SUPPORTING INFORMATION

Visible light driven α-sulfonylation of ketone-derived silyl enol ethers via electron donor-acceptor complex

Barakha Saxena,[a] Roshan I. Patel,[a] and Anuj Sharma*[a]

[a]Green Organic Synthesis Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee
Roorkee, 247667, Uttarakhand (India)
Tel: +91-1331-284751
E-mail: anujsharma.mcl@gmail.com, anuj.sharma@cy.iitr.ac.in

Table of Contents

1. General information…………………………………………………………………………S3

2. Detailed Optimization of Reaction Conditions…………………………………………S4

2.1 Screening of base…………………………………………………………………………**S4**

2.2 Screening of solvent………………………………………………………………………**S4**

2.3 Optimization of different equivalents of DABCO………………………………………**S4**

2.4 Screening of light irradiation ……………………………………………………………**S5**

2.5 Sensitivity assessment of reaction ………………………………………………………**S5**

3. General Procedure for Synthesis of Products…………………………………………S6

3.1 General procedure for the synthesis of silyl enol ethers ………………………………**S6**

3.2 General procedure for the synthesis of natural products………………………………**S8**

3.3 General procedure for the synthesis of unsymmetrical thiosulfonates ………………**S9**

3.4 General procedure for the synthesis of symmetrical thiosulfonates…………………… **S9**

3.5 General procedure **A** for the synthesis of β-keto sulfones …………………………… **S10**

3.6 General procedure **B** for the synthesis of β-keto sulfones …………………………… **S11**

3.7 Unsuitable substrates……………………………………………………………………**S11**

4. Procedure for the Gram Scale Synthesis of β-keto sulfones and recyclability of PhSSPh…S12

5. Mechanistic Studies……………………………………………………………………S12

5.1 UV-visible absorption spectra ……………………………………………………………**S13**

5.2. 1H-NMR titration experiment ……………………………………………………………**S13**

5.3 Job's plot ……………………………………………………………………………………**S15**

5.4 Determination of association constant (k_{EDA}) ……………………………………**S16**

5.5 Light-on/off experiment……………………………………………………………………**S18**

5.6 Radical Trapping Experiments ……………………………………………………………**S19**

5.7 Irradiation of natural sunlight ……………………………………………………………**S22**

5.8 Quantum Yield (Φ) …………………………………………………………………………**S23**

6. Calculations of Green Chemistry Metrics………………………………………………S26

7. Calculations of EcoScale…………………………………………………………………S34

8. NMR data…………………………………………………………………………………S38

8.1 Characterization data for products………………………………………………………**S39**

8.2 NMR copies of products……………………………………………………………………**S71**

9. References…………………………………………………………………………………S136

1. General Information

Reagents information: Commercially available reagents and analytical grade solvents were purchased from Sigma-Aldrich, Toyko Chemical Company (TCI), Alfa-Aesar, MolyChem, SRL chemicals, AVRA, BLD pharm, GLR innovations, LOBA Chemie and AVARICE and were used as received without further purification. 1,4-DIAZABICYCLO (2,2,2) OCTANE (DABCO) was purchased from Alfa Aesar (Assay 98%, Cas No. 280-57-9).

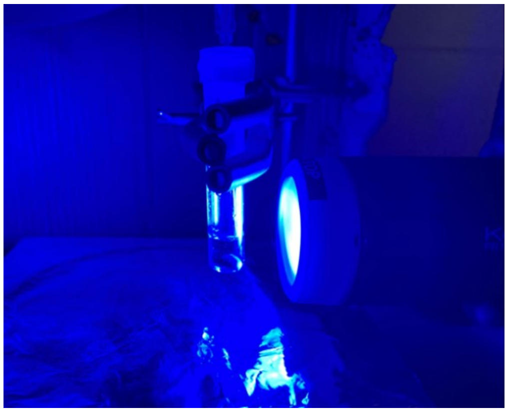
NMR Spectra: Nuclear magnetic resonance (NMR) spectra for ^{1}H, ^{13}C, and ^{19}F NMR were recorded on a JEOL (500 MHz ^{1}H, 126 MHz ^{13}C) spectrometer using $CDCl_3$ as a solvent with tetramethylsilane (TMS) as internal standard. In the evaluation of 1H NMR spectra, chemical shift has been assigned in units of parts per million (ppm), wherein, "s" stands for singlet, "br.s" for broad singlet "d" for doublet, "t" for triplet, "q" for quartet, "dd" for doublet of doublets", "tt" for triplet of triplets, "dt" for doublet of triplets", "td" for triplet of doublets" and "m" for multiplet. The units of coupling constant (J) has been assigned in Hz.

High Resolution Mass Spectrometry (HRMS): High resolution mass spectra (HRMS) were recorded with an Agilent LCQTOF spectrometer using ESI ionization.

Melting points (mp): Measurements were recorded on a OptiMelt, automated melting point apparatus (Stanford Research Systems, Inc.).

Chromatography: Reactions were monitored on Merck TLC silica gel 60 F254 plates and visualized using ultraviolet light of wavelength 254 nm. Column chromatography was performed on silica gel (100-200 mesh), eluted with hexane/ethyl acetate as a mobile phase.

Photoreactor: Visible light reaction was performed using a 40W Kessil PR160L lamp (456 nm), placed 3 cm away from reaction vials. The reaction setup was placed within a ventilated fume hood and using a fan to avoid overheating.



2. Detailed Optimization of Reaction Conditions

2.1 Screening of base

Entry	Base (2.0 equiv.)	Isolated Yield%
1	TMEDA	48
2	DBU	52
3	DMAP	30
4	Et_3N	trace
5	triphenylamine	trace
6	**DABCO**	**67**

Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol, 2.0 equiv.) and base (0.4 mmol, 2.0 equiv.) in MeCN (0.5 mL) under blue Kessil (λ = 456 nm) irradiation for 14 h at rt under argon atmosphere.

2.2 Screening of solvent

Entry	Base (2.0 equiv.)	Solvent	Isolated Yield%
1	DABCO	MeCN	67
2	DABCO	DMSO	72
3	DABCO	Acetone	38
4	DABCO	DCM	52
	DABCO	DMF	70
5	**DABCO**	**DMA**	**81**
6	DABCO	EtOH	nr
7	DABCO	DCE	55
8	DABCO	THF	42
9	DABCO	MeOH	nr

Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol, 2.0 equiv.), and DABCO (0.4 mmol, 2.0 equiv.) in solvent (0.5 mL) under blue Kessil (λ = 456 nm) irradiation for 14 h at rt under argon atmosphere; nr = no reaction

2.3 Optimization of different equivalents of DABCO

Entry	base	Equiv.	Isolated Yield%
1	DABCO	1 equiv.	55
2	DABCO	2 equiv.	81
3	DABCO	2.5 equiv.	81
4	**DABCO**	**3 equiv.**	**89**

Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol, 2.0 equiv.), and DABCO (x-equivalent) in DMA (0.5 mL) under blue Kessil (λ = 456 nm) irradiation for 14 h at rt under argon atmosphere.

2.4 Screening of light Irradiation

Entry	light	Isolated Yield%
1	White led	40
2	Blue LEDS (427 nm)	65
3	Blue LEDS (456 nm)	89
4	Blue LEDS (440 nm)	77
5	Purple LEDs (390 nm)	55
6	3 W Green LED Strips	72
7	Dark (no light)	nr
8	Blue LEDS (456 nm)	62[b]

Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol, 2.0 equiv.), and DABCO (0.4 mmol, 3.0 equiv.) in DMA (0.5 mL) under various light irradiation for 14 h at rt under argon atmosphere; [b]open-to-air 1a (0.2 mmol), 2a (0.24 mmol, 2.0 equiv.) and DABCO (0.4 mmol, 3.0 equiv.) in DMA (0.5 mL) under blue LED (456 nm) irradiation for 14 h at rt; nr = no reaction

2.5. Sensitivity assessment of reaction

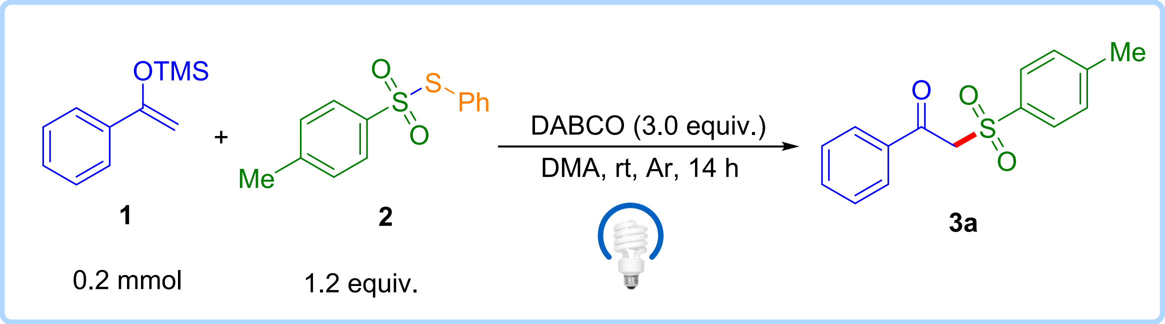


Table 1. Preparation of sensitivity assessment of reaction

Entry	Parameter	Variation	Description	Yield[a]
1	High concentration (+10%)	$c + 10\% c$	0.45 mL DMA	89%
2	Low concentration (-10%)	$c - 10\% c$	0.55 mL DMA	82%
3	High H_2O	$+H_2O$; $V_{H2O} = 1\% V_{rxn}$	5 µL H_2O in 0.5 mL DMA	85%
4	O_2 level	O_2 ballon	O_2 ballon instead of Ar	62%
5	Low temperature (T)	$T - 10$ °C	15 °C	74%
6	High temperature (T)	$T + 10$ °C	cooling fan turned off	81%
7	Low intensity (W)	d. 4	Distance: 12 cm	70%
8	High intensity (W)	d / 4	Distance: 0.75 cm	87%
9	Big Scale	n.20	6 mmol of 1a	52%

[a] Isolated yield.

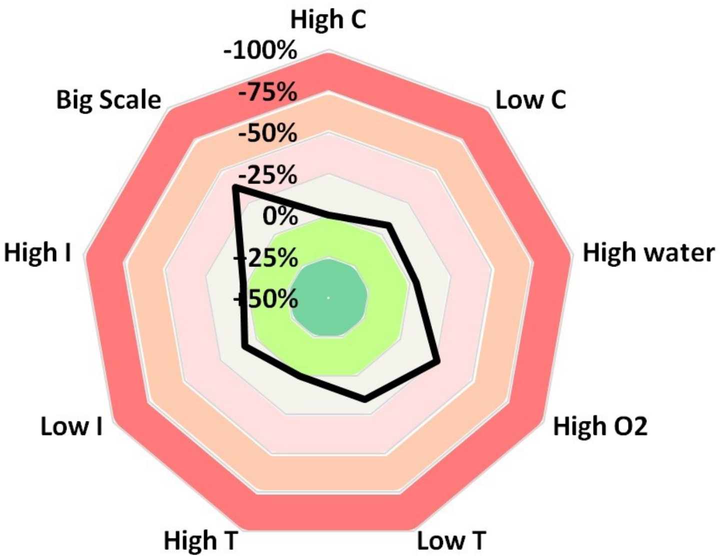


Figure 1: Sensitivity assessment of reaction towards concentration, water, oxygen, temperature, light intensity and large scale, is represented by a color-coded radar diagram. Deviation from standard reaction conditions is indicated by a black solid line.

3. General Procedure for Synthesis of Products

Silyl enol ethers **1z**,[1a] **1zf**,[1b] **1zh**,[1c] **1zi**,[1c] **1zj**[1c] and **1zk**[1d] were prepared according to synthesis procedures described in the literature.

3.1 General procedure for the synthesis of silyl enol ethers.

Unless otherwise noted in the experimental procedures, the silyl enol ethers (**1b**-**1zg**) were prepared from the corresponding ketones according to procedures described in the literature.[1e]

To an oven dried 100 mL round bottom flask, equipped with a magnetic stirrer, was charged with a mixture of substituted ketone (5.0 mmol, 1.0 equiv.) and anhydrous sodium iodide (899 mg, 6.0 mmol, 1.2 equiv.). The reaction vessel was evacuated and backfilled with N_2 (3 ×), then anhydrous MeCN (7.5 mL, 1.5

mL/mmol) was added. The round-bottom flask was stirred at rt for 5 min, and then added Et_3N (1.0 mL, 7.5 mmol, 1.5 equiv), followed by chlorotrimethylsilane (0.76 mL, 6.0 mmol, 1.2 equiv). The reaction mixture was stirred for 16 h at rt, then cooled to 0 °C and quenched with a mixture of Et_2O (20 mL) and saturated NH_4Cl(aq) solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic extract was sequentially washed with ice-water (20 mL) and saturated NH_4Cl(aq) solution (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was distilled under reduced pressure to provide pure silyl enol ethers.

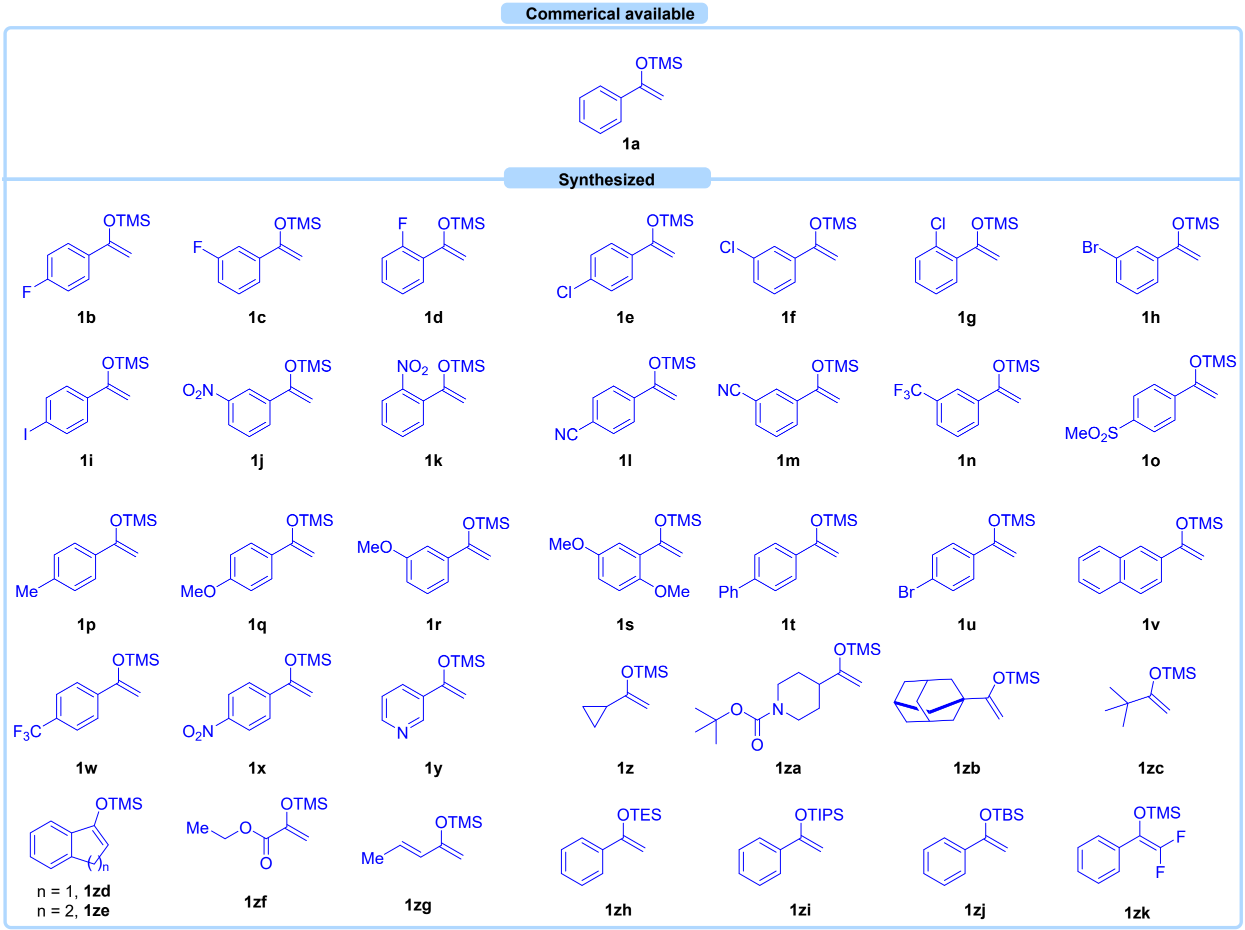
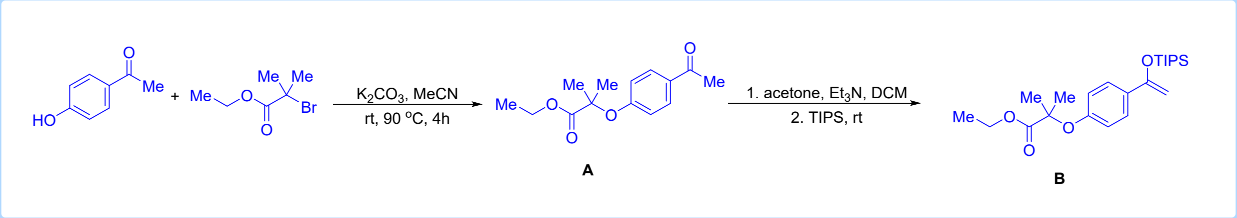


Figure 2: Various *O*-silyl enol ethers (**1a**-**1zk**) used in this experiment

3.2 General procedure for the synthesis of natural products

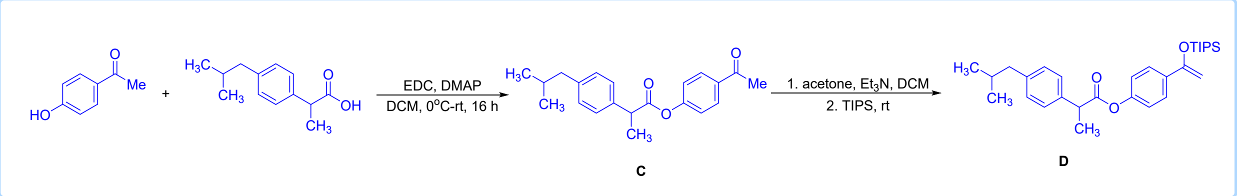
Synthesis of natural product B:[2]



General procedure: Charge an oven dried 50 mL round bottom flask with 4-hydroxy acetophenone (1.0 equiv.), substituted bromoester (1.1 equiv.) and acetonitrile (25 mL). Add K_2CO_3 (10.0 equiv.) and heat the reaction mixture to 90 °C for 4 h. Evaporate the acetonitrile in vacuo. Purify the residue by silica gel column chromatography (20% EtOAc/Hexane) to obtain the desired ketone A.

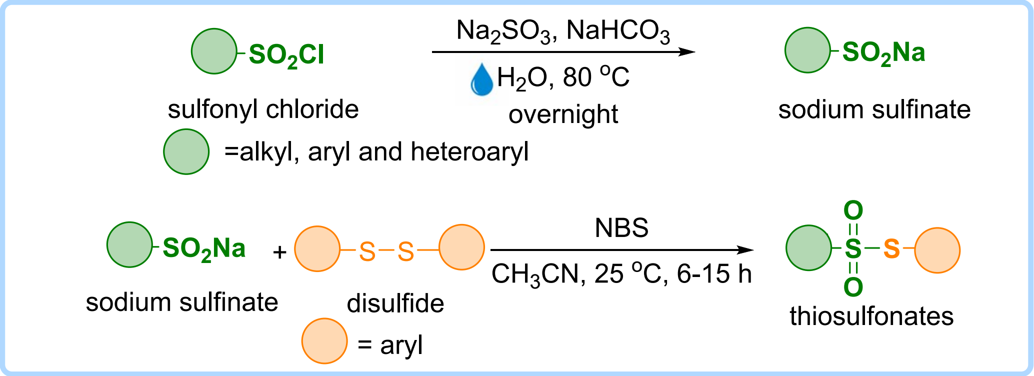
To a 50 mL round-bottom flask equipped with a stirring bar was added a solution of A (5.0 mmol) in dichloromethane (15 mL) and triethylamine (0.91 g, 9.0 mmol). The reaction mixture was stirred at room temperature for 40 min before triisopropylsilyl triflate (1.84 g, 6.0 mmol) was added slowly. Then the resulting mixture was stirred at room temperature for several minutes. Once the reaction was complete (reaction monitored by TLC), the reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and diluted with dichloromethane (15 mL). The organic layer was washed twice with a cooled saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over on basic alumina (pH 9.09.5) eluting with petroleum ether to afford the desired silyl enol ether B.

Synthesis of natural product D:[3]



General procedure: EDC (2.5 equiv.) and DMAP (0.5 equiv.) were added sequentially to an ice-cold solution of the 4′-hydroxy acetophenone (1.0 equiv.) and corresponding acid (2.5 equiv.) in DCM (0.1 M). After 30 min, the ice-water cooling bath was removed, and the resulting suspension was stirred vigorously at room temperature for 16 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane/EtOAc) afforded the desired ketone C. To a 50 mL round-bottom flask equipped with a stirring bar was added a solution of C (5.0 mmol) in dichloromethane (15 mL) and triethylamine (0.91 g, 9.0 mmol). The reaction mixture was stirred at room temperature for 40 min before triisopropylsilyl triflate (1.84 g, 6.0 mmol) was added slowly. Then the resulting mixture was stirred at room temperature for several minutes. Once the reaction was complete (reaction monitored by TLC), the reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and diluted with dichloromethane (15 mL). The organic layer was washed twice with a cooled saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over on basic alumina eluting with hexane/EtOAc to afford the desired silyl enol ether D.

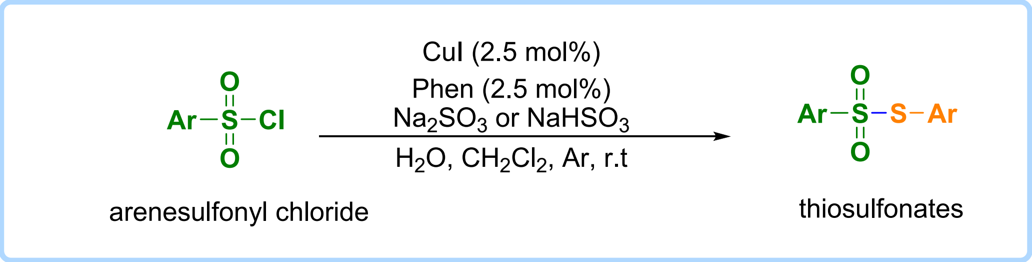
3.3 General procedure A for the synthesis of unsymmetrical thiosulfonates.



Synthesis of sodium sulfinate salts:[4a] To a oven dried 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with sulfonyl chloride (5 mmol), Na_2SO_3 (2.0 equiv.) followed by $NaHCO_3$ (2.0 equiv.) in water (5 mL). The round-bottom flask was sealed with a rubber septa and the resulting mixture was stirred at 80 ° for 10 h. Later, the reaction was cooled to room temperature and the water was removed in a vacuum. The residue was extracted in ethanol and recrystallization from ethanol furnished the sodium sulfinates as a white or light yellow solid.

Synthesis of thiosulfonates:[4b] To a solution of sodium sulfinate (0.8 mmol) and disulfide (0.2 mmol) in CH_3CN (3.0 ml) was added NBS (0.4 mmol) while mixing. the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (300-400 mesh) with hexane-EtOAc as eluent to provide the desired unsymmetrical thiosulfonates.

3.4 General procedure B for the synthesis of symmetrical thiosulfonates.[4c]



To a round-bottom flask equipped with a magnetic stir bar, aryl sulfonyl chlorides (1.0 equiv.), Na_2SO_3 (3.0 equiv.), CuI (2.5 mol %) and Phen (2.5 mol %) were added. The flask was then evacuated and flushed with argon. Degassed DCM (0.2 M) and H_2O (1.0 equiv.) were then added. The resulting mixture was stirred at room temperature overnight. After being diluted with DCM, the mixture was washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated by a rotary evaporator under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to afford the corresponding thiosulfonates.

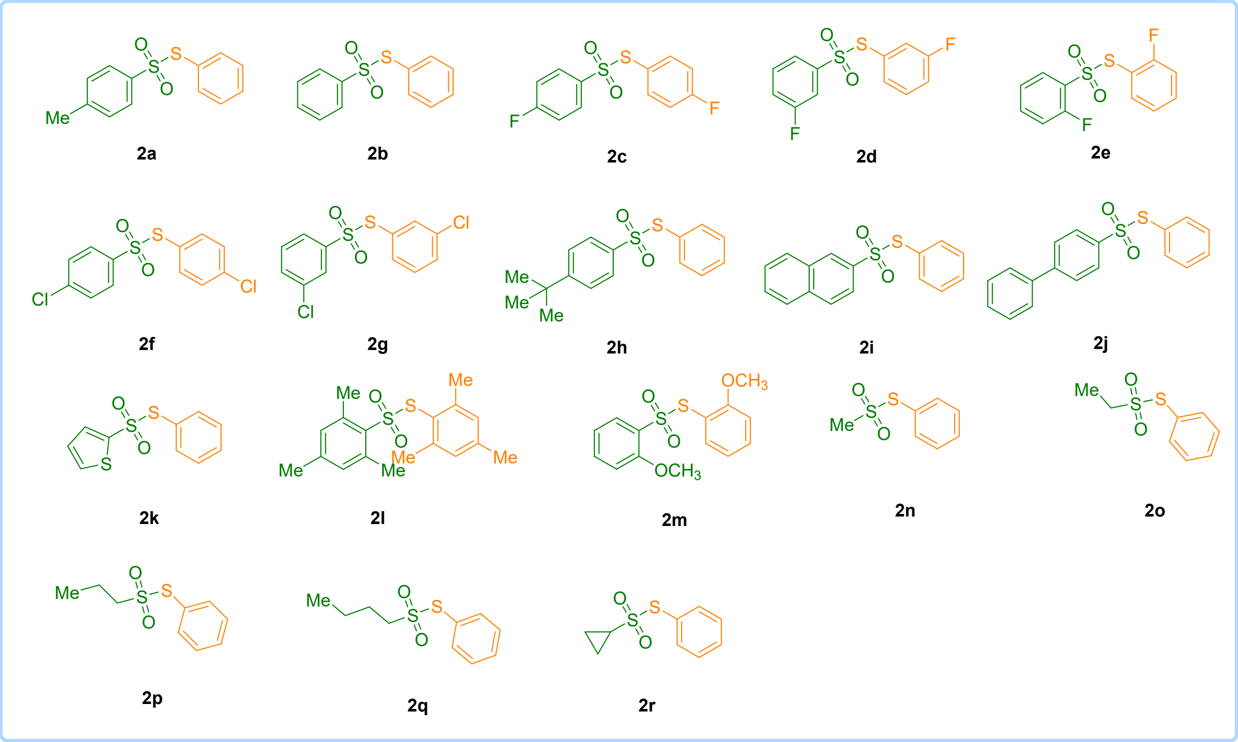
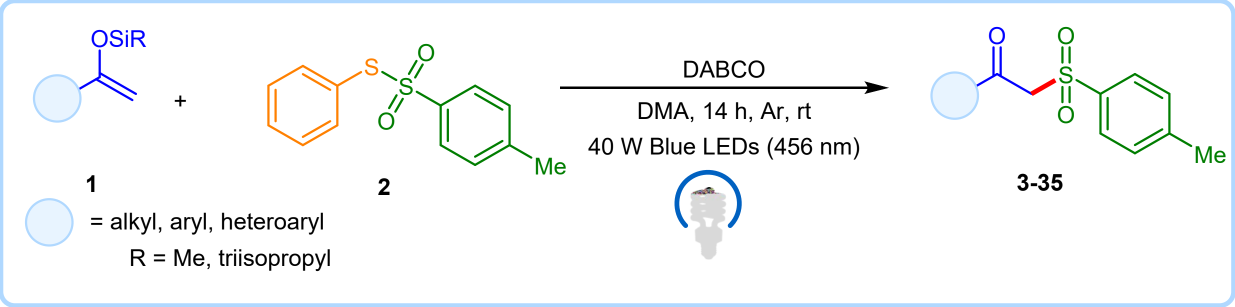


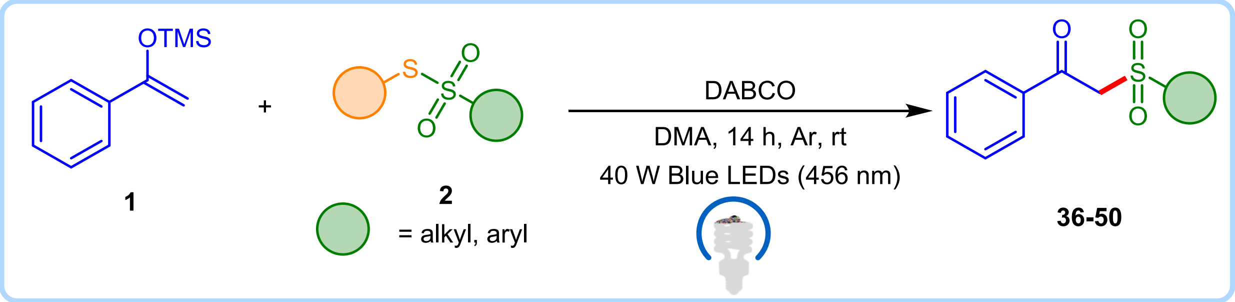
Figure 3: Various thiosulfonates (**2a**-**2r**) used in this experiment

3.5 General procedure A for the synthesis of β-keto sulfones using different *O*-silyl enol ethers.



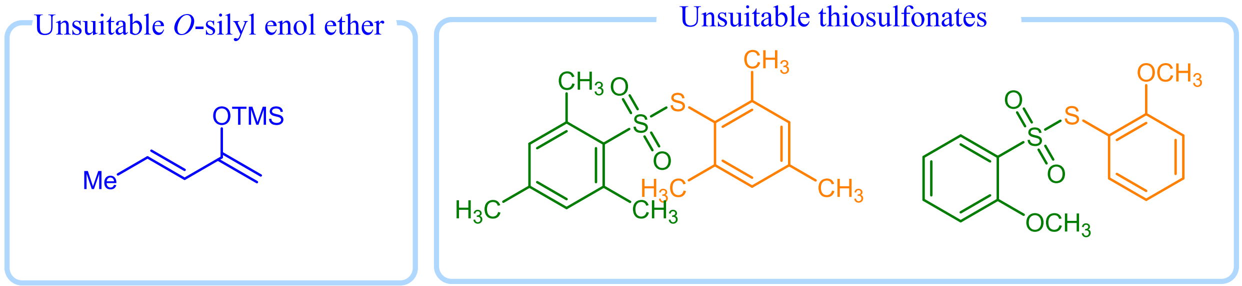
An oven-dried glass vial (10 mL) was equipped with a magnetic stir bar and charged with *O*-silyl enol ethers (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3 equiv.). The flask was evacuated and backfilled with argon and then DMA (0.5 mL) was added. The reaction mixture was irradiated with 40 W blue LED (456 nm) at room temperature for 14 h. After the reaction, the residue was diluted with water (40 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with hexane/EtOAc as eluent to afford the desired products **3-35**.

3.6 General procedure B for the synthesis of β-keto sulfones using different thiosulfonates.



An oven-dried glass vial (10 mL) was equipped with a magnetic stir bar and charged with ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane (0.2 mmol), thiosulfonates (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3 equiv.). The flask was evacuated and backfilled with argon and then DMA (0.5 mL) was added. The reaction mixture was irradiated with 40 W blue LED (456 nm) at room temperature for 14 h. After the reaction, the residue was diluted with water (40 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with hexane/EtOAc as eluent to afford the desired products **36-50**.

3.7 Unsuitable substrates



Scheme 1: Unsuitable substrates

4. Procedure for the gram-scale synthesis of β-keto sulfones and recyclability of PhSSPh.

The mixture of ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane (3.0 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (3.6 mmol, 1.2 equiv.), DABCO (9.0 mmol, 3.0 equiv.) and DMA (10 mL) were sequentially added in a 100 mL round bottom flask. Then the reaction system was carried out under 40 W blue LED (456 nm) at room temperature under an Ar atmosphere for 14 h. Once completed, the mixture was diluted with water (60 mL) and extracted with EtOAc (30 mL × 3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/EtOAc (5:1, v/v) as eluent to afford the desired product **3a** (0.63 g, 68%) and phenyl disulfide (0.47 g, 72%).

To demonstrate the recyclability of phenyl disulfide by-product, the recovered phenyl disulfide was recycled to afford the *S*-phenyl-4-methylbenzenesulfonothioate according to the General Procedure **A**, 3.3 mentioned above.

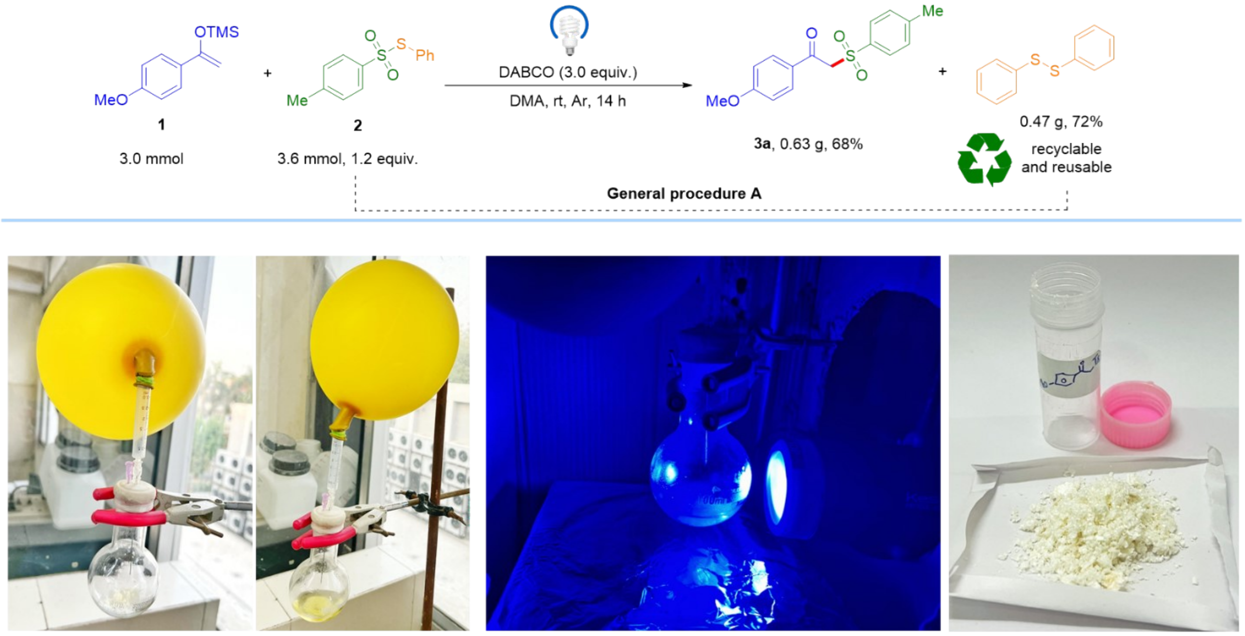


Figure 4: Gram-scale reaction of **3a**

5. Mechanistic Studies

5.1 UV-visible absorption spectra

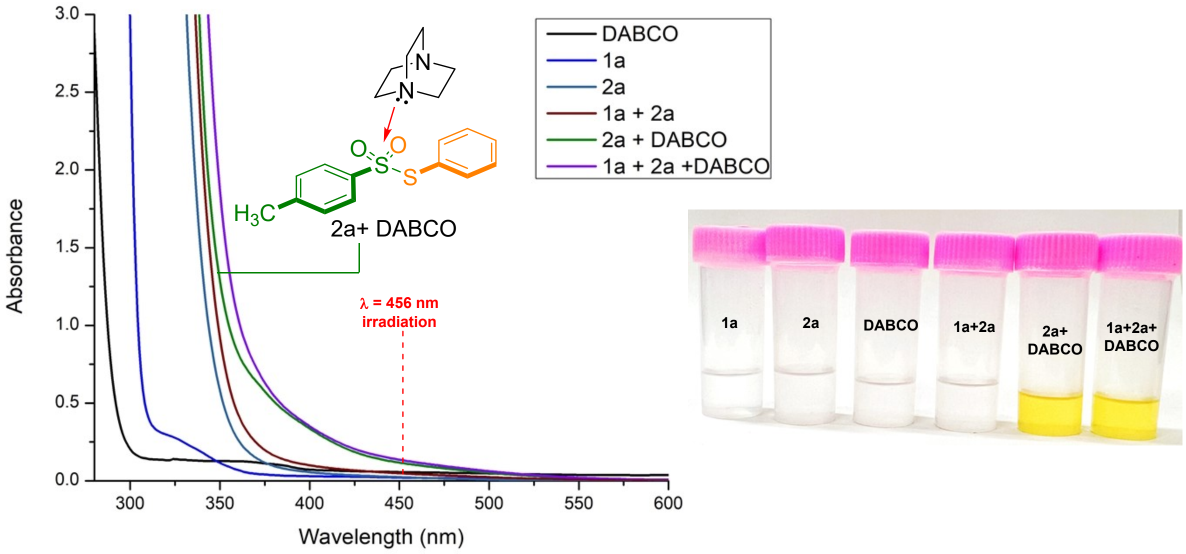


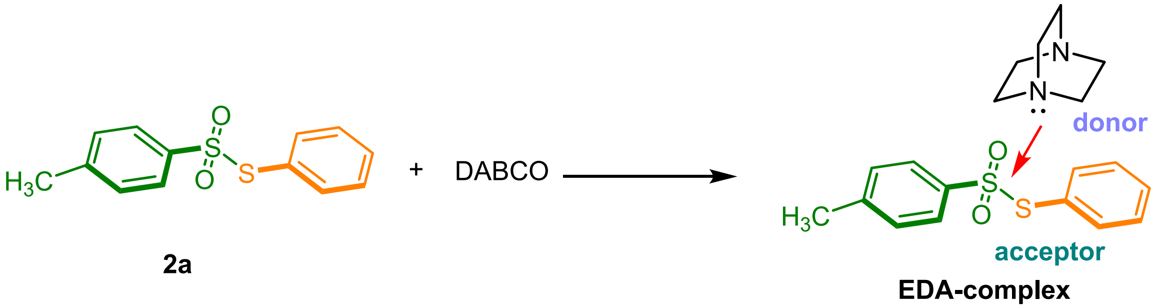
Figure 5: UV-visible spectra experiments measured in DMA and visual appearance of individual components and reaction mixture.

UV/vis absorption spectra was recorded using Shimadza UV-Vis 2600 spectrophotometer in the range of 200-800 nm in a 1 cm quartz cuvette. In order to identify light-absorbing species in this transformation, absorption spectra of the series of solutions were recorded (Figure 5). The results indicate, that none of the reaction components (**1a**, **2a** and DABCO) can individually absorb visible light. Combining silyl enol ether **1a** with **2a** led to just a small absorbance band in near UV region. In contrast, when aryl sulfonate S-ester **2a** in DMA was mixed with DABCO, the solution demonstrated a notable absorbance band in the visible region, thus, pointing on the possibility of the formation of an electron donor-acceptor (EDA) complex, presumably between **2a** and DABCO. Likewise, absorbance in the visible region was observed when **1a**, **2a**, and DABCO were mixed together.

The coloration of the prepared solutions additionally supports the formation of the EDA-complex (Figure 5). Individually, the components of the reaction remain clear even upon prolonged standing. In contrast, mixing **2a**, DABCO in DMA, rapidly develops the yellow color of the solution.

5.2 ^{1}H-NMR titration experiment

^{1}H NMR spectra of mixtures of *S*-phenyl-4-methylbenzenesulfonothioate **2a** and DABCO in $CDCl_3$ were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of *S*-phenyl-4-methylbenzenesulfonothioate **2a** (0.03 mmol) was kept constant at 0.05 M, and that of DABCO was varied from 0 to 0.2 M. The molar ratios of *S*-phenyl-4-methylbenzenesulfonothioate 2a: DABCO were 1:0, 1:1, 1:2, 1:3, 1:4 in $CDCl_3$. The ^{1}H NMR signal of *S*-phenyl-4-methylbenzenesulfonothioate 2a shifted upfield along with increasing the amount of DABCO, indicating the formation of EDA-complex between *S*-phenyl-4-methylbenzenesulfonothioate 2a with DABCO.



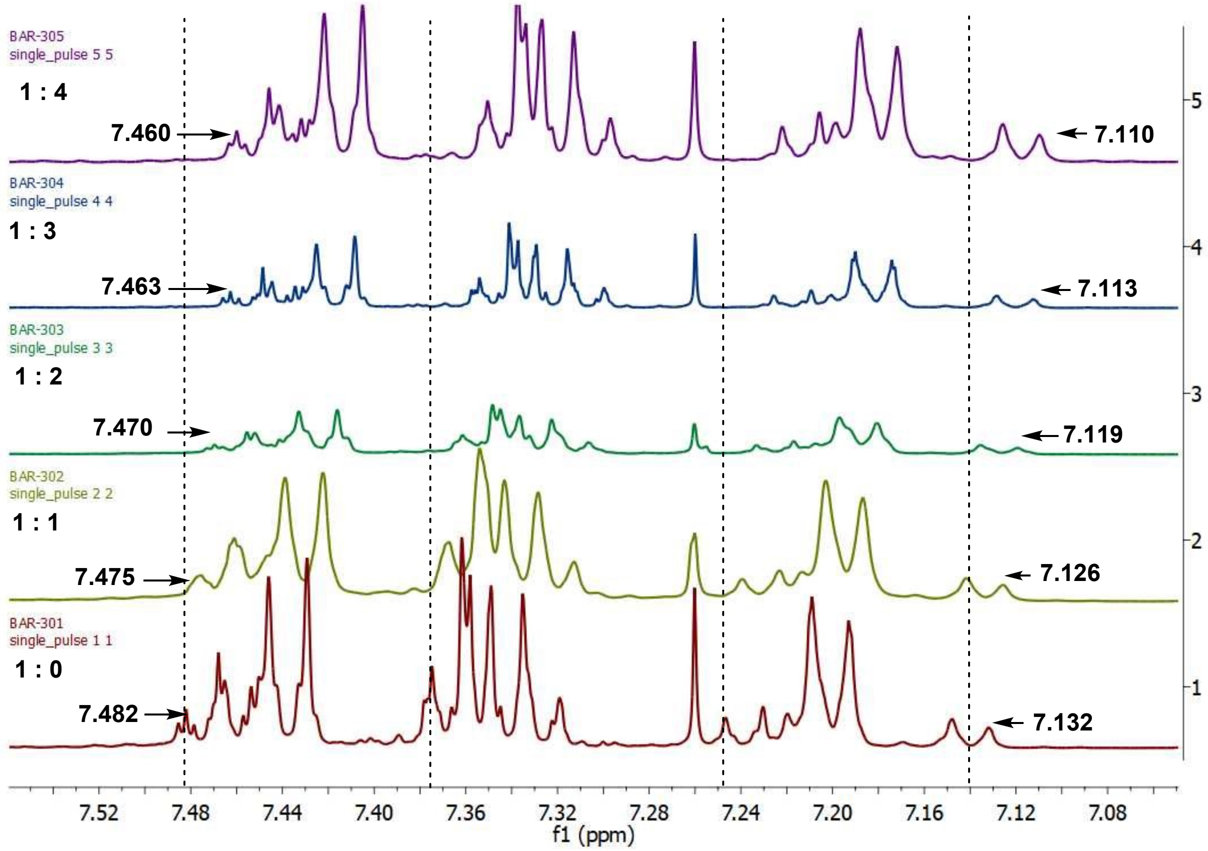


Figure 6: ^{1}H-NMR shift of *S*-phenyl-4-methylbenzenesulfonothioate **2a** with DABCO in aromatic region.

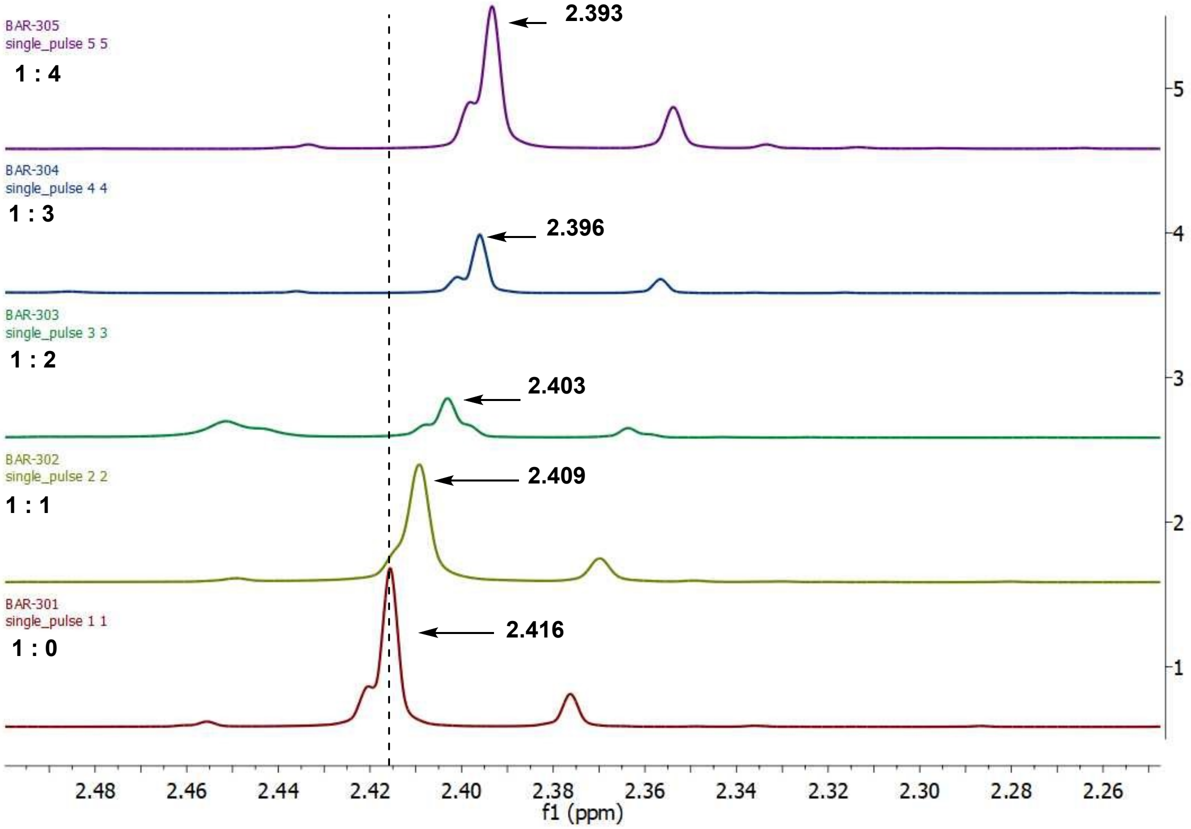


Figure 7: ^{1}H-NMR shift of *S*-phenyl-4-methylbenzenesulfonothioate **2a** with DABCO in aliphatic region.

5.3 Job's plot

The stoichiometry of the EDA complex formed between *S*-phenyl-4-methylbenzenesulfonothioate **2a** and DABCO in DMA was determined using the Job's plot method. The Job's plot was constructed by measuring the absorption at 456 nm of DMA solutions of different ratios of **2a** and DABCO, where the total concentration of the two components remained constant (Figure 8). A parabolic curve with a maximum absorbance value at 50% mol fraction was obtained, indicating a 1:1 EDA complex between **2a** and DABCO.

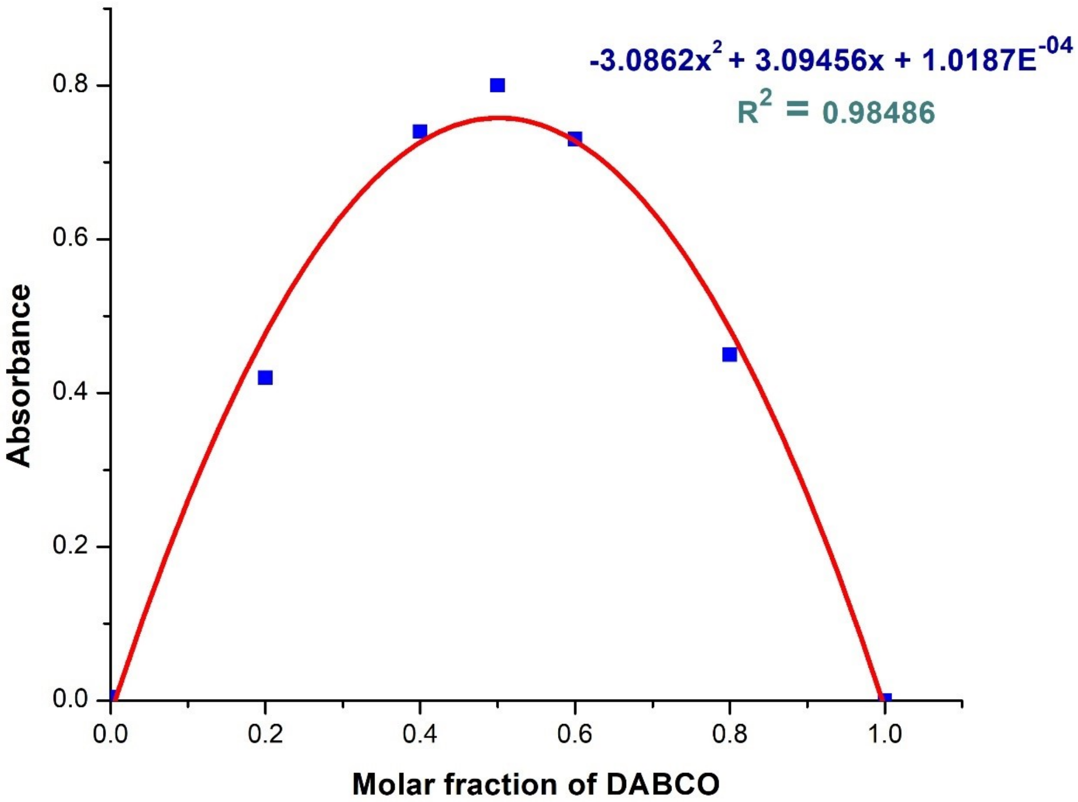
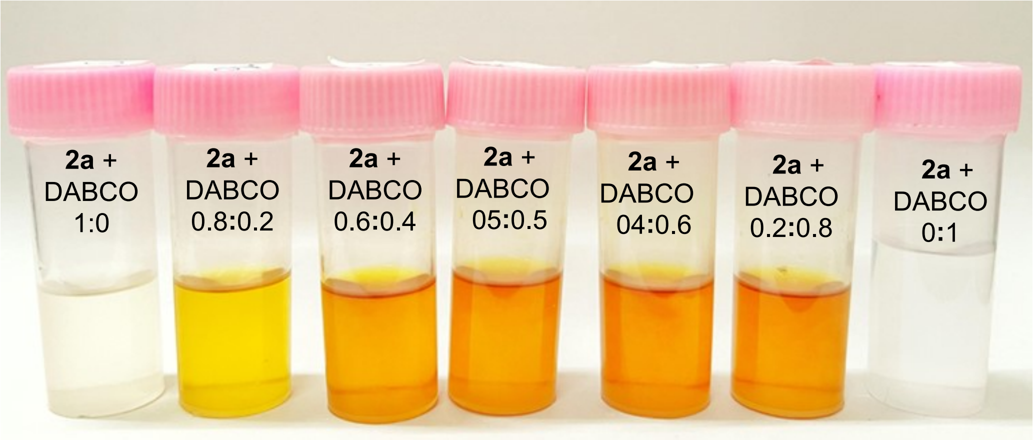


Figure 8: Job's plot of between *S*-phenyl-4-methylbenzenesulfonothioate **2a** and DABCO in DMA.



5.4 Determination of association constant (k_{EDA}):

The association constant for the EDA complex formed between *S*-phenyl-4-methylbenzenesulfonothioate **2a** and DABCO was determined by UV-vis measurements in DMA employing the Benesi Hildebrand[5] method. The absorbance of a constant concentration of **2a** (0.02 M) and an increasing concentration of DABCO (0.02-0.07 M) was recorded at 456 nm. The absorption spectra shown in Figure 9 were recorded in 1 cm path quartz cuvette.

To determine the k_{EDA}, the reciprocal concentration of DABCO was plotted against the reciprocal absorbance (A) of DABCO at 456 nm (Table 2 and Figure 9). A straight line was obtained, and by dividing the intercept through the slope: kEDA = 4.55 M^{-1} for **2a**/DABCO.

Table 2: Data obtained from the UV-vis absorption spectra of the EDA complex between **2a** and DABCO in DMA. The concentration of **2a** was kept at 0.02 M in DMA.

DABCO (M)	**1/DABCO (M^{-1})**	**Abs_{EDA}**	**1/ Abs_{EDA}-A_0**
0.02	50	0.024	41.54
0.03	33.3	0.036	27.54
0.04	25	0.047	20.97
0.05	20	0.069	14.33
0.06	16.7	0.106	9.43
0.07	14.3	0.114	8.76
0.08	12.5	0.131	7.66

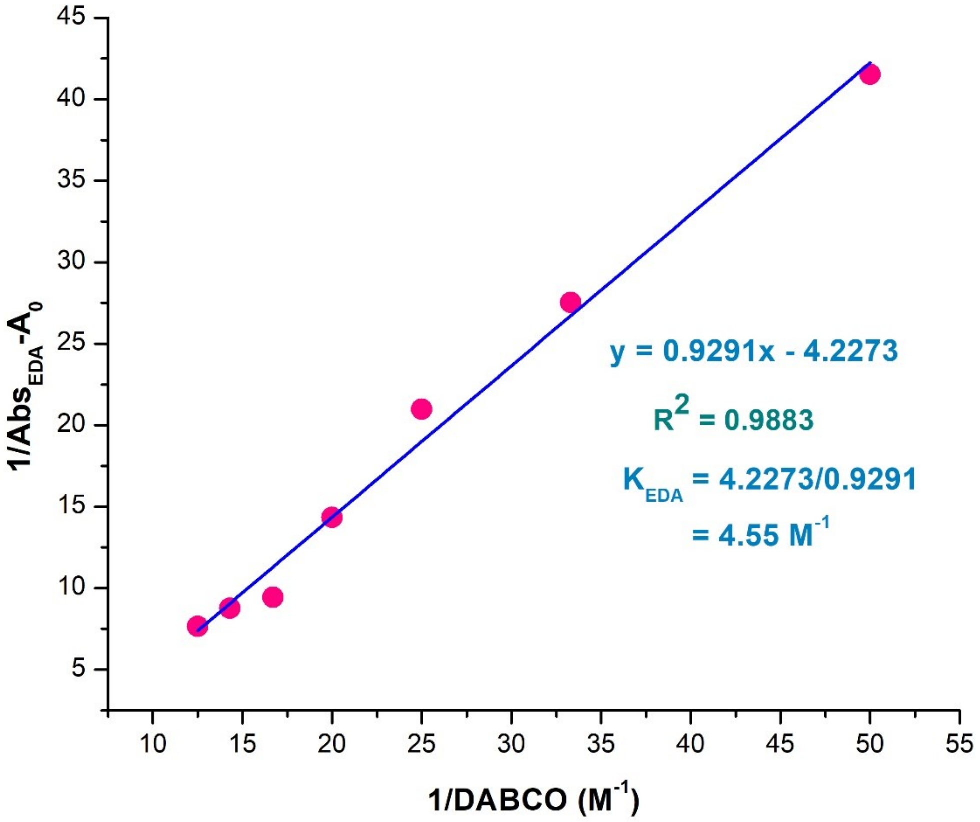


Figure 9: Benesi-Hildebrand plot for the EDA complex generated in DMA upon association of *S*-phenyl-4-methylbenzenesulfonothioate **2a** and DABCO.

5.5 Light-on/off experiment

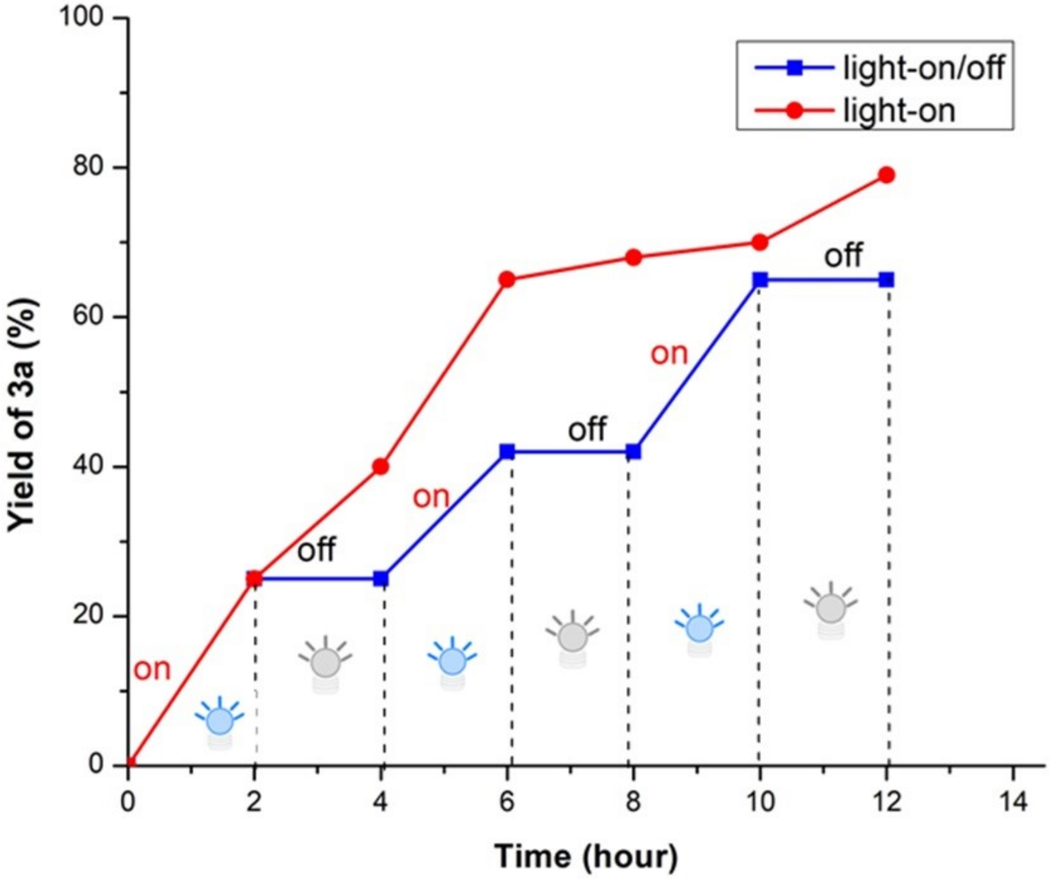
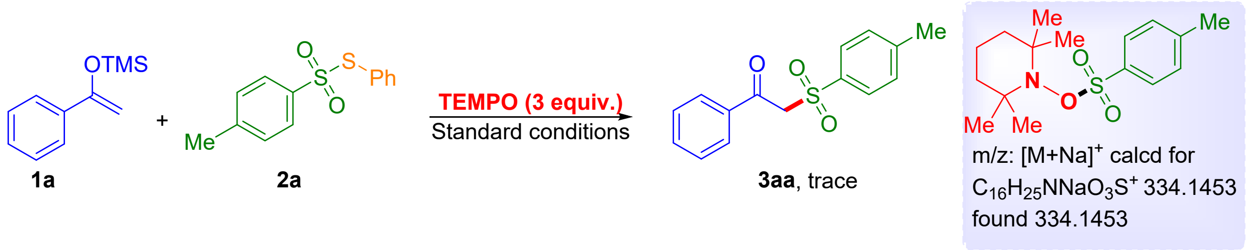


Figure 10: Light-on/off experiment of 1a (0.2 mmol), 2a (0.24 mmol, 1.2 equiv.) and DABCO (0.6 mmol, 3.0 equiv.) in DMA. The red line represents the yield of the reaction continuously irradiated with visible light. The blue line represents the yield of reaction under light turned on and off at intervals.

Six standard reaction mixtures were prepared in 10 mL vials, each containing ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane **1a** (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate **2a** (0.24 mmol, 1.2 equiv.), and DABCO (0.6 mmol, 3.0 equiv.) in DMA (0.5 mL). The vials were purged with argon for 10 minutes. The reactions were then stirred and irradiated under 456 nm blue LEDs at room temperature. After 2 hours of irradiation, the blue LEDs were turned off, and one vial was removed for analysis. The remaining five vials were stirred in the dark for an additional 2 hours. At this point, another vial was removed for analysis, and the blue LEDs were turned back on to irradiate the remaining four reaction mixtures. After another 2 hours of irradiation, the blue LEDs were turned off again, and a third vial was removed for analysis. The remaining three vials were stirred in the dark for an additional 2 hours. Then, one more vial was removed for analysis, and the blue LEDs were turned on once more for 2 hours of irradiation. After this final period of light exposure, one vial was removed for analysis, leaving the last vial to be stirred in the dark for an additional 2 hours before analysis. In Figure 10, the blue line represents the yield of the reaction during intervals of light exposure and darkness.

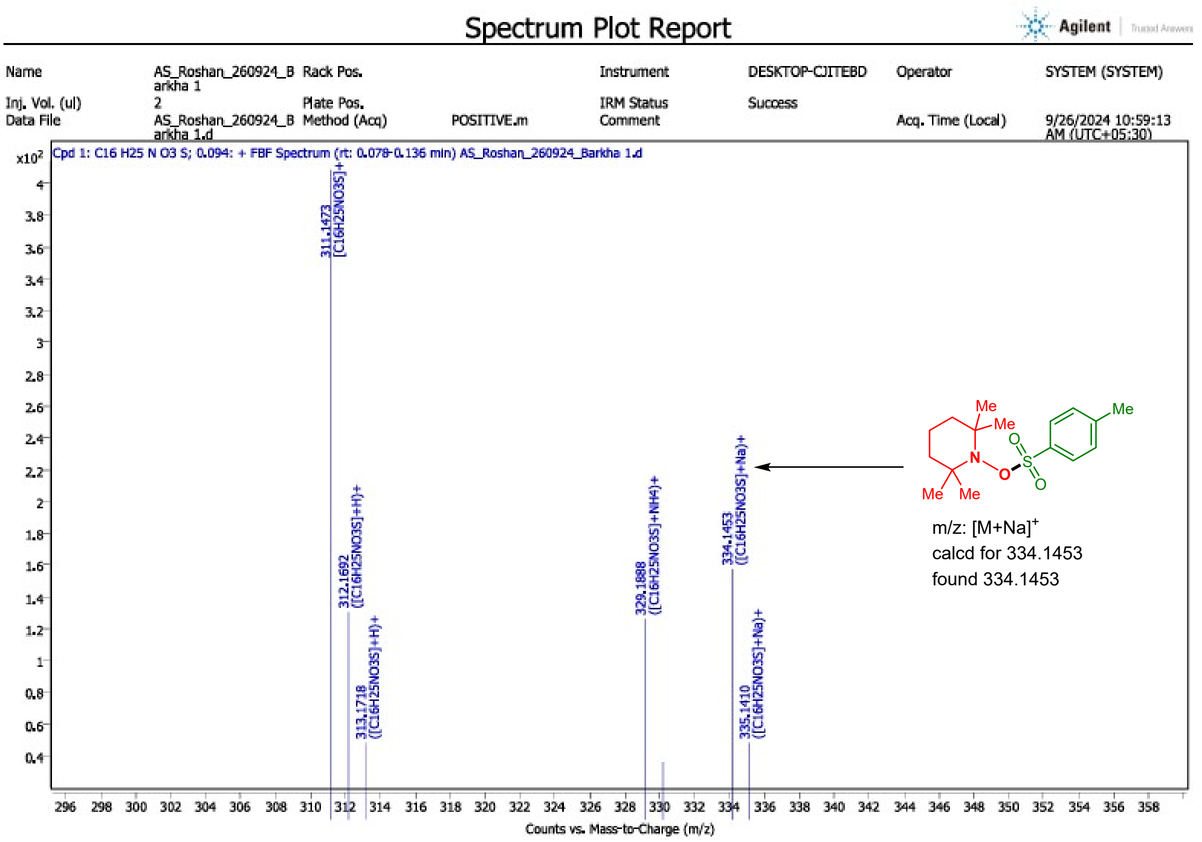
In continuously irradiated with blue LEDs, six standard reaction mixtures in 10 mL vial were charged with ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane **1a** (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate **2a** (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3.0 equiv.) in DMA (0.5 mL), and the vial was purged with Ar for 10 min. After every 2 h one tube was removed for analysis. In Figure 10 the red line represents the yield of the reaction continuously irradiated with visible light.

5.6 Radical Trapping Experiments



Scheme 2: Radical trapping experiment with TEMPO

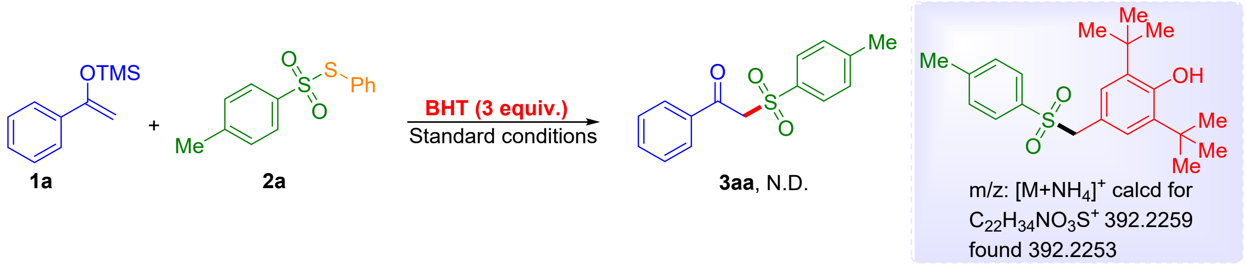
To a glass vial, charged with a magnetic stir bar, *O*-silyl enol ethers (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3 equiv.), TEMPO (193.3 mg, 0.9 mmol, 3.0 equiv), was added. The flask was evacuated and backfilled with argon and then DMA (0.5 mL) was added. The reaction mixture was stirred and irradiated with a 456 nm Kessil LED lamp (approximately 2 cm away from the light source) at room temperature for 14 h. The reaction was completely quenched and a trace amount of product **3a** was obtained. Furthermore, the TEMPO-adduct was detected by HRMS.



Spectrum Plot Report

Name	AS_Roshan_260924_Barkha 1	Rack Pos.		Instrument	DESKTOP-CJITEBD	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	AS_Roshan_260924_Barkha 1.d	Method (Acq)	POSITIVE.m	Comment		Acq. Time (Local)	9/26/2024 10:59:13 AM (UTC+05:30)

m/z: $[M+Na]^+$
calcd for 334.1453
found 334.1453

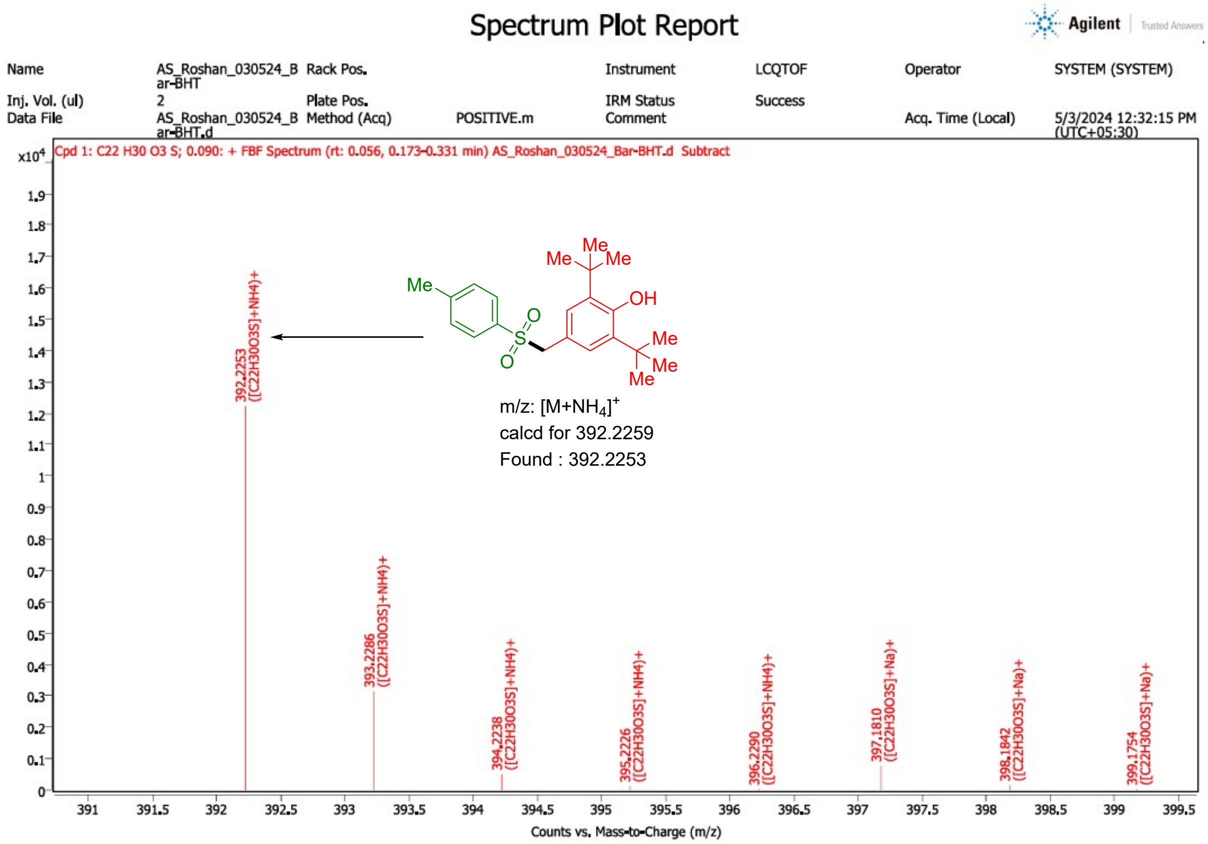


m/z: $[M+NH_4]^+$ calcd for $C_{22}H_{34}NO_3S^+$ 392.2259
found 392.2253

Scheme 3: Radical trapping experiment with BHT

To a glass vial, charged with a magnetic stir bar, *O*-silyl enol ethers (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3 equiv.), BHT (193.3 mg, 0.9 mmol, 3.0 equiv), was added. The flask was evacuated and backfilled with argon and then DMA (0.5 mL) was added. The reaction mixture was stirred and irradiated with a 456 nm Kessil LED lamp (approximately 2 cm away from the light source) at room temperature for 14 h. The reaction was completely quenched and product **3a** was not obtained. Furthermore, the BHT-adduct was detected by HRMS.

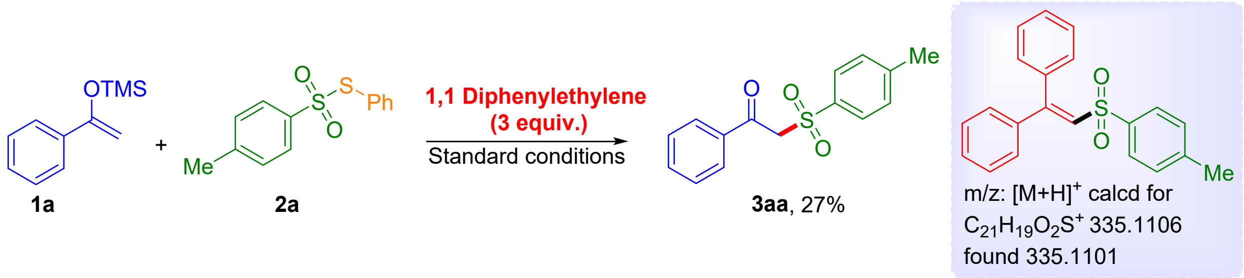
Spectrum Plot Report



Name	AS_Roshan_030524_Bar-BHT	Rack Pos.		Instrument	LCQTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	AS_Roshan_030524_Bar-BHT.d	Method (Acq)	POSITIVE.m	Comment		Acq. Time (Local)	5/3/2024 12:32:15 PM (UTC+05:30)

Cpd 1: C22 H30 O3 S; 0.090: + FBF Spectrum (rt: 0.056, 0.173-0.331 min) AS_Roshan_030524_Bar-BHT.d Subtract

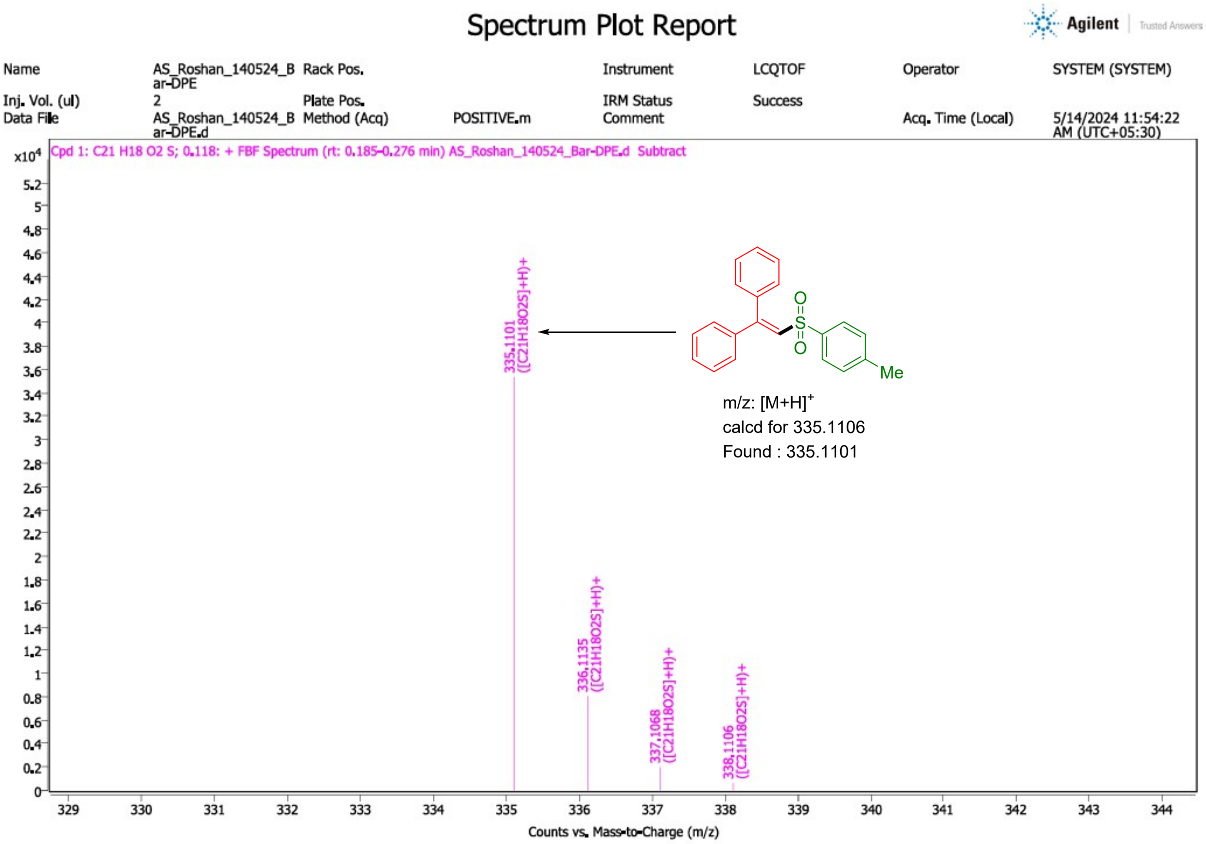
m/z: $[M+NH_4]^+$
calcd for 392.2259
Found : 392.2253



m/z: $[M+H]^+$ calcd for $C_{21}H_{19}O_2S^+$ 335.1106
found 335.1101

Scheme 4: Radical trapping experiment with 1,1-diphenylethylene

To a glass vial, charged with a magnetic stir bar, *O*-silyl enol ethers (0.2 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (0.24 mmol, 1.2 equiv.), DABCO (0.6 mmol, 3 equiv.), 1,1-diphenylethylene (193.3 mg, 0.9 mmol, 3.0 equiv), was added. The flask was evacuated and backfilled with argon and then DMA (0.5 mL) was added. The reaction mixture was stirred and irradiated with a 456 nm Kessil LED lamp (approximately 2 cm away from the light source) at room temperature for 14 h. The reaction was completely quenched and product **3a** was obtained in 27% yield. Furthermore, the DPE-adduct was detected by HRMS.



