Supporting Information

Electro-mechanochemical approach towards chloro sulfoximidations of allenes under solvent-free conditions in a ball mill

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1 Analytical Methods

1.1 Thin-Layer Chromatography Analysis

Thin-layer chromatography (TLC) analysis was performed using aluminum sheets coated with silica gel 60 F_{254} purchased from Merck. Substances were visualized using UV light (λ = 254 nm). If a mixture of solvents was used, it is always understood as volumetric ratio (*V*/*V*).

1.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance Neo 400, Bruker Avance Neo 600, Varian VNMRS 400 or Varian VNMRS 600 at ambient temperature (25 °C), if not mentioned otherwise. The program MestReNova was used for processing and analyzing the corresponding spectra.[1] Chemical shifts (δ) are given in ppm (parts per million) and are reported from downfield to upfield (decreasing ppm values). Carbon NMR spectra were recorded as proton broadband decoupled spectra, indicated as $^{13}C\{^{1}H\}$. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the solvent (residual) signal of the (non)-deuterated NMR solvent (^{1}H NMR: δ = 7.26 ppm for $CHCl_3$; $^{13}C\{^{1}H\}$ NMR: δ = 77.16 ppm for $CDCl_3$).[2] The spin-spin coupling constants (*J*) are reported in Hertz. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet), br (broad signal) and combinations thereof.

1.3 Infrared Spectroscopy

Infrared (IR) spectra were recorded neat on a PerkimElmer Spectrum 100 FT-IR spectrometer. Using an attached UATR device with a KRS-5 crystal for single reflection, the spectra were recorded in transmission mode.

1.4 Mass Spectrometry

High-resolution mass spectra (HRMS) were recorded on a ThermoFisher Scientific LTQ Orbitrap XL mass spectrometer as ESI (electrospray ionization) spectra in positive mode.

2 Materials and Equipment

2.1 Column Chromatography

Solvents for column chromatography were of technical grade and have been distilled prior to use. Solvent mixtures are always understood as volumetric ratios (*V*/*V*). Silica gel 60 M (0.04–0.063 mm and 0.06–0.2 mm) was purchased from Macherey-Nagel. Appropriate fractions were identified by using TLC analysis. The product was always impregnated on silica gel and placed on top of the column for purification to perform a *dry loaded column chromatography*.

2.2 Ball Mills

Mechanochemical reactions were performed using a RETSCH mixer mill MM400. The used milling containers and balls have always been of the same material. Yttrium-stabilized zirconia (ZrO_2-Y) was exclusively used for this purpose.

2.3 Glove Box

To perform mechanochemical reactions under inert atmosphere the milling containers were closed inside a glove box of the type MBraun Labmaster 130. Argon was used as inert gas.

2.4 Piezoelectric Materials

The piezoelectric materials [*tet*-$BaTiO_3$ (500 nm) and ZnO (18 nm)] used for this research project were purchased from US Research Nanomaterials, Inc. and stored in a desiccator over $CaCl_2$. $SrTiO_3$ (Aldrich 396141) and *cub*-$BaTiO_3$ (Aldrich 467634) were used as received and stored under ambient conditions.

2.5 Chemicals

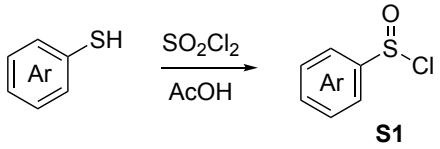
Unless otherwise mentioned, all other chemicals were obtained from commercial suppliers and were used as received.

3 General Synthetic Procedures

3.1 General Procedures for the Synthesis of Starting Materials

*General Procedure 1 (GP1): Synthesis of N-Tosylsulfoximidoyl Chlorides (**1**)*[3]

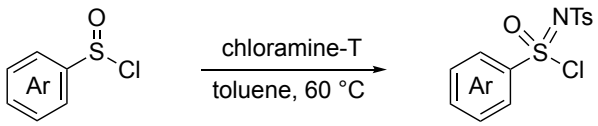
*Synthesis of Sulfinyl Chlorides (**S1**)*



S1

The thiophenol derivatives (9.90 mmol, 1.0 equiv.) and acetic acid (0.57 mL, 9.90 mmol, 1.0 equiv.) were charged into a 25 mL flask, and the reaction was stirred at –78 °C using dry ice/acetone for 10 min. Then, sulfuryl chloride (1.79 mL, 21.94 mmol, 2.2 equiv.) was added dropwise to the frozen mixture over a period of 30 min. When the addition was completed, the reaction mixture was stirred at the same temperature for 45 min, slowly warmed to room temperature and then stirred further for 3 h. The solution was concentrated under reduced pressure (**CAUTION:** without warming because of explosion risks) to give the desired crude sulfinyl chlorides **S1**, which was used in the next step without further purification.

*Synthesis N-Tosylsulfoximidoyl Chlorides (**1**)*

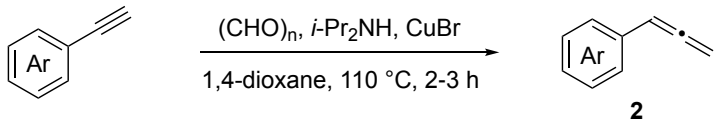


S1 **1**

Dried chloramine-T (2.79 g, 9.90 mmol, 1.0 equiv.) was added to sulfinic chloride **S1** (9.90 mmol, 1.0 equiv.) in dry toluene (25 mL). When the addition was completed, the reaction was heated at 60 °C for 3 h with stirring using an oil bath. After cooling to room temperature, the solids were filtered off and then washed with toluene. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (FCC, column diameter: 4 cm, column length: ca. 35 cm, SiO_2, 20:1 → 4:1 pentane:EtOAc) to afford the desired *N*-tosylsulfoximidoyl chlorides **1**.

Note*: *Chloramine-T trihydrate was dried for 8 h under high vacuum at 80 °C (oil bath).

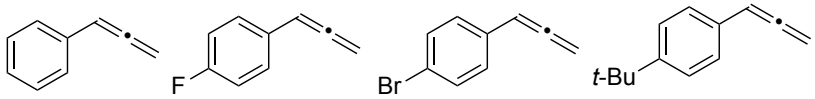
General Procedure 2 (GP2): Synthesis of Allenes ***2***[4]



2

To a solution of a terminal alkyne (5.0 mmol, 1.0 equiv.) in 1,4-dioxane (10 mL) at room temperature under argon, were added paraformaldehyde (0.9 g, 10.0 mmol, 2.0 equiv.), CuBr (360 mg, 2.5 mmol, 0.5 equiv.), and diisopropylamine (1.40 mL, 10.0 mmol, 1.0 equiv) under argon. The reaction mixture was heated at 110 °C for 2-3 h with stirring using an oil bath. The reaction was tracked by TLC analysis. Then, the reaction mixture was cooled to room temperature, was filtered and washed with *n*-pentane. The combined organic phases were diluted with 100 mL *n*-pentane, washed with water (5×100 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (column diameter: 5 cm, column length: ca. 40 cm) using pentane as an eluent to afford the pure terminal allene **2**.

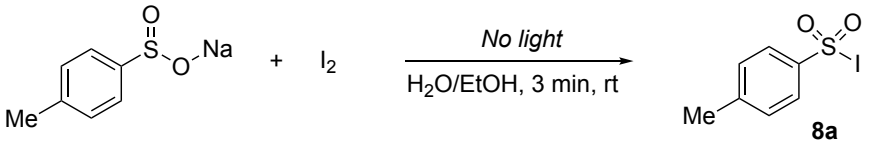
Allenes **2a**-**d** were prepared according to literature reports. The analytical data were in agreement with the reported values.[4]



2a **2b** **2c** **2d**

Note: *To prevent decomposition all allenes should be stored in the freezer.*

*Synthesis of 4-methylbenzenesulfonyl iodide (****8a****):*



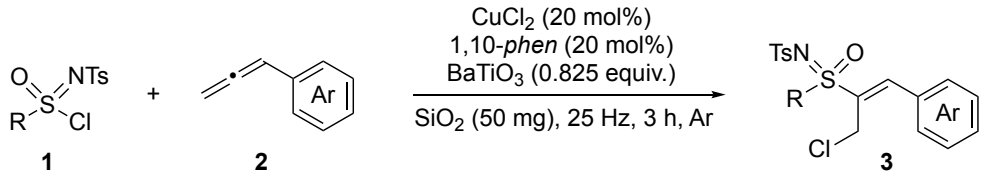
8a

Compound **8a** was synthesized according to a modified literature procedure.[5] To a solution of sodium *p*-toluenesulfinate (26.3 mmol, 4677 mg, 1.05 equiv.) in H_2O (250 mL) under the exclusion of light was added a solution of iodine (25.0 mmol, 6345 mg, 1.0 equiv.) in EtOH (50 mL) within approx. 3 min at room temperature. The resulting mixture was stirred for additional 3 min at ambient conditions. The precipitate was filtered in the dark and washed with H_2O and EtOH. The remaining solid was dried in the dark under vacuo. Compound **8a** was obtained as yellow solid (4.59 g, 16.3 mmol, 65%).

Note*: Compound* ***8a*** *should be stored under the strict exclusion of light in the freezer.*

3.2 General Procedures for the Electro-Mechanochemical ATRA

*General Procedure 3 (GP3): Synthesis of Vinyl Sulfoximines **3** (Method A)*



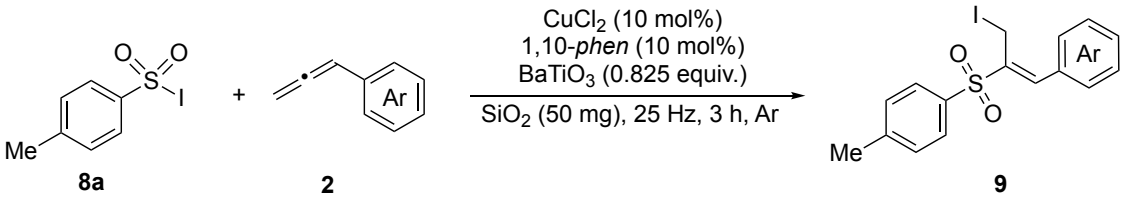
A 10 mL ZrO_2-Y milling vessel equipped with eight ZrO_2-Y milling balls (5 mm in Ø) was charged with *N*-tosylsulfoximidoyl chloride **1** (0.20 mmol, 1.0 equiv.), SiO_2 (50 mg), $CuCl_2$ (5.4 mg, 0.04 mmol, 20 mol%), 1,10-phen (7.2 mg, 0.04 mmol, 20 mol%), $BaTiO_3$ (tetragonal, 500 nm, 0.165 mmol, 38.5 mg, 0.825 equiv.), and the chosen allene **2** (0.30 mmol, 1.5 equiv.). Then, the jar was transferred to the glove box to exchange the atmosphere, by evacuating and flushing it slowly and carefully with argon (three times). The jar was closed inside the glove box. After transferring the milling vessel out of the glove box, the mechanochemical reaction was carried out for 2 × 90 minutes at 25 Hz. After milling, the crude mixture was transferred from the jars using CH_2Cl_2. The resulting reaction mixture was filtered over a short plug of celite using a borosilicate glass filter. The filtrate was analysed by ^{1}H NMR spectroscopy with 0.2 mmol of CH_2Br_2 as an internal standard. Product **3** was purified by column chromatography (column diameter: 2 cm, column length: ca. 20 cm).

*General Procedure 3 (GP3): Synthesis of Vinyl Sulfoximines **3** (Method B)*

A 10 mL ZrO_2-Y milling vessel equipped with eight ZrO_2-Y milling balls (5 mm in Ø) was charged with *N*-tosylsulfoximidoyl chloride **1** (0.20 mmol, 1.0 equiv.), SiO_2 (50 mg), $CuCl_2$ (5.4 mg, 0.04 mmol, 20 mol%), 1,10-phen (7.2 mg, 0.04 mmol, 20 mol%), and $BaTiO_3$ (tetragonal, 500 nm, 38.5 mg, 0.165 mmol, 0.825 equiv.). Then, the jar was transferred to the glove box to exchange the atmosphere, by evacuating and flushing it slowly and carefully with argon (three times). Next, *the chosen allene **2** was added inside the glove box* (0.22 mmol, 1.1 equiv.) using a single-channel pipette and the jar was closed. After transferring the milling vessel out of the glove box, the mechanochemical reaction was carried out for 2 × 90 minutes at 25 Hz. After milling, the crude mixture was transferred from the jars using CH_2Cl_2. The resulting reaction mixture was filtered over a short plug of celite using a borosilicate glass filter. The filtrate was analysed by ^{1}H NMR spectroscopy with 0.2 mmol of CH_2Br_2 as an internal standard. Product **3** was purified by column chromatography (column diameter: 2 cm, column length: ca. 20 cm).

Note: If not stated otherwise, GP3 (Method A) was used.

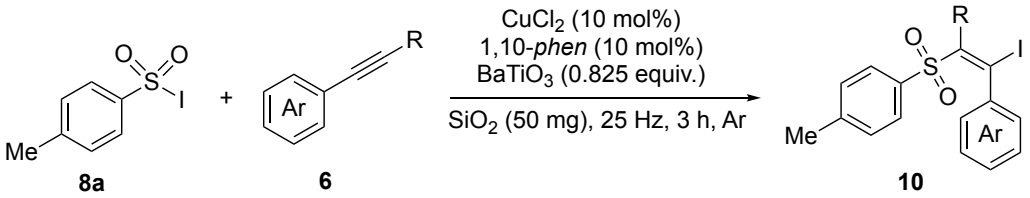
*General Procedure 4 (GP4): Synthesis of Vinyl Sulfones **9***



A 10 mL ZrO_2-Y milling vessel was charged with sulfonyl iodide **8a** (56.4 mg, 0.20 mmol, 1.0 equiv.), SiO_2 (50 mg), *tet*-$BaTiO_3$ (500 nm, 38.5 mg, 0.165 mmol, 0.825 equiv.), 1,10-phen (3.6 mg, 0.02 mmol, 10 mol%), and $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%) in the given order. The jar was equipped with eight ZrO_2-Y milling balls (5 mm in Ø). Then, the jar was transferred to the glove box to exchange the atmosphere, by evacuating and flushing it slowly and carefully with argon (three times). Next, the chosen allene **2** (0.24 mmol, 1.2 equiv.) was added inside the glove box using a single-channel pipette and the jar was closed. The mechanochemical reaction was carried out for 2 × 90 minutes at 25 Hz. After milling, the crude mixture was transferred from the jars using CH_2Cl_2. Product **9** was purified by column chromatography (column diameter: 2.5 cm, column length: ca. 35 cm).

***Note**: To prevent decomposition of sulfonyl iodide **8a** by light the milling jar was closed immediately after every addition of a reagent. The quality of sulfonyl iodide **8a** was frequently checked by ^1H NMR. Furthermore, vinyl sulfones **9** should be stored in the dark to prevent decomposition by light.*

*General Procedure 5 (GP5): Synthesis of Vinyl Sulfones **10***



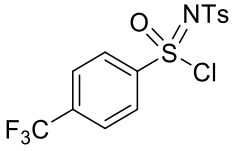
A 10 mL ZrO_2-Y milling vessel was charged with sulfonyl iodide **8a** (56,4 mg, 0.20 mmol, 1.0 equiv.), SiO_2 (50 mg), $BaTiO_3$ (tetragonal, 500 nm, 38.5 mg, 0.165 mmol, 0.825 equiv.), 1,10-phen (3.6 mg, 0.02 mmol, 10 mol%), and $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%) in the given order. The jar was equipped with eight ZrO_2-Y milling balls (5 mm in Ø). Then, the jar was transferred to the glove box to exchange the atmosphere, by evacuating and flushing it slowly and carefully with argon (three times). Next, the chosen acetylene **6** (0.24 mmol, 1.2 equiv.) was added inside the glove box using a single-channel pipettes and the jar was closed. The mechanochemical reaction was carried out for 2 × 90 minutes at 25 Hz. After milling, the crude mixture was transferred from the jars using CH_2Cl_2. Product **10** was purified by column chromatography (column diameter: 2.5 cm, column length: ca. 35 cm).

***Note**: To prevent decomposition of sulfonyl iodide **8a** by light the milling jar was closed immediately after every addition of reagents. The quality of sulfonyl iodide **8a** was frequently checked by ^{1}H NMR.*

4 Analytical Data

4.1 Starting Materials

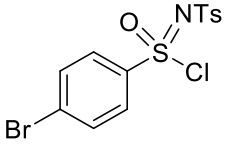
N-Tosyl-4-(trifluoromethyl)benzenesulfoximidoyl chloride (1b)



The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow solid (1.98 g, 4.97 mmol, 49% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.7, 145.0, 138.1, 137.1 (q, J = 33.8 Hz), 129.9, 127.6, 127.6, 127.2 (q, J = 3.6 Hz), 122.7 (q, J = 273.6 Hz), 21.8 ppm.
^{19}F NMR (565 MHz, $CDCl_3$): δ = –63.4 (s, 3F) ppm.
IR (ATR): ν = 3105, 2927, 2162, 1596, 1493, 1448, 1402, 1314, 1287, 1161, 1122, 1058, 1007, 843, 809, 739, 705, 666 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{11}ClF_3NNaO_3S_2^+$ 419.9713; found 419.9709.

4-Bromo-*N*-tosylbenzenesulfoximidoyl chloride (1c)

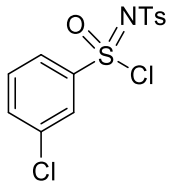


The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as an off-white solid (2.60 g, 6.36 mmol, 64% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 144.8, 141.6, 138.3, 133.3, 131.6, 129.9, 128.4, 127.6, 21.8 ppm.
IR (ATR): ν = 3094, 2922, 2176, 1919, 1595, 1564, 1494, 1465, 1391, 1331, 1280, 1157, 1109, 1064, 1002, 817, 725, 689 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{11}BrClNNaO_3S_2^+$ 429.8945; found 429.8943.

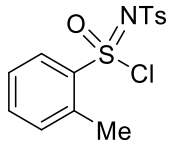
3-Chloro-*N*-tosylbenzenesulfoximidoyl chloride (1d)



The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (1.60 g, 4.39 mmol, 43% yield).

^1H NMR (600 MHz, $CDCl_3$): δ = 7.99 (t, *J* = 2.0 Hz, 1H), 7.95 – 7.90 (m, 3H), 7.72 – 7.68 (m, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H) ppm.
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 144.9, 143.7, 138.1, 136.0, 135.9, 131.2, 129.8, 127.5, 126.7, 125.0, 21.7 ppm.
IR (ATR): ν = 3105, 3071, 2923, 2857, 1593, 1460, 1410, 1336, 1285, 1160, 1101, 1073, 890, 796, 719, 666 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{11}Cl_2NNaO_3S_2^+$ 385.9449; found 385.9449.

2-Methyl-*N*-tosylbenzenesulfoximidoyl chloride (1e)



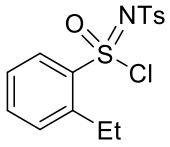
The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colourless solid (2.88 g, 8.37 mmol, 85% yield).

^1H NMR (600 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.70 (s, 3H), 2.44 (s, 3H) ppm.
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 144.6, 140.8, 138.6, 138.5, 135.7, 134.1, 129.8, 128.6, 127.6, 127.0, 21.8, 20.5 ppm.
IR (ATR): ν = 3095, 2929, 2164, 1595, 1563, 1466, 1378, 1335, 1283, 1206, 1159, 1106, 1036, 819,

774, 728, 687, 659 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{14}ClNNaO_3ClS_2^+$ 365.9996; found 365.9996.

2-Ethyl-*N*-tosylbenzenesulfoximidoyl chloride (1f)



The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (2.50 g, 6.98 mmol, 70% yield).

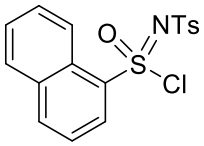
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.65 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.13 (dq, *J* = 14.9, 7.5 Hz, 1H), 3.05 (dq, *J* = 14.9, 7.5 Hz, 1H), 2.45 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.6, 144.4, 140.7, 138.6, 135.7, 132.3, 129.8, 128.6, 127.6, 126.7, 25.6, 21.8, 14.9 ppm.

IR (ATR): ν = 3357, 3259, 2982, 2983, 2879, 2162, 1594, 1467, 1331, 1282, 1157, 1117, 1083, 972, 902, 814, 768, 740, 714, 686, 661 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{16}ClNNaO_3S_2^+$ 380.0152; found 380.0150.

***N*-Tosylnaphthalene-1-sulfoximidoyl chloride (1g)**



The title compound was prepared following GP1. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as yellow solid (1.52 g, 4.00 mmol, 40% yield).

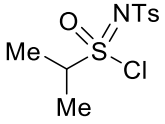
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 – 8.64 (m, 1H), 8.48 – 8.43 (m, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.84 – 7.76 (m, 3H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 2.46 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.8, 142.4, 138.6, 135.8, 131.9, 130.5, 129.9, 129.3, 129.0, 128.0, 127.7, 126.6, 126.2, 124.6, 124.4, 21.9 ppm.

IR (ATR): ν = 3356, 3261, 3063, 2924, 2858, 2160, 1726, 1592, 1559, 1451, 1371, 1337, 1278, 1160, 1069, 980, 901, 810, 761, 721, 679, 658 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{14}ClNNaO_3S_2^+$ 401.9996; found 401.9995.

***N*-Tosylpropane-2-sulfoximidoyl chloride (1h)**



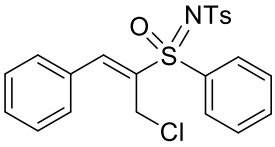
The title compound was prepared following GP2. After purification by column chromatography (SiO_2, 20:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow solid (2.20 g, 7.43 mmol, 73% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 3.86 (hept, J = 6.6 Hz, 1H), 2.43 (s, 3H), 1.61 – 1.57 (m, 6H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.4, 138.4, 129.7, 127.5, 69.6, 21.8, 17.2, 16.7 ppm.
IR (ATR): ν = 3357, 3260, 2918, 2161, 1925, 1596, 1455, 1390, 1333, 1270, 1159, 1090, 1055, 809, 727, 671 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{10}H_{14}ClNNaO_3S_2^+$ 317.9996, found 317.9993.

4.2 Products

4.2.1 Vinyl Sulfoximines

(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(phenyl)-λ^6-sulfaneylidene]-4 methylbenzene-sulfonamide (3aa)



According to GP3, method A: After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (80 mg, 0.17 mmol, 90% yield).

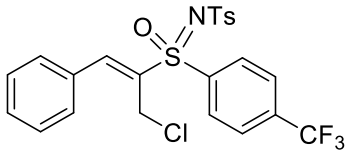
According to GP3, method B: After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (79 mg, 0.17 mmol, 89% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 – 8.03 (m, 3H), 7.87 (d, J = 8.3 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.65 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.51 – 7.46 (m, 3H), 7.29 – 7.22 (m, 2H), 4.66 (d, J = 13.3 Hz, 1H), 4.59 (d, J = 13.3 Hz, 1H), 2.39 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.9, 143.2, 140.8, 137.9, 136.2, 134.5, 132.2, 131.4, 130.5, 129.6, 129.4, 129.4, 128.8, 126.9, 37.5, 21.7 ppm.

IR (ATR): ν = 3060, 2922, 2324, 2161, 2081, 2031, 1990, 1948, 1905, 1613, 1492, 1446, 1314, 1235, 1151, 1060, 996, 922, 812,739, 684 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}ClNNaO_3S_2^+$ 468.0465; found 468.0458.

(*E*)-*N*-{(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)[4-(trifluoromethyl)phenyl]-λ⁶-sulfaneylidene}-4-methylbenzenesulfonamide (3ba)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (81 mg, 0.16 mmol, 79% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.4 Hz, 2H), 8.12 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.52 – 7.48 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.70 (d, *J* = 13.3 Hz, 1H), 4.62 (d, *J* = 13.3 Hz, 1H), 2.39 (s, 3H) ppm.

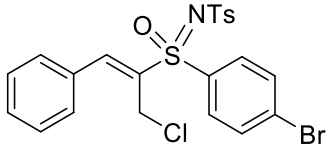
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 146.1, 143.5, 142.5, 140.4, 136.0 (q, *J* = 33.2 Hz), 135.4, 131.9, 131.7, 130.5, 129.51, 129.46, 129.4, 126.9, 126.6 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 273.2 Hz), 37.4, 21.6 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ = –63.2 (s, 3F) ppm.

IR (ATR): ν = 3061, 2925, 2165, 2029, 1808, 1731, 1610, 1494, 1449, 1403, 1319, 1241, 1149, 1098, 1059, 1009, 912, 843, 813, 728, 694, 665 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{19}ClF_3NNaO_3S_2^+$ 536.0339; found 536.0336.

(*E*)-*N*-[(4-Bromophenyl)(3-chloro-1-phenylprop-1-en-2-yl)(oxo)-λ⁶-sulfaneylidene]-4-methyl-benzenesulfonamide (3ca)

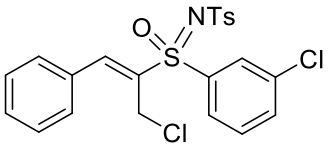


The title compound was prepared following GP3 (method A). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (80 mg, 0.15 mmol, 76% yield).

The title compound was prepared following GP3 (method B). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (76 mg, 0.14 mmol, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.91 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.63 – 7.60 (m, 2H), 7.52 – 7.46 (m, 3H), 7.26 (d, J = 7.9 Hz, 2H), 4.67 (d, J = 13.3 Hz, 1H), 4.59 (d, J = 13.2 Hz, 1H), 2.39 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.4, 143.3, 140.6, 137.2, 135.8, 132.9, 132.0, 131.6, 130.5, 130.2, 130.1, 129.5, 129.4, 126.9, 37.5, 21.7 ppm.
IR (ATR): ν = 3063, 2926, 2171, 2020, 1733, 1614, 1570, 1450, 1450, 1388, 1318, 1238, 1152, 1058, 1002, 922, 816, 752, 812,697, 664 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{19}BrClNNaO_3S_2^+$ 545.9571; found 545.9560.

(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(3-chlorophenyl)(oxo)-λ^6-sulfaneylidene]-4-methyl-benzenesulfonamide (3da)

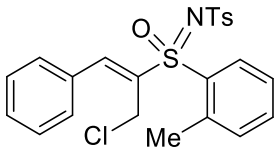


The title compound was prepared following GP3 (method A). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (88 mg, 0.18 mmol, 92% yield).

The title compound was prepared following GP3 (method B). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (71 mg, 0.15 mmol, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.99 (t, J = 2.0 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.50 – 7.46 (m, 4H), 7.24 (s, 2H), 4.66 (d, J = 13.3 Hz, 1H), 4.58 (d, J = 13.3 Hz, 1H), 2.38 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.7, 143.4, 140.6, 139.9, 135.9, 135.7, 134.6, 132.0, 131.6, 130.8, 130.6, 129.5, 129.5, 128.6, 127.0, 126.9, 37.5, 21.7 ppm.
IR (ATR): ν = 3066, 2926, 2161, 2024, 1913, 1733, 1613, 1576, 1493, 1454, 1413, 1373, 1319, 1239, 1153, 1062, 994, 921, 798, 759, 715, 667 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{19}Cl_2NNaO_3S_2^+$ 502.0076; found 502.0072.

(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(*o*-tolyl)- λ⁶-sulfaneylidene]-4-methylbenzene-sulfonamide (3ea)

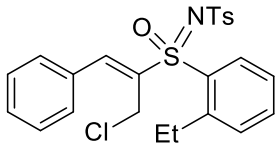


The title compound was prepared following GP3 (method A). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (88 mg, 0.19 mmol, 88% yield).

The title compound was prepared following GP3 (method B). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (80 mg, 0.17 mmol, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.37 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.08 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.47 – 7.43 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.50 (d, *J* = 13.4 Hz, 1H), 4.46 (d, *J* = 13.4 Hz, 1H), 2.55 (s, 3H), 2.39 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.4, 143.1, 141.0, 139.9, 134.8, 134.1, 133.9, 133.5, 132.1, 131.44, 131.43, 130.5, 129.44, 129.41, 127.1, 126.9, 37.5, 21.7, 20.3 ppm.
IR (ATR): ν = 3469, 3059, 2924, 2855, 2324, 2161, 2075, 2026, 1918, 1724, 1615, 1492, 1452, 1, 1151, 1060, 996, 922, 812,739, 684 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{22}ClNNaO_3S_2^+$ 482.0622; found 482.0616.

(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(2-ethylphenyl)(oxo)- λ⁶-sulfaneylidene]-4-methyl-benzenesulfonamide (3fa)

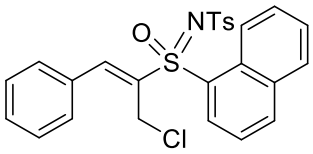


The title compound was prepared following GP3 (method A). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (79 mg, 0.17 mmol, 83% yield).

The title compound was prepared following GP3 (method B). After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (52 mg, 0.11 mmol, 55% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.36 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.06 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.62 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.45 – 7.41 (m, 1H), 7.40 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.49 (d, *J* = 13.4 Hz, 1H), 4.45 (d, *J* = 13.3 Hz, 1H), 3.02 (dq, *J* = 14.9, 7.5 Hz, 1H), 2.88 (dq, *J* = 14.9, 7.5 Hz, 1H), 2.38 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.9, 144.8, 143.0, 141.0, 134.90, 134.88, 133.8, 132.1, 131.42, 131.36, 130.4, 129.40, 129.38, 126.9, 126.8, 37.5, 25.3, 21.7, 14.9 ppm.
IR (ATR): ν = 2978, 2924, 2325, 2160, 2033, 1909, 1832, 1736, 1612, 1494, 1452, 1367, 1310, 1237, 1187, 1151, 1075, 1021, 951, 923, 807, 756, 718 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{24}ClNNaO_3S_2^+$ 496.0778; found 496.0781.

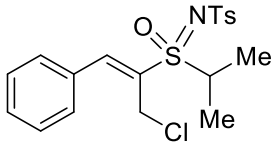
(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(naphthalen-1-yl)(oxo)- λ^6-sulfaneylidene]-4-methyl-benzenesulfonamide (3ga)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (83 mg, 0.17 mmol, 7.43 mmol, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 8.2 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 7.83 – 7.73 (m, 3H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.50 – 7.46 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.49 (d, *J* = 13.3 Hz, 1H), 4.45 (d, *J* = 13.3 Hz, 1H), 2.35 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.3, 143.1, 141.1, 140.5, 134.8, 132.4, 131.9, 131.6, 131.5, 130.4, 129.93, 129.87, 129.5, 129.4, 129.2, 128.2, 126.8, 126.0, 125.2, 124.2, 37.0, 21.6 ppm.
IR (ATR): ν = 3062, 2924, 2857, 2324, 2162, 2085, 1731, 1615, 1500, 1449, 1368, 1319, 1267, 1234, 1153, 1067, 983, 898, 814, 757, 716, 665 cm^{-1}.
HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{26}H_{22}ClKNO_3S_2^+$ 534.0361; found 534.0341.

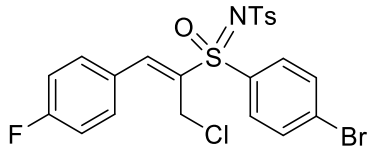
(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(isopropyl)(oxo)-λ^6-sulfaneylidene]-4-methylbenzene-sulfonamide (3ha)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (49 mg, 0.10 mmol, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.57 – 7.49 (m, 3H), 7.30 – 7.23 (m, 2H), 4.86 (d, J = 13.2 Hz, 1H), 4.69 (d, J = 13.2 Hz, 1H), 3.64 (hept, J = 6.8 Hz, 1H), 2.38 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H), 1.34 (d, J = 6.8 Hz, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 148.0, 142.9, 140.9, 132.3, 132.2, 131.5, 130.4, 129.42, 129.37, 126.7, 56.8, 38.6, 21.7, 14.8, 14.3 ppm.
IR (ATR): ν = 2962, 2871, 2254, 2160, 1803, 1605, 1504, 1461, 1368, 1312, 1225, 1151, 1067, 913, 875, 814, 767, 726, 683, 658 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{22}ClNNaO_3S_2^+$ 434.0622; found 434.0617.

(*E*)-*N*-{(4-Bromophenyl)[3-chloro-1-(4-fluorophenyl)prop-1-en-2-yl](oxo)-λ^6-sulfaneylidene}-4-methylbenzenesulfonamide (3cb)

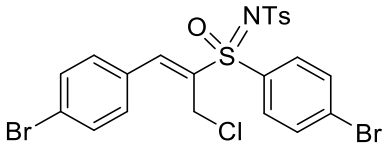


The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (85 mg, 0.16 mmol, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (s, 1H), 7.90 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 8.6 Hz, 2H), 4.65 (d, J = 13.4 Hz, 1H), 4.57 (d, J = 13.4 Hz, 1H), 2.40 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 164.5 (d, J = 254.9 Hz), 144.0, 143.4, 140.5, 137.0, 135.5, 132.93, 132.9 (d, J = 9.0 Hz), 130.20, 130.16, 129.5, 128.3 (d, J = 3.2 Hz), 126.8, 116.8 (d, J = 21.9 Hz), 37.4, 21.7 ppm.
^{19}F NMR (565 MHz, $CDCl_3$): δ = –106.4 - –106.5 (m, 1F) ppm.

IR (ATR): ν = 3087, 2922, 2853, 2323, 2246, 2213, 2172, 2098, 2026, 1989, 1956, 1722, 1596, 1570, 1507, 1467, 1387, 1316, 1234, 1152, 1058, 1002, 921, 820, 752, 703, 662 cm^{-1}.
HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{22}H_{18}BrClFKNO_3S_2^+$ 579.9216, found: 579.9206.

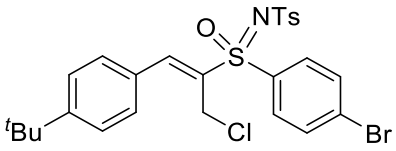
(*E*)-*N*-{(4-Bromophenyl)[1-(4-bromophenyl)-3-chloroprop-1-en-2-yl](oxo)-λ^6-sulfaneylidene}-4-methylbenzenesulfonamide (3cc)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (88 mg, 0.15 mmol, 73% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.29 – 7.23 (m, 2H), 7.10 – 7.00 (m, 2H), 4.42 (d, *J* = 13.4 Hz, 1H), 4.33 (d, *J* = 13.4 Hz, 1H), 2.18 (s, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 143.9, 143.3, 140.4, 136.7, 136.49, 136.46, 132.9, 132.6, 131.7, 130.8, 130.1, 129.4, 126.7, 126.3, 37.1, 21.6 ppm.
IR (ATR): ν = 3088, 2924, 2094, 2024, 1918, 1732, 1616, 1575, 1485, 1390, 1317, 1238, 1152, 1060, 1003, 922, 815, 758, 715, 662 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{18}Br_2ClNNaO_3S_2^+$ 623.8676; found 623.8663.

(*E*)-*N*-[(4-Bromophenyl){1-[4-(*tert*-butyl)phenyl]-3-chloroprop-1-en-2-yl}(oxo)-λ^6-sulfaneylidene]-4-methylbenzenesulfonamide (3cd)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (89 mg, 0.15 mmol, 76% yield).

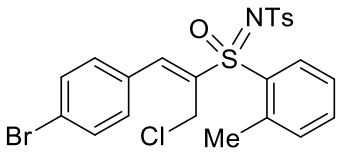
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 4.69 (d, *J* = 13.3 Hz, 1H), 4.62 (d, *J* = 13.3 Hz, 1H), 2.38 (s, 3H), 1.34 (s, 9H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 155.5, 145.2, 143.2, 140.6, 137.3, 134.2, 132.8, 130.6, 130.1, 129.9, 129.4, 129.2, 126.8, 126.4, 37.7, 35.2, 31.1, 21.6 ppm.

IR (ATR): ν = 3041, 2990, 2924, 2854, 2321, 2217, 2075, 2160, 2038, 1953, 1888, 1732, 1598, 1508, 1444, 1415, 1381, 1313, 1219, 1149, 1107, 1059, 938, 877, 832, 811, 770, 728, 698, 656 cm^{-1}.

HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{26}H_{27}BrClKNO_3S_2^+$ 617.9936, found: 617.9923.

(*E*)-*N*-{[1-(4-Bromophenyl)-3-chloroprop-1-en-2-yl](oxo)(*o*-tolyl)-λ^6-sulfaneylidene}-4-methylbenzenesulfonamide (3ec)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (92 mg, 0.17 mmol, 85% yield).

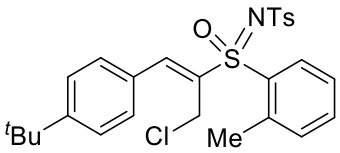
^1H NMR (600 MHz, $CDCl_3$): δ = 8.35 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.01 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.57 (td, *J* = 7.5, 1.3 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.45 (d, *J* = 13.5 Hz, 1H), 4.42 (d, *J* = 13.5 Hz, 1H), 2.53 (s, 3H), 2.39 (s, 3H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 144.0, 143.1, 140.9, 139.8, 134.9, 134.7, 133.7, 133.5, 132.7, 131.8, 131.4, 130.9, 129.4, 127.1, 126.8, 126.2, 37.2, 21.7, 20.3 ppm.

IR (ATR): ν = 3062, 2926, 2160, 1916, 1733, 1619, 1586, 1485, 1454, 1401, 1373, 1316, 1236, 1151, 1076, 923, 811, 754, 713, 658 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{21}BrClNNaO_3S_2^+$ 559.9727; found 559.9716.

(*E*)-*N*-({1-[4-(*tert*-Butyl)phenyl]-3-chloroprop-1-en-2-yl}(oxo)(*o*-tolyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (3ed)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (84 mg, 0.16 mmol, 81% yield).

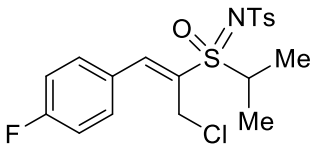
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.37 (dd, J = 8.2, 1.3 Hz, 1H), 8.03 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.56 (td, J = 7.6, 1.3 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 4.52 (d, J = 13.4 Hz, 1H), 4.48 (d, J = 13.4 Hz, 1H), 2.53 (s, 3H), 2.38 (s, 3H), 1.35 (s, 9H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 155.4, 145.3, 143.0, 141.0, 139.8, 134.7, 134.1, 133.41, 132.39, 131.38, 130.7, 129.4, 129.3, 127.0, 126.9, 126.5, 37.7, 35.2, 31.2, 21.7, 20.3 ppm.

