Supporting information

Photocatalytic 1,2-Thiosulfonylation of Alkenes with Thiophenols and Sulfonyl Chlorides Promoted by Directly Knitted Copper Polymers

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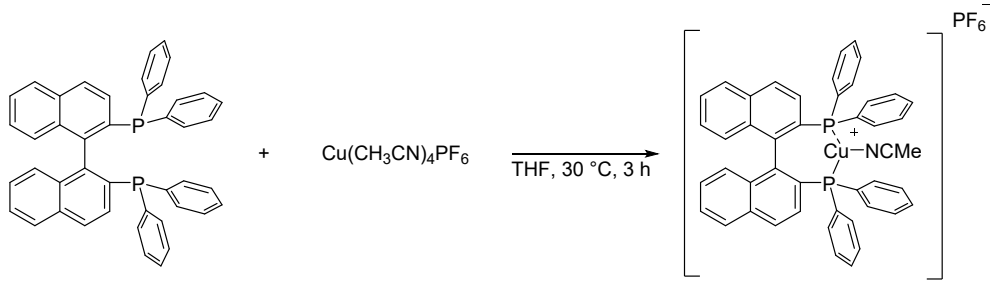
1. General experimental details

All reagents were commercially available unless otherwise noted. All reactions were carried out under N_2 atmosphere in dried glassware. Air and moisture sensitive liquids and solutions were transferred via a syringe. All solvents were dried and distilled by standard procedures. Solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished on silica gel Si 60® (300-400 mesh). Nuclear magnetic resonance spectra were acquired on a Bruker DRX 600 (600 MHz, and 150 MHz for ^{1}H, and ^{13}C respectively). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CDCl_3$). All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) were obtained with ^{1}H decoupling. Data for ^{1}H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s = singlet; brs = broad singlet; vbs = vary broad singlet; d = doublet; t= triplet; q = quartet; quint = quintet; sext = sextet; m = multiplet), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ in ppm), multiplicity, coupling constant (Hz). HR-MS spectra were obtained on a Finnigan MAT 8200 instrument. PXRD studies were performed on Rigaku SmartLab SE. SEM experiments were carried out on a Hitachi Regulus 8100 operated at 1 kV. TEM experiments were carried out on a FEI Talos F200x. XPS experiments were carried out on Thermo Scientific K-Alpha. N_2 sorption were performed on Micromeritics ASAP 2460. Thermogravimetric analysis experiments were collected on TA Q500. FT-IR spectra were recorded on Frontier of Thermo Scientific Nicolet iS5. The UV/Vis spectra were measured by UV-3600 Spectrophotometer (SHIMADZU). The fluorescence spectra were recorded by a fluorescence spectrometer of Perkinelmer FL 6500 with a 10 mm quartz cuvette.

2. Catalyst preparation

2.1 Synthesis of BINAP-Cu



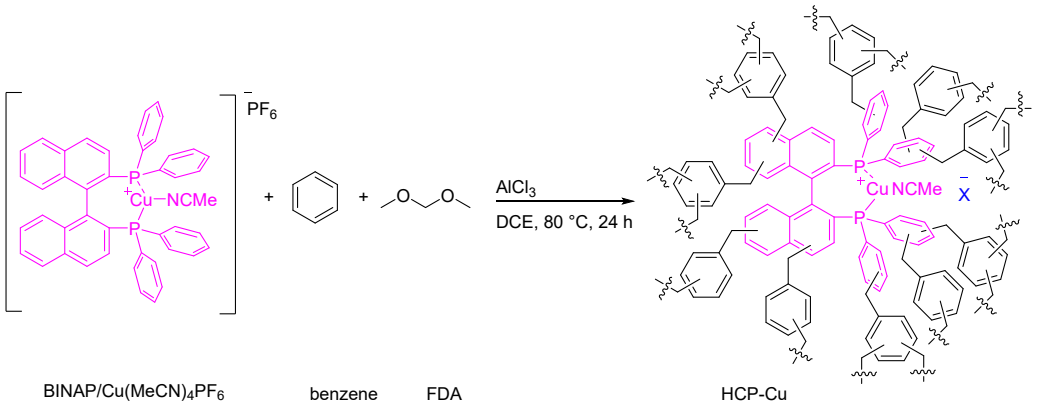
Scheme 1 The synthetic route of BINAP-Cu

A solution of $[Cu(CH_3CN)_4][PF_6]$ (0.194 g, 0.52 mmol) in 5 mL of THF was added to a THF solution (35 mL) of BINAP (0.330 g, 0.53 mmol) under N_2 atmosphere. The solution was stirred for 3 h. Then the solvent was reduced in vacuo to 15 mL, and 20 mL of hexanes was added leading a precipitation of a white solid. The resulted precipitates were collected by filtration and dried under reduced pressure affording BINAP-Cu as an ivory-white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 (s, 4H), 7.57-7.54 (m, 10H), 7.27 (s, 2H), 7.19

(s, 2H), 7.05 (s, 6H), 6.72 (s, 4H), 6.56 (s, 4H), 2.35 (s, 3H). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 36.15, 2.82, -142.86 (sept, J = 712.7 Hz, PF_6^-). Data is consistent with that reported in the literature.[1]

2.2 Synthesis of HCPs-Cu 1a-d[2]



Scheme 2 The synthetic route of HCPs-Cu **1a-d**

Synthesis of HCP-Cu 1a. To a dry Schlenk tube, a mixture of BINAP-Cu complex (0.3 mmol, 261.7 mg) and benzene (0.9 mmol, 70.3 mg) was added, then followed by dry 1,2-dichloroethane (2 mL) under nitrogen atmosphere. After stirring for several minutes, anhydrous $AlCl_3$ (0.9 mmol, 120 mg) and formaldehyde dimethyl acetal (FDA) (0.9 mmol, 68.5 mg) were added. The resulted mixture was heated to 80 °C and stirred for 24 h. After being cooled to room temperature, the precipitate was washed by methanol, distilled water, acetone, and dichloromethane successively. Further purification of the polymer was carried out by Soxhlet extraction from methanol for 24 h. The product was dried in vacuum for 24 h at 60 °C to give a gray-green powder and denoted as HCP-Cu **1a** (yield: 45%).

Synthesis of HCP-Cu 1b. Similar to the synthesis of HCP-Cu **1a**, with the exception of the use of 1.8 mmol FDA and $AlCl_3$ in place of 0.9 mmol FDA and $AlCl_3$. The product was a brown powder and denoted as HCP-Cu **1b** (yield: 32%).

Synthesis of HCP-Cu 1c. Similar to the synthesis of HCP-Cu **1a**, with the exception of the use of 3.6 mmol FDA and $AlCl_3$ in place of 0.9 mmol FDA and $AlCl_3$. The product was a dark brown powder and denoted as HCP-Cu **1c** (yield: 30%).

Synthesis of HCP-Cu 1d. Similar to the synthesis of HCP-Cu **1a**, with the exception of the use of 4.5 mmol FDA and $AlCl_3$ in place of 0.9 mmol FDA and $AlCl_3$. The product was a sepia powder and denoted as HCP-Cu **1d** (yield: 21%).

3. Characterization of HCPs-Cu

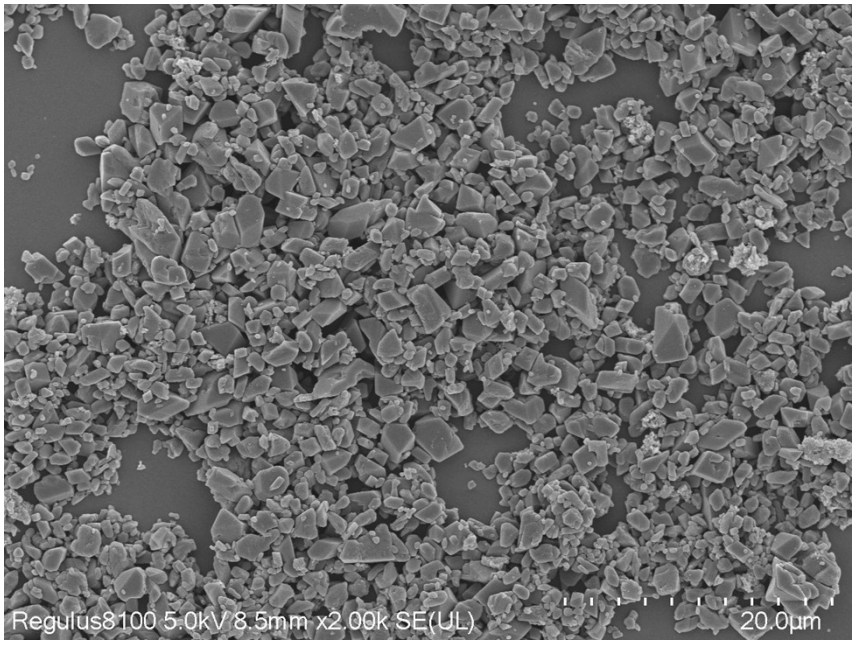


Figure S1 SEM image of HCP-Cu **1a**.

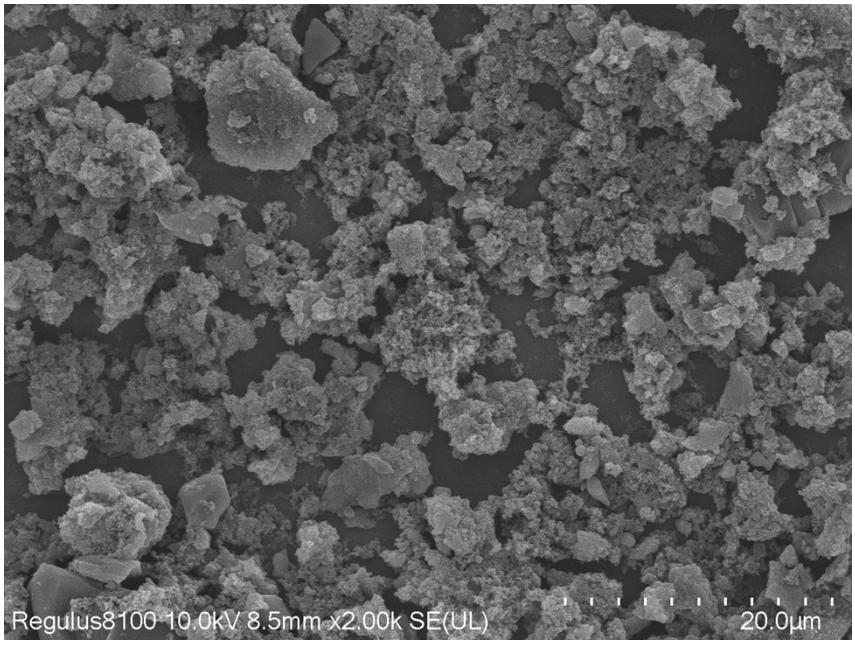


Figure S2 SEM image of HCP-Cu **1b**.

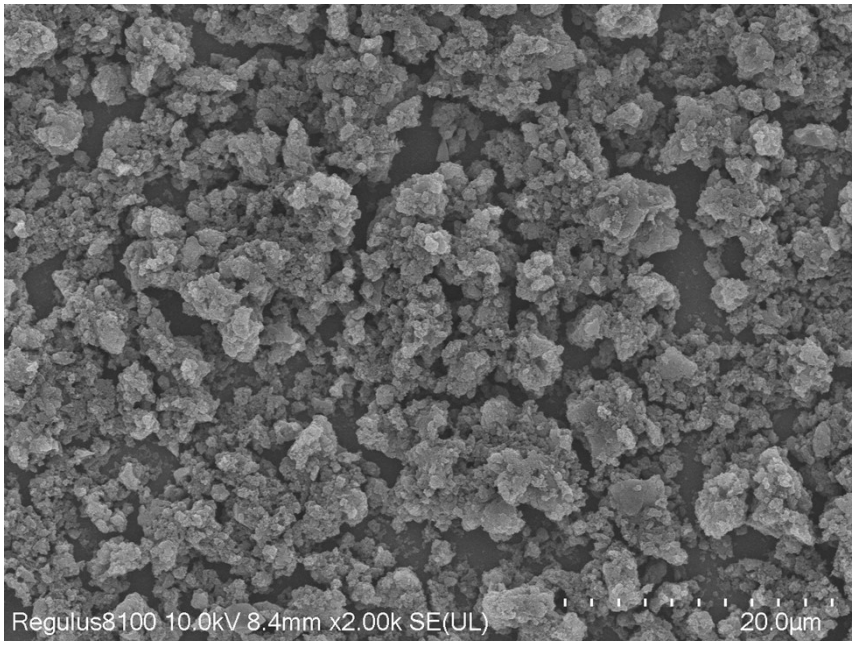


Figure S3 SEM image of HCP-Cu **1c**.

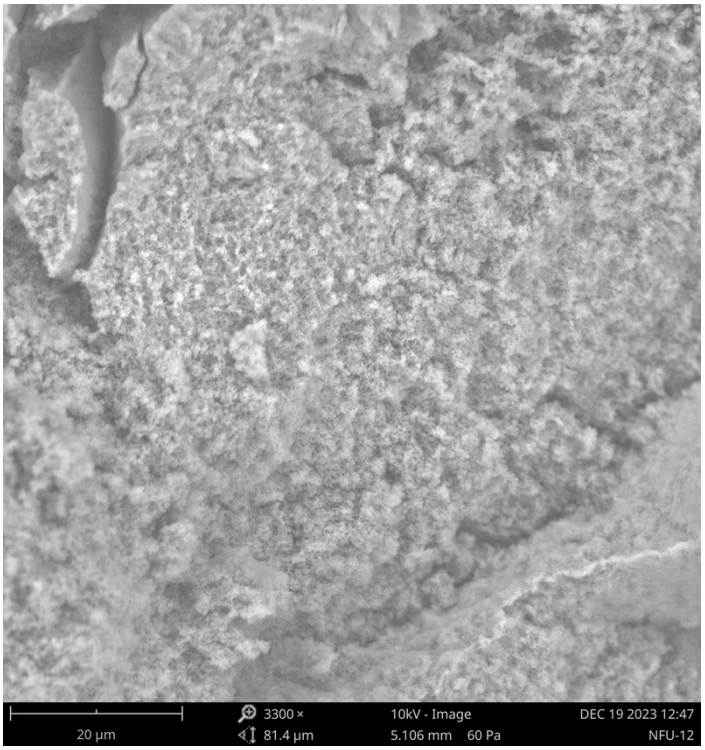


Figure S4 SEM image of HCP-Cu **1d**.

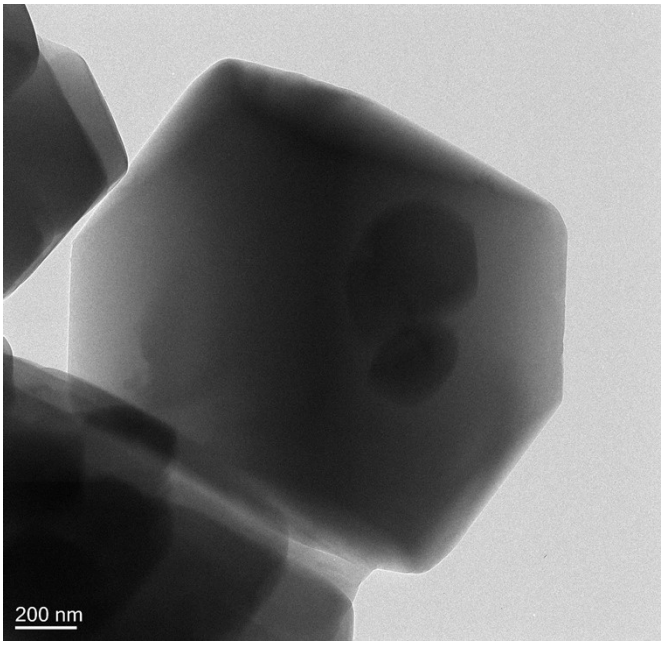


Figure S5 TEM image of HCP-Cu **1a.**

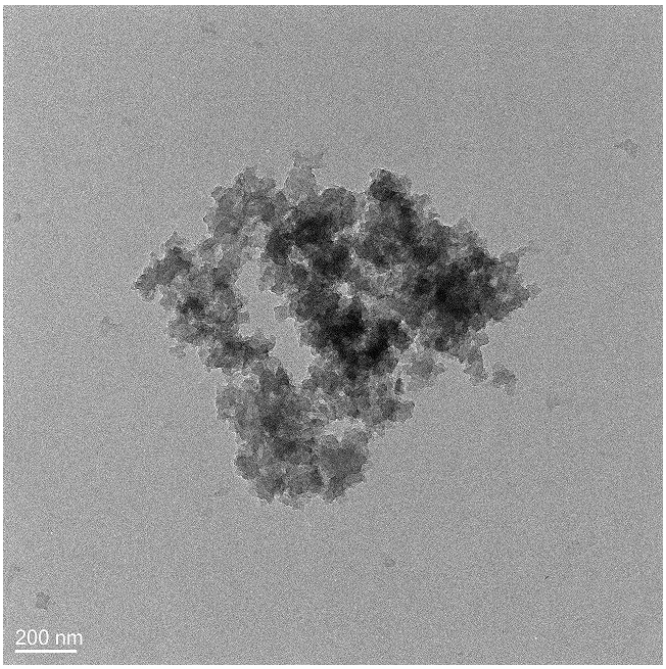


Figure S6 TEM image of HCP-Cu **1b.**

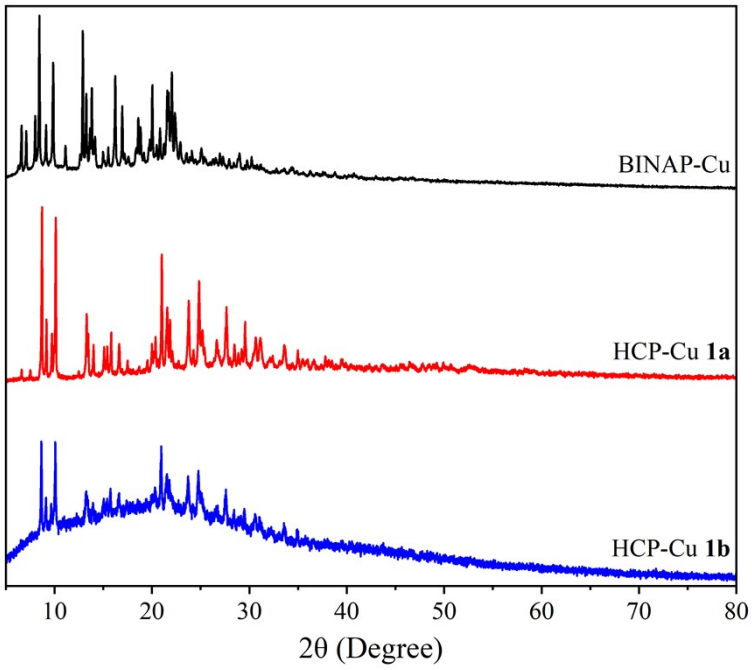


Figure S7 XRD spectra of BINAP-Cu, HCP-Cu **1a** and **1b**.

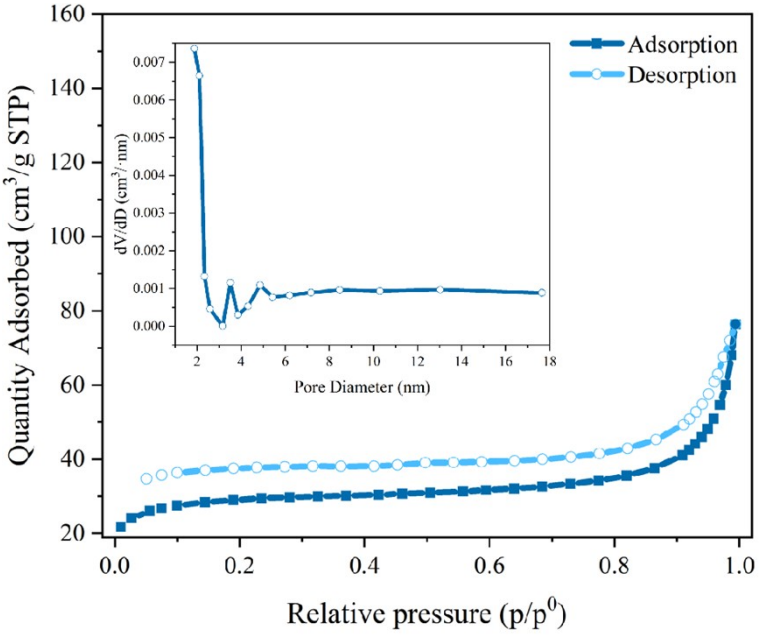


Figure S8 Nitrogen adsorption-desorption isotherms and pore width of HCP-Cu **1b**.

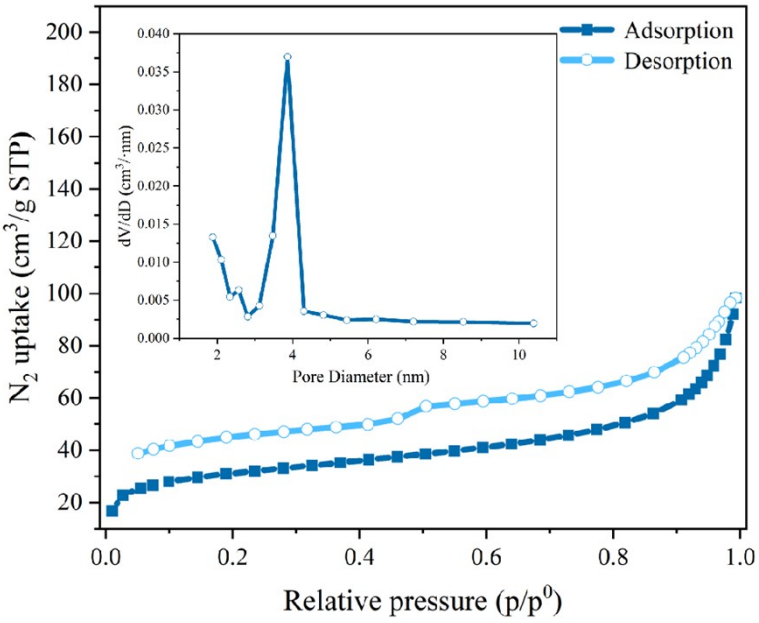


Figure S9 Nitrogen adsorption-desorption isotherms and pore width of HCP-Cu **1c**.

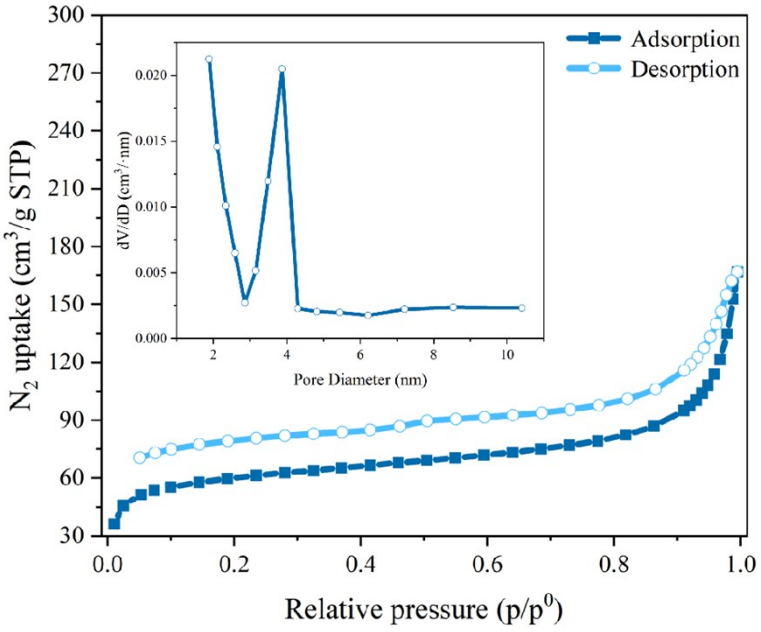


Figure S10 Nitrogen adsorption-desorption isotherms and pore width of HCP-Cu **1d**.

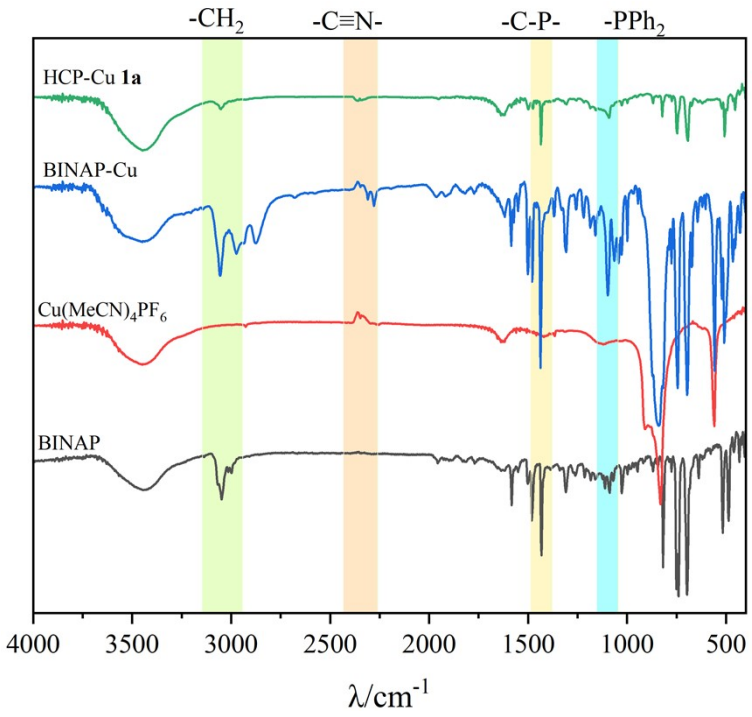


Figure S11 FT-IR spectra of BINAP, $Cu(MeCN)_4PF_6$, BINAP-Cu and HCP-Cu **1a**.

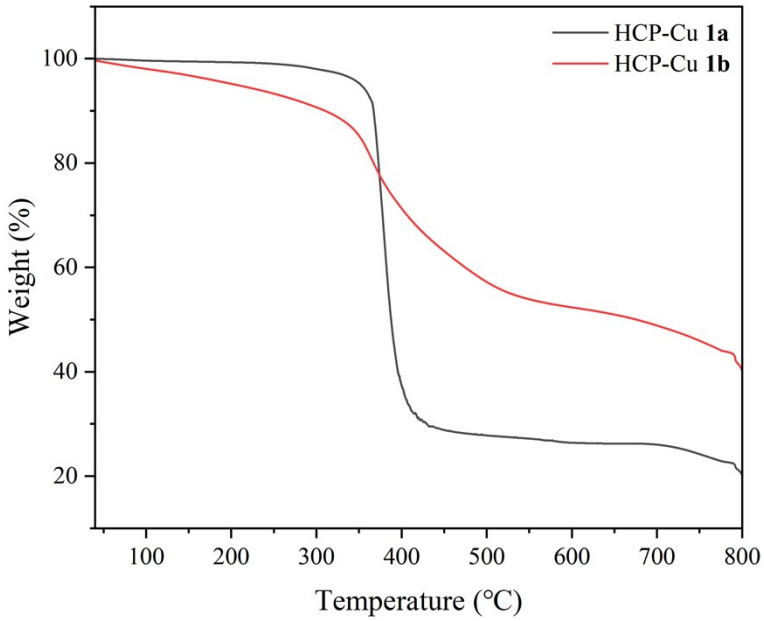


Figure S12 Thermogravimetric analysis of HCP-Cu **1a** and **1b**.

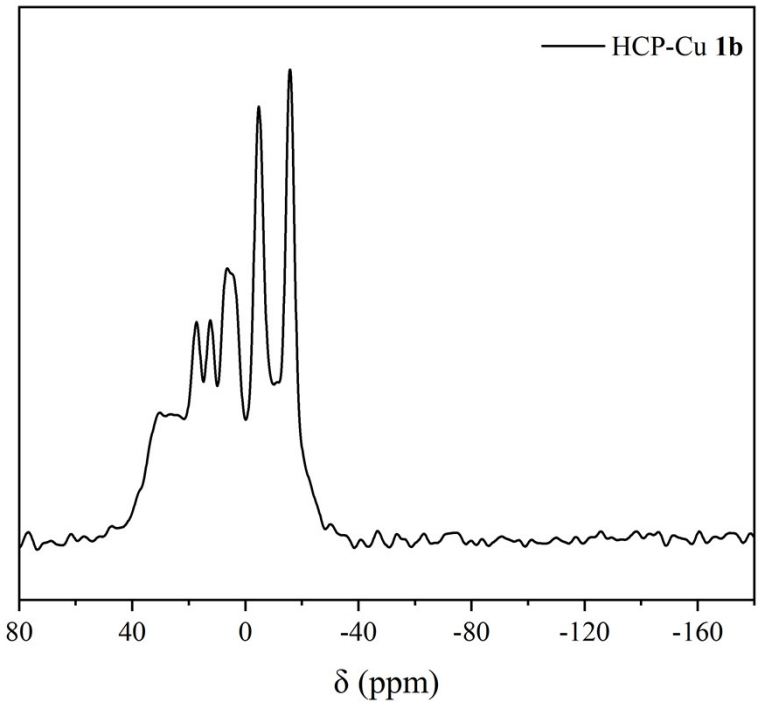


Figure S13 ^{31}P NMR spectrum of HCP-Cu **1b**.

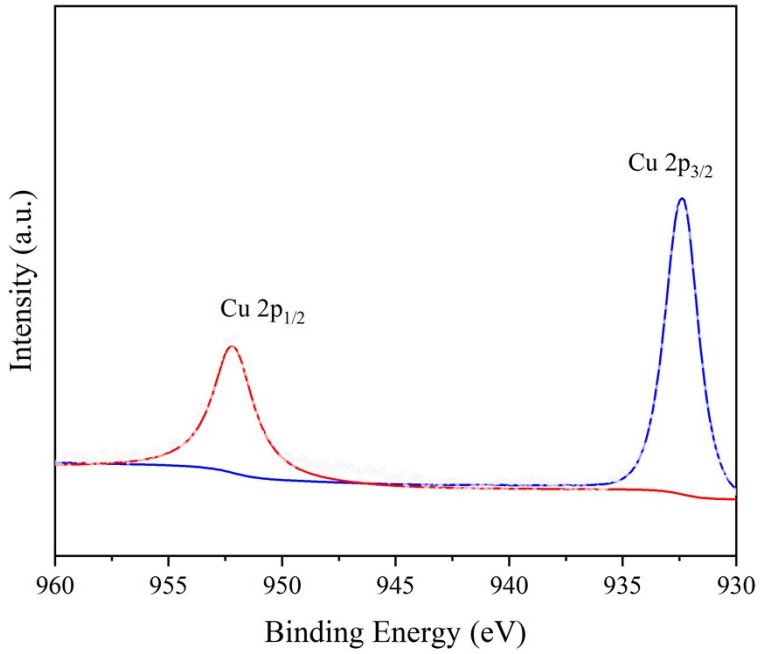


Figure S14 Cu 2p XPS spectrum of HCP-Cu **1b**.

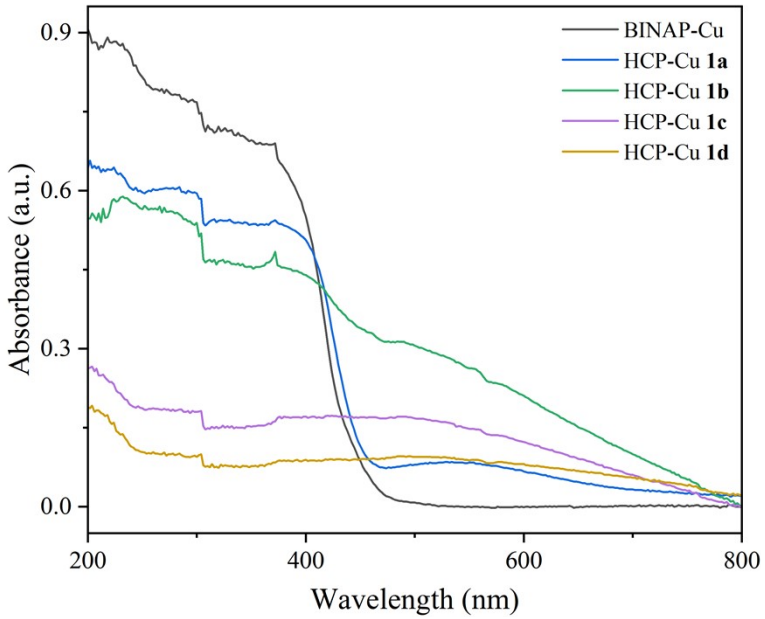


Figure S15 UV-Vis absorption spectra of BINAP-Cu and HCPs-Cu.

4. Characterization of recycled HCP-Cu 1a

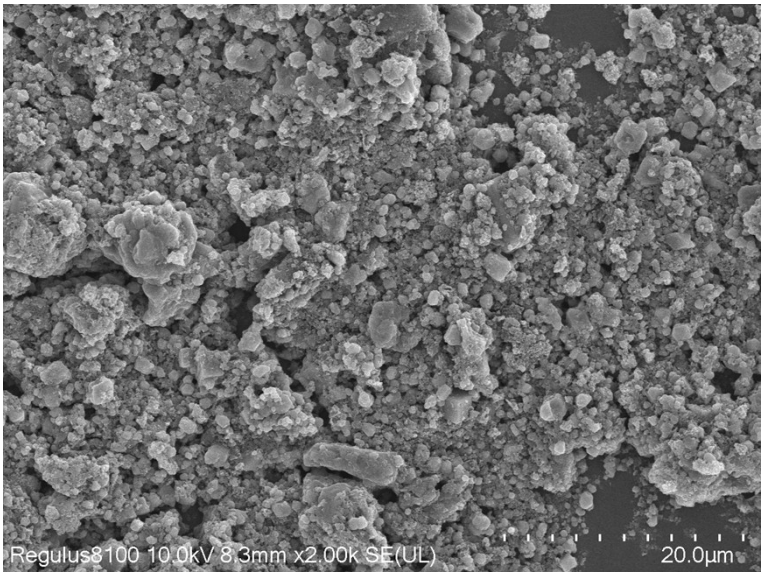


Figure S16 SEM image of recycled HCP-Cu **1a**.

Table S1 Measurement of metal content in fresh prepared and recycled HCP-Cu **1a**

Sample	Element	Element content (W)/%
HCP-Cu **1a**	Cu	14.91
Recycled HCP-Cu **1a**	Cu	9.07
	Fe	4.88

ICP-OES analysis of filtrate after continuous operation. After the reaction was quenched, the catalyst was separated by centrifugation.

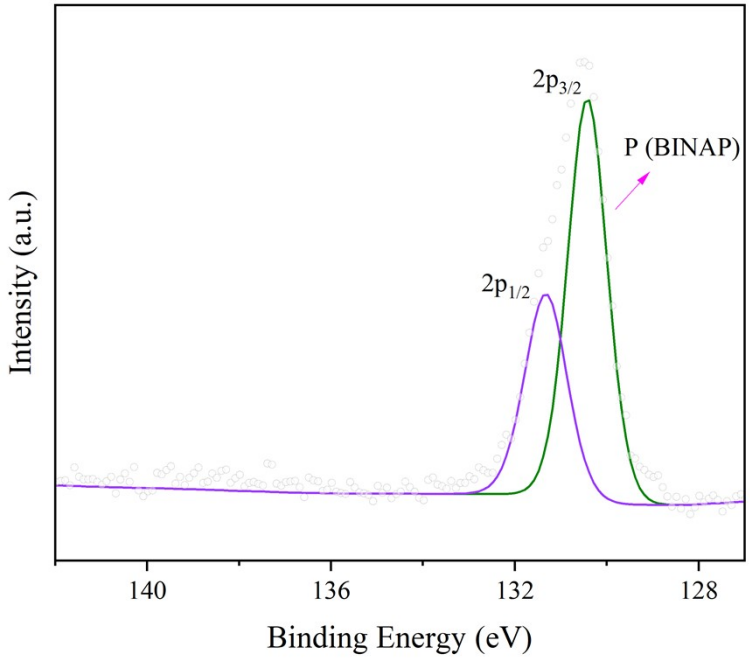


Figure S17 P 2p XPS spectrum of recycled HCP-Cu **1a**.

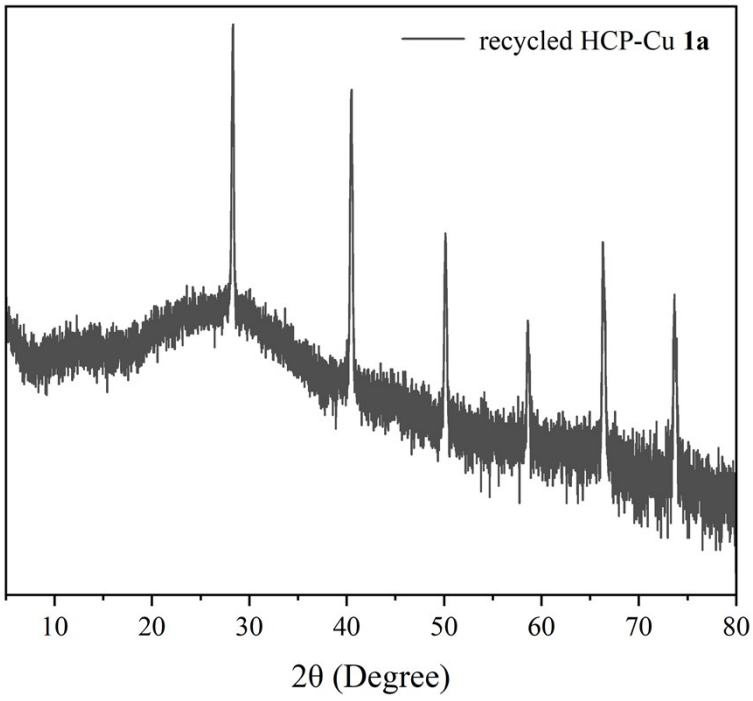


Figure S18 PXRD spectrum of recycled HCP-Cu **1a**.

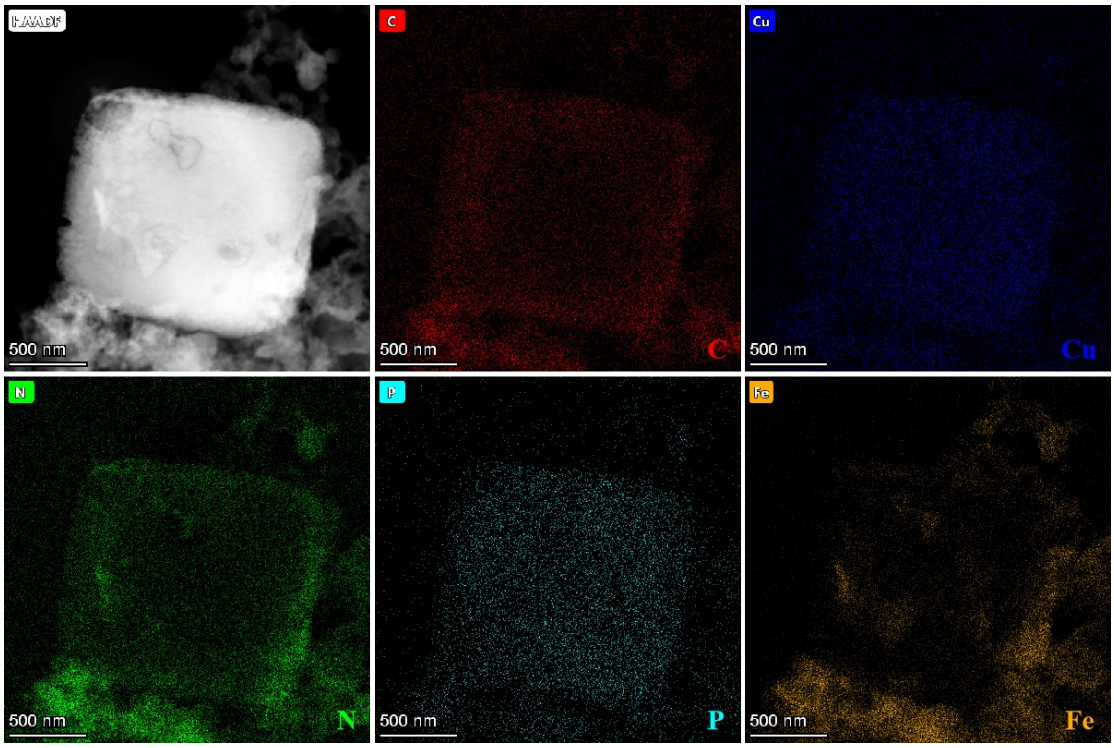


Figure S19 HAADF-STEM image of recycled HCP-Cu **1a** with the corresponding element distribution maps.

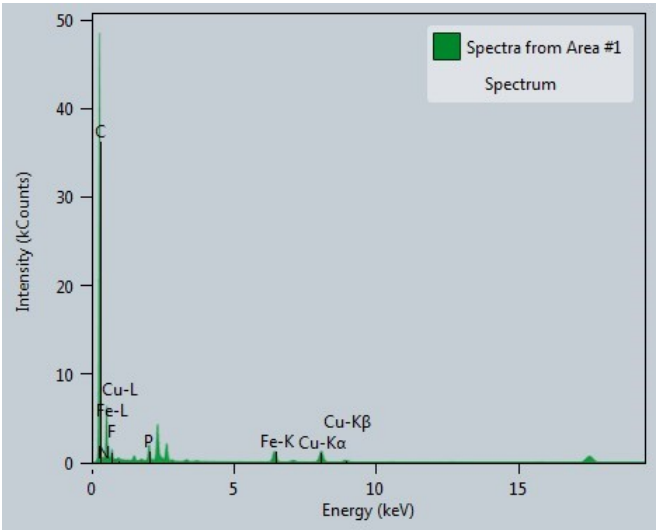


Figure S20 HAADF-STEM image of recycled HCP-Cu **1a** with the corresponding element distribution maps.

Table S2. Element analysis of HCP-Cu **1a** according to EDX

Z	Element	Family	Atomic Fraction (%)	Mass Fraction (%)	Fit error (%)
6	C	K	82.27	52.18	0.92
7	N	K	0.10	0.07	207.68
15	P	K	5.90	9.64	1.81
29	Cu	K	11.20	37.57	1.19

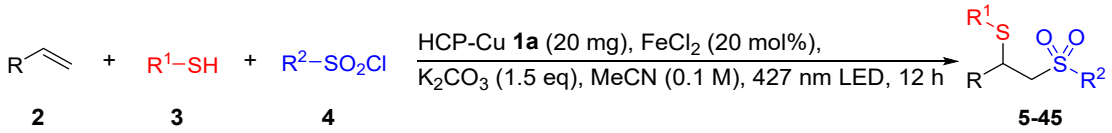
Note the content of elements determined by EDX is qualitatively.

Table S3. Element analysis of recycled HCP-Cu **1a** according to EDX

Z	Element	Family	Atomic Fraction (%)	Mass Fraction (%)	Fit error (%)
6	C	K	96.51	86.77	2.03
7	N	K	0.00	0.00	0.00
15	P	K	1.13	2.61	1.07
26	Fe	K	1.09	4.57	0.27
29	Cu	K	1.27	6.05	0.14

Note the content of elements determined by EDX is qualitatively.

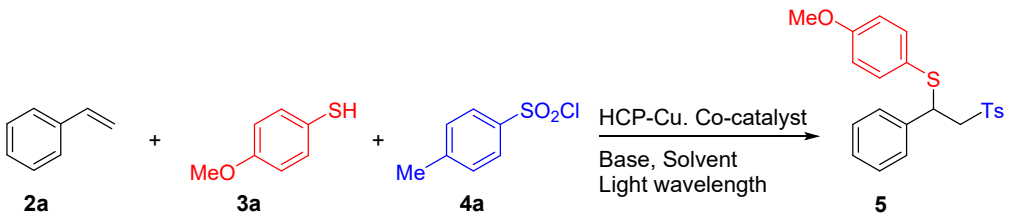
5. General procedure for the 1,2-thiosulfonylation



Scheme 3 1,2-Thiosulfonylation reaction of alkenes with thiophenols and sulfonyl chlorides.

To a 25 mL Schlenk tube containing a stir bar, HCP-Cu **1a** (20 mg), $FeCl_2$ (20 mol%, 0.04 mmol), K_2CO_3 (1.5 equiv., 0.3 mmol), and sulfonyl chloride **4** (2.0 equiv., 0.4 mmol) were added subsequently. Then the tube was evacuated and charged with argon three times. Olefin **2** (1.0 equiv., 0.2 mmol), thiophenol **3** (2.0 equiv., 0.4 mmol) and MeCN (2 mL) were added successively through a microinjector. Then the reaction mixture was stirred at room temperature for 12 h under irradiation of 20 W blue LEDs. After evaporation of organic solvents, the residue was purified by flash column chromatography on silica gel to yield the desired 1,2-thiosulfonylation product.[3]

6. Screening reaction conditions



Scheme 4 1,2-Thiosulfonylation reaction of styrene **2a** with thiophenol **3a** and sulfonyl

chloride **4a**.

Table S4 Screening the bases

Entry	base	Yield/%
1	Cs_2CO_3	19
2	**K_2CO_3**	**33**
3	Na_2CO_3	trace
4	LiOH	0
5	*t*BuOLi	trace
6	*t*BuOK	6
7	K_3PO_4	7
8	K_2HPO_4	13
9	Et_3N	trace
10	Quinuclidine	trace

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), Base (1.5 equiv.), H_2O (20 equiv.), DMF (2 mL), rt, 20 W, 427 nm, 12 h.

Table S5 Screening the equiv. of K_2CO_3

Entry	K_2CO_3/equiv.	Yield/%
1	**1.5**	**47**
2	2	42
3	2.5	37
4	1	29

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), K_2CO_3 (n equiv.), H_2O (20 equiv.), MeCN (2 mL), rt, 20 W, 427 nm, 12 h.

Table S6 Screening the solvents

Entry	solvent	Yield/%
1	DMF	33
2	DMSO	0
3	DMA	41
4	NMP	0
5	**MeCN**	**47**
6	DCM	37
7	DCE	31
8	THF	20
9	1,4-Dioxane	23
10	Toluene	16

11	EtOH	23

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), Solvent (2 mL), rt, 20 W, 427 nm, 12 h. DMF = *N*,*N*-Dimethylformamide. DMSO = Dimethyl sulfoxide. DMA = *N*,*N*-Dimethylacetamide. NMP = *N*-Methyl-2-pyrrolidone. DCM = Dichloromethane. DCE = 1,2-Dichloroethane. THF = Tetrahydrofuran.

Table S7 Screening the volume of MeCN

Entry	MeCN/mL	Yield/%
1	**2**	**47**
2	1.5	42
3	2.5	45
4	1	33

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), MeCN (x mL), rt, 20 W, 427 nm, 12 h.

Table S8 Screening the ratio of substrates

Entry	**2a**:**3a**:**4a** (x:y:z) 1eq = 0.2 mmol	Yield/%
1	**1:2:2**	**47**
2	1:1:1	29
3	2:1:1	41
4	2:2:1	16
5	2:1:2	39
6	1:3:3	32

Reaction conditions: **2a** (x equiv.), **3a** (y equiv.), **4a** (z equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), MeCN (2 mL), rt, 20 W, 427 nm, 12 h.

Table S9 Screening the Fe and other co-catalysts

Entry	co-catalyst	Yield/%
1	**$FeCl_2$**	**47**
2	$FeBr_2$	37
3	$FeSO_4 \cdot xH_2O$	36
4	$FeCl_3$	41
5	$Fe(acac)_3$	23
6	Dppf	11
7	CuCl	35
8	$CuCl_2 \cdot 2H_2O$	42

9	$Cu(CH_3CN)_4PF_6$	33
10	$NiCl_2$	45
11	$NiBr_2$	26
12	$NiBr_2$·DME	33
13	(Dppp)$NiCl_2$	36
14	$CoCl_2·6H_2O$	45

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), co-catalyst (20 mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), MeCN (2 mL), rt, 20 W, 427 nm, 12 h.

Table S10 Screening the catalyst-loading of $FeCl_2$

Entry	$FeCl_2$/mol%	Yield/%
1	**20**	**47**
2	15	45
3	25	44

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (x mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), MeCN (2 mL), rt, 20 W, 427 nm, 12 h.

Table S11 Screening the wavelength

Entry	wavelength/nm	Yield/%
1	390 (20 W)	38
2	**427 (20 W)**	**47/53[b]/82[c]**
3	440 (20 W)	33
4	525 (20 W)	trace
5	427 (10 W)	42
6	427 (30 W)	39

[a] Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (10 mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), H_2O (20 equiv.), MeCN (2 mL), rt, 12 h. [b] HCP-Cu **1a** (20 mg). [c] HCP-Cu **1a** (20 mg). Without H_2O.

Table S12 Screening the HCPs-Cu

Entry	HCPs	Yield/**5** [%]
1	**HCP-Cu 1a (20 mg)**	**82**
2	HCP-Cu **1b**	74
3	HCP-Cu **1c**	50
4	HCP-Cu **1d**	43
5	HCP-Cu **1a** (5 mg)	60
6	HCP-Cu **1a** (10 mg)	71

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCPs (20

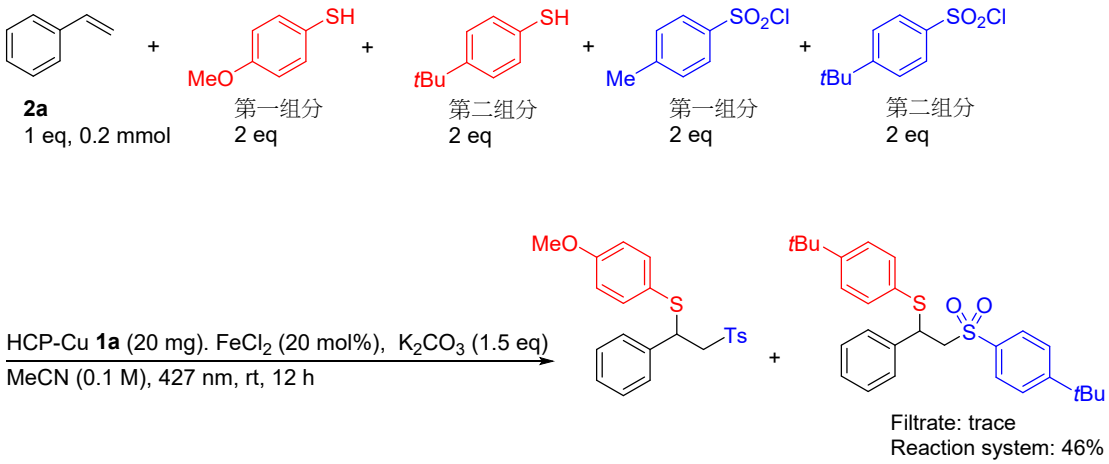
mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), MeCN (2 mL), rt, 20 W, 427 nm, 12 h.

7. Mechanism study

Table S13 Control experiment

Entry	Deviations from the reaction conditions	Yield/**5** [%]
1	Standard conditions	82
2	Without HCP-Cu **1a**	trace
3	Without $FeCl_2$	32
4	Without $FeCl_2$ and in dark	trace
5	In dark	trace
6	Without K_2CO_3	trace
7	Adding 2 eq TEMPO in dark	trace
8	Adding 2 eq TEMPO	trace
9	Under Air	26
10	5 mol% [Cu] [a]	57
11	1 equiv. [Cu] [a] and without $FeCl_2$	31
12	5 mol% [Cu] [b]	38
13	1 equiv. [Cu] [b] and without $FeCl_2$	32
14	Hantzsch Ester instead of $FeCl_2$	5

Reaction conditions: **2a** (1 equiv., 0.2 mmol), **3a** (2 equiv.), **4a** (2 equiv.), HCP-Cu **1a** (20 mg), $FeCl_2$ (20 mol%), K_2CO_3 (1.5 equiv.), MeCN (1.5 mL), 427 nm, rt, 12 h. [a] [Cu] = BINAP-Cu. [b] [Cu] = BINAP/$CuBr_2$.



Scheme 5 1,2-thiosulfonylation reaction of styrene **2a** with thiophenol **3a** and sulfonyl chloride **4a**.

UV-Vis spectroscopy study: The sample was prepared by mixing **2a** (2 mM), **3a** (4 mM), **4a** (4 mM), HCP-Cu **1a** (2 mg/100 mL) with MeCN in a light path quartz UV cuvette. The absorption was collected and the result was listed in **Figure S21**.

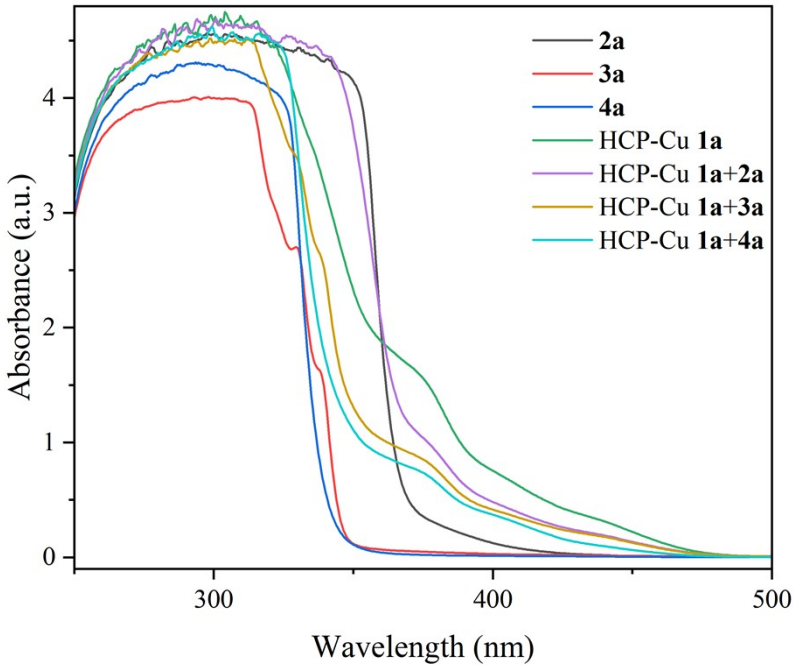


Figure S21 UV-Vis absorption spectra of mixture.

Fluorescence spectroscopy study: The excitation wavelength was fixed at 350 nm. The samples were prepared by mixing HCP-Cu **1a** (2 mg/100 mL) and different concentration of **2a**, **3a** and **4a** in MeCN in a light path quartz fluorescence cuvette. For each quenching experiment, 0.25 ml of quencher solution was titrated to a mixed solution of HCP-Cu **1a**. Then the emission intensity was collected and the results were presented in **Figure S22-S24**.

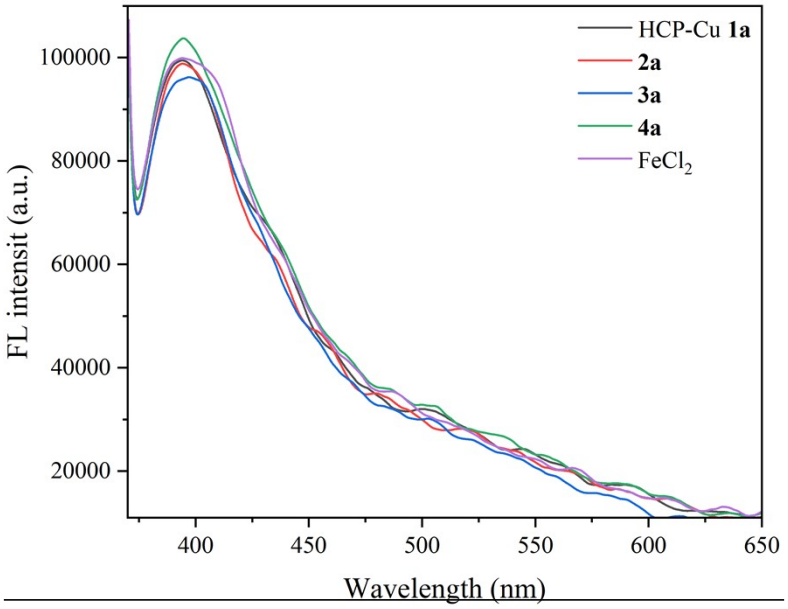


Figure S22 The fluorescent spectra of **1a** (2 mg/100 mL) in MeCN in the presence of **2a** (2 mM), **3a** (4 mM), **4a** (4 mM) or $FeCl_2$ (0.4 mM).

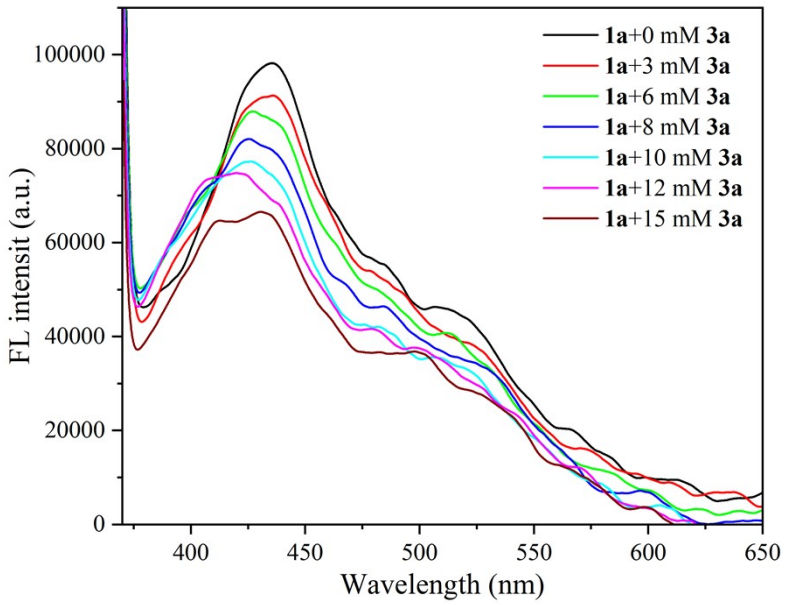


Figure S23 The fluorescent spectra of **1a** (2 mg/100 mL) in MeCN upon addition of different concentrations of **3a**.

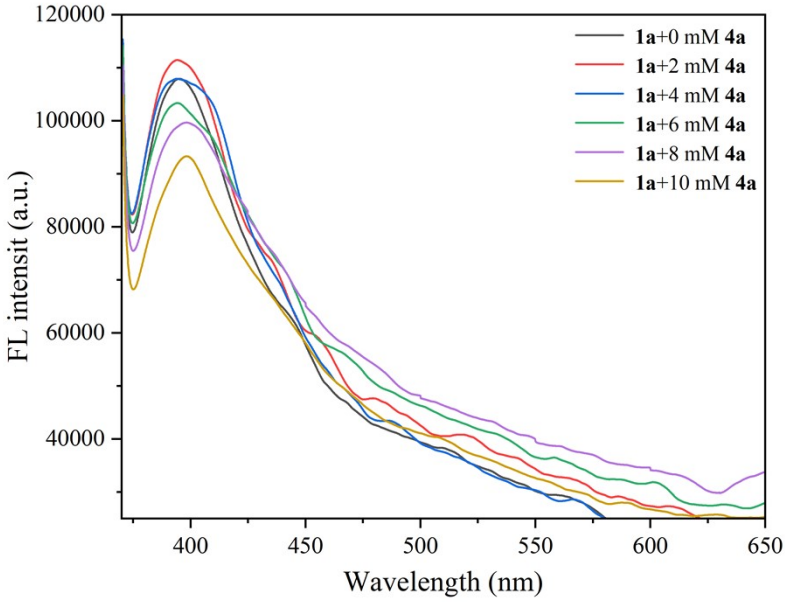
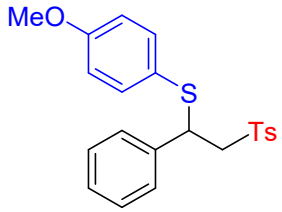


Figure S24 The fluorescent spectra of **1a** (2 mg/100 mL) in MeCN upon addition of different concentrations of **4a**.

EPR experiments: An oven-dried Schlenk tube equipped with a stir bar was charged with **2a** (0.2 mmol), **3a** (0.4 mmol), **4a** (0.4 mmol), K_2CO_3 (0.3 mmol), $FeCl_2$ (20 mol%), and HCP-Cu **1a** (20 mg) in anhydrous MeCN (2 mL) under N_2 atmosphere. The mixture was stirred in the dark for 5-10 min. Then, 1.5 equiv. DMPO was added and stirred for 5 min in dark. The solution sample was taken out into a small tube, then

analyzed by EPR, and obtained the black line. Subsequently, the reaction solution was irradiated with 20 W blue LED (427 nm) for 5 min, then analyzed by EPR again, as is shown by the red line. EPR spectrum was recorded at 295 K on EPR spectrometer operated at 9.82 GHz, scan width 100.0 G, center field 3500.00 G, scan time 30 s, power 6.325 mW.

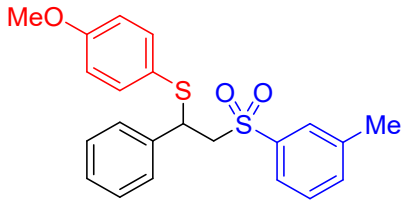
8. Characterization data of products



(4-methoxyphenyl)(1-phenyl-2-tosylethyl)sulfane (5): White solid, m = 59.8 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.2 Hz, 2H), 7.21-7.18 (m, 2H), 7.14-7.08 (m, 5H), 7.00 (d, J = 6.9 Hz, 2H), 6.78 (d, J = 8.7 Hz, 2H), 4.46 (dd, J = 10.4, 3.8 Hz, 1H), 3.79 (m, 4H), 3.63 (dd, J = 14.7, 3.8 Hz, 1H), 2.35 (s, 3H).

Data is consistent with that reported in the literature.[3]

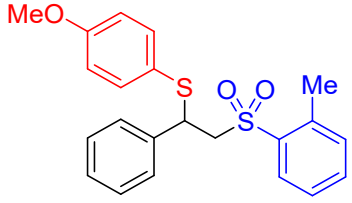


(4-methoxyphenyl)(1-phenyl-2-(*m*-tolylsulfonyl)ethyl)sulfane (6): White solid, m = 52.0 mg, 65% yield. **m.p.**: 139.5-141.5 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, J = 7.6 Hz, 1H), 7.26-7.19 (m, 5H), 7.12-7.08 (m, 3H), 7.01 (d, J = 5.9 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 4.47 (dd, J = 10.6, 3.7 Hz, 1H), 3.83-3.79 (m, 4H), 3.64 (dd, J = 14.7, 3.7 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 139.2, 139.0, 137.6, 136.5, 134.1, 128.8, 128.4, 128.3, 127.9, 127.8, 124.9, 122.9, 114.7, 60.5, 55.4, 48.3, 21.1.

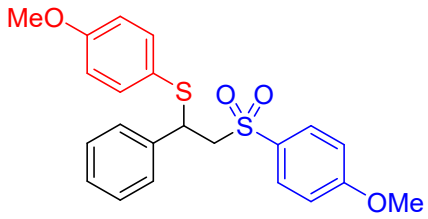
HR-MS (ESI, m/z): calcd for $C_{22}H_{22}O_3S_2$ $[M+Na]^+$: 421.0908. found: 421.0909.



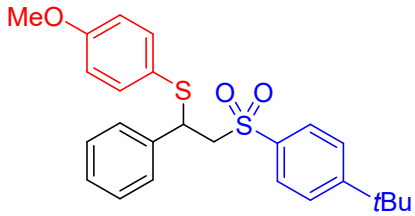
(4-methoxyphenyl)(1-phenyl-2-(*o*-tolylsulfonyl)ethyl)sulfane (7): White solid, m = 23.8 mg, 30% yield. **m.p.**: 109.8-123.9 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.3 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 8.7 Hz, 2H), 7.14-7.10 (m, 5H), 7.04-7.03 (m, 2H), 6.79 (d, J = 8.7 Hz, 2H), 4.45 (dd, J = 10.4, 3.6 Hz, 1H), 3.85 (dd, J = 14.6, 10.4 Hz, 1H), 3.80 (s, 3H), 3.65 (dd, J = 14.6, 3.6 Hz, 1H), 2.46 (s, 3H).

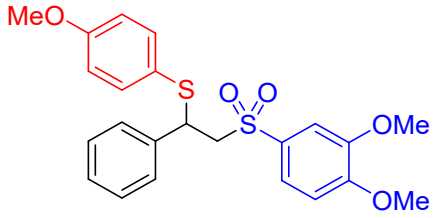
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 137.7, 137.5, 137.3, 136.3, 133.4, 132.3, 130.3, 128.4, 127.9, 127.7, 126.3, 123.1, 114.8, 59.3, 55.4, 48.3, 20.1.
HR-MS (ESI, m/z): calcd for $C_{22}H_{22}O_3S_2$ $[M+Na]^+$: 421.0908. found: 421.0912.



(4-methoxyphenyl)(2-((4-methoxyphenyl)sulfonyl)-1-phenylethyl)sulfane (8): White solid, m = 60.8 mg, 73% yield. **m.p.**: 140.1-143.7 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 7.13-7.10 (m, 3H), 7.01-6.99 (m, 2H), 6.78 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 4.45 (dd, J = 10.4, 3.7 Hz, 1H), 3.82-3.76 (m, 7H), 3.63 (dd, J = 14.7, 3.8 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.4, 160.3, 137.8, 136.5, 130.8, 130.1, 128.4, 127.9, 127.7, 122.9, 114.7, 114.1, 60.6, 55.6, 55.4, 48.4.
HR-MS (ESI, m/z): calcd for $C_{22}H_{22}O_4S_2$ $[M+Na]^+$: 437.0857. found: 437.0851.

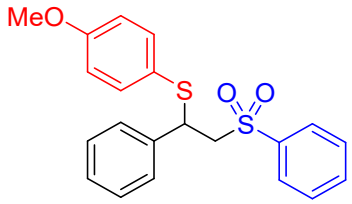


(2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (9): White solid, m = 74.8 mg, 85% yield. **m.p.**: 169.6-172.1 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.09-7.03 (m, 3H), 6.97 (d, J = 6.9 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 4.49 (dd, J = 10.3, 3.5 Hz, 1H), 3.83-3.79 (m, 4H), 3.64 (dd, J = 14.7, 3.6 Hz, 1H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 157.0, 137.5, 136.5, 136.2, 128.3, 127.9, 127.7, 125.8, 122.9, 114.7, 60.4, 55.4, 48.3, 35.1, 31.0.
HR-MS (ESI, m/z): calcd for $C_{25}H_{28}O_3S_2$ $[M+Na]^+$: 463.1378. found: 463.1382.

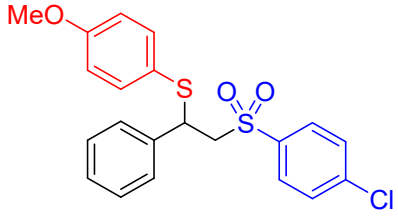


(2-((3,4-dimethoxyphenyl)sulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (10): White solid, m = 31.6 mg, 36% yield. **m.p.**: 112.0-113.4 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.20 (d, J = 8.7 Hz, 3H), 7.15-7.10 (m, 3H), 7.01 (d, J = 6.5 Hz, 2H), 6.89 (d, J = 1.8 Hz, 1H), 6.79-6.74 (m, 3H), 4.44 (dd, J = 10.6, 3.6 Hz, 1H), 3.90 (s, 3H), 3.84-3.80 (m, 4H), 3.77 (s, 3H), 3.64 (dd, J = 14.7, 3.6 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 153.1, 148.8, 137.7, 136.5, 130.9, 128.3,

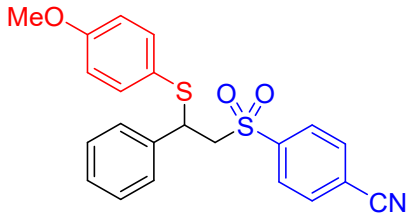
127.9, 127.8, 122.9, 122.2, 114.7, 110.5, 110.1, 60.6, 56.2, 56.0, 55.3, 48.4.
HR-MS (ESI, m/z): calcd for $C_{23}H_{24}O_5S_2$ $[M+Na]^+$: 463.0963. found: 467.0967.



(4-methoxyphenyl)(1-phenyl-2-(phenylsulfonyl)ethyl)sulfane (11): White solid, m = 46.4 mg, 60% yield. **m.p.**: 118.5-121.7 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.7 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.13-7.08 (m, 3H), 7.01 (d, J = 6.9 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 4.48 (dd, J = 10.5, 3.8 Hz, 1H), 3.84-3.80 (m, 4H), 3.66 (dd, J = 14.7, 3.8 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 139.3, 137.6, 136.5, 133.3, 128.9, 128.5, 127.9(1), 127.8(9), 122.8, 114.7, 60.5, 55.4, 48.3.
HR-MS (ESI, m/z): calcd for $C_{21}H_{20}O_3S_2$ $[M+Na]^+$: 407.0752. found: 407.0750.



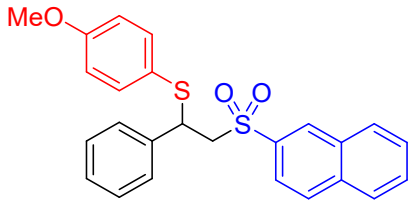
(2-((4-chlorophenyl)sulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (12): White solid, m = 41.8 mg, 50% yield. **m.p.**: 148.8-154.6 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 6.2 Hz, 4H), 7.16 (t, J = 7.2 Hz, 1H), 7.10 (t, J = 7.4 Hz, 2H), 6.98 (d, J = 7.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 4.45 (dd, J = 10.6, 3.2 Hz, 1H), 3.84-3.80 (m, 4H), 3.66 (dd, J = 14.8, 3.3 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 140.0, 137.7, 137.3, 136.6, 129.4, 129.1, 128.5, 127.9(4), 127.9(1), 122.6, 114.8, 60.6, 55.4, 48.4.
HR-MS (ESI, m/z): calcd for $C_{21}H_{19}ClO_3S_2$ $[M+Na]^+$: 441.0362. found: 441.0363.



4-((2-((4-methoxyphenyl)thio)-2-phenylethyl)sulfonyl)benzonitrile (13): White solid, m = 28.7 mg, 35% yield. **m.p.**: 136.4-140.6 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.07 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 7.4 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.47 (dd, J = 10.9, 3.7 Hz, 1H), 3.85 (dd, J = 15.0, 11.0 Hz, 1H), 3.81 (s, 3H), 3.70 (dd, J = 15.0, 3.7 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.6, 143.4, 137.0, 136.6, 132.4, 128.5(9), 128.5(5),

128.2, 128.0, 122.4, 117.1, 116.8, 114.9, 60.6, 55.4, 48.4.

HR-MS (ESI, m/z): calcd for $C_{21}H_{19}NO_3S_2$ $[M+Na]^+$: 432.0704. found: 432.0702.

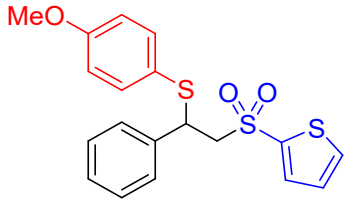


(4-methoxyphenyl)(2-(naphthalen-2-ylsulfonyl)-1-phenylethyl)sulfane (14): Yellow solid, m = 52.3 mg, 60% yield. **m.p.**: 155.2-159.7 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.78-7.76 (m, 2H), 7.63 (t, J = 7.0 Hz, 1H), 7.58-7.53 (m, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 7.3 Hz, 2H), 6.95 (t, J = 7.3 Hz, 2H), 6.89 (t, J = 7.1 Hz, 1H), 6.74 (d, J = 8.7 Hz, 2H), 4.50 (dd, J = 10.6, 3.6 Hz, 1H), 3.88 (dd, J = 14.8, 10.6 Hz, 1H), 3.78 (s, 3H), 3.72 (dd, J = 14.8, 3.7 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 137.4, 136.5, 136.0, 135.0, 131.9, 130.2, 129.4, 129.2(1), 129.1(7), 128.3, 127.8(4), 127.7(7), 127.4, 122.8, 122.3, 114.7, 60.4, 55.3, 48.4.

HR-MS (ESI, m/z): calcd for $C_{25}H_{22}O_3S_2$ $[M+Na]^+$: 457.0908. found: 457.0910.

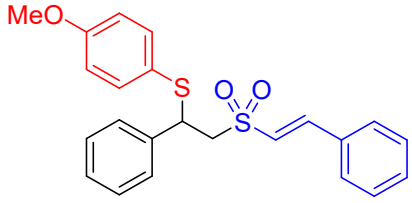


2-((2-((4-methoxyphenyl)thio)-2-phenylethyl)sulfonyl)thiophene (15): White solid, m = 40.4 mg, 52% yield. **m.p.**: 116.7-121.1 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (d, J = 4.9 Hz, 1H), 7.23 (d, J = 8.7 Hz, 3H), 7.17-7.14 (m, 3H), 7.08-7.07 (m, 2H), 6.87 (t, J = 4.5 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 4.52 (dd, J = 10.4, 3.8 Hz, 1H), 3.92 (dd, J = 14.8, 10.4 Hz, 1H), 3.80 (s, 3H), 3.74 (dd, J = 14.8, 3.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 140.3, 137.7, 136.5, 134.4, 134.0, 128.5, 127.9(1), 127.8(7), 127.6, 122.7, 114.8, 61.8, 55.4, 48.5.

HR-MS (ESI, m/z): calcd for $C_{19}H_{18}O_3S_3$ $[M+Na]^+$: 413.0316. found: 413.0315.



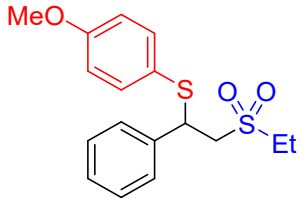
(*E*)-(4-methoxyphenyl)(1-phenyl-2-(styrylsulfonyl)ethyl)sulfane (16): Yellow solid, m = 52.3 mg, 60% yield. **m.p.**: 40.1-45.7 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 4H), 7.31 (t, J = 2.3 Hz, 5H), 7.25-7.22 (m, 1H), 7.18 (d, J = 7.1 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.01 (d, J = 15.4 Hz, 1H), 4.61 (dd, J = 10.6, 4.2 Hz, 1H), 3.85 (s, 3H), 3.75 (dd, J = 14.7, 10.6 Hz, 1H), 3.65 (dd, J = 14.7, 4.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 143.9, 138.3, 136.5, 136.3, 132.1, 131.2,

128.9(3), 128.8(6), 128.5, 128.4, 128.3(2), 128.2(9), 128.1(9), 125.5, 122.8, 114.9, 114.8, 60.8, 55.4, 48.7.

HR-MS (ESI, m/z): calcd for $C_{23}H_{22}O_3S_2$ $[M+Na]^+$: 433.0908. found: 433.0911.

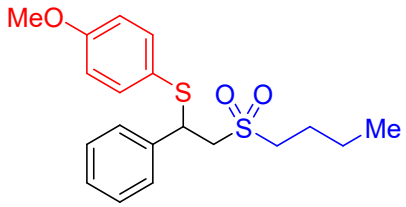


(2-(ethylsulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (17): White solid, m = 34.2 mg, 51% yield. **m.p.**: 105.2-107.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 7H), 6.82 (d, J = 8.4 Hz, 2H), 4.55 (dd, J = 10.2, 3.9 Hz, 1H), 3.80 (s, 3H), 3.61 (dd, J = 14.8, 10.3 Hz, 1H), 3.40 (dd, J = 14.9, 3.9 Hz, 1H), 2.45-2.31 (m, 2H), 1.12 (t, J = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 138.6, 136.4, 129.0, 128.5, 128.0, 122.8, 114.9, 57.3, 55.5, 48.5, 48.4, 6.4.

HR-MS (ESI, m/z): calcd for $C_{17}H_{20}O_3S_2$ $[M+Na]^+$: 359.0752. found: 359.0753.

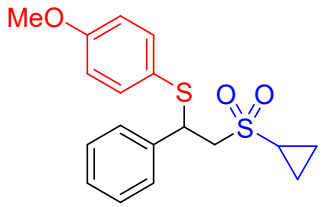


(2-(butylsulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (18): White solid, m = 43.1 mg, 59% yield. **m.p.**: 46.7-51.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 7H), 6.82 (d, J = 8.7 Hz, 2H), 4.55 (dd, J = 10.4, 3.8 Hz, 1H), 3.80 (s, 3H), 3.61 (dd, J = 14.8, 10.4 Hz, 1H), 3.39 (dd, J = 14.8, 3.8 Hz, 1H), 2.38-2.25 (m, 2H), 1.50-1.42 (m, 2H), 1.21-1.11 (m, 2H), 0.76 (t, J = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 138.6, 136.4, 129.0, 128.5, 128.0, 122.9, 114.9, 57.9, 55.4, 53.8, 48.5, 23.8, 21.5, 13.3.

HR-MS (ESI, m/z): calcd for $C_{19}H_{24}O_3S_2$ $[M+Na]^+$: 387.1065. found: 387.1067.

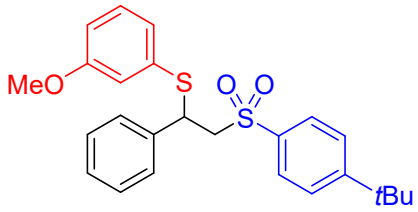


(2-(cyclopropylsulfonyl)-1-phenylethyl)(4-methoxyphenyl)sulfane (19): White solid, m = 38.5 mg, 55% yield. **m.p.**: 95.2-98.9 ℃.

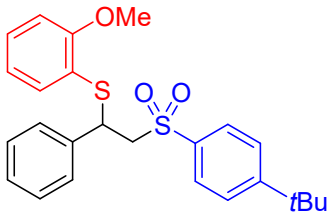
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32-7.27 (m, 7H), 6.82 (d, J = 8.7 Hz, 2H), 4.60 (dd, J = 10.5, 4.0 Hz, 1H), 3.80 (s, 3H), 3.70 (dd, J = 14.7, 10.6 Hz, 1H), 3.50 (dd, J = 14.7, 4.0 Hz, 1H), 1.64-1.59 (m, 1H), 1.12-1.08 (m, 1H), 1.00-0.96 (m, 1H), 0.72-0.61 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.4, 138.7, 136.5, 128.8, 128.3, 128.2, 122.9,

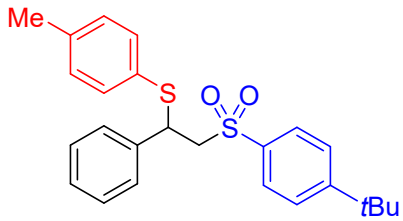
114.8, 59.1, 55.4, 48.5, 30.9, 5.5, 5.2.
HR-MS (ESI, m/z): calcd for $C_{18}H_{20}O_3S_2$ $[M+Na]^+$: 371.0752. found: 371.0756.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(3-methoxyphenyl)sulfane (20): White solid, m = 60.9 mg, 69% yield. **m.p.**: 85.2-96.5 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 8.9 Hz, 1H), 7.10-7.05 (m, 5H), 6.90 (d, J = 7.7 Hz, 1H), 6.82 (d, J = 6.5 Hz, 2H), 4.69 (dd, J = 10.7, 3.5 Hz, 1H), 3.83 (dd, J = 14.7, 10.7 Hz, 1H), 3.75 (s, 3H), 3.68 (dd, J = 14.8, 3.5 Hz, 1H), 1.28 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.9, 157.1, 137.2, 136.1, 134.0, 130.0, 128.5, 128.0, 127.9, 127.7, 125.9, 124.9, 117.7, 114.5, 60.4, 55.3, 47.1, 35.1, 31.0.
HR-MS (ESI, m/z): calcd for $C_{25}H_{28}O_3S_2$ $[M+Na]^+$: 463.1378. found: 463.1383.

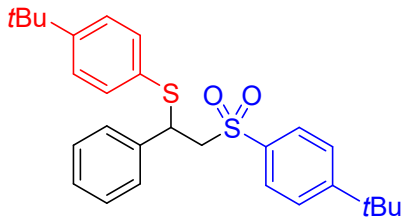


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(2-methoxyphenyl)sulfane (21): White solid, m = 60.4 mg, 69% yield. **m.p.**: 116.4-120.5 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.09-7.04 (m, 5H), 6.87 (t, J = 8.0 Hz, 2H), 4.83 (dd, J = 11.2, 3.0 Hz, 1H), 3.88-3.84 (m, 4H), 3.61 (dd, J = 14.8, 3.0 Hz, 1H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2, 156.9, 137.3, 136.2, 134.8, 130.2, 128.4, 127.9, 127.8, 127.7, 125.8, 121.1, 120.7, 111.1, 60.5, 55.8, 45.1, 35.1, 31.0.
HR-MS (ESI, m/z): calcd for $C_{25}H_{28}O_3S_2$ $[M+Na]^+$: 463.1378. found: 463.1382.