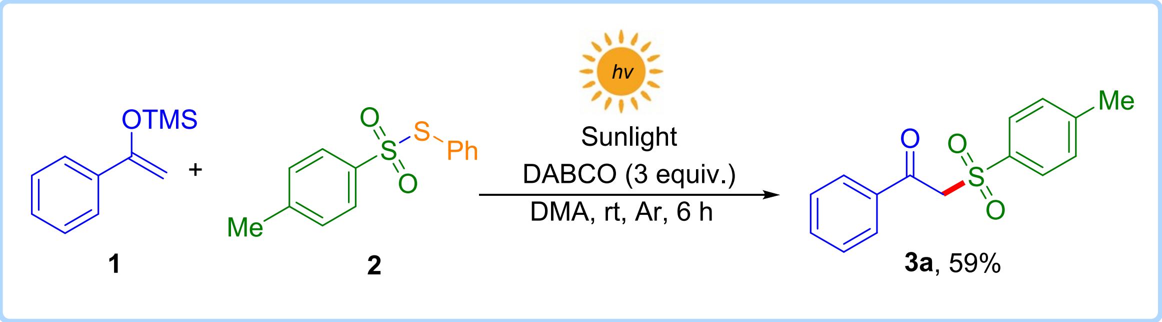
Spectrum Plot Report

Name	AS_Roshan_140524_Bar-DPE	Rack Pos.		Instrument	LCQTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	AS_Roshan_140524_Bar-DPE.d	Method (Acq)	POSITIVE.m	Comment		Acq. Time (Local)	5/14/2024 11:54:22 AM (UTC+05:30)

m/z: $[M+H]^+$
calcd for 335.1106
Found : 335.1101

5.7 Irradiation with natural sunlight

Figure 11: Typical reaction setup under sunlight



To a glass vial, charged with magnetic stir, *O*-silyl enol ethers (0.5 mmol), *S*-phenyl-4-methylbenzenesulfonothioate (0.6 mmol, 1.2 equiv.), DABCO (1.5 mmol, 3 equiv.) was added. The flask was evacuated and backfilled with argon and then DMA (1.0 mL) was added. Then the reaction was carried out under sunlight for 6 h (from 10:00 am to 16:00 pm, 26/04/2024, Roorkee, IIT Roorkee, Uttarakhand, India). After the completion of the reaction, the residue was diluted with water (40 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with hexane/ethyl acetate as eluent to afford the desired products **3a** in 59% yield (80.9 mg).

5.8. Photochemical Quantum Yield (φ):

A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure[6] outlined in the Handbook of Photochemistry.[7] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength.
The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

(1) **Ferrioxalate solution** (0.012 M): Potassium ferrioxalate hydrate (147.4 mg) was added to a flask wrapped in aluminum foil containing 69.5 µL H_2SO_4 (96%) to a 25 mL volumetric flask and filled to the mark with water. The flask was stirred for complete dissolution of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

(2) **Phenanthroline solution**: 0.2% by weight of 1,10-Phenanthroline in water (50 mg in 25 mL).

(3) **Buffer solution**: to a 100 mL volumetric flask, 4.94 g of NaOAc and 1.0 mL of H_2SO_4 (96%) were added and filled to the mark with water.

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (1.0 mL), and the stirred solution was irradiated for 90 s at λ = 456 nm. After irradiation, the actinometer solution was carefully transferred into a 10 mL volumetric flask, the phen solution (0.5 mL) and 2.0 mL of buffer solution was added and the flask was filled up with water and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance of the sample was measured at 510 nm to be 2.024.

A non-irradiated sample was also prepared and the absorbance at 510 nm was measured to be 0.193.

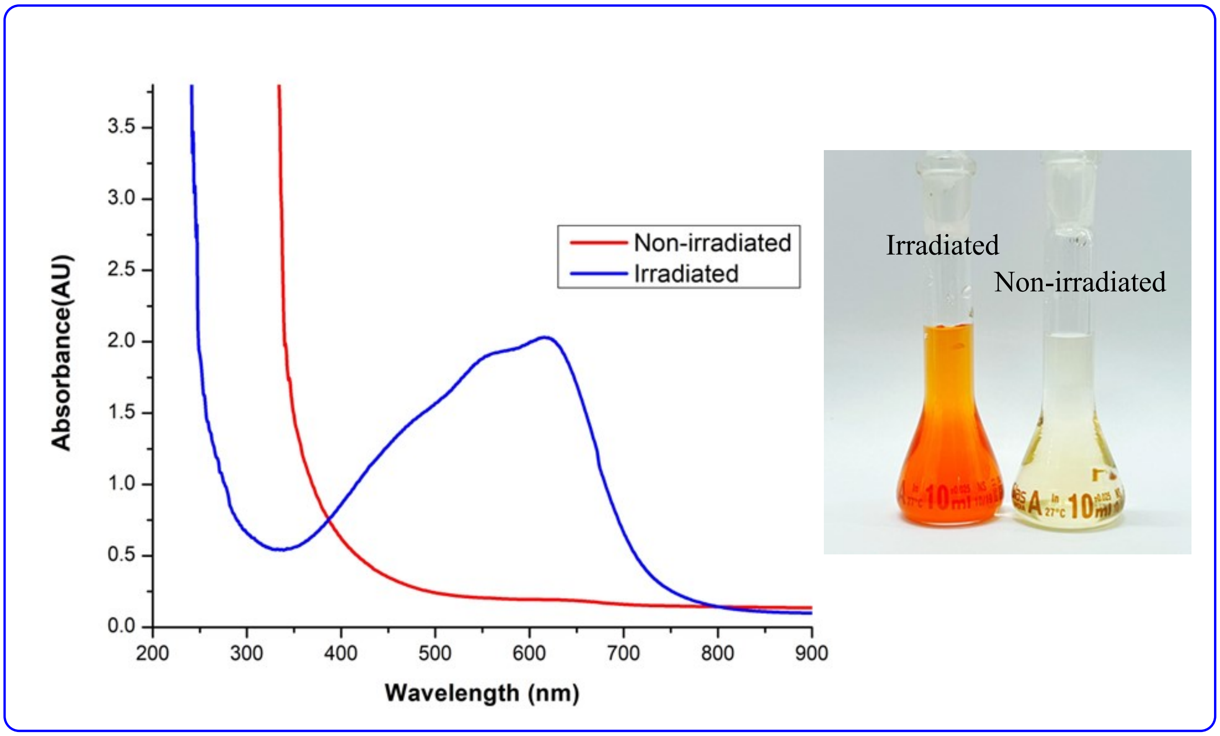


Figure 12: Absorption spectra for non-irradiated and irradiated samples of red $[Fe(phen)_3]^{+2}$

The quantum yield for our model photochemical reaction was determined using previously reported methods using equation 1:

$$\Phi(reaction\ at\ 456\ nm) = \frac{mol\ of\ product}{mol\ of\ photon\ flux.\ t.f} \qquad (1)$$

Where, Φ = quantum yield of the reaction,

t = time of the reaction (s),

f = incident light absorbed by the EDA Complex at 456 nm and

the photon flux is calculated by standard ferrioxalate actinometry.

The fraction of light, f, absorbed was determined according to equation 2:

$$f = 1 - 10^{-A} \qquad (2)$$

here A = absorbance of the EDA Complex in DMA at 456 nm.

Photon flux sample calculation

The photon flux is defined as shown in equation 3:

$$Photon\ Flux\ = \frac{mol\ Fe^{+2}}{\Phi(Fe^{+2}).t.f} \qquad (3)$$

Where $\boldsymbol{\Phi}$ is the quantum yield for the ferrioxalate actinometer (1.01 at λ = 438 nm), t is the time (s), and the mol of Fe^{+2} is calculated according to equation 4.

$$mol\left(Fe^{+2}\right) = \frac{V_1.V_3.\Delta A\ (510\ nm)}{10^3.V_2.\,l.\in(510\ nm)} \qquad (4)$$

V_1 = irradiated volume (1 mL) V_2 = aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 = final volume after complexation with phenanthroline (10 mL) l = optical path-length of the irradiation cell (1 cm) ΔA (510 nm) = optical difference in absorbance between the irradiated solution and that taken in the dark (2.024 – 0.193 = 1.831)

$$mol\left(Fe^{+2}\right) = \frac{1\ mL.10\ mL.1.831}{10^3.1\ mL.\,1\ cm.\,11100\ L\ mol^{-1}.cm^{-1}} \quad = 1.649\ x\ 10^{-6} \qquad (4)$$

fraction of light absorbed at 456 nm for the ferrioxalate solution are calculated by eq. 2.

$$f = 1 - 10^{-2.024}$$

$$f = \quad 0.990$$

Absorption of ferrioxalate solution at 456 nm = 2.024

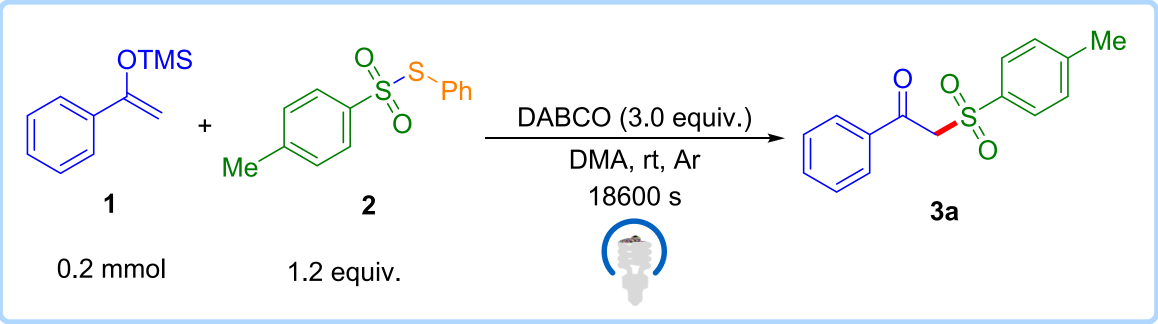
The photon flux can be calculated using eq 3.

$$Photon\ Flux\ = \frac{1.649\ x\ 10^{-6}}{1.01\ x\ 90\ x\ 0.990} \quad = 1.832\ x\ 10^{-8} \qquad (3)$$

Quantum yield determination of photochemical reaction

The quantum yield (ϕ) is calculated using eq 4.

$$quantum\ yield\ (reaction\ at\ 456\ nm) = \frac{mol\ of\ formed\ product}{mol\ of\ photon\ flux.\,t.\,f} \qquad (4)$$



On stirring the reaction under a 456 nm kessil lamp at room temperature for 18600 sec the reaction mixture produced 6.99 x 10-5 of the β-keto sulfones.

fraction of light absorbed at 456 nm for the photocatalytic reaction

$$f = 1 - 10^{-A} \qquad (2)$$

A = Absorption of photocatalytic reaction (0.125) **f = 0.2502**

$$quantum\ yield\ \Phi\ (reaction\ at\ 456\ nm) = \frac{6.99\ x\ 10^{-5}}{1.832\ x\ 10^{-8}\ x18600\ x\ 0.25}$$

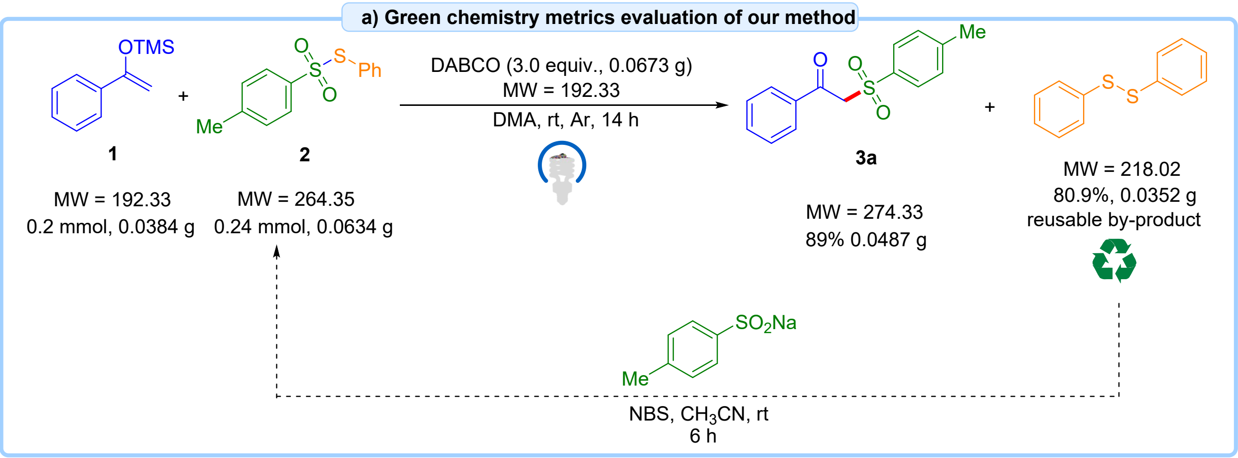
$$quantum\ yield\ \Phi\ (reaction\ at\ 456\ nm) = 0.82$$

Inference: The value of quantum yield is lower than unity suggesting the possibility of a closed chain pathway for the reaction.

6. Calculation of green chemistry metrics

The green chemistry metrics including Atom Economy (AE), Atom Efficiency (AEf), Effective Mass Yield (EMY), Carbon efficiency, Reaction Mass Efficiency (RME), Optimum Efficiency (OE), Process Mass Intensity (PMI), Mass Intensity (MI), Mass Productivity (MP), E-factor, Solvent Intensity (SI), Water Intensity (WI), Turnover Number (TON), and Turnover Frequency (TOF) were calculated according to literature.[8]

Green chemistry metrics evaluation of our method



This work

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{274.334}{192.33 + (1.2\ x\ 264.357)} \times 100 = 96.6\%$$

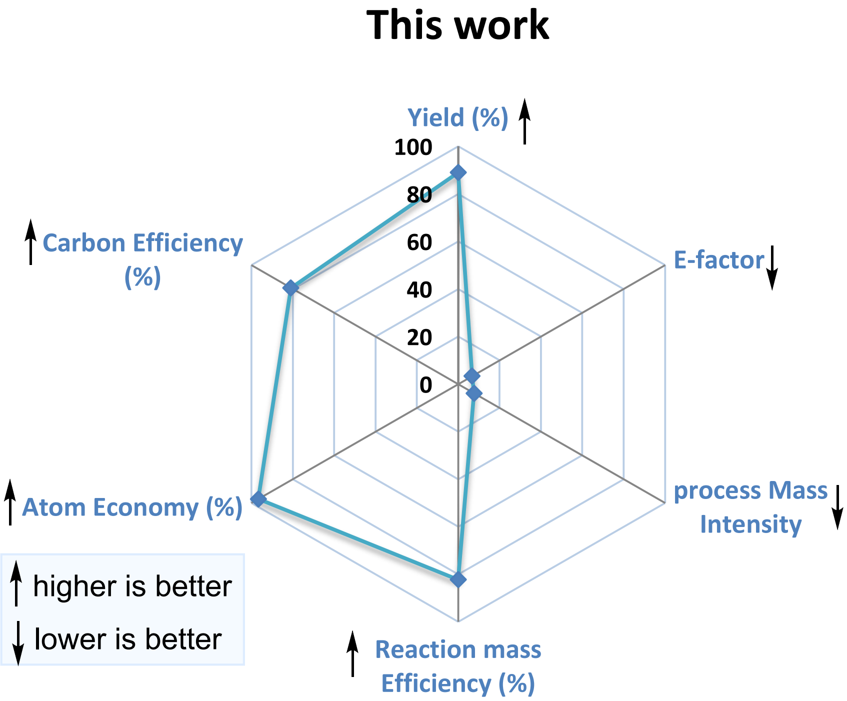
$$AEt\ (\%) = AE\ \times yield\% = 96.6\ \times 89\% = \ 85.9\%$$

$$Carbon\ efficiency\ (\%) = \frac{moles\ of\ products\ x\ no.\ of\ carbon\ of\ products}{moles\ of\ reactants\ x\ no.\ of\ carbon\ of\ reactants} \times 100 = \frac{(0.000177\ x\ 15) + (}{(0.0002\ x\ 11) + (0} \times 100 = 80.92\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100 = \frac{0.0472\ g + 0.035\ g}{0.0384\ g + 0.0634\ g} \times 100 = \ 82.22\%$$

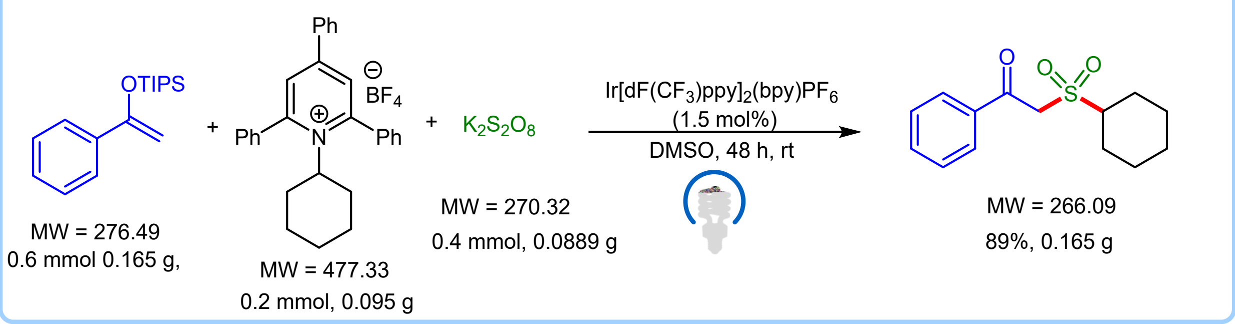
$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.0384\ g + 0.0634\ g + 0.47\ g + 0.0673g - 0.0487\ g - 0.035\ g}{0.0487\ g + 0.035\ g} = 6.7$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ solvents)}{Mass\ of\ product} = \frac{0.0}{} = 7.65$$



Green chemistry metrics evaluation of Ye, Wu and co-workers work[9a]

(b) Ye, Wu and co-workers (2019)



$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{266.0974}{477.3536 + (2\ x\ 222.33) + (3\ x} = 15.19\%$$

$$AEt\ (\%) = AE\ \times yield\% = 15.19\ \times 89\% =\ 13.52\%$$

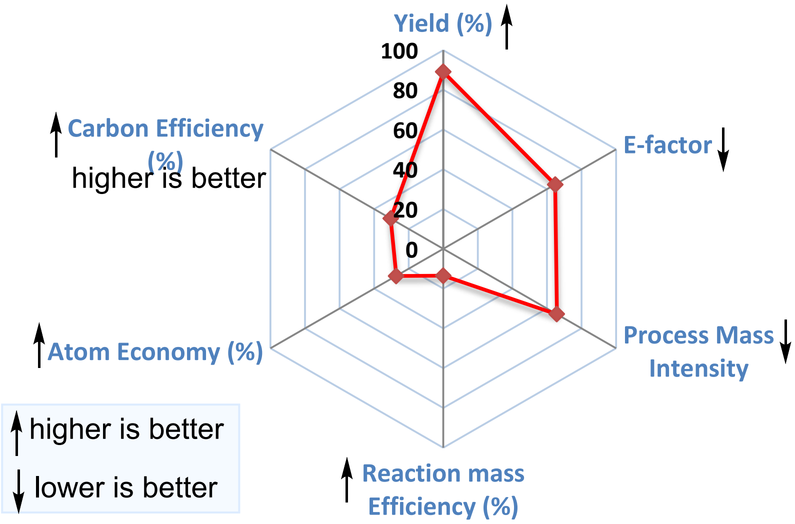
$$Carbon\ efficiency\ (\%) = \frac{moles\ of\ products\ x\ no.\ of\ carbon\ of\ products}{moles\ of\ reactants\ x\ no.\ of\ carbon\ of\ reactants} \times 100 = \frac{0.000177\ x\ 14}{0.0002\ x\ 29 + 0.0006\ x\ 17} \times 100 = 15.51\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100 = \frac{0.0472\ g}{0.0954\ g + 0.0889\ g + 0.165\ g} \times 100 =\ 13.51\%$$

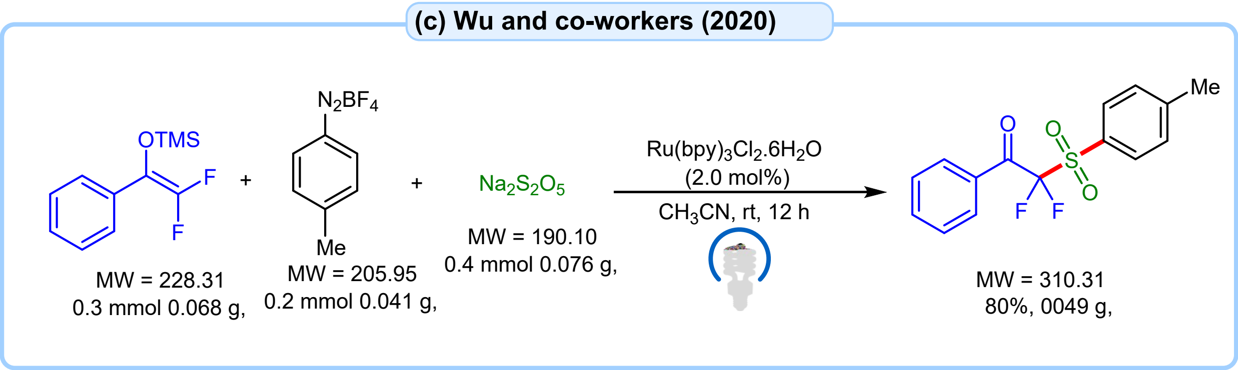
$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.0954\ g + 0.0889\ g + 0.165\ g + 0.003g + 2.75 - 0.0472\ g}{0.0472\ g} = 64.72$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ solvents)}{Mass\ of\ product} = \frac{0}{} = 65.72$$

Ye, and Wu's work (2019)



Green chemistry metrics evaluation of Wu and co-workers work[9b]



$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{310.3140}{205.9506 + 2\ x\ 190.107 + 1.5\ x\ 228.3138} = 33.41\%$$

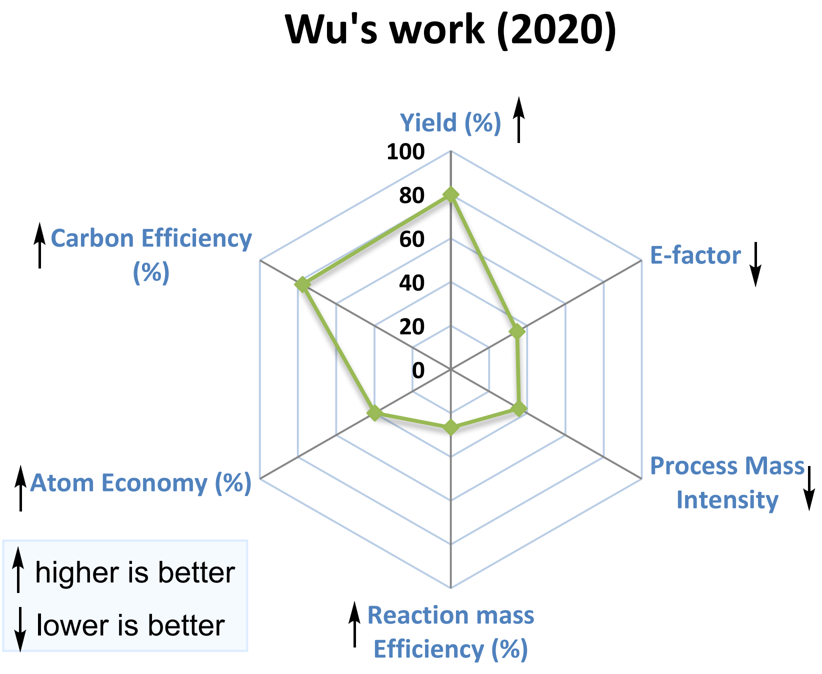
$$AEt\ (\%) = AE\ \times yield\% = 33.41\ \times 80\% =\ 26.73\%$$

$$Carbon\ efficiency\ (\%) = \frac{moles\ of\ products\ x\ no.\ of\ carbon\ of\ products}{moles\ of\ reactants\ x\ no.\ of\ carbon\ of\ reactants} \times 100 = \frac{0.000157\ x\ 14}{0.0002\ x\ 7 + 0.0003\ x\ 11} \times 100 = 47.03\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100 = \frac{0.049\ g}{0.041\ g + 0.076\ g + 0.068\ g} \times 100 =\ 26.48\%$$

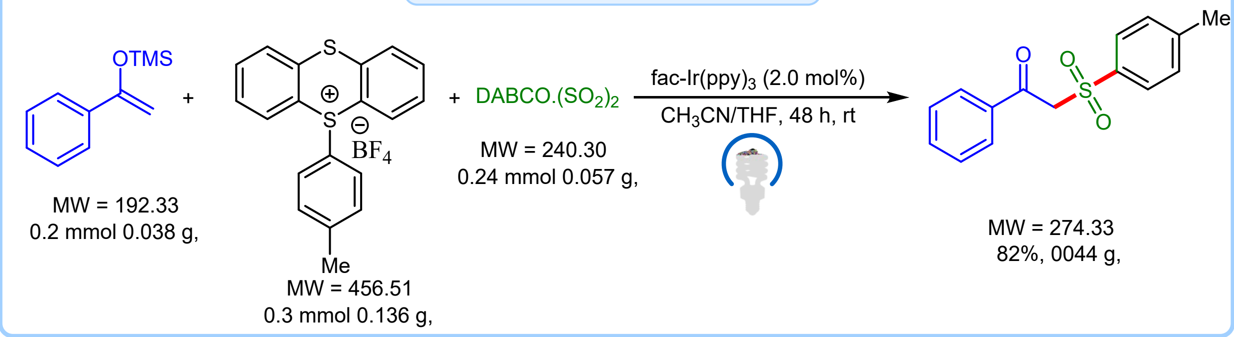
$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.041\ g + 0.076\ g + 0.068\ g + 0.0029\ g + 1.56 - 0.049\ g}{0.049\ g} = 34.67$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ solvents)}{Mass\ of\ product} = 35.67$$



Green chemistry metrics evaluation of He, Wu and co-workers work[9c]

(d) He, Wu and co-workers (2022)



$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{2}{1.5\ x\ 456.5122 + 1} = 23.54\%$$

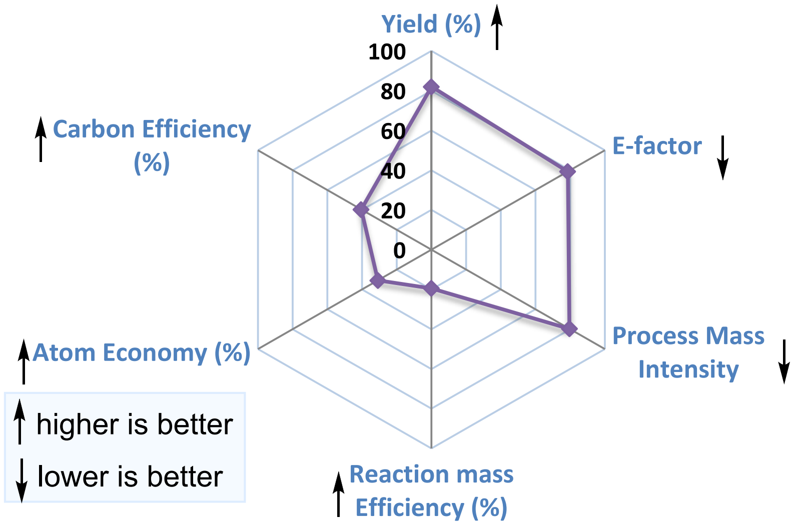
$$AEt\ (\%) = AE\ \times yield\% = 23.54\ \times 82\% =\ 19.30\%$$

$$Carbon\ efficiency\ (\%) = \frac{moles\ of\ products\ x\ no.\ of\ carbon\ of\ products}{moles\ of\ reactants\ x\ no.\ of\ carbon\ of\ reactants} \times 100 = \frac{}{0.0003} \times 100 = 25.36\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100 = \frac{0.0449\ g}{0.136\ g + 0.057\ g + 0.038\ g} \times 100 =\ 19.43\%$$

$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.136\ g + 0.057\ g + 0.038\ g + 0.0026\ g}{0.0449\ g} = 78.59$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ sol}{Mass\ of\ product} = 79.59$$



He, and Wu's work (2022)

Table 3: Green chemistry metrics summary of our method compared to reported literature[9]

Method	AE(%)	AEt(%)	Carbon efficiency (%)	RME(%)	E-factor	PMI
This work	**96.6**	**85.9**	**80.9**	**82.2**	**6.7**	**7.6**
Ye and Wu’s work (2019)	**15.1**	**13.5**	**15.5**	**13.5**	**64.7**	**65.7**
Wu’s work (2020)	**33.4**	**26.7**	**47.0**	**26.4**	**34.6**	**35.6**
He and Wu’s work (2022)	**23.5**	**19.3**	**25.3**	**19.4**	**78.5**	**79.5**

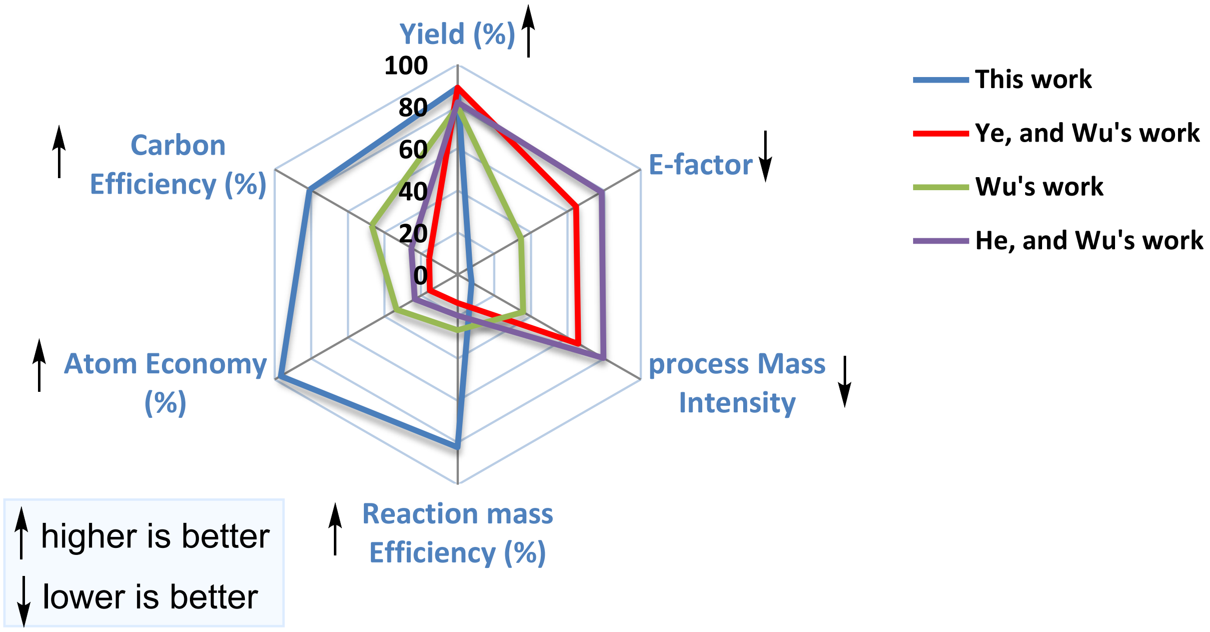
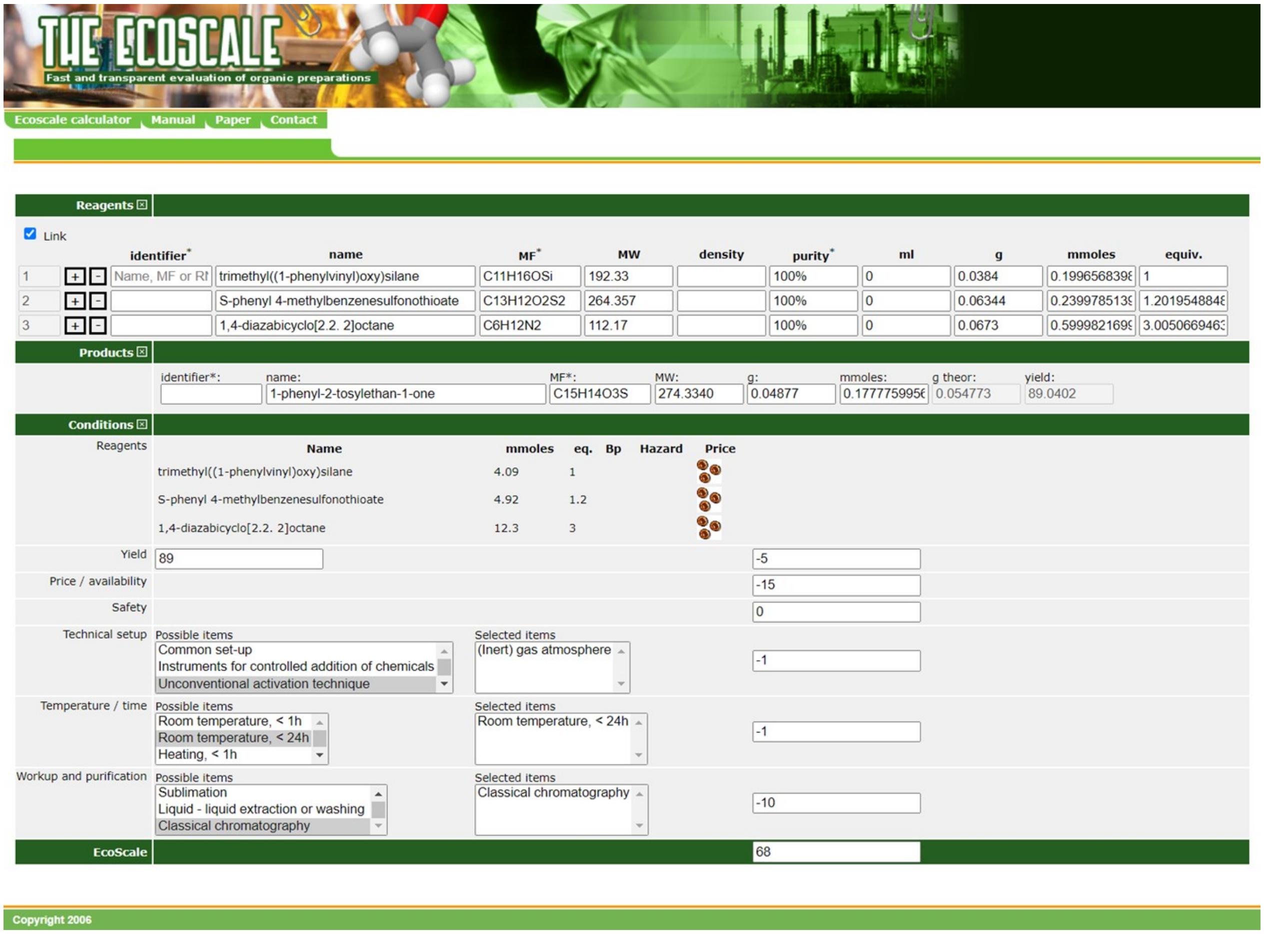


Figure 13: Summary of green chemistry metrics of our method compared to reported literature

7. Calculation of Ecoscale

Calculation of EcoScale of our method



Reagents ☒

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1	+ -	Name, MF or RI	trimethyl((1-phenylvinyl)oxy)silane	C11H16OSi	192.33		100%	0	0.0384	0.199656839	1
2	+ -		S-phenyl 4-methylbenzenesulfonothioate	C13H12O2S2	264.357		100%	0	0.06344	0.239978513	1.201954884
3	+ -		1,4-diazabicyclo[2.2. 2]octane	C6H12N2	112.17		100%	0	0.0673	0.599982169	3.005066946

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1-phenyl-2-tosylethan-1-one	C15H14O3S	274.3340	0.04877	0.177775995	0.054773	89.0402

Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
trimethyl((1-phenylvinyl)oxy)silane	4.09	1			●●●
S-phenyl 4-methylbenzenesulfonothioate	4.92	1.2			●●●
1,4-diazabicyclo[2.2. 2]octane	12.3	3			●●●

Yield	89		-5
Price / availability			-15
Safety			0
Technical setup	Possible items Common set-up Instruments for controlled addition of chemicals Unconventional activation technique	Selected items (Inert) gas atmosphere	-1
Temperature / time	Possible items Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Selected items Room temperature, < 24h	-1
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Classical chromatography	-10
EcoScale			68

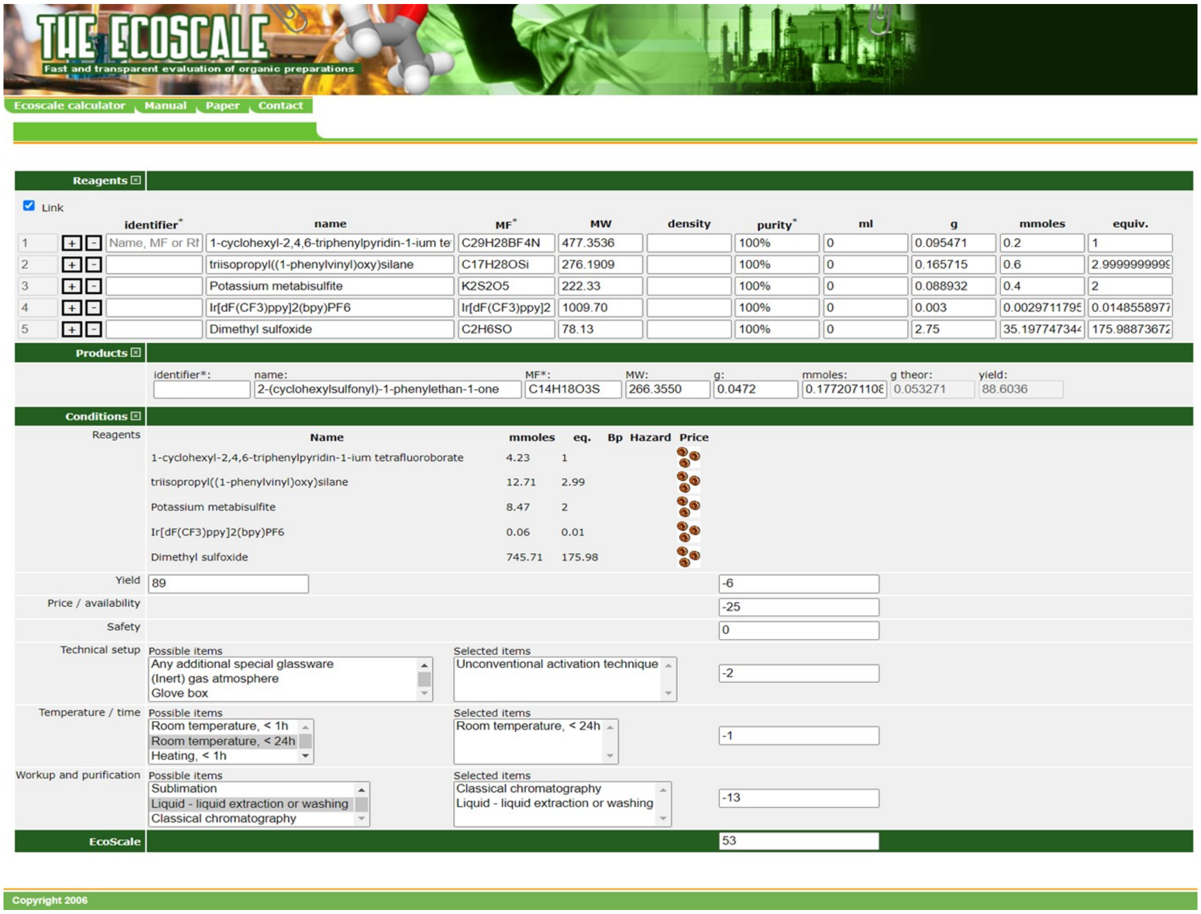
Copyright 2006

Figure 14: EcoScale of our method

Score on **EcoScale**; > 75, Excellent; >50, Acceptable; <50, Inadequate[8c]

EcoScale score = 68 (>50, it is an acceptable synthesis)

Calculation of EcoScale of Ye and Wu's work (2019)[9a]



Reagents ☒

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1	+ -	Name, MF or RI	1-cyclohexyl-2,4,6-triphenylpyridin-1-ium te	C29H28BF4N	477.3536		100%	0	0.095471	0.2	1
2	+ -		triisopropyl((1-phenylvinyl)oxy)silane	C17H28OSi	276.1909		100%	0	0.165715	0.6	2.999999999
3	+ -		Potassium metabisulfite	K2S2O5	222.33		100%	0	0.088932	0.4	2
4	+ -		Ir[dF(CF3)ppy]2(bpy)PF6	Ir[dF(CF3)ppy]2	1009.70		100%	0	0.003	0.002971179	0.014855897
5	+ -		Dimethyl sulfoxide	C2H6SO	78.13		100%	0	2.75	35.19774734	175.9887367

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	2-(cyclohexylsulfonyl)-1-phenylethan-1-one	C14H18O3S	266.3550	0.0472	0.177207110	0.053271	88.6036

Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate	4.23	1			●●●
triisopropyl((1-phenylvinyl)oxy)silane	12.71	2.99			●●●
Potassium metabisulfite	8.47	2			●●●
Ir[dF(CF3)ppy]2(bpy)PF6	0.06	0.01			●●●
Dimethyl sulfoxide	745.71	175.98			●●●

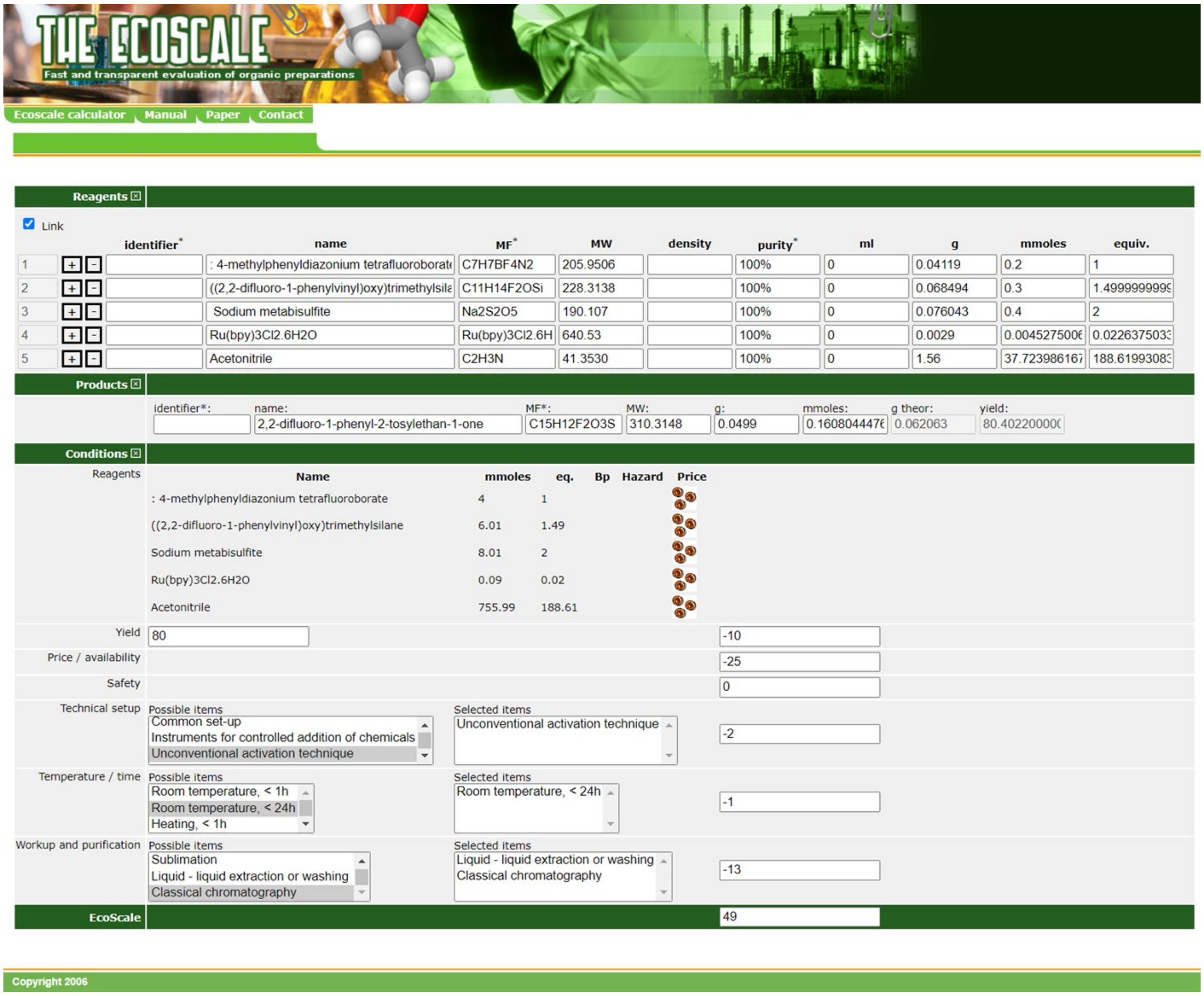
Yield	89		-6
Price / availability			-25
Safety			0
Technical setup	Possible items Any additional special glassware (Inert) gas atmosphere Glove box	Selected items Unconventional activation technique	-2
Temperature / time	Possible items Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Selected items Room temperature, < 24h	-1
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Classical chromatography Liquid - liquid extraction or washing	-13
EcoScale			53

Figure 15: EcoScale of Ye and Wu's work (2019)

Score on **EcoScale**; > 75, Excellent; >50, Acceptable; <50, Inadequate[8c]

EcoScale score = 53 (>50, it is an acceptable synthesis)

Calculation of EcoScale of Wu's work (2020)[9b]



Reagents ☒

☑ Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1 ⊞ ⊟		: 4-methylphenyldiazonium tetrafluoroborate	C7H7BF4N2	205.9506		100%	0	0.04119	0.2	1
2 ⊞ ⊟		((2,2-difluoro-1-phenylvinyl)oxy)trimethylsila	C11H14F2OSi	228.3138		100%	0	0.068494	0.3	1.499999999
3 ⊞ ⊟		Sodium metabisulfite	Na2S2O5	190.107		100%	0	0.076043	0.4	2
4 ⊞ ⊟		Ru(bpy)3Cl2.6H2O	Ru(bpy)3Cl2.6H	640.53		100%	0	0.0029	0.004527500	0.022637503
5 ⊞ ⊟		Acetonitrile	C2H3N	41.3530		100%	0	1.56	37.72398616	188.6199308

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	2,2-difluoro-1-phenyl-2-tosylethan-1-one	C15H12F2O3S	310.3148	0.0499	0.160804447	0.062063	80.40220000

Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
: 4-methylphenyldiazonium tetrafluoroborate	4	1			●●●
((2,2-difluoro-1-phenylvinyl)oxy)trimethylsilane	6.01	1.49			●●●
Sodium metabisulfite	8.01	2			●●●
Ru(bpy)3Cl2.6H2O	0.09	0.02			●●●
Acetonitrile	755.99	188.61			●●●

Yield	80		-10
Price / availability			-25
Safety			0
Technical setup	Possible items Common set-up Instruments for controlled addition of chemicals Unconventional activation technique	Selected items Unconventional activation technique	-2
Temperature / time	Possible items Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Selected items Room temperature, < 24h	-1
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Liquid - liquid extraction or washing Classical chromatography	-13
EcoScale			49

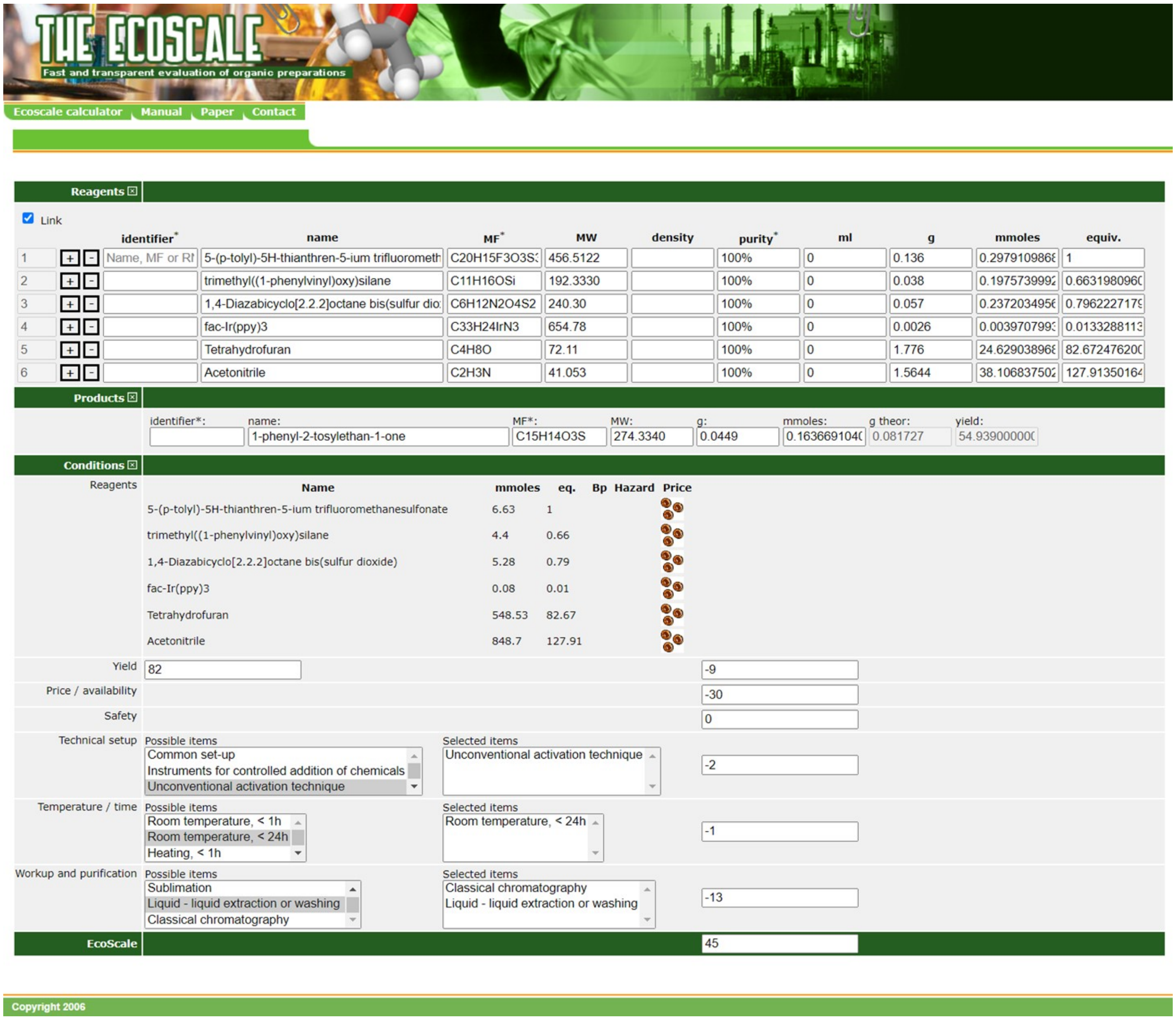
Copyright 2006

Figure 16: EcoScale of Wu's work (2020)

Score on **EcoScale**; > 75, Excellent; >50, Acceptable; <50, Inadequate[8c]

EcoScale score = 49 (<50, it is an inadequate synthesis)

Calculation of EcoScale of He and Wu's work (2022)[9c]



Reagents ☒

☑ Link

		identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1	+ -	Name, MF or RI	5-(p-tolyl)-5H-thianthren-5-ium trifluorometh	C20H15F3O3S3	456.5122		100%	0	0.136	0.2979109868	1
2	+ -		trimethyl((1-phenylvinyl)oxy)silane	C11H16OSi	192.3330		100%	0	0.038	0.1975739992	0.6631980960
3	+ -		1,4-Diazabicyclo[2.2.2]octane bis(sulfur dio:	C6H12N2O4S2	240.30		100%	0	0.057	0.2372034956	0.7962227179
4	+ -		fac-Ir(ppy)3	C33H24IrN3	654.78		100%	0	0.0026	0.0039707993	0.0133288113
5	+ -		Tetrahydrofuran	C4H8O	72.11		100%	0	1.776	24.629038968	82.672476200
6	+ -		Acetonitrile	C2H3N	41.053		100%	0	1.5644	38.106837502	127.91350164

Products ☒

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	1-phenyl-2-tosylethan-1-one	C15H14O3S	274.3340	0.0449	0.1636691040	0.081727	54.939000000

Conditions ☒

Reagents

Name	mmoles	eq.	Bp	Hazard	Price
5-(p-tolyl)-5H-thianthren-5-ium trifluoromethanesulfonate	6.63	1			●●●
trimethyl((1-phenylvinyl)oxy)silane	4.4	0.66			●●●
1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide)	5.28	0.79			●●●
fac-Ir(ppy)3	0.08	0.01			●●●
Tetrahydrofuran	548.53	82.67			●●●
Acetonitrile	848.7	127.91			●●●

Yield	82		-9
Price / availability			-30
Safety			0
Technical setup	Possible items Common set-up Instruments for controlled addition of chemicals Unconventional activation technique	Selected items Unconventional activation technique	-2
Temperature / time	Possible items Room temperature, < 1h Room temperature, < 24h Heating, < 1h	Selected items Room temperature, < 24h	-1
Workup and purification	Possible items Sublimation Liquid - liquid extraction or washing Classical chromatography	Selected items Classical chromatography Liquid - liquid extraction or washing	-13
EcoScale			45

Figure 17: EcoScale of He and Wu's work (2022)

Score on **EcoScale**; > 75, Excellent; >50, Acceptable; <50, Inadequate[8c]

EcoScale score = 45 (<50, it is an inadequate synthesis)

https://ecoscale.cheminfo.org/

summary of Ecoscale of our method compared to reported literature

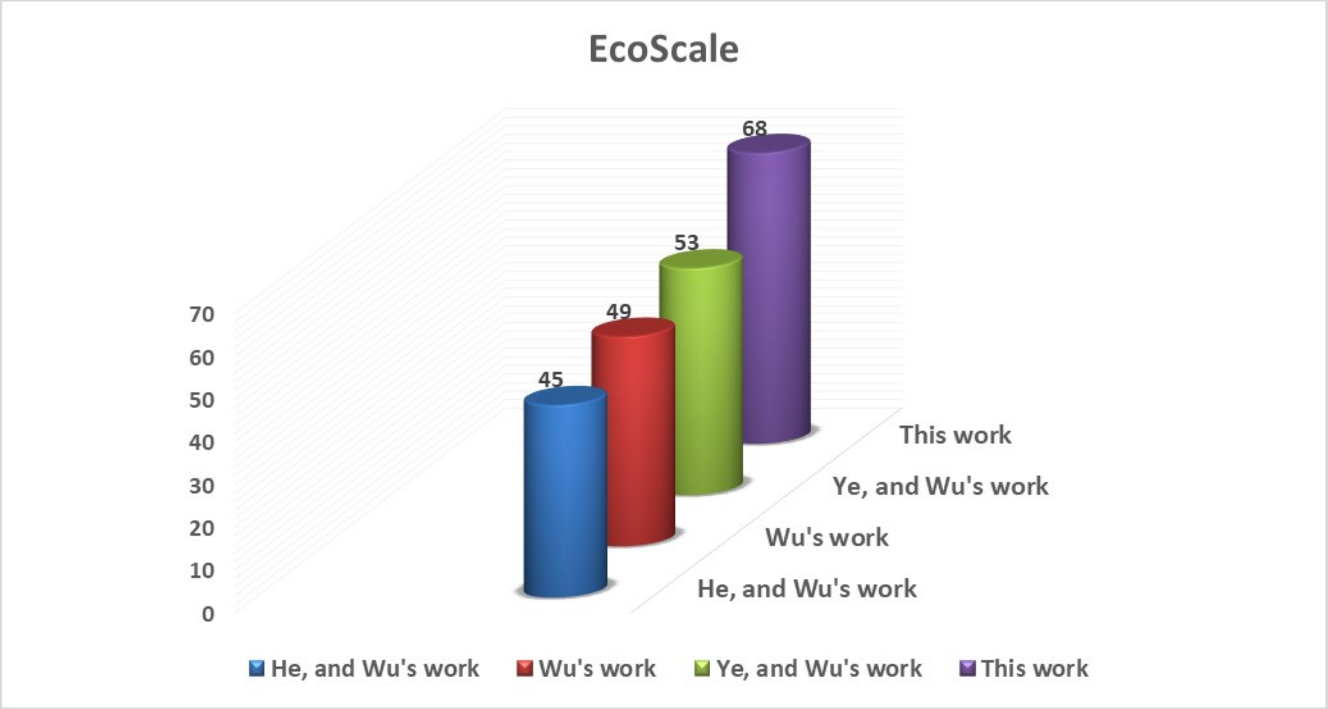
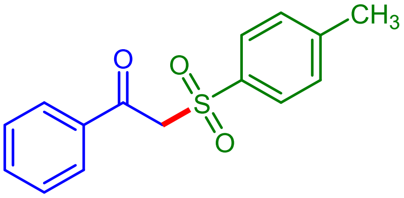


Figure 18: Summary of EcoScale compared to this work

8. NMR data

8.1 Characterization data of products

1-phenyl-2-tosylethan-1-one (3):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 89% (48.8 mg).

R$_f$: 0.37 (Mobile phase: 20% EtOAc in Hexane).

mp: 97-98 °C.

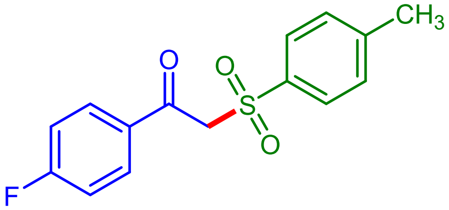
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.3, 145.5, 135.9, 135.8, 134.4, 129.9, 129.4, 128.9, 128.7, 63.6, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{14}NaO_3S$: $[M+Na]^+$, 297.0561; Found, 297.0557.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10a]

1-(4-fluorophenyl)-2-tosylethan-1-one (4):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 73% (42.7 mg).

R$_f$: 0.38 (Mobile phase: 20% EtOAc in Hexane).

mp: 138-139°C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 – 7.94 (m, 2H), 7.74 (dt, J = 8.5, 2.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.17-7.09 (m, 2H), 4.69 (s, 2H), 2.43 (s, 3H).

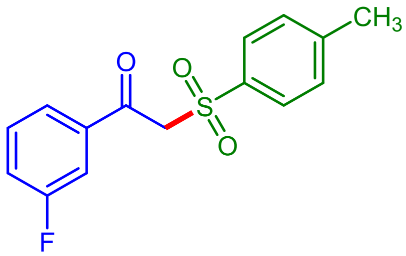
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 186.7, 166.5 (d, J = 258.2 Hz), 145.6, 135.7, 132.4 (d, J =10.1 Hz), 130.0, 128.6, 116.2 (d, J = 22.1 Hz), 63.7, 21.8.

^{19}F NMR (472 MHz, CDCl3, 300K): δ (ppm) = -102.4

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}FNaO_3S$: $[M+Na]^+$, 315.0467; Found, 315.0461.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10a]

1-(3-fluorophenyl)-2-tosylethan-1-one (5):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 69% (40.3 mg).

R$_f$: 0.42 (Mobile phase: 20% EtOAc in Hexane).

mp: 103-104 ^{o}C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.77 – 7.72 (m, 3H), 7.59 (dt, J = 9.5, 2.0 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.31-7.28 (m, 1H), 4.70 (s, 2H), 2.43 (s, 3H).

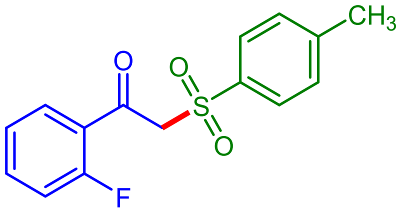
^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.1 (d, J = 3.4 Hz), 162.8 (d, J = 247.4 Hz), 145.7, 137.8 (d, J = 6.8 Hz), 135.6, 130.7 (d, J = 7.9 Hz), 130.0, 128.7, 125.5, 121.5 (d, J = 21.5 Hz), 115.9 (d, J = 22.6 Hz), 63.8, 21.8.

^{19}F NMR (472 MHz, CDCl3, 300K): δ (ppm) = -111.0

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}FNaO_3S$: [M+Na]$^+$, 315.0467; Found, 315.0461.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

1-(2-fluorophenyl)-2-tosylethan-1-one (6):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 65% (38.0 mg).

R$_f$: 0.36 (Mobile phase: 20% EtOAc in Hexane).

mp: 69-70 ^{o}C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.99-7.93 (m, 3H), 7.62 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.23-7.15 (m, 2H), 6.79 (d, *J* = 15.5 Hz, 1H), 2.45(s, 3H).

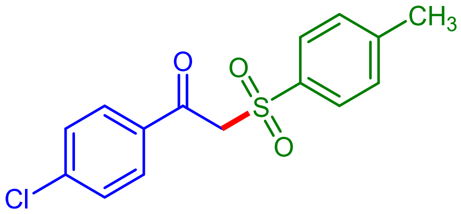
^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 140.8, 140.2, 138.3, 133.5, 131.3, 131.2, 131.1, 129.5,128.3, 127.7, 127.0, 126.6, 19.9.

^{19}F NMR (472 MHz, CDCl3, 300K): δ (ppm) = -108.9

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}FNaO_3S$: [M+Na]$^+$, 315.0467; Found, 315.0462.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10d]

1-(4-chlorophenyl)-2-tosylethan-1-one (7):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 79% (48.8 mg).

R$_f$: 0.43 (Mobile phase: 20% EtOAc in Hexane).

mp: 139-140^{o}C.

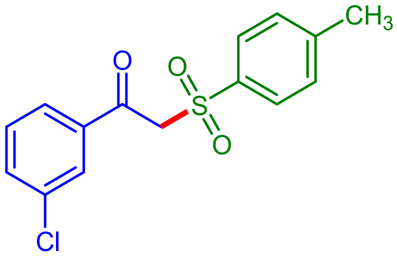
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (dt, J = 9.0, 2.0 Hz, 2H), 7.72 (dt, J = 8.5, 2.0 Hz, 2H), 7.41 (dt, J = 9.0, 2.5 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 4.69 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.2, 145.6, 141.1, 135.7, 134.2, 130.9, 130.0, 129.3, 128.6, 63.7, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}ClNaO_3S$: $[M+Na]^+$, 331.0172; Found, 331.0168.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

1-(3-chlorophenyl)-2-tosylethan-1-one (8):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 72% (44.8 mg).

R$_f$: 0.43 (Mobile phase: 20% EtOAc in Hexane).

mp: 127-128^{o}C.

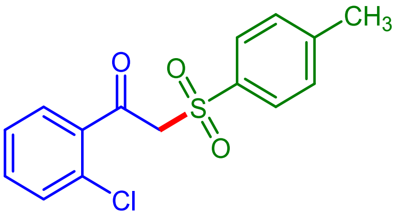
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 – 7.82 (m, 2H), 7.74 (dt, J = 8.0, 2.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.45-7.40 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 4.68 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.2, 145.7, 137.3, 135.6, 135.3, 134.3, 130.3, 130.0, 129.2, 128.7, 127.7, 63.8, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}ClNaO_3S$: $[M+Na]^+$, 331.0172; Found, 331.0167.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

1-(2-chlorophenyl)-2-tosylethan-1-one (9):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 43% (26.6 mg).

R$_f$: 0.41 (Mobile phase: 20% EtOAc in Hexane).

mp: 103-104°C.

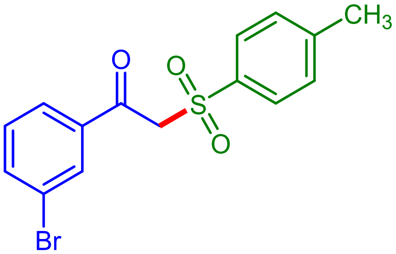
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.72 (d, J = 8.0 Hz, 2H), 7.50 (dd, J = 7.8, 1.5 Hz, 1H), 7.38 (td, J = 7.8, 2.0 Hz, 1H), 7.34-7.26 (m, 4H), 4.79 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.4, 145.5, 137.3, 136.0, 133.2, 131.6, 130.8, 130.7, 130.0, 128.6, 127.3, 66.4, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}ClNaO_3S$: $[M+Na]^+$, 331.0172; Found, 331.0169.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

1-(3-bromophenyl)-2-tosylethan-1-one (10):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 57% (40.3 mg).

R$_f$: 0.42 (Mobile phase: 20% EtOAc in Hexane).

mp: 128-129 °C.

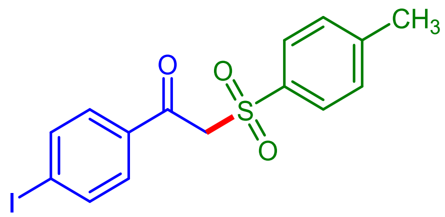
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (t, J = 2.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.76-7.71 (m, 3H), 7.39-7.31 (m, 3H), 4.68 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.1, 145.7, 137.5, 137.2, 135.6, 132.2, 130.5, 130.1, 128.7, 128.1, 123.2, 63.7, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}BrNaO_3S$: $[M+Na]^+$, 376.9646; Found, 376.9641.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10e]

1-(4-iodophenyl)-2-tosylethan-1-one (11):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 81% (64.8 mg).

R$_f$ = 0.45 (Mobile phase: 20% EtOAc in Hexane).

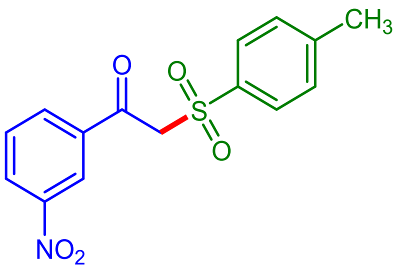
mp: 166-167 ^{o}C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.83 (dt, J = 8.5, 2.5 Hz, 2H), 7.72 (dt, J = 8.5, 2.0 Hz, 2H), 7.64 (dt, J = 8.5, 2.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 4.67 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.7, 145.7, 138.3, 135.6, 135.1, 130.7, 130.0, 128.6, 103.1, 63.7, 21.9.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}INaO_3S$: $[M+H]^+$, 422.9528; Found, 422.9523.

1-(3-nitrophenyl)-2-tosylethan-1-one (12):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 55% (35.2 mg).

R$_f$= 0.27 (Mobile phase: 20% EtOAc in Hexane).

mp = 133-134 ^{o}C.

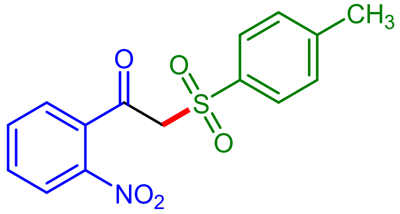
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.70 (t, J = 1.5 Hz, 1H), 8.44 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.33 (d, J = 8.5 Hz, 2H), 4.77 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 186.5, 148.5, 146.0, 137.0, 135.5, 135.0, 130.3, 130.1, 128.6, 128.4, 124.2, 63.9, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}NNaO_5S$: $[M+Na]^+$, 342.0412; Found, 342.0407.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

1-(2-nitrophenyl)-2-tosylethan-1-one (13):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow liquid.

Yield: 42% (26.8 mg).

R$_f$ = 0.26 (Mobile phase: 20% EtOAc in Hexane).

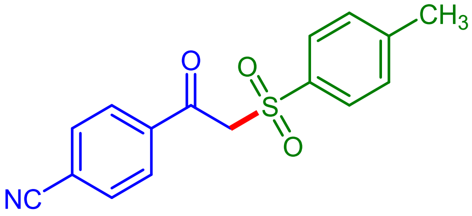
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.13 (dd, J = 8.3, 0.5 Hz, 1H), 7.82-7.74 (m, 3H), 7.68-7.63 (m, 1H), 7.61 (dd, J = 7.5, 1.5 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 4.59 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 190.1, 145.8, 145.3, 136.3, 135.9, 135.1, 131.7, 130.1, 129.1, 128.5, 124.3, 66.9, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}NNaO_5S$: [M+Na]$^+$, 342.0412; Found, 342.0409.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10b]

4-(2-tosylacetyl)benzonitrile (14):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 78% (46.7 mg).

R$_f$: 0.27 (Mobile phase: 20% EtOAc in Hexane).

mp: 154-155 °C.

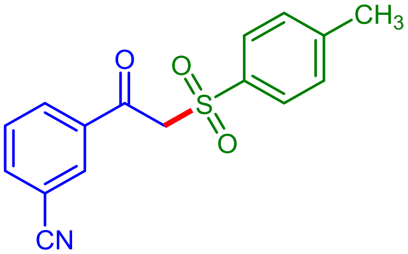
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.07 (dt, J = 8.5, 1.5 Hz, 2H), 7.78 (dt, J = 8.5, 1.5 Hz, 2H), 7.73 (dt, J = 8.0, 2.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.3, 146.0, 138.6, 135.4, 132.7, 130.1, 129.9, 128.6, 117.7, 117.5, 63.9, 21.9.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}NNaO_3S$: [M+Na]$^+$, 322.0514; Found, 322.0508.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10a]

3-(2-tosylacetyl)benzonitrile (15):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 85% (50.9 mg).

R$_f$: 0.23 (Mobile phase: 20% EtOAc in Hexane).

mp: 100-101 °C.

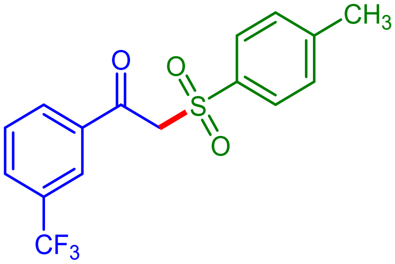
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.15 (dt, J = 8.0, 1.0 Hz, 1H), 8.12 (s, 1H), 7.81 (dt, J = 6.5, 1.0 Hz, 1H), 7.70 (dt, J = 6.5, 2.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 4.77 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 186.9, 145.9, 137.0, 136.5, 135.6, 133.4, 132.9, 130.1, 130.1, 128.6, 117.8, 113.3, 63.6, 21.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}NNaO_3S$: $[M+Na]^+$, 322.0514; Found, 322.0510.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10g]

2-tosyl-1-(3-(trifluoromethyl)phenyl)ethan-1-one (16):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 87% (59.6 mg).

R$_f$ = 0.36 (Mobile phase: 20% EtOAc in Hexane).

mp: 165-166 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.17 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H), 7.86 (t, J = 7.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 4.74 (s, 2H), 2.44 (s, 3H).

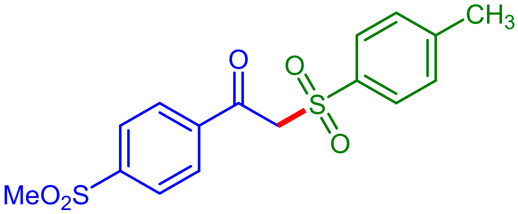
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.2, 145.9, 135.9 (d, J = 96.9 Hz), 132.7, 131.6 (d, J = 33.5 Hz), 130.7(q, J = 4.8 Hz), 130.1, 129.7, 128.7, 126.1 (q, J = 4.0 Hz), 124.6, 122.4, 63.8, 21.8.

^{19}F NMR (472 MHz, CDCl3, 300K): δ (ppm) = -62.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}F_3NaO_3S$: $[M+Na]^+$, 365.0435; Found, 365.0426.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10f]

1-(4-(methylsulfonyl)phenyl)-2-tosylethan-1-one (17):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 74% (52.2 mg).

R$_f$ = 0.22 (Mobile phase: 30% EtOAc in Hexane).