IR (ATR): ν = 3088, 2960, 2869, 2168, 1915, 1603, 1569, 1505, 1467, 1389, 1319, 1237, 1153, 1060, 1003, 922, 818, 761, 713, 669 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{30}ClNNaO_3S_2^+$ 538.1248, found: 538.1239.

(*E*)-*N*-{[3-Chloro-1-(4-fluorophenyl)prop-1-en-2-yl](isopropyl)(oxo)-λ^6-sulfaneylidene}-4-methyl-benzenesulfonamide (3hb)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (53 mg, 0.12 mmol, 62% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 – 7.79 (m, 3H), 7.70 – 7.65 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 8.5 Hz, 2H), 4.85 (d, J = 13.3 Hz, 1H), 4.65 (d, J = 13.3 Hz, 1H), 3.61 (hept, J = 6.8 Hz, 1H), 2.37 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H) ppm.

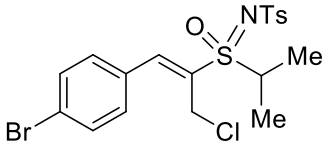
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 164.4 (d, J = 254.8 Hz), 146.5, 142.9, 140.8, 132.8 (d, J = 9.0 Hz), 131.8 (d, J = 1.9 Hz), 129.3, 128.4 (d, J = 3.4 Hz), 126.6, 116.7 (d, J = 21.9 Hz), 56.7, 38.3, 21.6, 14.7, 14.2 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ = –106.7 - –106.8 (m, 1F) ppm.

IR (ATR): ν = 3041, 2990, 2924, 2854, 2321, 2217, 2160, 2038, 1953, 1888, 1732, 1598, 1508, 1444, 1415, 1381, 1313, 1219, 1149, 938, 877, 832, 811, 770, 728, 698, 656 cm^{-1}.

HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{19}H_{21}ClFKNO_3S_2^+$ 468.0267; found 468.0261.

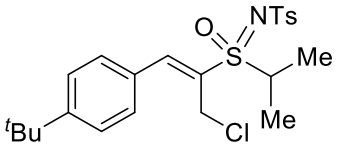
(*E*)-*N*-{[1-(4-Bromophenyl)-3-chloroprop-1-en-2-yl](isopropyl)(oxo)-λ^6-sulfaneylidene}-4-methyl-benzenesulfonamide (3hc)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (49 mg, 0.1 mmol, 50% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.3 Hz, 2H), 7.78 (s, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 4.83 (d, J = 13.3 Hz, 1H), 4.64 (d, J = 13.3 Hz, 1H), 3.61 (hept, J = 6.8 Hz, 1H), 2.38 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 146.5, 143.0, 140.8, 133.0, 132.7, 131.7, 131.0, 129.3, 126.6, 126.2, 56.7, 38.2, 21.6, 14.7, 14.3 ppm.
IR (ATR): ν = 3037, 2989, 2927, 2312, 2215, 2156, 2024, 1983, 1949, 1904, 1795, 1615, 1587, 1487, 1441, 1403, 1380, 1311, 1216, 1187, 1147, 1107, 1063, 936, 917, 873, 811, 769, 705, 658 cm^{-1}.
HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{19}H_{21}BrClKNO_3S_2^+$ 527.9466, found: 527.9458.

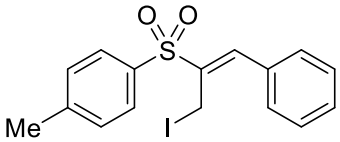
(*E*)-*N*-({1-[4-(*tert*-Butyl)phenyl]-3-chloroprop-1-en-2-yl}(isopropyl)(oxo)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (3hd)



The title compound was prepared following GP3. After purification by column chromatography (SiO_2, 6:1→4:1 *n*-pentane:EtOAc) the product was obtained as a pale-yellow foam (51 mg, 0.11 mmol, 55% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.81 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.25 – 7.23 (m, 2H), 4.88 (d, J = 13.2 Hz, 1H), 4.72 (d, J = 13.2 Hz, 1H), 3.62 (hept, J = 6.7 Hz, 1H), 2.37 (s, 3H), 1.49 (d, J = 6.8 Hz, 3H), 1.36 (s, 9H), 1.32 (d, J = 6.8 Hz, 3H) ppm.
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 155.4, 147.8, 142.9, 141.0, 130.68, 130.66, 129.5, 129.3, 126.7, 126.4, 56.74 38.8, 35.2, 31.2, 21.6, 14.7, 14.3 ppm.
IR (ATR): ν = 2962, 2871, 2254, 2160, 1803, 1605, 1504, 1461, 1368, 1312, 1225, 1151, 1067, 913, 875, 814, 767, 726, 683, 658 cm^{-1}.
HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{30}ClNNaO_3S_2^+$ 490.1248; found: 490.1241.

(*E*)-1-[(3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl]-4-methylbenzene (9a)



The title compound was prepared following GP4. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellowish solid (72 mg, 0.18 mmol, 90% yield).

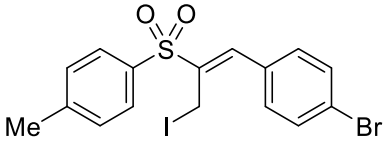
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.55 – 7.41 (m, 3H), 7.37 (d, J = 8.1 Hz, 2H), 4.30 (s, 3H), 2.45 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.0, 140.3, 138.8, 137.0, 133.2, 130.4, 130.1, 129.3, 128.8, 21.8, −5.8 ppm.

IR (ATR): ν = 3856, 3648, 3402, 3022, 2923, 2855, 2431, 2317, 2216, 2164, 2097, 2057, 2005, 1969, 1910, 1801, 1744, 1688, 1615, 1493, 1448, 1426, 1303, 1216, 1156, 1127, 1081, 1013, 929, 900, 851, 812, 752, 729, 688, 661 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}INaO_2S^+$ 420.9730; found 420.9725.

(*E*)-1-Bromo-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (9b)



The title compound was prepared following GP4. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellowish solid (79 mg, 0.17 mmol, 83% yield).

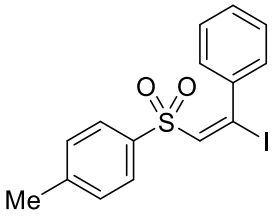
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.24 (s, 2H), 2.46 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.2, 139.6, 138.8, 136.7, 132.6, 132.0, 131.8, 130.1, 128.9, 125.0, 21.9, −6.4 ppm.

IR (ATR): ν = 3891, 3491, 3036, 2922, 2856, 2305, 2161, 2056, 2024, 1980, 1909, 1801, 1690, 1615, 1587, 1484, 1427, 1398, 1313, 1155, 1132, 1006, 903, 856, 806, 732, 703, 670 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{14}BrINaO_2S^+$ 498.8835; found 498.8830.

(*E*)-1-[(2-Iodo-2-phenylvinyl)sulfonyl]-4-methylbenzene (10a)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellowish solid (64 mg, 0.17 mmol, 83% yield).

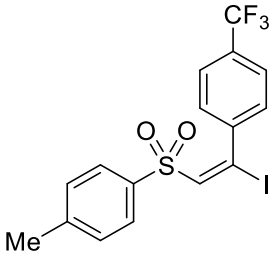
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.4 Hz, 2H), 7.36 (s, 1H), 7.34 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.7, 141.4, 139.8, 137.4, 129.9, 129.8, 128.03, 127.99, 127.8, 114.3, 21.8 ppm.

IR (ATR): ν = 3058, 2923, 2855, 2323, 2166, 2085, 1895, 1820, 1774, 1733, 1589, 1485, 1442, 1384, 1325, 1276, 1142, 1082, 1021, 926, 857, 802, 763, 689 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{13}INaO_2S^+$ 406.9573; found 406.9576.

(*E*)-1-({2-Iodo-2-[4-(trifluoromethyl)phenyl]vinyl}sulfonyl)-4-methylbenzene (10b)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (88 mg, 0.195 mmol, 97% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.40 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.23 – 7.17 (m, 2H), 2.40 (s, 3H) ppm.

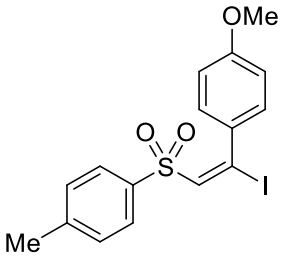
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 145.2, 143.3, 142.6, 137.0, 131.5 (q, J = 32.8 Hz), 130.0, 128.1, 128.0, 125.1 (q, J = 3.7 Hz), 123.7 (q, J = 272.5 Hz), 110.8, 21.7 ppm.

^{19}F NMR (564 MHz, $CDCl_3$): δ = –62.9 (s, 3F) ppm

IR (ATR): ν = 3039, 2926, 2323, 2166, 2079, 2023, 1913, 1734, 1597, 1505, 1447, 1406, 1321, 1148, 1116, 1064, 1017, 954, 748 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{12}F_3INaO_2S^+$ 474.9447; found 474.9449.

(*E*)-1-{[2-Iodo-2-(4-methoxyphenyl)vinyl]sulfonyl}-4-methylbenzene (10c)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (71 mg, 0.17 mmol, 86% yield).

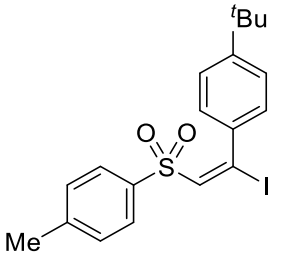
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 161.0, 144.6, 140.4, 137.7, 132.0, 130.1, 129.8, 128.0, 115.0, 113.4, 55.5, 21.8 ppm.

IR (ATR): ν = 3038, 2919, 2844, 2289, 2162, 2121, 1902, 1733, 1600, 1503, 1462, 1406, 1323, 1287, 1246, 1177, 1144, 1083, 1022, 867, 825, 790, 740, 711, 666 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}INaO_3S^+$ 436.9679; found 436.9681.

(*E*)-1-(*tert*-Butyl)-4-(1-iodo-2-tosylvinyl)benzene (10d)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellow oil (84 mg, 0.19 mmol, 95% yield).

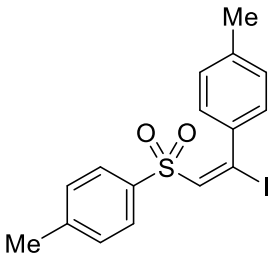
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H), 1.32 (s, 9H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 153.4, 144.4, 141.4, 137.4, 136.7, 129.6, 128.1, 127.9, 124.9, 114.9, 34.9, 31.3, 21.7 ppm.

IR (ATR): ν = 3039, 2960, 2869, 2325, 2164, 1912, 1798, 1595, 1498, 1462, 1401, 1365, 1318, 1142, 1083, 1019, 951, 910, 874, 814, 758 cm^{-1}.

HRMS (ESI): *m/z*: $[M + K]^+$ calcd for $C_{19}H_{21}IKO_2S^+$ 478.9939; found 478.9939.

(*E*)-1-{[2-Iodo-2-(*p*-tolyl)vinyl]sulfonyl}-4-methylbenzene (10e)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellowish solid (73 mg, 0.18 mmol, 92% yield).

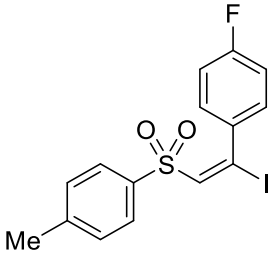
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.7, 140.7, 140.3, 137.6, 137.0, 129.8, 128.7, 128.0, 127.9, 114.9, 21.8, 21.6 ppm.

IR (ATR): ν = 3036, 2920, 2863, 2301, 2161, 2116, 2013, 1965, 1907, 1795, 1738, 1655, 1596, 1501, 1446, 1402, 1323, 1283, 1183, 1144, 1083, 1039, 1020, 868, 786, 734, 706, 666 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}INaO_2S^+$ 420.9730; found 420.9733.

(*E*)-1-Fluoro-4-(1-iodo-2-tosylvinyl)benzene (10f)



The title compound was prepared following GP4. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (76 mg, 0.19 mmol, 95% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.1 Hz, 2H), 7.34 (s, 1H), 7.26 – 7.23 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 8.6 Hz, 2H), 2.40 (s, 3H) ppm.

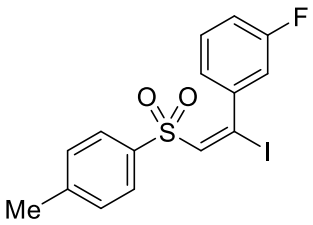
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 163.3 (d, J = 251.6 Hz), 144.9, 141.8, 137.4, 135.8 (d, J = 3.4 Hz), 130.2 (d, J = 8.7 Hz), 129.9, 128.0, 115.2 (d, J = 22.3 Hz), 112.7, 21.8 ppm.

^{19}F NMR (564 MHz, $CDCl_3$): δ = −109.8 – −109.9 (m, 1F) ppm.

IR (ATR): ν = 3039, 2923, 2857, 2321, 2165, 2104, 2036, 1908, 1791, 1741, 1668, 1591, 1498, 1453, 1400, 1317, 1288, 1230, 1183, 1145, 1084, 1040, 1016, 869, 830, 799, 739, 710, 668 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{12}FINaO_2S^+$ 424.9479; found 424.9468.

(*E*)-1-Fluoro-3-(1-iodo-2-tosylvinyl)benzene (10g)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (66 mg, 0.16 mmol, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.0 Hz, 2H), 7.36 (s, 1H), 7.28 (dd, J = 8.0, 5.8 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.6 Hz, 1H), 7.01 (td, J = 8.4, 2.5 Hz, 1H), 6.84 (d, J = 9.1 Hz, 1H), 2.41 (s, 3H) ppm.

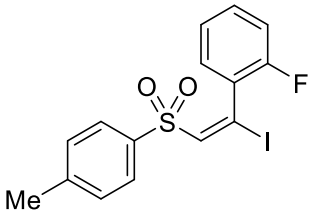
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 161.9 (d, J = 248.2 Hz), 145.1, 142.2, 141.6 (d, J = 8.2 Hz), 137.2, 129.9, 129.8 (d, J = 8.1 Hz), 128.0, 123.6 (d, J = 3.2 Hz), 116.9 (d, J = 21.2 Hz), 114.8 (d, J = 23.6 Hz), 111.4 (d, J = 2.4 Hz), 21.8 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ = −112.1 – −112.3 (m, 1F) ppm.

IR (ATR): ν = 3041, 2924, 2855, 2325, 2164, 2084, 1991, 1916, 1860, 1796, 1741, 1580, 1479, 1429, 1316, 1288, 1220, 1142, 1083, 1041, 936, 900, 832, 805, 781, 737, 703, 675 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{12}FINaO_2S^+$ 424.9479; found 424.9482.

(*E*)-1-Fluoro-2-(1-iodo-2-tosylvinyl)benzene (10h)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a yellowish oil (68 mg, 0.17 mmol, 85% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ=7.53 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 1.1 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.27 – 7.19 (m, 3H), 7.17 – 7.11 (m, 1H), 7.01 – 6.89 (m, 1H), 2.41 (s, 3H) ppm.

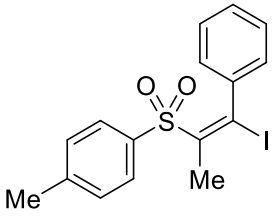
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 157.4 (d, J = 251.0 Hz), 145.0, 143.0, 136.9, 131.7 (d, J = 8.0 Hz), 129.9, 129.4 (d, J = 1.8 Hz), 128.0, 127.7 (d, J = 14.8 Hz), 123.9 (d, J = 3.7 Hz), 115.8 (d, J = 20.3 Hz), 104.6, 21.8 ppm.

^{19}F NMR (564 MHz, $CDCl_3$): δ = −110.8 - −110.9 (m, 1F) ppm.

IR (ATR): ν = 3044, 2924, 2854, 2323, 2163, 2082, 2012, 1920, 1809, 1739, 1622, 1592, 1479, 1445, 13225, 1285, 1220, 1184, 1144, 1082, 1028, 954, 871, 837, 810, 768, 724, 678 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{12}FINaO_2S^+$ 424.9479; found 424.9482.

(*E*)-1-[(1-Iodo-1-phenylprop-1-en-2-yl)sulfonyl]-4-methylbenzene (10i)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (71 mg, 0.18 mmol, 89% yield).

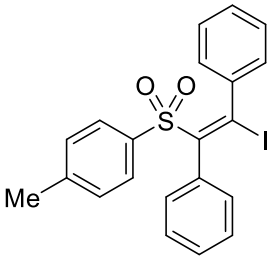
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.2 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.13 – 7.07 (m, 2H), 2.51 (s, 3H), 2.39 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 144.3, 144.1, 143.1, 137.5, 129.6, 128.8, 127.9, 127.8, 127.7, 115.9, 27.2, 21.7 ppm.

IR (ATR): ν = 3057, 2924, 2854, 2325, 2159, 2083, 1895, 1814, 1740, 1626, 1593, 1487, 1440, 1402, 1378, 1311, 1211, 1182, 1151, 1116, 1078, 995, 922, 847, 816, 760, 692 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}INaO_2S^+$ 420.9730; found 420.9732.

(*E*)-(1-iodo-2-tosylethene-1,2-diyl)dibenzene (10j)



The title compound was prepared following GP5. After purification by column chromatography (SiO_2, 20:1→10:1→4:1 *n*-pentane:EtOAc) the product was obtained as a colorless solid (65 mg, 0.14 mmol, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 – 7.23 (m, 8H), 7.21 – 7.17 (m, 2H), 7.12 – 7.08 (m, 2H), 7.02 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 149.3, 144.4, 142.7, 139.6, 137.0, 130.4, 129.3, 129.1 (2C), 128.7, 128.5, 128.0, 127.5, 118.2, 21.8 ppm.

IR (ATR): ν = 3055, 2924, 2855, 2593, 2318, 2164, 2056, 1996, 1912, 1816, 1737, 1619, 1594, 1490, 1444, 1402, 1319, 1234, 1149, 1086, 1030, 948, 908, 841, 812, 778, 730, 696, 669 cm^{-1}.

HRMS (ESI): *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{17}INaO_2S^+$ 482.9886; found 482.9873.

5 References

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6 Spectra

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1b**.

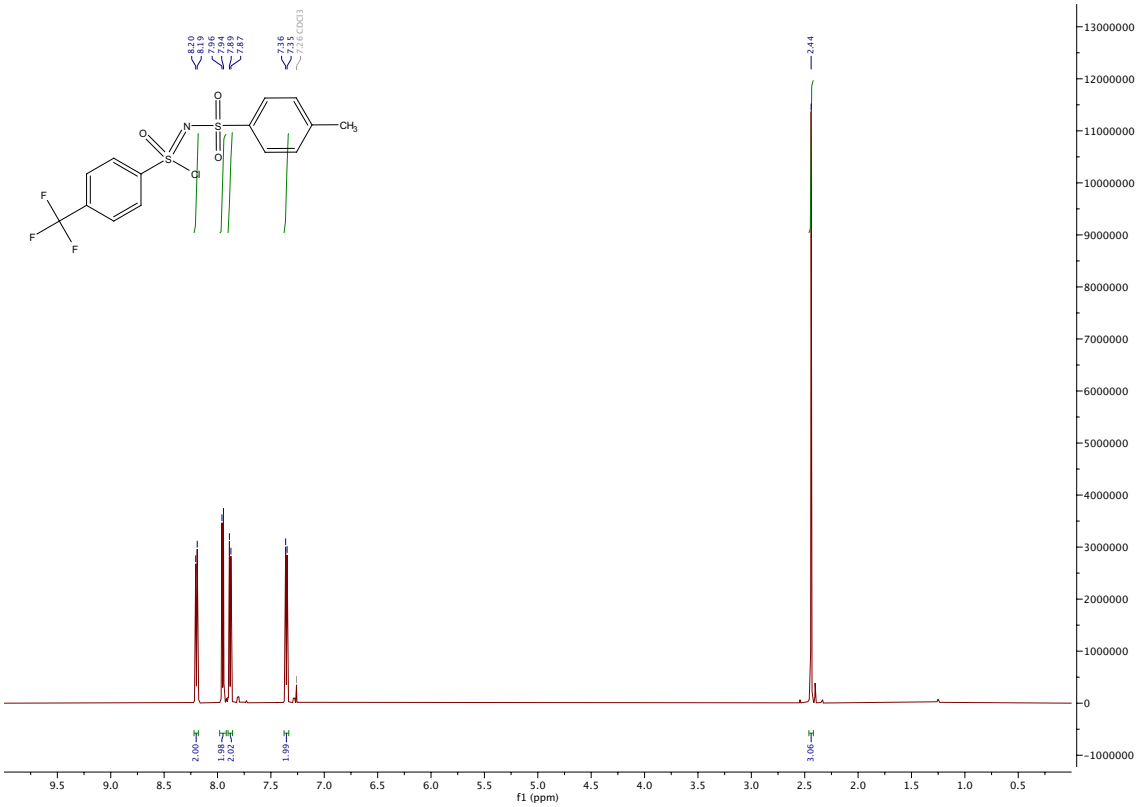

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1b**.

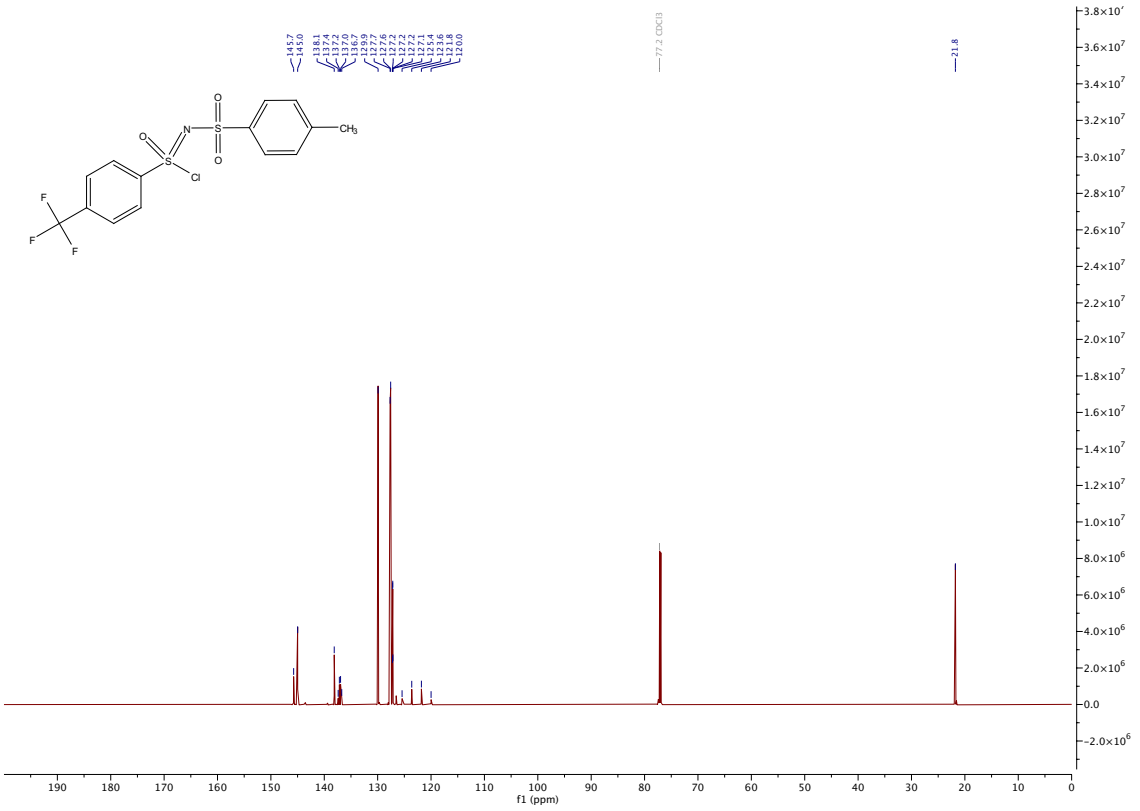

Figure S3. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **1b**.

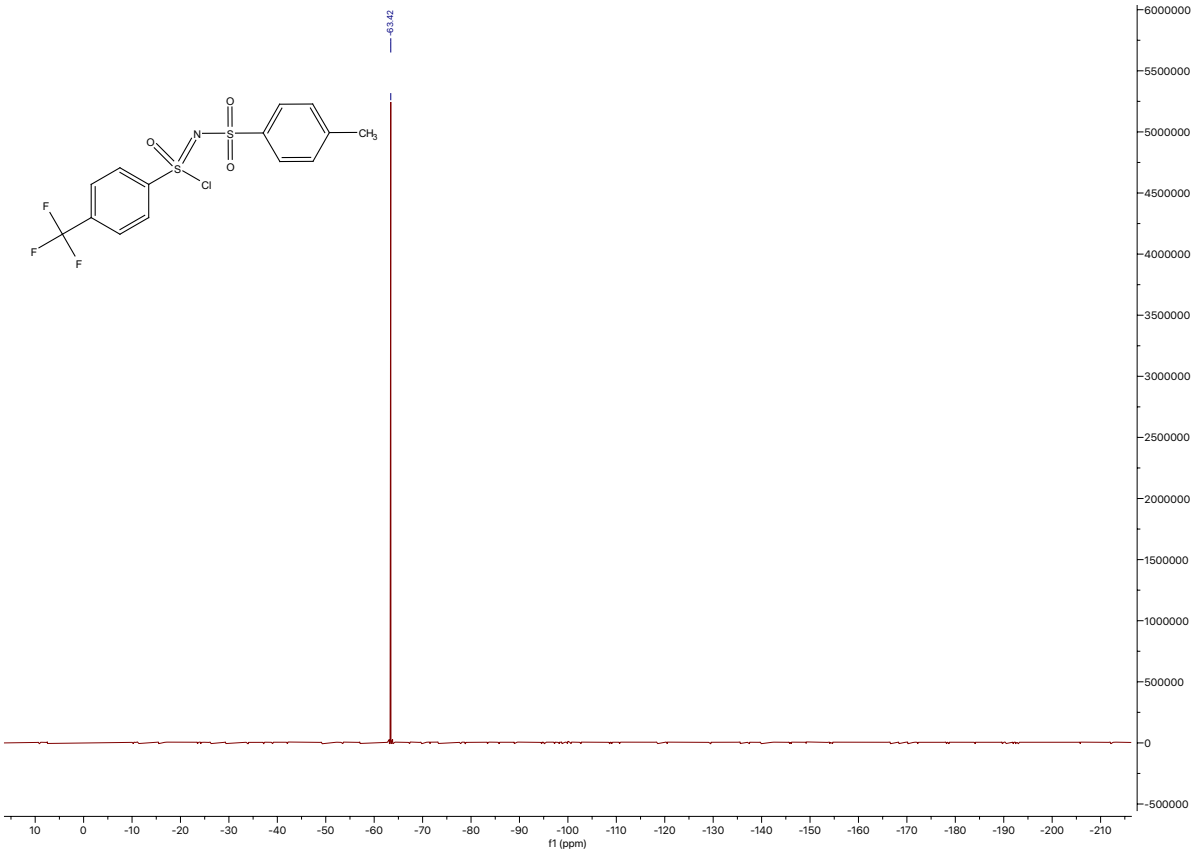

Figure S4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1c**.

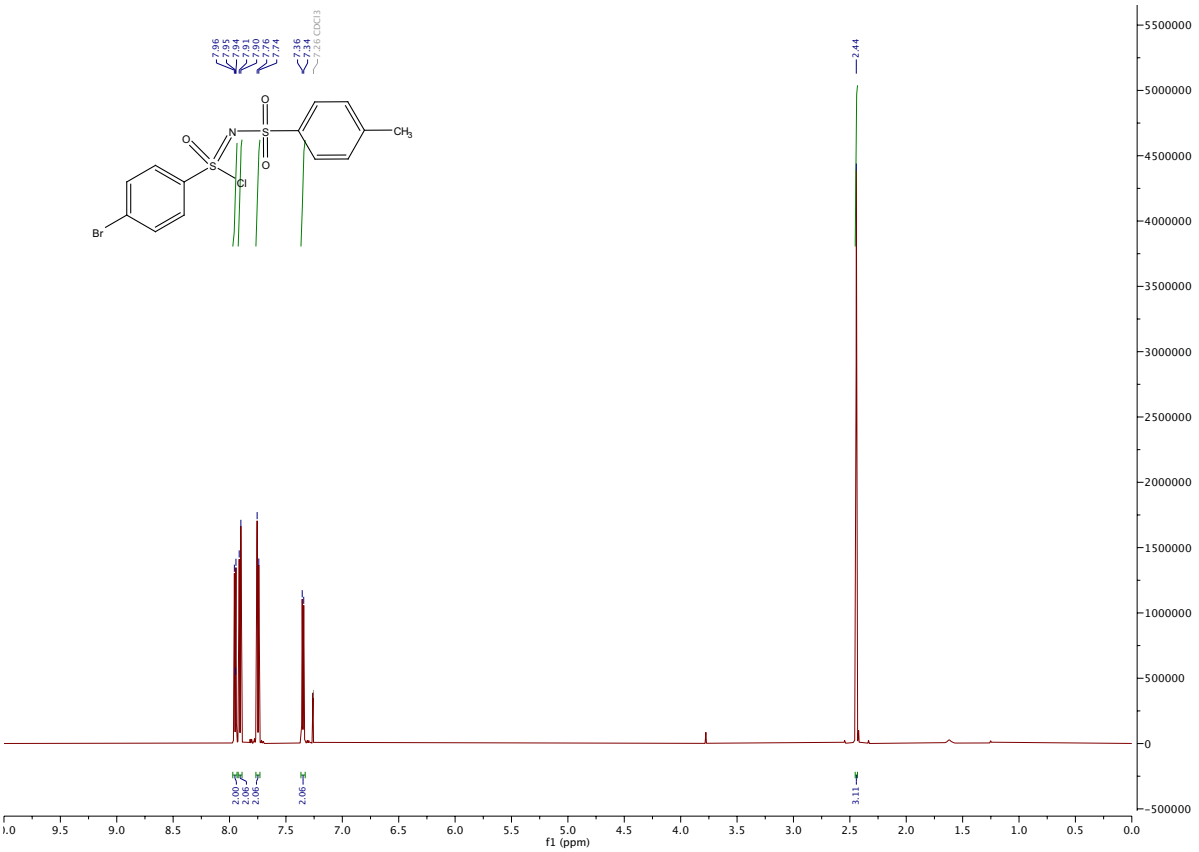

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1c**.

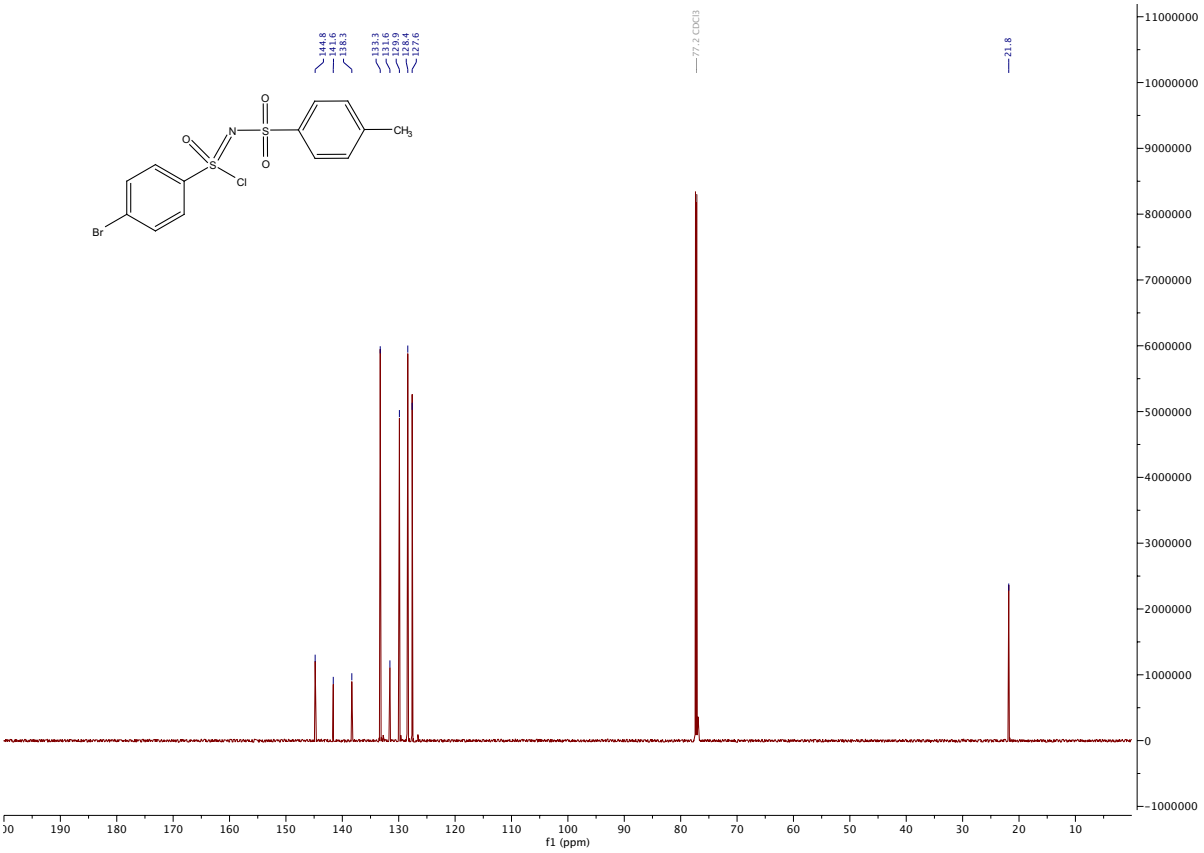

Figure S6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1d**.

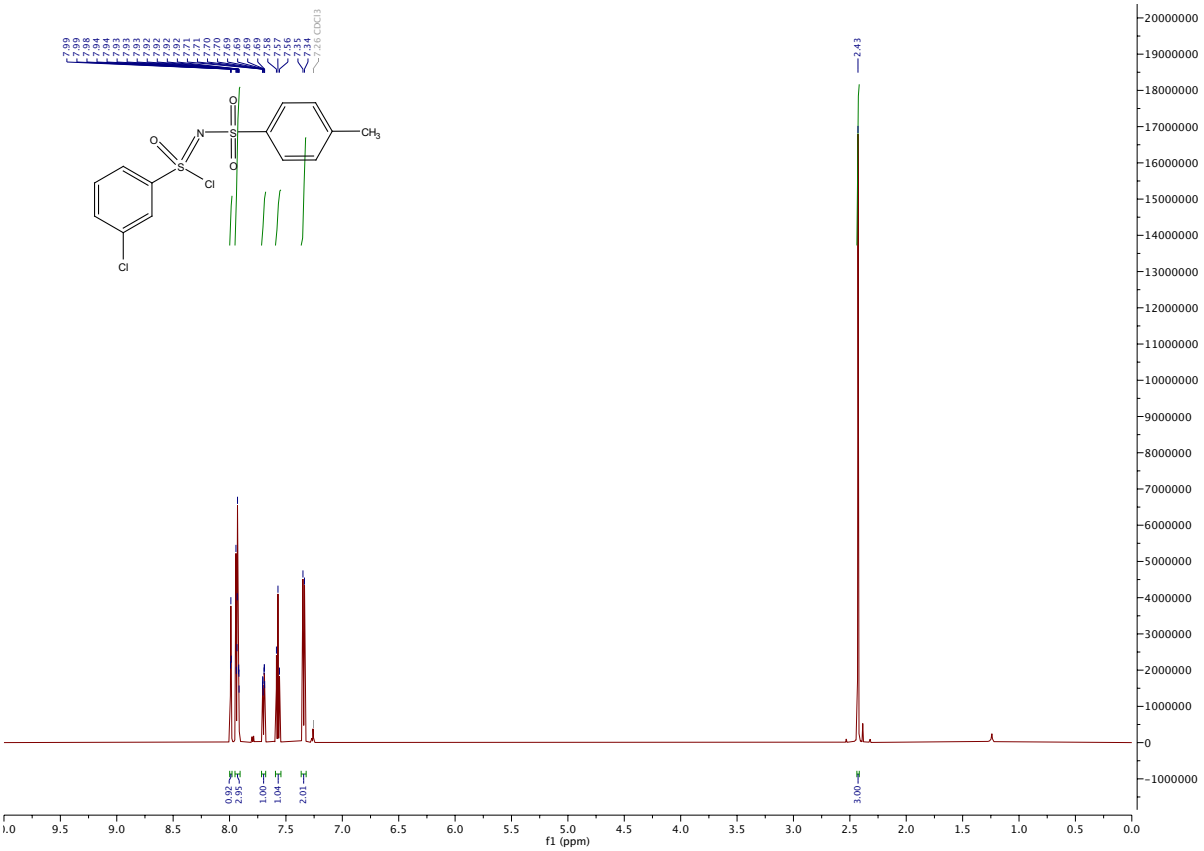

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1d**.