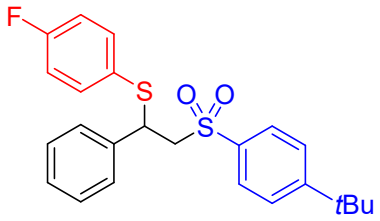


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(p-tolyl)sulfane (22): White solid, m = 69.9 mg, 82% yield. **m.p.**: 178.9-181.9 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.08-7.05 (m, 5H), 7.02 (d, J = 6.8 Hz, 2H), 4.59 (dd, J = 10.7, 3.3 Hz, 1H), 3.82 (dd, J = 14.7, 10.8 Hz, 1H), 3.64 (dd, J = 14.7, 3.4 Hz, 1H), 2.33 (s, 3H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.0, 138.7, 137.8, 136.2, 133.8, 130.0, 129.0,

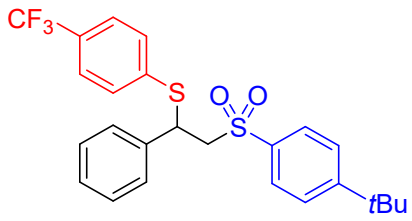
128.4, 127.9, 127.8, 127.7, 125.8, 60.4, 47.7, 35.1, 31.0, 21.2.
HR-MS (ESI, m/z): calcd for $C_{25}H_{28}O_2S_2$ $[M+Na]^+$: 447.1428. found: 447.1430.



(4-(*tert*-butyl)phenyl)(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)sulfane (23): White solid, m = 73.9 mg, 79% yield. **m.p.**: 149.1-152.5 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.25 (t, J = 7.9 Hz, 4H), 7.09-7.03 (m, 5H), 4.62 (dd, J = 10.9, 3.1 Hz, 1H), 3.83 (dd, J = 14.7, 11.0 Hz, 1H), 3.65 (dd, J = 14.8, 3.2 Hz, 1H), 1.31 (s, 9H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.0, 151.8, 137.2, 136.2, 133.2, 129.3, 128.4, 128.0, 127.9, 127.7, 126.4, 125.8, 60.5, 47.5, 35.1, 34.7, 31.2, 31.0.
HR-MS (ESI, m/z): calcd for $C_{28}H_{34}O_2S_2$ $[M+Na]^+$: 489.1898. found: 489.1901.

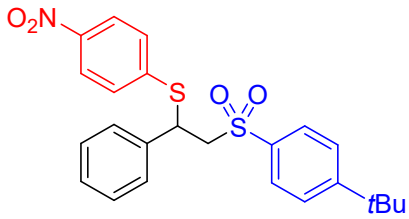


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(4-fluorophenyl)sulfane (24): White solid, m = 76.5 mg, 89% yield. **m.p.**: 118.2-126.4 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.25-7.22 (m, 2H), 7.10-7.05 (m, 3H), 6.98-6.93 (m, 4H), 4.56 (dd, J = 10.4, 3.8 Hz, 1H), 3.81 (dd, J = 14.7, 10.4 Hz, 1H), 3.64 (dd, J = 14.7, 3.8 Hz, 1H), 1.29 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.1 (d, J = 249.1 Hz), 157.2, 137.3, 136.3 (d, J = 8.3 Hz), 136.1, 128.4, 127.9 (2), 127.8, 127.6 (d, J = 3.3 Hz), 125.9, 116.3 (d, J = 21.9 Hz), 60.4, 48.1, 35.1, 31.0.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.97 (s).
HR-MS (ESI, m/z): calcd for $C_{24}H_{25}FO_2S_2$ $[M+Na]^+$: 451.1178. found: 451.1176.

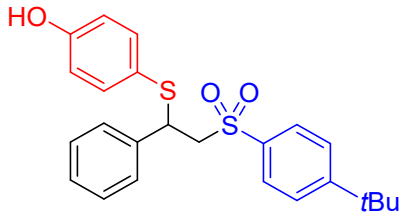


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(4-(trifluoromethyl)phenyl)sulfane (25): White solid, m = 73.7 mg, 77% yield. **m.p.**: 128.0-133.4 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51-7.49 (m, 4H), 7.36 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.13-7.09 (m, 5H), 4.81 (dd, J = 10.2, 3.6 Hz, 1H), 3.85 (dd, J = 14.7, 10.3 Hz, 1H), 3.65 (dd, J = 14.7, 3.6 Hz, 1H), 1.29 (s, 9H).

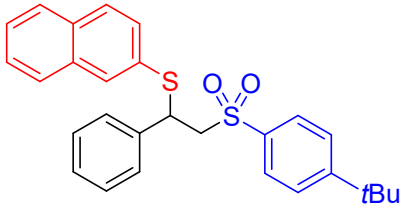
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.4, 138.4, 136.9, 136.0, 131.3, 129.6 (d, J = 32.1 Hz), 128.7, 128.2, 127.9, 127.8, 127.0 (d, J = 4.7 Hz), 126.0, 123.9 (d, J = 270.9 Hz), 60.5, 46.4, 35.2, 31.0.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.69 (s).
HR-MS (ESI, m/z): calcd for $C_{25}H_{25}F_3O_2S_2$ $[M+Na]^+$: 501.1146. found: 501.1150.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(4-nitrophenyl)sulfane (26): White solid, m = 36.8 mg, 40% yield. **m.p.**: 135.6-145.1 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 7.8 Hz, 4H), 7.15 (s, 5H), 4.94 (dd, J = 9.9, 3.7 Hz, 1H), 3.86 (dd, J = 14.7, 9.9, Hz, 1H), 3.66 (dd, J = 14.8, 3.7 Hz, 1H), 1.30 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.7, 146.4, 143.4, 136.6, 135.9, 129.6, 128.9, 128.5, 127.9, 127.8, 126.4, 126.1, 124.5, 124.2, 60.6, 45.7, 35.2, 31.0.
HR-MS (ESI, m/z): calcd for $C_{24}H_{25}NO_4S_2$ $[M+Na]^+$: 478.1123. found: 478.1125.



4-((2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)thio)phenol (27): White solid, m = 35.9 mg, 42% yield. **m.p.**: 138.7-152.7 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 7.09-7.04 (m, 3H), 6.97 (d, J = 7.0 Hz, 2H), 6.73 (d, J = 8.3 Hz, 2H), 5.23 (s, 1H), 4.49 (dd, J = 10.6, 3.5 Hz, 1H), 3.81 (dd, J = 14.7, 10.7 Hz, 1H), 3.65 (dd, J = 14.7, 3.5 Hz, 1H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.3, 157.0, 137.5, 136.8, 136.0, 128.5, 128.0, 127.9, 127.8, 126.0, 122.8, 116.4, 60.5, 48.4, 35.2, 31.1.
HR-MS (ESI, m/z): calcd for $C_{24}H_{26}O_3S_2$ $[M+Na]^+$: 449.1221. found: 449.1215.

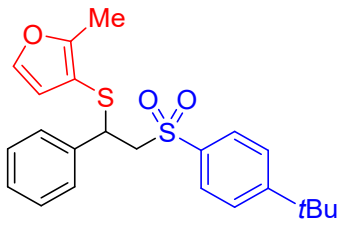


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(naphthalen-2-yl)sulfane (28): White solid, m = 51.3 mg, 56% yield. **m.p.**: 205.5-209.8 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82-7.80 (m, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.52-7.49 (m, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.35 (dd, J = 8.5, 1.7 Hz, 1H), 7.27 (d, J = 5.9

Hz, 2H), 7.11-7.08 (m, 5H), 4.79 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.88 (dd, *J* = 14.8, 10.7 Hz, 1H), 3.72 (dd, *J* = 14.8, 3.5 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.1, 137.3, 136.2, 133.6, 132.7, 132.3, 130.2, 129.8, 128.9, 128.5, 128.0, 127.8, 127.7(1), 127.6(5), 126.7, 125.9, 60.5, 47.1, 35.1, 31.0.

HR-MS (ESI, m/z): calcd for $C_{24}H_{26}O_3S_2$ $[M+Na]^+$: 483.1428. found: 483.1421.

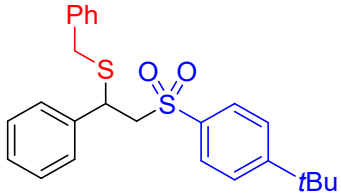


3-((2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)thio)-2-methylfuran (29): White solid, m = 52.8 mg, 64% yield. **m.p.**: 98.5-103.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 1.4 Hz, 1H), 7.10-7.04 (m, 3H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.16 (s, 1H), 4.33 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.81 (dd, *J* = 14.7, 10.6 Hz, 1H), 3.68 (dd, *J* = 14.7, 3.8 Hz, 1H), 1.95 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.8, 157.3, 141.0, 137.7, 136.2, 128.4, 127.9, 127.8, 126.0, 115.6, 107.6, 60.4, 47.4, 35.2, 31.1, 11.5.

HR-MS (ESI, m/z): calcd for $C_{23}H_{26}O_3S_2$ $[M+Na]^+$: 437.1221. found: 437.1219.

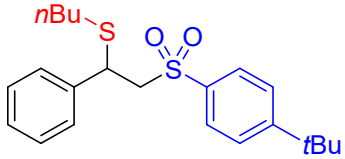


benzyl(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)sulfane (30): Colorless oil, m = 40.1 mg, 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.5 Hz, 2H), 7.33-7.30 (m, 4H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.16-7.14 (m, 3H), 7.09-7.08 (m, 2H), 4.23 (dd, *J* = 9.7, 4.4 Hz, 1H), 3.76 (dd, *J* = 14.7, 9.7 Hz, 1H), 3.64 (dd, *J* = 14.7, 4.4 Hz, 1H), 3.58 (d, *J* = 13.5 Hz, 1H), 3.50 (d, *J* = 13.5 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.1, 138.6, 137.2, 136.3, 129.0, 128.6(0), 128.5(6), 128.0, 127.8(1), 127.7(6), 127.3, 125.9, 61.3, 43.2, 36.1, 35.1, 31.1, 31.0.

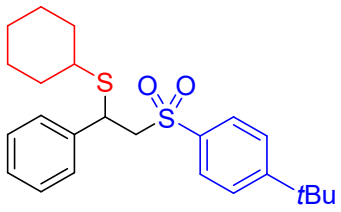
HR-MS (ESI, m/z): calcd for $C_{25}H_{28}O_2S_2$ $[M+Na]^+$: 447.1428. found: 447.1427.



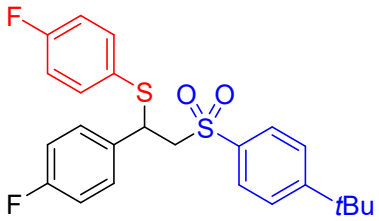
butyl(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)sulfane (31): White solid, m = 56.7 mg, 73% yield. **m.p.**: 60.5-63.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 5H), 4.32 (dd, *J* = 9.9, 4.2 Hz, 1H), 3.76 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.65 (dd, *J* = 14.7, 4.2 Hz, 1H), 2.36-2.27 (m, 2H), 1.48-1.41 (m, 2H), 1.29 (s, 11H), 0.83 (t, *J* =

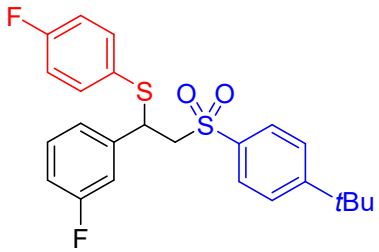
7.4 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.1, 138.9, 136.4, 128.5, 127.8, 127.7(4), 127.6(5), 125.9, 61.4, 43.3, 35.1, 31.2, 31.0(4), 30.9(9), 21.9, 13.6.
HR-MS (ESI, m/z): calcd for $C_{22}H_{30}O_2S_2$ $[M+Na]^+$: 413.1585. found: 413.1586.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylethyl)(cyclohexyl)sulfane (32): White solid, m = 52.2 mg, 63% yield. **m.p.**: 105.0-106.5 °C.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.10 (s, 5H), 4.40 (dd, J = 10.0, 4.0 Hz, 1H), 3.76 (dd, J = 14.7, 10.0 Hz, 1H), 3.64 (dd, J = 14.7, 4.0 Hz, 1H), 2.45-2.41 (m, 1H), 1.90 (d, J = 12.8 Hz, 1H), 1.73-1.63 (m, 3H), 1.53 (s, 1H), 1.28 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.1, 139.3, 136.4, 128.5, 127.7(3), 127.7(0), 127.6, 125.9, 61.8, 43.4, 41.9, 35.1, 33.3, 33.1, 31.0, 25.7.
HR-MS (ESI, m/z): calcd for $C_{24}H_{32}O_2S_2$ $[M+Na]^+$: 439.1741. found: 439.1743.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(4-fluorophenyl)ethyl)(4-fluorophenyl)sulfane (33): White solid, m = 63.4 mg, 71% yield. **m.p.**: 132.9-135.2 °C.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.25-7.23 (m, 2H), 6.98-6.91 (m, 4H), 6.73 (t, J = 8.5 Hz, 2H), 4.56 (dd, J = 10.8, 3.6 Hz, 1H), 3.77 (dd, J = 14.7, 10.9 Hz, 1H), 3.63 (dd, J = 14.7, 3.6 Hz, 1H), 1.29 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, J = 250.1 Hz), 162.0 (d, J = 247.3 Hz), 157.5, 136.4 (d, J = 8.3 Hz), 136.1, 133.1, 129.6 (d, J = 8.1 Hz), 127.7, 127.3 (d, J = 4.0 Hz), 125.9, 116.4 (d, J = 21.9 Hz), 115.3 (d, J = 21.7 Hz), 60.4, 47.4, 35.2, 31.0.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.58 (s), -113.54 (s).
HR-MS (ESI, m/z): calcd for $C_{24}H_{24}F_2O_2S_2$ $[M+Na]^+$: 469.1083. found: 469.1085.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(3-fluorophenyl)ethyl)(4-

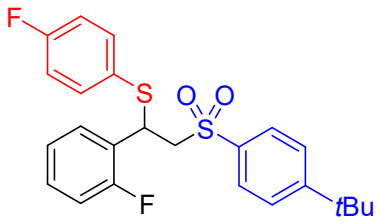
fluorophenyl)sulfane (34): White solid, m = 72.7 mg, 81% yield. **m.p.**: 106.5-110.6 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.25-7.22 (m, 2H), 7.07-7.03 (m, 1H), 6.96 (t, J = 8.6 Hz, 2H), 6.79-6.76 (m, 2H), 6.62 (d, J = 9.7 Hz, 1H), 4.54 (dd, J = 10.6, 3.6 Hz, 1H), 3.76 (dd, J = 14.7, 10.6 Hz, 1H), 3.63 (dd, J = 14.7, 3.7 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, J = 250.3 Hz), 162.4 (d, J = 246.8 Hz), 157.5, 140.0 (d, J = 7.3 Hz), 136.5 (d, J = 8.2 Hz), 136.0, 129.9 (d, J = 7.9 Hz), 127.7, 127.1 (d, J = 4.3 Hz), 126.0, 123.9, 116.4 (d, J = 21.6 Hz), 114.9 (d, J = 21.6 Hz), 114.7 (d, J = 22.3 Hz), 60.2, 47.7, 35.2, 30.9.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.44 (s), -112.30 (s).

HR-MS (ESI, m/z): calcd for $C_{24}H_{24}F_2O_2S_2$ $[M+Na]^+$: 469.1083. found: 469.1085.



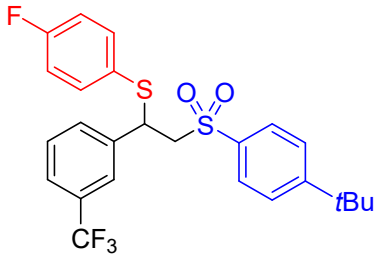
(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(2-fluorophenyl)ethyl)(4-fluorophenyl)sulfane (35): White solid, m = 63.5 mg, 71% yield. **m.p.**: 79.9-84.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.25-7.23 (m, 2H), 7.10-7.07 (m, 1H), 6.95-6.90 (m, 3H), 6.86 (t, J = 7.3 Hz, 1H), 6.79 (t, J = 10.1 Hz, 1H), 4.76 (dd, J = 10.9, 3.5 Hz, 1H), 3.94 (dd, J = 14.7, 10.9 Hz, 1H), 3.65 (dd, J = 14.7, 3.6 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, J = 249.9 Hz), 160.2 (d, J = 248.5 Hz), 157.4, 136.5 (d, J = 8.5 Hz), 135.7, 129.6 (d, J = 8.5 Hz), 129.2 (d, J = 2.0 Hz), 127.8, 127.4 (d, J = 2.7 Hz), 125.9, 124.9 (d, J = 12.6 Hz), 124.0 (d, J = 3.1 Hz), 116.3 (d, J = 21.7 Hz), 115.7 (d, J = 22.2 Hz), 59.1, 42.1, 35.2, 31.0.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.64 (s), -115.78 (s).

HR-MS (ESI, m/z): calcd for $C_{24}H_{24}F_2O_2S_2$ $[M+Na]^+$: 469.1083. found: 469.1084.

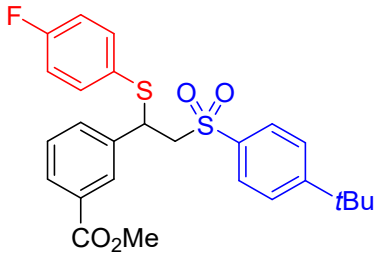


(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(3-(trifluoromethyl)phenyl)ethyl)(4-fluorophenyl)sulfane (36): White solid, m = 74.6 mg, 75% yield. **m.p.**: 92.8-97.9 °C.

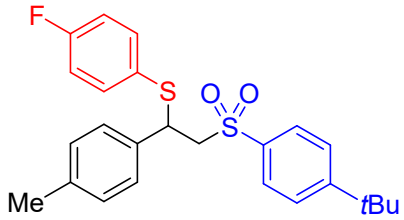
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.23-7.16 (m, 5H), 6.96 (t, J = 8.5 Hz, 2H), 4.62 (dd, J = 10.7, 3.6 Hz, 1H), 3.82 (dd, J = 14.8, 10.7 Hz, 1H), 3.69 (dd, J = 14.8, 3.6 Hz, 1H), 1.26 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.6, 156.4 (d, J = 206.6 Hz), 138.7, 136.8 (d, J =

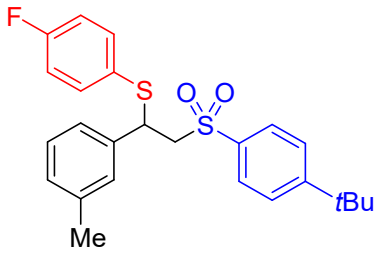
8.7 Hz), 135.9, 131.3, 128.9, 127.7, 126.7 (d, J = 2.5 Hz), 126.0, 124.7 (d, J = 22.1 Hz), 116.5 (d, J = 22.0 Hz), 60.0, 47.8, 35.1, 30.9.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.74 (s), -111.13 (s).
HR-MS (ESI, m/z): calcd for $C_{25}H_{24}F_4O_2S_2$ $[M+Na]^+$: 519.1052. found: 519.1057.



Methyl 3-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl) benzoate (37): Colorless oil, m = 79.1 mg, 81% yield. **m.p.**: 45.7-57.1 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77-7.75 (m, 1H), 7.63 (s, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.24-7.22 (m, 2H), 7.18-7.15 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H), 4.61 (dd, J = 10.7, 3.6 Hz, 1H), 3.88-3.83 (m, 4H), 3.66 (dd, J = 14.7, 3.6 Hz, 1H), 1.25 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.2, 163.2 (d, J = 250.5 Hz), 157.4, 137.9, 136.5 (d, J = 8.5 Hz), 135.9, 132.6, 130.3, 129.1, 128.9, 128.5, 127.8, 127.1, 125.9, 116.4 (d, J = 21.8 Hz), 60.0, 52.2, 47.8, 35.1, 30.9.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.47 (s).
HR-MS (ESI, m/z): calcd for $C_{26}H_{27}FO_4S_2$ $[M+Na]^+$: 509.1232. found: 509.1234.



(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(p-tolyl)ethyl)(4-fluorophenyl)sulfane (38): White solid, m = 85.4 mg, 96% yield. **m.p.**: 95.0-98.4 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.26-7.24 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.87 (s, 4H), 4.54 (dd, J = 10.6, 3.6 Hz, 1H), 3.80 (dd, J = 14.7, 10.6 Hz, 1H), 3.61 (dd, J = 14.7, 3.6 Hz, 1H), 2.24 (s, 3H), 1.29 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.0 (d, J = 249.2 Hz), 157.2, 137.5, 136.2, 136.1 (d, J = 8.1 Hz), 134.2, 129.1, 127.9 (d, J = 3.2 Hz), 127.8, 127.7, 125.8, 116.3 (d, J = 22.0 Hz), 60.5, 47.8, 35.1, 31.0, 21.1.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.14 (s).
HR-MS (ESI, m/z): calcd for $C_{25}H_{27}FO_2S_2$ $[M+Na]^+$: 465.1334. found: 465.1330.



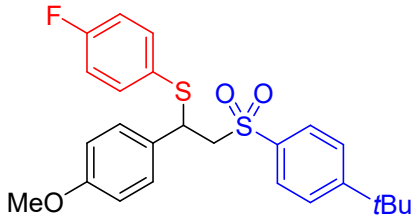
(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(m-tolyl)ethyl)(4-fluorophenyl)sulfane (39): White solid, m = 71.3 mg, 81% yield. **m.p.**: 61.4-66.7 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.27-7.24 (m, 2H), 6.98-6.94 (m, 3H), 6.89 (d, J = 7.5 Hz, 1H), 6.80 (t, J = 7.7 Hz, 2H), 4.53 (dd, J = 10.5, 3.7 Hz, 1H), 3.81 (dd, J = 14.7, 10.5 Hz, 1H), 3.61 (dd, J = 14.7, 3.7 Hz, 1H), 2.17 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.0 (d, J = 247.9 Hz), 157.1, 138.0, 137.1, 136.2 (d, J = 7.3 Hz), 128.7, 128.5, 128.4, 127.8, 127.5 (d, J = 4.6 Hz), 125,7, 125.1, 116.3 (d, J = 21.9 Hz), 60.4, 48.0, 35.1, 31.0, 21.3.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.07 (s).

HR-MS (ESI, m/z): calcd for $C_{25}H_{27}FO_2S_2$ $[M+Na]^+$: 465.1334. found: 465.1337.



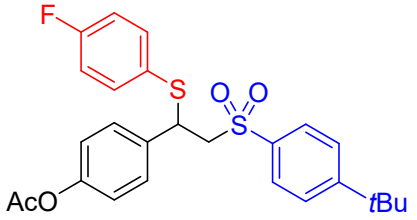
(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(4-methoxyphenyl)ethyl)(4-fluorophenyl)sulfane (40): White solid, m = 68.2 mg, 74% yield. **m.p.**: 78.6-90.9 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.26-7.23 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H), 4.55 (dd, J = 10.7, 3.6 Hz, 1H), 3.78 (dd, J = 14.7, 10.7 Hz, 1H), 3.73 (s, 3H), 3.61 (dd, J = 14.7, 3.6 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2 (d, J = 282.6 Hz), 136.2 (d, J = 8.3 Hz), 129.0, 127.9, 127.8, 125.8, 116.3 (d, J = 21.9 Hz), 113.8, 60.6, 55.1, 47.5, 35.1, 31.0.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.11 (s).

HR-MS (ESI, m/z): calcd for $C_{25}H_{27}FO_3S_2$ $[M+Na]^+$: 481.1283. found: 481.1285.



4-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl)phenyl acetate (41): White solid, m = 76.4 mg, 79% yield. **m.p.**: 123.9-127.0 ℃.

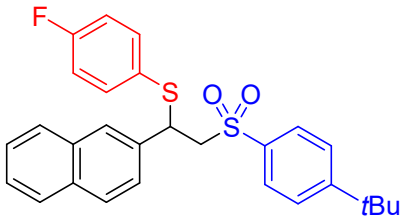
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 7.25-7.22 (m, 2H), 6.97-6.94 (m, 4H), 6.80 (d, J = 8.6 Hz, 2H), 4.57 (dd, J = 10.4, 4.0

Hz, 1H), 3.78 (dd, J = 14.7, 10.4 Hz, 1H), 3.64 (dd, J = 14.7, 4.0 Hz, 1H), 2.26 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.9, 163.1 (d, J = 249.9 Hz), 157.4, 150.1, 136.5 (d, J = 8.1 Hz), 136.2, 134.8, 128.9, 127.7, 127.4 (d, J = 3.7 Hz), 126.0, 121.5, 116.4 (d, J = 21.9 Hz), 60.5, 47.6, 35.2, 31.0, 29.7, 21.1.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.71 (s).

HR-MS (ESI, m/z): calcd for $C_{26}H_{27}FO_4S_2$ $[M+Na]^+$: 509.1232. found: 509.1236.



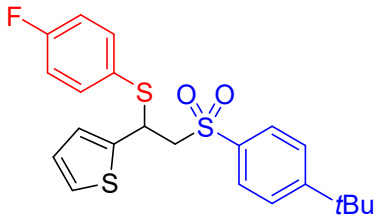
(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-(naphthalen-2-yl)ethyl)(4-fluorophenyl)sulfane (42): White solid, m = 54.9 mg, 57% yield. **m.p.**: 102.0-111.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.33 (s, 1H), 7.27-7.24 (m, 2H), 7.13-7.12 (m, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.93 (t, J = 8.6 Hz, 2H), 4.74 (dd, J = 10.8, 3.6 Hz, 1H), 3.93 (dd, J = 14.8, 10.8 Hz, 1H), 3.73 (dd, J = 14.8, 3.6 Hz, 1H), 1.08 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.1 (d, J = 249.5 Hz), 157.1, 136.4 (d, J = 8.2 Hz), 135.9, 134.4, 132.8, 132.7, 128.4, 127.8, 127.7, 127.6, 126.4, 126.3, 125.5, 125.0, 116.3 (d, J = 22.0 Hz), 60.4, 48.6, 34.9, 30.8.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.84 (s).

HR-MS (ESI, m/z): calcd for $C_{28}H_{27}FO_2S_2$ $[M+Na]^+$: 501.1334. found: 501.1339.



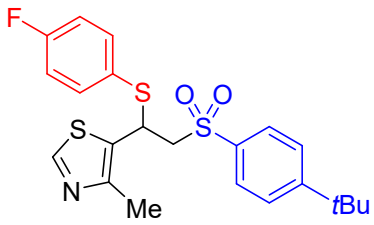
2-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl)thiophene (43): White solid, m = 60.2 mg, 69% yield. **m.p.**: 105.0-110.0 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.25-7.23 (m, 2H), 7.06 (d, J = 5.0 Hz, 1H), 6.96 (t, J = 8.6 Hz, 2H), 6.66-6.65 (m, 1H), 6.56 (d, J = 3.4 Hz, 1H), 4.88 (dd, J = 9.9, 4.0 Hz, 1H), 3.76 (dd, J = 14.6, 9.9 Hz, 1H), 3.68 (dd, J = 14.6, 4.0 Hz, 1H), 1.31 (s, 9H).

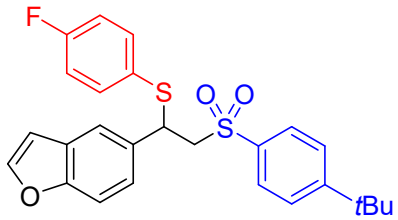
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, J = 250.0 Hz), 157.5, 141.4, 136.6 (d, J = 8.2 Hz), 136.1, 127.9, 127.3 (d, J = 3.2 Hz), 126.7, 126.4, 126.0, 125.6, 116.3 (d, J = 21.9 Hz), 61.7, 43.5, 35.2, 31.0.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.55 (s).

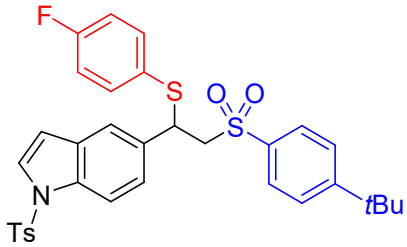
HR-MS (ESI, m/z): calcd for $C_{22}H_{23}FO_2S_3$ $[M+Na]^+$: 457.0742. found: 457.0746.



5-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl)-4-methylthiazole (44): White solid, m = 47.7 mg, 53% yield. **m.p.**: 91.5-98.4 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.27-7.24 (m, 2H), 6.97 (t, J = 8.6 Hz, 2H), 4.90 (dd, J = 10.6, 3.2 Hz, 1H), 3.73 (dd, J = 14.6, 3.7 Hz, 1H), 3.64 (dd, J = 14.7, 10.6 Hz, 1H), 2.16 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.5 (d, J = 251.0 Hz), 157.8, 151.3, 137.0 (d, J = 8.4 Hz), 135.9, 127.6, 126.8 (d, J = 2.8 Hz), 126.1, 116.5 (d, J = 21.9 Hz), 61.9, 41.3, 35.2, 31.0, 15.0.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -110.63 (s).
HR-MS (ESI, m/z): calcd for $C_{22}H_{24}FNO_2S_3$ $[M+H]^+$: 450.1031. found: 450.1034.



5-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl)benzofuran (45): White solid, m = 88.1 mg, 94% yield. **m.p.**: 112.9-118.9 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.38 (d, J = 8.2 Hz, 2H), 7.31-7.29 (m, 3H), 7.16 (t, J = 8.1 Hz, 3H), 6.99-6.94 (m, 3H), 6.64 (s, 1H), 4.72 (dd, J = 10.8, 3.2 Hz, 1H), 3.90 (dd, J = 14.5, 11.1 Hz, 1H), 3.71 (dd, J = 14.7, 3.0 Hz, 1H), 1.22 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.4 (d, J = 229.7 Hz), 140.6, 140.4, 126.3 (d, J = 7.4 Hz), 126.1, 125.7, 123.9, 123.8, 123.6, 121.2, 120.5 (d, J = 8.2 Hz), 120.4, 109.7, 109.5, 109.4, 31.6, 22.6, 14.1.
^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.00 (s).
HR-MS (ESI, m/z): calcd for $C_{26}H_{25}FNO_3S_2$ $[M+Na]^+$: 491.1127. found: 491.1130.



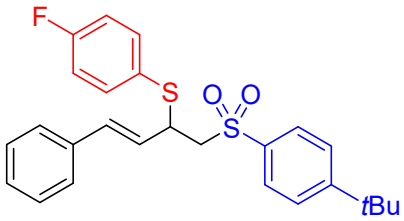
5-(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-((4-fluorophenyl)thio)ethyl)-1-tosyl-1*H*-indole (46): White solid, m = 104.9 mg, 84% yield. **m.p.**: 157.4-161.6 ℃.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (t, J = 8.6 Hz, 3H), 7.49 (d, J = 3.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.20-7.18 (m, 2H), 7.15 (s, 1H), 7.13

(d, J = 2.9 Hz, 2H), 7.03 (d, J = 8.6 Hz, 1H), 6.87 (t, J = 8.5 Hz, 2H), 6.45 (d, J = 3.6 Hz, 1H), 4.65 (dd, J = 10.5, 3.7 Hz, 1H), 3.84 (dd, J = 14.7, 10.5 Hz, 1H), 3.64 (dd, J = 14.7, 3.7 Hz, 1H), 2.36 (s, 3H), 1.19 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.0 (d, J = 249.7 Hz), 157.5, 145.2, 136.2 (d, J = 8.3 Hz), 136.0, 135.2, 134.2, 132.4, 130.7, 130.0, 127.7 (d, J = 4.3 Hz), 127.7, 127.0, 126.8, 125.7, 124.7, 120.8, 116.3 (d, J = 21.9 Hz), 113.6, 108.8, 60.8, 48.2, 35.0, 30.9, 21.6.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.91 (s).

HR-MS (ESI, m/z): calcd for $C_{33}H_{32}FNO_4S_3$ $[M+Na]^+$: 644.1375. found: 644.1378.



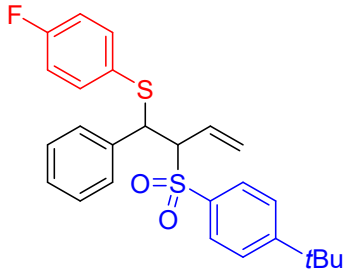
(*E*)-(1-((4-(*tert*-butyl)phenyl)sulfonyl)-4-phenylbut-3-en-2-yl)(4-fluorophenyl) sulfane (47a): White oil, m = 38.1 mg, 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.37-7.35 (m, 2H), 7.25-7.20 (m, 3H), 7.05 (d, J = 9.0 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 6.09 (d, J = 15.7 Hz, 1H), 5.63 (dd, J = 15.7, 9.2 Hz, 1H), 4.15 (td, J = 9.5, 4.0 Hz, 1H), 3.55-3.47 (m, 2H), 1.22 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, J = 248.8 Hz), 157.7, 137.2 (d, J = 8.1 Hz), 136.3, 135.9, 133.5, 128.5, 128.3, 128.0, 127.0 (d, J = 2.3 Hz), 126.4, 126.2, 125.8, 116.3 (d, J = 22.0 Hz), 60.0, 46.8, 35.2, 30.9.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -111.74 (s).

HR-MS (ESI, m/z): calcd for $C_{26}H_{27}FO_2S_2$ $[M+Na]^+$: 477.1334. found: 477.1333.



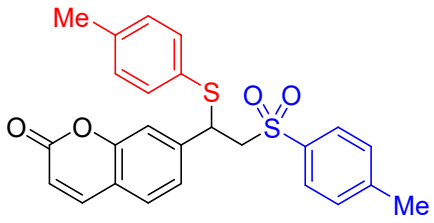
(2-((4-(*tert*-butyl)phenyl)sulfonyl)-1-phenylbut-3-en-1-yl)(4-fluorophenyl)sulfane (47b): White oil, m = 31.2 mg, 34% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.29-7.23 (m, 5H), 7.18 (d, J = 7.1 Hz, 2H), 6.94 (t, J = 8.6 Hz, 2H), 5.81 (dd, J = 15.2, 8.4 Hz, 1H), 5.45-5.40 (m, 1H), 4.64 (d, J = 8.3 Hz, 1H), 3.75-3.68 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.9 (d, J = 193.2 Hz), 157.6, 139.3, 139.1, 136.0 (d, J = 8.0 Hz), 135.1, 128.7, 128.3, 127.8, 127.7, 126.0, 118.5, 116.0 (d, J = 22.0 Hz), 59.5, 56.3, 35.2, 31.1.

^{19}F NMR (564 MHz, $CDCl_3$): δ = -113.04 (s).

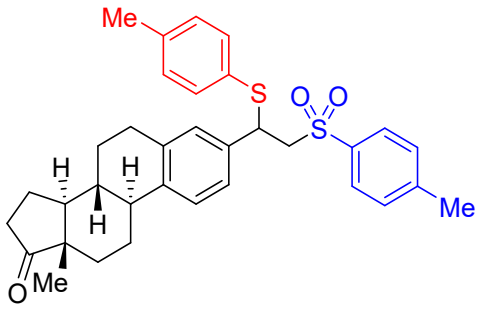
HR-MS (ESI, m/z): calcd for $C_{26}H_{27}FO_2S_2$ $[M+Na]^+$: 477.1334. found: 477.1331.



7-(1-(*p*-tolylthio)-2-tosylethyl)-2*H*-chromen-2-one (48): White solid, m = 67.8 mg, 75% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, J = 9.5 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.11-7.06 (m, 5H), 6.84 (d, J = 1.4 Hz, 1H), 6.39 (d, J = 9.5 Hz, 1H), 4.56 (dd, J = 10.8, 3.6 Hz, 1H), 3.76 (dd, J = 14.7, 10.8 Hz, 1H), 3.67 (dd, J = 14.7, 3.6 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H).

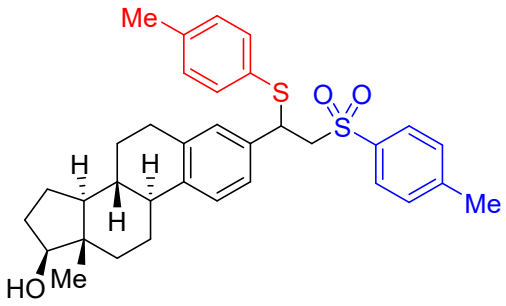
Data is consistent with that reported in the literature.[4]



(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-(*p*-tolylthio)-2-tosylethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (49): White solid, m = 99.0 mg, 89% yield, dr = 4:3.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39-7.36 (m, 2H), 7.24-7.22 (m, 2H), 7.11-7.05 (m, 5H), 6.91-6.90 (m, 1H), 6.72 (d, J = 7.1 Hz, 1H), 4.53-4.49 (m, 1H), 3.83-3.78 (m, 1H), 3.58 (dd, J = 14.8, 3.4 Hz, 1H), 2.80-2.73 (m, 1H), 2.65-2.57 (m, 1H), 2.54-2.49 (m, 1H), 2.43-2.35 (m, 7H), 2.22-2.04 (m, 3H), 1.99-1.96 (m, 2H), 1.66-1.60 (m, 1H), 1.55-1.44 (m, 4H), 1.35-1.26 (m, 1H), 0.93 (d, J = 8.8 Hz, 3H).

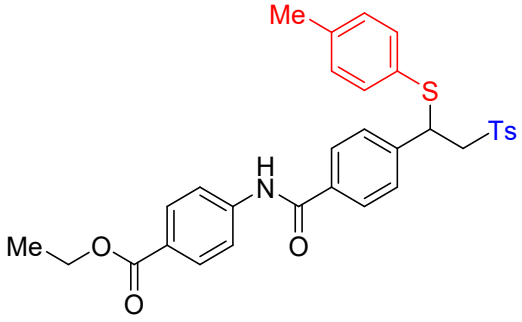
Data is consistent with that reported in the literature.[4]



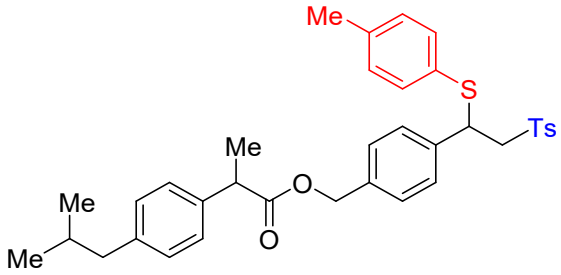
(8*R*,9*S*,13*S*,14*S*,17*S*)-13-methyl-3-(1-(*p*-tolylthio)-2-tosylethyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (50): White solid, m = 102.2 mg, 91% yield, dr = 1:1.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.13-7.04 (m, 5H), 6.93-6.88 (m, 1H), 6.67 (d, J = 37.4 Hz, 1H), 4.54-4.53 (m, 1H), 3.85-3.75 (m, 2H), 3.60 (dd, J = 14.8, 3.3 Hz, 1H), 2.76-2.41 (m, 2H), 2.39-2.20 (m,

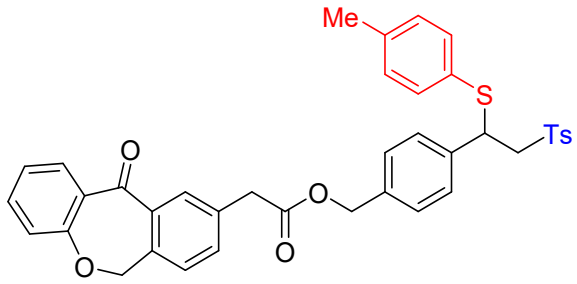
7H), 2.18-2.12 (m, 2H), 2.00-1.97 (m, 1H), 1.89-1.84 (m, 1H), 1.75-1.64 (m, 1H), 1.55-1.17 (m, 8H), 0.83 (d, J = 11.0 Hz, 3H).
Data is consistent with that reported in the literature.[4]



ethyl 4-(4-(1-(*p*-tolylthio)-2-tosylethyl)benzamido)benzoate (51): White solid, m = 89.0 mg, 65% yield. **m.p.**: 119.2-127.9 °C.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.7 Hz, 2H), 7.98 (s, 1H), 7.73 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.19-7.13 (m, 6H), 7.06 (d, J = 7.9 Hz, 2H), 4.58 (dd, J = 10.6, 3.6 Hz, 1H), 4.40-4.36 (m, 2H), 3.78 (dd, J = 14.6, 10.6 Hz, 1H), 3.66 (dd, J = 14.7, 3.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.2, 165.5, 145.0, 142.3, 139.1, 136.0, 134.0(1), 133.9(6), 130.8, 130.1, 129.8, 128.3, 128.2, 127.9, 127.5, 126.1, 119.3, 60.9, 60.2, 47.2, 21.6, 21.2, 14.4.
HR-MS (ESI, m/z): calcd for $C_{32}H_{31}NO_5S_2$ $[M+Na]^+$: 596.1541. found: 596.1544.



4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(4-isobutylphenyl)propanoate (52): White solid, m = 146.7 mg, 76% yield, dr > 99:1. **m.p.**: 101.2-112.3 °C.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 (d, J = 8.2 Hz, 2H), 7.22-7.20 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.11-7.10 (m, 2H), 7.07-7.03 (m, 4H), 6.99-6.95 (m, 4H), 5.05-4.99 (m, 2H), 4.53 (dd, J = 10.6, 3.6 Hz, 1H), 3.78-3.73 (m, 2H), 3.61 (dd, J = 14.7, 3.6 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 2.33 (d, J = 6.5 Hz, 6H), 1.87-1.83 (m, 1H), 1.55-1.52 (m, 5H), 0.91 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.5, 144.3, 140.7, 138.8, 137.6, 137.4(0), 137.3(5), 136.3, 135.8, 133.8, 130.0, 129.5, 129.4, 128.9, 128.0, 127.9, 127.6(2), 127.5(7), 127.2, 65.7, 60.6, 47.3, 45.2(0), 45.1(6), 45.0, 30.2, 22.4, 21.5, 21.2, 18.5(2), 18.4(7).
HR-MS (ESI, m/z): calcd for $C_{36}H_{40}O_4S_2$ $[M+Na]^+$: 623.2266. found: 623.2270.

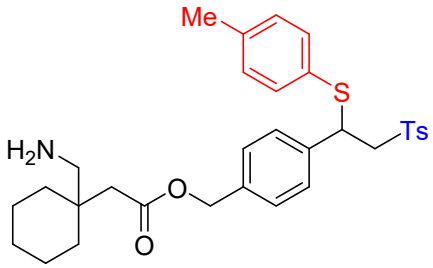


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-9-yl)acetate (53): White solid, m = 88.7 mg, 67% yield. **m.p.**: 44.6-55.4 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, J = 2.3 Hz, 1H), 7.90 (d, J = 6.7 Hz, 1H), 7.57 (t, J = 6.2 Hz, 1H), 7.48 (t, J = 8.6 Hz, 1H), 7.44 (dd, J = 8.4, 2.4 Hz, 1H), 7.40 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 7.3 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.09-7.04 (m, 9H), 5.19 (s, 2H), 5.07 (d, J = 2.7 Hz, 2H), 4.54 (dd, J = 10.5, 3.7 Hz, 1H), 3.77 (dd, J = 14.7, 10.5 Hz, 1H), 3.71 (s, 2H), 3.62 (dd, J = 14.7, 3.7 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.1, 170.4, 159.9, 143.6, 139.7, 138.1, 137.0, 135.6(1), 135.5(6), 134.8, 134.7, 133.1, 132.1, 131.8, 129.3, 128.8, 128.6, 128.2, 127.4, 127.3, 127.2, 127.1, 126.9, 124.5, 120.5, 72.9, 65.4, 59.8, 46.6, 39.5, 20.8, 20.5.

HR-MS (ESI, m/z): calcd for $C_{39}H_{34}O_6S_2$ $[M+Na]^+$: 685.1694. found: 685.1699.

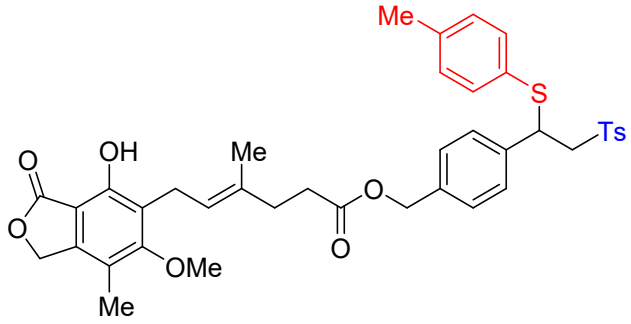


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(1-(aminomethyl)cyclohexyl)acetate (54): White oil, m = 79.8 mg, 71% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.1 Hz, 2H), 7.14 (t, J = 7.9 Hz, 4H), 7.04 (t, J = 8.3 Hz, 4H), 6.99 (d, J = 7.9 Hz, 2H), 4.54 (dd, J = 10.3, 3.7 Hz, 1H), 4.38-4.32 (m, 2H), 3.77 (dd, J = 14.6, 10.3 Hz, 1H), 3.62 (dd, J = 14.7, 3.7 Hz, 1H), 2.96 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 2.31 (s, 2H), 1.42-1.25 (m, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.1, 144.5, 138.8, 137.1, 136.3(1), 136.2(8), 133.9, 123.0, 129.5, 128.8, 128.3, 127.9, 60.5, 47.3, 46.0, 36.9(3), 36.9(1), 36.2, 25.6, 22.8, 21.6, 21.2.

HR-MS (ESI, m/z): calcd for $C_{32}H_{39}NO_4S_2$ $[M+H]^+$: 566.2399. found: 566.2398.

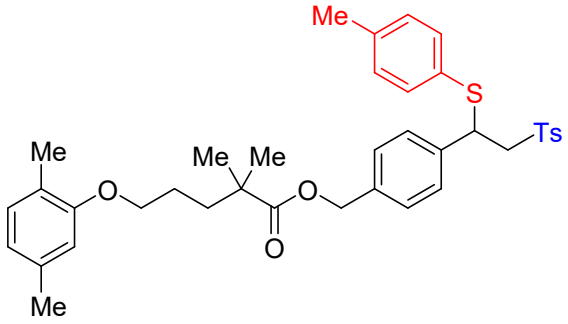


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl (*E*)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoate (55): White solid, m = 97.3 mg, 68% yield. **m.p.**: 43.2-44.1 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (s, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.10-7.04 (m, 8H), 5.25 (t, J = 6.0 Hz, 1H), 5.18 (s, 2H), 4.98 (s, 2H), 4.53 (dd, J = 10.5, 3.5 Hz, 1H), 3.77-3.73 (m, 4H), 3.60 (dd, J = 14.7, 3.6 Hz, 1H), 3.39 (d, J = 6.9 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H), 2.34 (d, J = 20.8 Hz, 8H), 2.13 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.1, 172.9, 163.7, 153.6, 144.4, 144.1, 138.8, 137.6, 136.3, 135.7, 134.1, 133.7, 130.0, 129.5, 128.9, 128.1, 128.0, 127.9, 122.9, 122.1, 116.8, 106.4, 70.1, 65.5, 61.0, 60.5, 47.3, 34.6, 33.1, 22.6, 21.6, 21.2, 16.2, 11.6.

HR-MS (ESI, m/z): calcd for $C_{40}H_{42}O_8S_2$ $[M+Na]^+$: 737.2219. found: 737.2219.

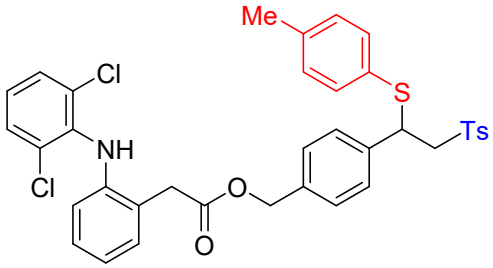


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (56): White solid, m = 85.3 mg, 66% yield. **m.p.**: 79.1-85.1 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = Hz, 2H), 7.16 (d, J = Hz, 2H), 7.11 (d, J = Hz, 4H), 7.07-7.05 (m, 4H), 7.00 (d, J = Hz, 1H), 6.66 (d, J = Hz, 1H), 6.60 (s, 1H), 5.03 (s, 2H), 4.54 (dd, J = Hz, 1H), 3.91 (t, J = Hz, 2H), 3.77 (dd, J = Hz, 1H), 3.61 (dd, J = Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 2.16 (s, 3H), 1.78-1.71 (m, 4H), 1.26 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 177.5, 157.0, 144.4, 138.8, 137.6, 136.5, 136.4, 136.1, 133.8, 130.3, 130.0, 129.5, 129.0, 128.1, 128.0, 127.7, 123.6, 120.8, 112.0, 67.9, 65.5, 60.6, 47.3, 42.2, 37.2, 25.2, 21.6, 21.4, 21.2, 15.8.

HR-MS (ESI, m/z): calcd for $C_{38}H_{44}O_5S_2$ $[M+Na]^+$: 667.2528. found: 667.2531.



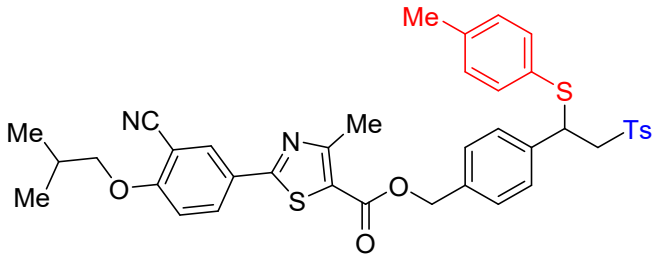
4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(2-((2,6-dichlorophenyl)amino)phenyl) acetate (57): White solid, m = 121 mg, 88% yield. **m.p.**: 63.6-73.7 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 6.4 Hz, 1H), 7.17-7.13 (m, 3H), 7.10-7.03 (m, 8H), 7.00-6.96 (m, 2H), 6.90 (s, 1H), 6.58 (d, J = 8.0 Hz, 1H), 5.10 (s, 2H), 4.54 (dd, J = 10.4, 3.7 Hz, 1H), 3.88 (s, 2H), 3.77 (dd, J = 14.7, 10.5 Hz, 1H), 3.62 (dd, J = 14.7, 3.7 Hz, 1H), 2.35 (s, 3H), 2.33

(s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.1, 144.4, 142.8, 138.8, 137.9, 137.8, 136.3, 135.3, 133.8, 130.9, 130.0, 129.5(0), 129.4(7), 128.9, 128.2, 128.1, 127.9, 124.2, 124.1, 122.2, 118.5, 66.4, 60.6, 47.3, 38.6, 21.6, 21.2.

HR-MS (ESI, m/z): calcd for $C_{37}H_{33}Cl_2NO_4S_2$ $[M+Na]^+$: 712.1126. found: 712.1129.

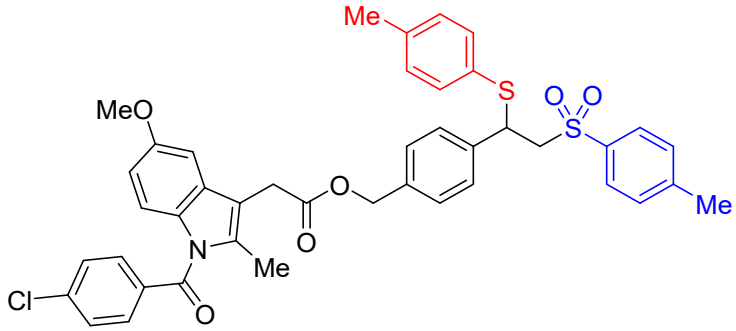


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (58): White solid, m = 104.1 mg, 73% yield. **m.p.**: 111.2-116.5 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, J = 2.3 Hz, 1H), 8.10 (dd, J = 8.9, 2.3 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.2 Hz, 4H), 7.07 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 1H), 5.26 (s, 2H), 4.57 (dd, J = 10.5, 3.6 Hz, 1H), 3.90 (d, J = 6.5 Hz, 2H), 3.79 (dd, J = 14.7, 10.5 Hz, 1H), 3.63 (dd, J = 14.7, 3.6 Hz, 1H), 2.79 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.23-2.18 (m, 1H), 1.10 (s, 1H), 1.08 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.5, 162.6, 161.8, 144.4, 138.8, 138.0, 136.4, 135.3, 133.8, 132.6, 132.1, 130.0, 129.5, 128.9, 128.5, 128.3, 128.1, 128.0, 125.9, 121.3, 115.4, 112.7, 103.0, 75.7, 66.3, 60.6, 47.3, 28.2, 21.6, 21.2, 19.1, 17.6.

HR-MS (ESI, m/z): calcd for $C_{39}H_{38}N_2O_5S_3$ $[M+Na]^+$: 733.1841. found: 733.1841.

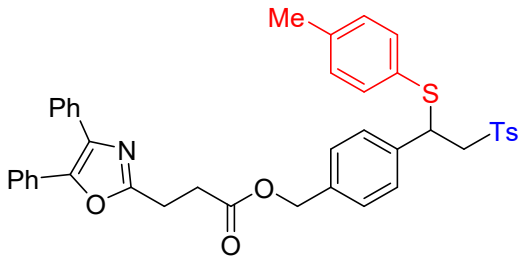


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (59): White solid, m = 74.4 mg, 50% yield. **m.p.**: 63.9-81.2 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.08-7.05 (m, 8H), 6.96 (d, J = 2.4 Hz, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.68 (dd, J = 9.0, 2.5 Hz, 1H), 5.07 (d, J = 1.4 Hz, 2H), 4.53 (dd, J = 10.5, 3.6 Hz, 1H), 3.79 (s, 3H), 3.77-3.73 (m, 3H), 3.60 (dd, J = 14.7, 3.6 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.6, 168.3, 156.1, 144.4, 139.3, 137.9, 136.3, 136.0, 135.5, 133.9, 133.7, 131.2, 130.8, 130.6, 130.1, 129.5, 129.2, 128.9, 128.1, 128.0, 127.9, 115.0, 112.3, 111.7, 101.4, 66.2, 60.5, 55.7, 47.2, 30.4, 21.5, 21.2, 13.4.

HR-MS (ESI, m/z): calcd for $C_{42}H_{38}ClNO_6S_2$ [M+Na]$^+$: 774.1727. found: 774.1728.

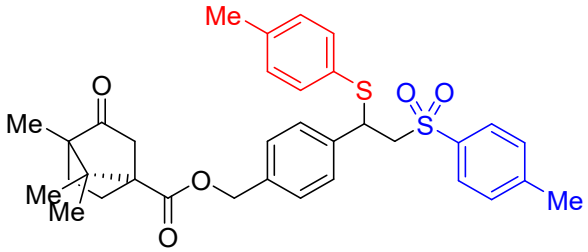


4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 3-(4,5-diphenyloxazol-2-yl)propanoate (60): White solid, m = 63.9 mg, 46% yield. **m.p.**: 95.1-105.3 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.1 Hz, 2H), 7.59 (d, J = 7.0 Hz, 2H), 7.40-7.32 (m, 8H), 7.18 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 8.5 Hz, 6H), 6.99 (d, J = 8.1 Hz, 2H), 5.13-5.08 (m, 2H), 4.54 (dd, J = 10.5, 3.7 Hz, 1H), 3.75 (dd, J = 14.7, 10.5 Hz, 1H), 3.62 (dd, J = 14.7, 3.7 Hz, 1H), 3.24 (t, J = 7.3 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.8, 161.7, 145.5, 144.4, 138.8, 137.7, 136.3, 135.5, 135.2, 133.8, 132.5, 130.1, 129.5, 129.0, 128.8, 128.7, 128.6(2), 128.5(5), 128.4(7), 128.4(1), 128.3(6), 128.1, 127.9(3), 127.8(7), 126.5, 126.3, 65.9, 60.5, 47.3, 31.1, 23.5, 21.6, 21.2.

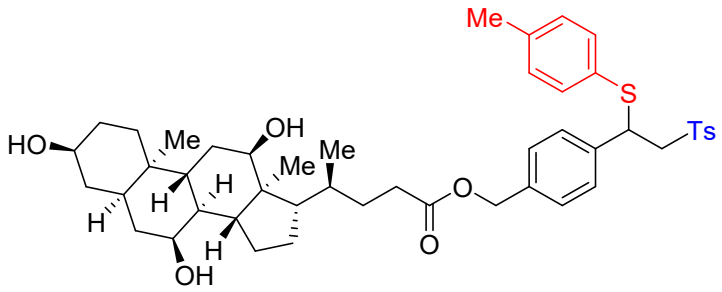
HR-MS (ESI, m/z): calcd for $C_{41}H_{37}NO_5S_2$ [M+Na]$^+$: 710.2011. found: 710.2014.



4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl (1*R*)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptane-1-carboxylate (61): White solid, m = 74.6 mg, 63% yield, dr > 99:1.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 9.8 Hz, 6H), 7.09 (d, J = 7.9 Hz, 2H), 7.05 (d, J = 7.6 Hz, 2H), 5.21-5.16 (m, 2H), 4.53 (dd, J = 10.4, 3.7 Hz, 1H), 3.76 (dd, J = 14.7, 10.4 Hz, 1H), 3.62 (dd, J = 14.7, 3.7 Hz, 1H), 2.47-2.42 (m, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.07-2.02 (m, 1H), 1.95-1.90 (m, 1H), 1.72-1.67 (m, 1H), 1.11 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H).

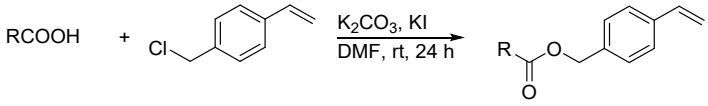
Data is consistent with that reported in the literature.[3]



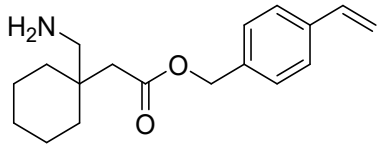
4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl (4*S*)-4-((3*S*,5*R*,7*S*,8*S*,9*R*,10*R*,12*R*,13*S*,14*R*,17*S*)-3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-17-yl)pentanoate (62): White oil, m = 123.6 mg, 77% yield, dr > 99:1.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.11-7.09 (m, 4H), 7.06 (d, J = 8.0 Hz, 4H), 5.02 (s, 2H), 4.54 (dd, J = 10.5, 3.6 Hz, 1H), 3.95 (s, 1H), 3.82 (s, 1H), 3.77 (dd, J = 14.7, 10.6 Hz, 1H), 3.60 (dd, J = 14.7, 3.6 Hz, 1H), 3.45-3.39 (m, 1H), 2.45-2.39 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.31-2.17 (m, 4H), 1.92-1.36 (m, 20H), 1.10-1.07 (m, 1H), 0.98 (d, J = 6.0 Hz, 4H), 0.86 (s, 3H), 0.65 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.1, 144.4, 138.8, 137.6, 133.7, 130.0, 129.5, 128.5, 128.1, 127.9, 126.4, 73.0, 71.9, 68.5, 65.5, 47.3, 47.0, 46.5, 41.7, 41.5, 39.6, 39.5, 35.2, 34.8, 34.7, 31.3, 30.9, 30.4, 27.5, 26.4, 23.2, 22.5, 21.6, 21.2, 17.3, 12.5.
HR-MS (ESI, m/z): calcd for $C_{47}H_{62}O_7S_2$ $[M+Na]^+$: 825.3835. found: 825.3834.

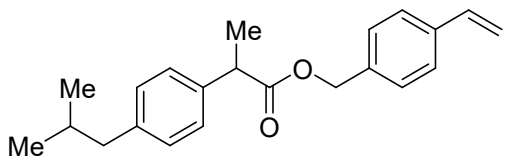
General procedure for the synthesis of complex olefin.



To a stirring suspension of complex substrate carboxylic acid (1.0 equiv.), K_2CO_3 (1.5 equiv.), and KI (1.5 equiv.) in DMF (0.5 M) was added 4-vinylbenzyl chloride (1.1 equiv.). The mixture was stirred for 24 h at room temperature, then diluted with water and extracted with ethyl acetate. The combined organic layers were washed for three times with water, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel with PE/EA to produce corresponding alkene (**61-71**).[3]

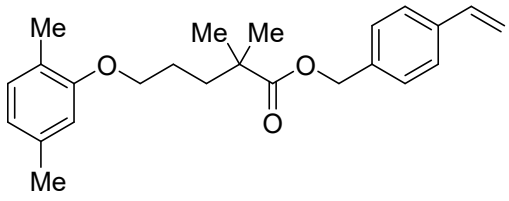


4-vinylbenzyl 2-(1-(aminomethyl)cyclohexyl)acetate (63): White oil, m = 113.5 mg, 16% yield.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 (d, J = Hz, 2H), 7.19 (d, J = Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.74 (d, J = Hz, 1H), 5.24 (d, J = Hz, 1H), 4.42 (s, 2H), 2.98 (s, 2H), 2.31 (s, 2H), 1.47-1.25 (m, 12H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.5, 137.0, 136.5, 127.2, 126.4, 113.9, 64.9, 36.8, 29.7, 25.6, 22.8.
HR-MS (ESI, m/z): calcd for $C_{18}H_{25}NO_2$ $[M+H]^+$: 288.1964. found: 288.1968.

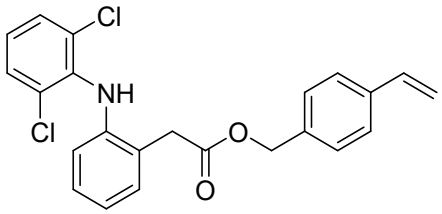


4-vinylbenzyl 2-(4-isobutylphenyl)propanoate (64): White oil, m = 750.7 mg, 93% yield.

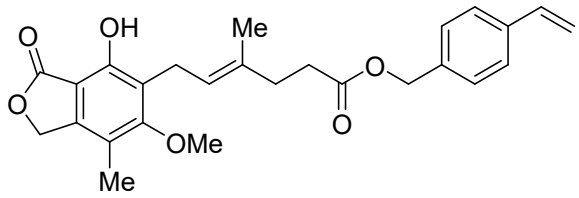
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.1 Hz, 2H), 7.21-7.18 (m, 4H), 7.09 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 5.11-5.06 (m, 2H), 3.76-3.73 (m, 1H), 2.46 (d, J = 7.2 Hz, 2H), 1.89-1.82 (m, 1H), 1.51 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.5, 140.6, 137.7, 137.4, 136.4, 135.7, 129.4, 128.1, 127.3, 126.3, 114.2, 66.1, 45.2, 45.1, 30.3, 22.4, 18.5.
HR-MS (ESI, m/z): calcd for $C_{22}H_{26}O_2$ $[M+Na]^+$: 345.1830. found: 345.1834.



4-vinylbenzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (65): White oil, m = 85.3 mg, 66% yield.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.4 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 6.66 (d, J = 7.4 Hz, 1H), 6.59 (s, 1H), 5.75 (d, J = 17.6, 10.9 Hz, 1H), 5.25 (d, J = Hz, 1H), 5.09 (s, 2H), 3.88 (t, J = 5.6 Hz, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 1.75-1.69 (m, 4H), 1.24 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 177.4, 157.2, 137.6, 136.6, 136.5, 136.2, 130.6, 128.4, 126.5, 123.7, 121.0, 114.3, 112.1, 68.0, 66.0, 42.3, 37.3, 25.4(0), 25.3(6), 21.6, 16.1.
HR-MS (ESI, m/z): calcd for $C_{27}H_{23}NO_3$ $[M+Na]^+$: 389.2093. found: 389.2096.



4-(1-(*p*-tolylthio)-2-tosylethyl)benzyl 2-(2-((2,6-dichlorophenyl)amino)phenyl) acetate (66): White oil, m = 373.2 mg, 36% yield.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.4 Hz, 1H), 7.15-7.12 (m, 1H), 6.99-6.95 (m, 2H), 6.87 (s, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 5.76 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.9 Hz, 1H), 5.17 (s, 2H), 3.86 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.2, 142.8, 137.9, 137.8, 136.4, 135.1, 131.0, 129.5, 128.9, 128.6, 128.1, 126.5, 124.3, 124.0, 122.1, 118.4, 114.5, 66.9, 38.7.
HR-MS (ESI, m/z): calcd for $C_{23}H_{19}Cl_2NO_2$ $[M+Na]^+$: 434.0691. found: 434.0695.



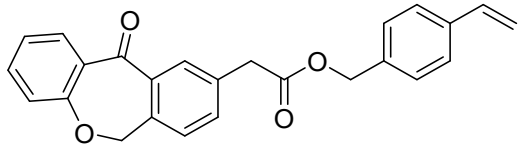
4-vinylbenzyl (*E*)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoate (67): White oil, m = 863.1 mg,

79% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ =7.67 (s, 1H), 7.38 (d, *J* = Hz, 2H), 7.27 (d, *J* = Hz, 2H), 6.72-6.68 (dd, *J* = Hz, 1H), 5.75 (d, *J* = Hz, 1H), 5.27-5.23 (m, 2H), 5.18 (s, 2H), 5.04 (s, 2H), 3.74 (s, 3H), 3.38 (d, *J* = Hz, 2H), 2.46-2.43 (m, 2H), 2.32 (t, *J* = Hz, 2H), 2.13 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.2, 172.9, 172.8, 163.7, 153.6, 153.5, 144.1, 144.0, 137.5, 136.3, 135.5, 134.1, 128.3, 128.1, 127.6, 126.3, 122.8, 122.1, 116.7, 114.3, 106.3, 70.1, 65.9, 61.0, 34.6, 33.1, 33.0, 22.6, 16.1, 11.6.

HR-MS (ESI, m/z): calcd for $C_{26}H_{28}O_6$ $[M+Na]^+$: 459.1784. found: 459.1786.

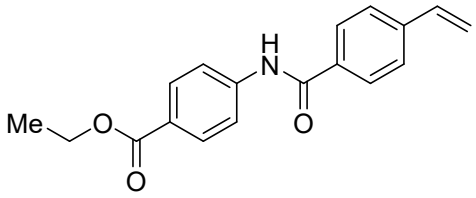


4-vinylbenzyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-9-yl)acetate (68): White solid, m = 935.4 mg, 97% yield. **m.p.**: 70.1-73.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.1 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43-7.36 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 5.19 (s, 2H), 5.13 (s, 2H), 3.69 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.8, 171.2, 160.5, 140.5, 137.7, 136.3(7), 136.3(5), 135.6, 135.2, 132.8, 132.5, 129.5, 129.3, 128.5, 127.8, 127.7, 126.4, 125.2, 121.1, 114.4, 73.6, 66.5, 40.2.

HR-MS (ESI, m/z): calcd for $C_{27}H_{23}NO_3$ $[M+Na]^+$: 407.1259. found: 407.1259.

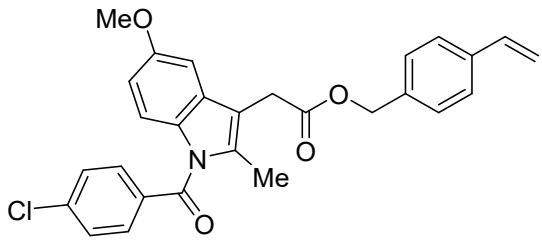


ethyl 4-(4-vinylbenzamido)benzoate (69): White solid, m = 687.9 mg, 78% yield. **m.p.**: 177.8-183.1 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.7 Hz, 2H), 8.01 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 4.39-4.35 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.2, 165.5, 142.2, 141.3, 135.8, 133.5, 130.8, 127.5, 126.6, 126.1, 122.9, 119.3, 116.5, 60.9, 31.5, 30.1, 14.4.

HR-MS (ESI, m/z): calcd for $C_{18}H_{13}NO_3$ $[M+Na]^+$: 318.1106. found: 318.1102.



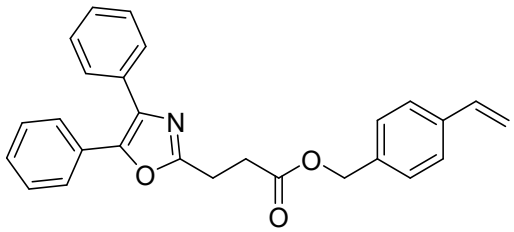
4-vinylbenzyl 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetate (70): White solid, m

= 894.1 mg, 75% yield. **m.p.**: 95.9-97.6 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 6.93-6.88 (m, 2H), 6.73-6.67 (m, 2H), 5.76 (d, J = 17.6 Hz, 1H), 5.28 (d, J = 10.9 Hz, 1H), 5.13 (s, 2H), 3.76 (s, 3H), 3.71 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.7, 168.3, 156.1, 139.3, 137.7, 136.3, 135.9, 135.2, 133.9, 131.2, 130.8, 130.6, 129.1, 128.5, 126.4, 115.0, 114.5, 112.5, 111.9, 101.2, 66.6, 55.6, 30.5, 13.4.

HR-MS (ESI, m/z): calcd for $C_{28}H_{24}ClNO_4$ $[M+Na]^+$: 496.1292. found: 496.1290.

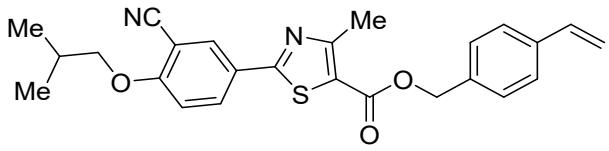


4-vinylbenzyl 3-(4,5-diphenyloxazol-2-yl)propanoate (71): White oil, m = 903.1 mg, 88% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62-7.61 (m, 2H), 7.56-7.54 (m, 2H), 7.37-7.29 (m, 10H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 5.16 (s, 2H), 3.21 (t, J = 7.3 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.9, 161.8, 145.5, 137.6, 136.4, 135.4, 135.2, 132.6, 130.0, 129.1, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 126.6, 126.4, 114.4, 66.3, 31.2, 23.6.

HR-MS (ESI, m/z): calcd for $C_{27}H_{23}NO_3$ $[M+Na]^+$: 432.1576. found: 432.1580.

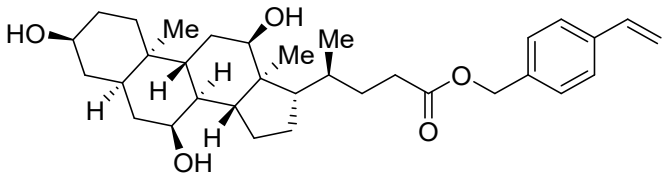


4-vinylbenzyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (72): White solid, m = 1.02 g, 95% yield. **m.p.**: 106.9-110.8 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, J = 2.2 Hz, 1H), 8.08 (dd, J = 8.8, 2.3 Hz, 1H), 7.44-7.38 (m, 4H), 7.00 (d, J = 8.9 Hz, 1H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.32 (s, 2H), 5.28 (d, J = 10.9 Hz, 1H), 3.90 (d, J = 6.5 Hz, 2H), 2.77 (s, 3H), 2.23-2.17 (m, 1H), 1.09 (d, J = 6.7 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.4, 162.5, 161.8, 161.6, 137.8, 136.3, 135.0, 132.6, 132.1, 128.5, 126.5, 125.9, 121.5, 115.4, 114.5, 112.6, 103.0, 75.7, 66.7, 28.2, 19.1, 17.6.

HR-MS (ESI, m/z): calcd for $C_{25}H_{24}N_2O_3S$ $[M+H]^+$: 433.1586. found: 433.1589.



4-vinylbenzyl (*S*)-4-((3*S*,5*R*,7*S*,8*S*,9*R*,10*R*,12*R*,13*S*,14*R*,17*S*)-3,7,12-trihydroxy-

10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (73): White solid, m = 791.3 mg, 60% yield. **m.p.**: 134.9-141.1 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ =7.40 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 18.1 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 5.11-5.06 (m, 2H), 3.95 (s, 1H), 3.83 (s, 1H), 3.45-3.42 (m, 1H), 2.44-2.39 (m, 1H), 2.31-2.16 (m, 6H), 1.94-1.23 (m, 20H), 1.12-1.05 (m, 1H), 0.97 (d, J = 6.1 Hz, 4H), 0.88 (s, 3H), 0.65 (s, 3H).

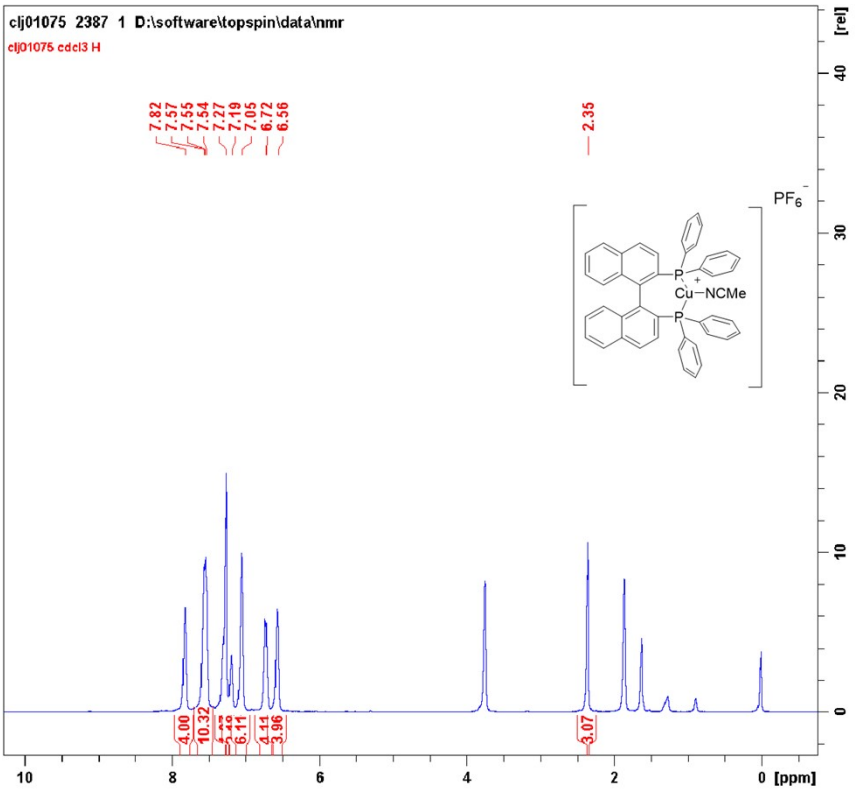
^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.2, 137.5, 136.4, 135.6, 128.5, 126.4, 114.3, 73.1, 71.9, 68.5, 65.8, 47.0, 46.4, 41.6, 41.5, 39.5, 35.3(2), 35.2(5), 34.8, 34.7, 31.4, 30.9, 30.4, 28.2, 27.5, 26.3, 23.2, 22.5, 17.3, 12.5.

HR-MS (ESI, m/z): calcd for $C_{33}H_{48}O_5$ $[M+Na]^+$: 547.3399. found: 547.3402.

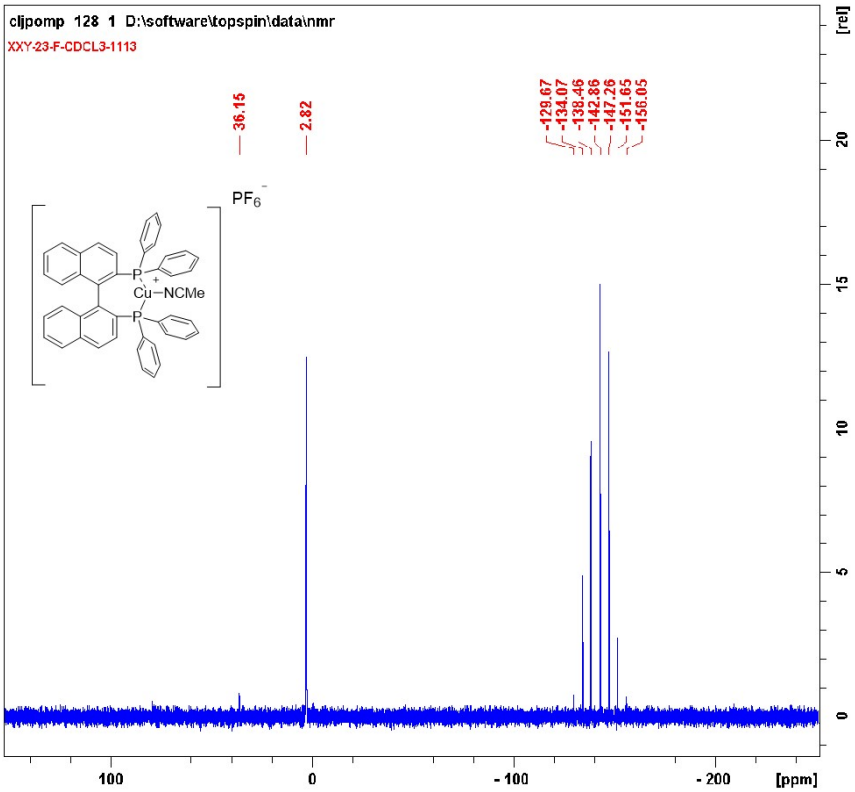
9. References

1. Q. Yan, W. Cui, X. Song, G. Xu, M. Jiang, K. Sun, J. Lv and D. Yang, *Org. Lett.*, 2021, **23**, 3663-3668.
2. Y. Shen, Q. Zheng, Z. N. Chen, D. Wen, J. H. Clark, X. Xu and T. Tu, *Angew. Chem. Int. Ed.*, 2021, **60**, 4125-4132.
3. F. Tang, Y.-S. Feng, W. Yang and H.-J. Xu, *Org. Lett.*, 2024, **26**, 236-240.
4. X. Zhou, Z. Peng, P. G. Wang, Q. Liu and T. Jia, *Org. Lett.*, 2021, **23**, 1054-1059.

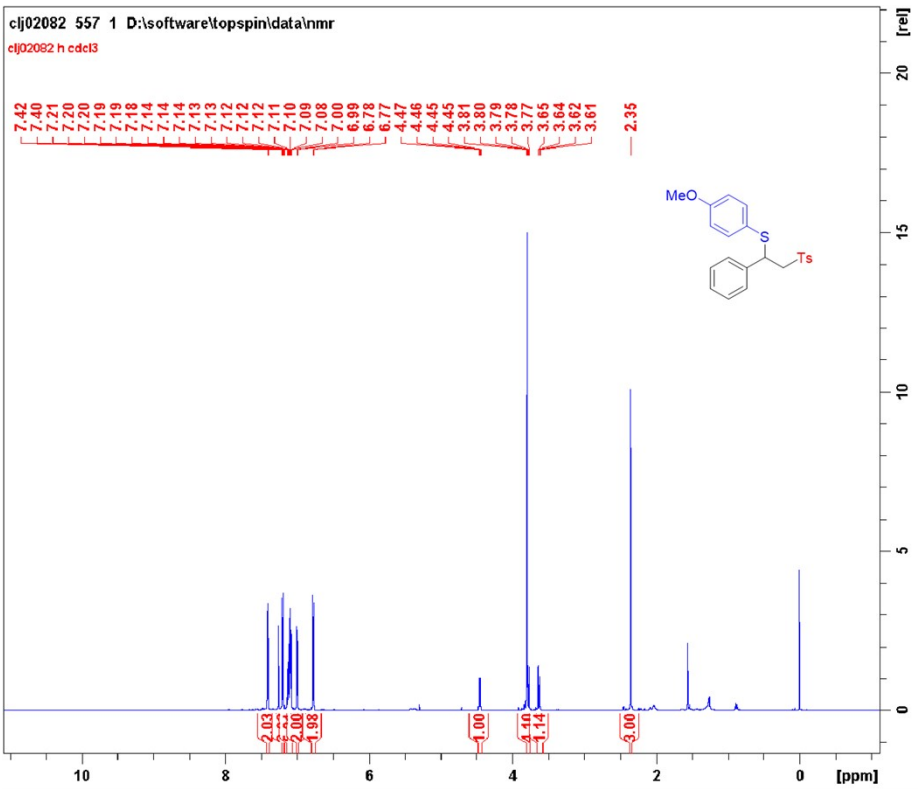
10. NMR and HR-MS (ESI) spectra



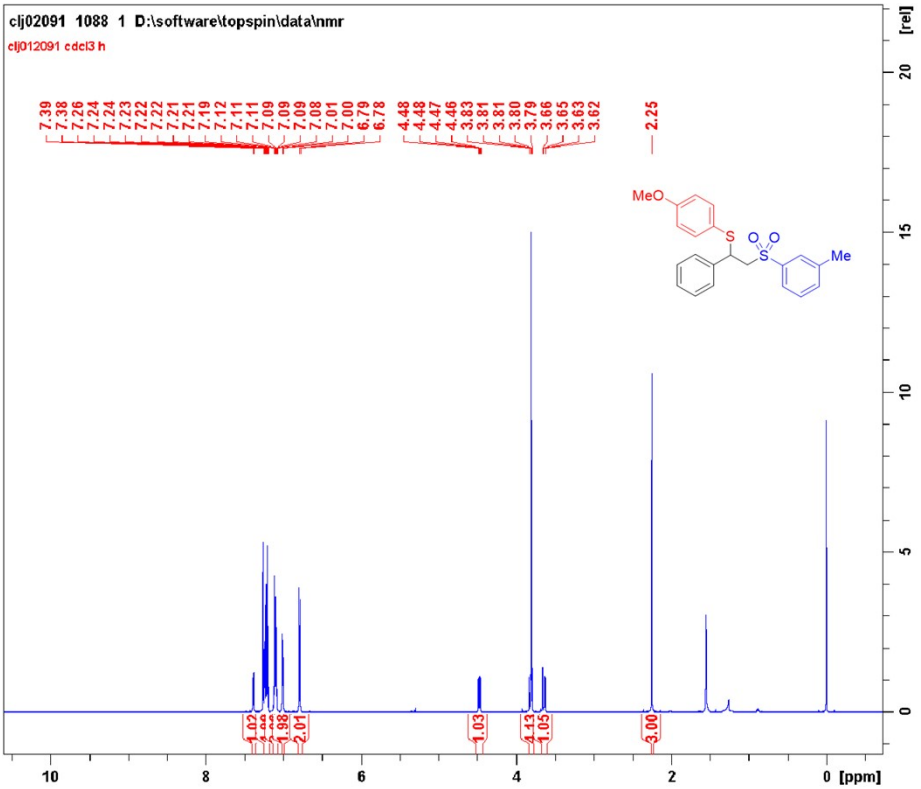
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **BINAP-Cu**.



