Supporting Information

Substrate-Initiated Radical Relay: Redox-Neutral Iodo/Bromo Sulfoximination of Alkynes

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1. General information

Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) data were recorded with Chloroform-*d* or DMSO-d_6 as solvent at room temperature unless specified otherwise. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) or Chloroform-*d* (δ= 7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm) as internal reference; ^{13}C NMR spectra was recorded with Chloroform-*d* (δ = 77.00 ppm) or DMSO (δ = 39.52 ppm) as internal reference. IR and HRMS were performed by the State-authorized Analytical Center in Soochow University.

2. General procedures

2.1 General process for esterification of vinyl sulfoximines

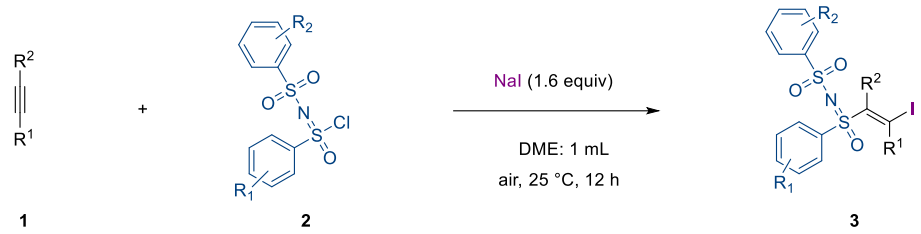


Figure S1: General process for esterification of (*E*)-*β*-iodoalkenyl sulfoximines.

The step is to add alkyne **1** (0.1 mmol), sulfoximidoyl chloride **2** (0.14 mmol) and sodium iodide (0.16 mmol), 1,2-Dimethoxyethane (1 mL), stirring for 12 hours at 25 ℃. After confirming the finish of the reaction by TLC, concentrated in vacuum and purified by column chromatography on silica gel to afford the desired products **3**.

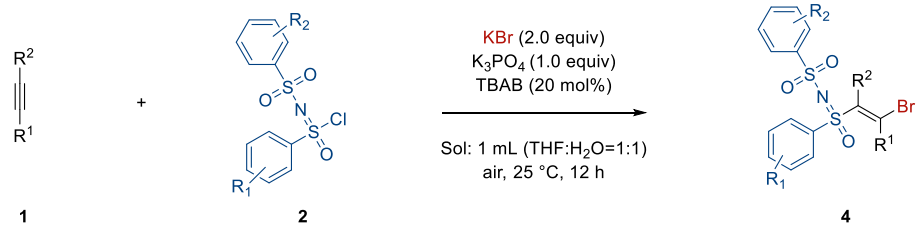


Figure S2: General process for esterification of (*E*)-*β*-bromoalkenyl sulfoximines.

The step is to add alkyne **1** (0.1 mmol), sulfoximidoyl chloride **2** (0.2 mmol) potassium bromide (0.2 mmol), potassium phosphate (0.1 mmol), tetrabutylammonium bromide (20 mol%), tetrahydrofuran (500 μL) and water (500 μL), stirring for 12 hours at 25 ℃. After confirming the finish of the reaction by TLC, the system was extracted with ethyl acetate, merge the organic phase, dried with anhydrous sodium sulfate, then concentrated in vacuum and purified by column chromatography on silica gel to afford the desired products **4**.

2.2 Gram scale reaction

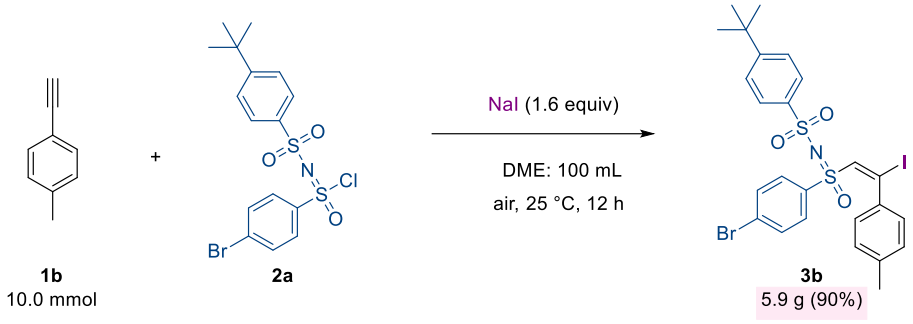


Figure S3: Gram-scale synthesis of (*E*)-*β*-iodoalkenyl sulfoximines.

In a 250 mL round-bottom flask, 4-ethynyltoluene **1b** (10.0 mmol), sulfoximidoyl chloride **2a** (14.0 mmol), sodium iodide (16.0 mmol) and 1,2-Dimethoxyethane (100 mL) were added separately under air. The mixture was stirred at 25 ℃ for 12 hours. After confirming the finish of the reaction by TLC, concentrated in vacuum and purified by column chromatography on silica gel to afford the desired product **3b** in 90% yield (5.9 g).

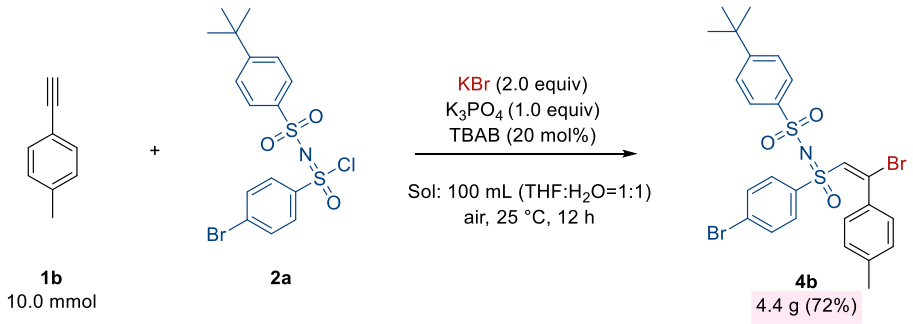


Figure S4: Gram-scale synthesis of (*E*)-*β*-bromoalkenyl sulfoximines.

In a 250 mL round-bottom flask, 4-ethynyltoluene **1b** (10.0 mmol), sulfoximidoyl chloride **2a** (20.0 mmol), potassium bromide (20.0 mmol), potassium phosphate (10.0 mmol), tetrabutylammonium bromide (2.0 mmol), tetrahydrofuran (50 mL) and water (50 mL), were added separately under air. The mixture was stirred at 25 ℃ for 12 hours. After confirming the finish of the reaction by TLC, the system was extracted with ethyl acetate, merge the organic phase, dried with anhydrous sodium sulfate, then

concentrated in vacuum and purified by column chromatography on silica gel to afford the desired product **4b** in 72% yield (4.4 g).

2.3 General procedure for the preparation of sulfoximidoyl chloride

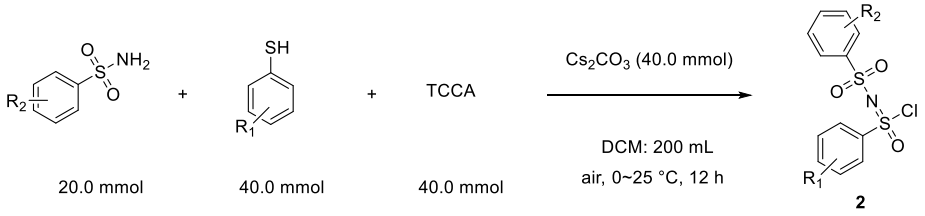
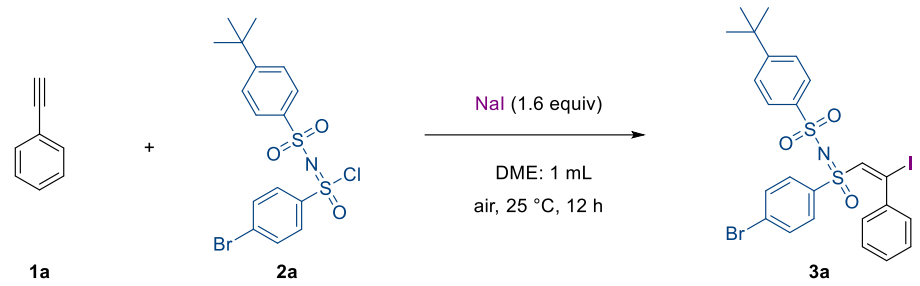


Figure S5: General procedure for the preparation of sulfoximidoyl chloride **2**.

In a 500 mL round-bottom flask, sulfonamide (20.0 mmol), thiophenols (40.0 mmol), trichloroisocyanuric acid (40 mmol), cesium carbonate (40.0 mmol) and dichloromethane (200 mL) were added separately under air. The mixture was stirred from 0 ℃ to 25 ℃ for 12 hours. After confirming the finish of the reaction by TLC, the system was extracted with ethyl acetate, merge the organic phase, dried with anhydrous sodium sulfate, then concentrated in vacuum and purified by column chromatography on silica gel to afford the desired product sulfoximidoyl chloride **2**.

3. Optimization of the reaction conditions



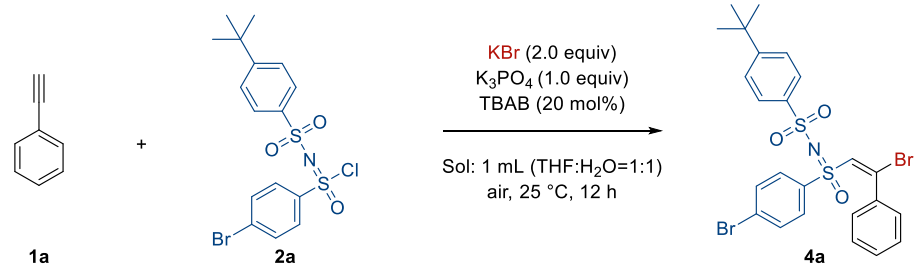
1a 2a 3a

Entry	Variation from the "standard conditions" [a]	Yield (%) [b]
1	none	96
2	no NaI	N.D.
3	DCM instead of DME	86
4	MeOH instead of DME	18
5	MeCN instead of DME	85
6	Acetone instead of DME	76
7	DMF instead of DME	40
8	NMP instead of DME	＜5
9	H_2O instead of DME	＜5
10	THF instead of DME	86
11	EA instead of DME	89
12	Toluene instead of DME	71
13	CuI instead of NaI	46
14	LiI instead of NaI	64
15	KI instead of NaI	70
16	NH_4I instead of NaI	74
17	TBAI instead of NaI	47
18	0.8 equiv I_2 instead of NaI	＜5
19	0.1 equiv of NaI	＜5

20	1.0 equiv of NaI	63

Table S1. Optimization of the iodination reaction conditions.

[a]General reaction conditions: **1a** (0.1 mmol), **2a** (0.14 mmol), NaI (0.16 mmol), using 1 mL of the solvent at 25 °C for 12 h. [b]Yields of isolated product.

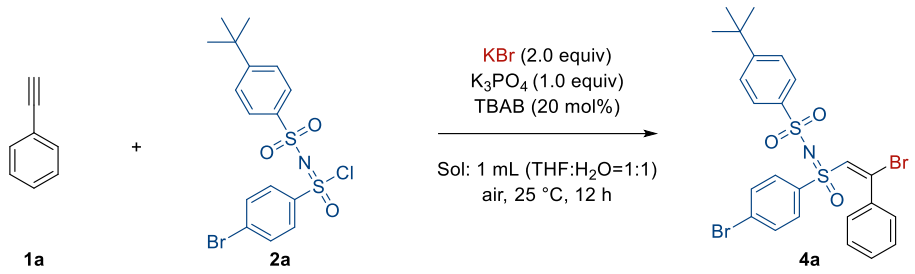


Entry	Variation from the "standard conditions" [a]	Yield (%) [b]
1	none	85
2	THF instead of THF/H_2O	54
3	H_2O instead of THF/H_2O	＜5
4	DMF instead of THF/H_2O	＜5
5	MeCN instead of THF/H_2O	35
6	MeOH instead of THF/H_2O	38
7	Acetone instead of THF/H_2O	47
8	DCM instead of THF/H_2O	11
9	EA instead of THF/H_2O	33
10	NaBr instead of KBr	64
11	LiBr instead of KBr	72
12	CuBr instead of KBr	29
13	NH_4Br instead of KBr	56
14	K_2CO_3 instead of K_3PO_4	73
15	$Ca(OH)_2$ instead of K_3PO_4	63
16	Et_3N instead of K_3PO_4	62

17	DMAP instead of K_3PO_4	65
18	CTAB instead of TBAB	76
19	$TBABr_3$ instead of TBAB	72
20	18-Crown-6 instead of TBAB	76

Table S2. Optimization of the bromination reaction conditions.

[a]General reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), KBr (0.2 mmol), K_3PO_4 (0.1 mmol), TBAB (20 mol%)，using 1 mL of the solvent at 25 °C for 12 h. [b]Yields of isolated product.



Entry	Controlled parameter	Yield (%)
1	Standard conditions	85
2	Without TBAB	56
3	Without K_3PO_4	63
4	Without KBr	＜5
5	Without KBr (TBAB 0.2 mmol)	48

Table S3. Control experiment of the bromination reaction conditions.

[a]General reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), KBr (0.2 mmol), K_3PO_4 (0.1 mmol), TBAB (20 mol%)，using 1 mL of the solvent at 25 °C for 12 h. [b]Yields of isolated product.

4. Mechanistic investigations

4.1 Radical trapping experiments

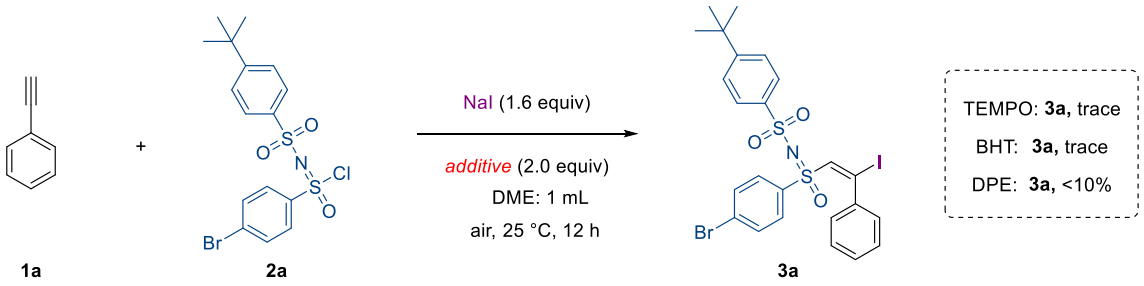


Figure S6: Radical quenching experiments under iodination conditions.

The step is to add phenylacetylene **1a** (0.1 mmol), sulfoximidoyl chloride **2a** (0.14 mmol) and sodium iodide (0.16 mmol) and TEMPO/BHT/1,1-diphenylethylene (0.2 mmol), 1,2-Dimethoxyethane (1 mL), stirring for 12 hours at 25 ℃. Under these conditions, only trace amounts of **3a** were obtained in the presence of TEMPO or BHT, while <10% yield of **3a** was detected with 1,1-diphenylethylene.

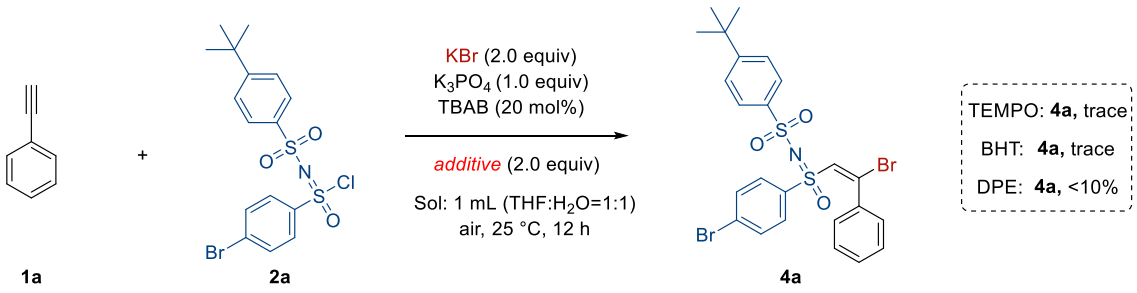


Figure S7: Radical quenching experiments under bromination conditions.

The step is to add phenylacetylene **1a** (0.1 mmol), sulfoximidoyl chloride **2a** (0.2 mmol), potassium bromide (0.2 mmol), potassium phosphate (0.1 mmol), tetrabutylammonium bromide (20 mol%), TEMPO/BHT/1,1-diphenylethylene (0.2 mmol), tetrahydrofuran (500 μL) and water (500 μL), stirring for 12 hours at 25 ℃. Under these conditions, only trace amounts of **4a** were obtained in the presence of

TEMPO or BHT, while <10% yield of **4a** was detected with 1,1-diphenylethylene. The crude residue was directly characterized by HRMS without further purification.

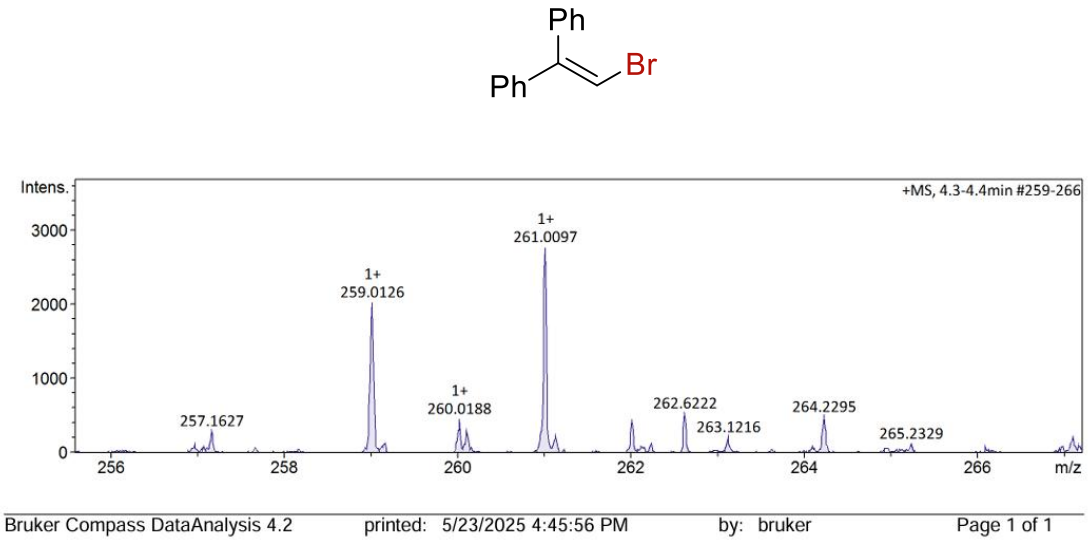


Figure S8: Radical trapping experiments under bromination conditions.

HRMS (ESI-TOF): Anal Calcd. For. $C_{14}H_{11}Br$ $[M+H]^+$: 259.0117 (100.0%), 261.0097 (97.3%), Found: 259.0126 (100.0%), 261.0097 (97.3%).

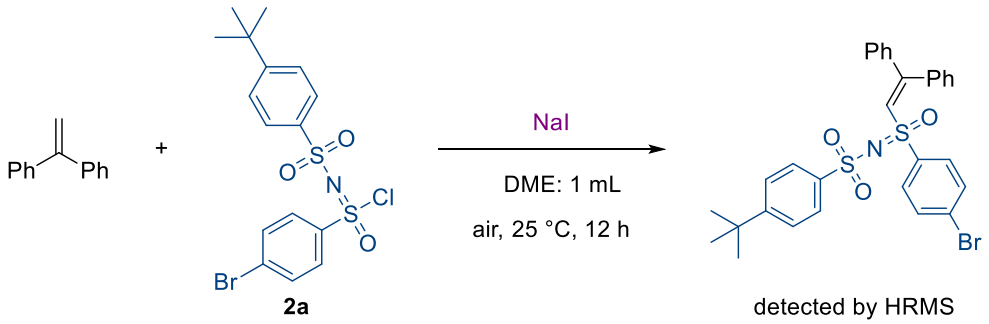


Figure S9: Radical trapping experiments.

The step is to add 1,1-diphenylethylene (0.2 mmol), sulfoximidoyl chloride **2a** (0.14 mmol) and sodium iodide (0.16 mmol) and 1,2-Dimethoxyethane (1 mL), stirring for 12 hours at 25 ℃. The crude residue was directly characterized by HRMS without further purification.

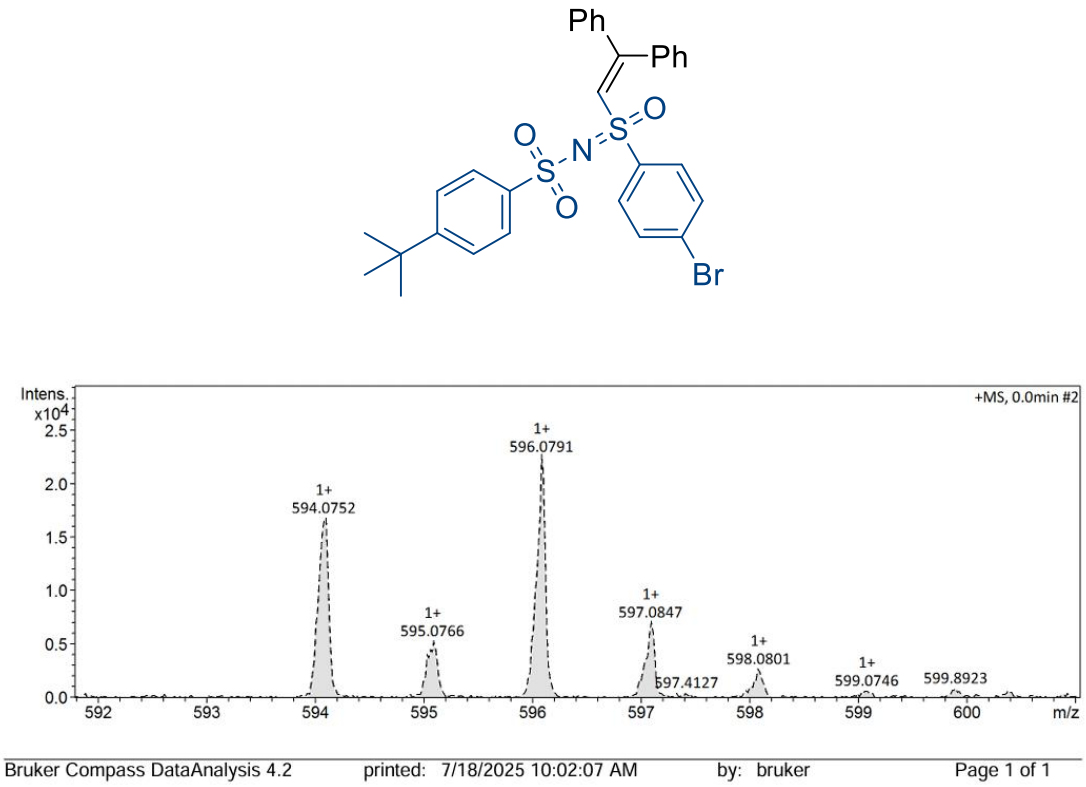


Figure S10: Radical trapping experiments under iodination conditions.

HRMS (ESI-TOF): Anal Calcd. For. $C_{30}H_{28}BrNO_3S_2$ $[M+H]^+$: 594.0767 (100.0%), 596.0747 (97.3%), Found: 594.0752 (100.0%), 596.0791 (97.3%).

4.2 Control experiments

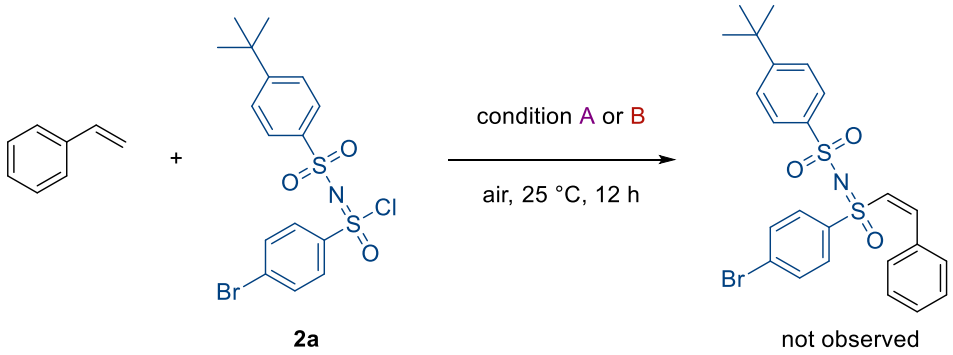


Figure S11: Reaction of styrene instead of phenylacetylene **1a**.

Condition A: The step is to add styrene (0.1 mmol), sulfoximidoyl chloride **2a** (0.14 mmol) , potassium phosphate (0.1 mmol) and sodium iodide (0.16 mmol) and

1,2-Dimethoxyethane (1 mL), stirring for 12 hours at 25 ℃. Condition B: The step is to add styrene (0.1 mmol), sulfoximidoyl chloride **2a** (0.2 mmol) potassium bromide (0.2 mmol), potassium phosphate (0.1 mmol), tetrabutylammonium bromide (20 mol%), tetrahydrofuran (500 μL) and water (500 μL), stirring for 12 hours at 25 ℃. The reaction progress was monitored by TLC, and the crude residue was directly analyzed by HRMS without further purification; no expected product was observed.

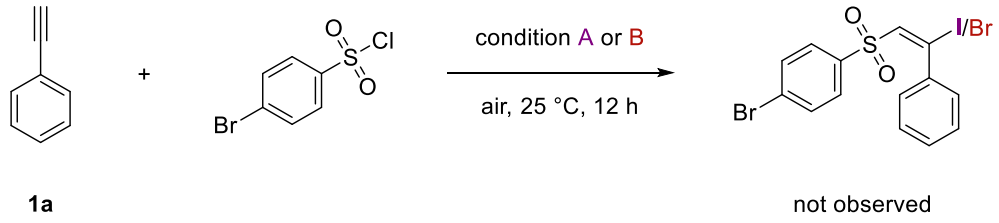


Figure S12: Reaction of 4-bromobenzenesulfonyl chloride instead of sulfoximidoyl chloride **2a**.

Condition A: The step is to phenylacetylene **1a** (0.1 mmol), 4-bromobenzenesulfonyl chloride (0.14 mmol) and sodium iodide (0.16 mmol) and 1,2-Dimethoxyethane (1 mL), stirring for 12 hours at 25 ℃. Condition B: The step is to add phenylacetylene **1a** (0.1 mmol), 4-bromobenzenesulfonyl chloride (0.2 mmol) potassium bromide (0.2 mmol), potassium phosphate (0.1 mmol), tetrabutylammonium bromide (20 mol%), tetrahydrofuran (500 μL) and water (500 μL), stirring for 12 hours at 25 ℃. The reaction progress was monitored by TLC, and the crude residue was directly analyzed by HRMS without further purification; no expected product was observed.

4.3 Cyclic voltammetry (CV) measurements

Linear scan voltammetry measurements were performed on a photoelectrochemical analysis CHI760E electrical workstation (Shanghai Chenhua) using a three-electrode cell set-up: tetrabutylammonium hexafluorophosphate ([(n-Bu)$_4$N]PF$_6$) (0.1 M) was used as the supporting electrolyte, the working electrode was

a glassy carbon, the counter electrode was a Pt wire and the reference electrode was Ag/AgCl.

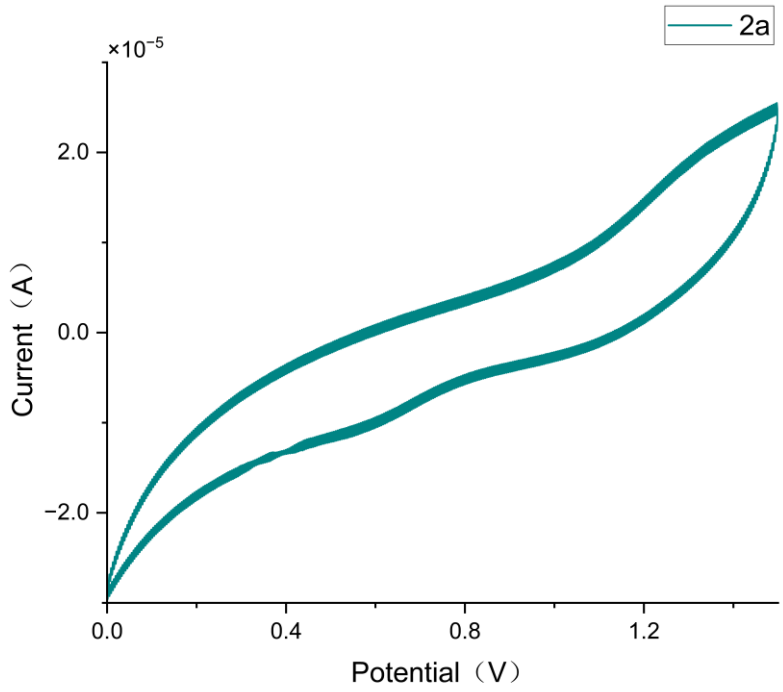


Figure S13: Cyclic voltammetry (CV) measurements.

Cyclic voltammetry of [**2a**] (0.1 mM) in MeCN. The scan rate was 200 mV/s. It shows an oxidation at $E_{1/2}$ = 1.38 V vs. Ag/AgCl.

4.4 Visual Color Observation Experiment

Sulfoximidoyl chloride **2a** (0.1 mmol) was dissolved in tetrahydrofuran (THF, 1.0 mL) at room temperature. Since potassium bromide is insoluble in THF, tetrabutylammonium bromide (TBAB) was employed instead. Separately, sodium iodide (0.1 mmol) and TBAB (0.1 mmol) were each dissolved in THF (1.0 mL). The colors of the individual solutions were noted, after which mixtures of **2a** with either sodium iodide or TBAB were prepared under the same conditions. The resulting solutions were photographed immediately after mixing under ambient laboratory lighting.

Figure S14: Photographs of THF solutions (from left to right): (a) sulfoximidoyl chloride **2a**, (b) sodium iodide (NaI), (c) tetrabutylammonium bromide (TBAB), (d) mixture of **2a** and NaI, (e) mixture of **2a** and TBAB.

4.5 In situ NMR study

At 25 ℃, **2a** (0.1 mmol) was stirred in $CDCl_3$(1.0 mL) for 10 min and then ^1H NMR monitoring was performed to obtain ^1H NMR spectra of (1). At 25 ℃, **2a** (0.1 mmol) and sodium iodide (0.15 mmol) were stirred in $CDCl_3$ (1.0 mL) for 10 min and then ^1H NMR monitoring was performed to obtain ^1H NMR spectra of (2). Since potassium bromide is insoluble in $CDCl_3$, tetrabutylammonium bromide was employed as a substitute. At 25 ℃, **2a** (0.1 mmol) and tetrabutylammonium bromide (0.1 mmol) were stirred in $CDCl_3$ (1.0 mL) for 10 min and then ^1H NMR monitoring was performed to obtain ^1H NMR spectra of (3).

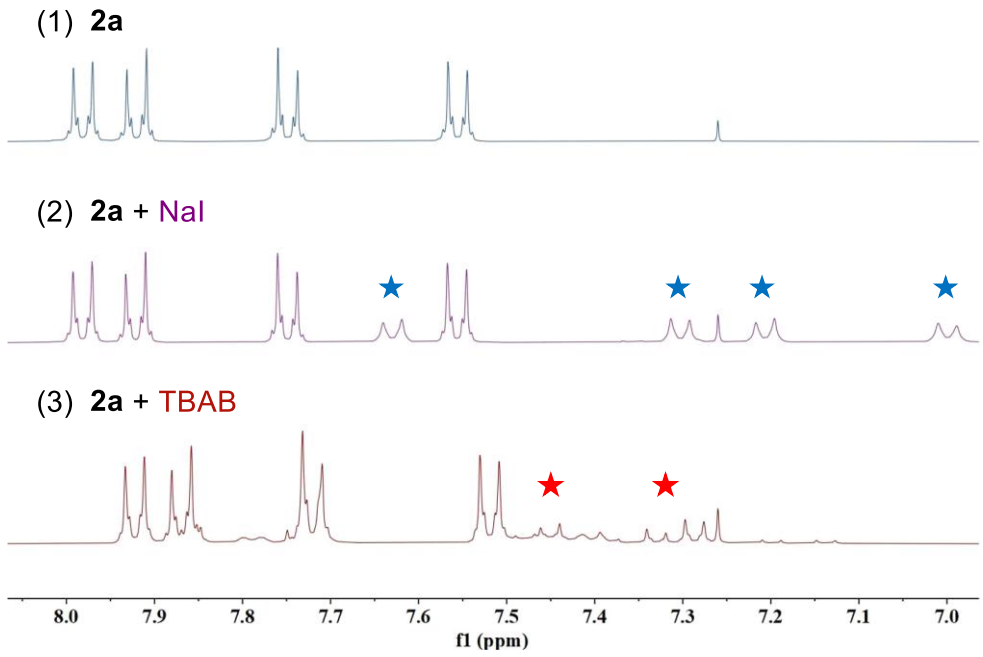
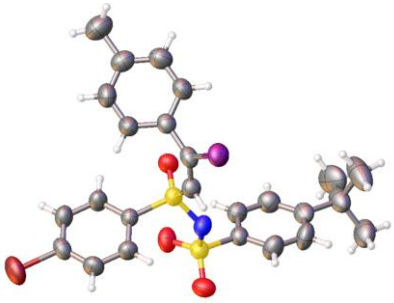


Figure S15: Comparison between ^{1}H NMR spectra of (1), (2), (3).

5. X-ray data

X-Ray single-crystal data of product **3b**



CCDC n° 2432150

Crystallography data for ***3b***

Empirical formula	$C_{25}H_{25}BrINO_3S_2$
Formula weight	658.39
Temperature/K	297
Crystal system	triclinic

Space group	P -1
a/Å	7.0173(4)
b/Å	14.2130(10)
c/Å	15.1454(10)
α/°	64.302(2)
β/°	81.405(2)
γ/°	77.696(2)
Volume/Å^3	1327.09(15)
Z	2
ρ_{calc}g/cm^3	1.648
μ/mm^{-1}	2.896
F(000)	652.0
Crystal size/mm^3	0.10 × 0.10 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.4140 to 29.1690
Index ranges	-7 ≤ h ≤ 8, -16≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	20091
Data/restraints/parameters	4640/0/302
Goodness-of-fit on F^2	1.033
Final R indexes (I>=2σ (I))	R_1 =0.0416, wR_2 = 0.0916
Final R indexes (all data)	R_1 = 0.0587, wR_2 = 0.1016
Largest diff. peak/hole / e Å^{-3}	0.647/-0.454

6. DFT calculation

6.1 DFT computational details

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[1] Molecular frontier orbital calculations were conducted at the B3LYP-D3/def2-QZVPP level of theory. Geometry optimizations for

all other intermediates and transition states, as well as calculations of electrostatic potential, orbital phase diagrams, and bond dissociation energies, employed the B3LYP-D3 functional. The 6-31G* basis set was used for C, H, O, N, S, and Cl atoms, and the def2-SVP basis set was used for Br and I atoms. Solvation effects were evaluated using the integral equation formalism polarizable continuum model (IEF-PCM) via the self-consistent reaction field (SCRF) approach.

For the iodo sulfoximination of alkynes, the mixed solvent was modeled using the intrinsic dielectric parameters of dimethoxyethane (DME): dynamic dielectric constant $\varepsilon = 7.2$ and static dielectric constant $\varepsilon\infty = 1.9$. For the bromo sulfoximination of alkynes, the mixed solvent was assigned a dynamic dielectric constant $\varepsilon = 42.8905$ and a static dielectric constant $\varepsilon\infty = 1.8800$, with both determined based on volume ratios. For other systems, the built-in tetrahydrofuran (THF) solvent parameters in Gaussian were applied.

Frequency analyses were performed at the same level to confirm the nature of stationary points (minima for intermediates; one imaginary frequency for transition states) and to provide thermal corrections at 298 K. Intrinsic reaction coordinate (IRC) analyses were performed at the same theoretical level as the geometry optimizations to verify reaction pathways.

Single-point energy calculations were performed on the optimized structures using the 6-311+G** basis set for C, H, O, N, S, and Cl atoms and the def2-TZVP basis set for Br and I atoms, with solvation effects evaluated using the SMD model under consistent solvent settings.

The expectation value of the total spin squared operator $\langle \hat{S}^2 \rangle$ and the g-tensor calculations were performed at the ωB97XD/def2-TZVPP level of theory. Electron adiabatic affinities were computed at the ωB97XD/aug-cc-pVDZ level. Both incorporated solvation effects in THF via the SCRF method with the SMD solvation model.

All molecular structure diagrams were generated using CYLview 20.[2] Electrostatic potential maps and orbital phase diagrams were produced with the Multiwfn 3.8 and VMD 2.0 programs.[3-5] The electrostatic potential involved in the

analyses was evaluated by Multiwfn based on the highly effective algorithm proposed in Ref.[6, 7]

6.2 Homolytic vs Heterolytic S–X Bond Cleavage: A DFT Study

The homolytic and heterolytic bond cleavage energies were determined by combining high-accuracy single-point energy calculations with thermodynamic corrections at 298 K. The optimized Cartesian coordinates for all structures are provided in the 6.6 section.

Bond type	Homolytic cleavage Energy (kcal/mol)	Heterolytic cleavage Energy (kcal/mol)
S-Cl	38.7	39.9
S-Br	32.4	52.8
S-I	24.7	44.5

Table S4: Summary of homolytic and heterolytic cleavage energies for S-X bond.

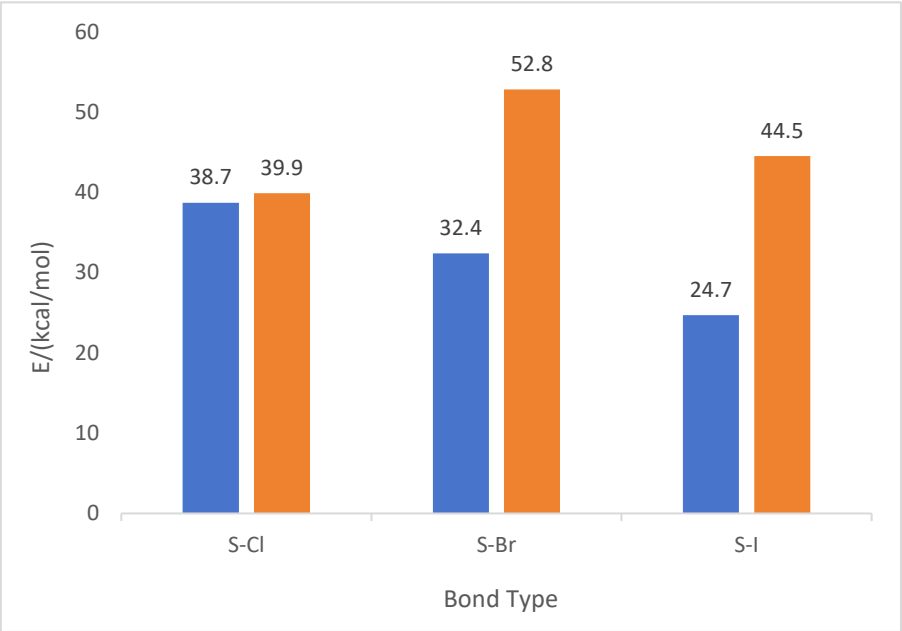


Figure S16: Comparison of homolytic (blue) and heterolytic (orange) cleavage energies for S-X bonds.

The high homolytic and heterolytic bond dissociation energies indicate that S–X

bond cleavage is thermodynamically unfavorable, suggesting that the generation of sulfur-centered radicals or cations via direct homolytic or heterolytic cleavage is energetically disfavored under the reaction conditions.

6.3 Theoretical Investigation of Frontier Molecular Orbital Energies

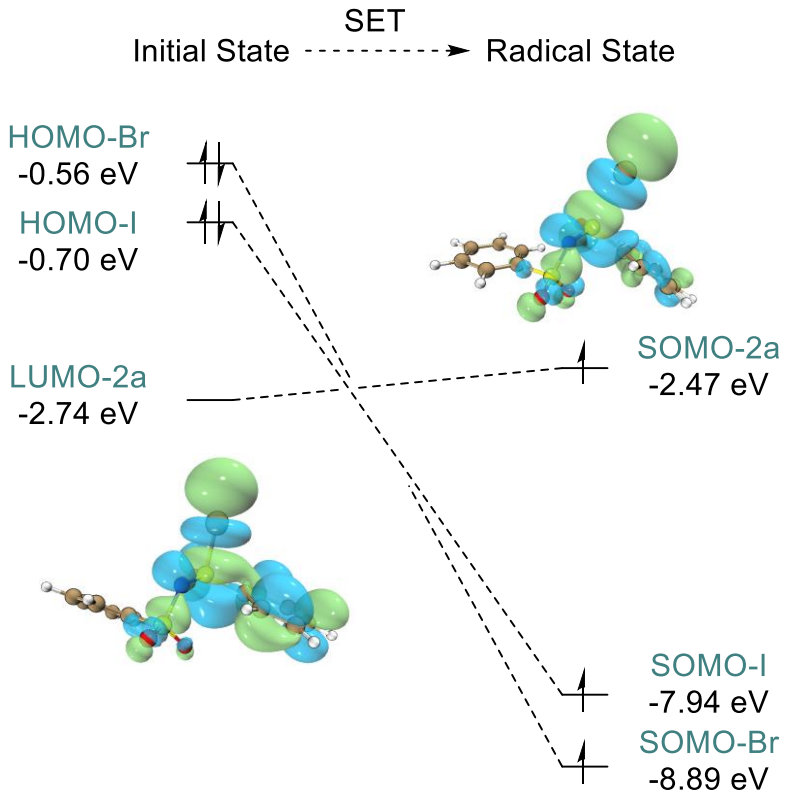


Figure S17: Orbital Energy Changes Before and After Electron Transfer.

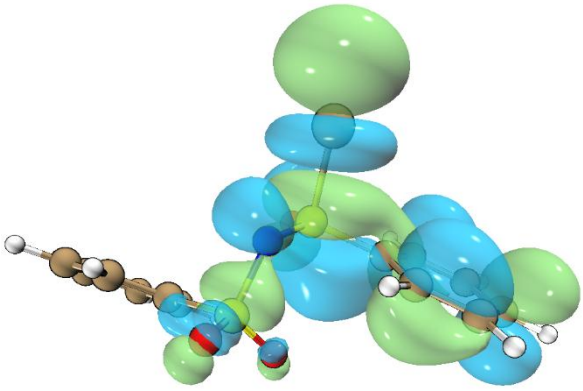


Figure S18: LUMO of molecule **2a** (−0.10082 a.u. / −2.74 eV).

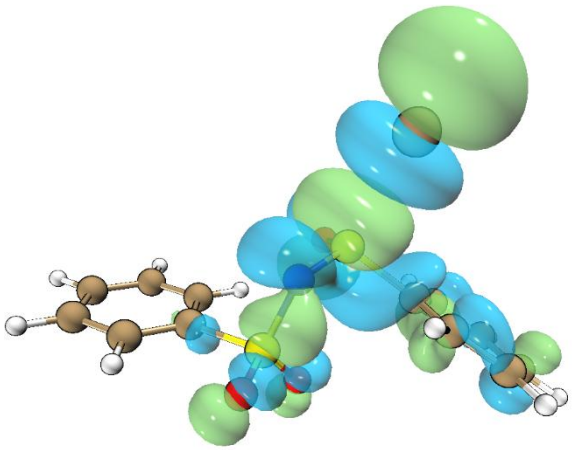


Figure S19: α-SOMO of molecule **2a**$^{\bullet-}$ (−0.09085 a.u. / −2.47 eV).

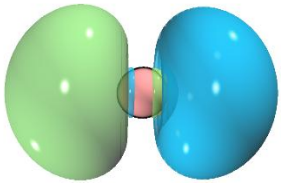


Figure S20: HOMO of iodide anion (**I**$^-$) (−0.02591 a.u. / −0.70 eV).

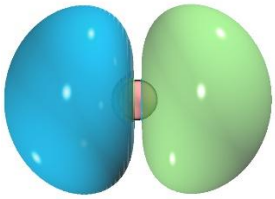


Figure S21: α-SOMO of Iodine radical (**I**$^\bullet$) (-0.29169 a.u. / -7.94 eV).

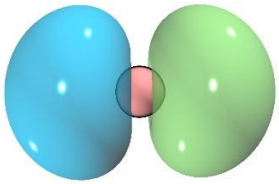


Figure S22: HOMO of Bromide anion (**Br**$^-$) (-0.02068 a.u. / -0.56 eV).

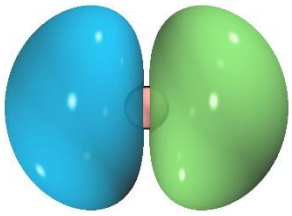


Figure S23: α-SOMO of Bromine radical (**Br•**) (-0.32685 a.u. / -8.89 eV).

The frontier molecular orbital energies of key species provide theoretical insights into the feasibility of the proposed SET process. As illustrated in Figure S17, the LUMO energy of molecule **2a** is considerably lower than the HOMO energies of both iodide (**I⁻**) and bromide (**Br⁻**) anions. This significant energy difference supports the redox potential disparity measured by cyclic voltammetry and suggests that electron transfer from the halide anions to the LUMO of **2a** is an energetically plausible pathway.

Furthermore, the α-SOMO energy of the resulting radical anion **2a•⁻** is significantly lower than the HOMOs of the halide anions, indicating that the SET process is thermodynamically favorable. The α-SOMOs of the halogen radicals (**I•**, **Br•**) generated concurrently are also positioned at much lower energies compared to their anionic counterparts (Figures S21, S23), completing the picture of the redox event.

The orbital energies were obtained from calculations at the B3LYP-D3/def2-QZVPP level of theory. Energy unit conversion was applied using a scale of 1 a.u. = 27.2114 eV. The optimized Cartesian coordinates for all structures are provided in the 6.6 section.

6.4 Formation of the 2a Radical Anion and Associated Calculations

To confirm that the formation of the **2a** radical anion is thermodynamically favorable, we computed its electron affinity (EA). The EA for the formation of **2a•⁻** was computed as the energy difference EA(radical anion) = E(radical anion) − E(neutral molecule) , where the energy of the electron is neglected for this qualitative discussion. This energy difference was derived from single-point energy calculations at the

ωB97XD-SMD/aug-cc-pVDZ level (THF solvent), combined with thermal corrections to enthalpy at 298 K obtained from frequency calculations at the B3LYP-D3-PCM/6-31G* level. The computed EA is −0.1640 Hartree (approximately −102.89 kcal/mol). This large negative value indicates that the formation of the **2a** radical anion is highly exothermic and thus thermodynamically favorable.

To further characterize the electronic structure of the optimized radical anion **2a**$^{\bullet-}$, we analyzed its spin properties. Calculations of the expectation value of $\langle \hat{S}^2 \rangle$ and the g-tensor were performed at the ωB97XD-SMD/def2-TZVPP level (THF solvent). The results show $\langle \hat{S}^2 \rangle$ = 0.7553 and g-tensor = 2.0023. These observed values are characteristic of a typical doublet state radical anion, thereby validating the electronic structure of the optimized intermediate and supporting the reliability of subsequent analyses such as orbital energy levels and spin density distributions. The Cartesian coordinates of all optimized structures and their corresponding single-point energies are provided in Section 6.6.

6.5 Analysis of Product Stereoselectivity

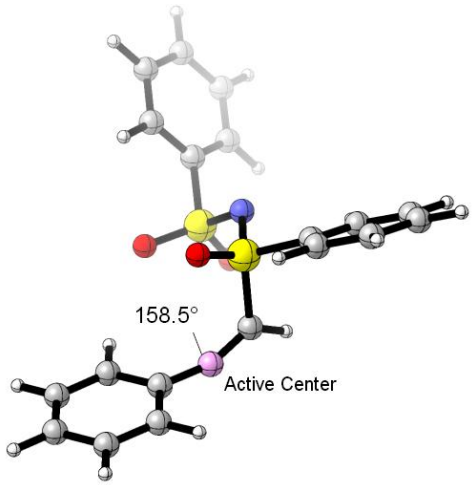


Figure S24: Schematic diagram of the structure of **Int5**.

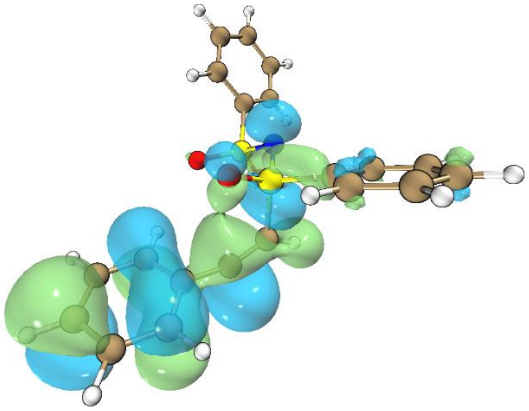


Figure S25: Orbital phase diagram of **Int5** (isovalue=0.02, positive=green/negative=blue).

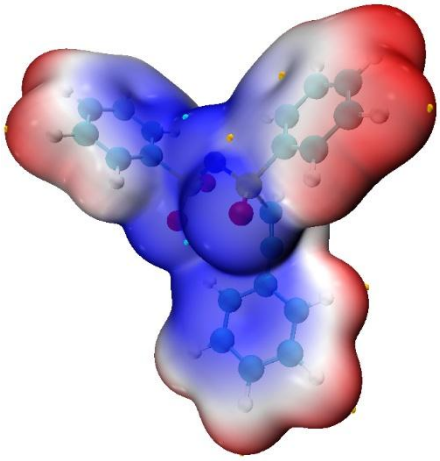


Figure S26: Front view MEP map of **Int5** (isovalue=0.002, positive=red/negative=blue).

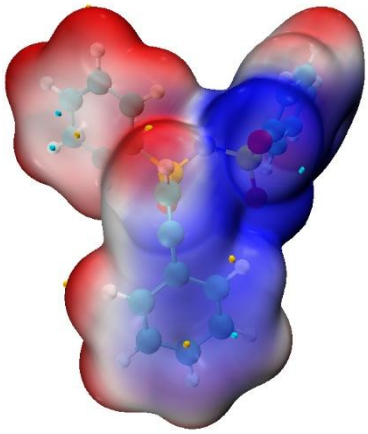


Figure S27: Back view MEP map of **Int5** (isovalue=0.002, positive=red/negative=blue).

As the radical coupling process does not involve well-defined transition states, it is challenging to quantitatively evaluate the steric differences for different attack directions using energy barriers. Therefore, we qualitatively analyzed the

stereoselectivity of the reaction from the following three aspects to demonstrate that the approach of the halogen radical from the back side of the molecule is more favorable than from the front side.

First, the reactive site was identified using Natural Population Analysis (NPA) (Figure S24). The results show a spin density of 0.527 on the pink carbon atom, indicating that the unpaired electron is primarily localized on this atom, thus confirming it as the reaction center for radical coupling.

Second, the feasibility of the attack direction was assessed based on spatial structure. For clarity, the view from the top-left to the bottom-right of the depicted structure is defined as the front side, and the opposite direction as the back side. Spatially, the bond angle of the alkyne moiety in the phenylethynyl unit bends from the initial 180° to 158.5°, resulting in compressed space on the front side and more available reaction space on the back side. To exclude potential bias from the initial conformation on structural optimization, we attempted to invert this bond angle to enhance frontal accessibility; however, the computational attempts failed to locate a stable intermediate configuration favoring front-side attack. Furthermore, structural features such as the phenyl ring and oxygen atom present on the front side pose additional steric hindrance to the approaching halogen radical compared to the back side.

Regarding electronic structure (Figure S25), frontier orbital phase analysis indicates that the frontal region, influenced by the negative phases of the adjacent phenyl ring and oxygen atom, is prone to forming a destructive interference area, which is unfavorable for overlap with the positive phase of the halogen radical in this region. Concurrently, the lack of a nodal plane between the phases in the region between the oxygen atom and the pink carbon atom may impair new bond formation capability in this area. In contrast, the negative phase distribution on the back side is more conducive to effective orbital overlap with the halogen radical.

Finally, analysis from the perspective of electrostatic interactions was conducted. In the Molecular Electrostatic Potential (MEP) map, blue and orange regions represent the extremes of negative and positive electrostatic potentials, respectively. The MEP

maps (Figures S26, S27) clearly reveal a significant region of negative electrostatic potential on the front side of the molecule, which would electrostatically repel the anion-stabilized halogen radical formed in the preceding SET process, thereby inhibiting its approach to the reaction center from the front.

The optimized Cartesian coordinates for all structures are provided in the 6.6 section.

6.6 Cartesian Coordinates for the Optimized Structures

The following are the optimized Cartesian coordinates of the structures involved in the reaction pathway.

Int1

C	3.79278	0.45962	1.85891
C	2.61249	-0.14665	1.43143
C	2.50692	-0.53118	0.09456
C	3.54167	-0.33065	-0.82009
C	4.71526	0.27641	-0.37672
C	4.83902	0.6714	0.95792
H	3.89497	0.7636	2.8958
H	1.78986	-0.31953	2.11471
H	3.42924	-0.65112	-1.84957
H	5.53272	0.43775	-1.07221
H	5.75561	1.14409	1.29736
C	-2.31458	0.13694	0.19169
C	-3.03863	0.605	1.28971
C	-2.76138	-0.89867	-0.63023
C	-4.25724	-0.00503	1.57607
H	-2.6519	1.40938	1.90427
C	-3.98259	-1.49421	-0.32408
H	-2.16667	-1.228	-1.47385
C	-4.72583	-1.04826	0.772

H	-4.83758	0.33152	2.42865
H	-4.35048	-2.30744	-0.94051
H	-5.67676	-1.51791	1.00263
O	1.28656	-2.13088	-1.62653
O	0.28053	-1.83771	0.68772
O	-0.19935	1.49214	1.05213
S	0.99193	-1.27903	-0.4728
S	-0.74672	0.89048	-0.16823
N	0.10883	0.01321	-1.13235
Cl	-1.28903	2.45325	-1.47987

Thermal correction to Gibbs Free Energy= 0.155499

Esolv(RB3LYP) = -2000.518105

Int2

C	4.02169	0.78216	1.51372
C	2.75833	0.34313	1.12377
C	2.63847	-0.40988	-0.04638
C	3.74792	-0.73133	-0.82523
C	5.00898	-0.28611	-0.42308
C	5.14565	0.4683	0.74288
H	4.12954	1.37261	2.41873
H	1.87522	0.59405	1.70232
H	3.61721	-1.3183	-1.72698
H	5.88153	-0.52868	-1.02234
H	6.12746	0.81518	1.0518
C	-2.26143	-0.11785	0.29655
C	-3.0357	-0.07748	1.45479
C	-2.5929	-0.93405	-0.78456
C	-4.15686	-0.9031	1.54062
H	-2.7522	0.5717	2.27535

C	-3.71577	-1.75402	-0.68471
H	-1.96923	-0.93845	-1.67113
C	-4.49665	-1.73871	0.47405
H	-4.7622	-0.89503	2.44209
H	-3.97848	-2.40642	-1.51189
H	-5.37142	-2.37827	0.54515
O	1.193	-1.74584	-1.80112
O	0.452	-1.73828	0.61774
O	-0.38487	1.28224	1.56107
S	1.01829	-1.00728	-0.53651
S	-0.85722	1.00757	0.15531
N	0.16812	0.37017	-0.90321
Cl	-2.05898	3.07555	-1.25868

Thermal correction to Gibbs Free Energy= 0.151005

Esolv(UB3LYP) = -2000.684867

Int3

C	3.29077	1.72583	1.60691
C	2.66958	0.48446	1.48719
C	2.30392	0.03883	0.21482
C	2.54192	0.7973	-0.93367
C	3.1653	2.03606	-0.79627
C	3.53625	2.49892	0.46876
H	3.58571	2.08755	2.58677
H	2.47806	-0.13493	2.35586
H	2.24358	0.423	-1.90499
H	3.36311	2.63801	-1.67742
H	4.02094	3.46535	0.5682
S	1.48178	-1.53389	0.05975
O	1.70033	-2.06036	-1.29595

O	1.81433	-2.35543	1.2261
N	-0.14839	-1.11677	0.27265
S	-0.99627	-0.60685	-1.00464
O	-0.46327	0.44208	-1.93417
C	-2.48435	0.0087	-0.20396
C	-3.08048	1.14256	-0.75372
C	-3.04045	-0.69307	0.8668
C	-4.26344	1.60886	-0.17996
H	-2.62072	1.65157	-1.59278
C	-4.22326	-0.21082	1.42352
H	-2.55211	-1.5755	1.26277
C	-4.8322	0.93483	0.90246
H	-4.7372	2.4993	-0.58049
H	-4.66818	-0.73121	2.2655
H	-5.75507	1.30096	1.34128

Thermal correction to Gibbs Free Energy= 0.153740

Esolv(UB3LYP) = -1540.277009

TS4

C	5.26539	-1.6255	0.47243
C	3.97775	-1.31396	0.90929
C	2.90606	-1.52667	0.04318
C	3.08593	-2.04538	-1.24013
C	4.37746	-2.35189	-1.66417
C	5.46391	-2.14091	-0.81031
H	6.11123	-1.46838	1.13449
H	3.79913	-0.92036	1.90338
H	2.22944	-2.20906	-1.88463
H	4.53572	-2.75778	-2.65843
H	6.46809	-2.38247	-1.14551

S	1.25338	-1.13006	0.58631
O	1.25428	-1.04611	2.06075
O	0.31177	-2.08631	-0.03453
N	1.13252	0.39438	-0.08324
S	-0.34722	1.01003	-0.23114
C	-0.00484	2.7611	-0.25289
C	-0.81871	3.57279	-1.04475
C	0.98215	3.28682	0.58432
C	-0.61377	4.95147	-1.01599
H	-1.57865	3.12671	-1.67593
C	1.17079	4.66735	0.60225
H	1.59564	2.6257	1.18509
C	0.37606	5.49666	-0.19459
H	-1.22626	5.59818	-1.63623
H	1.94105	5.09489	1.23631
H	0.52873	6.57133	-0.17413
O	-1.18336	0.66301	-1.41613
C	-5.68741	-1.44492	-0.29788
C	-4.79396	-0.63118	0.38527
C	-3.46668	-1.06998	0.59905
C	-3.05589	-2.33464	0.11256
C	-3.963	-3.13369	-0.57068
C	-5.27651	-2.69551	-0.77494
H	-6.70638	-1.10868	-0.46215
H	-5.09982	0.33974	0.76026
H	-2.02673	-2.64322	0.25905
H	-3.64783	-4.10017	-0.95159
H	-5.98011	-3.32678	-1.30915
C	-2.5436	-0.2668	1.28957
C	-1.61776	0.44473	1.69679

H	-1.01116	0.87618	2.46808

Thermal correction to Gibbs Free Energy= 0.253741

Esolv(UB3LYP) = -1848.793919

Int5

C	-1.8349	-4.07063	-1.61385
C	-1.10409	-3.65749	-0.50034
C	-1.28084	-2.35843	-0.02359
C	-2.1678	-1.46739	-0.62863
C	-2.89142	-1.89311	-1.74116
C	-2.72516	-3.19013	-2.23316
H	-1.71106	-5.0797	-1.99459
H	-0.41479	-4.32836	-0.00024
H	-2.28595	-0.46283	-0.24112
H	-3.58628	-1.21123	-2.22162
H	-3.2924	-3.51616	-3.09984
S	-0.32525	-1.81794	1.38844
O	-1.10077	-0.76397	2.06969
O	0.07223	-3.00728	2.15233
N	1.10104	-1.23383	0.75131
S	1.13897	0.21072	0.08511
O	0.31593	0.50726	-1.10751
C	2.87174	0.37793	-0.29672
C	3.19786	1.13652	-1.42126
C	3.8417	-0.18108	0.53711
C	4.54519	1.33188	-1.72218
H	2.41397	1.54836	-2.04674
C	5.18321	0.02801	0.22178
H	3.5492	-0.77702	1.39326
C	5.53283	0.78159	-0.90216

H	4.82122	1.91058	-2.59773
H	5.95464	-0.40281	0.85186
H	6.58025	0.93789	-1.14096
C	0.82858	1.52286	1.33086
H	1.56459	1.51981	2.13
C	-0.22911	2.2581	1.19613
C	-1.4283	2.66328	0.62716
C	-1.48449	3.7637	-0.27329
C	-2.63508	1.98759	0.97338
C	-2.69858	4.14886	-0.81937
H	-0.56756	4.28224	-0.53216
C	-3.83656	2.39235	0.41333
H	-2.58302	1.14784	1.65684
C	-3.87821	3.47024	-0.48231
H	-2.7332	4.98194	-1.51487
H	-4.75075	1.86586	0.67061
H	-4.82422	3.78006	-0.9152

Thermal correction to Gibbs Free Energy= 0.258108

Esolv(UB3LYP) = -1848.804067

TM

C	-5.84495	-0.79348	-0.11688
C	-4.82699	-0.28041	-0.92178
C	-3.51014	-0.66216	-0.66589
C	-3.18645	-1.54139	0.36962
C	-4.21301	-2.04386	1.16702
C	-5.53862	-1.67172	0.92485
H	-6.87513	-0.50802	-0.30583
H	-5.04303	0.39711	-1.73968
H	-2.15638	-1.81698	0.55807

H	-3.97685	-2.72775	1.97639
H	-6.33372	-2.06827	1.54906
S	-2.20472	0.00449	-1.68972
O	-1.18725	-1.05007	-1.86908
O	-2.82002	0.60394	-2.87932
N	-1.59972	1.28784	-0.8157
S	-0.46103	1.0457	0.25915
O	-0.70773	0.21928	1.45675
C	-0.0673	2.71655	0.74313
C	0.44231	2.8892	2.03102
C	-0.22432	3.7769	-0.15082
C	0.80032	4.1747	2.43503
H	0.54221	2.04001	2.69766
C	0.14065	5.05458	0.27137
H	-0.63593	3.60268	-1.13757
C	0.65151	5.25169	1.55743
H	1.19165	4.33366	3.43456
H	0.02148	5.89575	-0.4038
H	0.93236	6.25014	1.87786
C	1.05875	0.55174	-0.56022
H	1.31168	1.24657	-1.35266
C	1.81967	-0.47831	-0.19001
C	1.53799	-1.53808	0.79068
C	2.28153	-1.64038	1.97456
C	0.52834	-2.47173	0.51304
C	1.98907	-2.6469	2.89213
H	3.07495	-0.92713	2.17571
C	0.25152	-3.4843	1.43015
H	-0.03049	-2.38652	-0.41182
C	0.97497	-3.57051	2.62176

H	2.55516	-2.7135	3.81622
H	-0.53127	-4.20507	1.21285
H	0.7549	-4.35848	3.33585
I	3.70527	-0.67189	-1.22731

Thermal correction to Gibbs Free Energy= 0.258228

Esolv(RB3LYP) = -2146.670817

I^-

I	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.016848

Esolv(RB3LYP) = -297.979646

$I•--I^-$

I	0.	0.	1.66729
I	0.	0.	-1.66729

Thermal correction to Gibbs Free Energy= -0.027228

Esolv(UB3LYP) = -595.791542

Cl^-

Cl	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.015023

Esolv(RB3LYP) = -460.398265

1a

C	-1.51187	1.20944	0.00006
C	-0.11924	1.2143	0.00001
C	0.59269	-0.00001	-0.00025
C	-0.11923	-1.21427	0.00002
C	-1.51191	-1.20942	0.00005
C	-2.21167	-0.00001	-0.00003

H	-2.05235	2.15132	0.00015
H	0.42837	2.15126	0.00003
H	0.42827	-2.1513	0.00014
H	-2.05235	-2.15132	0.00008
H	-3.29759	0.00002	0.00001
C	2.02228	-0.00004	-0.00004
C	3.23312	0.00003	0.00007
H	4.30062	-0.00007	0.00029

Thermal correction to Gibbs Free Energy= 0.079151

Esolv(RB3LYP) = -308.517036

Int1′

C	3.76498	0.33317	1.91425
C	2.59555	-0.26129	1.44193
C	2.49184	-0.53727	0.07838
C	3.51741	-0.23898	-0.82039
C	4.67955	0.35554	-0.33244
C	4.8016	0.64158	1.03017
H	3.86591	0.55264	2.97226
H	1.78034	-0.50752	2.11153
H	3.40807	-0.47469	-1.8729
H	5.48949	0.59203	-1.01495
H	5.70942	1.10467	1.40428
C	-2.30274	0.13637	0.20341
C	-3.00451	0.57049	1.32999
C	-2.76998	-0.86811	-0.64606
C	-4.22037	-0.04451	1.61774
H	-2.60417	1.35273	1.964
C	-3.98813	-1.46851	-0.33792
H	-2.19404	-1.1699	-1.51257

C	-4.70856	-1.05759	0.78704
H	-4.78353	0.26516	2.4916
H	-4.37204	-2.25741	-0.9757
H	-5.65739	-1.53069	1.01872
O	1.30716	-2.06589	-1.73154
O	0.27098	-1.89042	0.5794
O	-0.16775	1.45854	1.06881
S	0.99087	-1.26845	-0.54376
S	-0.73904	0.89446	-0.15856
N	0.10359	0.04004	-1.15749
Cl	-1.2835	2.49373	-1.42216

Thermal correction to Gibbs Free Energy= 0.155657

Esolv(RB3LYP) = -2000.521889

Int2′

C	4.03866	0.78681	1.4937
C	2.77001	0.36032	1.10693
C	2.64291	-0.4089	-0.05227
C	3.74953	-0.75971	-0.82306
C	5.01573	-0.32676	-0.42351
C	5.15995	0.44364	0.73113
H	4.1532	1.38875	2.39004
H	1.89036	0.63127	1.68183
H	3.61486	-1.35855	-1.71628
H	5.88618	-0.5921	-1.01567
H	6.14577	0.78009	1.0379
C	-2.27184	-0.12493	0.30017
C	-3.04224	-0.11005	1.46235
C	-2.61089	-0.91037	-0.80206
C	-4.1658	-0.93406	1.53076

H	-2.75527	0.51731	2.29849
C	-3.73647	-1.72857	-0.71861
H	-1.99297	-0.89447	-1.69257
C	-4.51261	-1.74027	0.44373
H	-4.76761	-0.94691	2.4342
H	-4.00566	-2.35768	-1.56133
H	-5.38957	-2.37769	0.50146
O	1.17651	-1.72568	-1.80616
O	0.4525	-1.73393	0.61695
O	-0.39969	1.26118	1.59101
S	1.01871	-0.99649	-0.53371
S	-0.86695	0.99878	0.18167
N	0.16671	0.38761	-0.88198
Cl	-2.02533	3.10379	-1.25068

Thermal correction to Gibbs Free Energy= 0.150018

Esolv(UB3LYP) = -2000.697710

Int3′

C	3.25126	1.77444	1.5861
C	2.64279	0.5252	1.48431
C	2.29682	0.05044	0.21664
C	2.54147	0.7881	-0.94418
C	3.15229	2.035	-0.82453
C	3.50362	2.52667	0.43536
H	3.53055	2.15865	2.56185
H	2.4461	-0.0768	2.36399
H	2.2584	0.39227	-1.9115
H	3.35547	2.62086	-1.71514
H	3.978	3.49938	0.52099
S	1.488	-1.53034	0.08428

O	1.71586	-2.07854	-1.26226
O	1.82937	-2.33476	1.26144
N	-0.14344	-1.12764	0.2918
S	-0.99776	-0.64815	-0.99449
O	-0.45859	0.37082	-1.95332
C	-2.47923	-0.00381	-0.20613
C	-3.06374	1.12621	-0.77622
C	-3.04172	-0.68176	0.87676
C	-4.24089	1.61507	-0.20934
H	-2.60066	1.6155	-1.62501
C	-4.21859	-0.17699	1.42604
H	-2.5645	-1.56379	1.28688
C	-4.81548	0.96616	0.88547
H	-4.70544	2.50323	-0.62514
H	-4.66866	-0.67814	2.2768
H	-5.73391	1.34973	1.31841

Thermal correction to Gibbs Free Energy= 0.153764

Esolv(UB3LYP) = -1540.280560

TS4′

C	-5.27259	-1.55231	-0.44824
C	-3.98254	-1.24631	-0.88122
C	-2.90702	-1.53398	-0.04081
C	-3.08646	-2.12177	1.21248
C	-4.38096	-2.42295	1.63249
C	-5.47048	-2.13714	0.80489
H	-6.1209	-1.33701	-1.09024
H	-3.8069	-0.80012	-1.85343
H	-2.22846	-2.3427	1.83751
H	-4.53874	-2.88267	2.603

H	-6.47664	-2.37434	1.13682
S	-1.25277	-1.13855	-0.57852
O	-1.24879	-1.05482	-2.05379
O	-0.31253	-2.10074	0.03818
N	-1.12998	0.38149	0.09533
S	0.35028	1.00698	0.22126
C	-0.00053	2.75562	0.25218
C	0.81089	3.56829	1.04591
C	-0.99266	3.27908	-0.58078
C	0.59637	4.94568	1.02518
H	1.57671	3.12523	1.67197
C	-1.19065	4.65833	-0.59047
H	-1.60163	2.61848	-1.18662
C	-0.39953	5.4885	0.20935
H	1.20656	5.59308	1.64678
H	-1.96446	5.08415	-1.22116
H	-0.55923	6.56213	0.19484
O	1.19534	0.65856	1.40116
C	5.68569	-1.39524	0.32606
C	4.78519	-0.59361	-0.36232
C	3.47241	-1.06112	-0.60559
C	3.08438	-2.34232	-0.14334
C	3.99789	-3.12901	0.54546
C	5.29681	-2.66185	0.77912
H	6.69312	-1.03713	0.51291
H	5.07423	0.38927	-0.71876
H	2.06636	-2.67509	-0.31307
H	3.70027	-4.10835	0.90694
H	6.00593	-3.28341	1.31716
C	2.54364	-0.2685	-1.30003

C	1.61642	0.43759	-1.71319
H	1.01363	0.8772	-2.48292

Thermal correction to Gibbs Free Energy= 0.252879

Esolv(UB3LYP) = -1848.799403

Int5′

C	5.4054	-1.19452	0.39592
C	4.10603	-1.01086	0.86936
C	3.03689	-1.32072	0.02947
C	3.23064	-1.81125	-1.26286
C	4.53398	-1.99064	-1.72279
C	5.61779	-1.68139	-0.89581
H	6.24949	-0.96019	1.0368
H	3.91922	-0.64169	1.87124
H	2.37777	-2.05215	-1.88769
H	4.70345	-2.37388	-2.72403
H	6.63099	-1.82355	-1.25911
S	1.36999	-1.08656	0.62002
O	1.40185	-1.04414	2.09499
O	0.49683	-2.1038	-0.00533
N	1.08452	0.43833	0.00565
S	-0.4263	0.89476	-0.20118
C	-0.28013	2.66889	-0.20228
C	-1.16273	3.38207	-1.01457
C	0.64428	3.29872	0.63326
C	-1.10506	4.77488	-0.99377
H	-1.86438	2.85534	-1.65101
C	0.68424	4.69182	0.6435
H	1.32096	2.71075	1.24174
C	-0.18674	5.42593	-0.16657

H	-1.77566	5.34914	-1.6246
H	1.39891	5.20262	1.28055
H	-0.14788	6.51066	-0.15404
O	-1.17908	0.45171	-1.39355
C	-5.50674	-1.6284	-0.38579
C	-4.62037	-0.74524	0.20936
C	-3.30609	-1.17801	0.5465
C	-2.92678	-2.52542	0.27449
C	-3.83337	-3.38898	-0.31881
C	-5.1238	-2.95131	-0.65004
H	-6.50492	-1.29093	-0.64748
H	-4.91036	0.2786	0.4197
H	-1.9171	-2.8414	0.51163
H	-3.53673	-4.41107	-0.53404
H	-5.82647	-3.63631	-1.11389
C	-2.40934	-0.32367	1.16799
C	-1.39809	0.47517	1.29716
H	-0.96482	0.892	2.20207

Thermal correction to Gibbs Free Energy= 0.255722

Esolv(UB3LYP) = -1848.806733

TM′

C	5.87923	-0.72469	1.00181
C	4.50195	-0.70528	1.22617
C	3.64955	-1.07469	0.18625
C	4.13265	-1.46473	-1.0644
C	5.51039	-1.47894	-1.27448
C	6.38045	-1.10862	-0.24418
H	6.55815	-0.44234	1.80014
H	4.09143	-0.41677	2.18692

H	3.4436	-1.75496	-1.8498
H	5.90464	-1.78106	-2.23952
H	7.45277	-1.12241	-0.41335
S	1.8889	-1.0543	0.45899
O	1.63704	-1.01633	1.91239
O	1.27661	-2.16685	-0.29938
N	1.53662	0.42225	-0.22771
S	0.03497	0.75172	-0.61904
C	0.02866	2.53467	-0.59399
C	-0.83964	3.17937	-1.47641
C	0.83143	3.23021	0.31192
C	-0.89596	4.57236	-1.45074
H	-1.44308	2.60279	-2.16786
C	0.75936	4.62234	0.32424
H	1.50174	2.69394	0.97293
C	-0.10103	5.28945	-0.55273
H	-1.55829	5.0951	-2.13288
H	1.37825	5.18468	1.01569
H	-0.15013	6.37369	-0.53735
O	-0.52335	0.28107	-1.9003
C	-4.6177	-1.63344	-1.85537
C	-4.07077	-0.89939	-0.80683
C	-2.74408	-1.12766	-0.40742
C	-1.98288	-2.12024	-1.04401
C	-2.54497	-2.86283	-2.08133
C	-3.85674	-2.61883	-2.49251
H	-5.63863	-1.44228	-2.17109
H	-4.66239	-0.14278	-0.30167
H	-0.96409	-2.3061	-0.72319
H	-1.95522	-3.63387	-2.56774

H	-4.28937	-3.19835	-3.3026
C	-2.15776	-0.36156	0.70188
C	-1.02022	0.34226	0.76063
H	-0.65251	0.79422	1.67385
Br	-3.16369	-0.42685	2.34856

Thermal correction to Gibbs Free Energy= 0.257455

Esolv(RB3LYP) = -4423.054697

Br^-

Br	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.016176

Esolv(RB3LYP) = -2574.353241

$Br^{\bullet}$--Br^-

Br	0.	0.	1.47446
Br	0.	0.	-1.47446

Thermal correction to Gibbs Free Energy= -0.025324

Esolv(UB3LYP) = -5148.543687

$Cl^{-\prime}$

Cl	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.015023

Esolv(RB3LYP) = -460.410580

1a′

C	1.51187	1.20944	-0.00006
C	0.11924	1.2143	-0.00001
C	-0.59269	-0.00001	0.00025
C	0.11923	-1.21427	-0.00002
C	1.51191	-1.20942	-0.00005

C	2.21167	-0.00001	0.00003
H	2.05235	2.15132	-0.00015
H	-0.42837	2.15126	-0.00003
H	-0.42827	-2.1513	-0.00014
H	2.05235	-2.15132	-0.00008
H	3.29759	0.00002	-0.00001
C	-2.02228	-0.00004	0.00004
C	-3.23312	0.00003	-0.00007
H	-4.30062	-0.00007	-0.00029

Thermal correction to Gibbs Free Energy= 0.079168

Esolv(RB3LYP) = -308.518748

The following are the optimized Cartesian coordinates related to structures in supporting information 6.2.