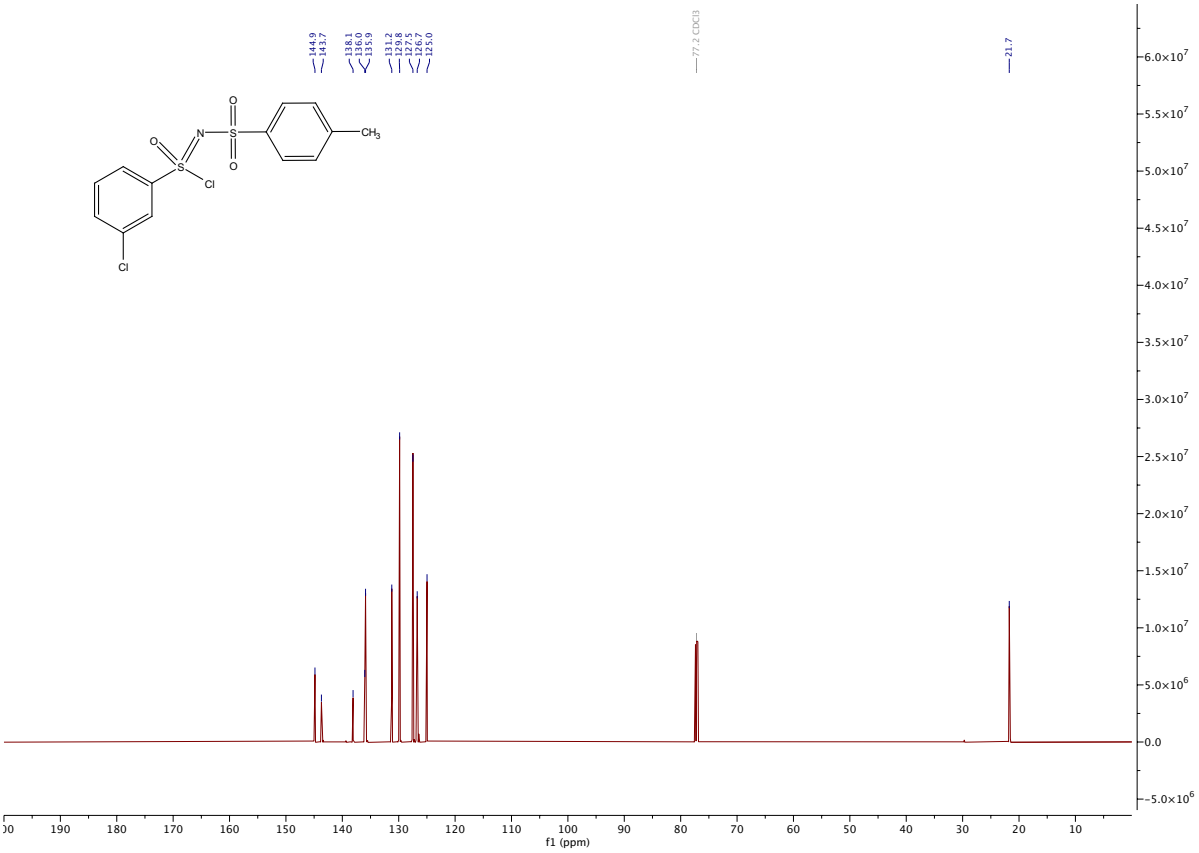

Figure S8. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1e**.

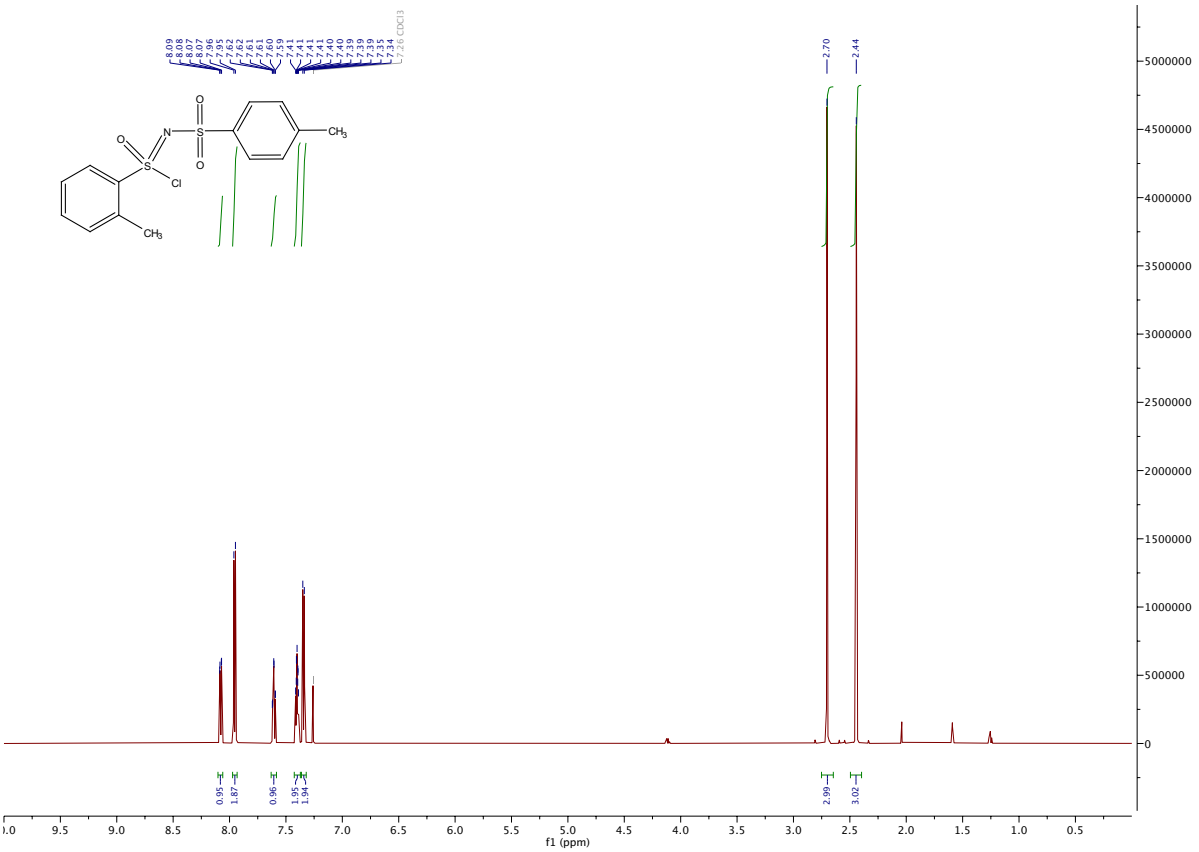

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1e**.

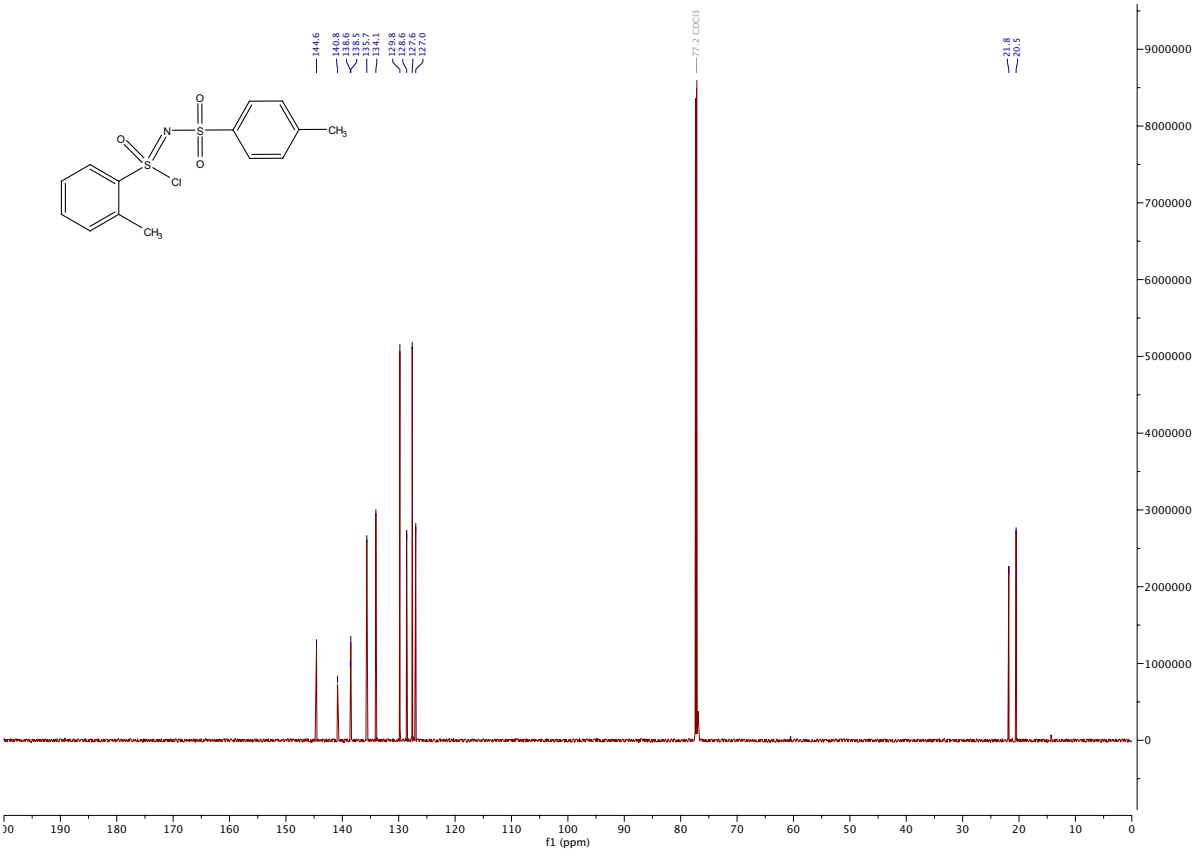

Figure S10. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1f**.

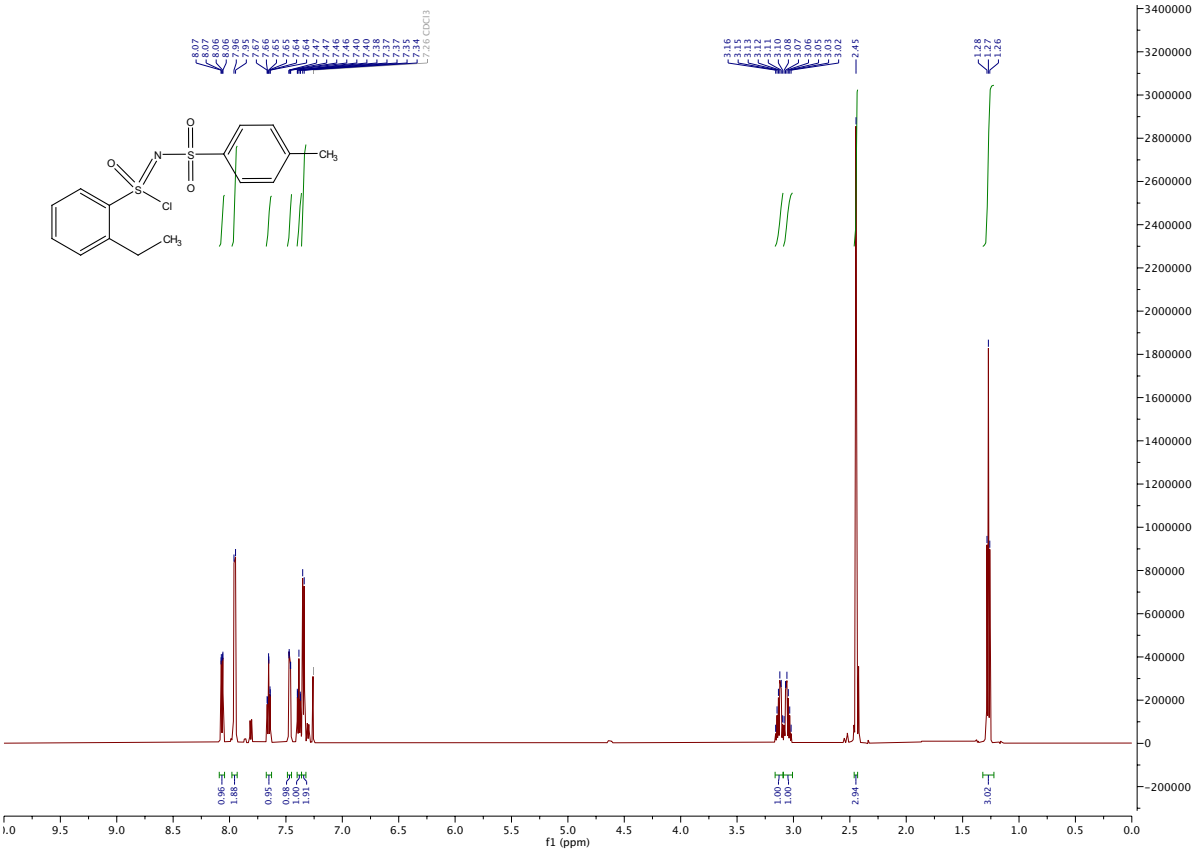

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1f**.

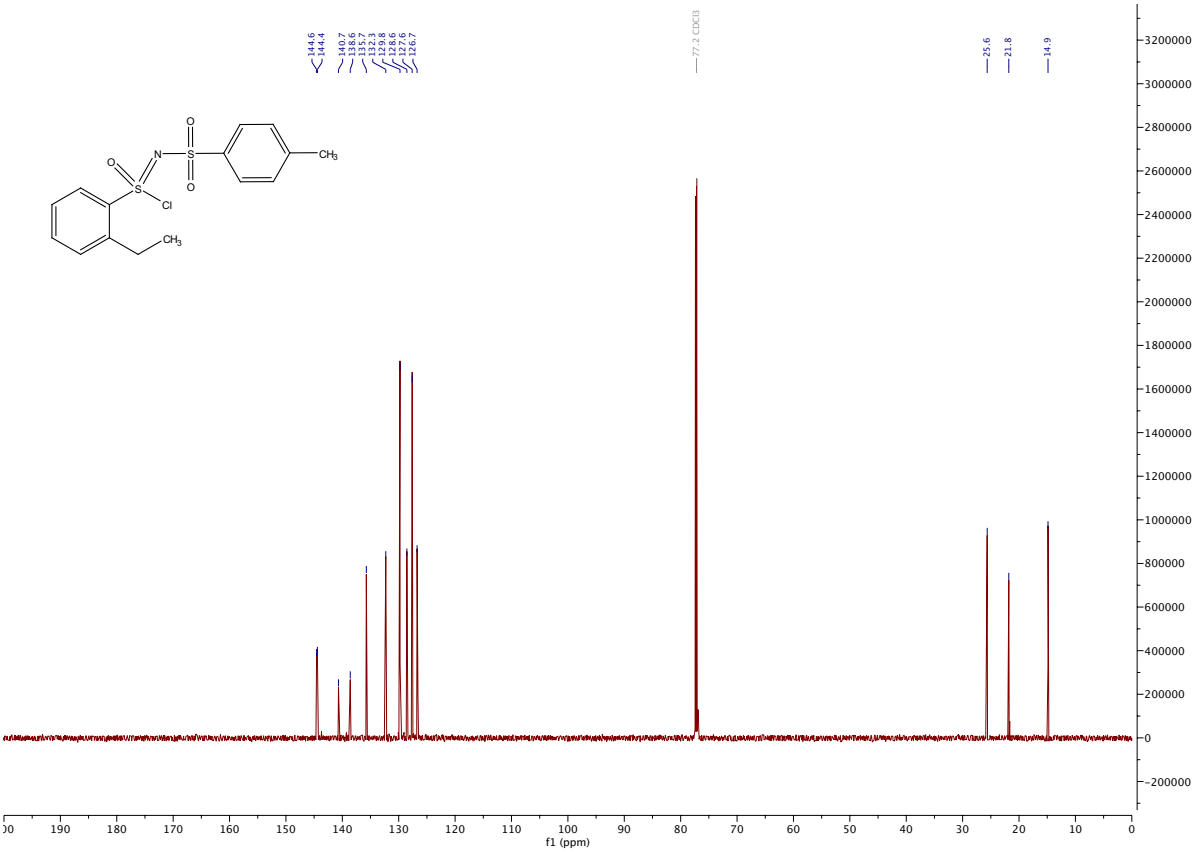

Figure S12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1g**.

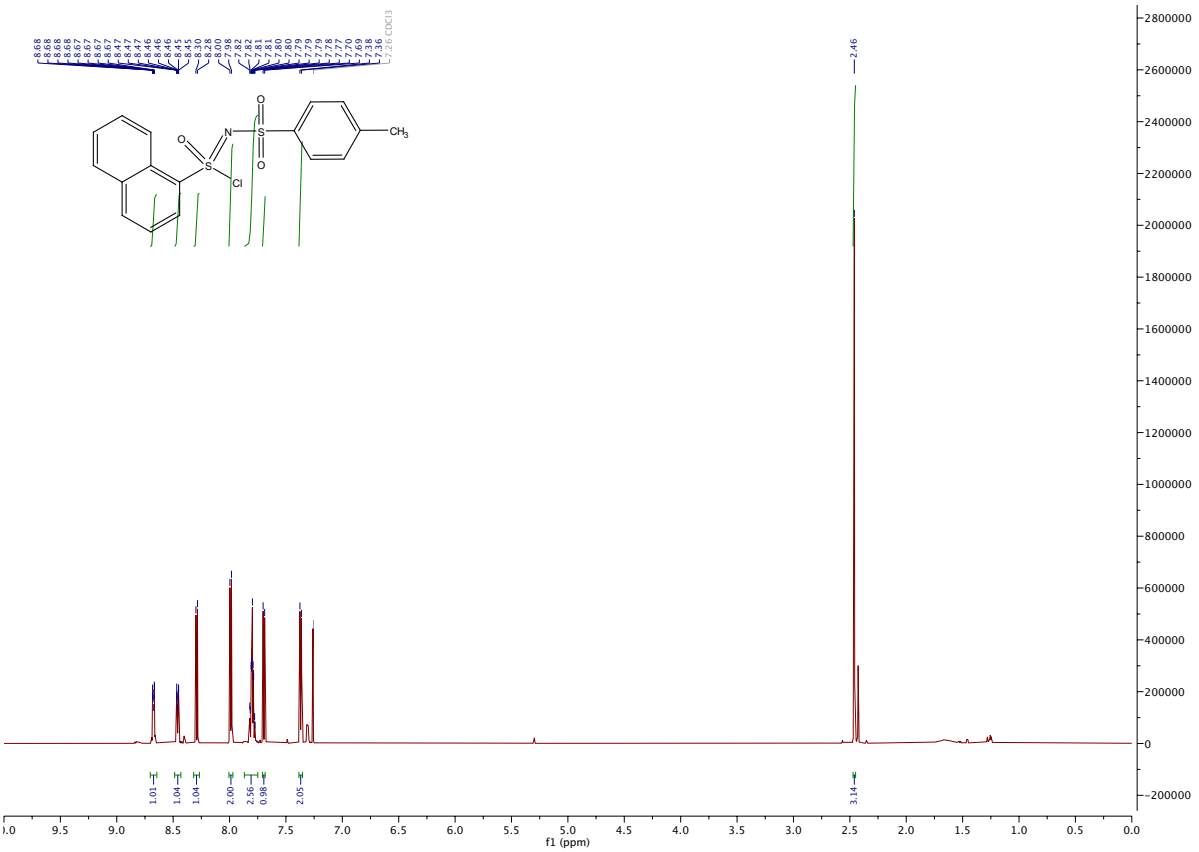

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1g**.

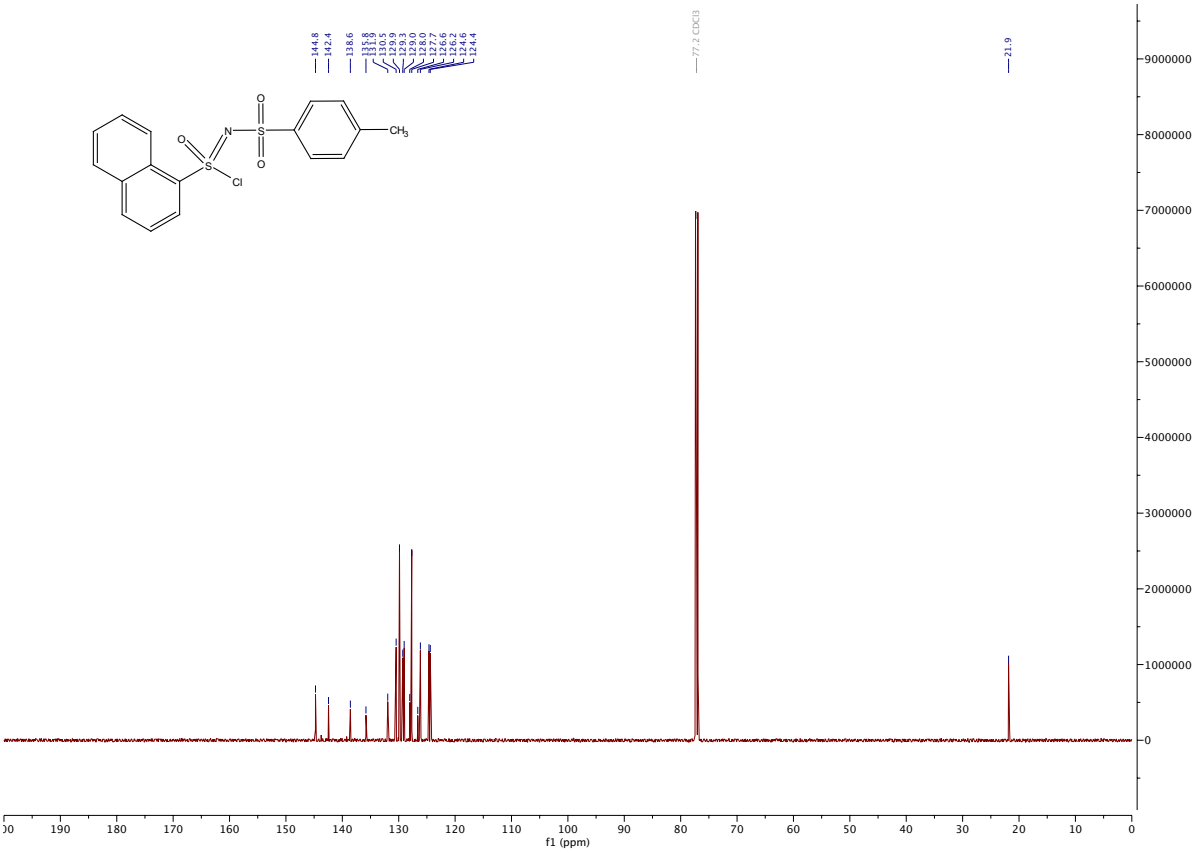

Figure S14. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **1h**.

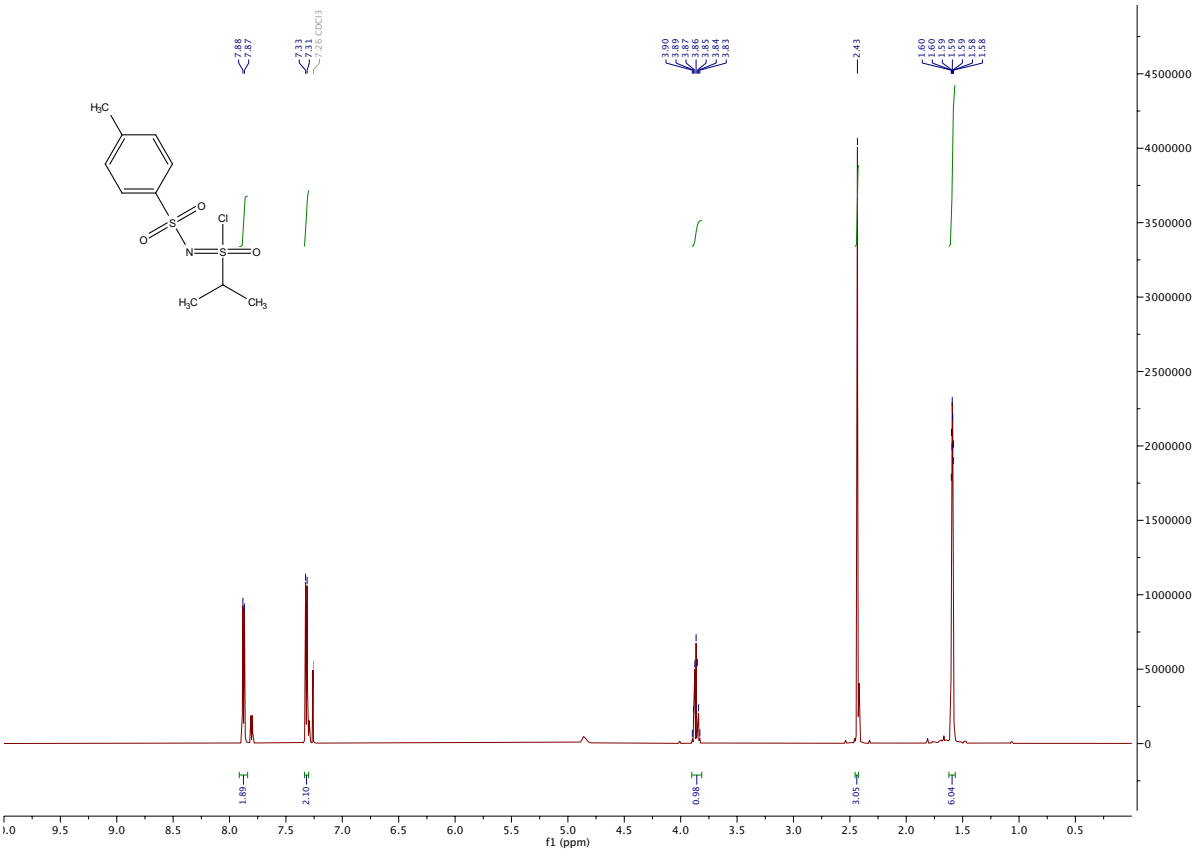

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **1h**.

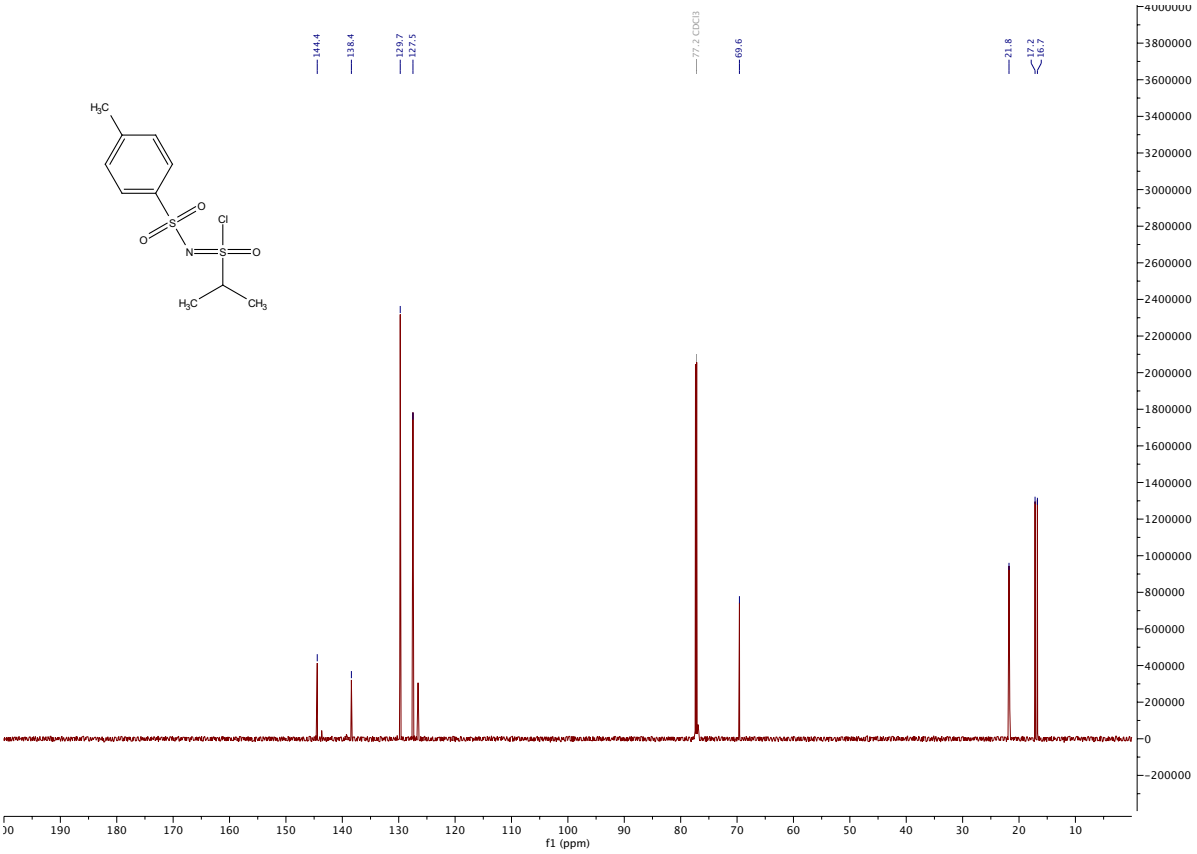

Figure S16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3aa**.

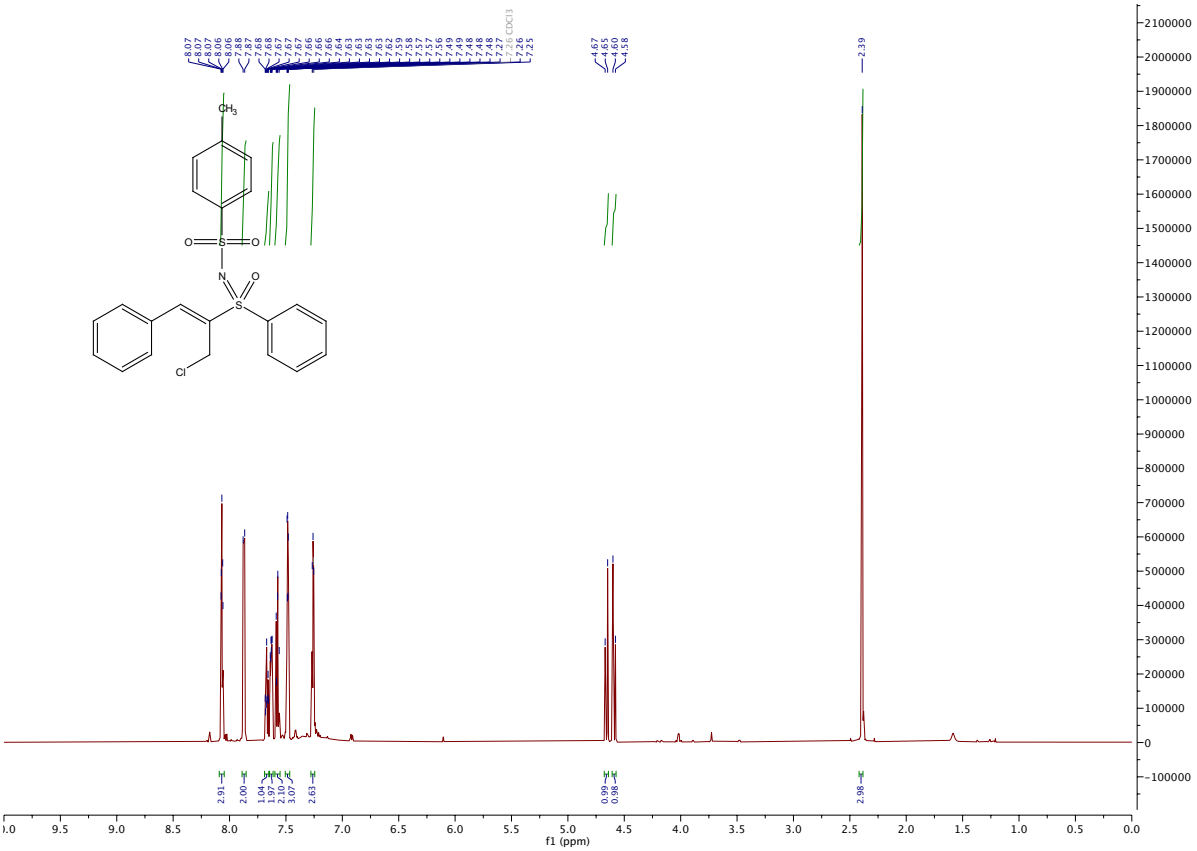

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3aa**.

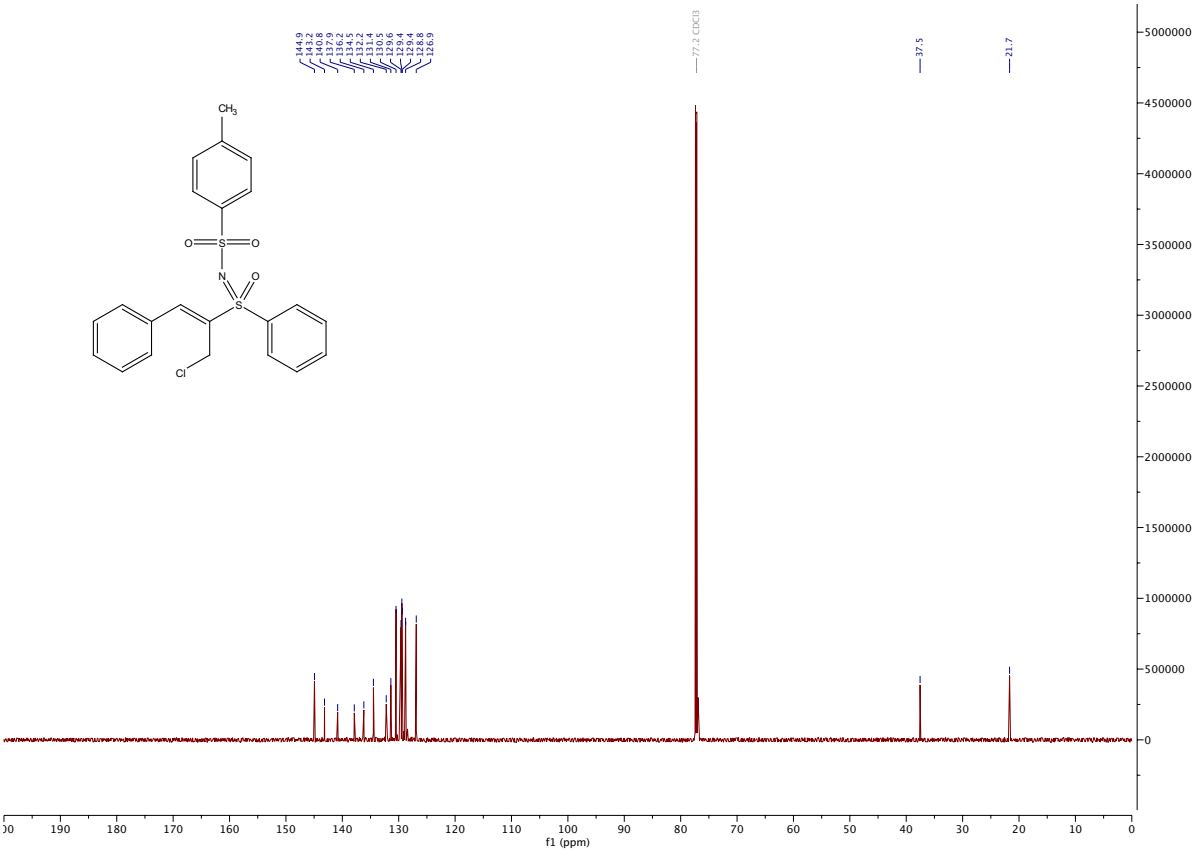

Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ba**.

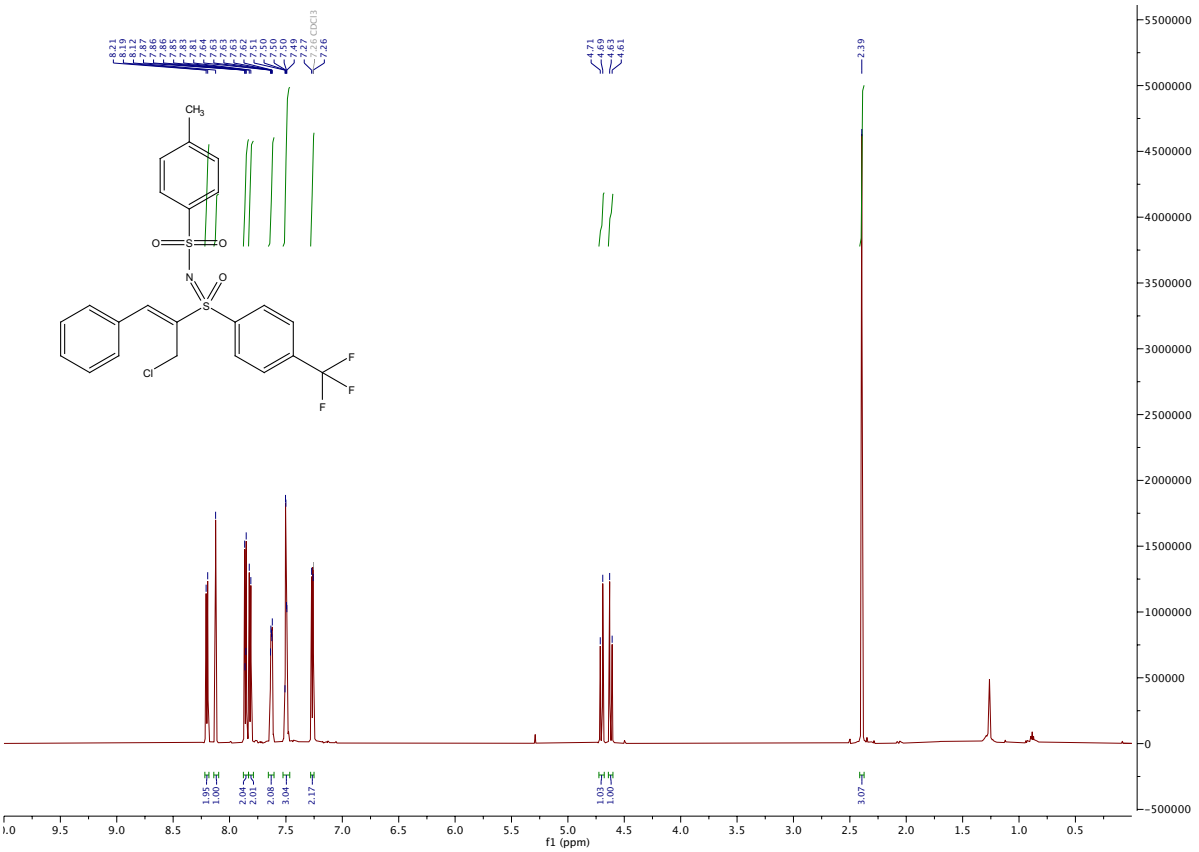

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ba**.