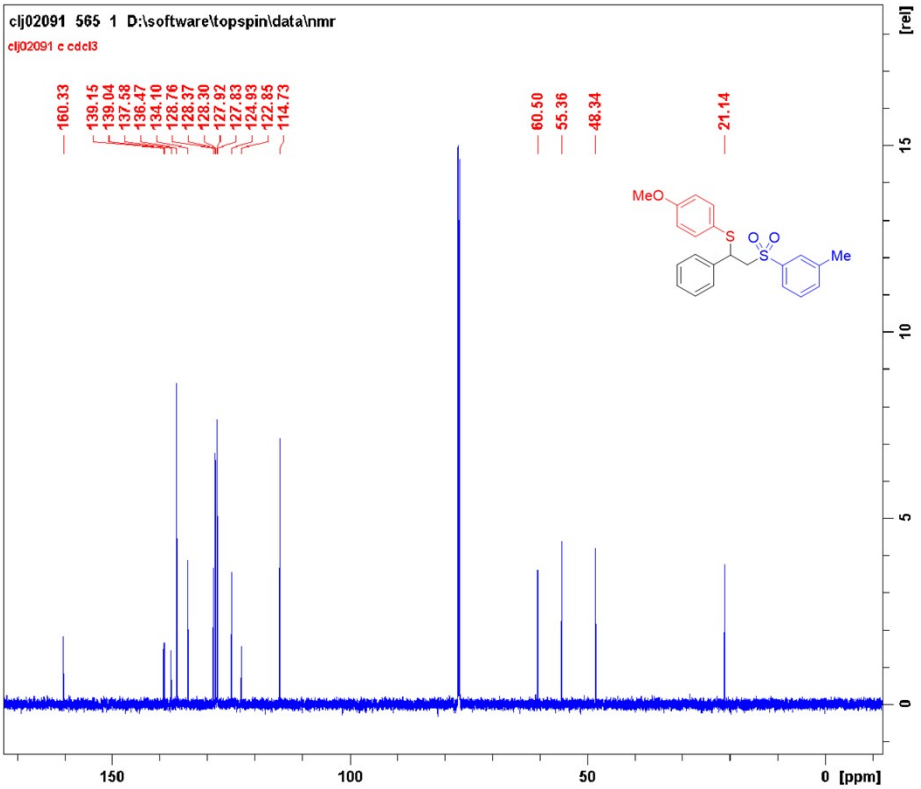
^{31}P NMR (243 MHz, $CDCl_3$) spectrum of **BINAP-Cu**.



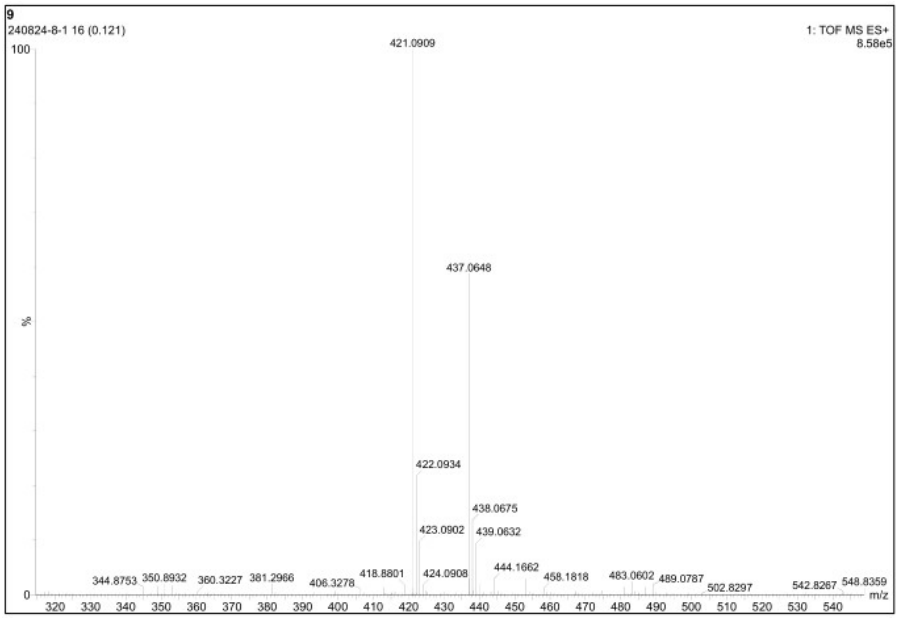
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5**.



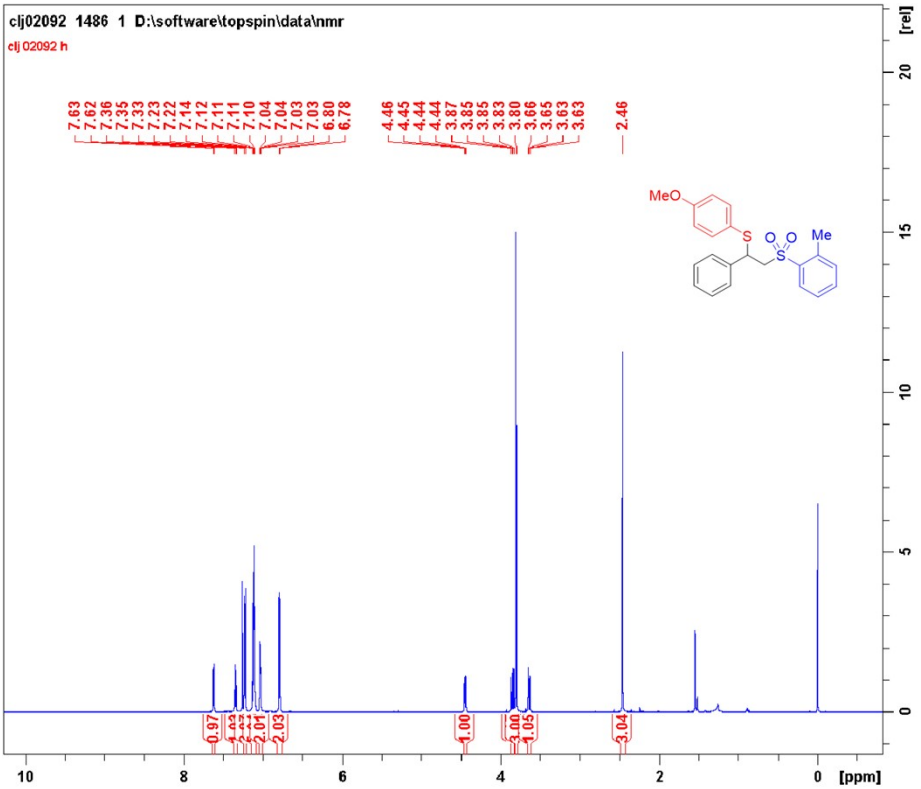
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6**.



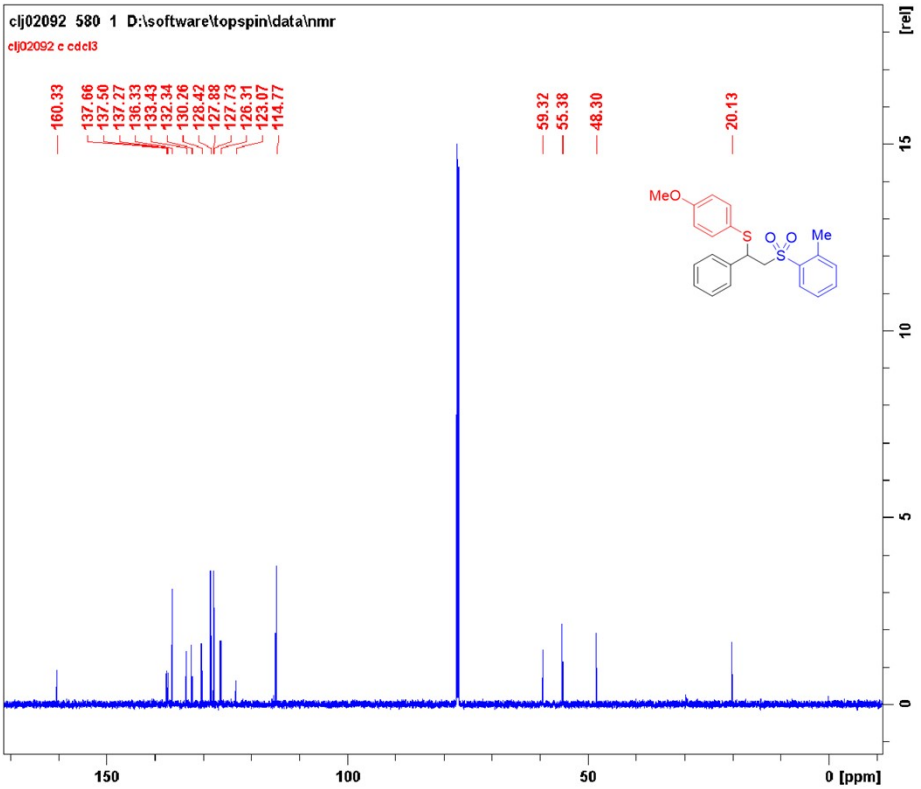
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6**.



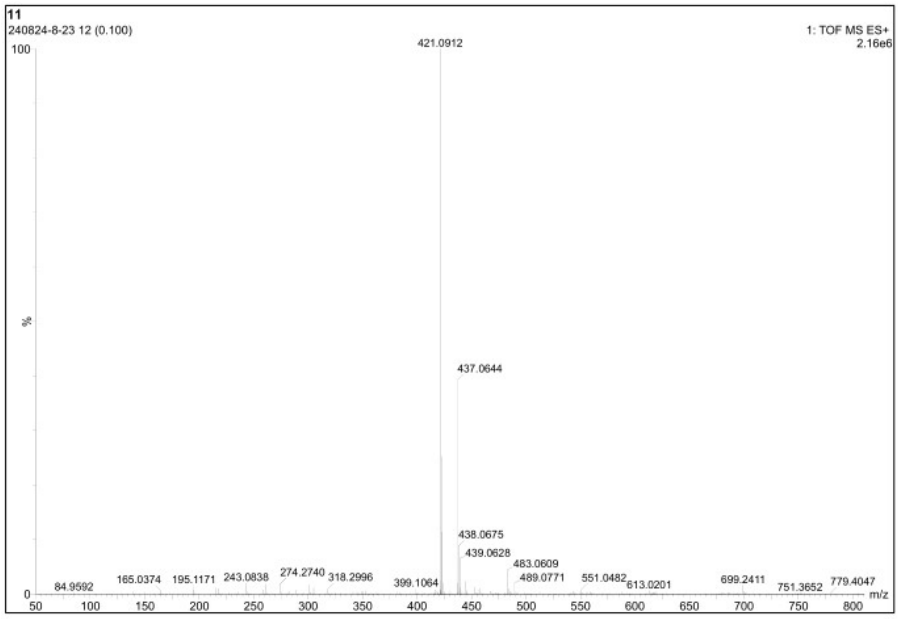
HR-MS (ESI) spectrum of **6**.



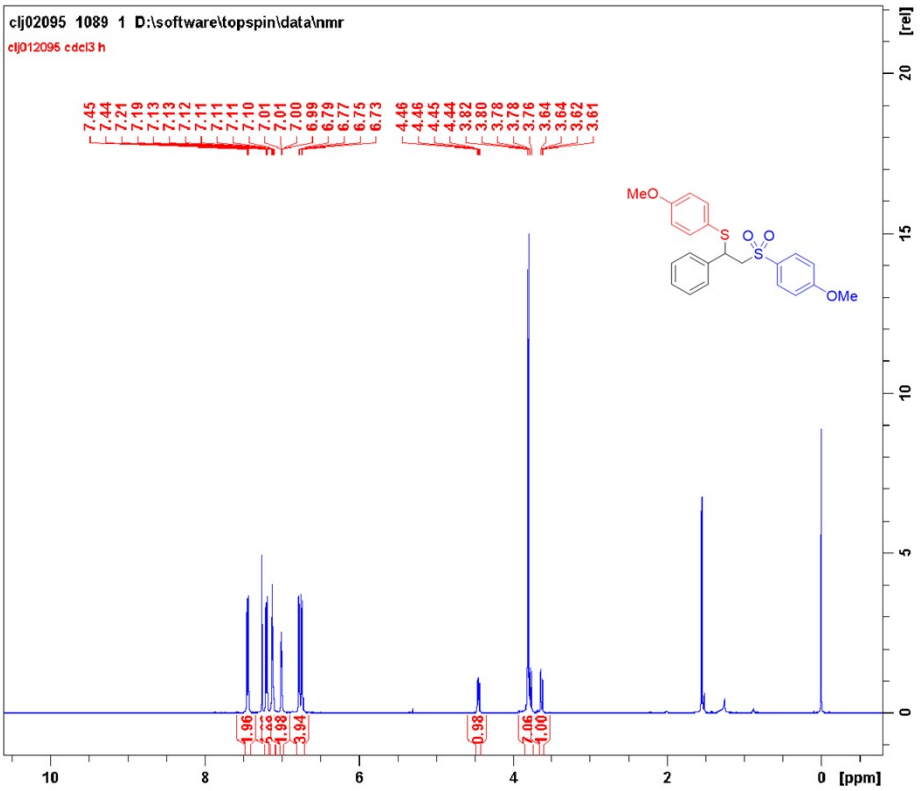
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **7**



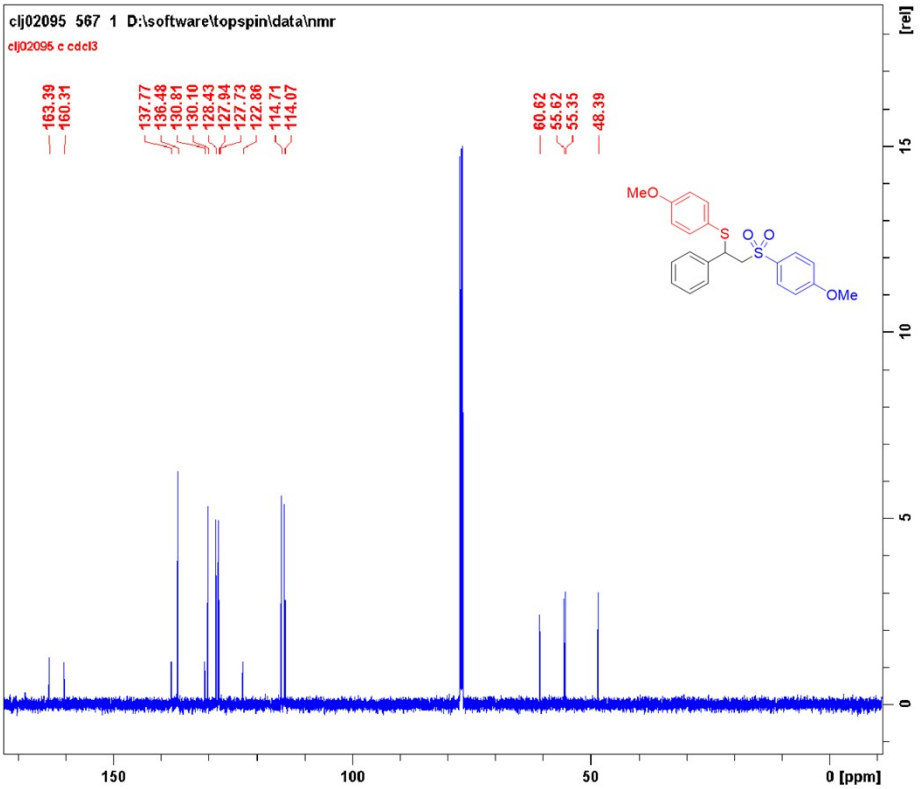
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **7**.



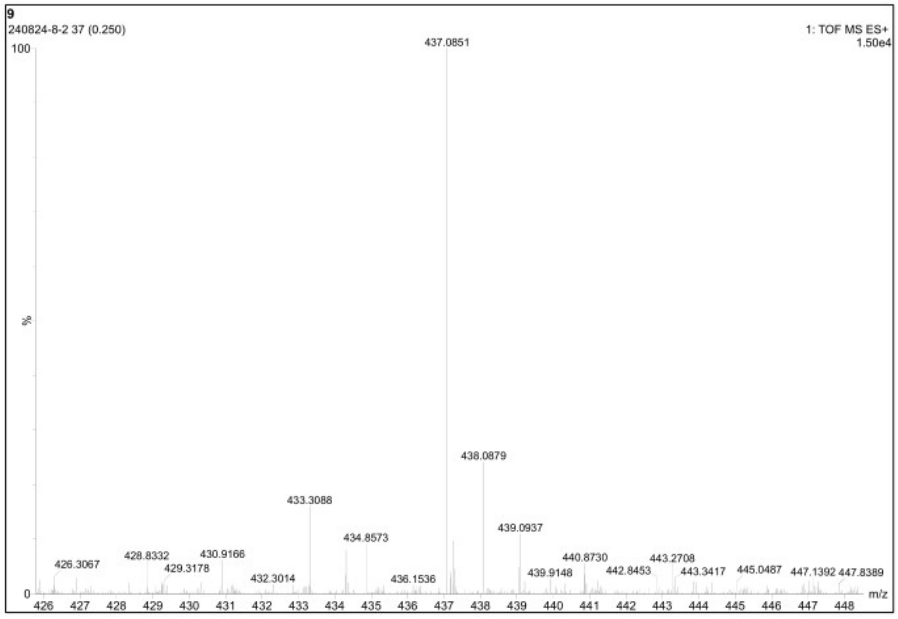
HR-MS (ESI) spectrum of **7**.



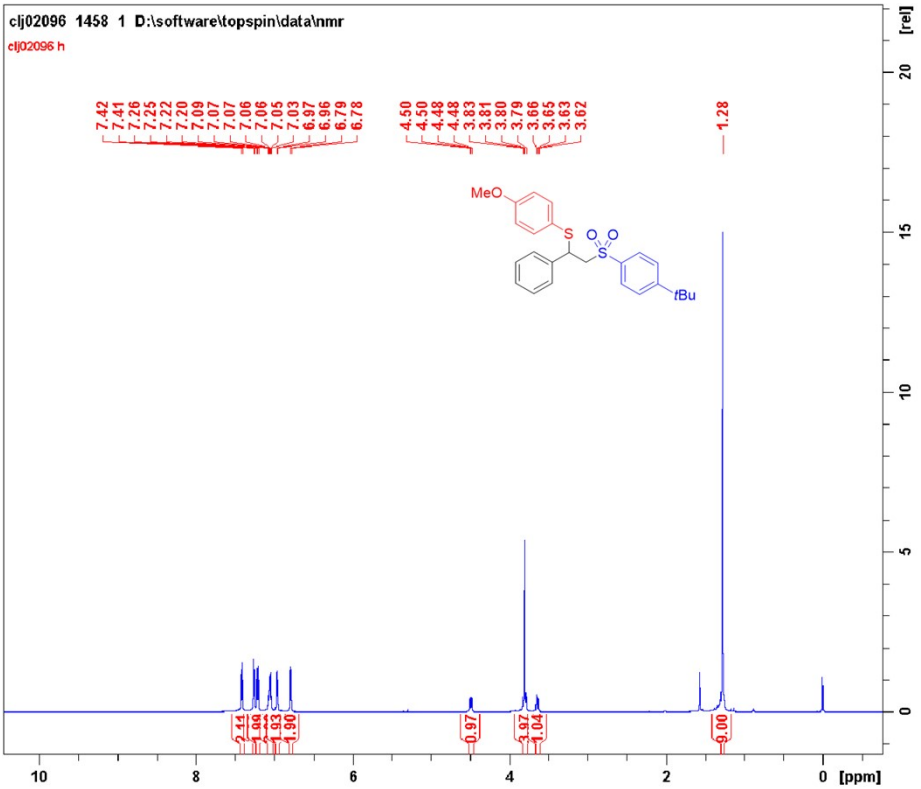
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **8**.



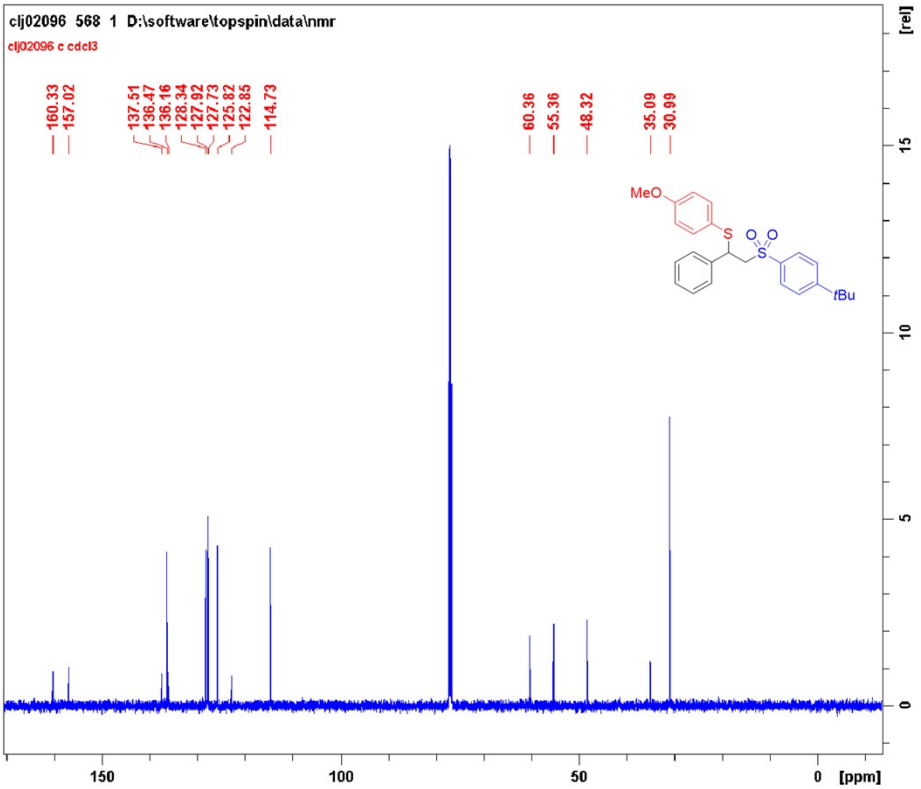
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **8**.



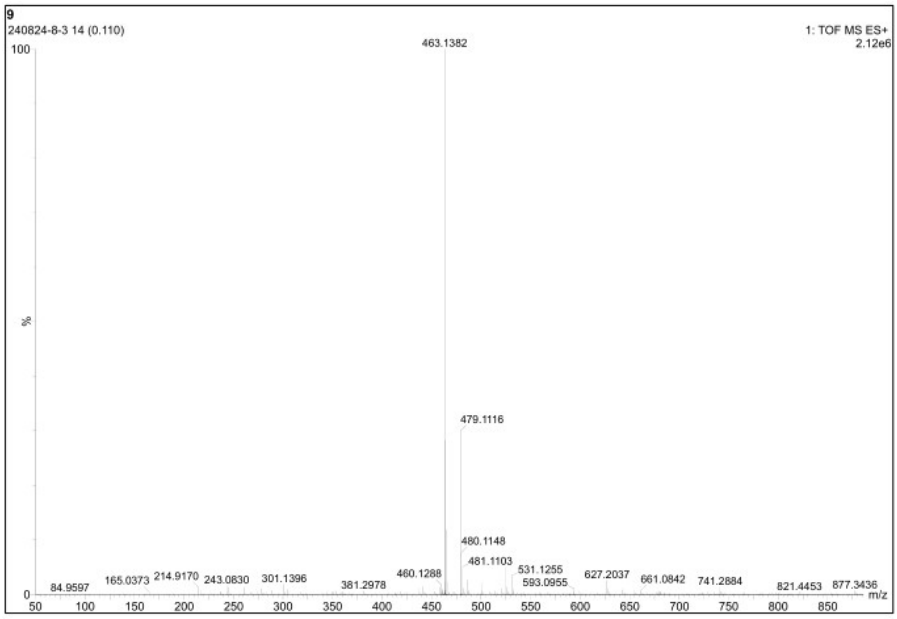
HR-MS (ESI) spectrum of **8**.



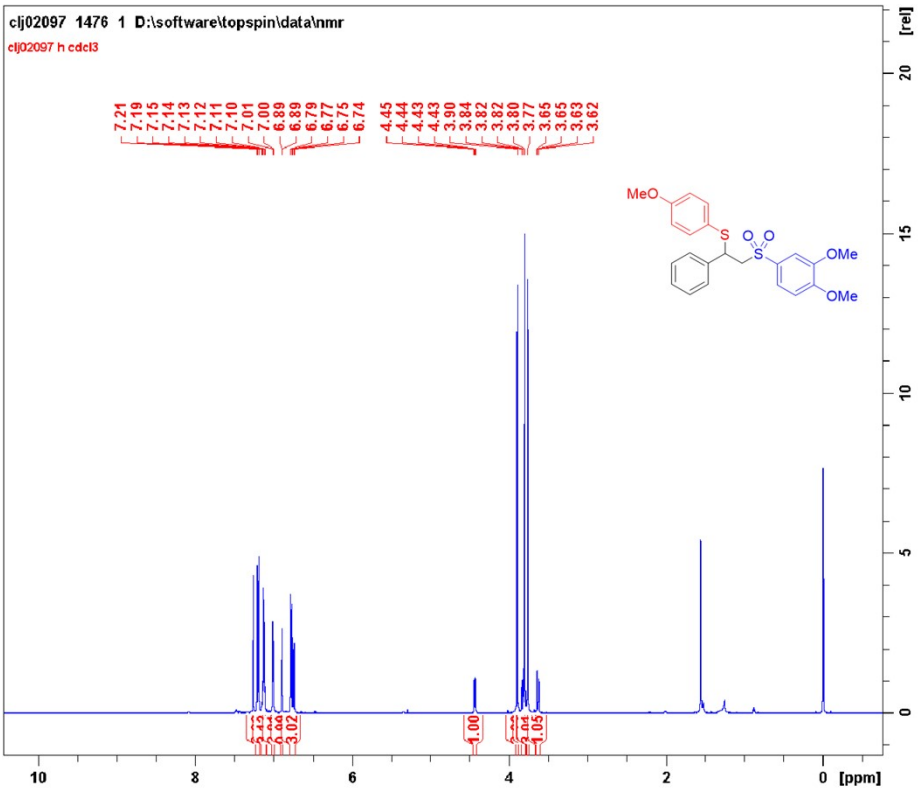
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9**.



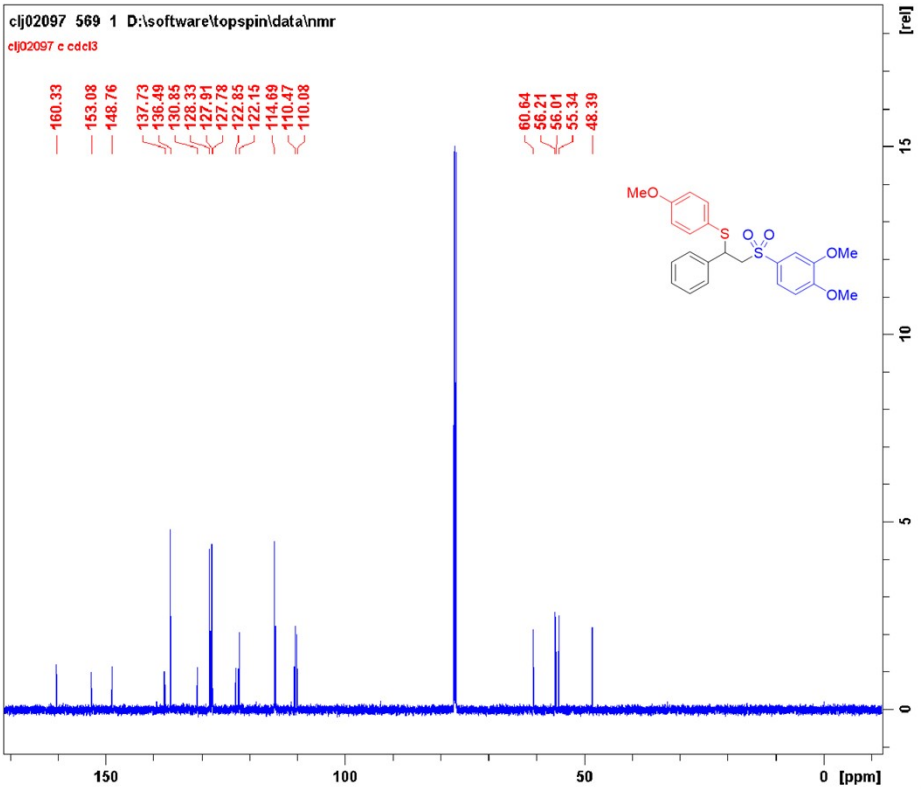
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **9**.



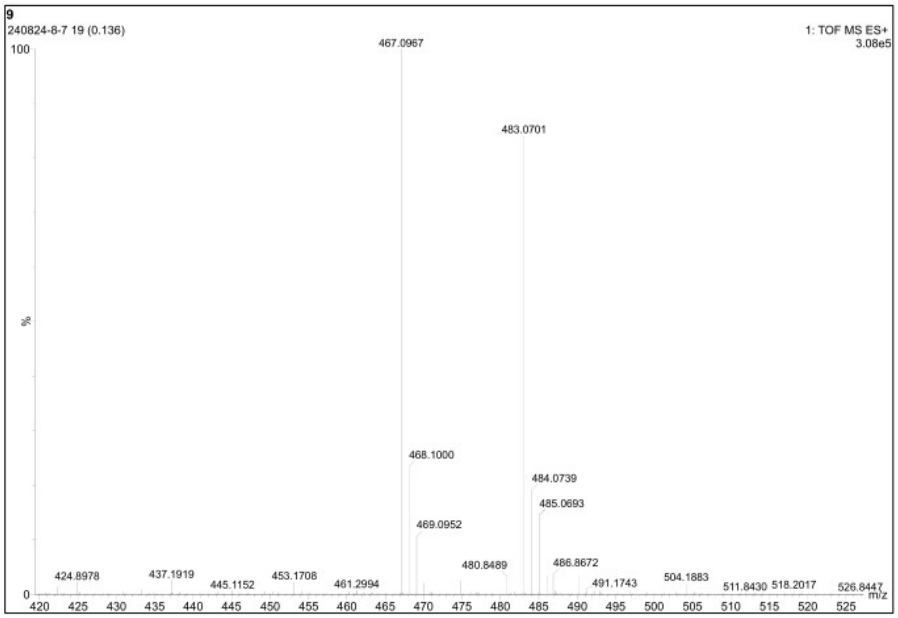
HR-MS (ESI) spectrum of **9**.



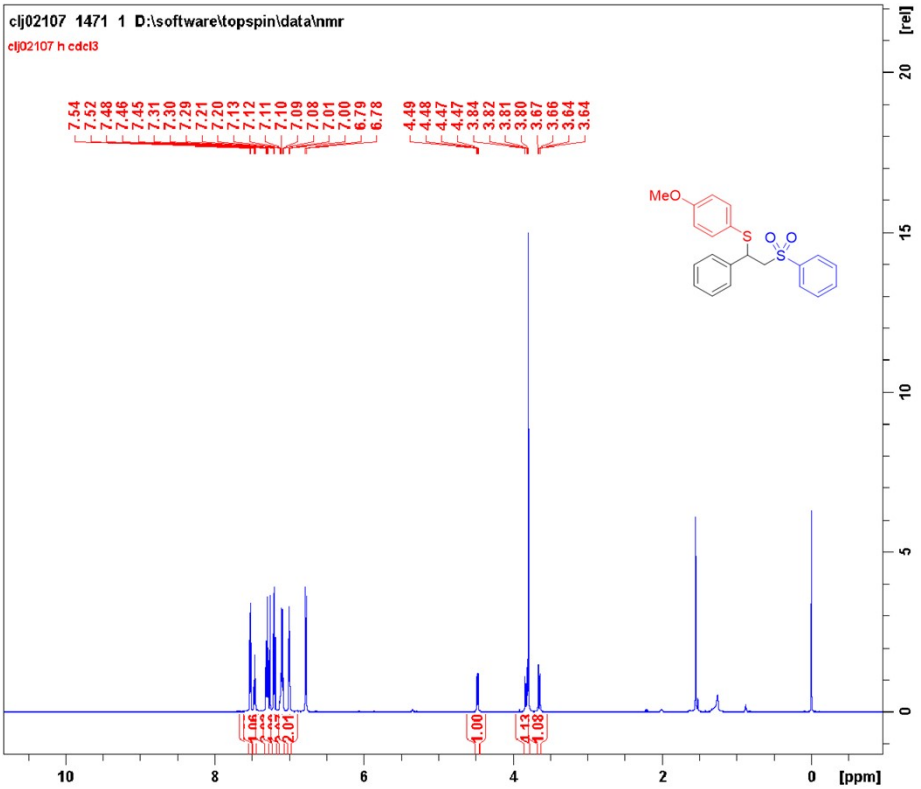
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **10**.



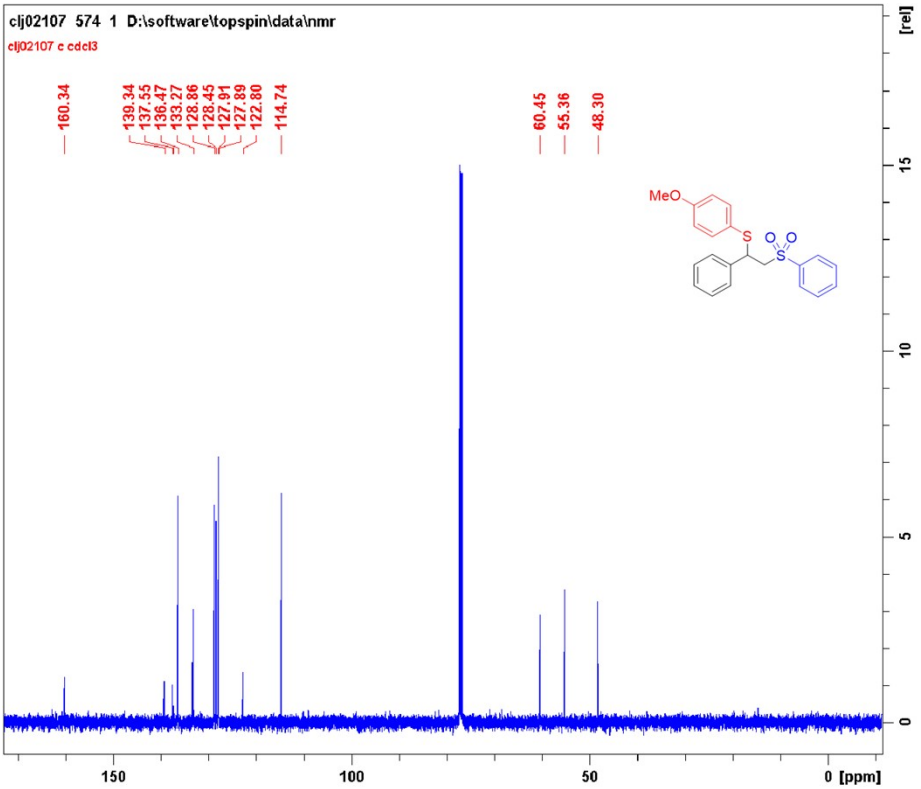
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **10**.



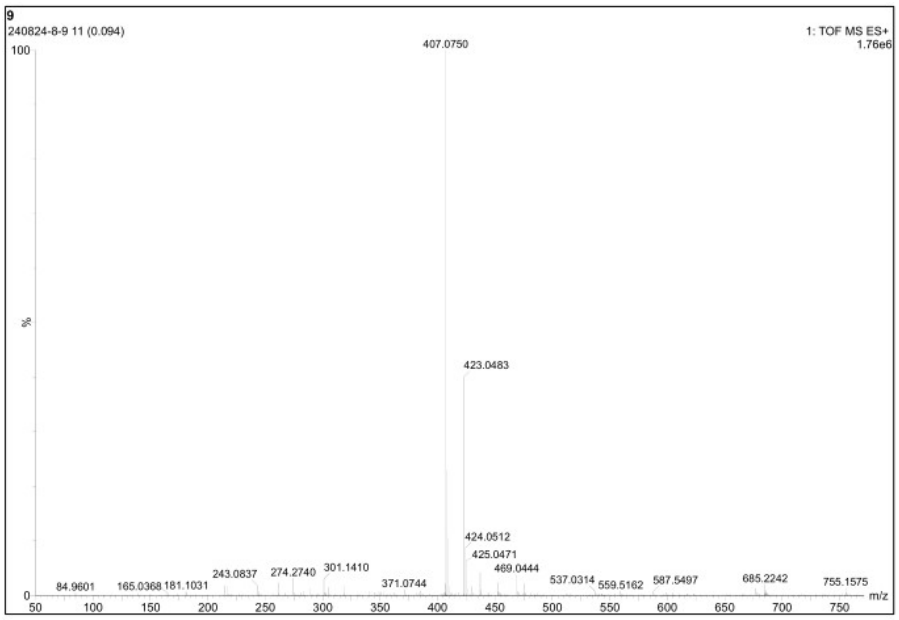
HR-MS (ESI) spectrum of **10**.



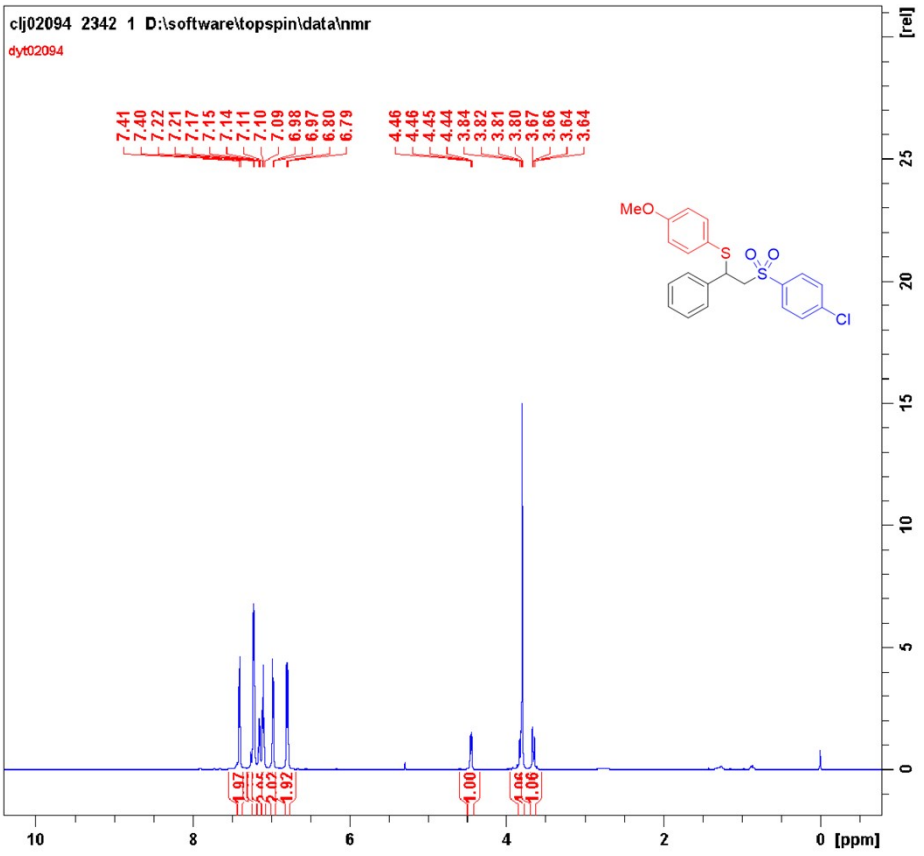
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **11**.



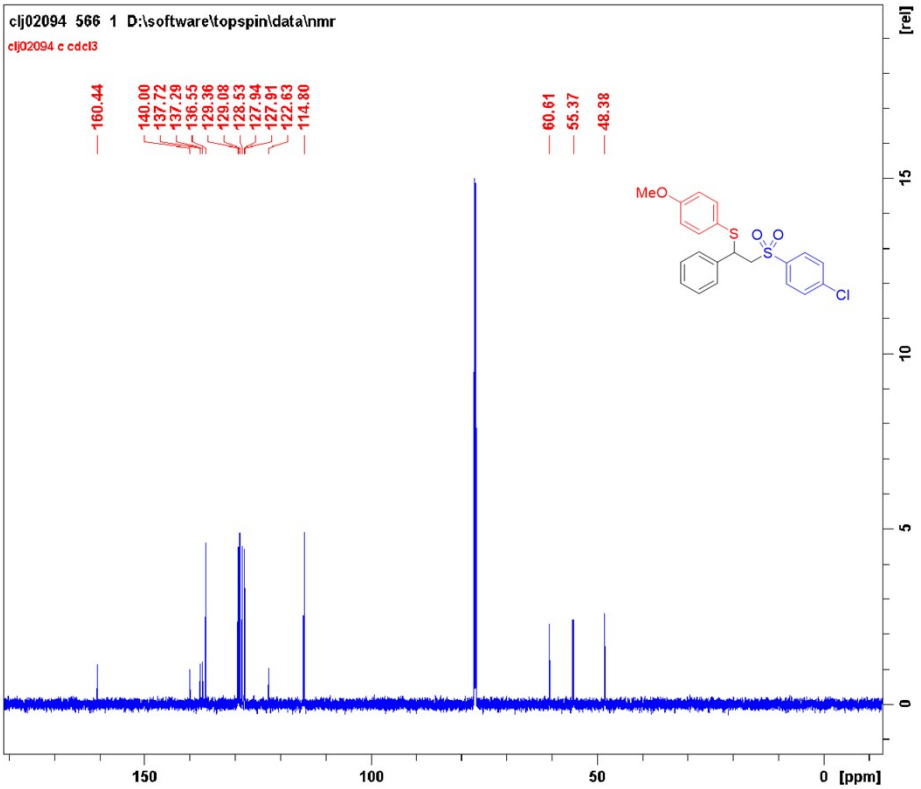
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **11**.



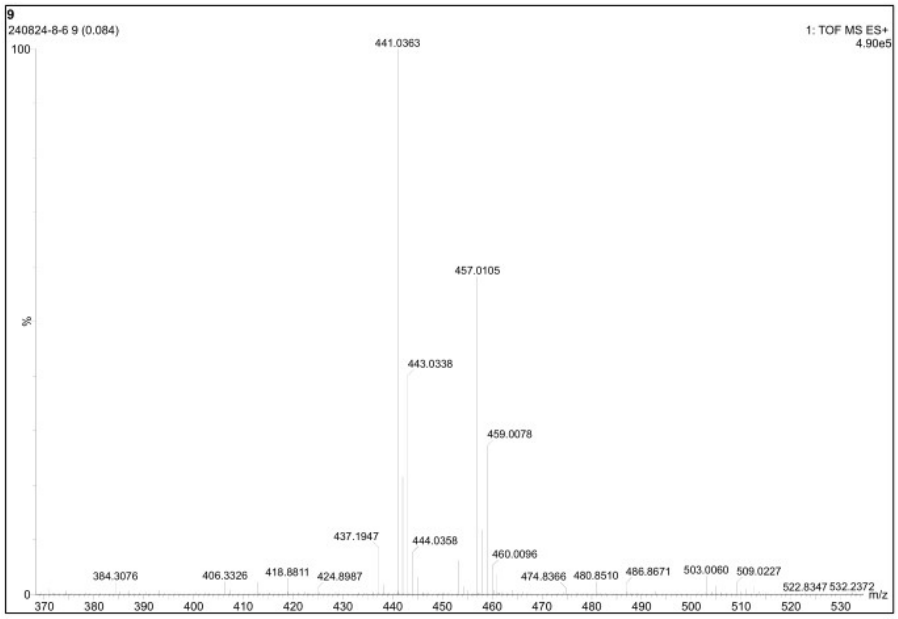
HR-MS (ESI) spectrum of **11**.



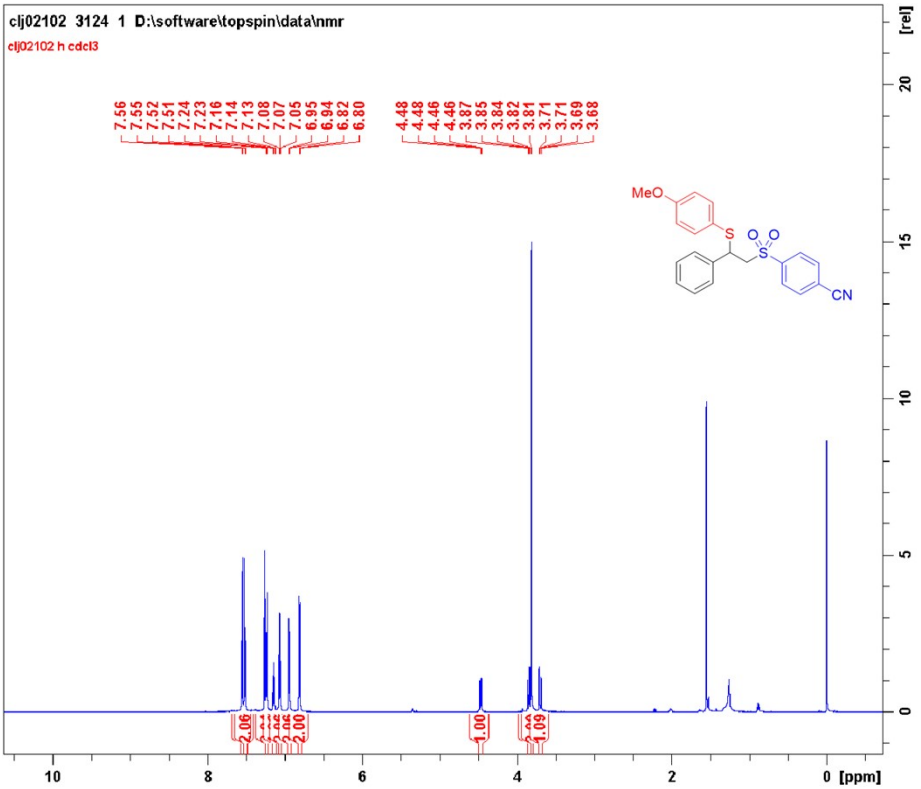
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **12**.



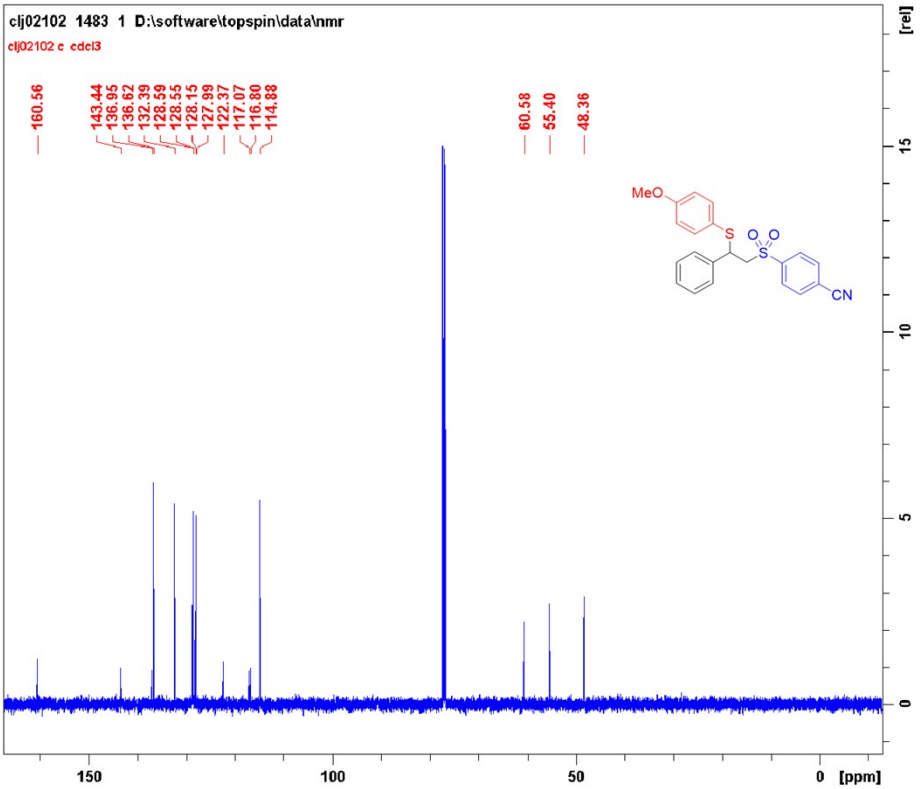
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **12**.



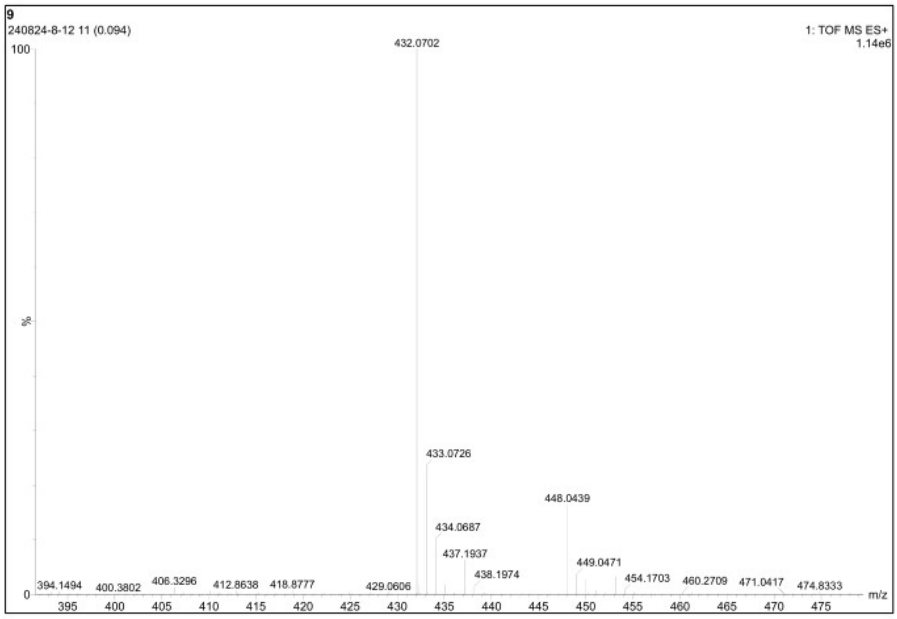
HR-MS (ESI) spectrum of **12**.



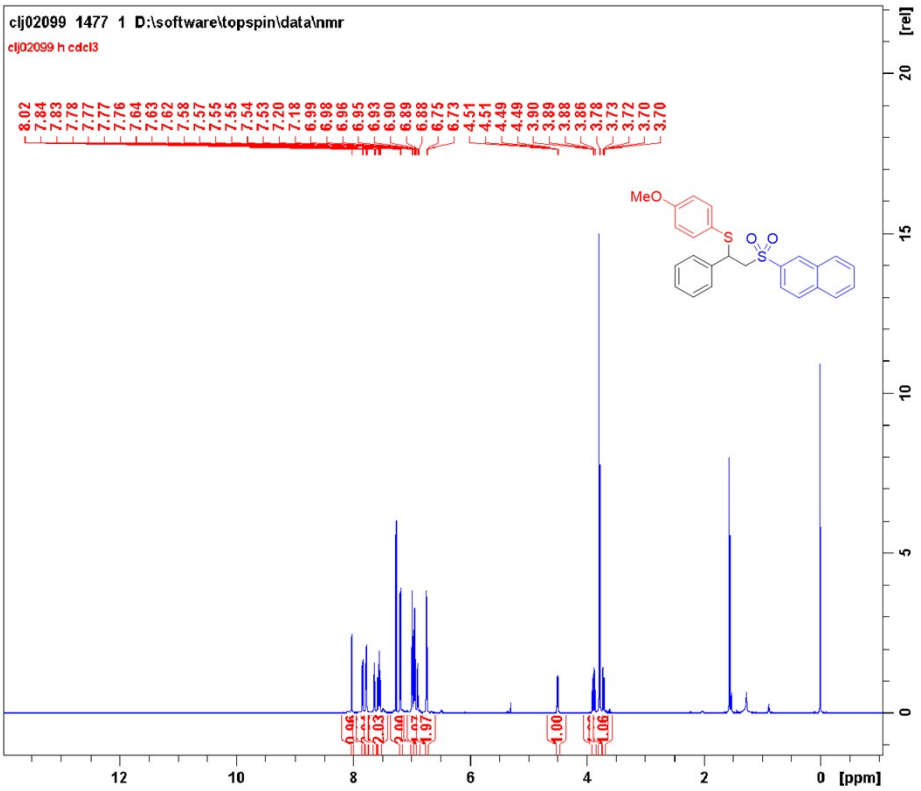
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **13**.



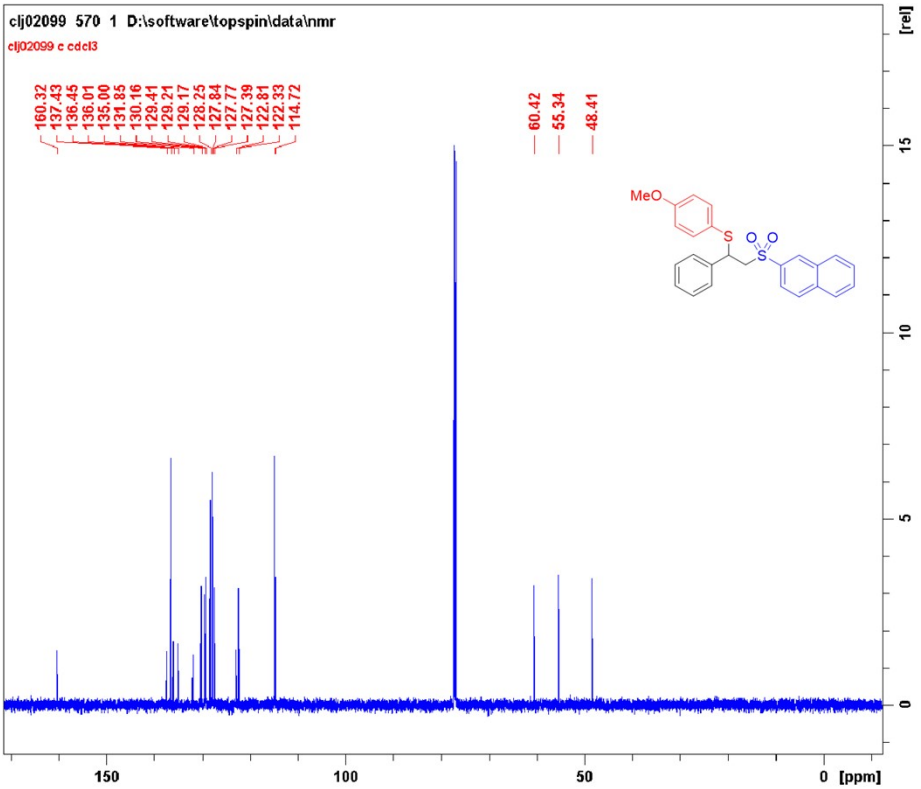
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **13**.



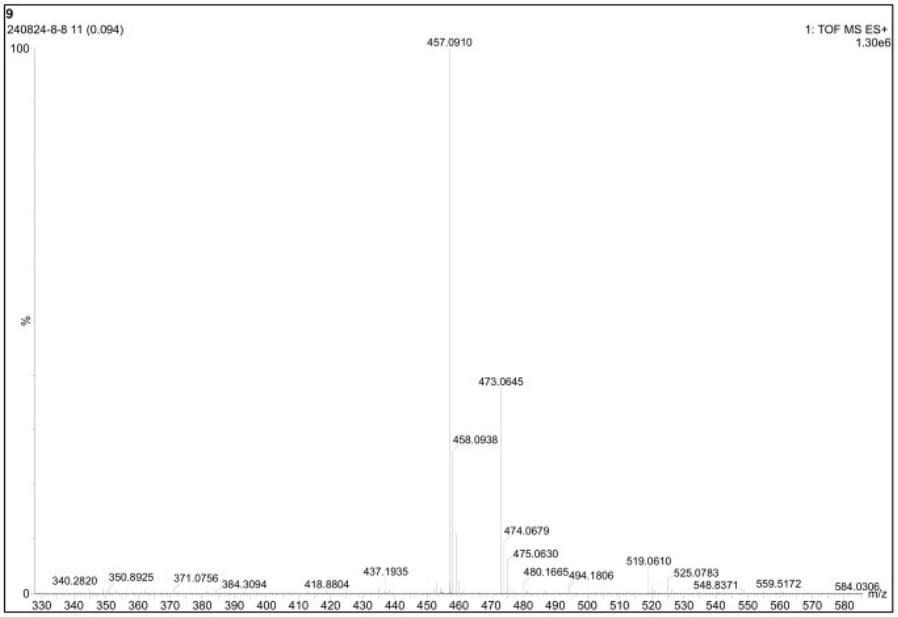
HR-MS (ESI) spectrum of **13**.



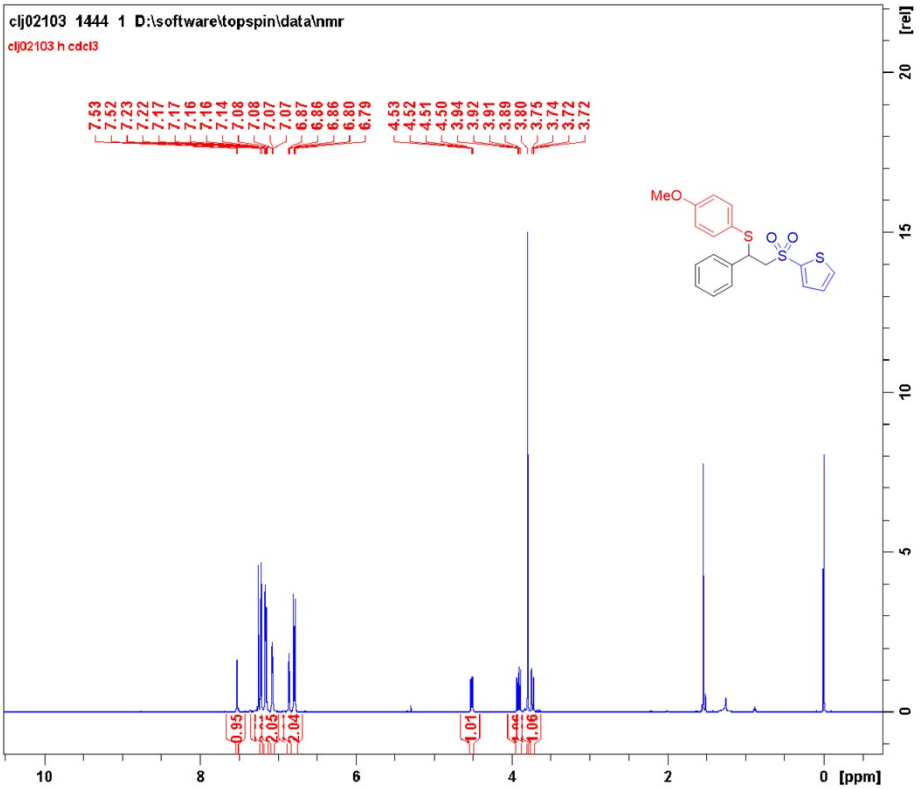
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14**.



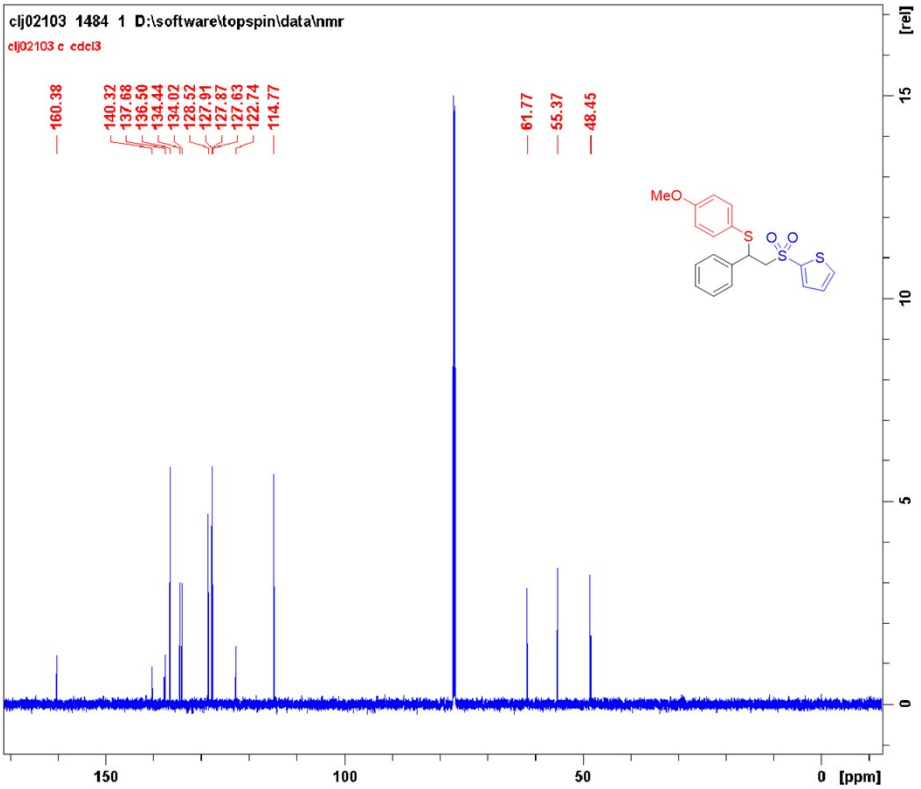
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14**.



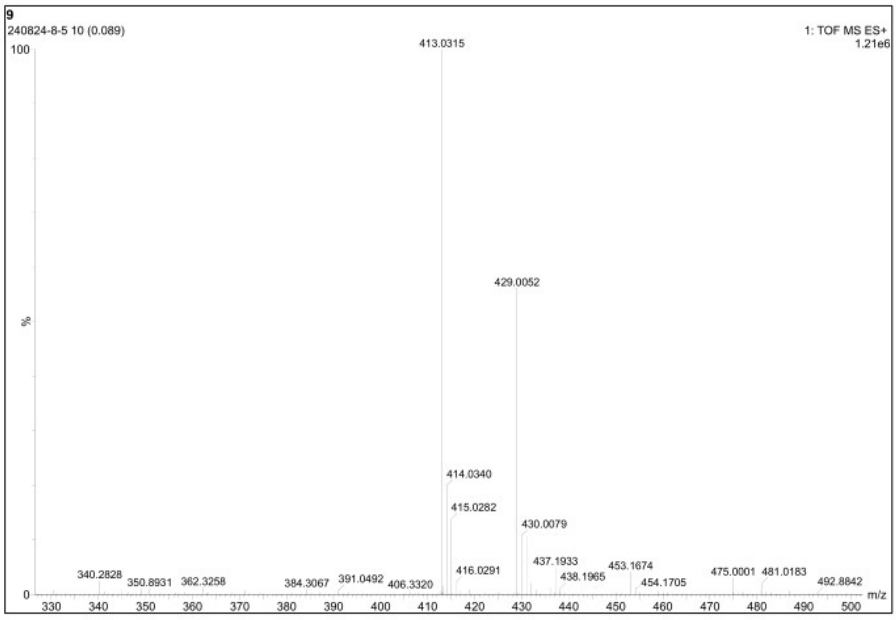
HR-MS (ESI) spectrum of **14**.



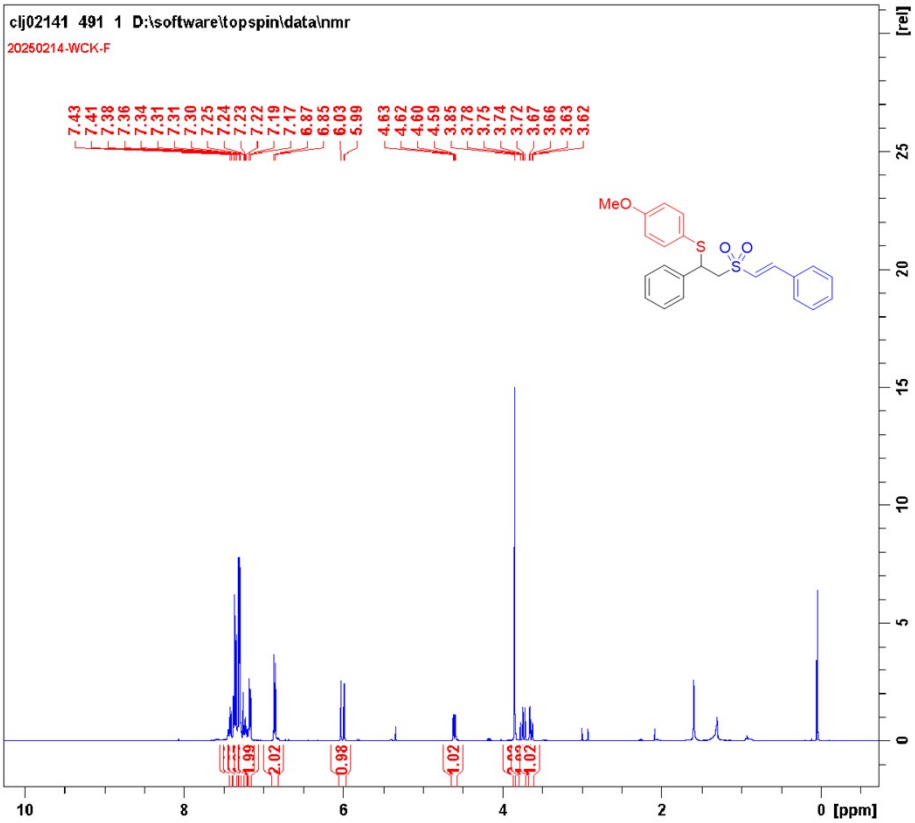
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **15**.



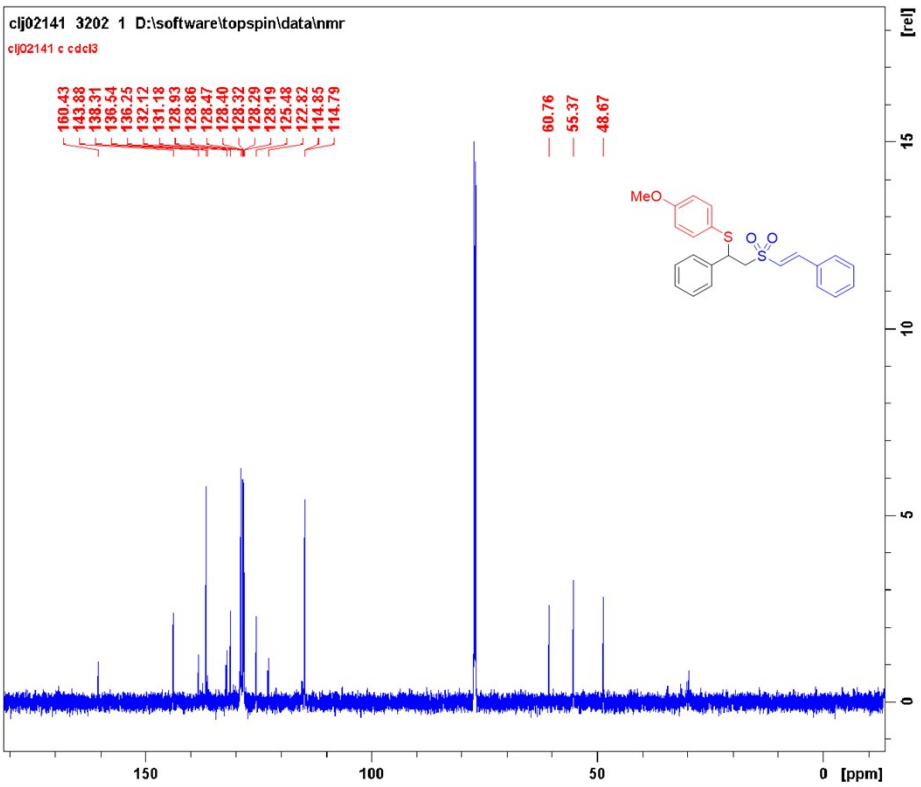
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **15**.



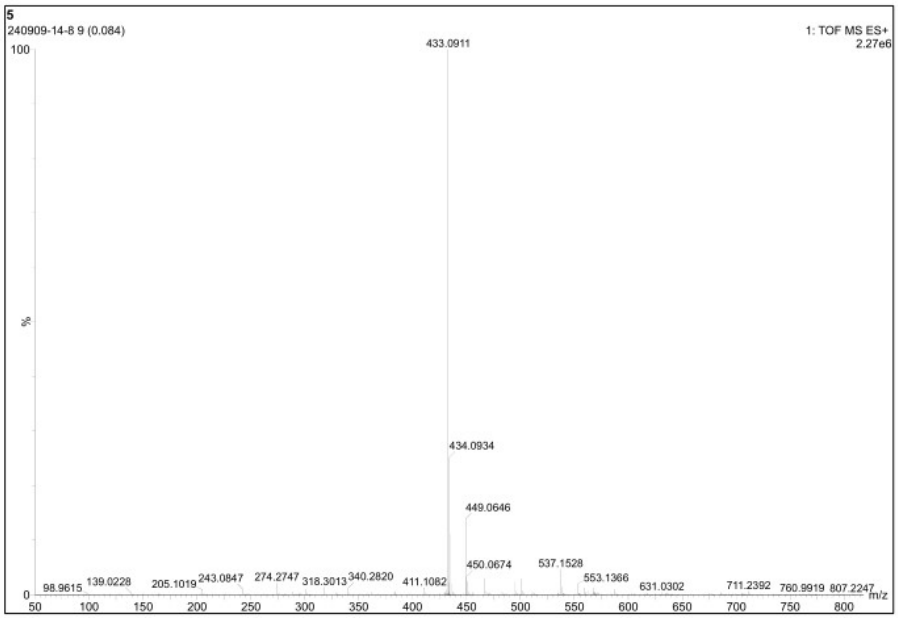
HR-MS (ESI) spectrum of **15**.



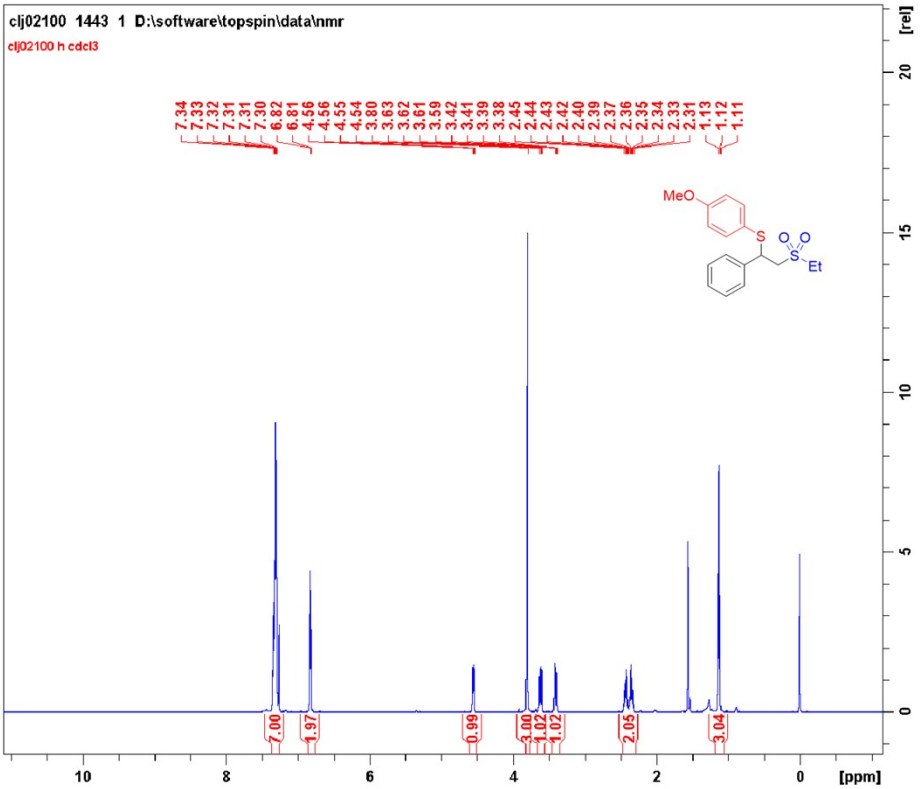
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16**.



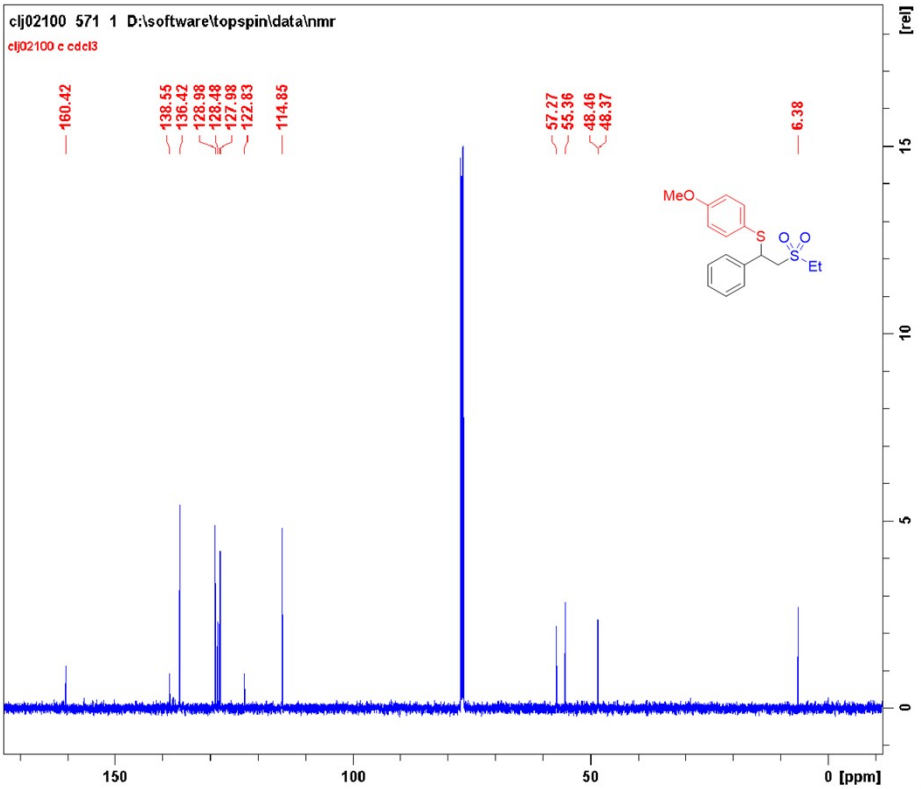
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **16**.



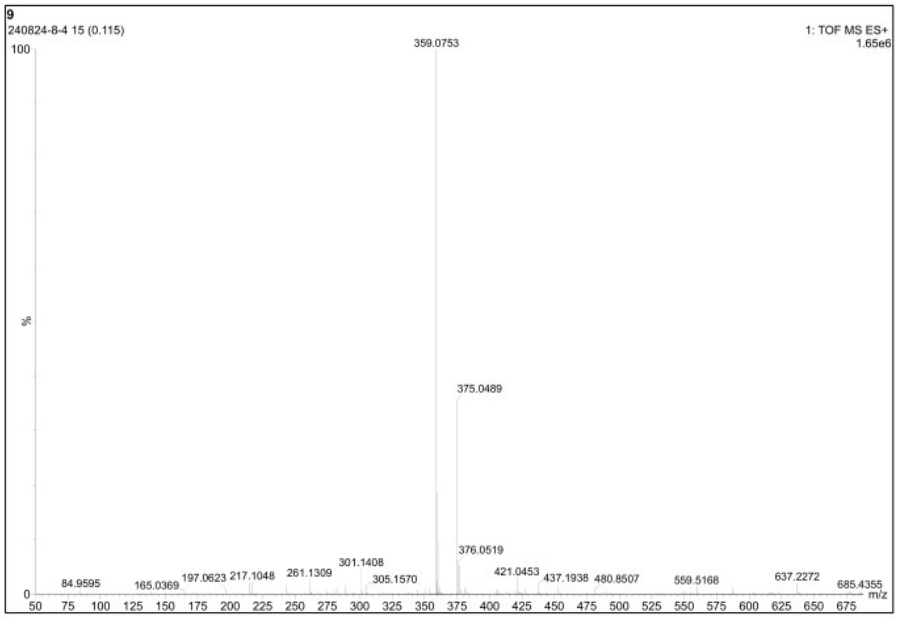
HR-MS (ESI) spectrum of **16**.



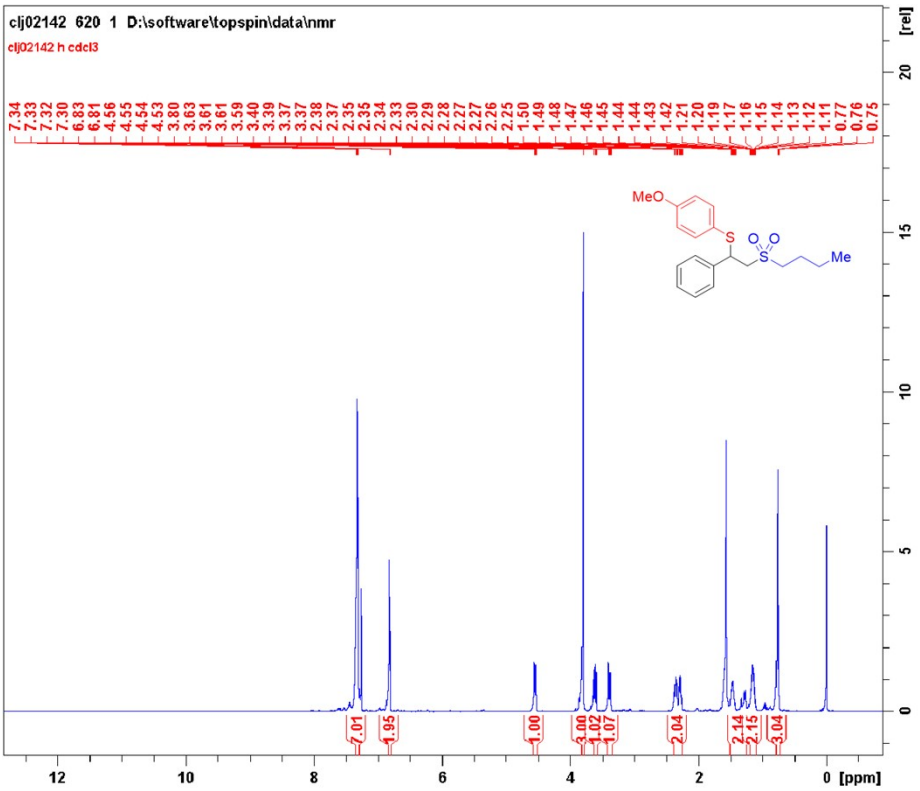
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **17**.