S-Cl

C	3.76685	1.12116	1.41304
C	3.04298	0.02936	0.93361
C	2.43978	0.12819	-0.31897
C	2.53931	1.27966	-1.10398
C	3.26154	2.36252	-0.60933
C	3.87269	2.28283	0.64613
H	4.24576	1.06237	2.38513
H	2.94251	-0.88024	1.51333
H	2.06518	1.32232	-2.07841
H	3.3509	3.26621	-1.20364
H	4.43468	3.13052	1.02594
S	1.49863	-1.25087	-0.93694
O	1.64321	-2.38078	-0.01172
O	1.7749	-1.42464	-2.36369
N	-0.08239	-0.62592	-0.89468

S	-1.07674	-0.9451	0.25017
C	-2.45593	0.1217	-0.06429
C	-3.72222	-0.3651	0.25808
C	-2.23581	1.39747	-0.58675
C	-4.81743	0.46648	0.0284
H	-3.84342	-1.36153	0.66584
C	-3.34498	2.20938	-0.80532
H	-1.23227	1.73258	-0.81941
C	-4.62852	1.74551	-0.49889
H	-5.81586	0.11179	0.261
H	-3.20695	3.20385	-1.2162
H	-5.48647	2.38711	-0.67275
O	-1.50951	-2.30056	0.59612
Cl	-0.30624	-0.13442	2.11024

Thermal correction to Gibbs Free Energy= 0.155832

Esolv(RB3LYP) = -2000.517122

S-Br

C	-3.76794	0.98776	-1.38284
C	-3.06953	-0.03148	-0.73405
C	-2.46093	0.25058	0.48781
C	-2.52977	1.51541	1.07849
C	-3.22578	2.52344	0.41611
C	-3.8426	2.2595	-0.81168
H	-4.25044	0.78658	-2.33392
H	-2.99201	-1.02392	-1.16089
H	-2.05108	1.70181	2.03362
H	-3.29029	3.5127	0.85779
H	-4.38395	3.04964	-1.32285
S	-1.55187	-1.03384	1.31974

O	-1.68553	-2.28234	0.55874
O	-1.86886	-1.00273	2.74862
N	0.02872	-0.42825	1.22718
S	1.06806	-0.94898	0.19512
C	2.404	0.21266	0.32138
C	3.69727	-0.28366	0.16273
C	2.12289	1.56346	0.5355
C	4.75663	0.6203	0.24038
H	3.86563	-1.34049	-0.00658
C	3.19685	2.44657	0.60702
H	1.10053	1.9034	0.64999
C	4.50651	1.97661	0.45975
H	5.77453	0.2617	0.13025
H	3.01116	3.50149	0.77912
H	5.33632	2.67392	0.51599
O	1.55833	-2.33245	0.18273
Br	0.30464	-0.5603	-1.97642

Thermal correction to Gibbs Free Energy= 0.154221

Esolv(RB3LYP) = -4114.482138

S-I

C	-3.96619	-1.06877	-0.68629
C	-3.26096	-0.23312	0.18009
C	-2.41849	0.73524	-0.36376
C	-2.26328	0.89328	-1.74408
C	-2.96764	0.04698	-2.59609
C	-3.81601	-0.93221	-2.06764
H	-4.62581	-1.82913	-0.28068
H	-3.34719	-0.33177	1.25548
H	-1.60044	1.65572	-2.13854

H	-2.85595	0.14996	-3.67069
H	-4.36048	-1.5907	-2.73742
S	-1.50484	1.79734	0.73414
O	-1.70018	1.3256	2.11131
O	-1.76567	3.19807	0.39525
N	0.08234	1.5408	0.21023
S	1.01973	0.47808	0.8709
C	2.43838	0.47737	-0.20203
C	3.68697	0.3158	0.39573
C	2.25936	0.59338	-1.58127
C	4.8087	0.29085	-0.43336
H	3.77511	0.22134	1.47145
C	3.39335	0.56311	-2.38864
H	1.26784	0.71036	-2.00158
C	4.66141	0.41228	-1.81661
H	5.79459	0.17647	0.0047
H	3.28703	0.65838	-3.46412
H	5.53881	0.38783	-2.455
O	1.42629	0.54589	2.28373
I	0.0999	-1.89665	0.5352

Thermal correction to Gibbs Free Energy= 0.153437

Esolv(RB3LYP) = -1838.104963

S-cation

C	-3.61095	1.2199	-1.7607
C	-2.86774	0.13624	-1.30147
C	-2.52154	0.10571	0.05323
C	-2.88386	1.11174	0.95506
C	-3.62533	2.18554	0.47161
C	-3.98483	2.23827	-0.87871

H	-3.90147	1.26681	-2.80457
H	-2.57274	-0.66816	-1.96511
H	-2.60174	1.04624	1.99927
H	-3.92584	2.97778	1.14867
H	-4.56427	3.07906	-1.24609
S	-1.58214	-1.25881	0.64914
O	-1.59495	-2.36829	-0.29221
O	-1.74313	-1.44478	2.08106
N	0.05583	-0.46884	0.56375
S	1.23716	-0.95341	-0.23953
C	2.63119	0.07051	-0.07232
C	3.77728	-0.30012	-0.79674
C	2.55996	1.19802	0.76405
C	4.89631	0.51221	-0.67269
H	3.78332	-1.18071	-1.42718
C	3.69847	1.98389	0.86284
H	1.65276	1.43603	1.30479
C	4.85642	1.64372	0.15006
H	5.79925	0.26169	-1.21756
H	3.68554	2.863	1.49696
H	5.73838	2.26911	0.23837
O	1.39851	-2.10034	-1.12297

Thermal correction to Gibbs Free Energy= 0.155801

Esolv(RB3LYP) = -1540.040995

Cl-anion

Cl	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.015023

Esolv(RB3LYP) = -460.397497

Br-anion

Br 0. 0. 0.

Thermal correction to Gibbs Free Energy= -0.016176

Esolv(RB3LYP) = -2574.342367

I-anion

I 0. 0. 0.

Thermal correction to Gibbs Free Energy= -0.016848

Esolv(RB3LYP) = -297.978497

S-radical

C	-3.53902	1.33936	-1.62664
C	-2.79061	0.22279	-1.25545
C	-2.42283	0.07886	0.08267
C	-2.78117	1.01545	1.05423
C	-3.52791	2.1266	0.66756
C	-3.90391	2.28846	-0.66893
H	-3.83942	1.46487	-2.66206
H	-2.50314	-0.52874	-1.98184
H	-2.48793	0.86881	2.0877
H	-3.81929	2.86322	1.40953
H	-4.48625	3.15602	-0.96381
S	-1.43511	-1.32685	0.56044
O	-1.53652	-2.34896	-0.4925
O	-1.74442	-1.67293	1.95138
N	0.11519	-0.64911	0.61276
S	1.16267	-0.9898	-0.55845
C	2.50388	0.1315	-0.16892
C	3.80869	-0.32103	-0.36473
C	2.21095	1.43828	0.22763
C	4.85757	0.5642	-0.11908

H	3.99223	-1.3403	-0.6838
C	3.27358	2.30673	0.46657
H	1.18352	1.75506	0.3634
C	4.59107	1.87172	0.29361
H	5.88172	0.22961	-0.24851
H	3.07176	3.32323	0.78845
H	5.41272	2.55628	0.47947
O	1.71408	-2.36753	-0.76398

Thermal correction to Gibbs Free Energy= 0.153132

Esolv(UB3LYP) = -1540.267731

Cl-radical

Cl	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.015677

Esolv(UB3LYP) = -460.169377

Br-radical

Br	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.01683

Esolv(UB3LYP) = -2574.144854

I-radical

I	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.017503

Esolv(UB3LYP) = -297.780098

The following are the optimized Cartesian coordinates related to structures in supporting information 6.3.

2a

C	3.84389100	0.43598900	1.80331300

C	2.63685600	-0.11006000	1.39114500
C	2.50357700	-0.52549800	0.07232600
C	3.54738600	-0.40870000	-0.83705600
C	4.74959000	0.13857000	-0.41225000
C	4.89669300	0.56141000	0.90409200
H	3.96205300	0.76170300	2.82656700
H	1.80928500	-0.21571300	2.07457300
H	3.41441100	-0.75137000	-1.85153700
H	5.57130100	0.23152800	-1.10749800
H	5.83505200	0.98667800	1.23062900
C	-2.28990200	0.12590700	0.19306000
C	-3.02404000	0.49897100	1.31161500
C	-2.70580300	-0.88078600	-0.66823000
C	-4.21331300	-0.16511900	1.57179500
H	-2.66031300	1.27704100	1.96408000
C	-3.89686800	-1.53416600	-0.39258000
H	-2.10182200	-1.15271100	-1.51969000
C	-4.64772600	-1.17632300	0.72176700
H	-4.79604300	0.10256900	2.44084900
H	-4.23295700	-2.32755800	-1.04348700
H	-5.57341400	-1.69236600	0.93231400
O	1.19492900	-2.01658700	-1.62327800
O	0.26925300	-1.74502800	0.66862800
O	-0.29353400	1.57100300	1.07691400
S	0.95985900	-1.20177200	-0.47094300
S	-0.75930700	0.95006900	-0.12813700
N	0.14592300	0.13487400	-1.03869500
Cl	-1.36618100	2.44865000	-1.41310300

Thermal correction to Gibbs Free Energy= 0.156459

E(RB3LYP) = -2000.769296

HOMO, energy: -0.272884 a.u. -7.425558 eV

LUMO, energy: -0.100816 a.u. -2.743331 eV

2a$^{\bullet-}$

C	3.91851500	0.45252600	1.69474000
C	2.67907500	0.06555400	1.20667600
C	2.57894300	-0.40511600	-0.09781800
C	3.69898100	-0.48896600	-0.91230700
C	4.93807800	-0.10054000	-0.41486800
C	5.04949300	0.36931800	0.88749700
H	4.00118400	0.82550200	2.70642800
H	1.79018600	0.14798700	1.81385900
H	3.58611900	-0.85840800	-1.91994600
H	5.81396200	-0.16415100	-1.04631400
H	6.01317800	0.67407700	1.27300600
C	-2.18630100	-0.12195200	0.30374700
C	-2.74605200	-0.36407700	1.54779700
C	-2.70832800	-0.69233400	-0.84867100
C	-3.83922100	-1.21679900	1.64201600
H	-2.31183100	0.09837600	2.42076600
C	-3.80057200	-1.53993900	-0.74488000
H	-2.25101500	-0.48126700	-1.80307700
C	-4.36705200	-1.80396500	0.49872800
H	-4.27529200	-1.42474800	2.60975900
H	-4.20806600	-1.99896300	-1.63502000
H	-5.21769700	-2.46765100	0.57492400
O	1.23410500	-1.48097900	-2.03875300
O	0.40647800	-1.79033700	0.27614200
O	-0.30235400	1.22645600	1.53785200
S	0.98411900	-0.92610800	-0.73015400

S	-0.81582100	1.03725200	0.16810600
N	0.16647000	0.45239800	-0.92477200
Cl	-2.16458600	3.06710600	-0.95918200

Thermal correction to Gibbs Free Energy= 0.150039

E(UB3LYP) = -2000.860737

alpha-HOMO, energy: -0.090850 a.u. -2.472149 eV

beta-HOMO, energy: -0.132853 a.u. -3.615122 eV

alpha-LUMO, energy: 0.061778 a.u. 1.681065 eV

beta-LUMO, energy: -0.006535 a.u. -0.177816 eV

I^-

I	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.016848

E(RB3LYP) = -297.899037

HOMO, energy: -0.025908 a.u. -0.704986 eV

LUMO, energy: 0.252774 a.u. 6.878319 eV

$I^•$

I	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.017503

E(UB3LYP) = -297.779440

alpha-HOMO, energy: -0.291686 a.u. -7.937183 eV

beta-HOMO, energy: -0.281020 a.u. -7.646946 eV

alpha-LUMO, energy: 0.053295 a.u. 1.450230 eV

beta-LUMO, energy: -0.216336 a.u. -5.886814 eV

Br^-

Br	0.	0.	0.

Thermal correction to Gibbs Free Energy= -0.016176

E(RB3LYP) = -2574.321754

HOMO, energy: -0.020680 a.u. -0.562722 eV

LUMO, energy: 0.381675 a.u. 10.385896 eV

Br•

Br 0. 0. 0.

Thermal correction to Gibbs Free Energy= -0.016830

E(UB3LYP) = -2574.194929

alpha-HOMO, energy: -0.326855 a.u. -8.894163 eV

beta-HOMO, energy: -0.313874 a.u. -8.540955 eV

alpha-LUMO, energy: 0.153648 a.u. 4.180984 eV

beta-LUMO, energy: -0.236009 a.u. -6.422137 eV

The following are the optimized Cartesian coordinates related to structures in supporting information 6.4.

E (radical anion)

C	3.9036	-0.11253	1.82606
C	2.68806	-0.46738	1.24295
C	2.57295	-0.44305	-0.14756
C	3.64443	-0.07519	-0.96073
C	4.85647	0.27771	-0.36615
C	4.98603	0.25957	1.02414
H	4.00572	-0.12725	2.90741
H	1.83537	-0.74526	1.851
H	3.52792	-0.07436	-2.03875
H	5.69851	0.56423	-0.98969
H	5.93102	0.53511	1.48392
C	-2.20714	-0.14826	0.31183
C	-2.78777	-0.48234	1.53334
C	-2.74557	-0.57536	-0.90196
C	-3.92088	-1.29697	1.53745

H	-2.34822	-0.12635	2.45836
C	-3.87864	-1.38658	-0.88313
H	-2.27612	-0.29036	-1.83697
C	-4.46543	-1.74781	0.3332
H	-4.37546	-1.57968	2.48268
H	-4.30229	-1.73774	-1.81953
H	-5.34892	-2.37981	0.34119
O	1.28728	-1.22537	-2.3102
O	0.37801	-1.90202	-0.04207
O	-0.19413	0.92121	1.68514
S	1.00409	-0.88005	-0.9061
S	-0.7813	0.96261	0.29824
N	0.14305	0.54144	-0.95103
Cl	-2.03291	3.27581	-0.61272

Thermal correction to Gibbs Free Energy= 0.150725

Esolv(UωB97XD) = -2000.159279

E (neutral molecule)

C	3.82657	0.20529	1.91096
C	2.66221	-0.40063	1.43951
C	2.49691	-0.54473	0.06256
C	3.45489	-0.10249	-0.85171
C	4.61117	0.50281	-0.36452
C	4.79558	0.65639	1.01258
H	3.97487	0.32343	2.97996
H	1.89837	-0.75529	2.12135
H	3.29937	-0.2326	-1.91717
H	5.36831	0.85234	-1.05964
H	5.69918	1.12909	1.386
C	-2.31515	0.13932	0.2067

C	-3.02836	0.5746	1.3256
C	-2.78666	-0.84507	-0.66348
C	-4.26009	-0.02042	1.58494
H	-2.62822	1.34258	1.97753
C	-4.0213	-1.4253	-0.38289
H	-2.20409	-1.14811	-1.5256
C	-4.75287	-1.01437	0.73432
H	-4.83196	0.29009	2.45338
H	-4.40872	-2.19945	-1.03717
H	-5.71445	-1.47256	0.94465
O	1.31333	-2.05676	-1.76588
O	0.29616	-1.93804	0.55893
O	-0.15788	1.3955	1.12341
S	1.00145	-1.29155	-0.55787
S	-0.72963	0.86883	-0.11979
N	0.09623	0.02745	-1.1368
Cl	-1.24621	2.52257	-1.34953

Thermal correction to Gibbs Free Energy= 0.154484

Esolv(RωB97XD) = -1999.999072

E (g-tensor)

C	4.02169	0.78216	1.51372
C	2.75833	0.34313	1.12377
C	2.63847	-0.40988	-0.04638
C	3.74792	-0.73133	-0.82523
C	5.00898	-0.28611	-0.42308
C	5.14565	0.4683	0.74288
H	4.12954	1.37261	2.41873
H	1.87522	0.59405	1.70232
H	3.61721	-1.3183	-1.72698

H	5.88153	-0.52868	-1.02234
H	6.12746	0.81518	1.0518
C	-2.26143	-0.11785	0.29655
C	-3.0357	-0.07748	1.45479
C	-2.5929	-0.93405	-0.78456
C	-4.15686	-0.9031	1.54062
H	-2.7522	0.5717	2.27535
C	-3.71577	-1.75402	-0.68471
H	-1.96923	-0.93845	-1.67113
C	-4.49665	-1.73871	0.47405
H	-4.7622	-0.89503	2.44209
H	-3.97848	-2.40642	-1.51189
H	-5.37142	-2.37827	0.54515
O	1.193	-1.74584	-1.80112
O	0.452	-1.73828	0.61774
O	-0.38487	1.28224	1.56107
S	1.01829	-1.00728	-0.53651
S	-0.85722	1.00757	0.15531
N	0.16812	0.37017	-0.90321
Cl	-2.05898	3.07555	-1.25868

Thermal correction to Gibbs Free Energy= 0.151005

Esolv(UωB97XD) = -2000.450107

The following are the optimized Cartesian coordinates related to structures in supporting information 6.5.

Int5 (THF solvent)

C	5.39991400	-1.39021200	0.40953200
C	4.10956700	-1.18992200	0.90230100
C	3.03339300	-1.29364200	0.02340600
C	3.20974800	-1.59523700	-1.32830400

C	4.50289900	-1.79143600	-1.80740400
C	5.59507800	-1.68838000	-0.94014300
H	6.24979400	-1.31455800	1.08064800
H	3.93231500	-0.96166600	1.94689100
H	2.35104000	-1.67577000	-1.98592300
H	4.65892900	-2.02684900	-2.85551200
H	6.60078300	-1.84332400	-1.31907500
S	1.37628900	-1.05826200	0.64253600
O	1.43411100	-1.00870300	2.11559100
O	0.49302300	-2.07509700	0.03287800
N	1.08078800	0.46554200	0.02738900
S	-0.43001600	0.90580800	-0.19906200
C	-0.30015000	2.68239600	-0.18854700
C	-1.18133700	3.39205800	-1.00503400
C	0.61075500	3.31658800	0.65800700
C	-1.13755800	4.78523900	-0.97602200
H	-1.87015800	2.86103700	-1.65196900
C	0.63713600	4.70996900	0.67682800
H	1.28893800	2.73043400	1.26665300
C	-0.23350200	5.44045400	-0.13666500
H	-1.80720600	5.35674600	-1.61054700
H	1.34178200	5.22402900	1.32254700
H	-0.20493200	6.52552900	-0.11798200
O	-1.16949300	0.46581500	-1.39959700
C	-5.47843900	-1.71830500	-0.39324200
C	-4.61340900	-0.81401500	0.20121100
C	-3.28652300	-1.21215900	0.53039200
C	-2.87140000	-2.54737200	0.25085100
C	-3.75761200	-3.43254600	-0.34122900
C	-5.06099800	-3.02920800	-0.66427100

H	-6.48671700	-1.40700200	-0.64902000
H	-4.93019800	0.20075600	0.41725400
H	-1.85111600	-2.83417000	0.47897300
H	-3.43370200	-4.44493900	-0.56310200
H	-5.74705000	-3.73123900	-1.12779900
C	-2.41007700	-0.33851600	1.15380400
C	-1.41255100	0.47620500	1.28962600
H	-0.98913000	0.89358500	2.19911000

Thermal correction to Gibbs Free Energy= 0.255521

Esolv(UB3LYP) = -1848.789284

[1] Gaussian 16. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

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7. Characterization data of products

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3a)

petroleum ether/ ethyl acetate = 5:1, white solid, 96% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.67 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.14 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 140.1, 139.5, 138.7, 136.8, 132.2, 130.1, 129.5, 129.3, 128.0, 127.5, 126.5, 125.7, 116.8, 35.1, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}BrINO_3S_2$ $[M+H]^+$: 643.9421, Found: 643.9411.

IR (neat, cm^{-1}): υ 3043, 1980, 1442, 1143, 1029, 1019, 1011, 924, 867, 807, 772, 732, 718, 661.

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(p-tolyl)vinyl)(oxo)- λ^6-sulfaneylidene)-4-(*tert*-butyl)benzeneesulfonamide (3b)

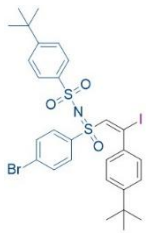
petroleum ether/ ethyl acetate = 5:1, white solid, 93% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.61 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.34 (m, 4H), 6.97 – 6.92 (m, 4H), 2.32 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.7, 140.1, 138.8, 136.8, 135.9, 132.1, 129.5, 129.2, 128.6, 127.6, 126.5, 125.6, 117.4, 35.0, 31.1, 21.4.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}BrINO_3S_2$ $[M+Na]^+$: 679.9397, Found: 679.9386.

IR (neat, cm^{-1}): υ 3087, 3049, 2955, 2869, 1610, 1592, 1467, 1322, 1251, 1158, 1093, 1052, 865, 654.



(*E*)-*N*-((4-bromophenyl)(2-(4-(*tert*-butyl)phenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3c)

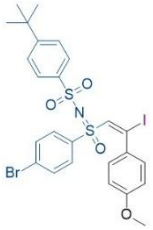
petroleum ether/ ethyl acetate = 5:1, white solid, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 153.8, 140.1, 139.6, 136.4, 135.7, 131.8, 129.5, 128.9, 127.4, 126.4, 125.6, 124.9, 117.1, 35.0, 34.7, 31.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{28}H_{31}BrINO_3S_2$ $[M+Na]^+$: 721.9866, Found: 721.9856.

IR (neat, cm^{-1}): υ 3057, 2964, 1596, 1570, 1390, 1363, 1313, 1265, 1236, 1177, 1157, 1055, 830, 653.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-methoxyphenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3d)

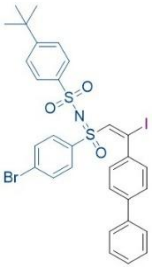
petroleum ether/ ethyl acetate = 5:1, brown solid, 79% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.59 (s, 1H), 7.46 – 7.35 (m, 6H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.0, 155.9, 140.1, 138.4, 136.9, 132.1, 130.8, 129.7, 129.4, 129.1, 126.4, 125.6, 117.6, 113.3, 55.4, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}BrINO_4S_2$ $[M+H]^+$: 673.9526, Found: 673.9516.

IR (neat, cm^{-1}): υ 3093, 3068, 2959, 2922, 2850, 1598, 1574, 1501, 1462, 1319, 1249, 1177, 833, 660.



(*E*)-*N*-((2-([1,1'-biphenyl]-4-yl)-2-iodovinyl)(4-bromophenyl)(oxo)- λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3e)

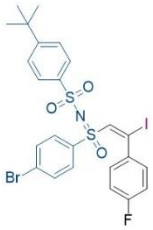
petroleum ether/ ethyl acetate = 4:1, yellow solid, 88% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.71 (s, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.41 (m, 5H), 7.39 – 7.44 (m, 6H), 7.11 (d, *J* = 8.4 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 143.1, 140.0, 139.6, 139.4, 137.5, 136.6, 132.1, 129.5, 129.2, 129.0, 128.2, 128.1, 127.0, 126.5, 126.4, 125.6, 116.3, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{30}H_{27}BrINO_3S_2$ $[M+H]^+$: 719.9734, Found: 719.9730.

IR (neat, cm^{-1}): υ 3053, 2960, 1568, 1483, 1469, 1443, 1391, 1312, 1250, 1234, 1157, 1095, 1050, 666.



(*E*)-*N*-((4-bromophenyl)(2-(4-fluorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)ben zeneesulfonamide (3f)

petroleum ether/ ethyl acetate = 5:1, white solid, 89% yield.

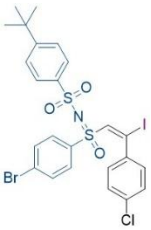
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.60 (s, 1H), 7.51 – 7.41 (m, 6H), 7.14 – 7.08 (m, 2H), 6.89 – 6.83 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.5, 162.0, 156.1, 140.0, 139.5, 136.9, 134.8 (d, *J* = 3.5 Hz), 132.4, 129.9 (d, *J* = 8.8 Hz), 129.5 (d, *J* = 17.4Hz), 126.5, 125.7, 115.3 (d, *J* = 5.5 Hz), 115.1, 35.0, 31.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.4.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}BrFINO_3S_2$ $[M+Na]^+$: 683.9146, Found: 683.9151.

IR (neat, cm^{-1}): υ 3095, 3051, 2967, 2869, 1604, 1594, 1567, 1498, 1466, 1321, 1251, 1156, 870, 652.



(*E*)-*N*-((4-bromophenyl)(2-(4-chlorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3g)

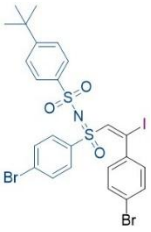
petroleum ether/ ethyl acetate = 4:1, white solid, 86% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.55 (s, 1H), 7.52 – 7.48 (m, 4H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 143.1, 139.7, 136.4, 132.8, 131.6, 130.1, 129.3, 128.0, 126.4, 125.7, 117.7, 113.5, 112.6, 35.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}BrClINO_3S_2$ $[M+Na]^+$: 699.8850, Found: 699.8836.

IR (neat, cm^{-1}): υ 3030, 2955, 1583, 1568, 1493, 1392, 1315, 1252, 1159, 1097, 1057, 867, 751, 655.



(*E*)-*N*-((4-bromophenyl)(2-(4-bromophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3h)

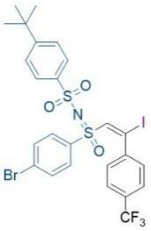
petroleum ether/ ethyl acetate = 5:1, white solid, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.59 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 140.0, 139.7, 137.7, 136.8, 132.5, 131.3, 129.7, 129.5, 129.1, 126.5, 125.8, 124.7, 114.7, 35.1, 31.2.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}Br_2INO_3S_2$ $[M+H]^+$: 723.8505, Found: 723.8497.

IR (neat, cm^{-1}): υ 2960, 1569, 1470, 1443, 1391, 1325, 1250, 1234, 1151, 1121, 1083, 1049, 1005, 868.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-(trifluoromethyl)phenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*ter t* -butyl)benzenesulfonamide (3i)

petroleum ether/ ethyl acetate = 4:1, white solid, 83% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.66 (s, 1H), 7.48 – 7.39 (m, 8H), 7.20 (d, *J* = 8.0 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 142.2, 140.3, 139.8, 136.3, 132.5, 131.8, 129.8, 129.4, 127.8, 126.4, 125.7, 125.0 (q, *J* = 7.6 Hz), 121.9, 113.2, 35.0, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.9.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{22}BrF_3INO_3S_2$ $[M+Na]^+$: 733.9114, Found: 733.9104.

IR (neat, cm^{-1}): υ 3382, 2965, 1594, 1567, 1498, 1462, 1405, 1389, 1322, 1251, 1173, 1153, 829, 645.

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-nitrophenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benz eneesulfonamide (3j)

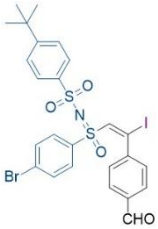
petroleum ether/ ethyl acetate = 4:1, white solid, 58% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.53 (m, 5H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 148.1, 145.0, 139.8, 139.7, 136.5, 133.0, 130.3, 129.4, 128.4, 126.4, 125.8, 123.2, 111.9, 35.1, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}BrIN_2O_5S_2$ $[M+Na]^+$: 710.9091, Found: 710.9078.

IR (neat, cm^{-1}): υ 3088, 3049, 2956, 2869, 1586, 1566, 1525, 1467, 1342, 1251, 1159, 1094, 1023, 655.



***(E)*-*N*-((4-bromophenyl)(2-(4-formylphenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)be nzenesulfonamide (3k)**

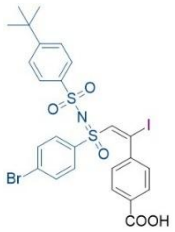
petroleum ether/ ethyl acetate = 3:1, white solid, 75% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 1H), 7.52 – 7.43 (m, 6H), 7.28 (d, *J* = 8.3 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.9, 156.2, 144.3, 139.8, 139.6, 136.7, 136.6, 132.6, 129.9, 129.4, 129.1, 128.0, 126.4, 125.7, 113.8, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}BrINO_4S_2$ $[M+H]^+$: 671.9370, Found: 671.9362.

IR (neat, cm^{-1}): υ 3051, 2956, 1736, 1587, 1567, 1531, 1463, 1390, 1324, 1251, 1158, 1111, 1059, 871.



(*E*)-4-(2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)-1-iodovinyl)benzoicacid (3l)

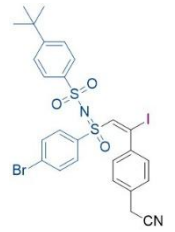
petroleum ether/ ethyl acetate = 2:1, white solid, 52% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.63 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.45 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 156.3, 143.8, 139.9, 139.7, 136.6, 132.7, 130.4, 129.9, 129.8, 129.5, 127.5, 126.5, 125.8, 114.2, 35.1, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}BrINO_5S_2$ $[M+H]^+$: 687.9319, Found: 687.9319.

IR (neat, cm^{-1}): υ 2960, 1727, 1568, 1469, 1443, 1390, 1312, 1234, 1152, 1122, 1083, 1047, 867, 631.



(*E*)-*N*-((4-bromophenyl)(2-(4-(cyanomethyl)phenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3m)

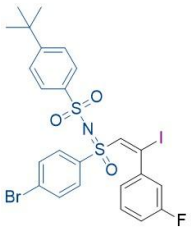
petroleum ether/ ethyl acetate = 2:1, white solid, 81% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.62 (s, 1H), 7.50 – 7.43 (m, 4H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 3.72 (s, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 139.9, 139.6, 138.7, 136.6, 132.4, 132.1, 129.6, 129.4, 128.2, 127.6, 126.4, 125.7, 117.1, 115.1, 35.0, 31.1, 23.4.

HRMS (ESI-TOF): Anal Calcd. For. $C_{26}H_{24}BrIN_2O_3S_2$ $[M+Na]^+$: 704.9349, Found: 704.9331.

IR (neat, cm^{-1}): υ 2959, 2921, 2850, 1573, 1500, 1412, 1327, 1252, 1157, 1109, 1053, 1009, 867, 662.



(*E*)-*N*-((4-bromophenyl)(2-(3-fluorophenyl)-2-iodovinyl)(oxo)- λ^6--sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3n)

petroleum ether/ ethyl acetate = 4:1, light yellow solid, 84% yield.

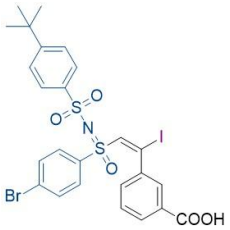
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.63 (s, 1H), 7.51 – 7.41 (m, 6H), 7.19 – 7.14 (m, 1H), 7.00 – 6.93 (m, 1H), 6.90 – 6.88 (m, 1H), 6.73 – 6.70 (m, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.8, 160.3, 156.1, 140.4 (d, *J* = 8.2 Hz), 139.9 (d, *J* = 5.6 Hz), 136.6, 132.4, 129.7 (t, *J* = 8.3 Hz), 129.4, 126.4, 125.7, 123.3 (d, *J* = 3.1 Hz), 117.0 (d, *J* = 21.0 Hz), 114.6, 114.4, 113.9 (d, *J* = 2.4 Hz), 35.0, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.2.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}BrFINO_3S_2$ $[M+Na]^+$: 683.9146, Found: 683.9131.

IR (neat, cm^{-1}): υ 3059, 2962, 2868, 1583, 1568, 1469, 1390, 1314, 1291, 1250, 1157, 1094, 1054, 881.



(*E*)-3-(2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)-1-iodovinyl)benzoicacid (3o)

petroleum ether/ ethyl acetate = 2:1, white solid, 72% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (s, 1H), 7.81 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.44 (m, 5H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.28 (dt, *J* = 7.7, 1.5 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 155.5, 139.9, 139.8, 137.4, 136.6, 132.6, 130.9, 130.5, 130.1, 129.4, 128.7, 128.4, 127.4, 126.0, 125.8, 118.2, 34.8, 30.8.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}BrINO_5S_2$ $[M+H]^+$: 687.9319, Found: 687.9315.

IR (neat, cm^{-1}): υ 3391, 3091, 2962, 1646, 1594, 1568, 1468, 1390, 1317, 1235, 1155, 1108, 1047, 625.

(*E*)-*N*-((4-bromophenyl)(2-(3,4-dimethoxyphenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3p)

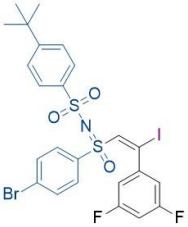
petroleum ether/ ethyl acetate = 3:1, yellow solid, 52% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.62 (s, 1H), 7.45 – 7.38 (m, 4H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.70 – 6.52 (m, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 150.6, 148.0, 140.0, 139.2, 136.7, 131.9, 130.9, 129.5, 129.0, 126.4, 125.6, 121.4, 117.1, 110.7, 110.0, 56.0, 55.9, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{26}H_{27}BrINO_5S_2$ $[M+Na]^+$: 725.9451, Found: 725.9452.

IR (neat, cm^{-1}): υ 3059, 2962, 2868, 1583, 1569, 1508, 1464, 1364, 1318, 1252, 1236, 1157, 1094, 829.



(*E*)-*N*-((4-bromophenyl)(2-(3,5-difluorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3q)

petroleum ether/ ethyl acetate = 5:1, light yellow solid, 72% yield.

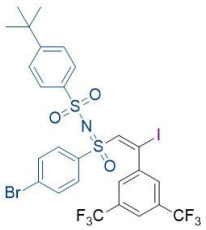
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.50 (m, 5H), 7.46 (d, *J* = 8.6 Hz, 2H), 6.72 (tt, *J* = 8.7, 2.3 Hz, 1H), 6.69 – 6.55 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 12.5 Hz), 160.7 (d, *J* = 12.4 Hz), 156.2, 141.3, 140.0, 139.9, 136.5, 132.7, 130.0, 129.4, 126.4, 125.7, 110.7 (q, *J* = 8.0 Hz), 105.3 (t, *J* = 24.8 Hz), 35.0, 31.0

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{21}BrF_2INO_3S_2$ $[M+Na]^+$: 701.9052, Found: 701.9045.

IR (neat, cm^{-1}): υ 3089, 3056, 1573, 1532, 1453, 1440, 1362, 1326, 1261, 1225, 1179, 1159, 1122, 871.



(*E*)-*N*-((2-(3,5-bis(trifluoromethyl)phenyl)-2-iodovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3r)

petroleum ether/ ethyl acetate = 4:1, yellow solid, 69% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.78 (m, 3H), 7.68 (s, 1H), 7.66 – 7.62 (m, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.50 – 7.43 (m, 4H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 140.9 (d, *J* = 19.7 Hz), 139.7, 136.1, 132.9, 131.6 (q, *J* = 33.9 Hz), 130.4, 129.2, 127.6 (d, *J* = 4.0 Hz), 126.4, 125.8, 123.9, 123.4, 121.2, 110.2, 35.0, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.9.

HRMS (ESI-TOF): Anal Calcd. For. $C_{26}H_{21}BrF_6INO_3S_2$ $[M+Na]^+$: 801.8988, Found: 801.8971.

IR (neat, cm^{-1}): υ 3092, 3061, 2959, 2921, 1625, 1589, 1567, 1469, 1326, 1279, 1243, 1179, 1159, 1093.

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(naphthalen-2-yl)vinyl)(oxo)-λ^6--sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3s)

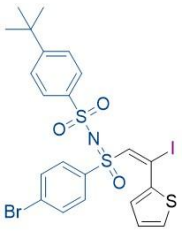
petroleum ether/ ethyl acetate = 5:1, light yellow solid, 82% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 4H), 7.72 – 7.69 (m, 1H), 7.61 – 7.52 (m, 4H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.97 (dd, *J* = 8.5, 1.9 Hz, 1H), 1.31 (s, 9H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 140.0, 140.0, 136.5, 135.7, 133.3, 131.9, 131.7, 129.4, 129.2, 128.5, 128.0, 127.9, 127.6, 127.3, 127.2, 126.4, 125.6, 124.1, 116.7, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{28}H_{25}BrINO_3S_2$ $[M+Na]^+$: 715.9397, Found: 715.9381.

IR (neat, cm^{-1}): υ 3052, 2961, 1573, 1470, 1454, 1393, 1371, 1326, 1312, 1234, 1150, 1121, 1082, 867.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(thiophen-2-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3t)

petroleum ether/ ethyl acetate = 4:1, brown solid, 78% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.59 (s, 1H), 7.51 – 7.39 (m, 8H), 6.86 (dd, *J* = 5.1, 3.7 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 140.5, 139.9, 138.7, 136.2, 132.2, 132.1, 131.3, 129.4, 129.3, 127.4, 126.4, 125.6, 106.7, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{22}H_{21}BrINO_3S_3$ $[M+Na]^+$: 671.8804, Found: 671.8806.

IR (neat, cm^{-1}): υ 2960, 1568, 1469, 1443, 1390, 1312, 1234, 1152, 1122, 1083, 1047, 1005, 867, 630.

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(thiophen-3-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3u)

petroleum ether/ ethyl acetate = 5:1, white solid, 86% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (s, 1H), 7.67 – 7.59 (m, 4H), 7.55 – 7.45 (m, 5H), 7.42 – 7.39 (m, 1H), 6.77 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 155.5, 140.0, 138.4, 136.7, 136.5, 132.3, 129.4, 128.4, 127.7, 127.5, 126.7, 126.0, 125.8, 113.6, 34.8, 30.8.

HRMS (ESI-TOF): Anal Calcd. For. $C_{22}H_{21}BrINO_3S_3$ $[M+Na]^+$: 671.8804, Found: 671.8795.

IR (neat, cm^{-1}): υ 3090, 2961, 2922, 2867, 1646, 1594, 1568, 1468, 1390, 1317, 1237, 1155, 1084, 876.

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(pyridin-2-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzeneesulfonamide (3v)

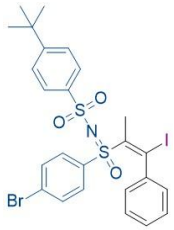
petroleum ether/ ethyl acetate = 2:1, brown solid, 60% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 – 8.36 (m, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.50 (m, 6H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.18 (m, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 155.2, 148.8, 140.0, 138.6, 136.7, 136.3, 132.6, 129.7, 129.5, 126.4, 125.7, 124.3, 123.7, 115.9, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{23}H_{22}BrIN_2O_3S_2$ $[M+H]^+$: 644.9373, Found: 644.9356.

IR (neat, cm^{-1}): υ 3053, 2958, 1578, 1567, 1531, 1462, 1390, 1325, 1255, 1158, 1119, 1064, 870, 638.



(*E*)-*N*-((4-bromophenyl)(1-iodo-1-phenylprop-1-en-2-yl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3w)

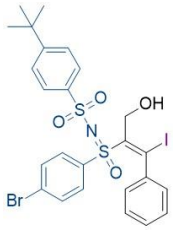
petroleum ether/ ethyl acetate = 5:1, white solid, 78% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.47 – 7.43 (m, 4H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.26 – 6.95 (m, 5H), 2.65 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 142.2, 142.0, 140.3, 137.1, 132.3, 129.2, 129.1, 128.8, 127.7, 126.3, 125.6, 117.1, 35.0, 31.0, 27.3.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}BrINO_3S_2$ $[M+Na]^+$: 679.9397, Found: 679.9394.

IR (neat, cm^{-1}): υ 3091, 3068, 2959, 1621, 1567, 1471, 1441, 1390, 1325, 1245, 1179, 1091, 660.



(*E*)-*N*-((4-bromophenyl)(3-hydroxy-1-iodo-1-phenylprop-1-en-2-yl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3x)

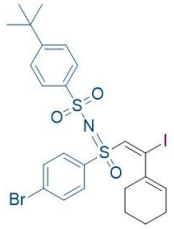
petroleum ether/ ethyl acetate = 2:1, yellow solid, 57% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.19 – 6.98 (m, 4H), 5.14 – 5.08 (m, 2H), 3.57 (t, *J* = 7.1 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 146.5, 141.0, 139.9, 137.0, 132.0, 129.3, 129.1, 128.9, 127.8, 127.4, 126.3, 125.7, 121.4, 67.9, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}BrINO_4S_2$ $[M+H]^+$: 673.9526, Found: 673.9523.

IR (neat, cm^{-1}): υ 1573, 1470, 1443, 1393, 1325, 1313, 1250, 1231, 1152, 1122, 1082, 1047, 1007, 867.



(*E*)-*N*-((4-bromophenyl)(2-(cyclohex-1-en-1-yl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3y)

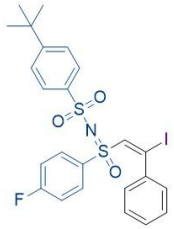
petroleum ether/ ethyl acetate = 5:1, yellow solid, 77% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.27 (s, 1H), 5.86 – 5.82 (m, 1H), 1.84 – 1.80 (m, 2H), 1.54 – 1.35 (m, 6H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.1, 138.1, 136.9, 136.6, 132.4, 131.8, 129.7, 129.2, 126.4, 125.6, 124.4, 35.0, 31.1, 27.0, 25.0, 21.2, 20.7.

HRMS (ESI-TOF): Anal Calcd. For $C_{24}H_{27}BrINO_3S_2$ $[M+H]^+$: 647.9734, Found: 647.9726.

IR (neat, cm^{-1}): υ 1573, 1470, 1443, 1392, 1326, 1312, 1250, 1233, 1151, 1121, 1082, 1047, 1006, 868.



(*E*)-4-(*tert*-butyl)-*N*-((4-fluorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3z)

petroleum ether/ ethyl acetate = 4:1, light yellow solid, 83% yield.

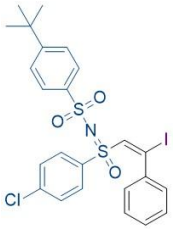
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.70 (s, 1H), 7.53 – 7.49 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.98 – 6.92 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 164.4, 156.0, 140.1, 139.8, 138.7, 133.4 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 9.8 Hz), 130.0, 128.0, 127.5, 126.5, 125.7, 116.3 (d, *J* = 22.7.0 Hz), 35.0, 31.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.4.

HRMS (ESI-TOF): Anal Calcd. For $C_{24}H_{23}FINO_3S_2$ $[M+H]^+$: 584.0221, Found: 584.0236.

IR (neat, cm^{-1}): υ 3053, 1579, 1531, 1492, 1462, 1441, 1362, 1325, 1256, 1179, 1157, 1082, 1009, 869.



(*E*)-4-(*tert*-butyl)-*N*-((4-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3aa)

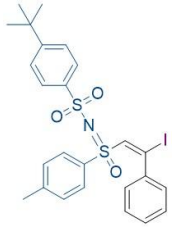
petroleum ether/ ethyl acetate = 4:1, yellow solid, 88% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.67 (s, 1H), 7.46 – 7.40 (m, 4H), 7.25 – 7.20 (m, 3H), 7.17 – 7.11 (m, 2H), 7.05 – 7.01 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.5, 140.0, 139.4, 138.6, 136.0, 130.0, 129.3, 129.2, 127.9, 127.4, 126.4, 125.6, 116.8, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For $C_{24}H_{23}ClINO_3S_2$ $[M+H]^+$: 599.9926, Found: 599.9924.

IR (neat, cm^{-1}): υ 3053, 2961, 1597, 1574, 1474, 1443, 1395, 1370, 1315, 1235, 1154, 1107, 1049, 868.



(*E*)-4-(tert-butyl)-*N*-((2-iodo-2-phenylvinyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)benzenesulfonamide (3ab)

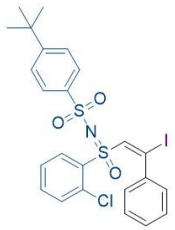
petroleum ether/ ethyl acetate = 3:1, yellow solid, 76% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.65 (s, 1H), 7.45 – 7.40 (m, 4H), 7.25 – 7.20 (m, 1H), 7.16 – 7.04 (m, 6H), 2.35 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7, 145.0, 140.4, 139.7, 138.8, 134.5, 129.8, 129.7, 128.0, 127.8, 127.5, 126.4, 125.5, 115.8, 35.0, 31.1, 21.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{26}INO_3S_2$ $[M+H]^+$: 580.0472, Found: 580.0471.

IR (neat, cm^{-1}): υ 3056, 2962, 2868, 1594, 1485, 1463, 1399, 1365, 1317, 1242, 1183, 1154, 1108, 1051.



(*E*)-4-(*tert*-butyl)-*N*-((2-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3ac)

petroleum ether/ ethyl acetate = 4:1, yellow solid, 48% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.37 – 7.33 (m, 2H), 7.13 – 7.08 (m, 1H), 7.06 – 6.97 (m, 5H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.0, 138.4, 138.4, 135.4, 134.5, 132.1, 131.7, 131.6, 130.0, 127.8, 127.1, 126.9, 126.5, 125.5, 116.5, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}ClINO_3S_2$ $[M+H]^+$: 599.9926, Found: 599.9922.

IR (neat, cm^{-1}): υ 1452, 1442, 1332, 1258, 1222, 1170, 1137, 1077, 1028, 923, 868, 774, 754, 718, 652.

(*E*)-*N*-((3-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3ad)

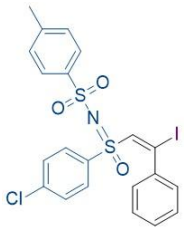
petroleum ether/ ethyl acetate = 4:1, light yellow solid, 84% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.69 (s, 1H), 7.59 – 7.52 (m, 2H), 7.47 – 7.43 (m, 3H), 7.31 – 7.26 (m, 1H), 7.22 – 7.14 (m, 3H), 7.04 – 7.00 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 140.0, 139.5, 139.5, 138.4, 136.7, 131.1, 130.4, 130.4, 128.0, 127.4, 126.5, 126.5, 125.7, 122.8, 117.1, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}BrINO_3S_2$ $[M+H]^+$: 643.9421, Found: 643.9404.

IR (neat, cm^{-1}): υ 2960, 1568, 1469, 1443, 1390, 1312, 1234, 1152, 1122, 1083, 1047, 1004, 967, 817.



(*E*)-*N*-((4-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-methylbenzenesulfonami

de (3ae)

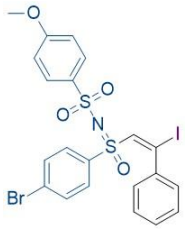
petroleum ether/ ethyl acetate = 3:1, light yellow solid, 80% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 5H), 7.16 (td, *J* = 7.9, 1.9 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.1, 140.6, 140.3, 139.5, 138.6, 136.1, 130.1, 129.4, 129.2, 129.2, 128.0, 127.4, 126.6, 116.8, 21.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{21}H_{17}ClINO_3S_2$ $[M+H]^+$: 557.9456, Found: 557.9461.

IR (neat, cm^{-1}): υ 2841, 2207, 1598, 1581, 1498, 1453, 1325, 1259, 1184, 1147, 1046, 999, 855, 813.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-methoxybenzenesulfonamide (3af)

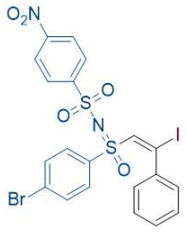
petroleum ether/ ethyl acetate = 2:1, light yellow solid, 72% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.68 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.18 – 7.13 (m, 2H), 7.05 – 7.02 (m, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.6, 139.5, 138.6, 136.7, 135.0, 132.2, 130.0, 129.4, 129.2, 128.8, 128.0, 127.4, 116.8, 113.8, 55.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{21}H_{17}BrINO_4S_2$ $[M+Na]^+$: 639.8720, Found: 639.8718.

IR (neat, cm^{-1}): υ 3041, 1579, 1444, 1326, 1314, 1302, 1237, 1182, 1150, 1083, 1051, 1008, 867, 770.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-nitrobenzenesulfonamide (3ag)

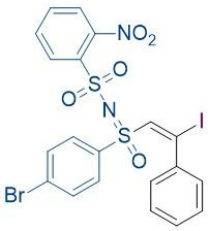
petroleum ether/ ethyl acetate = 3:1, white solid, 60% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 7.69 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.21 – 7.16 (m, 2H), 7.06 – 7.01 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.7, 148.6, 138.8, 138.5, 136.4, 132.5, 130.3, 129.8, 129.2, 128.1, 128.0, 127.3, 124.0, 118.2

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{14}BrIN_2O_5S_2$ $[M+Na]^+$: 654.8465, Found: 654.8471.

IR (neat, cm^{-1}): υ 3087, 2922, 1981, 1567, 1532, 1499, 1462, 1387, 1342, 1261, 1163, 1088, 1002, 872.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-2-nitrobenzenesulfonamide (3ah)

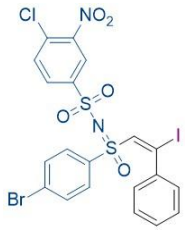
petroleum ether/ ethyl acetate = 3:1, light yellow solid, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.03 (m, 1H), 7.70 (s, 1H), 7.67 – 7.60 (m, 3H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.19 – 7.14 (m, 2H), 7.08 – 7.02 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 138.8, 138.6, 136.4, 135.8, 133.3, 132.4, 131.8, 130.2, 129.8, 129.7, 129.3, 128.1, 127.4, 123.9, 118.2.

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{14}BrIN_2O_5S_2$ $[M+H]^+$: 632.8645, Found: 632.8661.

IR (neat, cm^{-1}): υ 3055, 1572, 1531, 1484, 1440, 1362, 1334, 1261, 1179, 1122, 1046, 998, 872, 772.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-chloro-3-nitrobenzenesulfonamide (3ai)

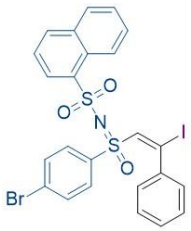
petroleum ether/ ethyl acetate = 5:1, yellow solid, 79% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 2.2 Hz, 1H), 8.00 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 – 7.17 (m, 2H), 7.07 – 7.03 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.5, 143.2, 138.6, 138.5, 136.3, 132.5, 132.4, 131.0, 130.8, 130.4, 129.9, 129.2, 128.1, 127.3, 124.3, 118.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{13}BrClIN_2O_5S_2$ $[M+Na]^+$: 688.8075, Found: 688.8067.

IR (neat, cm^{-1}): υ 3087, 3042, 2922, 1641, 1567, 1532, 1499, 1462, 1388, 1323, 1262, 1162, 1088, 788.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)naphthalene-1-sulfonamide (3aj)

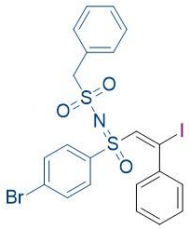
petroleum ether/ ethyl acetate = 3:1, white solid, 79% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, *J* = 2.1 Hz, 1H), 8.11 – 8.00 (m, 3H), 7.99 (s, 1H), 7.77 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.72 – 7.61 (m, 4H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.25 – 7.14 (m, 3H), 6.99 (d, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 139.9, 139.4, 136.6, 136.4, 134.2, 132.5, 131.6, 129.6, 129.5, 129.3, 129.2, 128.9, 128.7, 127.9, 127.8, 127.6, 126.8, 126.7, 122.1, 119.9.

HRMS (ESI-TOF): Anal Calcd. For $C_{24}H_{17}BrINO_3S_2$ $[M+Na]^+$: 659.8771, Found: 659.8773.

IR (neat, cm^{-1}): υ 3053, 2921, 2851, 1645, 1601, 1583, 1467, 1443, 1388, 1308, 1262, 1173, 1127, 871.



(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-1-phenylmethanesulfonamide(3ak)

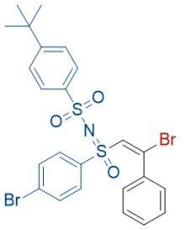
petroleum ether/ ethyl acetate = 5:1, yellow solid, 73% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.45 – 7.35 (m, 7H), 7.32 – 7.26 (m, 3H), 7.23 – 7.18 (m, 2H), 7.10 – 7.04 (m, 2H), 4.39 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.0, 138.7, 136.6, 132.2, 131.0, 130.1, 129.4, 129.3, 129.2, 128.5, 128.0, 127.4, 116.8, 63.0.

HRMS (ESI-TOF): Anal Calcd. For $C_{21}H_{17}BrINO_3S_2$ $[M+Na]^+$: 623.8771, Found: 623.8778.

IR (neat, cm^{-1}): υ 2841, 1598, 1581, 1498, 1453, 1325, 1259, 1184, 1147, 1046, 999, 906, 855, 772, 630



(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4a)

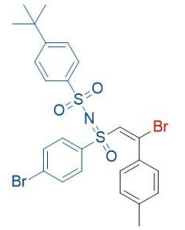
petroleum ether/ ethyl acetate = 5:1, white solid, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.30 (m, 8H), 7.22 – 7.17 (m, 2H), 7.16 – 7.10 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 141.1, 140.0, 136.7, 135.1, 133.1, 132.2, 130.7, 129.4, 129.3, 128.4, 128.0, 126.4, 125.6, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For $C_{24}H_{23}Br_2NO_3S_2$ $[M+Na]^+$: 619.9358, Found: 619.9353.

IR (neat, cm^{-1}): υ 3059, 2961, 2903, 2867, 1596, 1586, 1084, 1051, 829, 652.



(*E*)-*N*-((2-bromo-2-(p-tolyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4b)

petroleum ether/ ethyl acetate = 5:1, white solid, 76% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.38 (m, 7H), 7.04 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 141.6, 141.5, 140.1, 136.8, 132.4, 132.3, 132.1, 129.5, 129.3, 128.7, 128.5, 126.5, 125.6, 35.0, 31.1, 21.4.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}Br_2NO_3S_2$ $[M+Na]^+$: 633.9515, Found: 633.9516.

IR (neat, cm^{-1}): υ 3056, 2959, 2921, 2851, 1659, 1572, 1315, 1243, 1154, 1084, 797, 665.

(*E*)-*N*-((2-bromo-2-(4-(*tert*-butyl)phenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4c)

petroleum ether/ ethyl acetate = 6:1, white solid, 87% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.51 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.32– 7.28 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 154.6, 141.3, 140.0, 136.3, 133.2, 132.1, 131.8, 129.5, 129.0, 128.3, 126.4, 125.6, 125.0, 35.0, 34.8, 31.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{28}H_{31}Br_2NO_3S_2$ $[M+H]^+$: 654.0165, Found: 654.0176.

IR (neat, cm^{-1}): υ 2964, 1597, 1408, 1367, 1315, 1237, 1160, 1096, 1085, 1061, 833, 654, 622.

(*E*)-*N*-((2-bromo-2-(4-methoxyphenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4d)

petroleum ether/ ethyl acetate = 5:1, white solid, 52% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.39 (m, 6H), 7.36 (s, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.7, 156.0, 141.7, 140.1, 136.9, 132.1, 131.8, 130.7, 129.4, 129.2, 127.2, 126.5, 125.6, 113.4, 55.5, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}Br_2NO_4S_2$ $[M+H]^+$: 627.9645, Found: 627.9653.

IR (neat, cm^{-1}): υ 2921, 2851, 1597, 1567, 1502, 1249, 1157, 1111, 1086, 883, 830, 663, 622.

(*E*)-*N*-((2-([1,1'-biphenyl]-4-yl)-2-bromovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-but

yl)benzenesulfonamide (4e)

petroleum ether/ ethyl acetate = 5:1, white solid, 93% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 1H), 7.68 – 7.63 (m, 6H), 7.58 – 7.48 (m, 8H), 7.44 – 7.40 (m, 1H), 7.24 (d, J = 8.4 Hz, 2H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 155.6, 142.4, 140.3, 139.9, 138.9, 136.4, 134.4, 132.5, 131.6, 129.7, 129.1, 128.8, 128.7, 128.3, 126.9, 126.3, 126.1, 125.8, 34.8, 30.8.

HRMS (ESI-TOF): Anal Calcd. For. $C_{30}H_{27}Br_2NO_3S_2$ $[M+H]^+$: 673.9852, Found: 673.9849.

IR (neat, cm^{-1}): υ 3094, 2964, 1659, 1631, 1595, 1568, 1376, 1319, 1249, 1156, 1096, 1087, 826, 763.

(*E*)-*N*-((2-bromo-2-(4-chlorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4f)

petroleum ether/ ethyl acetate = 5:1, white solid, 84% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.50 – 7.44 (m, 4H), 7.37 (s, 1H), 7.21 – 7.12 (m, 4H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 139.9, 139.4, 137.1, 136.7, 133.5, 133.0, 132.5, 129.9, 129.7, 129.4, 128.3, 126.4, 125.7, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}Br_2ClNO_3S_2$ $[M+H]^+$: 631.9149, Found: 631.9153.

IR (neat, cm^{-1}): υ 3037, 2960, 1614, 1595, 1315, 1253, 1160, 1102, 1087, 1059, 841, 829, 715, 695, 623.

(*E*)-*N*-((2-bromo-2-(4-bromophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4g)

petroleum ether/ ethyl acetate = 5:1, white solid, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.47 (dd, J = 8.7, 2.0 Hz, 4H), 7.37 (s, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 139.9, 139.3, 136.7, 134.0, 133.1, 132.5, 131.3, 130.0, 129.8, 129.4, 126.5, 125.7, 125.5, 35.1, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}Br_3NO_3S_2$ $[M+H]^+$: 675.8644, Found: 675.8634.

IR (neat, cm^{-1}): υ 3036, 2961, 1613, 1595, 1567, 1315, 1253, 1159, 1099, 1058, 817, 774, 623.

(*E*)-*N*-((2-bromo-2-(4-(trifluoromethyl)phenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4h)

petroleum ether/ ethyl acetate = 5:1, white solid, 70% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.47 (m, 5H), 7.47 – 7.43 (m, 4H), 7.31 (d, *J* = 9.4 Hz, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.3, 139.8, 138.6, 138.1, 136.4, 134.0, 132.6, 132.2, 129.9, 129.4, 128.8, 126.5, 125.8, 125.1 (q, *J* = 3.7 Hz), 122.0, 35.1, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{22}Br_2F_3NO_3S_2$ [M+Na]$^+$: 687.9232, Found: 687.9229.

IR (neat, cm^{-1}): υ 3034, 2962, 1631, 1606, 1568, 1314, 1253, 1159, 1101, 1087, 835, 789, 745, 695, 623.

(*E*)-*N*-((2-bromo-2-(4-cyanophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4i)

petroleum ether/ ethyl acetate = 3:1, white solid, 46% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.56 – 7.51 (m, 4H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.34 (s, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 139.7, 139.5, 137.4, 136.5, 133.4, 132.8, 131.7, 130.2, 129.3, 129.1, 126.4, 125.8, 117.6, 114.2, 35.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{22}Br_2N_2O_3S_2$ [M+H]$^+$: 622.9491, Found: 622.9494.

IR (neat, cm^{-1}): υ 3076, 2962, 2926, 2226, 1596, 1567, 1317, 1253, 1159, 1098, 829, 704, 625.

(*E*)-*N*-((2-bromo-2-(4-nitrophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4j)

petroleum ether/ ethyl acetate = 4:1, white solid, 46% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.56 (m, 4H), 7.50 – 7.45 (m, 4H), 7.34 (s, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.5, 148.6, 141.4, 139.7, 136.9, 136.5, 133.5, 133.0, 130.4, 129.5, 129.4, 126.4, 125.8, 123.2, 35.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}Br_2N_2O_5S_2$ [M+H]$^+$: 664.9209, Found: 664.9198.

IR (neat, cm^{-1}): υ 3087, 2960, 2869, 1603, 1588, 1524, 1343, 1316, 1160, 1102, 842, 762, 638.

(*E*)-*N*-((2-bromo-2-(4-formylphenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4k)

petroleum ether/ ethyl acetate = 3:1, white solid, 60% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.02 (s, 1H), 7.82 – 7.75 (m, 4H), 7.53 – 7.44 (m, 6H), 7.41 – 7.38 (m, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.0, 156.3, 140.7, 139.8, 138.5, 137.2, 136.6, 133.4, 132.7, 130.0, 129.4, 129.1, 129.1, 126.4, 125.7, 35.1, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}Br_2NO_4S_2$ [M+Na]$^+$: 647.9307, Found: 647.9310.

IR (neat, cm^{-1}): υ 3087, 2965, 1693, 1659, 1630, 1595, 1567, 1314, 1253, 1159, 1098, 1007, 836, 774.

(*E*)-4-(1-bromo-2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)vinyl)benzoic acid (4l)

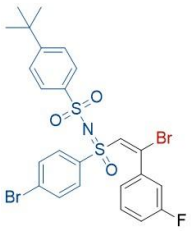
petroleum ether/ ethyl acetate = 2:1, white solid, 49% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.51 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 155.7, 139.9, 139.6, 139.0, 136.5, 132.8, 132.3, 131.9, 129.7, 129.0, 128.9, 128.2, 126.1, 125.9, 34.9, 30.8.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}Br_2NO_5S_2$ [M+Na]$^+$: 663.9257, Found: 663.9249.

IR (neat, cm^{-1}): υ 1650, 1597, 1571, 1470, 1390, 1319, 1251, 1157, 1099, 1024, 890, 826, 787, 704.



(*E*)-*N*-((2-bromo-2-(3-fluorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4m)

petroleum ether/ ethyl acetate = 5:1, white solid, 72% yield.

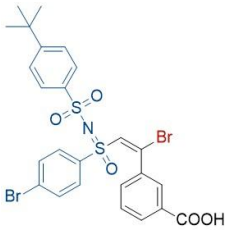
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.43 (s, 1H), 7.24 – 7.18 (m, 1H), 7.07 – 6.98 (m, 2H), 6.83 (dt, J = 8.9, 2.2 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.9, 160.5, 156.2, 139.9, 138.7, 136.8 (d, J = 8.2 Hz), 133.5, 132.5, 129.8 (t, J = 8.2 Hz), 129.4, 126.4, 125.7, 124.3 (d, J = 3.3 Hz), 117.7 (d, J = 20.9 Hz), 115.6, 115.3, 35.0, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.2.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{22}Br_2FNO_3S_2$ $[M+H]^+$: 615.9445, Found: 615.9431.

IR (neat, cm^{-1}): υ 3057, 2963, 2868, 1621, 1595, 1568, 1469, 1391, 1318, 1253, 1158, 1098, 821.



(*E*)-3-(1-bromo-2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)vinyl)benzoica cid (4n)

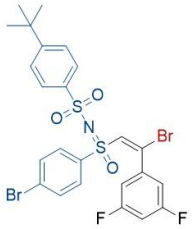
petroleum ether/ ethyl acetate = 2:1, white solid, 48% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (s, 1H), 7.96 – 7.91 (m, 1H), 7.69 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.6 Hz, 3H), 7.54 – 7.43 (m, 6H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 155.7, 139.9, 139.3, 136.3, 135.9, 132.7, 132.3, 132.1, 131.1, 130.7, 129.5, 129.0, 128.7, 128.6, 126.1, 125.9, 34.9, 30.8.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{23}Br_2NO_5S_2$ $[M+Na]^+$: 663.9257, Found: 663.9255.

IR (neat, cm^{-1}): υ 2966, 1693, 1659, 1594, 1530, 1468, 1391, 1367, 1291, 1241, 1151, 1084, 821, 759.



(*E*)-*N*-((2-bromo-2-(3,5-difluorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-but yl)benzenesulfonamide (4o)

petroleum ether/ ethyl acetate = 4:1, white solid, 60% yield.

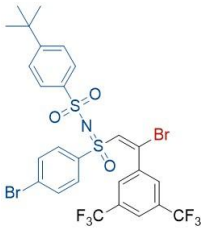
^{1}H NMR (400 MHz, Chloroform-*d*). δ 7.82 (d, J = 8.6 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.47 (d, J = 8.7 Hz, 2H), 7.37 (s, 1H), 6.84 – 6.72 (m, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*). δ 163.4 (d, J = 12.5 Hz), 160.9 (d, J = 12.4 Hz), 156.3, 139.8, 137.7, 136.5, 133.8, 132.8, 130.2, 129.4, 126.4, 125.8, 111.7 (q, J = 7.9 Hz), 106.0 (t, J = 24.7 Hz), 35.1, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) -107.5

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{21}Br_2F_2NO_3S_2$ $[M+H]^+$: 633.9350, Found: 633.9355.

IR (neat, cm^{-1}): υ 2964, 1594, 1568, 1479, 1391, 1367, 1257, 1159, 1097, 817, 742.



(*E*)-*N*-((2-(3,5-bis(trifluoromethyl)phenyl)-2-bromovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene) -4-(*tert*-butyl)benzenesulfonamide (4p)

petroleum ether/ ethyl acetate = 5:1, white solid, 72% yield.

^{1}H NMR (400 MHz, Chloroform-*d*). δ 7.88 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 1.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.49 – 7.44 (m, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*). δ 156.4, 139.7, 137.3, 136.1, 135.5, 134.7, 133.0, 131.8 (d, *J* = 34.1 Hz), 130.5, 129.2, 128.7, 126.4, 125.8, 124.0 (d, *J* = 14.1 Hz), 121.2, 35.1, 31.0.

^{19}F NMR (376 MHz, Chloroform-*d*) -62.9

HRMS (ESI-TOF): Anal Calcd. For. $C_{26}H_{21}Br_2F_6NO_3S_2$ $[M+Na]^+$: 755.9106, Found: 755.9096.

IR (neat, cm^{-1}): υ 3094, 2962, 1630, 1595, 1568, 1468, 1403, 1250, 1157, 1131, 1098, 828, 769, 744.

(*E*)-*N*-((2-bromo-2-(naphthalen-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4q)

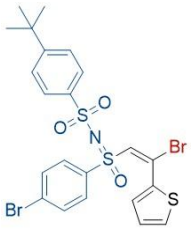
petroleum ether/ ethyl acetate = 5:1, yellow solid, 92% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.77 (m, 3H), δ 7.73 – 7.71 (m, 3H), 7.69 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.04 (dd, *J* = 8.5, 1.9 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 141.0, 140.0, 136.4, 133.6, 132.1, 131.9, 131.6, 129.4, 129.3, 129.0, 128.6, 128.2, 128.1, 127.6, 127.2, 126.4, 125.6, 124.3, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{28}H_{25}Br_2NO_3S_2$ $[M+H]^+$: 647.9695, Found: 647.9698.

IR (neat, cm^{-1}): υ 3022, 1621, 1504, 1357, 1307, 1254, 1161, 1125, 1031, 889, 810, 777, 708, 625.



(*E*)-*N*-((2-bromo-2-(thiophen-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4r)

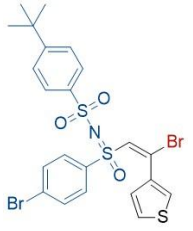
petroleum ether/ ethyl acetate = 5:1, brown solid, 59% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.50 – 7.43 (m, 5H), 7.34 (s, 1H), 6.90 (dd, *J* = 5.1, 3.8 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 140.0, 136.4, 136.3, 134.1, 132.7, 132.5, 132.3, 131.6, 129.5, 129.5, 127.3, 126.5, 125.7, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{22}H_{21}Br_2NO_3S_3$ $[M+Na]^+$: 625.8923, Found: 625.8924.

IR (neat, cm^{-1}): υ 1574, 1504, 1412, 1358, 1324, 1221, 1163, 1129, 1083, 1047, 858, 814, 767, 709, 644.



(*E*)-*N*-((2-bromo-2-(thiophen-3-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4s)

petroleum ether/ ethyl acetate = 4:1, white solid, 69% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.50 – 7.44 (m, 6H), 7.38 (s, 1H), 7.16 – 7.12 (m, 1H), 6.82 (dd, *J* = 5.1, 1.3 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 140.0, 136.6, 135.4, 134.6, 132.6, 132.2, 130.3, 129.4, 129.3, 127.8, 126.5, 126.1, 125.7, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{22}H_{21}Br_2NO_3S_3$ $[M+H]^+$: 603.9103, Found: 603.9106.

IR (neat, cm^{-1}): υ 3027, 2961, 2867, 1594, 1568, 1463, 1362, 1320, 1246, 1160, 1110, 1002, 823, 648.

(*E*)-*N*-((2-bromo-2-(pyridin-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benz enesulfonamide (4t)

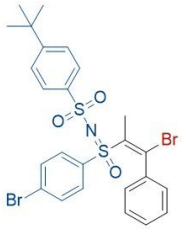
petroleum ether/ ethyl acetate = 3:1, brown solid, 68% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) 8.46 – 8.42 (m, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.70 (td, *J* = 7.7, 1.7 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.35 (s, 1H), 7.28 – 7.25 (m, 1H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 152.4, 148.9, 140.0, 138.9, 137.2, 136.5, 132.6, 132.6, 129.7, 129.5, 126.5, 125.7, 124.9, 124.8, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{23}H_{22}Br_2N_2O_3S_2$ $[M+H]^+$: 598.9491, Found: 598.9489.

IR (neat, cm^{-1}): υ 3053, 2962, 2922, 1595, 1568, 1493, 1429, 1365, 1319, 1246, 1155, 1108, 1005, 824.



