Visible-light-mediated β,β-thio- and selenosulfonylation of N-ethyl tertiary amines

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Contents:

1. General Information:

All the reagents were commercial grade and used without further purification unless otherwise stated. Thiosulfonates were prepared following the literature procedure from sodium salt of sulfinates and diphenyl disulfides.[1] All the reactions were carried out in an oven-dried 10 mL vial (see below). Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel plates ($60F_{254}$) and visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4). Column chromatography was performed to purify the crude product on silica gel 60–20 mesh using a mixture of petroleum ether and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [^1H, $^{13}C\{^1H\}$ NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform ($CDCl_3$), $^{13}C\{^1H\}$ were recorded in 500 (126) or 400 (101) MHz spectrometer and were calibrated using tetramethylsilane or residual undeuterated solvent for ^1H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm or $CHCl_3$: 7.260 ppm for ^1H NMR, 77.230 ppm for ^{13}C NMR}. ^{19}F and ^{77}Se NMR spectra were calibrated without an internal standard in $CDCl_3$. The chemical shifts are quoted in δ units, parts per million (ppm). ^1H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, integration and coupling constant(s) *J* in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded in neat and reported in the frequency of absorption (cm^{-1}). All UV experiments were performed in 3 mL quartz cuvettes of path length 1 cm at 25 °C in a UV-Vis spectrometer in HPLC-grade DMSO.

2. Light Information and Reaction Setup

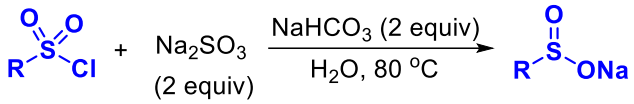
Philips 2 × 10 W white LEDs (light flux: 46 mW/cm²) were employed as the light source for this photoinduced reaction, and no optical filter was used. A 10 mL borosilicate vial served as the reaction vessel, positioned approximately 2–3 cm from the light source. A small air circulating fan was used to ventilate the setup and maintain the room temperature at 27–30 °C. The experimental setup for this photochemical reaction is shown in (Figure S1).

Figure S1. Photochemical reaction set-up

3. General Procedure:

(i) Procedure for the Synthesis of Sodium sulfinates:

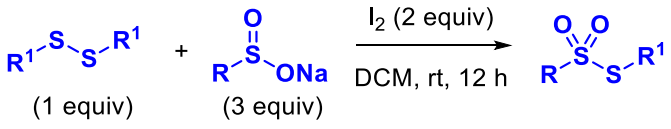
An oven-dried 50 mL round-bottom flask was charged with sulfonyl chloride (10 mmol), sodium sulfite (2.50 g, 20 mmol), and sodium bicarbonate (1.68 g, 20 mmol) in water (10 mL), and the mixture was stirred at 80 °C for 4 h. After complete consumption of sulfonyl chloride (as indicated by TLC analysis), the reaction mixture was concentrated under reduced pressure to remove water. The resulting solid residue was collected by filtration under vacuum and recrystallized from ethanol to afford the product as a white solid (Scheme S1).



Scheme S1. Synthesis of sodium sulfonate

(ii) Procedure for the Synthesis of Thiosulfonates (1):

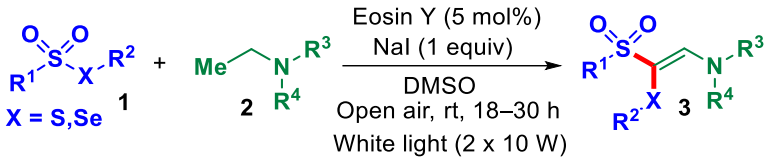
To an oven-dried 50 mL round-bottom flask were added disulfide (2 mmol), sulfinate (6 mmol), and iodine (1.01 g, 4 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 12 h. After complete consumption of disulfide (monitored by TLC), the reaction mixture was diluted with dichloromethane (10 mL) and washed sequentially with water (10 mL) followed by 5% aqueous sodium thiosulfate solution (10 mL). The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using 5% ethyl acetate in petroleum ether as eluent to afford the pure thiosulfonates (Scheme S2).



Scheme S2. Synthesis of thiosulfonates

(iii) Procedure for synthesis of *β, β*-thiosulfonylated/selenosulfonylated enamins (3)

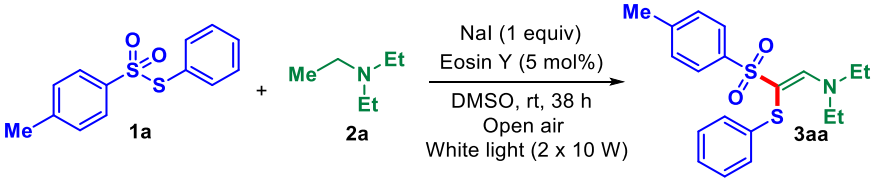
An oven-dried 10 mL vial was charged with thiosulfonate (**1)** (0.25 mmol), *N*-ethyl tertiary amine (**2**) (1.5 equiv, 0.375 mmol), sodium iodide (1 equiv, 0.25 mmol), and eosin Y (5 mol%) in dimethyl sulfoxide (1 mL). The reaction mixture was stirred at room temperature for 18–30 h, positioned approximately 2–3 cm from two 10 W white LED light sources. Reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction was quenched with water (5 mL), followed by extraction with ethyl acetate (3 × 10 mL). The combined organic layers were washed with 10 mL of 5% aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 15% ethyl acetate in petroleum ether as the eluent to yield the pure enamines (**3)** (Scheme S3).



Scheme S3. Synthesis of *β, β*-thiosulfonylated/selenosulfonylated enamines

Scale-up procedure

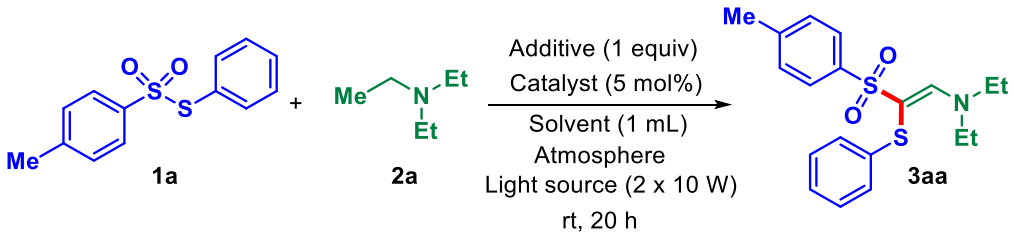
An oven-dried 25 mL vial was charged with *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) (330 mg, 1.25 mmol), triethyl amine (0.26 mL, 1.875 mmol), sodium iodide (188 mg, 1.25 mmol), and eosin Y (40 mg, 0.0625 mmol) in dimethyl sulfoxide (5 mL). The reaction mixture was stirred at room temperature for 38 h, positioned approximately 2–3 cm from two 10 W white LED light sources. Reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction was quenched with water (10 mL), followed by extraction with ethyl acetate (3 × 15 mL). The combined organic layers were washed with 10 mL of 5% aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 15% ethyl acetate in petroleum ether as the eluent to yield (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (**3a**) in 59% (268 mg) yield (Scheme S4).



Scheme S4. Scale-up synthesis of (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (**3aa**)

4. Optimization of the Reaction

Table S1. Optimisation of the reaction[a]



Entry	Solvent	Photocatalyst	Additive (1 equiv)	[b]Yield (%)
1	DMSO	Eosin Y	-	15
2	DMSO	-	-	n. r.
3	DMSO	Eosin Y	I_2	33
4	DMSO	Eosin Y	NH_4I	25
5	DMSO	Eosin Y	TBAI	65
6	DMSO	Eosin Y	LiI	55
7	DMSO	Eosin Y	CuI	0
8	DMSO	Eosin Y	NaI	71
9	DMSO	Eosin Y	TBAB	8
10	DMSO	Eosin Y	KBr	13
11	DMSO	Eosin Y	TBACl	Trace
12[c, d]	DMSO	Eosin Y	NaI	n. r.
13[e]	DMSO	Eosin Y	NaI	35
14[f]	DMSO	Eosin Y	NaI	Trace
15	DMSO	-	NaI	11
16	DMSO	$Ru(bpy)_3Cl_2$	NaI	Trace
17	DMSO	Riboflavin	NaI	32
18	DMSO	4CzIPN	NaI	34
19	DMSO	Rose Bengal	NaI	60
20	DMA	Eosin Y	NaI	15
21	DMC	Eosin Y	NaI	0
22	DMF	Eosin Y	NaI	18
23	CH_3CN	Eosin Y	NaI	53

[a]Reaction Conditions unless specified otherwise: **1a** (0.25 mmol), **2a** (0.375 mmol), Additive (0.25 mmol), solvent (1 mL) in 2 x 10 W white LEDs for 20 h. [b]Isolated yield, [c]reaction in dark, [d]N_2 atmosphere, [e](2 x 10 W) blue LEDs, [f](2 x 10 W) green LEDs, n. r. = no reaction.

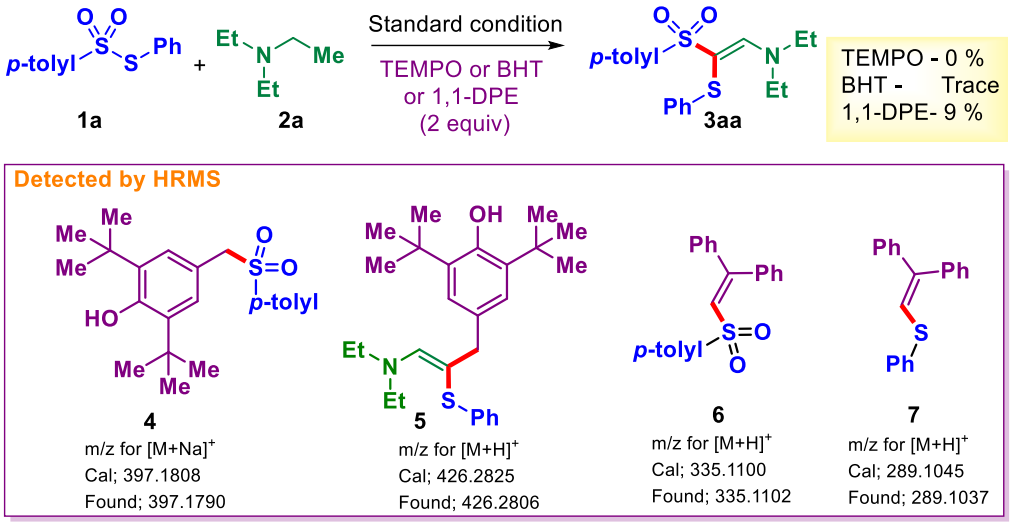
To find the optimal reaction condition, we commenced the investigation by selecting *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) and triethylamine (**2a**) as the model reacting partners. In our initial attempt, the anticipated *β,β*-thiosulfonylated product (**3aa**), was obtained in a modest yield of 15% when the reaction mixture containing *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) (0.25 mmol), and triethylamine (**2a**) (0.375 mmol), was subjected to irradiation under white light (2 × 10 W) in DMSO in the presence of eosin Y (5 mol%) under open-air conditions (Table S1, entry 1). The structure of the product (**3aa**) was confirmed by NMR spectroscopy (^1H and ^{13}C NMR) and further verified by single-crystal X-

ray diffraction (Scheme 2). The ideal condition for the maximum possible yield of (**3aa**) was established through systematic variation of additives, photocatalysts, solvents, atmospheric conditions, and light sources. No formation of (**3aa**) was observed in the absence of Eosin Y and NaI, with only the starting material recovered (Table S1, entry 2), suggesting their essential role. In contrast, the addition of I_2 afforded (**3aa**) in 33% yield (Table S1, entry 3). To examine the influence of additives, various iodide sources, such as ammonium iodide (NH_4I) (25%), tetra-n-butylammonium iodide (TBAI) (65%), lithium iodide (LiI) (55%), cuprous iodide (CuI) (00%), sodium iodide (NaI) (71%) along with the bromide sources, including tetrabutylammonium bromide (TBAB) (8%), potassium bromide (KBr) (13%), and the chloride source, such as tetrabutylammonium chloride (TBACl) (trace) were tested (Table S1, entries 4-11). Among which, NaI proved to be the most effective, delivering (**3aa**) in 71% yield (Table S1, entry 8). The reaction did not proceed under dark conditions or under a nitrogen atmosphere (Table S1, entry 12), confirming the essential roles of light and the involvement of oxygen. To assess the impact of the wavelength of light and its intensity, the standard reaction was conducted using 2 × 10 W blue (419 nm) and green (534 nm) LEDs separately. A moderate yield of 35% was obtained with blue light, whereas only trace formation of **3aa** was observed under green LED illumination (Table S1, entries 13–14). Further screening of alternative photocatalysts, including $Ru(bpy)_3Cl_2$(Trace), riboflavin (32%), 4CzIPN (34%), and rose Bengal (60%), did not furnish any significant improvements (Table S1, entries 16–19). Finally, screening of different solvents such as DMA, DMC, DMF, and CH_3CN revealed that only CH_3CN furnished **3aa** in appreciable yield, while others resulted in poor conversions (Table S1, entries 20–23).

5. General Procedures of Mechanistic Investigation

(a) Procedure for radical-trapping Experiments with TEMPO or BHT or 1,1-DPE

Three sets of oven-dried 10 mL vials were charged with *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) (66 mg, 0.25 mmol), triethylamine (**2a**) (38 mg, 0.375 mmol), sodium iodide (38 mg, 0.25 mmol), and eosin Y (8 mg, 0.0125 mmol, 5 mol%) in DMSO (1 mL). To each set, one of the following radical scavengers was added: (i) 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (78 mg, 0.5 mmol), (ii) Butylated hydroxytoluene (BHT) (110 mg, 0.5 mmol), or (iii) 1,1-diphenylethylene (90 mg, 0.5 mmol). The reaction mixtures were stirred at room temperature under open-air conditions while being irradiated with 2 × 10 W white LEDs placed approximately 2–3 cm away for 20 h.



Scheme S5. Radical trapping experiment

When TEMPO was used as a radical scavenger, the reaction failed to produce compound **3aa**, as confirmed by TLC analysis. In contrast, the reaction carried out in the presence of BHT afforded only a trace amount of **3aa**, also detected by TLC. However, in the presence of 1,1-diphenylethylene (1,1-DPE), the reaction proceeded to completion (monitored by TLC). After completion, the mixture was quenched with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with 10 mL of 5% aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using 15% ethylacetate in petroleum ether as the eluent to give (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (**3aa**) in 9% yield (8 mg). These observations clearly support the radical pathway of the reaction.

Two additional sets of identical reactions were performed separately in the presence of BHT and 1,1-diphenylethylene (1,1-DPE). After 2 h of irradiation, aliquots from each reaction mixture were analyzed by HRMS. The analyses revealed the formation of sulfonyl adducts (**4** and **6**) and a thio adduct (**7**), as confirmed by their corresponding HRMS spectra (Figures S2, S3, and S4). This confirms the involvement of both thiyl and sulfonyl radicals for the formation of **3aa**. Notably, the BHT-adduct, (*Z*)-2-(3-(*tert*-butyl)-5-(3-(diethylamino)-2-(phenylthio)allyl)-2-methylphenyl)propan-2-ol (**5**), was detected by HRMS, strongly supporting the involvement of intermediate **H** (Figure S5).

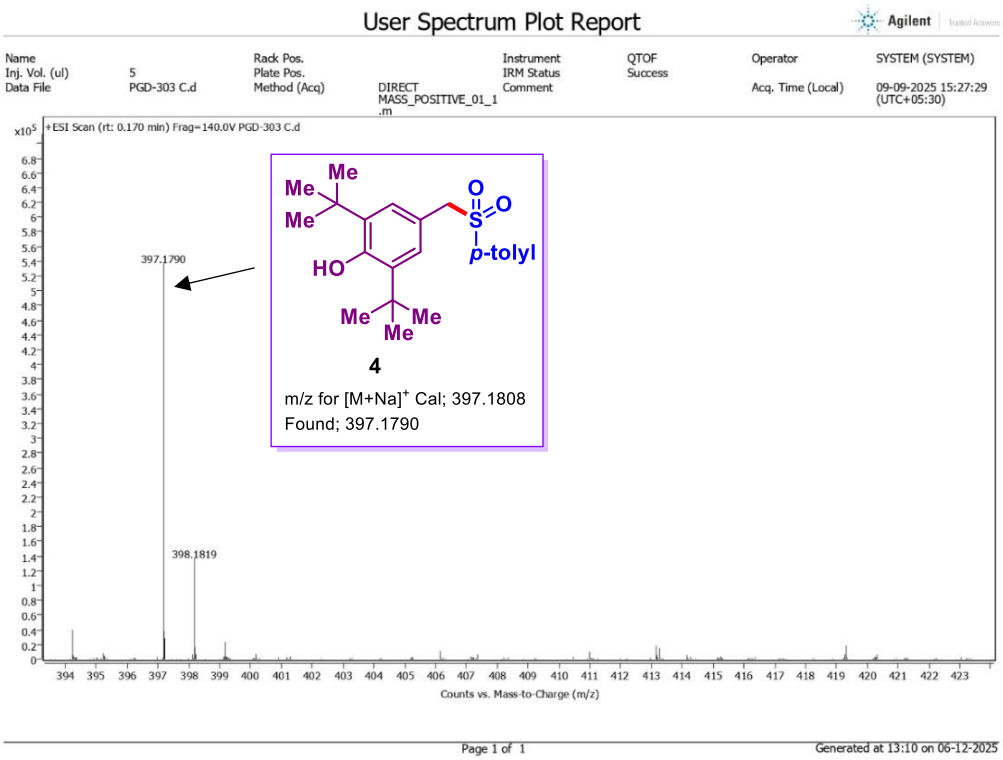


Figure S2. HRMS of BHT-tosyl adduct (**4**)

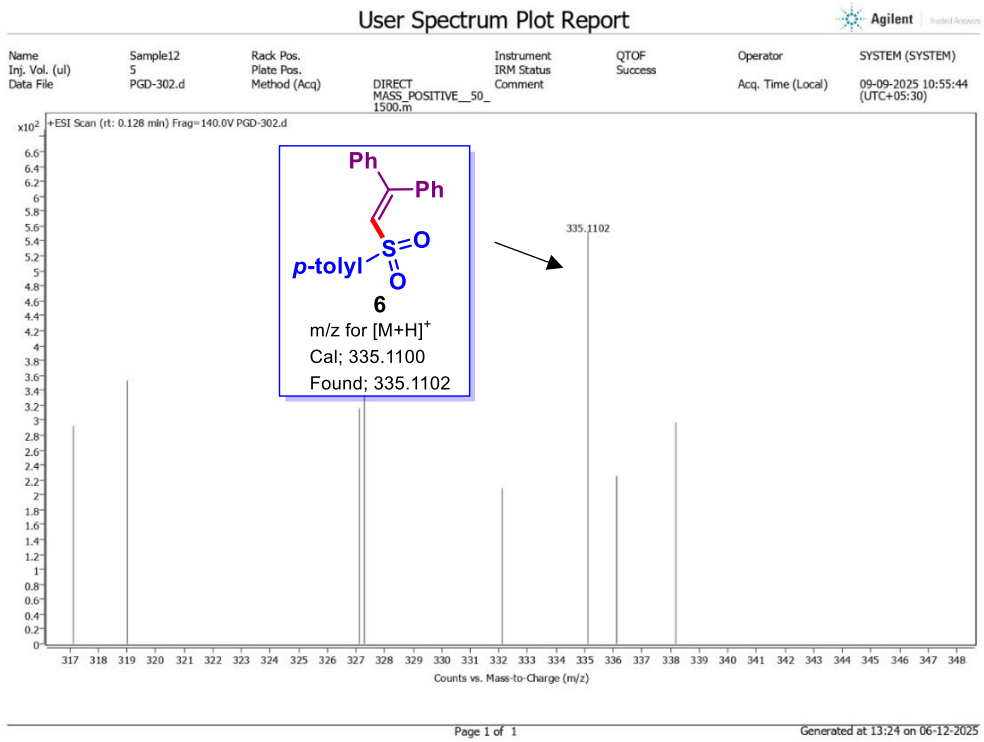


Figure S3. HRMS of 1,1-DPE-tosyl adduct (**6**)

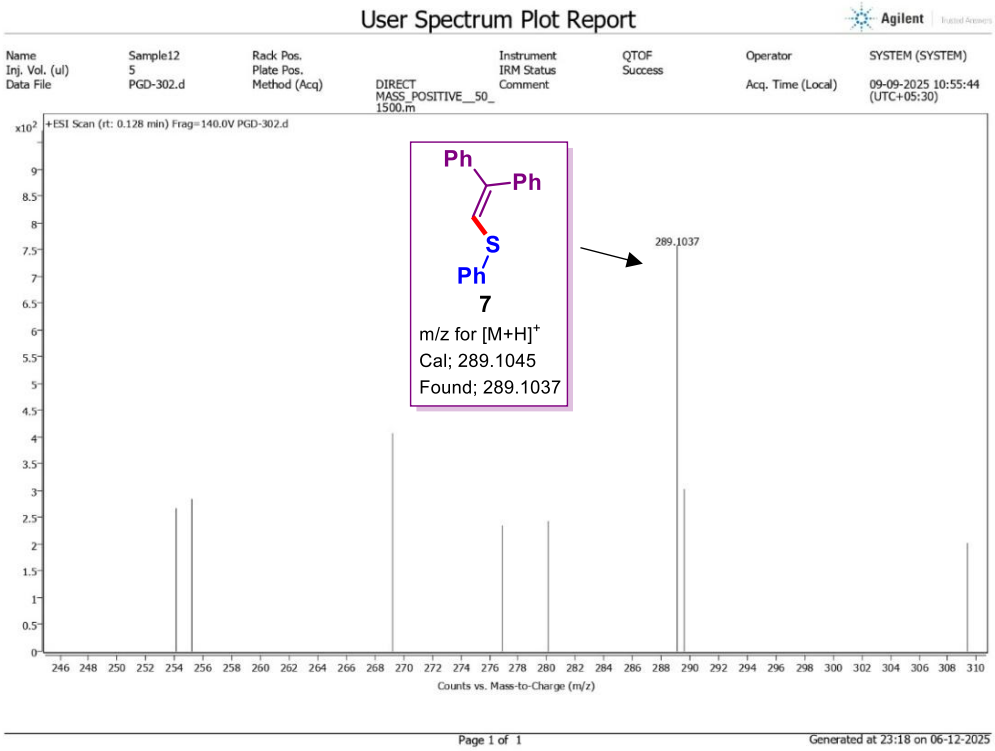


Figure S4. HRMS of 1,1-DPE-thio adduct (**7**)

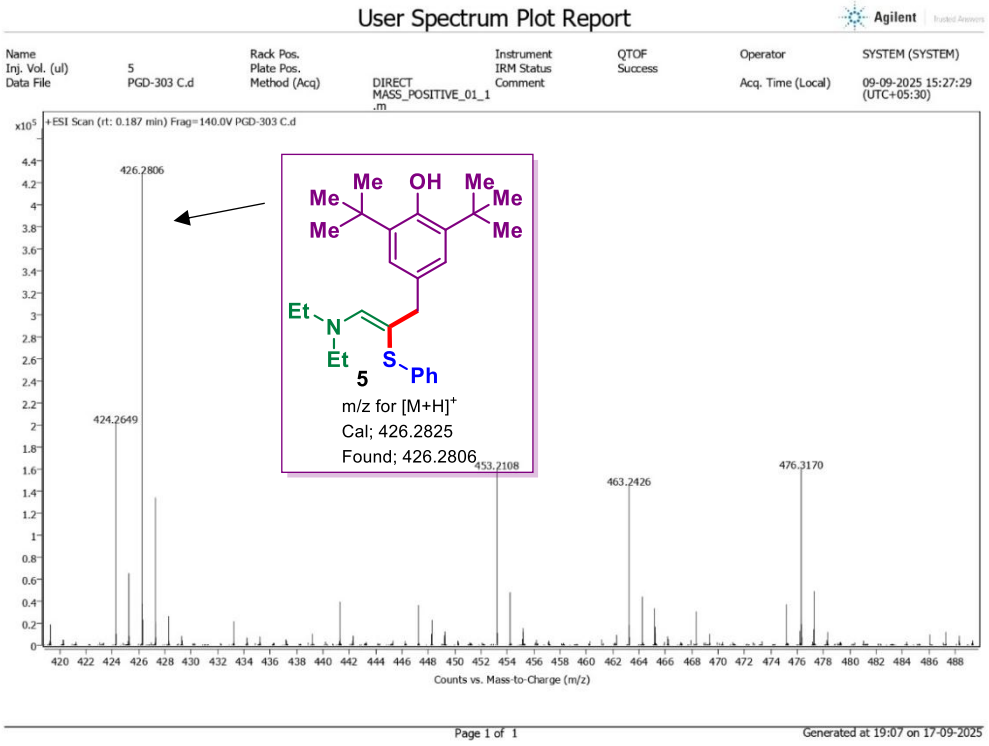
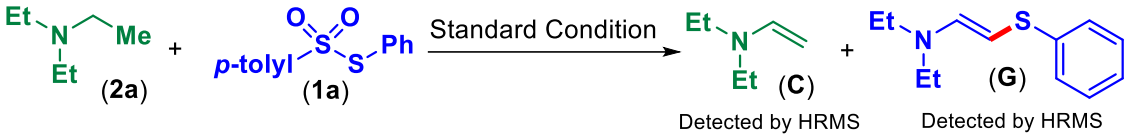


Figure S5. HRMS of BHT-intermediate adduct (**5**)

(b) Procedure for detection of intermediates

(i) Procedure for detection of *N*,*N*-diethylethenamine



Scheme S6. Detection of intermediate (**C**) and (**G**) by HRMS

An oven-dried 10 mL vial was charged with *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) (66 mg, 0.25 mmol), triethylamine (**2a**) (38 mg, 0.375 mmol), sodium iodide (38 mg, 0.25 mmol), and eosin Y (8 mg, 0.0125 mmol, 5 mol%) in DMSO (1 mL). The reaction mixture was irradiated at room temperature, positioned approximately 2–3 cm from 2 × 10 W white LED light sources. After 1 h, aliquots from reaction mixture were analyzed by HRMS, resulting in the detection of *N*,*N*-diethylethenamine ((m/z calcd. for $C_6H_{13}N$ $[M+H]^+$ 100.1121; Found 100.1108) and intermediate (*E*)-*N*,*N*-diethyl-2-(phenylthio)ethen-1-amine (m/z calcd. for $C_{12}H_{17}NS$ $[M]^+$ 207.1076; Found 207.1074). (Scheme S6, Fig. S6 and S7). These findings indicate the involvement of an *in situ* generated intermediate *N*,*N*-substituted ethenamine and intermediate (**G**).

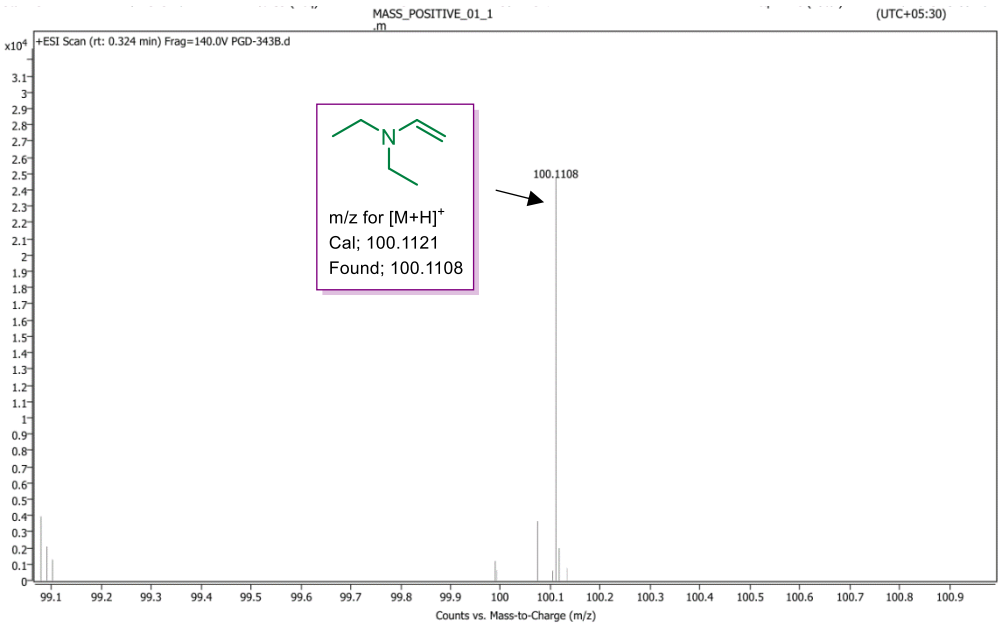


Figure S6. HRMS of intermediate *N*,*N*-diethylethenamine (**C**)

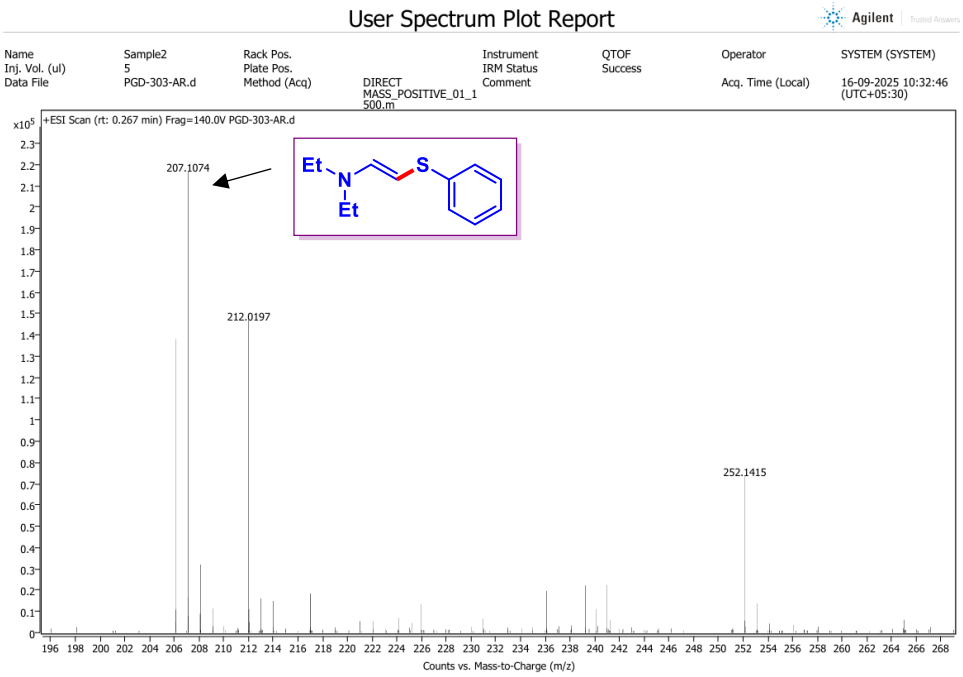
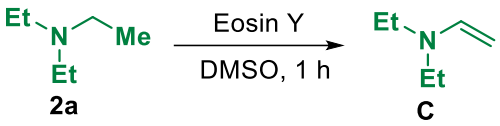


Figure S7. HRMS of intermediate (*E*)-*N*,*N*-diethyl-2-(phenylthio)ethen-1-amine



Scheme S7. Detection of *N*,*N*-diethylethenamine by HRMS

An oven-dried 10 mL vial was charged with triethyl amine (**2a**) (15 mg), and eosin Y (3 mg) in dimethyl sulfoxide (0.5 mL). The reaction mixture was irradiated at room temperature, positioned approximately 2–3 cm from 2 × 10 W white LED light sources. After 1 h, aliquots from the reaction mixture were analyzed by HRMS, resulting in the detection of *N*,*N*-diethylethenamine ((m/z calcd. for $C_6H_{13}N$ $[M+H]^+$ 100.1121; Found 100.1110) (Scheme S7, Fig. S8). This experiment confirms that the enamine intermediate is generated *in situ* from the oxidation of triethyl amine in the presence of eosin Y.

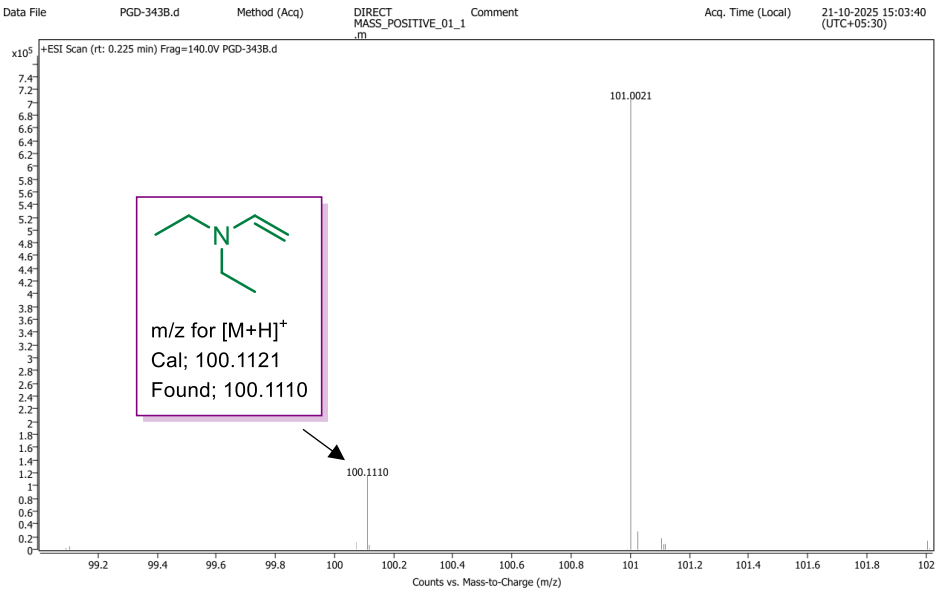
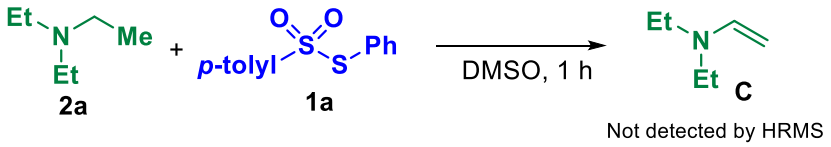


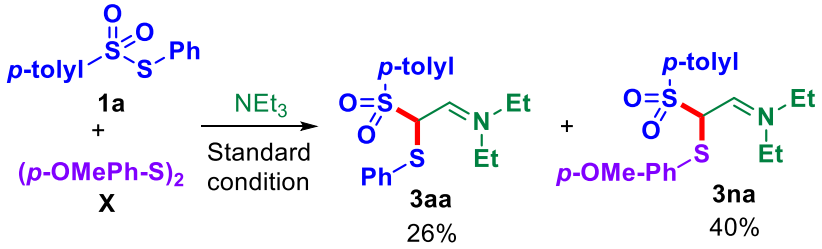
Figure S8. HRMS of intermediate *N*,*N*-diethylethenamine (**C**)



Scheme S8. Ruling out of generation of *N*,*N*-diethylethenamine by EDA formation

An oven-dried vial (10 mL) was charged with substrate **1a** (66 mg) and triethylamine (**2a**, 38 mg) in DMSO (1.0 mL). The mixture was stirred at room temperature under irradiation from 2 × 10 W white LED positioned approximately 2–3 cm from the reaction vessel for 20 h. Aliquots from the reaction mixture were analysed by HRMS. However, the formation of *N*,*N*-diethylethenamine could not be detected by HRMS. This experiment ruled out the generation of *N*,*N*-substituted ethenamine intermediate via an EDA complex between thiosulfonates and NEt_3 (Scheme S8).

(ii) Procedure to establish the source of thiyl radicals



Scheme S9. Procedure to establish the source of thiyl radicals

An oven-dried 10 mL vial was charged with *S*-phenyl 4-methylbenzenesulfonothioate (**1a)** (64 mg, 0.25 mmol), 1,2-*bis*(4-methoxyphenyl)disulfane (70 mg, 0.25 mmol), triethyl

amine (**2a**) (38 mg, 0.375 mmol), sodium iodide (38 mg, 0.25 mmol), and eosin Y (8 mg, 0.0125 mmol) in dimethyl sulfoxide (1 mL). The reaction mixture was stirred at room temperature for 20 h, positioned approximately 2–3 cm from 2 × 10 W white LED light sources. Reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction was quenched with water (5 mL), followed by extraction with ethyl acetate (3 × 10 mL). The combined organic layers were washed with 5% aqueous sodium thiosulfate solution, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 15% ethyl acetate in petroleum ether as the eluent to yield **3aa** and **3na** in 26% and 40%, respectively (Scheme S9). This observation indicates that, in addition to thiosulfonates, *in situ*-generated disulfides can also serve as a source of thiyl radicals during the reaction process.

(c) H_2O_2 Detection in the reaction mixture

(i) H_2O_2 detection in a reaction with KMnO4

An oven-dried vial (10 mL) was charged with triethylamine (**2a**, 38 mg) and eosin Y (8 mg) in DMSO (1 mL). The mixture was stirred at room temperature under irradiation from 2 × 10 W white LED lamps positioned approximately 2–3 cm from the reaction vessel for 20 h. In a separate test tube, a dilute aqueous $KMnO_4$ solution was freshly prepared. An aliquot of the photoreaction mixture was added to the $KMnO_4$ solution (Figure S9a). The immediate decolorization of the purple solution to pale yellow (Figure S9b) indicated the presence of H_2O_2 in the reaction mixture.

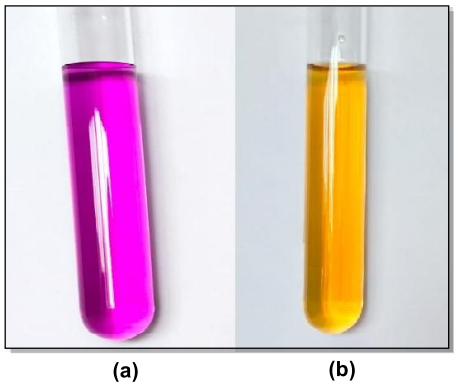


Figure S9. (a) $KMnO_4$ solution (b) $KMnO_4$ solution after addition of the reaction mixture.