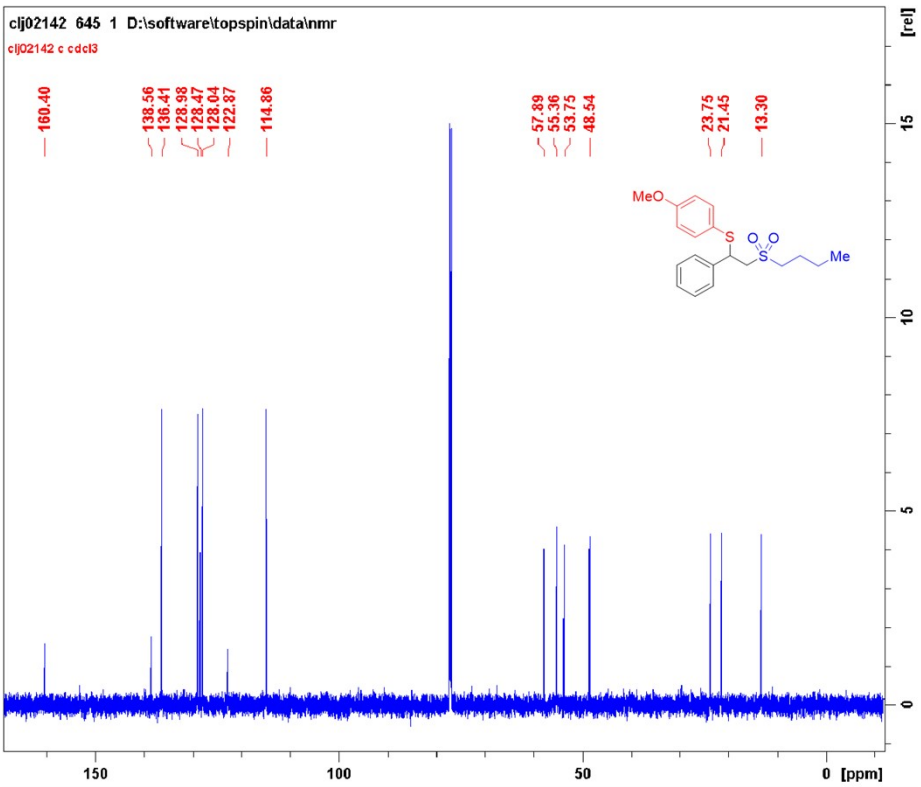
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **17**.



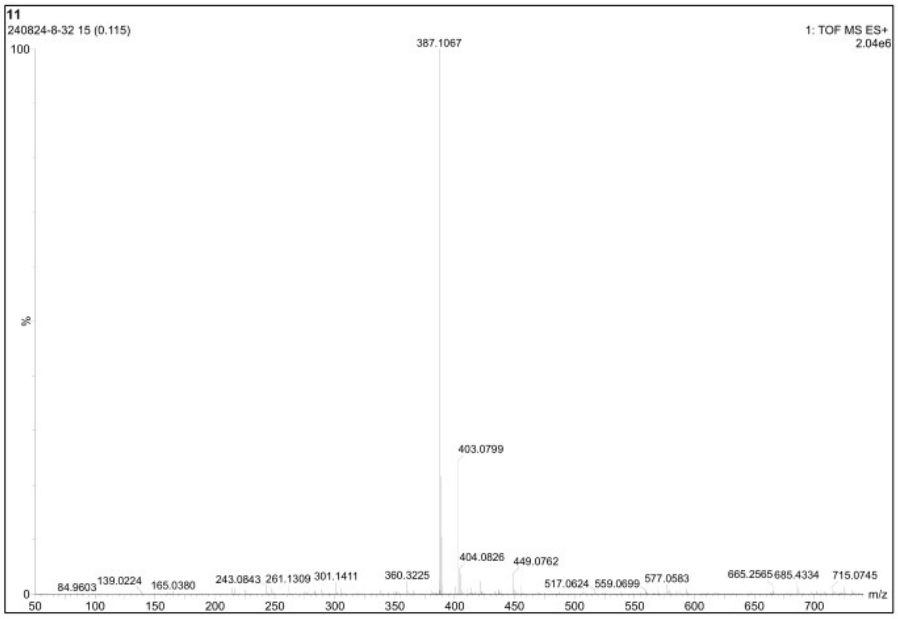
HR-MS (ESI) spectrum of **17**.



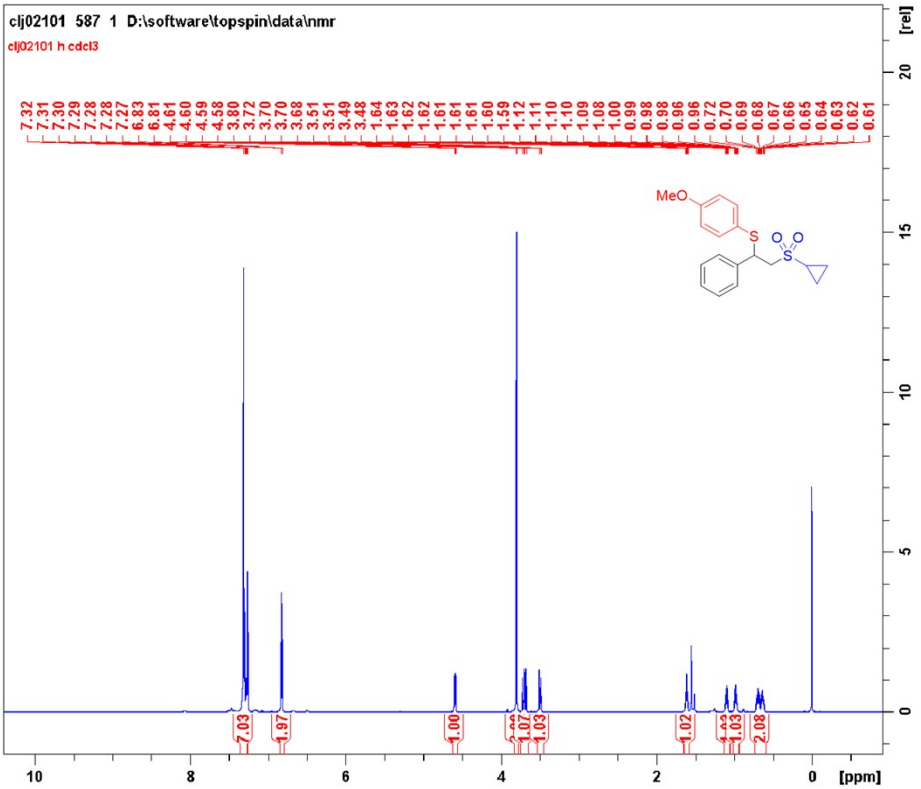
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **18**.



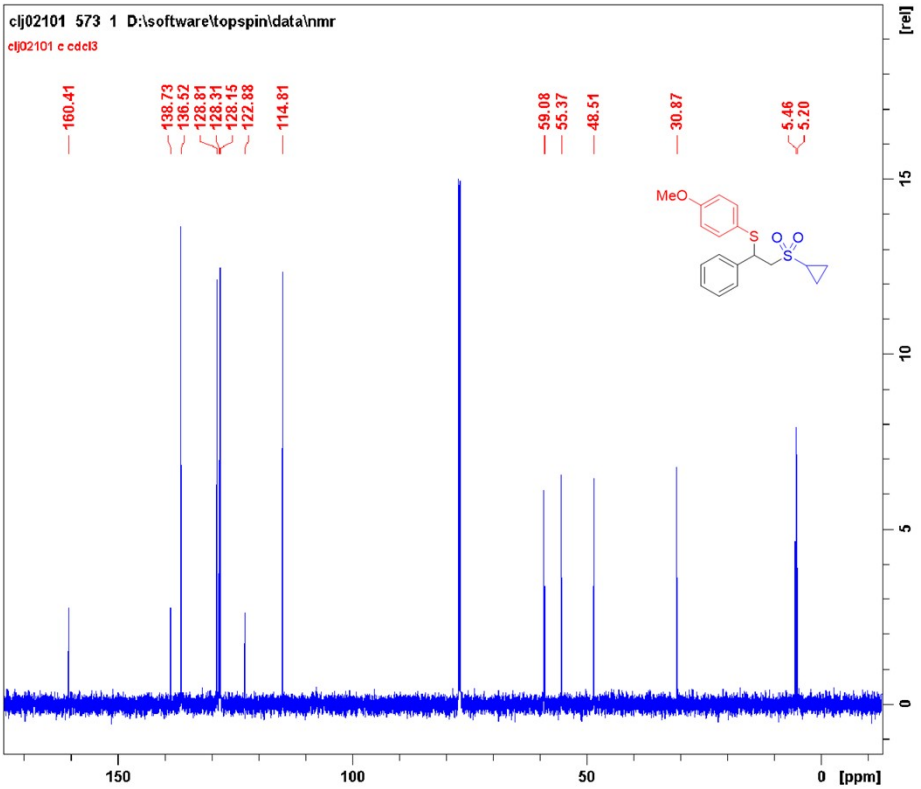
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **18**.



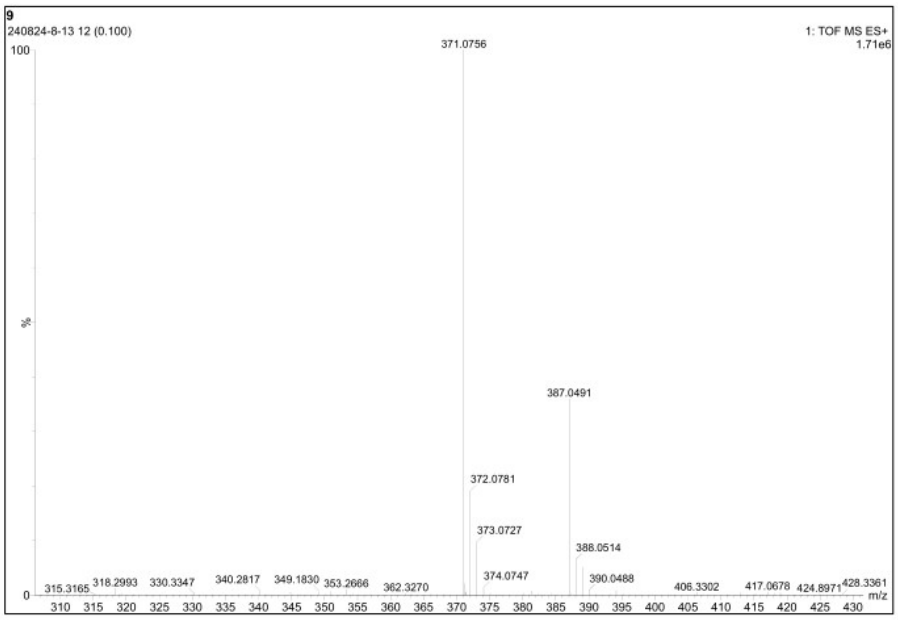
HR-MS (ESI) spectrum of **18**.



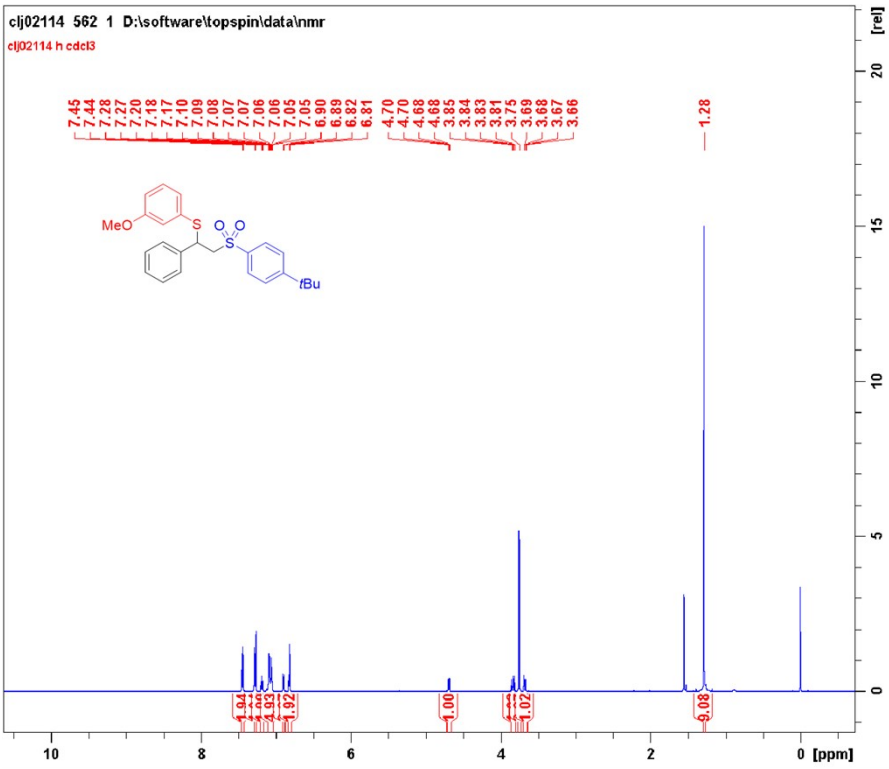
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **19**.



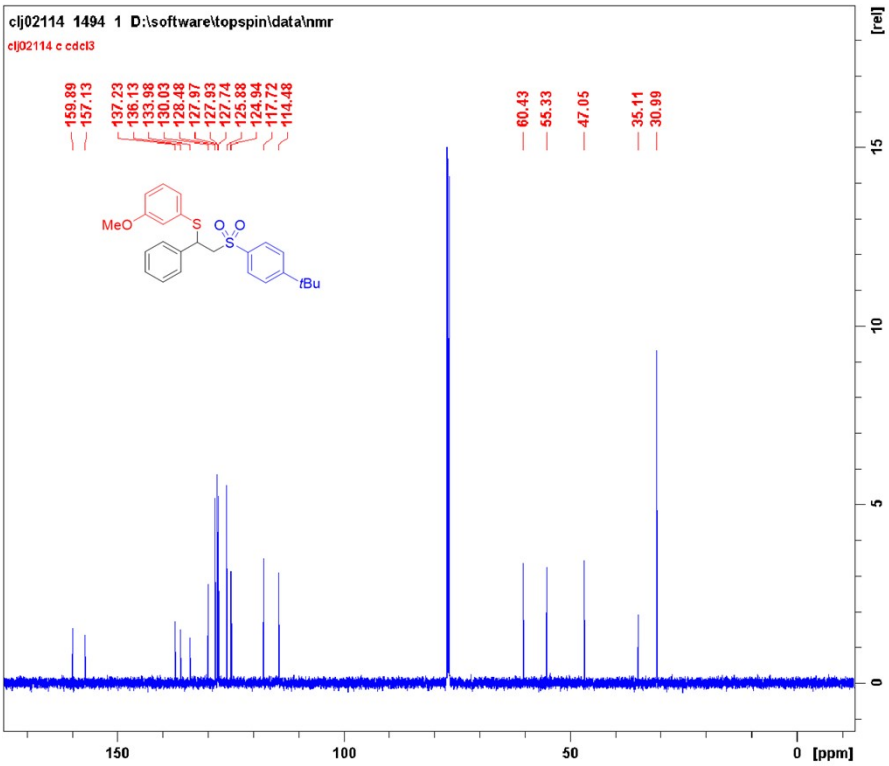
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **19**.



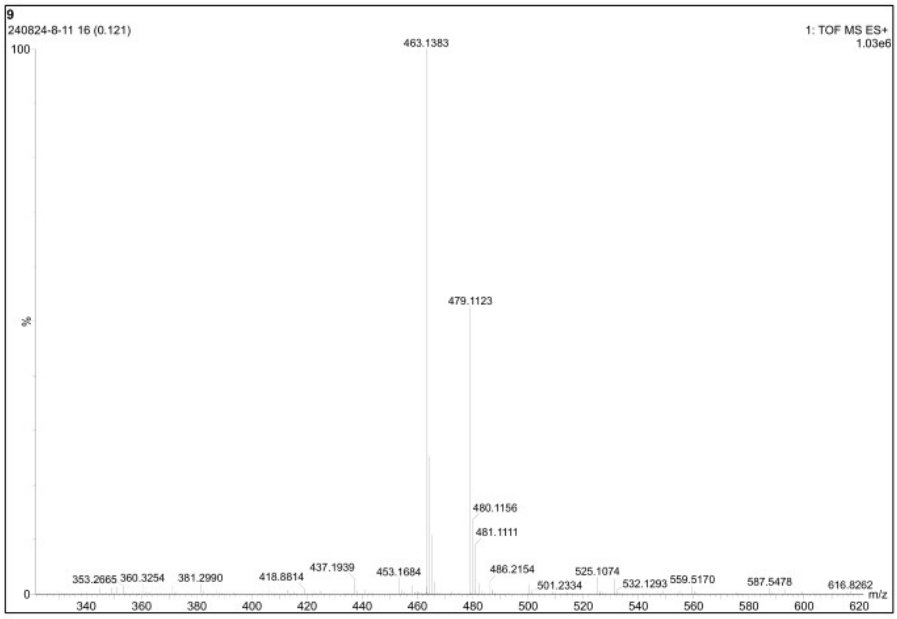
HR-MS (ESI) spectrum of **19**.



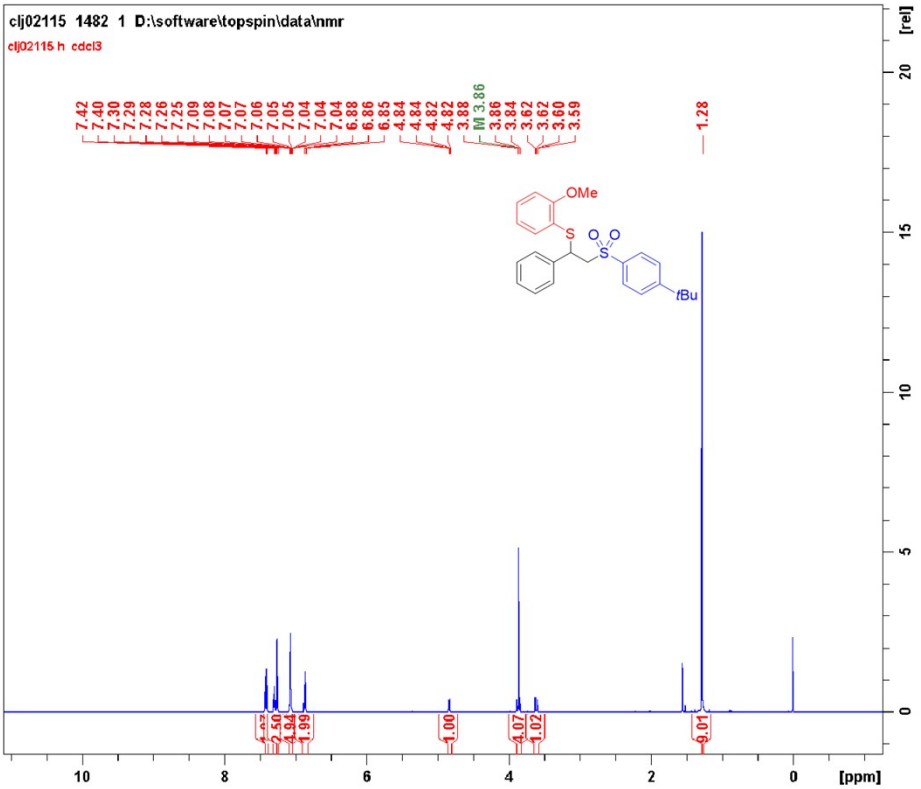
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20**.



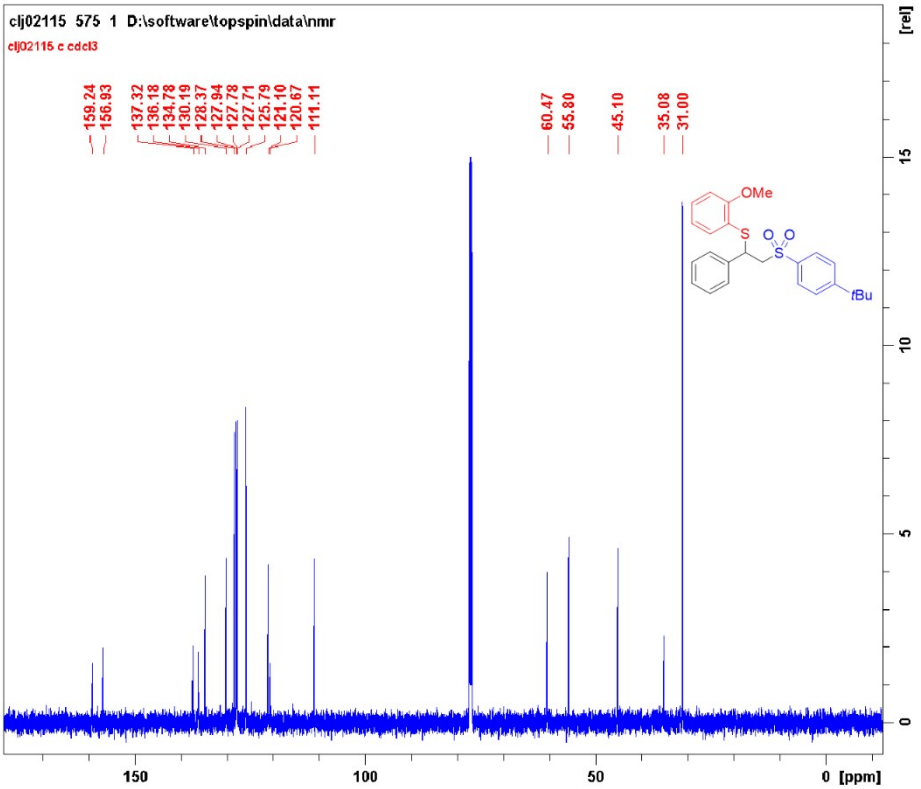
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **20**.



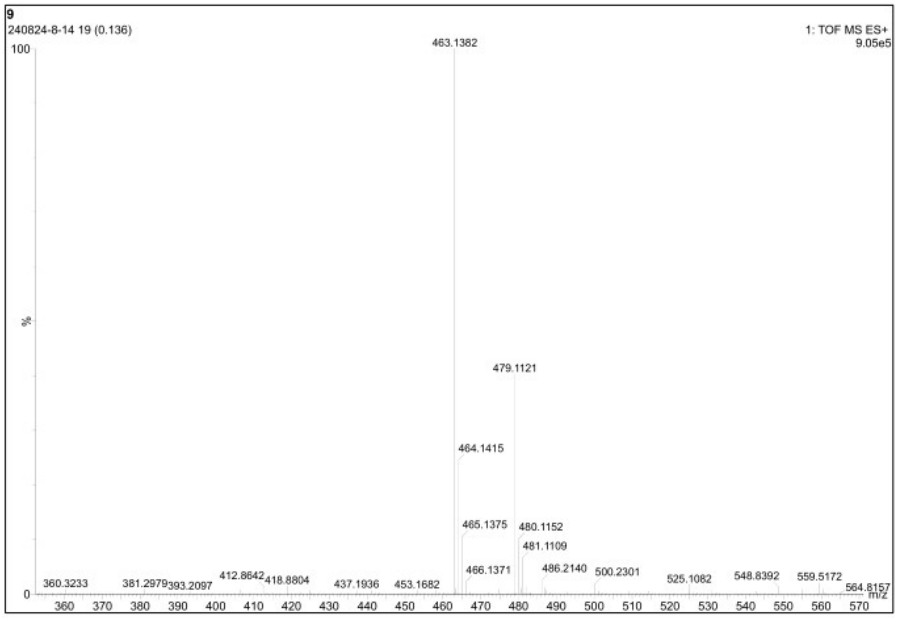
HR-MS (ESI) spectrum of **20**.



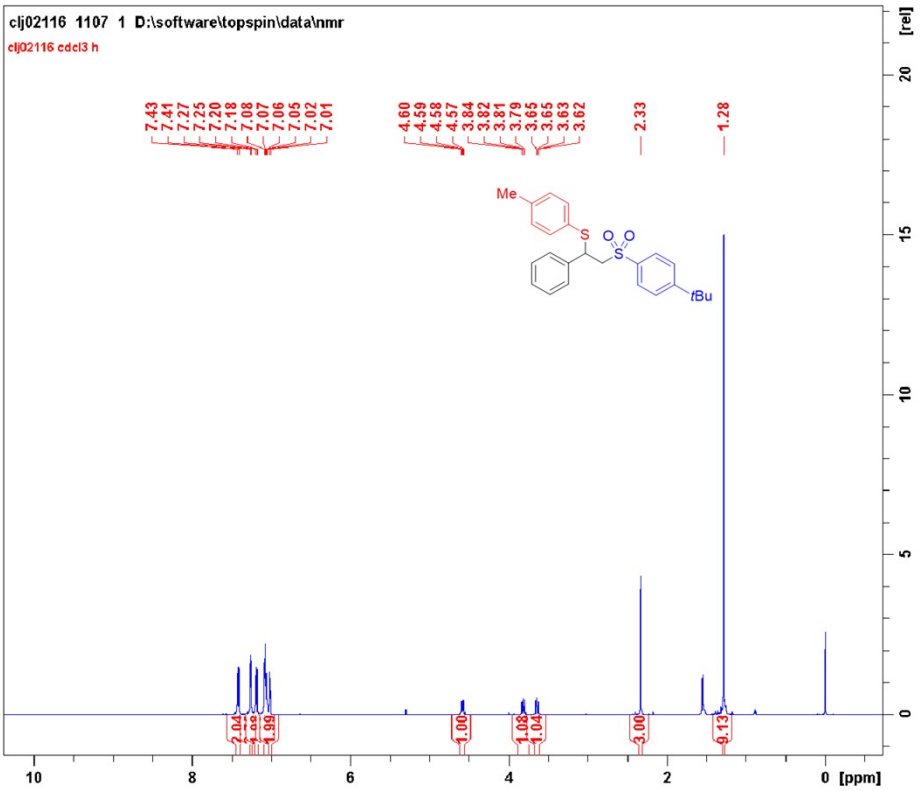
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **21**.



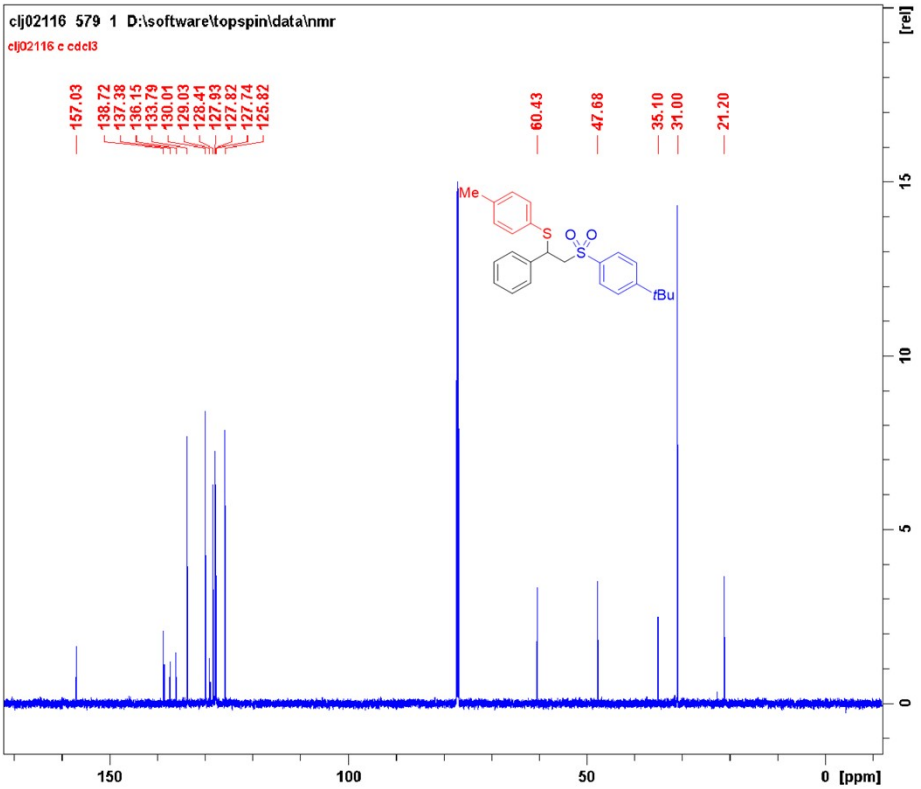
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **21**.



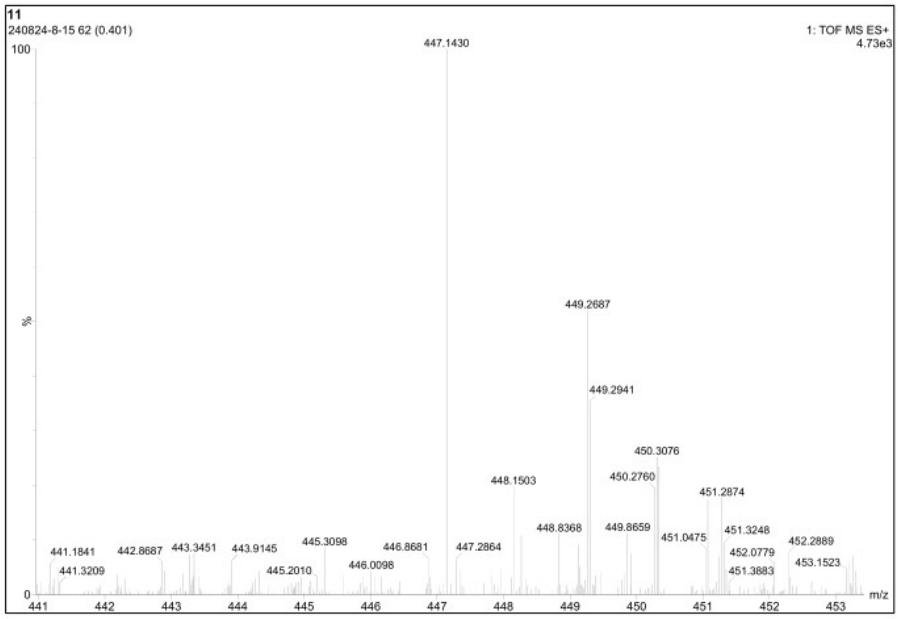
HR-MS (ESI) spectrum of **21**.



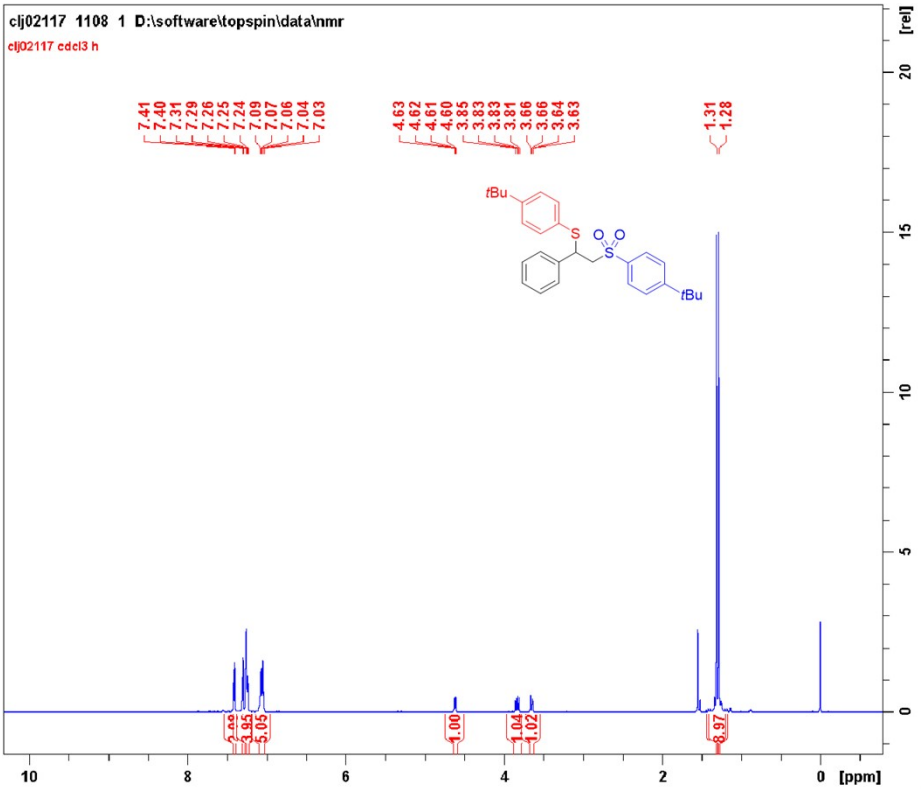
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **22**.



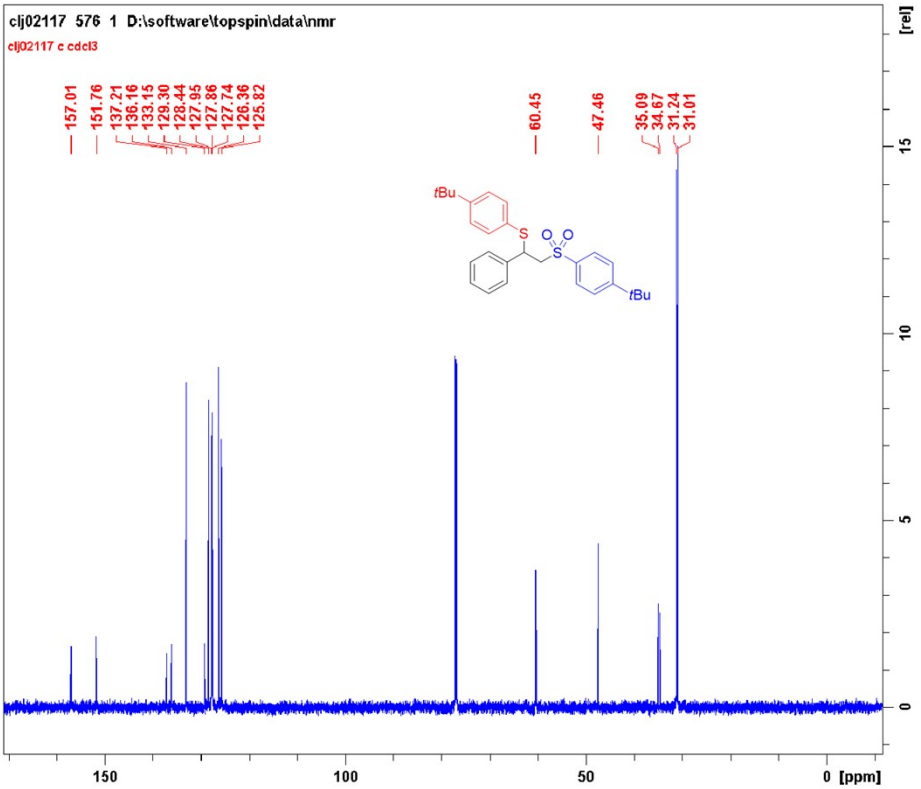
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **22**.



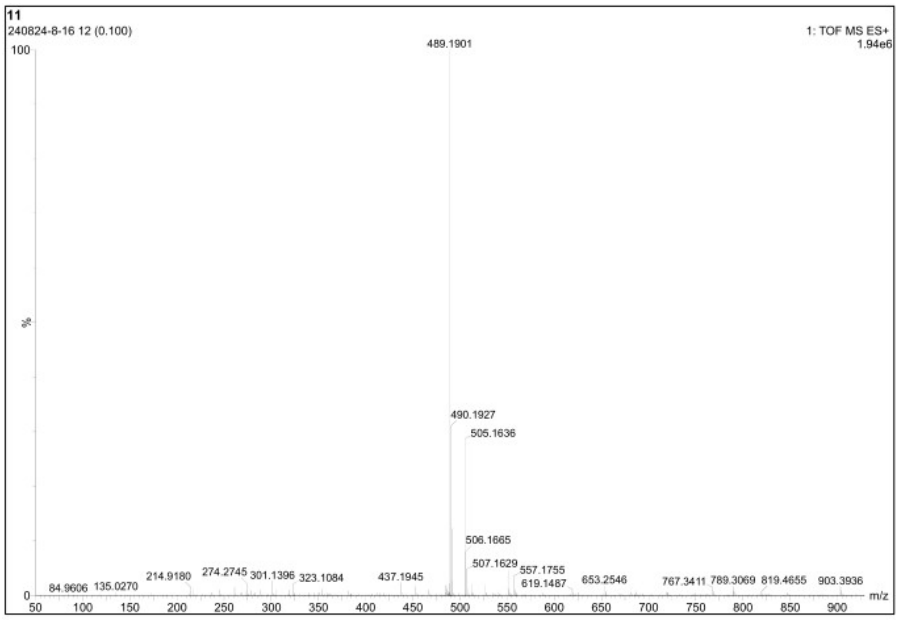
HR-MS (ESI) spectrum of **22**.



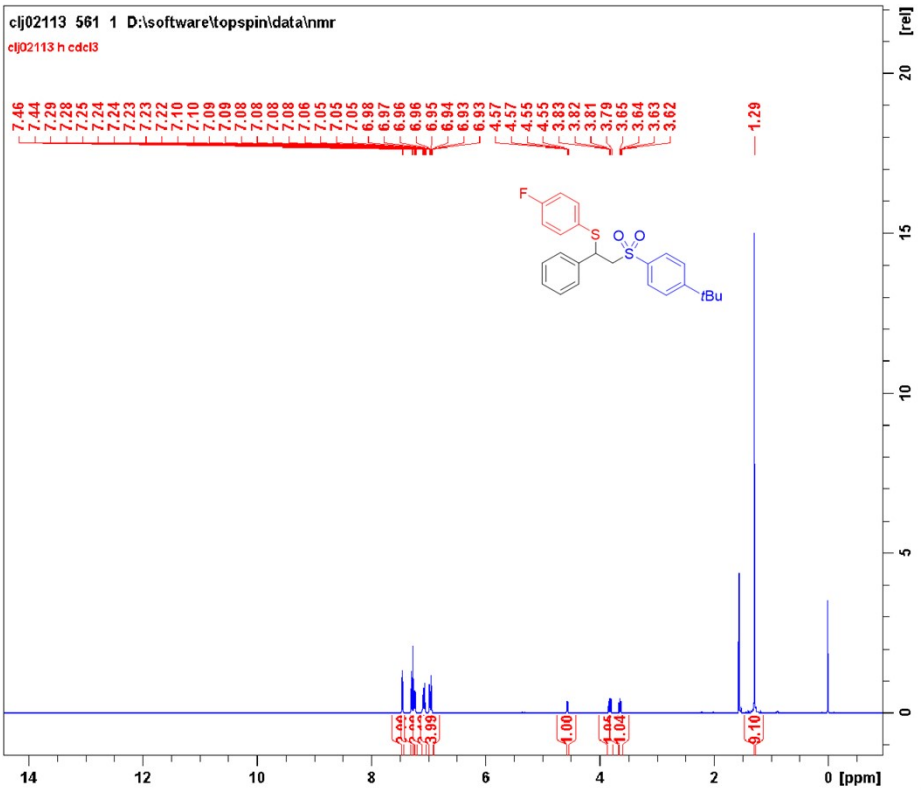
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **23**.



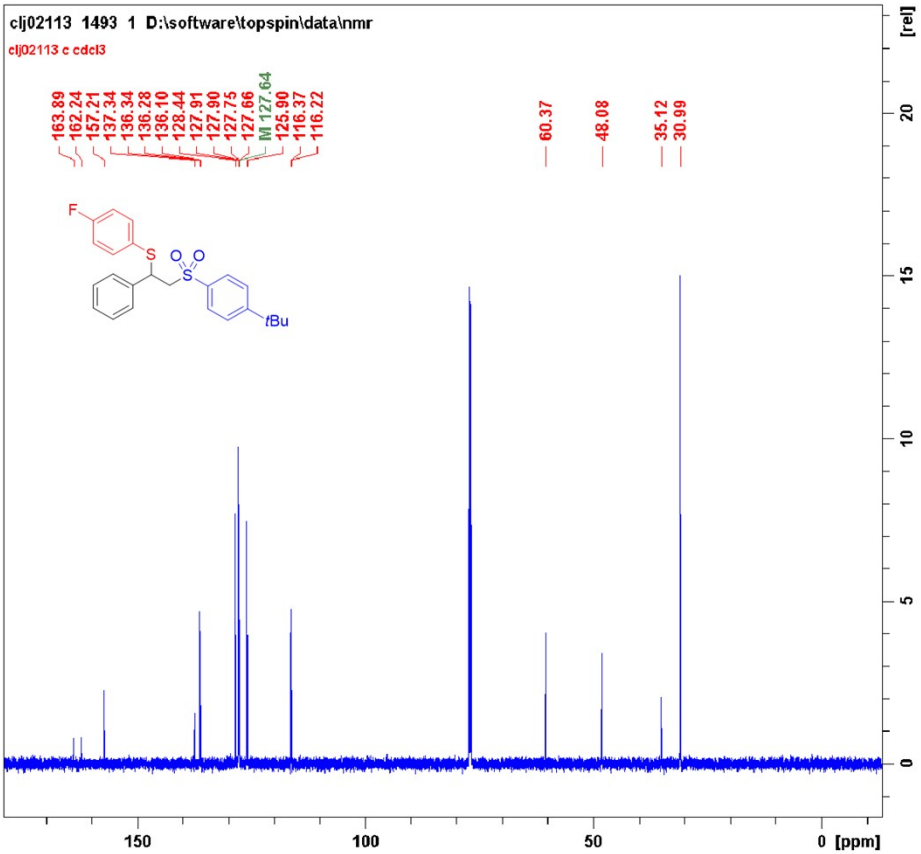
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **23**.



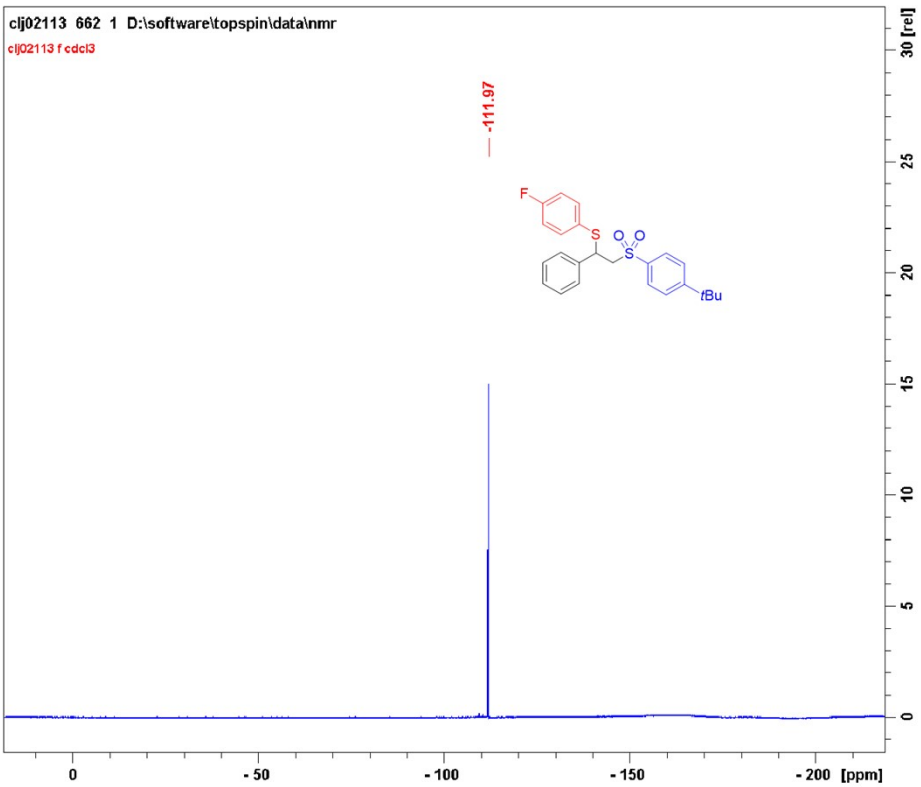
HR-MS (ESI) spectrum of **23**.



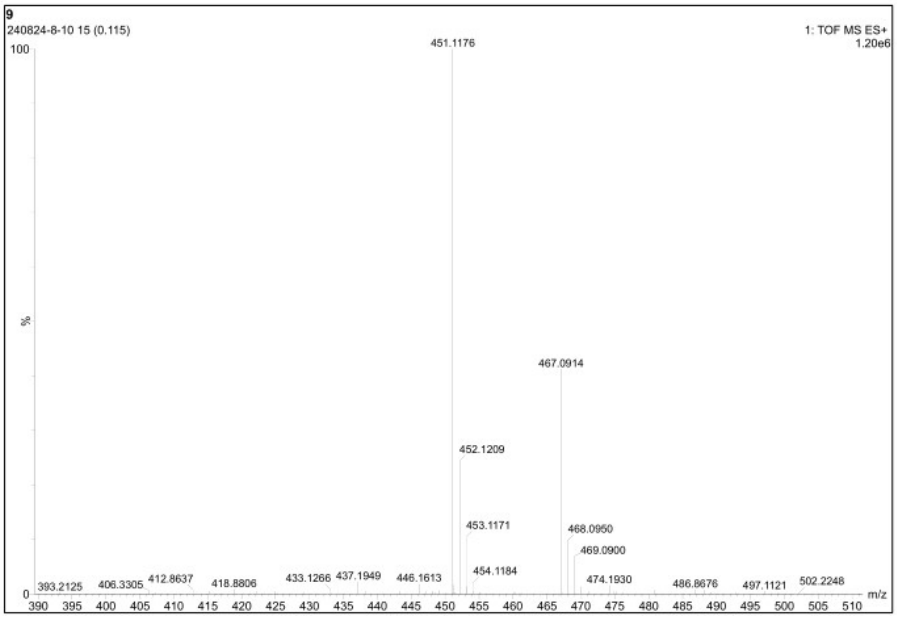
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **24**.



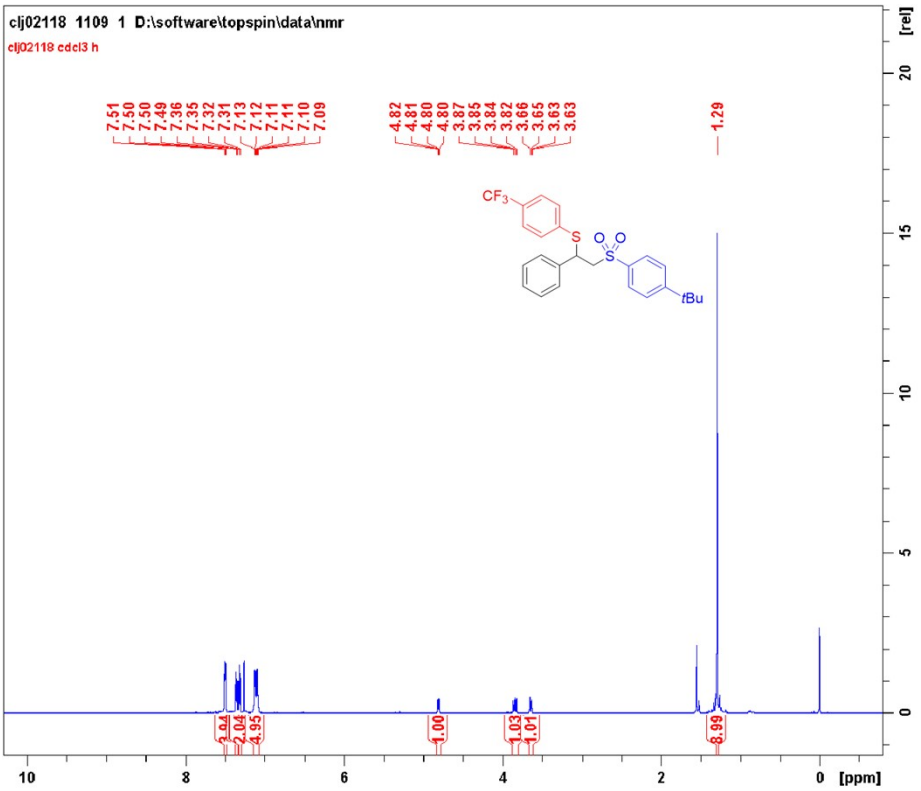
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **24**.



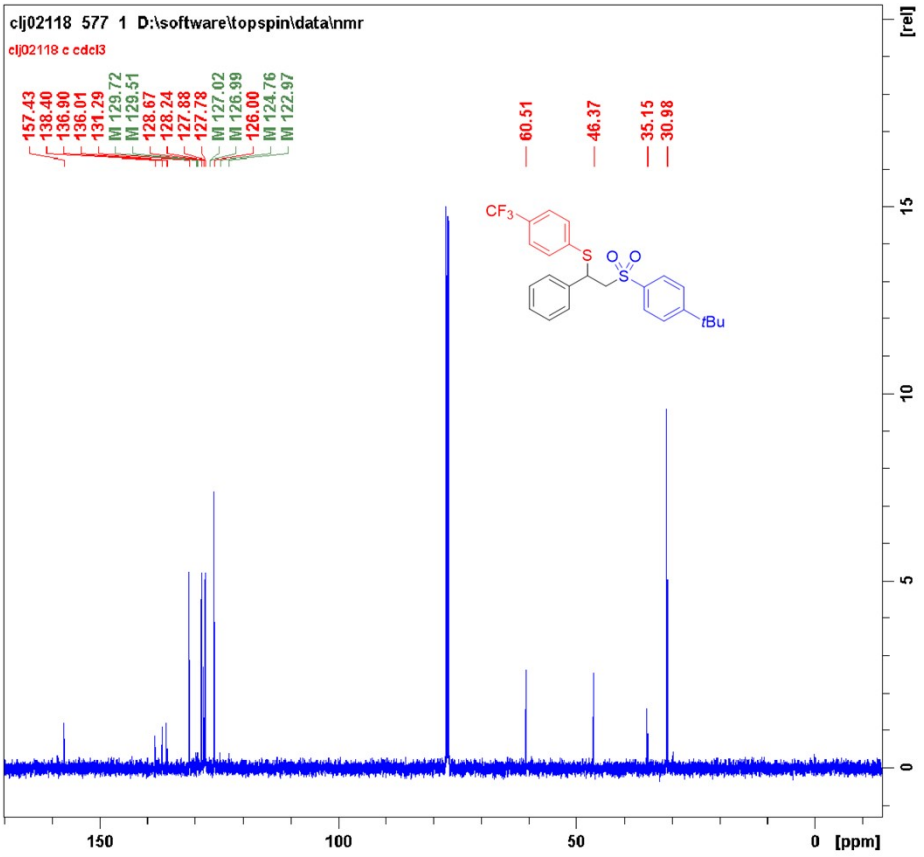
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **24**.



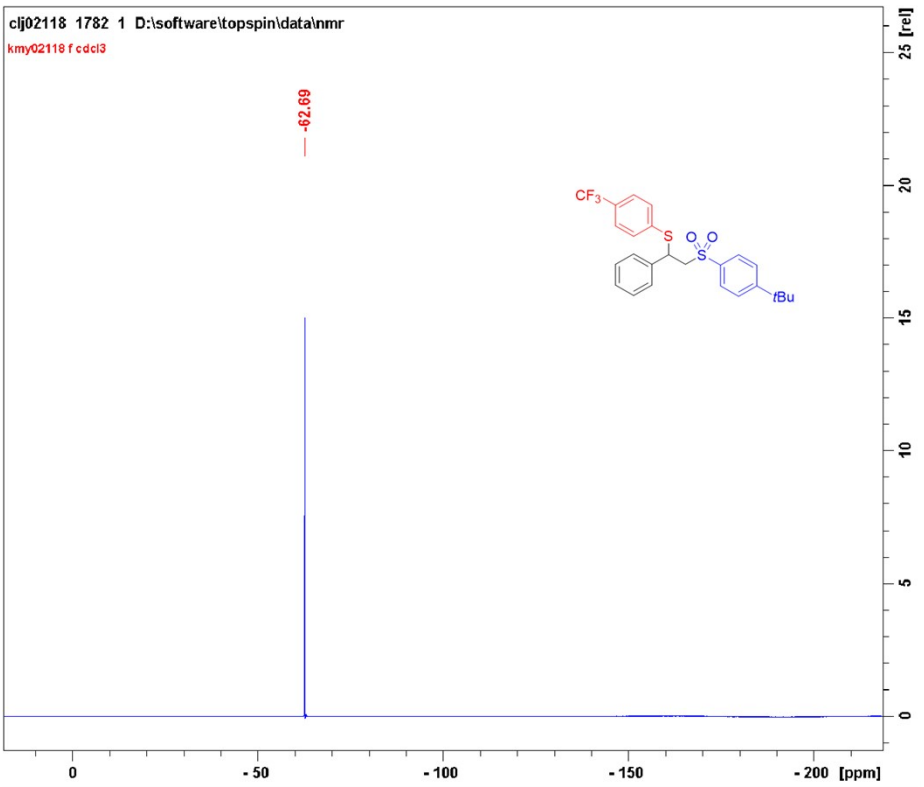
HR-MS (ESI) spectrum of **24**.



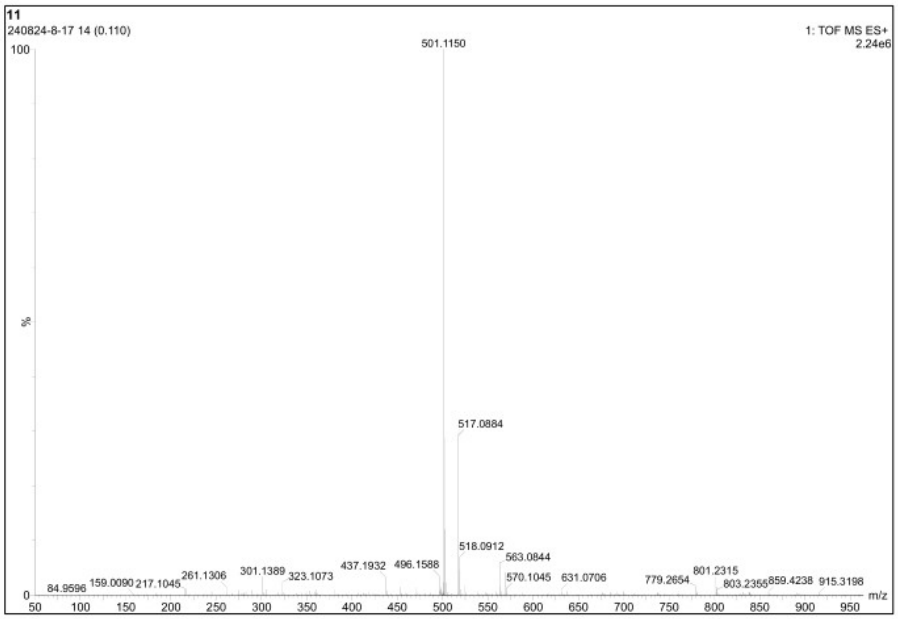
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **25**.



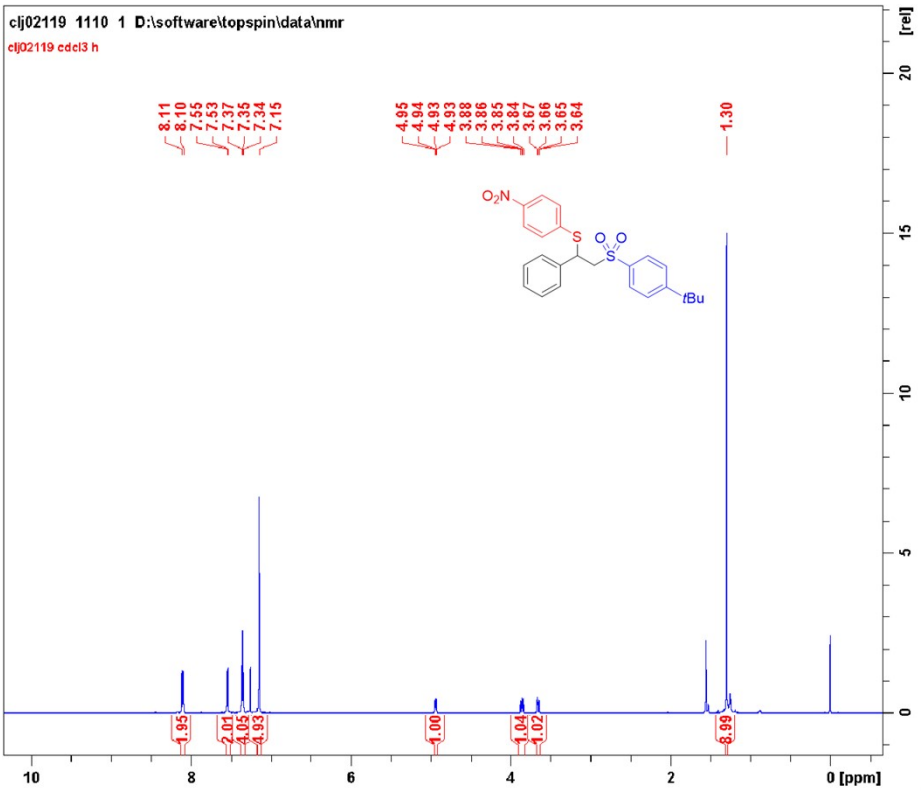
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **25**.



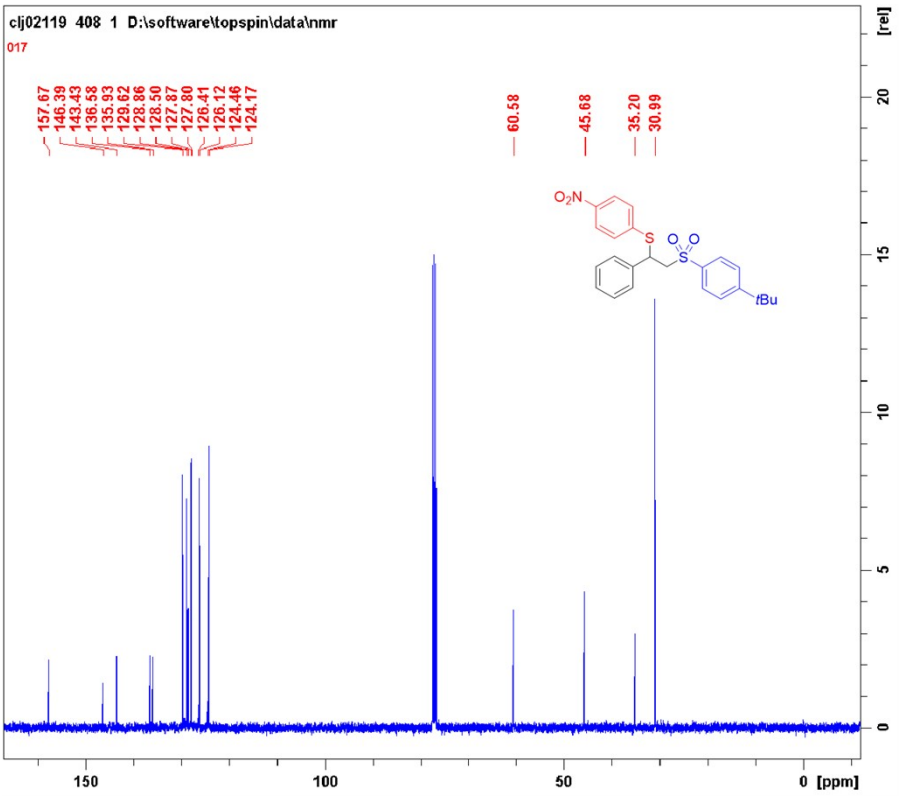
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **25**.



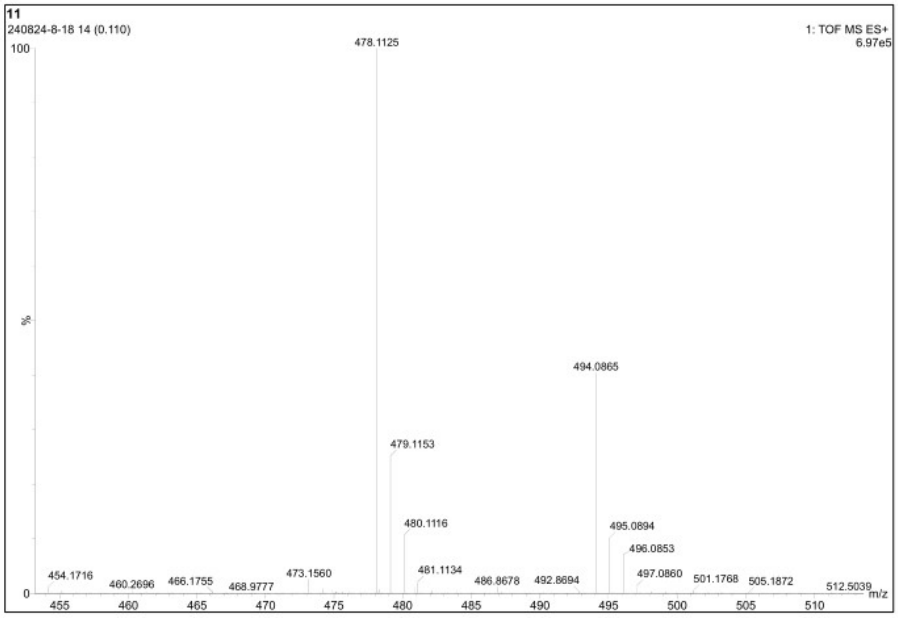
HR-MS (ESI) spectrum of **25**.



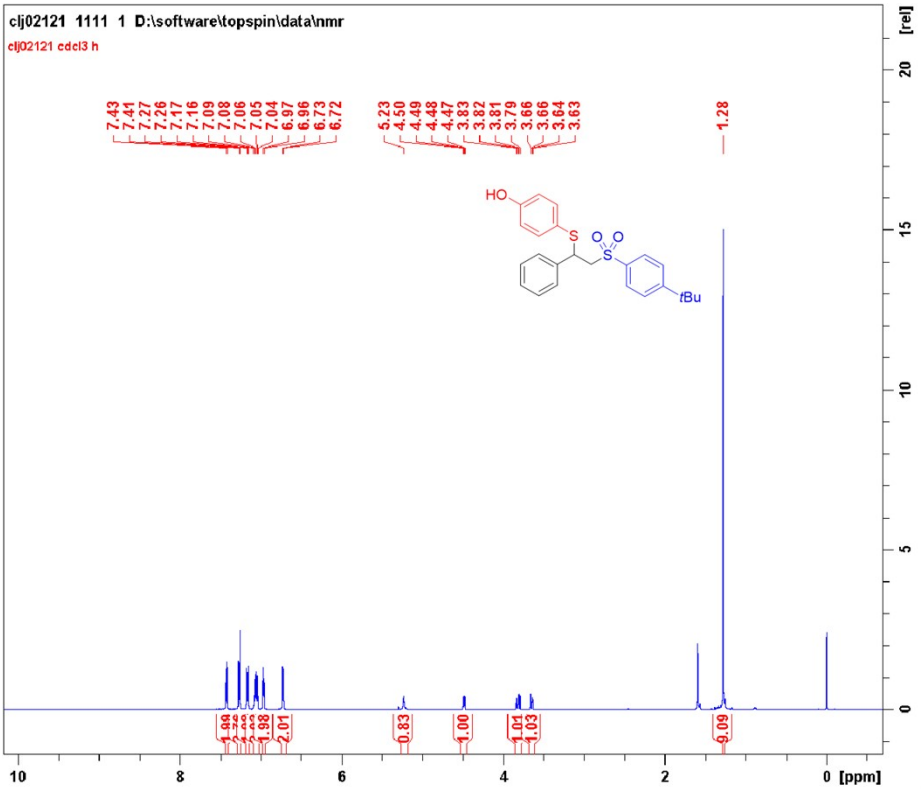
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **26**.



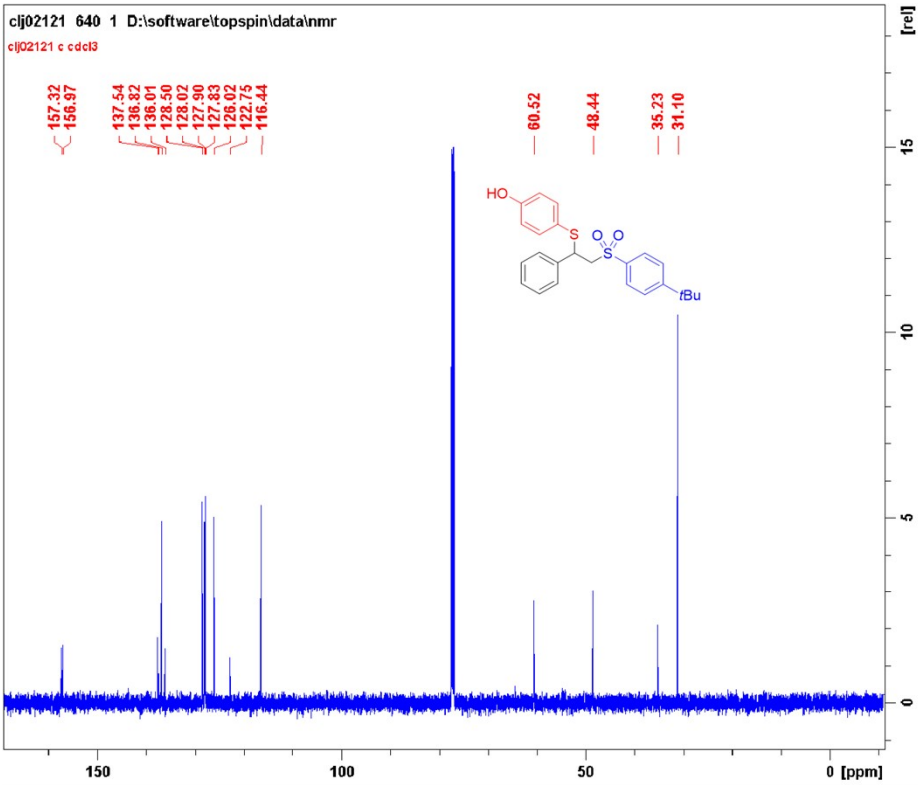
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **26**.



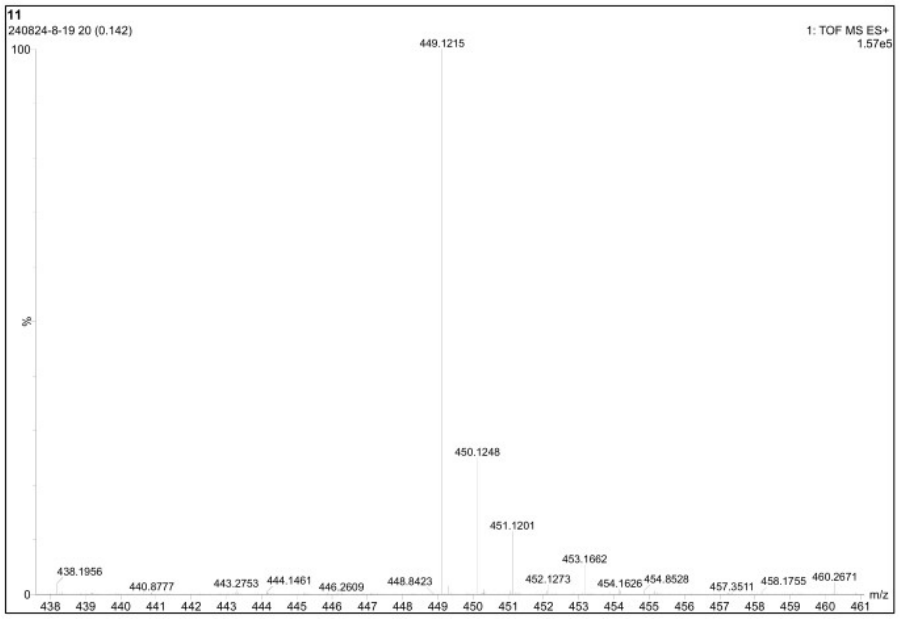
HR-MS (ESI) spectrum of **26**.



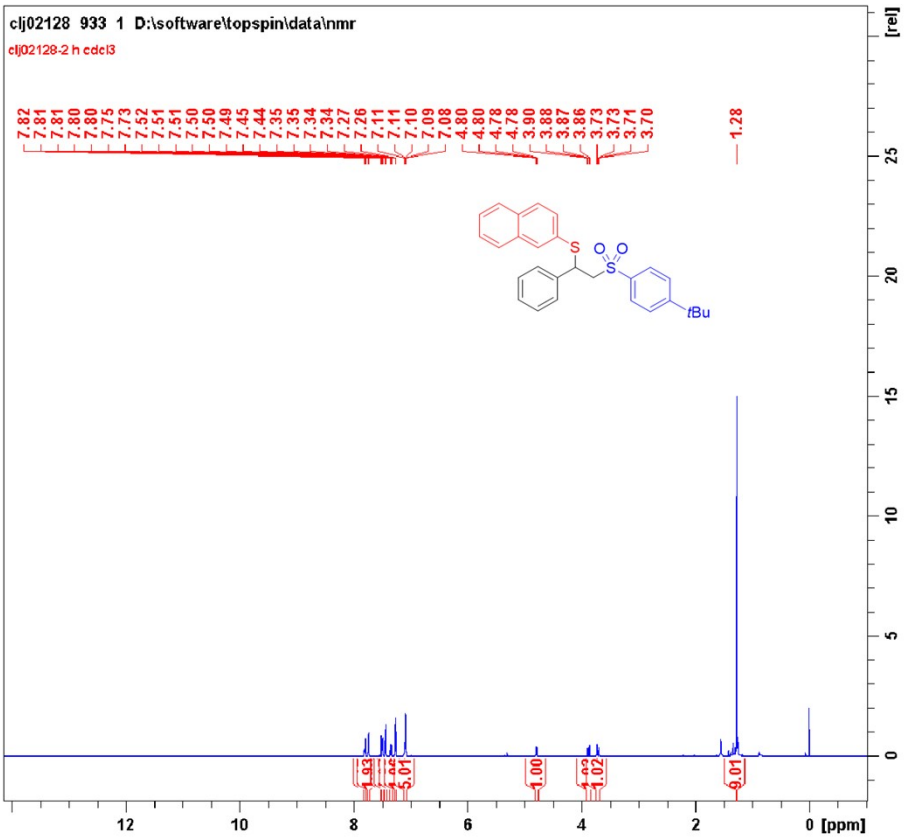
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **27**.



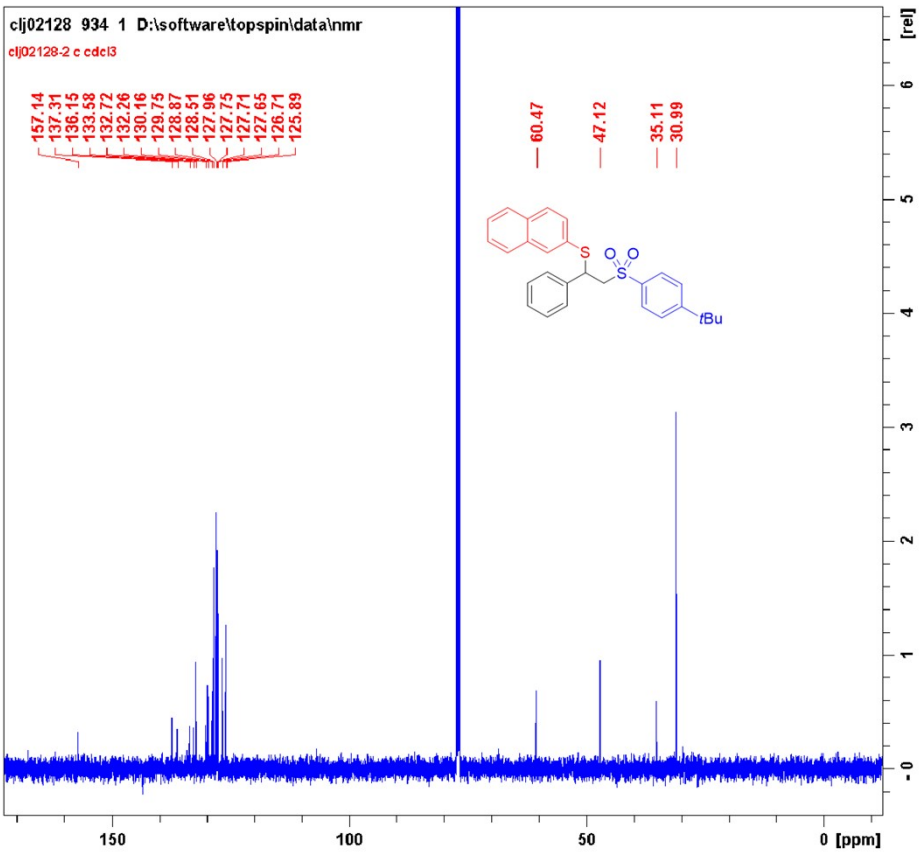
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **27**.



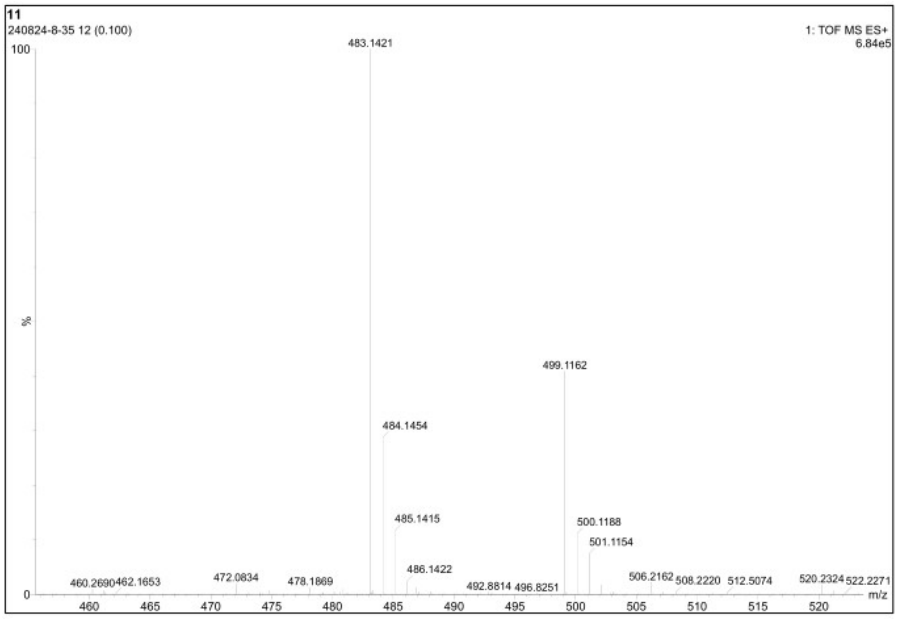
HR-MS (ESI) spectrum of **27**.



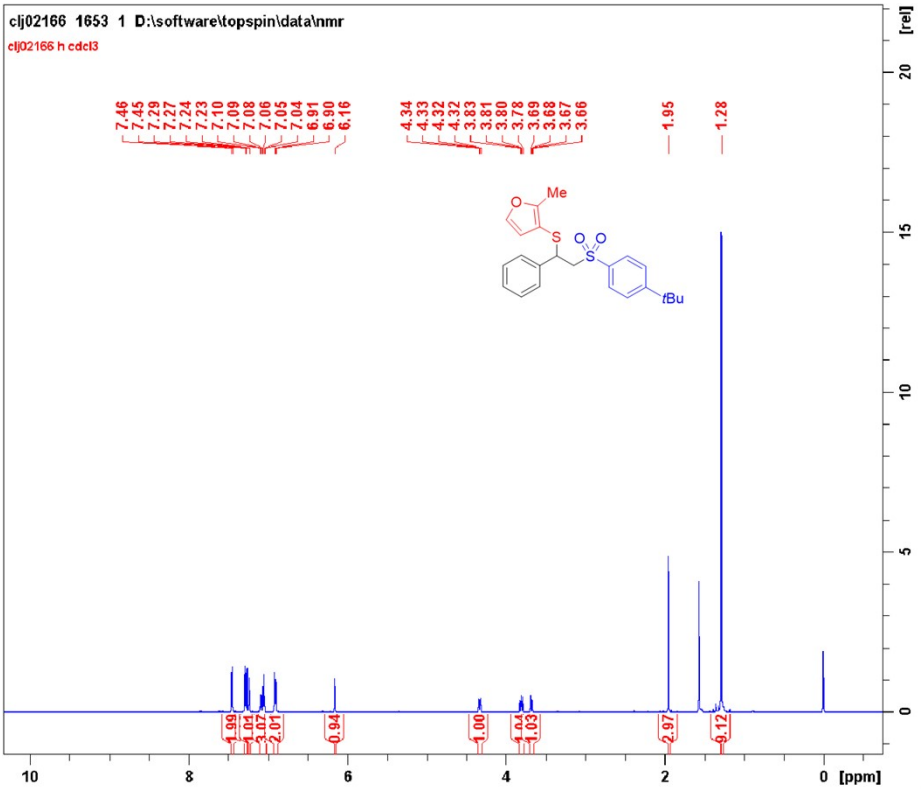
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **28**.



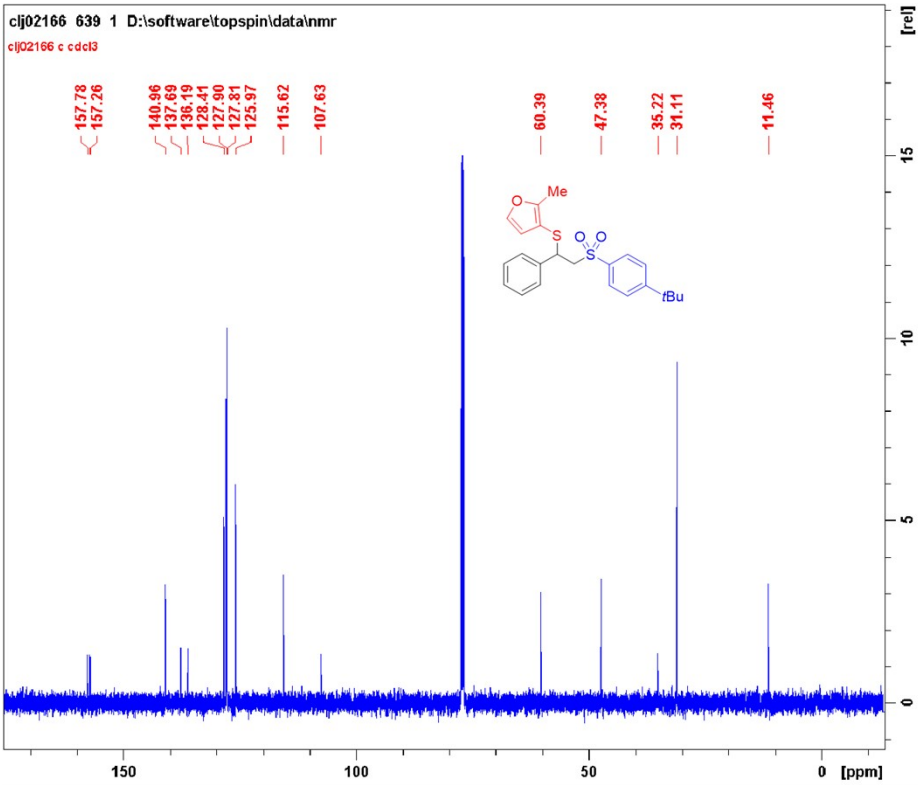
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **28**.