(*E*)-*N*-((1-bromo-1-phenylprop-1-en-2-yl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4u)

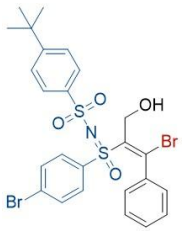
petroleum ether/ ethyl acetate = 5:1, white solid, 69% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.40 (m, 6H), 7.32 – 7.27 (m, 1H), 7.25 – 7.15 (m, 4H), 2.53 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.3, 138.9, 138.0, 138.0, 137.0, 132.3, 129.4, 129.3, 129.2, 128.5, 127.9, 126.4, 125.6, 35.0, 31.1, 21.7.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}Br_2NO_3S_2$ $[M+Na]^+$: 633.9515, Found: 633.9513.

IR (neat, cm^{-1}): υ 1631, 1568, 1503, 1412, 1358, 1324, 1247, 1161, 1125, 1084, 1001, 860, 817, 761.



(*E*)-*N*-((1-bromo-3-hydroxy-1-phenylprop-1-en-2-yl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4v)

petroleum ether/ ethyl acetate = 3:1, white solid, 64% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.20 – 7.17 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.94 (s, 2H), 5.03 – 4.92 (m, 2H), 3.48 (t, *J* = 7.3 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 143.6, 142.5, 139.9, 136.9, 132.0, 129.9, 129.2, 129.0, 128.5, 128.0, 126.4, 126.1, 125.8, 63.1, 35.1, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{25}H_{25}Br_2NO_4S_2$ [M+Na]$^+$: 649.9464, Found: 649.9479.

IR (neat, cm^{-1}): υ 3390, 3057, 2962, 2869, 1594, 1463, 1365, 1291, 1241, 1183, 1154, 1095, 1084, 1053.

(*E*)-*N*-((2-bromo-2-(cyclohex-1-en-1-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4w)

petroleum ether/ ethyl acetate = 5:1, brown solid, 40% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 1H), 5.96 – 5.92 (m, 1H), 1.98 – 1.88 (m, 2H), 1.52 – 1.35 (m, 4H), 1.32 (s, 9H), 1.30 – 1.19 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 146.4, 140.1, 138.0, 135.0, 133.8, 132.4, 130.8, 129.7, 129.3, 126.4, 125.6, 35.0, 31.1, 26.1, 25.1, 21.2, 20.6.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{27}Br_2NO_3S_2$ [M+H]$^+$: 601.9852, Found: 601.9854.

IR (neat, cm^{-1}): υ 3061, 2939, 2860, 1631, 1583, 1568, 1463, 1364, 1312, 1247, 1149, 1083, 702, 630.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-fluorophenyl)(oxo)-λ^{6}sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4x)

petroleum ether/ ethyl acetate = 5:1, yellow solid, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.49 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.23– 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 7.01 – 6.91 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.0, 164.4, 156.0, 140.8, 140.1, 135.1, 133.4, 131.0 (d, *J* = 9.8 Hz), 130.7, 128.4, 128.1, 126.5, 125.7, 116.5 (d, *J* = 22.9 Hz), 35.0, 31.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.3

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}BrFNO_3S_2$ $[M+Na]^+$: 558.0179, Found: 558.0168.

IR (neat, cm^{-1}): υ 3032, 2963, 2919, 2851, 1587, 1489, 1322, 1292, 1258, 1155, 1006, 841, 787, 627.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4y)

petroleum ether/ ethyl acetate = 5:1, white solid, 77% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.44 (m, 5H), 7.34 – 7.30 (m, 1H), 7.26 – 7.17 (m, 4H), 7.16 – 7.11 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 141.1, 140.7, 140.1, 136.1, 135.1, 133.2, 130.7, 129.4, 129.2, 128.4, 128.1, 126.5, 125.7, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}BrClNO_3S_2$ $[M+H]^+$: 552.0065, Found: 552.0057.

IR (neat, cm^{-1}): υ 3059, 2962, 2869, 1593, 1571, 1472, 1394, 1365, 1317, 1237, 1154, 1096, 627.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(2-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4z)

petroleum ether/ ethyl acetate = 4:1, white solid, 90% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.60 (s, 1H), 7.48 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.21 – 7.16 (m, 1H), 7.10 – 7.04 (m, 5H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 141.0, 139.9, 135.1, 134.8, 134.6, 132.1, 132.0, 131.7, 131.7, 130.6, 128.0, 127.9, 126.9, 126.5, 125.5, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}BrClNO_3S_2$ $[M+H]^+$: 552.0065, Found: 552.0065.

IR (neat, cm^{-1}): υ 3072, 2922, 2854, 1574, 1452, 1359, 1319, 1291, 1262, 1155, 1058, 999, 836, 778.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(2-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4aa)

petroleum ether/ ethyl acetate = 3:1, white solid, 66% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.65 (s, 1H), 7.54 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.19 – 7.14 (m, 1H), 7.11 – 7.03 (m, 5H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 140.8, 139.8, 136.6, 135.2, 134.8, 134.5, 132.0, 132.0, 130.5, 127.9, 127.8, 127.4, 126.5, 125.5, 120.3, 35.0, 31.0.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}Br_2NO_3S_2$ $[M+H]^+$: 597.9539, Found: 597.9523.

IR (neat, cm^{-1}): υ 3032, 2925, 2852, 1604, 1589, 1484, 1399, 1324, 1294, 1236, 1075, 1004, 842, 787.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(3-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4ab)

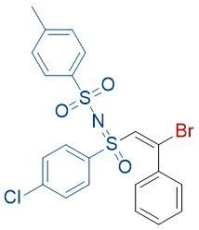
petroleum ether/ ethyl acetate = 5:1, white solid, 80% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.51 – 7.43 (m, 4H), 7.37 – 7.32 (m, 1H), 7.24 – 7.18 (m, 3H), 7.15 – 7.09 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 141.4, 140.0, 139.5, 136.8, 134.8, 133.2, 131.1, 131.0, 130.4, 128.3, 128.1, 126.5, 126.5, 125.7, 122.8, 35.0, 31.1.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{23}Br_2NO_3S_2$ $[M+Na]^+$: 619.9358, Found: 619.9358.

IR (neat, cm^{-1}): υ 3061, 2962, 2926, 2869, 1593, 1571, 1487, 1366, 1321, 1292, 1155, 993, 838, 781.



(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (4ac)

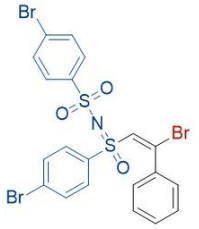
petroleum ether/ ethyl acetate = 5:1, white solid, 64% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.26 – 7.18 (m, 6H), 7.14 – 7.10 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.1, 141.1, 140.7, 140.3, 136.1, 135.1, 133.2, 130.7, 129.4, 129.3, 129.2, 128.4, 128.1, 126.7, 21.5.

HRMS (ESI-TOF): Anal Calcd. For. $C_{21}H_{17}BrClNO_3S_2$ $[M+Na]^+$: 531.9414, Found: 531.9427.

IR (neat, cm^{-1}): υ 3054, 2962, 2921, 2851, 1659, 1571, 1494, 1468, 1315, 1243, 1153, 1085, 1007, 781.



(*E*)-4-bromo-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (4ad)

petroleum ether/ ethyl acetate = 5:1, light yellow solid, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.40 – 7.31 (m, 3H), 7.24 – 7.19 (m, 2H), 7.17 – 7.09 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.2, 141.8, 136.6, 135.0, 132.8, 132.4, 131.9, 130.8, 129.6, 129.3, 128.3, 128.3, 128.1, 127.3.

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{14}Br_3NO_3S_2$ $[M+H]^+$: 619.8018, Found: 619.8022.

IR (neat, cm^{-1}): υ 3091, 3062, 1602, 1588, 1568, 1310, 1292, 1275, 1231, 1150, 1109, 1049, 1001, 840.

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-2-nitrobenzenesulfonamide (4ae)

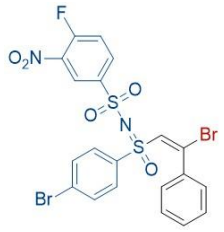
petroleum ether/ ethyl acetate = 3:1, white solid, 89% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 1H), 7.67 – 7.60 (m, 3H), 7.49 (s, 1H), 7.47 – 7.40 (m, 4H), 7.36 – 7.31 (m, 1H), 7.24 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 142.4, 136.3, 135.8, 135.0, 133.3, 132.4, 132.4, 131.8, 130.9, 129.8, 129.7, 129.3, 128.4, 128.1, 123.9.

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{14}Br_2N_2O_5S_2$ $[M+Na]^+$: 608.8583, Found: 608.8579.

IR (neat, cm^{-1}): υ 2923, 2854, 1575, 1452, 1359, 1319, 1291, 1262, 1156, 1059, 999, 921, 797, 778, 629.



(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-fluoro-3-nitrobenzenesulfonamide (4af)

petroleum ether/ ethyl acetate = 5:1, white solid, 83% yield.

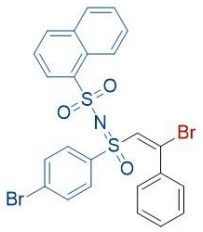
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, *J* = 6.8, 2.4 Hz, 1H), 8.18 – 8.14 (m, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.46 (s, 1H), 7.42 – 7.35 (m, 4H), 7.26 – 7.22 (m, 2H), 7.16 – 7.12 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.6, 155.9, 142.7, 140.4 (d, *J* = 4.6 Hz), 136.3, 135.0, 133.8 (d, *J* = 9.9 Hz), 132.5, 132.4, 131.0, 130.0, 129.3, 128.3 (d, *J* = 6.4 Hz), 125.6 (d, *J* = 2.0 Hz), 119.3, 119.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.7

HRMS (ESI-TOF): Anal Calcd. For. $C_{20}H_{13}Br_2FN_2O_5S_2$ $[M+H]^+$: 604.8669, Found: 604.8670.

IR (neat, cm^{-1}): υ 3096, 3060, 1609, 1593, 1569, 1536, 1348, 1312, 1281, 1265, 1231, 1167, 1138, 1121.



(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)naphthalene-1-sulfonamide (4ag)

petroleum ether/ ethyl acetate = 4:1, light yellow solid, 83% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.94 – 7.85 (m, 4H), 7.62 – 7.55 (m, 2H), 7.48 (s, 1H), 7.40 – 7.34 (m, 4H), 7.31 – 7.26 (m, 1H), 7.18 – 7.10 (m, 4H).

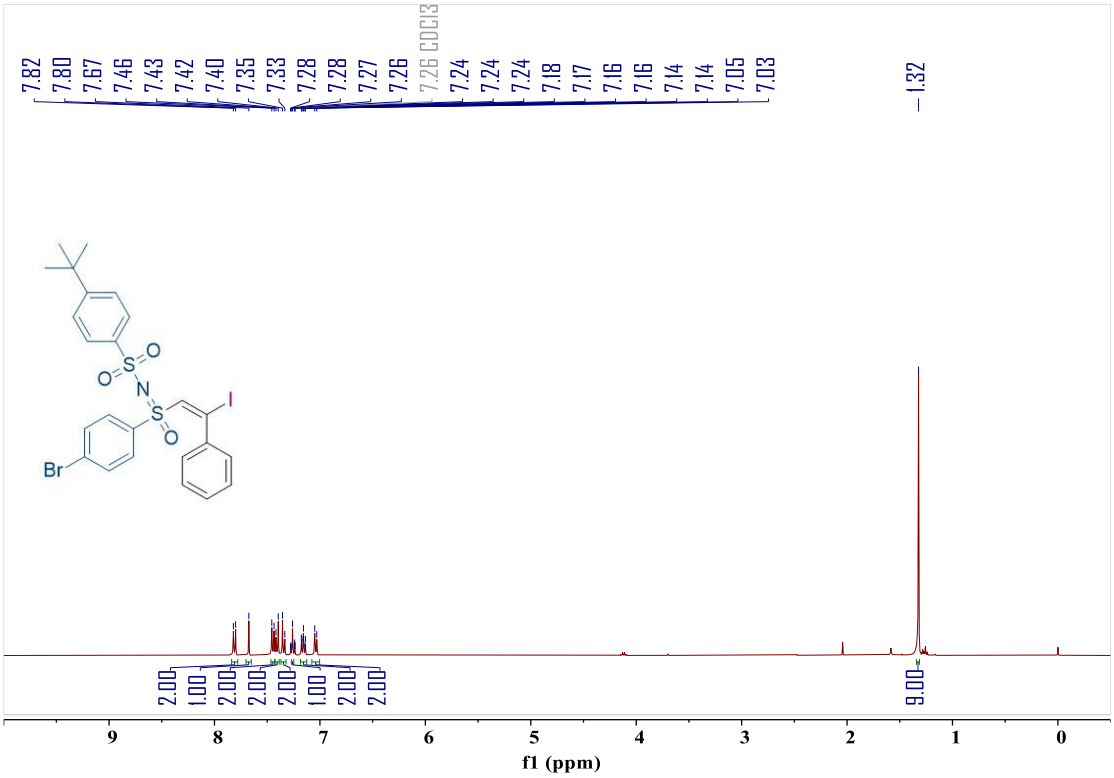
^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.4, 139.8, 136.5, 135.0, 134.6, 132.8, 132.2, 131.9, 130.7, 129.4, 129.3, 129.3, 129.0, 128.5, 128.3, 128.0, 127.8, 127.5, 127.2, 122.3.

HRMS (ESI-TOF): Anal Calcd. For. $C_{24}H_{17}Br_2NO_3S_2$ $[M+H]^+$: 591.9069, Found: 591.9073.

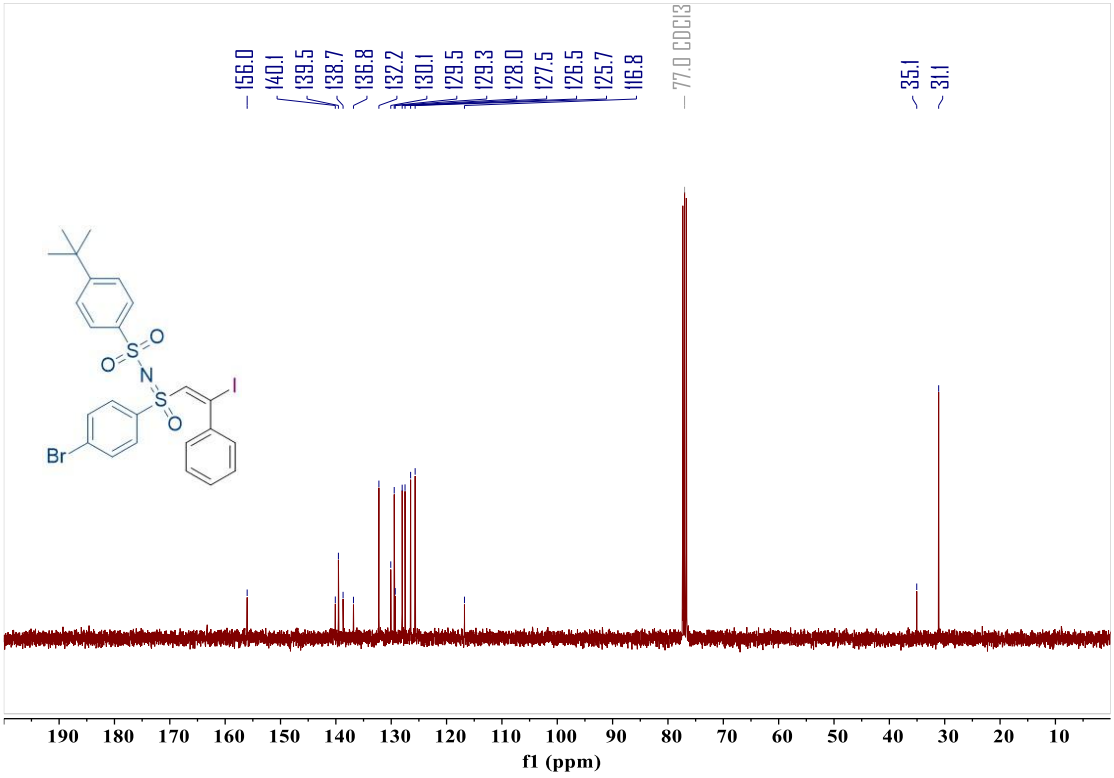
IR (neat, cm^{-1}): υ 3095, 3064, 2921, 2850, 1610, 1589, 1568, 1485, 1389, 1307, 1267, 1153, 1004, 814.

Spectra

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3a)

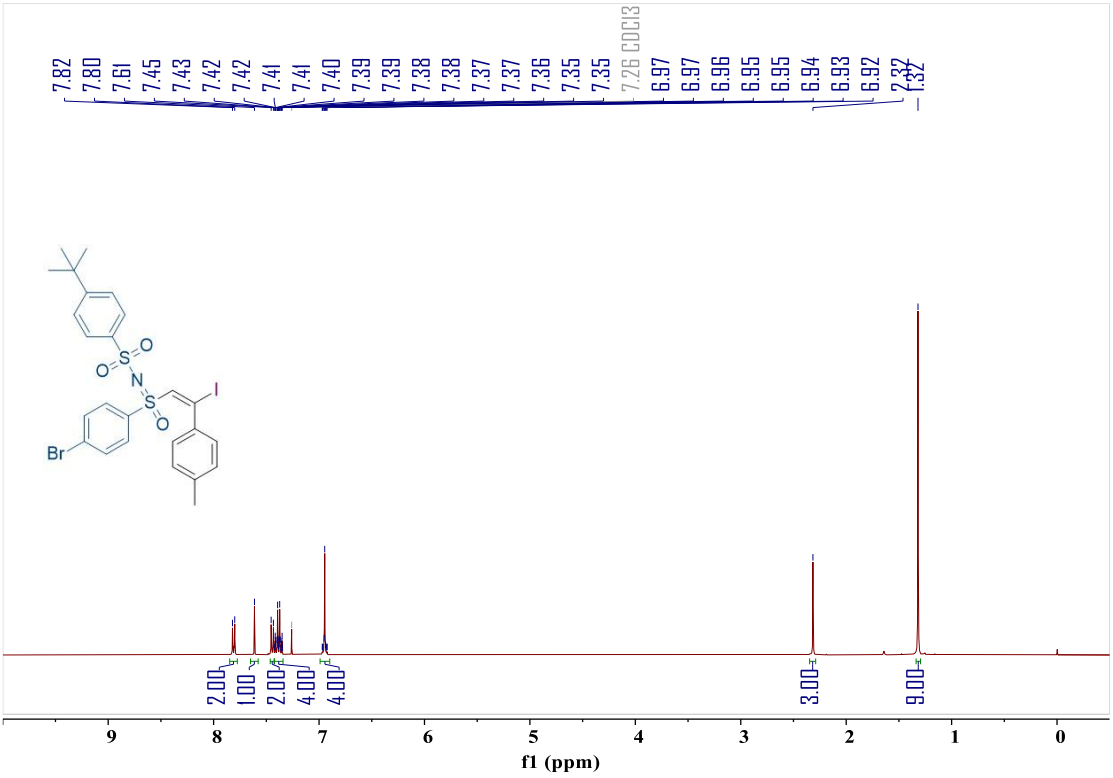


^{1}H NMR (400 MHz, $CDCl_3$)

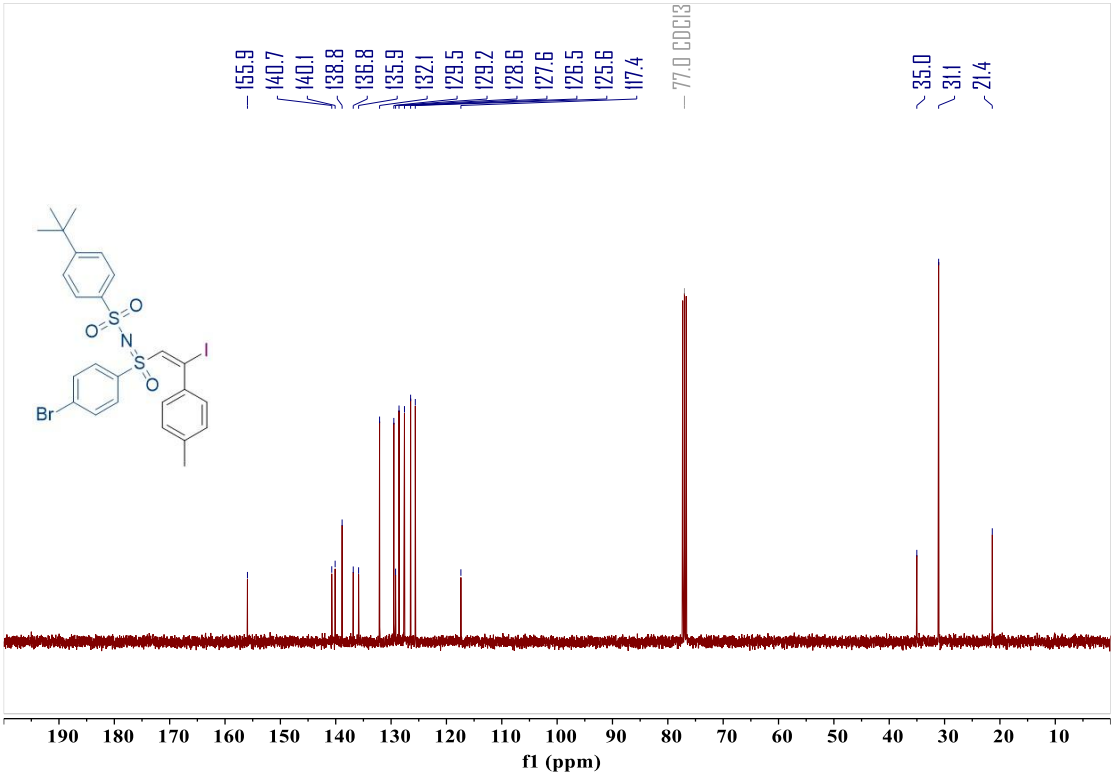


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(p-tolyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzeneesulfonamide (3b)

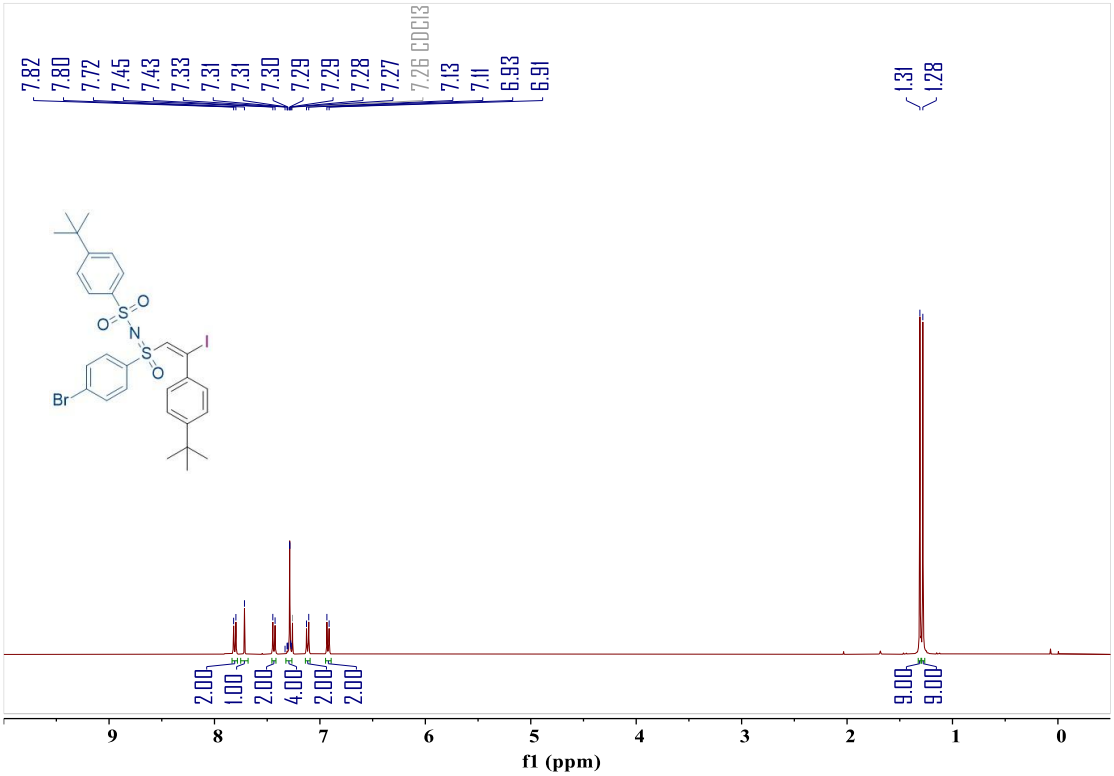


^{1}H NMR (400 MHz, $CDCl_3$)

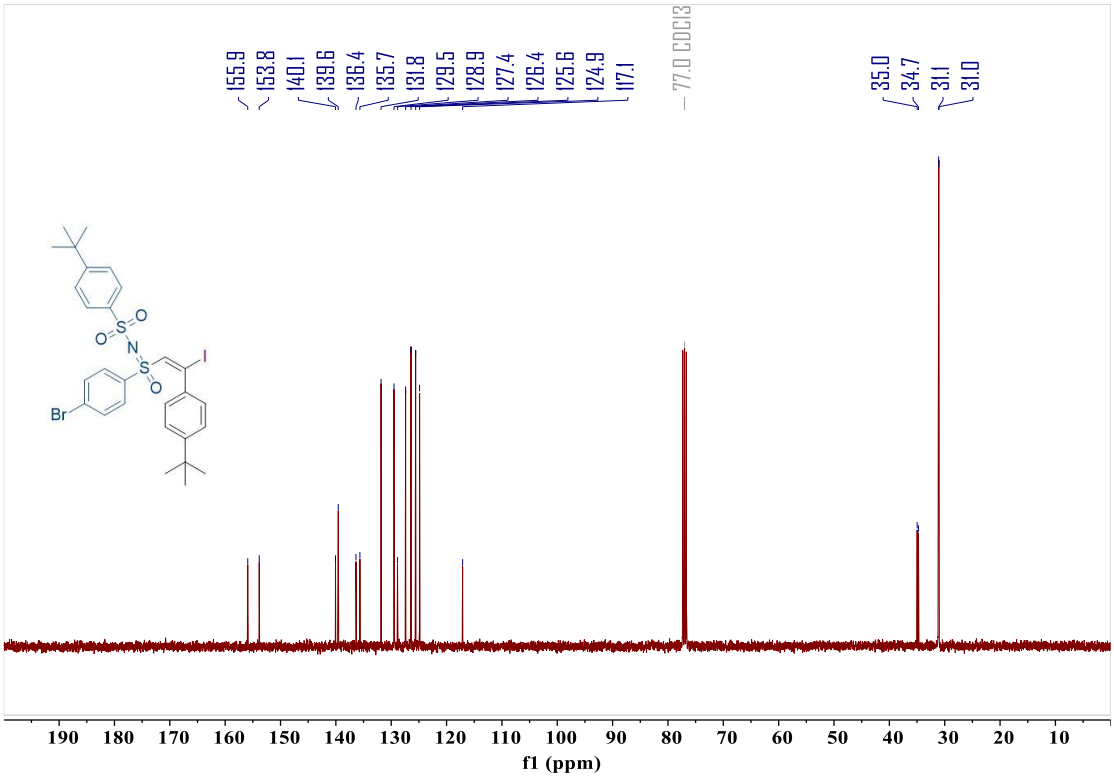


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-(4-(*tert*-butyl)phenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3c)

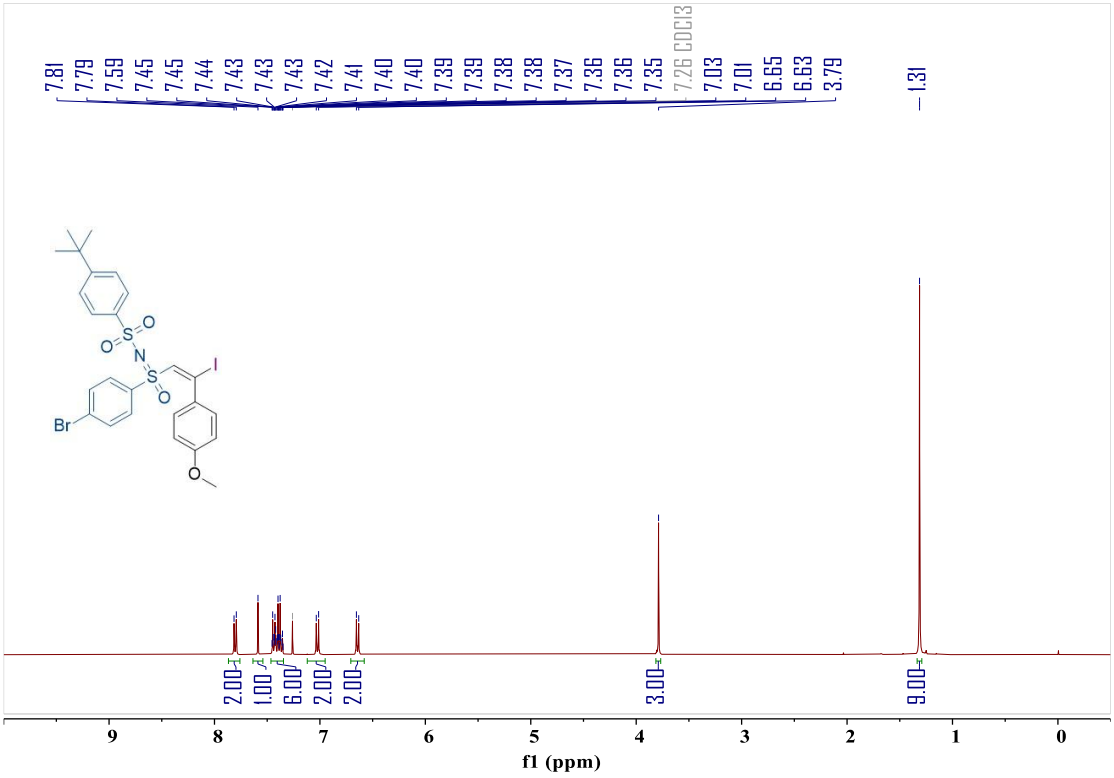


^{1}H NMR (400 MHz, $CDCl_3$)

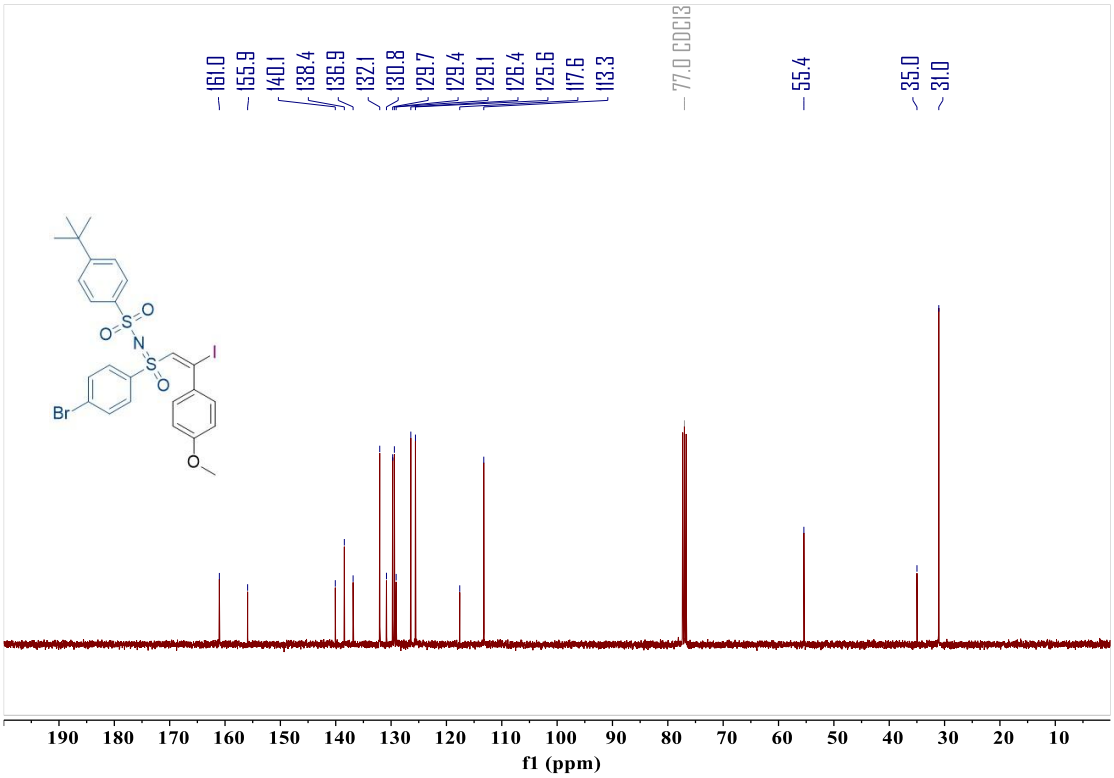


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-methoxyphenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3d)

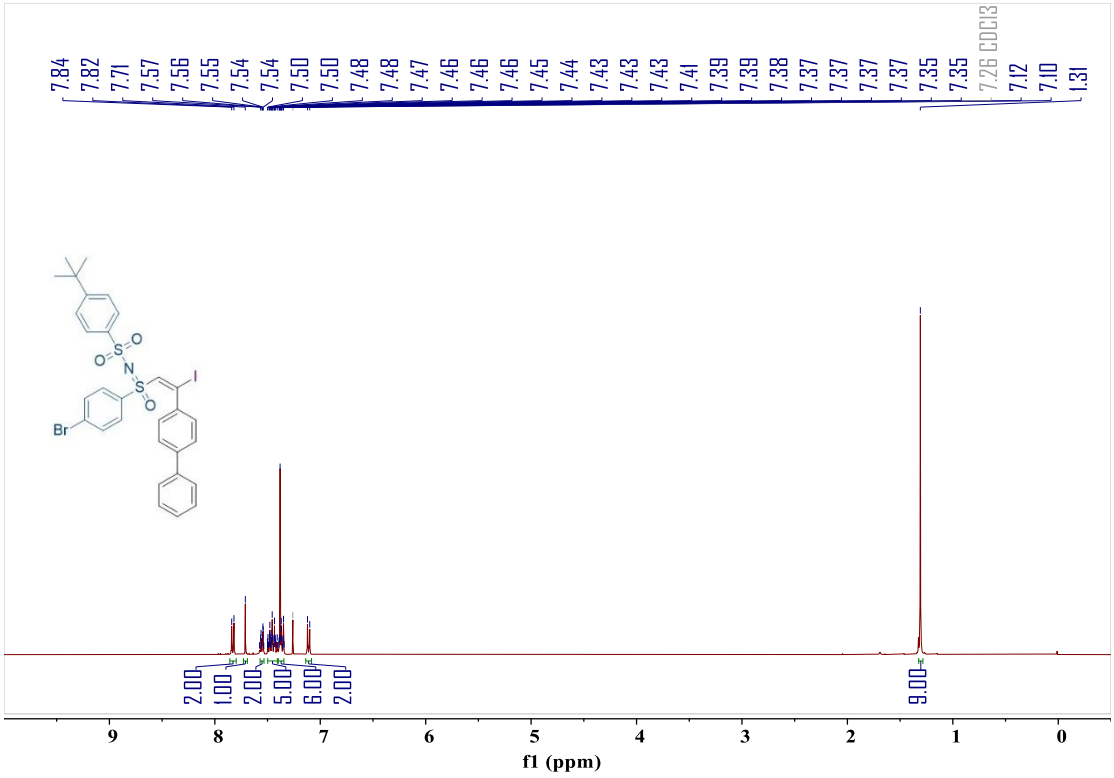


^{1}H NMR (400 MHz, $CDCl_3$)

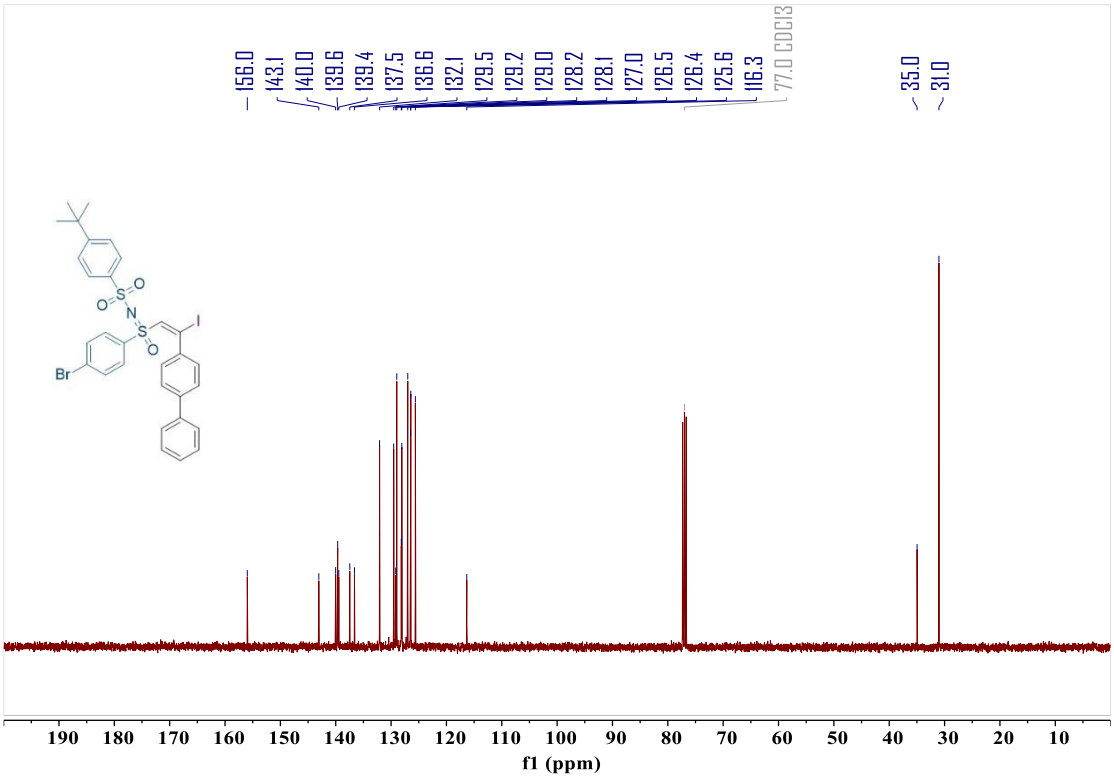


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-([1,1'-biphenyl]-4-yl)-2-iodovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3e)

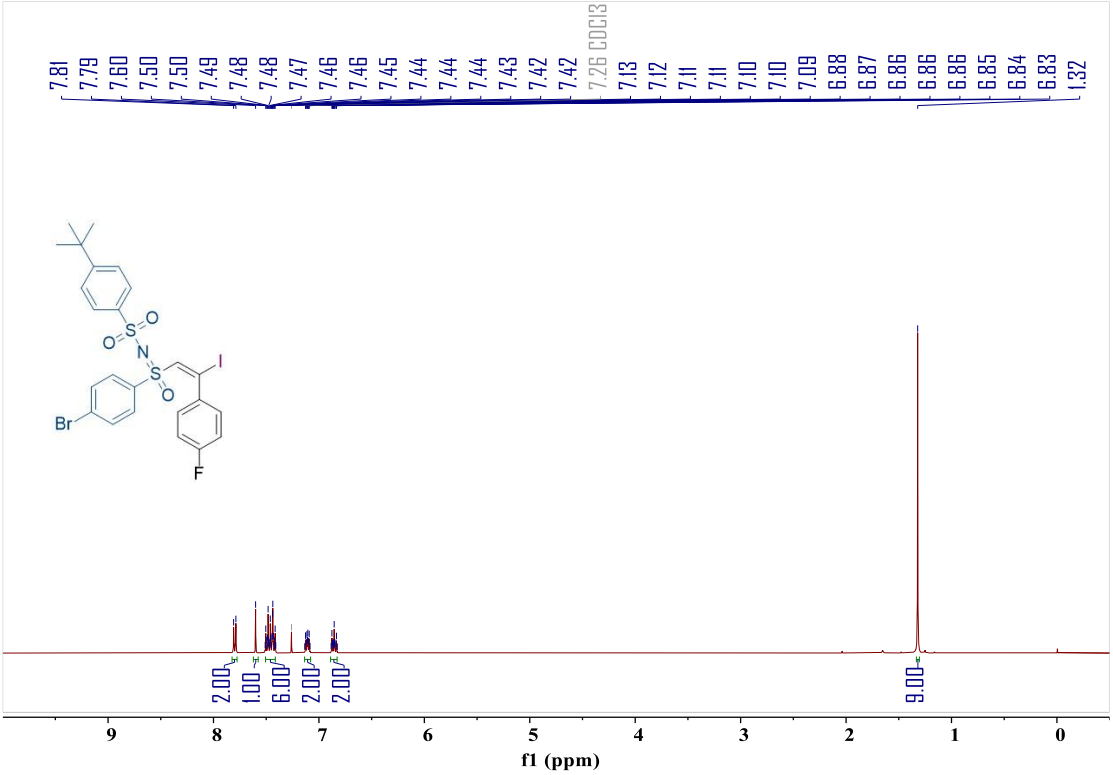


^{1}H NMR (400 MHz, $CDCl_3$)

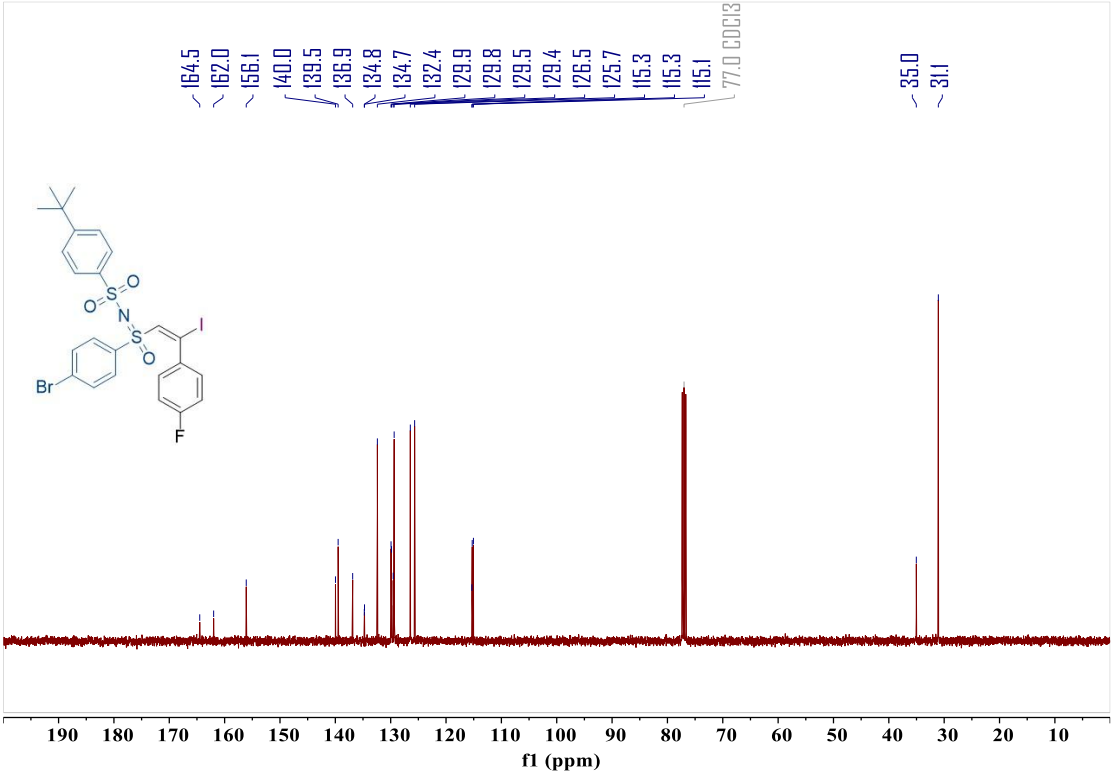


^{13}C NMR (100 MHz, $CDCl_3$)

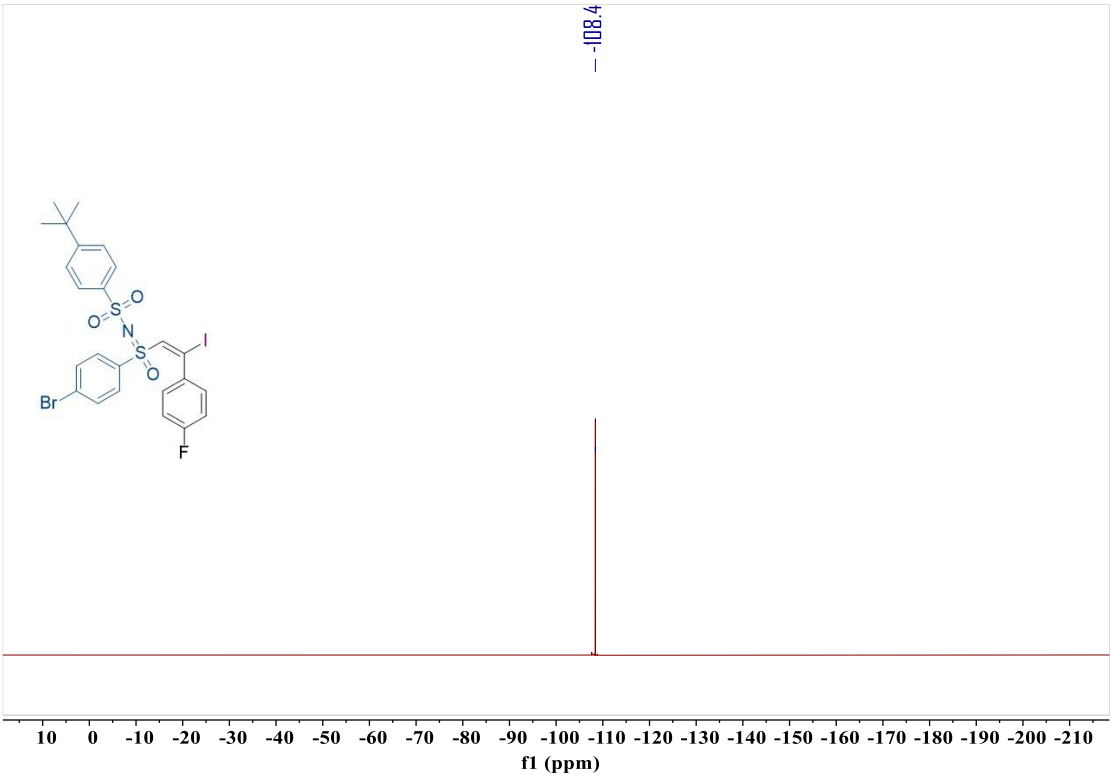
(*E*)-*N*-((4-bromophenyl)(2-(4-fluorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)ben zeneesulfonamide (3f)



^{1}H NMR (400 MHz, $CDCl_3$)

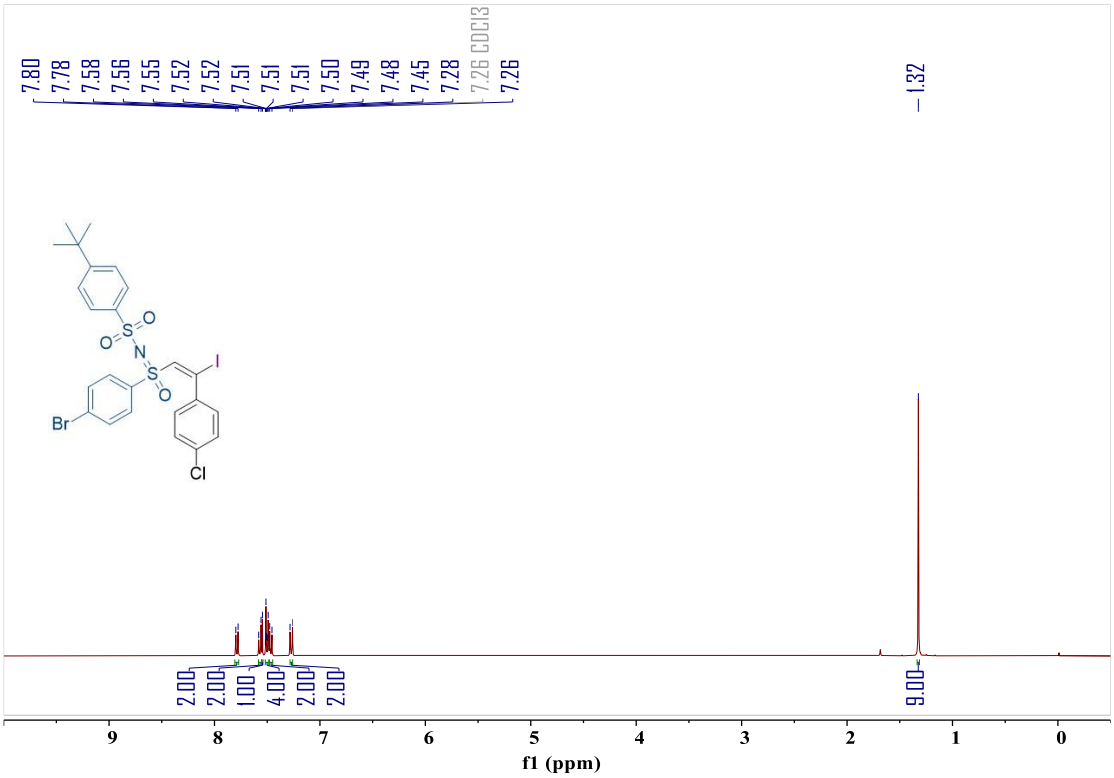


^{13}C NMR (100 MHz, $CDCl_3$)

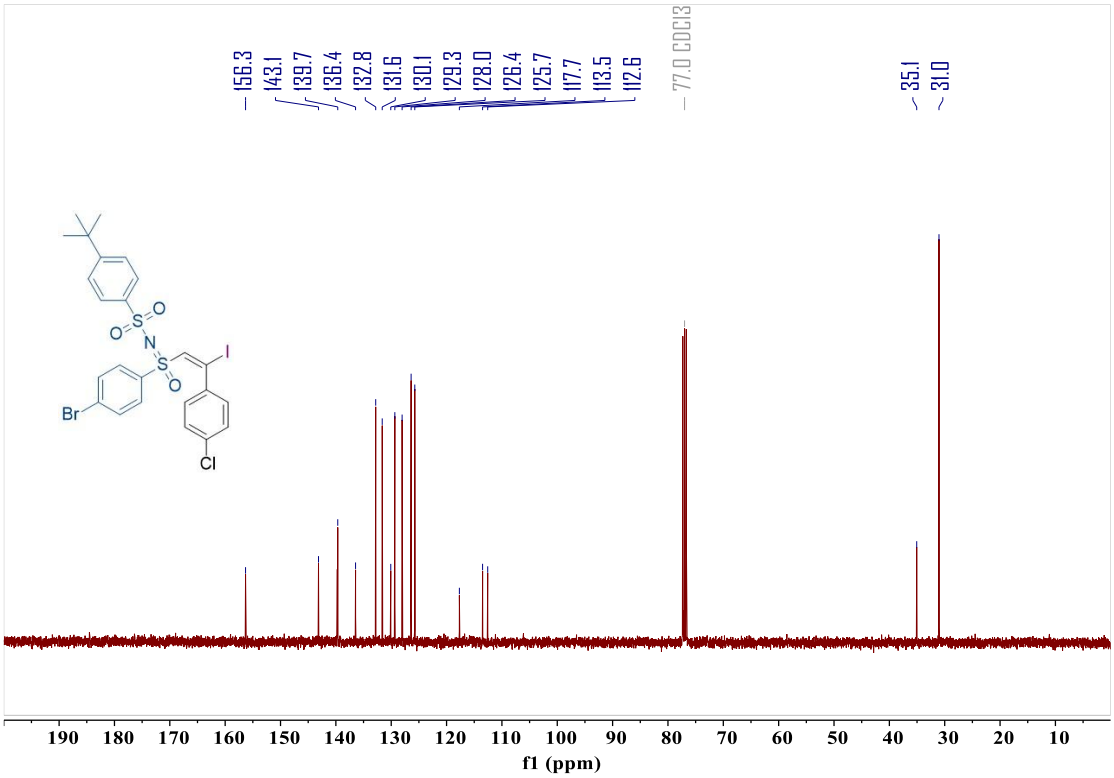


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-(4-chlorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3g)

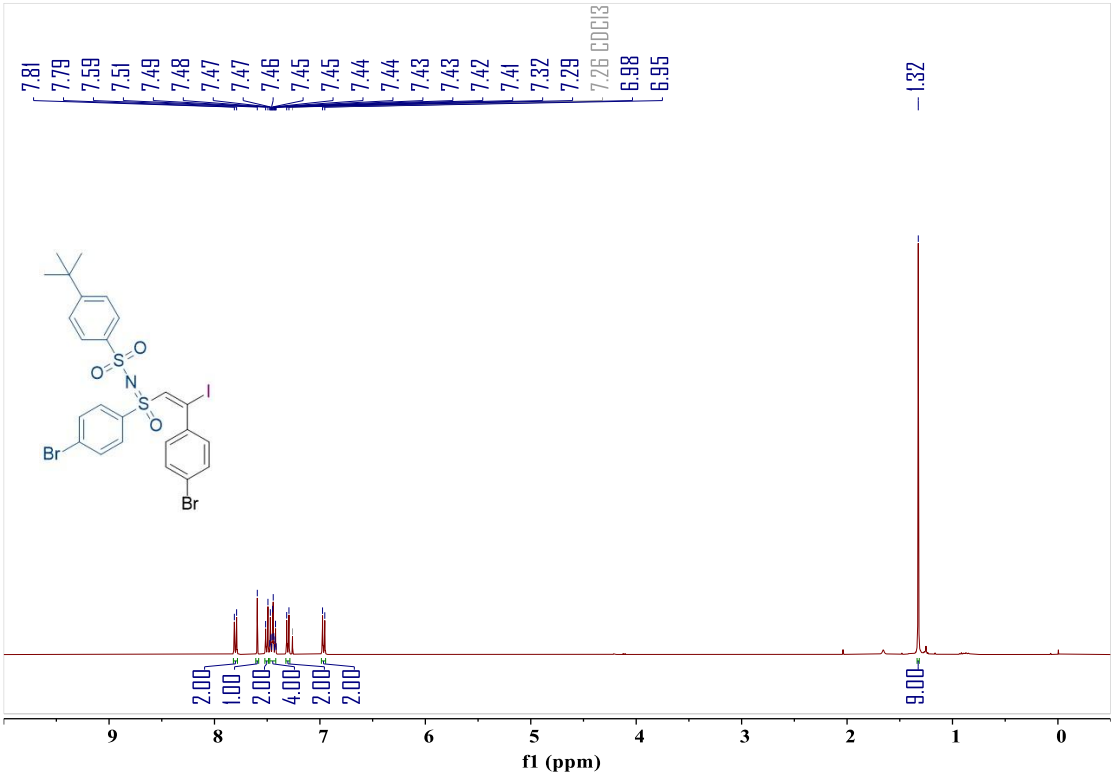


^{1}H NMR (400 MHz, $CDCl_3$)

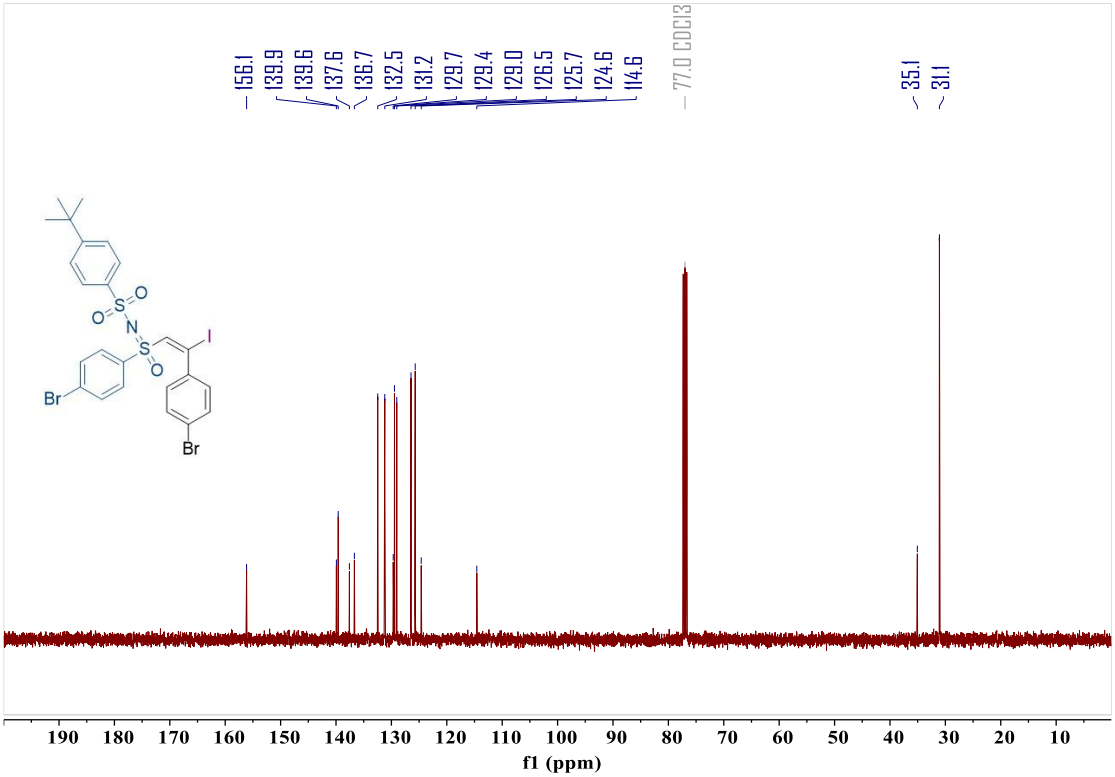


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-(4-bromophenyl)-2-iodovinyl)(oxo)- λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3h)

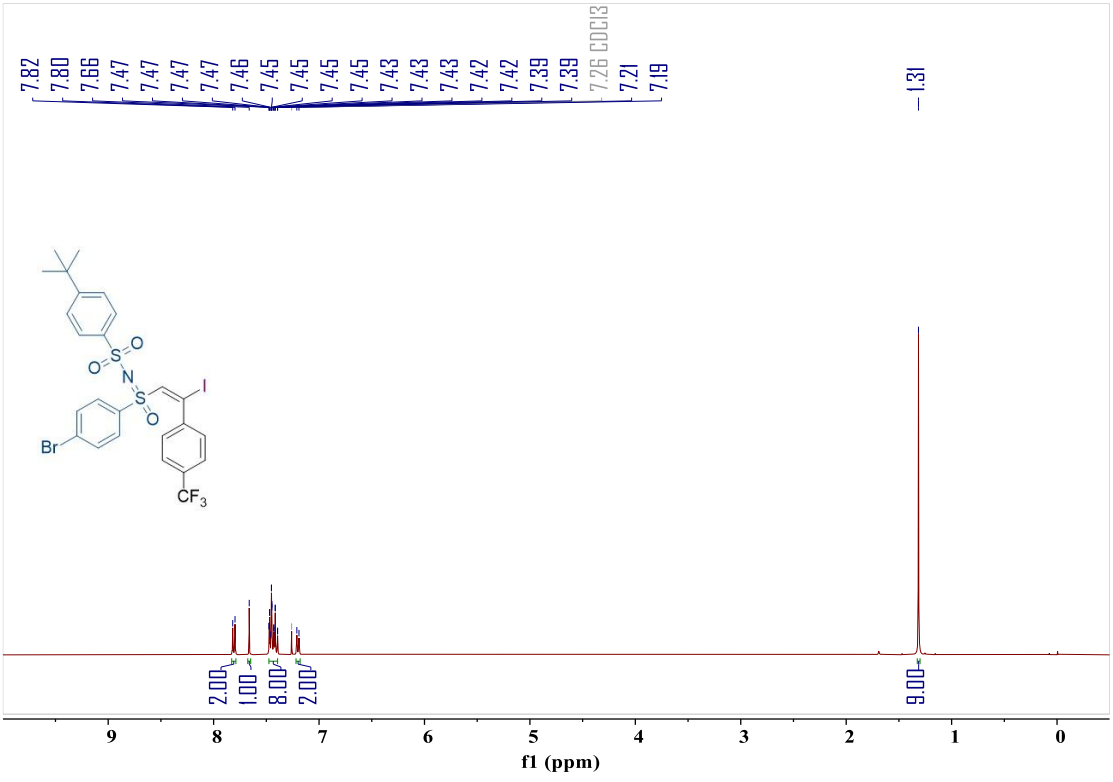


^{1}H NMR (400 MHz, $CDCl_3$)

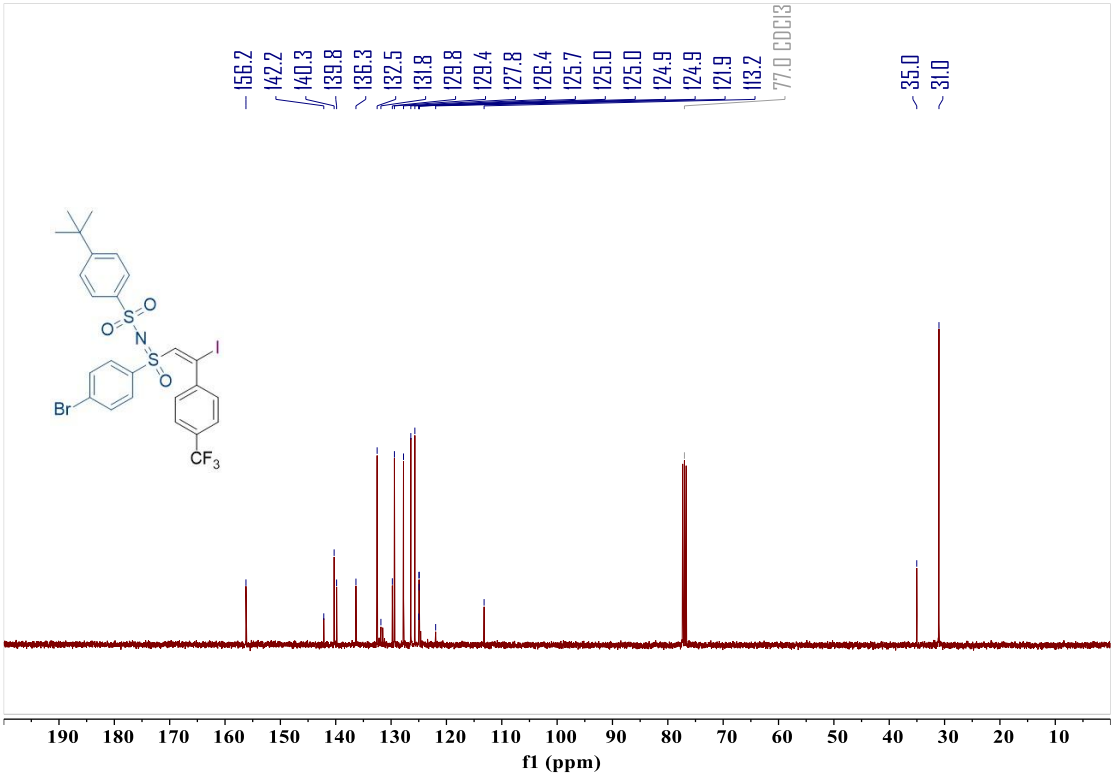


^{13}C NMR (100 MHz, $CDCl_3$)

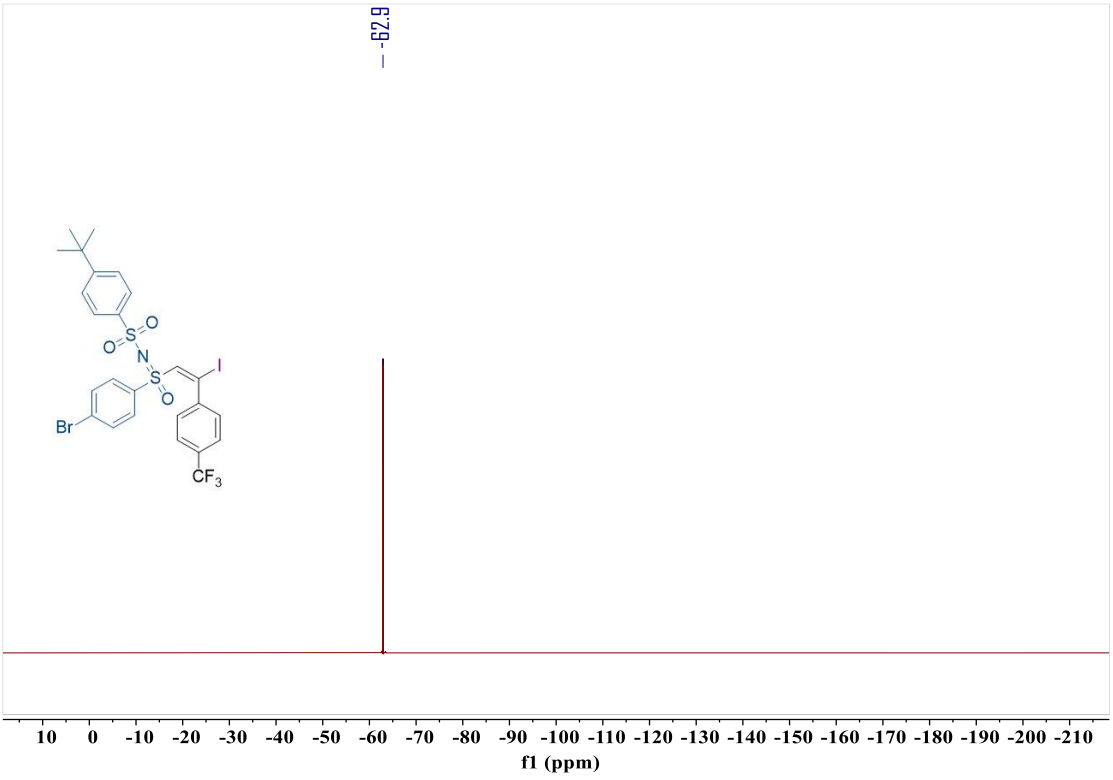
(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-(trifluoromethyl)phenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3i)



^{1}H NMR (400 MHz, $CDCl_3$)

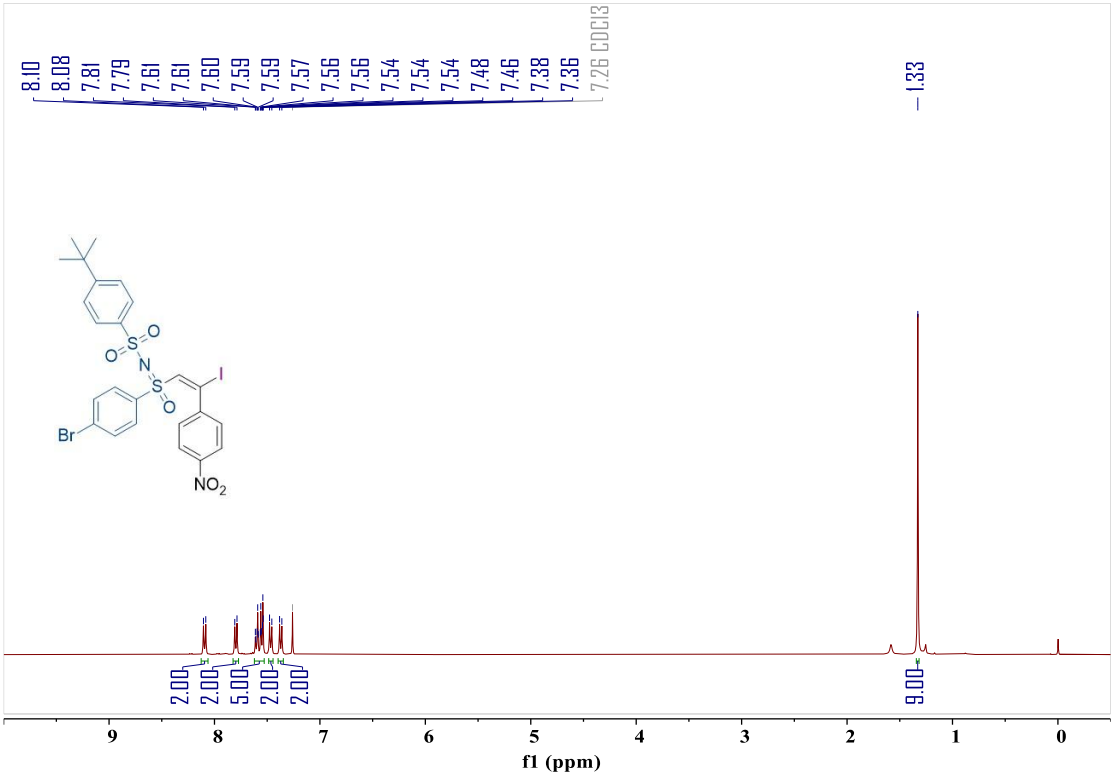


^{13}C NMR (100 MHz, $CDCl_3$)

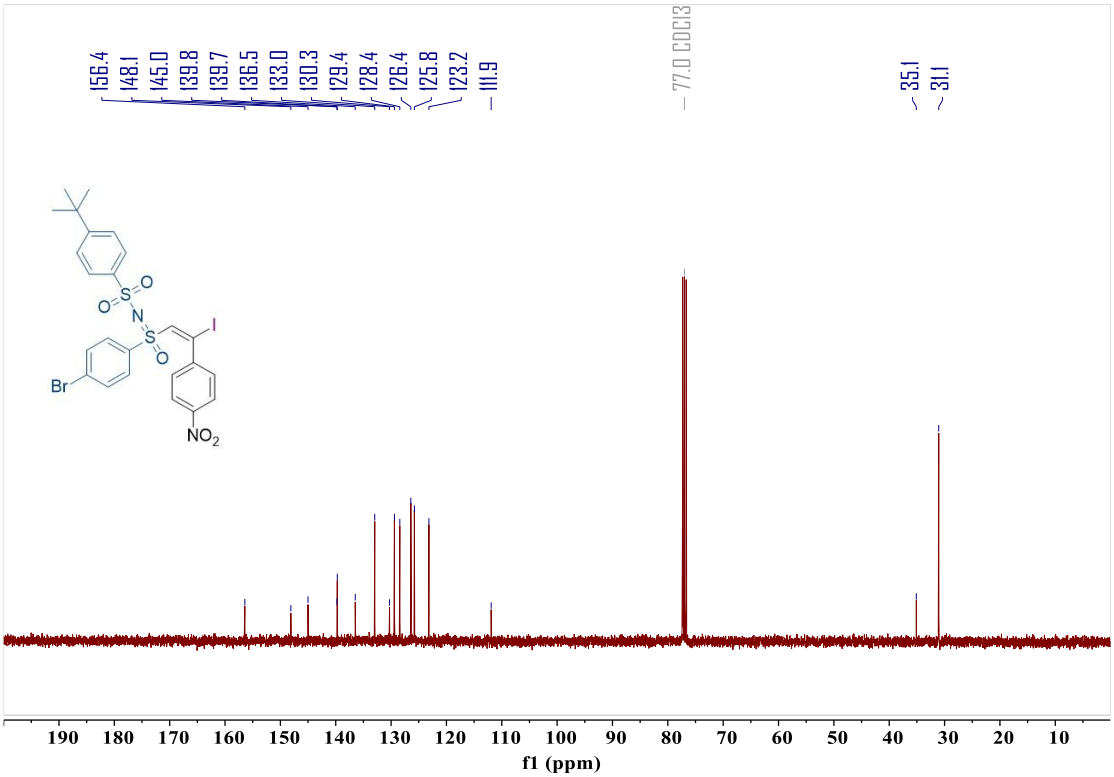


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(4-nitrophenyl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)ben zeneesulfonamide (3j)