(ii) H_2O_2 detection by iodometry

An oven-dried vial (10 mL) was charged with triethylamine (**2a**, 38 mg) and eosin Y (8 mg) in DMSO (1 mL). The mixture was stirred at room temperature under irradiation from two

10 W white LED lamps positioned approximately 2–3 cm from the reaction vessel for 20 h. In a separate test tube, a KI-starch solution was freshly prepared by combining aqueous KI solution (0.2 mmol in 1.5 mL H_2O), H_2SO_4 (0.02 M, 1.0 mL), and a freshly prepared starch solution (0.5 mL). An aliquot of the photoreaction mixture was added to the KI-starch reagent (Figure S10a) and vigorously stirred. The immediate development of a dark blue colour (Figure S10b) confirmed the presence of H_2O_2 in the reaction mixture.

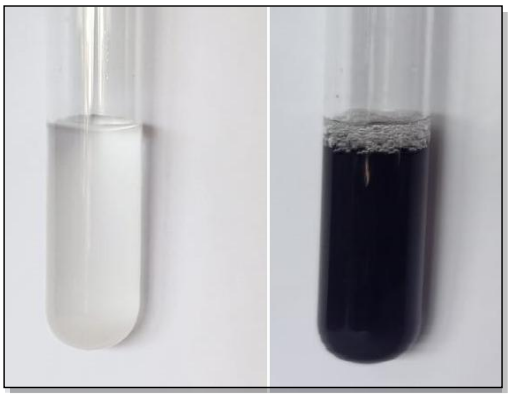


Figure S10. (a) Portion of the freshly prepared KI starch solution in 0.02 M H_2SO_4. (b) Appearance of dark blue colour due to the formation of I_2-starch complex (H_2O_2 detected).

(iii) Generation of H_2O_2 via EDA complex between 1a and NEt_3 by iodometry test

An oven-dried vial (10 mL) was charged with substrate **1a** (66 mg) and triethylamine (**2a**, 38 mg) in DMSO (1.0 mL). The mixture was stirred at room temperature under irradiation from two 10 W white LED lamps positioned approximately 2–3 cm from the reaction vessel for 20 h. In a separate test tube, a KI-starch reagent was freshly prepared by combining aqueous KI solution (0.2 mmol in 1.5 mL H_2O), H_2SO_4 (0.02 M, 1.0 mL), and a freshly prepared starch solution (0.5 mL). An aliquot of the photoreaction mixture was added to the KI-starch reagent (Figure S11a) and vigorously stirred. The absence of blue colour (Figure S11b) indicated that H_2O_2 was not present. This test rules out any reaction pathway involving H_2O_2 generation from the interaction between **1a** and NEt_3.

Figure S11. (a) Portion of the freshly prepared KI starch solution in 0.02 M H_2SO_4. (b) Non-appearance of dark blue colour (H_2O_2 not detected).

6. UV-Vis Experiments

Stock solutions (0.05 M, 10 mL) of *S*-phenyl 4-methylbenzenesulfonothioate (**1a**), NaI, and triethylamine (NEt_3) were prepared separately in DMSO. Initially, the UV-vis absorption spectra of individual components (**1a**, NaI, and NEt_3; 3.0 mL each) were recorded, none of which exhibited absorption in the visible region (Figure S12). Subsequently, binary combinations of (**1a** + NaI), (NaI + NEt_3), and (**1a** + NEt_3) were prepared at a 1:1 ratio (1.5 mL:1.5 mL) in 3.0 mL cuvettes. The (NaI + **2a**) mixture showed no absorption in the visible region. In contrast, the (**1a** + NaI) combination produced a yellow colouration with strong visible absorption, suggesting EDA complex formation between **1a** and NaI. Additionally, the (**1a** + NEt_3) mixture exhibited weak absorption in the visible region compared to (**1a** + NaI). A ternary mixture of **1a**, NaI, and NEt_3 (1.0 mL each) was then prepared in a 3.0 mL cuvette, which displayed an intense yellow colour with an absorption maximum in the visible region, further supporting EDA complex formation (Figure S12). These results demonstrate that both (**1a** + NaI) and (**1a** + NaI + NEt_3) absorb visible light, with the (**1a** + NaI) combination exhibiting significantly stronger absorption than (**1a** + NEt_3). This confirms that a strong EDA complex forms primarily between **1a** and NaI (Figure S12).

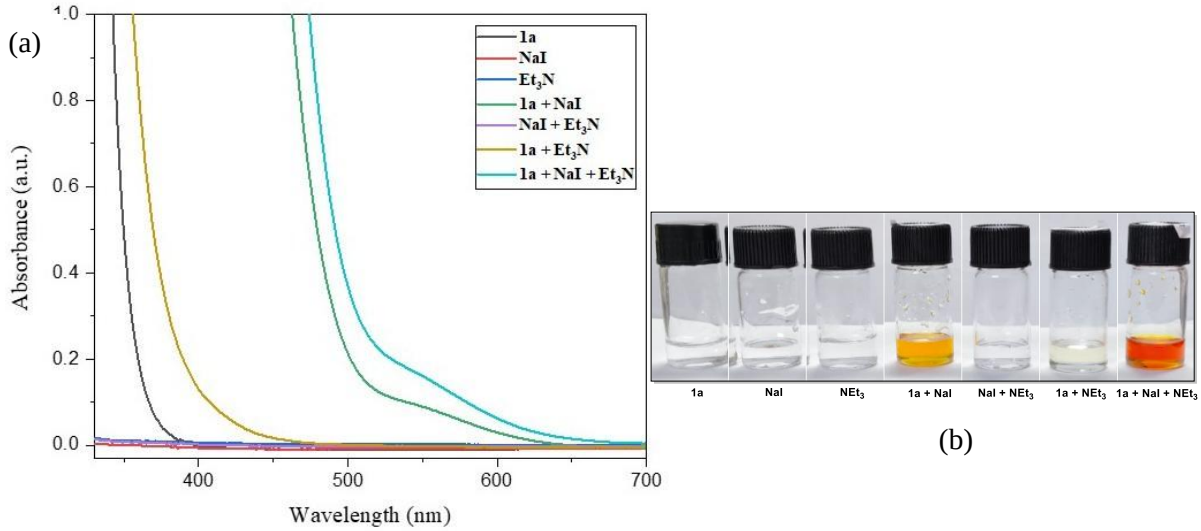


Figure S12. (a) UV-Vis spectra for EDA complexation (b) Colour change for the formation of EDA complex

7. ^{1}H NMR Experiments

To further confirm the formation of the EDA complex, a series of ^{1}H NMR experiments was performed in DMSO-d_6 using *S*-phenyl 4-methylbenzenesulfonothioate (**1a**) and NaI in different ratios. Solutions were prepared with a constant amount of **1a** (0.02 mmol) and increasing amounts of NaI (**1a** : NaI = 1:0, 1:1, 1:2, 1:3, 1:4, and 1:5). Each of the six mixtures was initially prepared in separate 1.5 mL microcentrifuge tubes. To each tube, 5 mg of **1a** was added. Tube 1 contained only **1a** (1:0). Varying amounts of NaI were then added to the remaining tubes to achieve the desired ratios: 3 mg for 1:1, 6 mg for 1:2, 9 mg for 1:3, 12 mg for 1:4, and 15 mg for 1:5. DMSO-d_6 was added to each tube to reach a final volume of 400 µL. The resulting solutions were transferred to NMR tubes, and ^{1}H NMR spectra were recorded. With increasing equivalents of NaI, the signal corresponding to the *para*-methyl group of **1a** progressively shifted upfield, consistent with an interaction between **1a** and NaI and indicative of EDA complex formation (Figures S13 and S14).

Table S2: ^{1}H NMR δ_{Me} (ppm) value for the ratio of la, NaI

Entry	**1a** (mmol)	NaI (mmol)	**1a** : NaI	δ_{Me} (ppm)
1	0.02	0	1:0	3.343
2	0.02	0.02	1:1	3.345
3	0.02	0.04	1:2	3.354
4	0.02	0.06	1:3	3.358
5	0.02	0.08	1:4	3.364
6	0.02	0.10	1:5	3.371

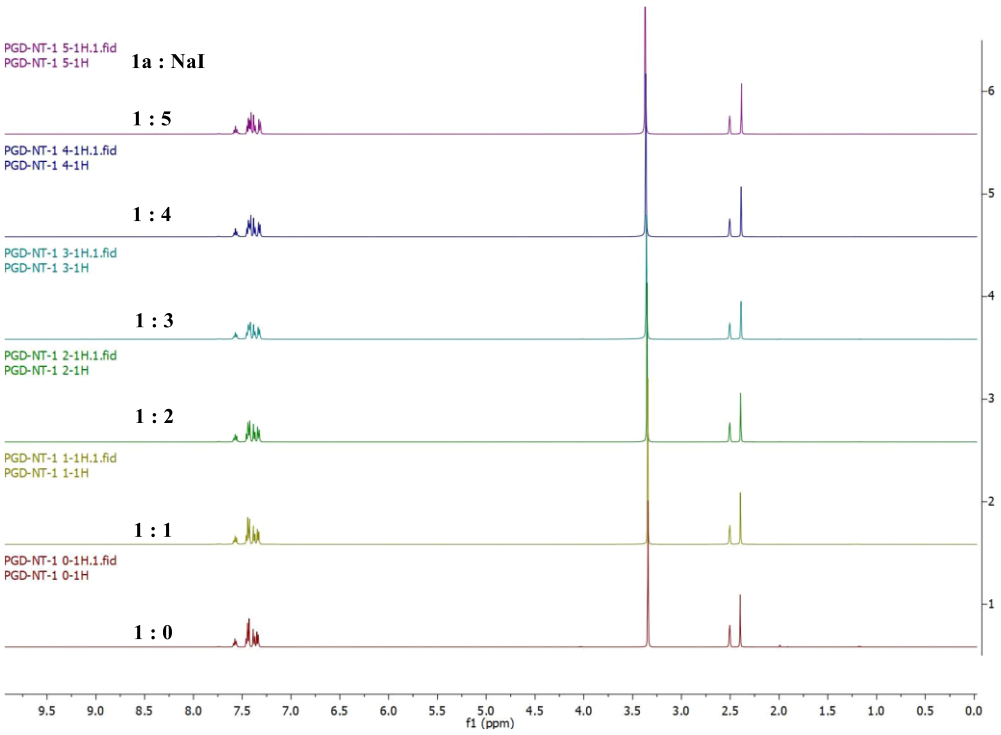


Figure S13. Full ^{1}H NMR spectra of **1a** and NaI in different ratios

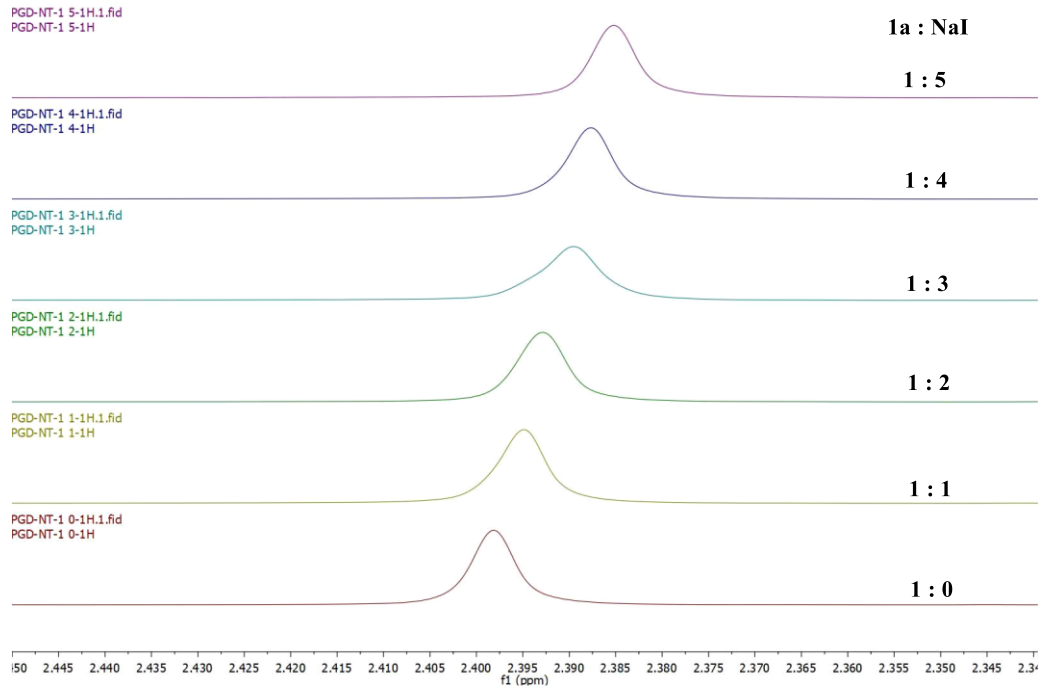


Figure S14. Evidence for the formation of EDA complex through ^{1}H NMR

8. Crystallographic Information

Sample Preparation:

The single crystal of compound **3aa** was prepared by the slow evaporation method for which 20 mg of the compound (**3a**) was dissolved in 0.2 mL methanol. The mouth of the glass vial was covered with a cap having a small hole and kept for slow evaporation at room temperature. Crystals of **3a** were obtained as white crystals after 3 days.

Data Collection:

Diffraction data were collected at 298 K with MoKα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator and Apex CD camera. The SMART software was used for data collection for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT[2,3] software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-97[4] software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections.

Crystallographic Description of (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (3aa):

$C_{19}H_{23}NO_2S_2$, Mr = 361.50, monoclinic, space group C 2/c, a = 34.921(3), b = 5.8632(6), c = 24.090(3) Å, α = 90, β = 131.034(5), γ = 90, *V* = 3720.6(7) $Å^3$, *Z* = 8, ρ_{calcd} = 1.291 g/cm^3, μ = 0.297 mm^{-1}, F(000)= 1536.0, reflection collected / unique = 3248 / 2698, refinement method = full-matrix least-squares on F2, final R indices [I> 2\s(I)]:R1 = 0.0691, wR2 = 0.1955, R indices (all data): R1 = 0.0867, wR2 = 0.2122, goodness of fit = 1.553. CCDC-2502000 for (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (**3aa**) contains the supplementary crystallographic data for this paper (Figure S15). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

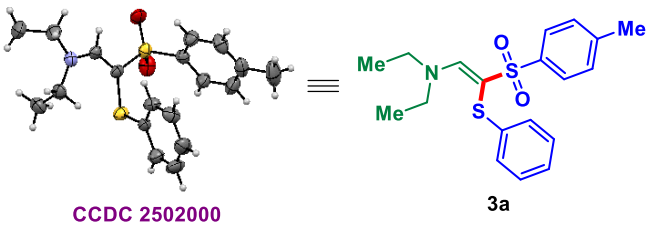


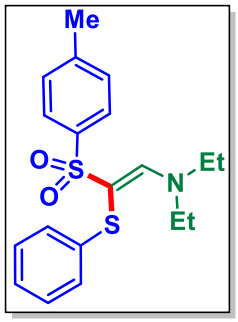
Figure S15. ORTEP diagram of (*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (**3aa**) (CCDC 2502000)

9. References:

1. D. Barik, N. Chakraborty, A. K. Sahoo, H. N. Dhara and B. K. Patel. *Chem. Commun.*, 2024, **60**, 12577.
2. R. H. Blessing, *Acta Crystallogr*., 1995, **A51**, 33–38.
3. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
4. G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr.*, 2008, **A64**, 112–122.

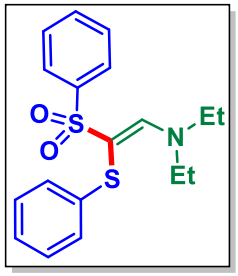
10. Spectral Data

(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (3aa)



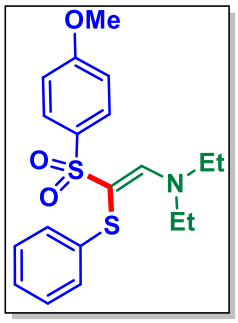
Compound **3aa** was obtained as a white solid (64 mg, 71% yield) by following the general procedure, after 20 h of reaction. mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.13–7.09 (m, 4H), 7.03–7.00 (m, 3H), 3.58 (s, 2H), 3.35 (s, 2H), 2.31 (s, 3H), 1.25 (s, 3H), 1.07 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.9, 142.6, 139.4, 138.9, 129.2, 128.8, 128.0, 125.1, 125.0, 91.6, 52.6, 42.2, 21.6, 15.1, 14.2; IR (neat, cm^{-1}): 3057, 2976, 2930, 2873, 1595, 1339, 1280, 1135, 1082, 903, 738, 657, 584, 555; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_2S_2$ $[M+H]^+$ 362.1243; Found 362.1235.

(*E*)-*N*,*N*-diethyl-2-(phenylsulfonyl)-2-(phenylthio)ethen-1-amine (3ba)



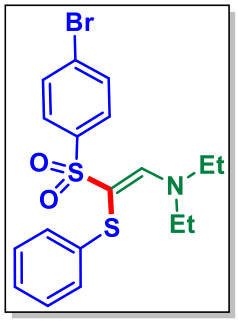
Compound **3ba** was obtained as a yellow solid (62 mg, 72% yield) by following the general procedure, after 20 h of reaction. mp 78–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.39–7.30 (m, 3H), 7.12–7.08 (m, 2H), 7.01 –6.98 (m, 3H), 3.58 (s, 2H), 3.34 (s, 2H), 1.26 (s, 3H), 1.06 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.1, 142.4, 138.7, 131.9, 128.8, 128.5, 127.9, 125.2, 124.8, 91.1, 52.6, 42.2, 15.1, 14.1; IR (neat, cm^{-1}): 3058, 2976, 1595, 1580, 1444, 1338, 1281, 1135, 1082, 903, 736, 687, 596, 566; HRMS (ESI) m/z calcd for $C_{18}H_{21}NO_2S_2$ $[M+H]^+$ 348.1086; Found 348.1085.

(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ca)



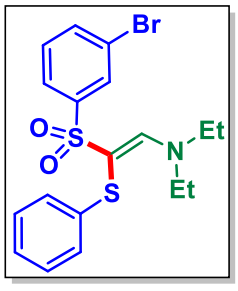
Compound **3ca** was obtained as a white solid (66 mg, 70% yield) by following the general procedure, after 18 h of reaction. mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.74 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.12–7.08 (m, 2H), 7.01-6.98 (m, 3H), 6.76 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 3.57 (s, 2H), 3.32 (s, 2H), 1.26–1.24 (m, 3H), 1.07–1.05 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.4, 151.5, 138.8, 133.9, 130.0, 128.8, 125.1, 124.9, 113.7, 91.6, 55.6, 52.6, 42.1, 15.0, 14.1; IR (neat, cm-1): 3057, 2975, 2935, 1592, 1495, 1282, 1254, 1131, 1083, 1023, 902, 737, 669, 584, 559; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_3S_2$ $[M+H]^+$ 378.1192; Found 378.1183.

(*E*)-2-((4-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3da)



Compound **3da** was obtained as a yellow solid (64 mg, 60% yield) by following the general procedure, after 22 h of reaction. mp 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.67 (d, J = 8 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8 Hz, 2H), 3.62–3.59 (m, 2H), 3.36–3.34 (m, 2H), 1.30–1.25 (m, 3H), 1.09–1.06 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.2, 141.3, 138.4, 131.7, 129.6, 128.9, 126.9, 125.4, 124.9, 90.9, 52.8, 42.3, 15.0, 14.1; IR (neat, cm^{-1}): 3058, 2976, 2934, 2875, 1596, 1298, 1136, 1081, 904, 762, 735, 610, 571; HRMS (ESI) m/z calcd for $C_{18}H_{20}BrNO_2S_2$ $[M+H]^+$ 426.0192; Found 426.0188.

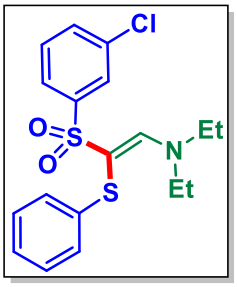
(*E*)-2-((3-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ea)



Compound **3ea** was obtained as a yellow solid (61 mg, 57% yield) by following the general procedure, after 23 h of reaction. mp 87–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.95–7.94 (m, 1H), 7.78–7.75 (m, 1H), 7.47–7.42 (m, 1H), 7.17–7.09 (m, 3H), 7.04–6.96 (m, 3H), 3.64–3.60 (m, 2H), 3.38–3.34 (m, 2H), 1.32–1.26 (m, 3H), 1.11–1.07 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.4, 144.2, 138.2, 134.8, 130.9, 129.9, 128.9, 126.7, 125.4, 124.9, 122.5, 90.6, 52.8, 42.3, 15.0, 14.1; IR (neat, cm^{-1}): 3059, 2976, 2934, 1597, 1460, 1285,

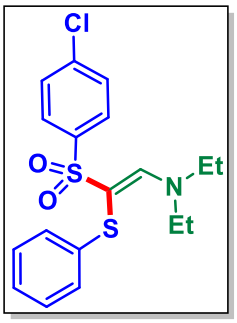
1139, 1076, 772, 679, 655, 604, 574; HRMS (ESI) m/z calcd for $C_{18}H_{20}BrNO_2S_2$ $[M+H]^+$ 426.0192; Found 426.0194.

(*E*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylthio)ethen-1-amine (3fa)



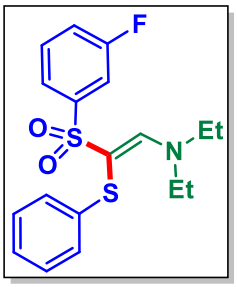
Compound **3fa** was obtained as a white solid (54 mg, 56% yield) by following the general procedure, after 26 h of reaction. mp 93–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.79–7.73 (m, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.21 (t, J = 8 Hz, 1H), 7.11 (t, J = 7.5 Hz, 2H), 7.03–6.97 (m, 3H), 3.62–3.60 (m, 2 H), 3.39–3.34 (m, 2H), 1.31–1.24 (m, 3H), 1.10–1.05 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.3, 144.1, 138.2, 134.6, 131.9, 129.7, 128.9, 128.1, 126.2, 125.4, 124.9, 90.6, 52.8, 42.3, 15.0, 14.0; IR (neat, cm^{-1}): 3060, 2977, 2935, 1596, 1579, 1338, 1285, 1141, 1074, 904, 759, 667, 605, 576; HRMS (ESI) m/z calcd for $C_{18}H_{20}ClNO_2S_2$ $[M+H]^+$ 382.0697; Found 382.0684.

(*E*)-2-((4-chlorophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ga)



Compound **3ga** was obtained as a white solid (59 mg, 62% yield) by following the general procedure, after 26 h of reaction. mp 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.77–7.72 (m, 2H), 7.27–7.22 (m, 2H), 7.14–7.08 (m, 2H), 7.06–7.00 (m, 1H), 7.00–6.95 (m, 2H), 3.61–3.57 (m, 2H), 3.36–3.32 (m, 2H), 1.30–1.24 (m, 3H), 1.09–1.03 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.1, 140.7, 138.39, 138.34, 129.4, 128.9, 128.7, 125.3, 124.9, 90.8, 52.7, 42.2, 15.0, 14.0; IR (neat, cm^{-1}): 3063, 2977, 2877, 1598, 1476, 1339, 1298, 1138, 1085, 904, 764, 621, 574; HRMS (ESI) m/z calcd for $C_{18}H_{20}ClNO_2S_2$ $[M+H]^+$ 382.0697; Found 382.0687.

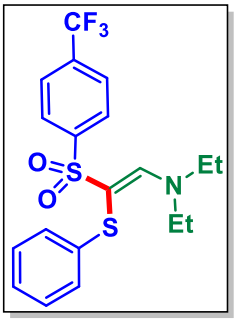
(*E*)-*N*,*N*-diethyl-2-((3-fluorophenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ha)



Compound **3ha** was obtained as a white solid (43 mg, 47% yield) by following the general procedure, after 26 h of reaction. mp 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.65–7.60 (m, 1H), 7.55–7.50 (m, 1H), 7.30–7.23 (m, 1H), 7.14–7.09 (m, 2H), 7.06–6.97

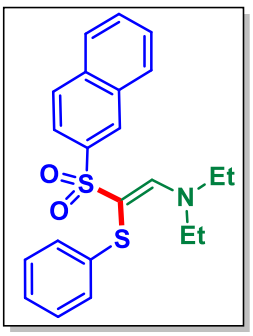
(m, 4H), 3.61 (s, 2H), 3.36 (s, 2H), 1.29–1.24 (m, 3H), 1.09–1.07 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 162.3 (d, J = 251.0 Hz), 152.3, 144.5 (d, J = 6.5 Hz), 138.3, 130.1 (d, J = 7.6 Hz), 128.9, 125.4, 124.9, 123.8 (d, J = 3.3 Hz), 119.0 (d, J = 21.4), 115.3 (d, J = 24.2 Hz), 90.6, 52.8, 42.3, 15.0, 14.1 ; ^{19}F NMR (471 MHz): –111.3; IR (neat, cm-1): 3072, 6978, 2877, 1595, 1474, 1289, 1129, 1080, 908, 689, 615, 532; HRMS (ESI) m/z calcd for $C_{18}H_{20}FNO_2S_2$ $[M+H]^+$ 366.0992; Found 366.0990.

(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3ia)



Compound **3ia** was obtained as a white solid (45 mg, 43% yield) by following the general procedure, after 30 h of reaction. mp 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8 Hz, 2H), 7.10–7.04 (m, 2H), 7.02–6.96 (m, 1H), 6.96–6.91 (m, 2H), 3.64–3.60 (m, 2H), 3.38–3.34 (m, 2H), 1.29–1.25 (m, 3H), 1.10–1.07 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 152.5, 145.9 (d, J = 1.5 Hz), 138.0, 133.5 (q, J = 32.8 Hz), 128.9, 128.5, 125.6–125.5 (m), 124.9, 122.1, 90.4, 52.8, 42.3, 15.0, 14.0; ^{19}F NMR (471 MHz): –63.0; IR (neat, cm^{-1}): 3055, 2979, 2934, 1596, 1402, 1319, 1129, 1060, 904, 760, 614, 597, 567; HRMS (ESI) m/z calcd for $C_{19}H_{20}F_3NO_2S_2$ $[M+H]^+$ 416.0960; Found 416.0960.

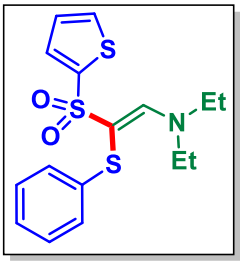
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylthio)ethen-1-amine (3ja)



Compound **3ja** was obtained as a white solid (65 mg, 65% yield) by following the general procedure, after 25 h of reaction. mp 124–126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.21 (s, 1H), 7.83 (d, J = 8 Hz, 1H), 7.79–7.76 (m, 3H), 7.56–7.48 (m, 2H), 7.02–6.96 (m, 4H), 6.88–6.84 (m, 1H), 3.60 (s, 2H), 3.36 (s, 2H), 1.28 (s, 3H), 1.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 152.2, 139.1, 138.5, 134.6, 132.2, 129.4, 129.3, 128.76, 128.71, 128.3, 127.7, 127.0, 125.1, 124.9, 123.3, 91.3, 52.7, 42.2, 15.0, 14.1; IR (neat, cm^{-1}): 2976, 2934, 2874, 1595,

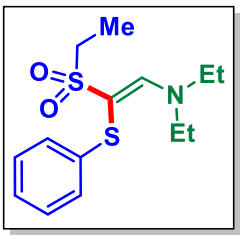
1343, 1287, 1139, 1121, 1068, 739, 655, 576, 555; HRMS (ESI) m/z calcd for $C_{22}H_{23}NO_2S_2$ $[M+H]^+$ 398.1243; Found 398.1242.

(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-(thiophen-2-ylsulfonyl)ethen-1-amine (3ka)



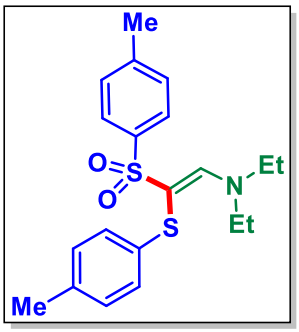
Compound **3ka** was obtained as a light brown solid (47 mg, 53% yield) by following the general procedure, after 22 h of reaction. mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H),7.52 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 7.39 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.16–7.10 (m, 2H), 7.03–7.00 (m, 3H), 6.87–6.83 (m, 1H), 3.59–3.57 (m, 2H), 3.35–3.31 (m, 2H), 1.28–1.22 (m, 3H), 1.09–1.04 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.9, 144.0, 138.7, 132.7, 131.6, 128.9, 127.1, 125.2, 124.6, 91.9, 52.8, 42.2, 15.1, 14.1; IR (neat, cm^{-1}): 3058, 2979, 2879, 1599, 1293, 1131, 1012, 904, 762, 603, 577; HRMS (ESI) m/z calcd for $C_{16}H_{19}NO_2S_3$ $[M+H]^+$ 354.0651; Found 354.0642.

(*E*)-*N*,*N*-diethyl-2-(ethylsulfonyl)-2-(phenylthio)ethen-1-amine (3la)



Compound **3la** was obtained as a light pink liquid (37 mg, 49% yield) by following the general procedure, after 20 h of reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.30–7.23 (m, 4H), 7.15–7.10 (m, 1H), 3.64 (s, 2H), 3.32 (s, 2H), 3.06–3.00 (m, 2H), 1.27–1.19 (m, 6H), 1.14–1.12 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.7, 139.0, 129.1, 125.6, 125.1, 87.8, 52.6, 46.7, 42.1, 14.9, 14.1, 7.6; IR (neat, cm^{-1}): 3363, 2977, 2877, 1599, 1343, 1289, 1118, 905, 741, 690, 601, 552; HRMS (ESI) m/z calcd for $C_{14}H_{21}NO_2S_2$ $[M+H]^+$ 300.1086; Found 300.1087.

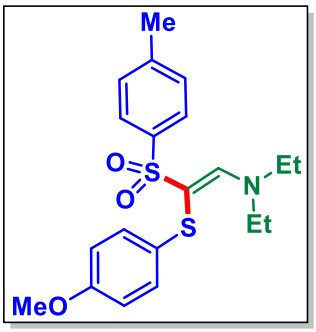
(*E*)-*N*,*N*-diethyl-2-(*p*-tolylthio)-2-tosylethen-1-amine (3ma)



Compound **3ma** was obtained as a white solid (65 mg, 69% yield) by following the general procedure, after 20 h of reaction. mp 77–79 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.70 (dd, J_1 = 8 Hz, J_2 = 3 Hz, 2H), 7.10 (dd, J_1 = 8 Hz, J_2 = 3 Hz, 2H), 6.93–6.90 (m, 4H), 3.58 (s, 2H), 3.33 (s, 2H), 2.31 (s, 3H), 2.22 (s, 3H), 1.24 (s, 3H), 1.07 (s,

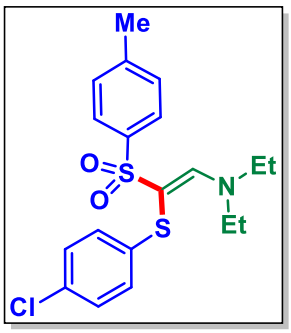
3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 151.7, 142.4, 139.4, 135.3, 134.8, 129.5, 129.1, 127.9, 125.1, 91.9, 52.5, 42.1, 21.5, 20.9, 15.0, 14.1; IR (neat, cm^{-1}): 3024, 2975, 2933, 2871, 1522, 1490, 1280, 1135, 1081, 902, 802, 759, 658, 584, 554; HRMS (ESI) m/z calcd for $C_{20}H_{25}NO_2S_2$ $[M+H]^+$ 376.1399; Found 376.1398.

(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)thio)-2-(m-tolylsulfonyl)ethen-1-amine (3na)



Compound **3na** was obtained as a yellow liquid (64 mg, 65% yield) by following the general procedure, after 20 h of reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 6.97 (d, J = 9 Hz, 2H), 6.67 (d, J = 9 Hz, 2H), 3.71 (s, 3H), 3.61 (s, 2H), 3.33 (s, 2H), 2.31 (s, 3H), 1.26–1.09 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 157.8, 151.5, 142.4, 139.5, 129.6, 129.1, 127.9, 126.8, 114.5, 92.6, 55.4, 52.5, 42.1, 21.5, 14.2; IR (neat, cm^{-1}): 2975, 293, 2835, 1593, 1491, 1280, 1242, 1136, 1083, 903, 760, 658, 585, 556; HRMS (ESI) m/z calcd for $C_{20}H_{25}NO_3S_2$ $[M+H]^+$ 392.1349; Found 392.1347.

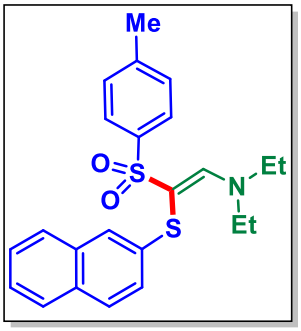
(*E*)-2-((4-chlorophenyl)thio)-*N*,*N*-diethyl-2-tosylethen-1-amine (3oa)



Compound **3oa** was obtained as a white solid (64 mg, 65% yield) by following the general procedure, after 22 h of reaction. mp 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 7.08–7.05 (m, 2H), 6.96–6.92 (m, 2H), 3.55 (s, 2H), 3.34 (s, 2H), 2.32 (s, 3H), 1.27–1.23 (m, 3H), 1.07–1.03 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 151.9, 142.8, 139.2, 137.4, 130.9, 129.2, 128.8, 127.9, 126.3, 91.1, 52.7, 42.2, 21.5, 15.0, 14.1; IR (neat, cm^{-1}): 2976, 2941, 2874, 1594, 147, 1280, 1280, 1084, 903, 810, 759, 657, 584, 561; HRMS (ESI) m/z calcd for $C_{19}H_{22}ClNO_2S_2$ $[M+H]^+$ 396.0853; Found 396.0852.

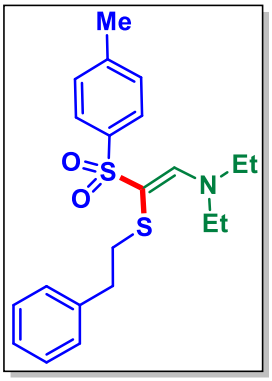
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylthio)-2-tosylethen-1-amine (3pa)

Compound **3pa** was obtained as a white solid (59 mg, 57% yield) by following the general procedure, after 26 h of reaction. mp 107–109



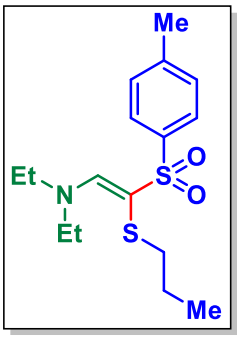
°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.74–7.67 (m, 3H), 7.58 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.42–7.31 (m, 2H), 7.26–7.24 (m, 1H), 7.15 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 1H), 6.99 (d, J = 8 Hz, 2H), 3.58 (s, 2H), 3.36 (s, 2H), 2.09 (s, 3H), 1.30–1.22 (m, 3H), 1.10–1.05 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.9, 142.6, 139.4, 136.2, 133.7, 131.5, 129.1, 128.3, 127.9, 127.7, 127.0, 126.4, 125.2, 123.6, 122.6, 91.6, 52.7, 42.2, 21.3, 15.1, 14.2; IR (neat, cm^{-1}): 3049, 2975, 2926, 1597, 1448, 1281, 1137, 1083, 903, 811, 760, 659, 585, 555; HRMS (ESI) m/z calcd for $C_{23}H_{25}NO_2S_2$ $[M+H]^+$ 412.1399; Found 412.1399.

(*E*)-*N*,*N*-diethyl-2-(phenethylthio)-2-tosylethen-1-amine (3qa)



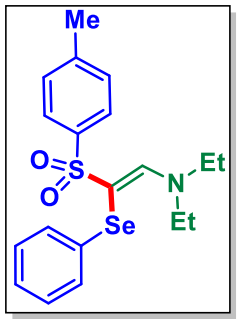
Compound **3qa** was obtained as a yellow liquid (46 mg, 47% yield) by following the general procedure, after 20 h of reaction. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.76 (d, J = 8 Hz, 2H), 7.28–7.22 (m, 4H), 7.18 (d, J = 7.6 Hz, 1H), 7.15–7.10 (m, 2H), 3.47 (s, 4H), 2.89–2.83 (m, 2H), 2.81–2.75 (m, 2H), 2.39 (s, 3H), 1.13 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 150.4, 142.5, 140.5, 139.6, 129.2, 128.7, 128.5, 127.9, 126.3, 94.5, 39.7, 35.2, 25.4, 21.6, 14.3; IR (neat, cm^{-1}): 3035, 2976, 1596, 1453, 1279, 1136, 1083, 902, 760, 658, 586, 549; HRMS (ESI) m/z calcd for $C_{21}H_{27}NO_2S_2$ $[M+H]^+$ 390.1556; Found 390.1558.

(*E*)-*N*,*N*-diethyl-2-(propylthio)-2-tosylethen-1-amine (3ra)



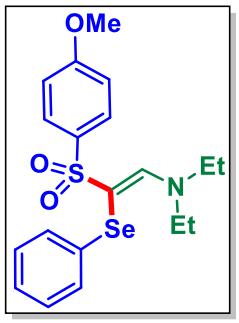
Compound **3ra** was obtained as a yellow liquid (37 mg, 45% yield) by following the general procedure, after 24 h of reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 3.56 (brs, 4H), 2.59 (t, J = 7.5 Hz, 2H), 2.39 (s, 3H), 1.52 (q, J = 7.5 Hz, 2H), 1.21–1.16 (m, 6H), 0.90 (t, J = 7 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.3, 142.4, 139.7, 129.2, 127.8, 94.9, 40.6, 22.3, 21.6, 14.2, 13.7; IR (neat, cm^{-1}): 2968, 292, 2872, 1594, 1347, 1277, 1082, 901, 760, 647, 584, 549; HRMS (ESI) m/z calcd for $C_{16}H_{25}NO_2S_2$ $[M+H]^+$ 328.1399; Found 328.1398.