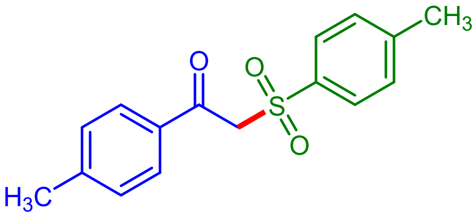
mp: 155-156 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.14 (dt, *J* = 9.0, 1.5 Hz, 2H), 8.05 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.74 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.75 (s, 2H), 3.10 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.4, 146.0, 145.2, 139.6, 135.5, 130.4, 130.1, 128.6, 128.0, 64.1, 44.3, 21.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{16}NaO_5S_2$: [M+Na]$^+$, 375.0337; Found, 375.0334.

1-(p-tolyl)-2-tosylethan-1-one (18):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 90% (51.9 mg).

R$_f$: 0.43 (Mobile phase: 20% EtOAc in Hexane).

mp: 108-109 °C.

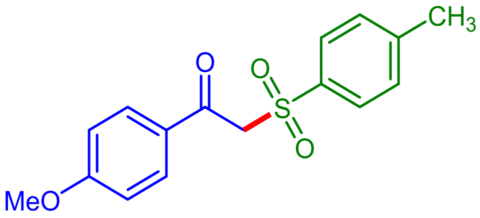
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.82 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.69 (s, 2H), 2.41 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.8, 145.6, 145.4, 135.9, 133.4, 129.9, 129.6, 129.6, 128.7, 63.5, 21.9, 21.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{16}NaO_3S$: [M+Na]$^+$, 311.0718; Found, 311.0711.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

1-(4-methoxyphenyl)-2-tosylethan-1-one (19):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow solid.

Yield: 93% (56.6 mg).

R_f = 0.30 (Mobile phase: 20% EtOAc in Hexane).

mp: 128-129 °C.

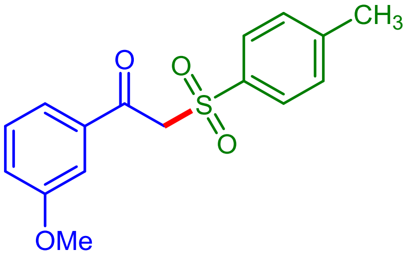
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (dt, J = 9.0, 2.5 Hz, 2H), 7.74 (dt, J = 8.5, 2.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.92 (dt, J = 9.0, 3.0 Hz, 2H), 4.66 (s, 2H), 3.86 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 186.4,164.6, 145.4, 135.9, 132.0, 129.9, 129.0, 128.6, 114.1, 63.6, 55.7, 21.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{16}NaO_4S$: $[M+Na]^+$, 327.0667; Found, 327.0662.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

1-(3-methoxyphenyl)-2-tosylethan-1-one (20):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow solid.

Yield: 89% (54.2 mg).

R_f = 0.28 (Mobile phase: 20% EtOAc in Hexane).

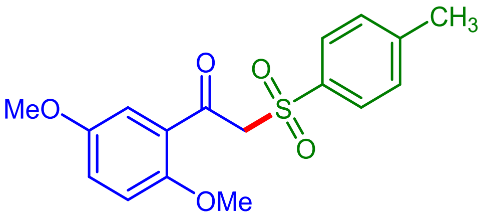
mp: 97-98 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.70 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.0 Hz, 1H), 7.34 (s, 1H), 7.31-7.20 (m, 3H), 7.09-7.02 (m, 1H), 4.69 (s, 2H), 3.73 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.2, 159.9, 145.4, 137.1, 136.0, 129.9, 128.6, 122.2, 121.0, 113.1, 63.6, 55.5, 21.7.

HRMS-ESI (m/z) calc'd for $C_{16}H_{16}NaO_4S$: $[M+Na]^+$, 327.0667; Found, 327.0664.

1-(2,5-dimethoxyphenyl)-2-tosylethan-1-one (21):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow solid.

Yield: 86% (57.5 mg).

R$_f$ = 0.24 (Mobile phase: 20% EtOAc in Hexane).

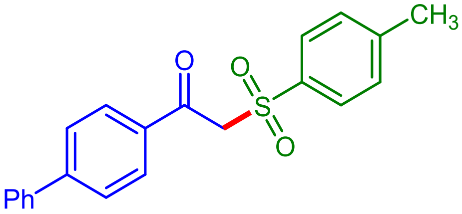
mp: 94-95 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.71 (dt, J = 8.5, 2.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 3.5 Hz, 1H), 7.00 (dd, J = 7.0, 3.5 Hz, 1H), 6.78 (d, J = 9.0 Hz, 1H), 4.90 (s, 2H), 3.76 (s, 3H), 3.70 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.8, 153.6, 153.5, 144.9, 136.8, 129.6, 128.5, 126.1, 122.3, 114.0, 113.3, 67.4, 56.1, 55.8, 21.7.

HRMS-ESI (m/z) calc'd for $C_{17}H_{18}NaO_5S$: [M+H]$^+$, 357.0773; Found, 357.0767.

1-([1,1'-biphenyl]-4-yl)-2-tosylethan-1-one (22):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 78% (54.7 mg).

R$_f$ = 0.41 (Mobile phase: 20% EtOAc in Hexane).

mp: 121-122 °C.

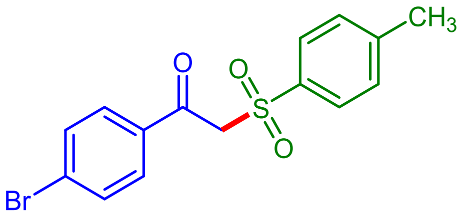
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (dt, J = 8.5, 2.0 Hz, 2H), 7.78 (dt, J = 8.5, 2.0 Hz, 2H), 7.70 (dt, J = 8.5, 2.0 Hz, 2H), 7.64-7.61 (m, 2H), 7.48 (t, J = 7.0 Hz, 2H), 7.42 (tt, J = 7.5, 1.5 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 4.75 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.8, 147.1, 145.5, 139.5, 135.8, 134.5, 130.1, 130.0, 129.1, 128.7, 128.7, 127.5, 127.4, 63.8, 21.8.

HRMS-ESI (m/z) calc'd for $C_{21}H_{18}NaO_3S$: [M+Na]$^+$, 373.0874; Found, 373.0866.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10d]

1-(4-bromophenyl)-2-tosylethan-1-one (23):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 79% (55.8 mg).

R$_f$: 0.51 (Mobile phase: 20% EtOAc in Hexane).

mp: 168-169 ^{o}C.

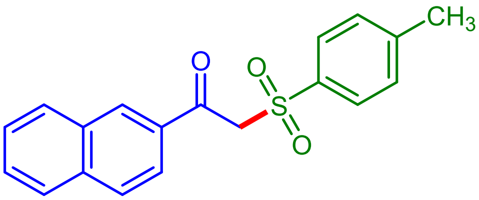
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.54 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 4.25 (s, 2H), 2.45 (s, 3H)

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 145.0, 134.8, 132.4, 131.8, 129.7, 128.6, 127.4, 123.2, 115.0, 62.1, 21.7.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}BrNaO_3S$: [M+Na]$^+$, 376.9646; Found, 376.9641.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

1-(naphthalen-2-yl)-2-tosylethan-1-one (24):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 65% (42.2 mg).

R$_f$: 0.41 (Mobile phase: 20% EtOAc in Hexane).

mp: 151-152 ^{o}C.

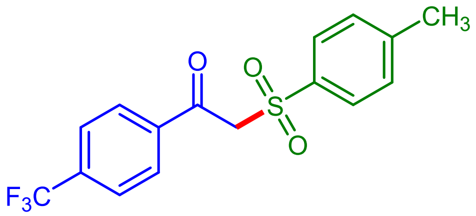
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.44 (s, 1H), 7.97-7.92 (m, 2H), 7.86 (dd, J= 8.5, 4.0 Hz, 2H), 7.77 (dt, J = 8.5, 2.0 Hz, 2H), 7.63 (td, J = 7.0, 1.5 Hz, 1H), 7.56 (td, J = 7.0, 1.5 Hz, 1H), 7.30 (d J = 8.0 Hz, 2H), 4.85 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.1, 145.5, 136.1, 135.8, 133.2, 132.4, 132.3, 130.1, 129.9, 129.5, 128.9, 128.7, 127.9, 127.2, 124.0, 63.8, 21.8.

HRMS-ESI (m/z) calc'd for $C_{19}H_{16}NaO_3S$: [M+Na]$^+$, 347.0718; Found, 347.0713.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (25):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 69% (47.3 mg).

R_f: 0.39 (Mobile phase: 20% EtOAc in Hexane).

mp: 135-136 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 (d, J = 9.0 Hz, 2H), 7.71 (t, J = 8.5 Hz, 4H), 7.31 (d, J = 8.0 Hz, 2H), 4.75 (s, 2H), 2.41 (s, 3H).

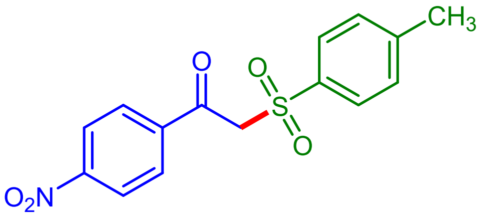
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.6, 145.8, 138.4, 135.3 (q, J = 32.5 Hz), 130.0, 129.8, 128.6, 128.5, 125.9 (q, J = 4.0 Hz), 123.5 (q, J = 273.9 Hz), 63.9, 21.7.

^{19}F NMR (472 MHz, CDCl3, 300K): δ (ppm) = -63.2.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}F_3NaO_3S$: $[M+Na]^+$, 365.0435; Found, 365.0428.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

1-(4-nitrophenyl)-2-tosylethan-1-one (26):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow solid.

Yield: 77% (49.2 mg).

R_f: 0.28 (Mobile phase: 20% EtOAc in Hexane).

mp: 142-143 °C.

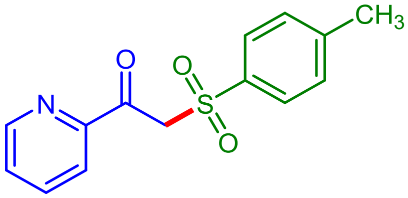
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.32 (dt, J = 9.0, 2.5 Hz, 2H), 8.14 (dt, J = 9.0, 2.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.76 (s, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.1, 150.9, 146.0, 140.0, 135.4, 130.6, 130.1, 128.6, 124.1, 64.2, 21.8.

HRMS-ESI (m/z) calc'd for $C_{15}H_{13}NNaO_5S$: $[M+Na]^+$, 342.0412; Found, 342.0415.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10b]

1-(pyridin-2-yl)-2-tosylethan-1-one (27):



The titled compound was synthesized according to the general procedure **A** and was obtained as a brown solid.

Yield: 71% (39.1 mg).

R$_f$: 0.27 (Mobile phase: 20% EtOAc in Hexane).

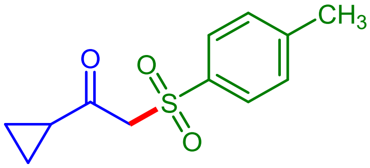
mp: 89-90 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.54-8.50 (m, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.79-7.71 (m 3H), 7.45-7.40 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 5.09 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.9, 151.9, 149.2, 145.1, 137.3, 136.7, 129.7, 128.6, 128.1, 122.6, 61.1, 21.7.

HRMS-ESI (m/z) calc'd for $C_{14}H_{13}NNaO_3S$: [M+Na]$^+$, 298.0514; Found, 298.0508.

1-cyclopropyl-2-tosylethan-1-one (28):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 84% (40.1mg).

R$_f$: 0.37 (Mobile phase: 20% EtOAc in Hexane).

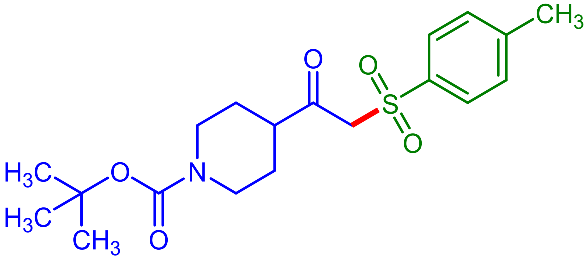
mp: 74-75 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.68 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.22 (s, 2H), 2.33 (s, 3H), 2.15–2.09 (m, 1H), 0.99–0.87 (m, 4H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 198.7, 145.4, 135.9, 130.0, 128.3, 68.1, 22.1, 21.7, 13.3.

HRMS-ESI (m/z) calc'd for $C_{12}H_{14}NaO_3S$: [M+Na]$^+$, 261.0561; Found, 261.0555.

tert-butyl 4-(2-tosylacetyl)piperidine-1-carboxylate (29):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow oil.

Yield: 39% (29.8 mg).

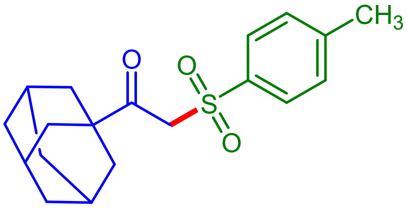
R$_f$: 0.38 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.71 (d, J = 8.0 Hz, 2H) 7.33(d, J = 8.0 Hz, 2H), 4.19 (s, 2H), 4.05 (m, 2H), 2.88-2.68 (m, 3H), 2.41 (s, 3H), 1.80 (m, 2H), 1.40 (s, 9H), 1.21 (s, 1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 200.0, 154.6, 145.6, 135.9, 130.1, 128.4, 79.8, 65.0, 49.3, 29.7, 28.4, 27.0, 21.8.

HRMS-ESI (m/z) calc'd for $C_{19}H_{31}N_2O_5S$: [M+NH$_4$]$^+$, 399.01954; Found, 399.1957.

1-(adamantan-1-yl)-2-tosylethan-1-one (30):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 66% (43.9 mg).

R$_f$: 0.51 (Mobile phase: 20% EtOAc in Hexane).

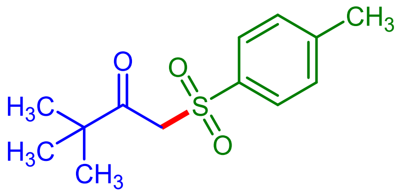
mp: 146-147 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.89 (dt, J = 8.5, 2.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H), 2.42 (s, 3H), 2.02 (s, 3H), 1.74-1.68 (m, 9H) 1.62(m, 3H), 1.23 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 203.1, 145.1, 136.7, 129.8, 128.7, 60.4, 47.6, 37.4, 36.3, 29.8, 27.6, 21.8.

HRMS-ESI (m/z) calc'd for $C_{19}H_{24}NaO_3S$: [M+Na]$^+$,355.1344; Found, 355.1336.

3,3-dimethyl-1-tosylbutan-2-one (31):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 39% (19.8 mg).

R_f: 0.43 (Mobile phase: 20% EtOAc in Hexane).

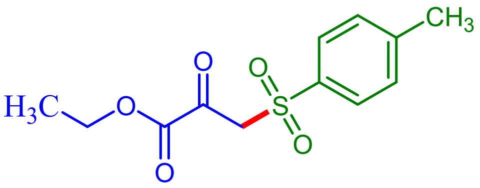
mp: 114-115 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (dt, *J* = 8.5, 1.5 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 4.30 (s, 2 H), 2.40 (s, 3 H), 1.06 (s, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 203.6, 145.1, 136.6, 129.8, 128.7, 60.9, 45.3, 25.6, 21.7.

HRMS-ESI (m/z) calc'd for $C_{13}H_{18}NaO_3S$: $[M+Na]^+$, 277.0874; Found, 277.0868.

ethyl 2-oxo-3-tosylpropanoate (32):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colorless liquid.

Yield: 26% (15.7 mg).

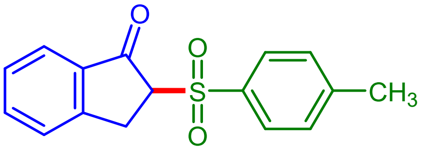
R_f: 0.28 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.32 (dt, *J* = 8.0 Hz, 2H), 4.62 (s, 2H), 4.37 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 1.36 (t, *J* =7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.2, 158.2, 144.5, 138.7, 129.5, 128.1, 64.0, 63.3, 21.7, 14.0.

HRMS-ESI (m/z) calc'd for $C_{12}H_{14}NaO_5S$: $[M+Na]^+$, 293.0460; Found, 293.0453.

(S)-2-tosyl-2,3-dihydro-1H-inden-1-one (33):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 62% (35.5 mg).

R$_f$: 0.27 (Mobile phase: 20% EtOAc in Hexane).

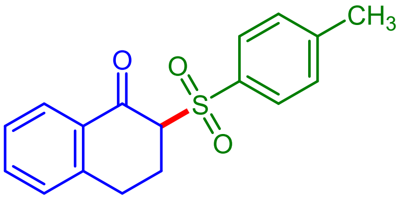
mp: 147-148 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 10.5 Hz, 2H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.62 (t, *J* = 10.0 Hz, 1H), 7.49 (d, *J* = 9.5 Hz, 1H), 7.37 (dd, *J* = 12.4, 7.8 Hz, 3H) 4.26 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.80 (dd, *J* = 18.5, 8.5 Hz, 1H), 3.52 (dd, *J* = 18.5, 8.5 Hz, 1H), 2.44 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.9, 145.3, 141.6, 137.9, 135.3, 130.2, 129.0, 128.7, 127.8, 124.6, 124.6, 72.8, 31.8, 21.8.

HRMS-ESI (m/z) calc'd for $C_{16}H_{14}NaO_3S$: $[M+Na]^+$, 309.0561; Found, 309.0553.

(S)-2-tosyl-3,4-dihydronaphthalen-1(2H)-one (34):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colorless liquid.

Yield: 40% (24.0 mg).

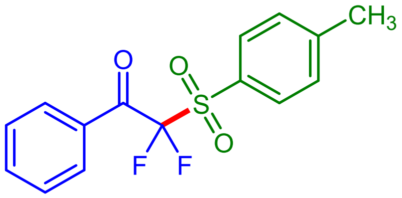
R$_f$: 0.29 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.41-7.24 (m, 4H), 4.09 (t, *J* = 7.0 Hz, 1H), 3.59-3.45 (m, 1H), 2.99 (dt, *J* = 16.9, 7.5 Hz, 1H) 2.93-2.81 (m, 1H), 2.72-2.61 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.0, 145.3, 141.6, 137.9, 135.3, 130.2, 129.0, 128.7, 127.8, 124.6, 124.6, 69.8, 31.8, 21.8.

HRMS-ESI (m/z) calc'd for $C_{17}H_{16}NaO_3S$: $[M+Na]^+$, 323.0718; Found, 323.0720.

2,2-difluoro-1-phenyl-2-tosylethan-1-one (35):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 80% (49.6 mg).

R$_f$: 0.56 (Mobile phase: 10% EtOAc in Hexane).

mp: 101-102 °C.

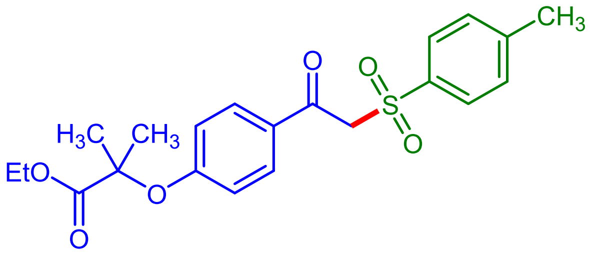
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.20-8.16 (m, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.69 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.533 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3 H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 184.1 (t, *J* = 23.2 Hz), 147.9, 135.5, 132.1, 131.0, 130.9 (t, *J* = 3.5 Hz), 130.4, 129.4, 128.9, 116.6 (t, *J* = 298.8 Hz), 22.0.

^{19}F NMR (471 MHz, CDCl$_3$, 300K): δ (ppm) = -101.6

HRMS-ESI (m/z) calc'd for $C_{15}H_{12}F_2NaO_3S$: [M+Na]$^+$, 333.0373; Found, 333.0369.

ethyl 2-methyl-2-(4-(2-tosylacetyl)phenoxy)propanoate (36):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colorless oil.

Yield: 63% (51.1 mg).

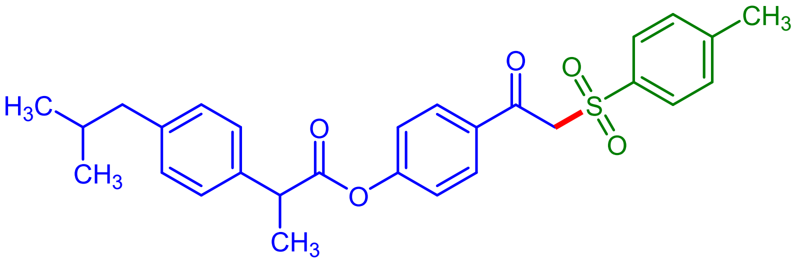
R$_f$ = 0.33 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.84 (dt, J = 9.0, 2.5 Hz, 2H), 7.72 (dt, J = 8.5, 2.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.78 (dt, J = 9.0, 3.0 Hz, 2H), 4.63 (s, 3H), 4.19 (q, J = 7.0 Hz, 2H), 2.39 (s, 3H), 1.63 (s, 6H), 1.18 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 186.5, 173.4, 160.9, 145.3, 136.0, 131.5, 129.9, 129.4, 128.6, 117.4, 79.6, 63.5, 61.8, 25.4, 21.7, 14.1.

HRMS-ESI (m/z) calc'd for $C_{21}H_{24}NaO_6S$: [M+Na]$^+$, 427.1191; Found, 427.1185.

4-(2-tosylacetyl)phenyl 2-(4-isobutylphenyl)propanoate (37):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 48% (46.0 mg).

R$_f$: 0.39 (Mobile phase: 20% EtOAc in Hexane).

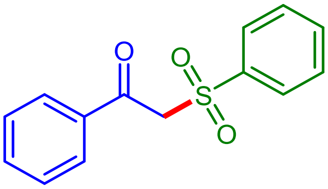
mp: 222-223 ^{o}C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.93 (dt, J = 9.0, 3.0 Hz, 2H), 7.73 (dt, J = 8.5, 2.0 Hz, 2H), 7.33-7.27 (m, 4H), 7.16 (dt, J = 8.0, 2.0 Hz, 2H), 7.11 (dt, J = 9.0, 2.5 Hz, 2H), 4.67 (s, 2H), 3.95 (q, J = 7.0 Hz, 1H), 2.48 (d, J = 7.0 Hz, 2H), 2.42 (s, 3H), 1.87 (septate, J = 6.5 Hz, 1H), 1.61 (d, J = 7.0 Hz, 3H), 0.92 (d, J = 6.5 Hz, 6H);

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.0, 172.5, 155.7, 145.6, 141.2, 136.8, 135.7, 133.2, 131.1, 130.0, 129.7, 128.7, 127.3, 122.0, 63.7, 45.4, 45.1, 30.3, 22.5, 21.8, 18.5.

HRMS-ESI (m/z) calc'd for $C_{28}H_{30}NaO_5S$: [M+Na]$^+$, 501.1712; Found, 501.1709.

1-phenyl-2-(phenylsulfonyl)ethan-1-one (38):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 90% (46.9 mg).

R$_f$ = 0.32 (Mobile phase: 20% EtOAc in Hexane).

mp: 95-96 ^{o}C.

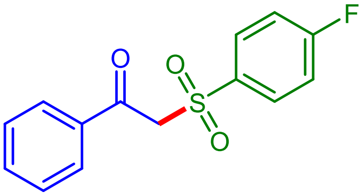
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.88 (t, J = 8.8 Hz, 4H), 7.64-7.54 (m, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 4.73 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.1, 138.9, 135.8, 134.4, 134.2, 129.3, 129.2, 128.9, 128.5, 63.4.

HRMS-ESI (m/z) calc'd for $C_{14}H_{12}NaO_3S$: [M+Na]$^+$, 283.0405; Found, 283.0400.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (39):



The titled compound was synthesized according to the general procedure **B** and was obtained as a yellow liquid.

Yield: 83% (46.2 mg).

R_f: 0.41 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96-7.89 (m, 4H), 7.63 (tt, J = 7.5, 1.0 Hz, 1H), 7.49 (tt, J = 8.5, 1.5 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H), 4.74 (s, 2H).

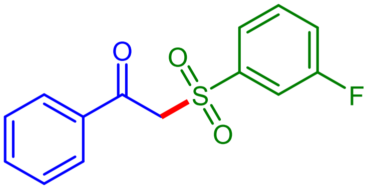
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.1, 166.2 (d, J = 257.9 Hz), 135.7, 134.7, 134.6, 131.8 (d, J = 10.2 Hz), 129.3, 129.0, 116.6 (d, J = 22.9), 63.5.

^{19}F NMR (471 MHz, $CDCl_3$, 300K): δ (ppm) = -102.2

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}FNaO_3S$: $[M+Na]^+$, 301.0311; Found, 301.0304.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10a]

2-((3-fluorophenyl)sulfonyl)-1-phenylethan-1-one (40):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 69% (38.4 mg).

R_f: 0.44 (Mobile phase: 20% EtOAc in Hexane).

mp: 98-99 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.66-7.58 (m, 2H), 7.56-7.51 (m, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.39-7.32 (m, 1H), 4.76 (s, 2H).

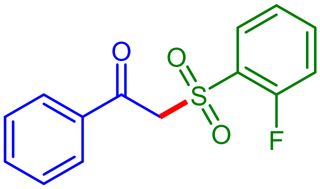
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.9, 162.4 (d, J = 253.0 Hz), 140.7(d, J = 7.2 Hz), 135.6, 134.7, 131.2 (d, J = 7.9 Hz), 129.3, 129.1, 124.6 (d, J = 3.8 Hz), 121.7 (d, J = 21.3 Hz), 116.1 (d, J = 24.7), 63.2.

^{19}F NMR (471 MHz, $CDCl_3$, 300K): δ (ppm) = -108.8

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}FNaO_3S$: $[M+Na]^+$, 301.0311; Found, 301.0305.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10f]

2-((2-fluorophenyl)sulfonyl)-1-phenylethan-1-one (41):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 91% (50.6 mg).

R$_f$: 0.42 (Mobile phase: 20% EtOAc in Hexane).

mp: 98-99 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.97-7.93 (m, 2H), 7.90-7.86 (m, 1H), 7.70-7.65 (m, 1H), 7.63 (tt, J = 7.0, 1.5 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.32 (td, J = 7.5, 1.0 Hz, 1H), 7.29-7.24 (m, 1H), 4.93 (s, 2H).

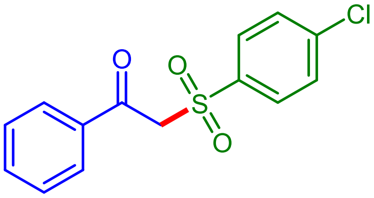
^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 187.8, 159.7 (d, J = 256.3 Hz), 136.8 (d, J = 8.7 Hz), 135.7, 134.6, 130.9, 129.3, 129.0, 126.8 (d, J = 14.4 Hz), 124.9 (d, J = 4.0 Hz), 117.2 (d, J = 21.2), 62.3 (d, J = 3.2 Hz).

^{19}F NMR (471 MHz, CDCl$_3$, 300K): δ (ppm) = -108.8

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}FNaO_3S$: $[M+Na]^+$, 301.0311; Found, 301.0304.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10f]

2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one (42):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 58% (34.2 mg).

R$_f$: 0.45 (Mobile phase: 20% EtOAc in Hexane).

mp: 126-127 °C.

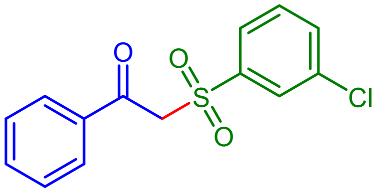
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.92 (dd, J = 8.3, 1.0 Hz, 2H), 7.83 (dt, J = 8.5, 2.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.53-7.45 (m, 4H), 4.75 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.1, 141.2, 137.2, 135.6, 134.6, 130.3, 129.6, 129.3, 129.0, 63.3.

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}ClNaO_3S$: $[M+Na]^+$, 317.0015; Found, 317.0014.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

2-((3-chlorophenyl)sulfonyl)-1-phenylethan-1-one (43):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 72% (42.4 mg).

$\mathbf{R_f}$: 0.43 (Mobile phase: 20% EtOAc in Hexane).

mp: 101-102 °C.

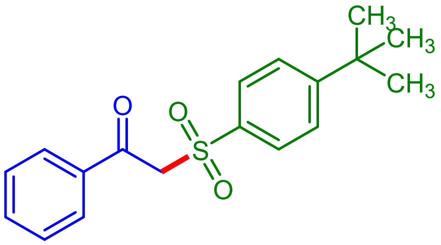
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93-7.89 (m, 2H), 7.88 (t, J = 2.0 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.65-7.58 (m, 2H), 7.51-7.44 (m, 3H), 4.77 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.9, 140.4, 135.6, 135.5, 134.7, 134.5, 130.6, 129.3, 129.0, 128.7, 126.9, 63.2.

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}ClNaO_3S$: $[M+Na]^+$, 317.0015; Found, 317.0007.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10e]

2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylethan-1-one (44):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 49% (31.0 mg).

$\mathbf{R_f}$: 0.33 (Mobile phase: 20% EtOAc in Hexane).

mp: 125-126 °C.

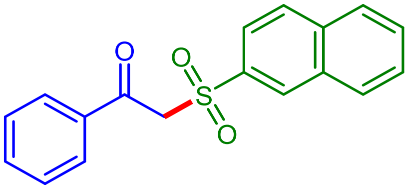
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94-7.89 (m, 2 H), 7.81 (dt, J = 9.0, 2.0 Hz, 2H), 7.60 (tt, J = 7.5, 1.5 Hz, 1H), 7.53 (dt, J = 9.0, 2.0 Hz, 2H), 7.46 (t, J = 6.5 Hz, 2H), 4.73 (s, 2H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.2, 158.3, 135.9, 135.9, 134.4, 129.4, 128.9, 128.5, 126.3, 63.6, 35.4, 31.1.

HRMS-ESI (m/z) calc'd for $C_{18}H_{20}NaO_3S$: $[M+Na]^+$, 339.1031; Found, 339.1023.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10c]

2-(naphthalen-2-ylsulfonyl)-1-phenylethan-1-one (45):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 92% (57.1 mg).

R$_f$: 0.36 (Mobile phase: 20% EtOAc in Hexane).

mp: 132-133 °C.

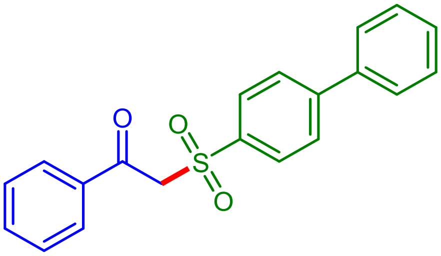
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.46 (s, 1H), 8.01-7.91 (m, 5H), 7.87 (dd, J = 9.0, 2.0 Hz, 1H), 7.68 (dt, J = 7.5, 1.0 Hz, 1H), 7.65-7.57 (m, 2H), 7.45 (t, J = 8.0 Hz, 2H), 4.82 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.1, 135.8, 135.7, 135.6, 134.5, 132.1, 130.8, 129.7, 129.6, 129.6, 129.4, 128.9, 128.1, 127.8, 123.0, 63.6.

HRMS-ESI (m/z) calc'd for $C_{18}H_{14}NaO_3S$: $[M+Na]^+$, 333.0561; Found, 333.0561.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

2-([1,1'-biphenyl]-4-ylsulfonyl)-1-phenylethan-1-one (46):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 79% (53.2 mg).

R$_f$: 0.39 (Mobile phase: 20% EtOAc in Hexane).

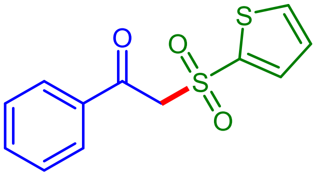
mp: 142-142 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.98-7.93 (m, 4H), 7.74 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.62 (t, *J* = 6.5 Hz, 3H), 7.49 (t, *J*=7.5 Hz, 5H), 4.78 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.2, 147.3, 139.1, 137.3, 135.8, 134.5, 129.4, 129.2, 129.2, 129.0, 128.8, 127.9, 127.5, 63.6.

HRMS-ESI (m/z) calc'd for $C_{20}H_{16}NaO_3S$: $[M+Na]^+$, 359.0718; Found, 359.0716.

1-phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one (47):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 66% (35.2 mg).

R$_f$: 0.36 (Mobile phase: 20% EtOAc in Hexane).

mp: 132-133 °C.

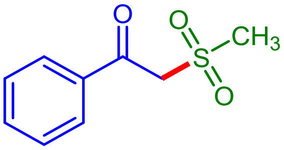
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.95-7.91 (m, 2H), 7.75-7.67 (m, 2H), 7.62 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.48 (tt, *J* = 8.0, 1.5 Hz, 2H), 7.16-7.10 (m, 1H), 4.83 (s, 2H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 188.1, 139.5, 135.6, 135.5, 135.3, 134.5, 129.2, 129.0, 128.1, 64.2.

HRMS-ESI (m/z) calc'd for $C_{12}H_{10}NaO_3S_2$: [M+Na]$^+$, 288.9969; Found, 288.9973.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10a]

2-(methylsulfonyl)-1-phenylethan-1-one (48):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 95% (37.7 mg).

R$_f$: 0.24 (Mobile phase: 20% EtOAc in Hexane).

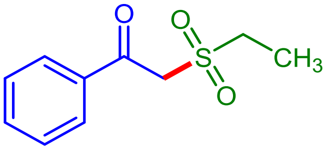
mp: 104-105 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.00-7.91 (m, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.47 (d,*J* = 11.0 Hz,2H), 7.43-7.25 (m, 3H), 7.24-7.15 (m,2H), 6.87 (d, *J*=15.0 Hz,1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 165.7 (d, *J*=254.4 Hz), 142.8, 136.9 d *J* = 3.3 Hz) , 132.3, 131.4, 130.6 (d, *J*=9.6 Hz), 129.2, 128.7, 127.2, 116.7 (d, *J*=22.5 Hz).

HRMS-ESI (m/z) calc'd for $C_9H_{10}NaO_3S$: [M+Na]$^+$, 221.0248; Found, 221.0243.

2-(ethylsulfonyl)-1-phenylethan-1-one (49):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 87% (36.9 mg).

R$_f$: 0.31 (Mobile phase: 20% EtOAc in Hexane).

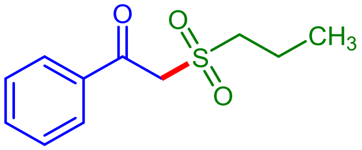
mp: 79-80 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 15.5 Hz, 1H), 7.64 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.56-7.46 (m, 3H), 7.44-7.36 (m, 3H), 7.30 (td, *J* = 8.5, 2.5 Hz, 1H), 6.87 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 162.6 (d, *J* = 250.6Hz), 143.6, 142.9 (d, *J* = 6.6 Hz), 132.2, 131.6, 131.4 (d, *J* = 7.6 Hz), 129.2, 128.8, 126.6, 123.6 (d, *J* = 3.5 Hz), 120.8, 120.7, 115.0 (d, *J* = 24.3 Hz).

HRMS-ESI (m/z) calc'd for $C_{10}H_{12}NaO_3S$: $[M+Na]^+$, 235.0405; Found, 235.0402.

1-phenyl-2-(propylsulfonyl)ethan-1-one (50):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 89% (40.3 mg).

R$_f$: 0.37 (Mobile phase: 20% EtOAc in Hexane).

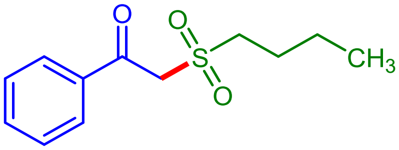
mp: 68-69 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.09 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 15.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.46-7.39 (m, 3H), 6.85 (d, *J*=15.5 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 144.3 (d, *J* = 31.5 Hz), 135.2 (d, *J* = 32.9 Hz), 132.1, 131.7, 129.3, 128.8, 128.3, 126.6 (d, *J*=3.9 Hz), 126.3, 124.3, 122.1.

HRMS-ESI (m/z) calc'd for $C_{11}H_{14}NaO_3S$: $[M+Na]^+$, 249.0561; Found, 249.0556.

2-(butylsulfonyl)-1-phenylethan-1-one (51):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 47% (22.7 mg).

R$_f$: 0.43 (Mobile phase: 20% EtOAc in Hexane).

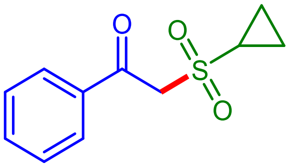
mp: 84-85 ^{o}C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.46-7.35 (m, 5H), 6.85 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 152.8, 143.4, 139.1, 132.2, 131.6, 130.0, 129.3, 128.8, 126.8, 121.3 (d, *J*=1.4 Hz), 119.2.

HRMS-ESI (m/z) calc'd for $C_{12}H_{17}O_3S$: [M+NH$_4$]$^+$, 258.1164; Found, 258.1159.

2-(cyclopropylsulfonyl)-1-phenylethan-1-one (52):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 77% (34.5 mg).

R$_f$ = 0.23 (Mobile phase: 20% EtOAc in Hexane).

mp: 67-68 ^{o}C.

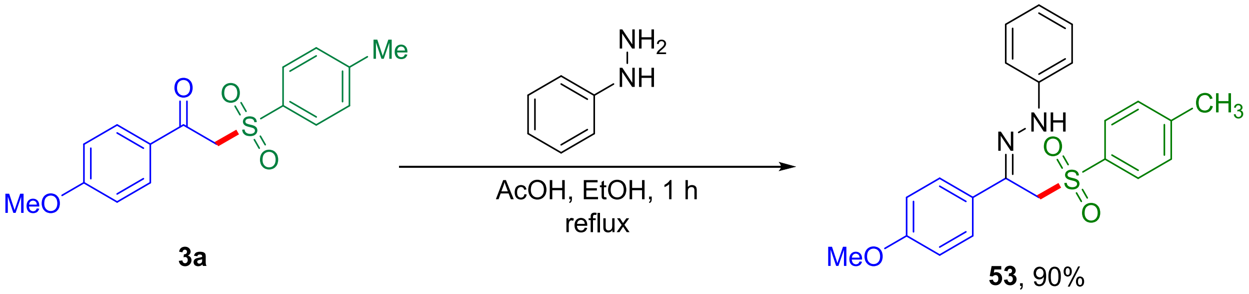
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 8.55 (br.s, 1H), 7.99 (t, *J* = 7.3 Hz, 2H), 7.93-7.87 (m, 2H), 7.75 (d, *J* = 15.0 Hz, 1H), 7.68-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.42-7.36 (m, 3H), 6.92 (d, *J*=15.5 Hz,1H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 142.7, 137.6, 135.3, 132.5, 132.4, 131.3, 129.8, 129.5, 129.3, 129.3, 129.2, 128.7, 128.1, 127.8, 127.4, 122.7.

HRMS-ESI (m/z) calc'd for $C_{11}H_{12}NaO_3S$: [M+Na]$^+$, 247.0405; Found, 247.0405.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[10c]

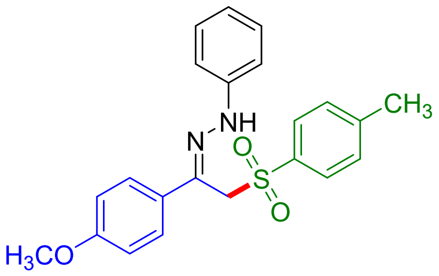
(Z)-1-(1-(4-methoxyphenyl)-2-tosylethylidene)-2-phenylhydrazine (53):



3a

53, 90%

Compound **53** was prepared according to the synthesis procedure described in the literature.[11] To an oven-dried 10 mL round bottom flask, **3a** (274 mg, 1.0 mmol) in ethanol (5.0 mL) and phenylhydrazine (108.1 mg, 1 mmol) and catalytic amount of acetic acid were added. The reaction mixture was refluxed for 1 h. After cooling, the precipitated product was filtered off, washed with ethanol and dried. Recrystallization from EtOH afforded compound **53** as a white solid.



Yield: 90% (319.5 mg).

R_f = 0.43 (Mobile phase: 20% EtOAc in Hexane).

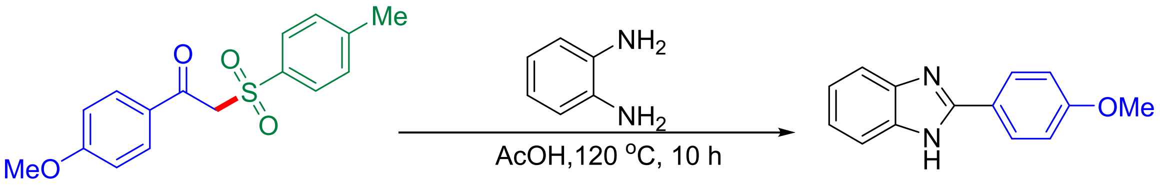
mp: 140-141 °C.

^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ (ppm) = 8.57 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.73 (dt, *J* = 9.0, 3.0 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 2H), 6.31 (t, *J* = 8.5 Hz, 2H), 6.15 (d, *J* = 8.0 Hz, 2H), 5.94 (d, *J* = 9.0 Hz, 2H), 5.88 (t, *J* = 7.0 Hz, 2H), 4.15 (s, 2H), 2.85 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6, 300 K): δ (ppm) = 159.4, 145.4, 145.1, 136.9, 130.8, 130.3, 129.9, 129.4, 128.7, 127.6, 120.0, 113.9, 113.3, 55.7, 52.6, 21.5.

HRMS-ESI (m/z) calc'd for $C_{22}H_{22}N_2NaO_3S$: $[M+Na]^+$, 417.1249; Found, 417.1250.

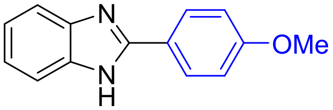
2-(4-methoxyphenyl)-1H-benzo[d]imidazole (54):



3a

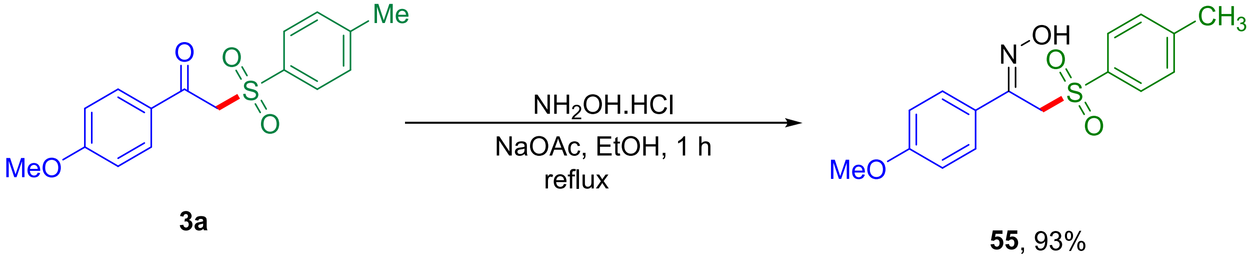
54, 76%

Compound **54** was prepared according to the synthesis procedure described in the literature.[12] To an oven-dried 10 mL round bottom flask, **3a** (54.8 mg, 0.2 mmol), acetic acid (1.0 mL) and *o*-phenylendiamine (38.2 mg, 0.2 mmol, 1.0 equiv) were added in this sequence. The resulting mixture was stirred at 120 °C for 10 h. Finally, all volatile components were removed in vacuum and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford the product **54** as a peach color solid.



Yield: 76% (30.7 mg).
R$_f$ = 0.34 (Mobile phase: 50% EtOAc in Hexane).
mp: 224-225 °C.
^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ (ppm) = 8.10 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 2H), 7.31 (s, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H).
^{13}C NMR (126 MHz, DMSO-d_6, 300 K): δ (ppm) = 162.8, 150.1, 134.6, 129.8, 124.8, 117.8, 115.3, 114.7, 56.1.
HRMS-ESI (m/z) calc'd for $C_{14}H_{12}N_2NaO$: $[M+Na]^+$, 247.0847; Found, 247.0849.

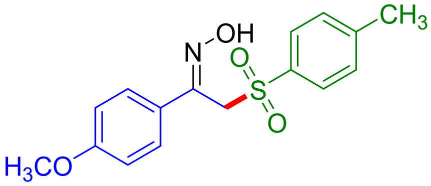
(Z)-1-(4-methoxyphenyl)-2-tosylethan-1-one oxime (55):



3a

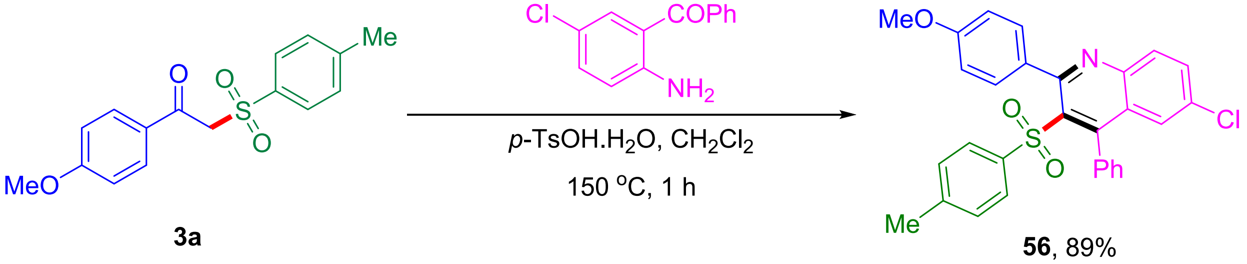
55, 93%

Compound **55** was prepared according to the synthesis procedure described in the literature.[11] To an oven-dried 10 mL round bottom flask, **3a** (274 mg, 1 mmol), NH_2OH. HCl (105 mg, 1.5 mmol), anhydrous NaOAc (123 mg, 1.5 mmol) and 5 mL of EtOH were taken. The flask was fitted with a condenser and the reaction mixture was stirred in a preheated oil bath at 80 °C for 1 h. Next, the reaction mixture was cooled to room temperature. Following that, it was poured into cold water and the solid product was filtered off and washed with water to afford the product **55** as a white solid.

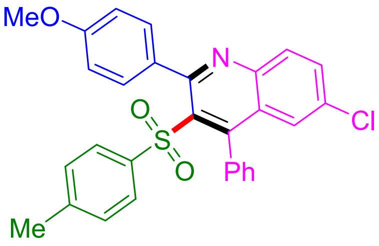


Yield: 93% (267.4 mg).
R$_f$ = 0.29 (Mobile phase: 20% EtOAc in Hexane).
mp: 163-164 °C.
^{1}H NMR (500 MHz, DMSO-*d*$_6$, 300 K): δ (ppm) = 11.5 (s, 1H), 7.58-7.51 (m, 4H), 7.30 (d, *J* = 7.5 Hz, 2H), 6.85 (dt, *J* = 9.0, 3.0 Hz, 2H), 4.82 (s, 2H), 3.72 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (126 MHz, DMSO-*d*$_6$, 300 K): δ (ppm) = 160.5, 145.7, 144.9, 137.4, 130.0, 128.4, 128.3, 127.5, 114.1, 55.7, 51.9, 21.6.
HRMS-ESI (m/z) calc'd for $C_{16}H_{17}NNaO_4S$: [M+Na]$^+$, 342.0776; Found, 342.0770.

6-chloro-2-(4-methoxyphenyl)-4-phenyl-3-tosylquinoline (56):



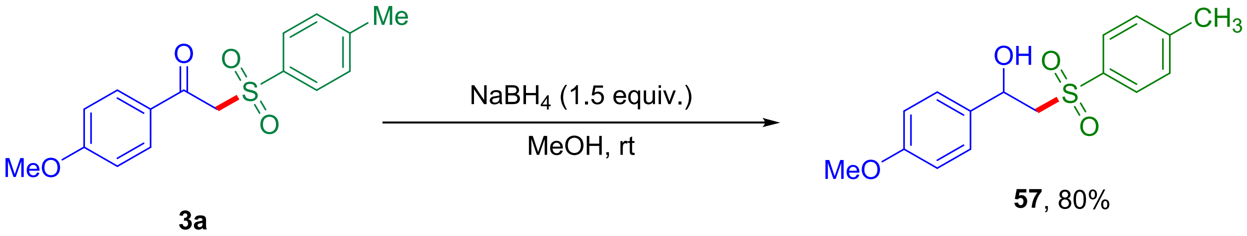
Compound **56** was prepared according to the synthesis procedure described in the literature.[13] A mixture of 2-aminobenzophenones (0.6 mmol), β-ketosulfones **3a** (0.5 mmol), and *p*-toluenesulfonic acid monohydrate (0.1 mmol) in dichloromethane (10 mL) was added and flask was stirred at 150 °C for 1 h. The consumption of the starting materials was confirmed by TLC. The reaction mixture was cooled to 25 °C, and the mixture containing the crude product was transferred to a 100 mL round bottom flask and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted using CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude products under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1) afforded compound **56** as a white solid.



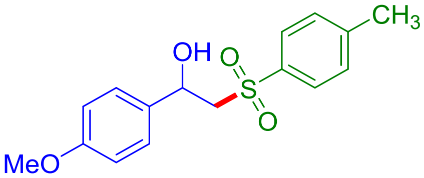
Yield: 89% (222.5 mg).
R$_f$ = 0.58 (Mobile phase: 20% EtOAc in Hexane).
mp: 230-231 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.71 (dt, *J* = 9.0, 2.5 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.49-7.44 (m, 1H), 7.43-7.38 (m, 3H), 7.23 (t, *J* = 7.5 Hz, 2H), 6.98-6.84 (m, 6H), 3.86 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 160.4, 157.9, 150.5, 146.1, 143.1, 139.0, 134.4, 134.3, 133.5, 133.3, 132.9, 131.1, 131.0, 130.3, 128.9, 128.1, 127.2, 127.1, 126.0, 113.4, 55.4, 21.6.
HRMS-ESI (m/z) calc'd for $C_{29}H_{23}ClNO_3S$: $[M+H]^+$, 500.1087; Found, 500.1083.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[13]

1-(4-methoxyphenyl)-2-tosylethan-1-ol (57):

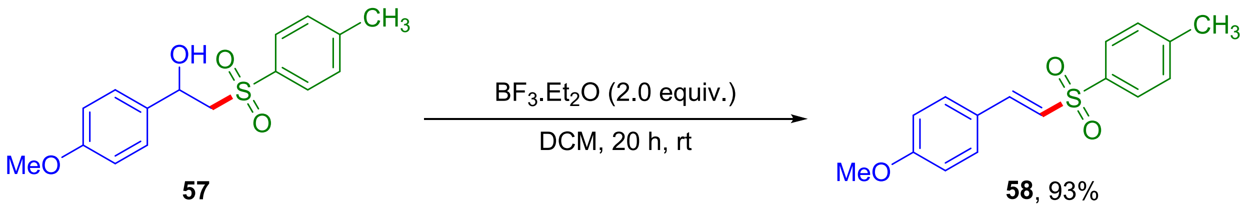


Compound **57** was prepared according to the synthesis procedure described in the literature.[14a] To an oven-dried 10 mL round bottom flask, Sodium borohydride (0.3 mmol, 1.5 equiv.) was gradually added to a solution of **3a** (56 mg, 0.2 mmol, 1.0 equiv.) in anhydrous methanol (2.0 mL) and stirred at room temperature for an hour. TLC analysis was used to trace the course of the reaction, and once it was finished, the solvent was removed under reduced pressure, and the crude was given an ice-cold water treatment. Ethyl acetate (3 x 10 mL) was used to remove the aqueous layer after it had been made acidic (pH 2). The mixed organic layers were concentrated after being dried over sodium sulfate. Hexanes/ethyl acetate (9:1, v/v) was used as the eluent in column chromatographic to purify the reaction mixture. The compound **57** was obtained as a yellow oil.

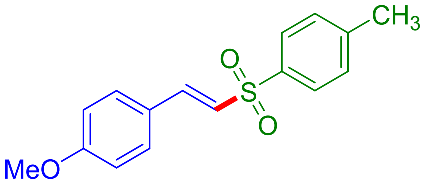


Yield: 80% (45.1 mg).
R$_f$ = 0.41 (Mobile phase: 20% EtOAc in Hexane).
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.81 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (dt, *J* = 6.5, 2.5 Hz, 2H), 6.82 (dt, *J* = 9.0, 3.0 Hz, 2H), 5.18 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.76 (s, 3H), 3.72 (d, *J* = 5.5 Hz, 1H), 3.47 (q, *J* = 4.0 Hz, 1H), 3.28 (q, *J* = 14.3 Hz, 1H), 2.45 (s, 3H).
^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 159.6, 145.3, 136.3, 133.0, 130.2, 128.1, 127.1, 114.2, 68.2, 64.0, 55.4, 21.8.
HRMS-ESI (m/z) calc'd for $C_{16}H_{18}NaO_4S$: $[M+Na]^+$, 329.0823; Found, 329.0827.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[14b]

(E)-1-methoxy-4-(2-tosylvinyl)benzene (58):



Compound **58** was prepared according to the synthesis procedure described in the literature.[14c] To an oven-dried 10 mL round bottom flask, reduced product **57** (0.1 mmol) was added, followed by the addition of $BF_3.Et_2O$ (0.2 mmol) and DCM solvent. The reaction was stirred at room temperature for 20 hours. The dehydration of compound **57** led to the desired vinyl sulfone **58**. After the completion of the reaction, the solvent was evaporated in vacuo. The crude product was purified by column chromatography, eluting with Hexane/EtOAc to afford the desired product **58** as a white solid.



Yield: 93% (26.8 mg).

$\mathbf{R_f}$ = 0.58 (Mobile phase: 20% EtOAc in Hexane).

mp: 96-97 °C.

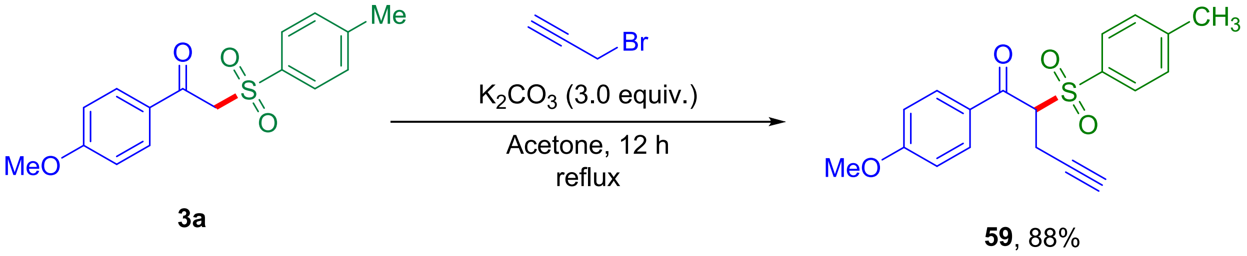
^{1}**H NMR** (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83-7.79 (m, 2H), 7.59 (d, *J* = 15.5, 1H), 7.41(dt, *J* = 9.0, 3.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.88 (dt, *J* = 9.0, 3.0 Hz, 2H), 6.69 (d, *J* = 15.5 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.1, 144.3, 141.9, 138.2, 130.4, 130.0, 127.6, 125.1, 124.8, 114.6, 55.5, 21.7.

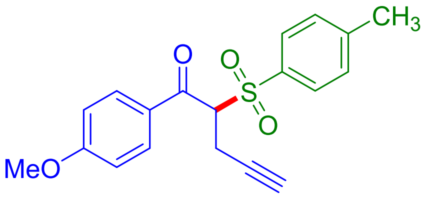
HRMS-ESI (m/z) calc'd for $C_{16}H_{16}NaO_3S$: $[M+Na]^+$, 311.0718; Found, 311.0721.

^{1}**H** and ^{13}**C NMR** of the product are in agreement with the literature.[14d]

(S)-1-(4-methoxyphenyl)-2-tosylpent-4-yn-1-one (59):

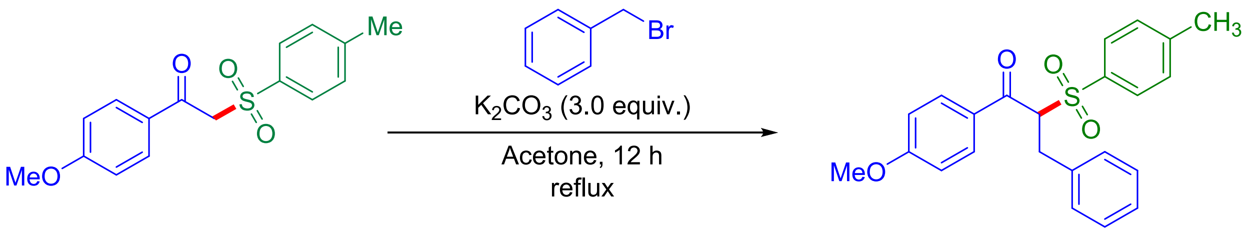


Compound **59** was prepared according to the synthesis procedure described in the literature.[15] To an oven-dried 10 mL round bottom flask, K_2CO_3 (3.0 equiv.) was added to a solution of **3a** (0.5 mmol, 1.0 equiv.) in acetone (2 mL). The reaction mixture was agitated at room temperature for 10 minutes. After that, propargylic bromide (1.1 equiv.) was added to the reaction mixture at room temperature. The reaction mixture was stirred at reflux for 12 hours. The reaction mixture was cooled to room temperature before being concentrated and extracted with EtOAc. The mixed organic layers were washed with brine, dried, filtered, and evaporated to obtain a crude product at reduced pressure. Purification on silica gel (hexanes/EtOAc) afforded the product **59** as a white solid.



Yield: 88% (150.7 mg).
$\mathbf{R_f}$ = 0.31 (Mobile phase: 20% EtOAc in Hexane).
mp: 114-115 ^{o}C.
^{1}**H NMR** (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (dt, *J* = 9.0, 3.0 Hz, 2H), 7.59 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.90 (dt, *J* = 9.0, 3.0 Hz, 2H), 5.19 (dd, *J* = 9.8, 4.5 Hz, 1H), 3.83 (s, 3H), 2.98-2.86 (m, 2H), 2.37 (s, 3H), 1.86 (t, *J* = 2.5 Hz, 1H).
^{13}**C NMR** (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.9, 164.6, 145.9, 133.0, 131.8, 129.9, 129.8, 129.7, 114.1, 78.5, 71.2, 67.9, 55.7, 21.8, 18.3.
HRMS-ESI (m/z) calc'd for $C_{19}H_{18}NaO_4S$: $[M+Na]^+$, 365.0823; Found, 365.0822.

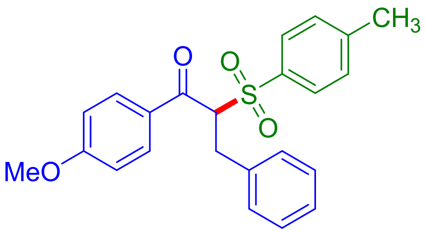
(S)-1-(4-methoxyphenyl)-3-phenyl-2-tosylpropan-1-one (58):



3a

60, 72%

Compound **60** was prepared according to the synthesis procedure described in the literature.[16] To an oven-dried 10 mL round bottom flask, K_2CO_3 (3.5 equiv.) was added to a solution of **3a** (0.5 mmol, 1.0 equiv.) in acetone (2 mL). For 10 minutes, the reaction mixture was agitated at room temperature. After that, benzyl bromide (1.1 equiv.) was added to the reaction mixture at room temperature. For 12 hours, the reaction mixture was stirred at reflux. The reaction mixture was cooled to room temperature before being concentrated and extracted with EtOAc/Hexane. The mixed organic layers were washed with brine, dried, filtered, and evaporated to obtain a crude product at reduced pressure. Purification on silica gel (hexanes/EtOAc) afforded the benzyl product **60** as a white solid.



Yield: 72% (140.0 mg).

R$_f$ = 0.43 (Mobile phase: 20% EtOAc in Hexane).

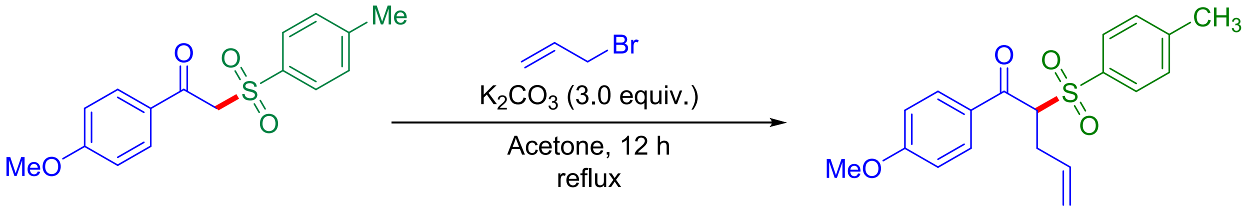
mp: 108-109 °C.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.76 (dt, *J* = 9.0, 3.0 Hz, 2H), 7.69 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17-7.11 (m, 2H), 7.11-7.05 (m, 3H), 6.81 (dt, *J* = 9.0, 2.5 Hz, 2H), 5.25 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.80 (s, 3H), 3.44 (dd, *J* = 13.3, 3.0 Hz, 1H), 3.33 (t, *J* = 11.5 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 190.2, 164.2, 145.5, 136.3, 133.5, 131.5, 130.4, 129.9, 129.7, 129.0, 128.8, 127.0, 113.9, 71.2, 55.6, 34.0, 21.8.

HRMS-ESI (m/z) calc'd for $C_{23}H_{22}NaO_4S$: $[M+Na]^+$, 417.1136; Found, 417.1129.

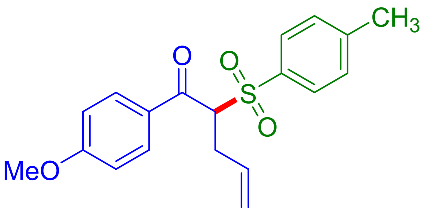
(S)-1-(4-methoxyphenyl)-2-tosylpent-4-en-1-one (61):



3a

61, 90%

Compound **61** was prepared according to the synthesis procedure described in the literature.[17] At room temperature, K_2CO_3 (2.0 equiv.) was added to a solution of **3a** (0.5 mmol, 1.0 equiv.) in acetone (2 mL). For 10 minutes, the reaction mixture was agitated at room temperature. Afterward, allyl bromide (1.1 equiv.) was added to the reaction mixture at room temperature. For 16 hours, the reaction mixture was stirred at reflux. The reaction mixture was cooled to room temperature before being concentrated and extracted with EtOAc/Hexane. The mixed organic layers were washed with brine, dried, filtered, and evaporated to obtain a crude product at reduced pressure. Purification on silica gel (hexanes/EtOAc) afforded the allyl product **61** as a yellow liquid.



Yield: 90% (154.9 mg).

R$_f$ = 0.41 (Mobile phase: 20% EtOAc in Hexane).

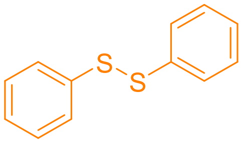
^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.91 (dt, *J* = 12.0, 3.0 Hz, 2H), 7.62 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.89 (dt, *J* = 9.0, 2.5 Hz, 2H), 5.59-5.50 (m, 1H), 5.08 (dd, *J* = 10.3, 4.5 Hz, 1H), 4.99 (dd, *J* = 18.5, 1.5 Hz, 1H), 4.91 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.81 (s, 3H), 2.83-2.72 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 190.0, 164.4, 145.4, 133.5, 132.3, 131.6, 130.3, 129.8, 129.6, 118.8, 114.4, 60.0, 55.7, 33.4, 21.7.

HRMS-ESI (m/z) calc'd for $C_{19}H_{20}NaO_4S$: [M+Na]$^+$, 367.0980; Found, 367.0977.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[17]

1,2-diphenyldisulfane

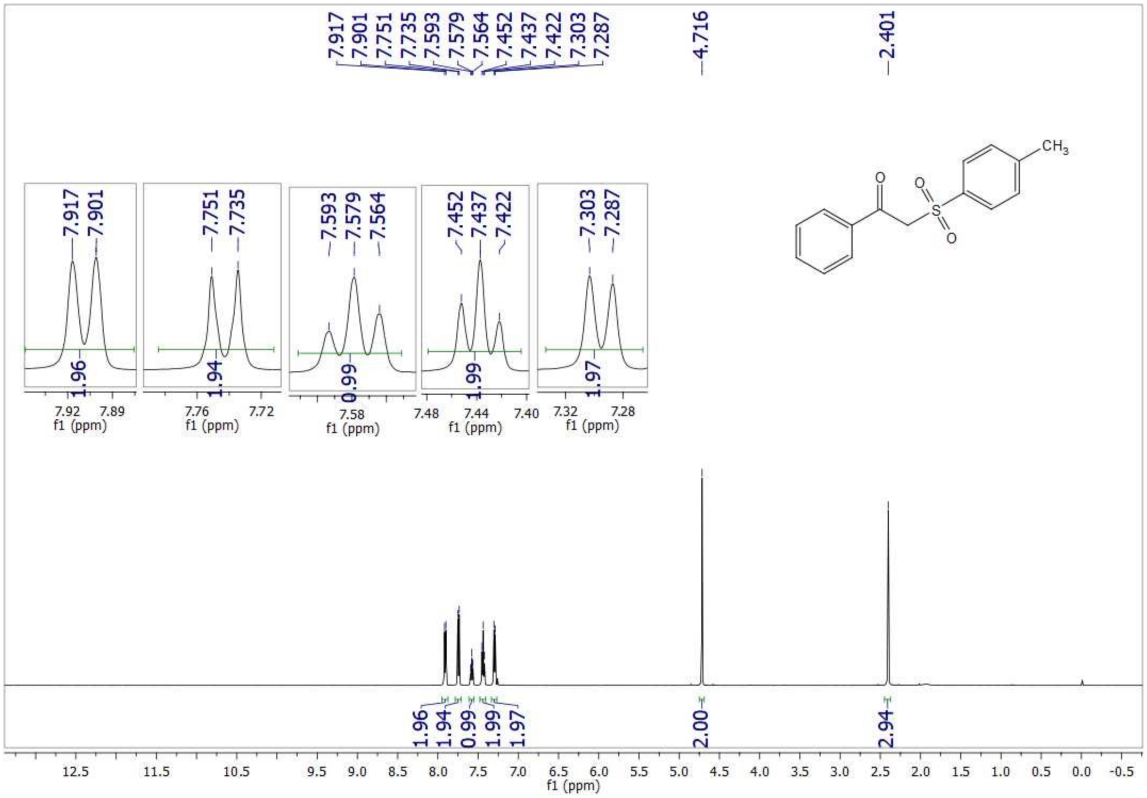


^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ (ppm) = 7.67–7.50 (m, 4H), 7.44–7.31 (m, 4H), 7.30–7.22 (m, 2H).

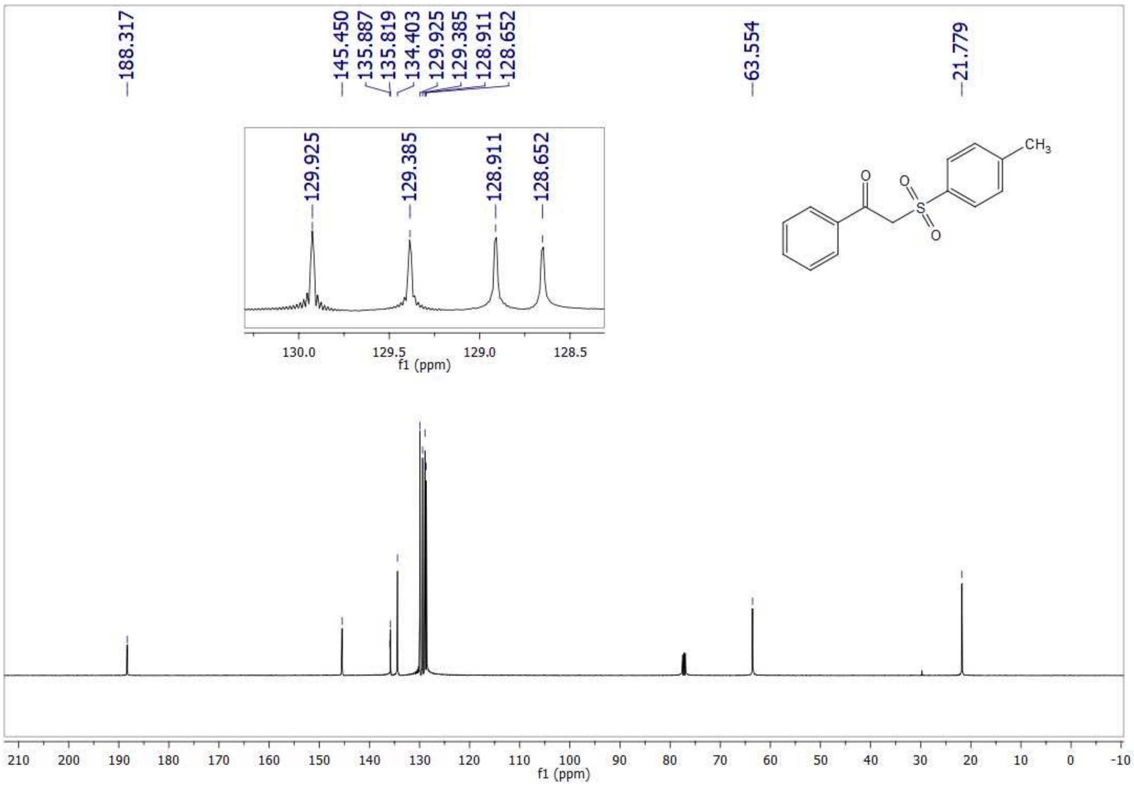
^{13}C NMR (126 MHz, CDCl$_3$, 300 K): δ (ppm) = 137.2, 129.3, 127.7, 127.3.

HRMS-ESI (m/z) calc'd for $C_{12}H_{10}NaS_2$: [M+Na]$^+$, 241.0122; Found, 241.0128.

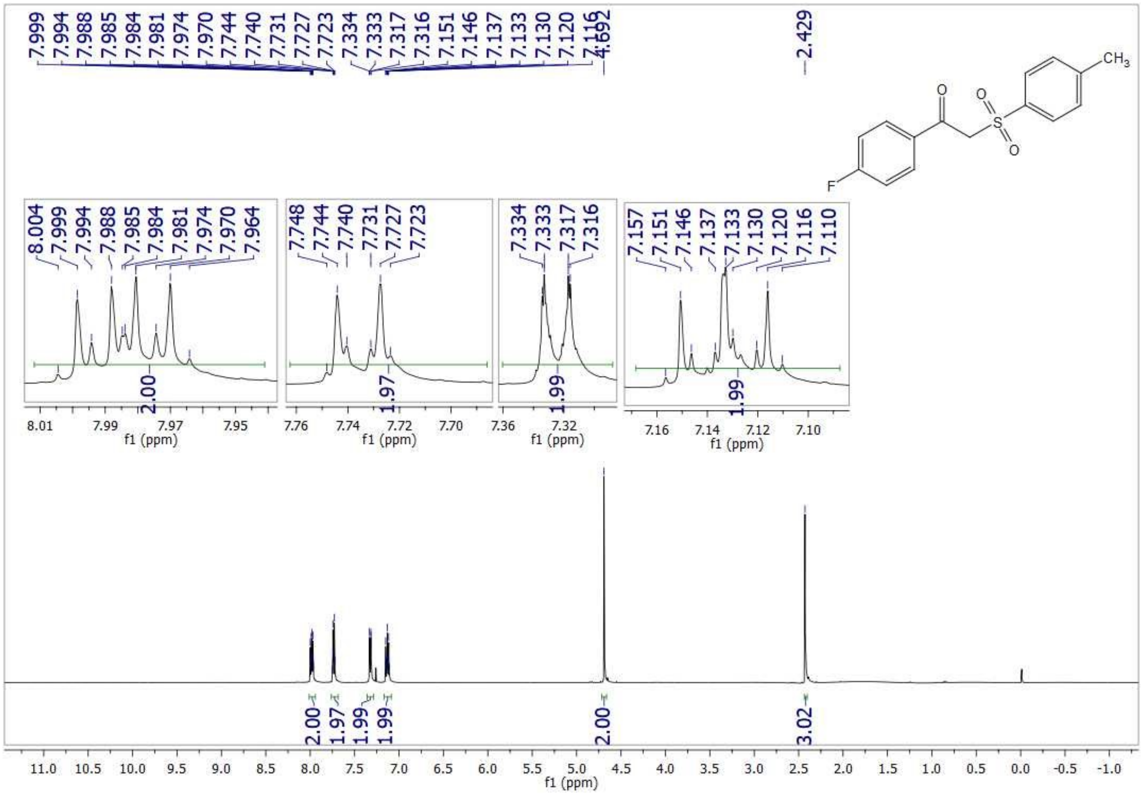
8.2 NMR copies of products



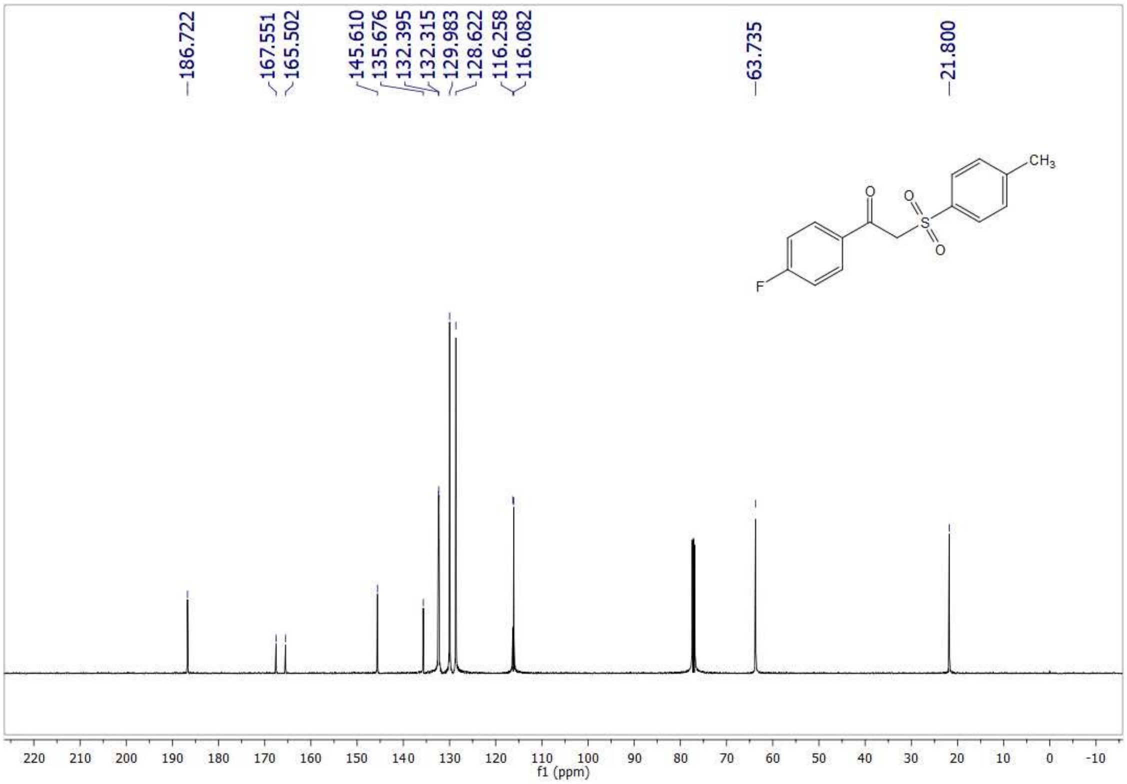
^{1}H NMR (500 MHz, CDCl$_3$) of compound **3**.