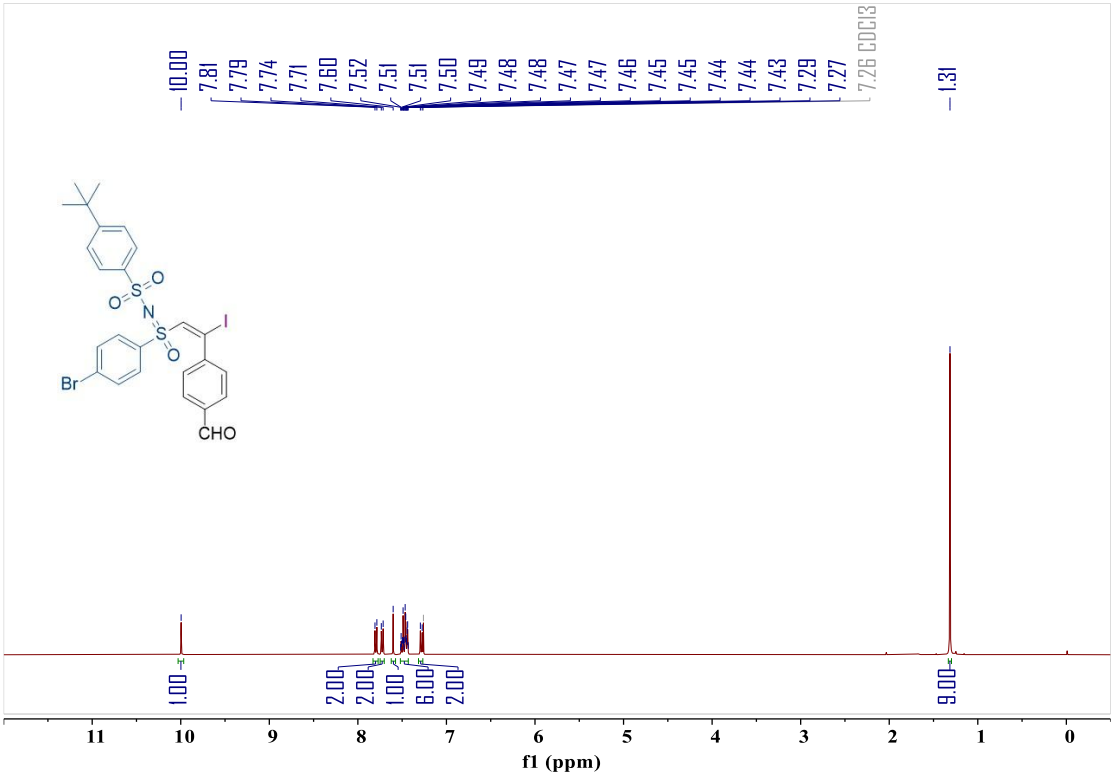


^{1}H NMR (400 MHz, $CDCl_3$)

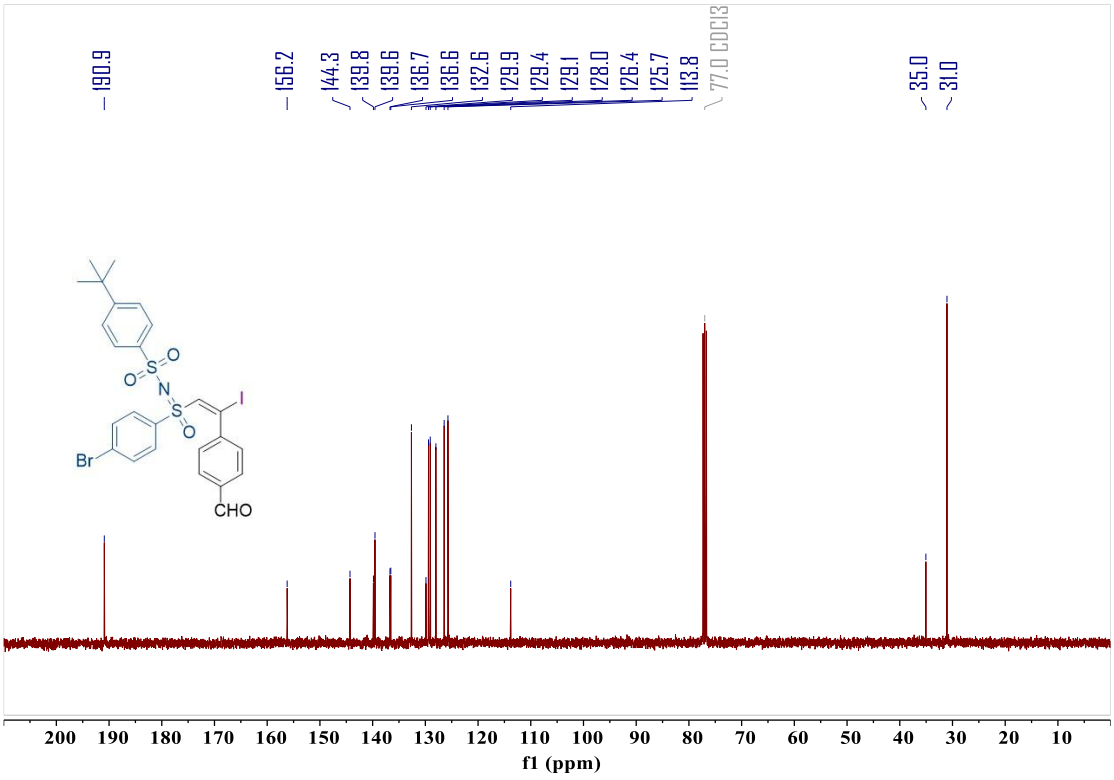


^{13}C NMR (100 MHz, $CDCl_3$)

***(E)*-*N*-((4-bromophenyl)(2-(4-formylphenyl)-2-iodovinyl)(oxo)- λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3k)**

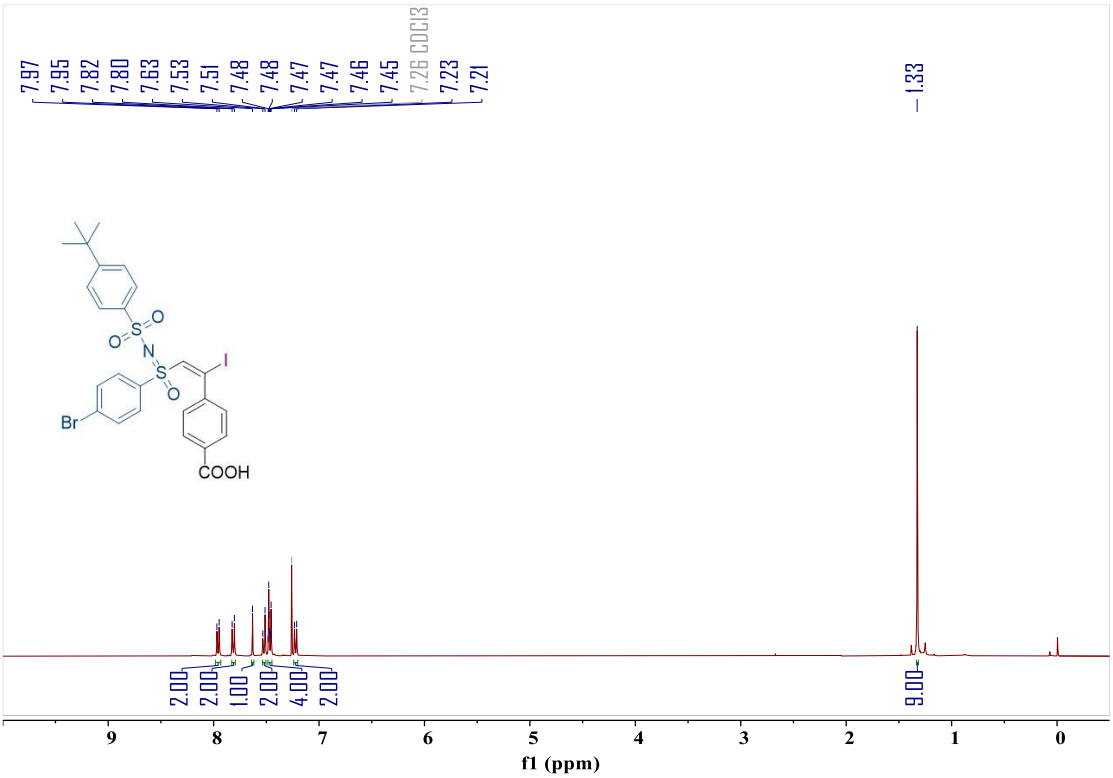


^{1}H NMR (400 MHz, $CDCl_3$)

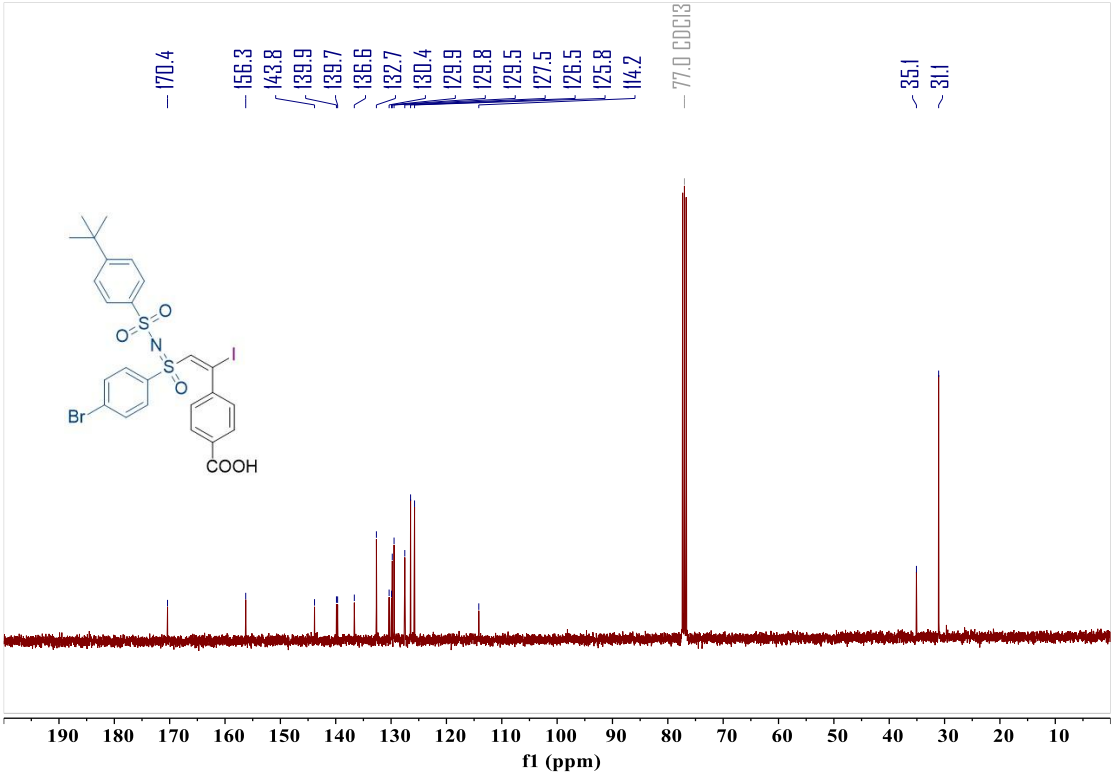


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-4-(2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)-1-iodovinyl)benzoicacid (3l)

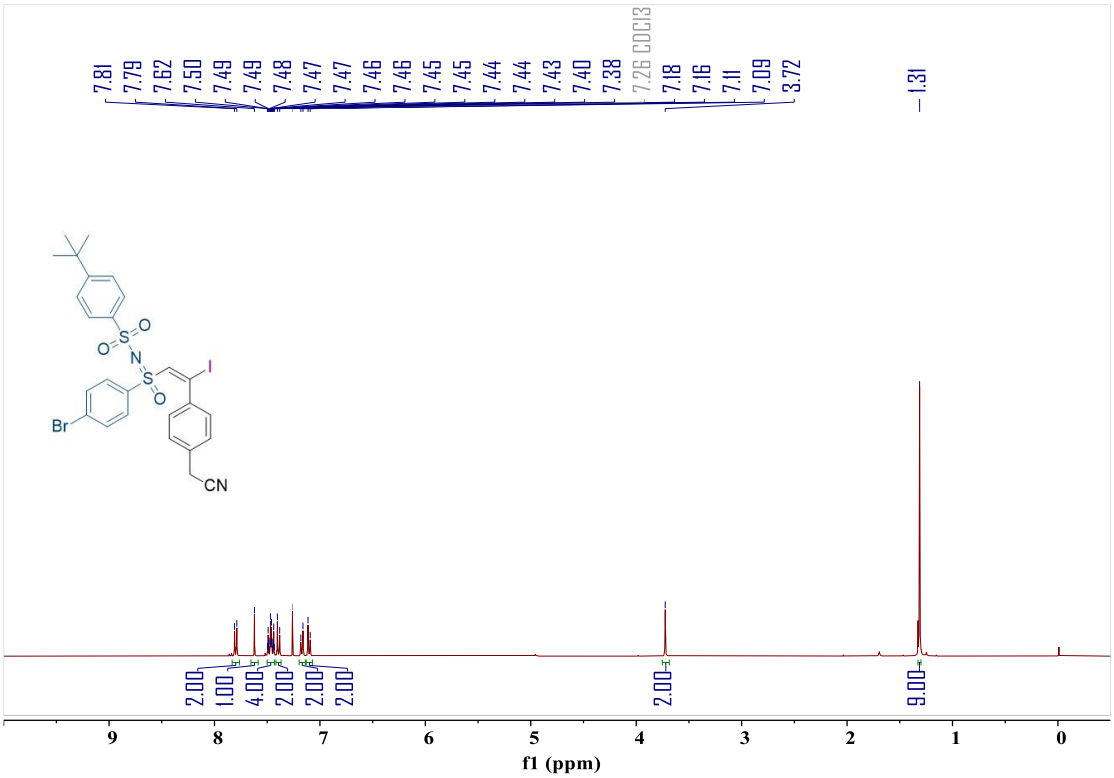


^{1}H NMR (400 MHz, $CDCl_3$)

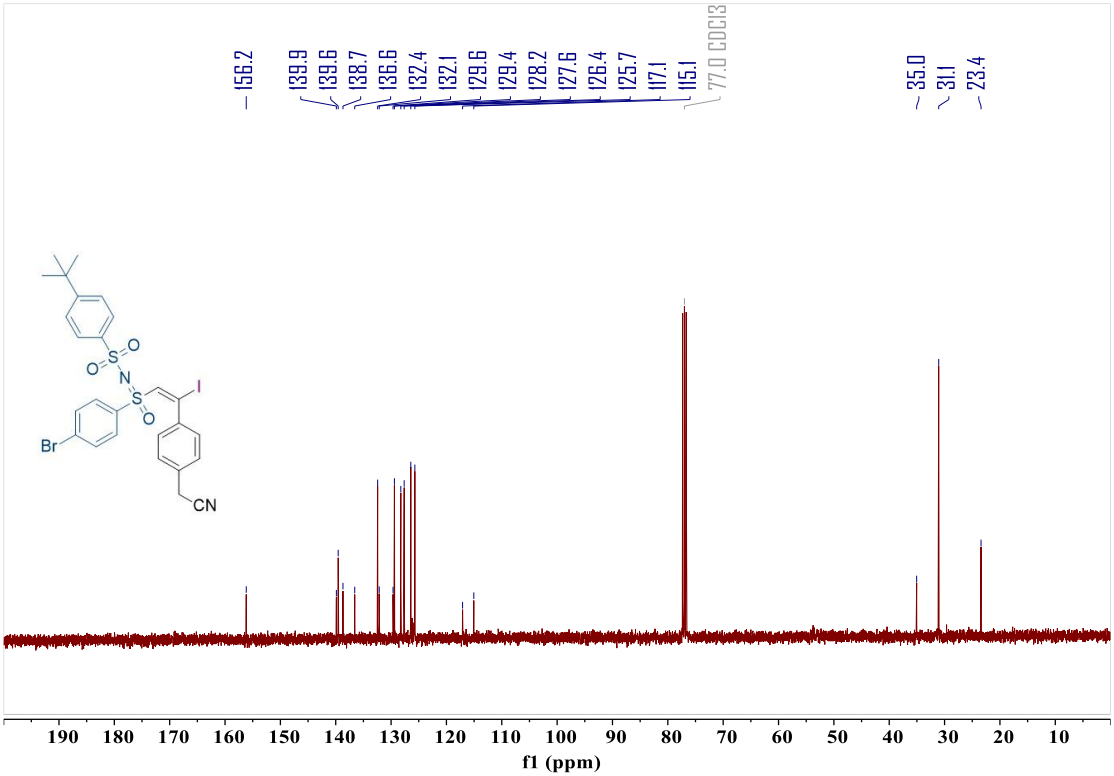


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-(4-(cyanomethyl)phenyl)-2-iodovinyl)(oxo)- λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3m)

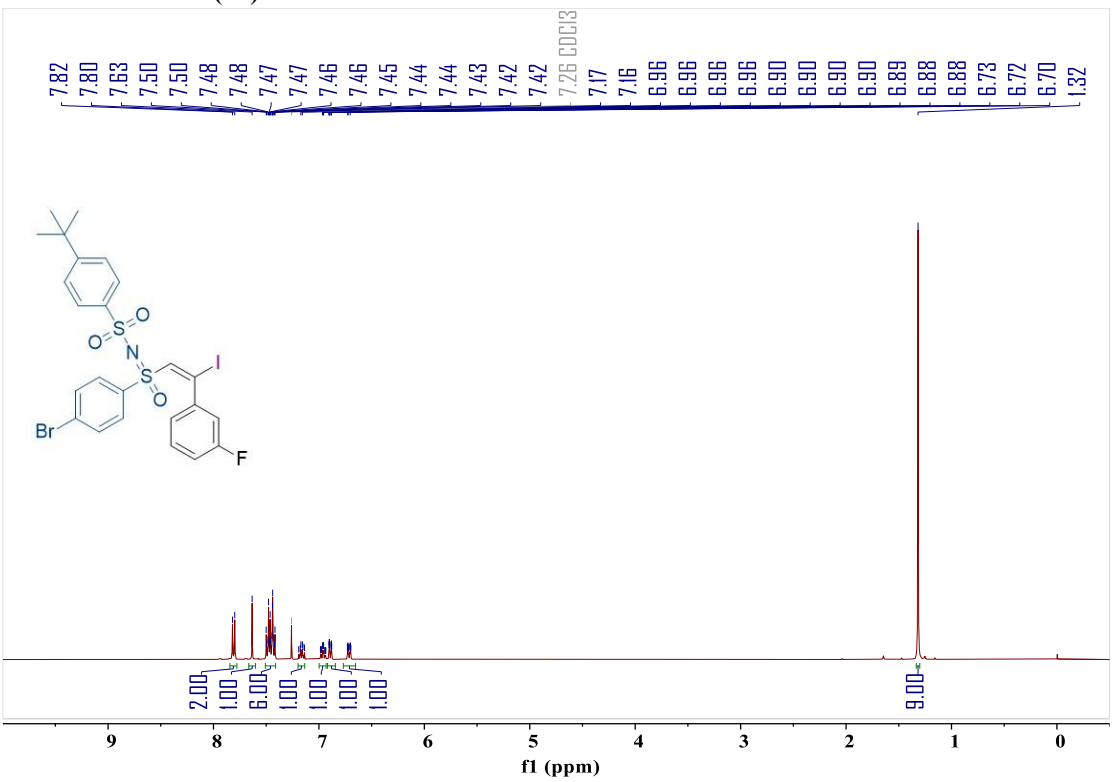


^{1}H NMR (400 MHz, $CDCl_3$)

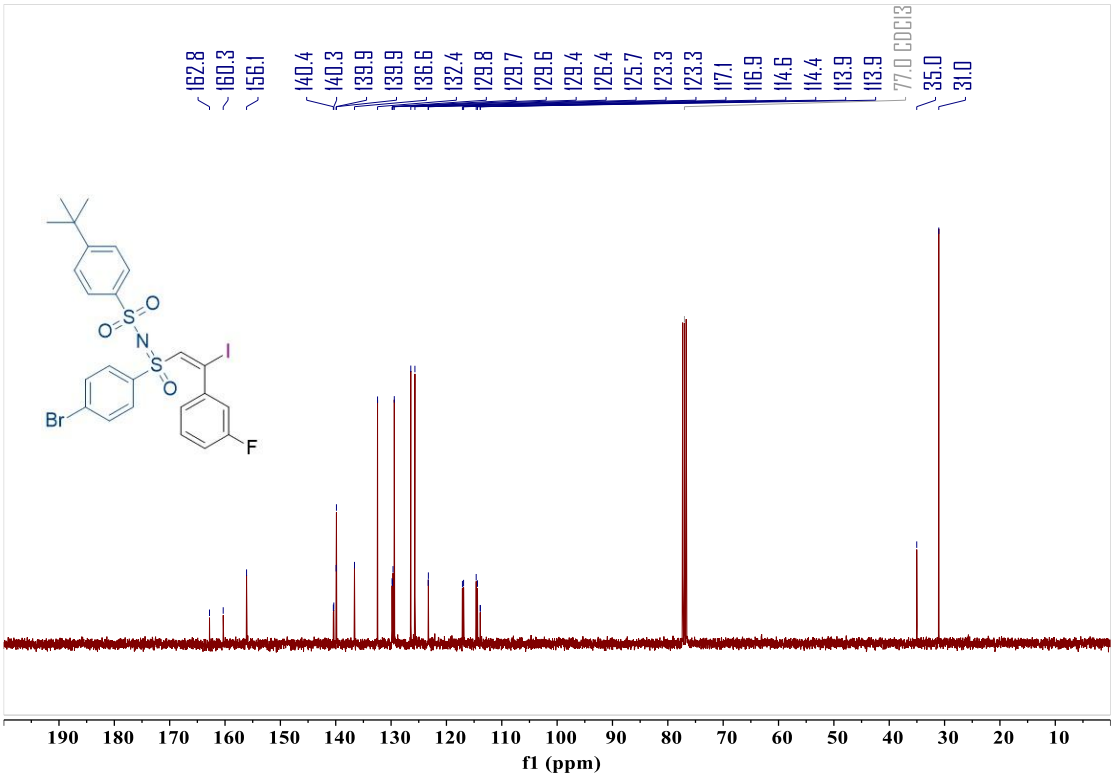


^{13}C NMR (100 MHz, $CDCl_3$)

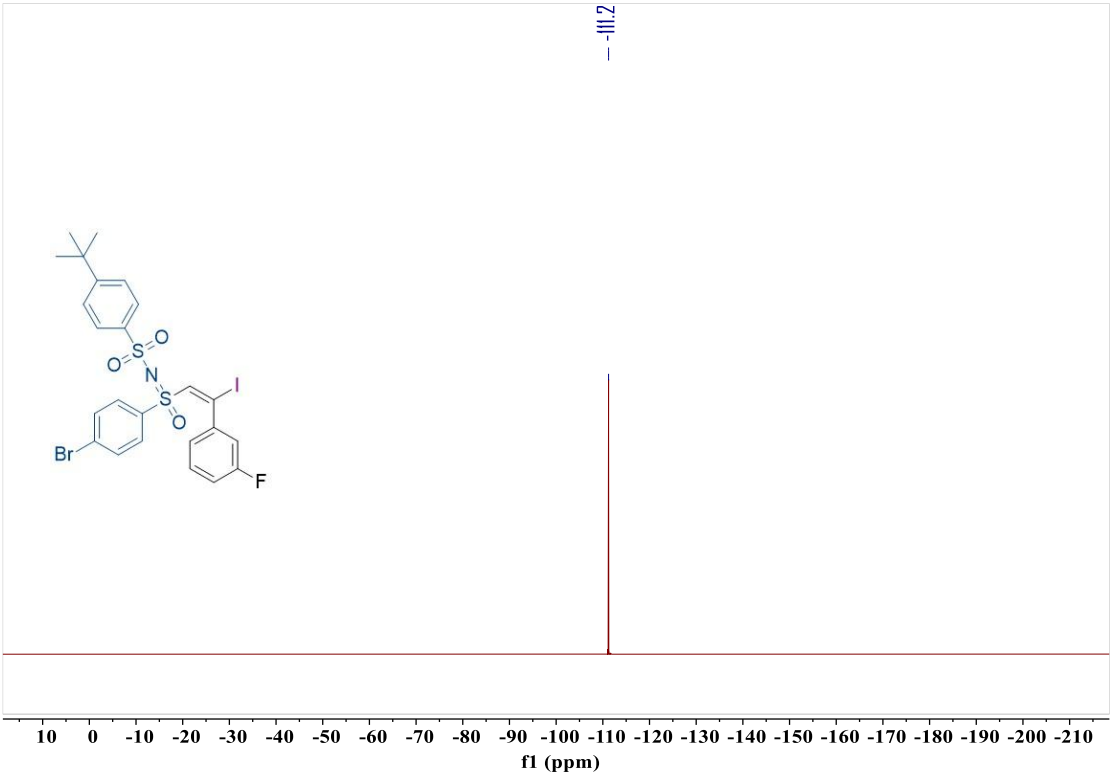
(*E*)-*N*-((4-bromophenyl)(2-(3-fluorophenyl)-2-iodovinyl)(oxo)- λ^6--sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3n)



^{1}H NMR (400 MHz, $CDCl_3$)

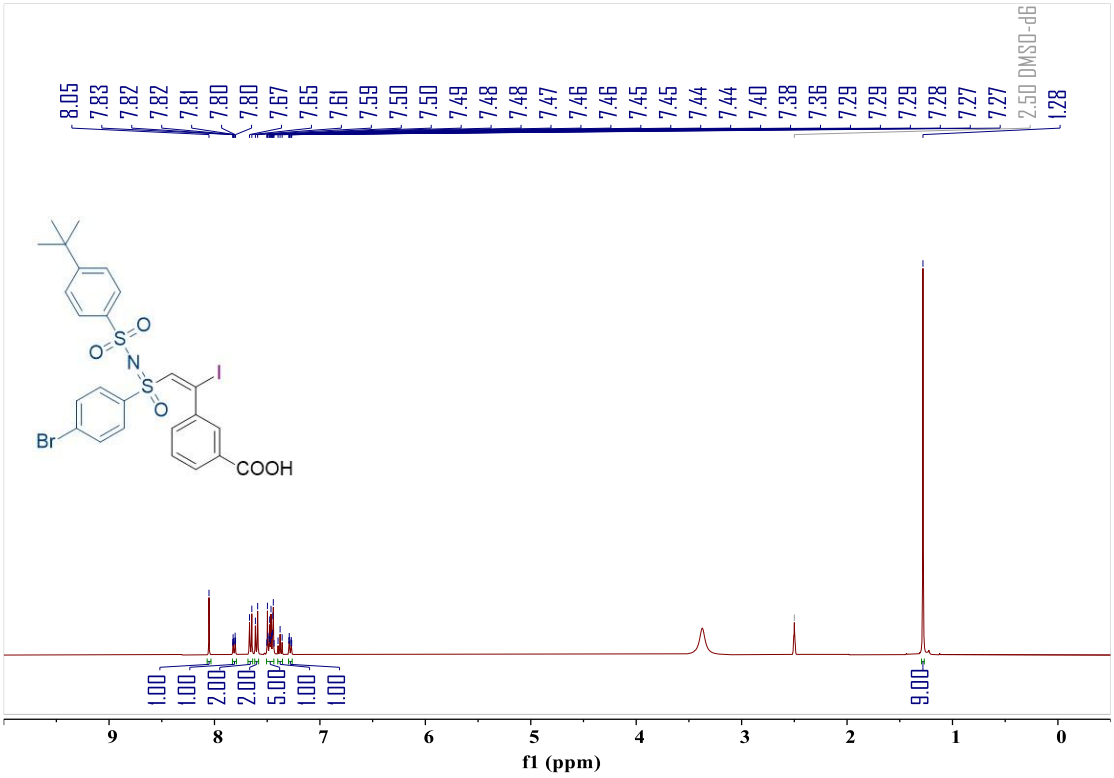


^{13}C NMR (100 MHz, $CDCl_3$)

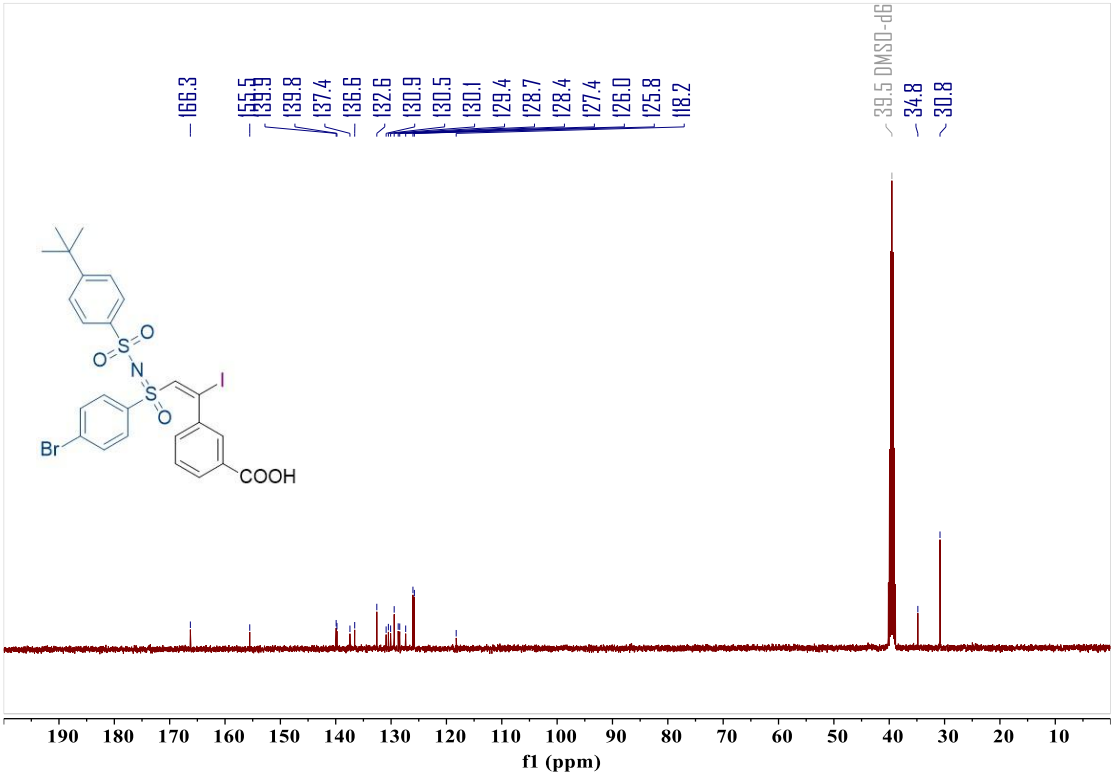


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-3-(2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)-1-iodovinyl)benzoicacid (3o)

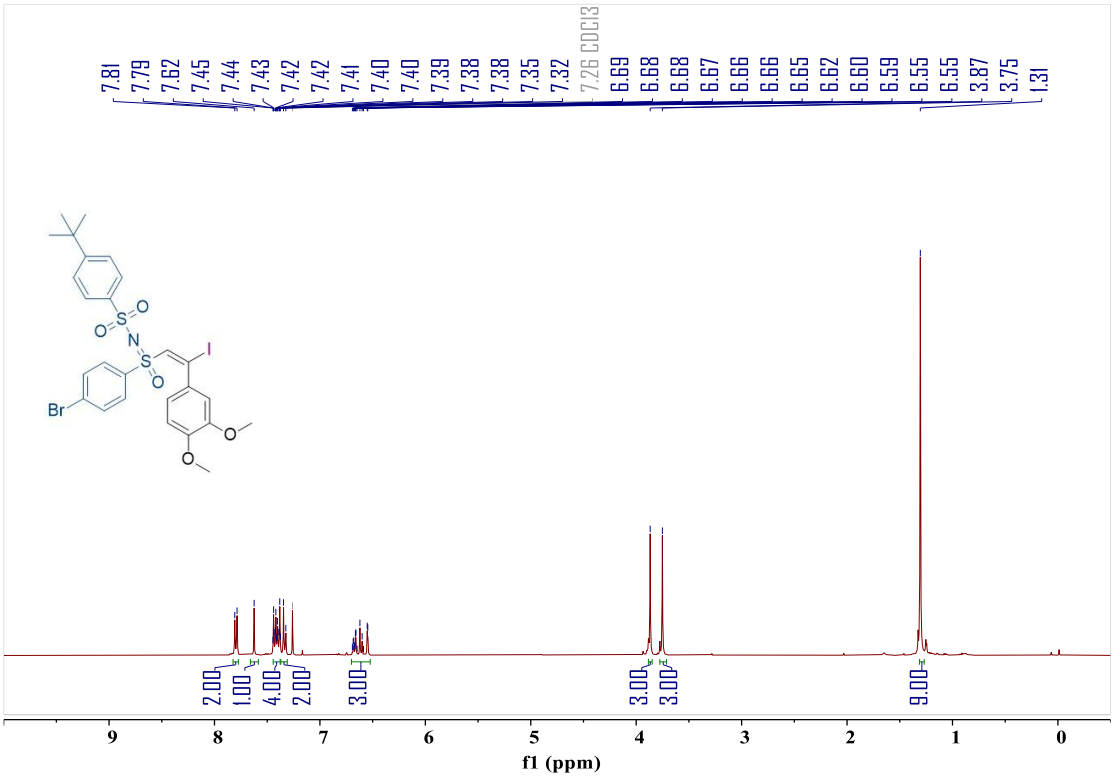


^{1}H NMR (400 MHz, DMSO-d_6)

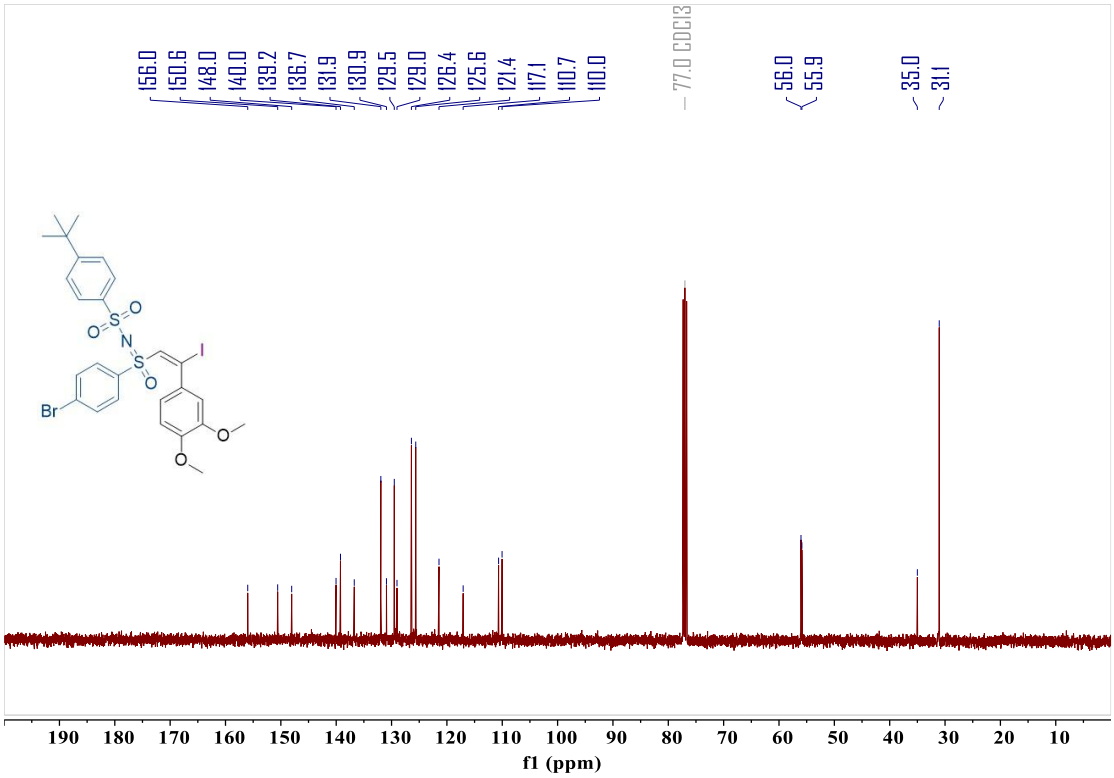


^{13}C NMR (100 MHz, DMSO-d_6)

(*E*)-*N*-((4-bromophenyl)(2-(3,4-dimethoxyphenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3p)

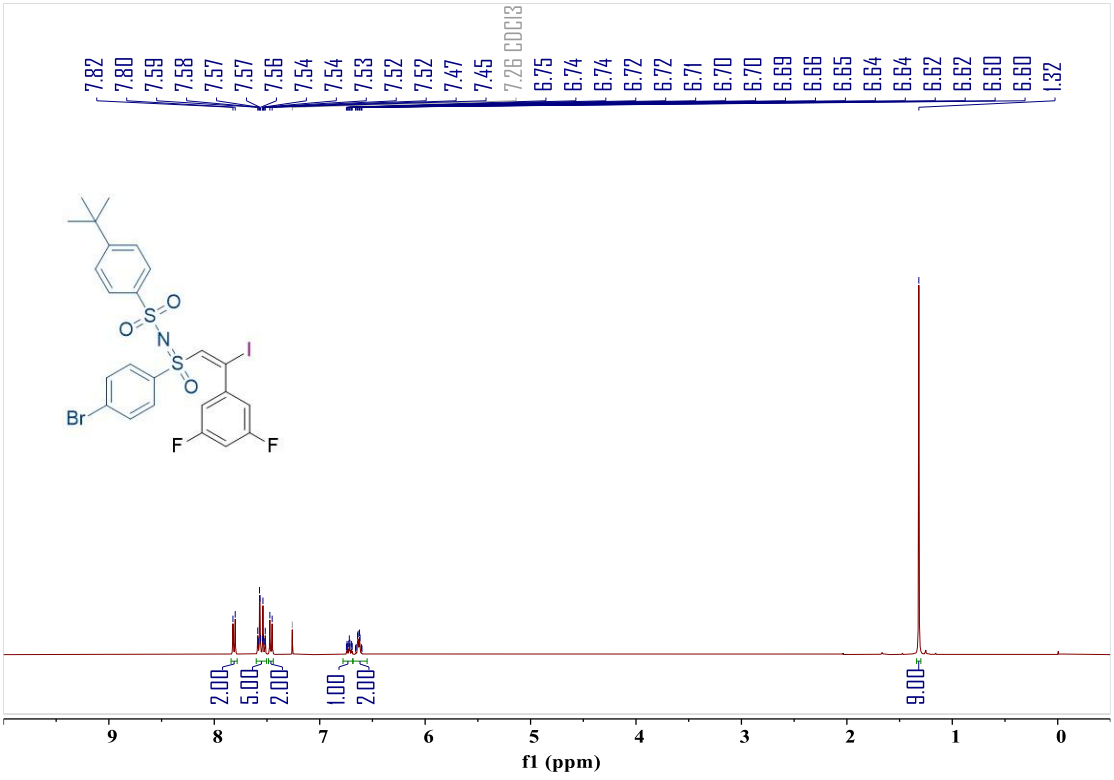


^{1}H NMR (400 MHz, $CDCl_3$)

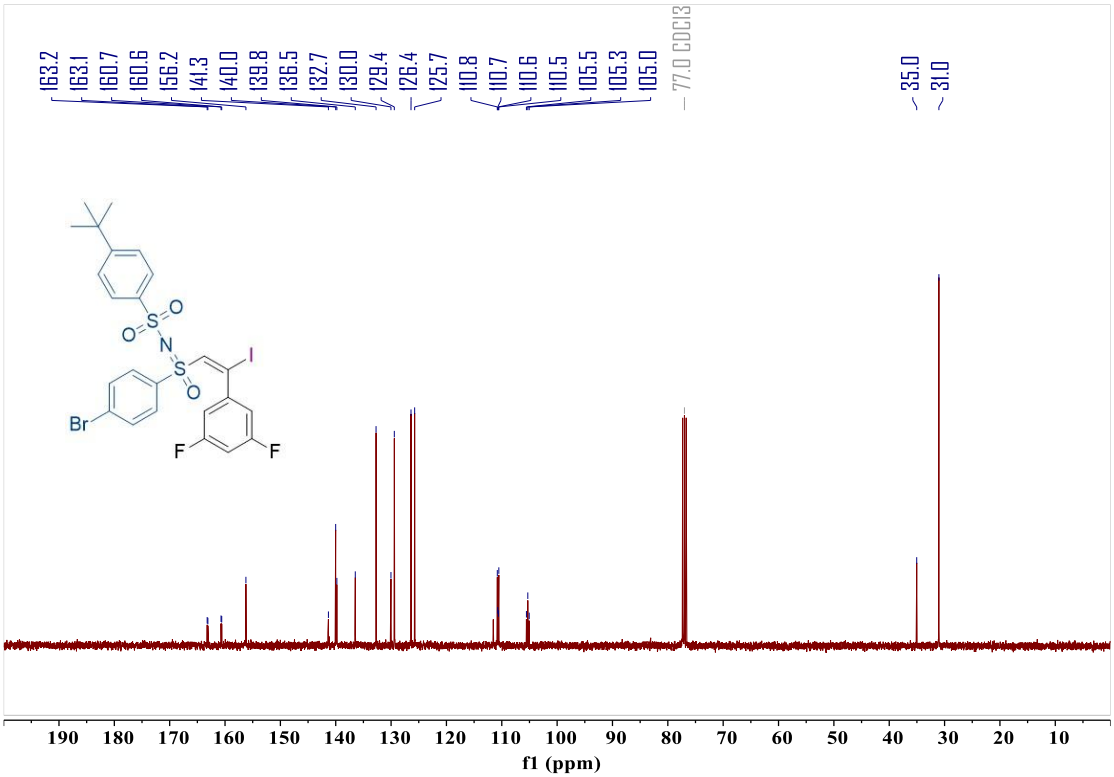


^{13}C NMR (100 MHz, $CDCl_3$)

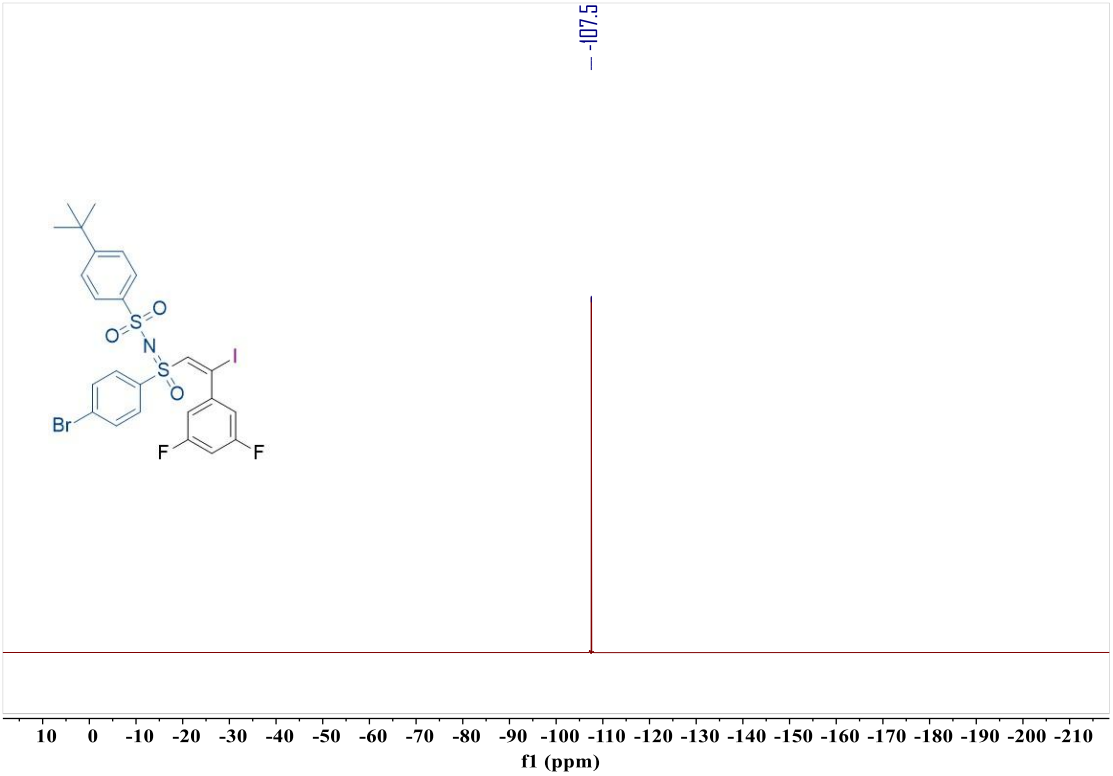
(*E*)-*N*-((4-bromophenyl)(2-(3,5-difluorophenyl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3q)



^{1}H NMR (400 MHz, $CDCl_3$)

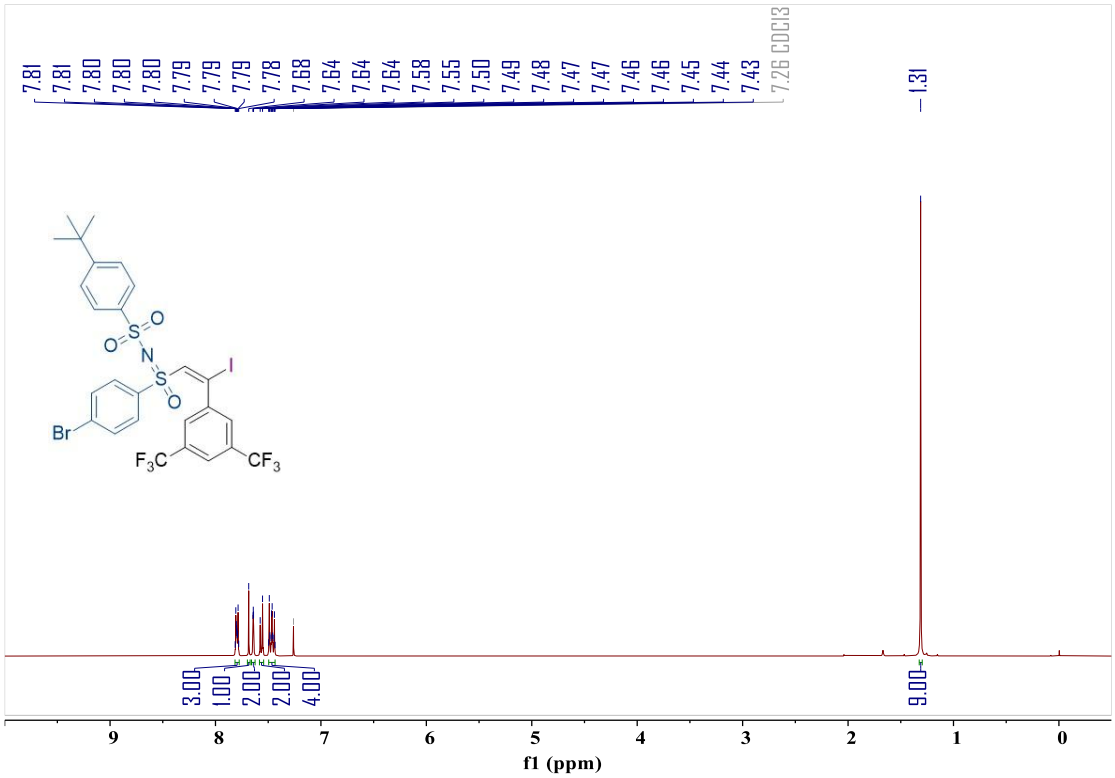


^{13}C NMR (100 MHz, $CDCl_3$)

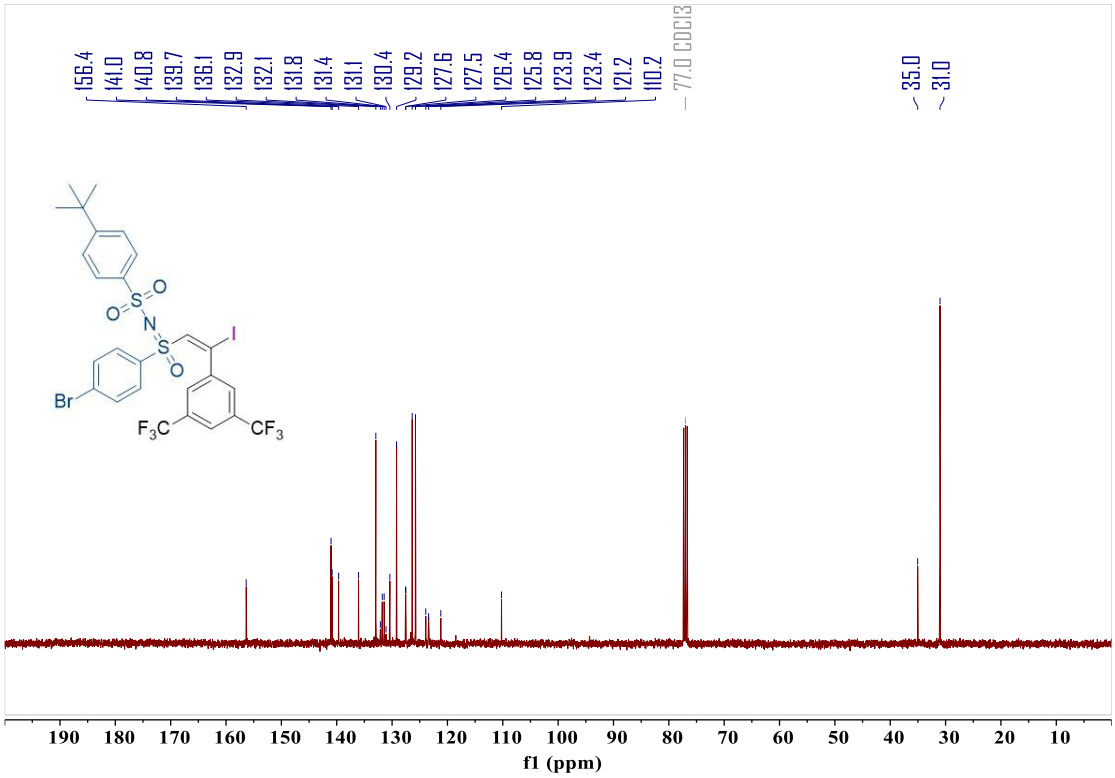


^{19}F NMR (376 MHz, $CDCl_3$)

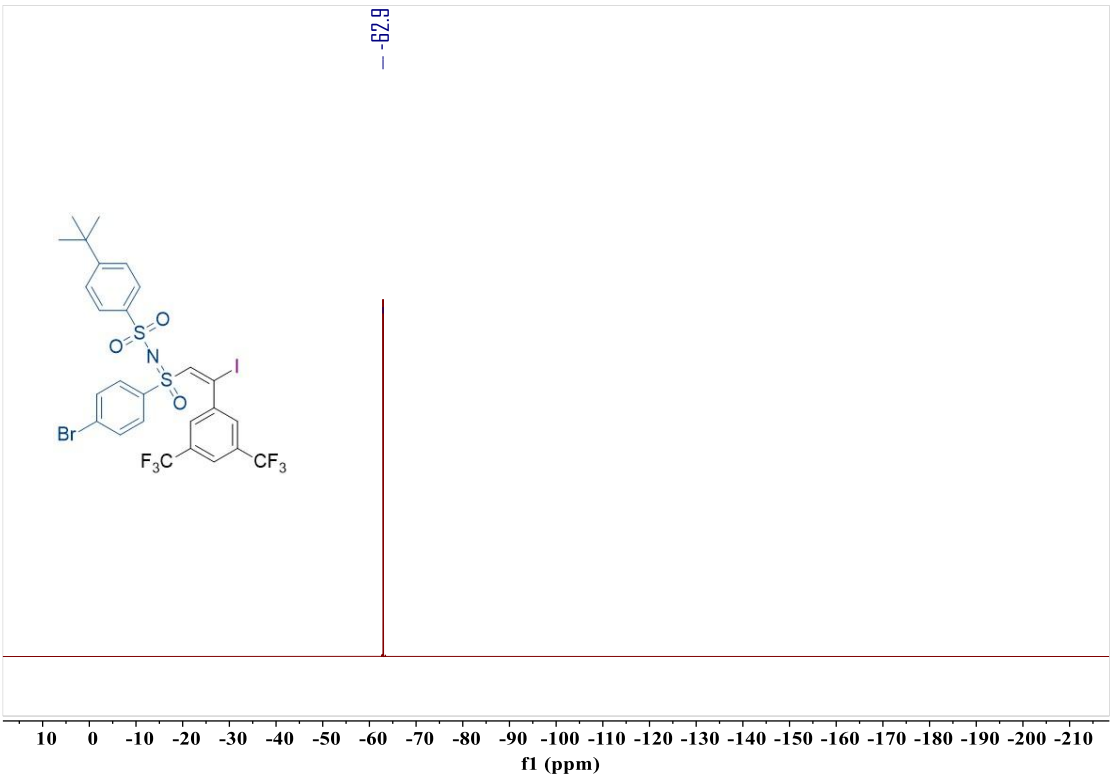
(*E*)-*N*-((2-(3,5-bis(trifluoromethyl)phenyl)-2-iodovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3r)



^{1}H NMR (400 MHz, $CDCl_3$)

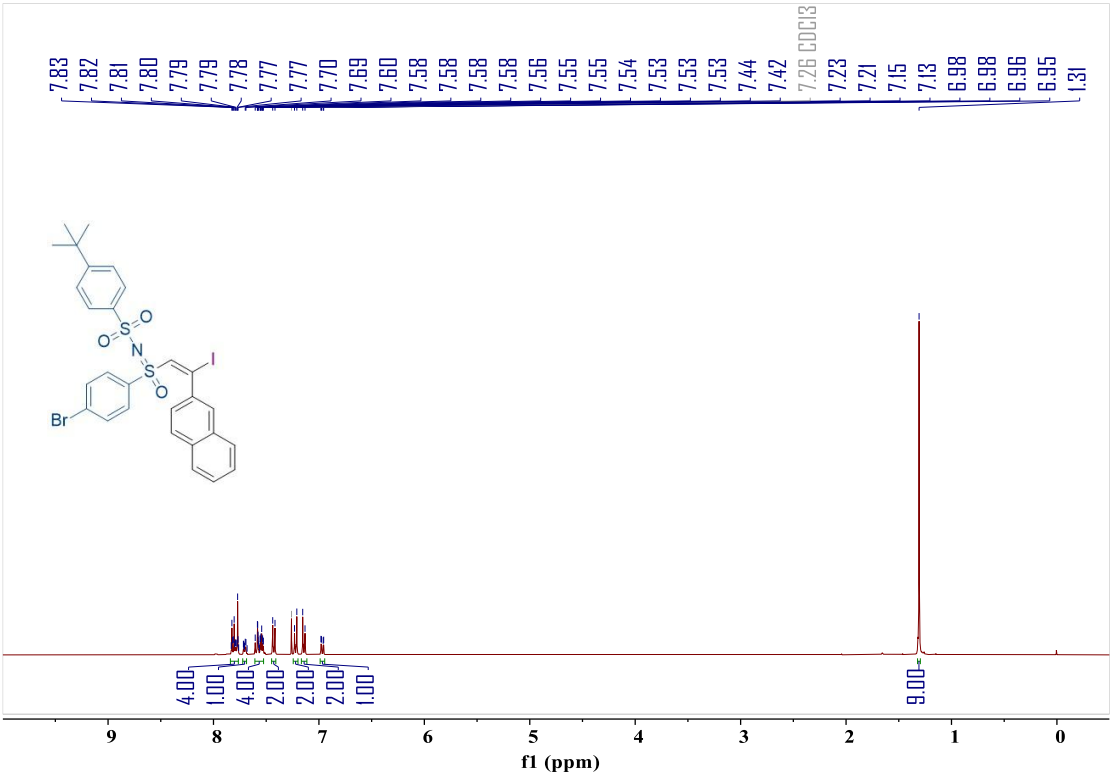


^{13}C NMR (100 MHz, $CDCl_3$)

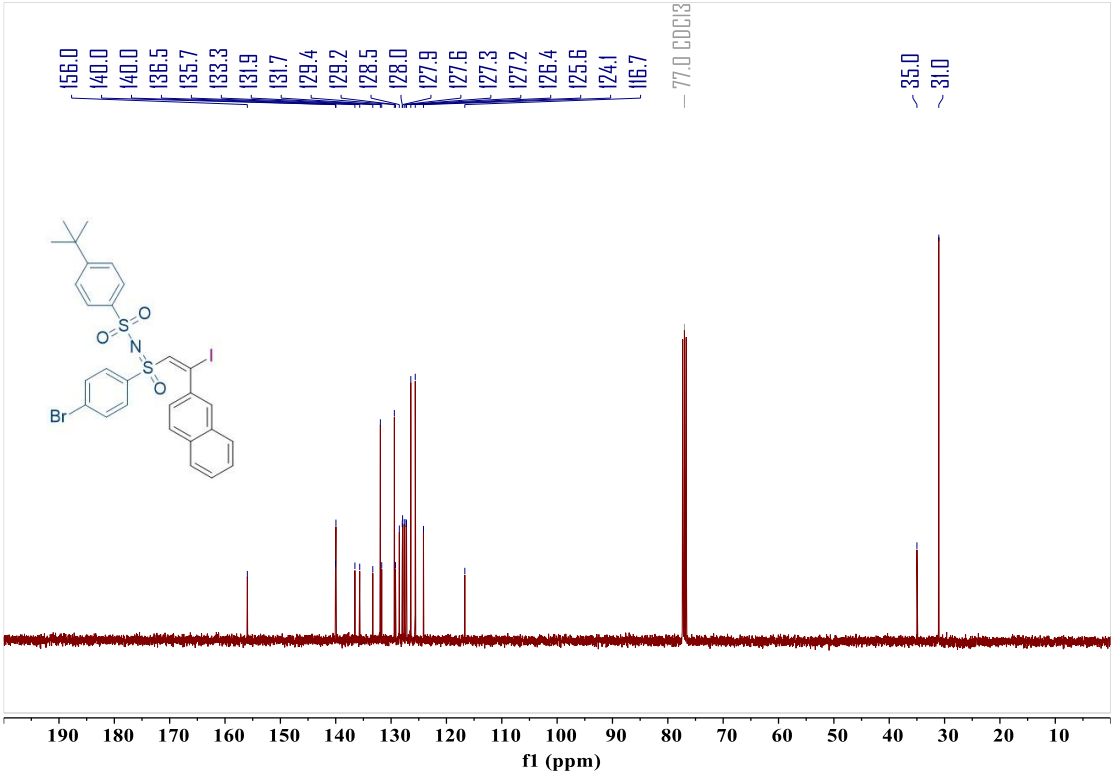


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(naphthalen-2-yl)vinyl)(oxo)-λ^6--sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3s)

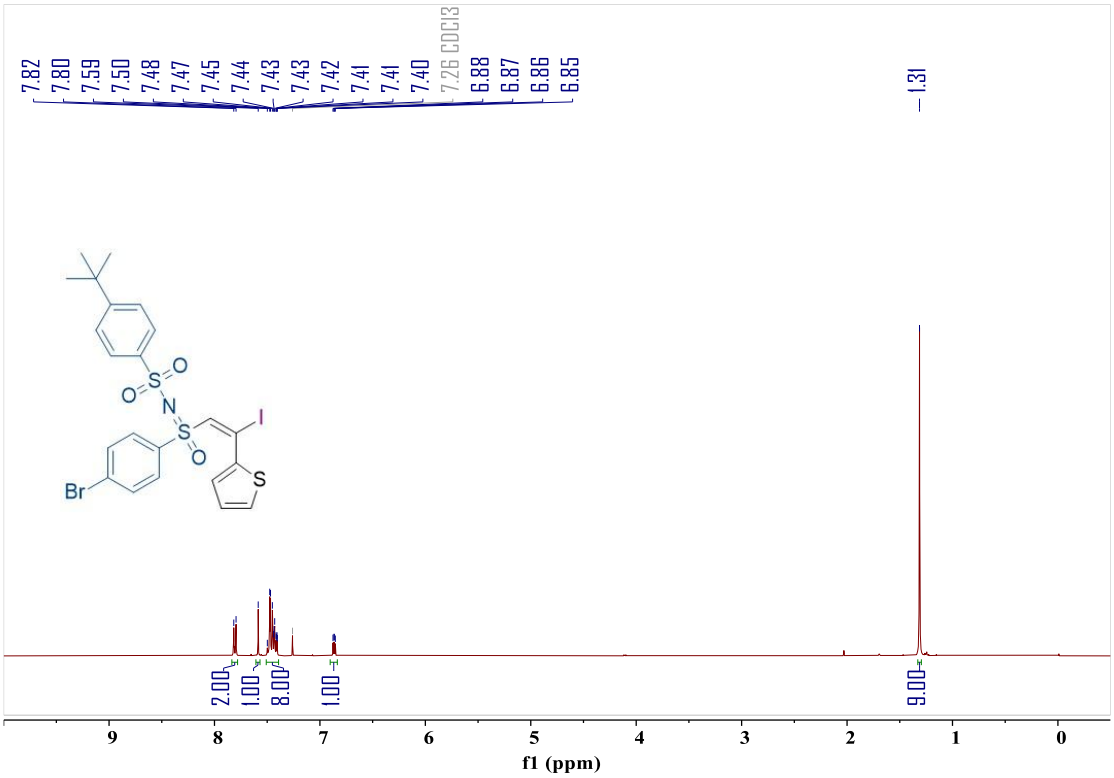


^{1}H NMR (400 MHz, $CDCl_3$)

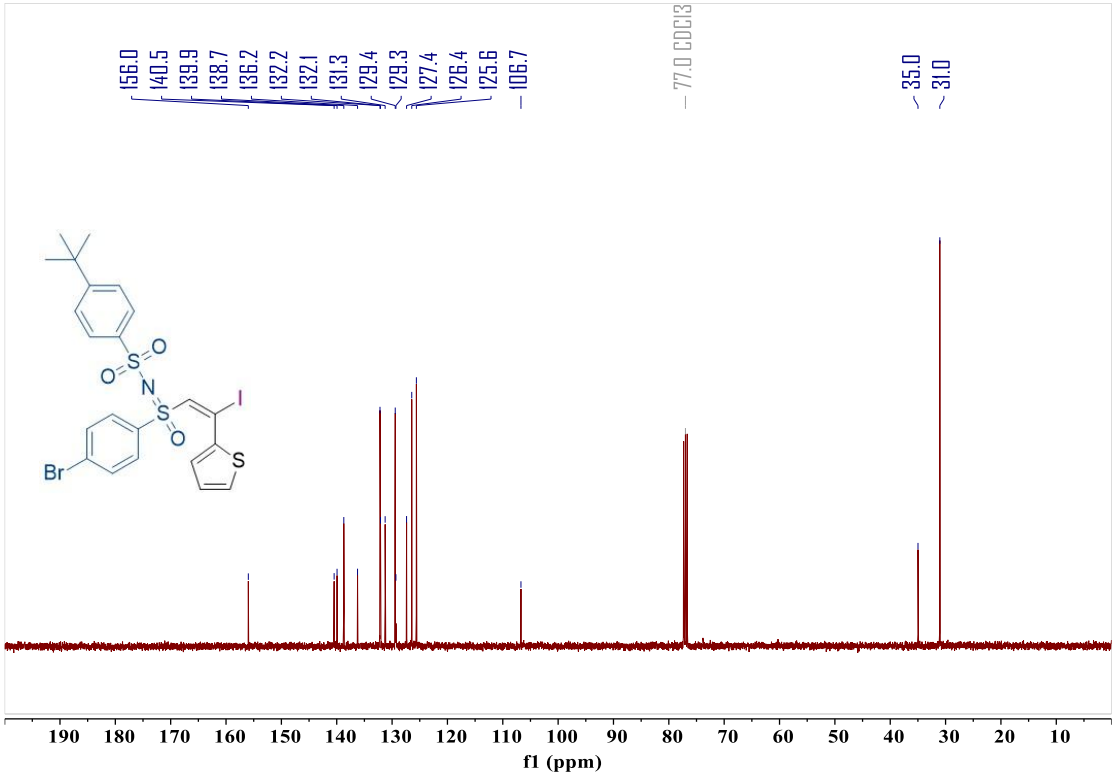


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(thiophen-2-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3t)

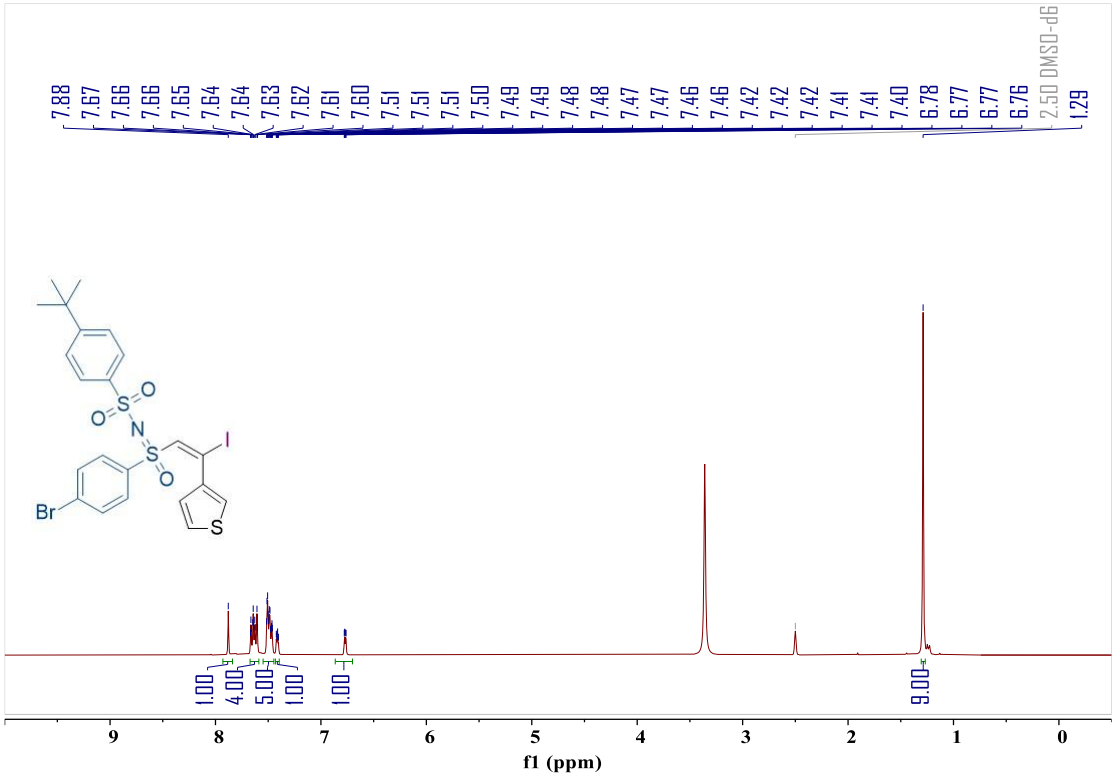


^{1}H NMR (400 MHz, $CDCl_3$)

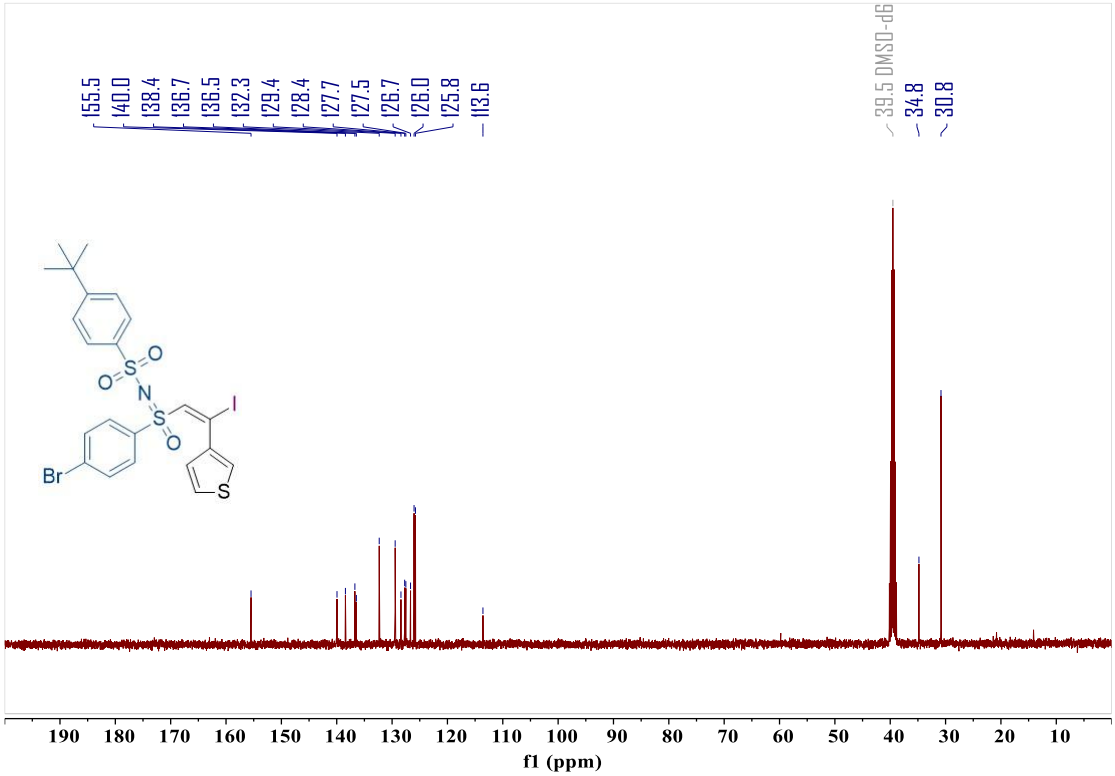


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(thiophen-3-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3u)

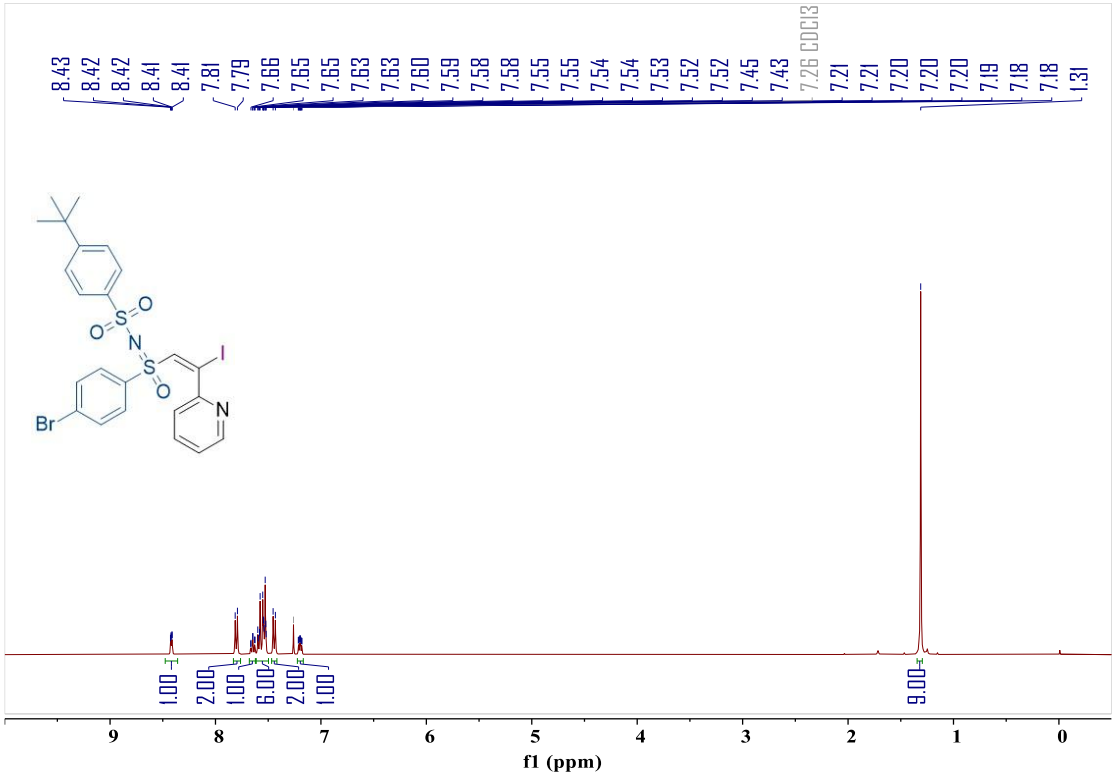


^{1}H NMR (400 MHz, DMSO-*d*$_6$)