(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-tosylethen-1-amine (3sa)



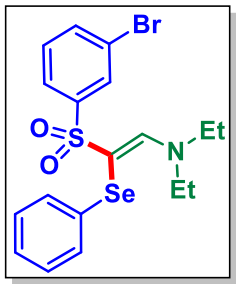
Compound **3sa** was obtained as a light yellow solid (56 mg, 55% yield) by following the general procedure, after 22 h of reaction. mp 96–98 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.70 (d, J = 8 Hz, 2H), 7.09–7.03 (m, 7H), 3.45 (s, 4H), 2.28 (s, 3H), 1.18–1.10 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.4, 142.3, 139.4, 134.1, 129.05, 129.00, 128.0, 127.5, 125.7, 88.3, 42.4, 21.5, 14.4; ^{77}Se NMR (95 MHz): 266.2; IR (neat, cm^{-1}): 3056, 2974, 2932, 1591, 1437, 1278, 1134, 1081, 734, 649, 579, 545; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_2SSe$ $[M+H]^+$ 410.0687; Found 410.0685.

(*Z*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylselanyl)ethen-1-amine (3ta)



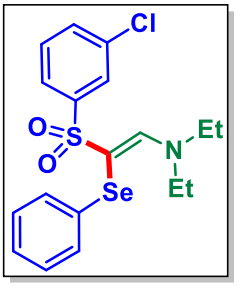
Compound **3ta** was obtained as a white solid (60 mg, 57% yield) by following the general procedure, after 20 h of reaction. mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.04–7.02 (m, 5H), 6.73 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 3.45 (s, 4H), 1.13 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 162.2, 151.1, 134.1, 134.0, 130.0, 128.9, 127.4, 125.7, 113.5, 88.7, 55.5, 52.7, 41.8, 14.4; ^{77}Se NMR (95 MHz): 266.2; IR (neat, cm^{-1}): 3063, 2975, 2879, 2838, 1592, 1496, 1280, 1255, 1133, 1083, 735, 666, 582, 553; HRMS (ESI) m/z calcd for $C_{19}H_{23}NO_3SSe$ $[M+H]^+$ 426.0637; Found 426.0637.

(*Z*)-2-((3-bromophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ua)



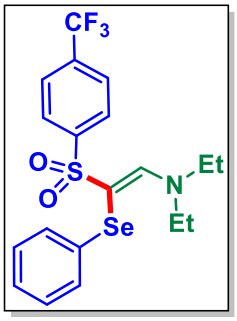
Compound **3ua** was obtained as a light yellow solid (49 mg, 41% yield) by following the general procedure, after 22 h of reaction. mp 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.94 (s, 1H), 7.76 (d, J = 8 Hz, 1H), 7.40 (d, J = 8 Hz, 1H), 7.14–7.00 (m, 6H), 3.64 (s, 2H), 3.35 (s, 2H), 1.24 (s, 3H), 1.08 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.0, 144.2, 134.6, 133.6, 130.9, 129.8, 129.1, 127.4, 126.7, 126.1, 122.4, 87.1, 52.9, 41.8, 14.9, 13.8; ^{77}Se NMR (95 MHz): 266.9; IR (neat, cm^{-1}): 3057, 2975, 2934, 2874, 1592, 1337, 1282, 1136, 1065, 732, 678, 599, 566; HRMS (ESI) m/z calcd for $C_{18}H_{20}BrNO_2SSe$ $[M+H]^+$ 473.9605; Found 473.9636.

(*Z*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3va)



Compound **3va** was obtained as a light yellow solid (45 mg, 42% yield) by following the general procedure, after 22 h of reaction. mp 102–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.80–7.79 (m, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.28–7.24 (m, 1H), 7.18 (t, J = 8 Hz, 1H), 7.10–7.01 (m, 5H), 3.64 (s, 2H), 3.38 (s, 2H), 1.26–1.10 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.0, 144.2, 134.5, 133.6, 131.8, 129.6, 129.1, 128.1, 127.4, 126.3, 126.1, 87.2, 52.9, 41.8, 14.9, 13.9; ^{77}Se NMR (95 MHz): 267.3; IR (neat, cm^{-1}): 3059, 2976, 2944, 2876, 1594, 1338, 1283, 1140, 1074, 734, 668, 603, 569; HRMS (ESI) m/z calcd for $C_{18}H_{20}ClNO_2SSe$ $[M+H]^+$ 430.0117; Found 430.0141.

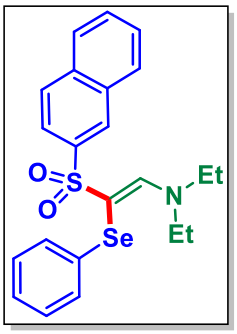
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3wa)



Compound **3wa** was obtained as a light pink solid (39 mg, 38% yield) by following the general procedure, after 28 h of reaction. mp 93–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.92 (d, J = 8 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.04–7.01 (m, 3H), 6.99–6.96 (m, 2H), 3.66 (s, 2H), 3.36 (s, 2H), 1.29–1.23 (m, 3H), 1.10–1.08 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.2, 145.9, 133.5, 133.3 (q, J = 32.7 Hz), 129.1, 128.5, 127.4 (t, J = 6.7 Hz), 126.2, 125.4 (q, J = 3.7 Hz), 123.3 (q, J = 273.2 Hz), 87.0, 52.9, 41.8, 15.0, 13.7; ^{19}F NMR (471 MHz): –63.0; ^{77}Se NMR (95 MHz): 267.0; IR (neat, cm^{-1}): 3069, 2978, 2878, 1593, 1402, 1320, 1286, 1129, 1060, 1084, 709, 612, 596, 562; HRMS (ESI) m/z calcd for $C_{19}H_{20}F_3NO_2SSe$ $[M+H]^+$ 464.0405; Found 464.0398.

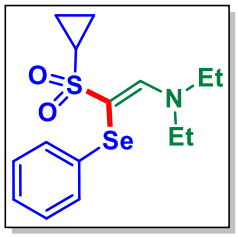
(*Z*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylselanyl)ethen-1-amine (3xa)

Compound **3xa** was obtained as a white solid (51 mg, 46% yield) by following the general procedure, after 24 h of reaction. mp 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.25 (s, 1H), 7.83 (d, J =



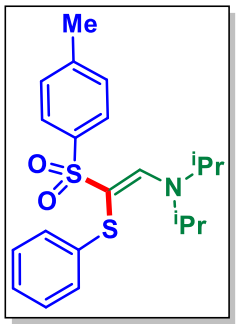
7.2 Hz, 1H), 7.80–7.71 (m, 3H), 7.56–7.46 (m, 2H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.95–6.86 (m, 3H), 3.60–3.41 (m, 4H), 1.17–1.14 (m, 6H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 151.9, 139.2, 134.5, 133.9, 132.2, 129.5, 129.3, 128.9, 128.7, 128.2, 127.7, 127.6, 127.0, 125.8, 123.3, 88.2, 52.8, 42.4, 14.4; ^{77}Se NMR (95 MHz): 267.1; IR (neat, cm^{-1}): 3055, 2976, 2933, 2879, 1594, 1344, 1285, 1120, 1068, 758, 660, 572, 546; HRMS (ESI) m/z calcd for $C_{22}H_{23}NO_2SSe$ $[M+H]^+$ 446.0662; Found 446.0687.

(*Z*)-2-(cyclopropylsulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ya)



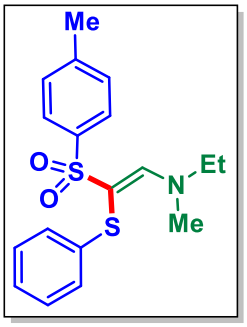
Compound **3ya** was obtained as a yellowish liquid (44 mg, 49% yield) by following the general procedure, after 18 h of reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.34 (dd, J_1 = 7.5 Hz, J_2 = 2 Hz, 2H), 7.28–7.22 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.59–3.39 (m, 4H), 2.48–2.43 (m, 1H), 1.19–1.13 (m, 8H), 0.74–0.70 (m, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 151.3, 134.8, 129.3, 127.4, 126.0, 86.6, 52.6, 41.6, 31.5, 14.3, 6.4; ^{77}Se NMR (95 MHz): 267.5; IR (neat, cm^{-1}): 3049, 2976, 2935, 2876, 1596, 1438, 1275, 1117, 894, 737, 692, 590, 537; HRMS (ESI) m/z calcd for $C_{15}H_{21}NO_2SSe$ $[M+H]^+$ 360.0531; Found 360.0532.

(*E*)-*N*-isopropyl-*N*-(2-(phenylthio)-2-tosylvinyl)propan-2-amine (3ab)



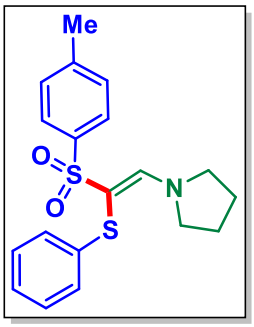
Compound **3ab** was obtained as a white solid (33 mg, 34% yield) by following the general procedure, after 24 h of reaction. mp 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.71 (d, *J* = 8 Hz, 2H), 7.13–7.07 (m, 4H), 7.01–6.97 (m, 3H), 5.37–5.32 (m, 1H), 3.62–3.57 (m, 1H), 2.31 (s, 3H), 1.32 (d, *J* = 6.4 Hz, 6H), 0.98 (d, *J* = 6 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 148.1, 142.4, 139.5, 138.0, 129.1, 128.7, 127.9, 125.17, 125.12, 91.3, 48.1, 47.4, 24.0, 21.5, 20.6; IR (neat, cm^{-1}): 3058, 2978, 2933, 1590, 1346, 1279, 1137, 1083, 929, 742, 658, 589, 557; HRMS (ESI) m/z calcd for $C_{21}H_{27}NO_2S_2$ $[M+H]^+$ 390.1556; Found 390.1559.

(*E*)-*N*-ethyl-*N*-methyl-2-(phenylthio)-2-tosylethen-1-amine (3ac)



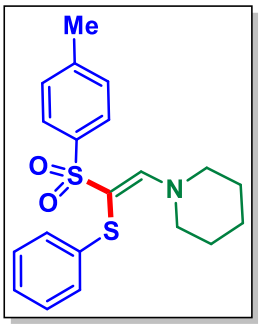
Compound **3ac** was obtained as a white solid, though contaminated with minor impurities (13 mg, 15% yield) by following the general procedure, after 24 h of reaction. mp 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.71 (dd, J_1 = 6.8 Hz, J_2 = 2 Hz, 2H), 7.14–7.08 (m, 4H), 7.05–7.00 (m, 3H), 3.47–3.31 (m, 2H), 3.15 (s, 3H), 2.30 (s, 3H), 1.19 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.8, 142.5, 139.2, 131.9, 129.1, 128.8, 128.0, 125.1, 125.0, 92.2, 55.7, 35.4, 21.5, 14.0; IR (neat, cm^{-1}): 2980, 2926, 2876, 1601, 1281, 1136, 1082, 740, 659, 585, 555; HRMS (ESI) m/z calcd for $C_{18}H_{21}NO_2S_2$ $[M+H]^+$ 348.1086; Found 348.1085.

(*E*)-1-(2-(phenylthio)-2-tosylvinyl)pyrrolidine (3ad)



Compound **3ad** was obtained as a white solid, though contaminated with minor impurities (24 mg, 27% yield) by following the general procedure, after 24 h of reaction. mp 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.72 (d, J = 8 Hz, 2H), 7.15–7.09 (m, 4H), 7.08–7.00 (m, 3H), 3.70–3.59 (m, 4H), 2.31 (s, 3H), 1.85–1.81 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 150.9, 142.5, 140.1, 139.4, 129.1, 128.8, 127.9, 125.03, 125.01, 92.3, 55.2, 47.3, 26.2, 24.2, 21.5; IR (neat, cm^{-1}): 2985, 2923, 2861, 1596, 1282, 1148, 1133, 1083, 669, 566, 553; HRMS (ESI) m/z calcd for $C_{19}H_{21}NO_2S_2$ $[M+H]^+$ 360.1086; Found 360.1085.

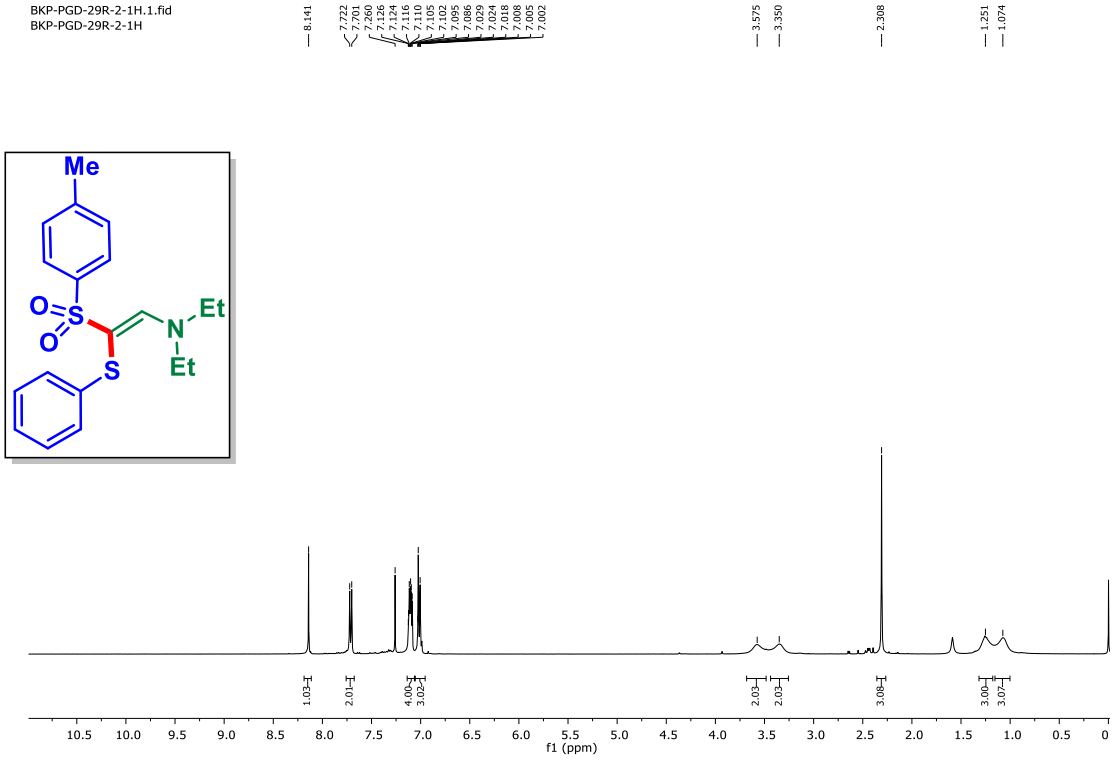
(*E*)-1-(2-(phenylthio)-2-tosylvinyl)piperidine (3ae)



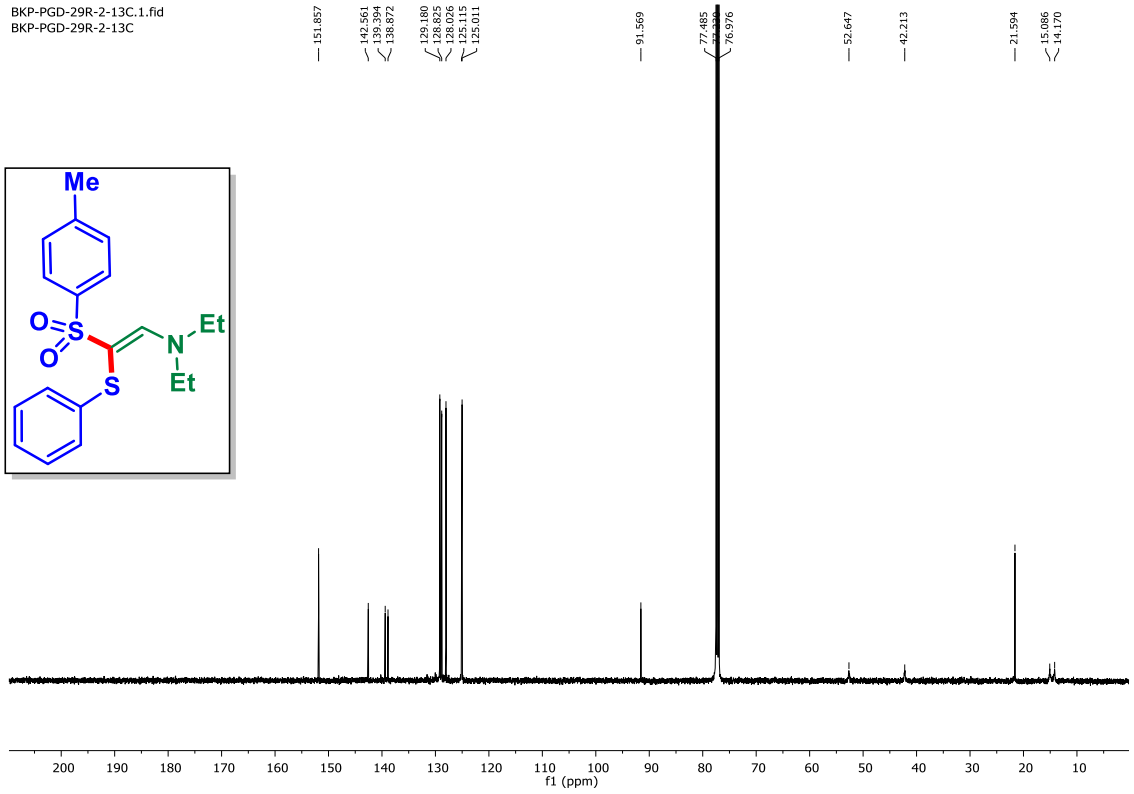
Compound **3ae** was obtained as a white solid (22 mg, 24% yield) by following the general procedure, after 24 h of reaction. mp 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.72 (d, J = 8 Hz, 2H), 7.13–7.08 (m, 4H), 7.04–7.01 (m, 3H), 3.66–3.64 (m, 4H), 2.31 (s, 3H), 1.59–1.50 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.5, 142.5, 139.4, 138.0, 129.1, 128.8, 128.0, 125.3, 125.2, 91.4, 26.5, 24.2, 21.5; IR (neat, cm^{-1}): 3066, 2939, 2858, 1597, 1439, 1137, 1082, 934, 738, 658, 593, 553; HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_2S_2$ $[M+H]^+$ 374.1243; Found 374.1239.

11. NMR Spectra

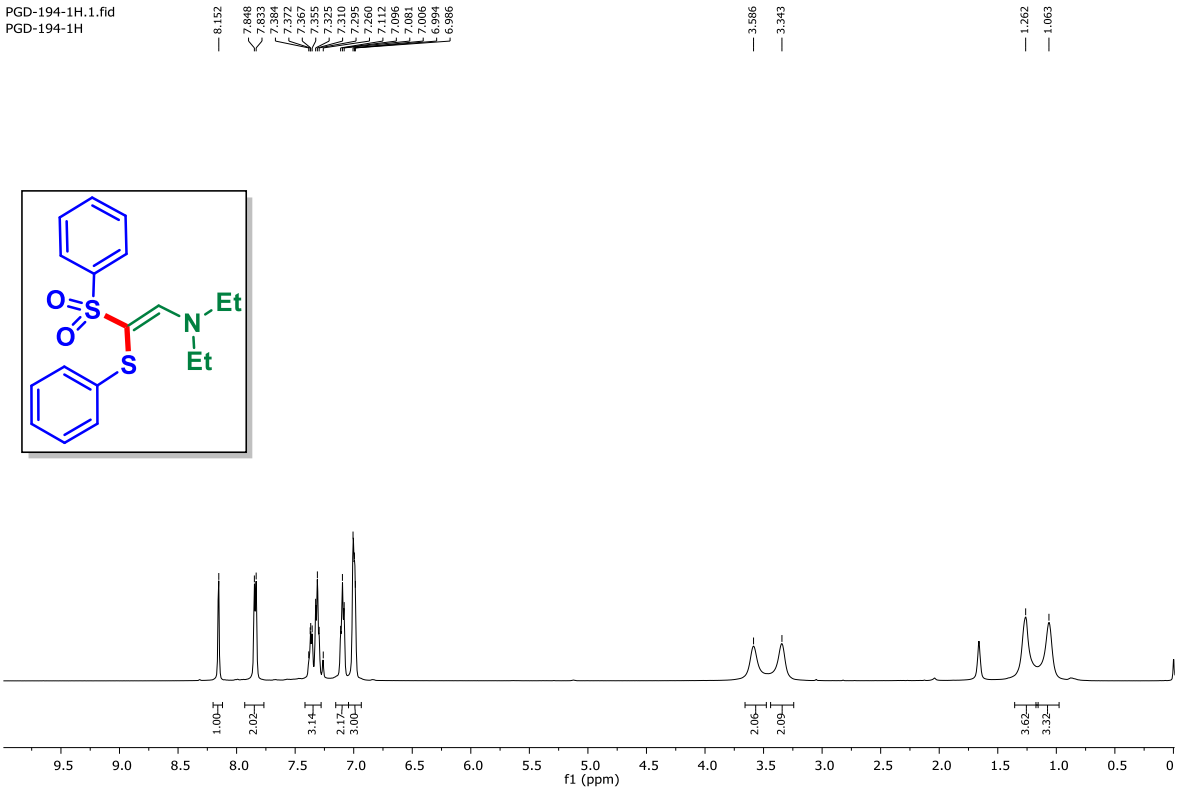
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (3aa): ^{1}H NMR ($CDCl_3$, 400 MHz)



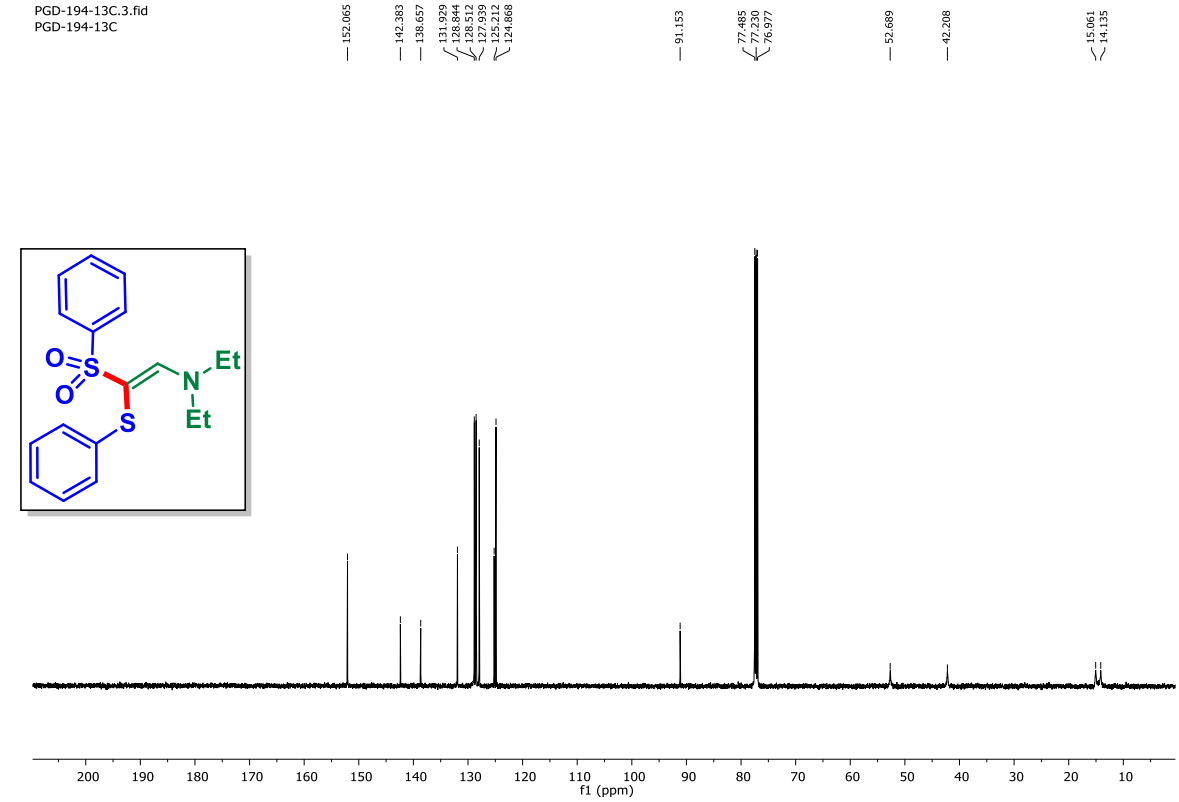
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-tosylethen-1-amine (3aa): ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz)



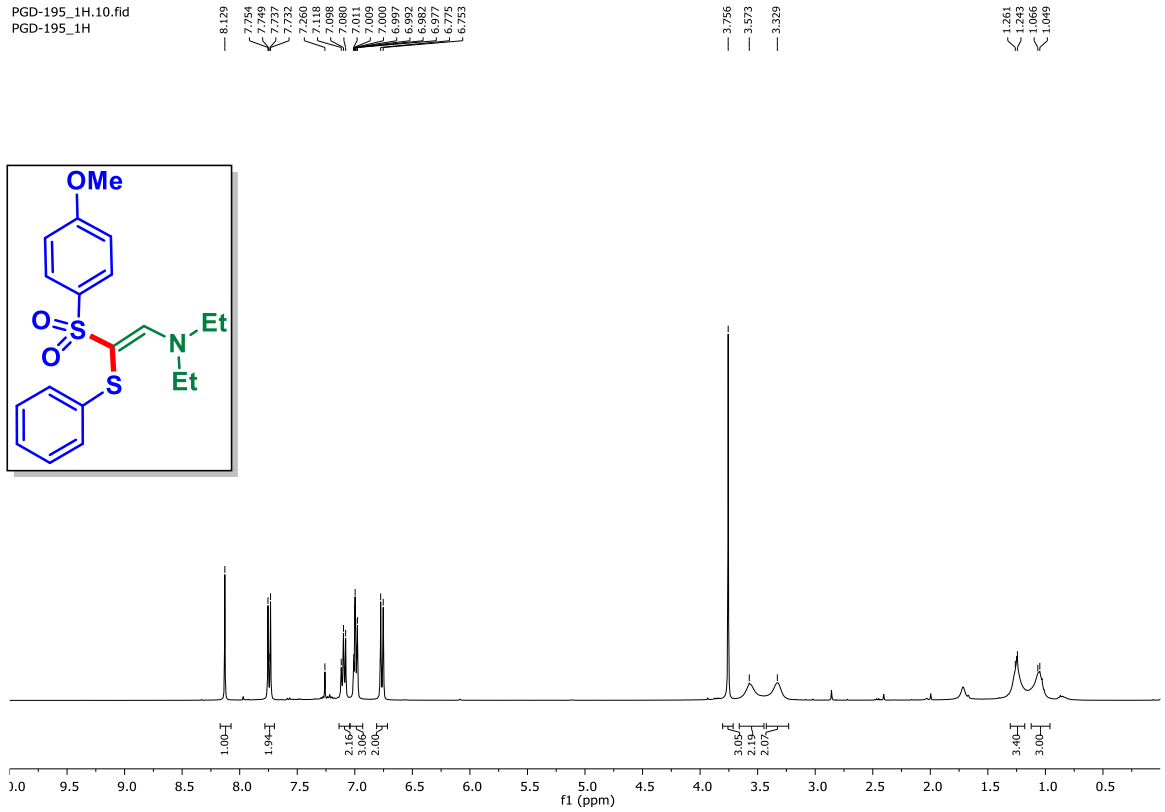
(*E*)-*N*,*N*-diethyl-2-(phenylsulfonyl)-2-(phenylthio)ethen-1-amine (3ba): ^{1}H NMR (CDCl$_3$, 500 MHz)



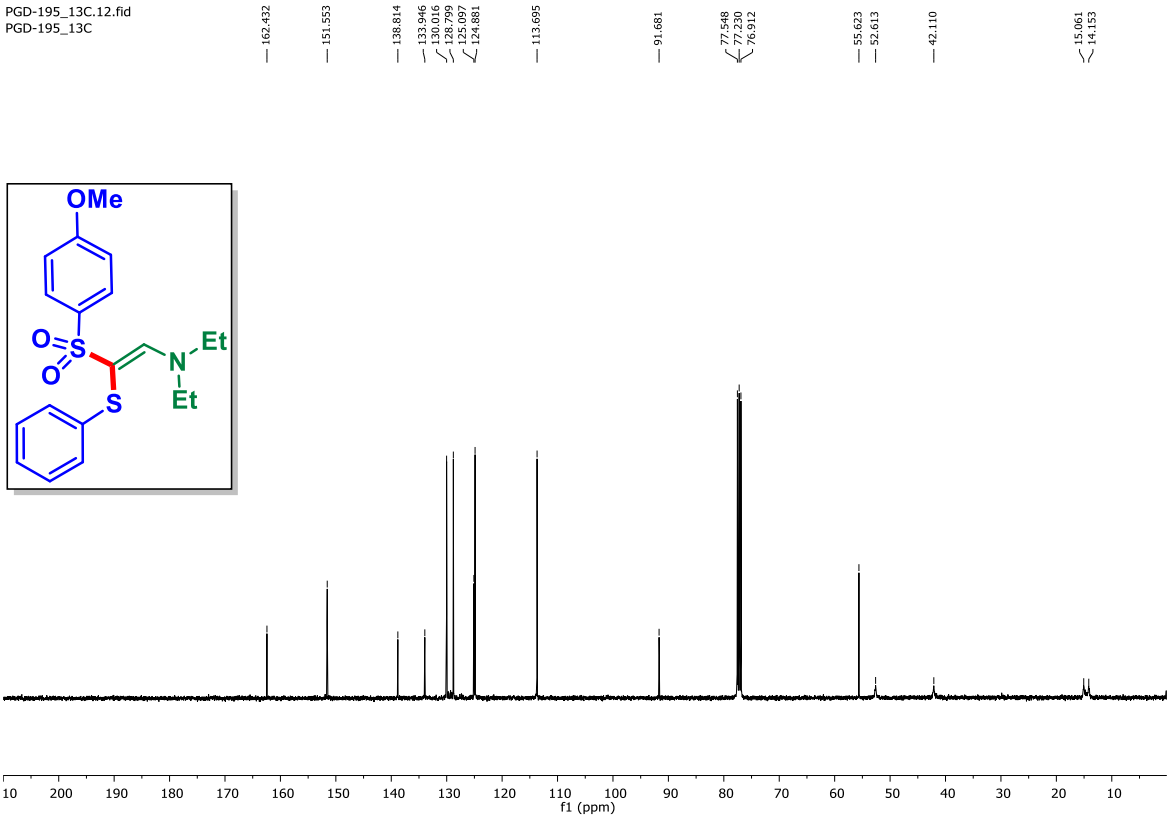
(*E*)-*N*,*N*-diethyl-2-(phenylsulfonyl)-2-(phenylthio)ethen-1-amine (3ba): ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz)



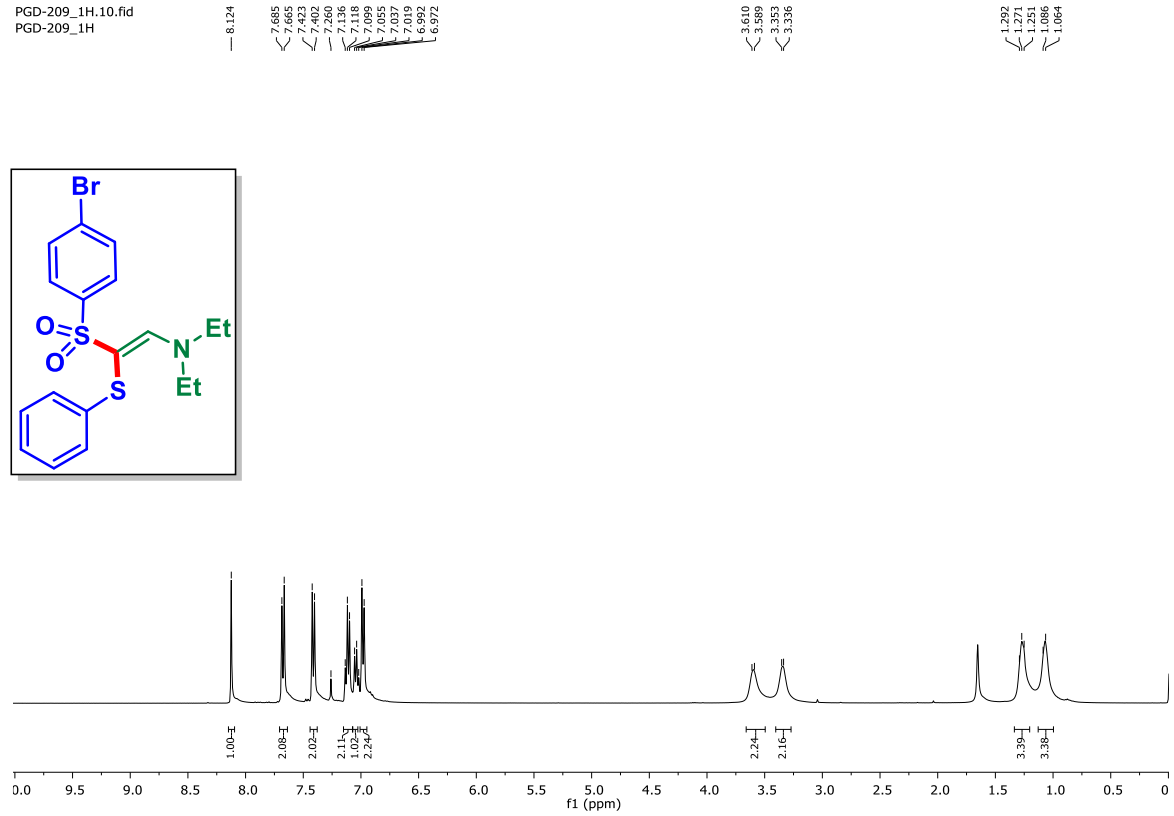
(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ca): ^{1}H NMR ($CDCl_3$, 400 MHz)



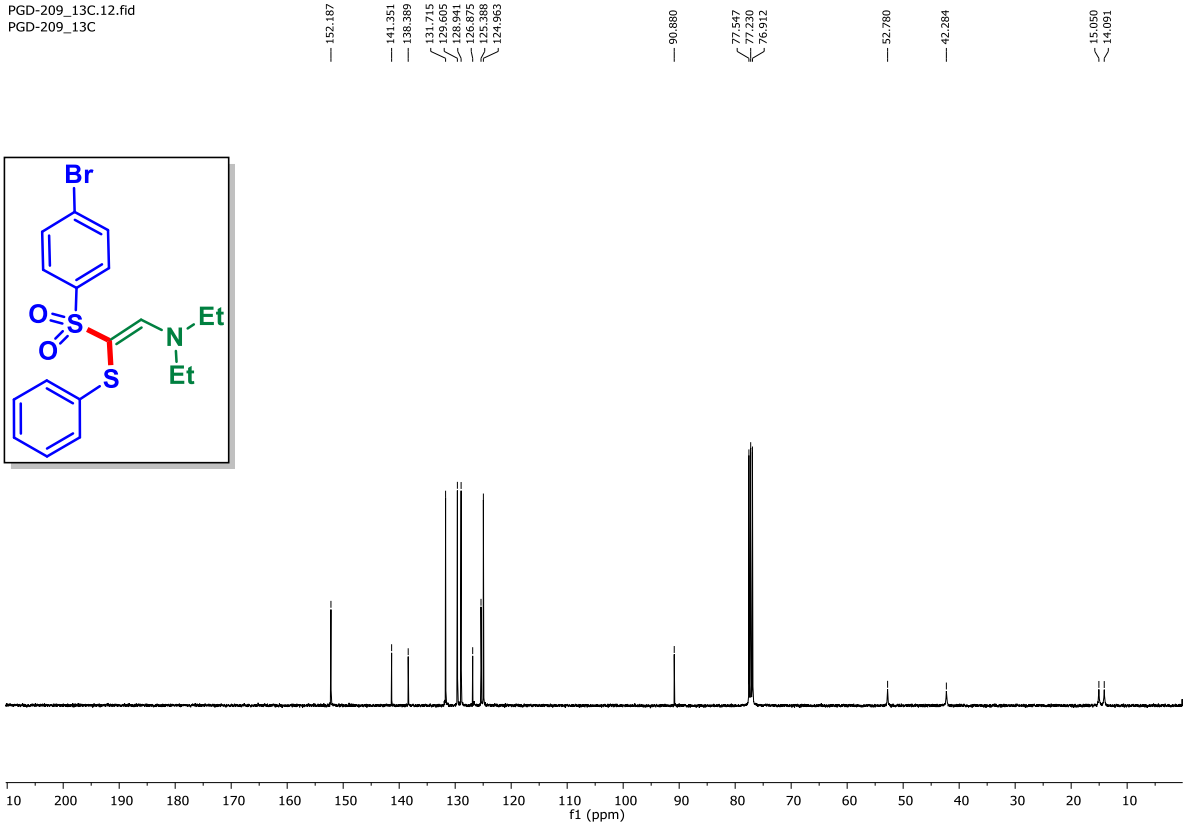
(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ca): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



