Supplementary Information (SI) for Chemical Communications.

Electron-donor-acceptor (EDA) complex-driven regioselective vicinal and oxidative geminal functionalization of alkynes

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Contents:

1. General Information:

All the reagents were commercial grade and purified according to the established procedures. 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. All the reactions were carried out in an oven-dried 10 mL vial (see below). Reactions were monitored by thin layer chromatography (TLC) on a 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 60−120 mesh using a mixture of hexane and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [^{1}H, ^{13}C{^{1}H} NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform ($CDCl_3$) and in some cases deuterated Methanol-d_4. ^{1}H, ^{13}C{^{1}H} were recorded in 500 (125) or 400 (100) MHz spectrometer and were calibrated using tetramethylsilane or residual undeuterated solvent for ^{1}H NMR, deuterochloroform for ^{13}C NMR as an internal reference {$Si(CH_3)_4$: 0.00 ppm or $CHCl_3$: 7.260 ppm for ^{1}H NMR, 77.230 ppm for ^{13}C NMR}. ^{19}F NMR was calibrated without any internal standard in $CDCl_3$. The chemical shifts are quoted in δ units, parts per million (ppm). ^{1}H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), 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 ^{o}C in a UV-Vis spectrometer in HPLC grade DMSO and DMF.

2. Light Information and Reaction Setup:

Philips 2 x 10 W blue LEDs (448 nm) and 2 x 10 W white LEDs (flux 46 mW/cm^2) were used as the light source for this light-promoted reaction and no filter was used. Borosilicate 10 mL vial was used as the reaction vessel. The distance from the light source to the irradiation vessel was ~6–8 cm. Regular fan was used to ventilate the area to maintain the room temperature (27–30 ^{o}C). The reaction set-up for this photochemical reaction is shown below (Figure S1).

Figure S1. Photochemical reaction set-up

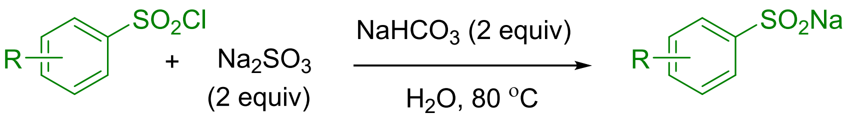
3. General Procedure:

(A) General Procedure for the Synthesis of Thiosulfonates (a-s):

Compounds (**a-s**) were synthesized by following the slightly modifying literature procedures.[1]

(i) Procedure for the Synthesis of Sodium sulfinates:

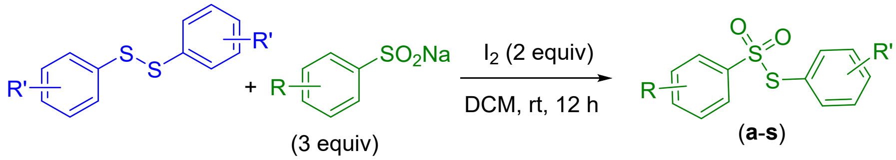
An oven-dried 50 mL round bottom flask was added 4-methylbenzenesulphonyl chloride (1.90 g, 10 mmol), sodium sulfite (2.50g, 20 mmol), sodium bicarbonate (1.68 g, 20 mmol) in 10 mL H_2O and stirred at 80 °C for 4 h. After completion of the reaction (monitored by TLC analysis) water was removed by rotary evaporator. Then the remaining solid was extracted using a vacuum pump and recrystallized using ethanol to get a white solid product (Scheme S1).



Scheme S1. Synthesis of sodium sulfinate

(ii) Procedure for the Synthesis of Thiosulfonates (a-s):

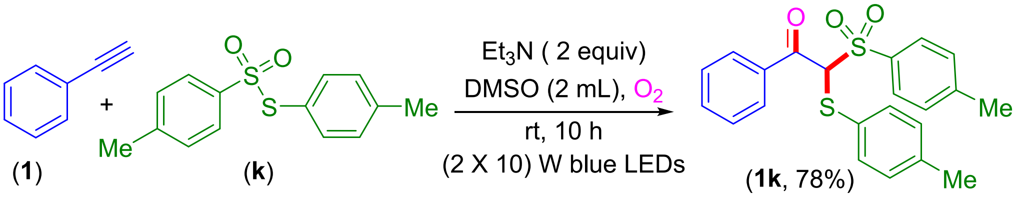
An oven-dried 50 mL round bottom flask was added *p*-tolyl disulfide (0.49 g, 2 mmol), 4-methylbenzenesulfinate (1.06 g, 6 mmol), I_2 (1.01 g, 4 mmol) in DCM (10 mL). The reaction was stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with DCM (25 mL) and washed with water (10 mL), followed by 5% sodium thiosulfate (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 5% ethyl acetate in hexane to give pure thiosulfonates (**k**) (0.505 g, 91%) (Scheme S2).



Scheme S2. Synthesis of thiosulfonates

(B) Procedure for the Synthesis of 1-Phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (1k):

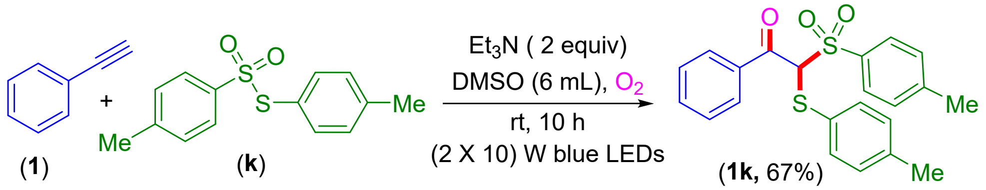
An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.025 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 78% yield (77 mg) (Scheme S3). The identity and purity of the product were confirmed by spectroscopic analysis.



Scheme S3. Synthesis of 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**)

(C) Large-scale Synthesis of 1-Phenyl-2-(p-tolylthio)-2-tosylethan-1-one (1k):

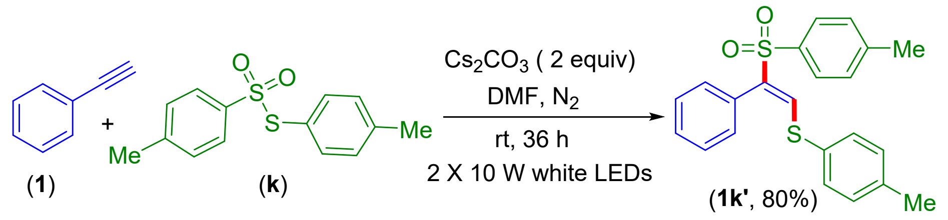
An oven-dried 25 mL round bottom flask was added phenylacetylene (**1**) (0.255 g, 270 µL, 2.5 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (1.391 g, 5 mmol), Et_3N (0.505 g, 700 µL, 5 mmol) in DMSO (6 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6−8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (40 mL) and washed with ice-cooled water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 67% yield (700 mg) (Scheme S4).



Scheme S4. Large-scale synthesis of 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**)

(D) Procedure for the Synthesis of (*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (1k′):

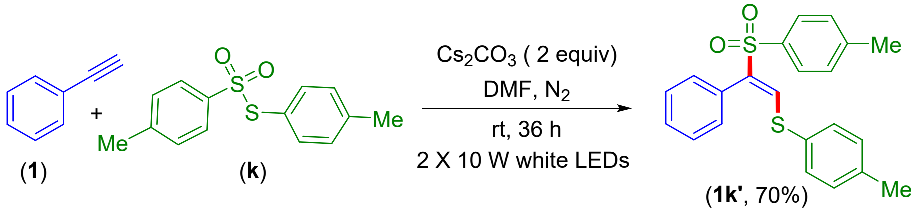
An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.025 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Cs_2CO_3 (0.16 g, 0.5 mmol), in DMF (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 5% ethyl acetate in hexane to give pure (*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (**1k′**) in 80% yield (76 mg) (Scheme S5). The identity and purity of the product was confirmed by spectroscopic analysis.



Scheme S5. Synthesis of (*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (**1k′**)

(E) Large-scale Synthesis of (*E*)-(2-phenyl-2-tosylvinyl)(p-tolyl)sulfane (1k′)

An oven-dried 50 mL round bottom flask was added phenylacetylene (**1**) (0.255 g, 270 µL 2.5 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (1.391 g, 5 mmol), Cs_2CO_3 (1.629 g, 5 mmol) in DMF (6 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (40 mL) and washed with ice-cooled water (20 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 5% ethyl acetate in hexane to give pure (*E*)-(2-phenyl-2-tosylvinyl)(p-tolyl)sulfane (**1k′**) in 70% yield (665 mg) (Scheme S6). The identity and purity of the product was confirmed by spectroscopic analysis.



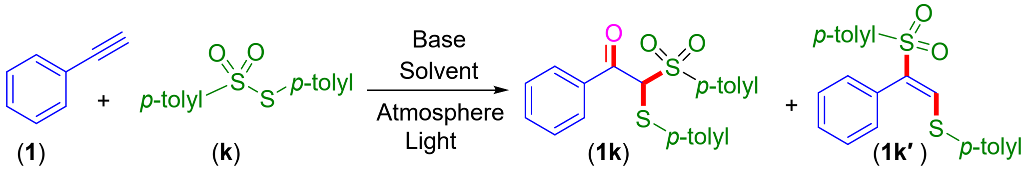
Scheme S6. Large-scale synthesis of (*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (**1k′**)

4. Optimization of the Reaction:

To find the optimal reaction condition for the exclusive formation of **1k** and **1k′**, various reaction parameters such as solvent, base, atmospheric condition, and light sources were screened. Initially, different solvents such as DMF, DMA, DCE, CH_3CN, DCM, 1,4-dioxane, and EtOH were screened but none of them were able to improve the yield of the trifunctionalized product **1k** (Table S1, entries 1-8). Next, different organic and inorganic bases were employed and it was observed that the use of inorganic bases such as K_2CO_3 and KOH (Table S1, entries 9 and 10) failed to give any tri- or di- functionalized product (**1k** or **1k′**). On the other hand, organic bases such as DBU, DABCO, and DIPEA resulted in the formation of the trifunctionalized product **1k** in lower yields of 29%, 34%, and 30% respectively. However, using these bases, the difunctionalized product was not formed at all or formed in a paltry amount (Table S1, entries 11-13). To our delight, the reaction when conducted using Et_3N (2 equiv) led to an increment in the yield of **1k** to 61% (Table S1, entry 14). Increasing the Et_3N loading to 4 equiv had no major impact on the product yield, however, decreasing it to 1 equiv suppressed the yield to 43% (Table S1, entries 15-16). Thus, all further reactions were carried out using 2 equiv of Et_3N. Since, product **1k** is an oxidative trifunctionalized product, the oxygen atmosphere might improve the product formation. To check this, a reaction was performed under an oxygen atmosphere, and as expected the yield of **1k** improved to 78%. (Table S1, entry 17). To corroborate the effect of wavelength and intensity of light on the formation of **1k**, the standard reaction was carried out using 2 x 10 W white (46 mW/cm^2) and green (534 nm) LEDs. A comparable yield of 70% was observed using white LEDs, but the product formation dropped to 27% with green LEDs (27%) (Table S1, entries 18 and 19). Further, the reaction in the absence of light produces a trace amount of product (**1k**), suggesting the essential role of light in this reaction (Table S1, entry 20). Thus, the optimized condition for the formation of tri-functionalized product **1k** is the use of phenylacetylene (**1**, 0.25 mmol) with S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**, 2 equiv, 0.50 mmol) in the presence of Et_3N (2 equiv, 0.50 mmol) in DMSO (2 mL) under the irradiation of 2 × 10 W blue LEDs for 10 h under O_2 atmosphere at room temperature (Table S1, entry 17). The surrounding temperature of the reaction set-up was maintained using a circulating fan.

In all the above conditions there was no substantial enhancement in the yield of the difunctionalized product **1k′**, hence, we focused on improving its yield. Since the vicinal difunctionalized product is a non-oxidative process, thus performing the reaction in an atmosphere devoid of oxygen might enhance the yield. Hence, a reaction was performed under a nitrogen atmosphere using 2 x 10 W blue LEDs and prolonging the reaction time to 36 h due to unconsume of starting material. This improved the yield of **1k′** to 44%, simultaneously suppressing the formation of oxidative trifunctionalized product **1k** (Table S1, entry 21). As observed from entry 2, the vicinal difunctionalized product **1k′** was obtained in a comparatively better yield using Cs_2CO_3, hence the reaction was repeated using the same in an atmosphere of nitrogen. As expected, the product yield improved to 52% (Table S1, entry 22). Next, for improving the yield, a reaction was performed using white LEDs instead of blue LEDs keeping all other parameters the same giving a better yield of 64% (Table S1, entry 23). Further, switching the solvent to DMF, significantly improved the yield of **1k′** to 80% (Table S1, entry 24). Further, a reaction in the absence of light gives a trace amount of product (**1k′**), suggesting the necessity of light in this protocol (Table S1, entry 25). Thus, the optimal condition for the di-functionalized product (**1k′**) is the use of phenylacetylene (**1**, 0.25 mmol) with S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**, 2 equiv, 0.50 mmol), Cs_2CO_3 (2 equiv, 0.50 mmol) in DMF (2 mL) under the irradiation of 2 × 10 W white LEDs for 36 h under N_2 atmosphere (Table S1, entry 24).

Table S1. Optimization of the reaction conditions[a-f]



Entry	**Solvent**	**Base (equiv)**	**Atmosphere**	**Yield (%) 1k/1k′**
1	DMSO	Cs_2CO_3 (2)	Open-air	37/21
2	DMF	Cs_2CO_3 (2)	Open-air	27/24
3	DMA	Cs_2CO_3 (2)	Open-air	23/15
4	DCE	Cs_2CO_3 (2)	Open-air	N.D/N.D
5	CH_3CN	Cs_2CO_3 (2)	Open-air	N.D/N.D
6	DCM	Cs_2CO_3 (2)	Open-air	trace/trace
7	1,4-dioxane	Cs_2CO_3 (2)	Open-air	N.D/N.D
8	Ethanol	Cs_2CO_3 (2)	Open-air	N.D/N.D
9	DMSO	K_2CO_3 (2)	Open-air	trace/15
10	DMSO	KOH (2)	Open-air	16/trace
11	DMSO	DBU (2)	Open-air	29/N.D
12	DMSO	DABCO (2)	Open-air	34/N.D
13	DMSO	DIPEA (2)	Open-air	30/12

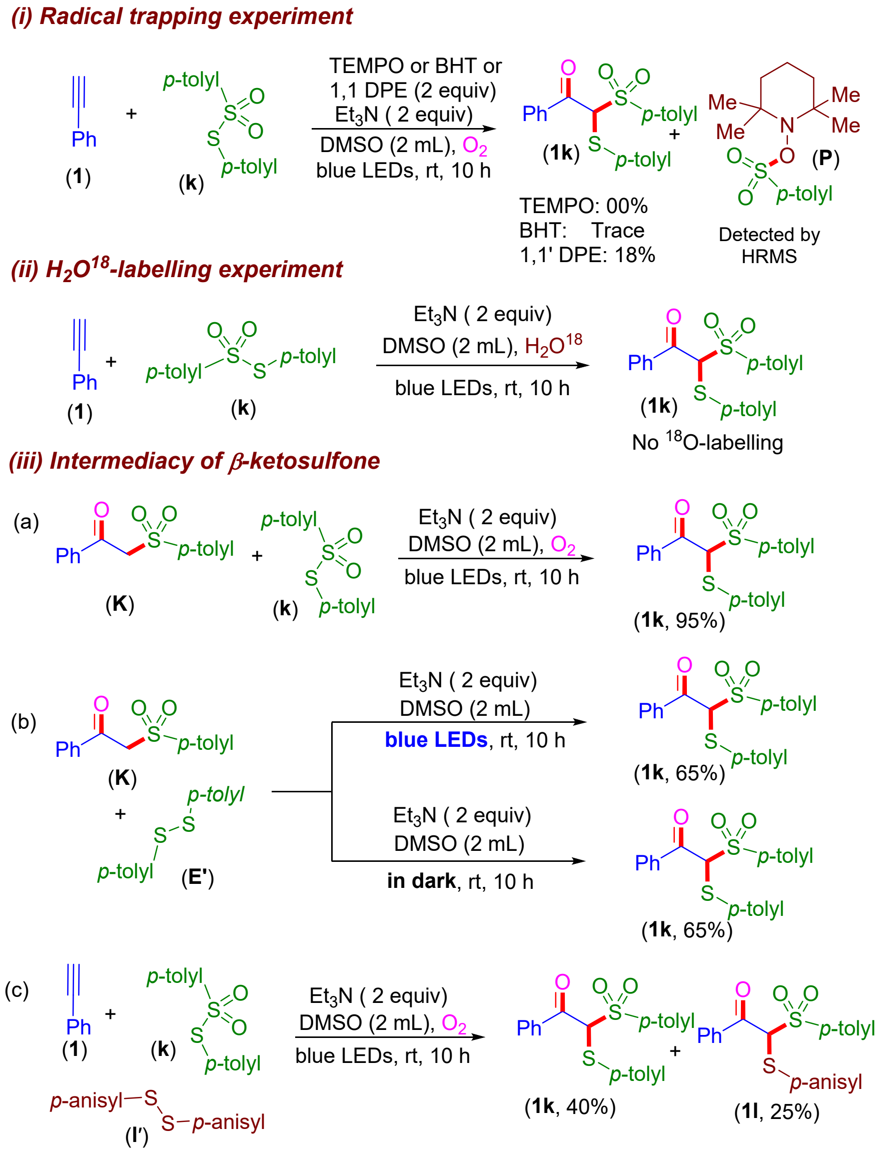
14	DMSO	Et_3N (2)	Open-air	61/17
15	DMSO	Et_3N (4)	Open-air	64/19
16	DMSO	Et_3N (1)	Open-air	43/14
17	**DMSO**	**Et_3N (2)**	**Oxygen**	**78/11**
18[c]	DMSO	Et_3N (2)	Oxygen	70/18
19[d]	DMSO	Et_3N (2)	Oxygen	**27**/trace
20[e]	DMSO	Et_3N (2)	Oxygen	trace/trace
21[f]	DMSO	Et_3N (2)	Nitrogen	N.D/44
22[f]	DMSO	Cs_2CO_3 (2)	Nitrogen	N.D/52
23[c,f]	DMSO	Cs_2CO_3 (2)	Nitrogen	N.D/64
24[c,f]	**DMF**	**Cs_2CO_3** (2)	**Nitrogen**	**N.D/80**
25[e,f]	DMF	Cs_2CO_3 (2)	Nitrogen	N.D/trace

[a]Reaction Conditions unless specified otherwise: **1** (0.25 mmol), **k** (0.5 mmol), base (2 equiv), solvent (2 mL) in 2 x 10 W blue LEDs for 10 h. [b]Isolated yield, [c](2 x 10 W) white LEDs, [d](2 x 10 W) green LEDs, [e]reaction in dark, [f]reaction for 36 h, N.D. = not detected.

5. Control Experiments:

(A) Control Experiments for Tri-functionalization of Alkyne:

To gain insight into the mechanistic steps involved in this photoinduced strategy, various control experiments were conducted taking phenylacetylene (**1**) and thiosulfonate (**k**) as the reacting partners. Initially, we sought to investigate a plausible mechanism for the formation of trifunctionalized product **1k**. The reactions when performed in the presence of radical scavengers, such as TEMPO, BHT, and 1,1′-diphenylethylene, keeping other reaction conditions fixed, suppressed the formation of product (**1k**), indicating the radical nature of the reaction. Further, a TEMPO-trapped tosyl radical adduct (**P**) has been detected by the HRMS analysis of the reaction aliquots, suggesting the involvement of tosyl radical [Scheme S7(i) and Figure S2]. Next, to ascertain the source of the carbonyl oxygen (moisture or atmospheric oxygen), a reaction was performed using H_2O^{18} (2 equiv) under standard conditions. From the HRMS and ^{13}C NMR analysis, no ^{18}O-labelled product (**1k**) could be detected, confirming the non-involvement of moisture in the reaction [Scheme S7(ii) and Figure S4 and S5]. Further, suppression of the product under N_2 atmosphere indorses atmospheric O_2 as the source of the carbonyl oxygen.



Scheme S7 Control experiments for trifunctionalization of alkyne

A retrosynthetic analysis of the product (**1k**) suggests *β*-keto sulfone (**K**) as one of the possible intermediates, the formation of which has also been observed by the HRMS analysis of the reaction aliquot (Figure S6). To ascertain the intermediacy of *β*-keto sulfone (**K**), a reaction between presynthesized (**K**) and thiosulfonate (**k**) was performed under standard condition. The trifunctionalized product (**1k**) was formed in an improved yield of 95%, supporting its intermediacy [Scheme S7(iii)a]. The enhanced yield of the product is due to the facile generation of the *β*-keto sulfonate anion which attacks the S–S bond of thiosulfonate **k** displacing the better leaving tosyl anion and introducing the thiyl functionality at the germinal position. Now the question arises whether the thiyl functionality originates only from the thiosulfonate (**k**) or there is some contribution from the *in situ* generated disulphide (**E'**)?

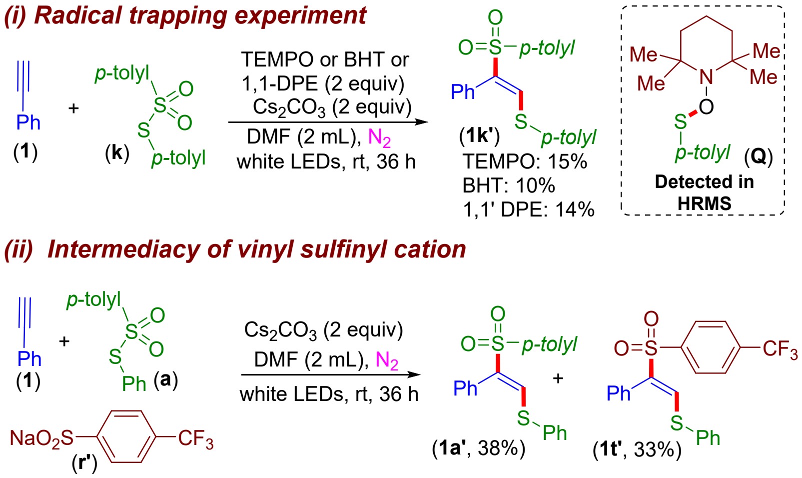
To ascertain the participation of disulphide **E′**, *β*-keto sulfone (**K**) was treated with *p*-tolyldiphenyl disulfide (**E′**) under the reaction condition (blue light irradiation) and the trifunctionalized product (**1k**) was isolated in a comparatively lower yield of 65% [Scheme S7(iii)b]. This suggests that in addition to thiosulfonate (**k**), the *in situ* generated disulfide (**E′**) also serves as the thiyl source. The lower yield of the product is due to the poor leaving ability of the thiolate compared to sulfonate (tosyl) during nucleophilic attack of *β*-keto sulfonate anion. Moreover, the same reaction proceeded with equal efficiency when performed in the absence of light (dark) suggesting the non-radical nature of this step [Scheme S7(iii)b]. Further, in another competitive reaction between (**1**) and an equimolar amount of thiosulfonate (**k**) and disulphide (**l'**) provided a mixture of (**1k**, 40%) and (**1l**, 25%), reconfirming the origin of thiol functionality from both the sources [Scheme S7(iii)c].

To gain further insight into the mechanism, UV-Vis spectroscopic measurements were performed using various combinations of phenylacetylene (**1**), thiosulfonate (**k**), and Et_3N in DMSO. No absorption band was observed individually for the reaction components (**1**), (**k**) and Et_3N in the visible region. However, when (**k**) was mixed with an equimolar amount of Et_3N, the mixture turned light yellow and showed a bathochromic shift in the visible region (Figures S9a and S9b). Upon the addition of phenylacetylene (**1**), the mixture turns to a light brown colour showing absorption in the visible region, indicating the progress of the reaction (Figures S9a and S9b). To further confirm the EDA complexation between thiosulfonate and Et_3N, a ^1H NMR titration experiment was conducted between *S*-(4-methoxyphenyl)-4-methylbenzenesulfonothioate (**l**) with increasing concentrations of Et_3N. The chemical shift of the –OMe group of thiosulfonate (**l**) gradually shifted upfield with increasing ratios of Et_3N. This upfield shift of the –OMe group is due to the enhanced electron density on the thiosulfonate owing to EDA complexation with the base (Figure S11 and S12).

(B) Control Experiments for Di-functionalization of Alkyne:

To decipher the mechanism of the di-functionalized product (**1k'**), reactions were performed in the presence of radical scavengers, such as TEMPO, BHT, and 1,1-

diphenylethylene, under standard reaction condition. In all the cases, the formation of the product was drastically suppressed indicating the radical pathway. Further, a TEMPO-trapped thiyl radical adduct (**Q**) was detected by the HRMS analysis of the reaction mixtures (Figure S3), suggesting the involvement of thiyl radical (Scheme 8 i). After the attack of the thiyl radical onto the alkyne, a vinylic radical is generated. This vinyl radical may undergo cross-coupling with the other radical partner (tosyl) or it may oxidize to a vinylic carbocation which is attacked by the nucleophilic tosylate anion. To check whether the reaction proceeds *via* the formation of a vinylic radical or a vinylic carbocation, a reaction was performed between (**1**), thiosulfonate (**k**), and sodium salt of substituted sulfinate (**r'**). The formation of a mixture of difunctionalized product having tolyl (**1a'**, 38%) and *p*-trifluoro (**1t'**, 33%) supports the intermediacy of vinyl carbocation (Scheme 8 ii). Here also the formation of EDA complex between thiosulfonate (**k**) and Cs_2CO_3 has been confirmed by UV-Vis spectroscopy. Appearance of a distinct yellow color having an absorption at 470 nm is consonant with the formation of an EDA complex between the thiosulfonate (**k**) and Cs_2CO_3 (Figure S10a and S10b). Here again, in a ^{1}H NMR titration of *S*-(4-methoxyphenyl)-4-methylbenzenesulfonothioate (**l**) and various concentrations of Cs_2CO_3, the chemical shift of the –Me group of (**l**), distinctly moved upfield with increasing ratios of Cs_2CO_3. This shift is due to increase in the electron density, confirming the formation of an EDA complex (Figure S13 and S14).



Scheme 8 Control experiments for vicinal difunctionalization strategy

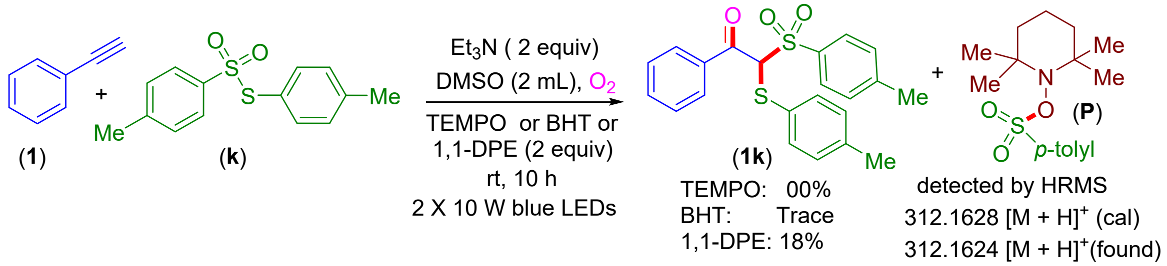
6. General Procedures of Mechanistic Investigation:

(A) Radical-trapping Experiments with TEMPO or BHT or 1,1-DPE for Tri-functionalization:

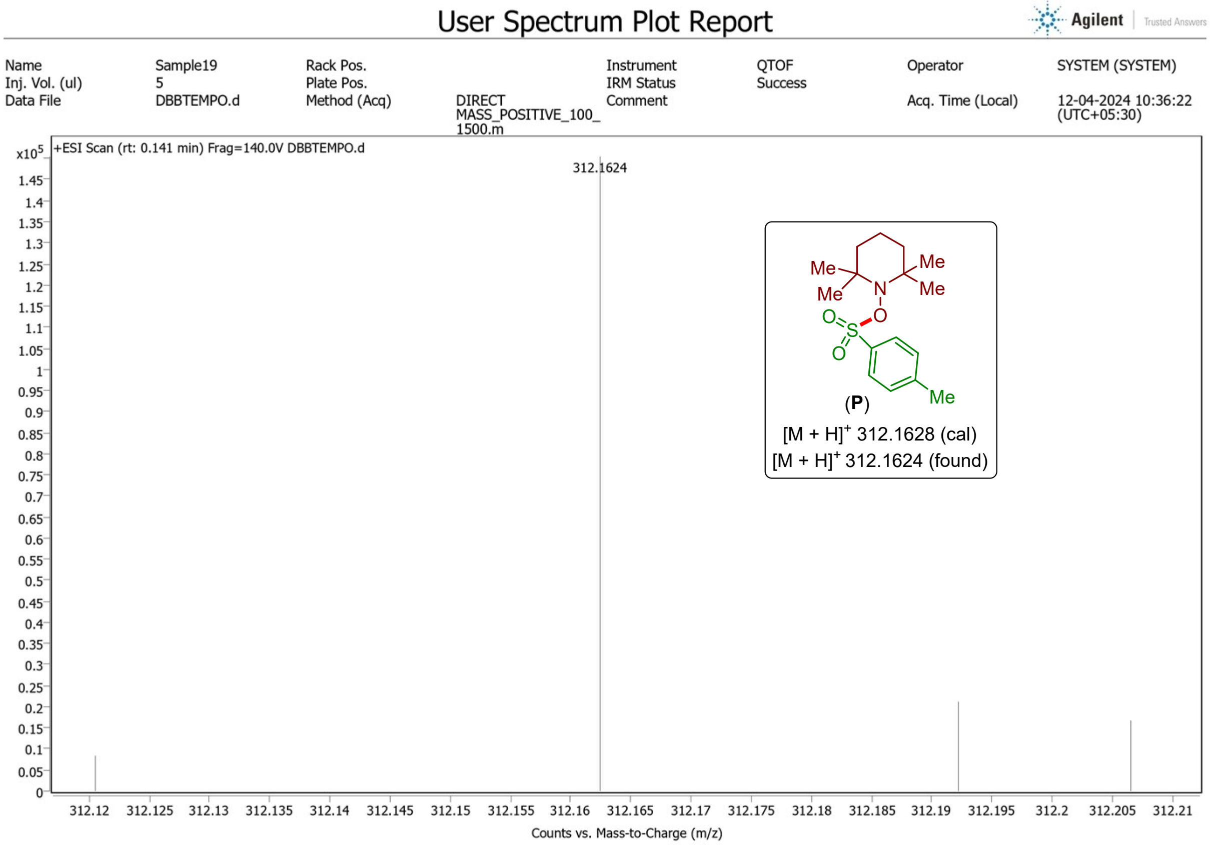
Three sets of oven-dried 10 mL vials were added phenylacetylene (**1**) (0.025 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol). To each of these three sets, a radical scavenger (i) (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.07 g, 2 equiv, 0.5 mmol), or (ii) BHT (0.11 g, 2 equiv, 0.5 mmol), or (iii) 1,1-diphenylethylene (DPE) (0.09 g, 2 equiv, 0.5 mmol) in DMSO (2 mL) under oxygen atmosphere. The three reaction mixtures were stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h.

In the case of TEMPO, the reaction failed to give the product (**1k**) which was monitored by TLC analysis. However, the reaction in the presence of BHT gave a trace amount of the product (**1k**) which was also monitored by TLC analysis. Whereas, in the presence of 1,1-DPE, after completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give 18% (17mg) of pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**). These results suggest that the reaction goes through a radical pathway (Scheme S9).

In another set of identical reaction in the presence of TEMPO, the formation of TEMPO-tosyl adduct (**P**) was monitored. Each time (10 µL) of reaction aliquot was taken at a time interval of 30 minutes and subjected to HRMS analysis. A TEMPO-tosyl adduct (**P**) was detected through HRMS after 2 h, which is given in Figure S2.



Scheme S9. Reaction in the presence of radical scavengers



User Spectrum Plot Report

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Figure S2. HRMS of TEMPO-tosyl adduct (**P**)

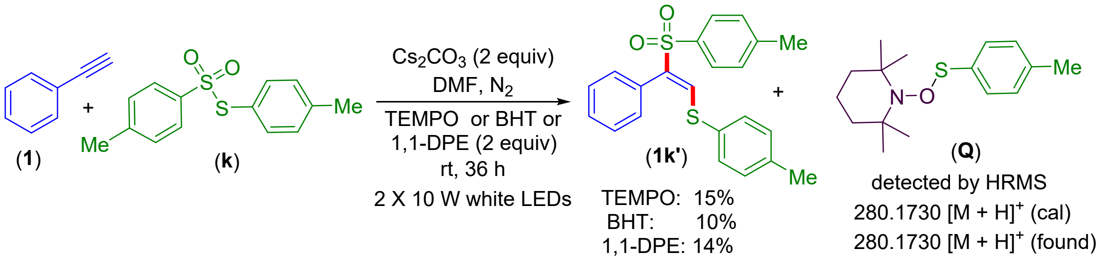
(B) Radical-trapping Experiments with TEMPO or BHT or 1,1-DPE for Di-functionalization:

Three sets of oven-dried 10 mL vials were added phenylacetylene (**1**) (0.025 g, 27 µL 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Cs_2CO_3 (0.16 g, 0.5 mmol). To each of this three sets, a radical scavenger (i) (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.07 g, 2 equiv, 0.5 mmol), or (ii) BHT (0.11 g, 2 equiv, 0.5 mmol), or (iii) 1,1-diphenylethylene (DPE) (0.09 g, 2 equiv, 0.5 mmol) in DMF (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6−8 cm from two 10 W white LEDs for 36 h.

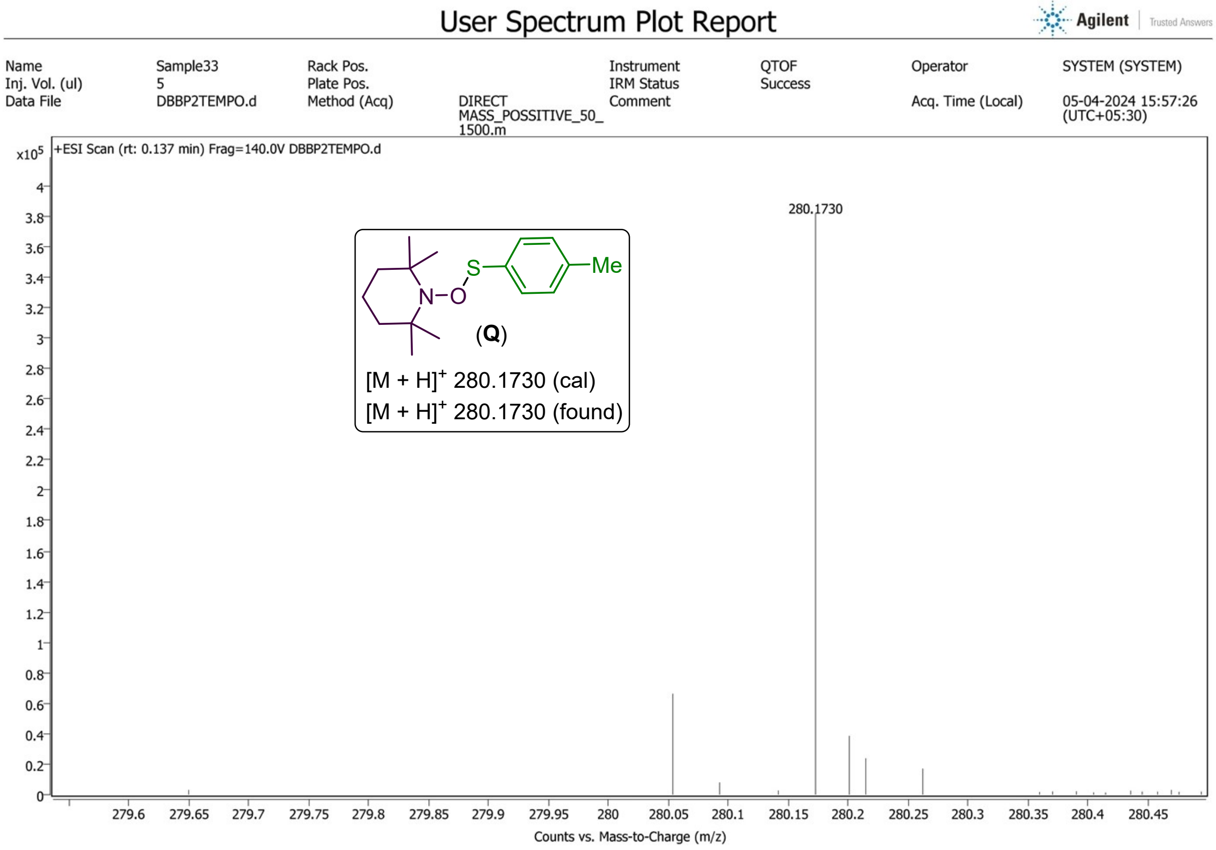
After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using

5% ethyl acetate in hexane to give 15% (14 mg) for TEMPO, 10% (10 mg) for BHT, and 14% (13 mg) for 1,1-DPE of pure (*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (**1k′**). These results suggest that the reaction followed a radical mechanism (Scheme S10).

In another set of identical reaction in the presence of TEMPO, the formation of TEMPO-thio adduct (**Q**) was monitored. Each time (10 μL) of reaction aliquot were withdrawn at a time interval of 1 h and subjected to HRMS analysis. A TEMPO-thio adduct (**Q**) was detected at 5 h through HRMS which is given in Figure S3.



Scheme S10. Reaction in the presence of radical scavengers



User Spectrum Plot Report

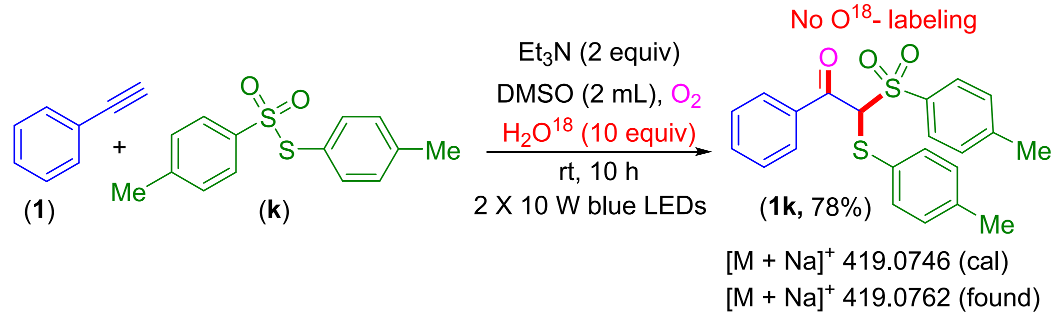
Name	Sample33	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
Data File	DBBP2TEMPO.d	Method (Acq)	DIRECT MASS_POSSITIVE_50_1500.m	Comment		Acq. Time (Local)	05-04-2024 15:57:26 (UTC+05:30)

Figure S3. HRMS of TEMPO-thio adduct (**Q**)

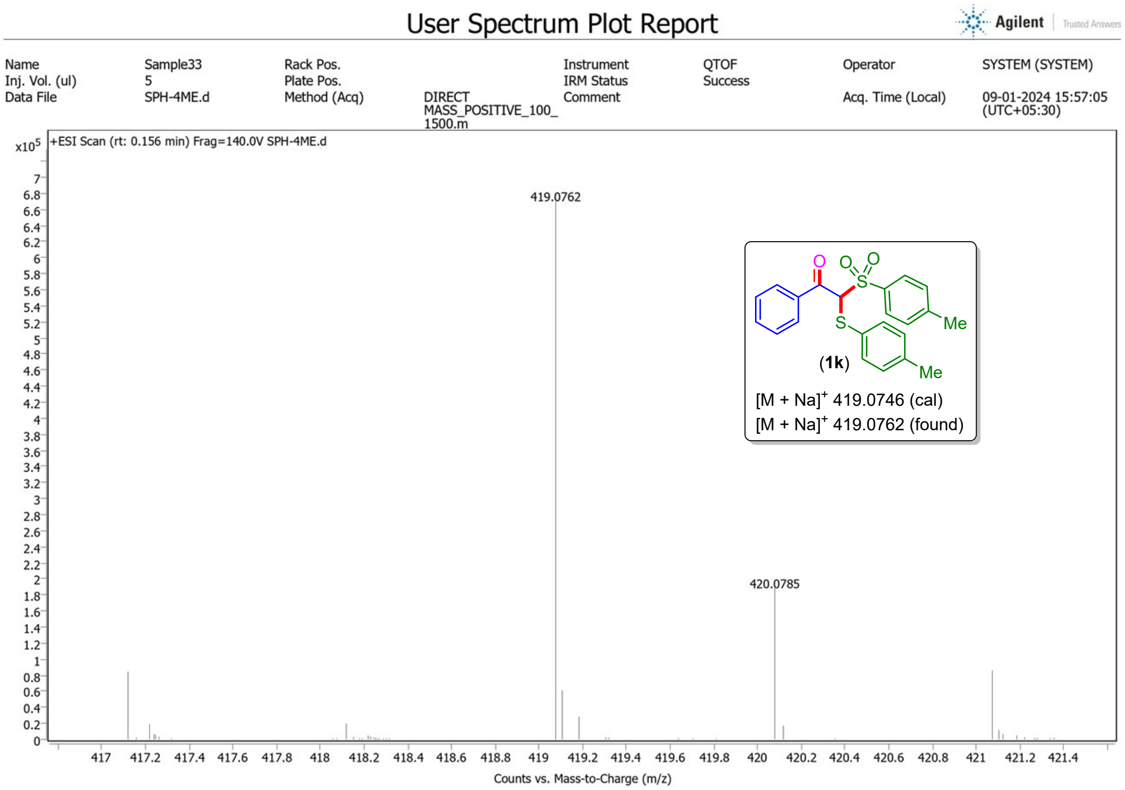
(C) Procedure for Investigation of Origin of Oxygen in Keto Functionality

(i) H_2O^{18} Labelling Experiment:

An oven-dried 10 mL vial was added with phenylacetylene (**1**) (0.02 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), H_2O^{18} (10 equiv, 2.5 mmol, 50 mg) in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6−8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane and analyzed by HRMS analysis and $^{13}C\{^1H\}$ NMR (Figure S4 and S5). The results showed that no O^{18} labeled **1k** was present; only 78% of pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) was obtained (Scheme S11). This results confirms the non-involvement of moisture in the reaction.



Scheme S11. Reaction in the presence of H_2O^{18}



User Spectrum Plot Report

Name	Sample33	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
Data File	SPH-4ME.d	Method (Acq)	DIRECT MASS_POSITIVE_100_1500.m	Comment		Acq. Time (Local)	09-01-2024 15:57:05 (UTC+05:30)

Figure S4. HRMS of O^{18} labelled experiment

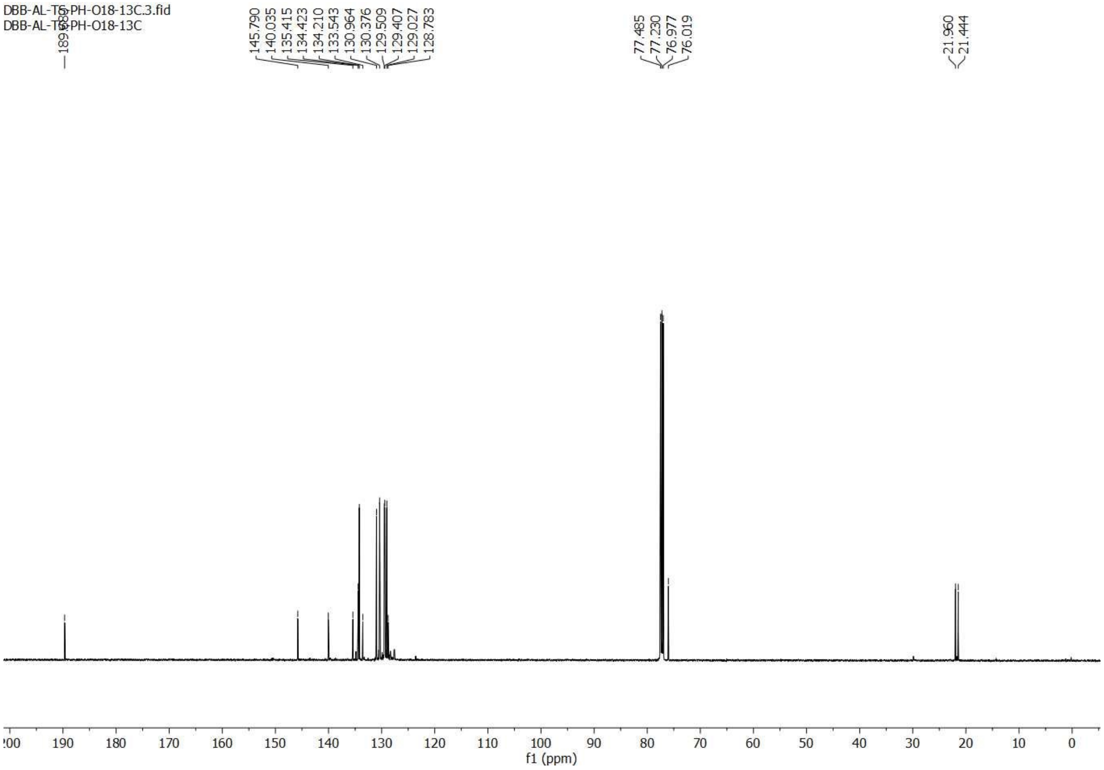
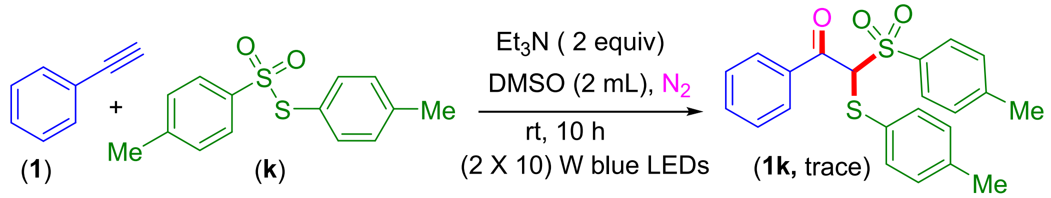


Figure S5. $^{13}C\{^1H\}$ NMR spectra of O^{18} labeled experiment

(ii) Reaction under Nitrogen Atmosphere:

An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.02 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol) in anhydrous DMSO (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), it was found that a trace amount of product 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) was formed (Scheme S12).

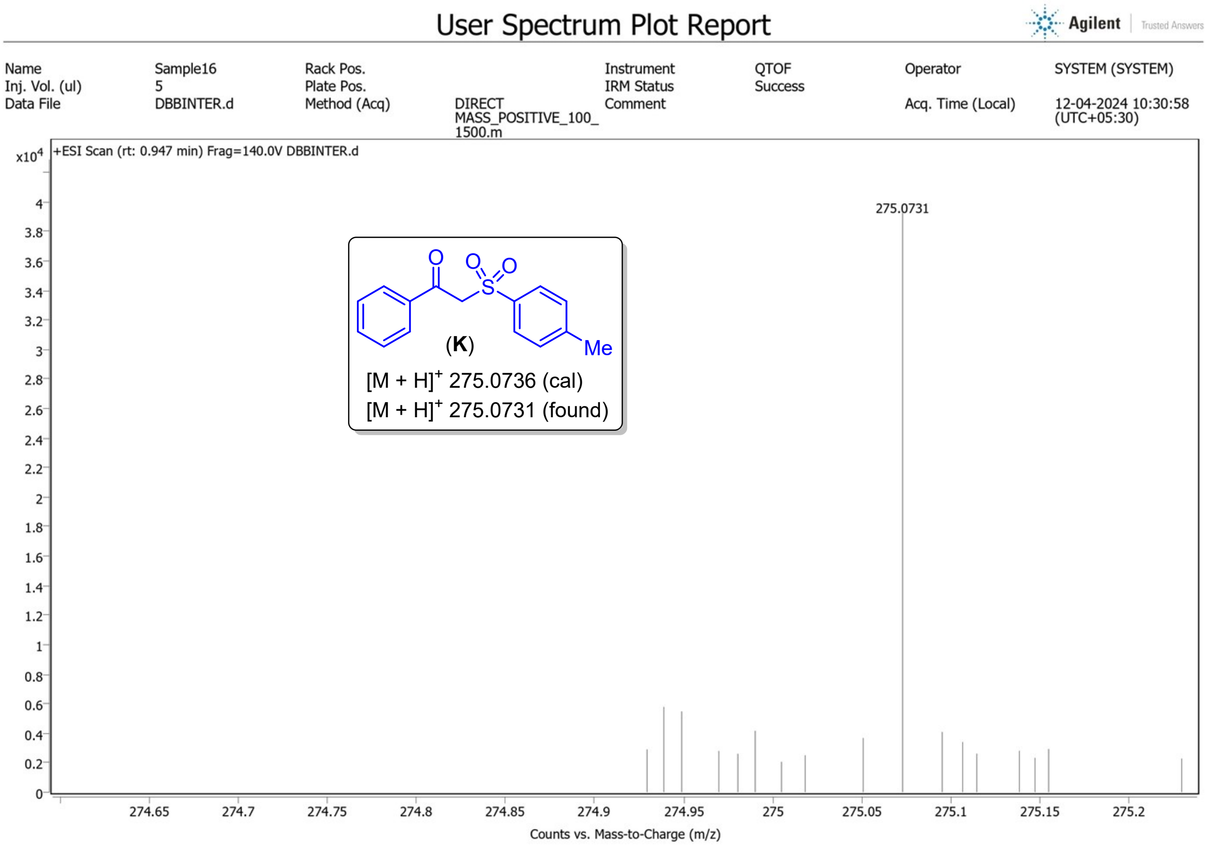


Scheme S12. Reaction under N_2 atmosphere

(D) Intermediacy of *β*-keto sulfone:

(i) Intermediacy of *β*-keto sulfone (K) from reaction mixture:

An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.025 g, 27 µL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs. Each time (10 µL) of reaction aliquot was withdrawn at a time interval of 30 minutes and subjected to HRMS analysis. The results suggest that *β*-keto sulfone is one of the intermediates of the tri-functionalized protocol, which is detected from HRMS analysis (Figure S6).



User Spectrum Plot Report

Name	Sample16	Rack Pos.		Instrument	QTOF	Operator	SYSTEM (SYSTEM)
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Data File	DBBINTER.d	Method (Acq)	DIRECT MASS_POSITIVE_100_1500.m	Comment		Acq. Time (Local)	12-04-2024 10:30:58 (UTC+05:30)

+ESI Scan (rt: 0.947 min) Frag=140.0V DBBINTER.d

(**K**)

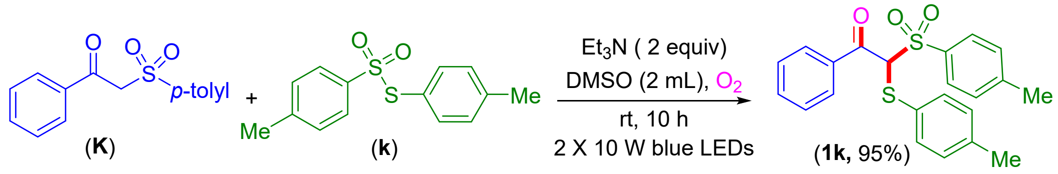
$[M + H]^+$ 275.0736 (cal)

$[M + H]^+$ 275.0731 (found)

Figure S6. HRMS of reaction mixture for detection of *β*-keto sulfone

(ii) Reaction of *β*-keto sulfone (K) with S-(*p*-tolyl) 4-methylbenzenesulfonothioate (k):

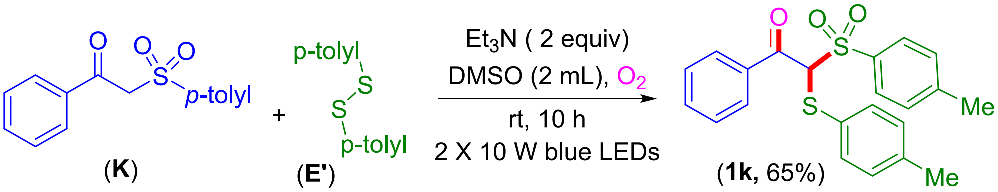
An oven-dried 10 mL vial was added *β*-keto sulfone (**K**) (0.07 g, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 95% yield (90 mg) (Scheme S13).



Scheme S13. Synthesis of 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) from *β*-keto sulfone and thiosufonate (**K**)

(iii) Reaction of *β*-keto sulfone (K) with 1,2-di-*p*-tolyldisulfane (E′):

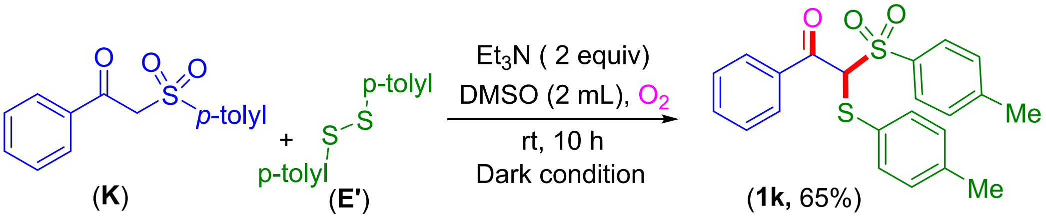
An oven-dried 10 mL vial was added *β*-keto sulfone (**K**) (0.07 g, 0.25 mmol), 1,2-di-*p*-tolyldisulfane (**E′**) (0.12 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 65% yield (61 mg) (Scheme S14).



Scheme S14. Synthesis of 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) from from *β*-keto sulfone and diphenyldisulfide (**E′**)

(iii) Reaction of *β*-keto sulfone (K) with 1,2-Di-*p*-tolyldisulfane (E′) in Dark Condition:

An oven-dried 10 mL vial was added *β*-keto sulfone (**K**) (0.07 g, 0.25 mmol), 1,2-di-*p*-tolyldisulfane (**E′**) (0.12 g, 0.5 mmol), Et_3N (0.05 g, 70 μL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred in a dark condition at room temperature for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give pure 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 65% yield (61 mg) (Scheme S15). This result suggests that the reaction follows the nucleophilic mechanism and the thiyl source originated from both thiosulfonate (**k**), and the *in situ* generated disulfide (**E'**).

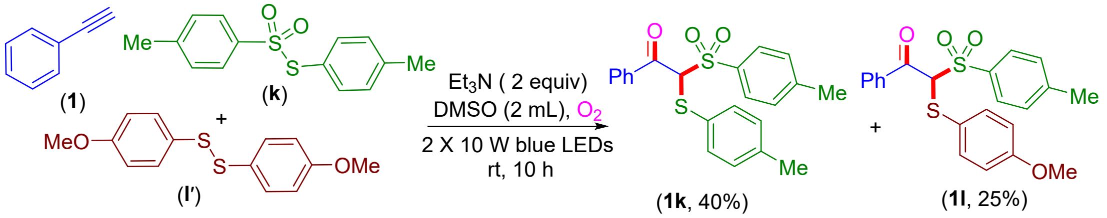


Scheme S15. Reaction of *β*-keto sulfone (**K**) with 1,2-di-*p*-tolyldisulfane (**E′**) in dark

(E) Procedure for Competitive Reaction of Phenylacetylene (1), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (k), 1,2-Bis(4-methoxyphenyl)disulfane (l′):

An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.025 g, 27 μL, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.14 g, 0.5 mmol), 1,2-bis(4-

methoxyphenyl)disulfane (**l′**) (0.14 g, 0.5 mmol), Et_3N (0.05 g, 70 µL, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs for 10 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 15% ethyl acetate in hexane to give 1-phenyl-2-(*p*-tolylthio)-2-tosylethan-1-one (**1k**) in 40% yield (40 mg) and 2-((4-methoxyphenyl)thio)-1-phenyl-2-tosylethan-1-one (**1l**) in 25% yield (26 mg) (Scheme S16). The identity and purity of the product were confirmed by spectroscopic analysis. The result confirms the origin of thiol functionality from both the sources of (**k**) and (**l′**).

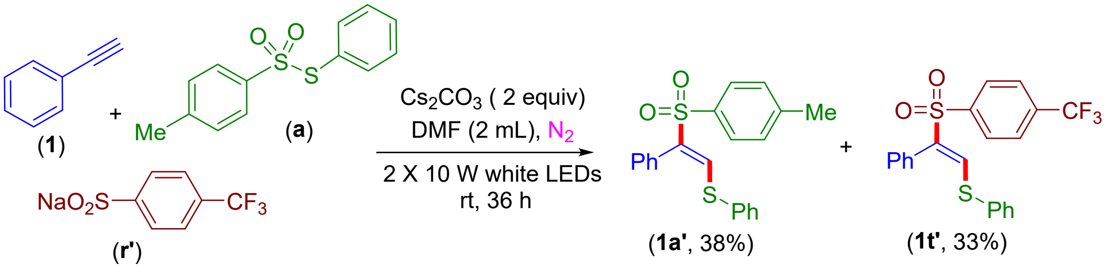


Scheme S16. Competitive Reaction of (**1**), (**k**), and (**l′**)

(F) Procedure for Competitive Reaction of Phenylacetylene (1), S-phenyl 4-methylbenzenesulfonothioate (a), Sodium 4-(trifluoromethyl)benzenesulfinate (r′):

An oven-dried 10 mL vial was added phenylacetylene (**1**) (0.02 g, 27 µL, 0.25 mmol), S-phenyl 4-methylbenzenesulfonothioate (**a**) (0.13 g, 0.5 mmol), sodium 4-(trifluoromethyl)benzenesulfinate (**r′**) (0.12 g, 0.5 mmol), Cs_2CO_3 (0.16 g, 0.5 mmol), in DMF (2 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W white LEDs for 36 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was admixed with ethyl acetate (20 mL) and washed with ice-cooled water (10 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel using 5% ethyl acetate in hexane to give (*E*)-phenyl(2-phenyl-2-tosylvinyl)sulfane (**1a′**) in 38% yield (35 mg) and (*E*)-phenyl(2-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (**1t′**) in 33% yield (34 mg)

(Scheme S17). The identity and purity of the product were confirmed by spectroscopic analysis. The formation of a mixture of difunctionalized products having tolyl (**1a'**, 38%) and *p*-trifluoro (**1t'**, 33%) supports the intermediacy of vinyl carbocation.



Scheme S17. Competitive reaction of (**1**), (**a**), and (**r′**)

(G) H_2O_2 Detection in the reaction mixture:

(i) H_2O_2 detection by Mohr's Salt:

An oven-dried 10 mL vial was charged with phenylacetylene (**1**) (0.02 g, 27 µL 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.13 g 0.5 mmol), Et_3N (0.05 g, 70 µL 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6–8 cm from two 10 W blue LEDs. After around 4 hours, a 100 µL solution of Mohr's Salt (10 mg in 100 µL H_2O) was added through a syringe to the reaction mixture. After 10 min, a rapid setting of $Fe(OH)_3$ floc was observed [Figure S7 (b)]. The floc observed was because of the rapid oxidation of Fe(II) to Fe(III) due to the presence of hydrogen peroxide, and H_2O_2 in the medium.

(a) **(b)**

Figure S7. (a) Reaction mixture before addition of Fe(II) solution (Mohr's Salt) (b) Reaction mixture after addition of Fe(II) solution (Mohr's Salt)

(ii) H_2O_2 detection in a reaction with $KMnO_4$:

An oven-dried 10 mL vial was added with phenylacetylene (**1**) (0.0255 g, 0.25 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**) (0.1391 g 0.5 mmol), Et_3N (0.0505 g, 0.5 mmol), in DMSO (2 mL) under oxygen atmosphere. The reaction mixture was stirred at room temperature, maintaining an approximate distance of ~6−8 cm from two 10 W blue LEDs. A small portion of the reaction mixture was taken out from the reaction vial using a syringe which was added to a separately prepared $KMnO_4$ solution (300 μM) in H_2O (10 mL). Instantly, the aqueous $KMnO_4$ solution of turned to pale yellow colour [Figure S8 (b)] indicating the presence of H_2O_2.

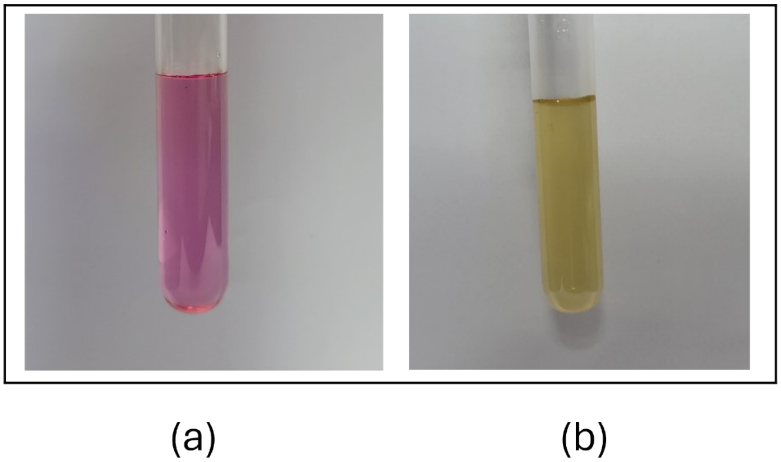


Figure S8. (a) $KMnO_4$ solution (b) $KMnO_4$ solution after adding a portion of the reaction mixture

7. UV-vis Experiments:

(i) UV-vis Experiments for Tri-functionalized Condition:

10 mL stock solutions of phenylacetylene (**1**, 50 mM), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**, 50 mM), and Et_3N (50 mM) were prepared separately in DMSO. At first, the UV absorption of **1**, **k**, and Et_3N each of 3 mL were taken individually, none of which showed any absorption in the visible region (Figure S9). Next, the combinations of (**1** + **k**), (**k** + Et_3N), and (**1** + Et_3N) were taken separately each ratio of 1:1 (1.5 mL : 1.5 mL) in 3 mL cuvette. The combination of (**1** + **k**) and (**1** + Et_3N) showed no absorption in the visible region. However, with the combination of (**k** + Et_3N), the solution turned to light yellow colour and showed absorption in the visible region, suggesting the formation of an EDA complex between **k** and Et_3N. Next, a combination of **1**, **k**, and Et_3N (1 mL each) was taken in a 3 mL UV cuvette. The

solution turned yellow, with an absorption maximum in the visible region, suggesting the formation of an electron donor-acceptor complex (Figure S9). These results indicate that the combinations of (**k** + Et_3N) and (**1** + **k** + Et_3N) absorb light and show absorption in the visible region, whereas (**1** + Et_3N) does not. This confirms that an EDA complex is formed between **k** and Et_3N (Figure S9).