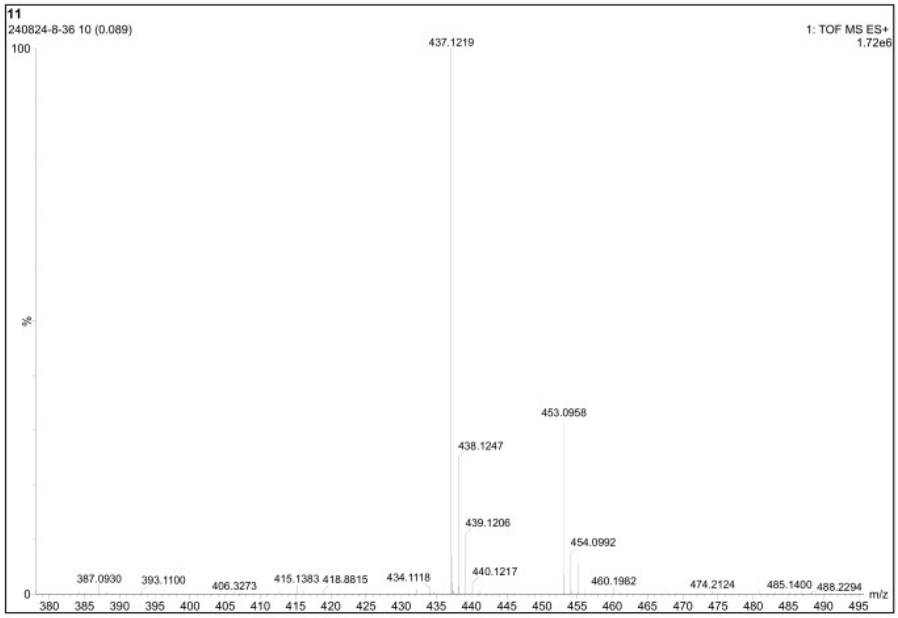
HR-MS (ESI) spectrum of **28**.



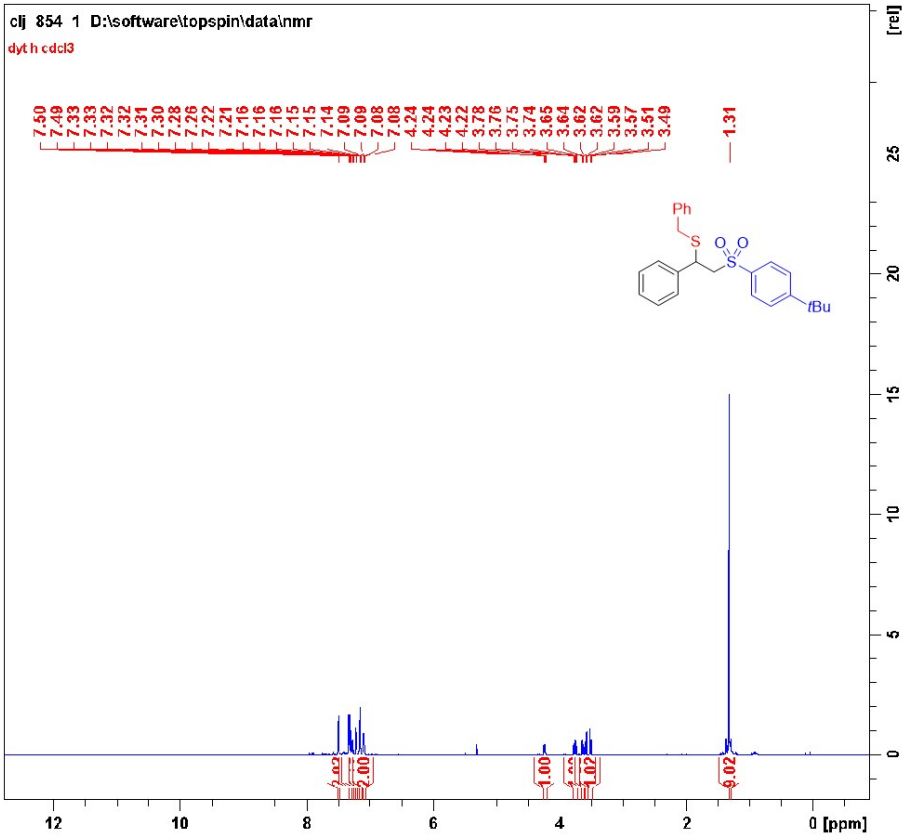
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **29**.



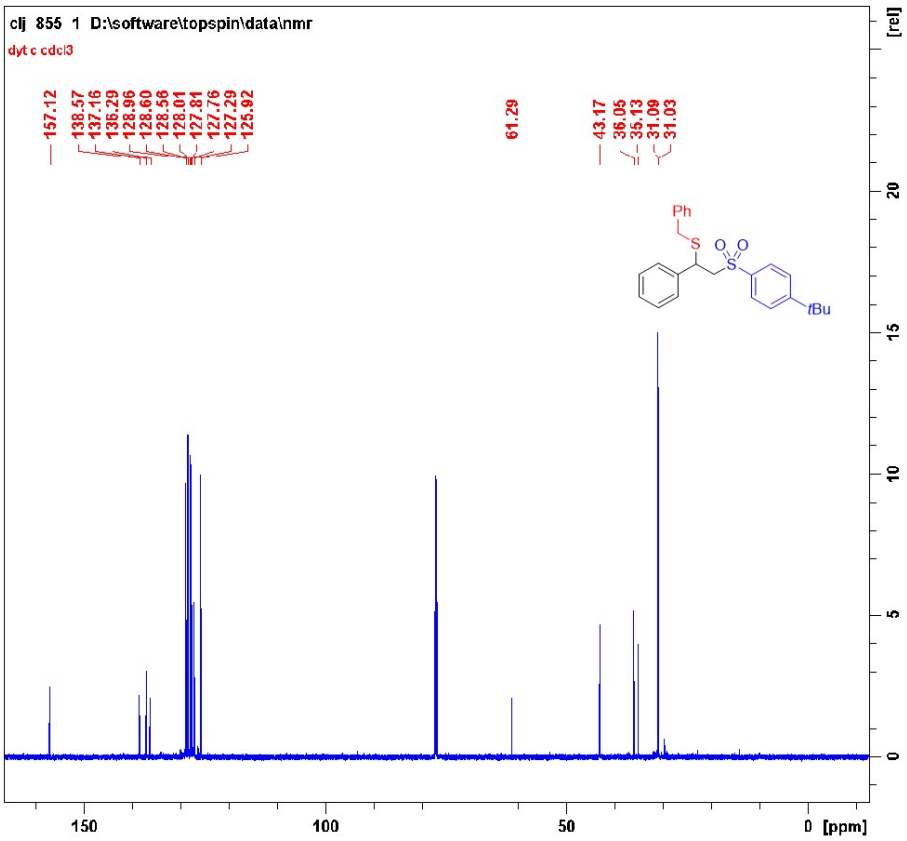
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **29**.



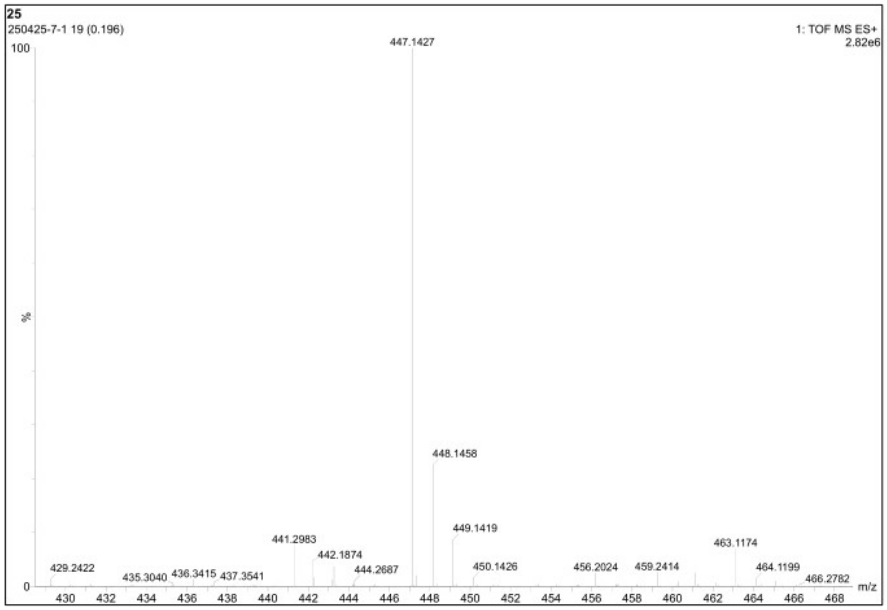
HR-MS (ESI) spectrum of **29**.



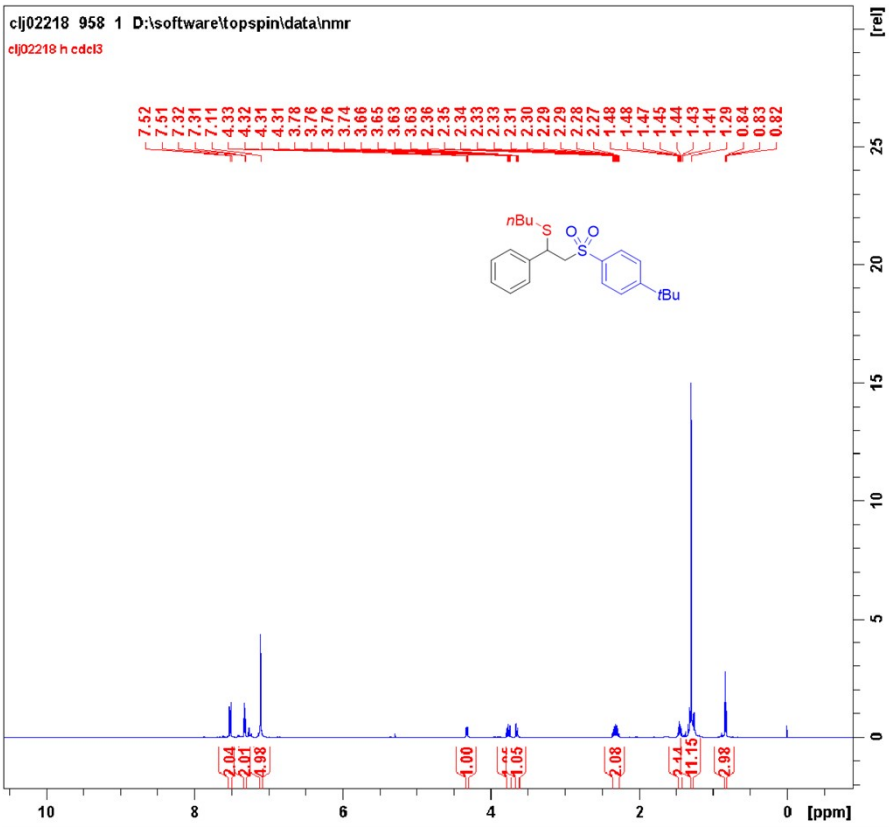
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **30**.



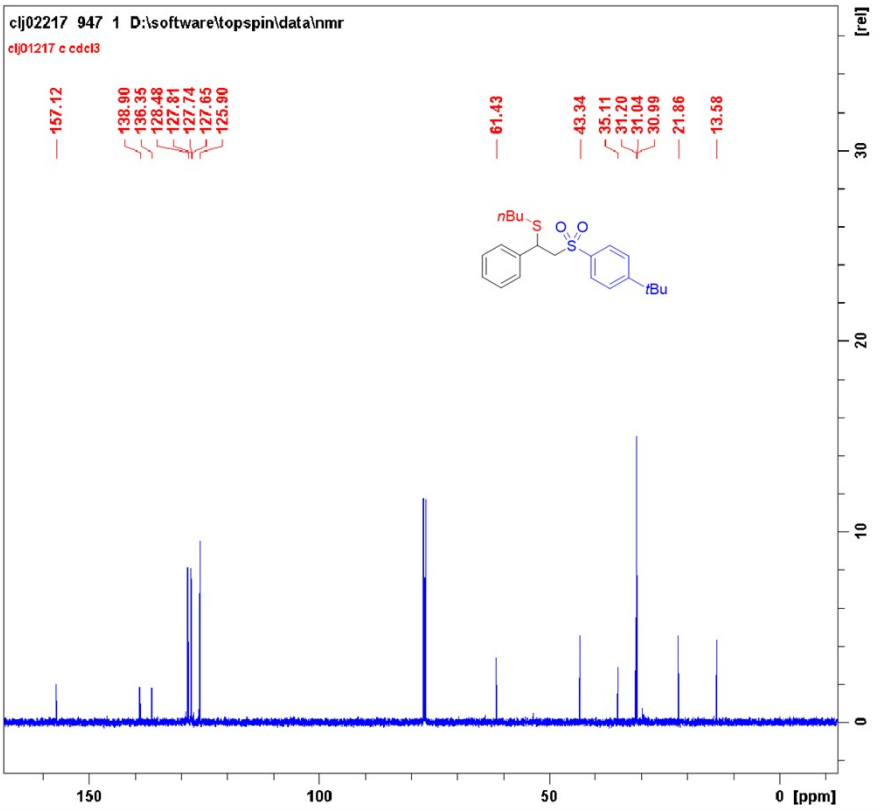
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **30**.



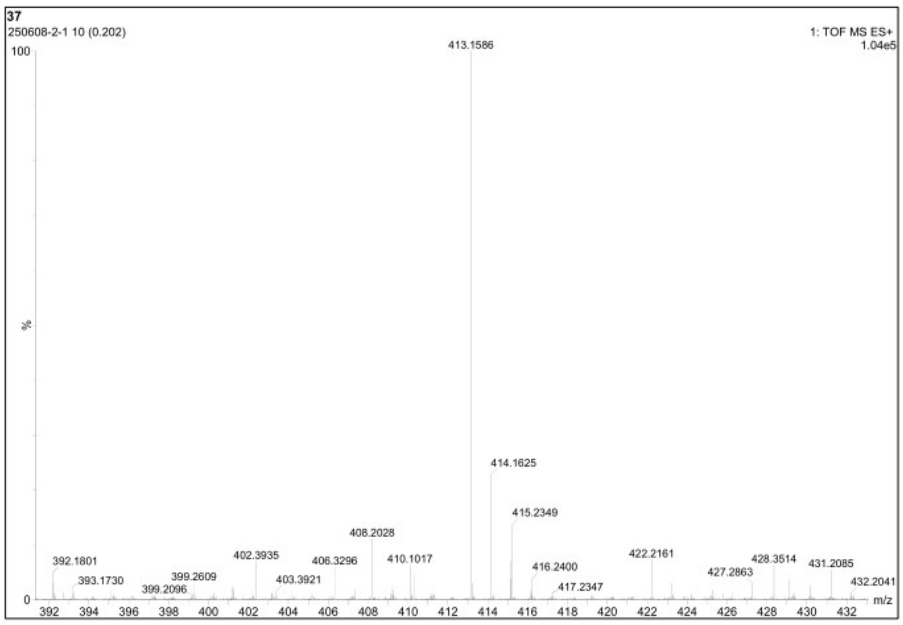
HR-MS (ESI) spectrum of **30**.



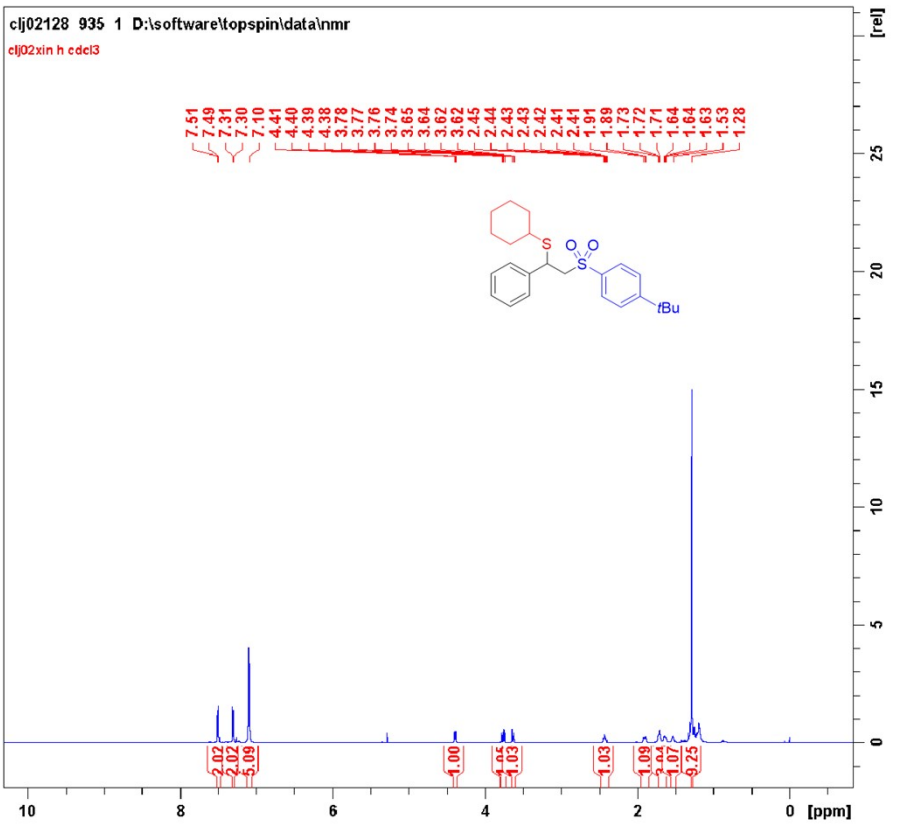
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **31**.



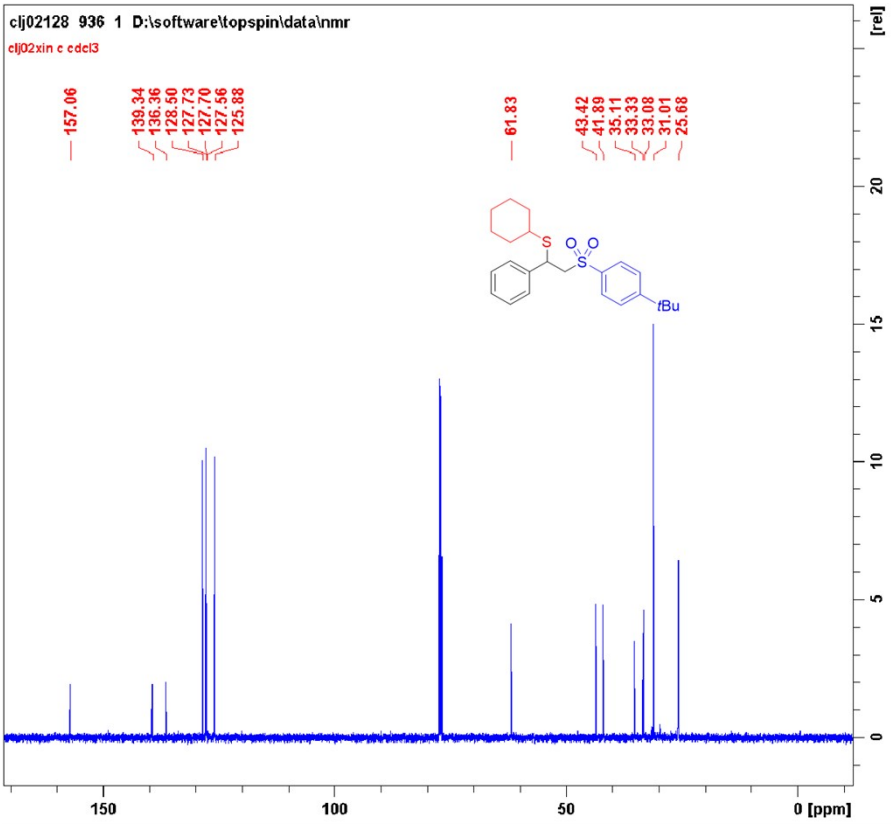
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **31**.



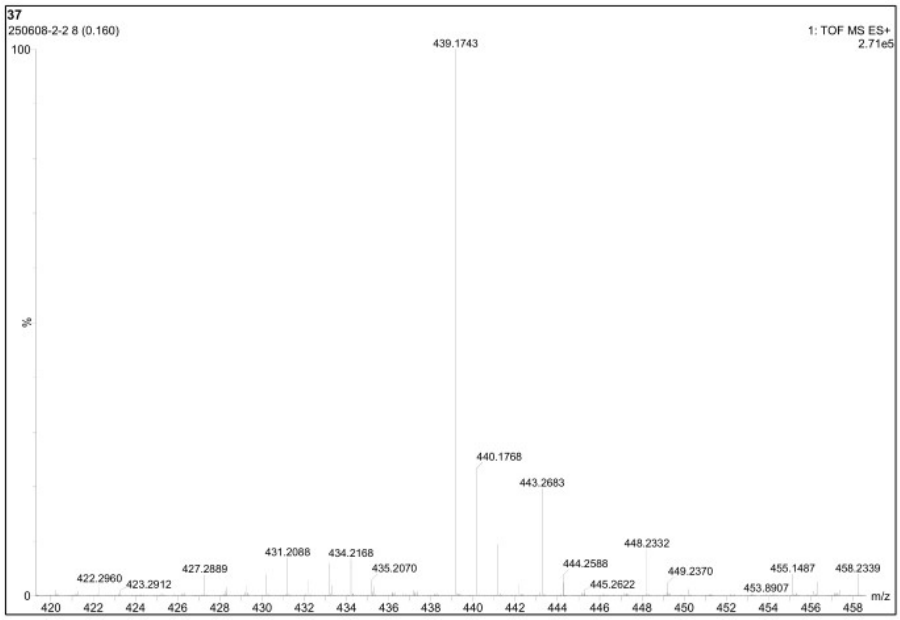
HR-MS (ESI) spectrum of **31**.



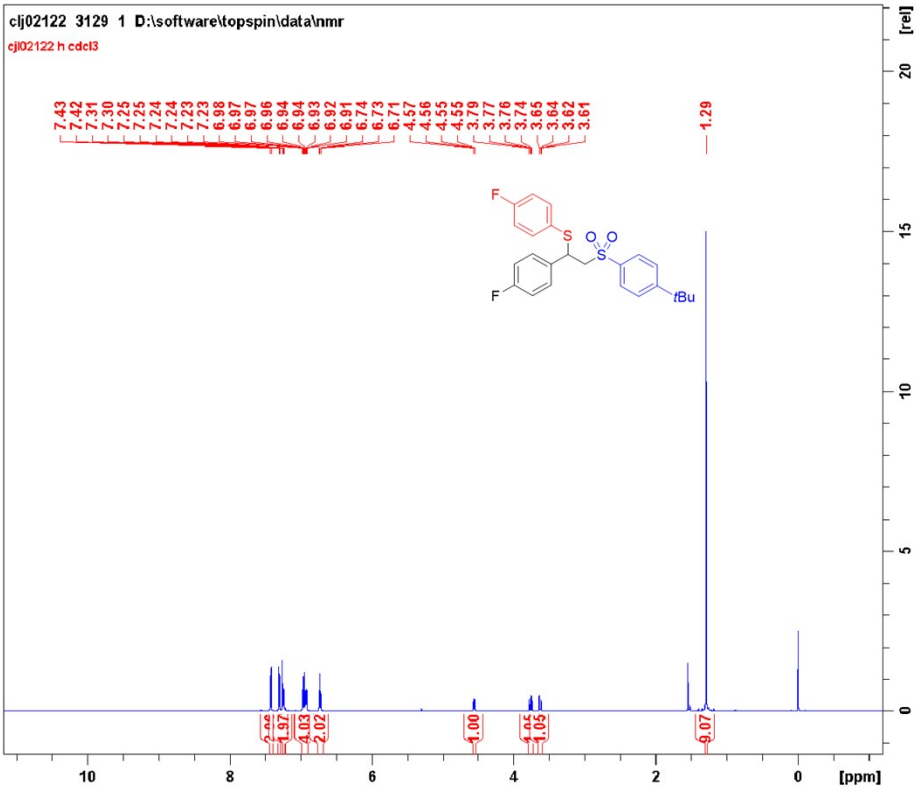
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **32**.



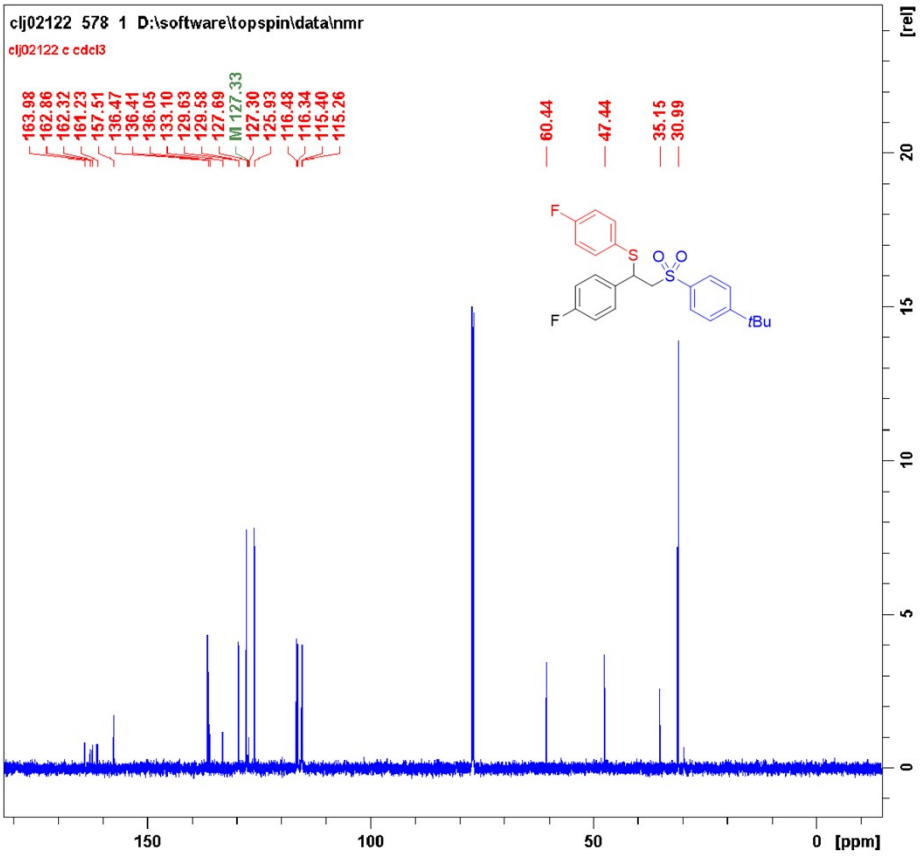
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **32**.



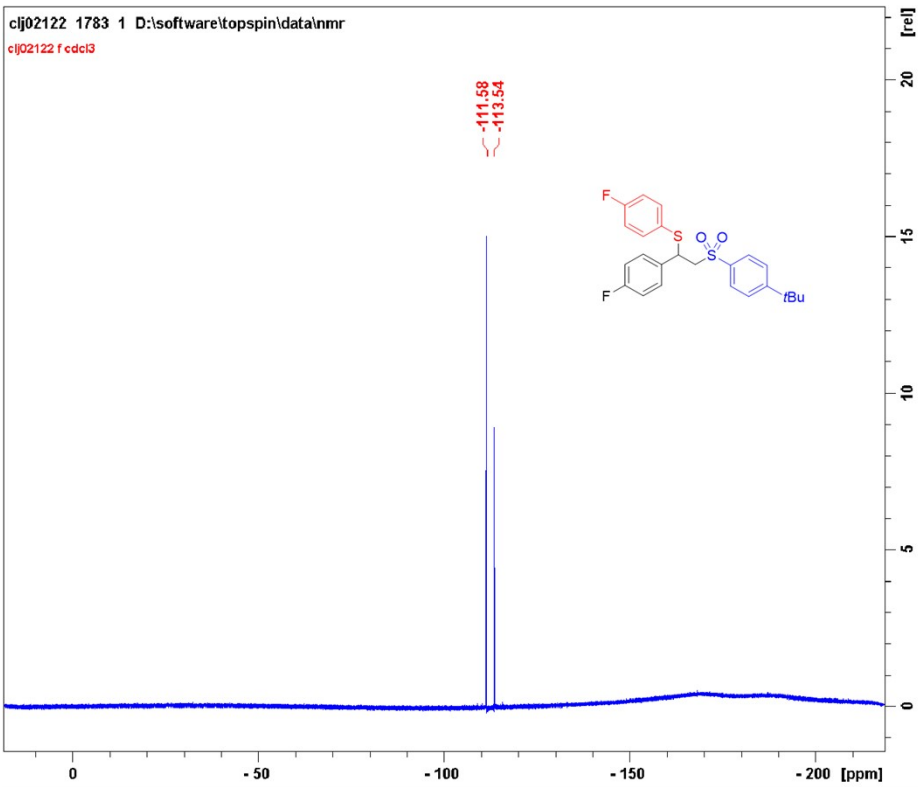
HR-MS (ESI) spectrum of **32**.



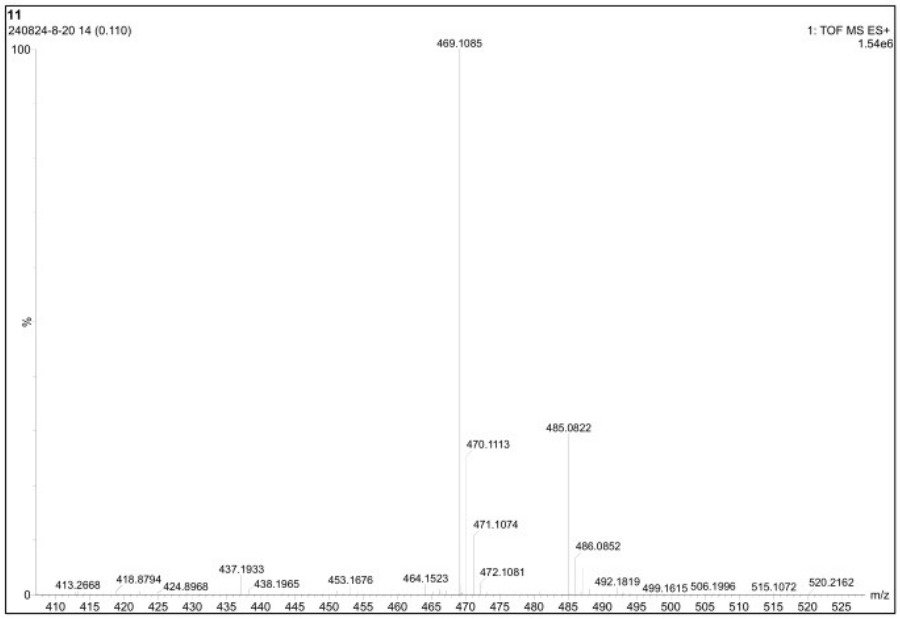
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **33**.



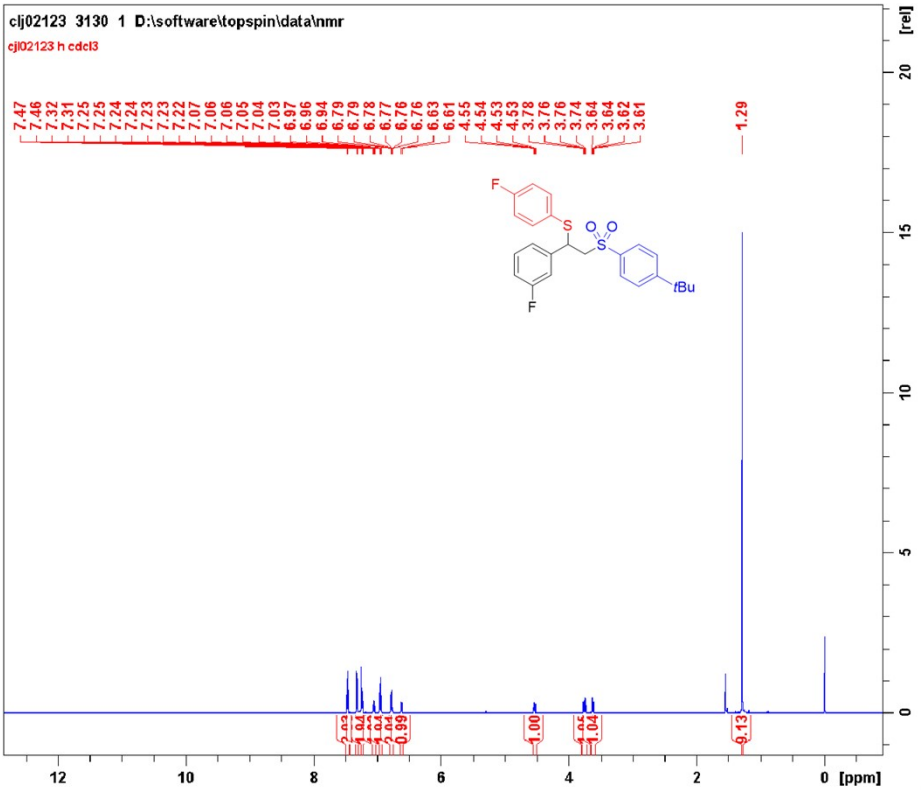
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **33**.



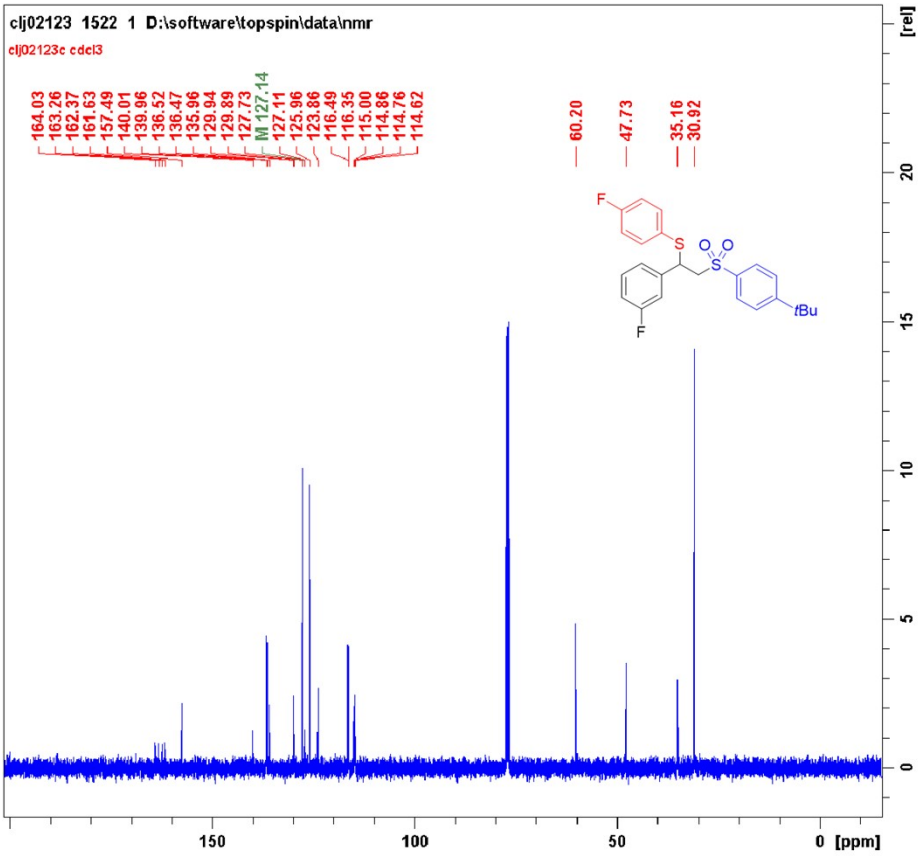
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **33**.



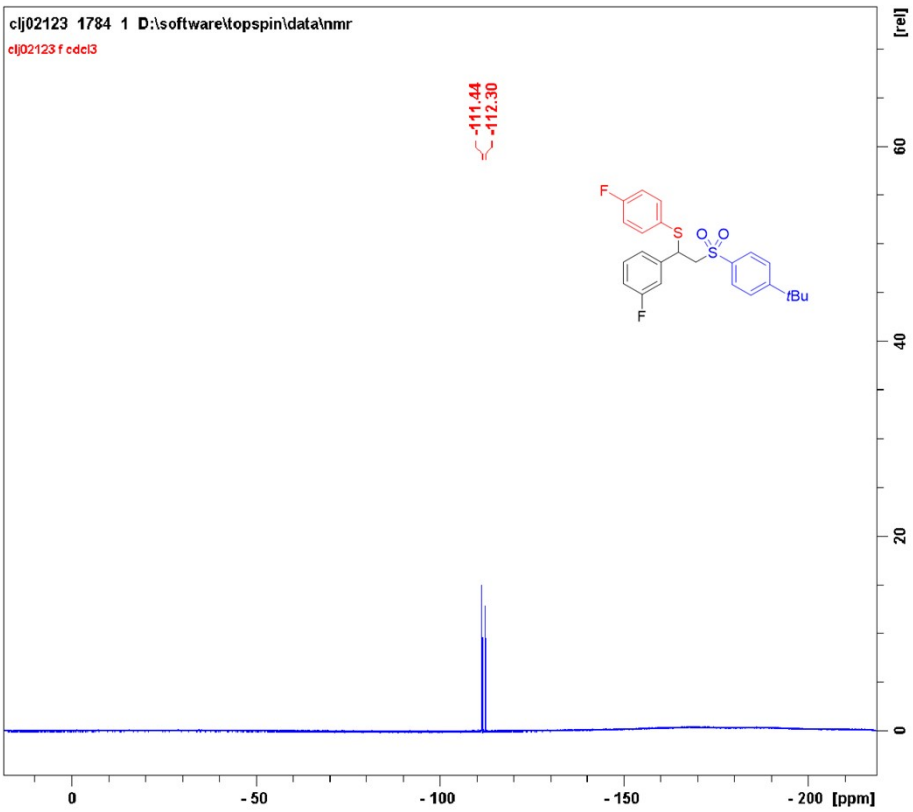
HR-MS (ESI) spectrum of **33**.



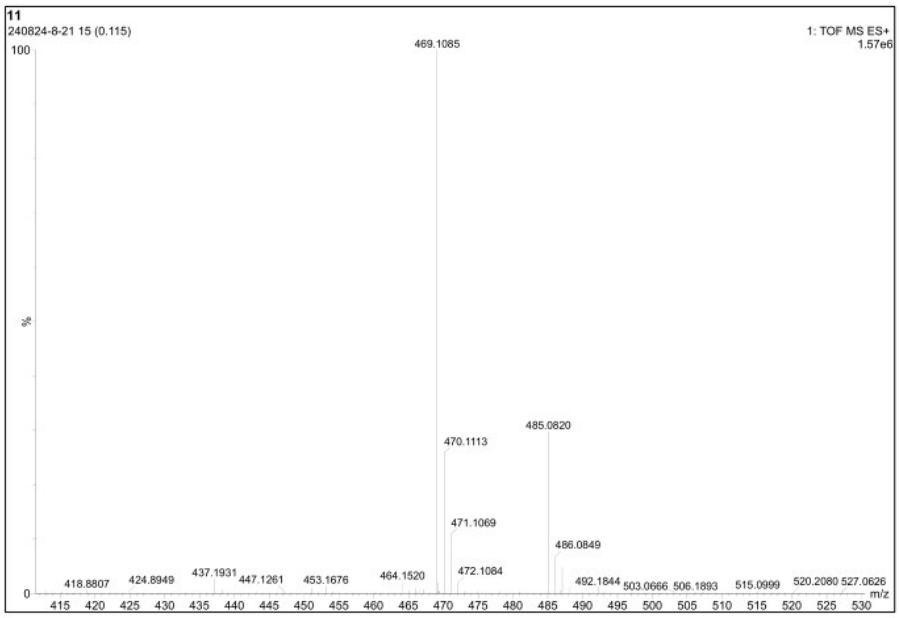
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **34**.



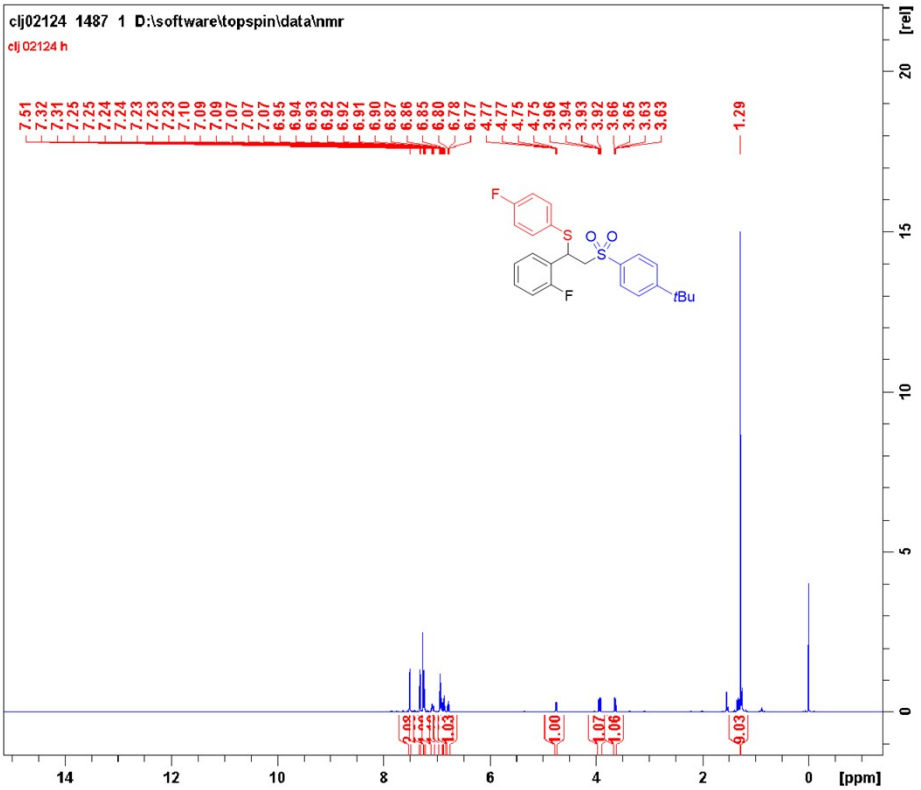
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **34**.



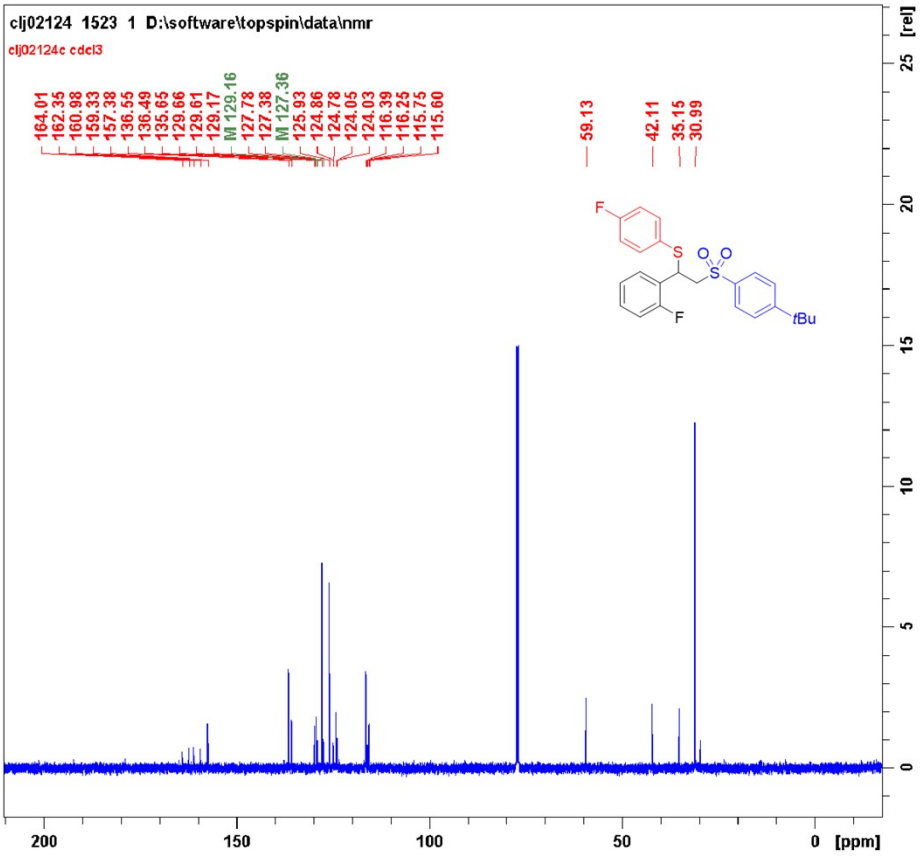
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **34**.



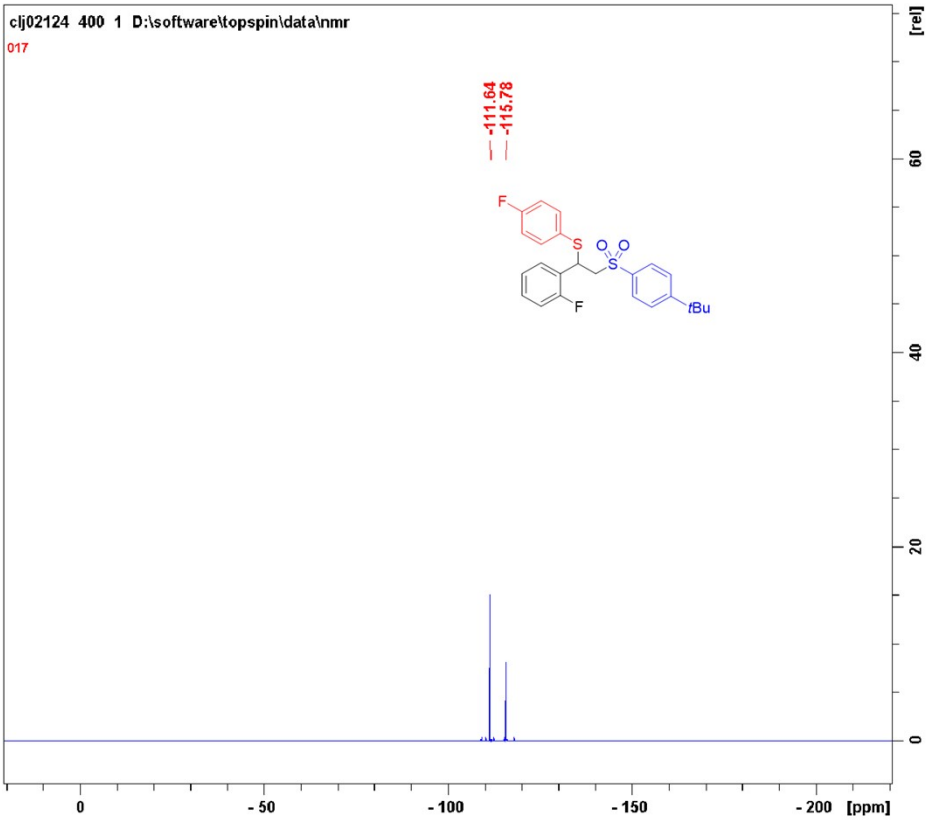
HR-MS (ESI) spectrum of **34**.



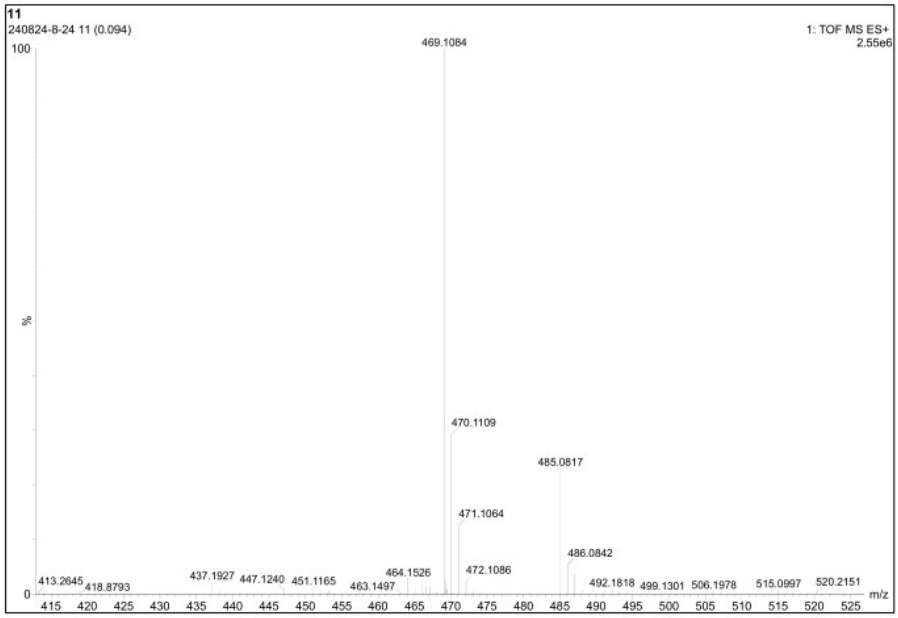
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **35**.



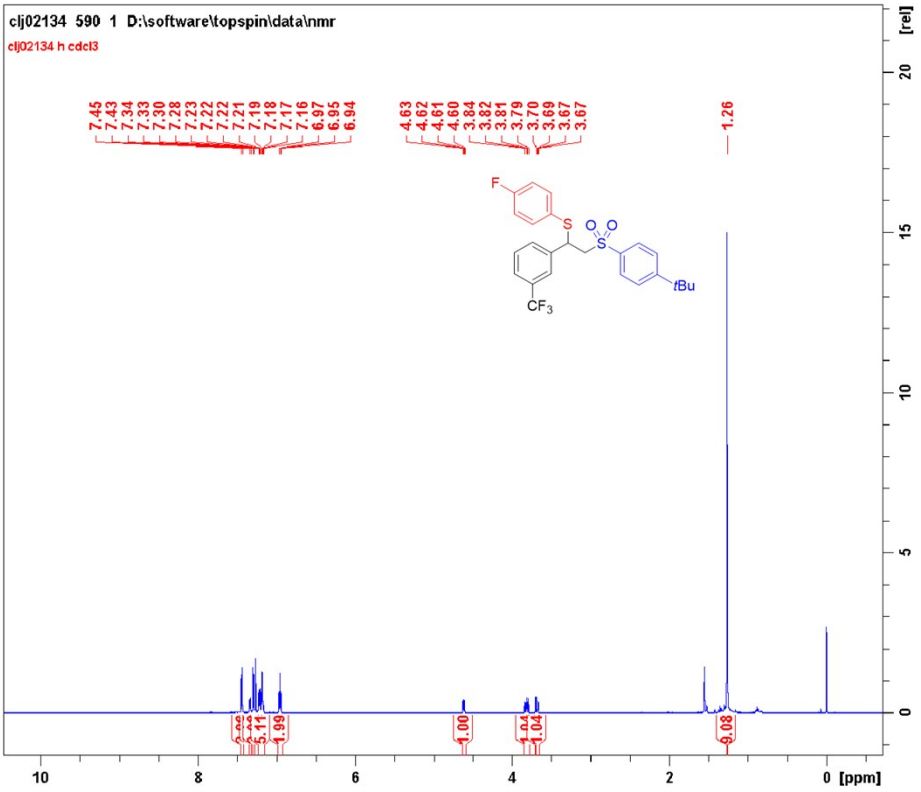
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **35**.



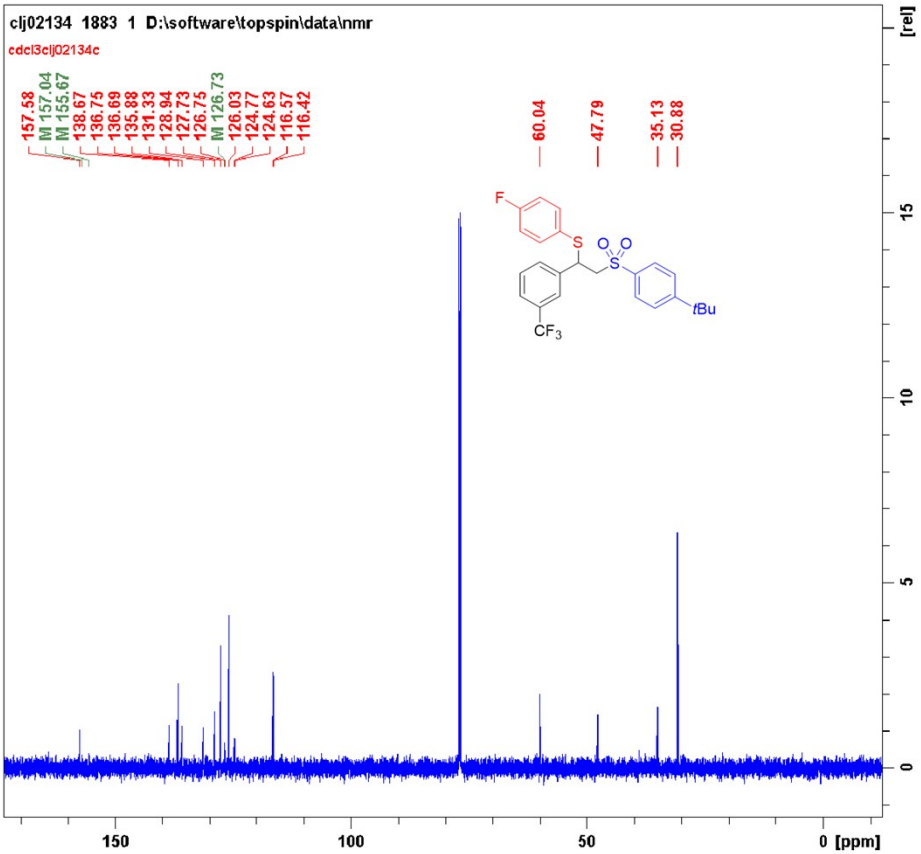
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **35**.



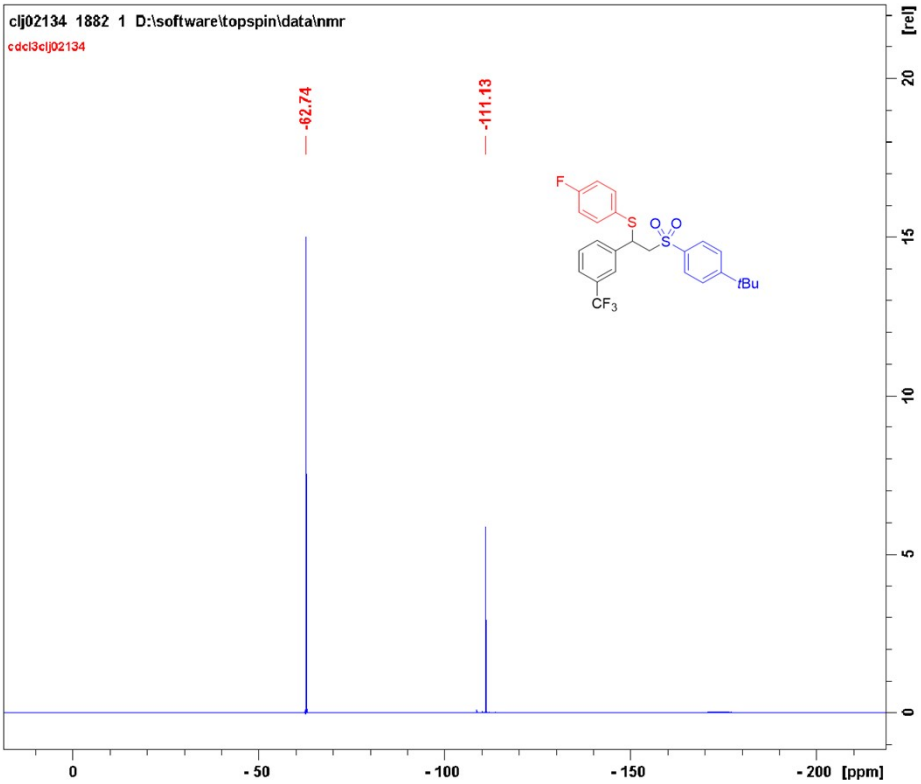
HR-MS (ESI) spectrum of **35**



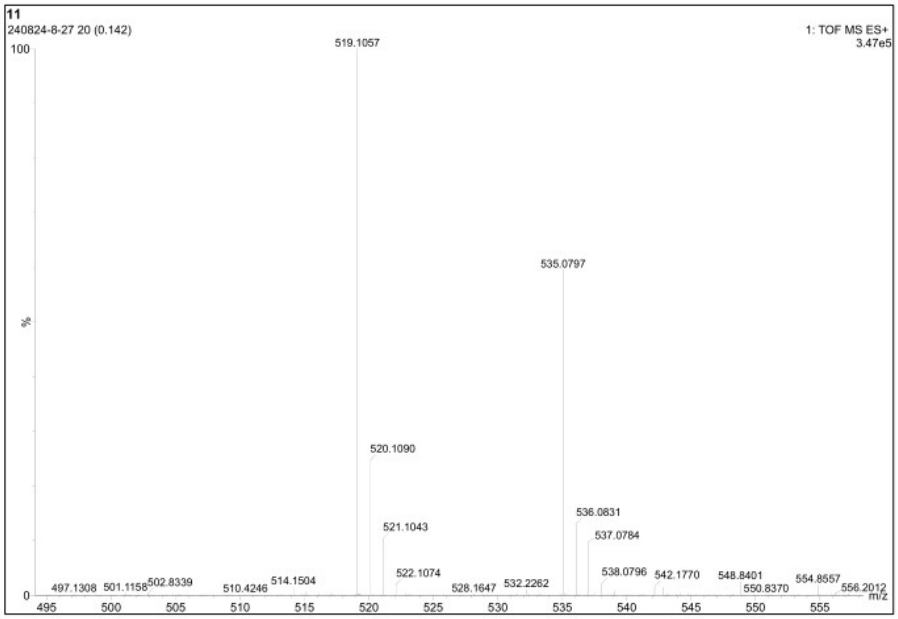
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **36**.



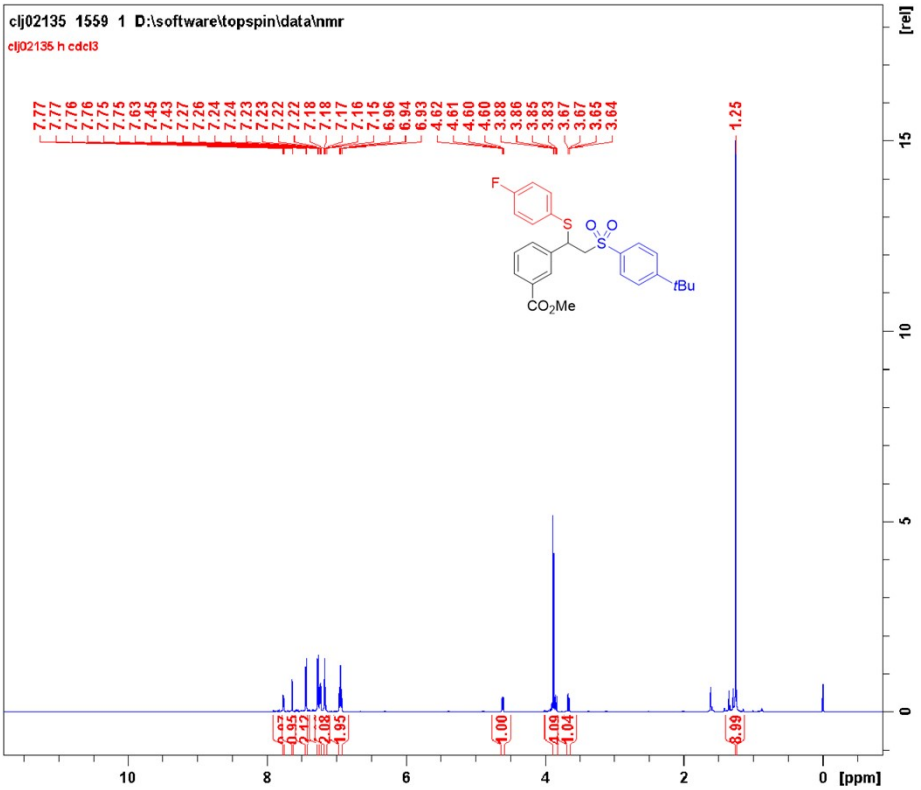
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **36**.



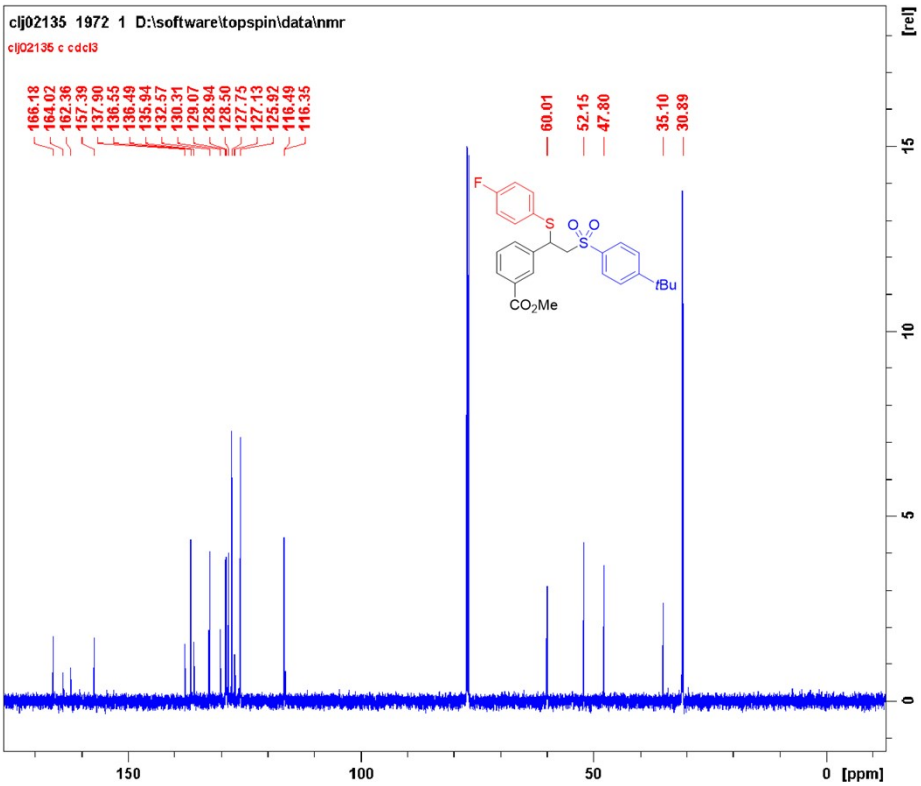
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **36**.



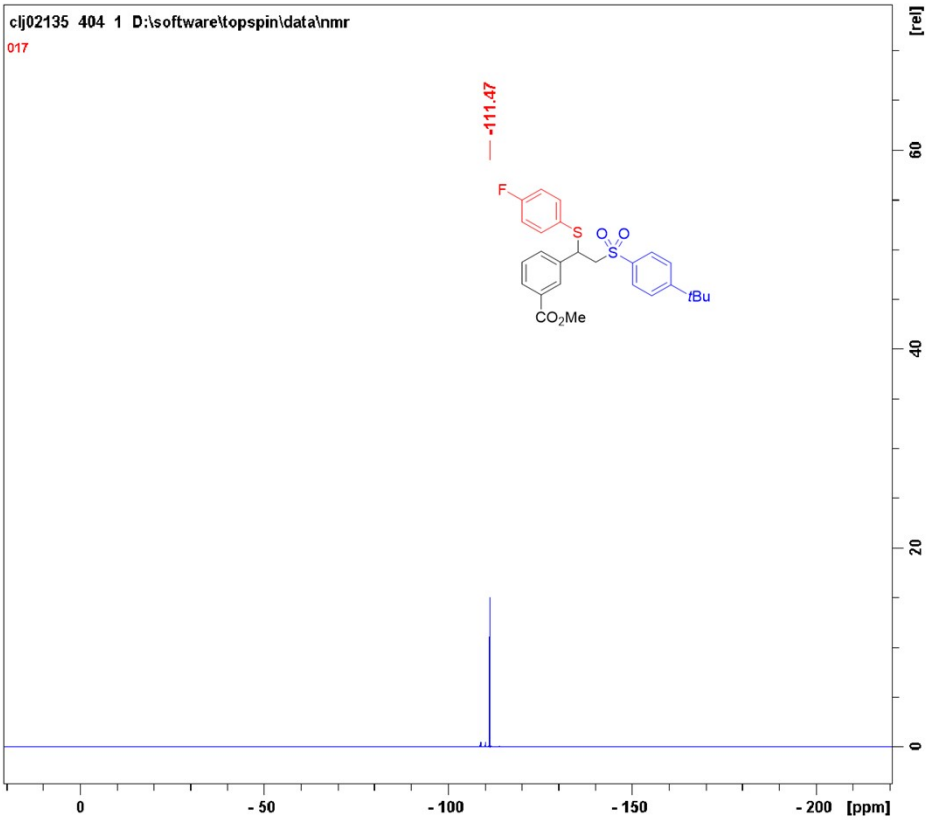
HR-MS (ESI) spectrum of **36**.



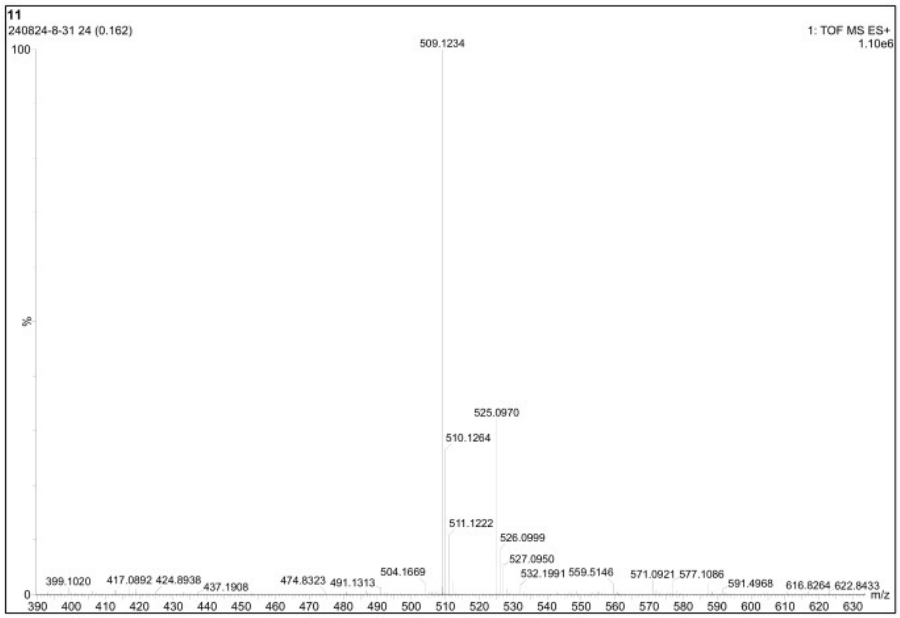
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **37**.



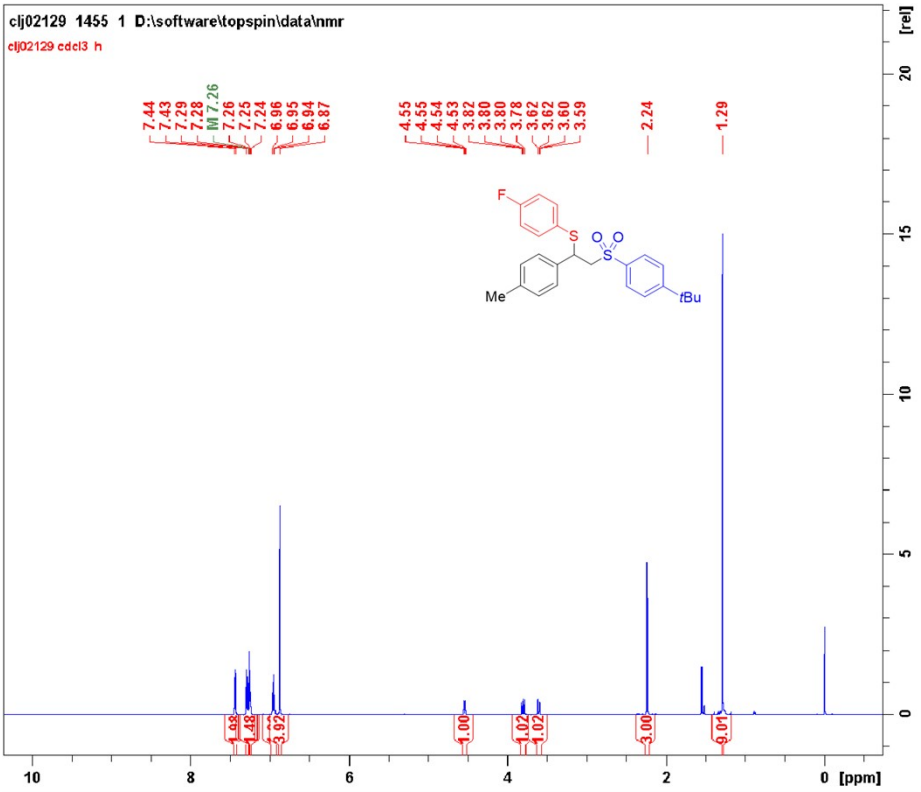
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **37**.



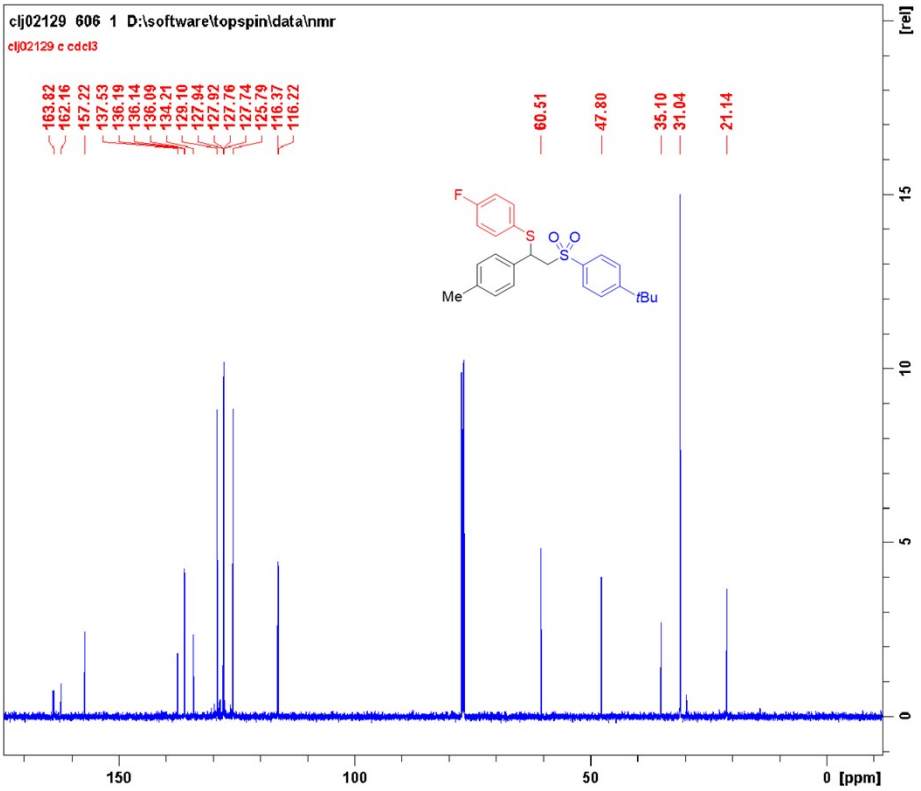
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **37**.



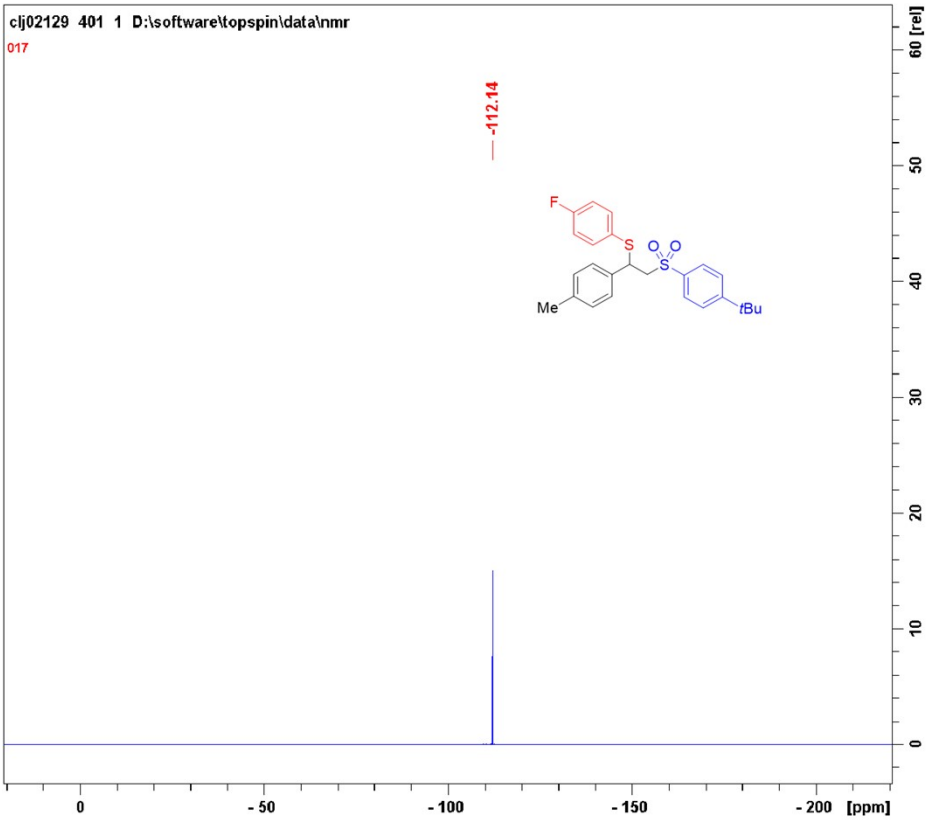
HR-MS (ESI) spectrum of **37**.



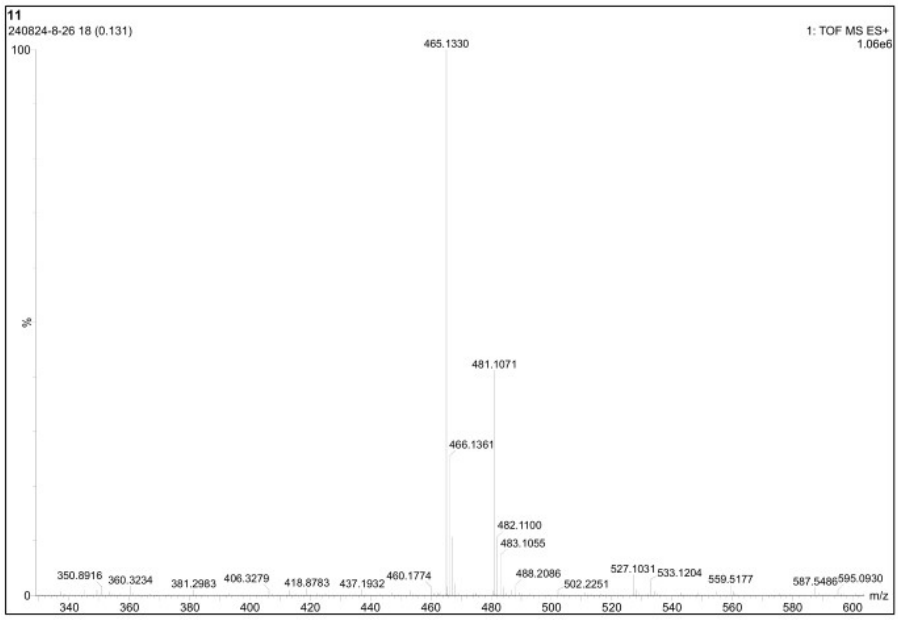
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **38**.



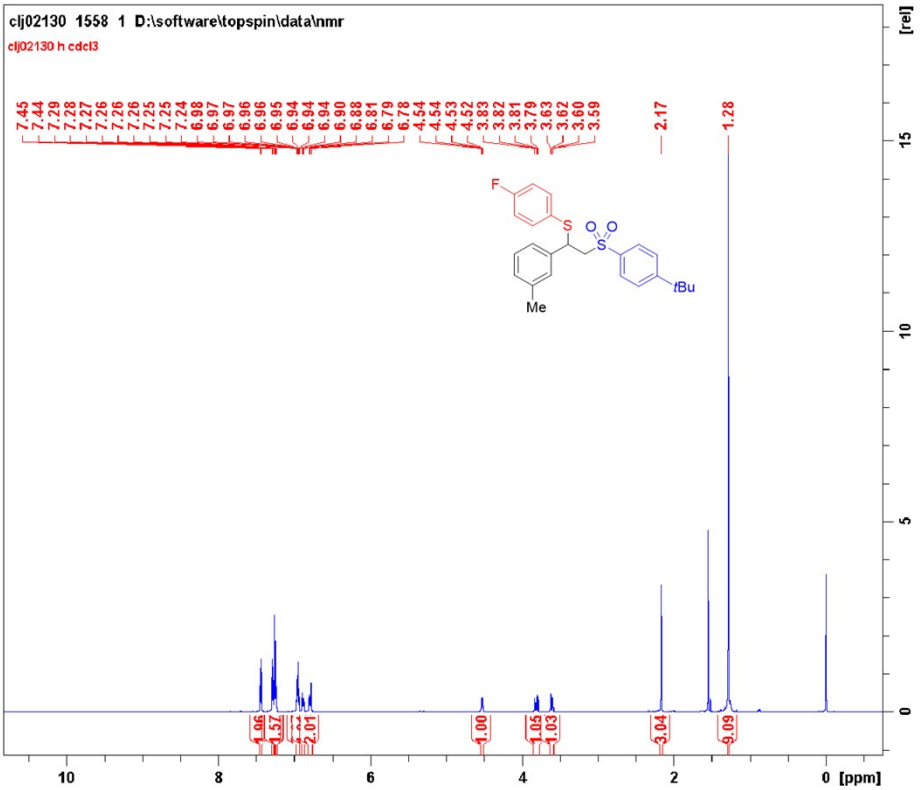
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **38**.



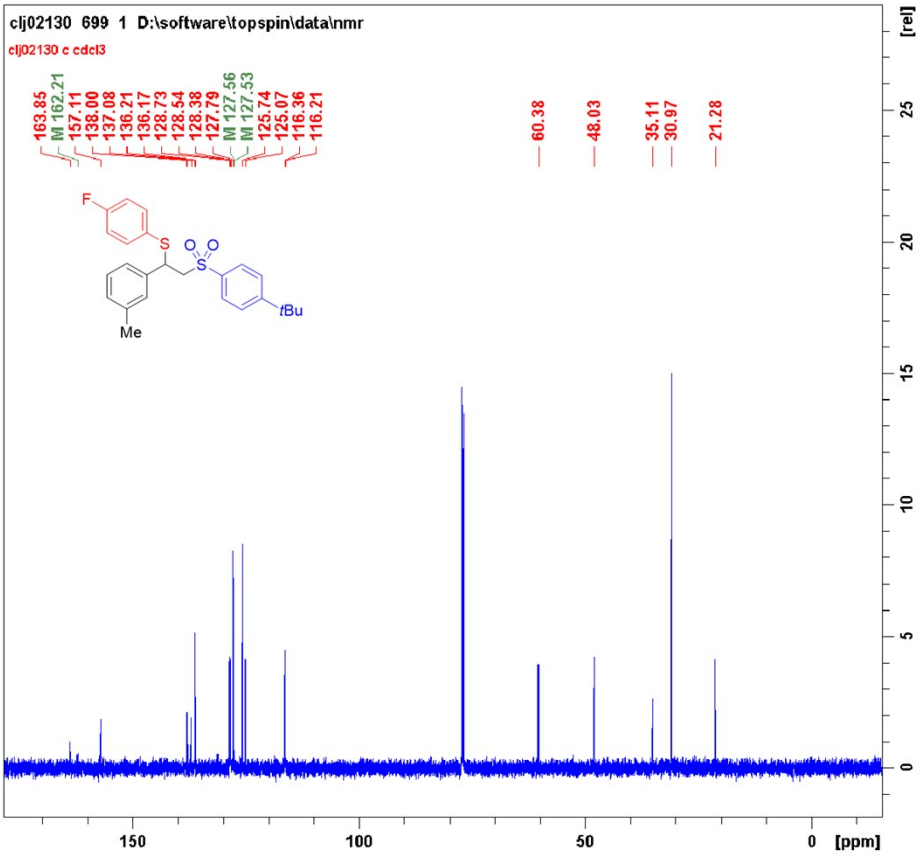
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **38**.