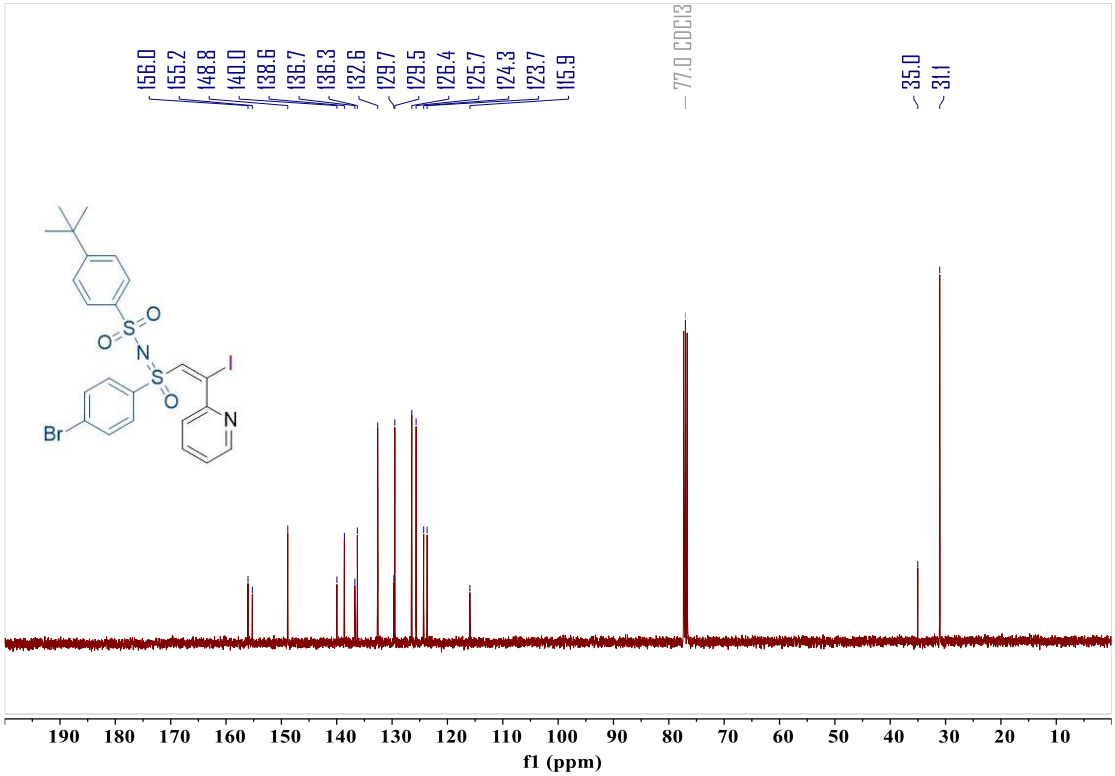


^{13}C NMR (100 MHz, DMSO-*d*$_6$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-(pyridin-2-yl)vinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benz eneeeesulfonamide (3v)

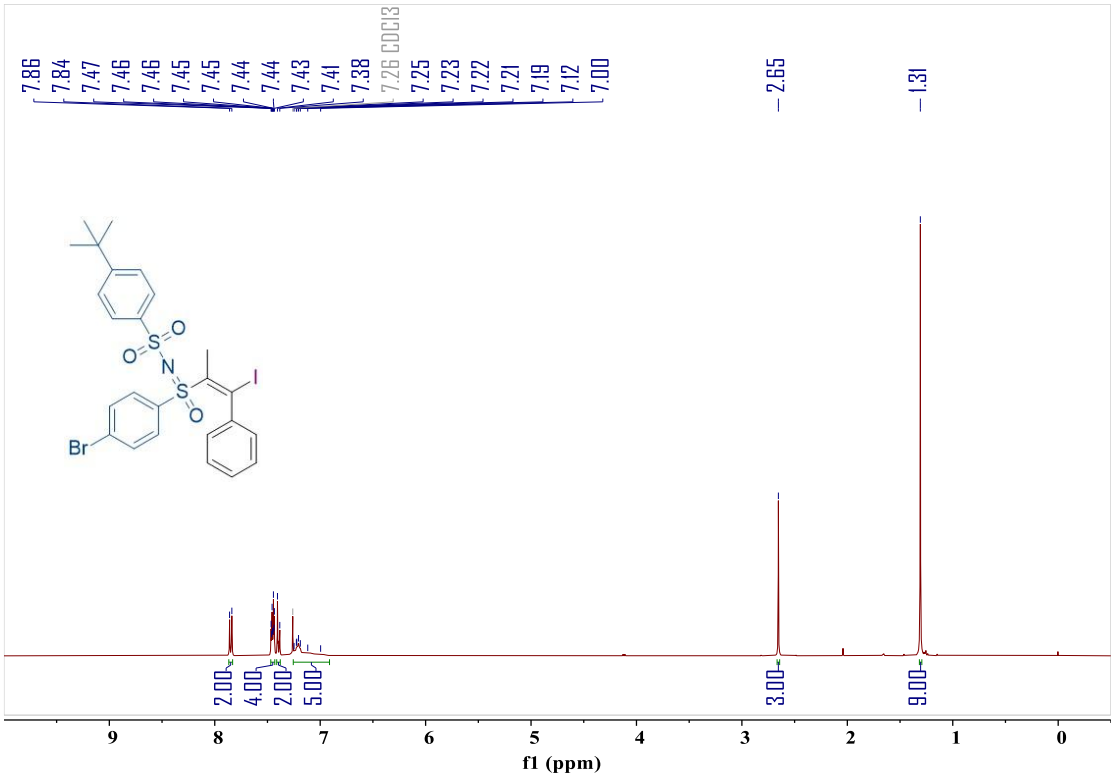


^{1}H NMR (400 MHz, CDCl$_3$)

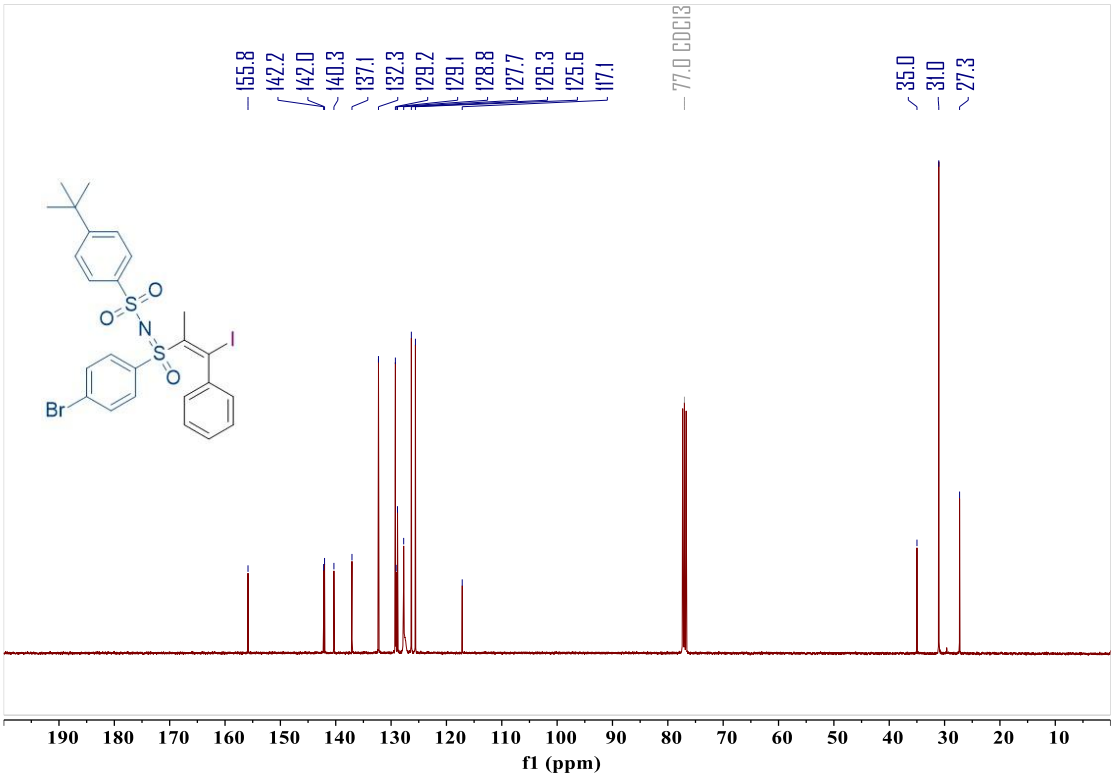


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(1-iodo-1-phenylprop-1-en-2-yl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3w)

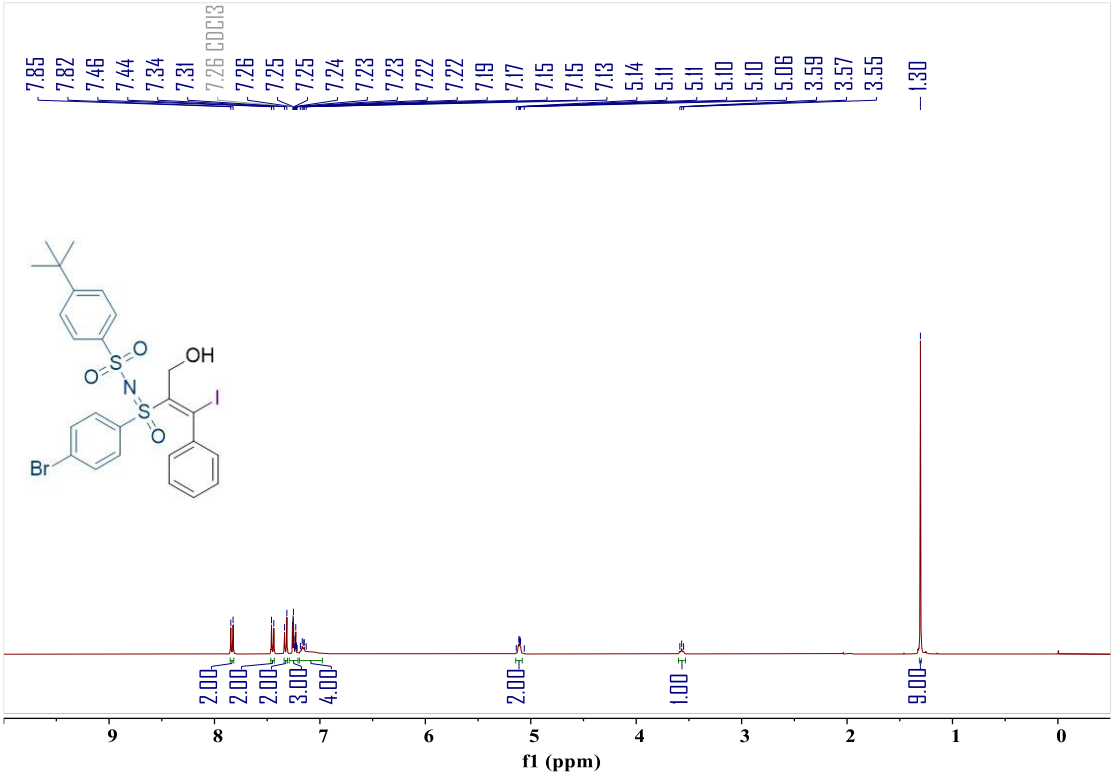


^{1}H NMR (400 MHz, $CDCl_3$)

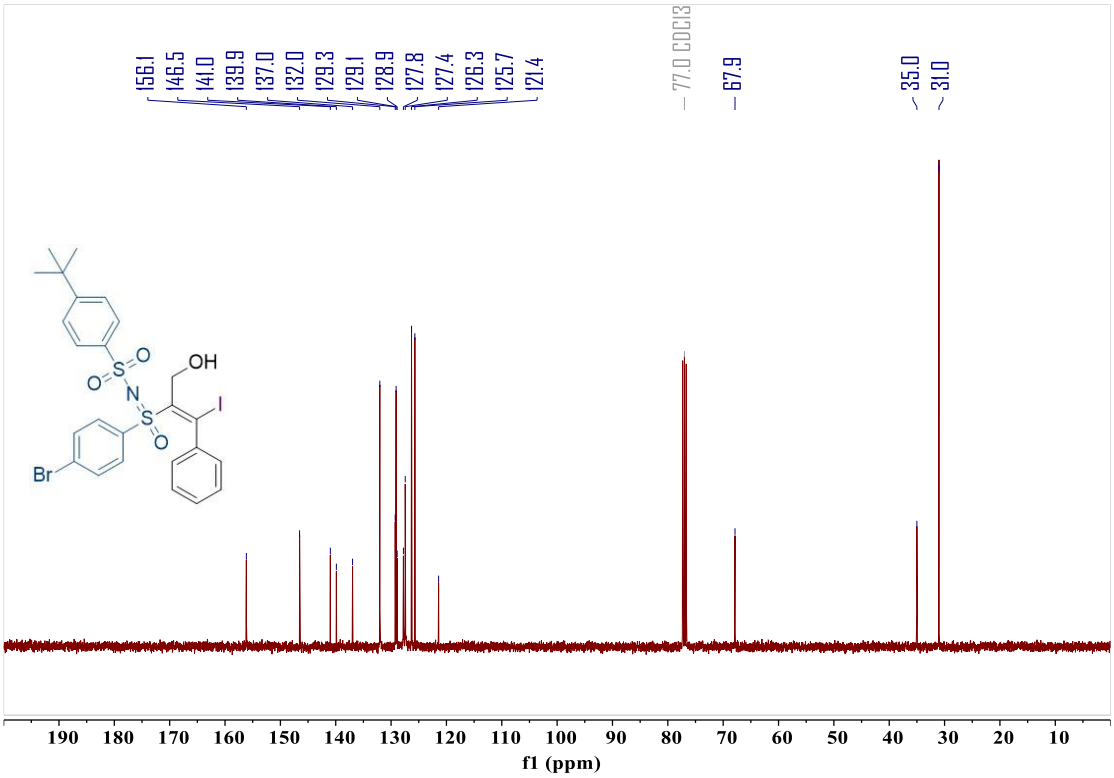


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(3-hydroxy-1-iodo-1-phenylprop-1-en-2-yl)(oxo)-λ^6-sulfaneylidene)-4-(*ter t*-butyl)benzenesulfonamide (3x)

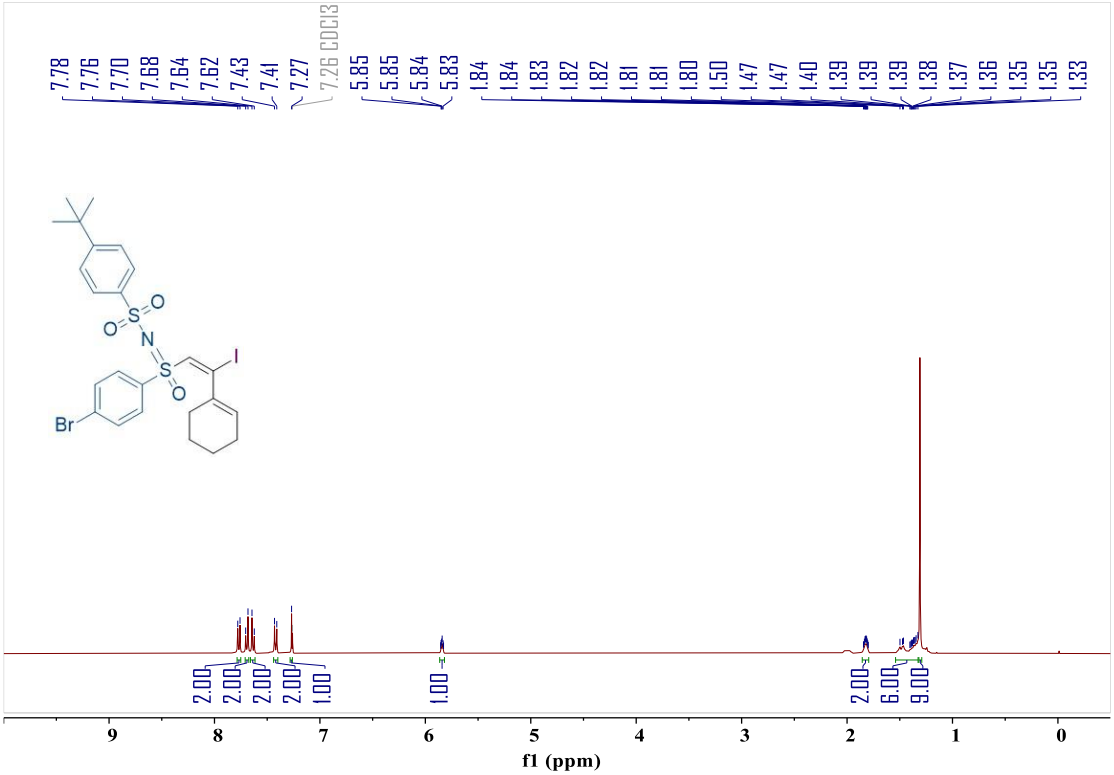


^{1}H NMR (400 MHz, $CDCl_3$)

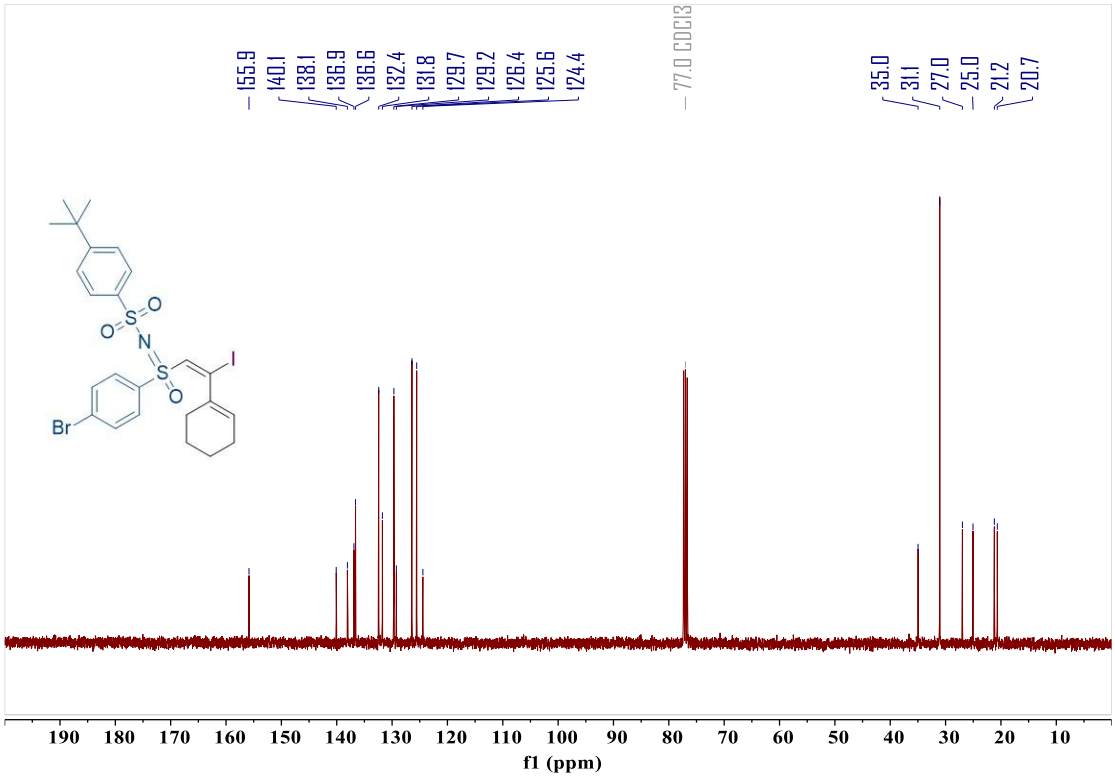


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-(cyclohex-1-en-1-yl)-2-iodovinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (3y)

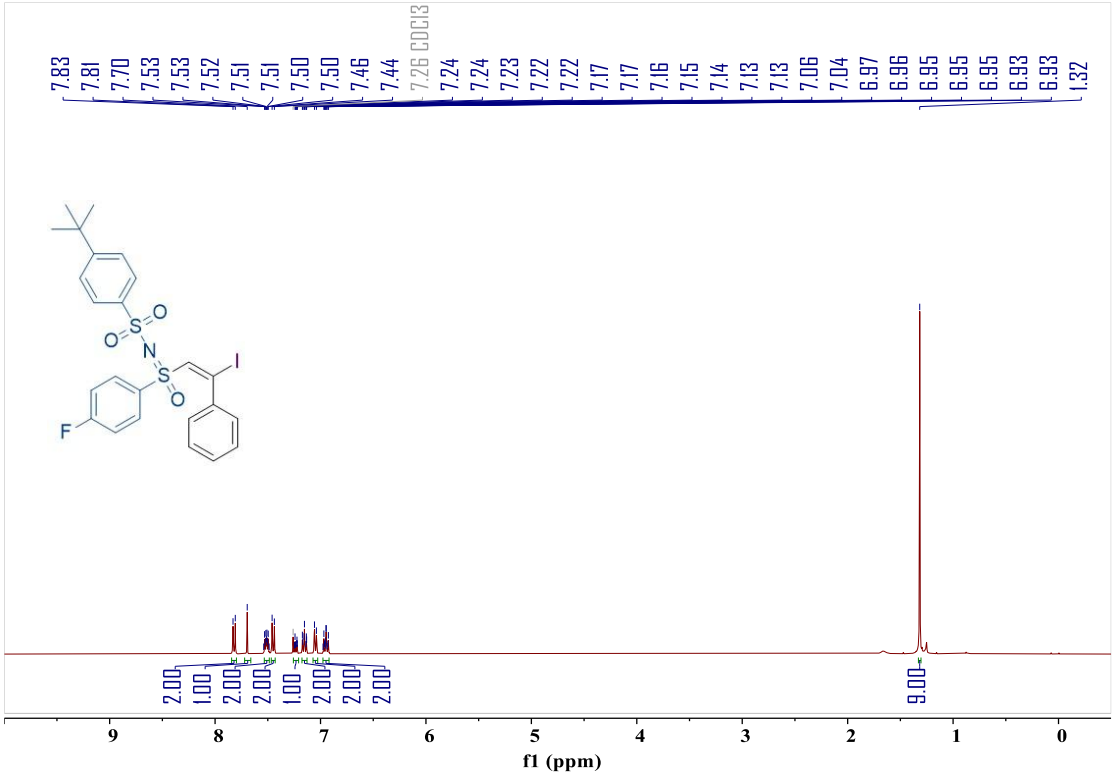


^{1}H NMR (400 MHz, $CDCl_3$)

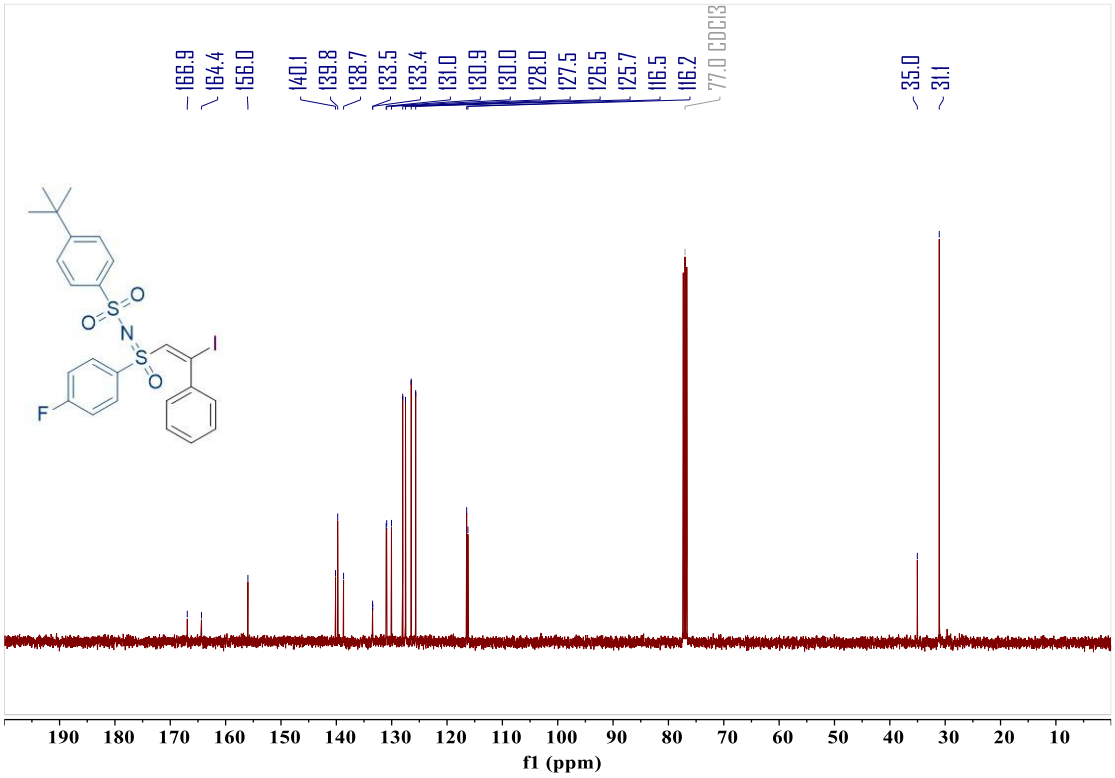


^{13}C NMR (100 MHz, $CDCl_3$)

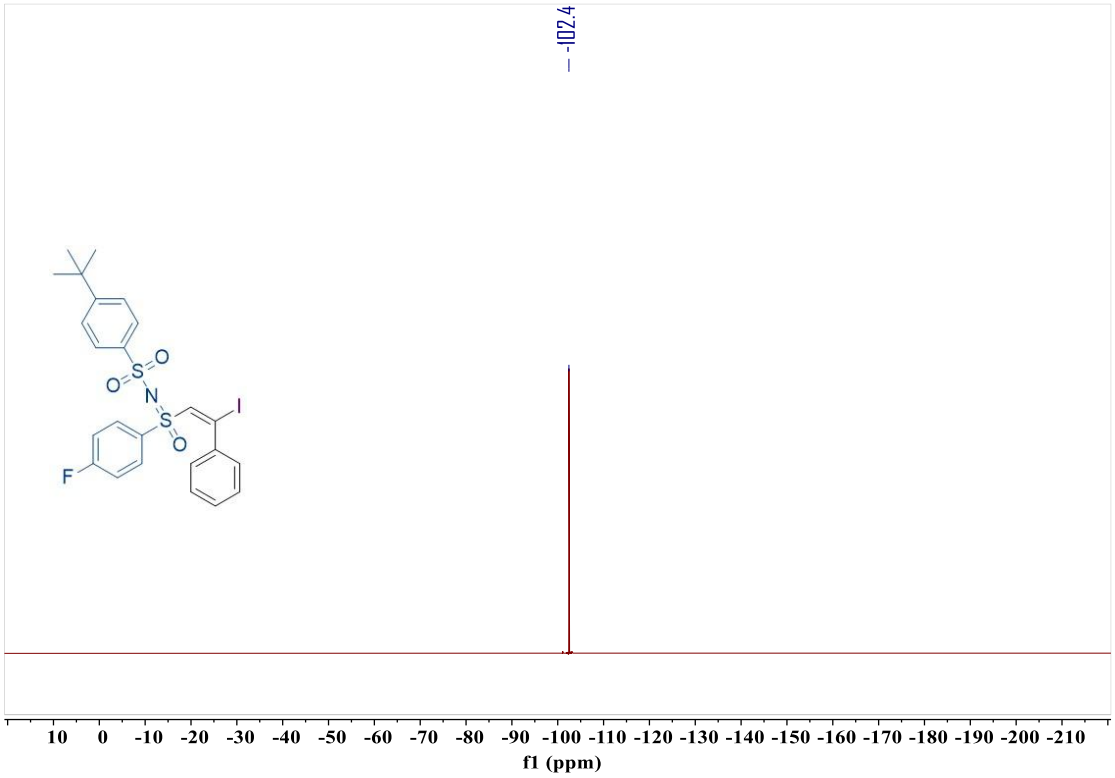
(*E*)-4-(*tert*-butyl)-*N*-((4-fluorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3z)



^{1}H NMR (400 MHz, $CDCl_3$)

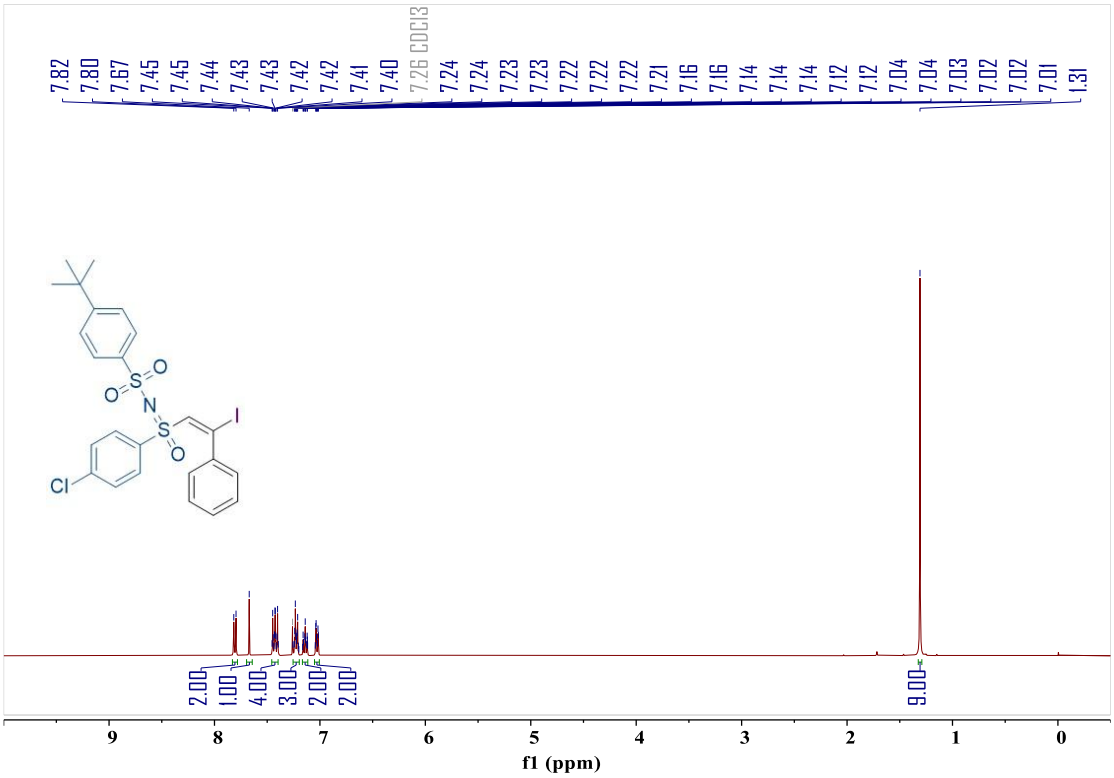


^{13}C NMR (100 MHz, $CDCl_3$)

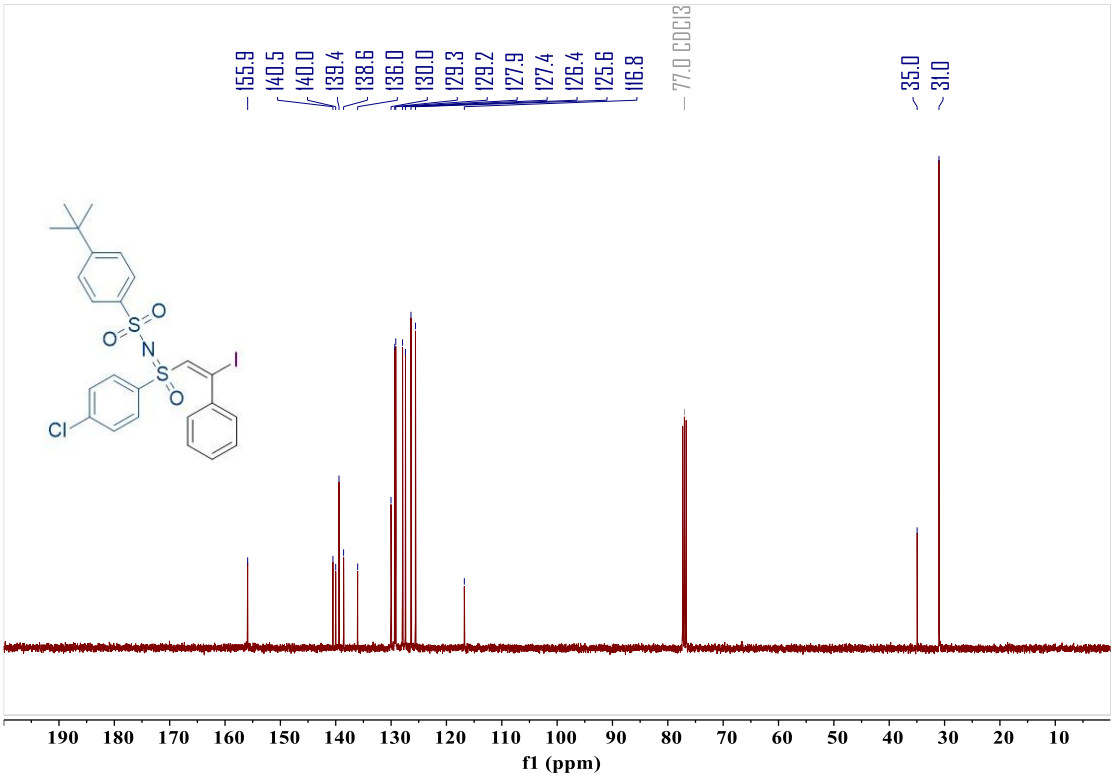


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-4-(*tert*-butyl)-*N*-((4-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3aa)

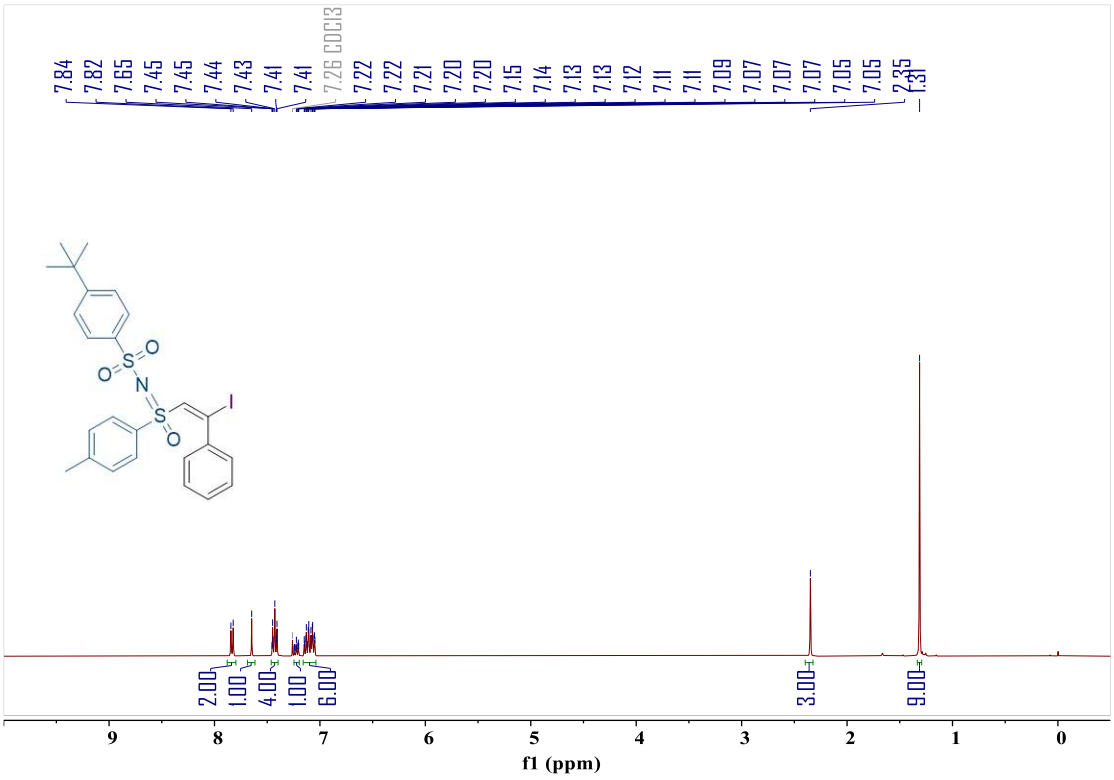


^{1}H NMR (400 MHz, $CDCl_3$)

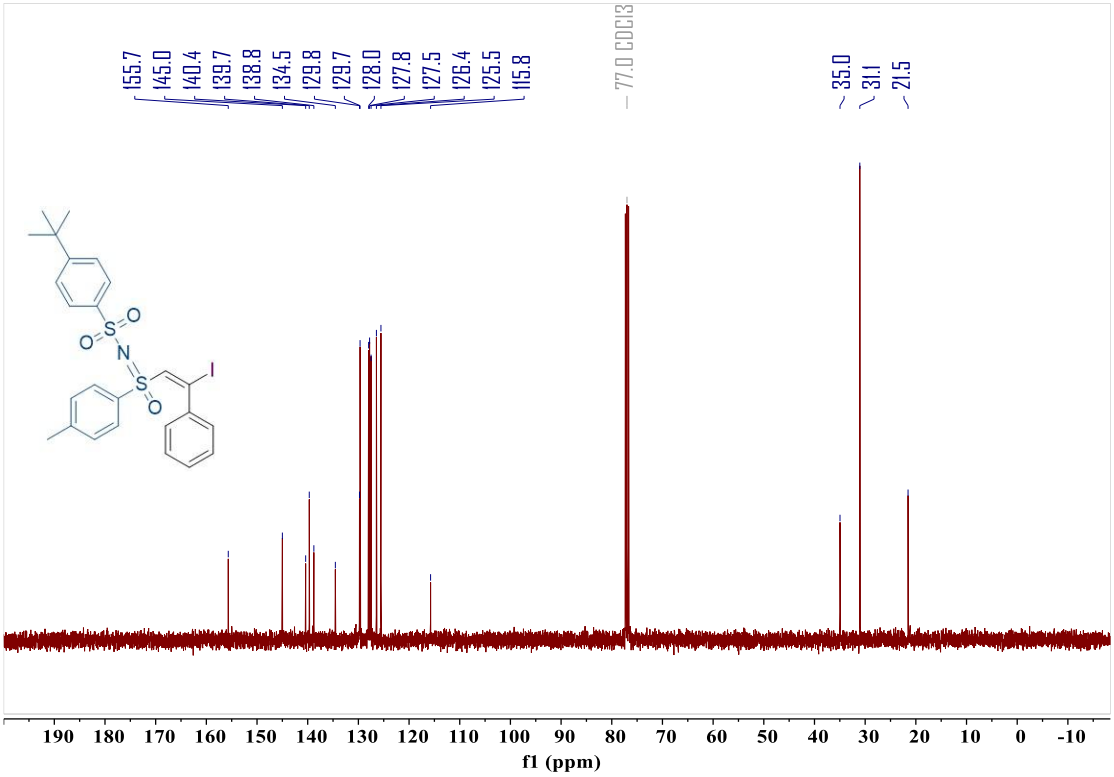


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-4-(tert-butyl)-*N*-((2-iodo-2-phenylvinyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)benzenesulfonamide (3ab)

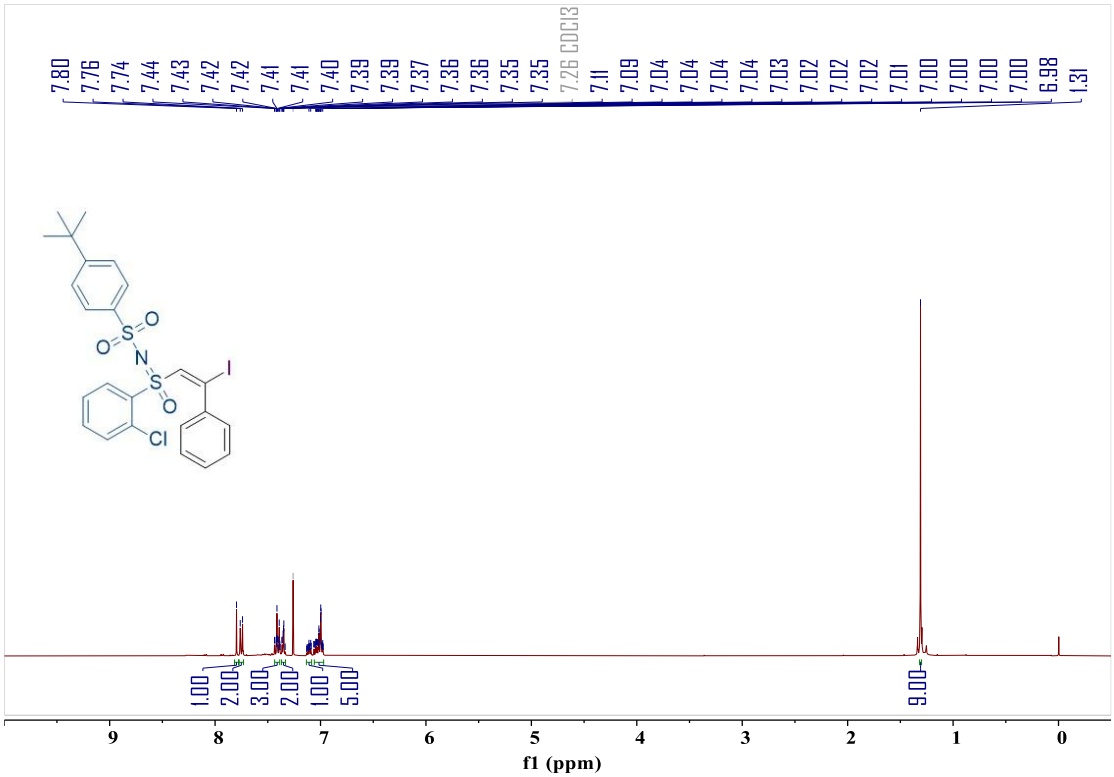


^{1}H NMR (400 MHz, $CDCl_3$)

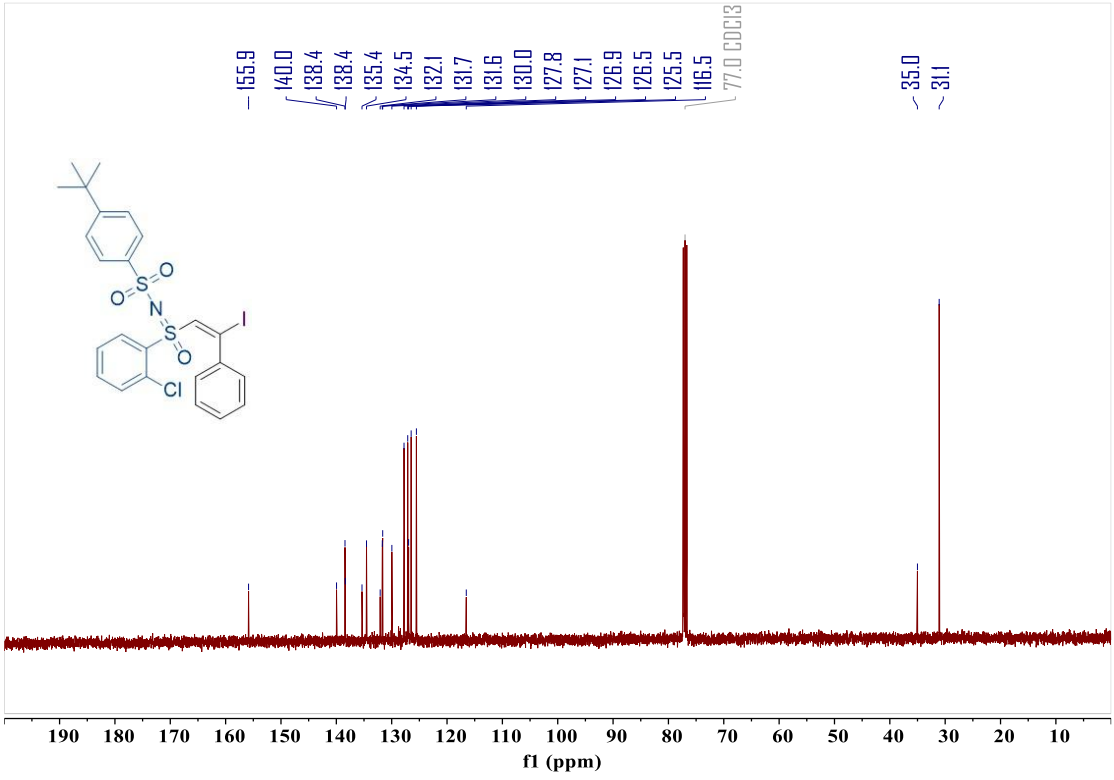


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-4-(*tert*-butyl)-*N*-((2-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (3ac)

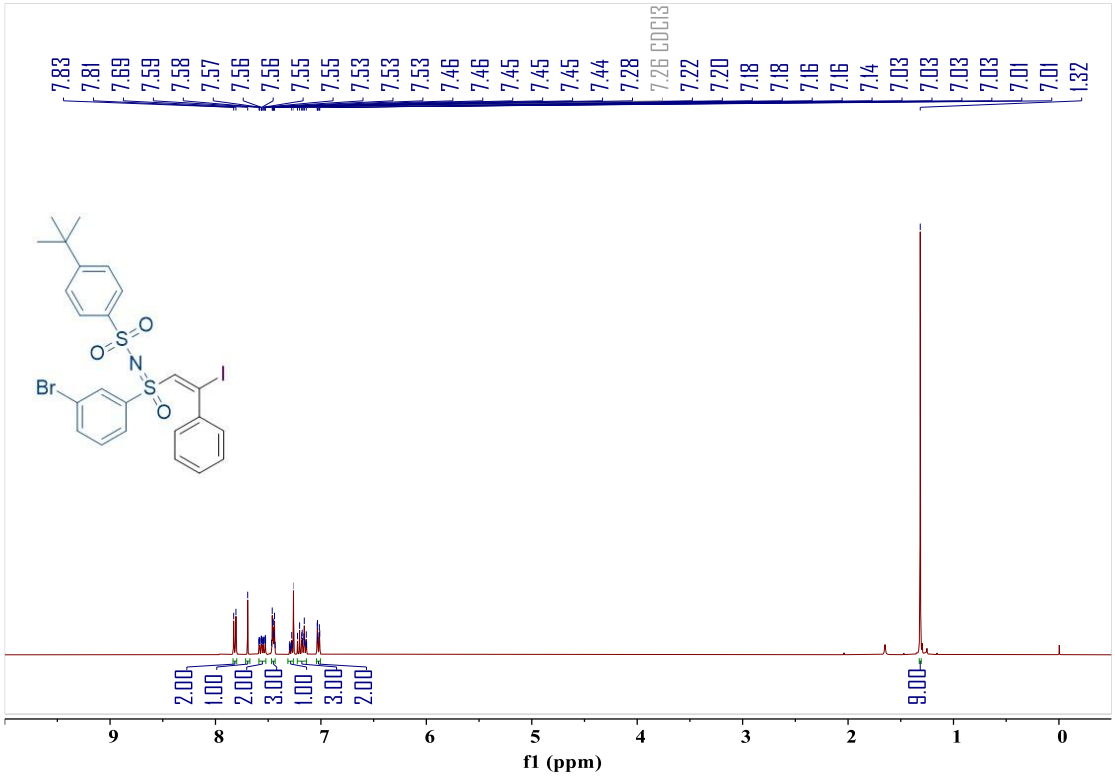


^{1}H NMR (400 MHz, $CDCl_3$)

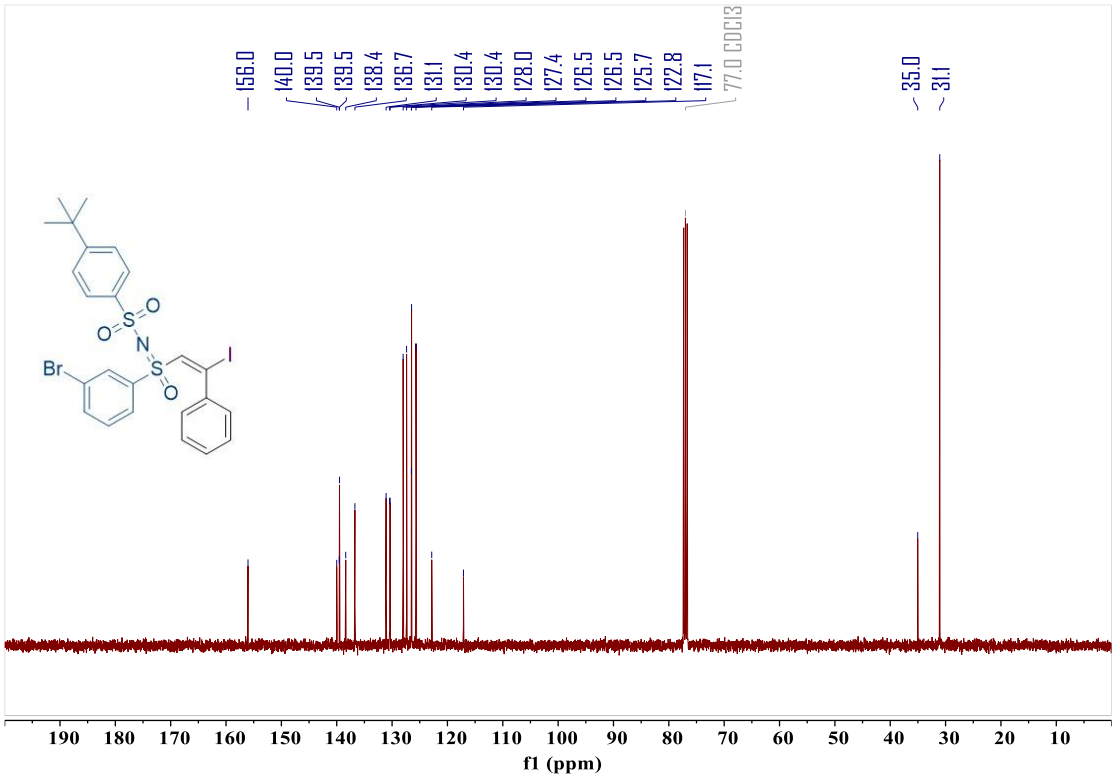


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((3-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (3ad)

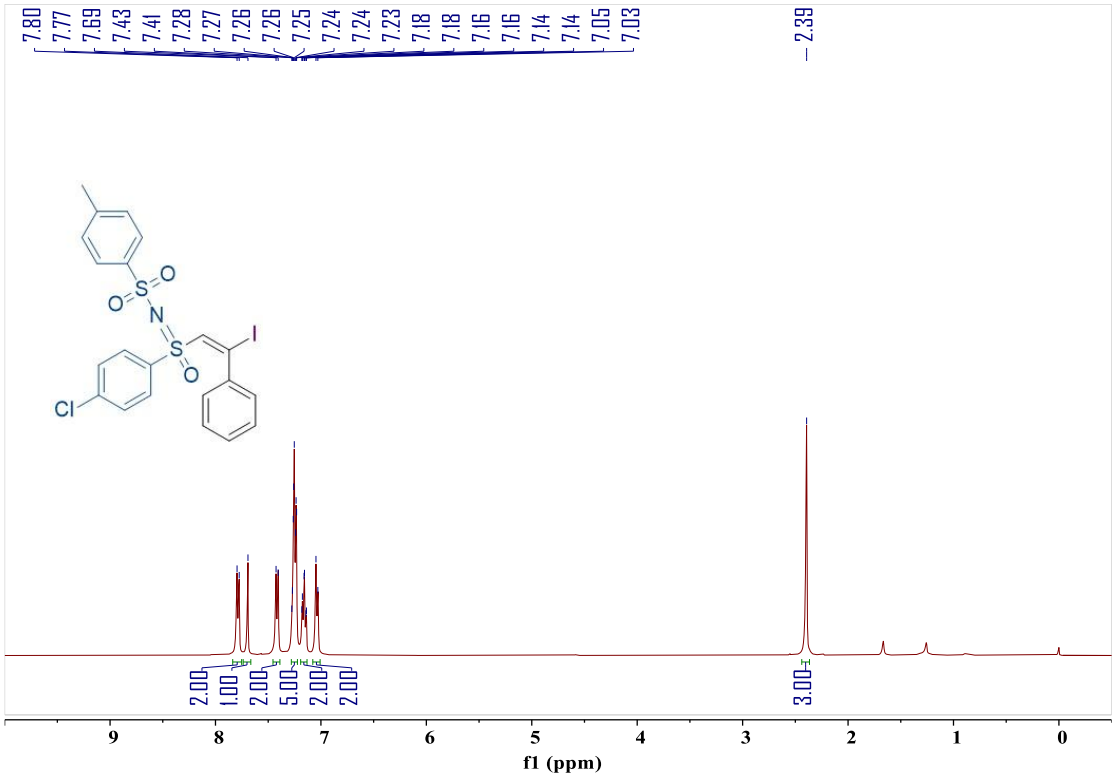


^{1}H NMR (400 MHz, $CDCl_3$)

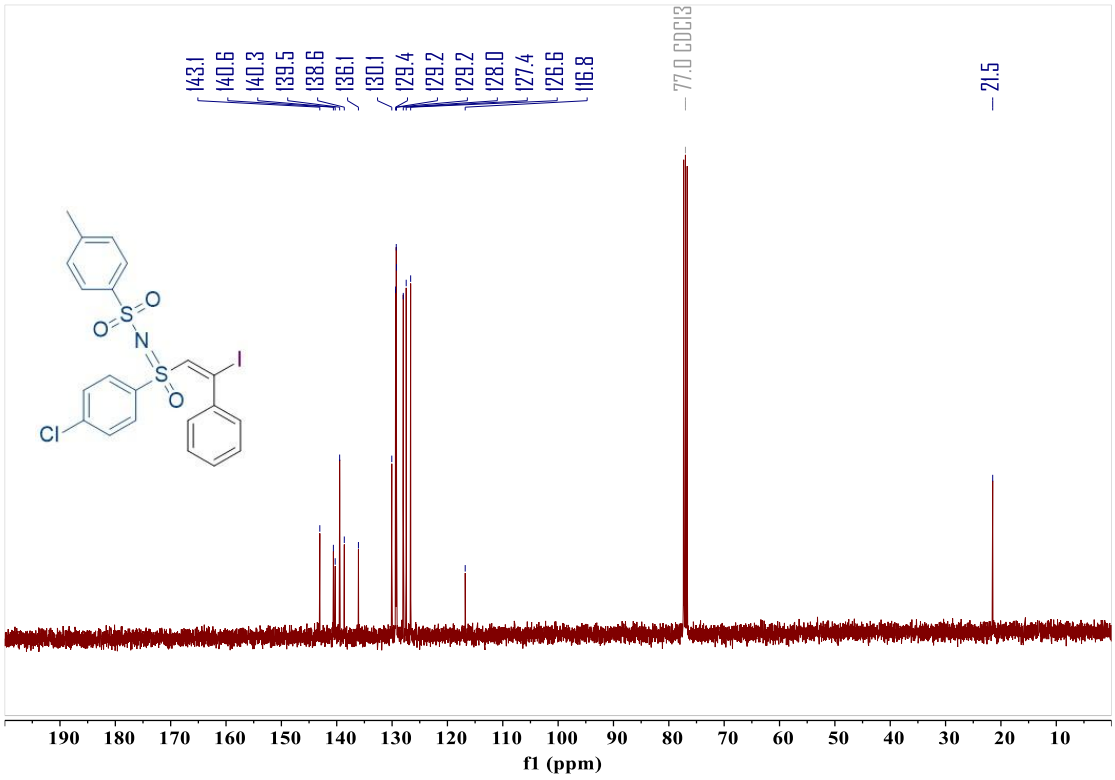


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-chlorophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (3ae)

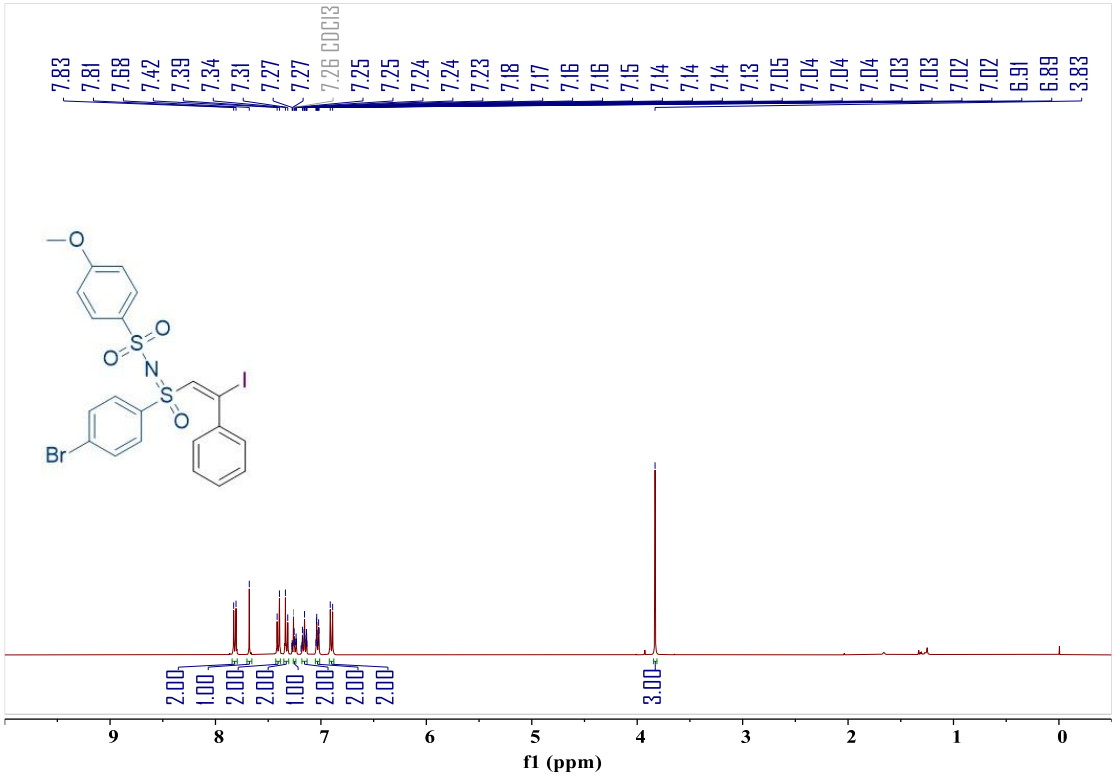


^{1}H NMR (400 MHz, $CDCl_3$)

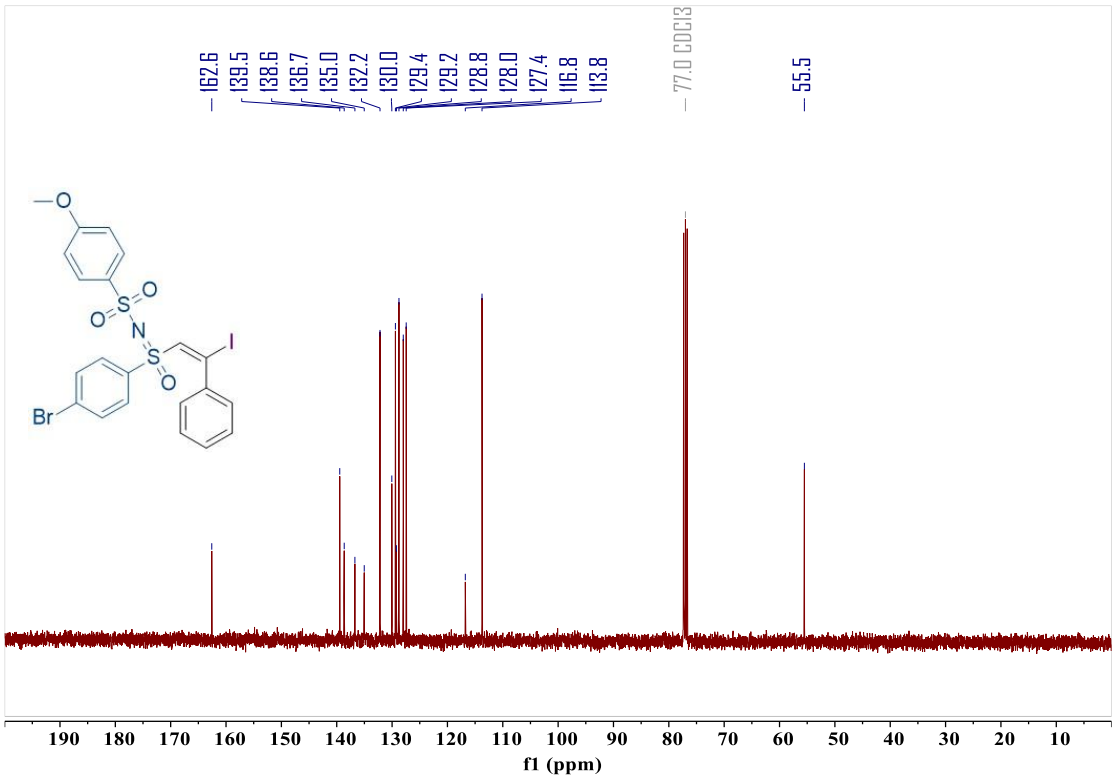


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-methoxybenzenesulfonamide (3af)

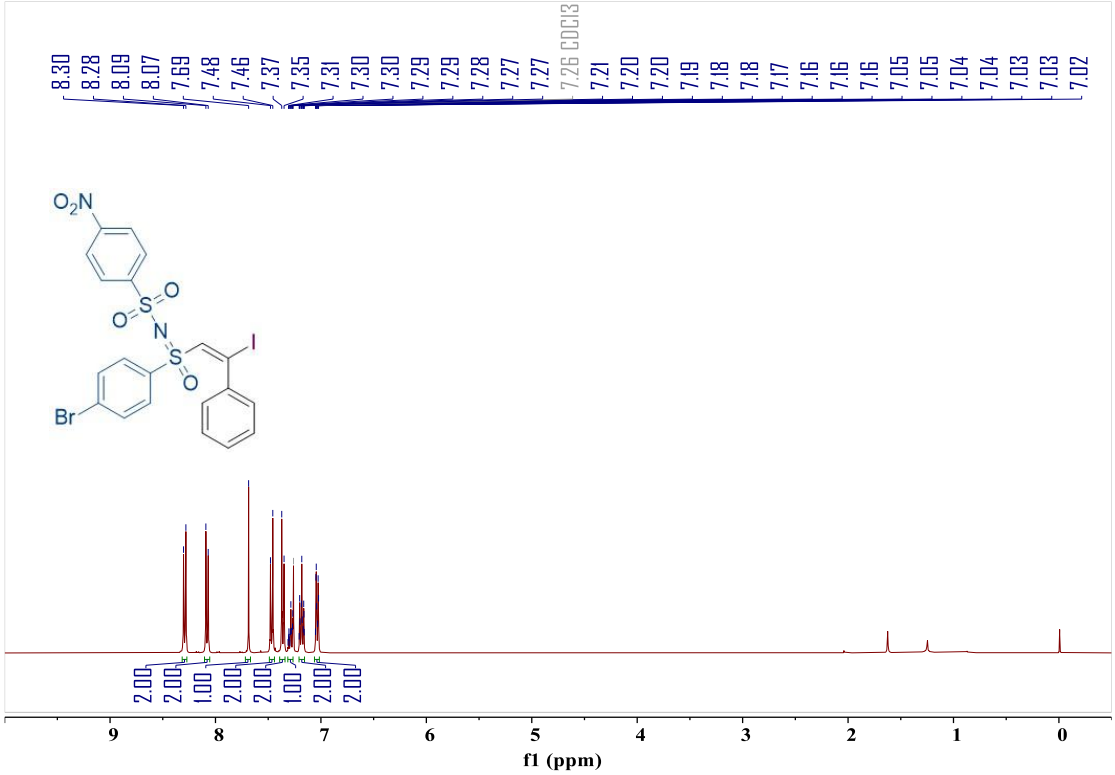


^{1}H NMR (400 MHz, $CDCl_3$)

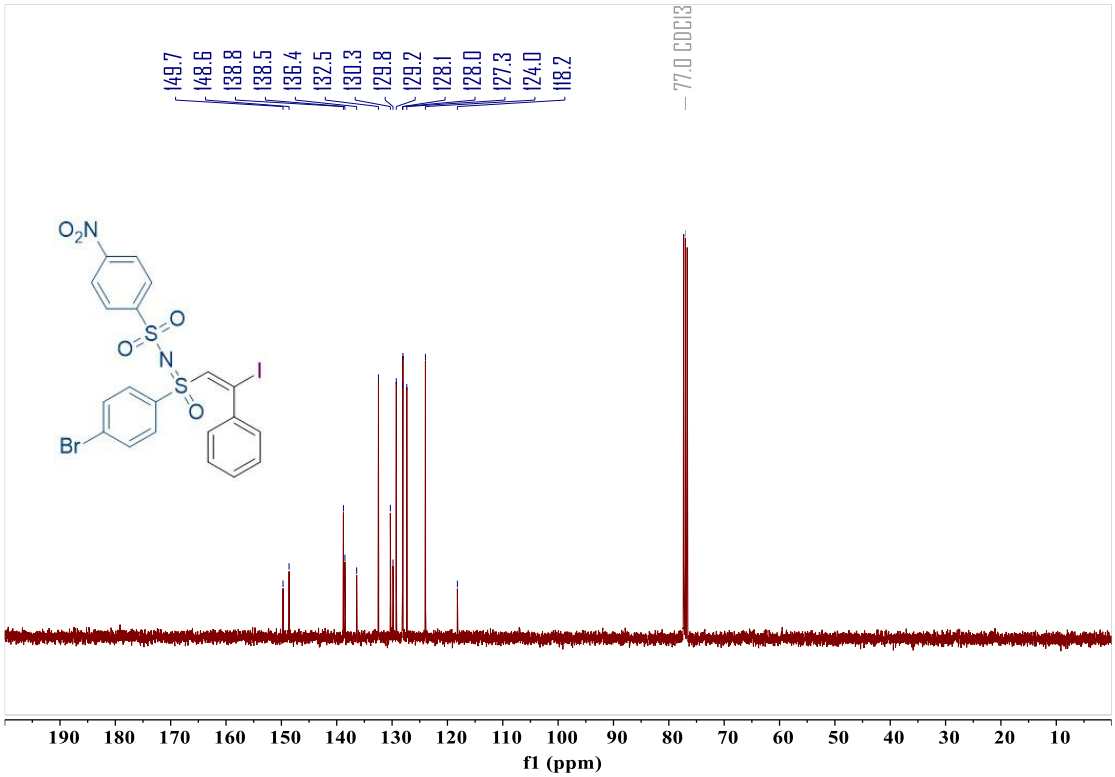


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-nitrobenzenesulfona mide (3ag)

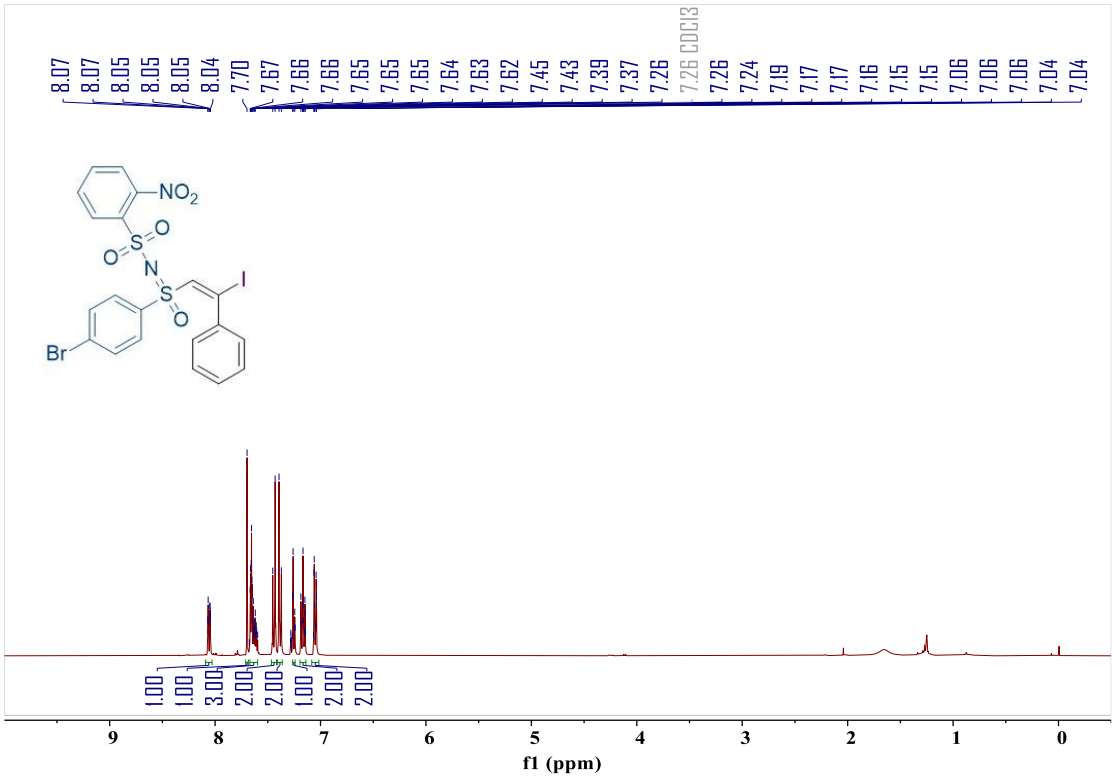


^{1}H NMR (400 MHz, $CDCl_3$)

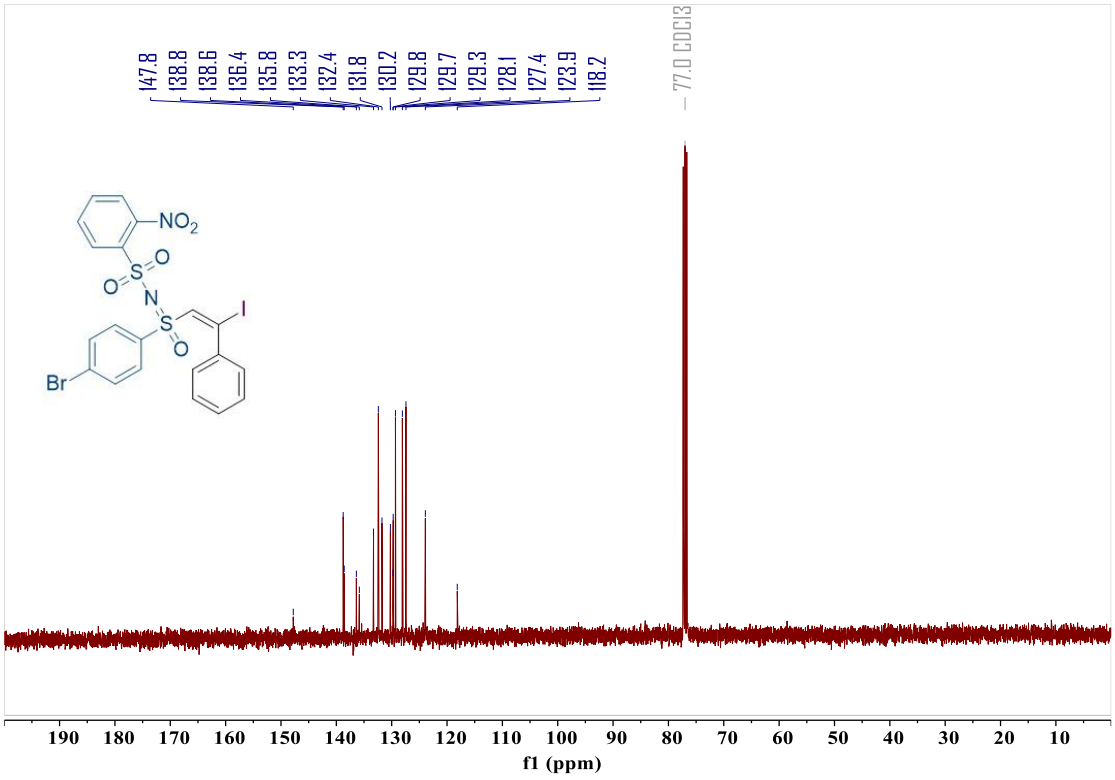


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-2-nitrobenzenesulfonamide (3ah)

