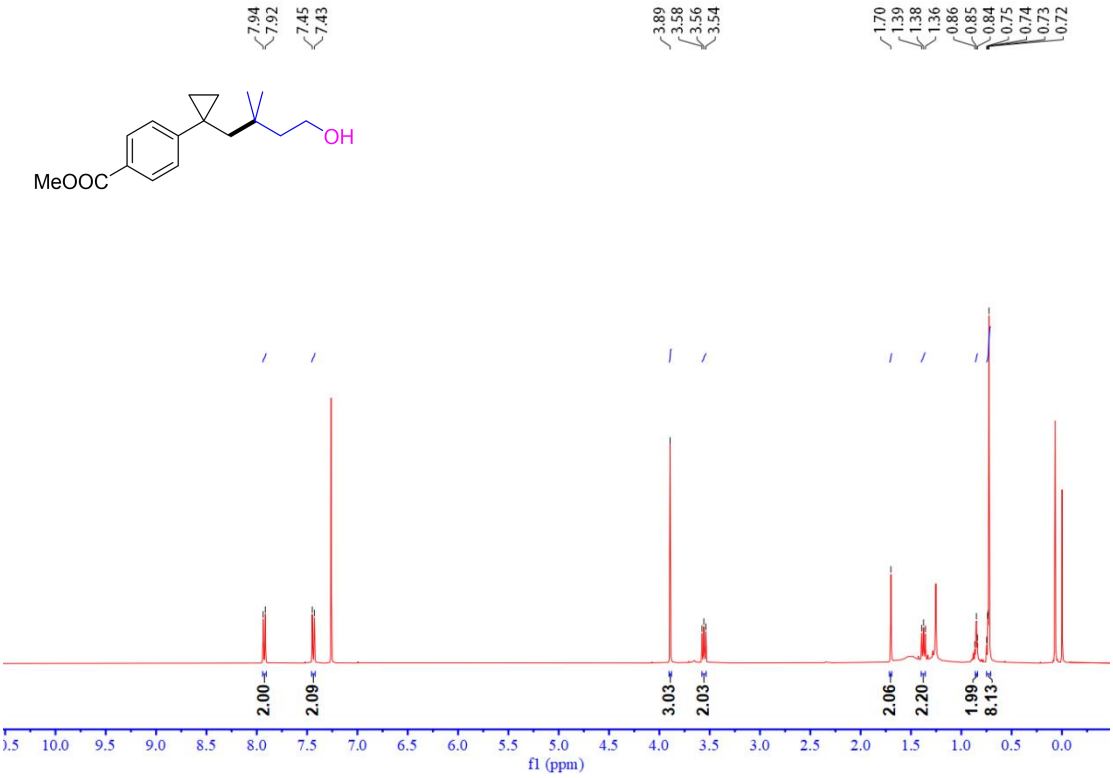
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4e**



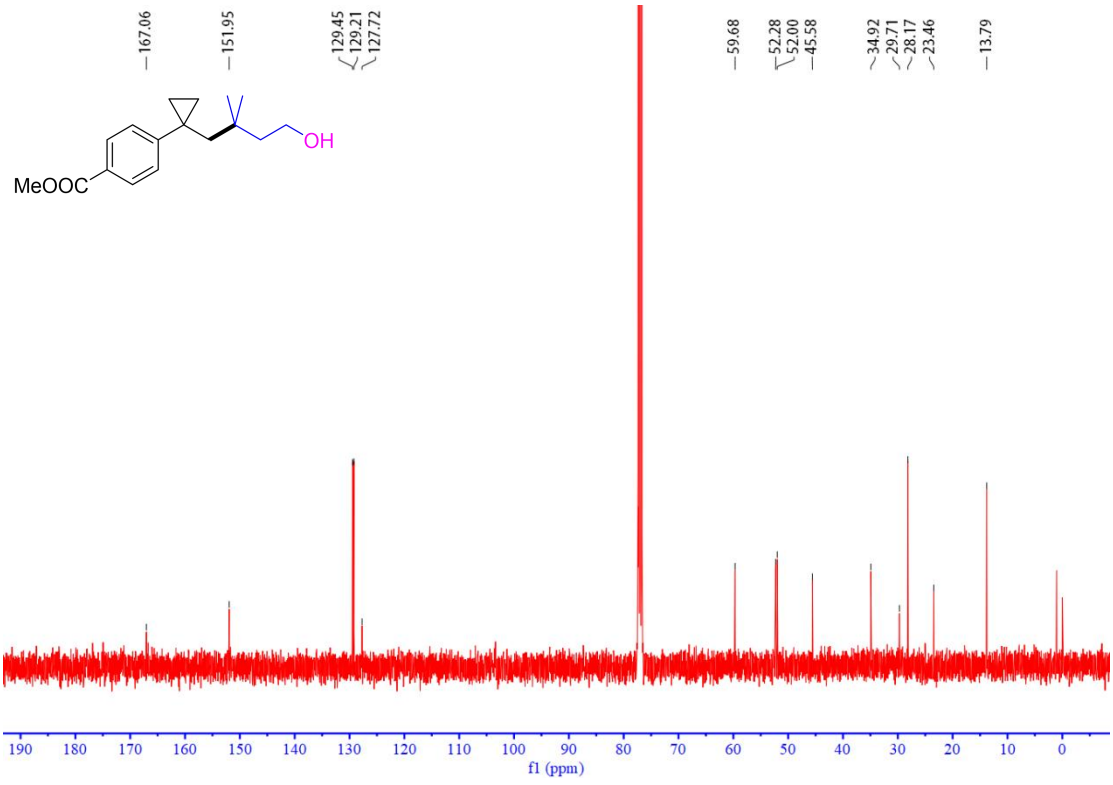
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4e**