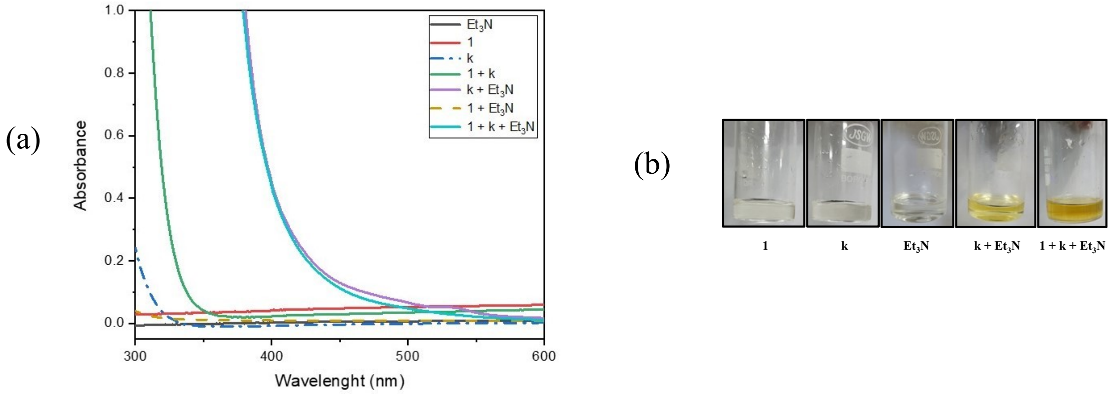


Figure S9. (a) UV-Vis spectra for the tri-functionalized protocol (b) Colour change for the formation of EDA complex

(ii) UV-Vis Experiments for Di-functionalized Condition:

10 mL stock solutions of phenylacetylene (**1**, 50 mM), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (**k**, 50 mM), and Cs_2CO_3 (50 mM) were prepared separately in DMF. At first, the UV absorption of **1**, **k**, and Cs_2CO_3 were taken individually, none of which showed any absorption in the visible region (Figure S10). Next, the combinations of (**1** + **k**), (**k** + Cs_2CO_3), and (**1** + Cs_2CO_3) were taken separately each ratio of 1:1 (1.5 mL : 1.5 mL) in a 3 mL cuvette. The combination of (**1** + **k**) and (**1** + Cs_2CO_3) showed no absorption in the visible region. Whereas, the combination of (**k** + Cs_2CO_3) solution turned a light yellow colour and showed absorption in the visible region suggesting the formation of an EDA complex between **k** and Cs_2CO_3. Next, a combination of **1**, **k**, and Cs_2CO_3 (1 mL each of **1**, **k**, and Cs_2CO_3) was taken in a 3 mL UV cuvette, which was also turned to yellow with an absorption maximum in the visible region, suggesting the formation of an electron donor-acceptor complex (Figure S10). From these results, the combinations of (**k** + Cs_2CO_3) and (**1** + **k** + Cs_2CO_3) absorb light and show absorption in the visible region, whereas (**1** + Cs_2CO_3) does not. This confirms that an EDA complex is formed only between **k** and Cs_2CO_3 (Figure S10).

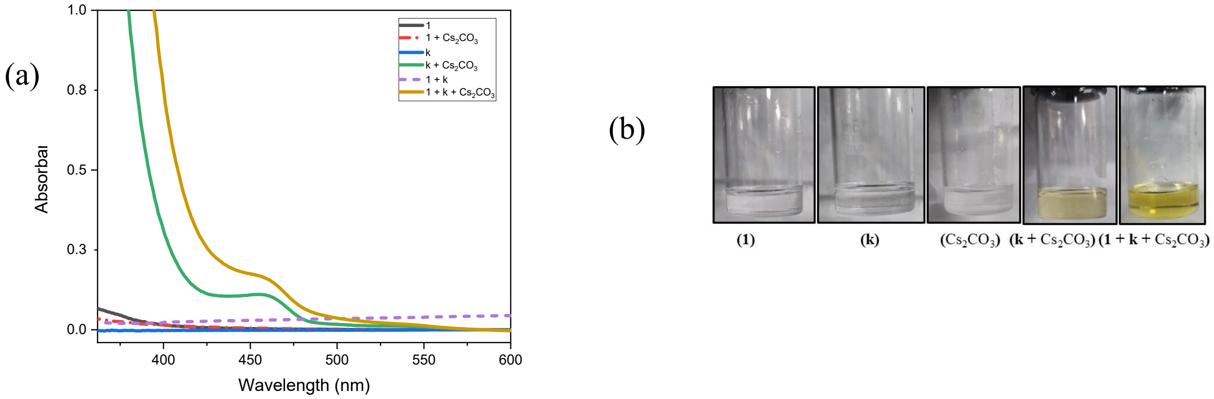


Figure S10. (a) UV-Vis spectra for di-functionalized protocol (b) Colour change for the formation of EDA complex

8. ^{1}H NMR Experiments:

(i) ^{1}H NMR Titration for Tri-functionalized Condition:

Further to confirm the formation of the EDA complex ^{1}H NMR experiment was performed by the preparation of $CDCl_3$ solutions containing S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) and Et_3N in different ratios, keeping the amount of S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) constant (0.02 mmol) and increasing the amount of Et_3N (**l** : Et_3N = 1 : 0, 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5). Each of the six ratios was prepared separately in 2 mL microcentrifuge tubes. Initially, 5.88 mg (~6 mg) of compound (**l**) was added to each tube. Microcentrifuge tube 1 contained only compound (**l**), maintaining a 1:0 ratio. Varying amounts of Et_3N were then added to other tubes to achieve the desired ratios: 2 mg (3.0 μL) for a 1:1 ratio, 4 mg (6.0 μL) for a 1:2 ratio, 6 mg (8.0 μL) for a 1:3 ratio, 8 mg (11 μL) for a 1:4 ratio, and 10 mg (14 μL) for a 1:5 ratio. Each ratio was prepared in $CDCl_3$, with the volume of each solution fixed at 400 μL. The solutions were then transferred to NMR tubes, and the data was recorded. Due to the interaction between (**l**) and Et_3N, the chemical shift of the –OMe group of (**l**) progressively shifted upfield with increasing amounts of Et_3N, as shown in Figures S11 and S12.

Table S2: ^{1}H NMR δ_{OMe} (ppm) value for the ratio of l, Et_3N

Entry	**l** (mmol)	Et_3N (mmol)	**l** : Et_3N	δ_{OMe} (ppm)
1	0.02	0	1: 0	3.8324
2	0.02	0.02	1: 1	3.8222
3	0.02	0.04	1: 2	3.8022
4	0.02	0.06	1: 3	3.7991
5	0.02	0.08	1: 4	3.7924
6	0.02	0.10	1: 5	3.7869

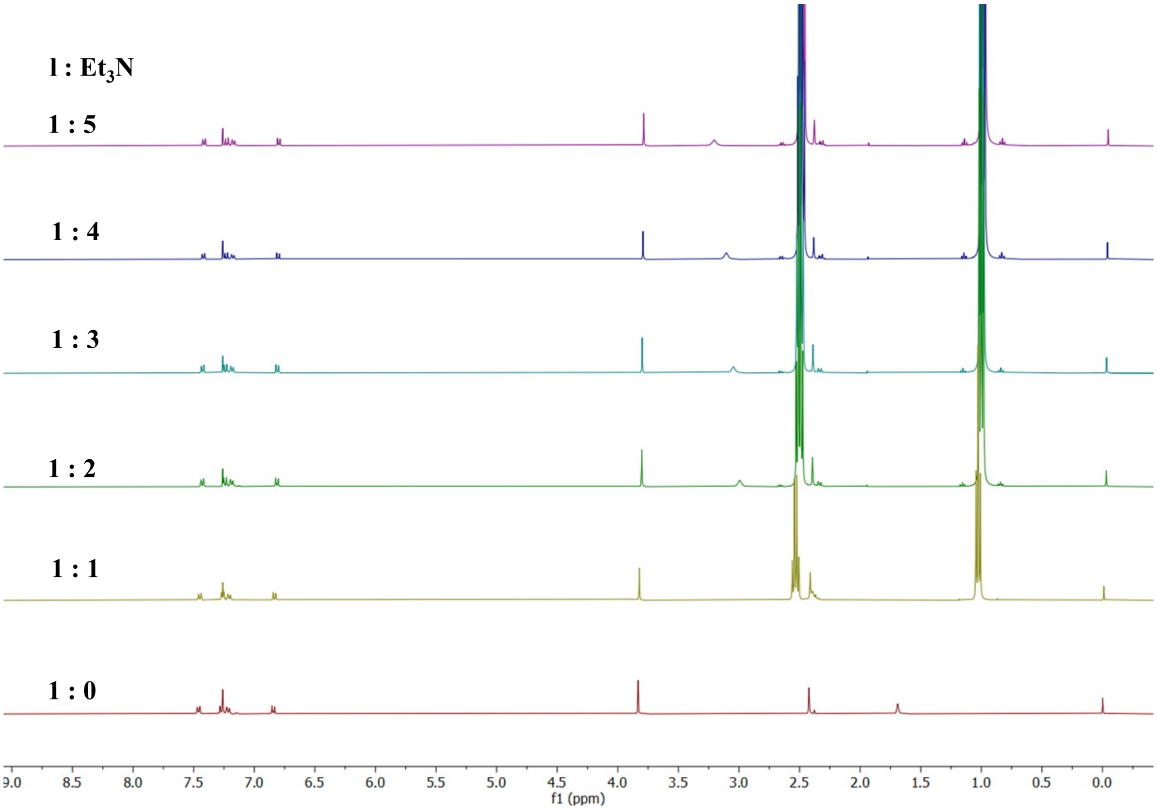


Figure S11. Full ^{1}H NMR spectra of S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) and Et_3N in different ratios

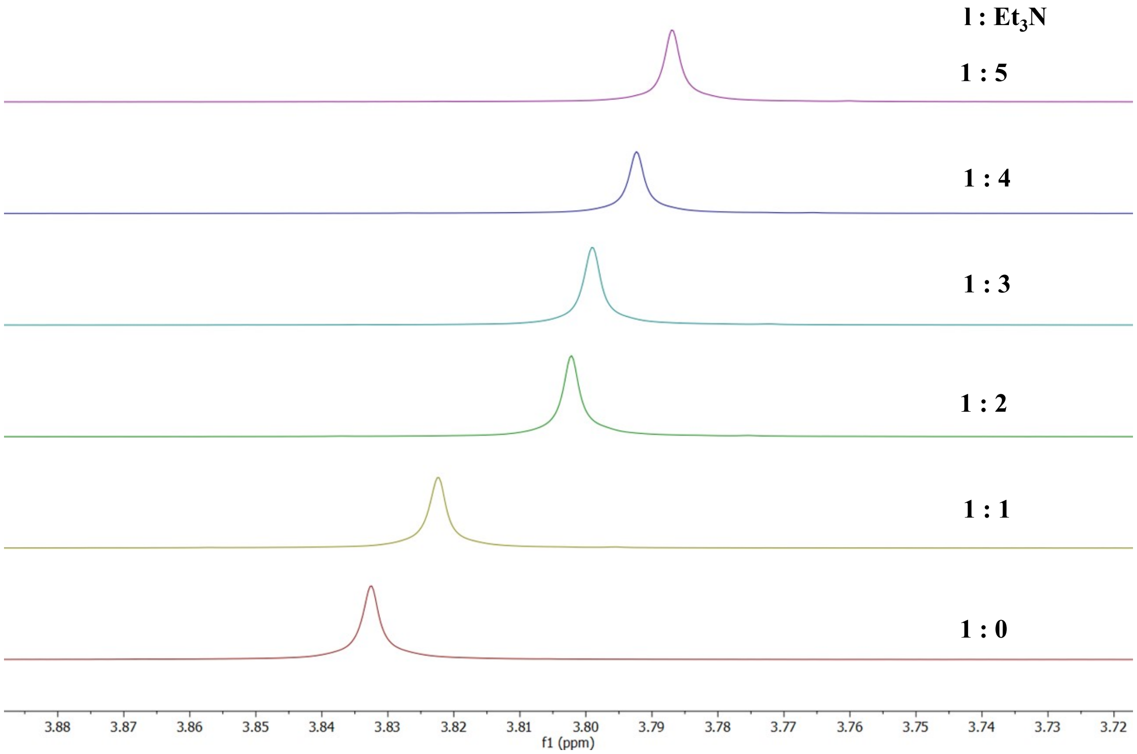


Figure S12. Evidence for the formation of EDA complex through ^{1}H NMR

(ii) ^{1}H NMR Titration for Di-functionalized Condition:

Further to confirm the formation of the EDA complex in case of di-functionalization, ^{1}H NMR experiment was performed by the preparation of CD_3OD solutions containing S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) and Cs_2CO_3 in different ratios keeping the amount of S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) constant (0.02 mmol) and increasing the amount of Cs_2CO_3 (**l** : Cs_2CO_3 = 1 : 0, 1 : 1, 1 : 2, 1 : 3, and 1 : 4). The five ratios were prepared separately in 2 mL microcentrifuge tubes. Initially, 5.88 mg (~6 mg) of compound (**l**) was added to each tube. Microcentrifuge tube 1 contained only compound (**l**), maintaining a 1:0 ratio. Varying amounts of Cs_2CO_3 were then added to other tubes to achieve the desired ratios: 6.5 mg for a 1:1 ratio, 13 mg for a 1:2 ratio, 19.5 mg for a 1:3 ratio, and 26 mg for a 1:4 ratio. Each ratio was prepared in Methanol-d$_4$, with the volume of each solution fixed at 400 µL. The solutions were then transferred to NMR tubes, and the data was recorded. Due to the formation of the EDA complex between **l** and Cs_2CO_3, the chemical shift of –Me group of **l** progressively shifted upfield with increasing amounts of Cs_2CO_3, as shown in Figures S13 and S14.

Table S3: ^{1}H NMR δ_{Me} (ppm) value for the ratio of l, Cs_2CO_3

Entry	**l** (mmol)	Cs_2CO_3 (mmol)	**l** : Cs_2CO_3	δ_{Me} (ppm)
1	0.02	0	1 : 0	2.2928
2	0.02	0.02	1 : 1	2.2246
3	0.02	0.04	1 : 2	2.1335
4	0.02	0.06	1 : 3	2.0947
5	0.02	0.08	1 : 4	2.0375

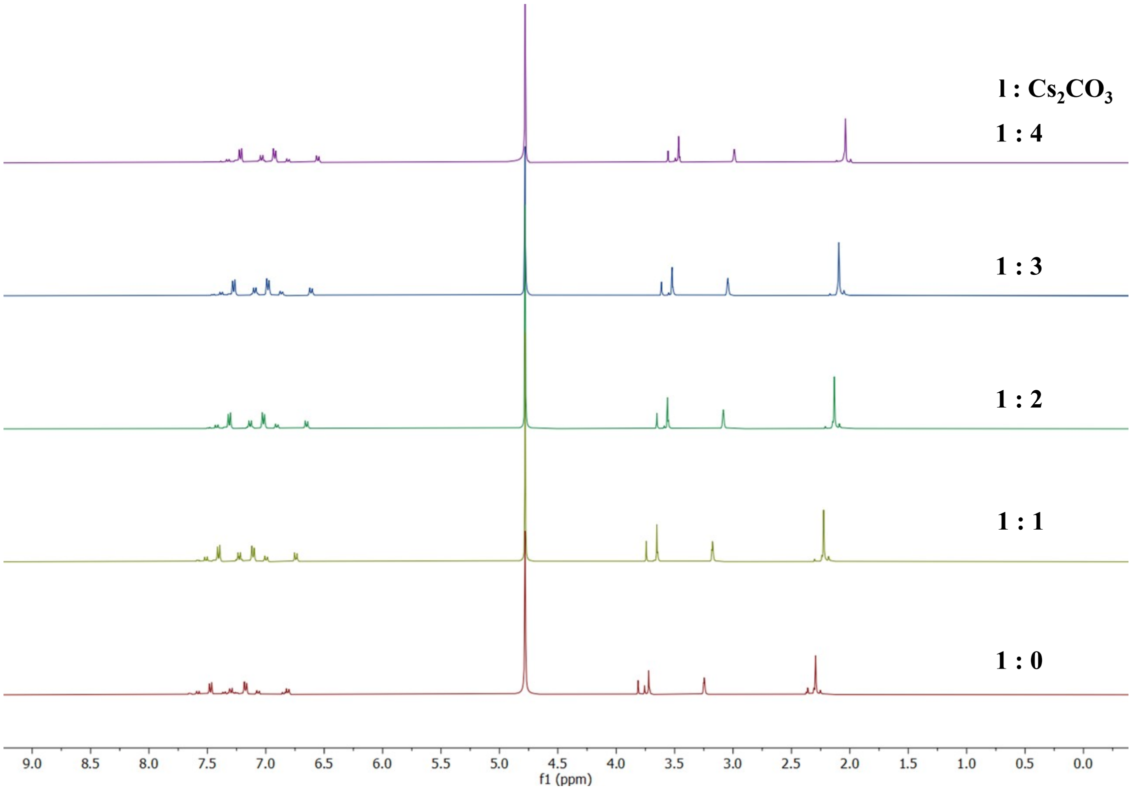


Figure S13. Full ^{1}H-NMR spectra of S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (**l**) and Cs_2CO_3 in different ratios

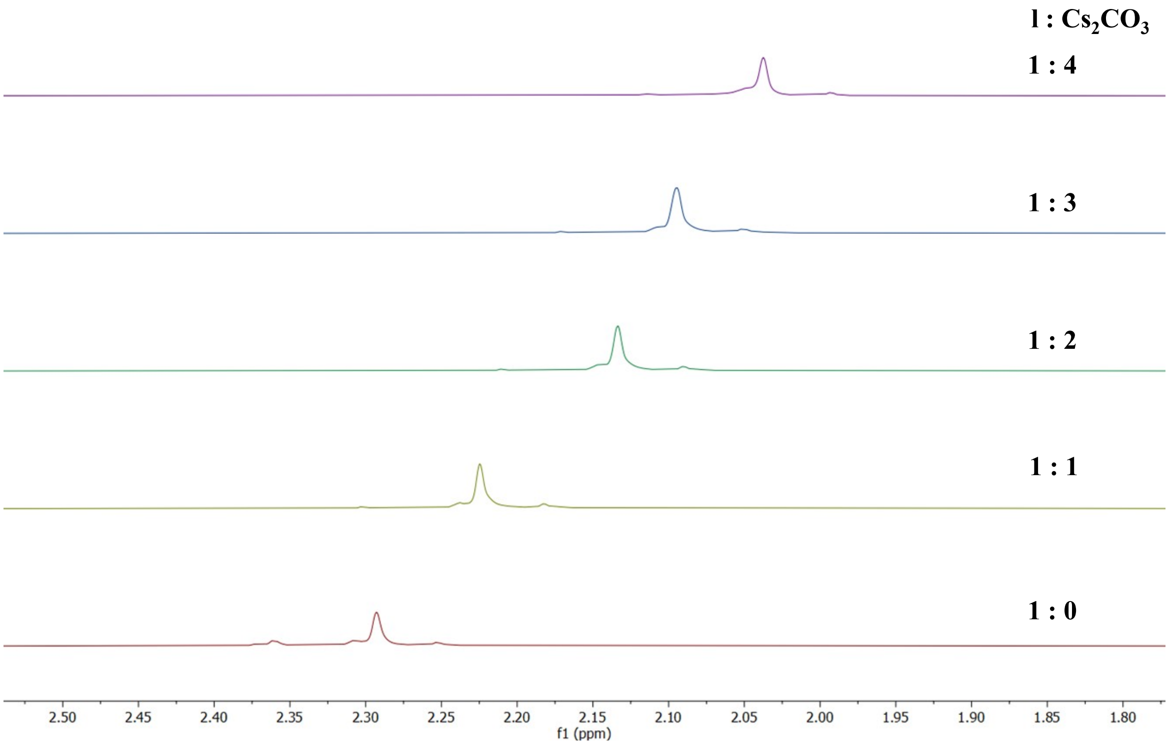
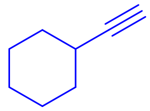
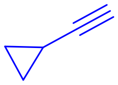


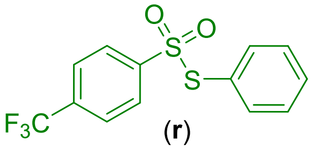
Figure S14. Evidence for the formation of EDA complex through ^{1}H-NMR

9. Unsuccessful Substrates

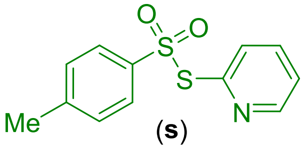
(i) Unsuccessful Substrates under Tri-functionalization Statergy:


(**15**)


(**16**)



(**r**)



(**s**)

Aliphatic alkynes **15** and **16** failed to react under this tri-functionalized condition, giving no products (**15a**, 00%) and (**16a**, 00%). This is possibly because of their inability to stabilize the generated aliphatic vinyl radical intermediates. Moreover, a strong electron-withdrawing group ($-CF_3$) (**r**) on the sulfonyl side and pyridyl (**s**) system on the thiol side of thiosulfonate, both failed to react. This is possibly because of their poor ability to form an EDA complex with Et_3N. No significant bathochromic shift in the UV-Vis spectra were observed for these thiosulfonates (**r**) and (**s**) on treatment with Et_3N, endorsing their inability to form EDA complex essential for driving this reaction.

To confirm the reason for unsuccessful substrates (**r** and **s**), an UV-Vis experiment was conducted. A 10 mL stock solution of phenylacetylene (**1**, 50 mM), S-Phenyl 4-(trifluoromethyl)benzenesulfonothioate (**r**, 50 mM), and Et_3N (50 mM) were prepared separately in DMSO. The UV spectra with equal ratios of the combinations of **r**, (**r** + Et_3N), and (**1** + **r** + Et_3N) were recorded in a 3 mL cuvette. No significant bathochromic shift was observed in the visible region which is shown in Figure S15(a). The result suggests an inability of EDA complexation between (**r**) and Et_3N.

Similarly, A 10 mL stock solution of phenylacetylene (**1**, 50 mM), S-(pyridin-2-yl) 4-methylbenzenesulfonothioate (**s**, 50 mM), and Et_3N (50 mM) were prepared separately in DMSO. The UV spectra with equal ratios of the combinations of **s**, (**s** + Et_3N), and (**1** + **s** + Et_3N) were recorded in a 3 mL cuvette. No significant bathochromic shift was observed in the visible region which is shown in Figure S15(b). The result suggests an inability of EDA complexation between (**s**) and Et_3N.

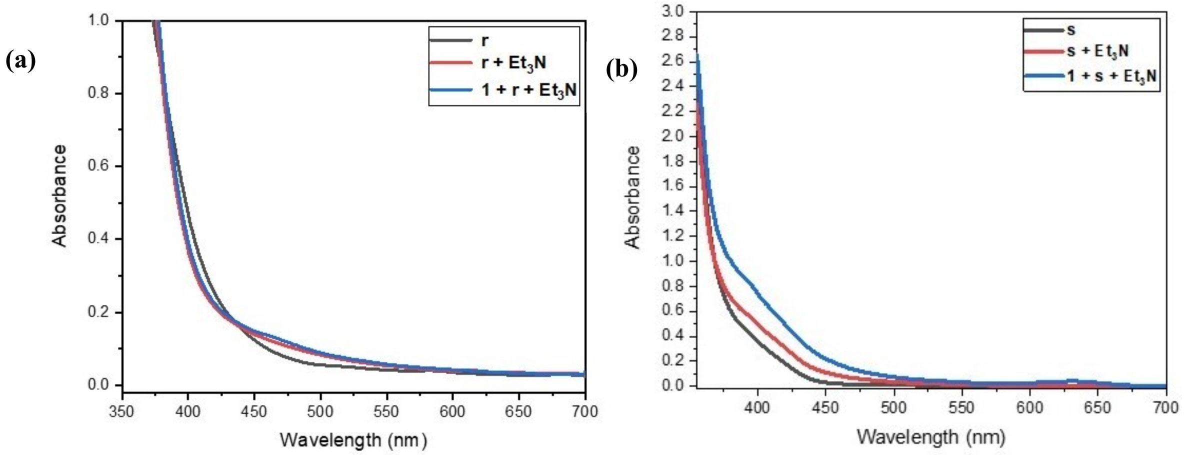
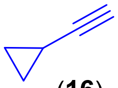
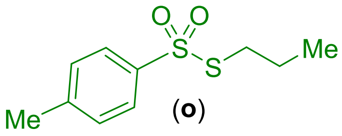


Figure S15. (a) UV-Vis spectra of the combibation of **r**, (**r** + Et_3N), and (**1** + **r** + Et_3N) (b) UV-Vis spectra of the combibation of **s**, (**s** + Et_3N), and (**1** + **s** + Et_3N)

(ii) Unsuccessful Substrates under Di-functionalization Statergy:



(**16**)



(**o**)

The di-functionalized statergy was unsuccessful for ethynylcyclopropane (**16**) which may be attributed to poor vinyl radical stability after the attack of thiyl radical at the terminal position of alkyne. Though thiosulfonates derived from aliphatic thiol (**o**) is capable of EDA complexation with base to deliver trifunctionalized product (**1o**) (Scheme 2), it fails to provide the difunctionalized product. This is possibly because of their inability to undergo S−S bond cleavage owing to the poor radical stability of the resulting thiyl radical ($MeCH_2CH_2S^{\bullet}$) essential for this difunctionalization.

10. Crystallographic Information:

(A) Crystallographic Information of 1-(3-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (12a):

(i) Sample Preparation: The single crystal of compound **12a** was prepared by the slow evaporation method for which 10 mg of the compound (**12a**) was dissolved in 1 mL ethyl acetate. 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 **12a** were obtained as light-yellow crystals after around 4−5 days.

(ii) 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.

(iii) Crystallographic Description of 1-(3-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (12a):

$C_{21}H_{17}ClO_3S_2$, crystal dimensions 0.24 x 0.20 x 0.15 mm, $M_r = 69.49$, triclinic, space group P −1, $a = 8.2512$ (5), $b = 11.5639$ (8), $c = 11.6055$ (8) Å, $\alpha = 117.3240$ (10), $\beta = 97.055$ (2), $\gamma = 94.082$ (2), $V = 966.08$ (11) Å^3, $Z = 12$, $\rho_{\text{calcd}} = 1.433$ g/cm^3, $\mu = 0.433$ mm^{-1}, $F(000) = 432.0$, reflection collected / unique = 3336 / 2935, refinement method = full-matrix least-squares on F^2, final R indices [I> 2\s(I)]:$R_1 = 0.0433$, $wR_2 = 0.1605$, R indices (all data): $R_1 = 0.0506$, $wR_2 = 0.1735$, goodness of fit = 1.421. **CCDC-2372790** for **1-(3-chlorophenyl)-2-(phenylthio)-2-tosylethan-1-**

one (12a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

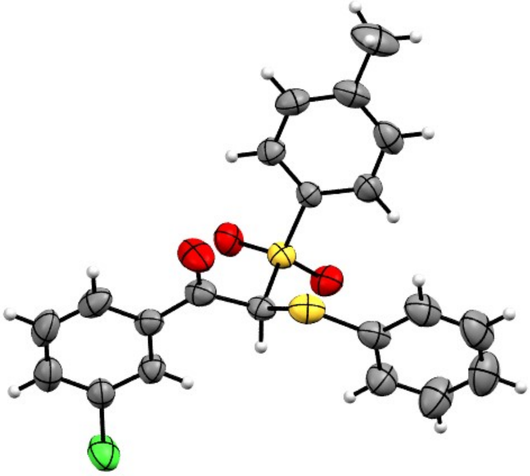


Figure S16. ORTEP diagram of 1-(3-chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (**12a**) with 50% ellipsoid probability (CCDC 2372790)

(A) Crystallographic Information of (*E*)-2-(2-(phenylthio)-1-tosylvinyl)pyridine (18a′):

(i) Sample Preparation: The single crystal of compound **18a′** was prepared by the slow evaporation method for which 10 mg of the compound (**18a′**) was dissolved in 1 mL ethyl acetate. 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 **18a′** were obtained as colourless crystals after around 4−5 days.

(ii) 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.

(iii) Crystallographic Description of (*E*)-2-(2-(phenylthio)-1-tosylvinyl)pyridine (18a′): $C_{20}H_{17}NO_2S_2$, crystal dimensions 0.20 x 0.17 x 0.14 mm, M_r = 61.24, orthorhombic, space group P n a 21, *a* = 11.753 (6), *b* = 8.710 (5), *c* = 17.811 (9) Å, α = 90, β = 90, γ = 90, *V* = 1823.3 (17) Å^3, *Z* = 24, ρ_{calcd} = 1.339 g/cm^3, μ = 0.305 mm^{-1}, *F*(000)=768, reflection collected / unique = 4019 / 3227, refinement method = full-matrix least-squares on F^2, final *R* indices [*I*> 2\s(*I*)]:R_1 = 0.0621, wR_2 = 0.1592, *R* indices (all data): R_1 = 0.0945, wR_2 = 0.1939, goodness of fit = 1.266. **CCDC-2374121** for **(*E*)-2-(2-(phenylthio)-1-tosylvinyl)pyridine (18a′)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

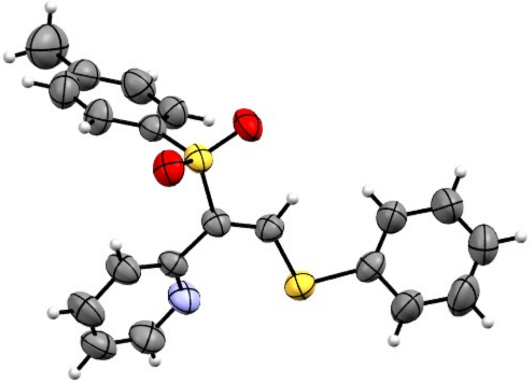


Figure S17. ORTEP diagram of (*E*)-2-(2-(phenylthio)-1-tosylvinyl)pyridine (**18a′**) with 50% ellipsoid probability (CCDC 2374121)

11. References:

1. (a) B. Du, P. Qian, Y. Wang, H. Mei, J. Han and Y. Pan, *Org. Lett.,* 2016, **18**, 4144−4147.

(b) Z. Tan, F. Chen, G. Huang, Y. Li, H. Jiang and W. Zeng, *Org. Lett.*, 2023, **25**, 2846−2851.

2. R. H. Blessing, *Acta Crystallogr.,* 1995, **A51**, 33–38.

3. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.

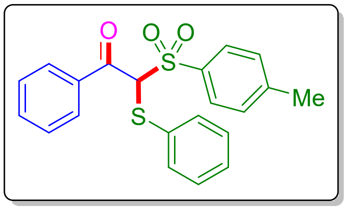
4. G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr.*, 2008, **A64**, 112–122.

12. Author contributions

D.B.– conceptualization, investigation, data curation, methodology, writing original work; N.C., A.K.S., and H.N.D.– investigation, characterization, validation, writing- review and editing; B.K.P.– supervision, resources, funding acquisition, writing- review, and editing.

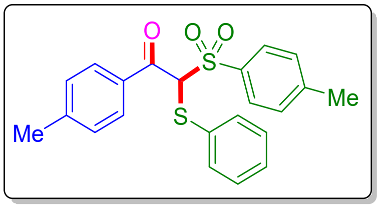
13. Spectral Data:

1-Phenyl-2-(phenylthio)-2-tosylethan-1-one (1a):



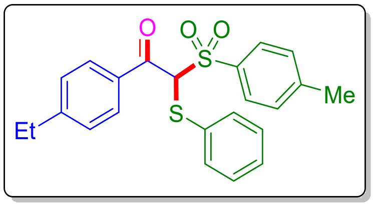
As yellow liquid (71 mg, 74% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88 (dd, J_1 = 8.2 Hz, J_2 = 4.2 Hz, 4H), 7.60 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.0 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.34–7.28 (m, 5H), 5.82 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 189.5, 145.8, 135.3, 134.4, 133.6, 133.4, 132.4, 130.8, 129.6, 129.5, 129.4, 129.3, 129.0, 75.7, 21.9; IR (neat, cm^{-1}): 3062, 2916, 2850, 1682, 1579, 1474, 1322, 1265, 1152, 1081, 733; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{19}O_3S_2$, [M + H]$^+$: 383.0770, found: 383.0760.

2-(Phenylthio)-1-(*p*-tolyl)-2-tosylethan-1-one (2a):



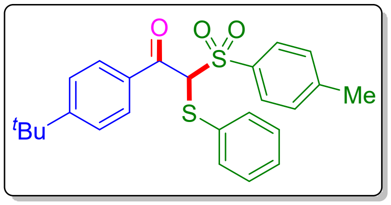
As yellow liquid (75mg, 76% yield); purified over a column of silica gel (15% EtOAc in Hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 4H), 7.30 (s, 1H), 7.25 (d, J = 5.5 Hz, 2H), 5.77 (s, 1H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 189.2, 145.8, 145.7, 133.7, 133.4, 132.8 132.6, 130.9, 129.8, 129.63, 129.60, 129.5, 129.4, 75.8, 22.0, 21.9; IR (neat, cm^{-1}): 2956, 2924, 2869, 1676, 1604, 1441, 1321, 1275, 1150, 1082, 748; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_3S_2$, [M + H]$^+$: 397.0927, found: 397.0918.

1-(4-Ethylphenyl)-2-(phenylthio)-2-tosylethan-1-one (3a):



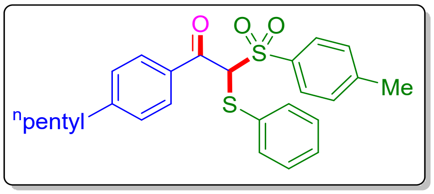
As yellow gummy (75 mg, 73% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.87 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.35–7.32 (m, 3H), 7.28 (q, J = 7.8 Hz, 4H), 5.80 (s, 1H), 2.71 (q, J = 7.5 Hz, 2H), 2.45 (s, 3H), 1.25 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 189.2, 151.8, 145.8, 133.6, 133.4, 133.0, 132.6, 130.9, 129.7, 129.6, 129.5, 129.4, 128.6, 75.8, 29.2, 21.9, 15.2; IR (neat, cm^{-1}): 2965, 2874, 1676, 1602, 1441, 1321, 1270, 1182, 1149, 1082, 729; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{23}H_{23}O_3S_2$, [M + H]$^+$: 411.1083, found: 411.1085.

1-(4-(Tert-butyl)phenyl)-2-(phenylthio)-2-tosylethan-1-one (4a):



As yellow gummy (77 mg, 70% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (t, J = 7.8 Hz, 4H), 7.55 (d, J = 6.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.35–7.30 (m, 5H), 5.80 (s, 1H), 2.45 (s, 3H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.2, 158.6, 145.8, 133.6, 133.3, 132.7, 131.0, 129.6, 129.5, 129.4, 129.3, 128.8, 126.1, 75.8, 35.5, 31.2, 22.0; IR (neat, cm^{-1}): 3059, 2965, 1677, 1602, 1475, 1321, 1266, 1196, 1082, 733; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{25}H_{26}O_3S_2Na$, [M + Na]$^+$: 461.1216, found: 461.1224.

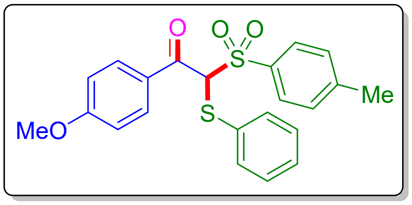
1-(4-Pentylphenyl)-2-(phenylthio)-2-tosylethan-1-one (5a):



As reddish liquid (83 mg, 73% yield); purified over a column of silica gel (15 % EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 9.5 Hz, 4H), 7.30 (s, 1H), 7.26 (d, J = 7.0 Hz, 2H), 5.79 (s, 1H), 2.66 (t, J = 7.8 Hz, 2H), 2.45 (s, 3H), 1.34–1.32 (m, 5H), 0.89 (t, J = 6.8 Hz, 4H); ^{13}C{^{1}H} NMR (125

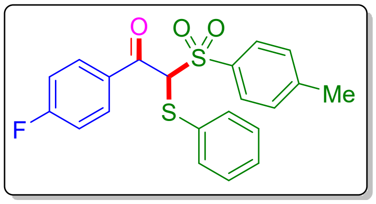
MHz, $CDCl_3$): δ 189.2, 150.7, 145.8, 133.6, 133.4, 133.1, 132.7, 130.9, 129.7, 129.6, 129.5, 129.4, 129.1, 75.8, 36.2, 31.6, 30.8, 22.7, 21.9, 14.2; IR (neat, cm^{-1}): 2927, 2857, 1676, 1601, 1414, 1321, 1269, 1150, 1082, 746; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{26}H_{29}O_3S_2$, $[M + H]^+$: 453.1553, found: 453.1555.

1-(4-Methoxyphenyl)-2-(phenylthio)-2-tosylethan-1-one (6a):



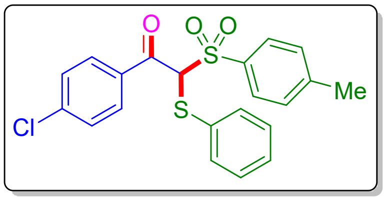
As yellow liquid (71 mg, 69% yield); purified over a column of silica gel (15% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.35–7.28 (m, 5H), 6.92 (d, J = 9.0 Hz, 2H), 5.77 (s, 1H), 3.86 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 187.9, 164.7, 145.7, 133.5, 133.4, 132.7, 132.0, 130.8, 129.5, 129.4, 129.3, 128.2, 114.3, 75.9, 55.8, 21.9; IR (neat, cm^{-1}): 3058, 2916, 2844, 1668, 1573, 1440, 1318, 1262, 1170, 1081, 735; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_4S_2$, $[M + H]^+$: 413.0876, found: 413.0882

1-(4-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (7a):



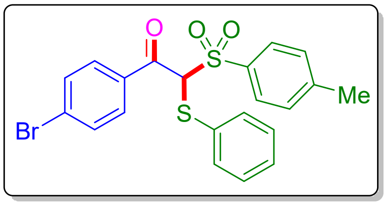
As gummy (67 mg, 67% yield); purified over a column of silica gel (15% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.96–7.93 (m, 2H), 7.86 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 3H), 7.31 (t, J = 7.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 5.70 (s, 1H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.2, 166.7 (d, J = 256.1 Hz), 146.0, 133.7, 133.2, 132.43, 132.41, 132.3, 131.7 (d, J = 2.9 Hz), 130.9, 129.6 (d, J = 12.1 Hz), 129.5, 116.3 (d, J = 22 Hz), 76.2, 22.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ –102.4 (s); IR (neat, cm^{-1}): 2917, 2850, 1683, 1589, 1440, 1322, 1274, 1148, 1081, 749; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{18}FO_3S_2$, $[M + H]^+$: 401.0676, found: 401.0681.

1-(4-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (8a):



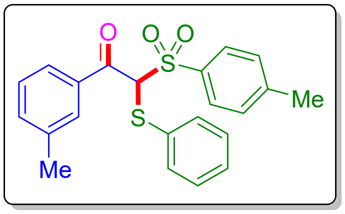
As yellow gummy (74 mg, 71% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (t, J = 8.0 Hz, 4H), 7.50 (d, J = 7.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 3H), 7.30 (t, J = 7.3 Hz, 2H), 5.70 (s, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 188.6, 146.1, 141.3, 133.7, 133.6, 133.3, 132.3, 131.7, 130.9, 129.7, 129.6, 129.4, 129.2, 76.1 22.0; IR (neat, cm^{-1}): 3060, 2921, 1680, 1587, 1440, 1320, 1264, 1148, 980, 736; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{18}O_3S_2Cl$, [M + H]$^+$: 417.0380, found: 417.0380.

1-(4-Bromophenyl)-2-(phenylthio)-2-tosylethan-1-one (9a):



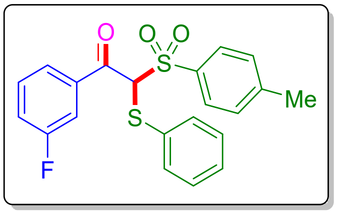
As yellow gummy (71 mg, 62% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 7.35–7.29 (m, 5H), 5.69 (s, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 188.8, 146.1, 135.5, 134.1, 133.7, 133.3, 132.4, 132.3, 130.9, 130.8, 130.1, 129.7, 129.6, 76.1, 22.0; IR (neat, cm^{-1}): 3059, 2917, 1680, 1582, 1481, 1396, 1264, 1148, 1071, 735; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{17}O_3S_2BrNa$, [M + Na]$^+$: 482.9695, found: 482.9695.

2-(Phenylthio)-1-(m-tolyl)-2-tosylethan-1-one (10a):



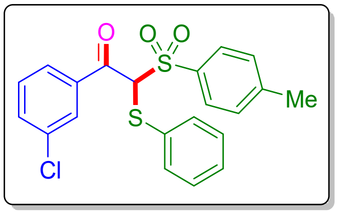
As yellow gummy (69 mg, 70% yield); m.p. 128–130 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.5 Hz, 1H), 7.65 (s, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.36–7.30 (m, 6H), 5.78 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.8, 145.8, 138.9, 135.4, 135.3, 133.7, 133.4, 132.6, 131.0, 129.9, 129.6, 129.5, 129.4, 128.9, 126.7, 75.7, 21.9, 21.5; IR (neat, cm^{-1}): 2917, 2850, 1680, 1597, 1440, 1321, 1275, 1148, 1082, 748; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_3S_2$, [M + H]$^+$: 397.0927, found: 397.0931.

1-(3-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (11a):



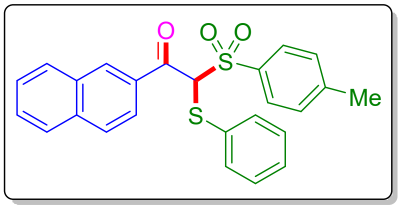
As brown gummy (64 mg, 64% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 9.5 Hz, 1H), 7.51 (d, J = 7.0 Hz, 2H), 7.47–7.43 (m, 1H), 7.35 (d, J = 8.5 Hz, 3H), 7.32 (t, J = 7.3 Hz, 3H), 5.70 (s, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.6 (d, J = 2.3 Hz), 163.0 (d, J = 7.8 Hz), 146.1, 137.4 (d, J = 6.4 Hz), 133.8, 133.3, 132.2, 130.9, 130.7 (d, J = 7.6 Hz), 129.7, 129.67, 129.6, 125.3 (d, J = 3.3 Hz), 121.6 (d, J = 21.4 Hz), 116.1 (d, J = 22.9 Hz), 76.0, 22.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ −110.9 (s); IR (neat, cm^{-1}): 2917, 2850, 1683, 1589, 1440, 1322, 1274, 1148, 1081, 749; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{18}FO_3S_2$, [M + H]$^+$: 401.0676, found: 401.0682.

1-(3-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (12a):



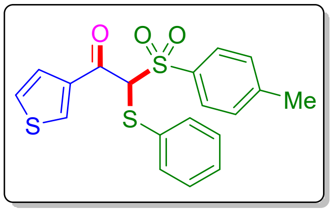
As yellow gummy (72 mg, 69% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 10.0 Hz, 2H), 7.82 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.36–7.31 (m, 5H), 5.69 (s, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.6, 146.1, 136.8, 135.5, 134.4, 133.8, 133.2, 132.1, 130.9, 130.3, 129.74, 129.72, 129.6, 129.3, 127.5, 75.9, 22.0; IR (neat, cm^{-1}): 3069, 2918, 2850, 1685, 1596, 1470, 1320, 1148, 1084, 749; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{17}O_3S_2ClNa$, [M + Na]$^+$: 439.0200, found: 439.0196.

1-(Naphthalen-2-yl)-2-(phenylthio)-2-tosylethan-1-one (13a):



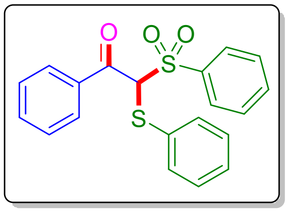
As white solid (59 mg, 55% yield); m.p. 112–114 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.36 (s, 1H), 7.95–7.87 (m, 6H), 7.63 (t, J = 7.8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 3H), 7.37–7.31 (m, 5H), 5.94 (s, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.6, 145.9, 136.2, 133.9, 133.4, 132.65, 132.63, 132.4, 131.9, 131.0, 130.1, 129.7, 129.6, 129.1, 128.0, 127.3, 124.3, 76.1, 21.9; IR (neat, cm^{-1}): 3058, 2923, 2854, 1674, 1595, 1440, 1320, 1279, 1149, 1081, 734; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{25}H_{20}O_3S_2Na$, $[M + Na]^+$: 455.0746, found: 455.0742.

2-(Phenylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one (14a):



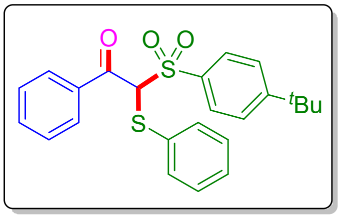
As black solid (61 mg, 63% yield); m.p. 72–74 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.14 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.52–7.50 (m, 3H), 7.34–7.29 (m, 6H), 5.52 (s, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 183.3, 145.9, 140.1, 135.5, 133.6, 133.4, 132.6, 130.7, 129.6, 129.5, 129.4, 127.7, 127.0, 78.1, 21.9; IR (neat, cm^{-1}): 3105, 2925, 1667, 1595, 1508, 1440, 1320, 1263, 1147, 1080, 732; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{19}H_{17}O_3S_3$, $[M + H]^+$: 389.0334, found: 389.0340.

1-Phenyl-2-(phenylsulfonyl)-2-(phenylthio)ethan-1-one (1b):



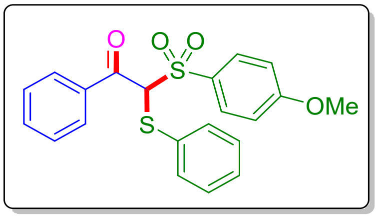
As white solid (64 mg, 70% yield); m.p. 135–137 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.01 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.0 Hz, 1H), 7.31 (t, J = 7.3 Hz, 2H), 5.81 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.5, 136.5, 135.3, 134.7, 134.6, 133.8, 132.3, 130.9, 129.7, 129.6, 129.4, 129.1, 128.9, 75.7; IR (neat, cm^{-1}): 2918, 2850, 1682, 1596, 1448, 1322, 1268, 1150, 1082, 746; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{16}O_3S_2Na$, $[M + Na]^+$: 391.0433, found: 391.0443.

2-((4-*(Tert*-butyl)phenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1c):



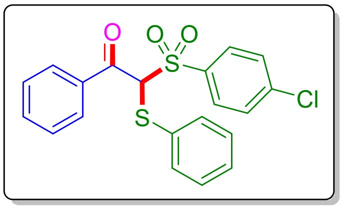
As yellow gummy (76 mg, 72% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.92 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.45 (t, J = 7.0 Hz, 4H), 7.32 (d, J = 7.0 Hz, 1H), 7.28 (d, J = 7.5 Hz, 2H), 5.80 (s, 1H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl$_3$): δ 189.6, 158.7, 135.4, 134.4, 133.7, 133.6, 132.4, 130.7, 129.6, 129.5, 129.4, 129.0, 125.9, 75.7, 35.5, 31.2; IR (neat, cm^{-1}): 3060, 2963, 2919, 1683, 1593, 1474, 1320, 1263, 1151, 1081, 735; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{24}H_{25}O_3S_2$, $[M + H]^+$: 425.1240, found: 425.1244.

2-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1d):



As yellow liquid (73 mg, 73% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.92 (d, J = 7.5, 2H), 7.89 (d, J = 8.0, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.35–7.29 (m, 3H), 7.00 (d, J = 8.5 Hz, 2H), 5.81 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 189.9, 164.7, 135.4, 134.5, 133.6, 133.2, 132.6, 129.6, 129.43, 129.41, 129.0, 127.7, 114.1, 75.7, 55.9; IR (neat, cm^{-1}): 3060, 2944, 2842, 1681, 1592, 1577, 1495, 1260, 1143, 1083, 736; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{19}O_4S_2$, $[M + H]^+$: 399.0719, found: 399.0718.

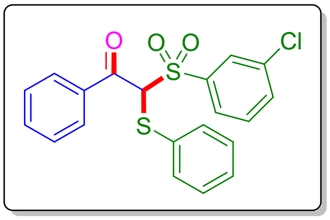
2-((4-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1e):



As yellow gummy (69 mg, 69% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.95 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 7.0 Hz, 2H), 7.63 (t, J =

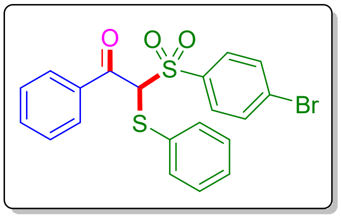
7.3 Hz, 1H), 7.54–7.52 (m, 4H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.38–7.32 (m, 3H), 5.82 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): *δ* 189.5, 141.7, 135.2, 134.7, 133.7, 132.5, 132.1, 129.8, 129.7, 129.4, 129.2, 75.6; IR (neat, cm^{-1}): 3062, 2916, 2850, 1682, 1578, 1474, 1322, 1265, 1175, 1081, 734; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{16}O_3S_2Cl$, $[M + H]^+$: 403.0224, found: 403.0223.

2-((3-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1f):



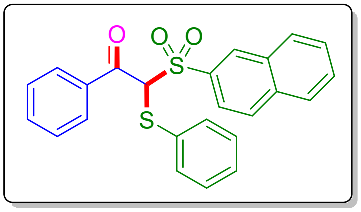
As yellow gummy (66 mg, 66% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.01 (s, 1H), 7.89 (t, *J* = 9.0 Hz, 3H), 7.63 (t, *J* = 6.8 Hz, 2H), 7.52 (t, *J* = 6.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 3H), 7.37–7.31 (m, 3H), 5.83 (s, 1H); ^{13}C $\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): *δ* 189.2, 138.2, 135.1, 135.0, 134.74, 134.72, 133.8, 131.9, 130.9, 130.1, 129.8, 129.7, 129.4, 129.2, 129.1, 75.7; IR (neat, cm^{-1}): 3063, 2927, 1682, 1570, 1440, 1323, 1265, 1150, 1075, 732; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{15}O_3S_2ClNa$, $[M + Na]^+$: 425.0043, found: 425.0034.

2-((4-Bromophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1g):



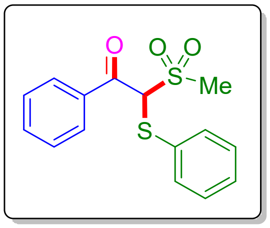
As white solid (71 mg, 64% yield); m.p. 98–100 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.88 (dd, J_1 = 8.2 Hz, J_2 = 4.3 Hz, 4H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.38–7.31 (m, 3H), 5.82 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): *δ* 189.4, 135.3, 135.2, 134.7, 133.7, 132.5, 132.2, 132.1, 130.4, 129.8, 129.7, 129.4, 129.2, 75.6; IR (neat, cm^{-1}): 3060, 2917, 1682, 1595, 1440, 1321, 1266, 1176, 1080, 735; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{16}BrO_3S_2$, $[M + H]^+$: 446.9716, found: 446.9718.

2-(Naphthalen-2-ylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1h):



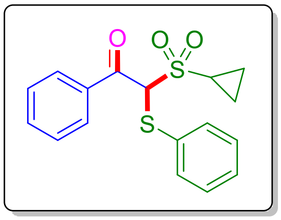
As white solid (62 mg, 59% yield); m.p. 112–114 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.98 (s, 2H), 7.94 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 7.5 Hz, 2H), 7.70 (t, J = 7.0 Hz, 1H), 7.64 (t, J = 6.0 Hz, 1H), 7.61 (t, J = 6.3 Hz, 1H), 7.52 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.0 Hz, 1H), 7.28 (d, J = 7.5 Hz, 2H), 5.91 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 189.5, 135.9, 135.3, 134.5, 133.7, 133.6, 133.2, 132.3, 132.0, 129.9, 129.8, 129.6, 129.5, 129.4, 129.1, 128.9, 128.1, 127.7, 125.1, 76.0; IR (neat, cm^{-1}): 3058, 2923, 2853, 1681, 1593, 1446, 1318, 1263, 1125, 1023, 734; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{24}H_{18}O_3S_2Na$, $[M + Na]^+$: 441.0590, found: 441.0583.

2-(Methylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1i):



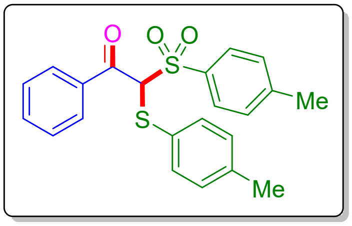
As yellow gummy (57 mg, 75% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.67–7.64 (m, 3H), 7.50 (t, J = 8.0 Hz, 2H), 7.42–7.37 (m, 3H), 5.57 (s, 1H), 3.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 190.4, 134.95, 134.91, 134.1, 131.8, 130.1, 129.9, 129.4, 129.3, 73.2, 38.1; IR (neat, cm^{-1}): 3060, 2918, 2851, 1679, 1595, 1448, 1309, 1276, 1113, 1024, 686; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{15}H_{14}O_3S_2Na$, $[M + Na]^+$: 329.0277, found: 329.0276.

2-(Cyclopropylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1j):



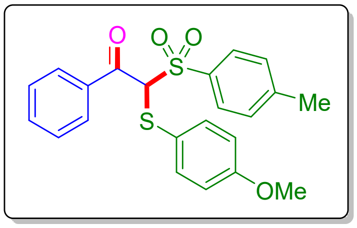
As yellow gummy (60 mg, 72% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 6.5 Hz, 3H), 7.48 (t, J = 7.8 Hz, 2H), 7.38–7.33 (m, 3H), 5.70 (s, 1H), 2.97–2.92 (m, 1H), 1.49–1.43 (m, 1H), 1.32–1.26 (m, 1H), 1.22–1.16 (m, 1H), 1.10–1.04 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 190.0, 135.2, 134.7, 133.9, 132.4, 129.7, 129.6, 129.4, 129.1, 74.2, 28.6, 6.7, 4.9; IR (neat, cm^{-1}): 3060, 2920, 2852, 1681, 1596, 1446, 1320, 1266, 1136, 1072, 687; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{17}H_{16}O_3S_2Na$, [M + Na]$^+$: 355.0433, found: 355.0440.

1-Phenyl-2-(p-tolylthio)-2-tosylethan-1-one (1k):



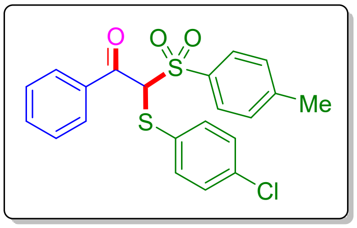
As red gummy (77 mg, 78% yield); purified over a column of silica gel (15% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 4H), 7.60 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.5Hz, 2H), 5.74 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.6, 145.8, 140.0, 135.4, 134.4, 134.2, 133.6, 130.9, 130.4, 129.5, 129.4, 129.0, 128.7, 75.9, 21.9, 21.4; IR (neat, cm^{-1}): 2923, 2853, 1681, 1596, 1448, 1303, 1321, 1267, 1151, 1084, 739; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{20}O_3S_2Na$, [M + Na]$^+$: 419.0746, found: 419.0762.

2-((4-Methoxyphenyl)thio)-1-phenyl-2-tosylethan-1-one (1l):



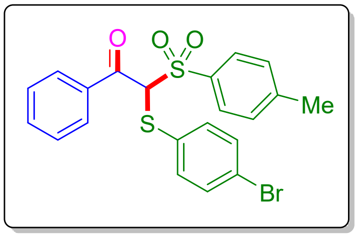
As yellow gummy (75 mg, 73% yield); purified over a column of silica gel (20% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.46–7.43 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 5.65 (s, 1H), 3.81 (s, 3H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.6, 161.2, 145.8, 136.8, 135.5, 134.4, 133.7, 130.9, 129.5, 129.4, 129.0, 122.5, 115.1, 76.3, 55.6, 22.0; IR (neat, cm^{-1}): 2918, 2850, 1682, 1592, 1493, 1465, 1321, 1249, 1149, 1082, 742; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{20}O_4S_2Na$, [M + Na]$^+$: 435.0695, found: 435.0684.

2-((4-Chlorophenyl)thio)-1-phenyl-2-tosylethan-1-one (1m):



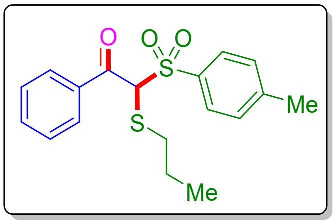
As white solid (74 mg, 71% yield); m.p. 96–98 °C; purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.49–7.46 (m, 4H), 7.34 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.75 (s, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.3, 146.0, 136.1, 135.3, 135.2, 134.6, 133.3, 130.9, 130.7, 129.8, 129.6, 129.4, 129.1, 75.6, 22.0; IR (neat, cm^{-1}): 3064, 2921, 1681, 1594, 1475, 1448, 1321, 1267, 1148, 1082, 738; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{18}ClO_3S_2$, [M + H]$^+$: 417.0380, found: 417.0374.

2-((4-Bromophenyl)thio)-1-phenyl-2-tosylethan-1-one (1n):



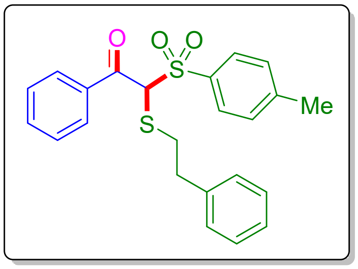
As yellow gummy (80 mg, 69% yield); purified over a column of silica gel (15 % EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.88 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.49–7.39 (m, 6H), 7.33 (d, J = 8.5 Hz, 2H), 5.76 (s, 1H), 2.45 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.3, 146.0, 135.4, 135.2, 134.6, 133.3, 132.7, 131.3, 130.9, 129.6, 129.4, 129.1, 124.2, 75.4, 21.9; IR (neat, cm^{-1}): 3064, 2919, 2852, 1682, 1595, 1473, 1448, 1321, 1263, 1149, 1082, 736; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{17}BrO_3S_2Na$, [M + Na]$^+$: 482.9695, found: 482.9696.

1-Phenyl-2-(propylthio)-2-tosylethan-1-one (1o):



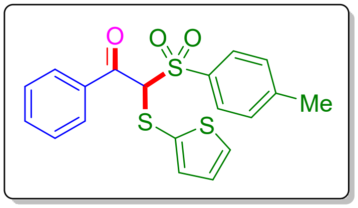
As yellow gummy (63 mg, 72% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.96 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.56 (s, 1H), 2.91–2.85 (m, 1H), 2.76–2.71 (m, 1H), 2.44 (s, 3H), 1.62–1.53 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.4, 145.7, 135.3, 134.4, 133.4, 130.8, 129.5, 129.2, 129.0, 70.9, 34.9, 22.5, 21.9, 13.4; IR (neat, cm^{-1}): 3063, 2963, 2932, 1682, 1595, 1448, 1318, 1268, 1082, 735; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{18}H_{20}O_3S_2Na$, $[M + Na]^+$: 371.0746, found: 371.0751.

2-(Phenethylthio)-1-phenyl-2-tosylethan-1-one (1p):



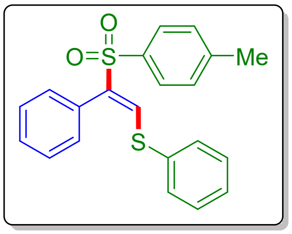
As gummy (72 mg, 70% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.93 (d, J = 7.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.21 (d, J = 7.0 Hz, 2H), 5.58 (s, 1H), 3.30–3.24 (m, 1H), 3.15–3.11 (m, 1H), 2.96–2.89 (m, 2H), 2.51 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.4, 145.7, 139.4, 135.3, 134.5, 133.1, 130.8, 129.5, 129.3, 129.0, 128.8, 128.7, 126.9, 70.8, 35.7, 33.9, 21.9; IR (neat, cm^{-1}): 2918, 2852, 1682, 1596, 1496, 1320, 1265, 1148, 1082, 733; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{23}H_{22}O_3S_2Na$, $[M + Na]^+$: 433.0903, found: 433.0902.

1-phenyl-2-(thiophen-2-ylthio)-2-tosylethan-1-one (1q):



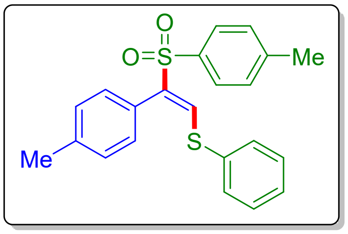
As black gummy (60 mg, 61% yield); purified over a column of silica gel (15% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.90 (t, J = 8.5 Hz, 4H), 7.62 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 7.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 5.5 Hz, 1H), 6.96 (dd, J_1 = 5.5 Hz, J_2 = 3.5 Hz, 1H), 5.70 (s, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 189.2, 145.9, 138.0, 135.4, 134.6, 133.4, 132.8, 131.0, 129.6, 129.4, 129.2, 129.1, 128.1,76.8, 21.9; IR (neat, cm^{-1}): 3063, 2923, 2851, 1681, 1593, 1448, 1322, 1263, 1146, 1083, 743; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{19}H_{16}O_3S_3Na$, $[M + Na]^+$: 411.0154, found: 411.0152.