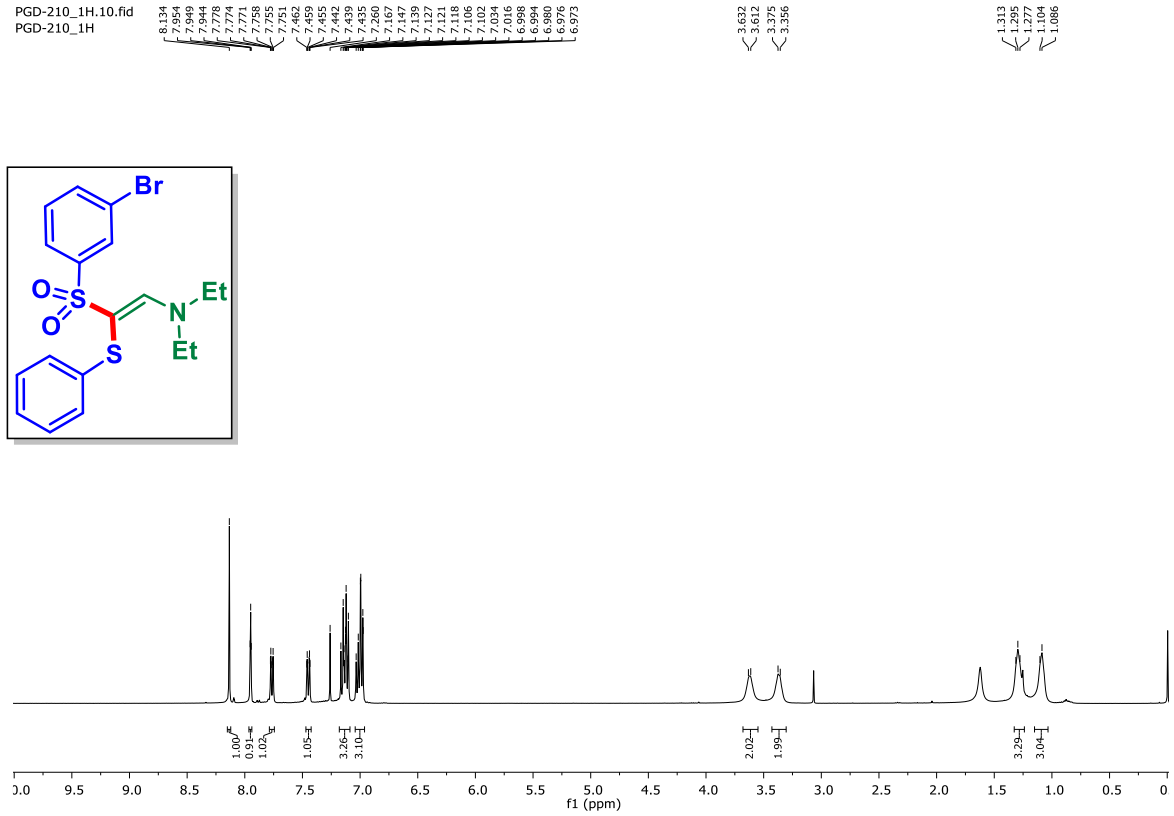
(*E*)-2-((4-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3da): ^{1}H NMR ($CDCl_3$, 400 MHz)



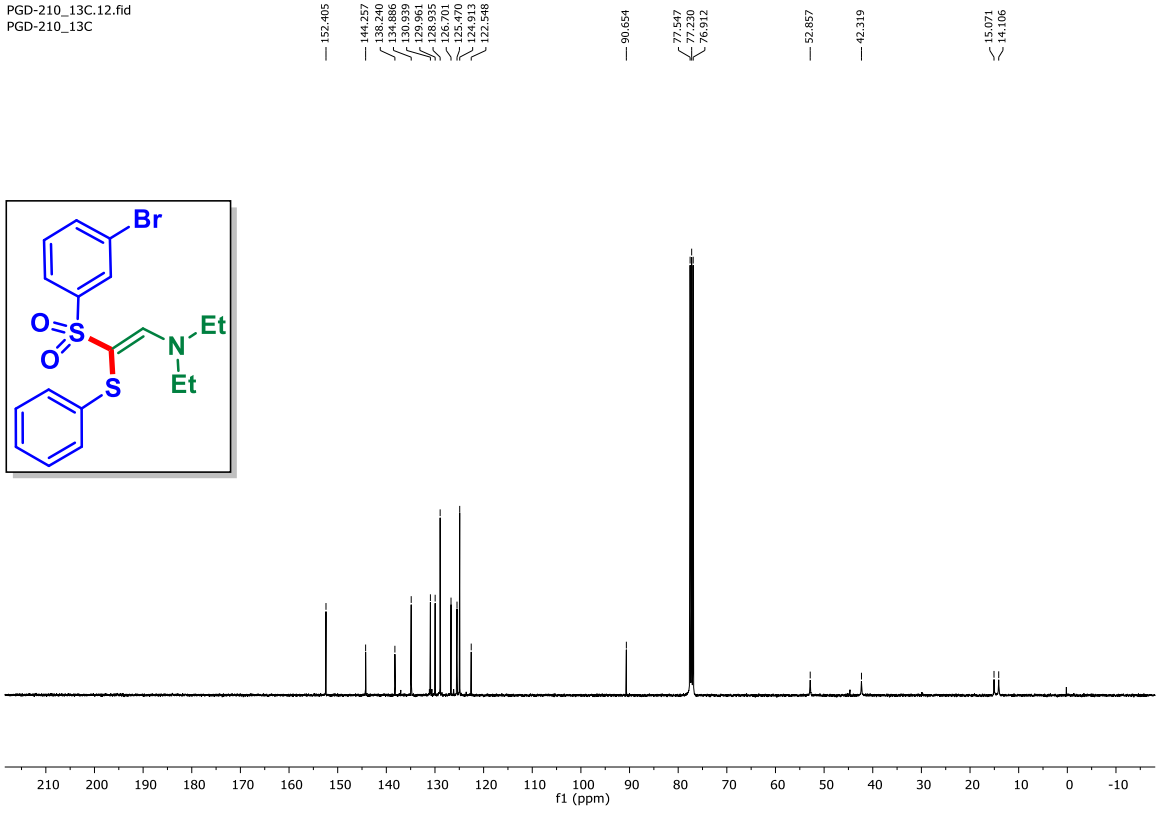
(*E*)-2-((4-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3da): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



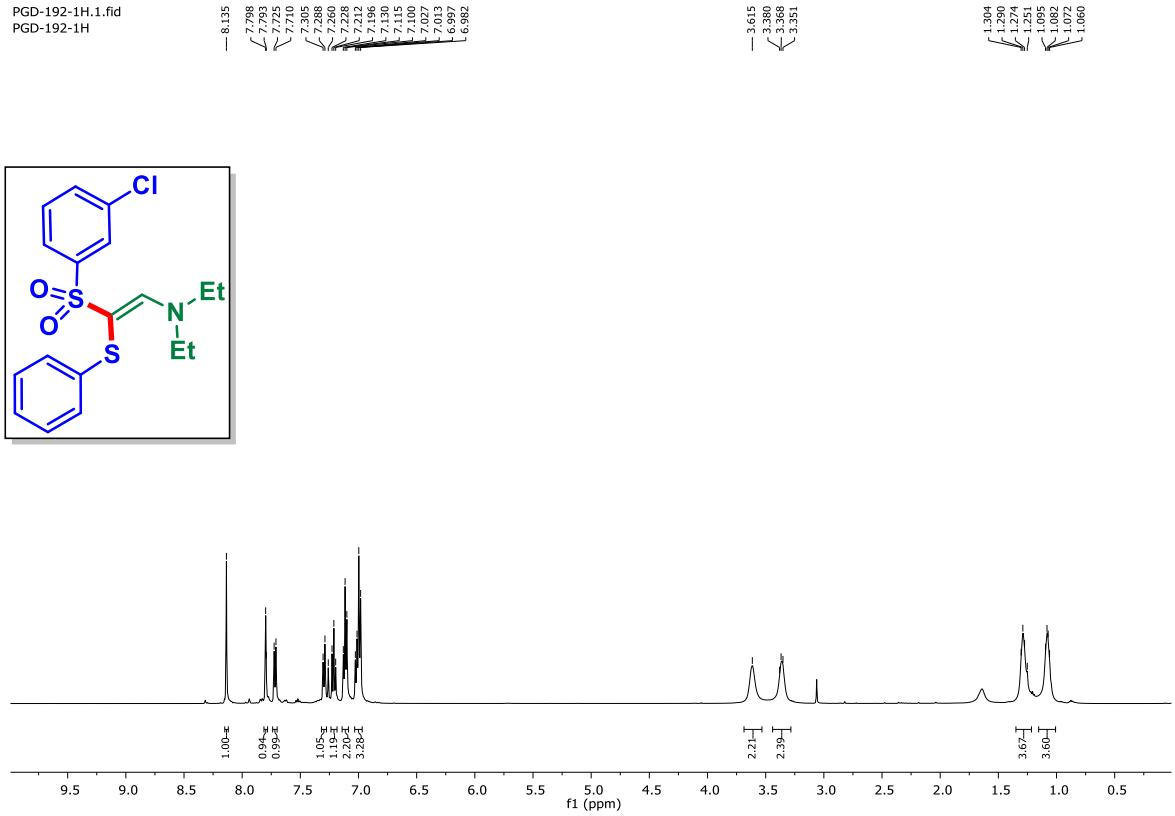
(*E*)-2-((3-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ea): ^{1}H NMR ($CDCl_3$, 400 MHz)



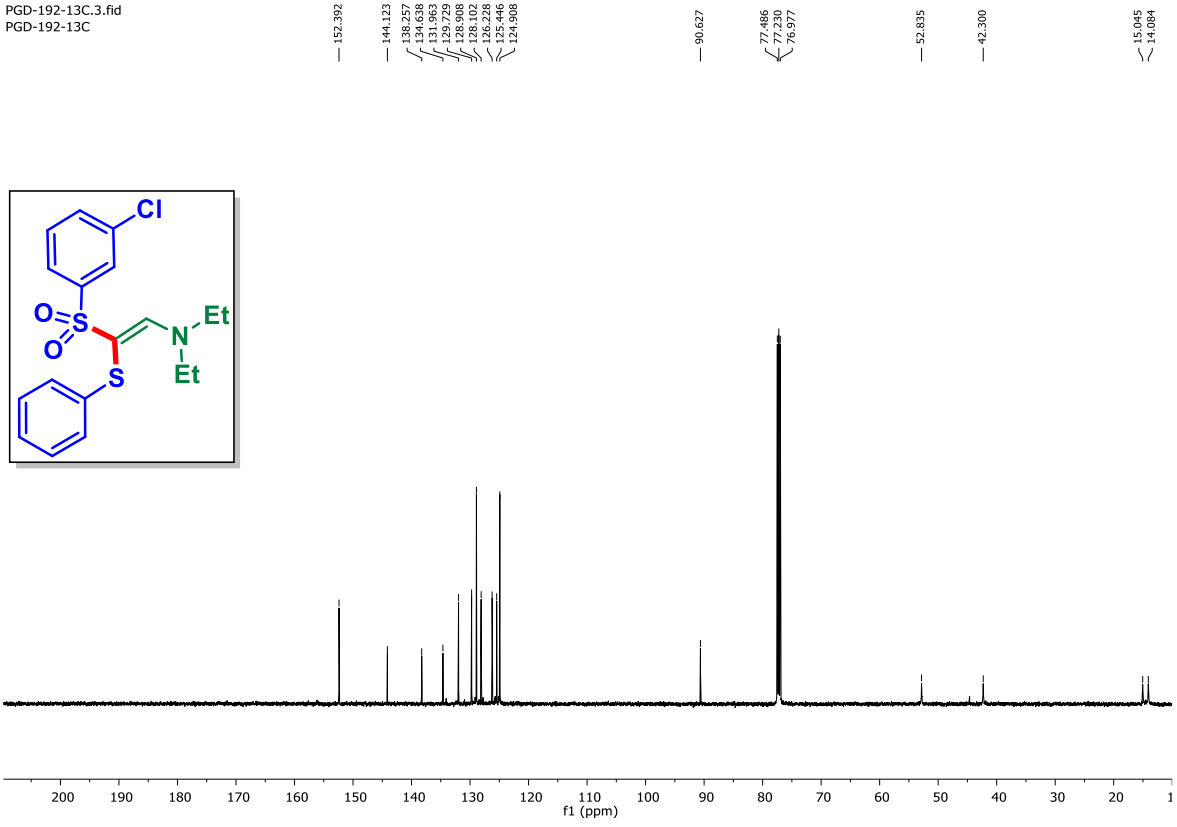
(*E*)-2-((3-bromophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ea): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



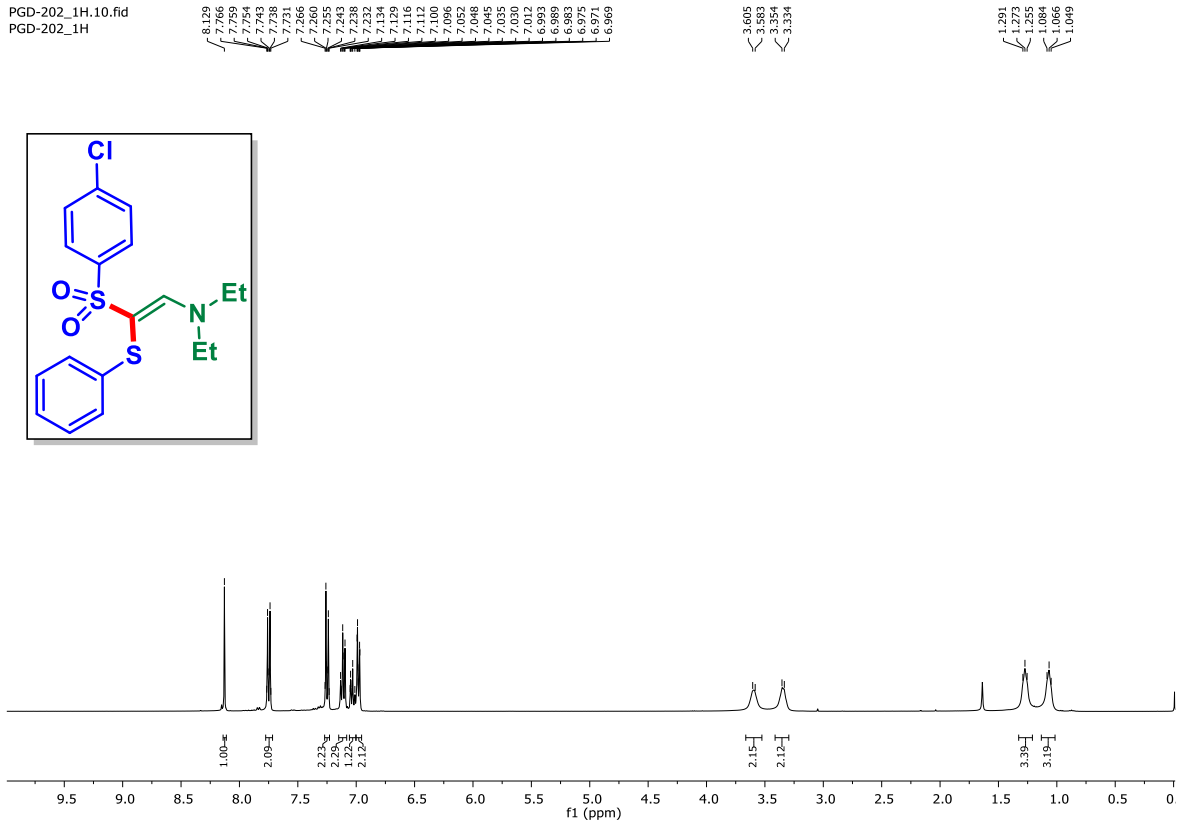
(*E*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylthio)ethen-1-amine (3fa): ^{1}H NMR (CDCl$_3$, 500 MHz)



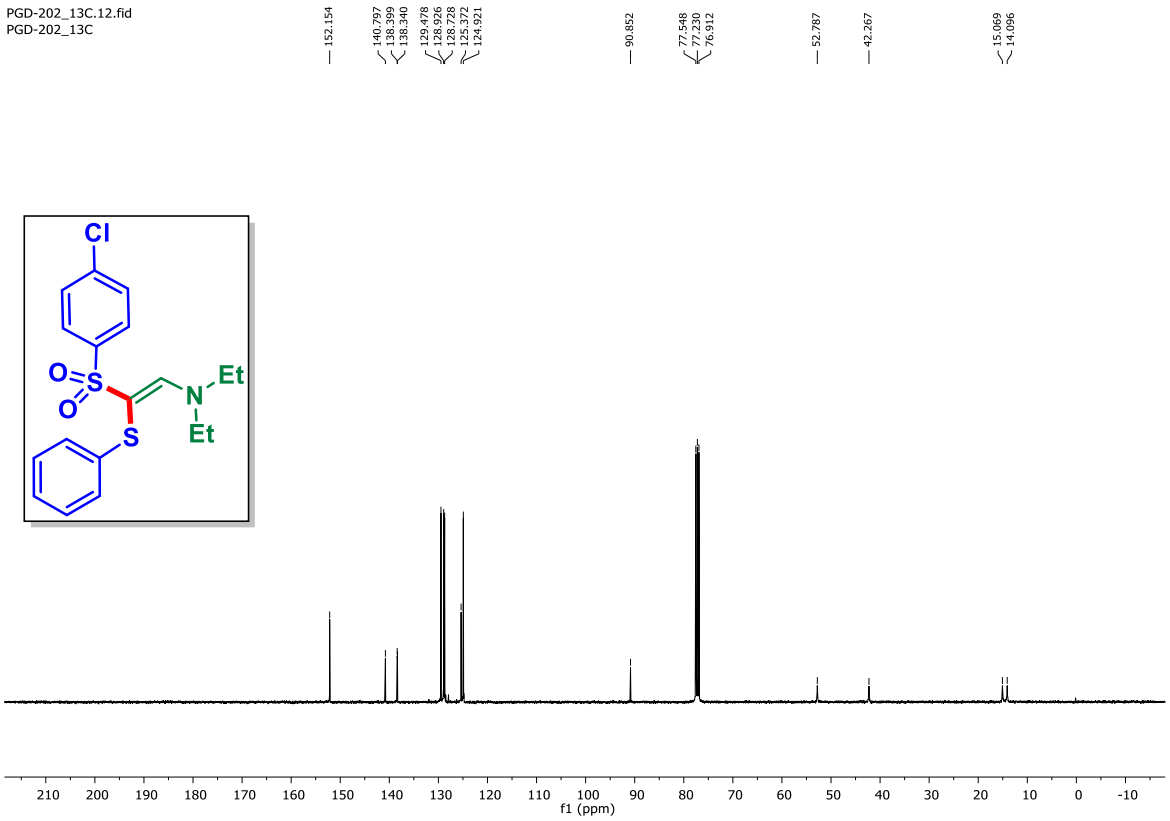
(*E*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylthio)ethen-1-amine (3fa): ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz)



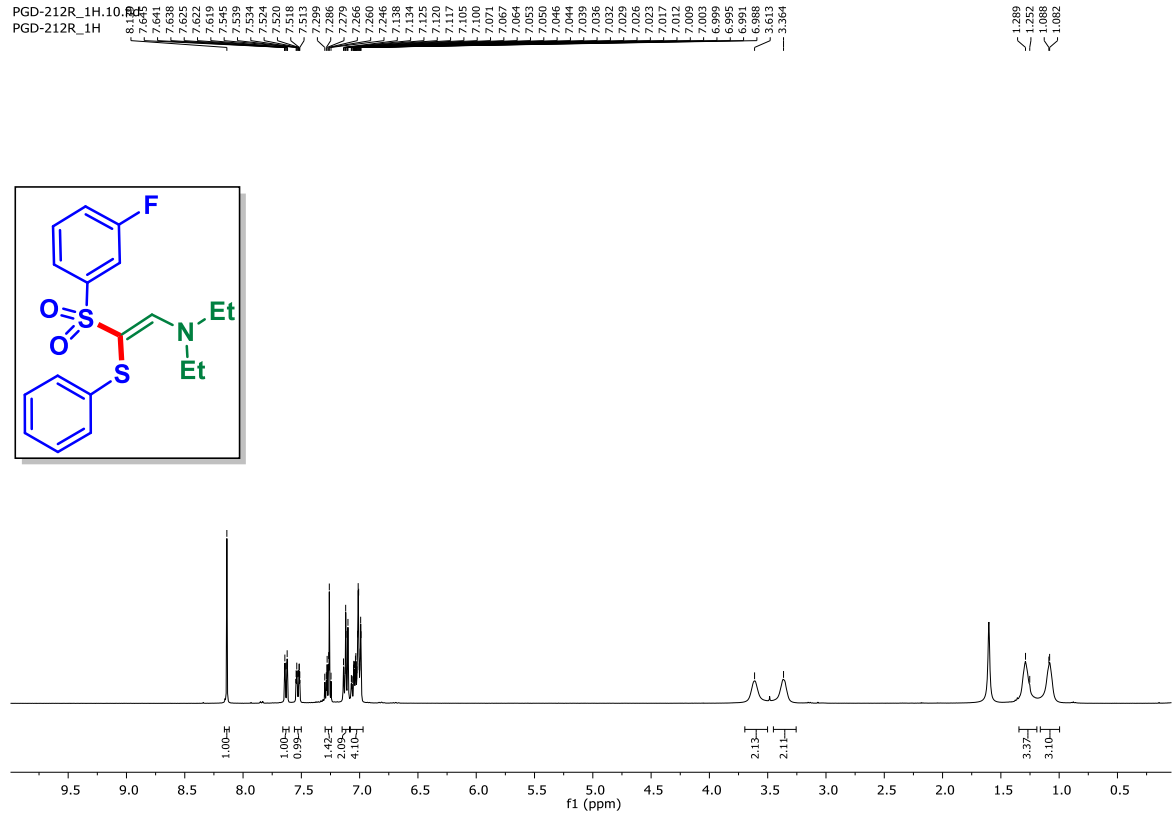
(*E*)-2-((4-chlorophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ga): ^{1}H NMR ($CDCl_3$, 400 MHz)



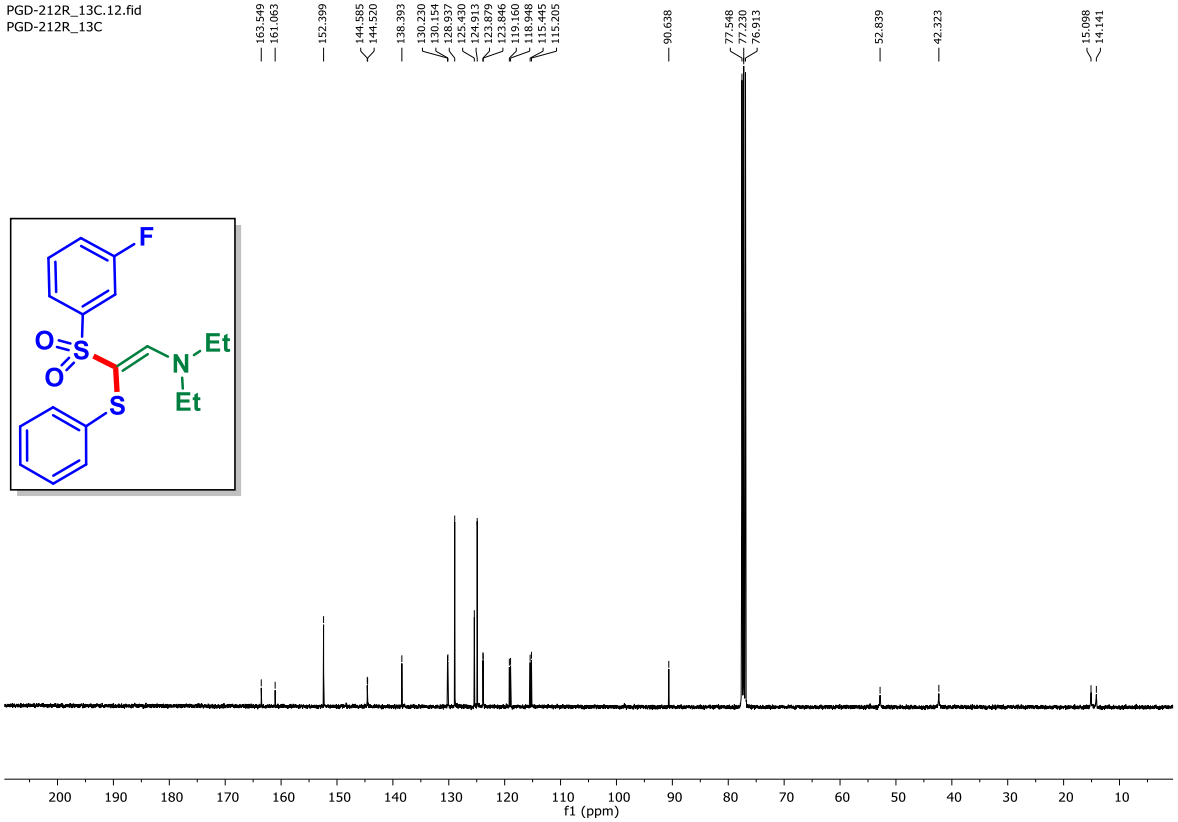
(*E*)-2-((4-chlorophenyl)sulfonyl)-N,N-diethyl-2-(phenylthio)ethen-1-amine (3ga): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



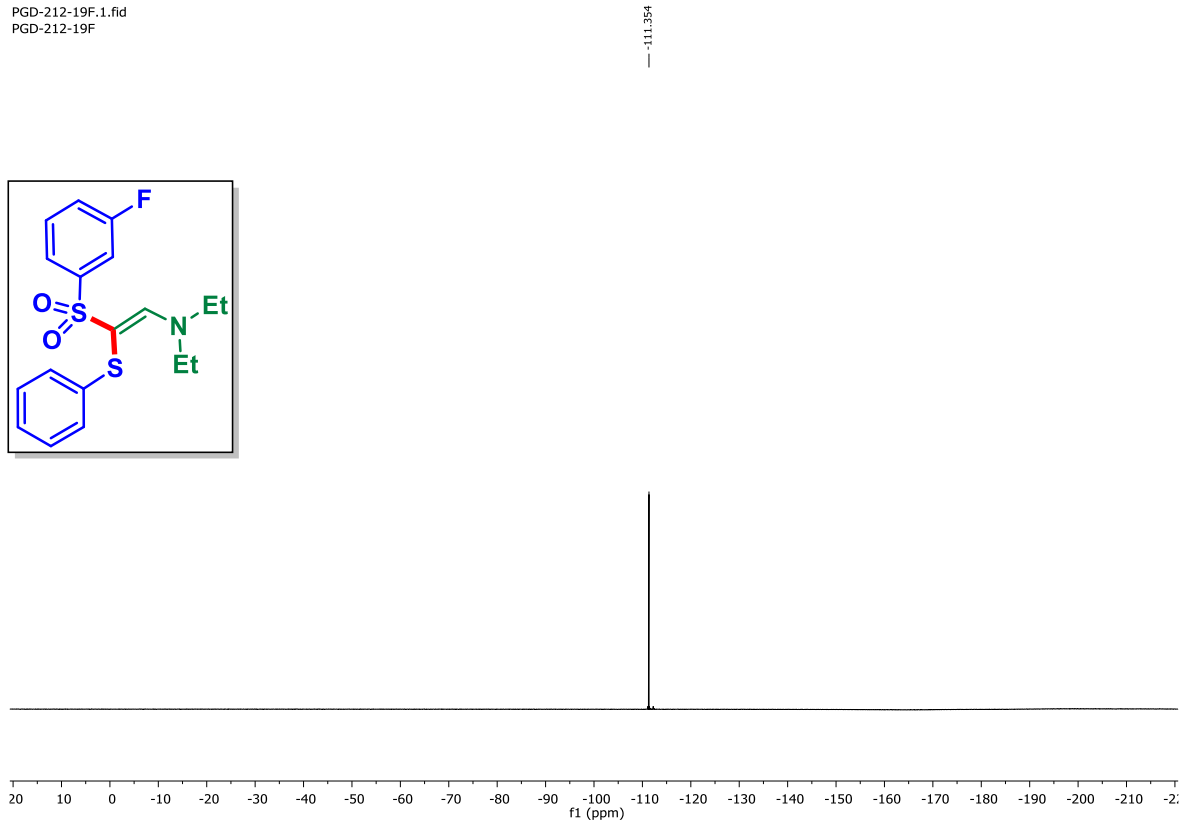
(*E*)-*N*,*N*-diethyl-2-((3-fluorophenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ha): ^{1}H NMR ($CDCl_3$, 400 MHz)



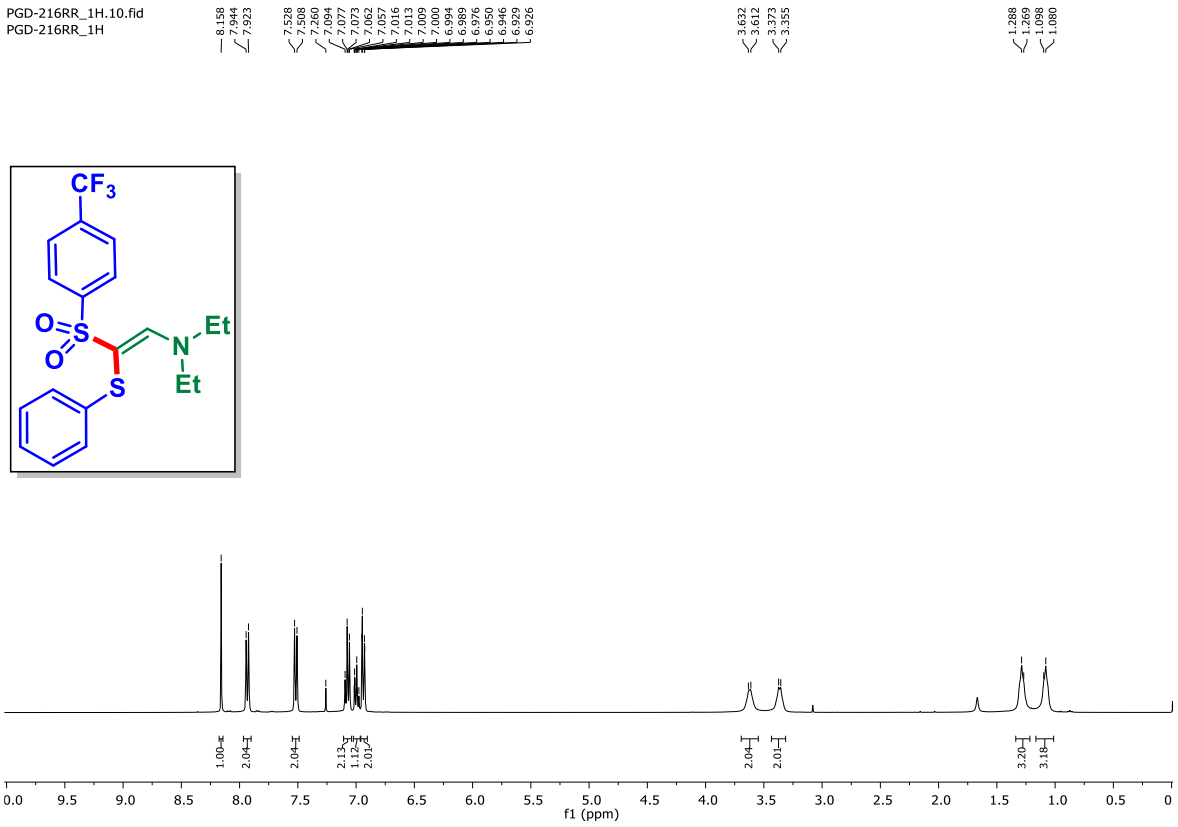
(*E*)-*N*,*N*-diethyl-2-((3-fluorophenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ha): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



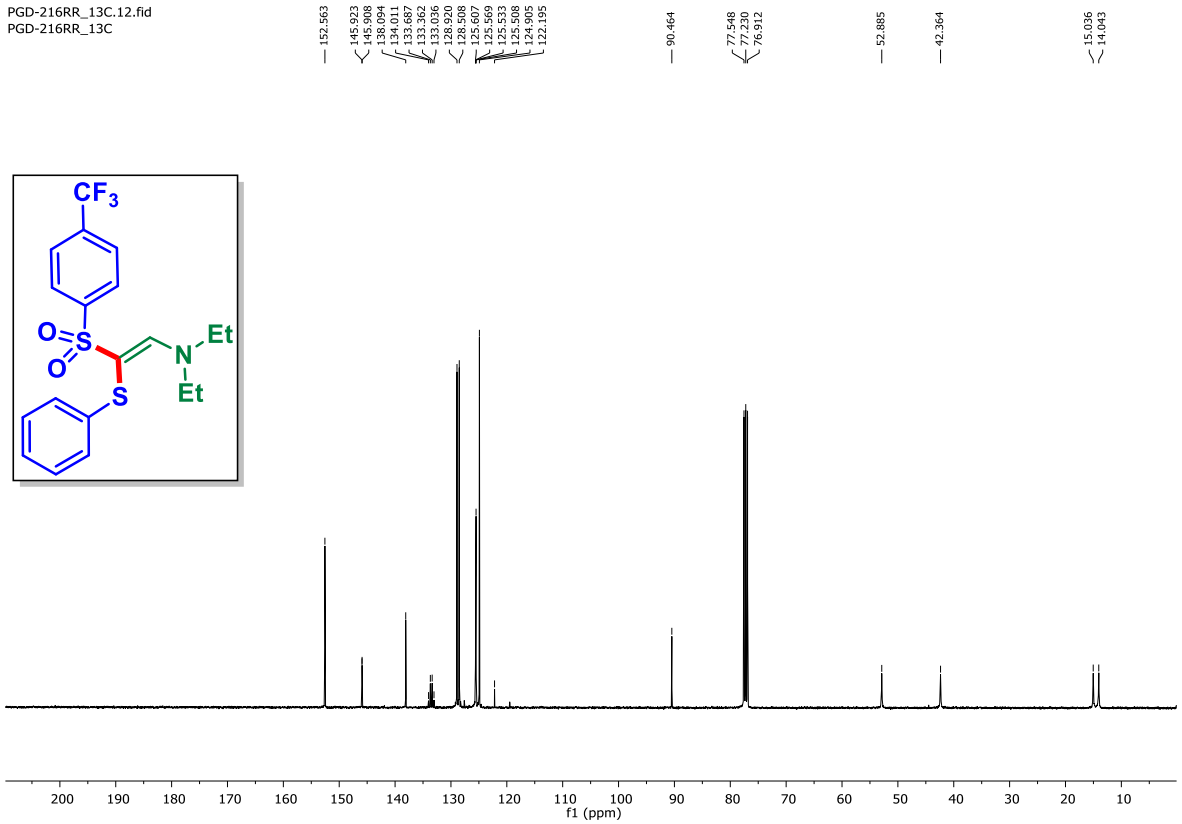
(*E*)-*N*,*N*-diethyl-2-((3-fluorophenyl)sulfonyl)-2-(phenylthio)ethen-1-amine (3ha): ^{19}F NMR (CDCl$_3$, 471 MHz)



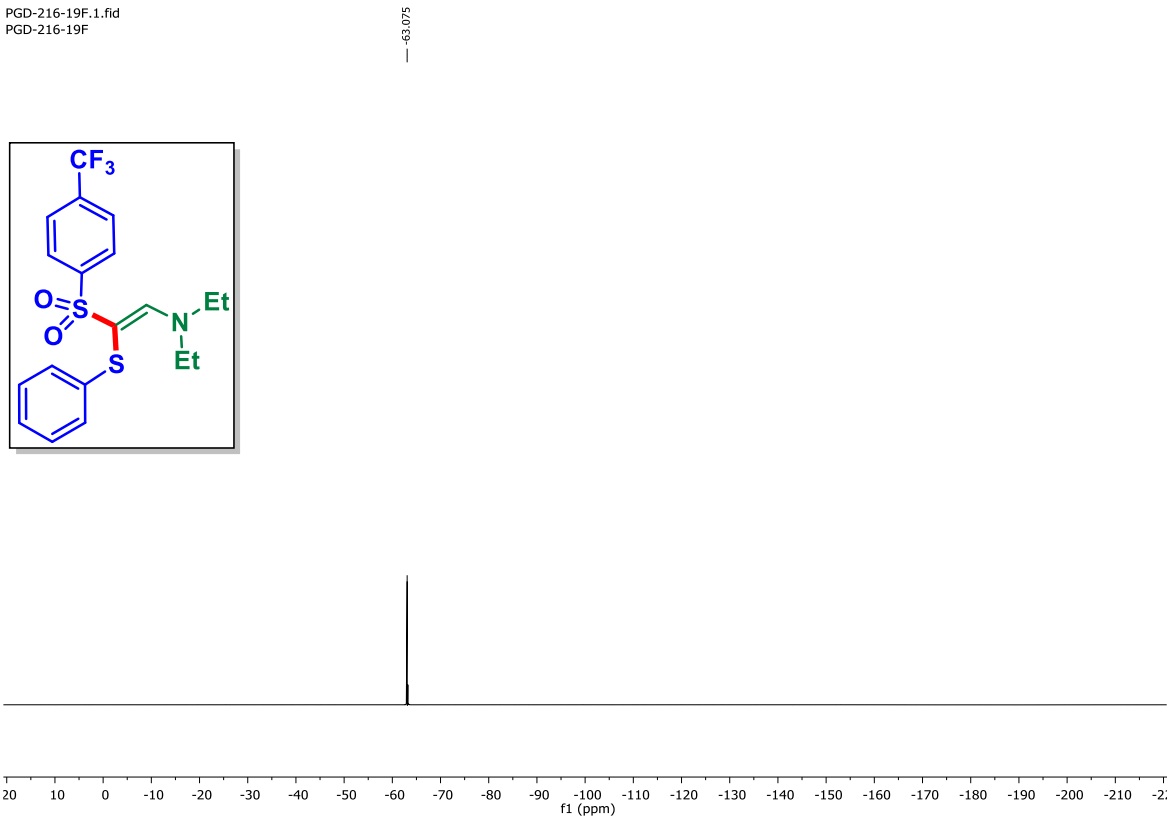
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3ia): ^{1}H NMR (CDCl$_3$, 400 MHz)