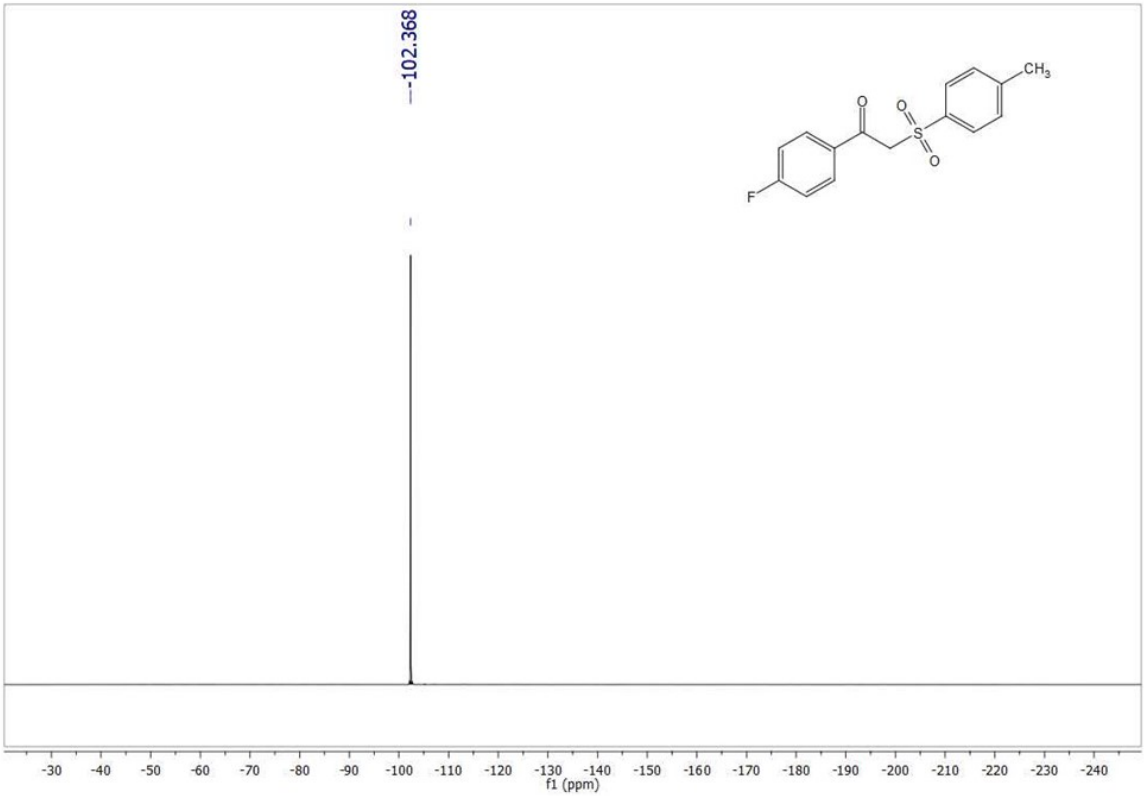
^{13}C NMR (126 MHz, CDCl$_3$) of compound **3**.



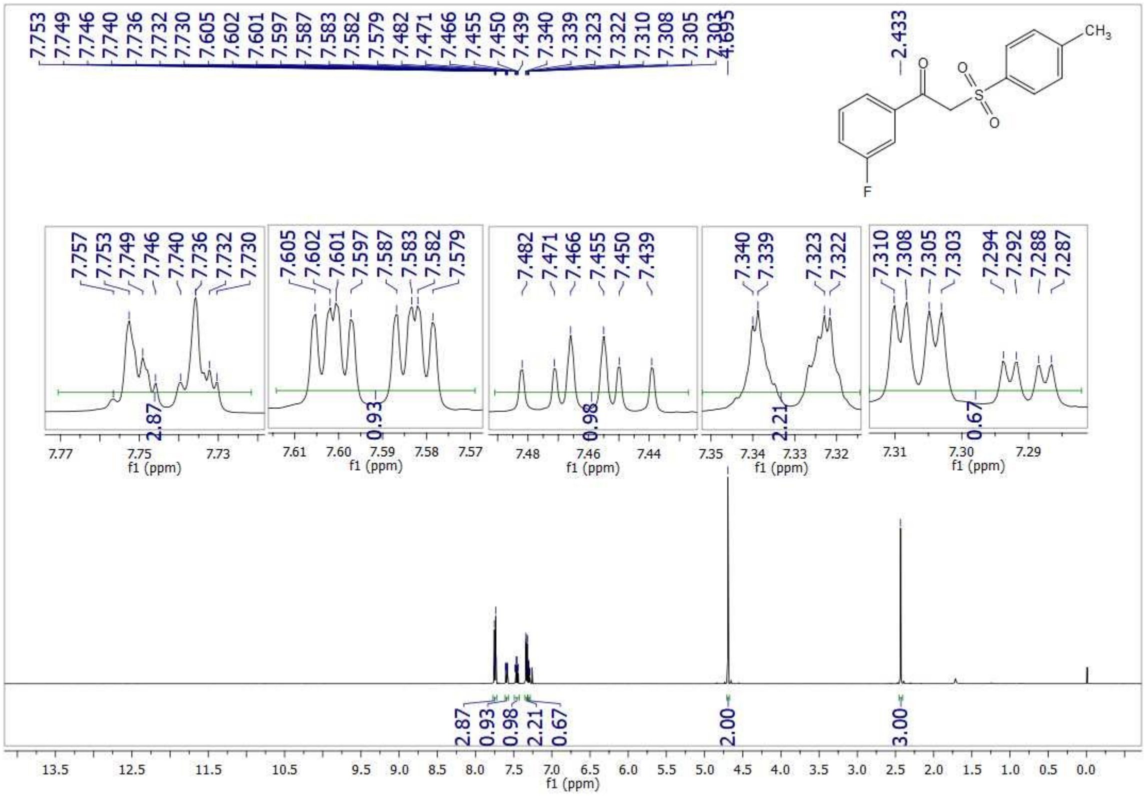
^{1}H NMR (500 MHz, CDCl$_3$) of compound **4**.



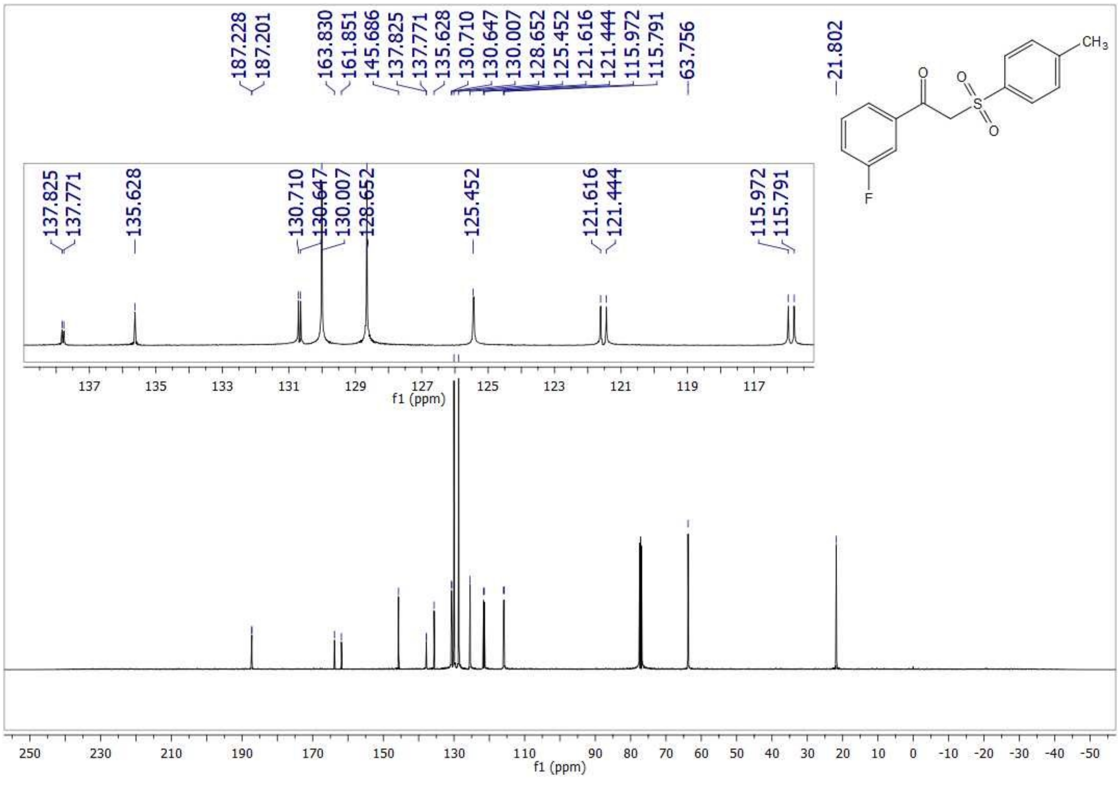
^{13}C NMR (126 MHz, CDCl$_3$) of compound **4**.



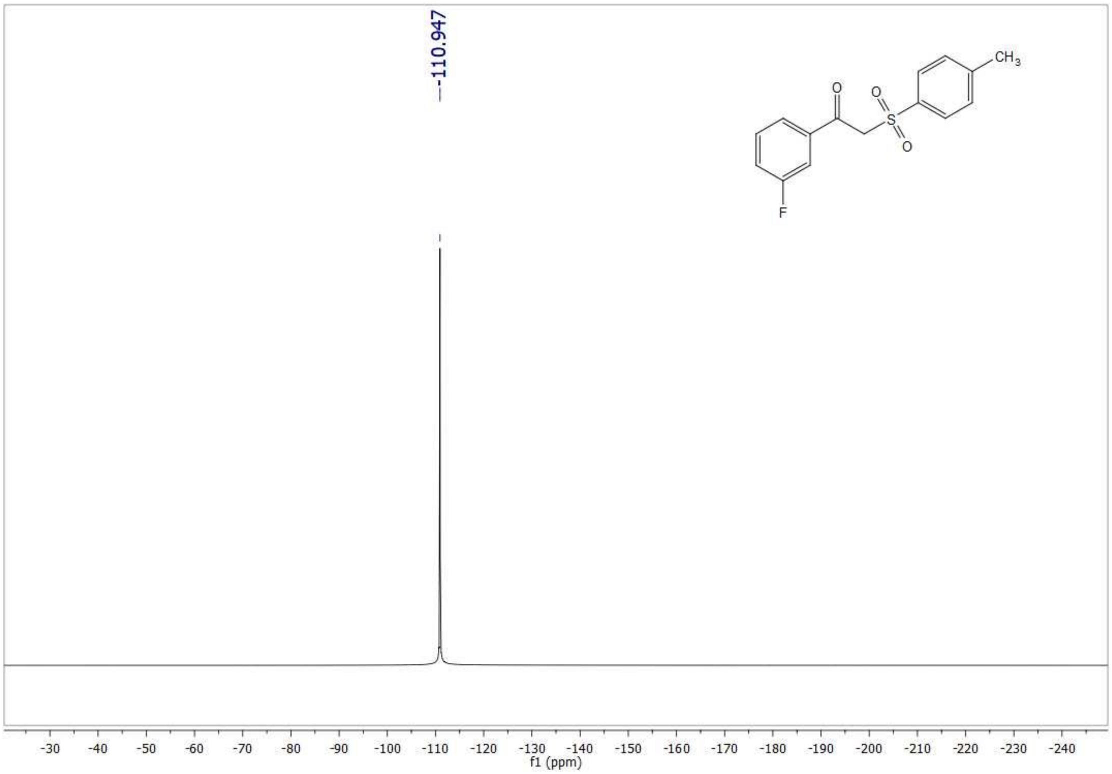
^{19}F NMR (472 MHz, CDCl$_3$) of compound **4**.



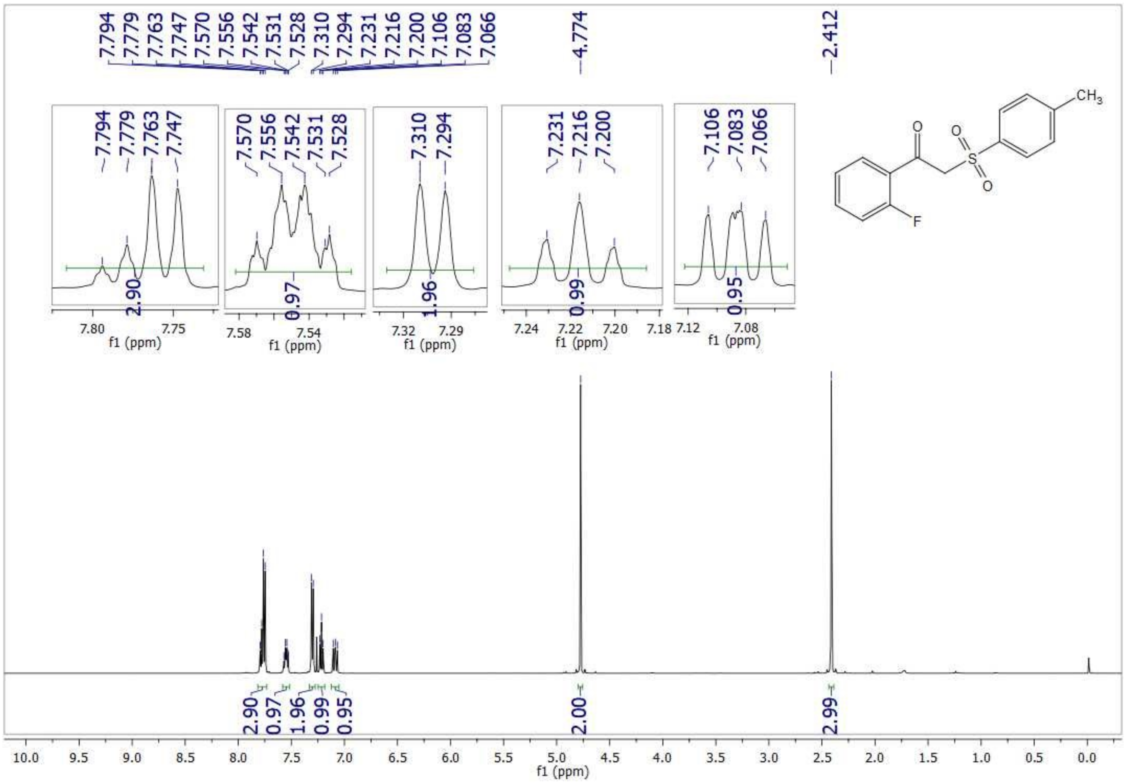
^{1}H NMR (500 MHz, CDCl$_3$) of compound **5**.



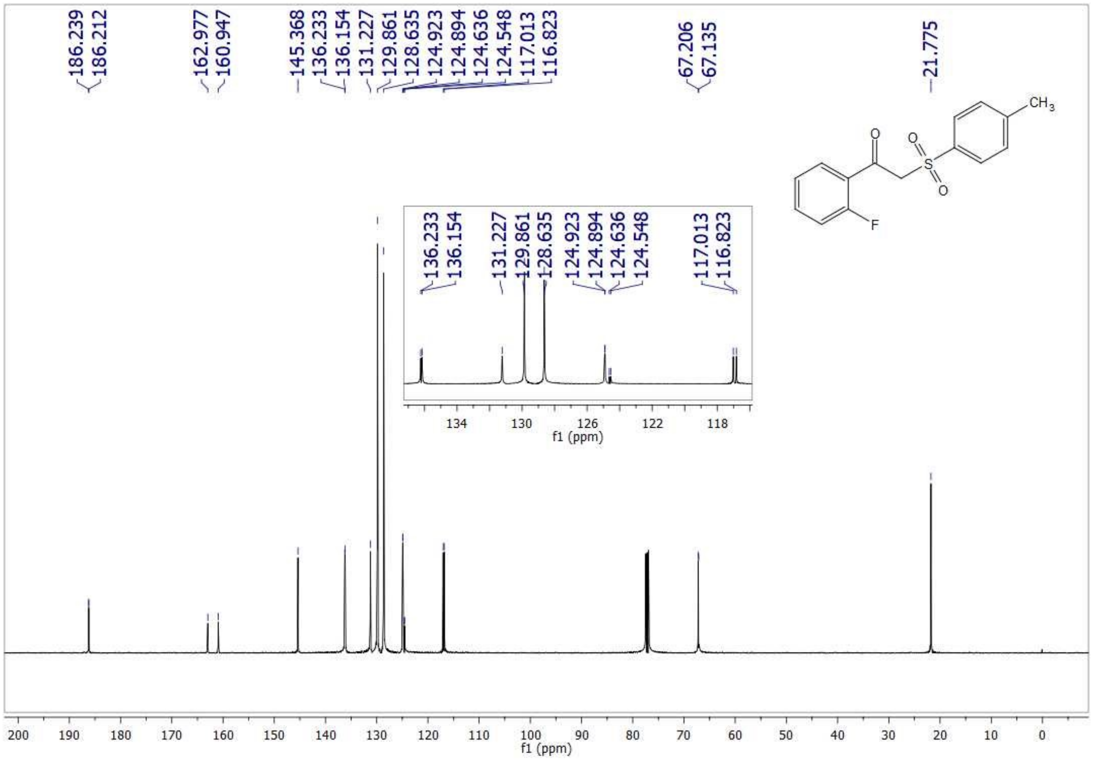
^{13}C NMR (126 MHz, CDCl$_3$) of compound **5**.



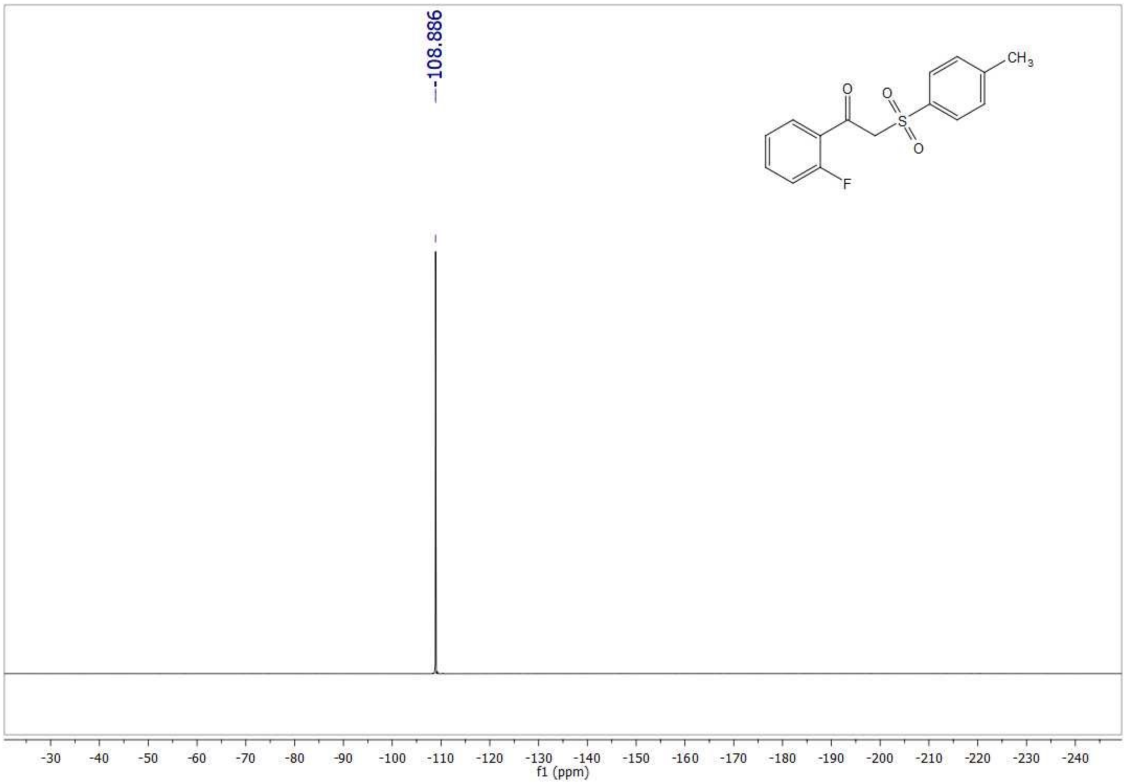
^{19}F NMR (472 MHz, CDCl$_3$) of compound **5**.



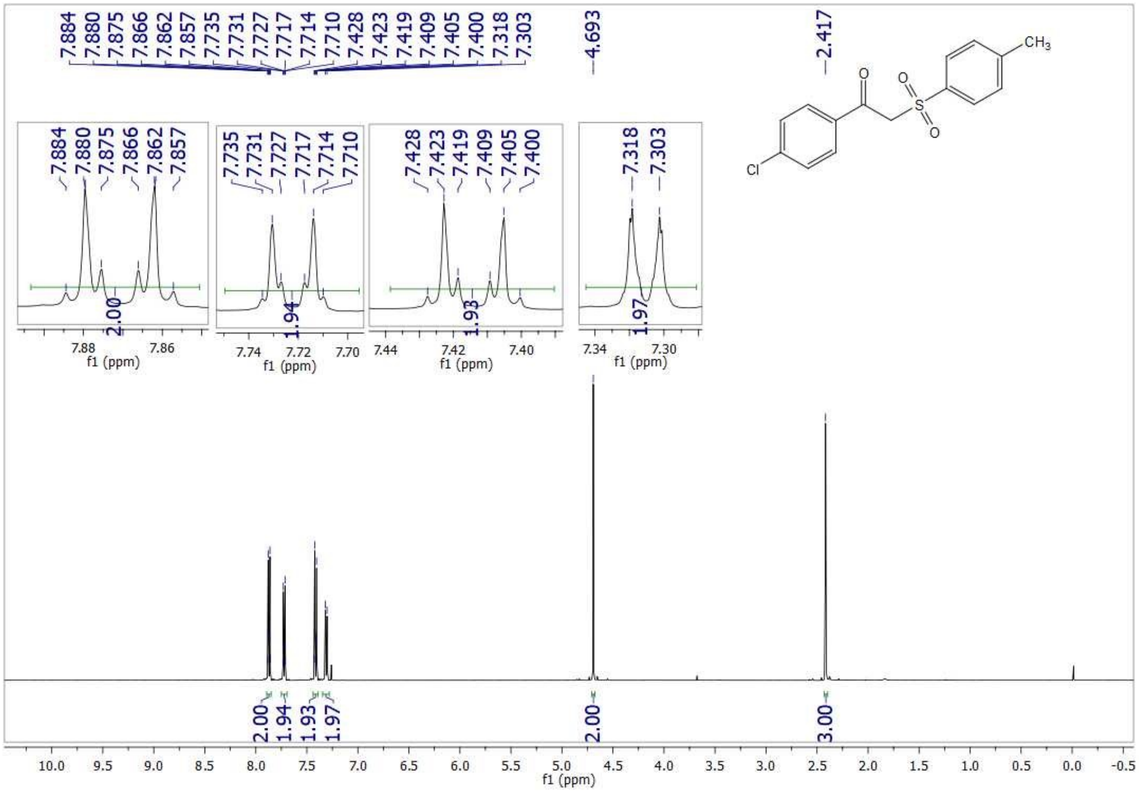
^{1}H NMR (500 MHz, CDCl$_3$) of compound **6**.



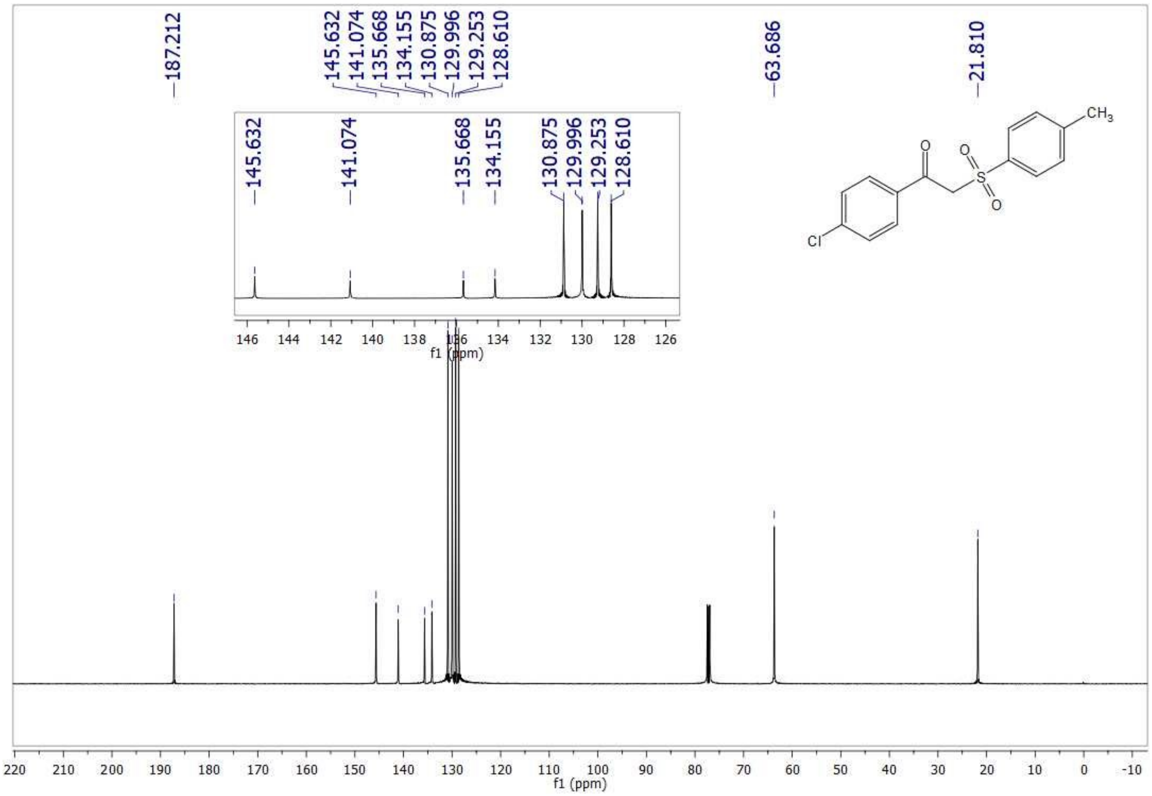
^{13}C NMR (126 MHz, CDCl$_3$) of compound **6**.



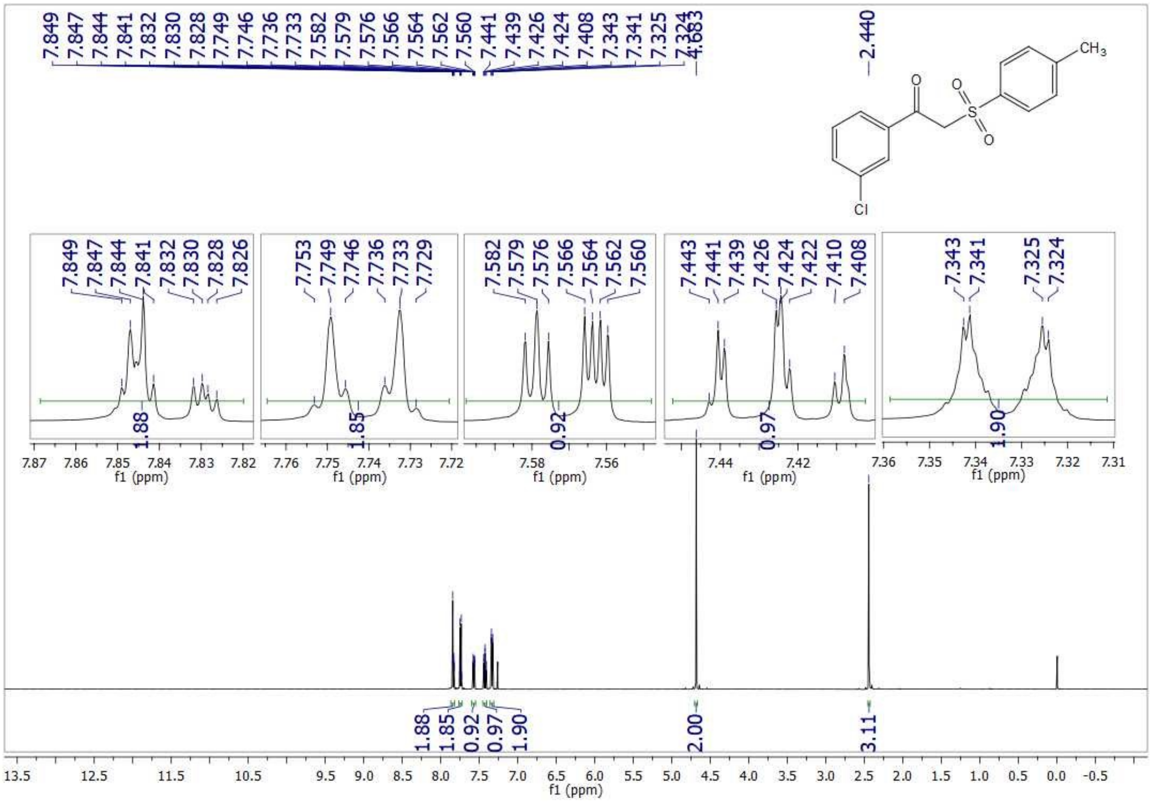
^{19}F NMR (472 MHz, CDCl$_3$) of compound **6**.



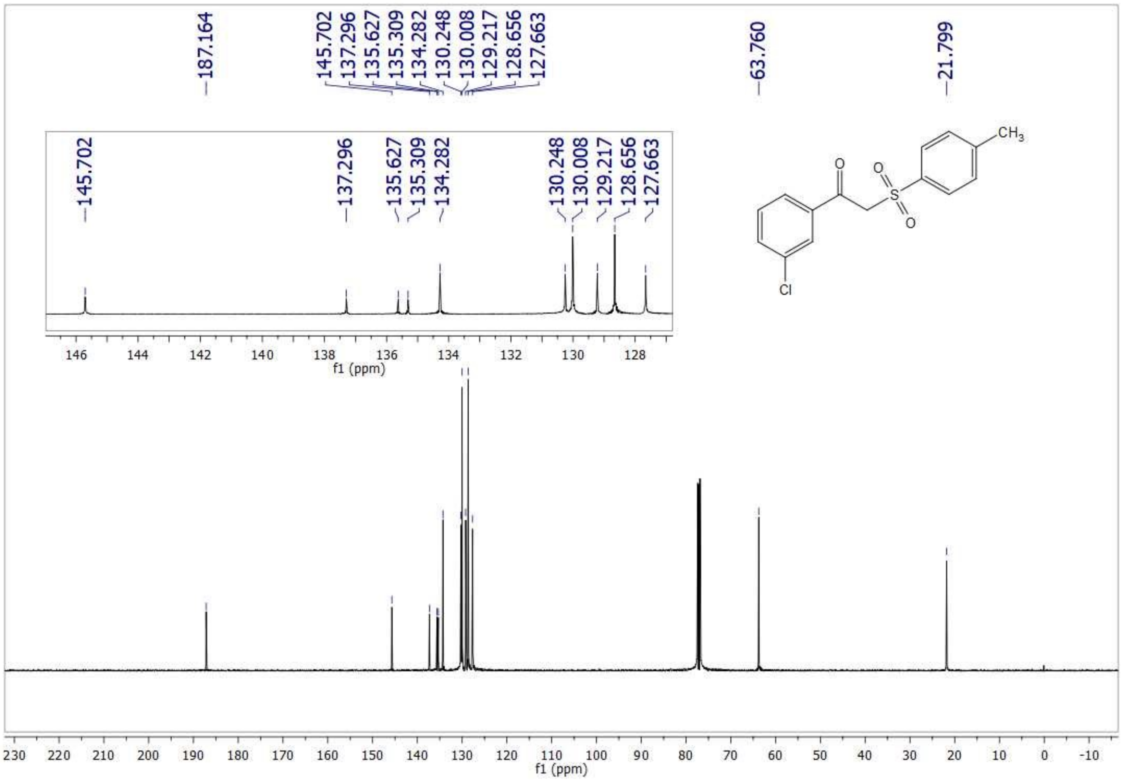
^{1}H NMR (500 MHz, CDCl$_3$) of compound **7**.



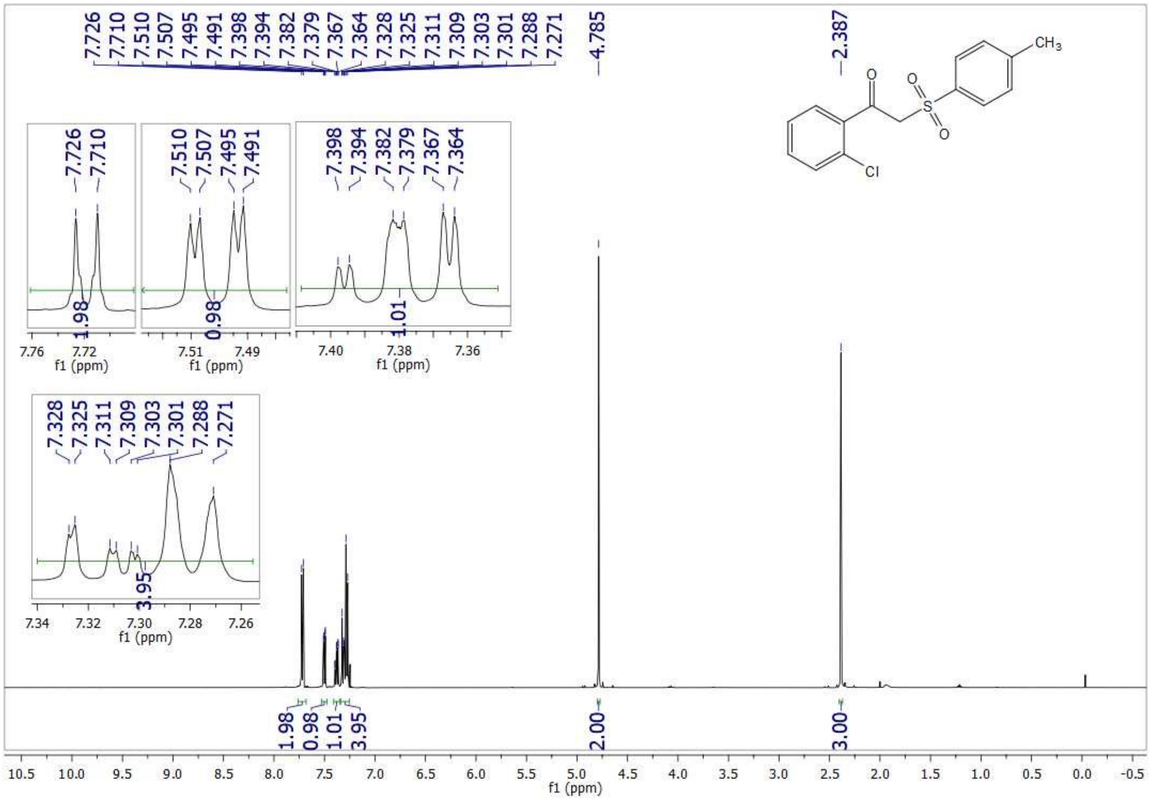
^{13}C NMR (126 MHz, CDCl$_3$) of compound **7**.



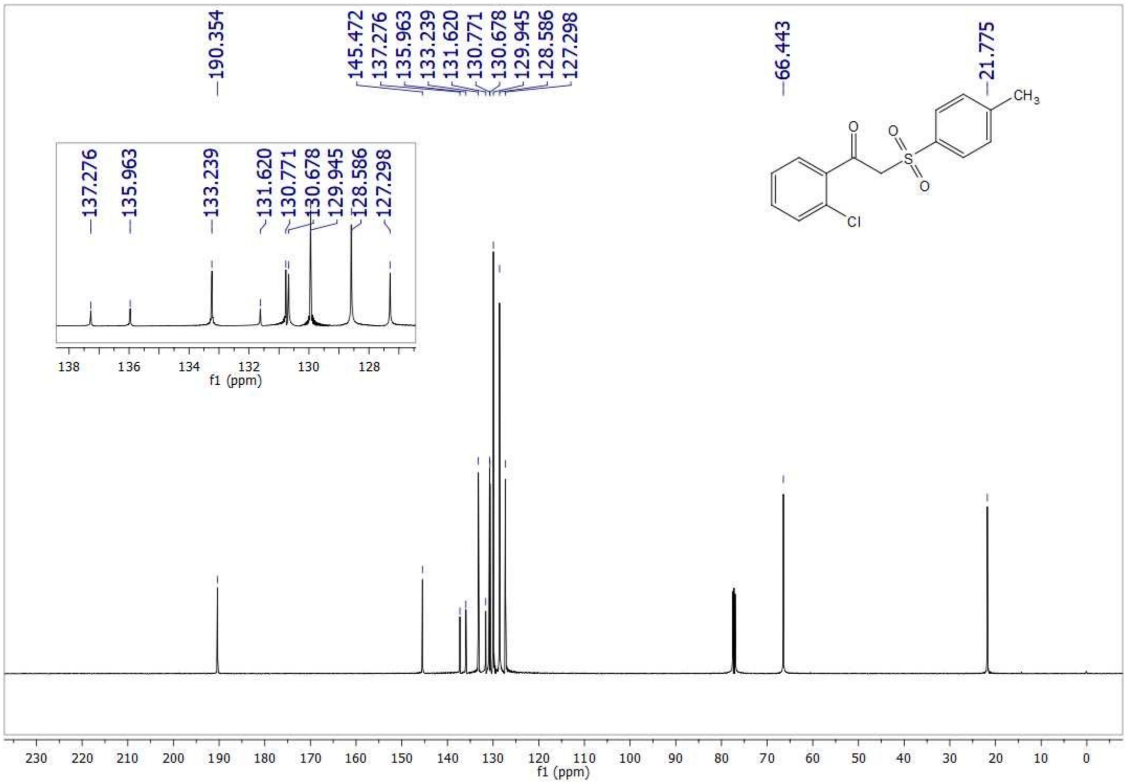
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



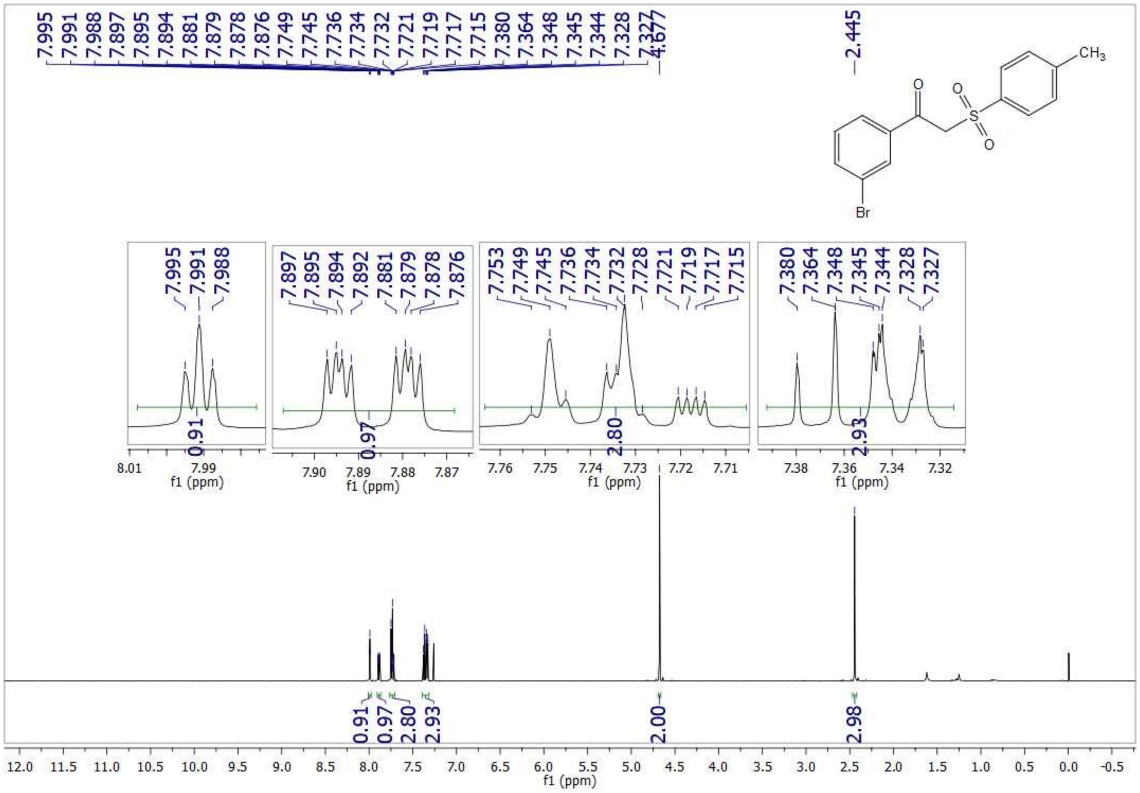
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**.



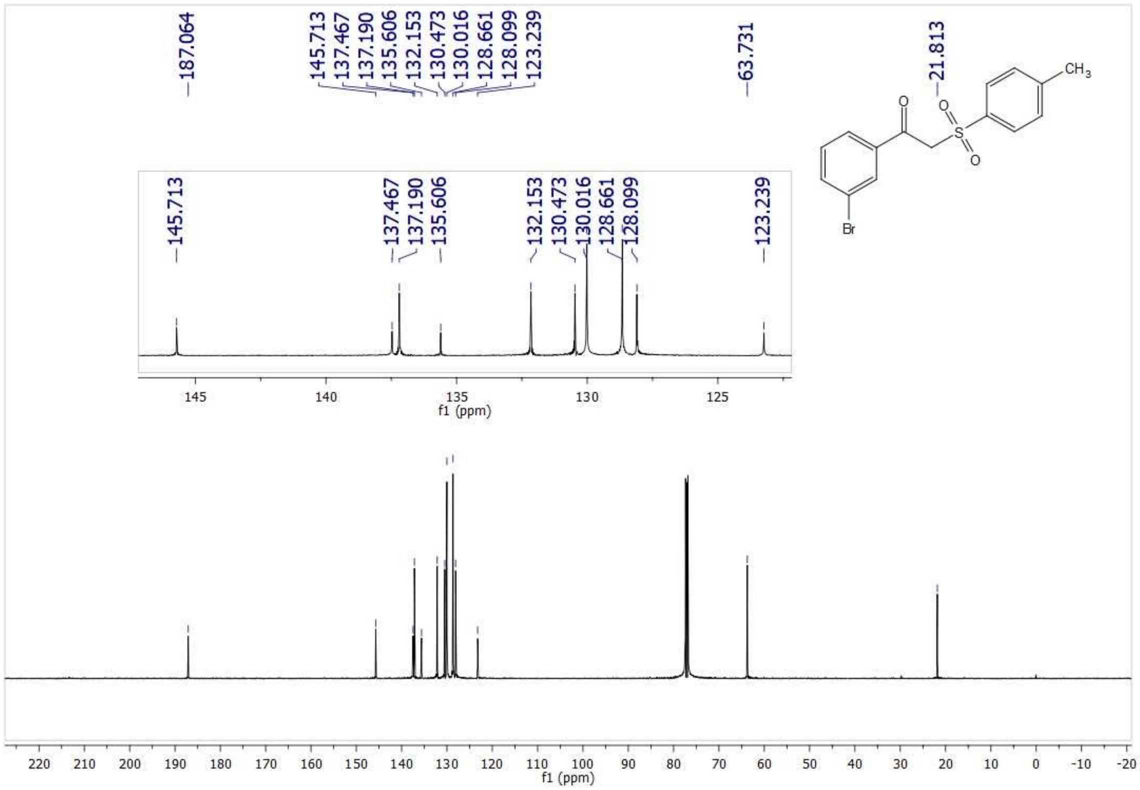
^{1}H NMR (500 MHz, CDCl$_3$) of compound **9**.



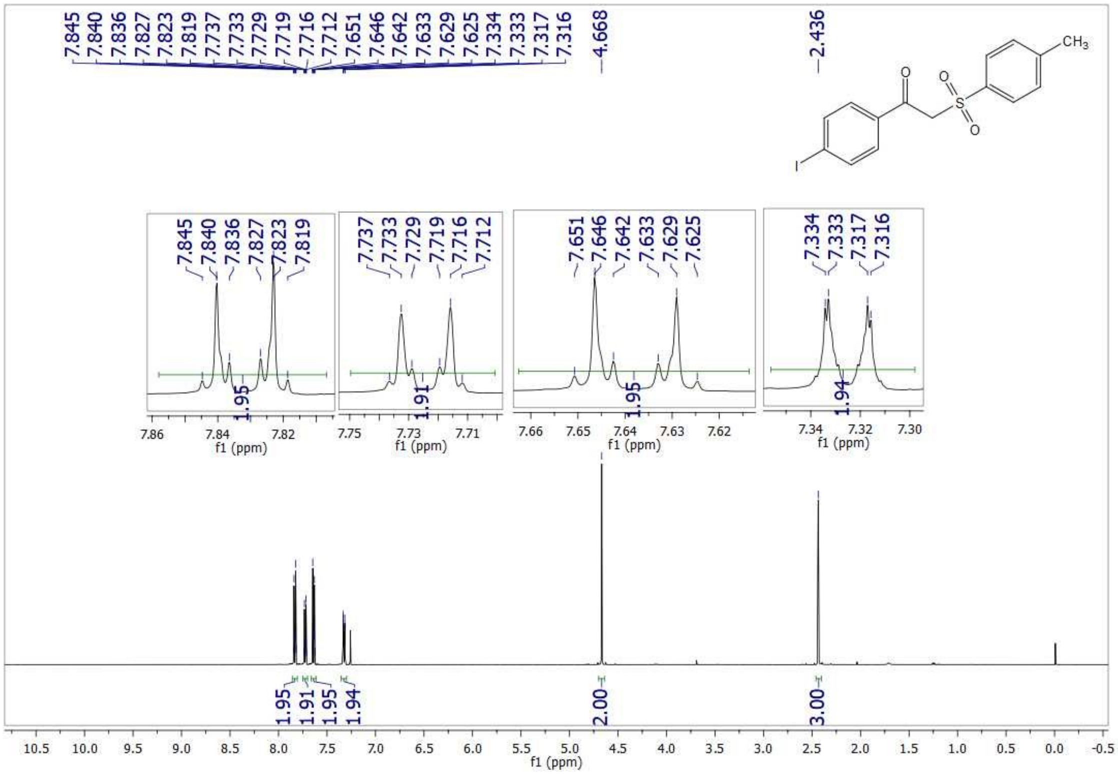
^{13}C NMR (126 MHz, CDCl$_3$) of compound **9**.



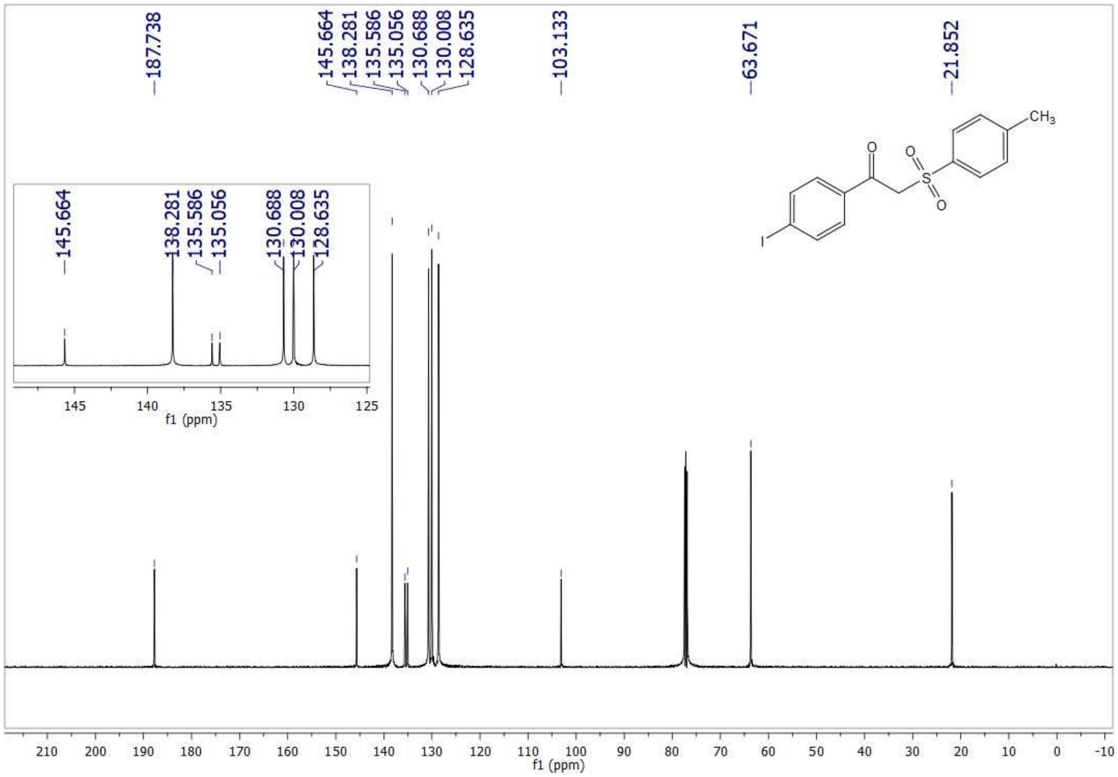
^{1}H NMR (500 MHz, CDCl$_3$) of compound **10**.



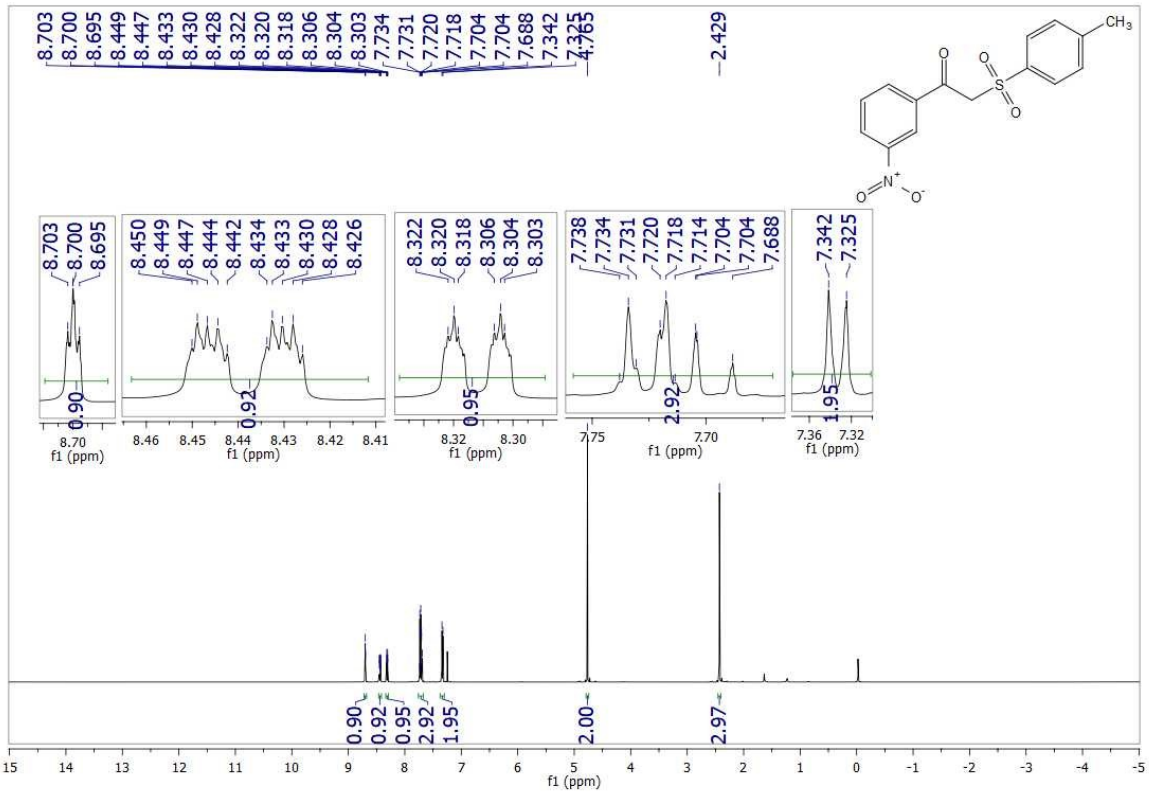
^{13}C NMR (126 MHz, CDCl$_3$) of compound **10**.



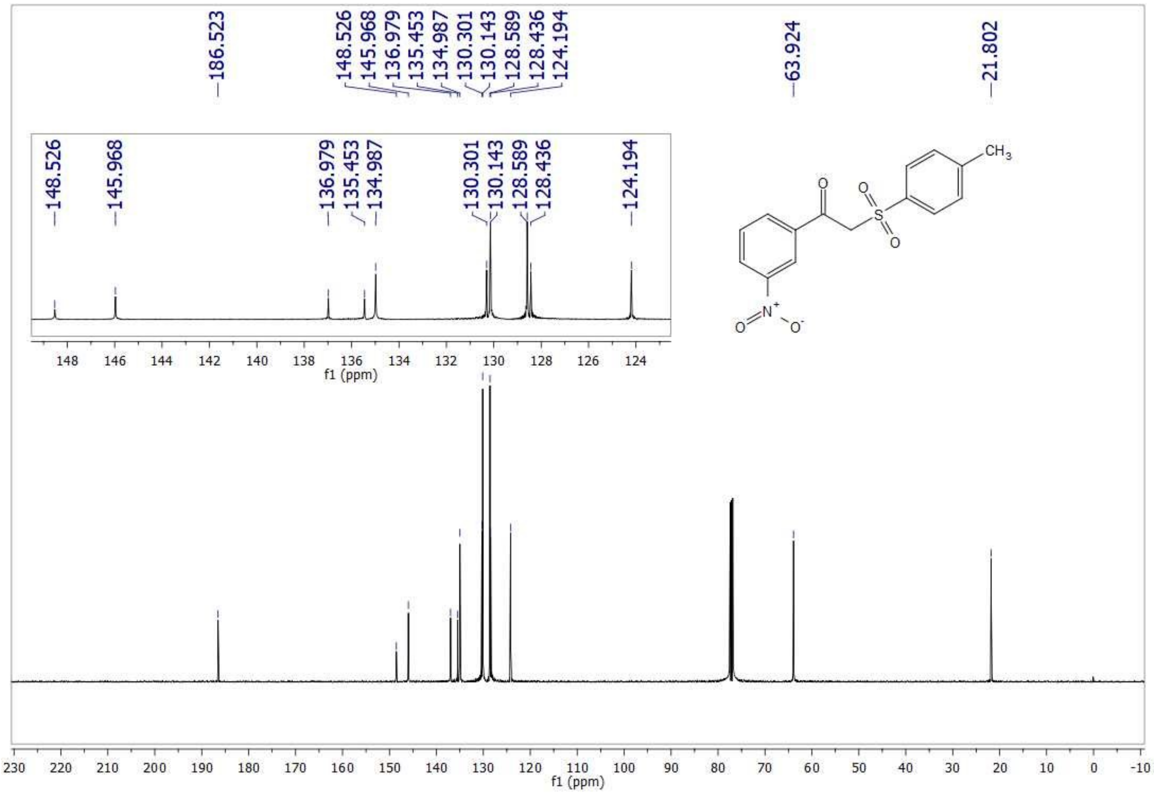
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



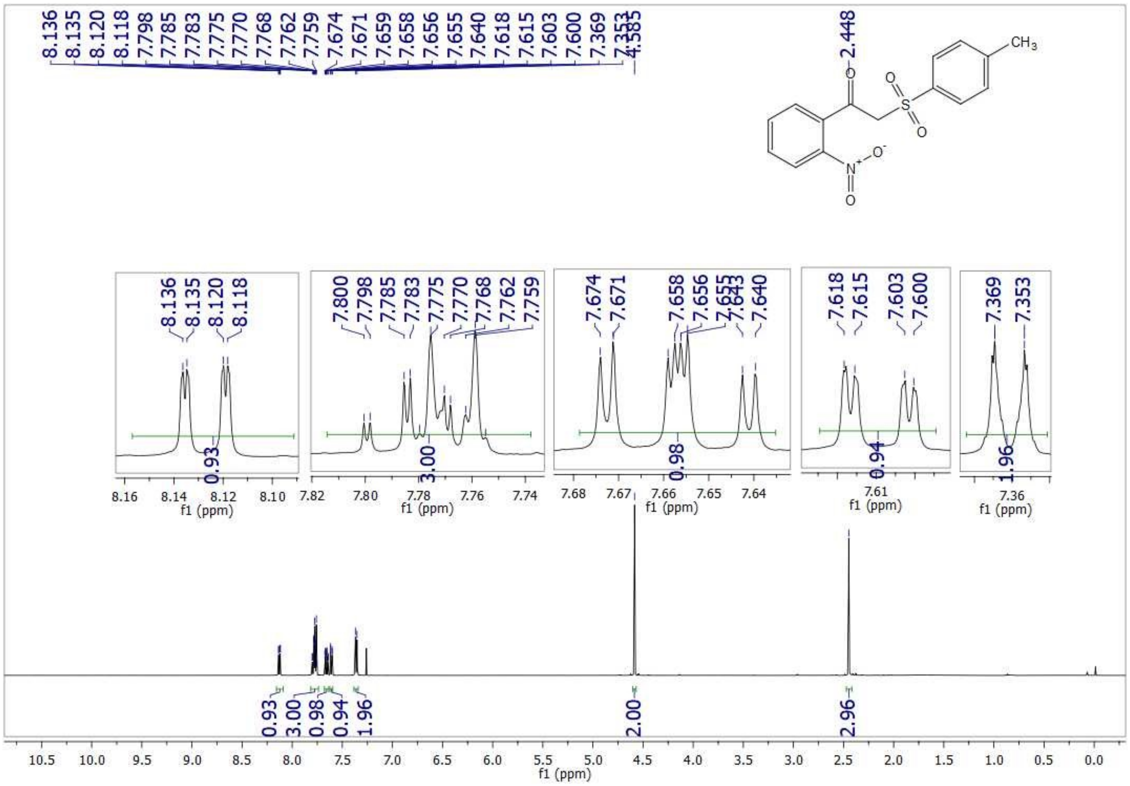
^{13}C NMR (126 MHz, $CDCl_3$) of compound **11**.



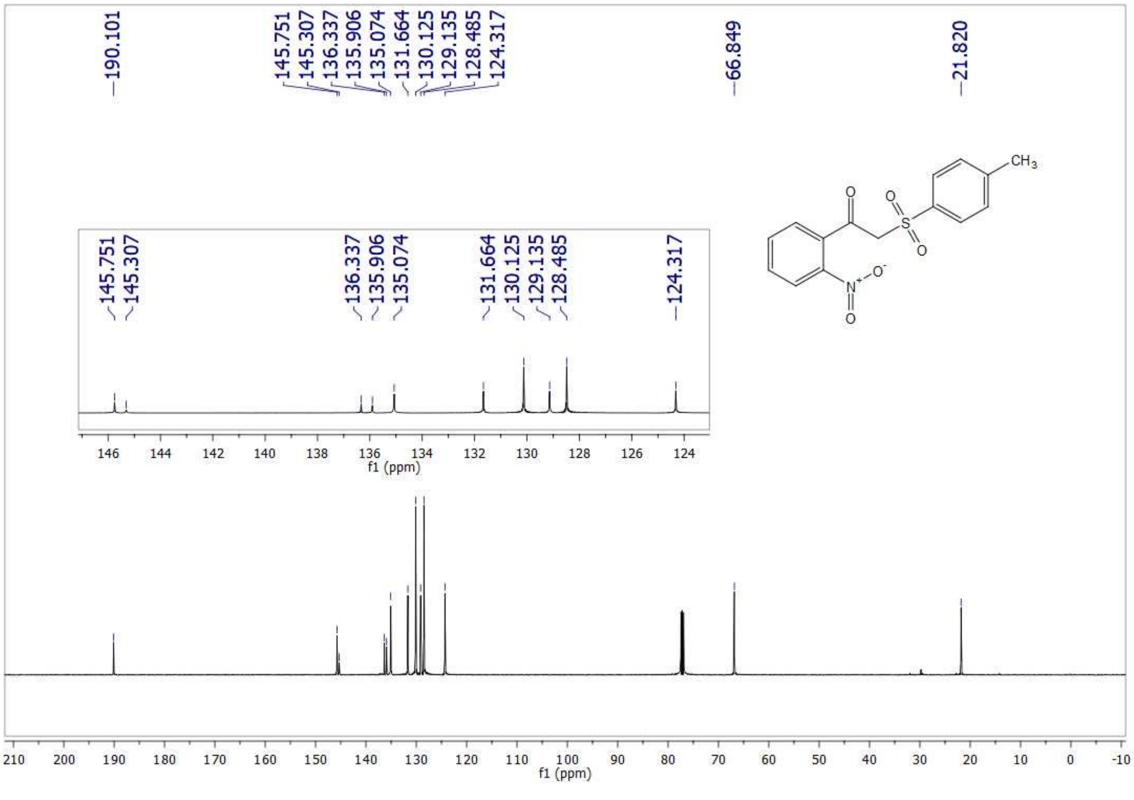
^{1}H NMR (500 MHz, CDCl$_3$) of compound **12**.



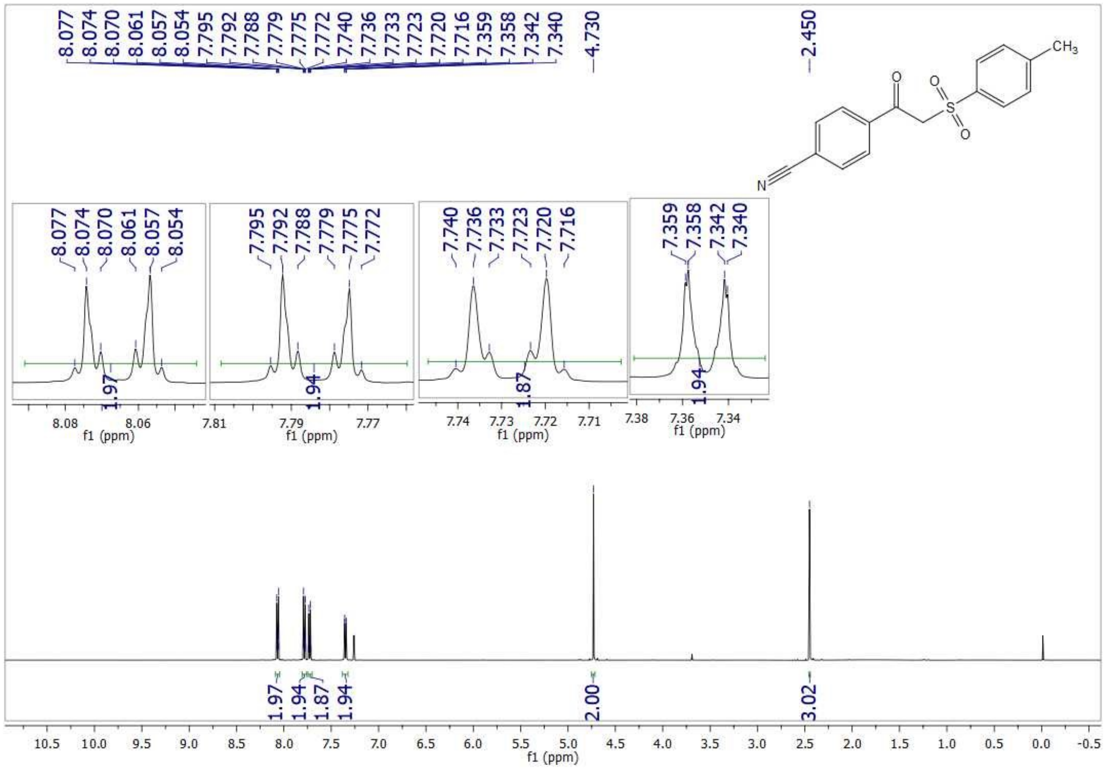
^{13}C NMR (126 MHz, CDCl$_3$) of compound **12**.



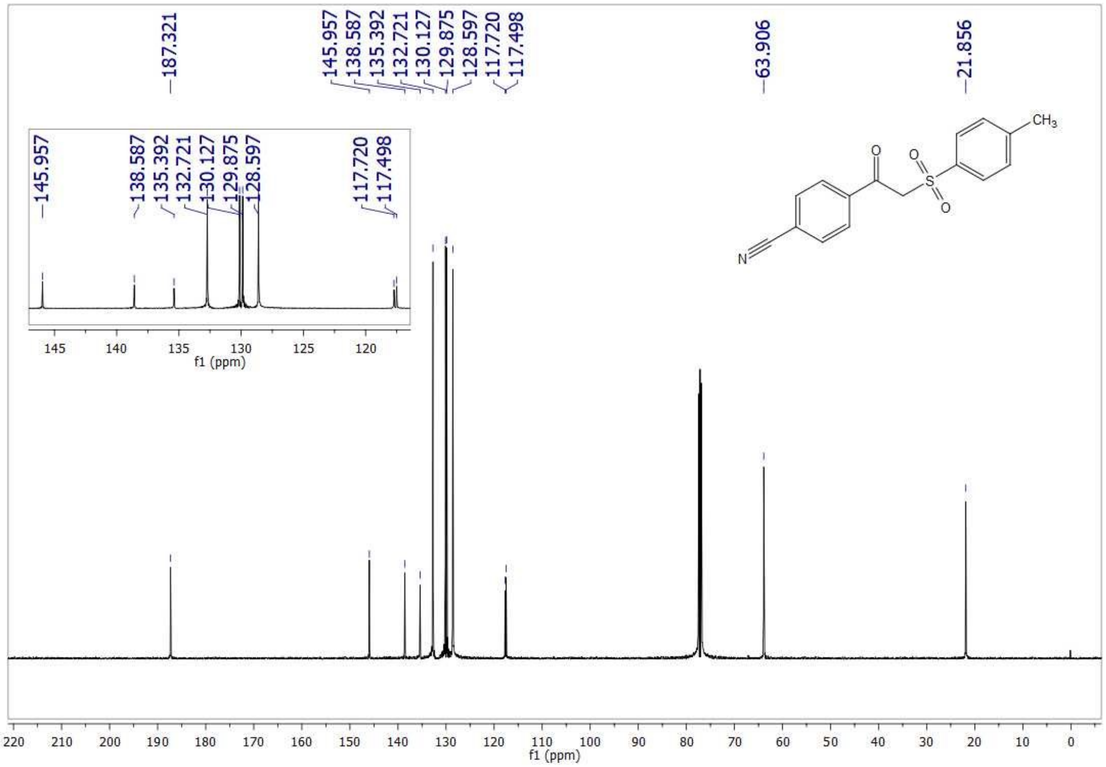
^{1}H NMR (500 MHz, CDCl$_3$) of compound **13**.



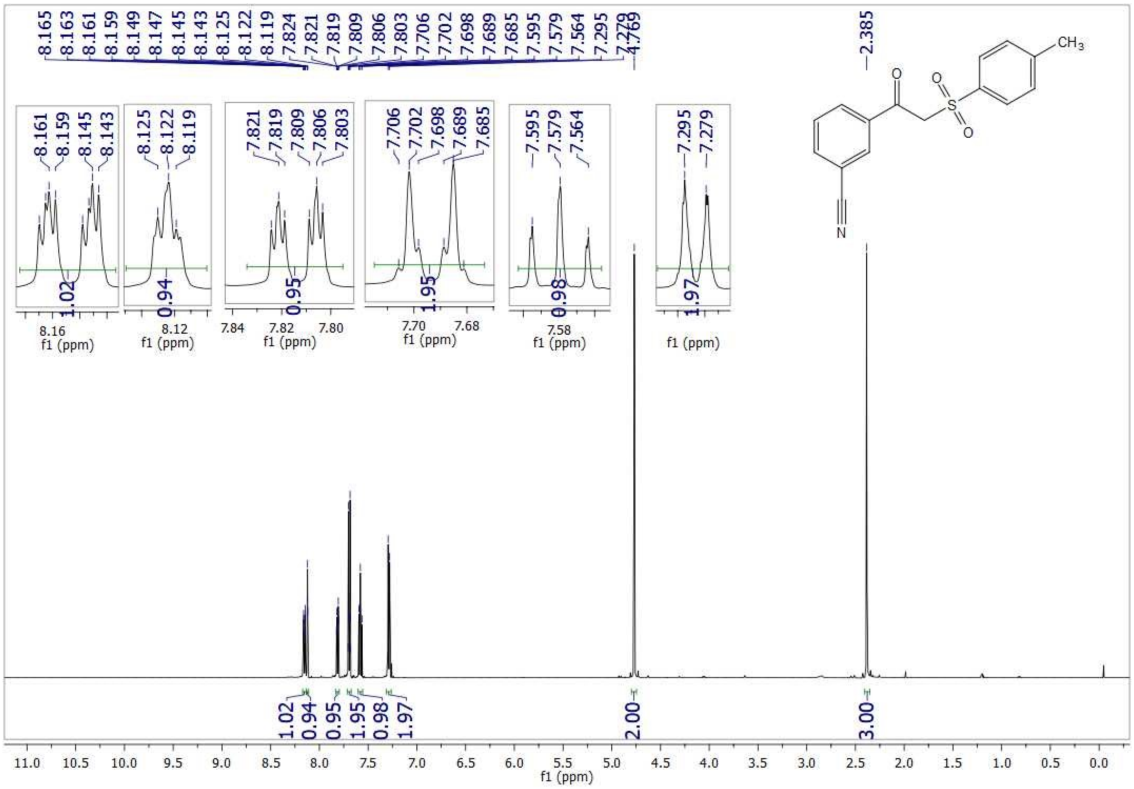
^{13}C NMR (126 MHz, CDCl$_3$) of compound **13**.



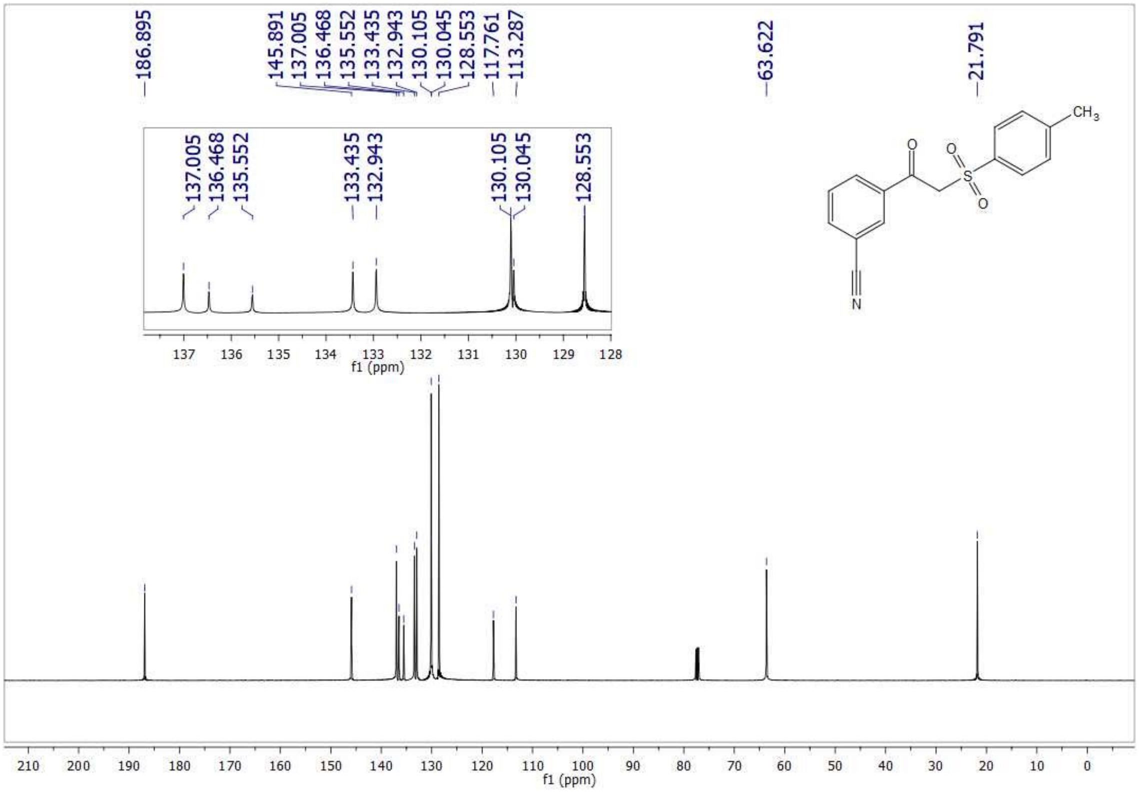
^{1}H NMR (500 MHz, CDCl$_3$) of compound **14**.