(*E*)-phenyl(2-phenyl-2-tosylvinyl)sulfane (1a′):



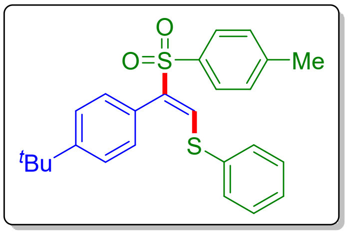
As white solid (69 mg, 75% yield); m.p. 112–114 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.10 (s, 1H), 7.50–7.46 (m, 4H), 7.38–7.33 (m, 6H), 7.22–7.17 (m, 4H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.2, 143.6, 136.6, 133.1, 131.3, 130.9, 130.4, 129.8, 129.7, 129.6, 129.0, 128.8, 128.8, 128.4, 21.8; IR (neat, cm^{-1}): 2963, 2929, 2854, 1572, 1461, 1310, 1271, 1152, 1083, 755; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{19}O_2S_2$, [M + H]$^+$: 367.0821, found: 367.0813.

(*E*)-phenyl(2-(p-tolyl)-2-tosylvinyl)sulfane (2a′):



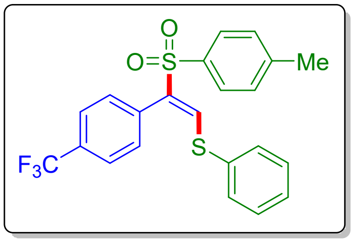
As white solid (70 mg, 74% yield); m.p. 109–111 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.09 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.5 Hz, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.11–7.09 (m, 2H), 2.38 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.1, 143.4, 139.6, 136.7, 136.6, 133.2, 131.3, 130.2, 129.7, 129.6, 129.6, 128.7, 128.4, 127.8, 21.8, 21.6; IR (neat, cm^{-1}): 2960, 2926, 2859, 1574, 1464, 1300, 1261, 1142, 1081, 750; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_2S_2$, [M + H]$^+$: 381.0977, found: 381.0974.

(*E*)-(2-(4-(*tert*-butyl)phenyl)-2-tosylvinyl)(phenyl)sulfane (4a′):



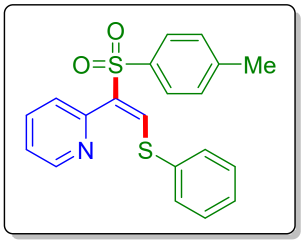
As colourless solid (74 mg, 70% yield); m.p. 148–150 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.08 (s, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 6.5 Hz, 2H), 7.38–7.33 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 2.39 (s, 3H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 152.7, 144.1, 143.5, 136.9, 136.6, 133.3, 131.3, 129.9, 129.7, 129.6, 128.7, 128.4, 127.8, 125.8, 34.9, 31.4, 21.8; IR (neat, cm^{-1}): 2957, 2916, 2869, 1578, 1463, 1302, 1265, 1143, 1084, 744; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{25}H_{27}O_2S_2$, $[M + H]^+$: 423.1447, found: 423.1451.

(*E*)-phenyl(2-tosyl-2-(4-(trifluoromethyl)phenyl)vinyl)sulfane (17a′):



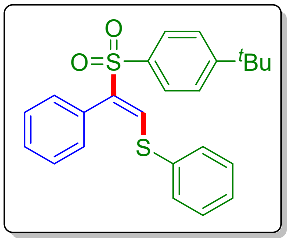
As gummy yellow solid (61 mg, 60% yield); purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.48–7.46 (m, 2H), 7.40–7.39 (m, 3H), 7.35 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 144.9, 144.6, 136.3, 135.2, 134.8, 132.5, 131.5, 130.9, 129.93, 129.90, 129.8, 129.1, 128.4, 127.8, 125.8 (q, J = 3.8 Hz), 21.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.8 (s); IR (neat, cm^{-1}): 2919, 1617, 1579, 1441, 1321, 1303, 1276, 1144, 1066, 746; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{18}F_3O_2S_2$, $[M + H]^+$: 435.0695, found: 435.0695.

(*E*)-2-(2-(phenylthio)-1-tosylvinyl)pyridine (18a′):



As colourless solid (56 mg, 61% yield); m.p. 177–179 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (d, J = 5.0 Hz, 1H), 8.46 (s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.69–7.65 (m, 3H), 7.56 (d, J = 7.0 Hz, 2H), 7.41–7.37 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.18–7.15 (m, 1H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.2, 149.2, 148.8, 144.1, 137.6, 136.6, 135.7, 132.8, 131.3, 129.8, 129.7, 128.8, 127.7, 123.5, 122.8, 21.6; IR (neat, cm^{-1}): 2957, 2920, 1580, 1463, 1275, 1260, 1144, 1086, 764; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{18}NO_2S_2$, $[M + H]^+$: 368.0773, found: 368.0776.

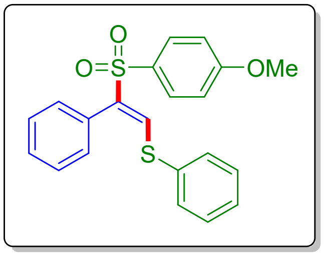
(*E*)-(2-((4-(tert-butyl)phenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1c′):



As white solid (74 mg, 73% yield); m.p. 110–112 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500

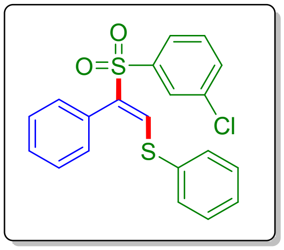
MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.39–7.33 (m, 6H), 7.22 (d, *J* = 7.5 Hz, 2H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 157.2, 143.7, 136.6, 136.5, 133.1, 131.3, 130.9, 130.4, 129.8, 129.6, 128.8, 128.7, 128.2, 126.0, 35.4, 31.2; IR (neat, cm^{-1}): 3057, 2964, 2869, 1593, 1488, 1313, 1291, 1146, 1083, 939; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{24}H_{25}O_2S_2$, $[M + H]^+$: 409.1290, found: 409.1283.

(*E*)-(2-((4-methoxyphenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1d′):



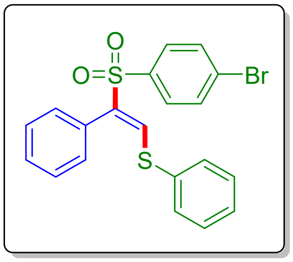
As white solid (66 mg, 69% yield); m.p. 139–141°C; purified over a column of silica gel (5% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 2H), 7.38–7.34 (m, 6H), 7.20 (d, *J* = 6.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 163.5, 143.0, 136.9, 133.1, 131.3, 131.0, 130.6, 130.4, 129.8, 129.6, 128.9, 128.8, 114.2, 55.8; IR (neat, cm^{-1}): 3066, 2926, 2844, 1594, 1496, 1313, 1203, 1140, 1086, 734; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{19}O_3S_2$, $[M + H]^+$: 383.0770, found: 383.0747.

(*E*)-(2-((3-chlorophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1f′):



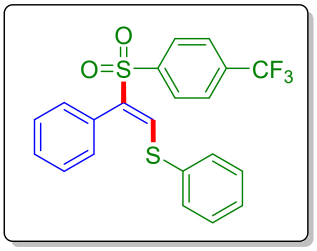
As white solid (65 mg, 67% yield); m.p. 130–132 °C; purified over a column of silica gel (5% EtOAc in hexane); ^1H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.62 (s, 1H), 7.49–7.45 (m, 5H), 7.40–7.36 (m, 5H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.4, 141.3, 135.5, 135.3, 133.4, 132.8, 131.5, 130.45, 130.40, 130.2, 129.9, 129.8, 129.0, 128.3, 126.6; IR (neat, cm^{-1}): 3060, 2853, 1578, 1480, 1441, 1318, 1275, 1148, 1106, 941; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{16}ClO_2S_2$, $[M + H]^+$: 387.0275, found: 387.0248.

(*E*)-(2-((4-bromophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1g′):



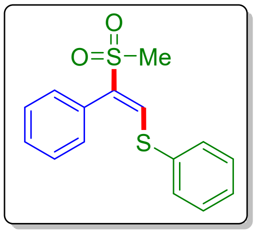
As white solid (69 mg, 64% yield); m.p. 150–152 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.13 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.8 Hz, 4H), 7.40–7.36 (m, 6H), 7.22 (d, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 145.1, 138.6, 135.6, 132.8, 132.3, 131.5, 130.5, 130.4, 129.9, 129.8, 129.0, 128.9, 128.6; IR (neat, cm^{-1}): 2916, 2849, 1572, 1469, 1309, 1265, 1142, 1083, 940; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{20}H_{16}BrO_2S_2$, [M + H]$^+$: 430.9770, found: 430.9770.

(*E*)-phenyl(2-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (1t′):



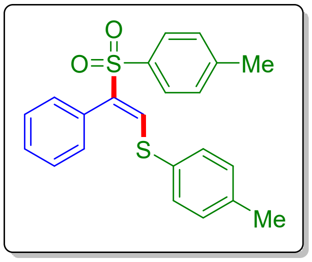
As white solid (57 mg, 54% yield); m.p. 116–118 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.41–7.35 (m, 6H), 7.23 (d, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 146.2, 143.3, 136.8, 135.1, 134.8, 132.7, 131.5, 130.5, 130.3, 130.0, 129.9, 129.1, 129.0, 128.9, 126.14 (q, J = 3.6 Hz); ^{19}F (471 MHz, CDCl$_3$): δ –63.1 (s); IR (neat, cm^{-1}): 3058, 2850, 1606, 1567, 1481, 1403, 1321, 1169, 1147, 1081, 708; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{16}F_3O_2S_2$, [M + H]$^+$: 421.0538, found: 421.0538.

(*E*)-(2-(methylsulfonyl)-2-phenylvinyl)(phenyl)sulfane (1i′):



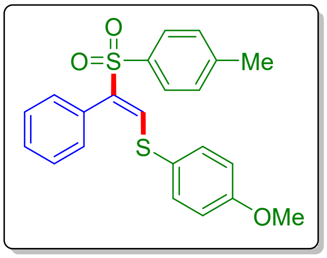
As yellow gummy (37 mg, 51% yield); purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.51–7.46 (m, 5H), 7.37 (d, J = 5.0 Hz, 3H), 2.80 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.7, 135.2, 132.8, 131.6, 130.9, 130.1, 130.0, 129.8, 129.4, 128.9, 41.1; IR (neat, cm^{-1}): 3056, 2852, 1603, 1561, 1479, 1423, 1325, 1159, 1130, 1079, 728; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{15}H_{15}O_2S_2$, $[M + H]^+$: 291.0508, found: 291.0501.

(*E*)-(2-phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (1k′):



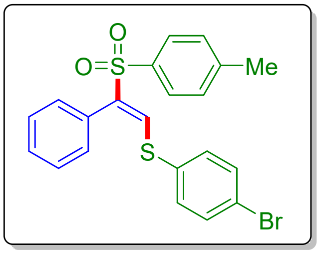
As white solid (76 mg, 80% yield); m.p. 168–170 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.07 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 9.0 Hz, 5H), 7.22–7.17 (m, 6H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.6, 144.1, 139.1, 136.6, 135.9, 131.6, 130.9, 130.5, 130.4, 129.6, 129.5, 129.4, 128.8, 128.4, 21.8, 21.3; IR (neat, cm^{-1}): 2914, 2852, 1572, 1491, 1315, 1275, 1260, 1141, 1085, 764; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_2S_2$, $[M + H]^+$: 381.0977, found: 381.0975.

(*E*)-(4-methoxyphenyl)(2-phenyl-2-tosylvinyl)sulfane (1l′):



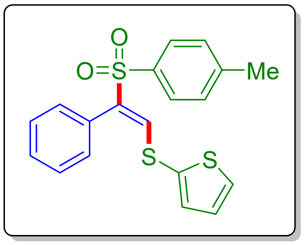
As white solid (71 mg, 72% yield); m.p. 174–176 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.00 (s, 1H), 7.48 (d, J =8.0 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.35–7.31 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 160.6, 145.5, 144.1, 136.7, 135.4, 134.0, 130.9, 130.4, 129.6, 129.5, 128.8, 128.4, 123.4, 115.3, 55.7, 21.8; IR (neat, cm^{-1}): 3033, 2837, 1592, 1572, 1493, 1300, 1249, 1142, 1086, 764; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{22}H_{21}O_3S_2$, $[M + H]^+$: 397.0927, found: 397.0927.

(*E*)-(4-bromophenyl)(2-phenyl-2-tosylvinyl)sulfane (1n′):



As white solid (79 mg, 71% yield); m.p. 170–172 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.01 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.37–7.32 (m, 5H), 7.19 (d, J = 7.0 Hz, 4H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): δ 144.3, 142.3, 137.4, 136.4, 132.9, 132.8, 132.2, 130.7, 130.3, 129.7, 128.9, 128.5, 123.2, 21.8; IR (neat, cm^{-1}): 2956, 2917, 1597, 1579, 1473, 1313, 1142, 1085, 753; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{21}H_{18}O_2S_2Br$, [M + H]$^+$: 444.9926, found: 444.9931.

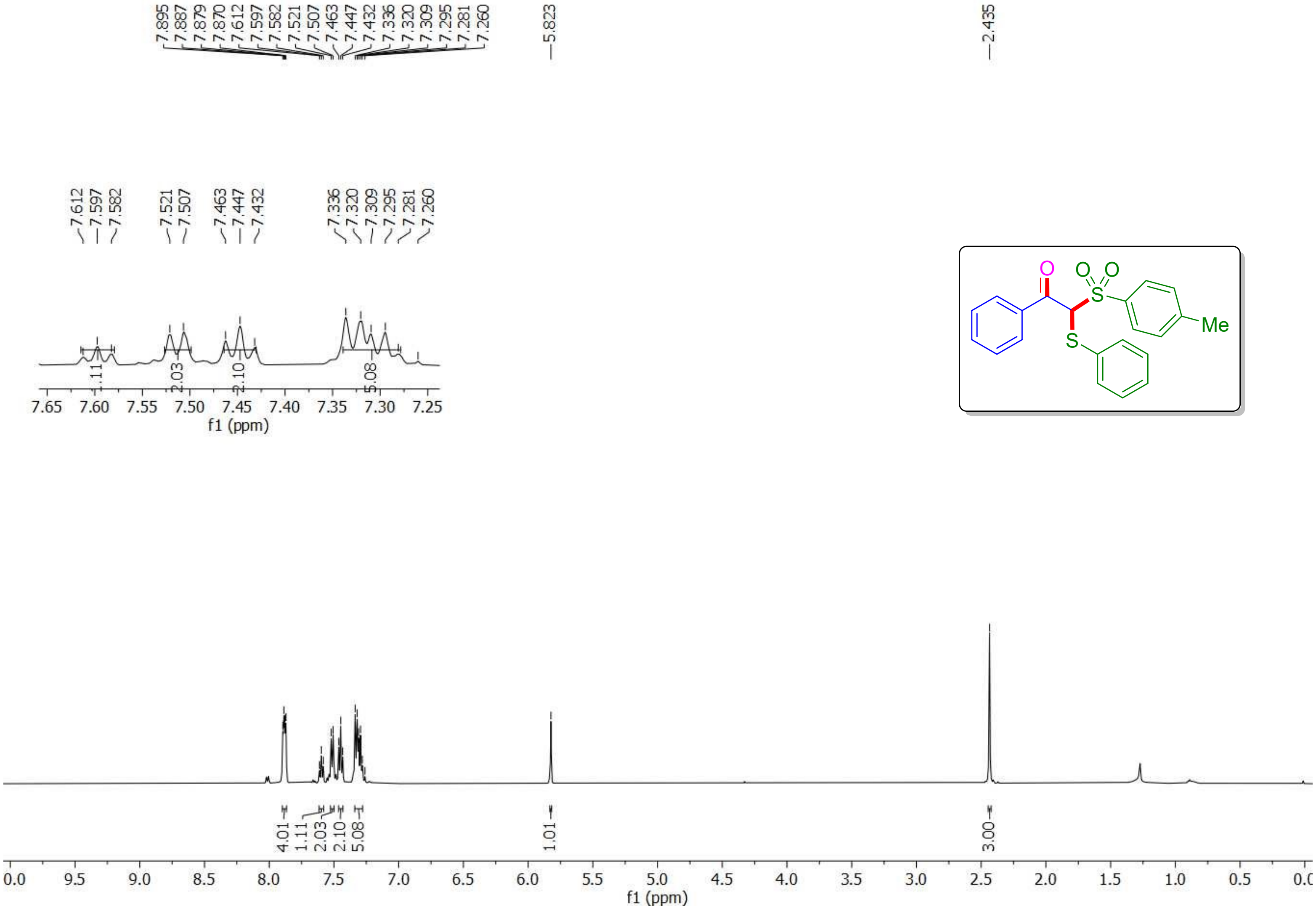
(*E*)-2-((2-phenyl-2-tosylvinyl)thio)thiophene (1q′):



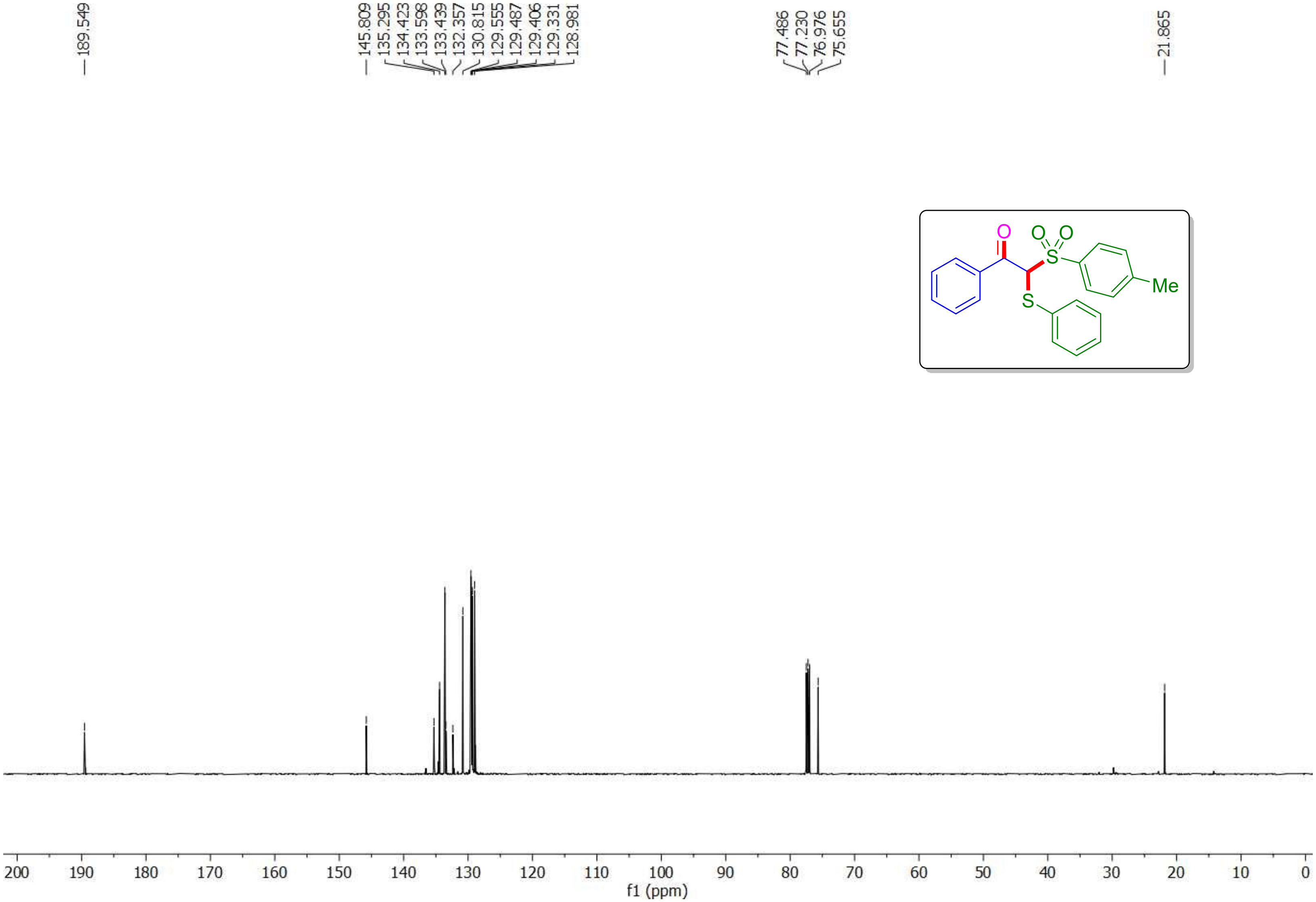
As white solid (60 mg, 64% yield); m.p. 138–140 °C; purified over a column of silica gel (5% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.47 (t, *J* = 7.8 Hz, 3H), 7.36–7.32 (m, 3H), 7.24 (d, *J* = 3.5 Hz, 1H), 7.19–7.18 (m, 4H), 7.04 (t, *J* = 4.5 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.2, 144.3, 136.4, 136.2, 135.3, 131.4, 130.5, 130.4, 129.7, 129.6, 128.9, 128.5, 128.2, 21.8; IR (neat, cm^{-1}): 3034, 2956, 2916, 1577, 1489, 1310, 1218, 1141, 1084, 766; HRMS (ESI/Q-TOF) (m/z): calcd. for $C_{19}H_{17}O_2S_3$, [M + H]$^+$: 373.0385, found: 373.0385.

14. Spectra of all compounds:

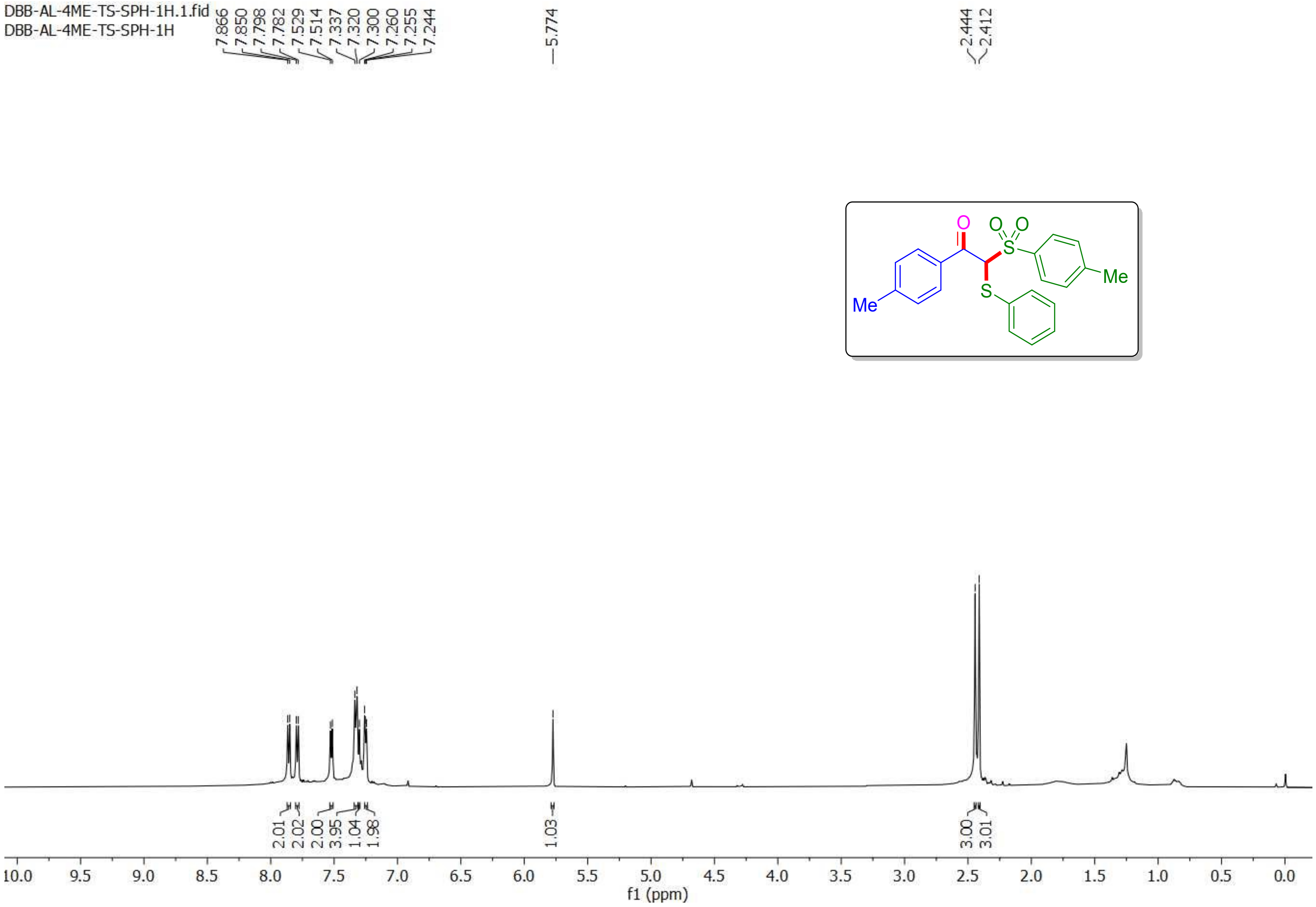
1-Phenyl-2-(phenylthio)-2-tosylethan-1-one (1a): ^{1}H NMR (CDCl$_3$, 500 MHz)



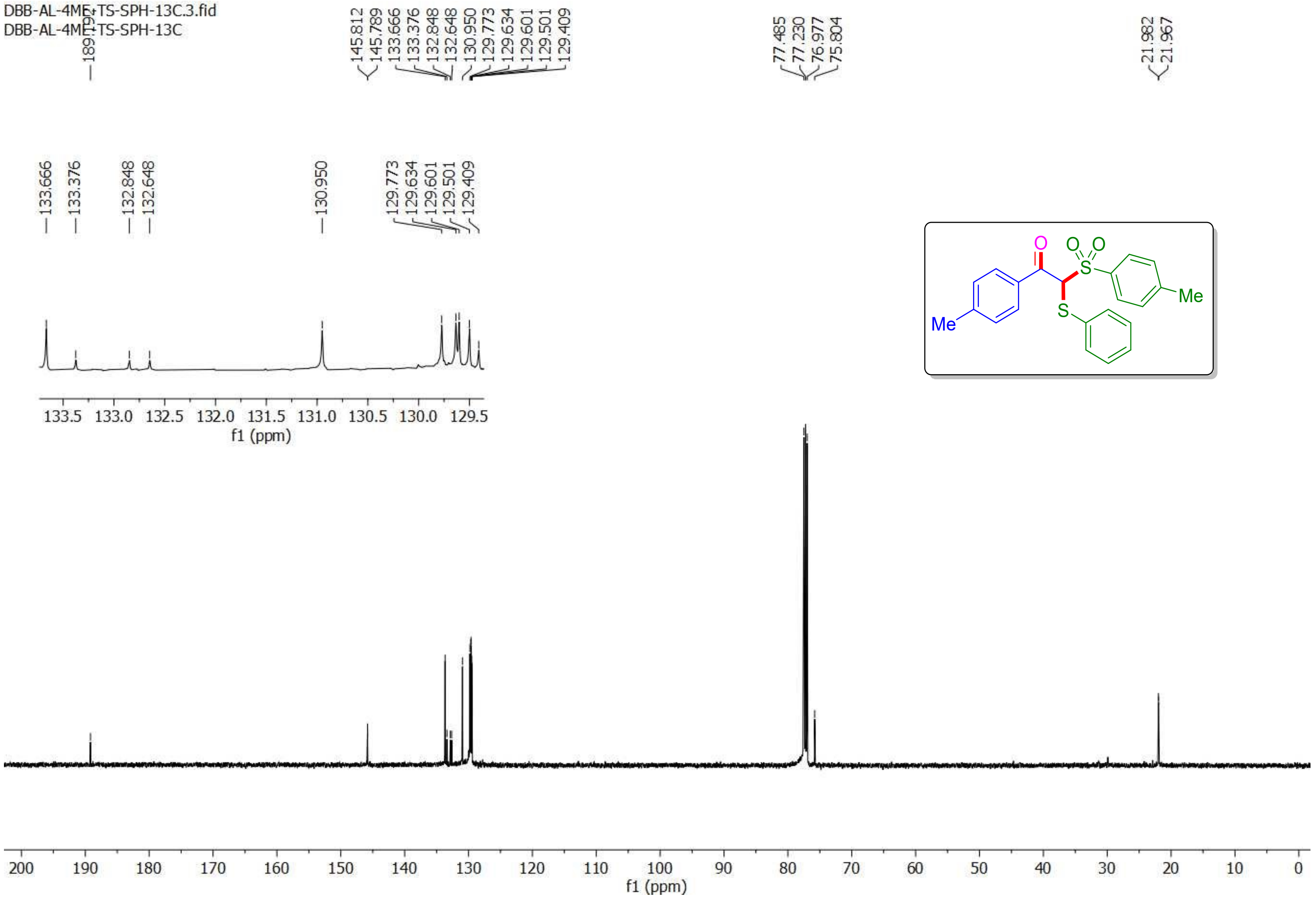
1-Phenyl-2-(phenylthio)-2-tosylethan-1-one (1a): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



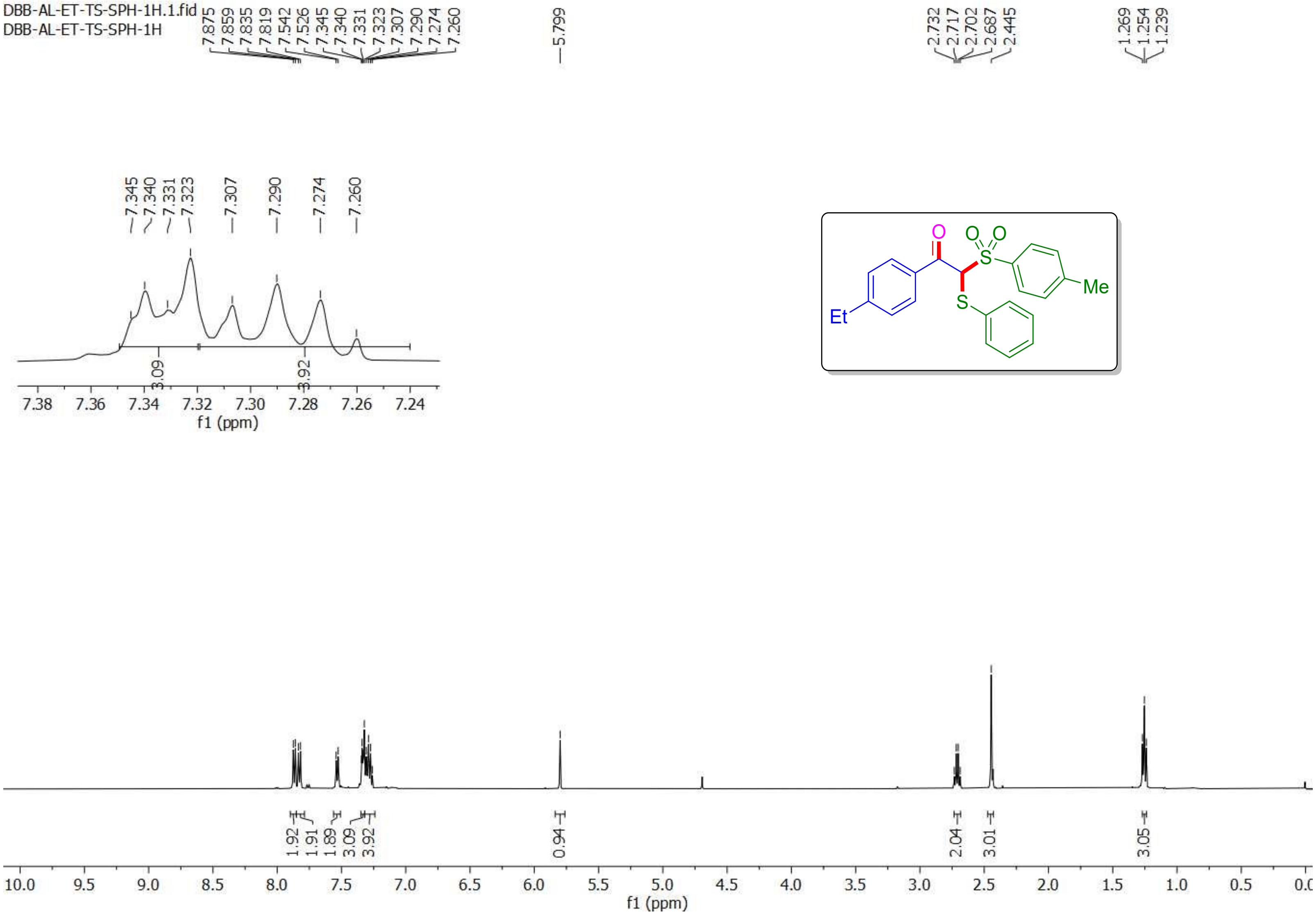
2-(Phenylthio)-1-(p-tolyl)-2-tosylethan-1-one (2a): ^{1}H NMR ($CDCl_3$, 500 MHz)



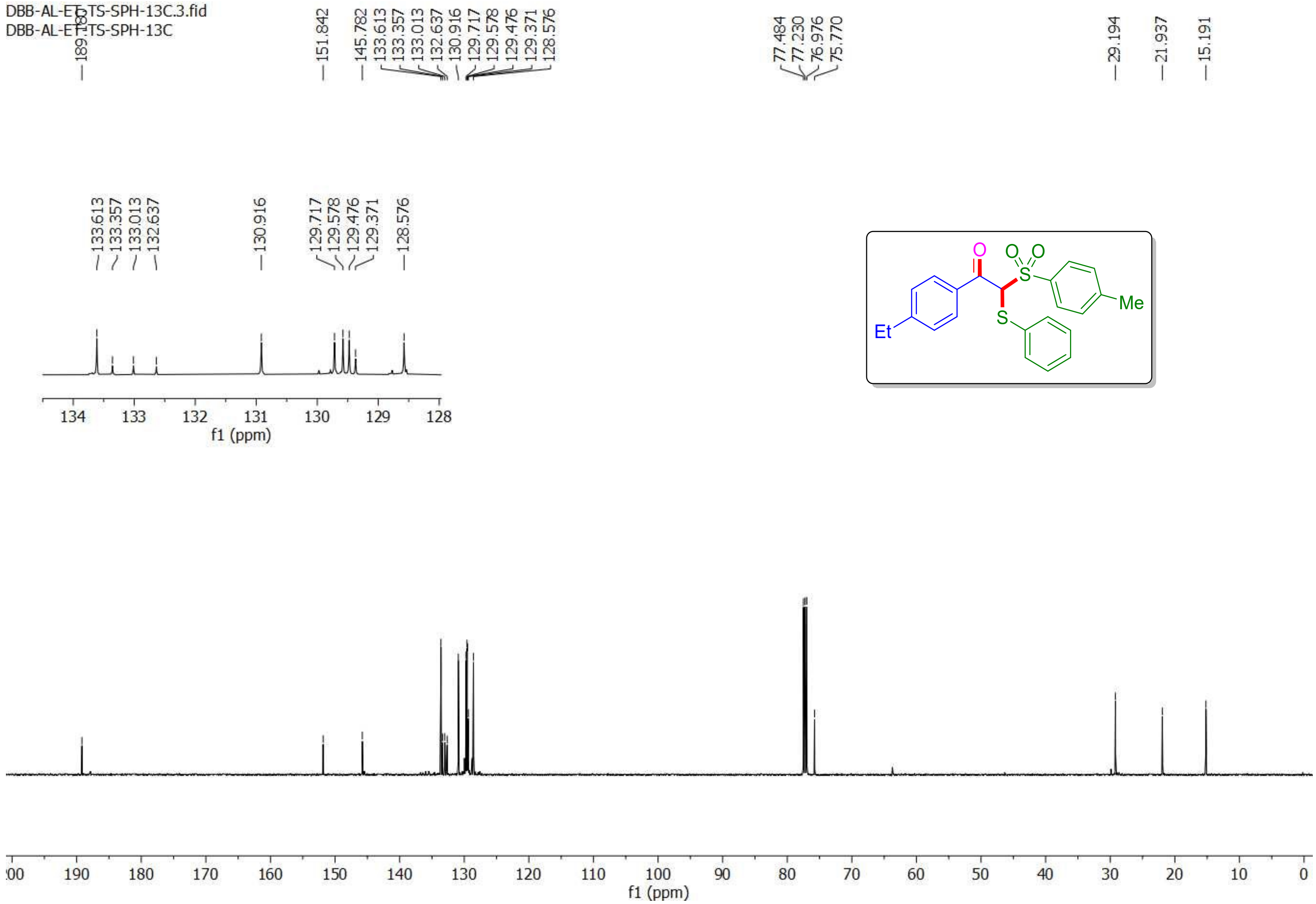
2-(Phenylthio)-1-(p-tolyl)-2-tosylethan-1-one (2a): ${}^{13}C\{{}^{1}H\}$ *NMR* ($CDCl_3$, *125 MHz)*



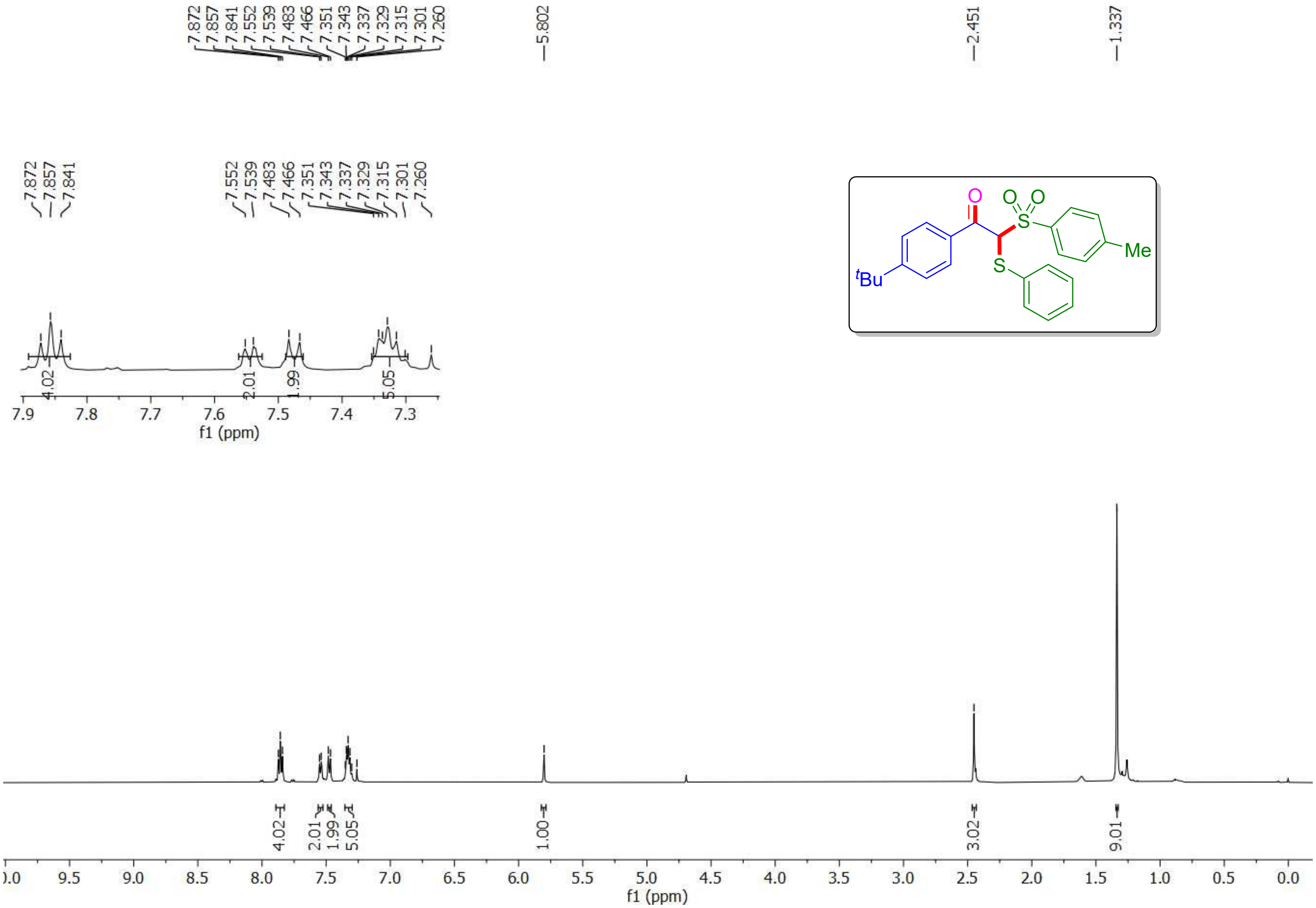
1-(4-Ethylphenyl)-2-(phenylthio)-2-tosylethan-1-one (3a): ^{1}*H NMR (CDCl$_3$, 500 MHz)*



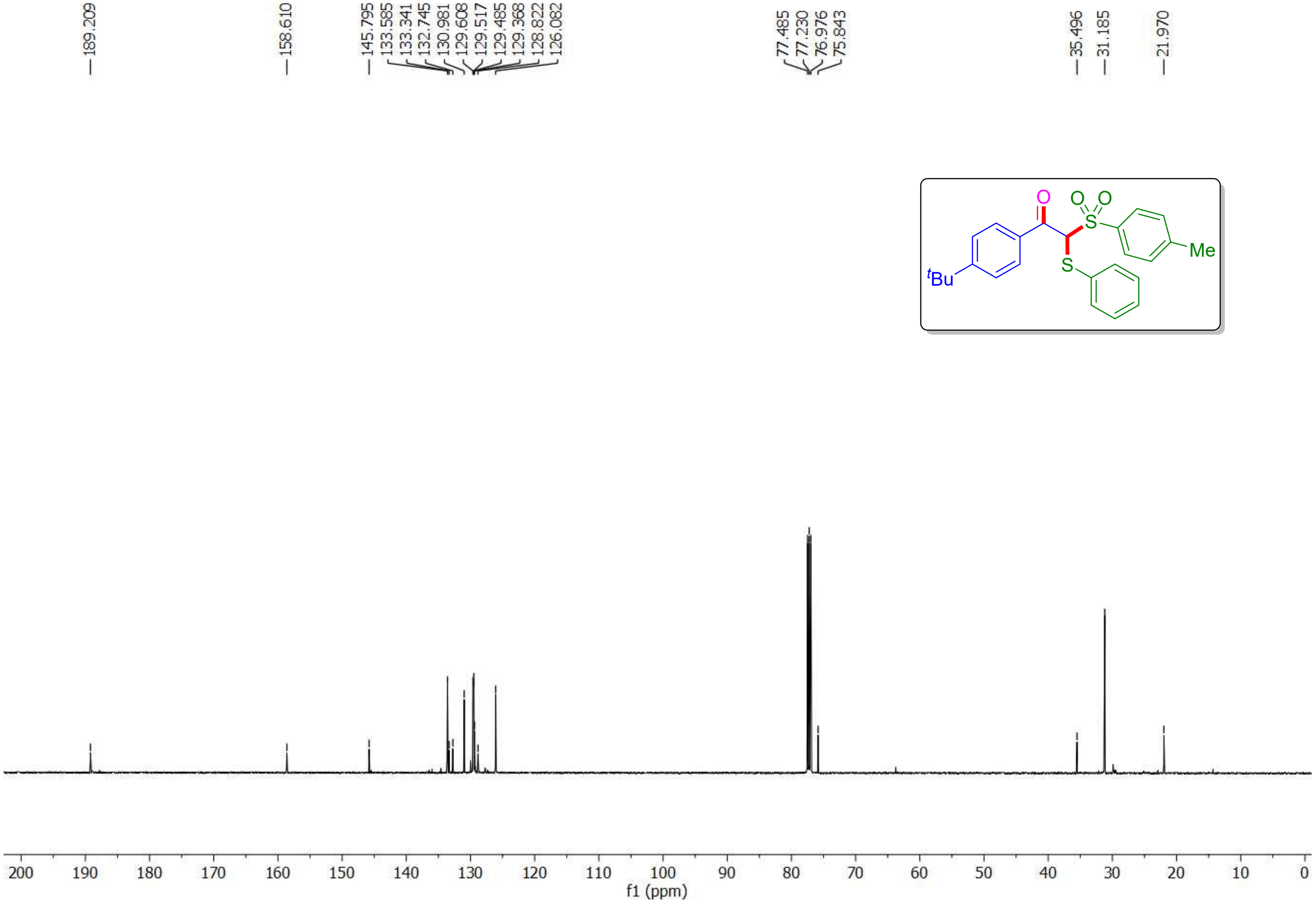
1-(4-Ethylphenyl)-2-(phenylthio)-2-tosylethan-1-one (3a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



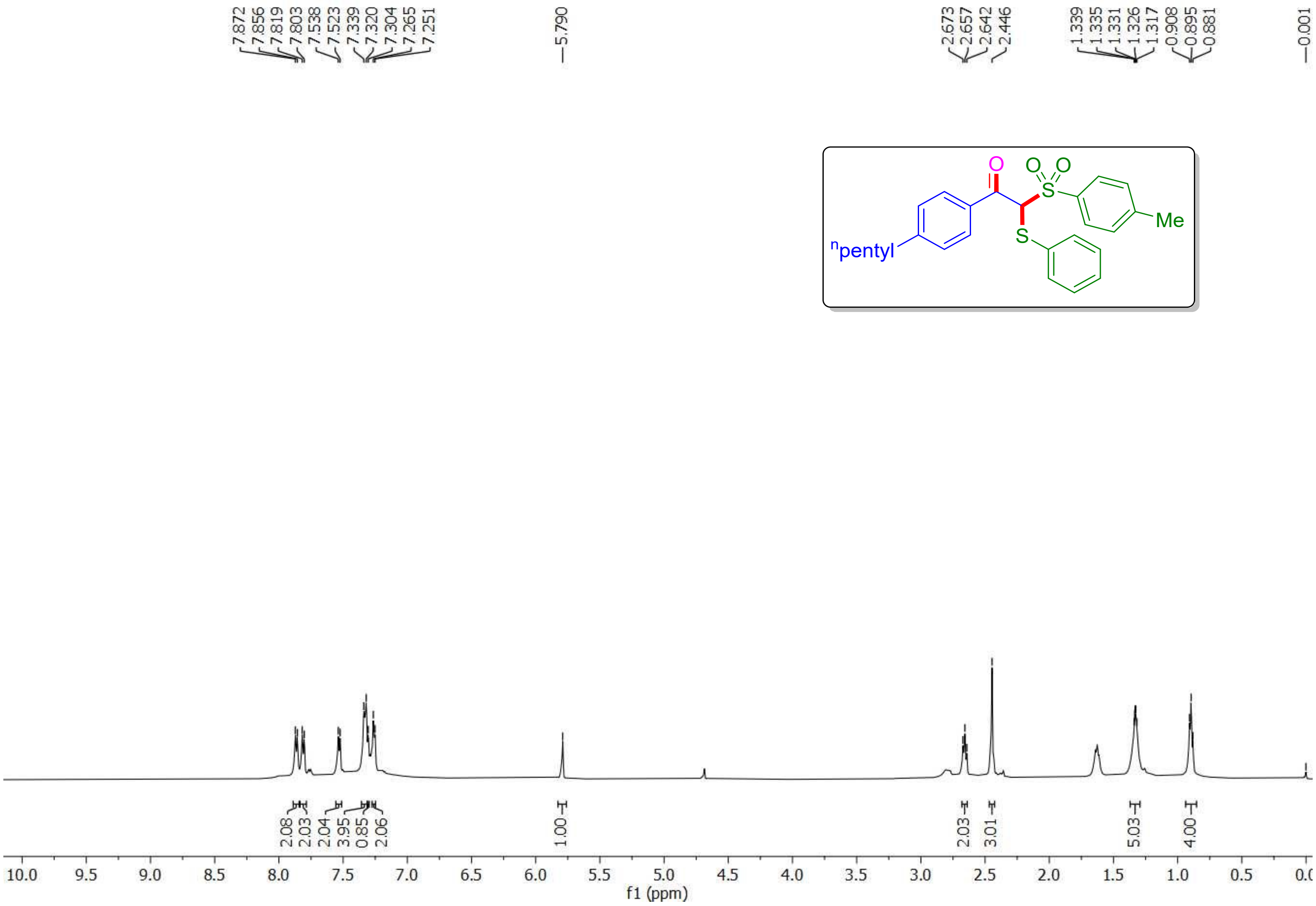
1-(4-(tert-Butyl)phenyl)-2-(phenylthio)-2-tosylethan-1-one (4a): ^{1}H NMR (CDCl$_3$, 500 MHz)



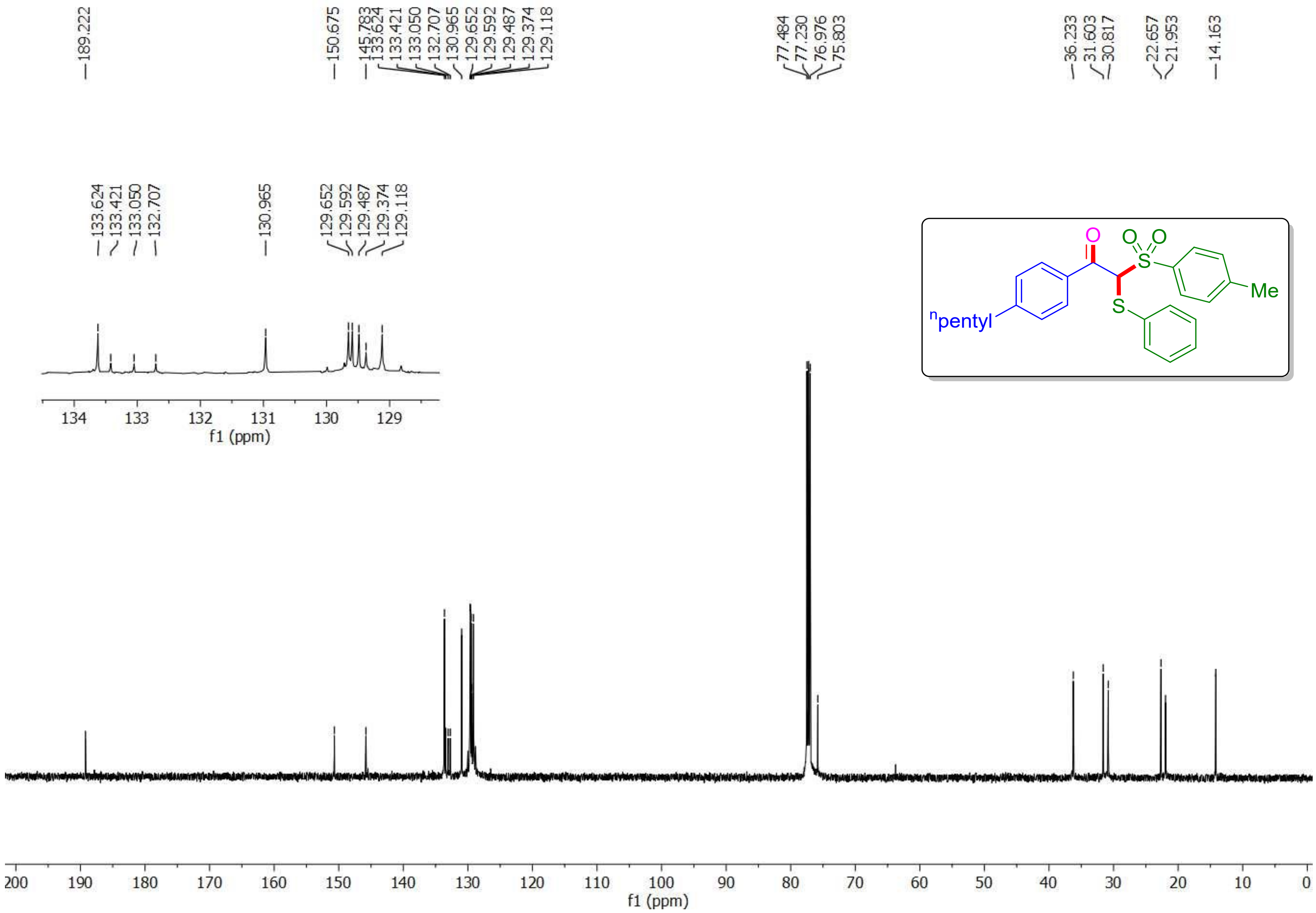
1-(4-(tert-Butyl)phenyl)-2-(phenylthio)-2-tosylethan-1-one (4a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



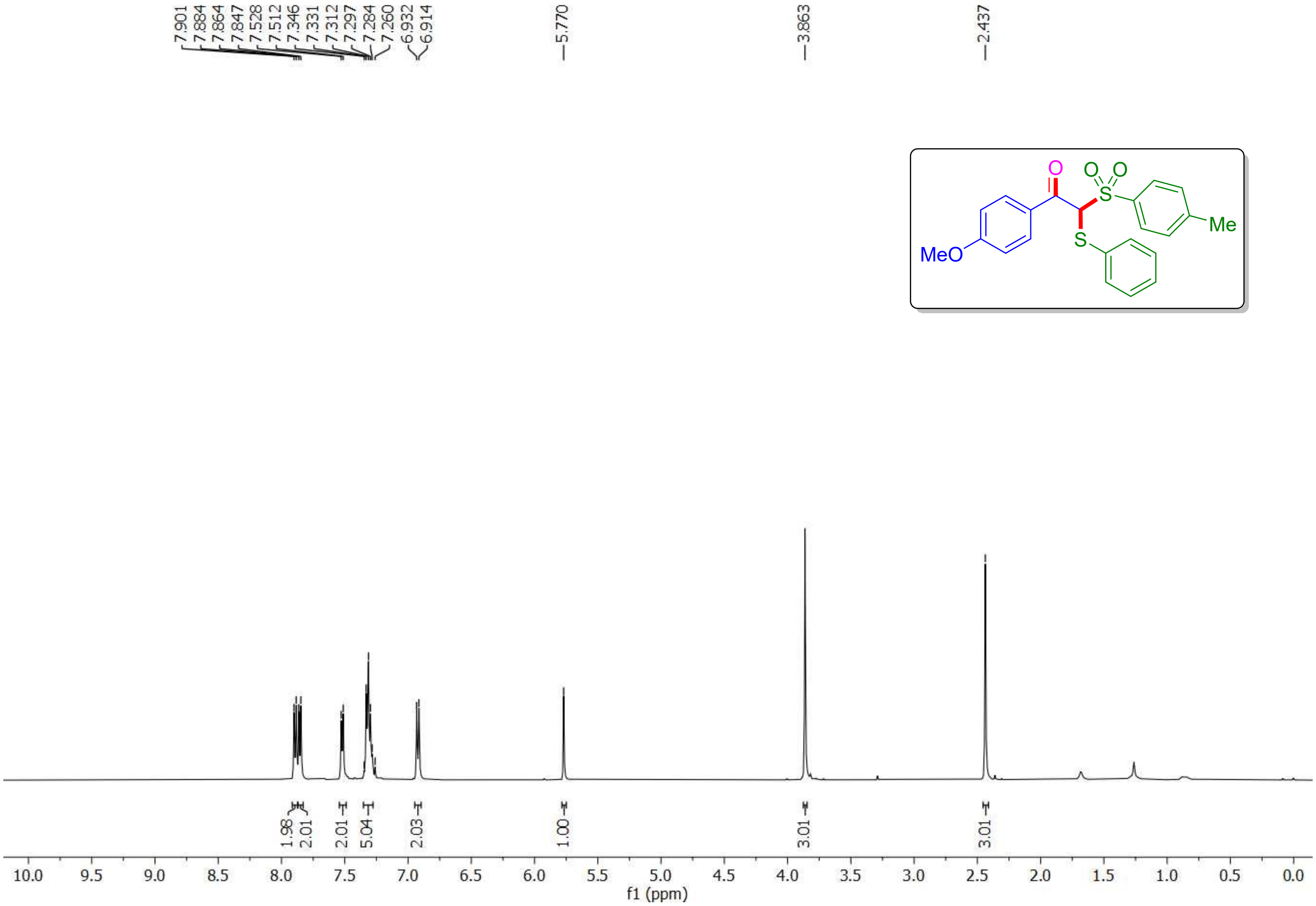
1-(4-Pentylphenyl)-2-(phenylthio)-2-tosylethan-1-one (5a): ^{1}H NMR (CDCl$_3$, 500 MHz)



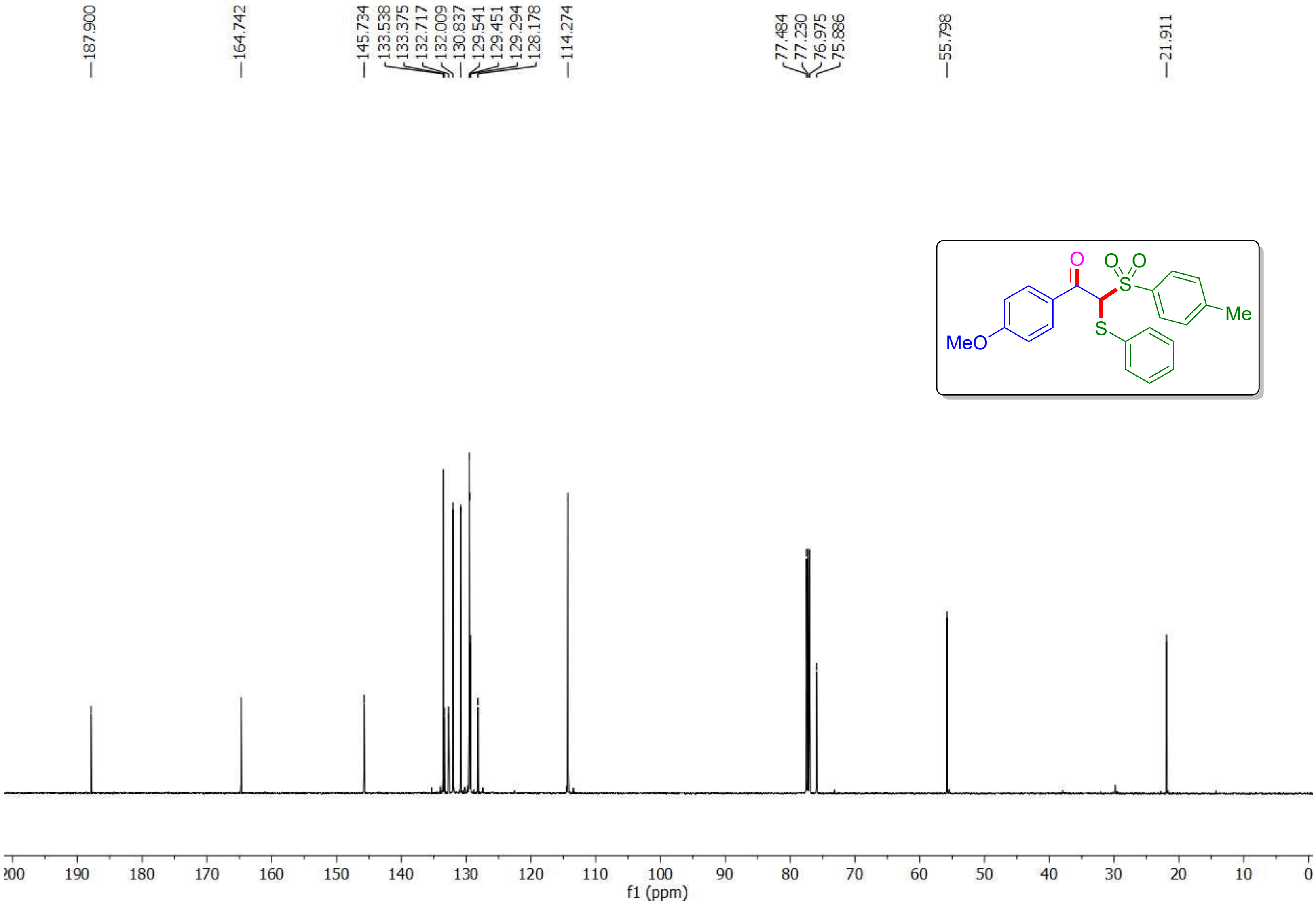
1-(4-Pentylphenyl)-2-(phenylthio)-2-tosylethan-1-one (5a): $^{13}C\{^1H\}$ NMR (CDCl$_3$, 125 MHz)



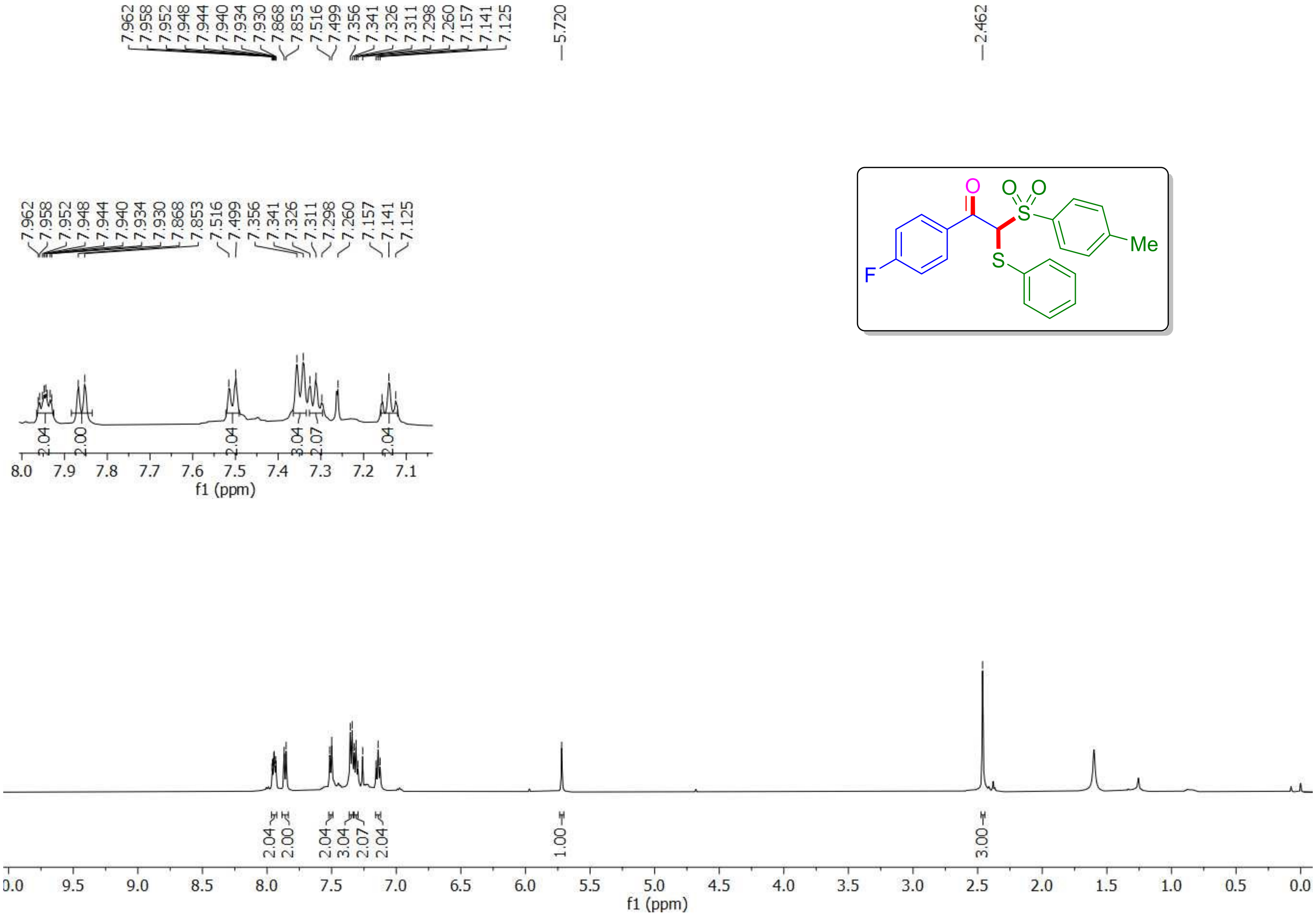
1-(4-Methoxyphenyl)-2-(phenylthio)-2-tosylethan-1-one (6a): ^{1}H NMR (CDCl$_3$, 500 MHz)