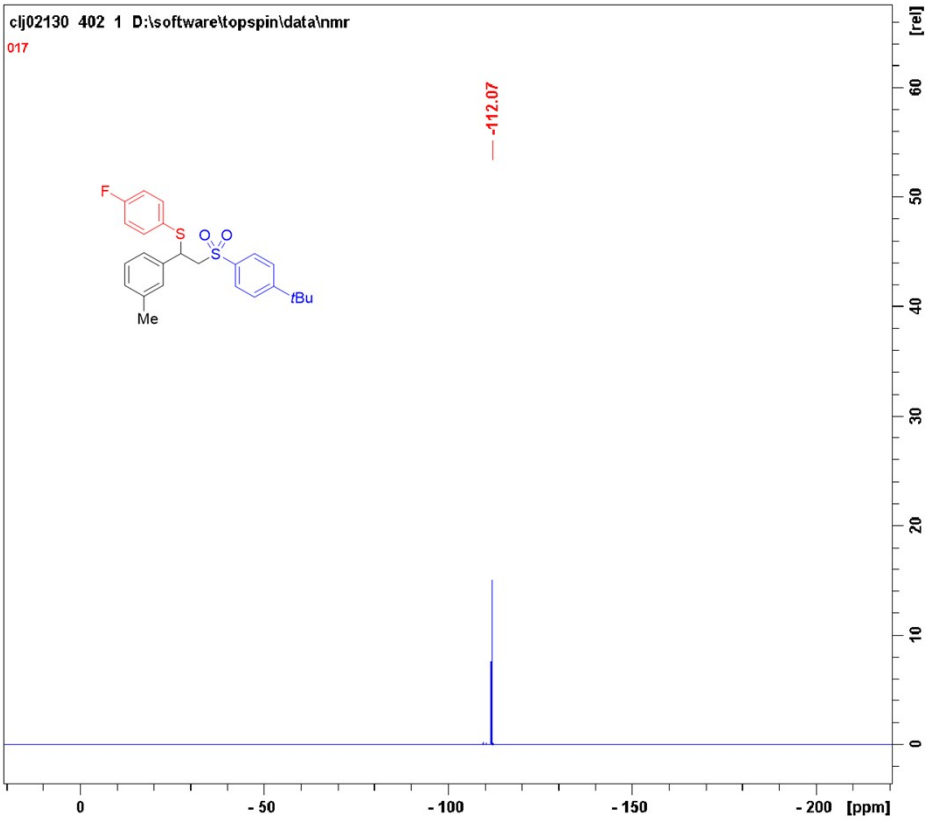
HR-MS (ESI) spectrum of **38**.



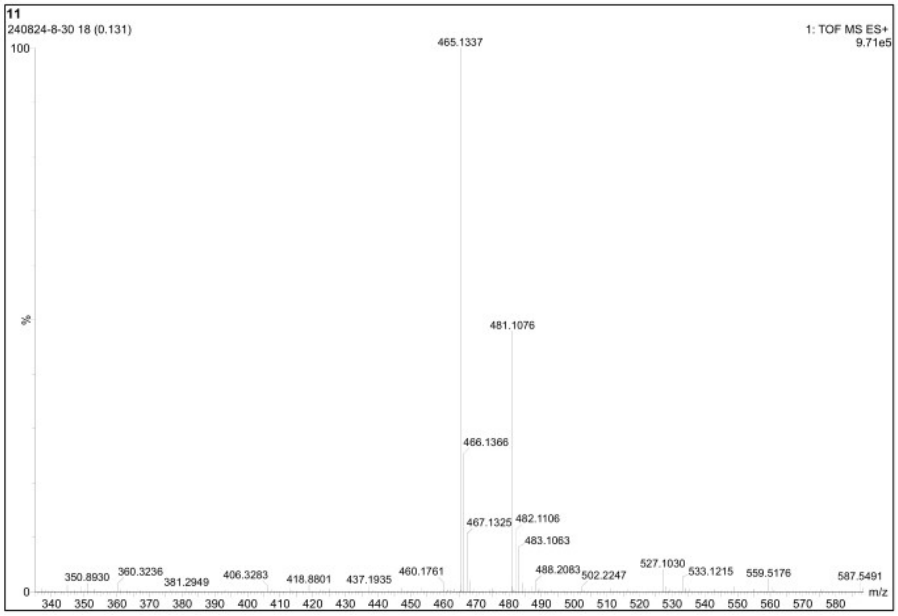
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **39**.



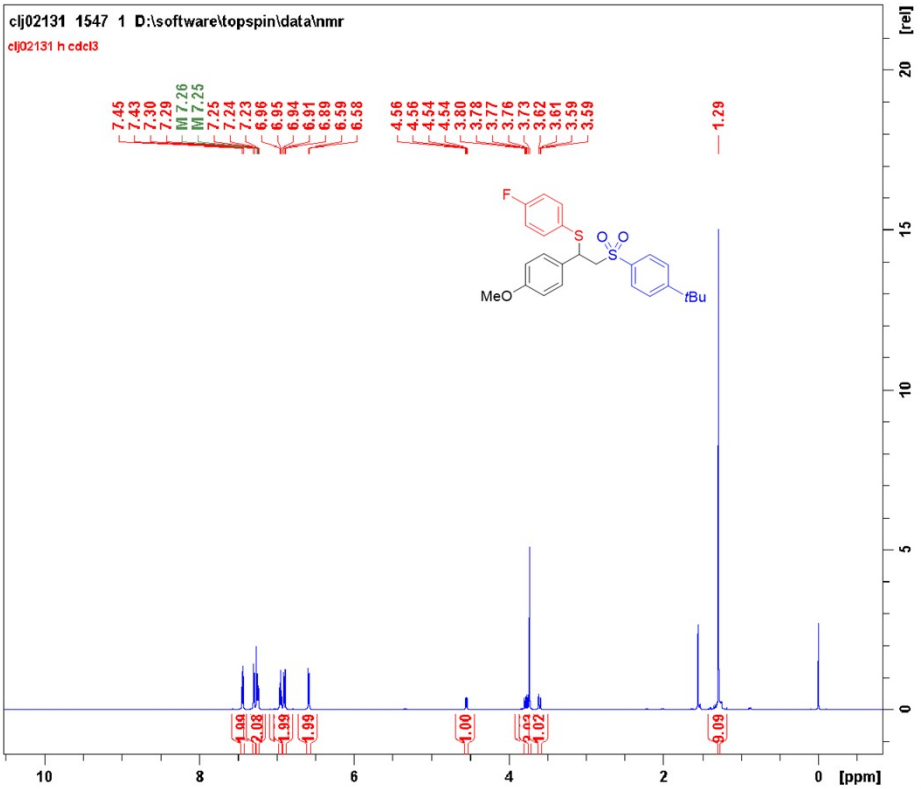
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **39**.



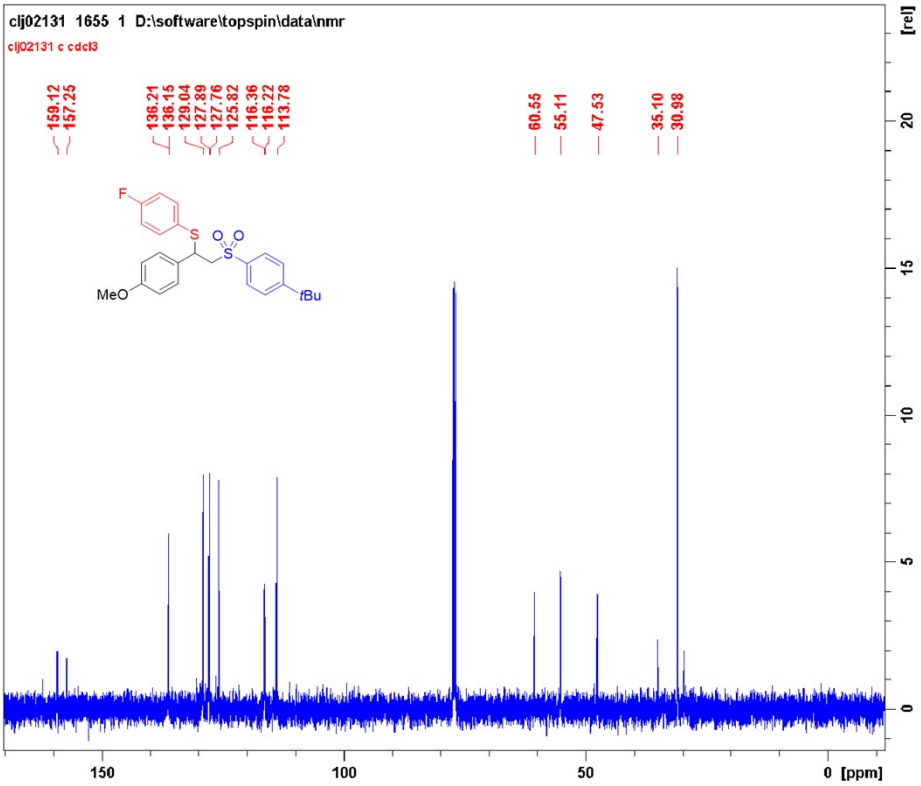
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **39**.



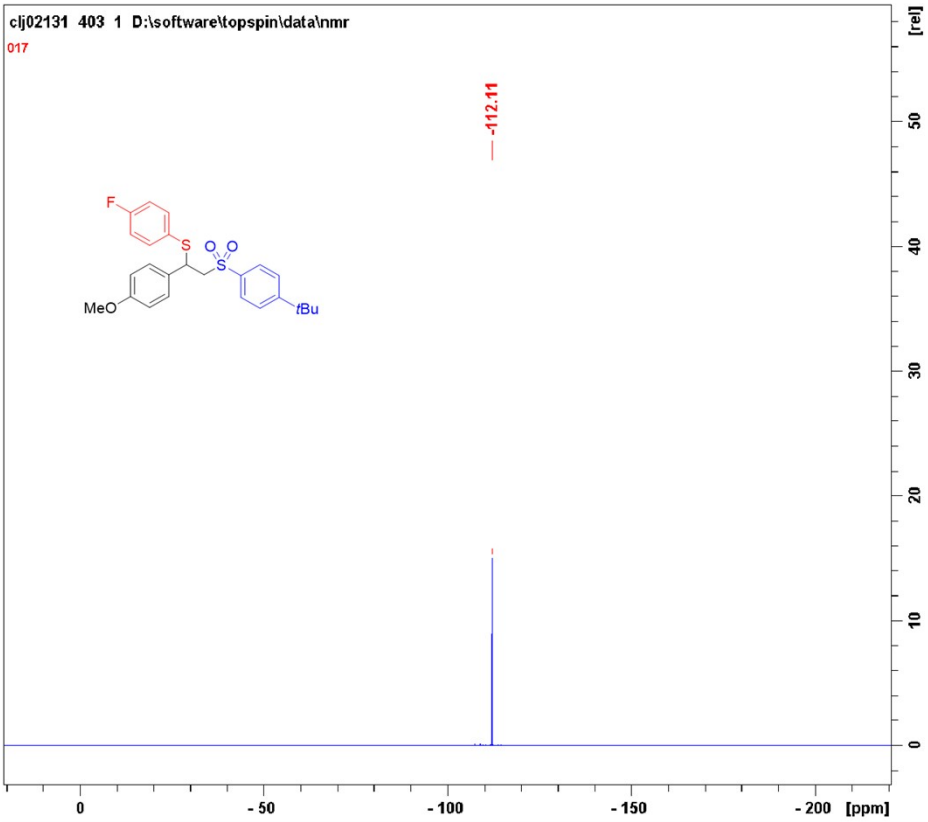
HR-MS (ESI) spectrum of **39**.



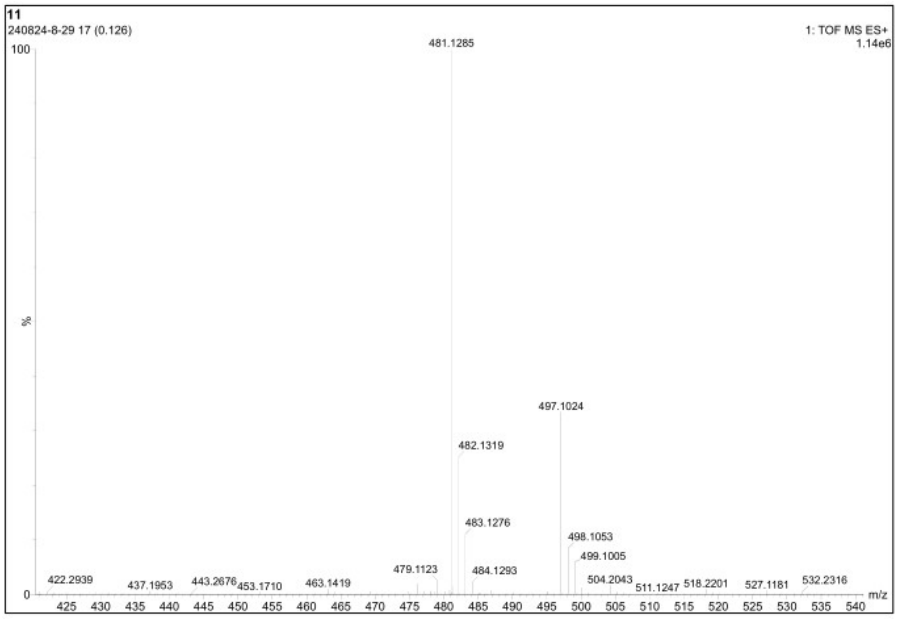
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **40**.



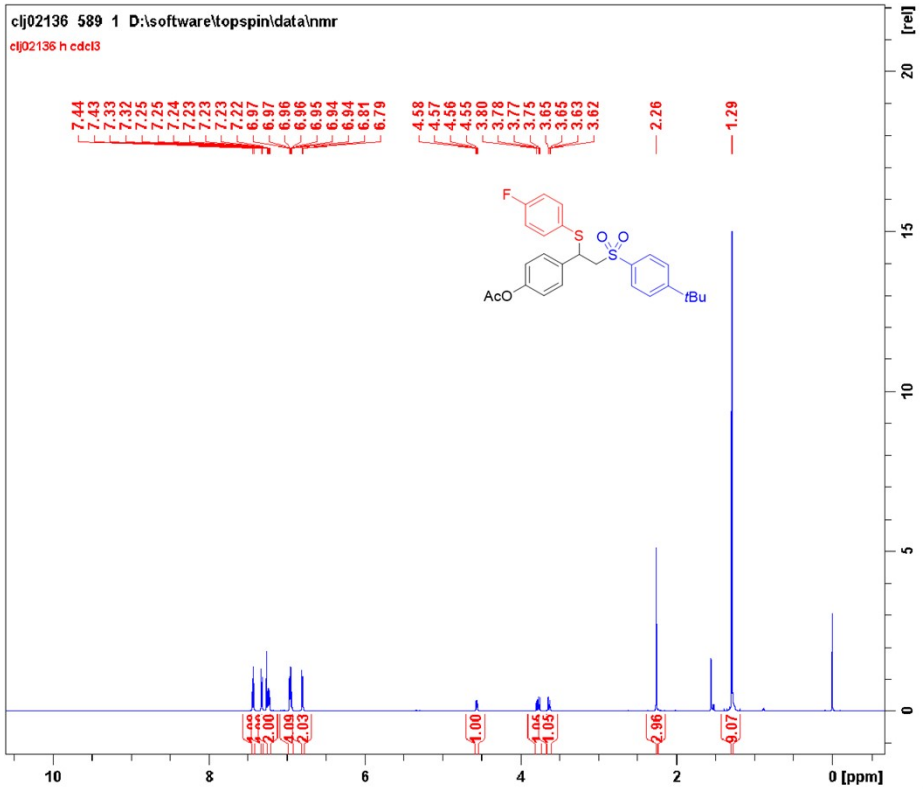
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **40**.



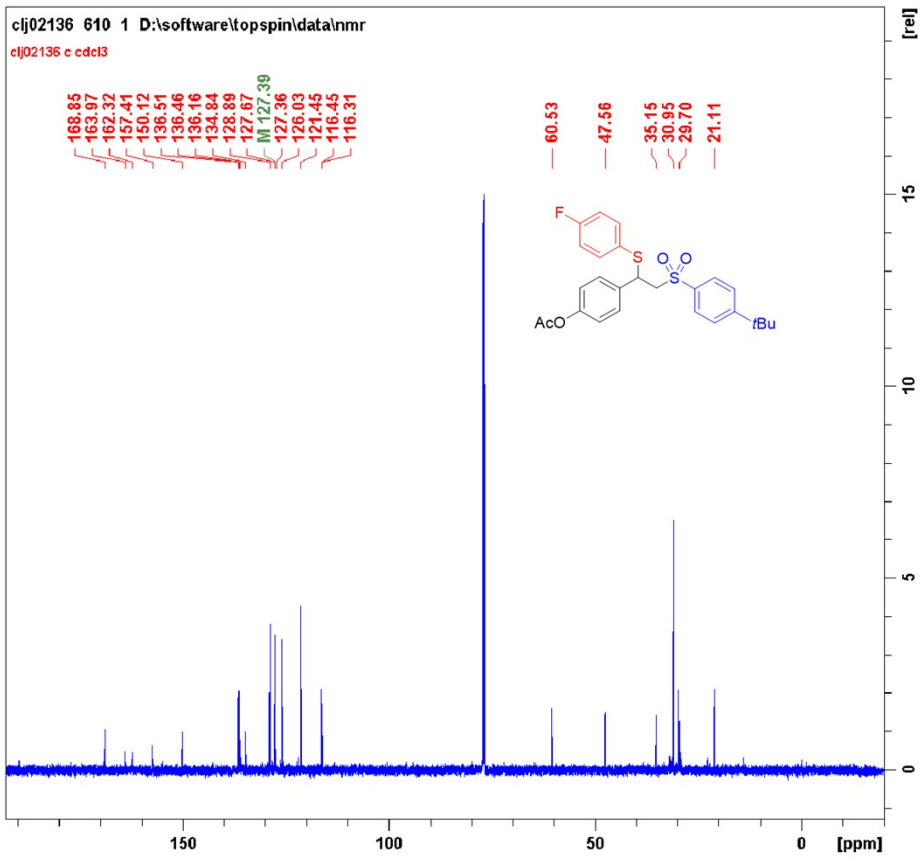
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **40**.



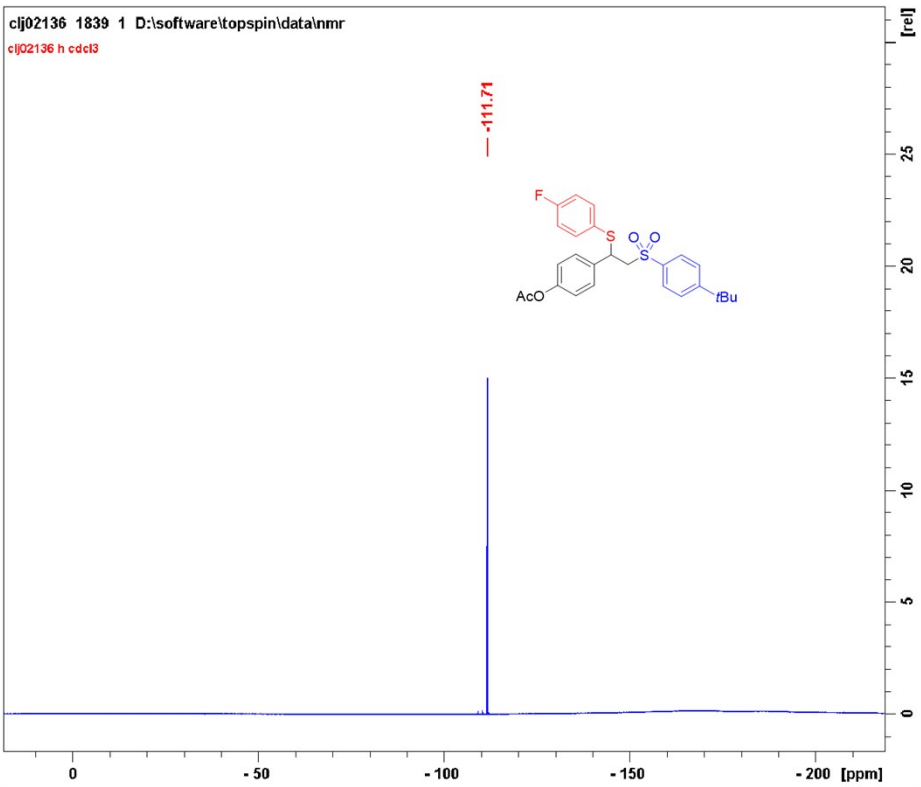
HR-MS (ESI) spectrum of **40**.



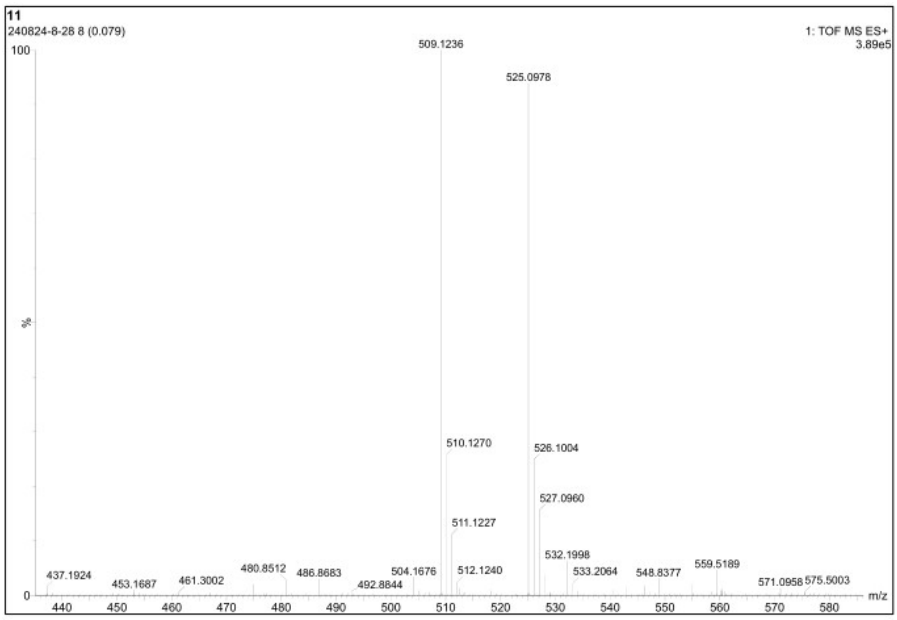
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **41**.



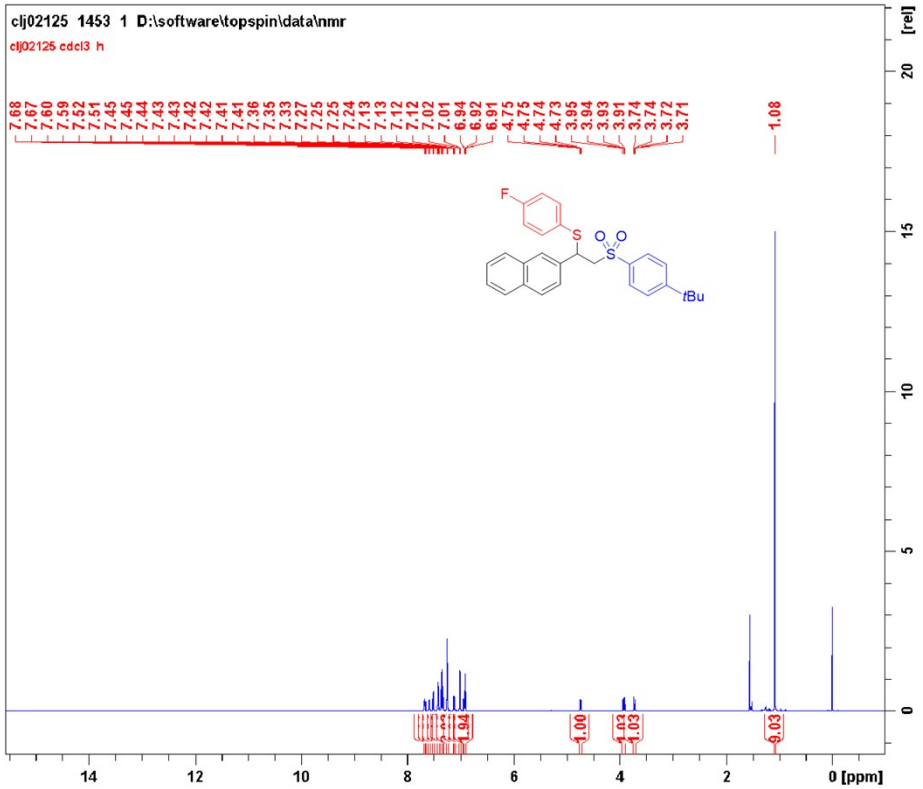
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **41**.



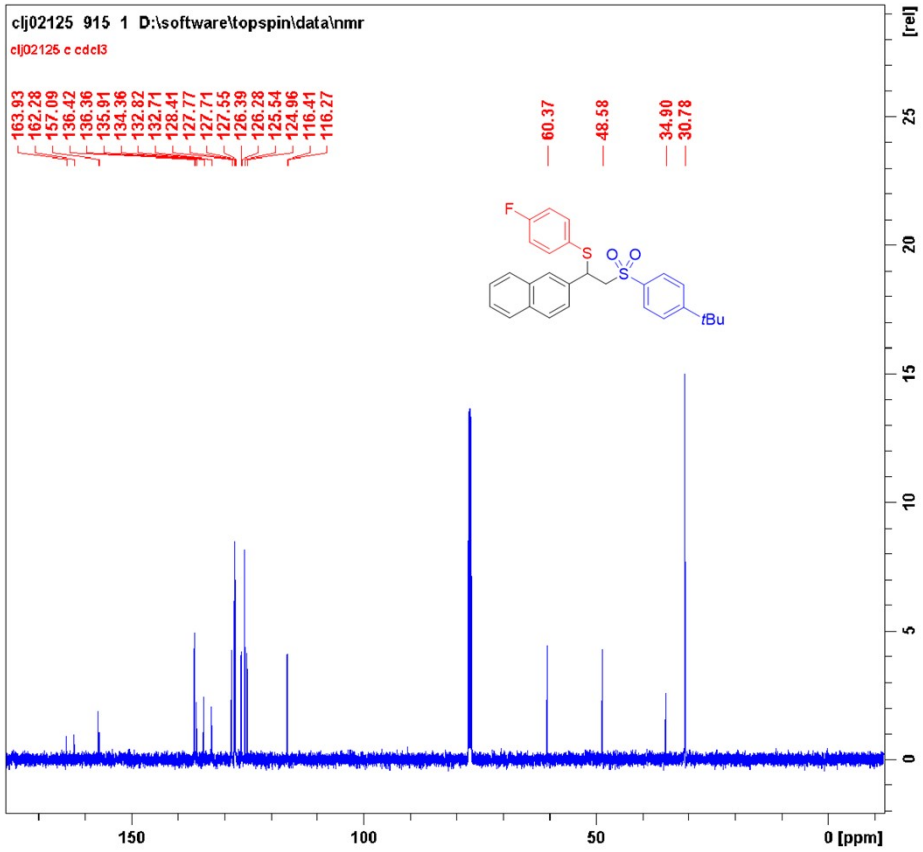
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **41**.



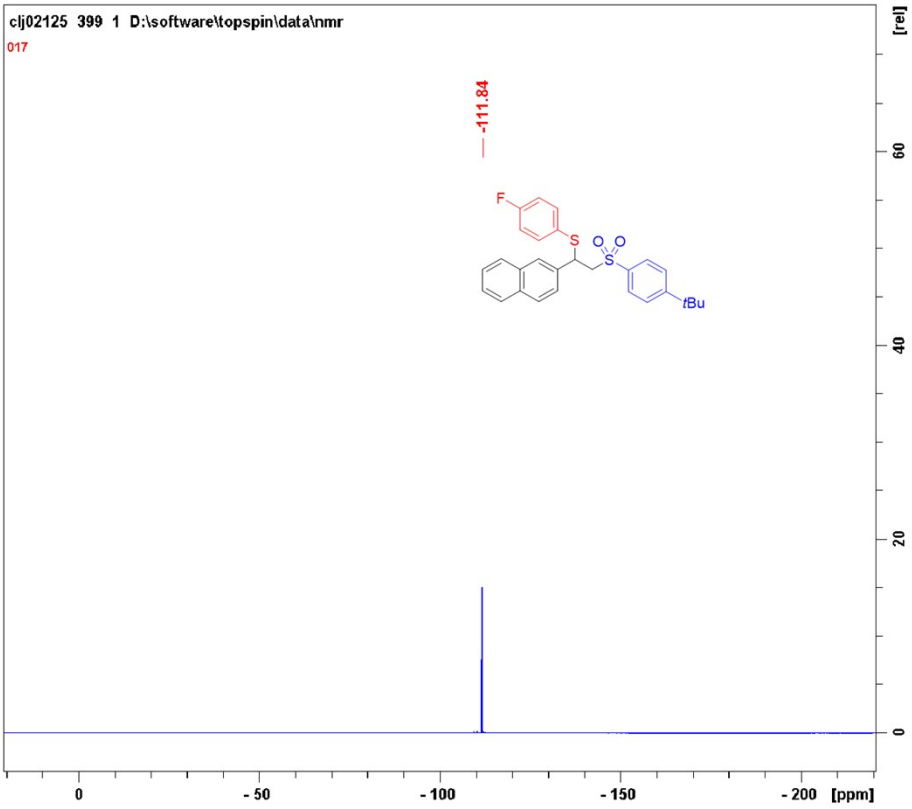
HR-MS (ESI) spectrum of **41**.



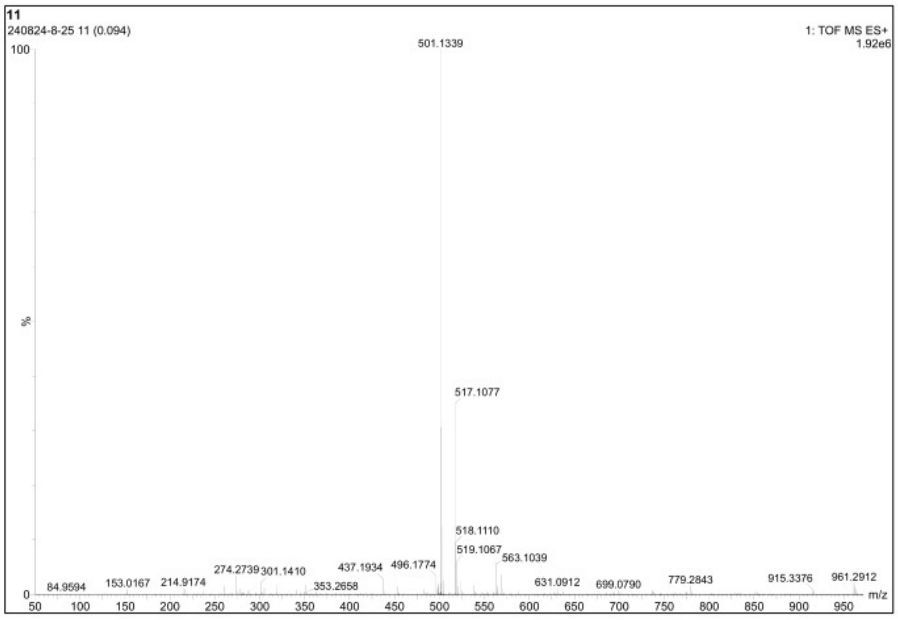
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **42**.



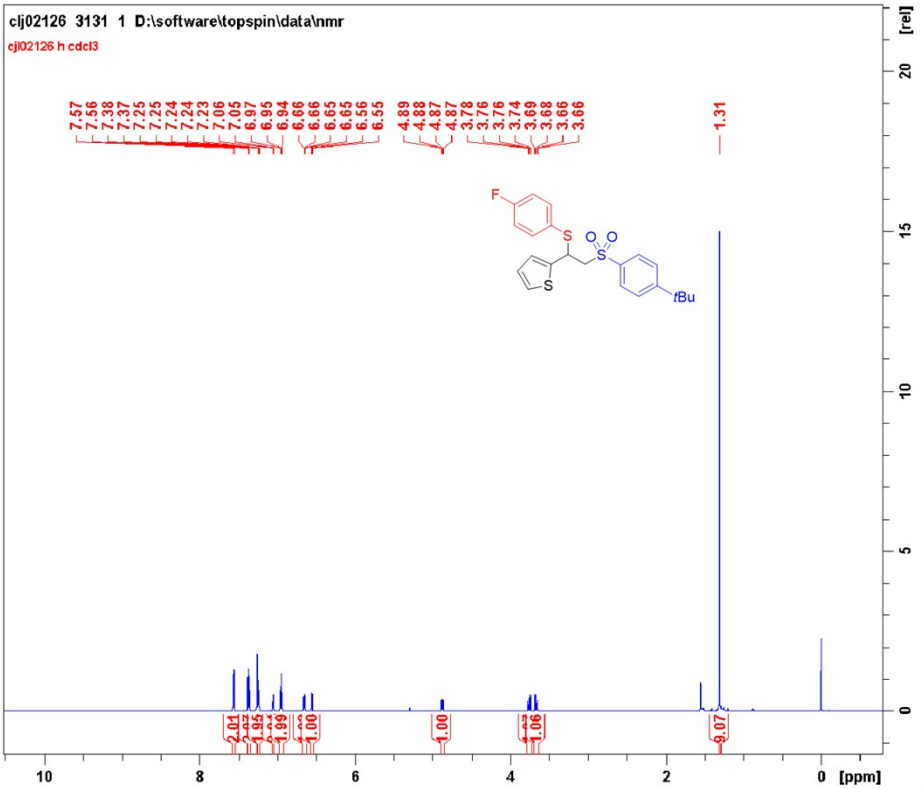
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **42**.



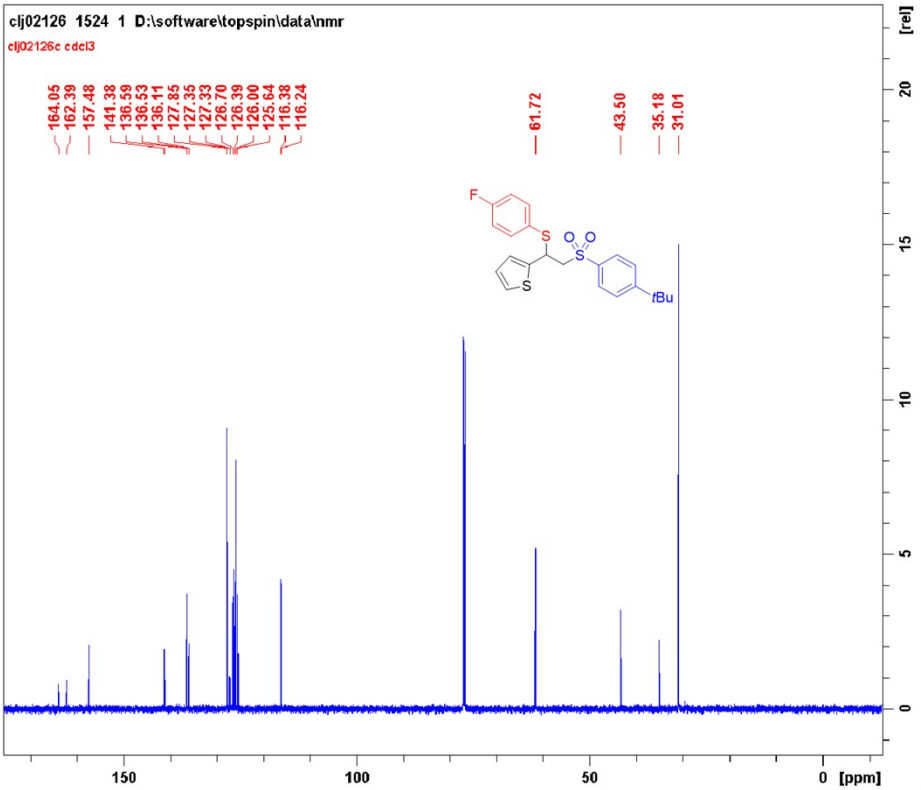
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **42**.



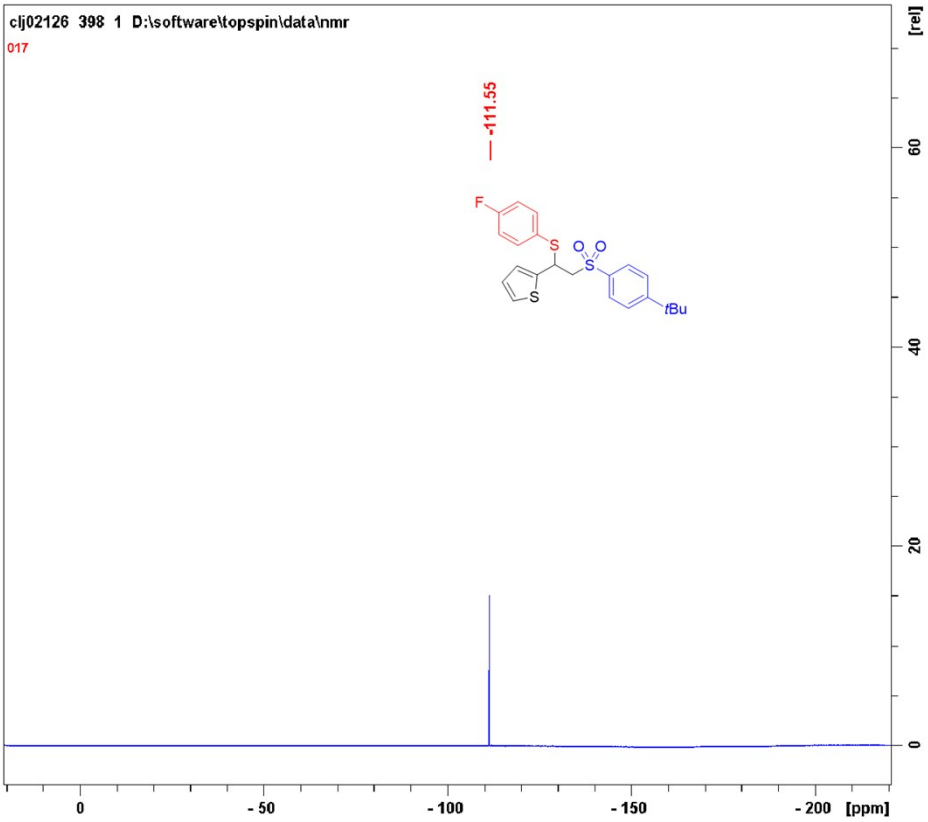
HR-MS (ESI) spectrum of **42**.



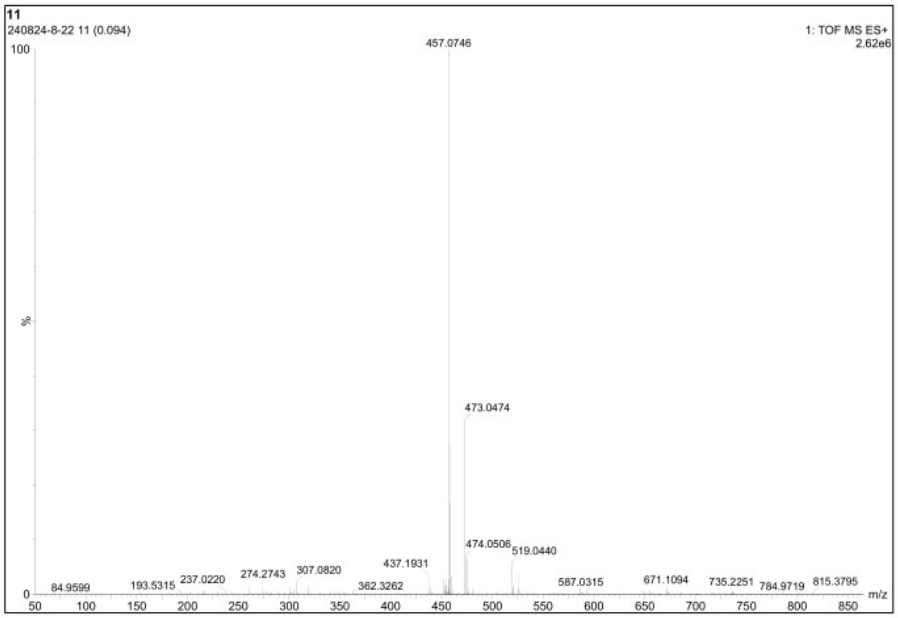
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **43**.



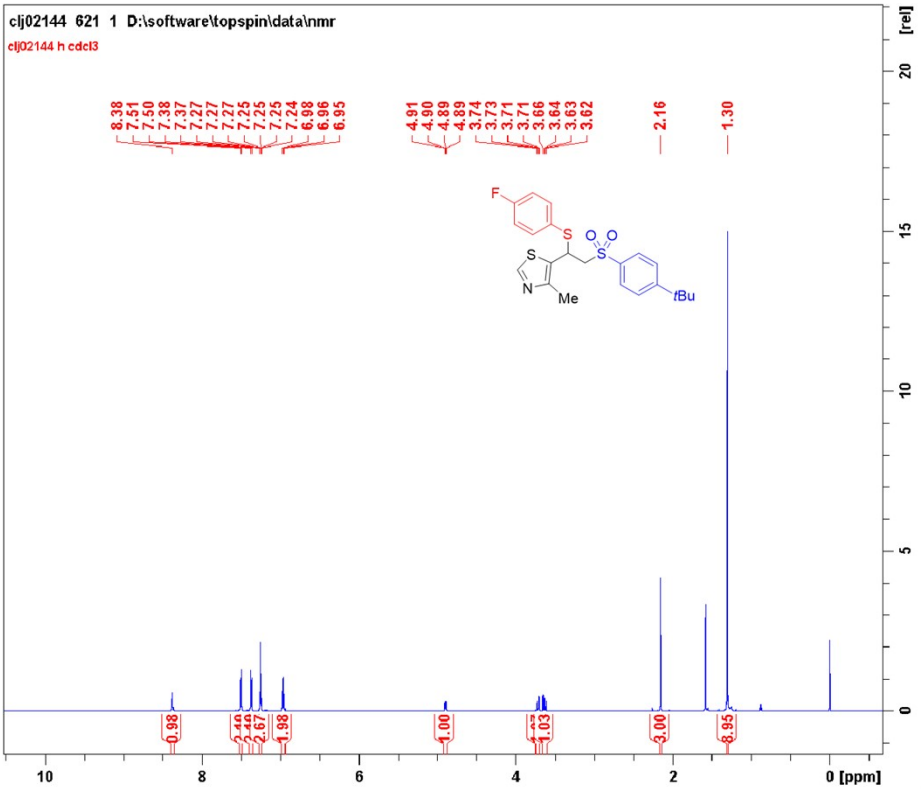
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **43**.



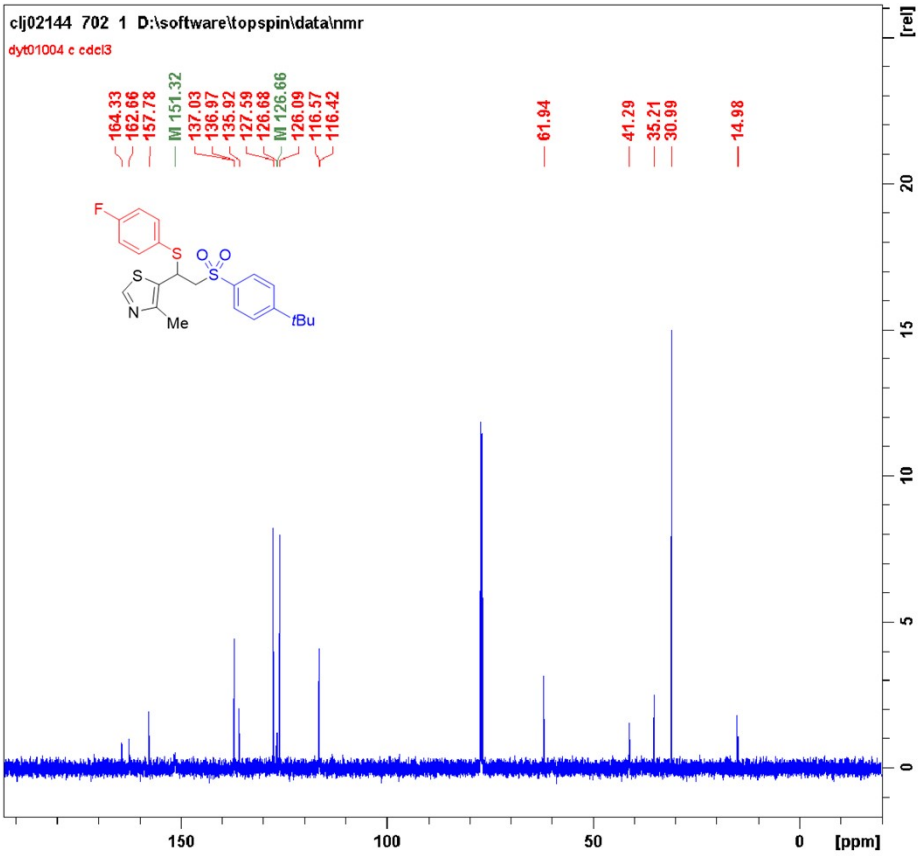
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **43**.



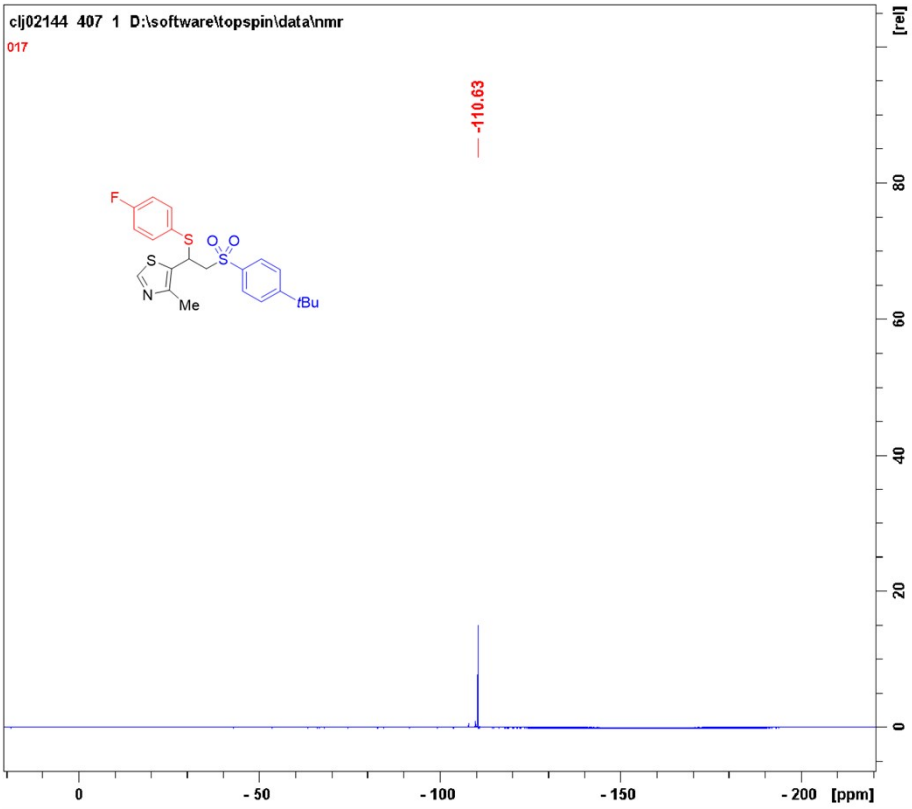
HR-MS (ESI) spectrum of **43**.



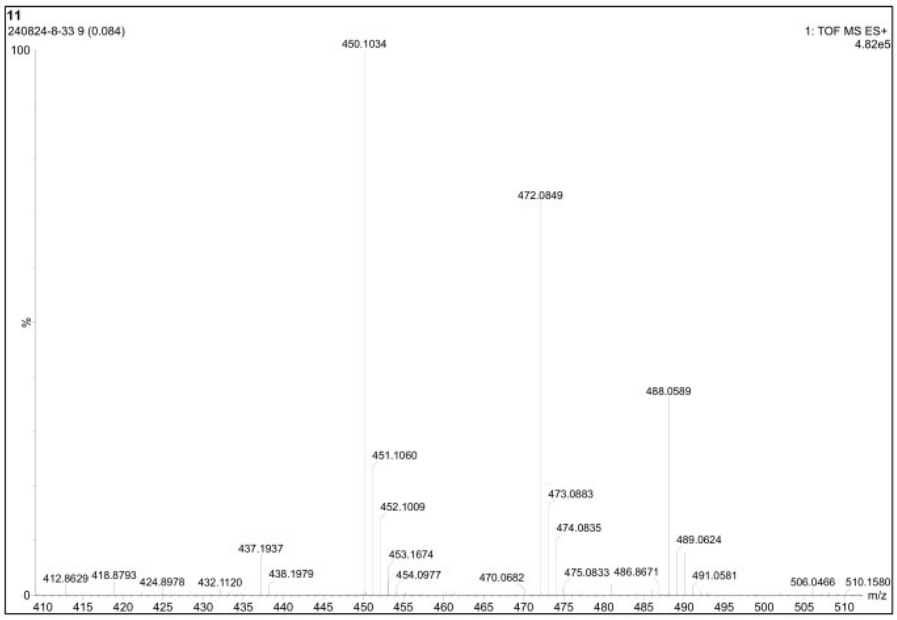
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **44**.



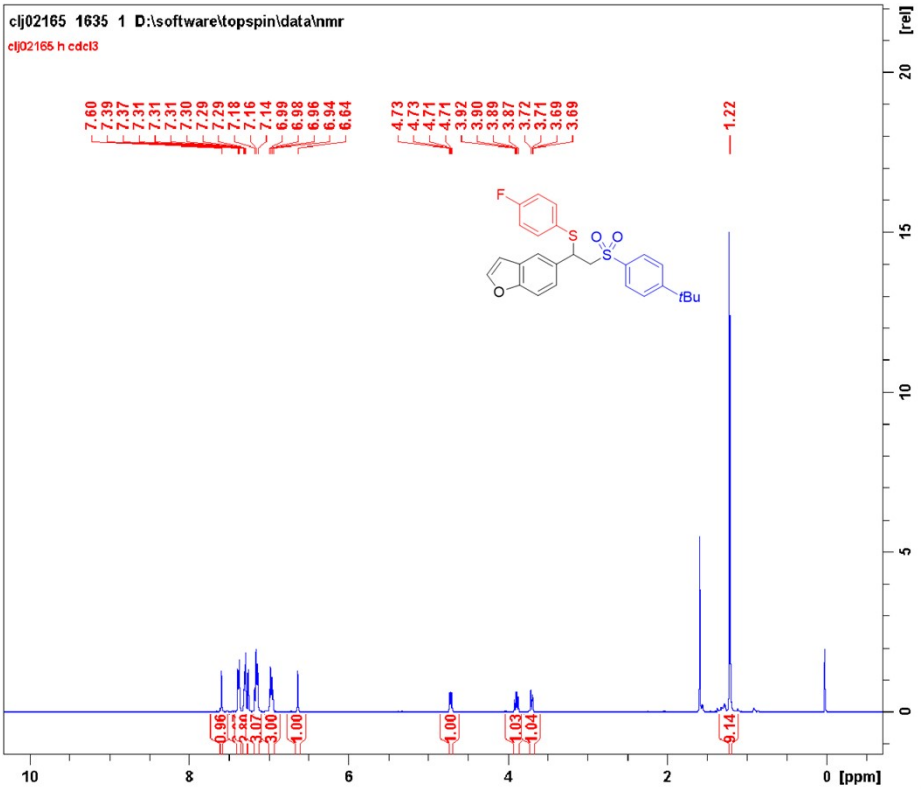
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **44**.



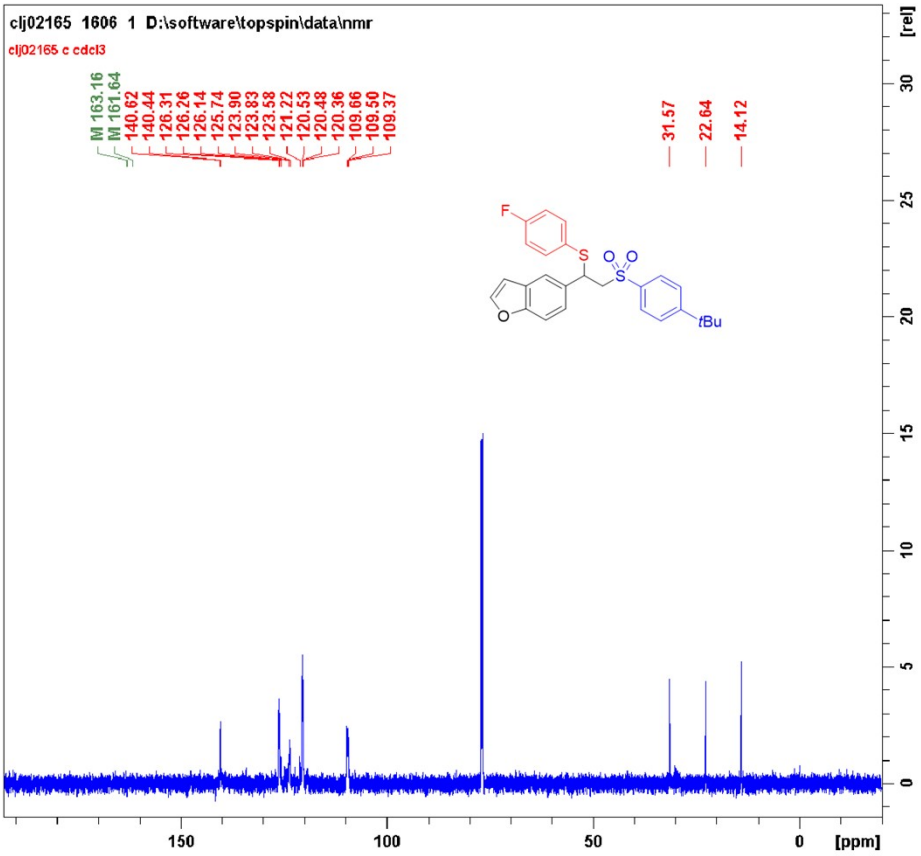
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **44**.



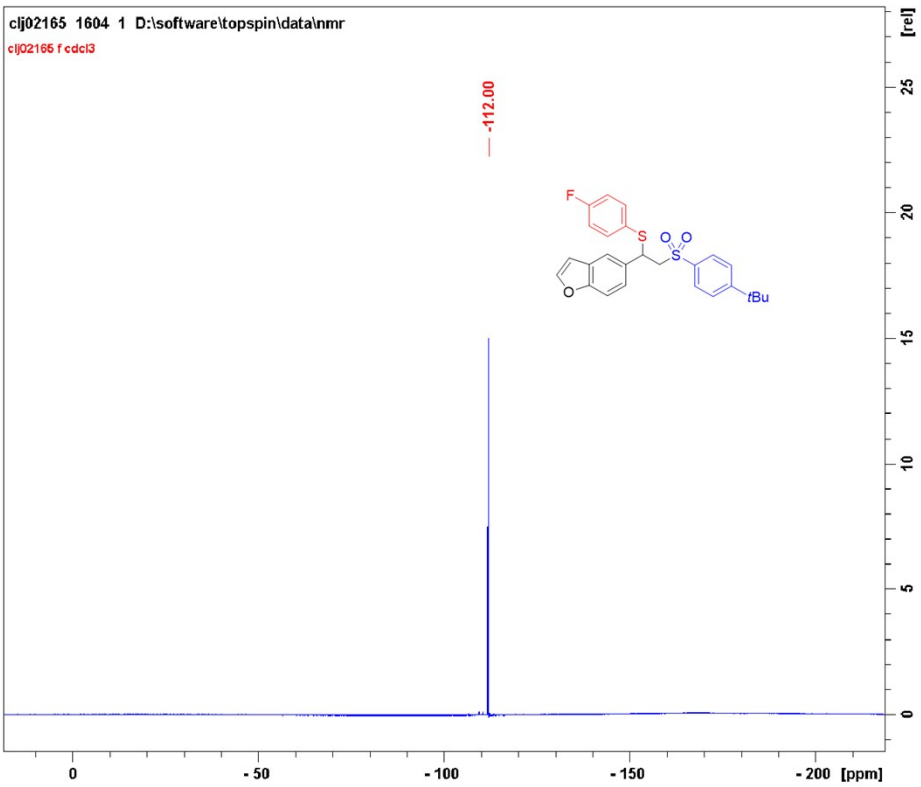
HR-MS (ESI) spectrum of **44**.



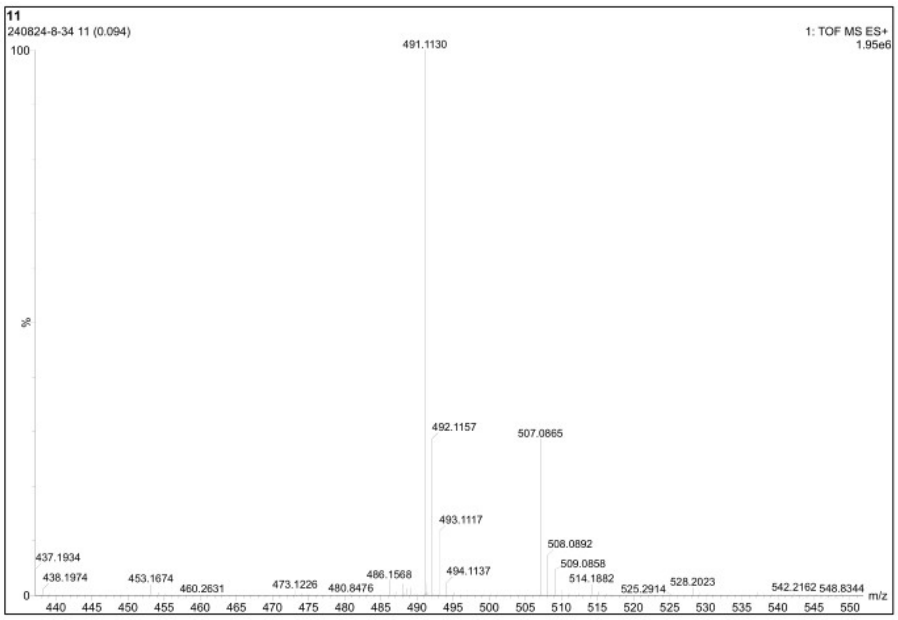
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **45**.



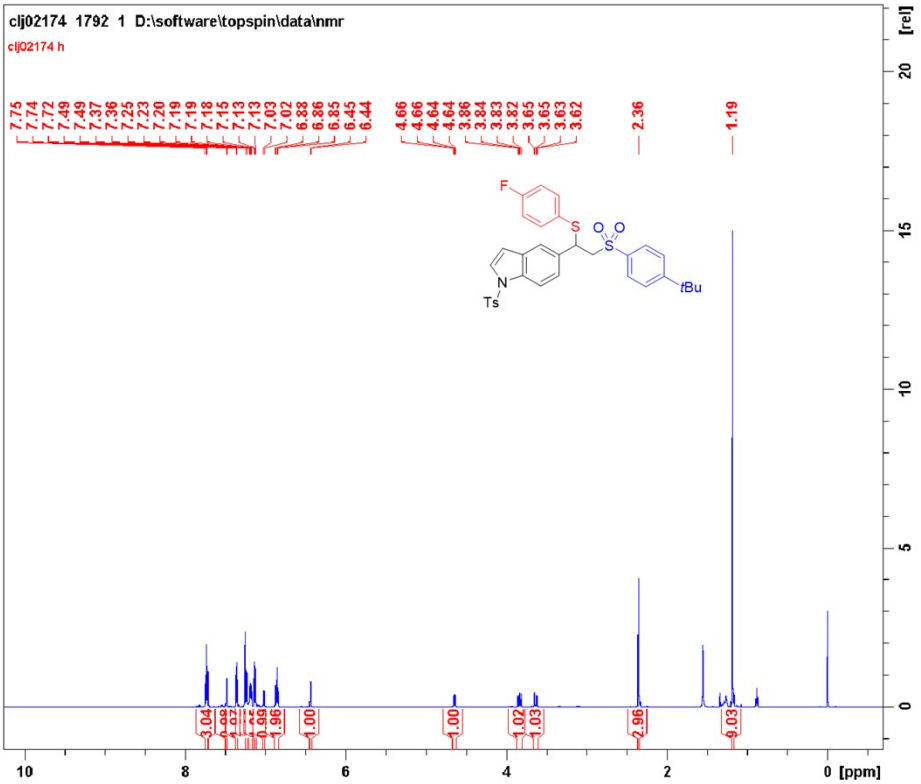
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **45**.



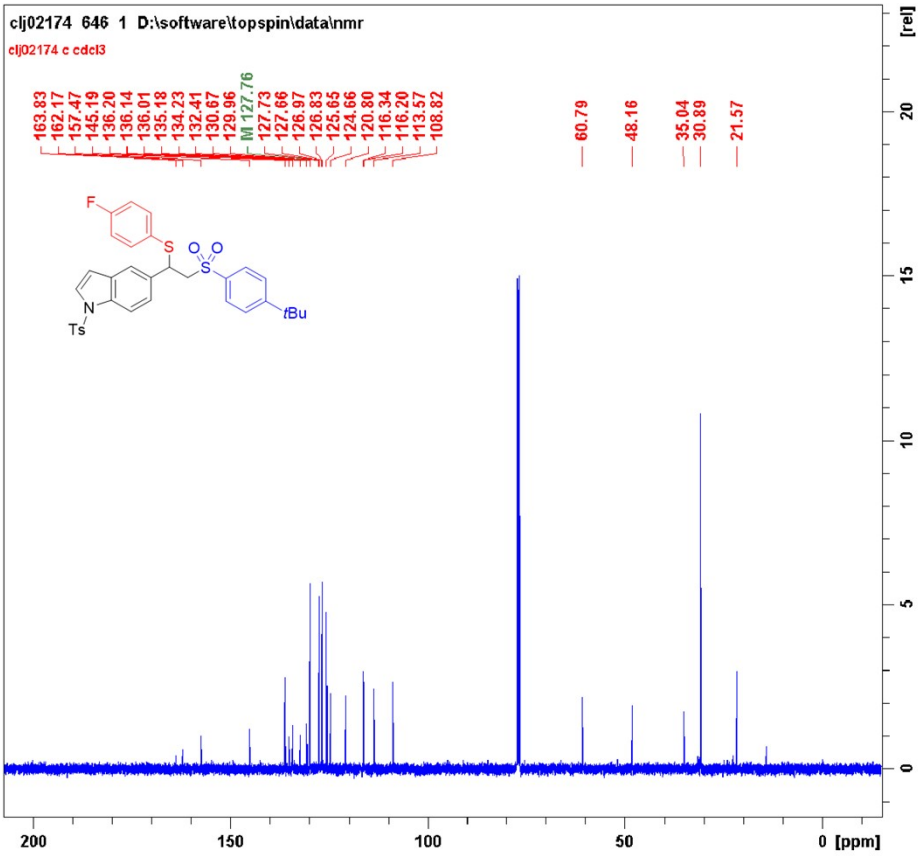
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **45**.



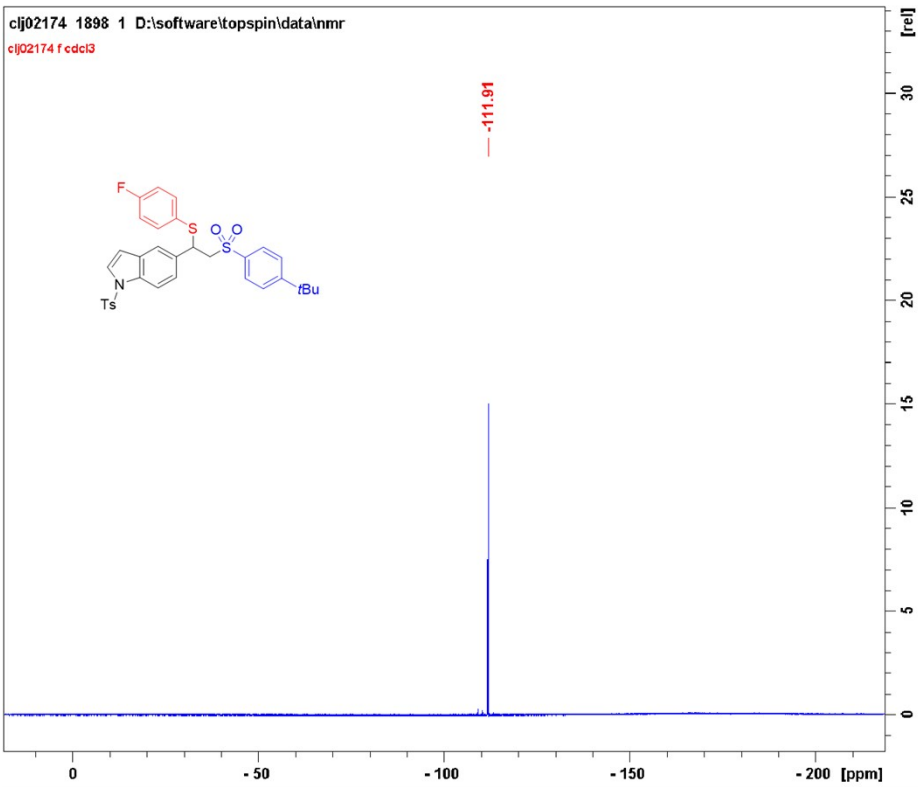
HR-MS (ESI) spectrum of **45**.



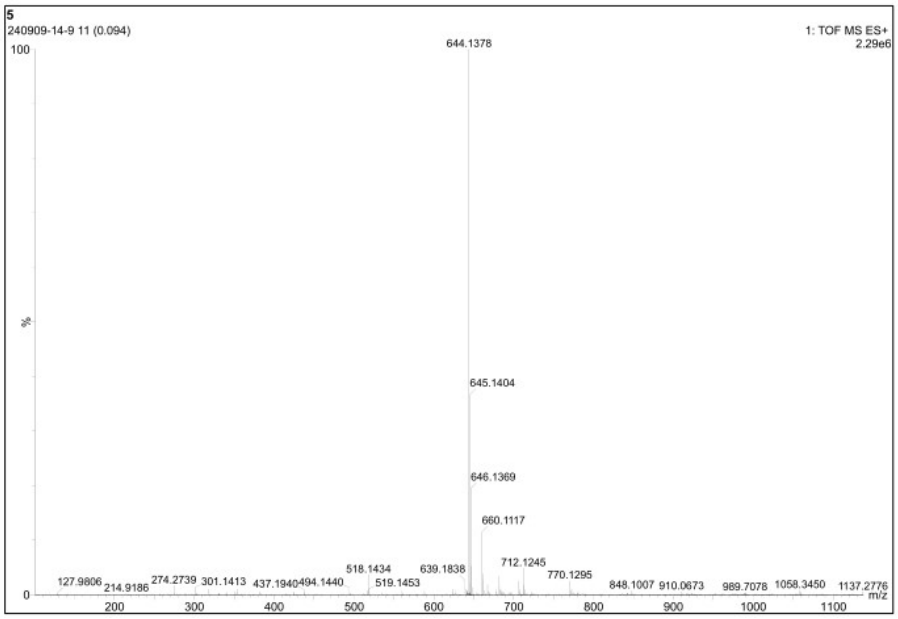
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **46**.



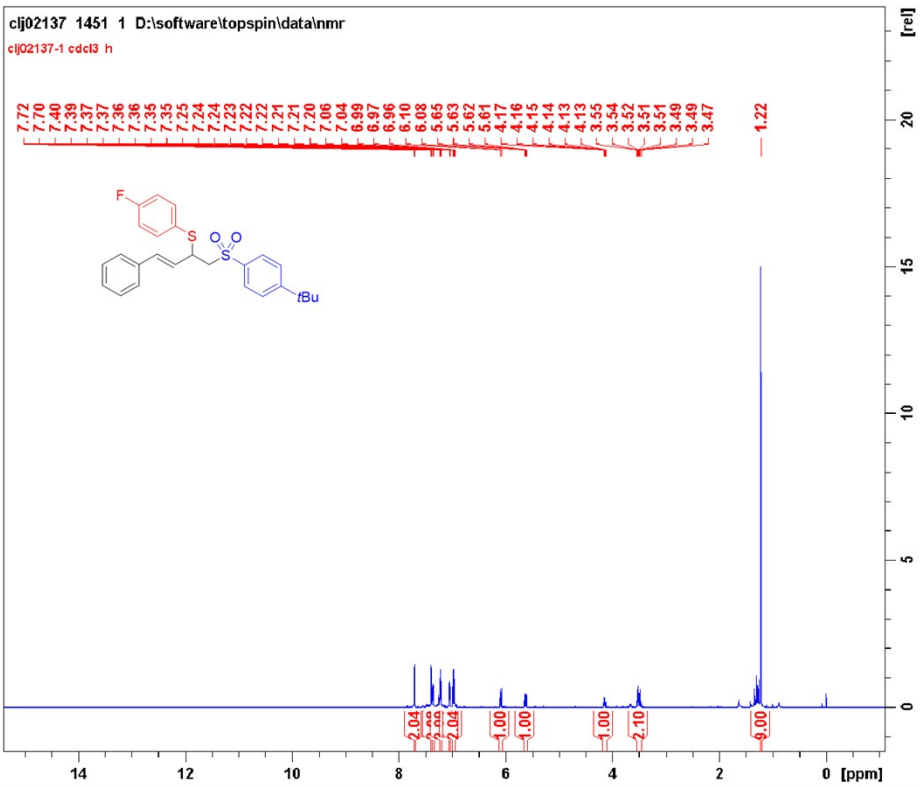
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **46**.



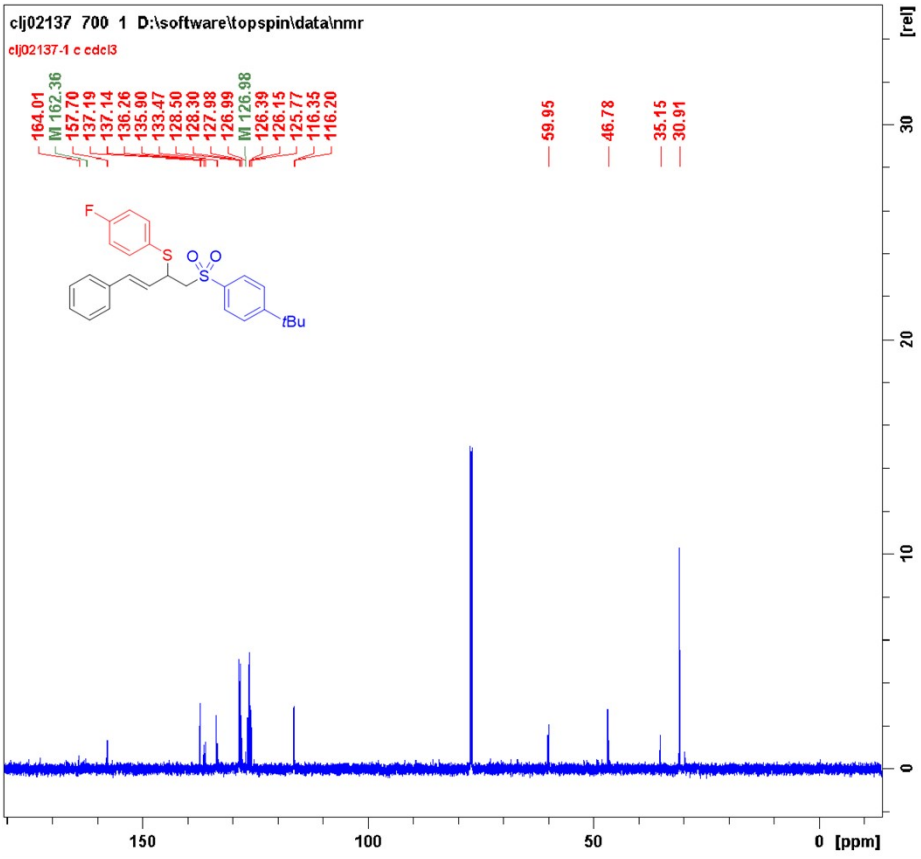
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **46**.



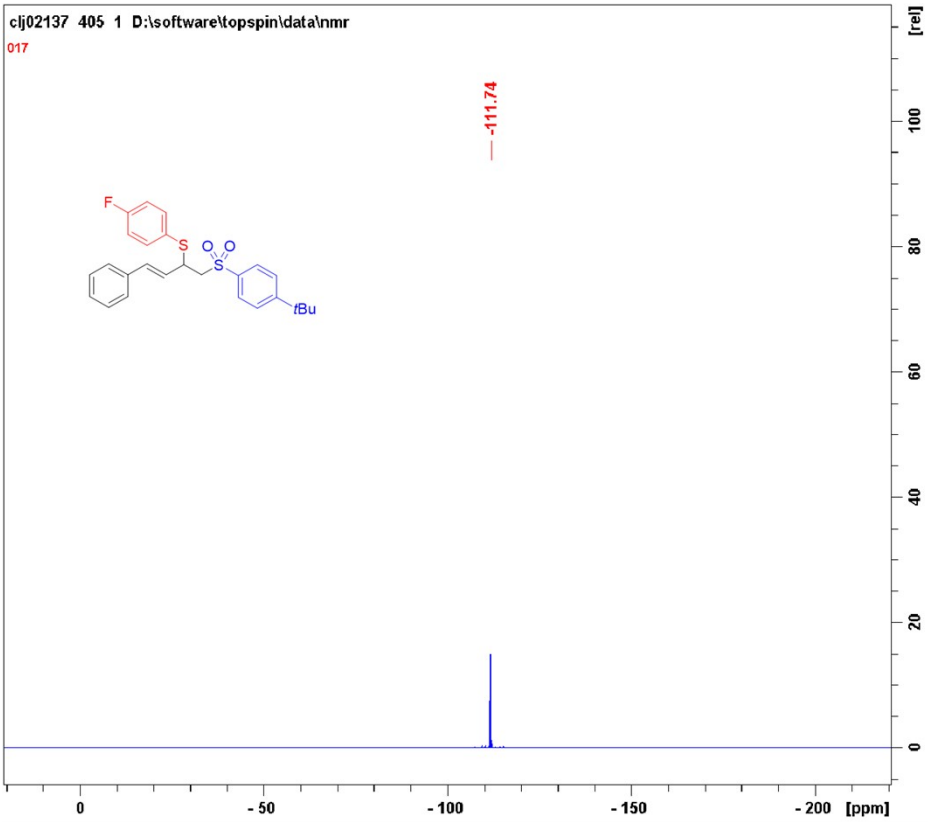
HR-MS (ESI) spectrum of **46**.



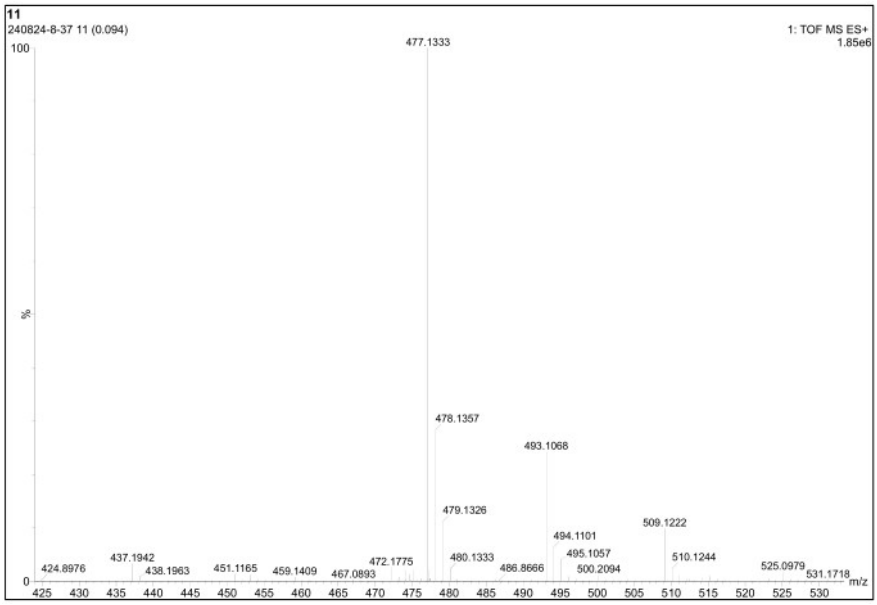
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **47a**.



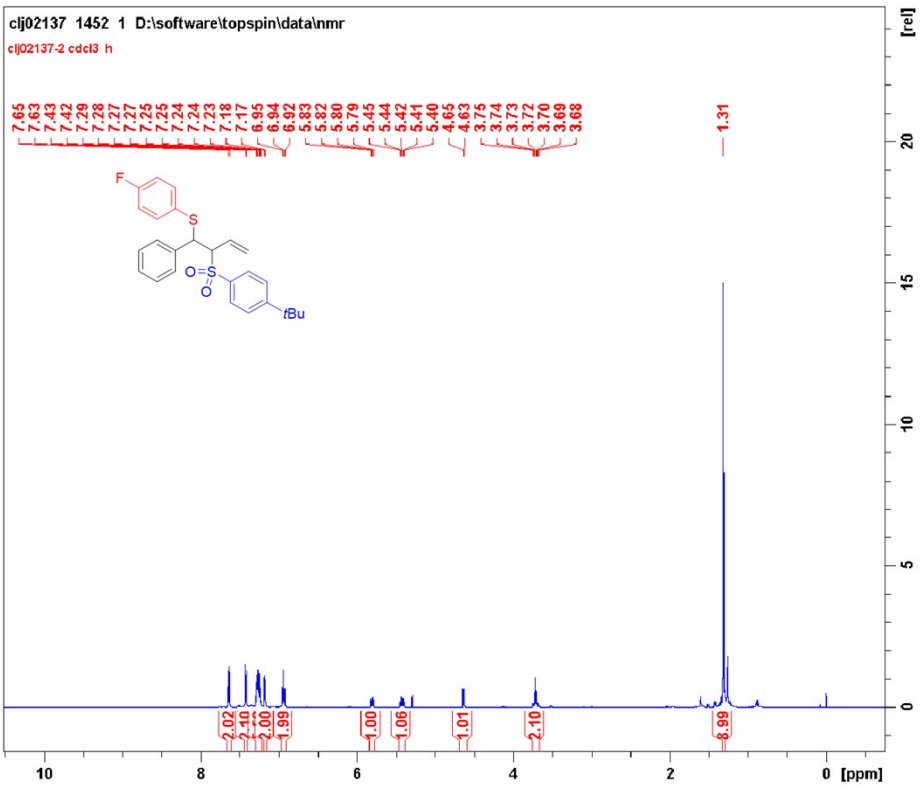
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **47a**.



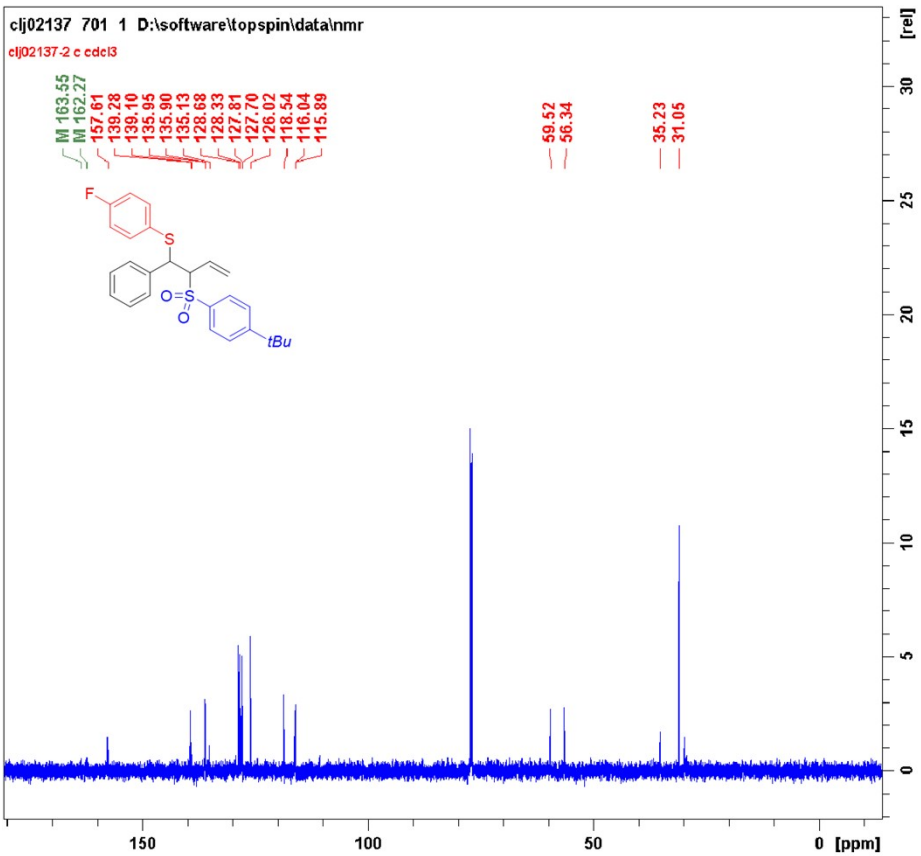
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **47a**.