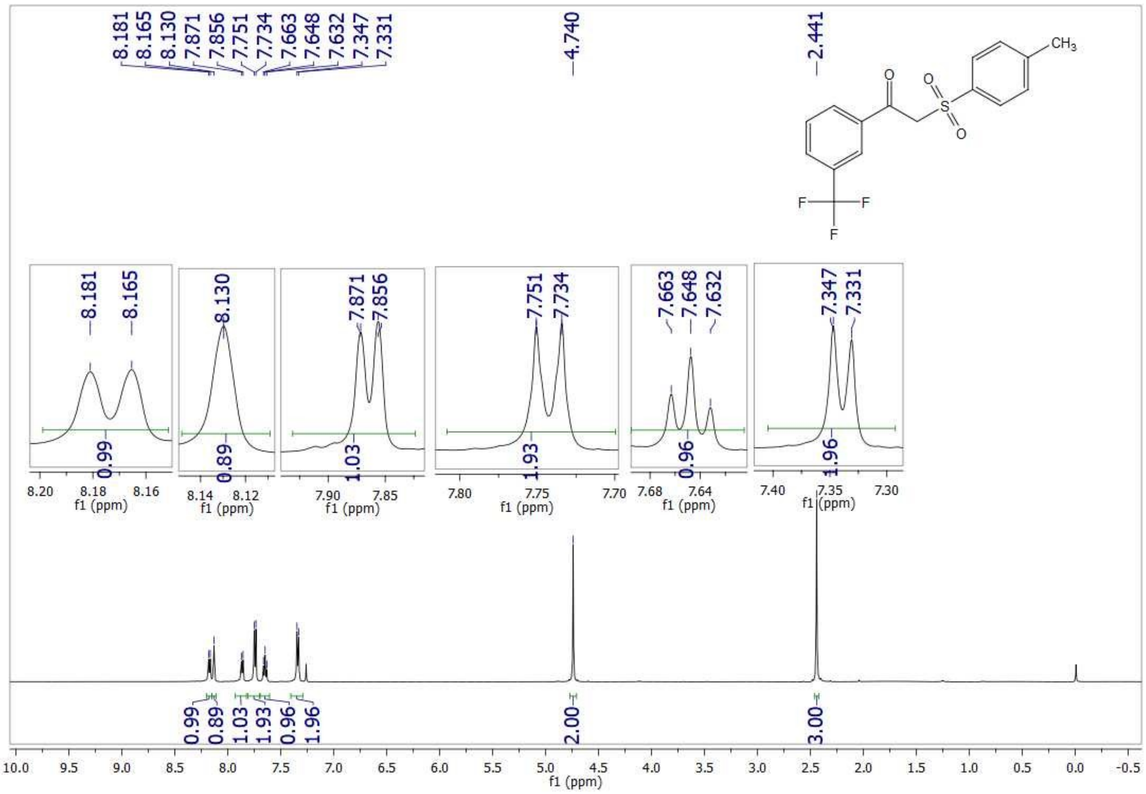
^{13}C NMR (126 MHz, CDCl$_3$) of compound **14**.



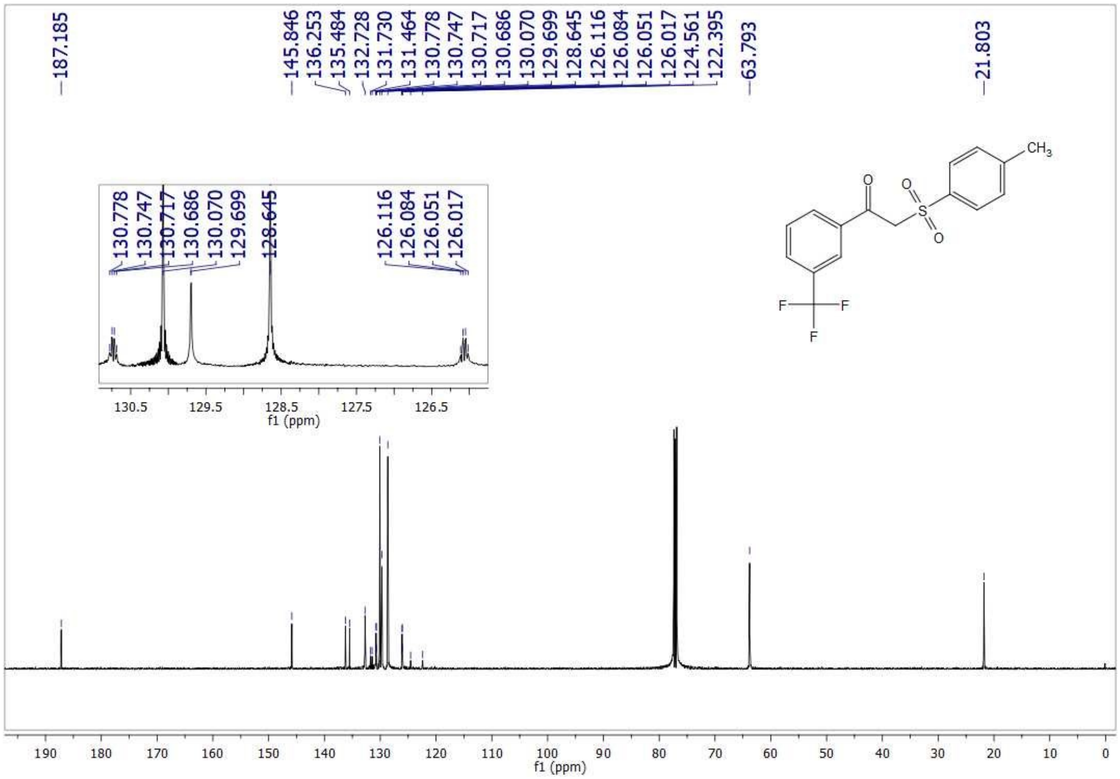
^{1}H NMR (500 MHz, CDCl$_3$) of compound **15**.



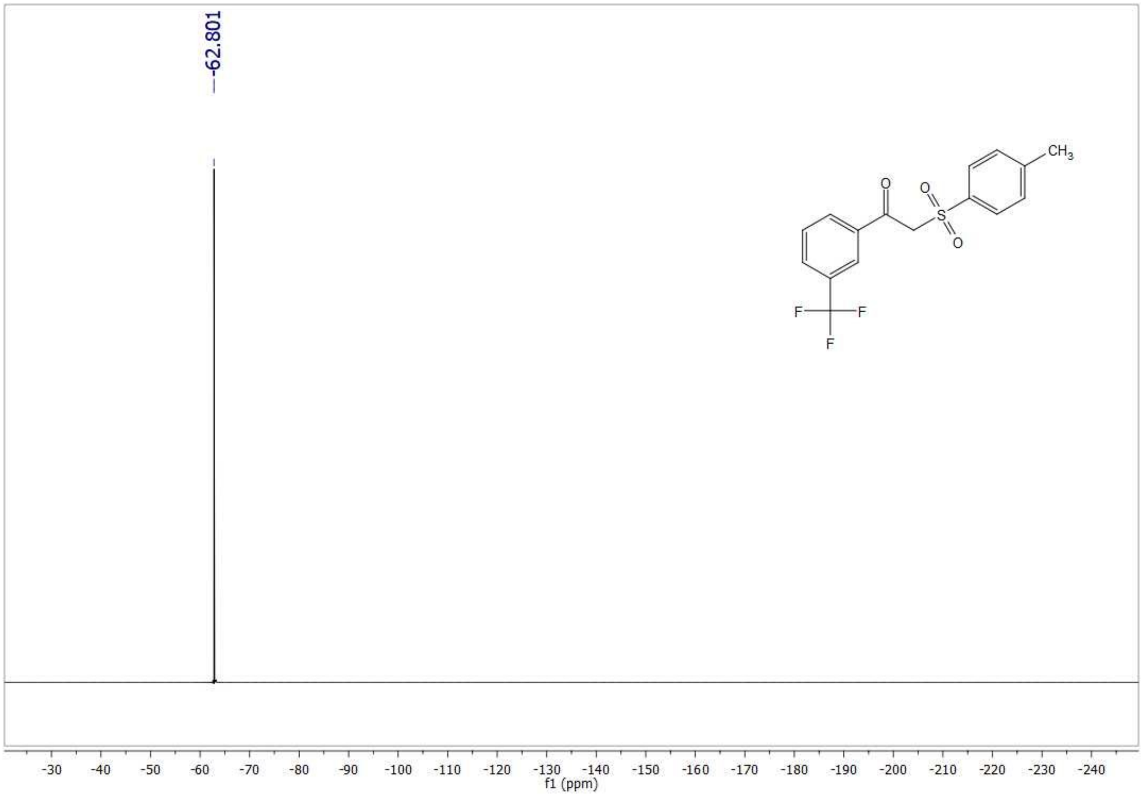
^{13}C NMR (126 MHz, CDCl$_3$) of compound **15**.



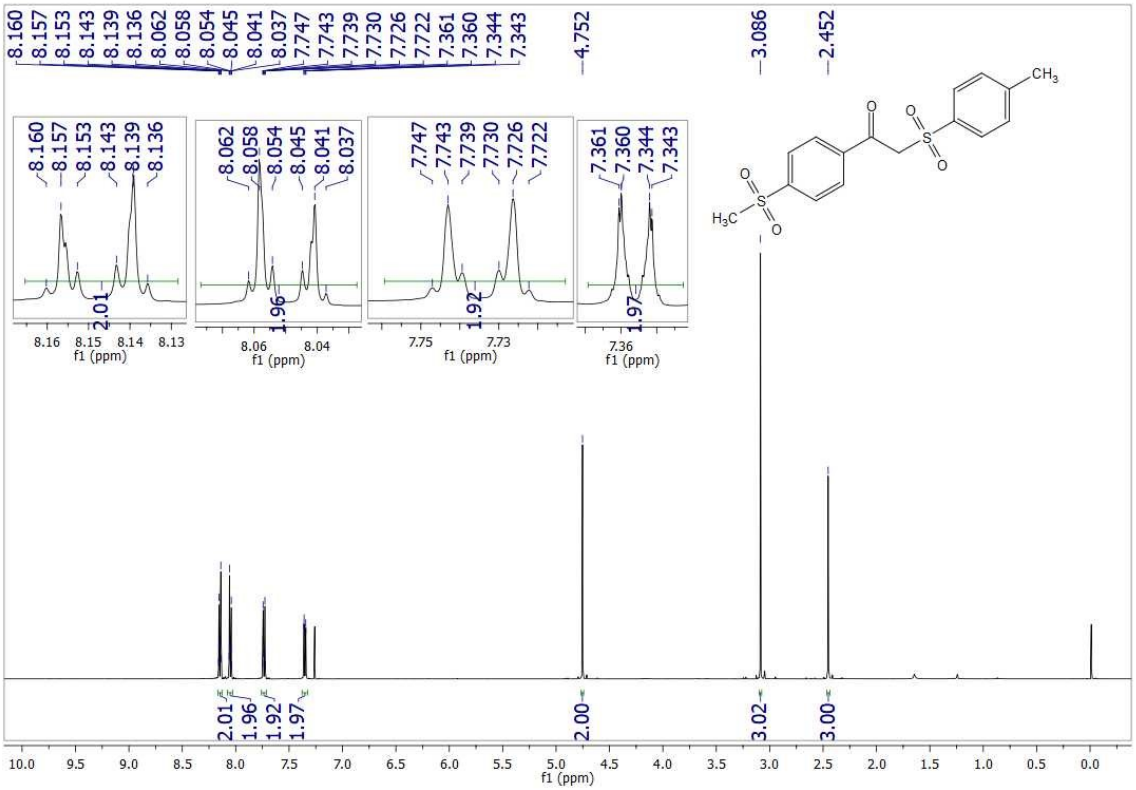
^{1}H NMR (500 MHz, CDCl$_3$) of compound **16**.



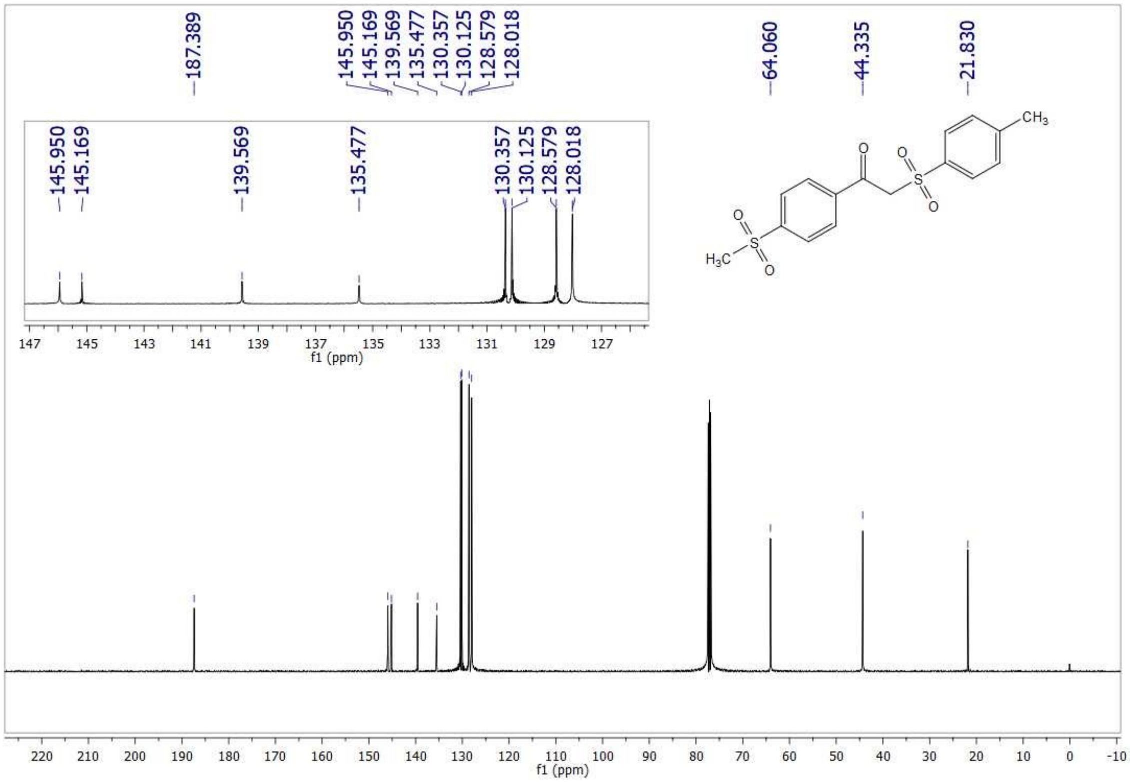
^{13}C NMR (126 MHz, CDCl$_3$) of compound **16.**



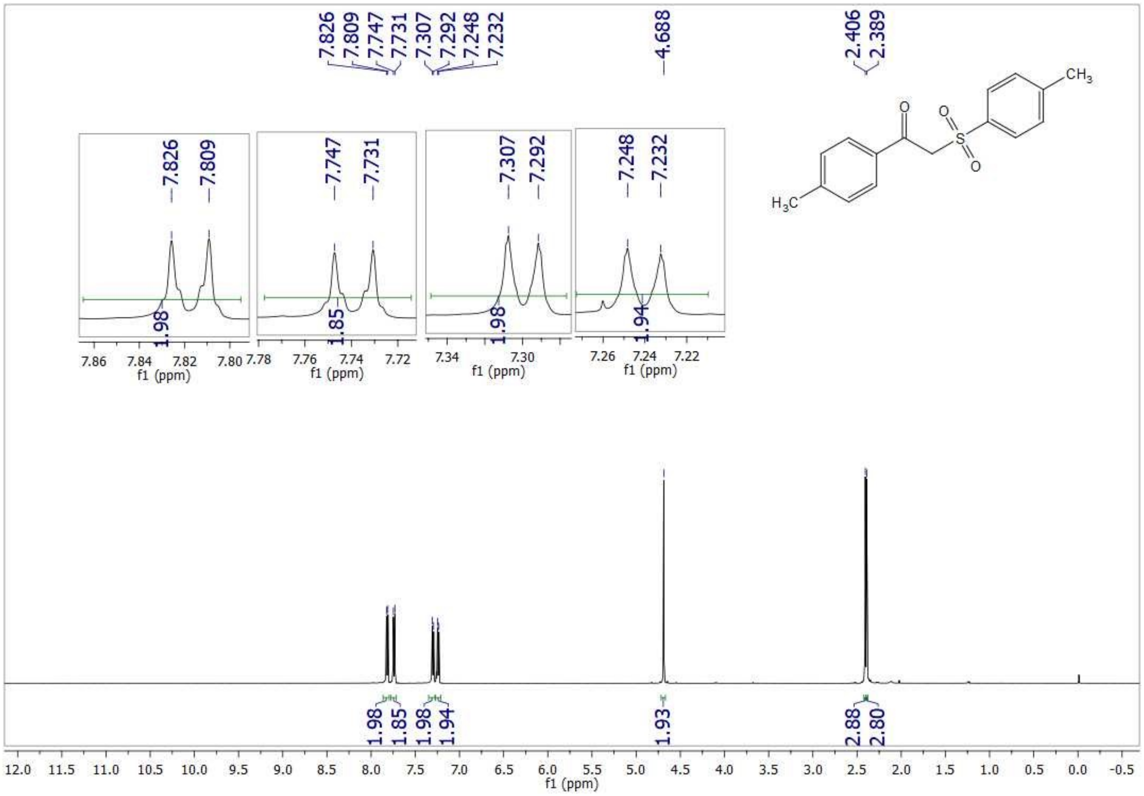
^{19}F NMR (472 MHz, CDCl$_3$) of compound **16**.



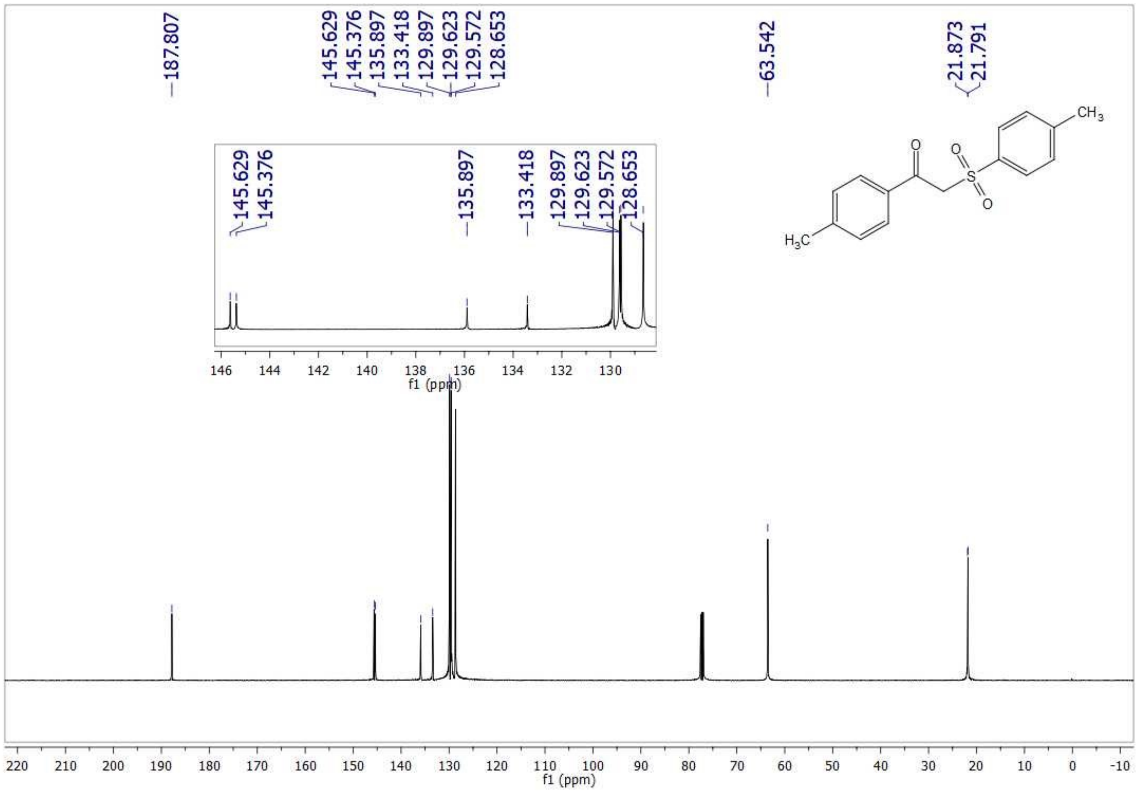
^{1}H NMR (500 MHz, CDCl$_3$) of compound **17**.



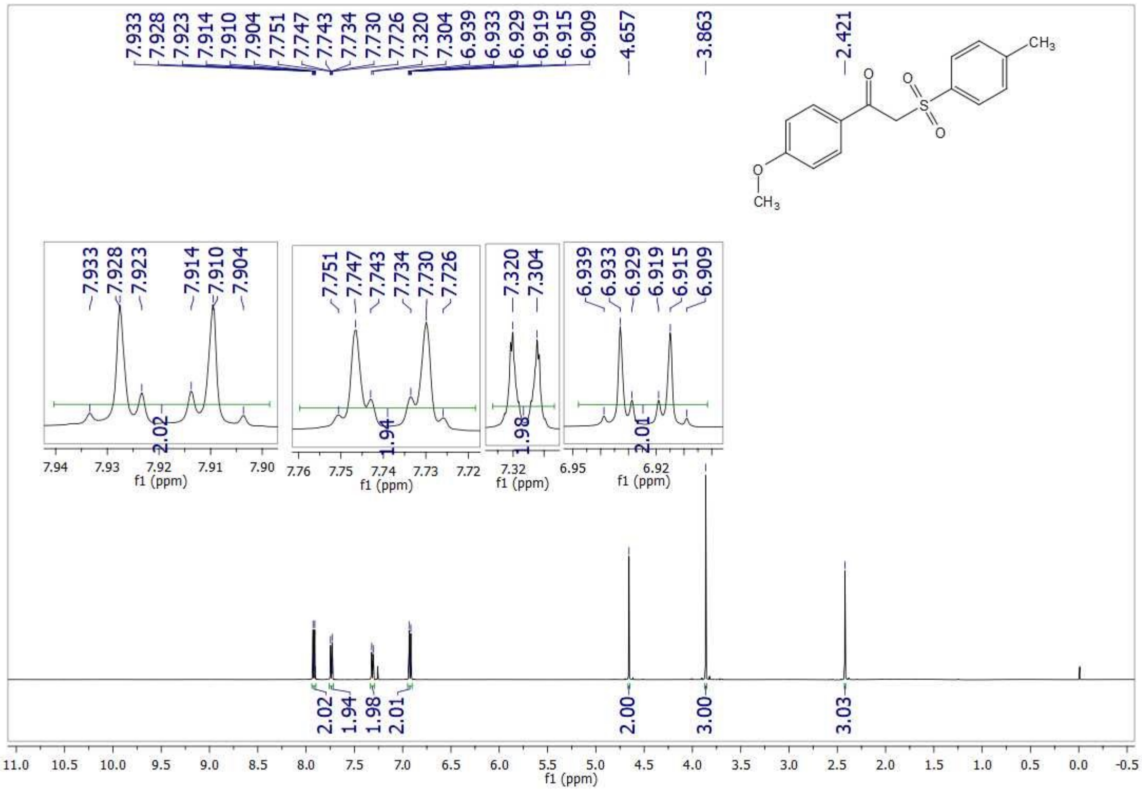
^{13}C NMR (126 MHz, CDCl$_3$) of compound **17**.



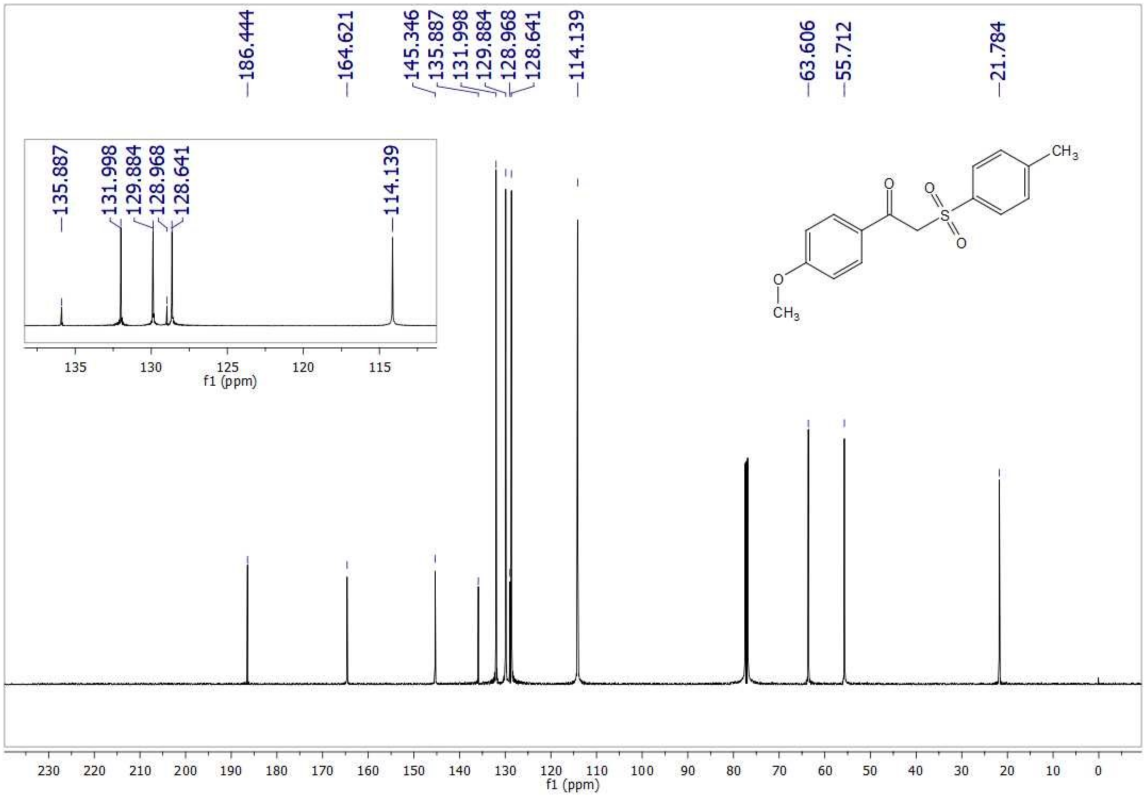
^{1}H NMR (500 MHz, CDCl$_3$) of compound **18**.



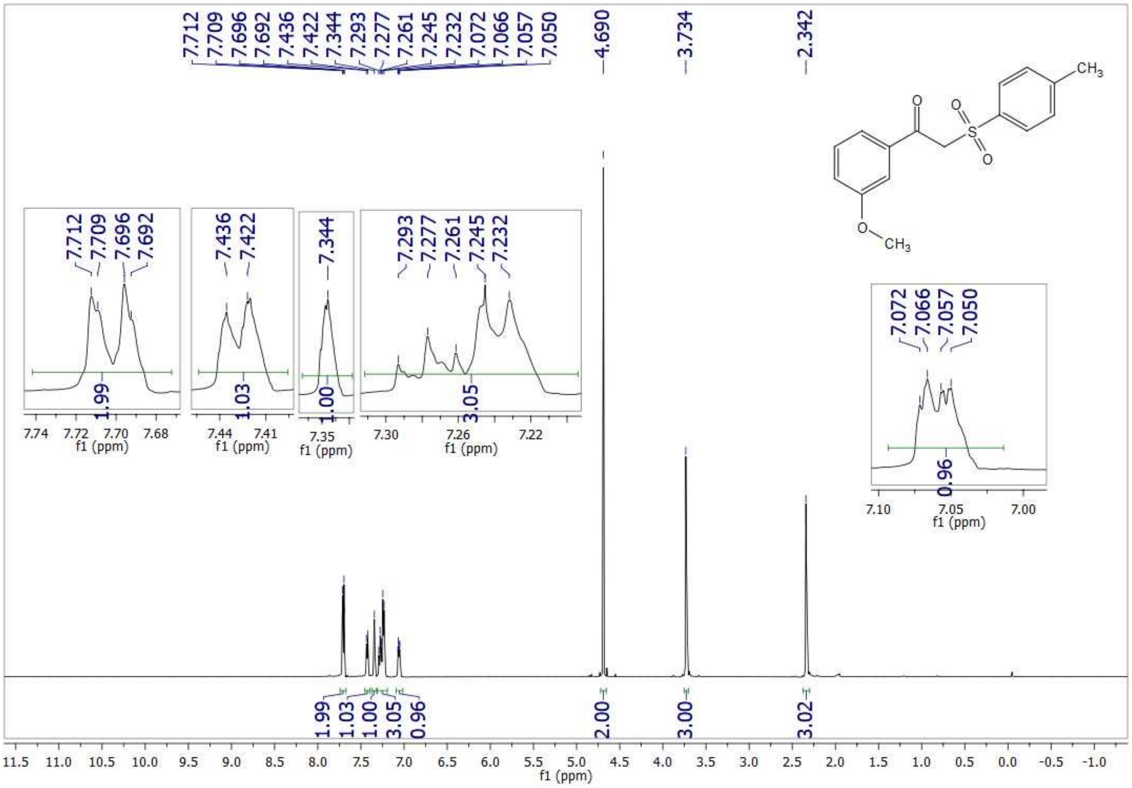
^{13}C NMR (126 MHz, CDCl$_3$) of compound **18**.



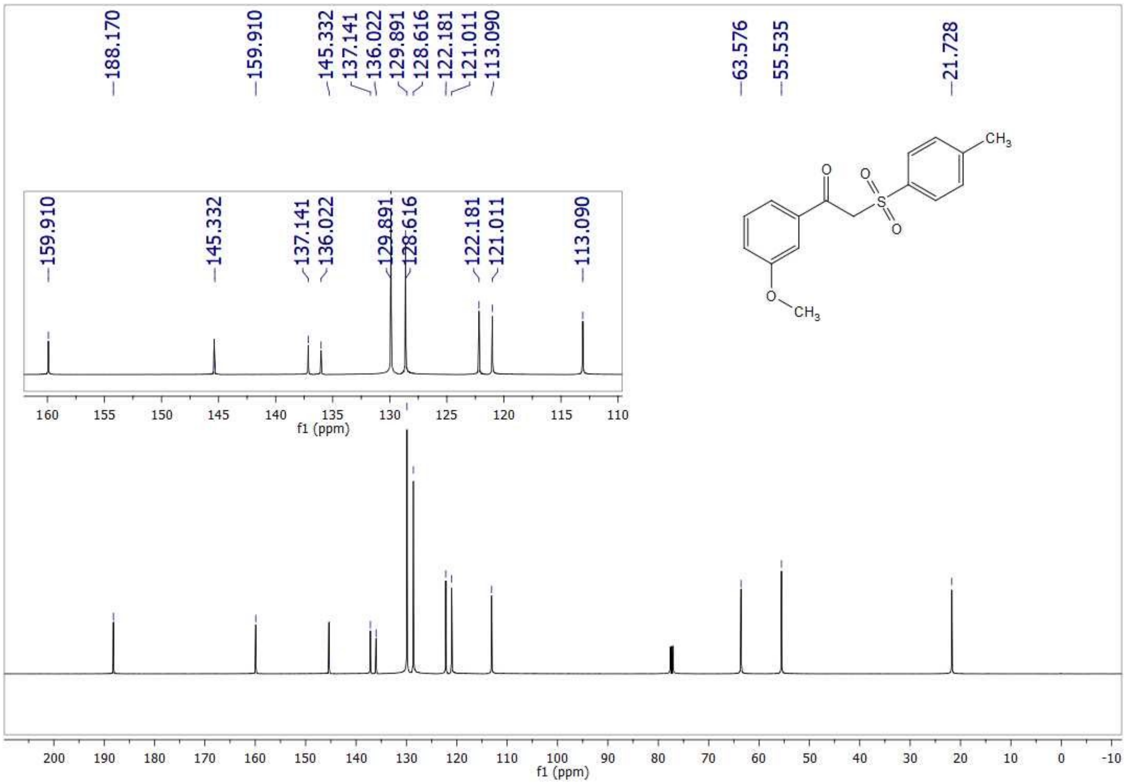
^{1}H NMR (500 MHz, CDCl$_3$) of compound **19**.



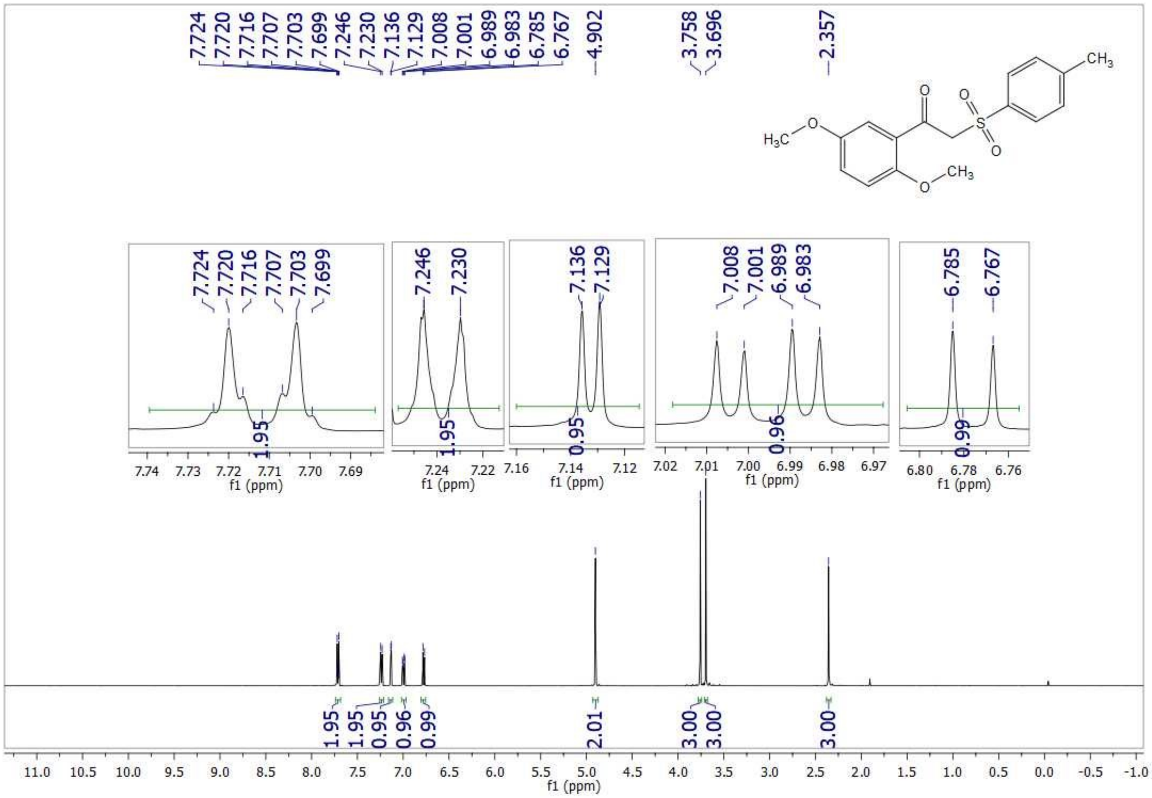
^{13}C NMR (126 MHz, CDCl$_3$) of compound **19**.



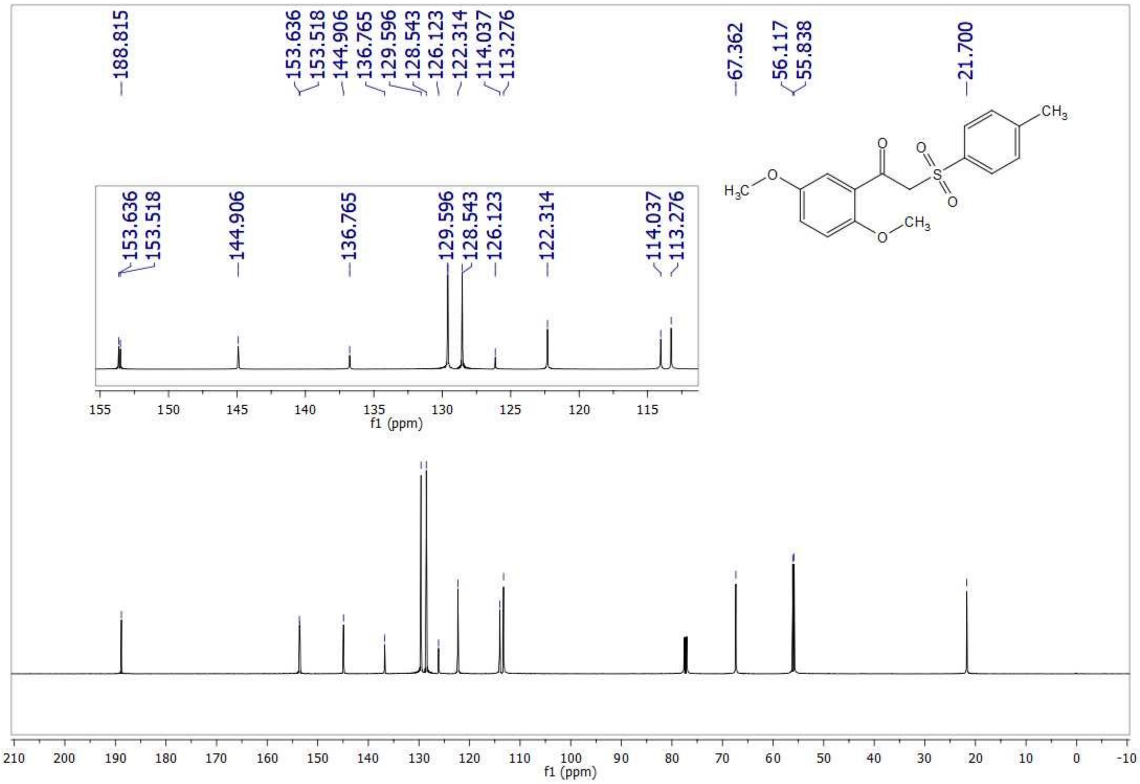
^{1}H NMR (500 MHz, CDCl$_3$) of compound **20**.



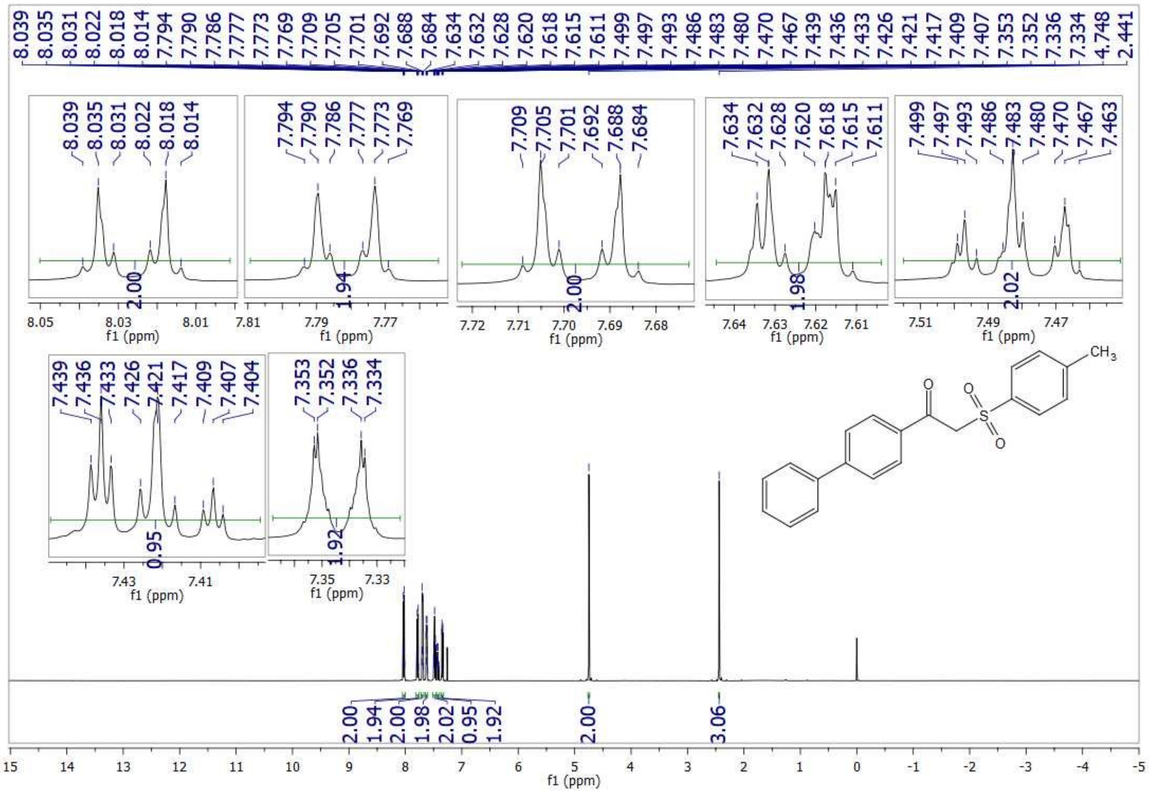
^{13}C NMR (126 MHz, CDCl$_3$) of compound **20**.



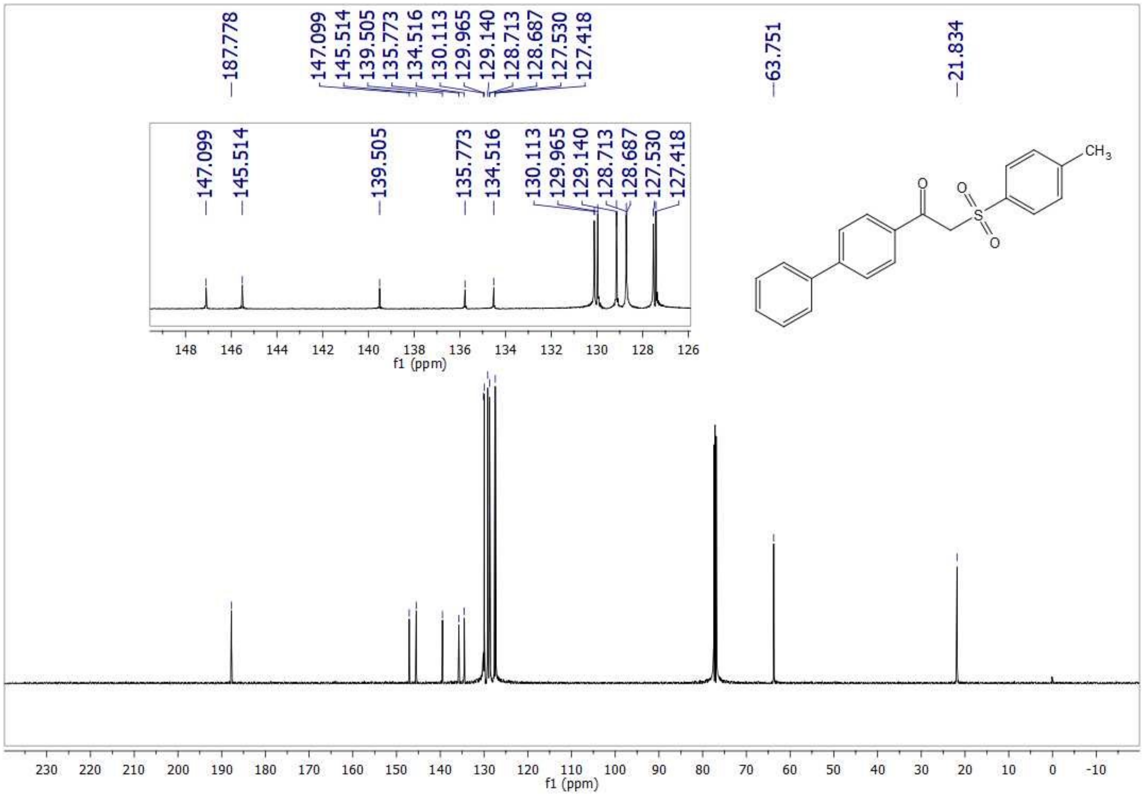
^{1}H NMR (500 MHz, CDCl$_3$) of compound **21**.



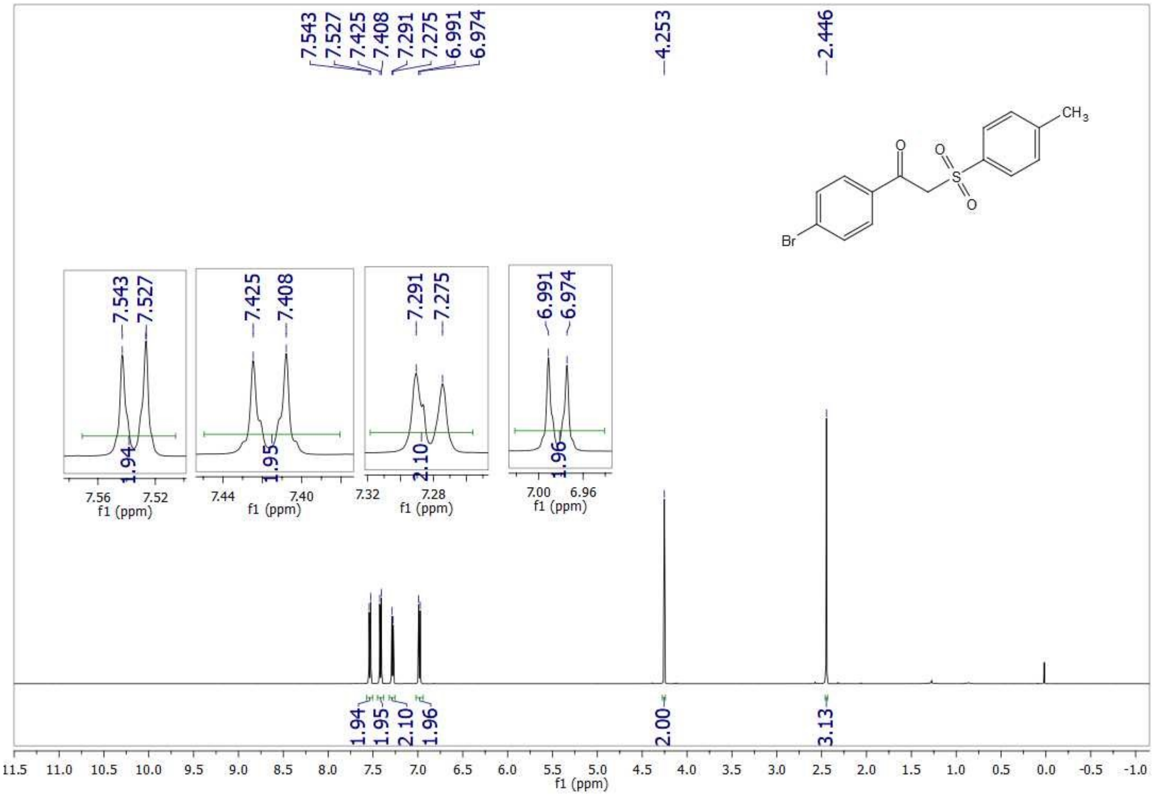
^{13}C NMR (126 MHz, CDCl$_3$) of compound **21**.



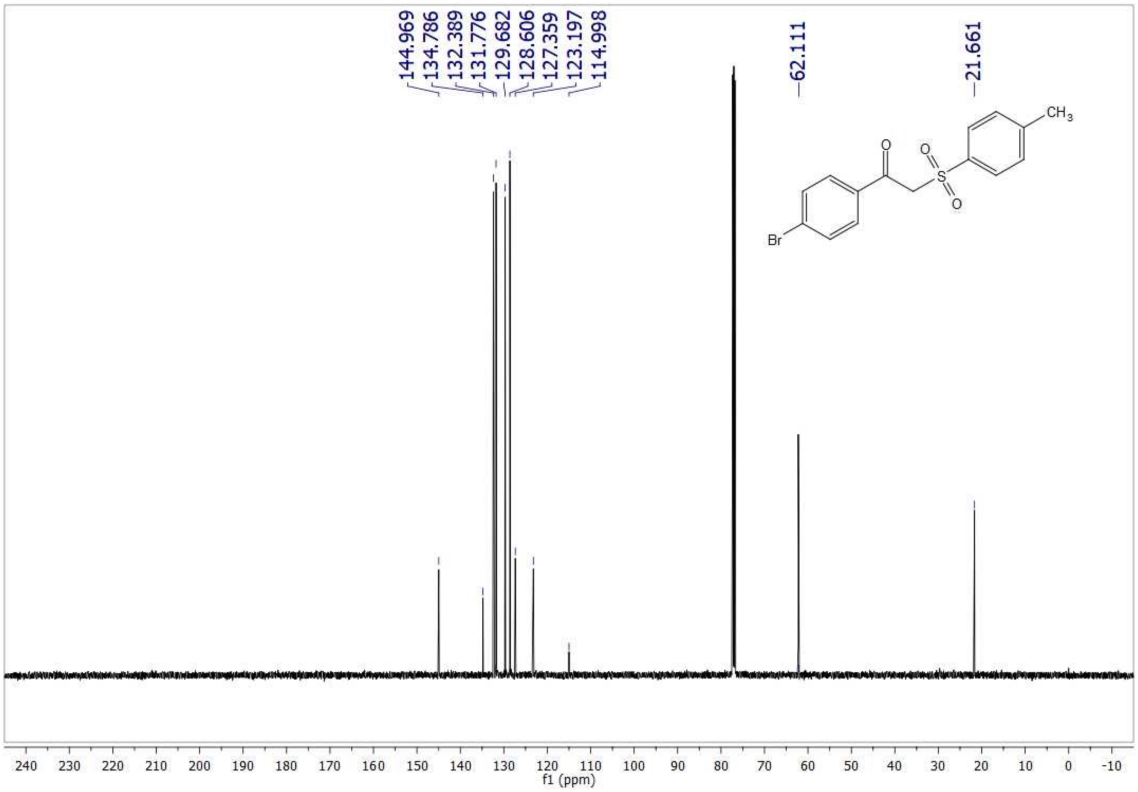
^{1}H NMR (500 MHz, CDCl$_3$) of compound **22**.



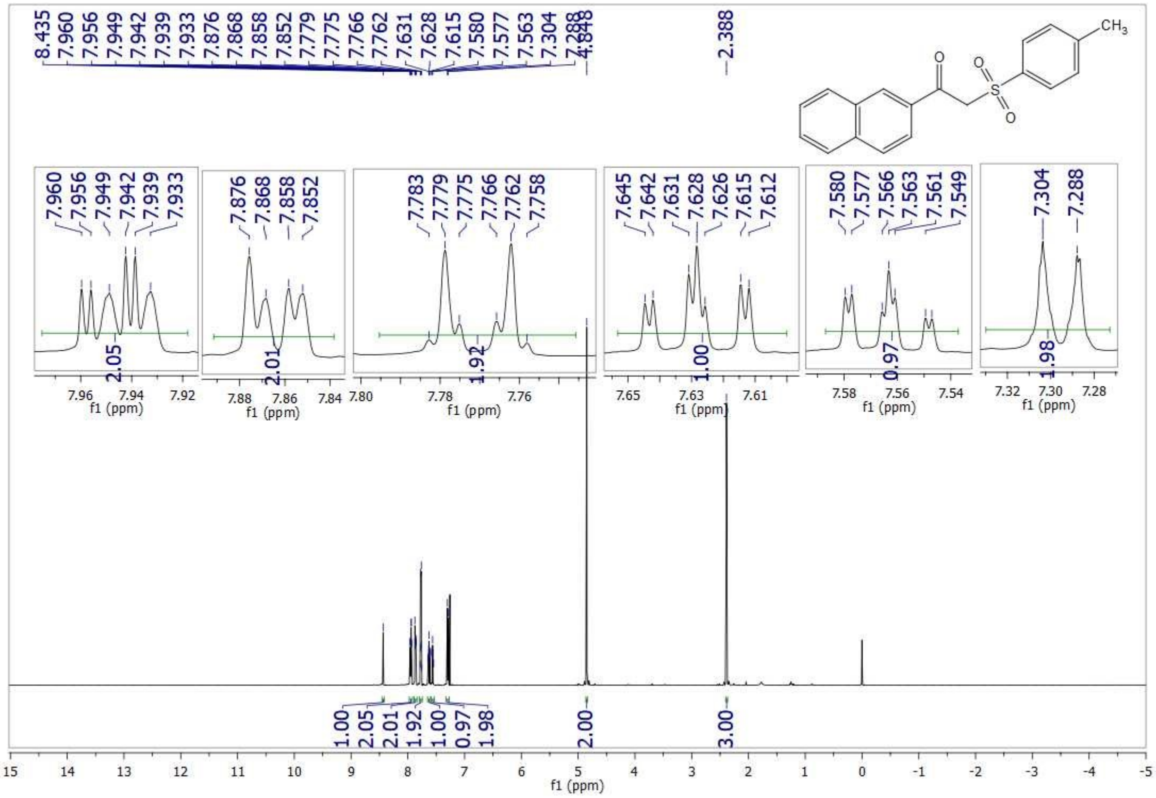
^{13}C NMR (126 MHz, CDCl$_3$) of compound **22**.



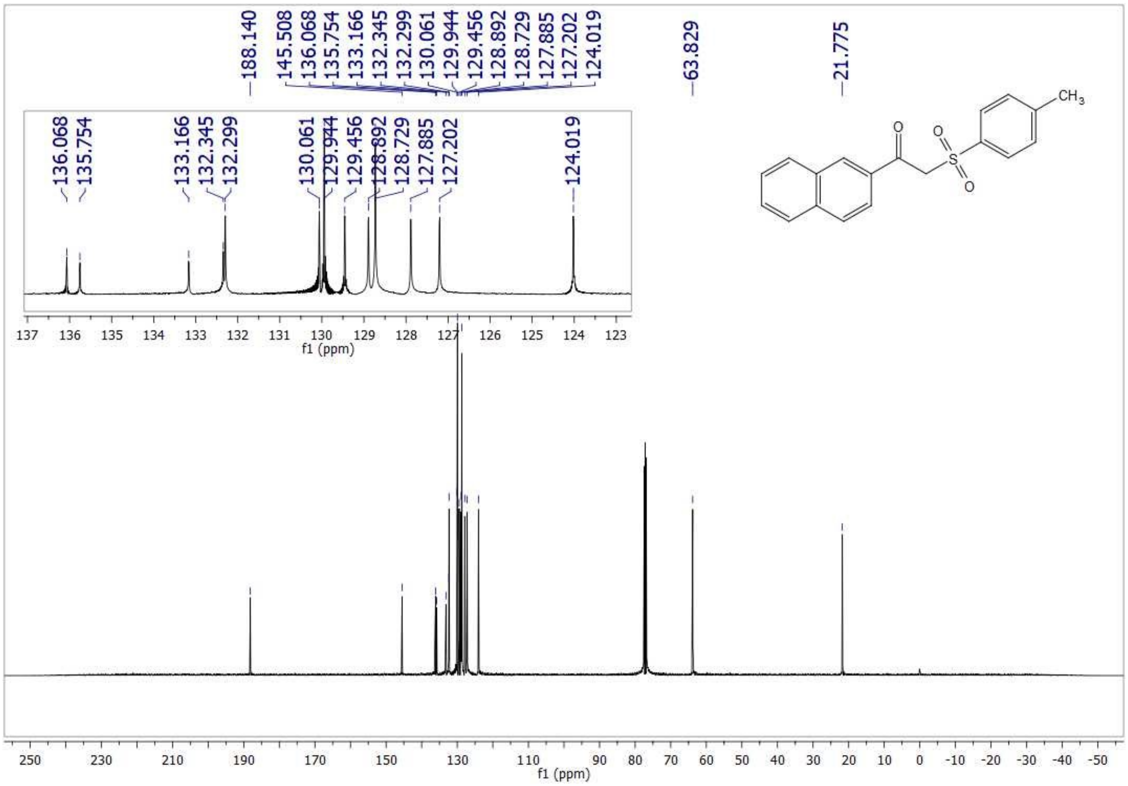
^{1}H NMR (500 MHz, CDCl$_3$) of compound **23**.



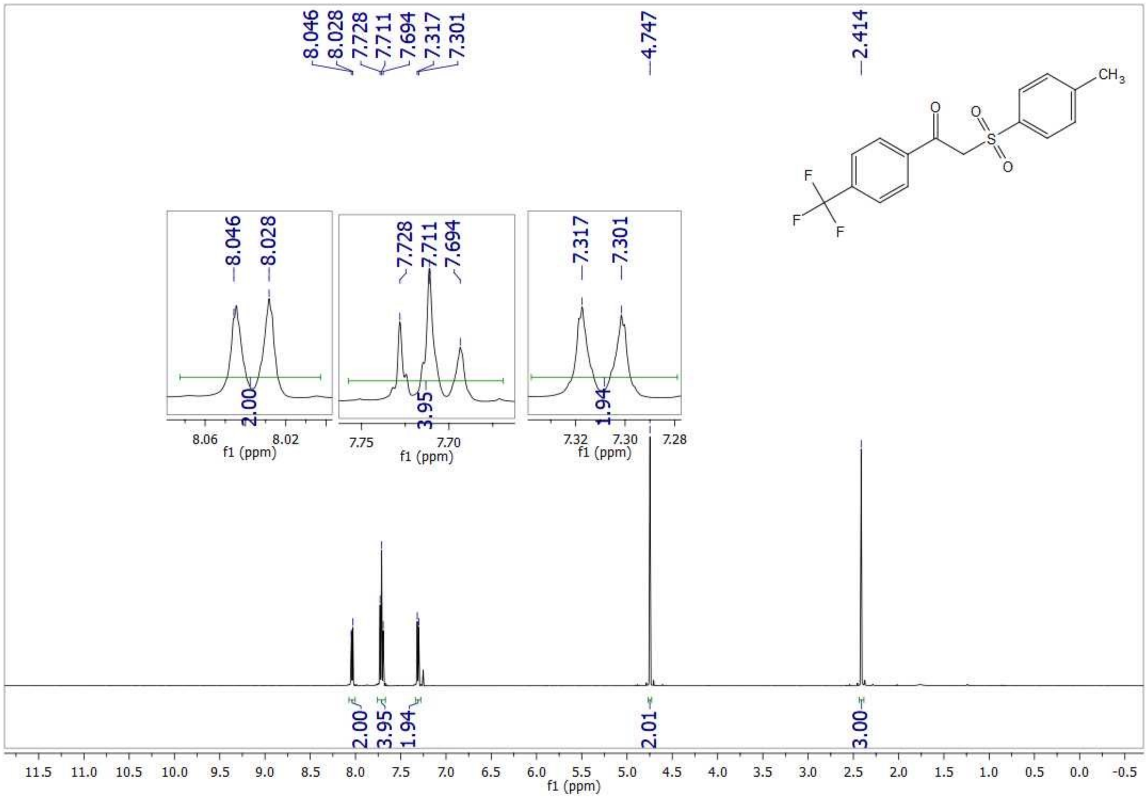
^{13}C NMR (126 MHz, CDCl$_3$) of compound **23**.



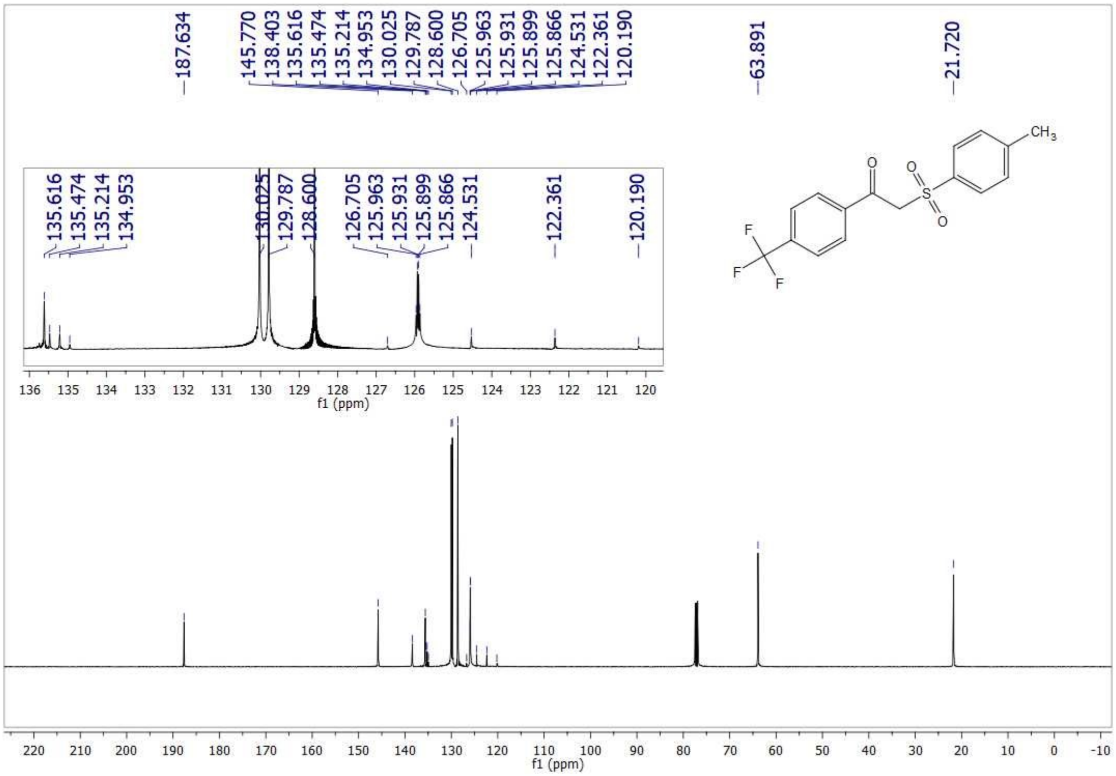
^{1}H NMR (500 MHz, CDCl$_3$) of compound **24**.



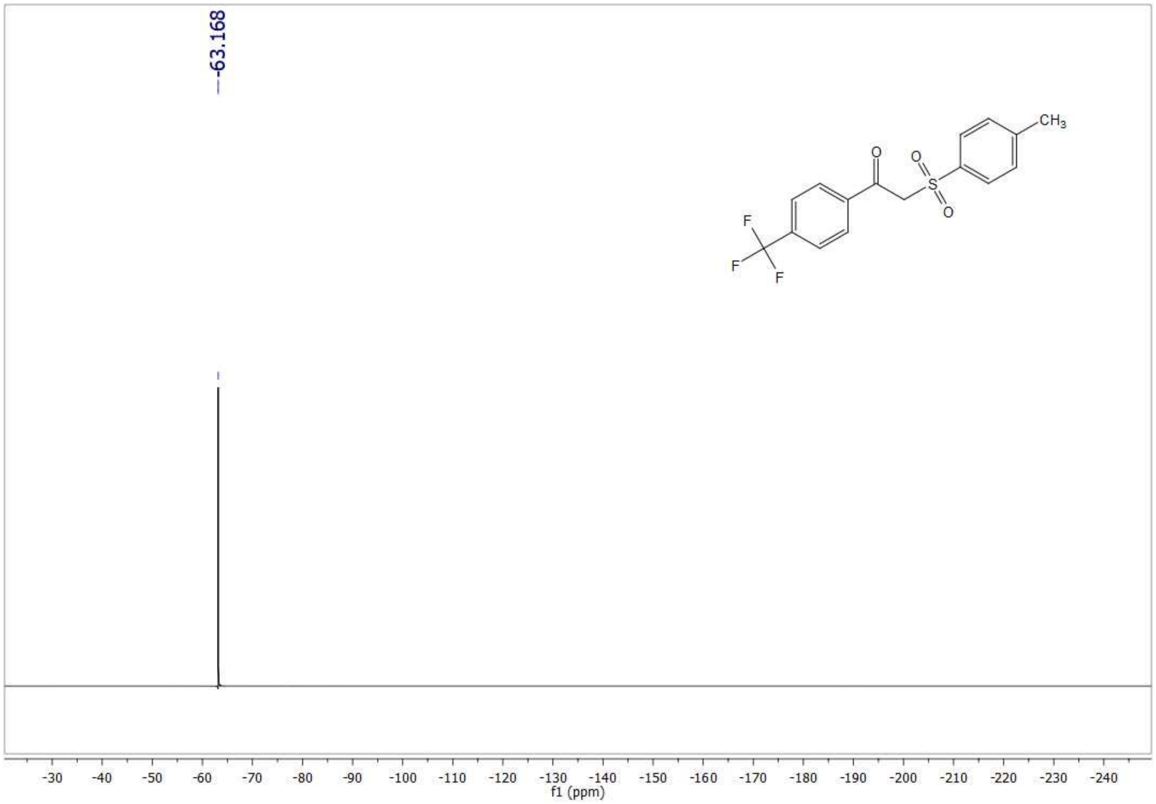
^{13}C NMR (126 MHz, CDCl$_3$) of compound **24**.



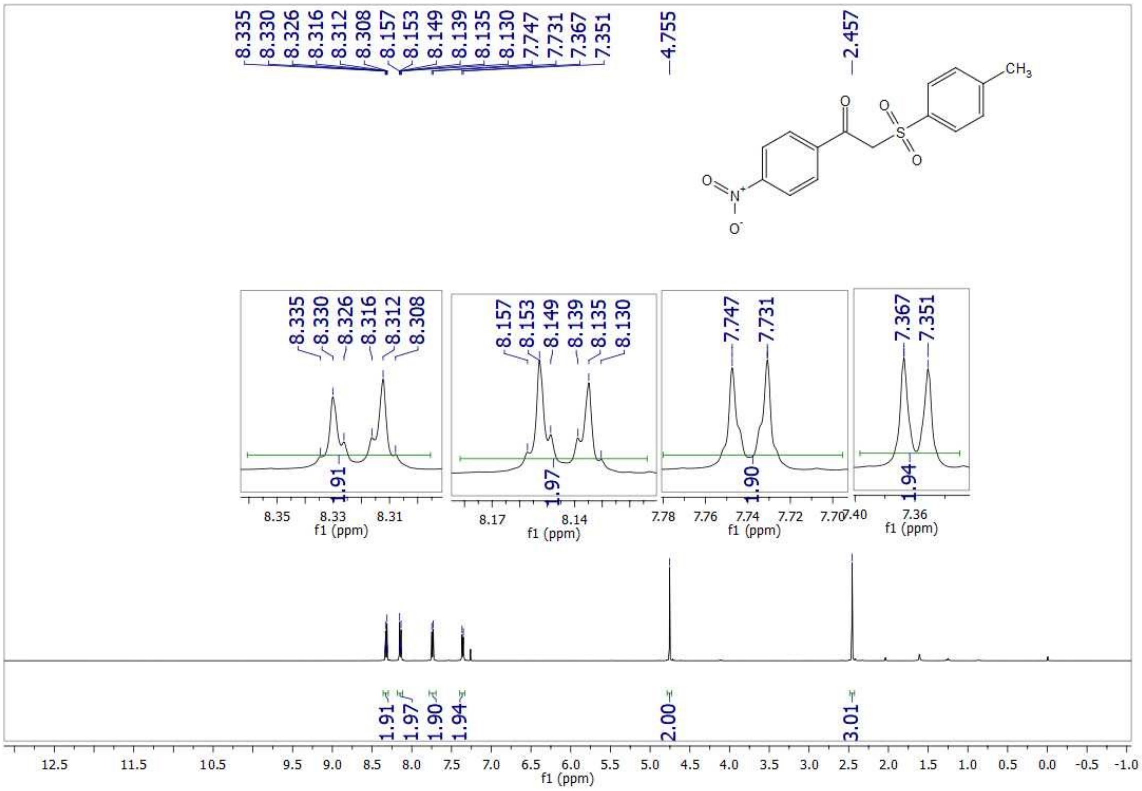
^{1}H NMR (500 MHz, CDCl$_3$) of compound **25**.



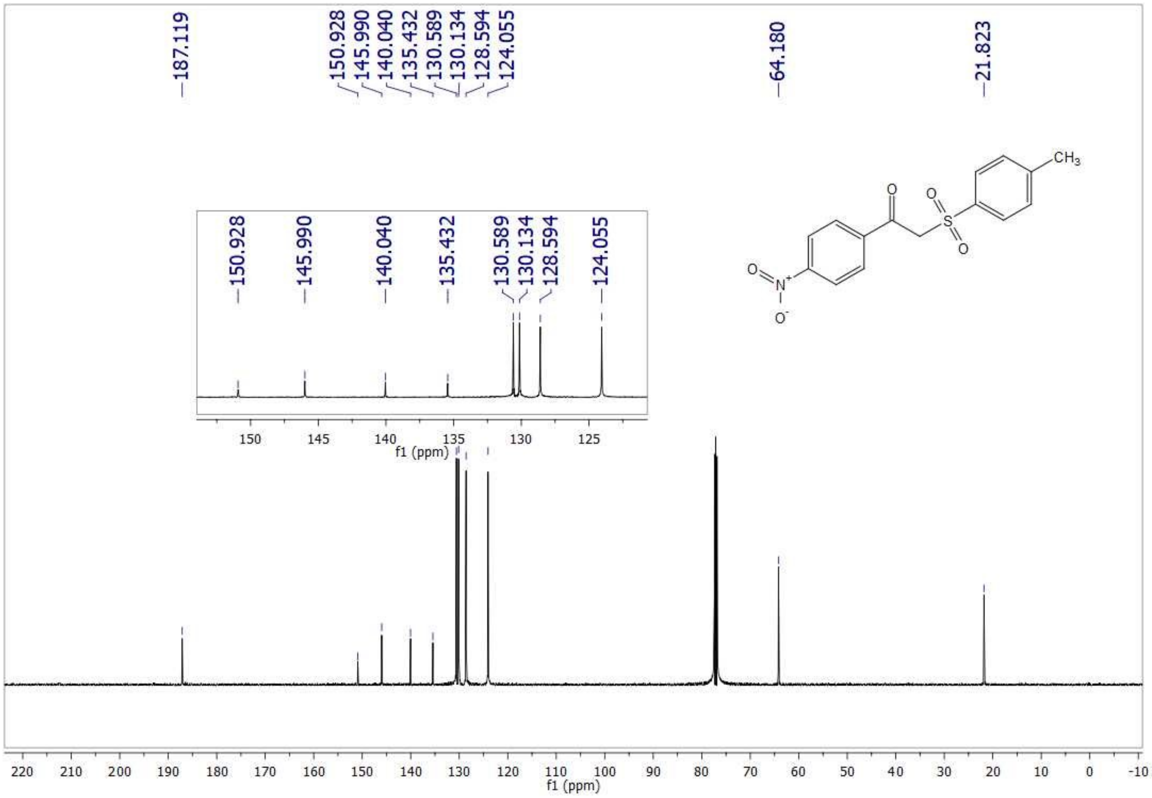
^{13}C NMR (126 MHz, CDCl$_3$) of compound **25**.



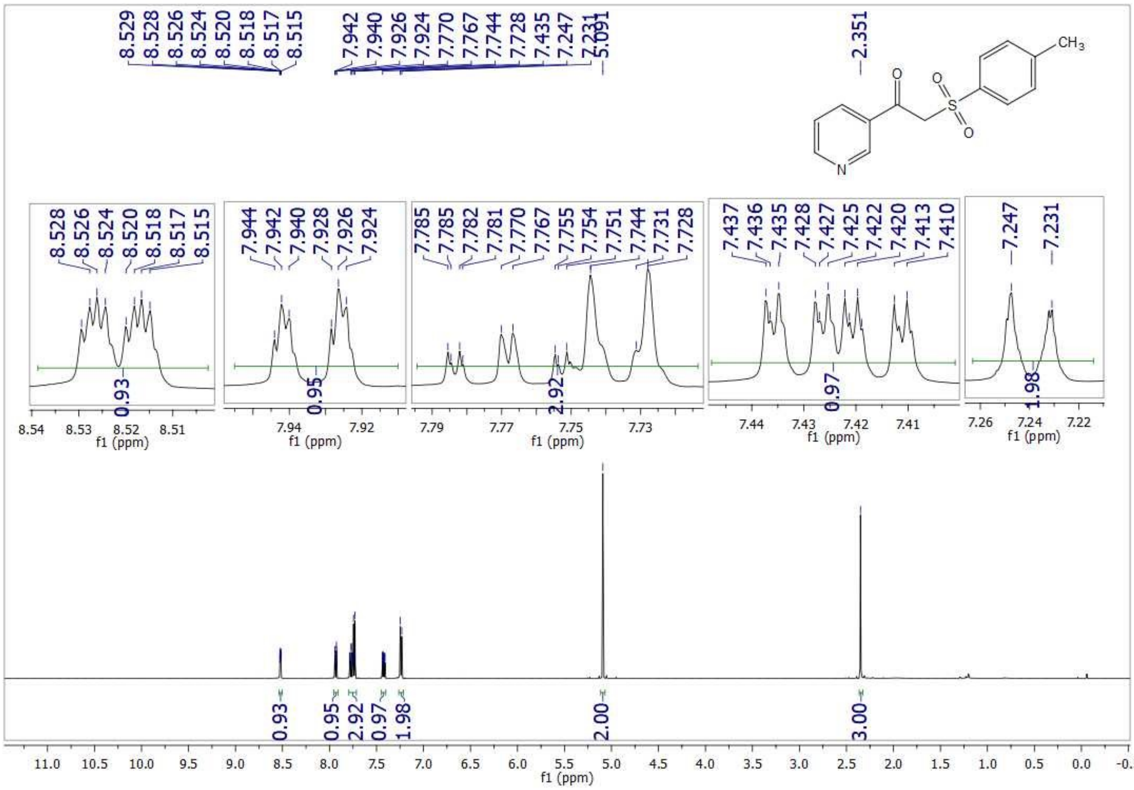
^{19}F NMR (472 MHz, CDCl$_3$) of compound **25**.