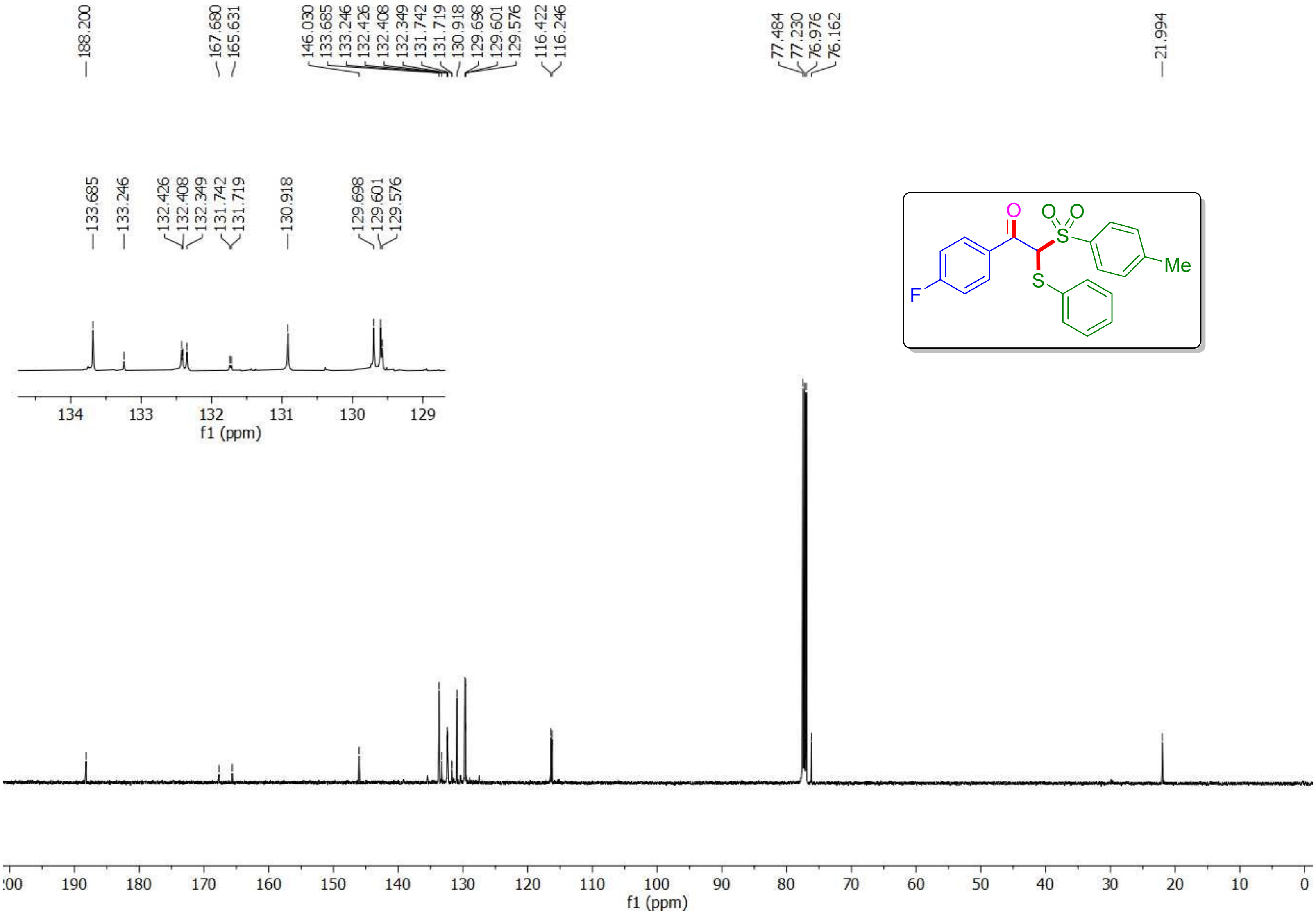
1-(4-Methoxyphenyl)-2-(phenylthio)-2-tosylethan-1-one (6a): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



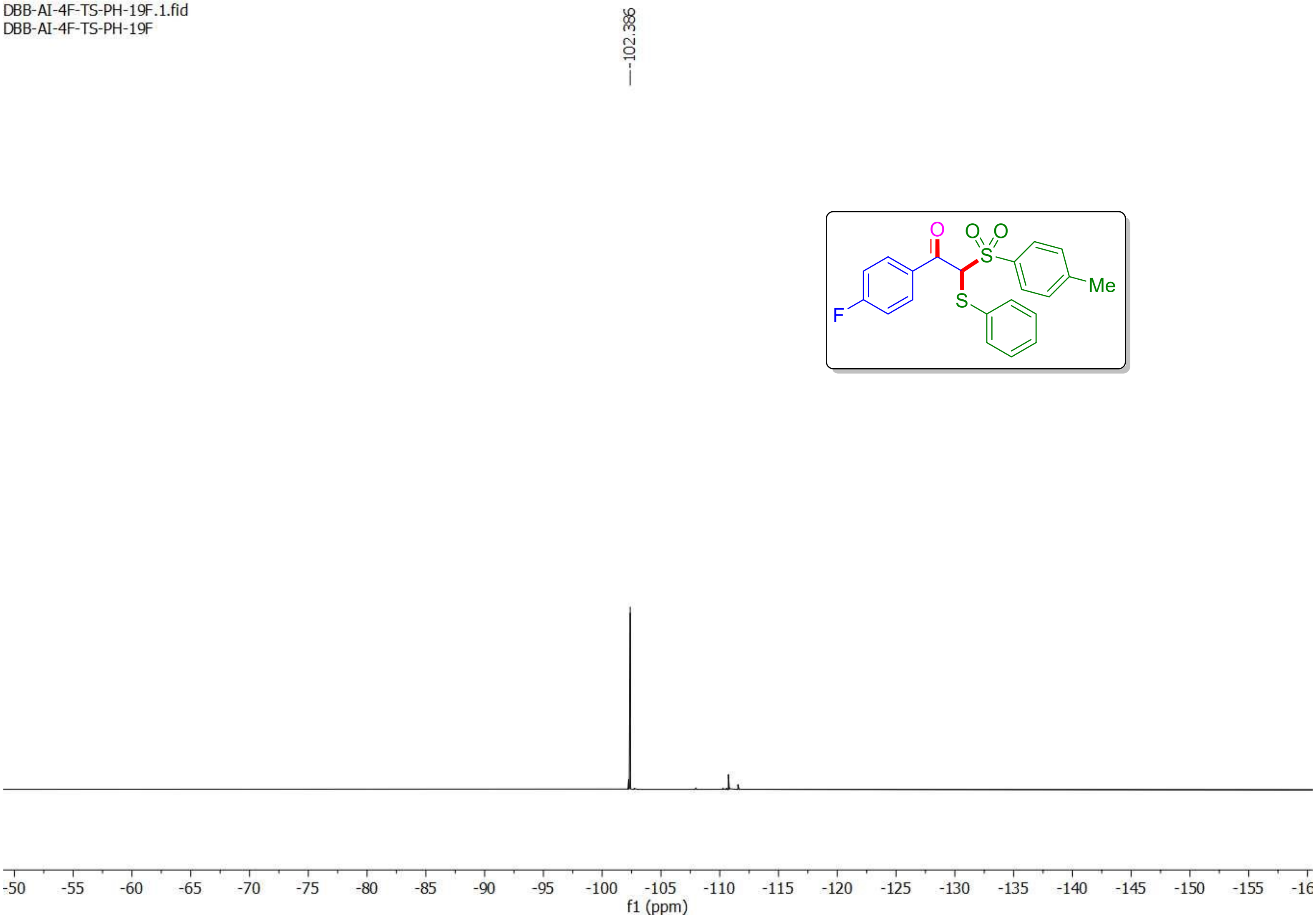
1-(4-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (7a): ^{1}H NMR (CDCl$_3$, 500 MHz)



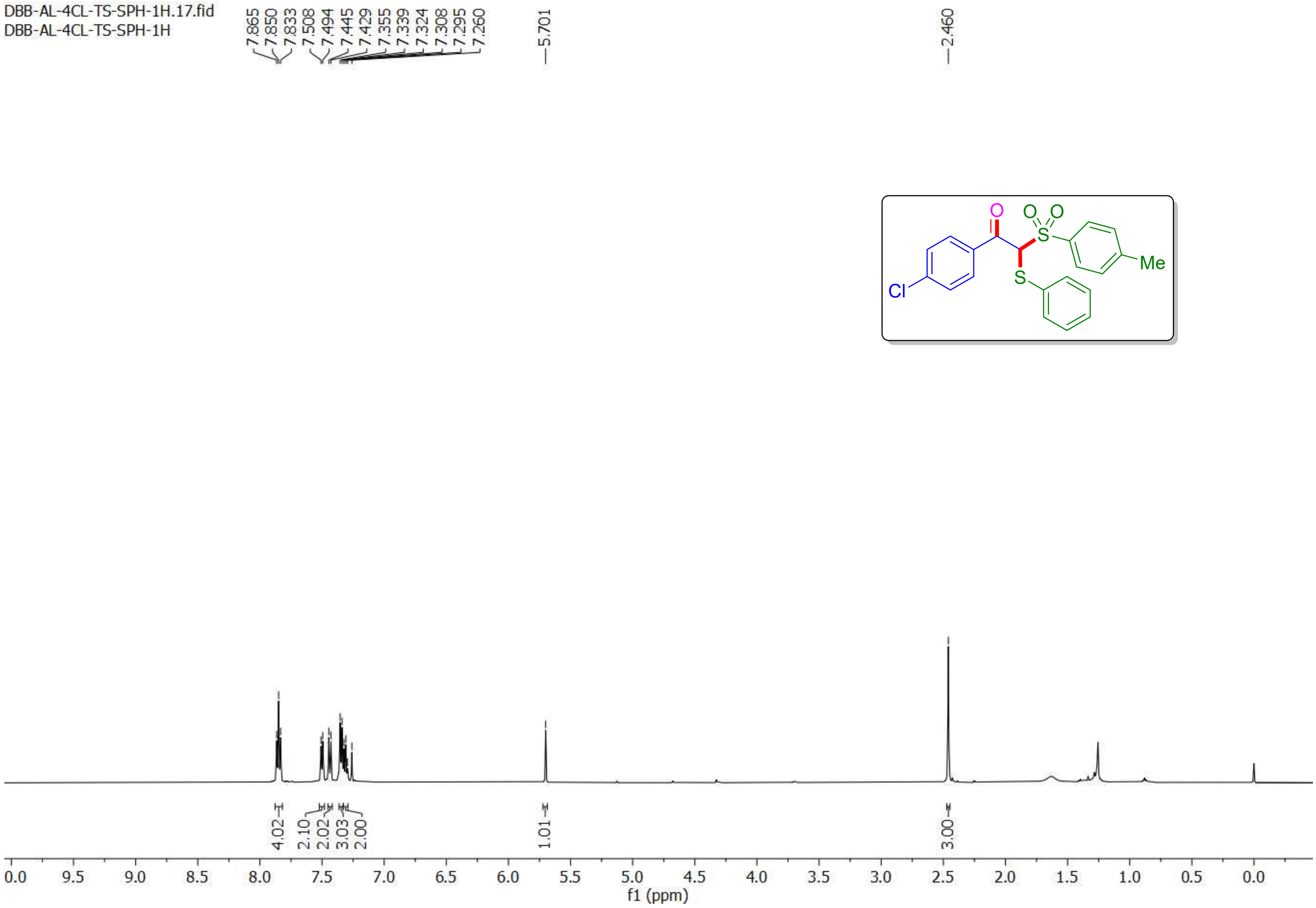
1-(4-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (7a): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



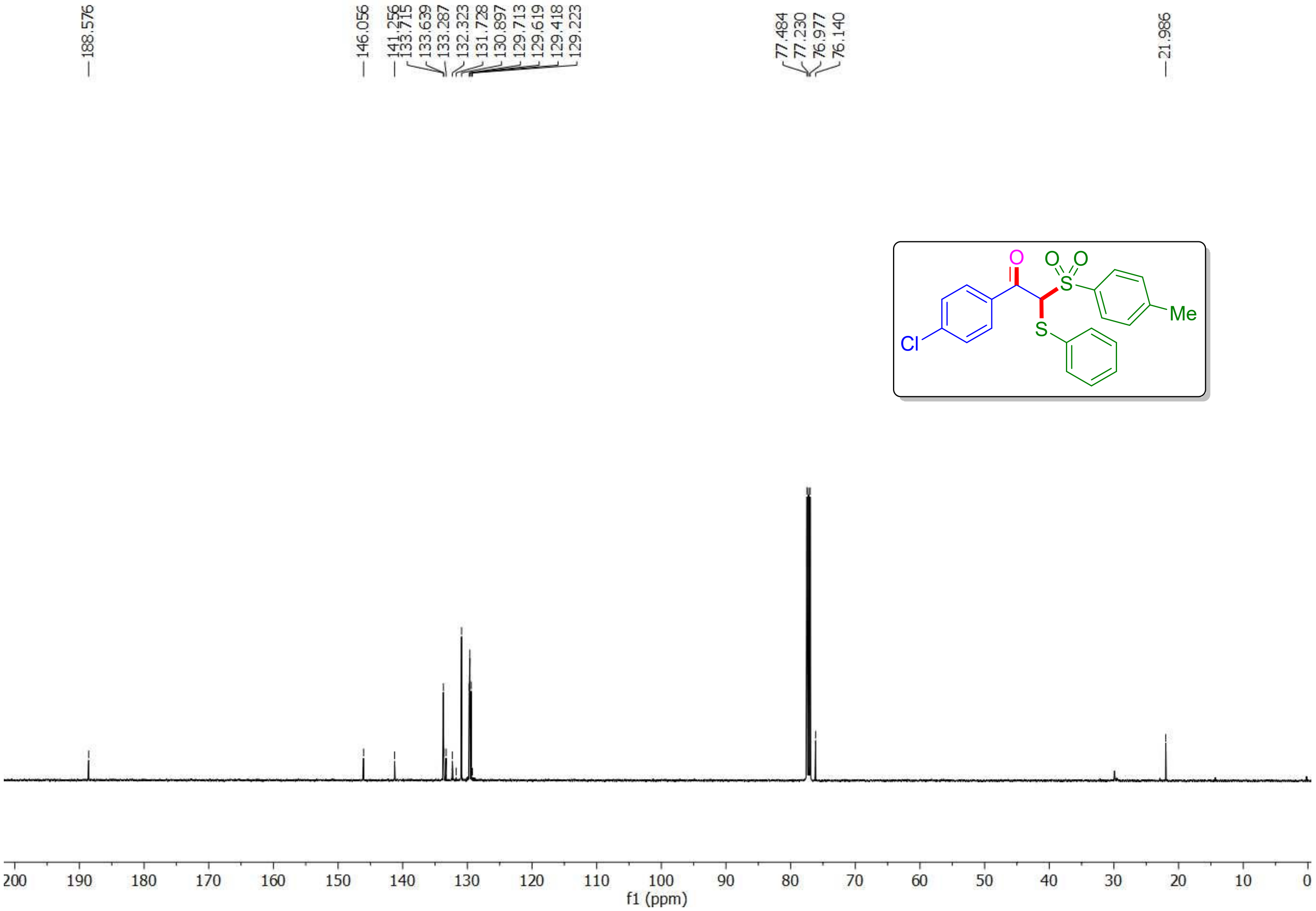
1-(4-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (7a): ^{19}F NMR (CDCl$_3$, 471 MHz)



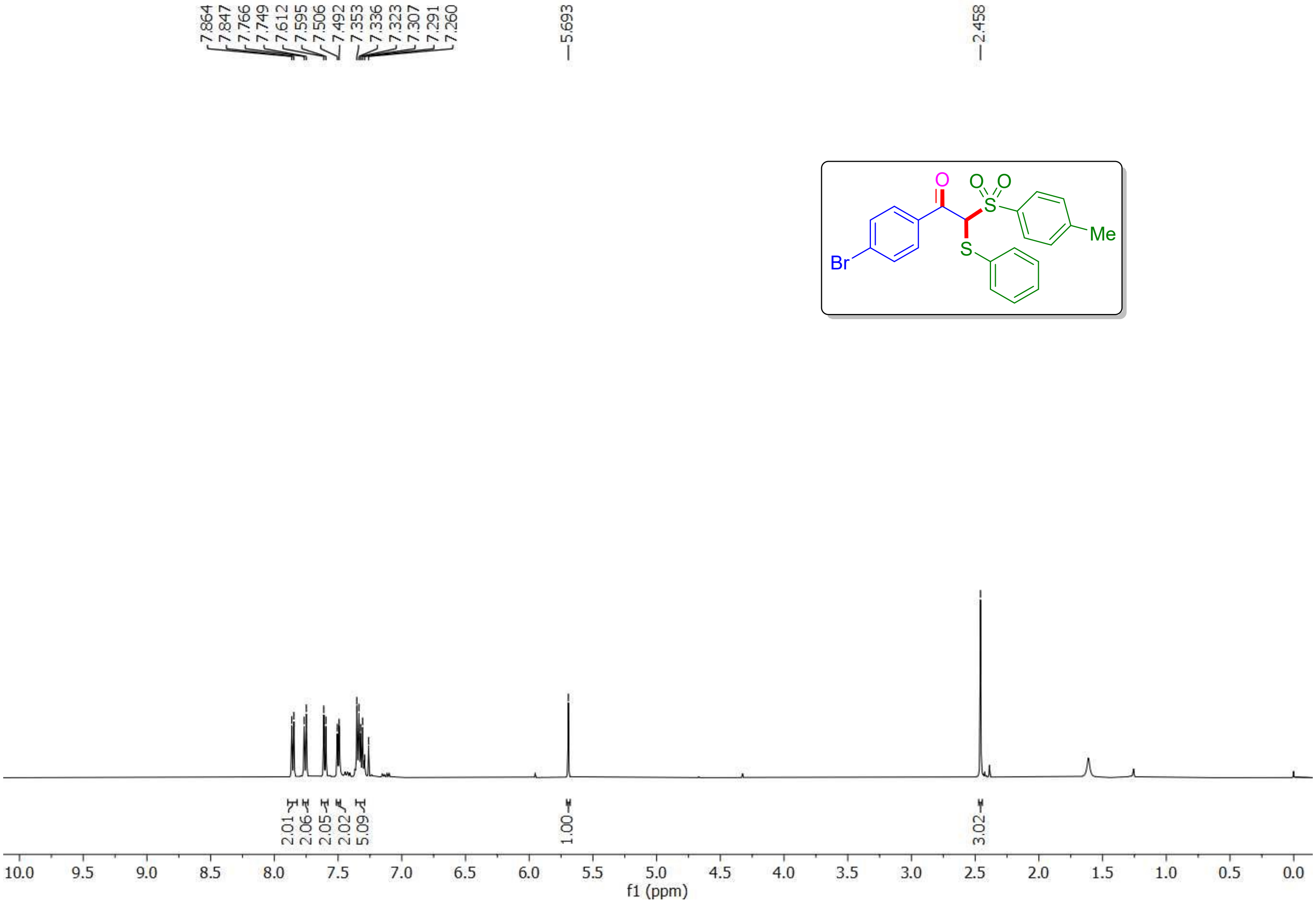
1-(4-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (8a): ^1H NMR ($CDCl_3$, 500 MHz)



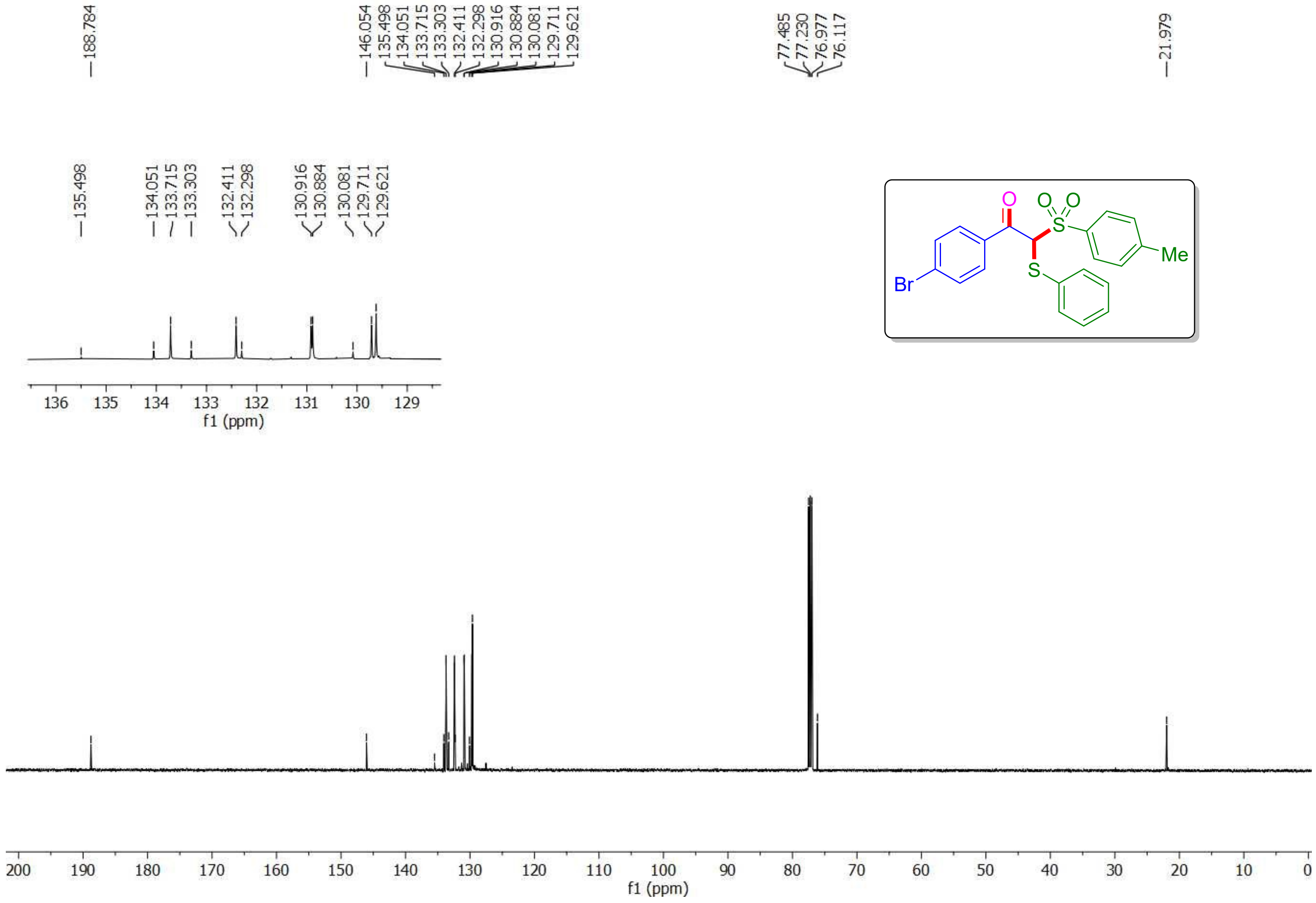
1-(4-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (8a): $^{13}C\{^1H\}$ *NMR* ($CDCl_3$, *125 MHz)*



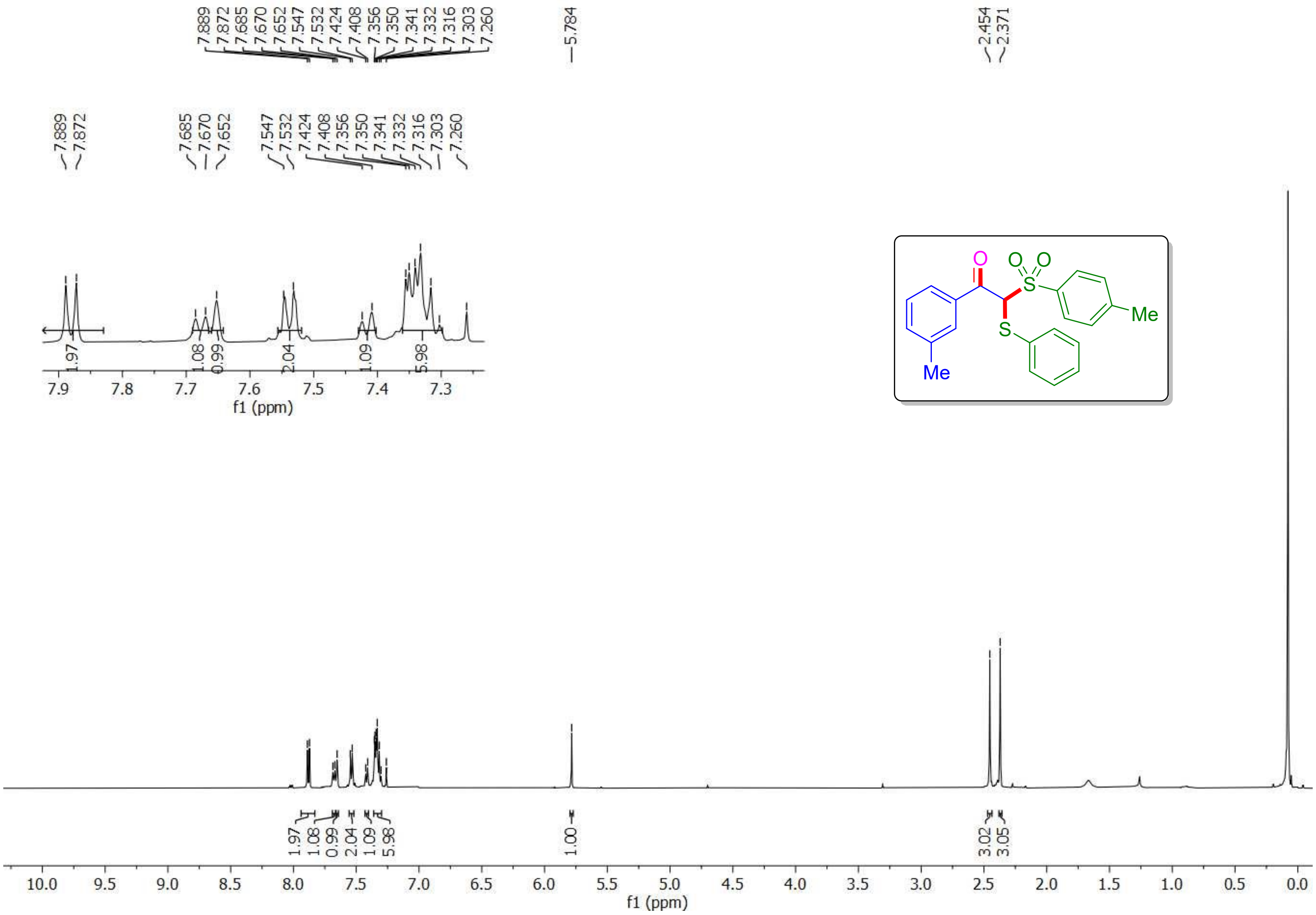
1-(4-Bromophenyl)-2-(phenylthio)-2-tosylethan-1-one (9a): ^{1}H NMR (CDCl$_3$, 500 MHz)



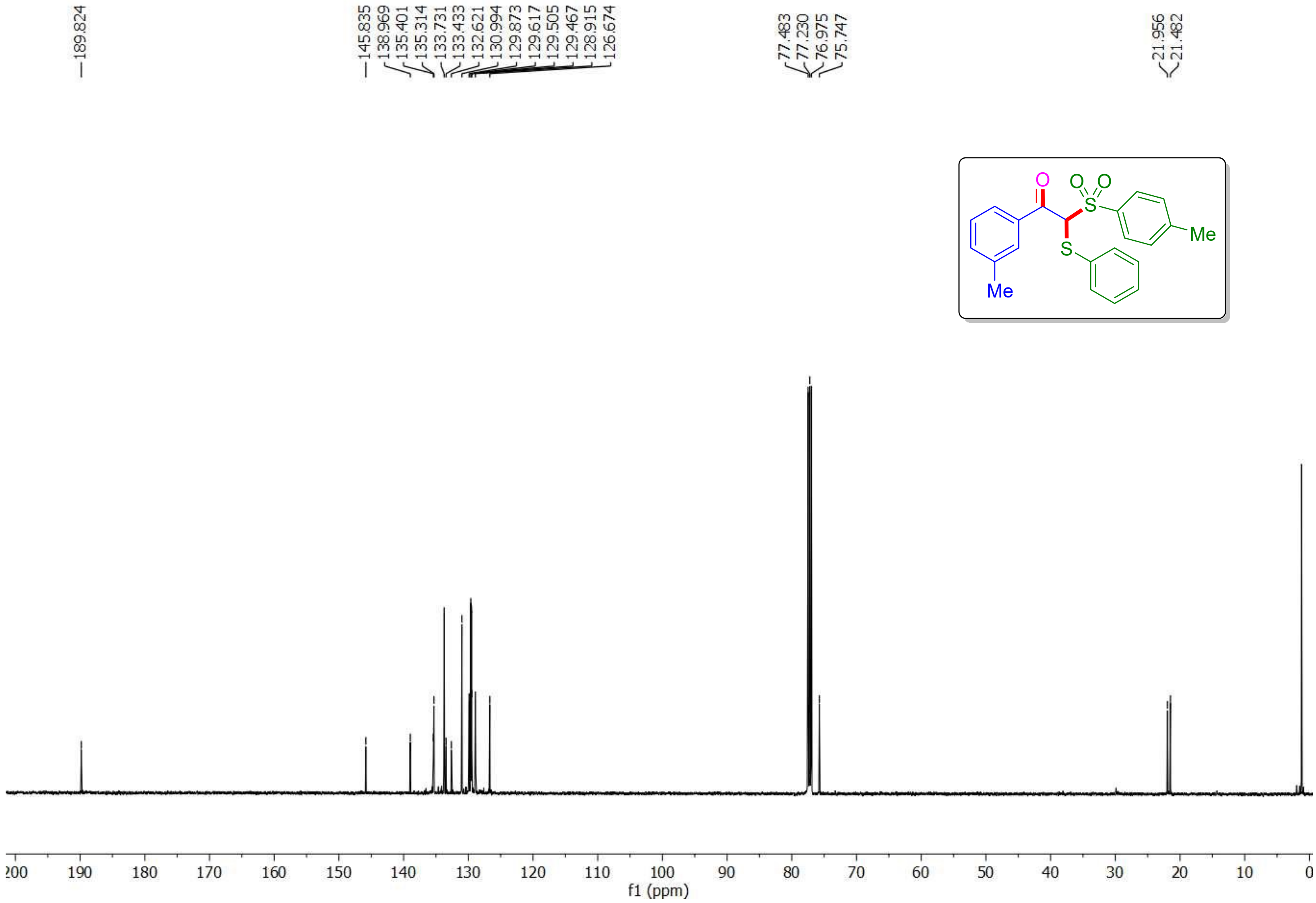
1-(4-Bromophenyl)-2-(phenylthio)-2-tosylethan-1-one (9a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



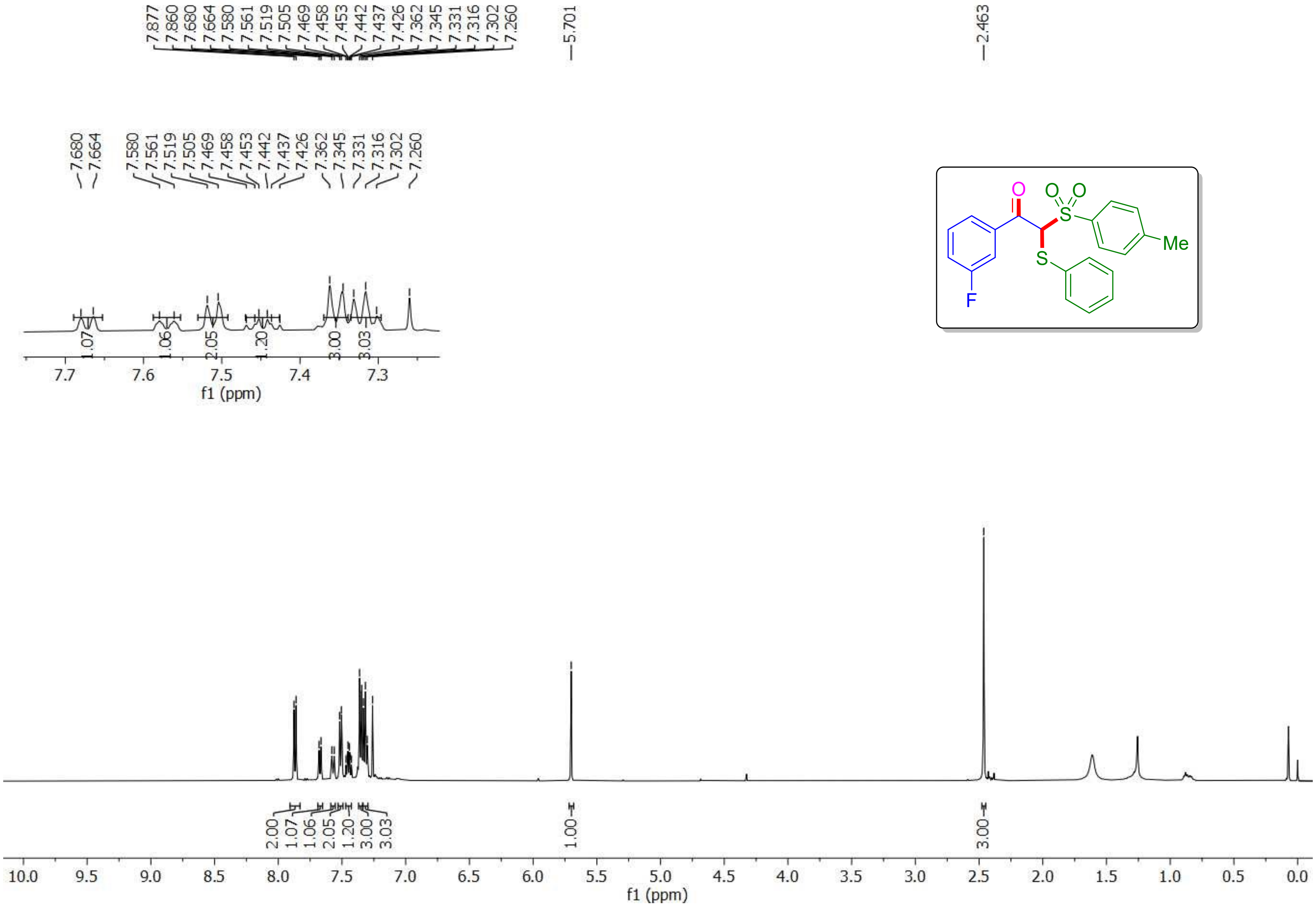
2-(Phenylthio)-1-(m-tolyl)-2-tosylethan-1-one (10a): ^{1}H NMR (CDCl3, 500 MHz)



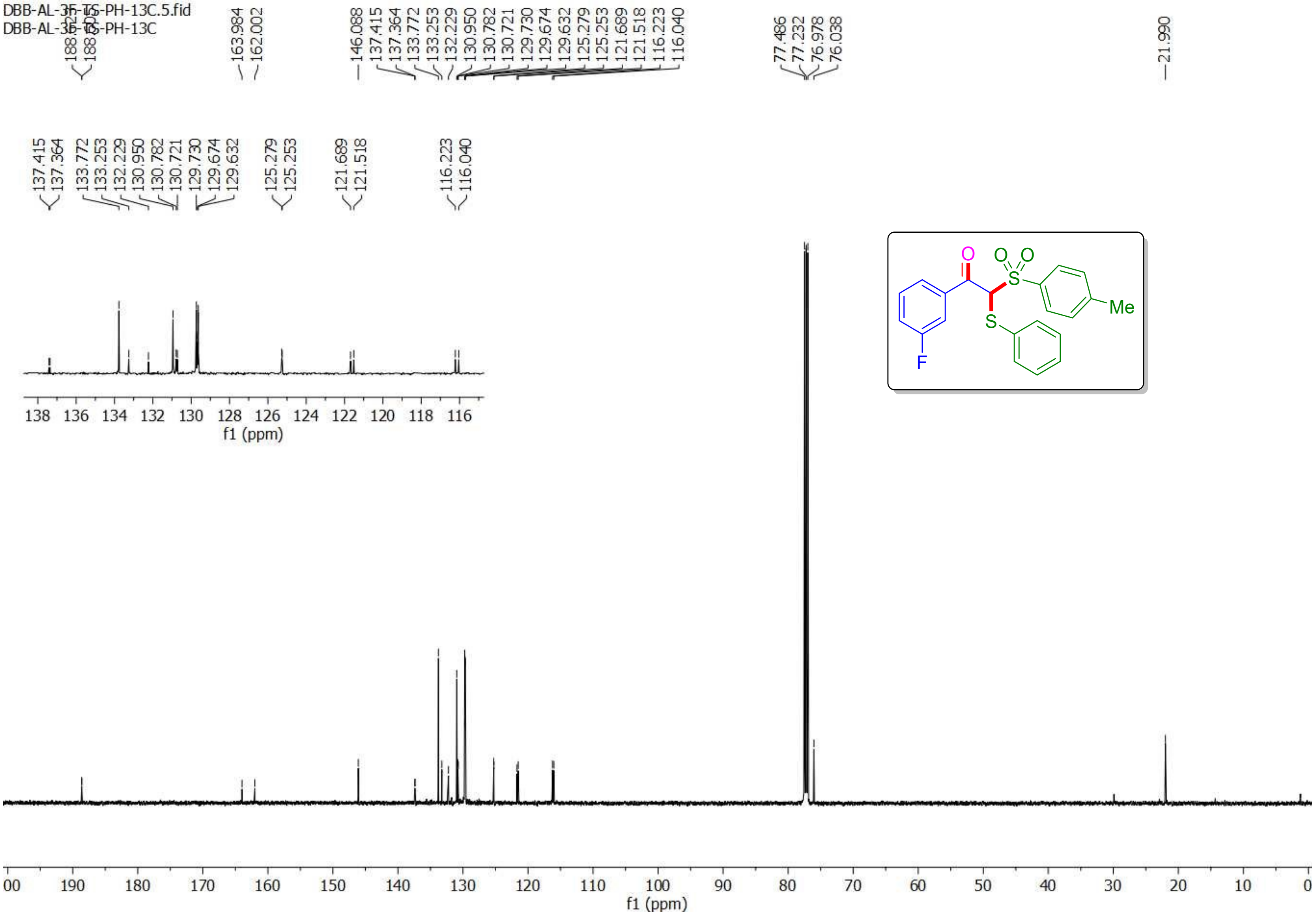
2-(Phenylthio)-1-(m-tolyl)-2-tosylethan-1-one (10a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



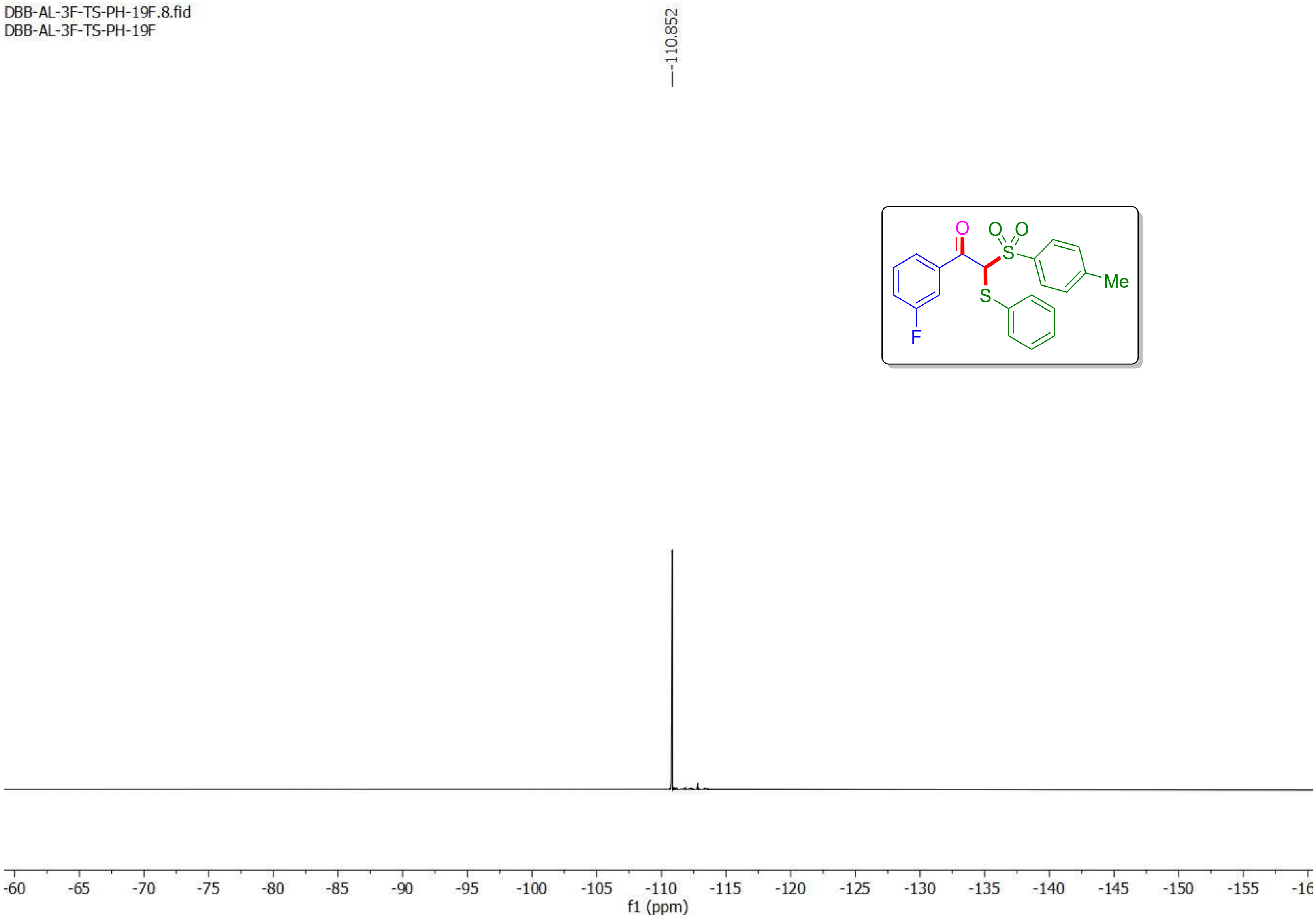
1-(3-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (11a): ^{1}H NMR ($CDCl_3$, 500 MHz)



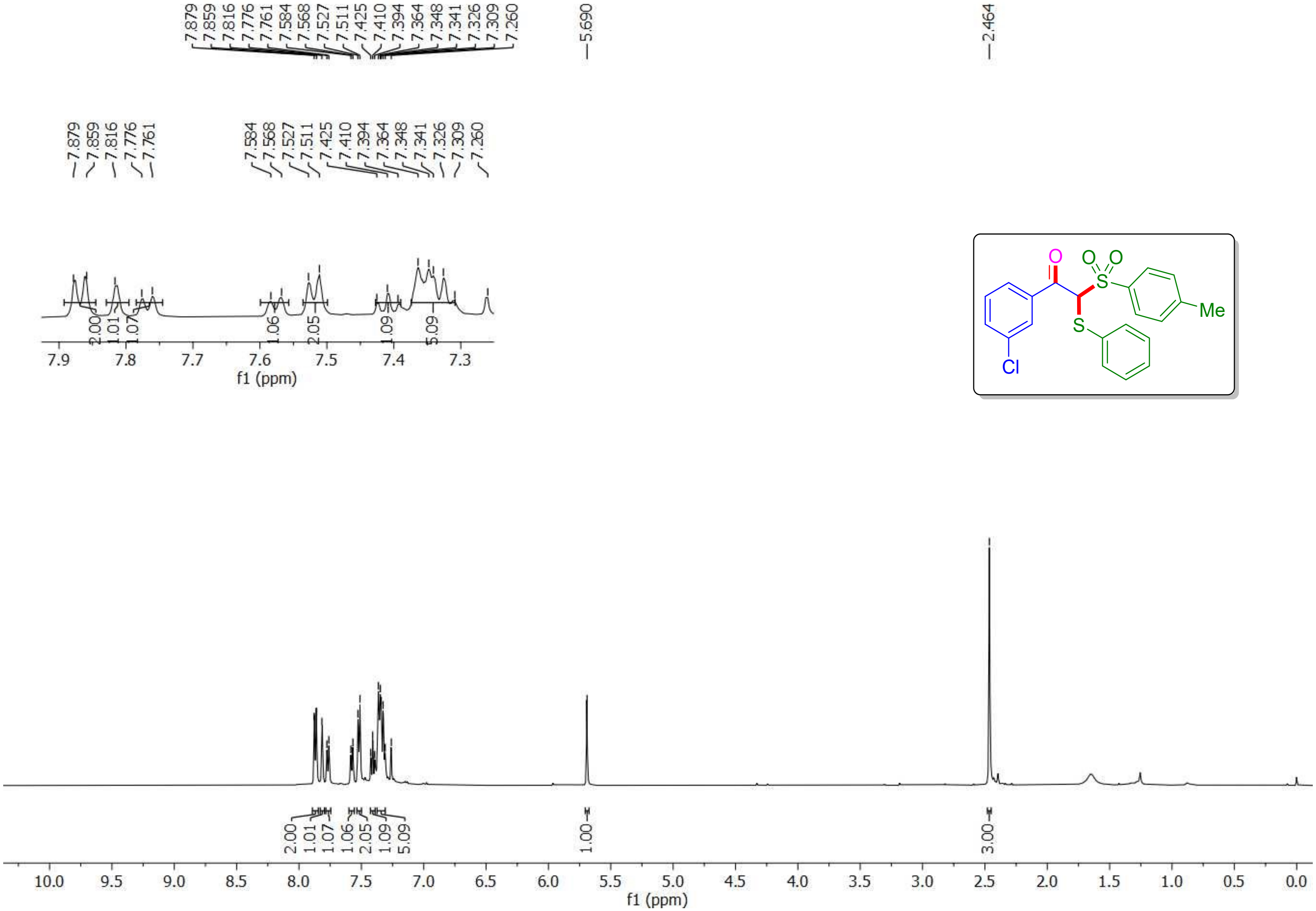
1-(3-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (11a): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



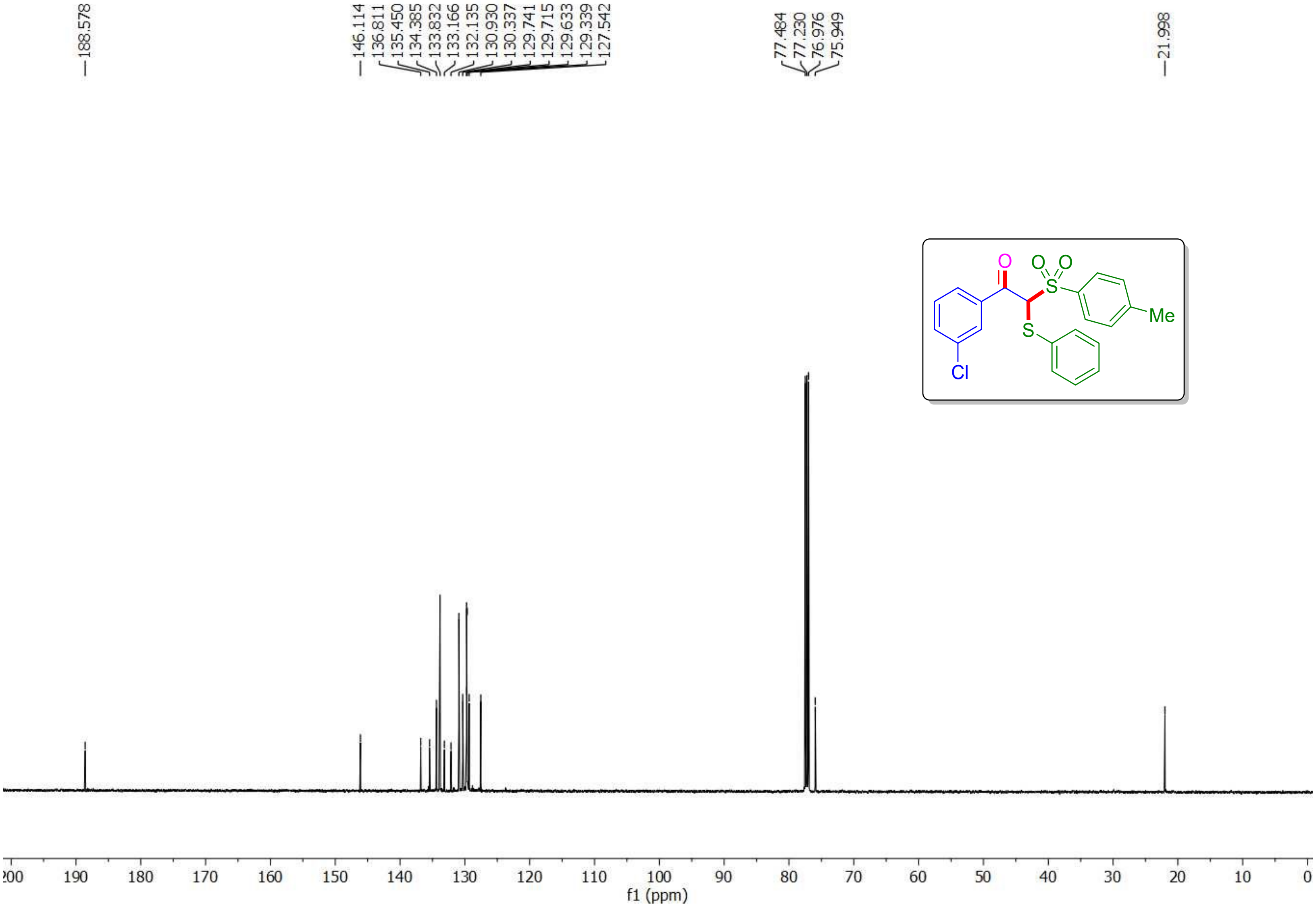
1-(3-Fluorophenyl)-2-(phenylthio)-2-tosylethan-1-one (11a): ^{19}*F NMR (CDCl*$_3$*, 471 MHz)*



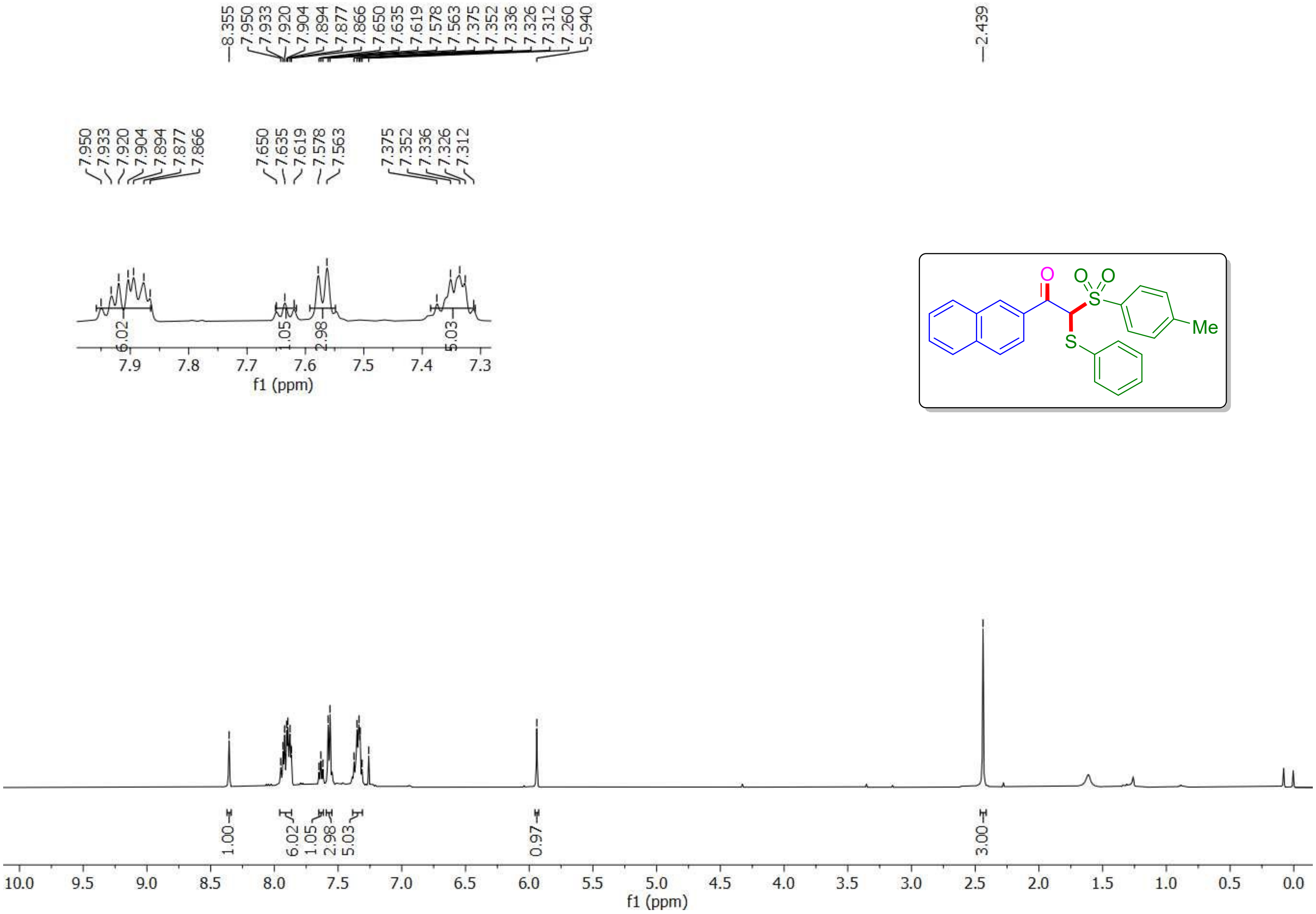
1-(3-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (12a): ^{1}H NMR (CDCl$_3$, 500 MHz)



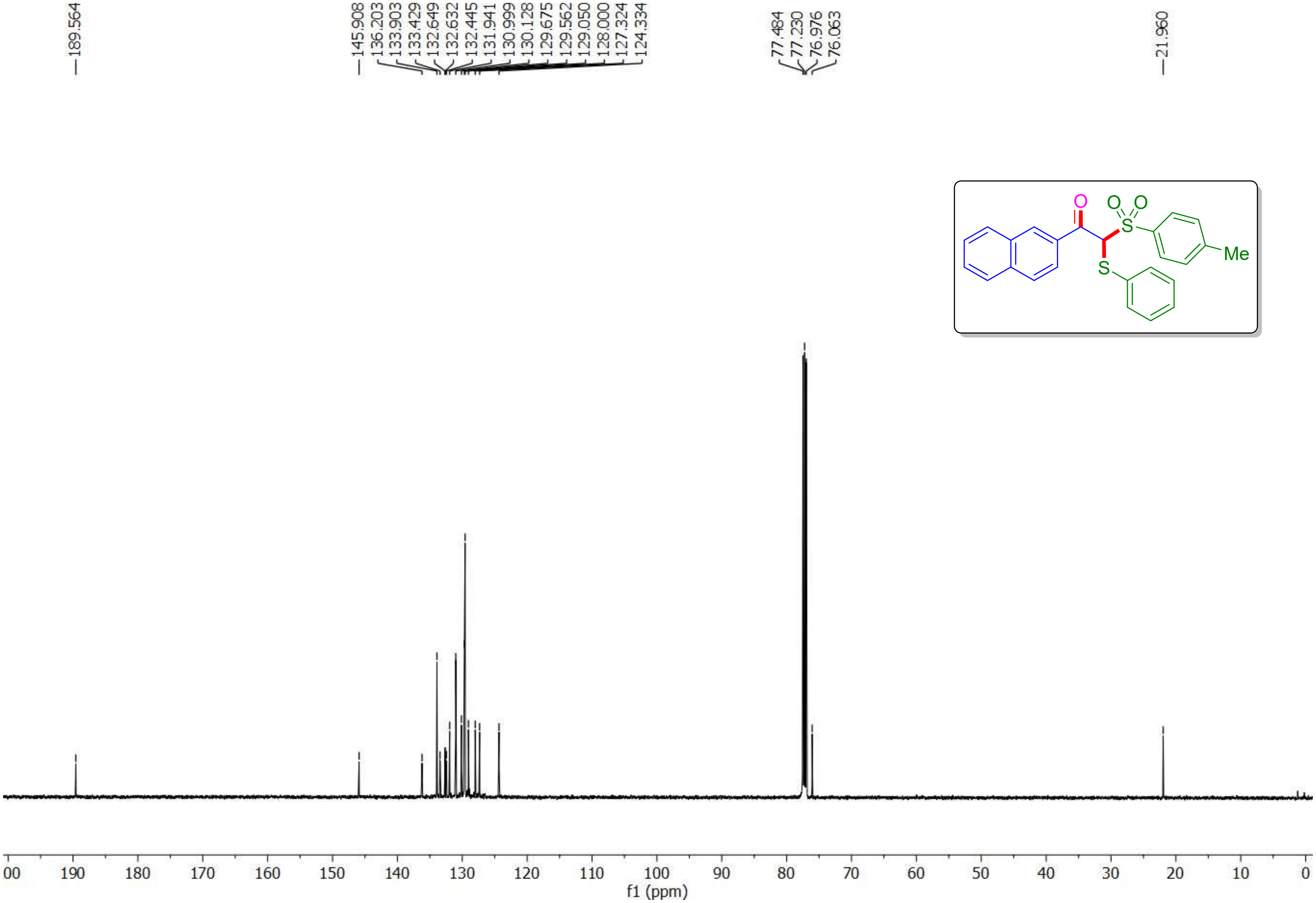
1-(3-Chlorophenyl)-2-(phenylthio)-2-tosylethan-1-one (12a): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



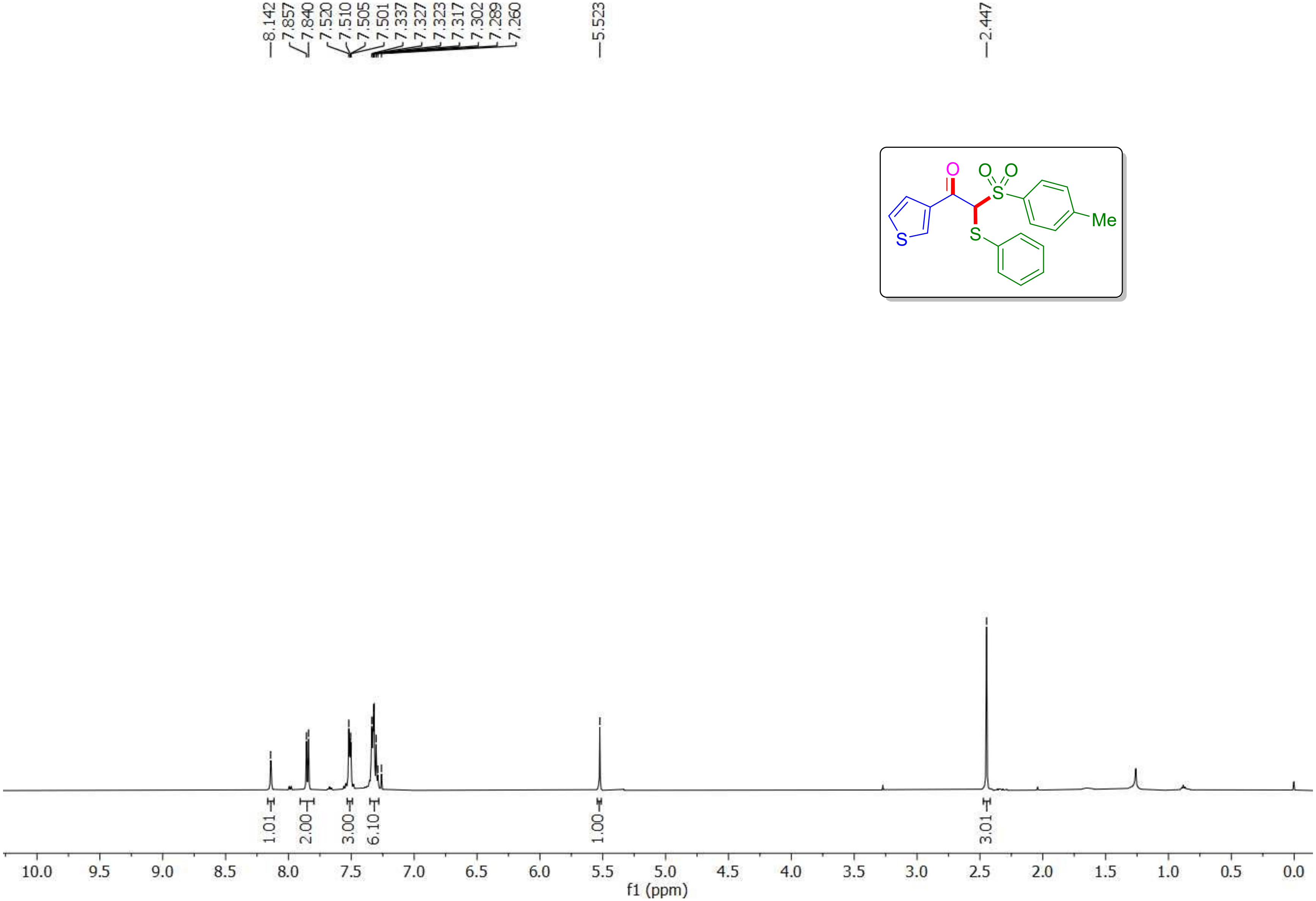
1-(Naphthalen-2-yl)-2-(phenylthio)-2-tosylethan-1-one (13a): ^{1}H NMR (CDCl$_3$, 500 MHz)