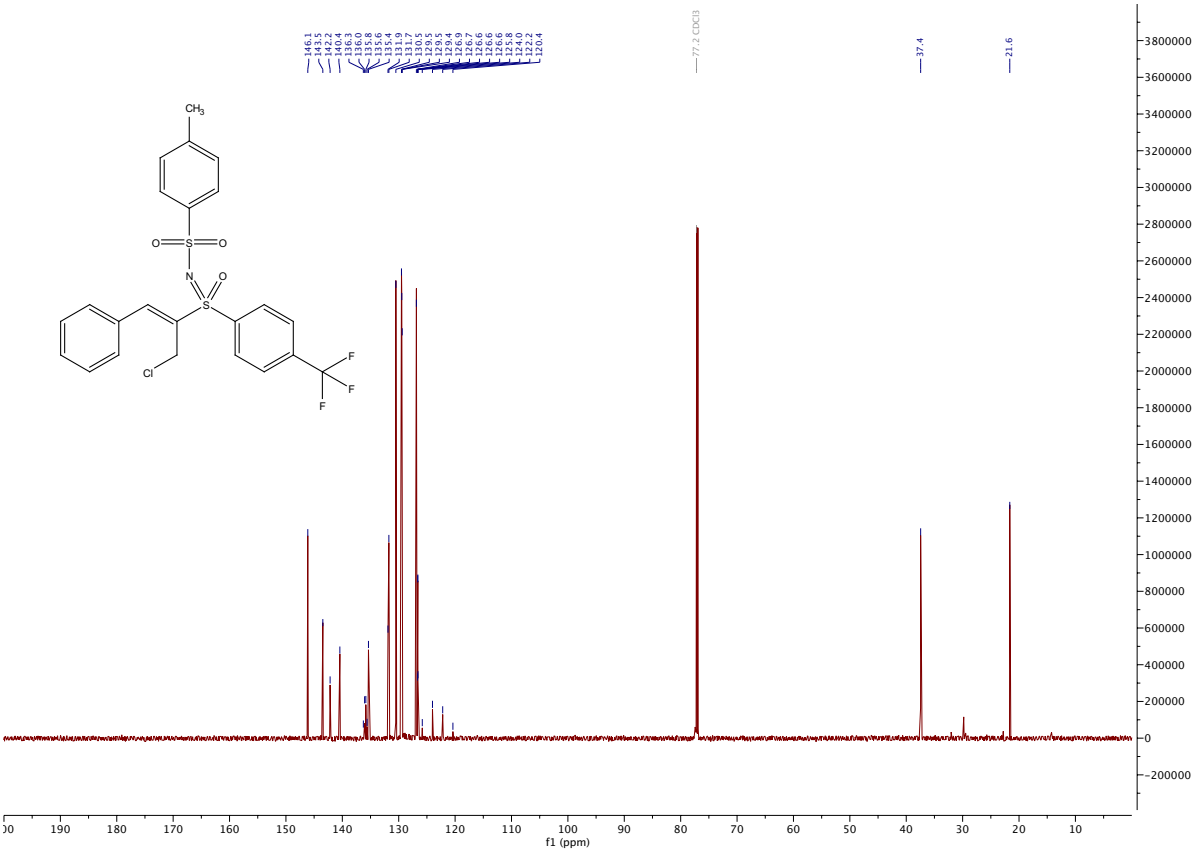

Figure S20. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **3ba**.

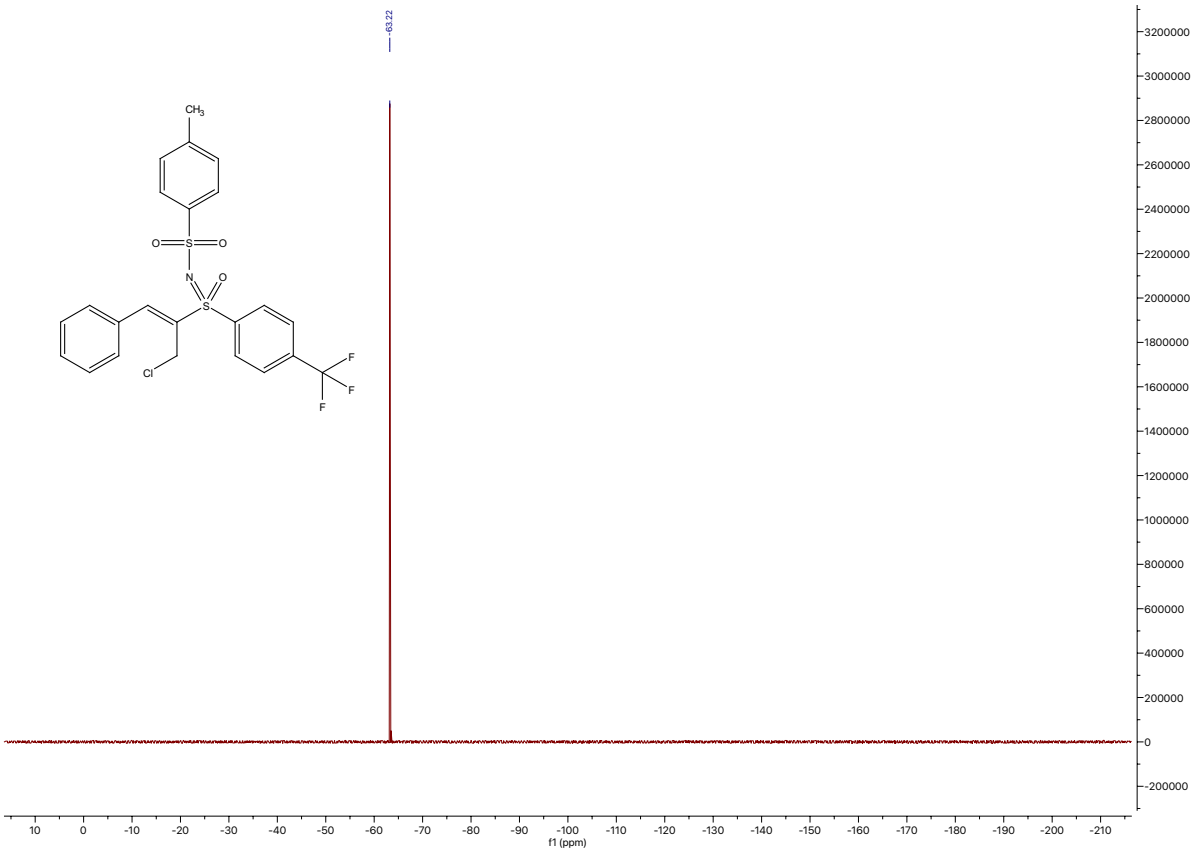

Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ca**.

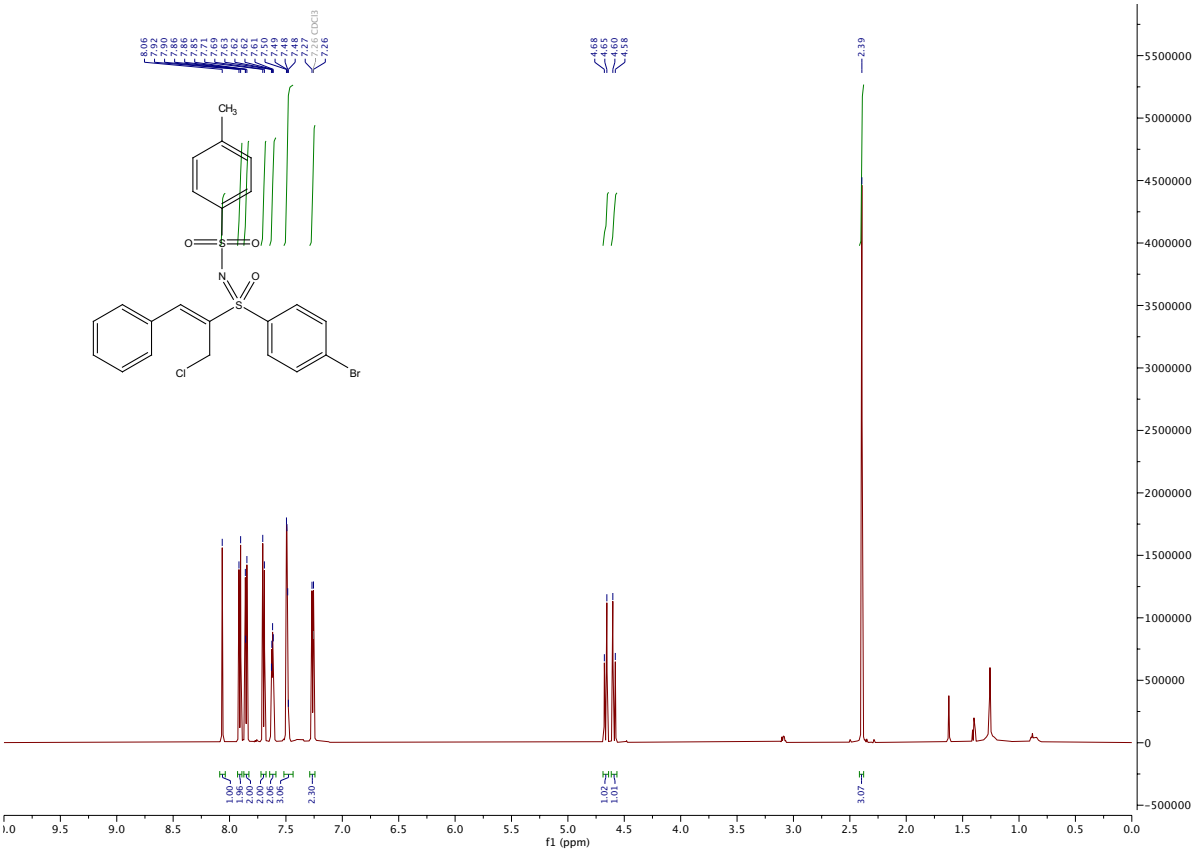

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ca**.

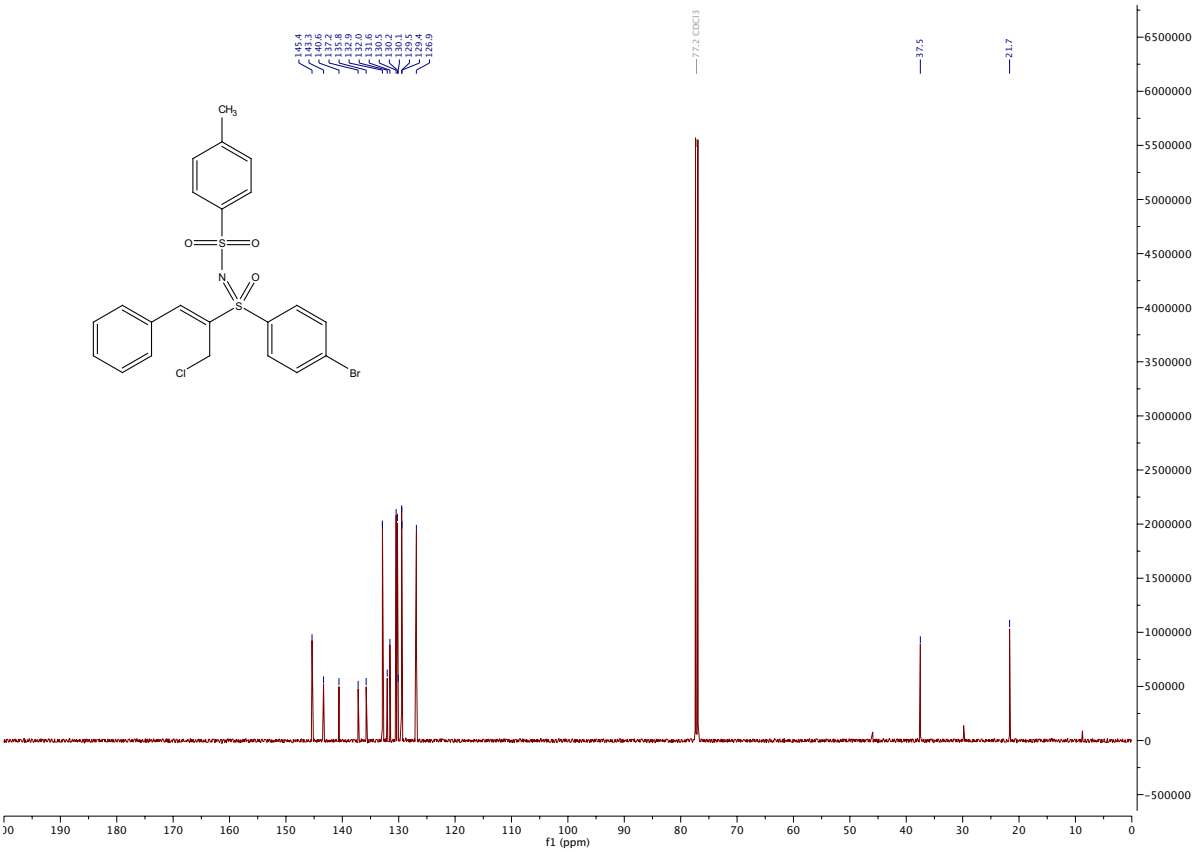

Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3da**.

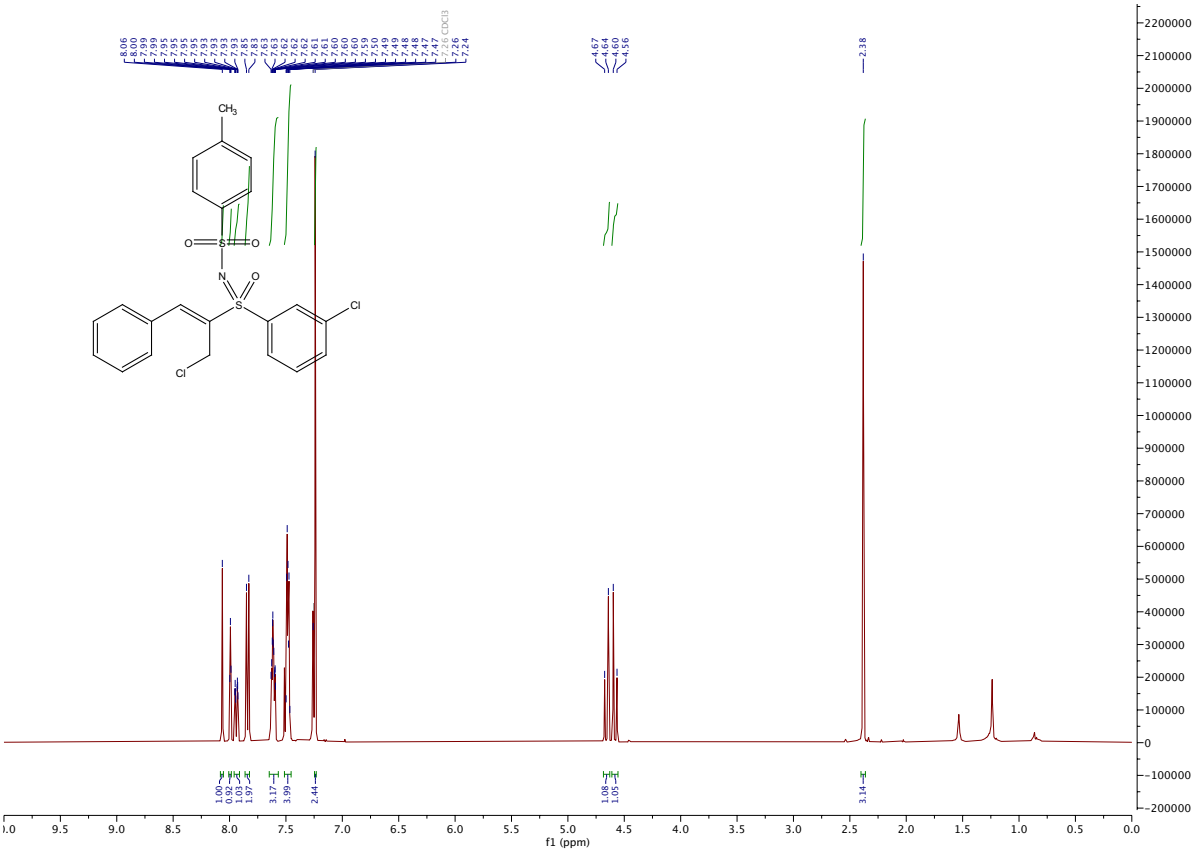

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3da**.

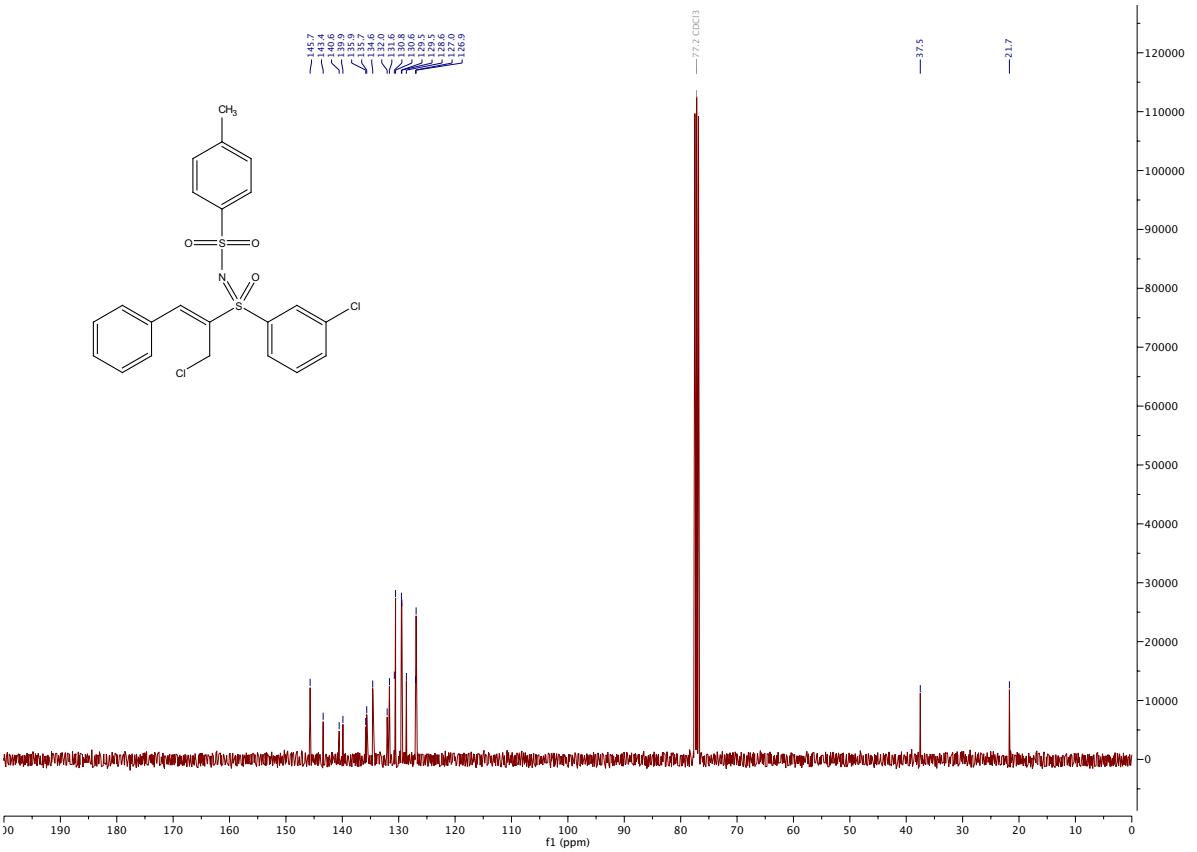

Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ea**.

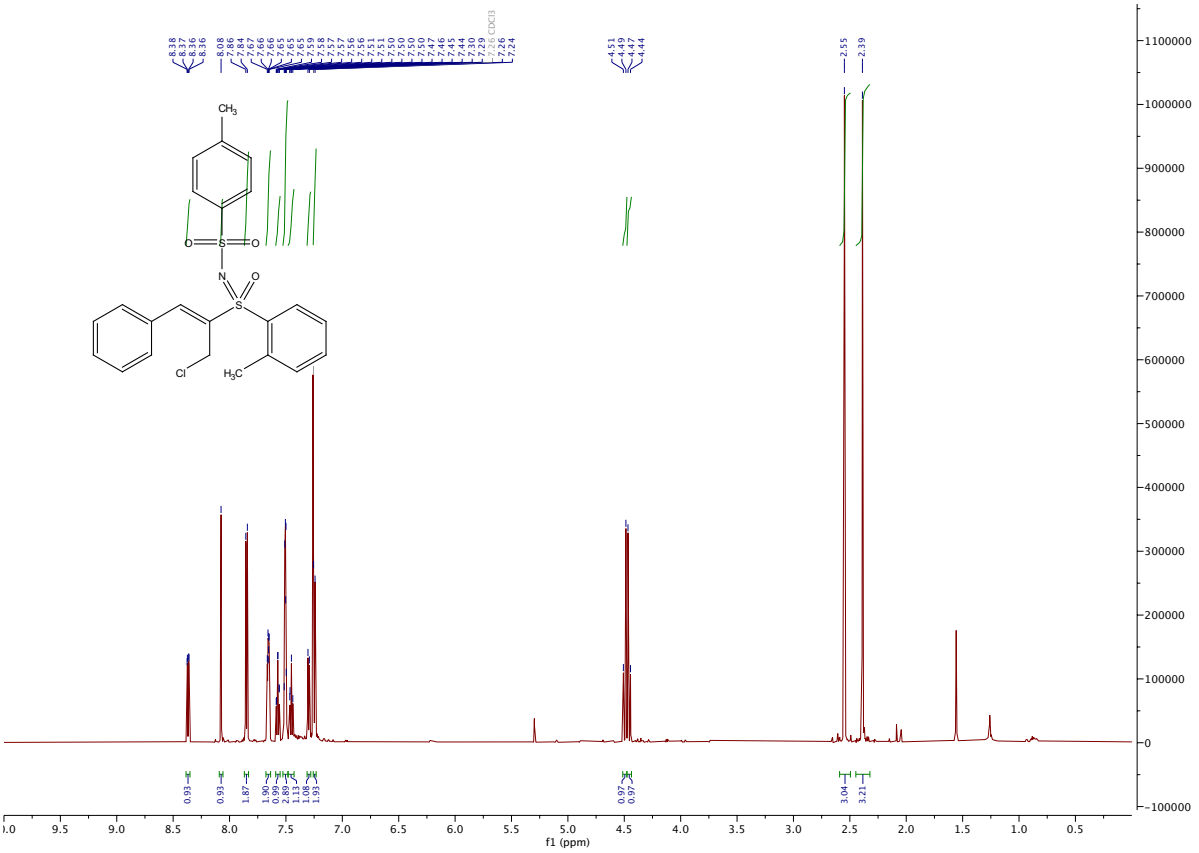

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ea**.

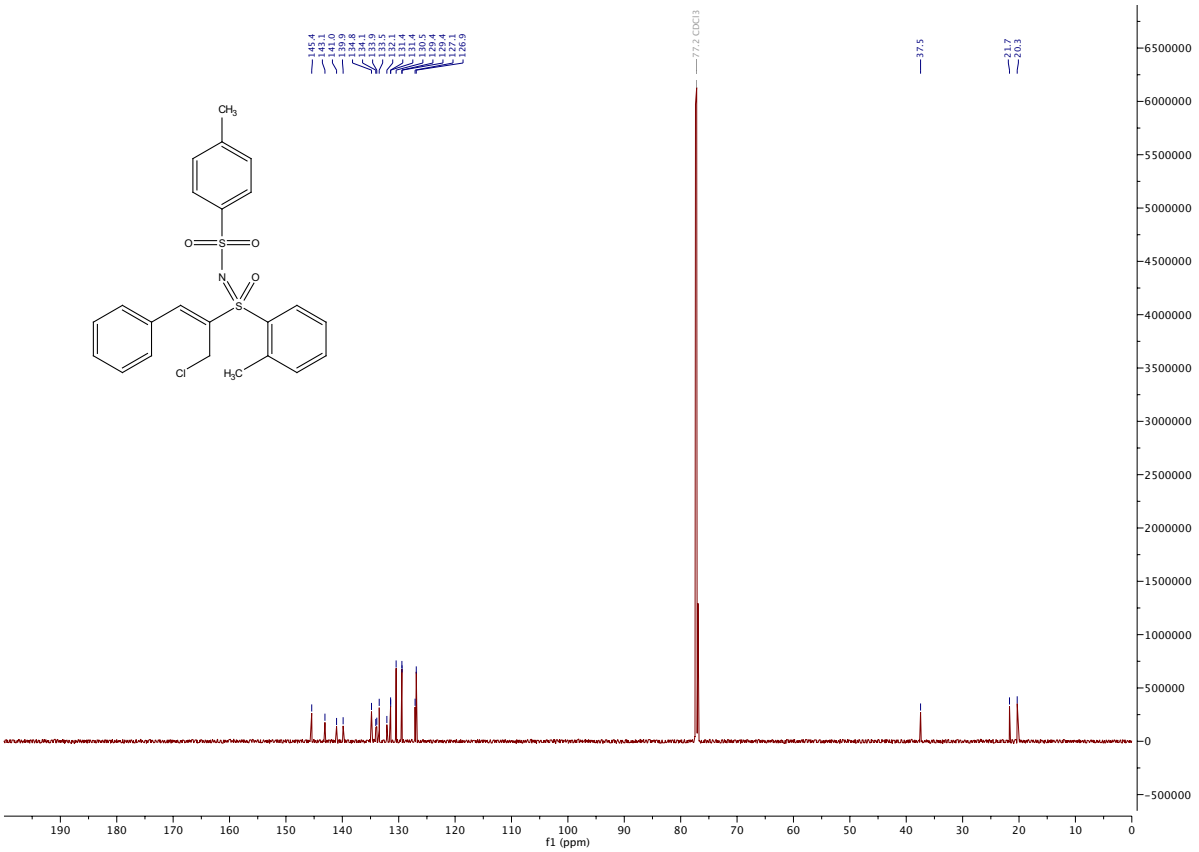

Figure S27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3fa**.

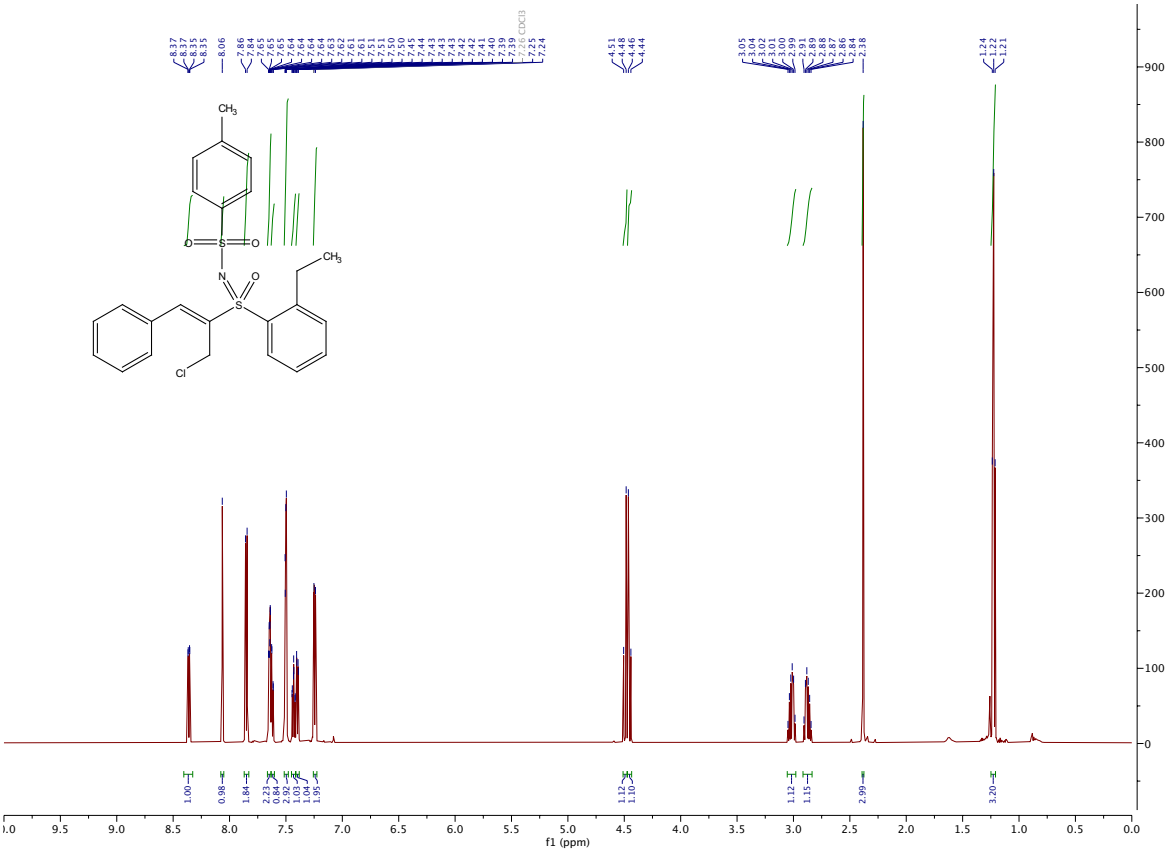

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3fa**.

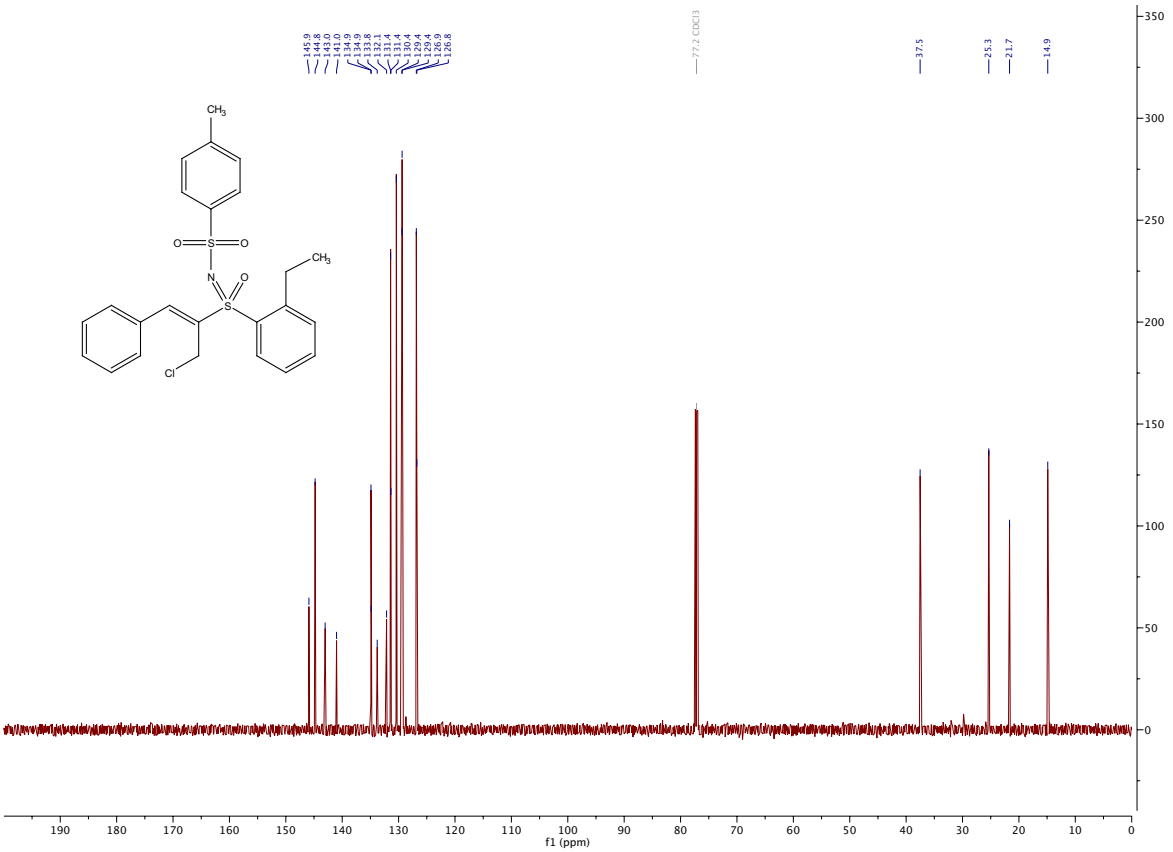

Figure S29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ga**.

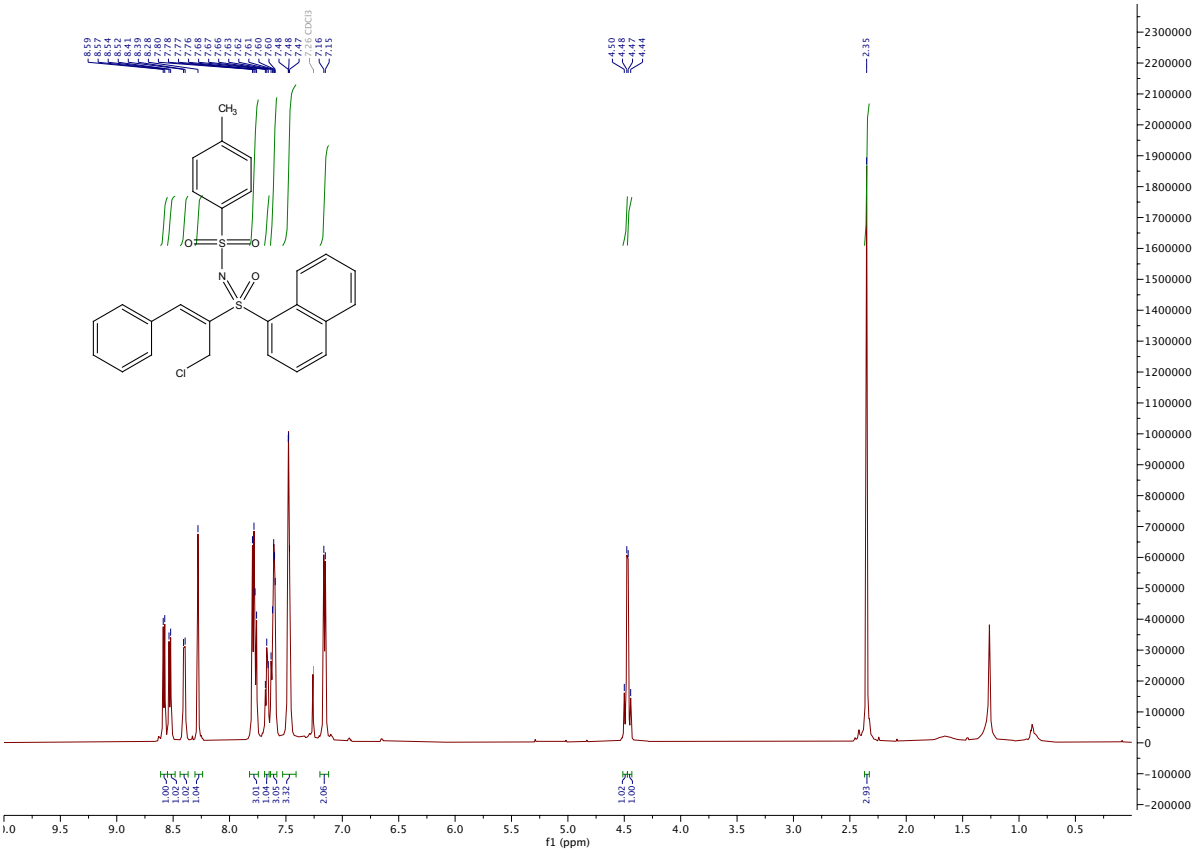

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ga**.