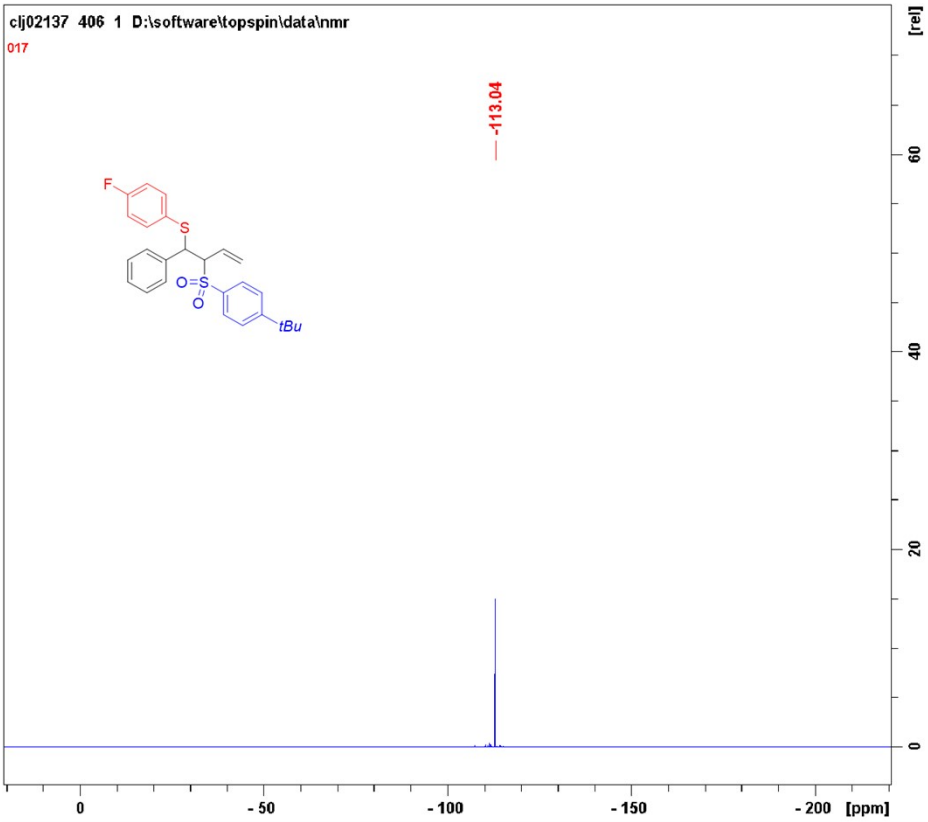
HR-MS (ESI) spectrum of **47a**.



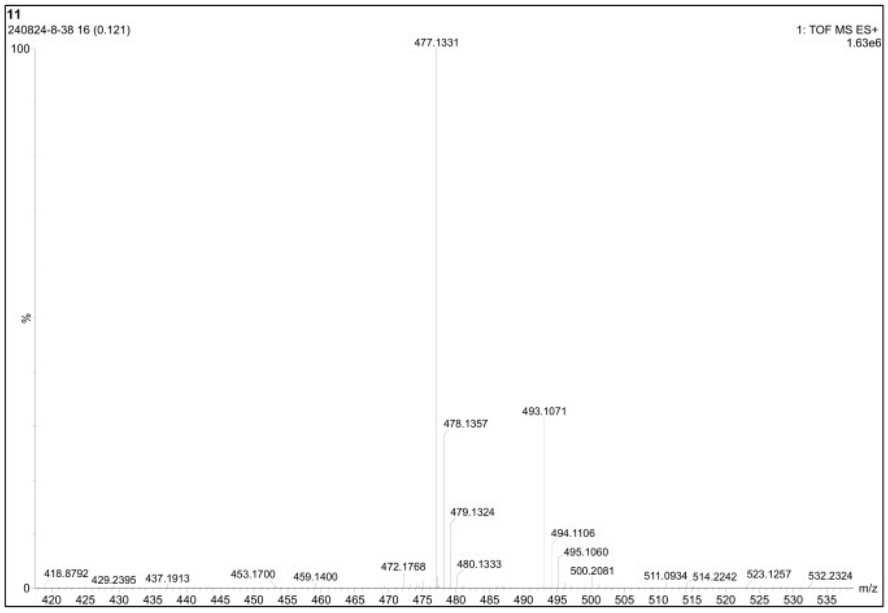
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **47b**.



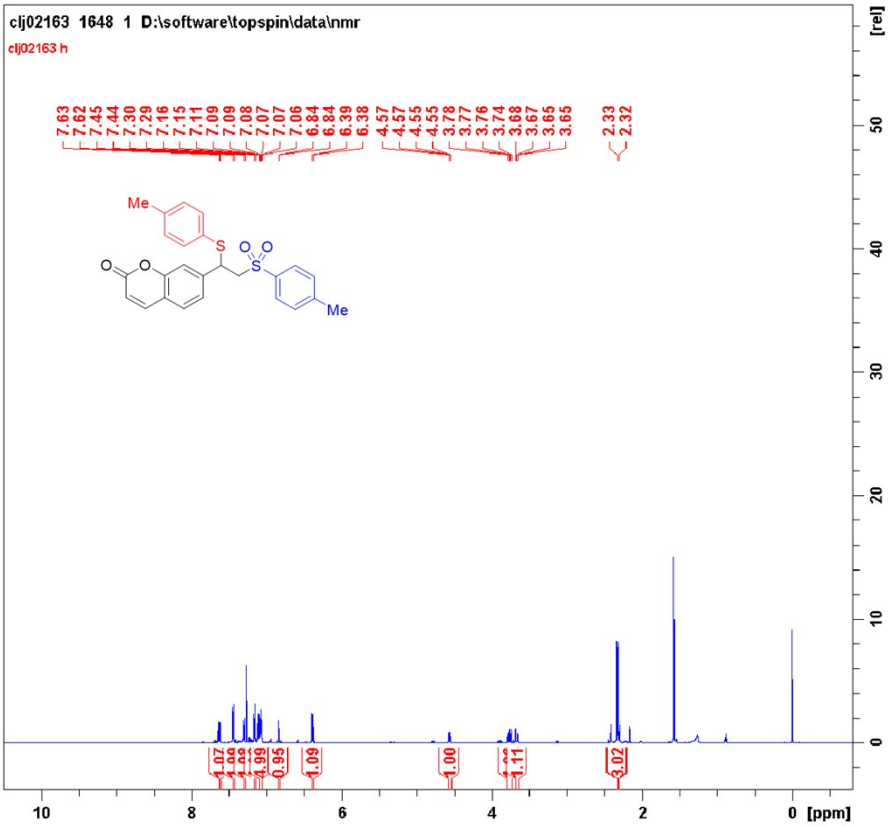
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **47b**.



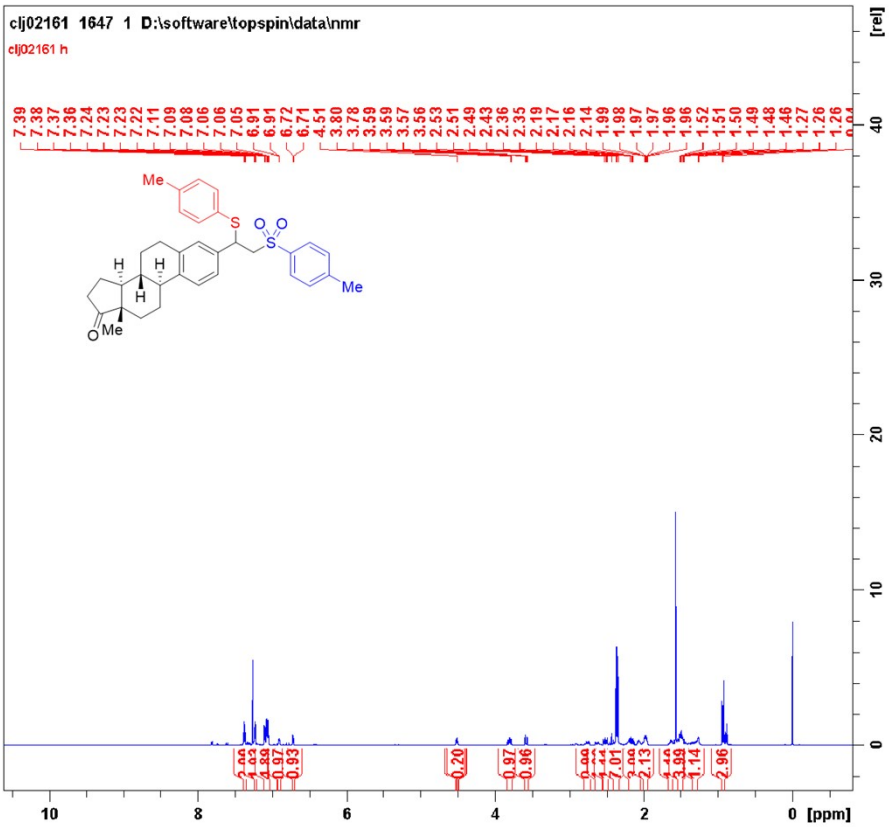
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **47b**.



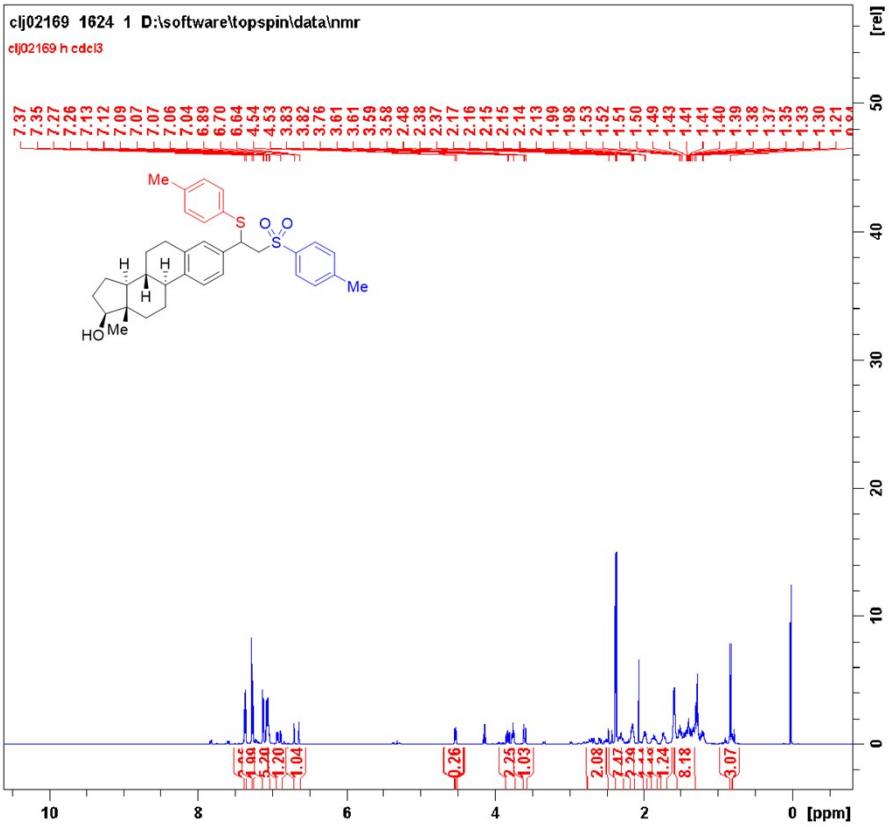
HR-MS (ESI) spectrum of **47b**.



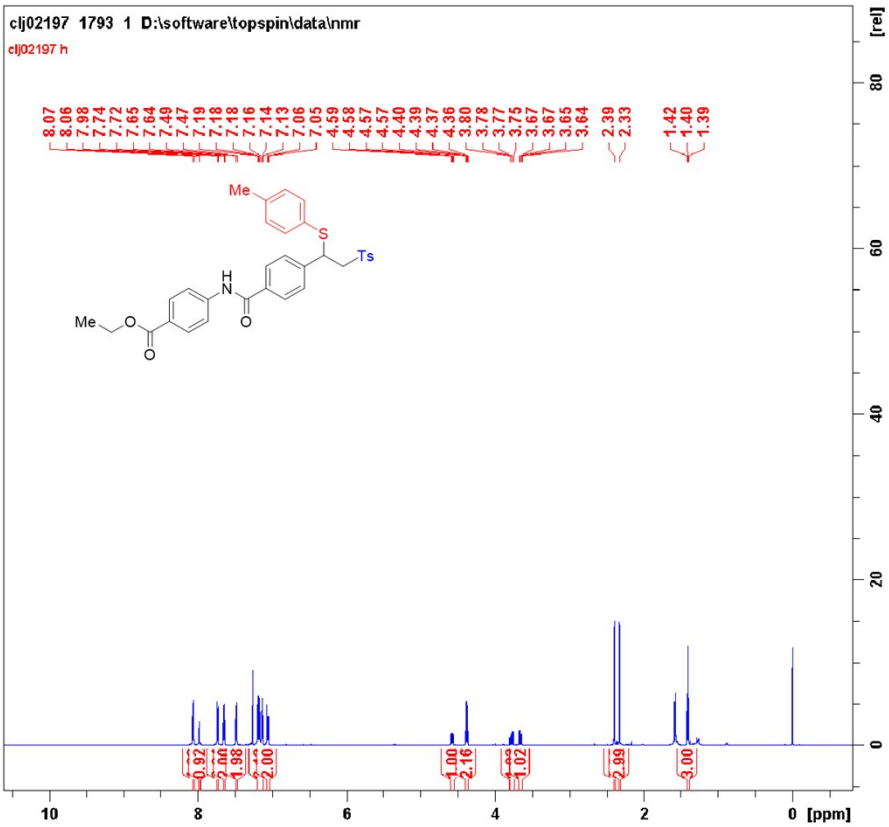
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **48**.



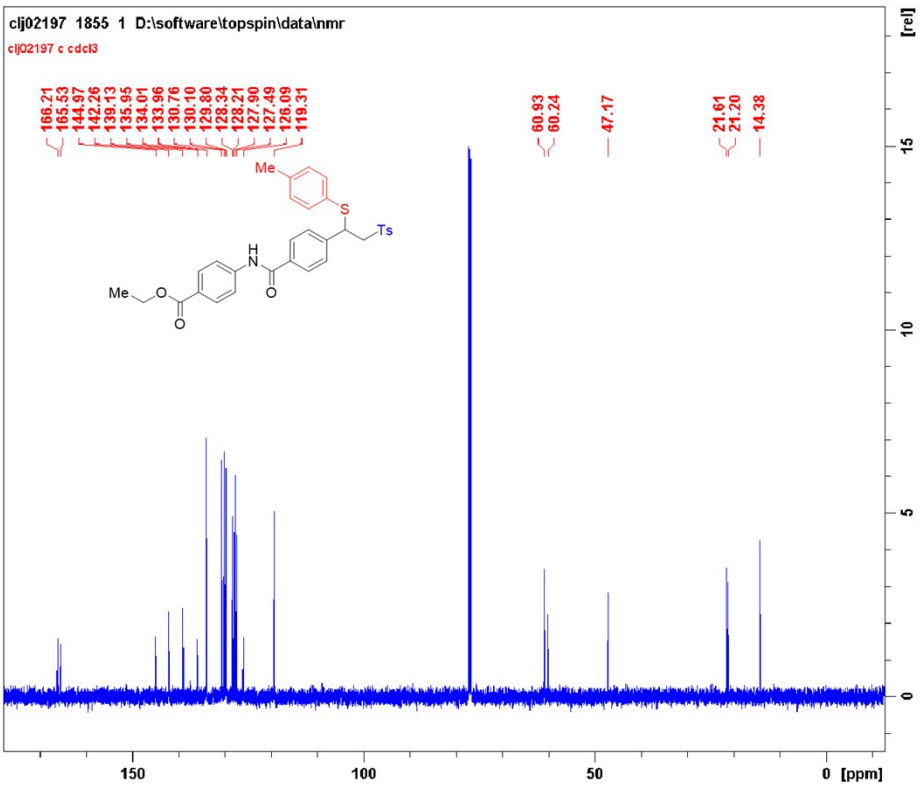
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **49**.



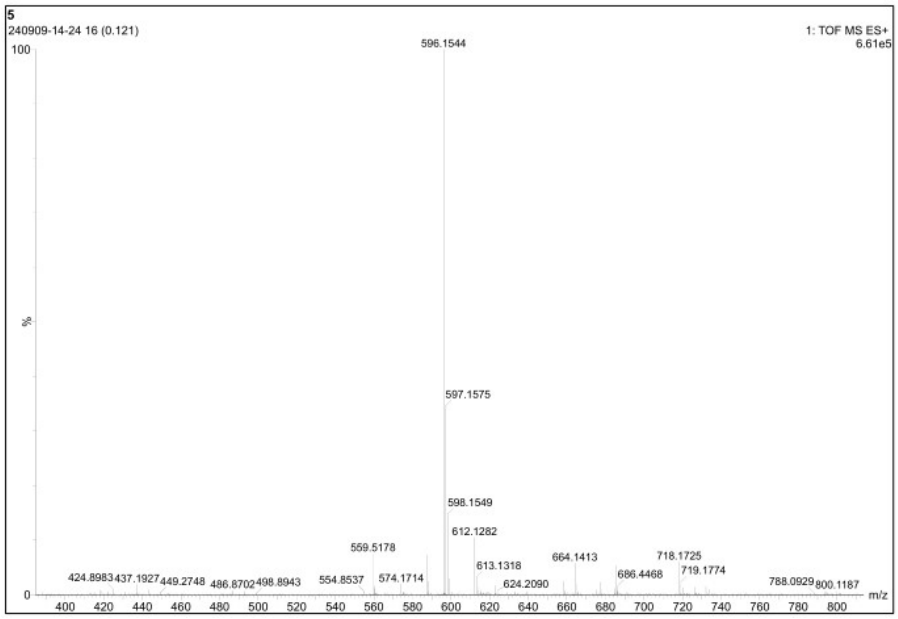
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **50**.



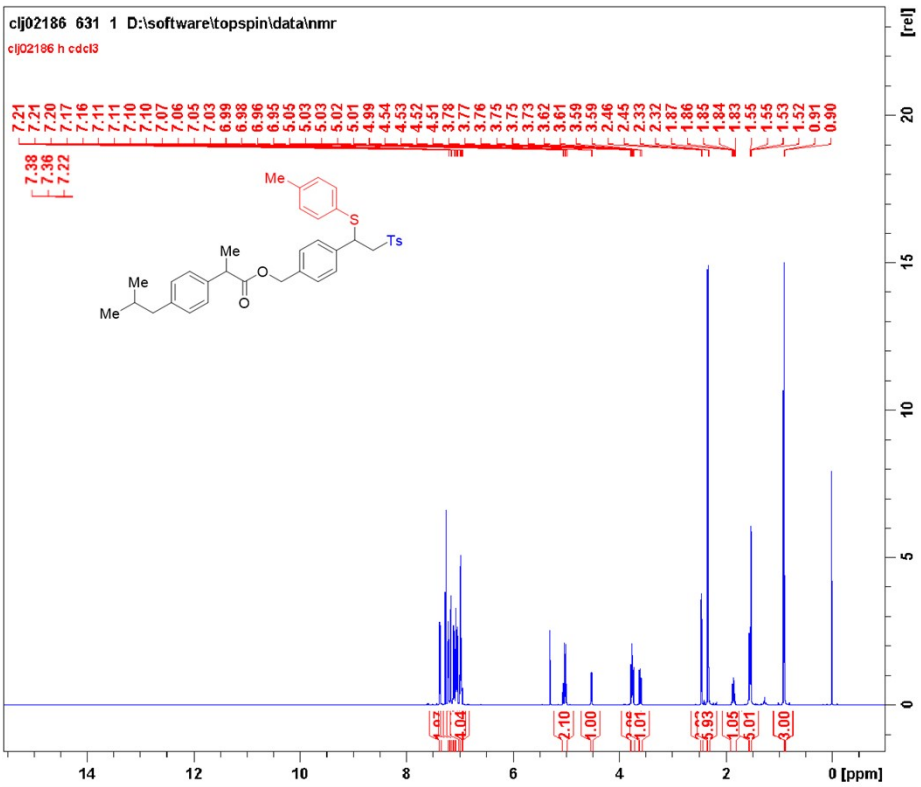
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **51**.



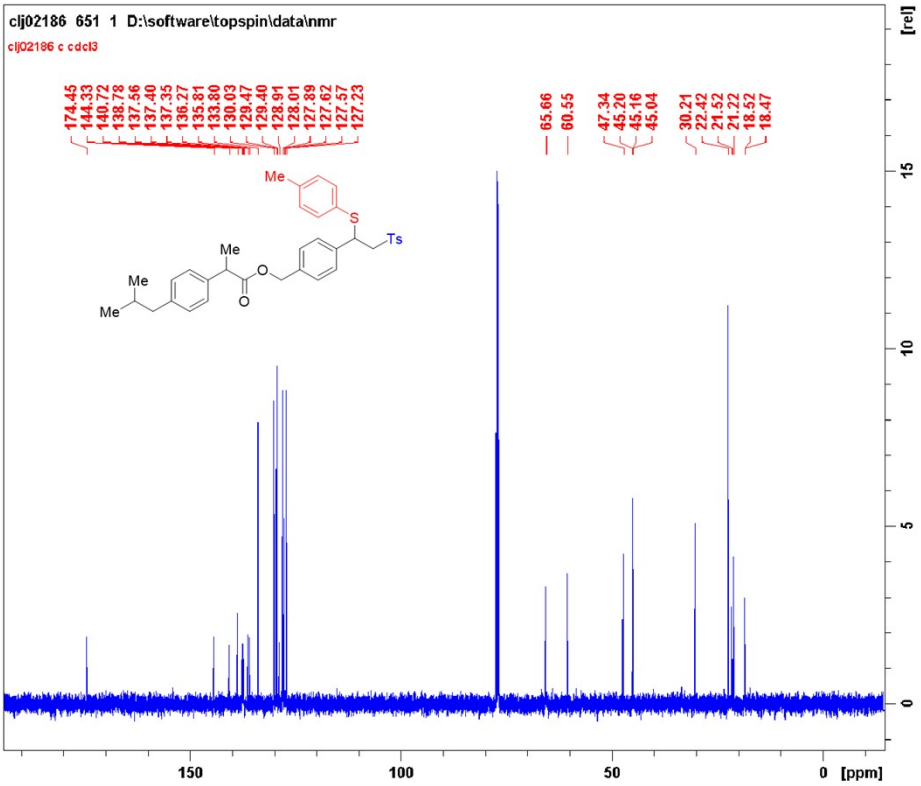
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **51**.



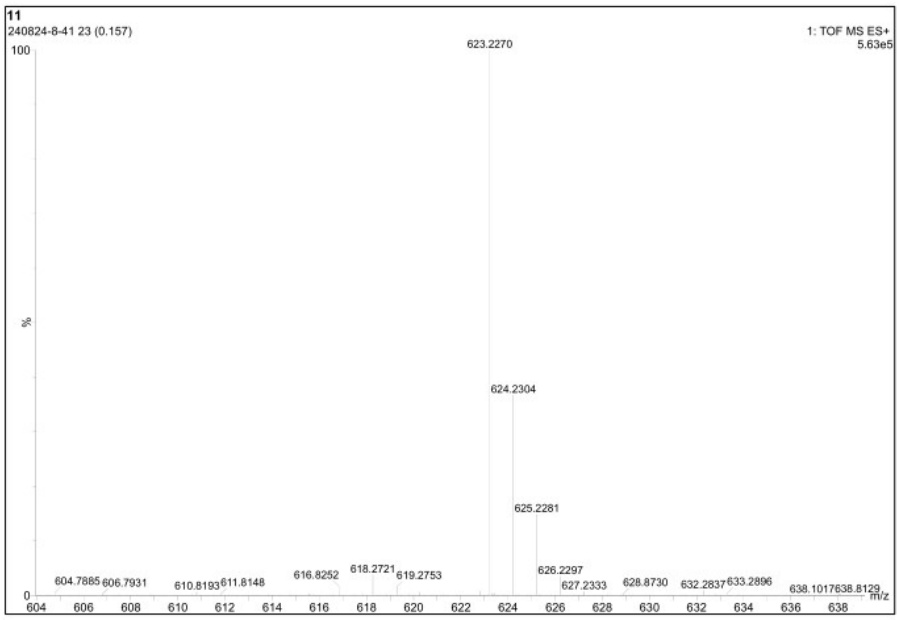
HR-MS (ESI) spectrum of **51**.



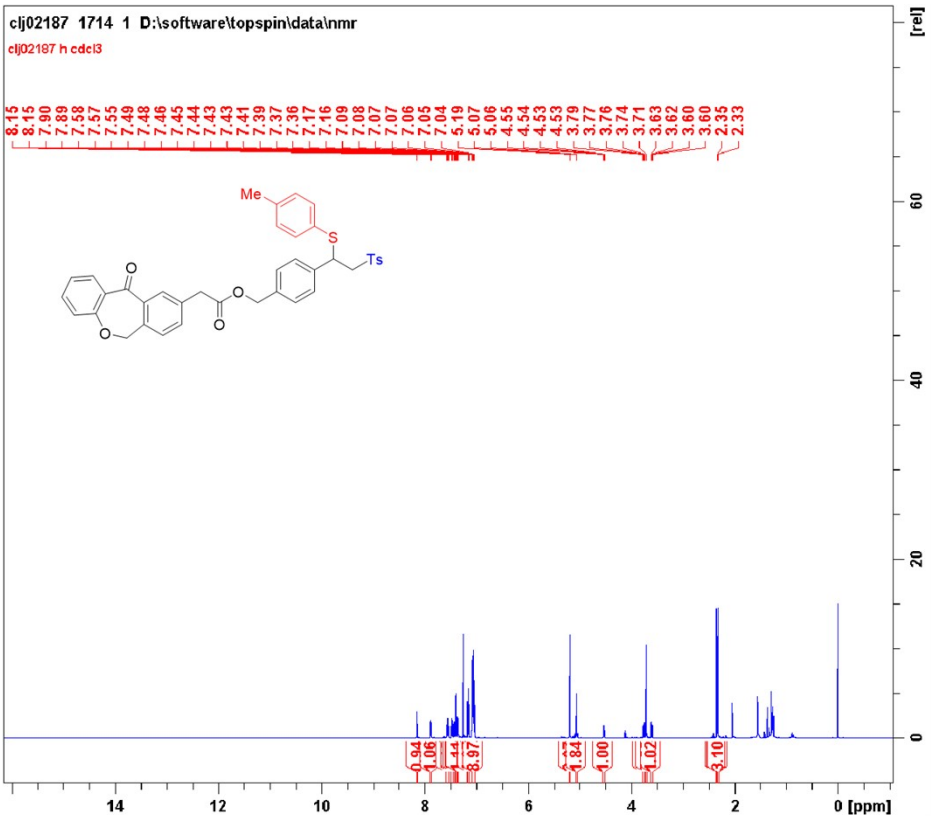
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **52**.



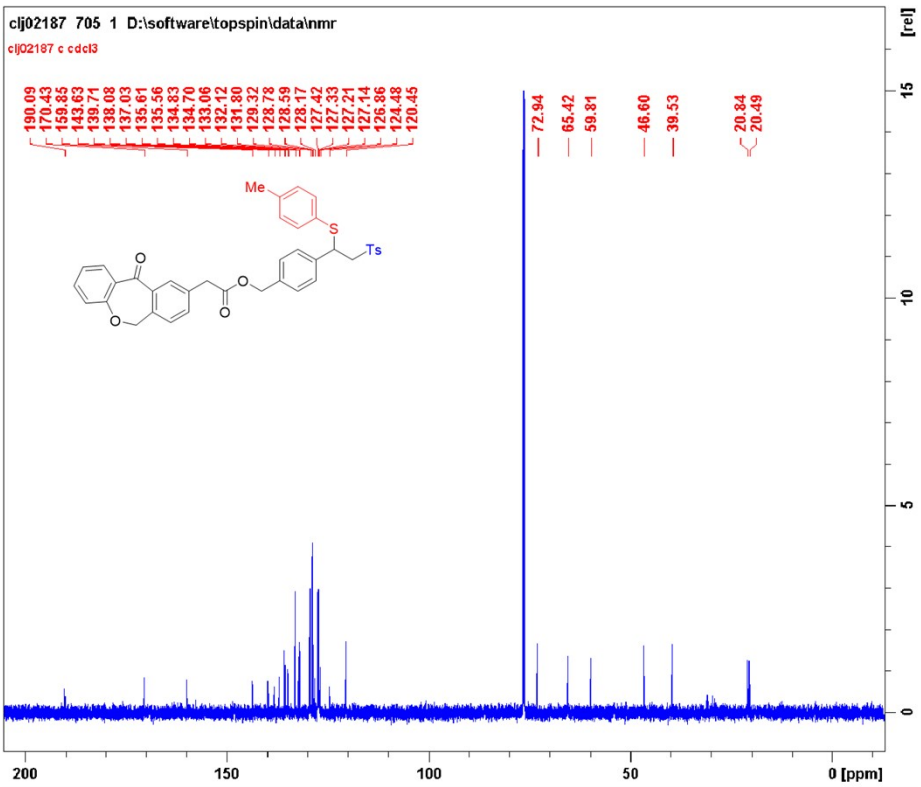
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **52**.



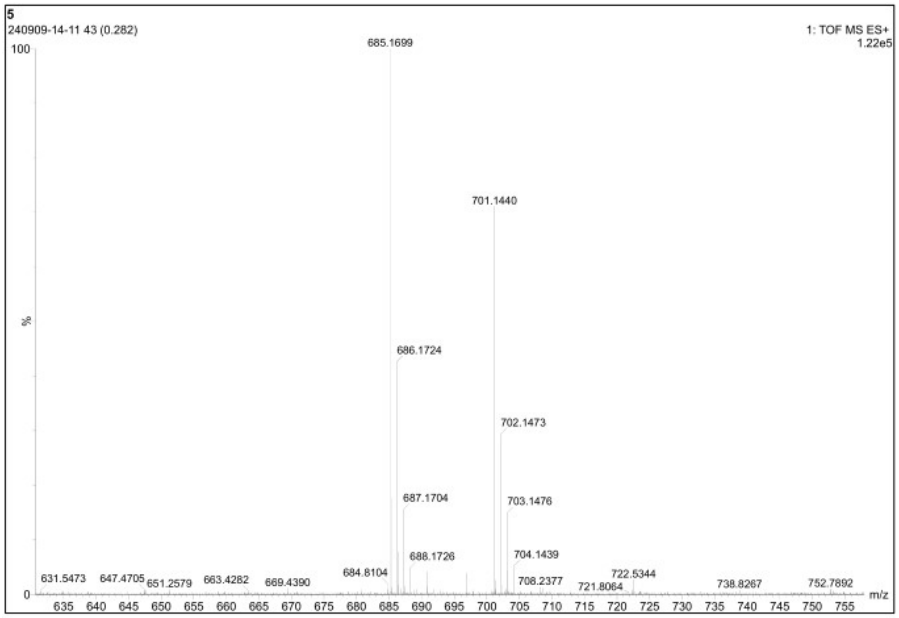
HR-MS (ESI) spectrum of **52**.



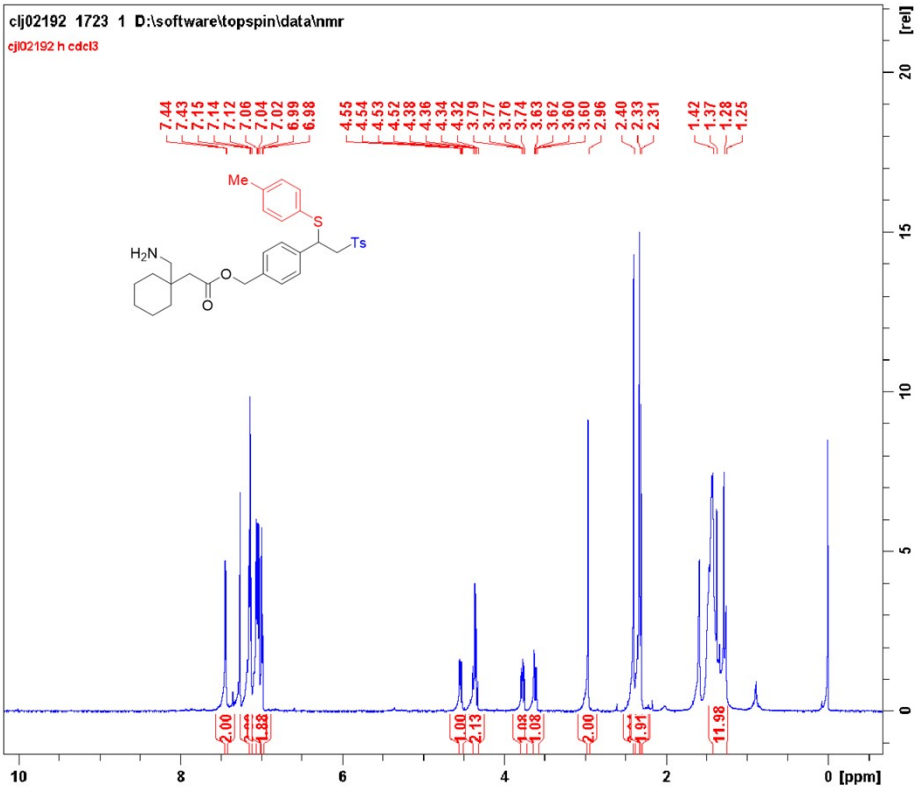
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **53**.



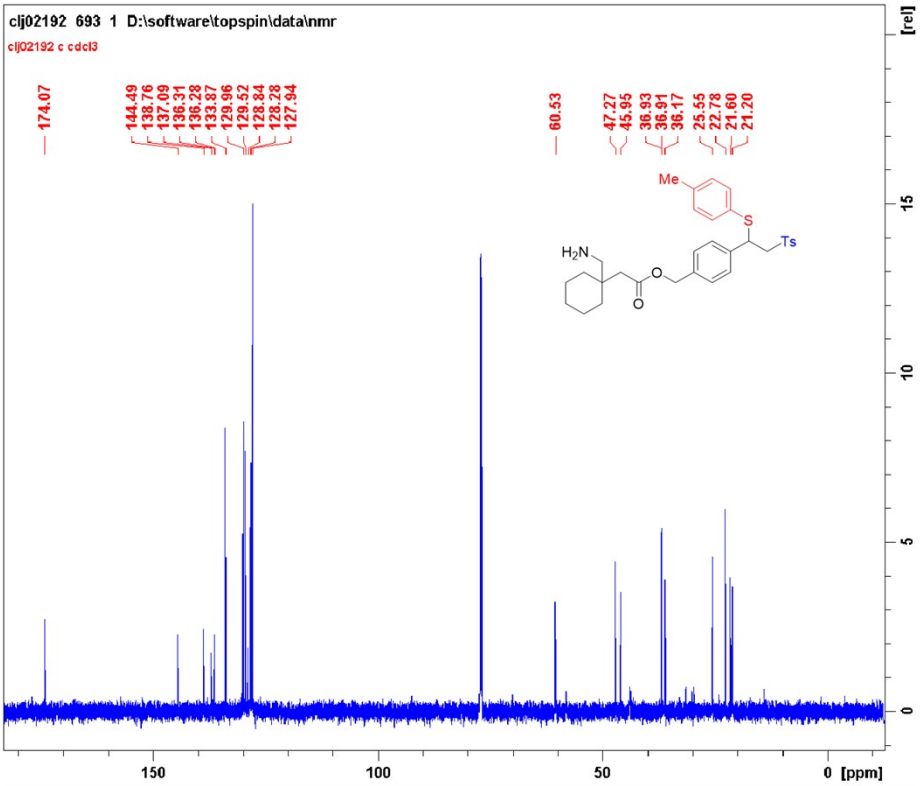
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **53**.



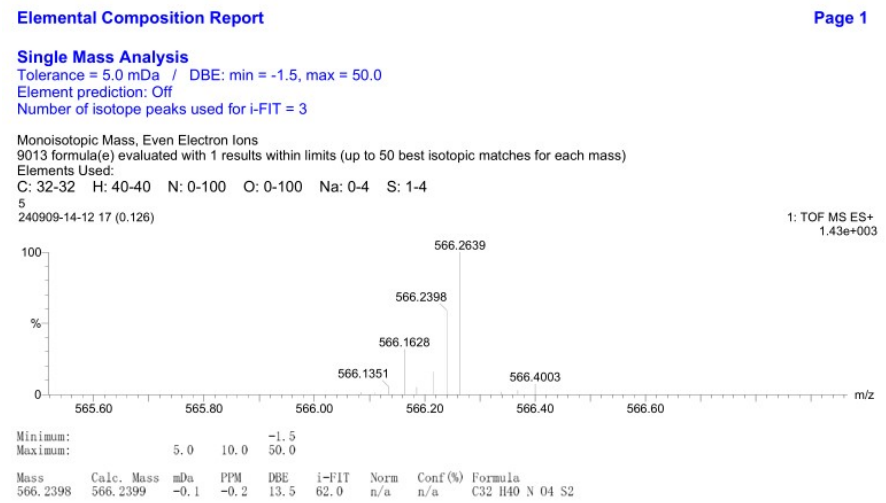
HR-MS (ESI) spectrum of **53**.



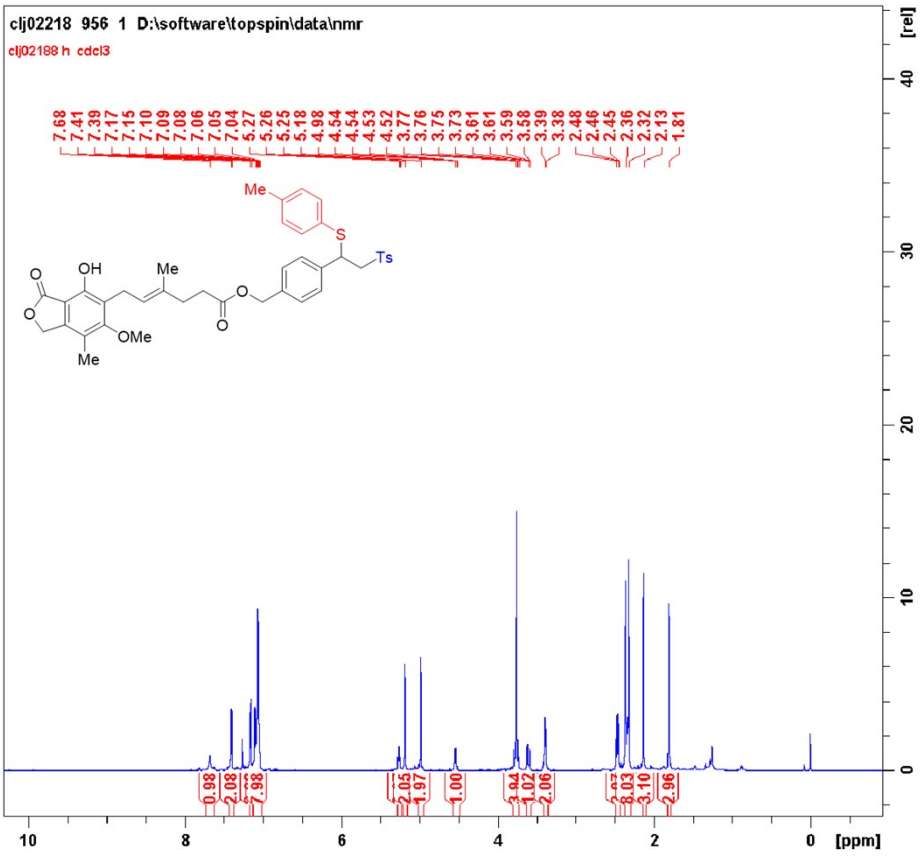
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **54**.



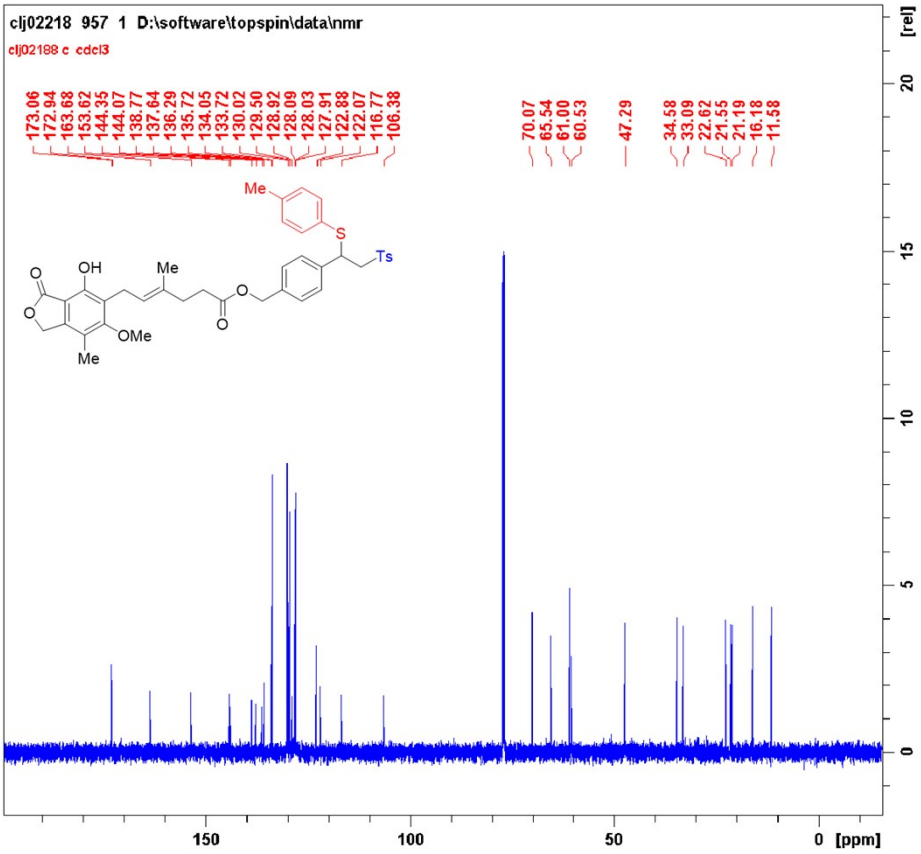
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **54**.



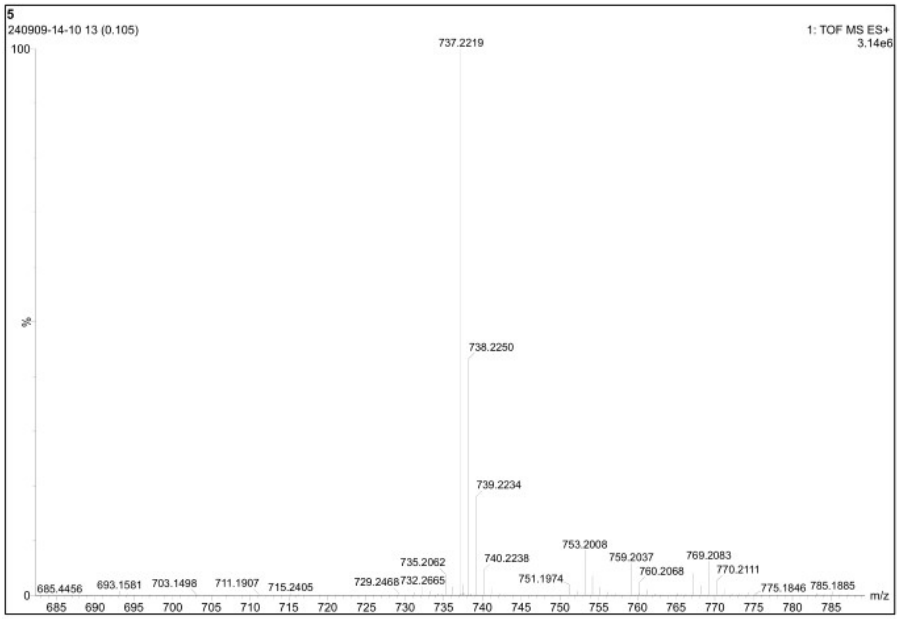
HR-MS (ESI) spectrum of **54**.



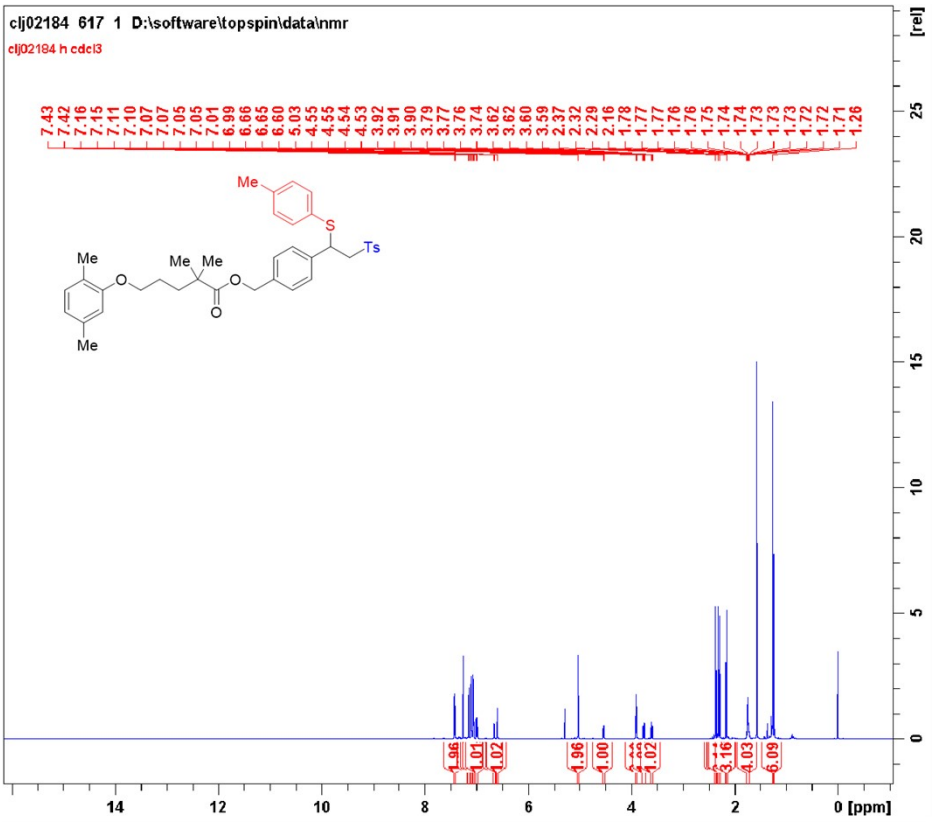
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **55**.



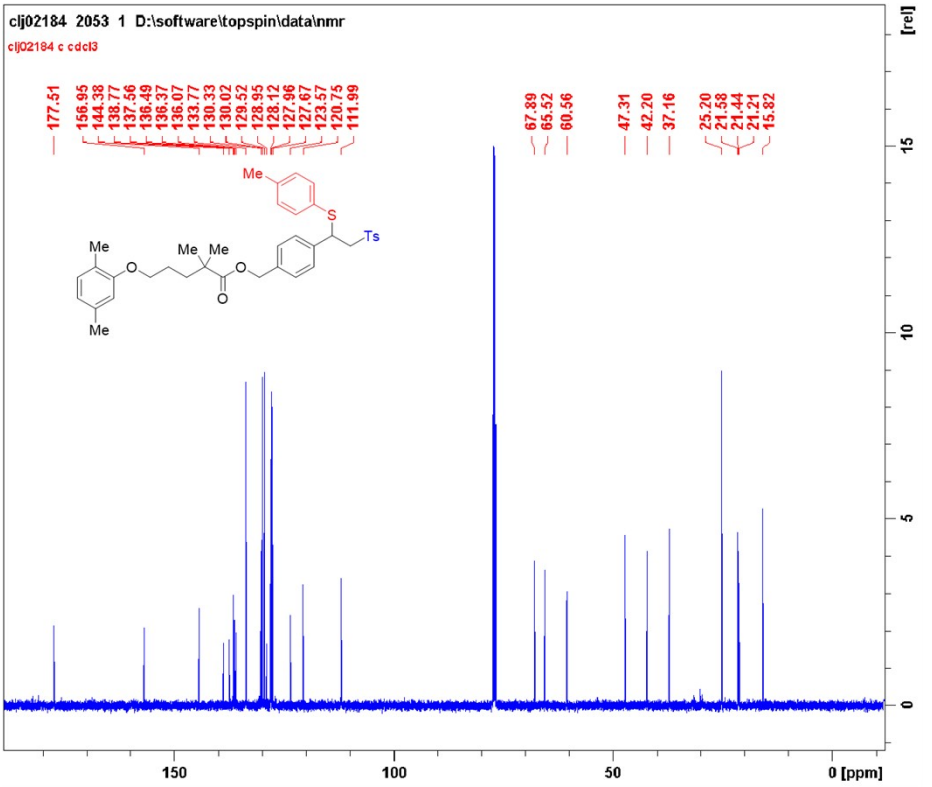
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **55**.



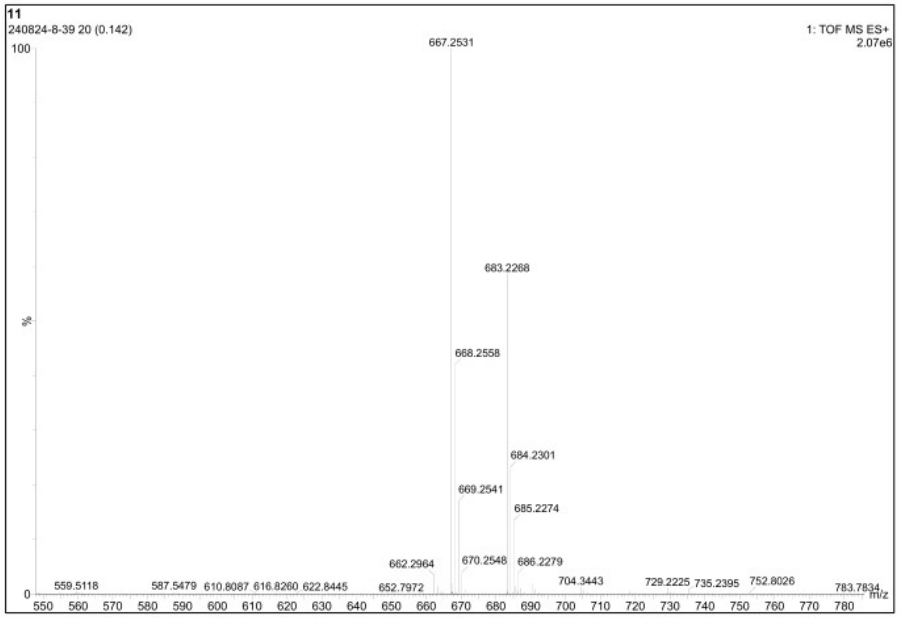
HR-MS (ESI) spectrum of **55**.



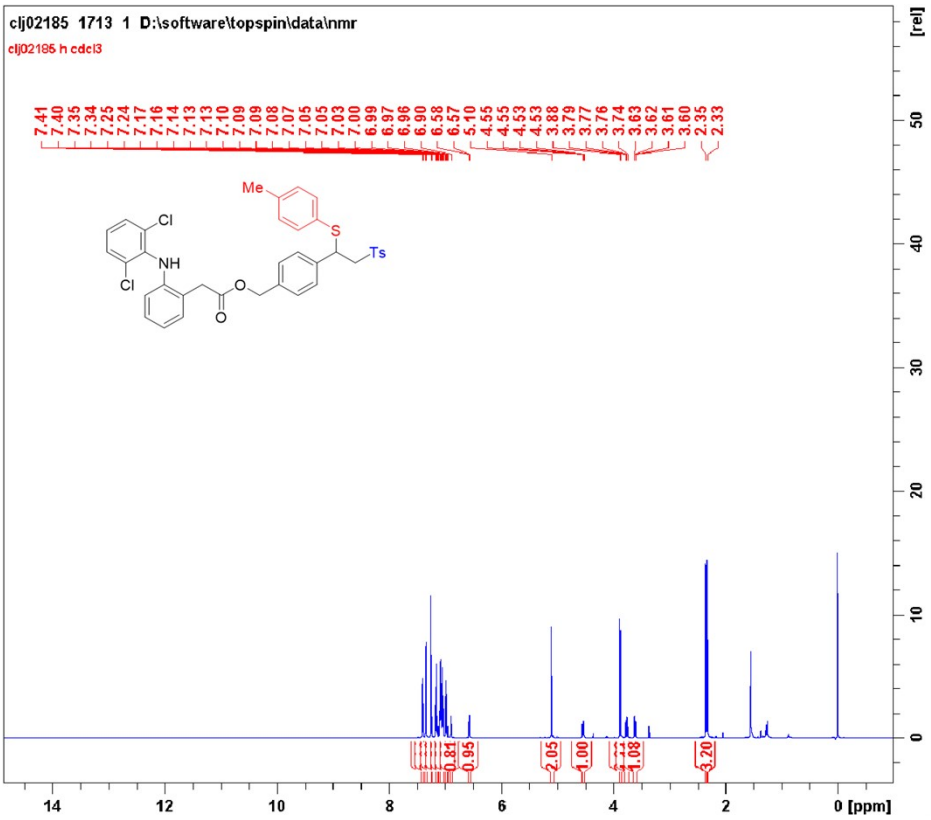
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **56**.



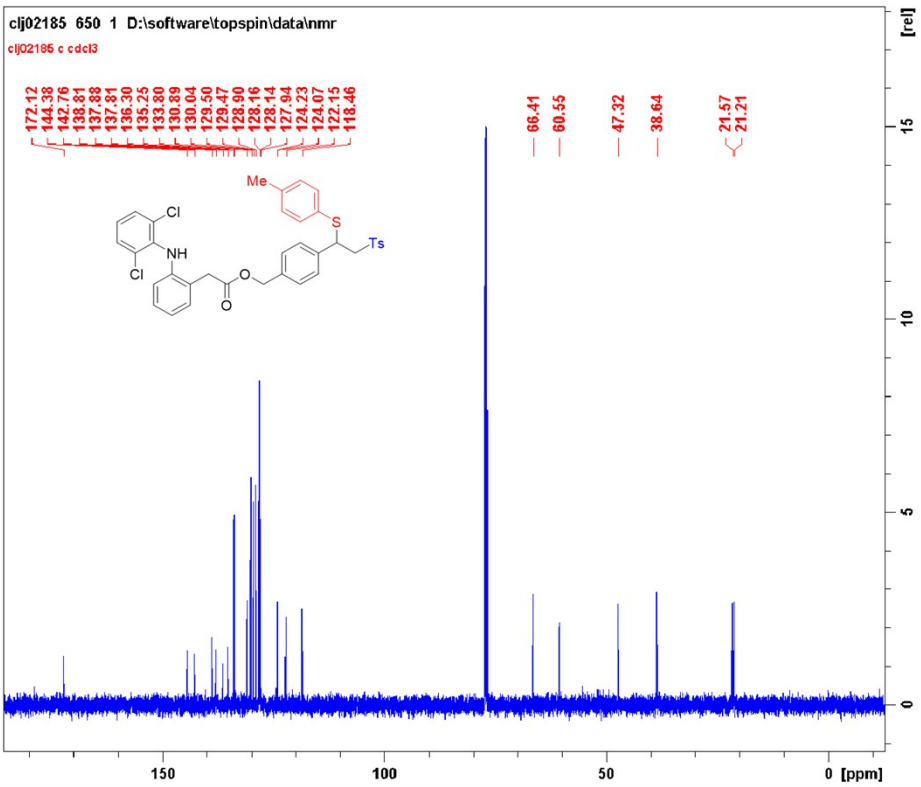
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **56**.



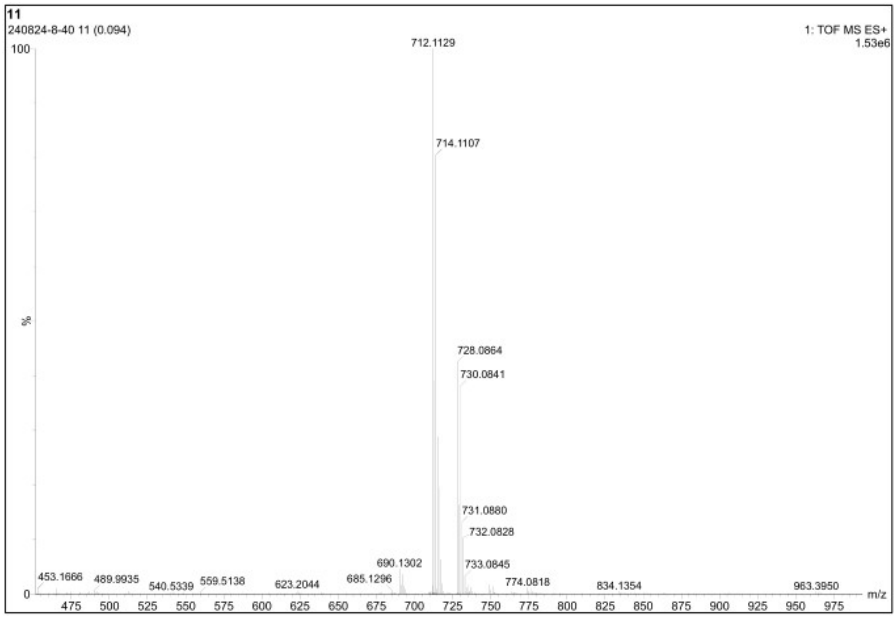
HR-MS (ESI) spectrum of **56**.



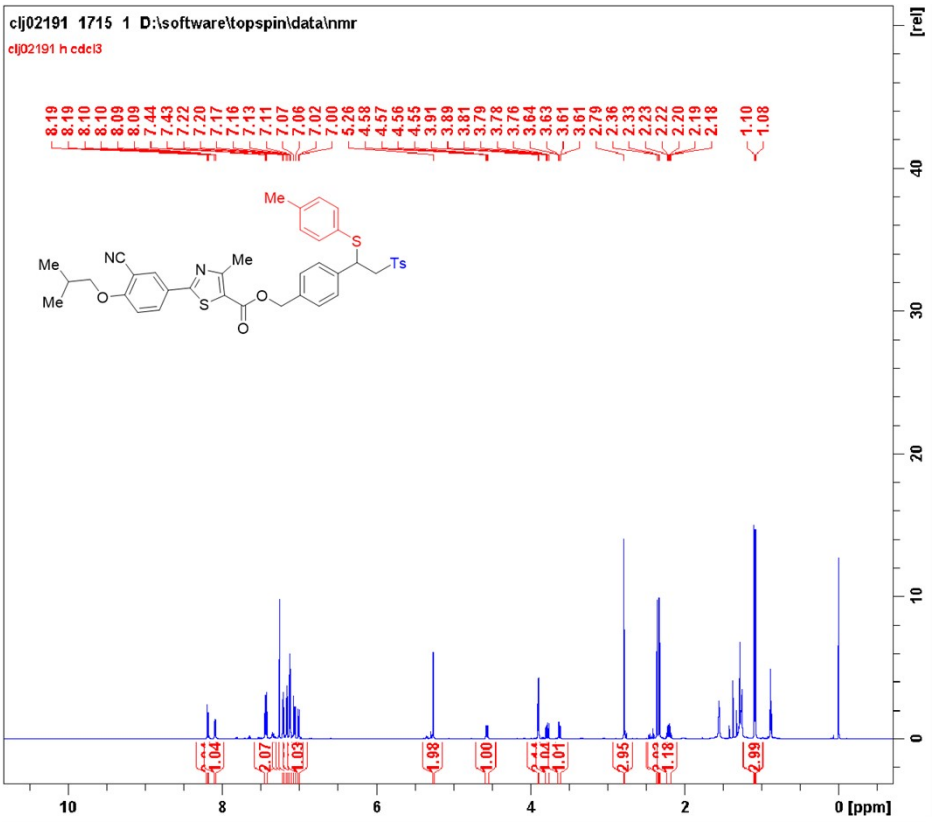
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **57**.



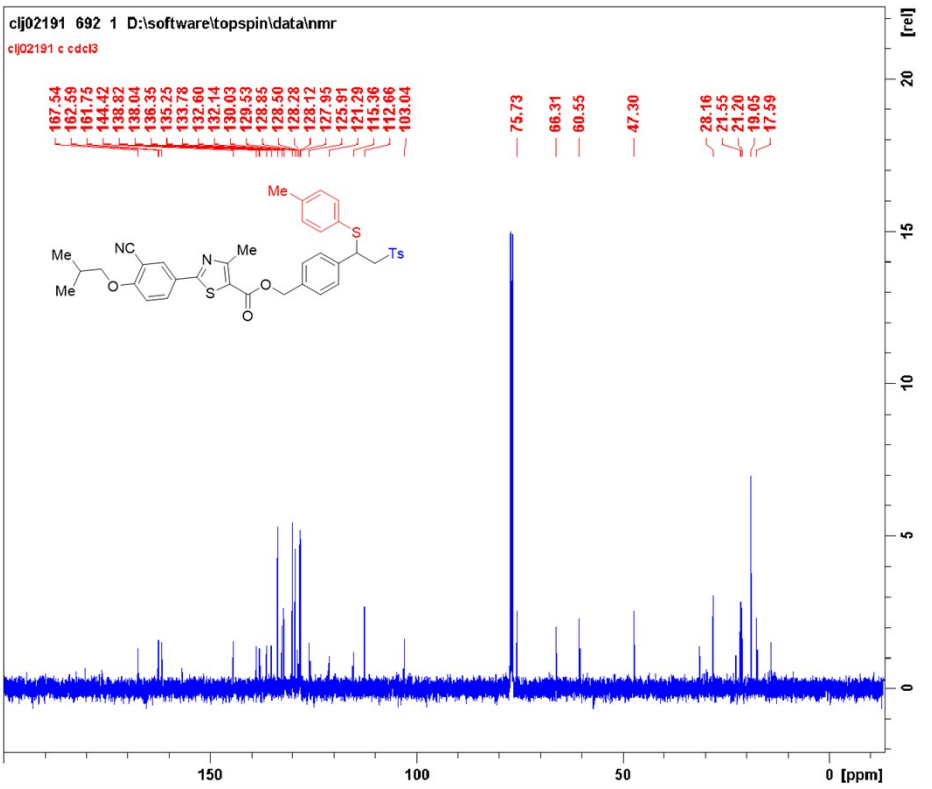
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **57**.



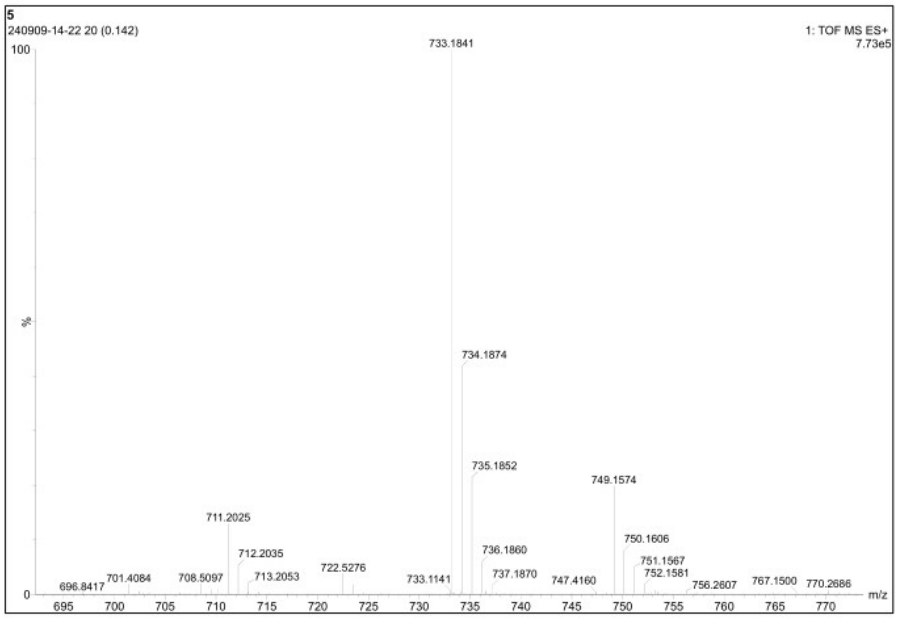
HR-MS (ESI) spectrum of **57**.



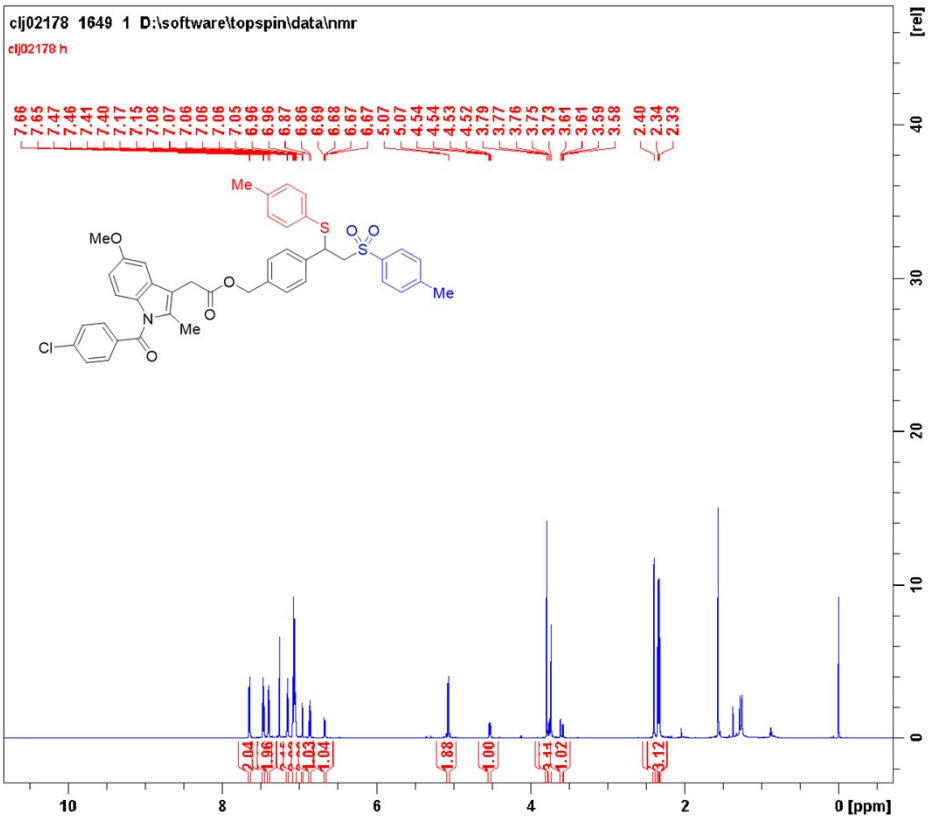
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **58**.



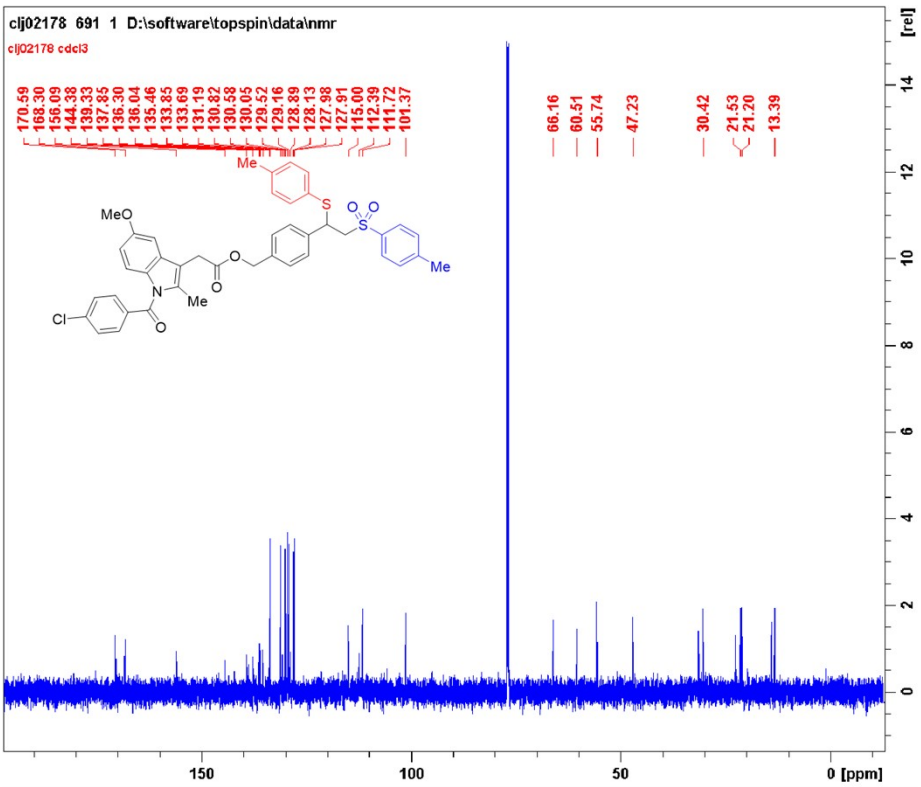
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **58**.



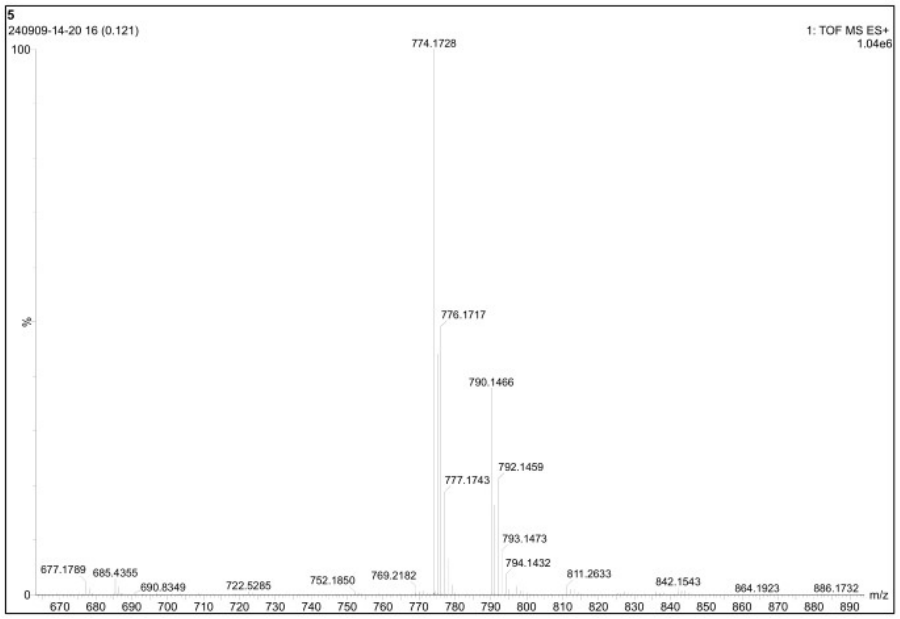
HR-MS (ESI) spectrum of **58**.



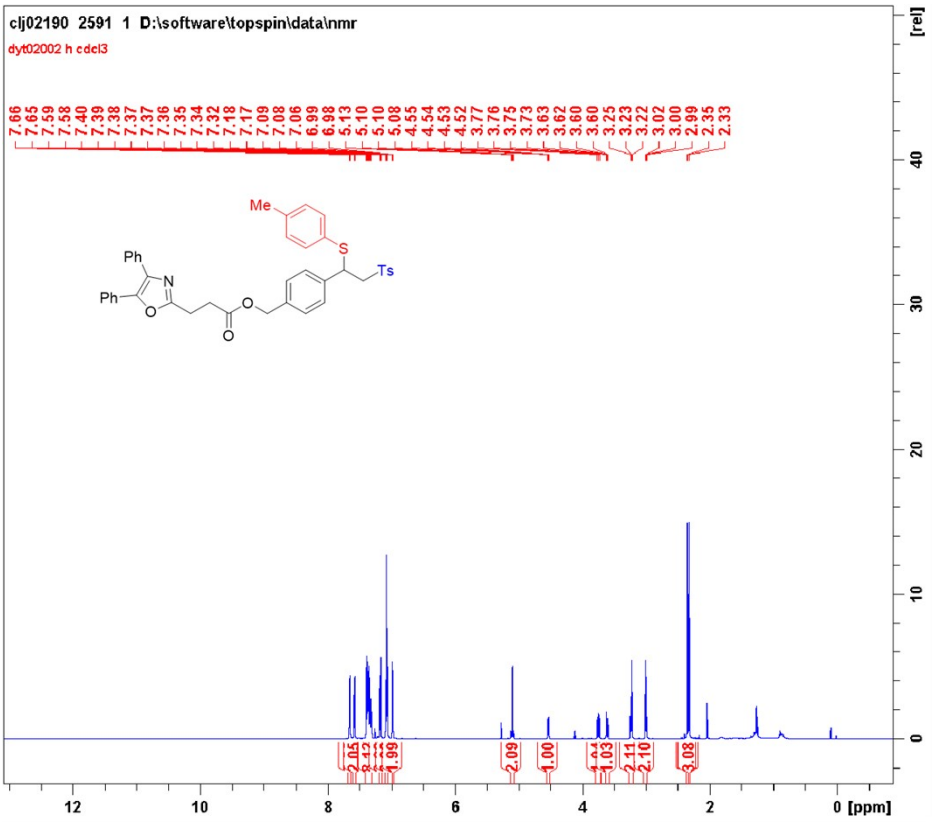
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **59**.



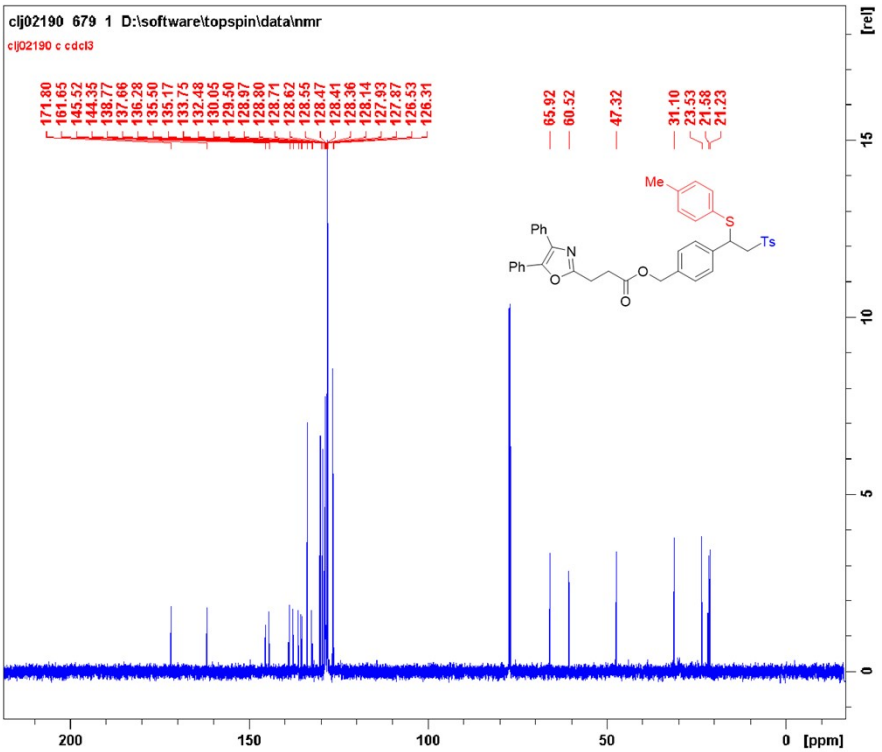
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **59**.



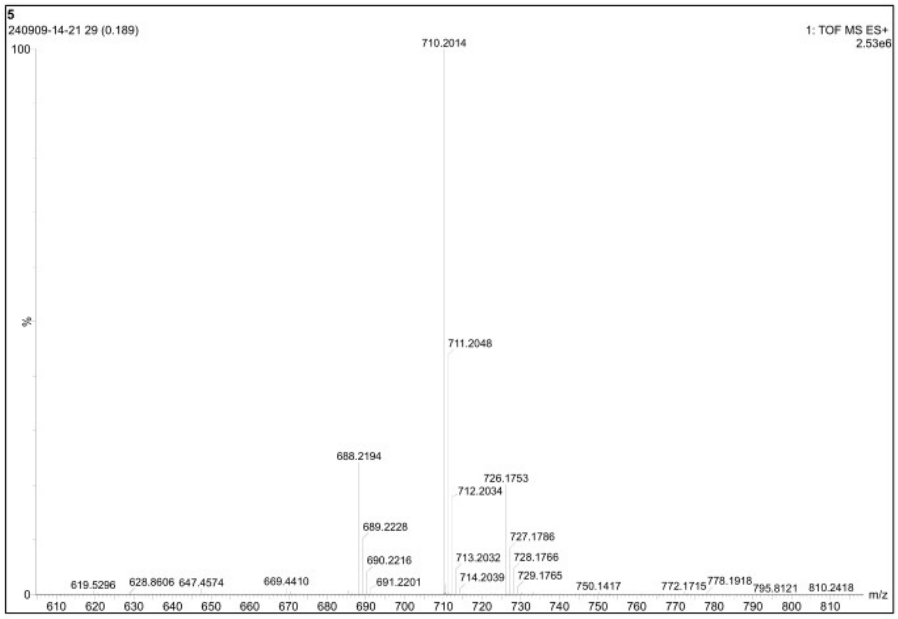
HR-MS (ESI) spectrum of **59**.



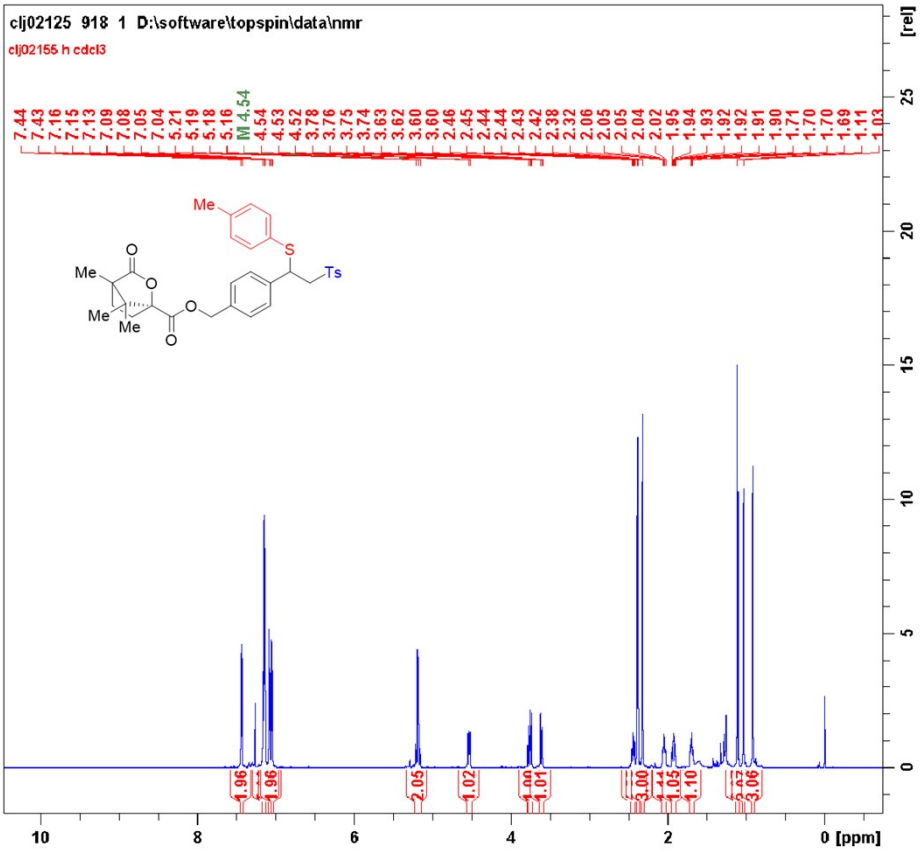
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **60**.