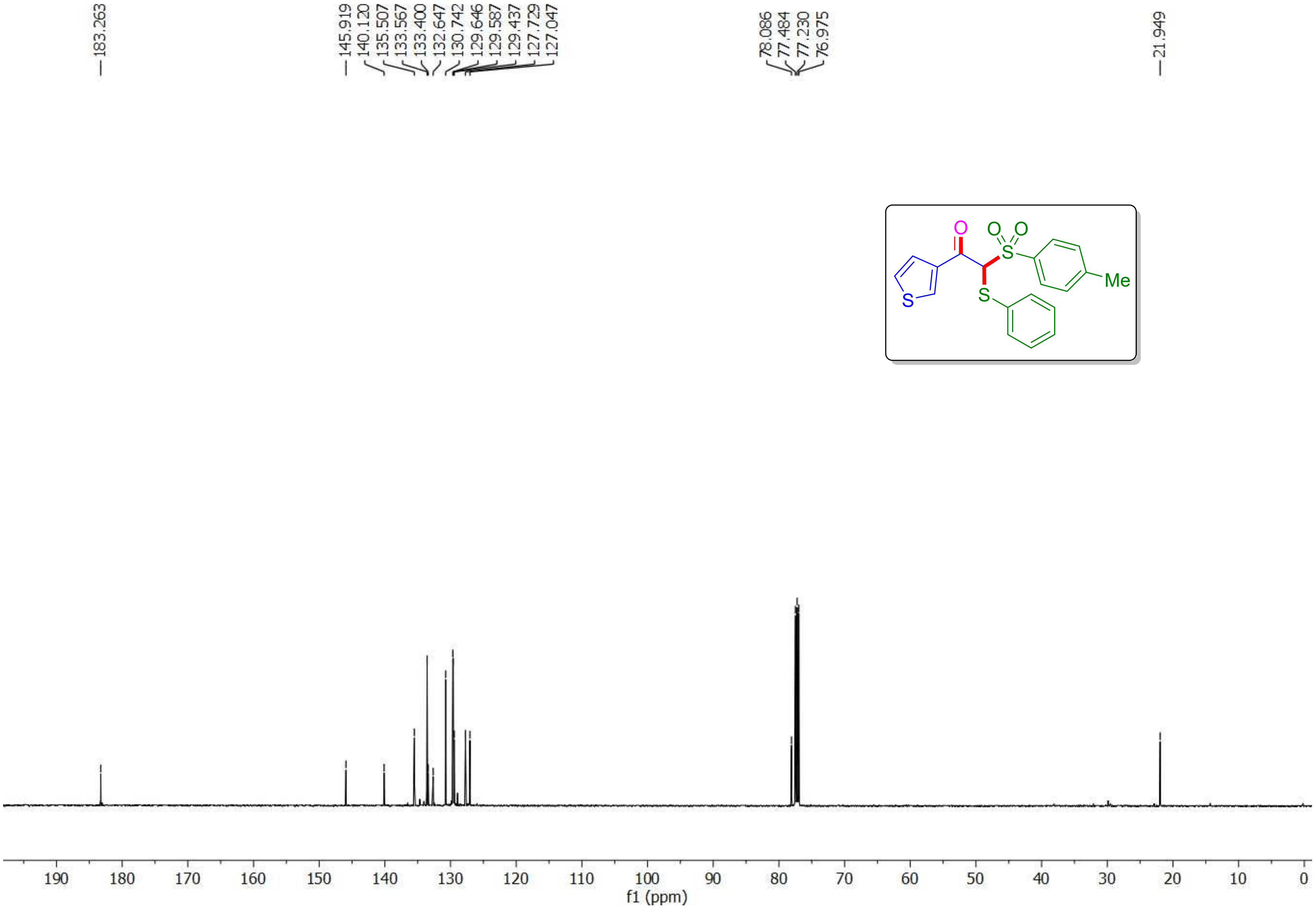
1-(Naphthalen-2-yl)-2-(phenylthio)-2-tosylethan-1-one (13a): $^{13}C\{^1H\}$ *NMR (CDCl$_3$, 125 MHz)*



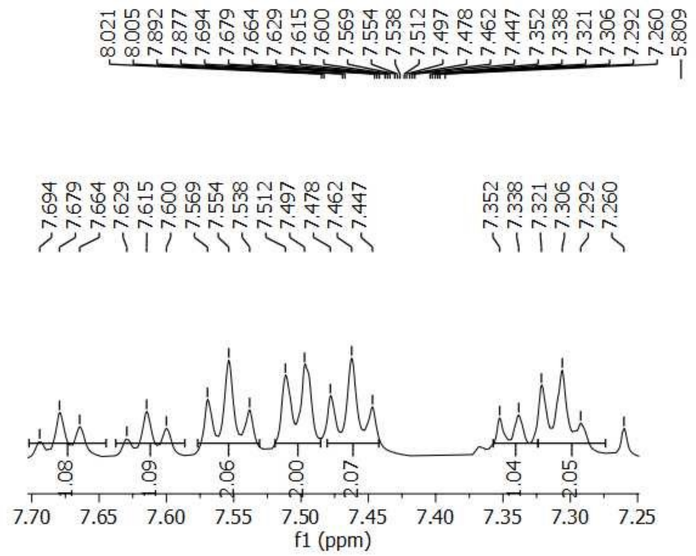
2-(Phenylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one (14a): ^{1}H NMR ($CDCl_3$, 500 MHz)

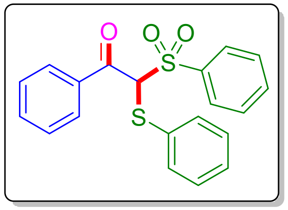


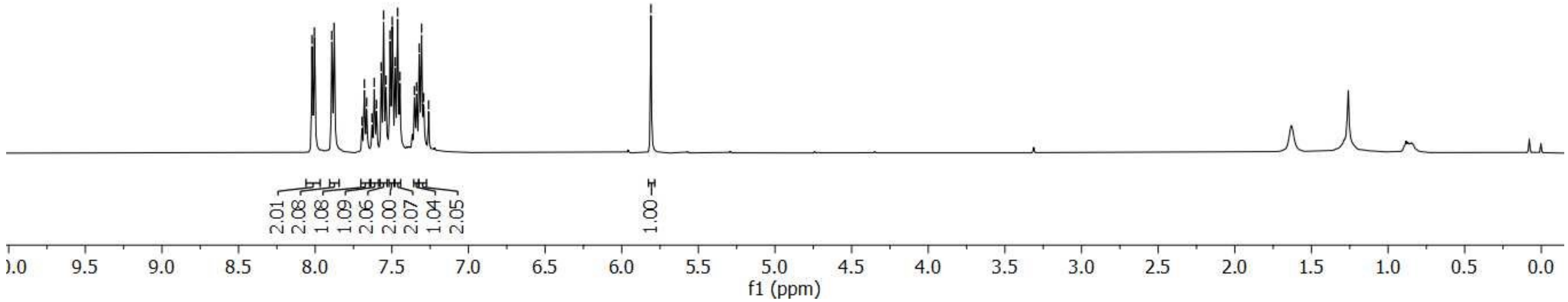
2-(Phenylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one (14a): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



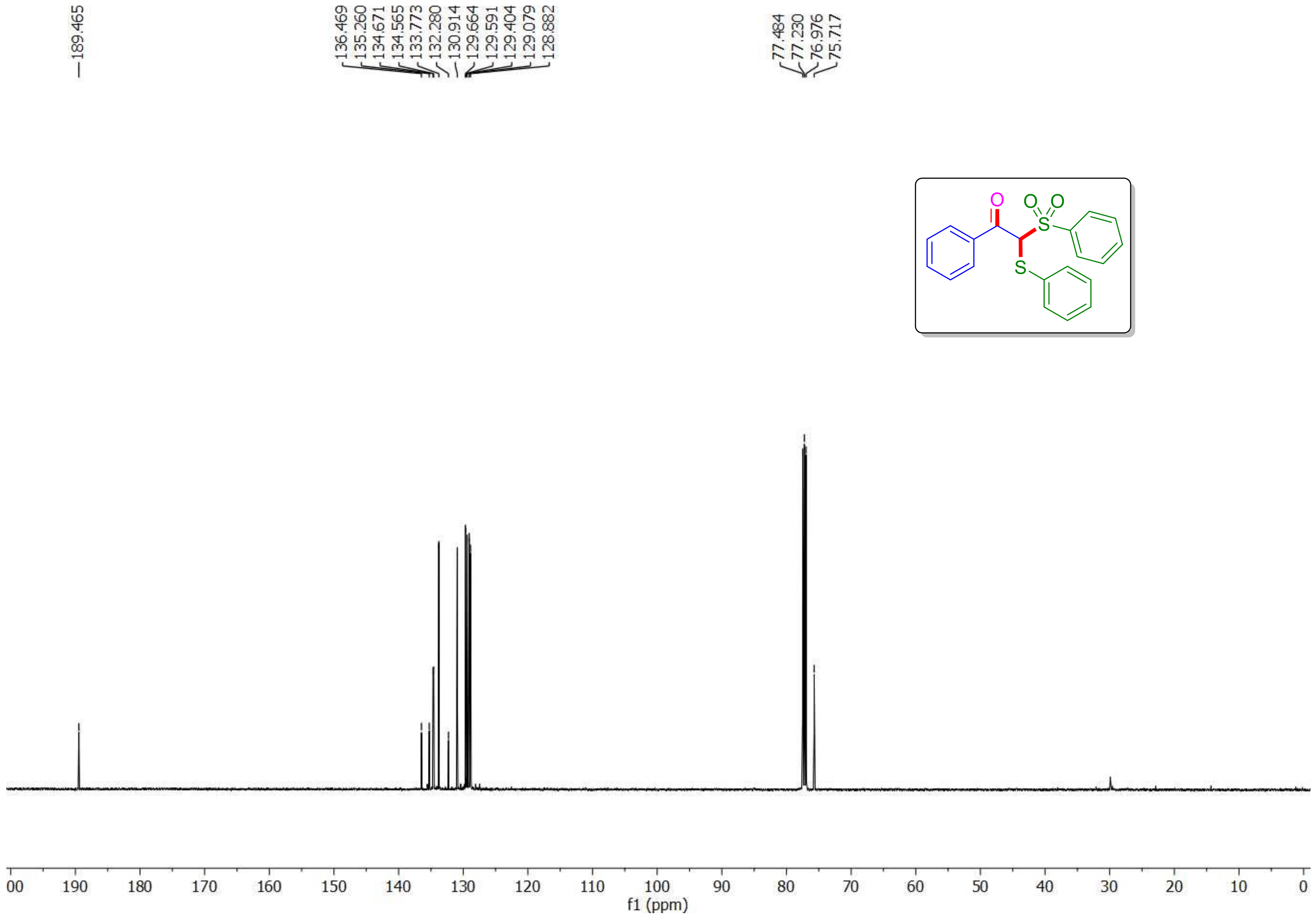
1-Phenyl-2-(phenylsulfonyl)-2-(phenylthio)ethan-1-one (1b): ^{1}H NMR ($CDCl_3$, 500 MHz)



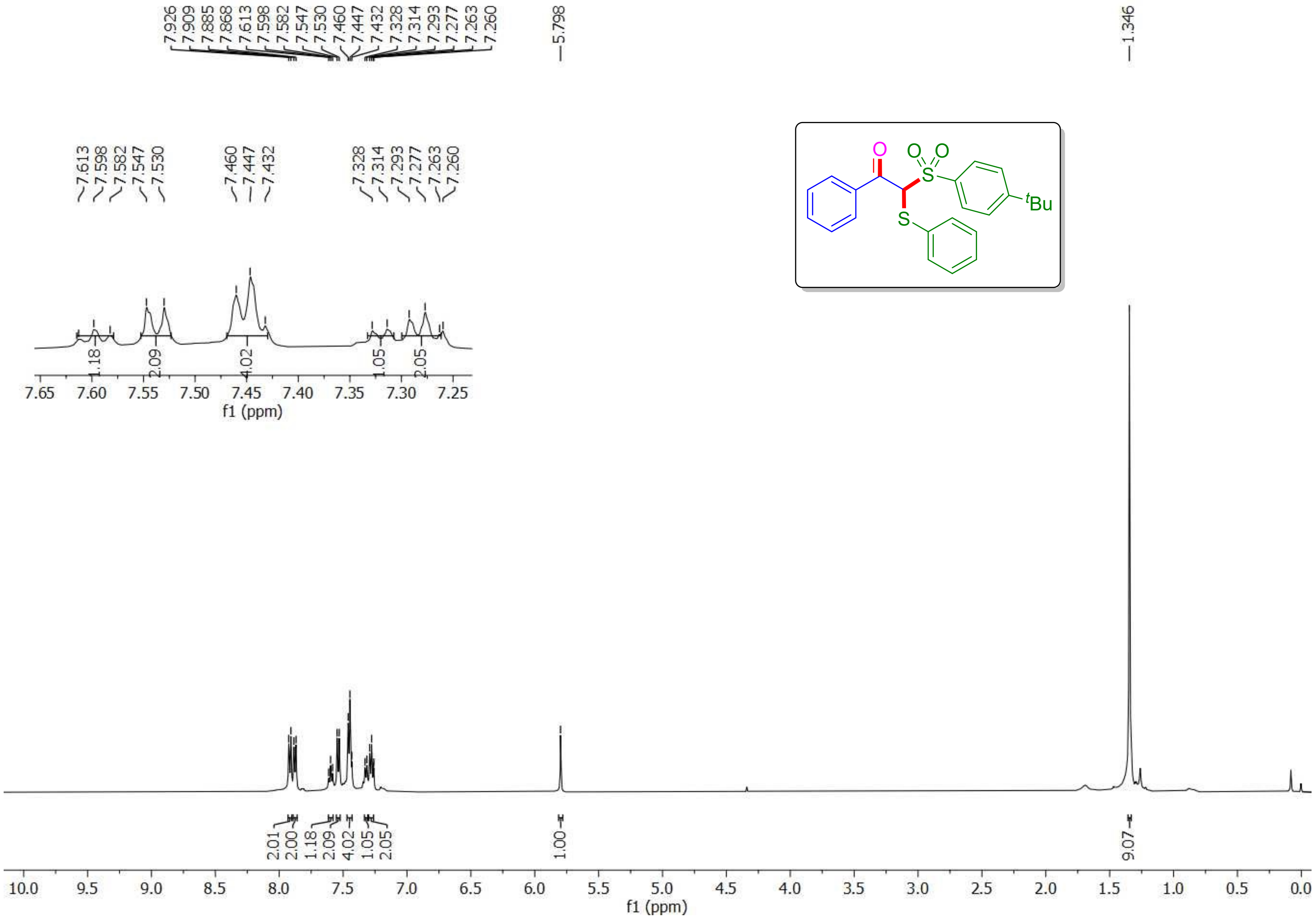




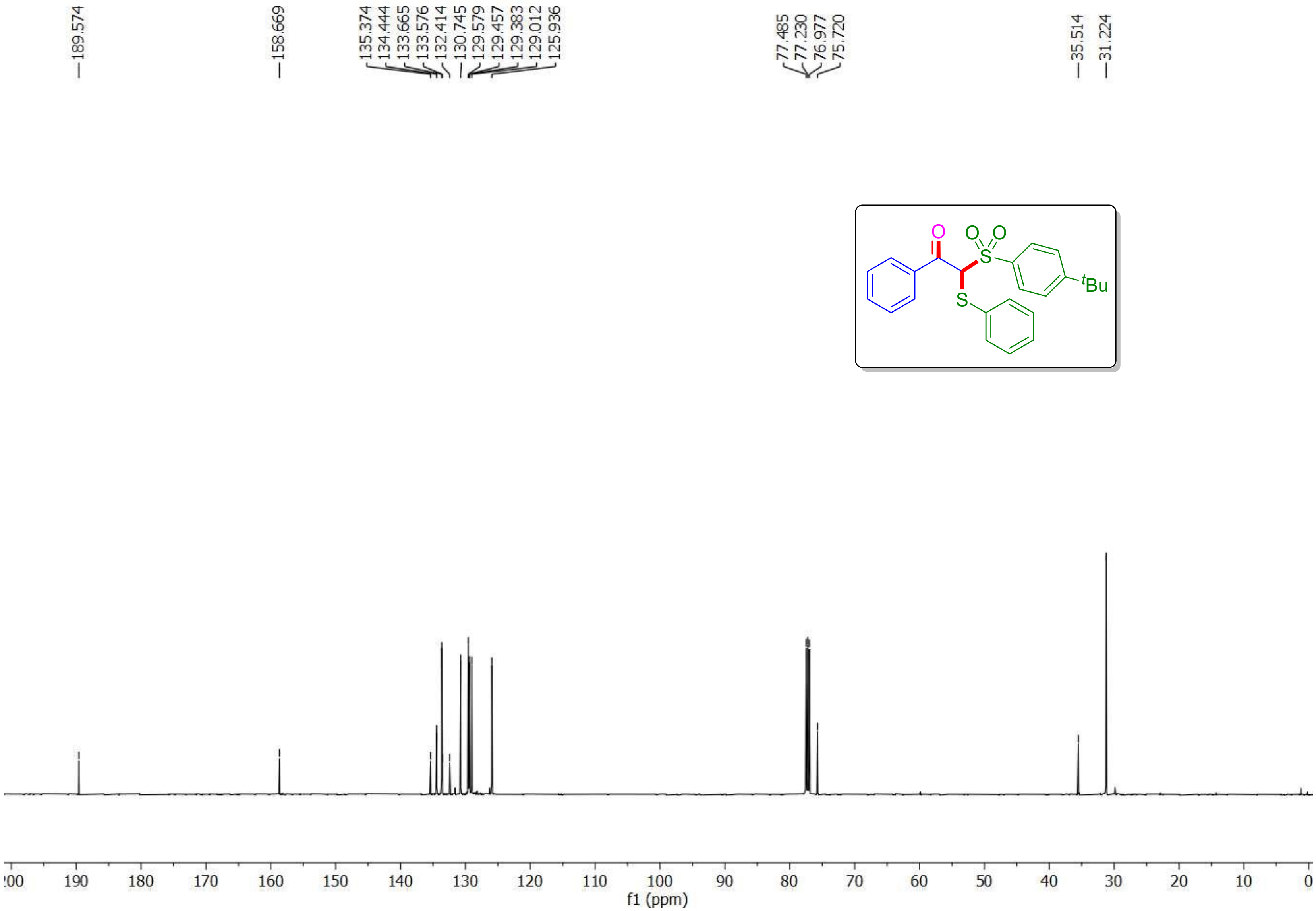
1-Phenyl-2-(phenylsulfonyl)-2-(phenylthio)ethan-1-one (1b): $^{13}C\{^{1}H\}$ *NMR* ($CDCl_3$, *125 MHz)*



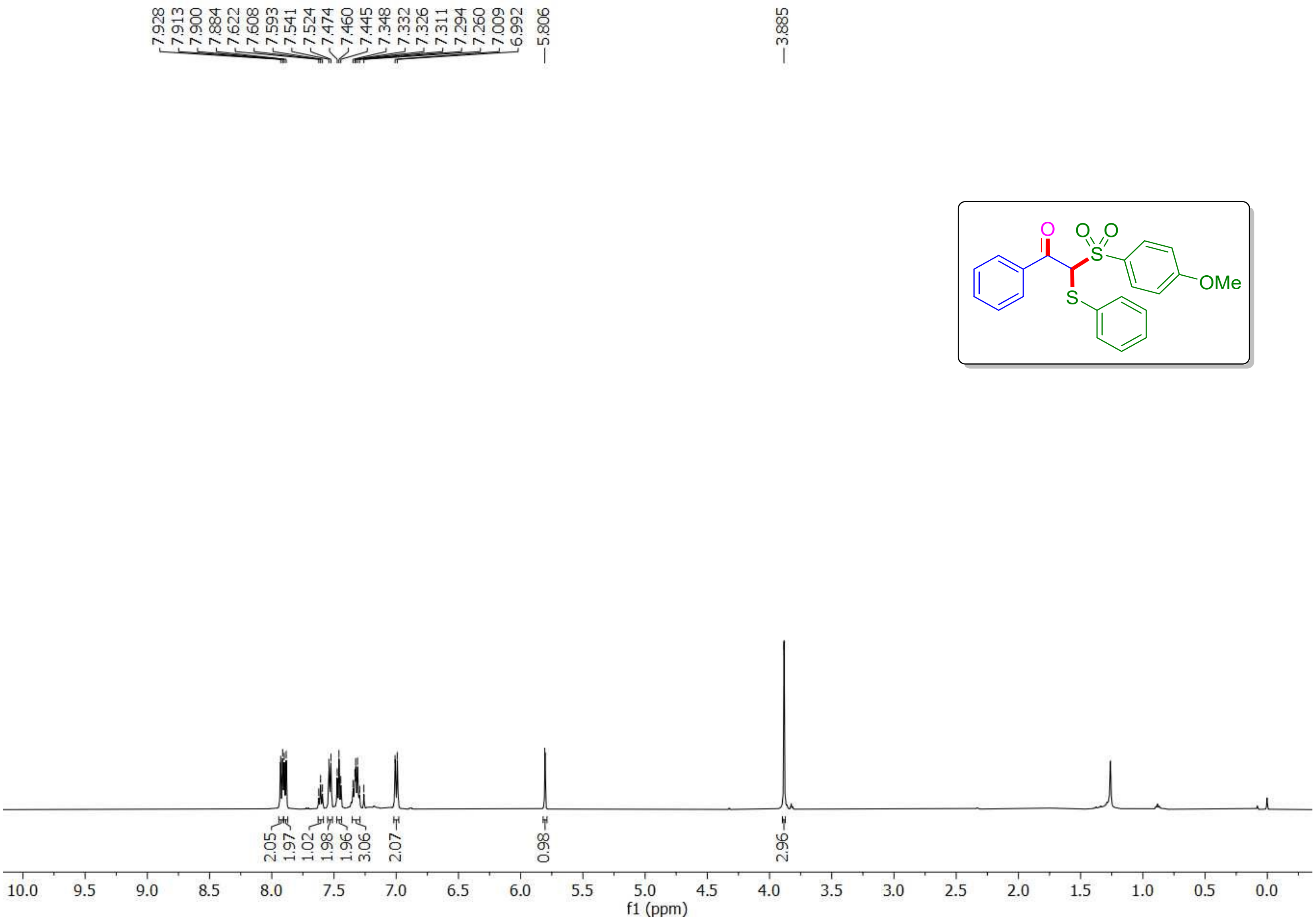
2-((4-(tert-Butyl)phenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1c): ^{1}H NMR (CDCl$_3$, 500 MHz)



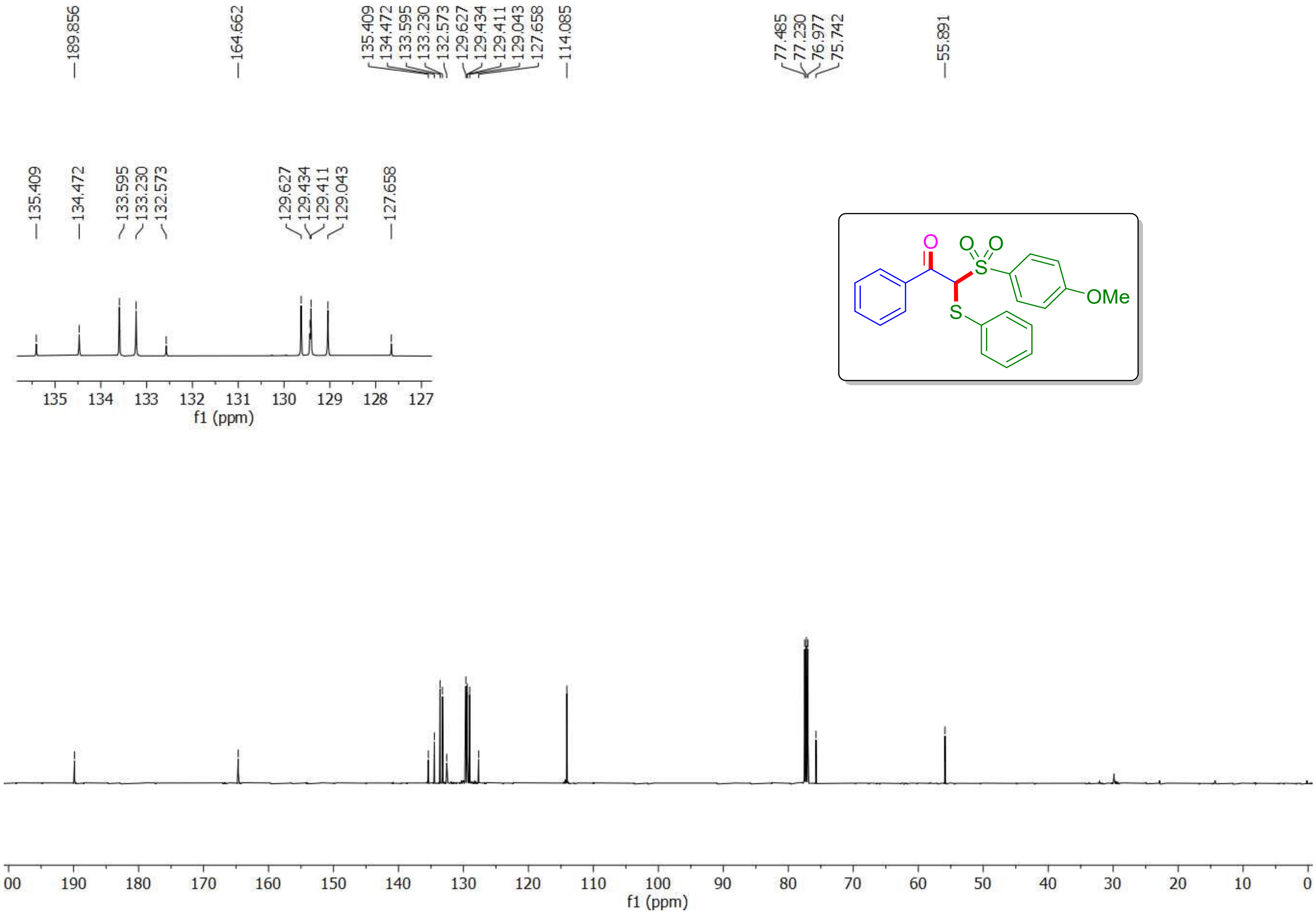
2-((4-(tert-Butyl)phenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1c): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



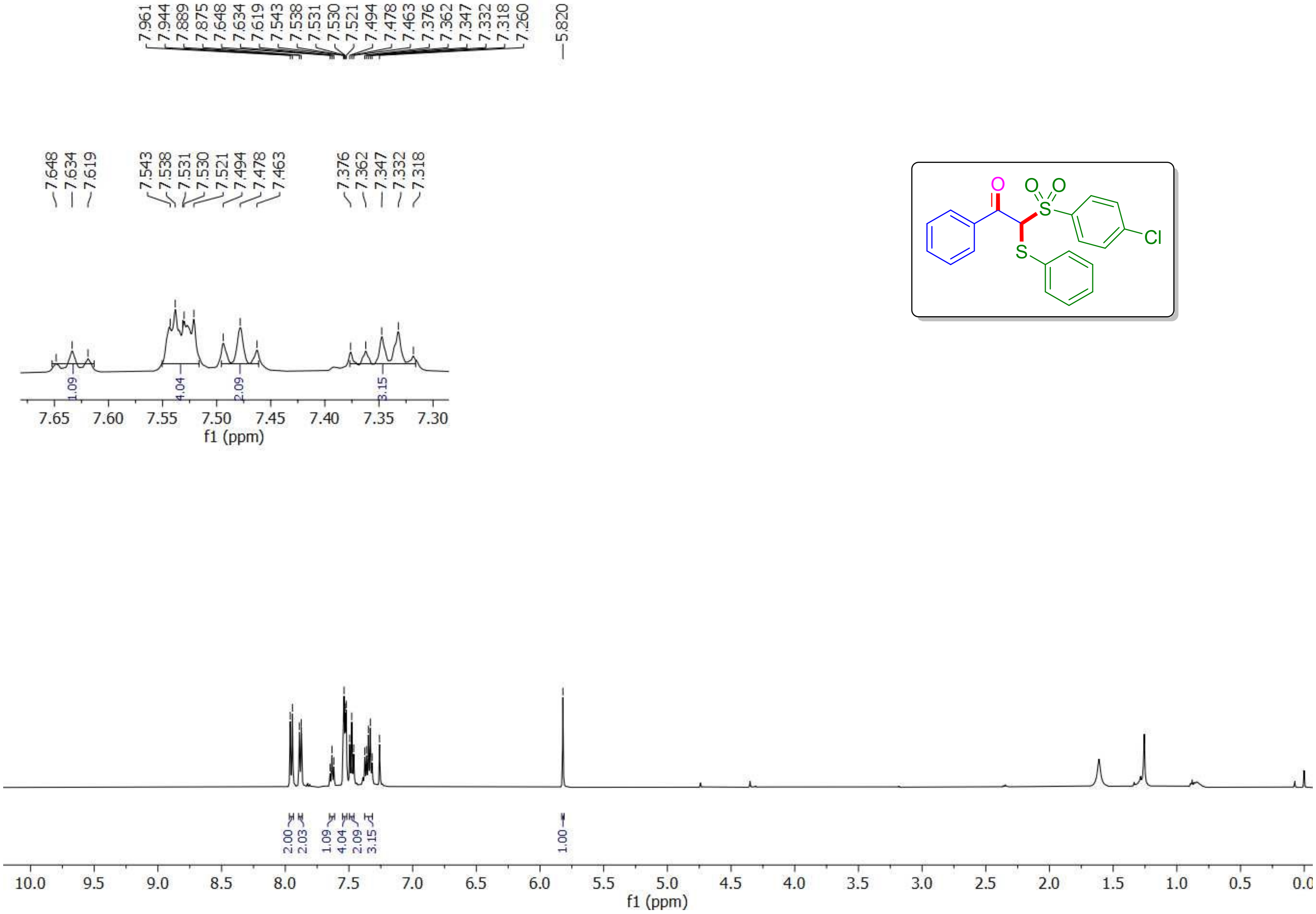
2-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1d): ^{1}H NMR (CDCl$_3$, 500 MHz)



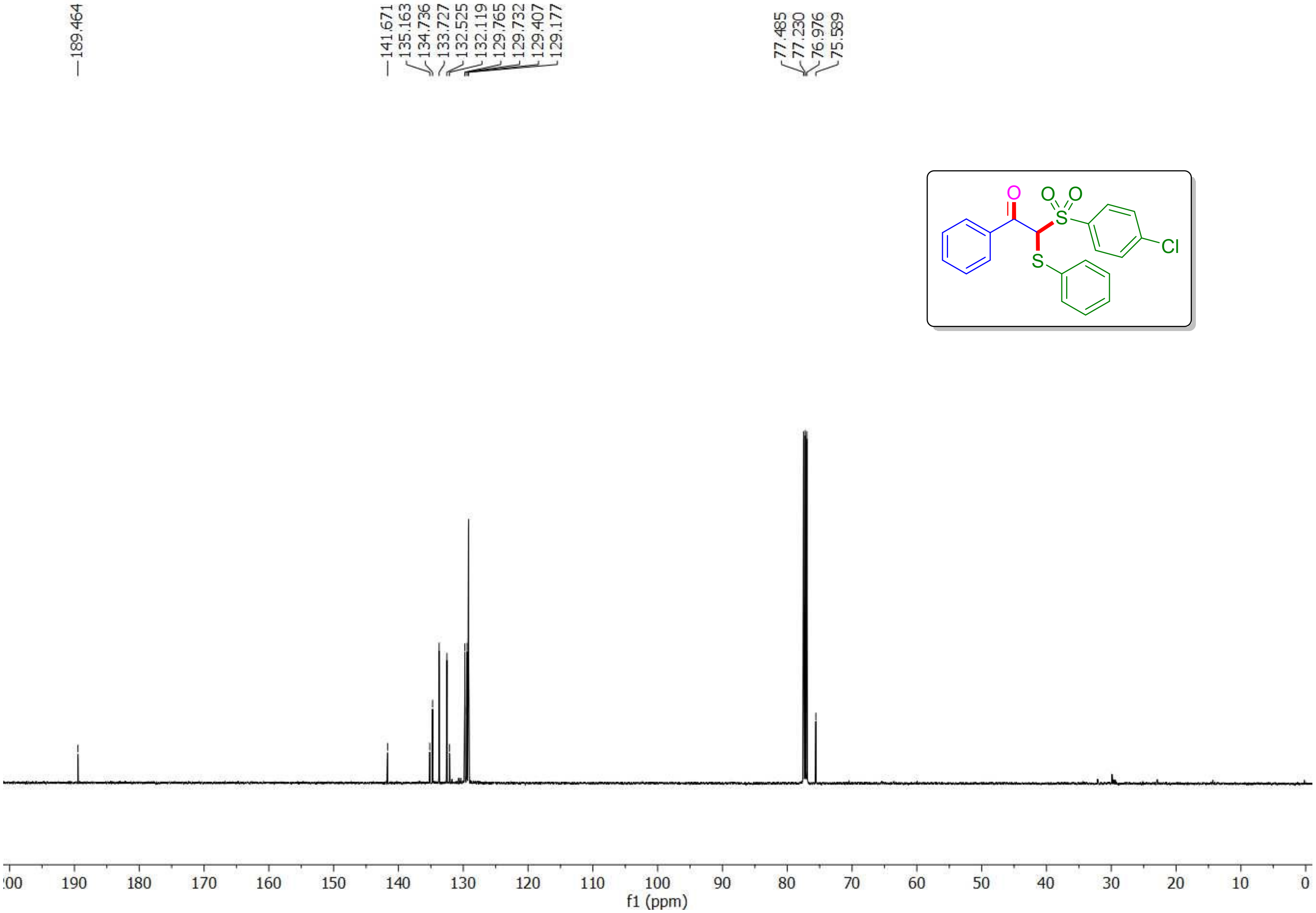
2-((4-Methoxyphenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1d): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



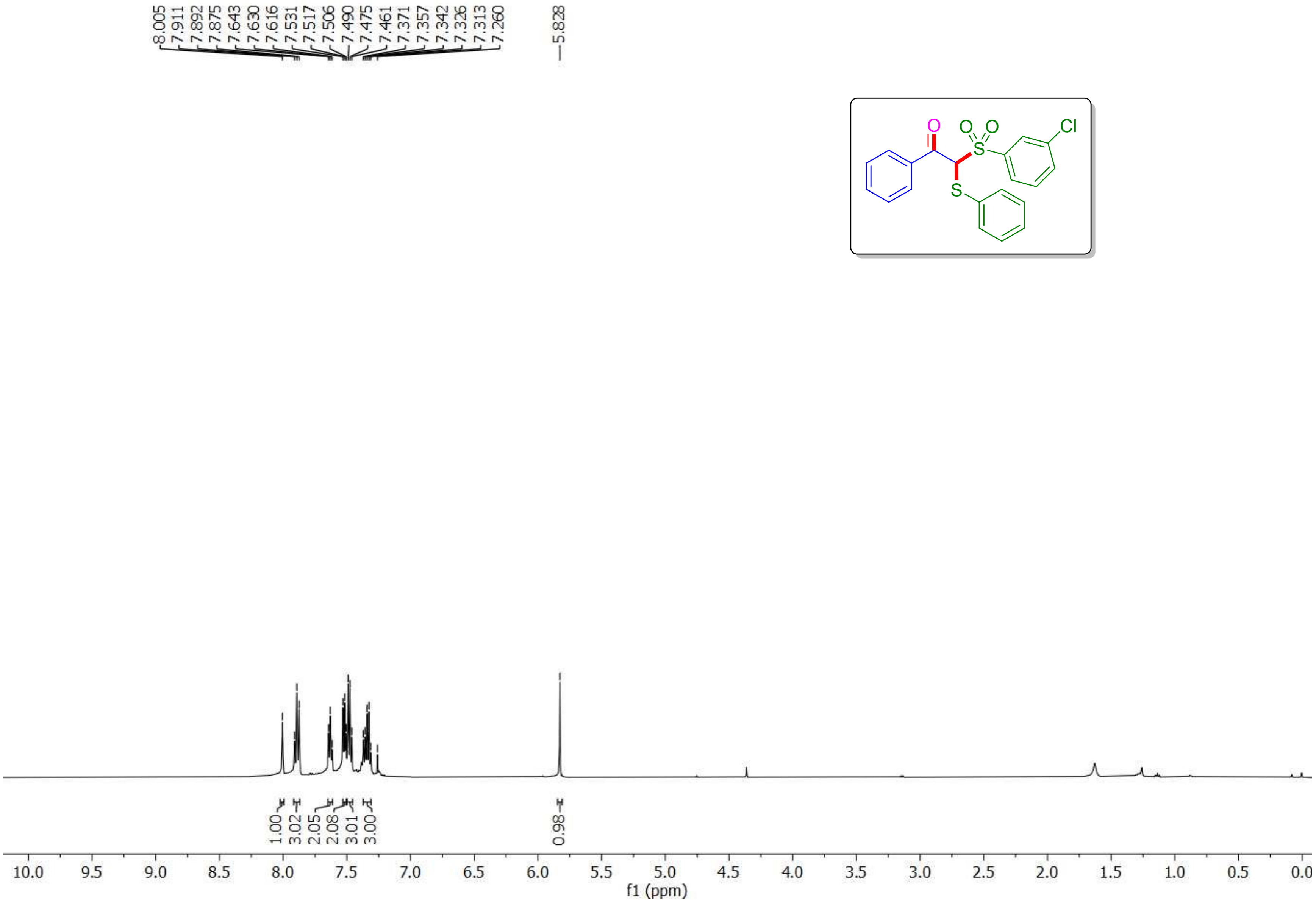
2-((4-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1e): ^{1}H NMR ($CDCl_3$, 500 MHz)



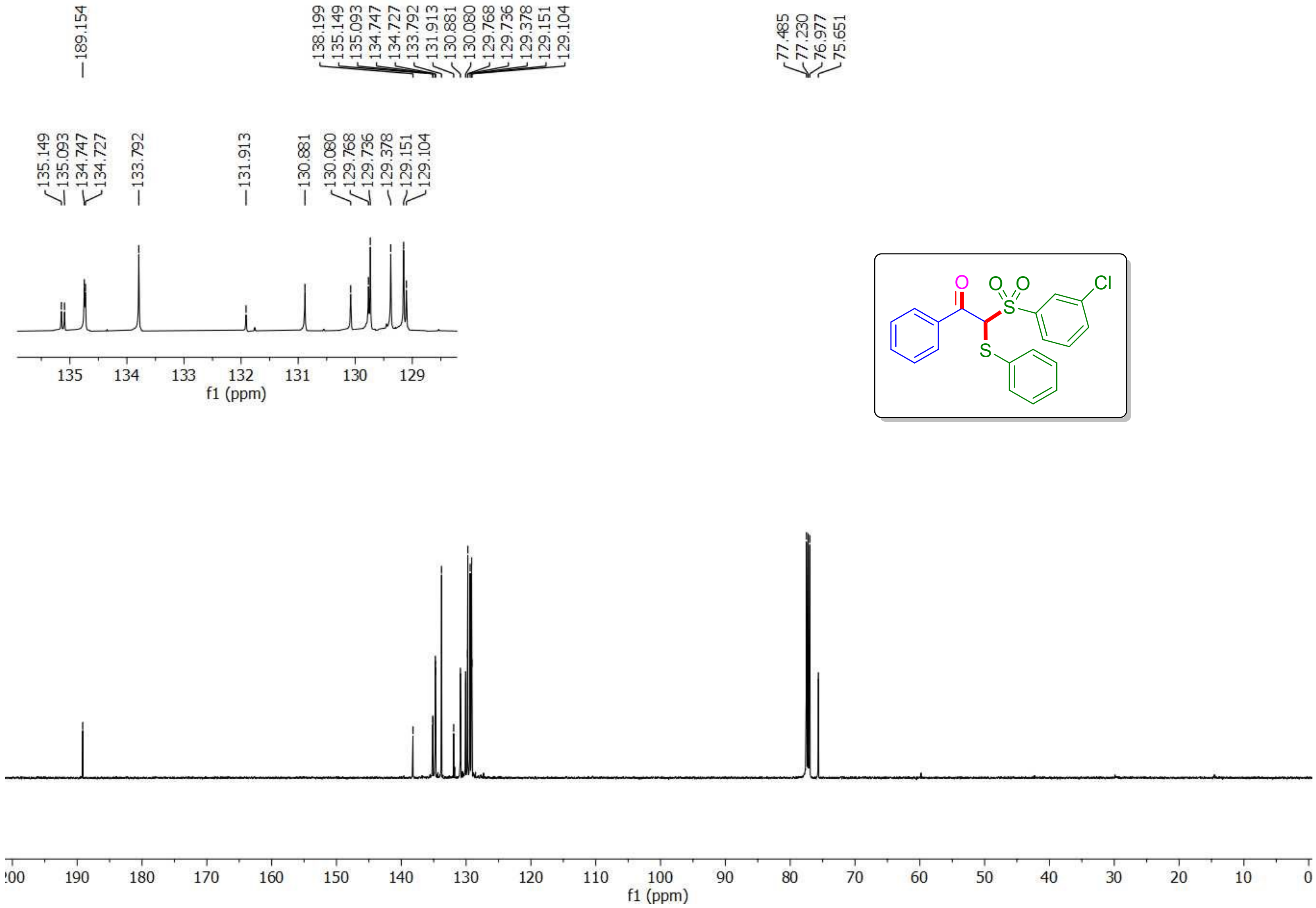
2-((4-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1e): ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz)



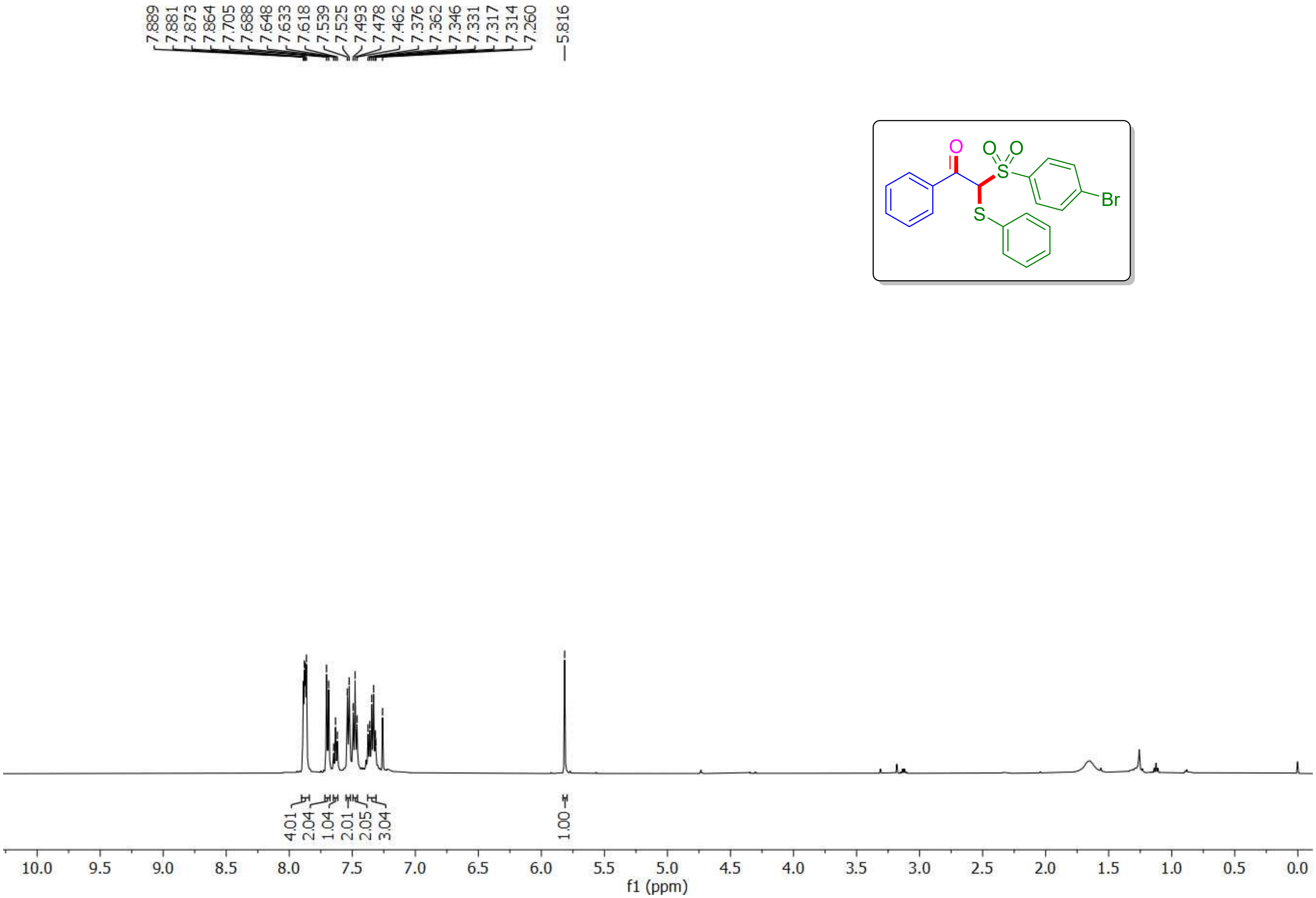
2-((3-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1f): ^{1}H NMR (CDCl$_3$, 500 MHz)



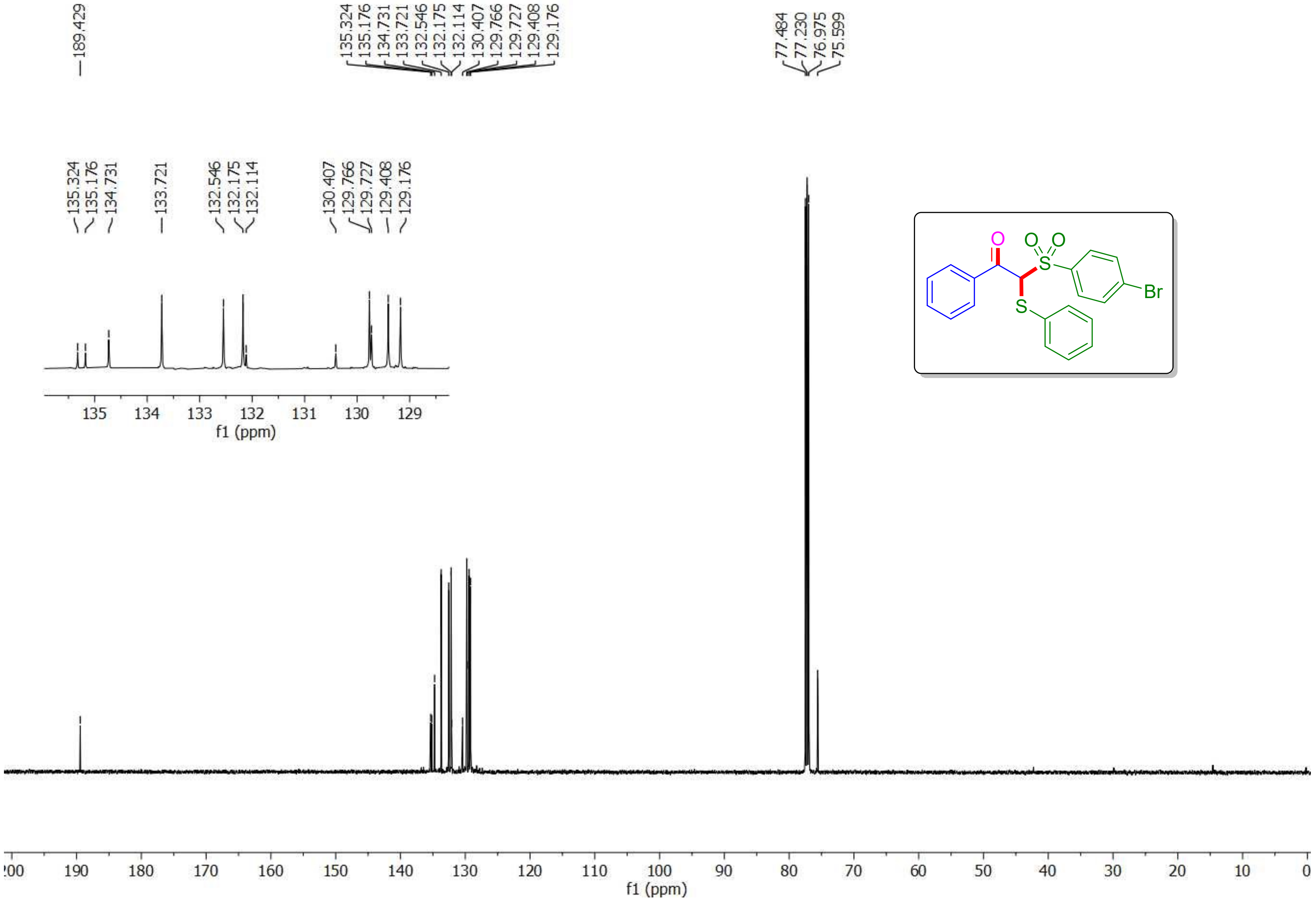
2-((3-Chlorophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1f): ^{13}C NMR (CDCl$_3$, 125 MHz)



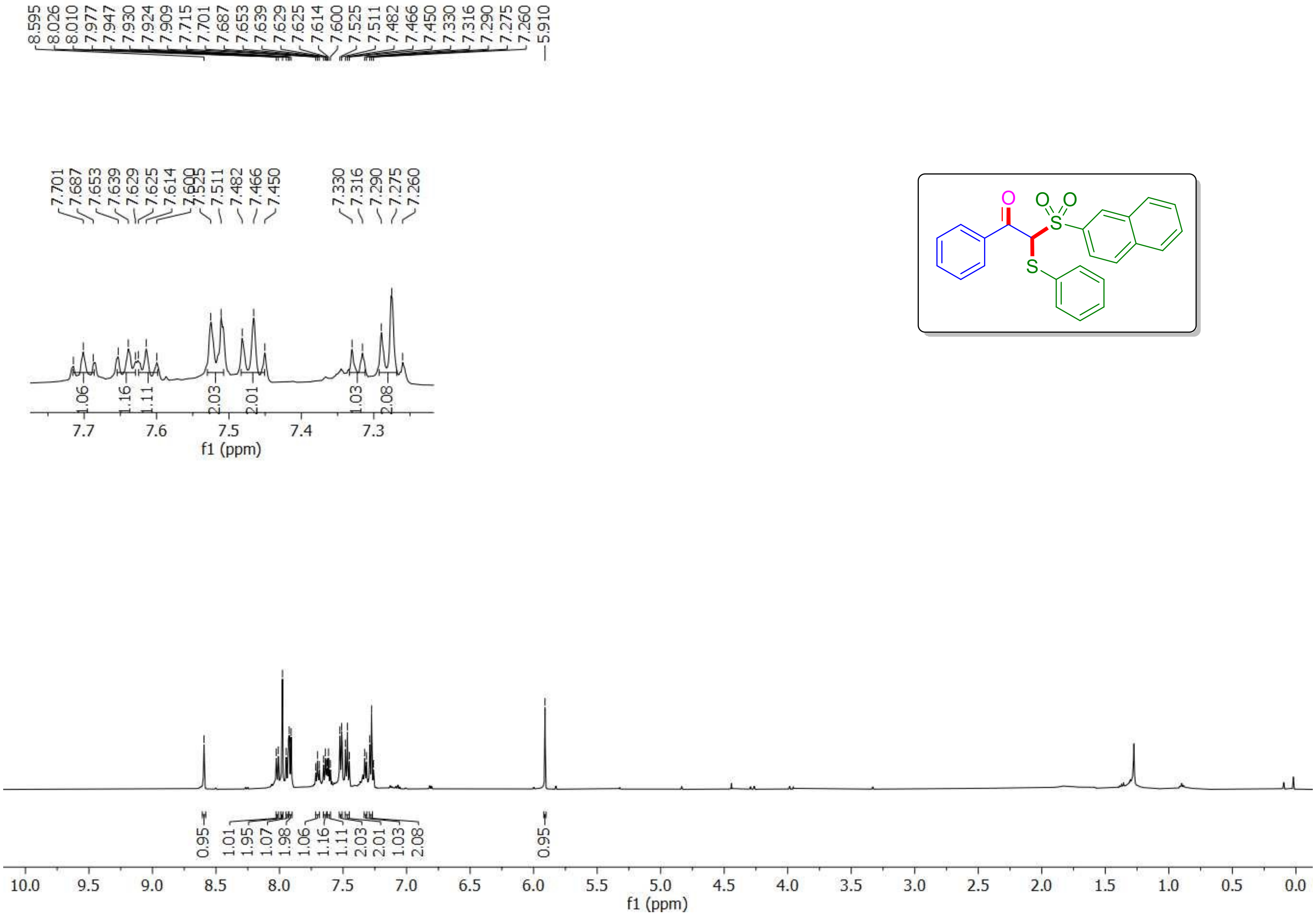
2-((4-Bromophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1g): ^{1}H NMR ($CDCl_3$, 500 MHz)



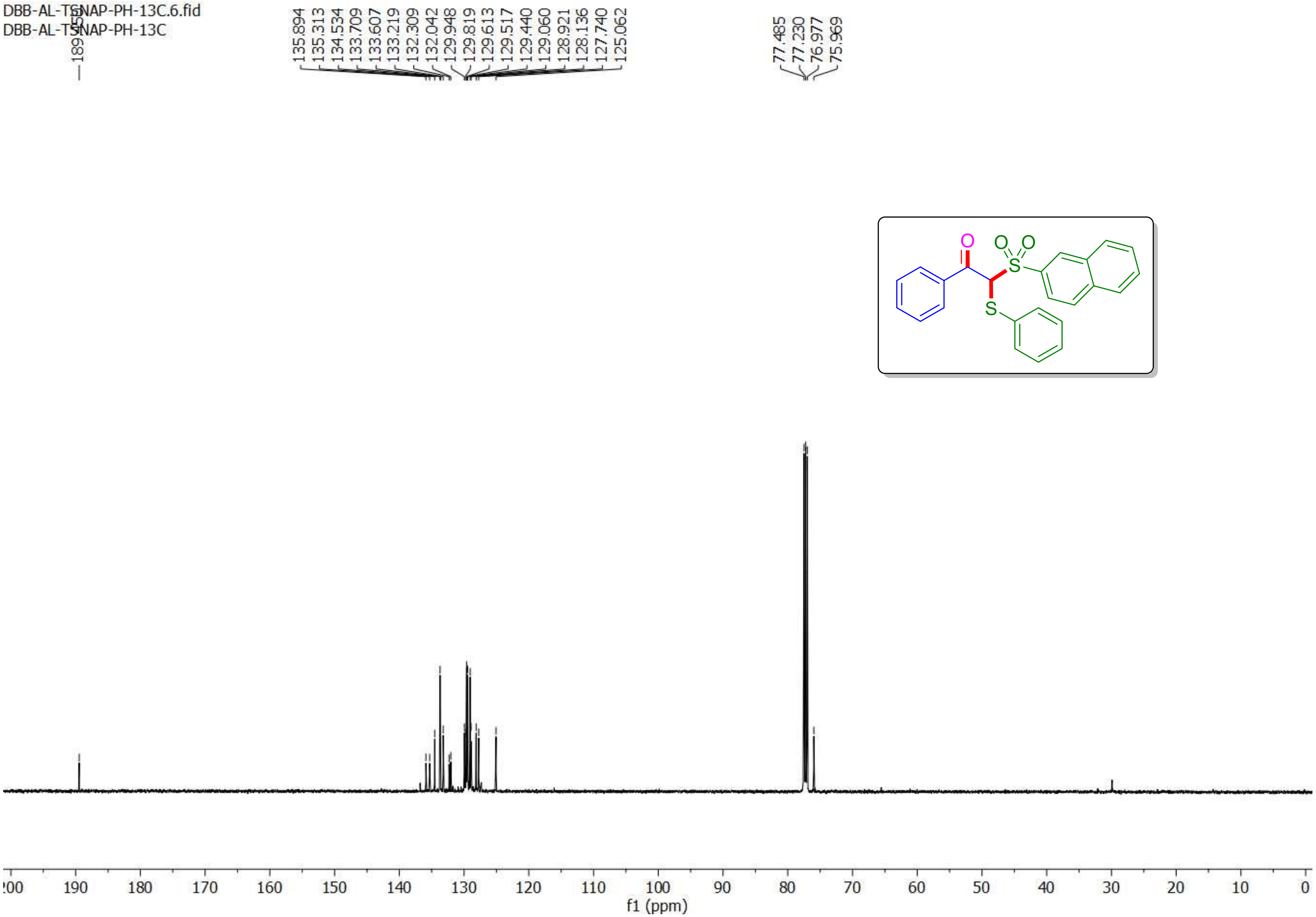
2-((4-Bromophenyl)sulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1g): ^{13}C NMR (CDCl$_3$, 125 MHz)



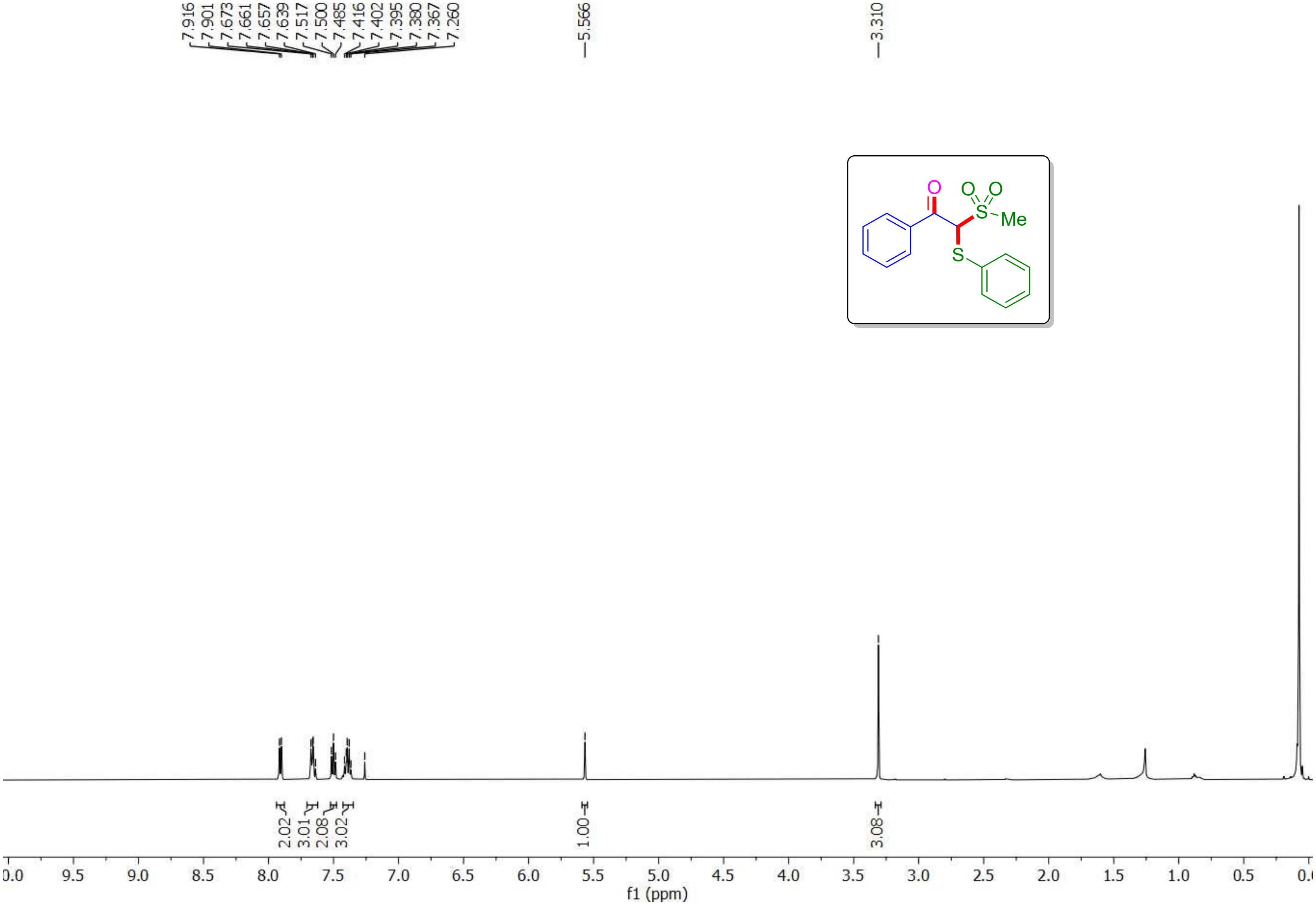
2-(Naphthalen-2-ylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1h): ^{1}H NMR (CDCl$_3$, 500 MHz)