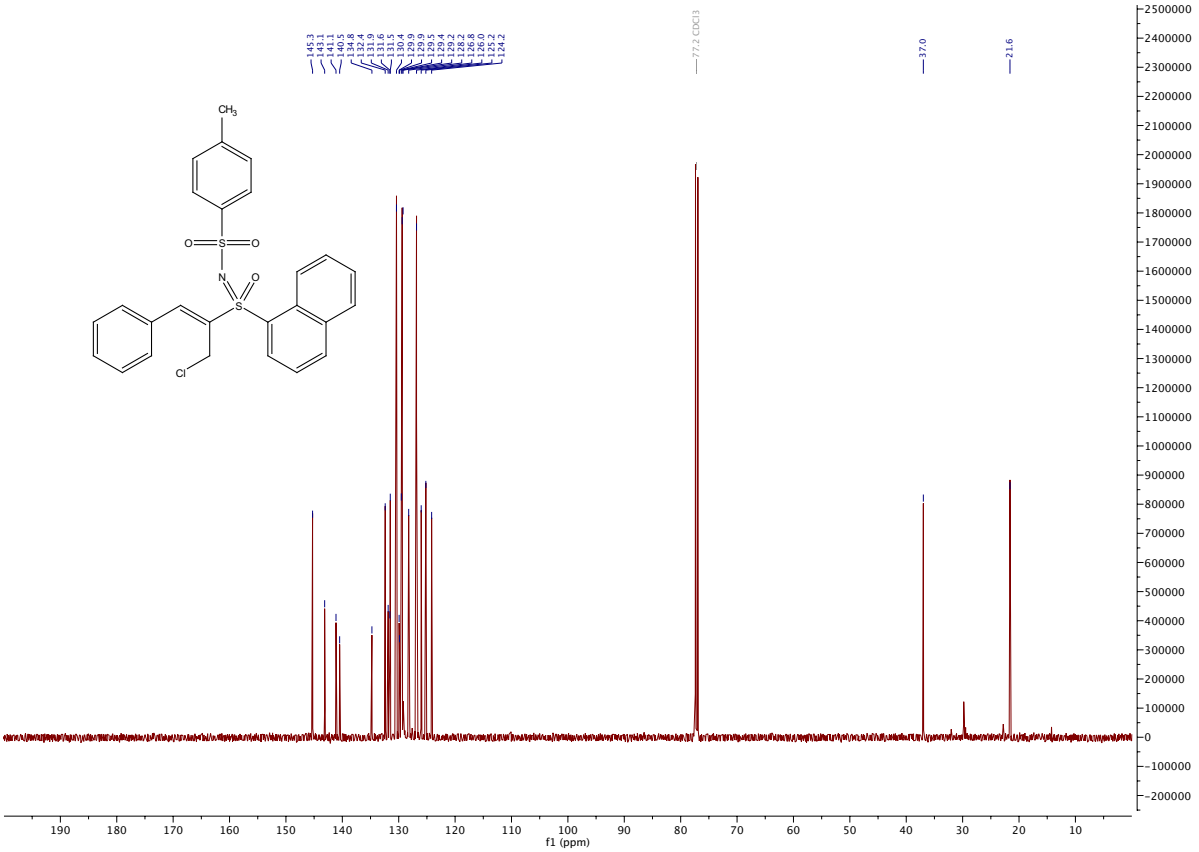

Figure S31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ha.**

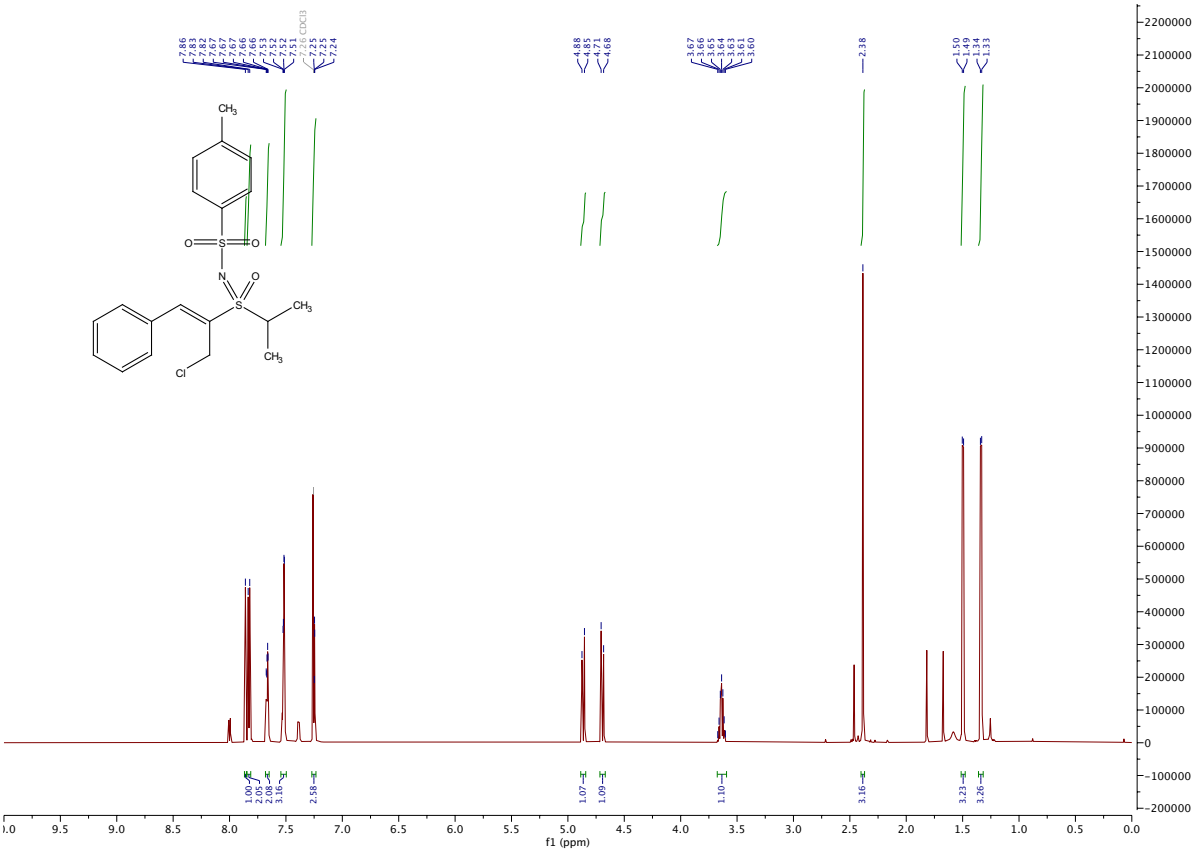

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ha**.

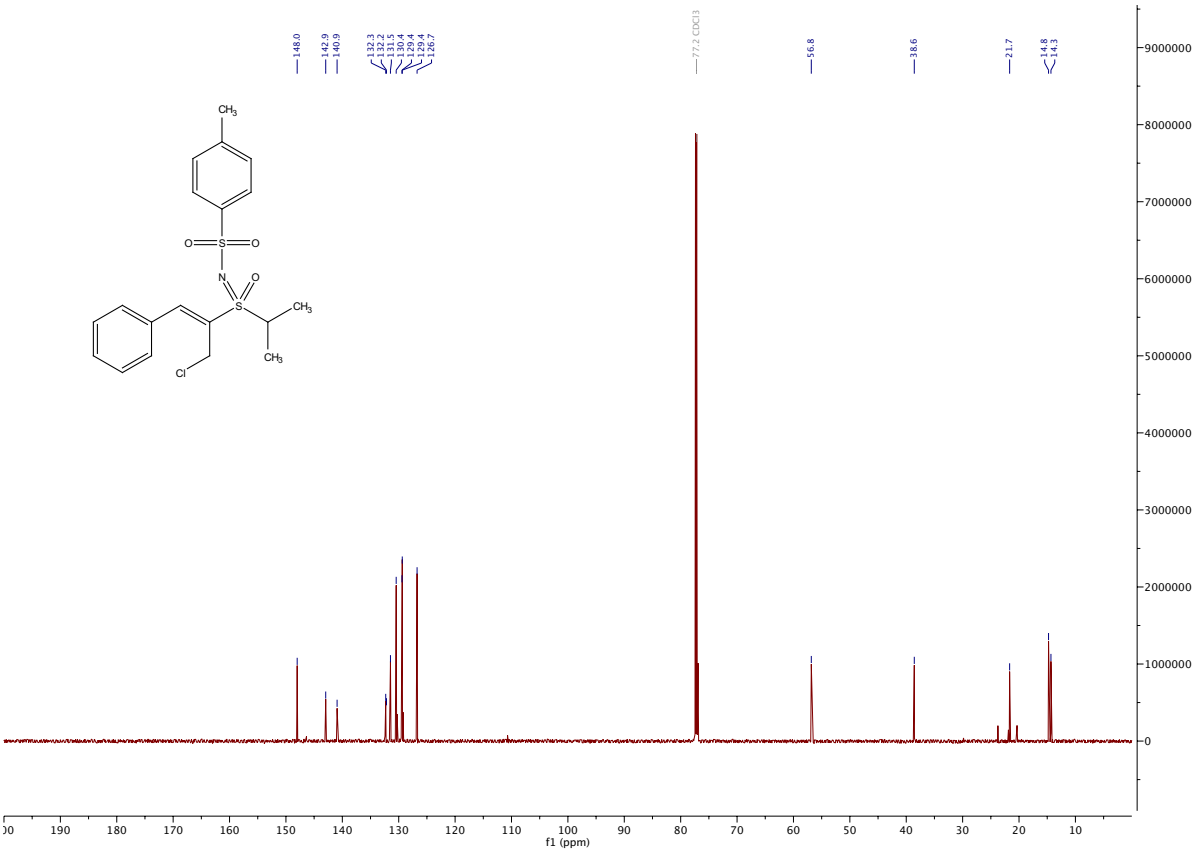

Figure S33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3cb**.

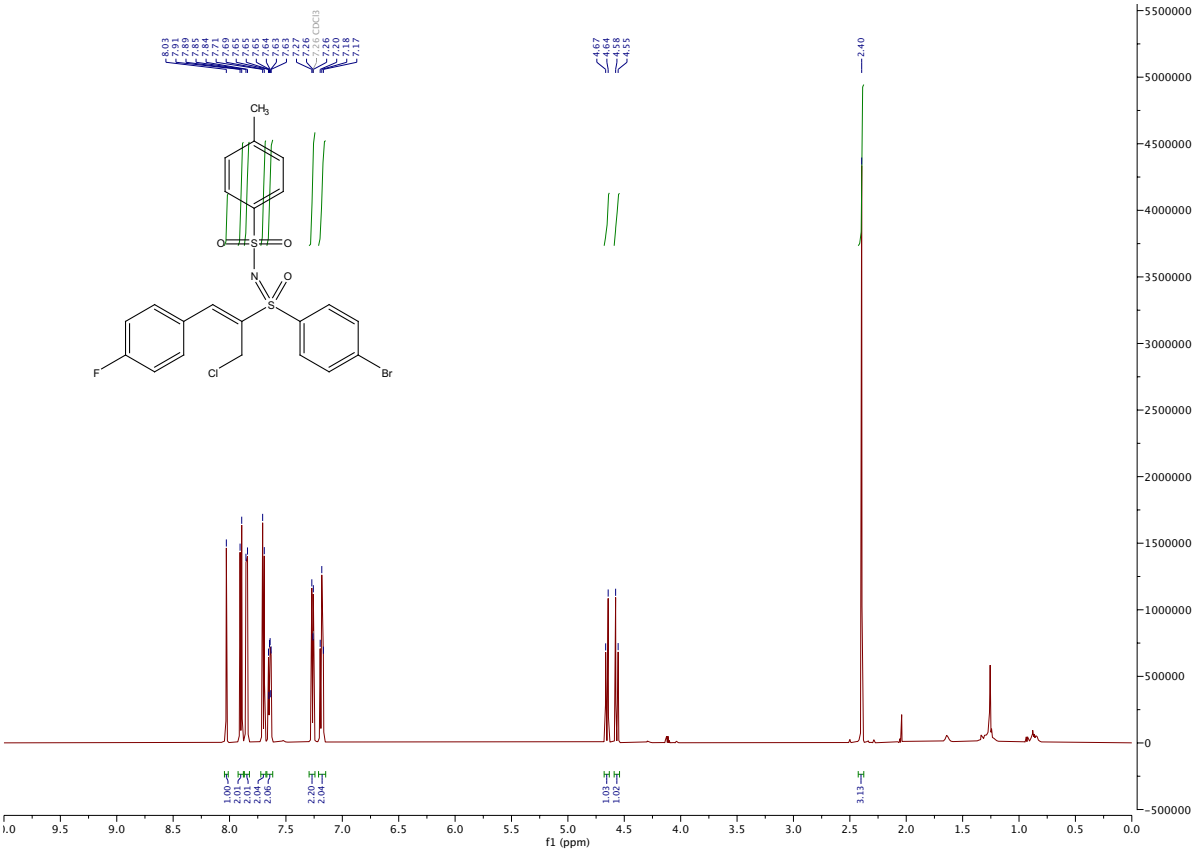

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3cb**.

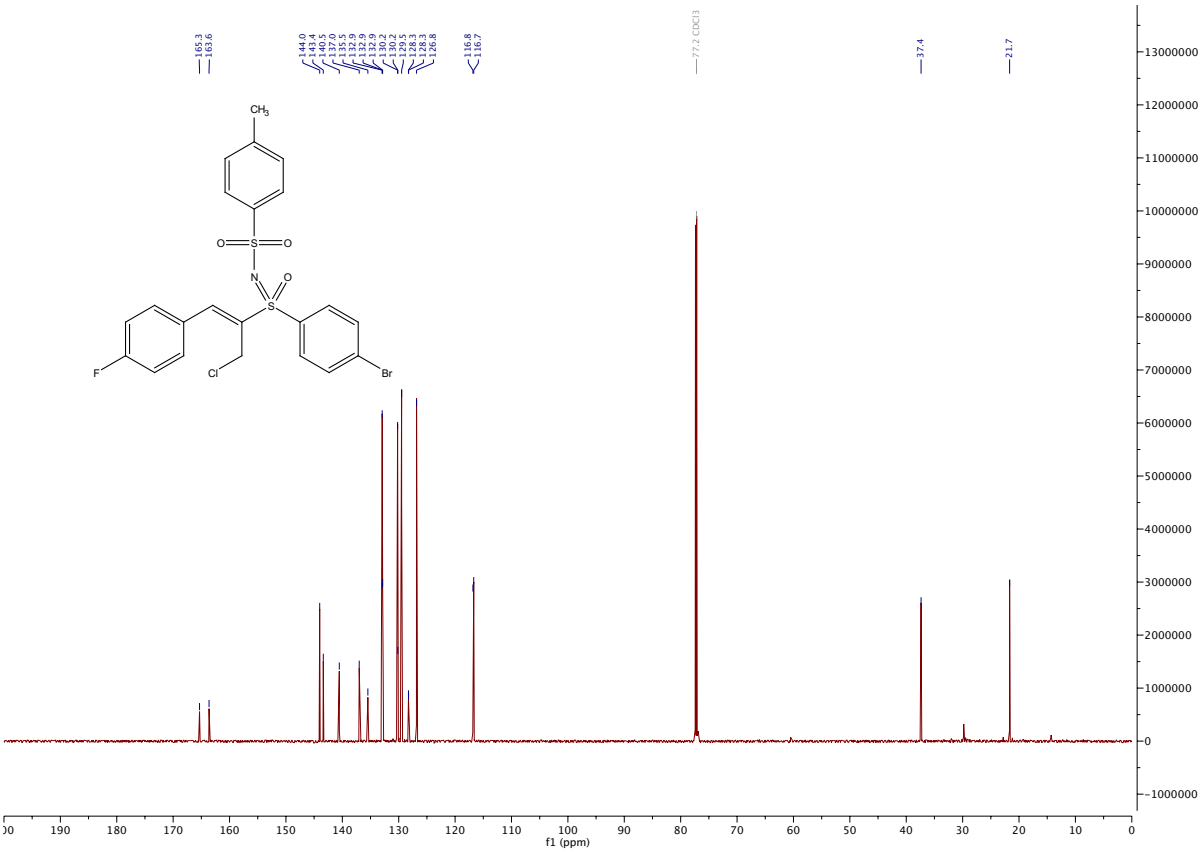

Figure S35. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **3cb**.

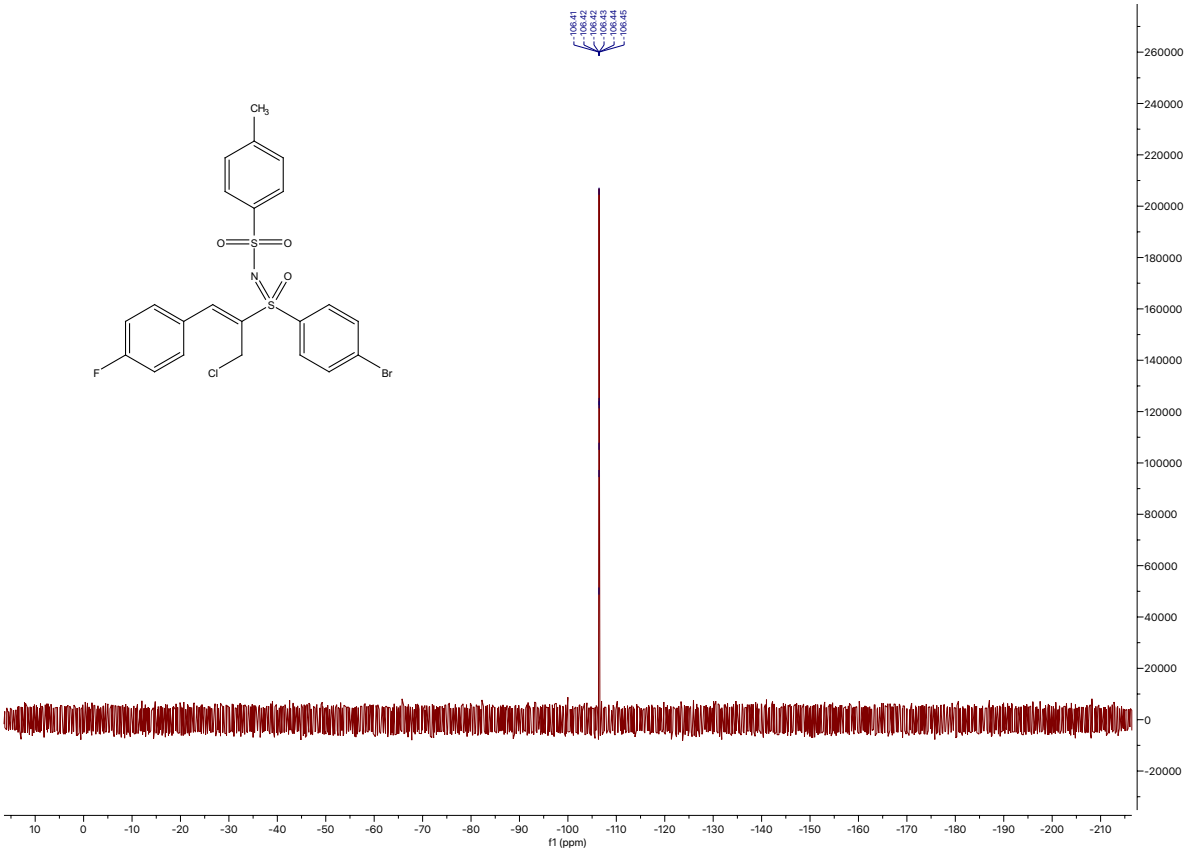

Figure S36. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3cc**.

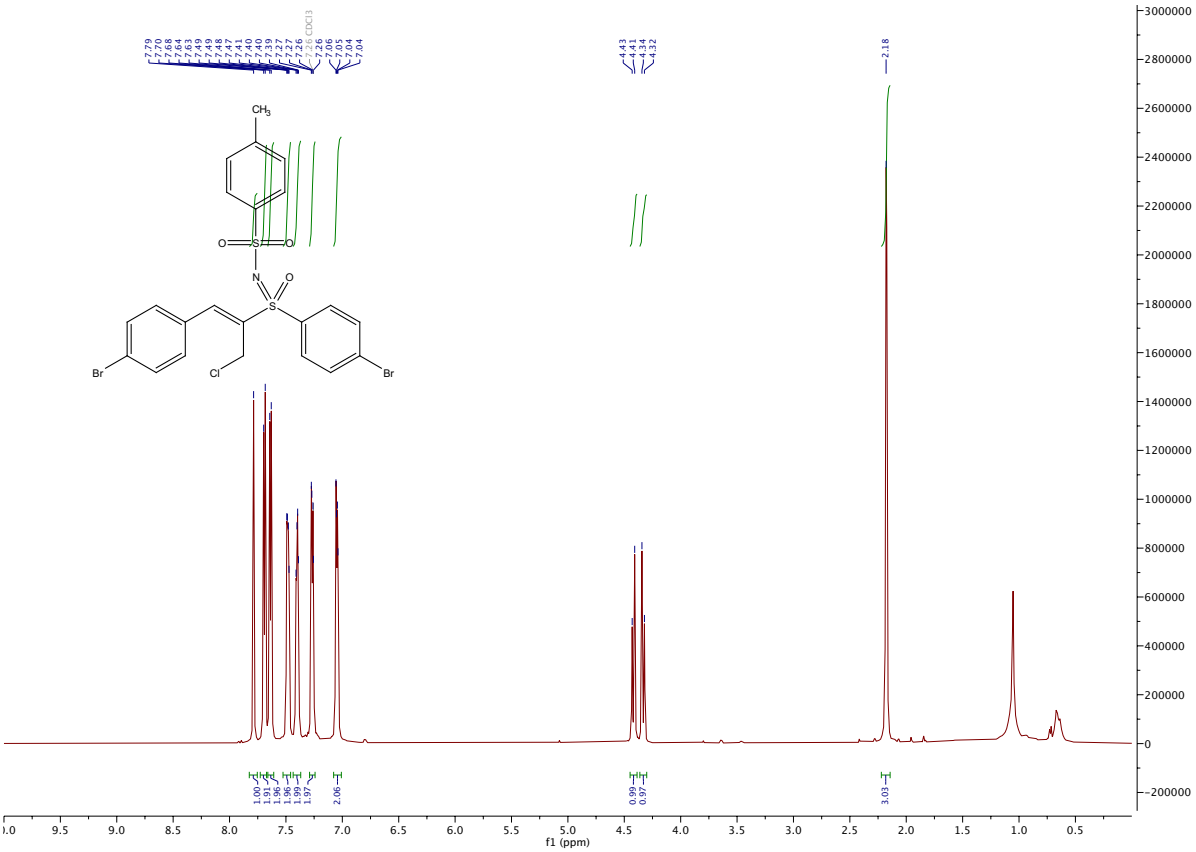

Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3cc**.

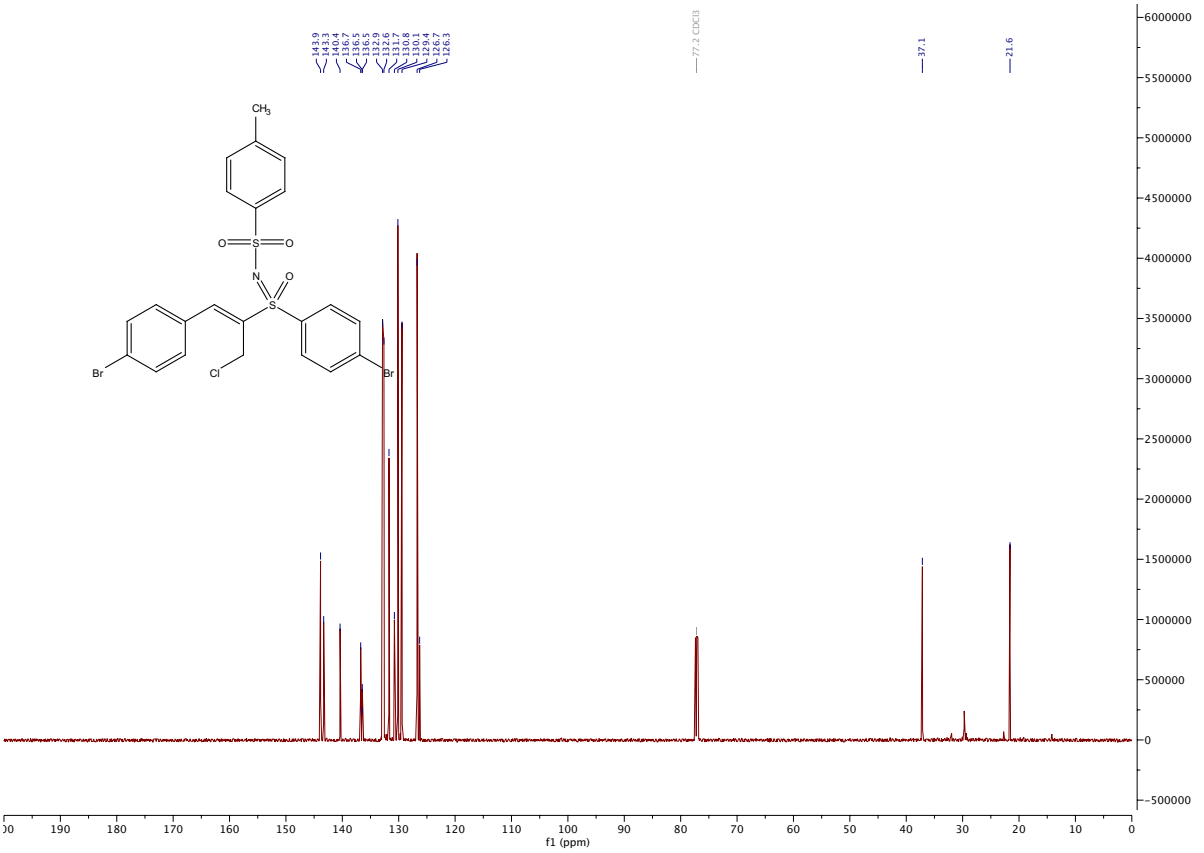

Figure S38. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3cd**.

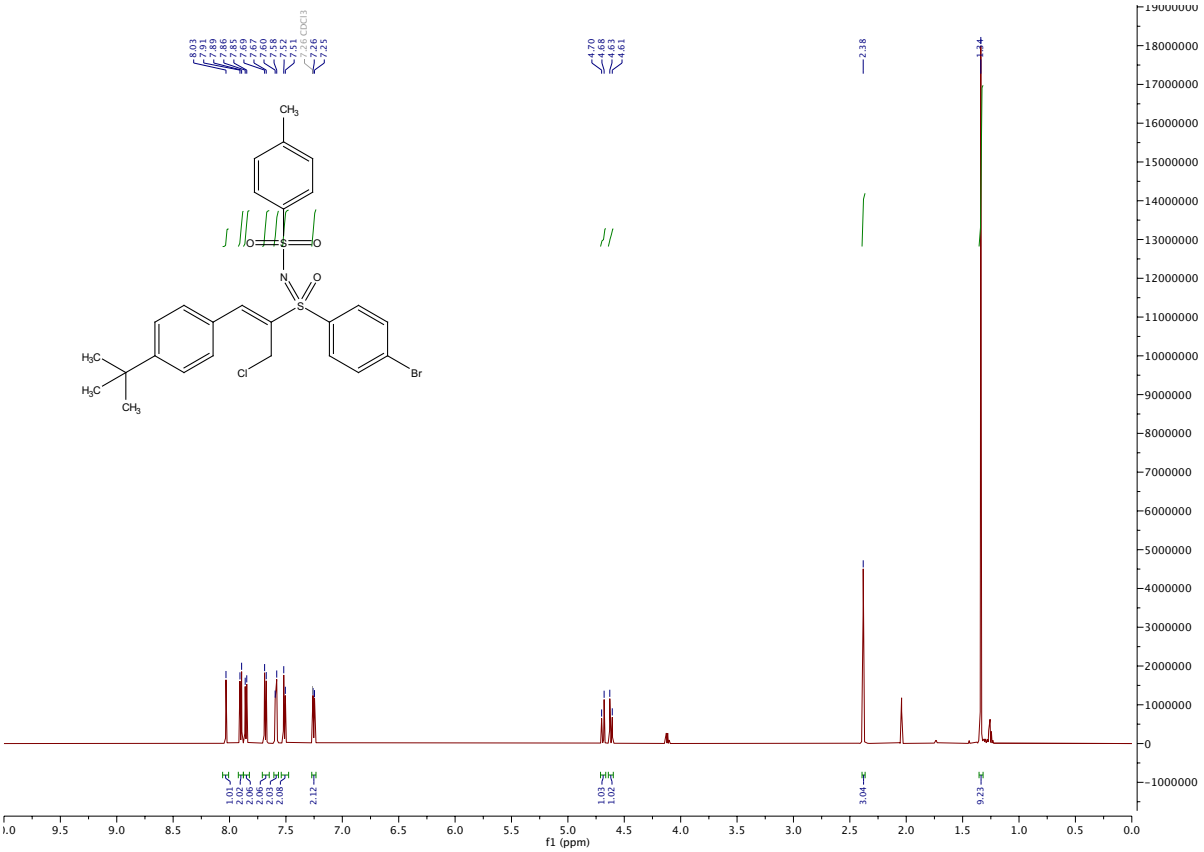

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3cd**.

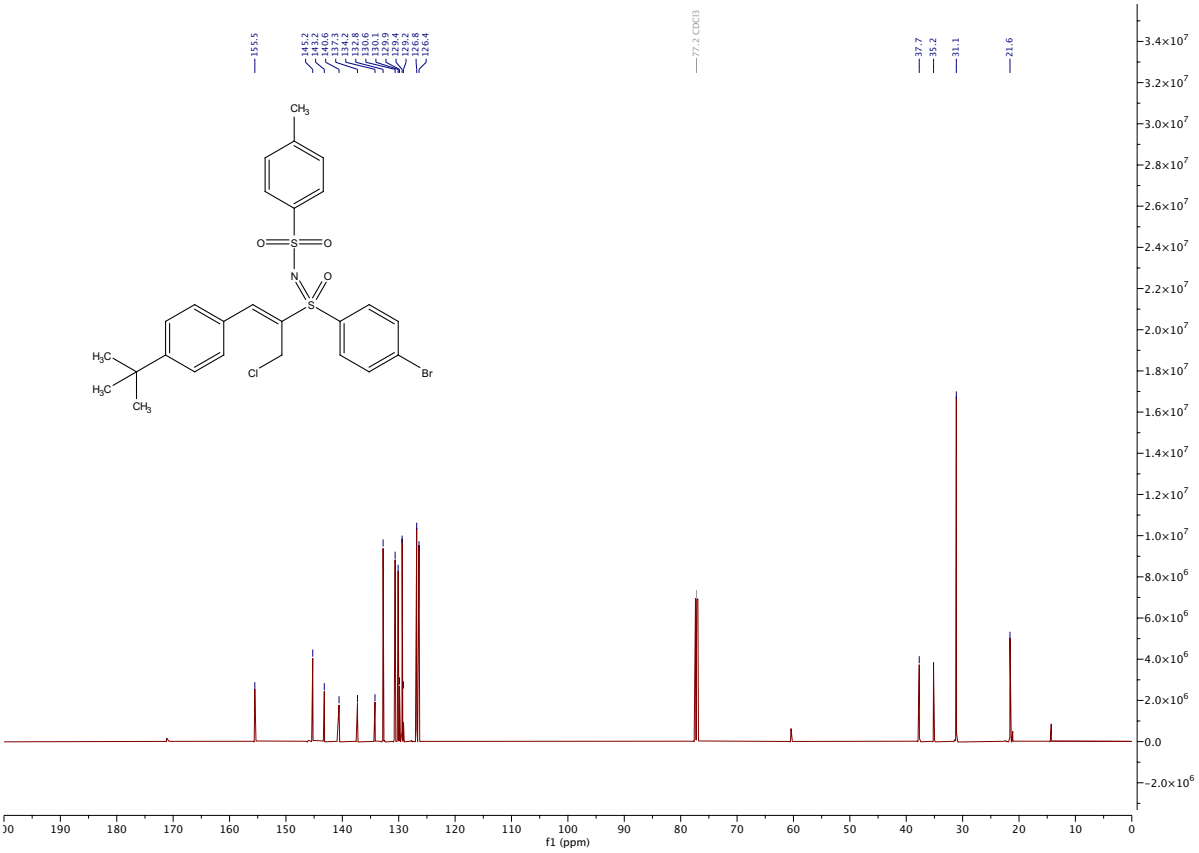

Figure S40. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ec**.

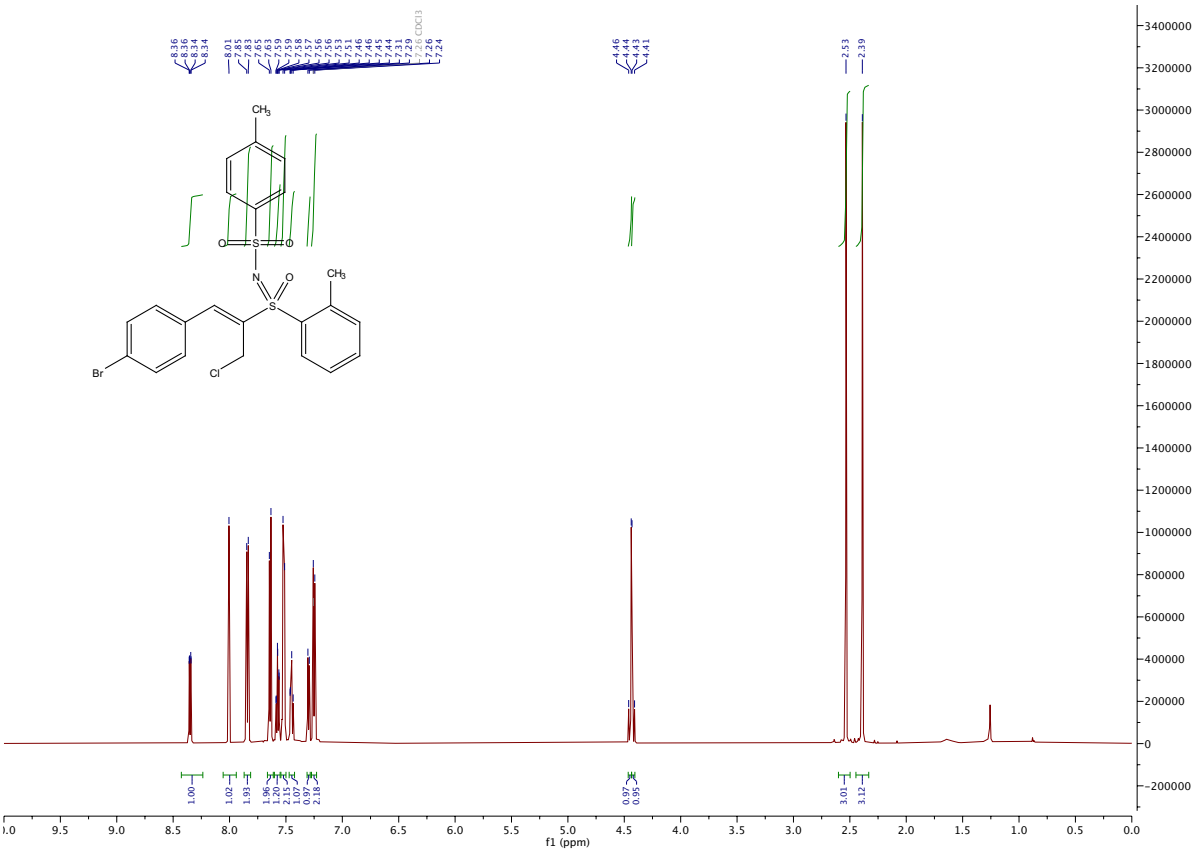

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ec**.

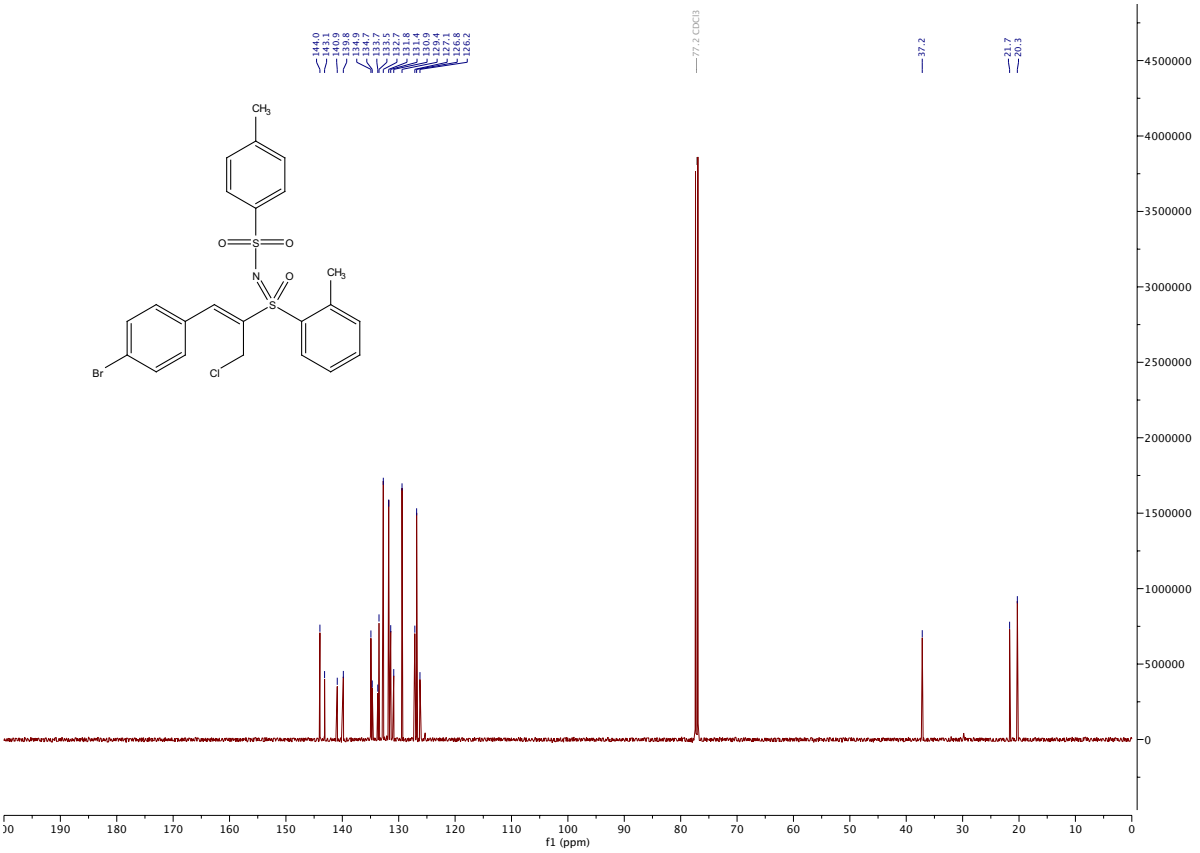

Figure S42. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3ed**.

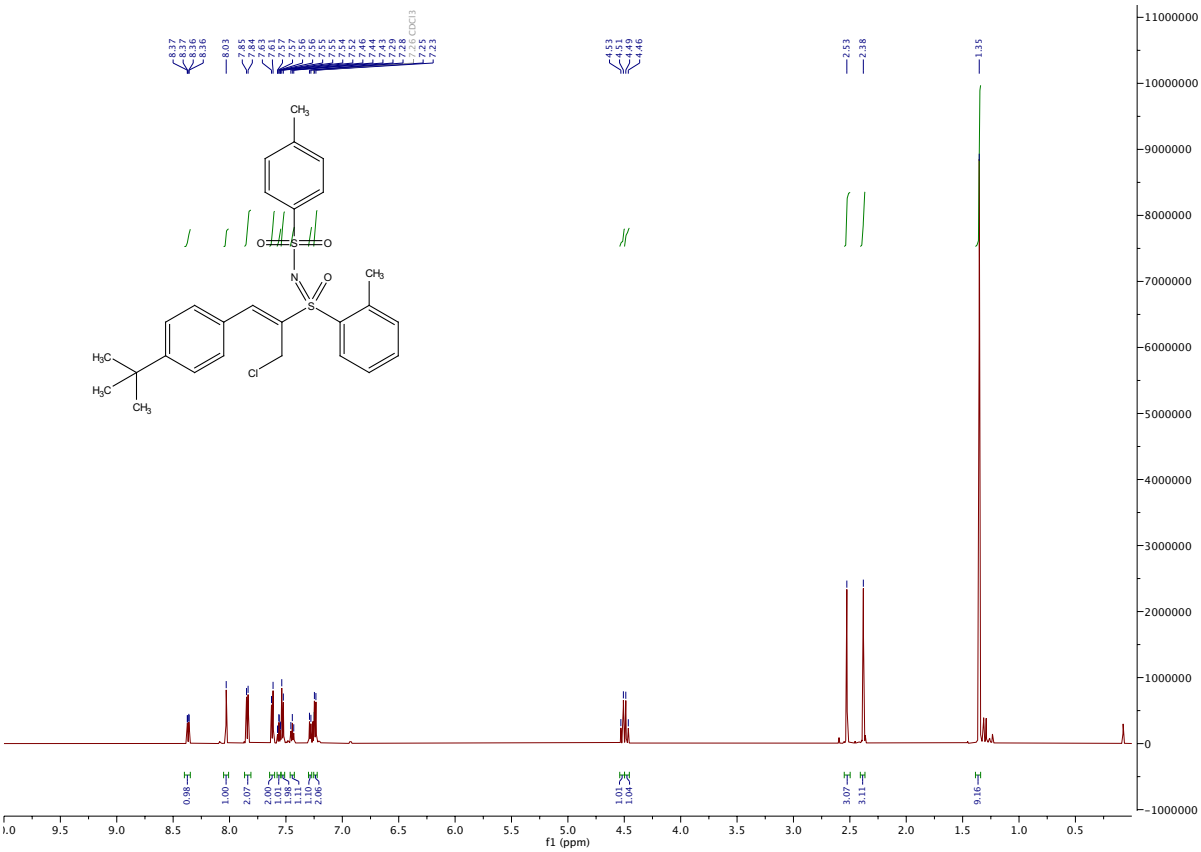

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3ed**.