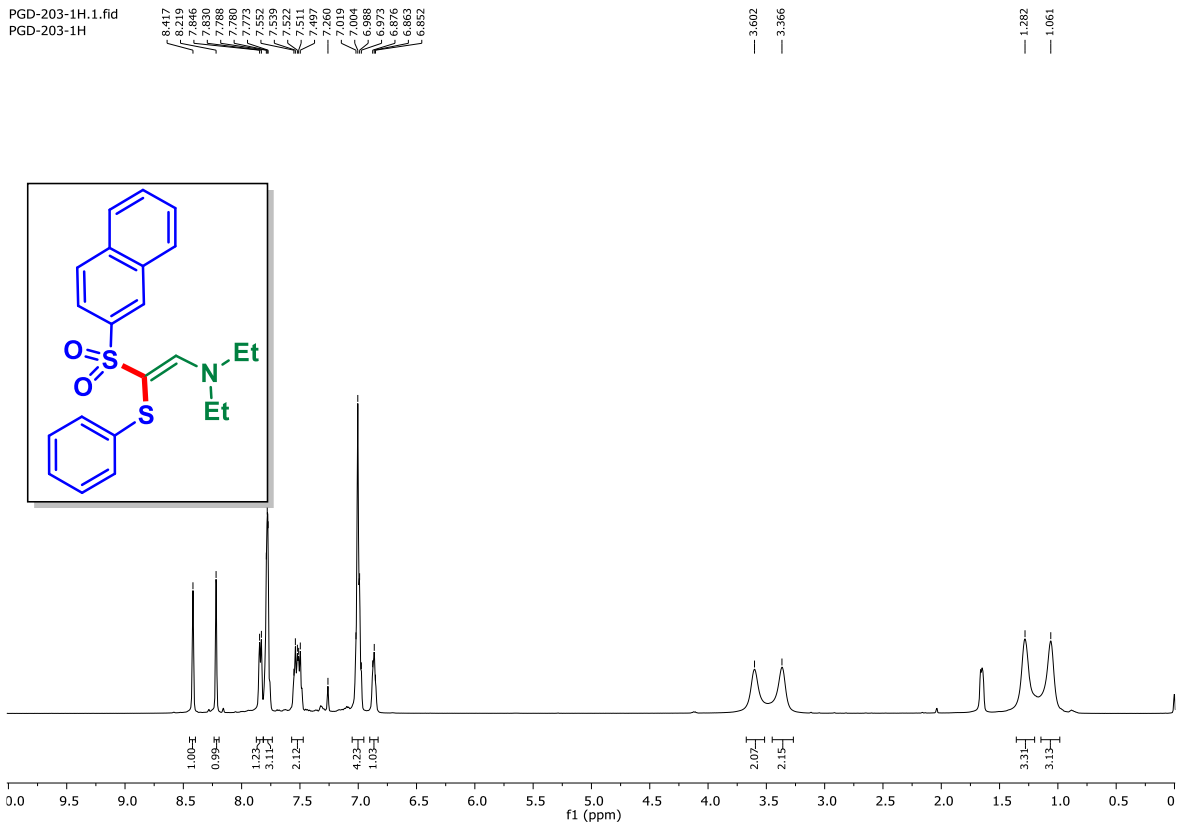
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3ia): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



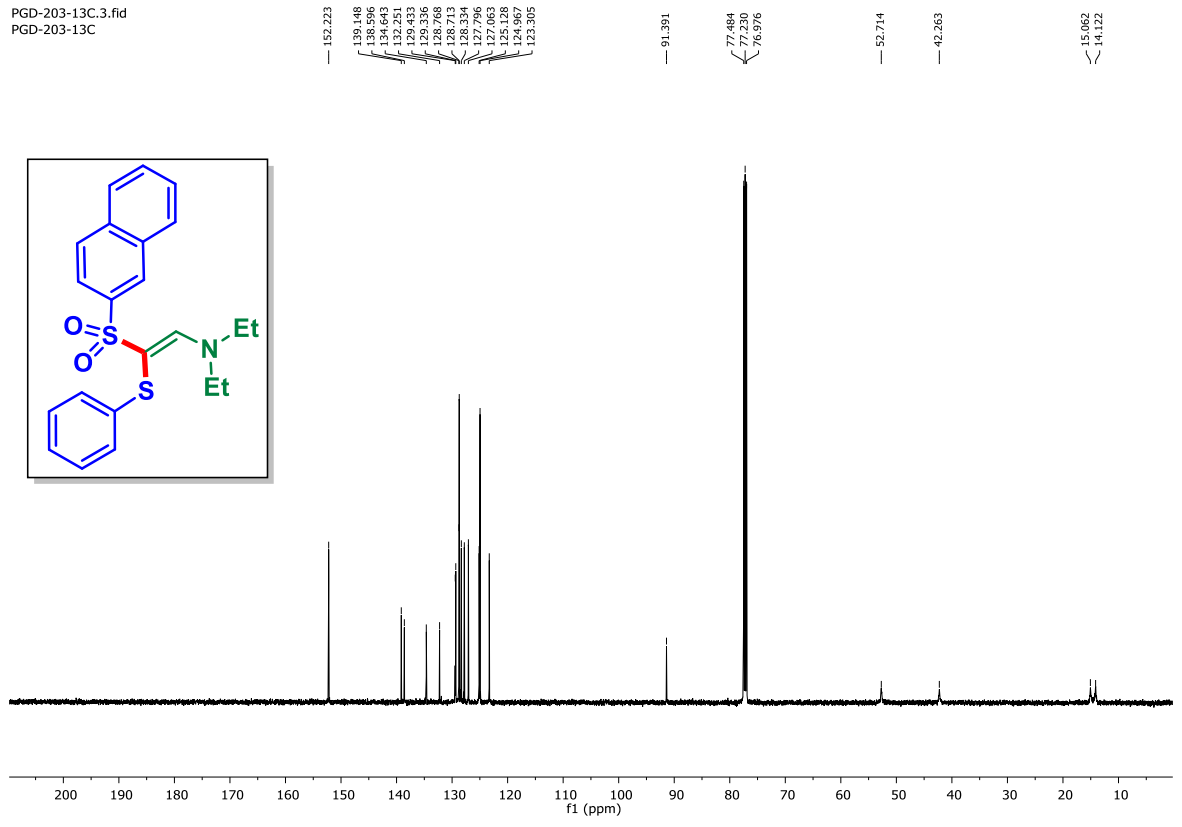
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3ia): ^{19}F NMR ($CDCl_3$, 471 MHz)



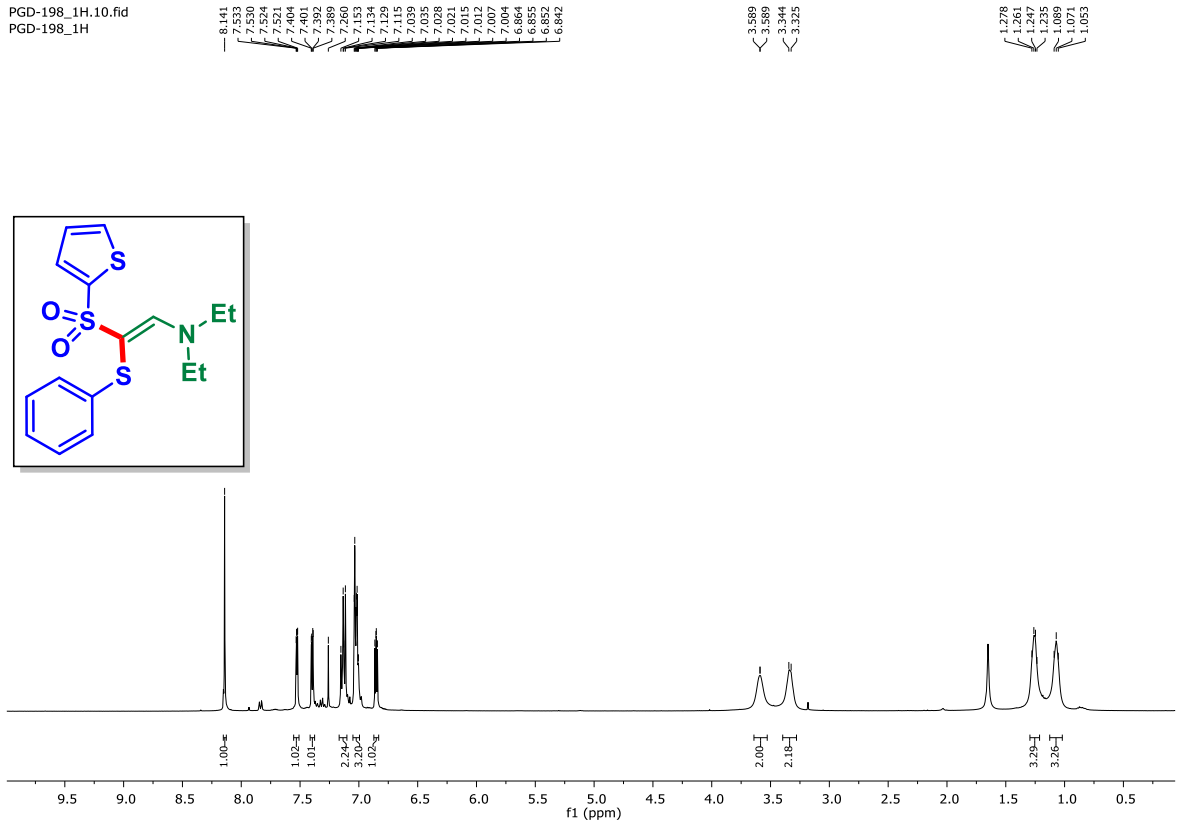
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylthio)ethen-1-amine (3ja): ^{1}H NMR (CDCl$_3$, 500 MHz)



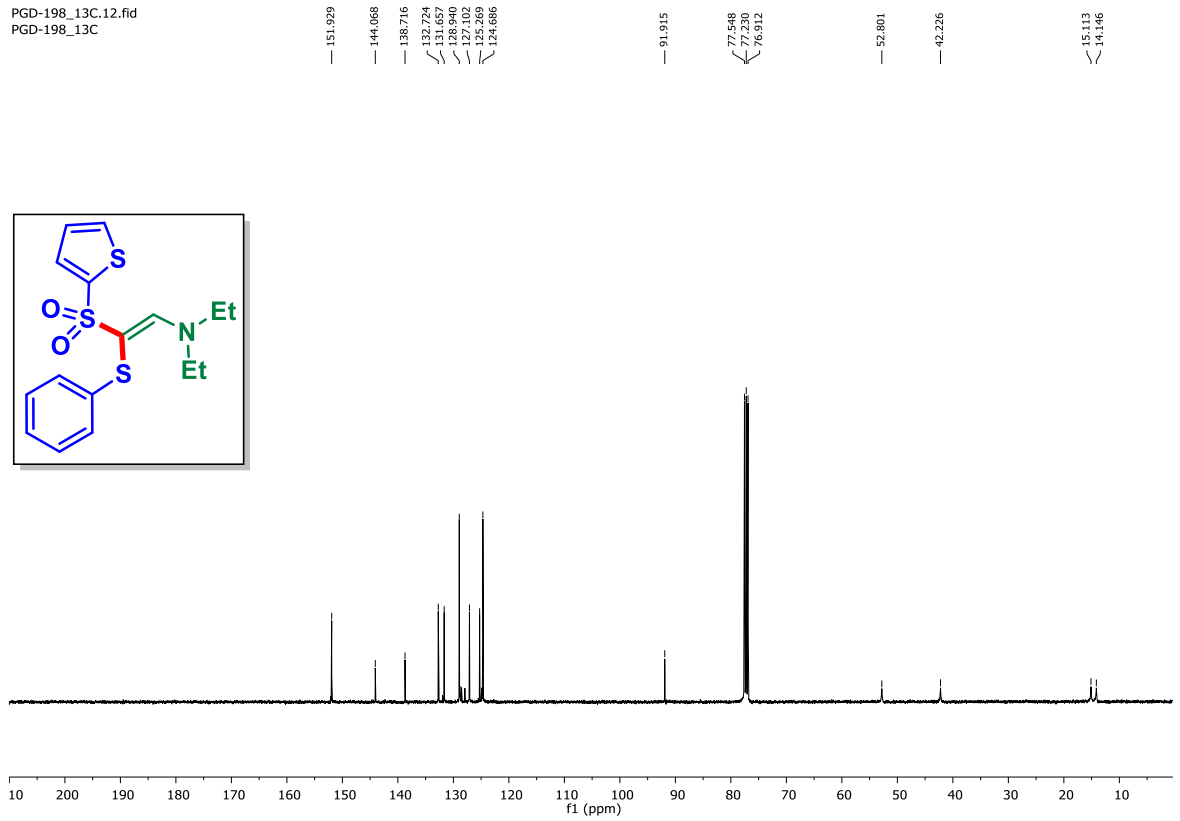
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylthio)ethen-1-amine (3ja): ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz)



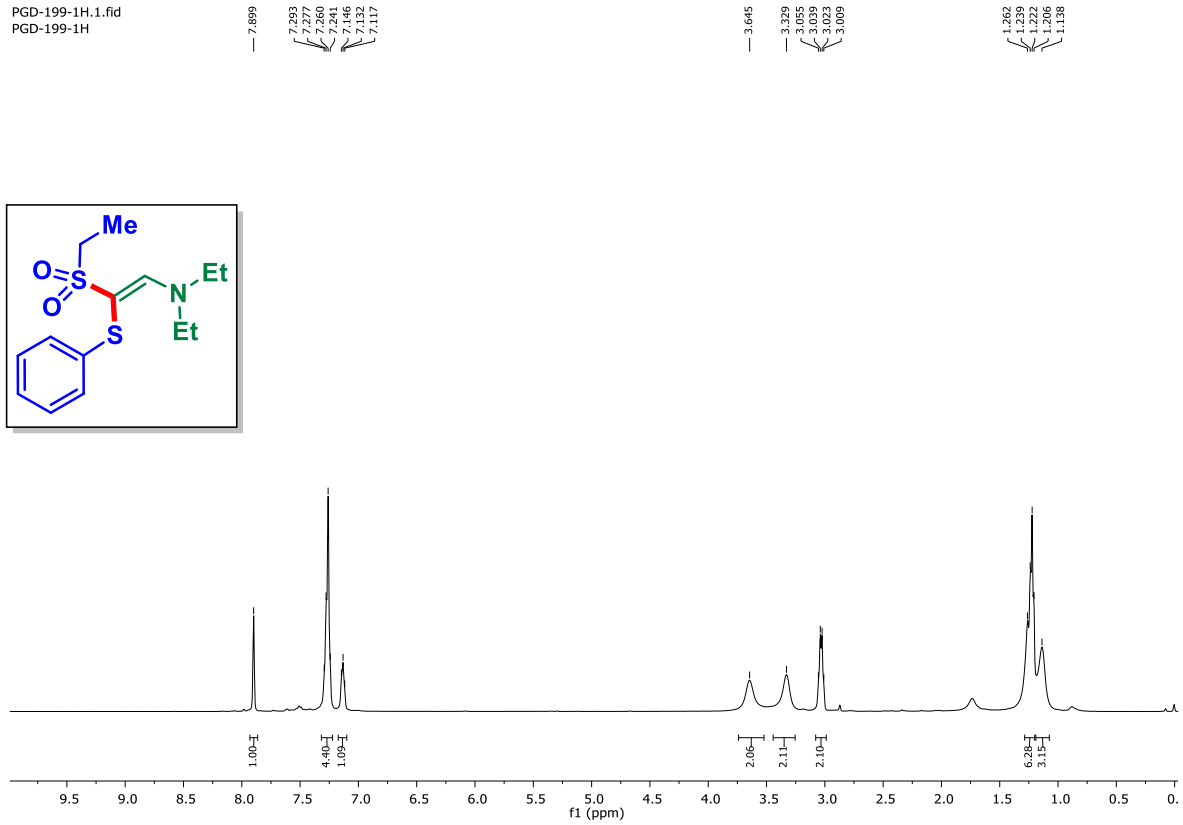
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-(thiophen-2-ylsulfonyl)ethen-1-amine (3ka): ^{1}H NMR (CDCl$_3$, 400 MHz)



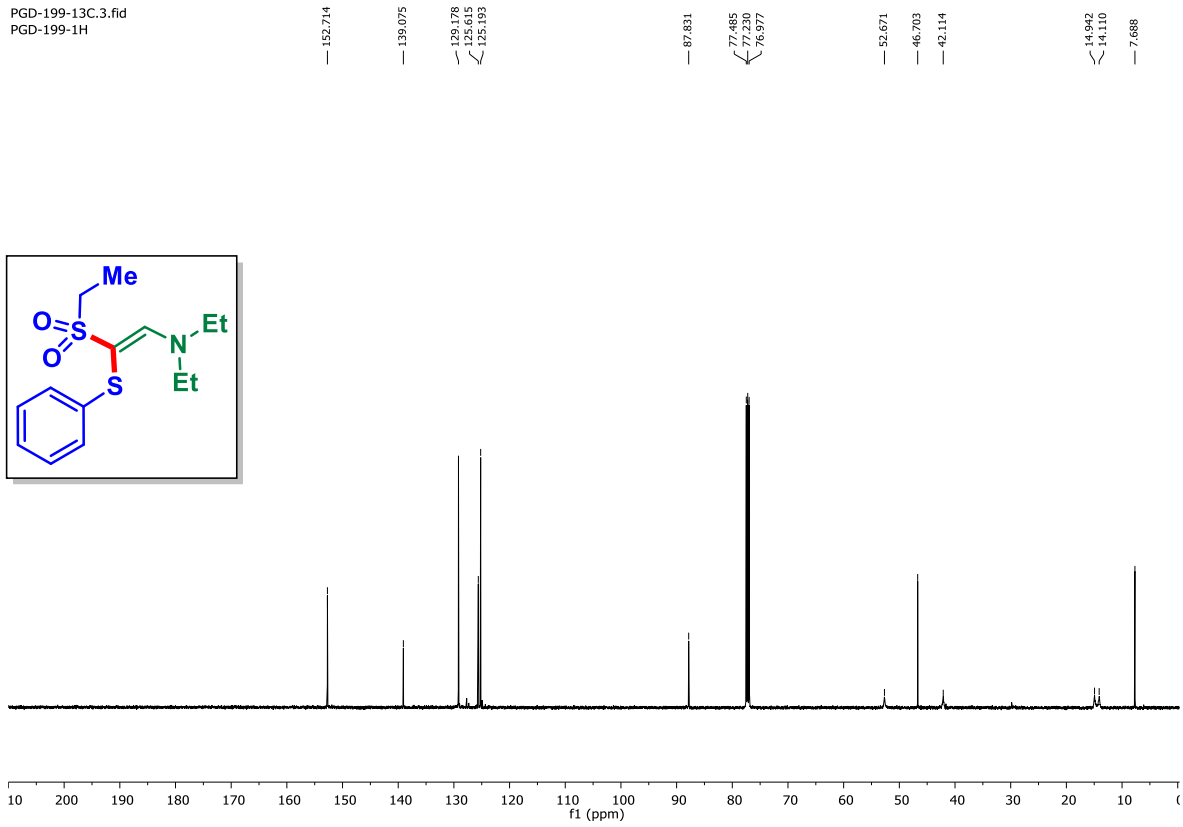
(*E*)-*N*,*N*-diethyl-2-(phenylthio)-2-(thiophen-2-ylsulfonyl)ethen-1-amine (3ka): ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz)



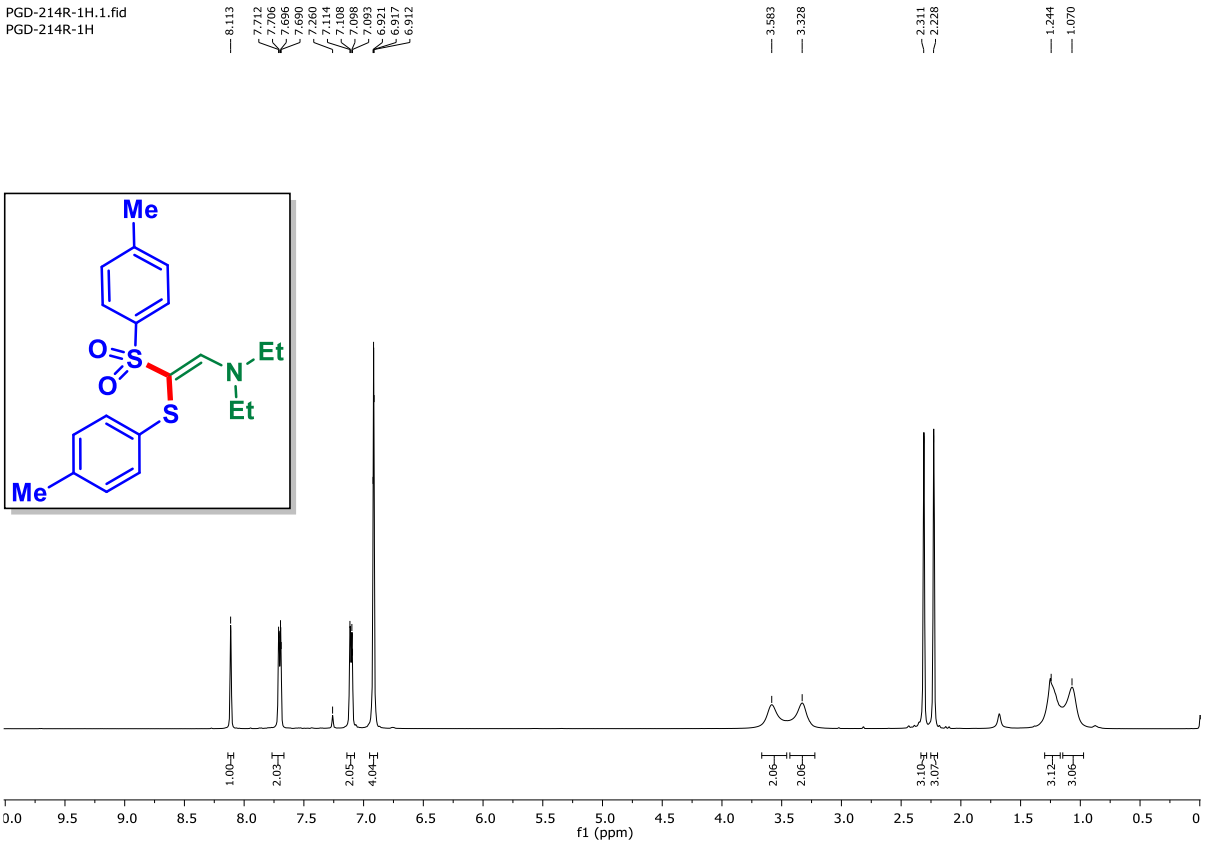
(*E*)-*N*,*N*-diethyl-2-(ethylsulfonyl)-2-(phenylthio)ethen-1-amine (3la): ^{1}H NMR ($CDCl_3$, 500 MHz)



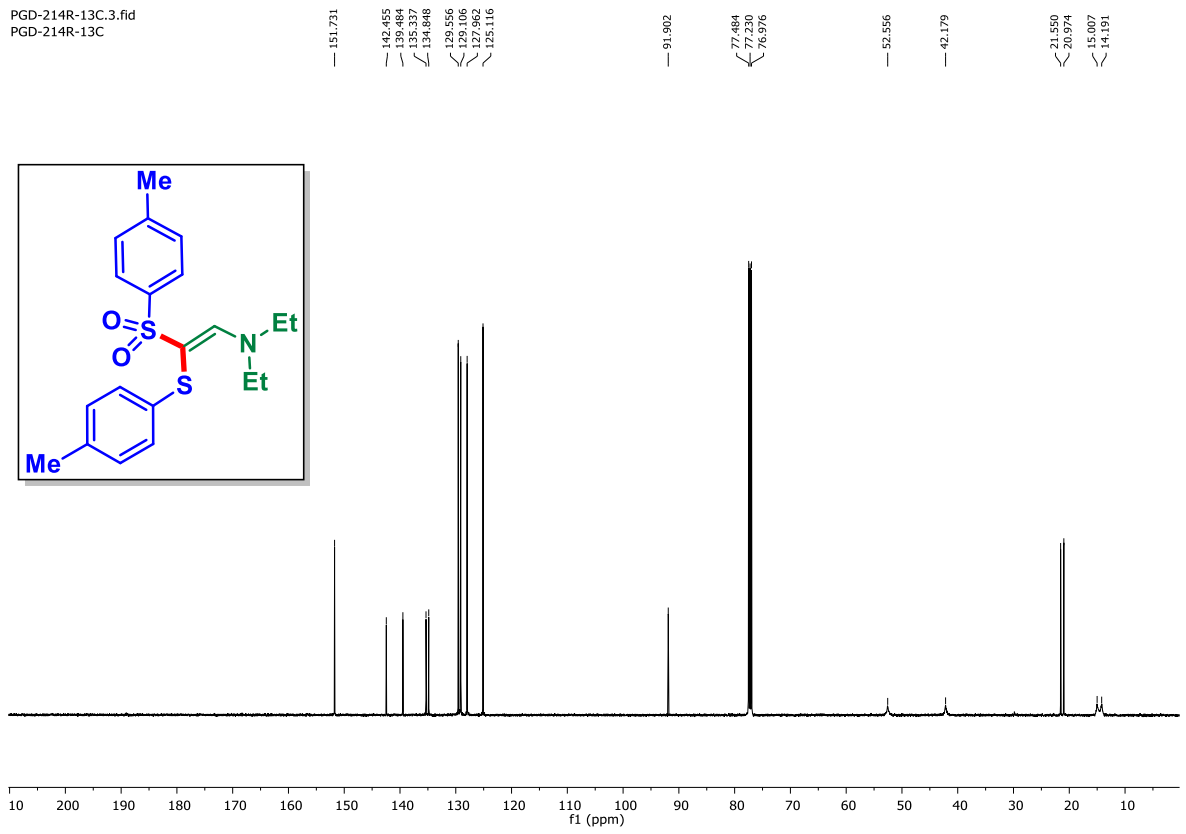
(*E*)-*N*,*N*-diethyl-2-(ethylsulfonyl)-2-(phenylthio)ethen-1-amine (3la): ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz)



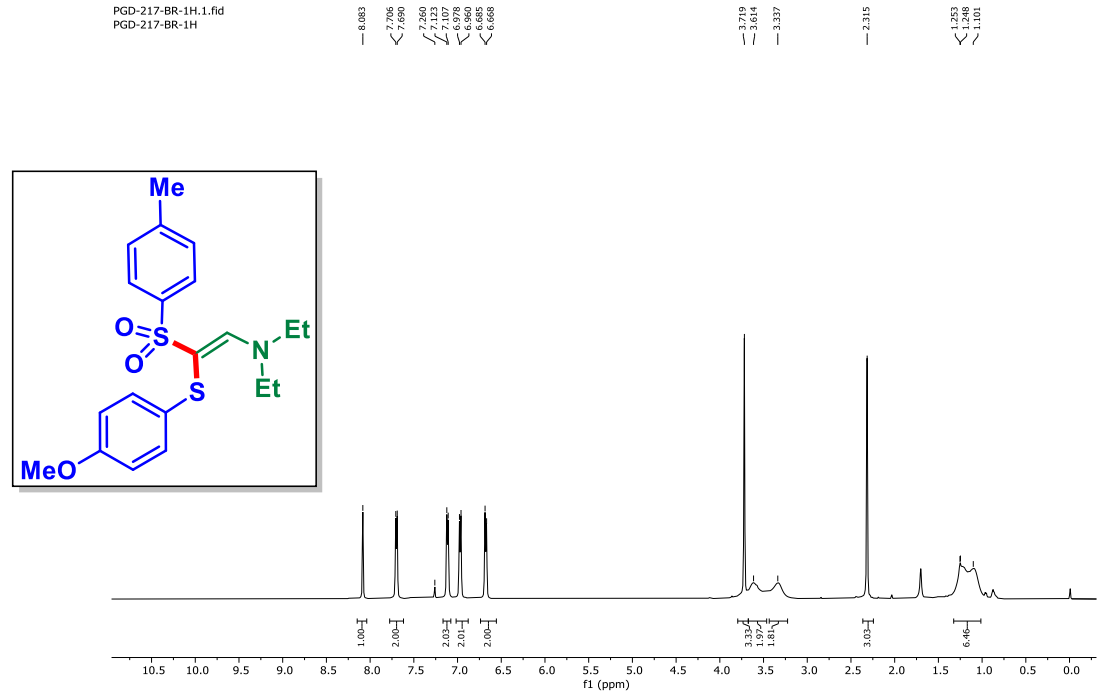
(*E*)-*N*,*N*-diethyl-2-(*p*-tolylthio)-2-tosylethen-1-amine (3ma): ^{1}H NMR (CDCl$_3$, 500 MHz)



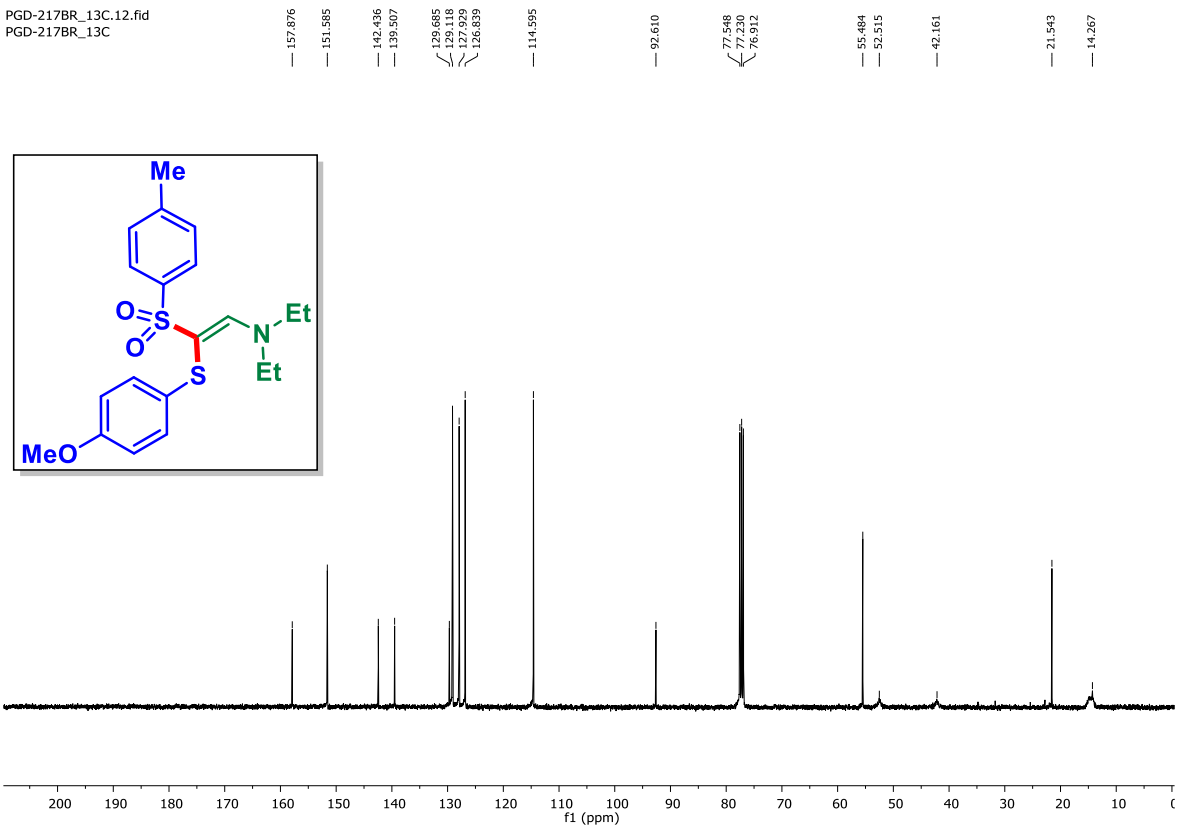
(*E*)-*N*,*N*-diethyl-2-(*p*-tolylthio)-2-tosylethen-1-amine (3ma): ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz)



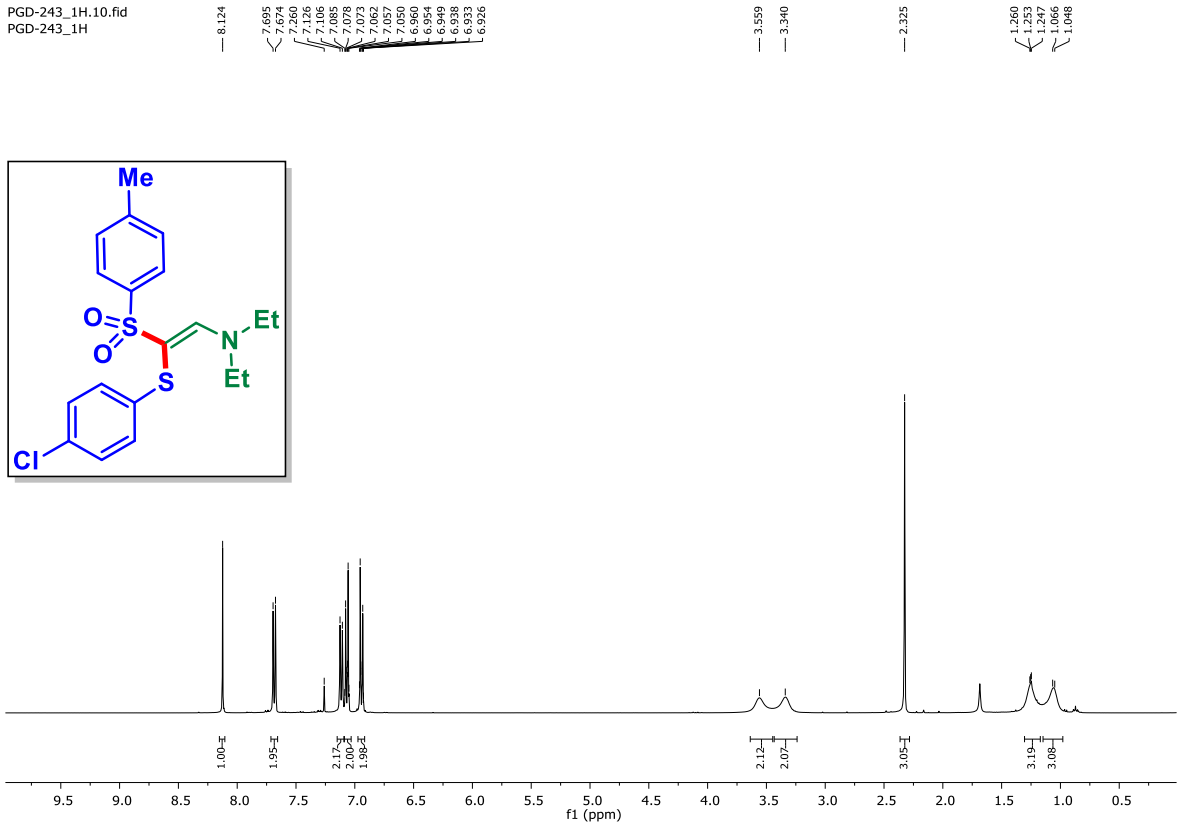
(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)thio)-2-(m-tolylsulfonyl)ethen-1-amine (3na): ^{1}H NMR ($CDCl_3$, 500 MHz)



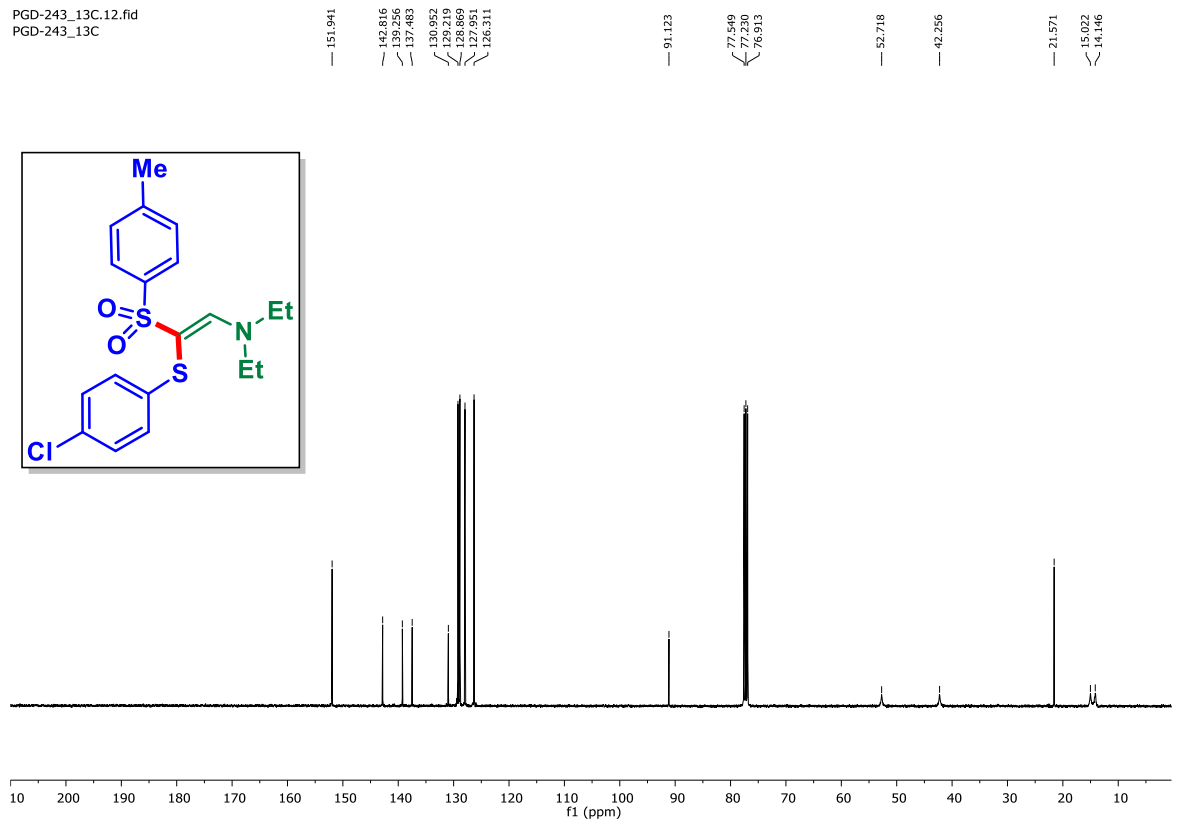
(*E*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)thio)-2-(m-tolylsulfonyl)ethen-1-amine (3na): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