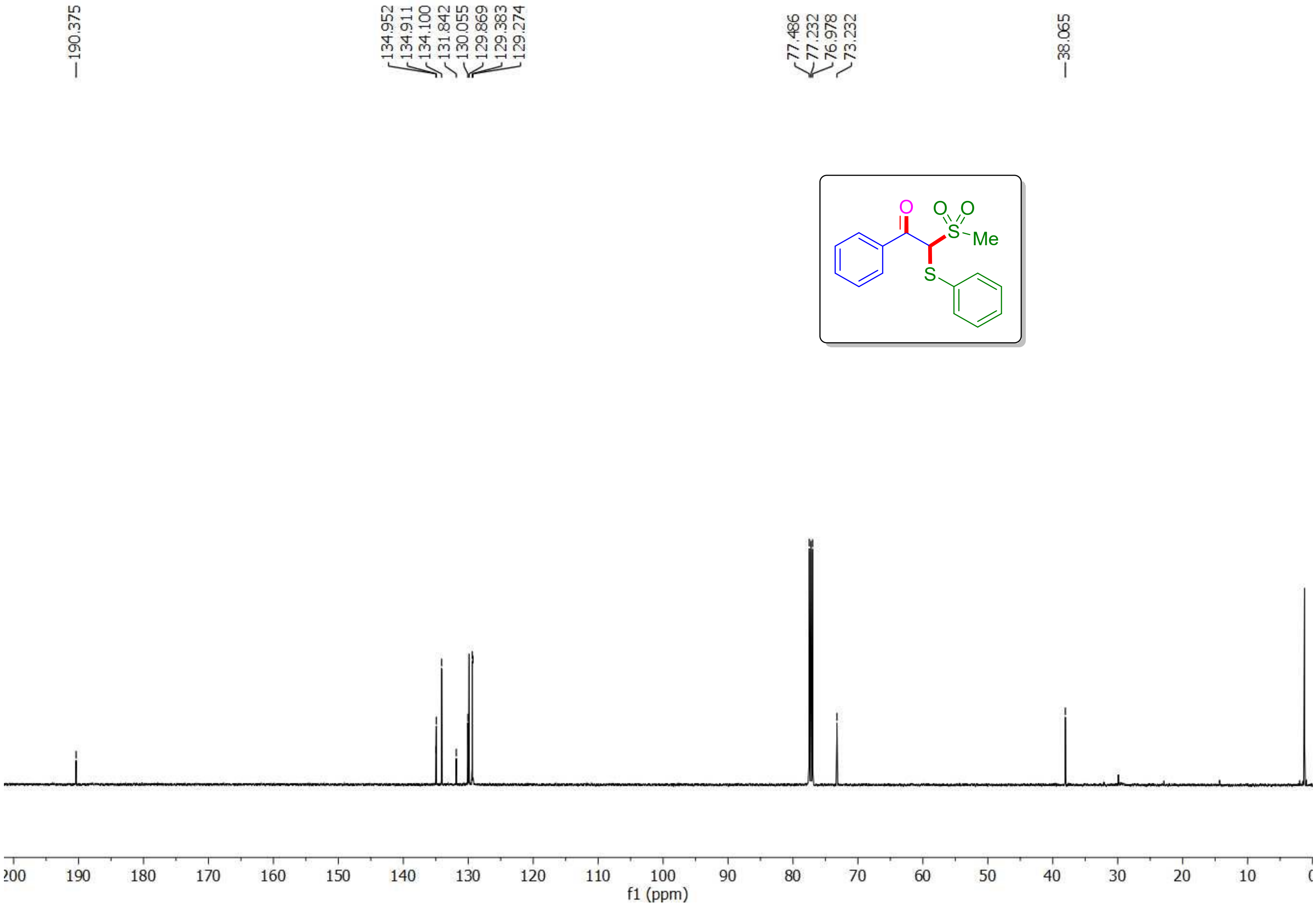
2-(Naphthalen-2-ylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1h): ^{13}C NMR (CDCl$_3$, 125 MHz)



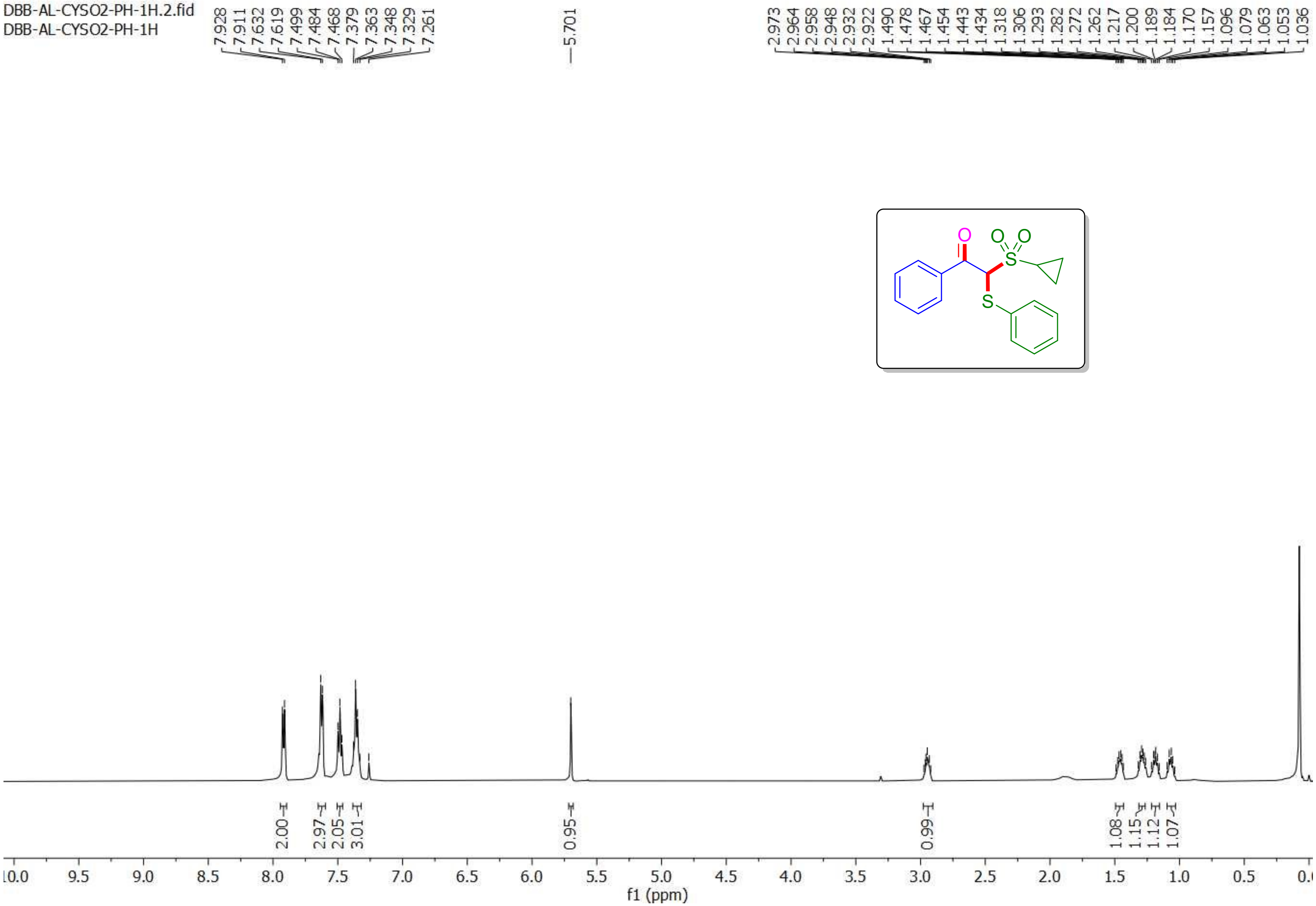
2-(Methylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1i): ^{1}H NMR (CDCl$_3$, 500 MHz)



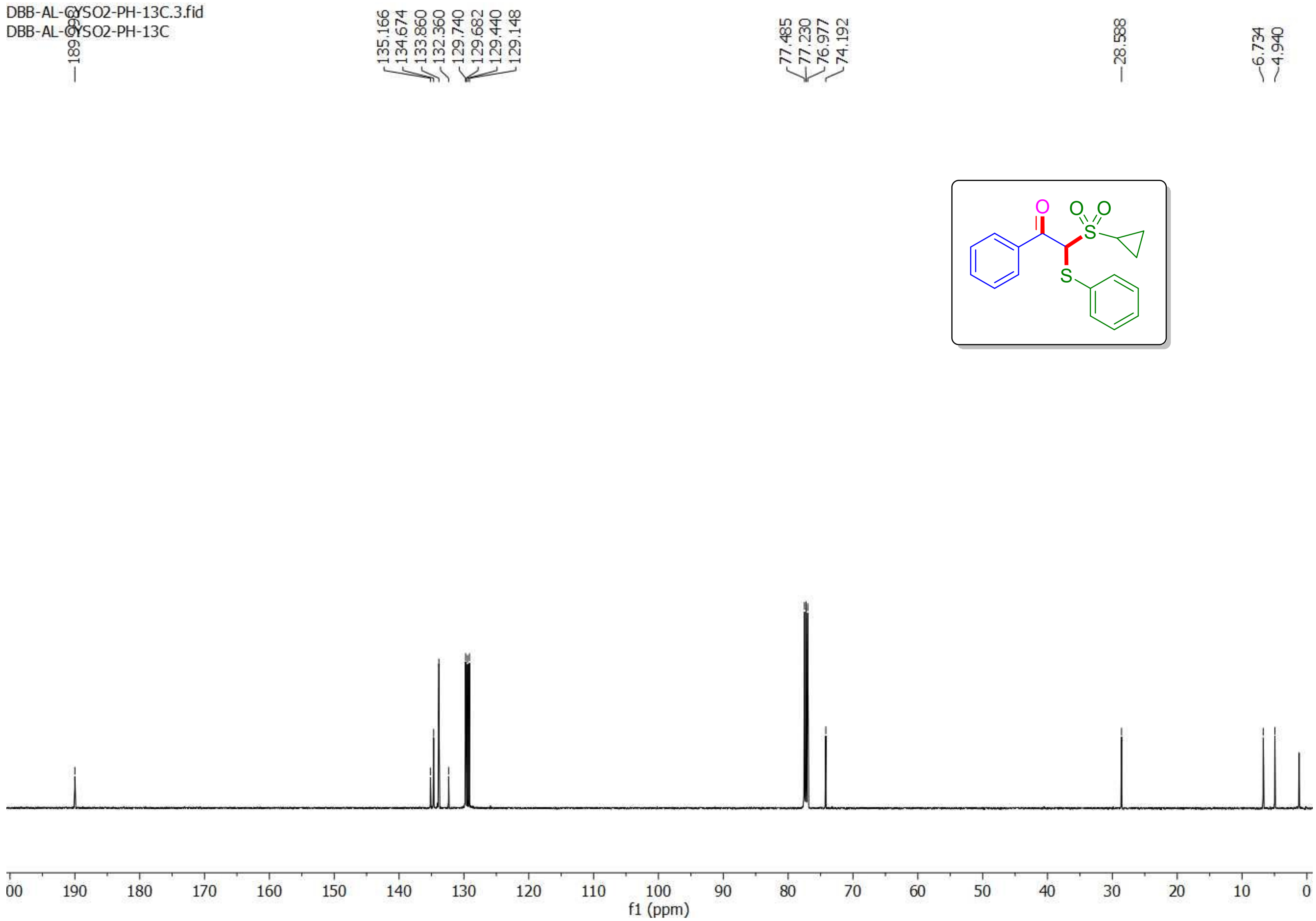
2-(Methylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1i): ^{13}C NMR (CDCl$_3$, 125 MHz)



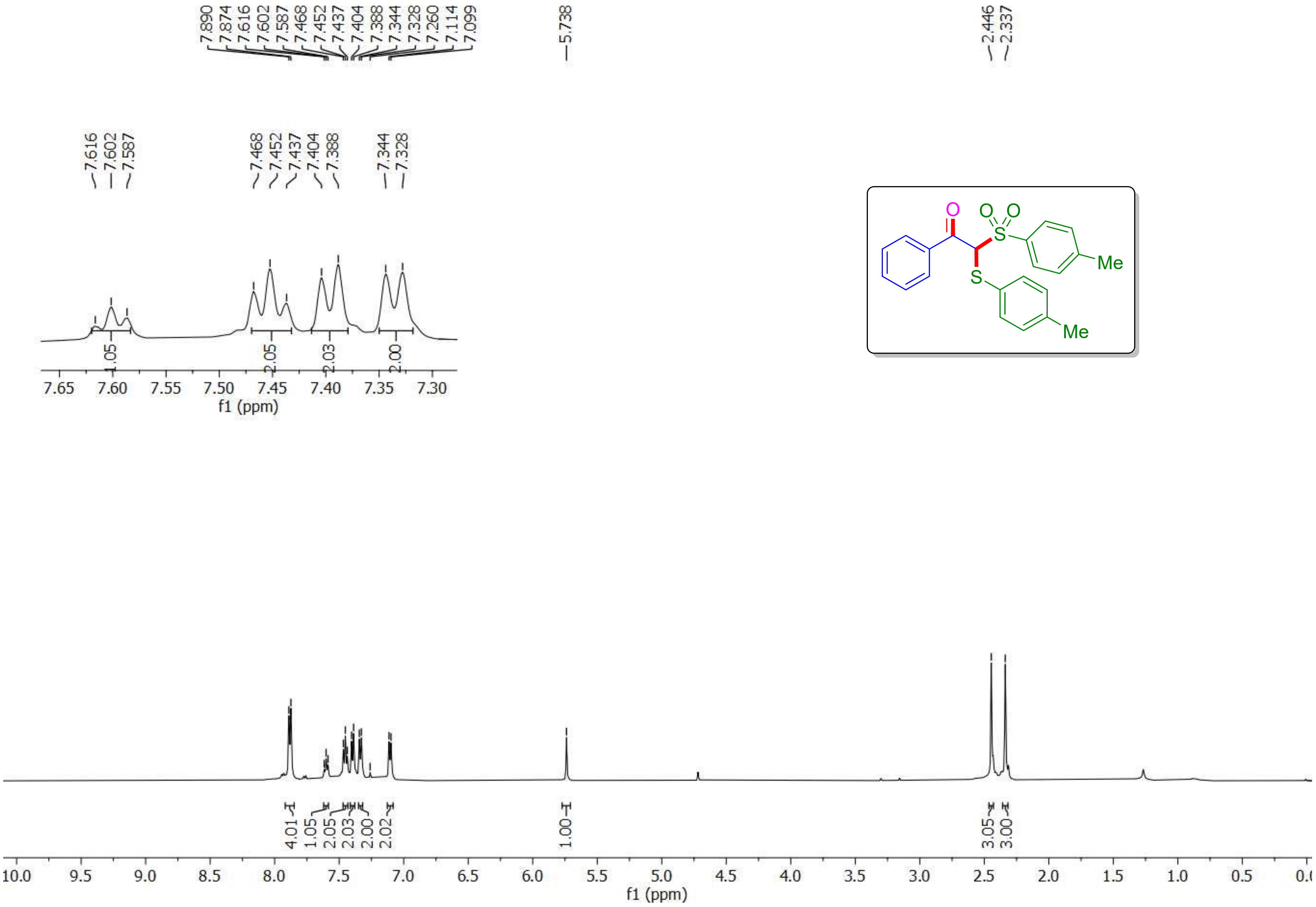
2-(Cyclopropylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1j): ¹H NMR (CDCl₃, 500 MHz)



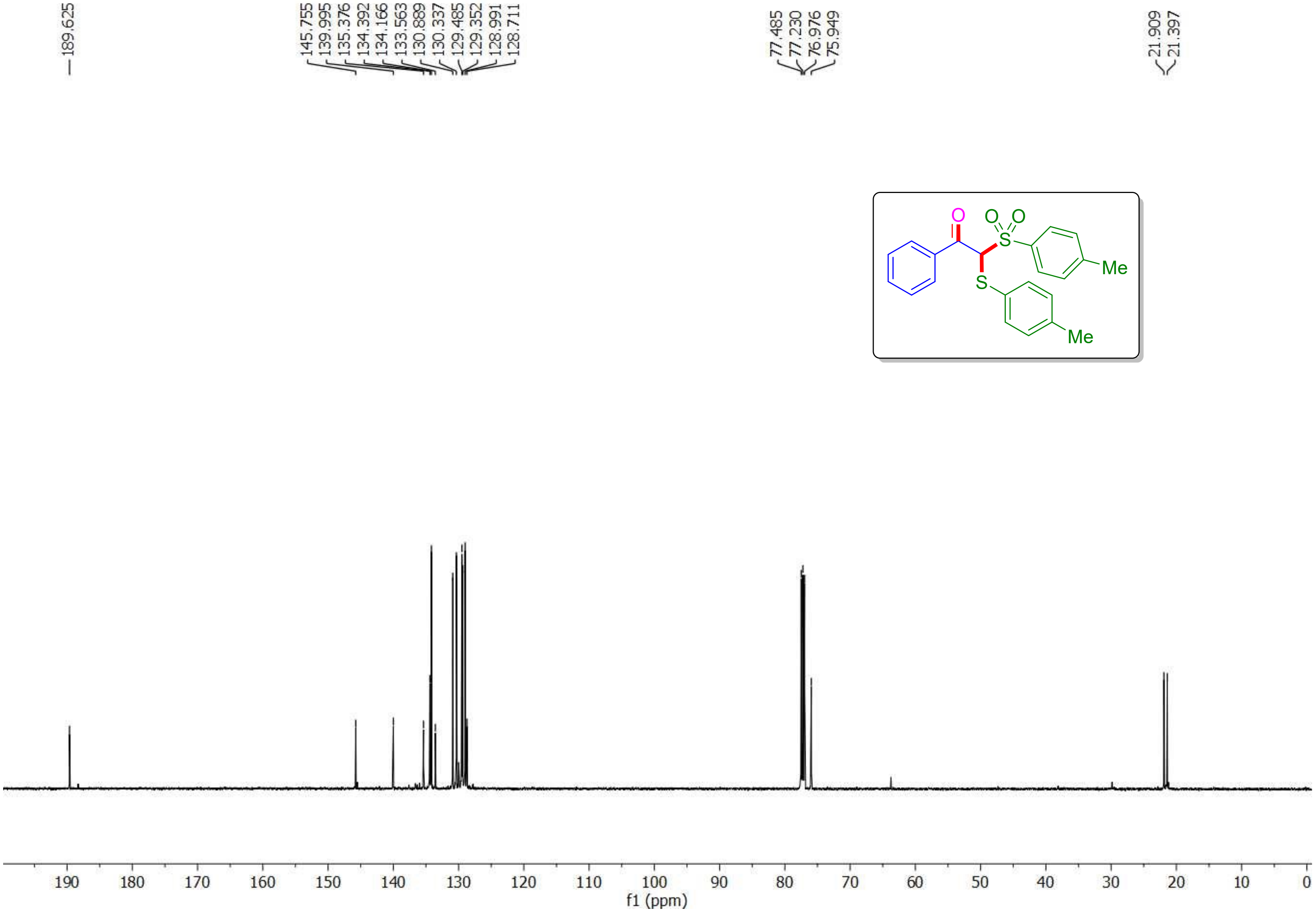
2-(Cyclopropylsulfonyl)-1-phenyl-2-(phenylthio)ethan-1-one (1j): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



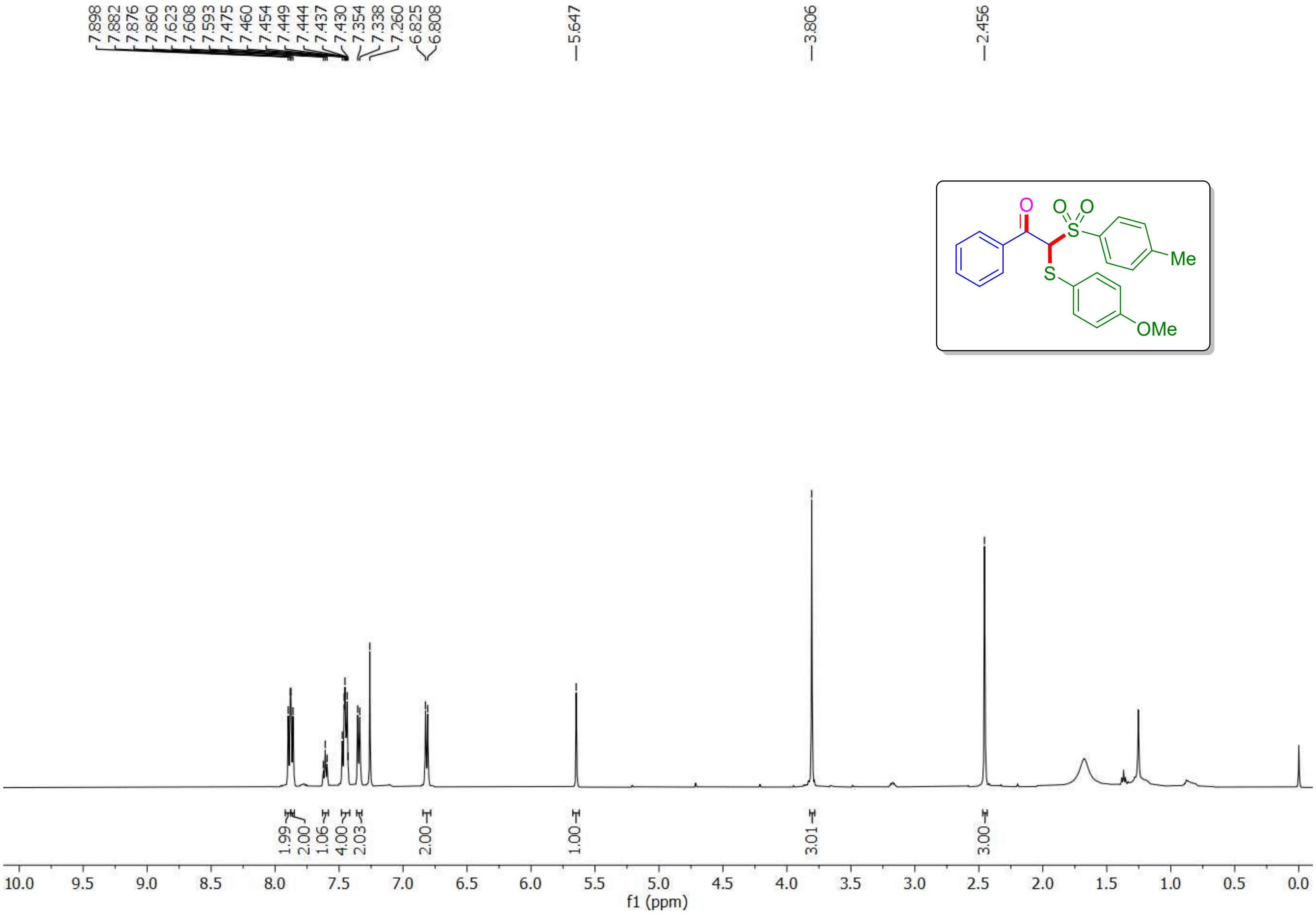
1-Phenyl-2-(p-tolylthio)-2-tosylethan-1-one (1k): ^{1}H NMR (CDCl$_3$, 500 MHz)



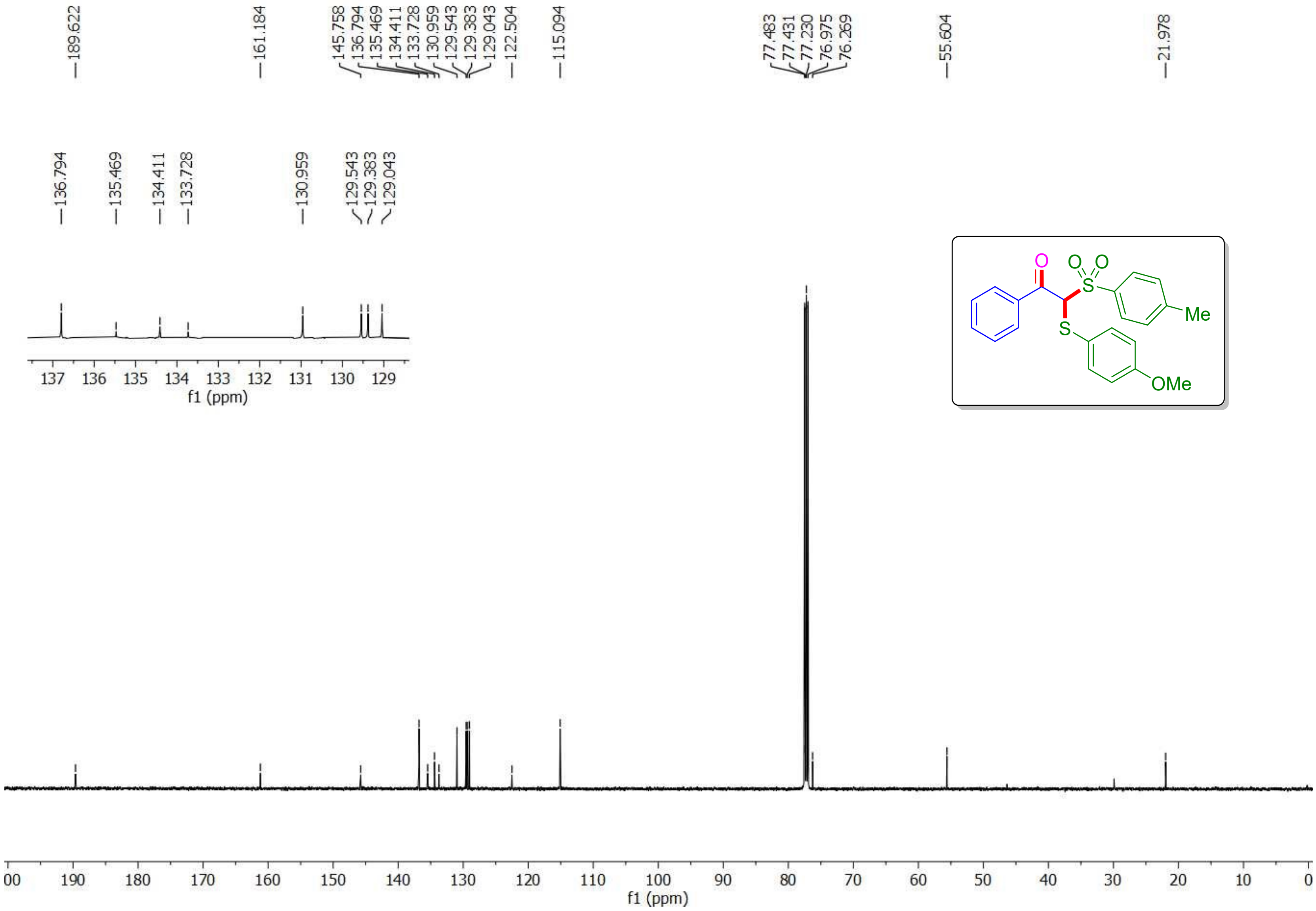
1-Phenyl-2-(p-tolylthio)-2-tosylethan-1-one (1k): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



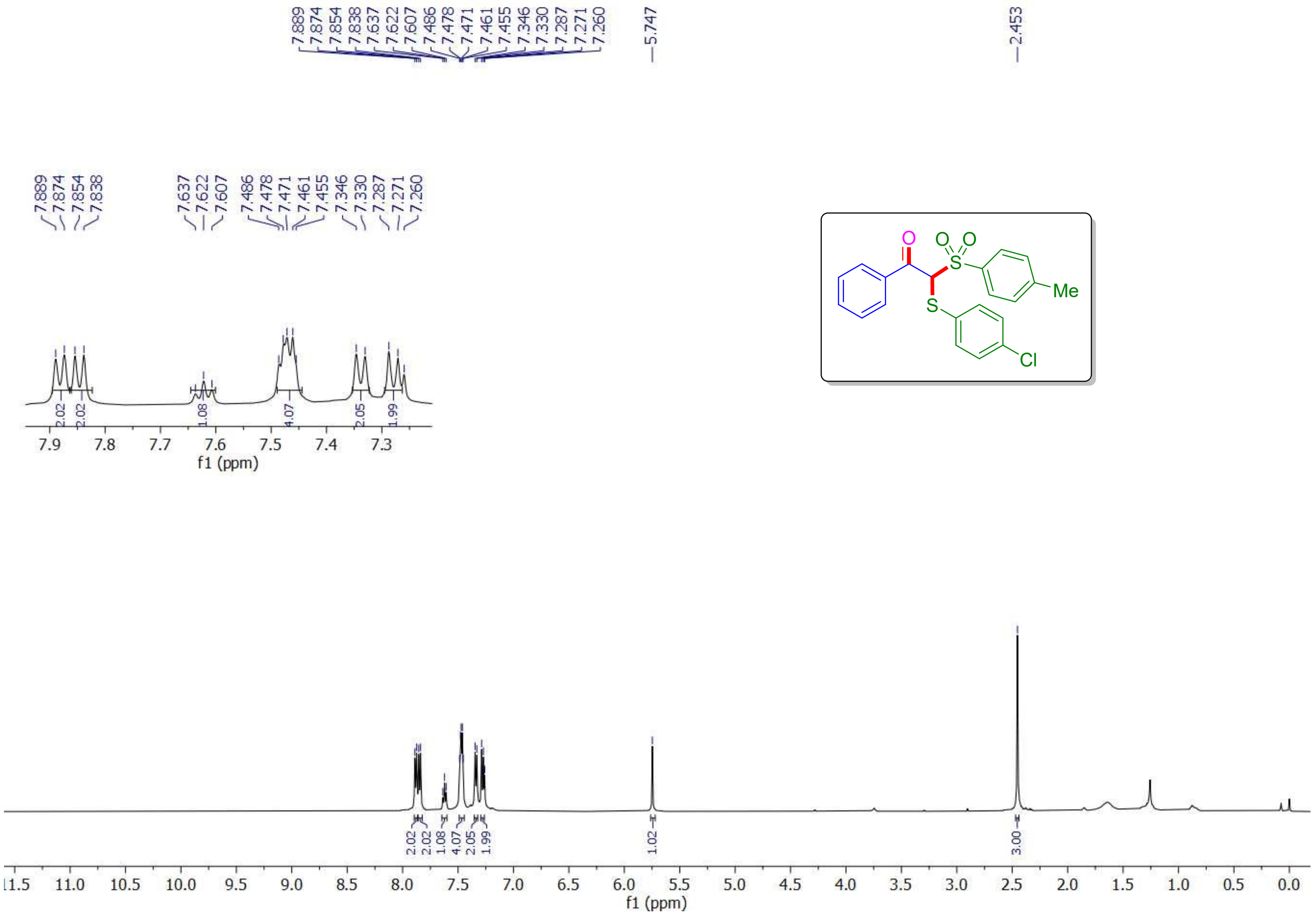
2-((4-Methoxyphenyl)thio)-1-phenyl-2-tosylethan-1-one (1l): ^{1}H NMR (CDCl$_3$, 500 MHz)



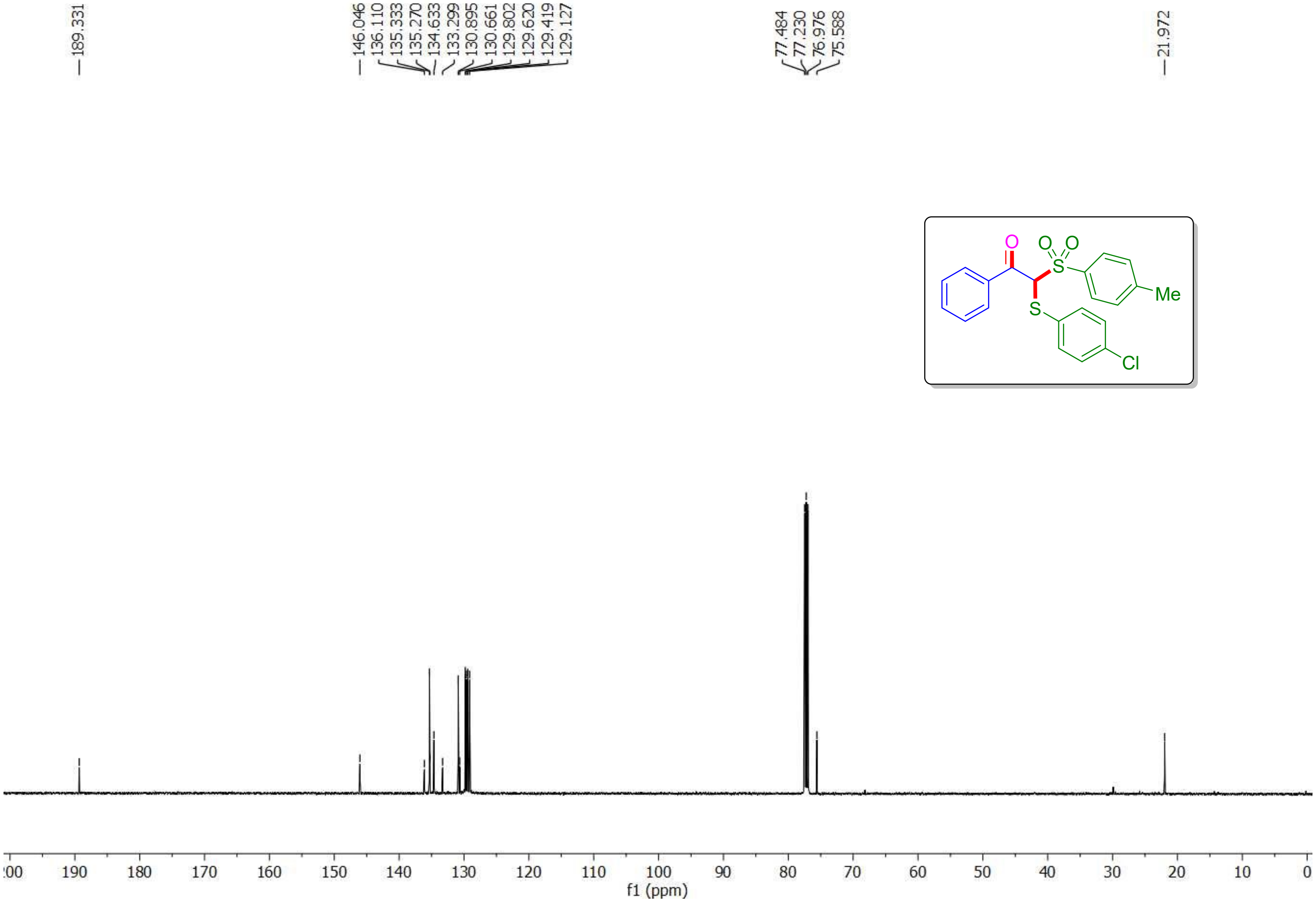
2-((4-Methoxyphenyl)thio)-1-phenyl-2-tosylethan-1-one (1l): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



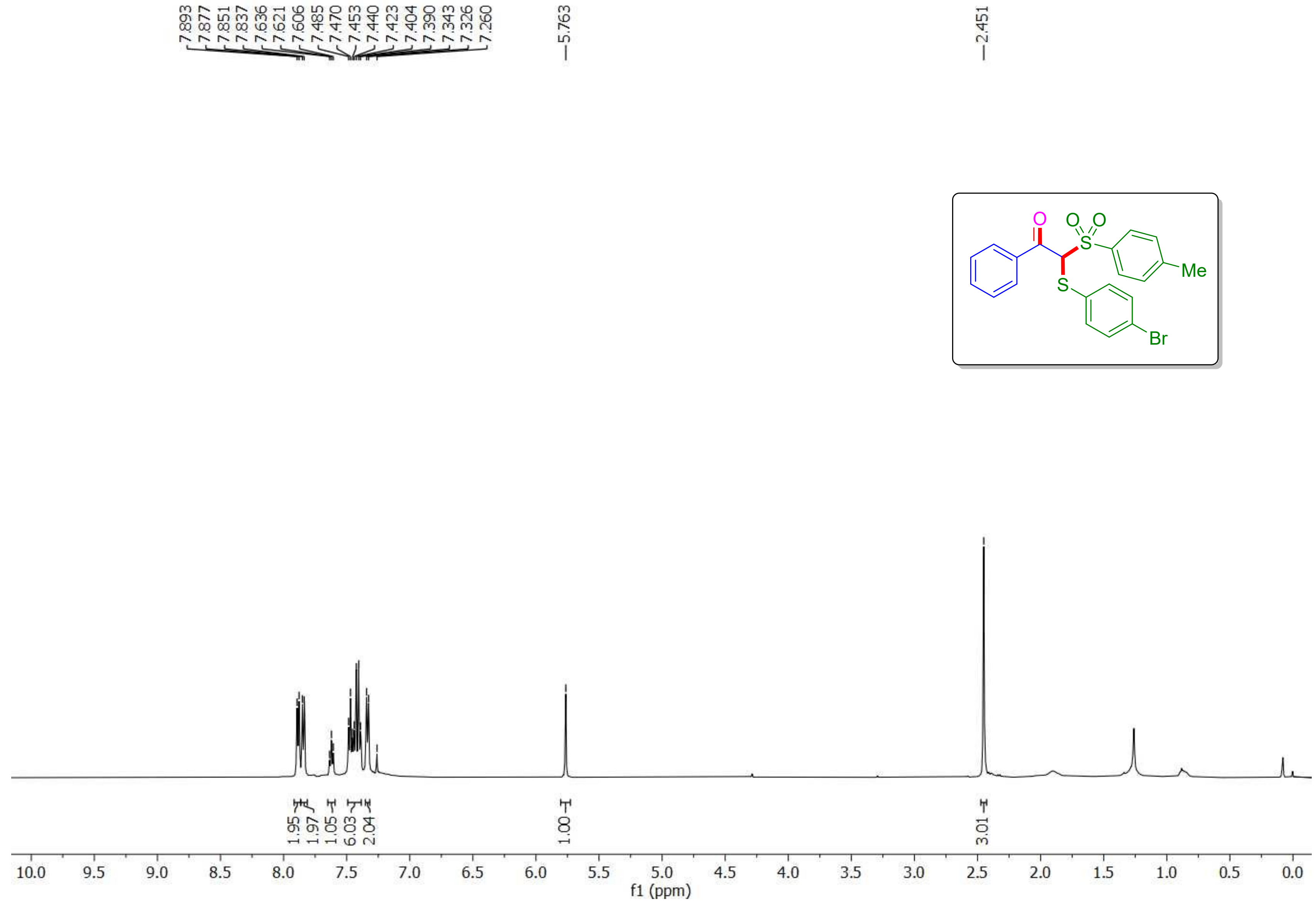
2-((4-Chlorophenyl)thio)-1-phenyl-2-tosylethan-1-one (1m): ^{1}*H NMR (CDCl$_3$, 500 MHz)*



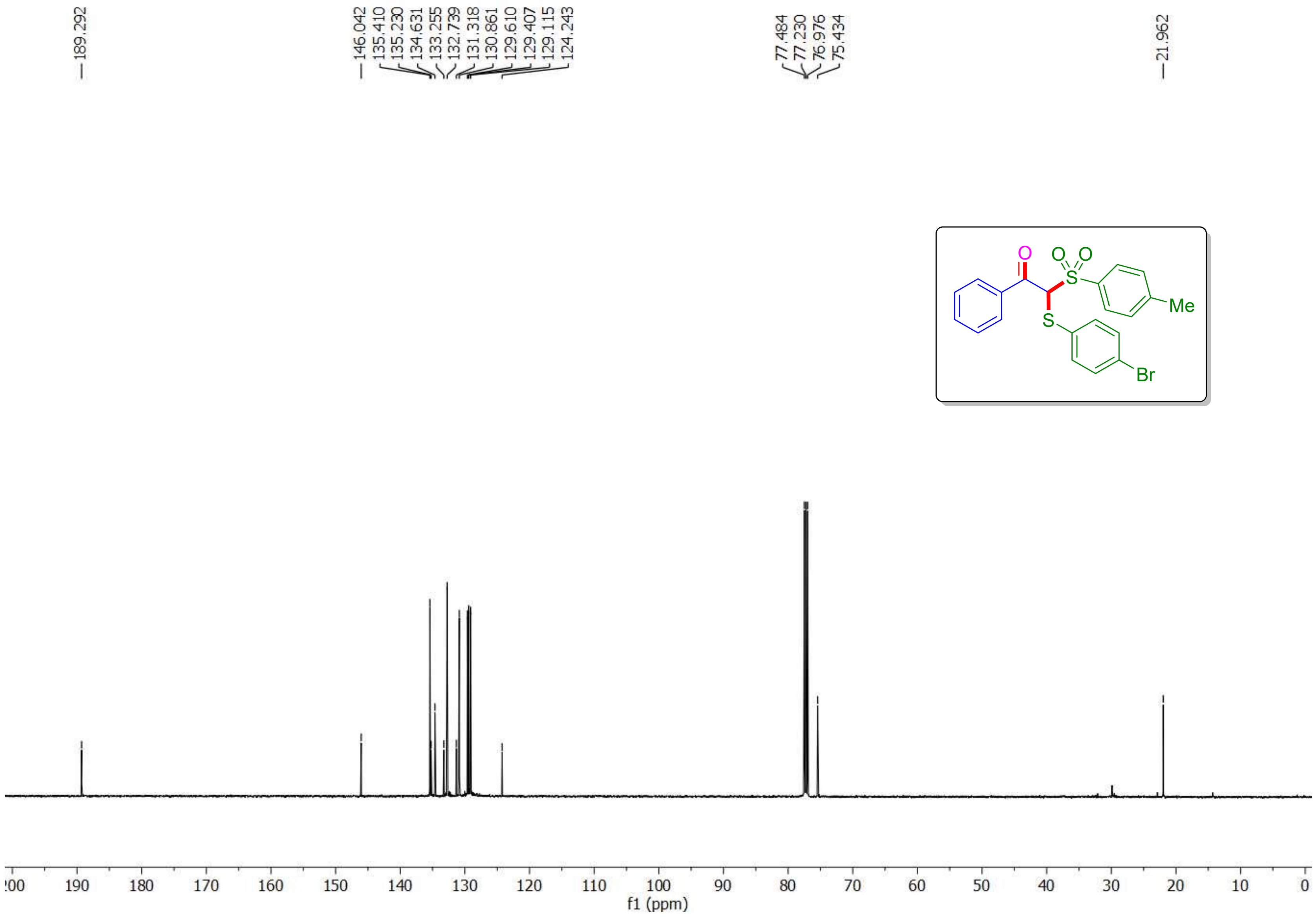
2-((4-Chlorophenyl)thio)-1-phenyl-2-tosylethan-1-one (1m): ^{13}C NMR (CDCl$_3$, 125 MHz)



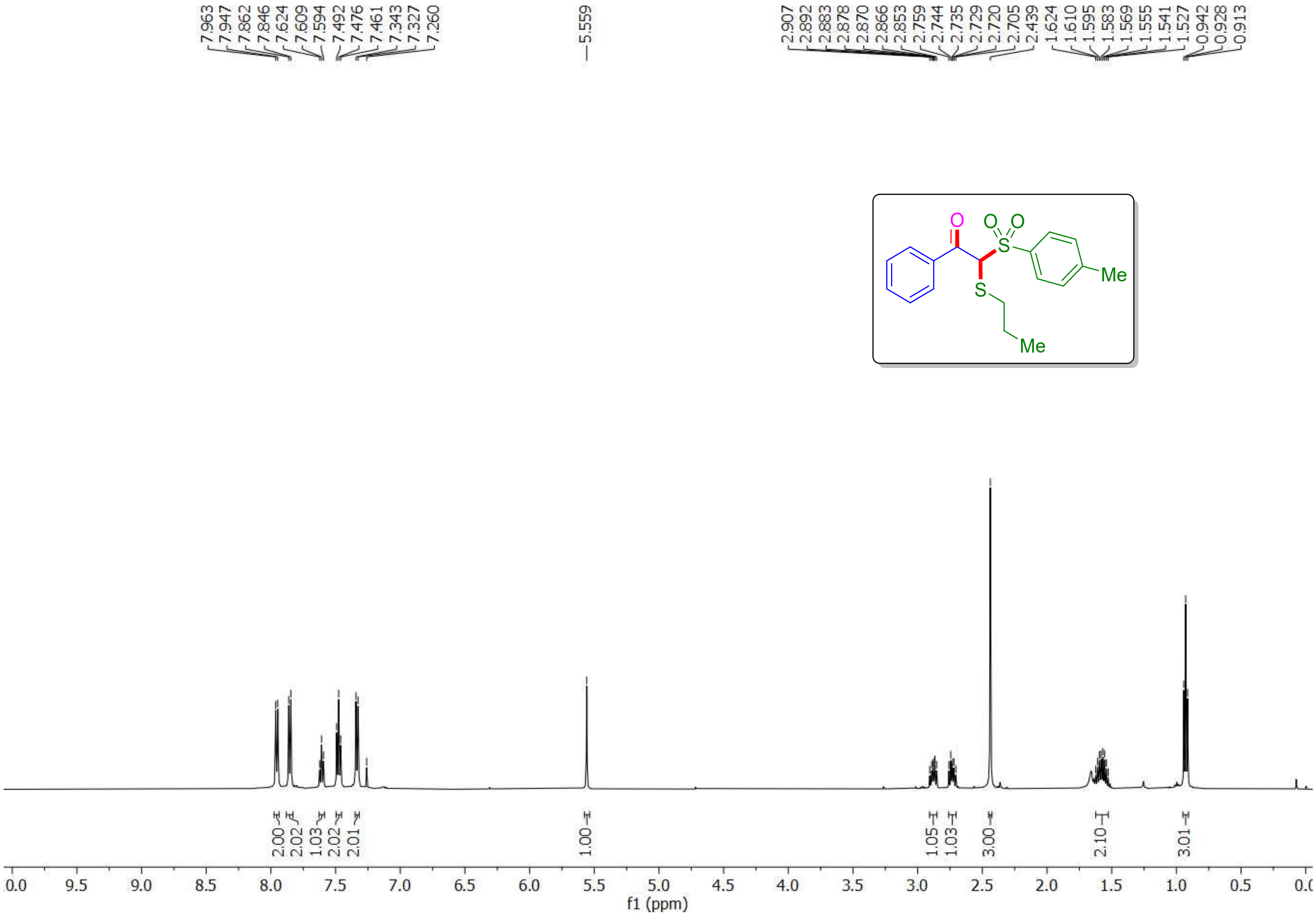
2-((4-Bromophenyl)thio)-1-phenyl-2-tosylethan-1-one (1n): ^{1}H NMR (CDCl$_3$, 500 MHz)



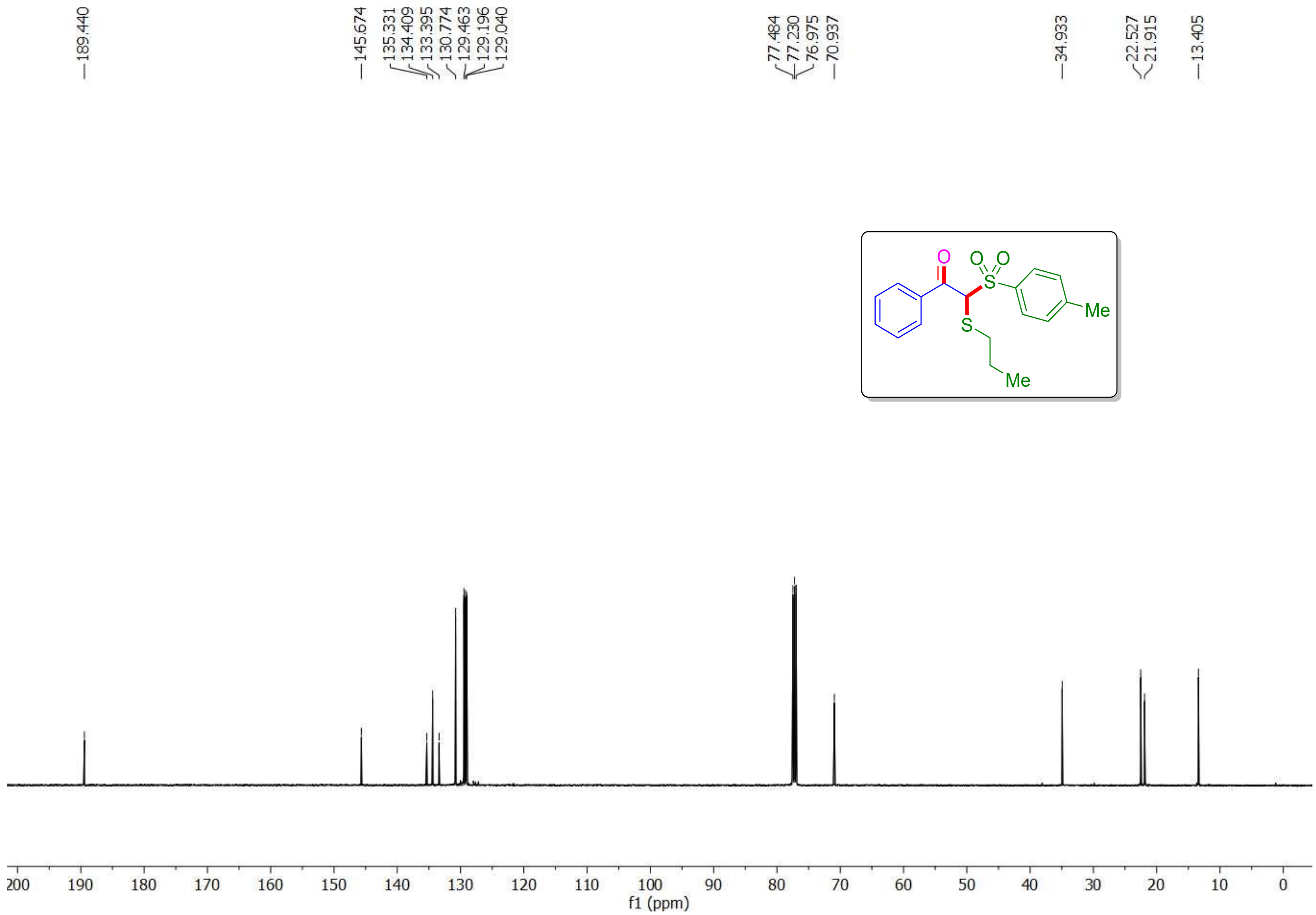
2-((4-Bromophenyl)thio)-1-phenyl-2-tosylethan-1-one (1n): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



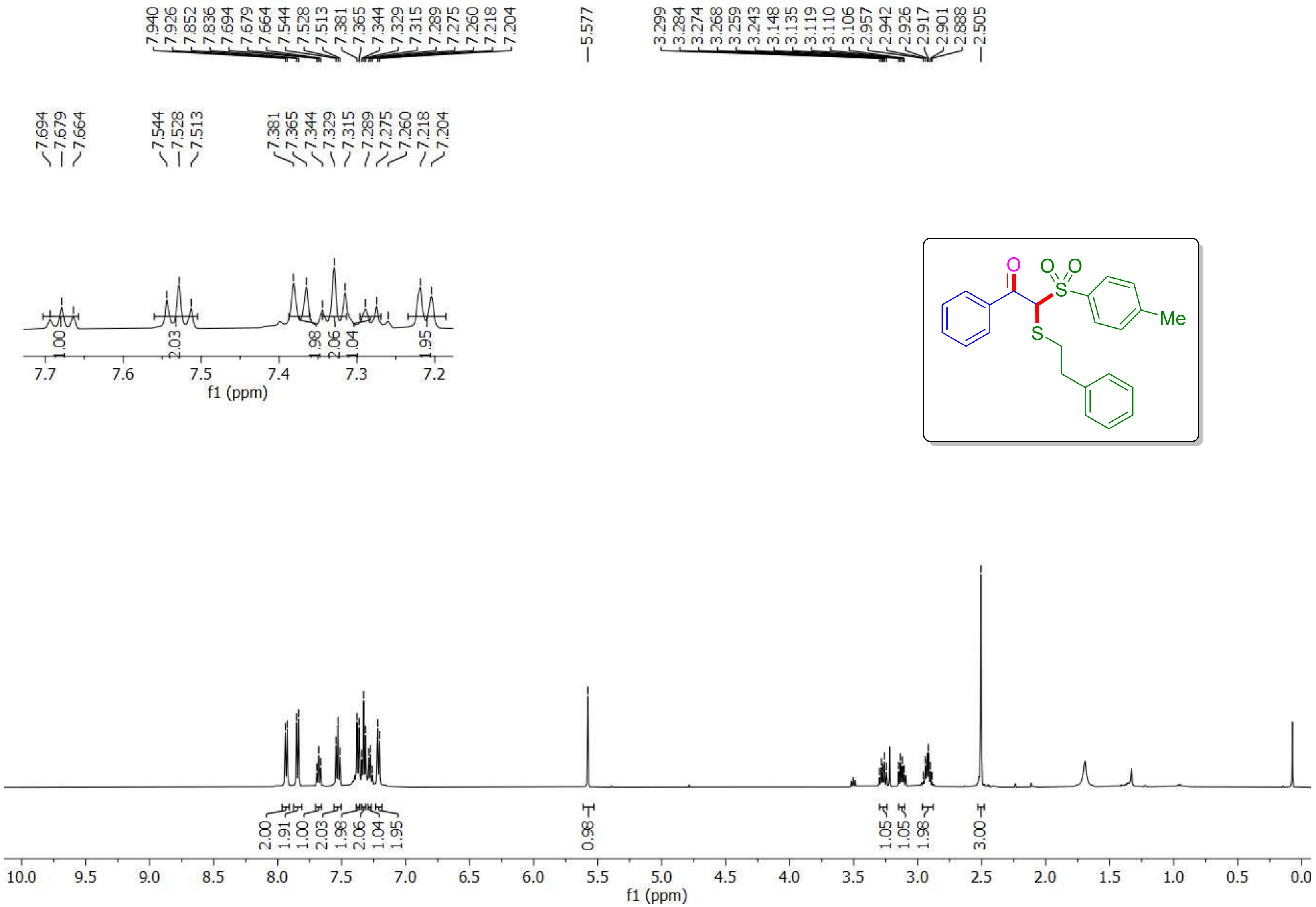
1-Phenyl-2-(propylthio)-2-tosylethan-1-one (1o): ^{1}H NMR (CDCl$_3$, 500 MHz)



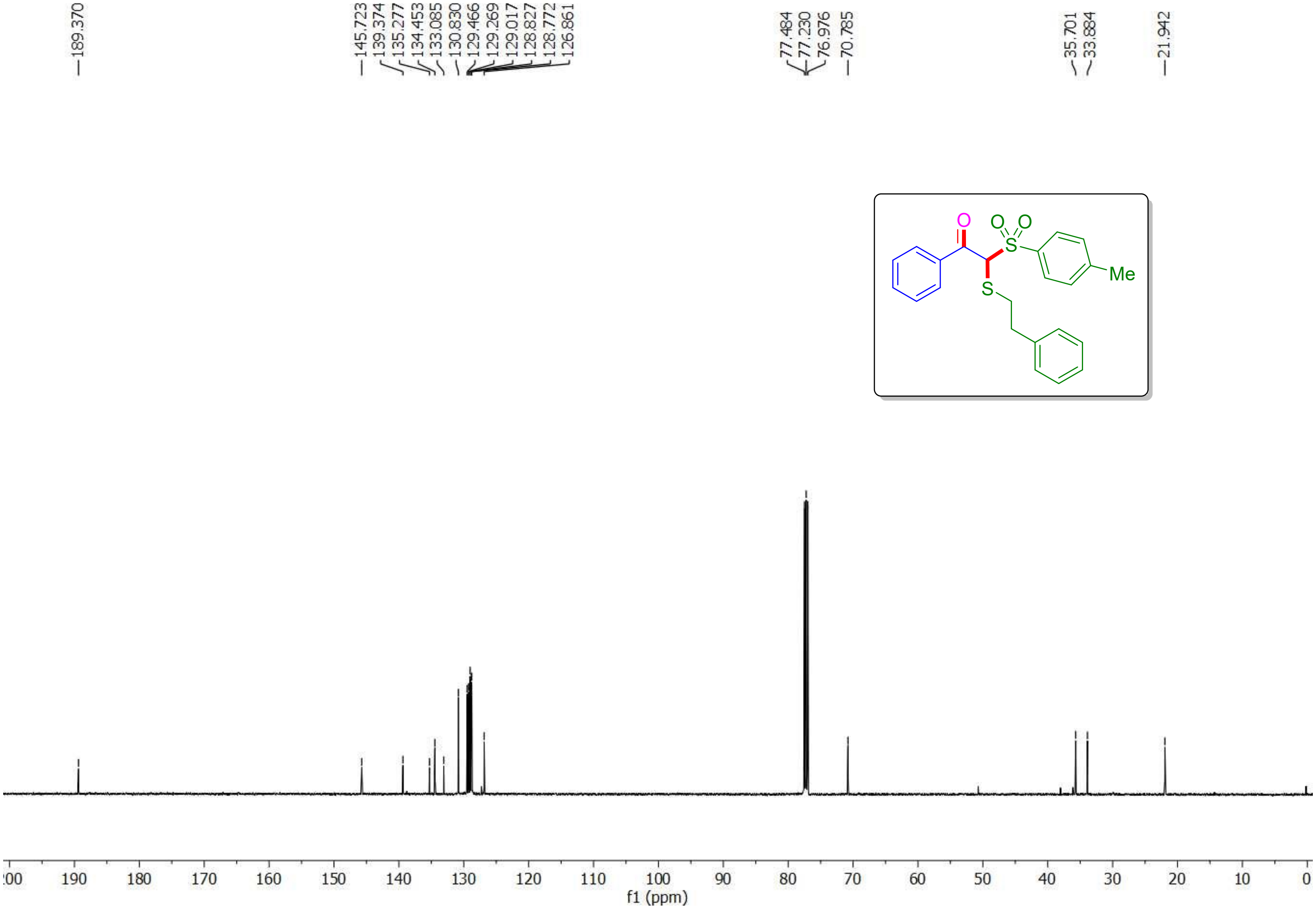
1-Phenyl-2-(propylthio)-2-tosylethan-1-one (1o): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz)



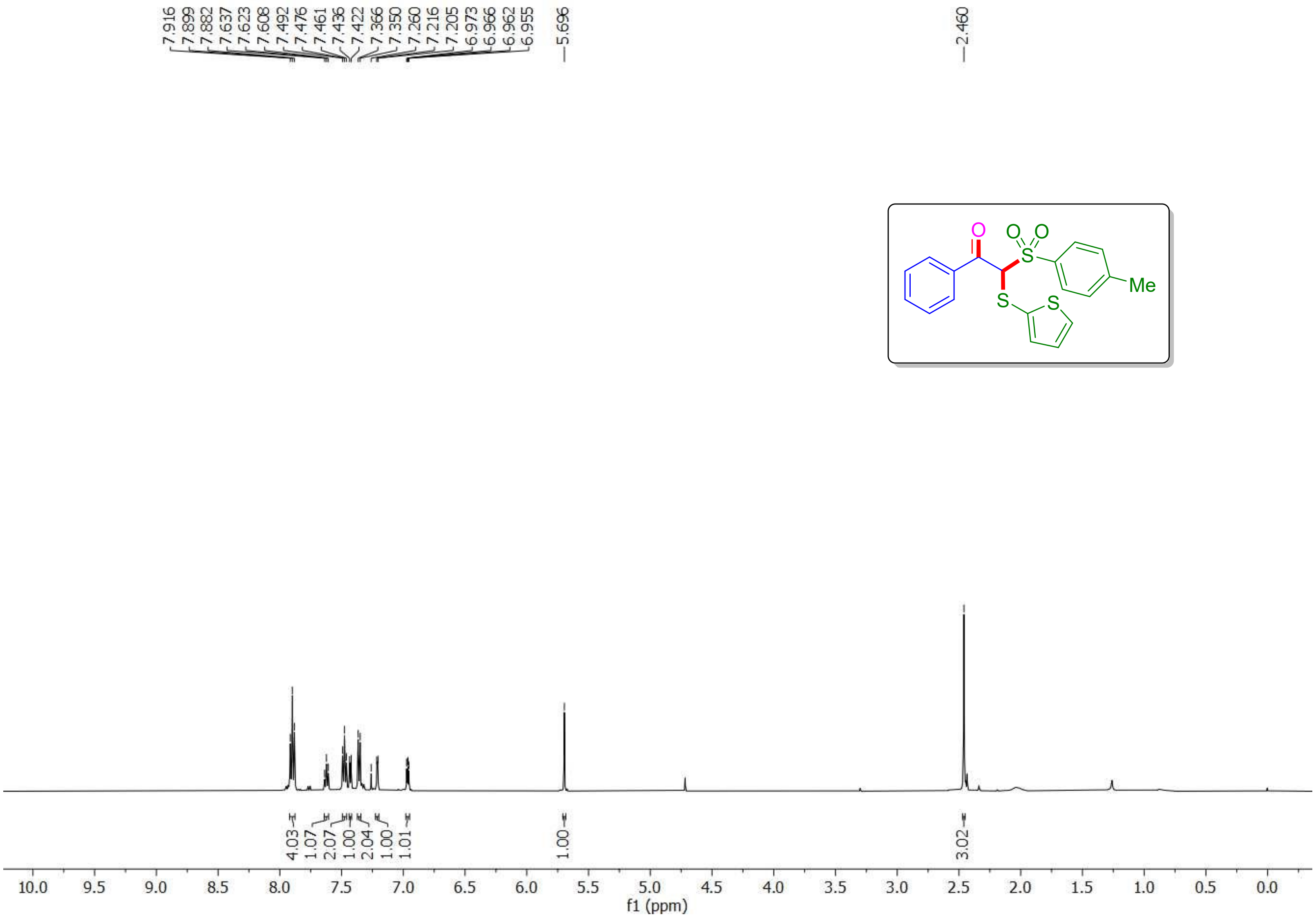
2-(Phenethylthio)-1-phenyl-2-tosylethan-1-one (1p): ^{1}H NMR (CDCl$_3$, 500 MHz)