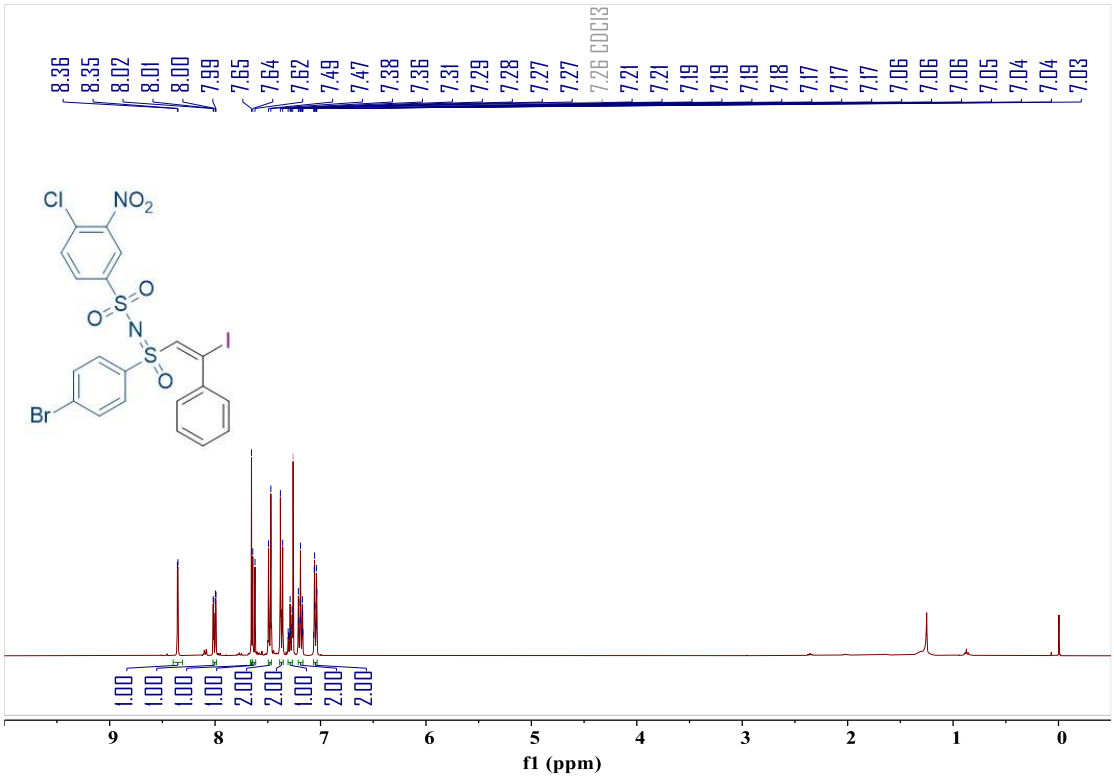


^{1}H NMR (400 MHz, $CDCl_3$)

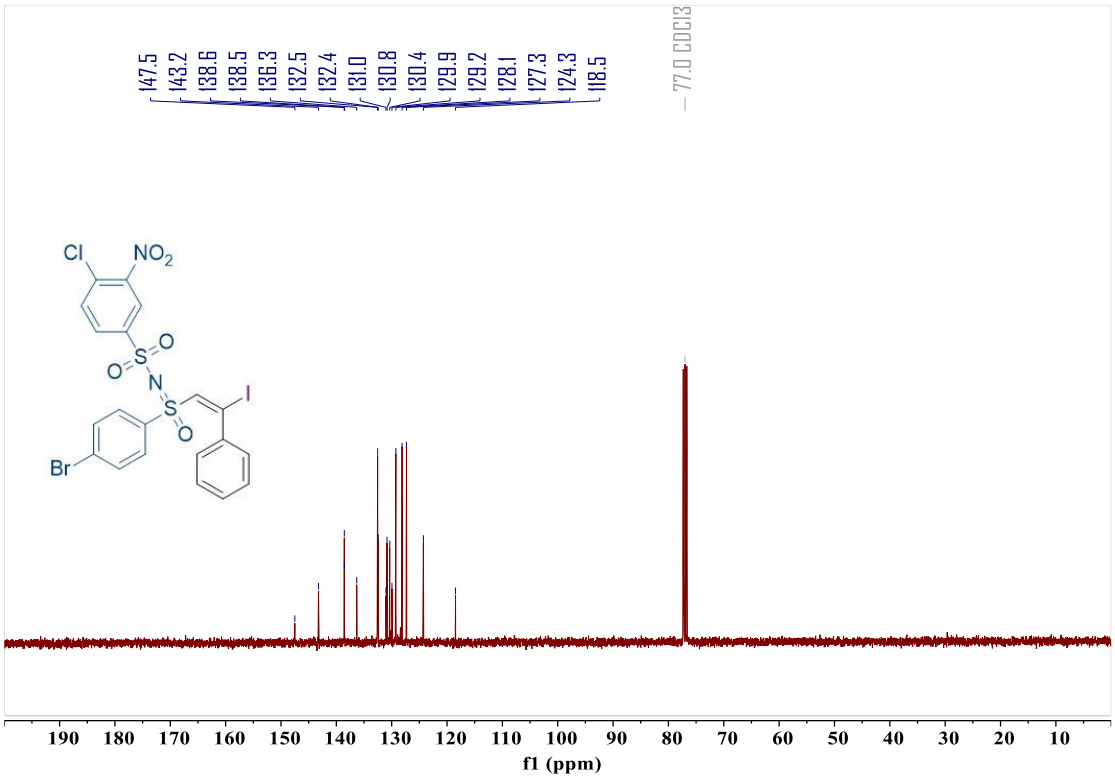


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-4-chloro-3-nitrobenzenesulfonamide (3ai)

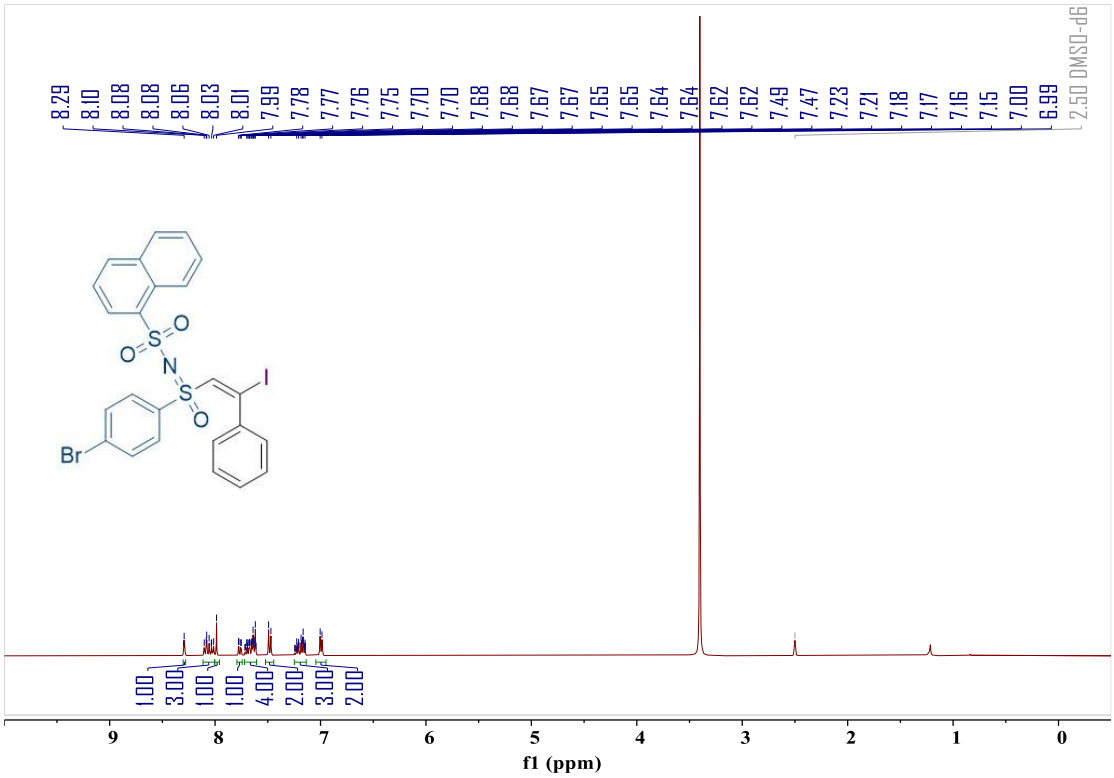


^{1}H NMR (400 MHz, $CDCl_3$)

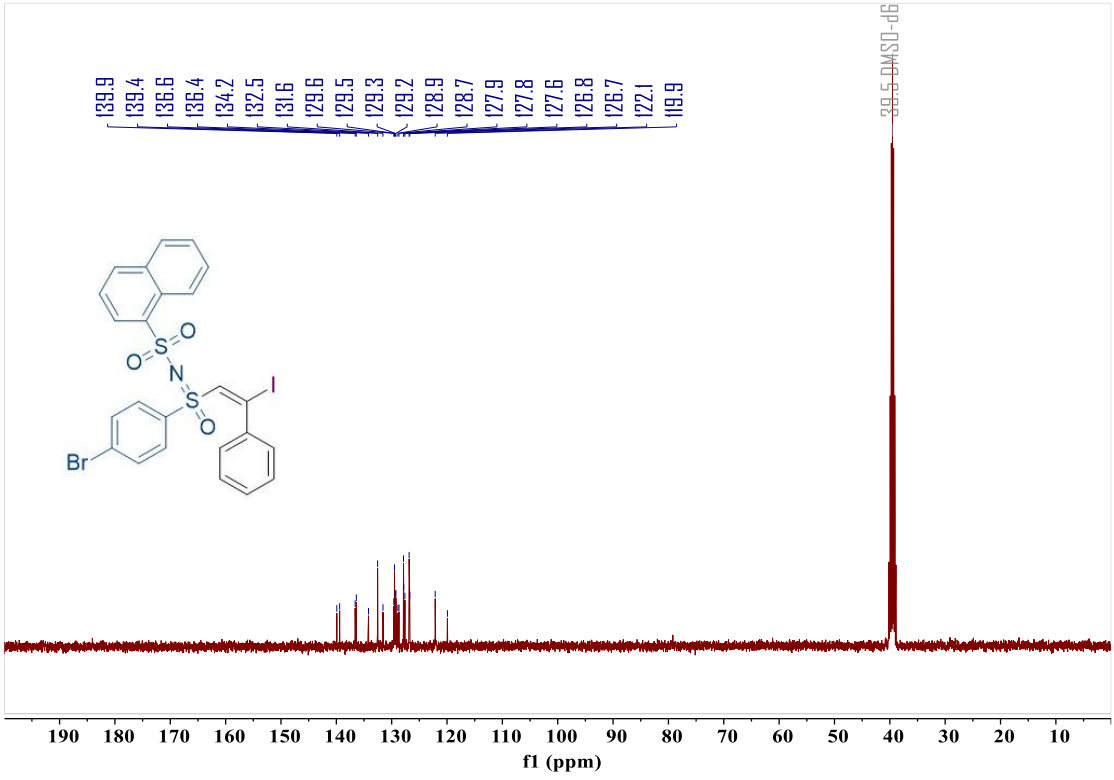


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)naphthalene-1-sulfonamide (3aj)

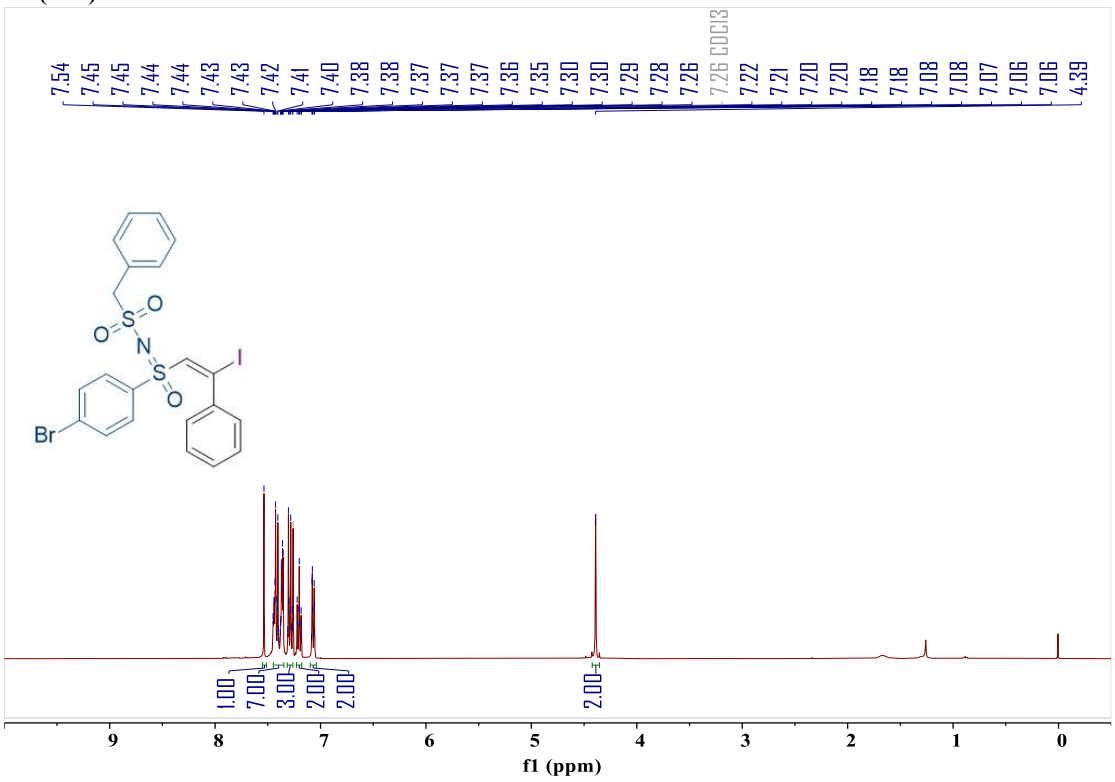


^{1}H NMR (400 MHz, DMSO-*d*$_6$)

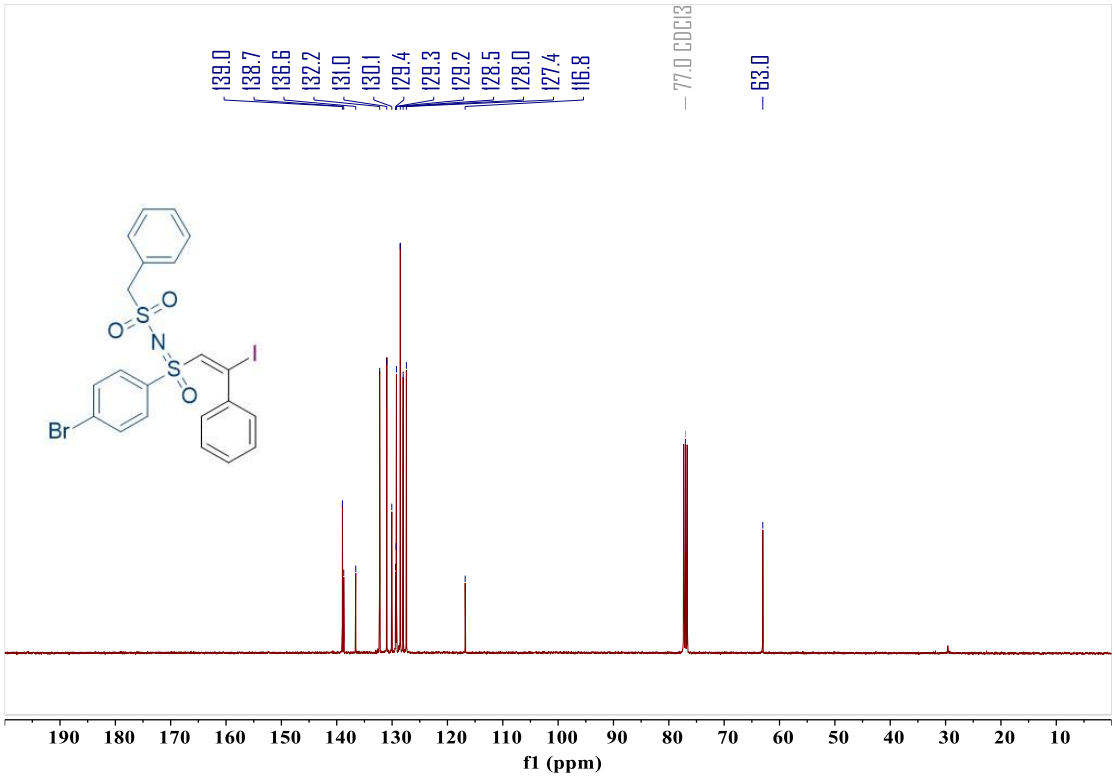


^{13}C NMR (100 MHz, DMSO-*d*$_6$)

(*E*)-*N*-((4-bromophenyl)(2-iodo-2-phenylvinyl)(oxo)-λ^6-sulfaneylidene)-1-phenylmethanesulfonamide(3ak)

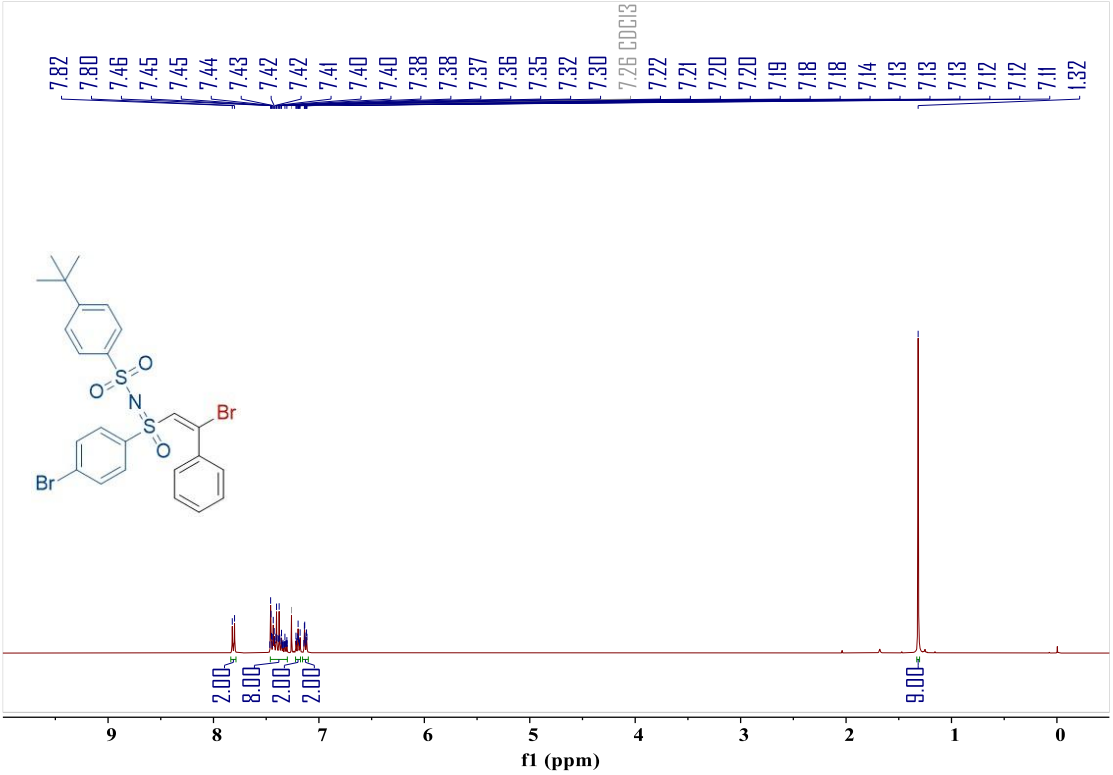


^{1}H NMR (400 MHz, $CDCl_3$)

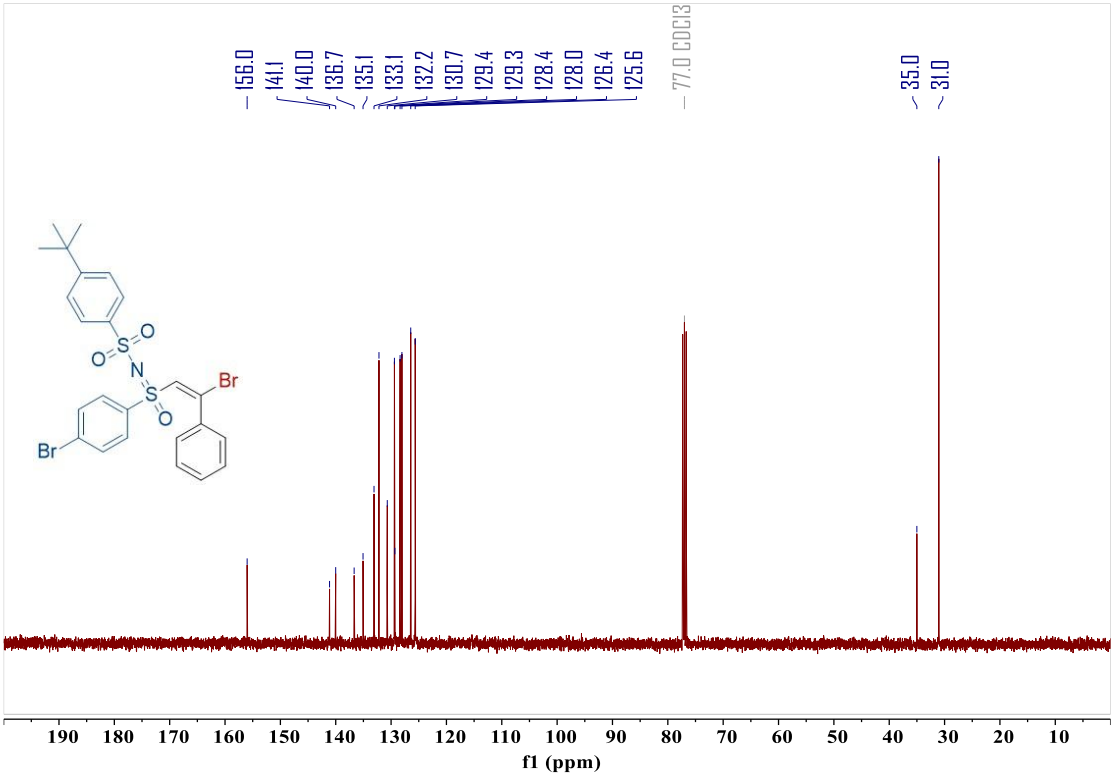


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4a)

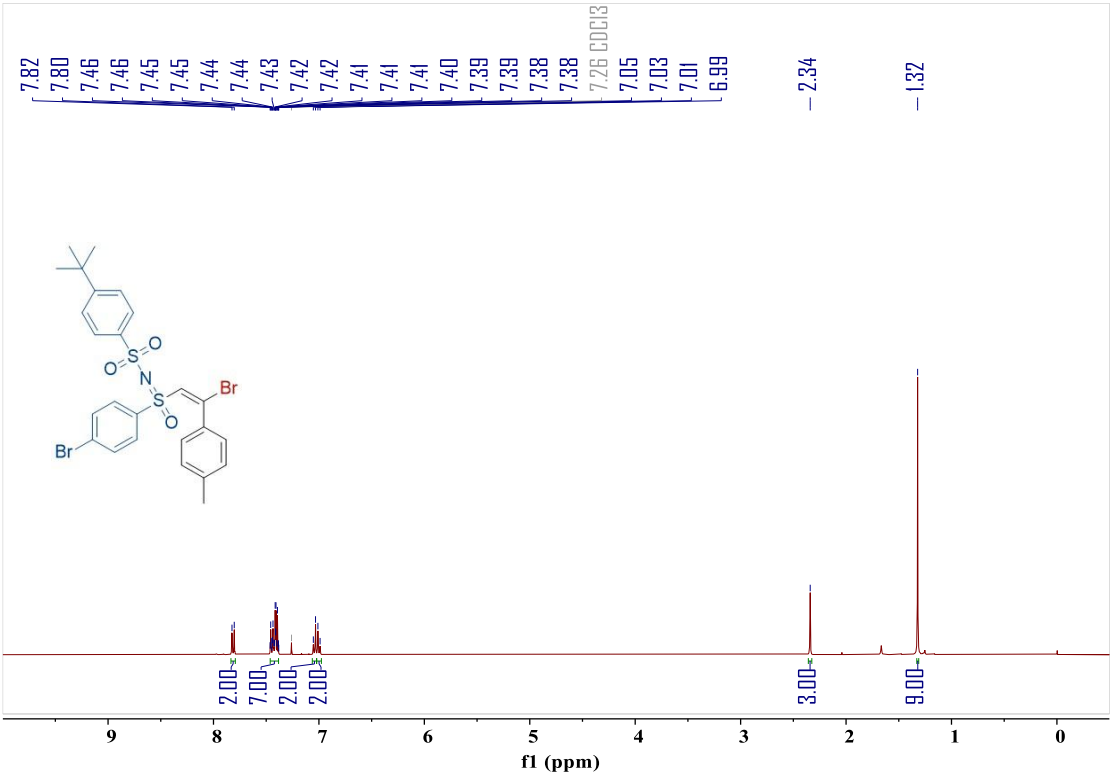


^{1}H NMR (400 MHz, $CDCl_3$)

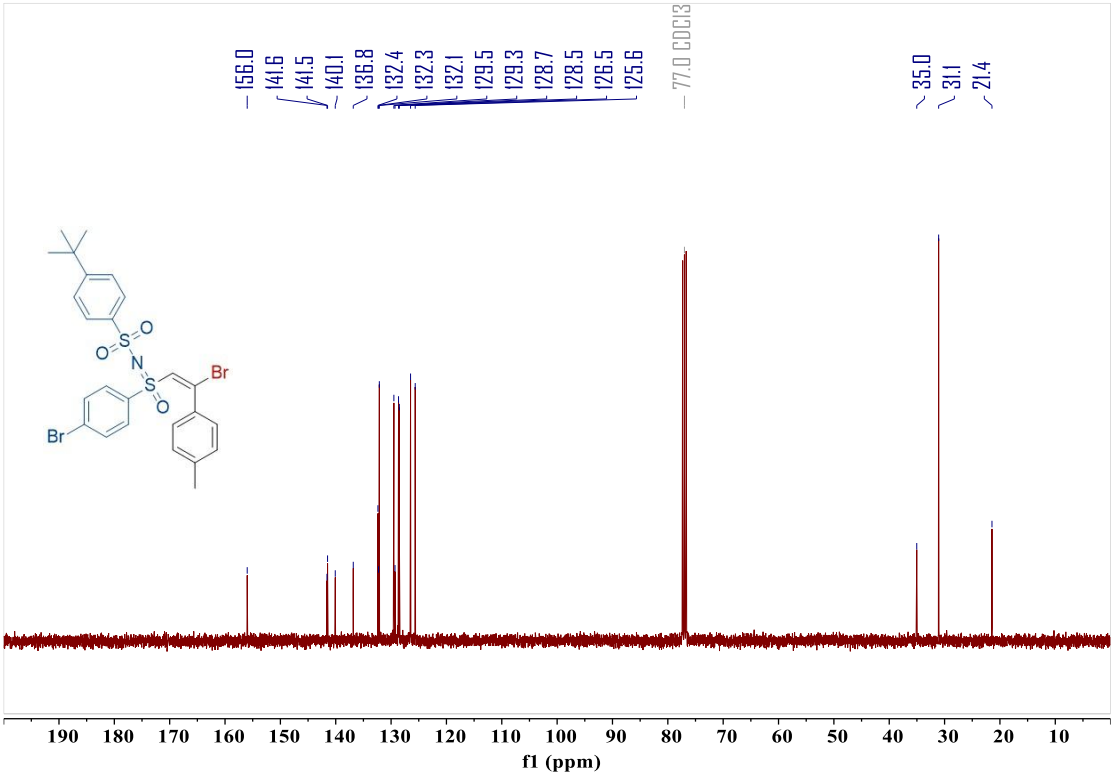


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(p-tolyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzene sulfonamide (4b)

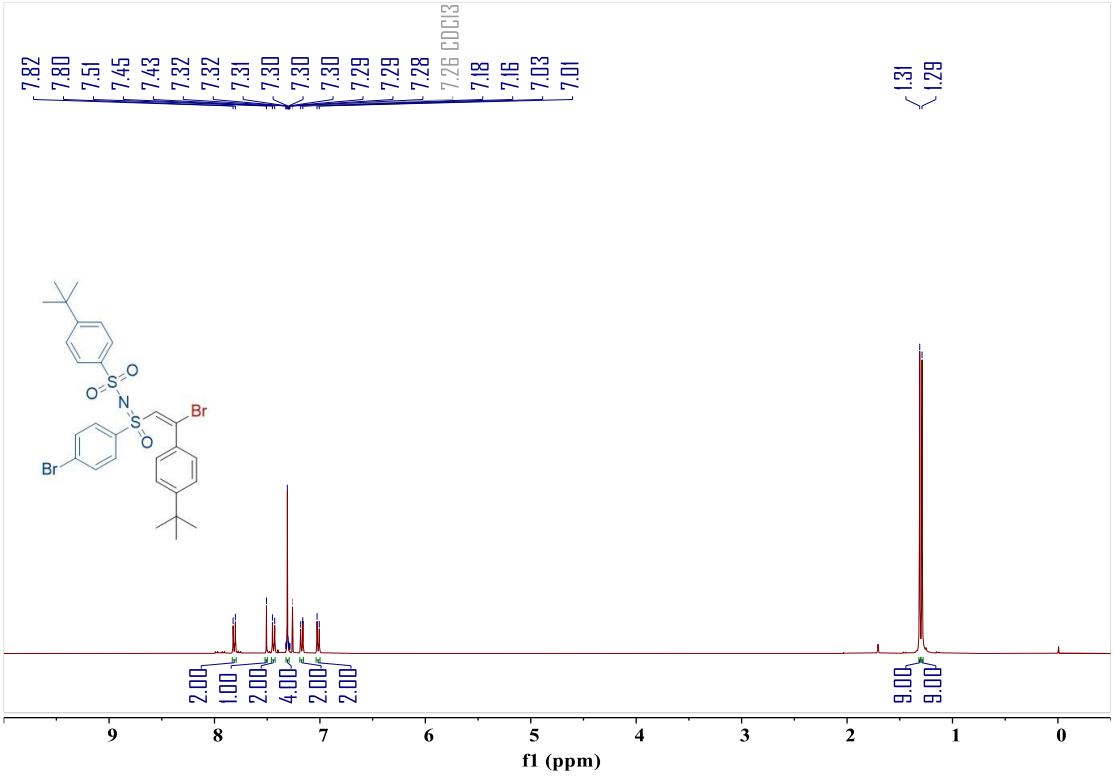


^{1}H NMR (400 MHz, $CDCl_3$)

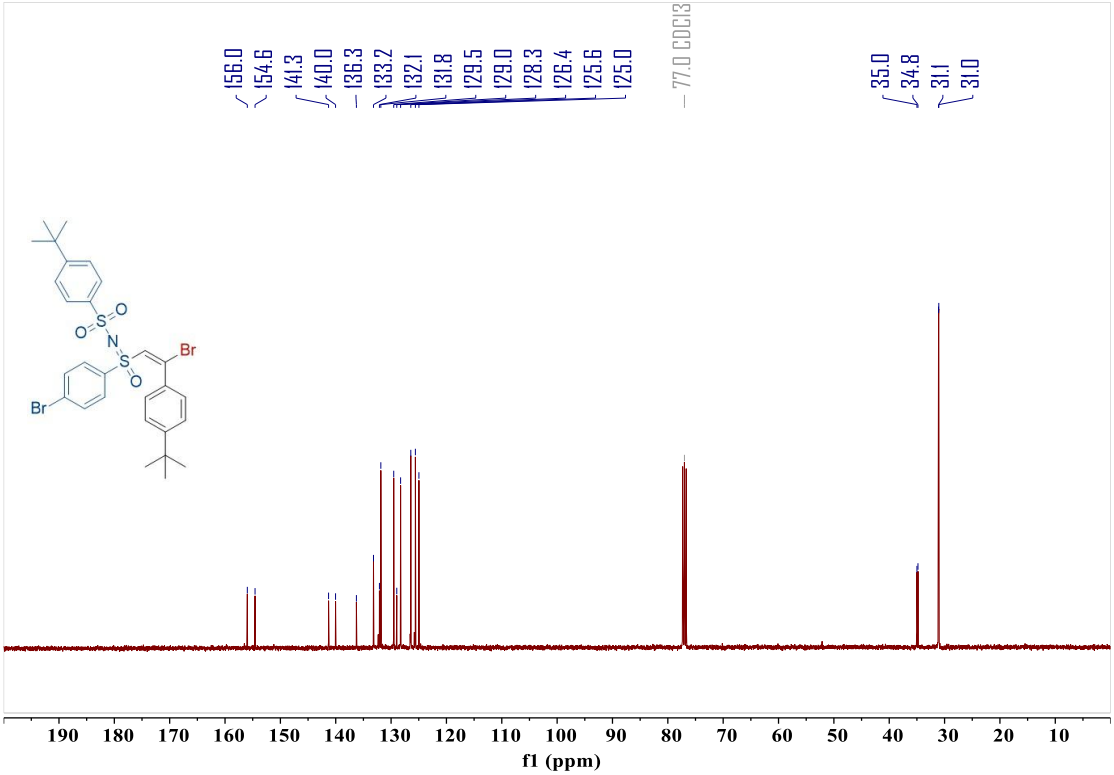


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-(*tert*-butyl)phenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4c)

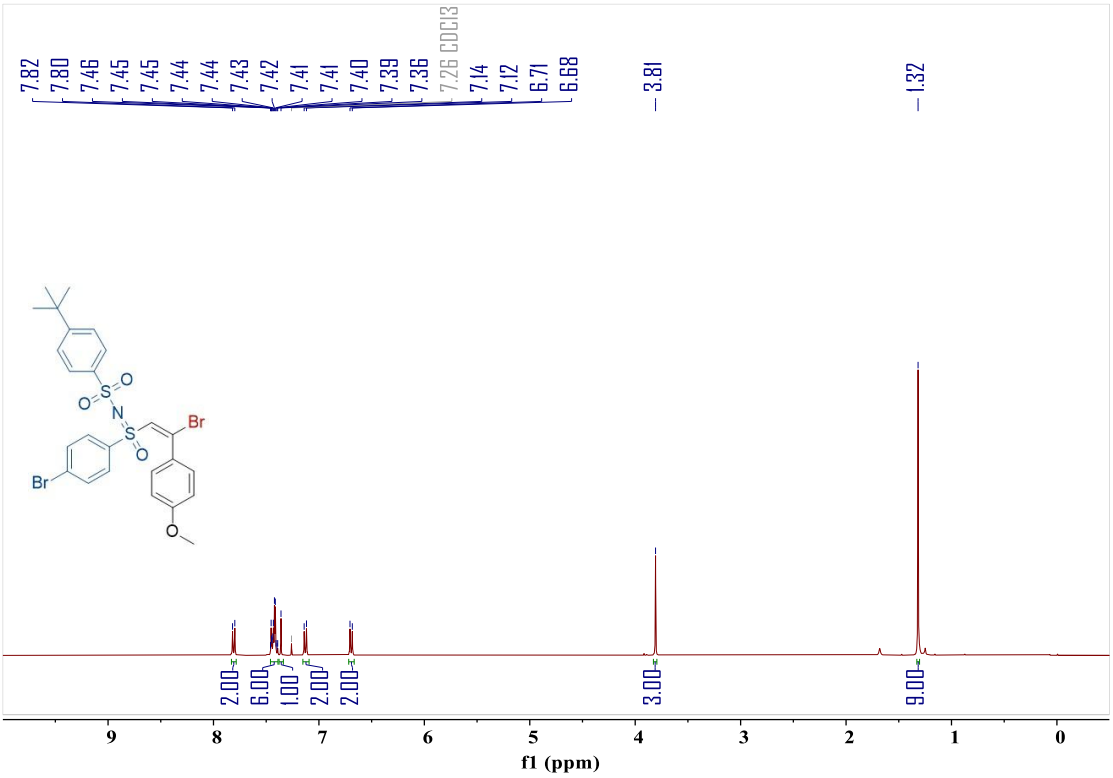


^{1}H NMR (400 MHz, $CDCl_3$)

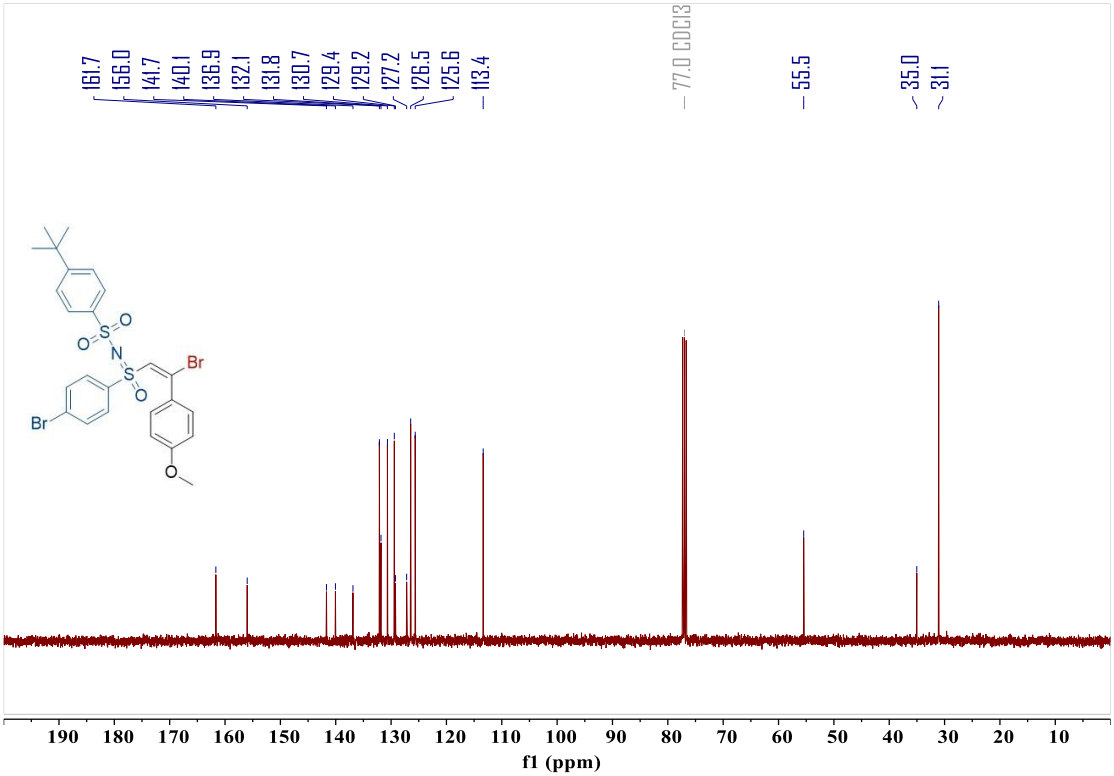


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-methoxyphenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4d)

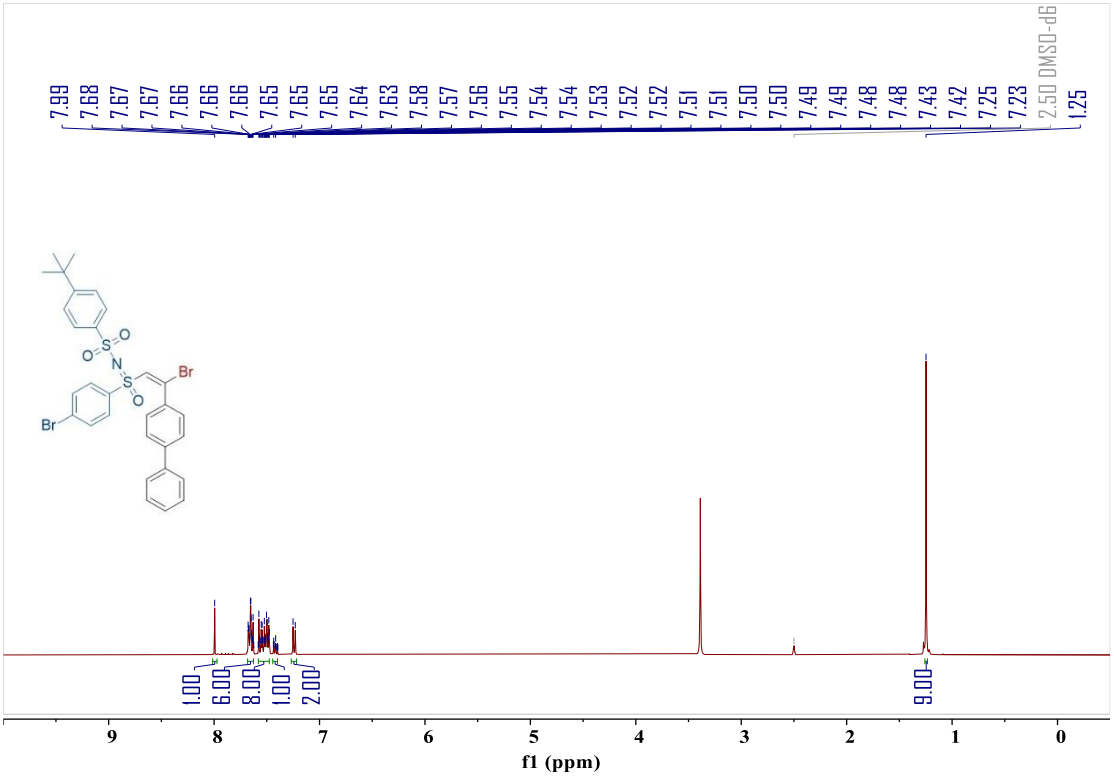


^{1}H NMR (400 MHz, $CDCl_3$)

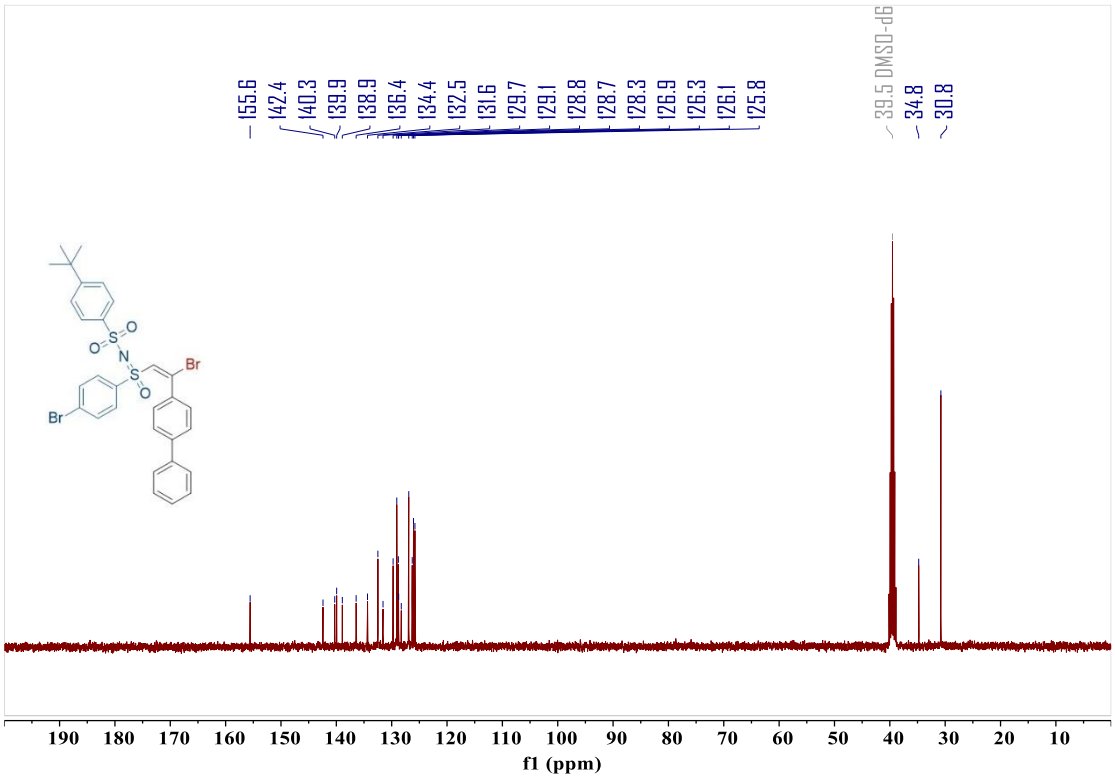


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-([1,1'-biphenyl]-4-yl)-2-bromovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4e)

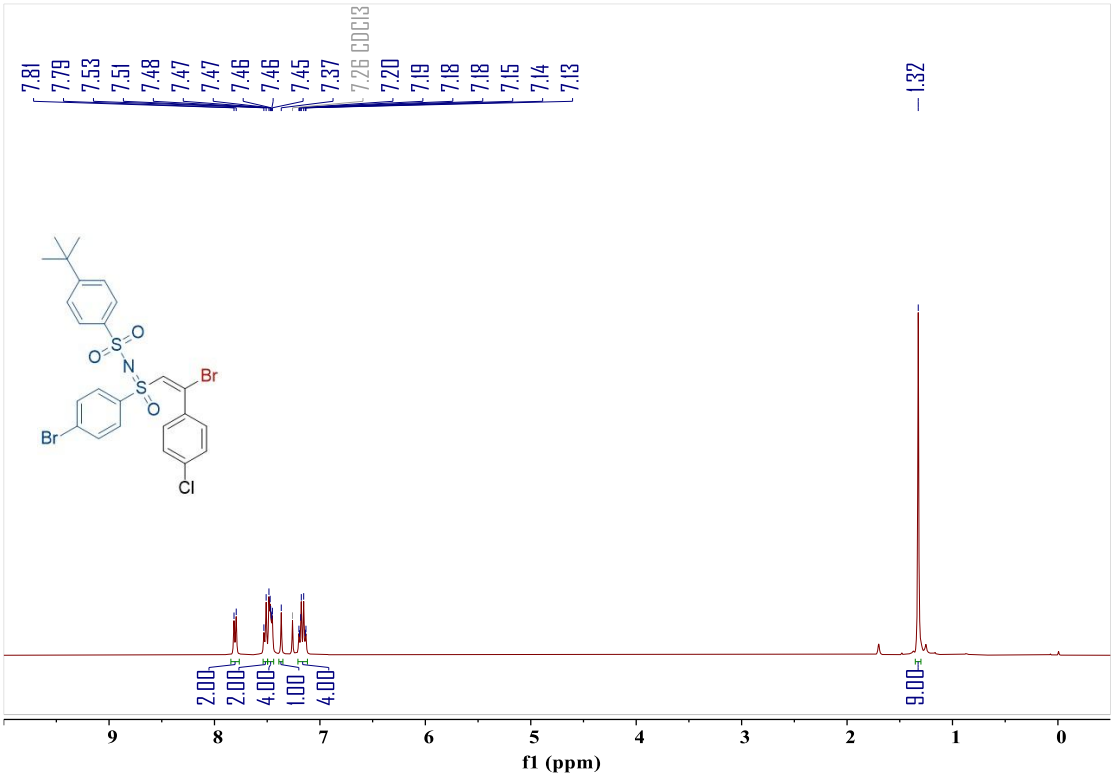


^{1}H NMR (400 MHz, DMSO-*d*$_6$)

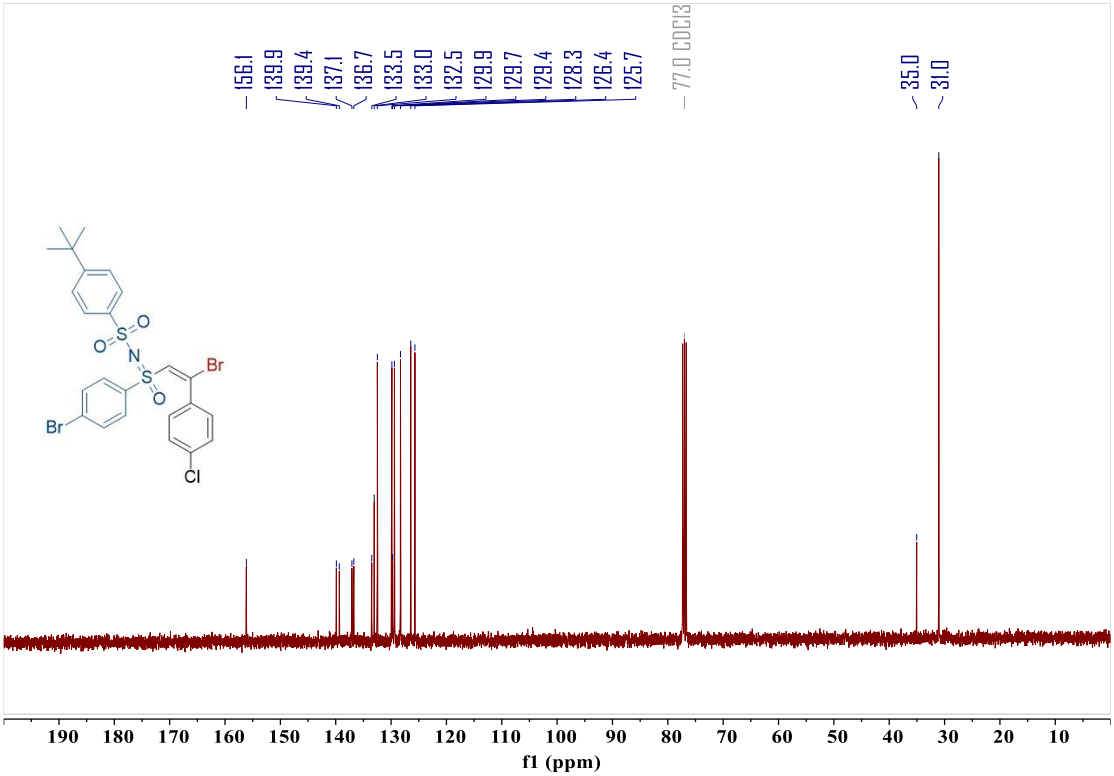


^{13}C NMR (100 MHz, DMSO-*d*$_6$)

(*E*)-*N*-((2-bromo-2-(4-chlorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4f)

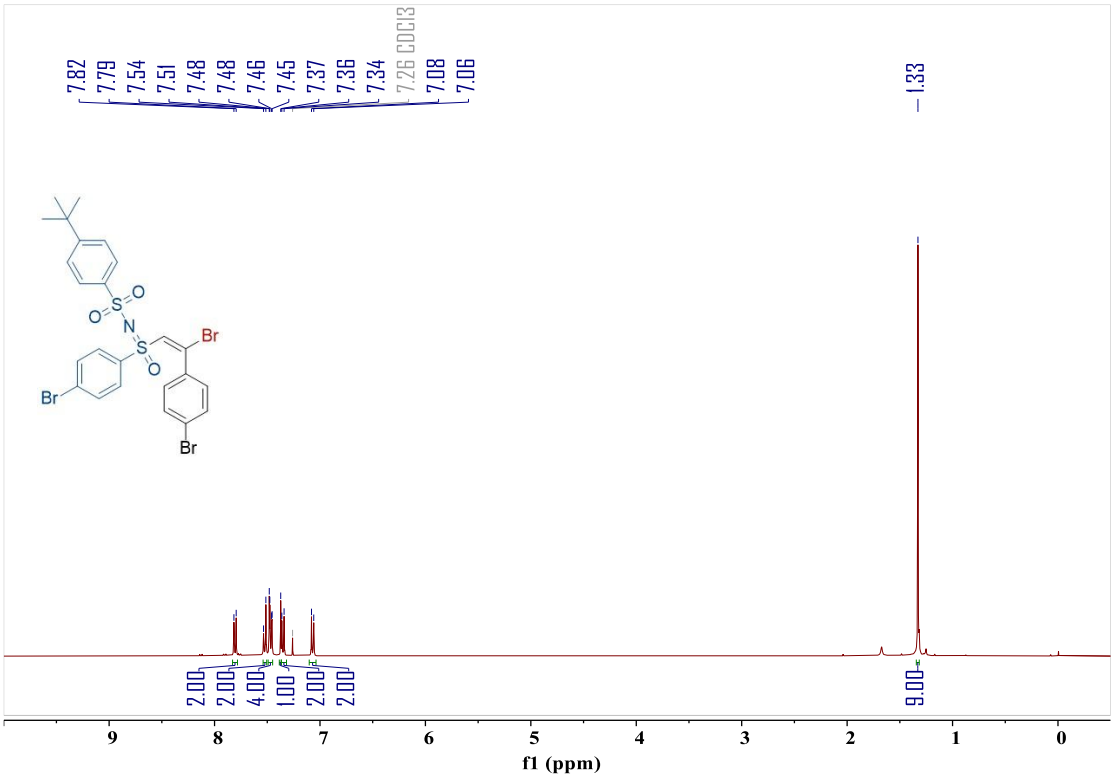


^{1}H NMR (400 MHz, $CDCl_3$)

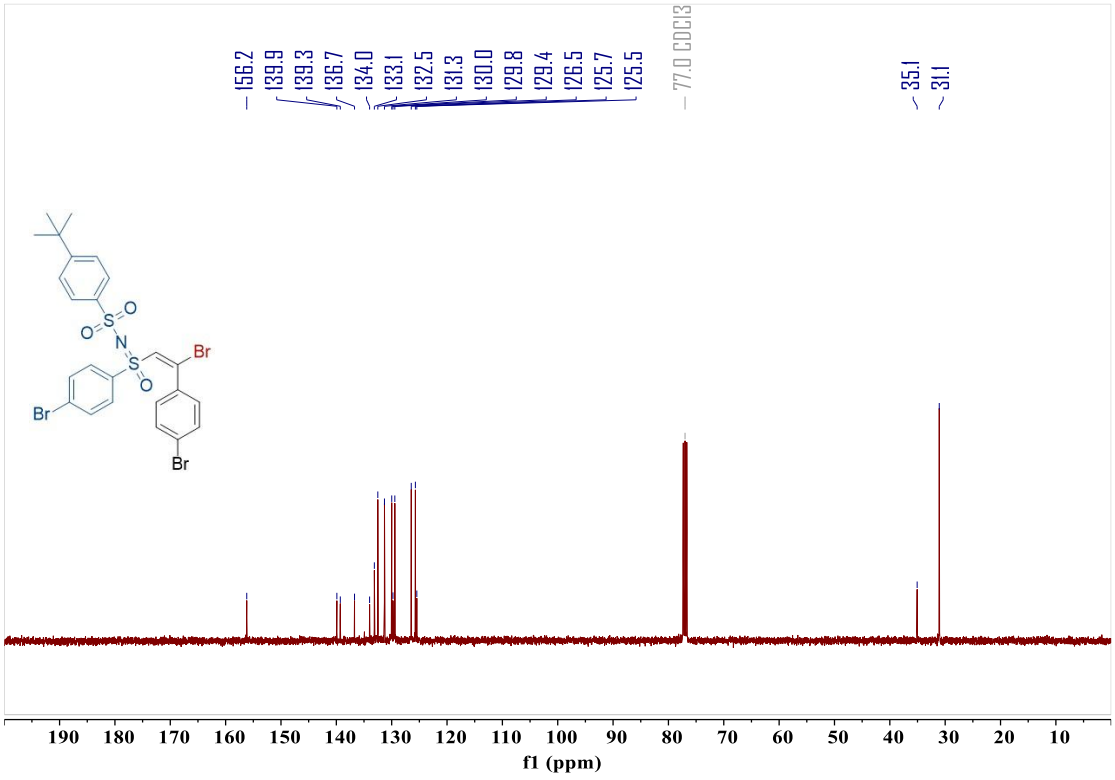


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-bromophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4g)

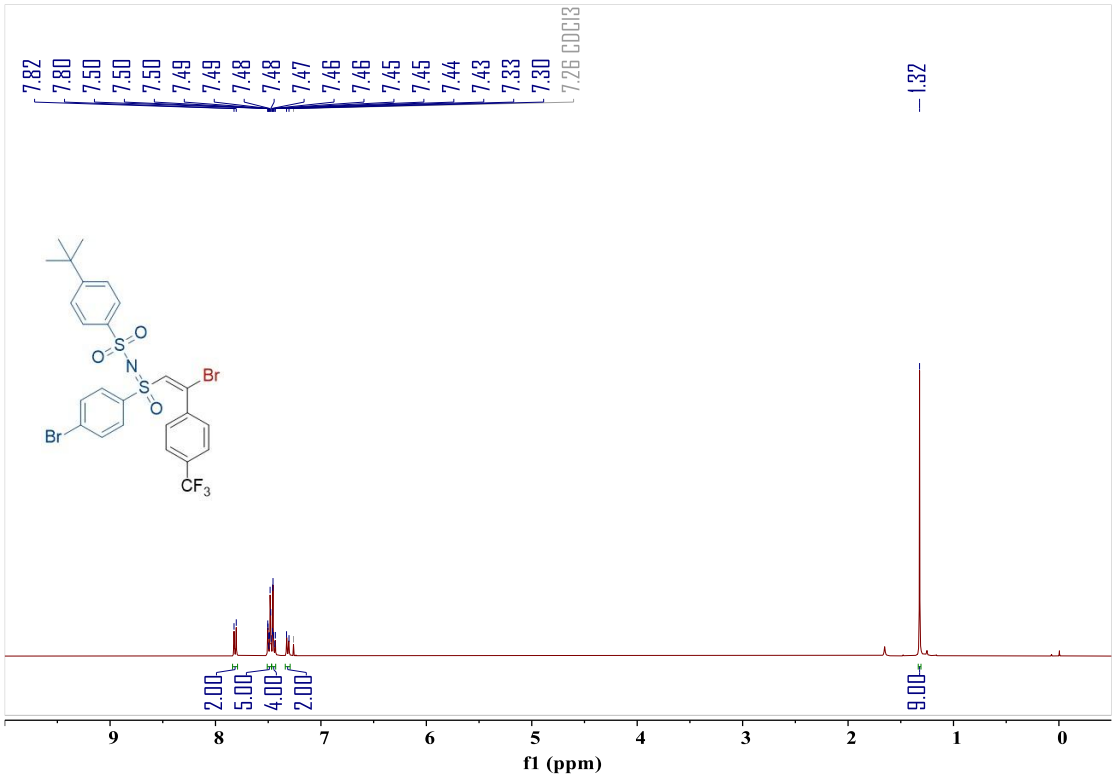


^{1}H NMR (400 MHz, $CDCl_3$)

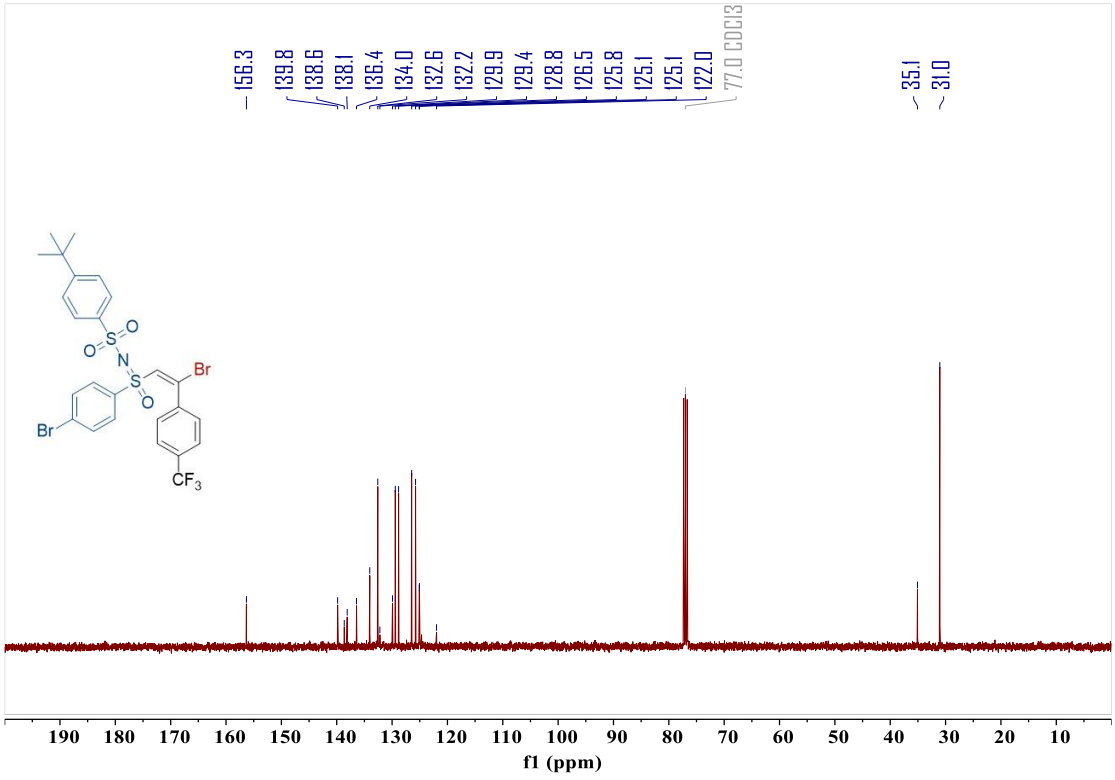


^{13}C NMR (100 MHz, $CDCl_3$)

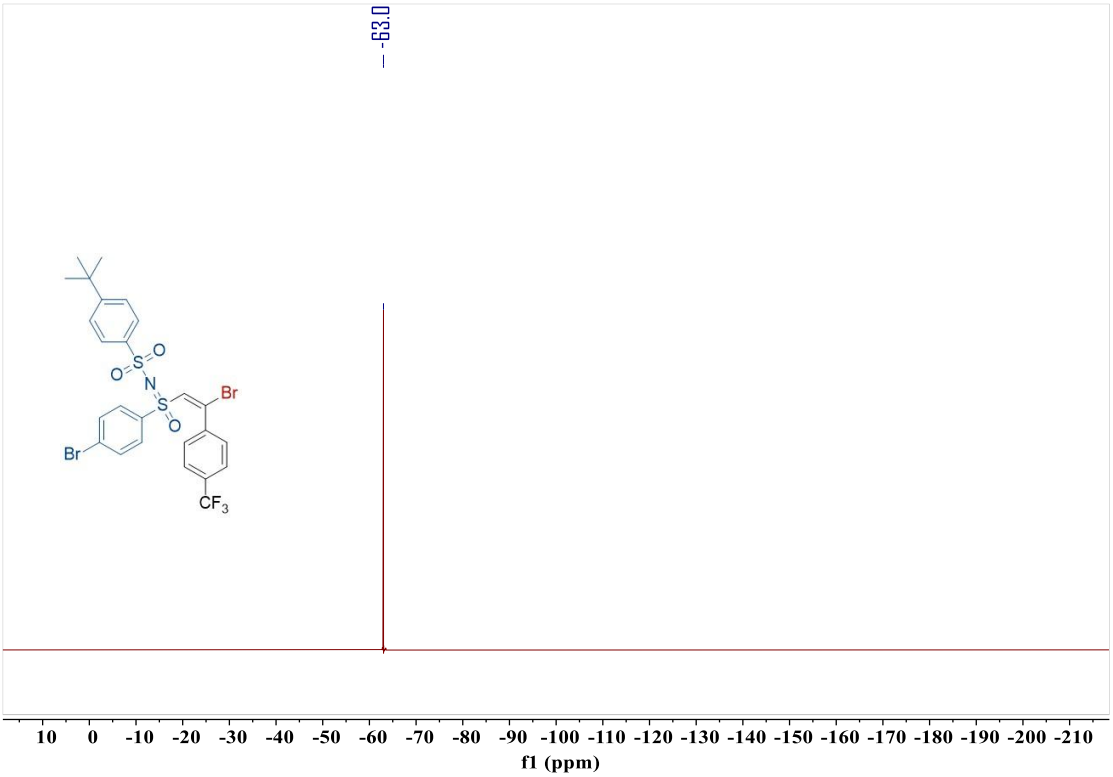
(*E*)-*N*-((2-bromo-2-(4-(trifluoromethyl)phenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide(4h)



^{1}H NMR (400 MHz, $CDCl_3$)

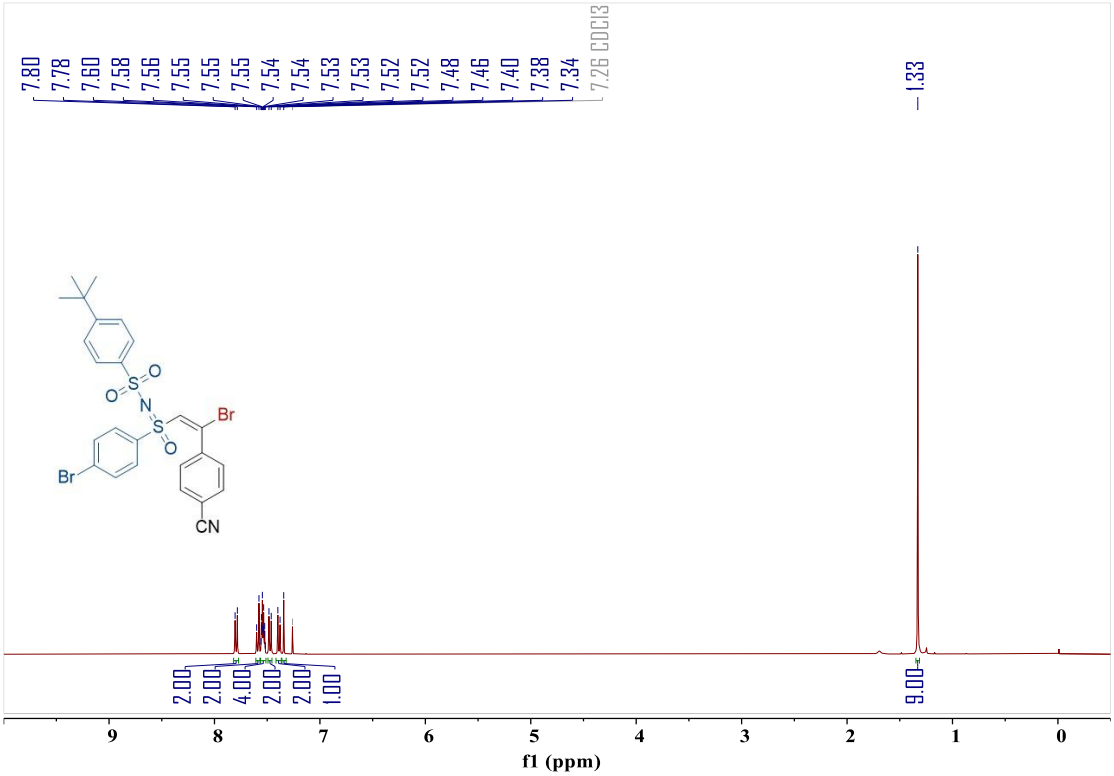


^{13}C NMR (100 MHz, $CDCl_3$)

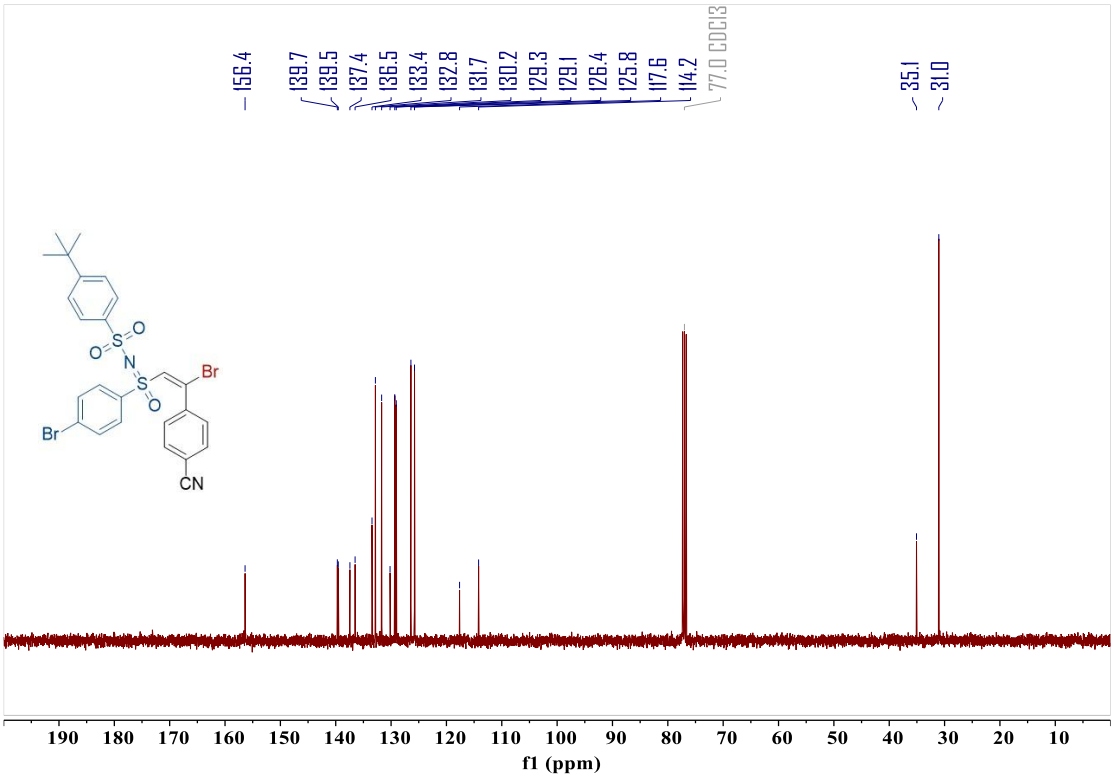


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-cyanophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4i)

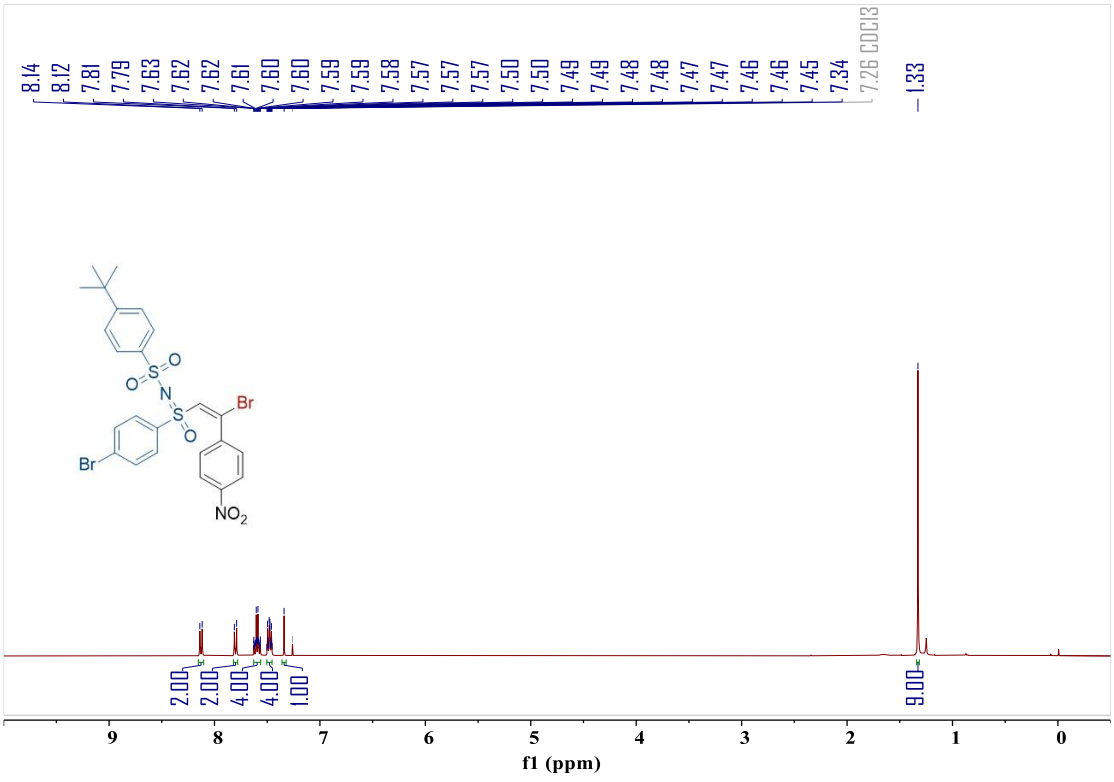


^{1}H NMR (400 MHz, $CDCl_3$)