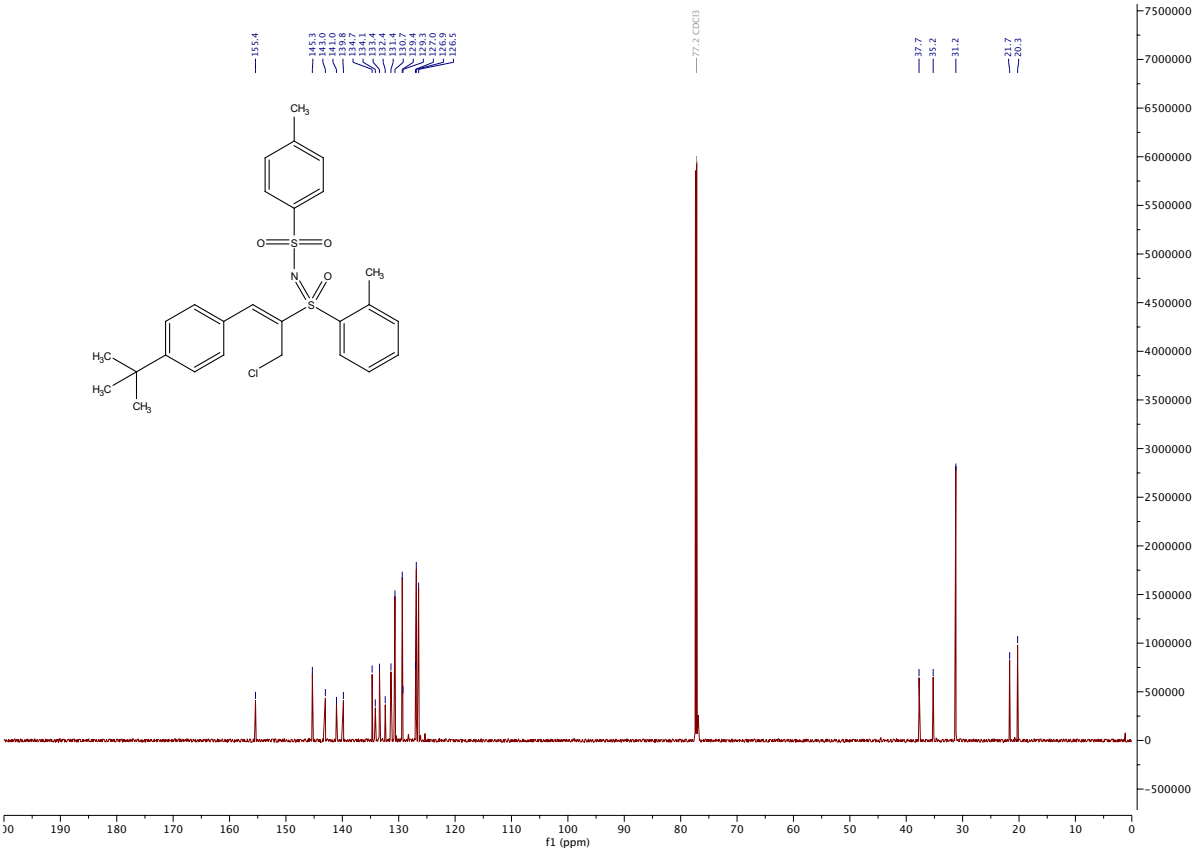

Figure S44. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3hb**.

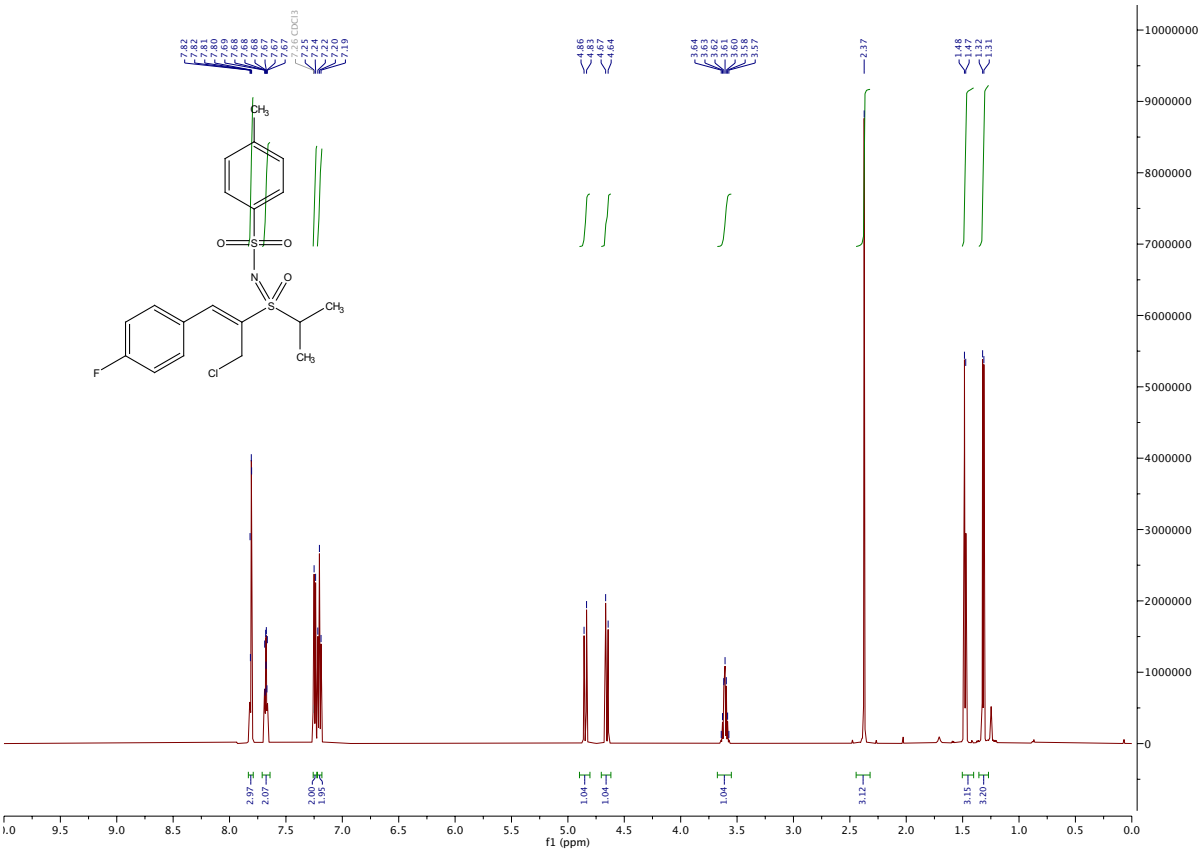

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3hb**.

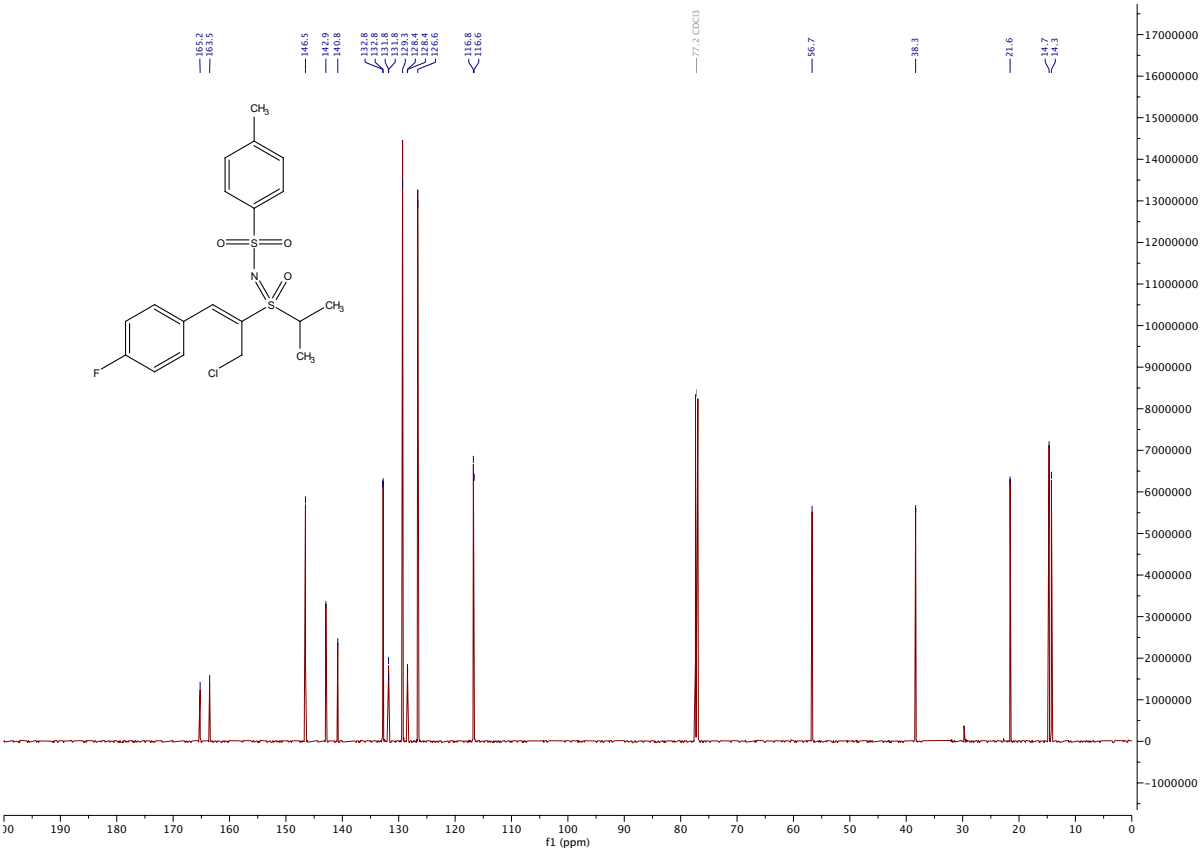

Figure S46. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **3hb**.

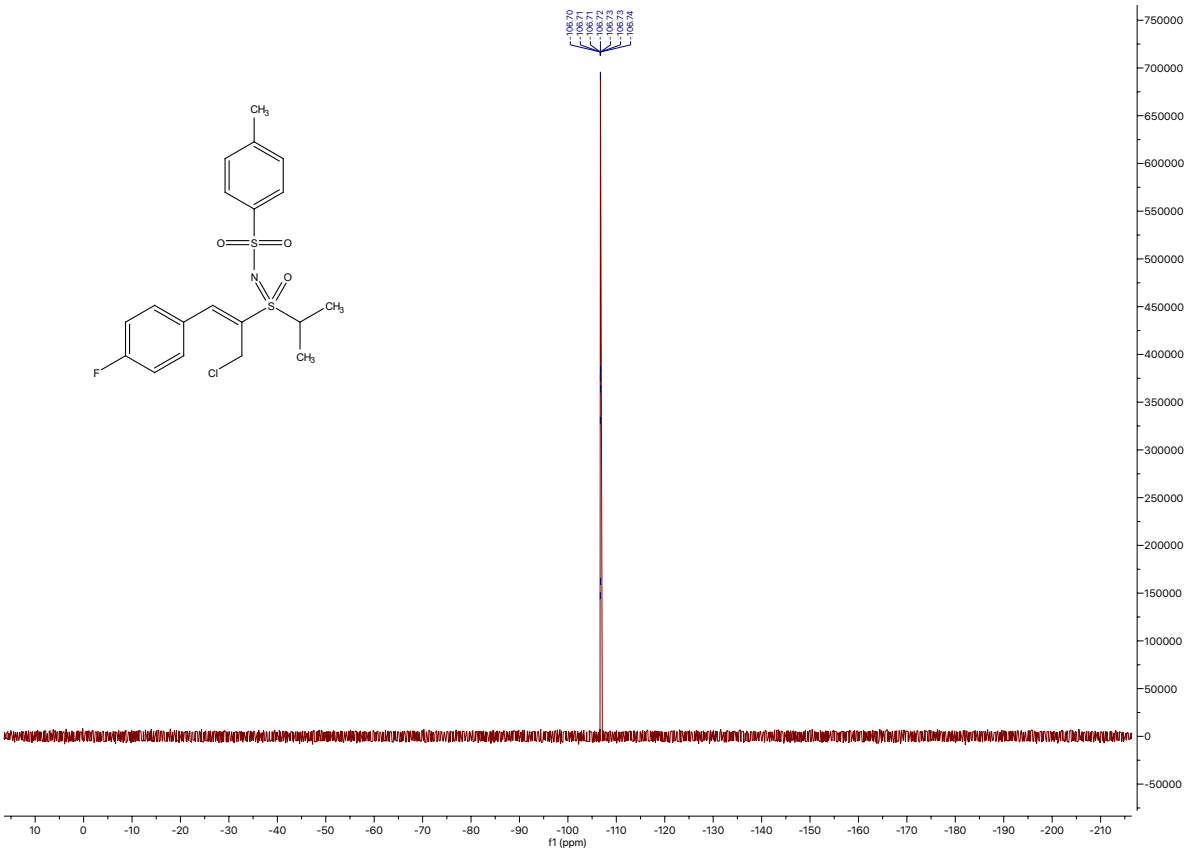

Figure S47. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3hc**.

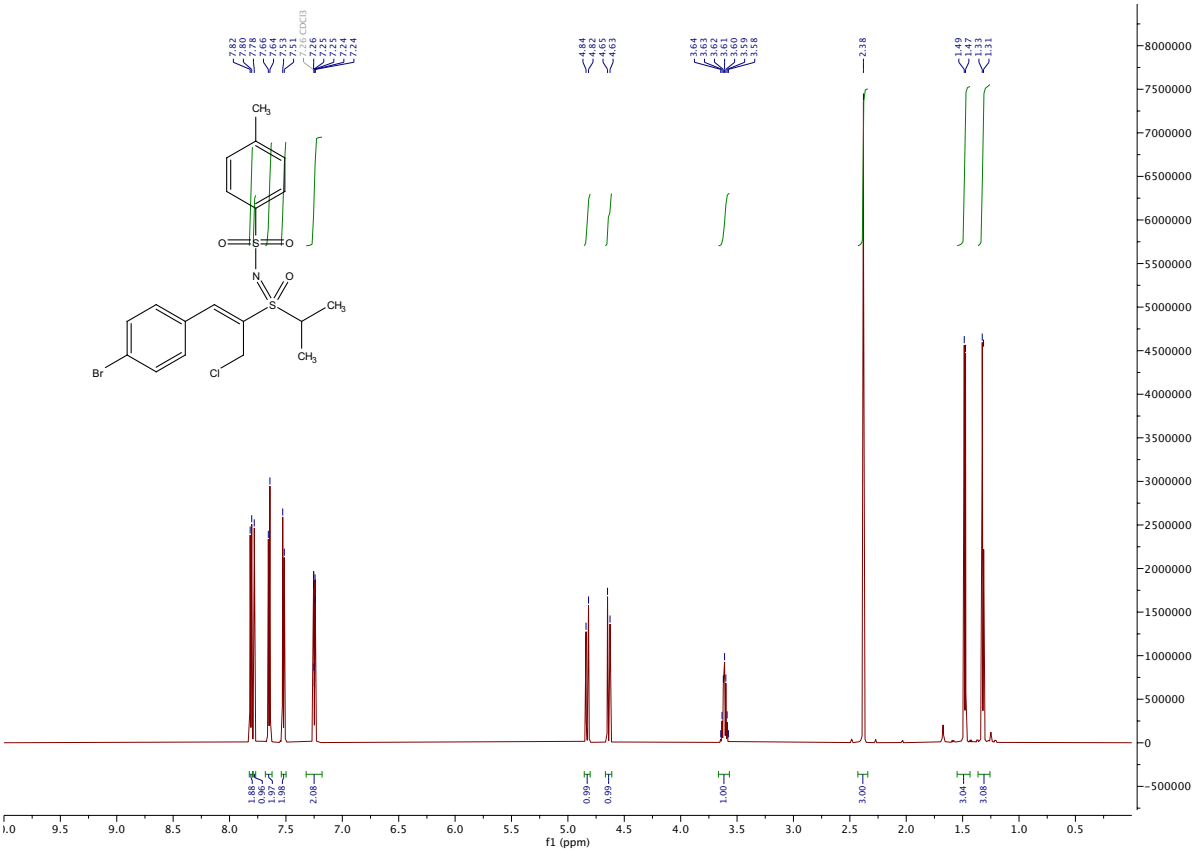

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3hc**.

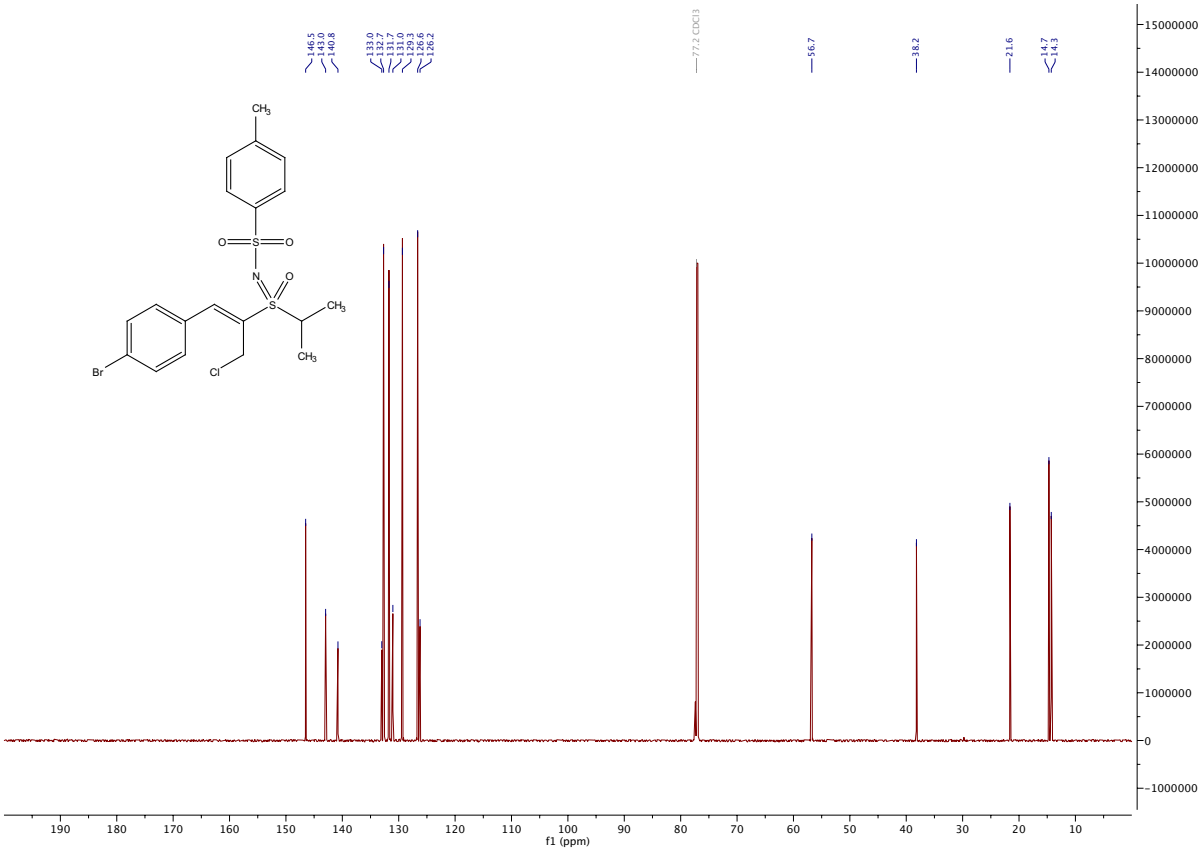

Figure S49. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **3hd**.

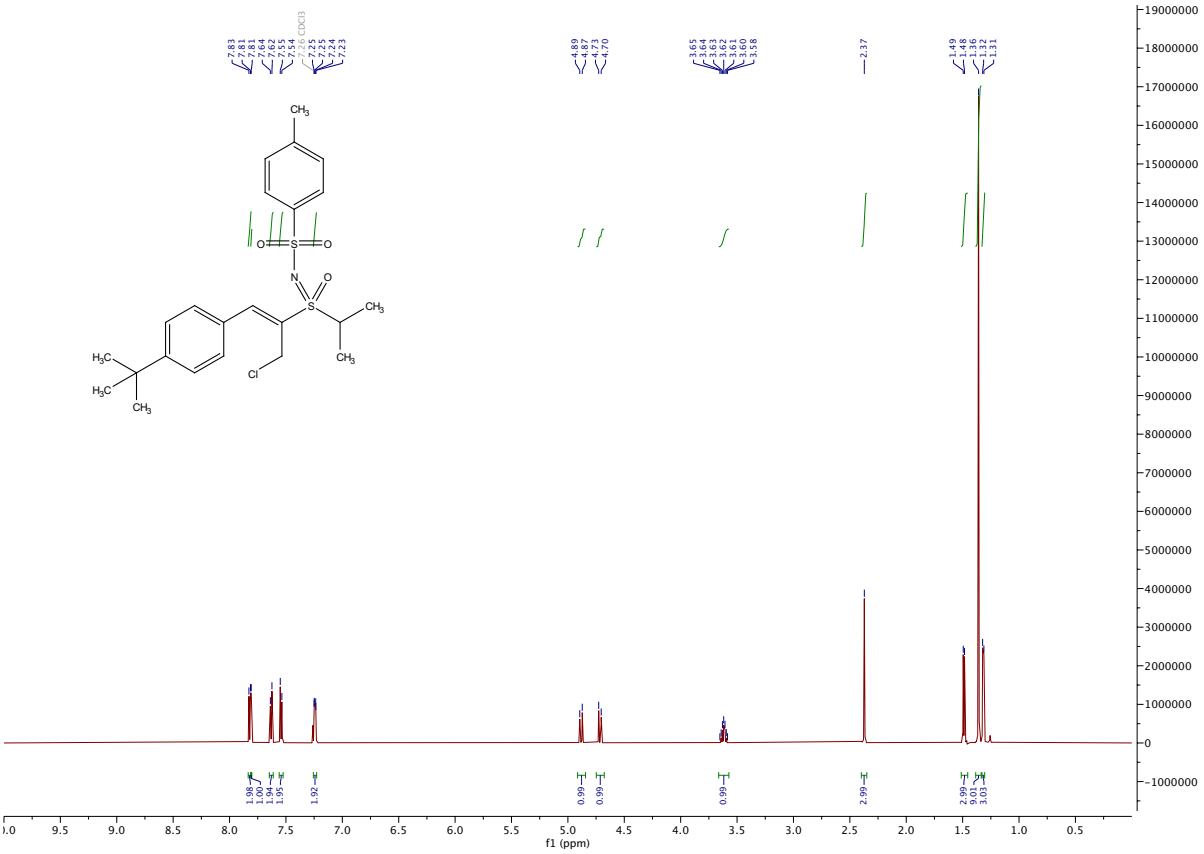

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **3hd**.

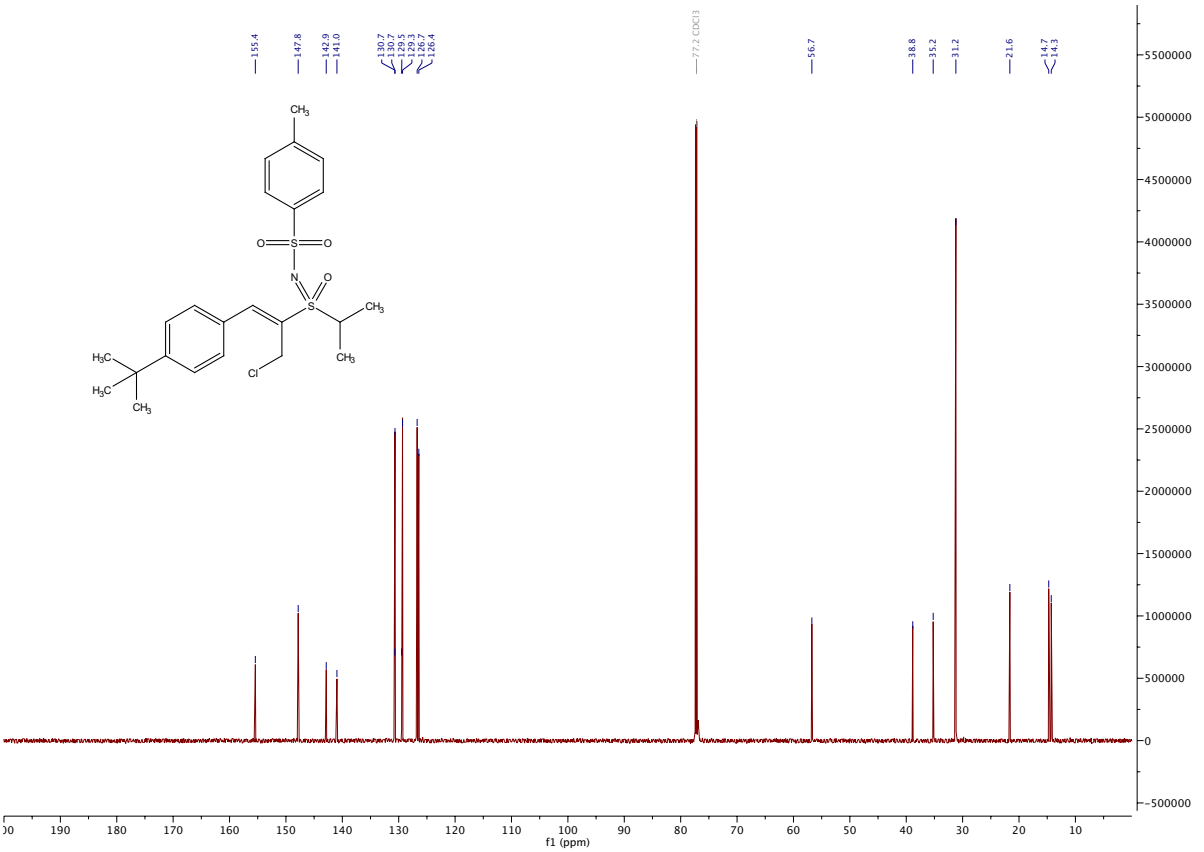

Figure S51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **9a**.

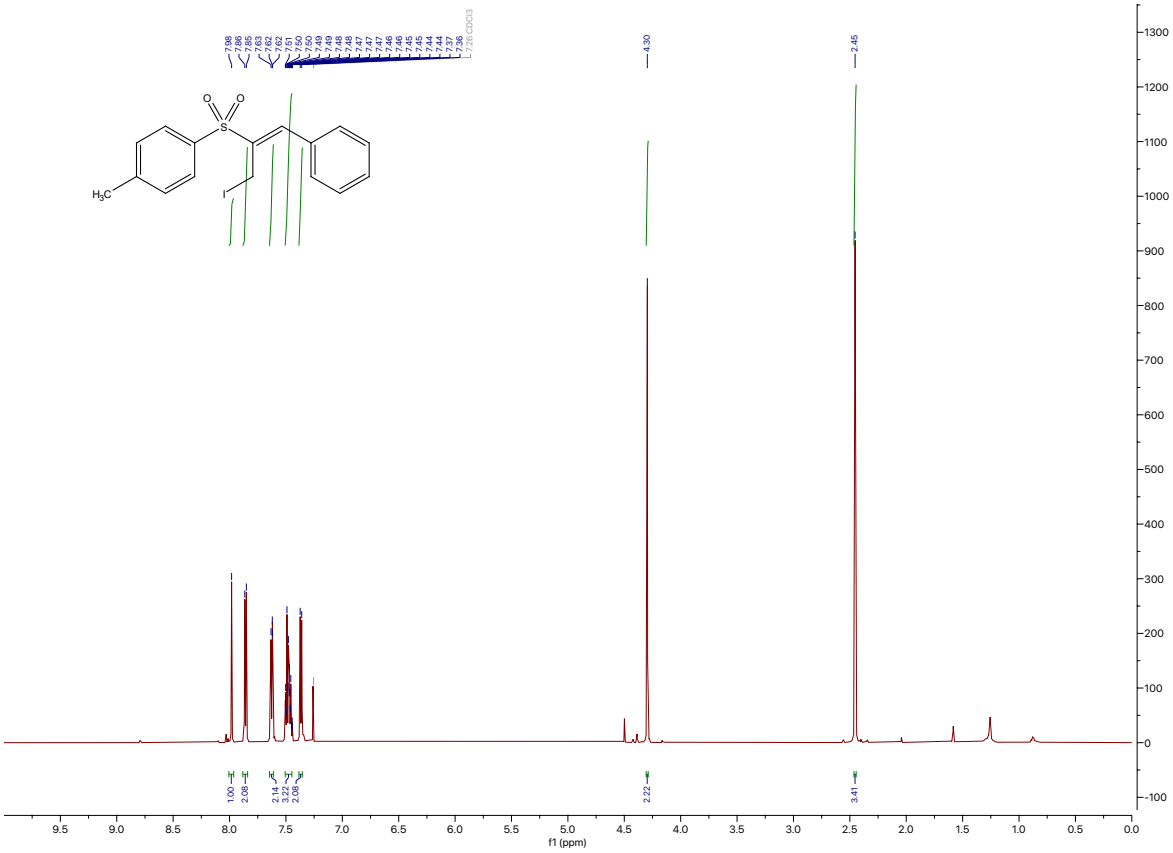

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **9a**.

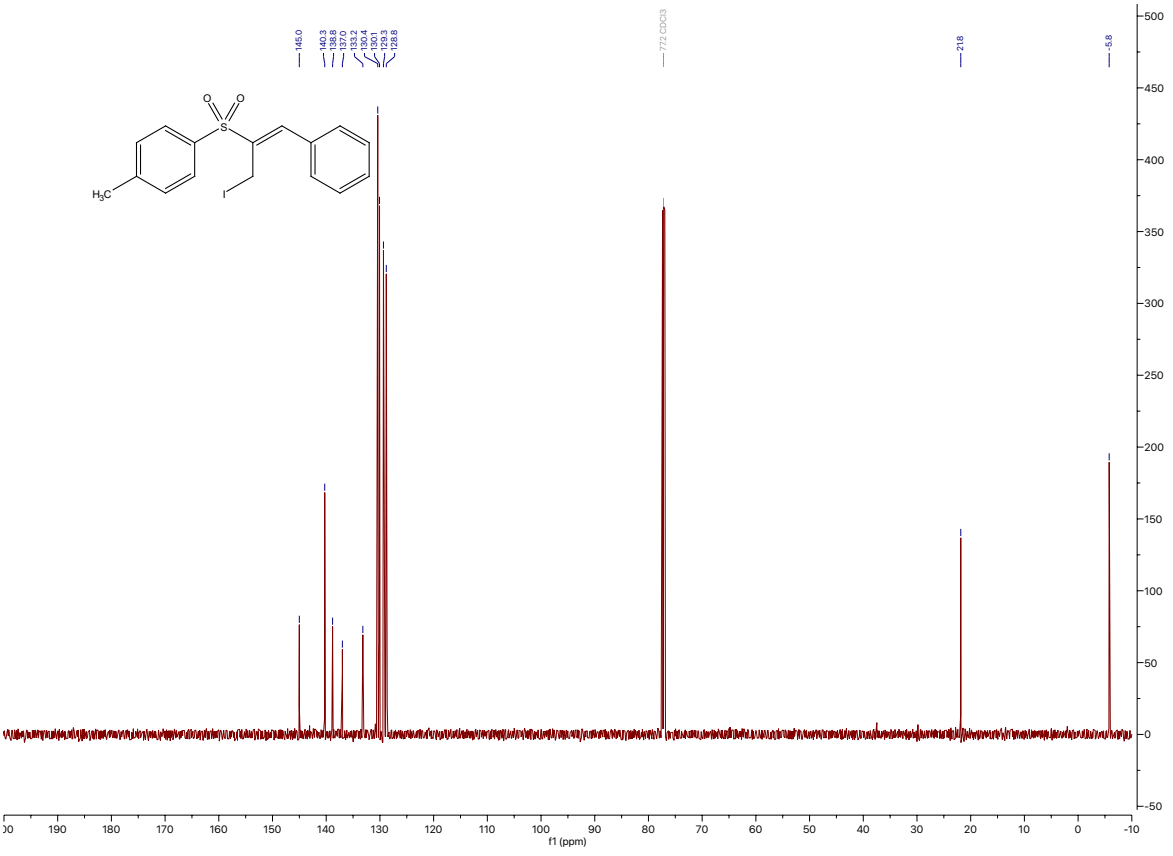

Figure S53. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **9b**.

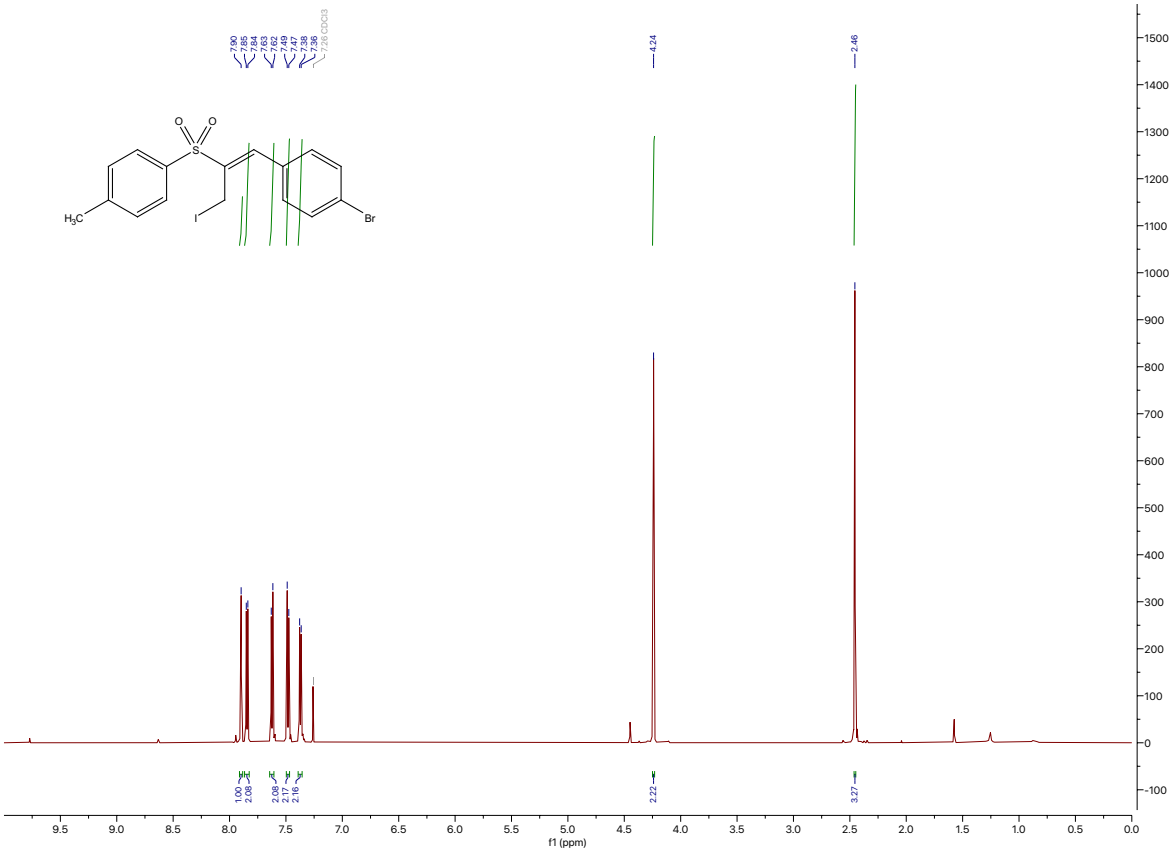

Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **9b**.