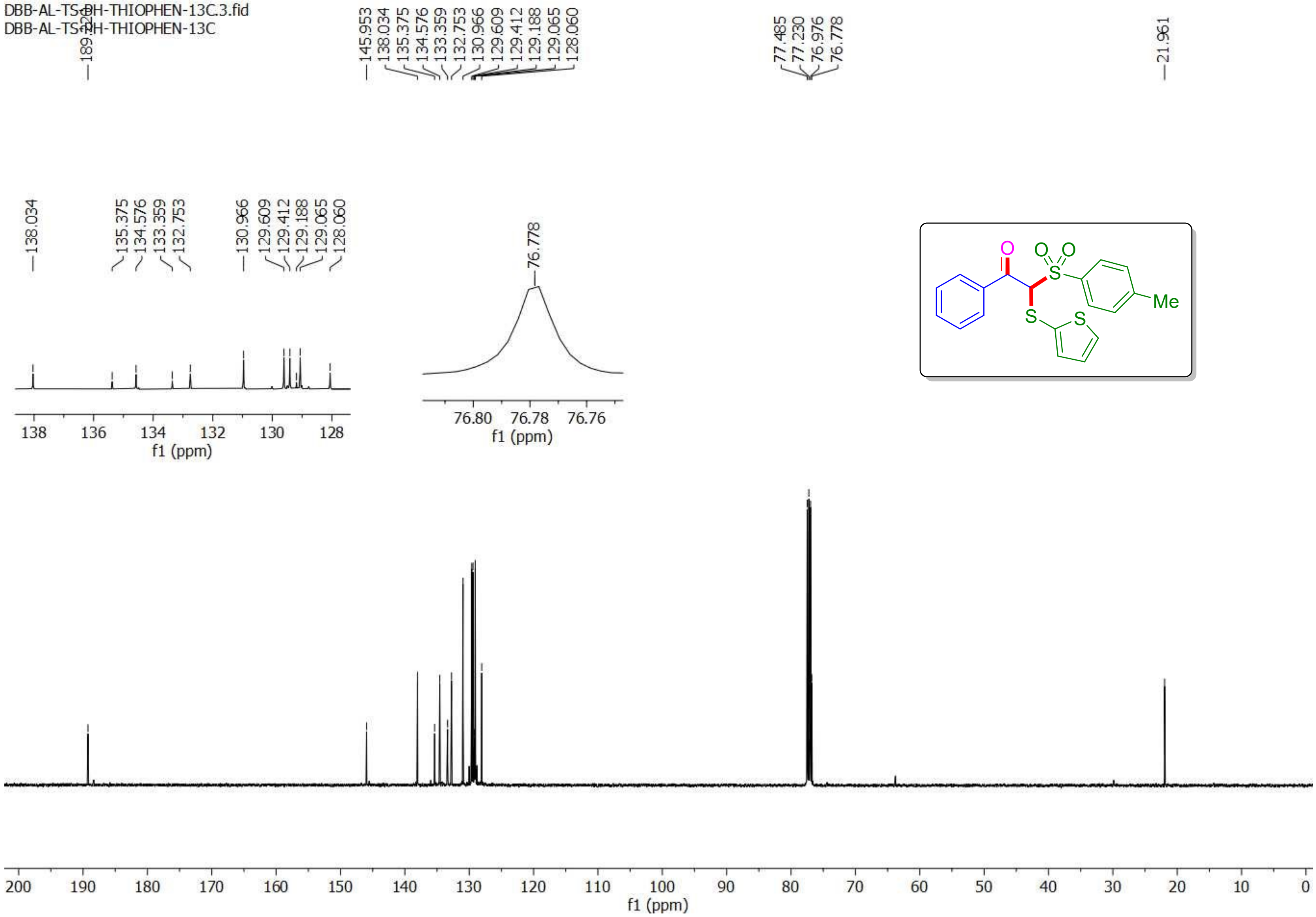
2-(Phenethylthio)-1-phenyl-2-tosylethan-1-one (1p): $^{13}C\{^1H\}$ *NMR* ($CDCl_3$, *125 MHz)*



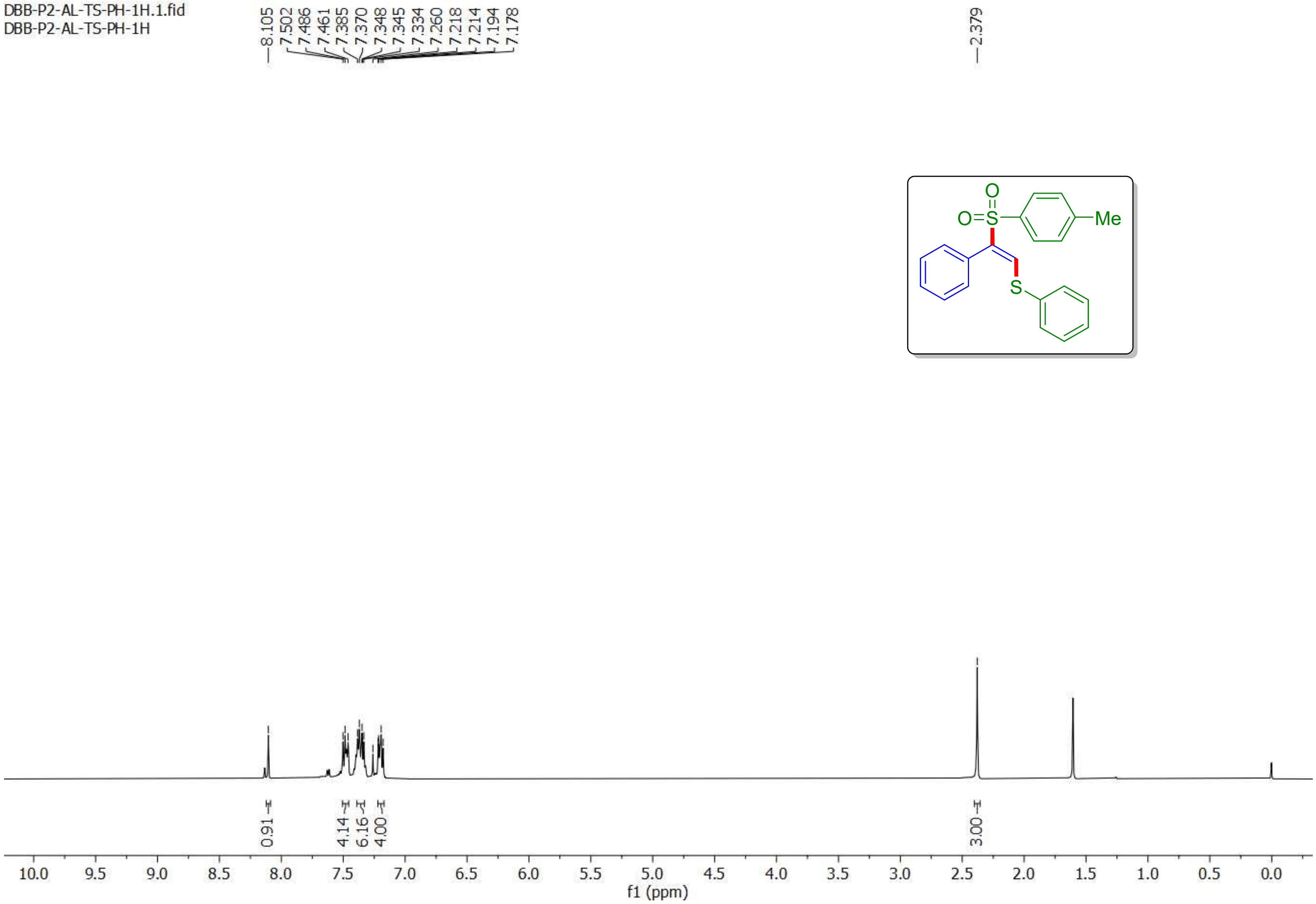
1-Phenyl-2-(thiophen-2-ylthio)-2-tosylethan-1-one (1q): ^{1}H NMR (CDCl$_3$, 500 MHz)



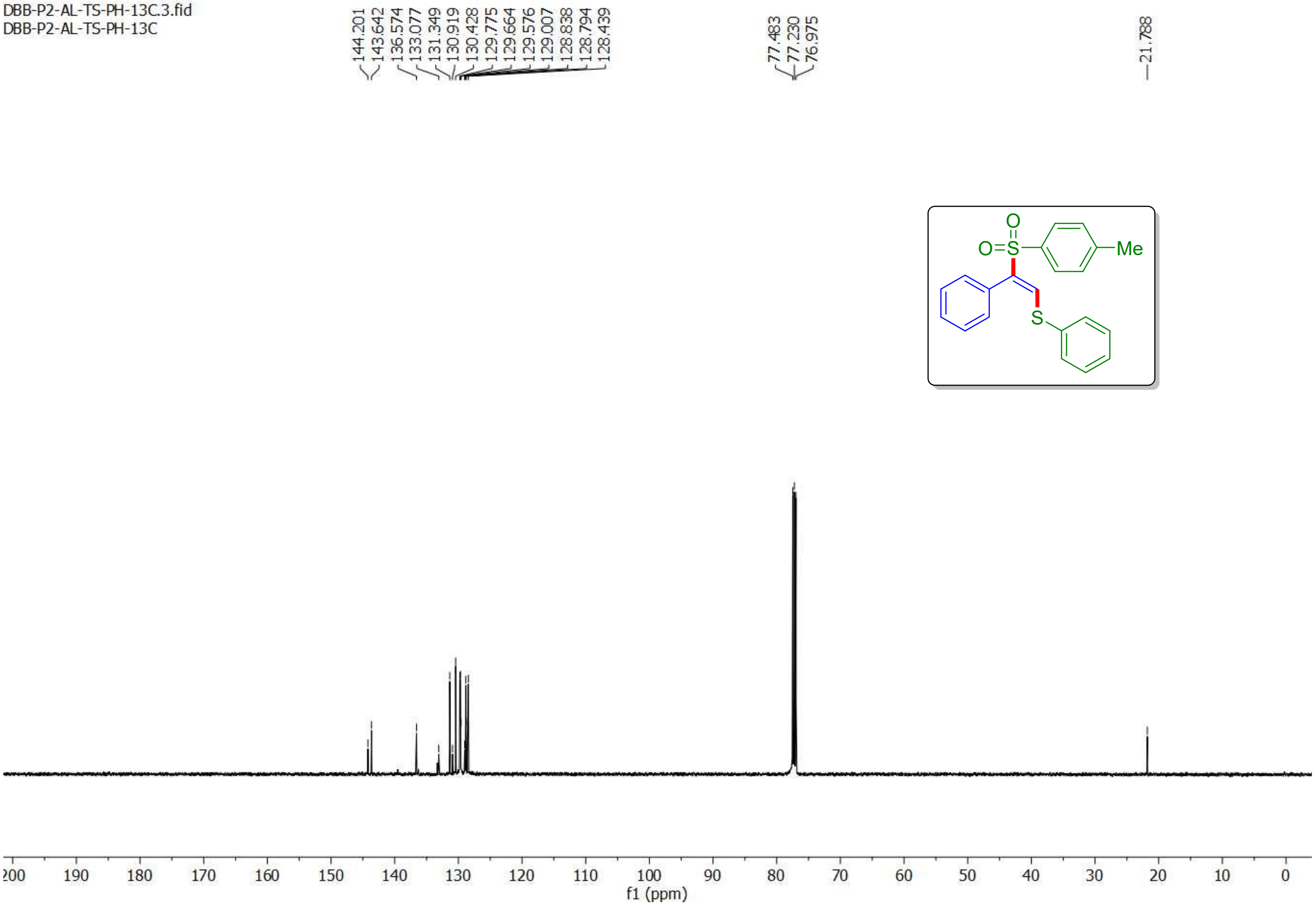
1-Phenyl-2-(thiophen-2-ylthio)-2-tosylethan-1-one (1q): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



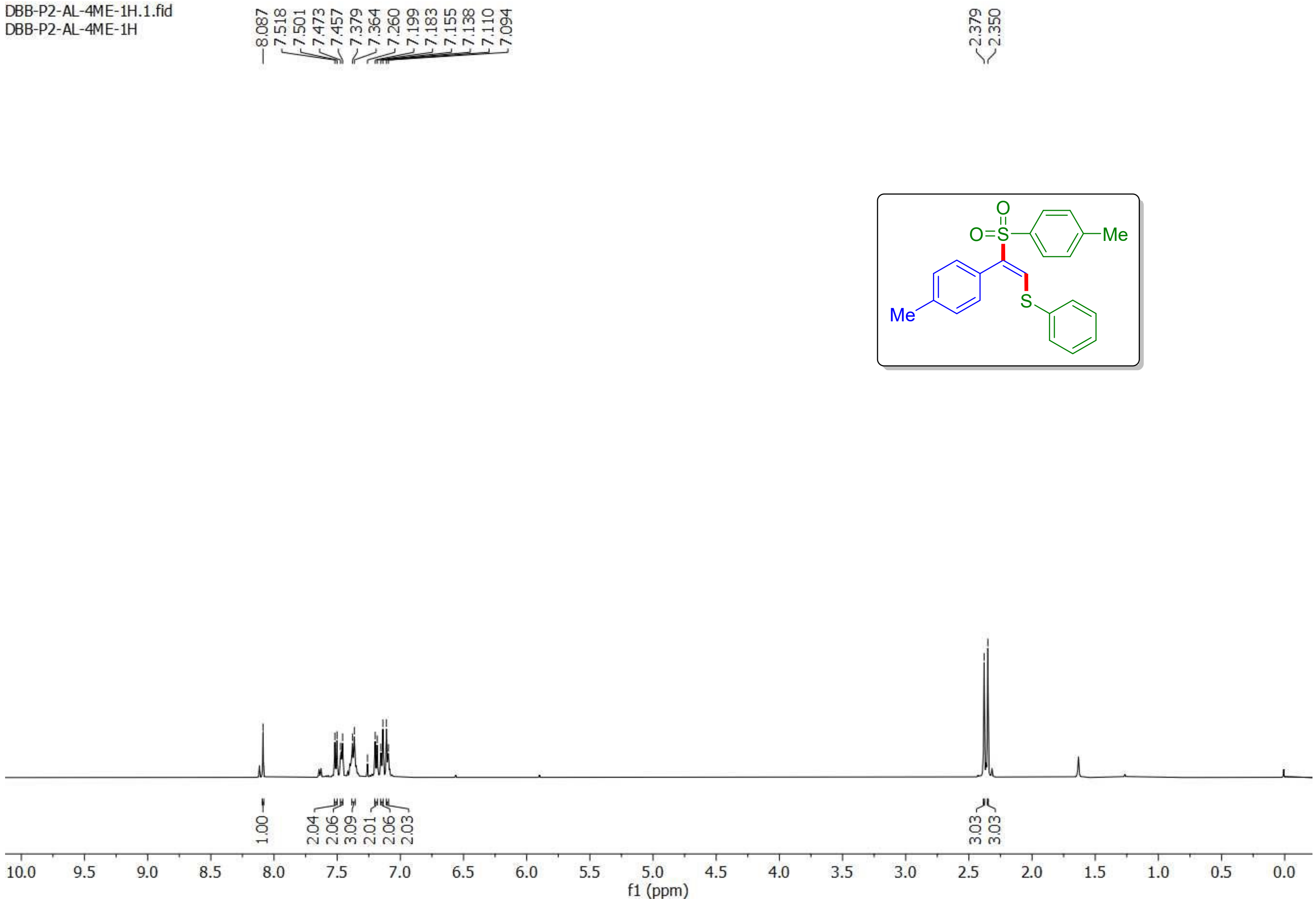
(E)-Phenyl(2-phenyl-2-tosylvinyl)sulfane (1a'): ^{1}H NMR (CDCl$_3$, 500 MHz)



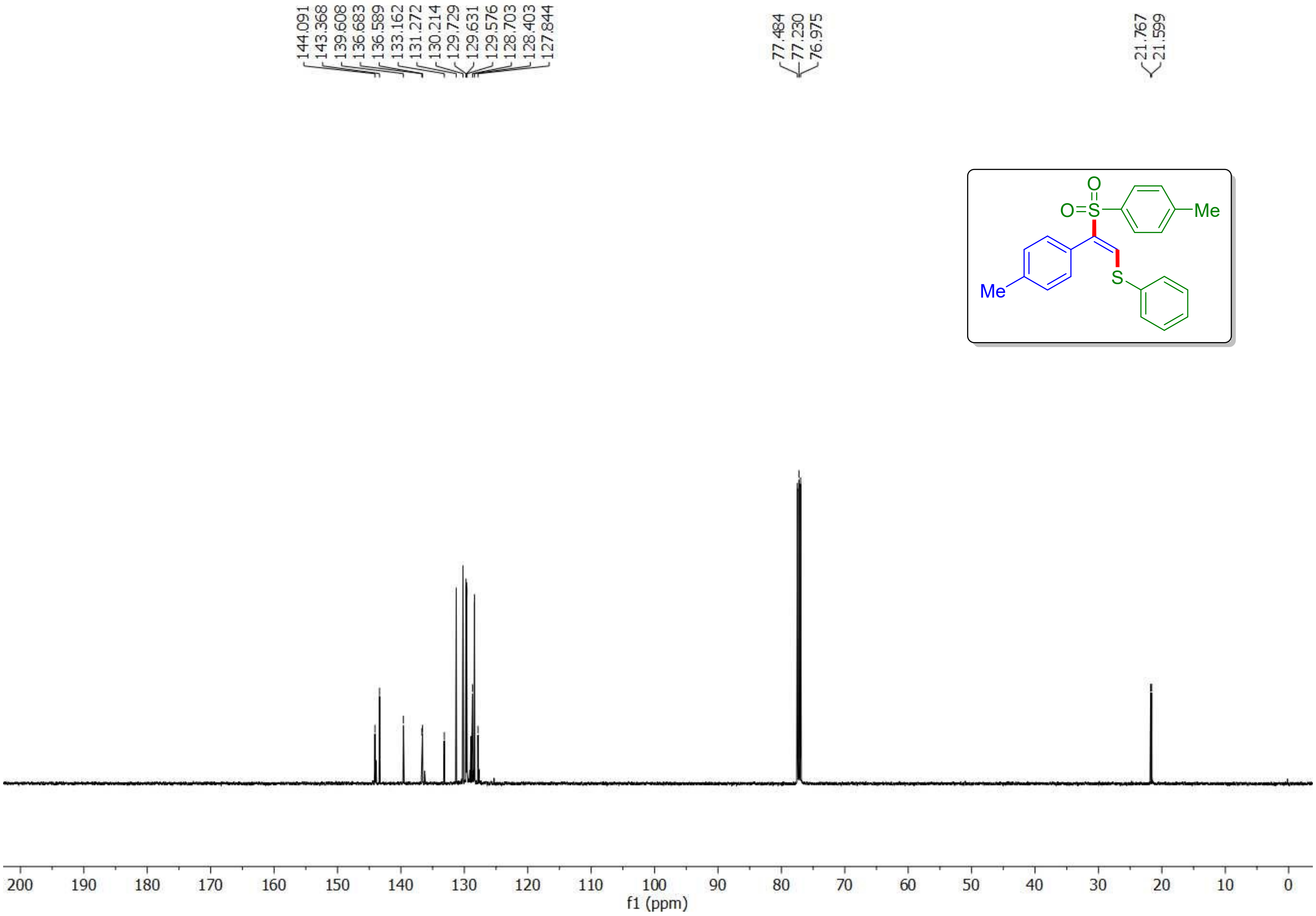
(E)-Phenyl(2-phenyl-2-tosylvinyl)sulfane (1a'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



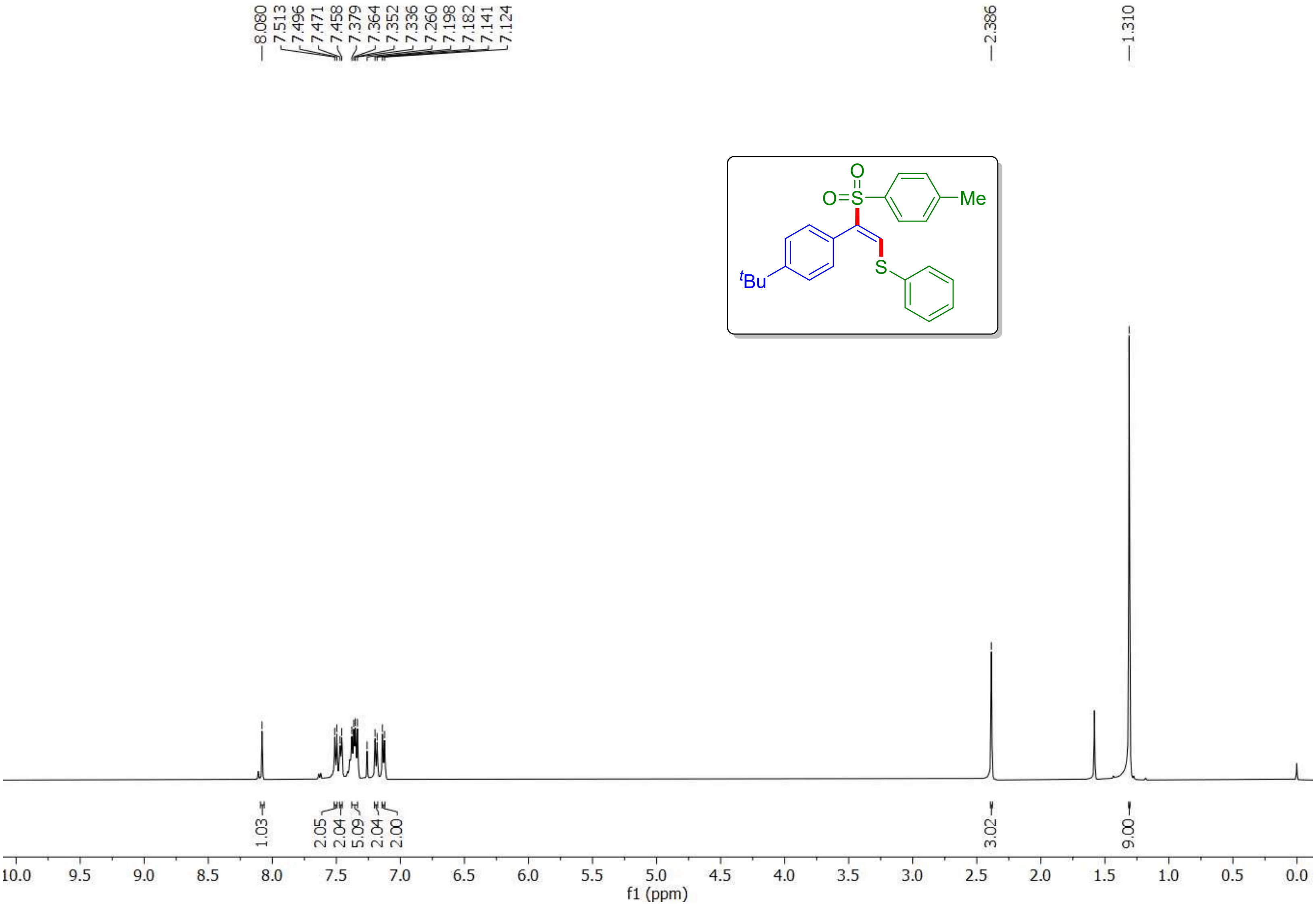
(E)-Phenyl(2-(p-tolyl)-2-tosylvinyl)sulfane (2a'): ^{1}H NMR ($CDCl_3$, 500 MHz)



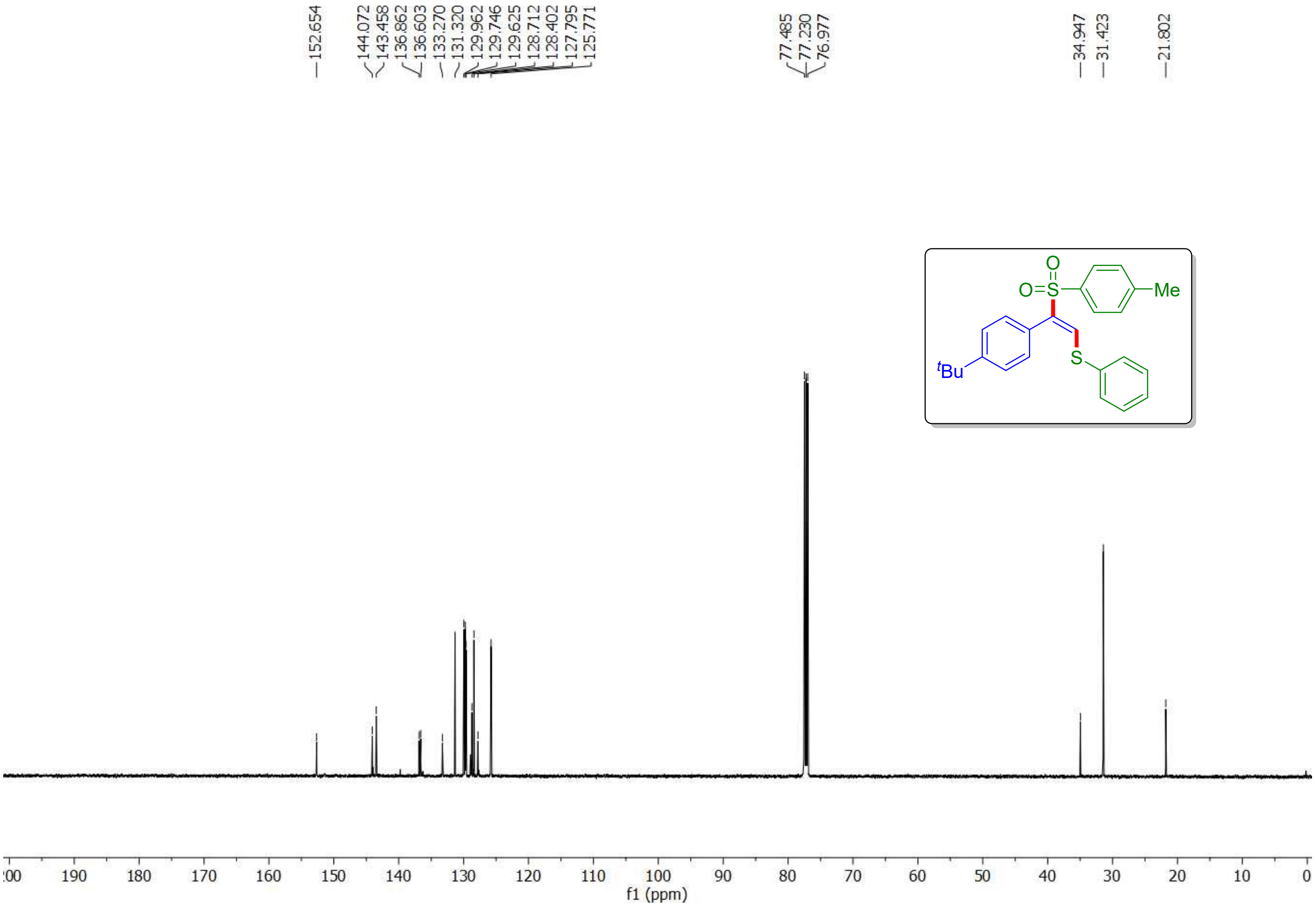
(E)-Phenyl(2-(p-tolyl)-2-tosylvinyl)sulfane (2a'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



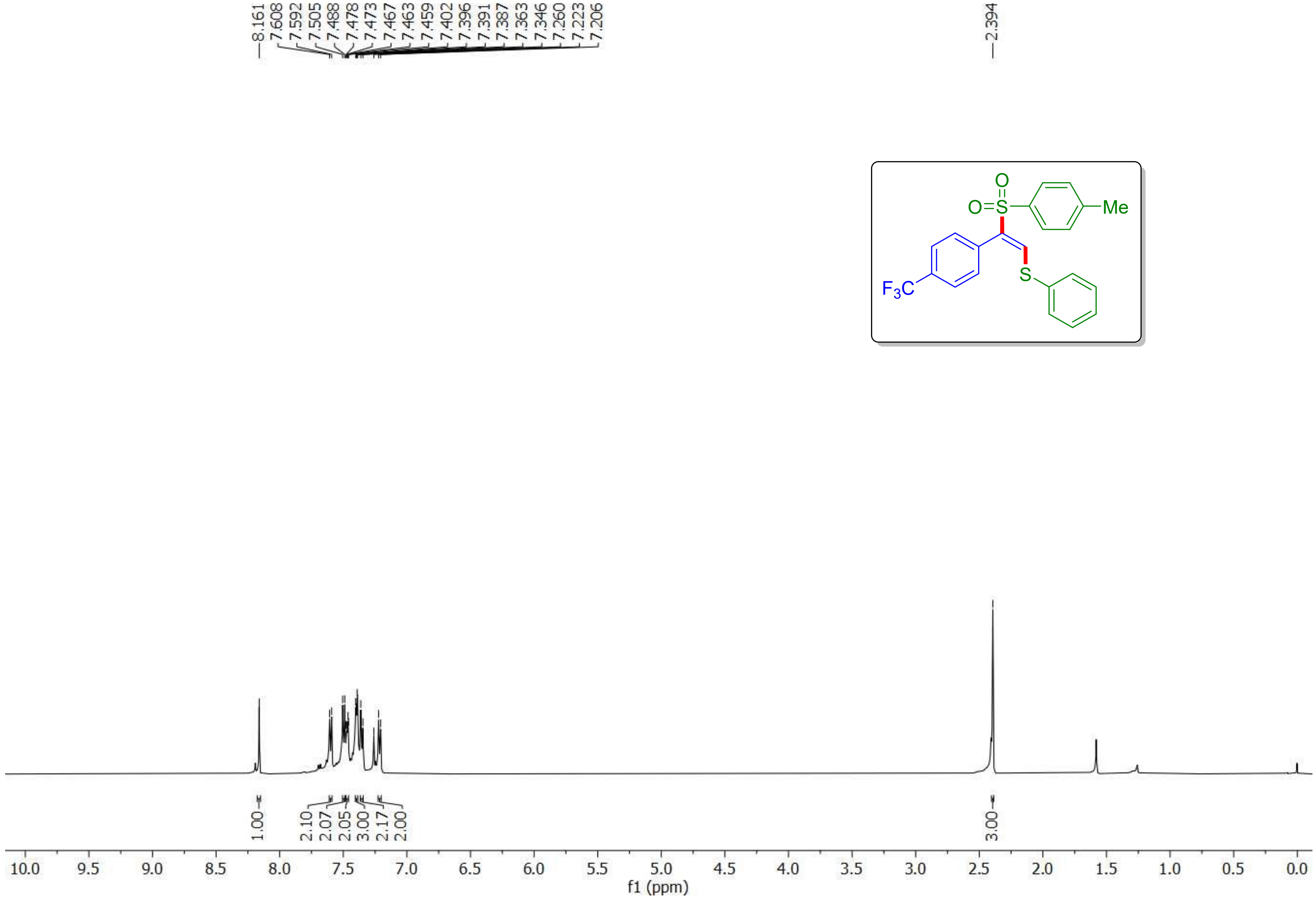
(E)-(2-(4-(tert-Butyl)phenyl)-2-tosylvinyl)(phenyl)sulfane (4a'): ^{1}H NMR (CDCl$_3$, 500 MHz)



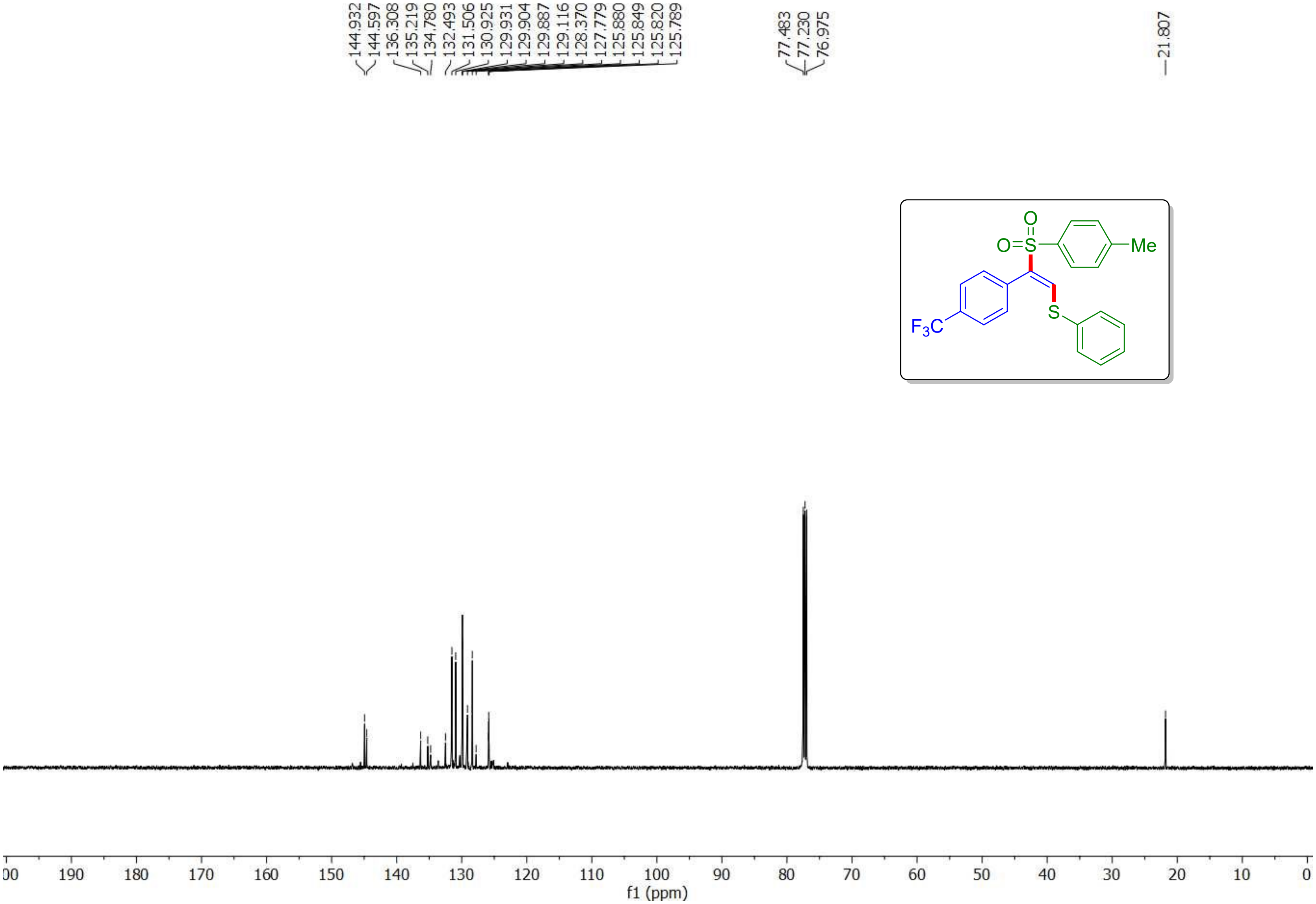
(E)-(2-(4-(tert-Butyl)phenyl)-2-tosylvinyl)(phenyl)sulfane (4a'): $^{13}C\{^1H\}$ *NMR* ($CDCl_3$, *125 MHz)*



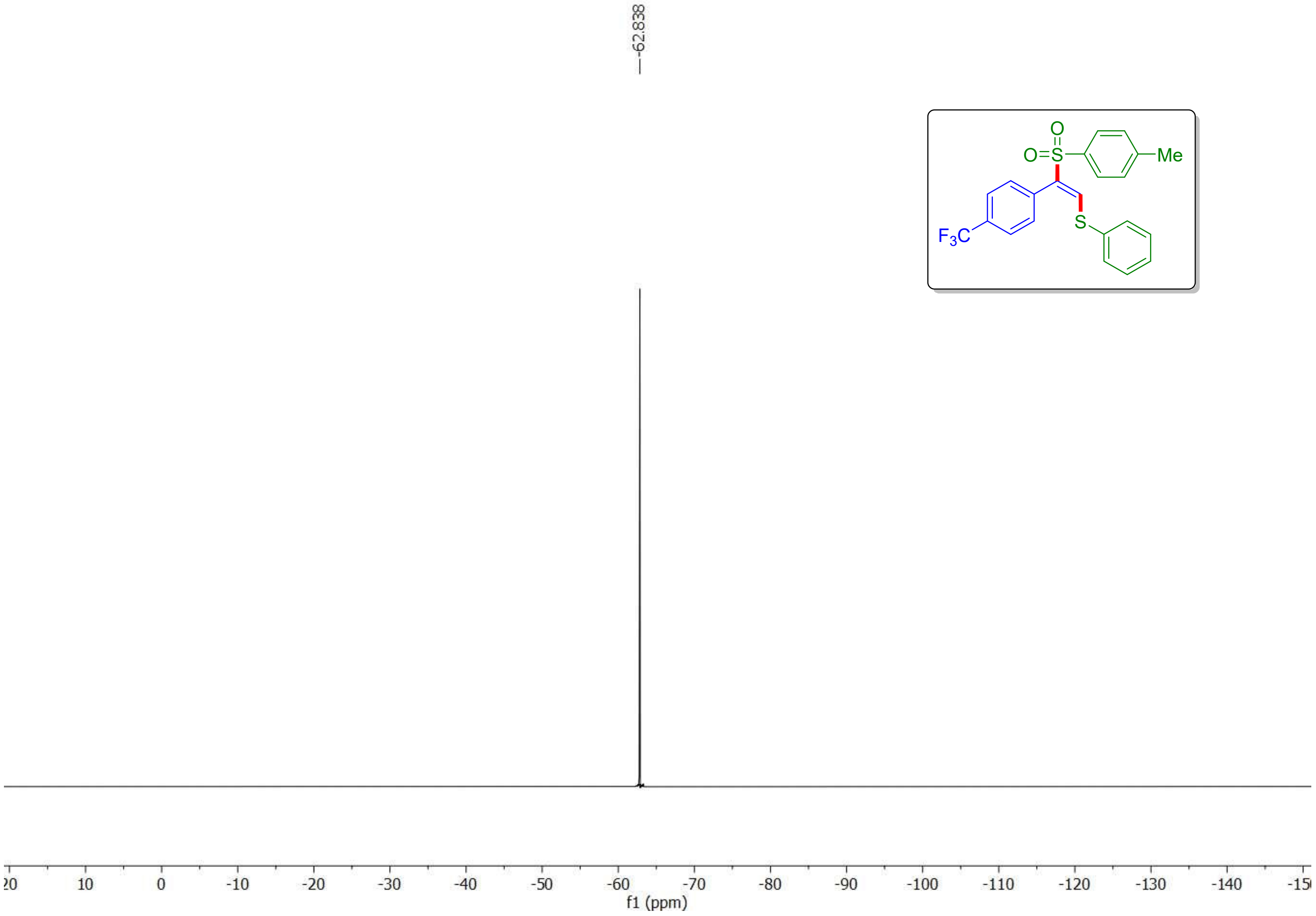
(E)-Phenyl(2-tosyl-2-(4-(trifluoromethyl)phenyl)vinyl)sulfane (17a'): ^{1}H NMR (CDCl$_3$, 500 MHz)



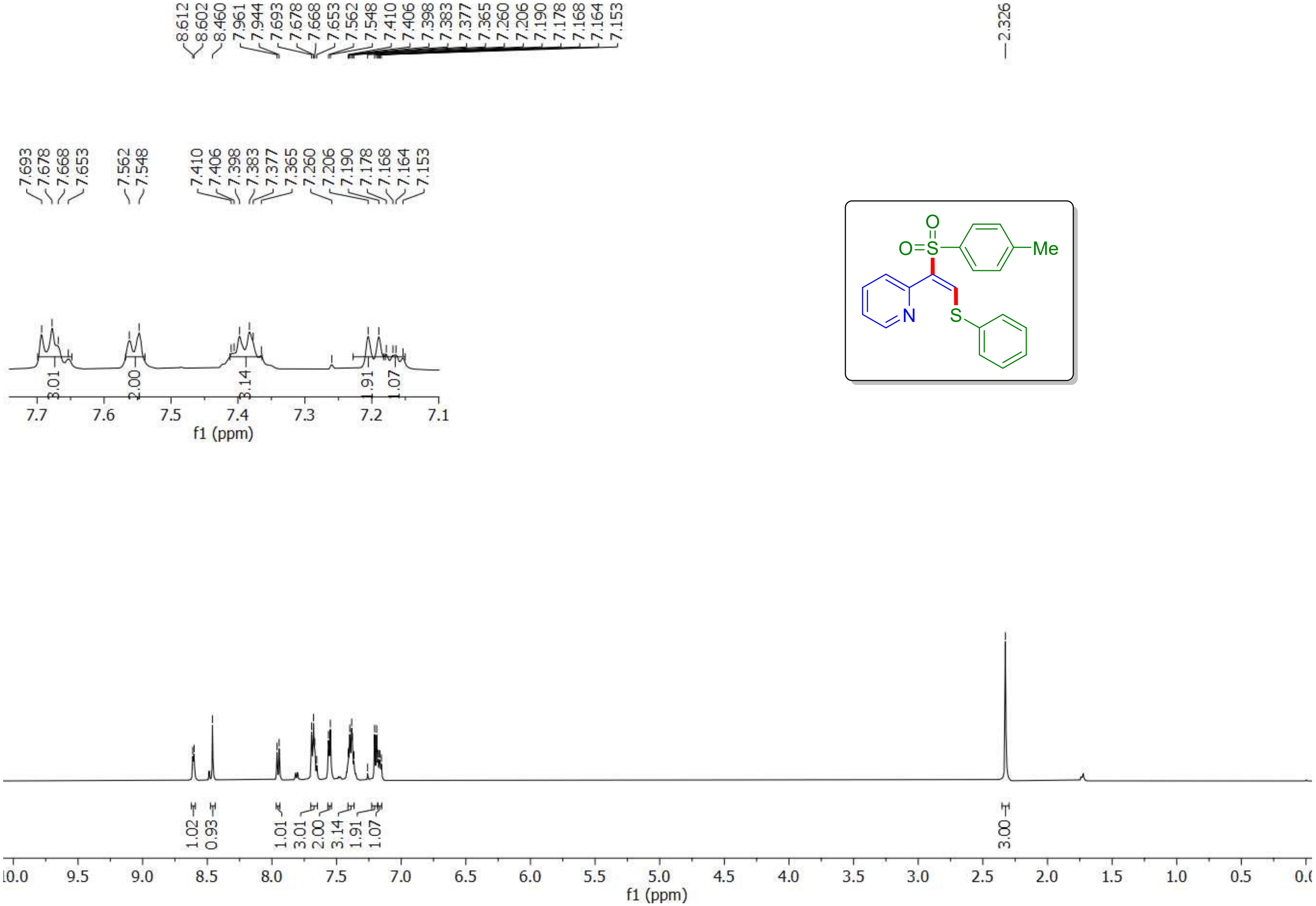
(E)-Phenyl(2-tosyl-2-(4-(trifluoromethyl)phenyl)vinyl)sulfane (17a'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



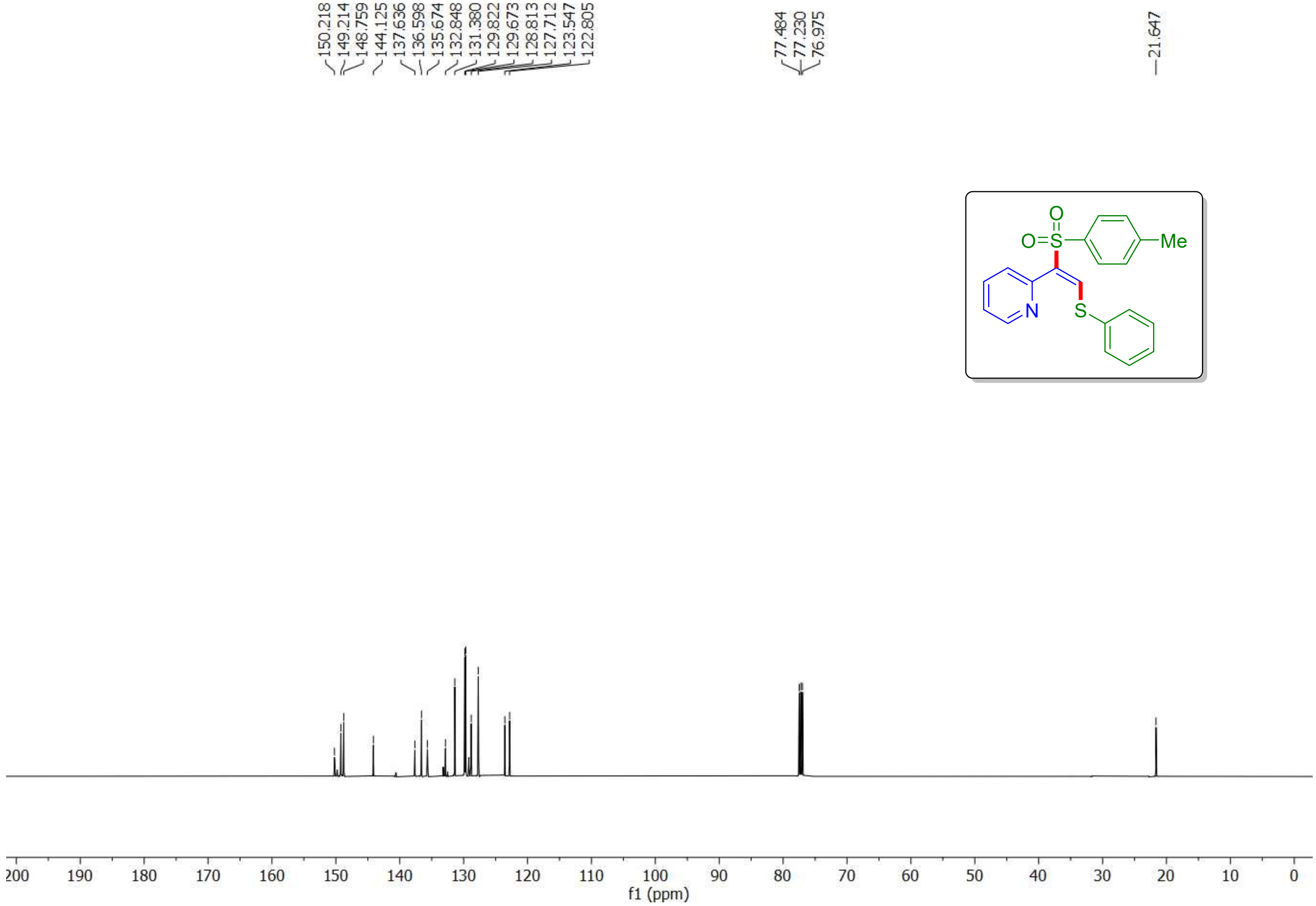
(E)-Phenyl(2-tosyl-2-(4-(trifluoromethyl)phenyl)vinyl)sulfane (17a'): ^{19}F NMR (CDCl$_3$, 471 MHz)



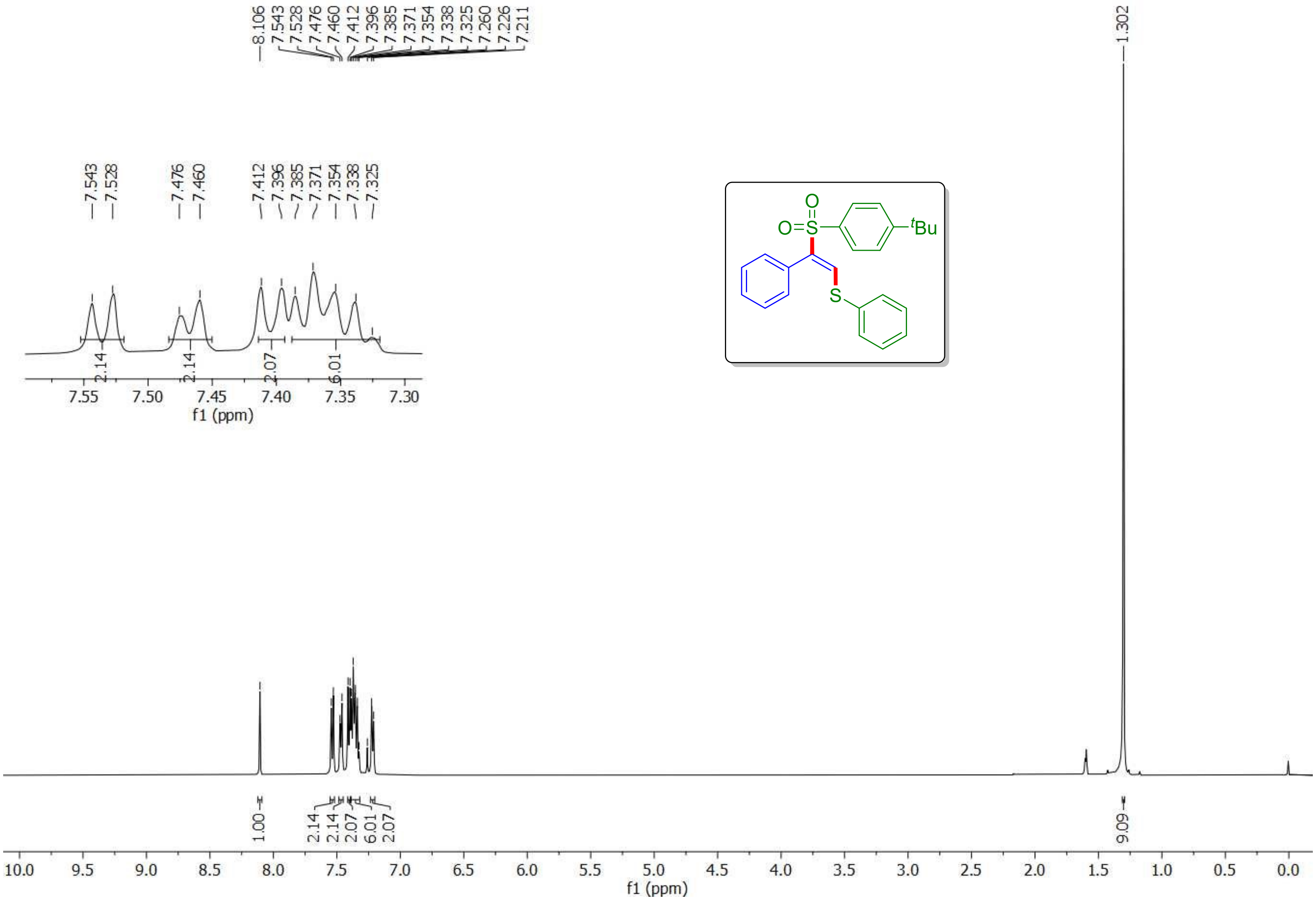
(E)-2-(2-(Phenylthio)-1-tosylvinyl)pyridine (18a'): ^{1}H NMR (CDCl$_3$, 500 MHz)



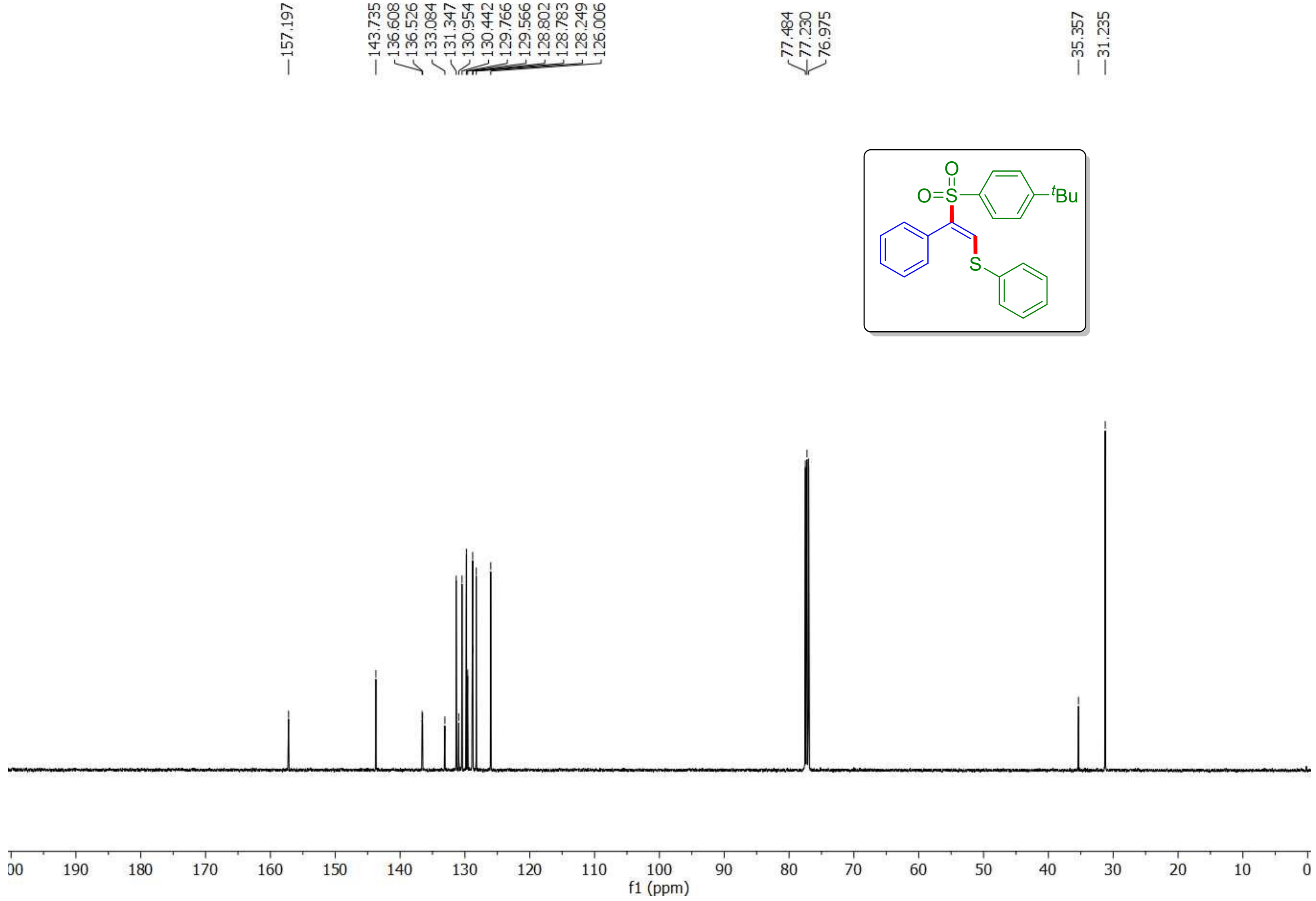
(E)-2-(2-(Phenylthio)-1-tosylvinyl)pyridine (18a'): $^{13}C\{^{1}H\}$ *NMR (*$CDCl_3$*, 125 MHz)*



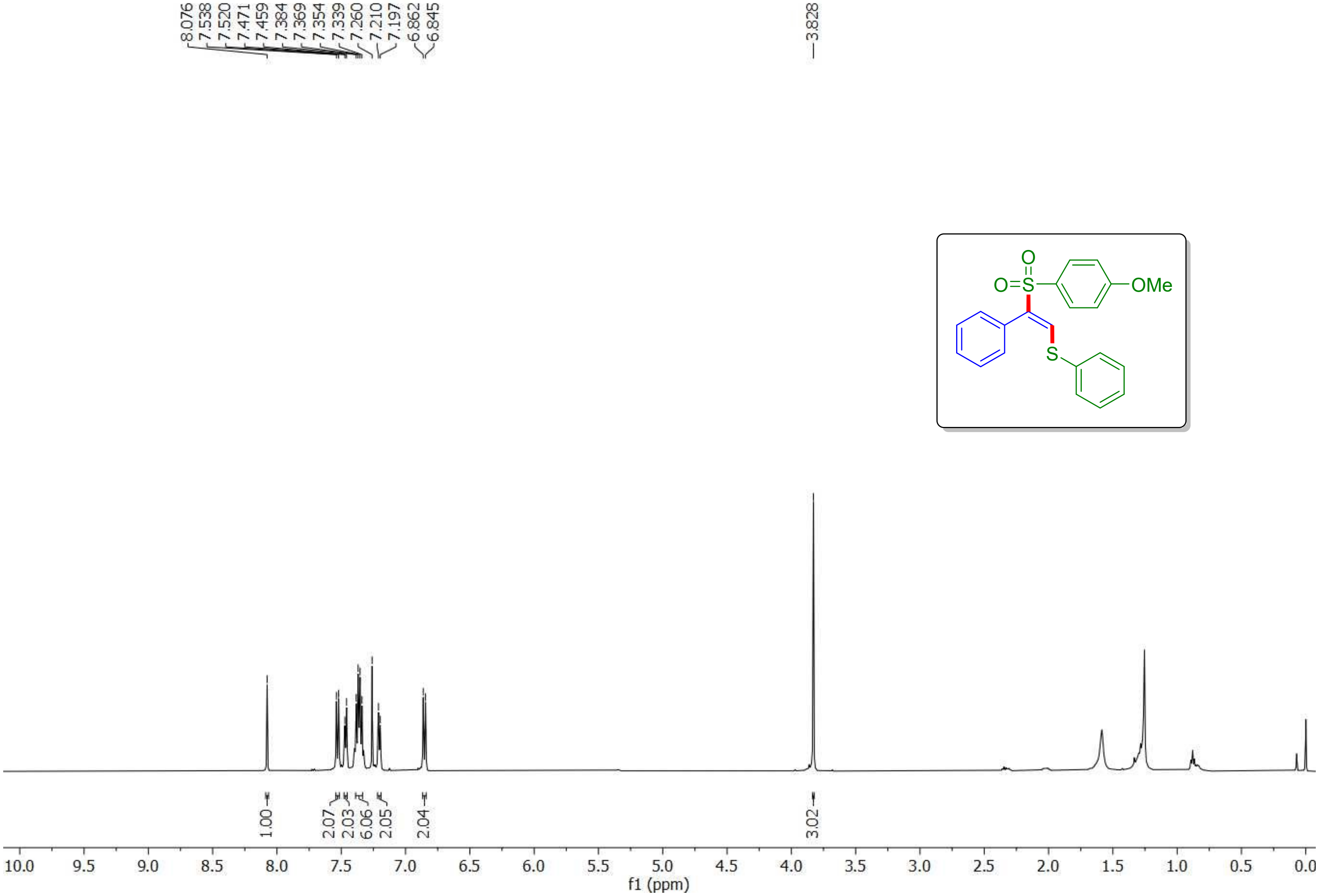
(E)-(2-((4-(tert-Butyl)phenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1c'): ^{1}H NMR (CDCl$_3$, 500 MHz)



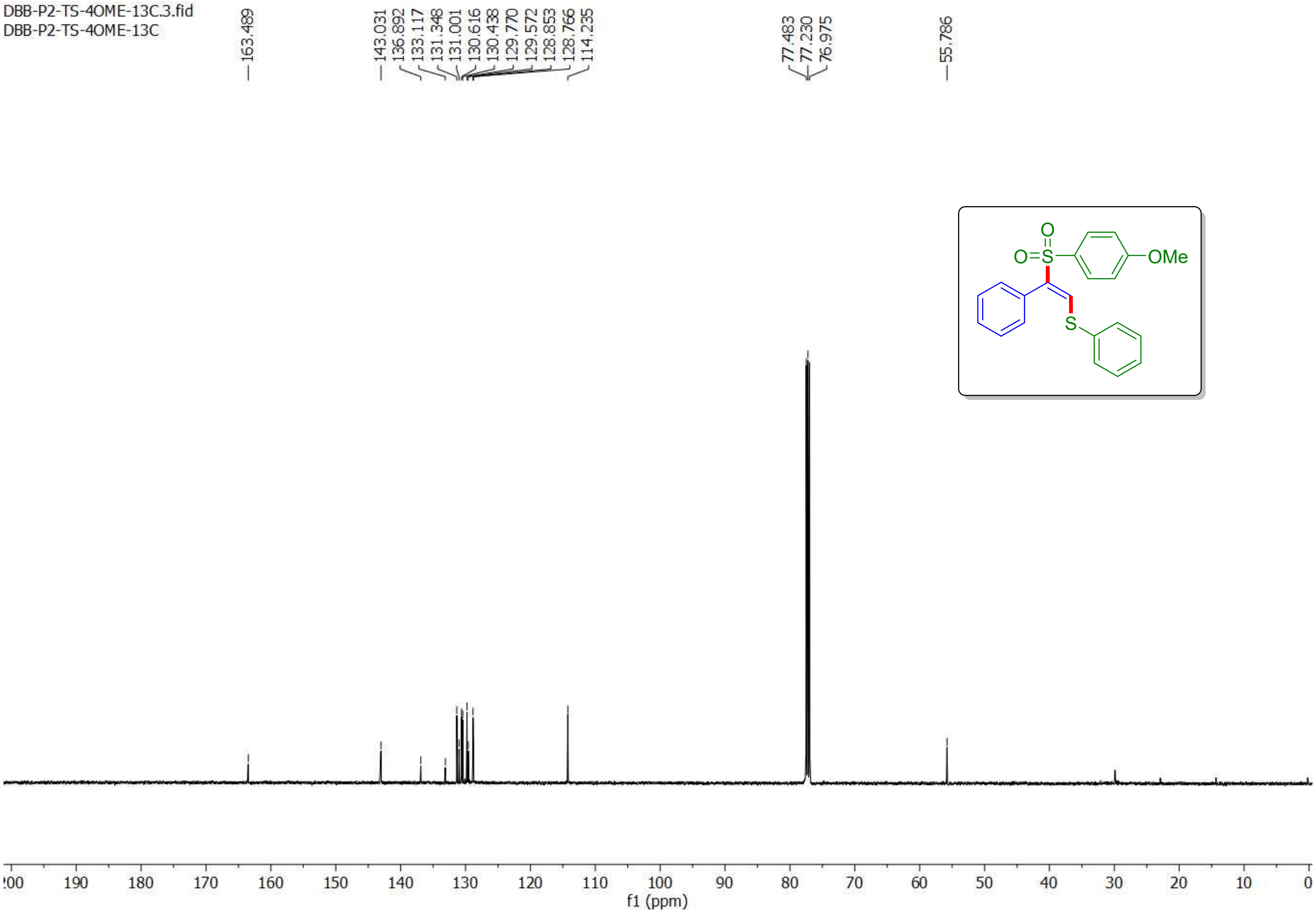
(E)-(2-((4-(tert-Butyl)phenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1c'): $^{13}C\{^{1}H\}$ NMR (CDCl$_3$, 125 MHz)