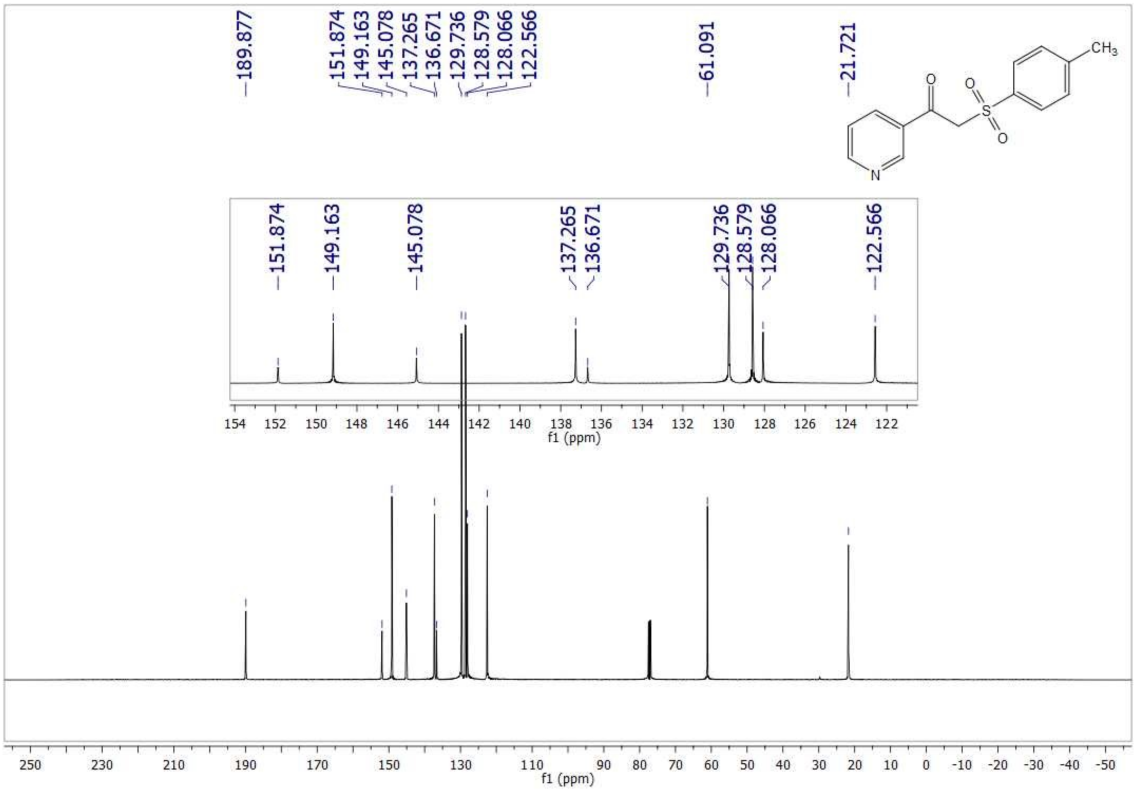
^{1}H NMR (500 MHz, CDCl$_3$) of compound **26**.



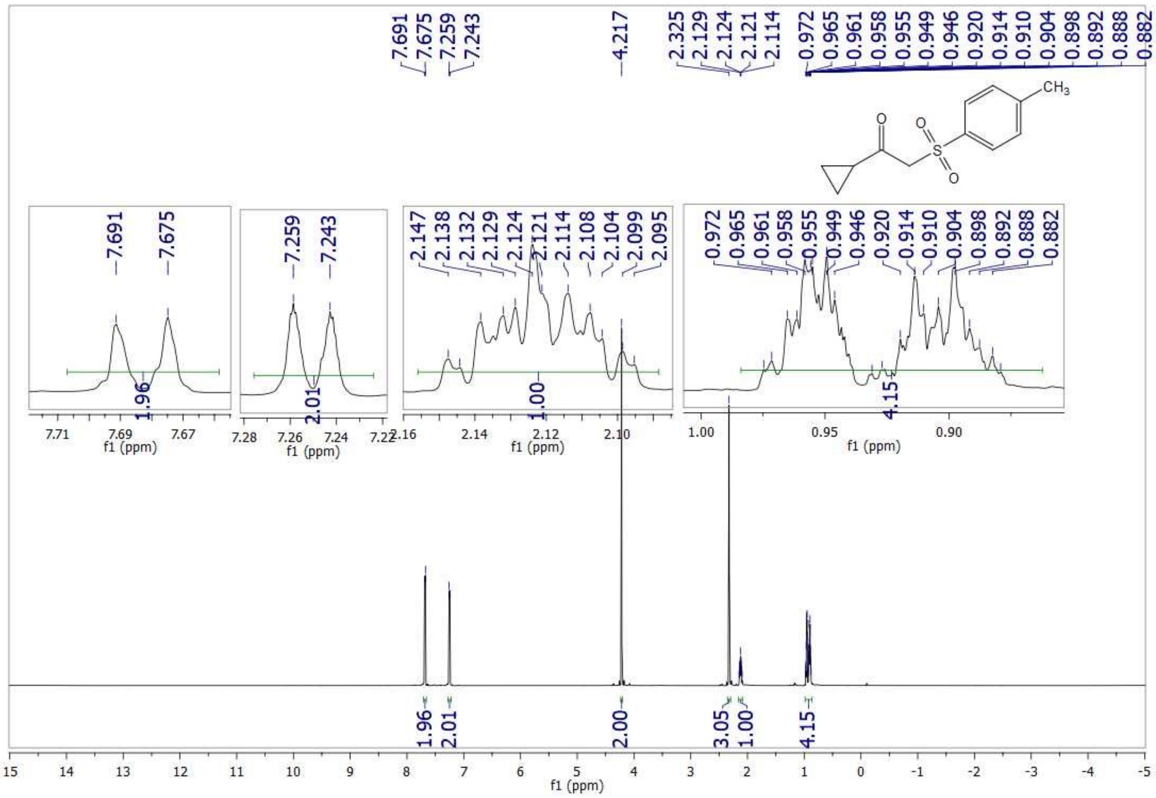
^{13}C NMR (126 MHz, CDCl$_3$) of compound **26**.



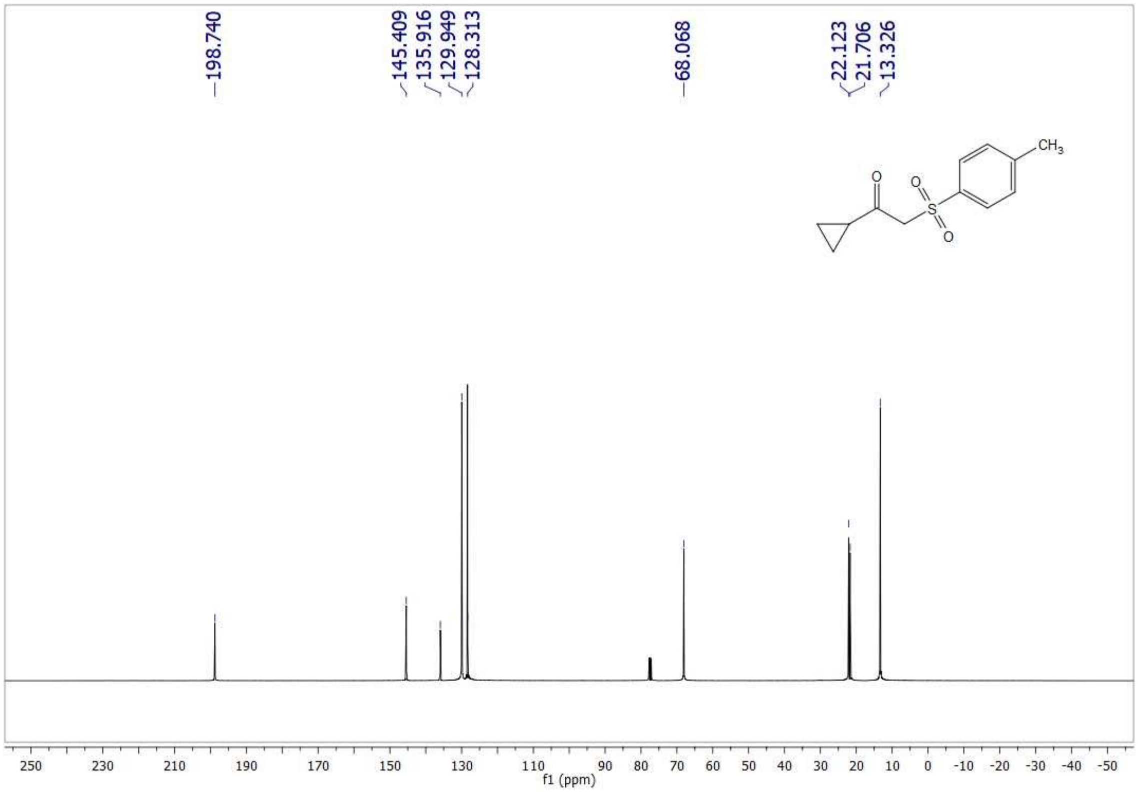
^{1}H NMR (500 MHz, CDCl$_3$) of compound **27**.



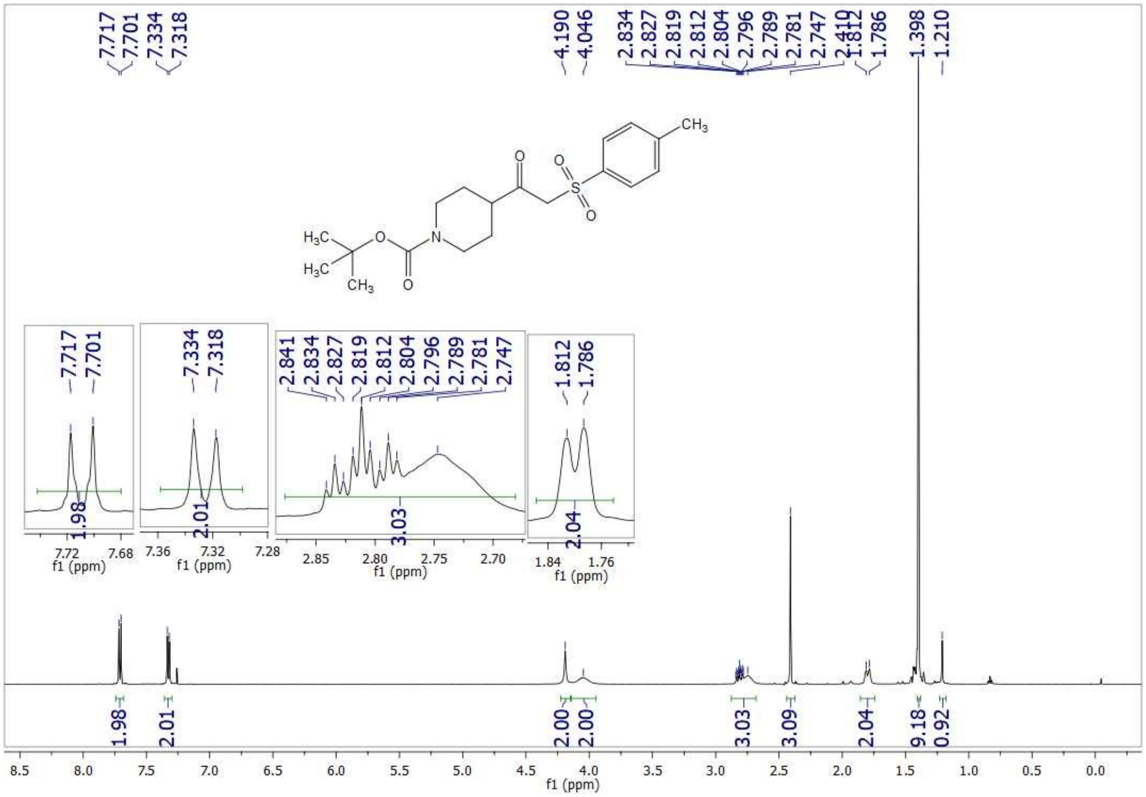
^{13}C NMR (126 MHz, CDCl$_3$) of compound **27**.



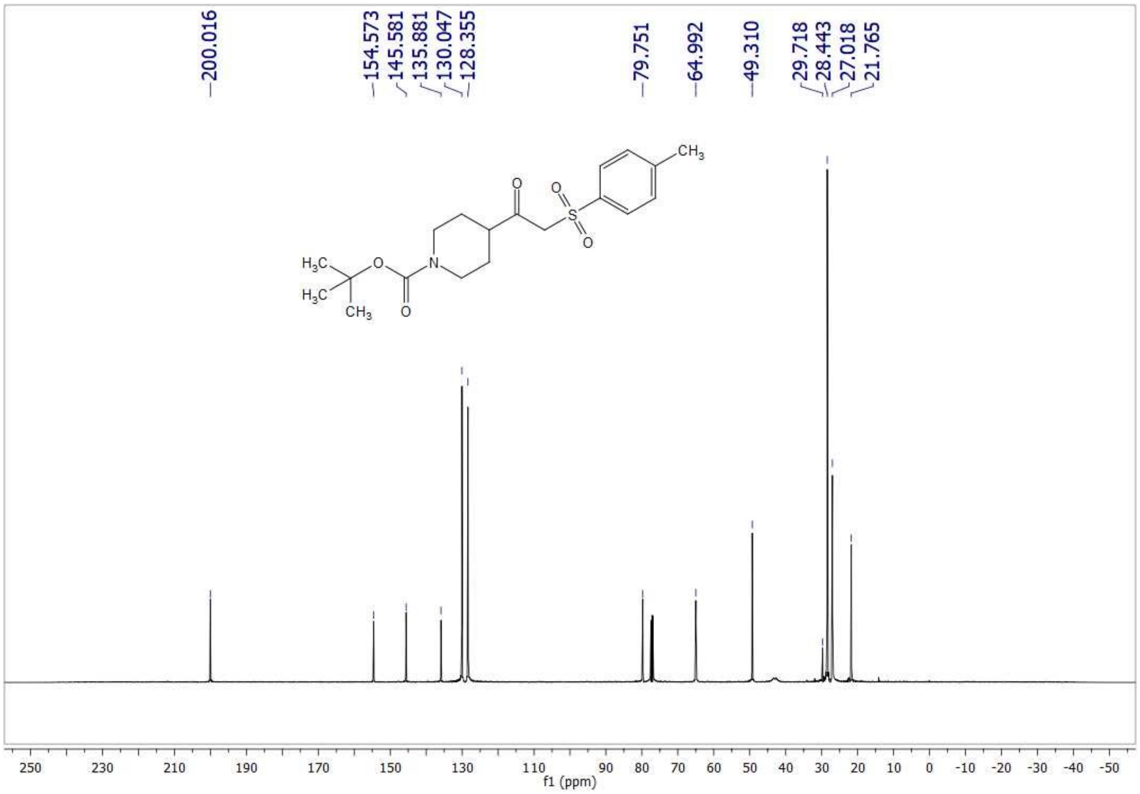
^{1}H NMR (500 MHz, CDCl$_3$) of compound **28**.



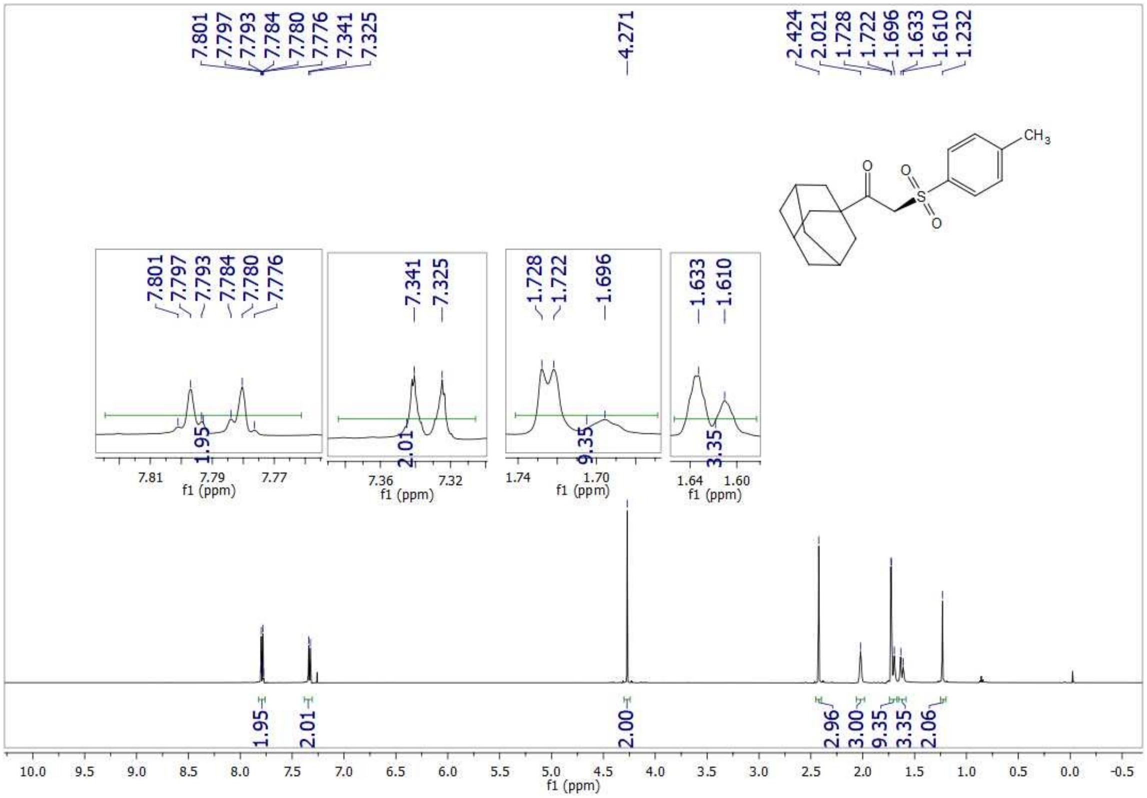
^{13}C NMR (126 MHz, CDCl$_3$) of compound **28**.



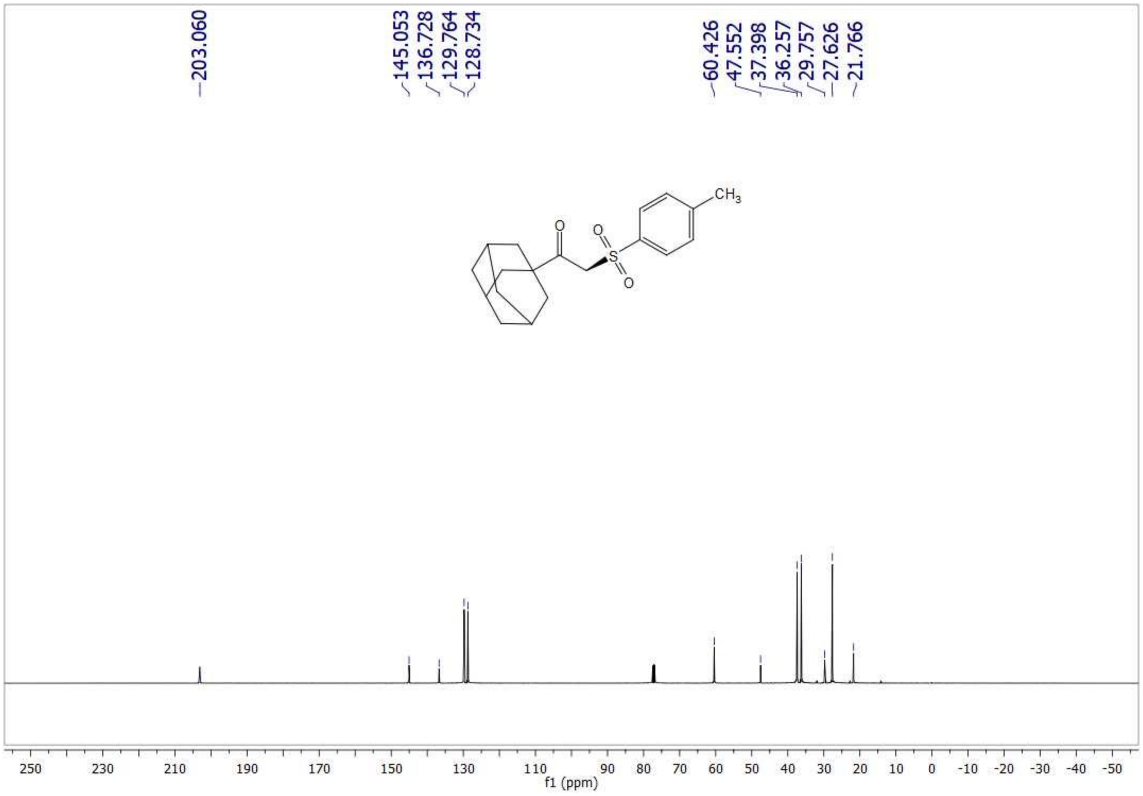
^{1}H NMR (500 MHz, CDCl$_3$) of compound **29**.



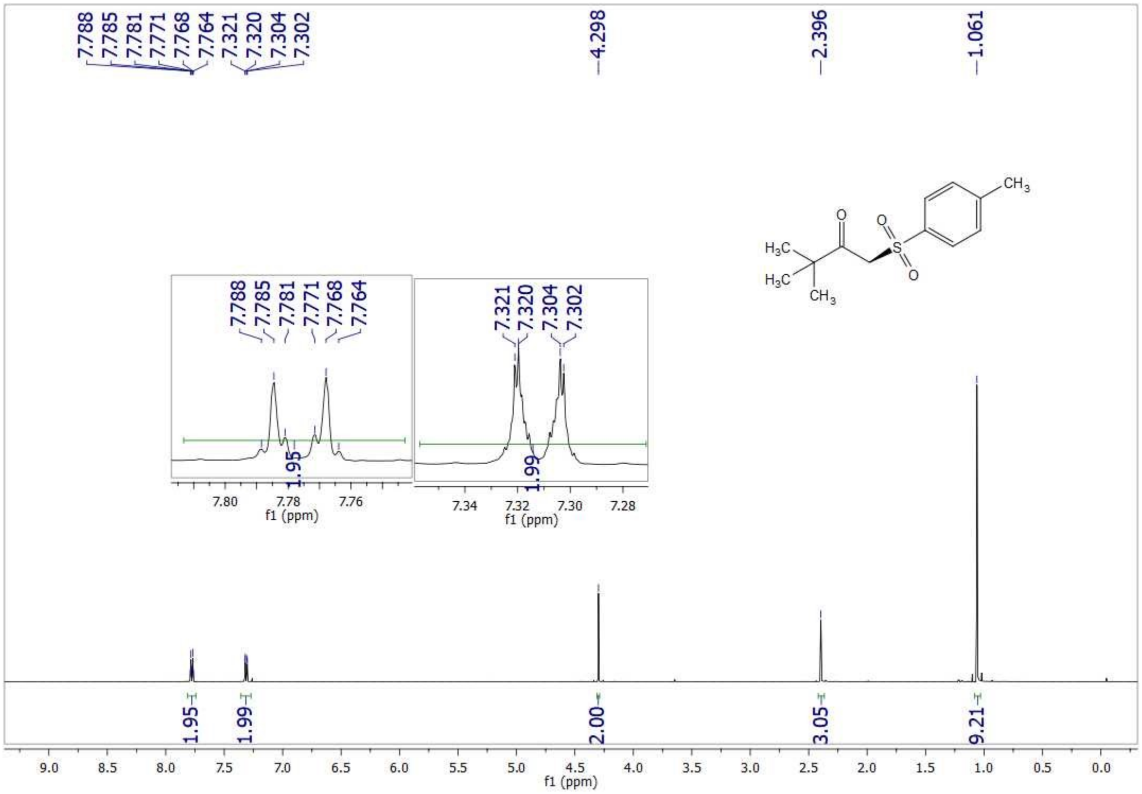
^{13}C NMR (126 MHz, CDCl$_3$) of compound **29**.



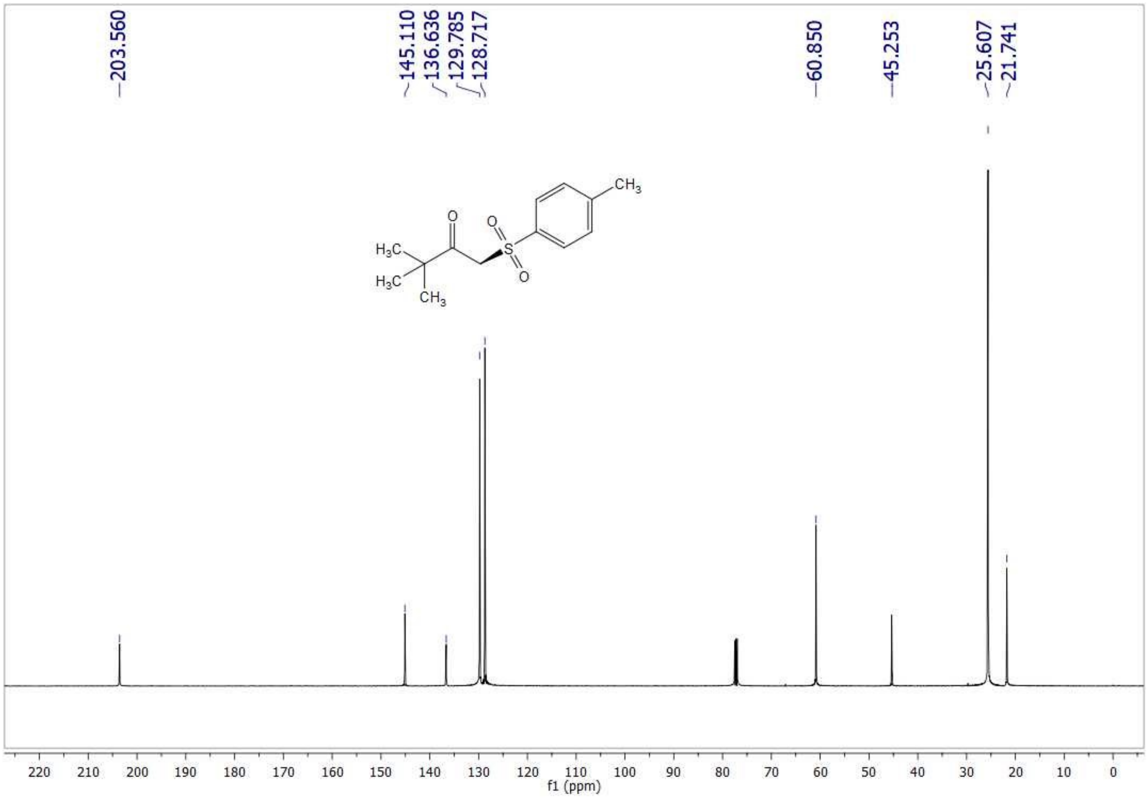
^{1}H NMR (500 MHz, CDCl$_3$) of compound **30**.



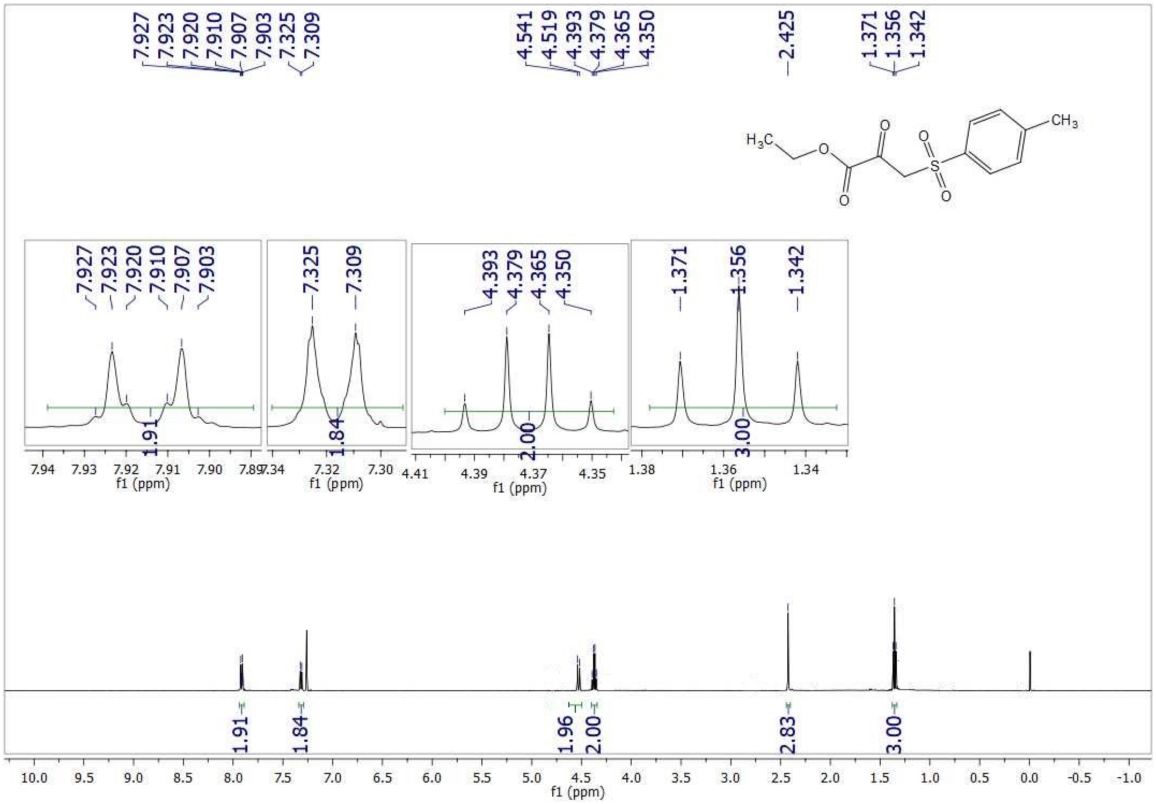
^{13}C NMR (126 MHz, CDCl$_3$) of compound **30**.



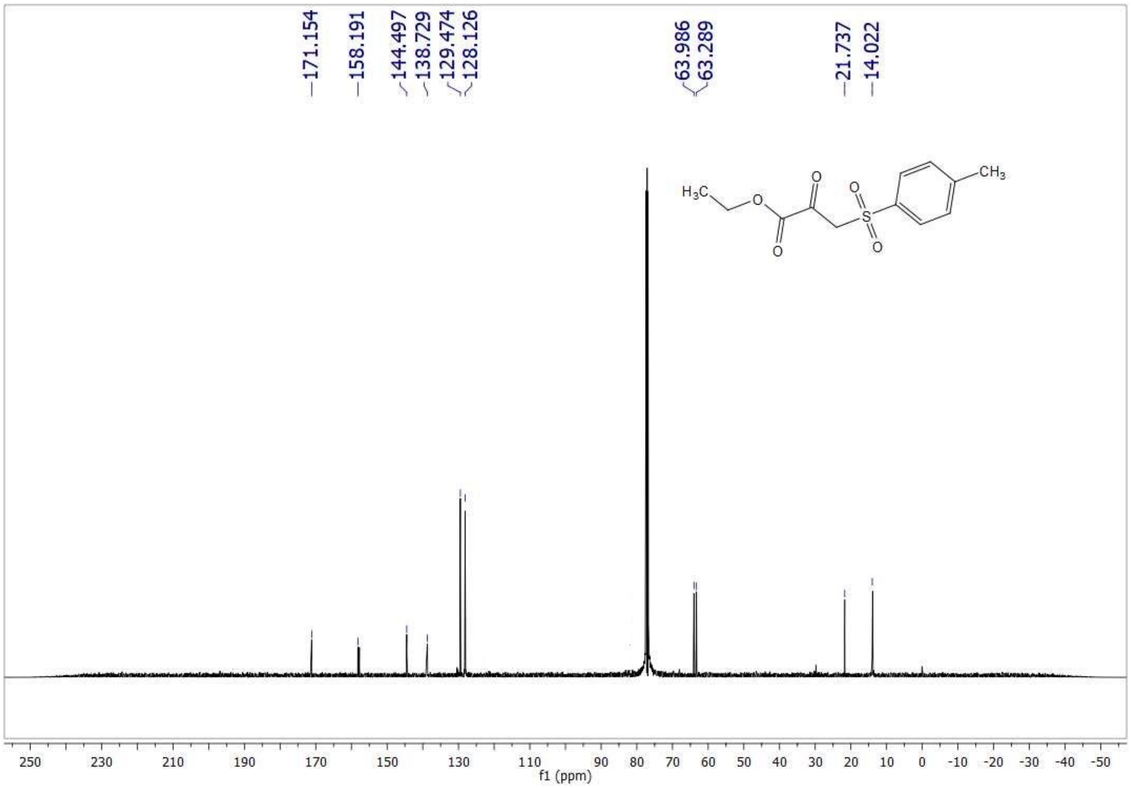
^{1}H NMR (500 MHz, CDCl$_3$) of compound **31**.



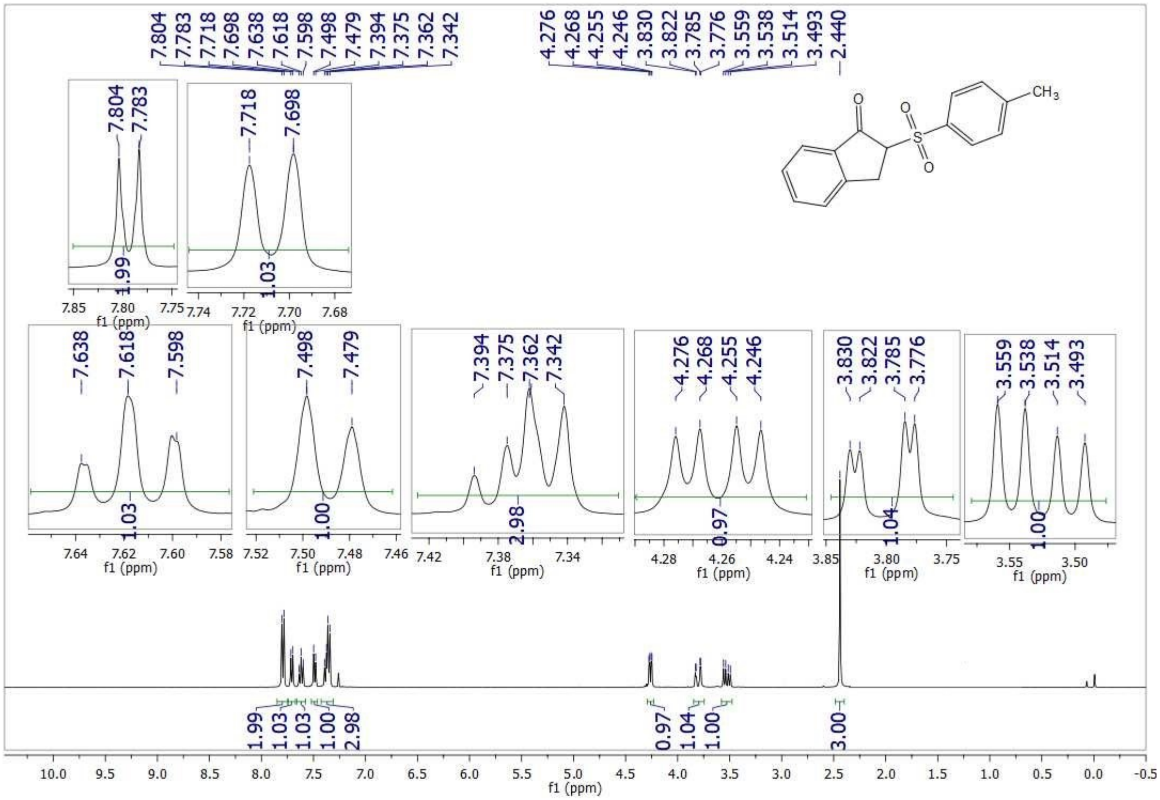
^{13}C NMR (126 MHz, CDCl$_3$) of compound **31**.



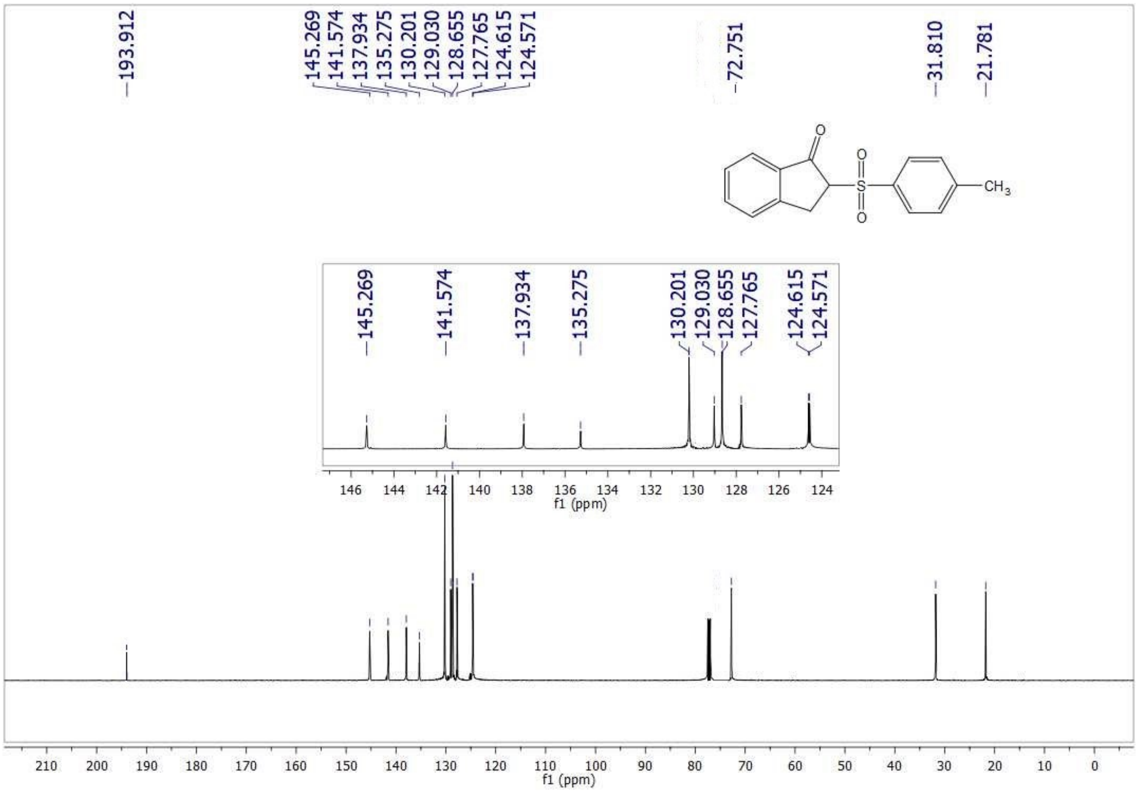
^{1}H NMR (500 MHz, CDCl$_3$) of compound **32**.



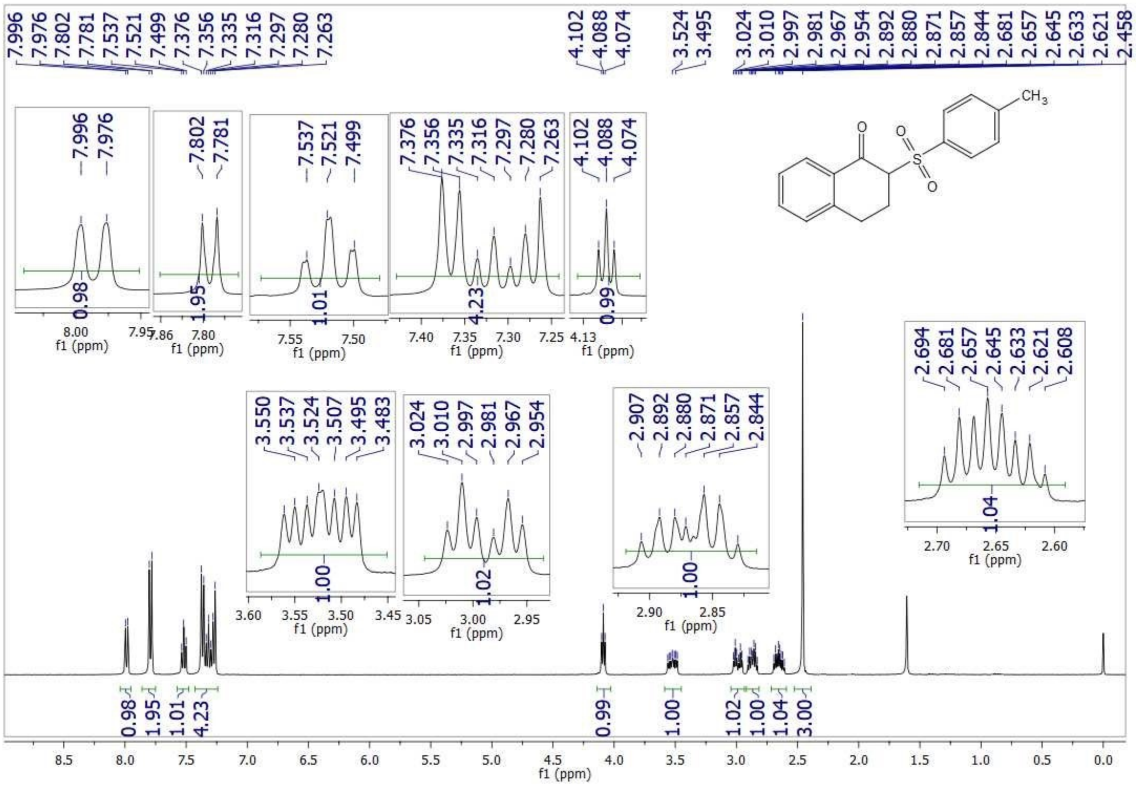
^{13}C NMR (126 MHz, CDCl$_3$) of compound **32**.



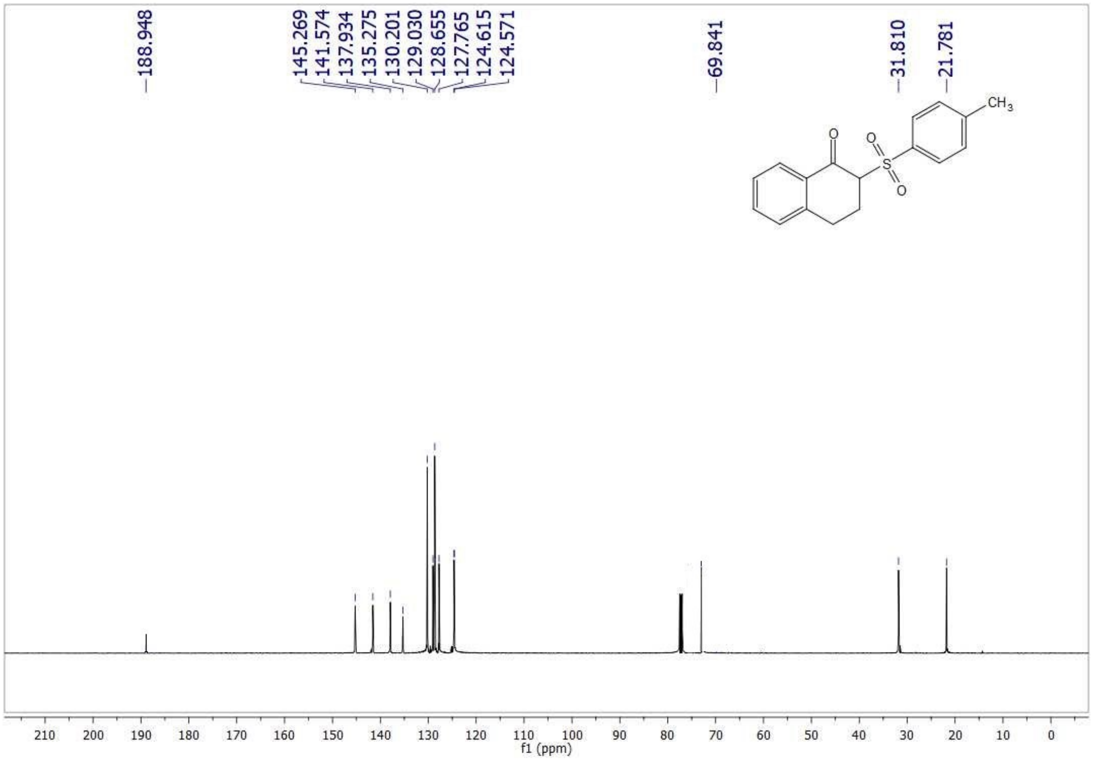
^{1}H NMR (500 MHz, CDCl$_3$) of compound **33**.



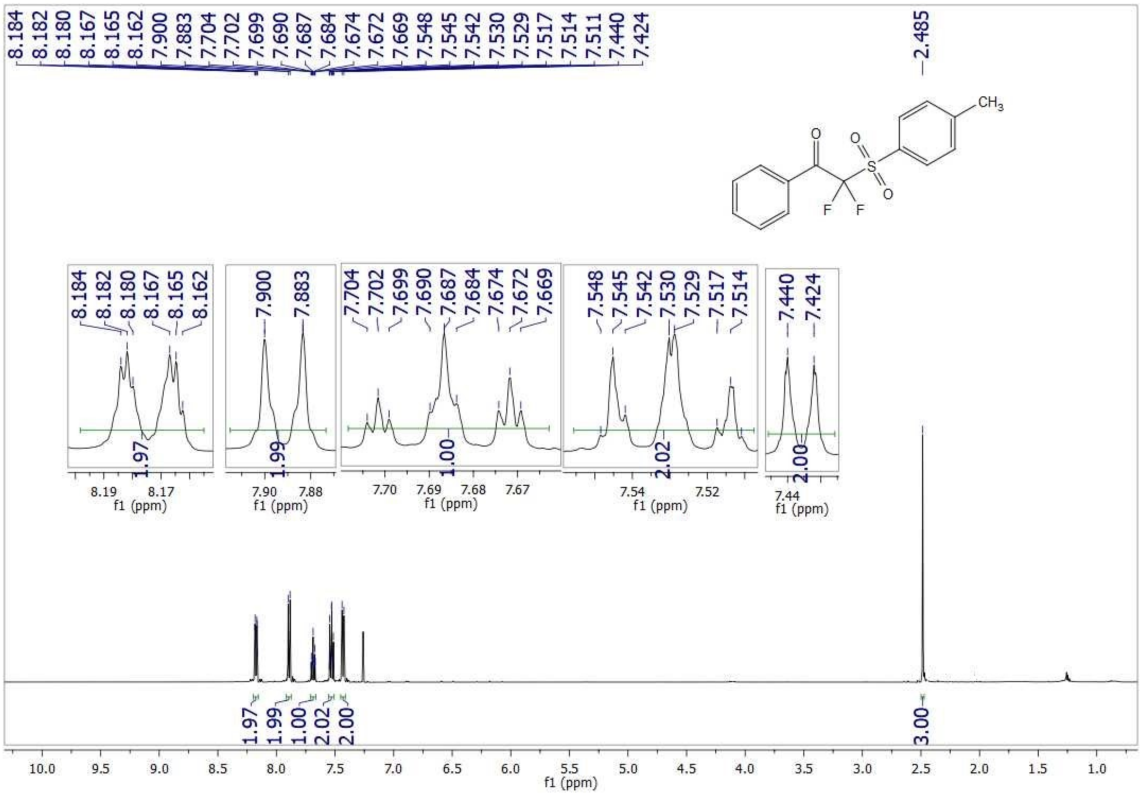
^{13}C NMR (126 MHz, CDCl$_3$) of compound **33**.



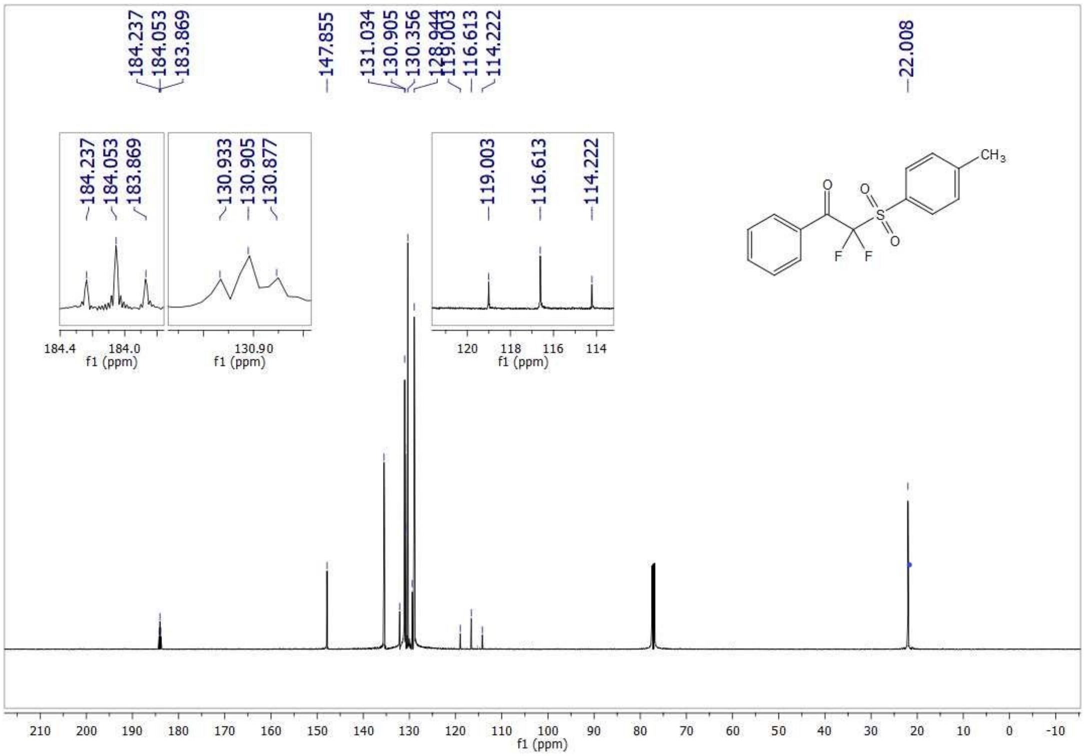
^{1}H NMR (500 MHz, $CDCl_3$) of compound **34**.



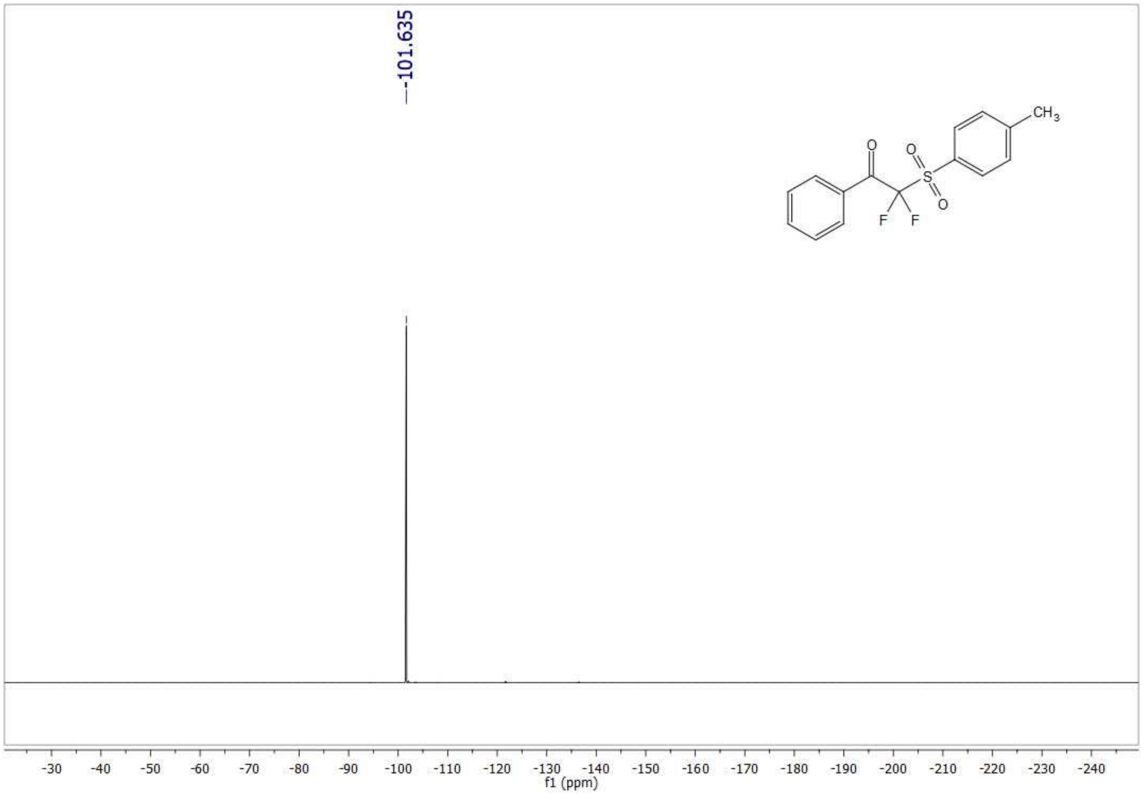
^{13}C NMR (126 MHz, $CDCl_3$) of compound **34**.



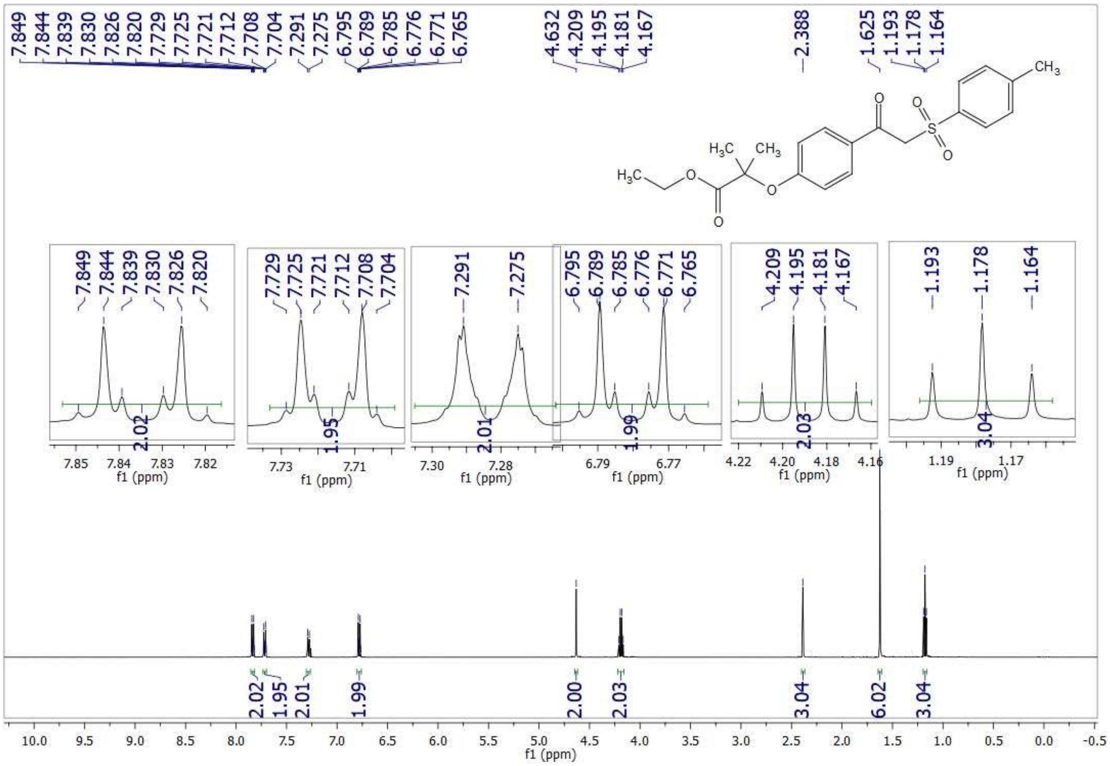
^{1}H NMR (500 MHz, CDCl$_3$) of compound **35**.



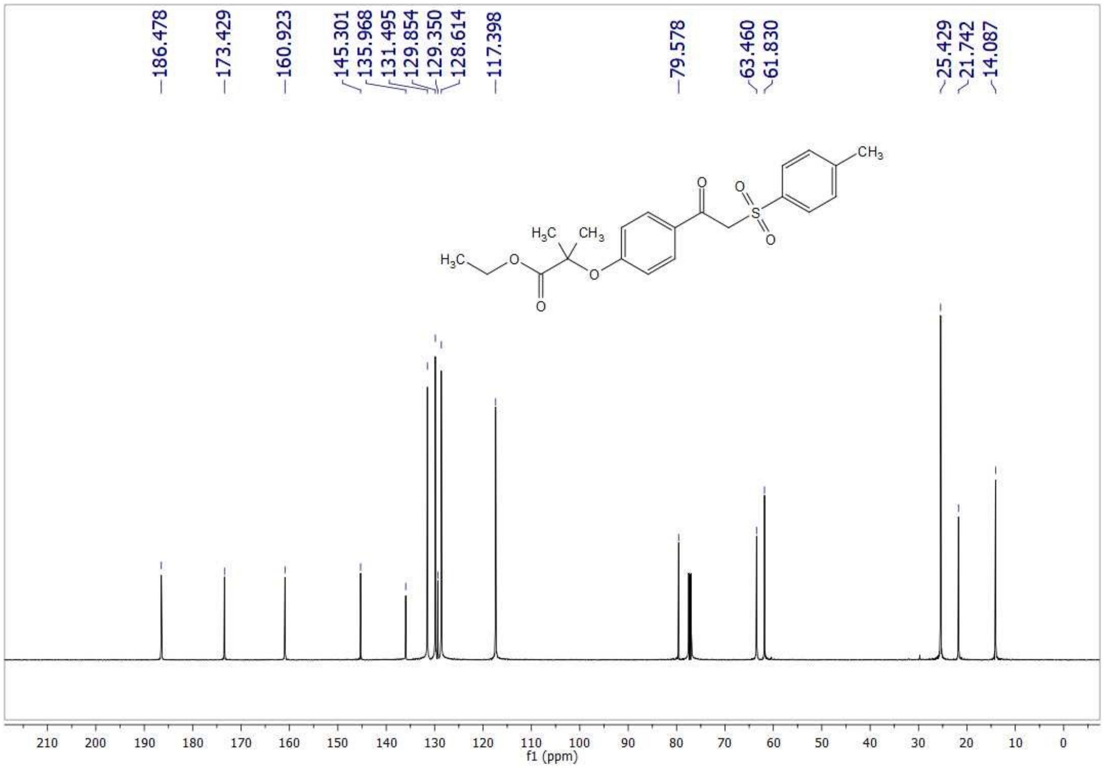
^{13}C NMR (126 MHz, CDCl$_3$) of compound **35**.



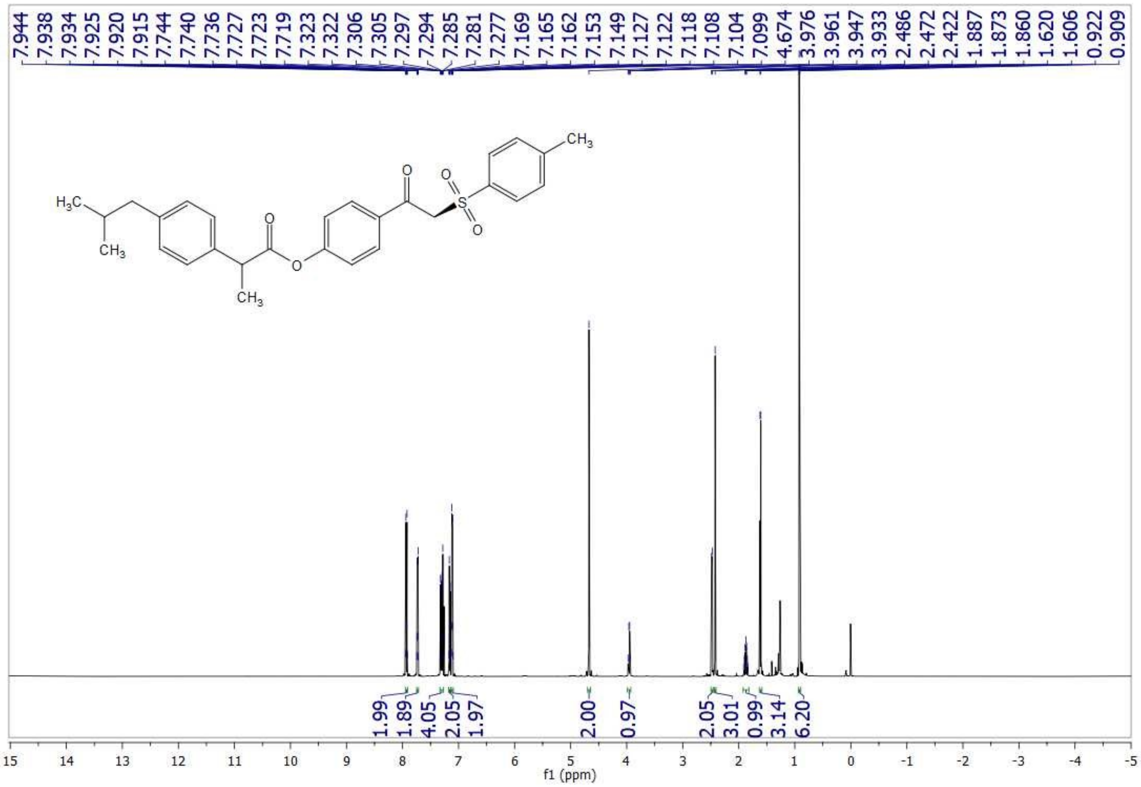
^{19}F NMR (472 MHz, CDCl$_3$) of compound **35**.



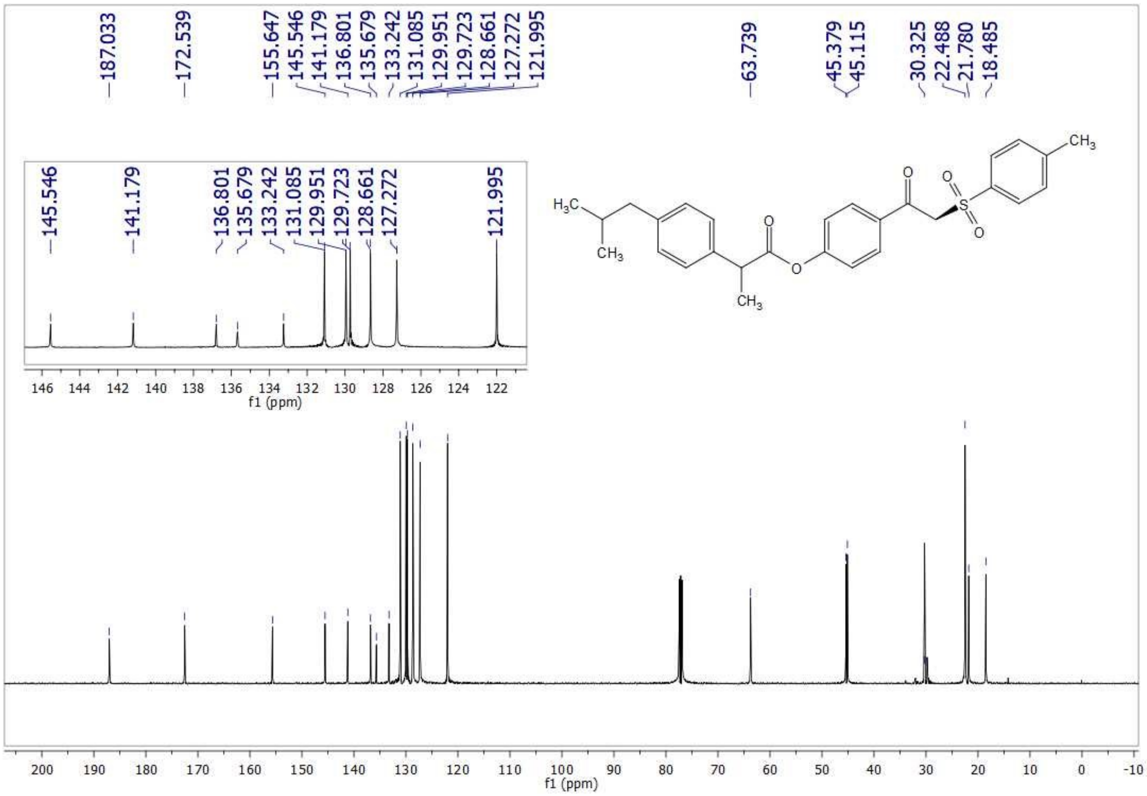
^{1}H NMR (500 MHz, CDCl$_3$) of compound **36**.



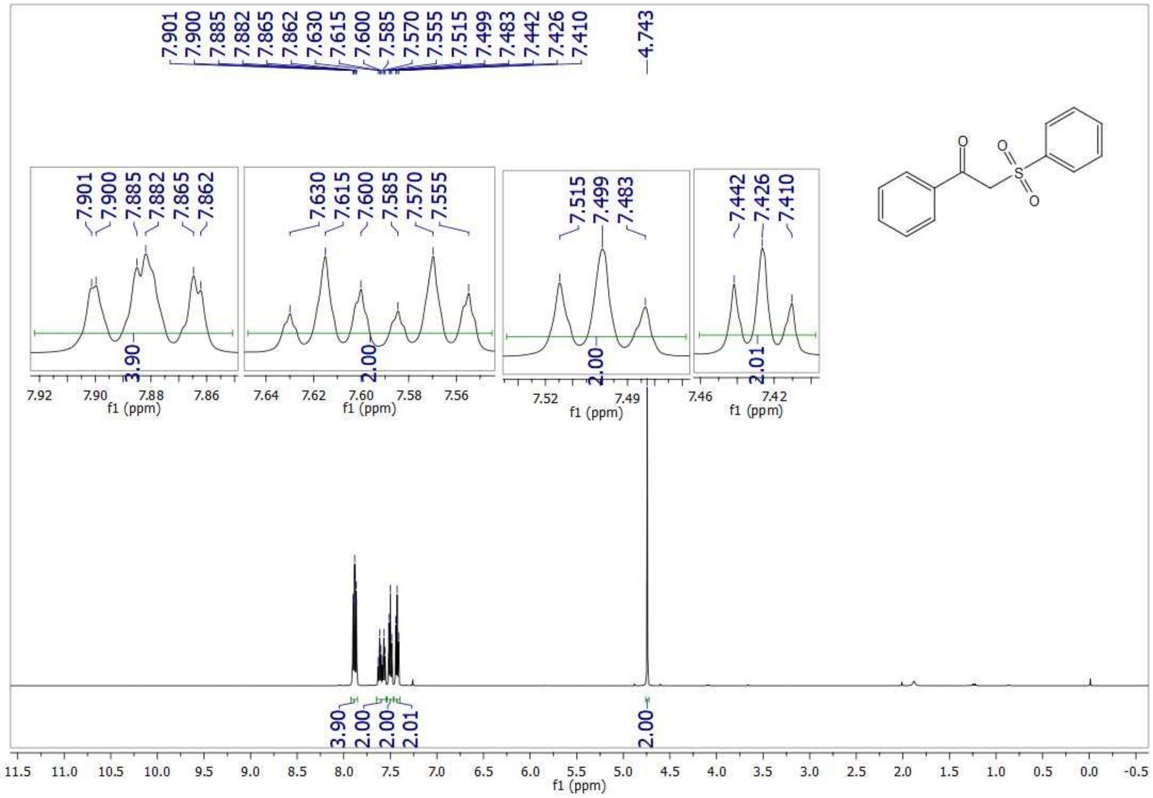
^{13}C NMR (126 MHz, CDCl$_3$) of compound **36**.



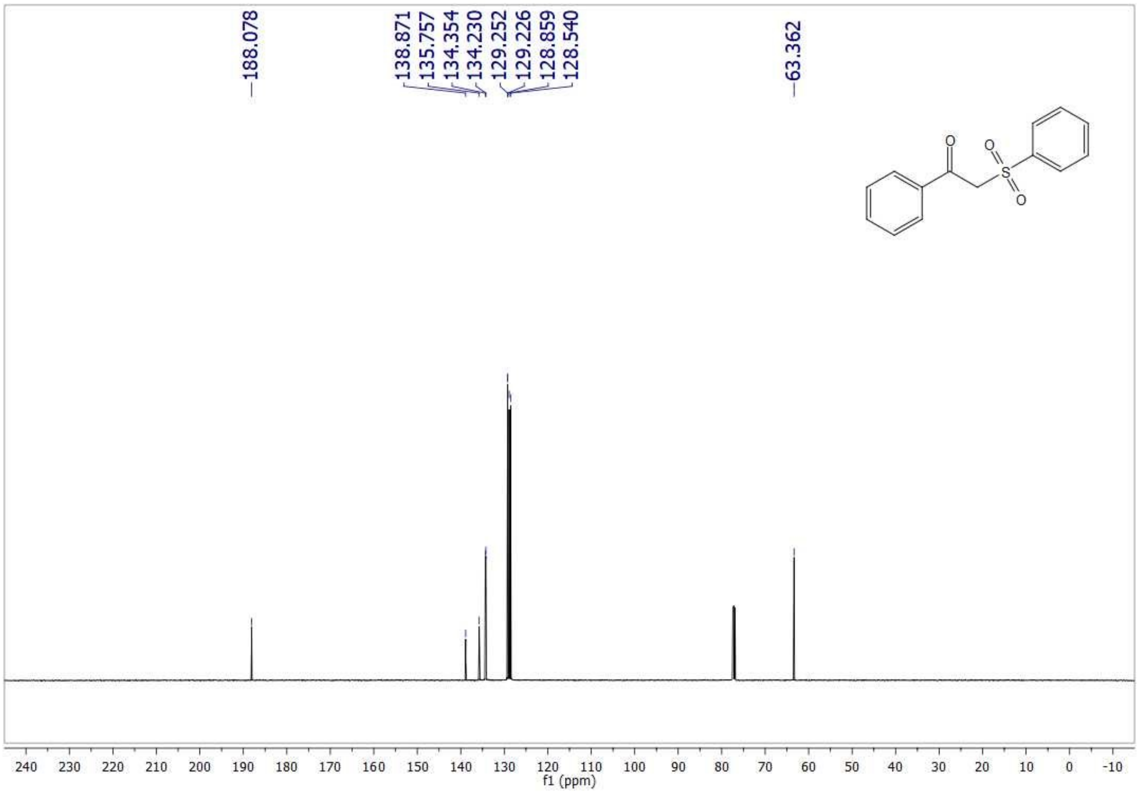
^{1}H NMR (500 MHz, CDCl$_3$) of compound **37**.



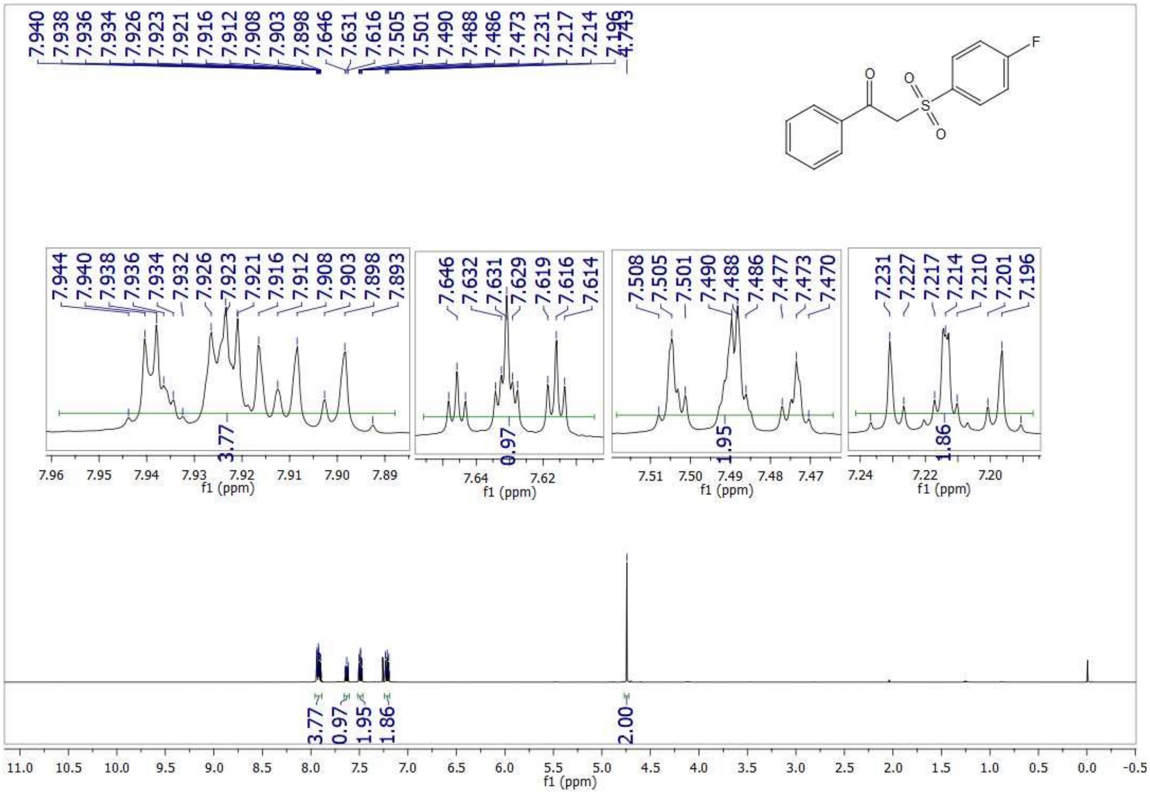
^{13}C NMR (126 MHz, $CDCl_3$) of compound **37**.



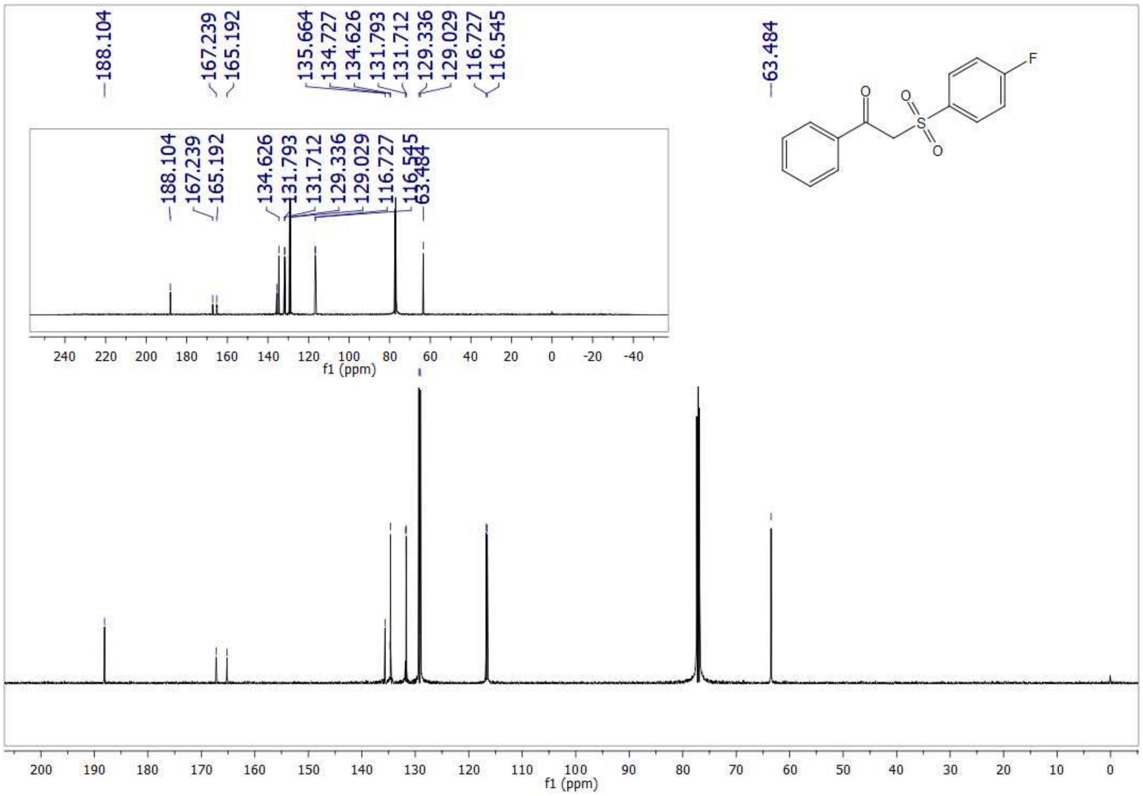
^{1}H NMR (500 MHz, $CDCl_3$) of compound **38**.