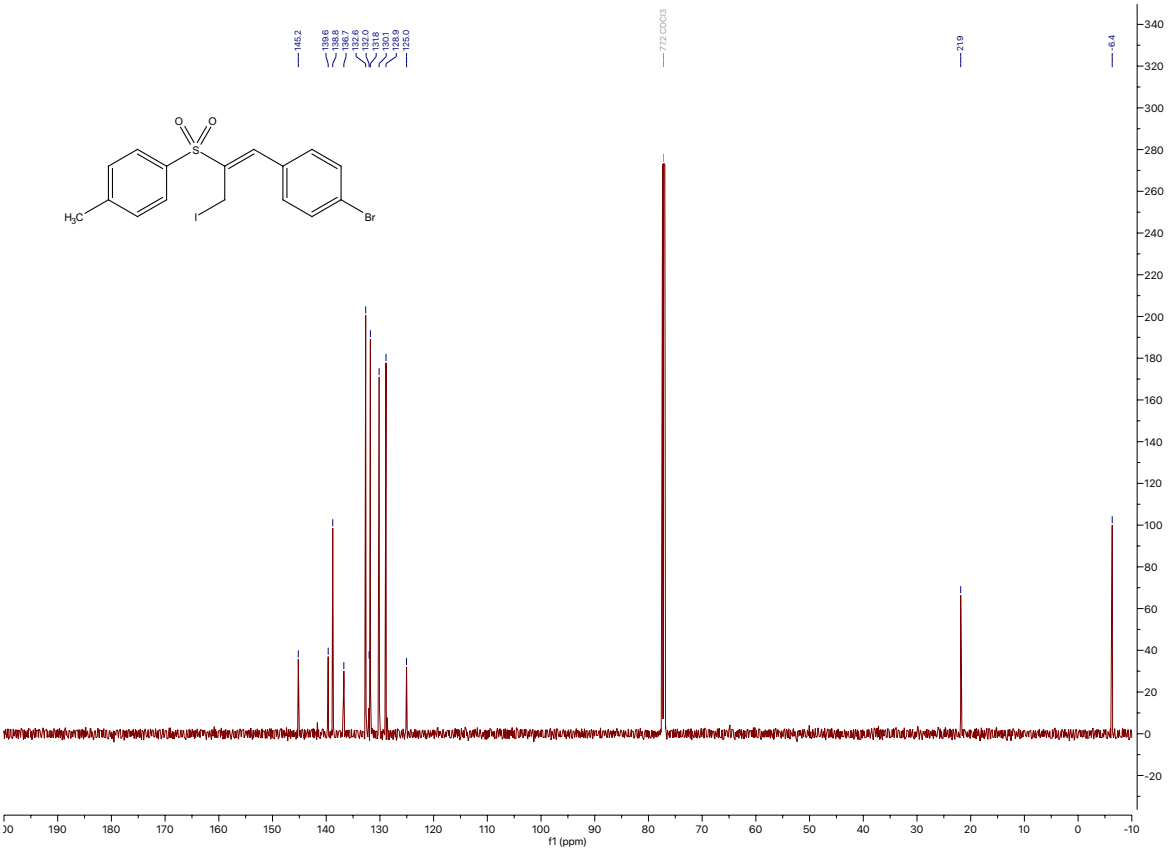

Figure S55. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10a**.

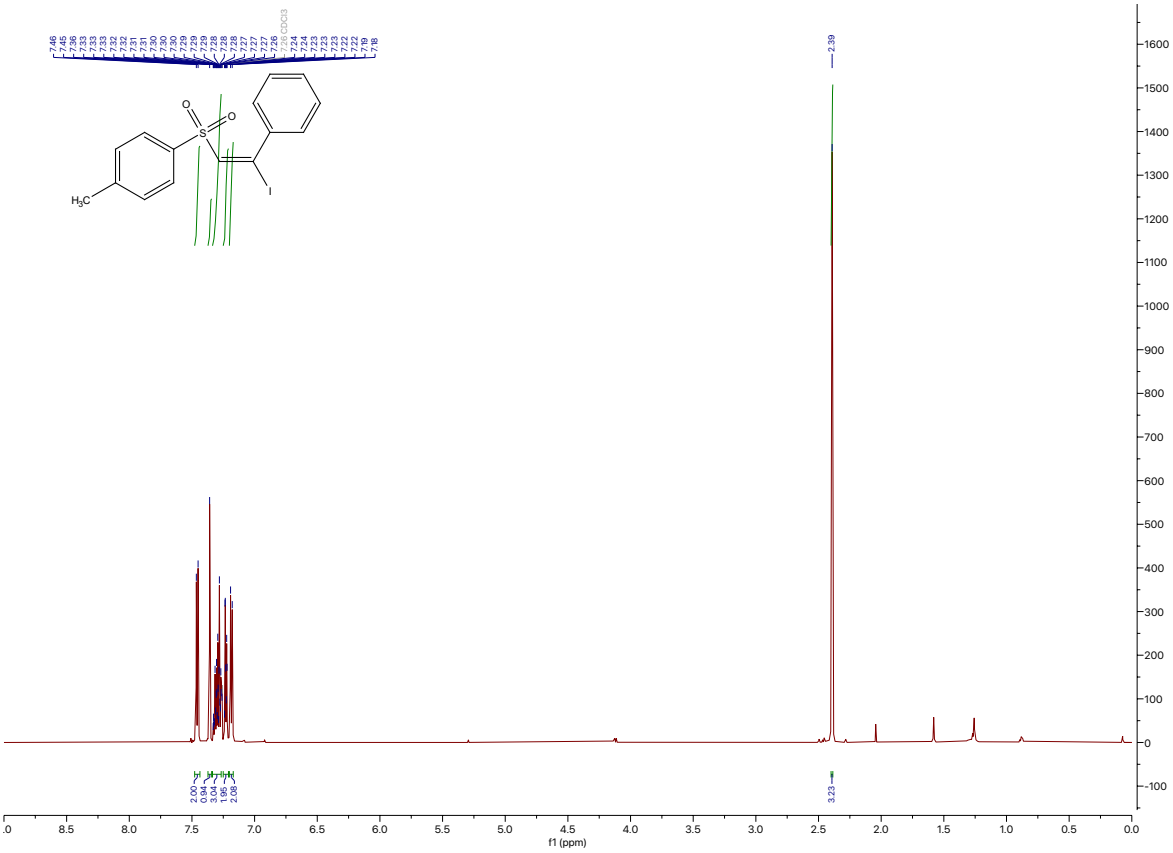

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10a**.

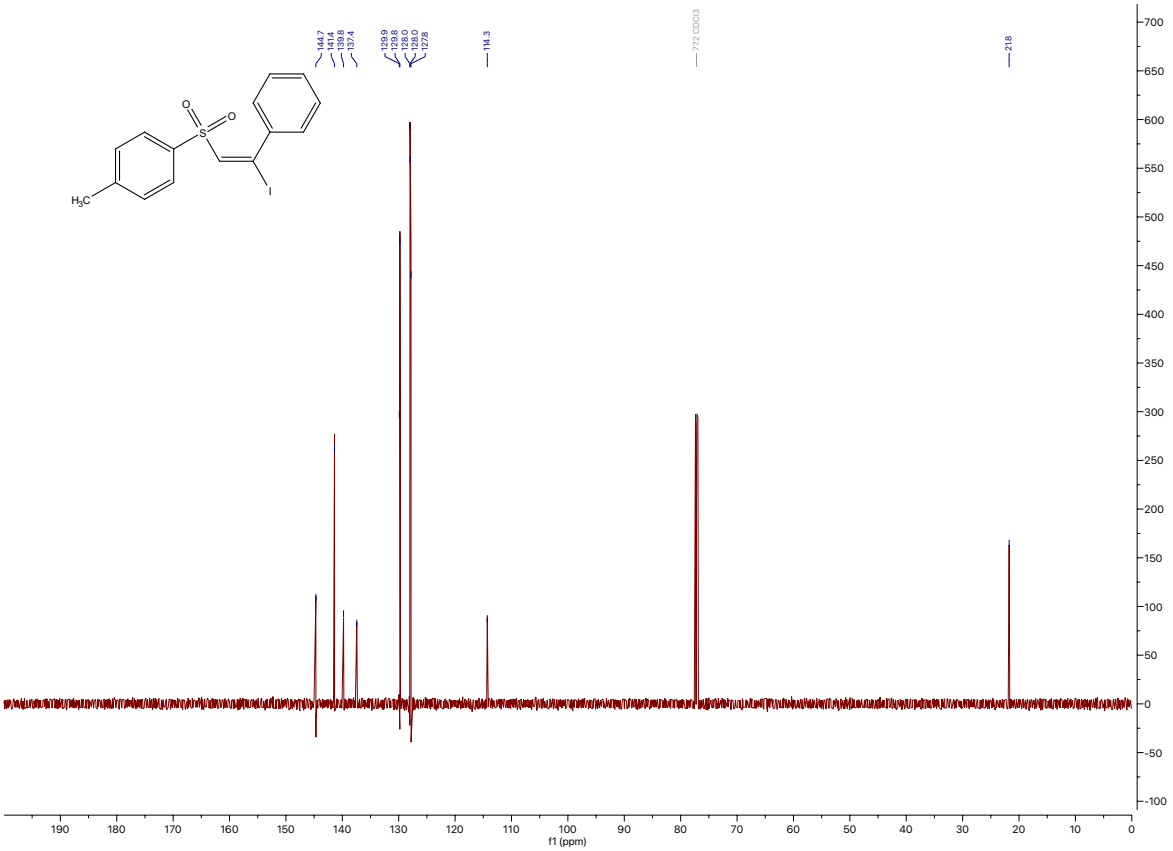

Figure S57. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10b**.

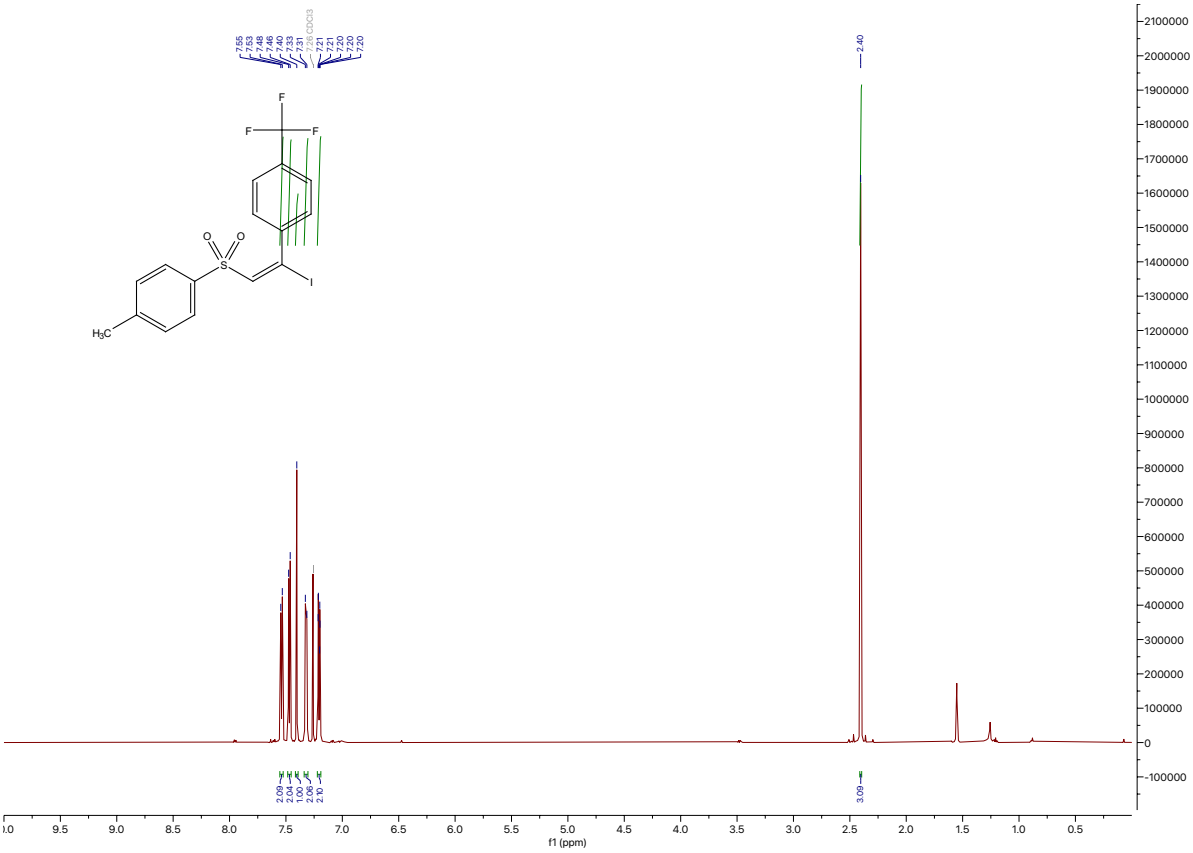

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10b**.

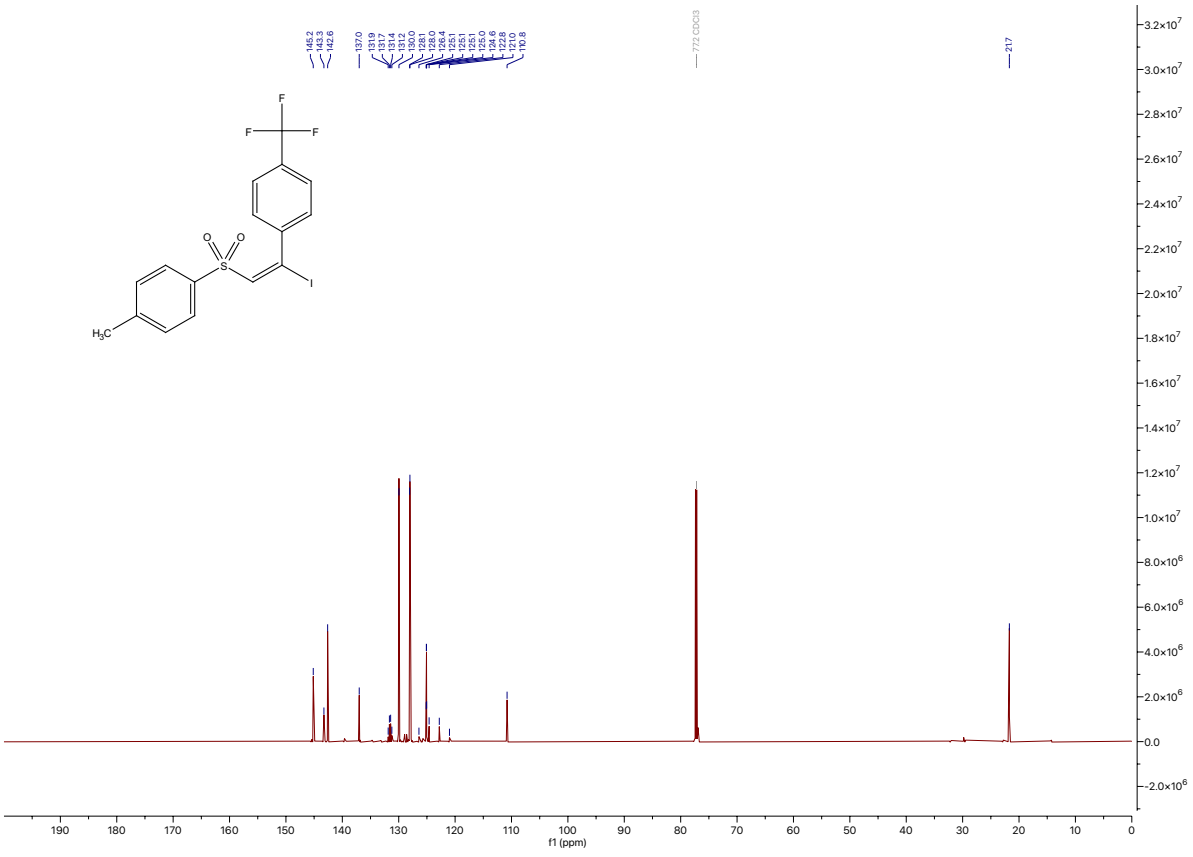

Figure S59. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **10b**.

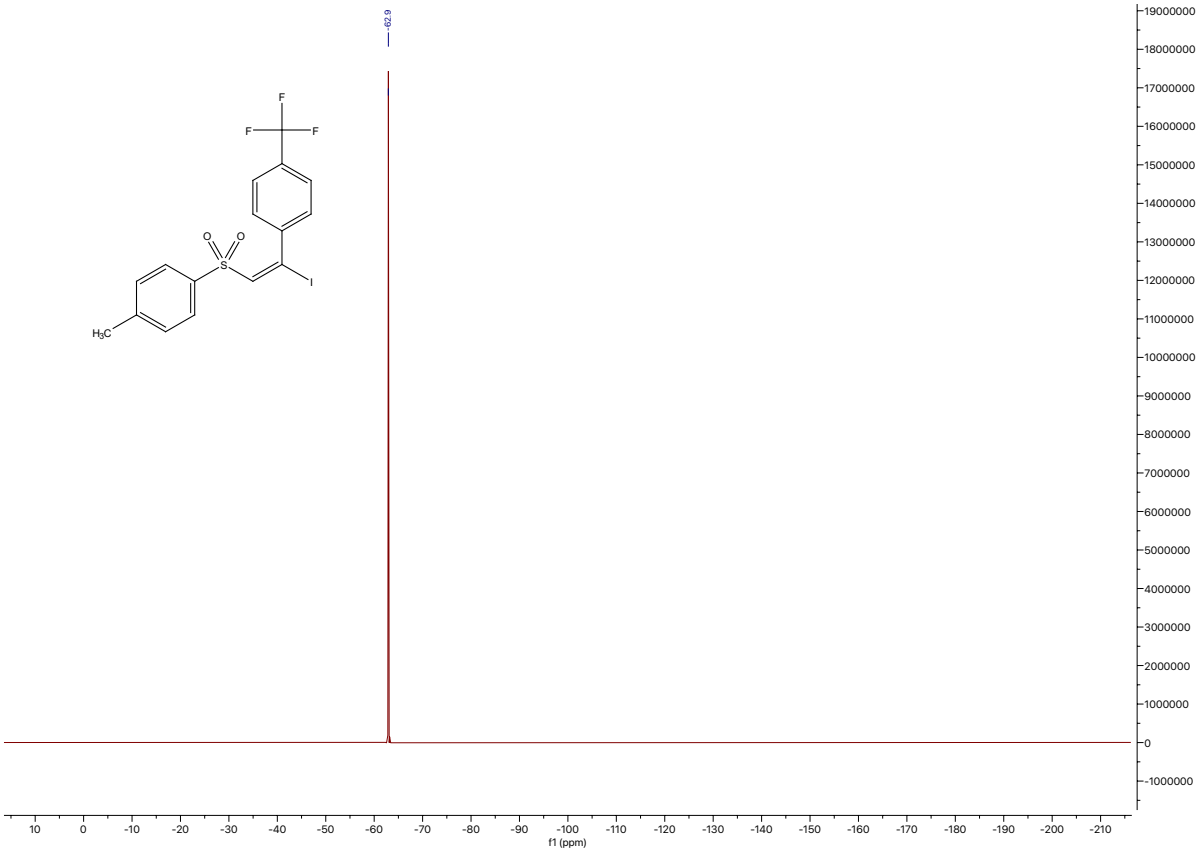

Figure S60. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10c**.

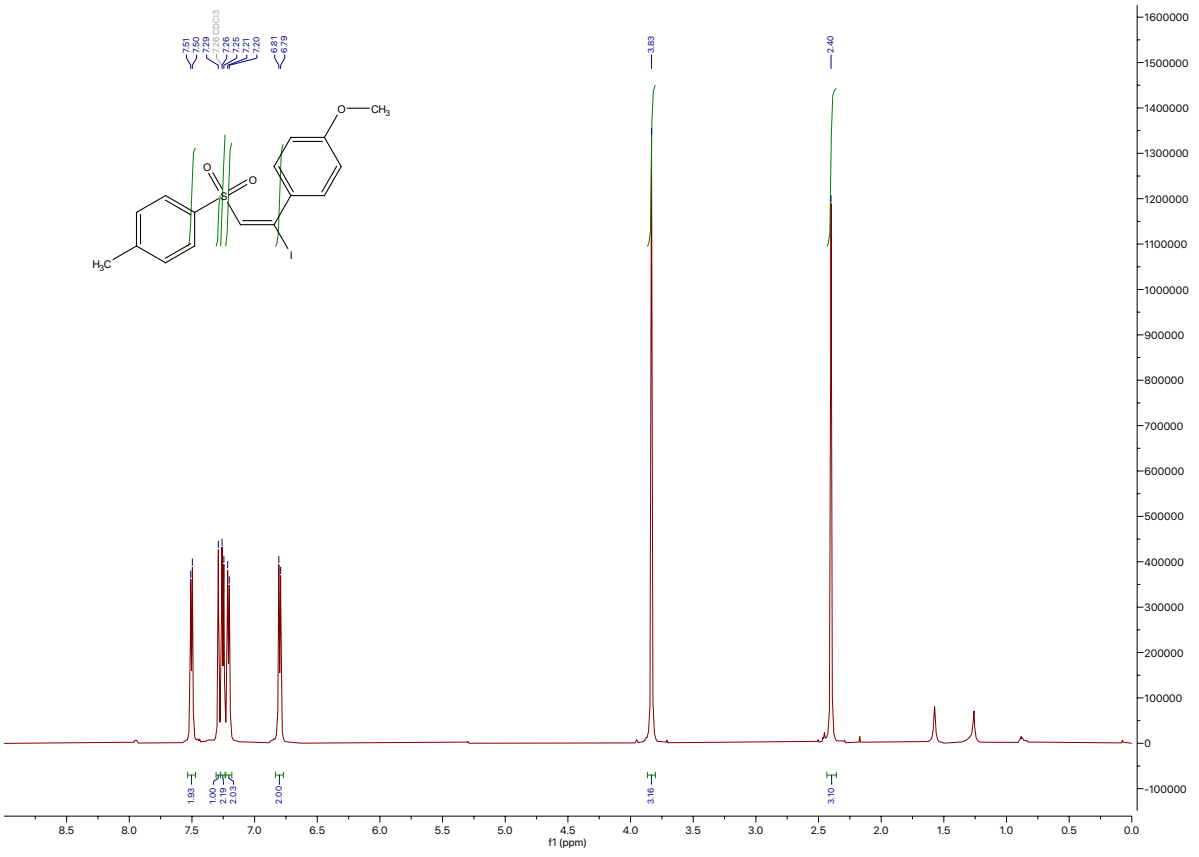

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10c**.

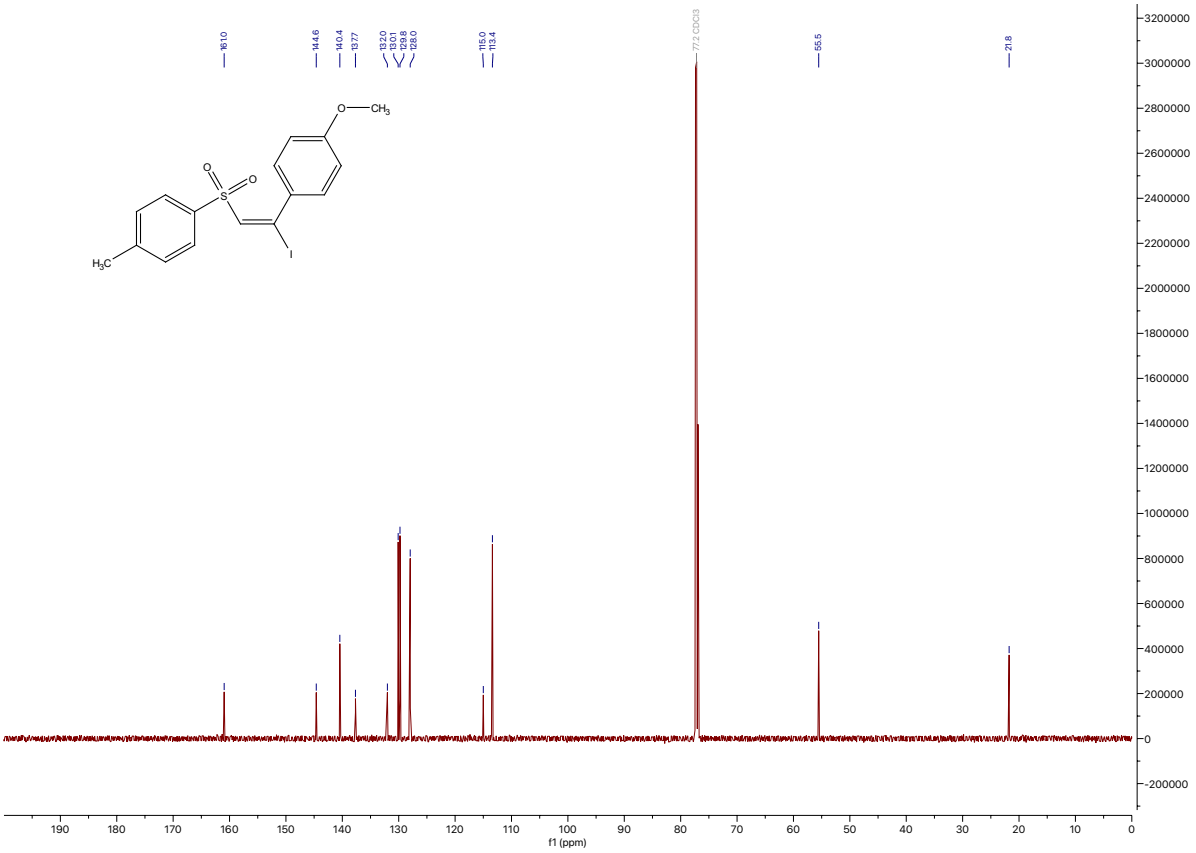

Figure S62. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10d**.

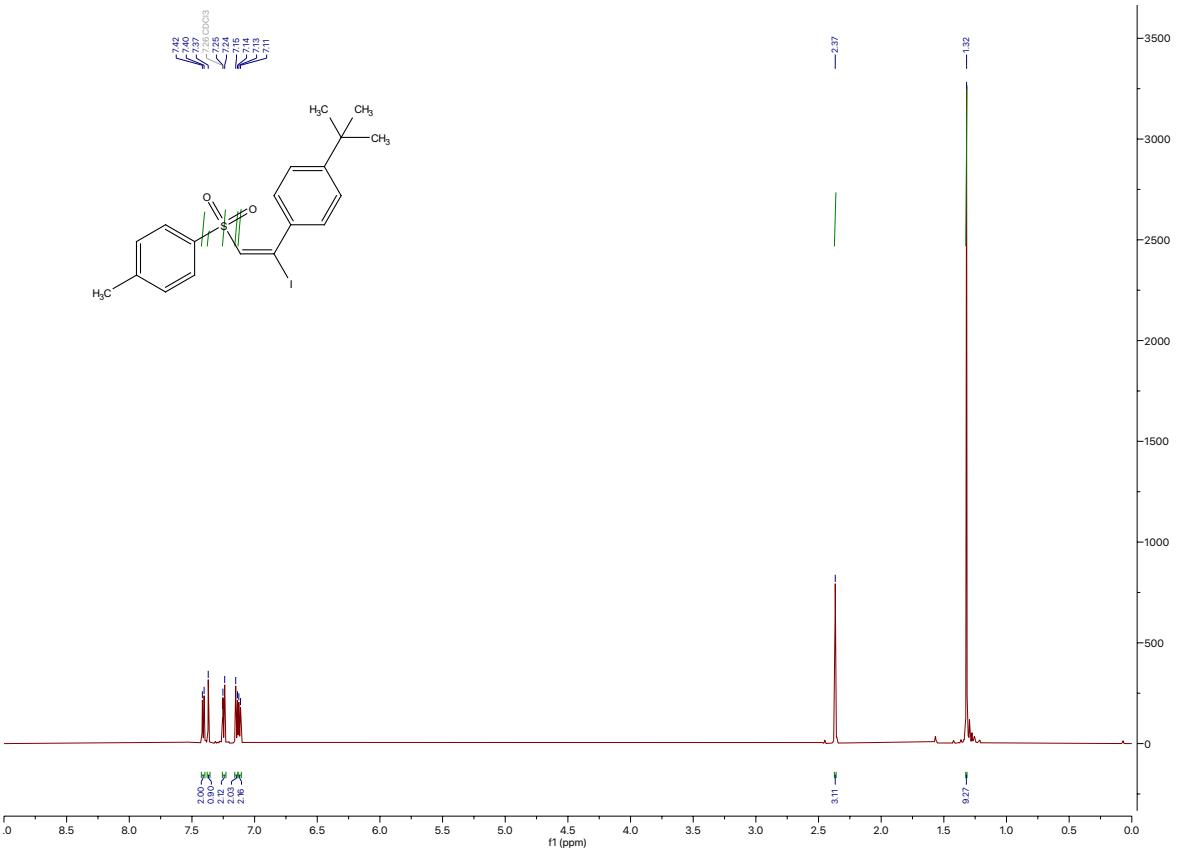

Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10d**.

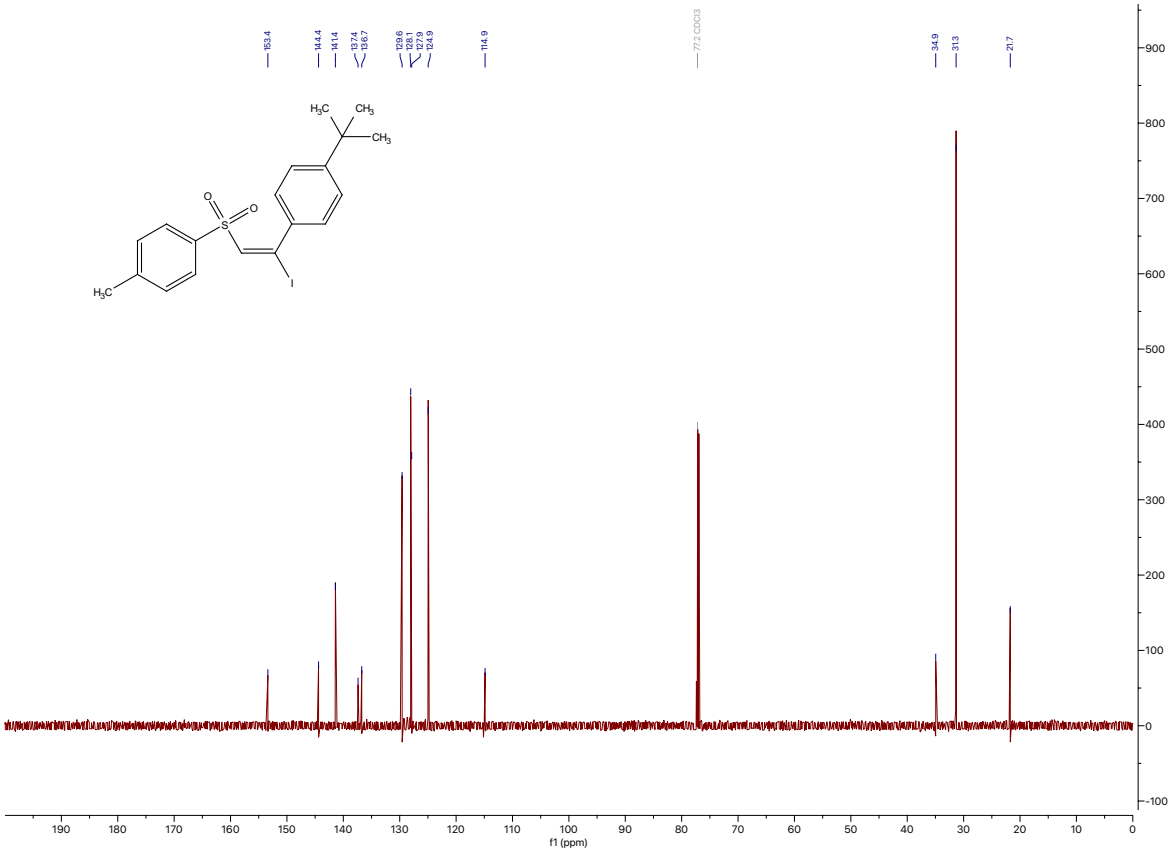

Figure S64. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10e**.

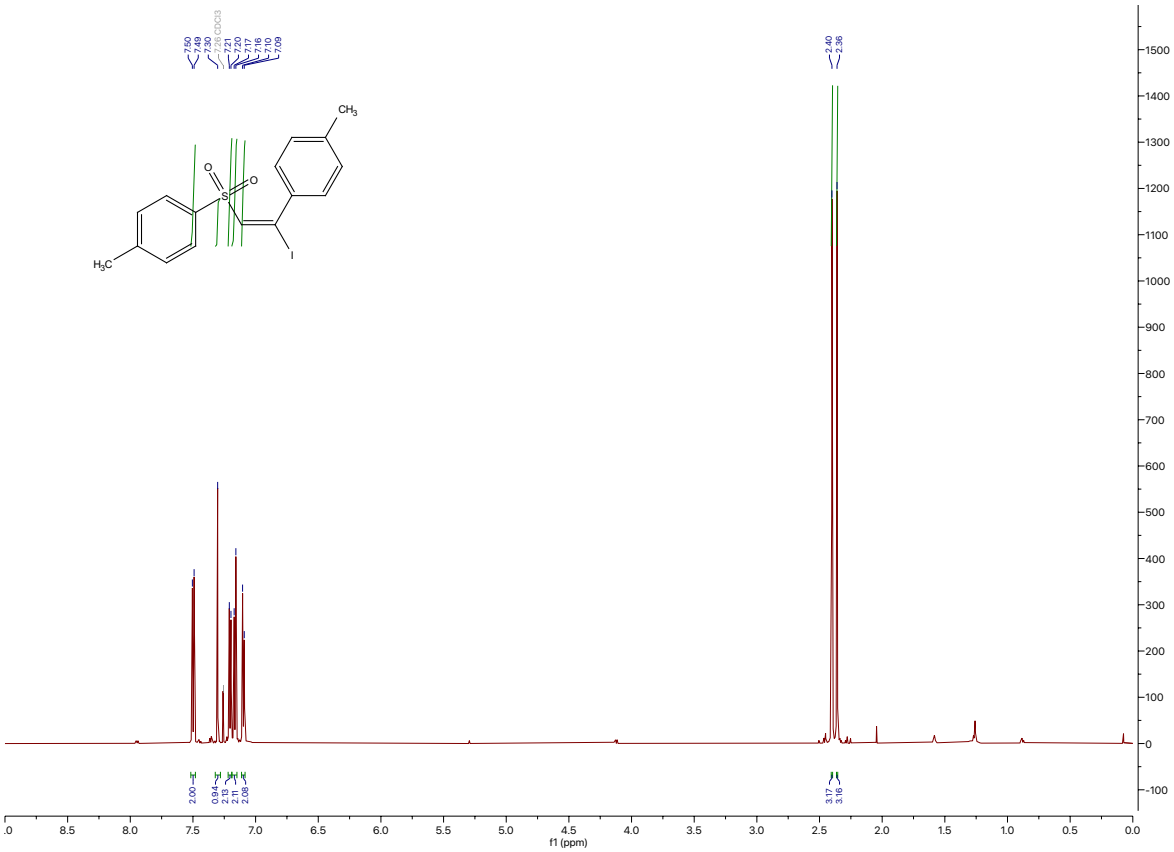

Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10e**.

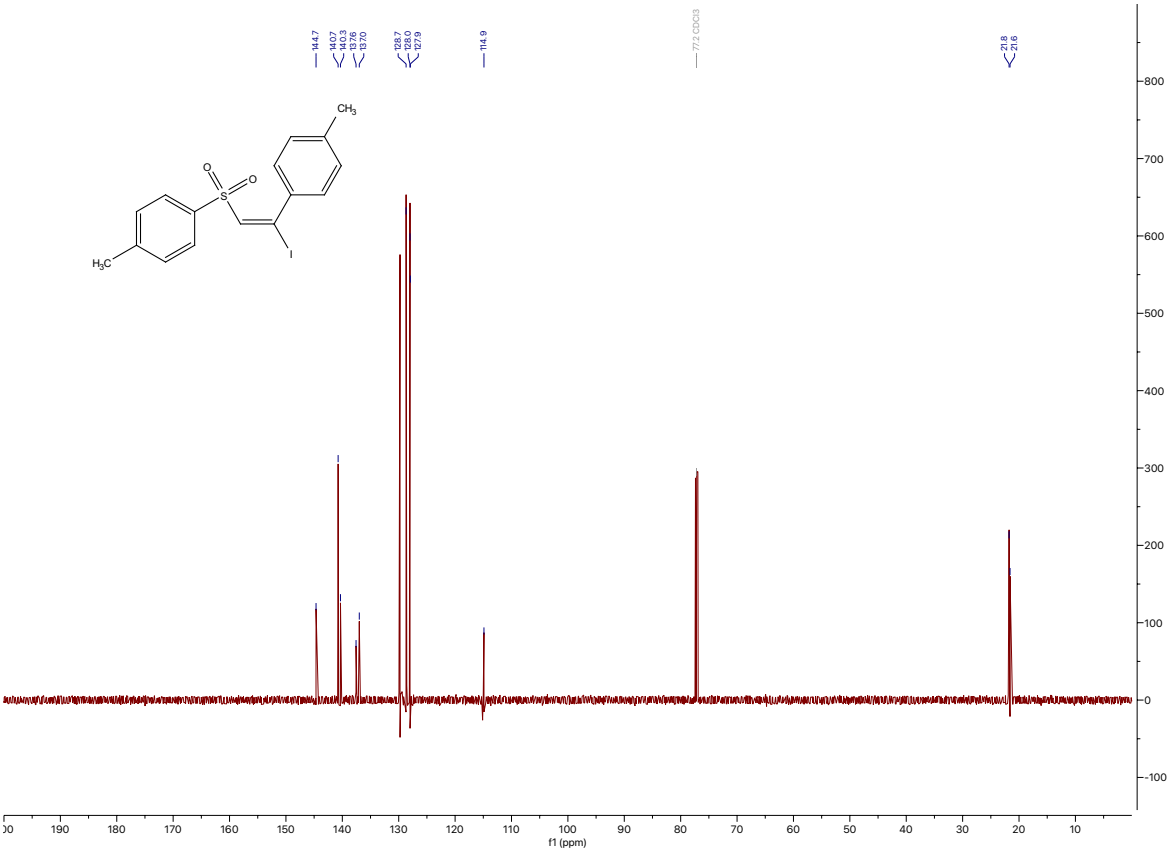

Figure S66. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10f**.