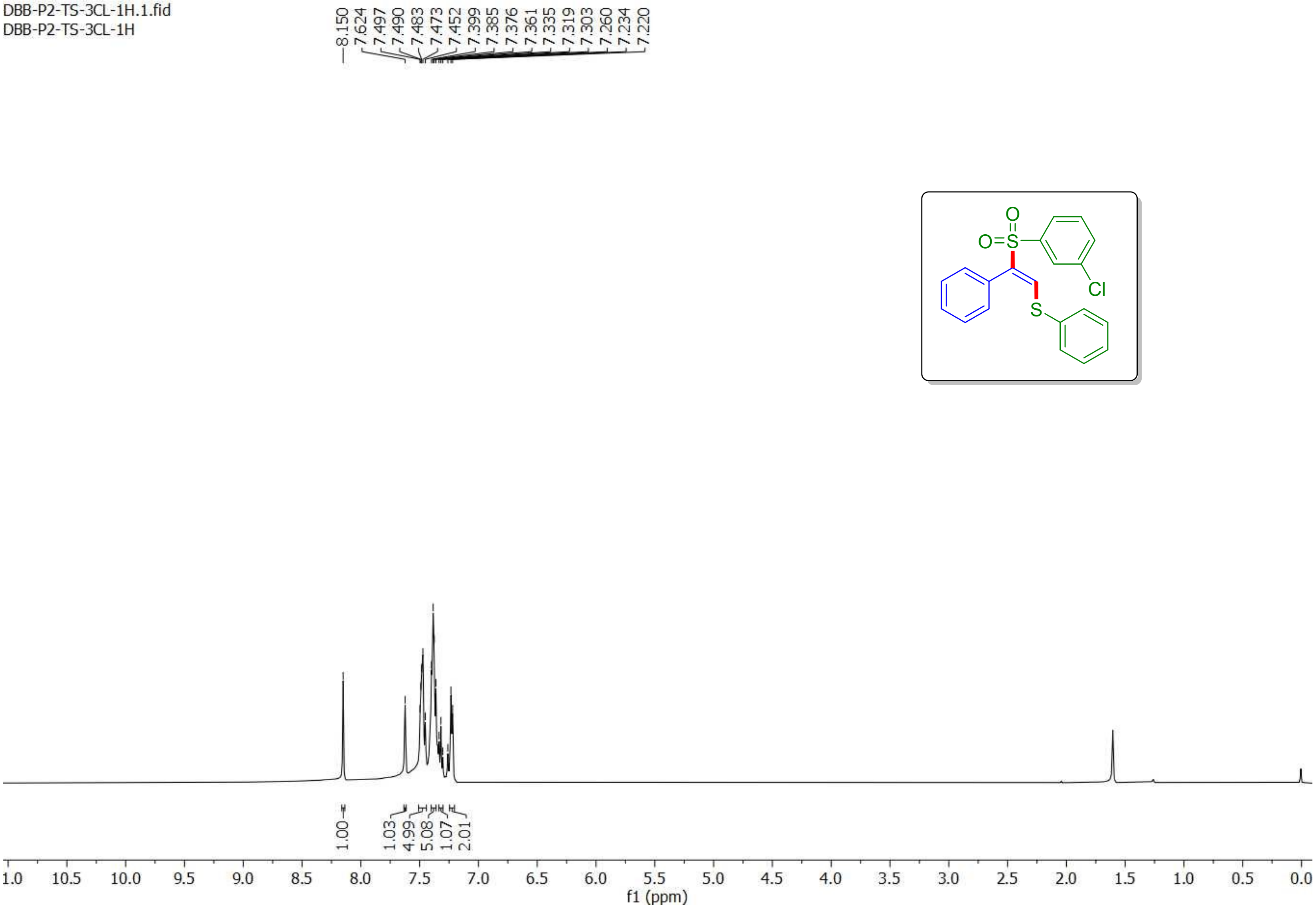
(E)-(2-((4-Methoxyphenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1d'): ^{1}*H NMR (CDCl*$_3$*, 500 MHz)*



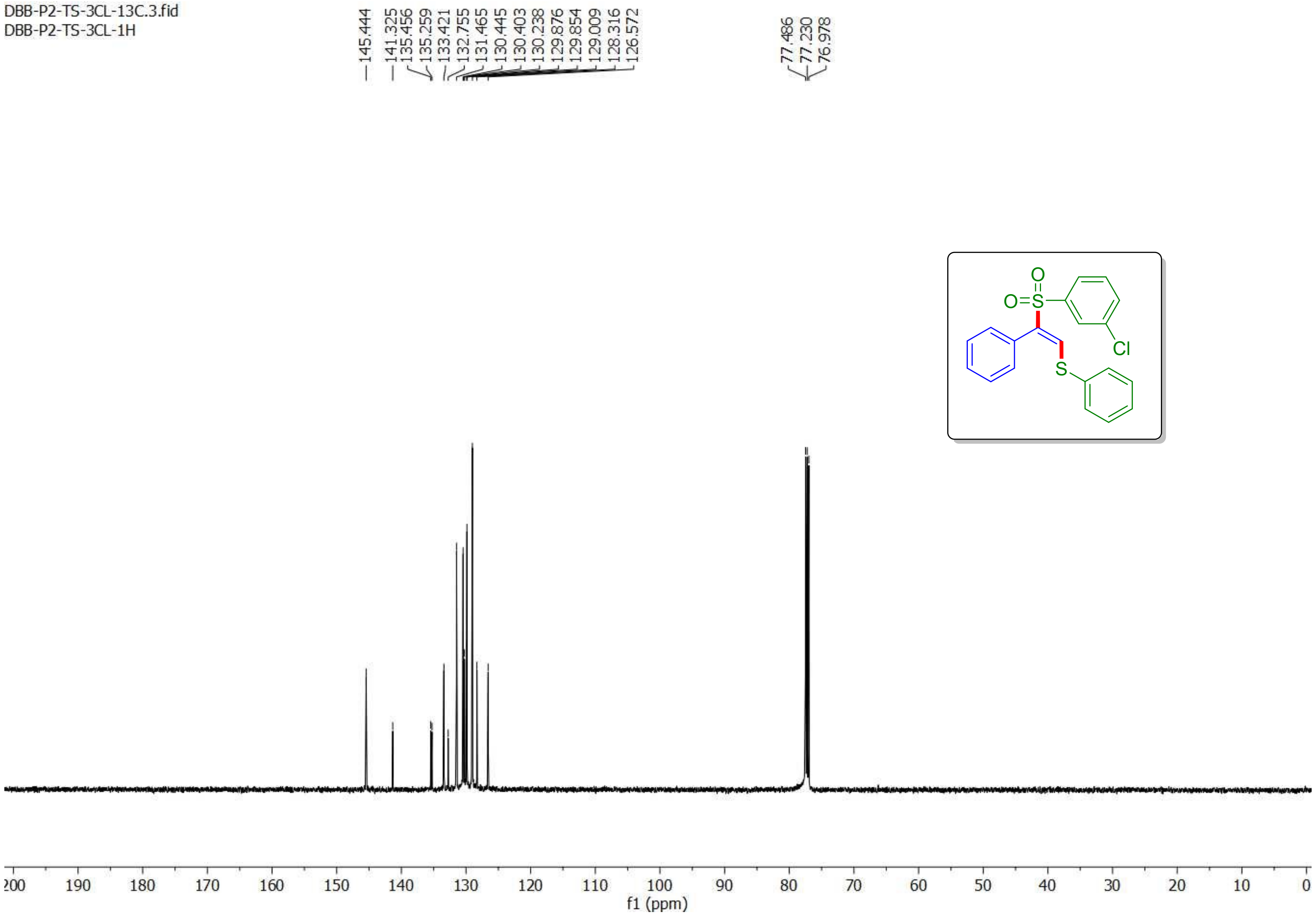
(E)-(2-((4-Methoxyphenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1d'): $^{13}C\{^{1}H\}$ *NMR ($CDCl_3$, 125 MHz)*



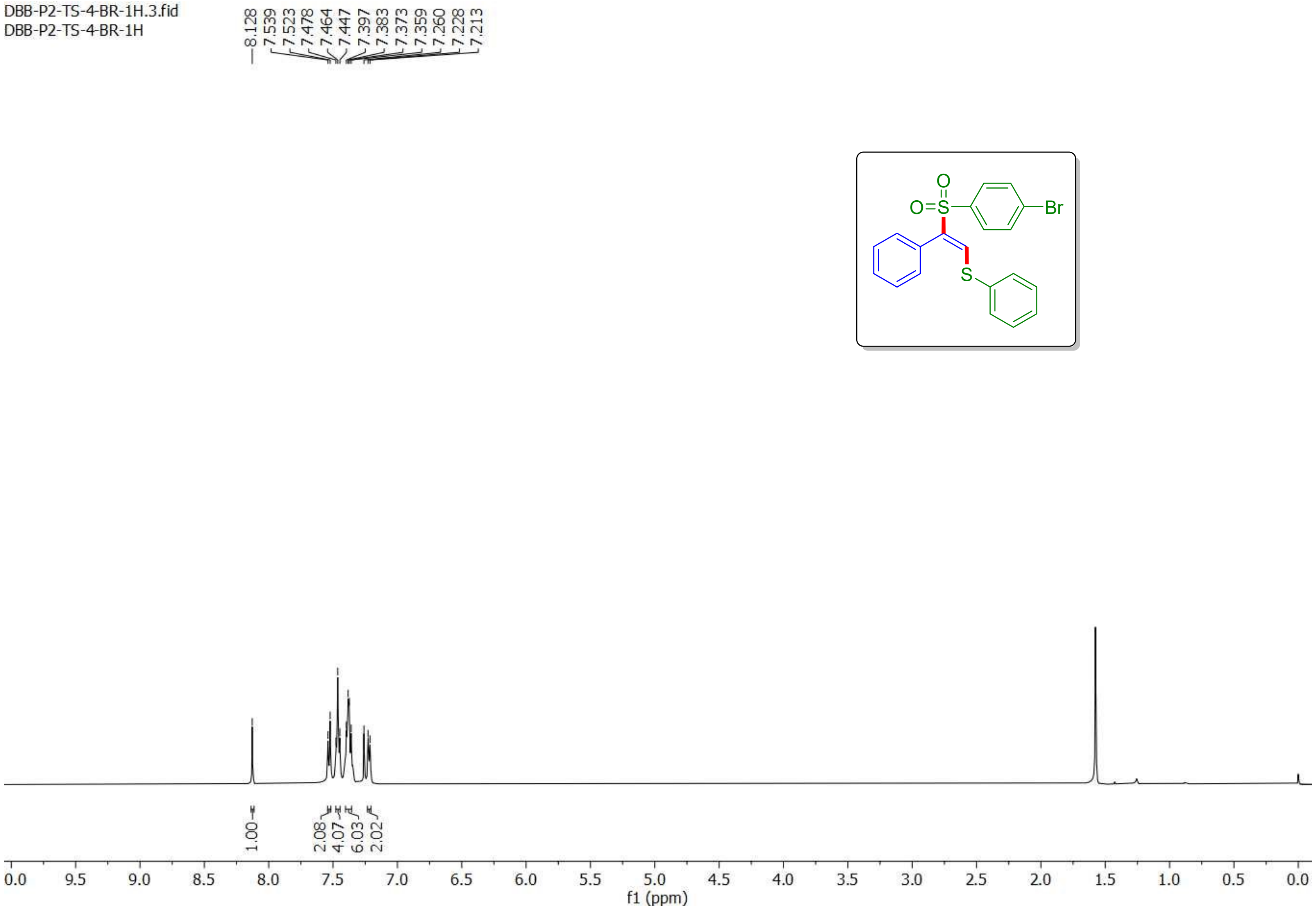
(E)-(2-((3-Chlorophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1f'): ^{1}H NMR (CDCl3, 500 MHz)



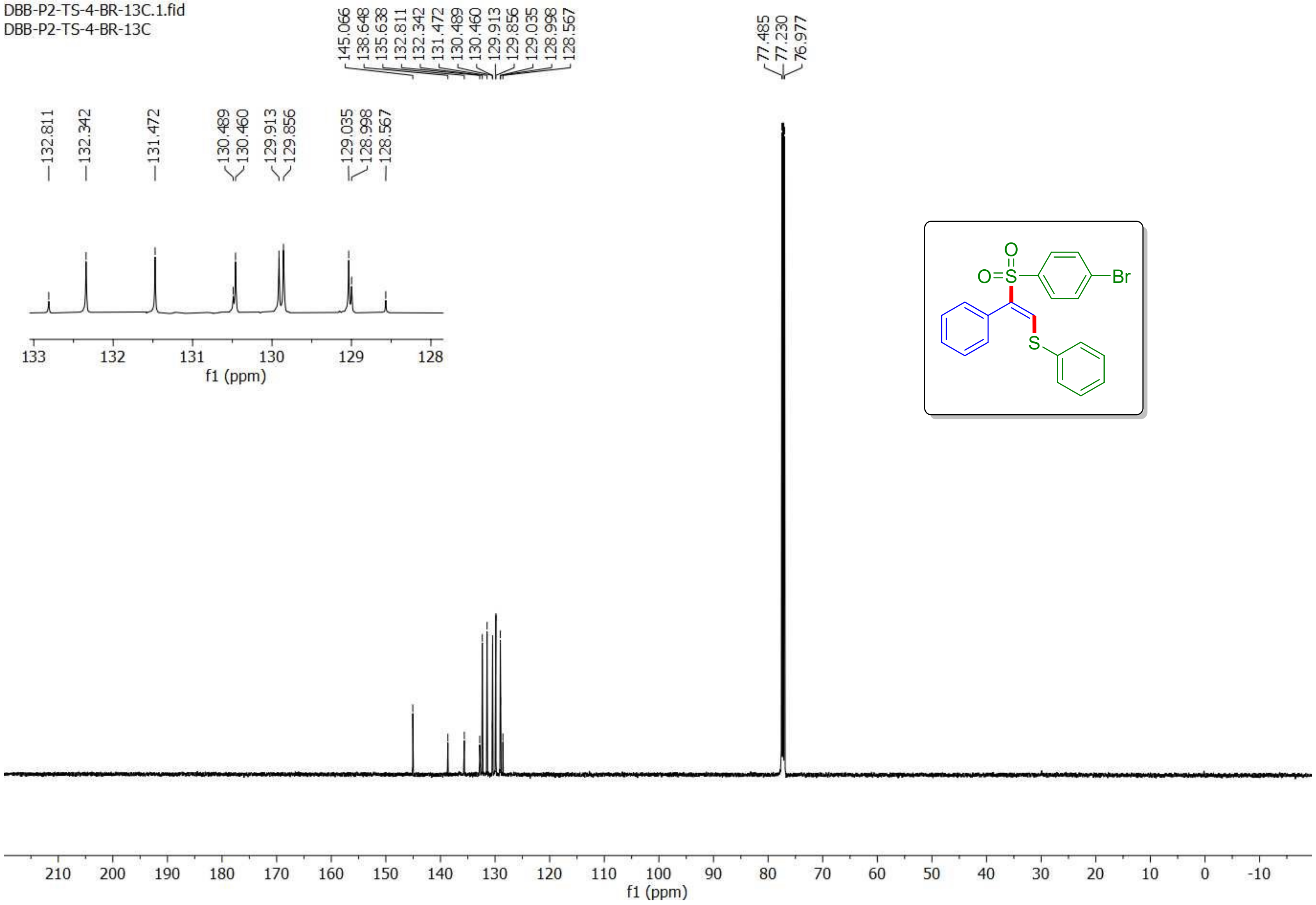
(E)-(2-((3-Chlorophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1f'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



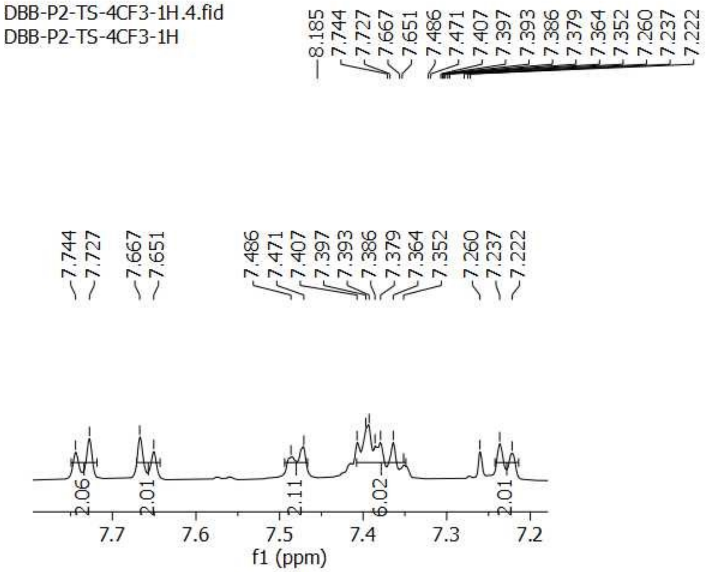
(E)-(2-((4-Bromophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1g'): ^{1}H NMR (CDCl$_3$, 500 MHz)

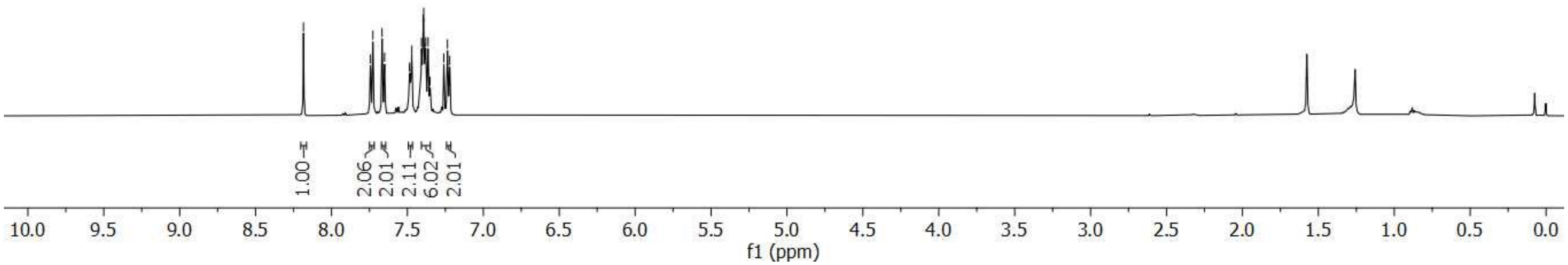


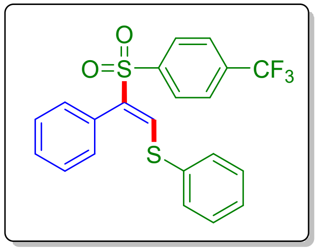
(E)-(2-((4-Bromophenyl)sulfonyl)-2-phenylvinyl)(phenyl)sulfane (1g'): $^{13}C\{^{1}H\}$ NMR (CDCl$_3$, 125 MHz)



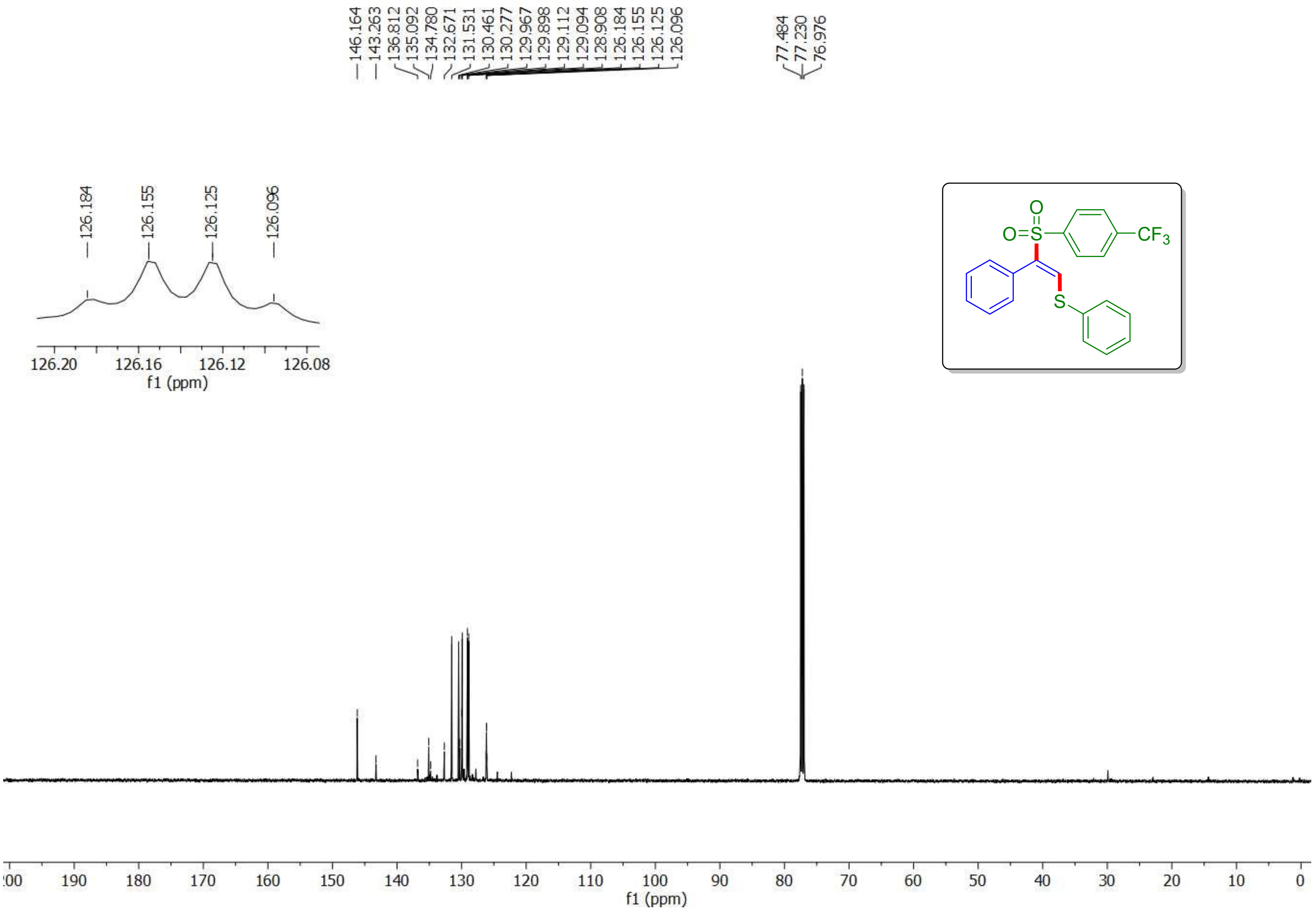
(E)-Phenyl(2-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (1t'): ^{1}*H NMR (CDCl*$_3$*, 500 MHz)*



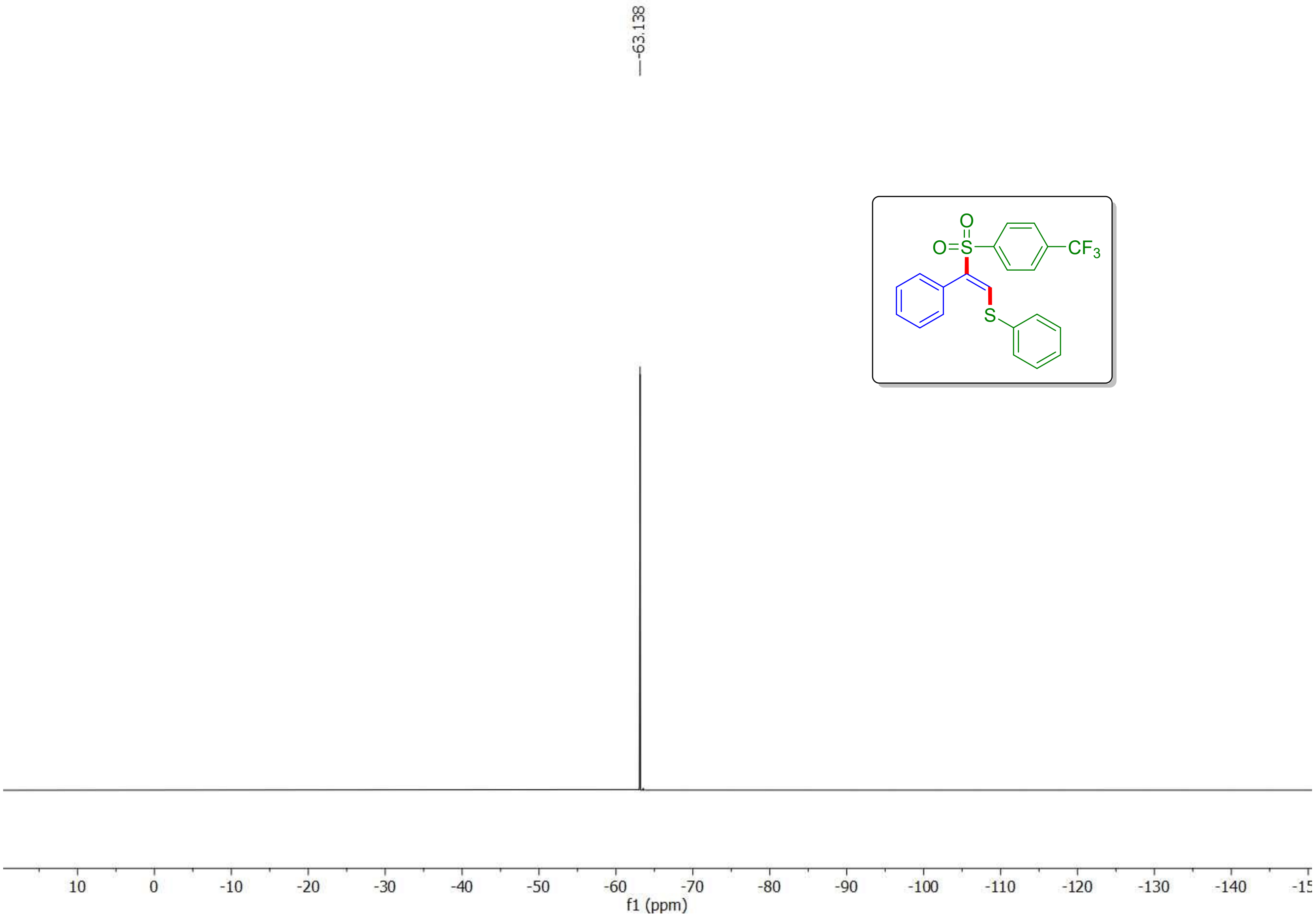




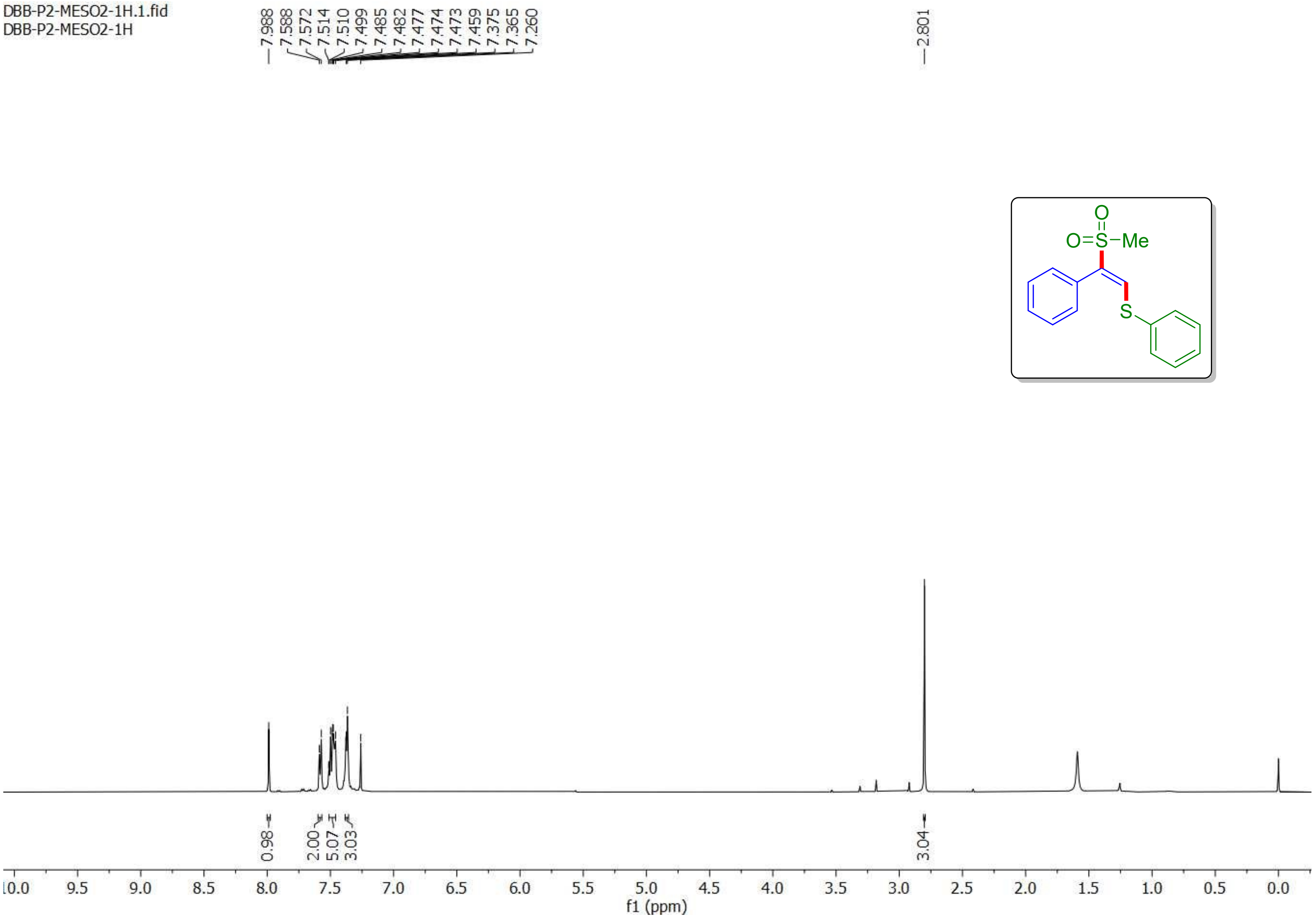
(E)-Phenyl(2-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (1t'): $^{13}C\{^{1}H\}$ *NMR ($CDCl_3$, 125 MHz)*



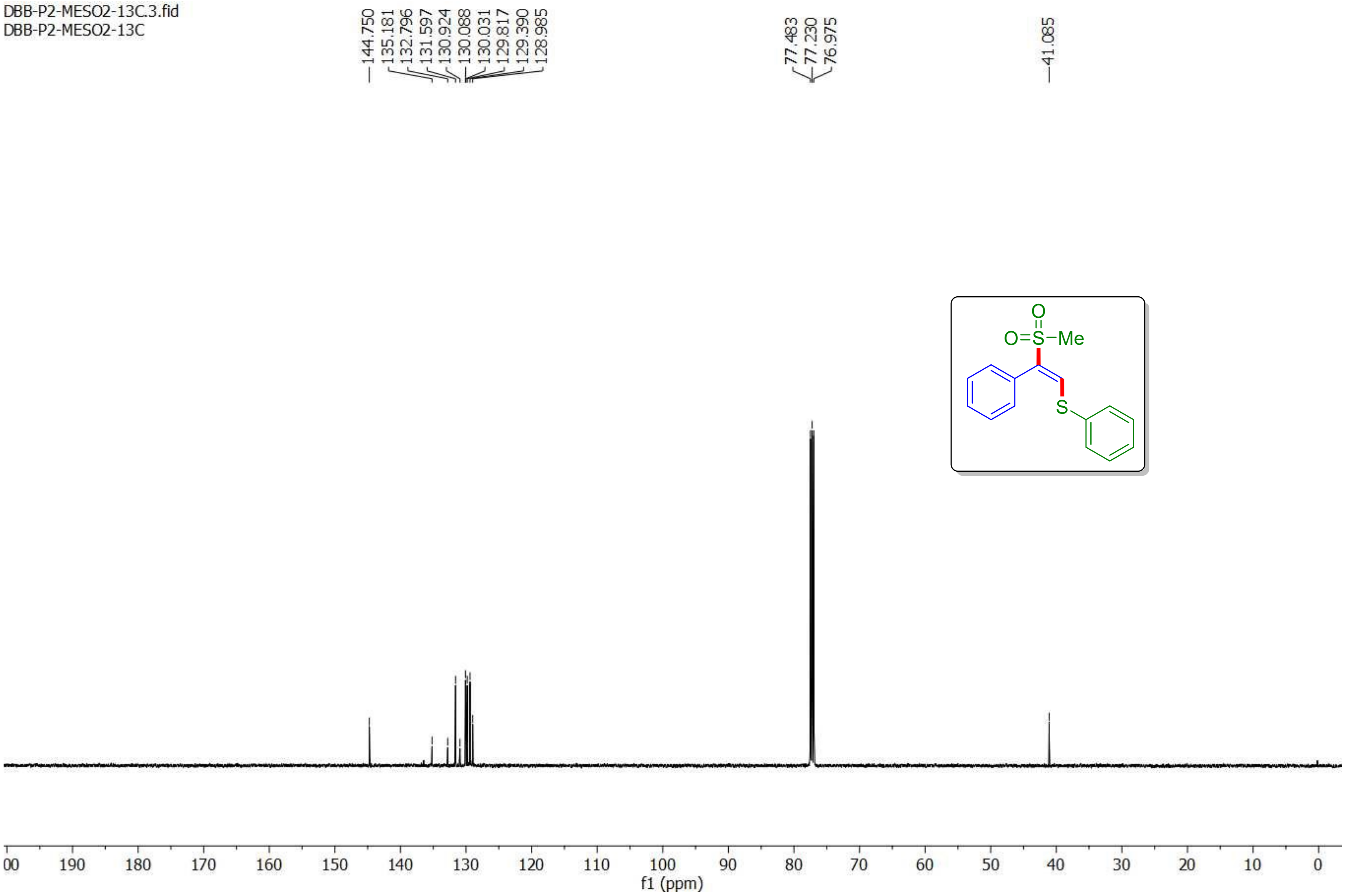
(E)-Phenyl(2-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (1t'): ^{19}F NMR (CDCl$_3$, 471 MHz)



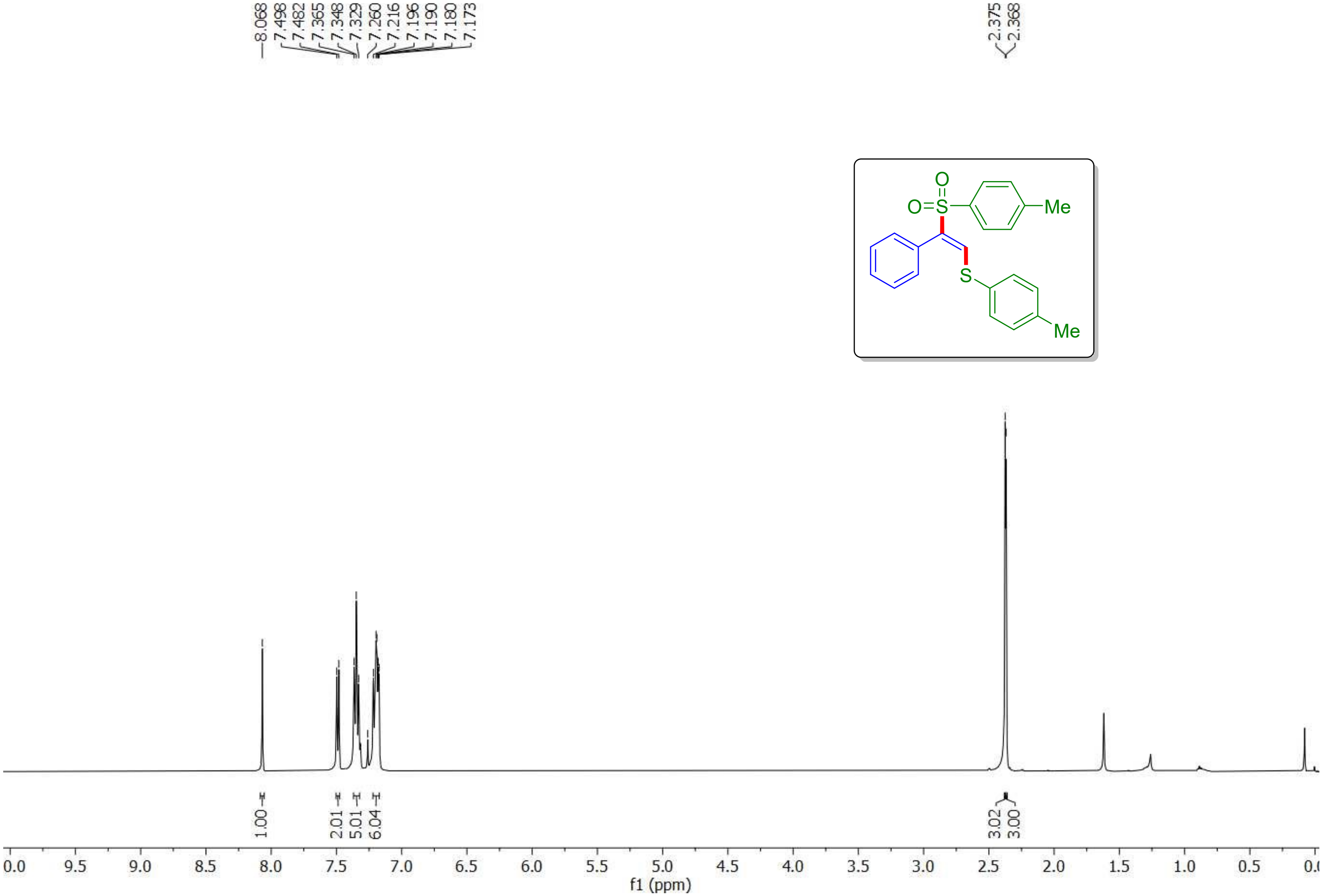
(E)-(2-(Methylsulfonyl)-2-phenylvinyl)(phenyl)sulfane (1i'): ^{1}*H NMR (CDCl*$_3$*, 500 MHz)*



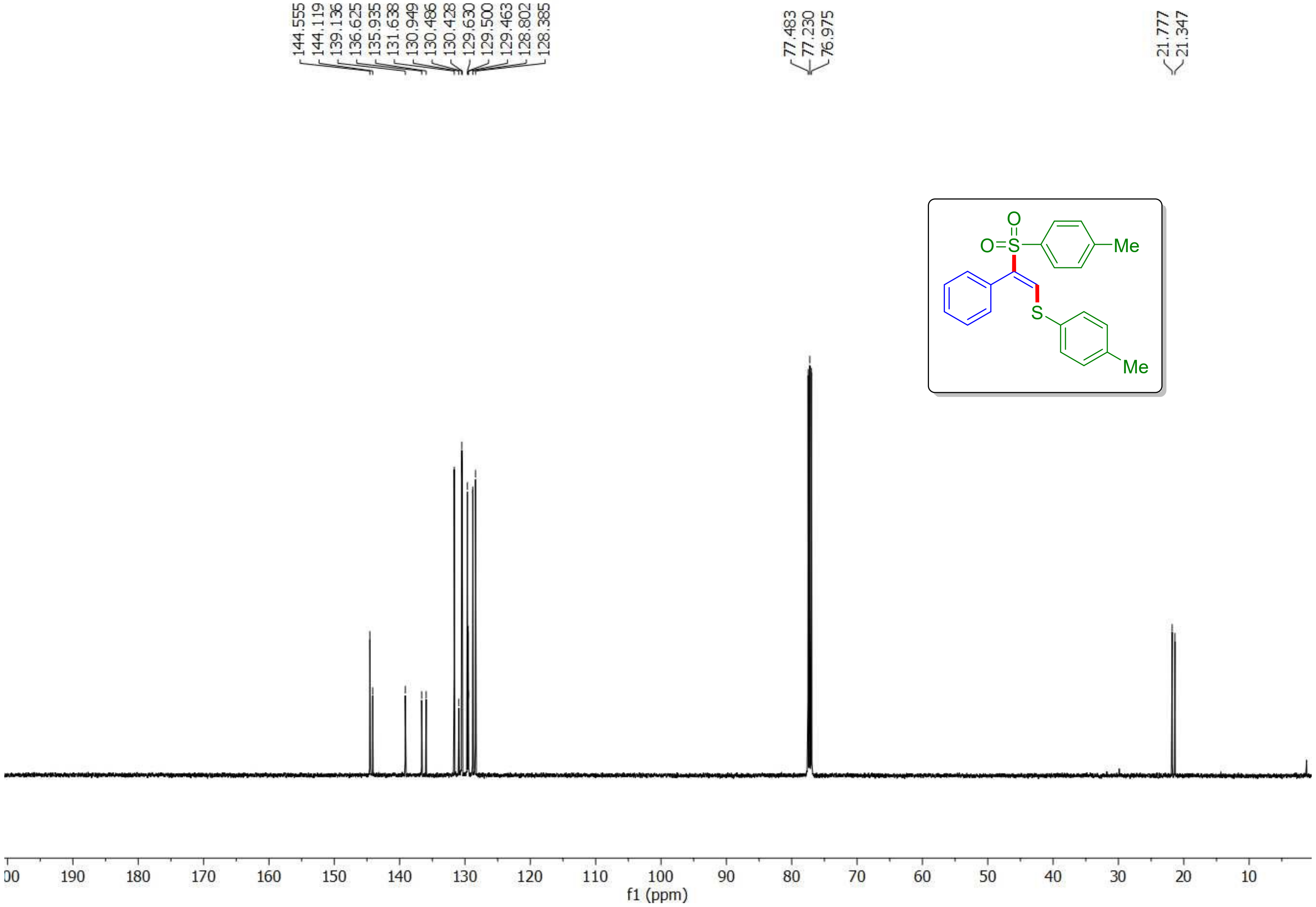
(E)-(2-(Methylsulfonyl)-2-phenylvinyl)(phenyl)sulfane (1i'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



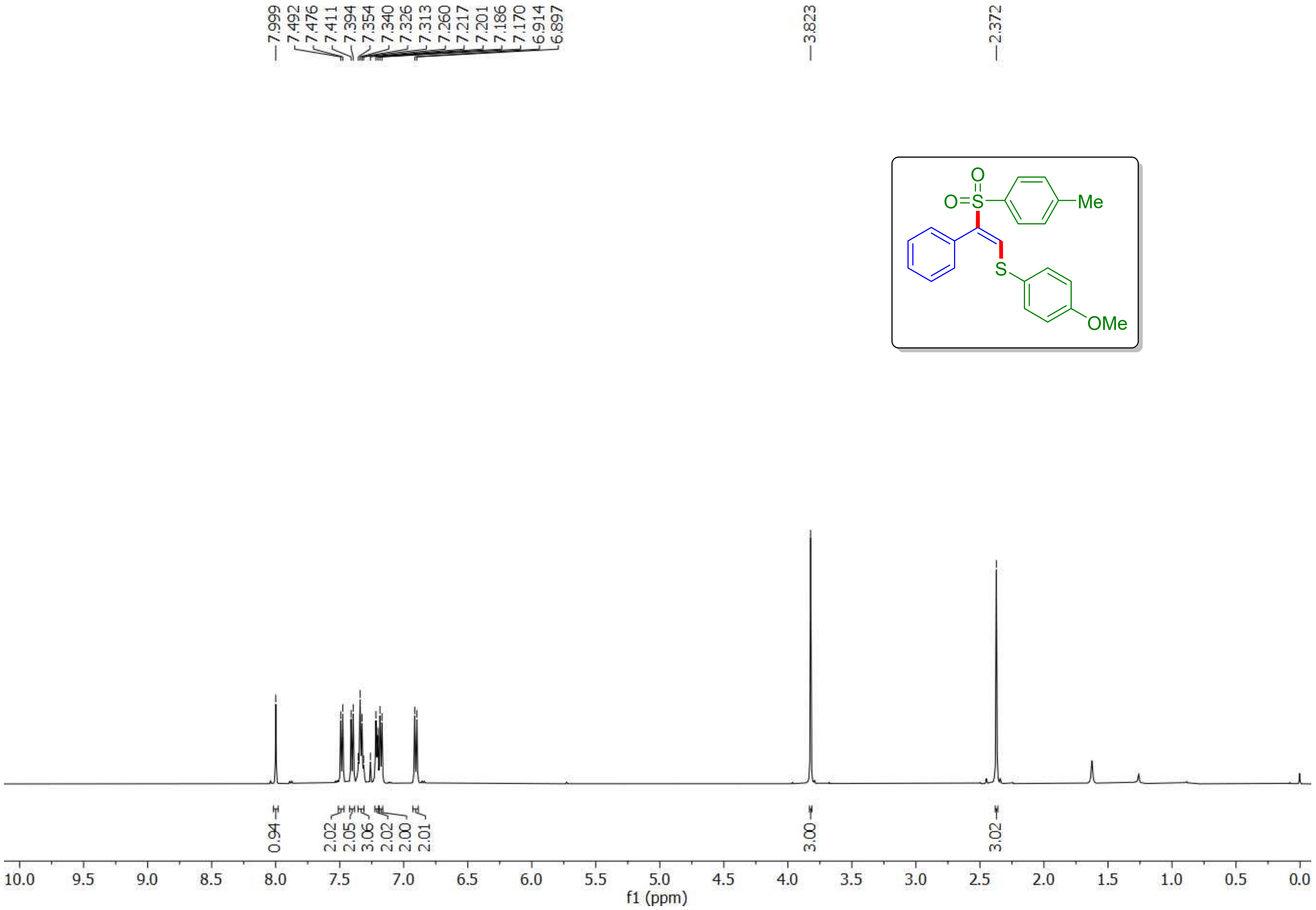
(E)-(2-Phenyl-2-tosylvinyl)(p-tolyl)sulfane (1k'): ^{1}H NMR (CDCl$_3$, 500 MHz)



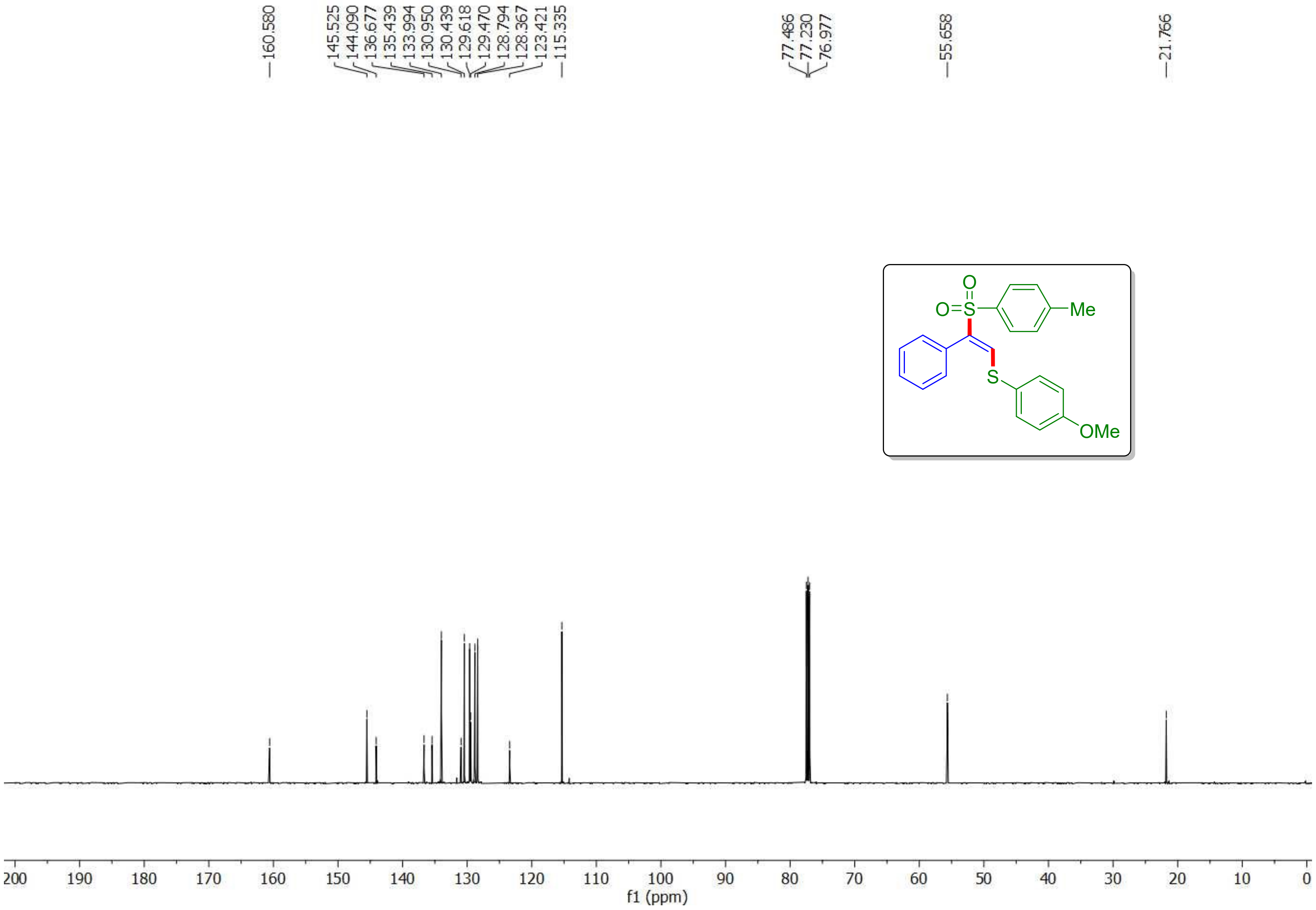
(E)-(2-Phenyl-2-tosylvinyl)(p-tolyl)sulfane (1k'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*



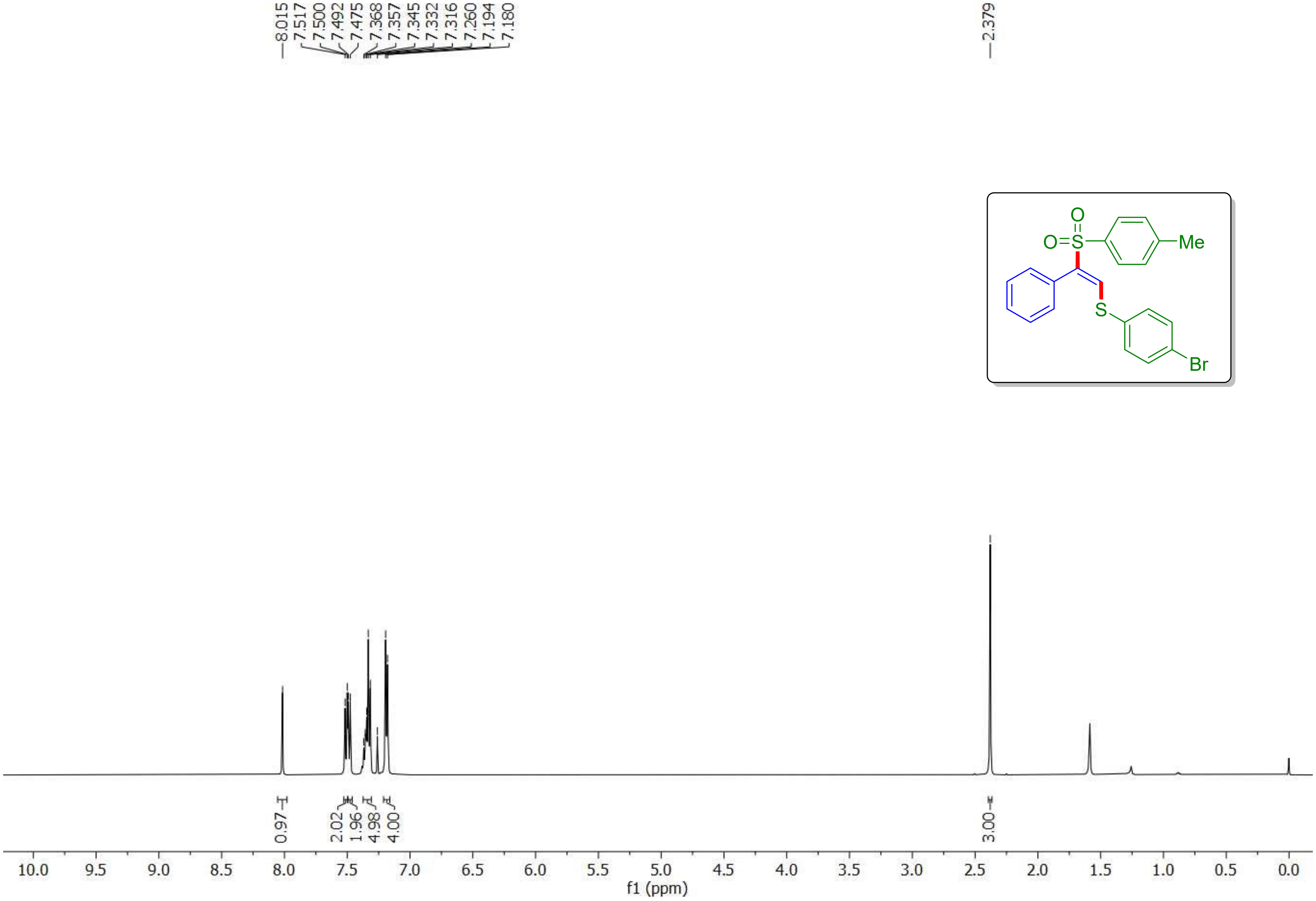
(E)-(4-Methoxyphenyl)(2-phenyl-2-tosylvinyl)sulfane (1l'): ^{1}H NMR ($CDCl_3$, 500 MHz)



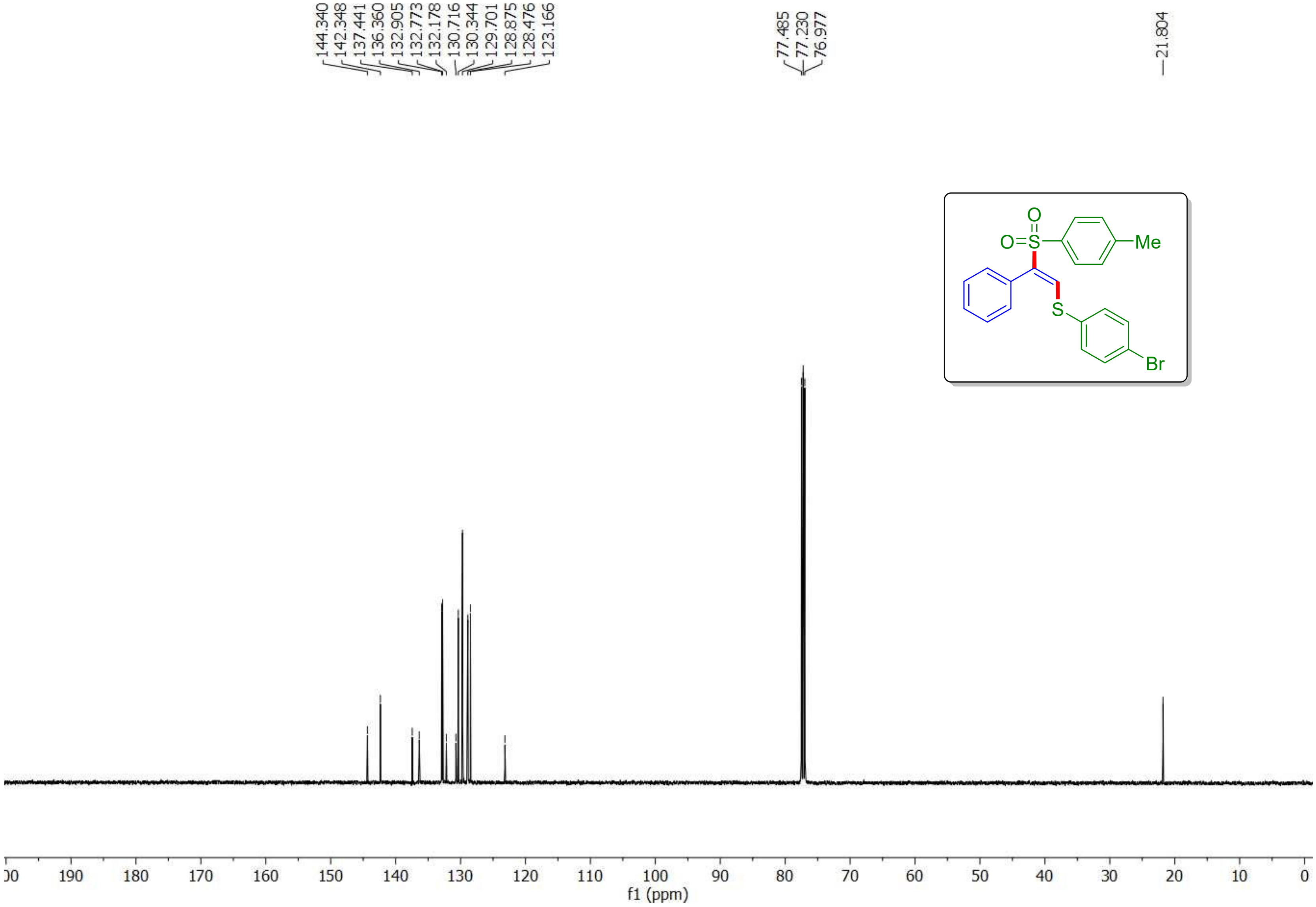
(E)-(4-Methoxyphenyl)(2-phenyl-2-tosylvinyl)sulfane (1l'): $^{13}C\{^{1}H\}$ *NMR* ($CDCl_3$*, 125 MHz)*



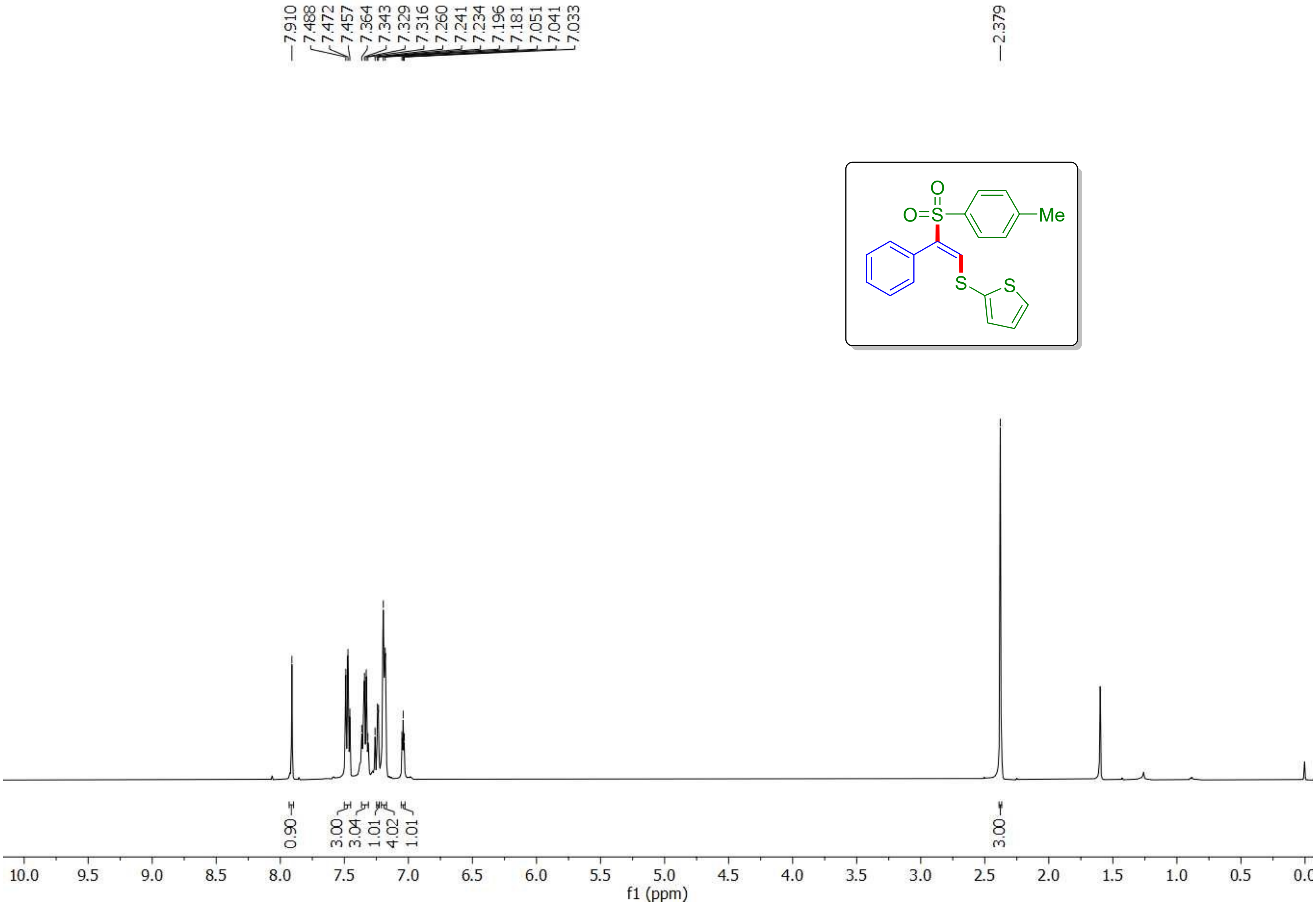
(E)-(4-Bromophenyl)(2-phenyl-2-tosylvinyl)sulfane (1n'): ^{1}*H NMR (CDCl*$_3$*, 500 MHz)*



(E)-(4-Bromophenyl)(2-phenyl-2-tosylvinyl)sulfane (1n'): $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



(E)-2-((2-Phenyl-2-tosylvinyl)thio)thiophene (1q'): ^{1}*H NMR (CDCl*$_3$*, 500 MHz)*



(E)-2-((2-Phenyl-2-tosylvinyl)thio)thiophene (1q'): $^{13}C\{^{1}H\}$ *NMR (CDCl$_3$, 125 MHz)*