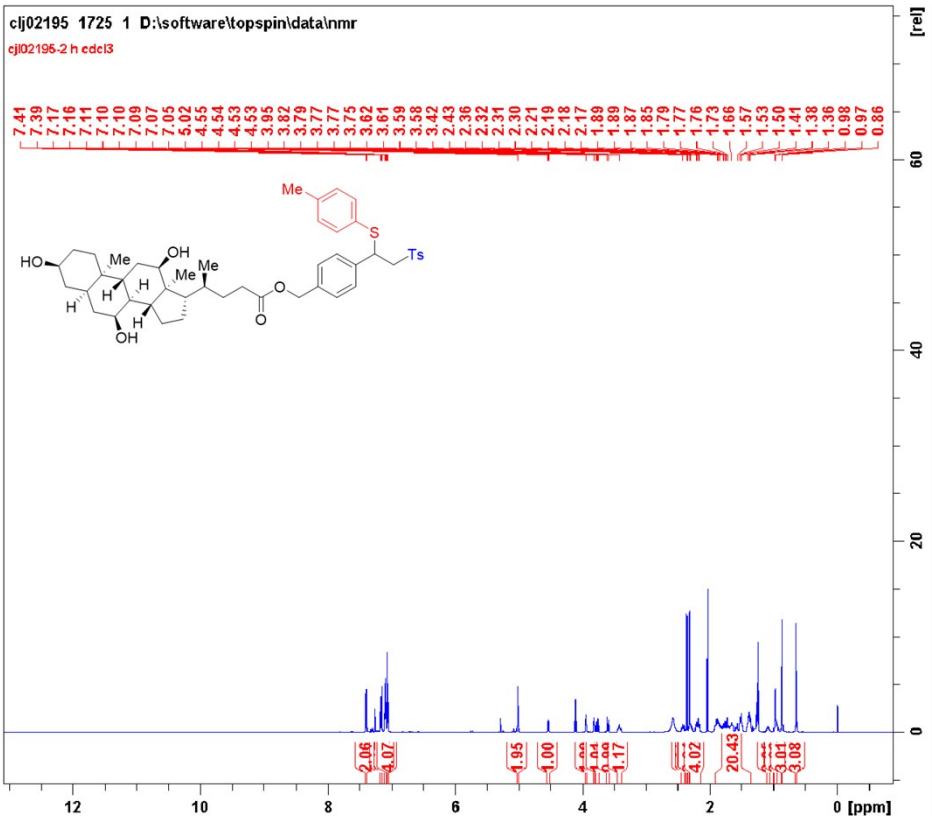
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **60**.



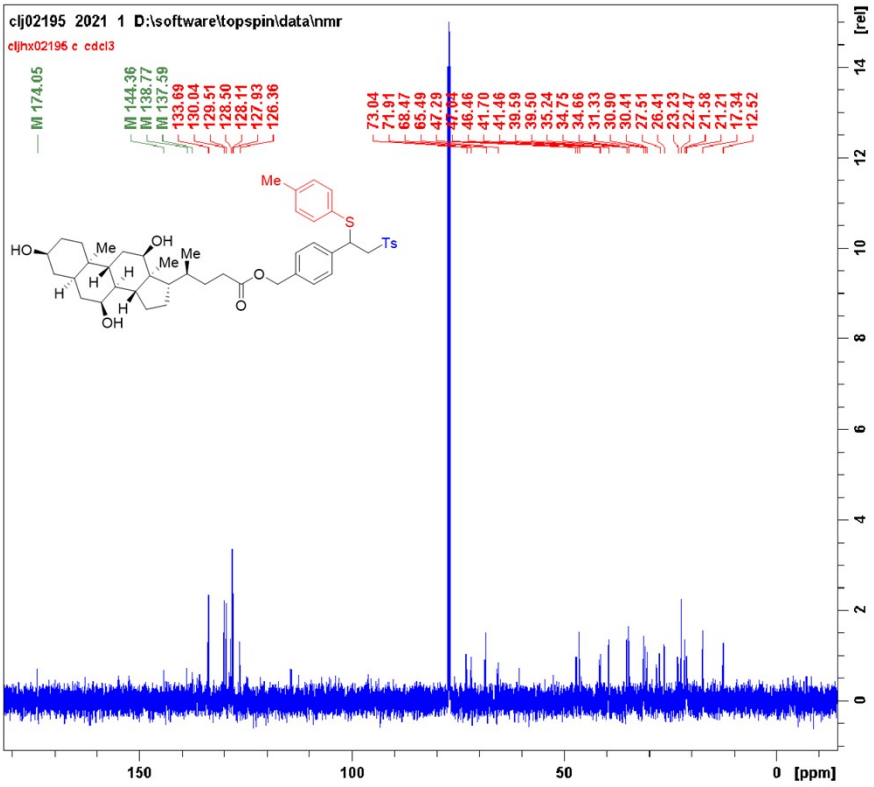
HR-MS (ESI) spectrum of **60**.



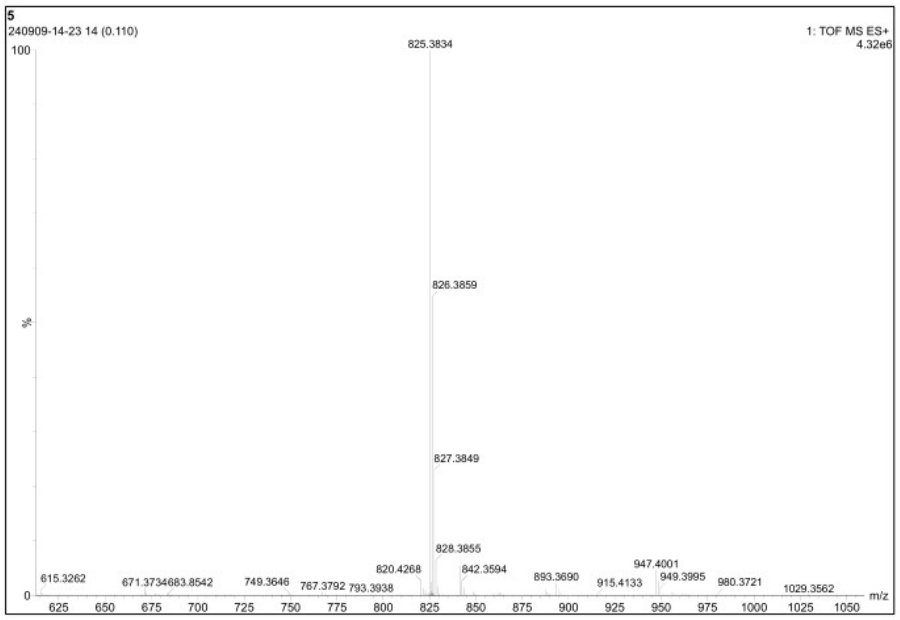
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **61**.



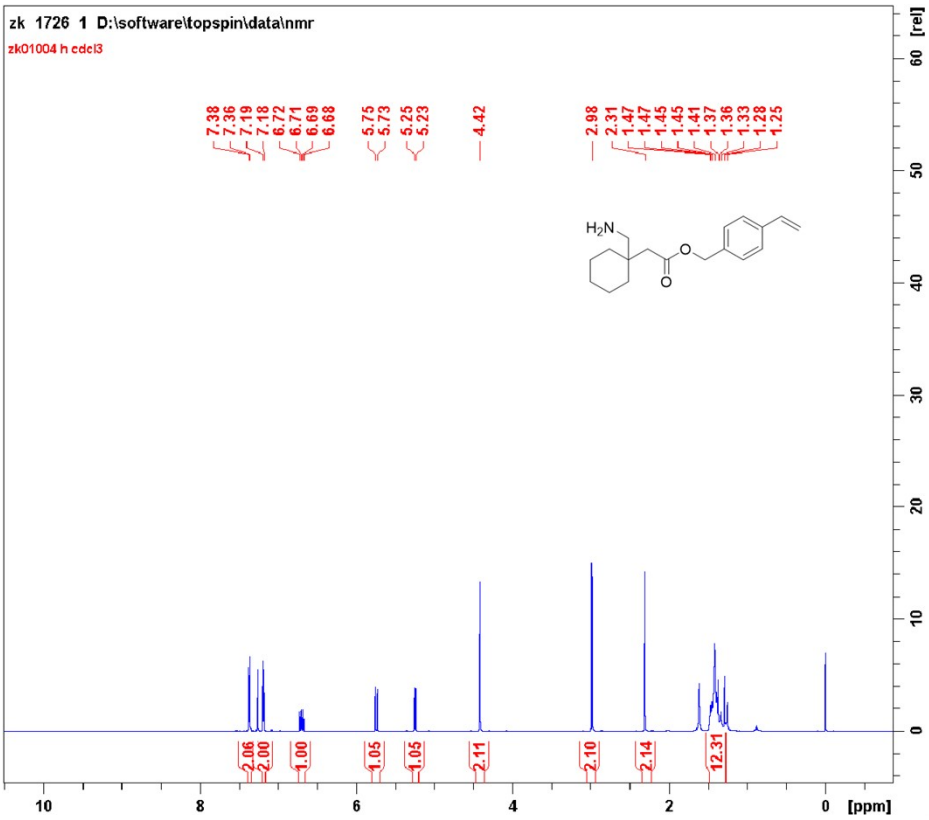
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **62**.



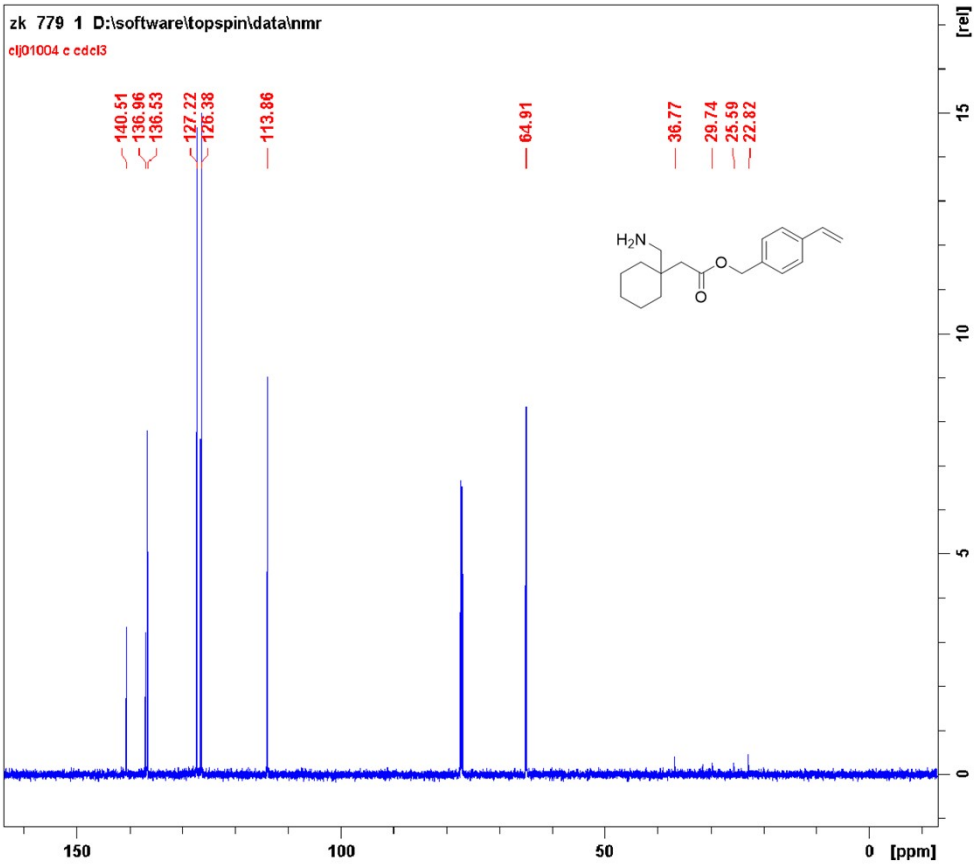
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **62**.



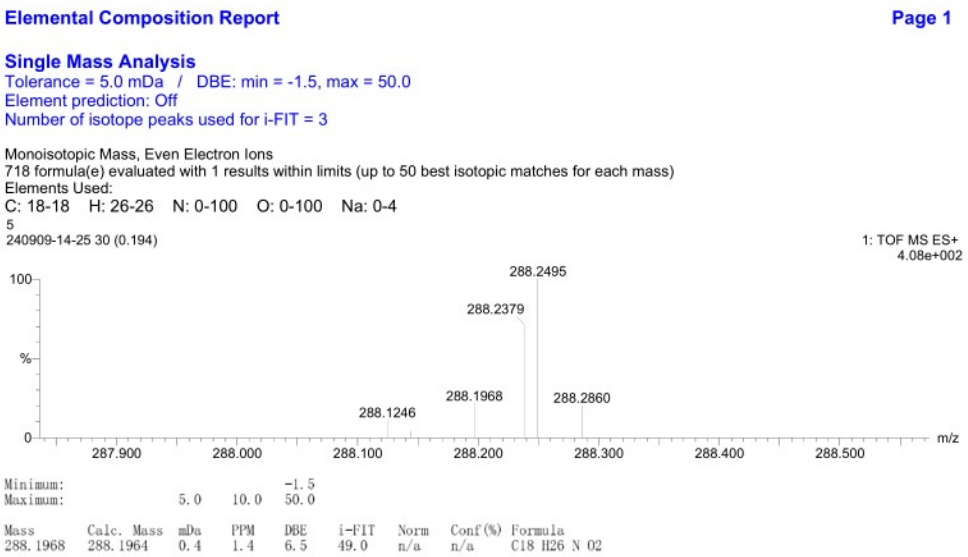
HR-MS (ESI) spectrum of **62**.



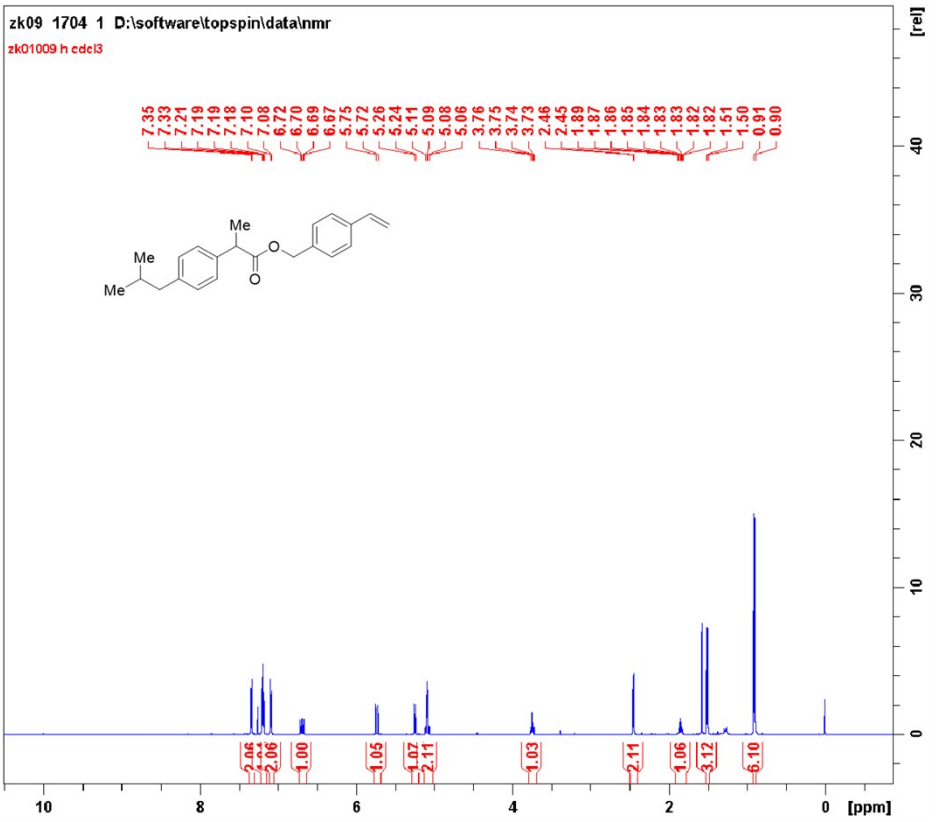
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **63**.



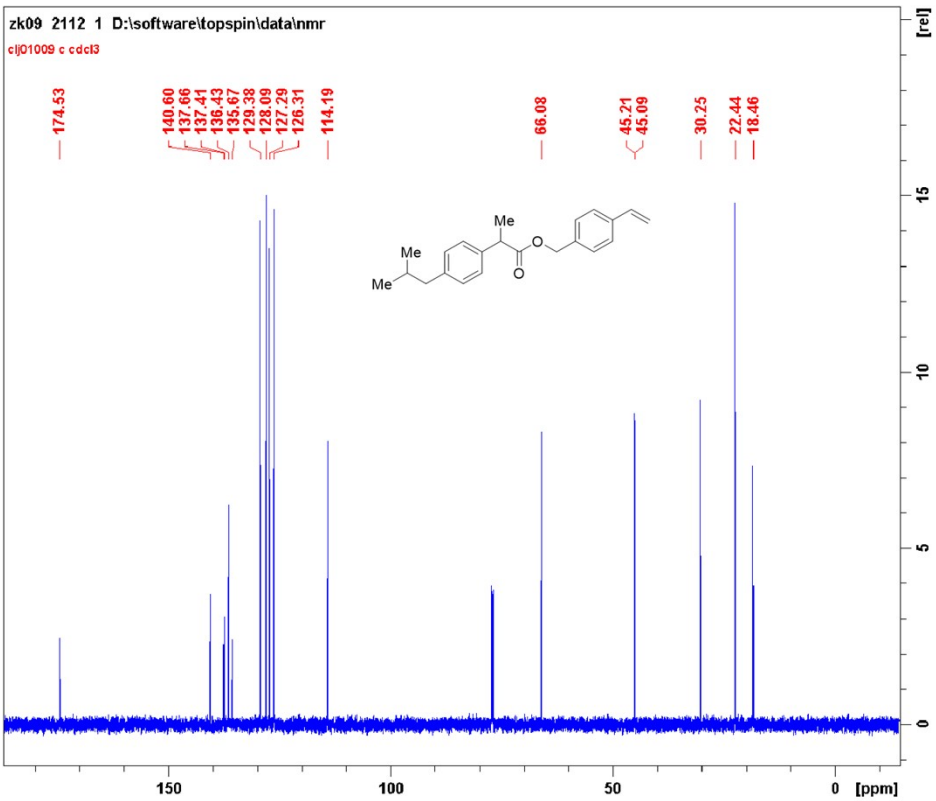
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **63**.



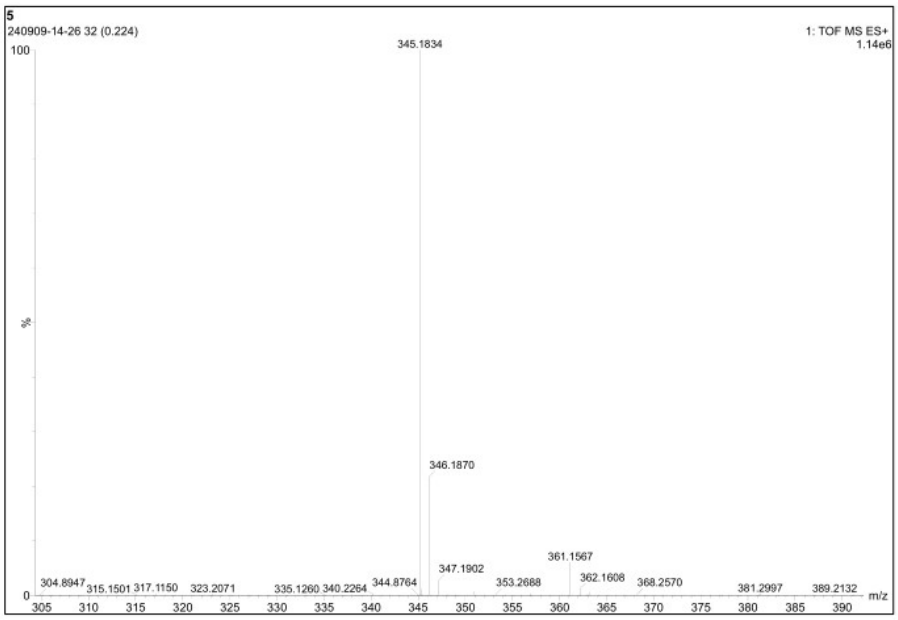
HR-MS (ESI) spectrum of **63**.



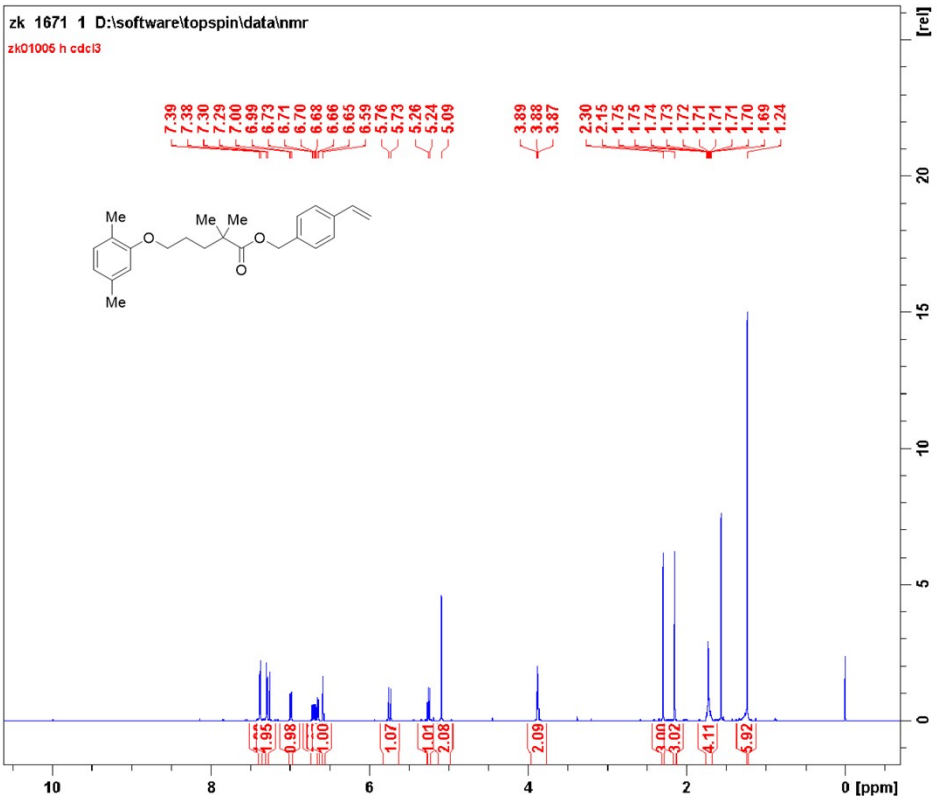
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **64**.



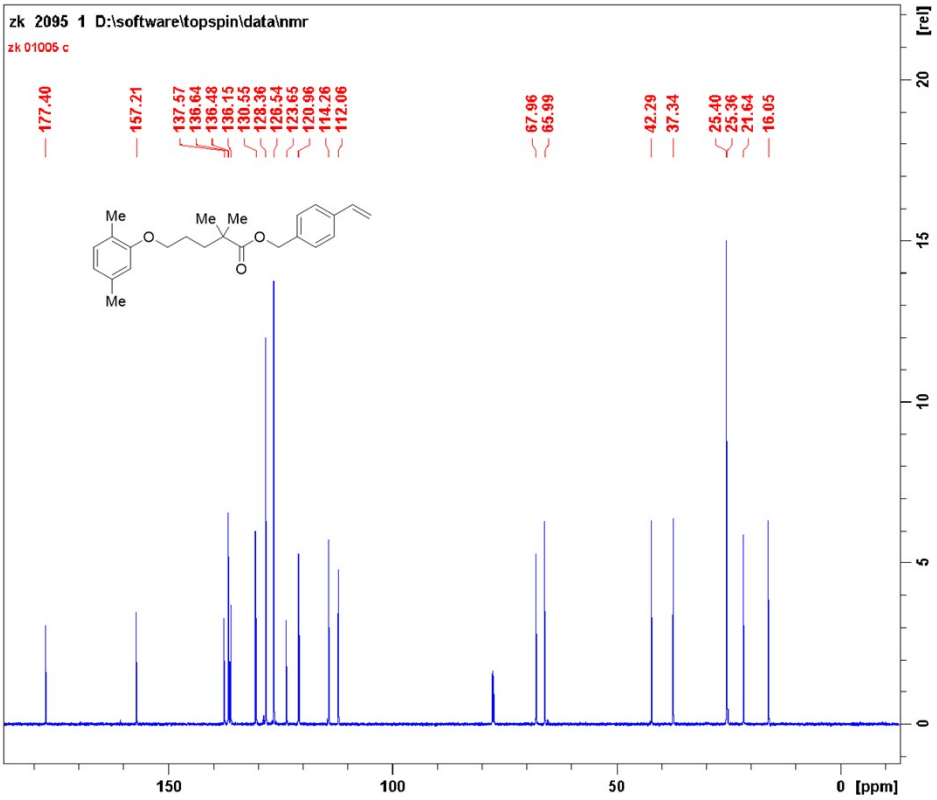
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **64**.



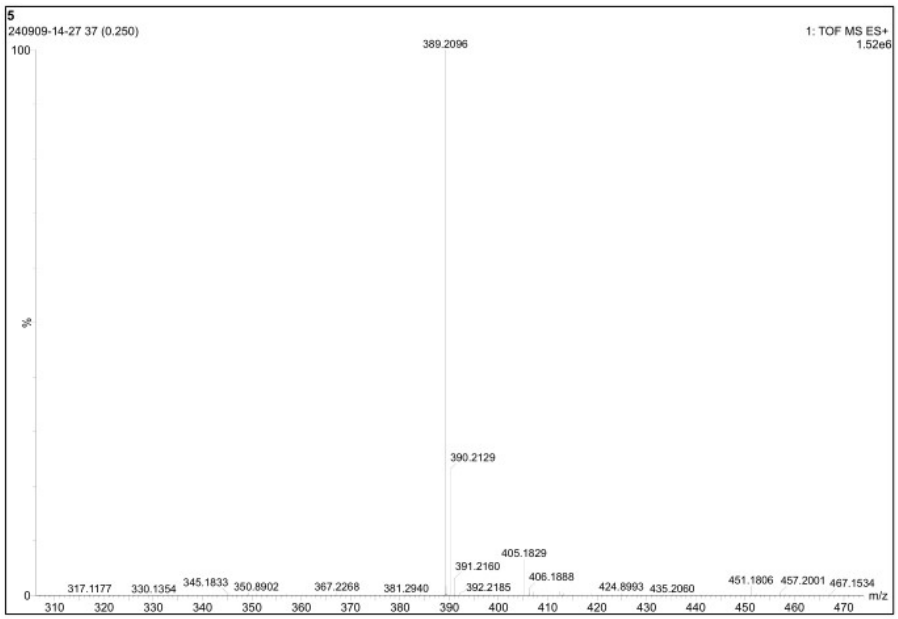
HR-MS (ESI) spectrum of **64**.



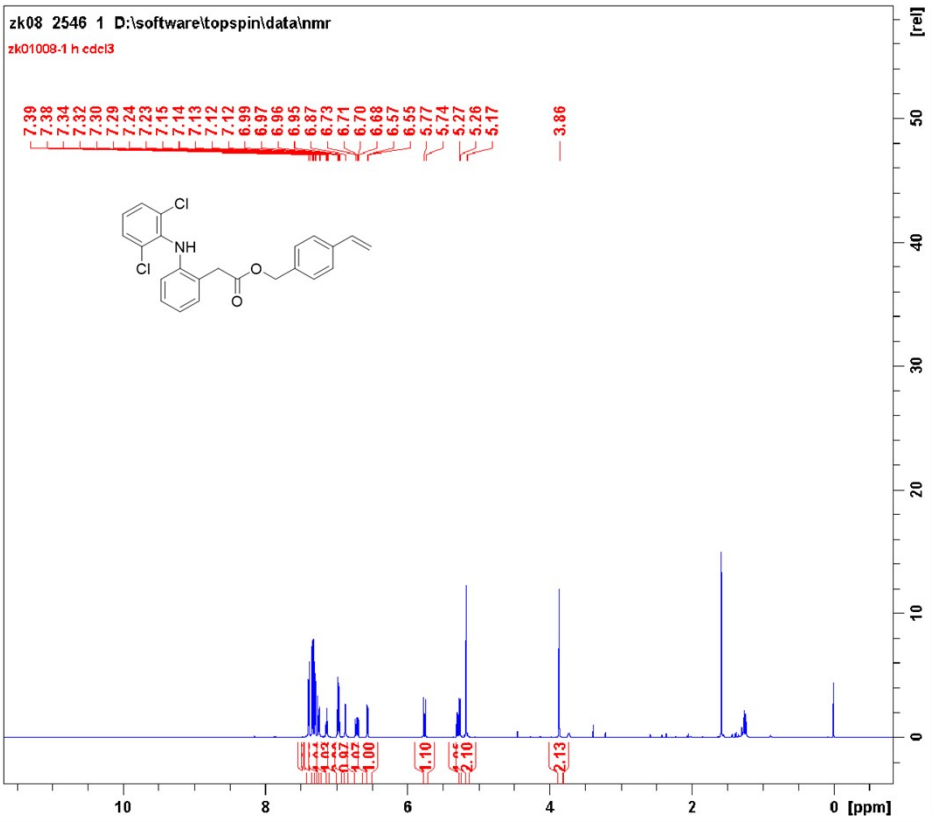
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **65**.



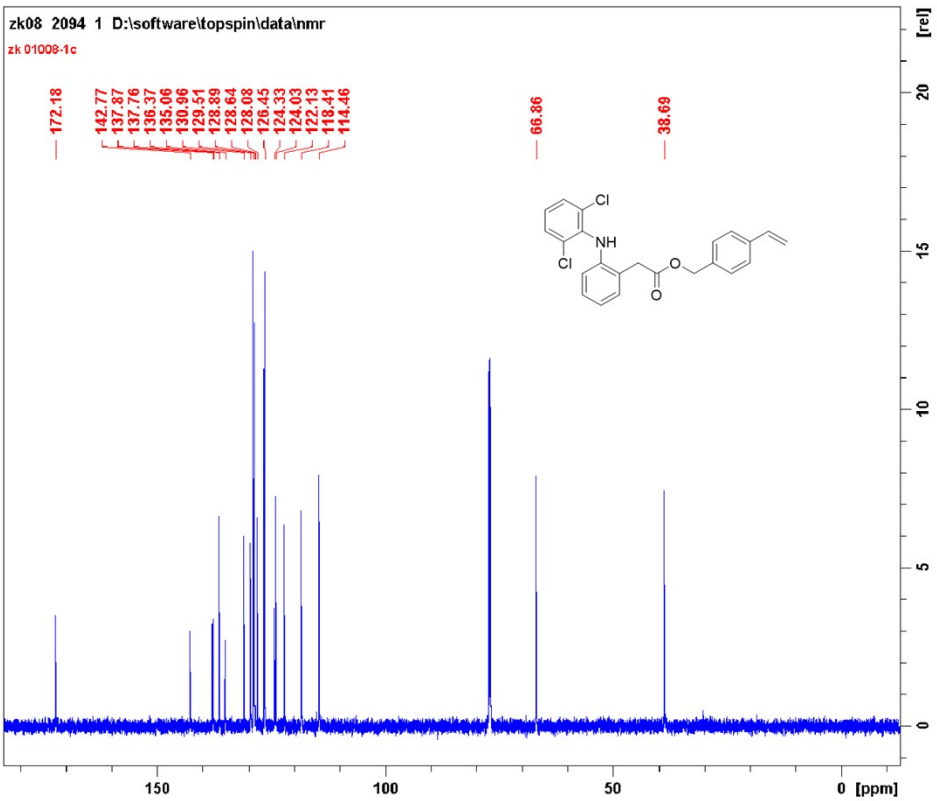
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **65**.



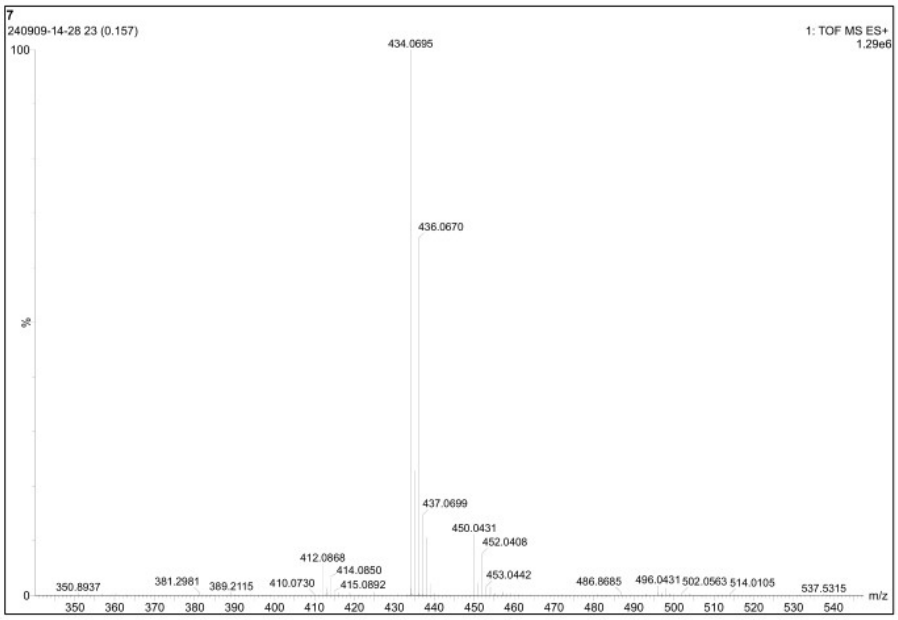
HR-MS (ESI) spectrum of **65**.



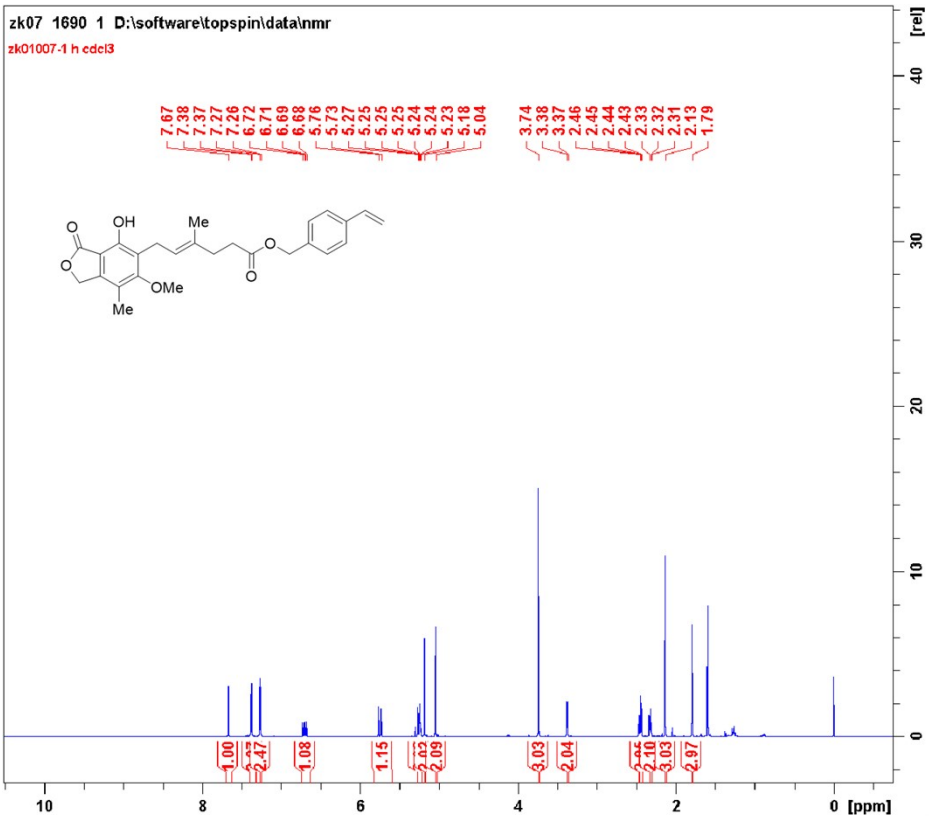
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **66**.



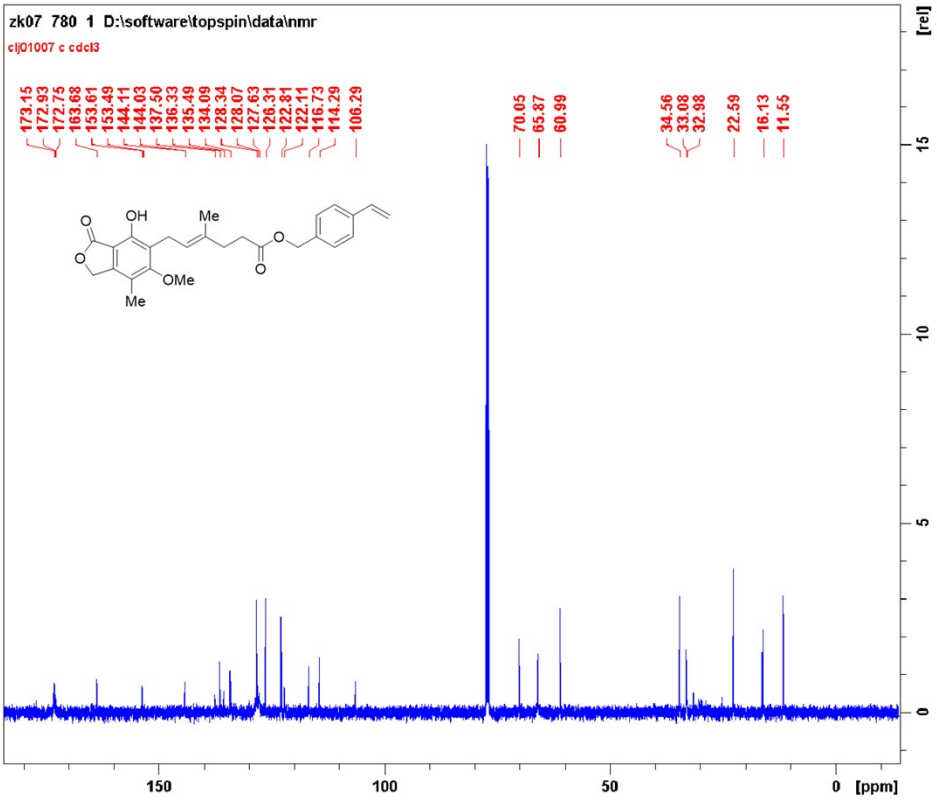
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **66**.



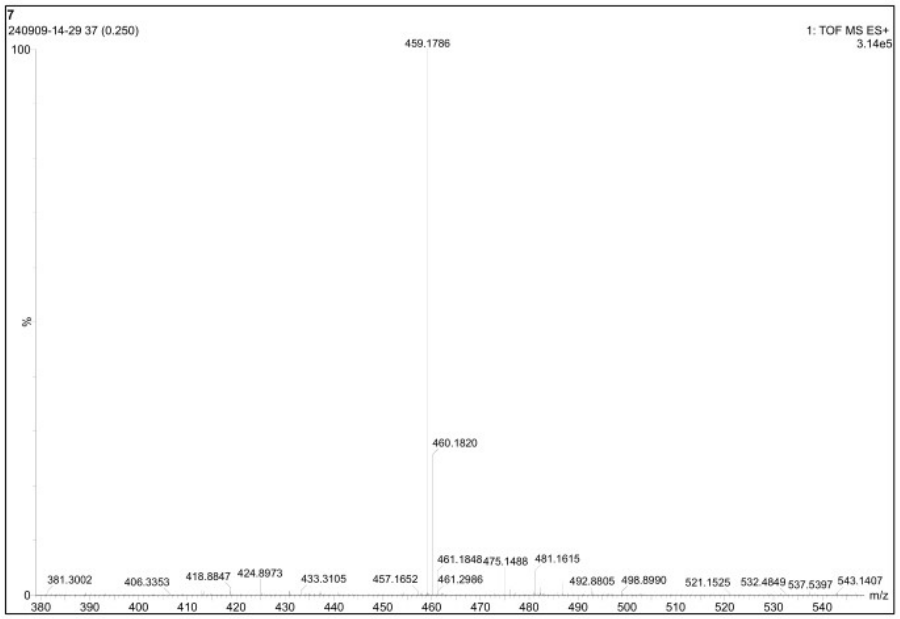
HR-MS (ESI) spectrum of **66**.



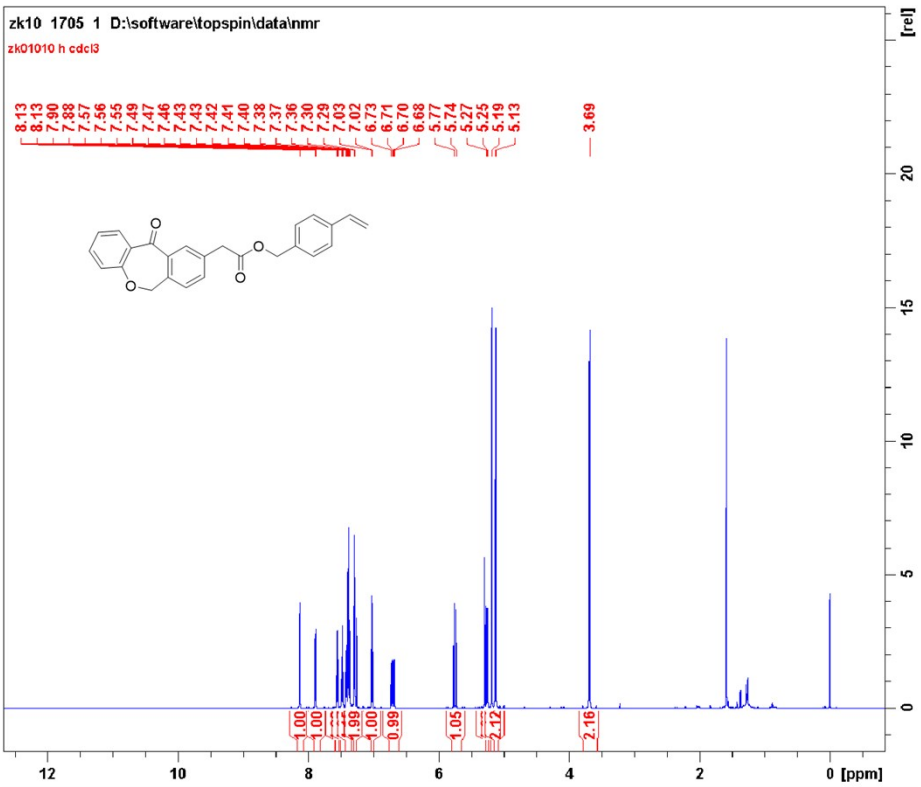
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **67**.



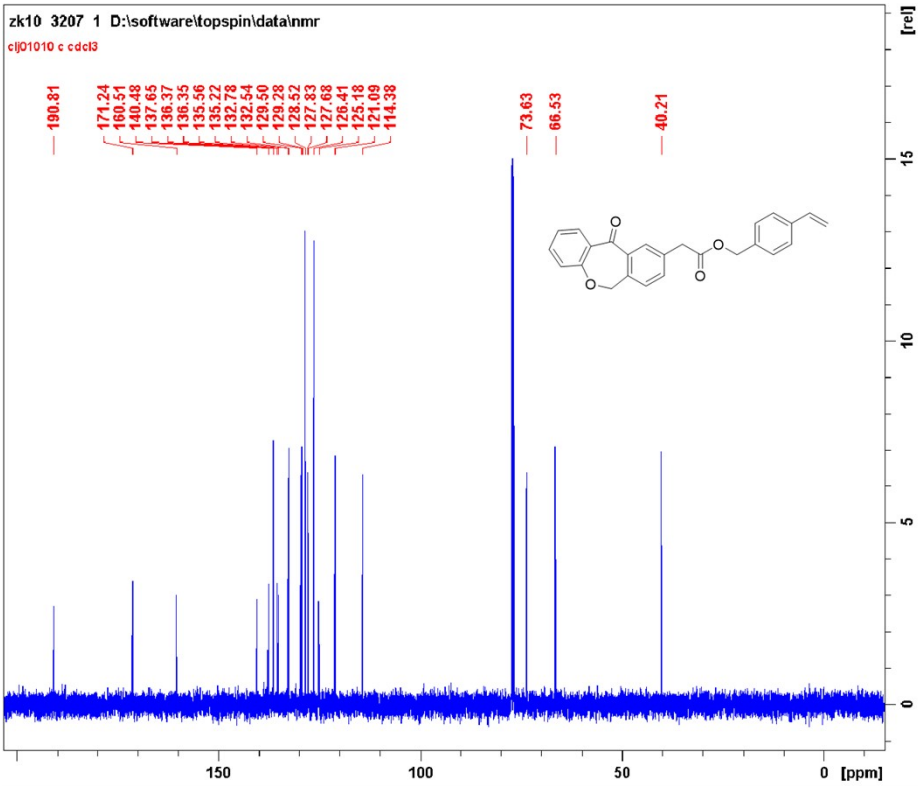
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **67**.



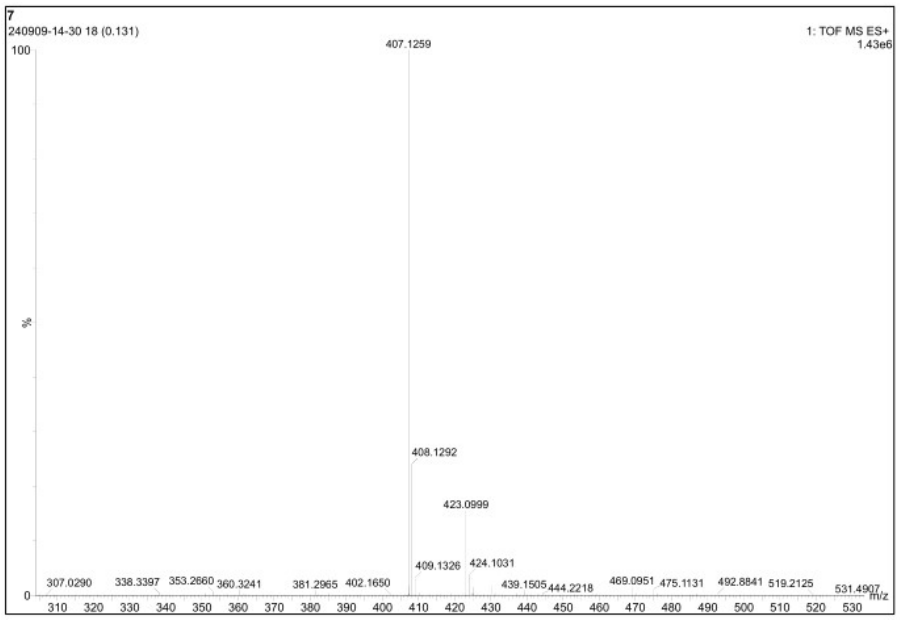
HR-MS (ESI) spectrum of **67**.



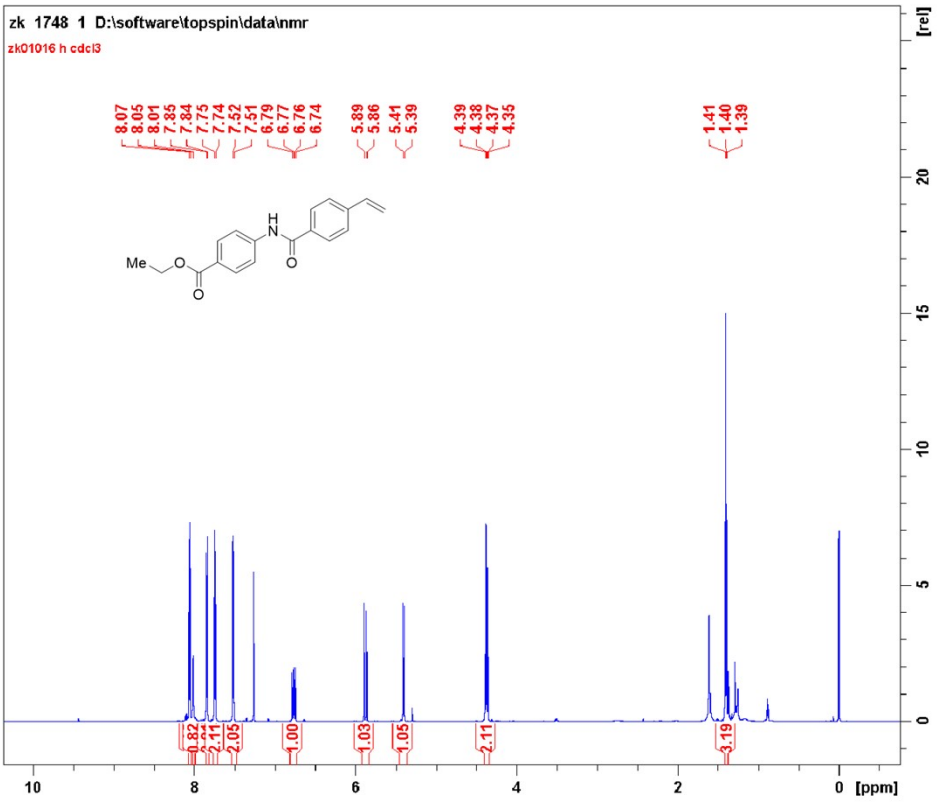
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **68**.



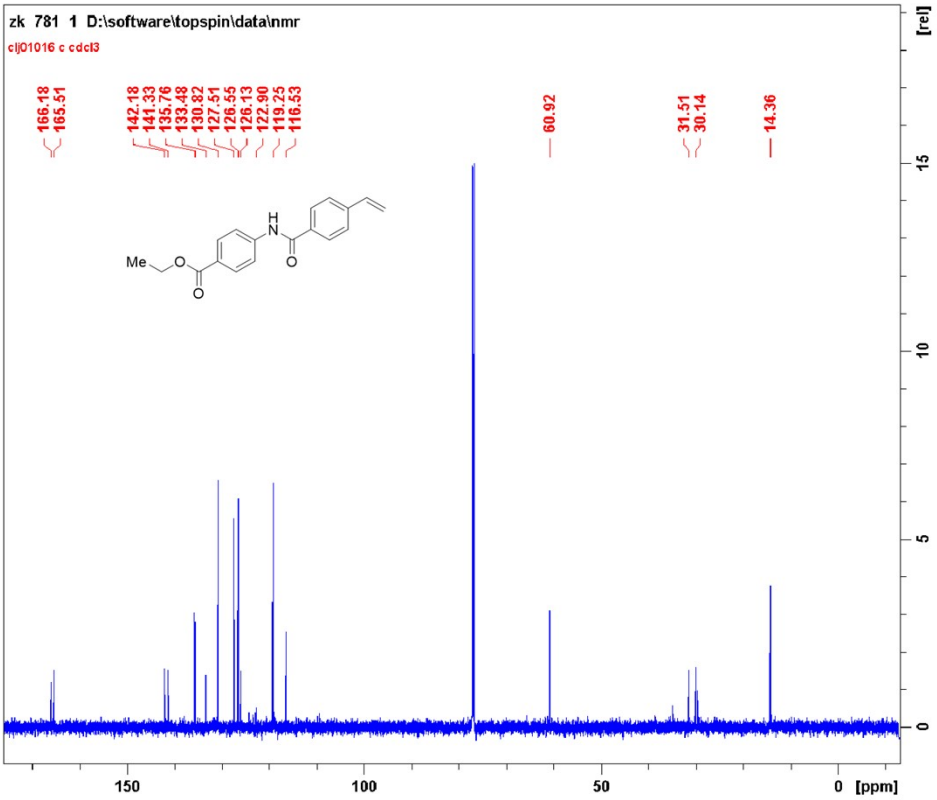
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **68**.



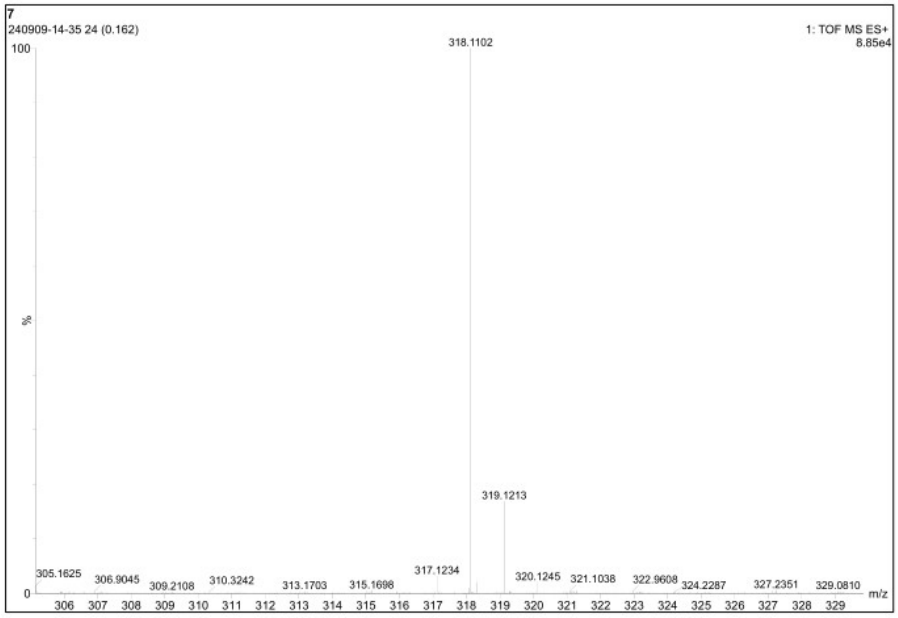
HR-MS (ESI) spectrum of **68**.



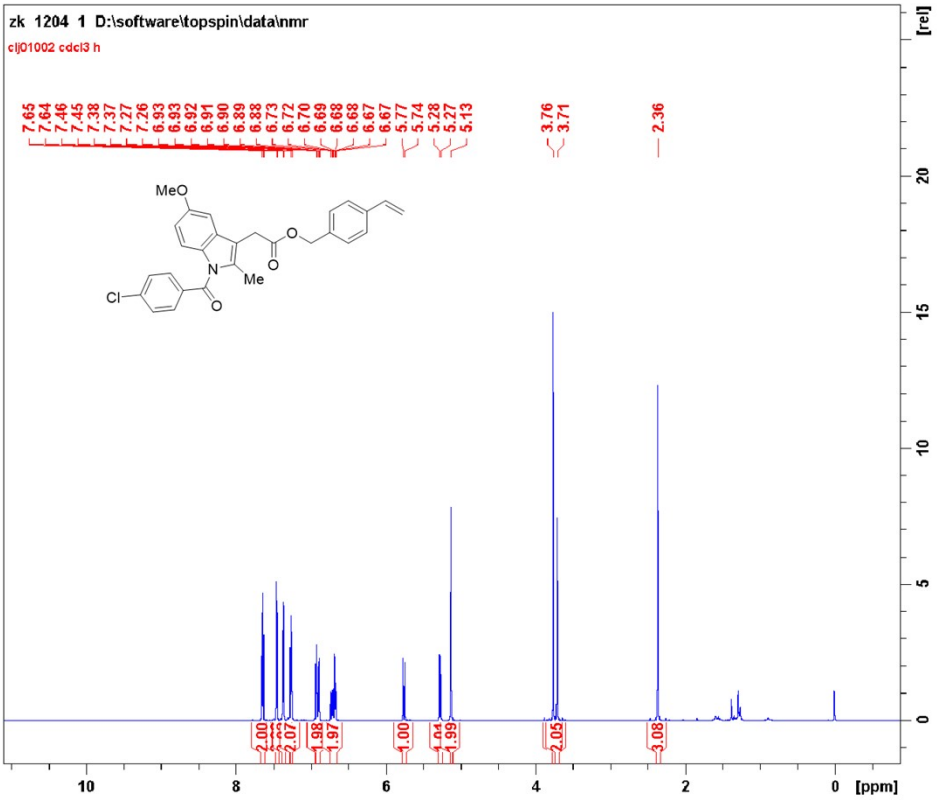
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **69**.



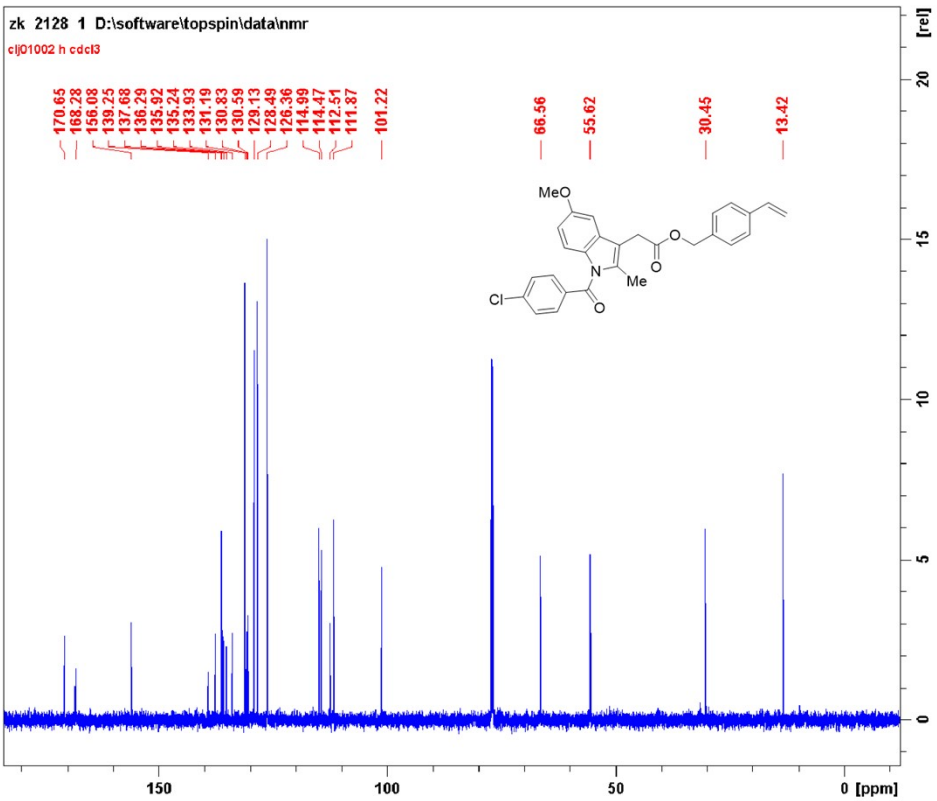
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **69**.



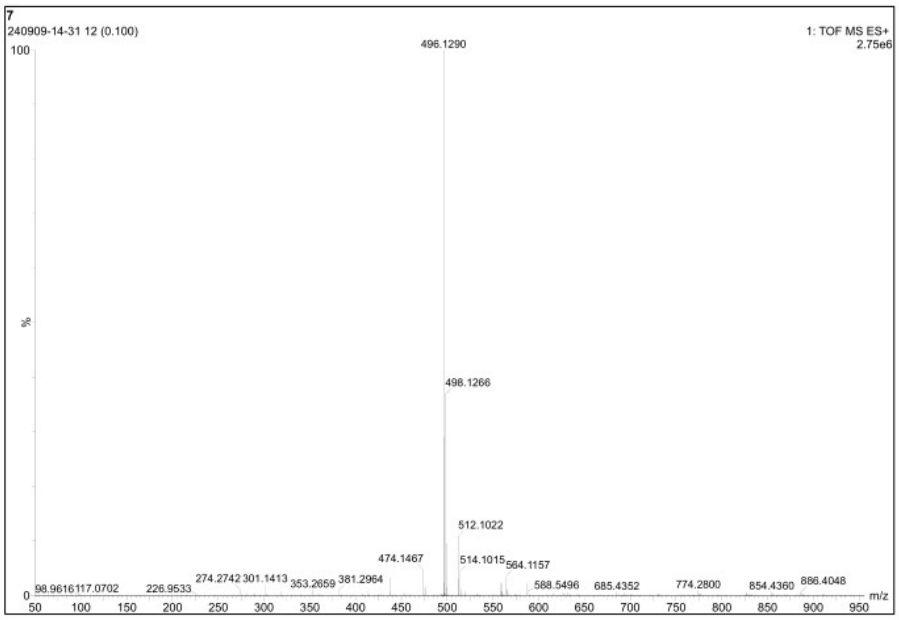
HR-MS (ESI) spectrum of **69**.



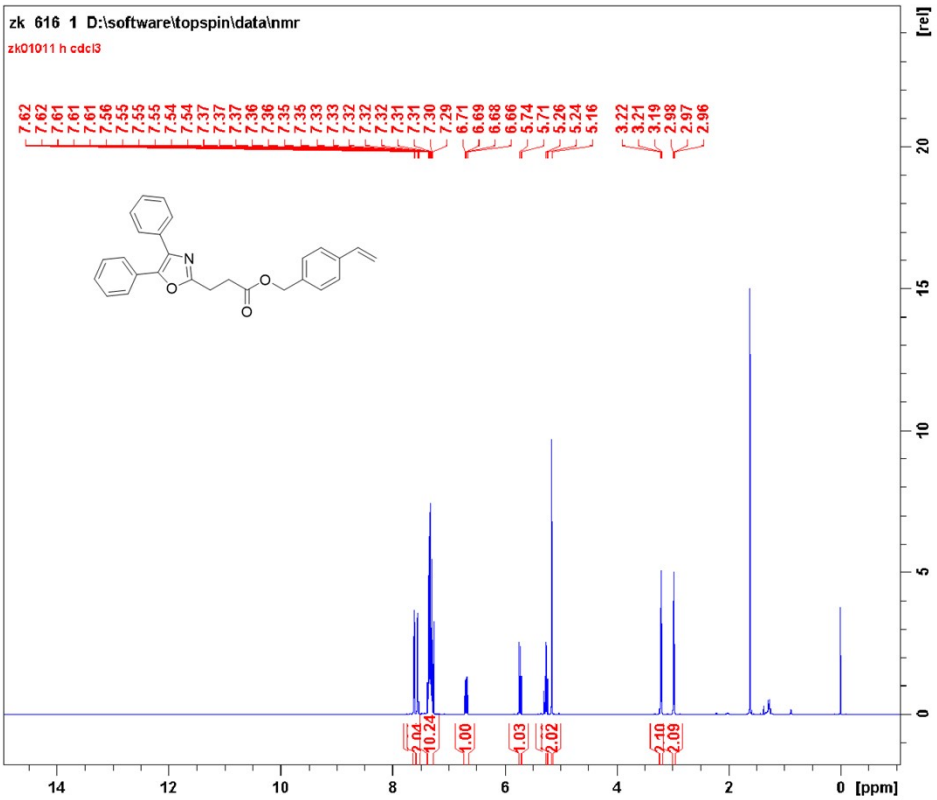
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **70**.



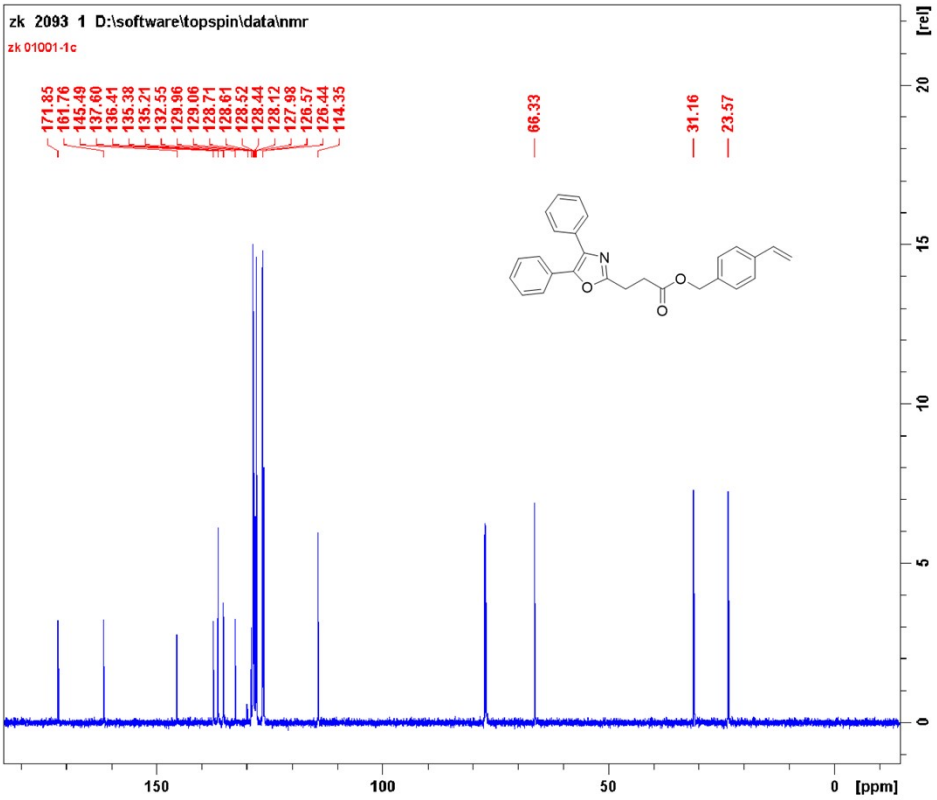
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **70**.



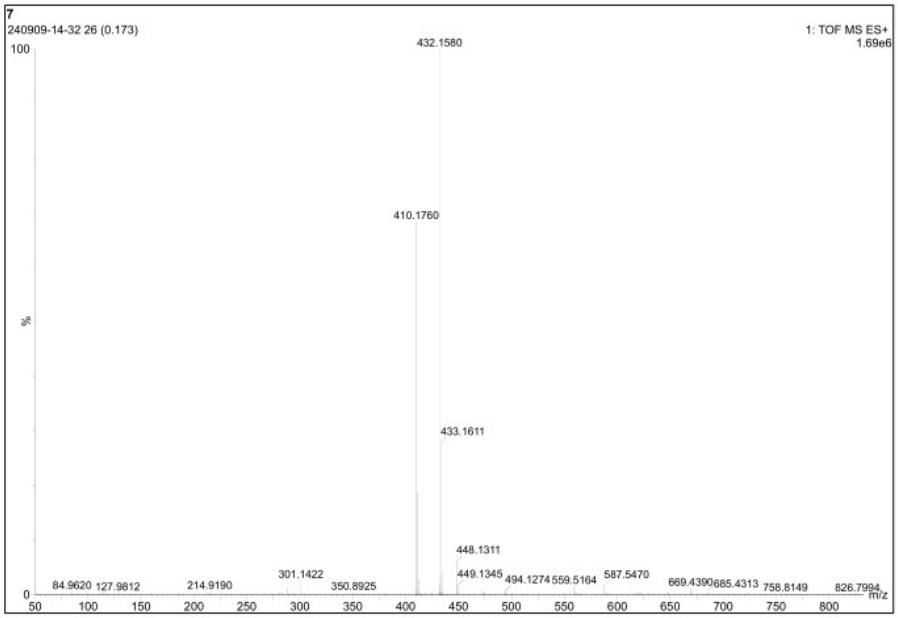
HR-MS (ESI) spectrum of **70**.



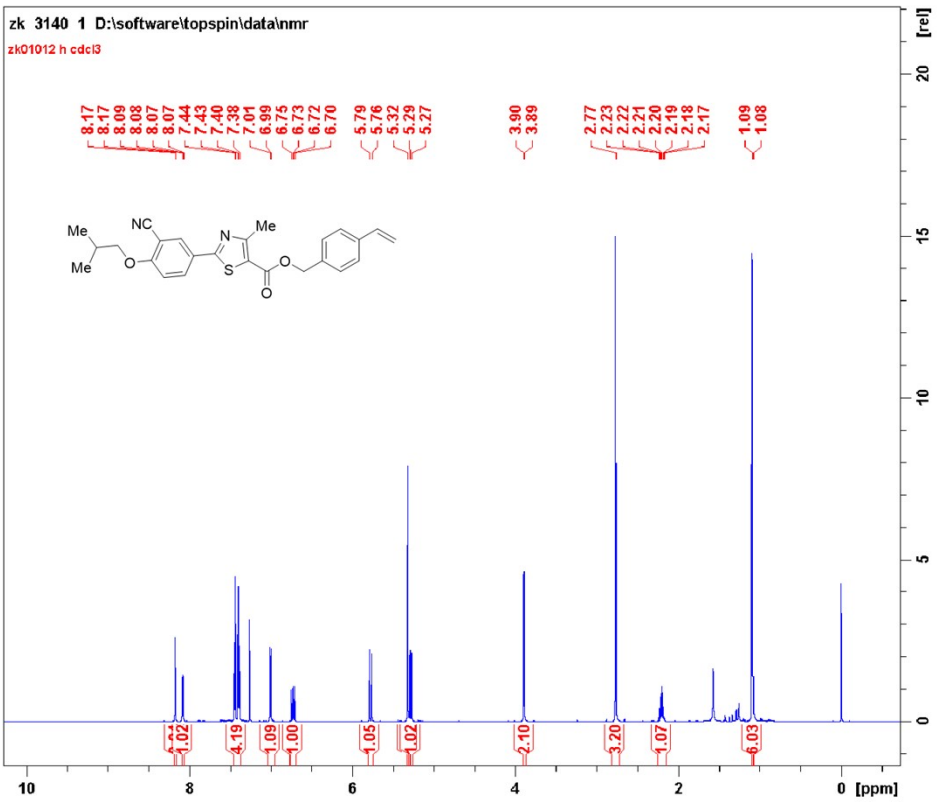
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **71**.



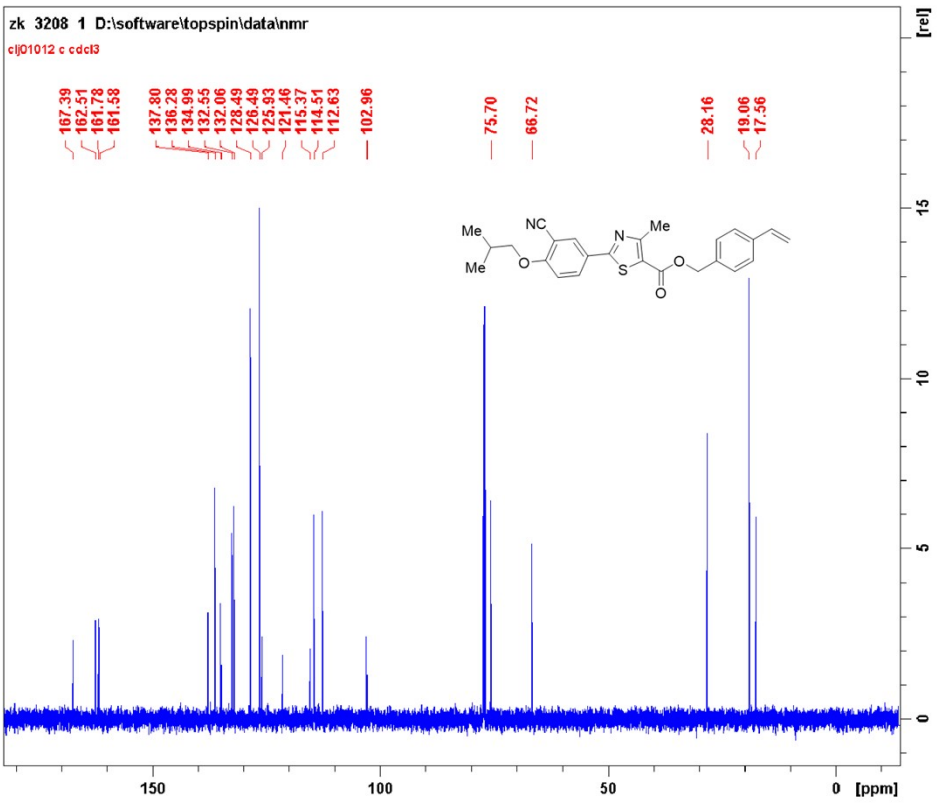
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **71**.



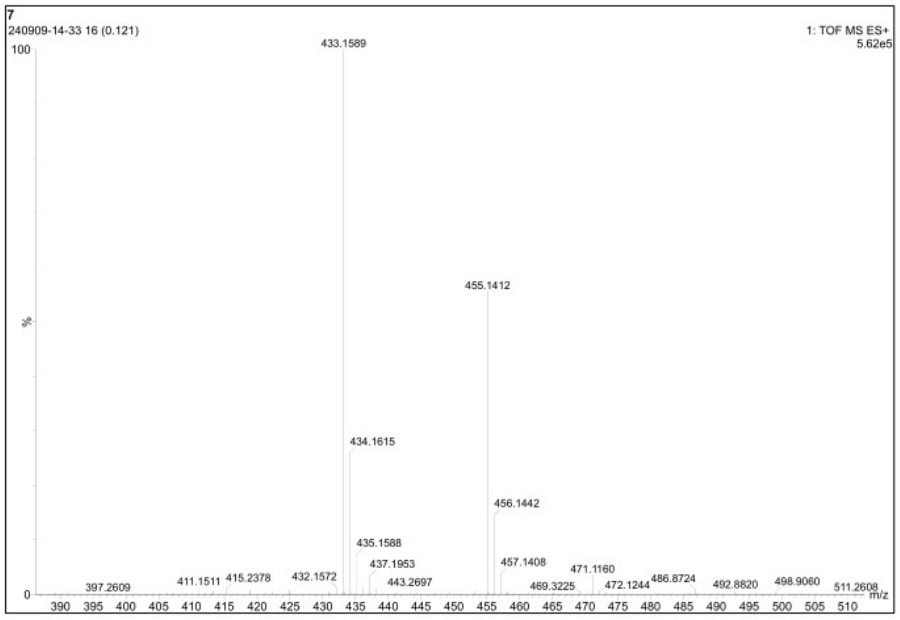
HR-MS (ESI) spectrum of **71**.



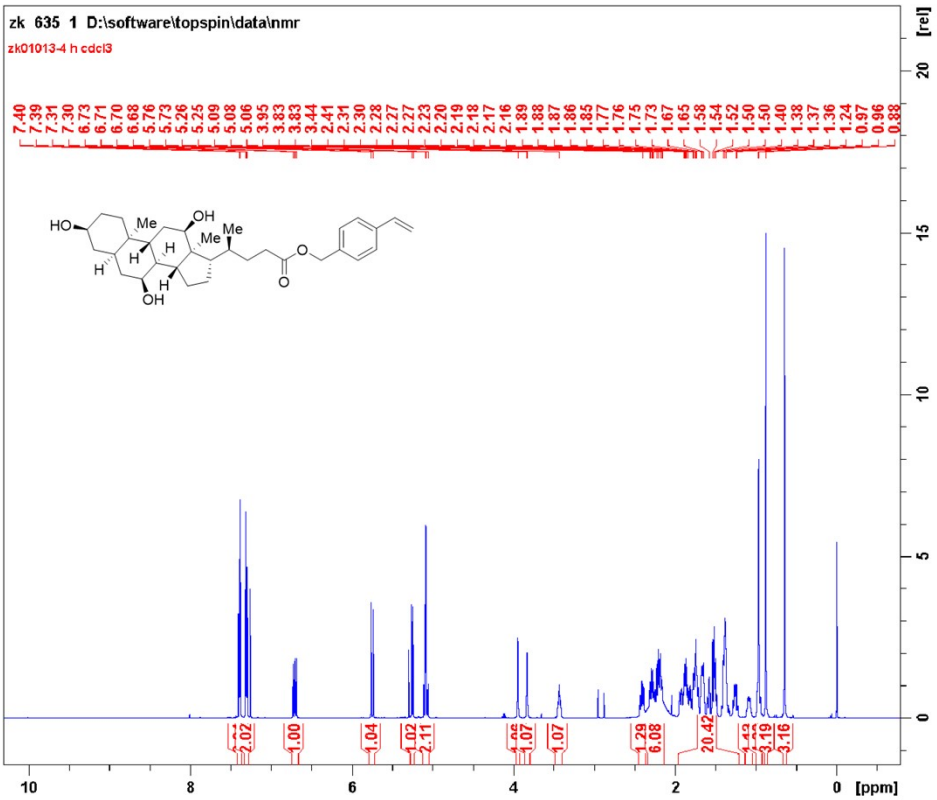
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **72**.



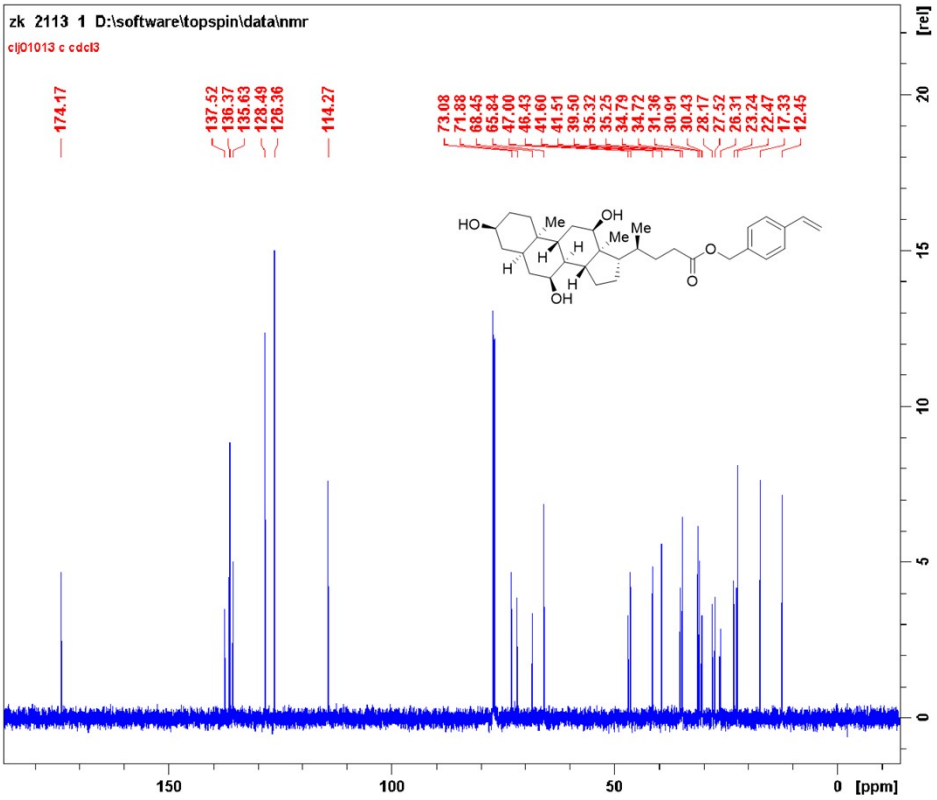
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **72**.



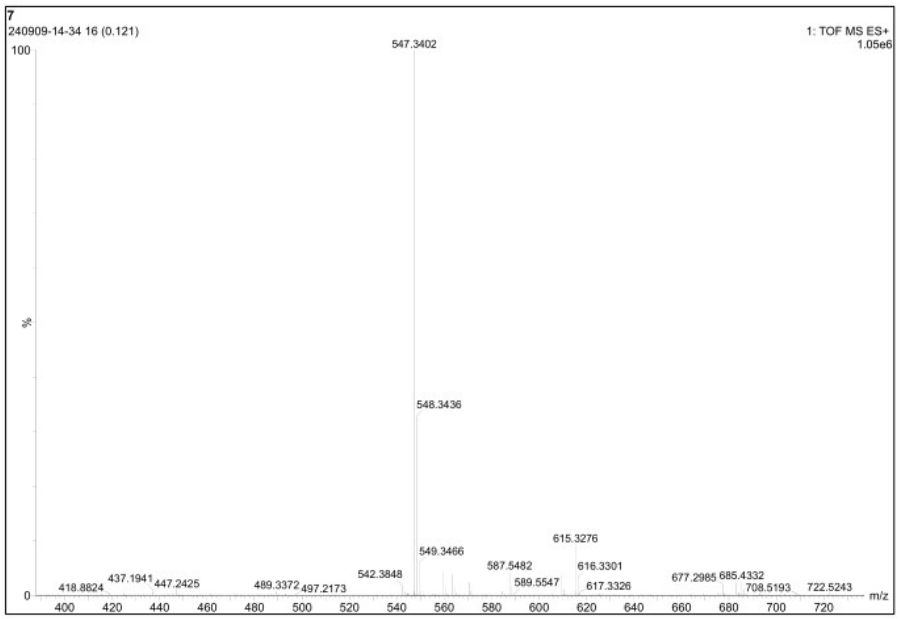
HR-MS (ESI) spectrum of **72**.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **73**.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **73**.



HR-MS (ESI) spectrum of **73**.