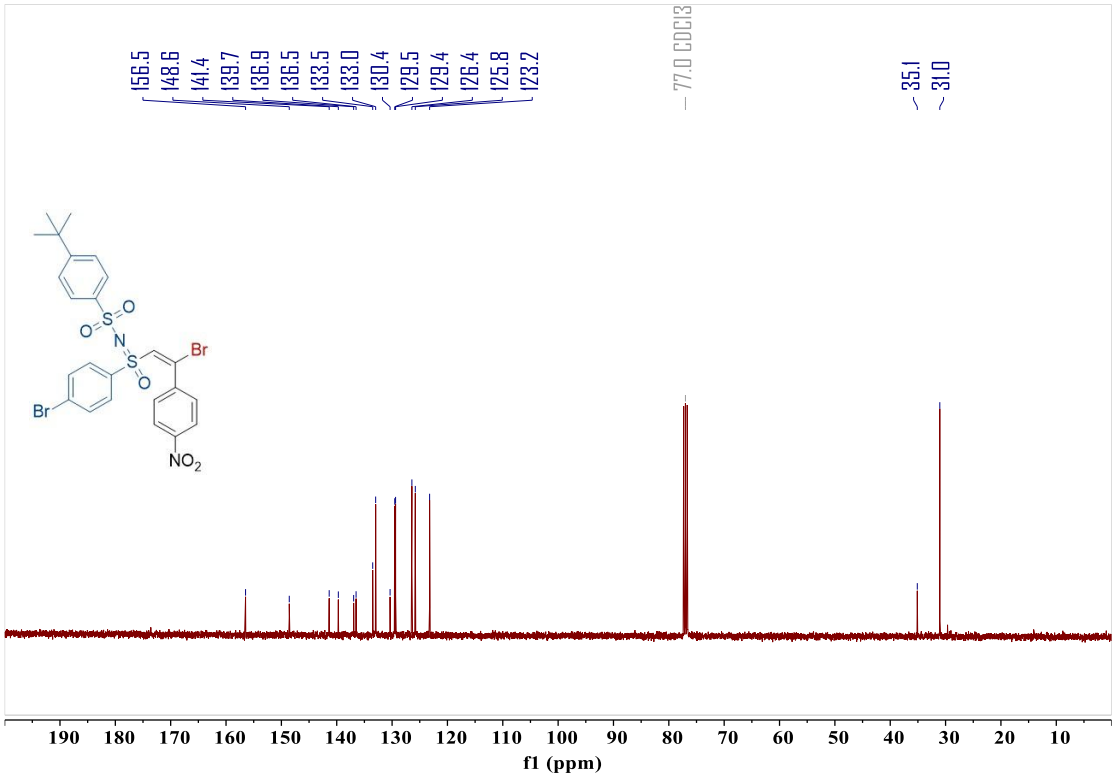


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-nitrophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4j)

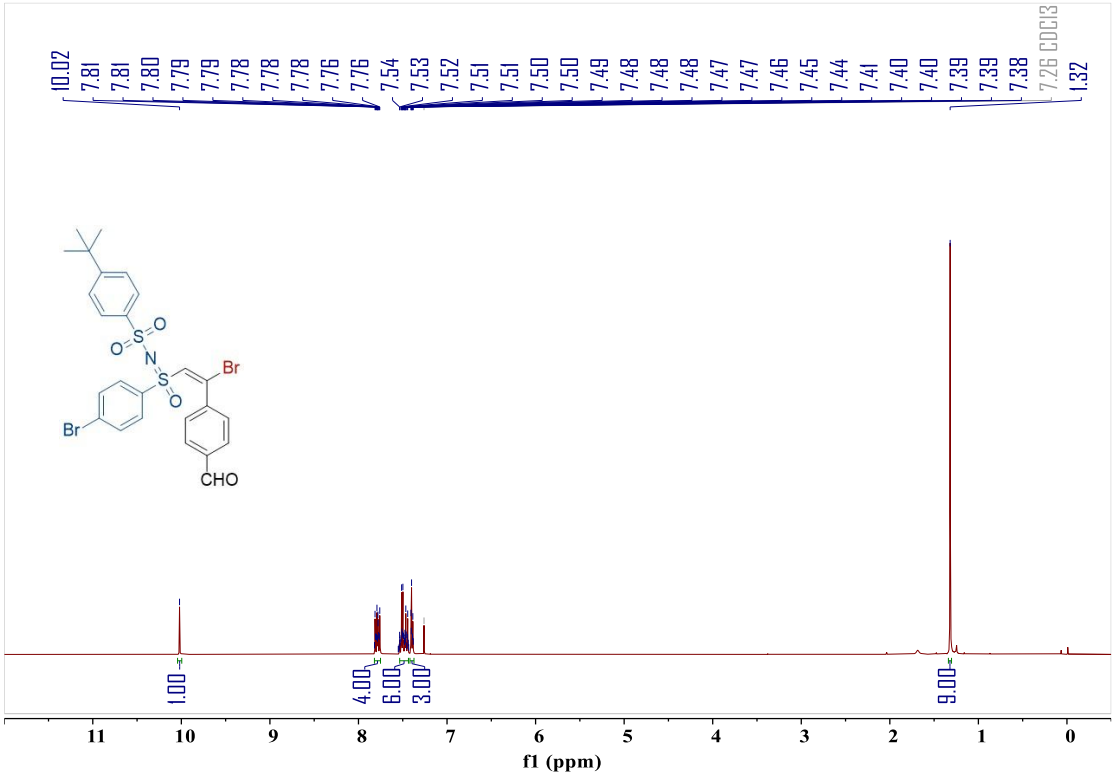


^{1}H NMR (400 MHz, $CDCl_3$)

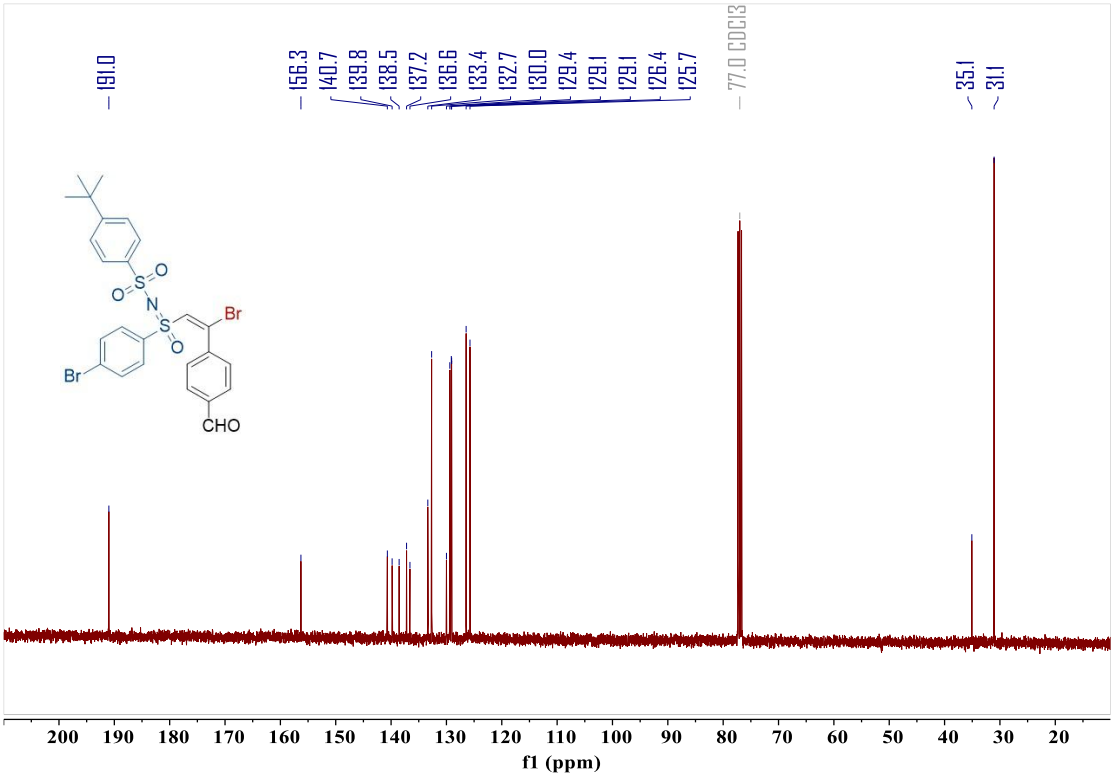


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(4-formylphenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4k)

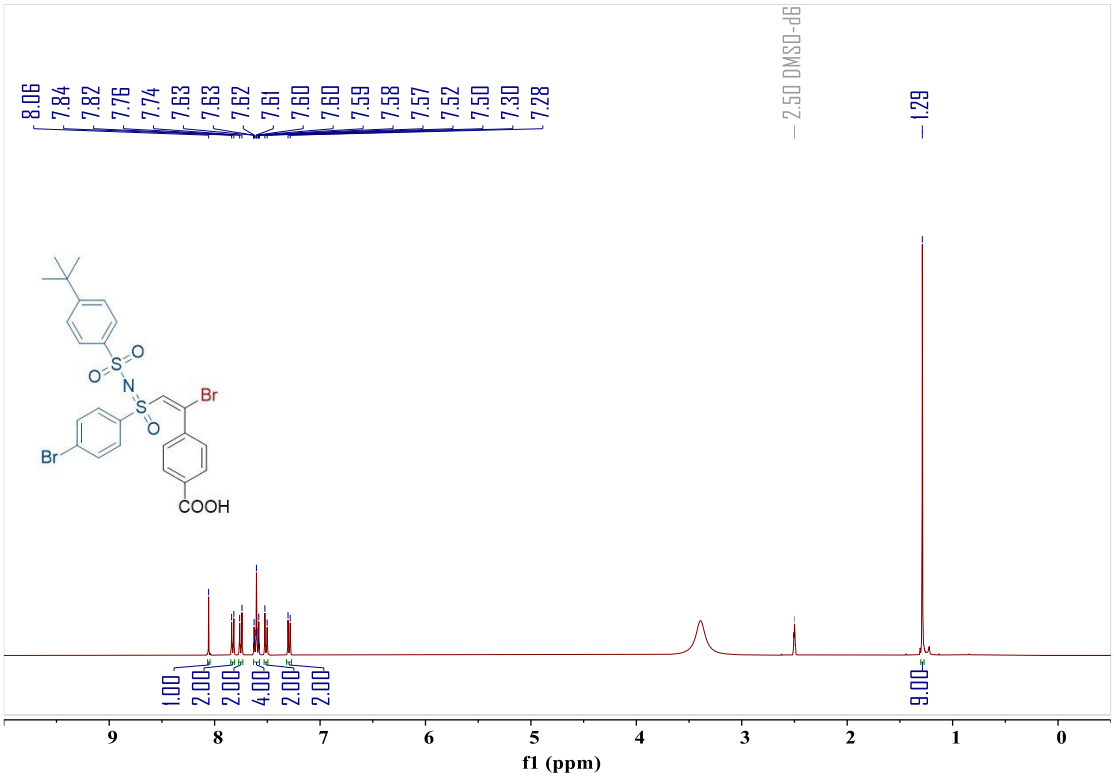


^{1}H NMR (400 MHz, $CDCl_3$)

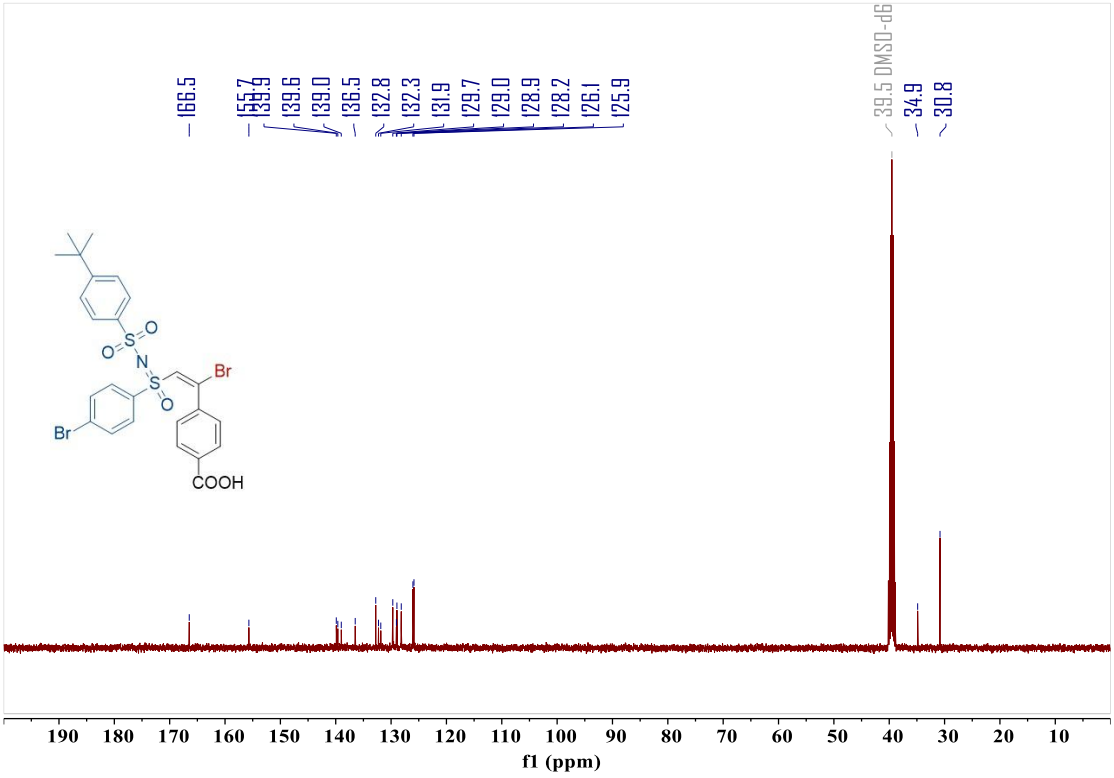


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-4-(1-bromo-2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)vinyl)benzoic acid (4l)

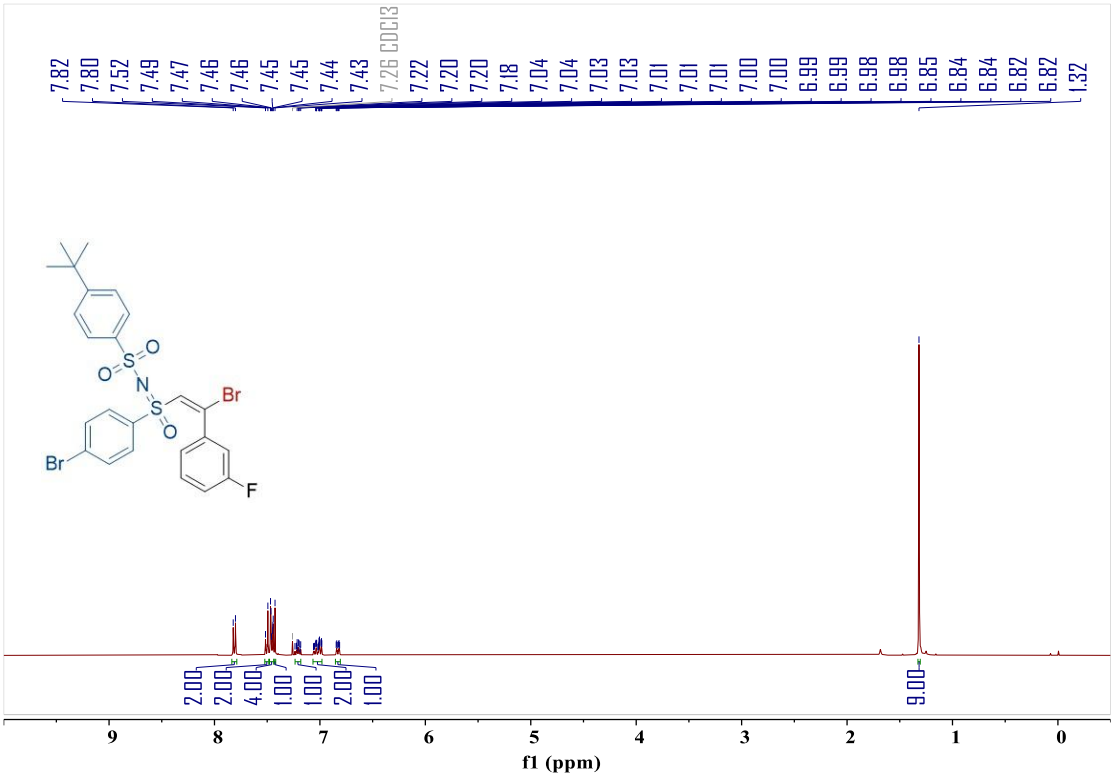


^{1}H NMR (400 MHz, DMSO-*d*$_6$)

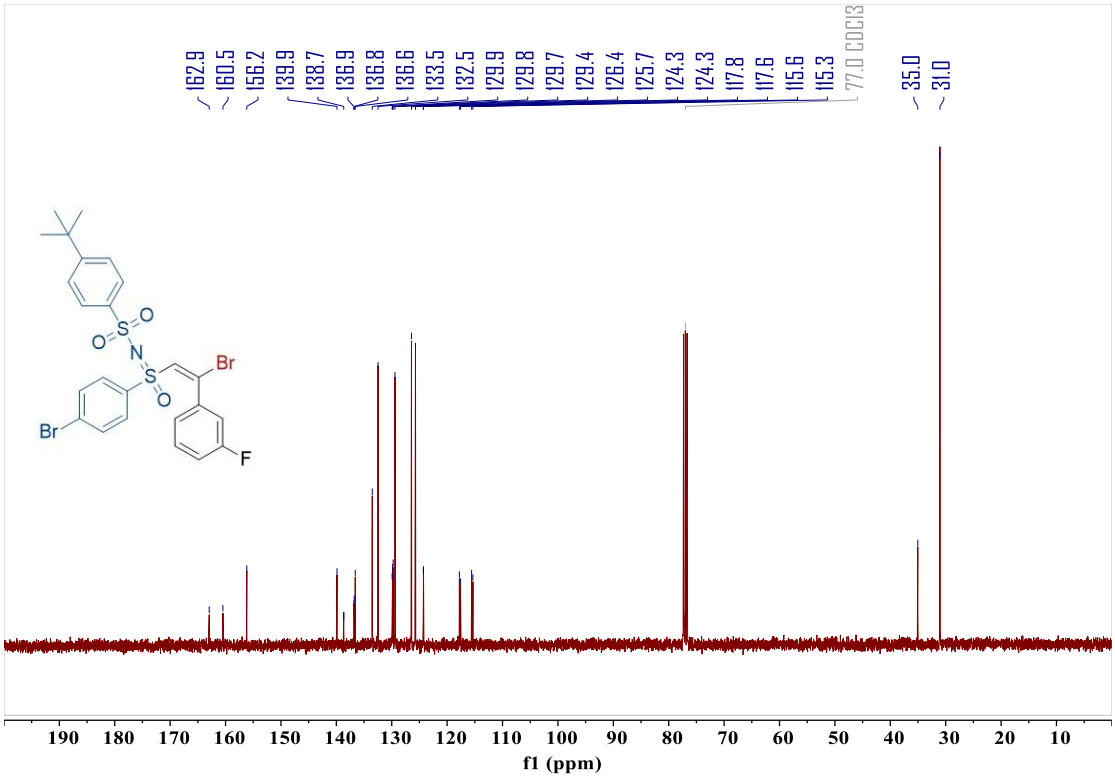


^{13}C NMR (100 MHz, DMSO-*d*$_6$)

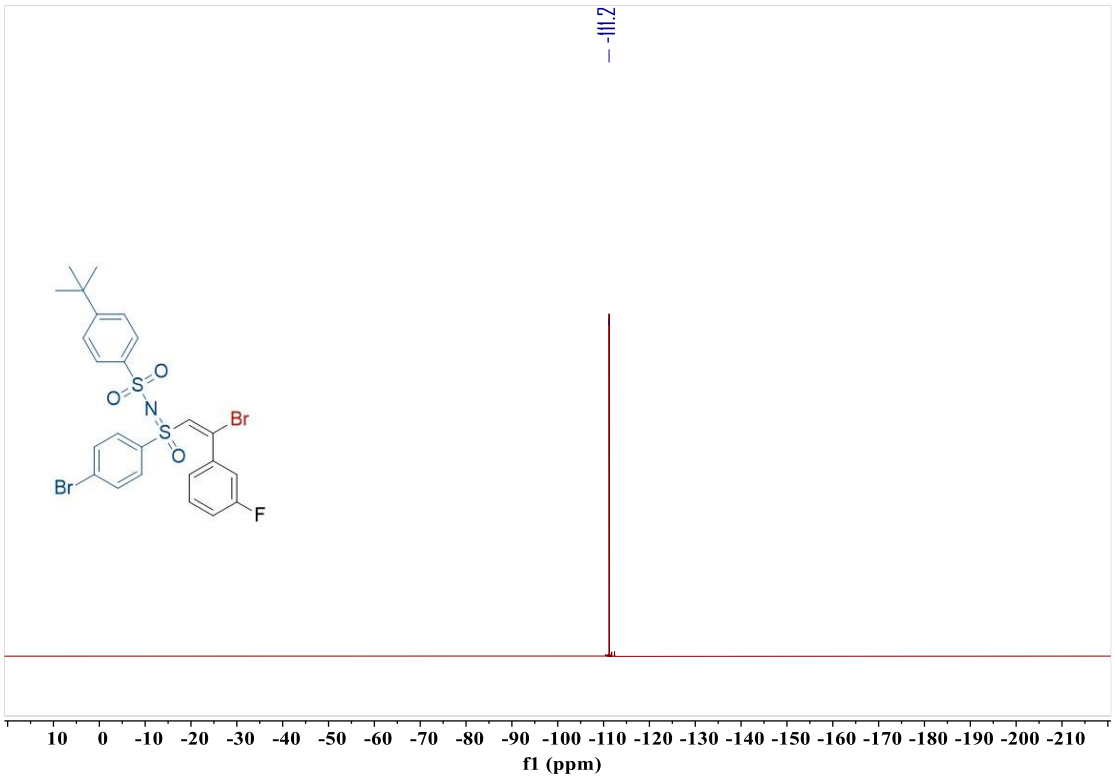
(*E*)-*N*-((2-bromo-2-(3-fluorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4m)



^{1}H NMR (400 MHz, CDCl$_3$)

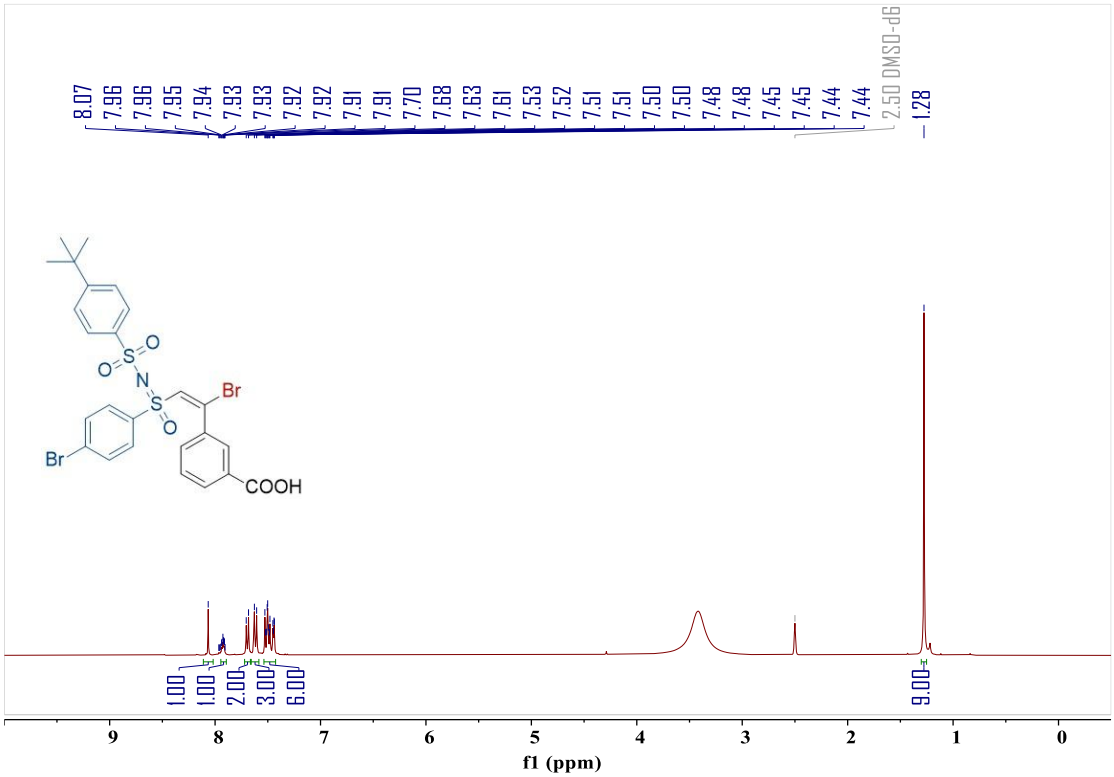


^{13}C NMR (100 MHz, $CDCl_3$)

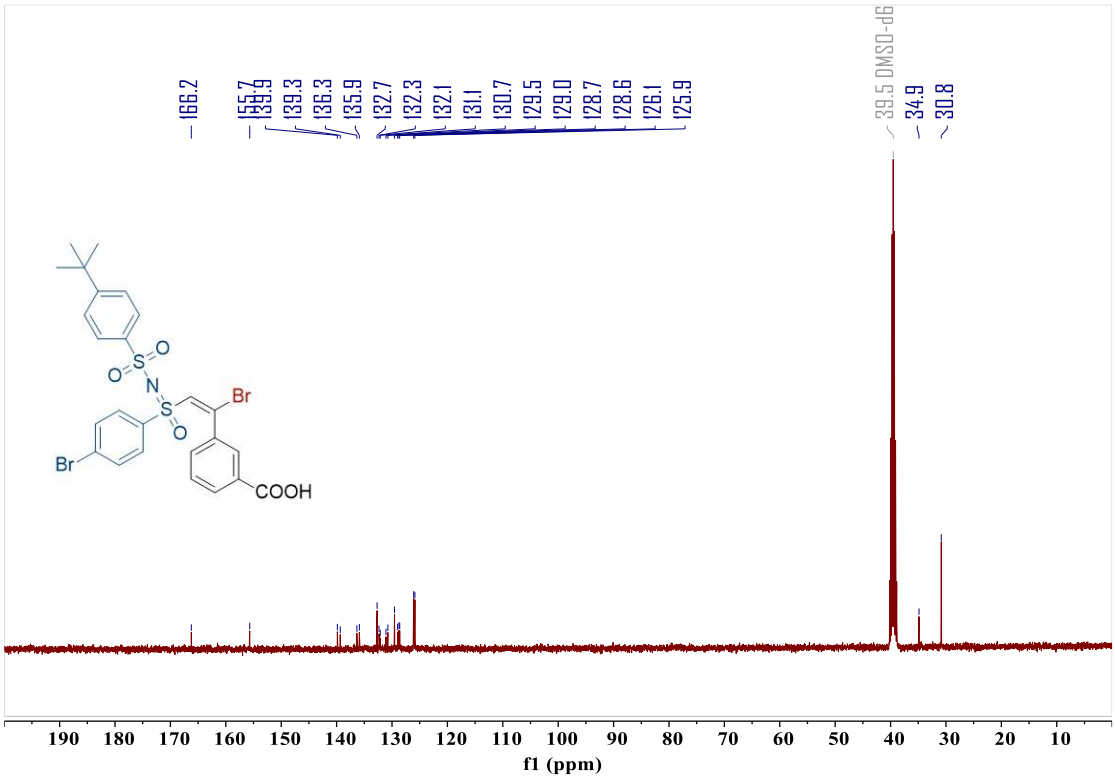


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-3-(1-bromo-2-(4-bromo-*N*-((4-(*tert*-butyl)phenyl)sulfonyl)phenylsulfonimidoyl)vinyl)benzoic acid (4n)

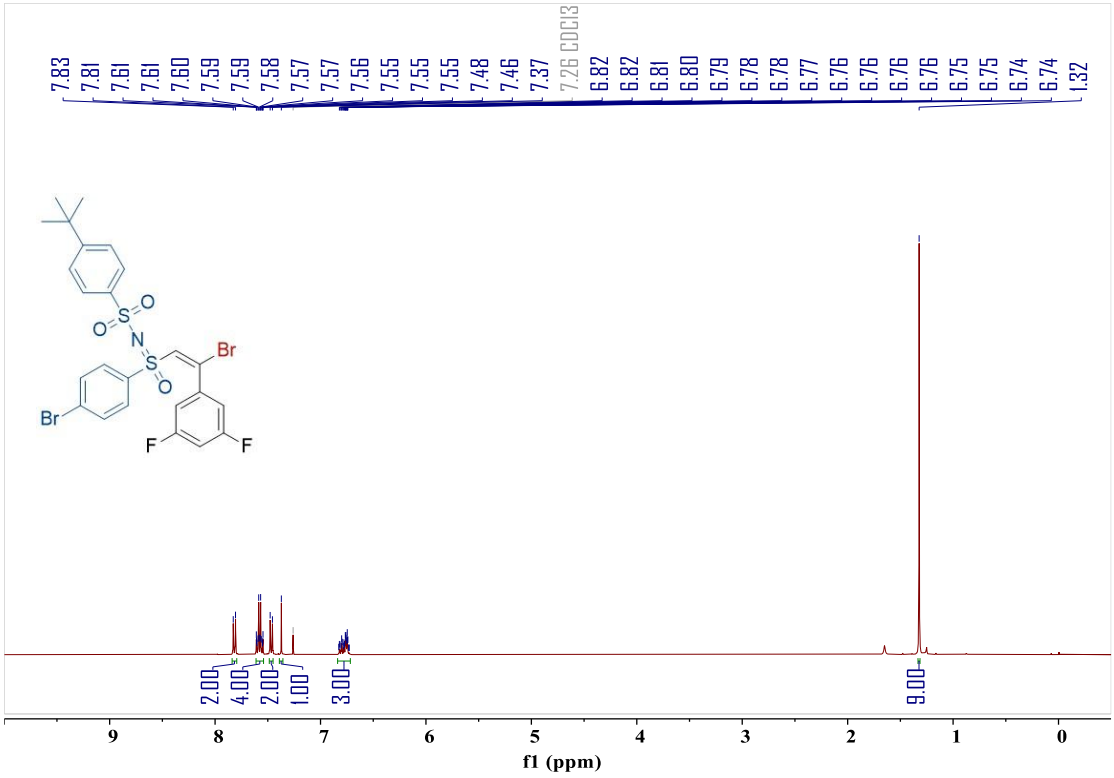


^{1}H NMR (400 MHz, DMSO-d_6)

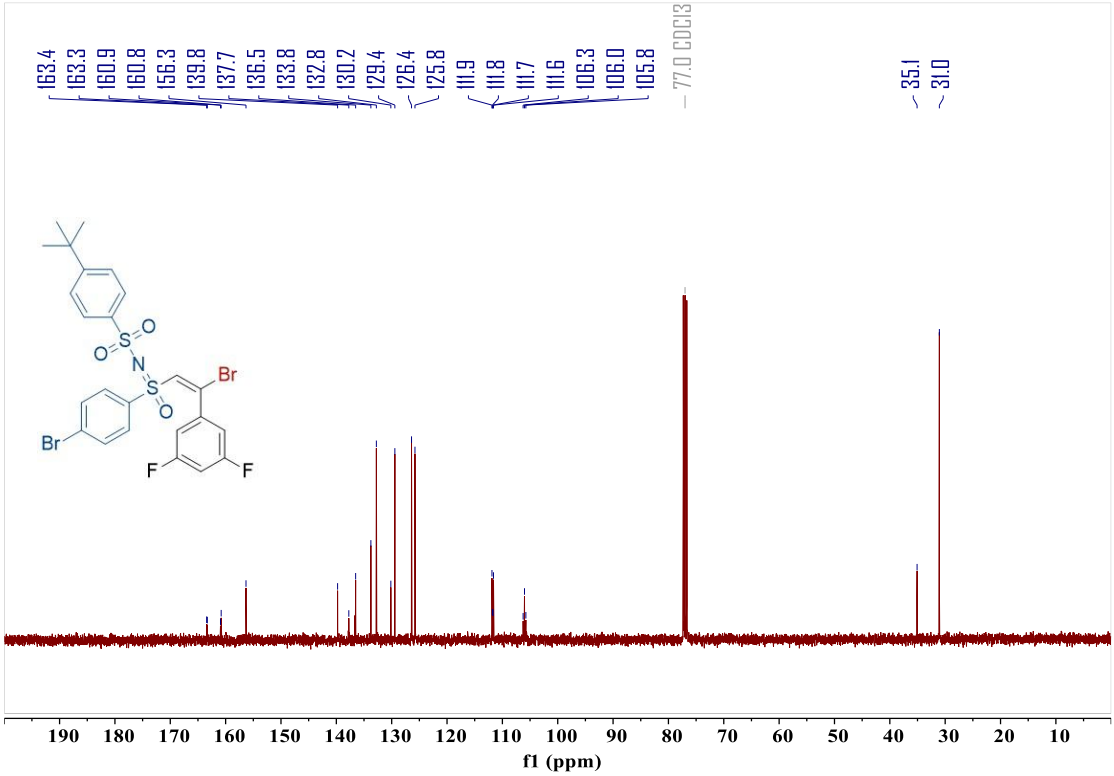


^{13}C NMR (100 MHz, DMSO-d_6)

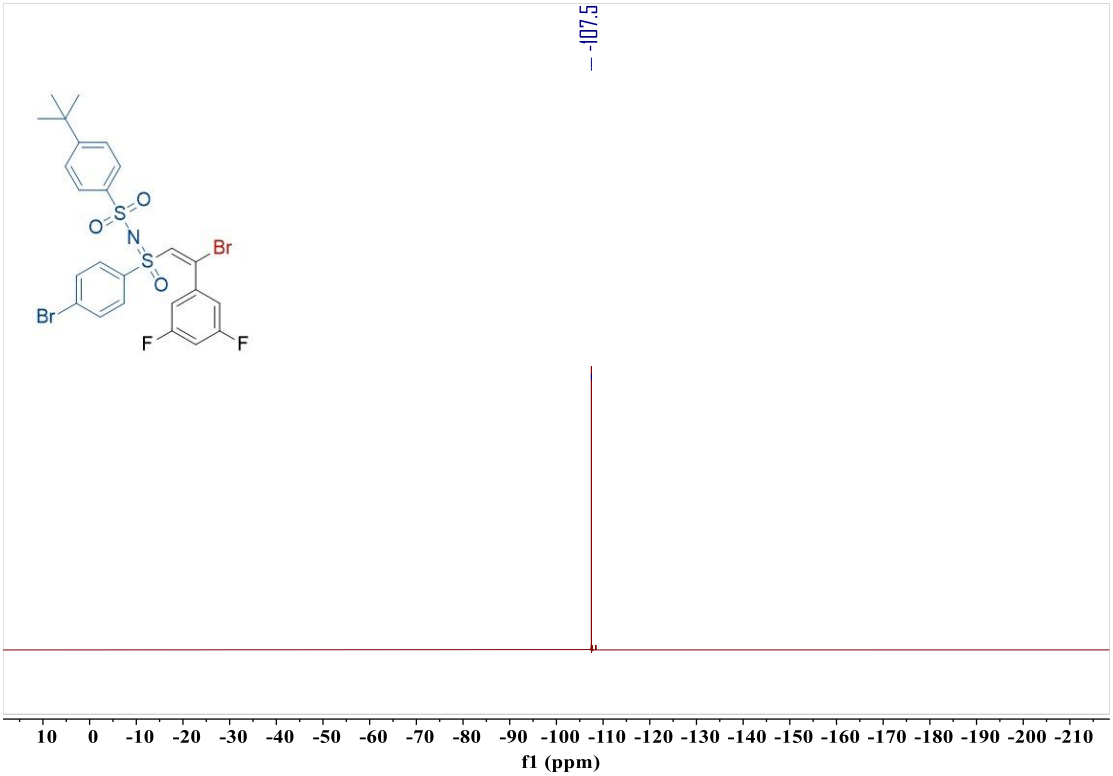
(*E*)-*N*-((2-bromo-2-(3,5-difluorophenyl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4o)



^{1}H NMR (400 MHz, $CDCl_3$)

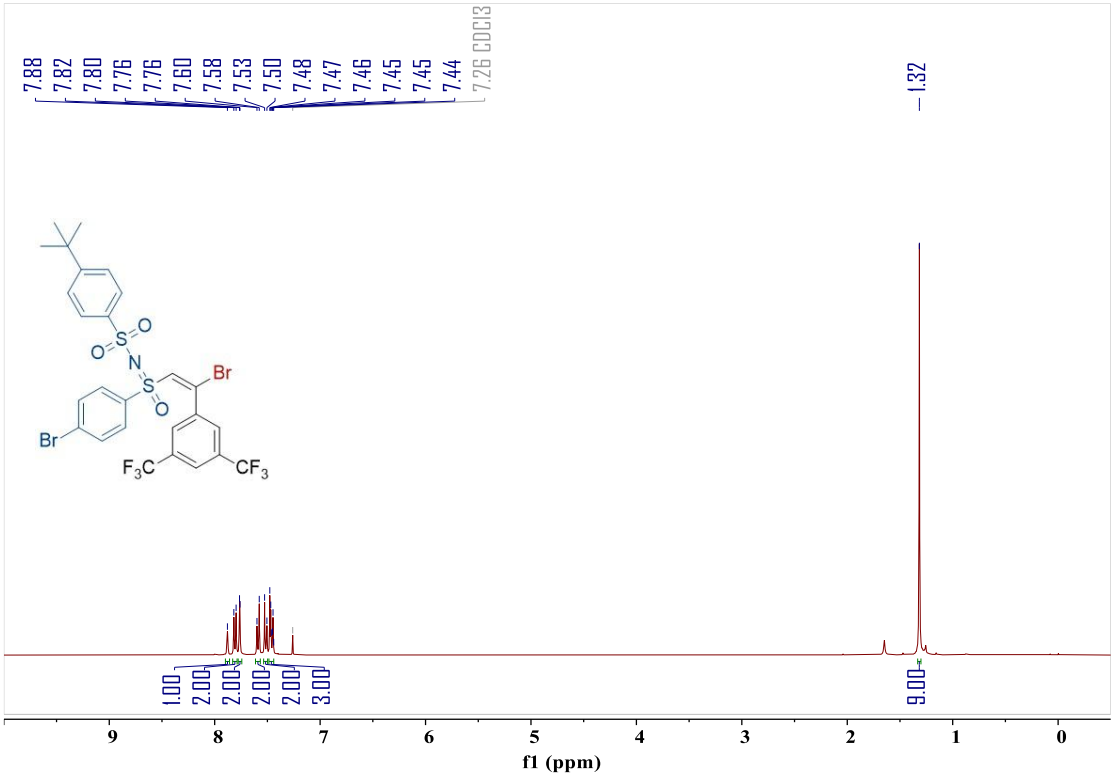


^{13}C NMR (100 MHz, $CDCl_3$)

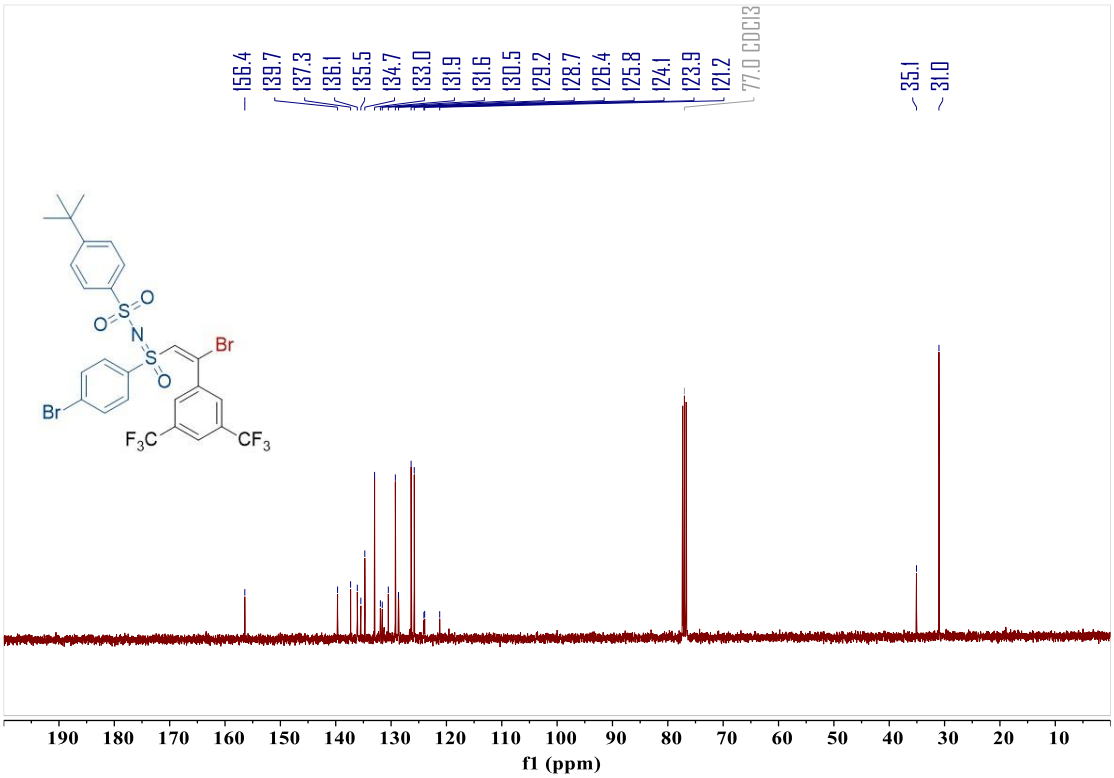


^{19}F NMR (376 MHz, $CDCl_3$)

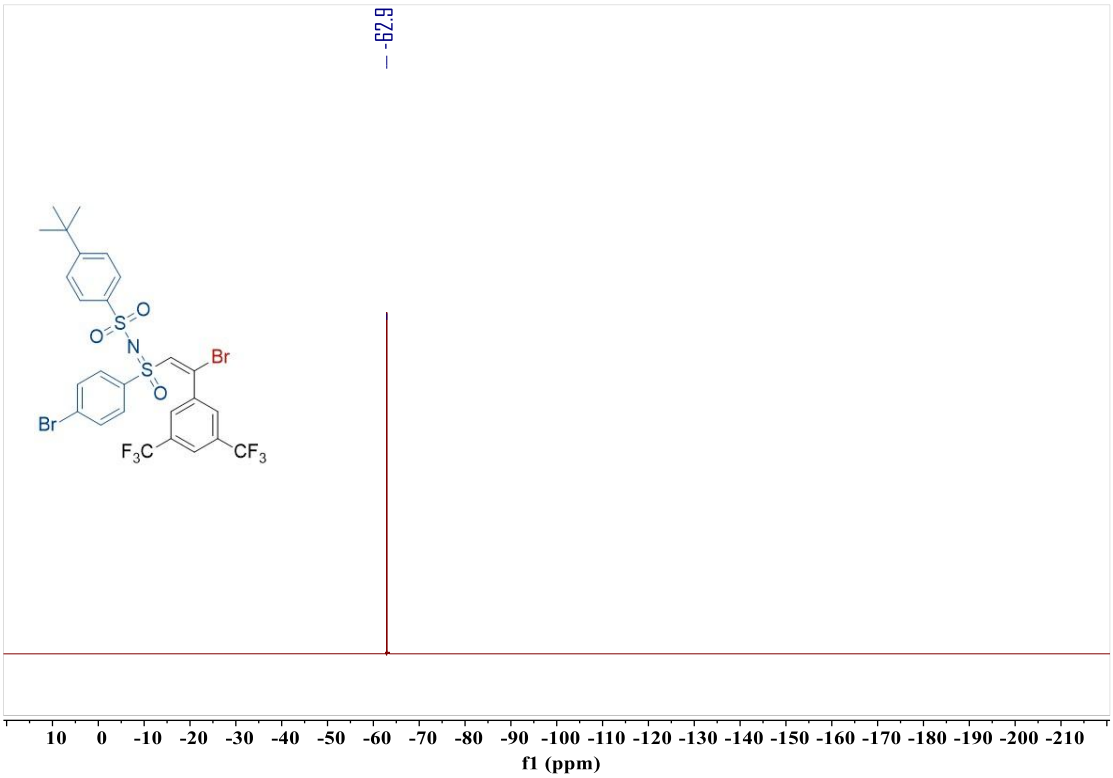
(*E*)-*N*-((2-(3,5-bis(trifluoromethyl)phenyl)-2-bromovinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene) -4-(*tert*-butyl)benzenesulfonamide (4p)



^{1}H NMR (400 MHz, $CDCl_3$)

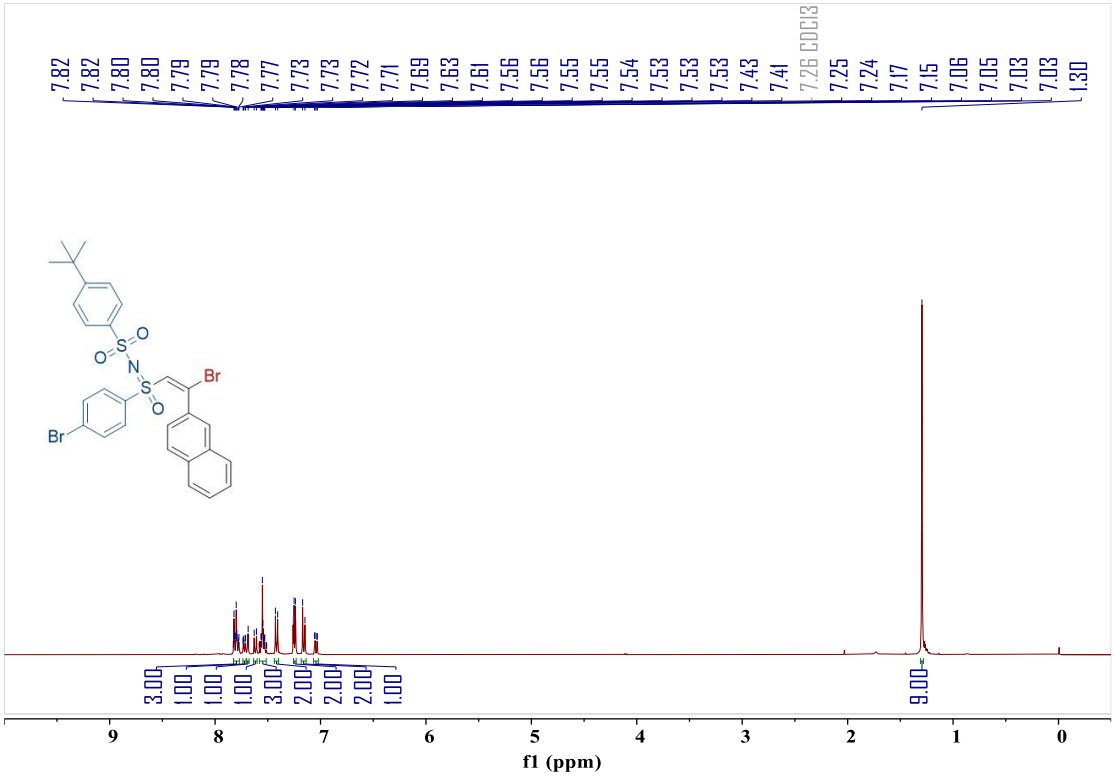


^{13}C NMR (100 MHz, $CDCl_3$)

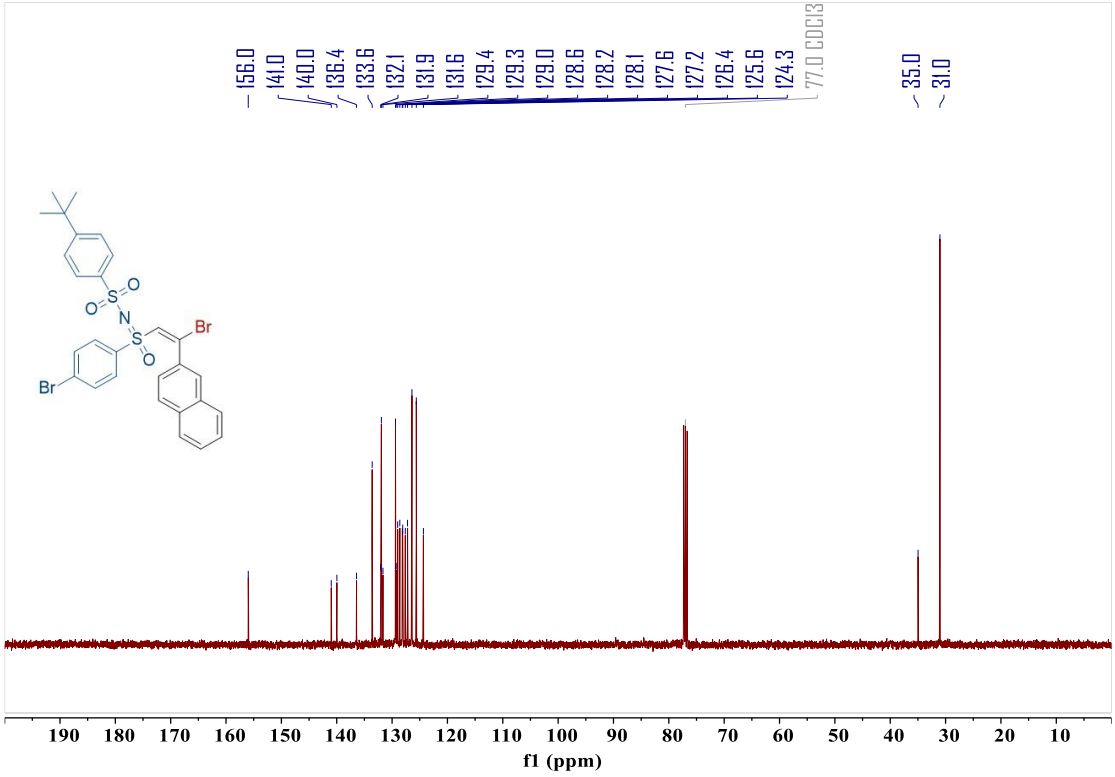


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(naphthalen-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4q)

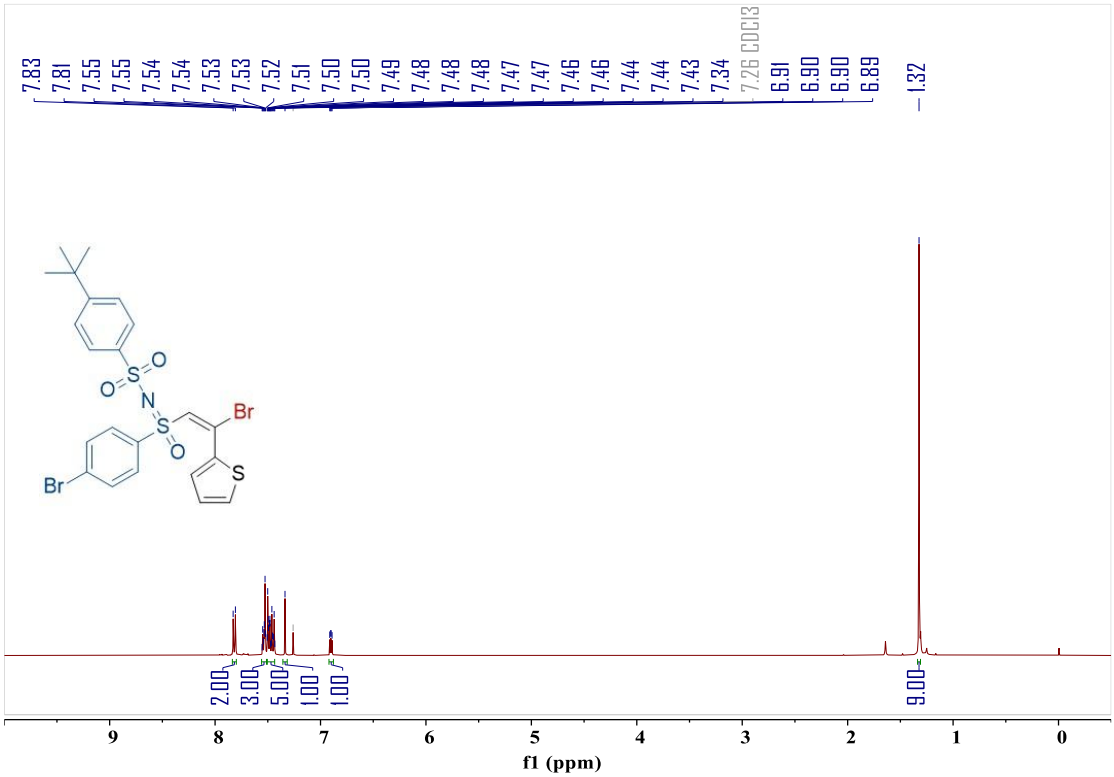


^{1}H NMR (400 MHz, $CDCl_3$)

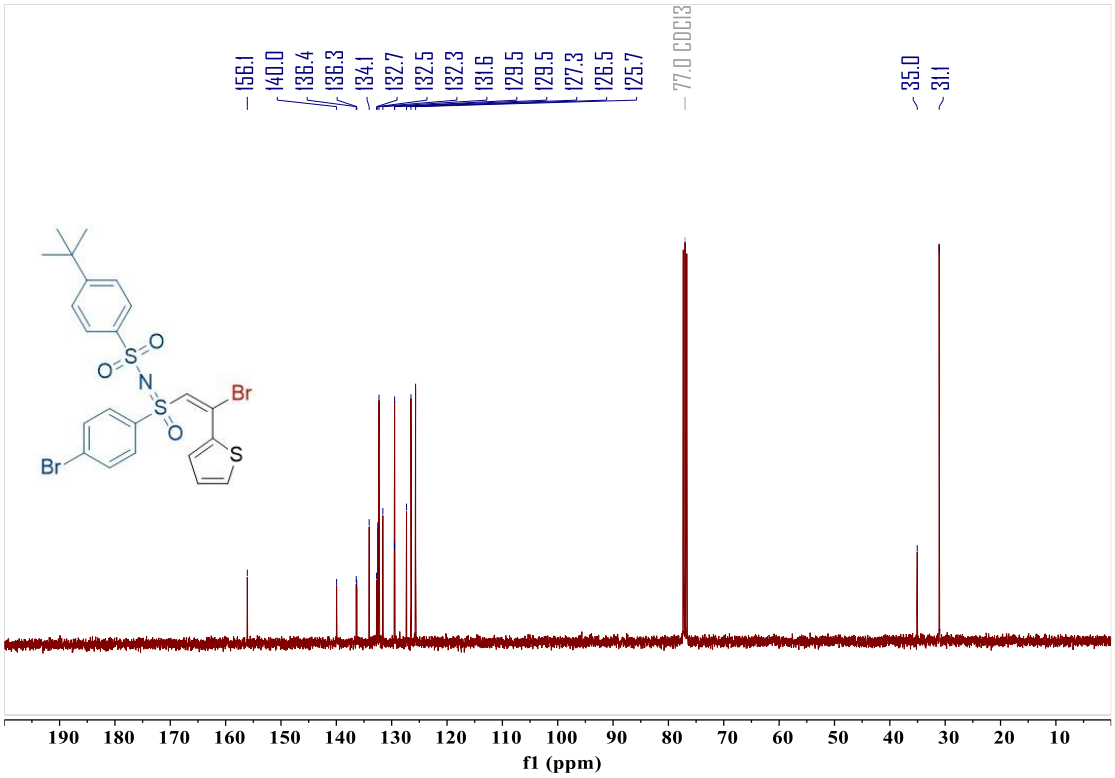


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(thiophen-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4r)

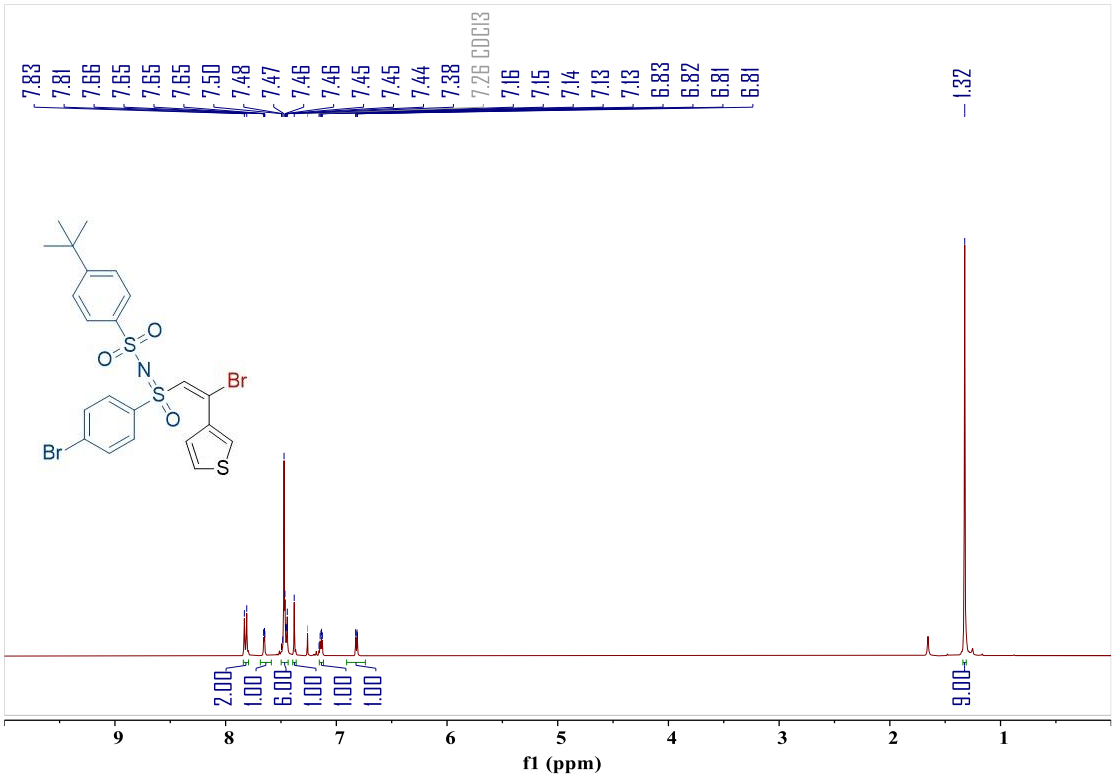


^{1}H NMR (400 MHz, $CDCl_3$)

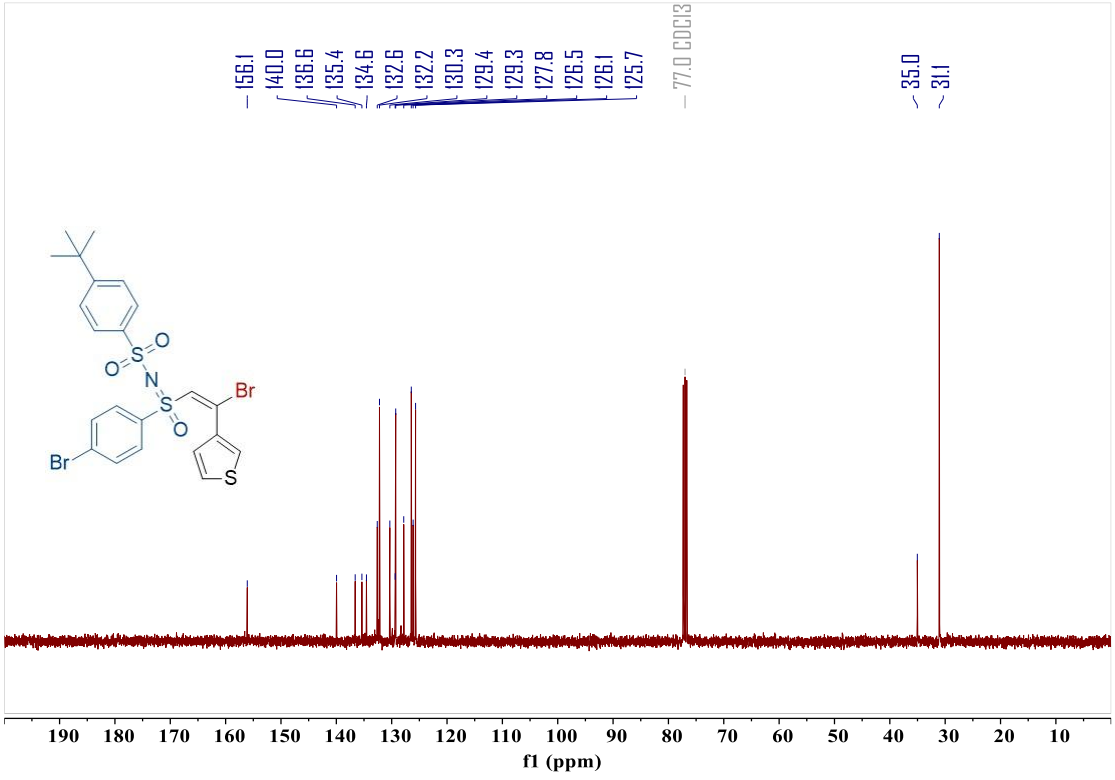


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(thiophen-3-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4s)

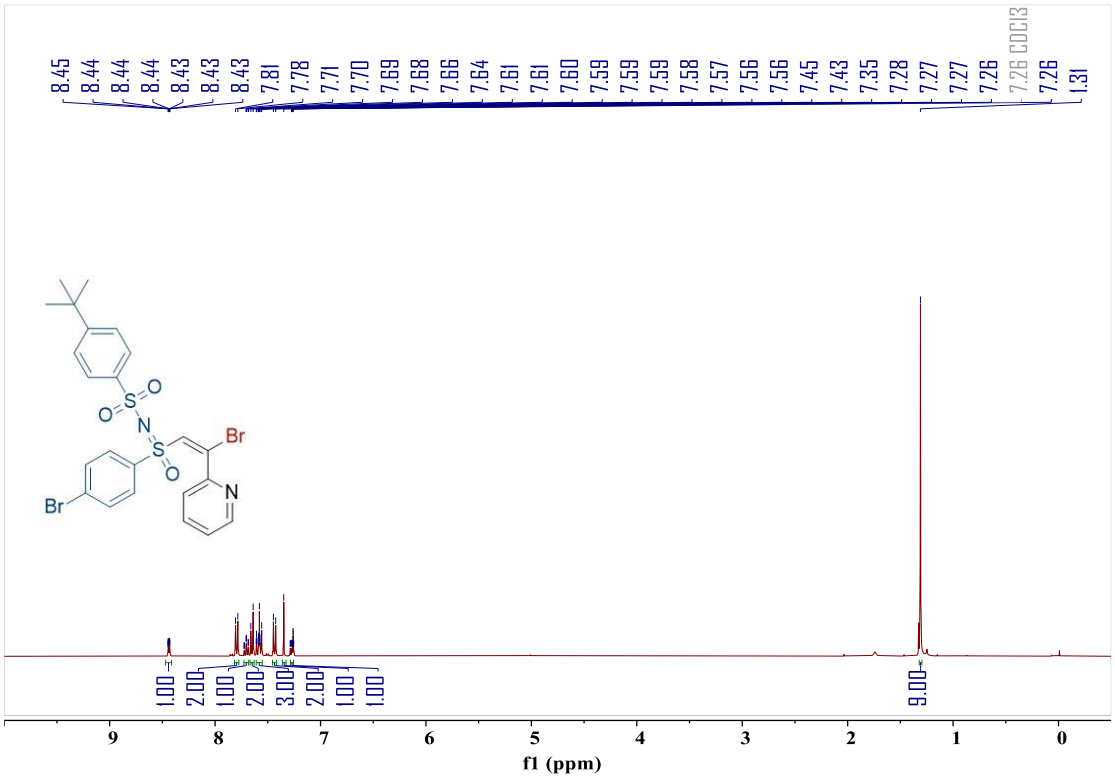


^{1}H NMR (400 MHz, $CDCl_3$)

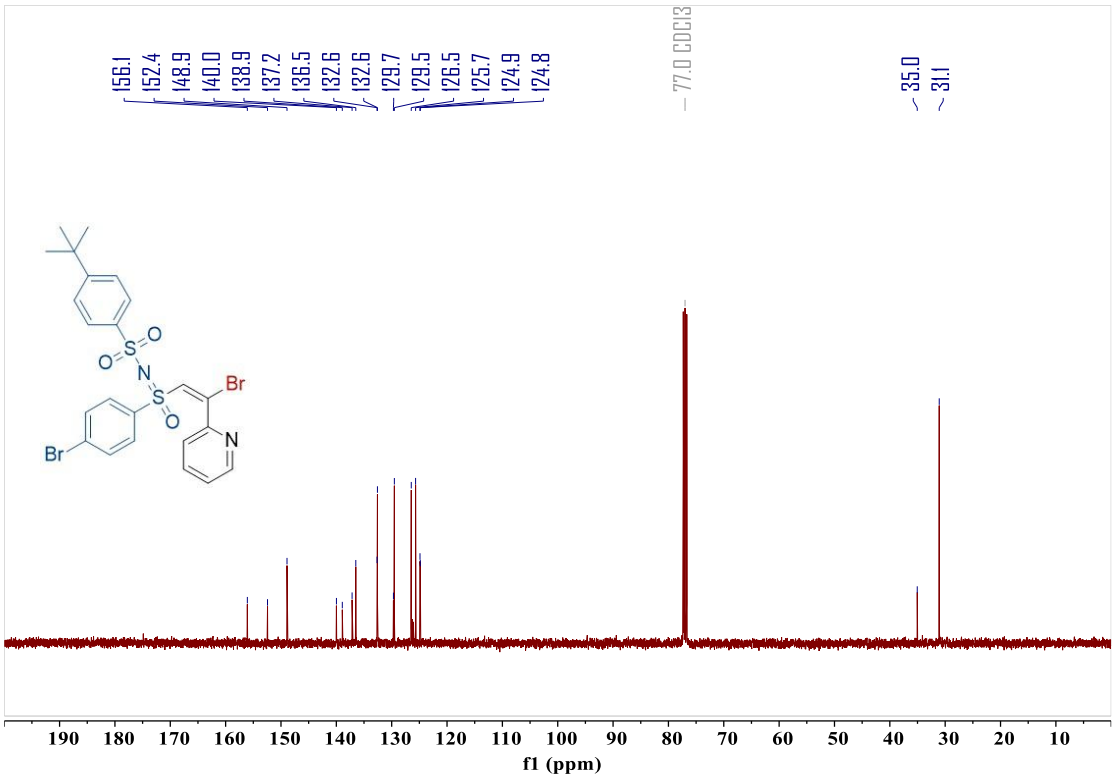


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(pyridin-2-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4t)

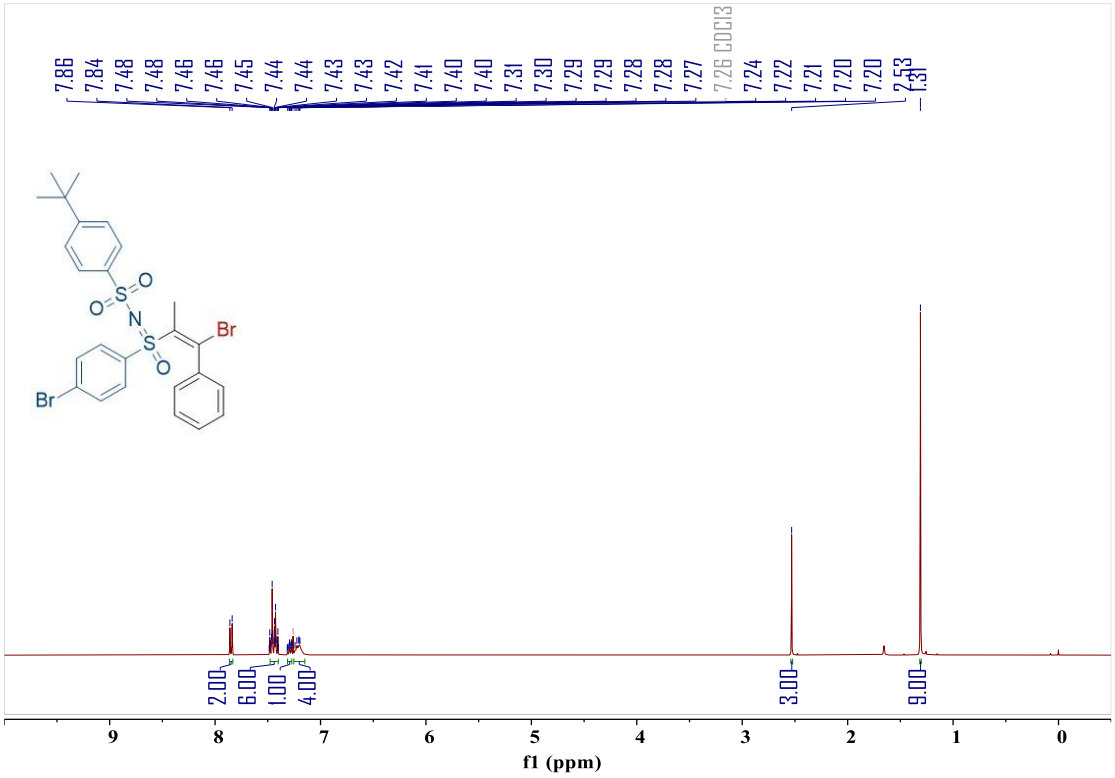


^{1}H NMR (400 MHz, $CDCl_3$)

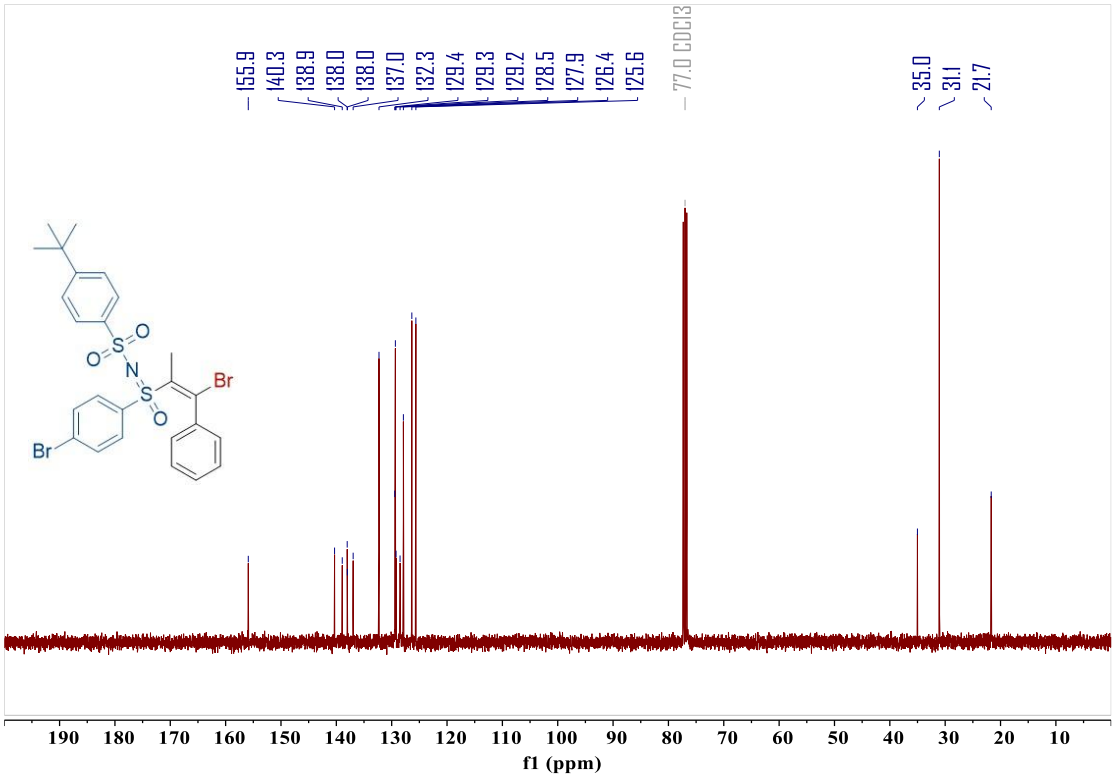


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((1-bromo-1-phenylprop-1-en-2-yl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl) benzenesulfonamide (4u)