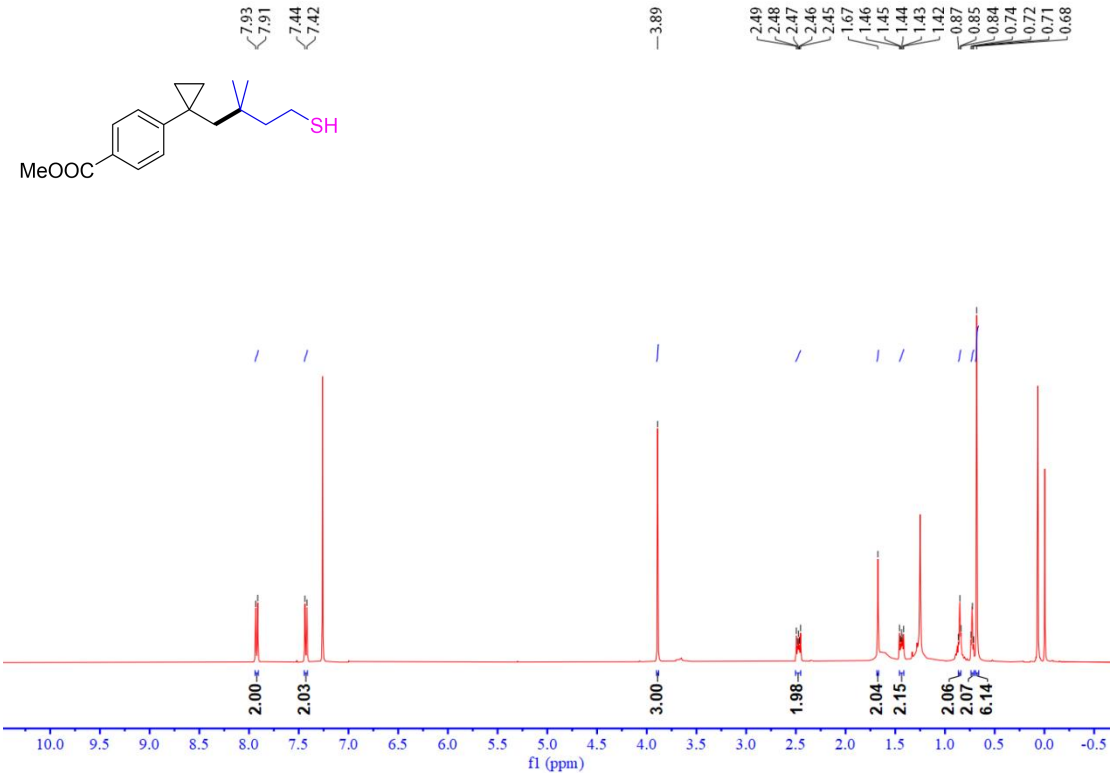
^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4f**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4f**



^{1}H NMR ($CDCl_3$, 400 MHz) spectra of compound **4g**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **4g**