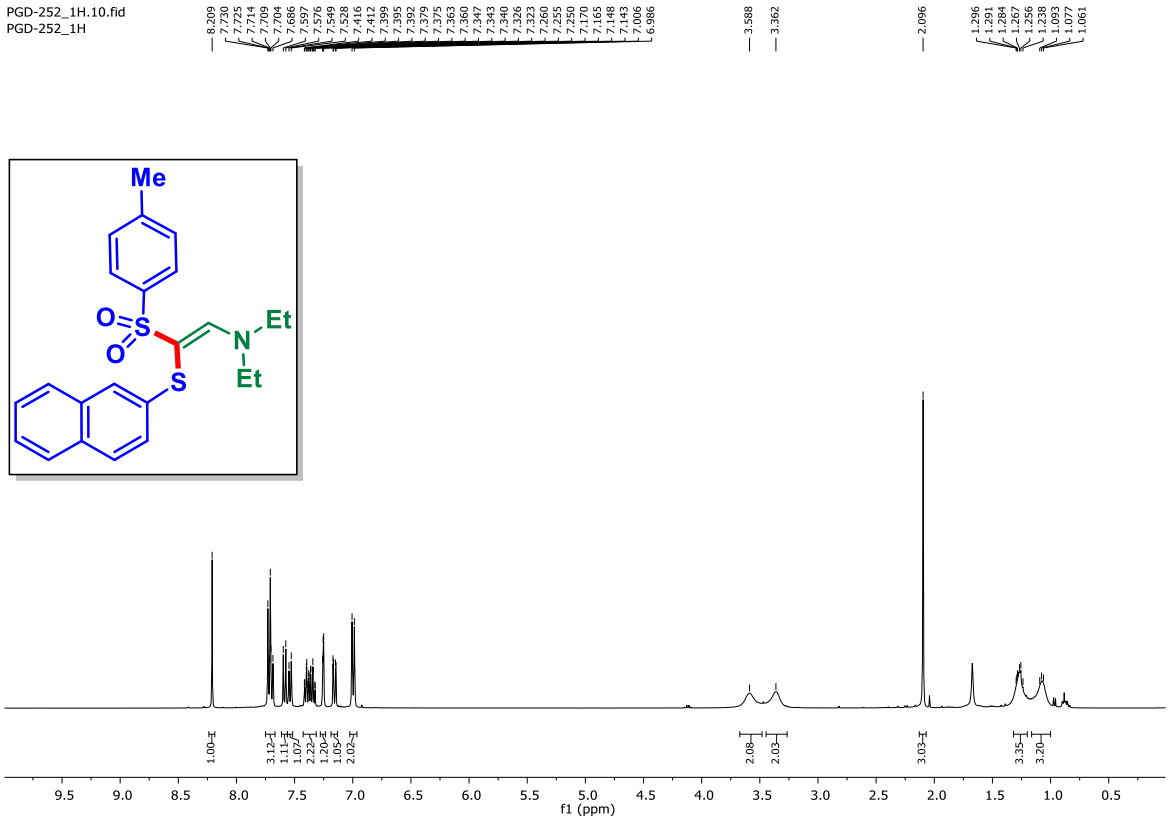
(*E*)-2-((4-chlorophenyl)thio)-*N*,*N*-diethyl-2-tosylethen-1-amine (3oa): ^{1}H NMR ($CDCl_3$, 400 MHz)



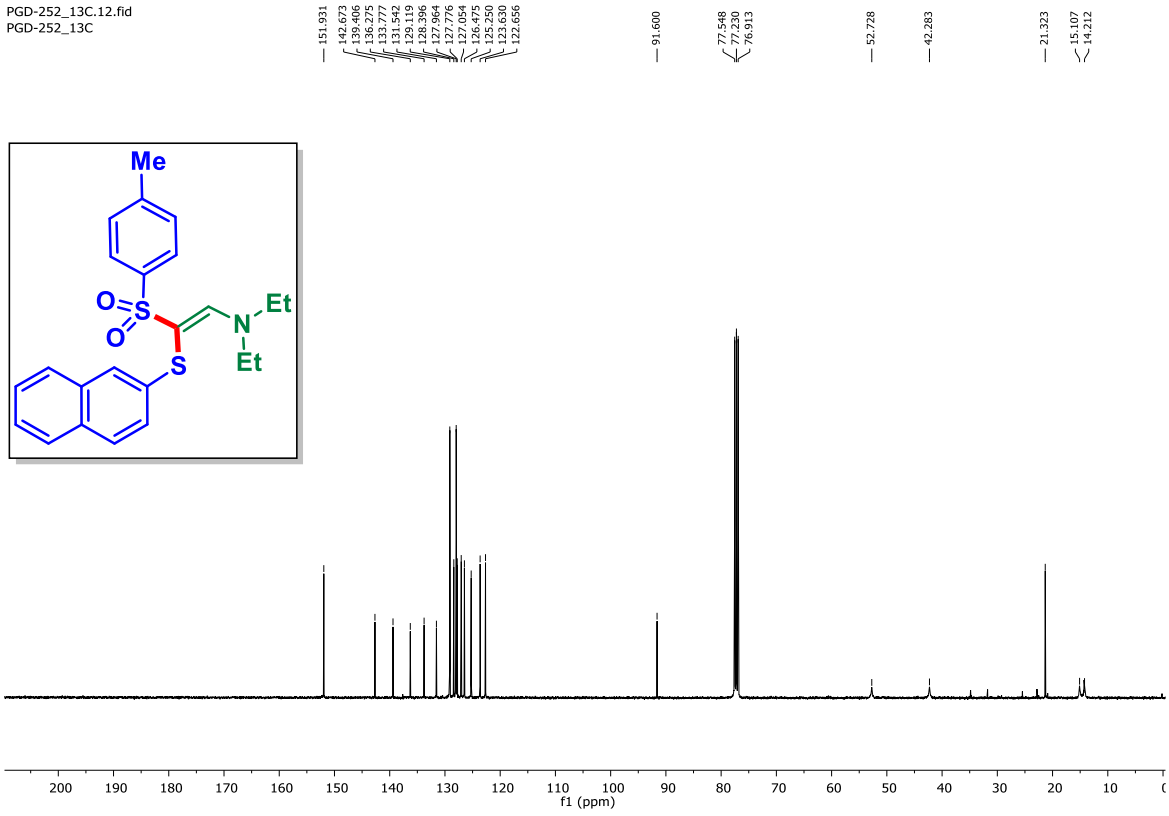
(*E*)-2-((4-chlorophenyl)thio)-*N*,*N*-diethyl-2-tosylethen-1-amine (3oa): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



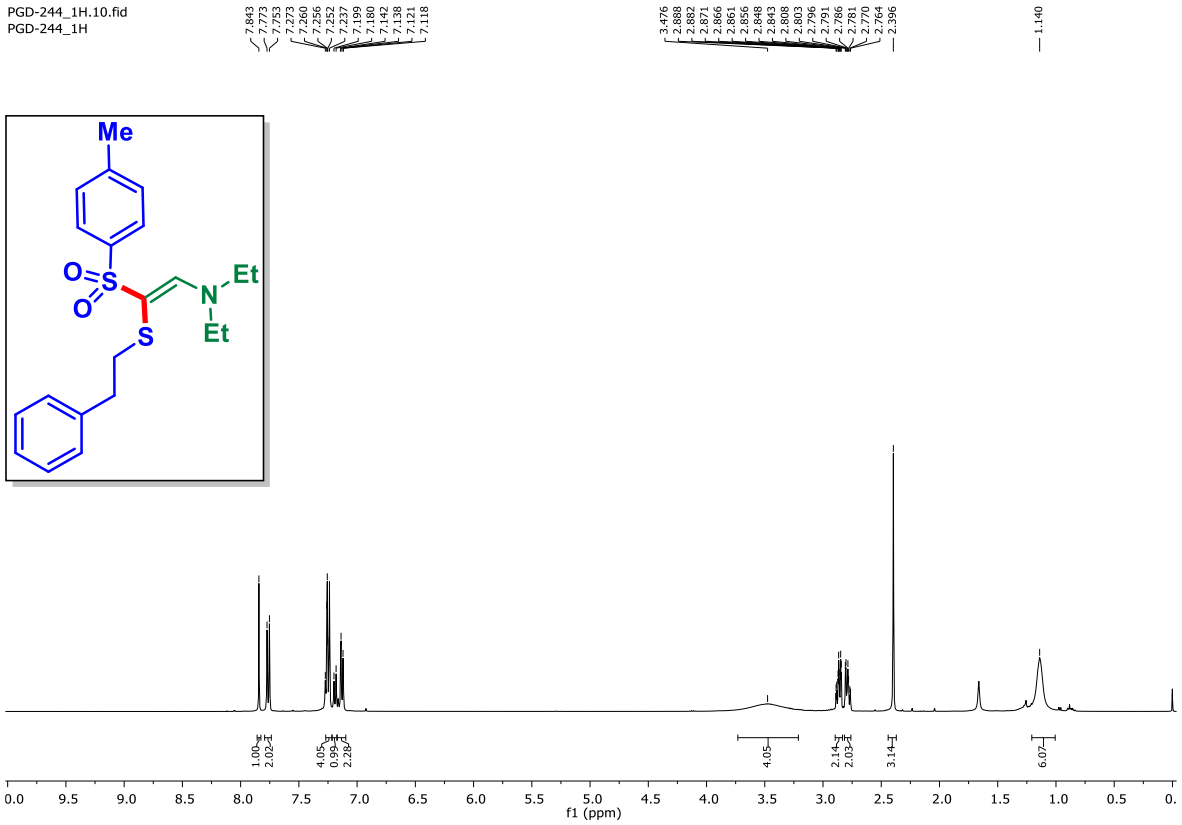
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylthio)-2-tosylethen-1-amine (3pa): ^{1}H NMR ($CDCl_3$, 400 MHz)



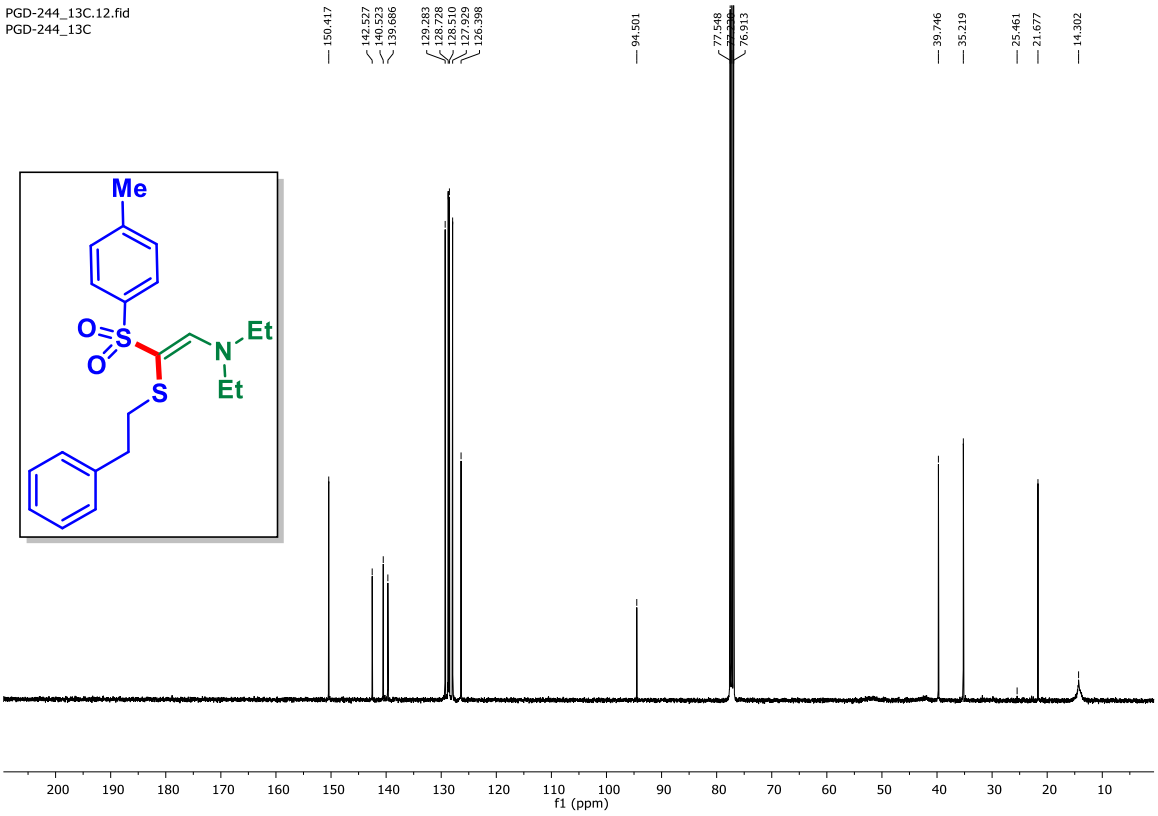
(*E*)-*N*,*N*-diethyl-2-(naphthalen-2-ylthio)-2-tosylethen-1-amine (3pa): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



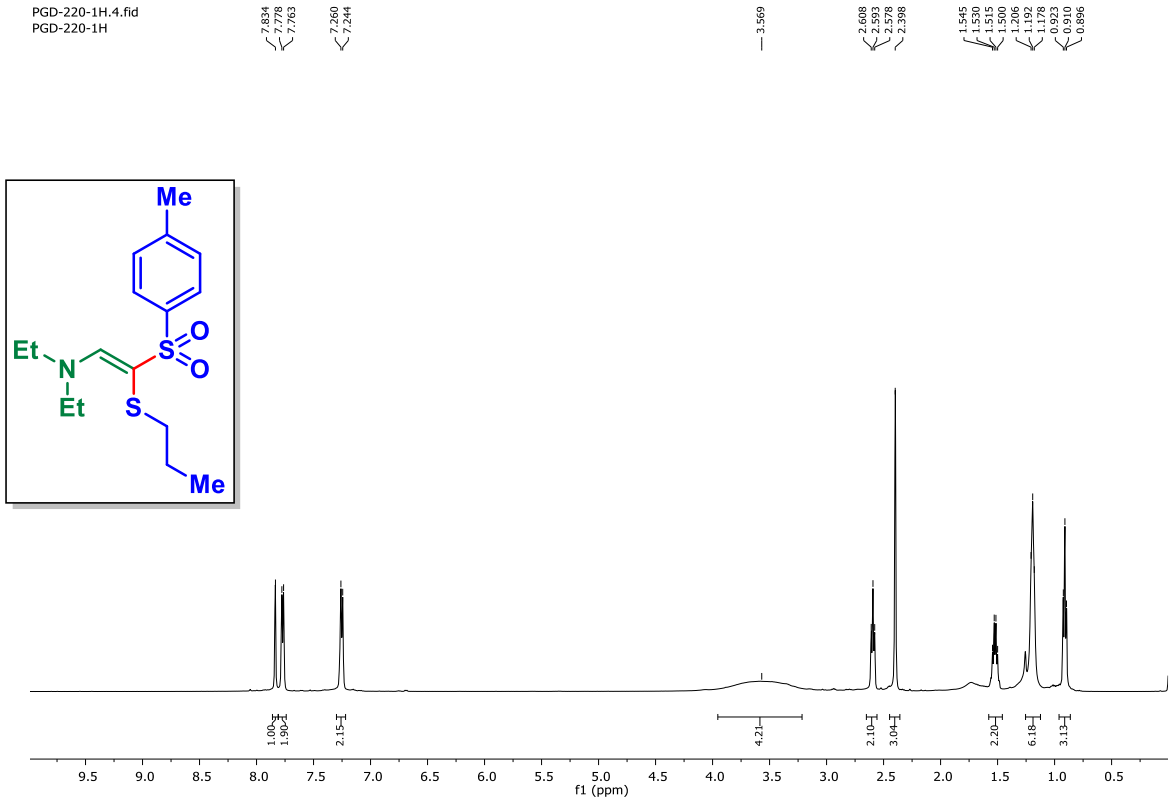
(*E*)-*N*,*N*-diethyl-2-(phenethylthio)-2-tosylethen-1-amine (3qa): ^{1}H NMR ($CDCl_3$, 400 MHz)



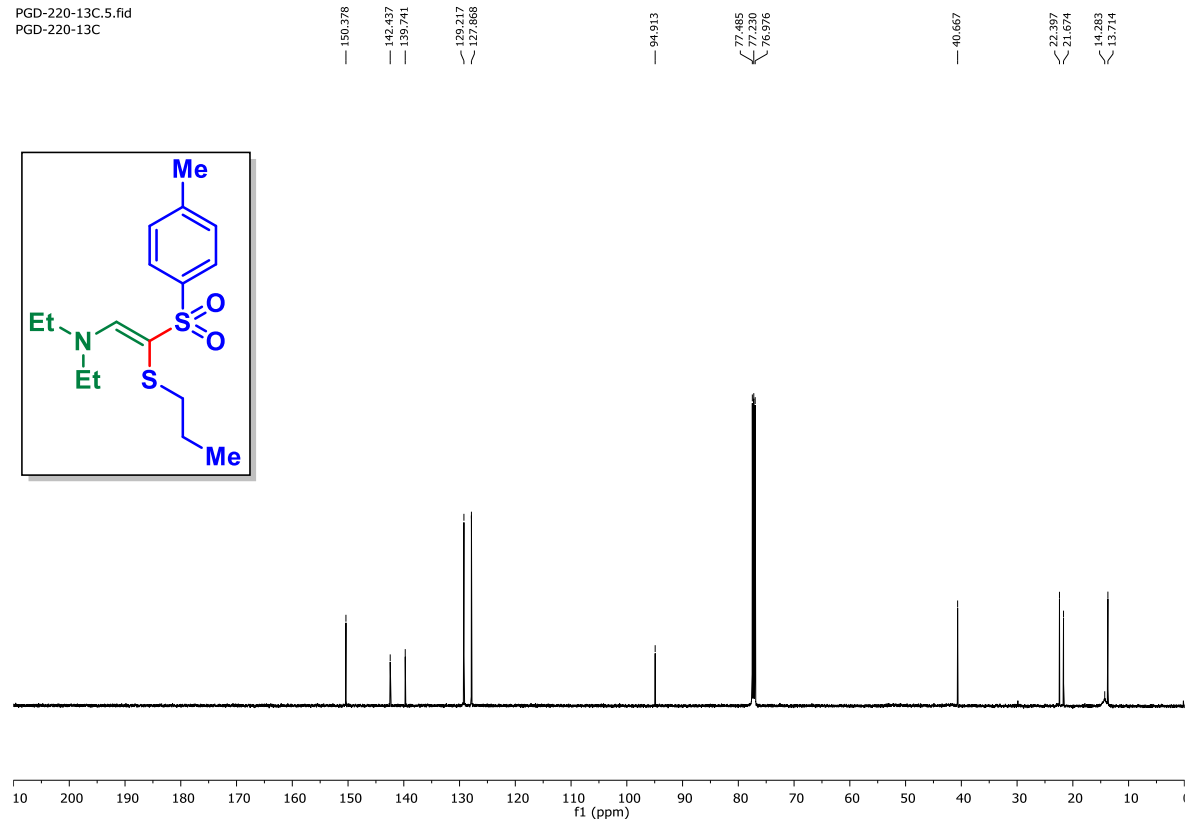
(*E*)-*N*,*N*-diethyl-2-(phenethylthio)-2-tosylethen-1-amine (3qa): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



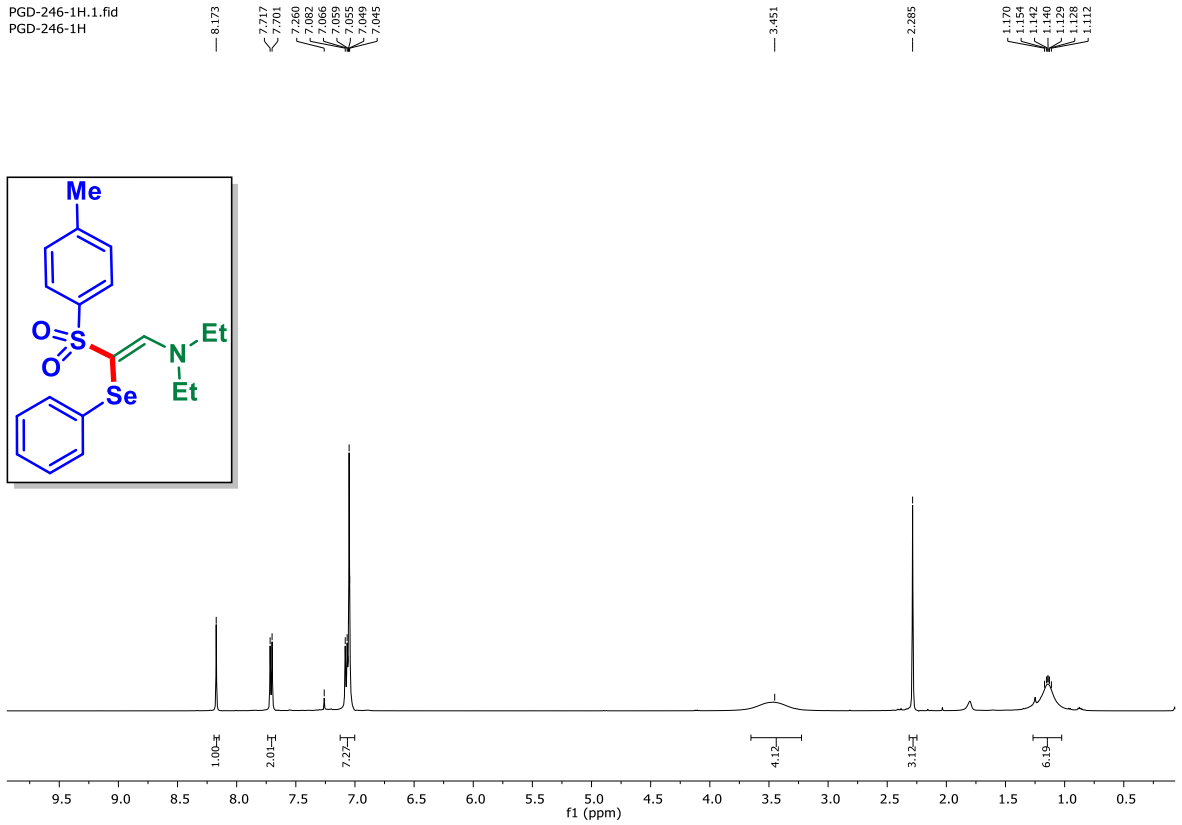
(*E*)-*N*,*N*-diethyl-2-(propylthio)-2-tosylethen-1-amine (3ra): ^{1}H NMR (CDCl$_3$, 500 MHz)



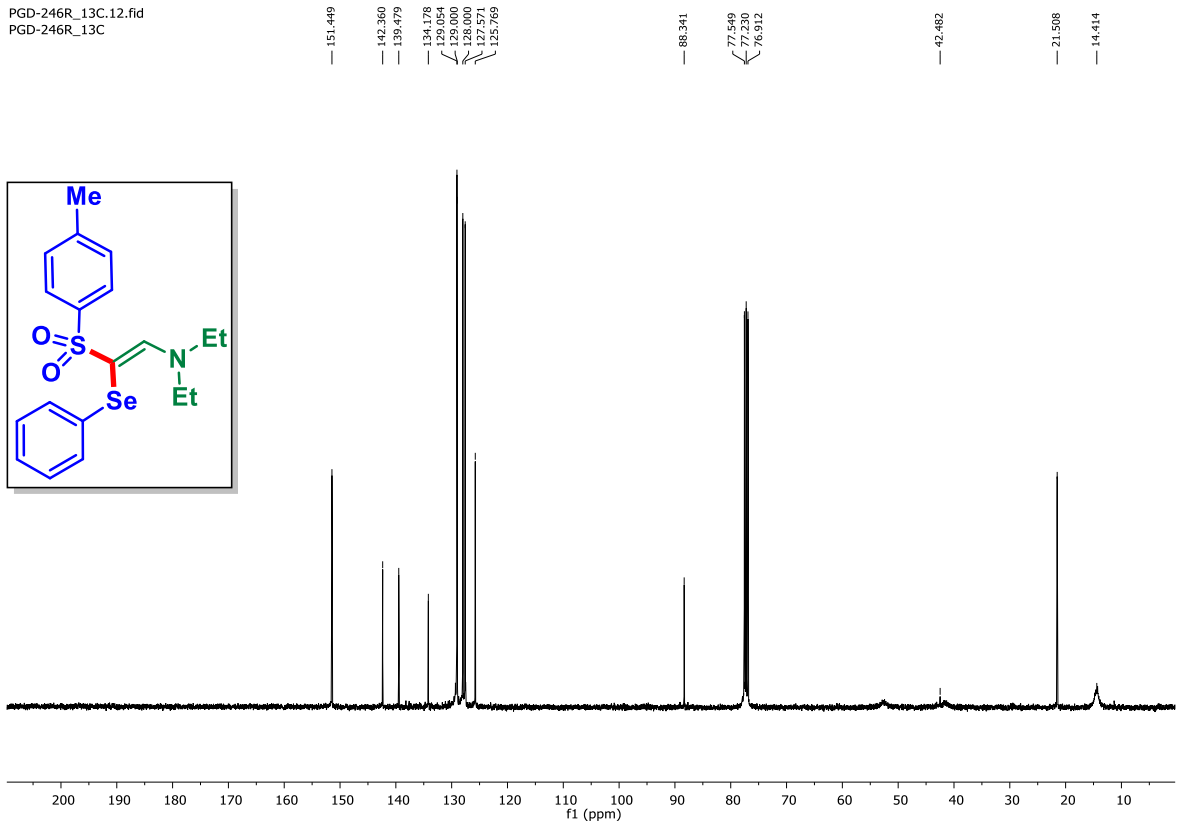
(*E*)-*N*,*N*-diethyl-2-(propylthio)-2-tosylethen-1-amine (3ra): ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz)



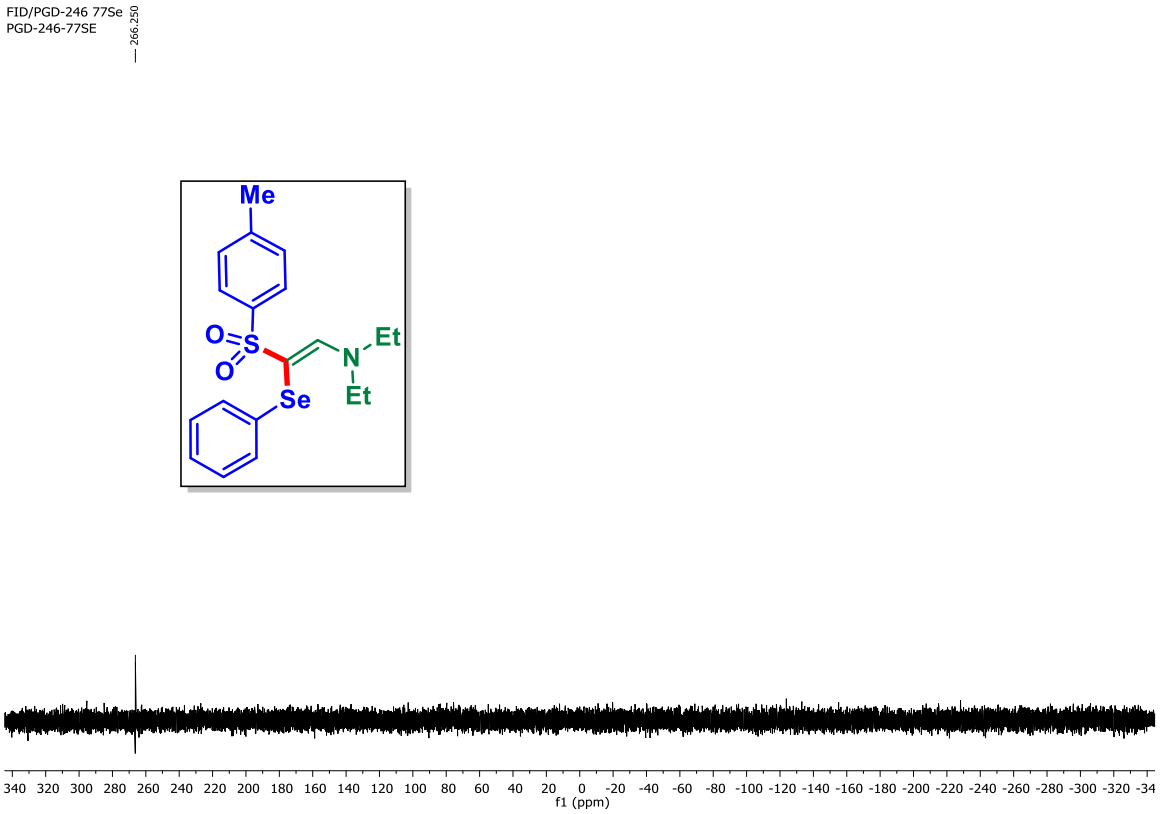
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-tosylethen-1-amine (3sa): ^{1}H NMR ($CDCl_3$, 500 MHz)



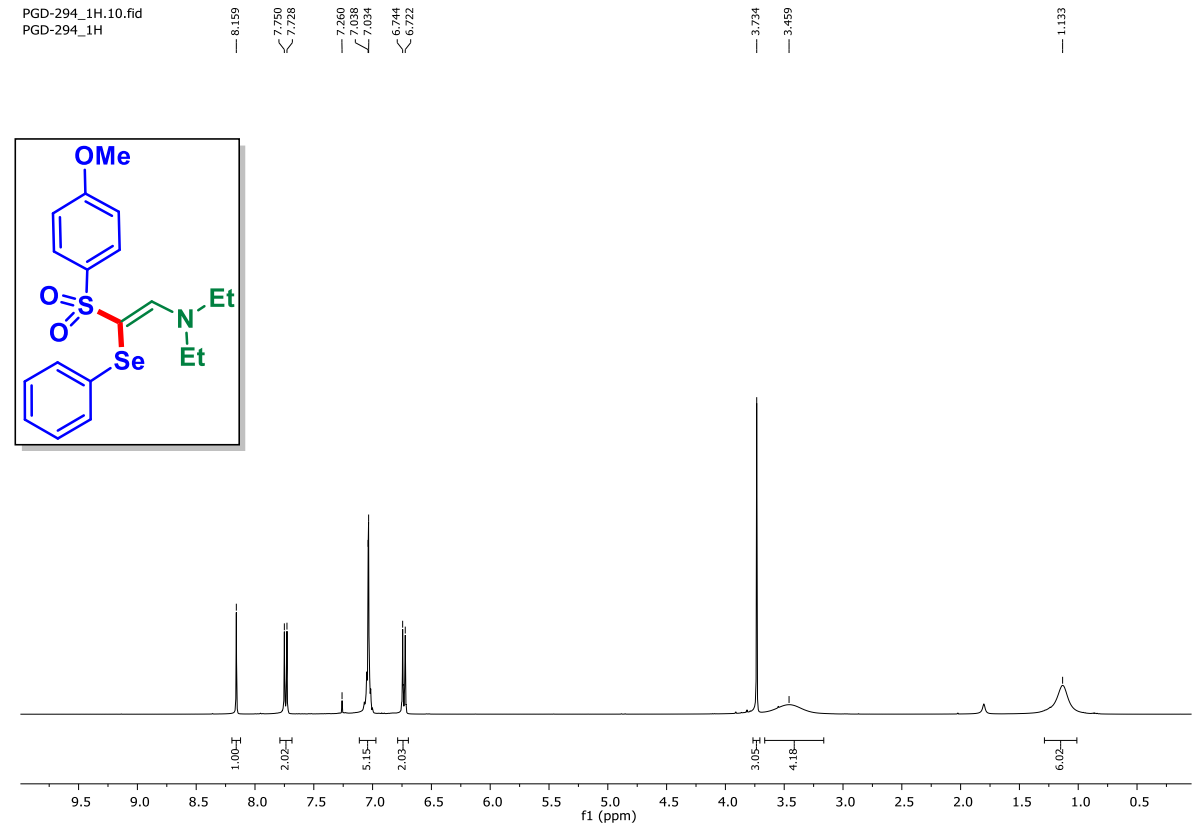
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-tosylethen-1-amine (3sa): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



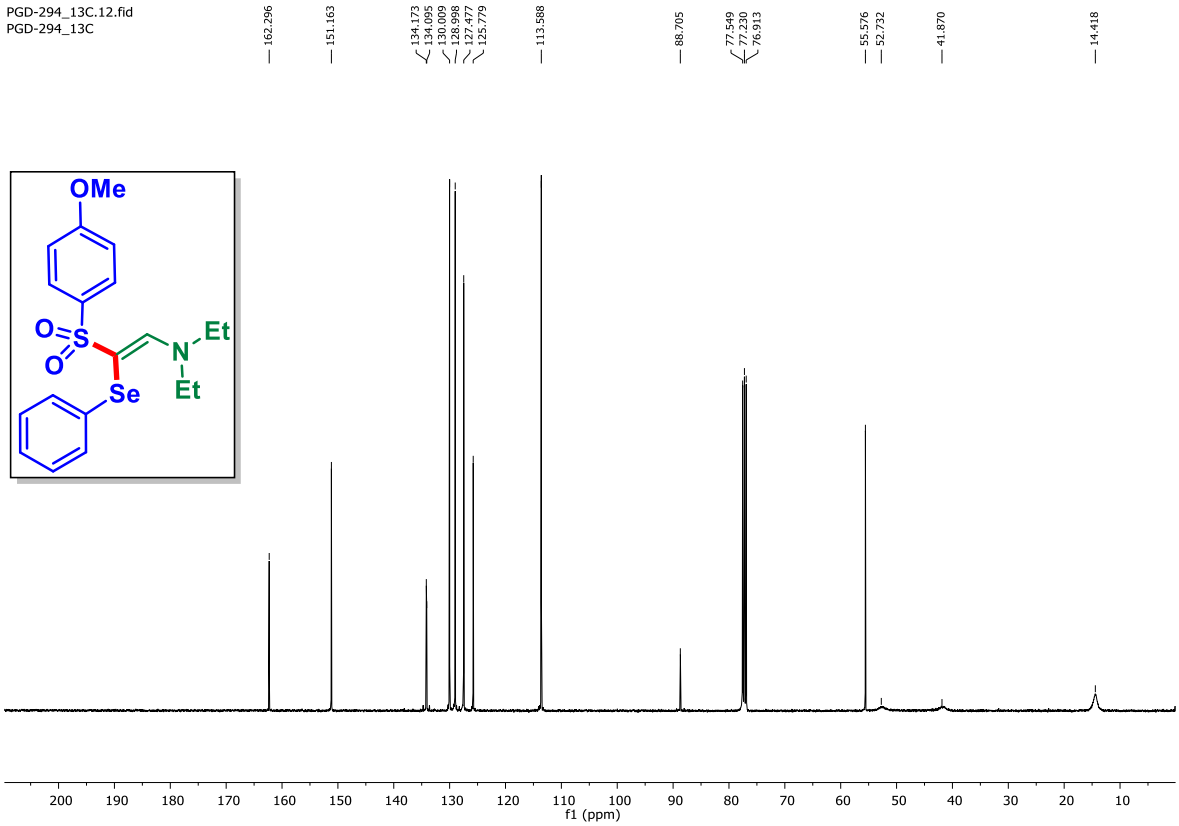
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-tosylethen-1-amine (3sa): ^{77}Se NMR (CDCl$_3$, 95 MHz)



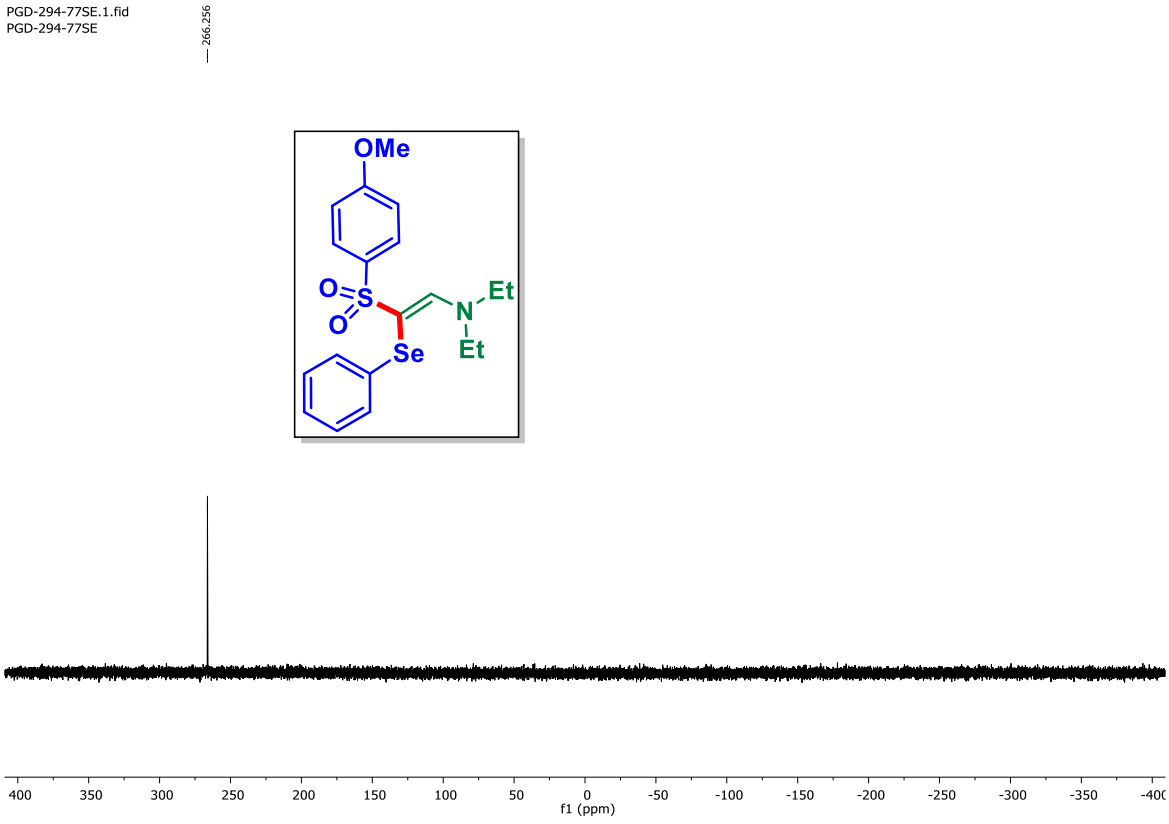
(*Z*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylselanyl)ethen-1-amine (3ta): ^{1}H NMR (CDCl$_3$, 400 MHz)