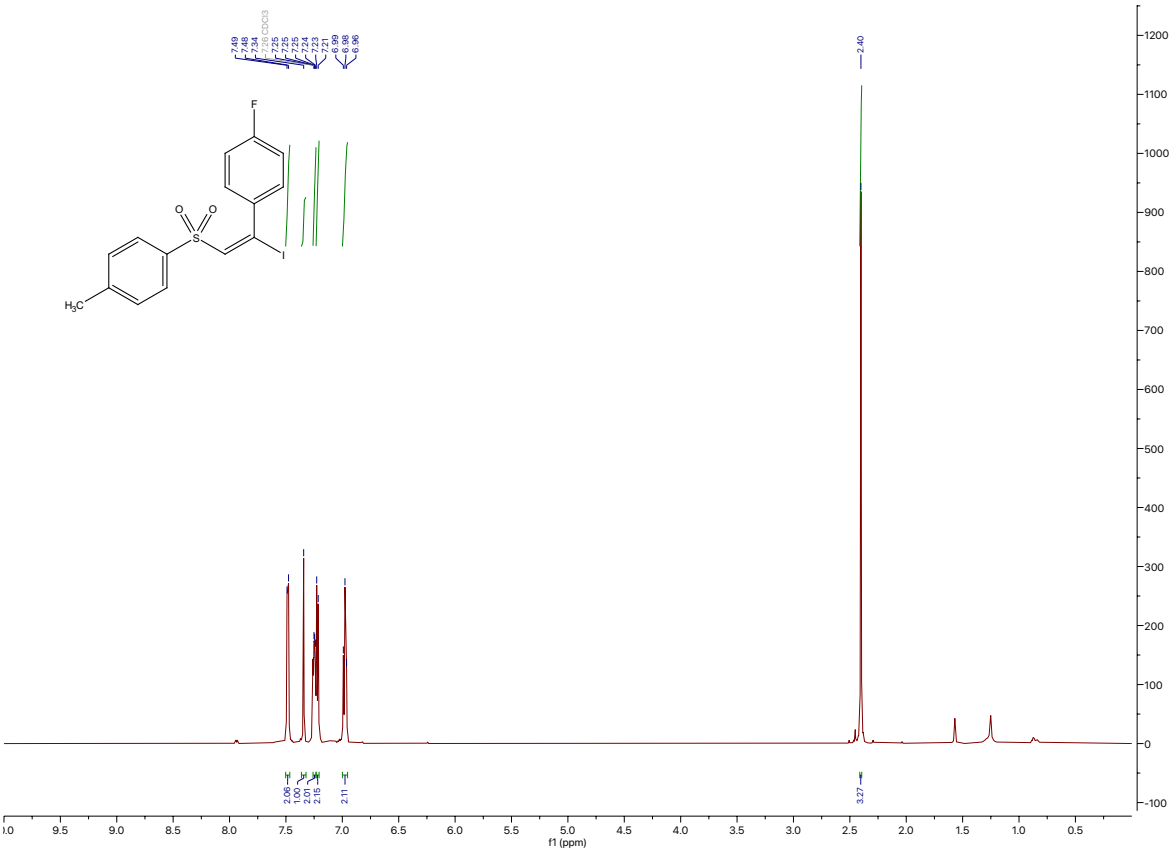

Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10f**.

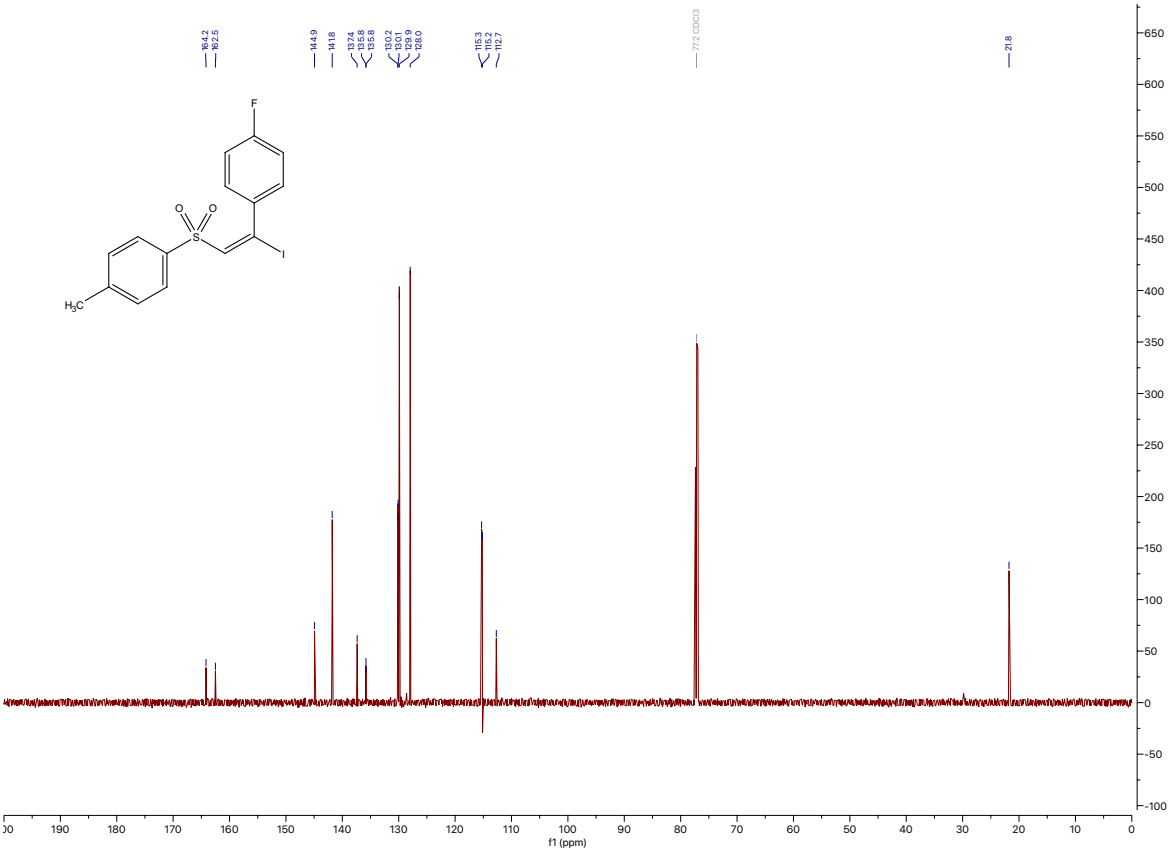

Figure S68. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **10f**.

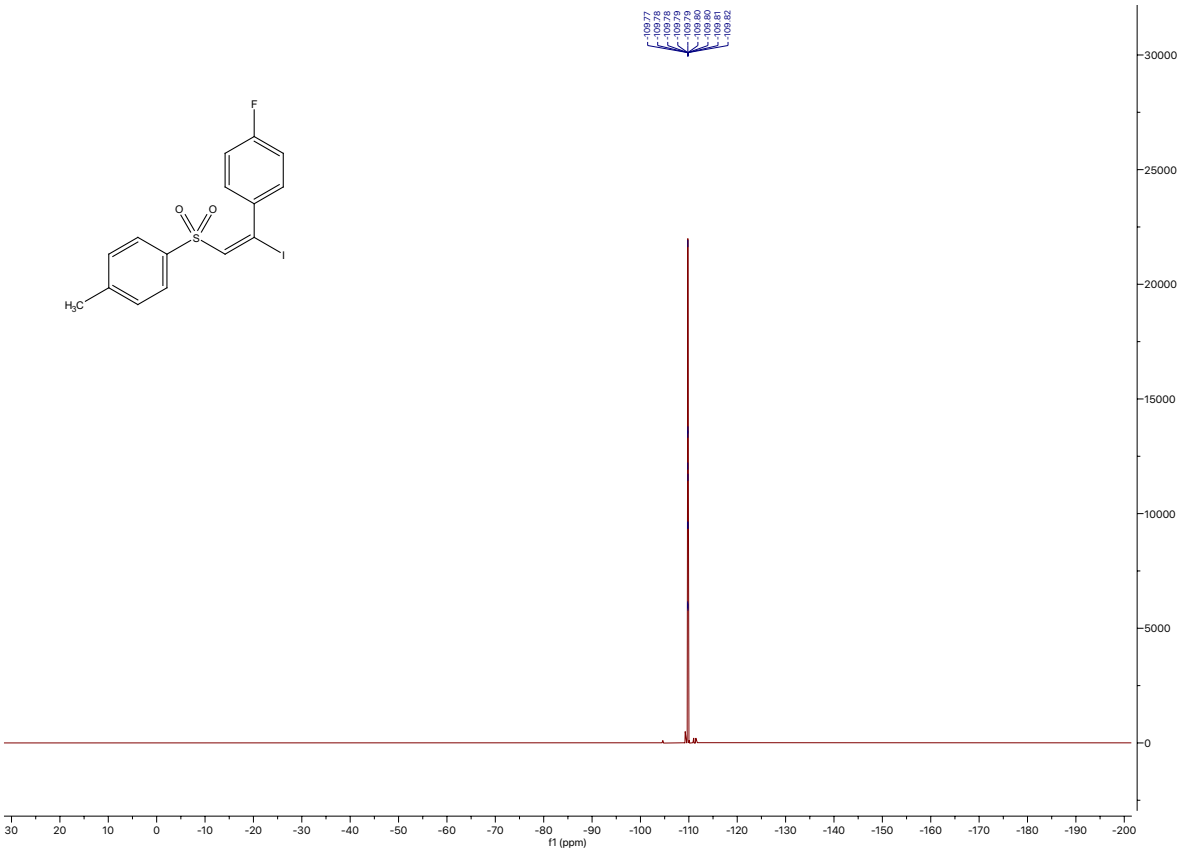

Figure S69. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10g**.

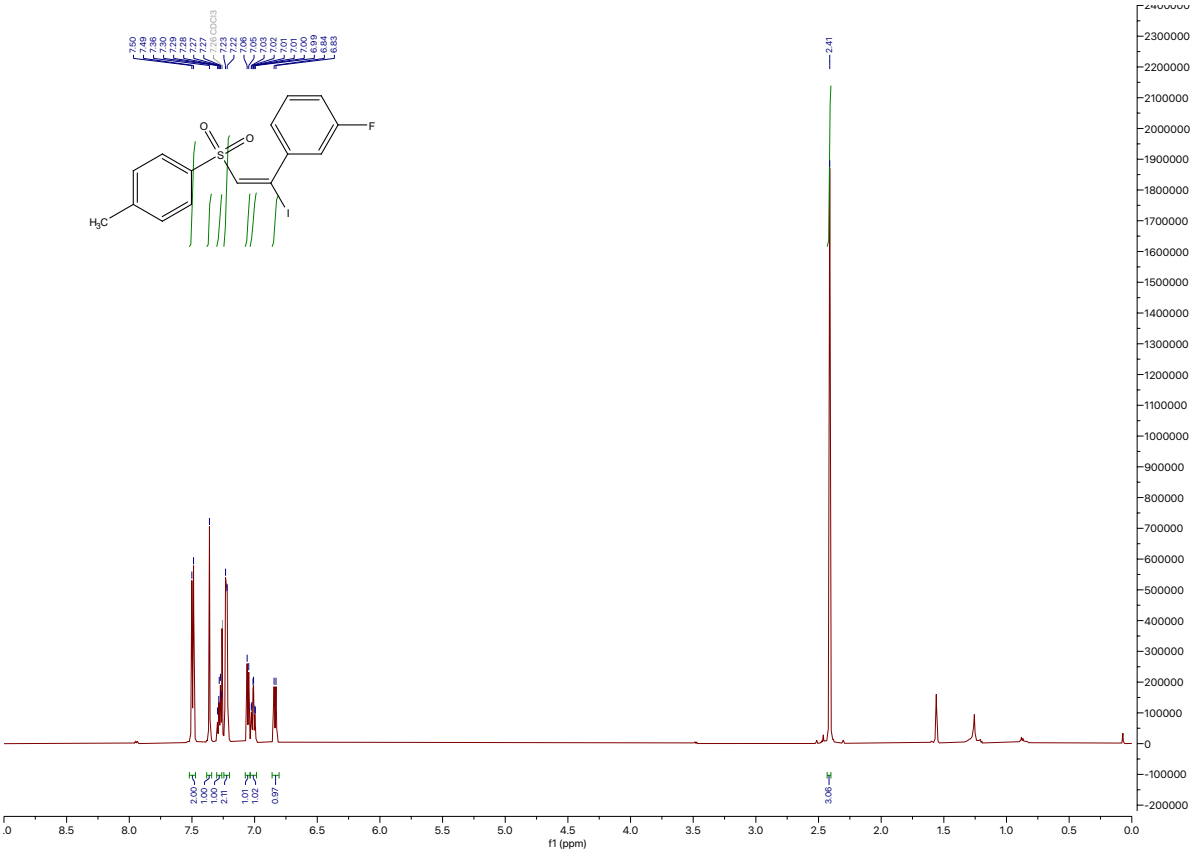

Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10g**.

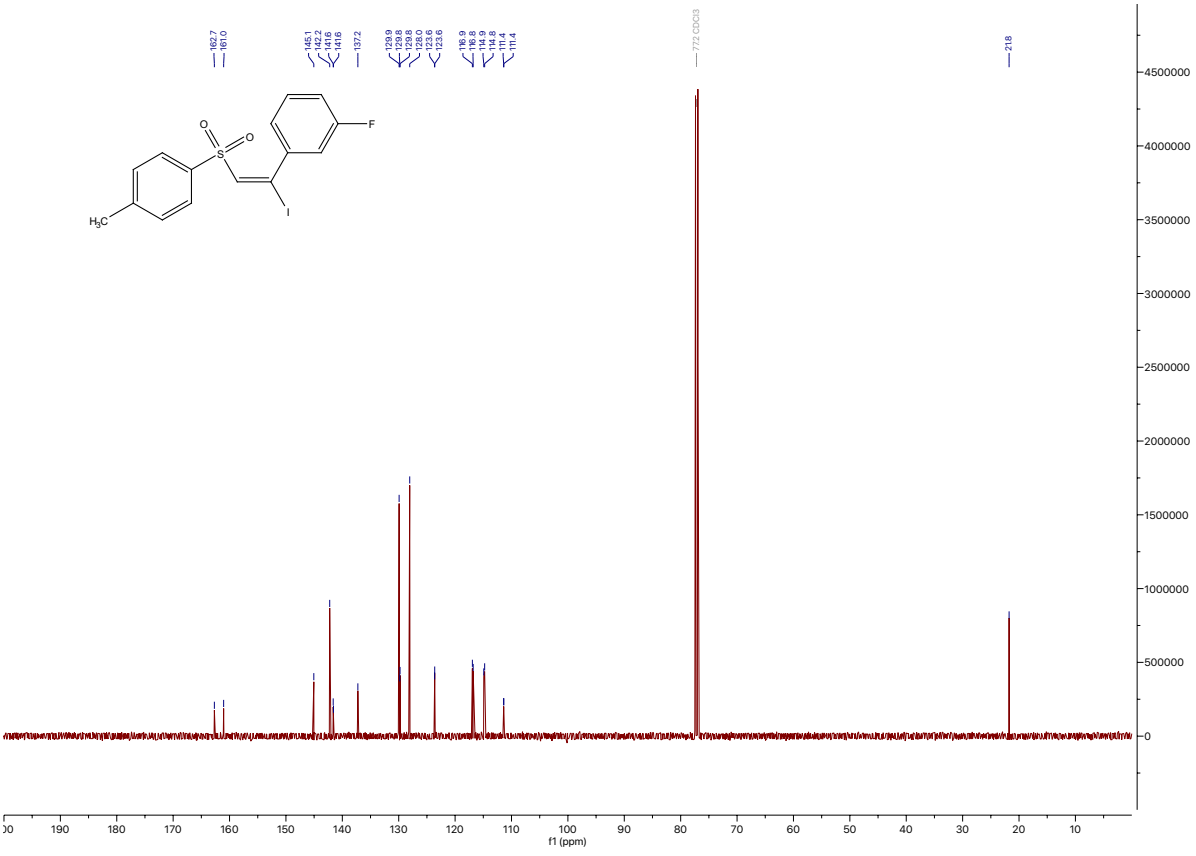

Figure S71. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **10g**.

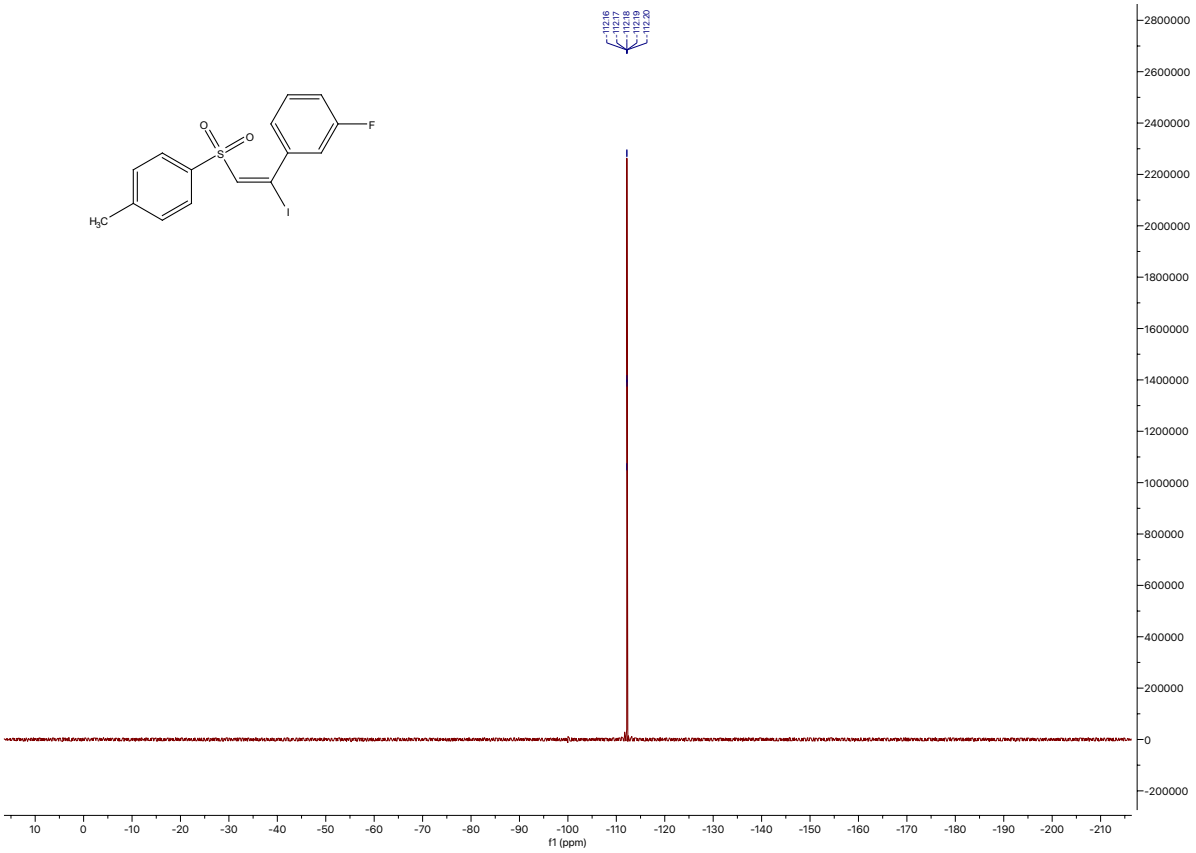

Figure S72. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10h**.

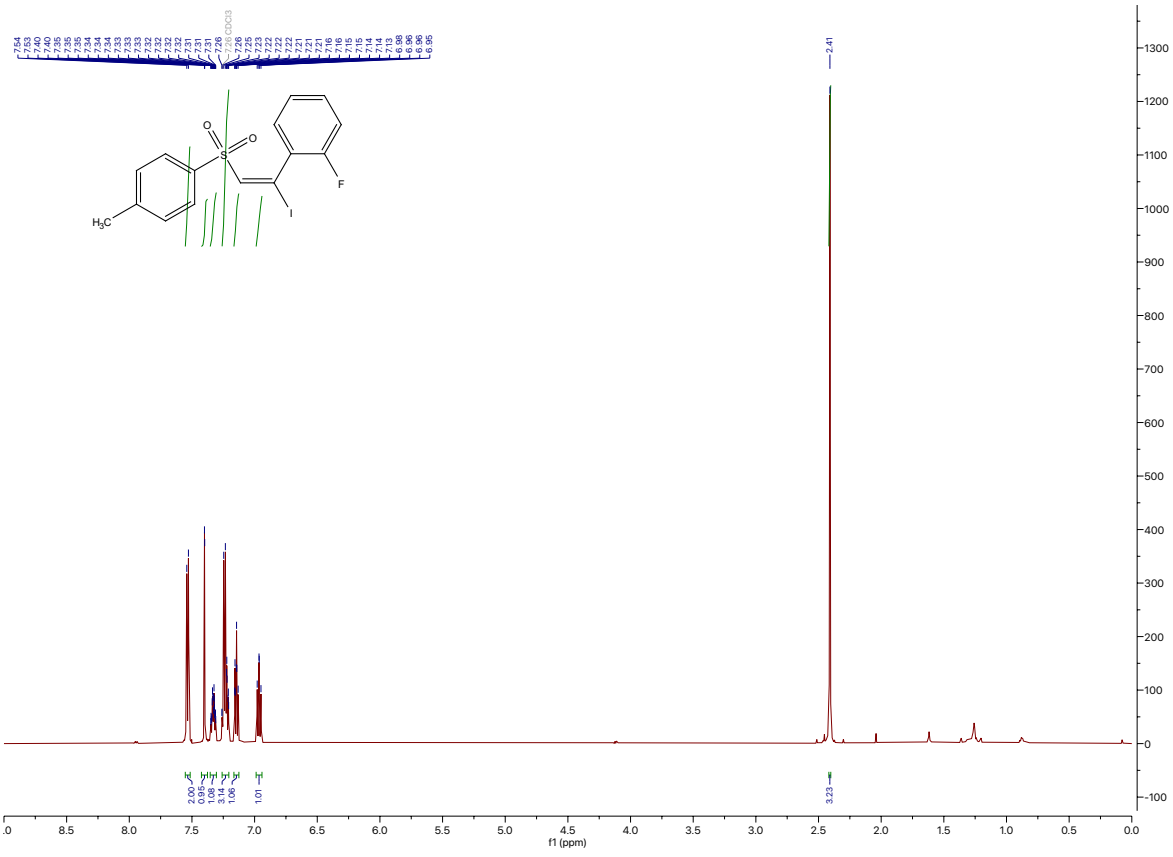

Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10h**.

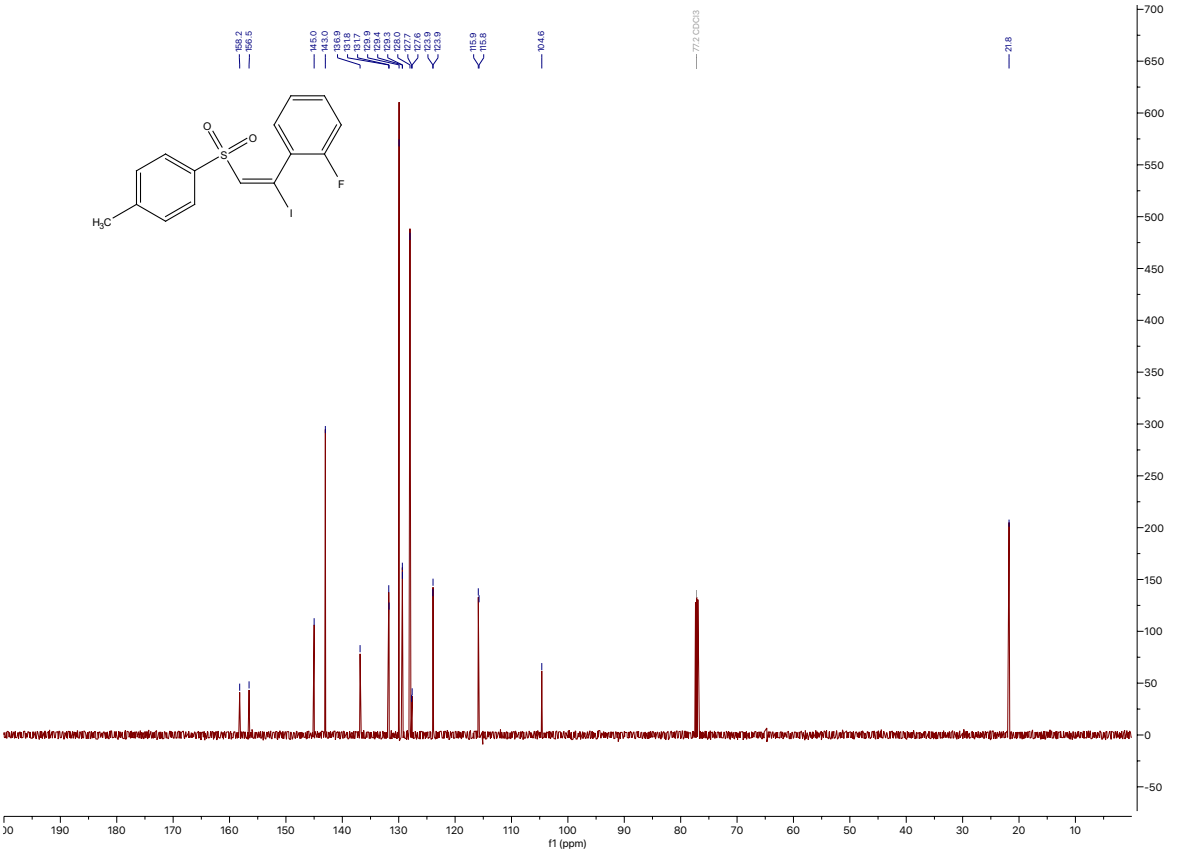

Figure S74. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of compound **10h**.

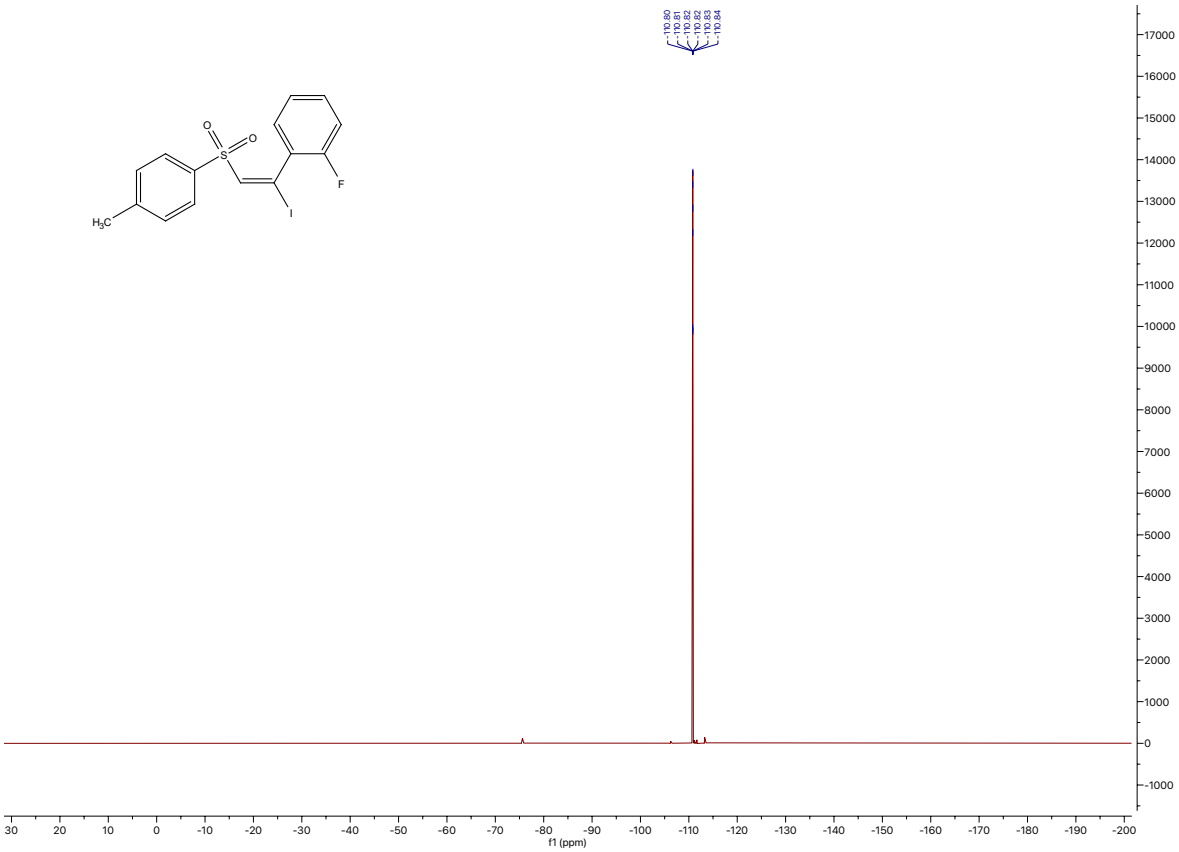

Figure S75. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10i**.

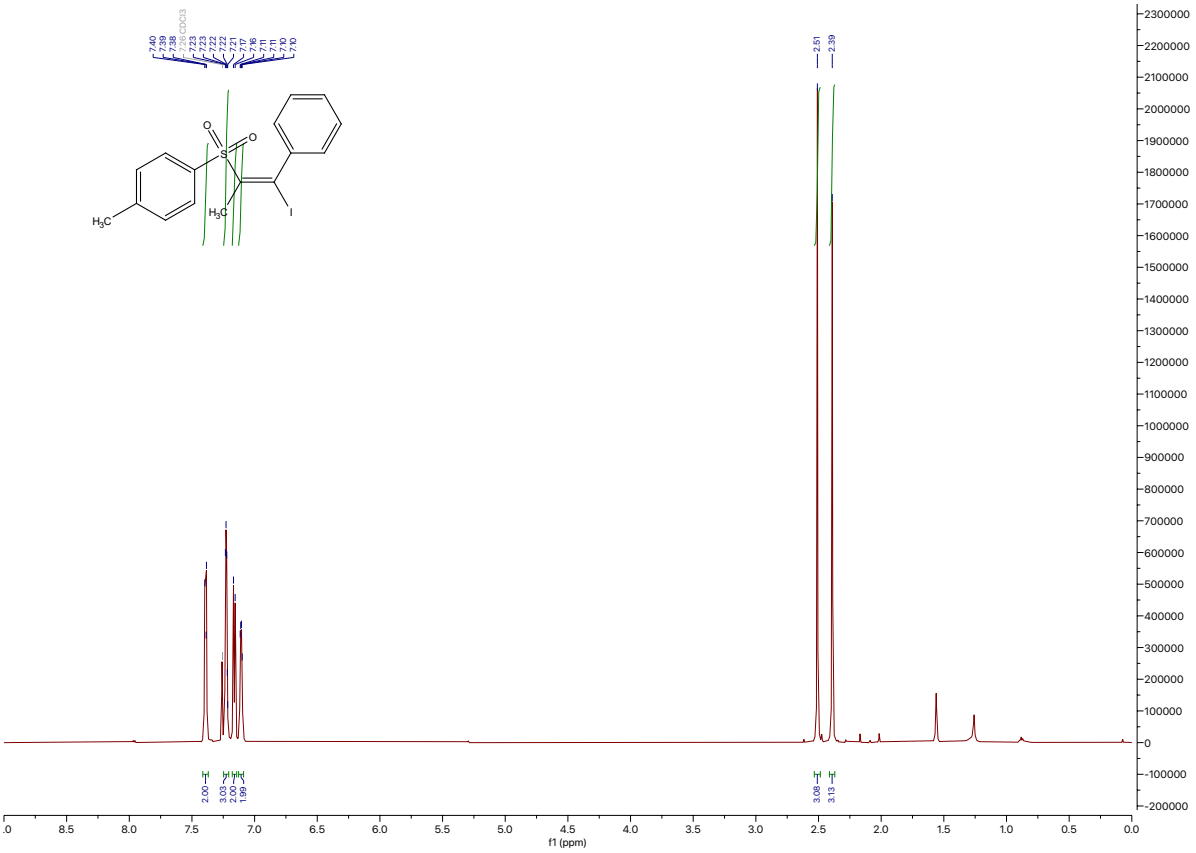

Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10i**.

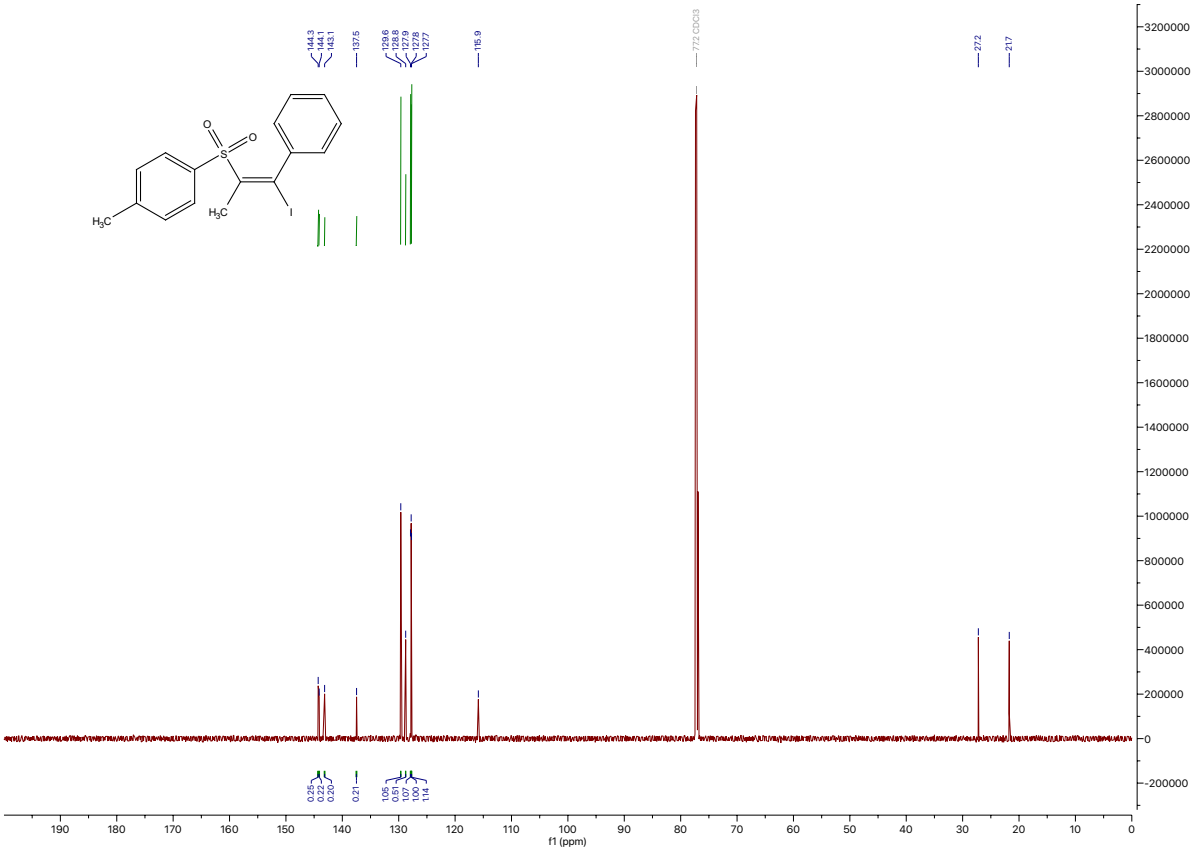

Figure S77. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **10j**.

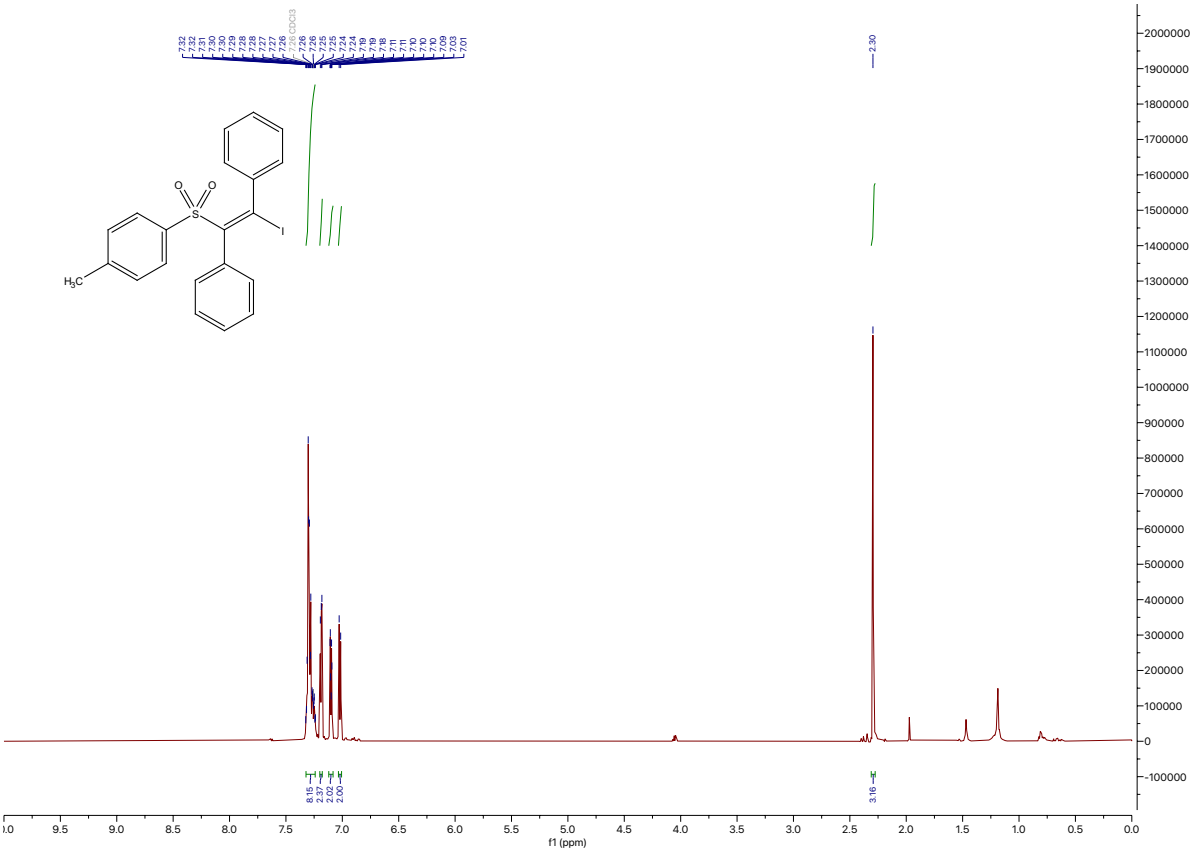

Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of compound **10j**.