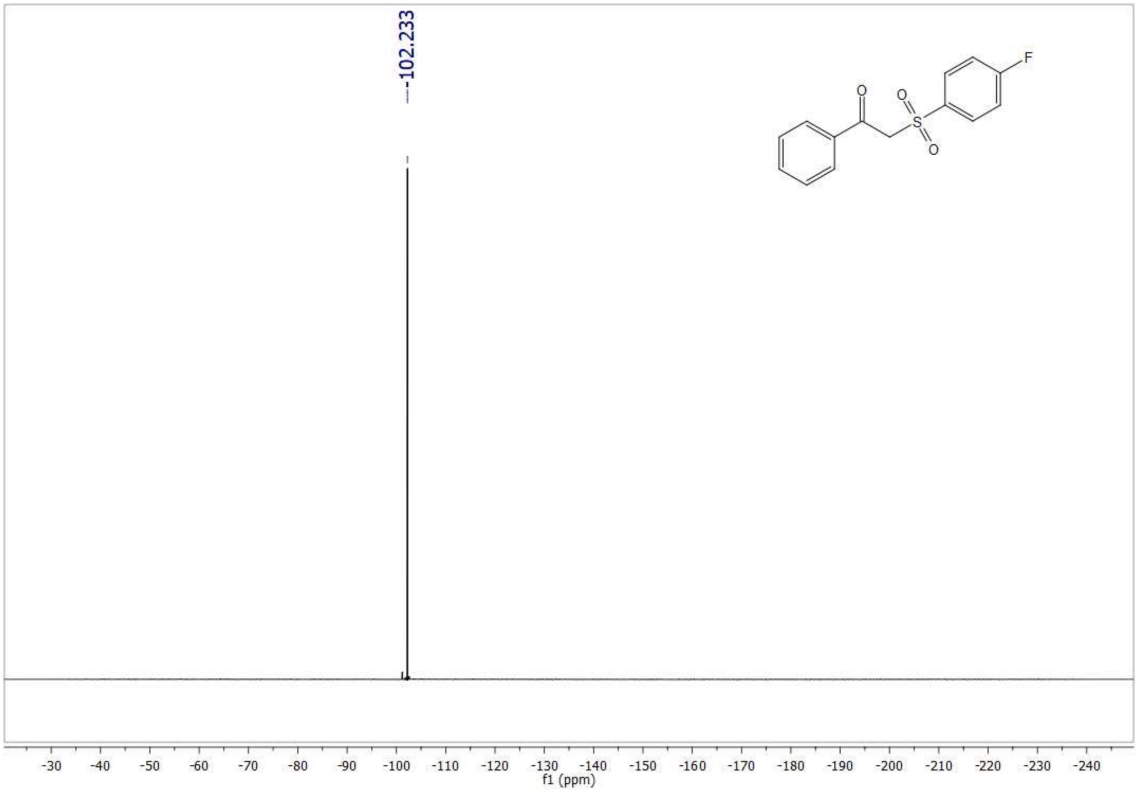
^{13}C NMR (126 MHz, CDCl$_3$) of compound **38**.



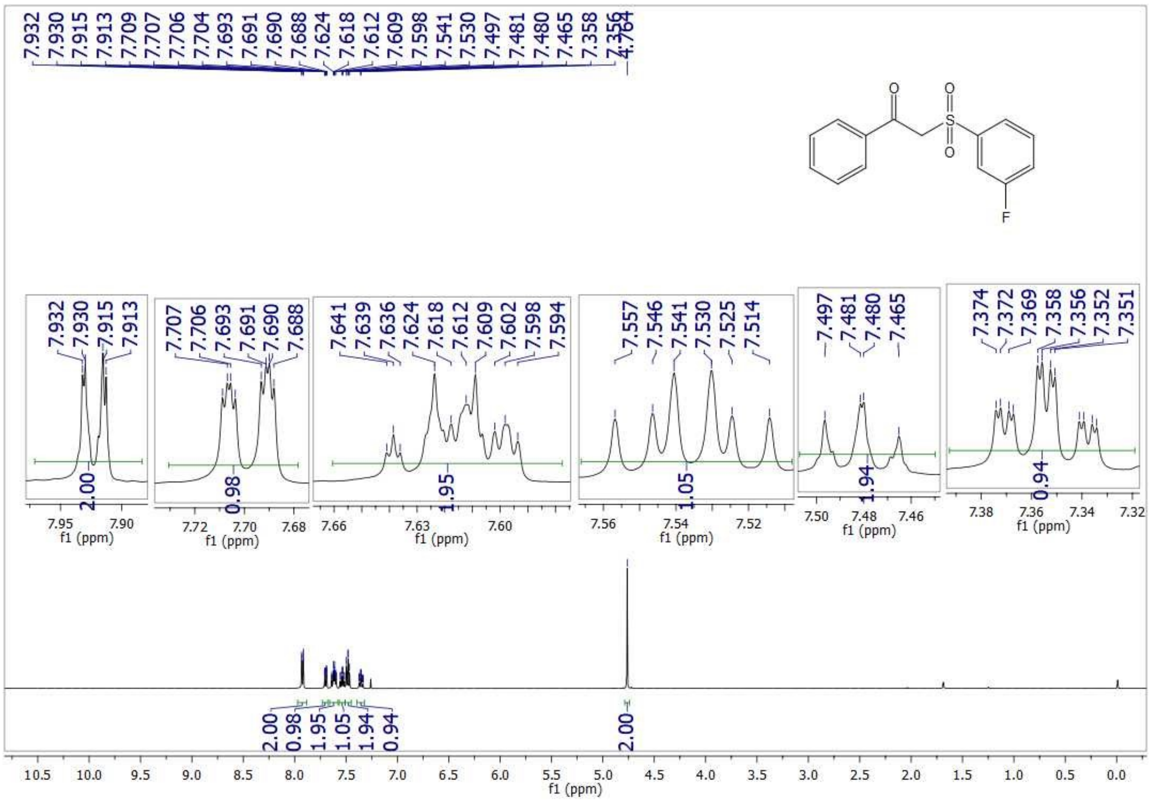
^{1}H NMR (500 MHz, CDCl$_3$) of compound **39**.



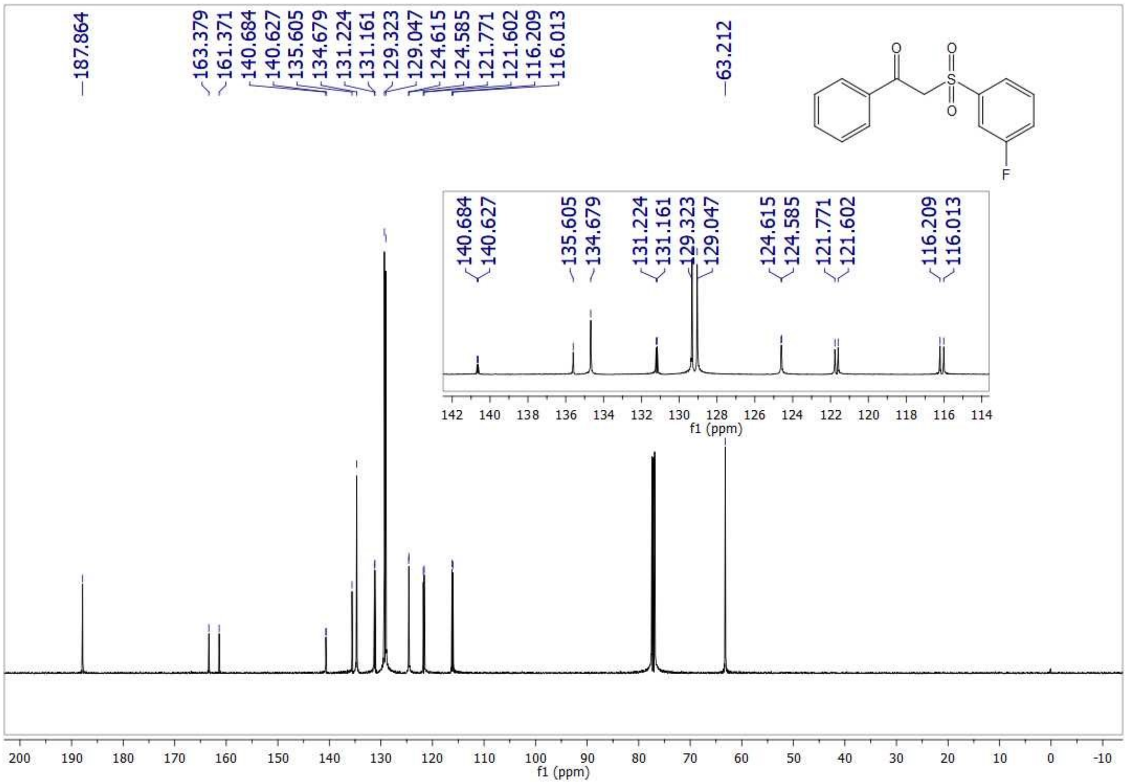
^{13}C NMR (126 MHz, CDCl$_3$) of compound **39**.



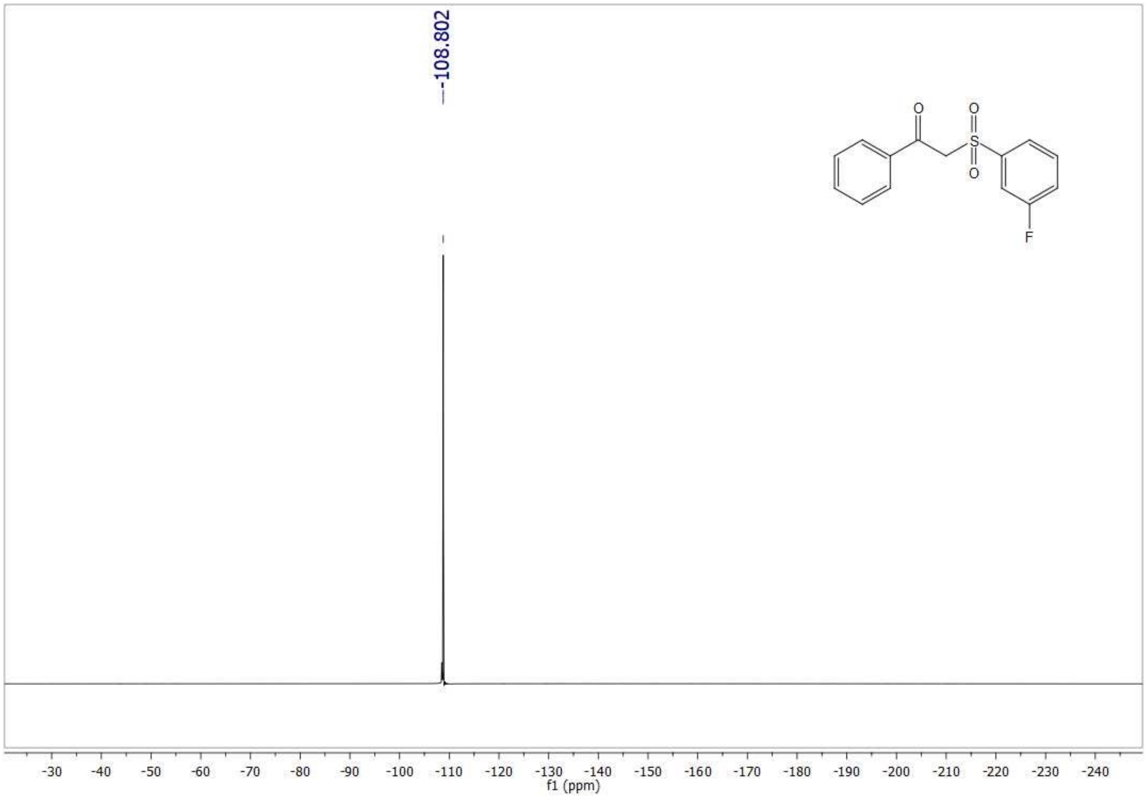
^{19}F NMR (472 MHz, CDCl$_3$) of compound **39**.



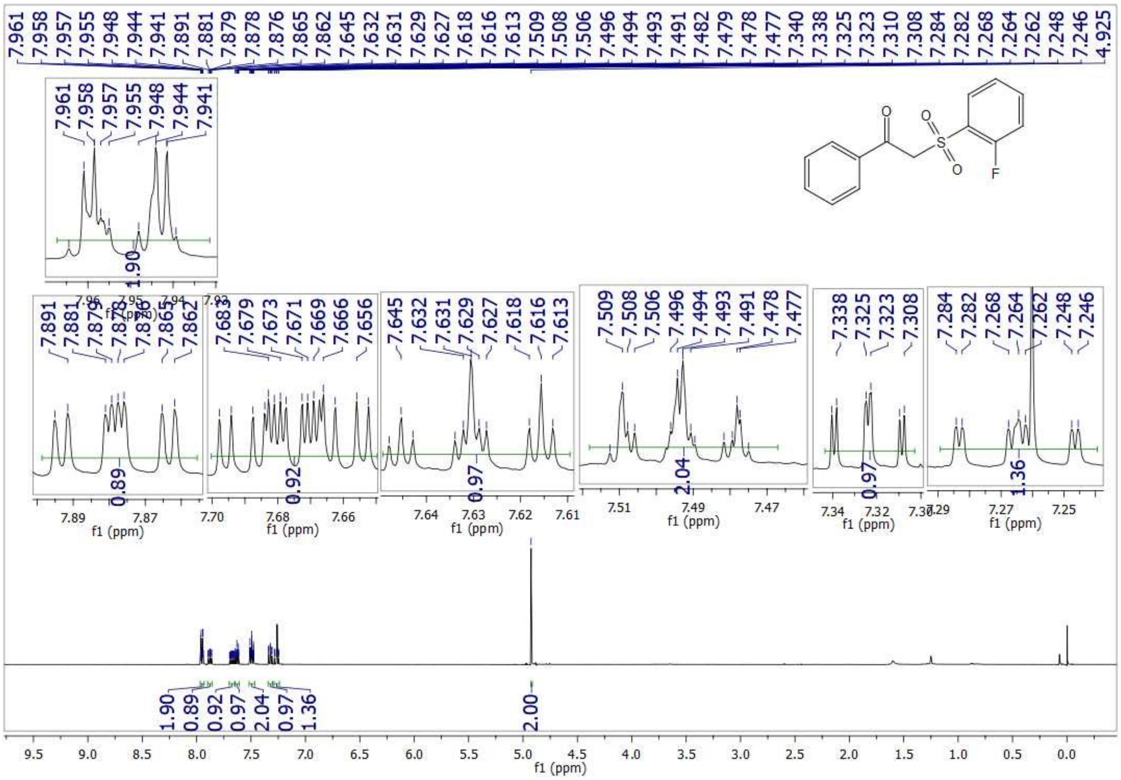
^1H NMR (500 MHz, $CDCl_3$) of compound **40**.



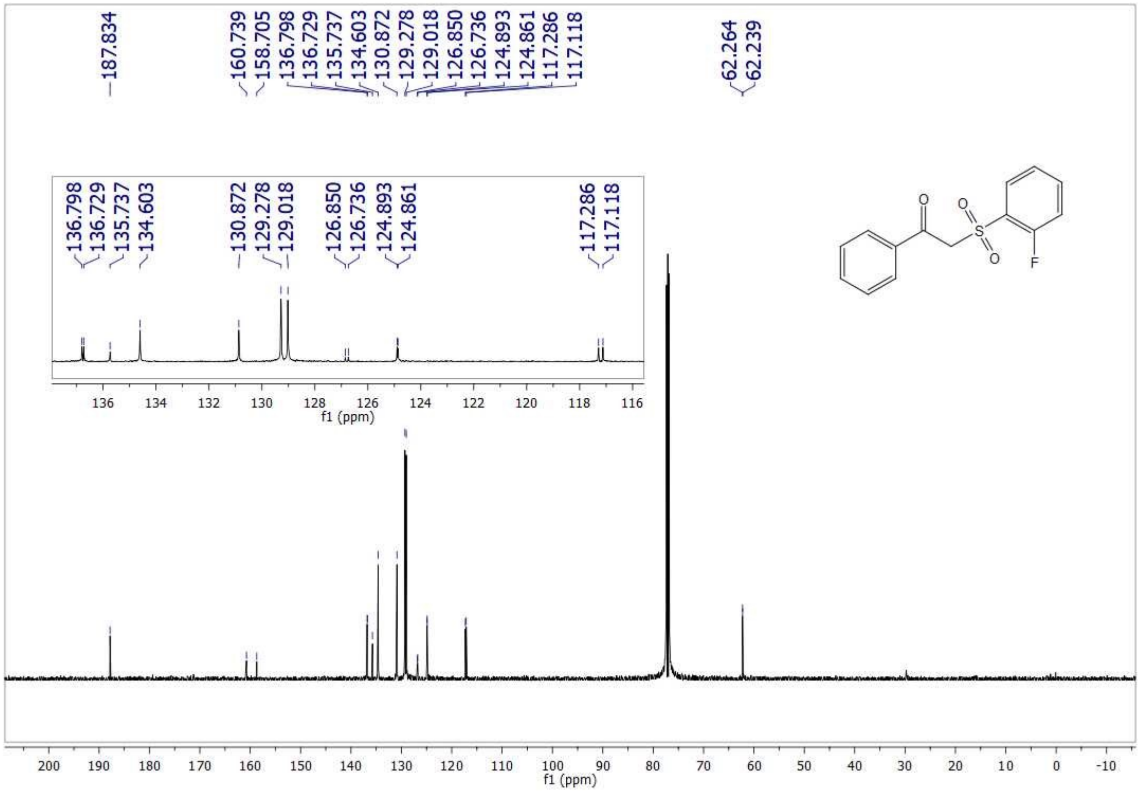
^{13}C NMR (126 MHz, $CDCl_3$) of compound **40**.



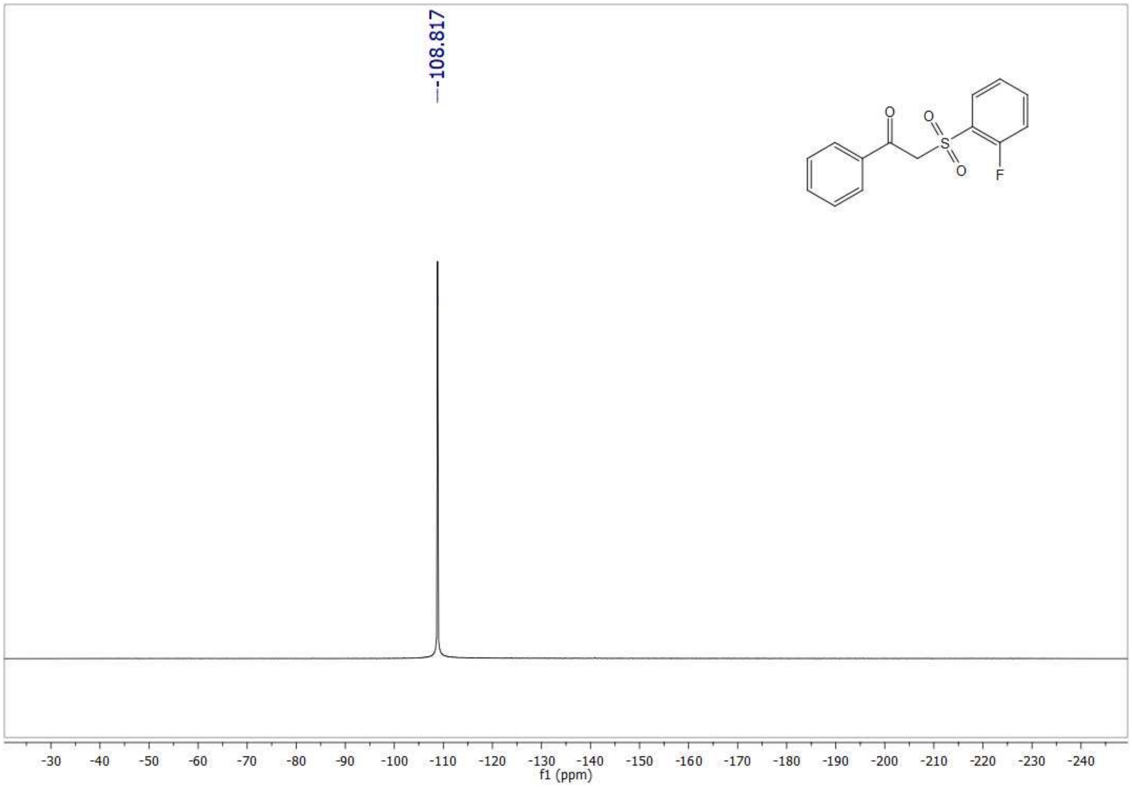
^{19}F NMR (472 MHz, $CDCl_3$) of compound **40**.



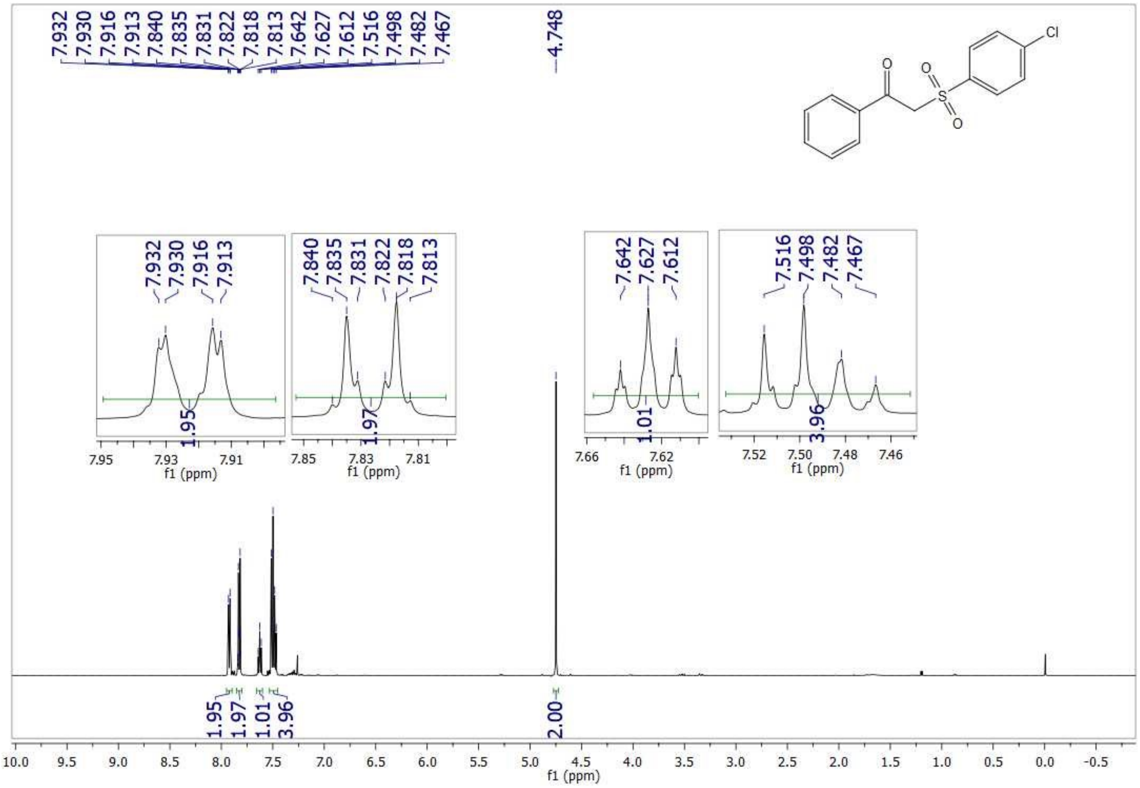
^{1}H NMR (500 MHz, $CDCl_3$) of compound **41**.



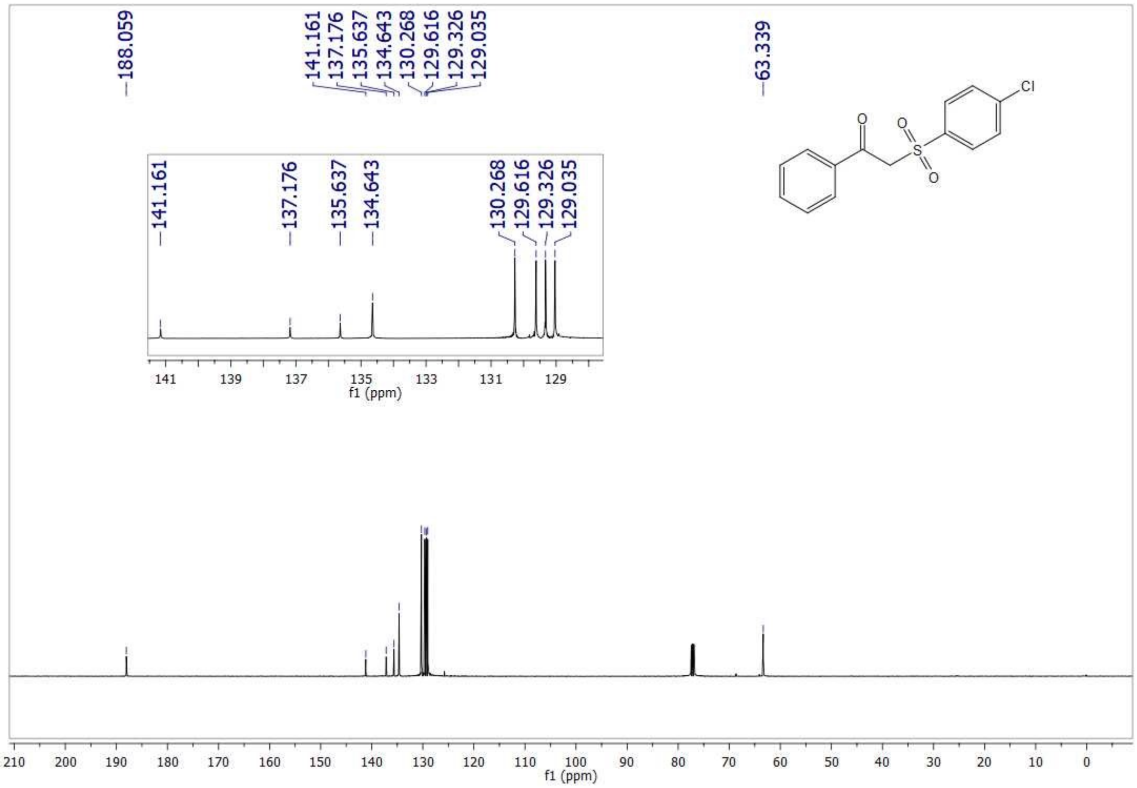
^{13}C NMR (126 MHz, CDCl$_3$) of compound **41**.



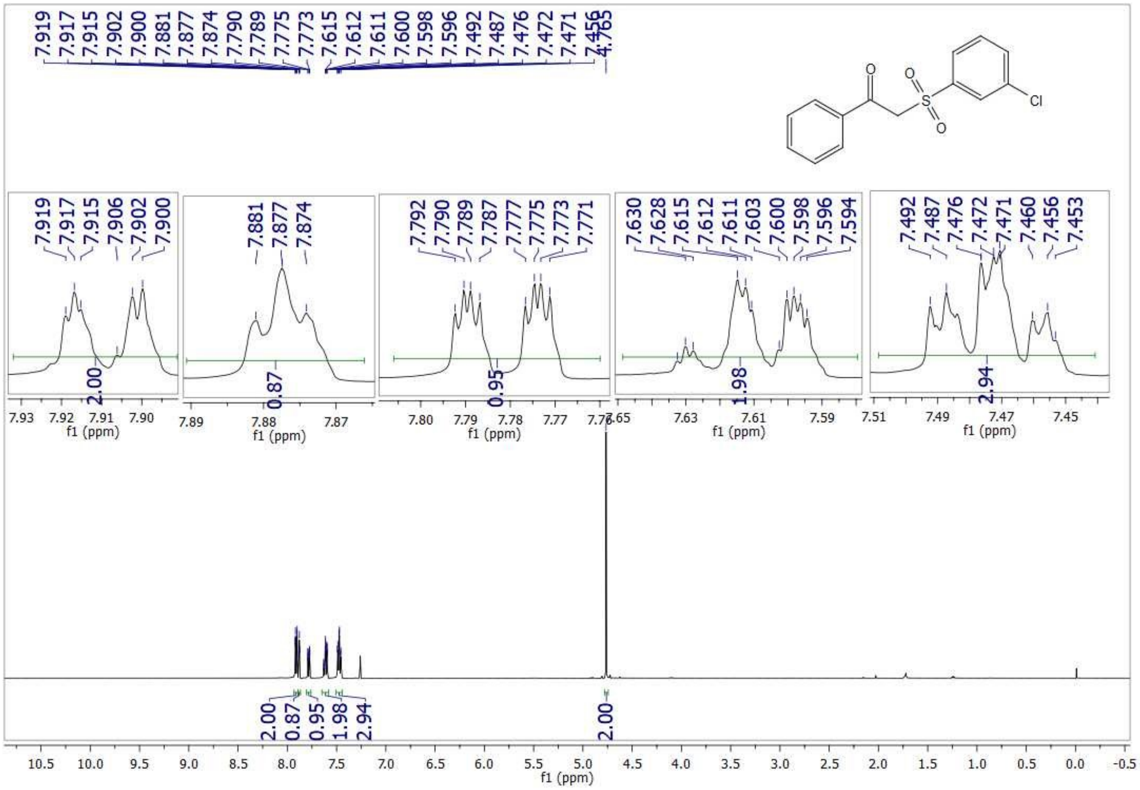
^{19}F NMR (472 MHz, CDCl$_3$) of compound **41**.



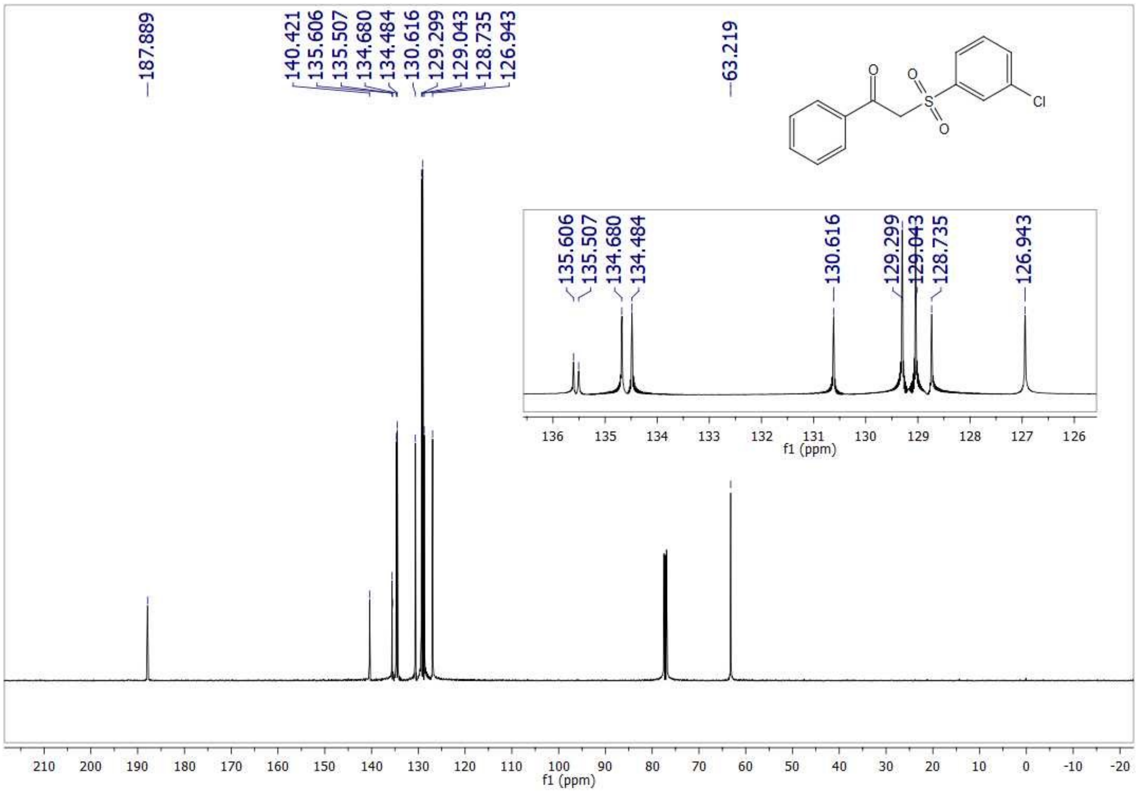
^{1}H NMR (500 MHz, CDCl$_3$) of compound **42**.



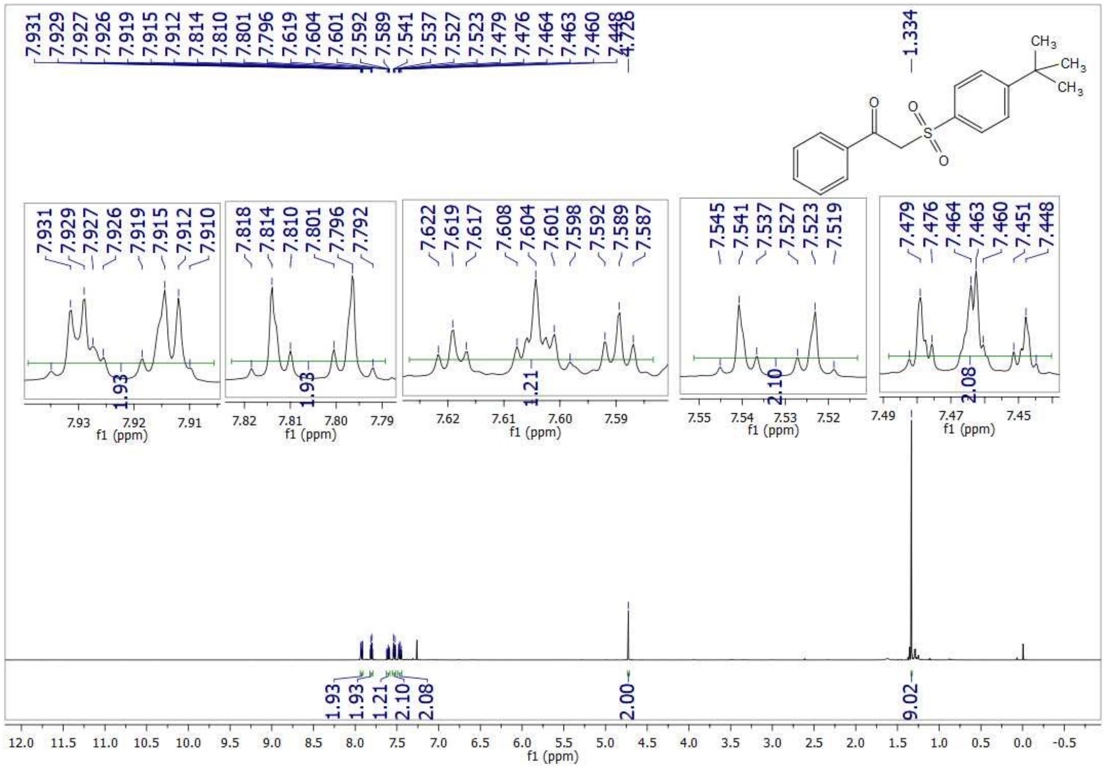
^{13}C NMR (126 MHz, CDCl$_3$) of compound **42**.



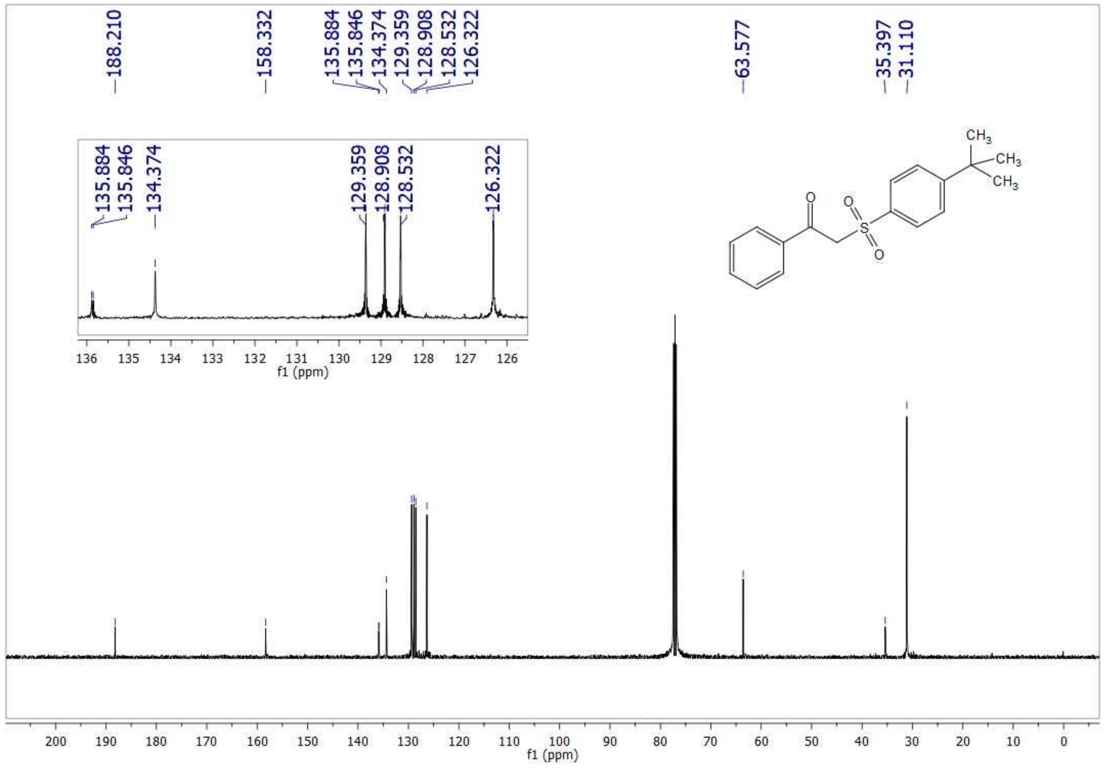
^{1}H NMR (500 MHz, CDCl$_3$) of compound **43**.



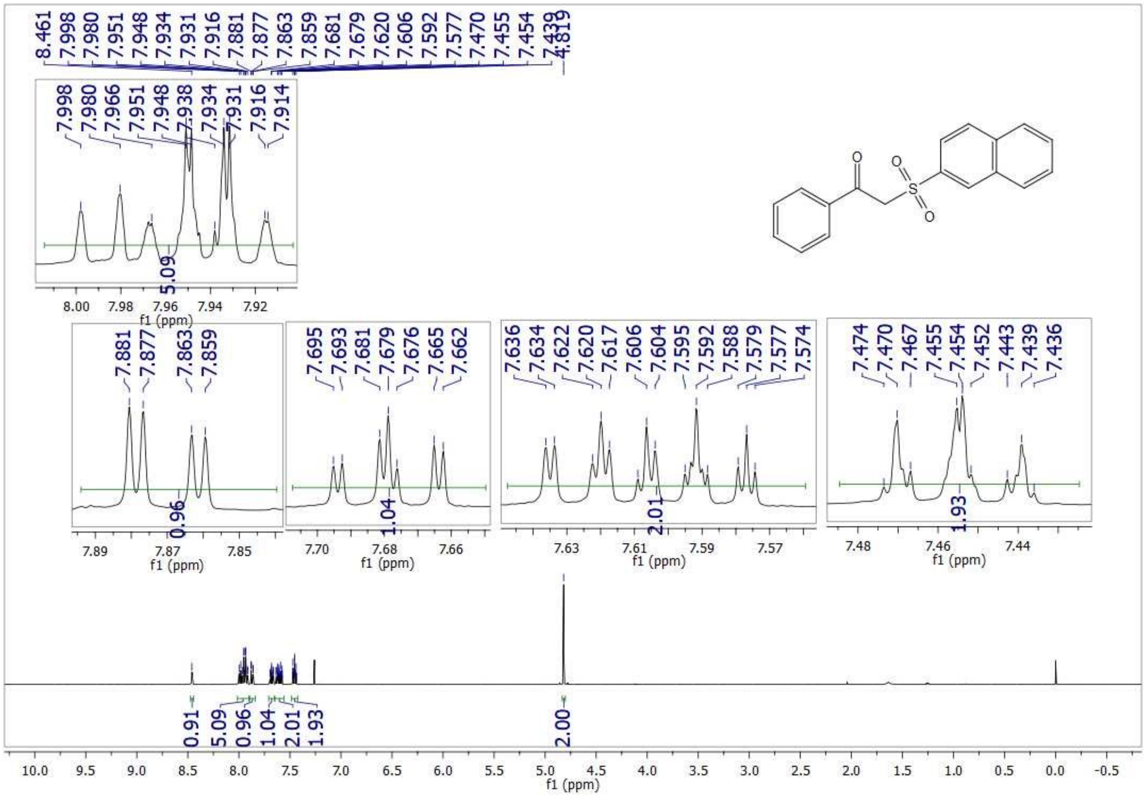
^{13}C NMR (126 MHz, CDCl$_3$) of compound **43**.



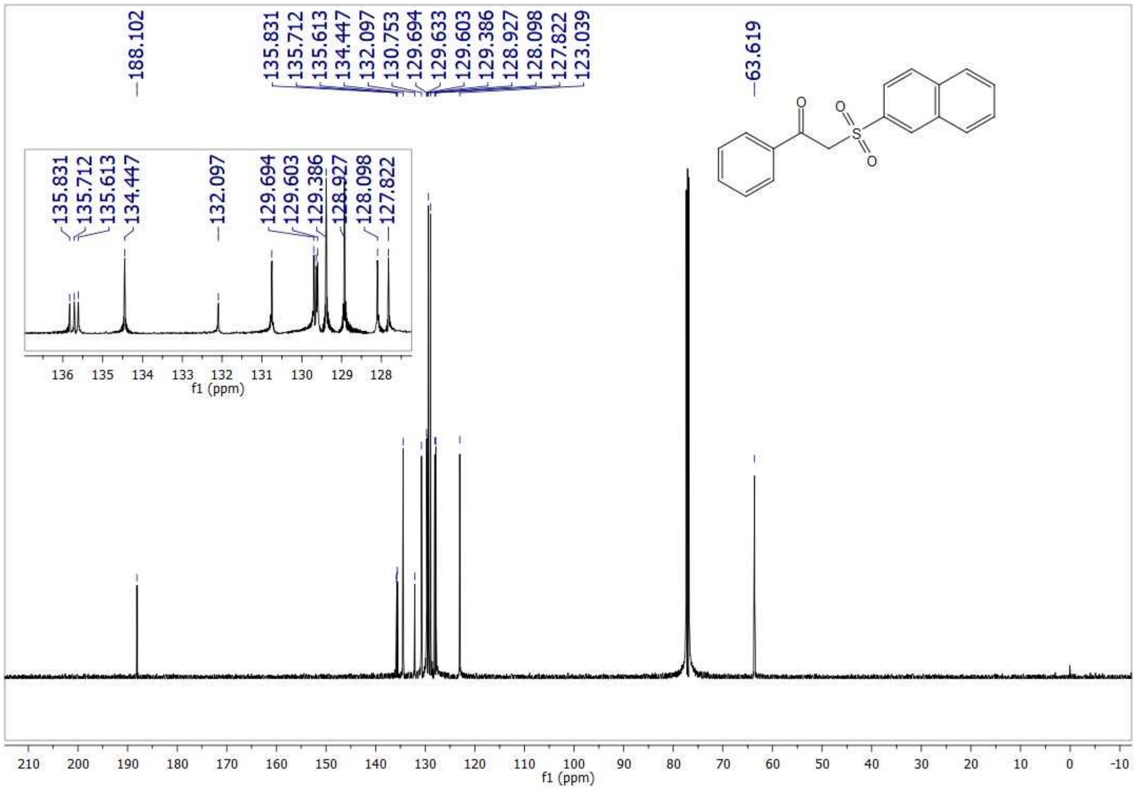
^{1}H NMR (500 MHz, CDCl$_3$) of compound **44**.



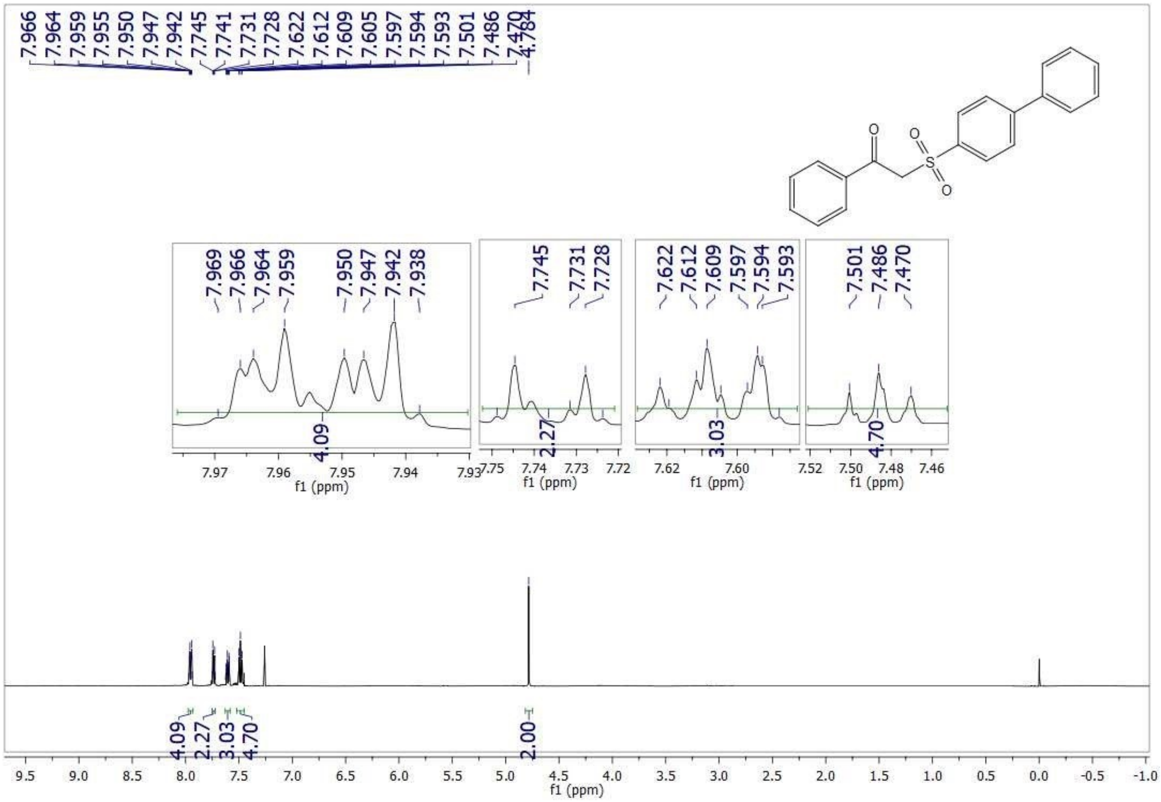
^{13}C NMR (126 MHz, CDCl$_3$) of compound **44**.



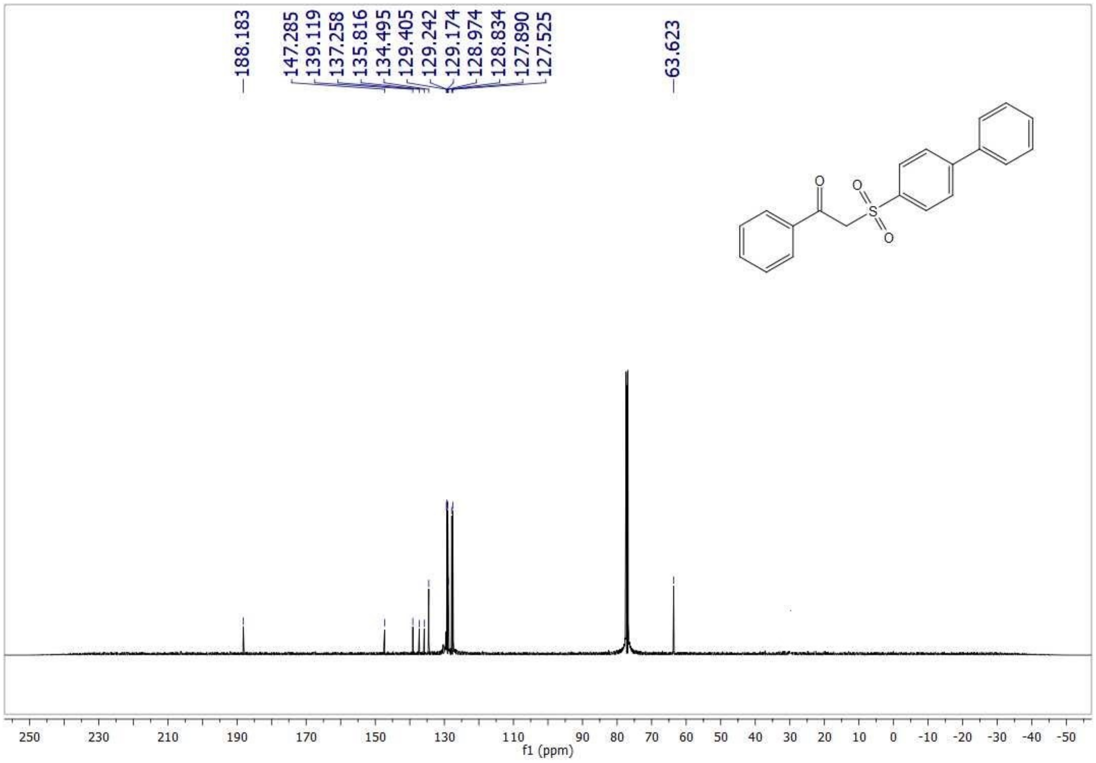
^{1}H NMR (500 MHz, $CDCl_3$) of compound **45.**



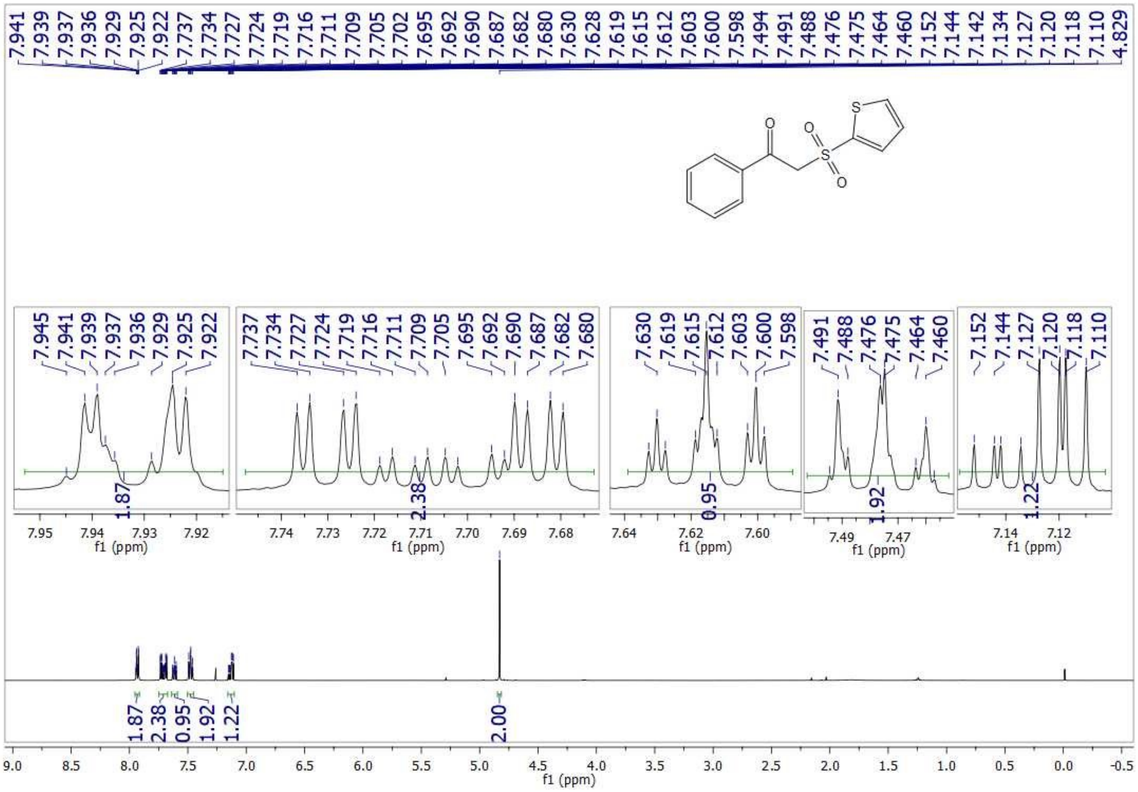
^{13}C NMR (126 MHz, $CDCl_3$) of compound **45.**



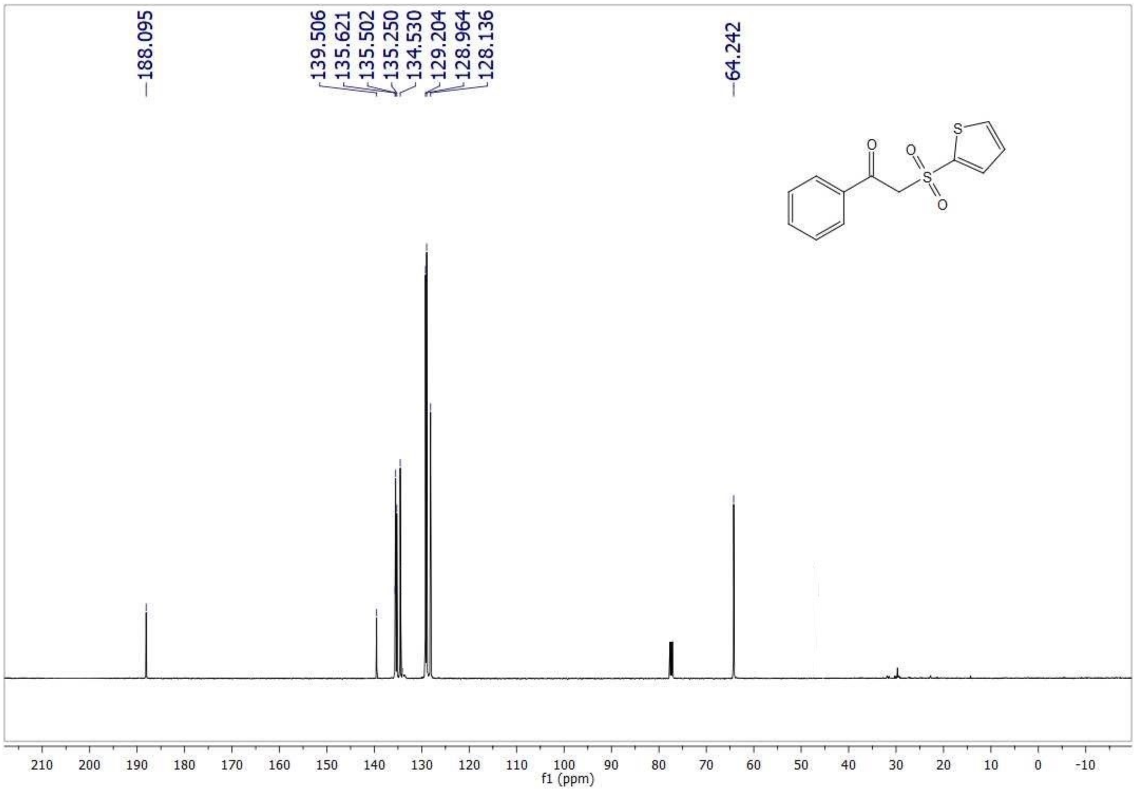
^{1}H NMR (500 MHz, CDCl$_3$) of compound **46**.



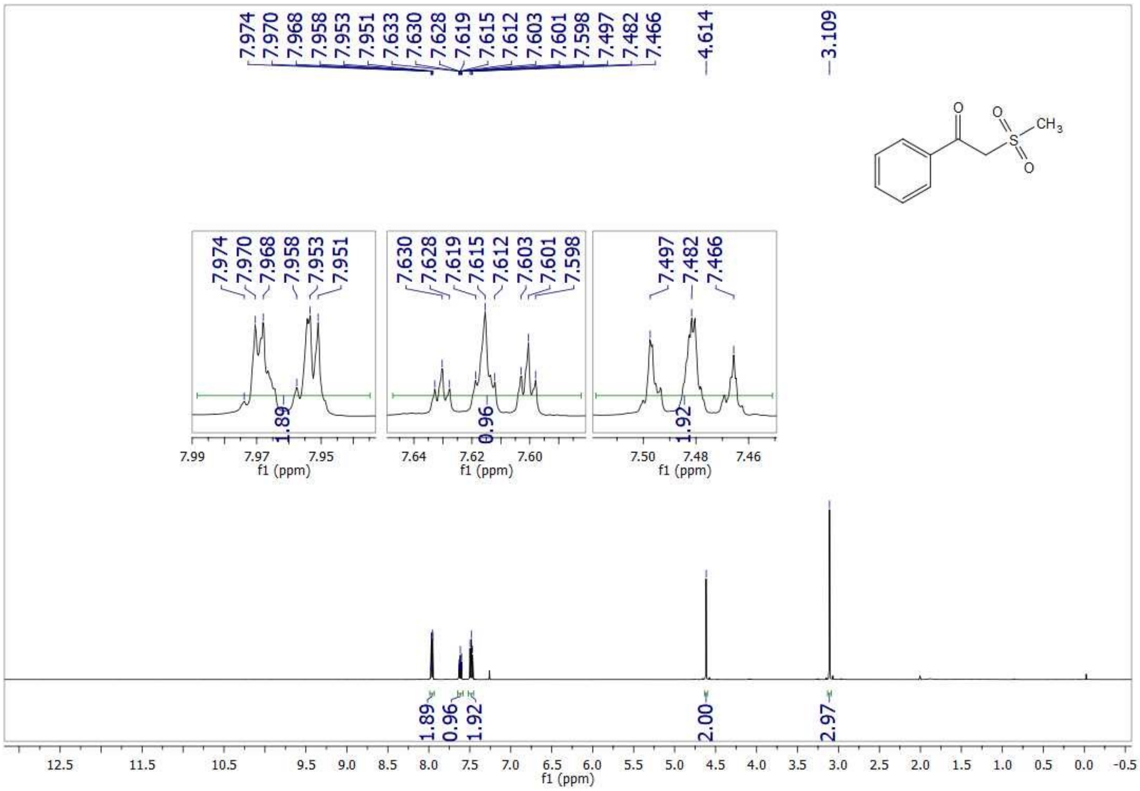
^{13}C NMR (126 MHz, CDCl$_3$) of compound **46**.



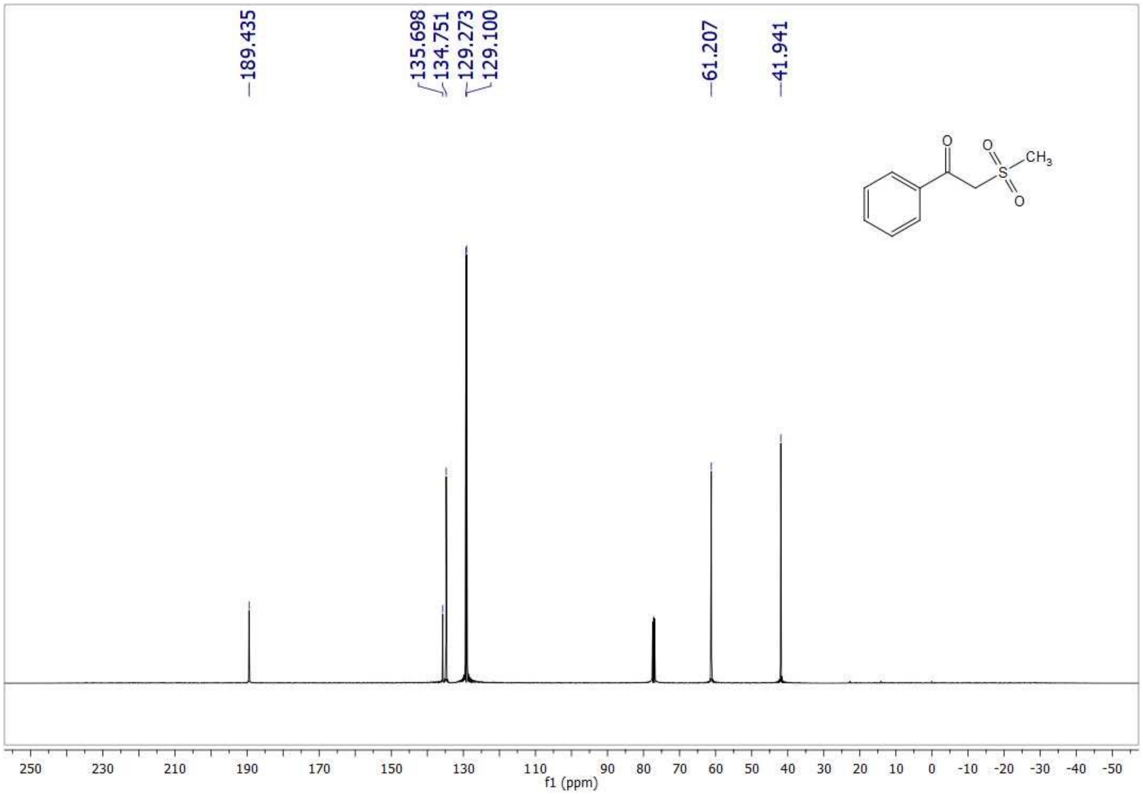
^{1}H NMR (500 MHz, CDCl$_3$) of compound **47**.



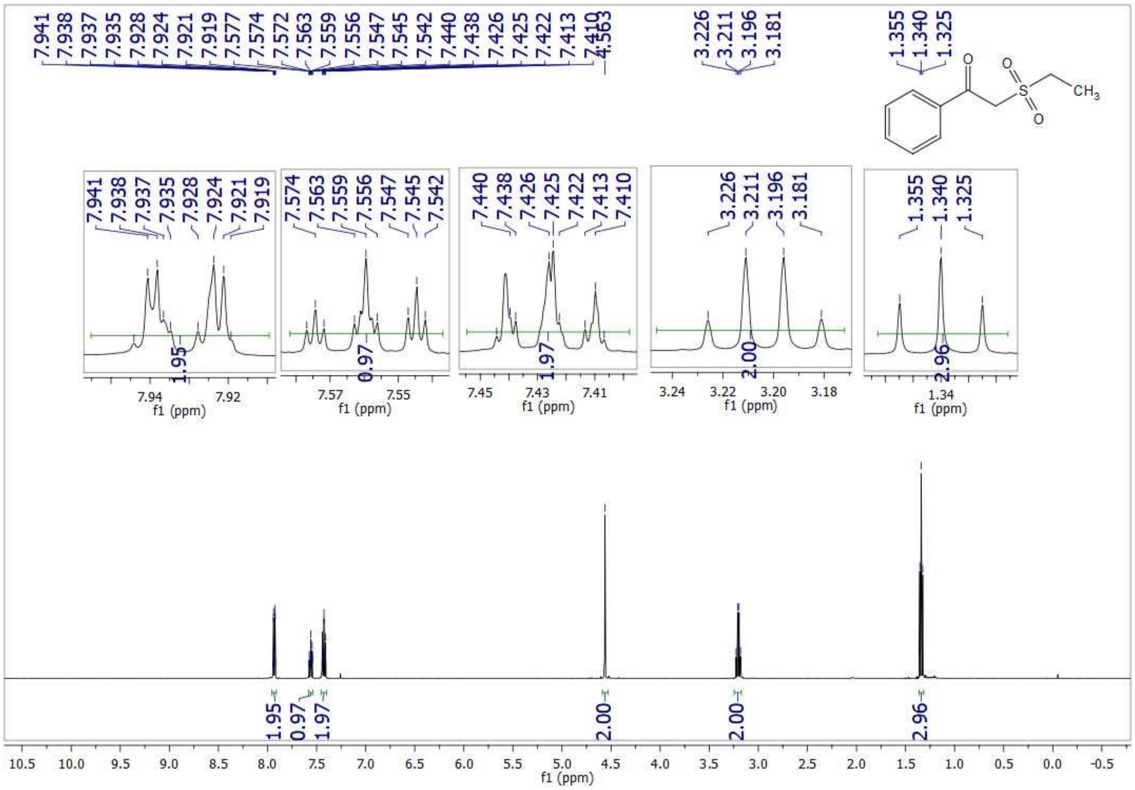
^{13}C NMR (126 MHz, CDCl$_3$) of compound **47**.



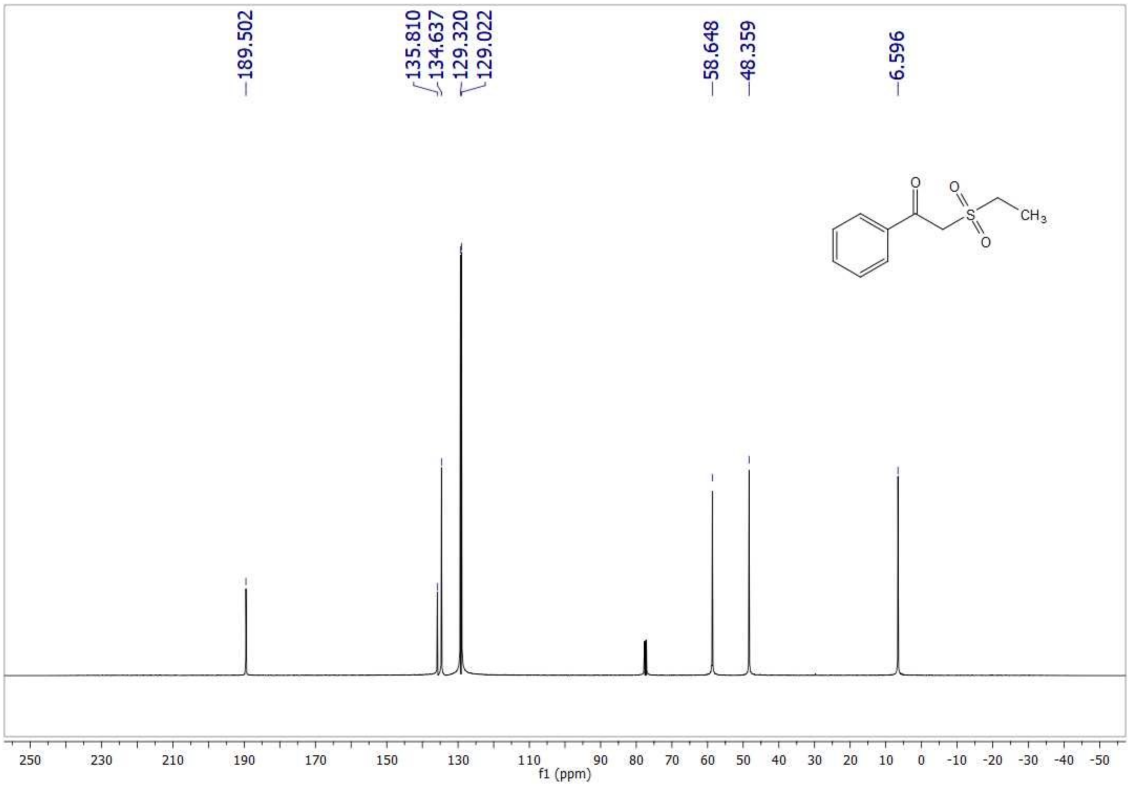
^{1}H NMR (500 MHz, CDCl$_3$) of compound **48**.



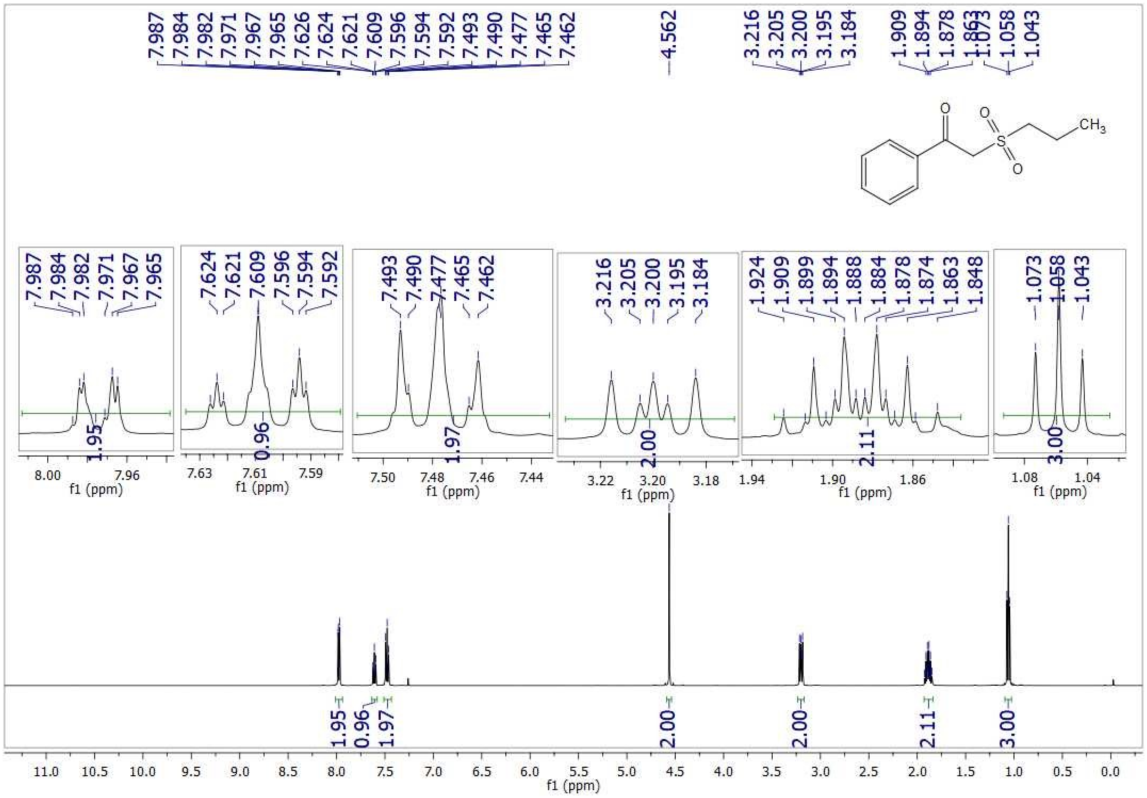
^{13}C NMR (126 MHz, CDCl$_3$) of compound **48**.



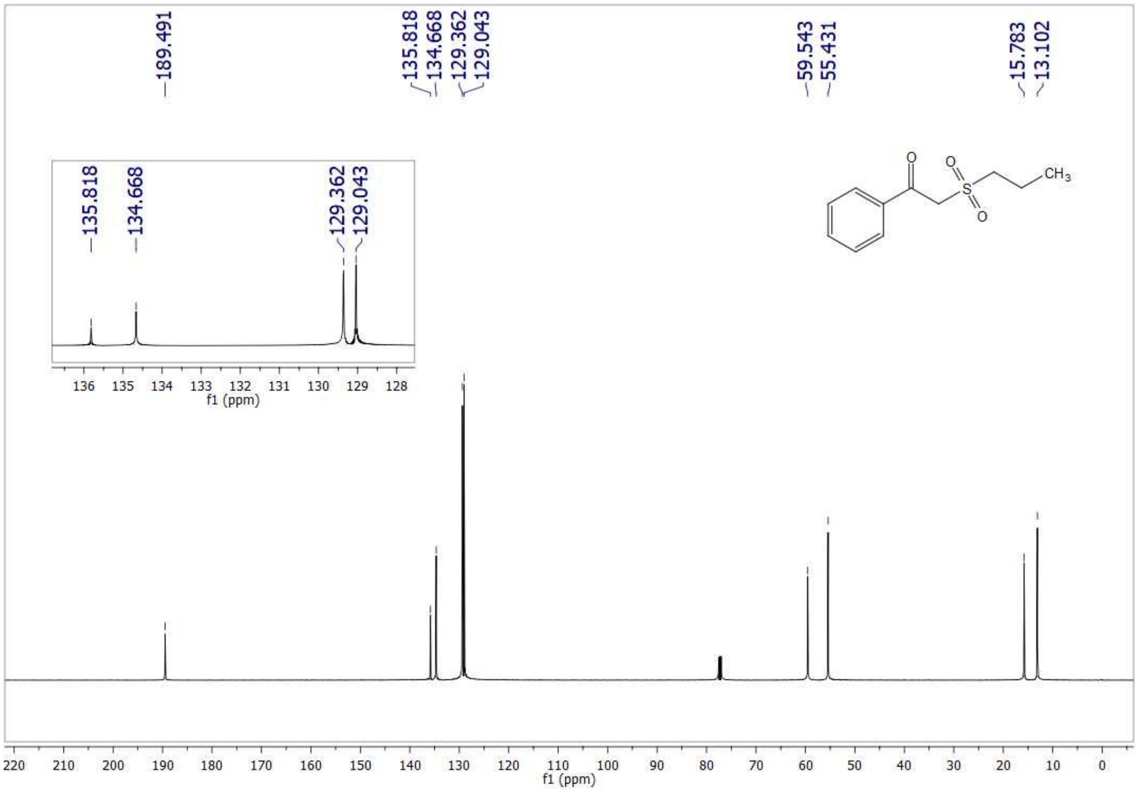
^{1}H NMR (500 MHz, CDCl$_3$) of compound **49**.