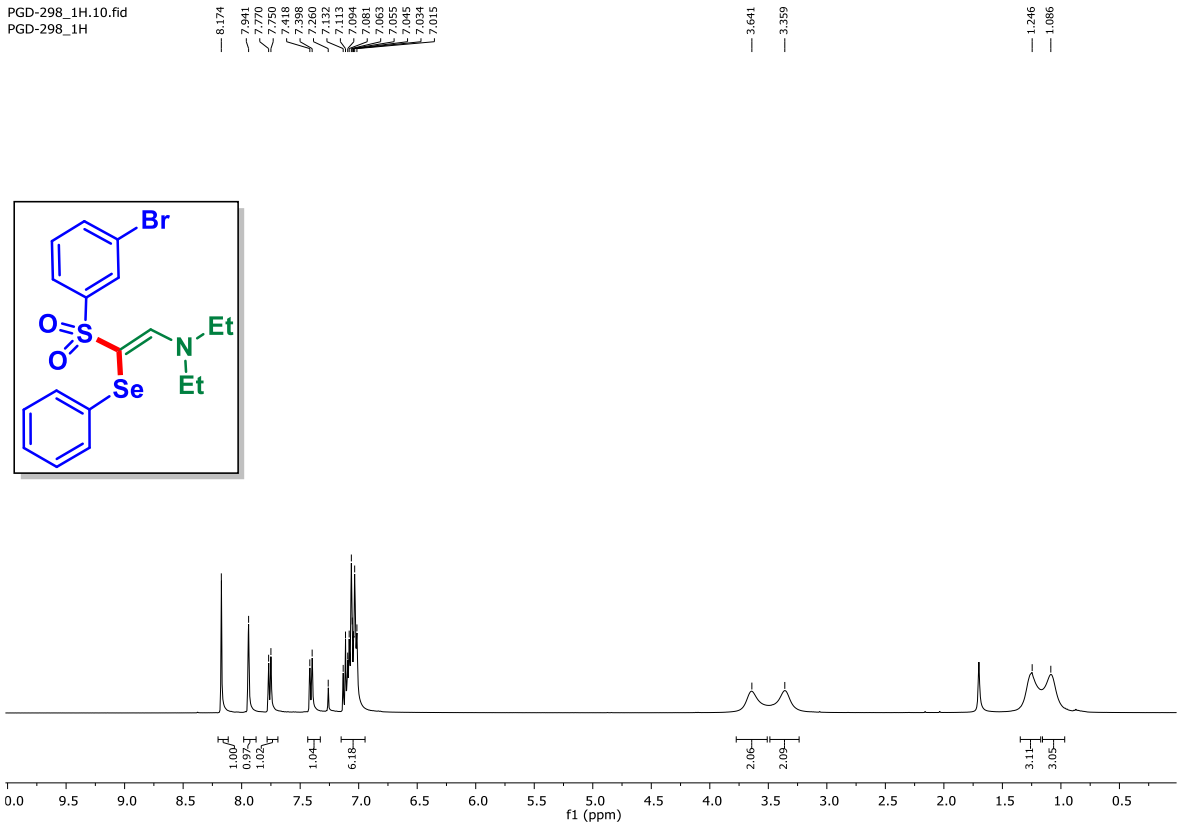
(*Z*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylselanyl)ethen-1-amine (3ta): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



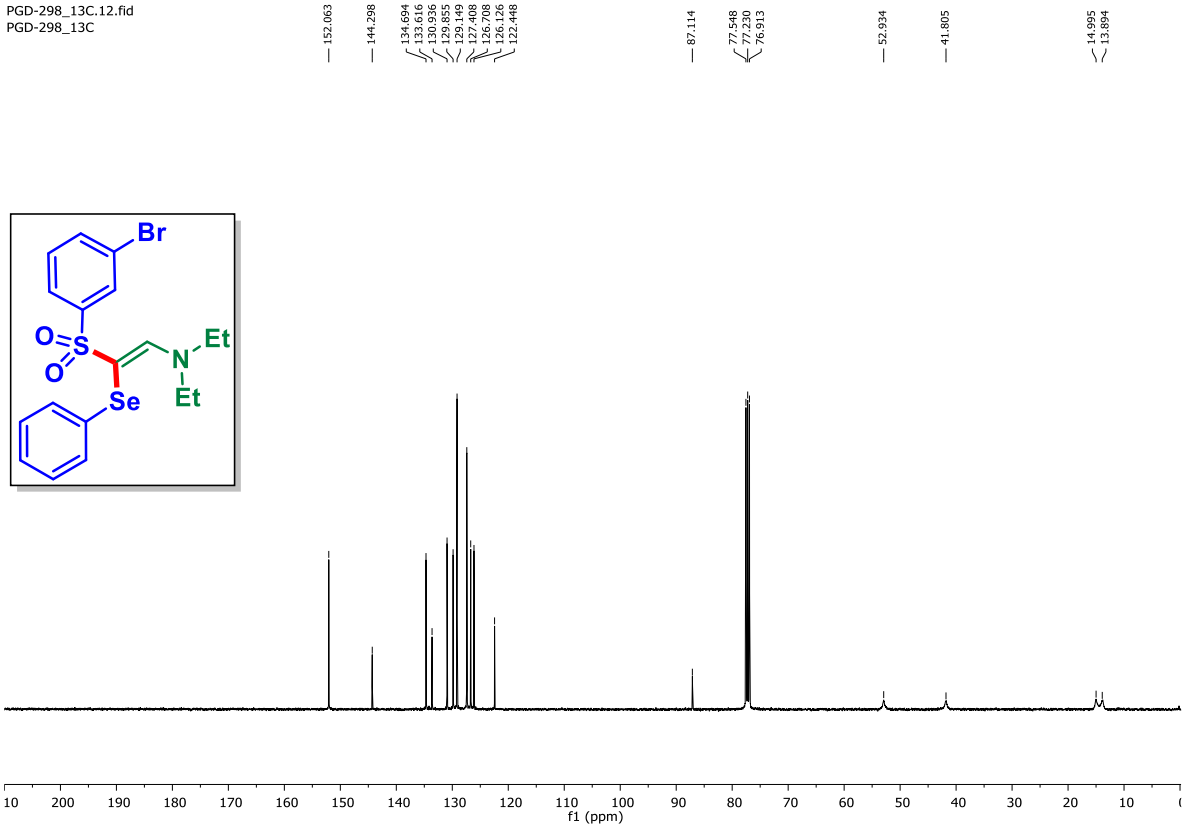
(*Z*)-*N*,*N*-diethyl-2-((4-methoxyphenyl)sulfonyl)-2-(phenylselanyl)ethen-1-amine (3ta): ^{77}Se NMR ($CDCl_3$, 95 MHz)



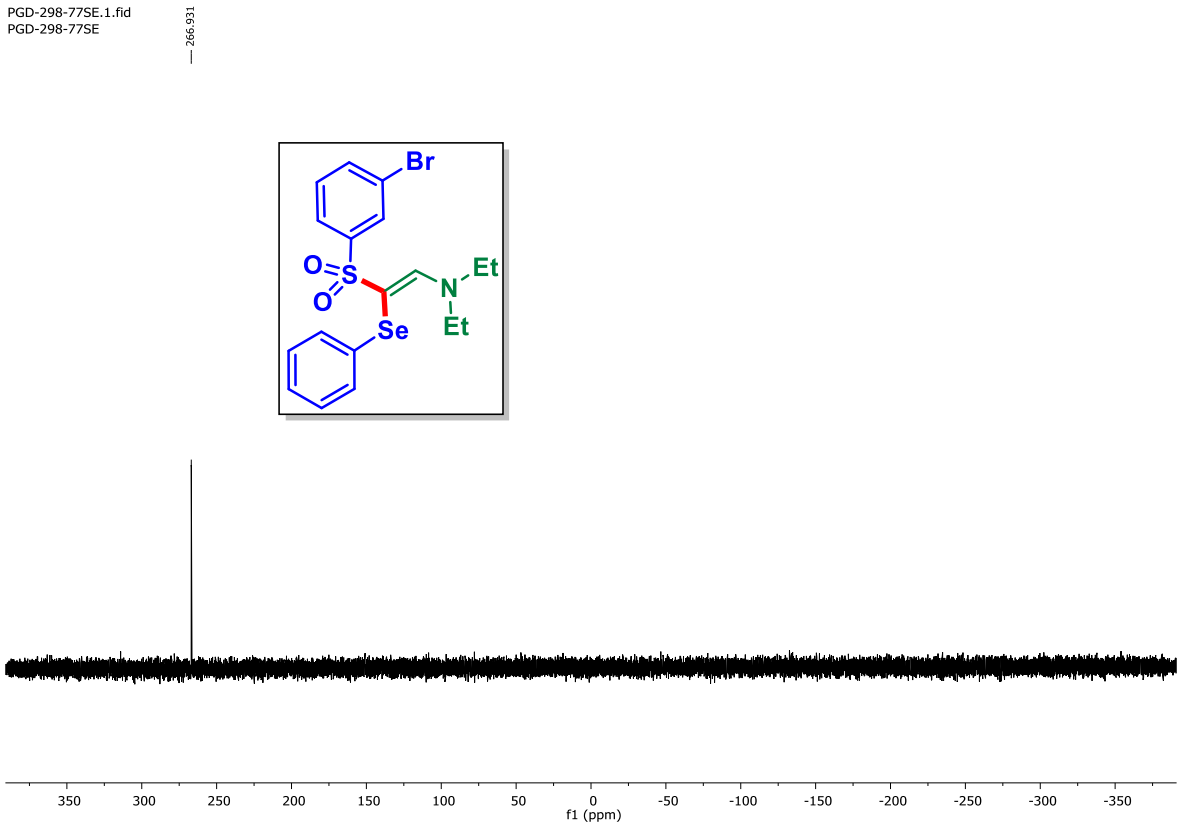
(*Z*)-2-((3-bromophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ua): ^{1}H NMR ($CDCl_3$, 400 MHz)



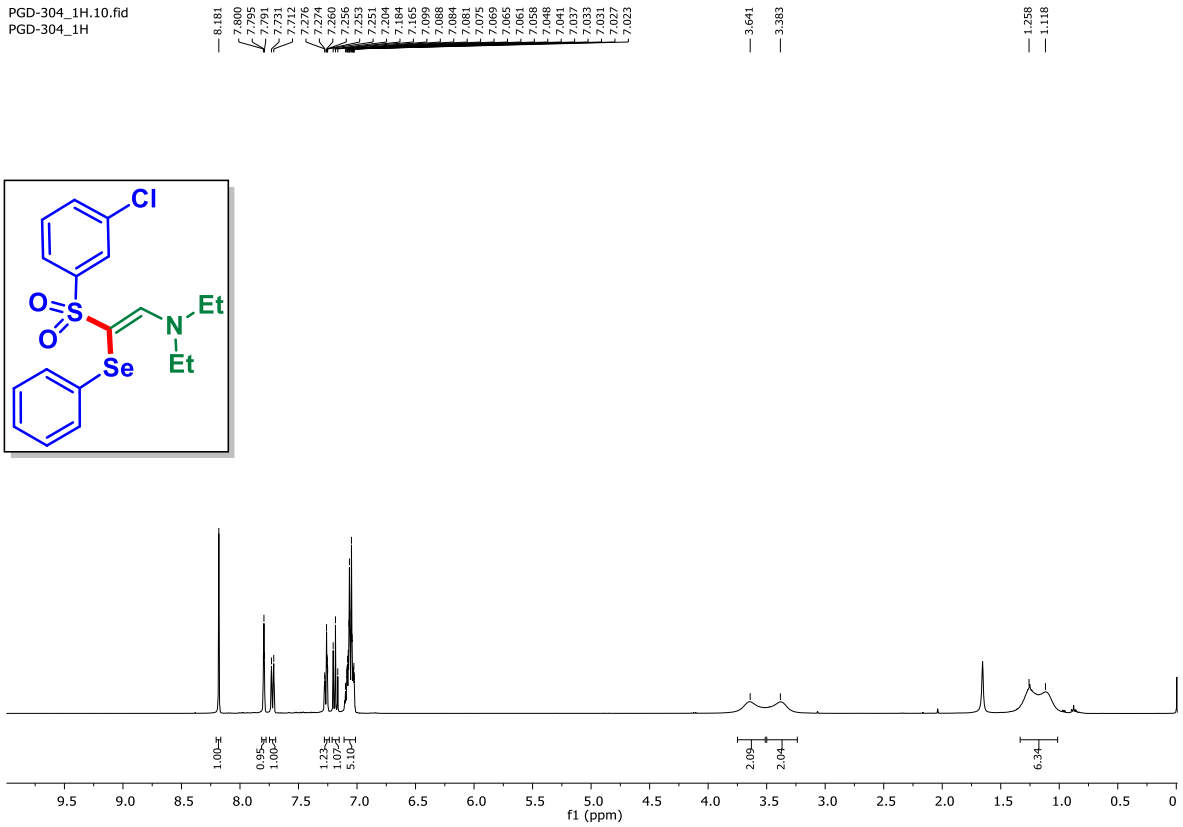
(*Z*)-2-((3-bromophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ua): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



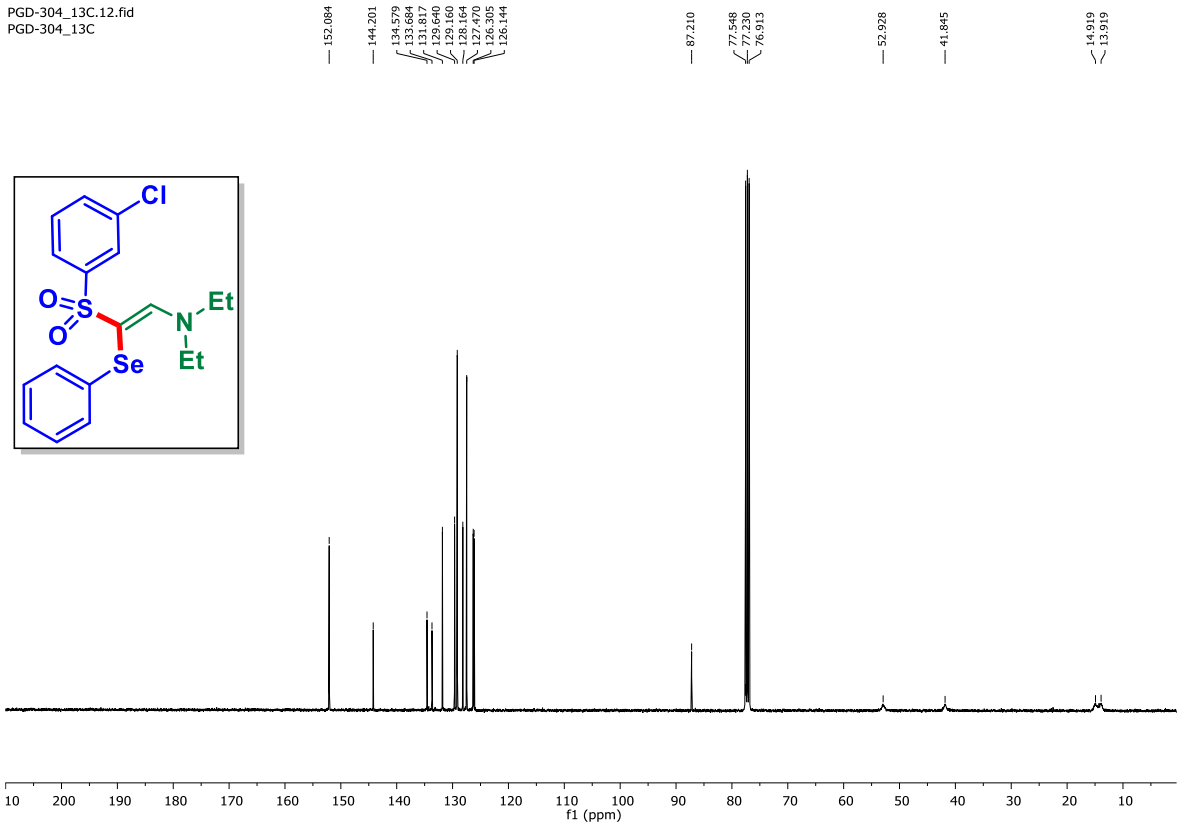
(*Z*)-2-((3-bromophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ua): ^{77}Se NMR ($CDCl_3$, 95 MHz)



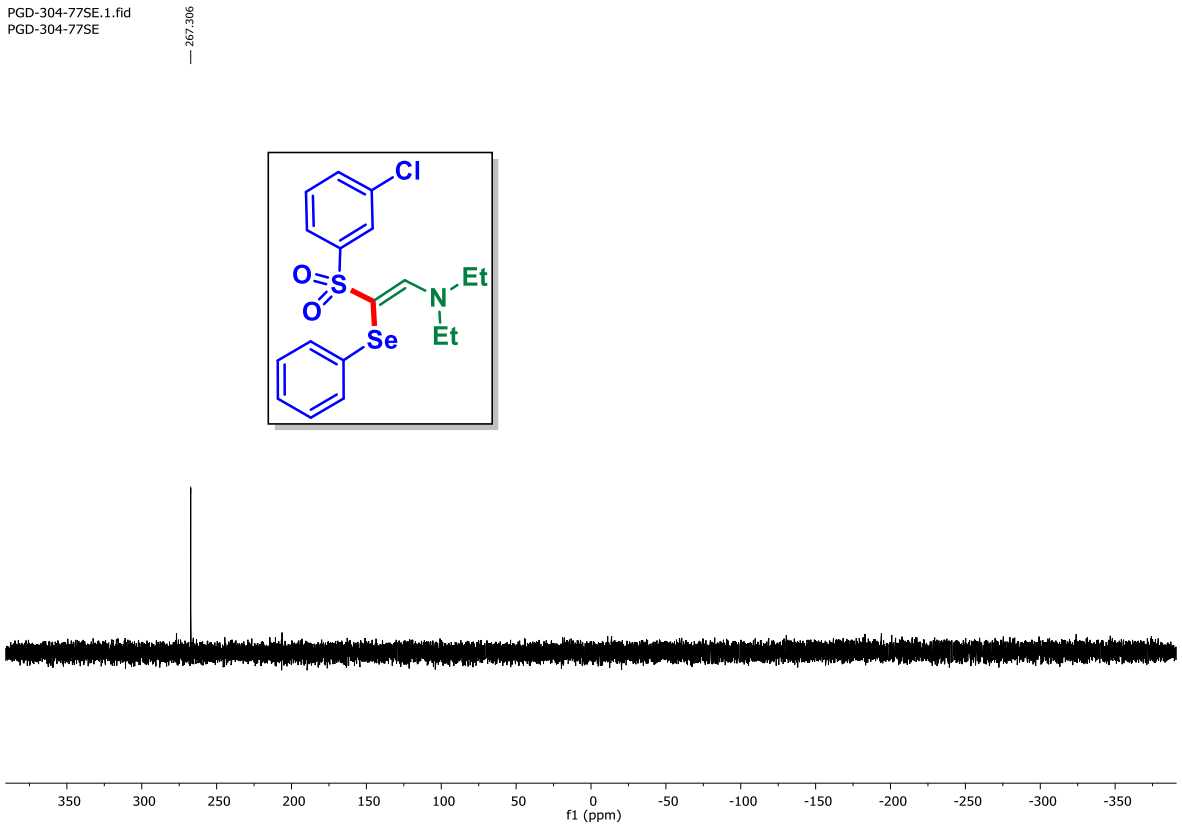
(*Z*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3va): ^{1}H NMR ($CDCl_3$, 400 MHz)



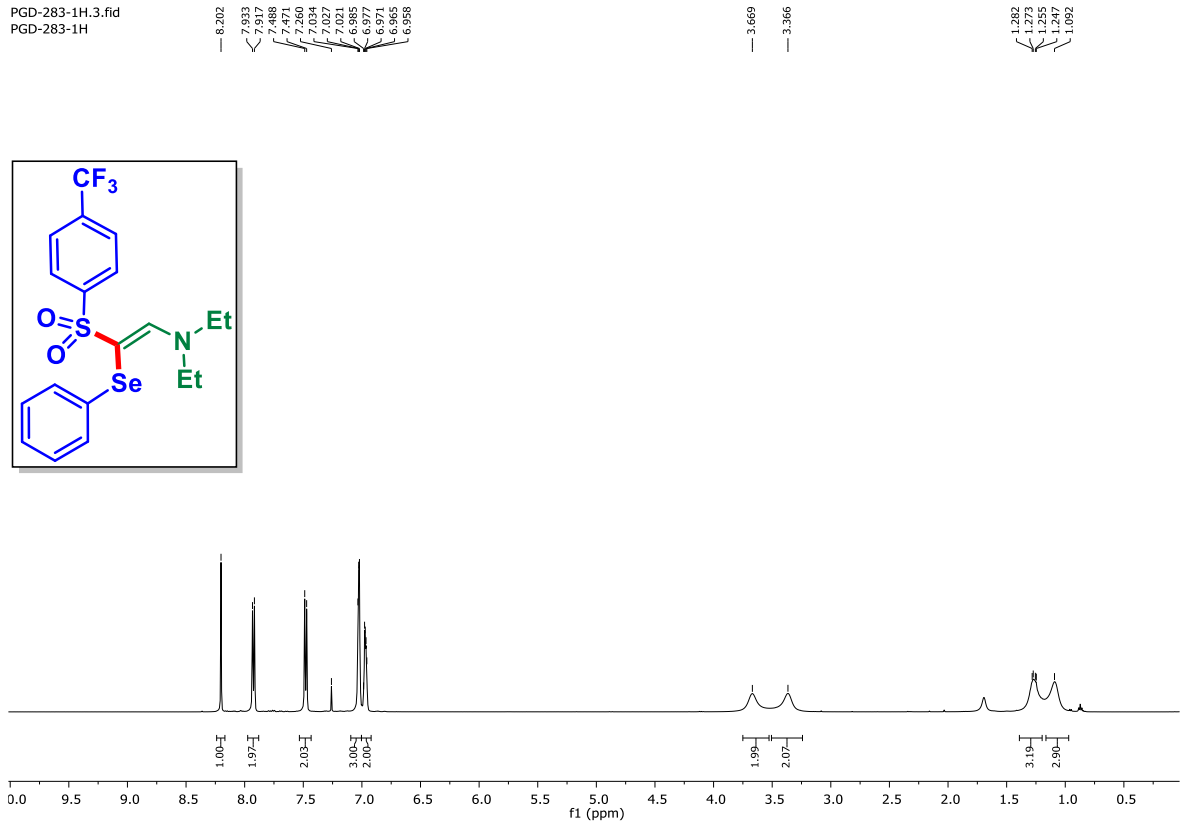
(*Z*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3va): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



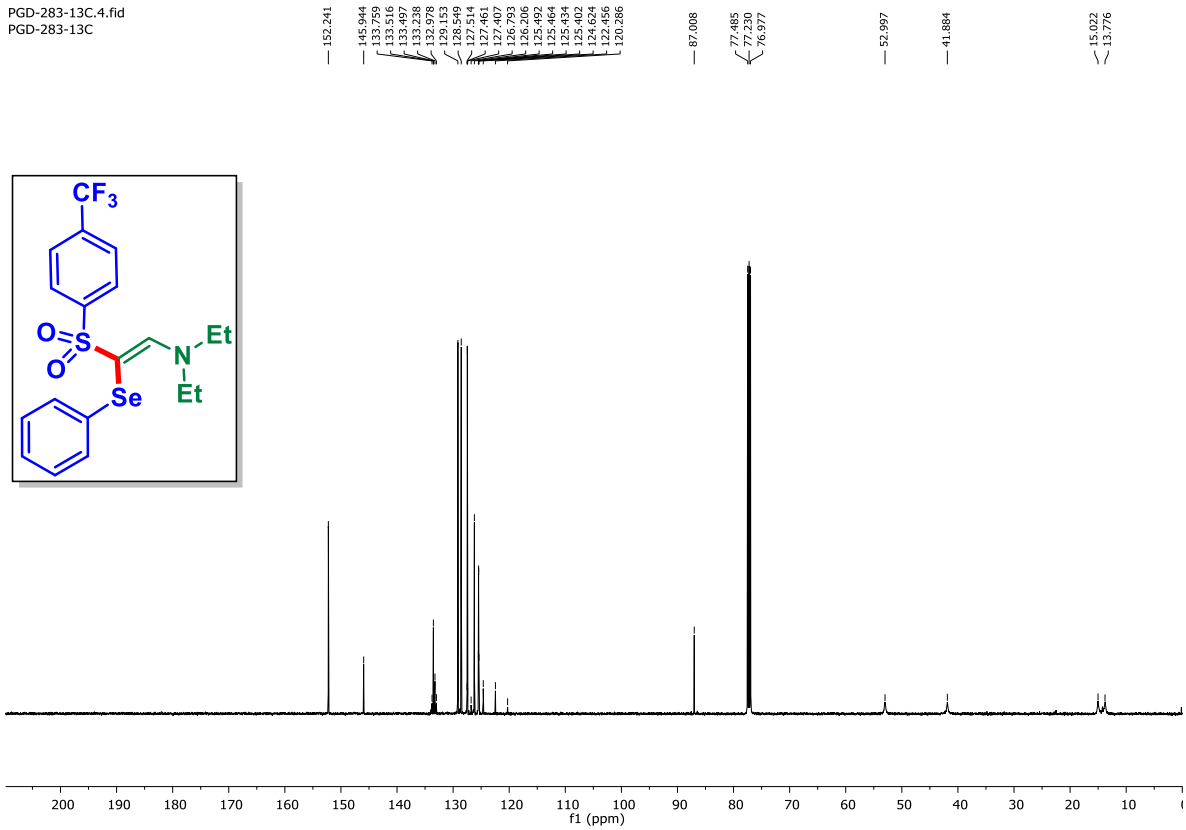
(*Z*)-2-((3-chlorophenyl)sulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3va): ^{77}Se NMR ($CDCl_3$, 95 MHz)



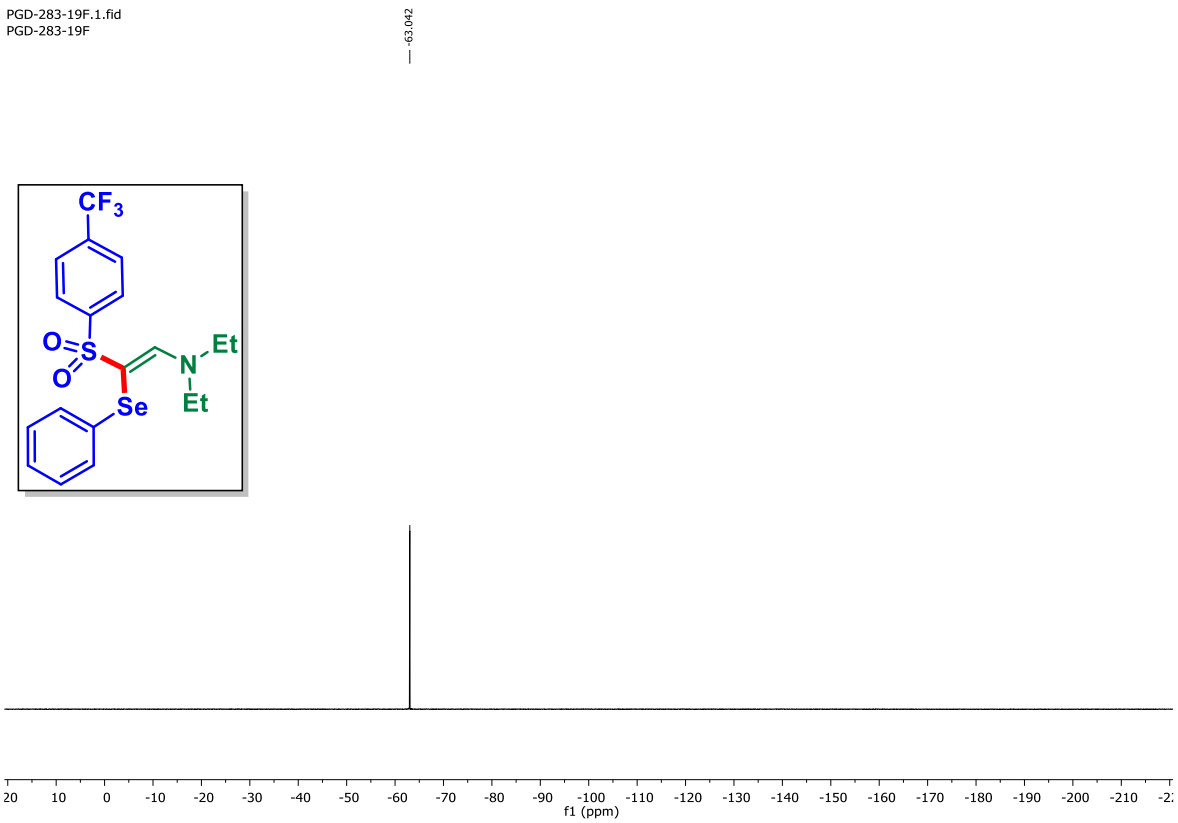
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3wa): ^{1}H NMR ($CDCl_3$, 400 MHz)



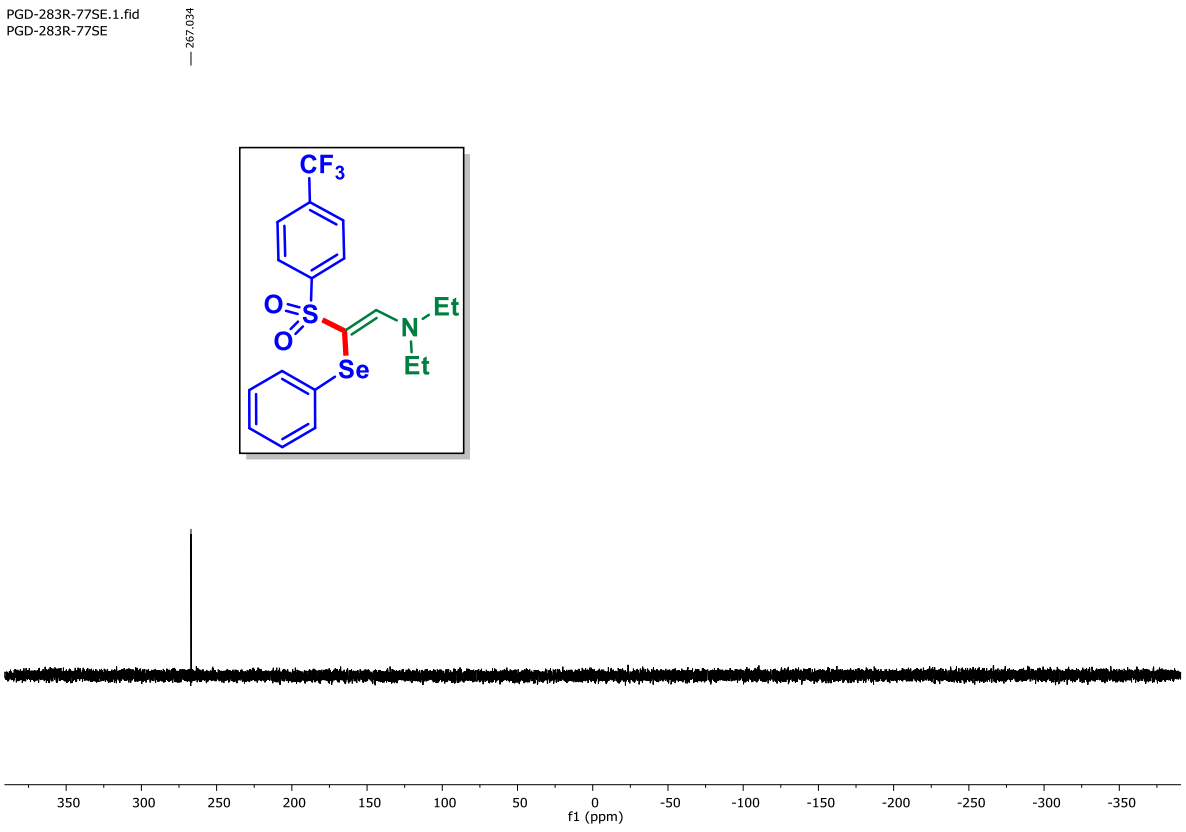
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3wa): ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz)



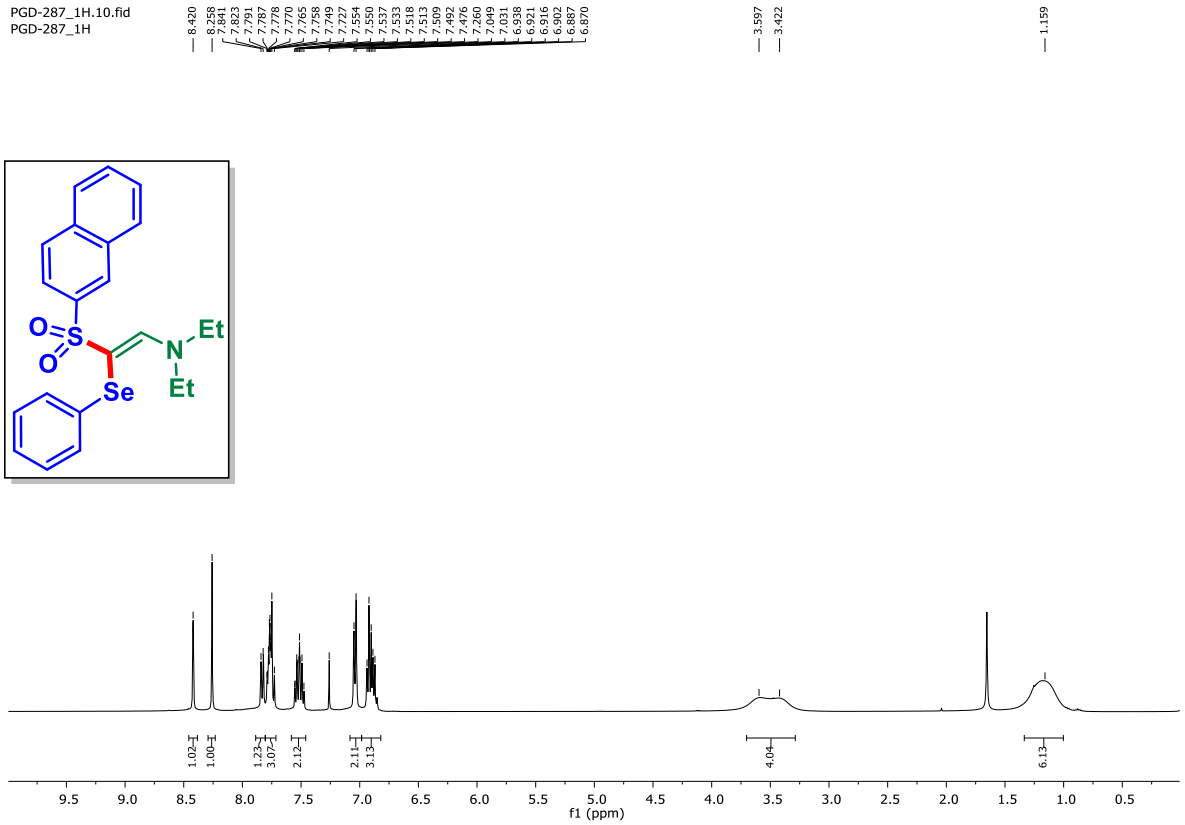
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3wa): ^{19}F NMR ($CDCl_3$, 471 MHz)



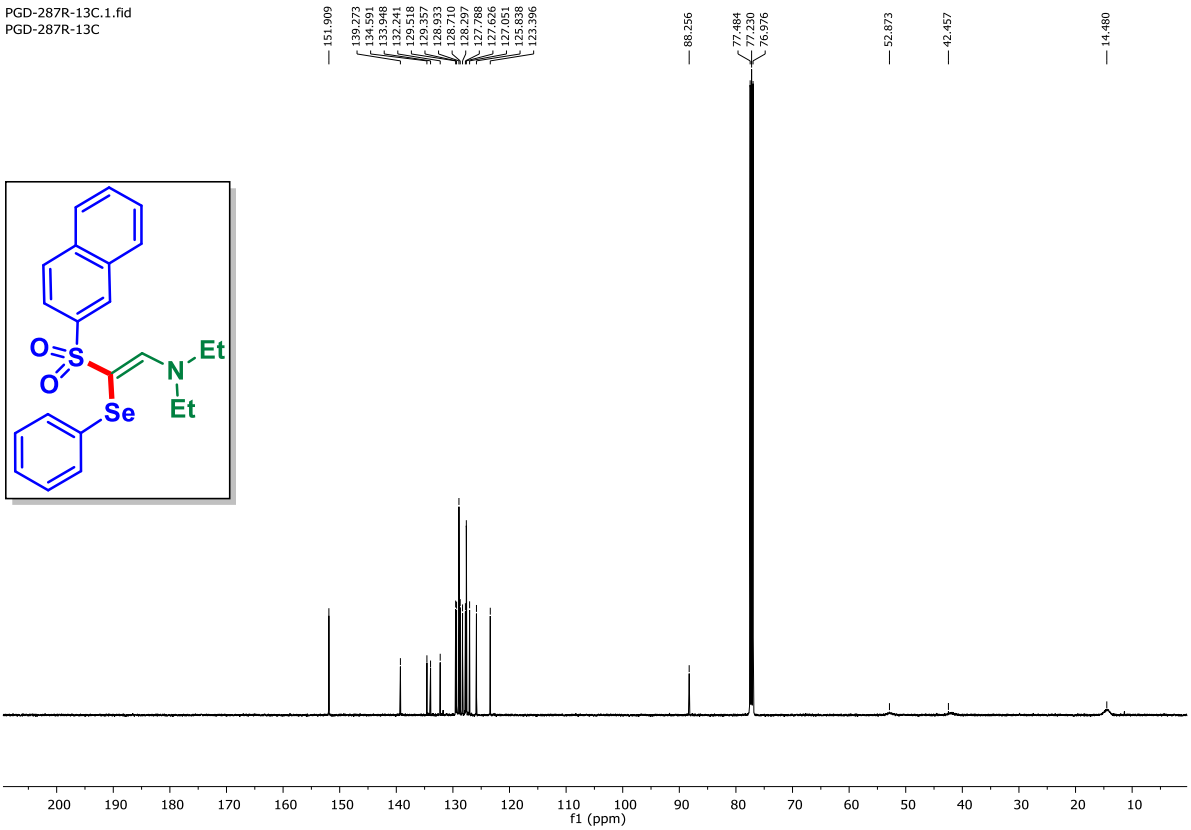
(*Z*)-*N*,*N*-diethyl-2-(phenylselanyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethen-1-amine (3wa): ^{77}Se NMR ($CDCl_3$, 95 MHz)