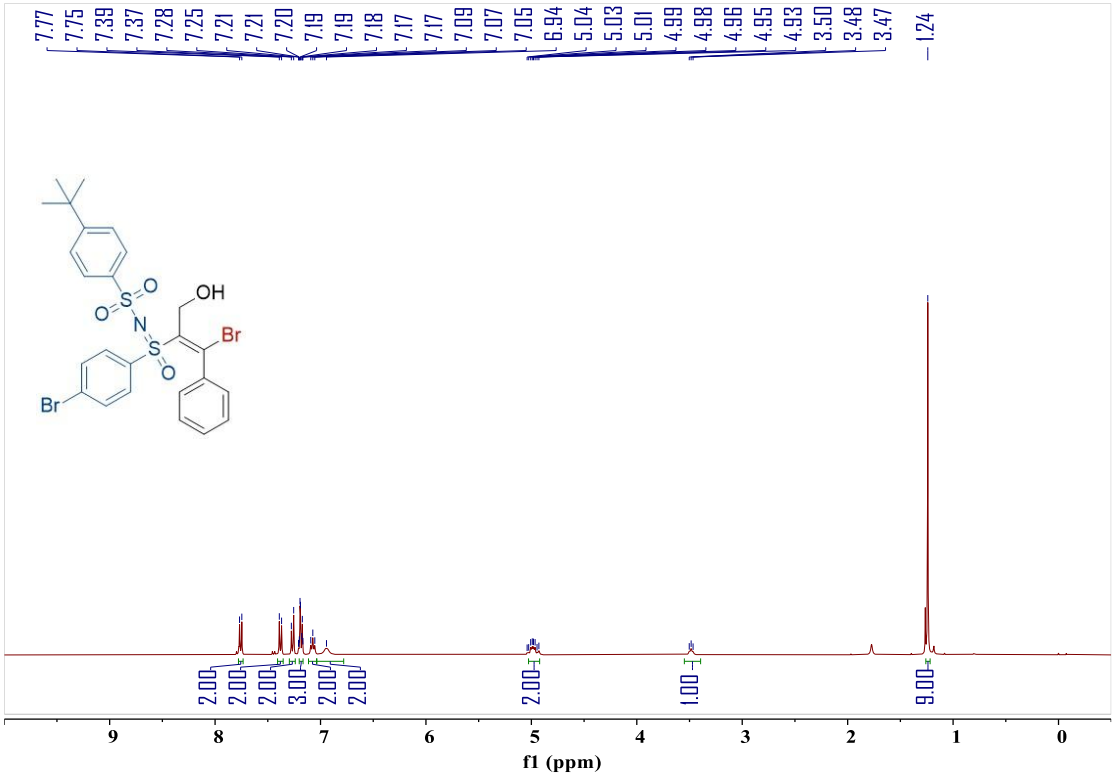


^{1}H NMR (400 MHz, $CDCl_3$)

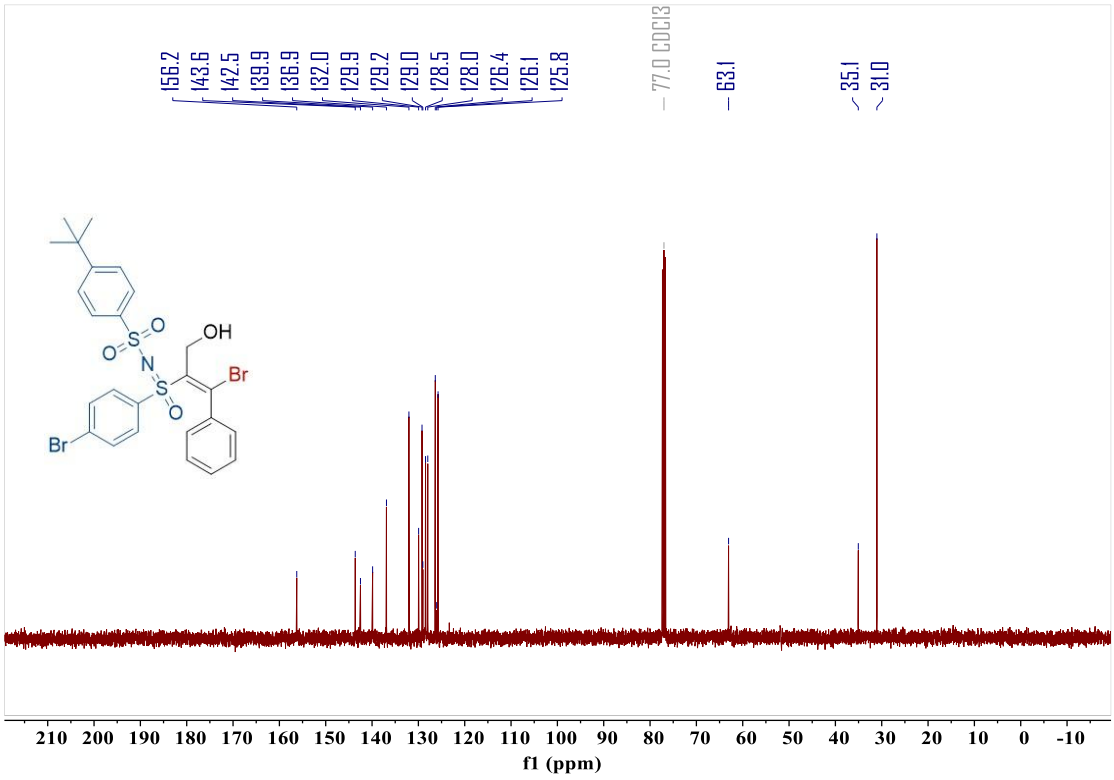


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((1-bromo-3-hydroxy-1-phenylprop-1-en-2-yl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4v)

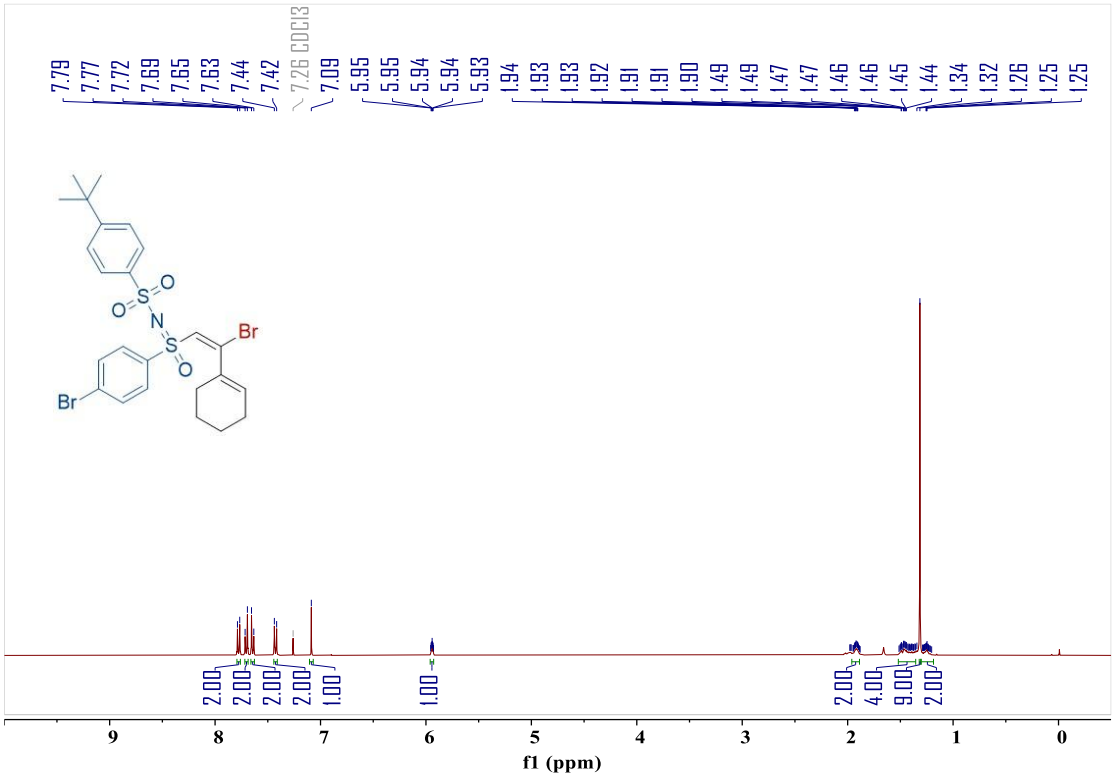


^{1}H NMR (400 MHz, $CDCl_3$)

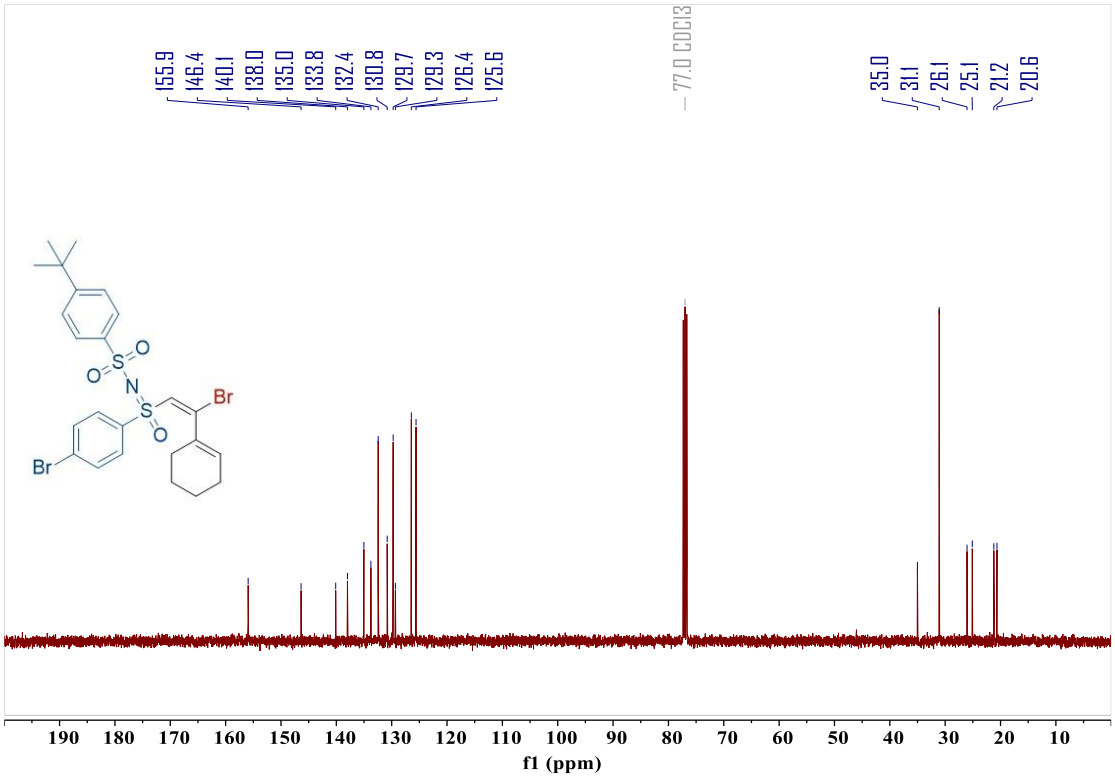


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-(cyclohex-1-en-1-yl)vinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4w)

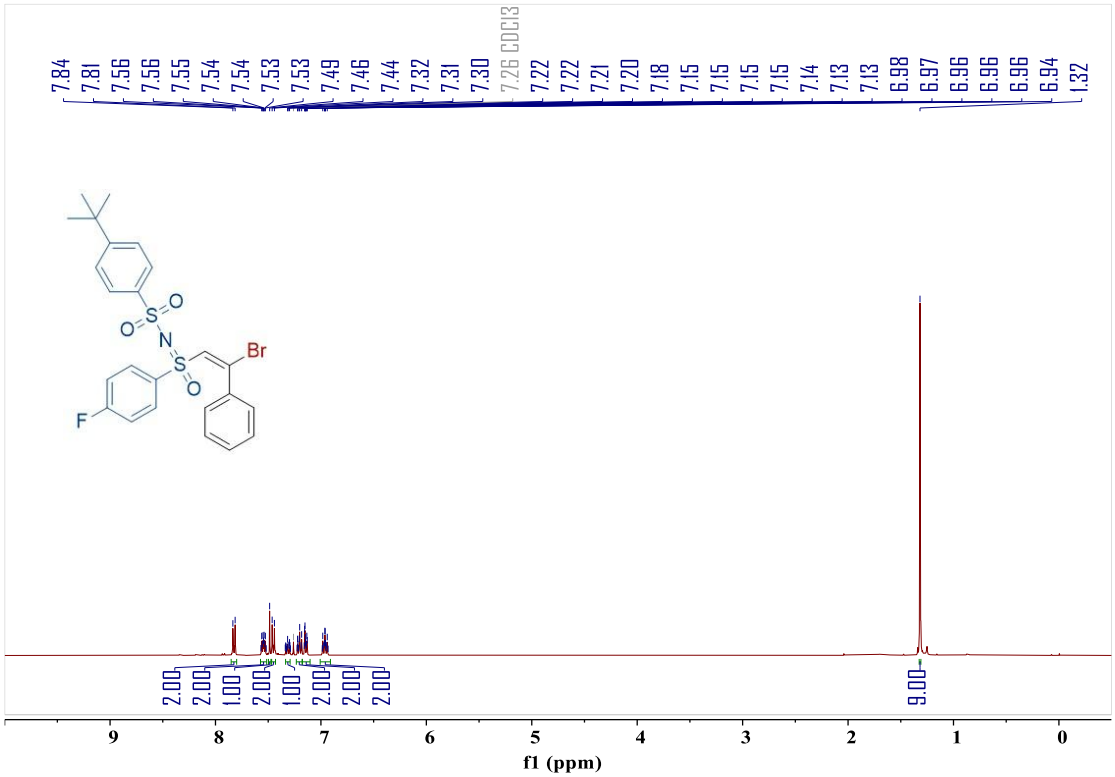


^{1}H NMR (400 MHz, $CDCl_3$)

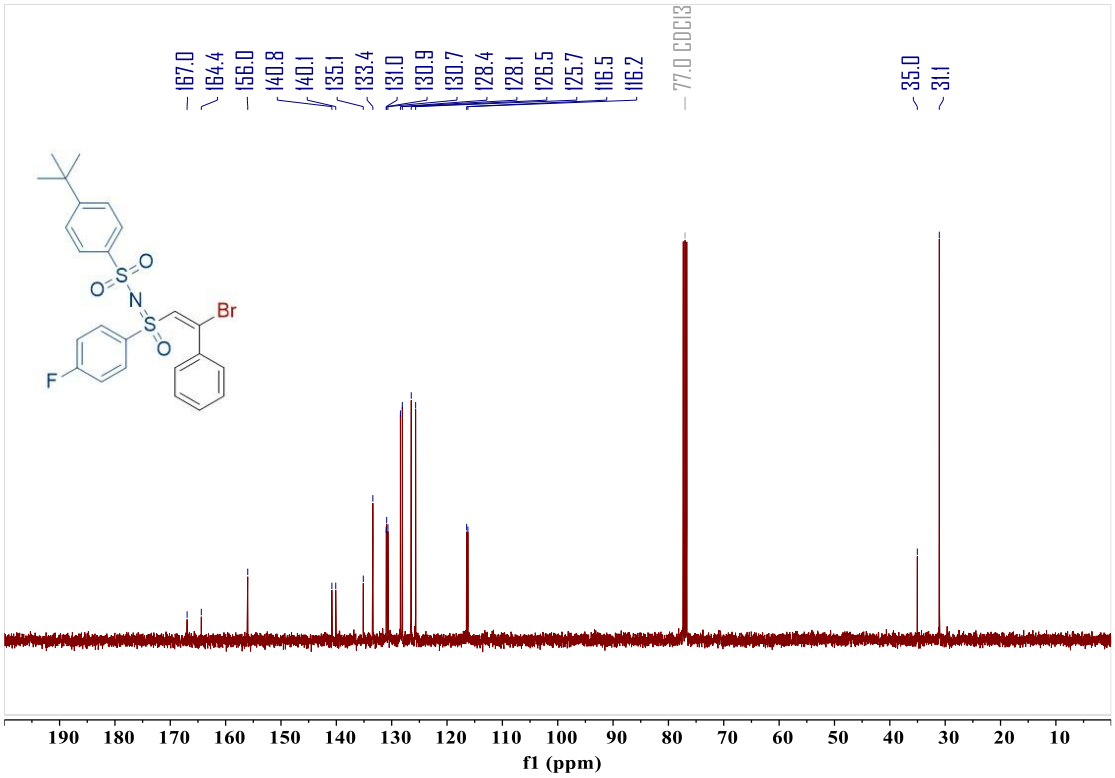


^{13}C NMR (100 MHz, $CDCl_3$)

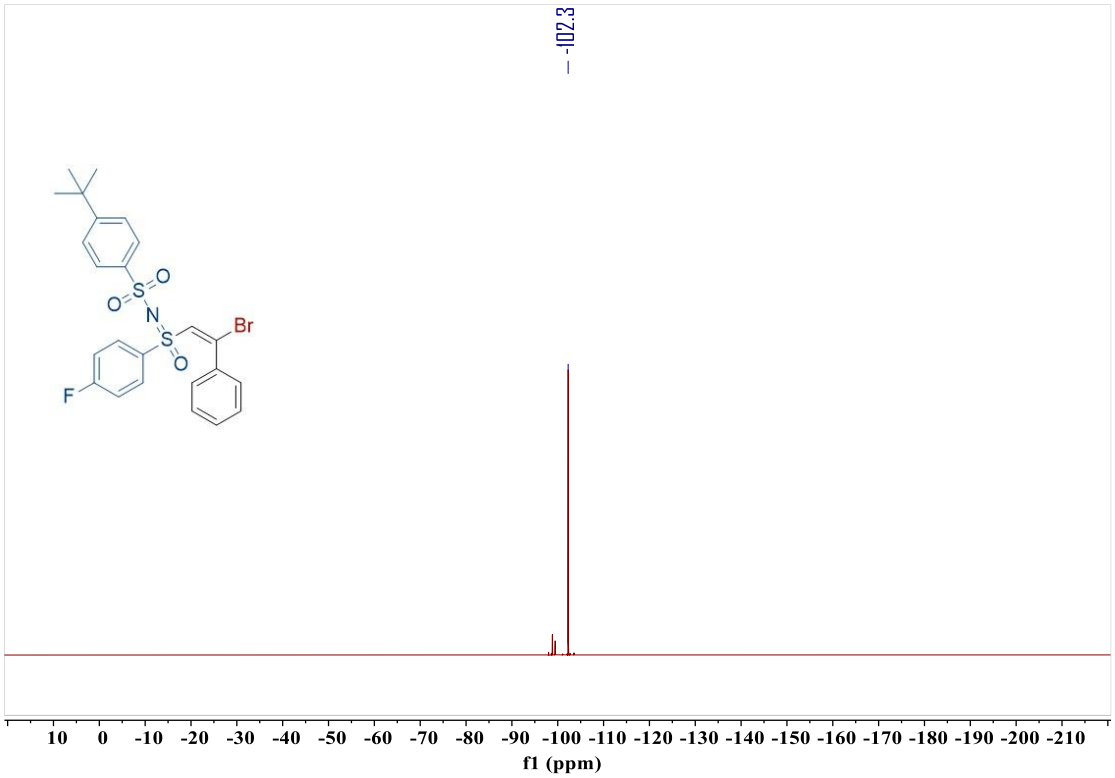
(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-fluorophenyl)(oxo)-λ^{6}sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4x)



^{1}H NMR (400 MHz, $CDCl_3$)

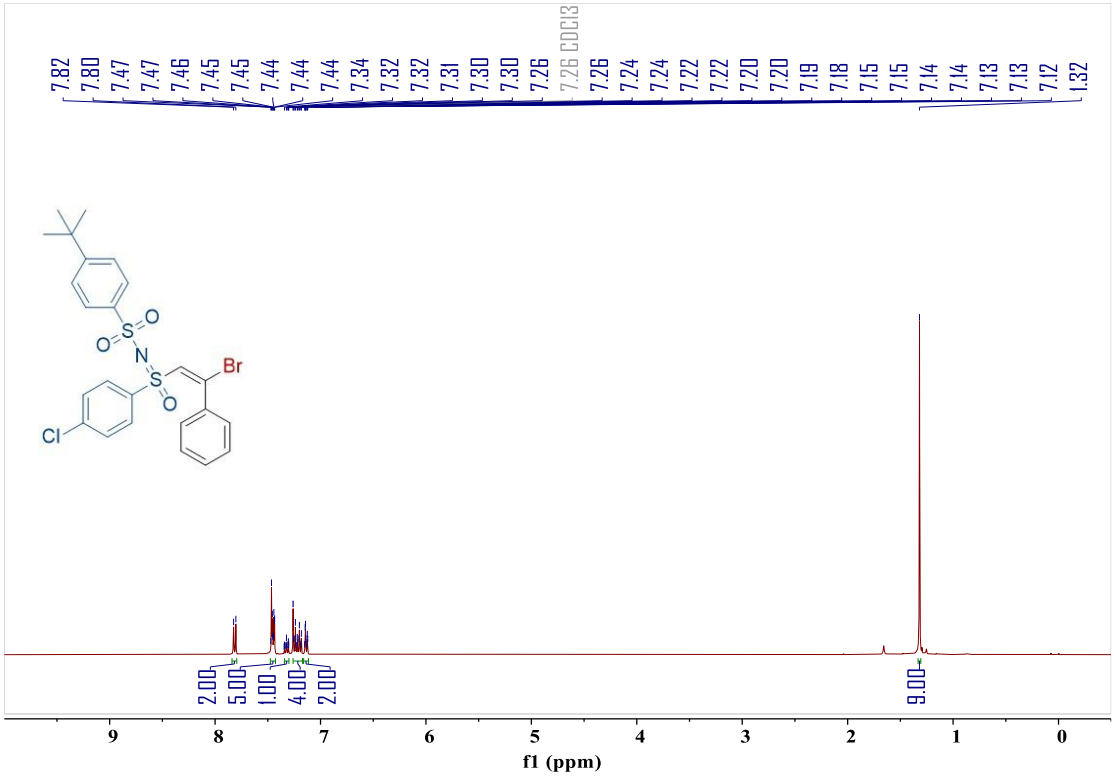


^{13}C NMR (100 MHz, $CDCl_3$)

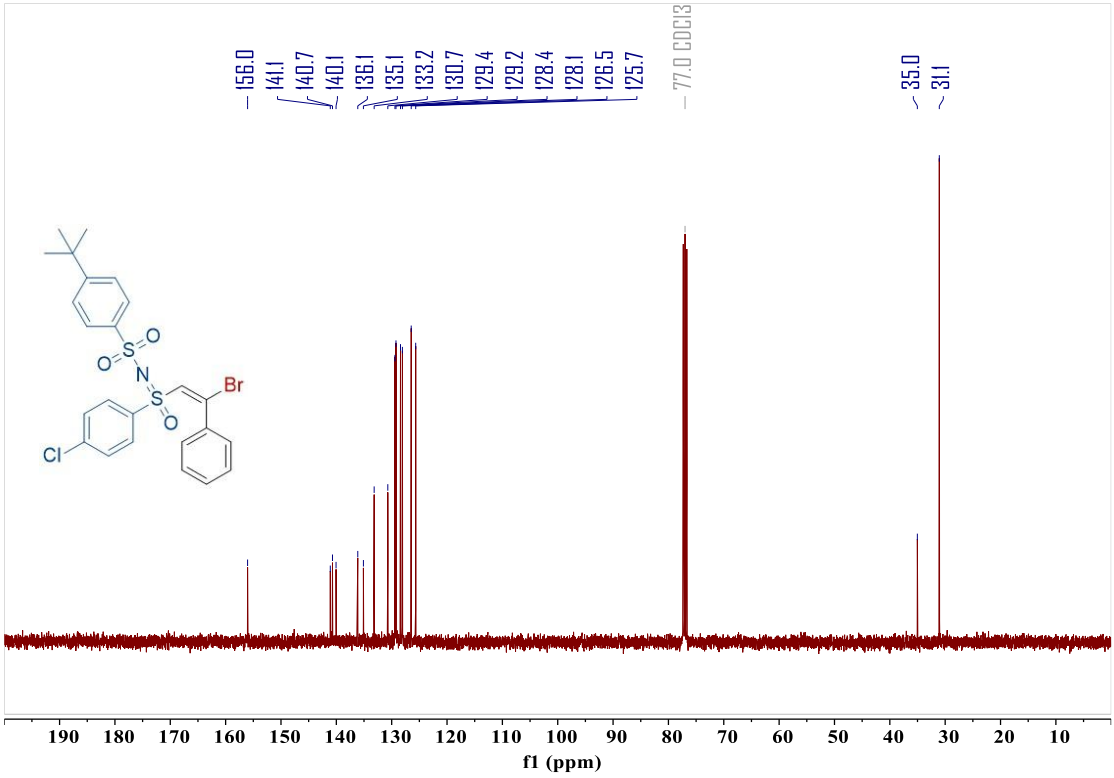


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4y)

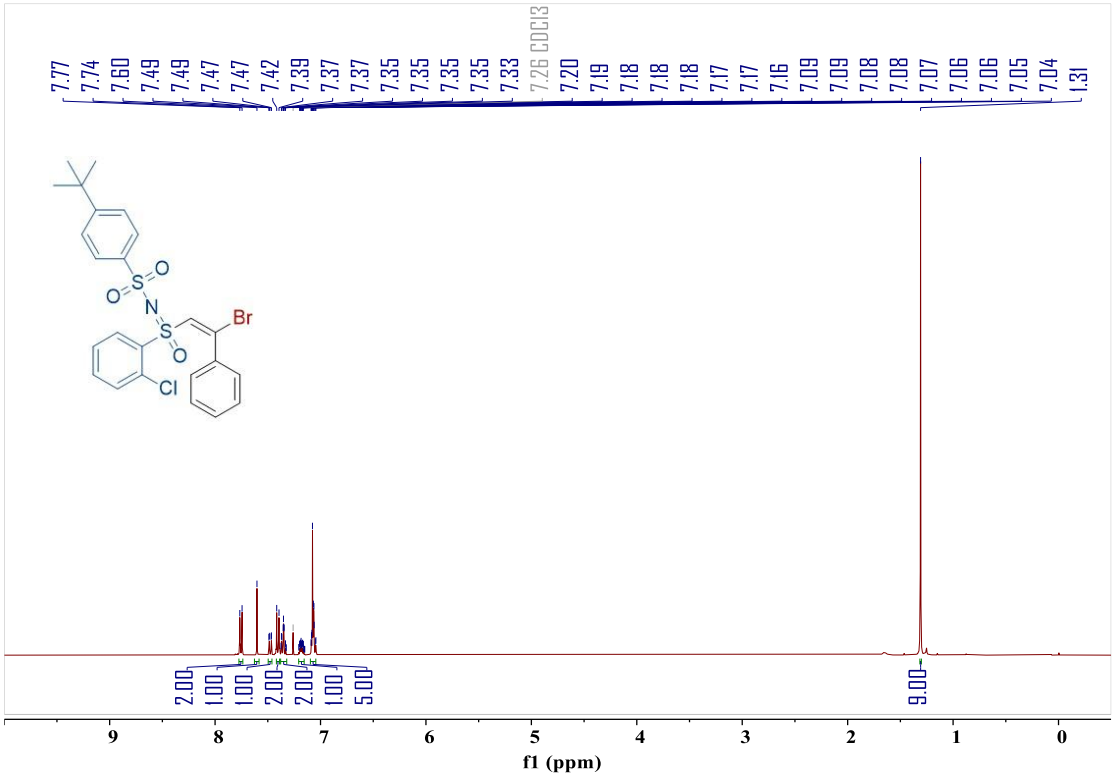


^{1}H NMR (400 MHz, $CDCl_3$)

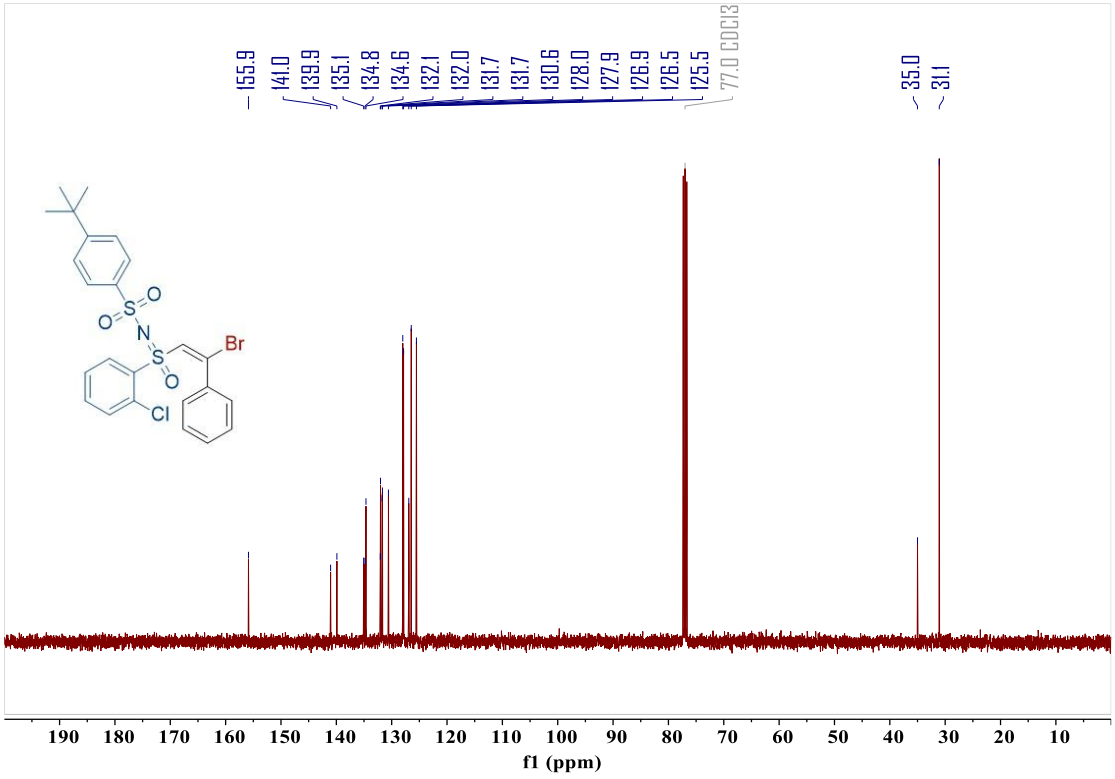


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(2-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4z)

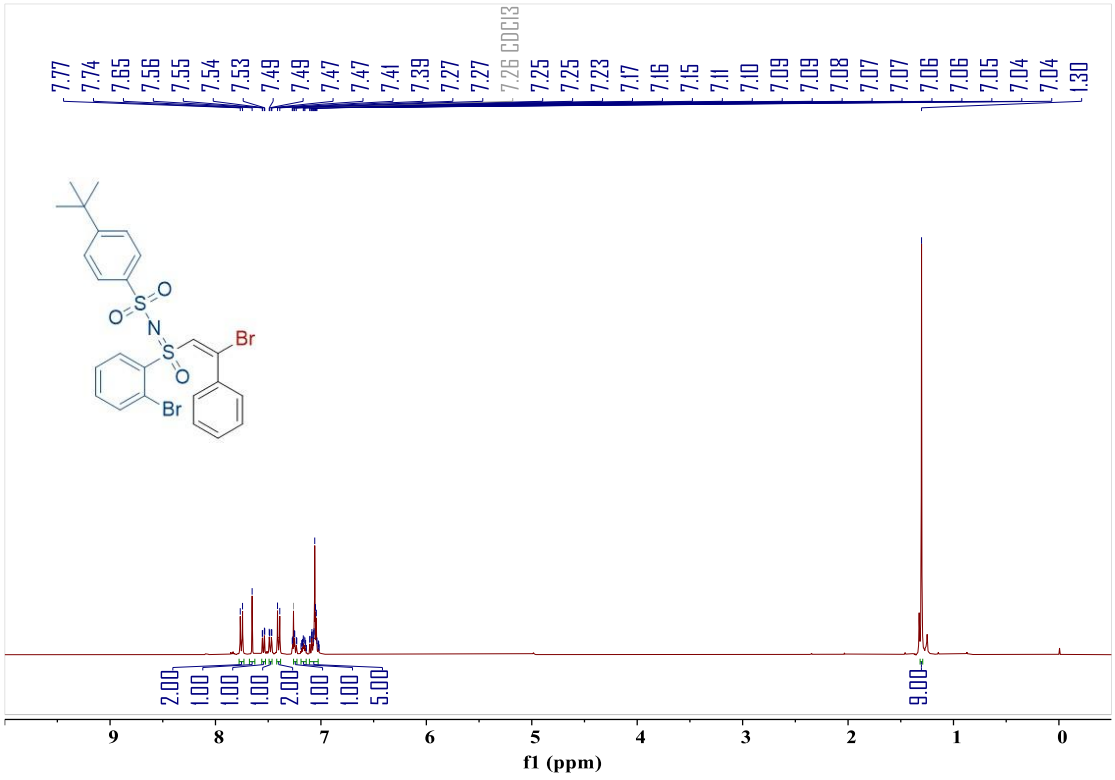


^{1}H NMR (400 MHz, $CDCl_3$)

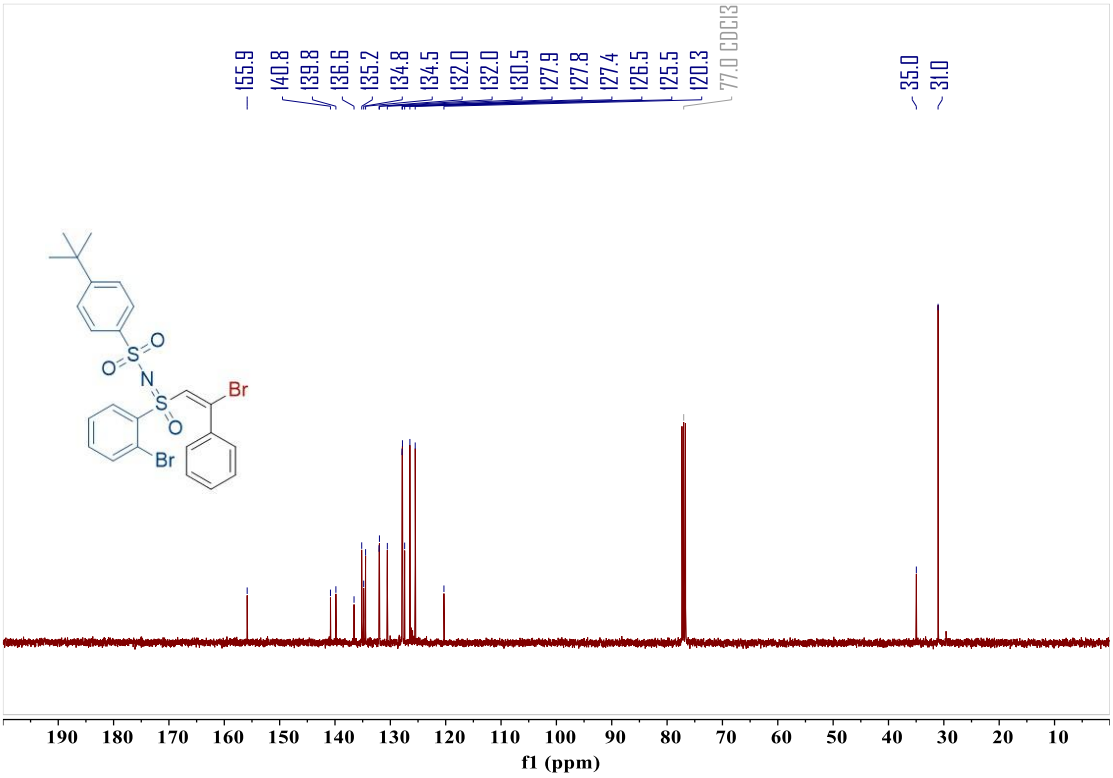


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(2-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4aa)

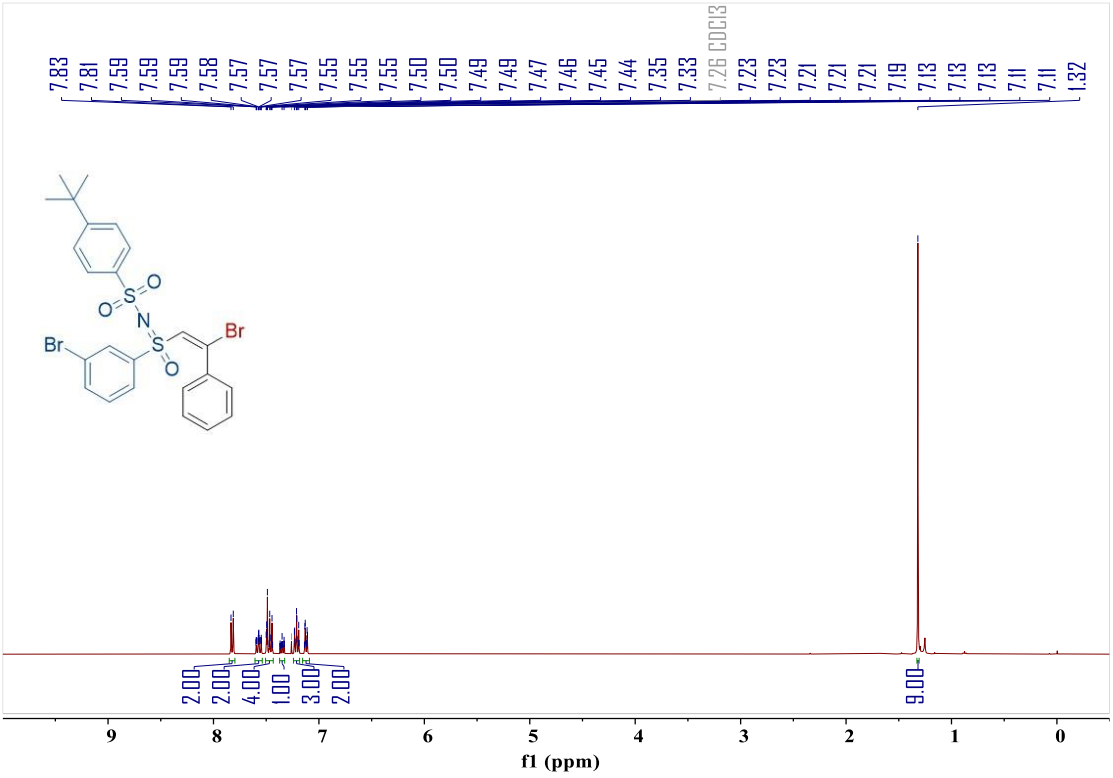


^{1}H NMR (400 MHz, $CDCl_3$)

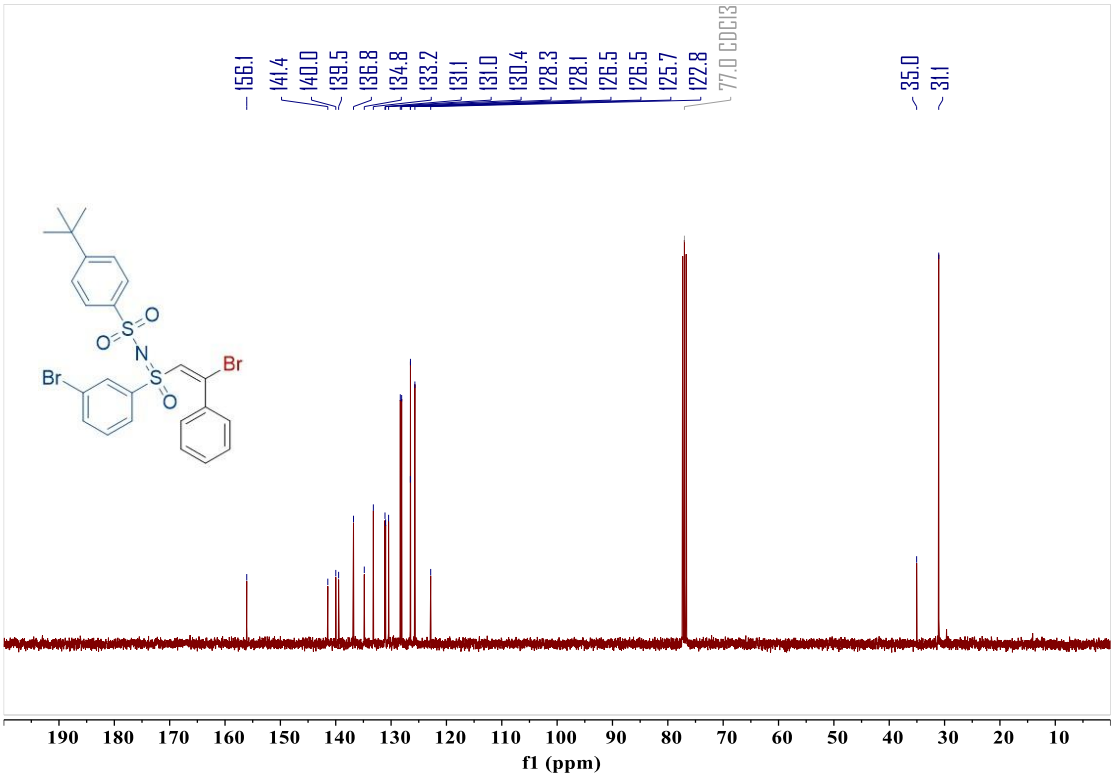


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(3-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-(*tert*-butyl)benzenesulfonamide (4ab)

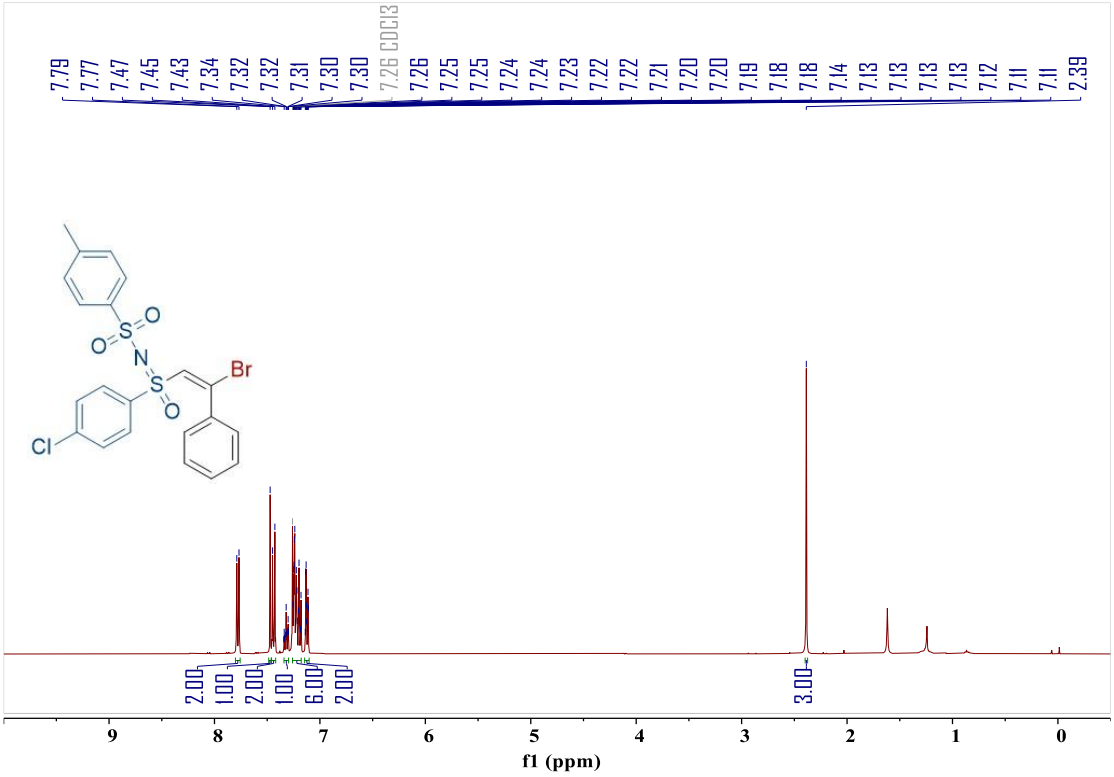


^{1}H NMR (400 MHz, $CDCl_3$)

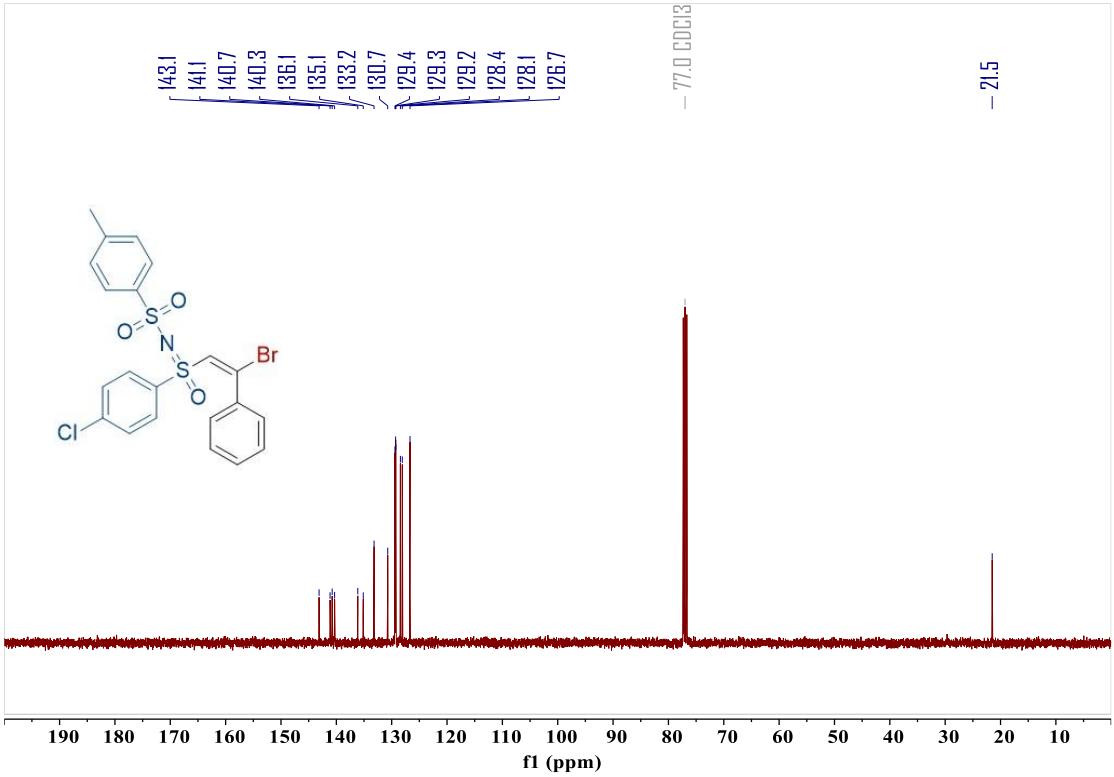


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-chlorophenyl)(oxo)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (4ac)

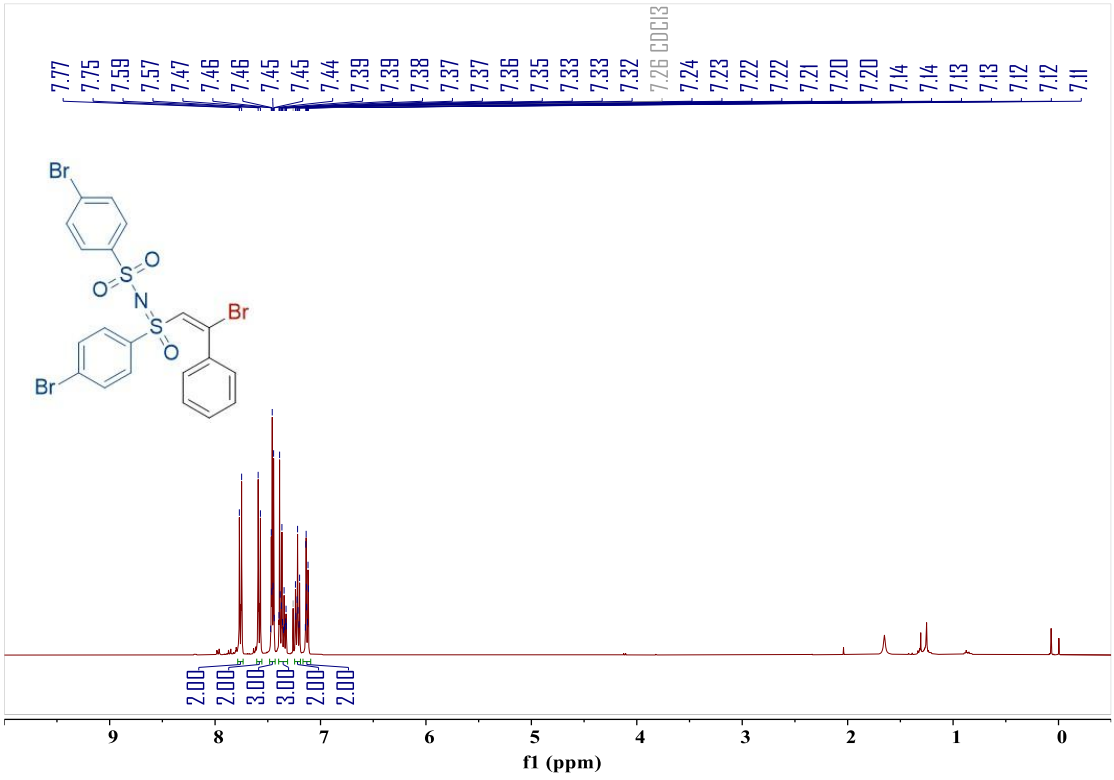


^{1}H NMR (400 MHz, $CDCl_3$)

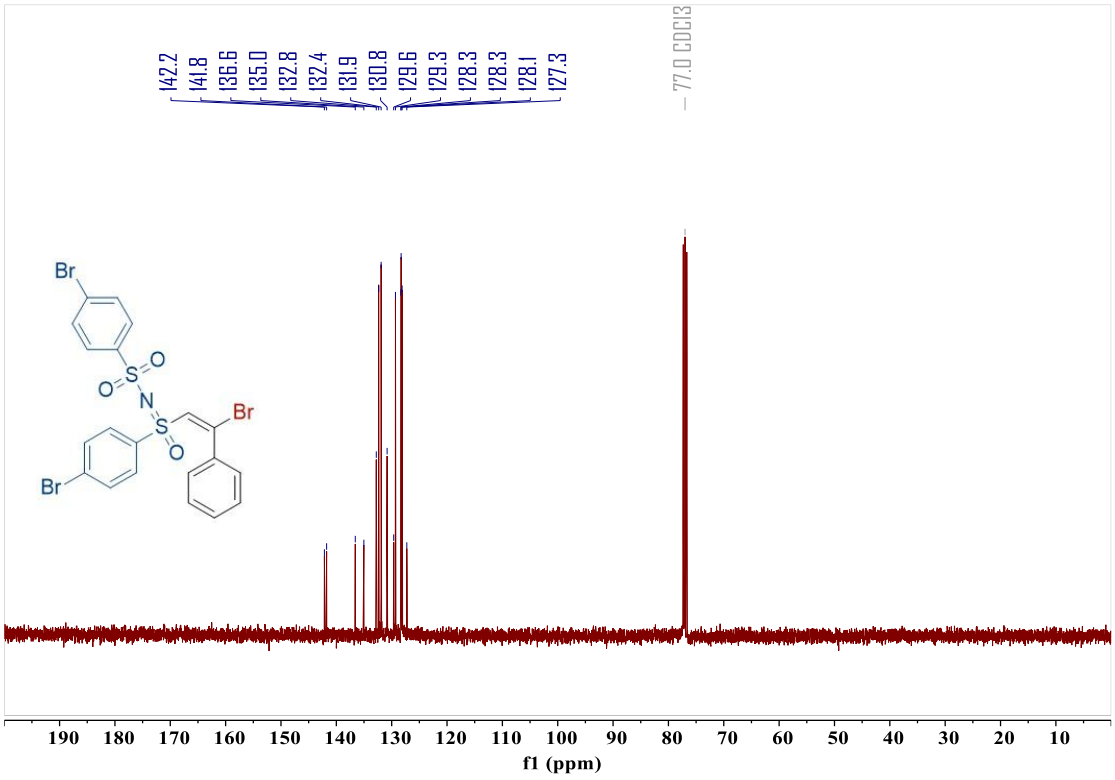


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-4-bromo-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)benzenesulfonamide (4ad)

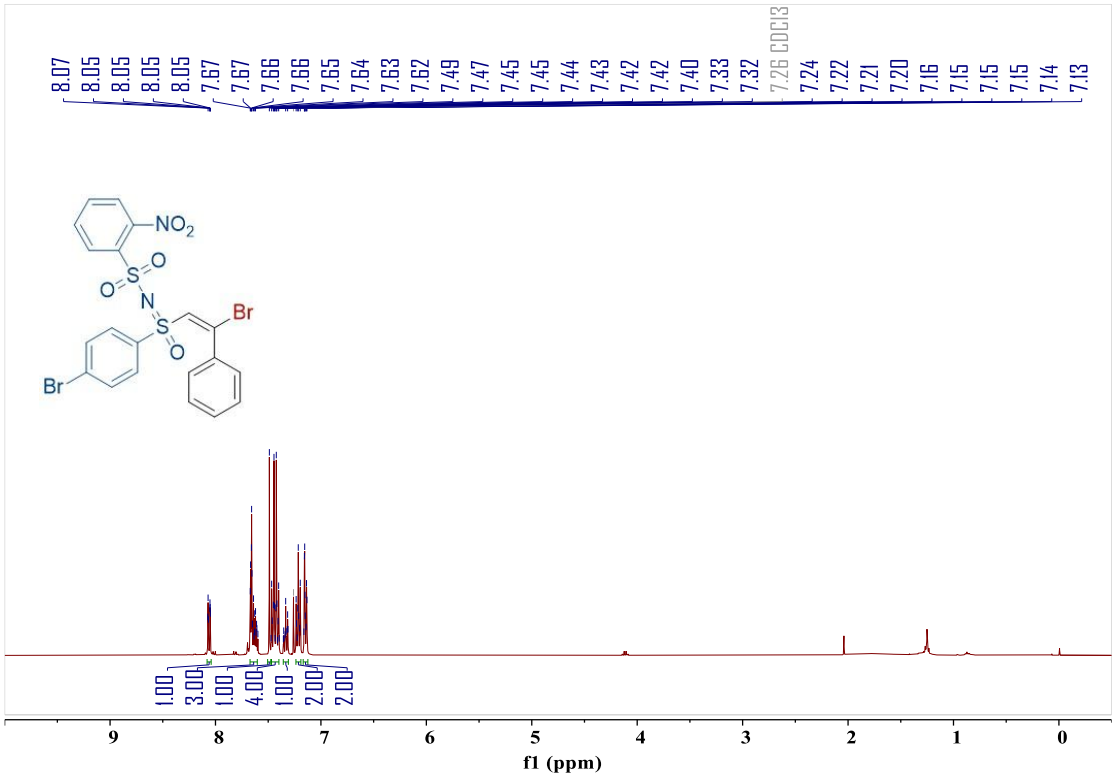


^{1}H NMR (400 MHz, $CDCl_3$)

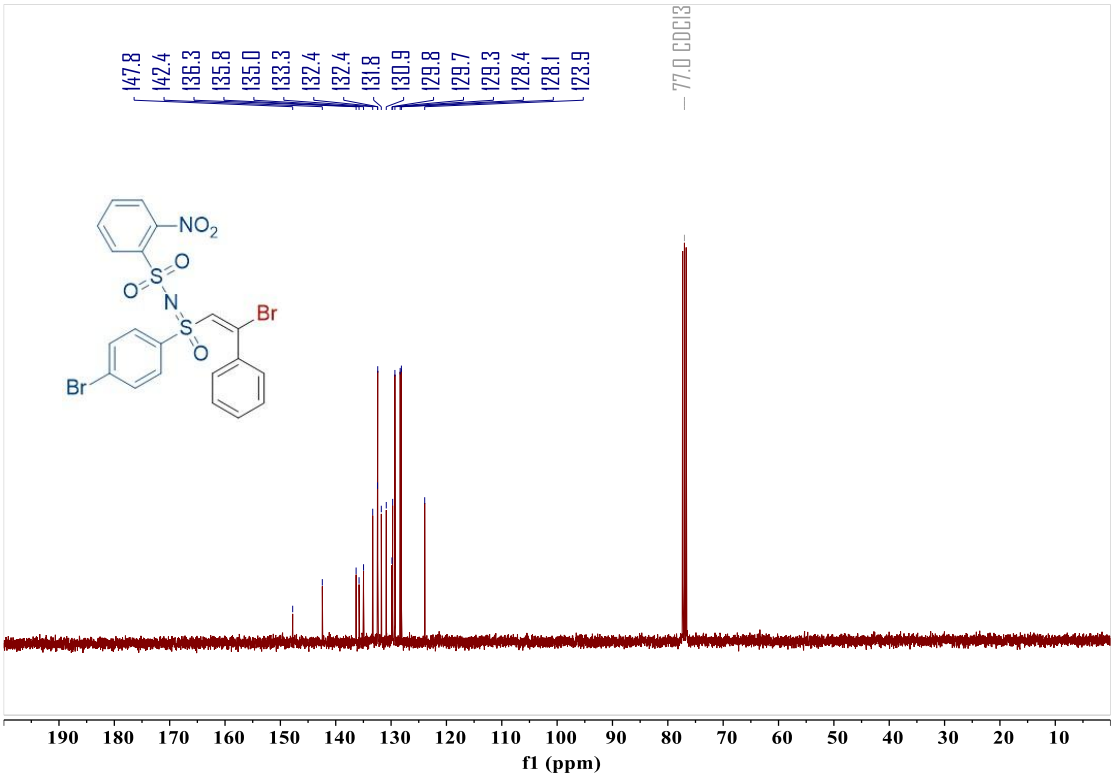


^{13}C NMR (100 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-2-nitrobenzenesulfon amide (4ae)

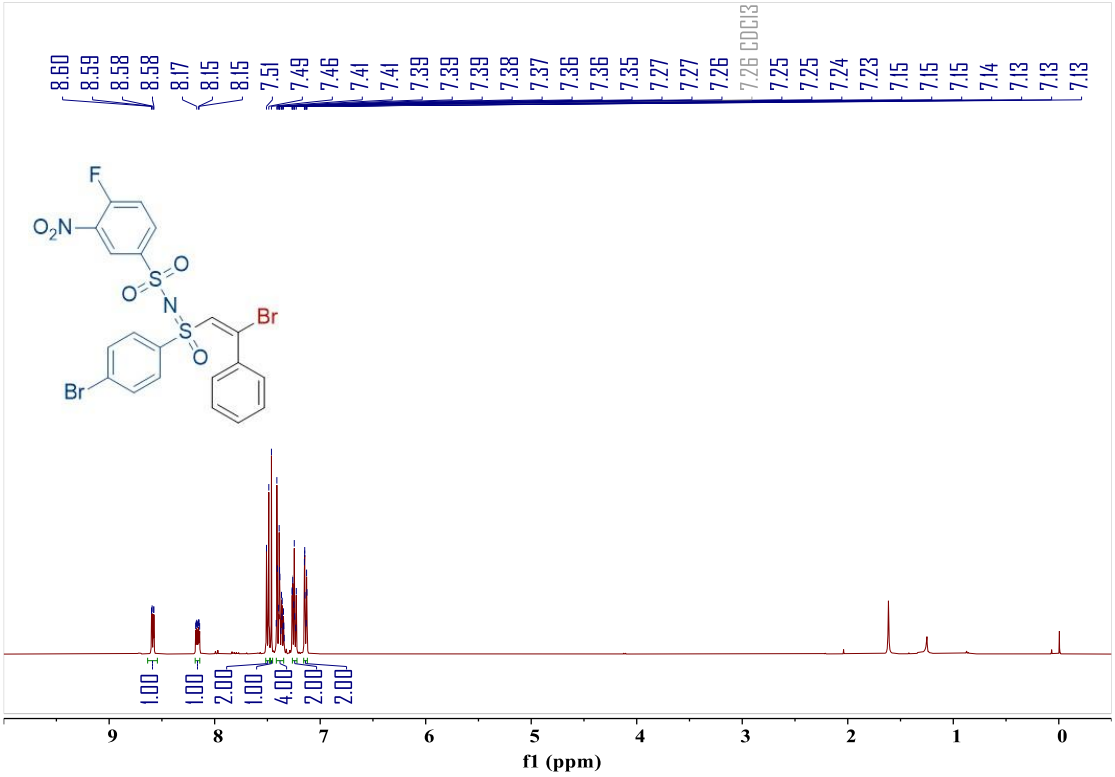


^{1}H NMR (400 MHz, $CDCl_3$)

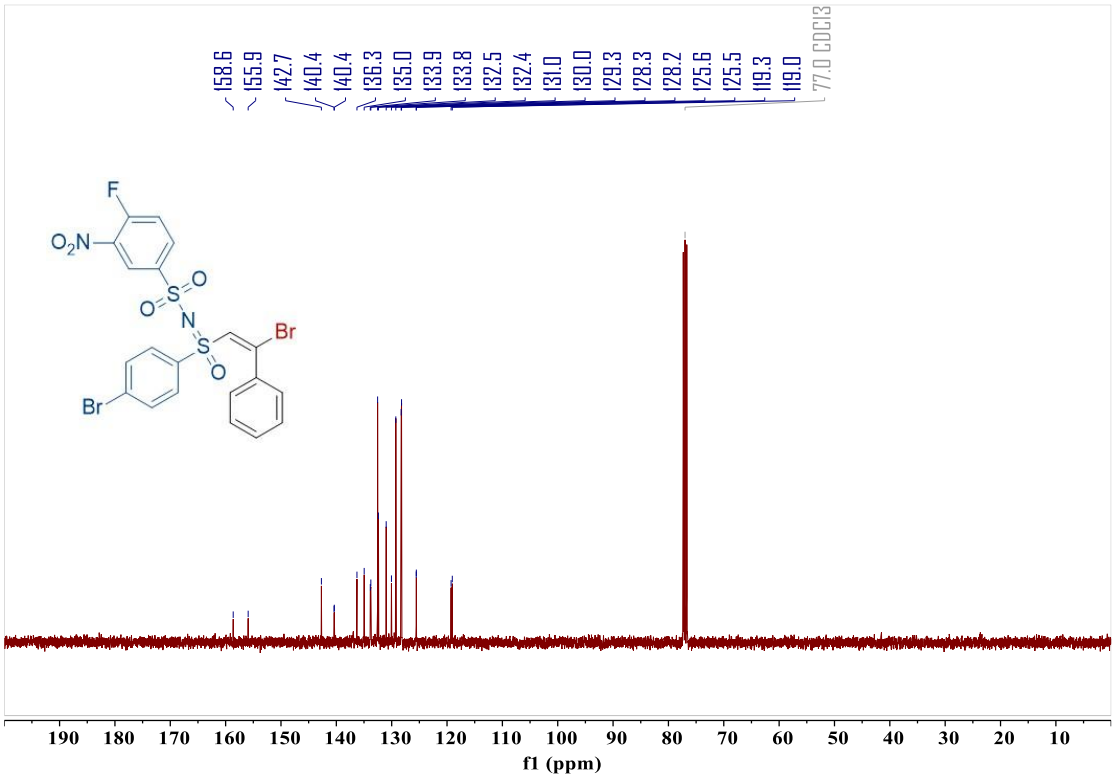


^{13}C NMR (100 MHz, $CDCl_3$)

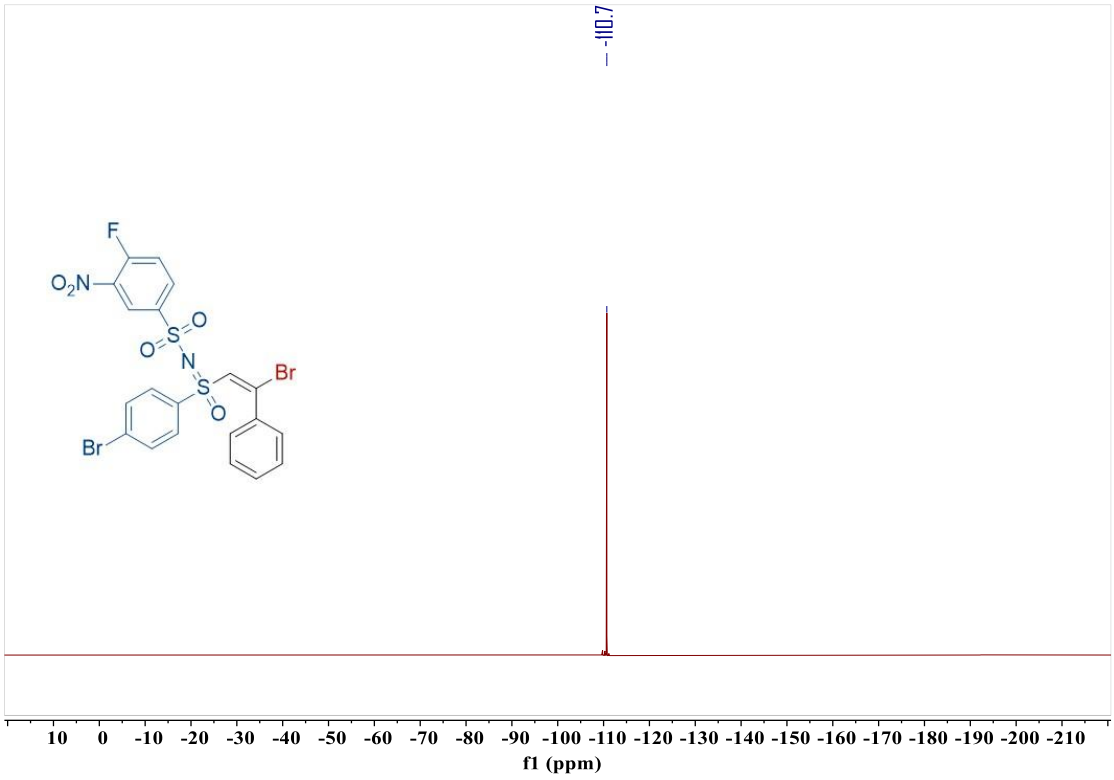
(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)-4-fluoro-3-nitrobenzene sulfonamide (4af)



^{1}H NMR (400 MHz, $CDCl_3$)

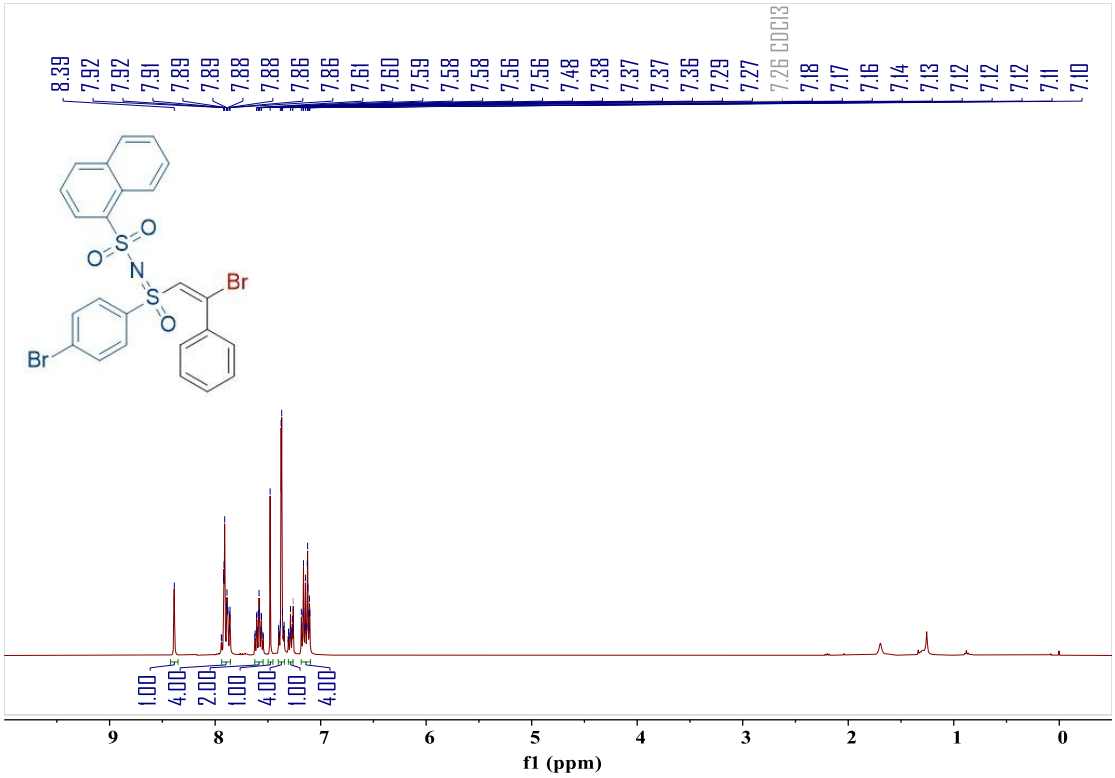


^{13}C NMR (100 MHz, $CDCl_3$)

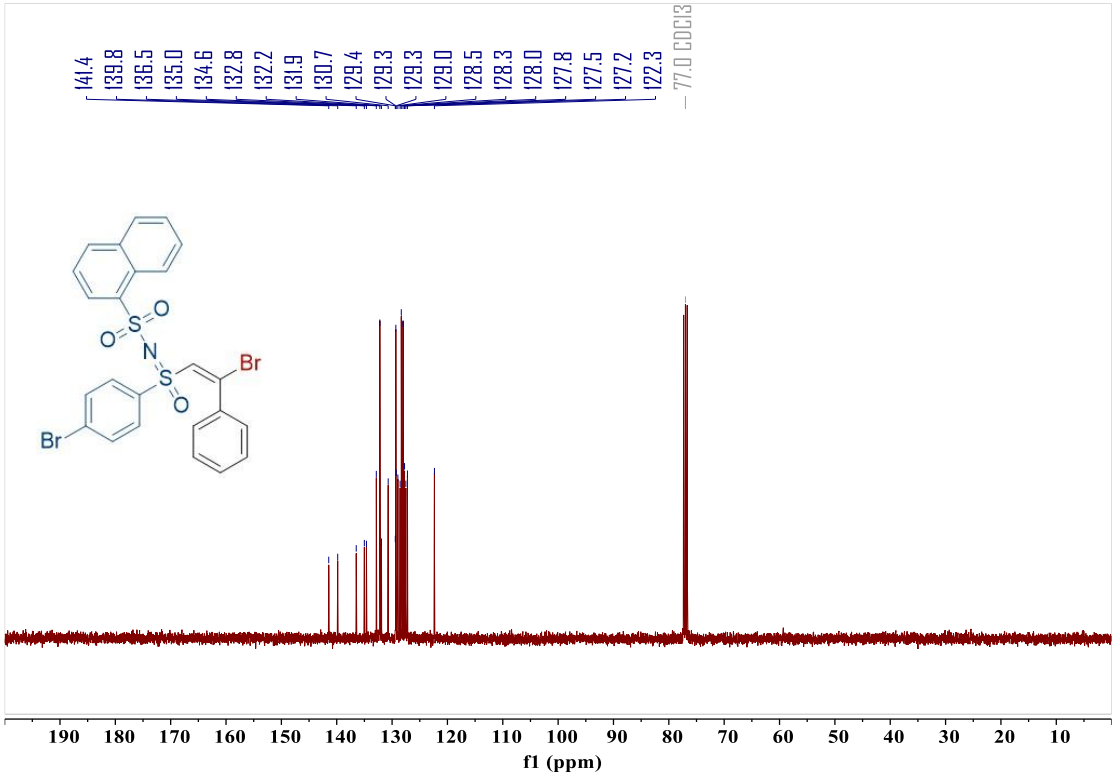


^{19}F NMR (376 MHz, $CDCl_3$)

(*E*)-*N*-((2-bromo-2-phenylvinyl)(4-bromophenyl)(oxo)-λ^6-sulfaneylidene)naphthalene-1-sulfon amide (4ag)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)