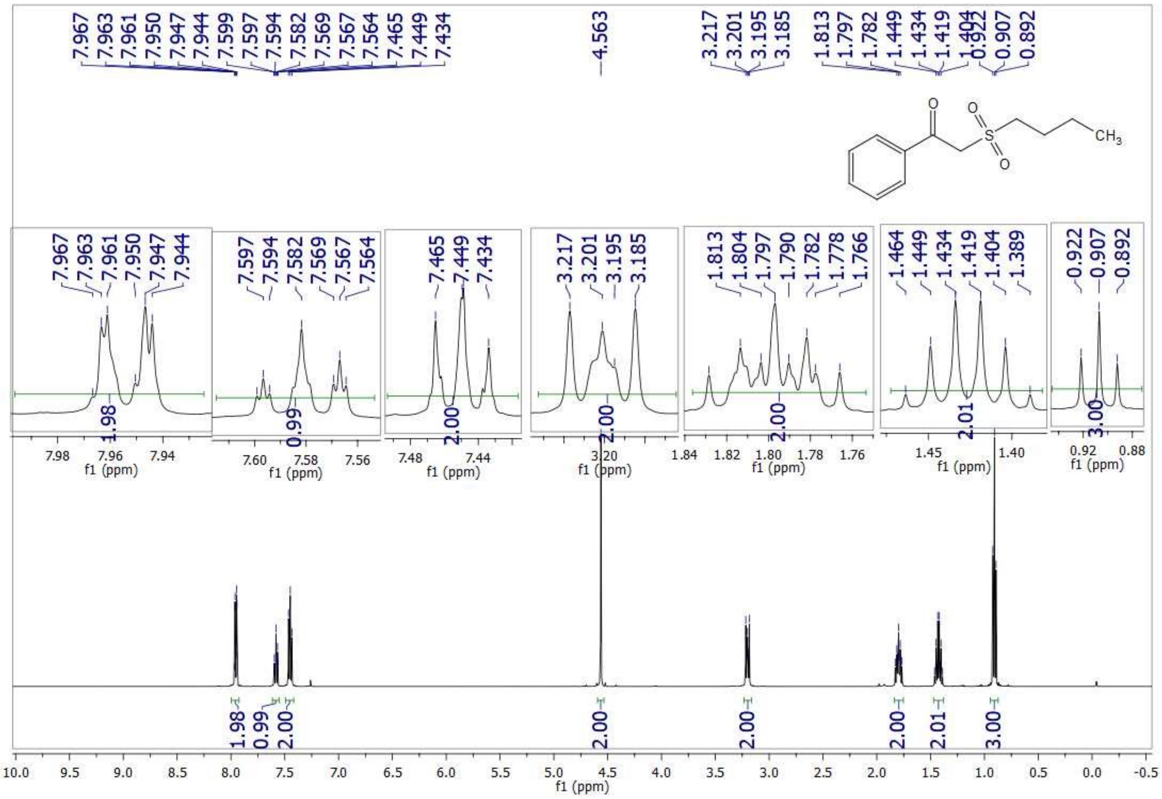
^{13}C NMR (126 MHz, CDCl$_3$) of compound **49**.



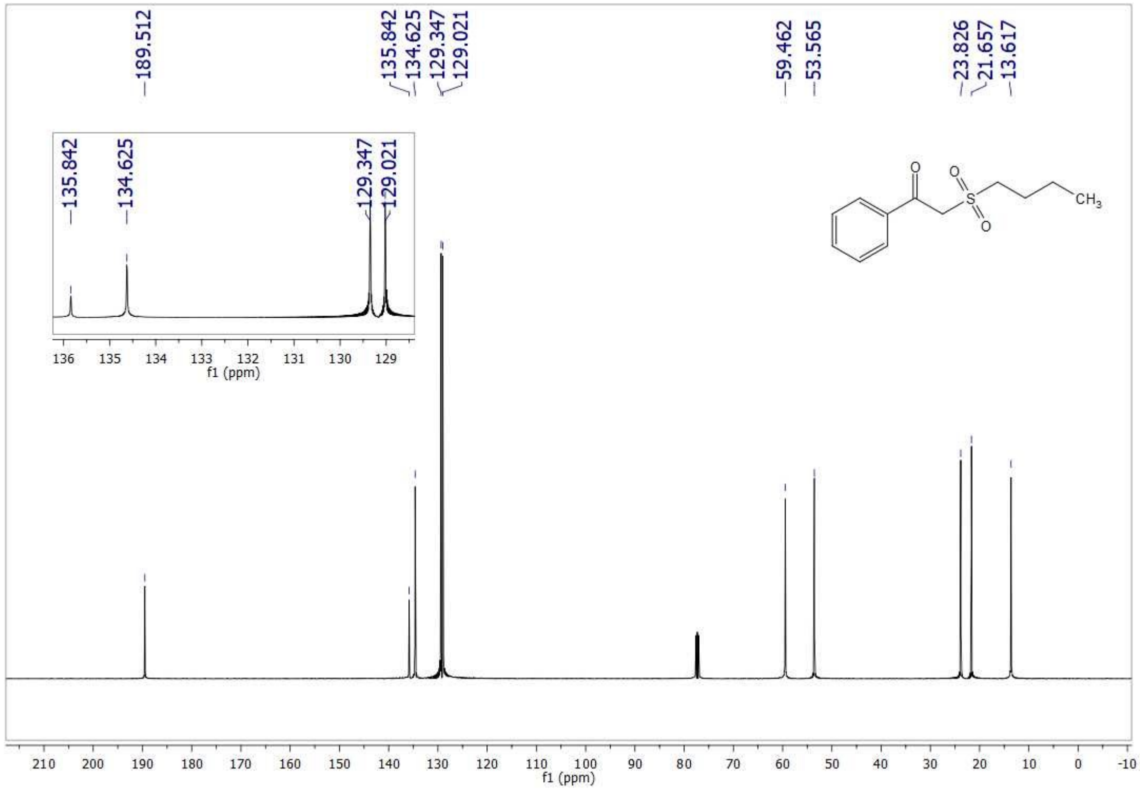
^{1}H NMR (500 MHz, CDCl$_3$) of compound **50**.



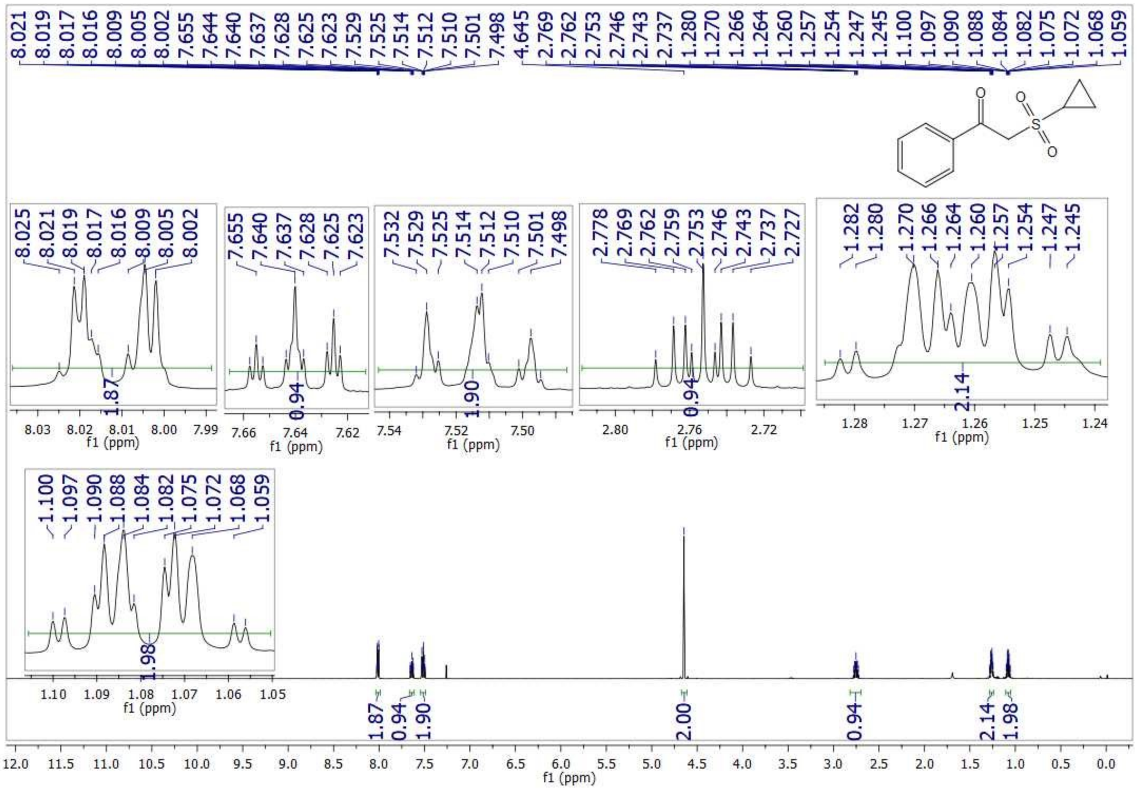
^{13}C NMR (126 MHz, CDCl$_3$) of compound **50**.



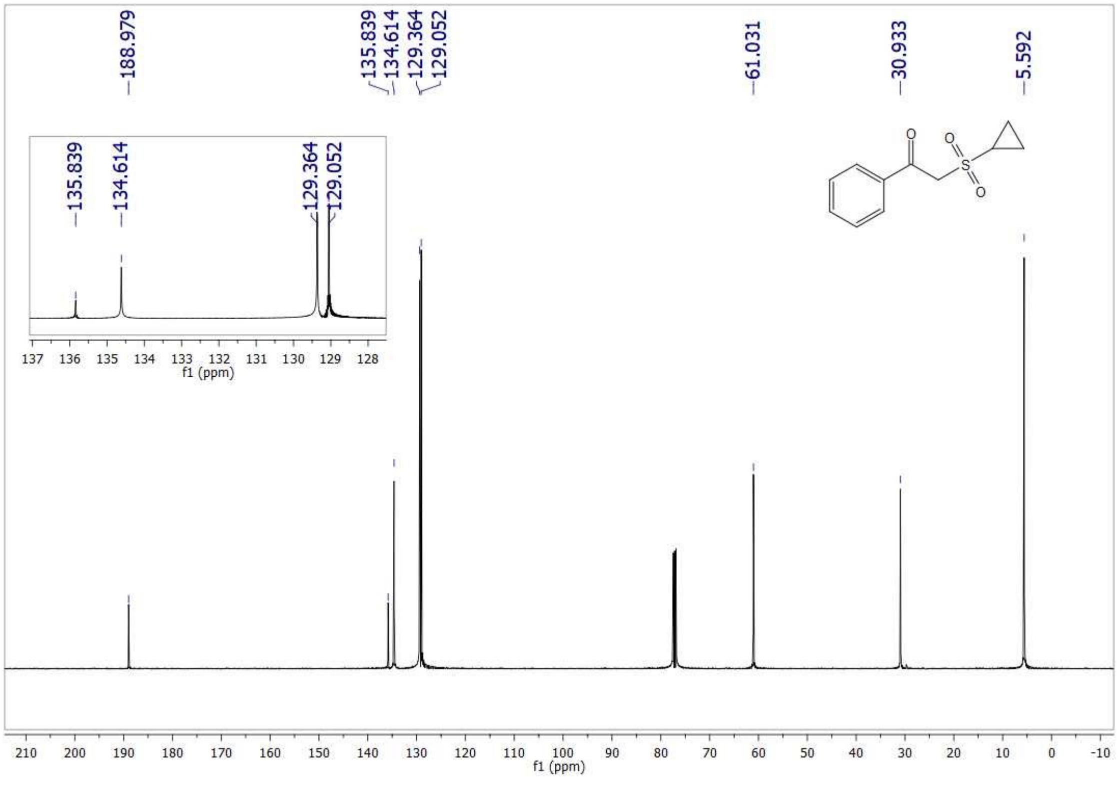
^{1}H NMR (500 MHz, CDCl$_3$) of compound **51**.



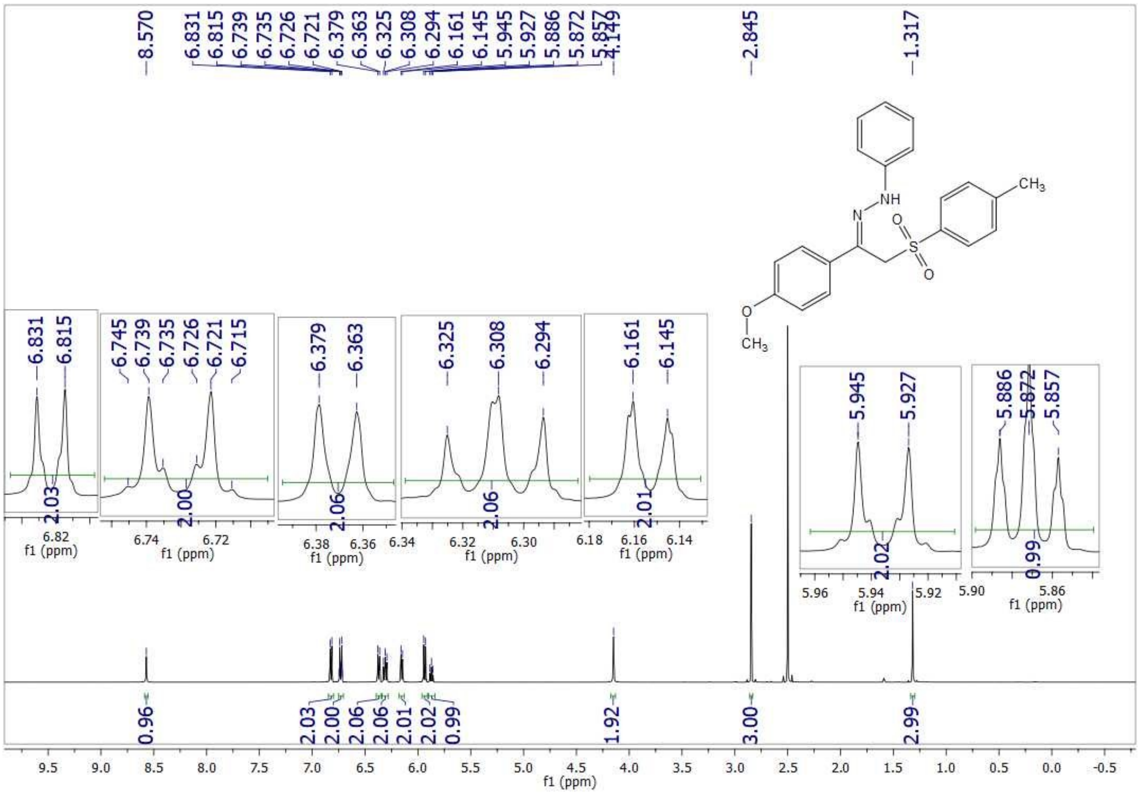
^{13}C NMR (126 MHz, CDCl$_3$) of compound **51**.



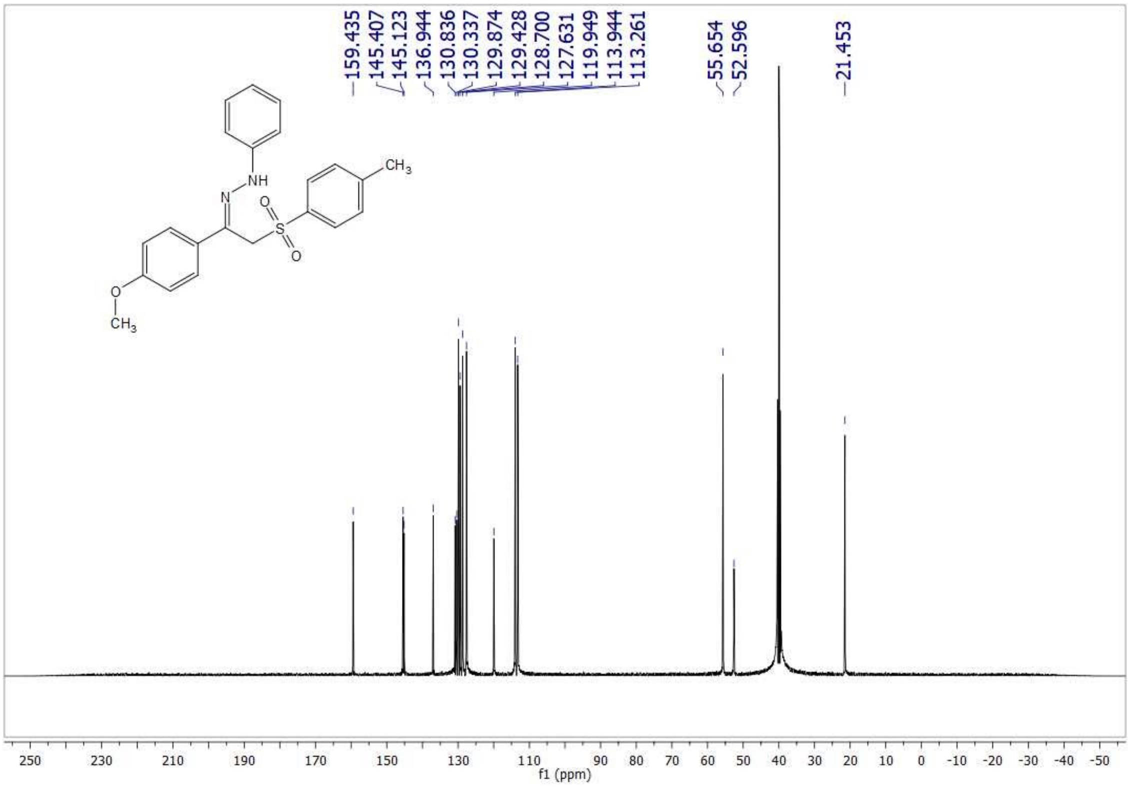
^{1}H NMR (500 MHz, CDCl$_3$) of compound **52**.



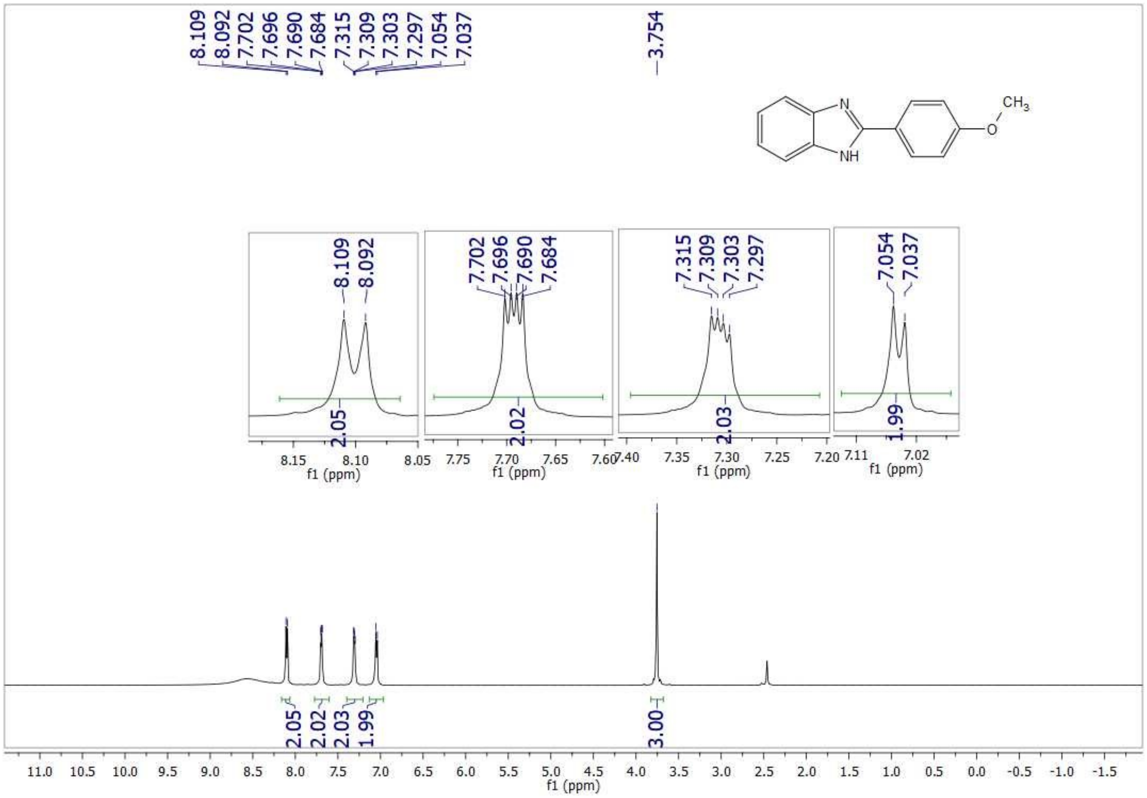
^{13}C NMR (126 MHz, CDCl$_3$) of compound **52**.



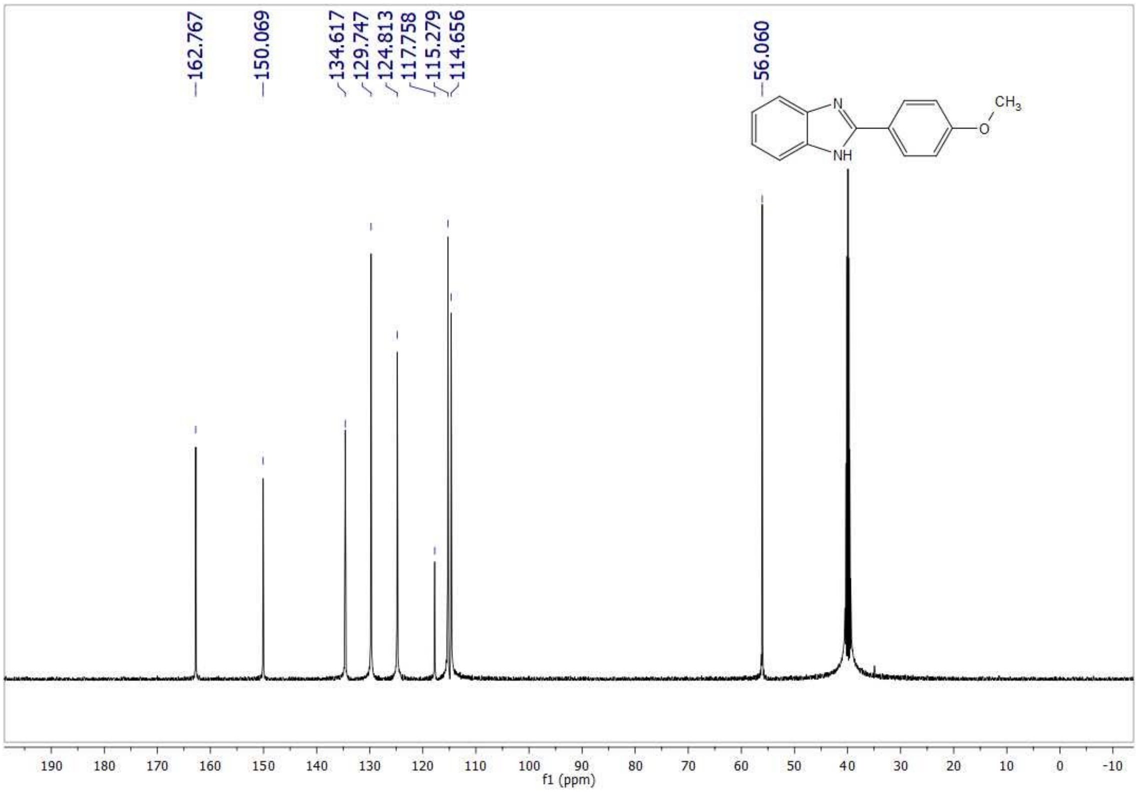
^{1}H NMR (500 MHz, DMSO -d_6) of compound **53**.



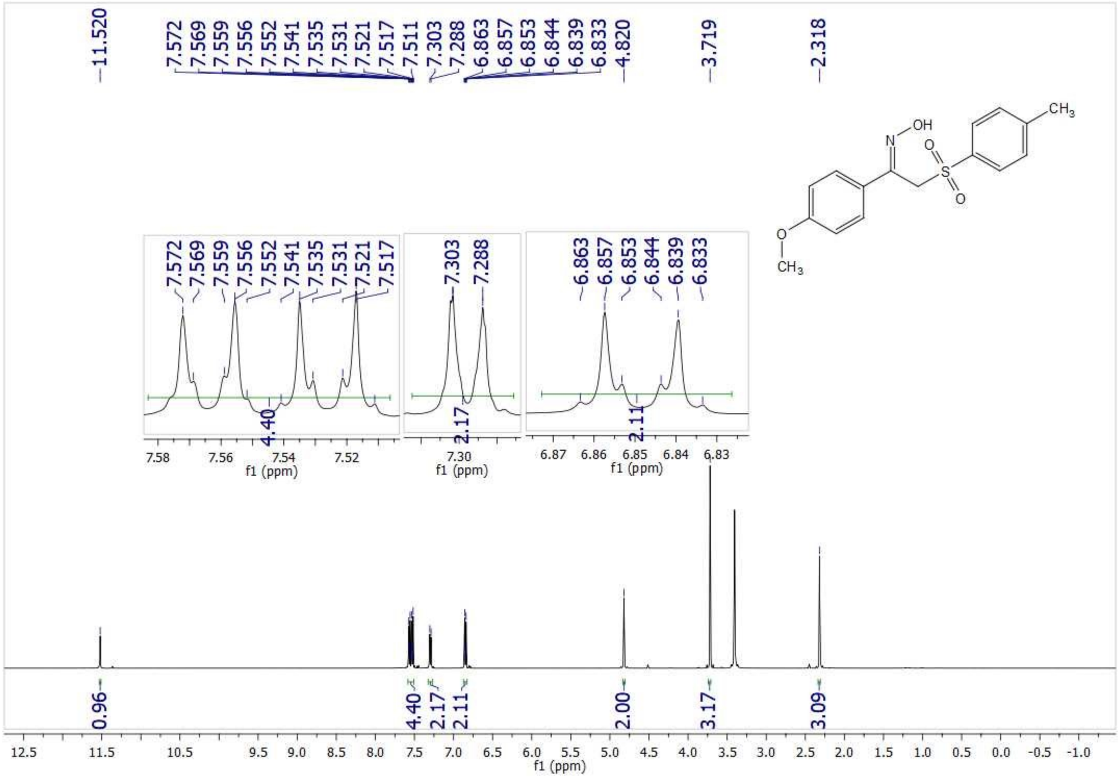
^{13}C NMR (126 MHz, DMSO -d_6) of compound **53**.



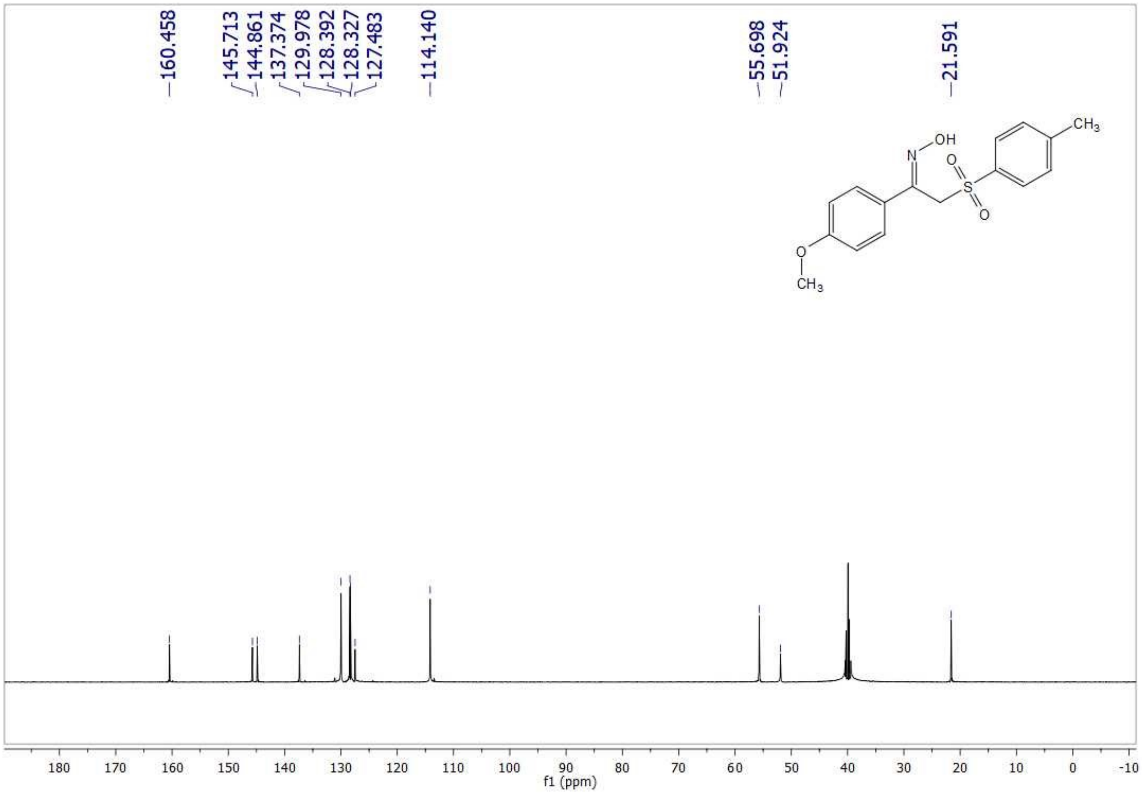
^{1}H NMR (500 MHz, DMSO -d_6) of compound **54**.



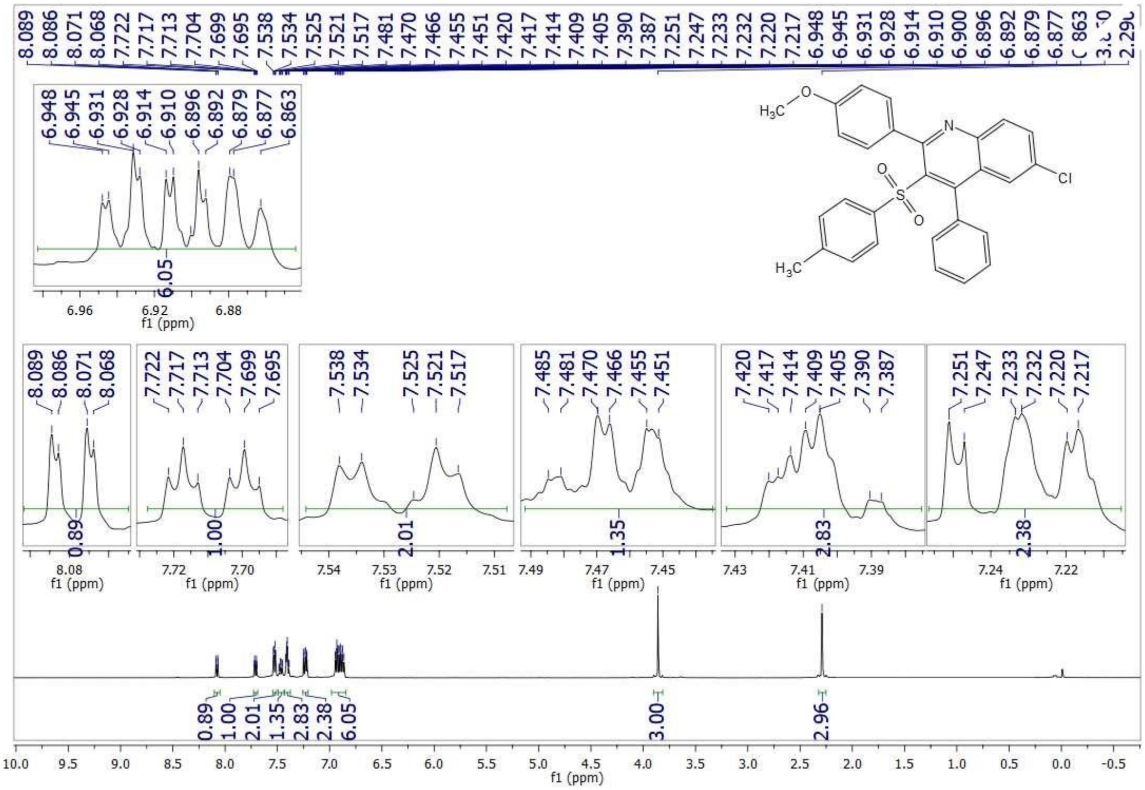
^{13}C NMR (126 MHz, DMSO -d_6) of compound **54**.



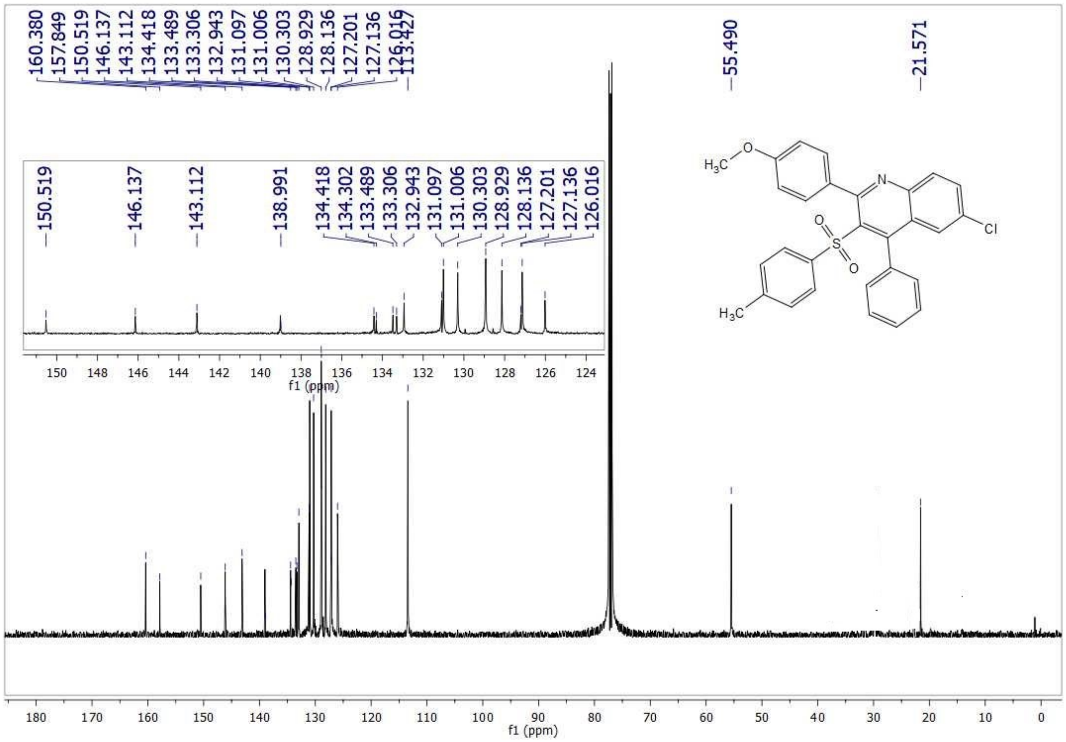
^{1}H NMR (500 MHz, DMSO -d_6) of compound **55**.



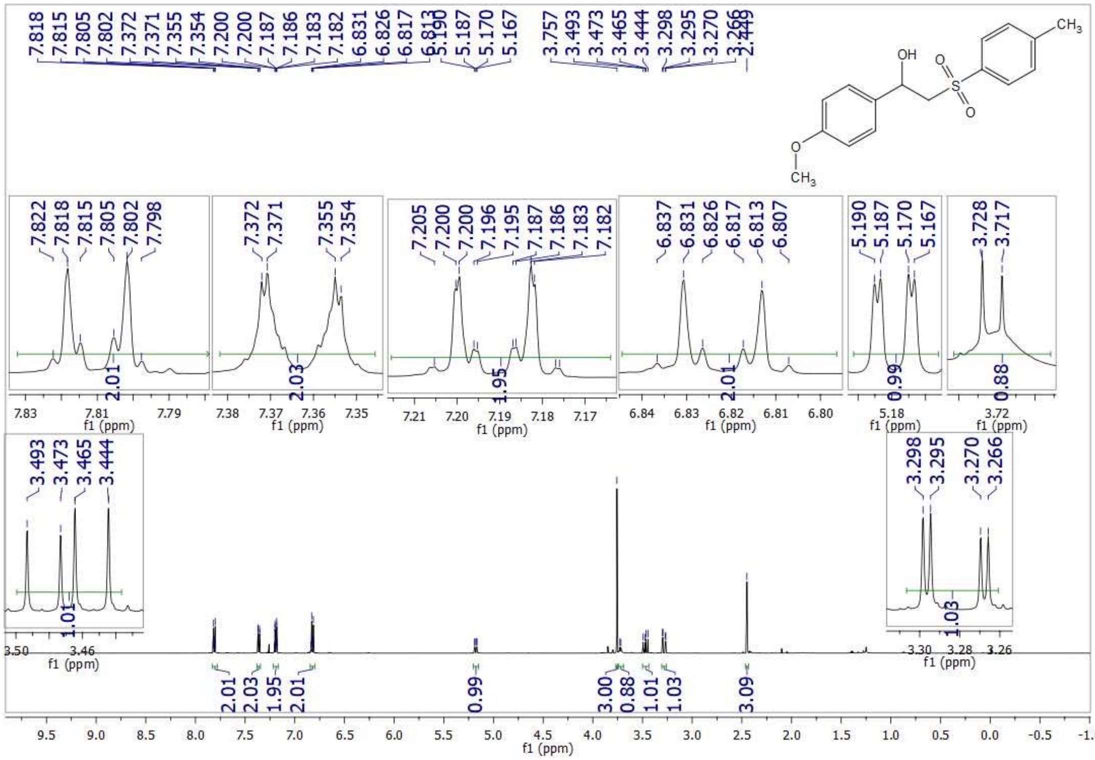
^{13}C NMR (126 MHz, DMSO -d_6) of compound **55**.



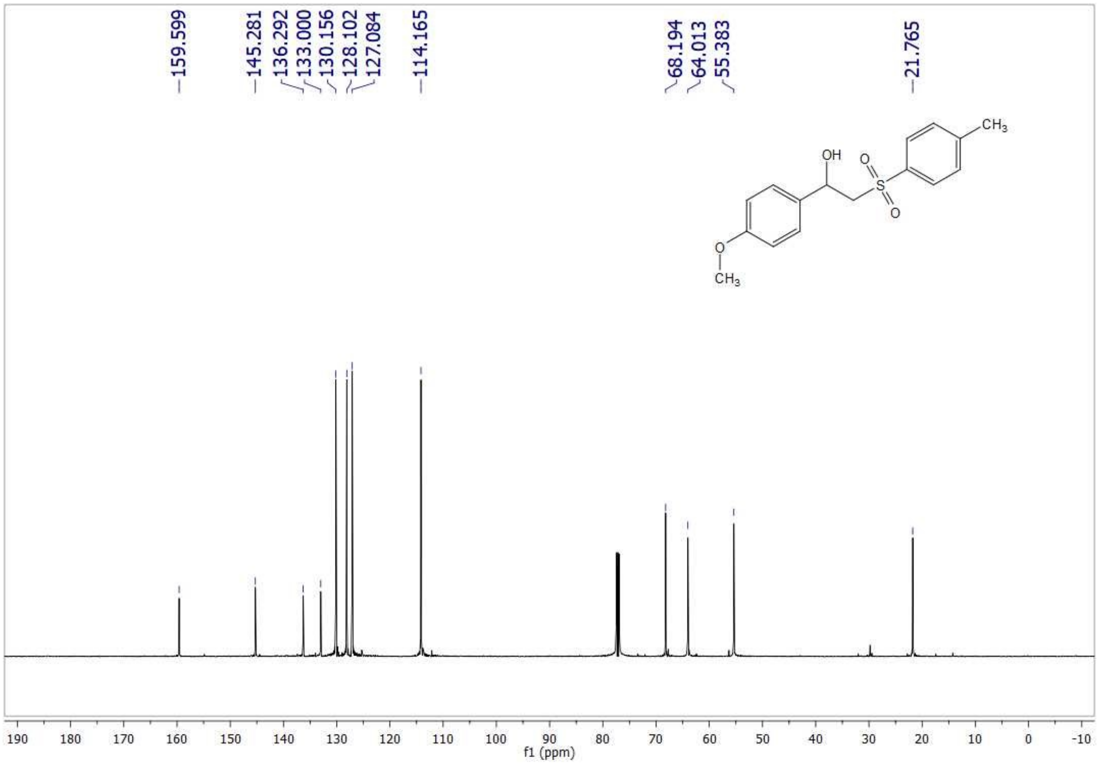
^{1}H NMR (500 MHz, $CDCl_3$) of compound **56**.



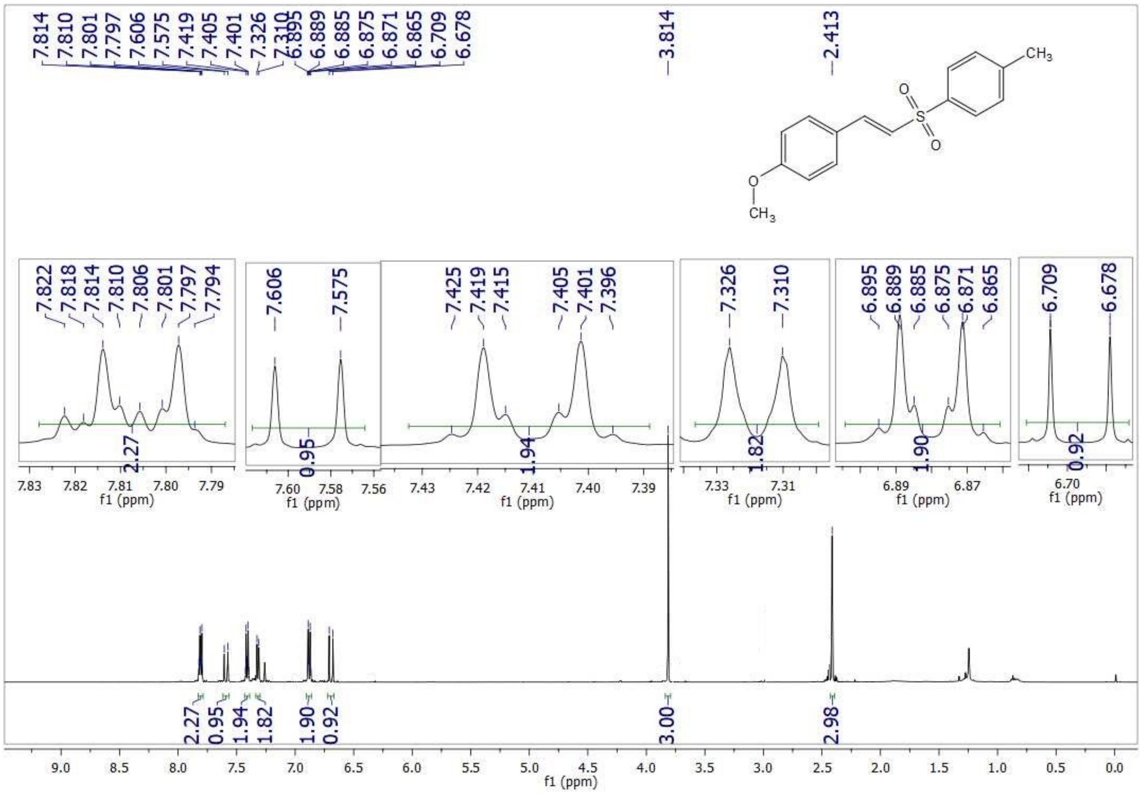
^{13}C NMR (126 MHz, $CDCl_3$) of compound **56**.



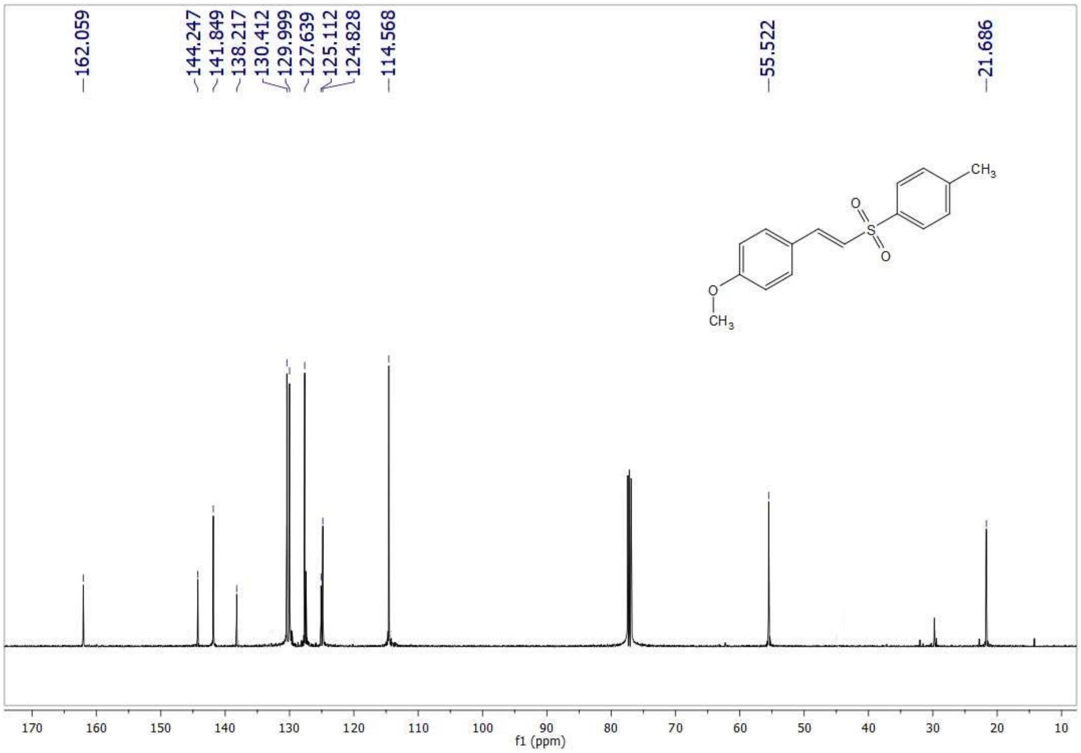
^{1}H NMR (500 MHz, CDCl$_3$) of compound **57**.



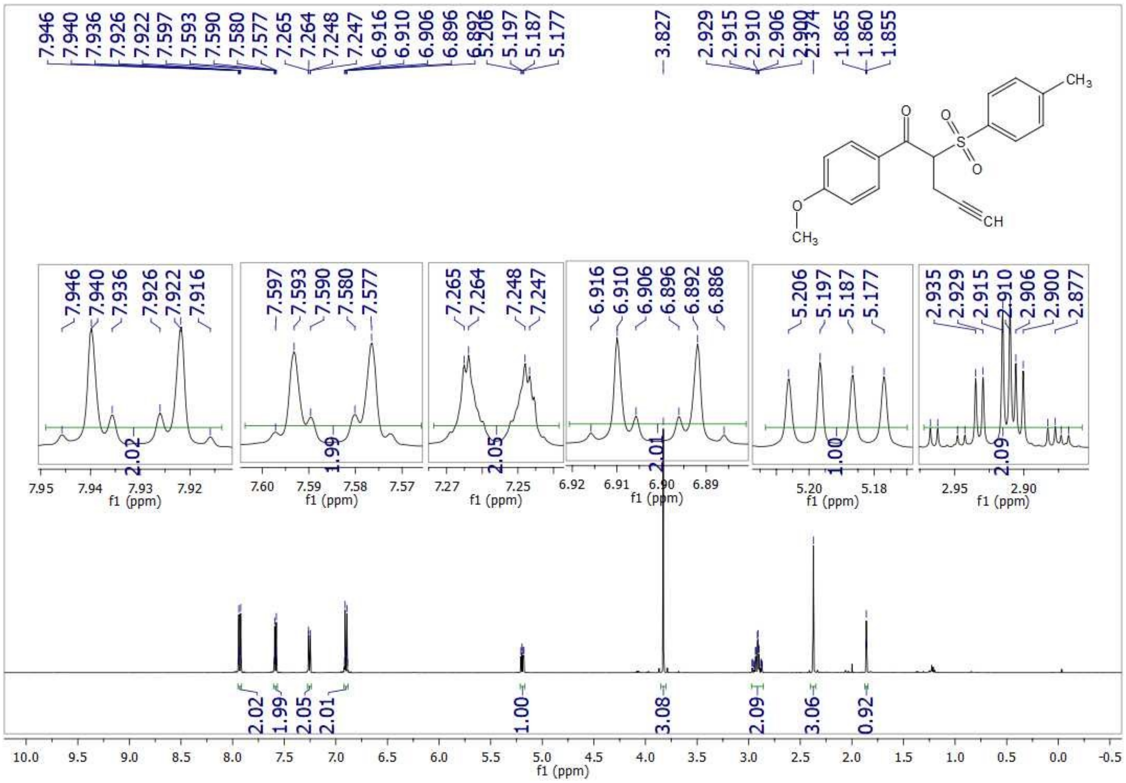
^{13}C NMR (126 MHz, CDCl$_3$) of compound **57**.



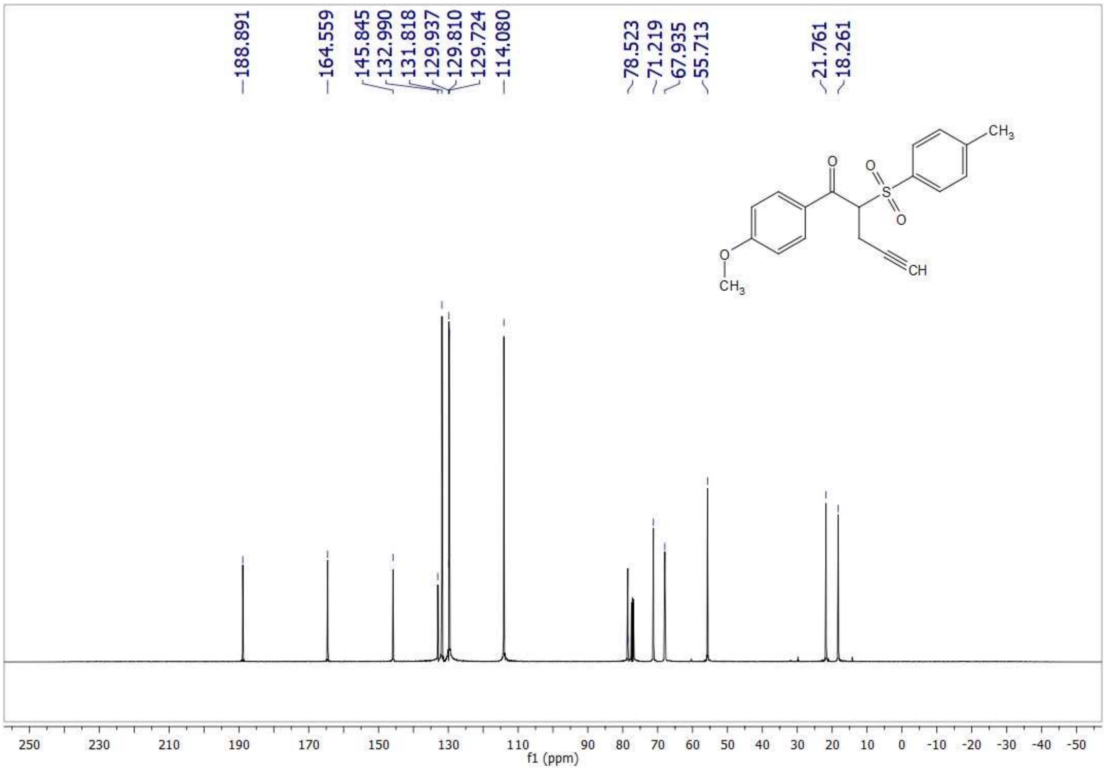
^{1}H NMR (500 MHz, CDCl$_3$) of compound **58**.



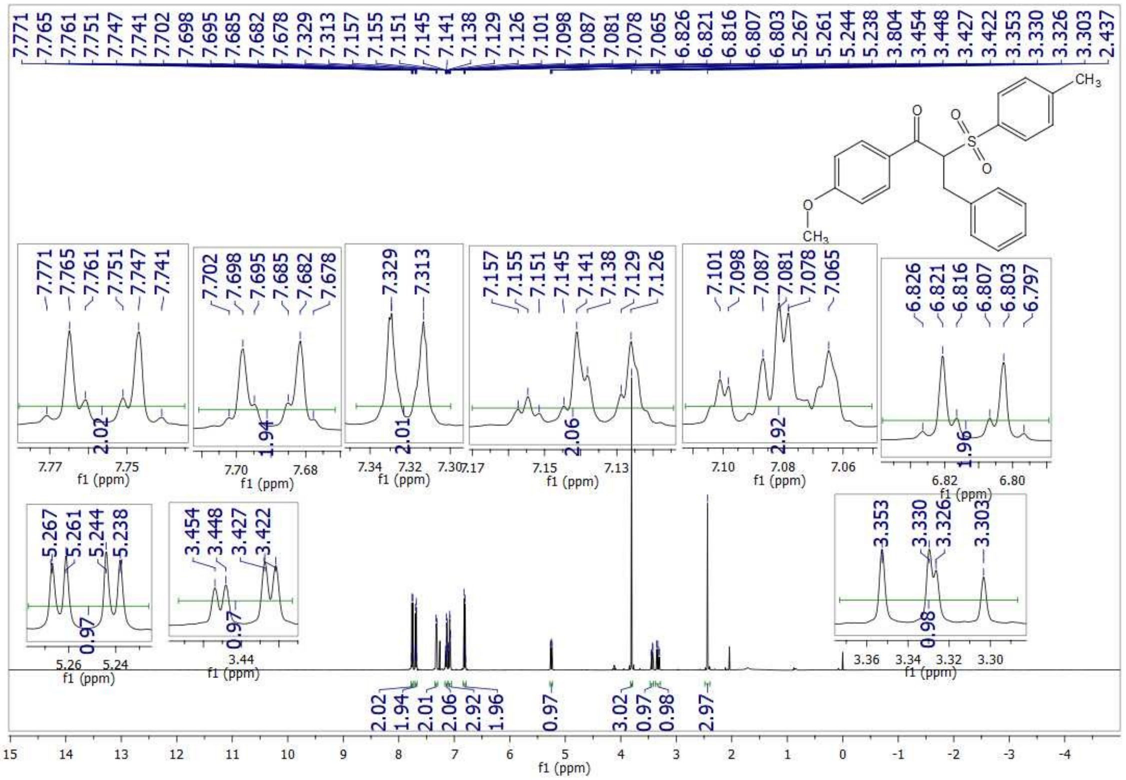
^{13}C NMR (126 MHz, CDCl$_3$) of compound **58**.



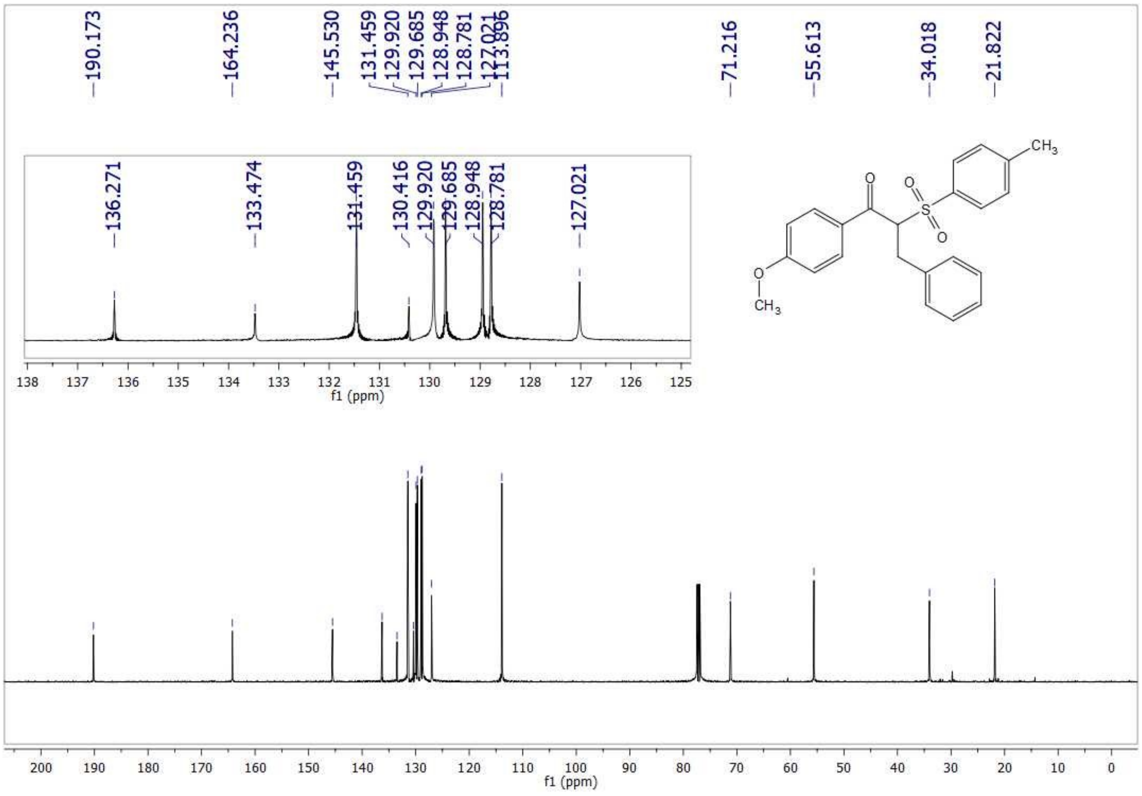
^{1}H NMR (500 MHz, CDCl$_3$) of compound **59**.



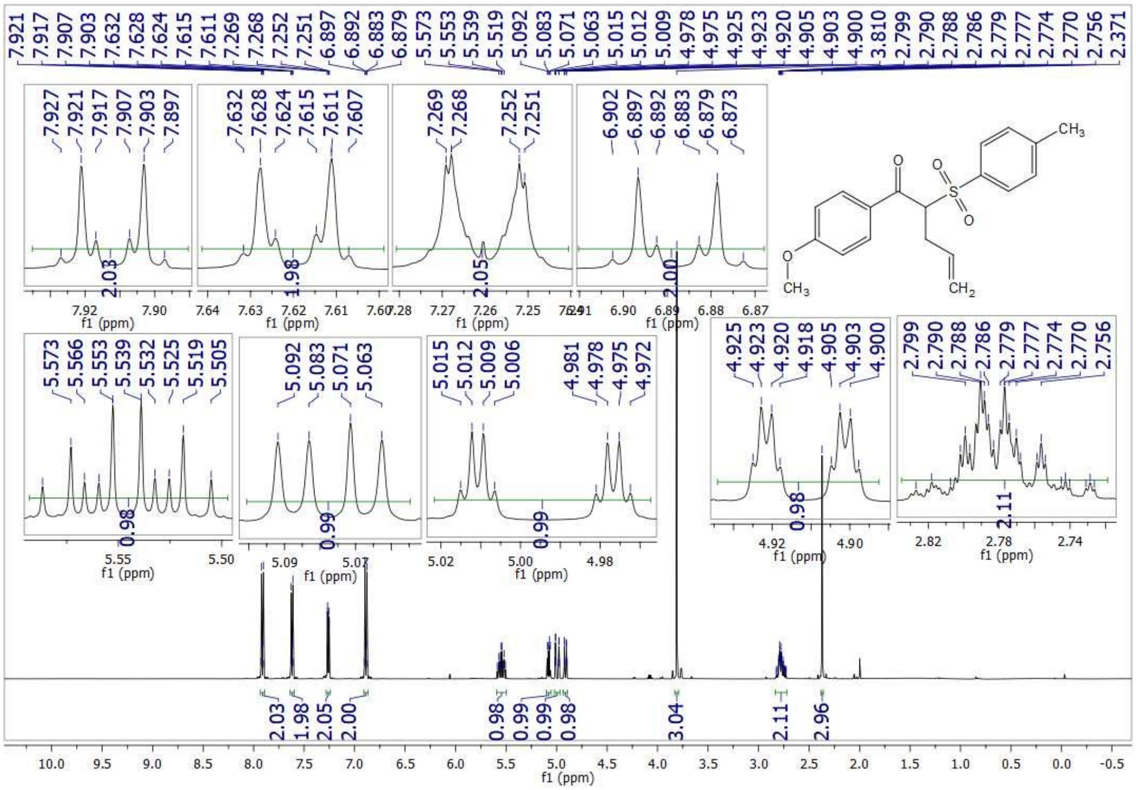
^{13}C NMR (126 MHz, CDCl$_3$) of compound **59**.



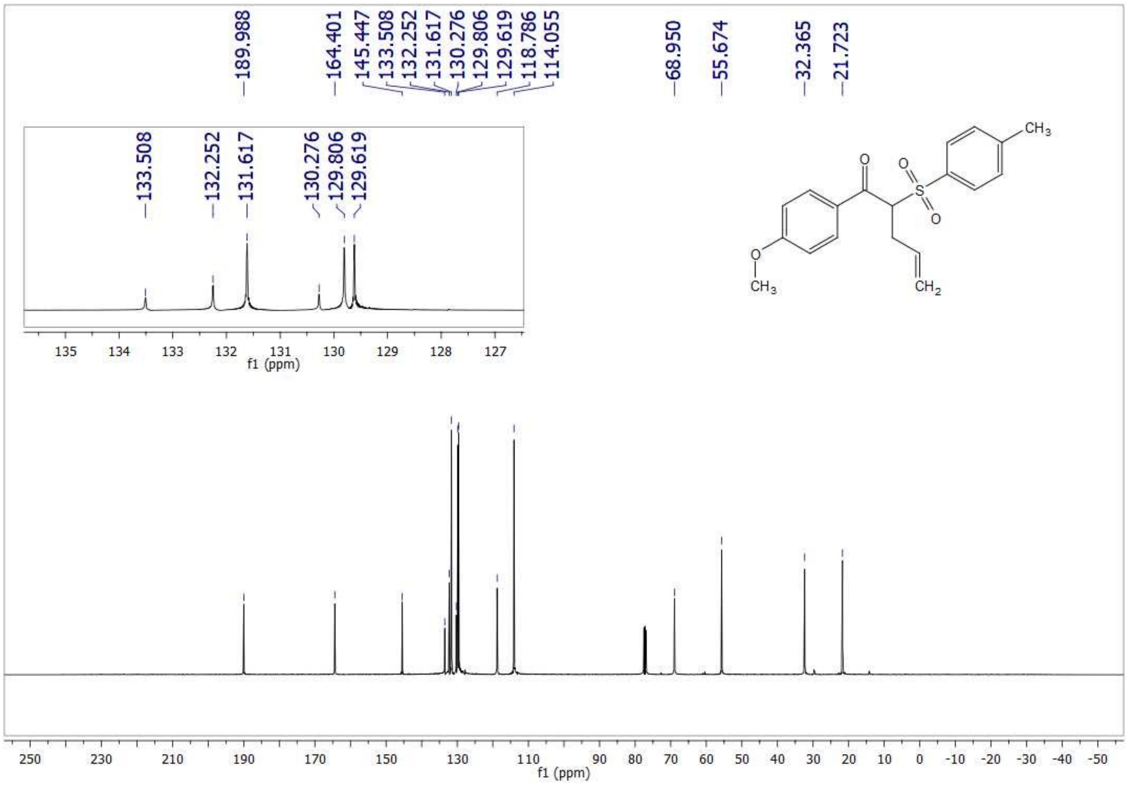
^{1}H NMR (500 MHz, CDCl$_3$) of compound **60**.



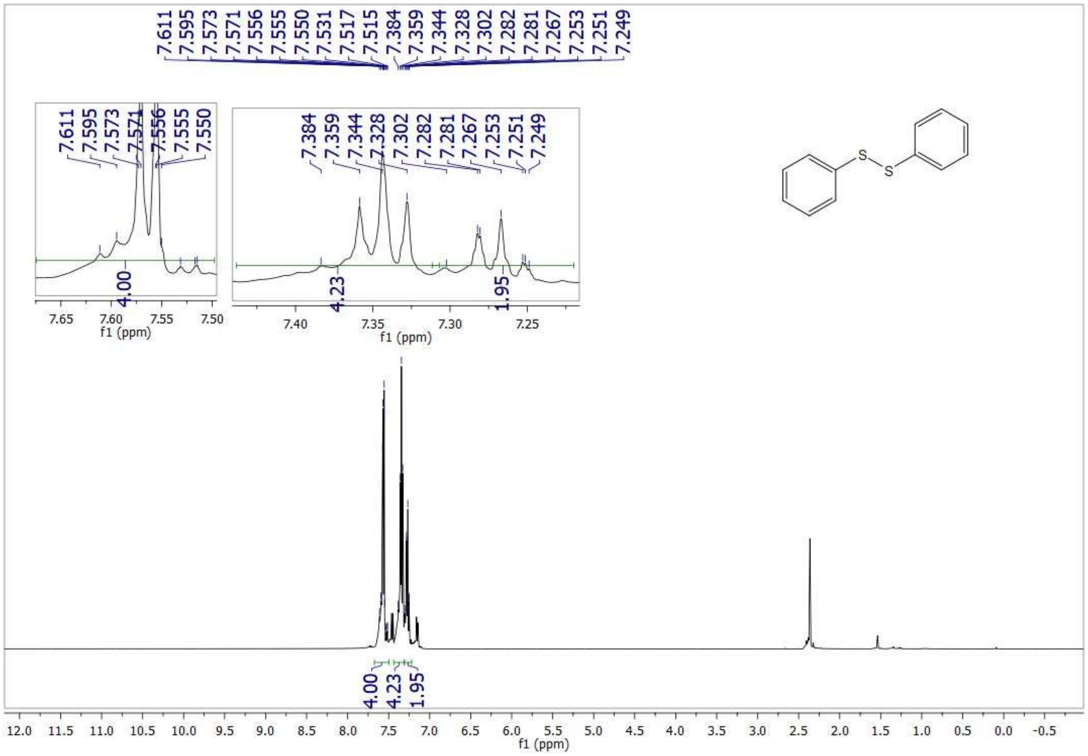
^{13}C NMR (126 MHz, CDCl$_3$) of compound **60**.



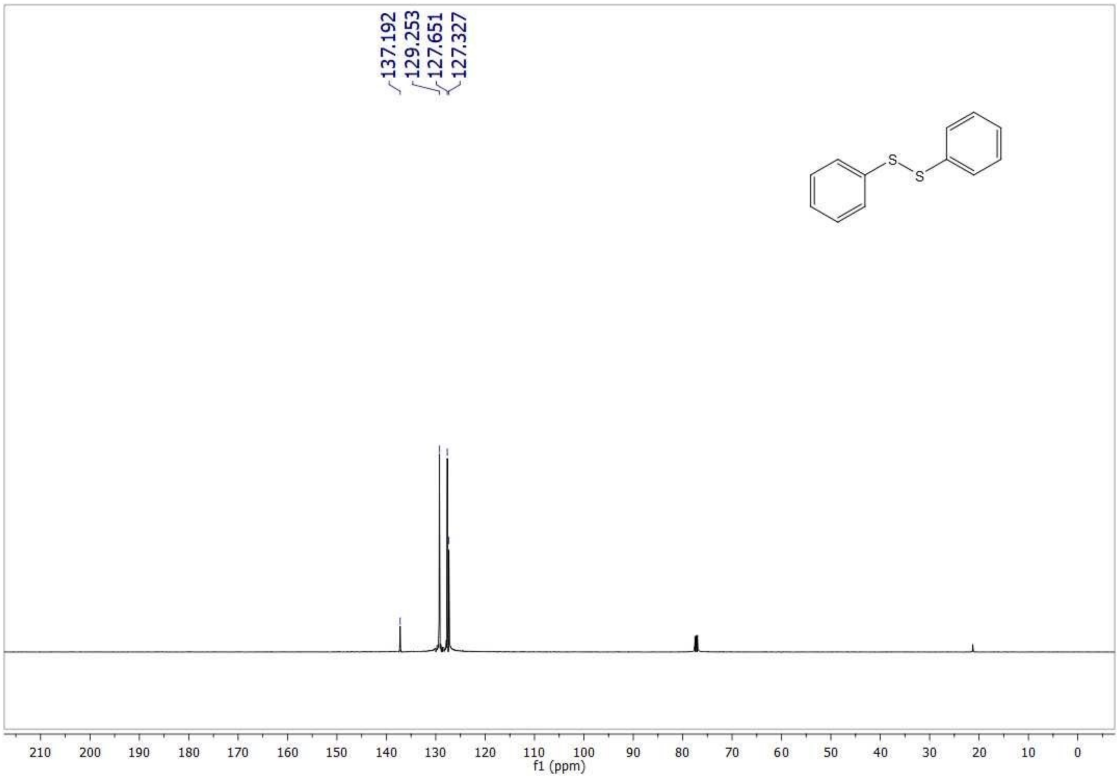
^{1}H NMR (500 MHz, CDCl$_3$) of compound **61**.



^{13}C NMR (126 MHz, CDCl$_3$) of compound **61**.



^{1}H NMR (500 MHz, CDCl$_3$) of **1,2-diphenyldisulfane**.



^{13}C NMR (126 MHz, CDCl$_3$) of **1,2-diphenyldisulfane**.

9. References

1. (a) H. Cao, S. Ma, Y. Feng, Y. Guo and P. Jiao, *Chem. Commun.*, 2022, **58**, 1780-1783; (b)Y. Hu, Y. Li, S. Zhang, C. Li, L. Li, Z. Zha, and Z. Wang, *Org. Lett.*, 2015, **17**, 4018–4021; (c) I. Khan, B. G. Reed-Berendt, R. L. Melen, and L. C. Morrill, *Angew. Chem. Int. Ed.*, 2018, **57**, 12356-12359; (d) R. Doi, K. Kajiwara, T. Negoro, K. Koh and S. Ogoshi, *Org. Lett.*, 2023, **25**, 5542-5547; (e) X. Kou and K. G. M. Kou, *ACS Catal.*, 2020, **10**, 3103−3109.
2. (a) X. Kou and K. G. M. Kou, ACS Catal., 2021, 11, 11510; (b) K. Maji, P. R. Thorve, P. Raia and B. Maji, Chem. Commun., 2022, 58, 9516-9519.
3. R. Ma, Z. Deng, K.-H. Wang, J. Wang, D. Huang, Y. Su, Y. Hu and X. Lv, ACS Omega., 2022, 7, 14357-14362.
4. (a) G. Bogonda, D. V. Patil, H. Y. Kim, K. Oh, *Org. Lett.*, 2019, **21**, 3774-3779; (b) Y. Fang, T. Rogge, L. Ackermann, S.-Y. Wang and S.-J. Ji, *Nat Commun.*, 2018, **9**, 2240; (c) Z. Xuna, L. Tong-Xin and Z. Guisheng, *Asian J. Org. Chem*., 2017, **6**, 677–681.
5. H. A. Benesi, J. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703-2707.
6. C. G. Hatchard, C. A. Parker, Proc. R. Soc. (London), 1956, 235, 518-536.
7. M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, Handbook of Photochemistry, Taylor Francis, 2006.
8. (a) N. Mukherjee and T. Chatterjee, *Green Chem.*, 2021, **23**, 10006-10013; (b) A. N. V. Satyanarayana, N. Mukherjee and T. Chatterjee, *Green Chem.*, 2023, **25**, 779-788; (c) K. Van Aken, L. Strekowski, L. Patiny, *Beilstein J. Org. Chem.*, 2006, **2**, 3; (d) A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez and F. Lamaty, *Green Chem.*, 2018, **20**, 964–968;(e) B. Saxena, R. I. Patel, S. Sharma and A. Sharma, *Green Chem.*, 2024, **26**, 2721-2729.
9. (a) X. Wang, Y. Kuang, S. Ye and J Wu, *Chem. Commun*., 2019, **55**, 14962-14964; (b) F.-S. He, Y. Yao, W. Xie and Jie Wu, *Chem.Commun*., 2020, **56**, 9469-9472; (c) F.-S. He, P. Bao, Z. Tang, F. Yu, W.-P. Deng, and Jie Wu, *Org. Lett.*, 2022, **24**, 2955-2960.
10. (a) V. K. K. Pampana, V. P. Charpe, A. Sagadevan, D. K. Das, C.-C. Lin, J. R. Hwu and K. C. Hwang, *Green Chem*., 2021, **23**, 3569–3574; (b) B. Dam, A. K. Sahoo and B. K. Patel, *Green Chem*., 2022, **24**, 7122–7130. (c) W.-H. Rao, C. Gao, L.-L. Jiang, F.-Y. Zhou, J.-F. Liu, and G.-D. Zou, *J. Org. Chem.*, 2024, https://doi.org/10.1021/acs.joc.4c01660; (d) C. Liu, Z. Liang, A. Jialingbieke, J. Gao, and D. Du, *Org. Lett.*, 2023, **25**, 2657−2662; (e) R. Chen, Y. Tang, X. He, K.-K. Wang, L. Ding, and L. Liu, *Org. Lett.*, 2023, **25**, 5454−545; (f) J. Xu, C. Shen, X. Qin, J. Wu, P. Zhang, and X. Liu*, J. Org. Chem.*, 2021, **86**, 3706−3720; (g) S. Handa, J. C. Fennewald, B. H. Lipshutz, *Angew. Chem. Int. Ed.*, 2014, **53**, 3432 –3435.
11. H. A. A. Aziz, K. A. A. Rashood, K. H. El-Tahir and G. M. Suddek, *Eur. J. Med. Chem*., 2014, **80**, 416–422.
12. M.-Y. Chang, C.-K. Chan and Y.-C. Chen, *Heterocycles*, 2014, **89**, 1237.
13. C.-K. Chan, C.-Y. Lai, W.-C. Lo, Y.-T. Cheng, M.-Y. Chang and C.-C. Wang, *Org. Biomol. Chem*., 2020, **18**, 305–315.
14. (a) Y.-S. Lin, Y.-C. Kuo, C.-H. Kuei, M.-Y. Chang, *Tetrahedron*, 2017, **73**, 1275–1282; (b) N. Taniguchi, *J. Org. Chem*., 2015, **80**, 7797−7802; (c) Y. Wang, Y. Zhao, C. Cai, L. Wang, H. Gong, *Org.*

Lett., 2021, **23**, 8296–8301; (d) Z. Jiang, K. You, H. Wu, M. Xu, T. Wang, and J. Luo, *Org. Lett.*, 2024, **26**, 636−641

15. M.-Y. Chang, Y.-C. Cheng, Y.-J. Lu, *Org. Lett.*, 2015, **17**, 1264–1267.
16. M.-Y. Chang, Y.-C. Chen, C.-K. Chan, *Synlett*, 2014, **25**, 1739–1744.
17. M.-Y. Chang, Y.-C. Cheng, Y.-J. Lu, *Org. Lett.*, 2014, **16**, 6252–6255.