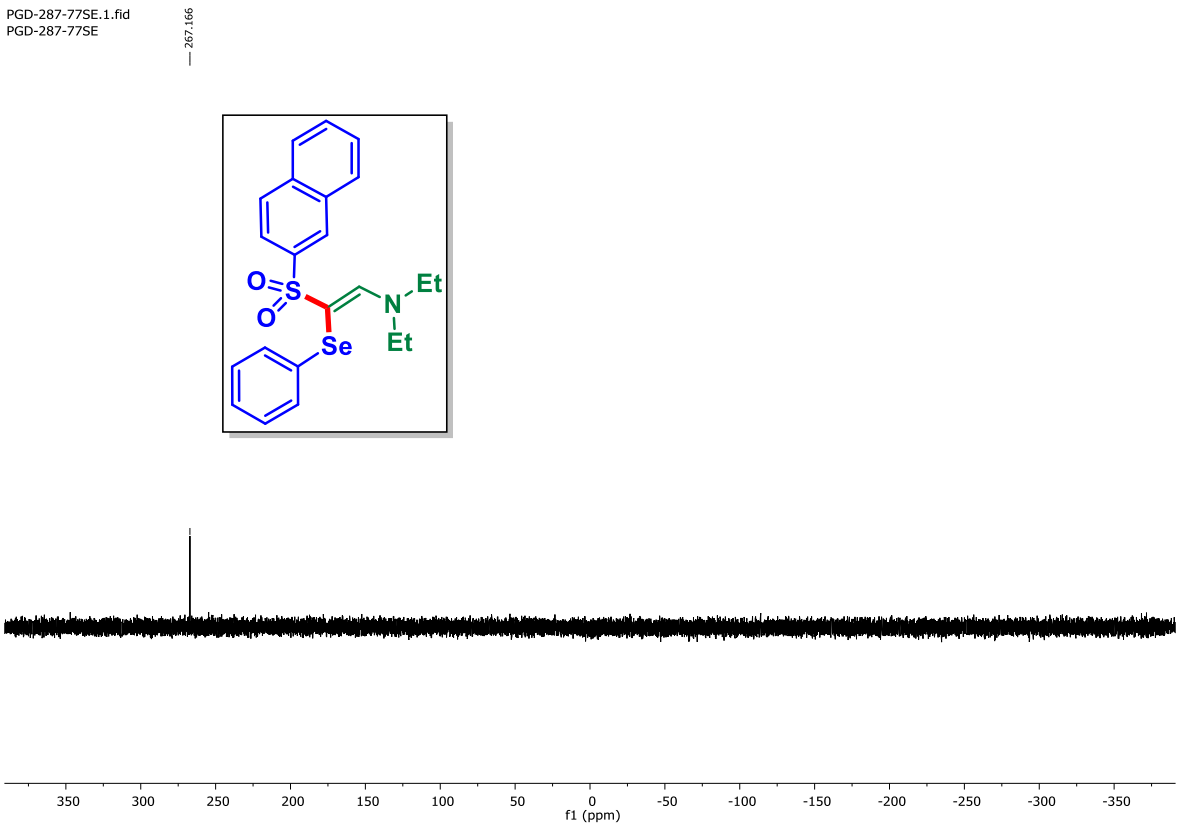
(*Z*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylselanyl)ethen-1-amine (3xa): ^{1}H NMR ($CDCl_3$, 400 MHz)



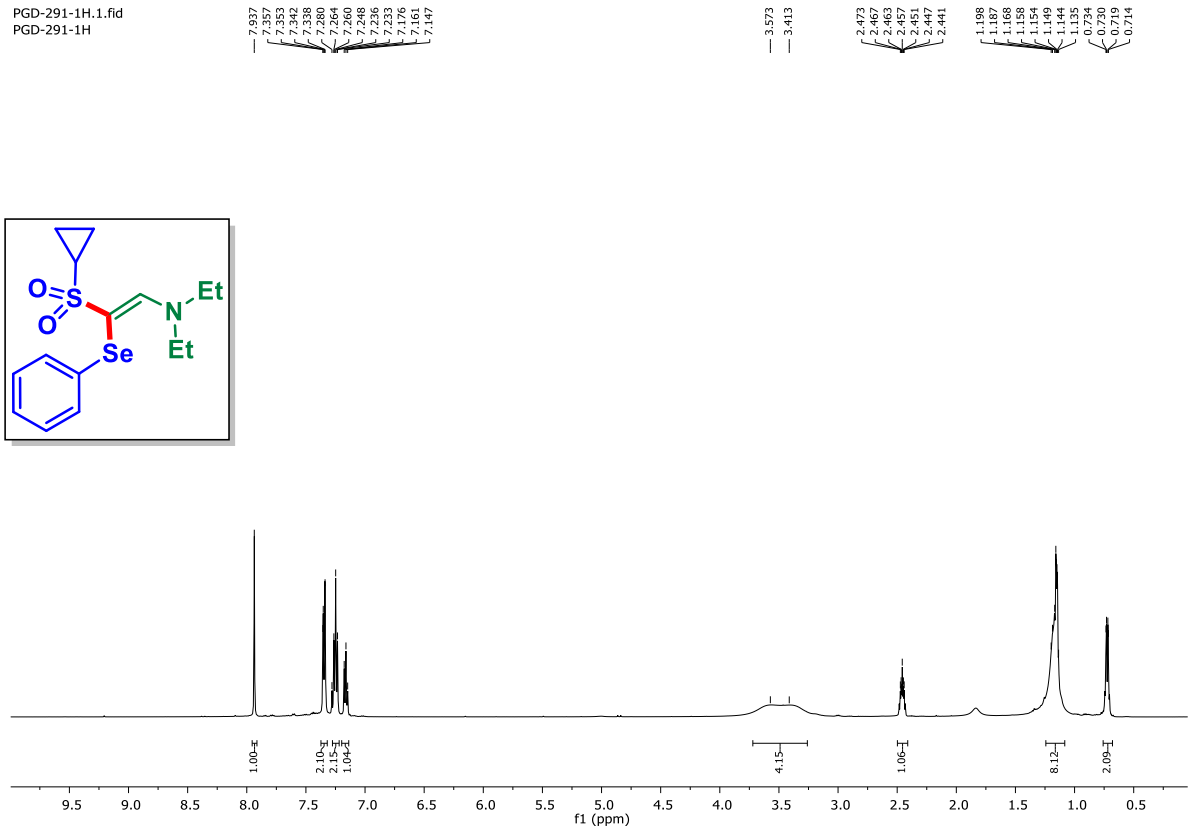
(*Z*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylselanyl)ethen-1-amine (3xa): ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz)



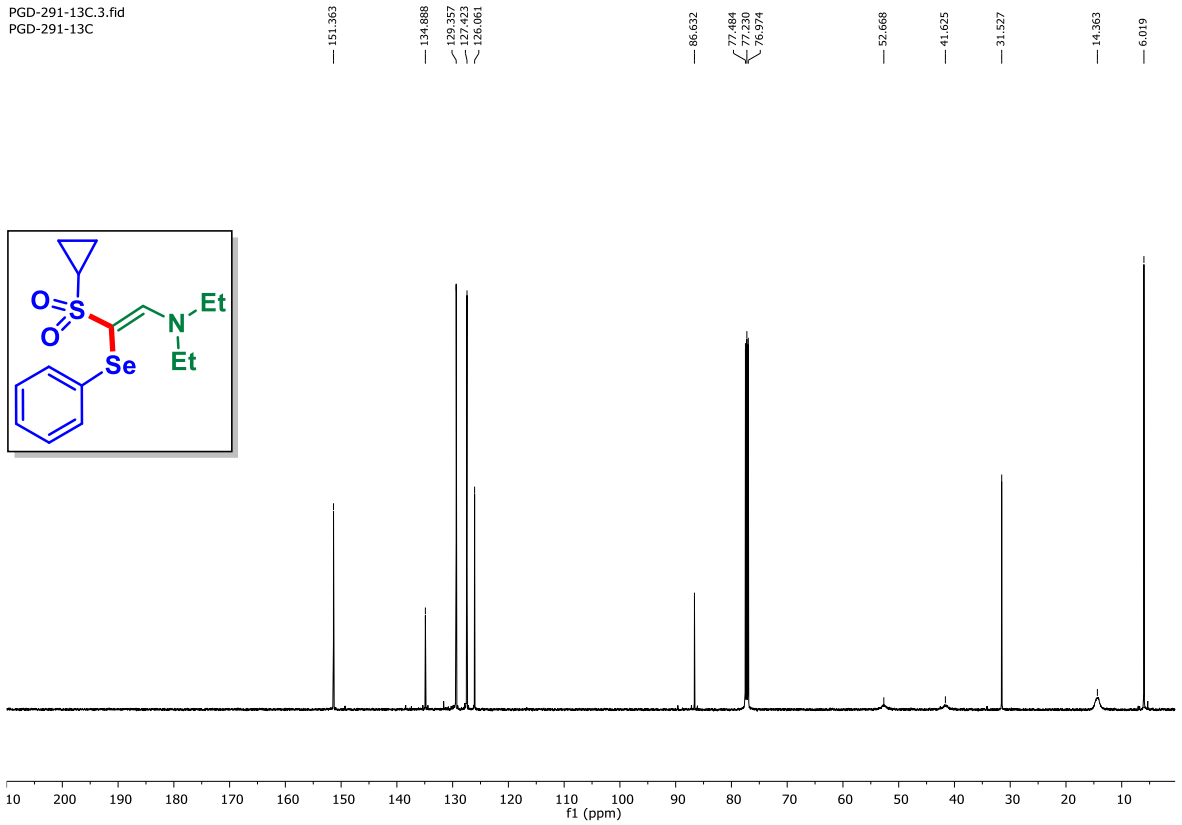
(*Z*)-*N*,*N*-diethyl-2-(naphthalen-2-ylsulfonyl)-2-(phenylselanyl)ethen-1-amine (3xa): ^{77}Se NMR ($CDCl_3$, 95 MHz)



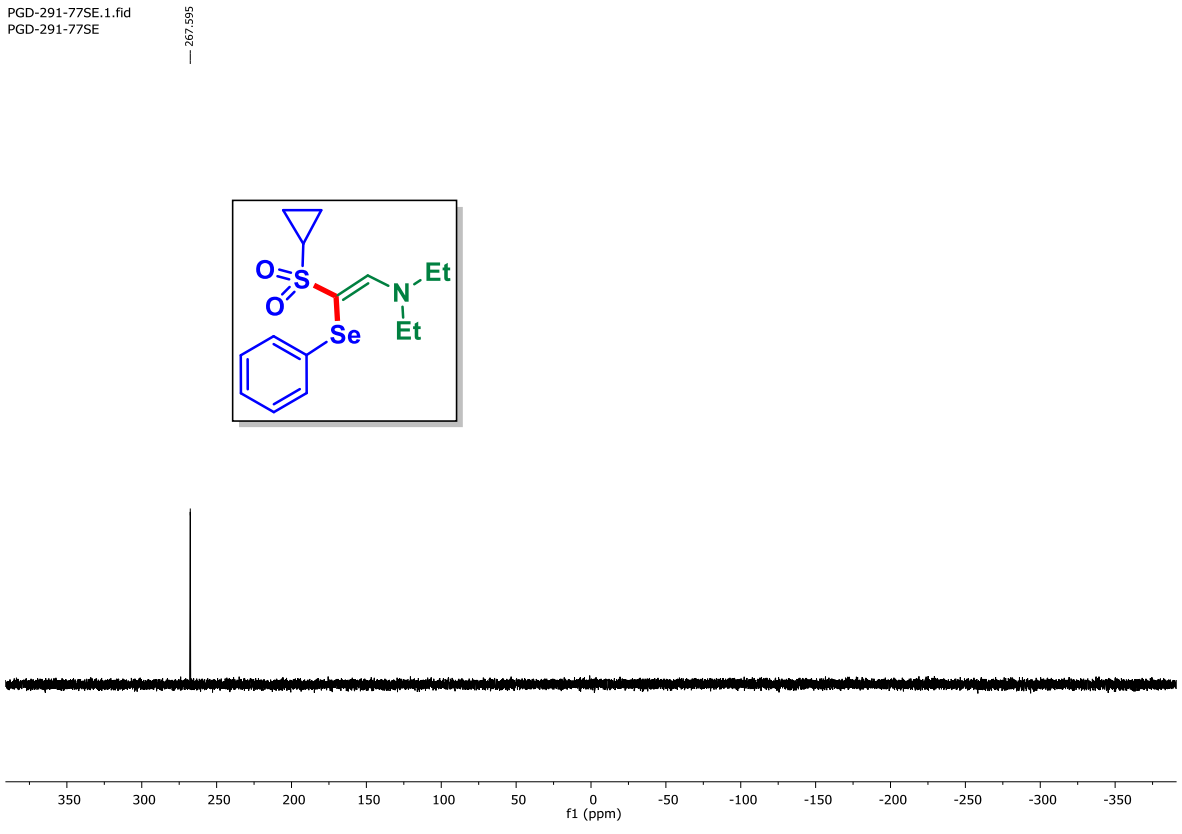
(*Z*)-2-(cyclopropylsulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ya): ^{1}H NMR ($CDCl_3$, 500 MHz)



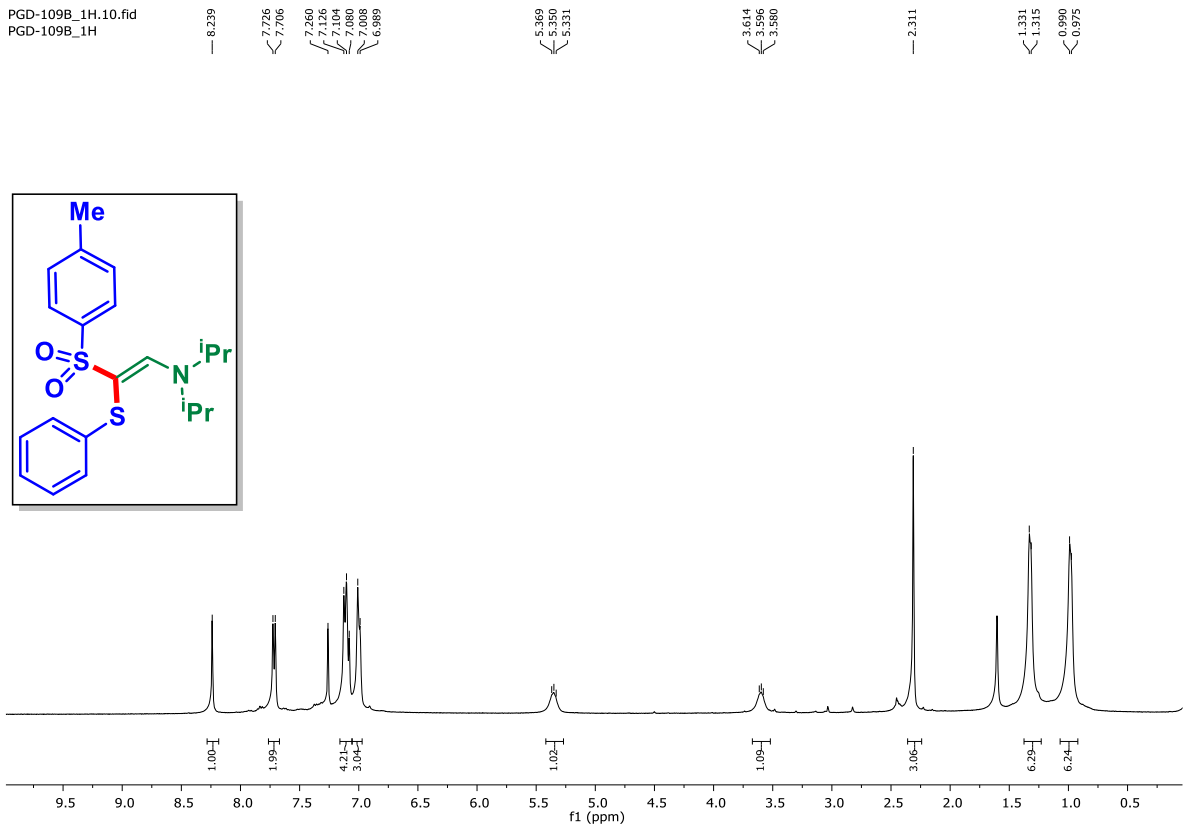
(*Z*)-2-(cyclopropylsulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ya): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)



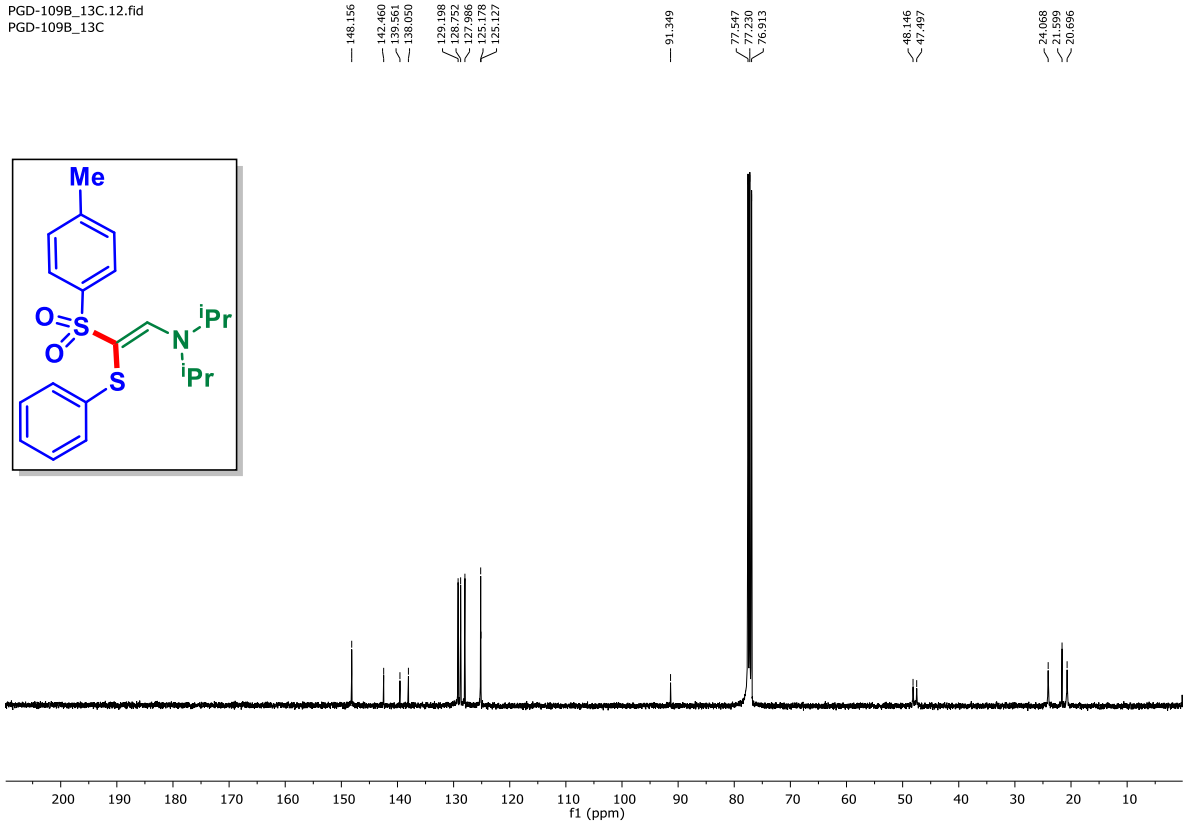
(*Z*)-2-(cyclopropylsulfonyl)-*N*,*N*-diethyl-2-(phenylselanyl)ethen-1-amine (3ya): ^{77}Se NMR ($CDCl_3$, 95 MHz)



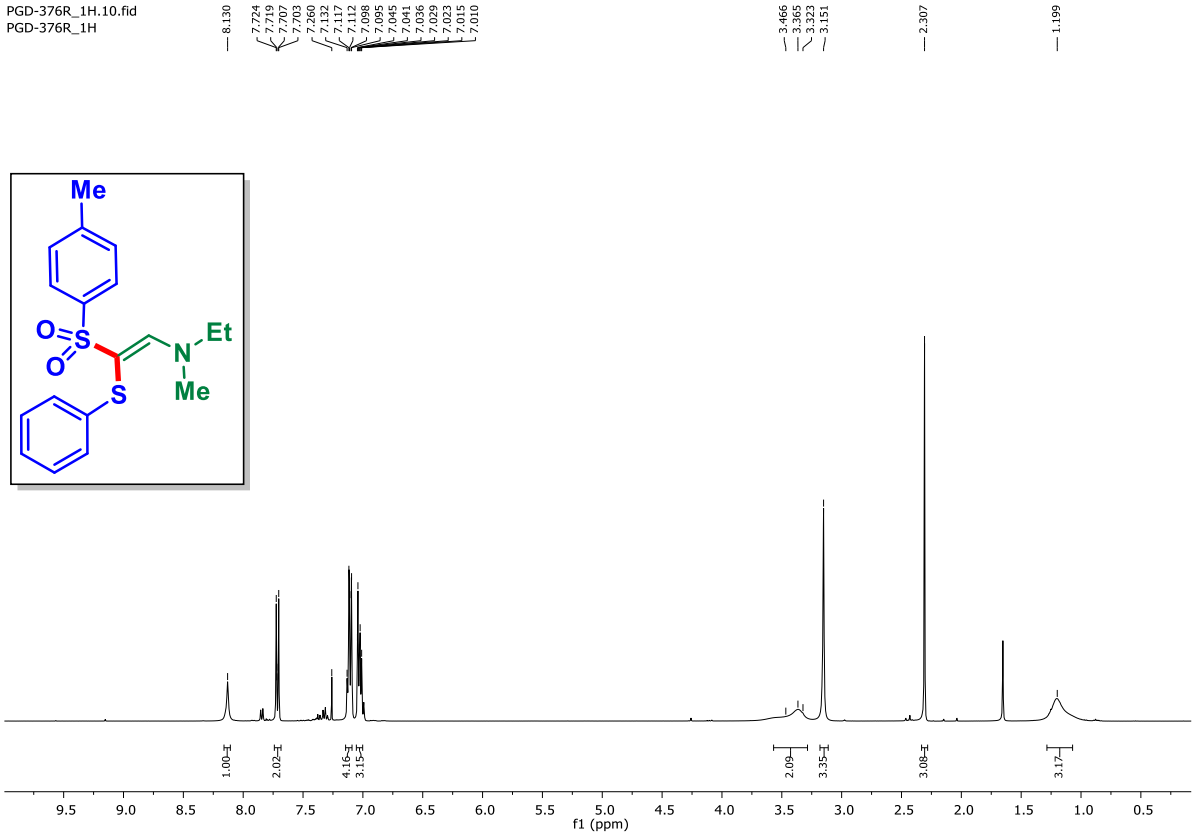
(*E*)-*N*-isopropyl-*N*-(2-(phenylthio)-2-tosylvinyl)propan-2-amine (3ab): ^{1}H NMR ($CDCl_3$, 400 MHz)



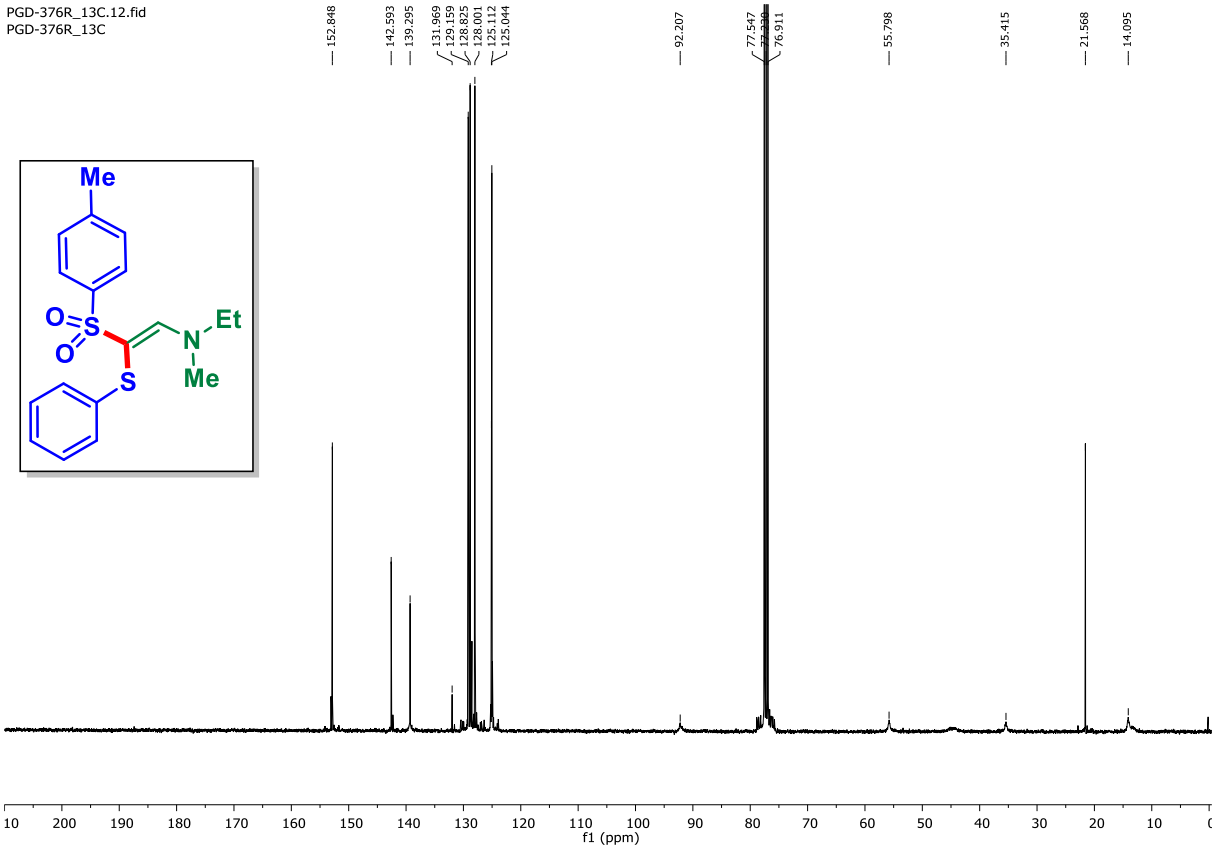
(*E*)-*N*-isopropyl-*N*-(2-(phenylthio)-2-tosylvinyl)propan-2-amine (3ab): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



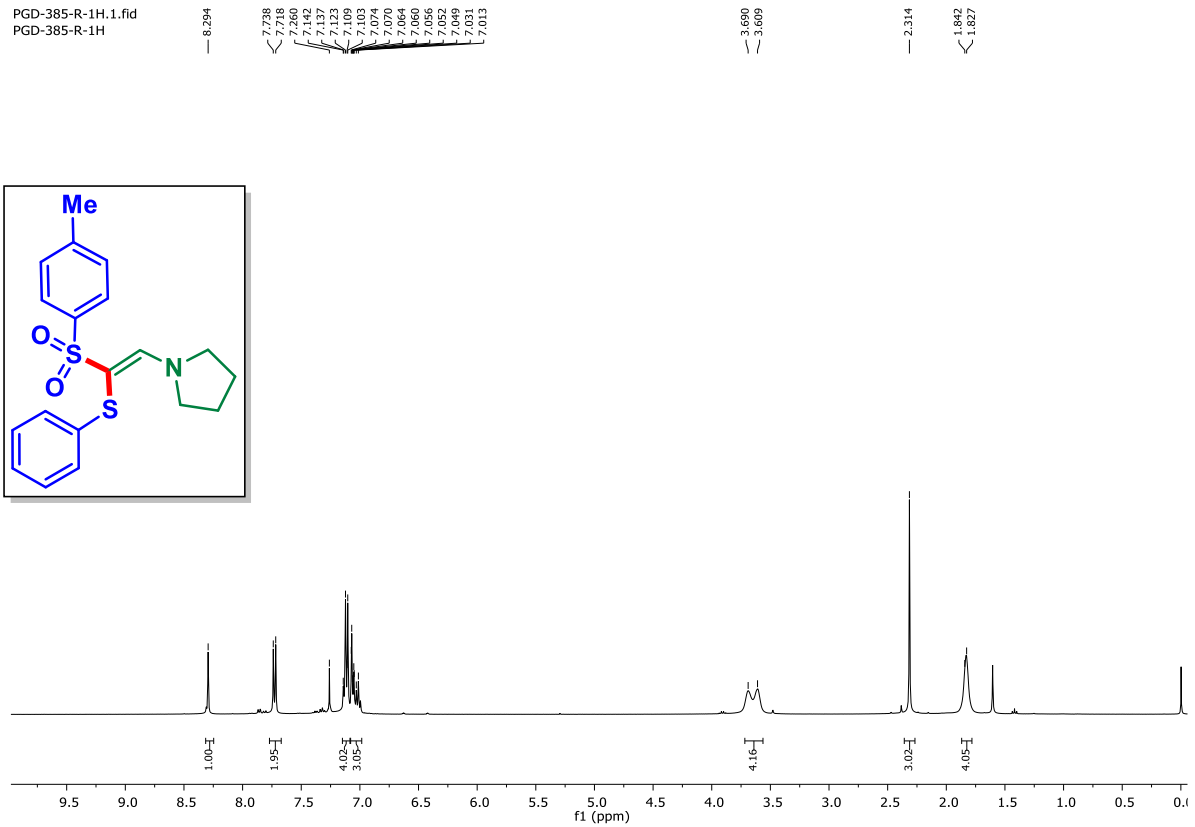
(*E*)-*N*-ethyl-*N*-methyl-2-(phenylthio)-2-tosylethen-1-amine (3ac): ^{1}H NMR ($CDCl_3$, 400 MHz)



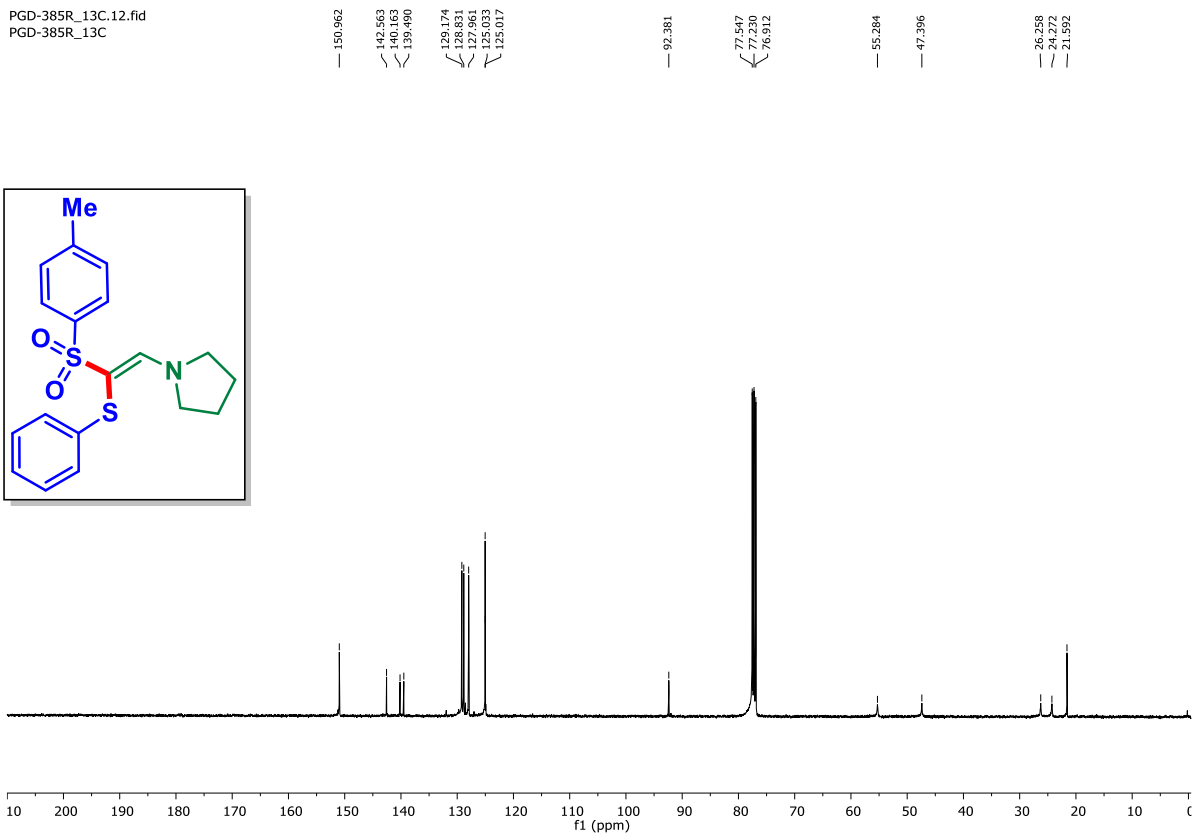
(*E*)-*N*-ethyl-*N*-methyl-2-(phenylthio)-2-tosylethen-1-amine (3ac): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



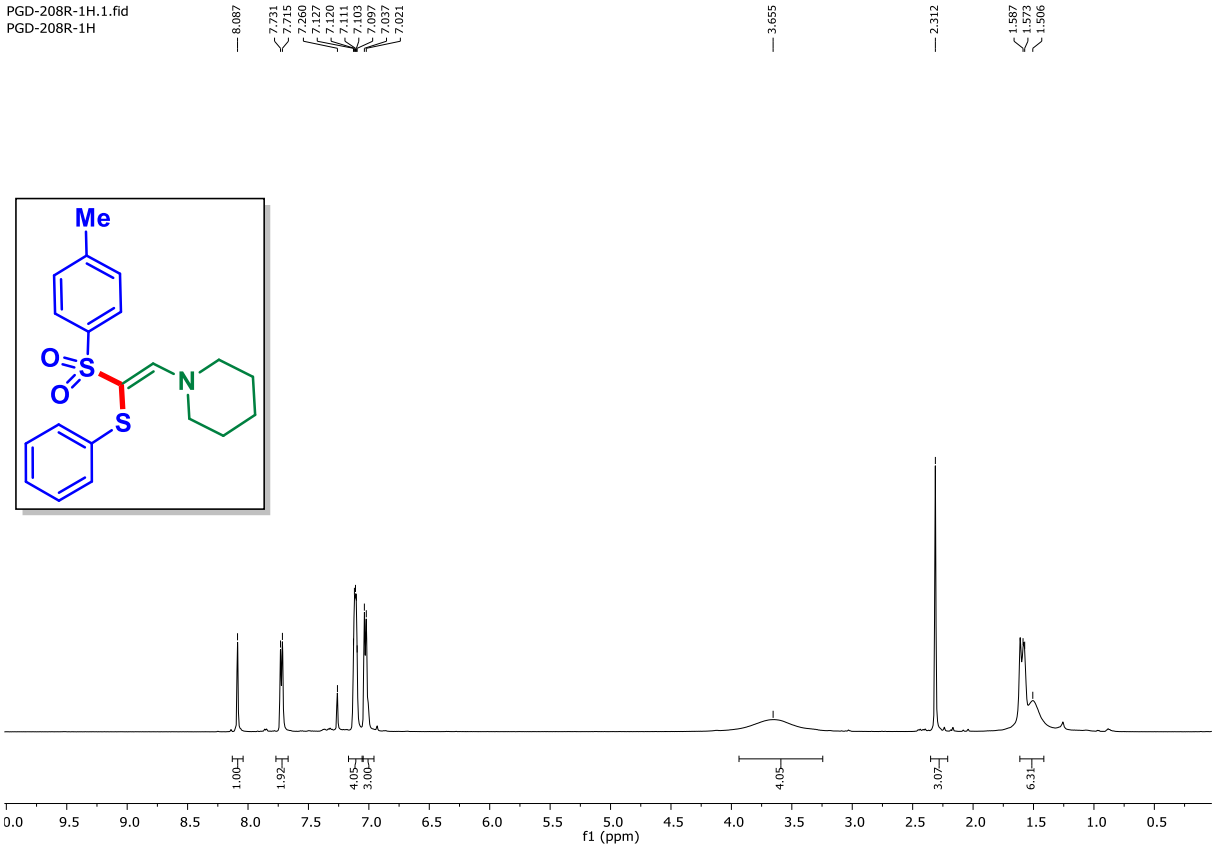
(*E*)-1-(2-(phenylthio)-2-tosylvinyl)pyrrolidine (3ad): ^{1}H NMR ($CDCl_3$, 400 MHz)



(*E*)-1-(2-(phenylthio)-2-tosylvinyl)pyrrolidine (3ad): ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



(*E*)-1-(2-(phenylthio)-2-tosylvinyl)piperidine (3ae): ^{1}H NMR ($CDCl_3$, 500 MHz)



(*E*)-1-(2-(phenylthio)-2-tosylvinyl)piperidine (3ae): ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz)