Supporting Information

Electrochemical Sulfinylation-Driven Skeletal Rearrangement of Baylis-Hillman Adducts

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1. General. All solvents used in this study were distilled and dried before use, according to standard procedures. ^{1}H, ^{13}C and ^{19}F NMR spectra were collected at Varian Unity Inova-600 or a Varian Mercury-400 NMR instrument using $CDCl_3$ as solvent. Chemical shifts were reported in δ (ppm), relative to the internal standard, TMS. The signals observed are described as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants are reported as *J* values in Hz. Mass spectrometry was obtained using a Jeol JMS-HX 110 spectrometer. LC analyses were performed on SHIMADZU Model: LC-2050C 3D, and the LC mass spectra (LC-MS) analyses were recorded on DPiMS-2020. The Liquid chromatography-tandem mass spectra (LC-MSMS) analyses were recorded on LC-8045. Mass analyses were performed on a Waters SYNAPT HDMS Q-TOF mass spectrometer (ESI-Q-TOF) to determine the molecular weights of the synthesized molecules. The X-ray diffraction measurements were carried out using a Bruker D8 VENTURE XRD instrument. Cyclic voltammetry was performed on a CHI Instruments 750A potentiostat using acetonitrile as solvent. The melting points were recorded on a Büchi 535 melting point apparatus and are uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 F_{254} (Merck) plates. An undivided electrochemical cell equipped with platinum electrodes (IKA) was used, with dimensions of 0.7 cm × 0.7 cm × 0.2 cm for small-scale reactions and 2.8 cm × 0.7 cm × 0.2 cm for larger-scale reactions. A GW Instek GPS-2303 Laboratory DC Power Supply (350 watts, 450 VA, 50/60 Hz) was employed as the power source.

2. General Procedure for the Synthesis of Compounds 3

An oven-dried 10 mL glass vessel was sequentially charged with the Baylis-Hillman skeletons (**1**, 1.0 mmol), the corresponding thiols (**2**, 1.0 mmol), and 5 mL of a 0.1 M KI electrolyte solution in acetonitrile (CH_3CN), along with a magnetic stir bar. The reaction mixture was purged with nitrogen for approximately 10 s, after which the vessel was sealed with a rubber stopper fitted with a nitrogen balloon. Platinum plates (working dimensions: 0.7 cm × 0.7 cm × 0.2) were introduced into the vessel as both the anode and cathode, positioned 0.5 cm apart to form an undivided electrochemical cell. A constant direct current (10 mA) was applied to the stirred reaction mixture at room temperature for 5 h. Reaction progress was monitored periodically by thin-layer chromatography (TLC). Upon completion, 20 mL of a mixture of ethyl acetate and water (3:1, *v*/*v*) was added, and the resulting mixture was transferred to a separatory funnel and vigorously shaken. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc-Hexane mixtures as eluents to afford the desired product **3** (**3aa**-**3fi**) in each case. In total, 34 derivatives were synthesized and fully characterized by detailed spectroscopic analysis, including ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS.

3. Gram-scale synthesis of compound 3aa

Methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**, 5.0 mmol, 0.960 g), benzenethiol (**2a**, 5.0 mmol, 0.550 g), 15 mL of 0.2 M potassium iodide (KI) in acetonitrile (CH_3CN), and a magnetic stir bar were sequentially transferred into an oven-dried glass vessel. The reaction mixture was purged with nitrogen (N_2) for approximately 1 min and then sealed with a stopper fitted with a vertical channel connected to an N_2 balloon. Platinum electrode plates (2.8 × 0.7 × 0.2 cm) were inserted into the vessel, positioned 0.5 cm apart, to assemble an undivided electrochemical cell. A constant direct current (DC) of 10 mA was applied while stirring the reaction mixture at ambient temperature (25-28 °C) for 13 h. Reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was quenched by adding 40 mL of a 3:1 (*v*/*v*) ethyl acetate/water mixture and extracted in a separatory funnel. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. The residue was purified by column chromatography on silica gel using EtOAc-Hexane mixtures as eluents, yielding the desired product, methyl (*Z*)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3aa**), in 75% yield (1.125 g).

4. General procedure for cyclic voltammetry

Electrochemical tests were performed on a CHI Instruments 750A potentiostat using acetonitrile as solvent. A standard cyclic voltammetric (CV) experiment based on a three-electrode system is conducted. The working electrode uses BAS glassy carbon (3 mm diameter), while the reference and auxiliary electrodes use Ag/AgCl (saturated) and platinum wire, respectively. Potentials are reported *vs*. Ag/AgCl (saturated). The working electrode was polished with 0.03 μm aluminium on felt pads (Buehler) before each experiment. The reference is Ag/Ag^+ electrode, and 10 mL of electrolyte solution containing 300 mg $^n Bu_4NBF_4$ in CH_3CN was poured into the electrochemical cell in all experiments. 1 mg of each of the samples, such as methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**), benzenethiol (**2a**), KI, and other mixtures, was used for the purpose. The potential scan ranged from −2.0 to +2.0 V at a scan rate of 0.1 V/s for each case. CV plotting convention is IUPAC.

5. Cyclic voltammograms of methyl 2-(hydroxy(phenyl)methyl)acrylate (1a), benzenethiol (2a), KI, and other mixtures:

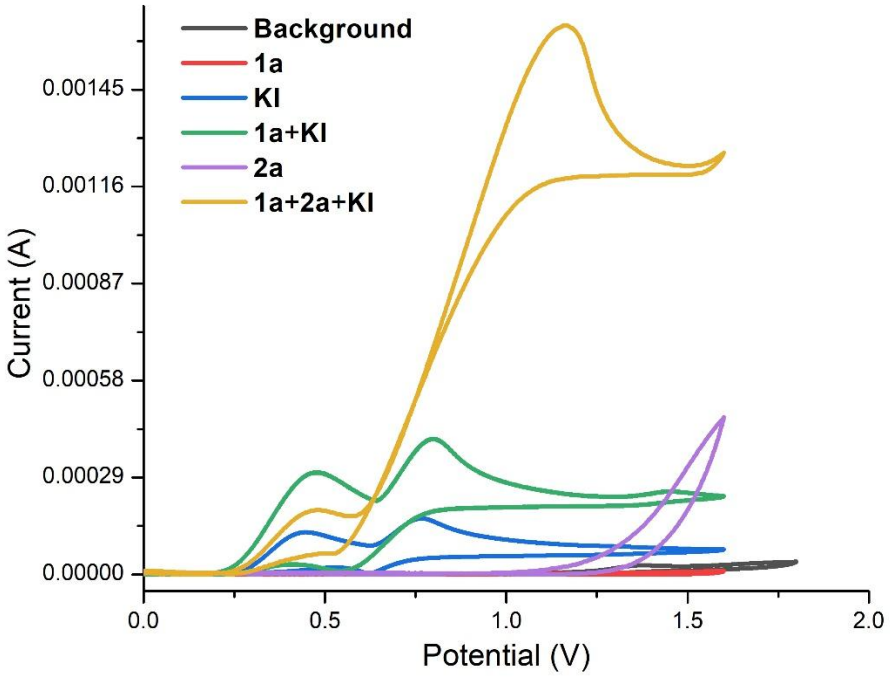


Figure S1. Cyclic voltammetry

6. The EPR Experiment

Electron paramagnetic resonance (EPR) measurements were performed using a Bruker EMX-Plus EPR spectrometer operating in the X-band frequency range. The EPR spectra were acquired and analyzed with the following instrumental parameters: sampling time of 40 s, field modulation amplitude of 0.0001 T, field modulation frequency of 100 Hz, microwave frequency of 9.741 GHz, microwave power of 40.36 mW, receiver gain of 30, and a receiver time constant of 40.96 ms.

Radical trapping in reaction: A mixture of methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**, 1.0 mmol), benzenethiol (**2a**, 1.0 mmol), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 1.0 equiv), and 5 mL of 0.1 M potassium iodide (KI) in acetonitrile (CH_3CN) was placed in an oven-dried glass vessel equipped with a magnetic stir bar. The vessel was evacuated and backfilled with nitrogen using a balloon.Platinum electrode plates (2.8 × 0.7 × 0.2 cm) were introduced into the vessel as both the anode and cathode, positioned 0.5 cm

apart to form an undivided electrochemical cell. A constant direct current (10 mA) was applied to the stirred reaction mixture at room temperature for 0-15 min. Later, a small amount of the mixture was quickly transferred to the small tube for EPR analysis. The radical was trapped with an intense, prominent signal of radical species (Figure S2). Then, the crude reaction mixture was also analyzed by EI-HRMS, and the benzenethiol radical intermediates trapped by DMPO were detected (Figure S80).

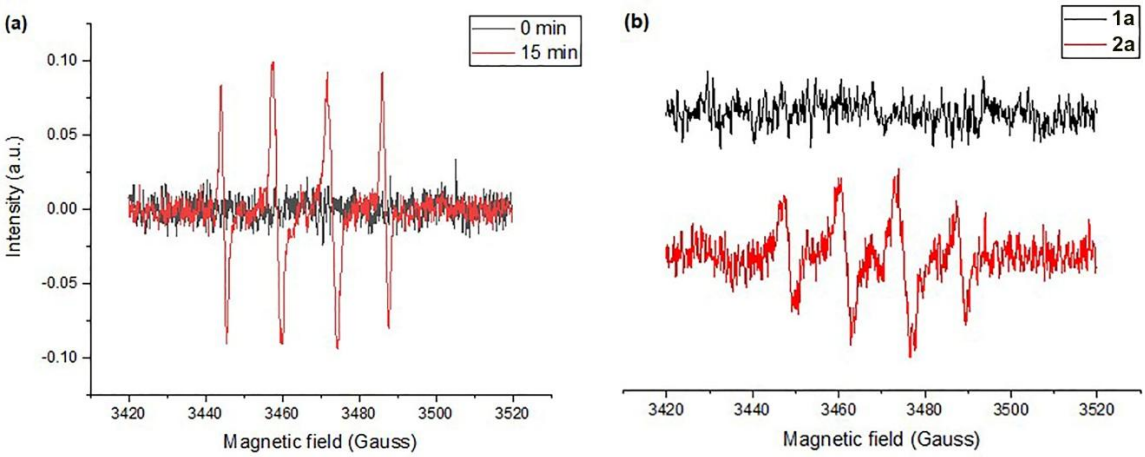


Figure 2. EPR diagram

7. Single X-ray crystal structure analysis of methyl (Z)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (3fc)

Preparation of single crystals of compound 3fc

For preparing single crystals of compound **3fc**, 50 mg of the sample was dissolved in 5 mL of commercial chloroform, and the solution was left for 15 days for slow evaporation at ambient temperature to yield colourless block-shaped crystals.

CCDC 2375469 (Compound **3fc**) 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

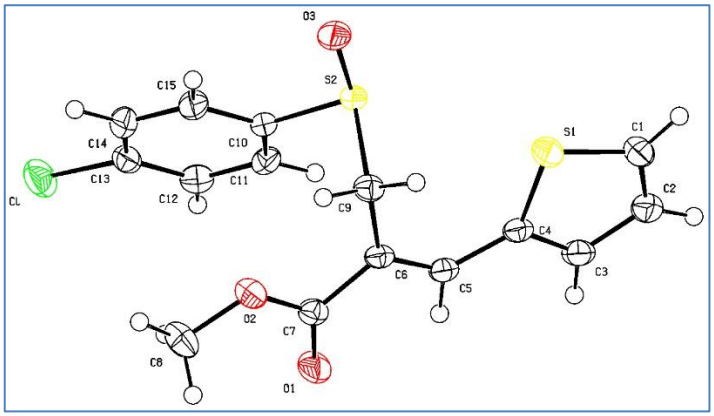
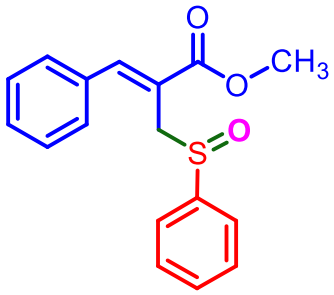


Figure. S3 *ORTEP* view of the molecule, showing the atom-labelling scheme
Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

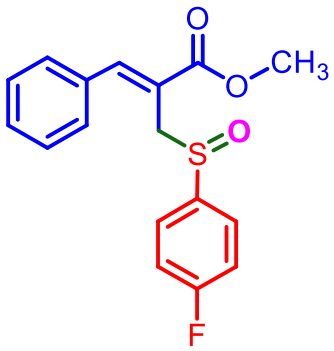
Table S1. Crystal data and structure refinement for methyl (Z)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (3fc)

CCDC	2375469	
Empirical formula	$C_{15}H_{13}ClO_3S_2$	
Formula weight	340.82	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.2579(12) Å	α= 90°.
	b = 12.7858(7) Å	β= 105.9390(16)°.
	c = 11.3836(5) Å	γ = 90°.
Volume	3115.1(3) $Å^3$	
Z	8	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	1408	
Crystal size	0.490 x 0.190 x 0.180 mm^3	
Theta range for data collection	3.187 to 27.899°.	
Index ranges	-29<=h<=29, -16<=k<=16, -14<=l<=13	
Reflections collected	68816	
Independent reflections	3722 [R(int) = 0.0489]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6707	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3722 / 0 / 190	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0767	
R indices (all data)	R1 = 0.0387, wR2 = 0.0862	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.301 and -0.339 $e.Å^{-3}$	
Software for solve and refine	Olex2[1]	
Software for structure solution	SHELXS[2]	
Software for refinement	SHELXL[3]	

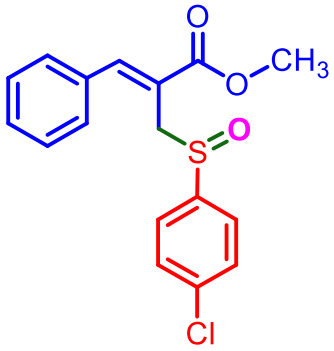
8. The Physical and Spectral Data of the Synthesized Compounds 3 are given below:



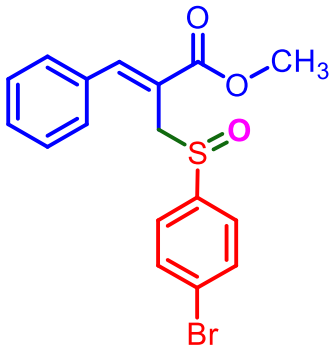
Methyl (*Z*)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3aa). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), thiophenol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3aa** as a yellow oil; yield: 83% (0.294 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (s, 1H), 7.68 – 7.65 (m, 2H), 7.55 – 7.53 (m, 2H), 7.47 – 7.46 (m, 3H), 7.39 – 7.36 (m, 3H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.75 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.35, 146.36, 143.90, 134.10, 131.36, 129.68, 129.50 (2*C*), 129.22 (2*C*), 128.77 (2*C*), 124.36 (2*C*), 122.30, 56.84, 52.57 ppm. HRMS (EI) calcd for $C_{17}H_{16}O_3S$ $[M]^+$ 300.0820, found 300.0829.



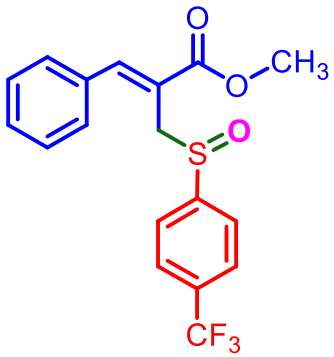
Methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-phenylacrylate (3ab). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ab** as a yellow oil; yield: 55% (0.175 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (s, 1H), 7.66 – 7.61 (m, 2H), 7.51 – 7.49 (m, 2H), 7.39 – 7.36 (m, 3H), 7.17 – 7.11 (m, 2H), 4.18 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.21, 164.55 (d, J_{CF} = 250 Hz), 146.29, 139.12, 133.94, 129.67, 129.33 (2*C*), 128.72 (2*C*), 126.65 (d, J_{CF} = 9 Hz, 2*C*), 121.96, 116.41 (d, J_{CF} = 22 Hz, 2*C*), 56.81, 52.56 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -108.20 ppm. HRMS (EI) calcd for $C_{17}H_{15}FO_3S$ $[M]^+$ 318.0726, found 318.0741.



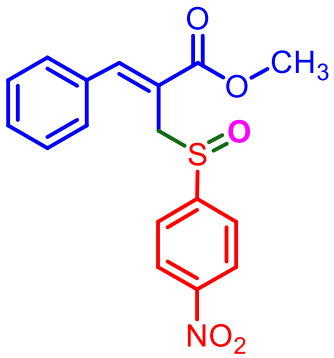
Methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-phenylacrylate (3ac). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), 4-chlorobenzenethiol (**2c**, 1.0 mmol, 0.145 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ac** as a yellow oil; yield: 80% (0.269 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (s, 1H), 7.49 – 7.48 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.27 – 7.15 (m, 4H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.93 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.22, 146.46, 142.75, 133.89, 132.29 (2*C*), 129.69, 129.30 (2*C*), 128.74 (2*C*), 125.95 (2*C*), 125.90, 121.83, 56.69, 52.63 ppm. HRMS (EI) calcd for $C_{17}H_{15}ClO_3S$ $[M]^+$ 334.0430, found 334.0441.



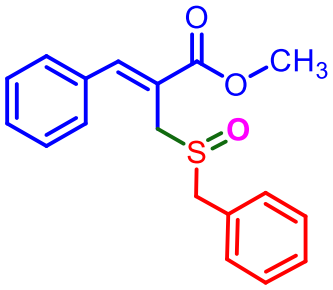
Methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ad**). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ad** as a yellow oil; yield: 67% (0.254 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.36 – 7.32 (m, 5H), 4.13 (d, *J* = 12.4 Hz, 1H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.74 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.19, 146.39, 142.18, 137.54, 133.88, 129.66, 129.34 (2*C*), 129.28 (2*C*), 128.70 (2*C*), 125.74 (2*C*), 121.85, 56.75, 52.58 ppm. HRMS (EI) calcd for $C_{17}H_{15}BrO_3S$ $[M]^+$ 377.9925, found 377.9937.



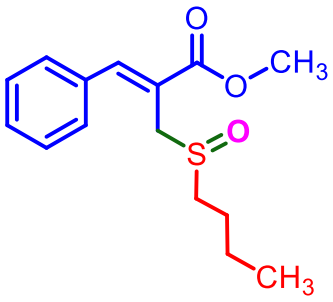
Methyl (*Z*)-3-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfinyl)methyl)acrylate (**3ae**). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), 4-(trifluoromethyl)benzenethiol (**2e**, 1.0 mmol, 0.178 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ae** as a yellow oil; yield: 54% (0.198 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03 (s, 1H), 7.76 – 7.68 (m, 4H), 7.45 – 7.43 (m, 2H), 7.36 – 7.34 (m, 3H), 4.20 (d, *J* = 12.4 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.78 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.23, 148.20, 146.69 (2*C*), 133.86, 133.47, 129.80, 129.30 (2*C*), 128.83 (2*C*), 126.15 – 126.04 (m), 124.88 (2*C*), 123.59 (d, J_{CF} = 271 Hz, *C*F_3), 121.73, 56.76, 52.67 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -62.75 ppm. HRMS (EI) calcd for $C_{18}H_{15}F_3O_3S$ $[M]^+$ 368.0694, found 368.0682.



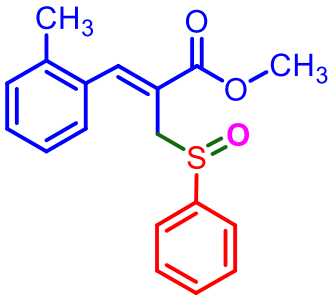
Methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-phenylacrylate (**3af**). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), 4-nitrobenzenethiol (**2f**, 1.0 mmol, 155 mg), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3af** as a yellow oil; yield: 64% (0.221 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.26 (d, *J* = 8.4 Hz, 2H), 8.05 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.37 – 7.33 (m, 3H), 4.21 (d, *J* = 12.8 Hz, 1H), 4.11 (d, *J* = 12.8 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H}□NMR ($CDCl_3$, 100 MHz): δ = 167.20, 151.46, 149.71, 146.86, 133.74, 129.92, 129.31 (2*C*), 128.82 (2*C*), 125.42 (2*C*), 124.15 (2*C*), 121.50, 56.94, 52.79 ppm. HRMS (EI) calcd for $C_{17}H_{15}NO_5S$ $[M]^+$ 345.0671, found 345.0683.



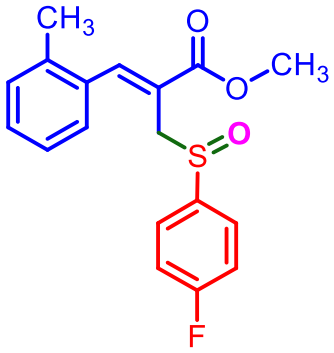
Methyl (*Z*)-2-((benzylsulfinyl)methyl)-3-phenylacrylate (**3ag**). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), phenylmethanethiol (**2g**, 1.0 mmol, 0.124 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ag** as a yellow oil; yield: 50% (0.157 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.53 – 7.50 (m, 2H), 7.37 – 7.29 (m, 8H), 4.12 (d, *J* = 12.8 Hz, 1H), 4.07 (d, *J* = 12.8 Hz, 1H), 3.97 (d, *J* = 12.8 Hz, 1H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.42, 146.31, 133.99, 130.39 (2*C*), 129.79, 129.67, 129.61 (2*C*), 128.93 (2*C*), 128.75 (2*C*), 128.49, 122.45, 58.73, 52.59, 50.03 ppm. HRMS (EI) calcd for $C_{18}H_{18}O_3S$ $[M]^+$ 314.0977, found 314.0984.



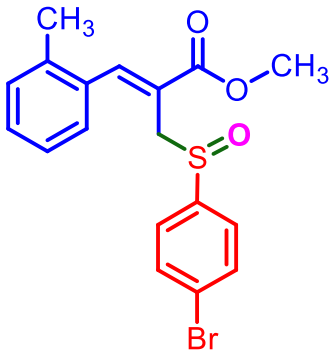
Methyl (*Z*)-2-((butylsulfinyl)methyl)-3-phenylacrylate (**3ah**). Following the general procedure, using methyl 2-(hydroxy(phenyl)methyl)acrylate (**1a**; 1.0 mmol, 0.192 g), butane-1-thiol (**2h**, 1.0 mmol, 0.090 mg), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ah** as a yellow oil; yield: 62% (0.174 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.63 – 7.60 (m, 2H), 7.43 – 7.39 (m, 3H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.91 (d, *J* = 12.8 Hz, 1H), 3.85 (s, 3H), 2.76 – 2.72 (m, 2H), 1.78 – 1.70 (m, 2H), 1.52 – 1.37 (m, 2H), 0.94 – 0.90 (m, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.49, 146.00, 134.16, 129.73, 129.60 (2*C*), 128.85 (2*C*), 122.72, 52.72, 52.63, 51.31, 24.59, 22.12, 13.76 ppm. HRMS (EI) calcd for $C_{15}H_{20}O_3S$ $[M]^+$ 280.1133, found 280.1145.



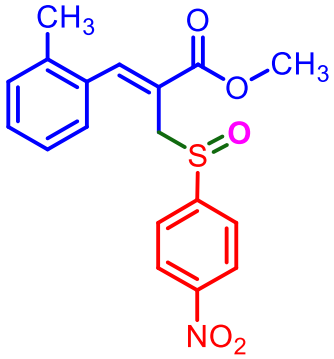
Methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3ba**). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), benzenethiol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ba** as a yellow oil; yield: 75% (0.236 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.59 – 7.57 (m, 2H), 7.49 – 7.48 (m, 1H), 7.45 – 7.41 (m, 3H), 7.27 – 7.18 (m, 2H), 7.16 – 7.14 (m, 1H), 4.05 (dd, *J* = 12.4 and 0.8 Hz, 1H), 3.89 (dd, *J* = 12.4 and 0.8 Hz, 1H), 3.78 (s, 3H), 2.18 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.06, 145.70, 144.02, 136.98, 133.31, 131.25, 130.20, 129.37, 129.15 (2*C*), 129.06, 126.00, 124.29 (2*C*), 123.08, 56.72, 52.50, 20.09 ppm. HRMS (EI) calcd for $C_{18}H_{18}O_3S$ $[M]^+$ 314.0977, found 314.0989.



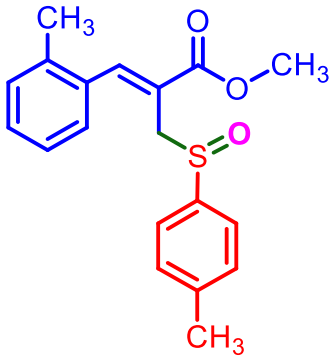
Methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bb**). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3bb** as a yellow oil; yield: 67% (0.223 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.06 (s, 1H), 7.58 – 7.54 (m, 2H), 7.46 – 7.43 (m, 1H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.08 (m, 2H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.92 (d, *J* = 12.4 Hz, 1H), 3.79 (s, 3H), 2.18 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.02, 164.51 (d, J_{CF} = 250 Hz), 145.78, 139.22 (d, J_{CF} = 3 Hz), 136.98, 133.20, 130.28, 129.46, 128.91, 126.70 (d, J_{CF} = 9 Hz, 2*C*), 126.03, 122.75, 116.44 (d, J_{CF} = 23 Hz, 2*C*), 56.71, 52.58, 20.05 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -108.13 ppm. HRMS (EI) calcd for $C_{18}H_{17}FO_3S$ $[M]^+$ 332.0882, found 332.0897.



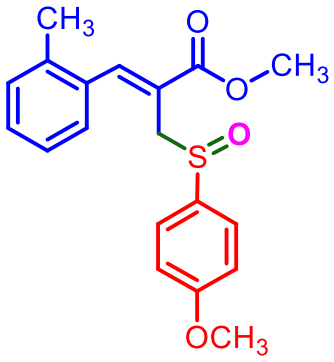
Methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bd**). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3bd** as a yellow oil; yield: 71% (0.280 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (s, 1H), 7.52 – 7.50 (m, 2H), 7.41 – 7.38 (m, 3H), 7.24 – 7.22 (m, 1H), 7.20 – 7.14 (m, 2H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.94 (d, *J* = 12.4 Hz, 1H), 3.79 (s, 3H), 2.15 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.03, 145.91, 142.86, 137.03, 133.15, 132.34 (2*C*), 130.35, 129.52, 128.88, 126.05, 125.98 (2*C*), 125.89, 122.62, 56.61, 52.66, 20.08 ppm. HRMS (EI) calcd for $C_{18}H_{17}BrO_3S$ $[M]^+$ 392.0082, found 392.0098.



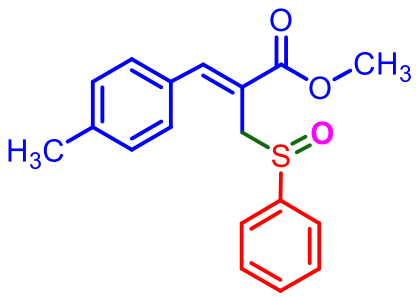
Methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bf**). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), 4-nitrobenzenethiol (**2f**, 1.0 mmol, 0.155 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3bd** as a yellow oil; yield: 72% (0.259 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.27 – 8.24 (m, 2H), 8.13 (s, 1H), 7.78 – 7.74 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 4.07 (d, *J* = 12.4 Hz, 1H), 4.02 (d, J = 12.4 Hz, 1H), 3.85 (s, 3H), 2.19 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.03, 151.83, 149.64, 146.34, 137.07, 133.05, 130.42, 129.74, 128.90, 126.15, 125.34 (2*C*), 124.19 (2*C*), 122.37, 56.95, 52.79, 20.17 ppm. HRMS (EI) calcd for $C_{18}H_{17}NO_5S$ $[M]^+$ 359.0827, found 359.0816.



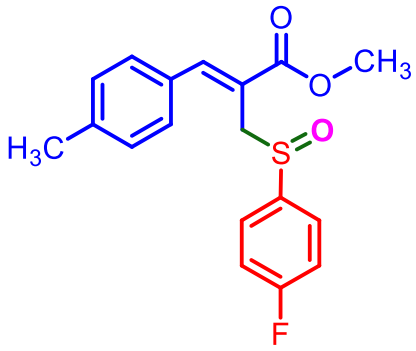
Methyl (*Z*)-3-(*o*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (3bi). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), 4-methylbenzenethiol (**2i**, 1.0 mmol, 0.124 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3bi** as a yellow oil; yield: 60% (0.197 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (s, 1H), 7.47 – 7.44 (m, 3H), 7.25 – 7.19 (m, 4H), 7.14 (d, *J* = 7.2 Hz, 1H), 4.05 (d, *J* = 12.0 Hz, 1H), 3.88 (d, *J* = 12.0 Hz, 1H), 3.78 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.13, 145.55, 141.77, 140.68, 137.02, 133.35, 130.16, 129.84 (2*C*), 129.35, 129.09, 126.01, 124.41 (2*C*), 123.13, 56.71, 52.52, 21.50, 20.08 ppm. HRMS (EI) calcd for $C_{19}H_{20}O_3S$ $[M]^+$ 328.1133, found 328.1141.



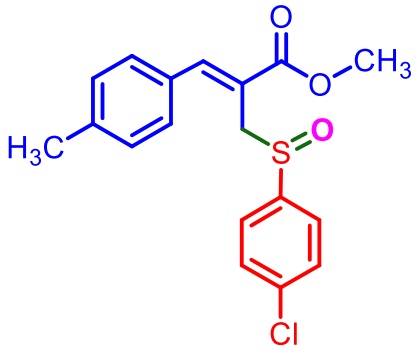
Methyl (*Z*)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-(o-tolyl)acrylate (3bj). Following the general procedure, using methyl 2-(hydroxy(*o*-tolyl)methyl)acrylate (**1b**; 1.0 mmol, 0.206 g), 4-methylbenzenethiol (**2j**, 1.0 mmol, 0.140 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3bj** as a yellow oil; yield: 56% (0.193 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.03 (s, 1H), 7.50 – 7.47 (m, 2H), 7.45 (d, *J* = 6.4 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.92 – 6.89 (m, 2H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.92 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.16 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.15, 162.25, 145.50, 137.06, 134.59, 133.41, 130.26, 129.38, 129.06, 126.42 (2*C*), 126.06, 123.11, 114.68 (2*C*), 56.57, 55.63, 52.57, 20.11 ppm. HRMS (EI) calcd for $C_{19}H_{20}O_4S$ $[M]^+$ 344.1082, found 344.1093.



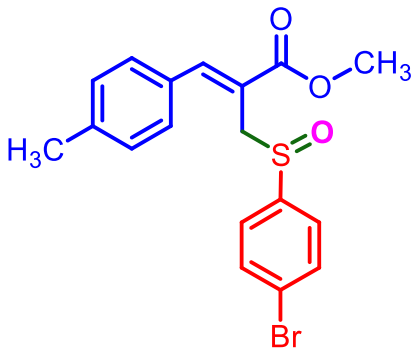
Methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*p*-tolyl)acrylate (3ca). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), benzenethiol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ca** as a yellow oil; yield: 66% (0.208 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (s, 1H), 7.69 – 7.65 (m, 2H), 7.49 – 7.46 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.20 (d, *J* = 12.8 Hz, 1H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.45, 146.34, 143.97, 140.12, 131.28, 131.26, 129.64 (2*C*), 129.49 (2*C*), 129.16 (2*C*), 124.34 (2*C*), 121.23, 56.93, 52.45, 21.50 ppm. HRMS (EI) calcd for $C_{18}H_{18}O_3S$ $[M]^+$ 314.0977, found 314.0990.



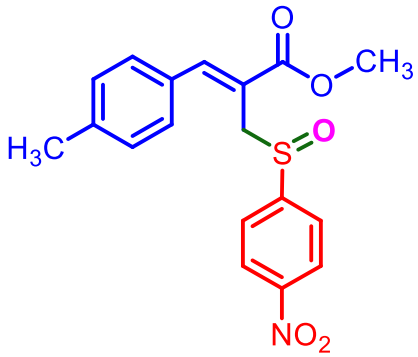
Methyl (Z)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (3cb). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3cb** as a yellow oil; yield: 67% (0.223 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 1H), 7.66 – 7.61 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.11 (m, 2H), 4.20 (d, *J* = 12.8 Hz, 1H), 4.03 (d, J = 12.4 Hz, 1H), 3.75 (s, 3H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.43, 164.82 (d, J_{CF} = 250 Hz), 146.41, 140.25, 139.21 (d, J_{CF} = 4 Hz), 131.19, 129.57 (2*C*), 129.54 (2*C*), 126.74 (d, J_{CF} = 9 Hz, 2*C*), 120.95, 116.44 (d, J_{CF} = 23 Hz, 2*C*), 56.99, 52.55, 21.52 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -108.26 ppm. HRMS (EI) calcd for $C_{18}H_{17}FO_3S$ $[M]^+$ 332.0882, found 332.0890.



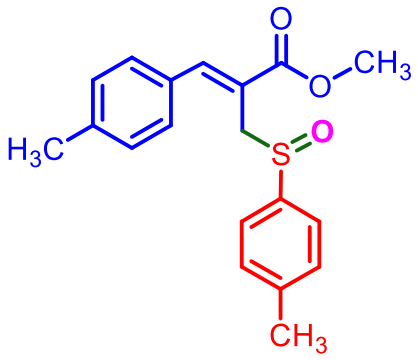
Methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (3cc). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), 4-chlorobenzenethiol (**2c**, 1.0 mmol, 0.145 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3cc** as a yellow oil; yield: 62% (0.217 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 1H), 7.59 – 7.56 (m, 2H), 7.42 – 7.39 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.19 (d, *J* = 12.8 Hz, 1H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.76 (s, 3H), 2.38 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.42, 146.51, 142.34, 140.25, 137.59, 131.14, 129.52 (4*C*), 129.36 (2*C*), 125.82 (2*C*), 120.85, 56.94, 52.57, 21.53 ppm. HRMS (EI) calcd for $C_{18}H_{17}ClO_3S$ $[M]^+$ 348.0587, found 348.0592.



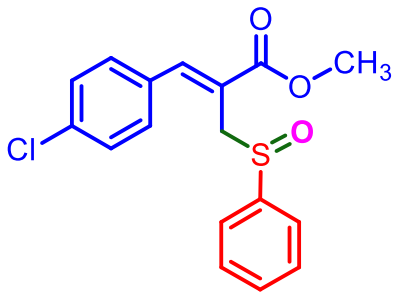
Methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (3cd). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3cd** as a yellow oil; yield: 63% (0.248 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 1H), 7.58 – 7.55 (m, 2H), 7.51 – 7.48 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.19 (d, *J* = 12.8 Hz, 1H), 4.04 (d, *J* = 12.4 Hz, 1H), 3.76 (s, 3H), 2.38 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.43, 146.55, 142.98, 140.27, 132.29 (2*C*), 131.15, 129.53 (4*C*), 126.01 (2*C*), 125.91, 120.84, 56.91, 52.60, 21.56 ppm. HRMS (EI) calcd for $C_{18}H_{17}BrO_3S$ $[M]^+$ 392.0082, found 392.0093.



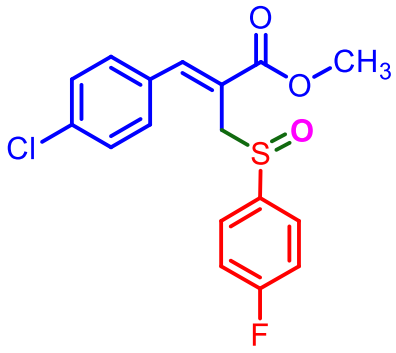
Methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cf**). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), 4-nitrobenzenethiol (**2f**, 1.0 mmol, 0.155 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3cf** as a yellow oil; yield: 67% (0.241 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.28 – 8.24 (m, 2H), 8.01 (s, 1H), 7.84 – 7.80 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.23 (d, *J* = 12.4 Hz, 1H), 4.14 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.38, 151.57, 149.73, 146.92, 140.57, 130.95, 129.58 (2*C*), 129.49 (2*C*), 125.48 (2*C*), 124.11 (2*C*), 120.44, 57.08, 52.73, 21.52 ppm. HRMS (EI) calcd for $C_{18}H_{17}NO_5S$ $[M]^+$ 359.0827, found 359.0834.



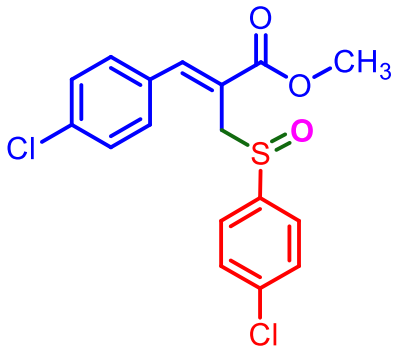
Methyl (*Z*)-3-(*p*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3ci**). Following the general procedure, using methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate (**1c**; 1.0 mmol, 0.206 g), 4-methylbenzenethiol (**2i**, 1.0 mmol, 0.124 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ci** as a yellow oil; yield: 85% (0.279 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.21 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.43 (d, *J* = 12.4 Hz, 1H), 4.22 (d, *J* = 12.4 Hz, 1H), 3.96 (s, 3H), 2.62 (s, 3H), 2.61 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.52, 146.22, 141.79, 140.65, 140.07, 131.32, 129.83 (2*C*), 129.65 (2*C*), 129.44 (2*C*), 124.40 (2*C*), 121.32, 56.93, 52.46, 21.53 (2*C*) ppm. HRMS (EI) calcd for $C_{19}H_{20}O_3S$ $[M]^+$ 328.1133, found 328.1141.



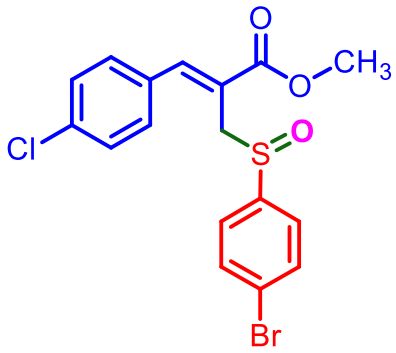
Methyl (*Z*)-3-(4-chlorophenyl)-2-((phenylsulfinyl)methyl)acrylate (**3da**). Following the general procedure, using methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (**1d**; 1.0 mmol, 0.227 g), benzenethiol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3da** as a yellow oil; yield: 86% (0.289 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 1H), 7.67 – 7.64 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.47 (m, 3H), 7.35 – 7.32 (m, 2H), 4.07 (d, *J* = 12.8 Hz, 1H), 3.93 (d, *J* = 12.8 Hz, 1H), 3.77 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.08, 145.07, 143.90, 135.79, 132.45, 131.38, 130.82 (2*C*), 129.28 (2*C*), 128.96 (2*C*), 124.18 (2*C*), 122.92, 56.80, 52.62 ppm. HRMS (EI) calcd for $C_{17}H_{15}ClO_3S$ $[M]^+$ 334.0430, found 334.0439.



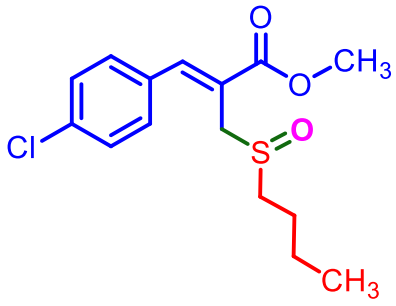
Methyl (*Z*)-3-(4-chlorophenyl)-2-(((4-fluorophenyl)sulfinyl)methyl)acrylate (**3db**). Following the general procedure, using methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (**1d**; 1.0 mmol, 0.227 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3db** as a yellow oil; yield: 67% (0.237 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (s, 1H), 7.66 – 7.63 (m, 2H), 7.53 – 7.50 (m, 2H), 7.46 – 7.43 (m, 2H), 7.19 – 7.15 (m, 2H), 4.06 (d, J = 12.4 Hz, 1H), 3.94 (d, J = 12.8 Hz, 1H), 3.79 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.07, 164.66 (d, J_{CF} = 250 Hz), 145.21, 139.26 (d, J_{CF} = 3 Hz), 132.85, 132.01 (2*C*), 130.98 (2*C*), 126.58 (d, J_{CF} = 9 Hz, 2*C*), 124.29, 122.81, 116.62 (d, J_{CF} = 22 Hz, 2*C*), 56.97, 52.73 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -107.95. HRMS (EI) calcd for $C_{17}H_{14}ClFO_3S$ $[M]^+$ 352.0336, found 352.0341.



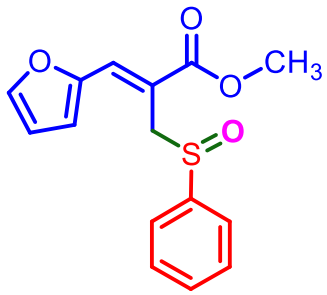
Methyl (*Z*)-3-(4-chlorophenyl)-2-(((4-chlorophenyl)sulfinyl)methyl)acrylate (**3dc**). Following the general procedure, using methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (**1d**; 1.0 mmol, 0.227 g), 4-chlorobenzenethiol (**2c**, 1.0 mmol, 0.145 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3dc** as a yellow oil; yield: 65% (0.240 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 1H), 7.60 – 7.57 (m, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 2H), 7.38 – 7.34 (m, 2H), 4.07 (d, J = 12.4 Hz, 1H), 3.96 (d, J = 12.4 Hz, 1H), 3.79 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.09, 145.27, 142.35, 137.75, 135.97, 132.37, 130.75 (2*C*), 129.54 (2*C*), 129.05 (2*C*), 125.71 (2*C*), 122.61, 56.92, 52.76 ppm. HRMS (EI) calcd for $C_{17}H_{14}Cl_2O_3S$ $[M]^+$ 368.0041, found 368.0037.



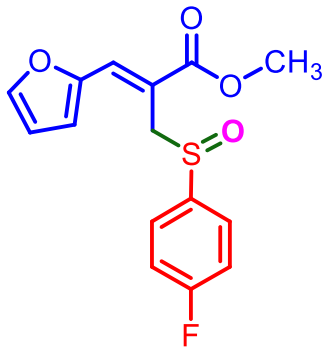
Methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dd**). Following the general procedure, using methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (**1d**; 1.0 mmol, 0.227 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3dd** as a yellow oil; yield: 64% (0.265 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1H), 7.61 – 7.58 (m, 2H), 7.52 – 7.46 (m, 4H), 7.37 – 7.34 (m, 2H), 4.07 (d, J = 12.8 Hz, 1H), 3.96 (d, J = 12.8 Hz, 1H), 3.79 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.06, 145.26, 142.93, 135.95, 132.44 (2*C*), 132.35, 130.72 (2*C*), 129.04 (2*C*), 126.01, 125.86 (2*C*), 122.56, 56.81, 52.75 ppm. HRMS (EI) calcd for $C_{17}H_{14}BrClO_3S$ $[M]^+$ 411.9536, found 411.9543.



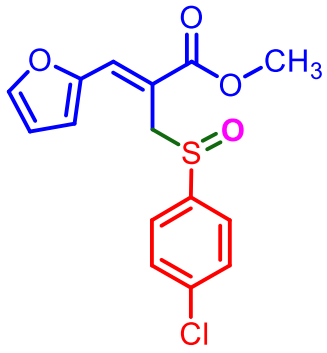
Methyl (Z)-2-((butylsulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dh**). Following the general procedure, using methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (**1d**; 1.0 mmol, 0.227 g), butane-1-thiol (**2h**, 1.0 mmol, 0.090 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3dh** as a yellow oil; yield: 52% (0.164 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (s, 1H), 7.54 (s, 4H), 3.90 (d, *J* = 12.8 Hz, 1H), 3.86 (s, 3H), 3.83 (d, *J* = 12.4 Hz, 1H), 2.79 – 2.75 (m, 2H), 1.79 – 1.75 (m, 2H), 1.53 – 1.42 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.30, 144.91, 133.02, 132.09 (2*C*), 131.23 (2*C*), 124.31, 123.49, 53.13, 52.76, 51.36, 24.69, 22.19, 13.82 ppm. HRMS (EI) calcd for $C_{15}H_{19}ClO_3S$ $[M]^+$ 314.0743, found 314.0738.



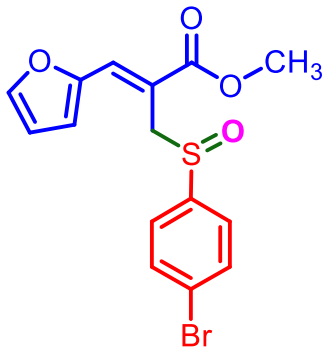
Methyl (*Z*)-3-(furan-2-yl)-2-((phenylsulfinyl)methyl)acrylate (**3ea**). Following the general procedure, using methyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**1e**; 1.0 mmol, 0.182 g), benzenethiol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ea** as a yellow oil; yield: 80% (0.232 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.62 – 7.59 (m, 2H), 7.54 (s, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.42 – 7.38 (m, 3H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.45 – 6.44 (m, 1H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.57 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.21, 150.57, 145.95, 143.52, 131.32, 130.12, 128.77 (2*C*), 124.52 (2*C*), 118.70, 116.34, 112.41, 56.63, 52.42 ppm. HRMS (EI) calcd for $C_{15}H_{14}O_4S$ $[M]^+$ 290.0613, found 290.0621.



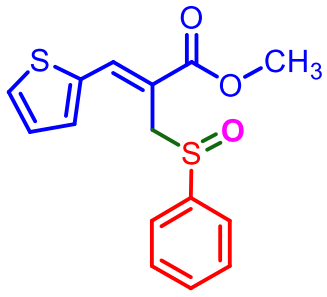
Methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3eb**). Following the general procedure, using methyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**1e**; 1.0 mmol, 0.182 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3eb** as a yellow oil; yield: 61% (0.188 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.64 – 7.57 (m, 2H), 7.54 (s, 1H), 7.51 (s, 1H), 7.13 – 7.07 (m, 2H), 6.69 (d, *J* = 3.2 Hz, 1H), 6.48 – 6.46 (m, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 3.62 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.16, 164.58 (d, J_{CF} = 251 Hz), 150.53, 145.95, 139.06 (d, J_{CF} = 3 Hz), 130.13, 126.84 (d, J_{CF} = 9 Hz, 2*C*), 118.86, 116.13, 116.02 (d, J_{CF} = 23 Hz, 2*C*), 112.51, 56.79, 52.49 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -108.34 ppm. HRMS (EI) calcd for $C_{15}H_{13}FO_4S$ $[M]^+$ 308.0519, found 308.0526.



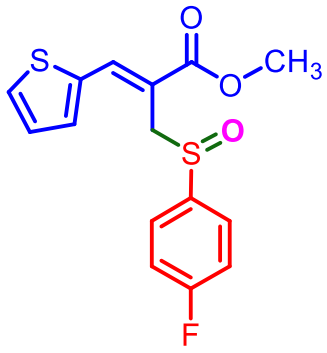
Methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ec**). Following the general procedure, using methyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**1e**; 1.0 mmol, 0.182 g), 4-chlorobenzenethiol (**2c**, 1.0 mmol, 0.145 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ec** as a yellow oil; yield: 60% (0.195 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 – 7.53 (m, 3H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.36 (m, 2H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.48 – 6.47 (m, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.16, 150.51, 146.10, 142.20, 137.49, 130.26, 128.87, 125.93, 118.95 (2*C*), 116.00 (2*C*), 112.50, 56.81, 52.55 ppm. HRMS (EI) calcd for $C_{15}H_{13}ClO_4S$ $[M]^+$ 324.0223, found 324.0229.



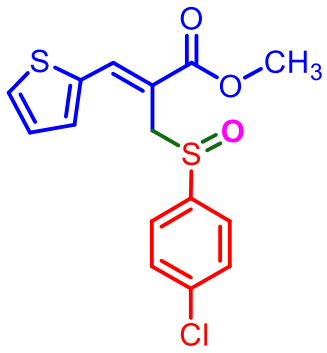
Methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ed**). Following the general procedure, using methyl 2-(furan-2-yl(hydroxy)methyl)acrylate (**1e**; 1.0 mmol, 0.182 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3ed** as a yellow oil; yield: 75% (0.277 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.52 – 7.44 (m, 6H), 6.66 (d, *J* = 3.2 Hz, 1H), 6.45 (s, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 3.60 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.15, 150.50, 145.85, 142.83, 131.91, 130.27, 126.07, 125.78, 118.97 (2*C*), 115.97 (2*C*), 112.47, 56.77, 52.57 ppm. HRMS (EI) calcd for $C_{15}H_{13}BrO_4S$ $[M]^+$ 367.9718, found 367.9723.



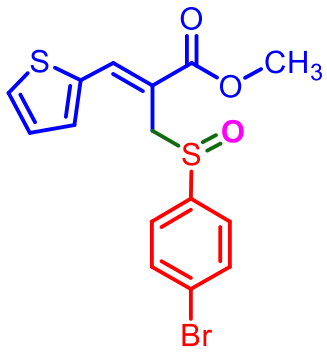
Methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fa**). Following the general procedure, using methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate (**1f**; 1.0 mmol, 0.198 g), benzenethiol (**2a**, 1.0 mmol, 0.110 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3fa** as a yellow oil; yield: 85% (0.245 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.71 – 7.68 (m, 2H), 7.54 – 7.53 (m, 1H), 7.49 – 7.46 (m, 4H), 7.12 – 7.09 (m, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 4.21 (d, *J* = 12.8 Hz, 1H), 3.61 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.23, 143.86, 137.56, 137.34, 134.27, 131.44, 130.84, 129.11 (2*C*), 127.85, 124.57 (2*C*), 117.60, 57.18, 52.49 ppm. HRMS (EI) calcd for $C_{15}H_{14}O_3S_2$ $[M]^+$ 306.0384, found 306.0390.



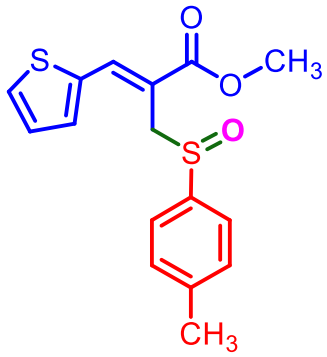
Methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fb**). Following the general procedure, using methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate (**1f**; 1.0 mmol, 0.198 g), 4-fluorobenzenethiol (**2b**, 1.0 mmol, 0.128 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3fb** as a yellow oil; yield: 60% (0.195 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.07 (s, 1H), 7.71 – 7.66 (m, 2H), 7.55 – 7.53 (m, 1H), 7.45 – 7.44 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.09 (m, 1H), 4.40 (d, J = 12.8 Hz, 1H), 4.21 (d, J = 12.4 Hz, 1H), 3.64 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.16, 164.71 (d, J_{CF} = 250 Hz), 139.18 (d, J_{CF} = 3 Hz), 137.65, 137.20, 134.41, 130.91, 127.88, 126.92 (d, J_{CF} = 9 Hz, 2*C*), 117.26, 116.38 (d, J_{CF} = 23 Hz, 2*C*), 57.26, 52.54 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -108.09 ppm. HRMS (EI) calcd for $C_{15}H_{13}FO_3S_2$ $[M]^+$ 324.0290, found 324.0298.



Methyl (Z)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fc**). Following the general procedure, using methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate (**1f**; 1.0 mmol, 0.198 g), 4-chlorobenzenethiol (**2c**, 1.0 mmol, 0.145 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3fc** as a yellow oil; yield: 63% (0.215 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.64 – 7.61 (m, 2H), 7.55 – 7.54 (m, 1H), 7.47 – 7.43 (m, 3H), 7.13 – 7.11 (m, 1H), 4.40 (d, J = 12.4 Hz, 1H), 4.21 (d, J = 12.8 Hz, 1H), 3.65 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.17, 142.37, 137.80, 137.70, 137.19, 134.47, 130.94, 129.35 (2*C*), 127.90, 126.02 (2*C*), 117.18, 57.31, 52.58 ppm. HRMS (EI) calcd for $C_{15}H_{13}ClO_3S_2$ $[M]^+$ 339.9995, found 339.9989.



Methyl (Z)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fd**). Following the general procedure, using methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate (**1f**; 1.0 mmol, 0.198 g), 4-bromobenzenethiol (**2d**, 1.0 mmol, 0.189 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3fd** as a yellow oil; yield: 62% (0.239 g; 1.0 mmol scale). ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.62 – 7.59 (m, 2H), 7.57 – 7.54 (m, 3H), 7.45 (d, J = 3.6 Hz, 1H), 7.13 – 7.11 (m, 1H), 4.40 (d, J = 12.4 Hz, 1H), 4.22 (d, J = 12.4 Hz, 1H), 3.65 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 167.11, 142.84, 137.78, 137.11, 134.44, 132.23 (2*C*), 130.91, 127.86, 126.13 (2*C*), 125.95, 117.08, 57.13, 52.54 ppm. HRMS (EI) calcd for $C_{15}H_{13}BrO_3S_2$ $[M]^+$ 383.9489, found 383.9495.



Methyl (*Z*)-3-(thiophen-2-yl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3fi**). Following the general procedure, using methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate (**1f**; 1.0 mmol, 0.198 g), 4-methylbenzenethiol (**2i**, 1.0 mmol, 0.124 g), KI (0.1 M, 0.083 g), and 5 mL of CH_3CN then purified by column chromatography (SiO_2, 15-20% ethyl acetate in hexanes) to provide **3fi** as a yellow oil; yield: 70% (0.224 g; 1.0 mmol scale). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.06 (s, 1H), 7.58 – 7.55 (m, 2H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H), 7.27 (m, *J* = 8.0 Hz, 2H), 7.11 – 7.09 (m, 1H), 4.39 (d, *J* = 12.8 Hz, 1H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.60 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 167.24, 141.91, 140.55, 137.41, 137.36, 134.16, 130.74, 129.76 (2*C*), 127.79, 124.57 (2*C*), 117.74, 57.19, 52.43, 21.53 ppm. HRMS (EI) calcd for $C_{16}H_{16}O_3S_2$ $[M]^+$ 320.0541, found 320.0548.

9. Scanned copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR (for 3ab, 3ae, 3bb, 3cb, 3db, 3eb, and 3fb) spectra for all the synthesized compounds 3 (3aa - 3fi) (Figure S4 – S78); Mass spectra of adduct 4, 5, II-aaI, 9, 3aa-O^{18} and 3aa (Figure S79 – S84)

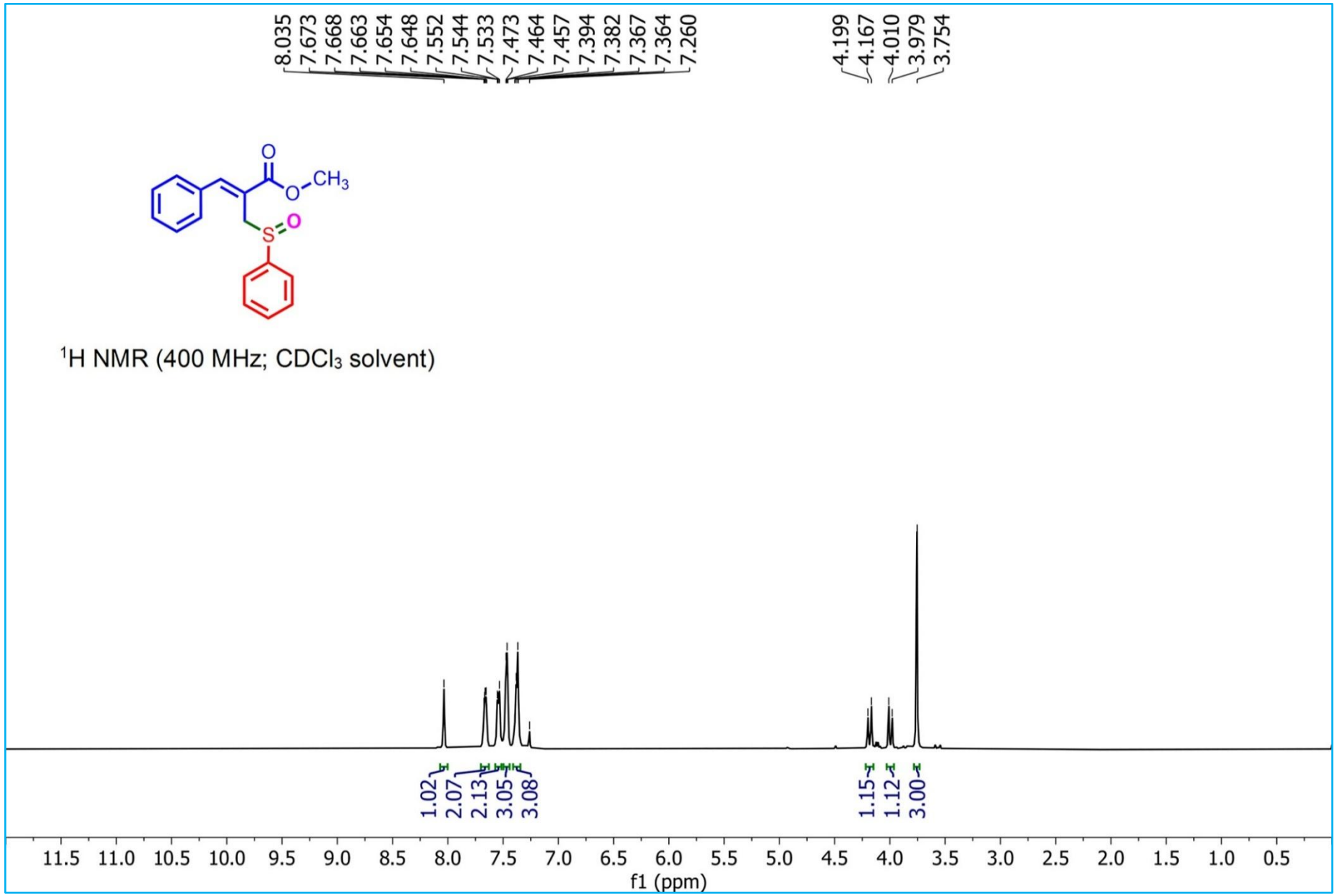


Figure S4. ^{1}H NMR spectrum of methyl (*Z*)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3aa**)

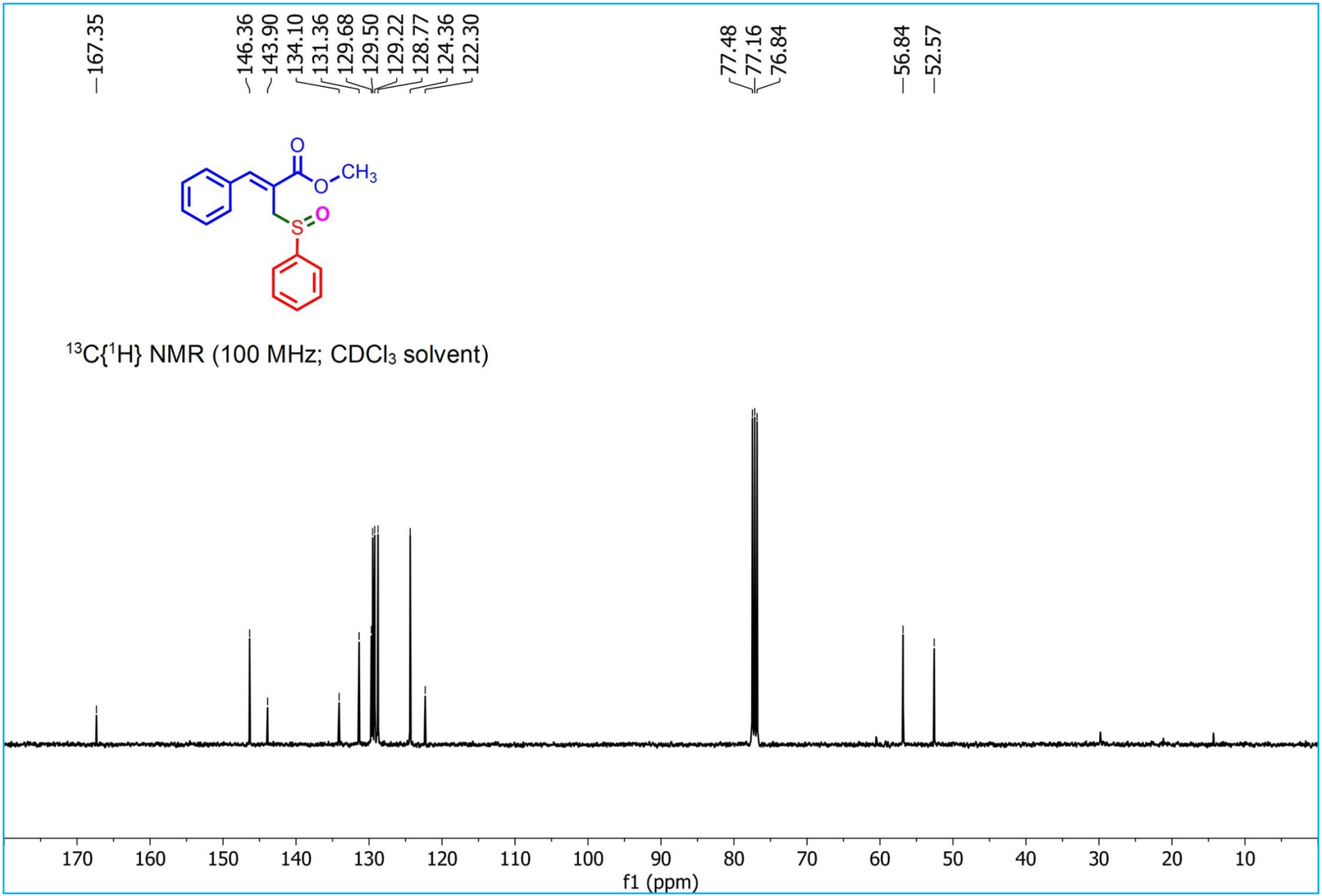


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3aa**)

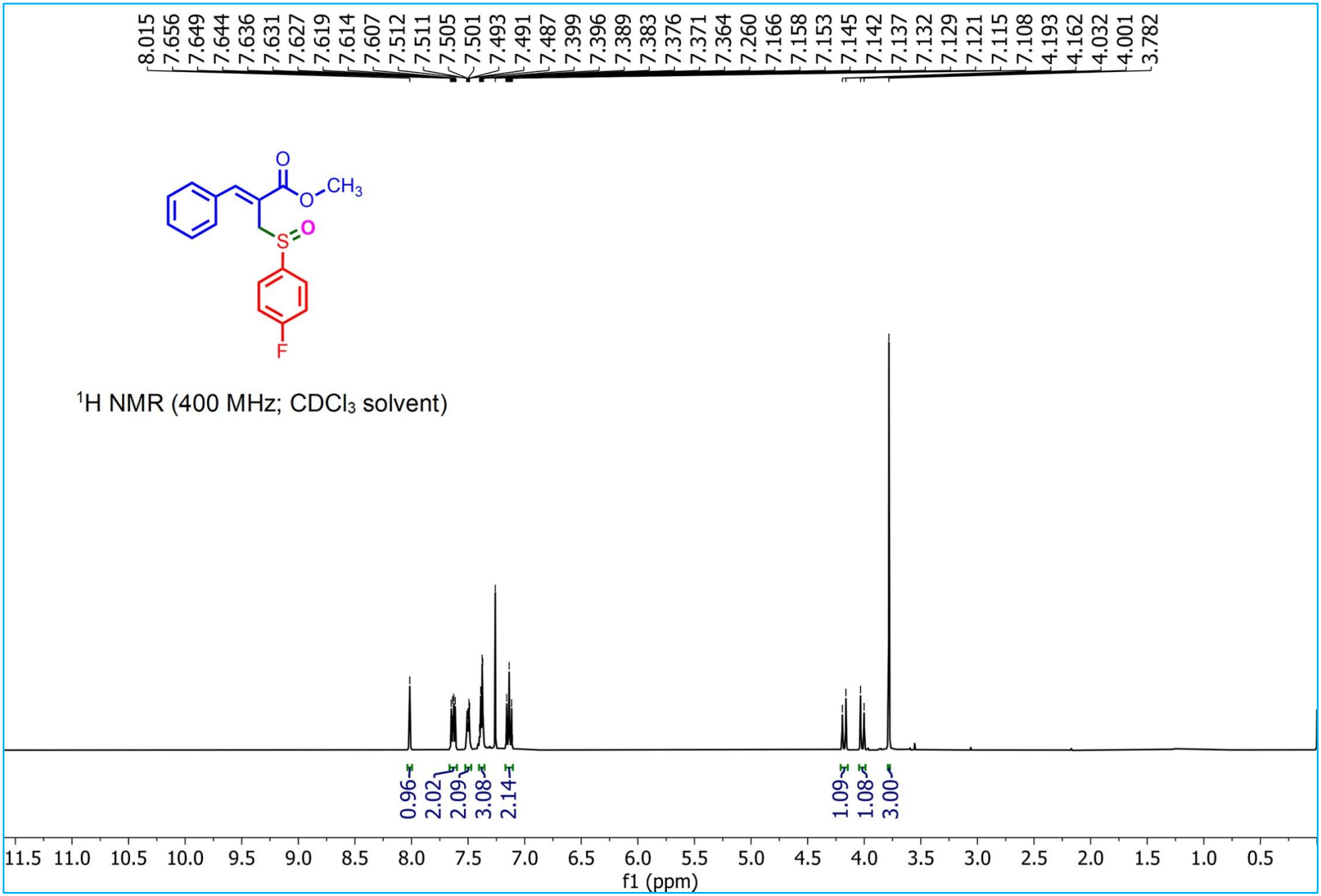


Figure S6. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ab**)

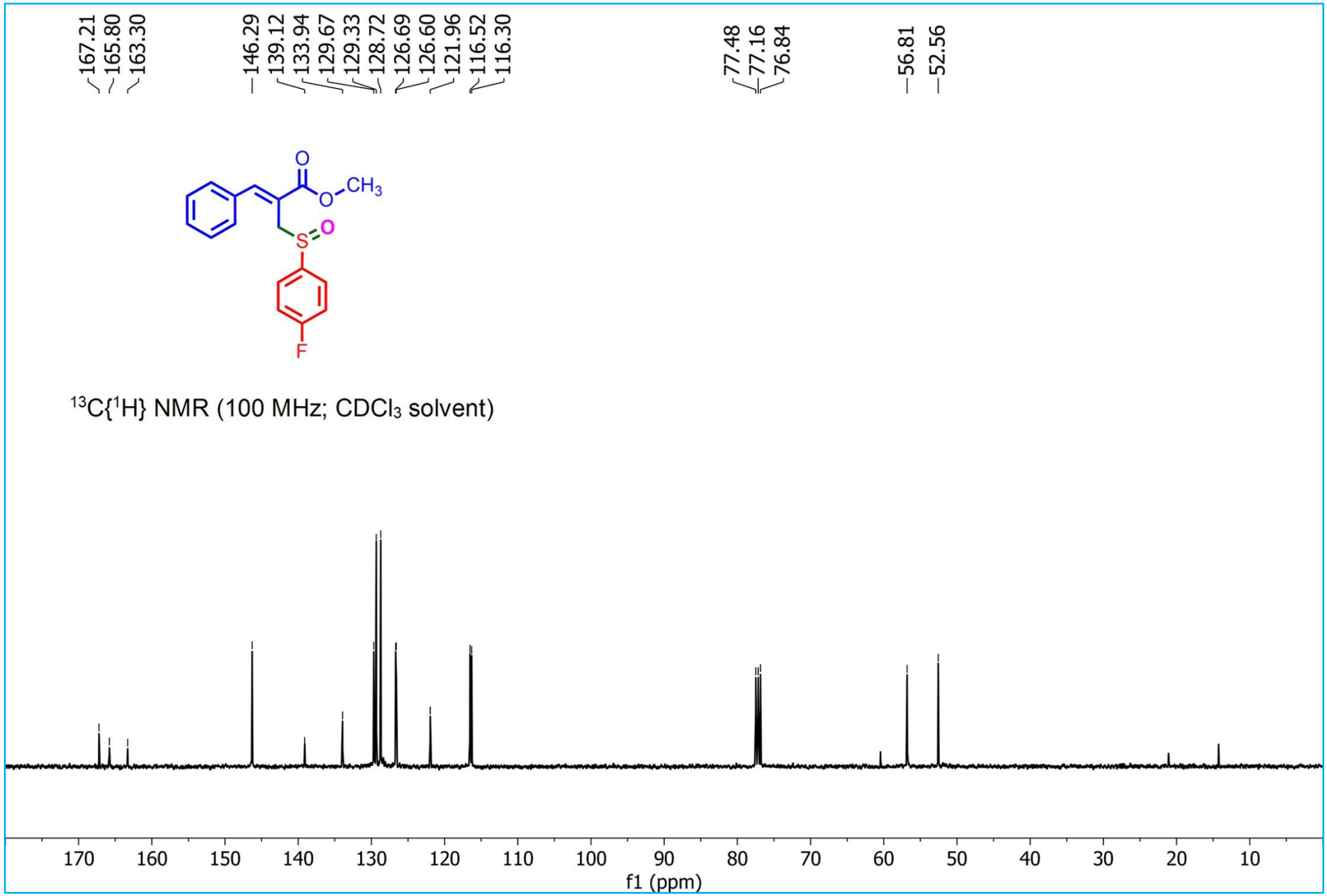


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ab**)

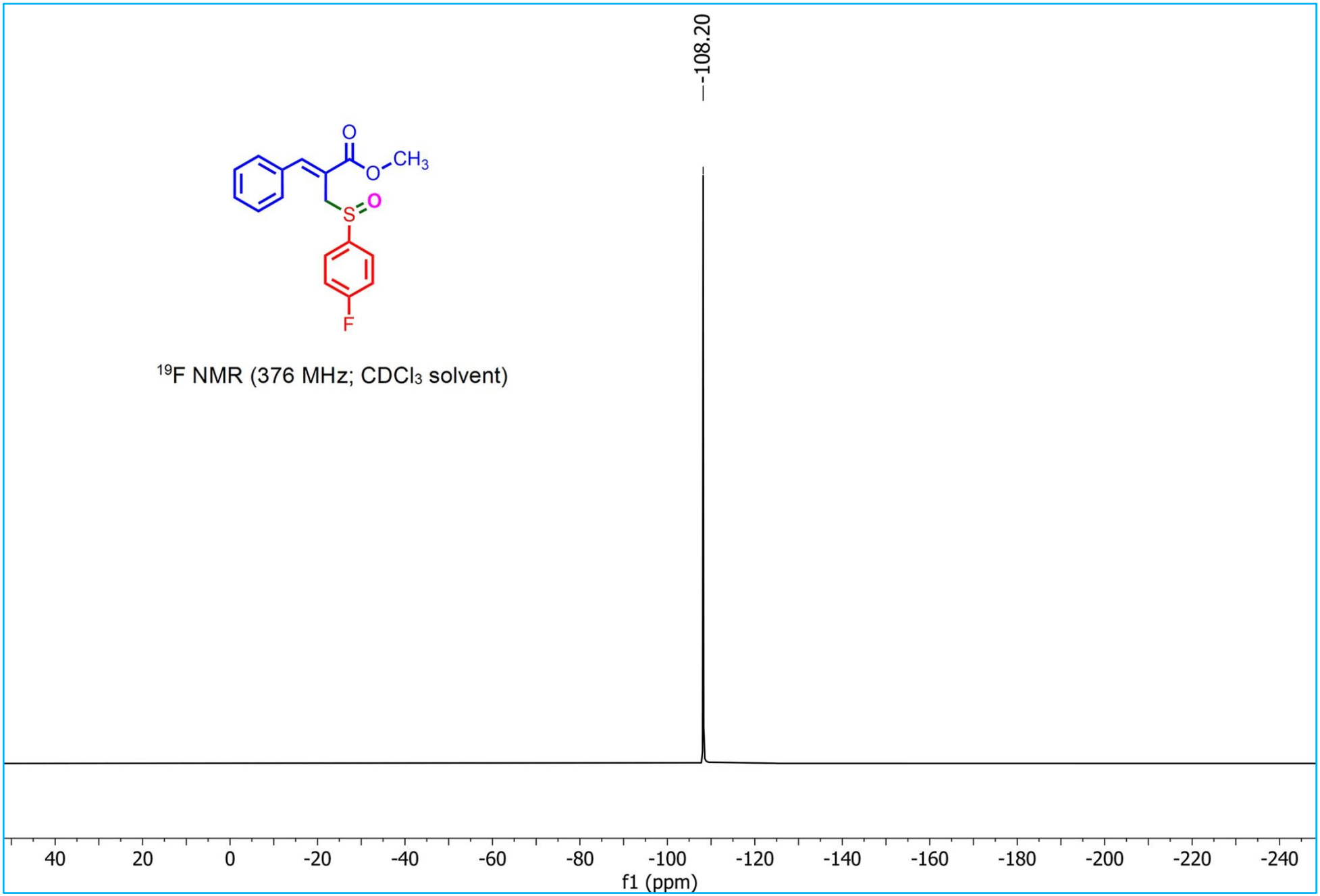


Figure S8. ^{19}F NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ab**)

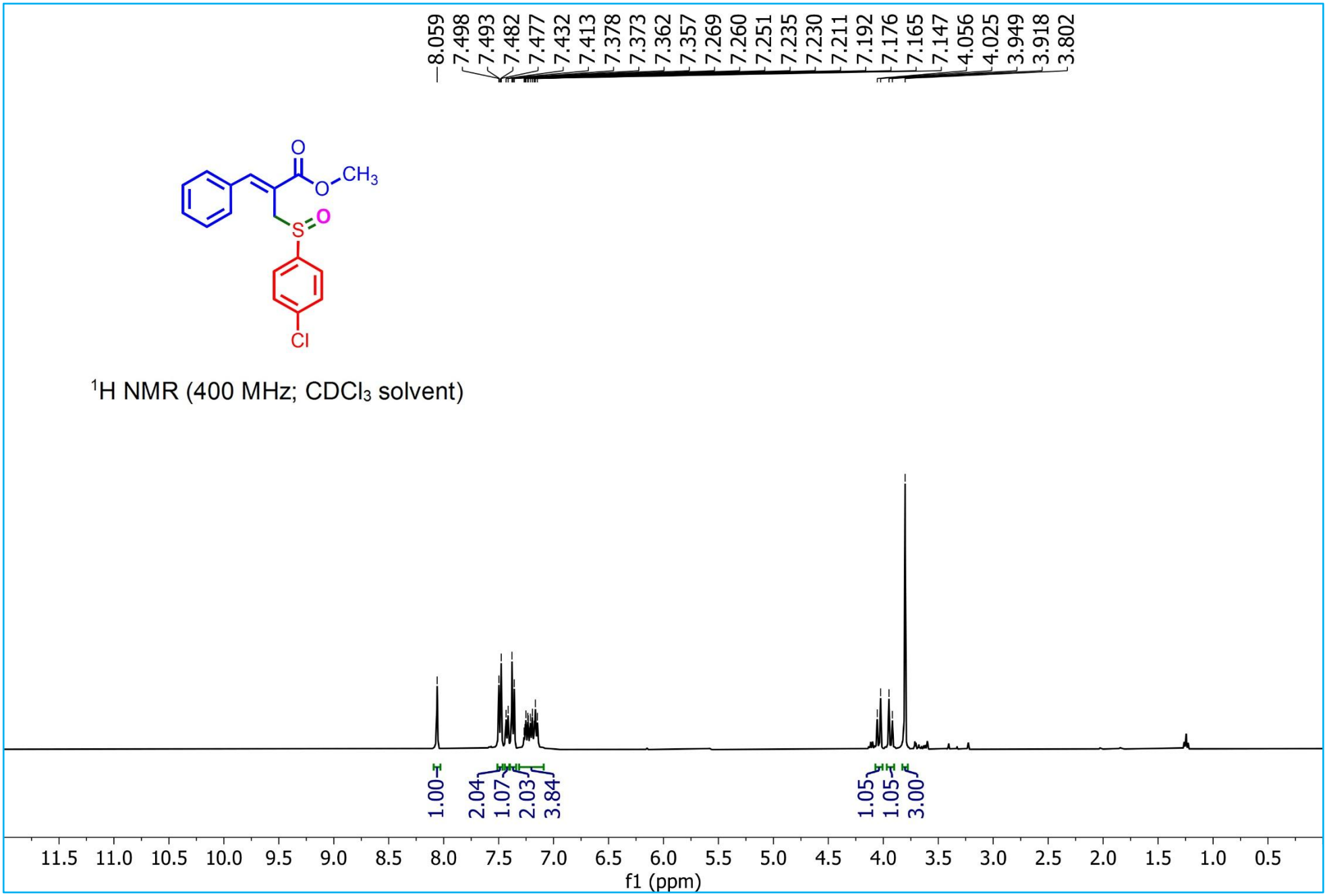


Figure S9. [1]H NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ac**)

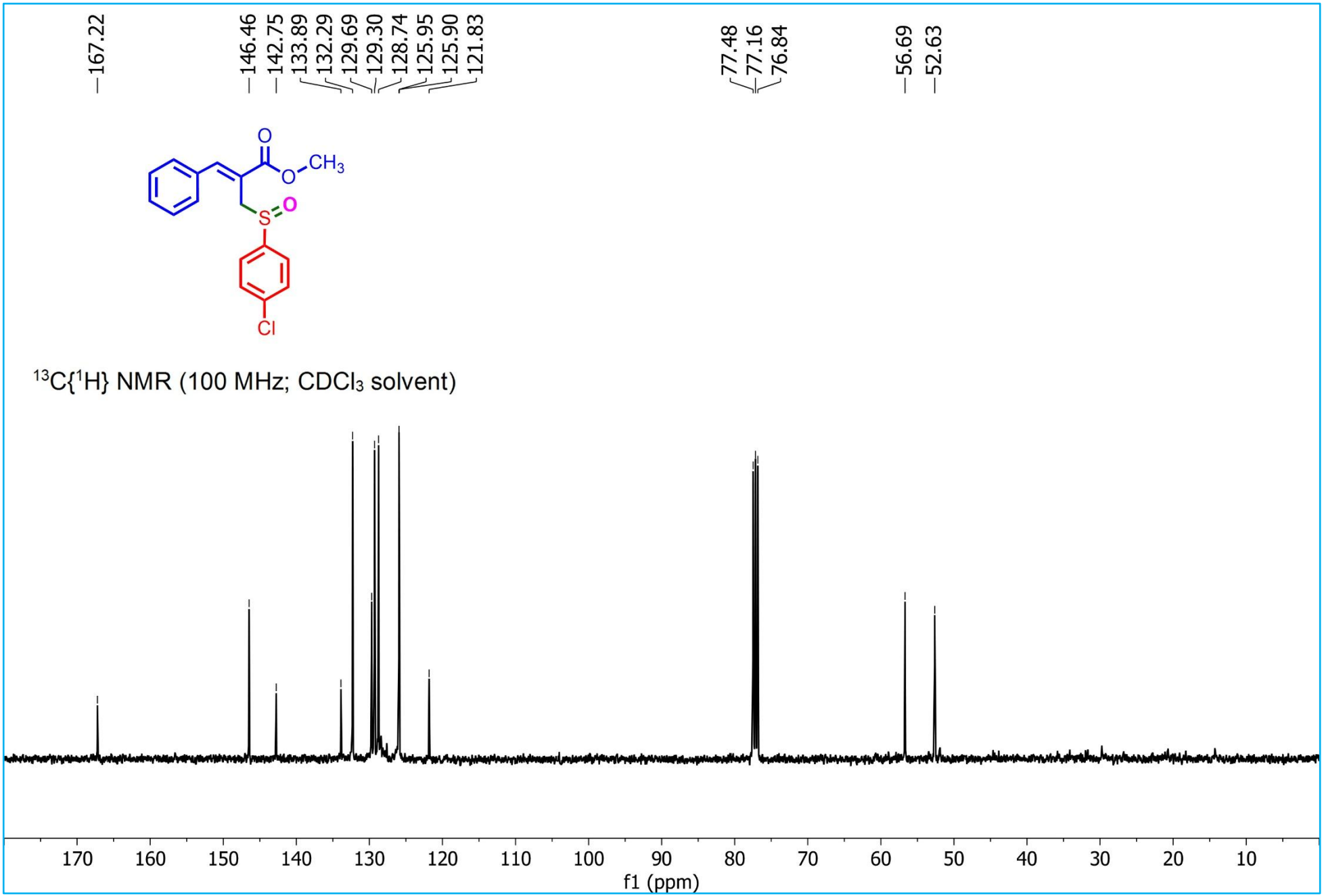


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ac**)

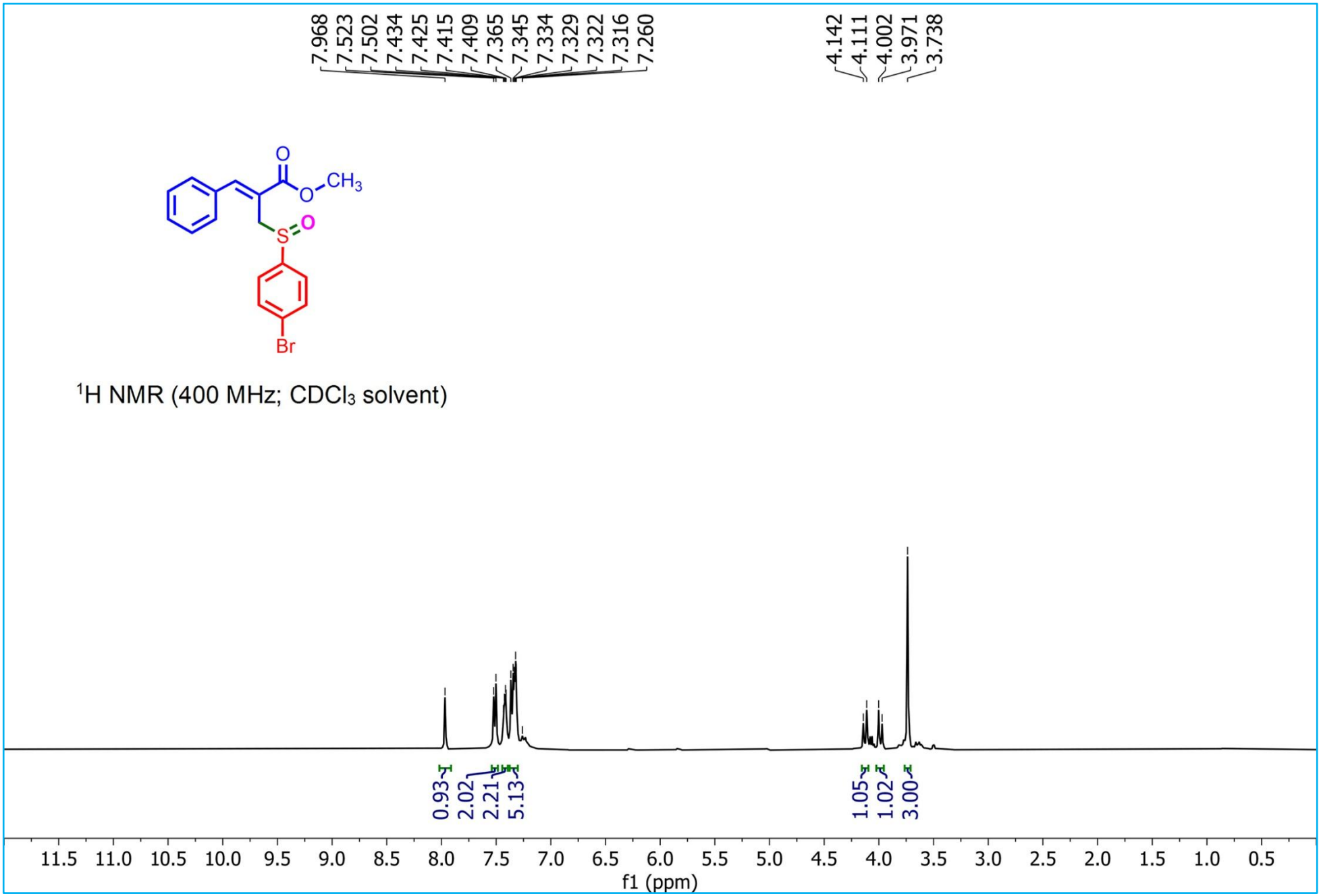


Figure S11. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ad**)

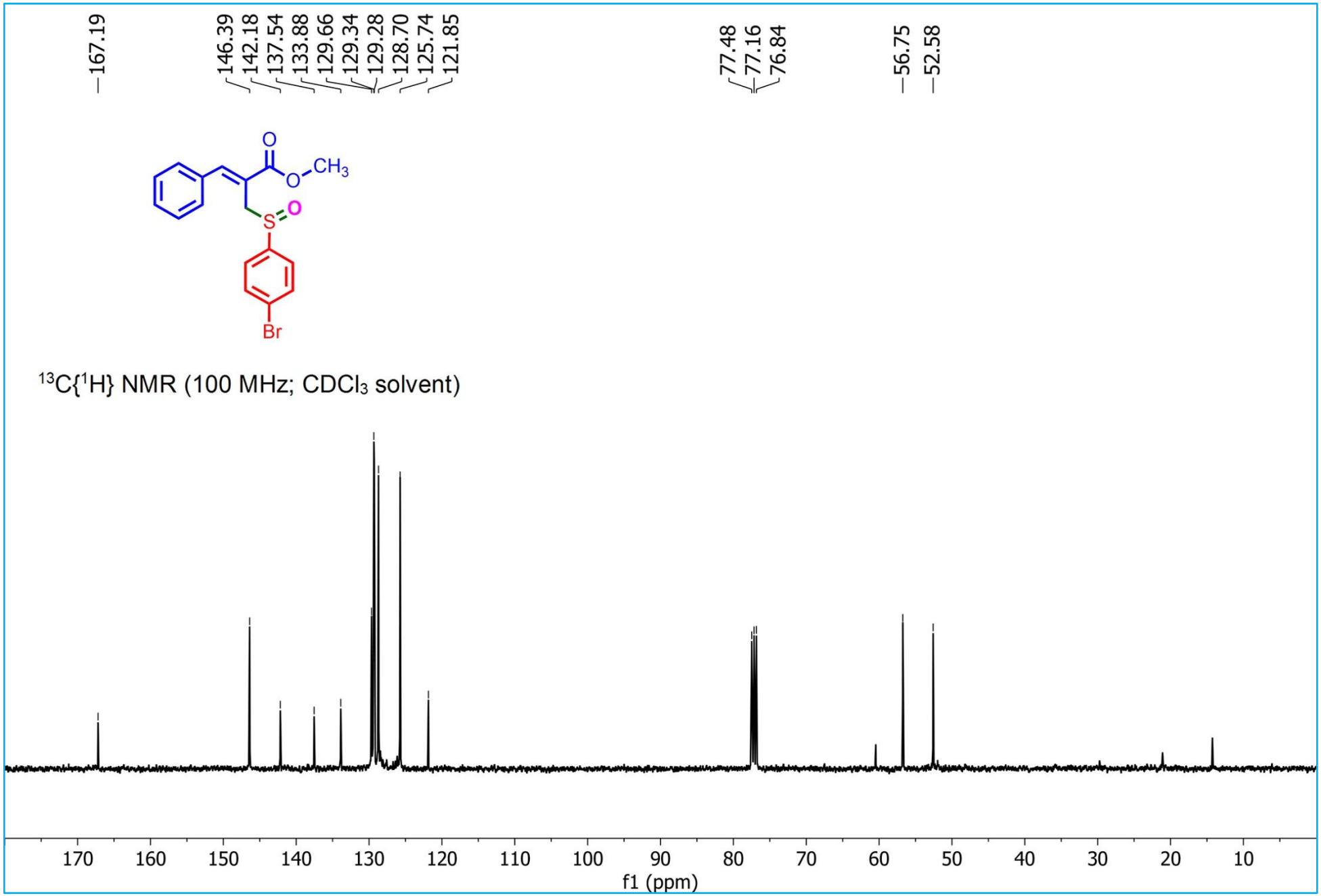


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-phenylacrylate (**3ad**)

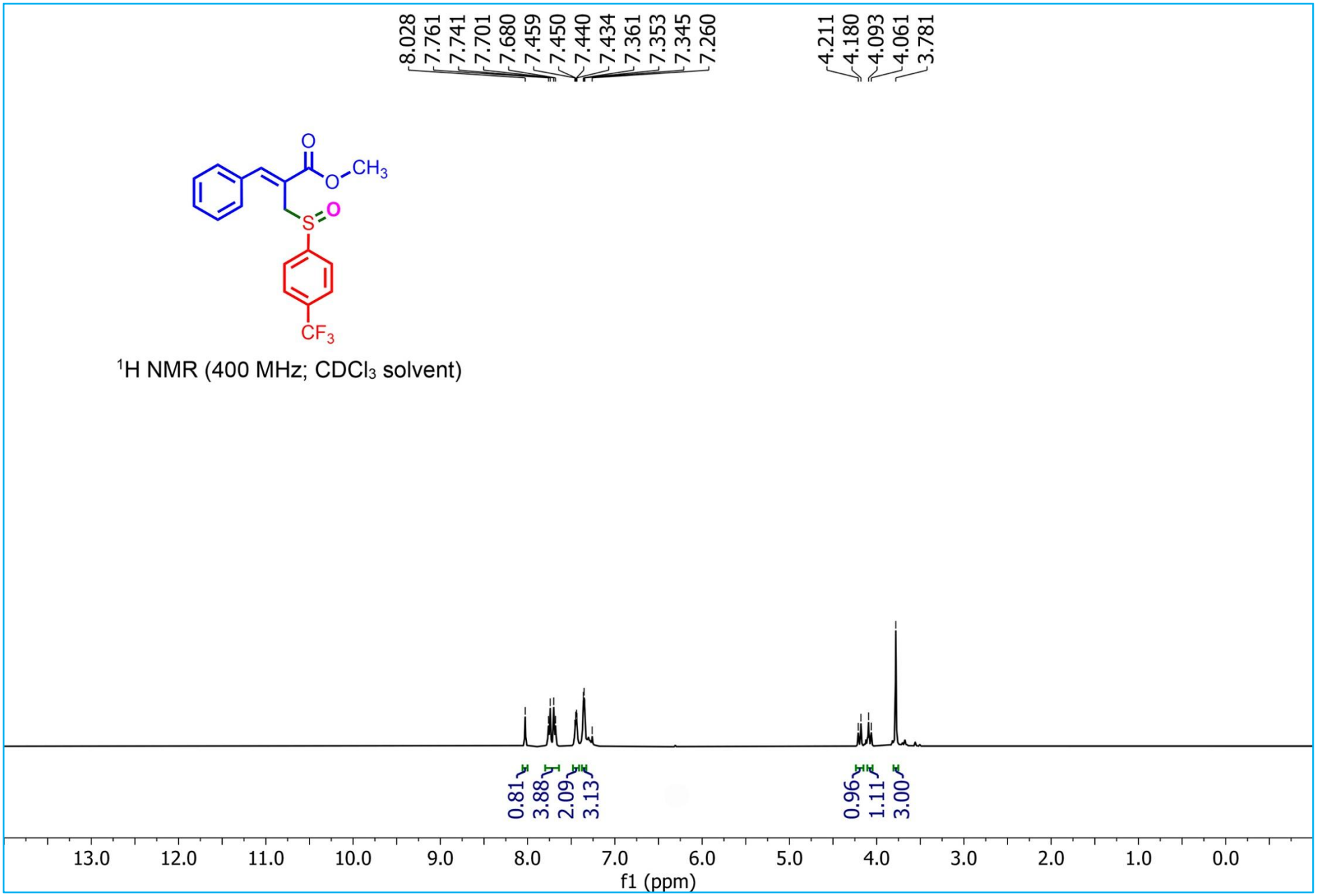


Figure S13. ^{1}H NMR spectrum of methyl (*Z*)-3-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfinyl)methyl)acrylate (**3ae**)

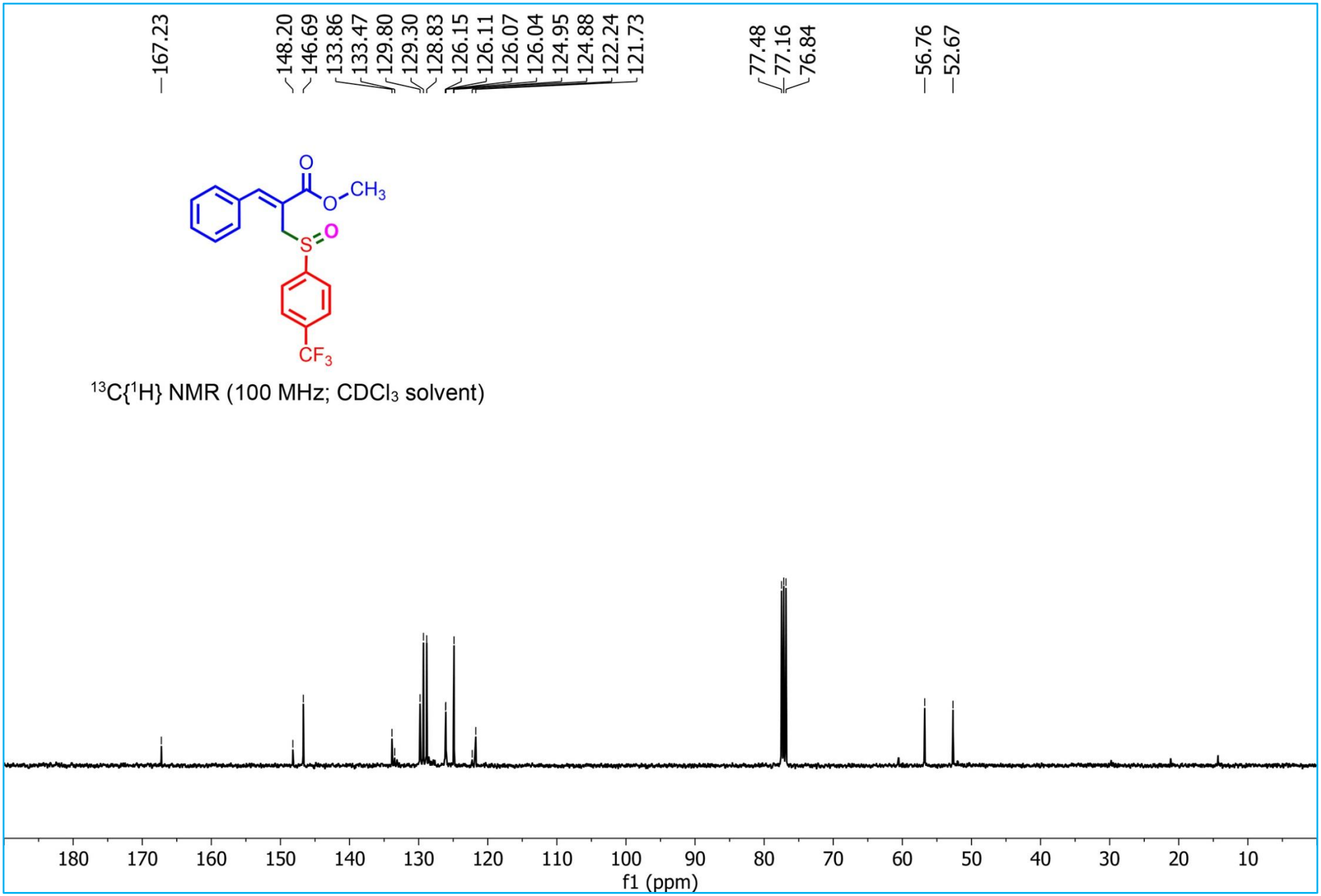


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfinyl)methyl)acrylate (**3ae**)

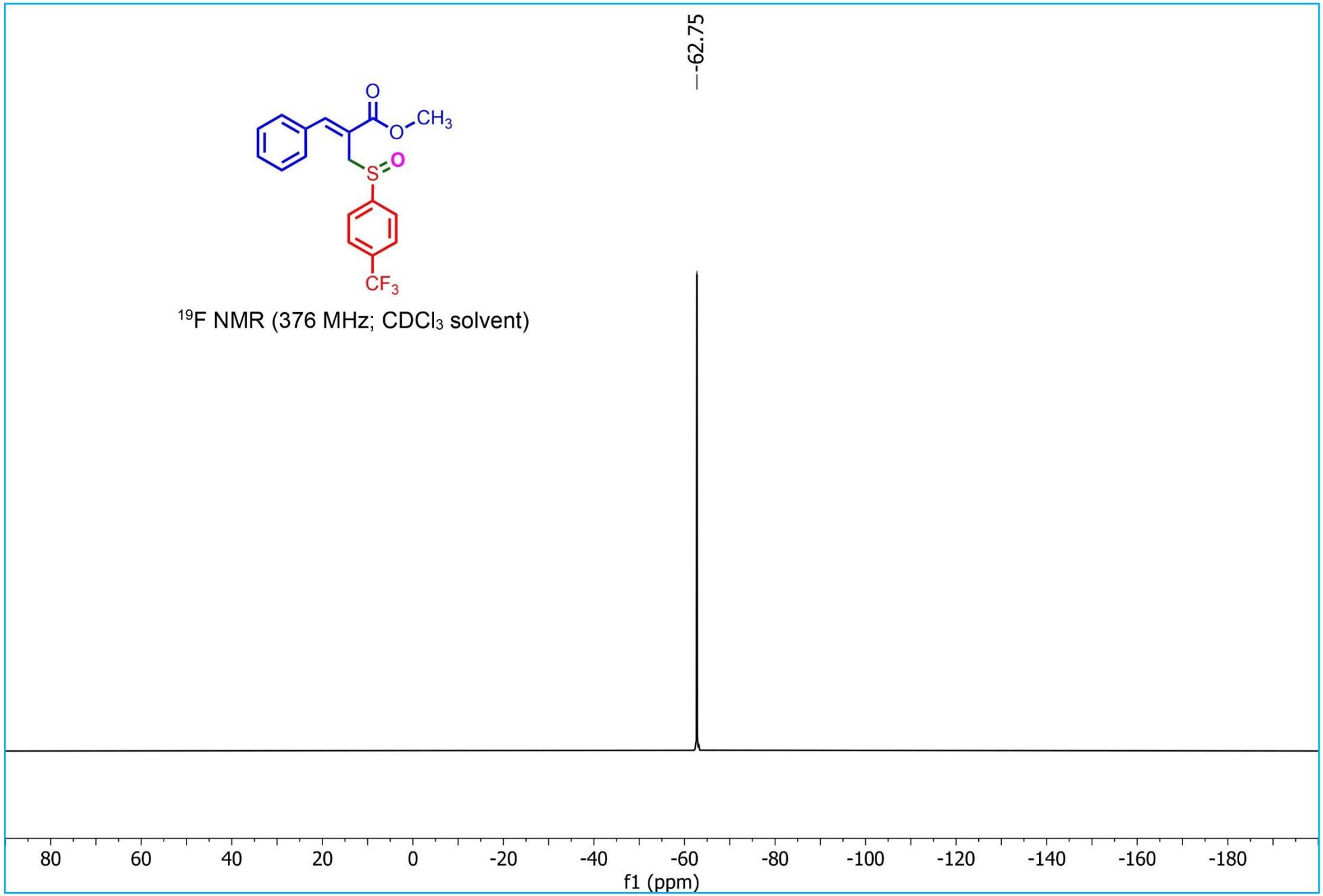


Figure S15. ^{19}F NMR spectrum of methyl (*Z*)-3-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfinyl)methyl)acrylate (**3ae**)

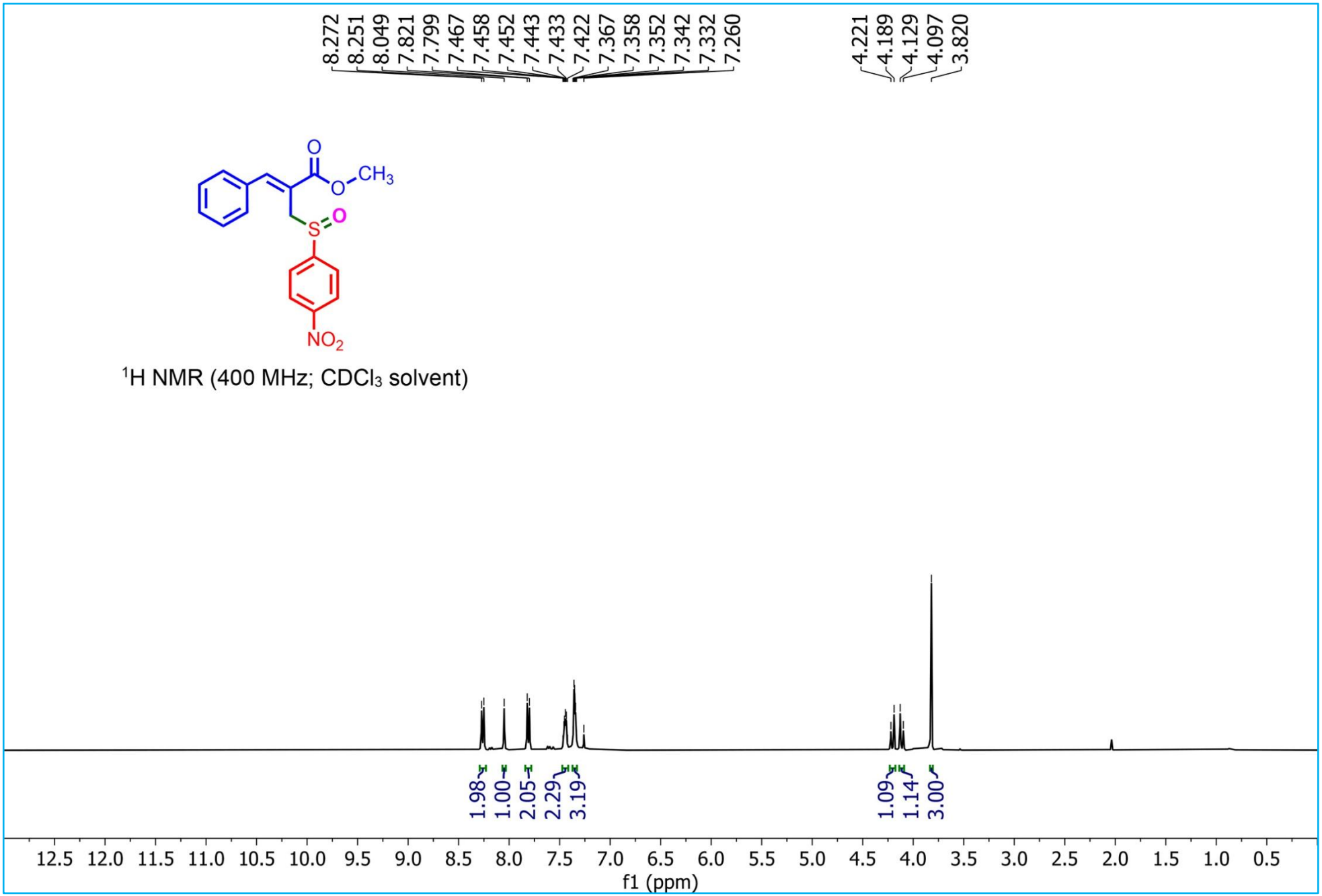


Figure S16. [1]H NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-phenylacrylate (**3af**)

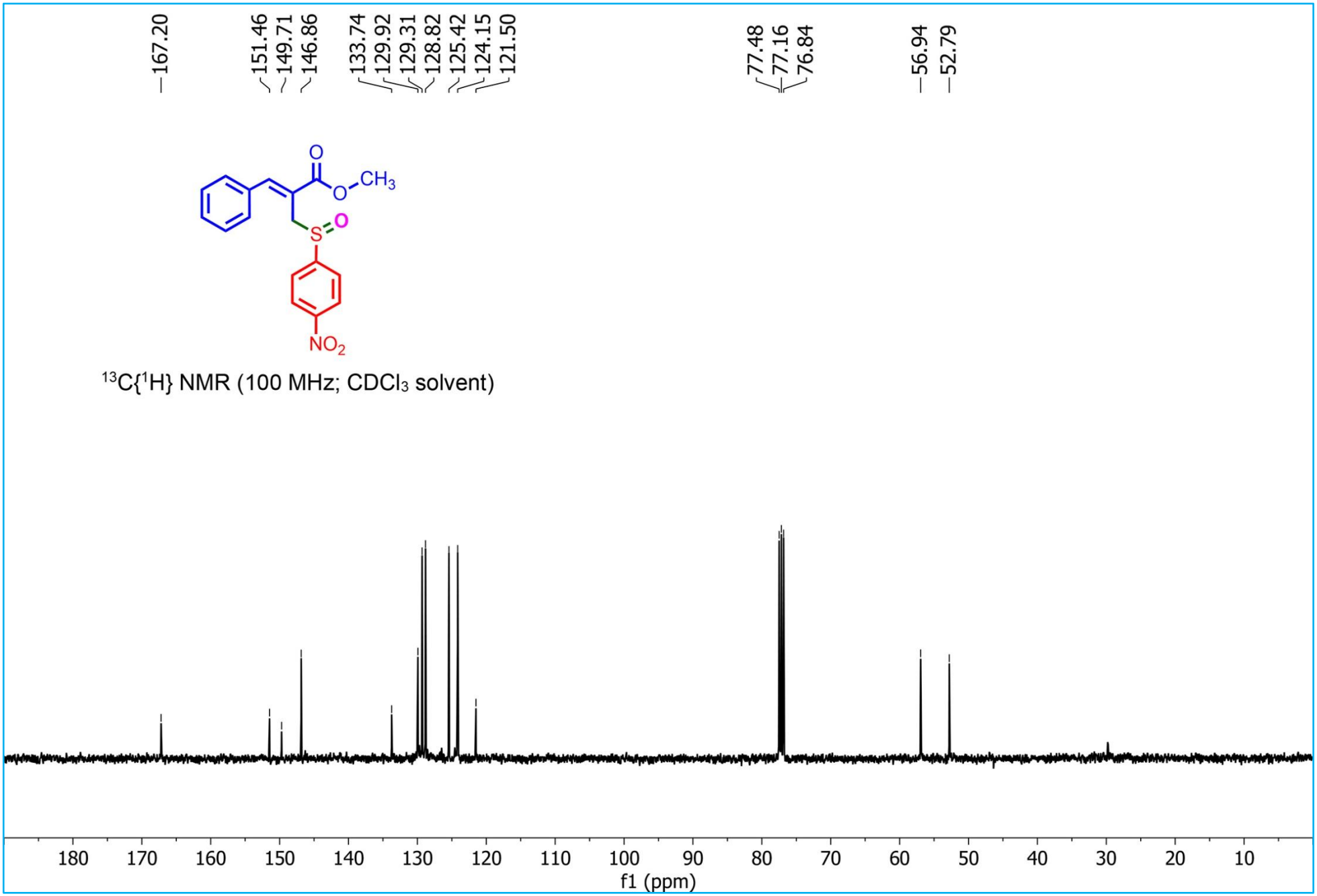


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-phenylacrylate (**3af**)

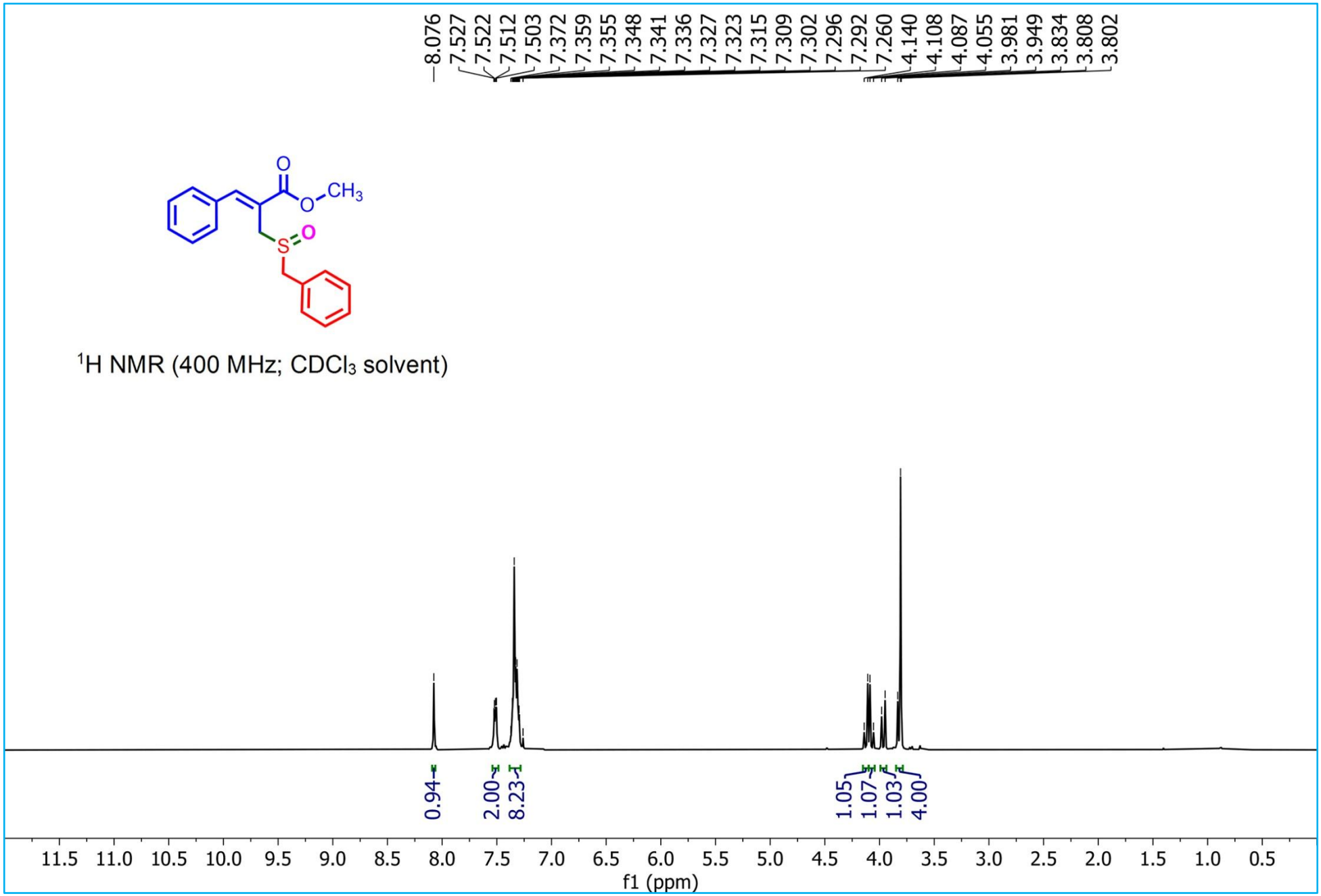


Figure S18. ^{1}H NMR spectrum of methyl (*Z*)-2-((benzylsulfinyl)methyl)-3-phenylacrylate (**3ag**)

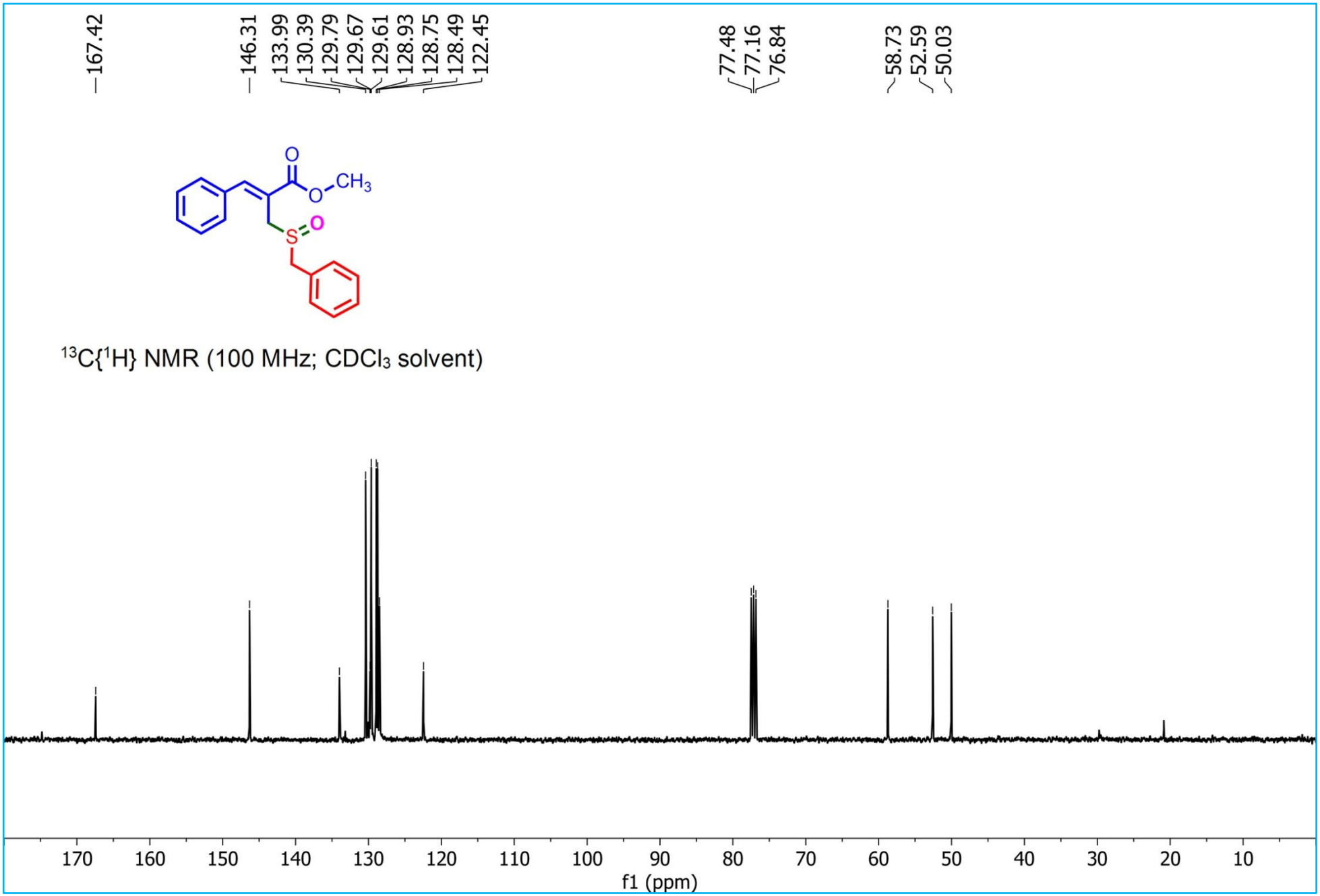


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((benzylsulfinyl)methyl)-3-phenylacrylate (**3ag**)

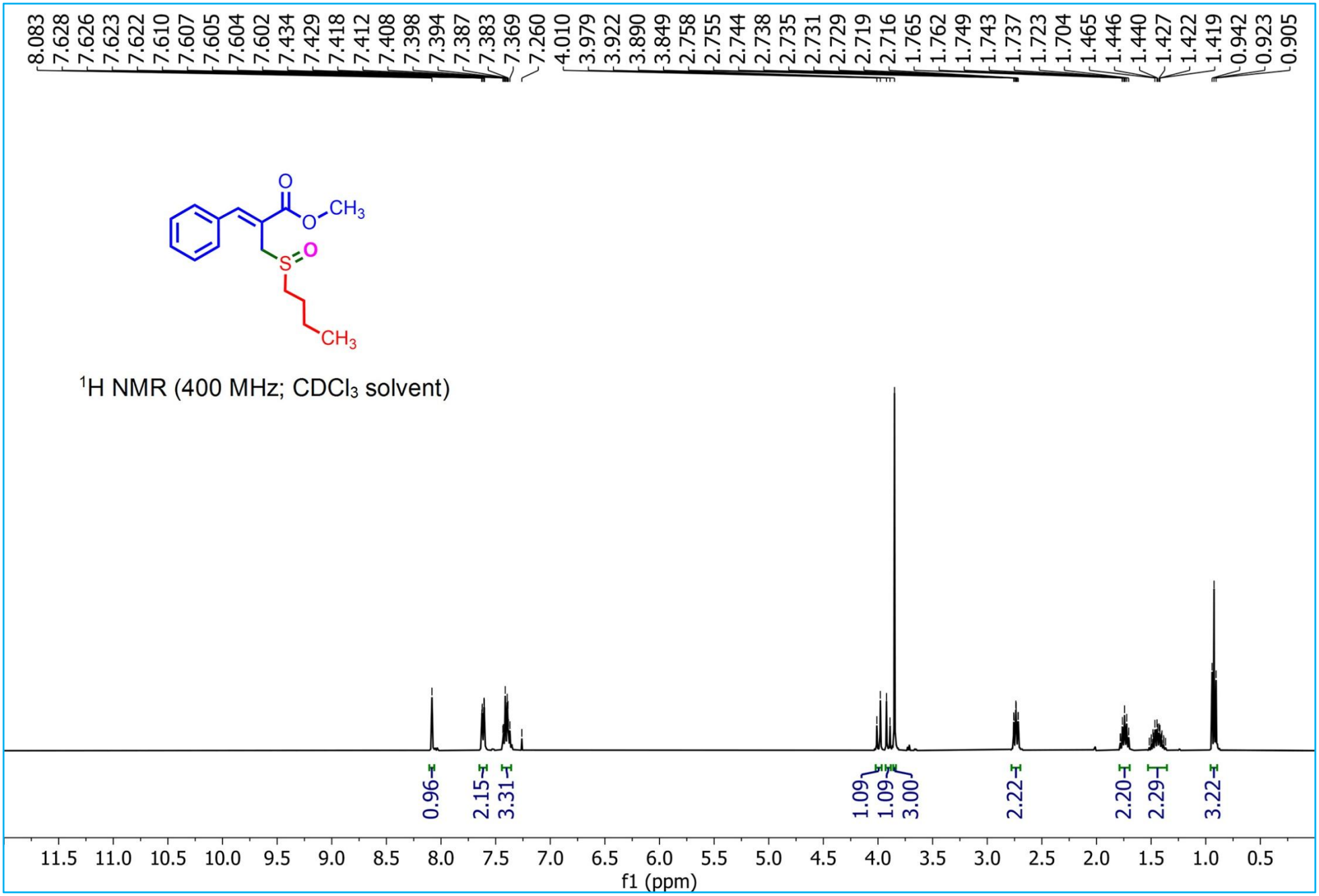


Figure S20. ^{1}H NMR spectrum of methyl (*Z*)-2-((butylsulfinyl)methyl)-3-phenylacrylate (**3ah**)

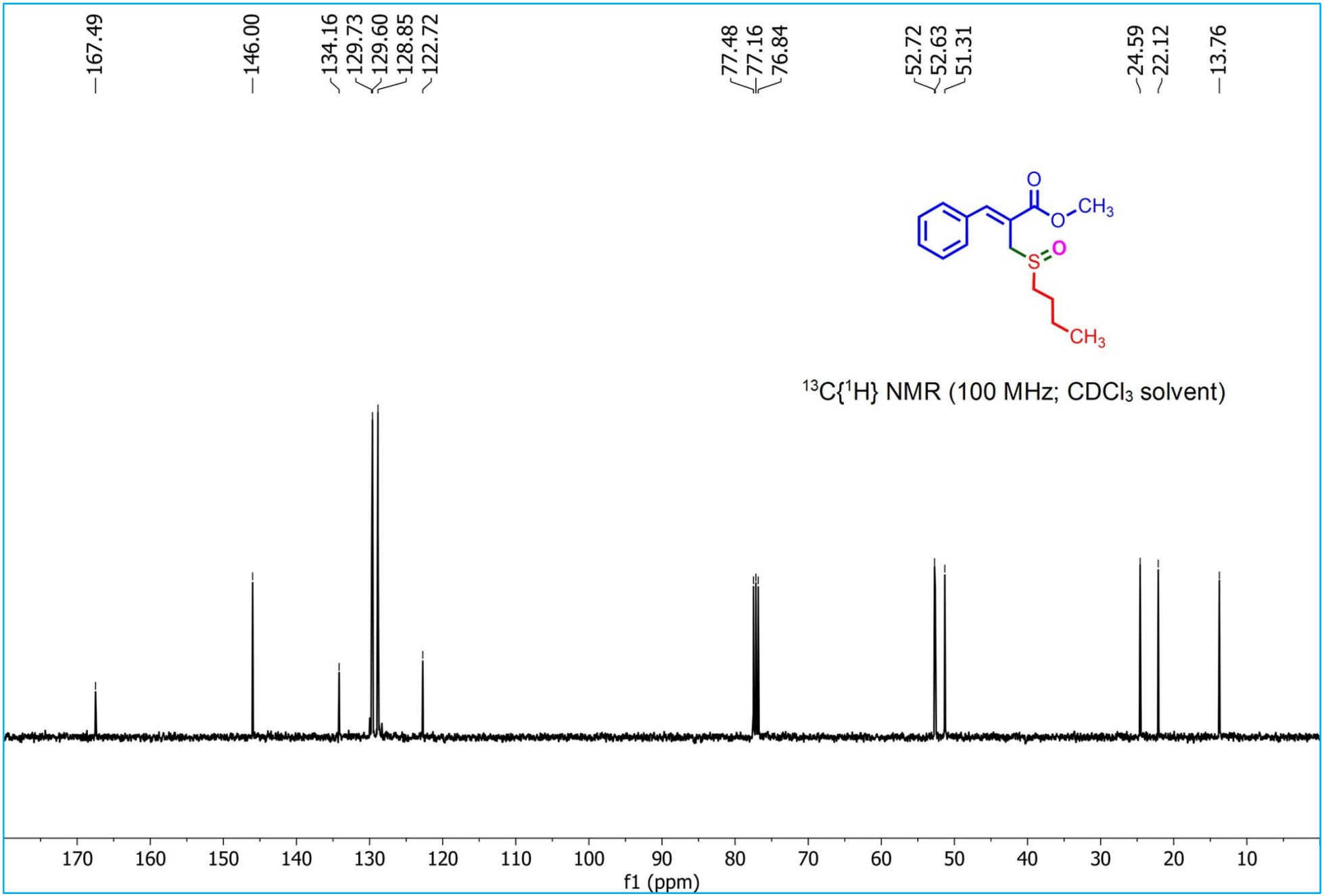


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((butylsulfinyl)methyl)-3-phenylacrylate (**3ah**)

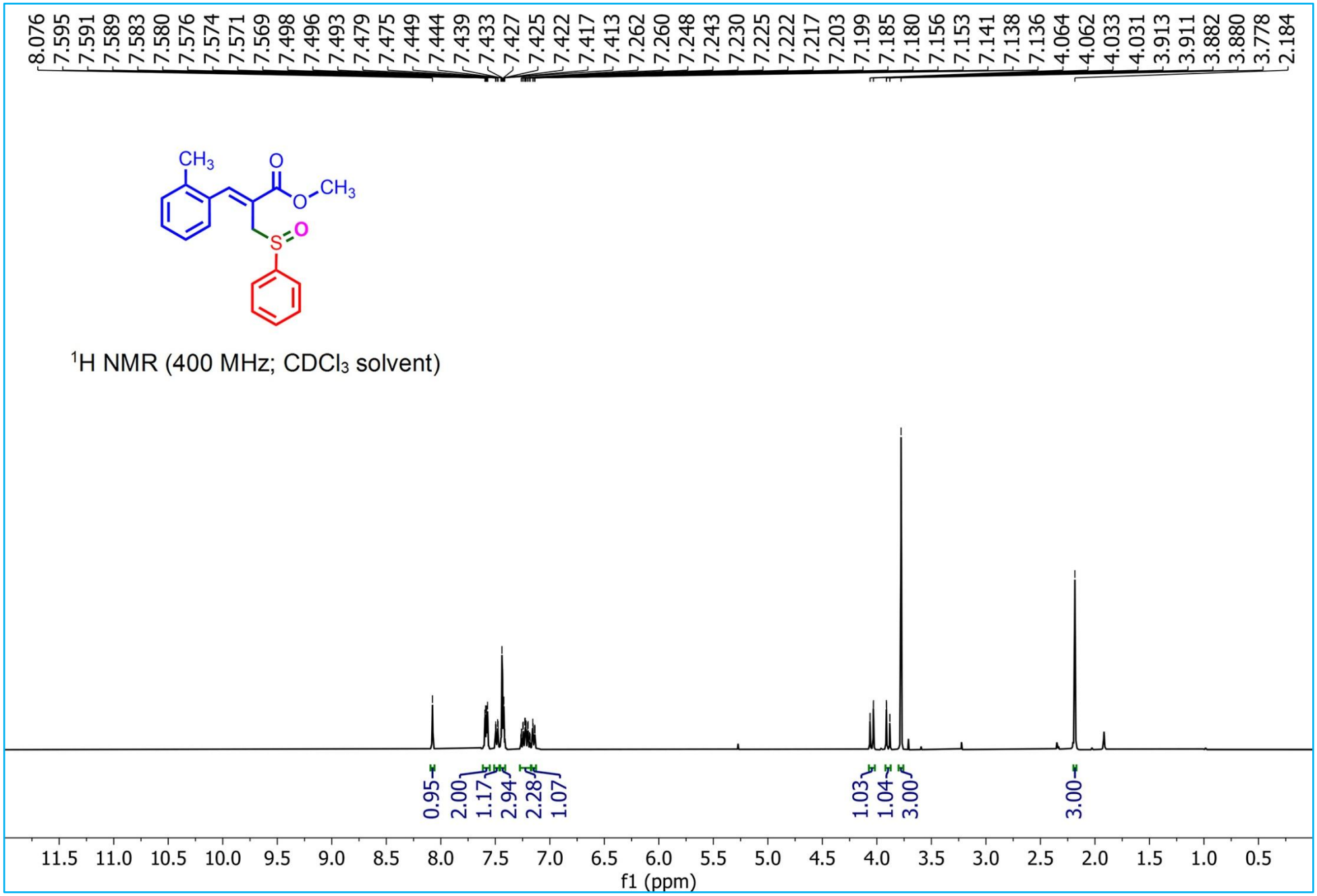


Figure S22. ^{1}H NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3ba**)

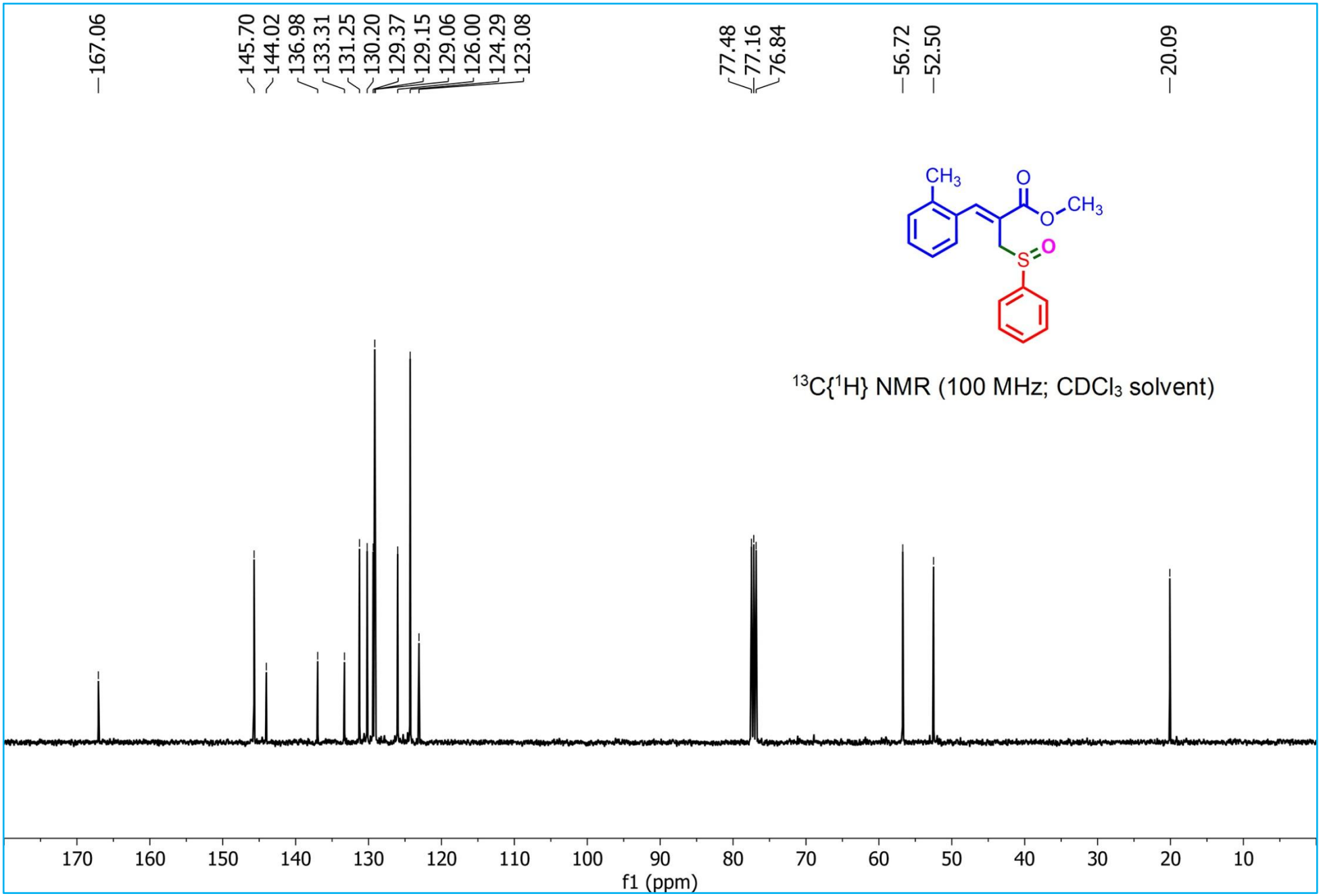


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3ba**)

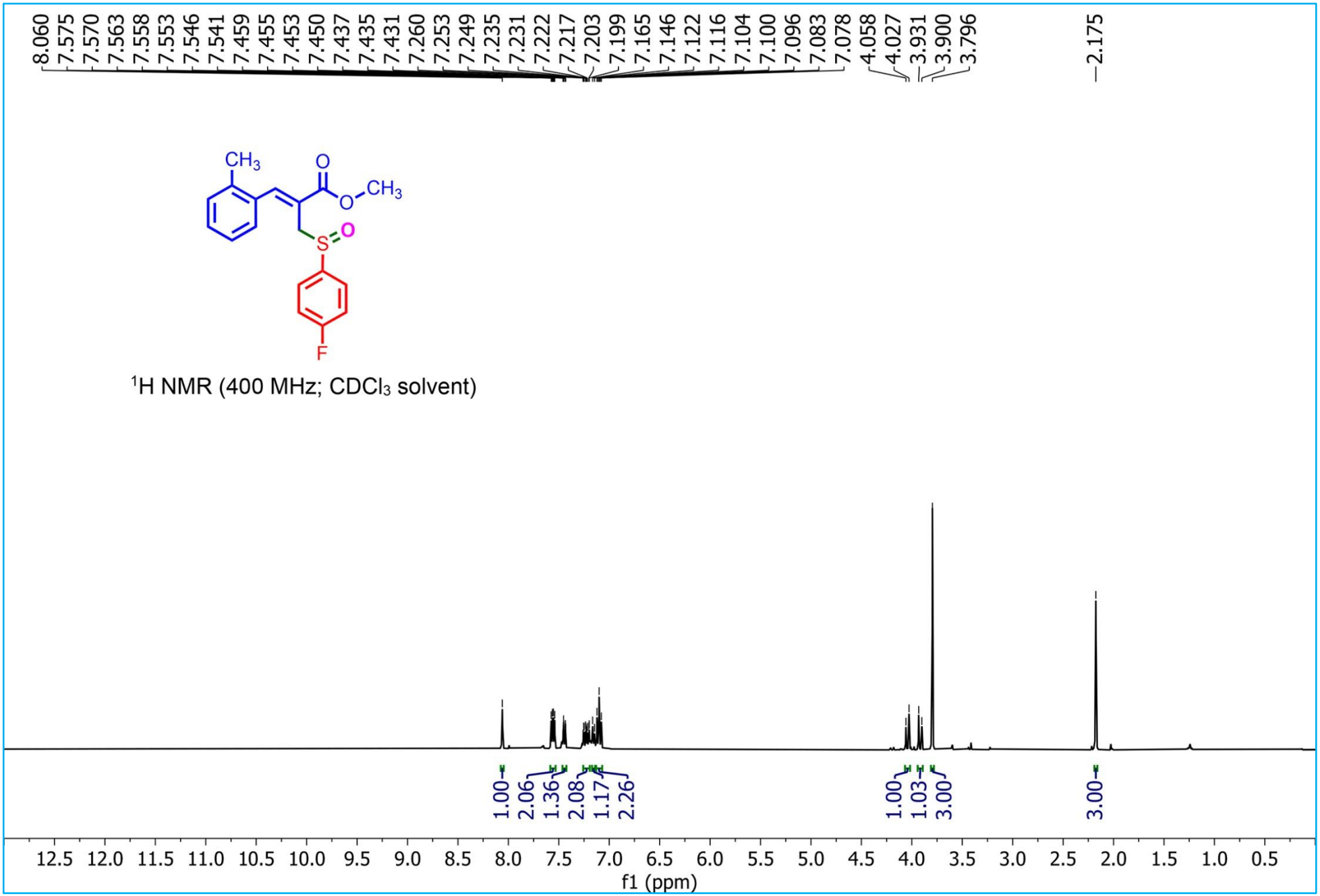


Figure S24. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bb**)

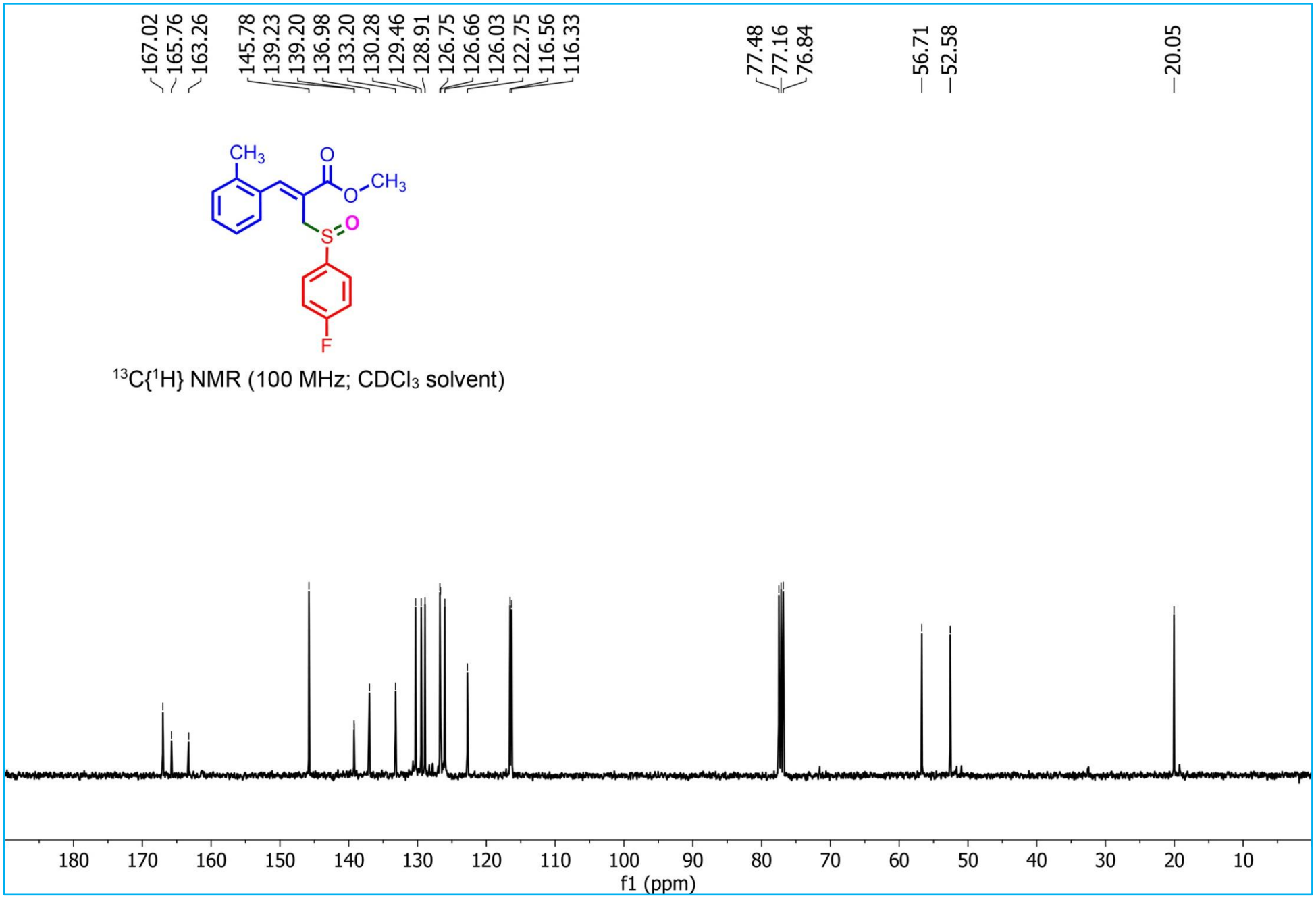


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bb**)

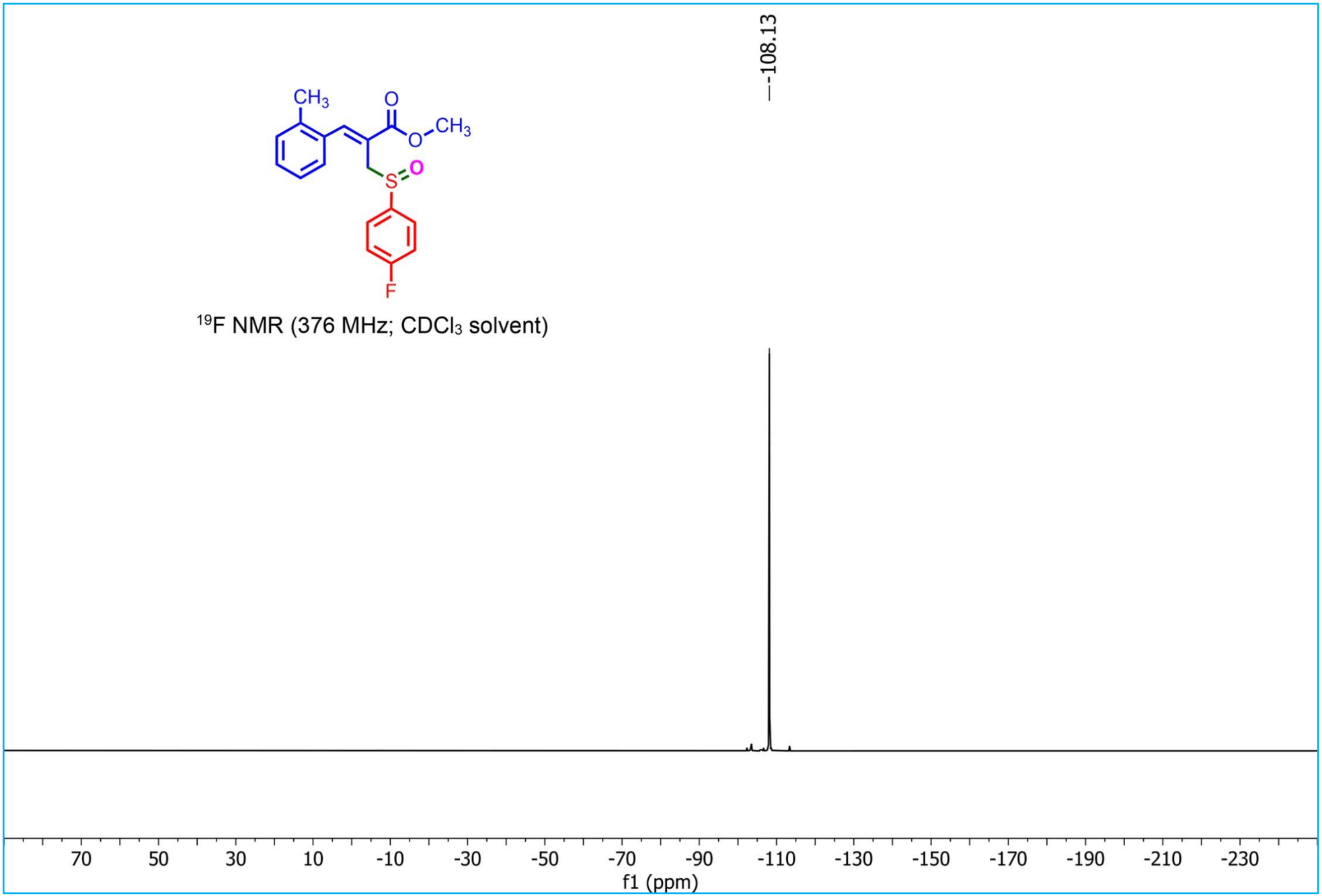


Figure S26. ^{19}F NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bb**)

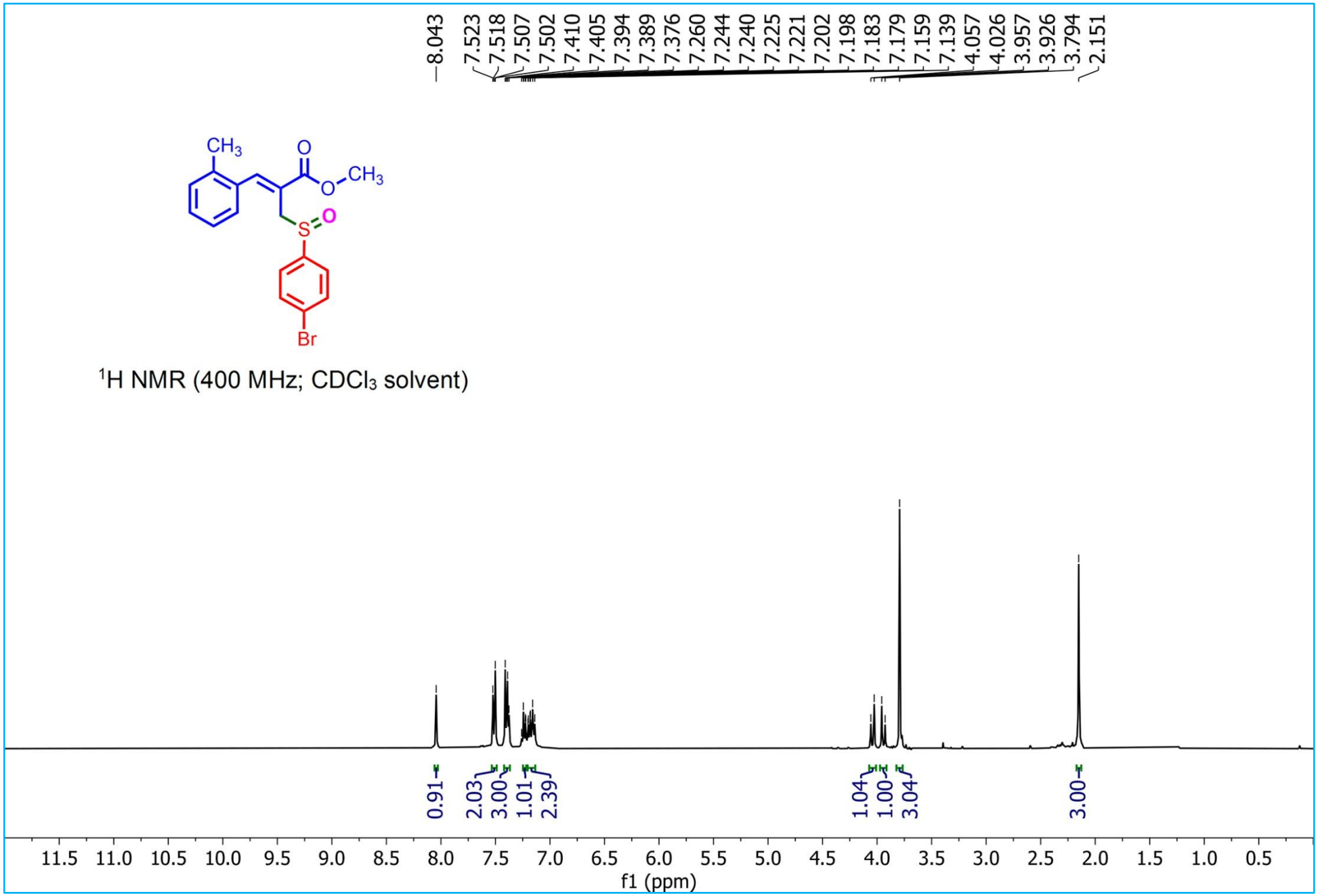


Figure S27. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bd**)

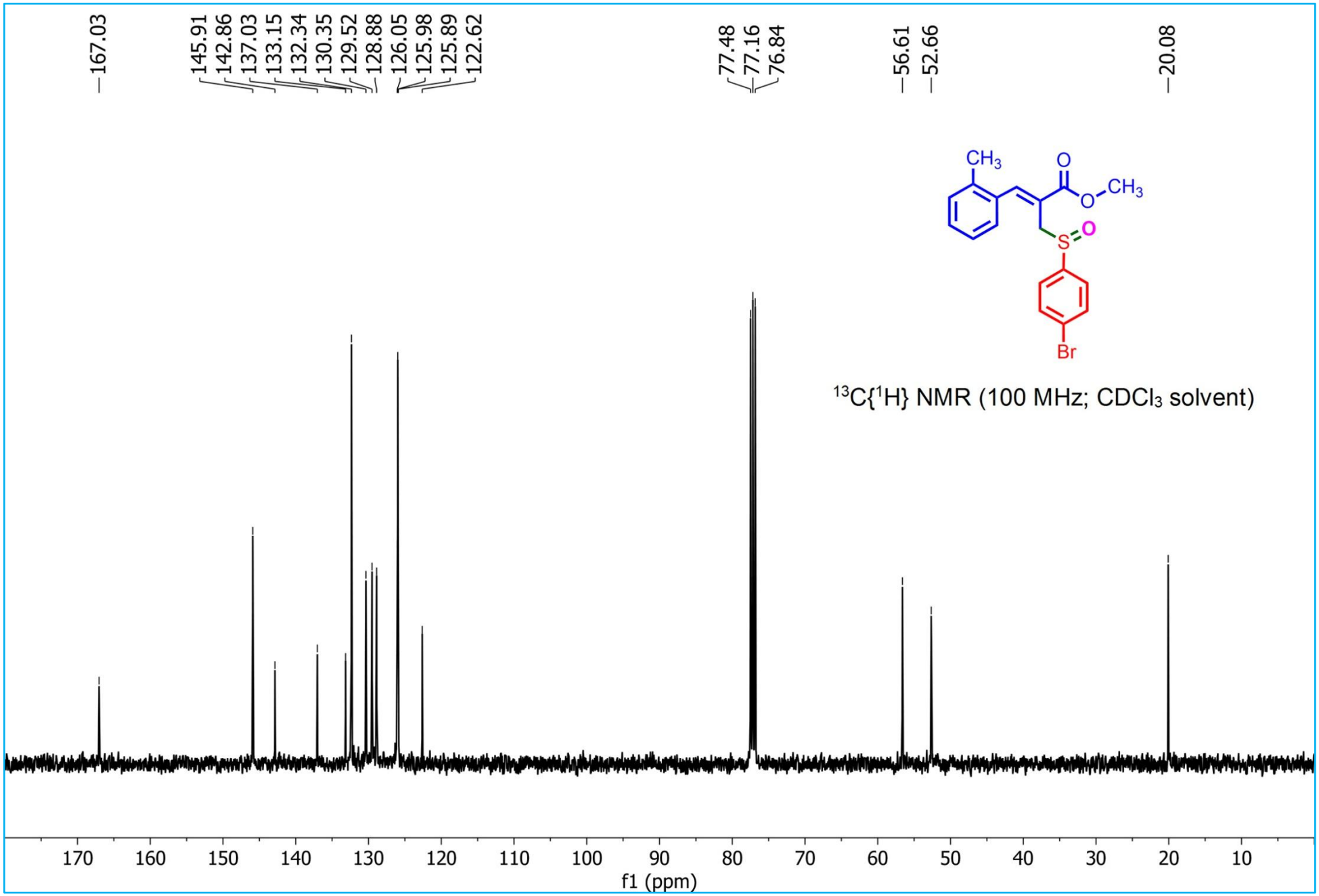


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bd**)

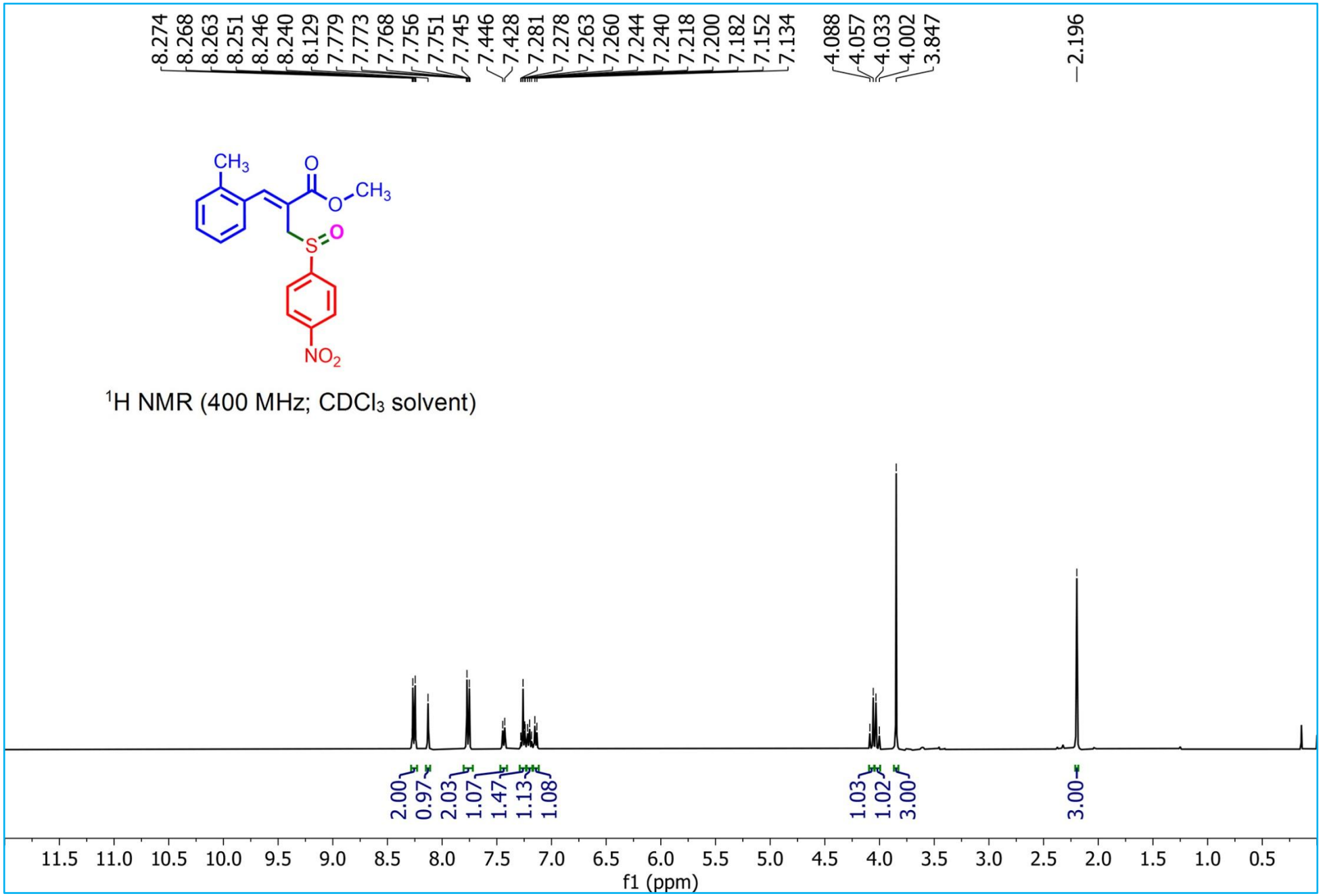


Figure S29. [1]H NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bf**)

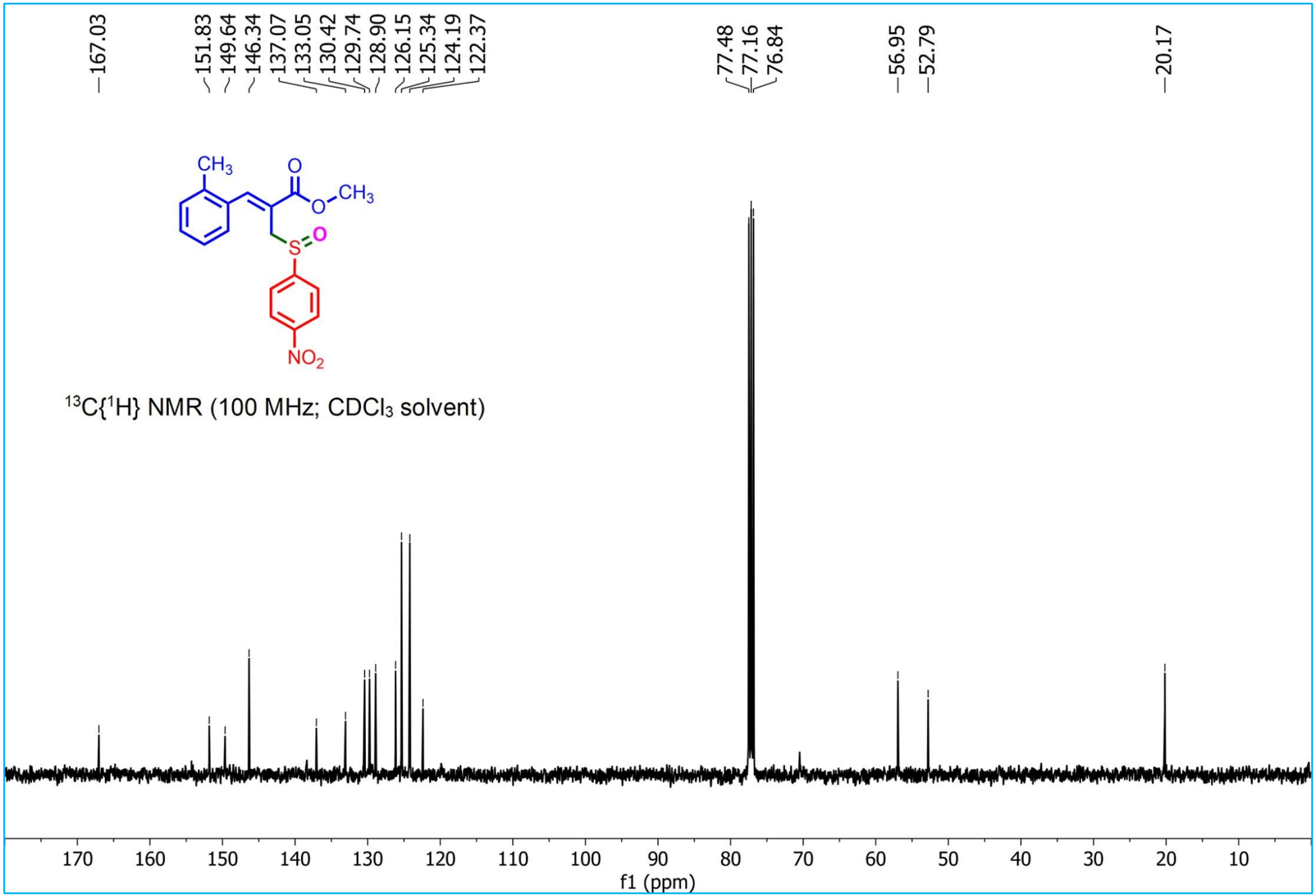


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bf**)

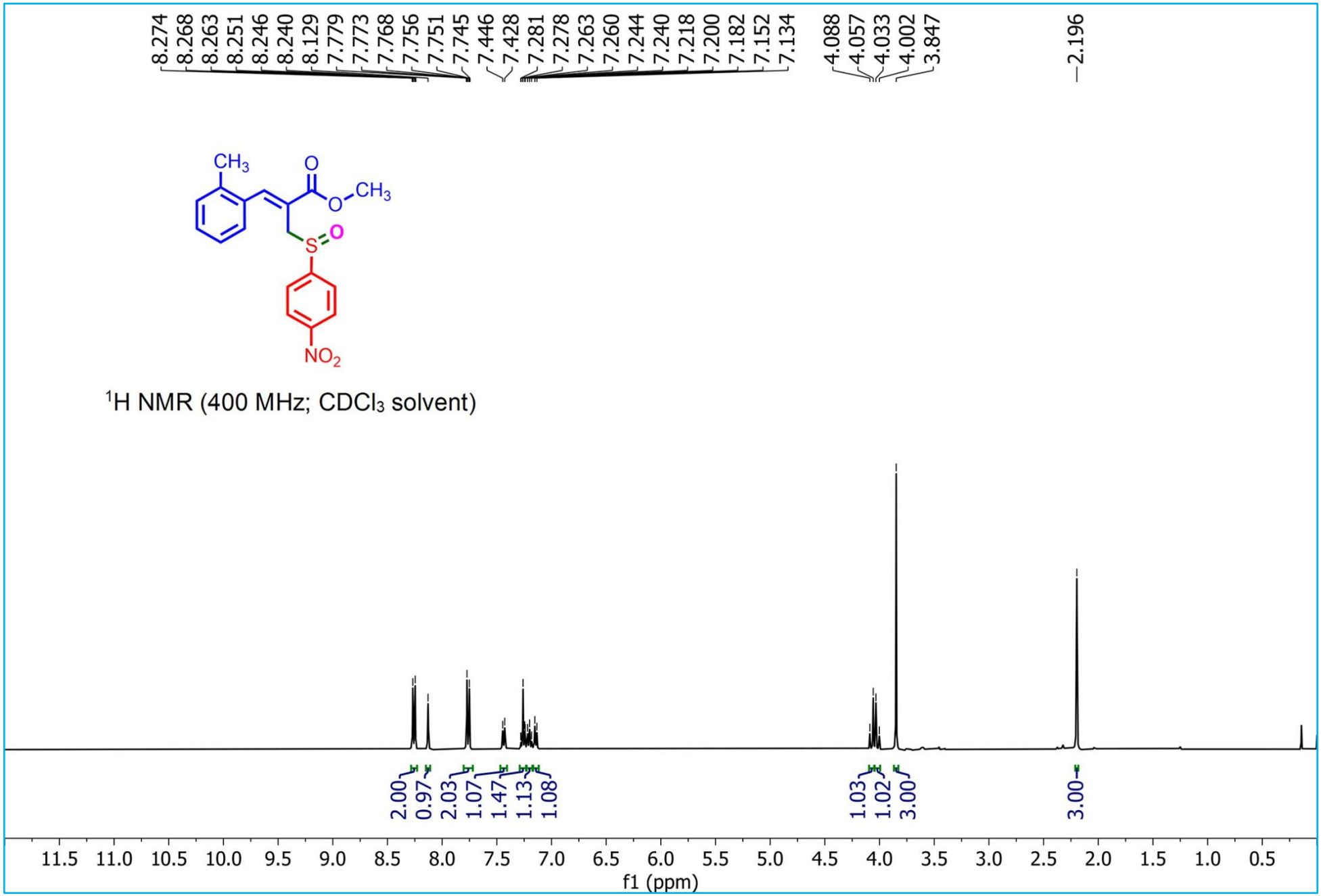


Figure S31. ^{1}H NMR spectrum of methyl (*Z*)-3-(*o*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3bi**)

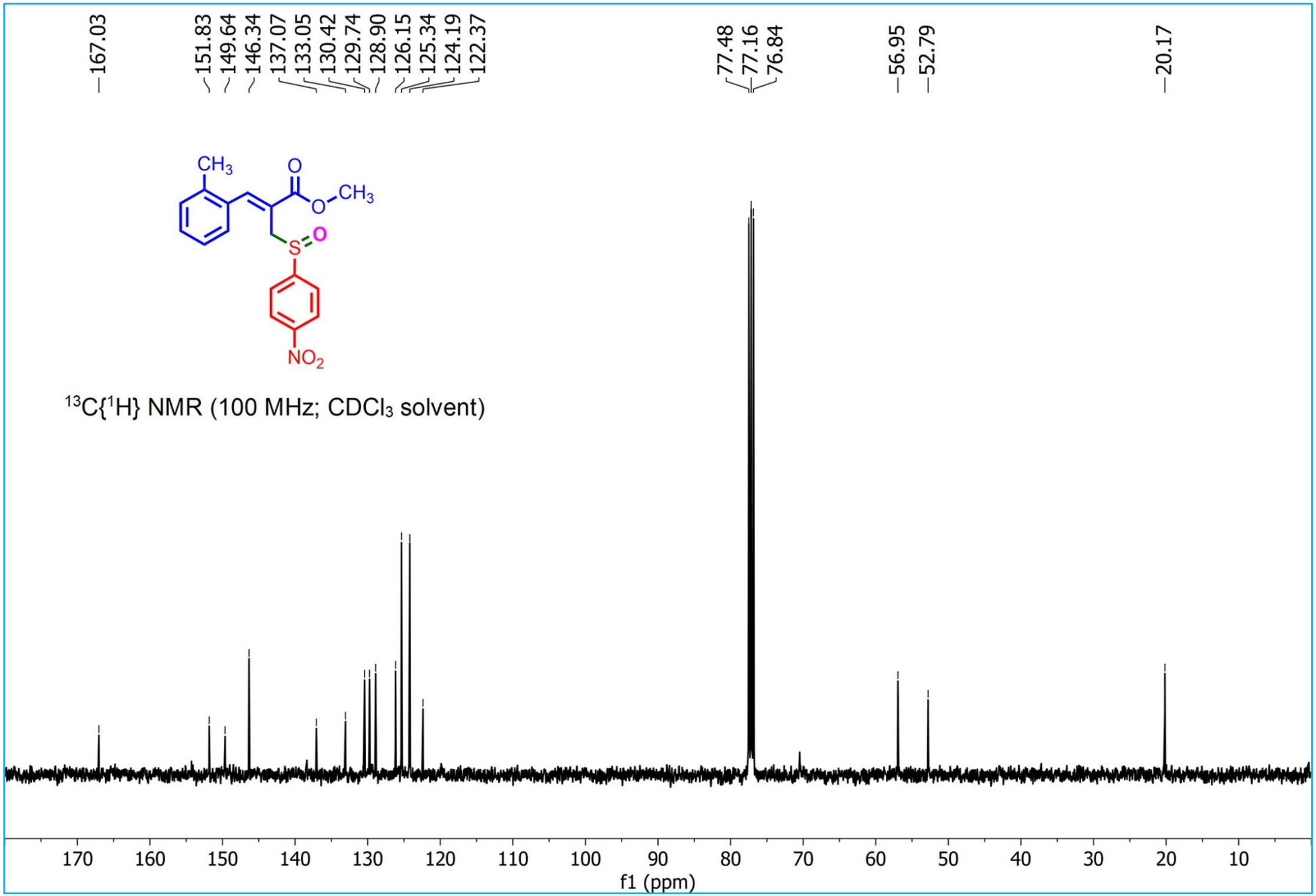


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(*o*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3bi**)

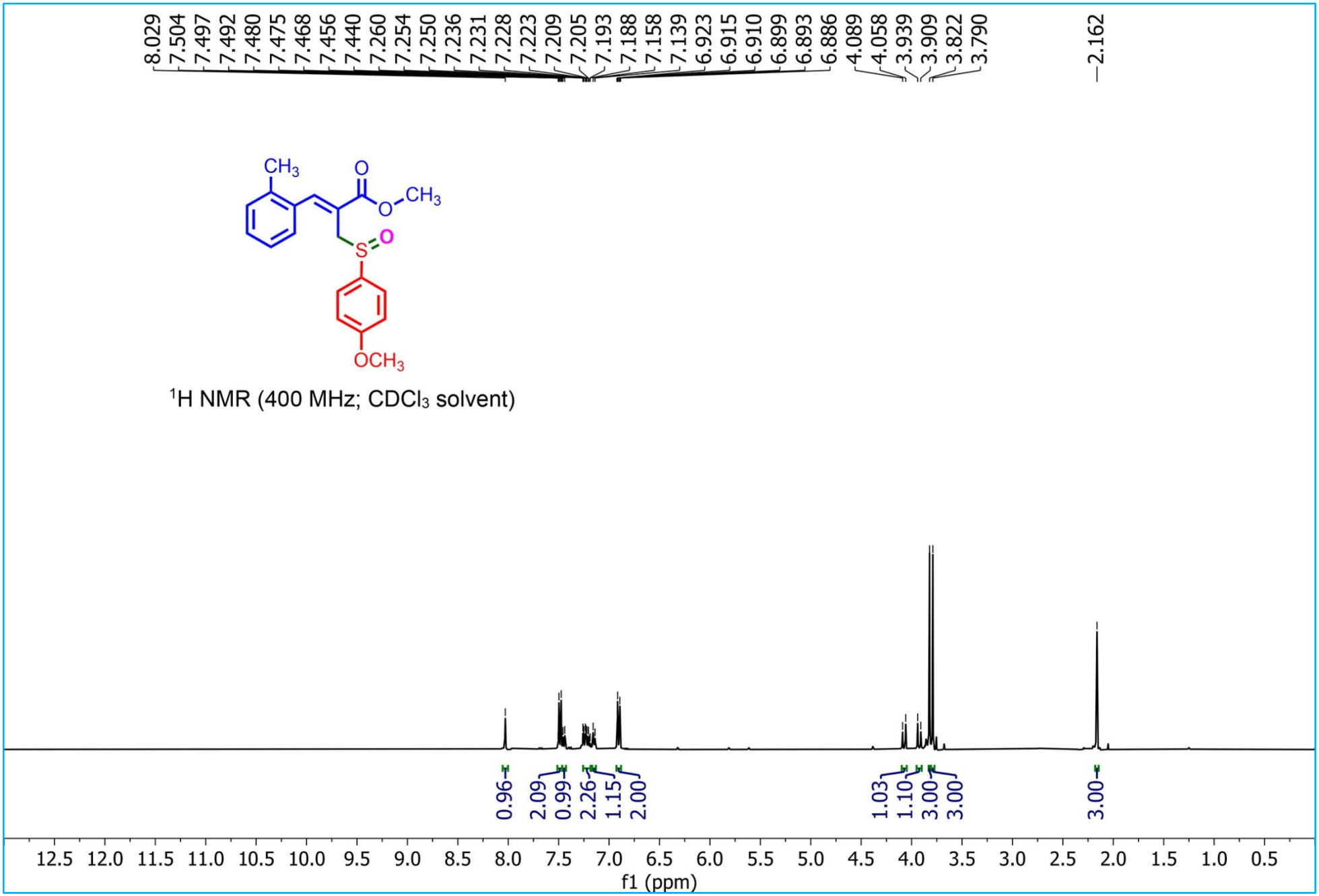


Figure S33. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bj**)

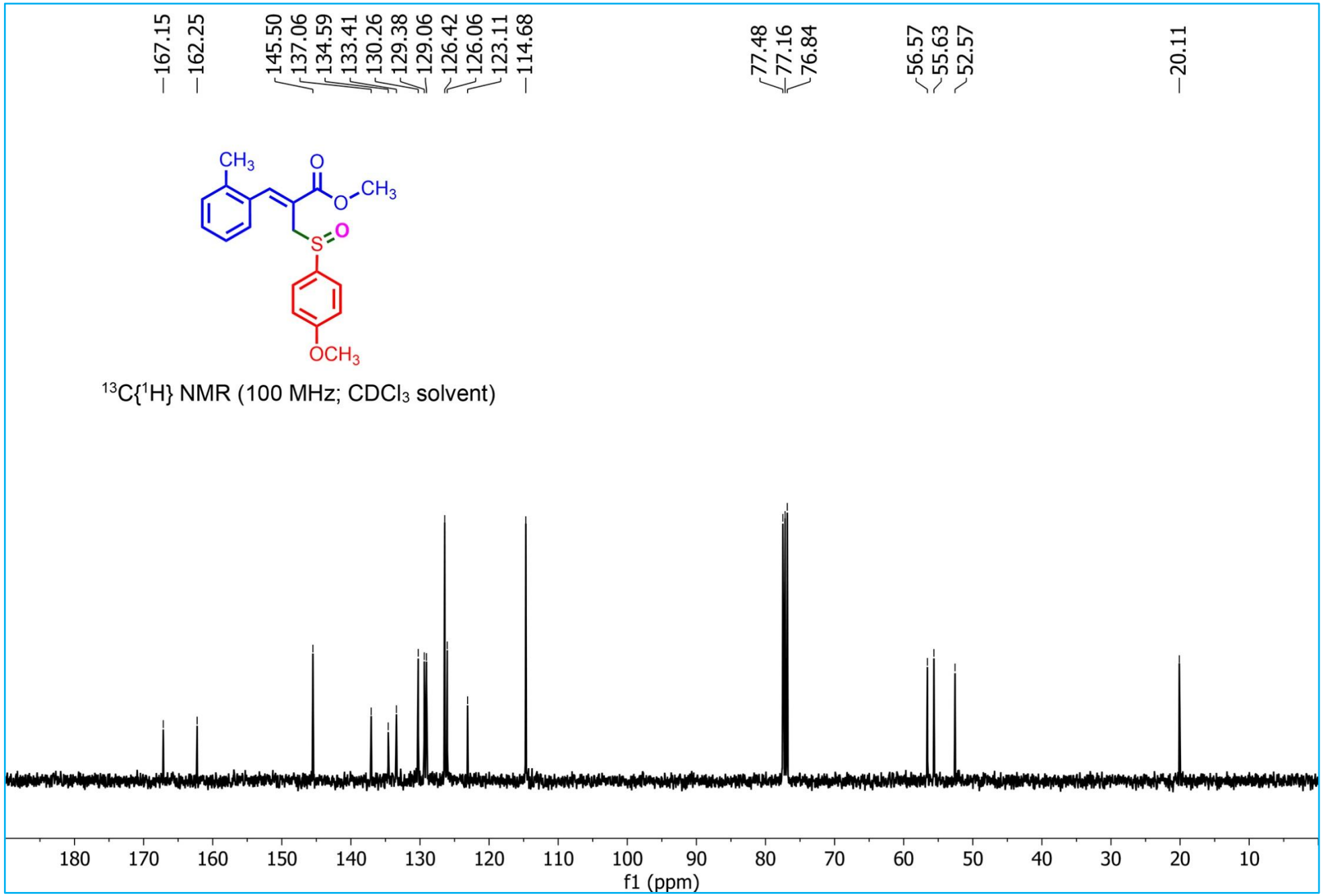


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-(*o*-tolyl)acrylate (**3bj**)

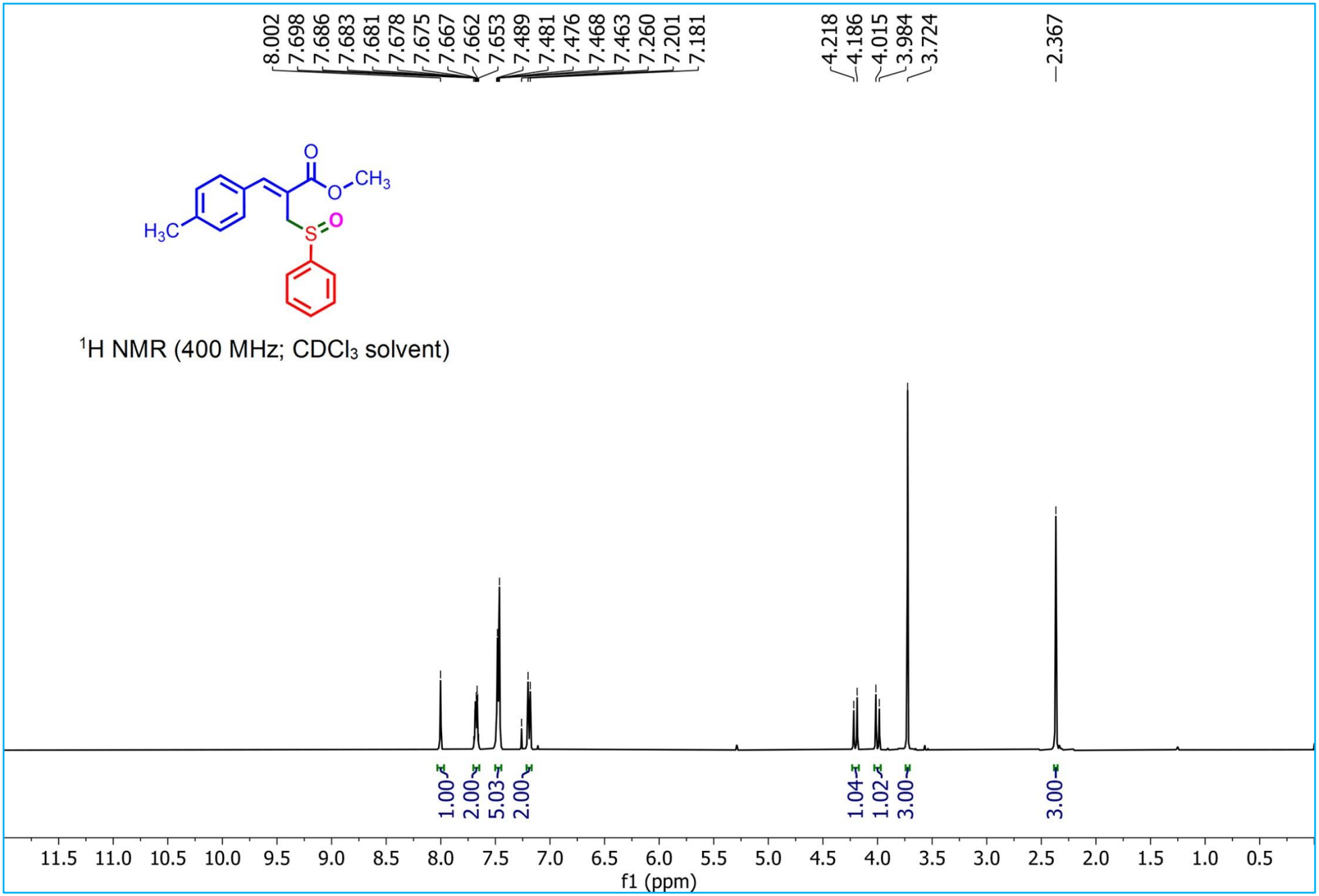


Figure S35. ^{1}H NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3ca**)

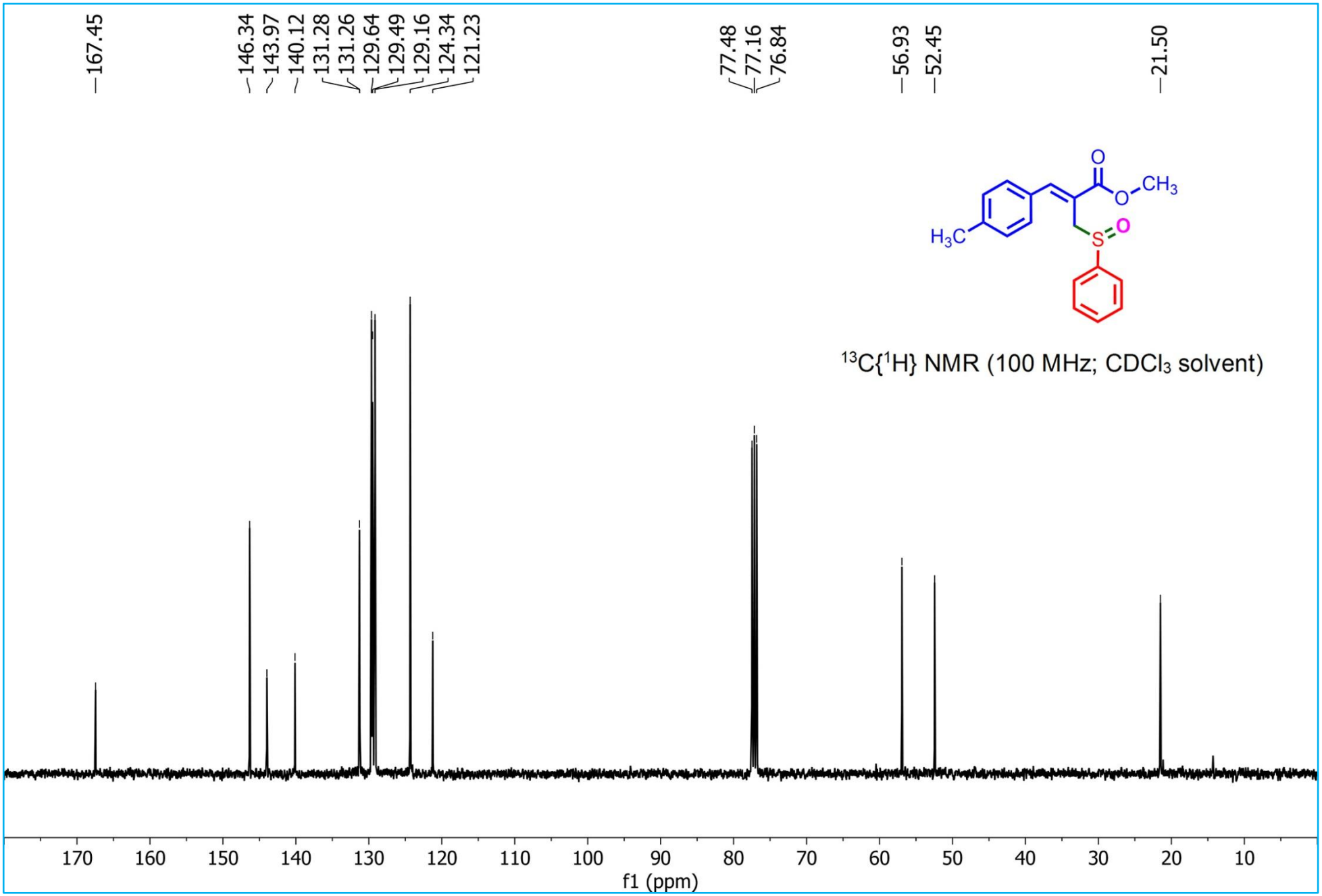


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3ca**)

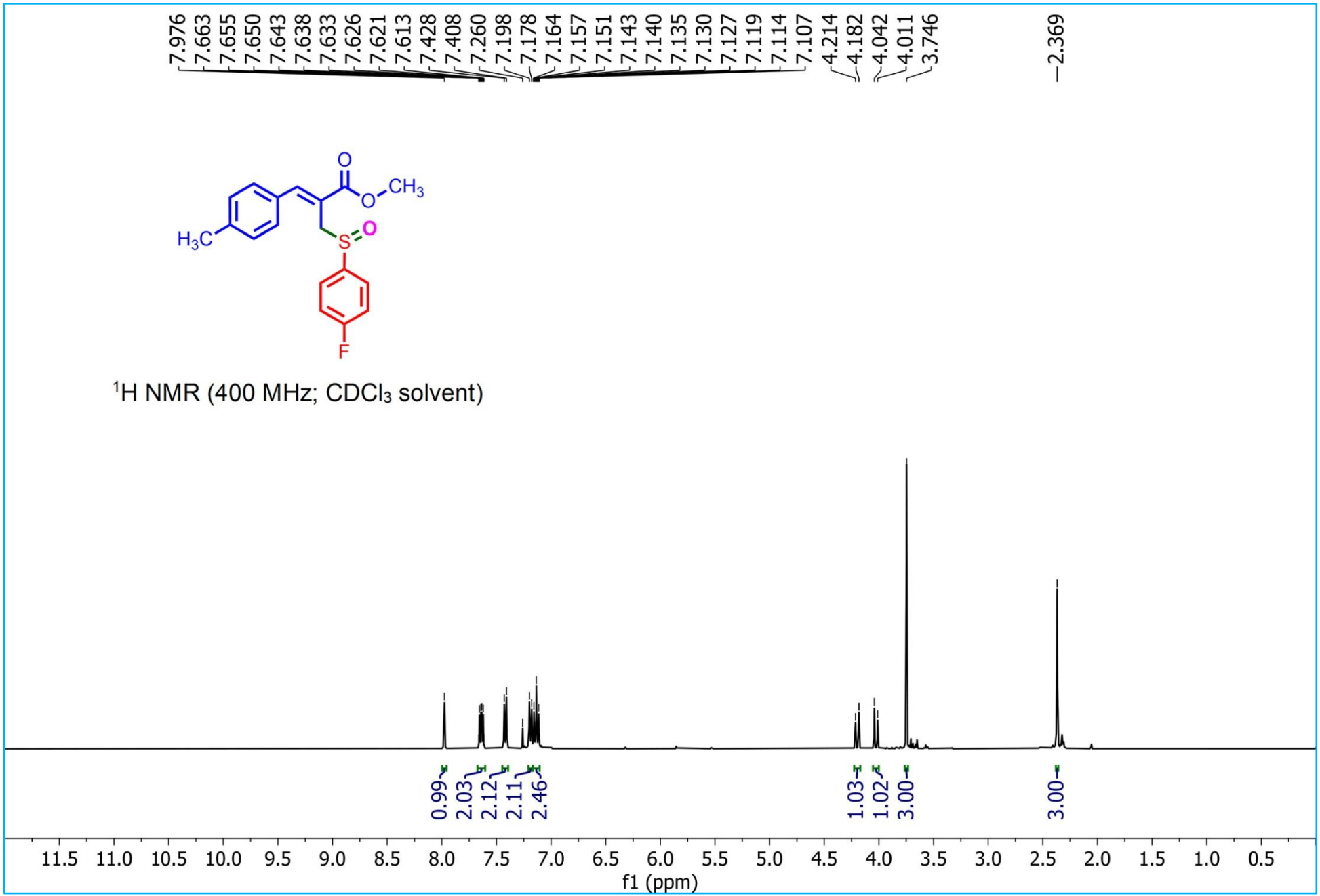


Figure S37. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cb**)

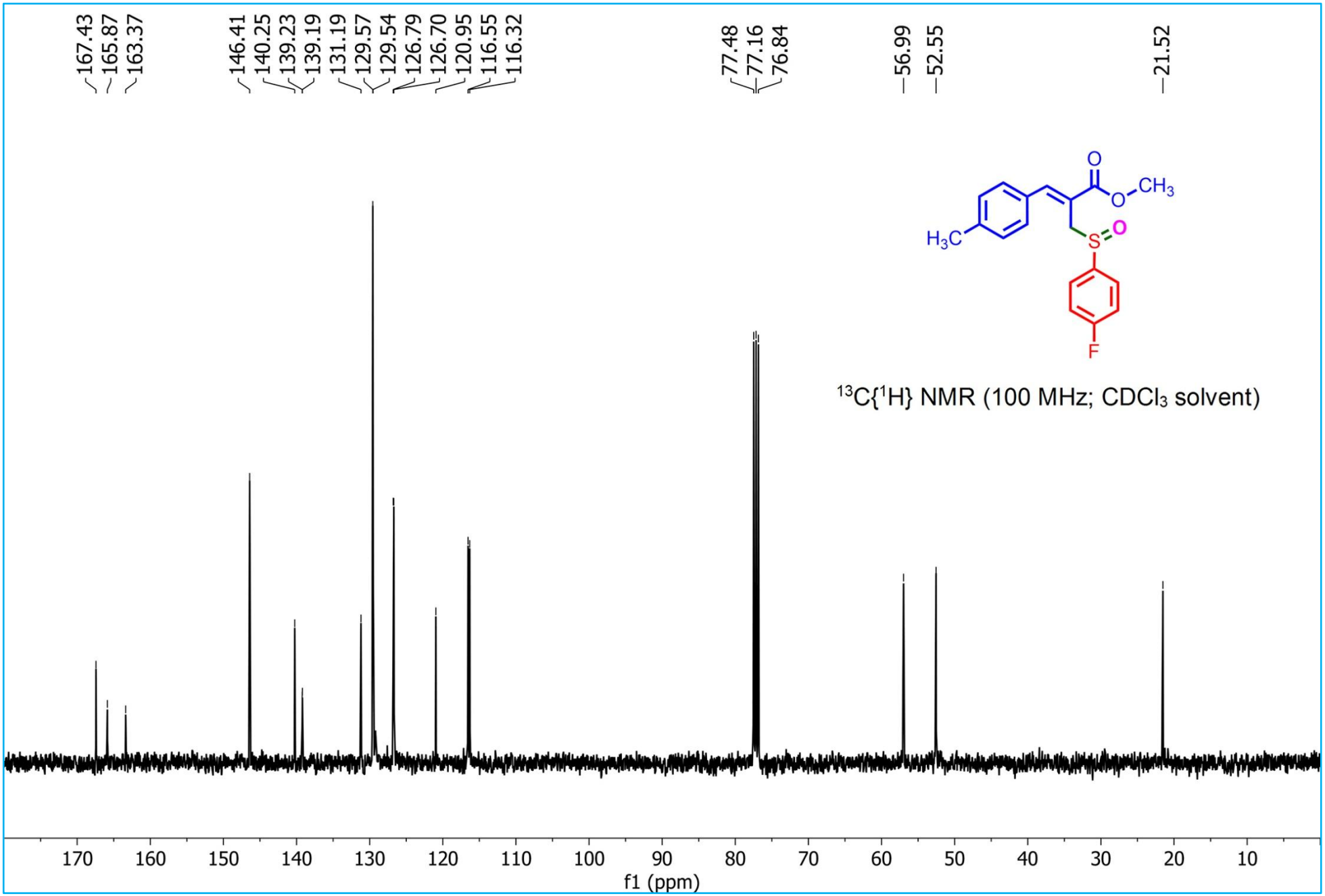


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cb**)

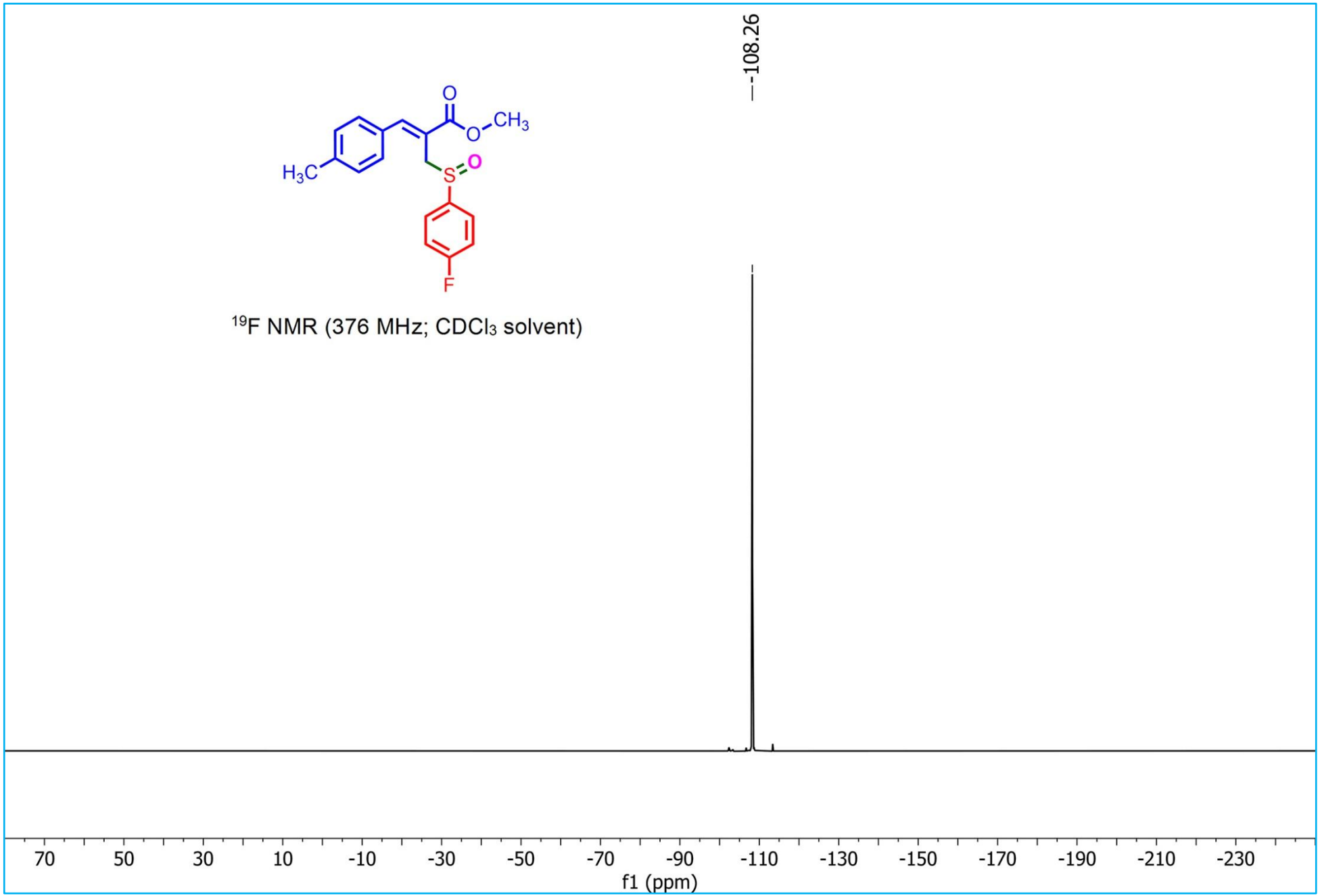


Figure S39. ^{19}F NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cb**)

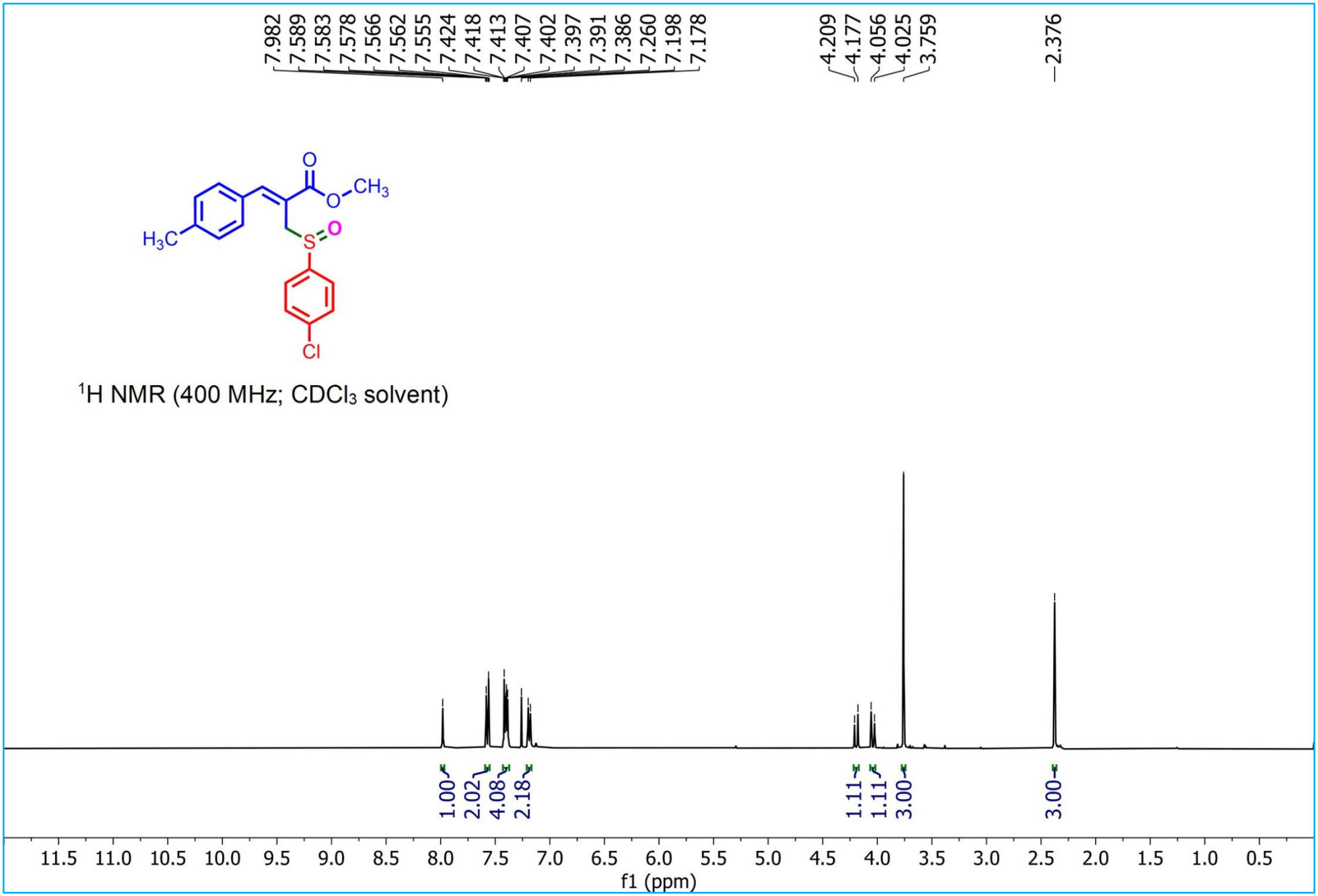


Figure S40. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cc**)

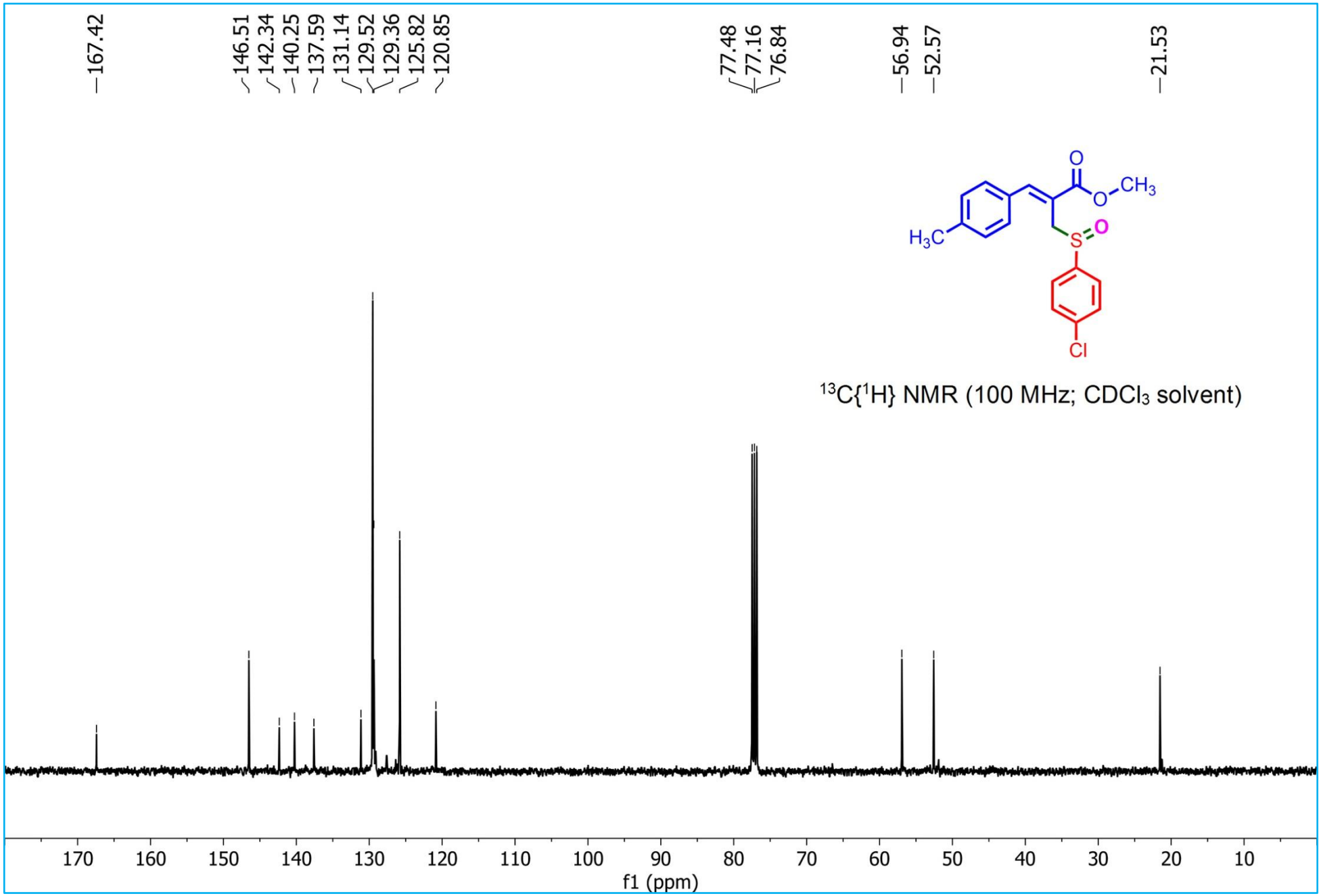


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cc**)

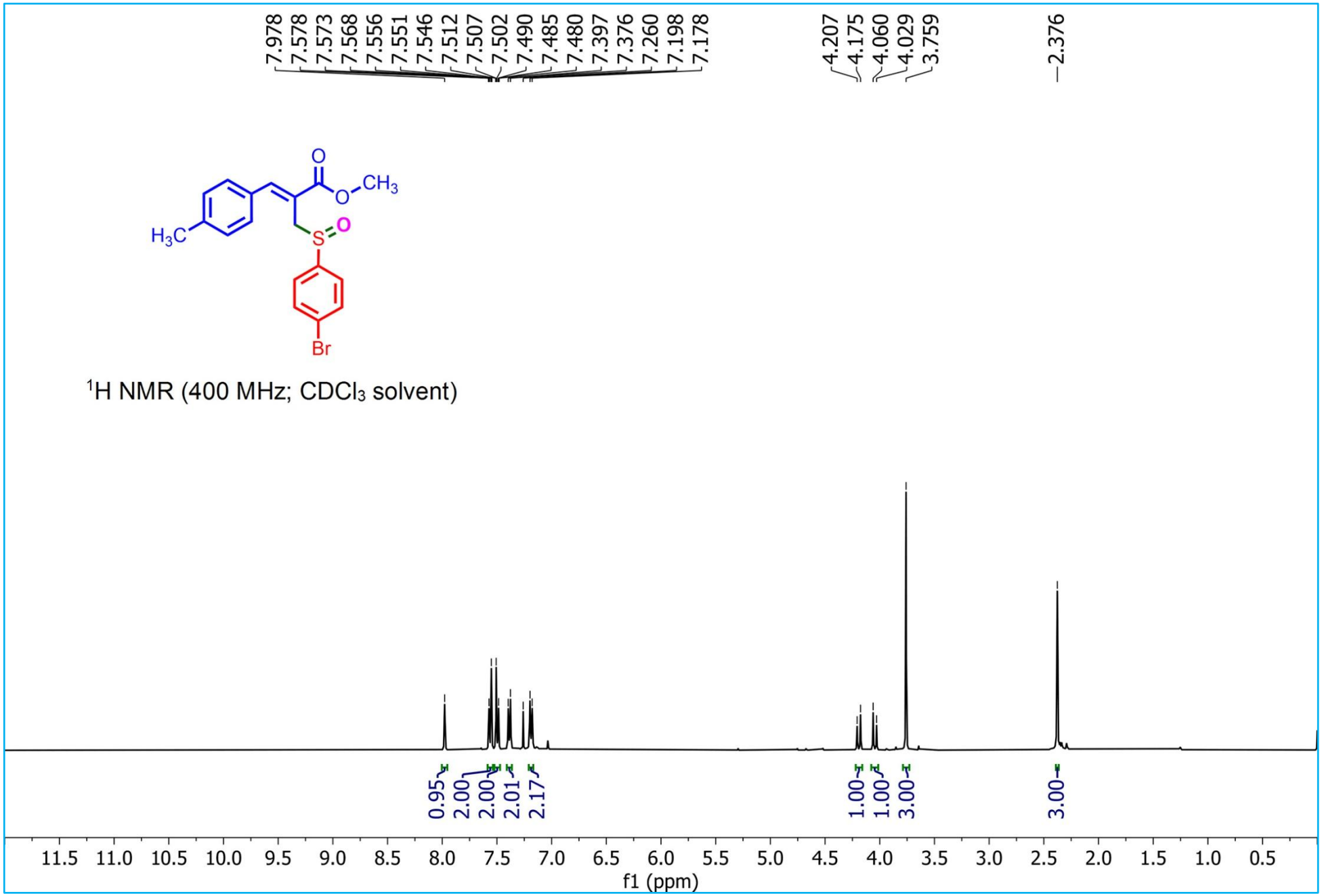


Figure S42. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cd**)

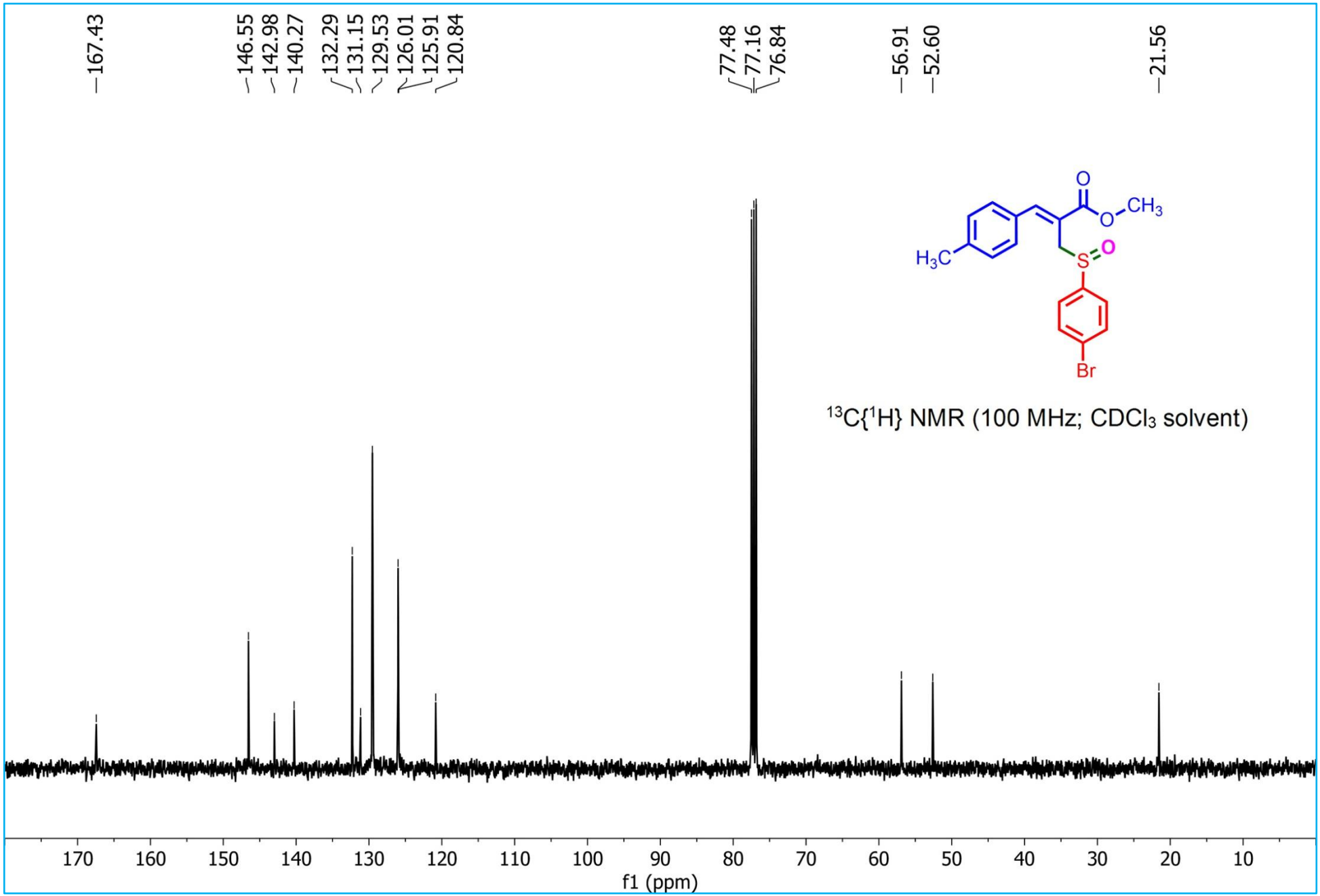


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cd**)

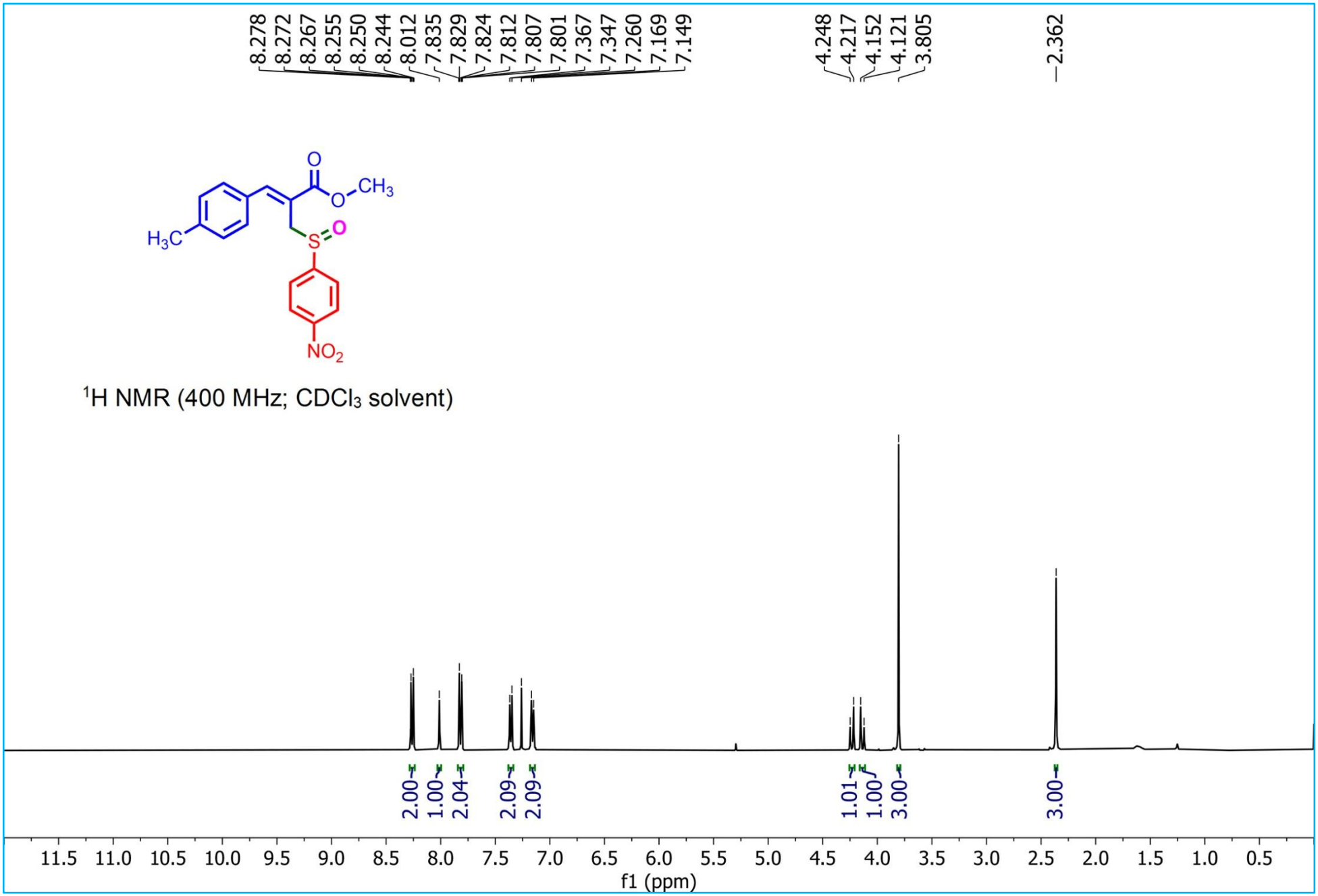


Figure S44. [1]H NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cf**)

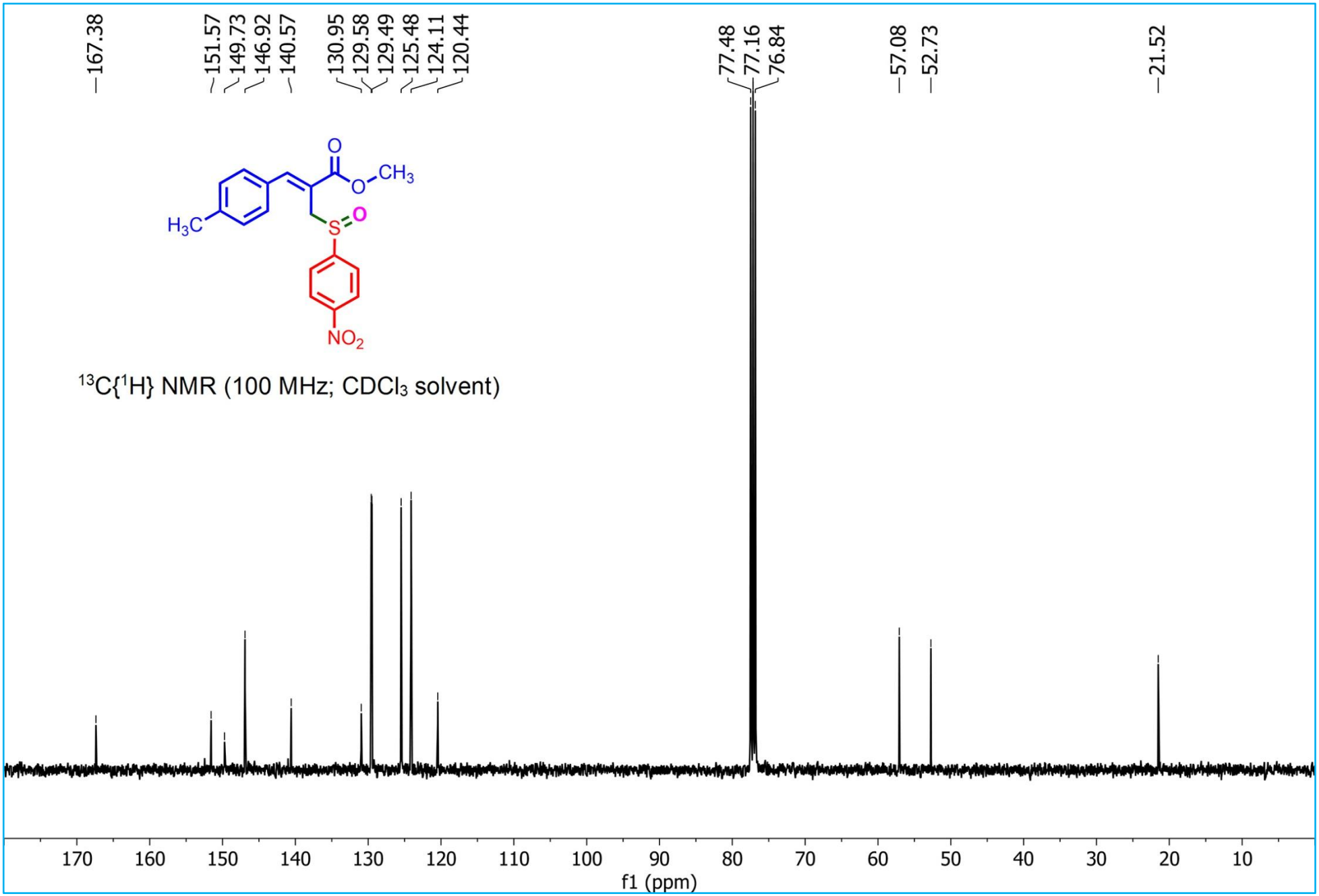


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-(*p*-tolyl)acrylate (**3cf**)

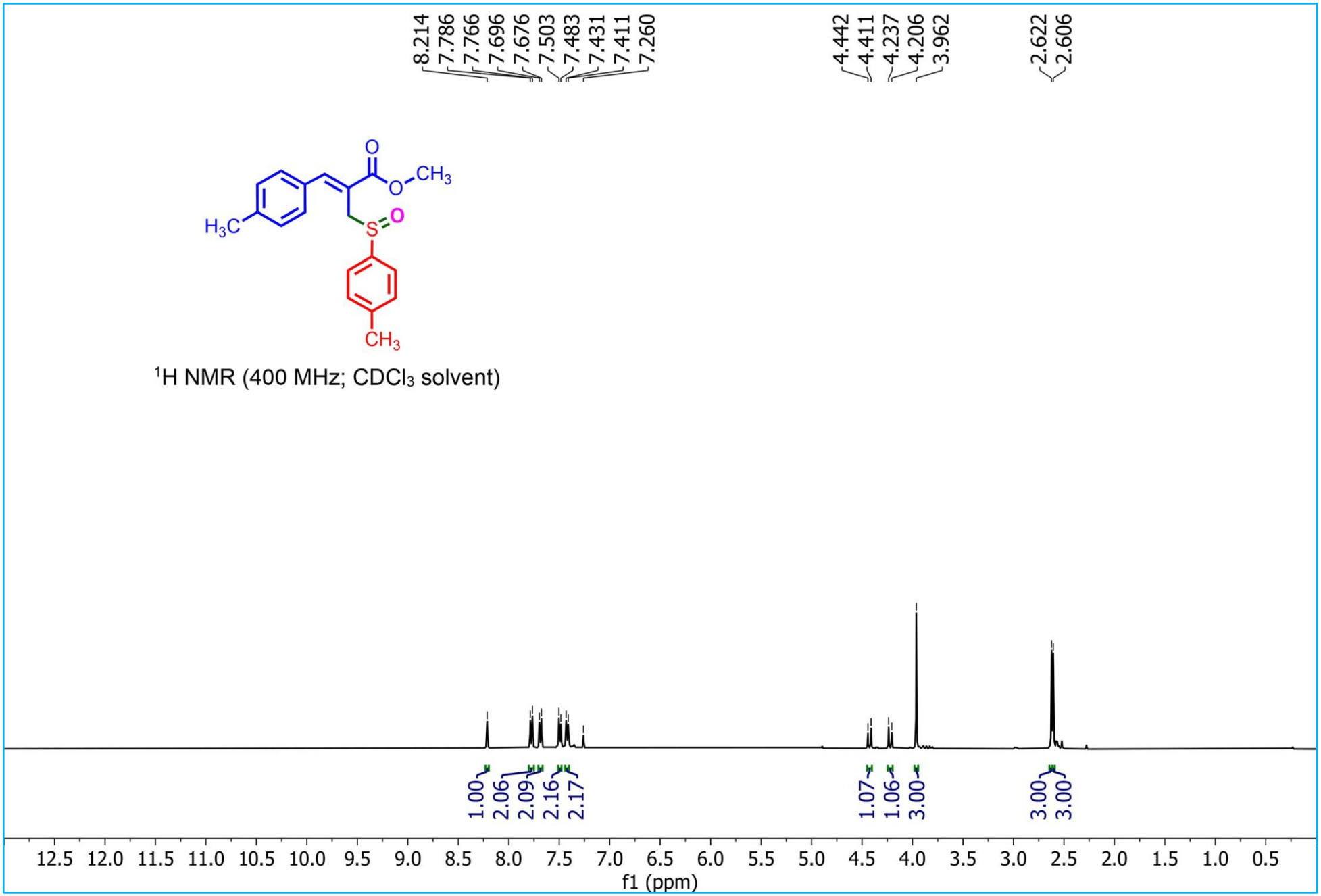


Figure S46. ^{1}H NMR spectrum of methyl (*Z*)-3-(*p*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3ci**)

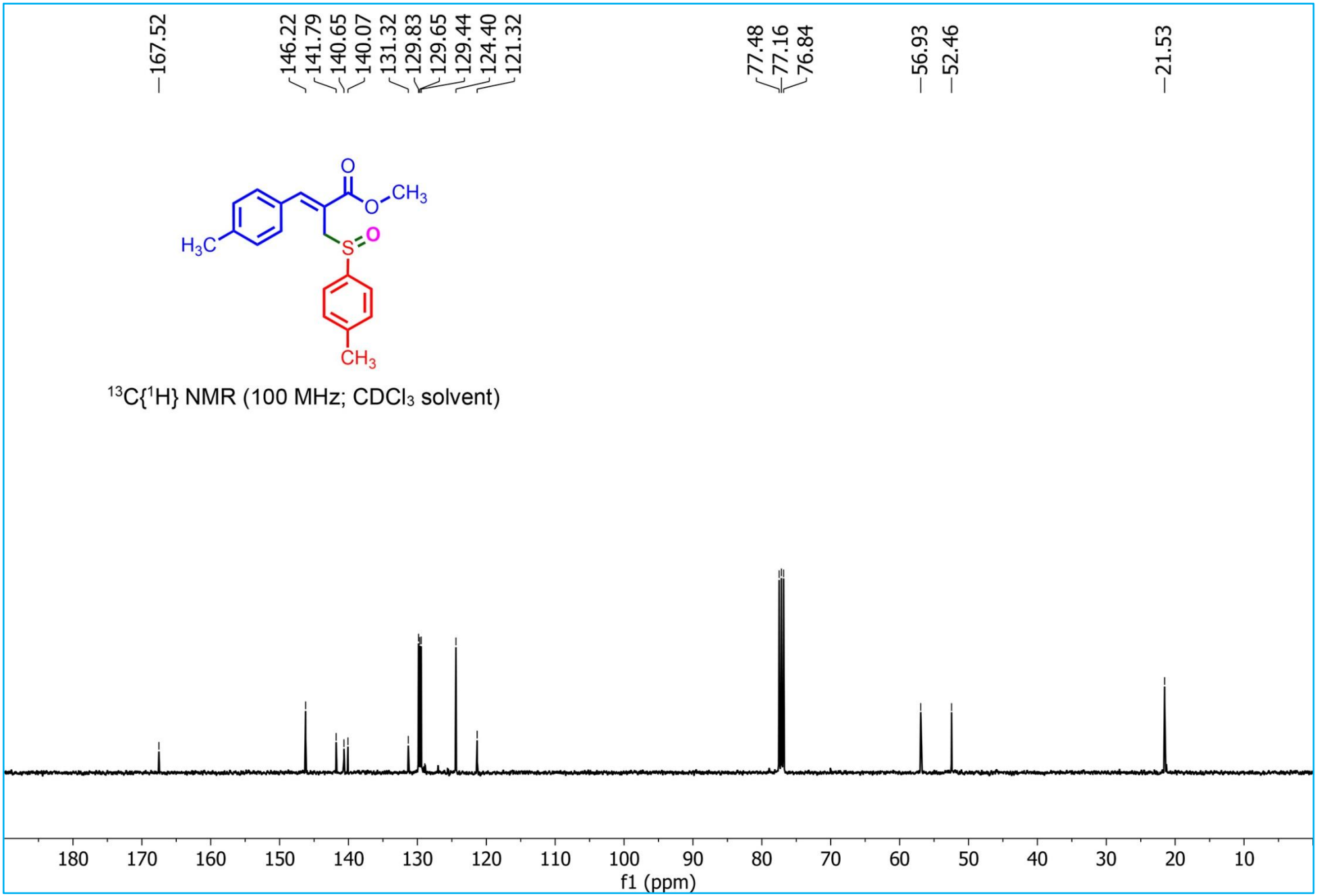


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(*p*-tolyl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3ci**)

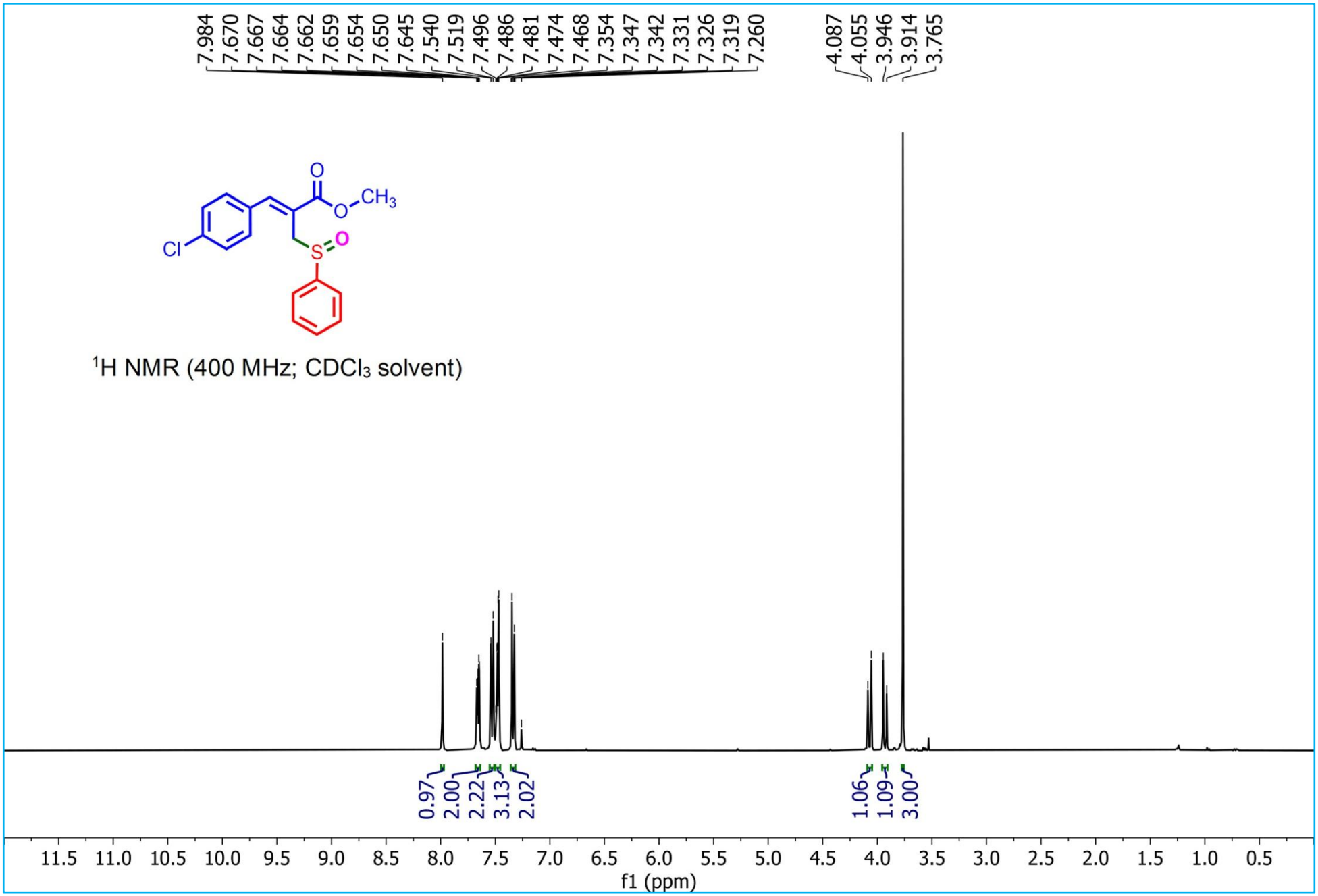


Figure S48. [1]H NMR spectrum of methyl (*Z*)-3-(4-chlorophenyl)-2-((phenylsulfinyl)methyl)acrylate (**3da**)

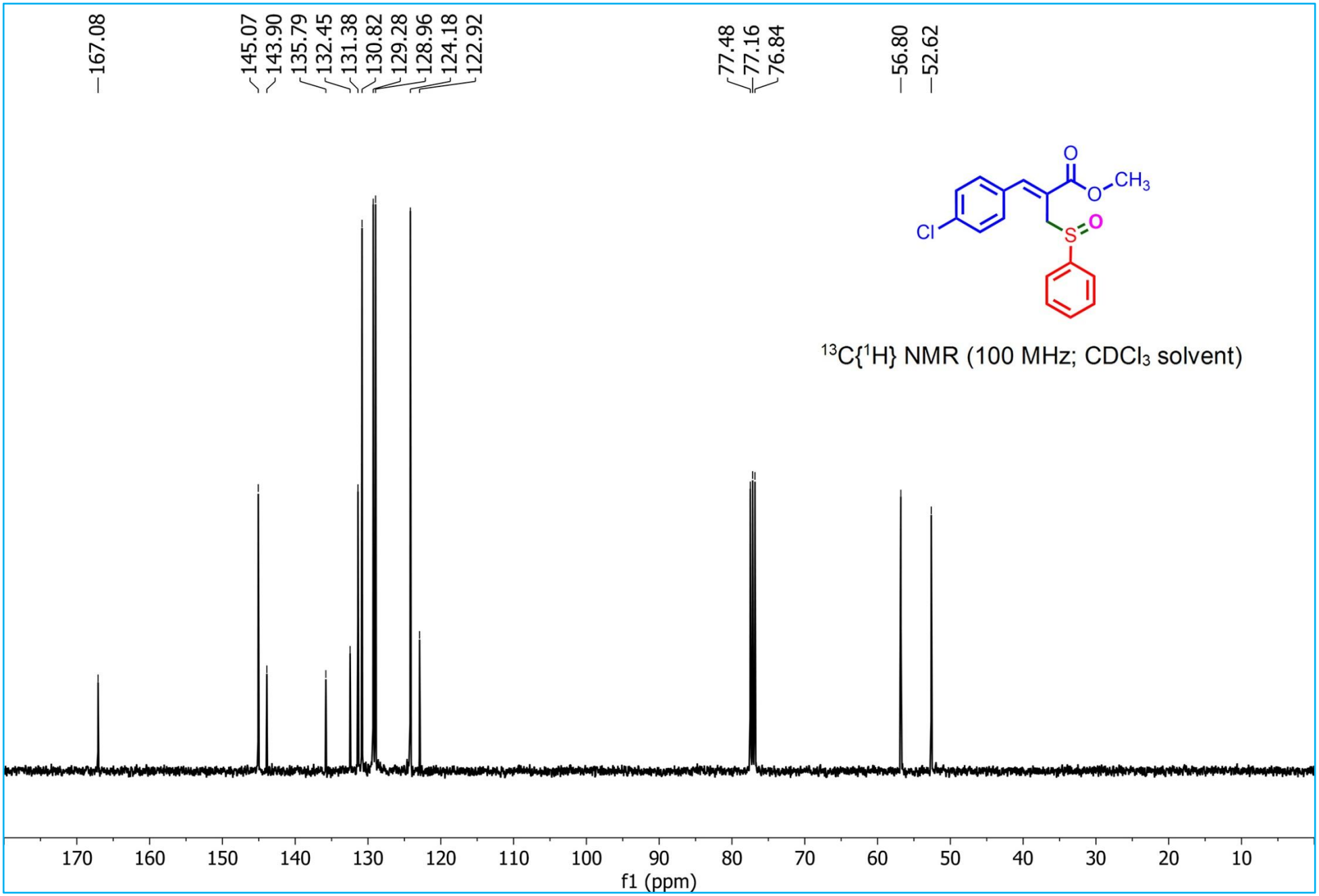


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(4-chlorophenyl)-2-((phenylsulfinyl)methyl)acrylate (**3da**)

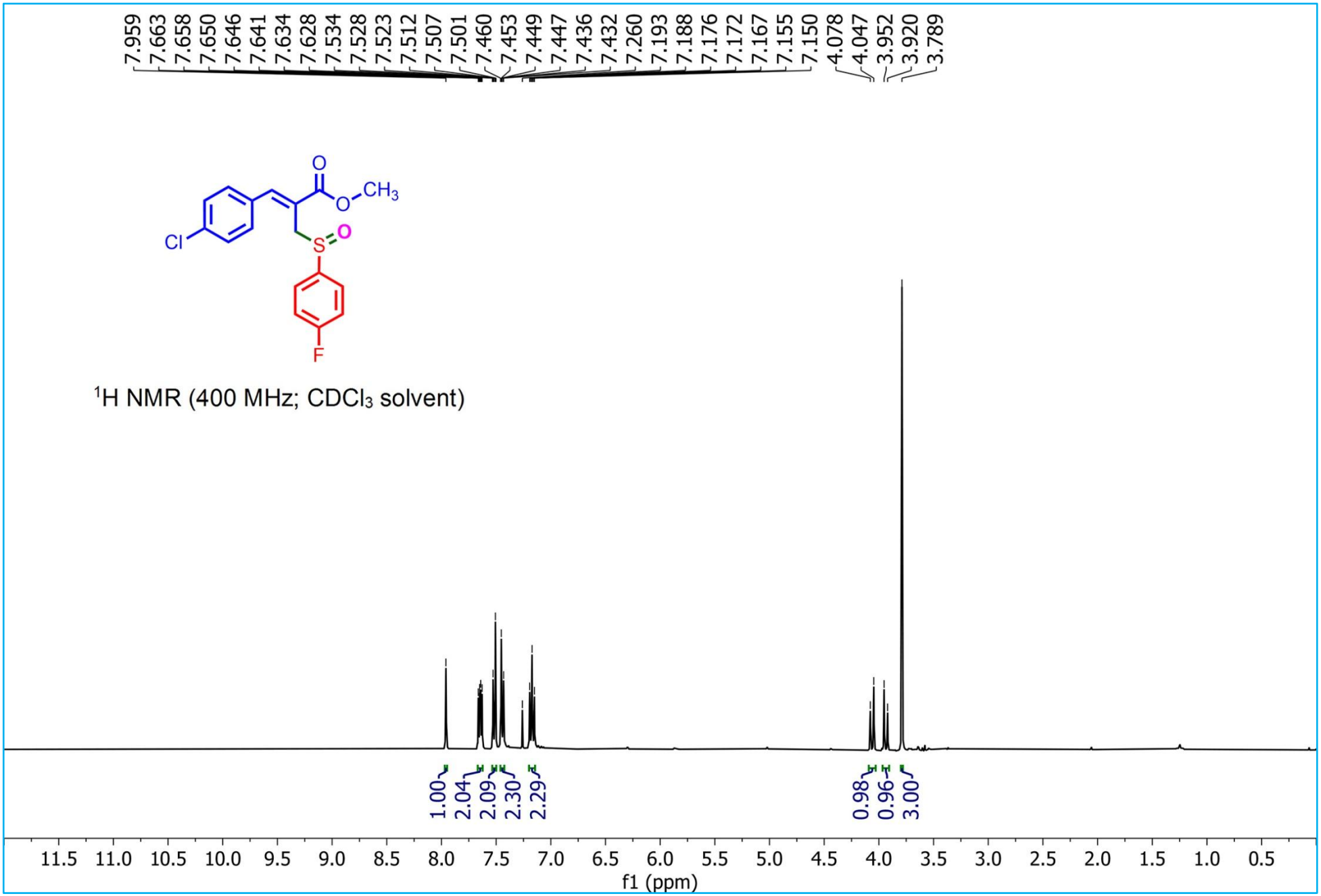


Figure S50. ^{1}H NMR spectrum of methyl (*Z*)-3-(4-chlorophenyl)-2-(((4-fluorophenyl)sulfinyl)methyl)acrylate (**3db**)

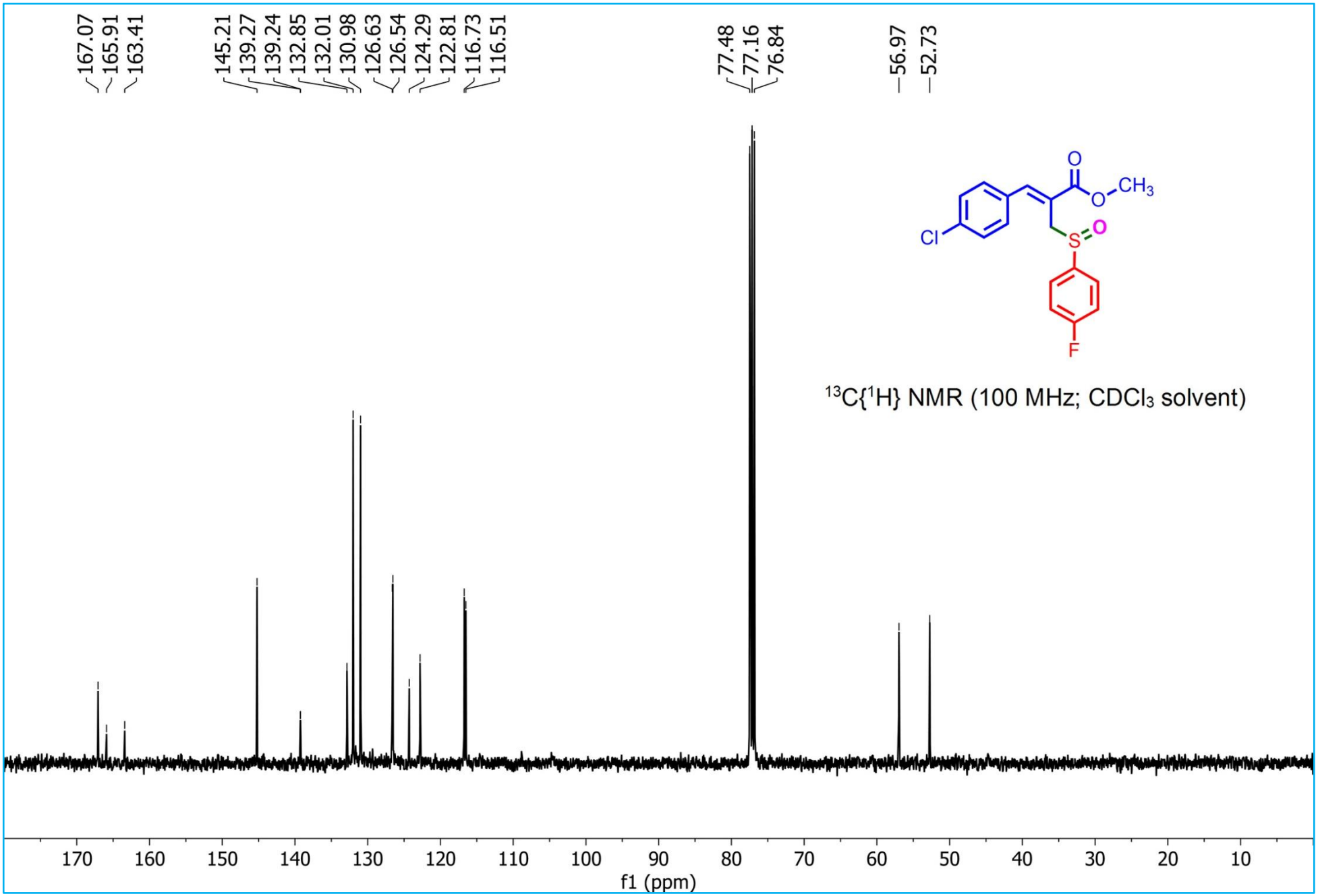


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(4-chlorophenyl)-2-(((4-fluorophenyl)sulfinyl)methyl)acrylate (**3db**)

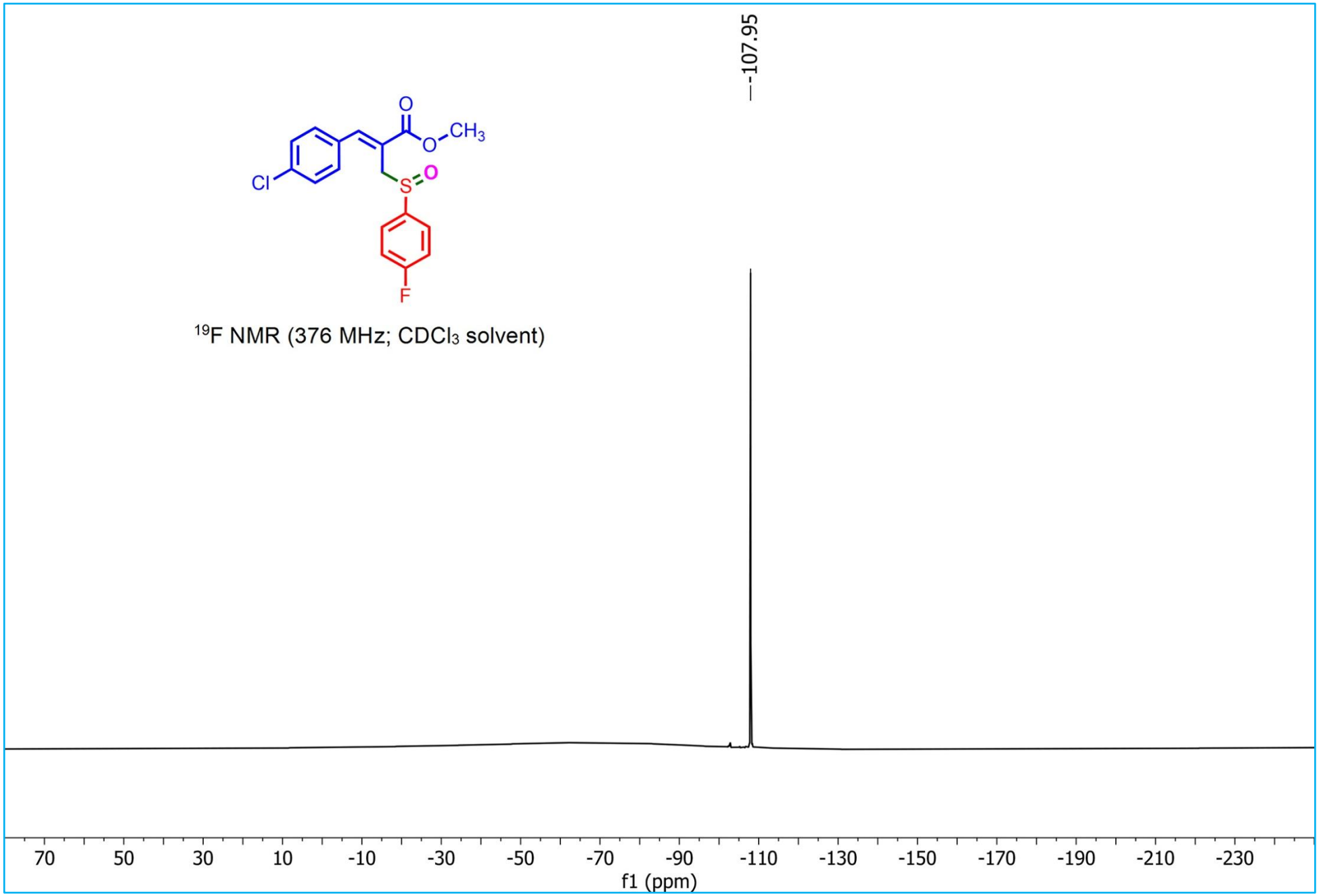


Figure S52. ^{19}F NMR spectrum of methyl (*Z*)-3-(4-chlorophenyl)-2-(((4-fluorophenyl)sulfinyl)methyl)acrylate (**3db**)

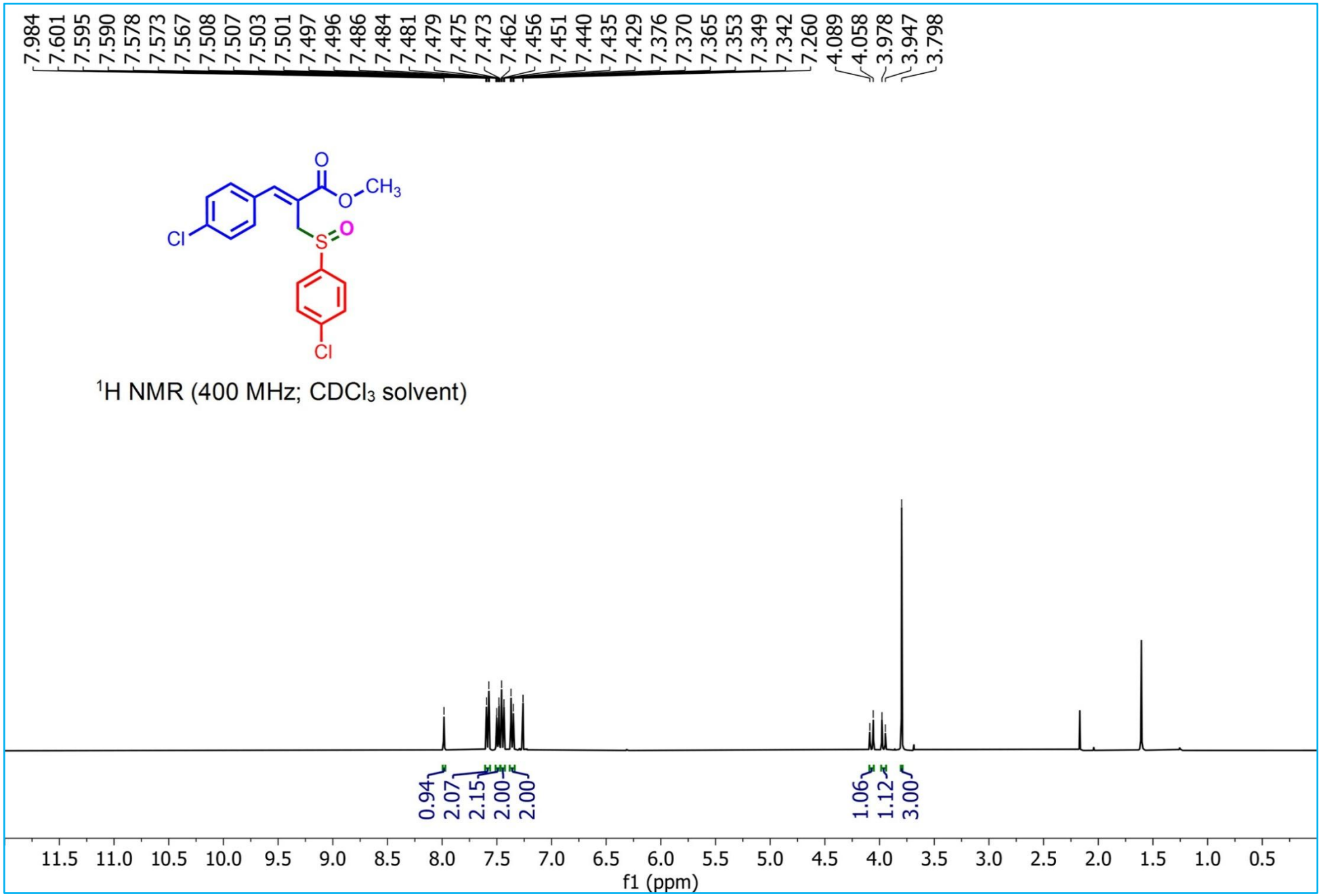


Figure S53. [1]H NMR spectrum of methyl (Z)-3-(4-chlorophenyl)-2-(((4-chlorophenyl)sulfinyl)methyl)acrylate (**3dc**)

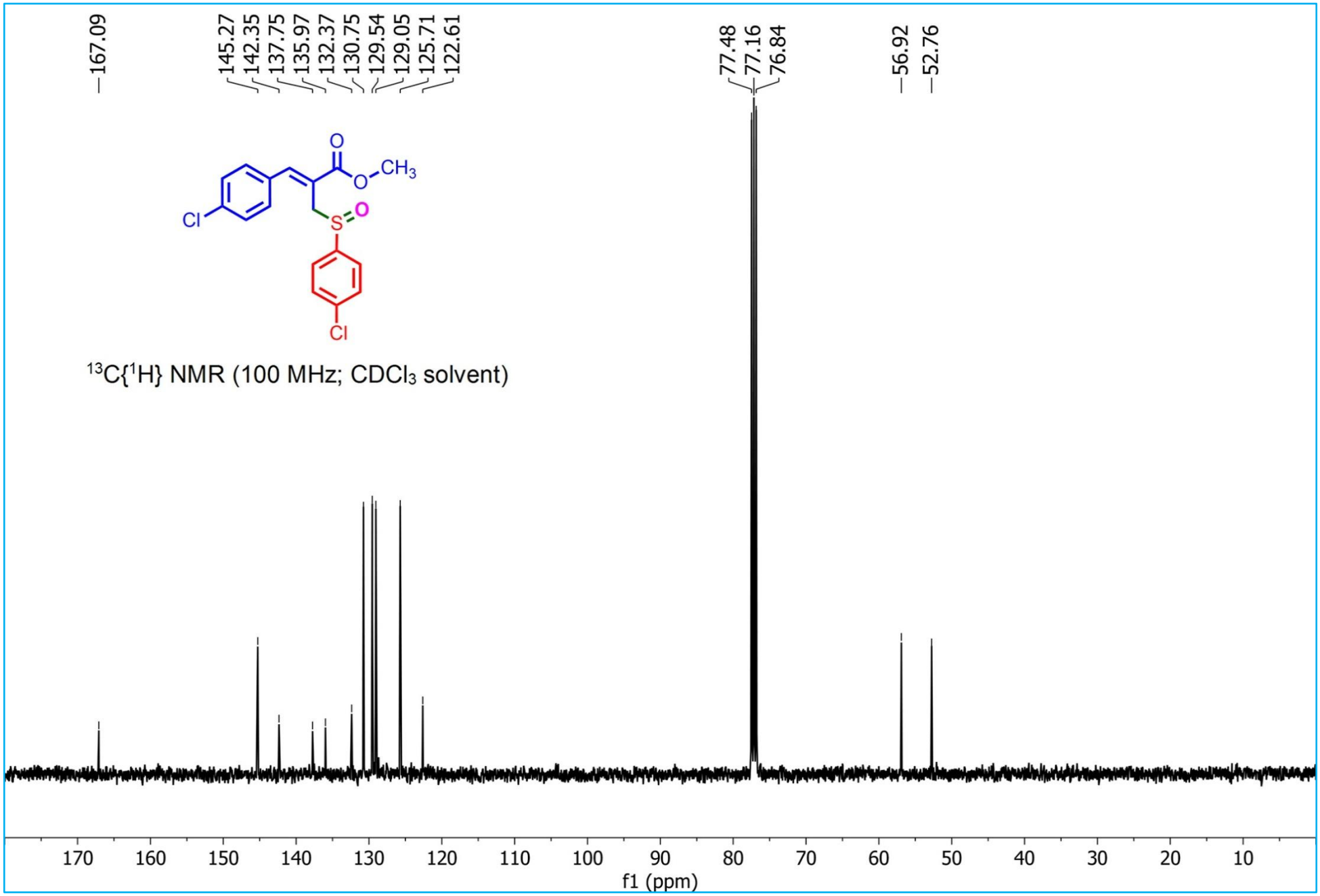


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (Z)-3-(4-chlorophenyl)-2-(((4-chlorophenyl)sulfinyl)methyl)acrylate (**3dc**)

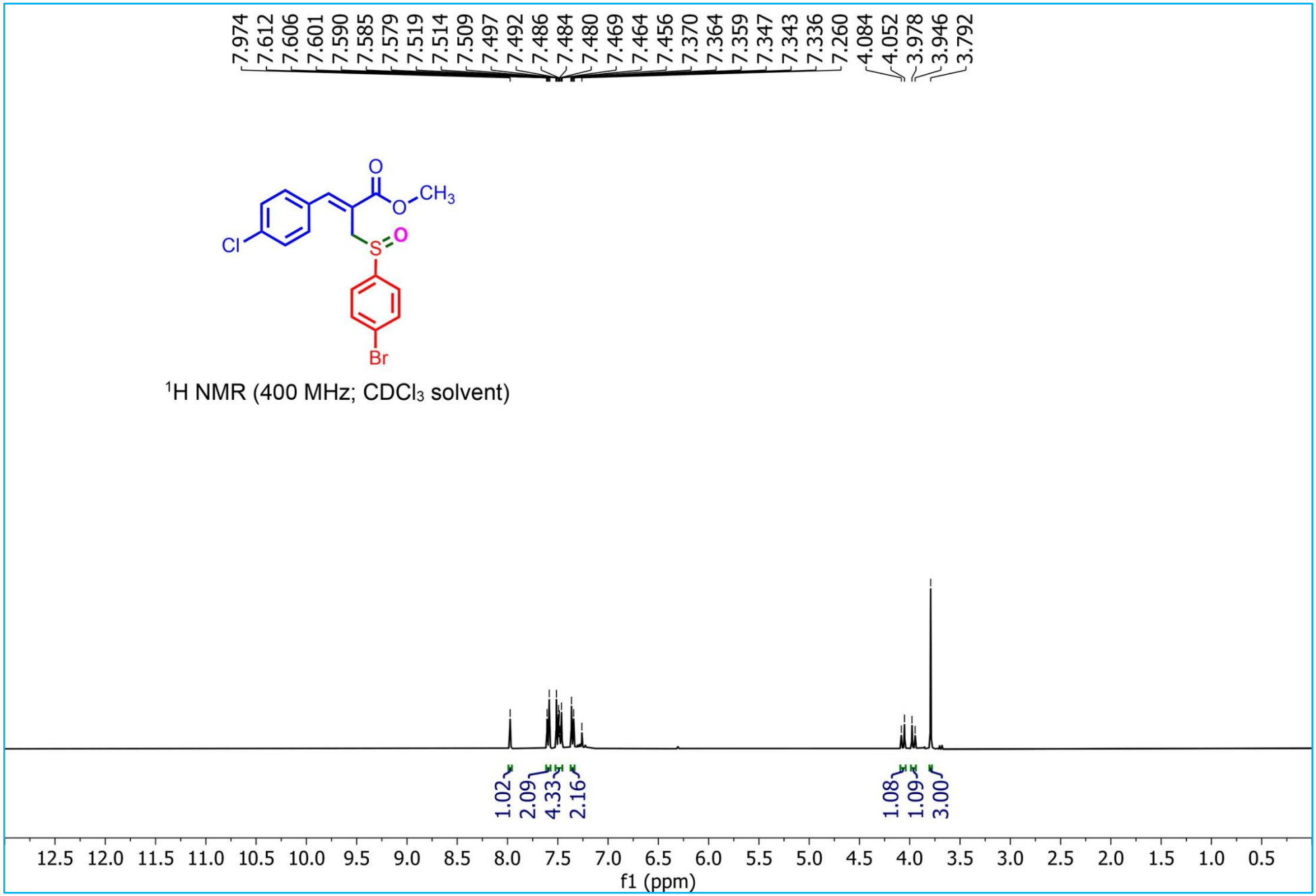


Figure S55. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dd**)

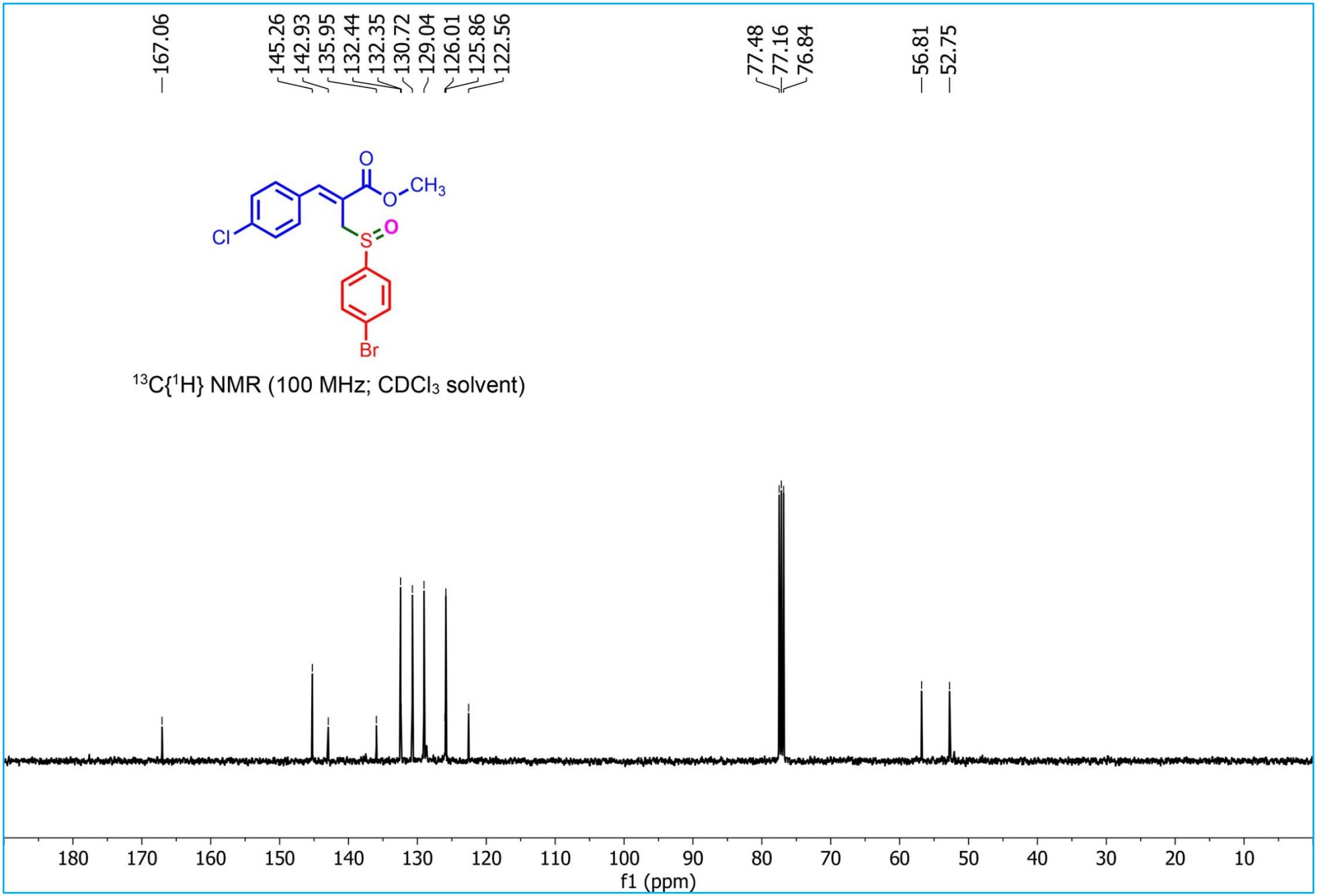


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dd**)

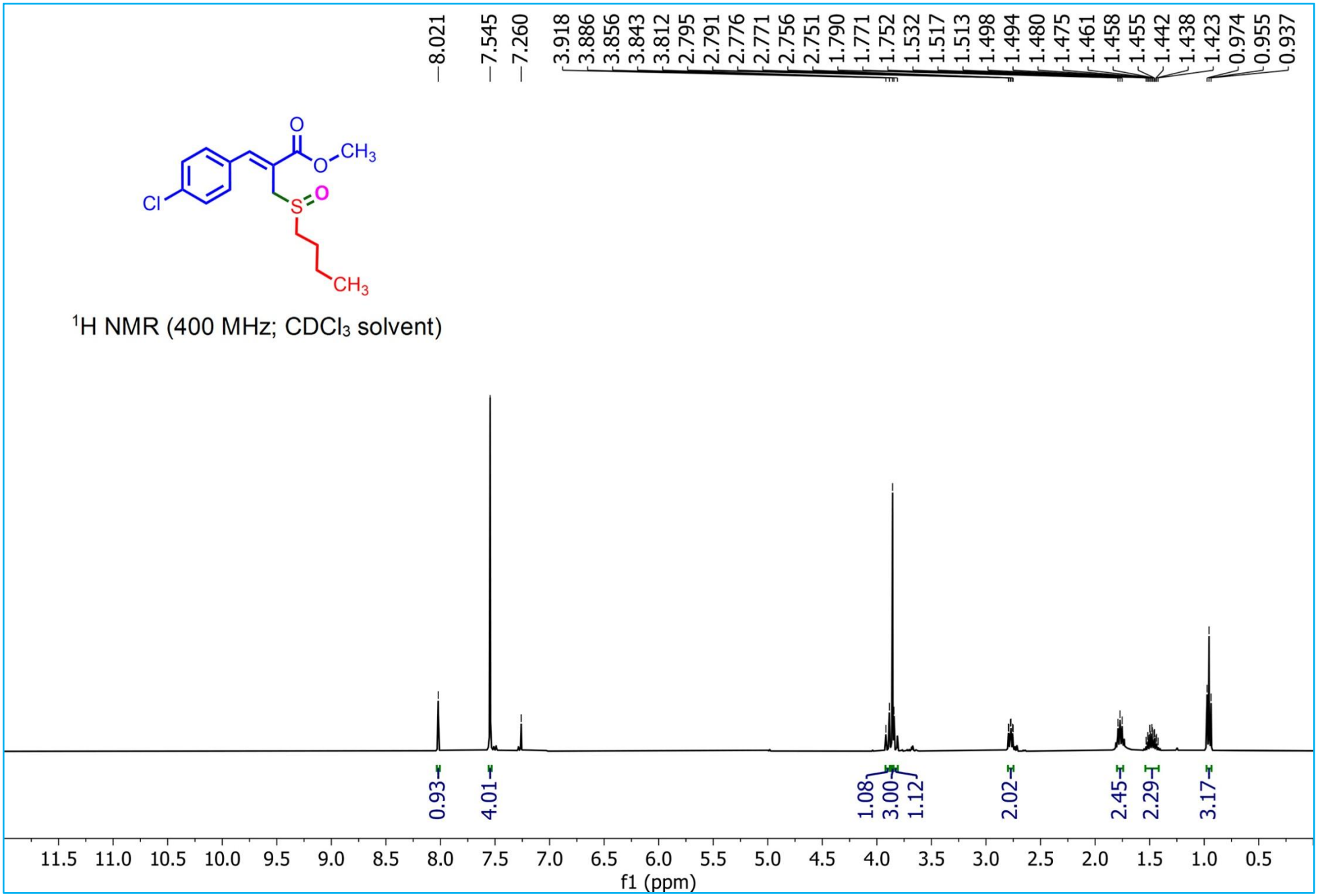


Figure S57. ^{1}H NMR spectrum of methyl (*Z*)-2-((butylsulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dh**)

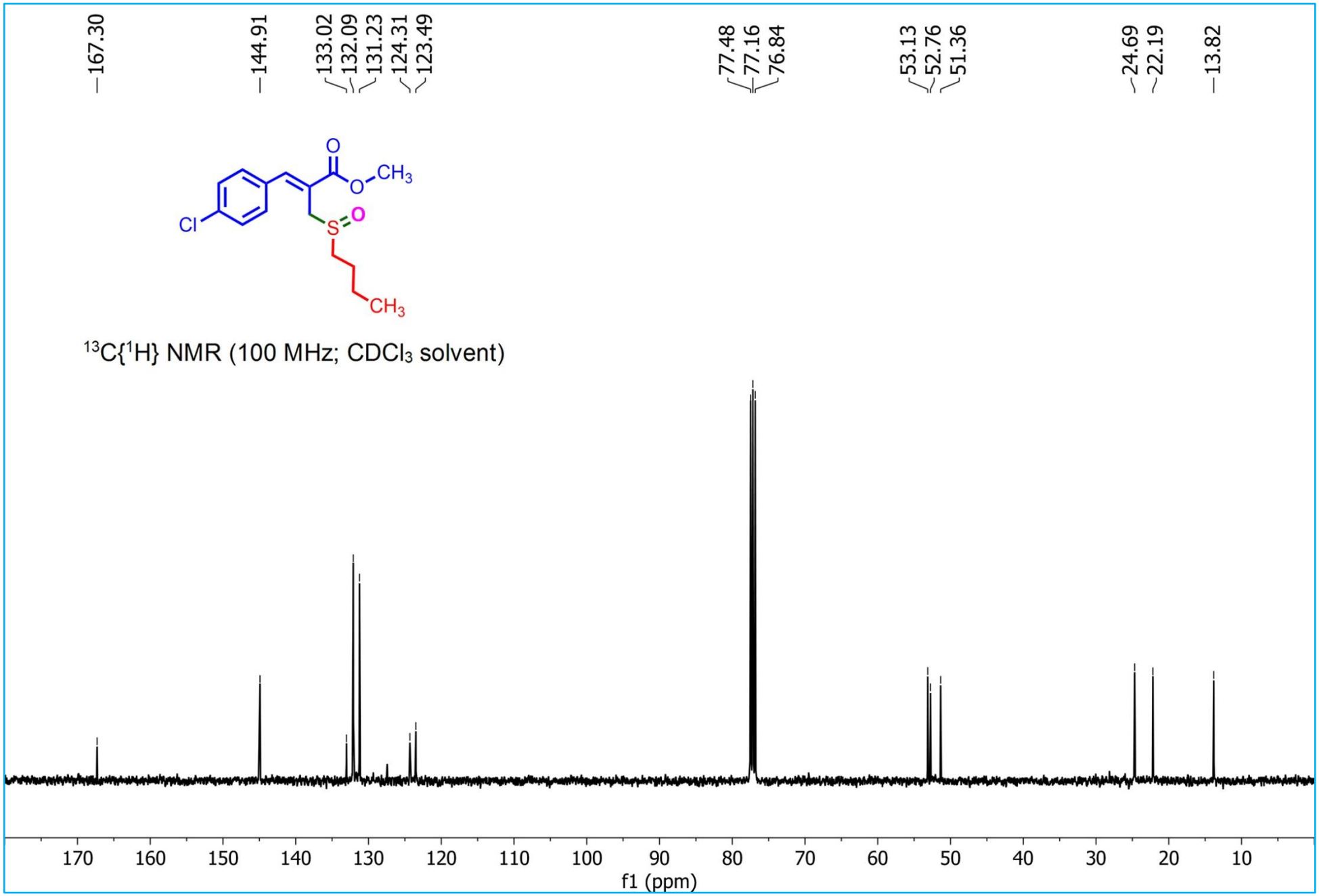


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((butylsulfinyl)methyl)-3-(4-chlorophenyl)acrylate (**3dh**)

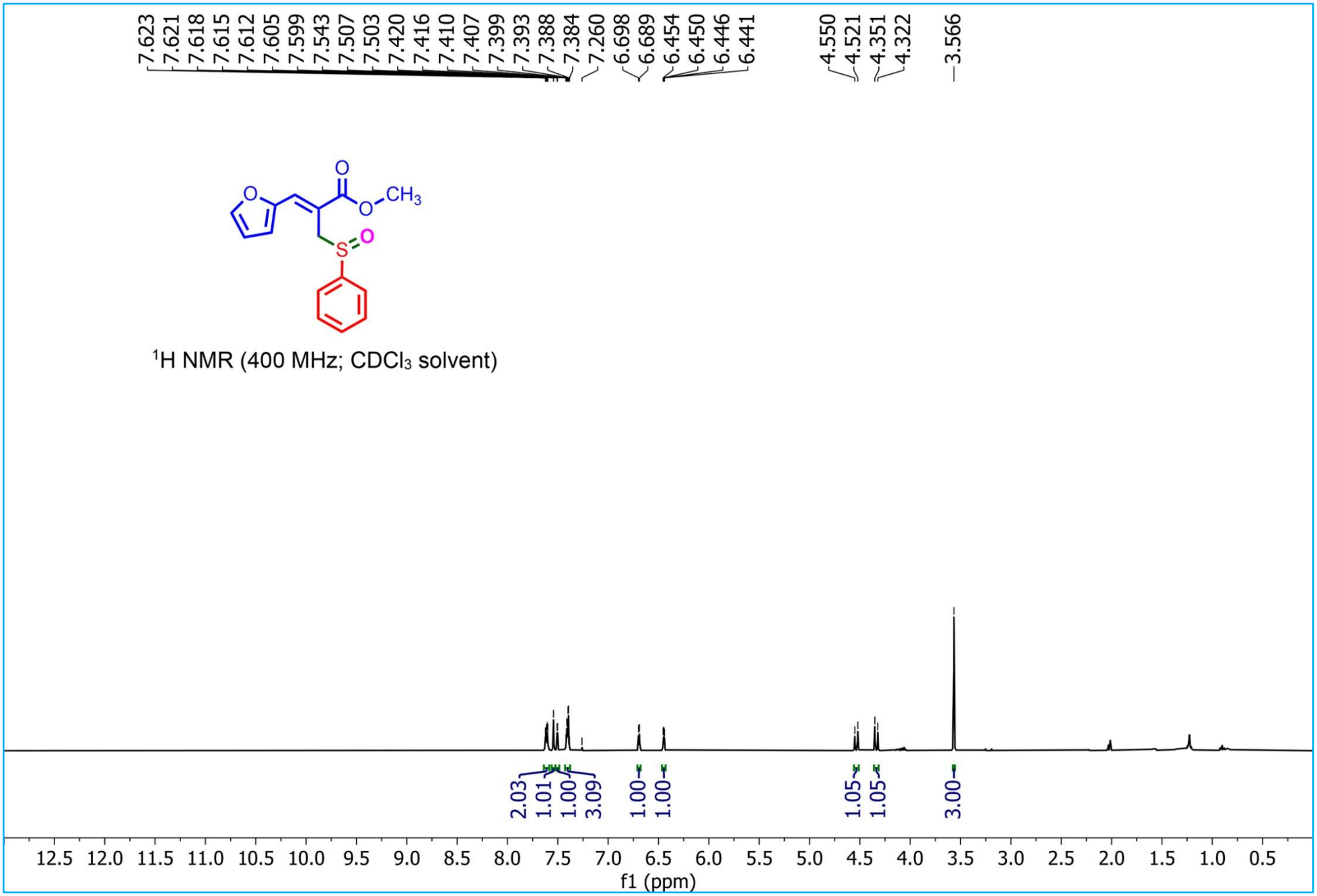


Figure S59. ^{1}H NMR spectrum of methyl (*Z*)-3-(furan-2-yl)-2-((phenylsulfinyl)methyl)acrylate (**3ea**)

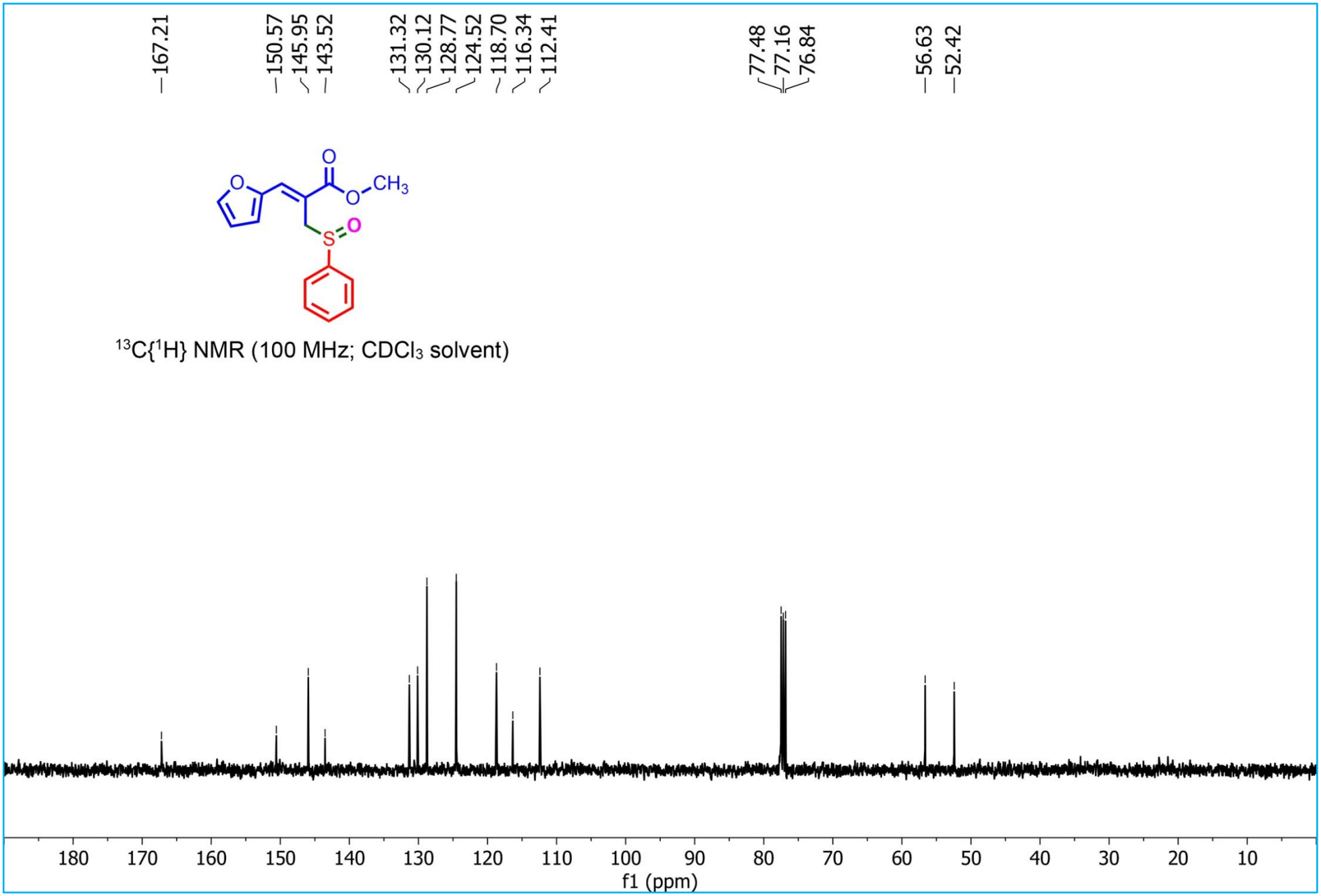


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(furan-2-yl)-2-((phenylsulfinyl)methyl)acrylate (**3ea**)

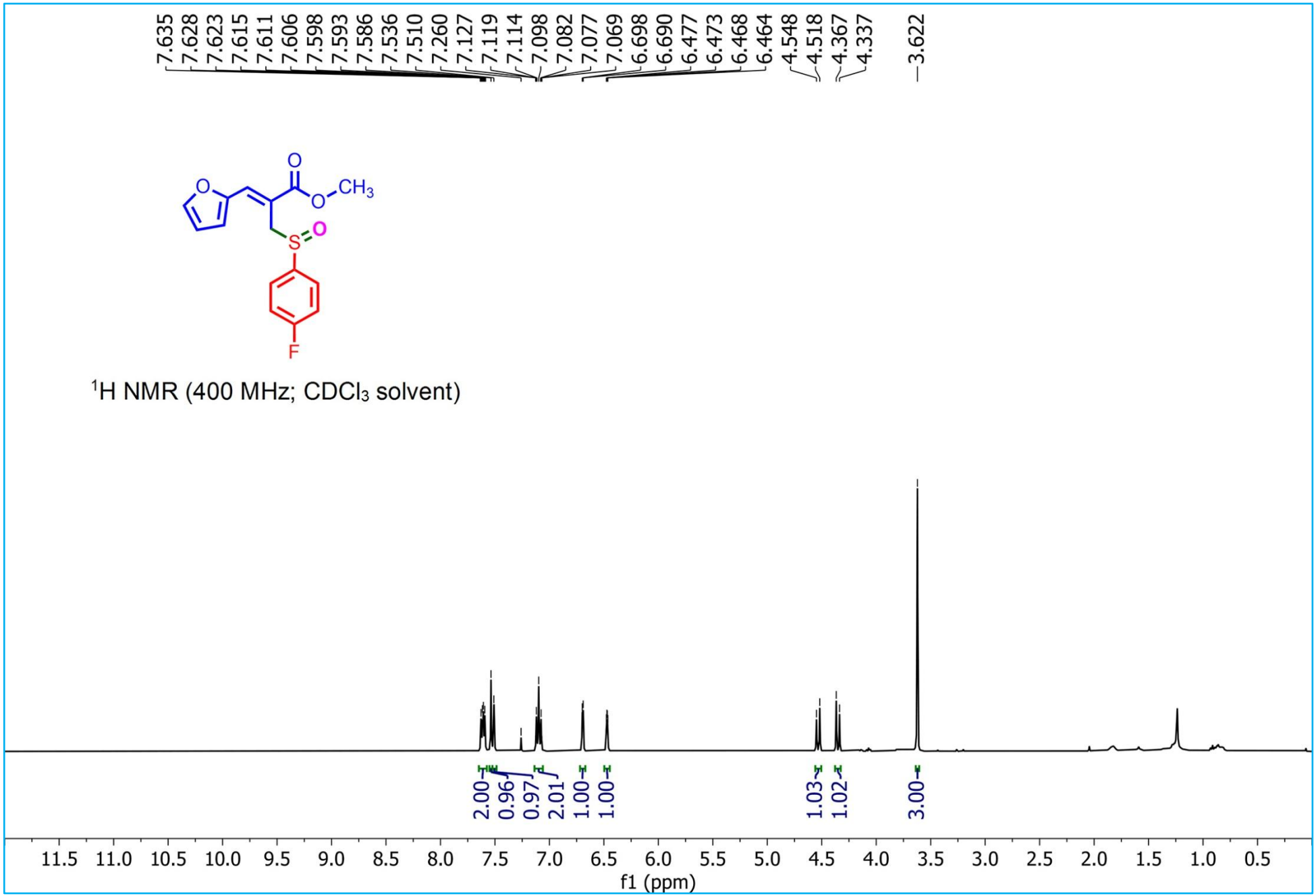


Figure S61. [1]H NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3eb**)

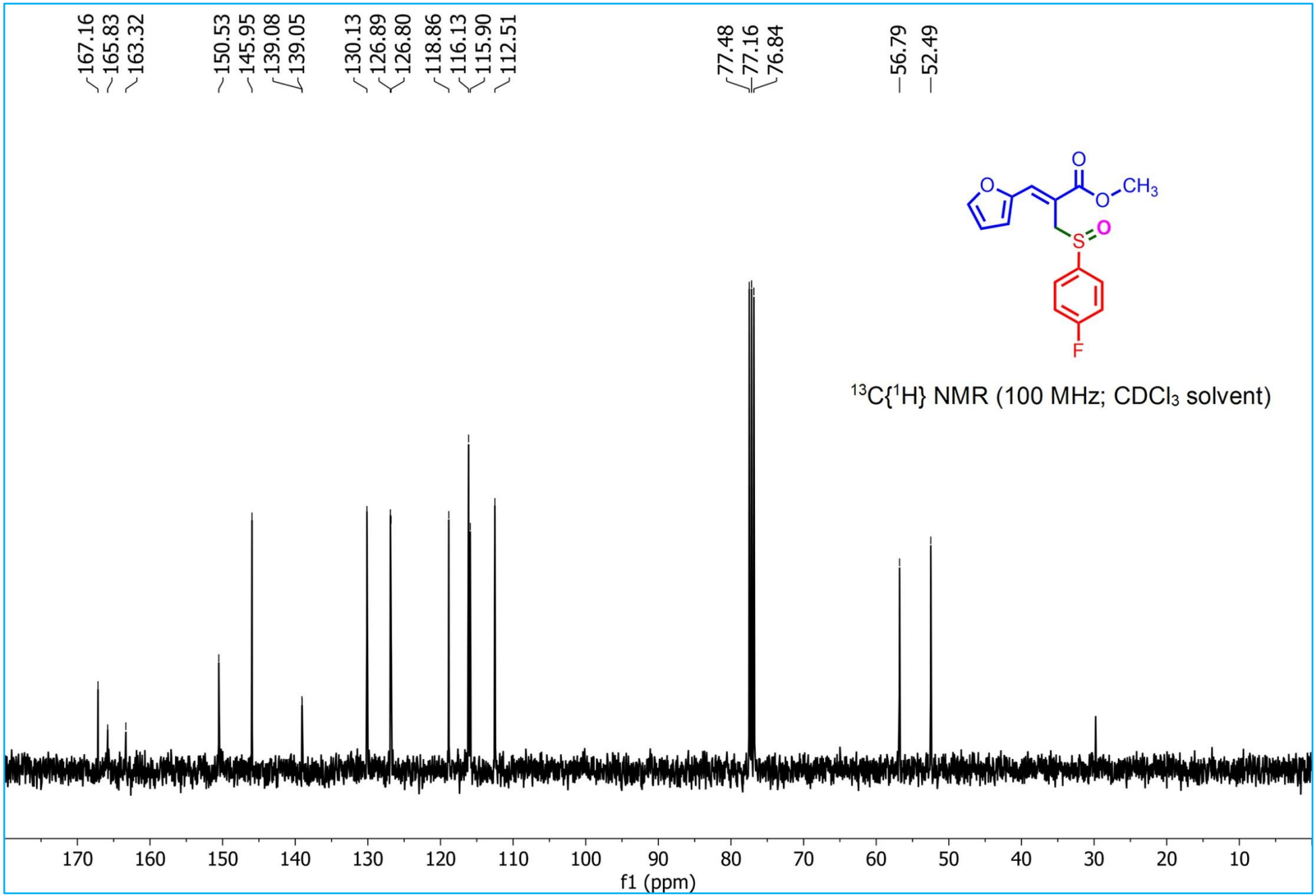


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3eb**)

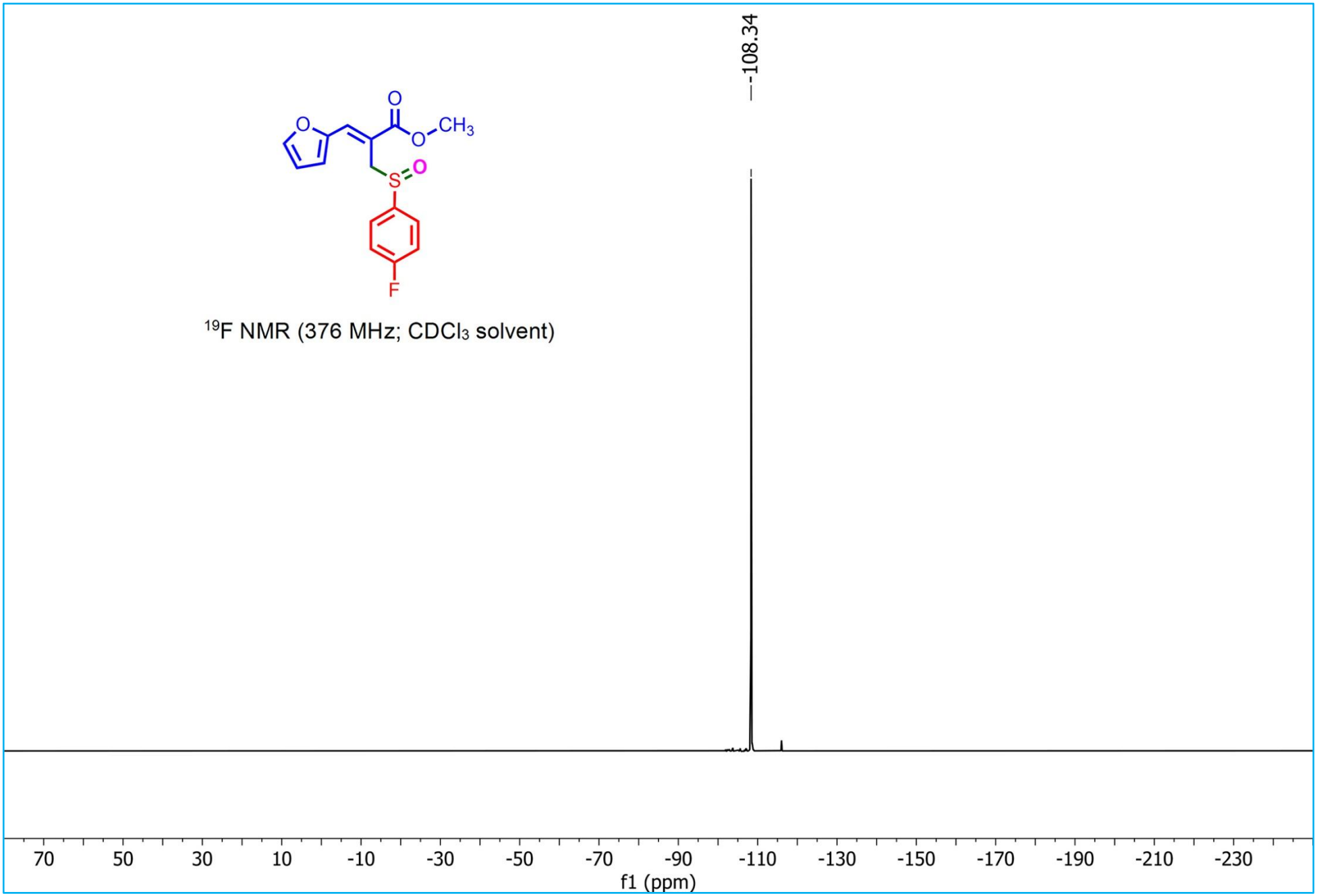


Figure S63. ^{19}F NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3eb**)

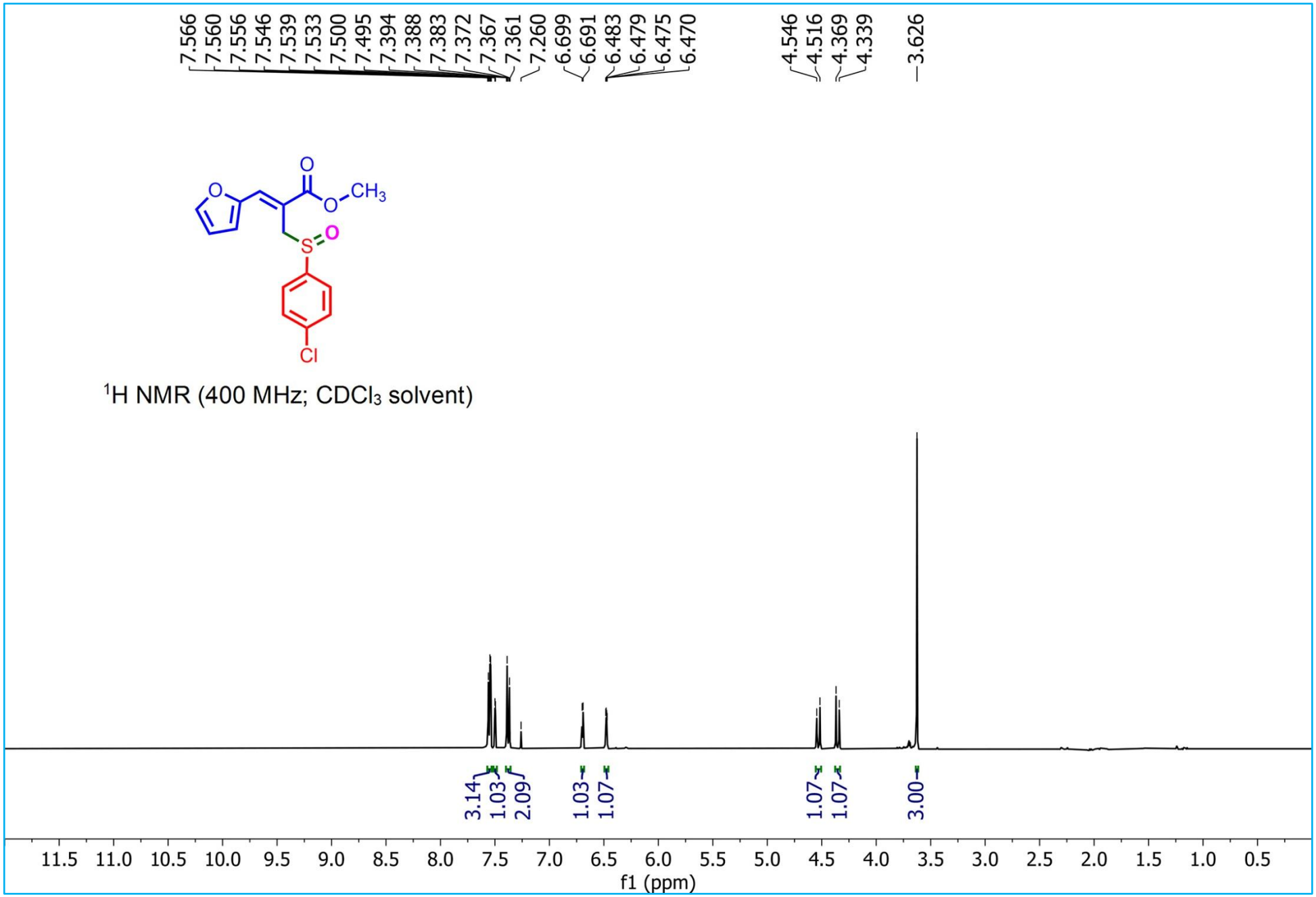


Figure S64. [1]H NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ec**)

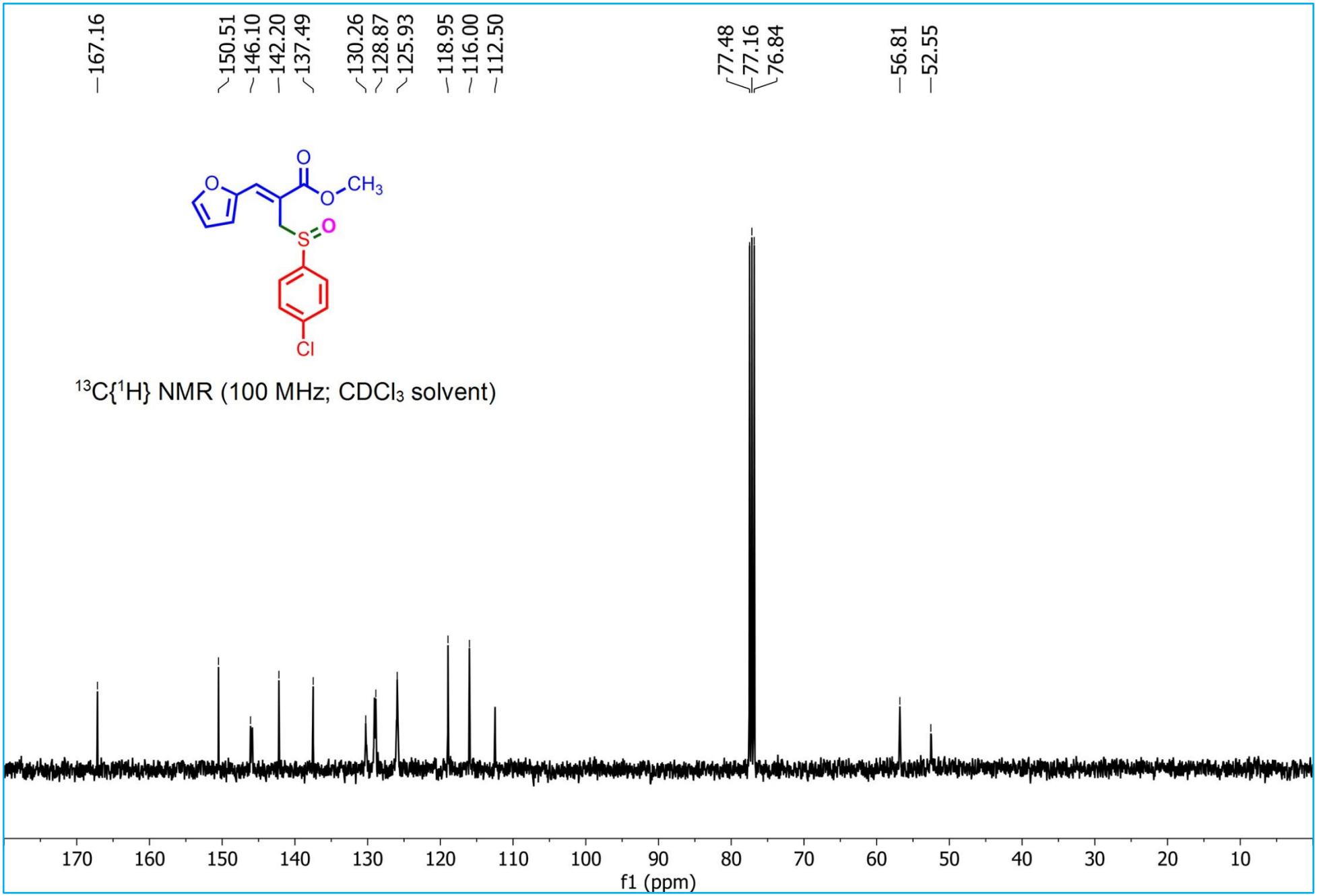


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ec**)

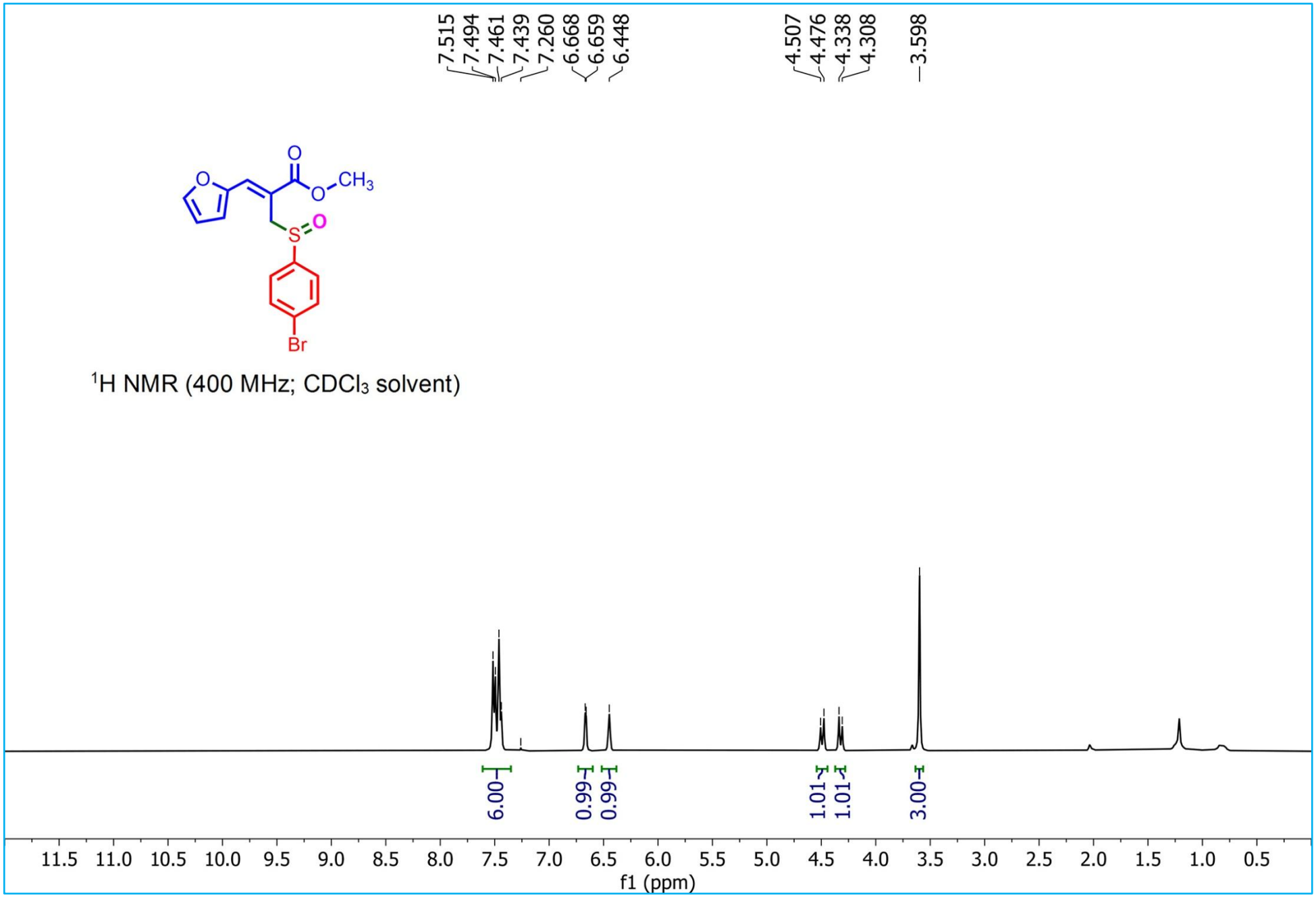


Figure S66. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ed**)

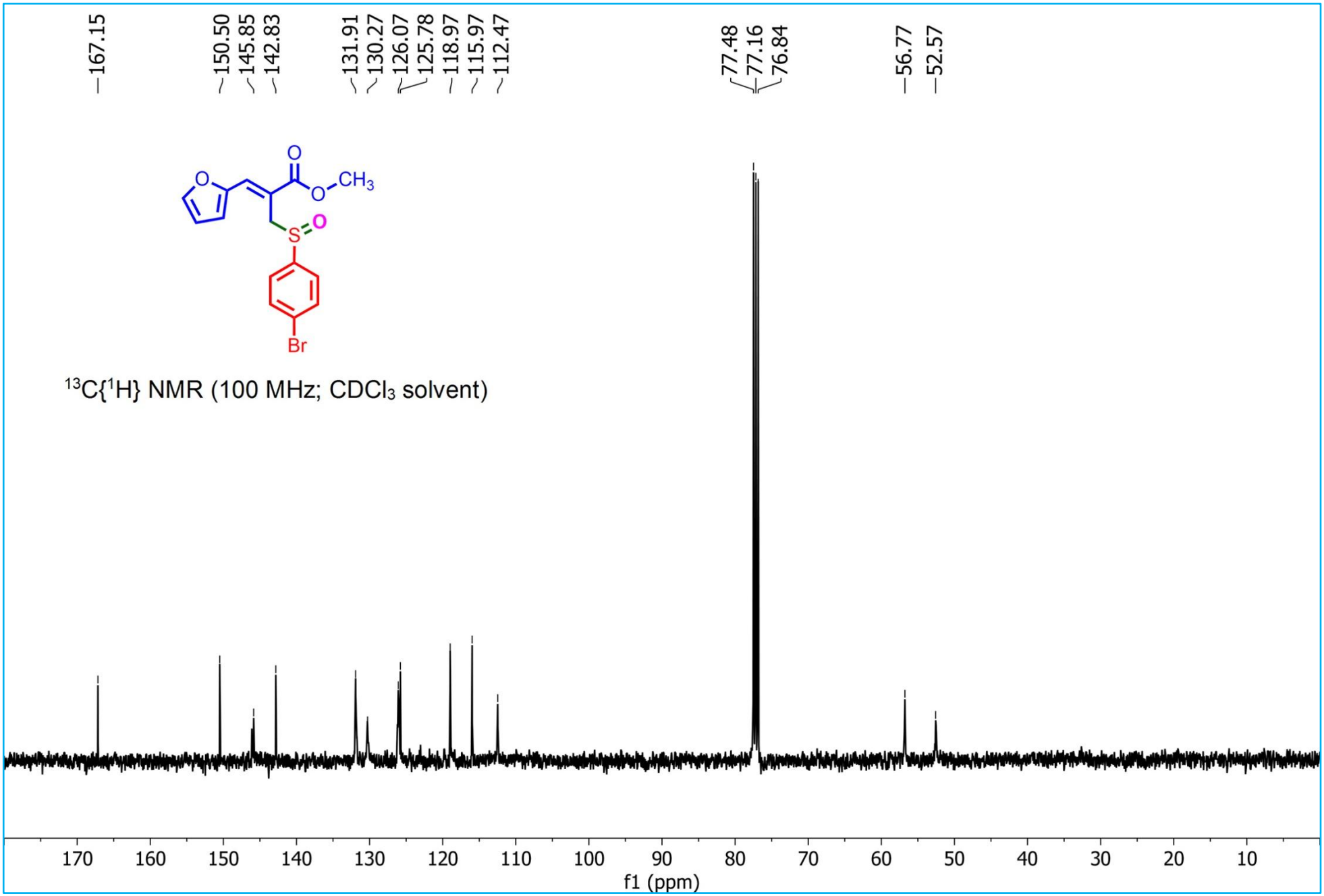


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(furan-2-yl)acrylate (**3ed**)

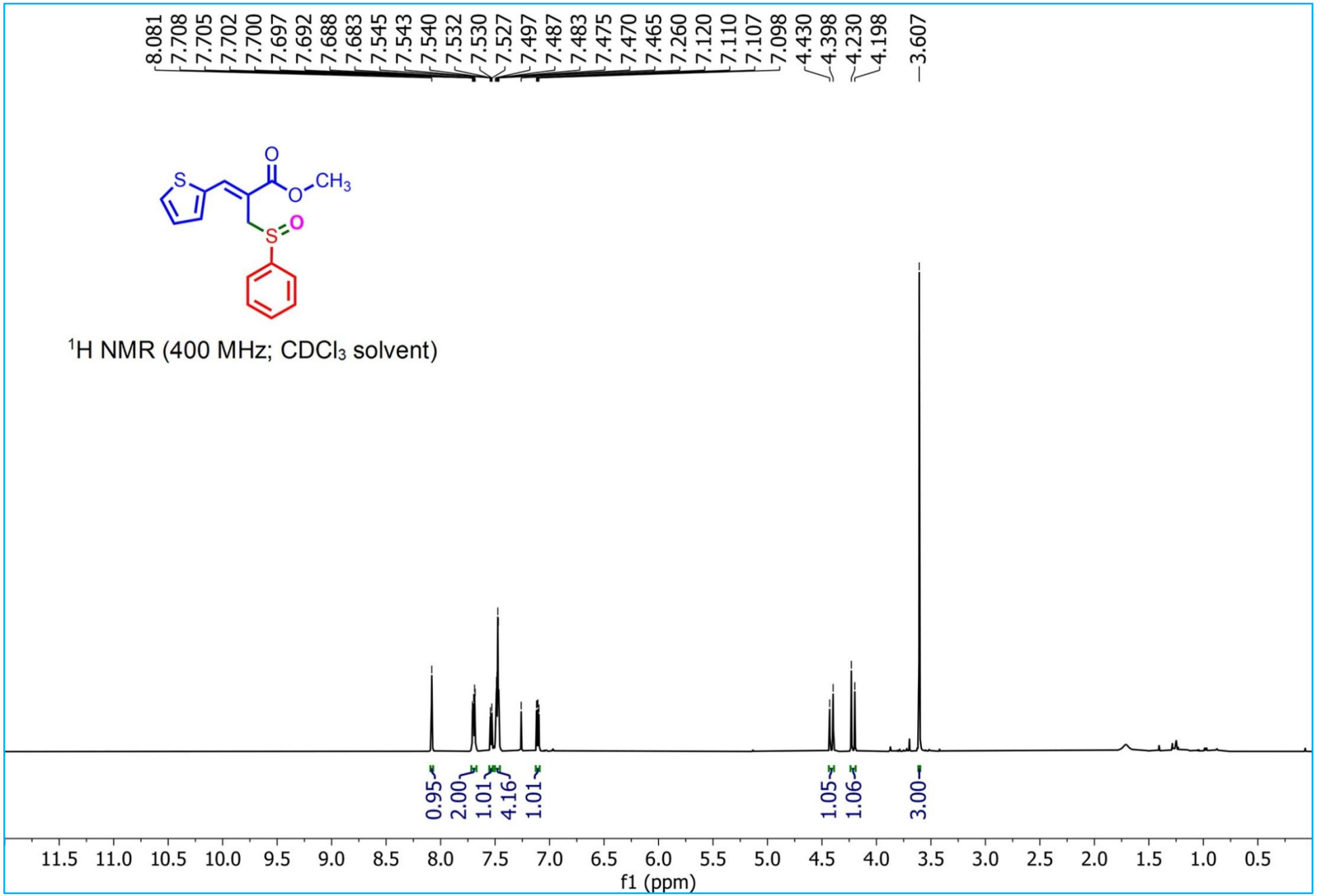


Figure S68. [1]H NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fa**)

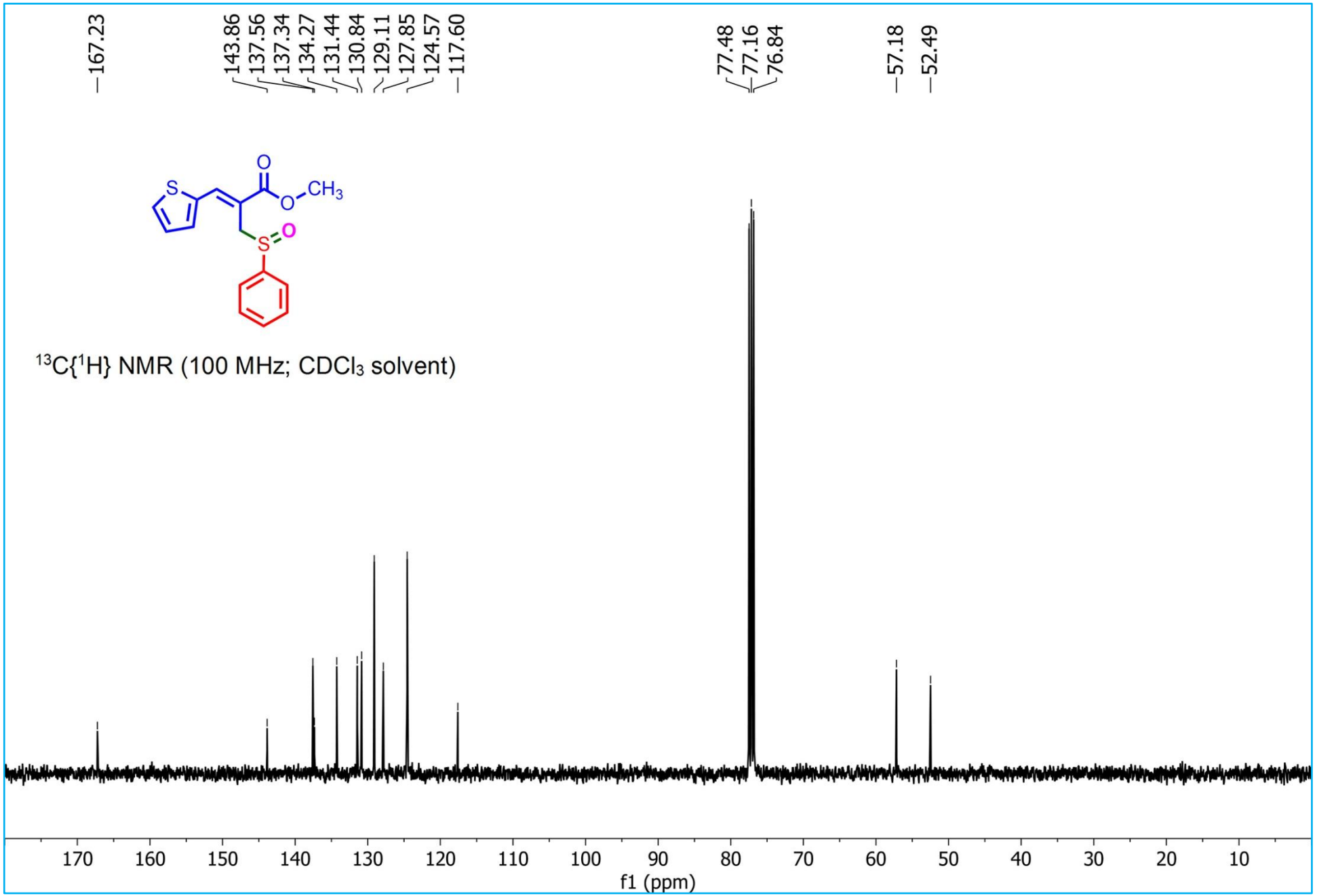


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-((phenylsulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fa**)

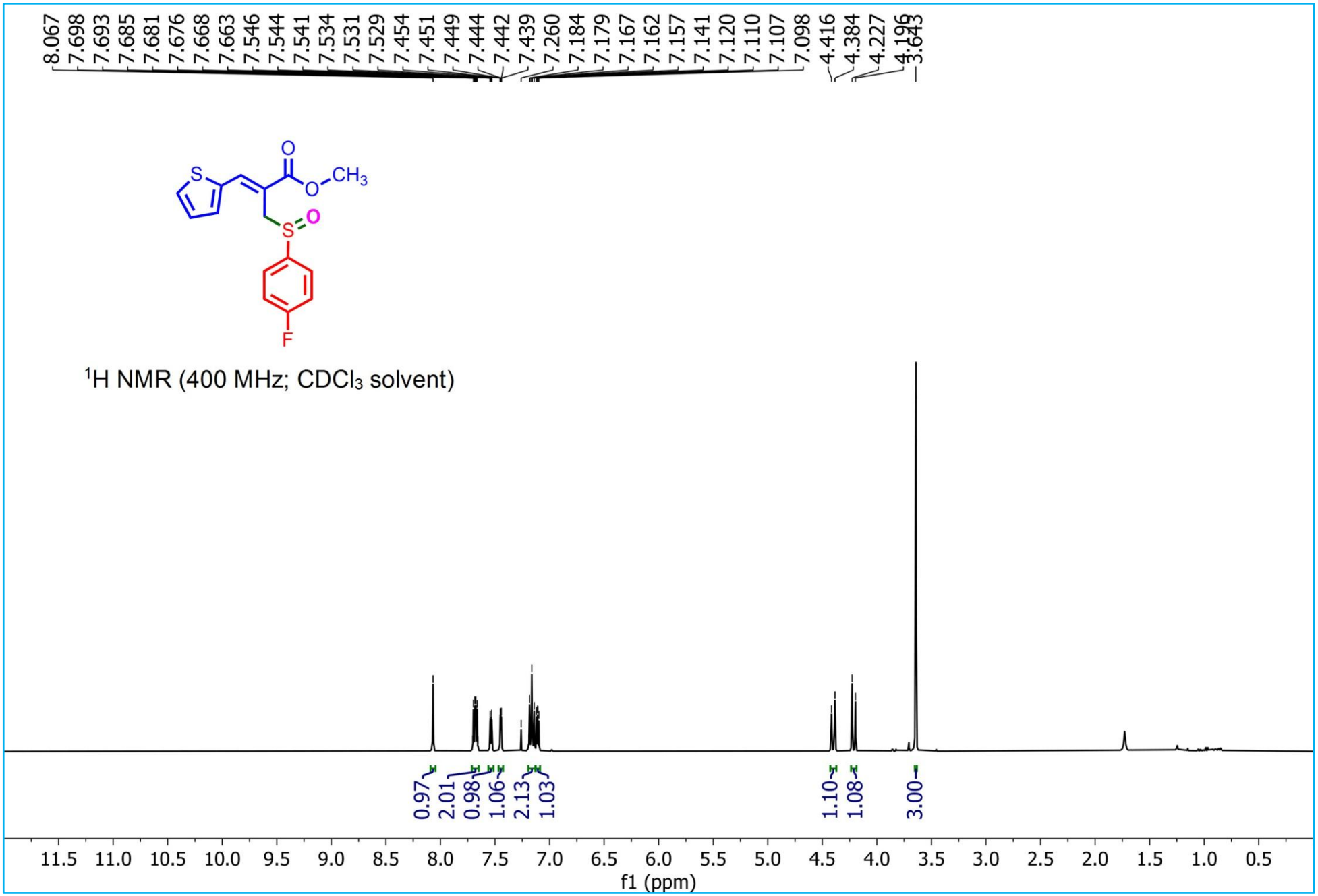


Figure S70. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fb**)

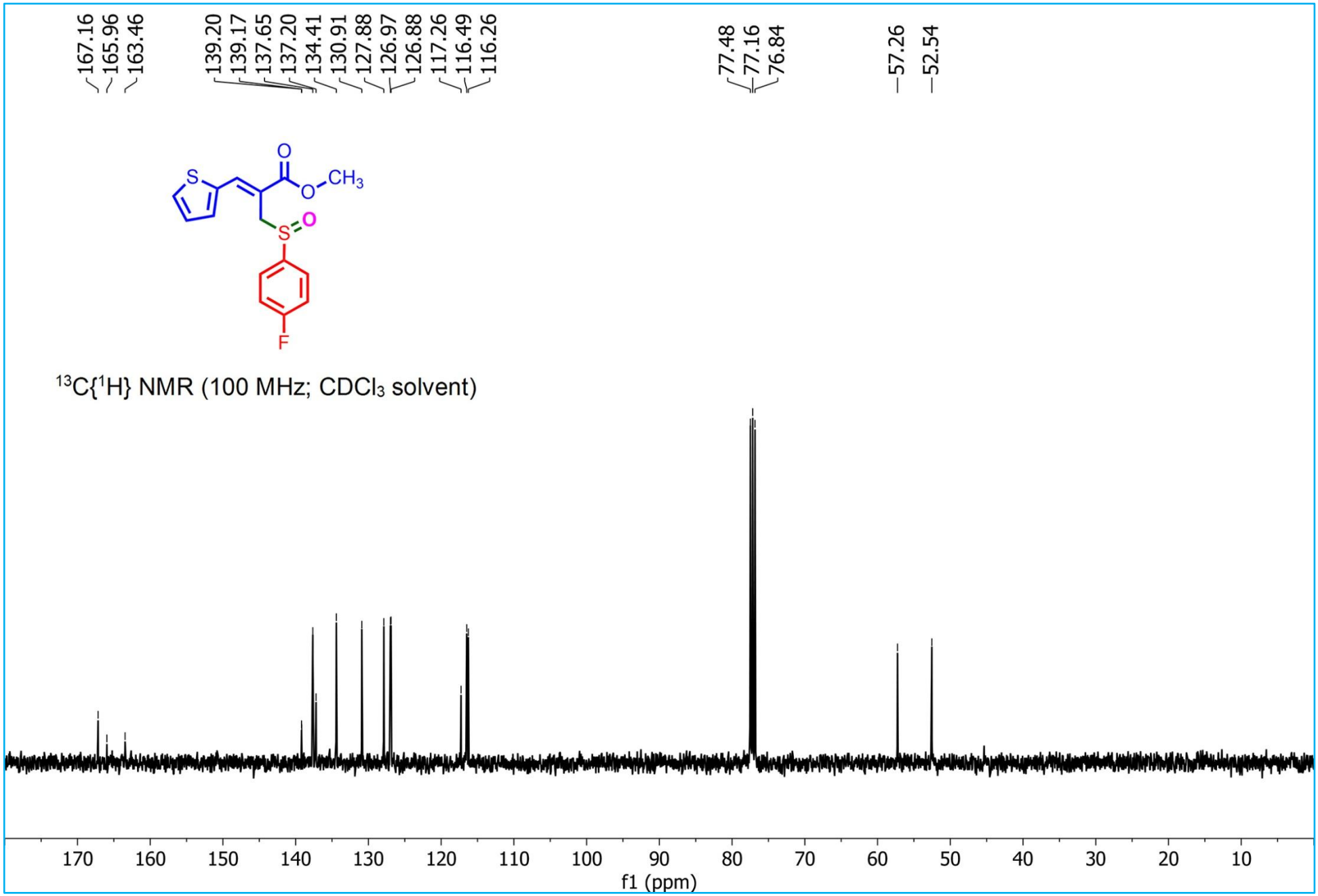


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fb**)

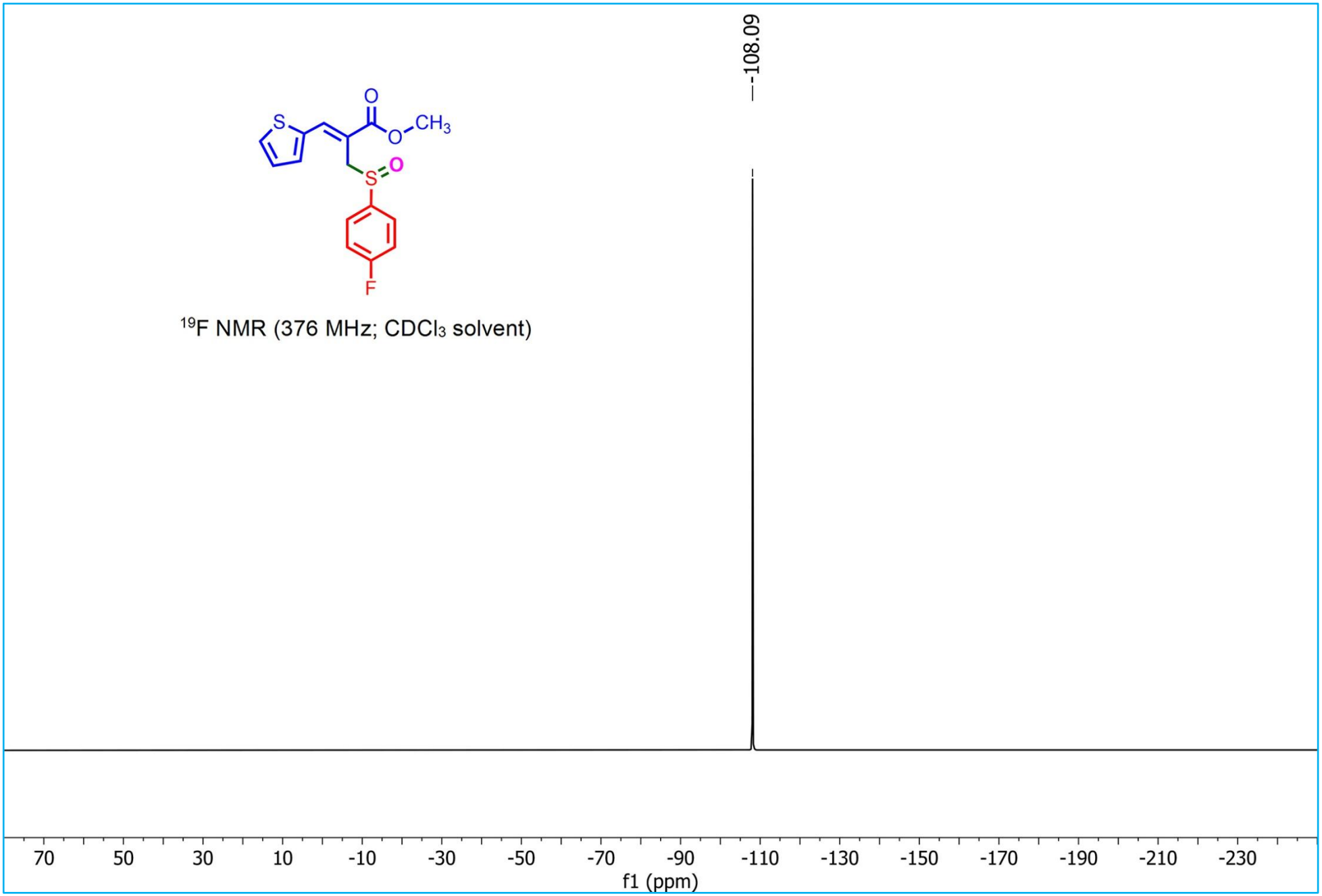


Figure S72. ^{19}F NMR spectrum of methyl (*Z*)-2-(((4-fluorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fb**)

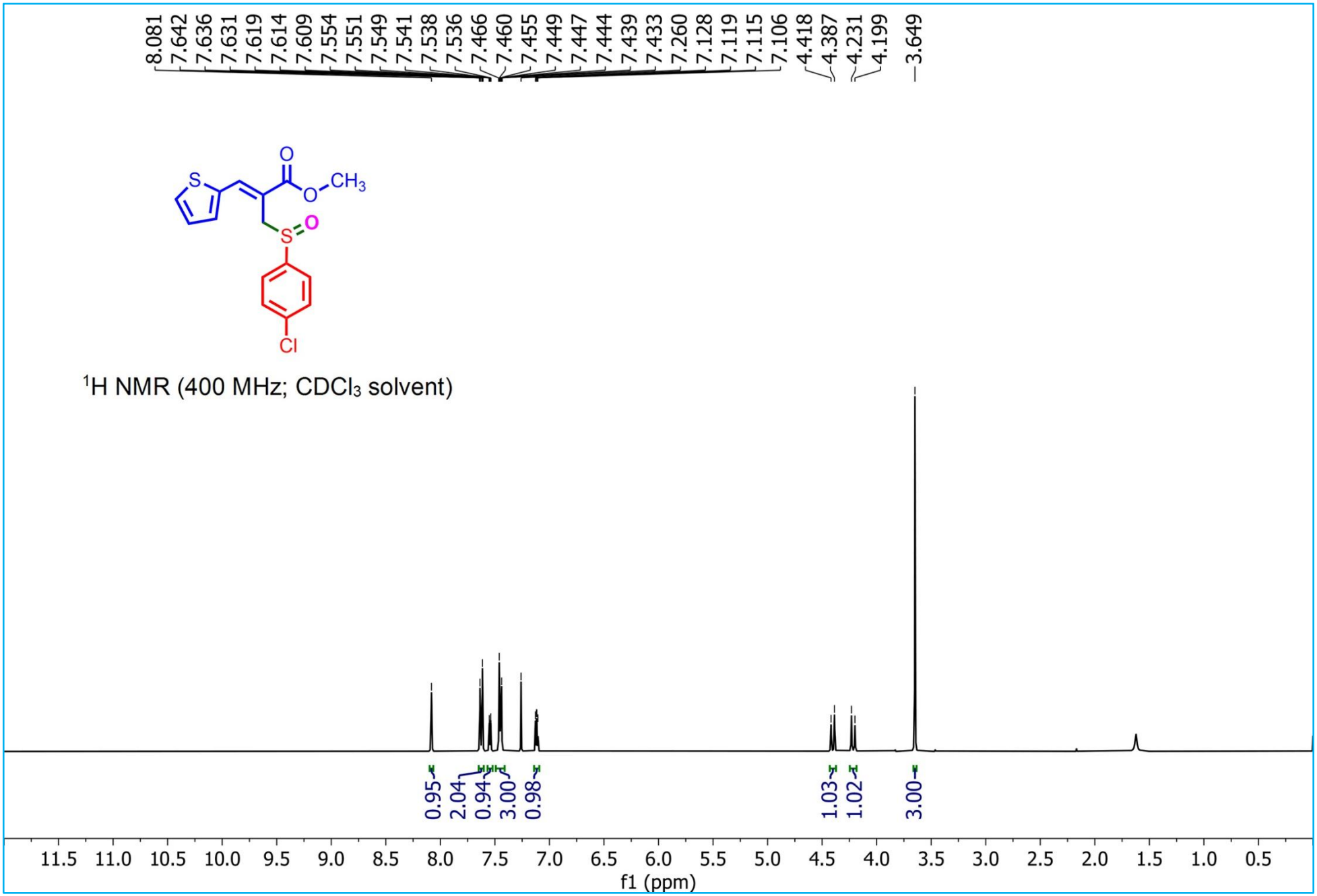


Figure S73. [1]H NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fc**)

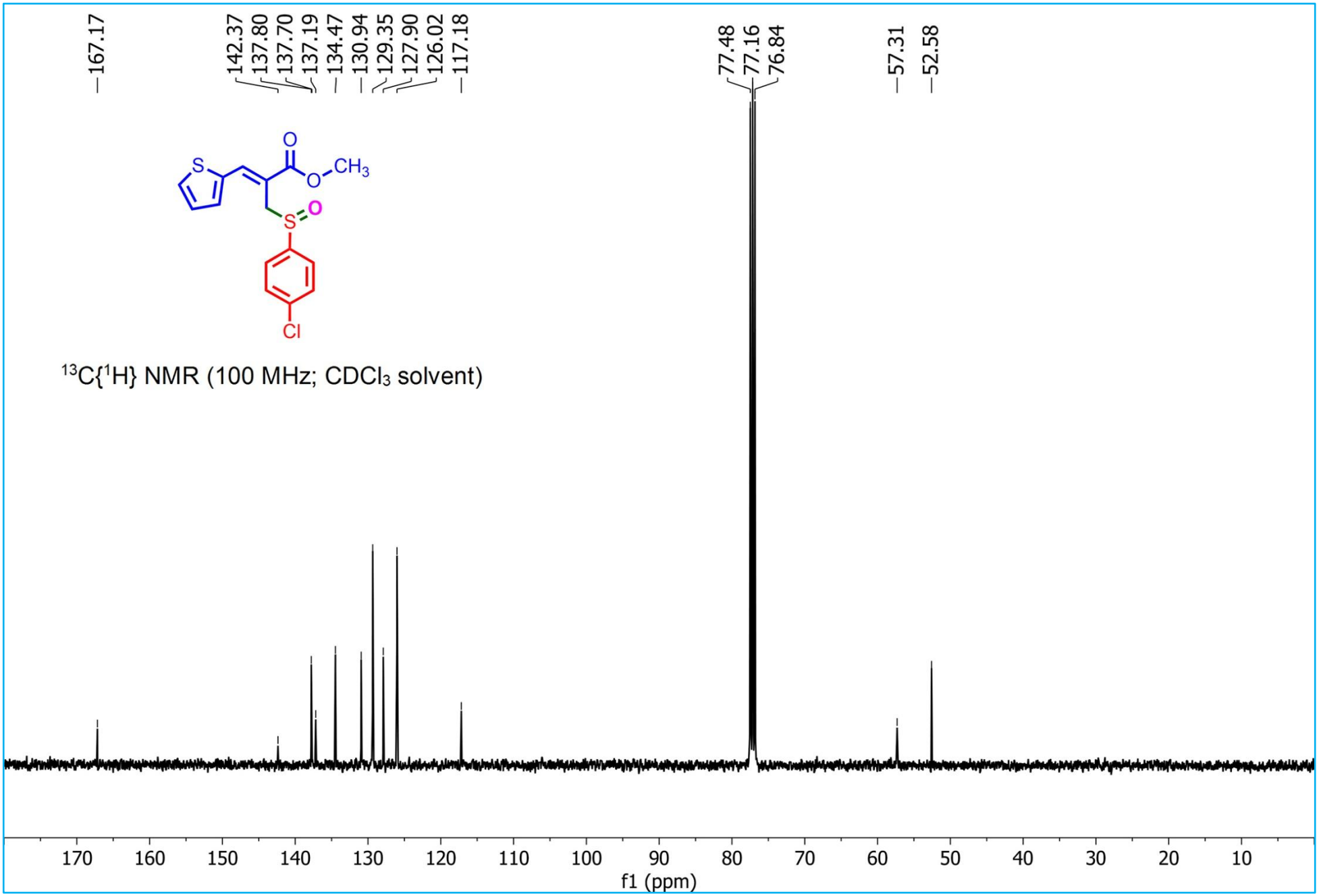


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-chlorophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fc**)

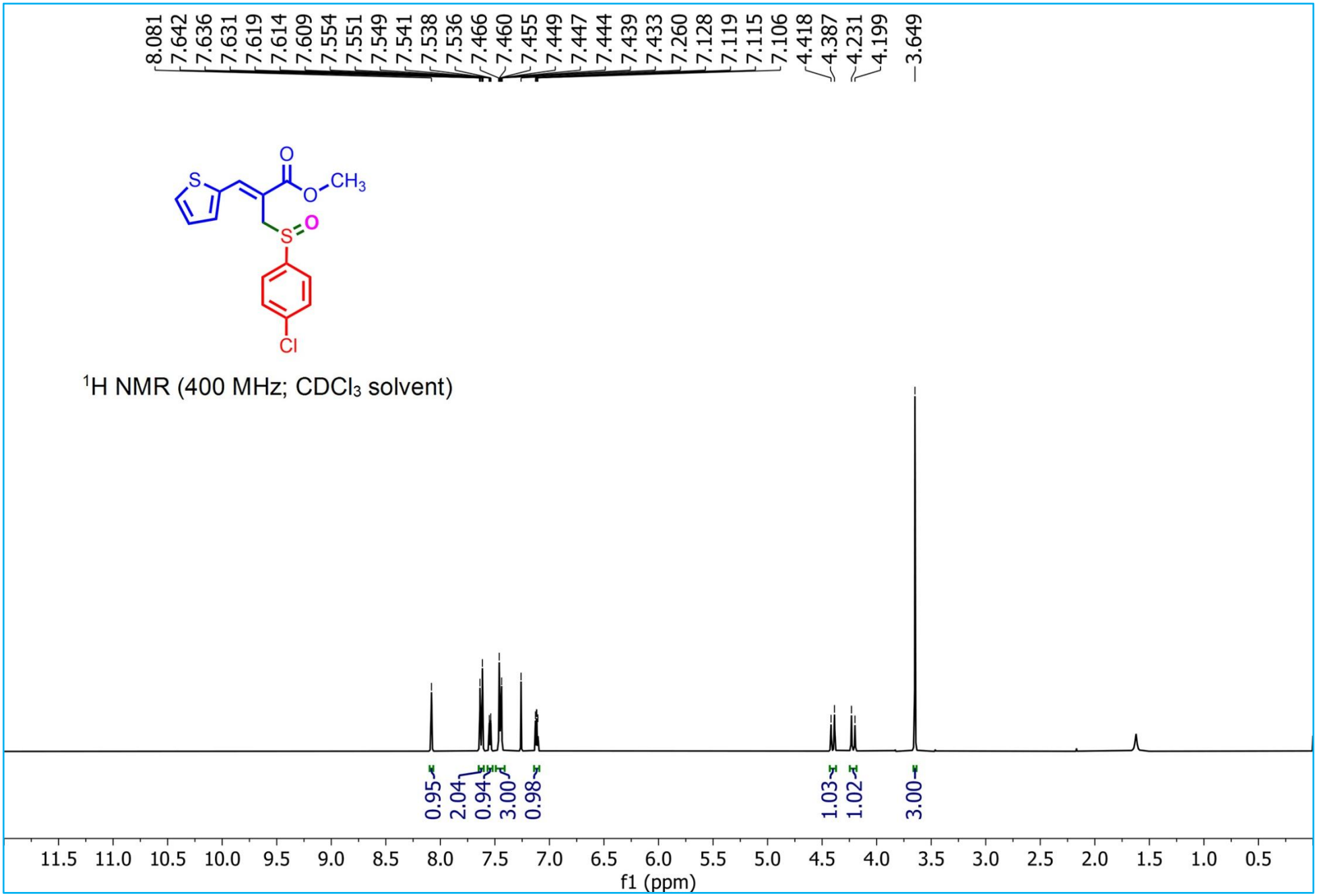


Figure S75. ^{1}H NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fd**)

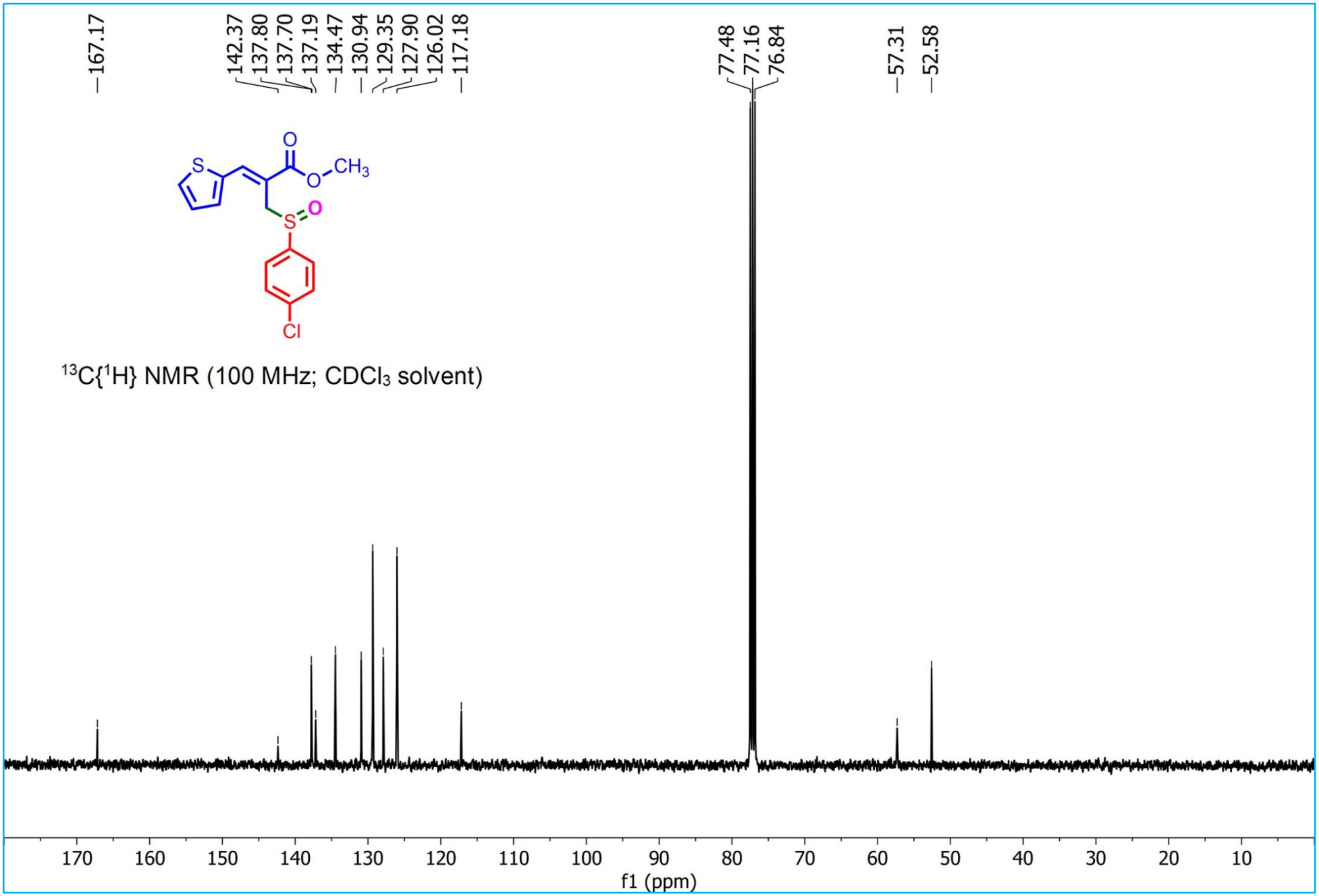


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-2-(((4-bromophenyl)sulfinyl)methyl)-3-(thiophen-2-yl)acrylate (**3fd**)

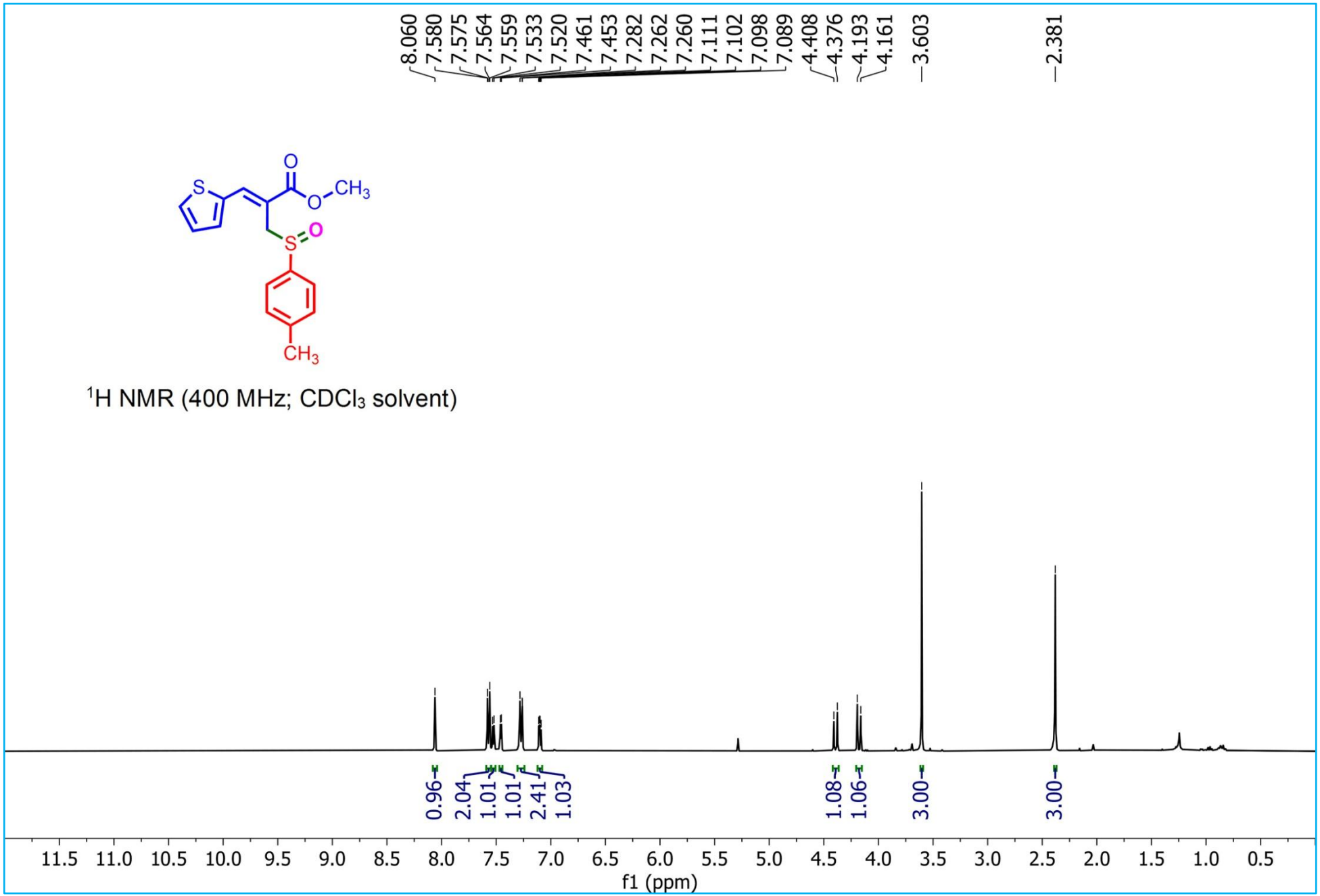


Figure S77. [1]H NMR spectrum of methyl (*Z*)-3-(thiophen-2-yl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3fi**)

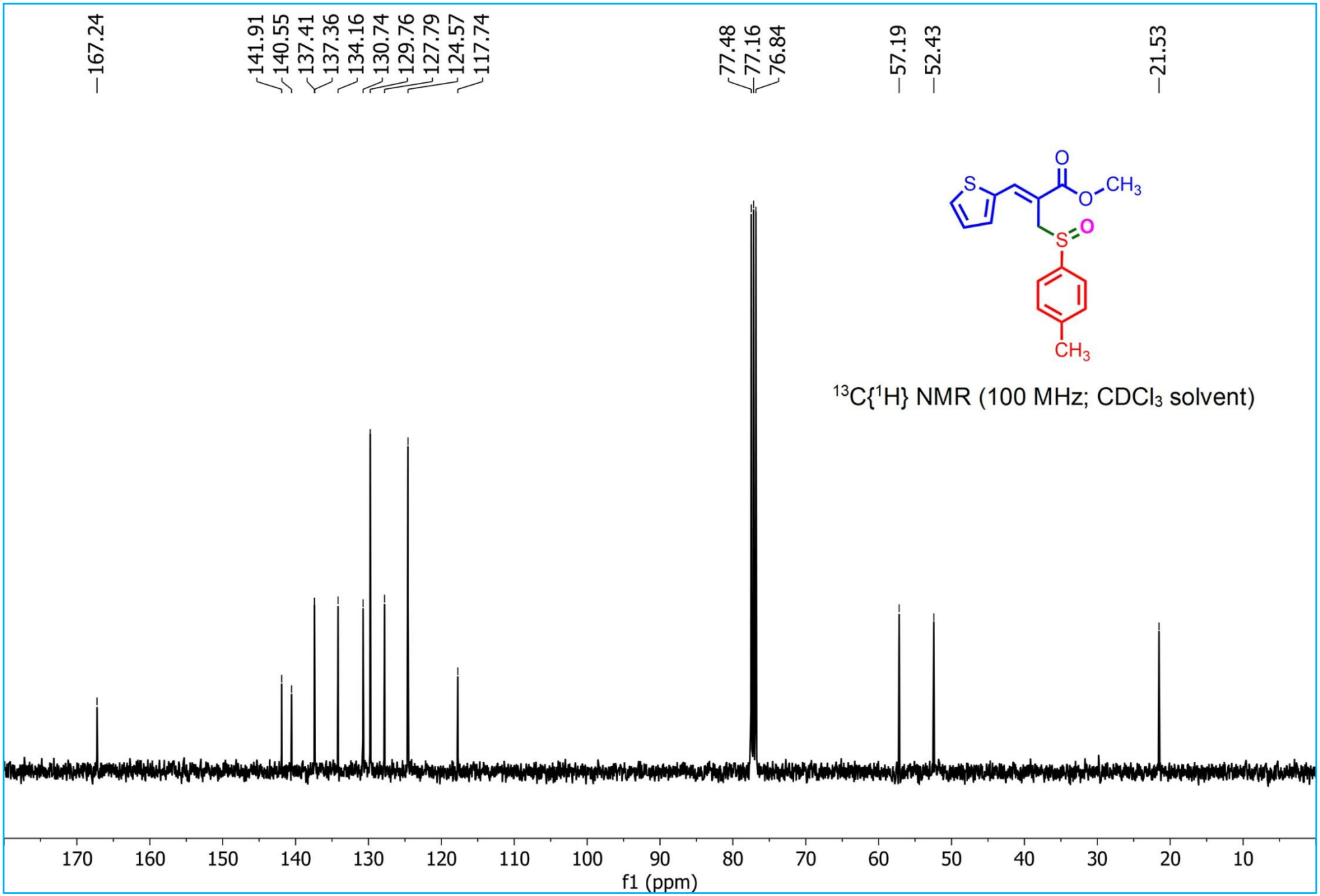


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (*Z*)-3-(thiophen-2-yl)-2-((*p*-tolylsulfinyl)methyl)acrylate (**3fi**)

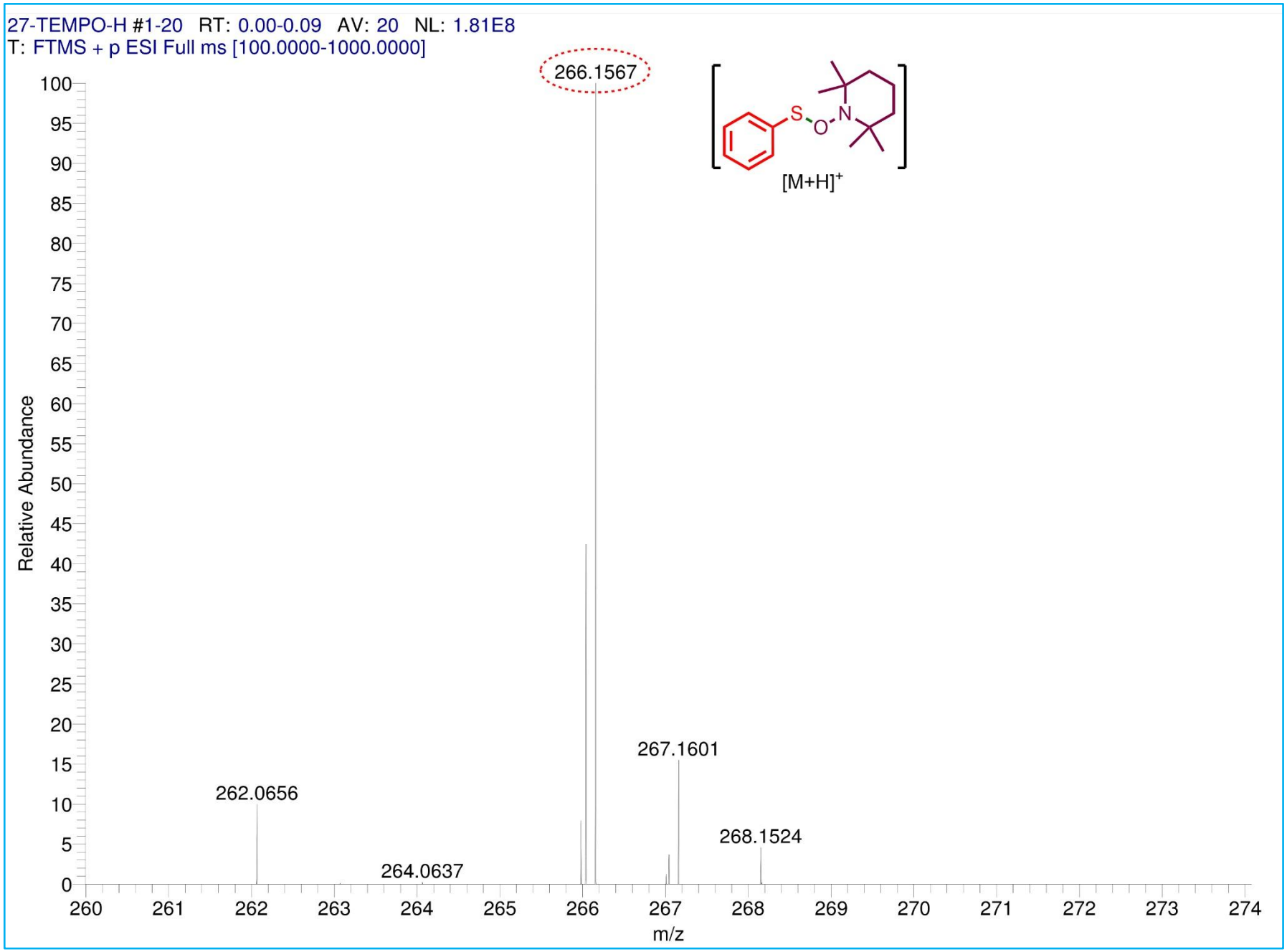


Figure S79. Mass spectrum of adduct **4**

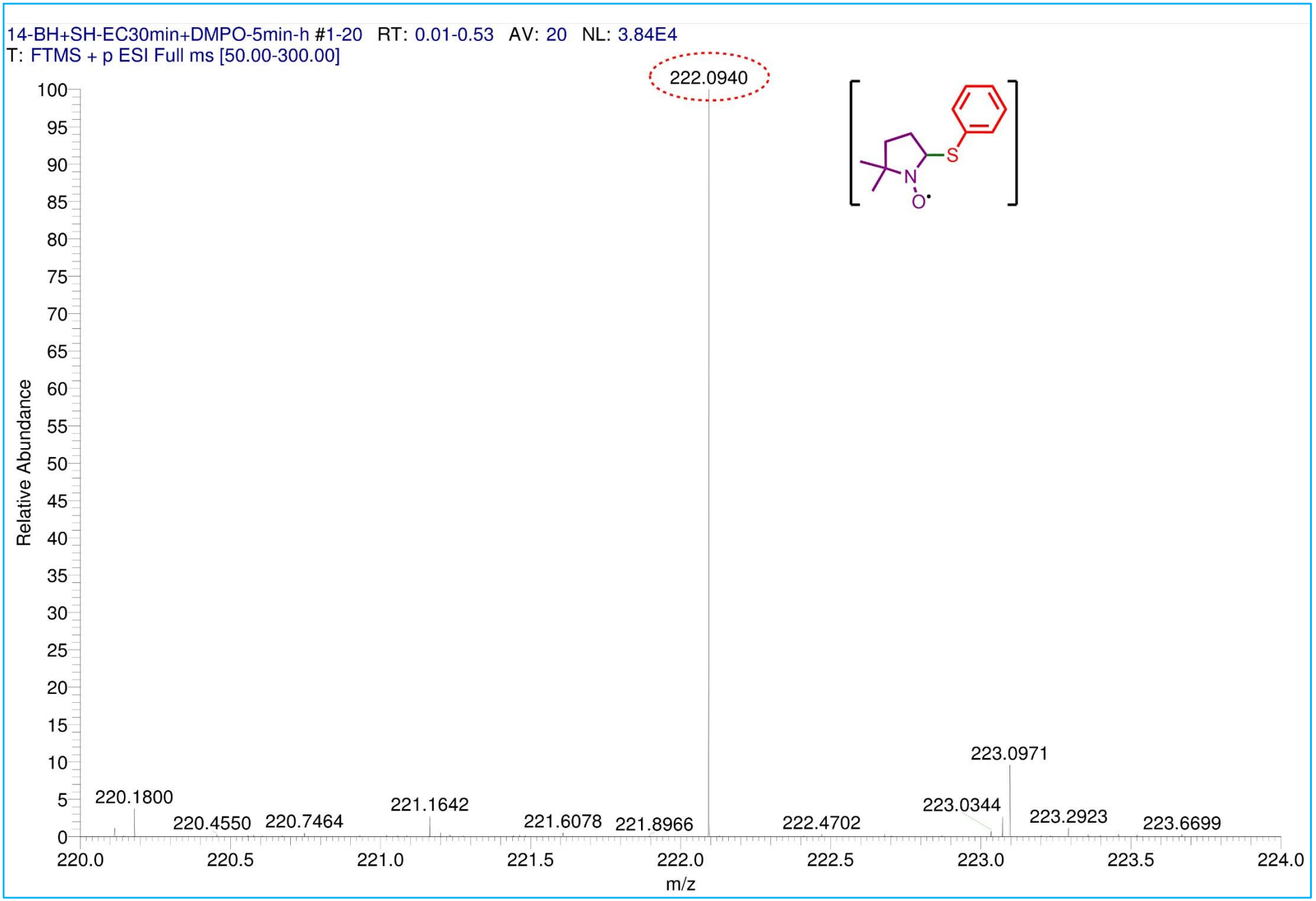


Figure S80. Mass spectrum of adduct **5**

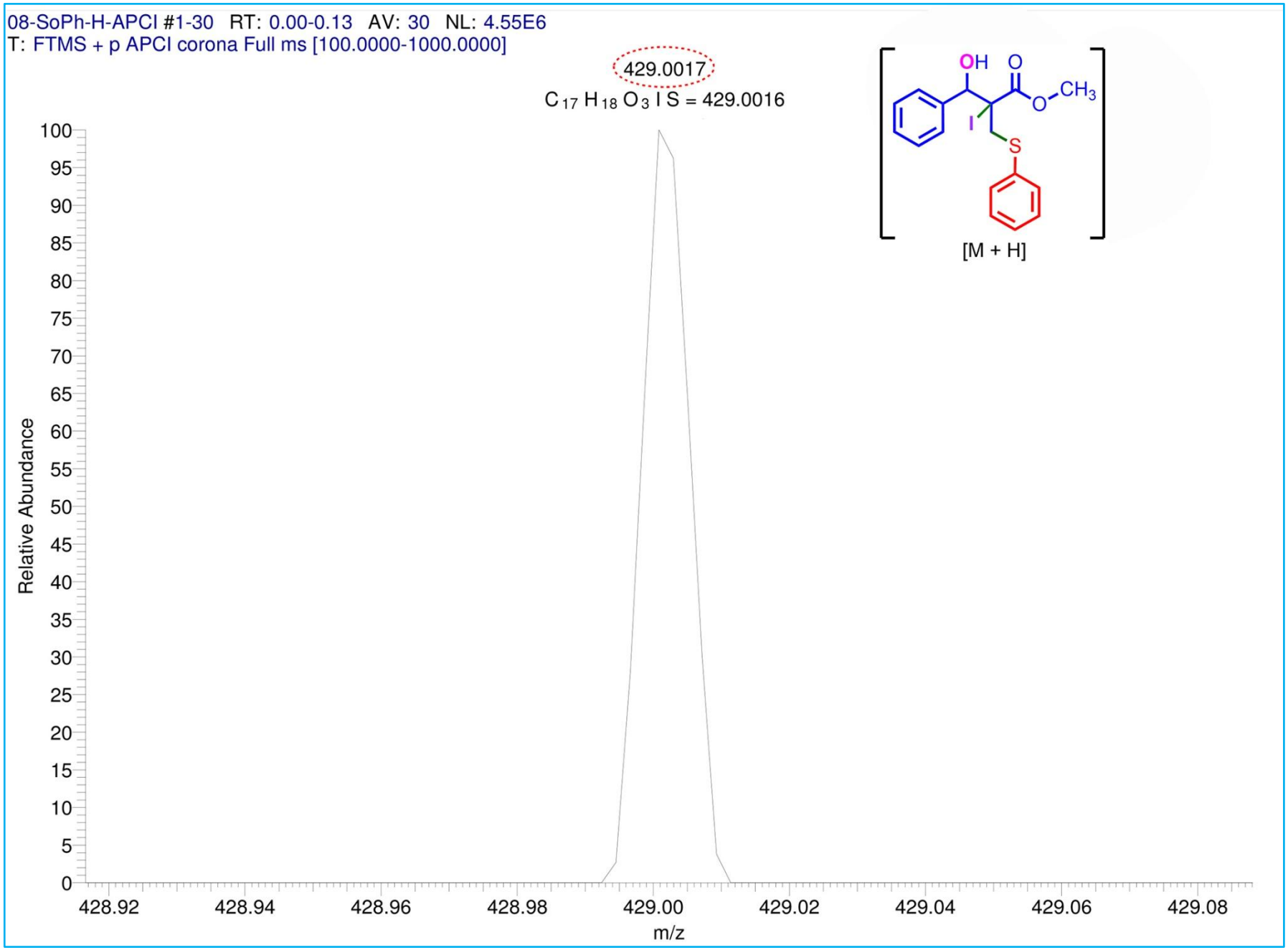


Figure S81. Mass spectrum of adduct **II-aaI**

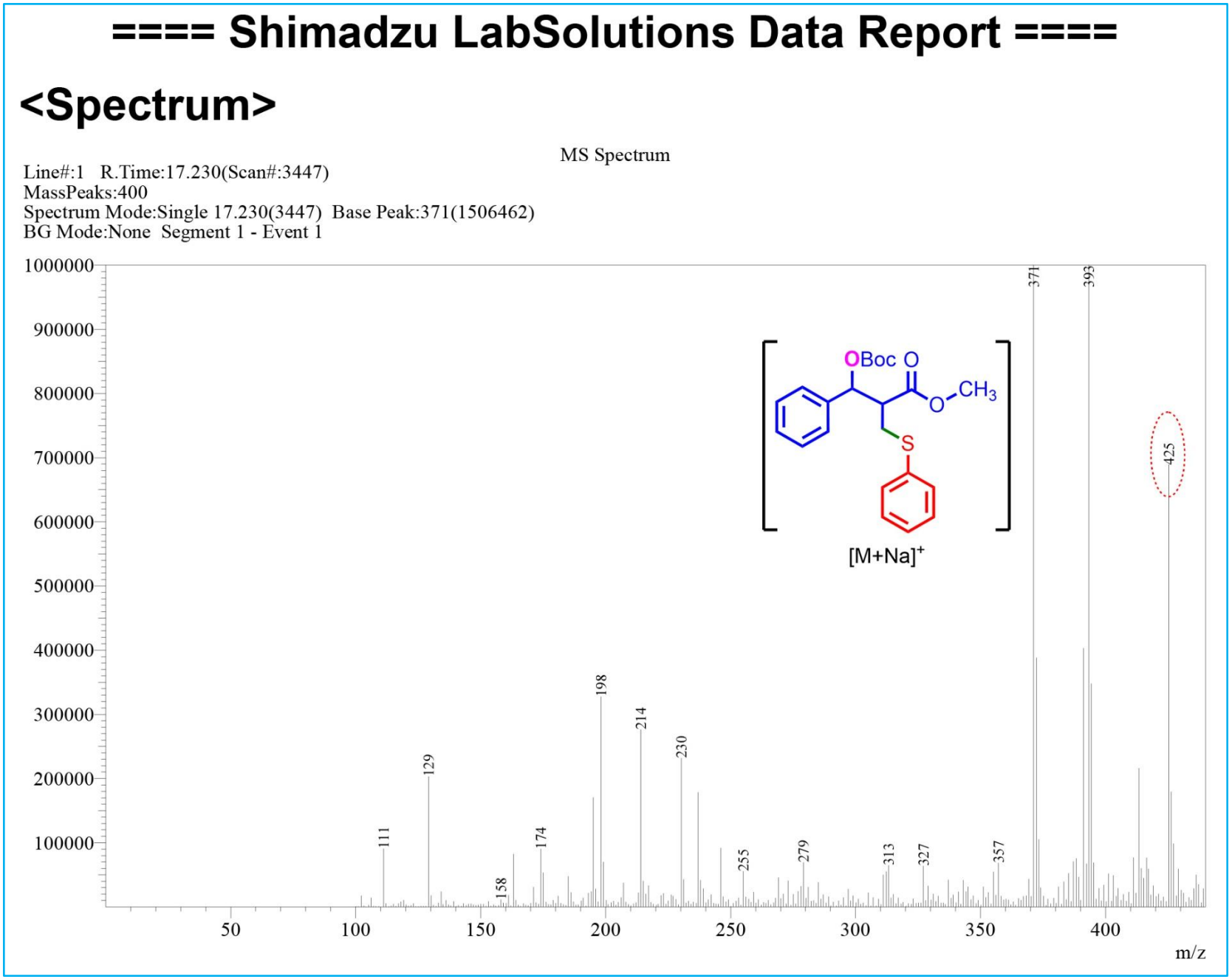


Figure S82. Mass spectrum of compound **9**

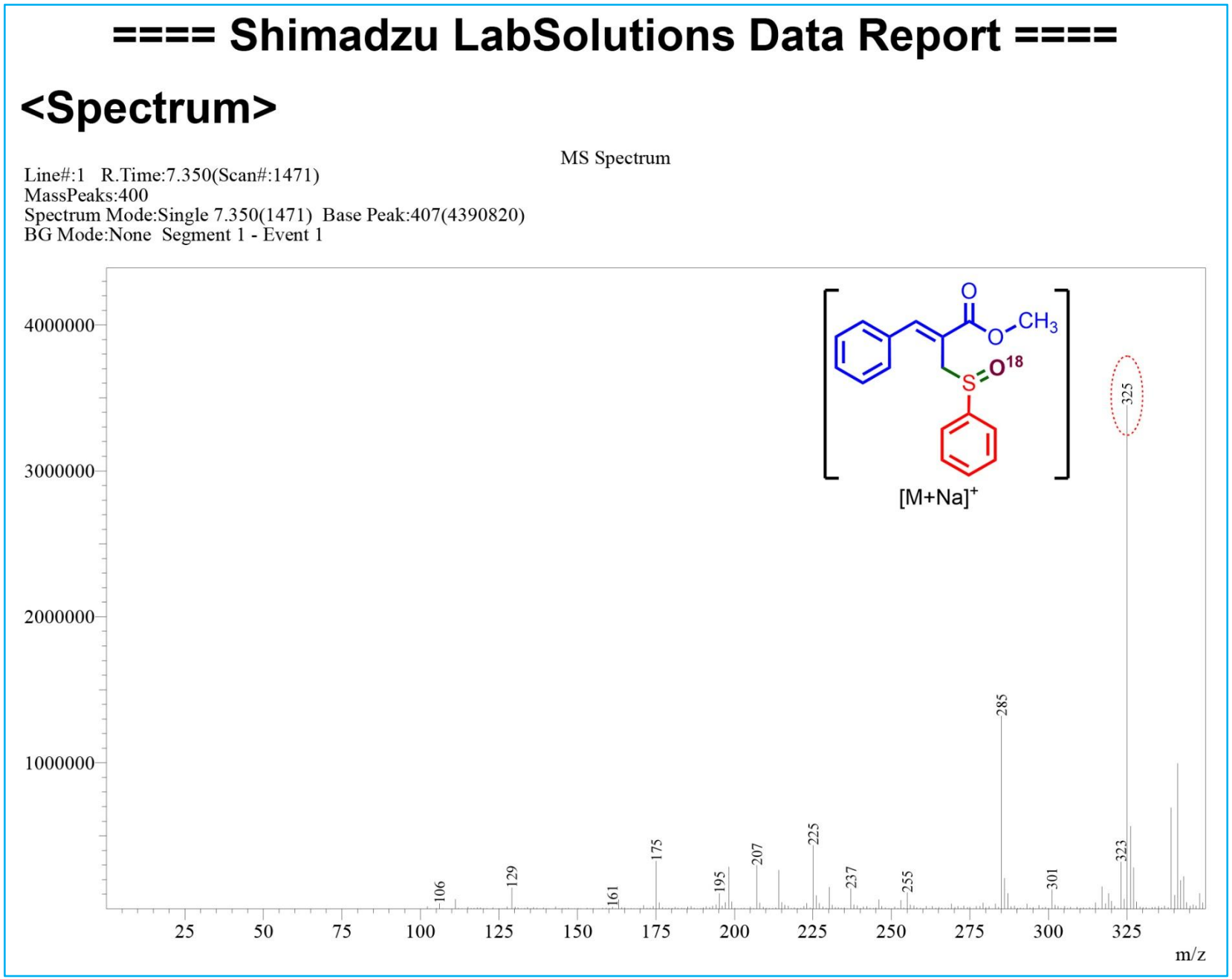


Figure S83. Mass spectrum of compound **3aa-O^{18}**

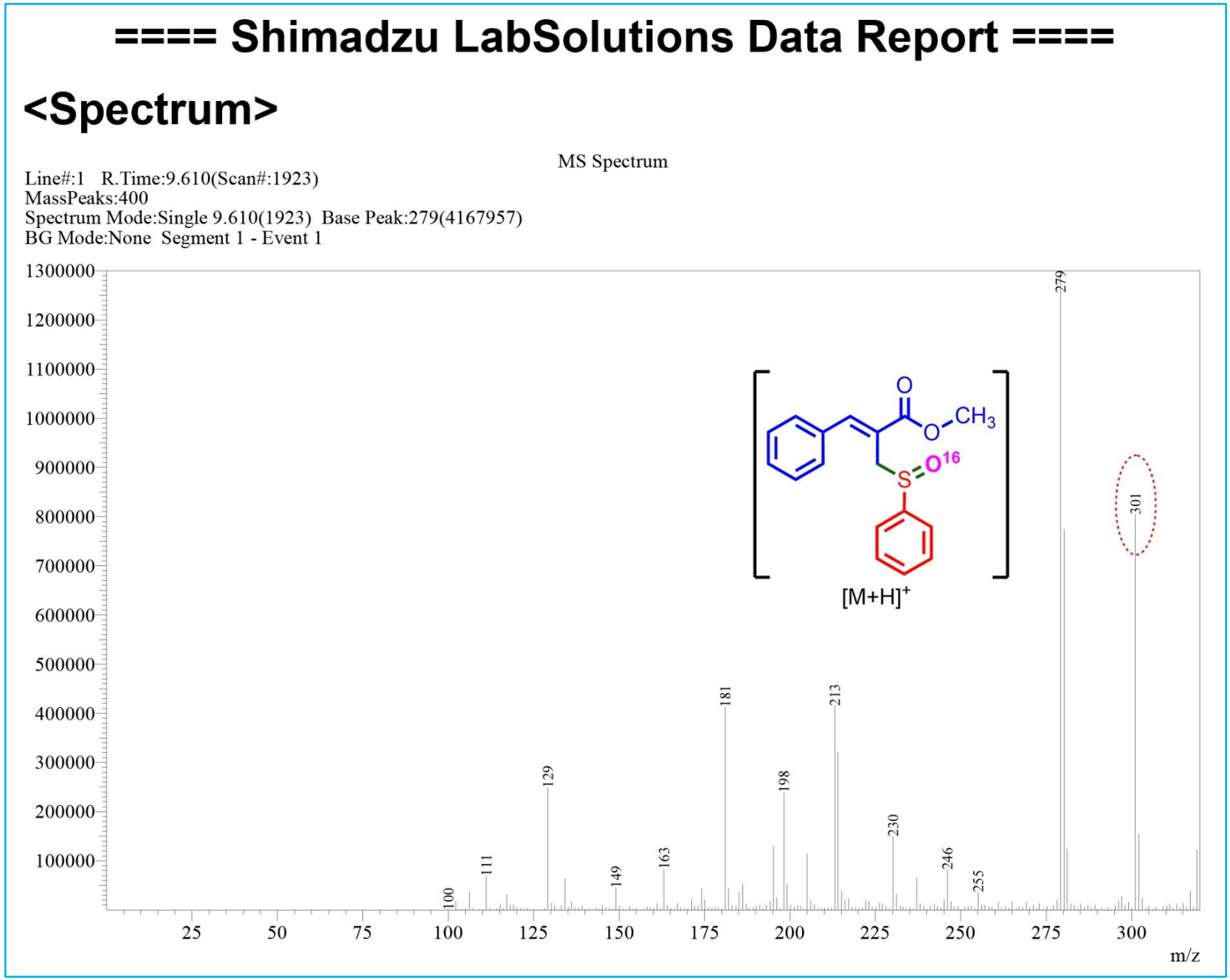


Figure S84. Mass spectrum of compound **3aa**

10. Computational details

Density functional theory (DFT) calculations were carried out using the Gaussian 09 program. Main-group atoms were described using the 6-31G (for C, H) and 6-311G** (for O, S) basis sets. For iodine, the aug-cc-pVDZ-PP relativistic pseudopotential basis set was used, with parameters obtained from the Basis Set Exchange (BSE). The corresponding pseudopotential references (Peterson et al. 2003, 2006) and database references (Pritchard et al. 2019; Feller 1996; Schuchardt 2007) are cited accordingly.[4-8] All reported free energies include thermal corrections at 298 K. Solvation effects (MeCN) were computed using the SMD implicit solvent model. All stationary points were characterized by vibrational analysis: Minima exhibit no imaginary frequencies. Transition states (TS) exhibit a single imaginary frequency, and were validated by IRC calculations connecting reactant and product minima. Thermal corrections to Gibbs free energies (ΔG) were obtained at 298 K and 1 atm.

11. Iodide-Assisted Hydrogen Relay (II′ → III–HI)

To examine the feasibility of the proton/hydrogen shift between the hydroxyl group and iodide, a relaxed potential energy surface (PES) scan was performed along the O–H···I coordinate using the modredundant opt scan protocol. The scan was carried out by incrementally elongating the O–H distance while allowing all other internal coordinates to relax.

Results: The PES shows a smooth, monotonic increase from **II′** to **III–HI**. No first-order saddle point was detected anywhere along the coordinate. The total barrier along the scan is only 6.8 kcal mol^{-1}, distributed over several small increments (1.9 → 1.7 → 1.6 → 1.4 → 1.3 kcal mol^{-1}). These results indicate that the hydrogen relay occurs on a flat PES without a resolvable transition state, consistent with an iodide-mediated H-shuttle rather than a discrete proton-transfer TS.

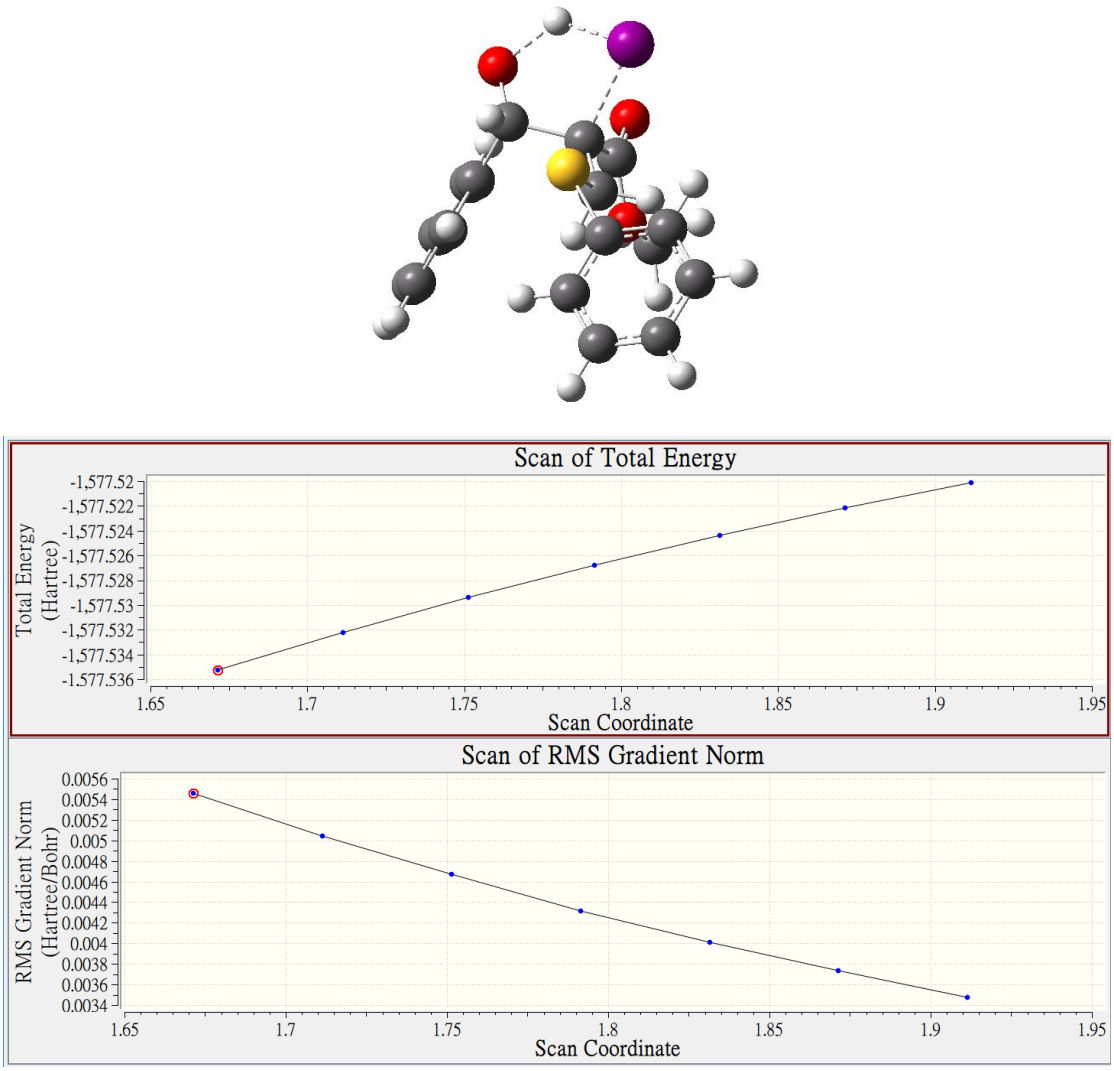
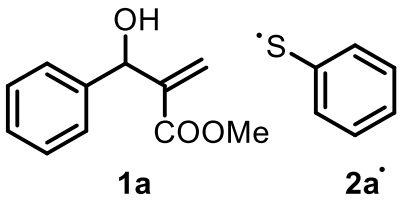


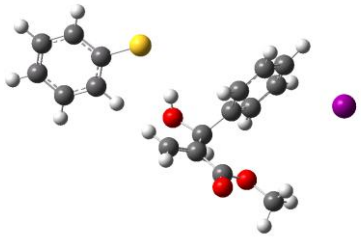
Figure S85. Relaxed potential energy surface (PES) scan for the I^--assisted hydrogen-relay step from **II′** to **III–HI**. The total energy increases smoothly with no discernible maximum, and the RMS gradient norm decreases monotonically along the scan coordinate. Together, these data confirm the absence of a resolvable first-order saddle point, consistent with a barrierless iodide-mediated H-shuttle rather than a discrete proton-transfer transition state.

12. Optimized structures and Cartesian coordinates:

Starting state (1a + 2a$^{\cdot}$)



1a **2a$^{\cdot}$**



Electronic Energy: -1577.556389 Hartree
RMS Gradient Norm: 0.000503 Hartree/Bohr

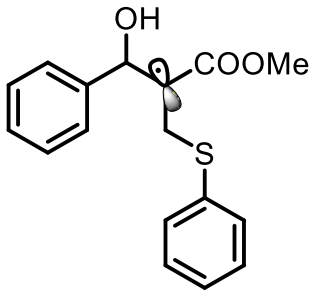
Cartesian coordinates of the optimized structure

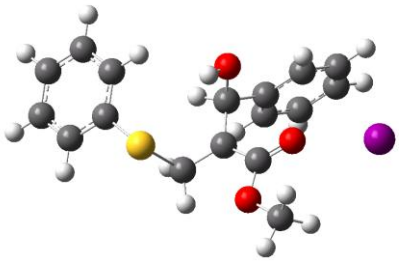
0 3

Atom	X	Y	Z
C	1.481827	-1.663823	-0.87958
C	0.641788	-0.564565	-0.695361
C	0.391464	-0.066605	0.597144
C	0.99239	-0.69508	1.705577
C	1.833578	-1.79197	1.531926
C	2.089654	-2.284722	0.23351
H	1.669327	-2.044141	-1.878354
H	0.187105	-0.082008	-1.555741
H	0.794964	-0.314948	2.703405
H	2.293141	-2.271048	2.391003
H	2.686293	-3.180302	0.099287
C	-0.585148	1.085731	0.829251
C	-0.546997	2.151113	-0.26146
H	-0.328951	1.560549	1.781703
C	0.712658	2.938746	-0.444704
O	0.927448	3.732416	-1.345862
O	1.6144	2.674974	0.544971
C	2.891293	3.37058	0.44065
H	2.738813	4.451037	0.498209

H	3.480184	3.011095	1.283286
H	3.378249	3.123656	-0.505062
S	-3.689571	-1.500068	-1.046576
C	-5.190268	-0.947018	-0.369434
C	-6.428719	-1.481787	-0.837034
C	-5.220417	0.041917	0.657944
C	-7.639363	-1.044972	-0.301715
H	-6.406238	-2.234628	-1.616923
C	-6.439569	0.469352	1.185018
H	-4.284116	0.453212	1.025068
C	-7.649836	-0.068823	0.710011
H	-8.576388	-1.458267	-0.664752
H	-6.453288	1.22127	1.967074
H	-8.596342	0.269412	1.125953
H	-2.125458	-0.091729	0.337807
O	-1.918189	0.561748	1.031824
I	4.891165	-0.9562	-0.14592
C	-1.597563	2.445271	-1.041677
H	-1.521239	3.221149	-1.79604
H	-2.544545	1.932198	-0.924799

Int. I





Electronic Energy: -1577.547038 Hartree
RMS Gradient Norm: 0.000006 Hartree/Bohr
Dipole Moment: 5.730235 Debye

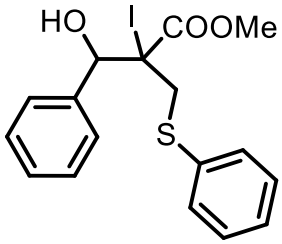
Cartesian coordinates of the optimized structure

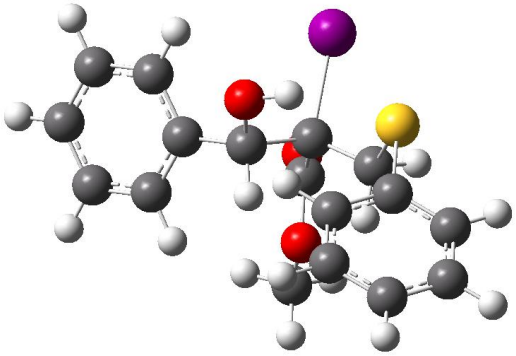
0 3

Atom	X	Y	Z
C	1.7718	-3.54982	-0.270455
C	1.00658	-2.43867	-0.641577
C	-0.093989	-2.05463	0.136226
C	-0.420958	-2.79645	1.28299
C	0.349825	-3.90125	1.65759
C	1.45027	-4.28061	0.879816
H	2.62146	-3.84164	-0.879459
H	1.25176	-1.86536	-1.52556
H	-1.28374	-2.51444	1.88192
H	0.088271	-4.46666	2.54663
H	2.04899	-5.1398	1.16545
C	-0.956468	-0.854321	-0.237461
C	-0.702791	0.375679	0.614536
H	-2.00594	-1.13684	-0.070693
C	-1.85176	1.02468	1.28536
H	-2.56417	0.308252	1.70018
H	-1.55463	1.74336	2.04563
C	0.610063	1.01734	0.609615
O	1.60103	0.574787	0.021874

O	0.622988	2.1774	1.33412
C	1.88511	2.90155	1.38695
H	2.21245	3.17231	0.380964
H	1.67375	3.79177	1.97792
H	2.65516	2.29226	1.8649
S	-2.84121	2.01972	-0.024453
C	-4.29629	0.989776	-0.272885
C	-5.41836	1.16276	0.558104
C	-4.34339	0.048266	-1.31694
C	-6.56944	0.395538	0.350985
H	-5.38727	1.90098	1.35209
C	-5.49834	-0.71582	-1.51844
H	-3.47972	-0.094659	-1.95712
C	-6.61108	-0.544001	-0.686578
H	-7.43218	0.535367	0.994333
H	-5.52623	-1.44265	-2.32359
H	-7.50585	-1.13661	-0.847125
H	-1.09162	0.338382	-1.81019
O	-0.777429	-0.563718	-1.64724
I	4.47739	0.699106	-0.503435

Int. II





Electronic Energy: -1577.595697 Hartree
RMS Gradient Norm: 0.000295 Hartree/Bohr
Dipole Moment: 5.732181 Debye

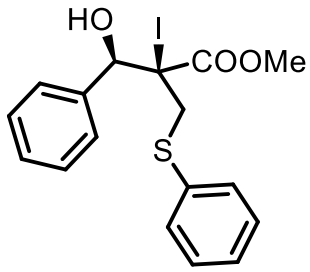
Cartesian coordinates of the optimized structure

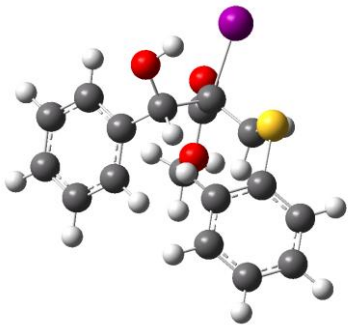
0 1

Atom	X	Y	Z
C	3.96456	-1.3973	-1.88986
C	2.69665	-0.830457	-1.71858
C	1.79993	-1.37131	-0.78195
C	2.18236	-2.50847	-0.04779
C	3.45173	-3.07326	-0.217843
C	4.34912	-2.51417	-1.13582
H	4.64907	-0.969564	-2.61655
H	2.38636	0.016185	-2.31956
H	1.48012	-2.95919	0.648076
H	3.73381	-3.95302	0.354814
H	5.3338	-2.95189	-1.2712
C	0.421429	-0.758632	-0.587395
C	0.343552	0.374707	0.517046
H	-0.249188	-1.54322	-0.196687
C	-1.11227	0.67576	0.969012
H	-1.55338	-0.24589	1.35877
H	-1.09242	1.41341	1.77532

C	1.13513	-0.060589	1.7679
O	2.15103	0.424402	2.20906
O	0.498682	-1.12298	2.35164
C	1.16073	-1.67333	3.53208
H	1.25712	-0.905407	4.30304
H	0.51455	-2.48411	3.866
H	2.15273	-2.04506	3.2644
S	-2.27616	1.32316	-0.341048
C	-3.5671	0.057832	-0.332324
C	-4.74936	0.286817	0.394045
C	-3.42802	-1.12039	-1.08868
C	-5.77988	-0.660871	0.37268
H	-4.85905	1.20306	0.96513
C	-4.45918	-2.06714	-1.09905
H	-2.52545	-1.28872	-1.66912
C	-5.63489	-1.83919	-0.370351
H	-6.69218	-0.477268	0.933358
H	-4.34717	-2.97546	-1.68355
H	-6.43543	-2.57252	-0.386792
H	-0.795466	0.295984	-1.73179
O	-0.042605	-0.310699	-1.86437
I	1.24447	2.26842	-0.215211

Int. II′





Electronic Energy: -1577.579313 Hartree

Dipole Moment: 5.4666509 Debye

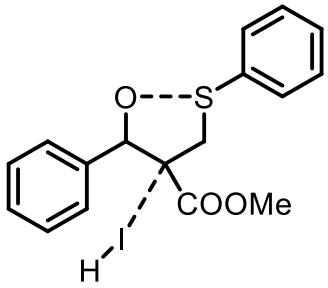
Cartesian coordinates of the optimized structure

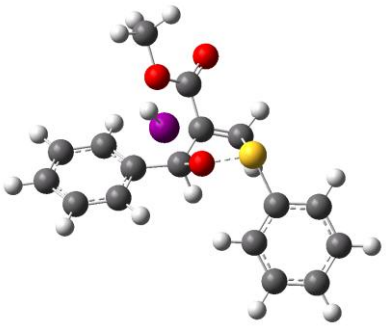
0 1

Atom	X	Y	Z
C	-3.287116	3.010293	-1.056113
C	-2.612926	1.792475	-1.199775
C	-1.263568	1.681618	-0.824496
C	-0.594346	2.818841	-0.337421
C	-1.270139	4.035902	-0.191583
C	-2.621548	4.132639	-0.545016
H	-4.330411	3.083066	-1.349067
H	-3.11715	0.930337	-1.620178
H	0.460321	2.753661	-0.084536
H	-0.740473	4.907387	0.184538
H	-3.147522	5.076426	-0.434883
C	-0.524919	0.360453	-0.974201
C	-0.591038	-0.589477	0.292123
H	0.552019	0.580362	-1.073195
C	0.792676	-0.7838	0.971758
H	1.175069	0.196577	1.269347
H	0.668095	-1.390428	1.872389
C	-1.543364	0.012275	1.346488
O	-2.607367	-0.423786	1.720165

O	-0.993623	1.165841	1.83797
C	-1.808574	1.873617	2.822626
H	-2.004209	1.229892	3.683276
H	-1.215148	2.740795	3.109449
H	-2.757332	2.17677	2.37333
S	2.12256	-1.595345	-0.05918
C	3.396814	-0.313307	-0.076378
C	4.472663	-0.401125	0.825076
C	3.355831	0.732494	-1.016724
C	5.493838	0.556336	0.793209
H	4.508336	-1.216956	1.539797
C	4.376177	1.690709	-1.037597
H	2.537964	0.78919	-1.729302
C	5.445223	1.604113	-0.134876
H	6.324022	0.481773	1.490052
H	4.34002	2.496617	-1.764533
H	6.238485	2.345097	-0.159039
H	-0.736663	-1.215321	-2.146717
O	-1.004571	-0.277001	-2.161734
I	-1.380491	-2.593292	-0.251465

Int. III-HI





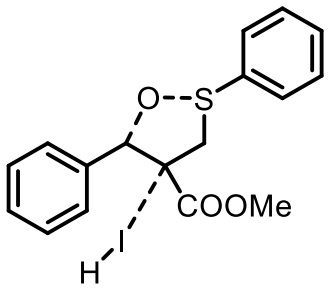
Electronic Energy: -1577.548500 Hartree
RMS Gradient Norm: 0.001398 Hartree/Bohr
Dipole Moment: 2.502648 Debye

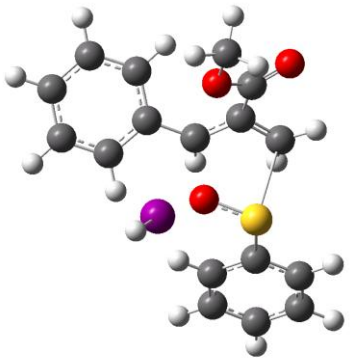
Cartesian coordinates of the optimized structure

0 1

Atom	X	Y	Z
C	-2.174144	0.010498	-3.308291
C	-1.107264	0.27462	-2.4447
C	-1.163978	1.332332	-1.518484
C	-2.307822	2.157264	-1.523607
C	-3.374098	1.897112	-2.39411
C	-3.317976	0.815732	-3.280905
H	-2.109944	-0.823848	-3.999271
H	-0.22829	-0.359822	-2.46923
H	-2.371918	3.002681	-0.849844
H	-4.247978	2.540818	-2.375467
H	-4.149163	0.609764	-3.947782
C	0.049343	1.580245	-0.651745
C	0.059186	2.454608	0.537941
H	0.912922	1.810294	-1.281647
C	1.266274	2.915885	0.950556
H	2.141528	2.874278	0.312366
H	1.376901	3.386467	1.920771
C	-1.04119	2.54784	1.543185

O	-1.021331	3.314584	2.494098
O	-2.051814	1.665969	1.330043
C	-3.126151	1.692288	2.313539
H	-3.580666	2.685021	2.354558
H	-3.840341	0.946513	1.969023
H	-2.739144	1.434837	3.301839
S	1.787479	0.059105	1.039379
C	3.289311	0.12449	0.056483
C	4.478568	0.544462	0.681892
C	3.307222	-0.274444	-1.287626
C	5.678268	0.547022	-0.038064
H	4.466944	0.867803	1.718828
C	4.50752	-0.24577	-2.004523
H	2.390153	-0.612951	-1.756176
C	5.695839	0.158675	-1.38369
H	6.594519	0.865483	0.448986
H	4.515699	-0.552278	-3.045834
H	6.62581	0.171337	-1.942427
O	0.558689	0.084397	-0.064522
I	-1.177317	-2.524274	0.633179
H	-1.938687	-3.921105	1.019183





IRC calculations confirm **TS** connects **III** and the sulfoxide product **3**. The computed barrier is +8.9 kcal mol^{-1}.

Electronic Energy: -1577.542174 Hartree
RMS Gradient Norm: 0.000079 Hartree/Bohr
Dipole Moment: 2.680584 Debye

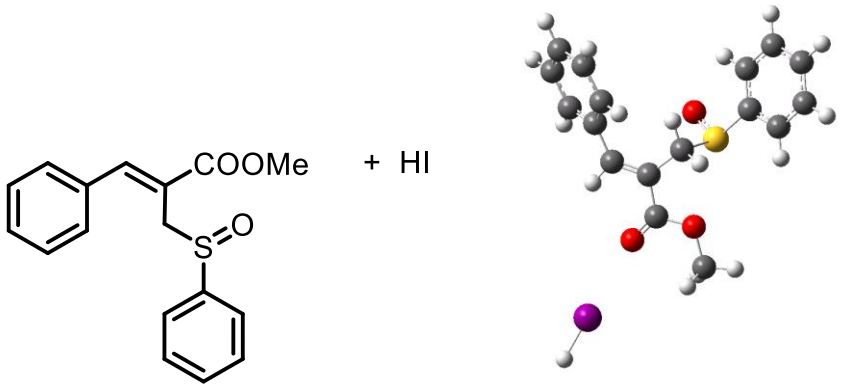
Cartesian coordinates of the optimized structure

0 1

Atom	X	Y	Z
C	-2.17833	0.019694	-3.30972
C	-1.11554	0.326705	-2.45817
C	-1.20488	1.40196	-1.54907
C	-2.37751	2.18407	-1.54752
C	-3.43198	1.88675	-2.4133
C	-3.34143	0.79919	-3.29061
H	-2.0981	-0.823172	-3.98847
H	-0.216874	-0.279702	-2.47018
H	-2.45482	3.03642	-0.883721
H	-4.32343	2.50584	-2.40487
H	-4.16533	0.566632	-3.95773
C	-0.029028	1.73443	-0.727476
C	0.0511973	2.43702	0.503831
H	0.896468	1.7553	-1.29798
C	1.32022	2.73006	0.97603
H	2.17002	2.78782	0.305874

H	1.45444	3.11621	1.97953
C	-1.03999	2.54347	1.52294
O	-0.994737	3.29896	2.48247
O	-2.06368	1.67545	1.31845
C	-3.12629	1.7039	2.3139
H	-3.57749	2.69791	2.36348
H	-3.84708	0.961769	1.97512
H	-2.72972	1.44147	3.29714
S	1.80099	0.110055	1.05766
C	3.31076	0.139943	0.077819
C	4.50593	0.54842	0.693822
C	3.30728	-0.261829	-1.2654
C	5.69595	0.550591	-0.039656
H	4.50763	0.862188	1.73416
C	4.50207	-0.246942	-1.9932
H	2.37967	-0.591573	-1.71916
C	5.69687	0.156994	-1.38466
H	6.61945	0.864587	0.43624
H	4.50058	-0.558765	-3.03292
H	6.6218	0.163376	-1.95187
O	0.641447	-0.084135	0.018434
I	-1.17605	-2.52415	0.634005
H	-1.99102	-3.89686	1.00673

3aa (*Z*-form) - more stable



Electronic Energy: -1577.569576 Hartree
RMS Gradient Norm: 0.000091 Hartree/Bohr
Dipole Moment: 4.750989 Debye

Cartesian coordinates of the optimized structure

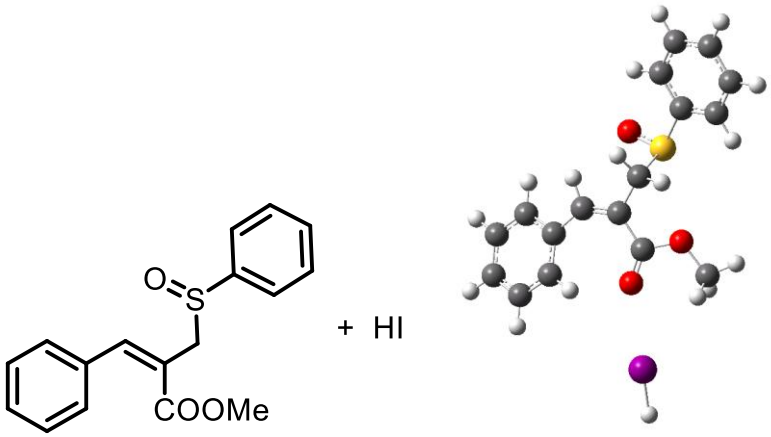
0 1

Atom	X	Y	Z
C	-0.20244100	1.56454700	-0.03164400
C	1.43264200	-0.31316900	0.47274000
H	2.15472100	0.45293100	0.75035800
H	1.41415300	-1.10659700	1.22268800
C	-1.05470500	-0.69824200	-0.01267200
O	-2.20502400	-0.38783600	-0.29967500
O	-0.67490600	-1.99354600	0.18192500
C	-1.71738000	-2.99658400	0.00331400
H	-2.14777500	-2.92163900	-0.99744800
H	-1.21601400	-3.95380300	0.14032200
H	-2.50599600	-2.86037800	0.74688900
S	2.17088700	-1.09839500	-1.09814400

C	3.74174600	-1.59933900	-0.30513500
C	3.81357000	-2.77600200	0.45066500
C	4.87104200	-0.80421100	-0.52025300
C	5.03767600	-3.14793300	1.01841000
H	2.93283200	-3.39725300	0.59056100
C	6.09182000	-1.18595600	0.04834700
H	4.77750300	0.08440200	-1.13644100
C	6.17470500	-2.35300700	0.81849300
H	5.10593300	-4.05694300	1.60724200
H	6.97596700	-0.57716500	-0.11226100
H	7.12365700	-2.64796700	1.25494000
O	2.49888600	0.04404100	-2.02510700
C	0.07796900	0.25149200	0.17753100
I	-5.25463600	-0.41996900	0.11706500
H	-6.87059800	-0.45490700	0.37743100
H	-1.21317200	1.77606700	-0.37871300
C	0.66240900	2.74070100	0.13866600
C	0.57490200	3.78780900	-0.80380600
C	1.53068400	2.90059300	1.23937900
C	1.36694200	4.93085900	-0.67919500
H	-0.10377200	3.68755600	-1.64511700
C	2.30932900	4.05323200	1.37144800
H	1.56136200	2.14143100	2.01403400
C	2.24004600	5.06645600	0.40722400
H	1.30073800	5.71622700	-1.42538400

H	2.96354000	4.16415000	2.23035900
H	2.85102600	5.95778400	0.50820900

3aa (*E*-form) -less stable



Electronic Energy: -1577.567140 Hartree
RMS Gradient Norm: 0.000356 Hartree/Bohr
Dipole Moment: 3.718572 Debye

Cartesian coordinates of the optimized structure

0 1

Atom	X	Y	Z
C	-3.24502	3.075424	0.544348
C	-2.184831	2.184369	0.728539
C	-0.866357	2.558727	0.382454
C	-0.658686	3.864147	-0.132568
C	-1.722352	4.742003	-0.331835
C	-3.023919	4.349515	0.007576
H	-4.248911	2.770176	0.822482
H	-2.368897	1.204281	1.140543
H	0.350266	4.172519	-0.391628
H	-1.538285	5.729552	-0.742814
H	-3.854996	5.032454	-0.137933
C	0.34344	1.75069	0.555525

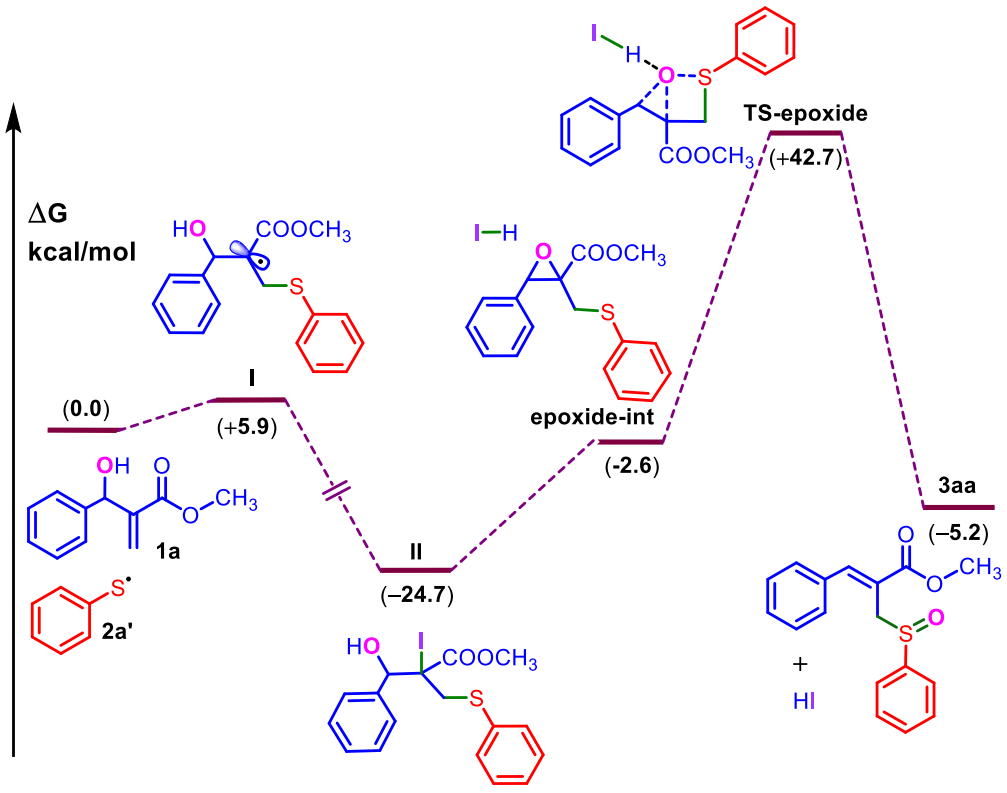
H	1.234763	2.376969	0.556497
C	2.103337	0.05253	0.766423
H	2.667978	0.802015	1.32782
H	2.266051	-0.935399	1.196258
C	-0.309815	-0.702728	0.519037
O	-1.533463	-0.65935	0.59464
O	0.345748	-1.883016	0.276793
C	-0.497769	-3.05656	0.10178
H	-1.140372	-2.93697	-0.773524
H	0.195473	-3.885211	-0.039876
H	-1.119373	-3.215463	0.986163
S	2.923753	0.053646	-0.943781
C	4.590133	-0.399001	-0.345466
C	4.904235	-1.736461	-0.072634
C	5.545251	0.613237	-0.213423
C	6.195372	-2.058467	0.360673
H	4.157885	-2.51624	-0.200362
C	6.835316	0.281169	0.216795
H	5.268245	1.632697	-0.462822
C	7.159094	-1.05076	0.506211
H	6.450466	-3.091132	0.576621
H	7.586254	1.058124	0.32168
H	8.161197	-1.305288	0.836295
O	2.988537	1.508864	-1.348476
C	0.645665	0.418713	0.653902
I	-4.419053	-1.634754	-0.206998
H	-5.923156	-2.160702	-0.611686

13. Stereochemical Considerations

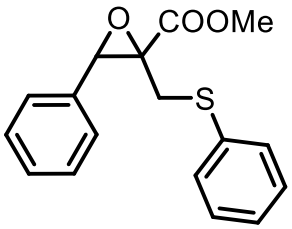
The experimentally observed exclusive *Z*-selectivity can be rationalized by steric considerations and thermodynamic stability. Qualitative analysis suggests that the *Z*-orientation minimizes steric repulsion between the bulky sulfinyl substituent and the ester group, whereas the *E*-orientation would lead to unfavorable steric congestion between the phenyl ring and the ester moiety. This preference is consistent with DFT calculations, which indicate that the *Z*-isomer is thermodynamically more stable than the *E*-isomer by 1.5 kcal/mol. Furthermore, the *Z*-configuration was unambiguously confirmed by the X-ray crystal structure of **3fc**.

14. Alternative Epoxide Pathway

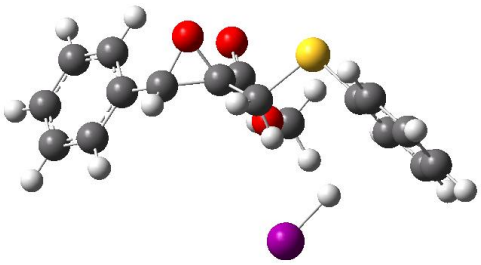
A putative epoxide intermediate (**epoxide-int**) was successfully optimized and is slightly stabilized relative to the starting materials (ΔG = -2.6 kcal/mol). However, attempts to locate a feasible transition state (**TS-epoxide**) for the subsequent conversion of this epoxide to the sulfoxide product resulted in barriers exceeding 40 kcal/mol. This corresponds to a prohibitive activation energy for the product-forming step. Consequently, even if the epoxide is formed reversibly, it cannot proceed to the final product. Given these energetics, the epoxidation route is considered a non-productive pathway, supporting the operation of the alternative iodide-assisted mechanism.



Epoxide-int.



+ HI



Electronic Energy: -1577.565859 Hartree

RMS Gradient Norm: 0.005459 Hartree/Bohr

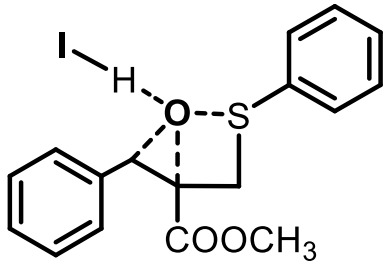
Cartesian coordinates of the optimized structure

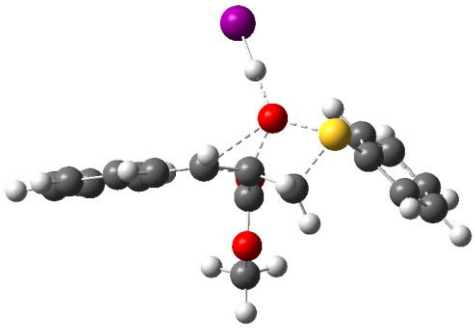
0 1

Atom	X	Y	Z
C	-1.76990000	-0.59621600	-0.61251700
C	-0.25910200	-0.53603600	-0.65663800
H	0.06073300	0.25858400	-1.33445200
H	0.13273800	-0.34654400	0.34410000
C	-2.38318500	-1.55428100	0.38103900
O	-3.34459100	-2.26551800	0.18410700
O	-1.71355900	-1.49234700	1.56731200
C	-2.21864600	-2.37541300	2.61168800
H	-2.15366200	-3.41692800	2.28822400
H	-1.57805300	-2.19362200	3.47346500
H	-3.25895800	-2.13357600	2.84073800
C	-2.55849200	0.62547100	-1.03690800
H	-1.93929600	1.46678700	-1.35088800
C	-3.89952300	1.01025700	-0.51701200
C	-4.03202300	2.23577700	0.15969100
C	-5.03201600	0.20218800	-0.71064300
C	-5.27391400	2.63949700	0.65586800
H	-3.16200900	2.87251900	0.29598400
C	-6.27452600	0.61280100	-0.21722600
H	-4.92656500	-0.73720700	-1.23850200
C	-6.39910900	1.82716000	0.46818700
H	-5.36502800	3.58591000	1.17944900

H	-7.14572900	-0.01591900	-0.37136100
H	-7.36556000	2.14156300	0.84886100
O	-2.44021400	-0.53835700	-1.89029700
H	3.70968600	0.78334600	-0.22210000
I	3.48302300	2.34330000	0.21593100
S	0.44088800	-2.16057500	-1.24776800
C	2.09965800	-2.05333600	-0.55372500
C	2.33480600	-2.37083700	0.79600600
C	3.17977000	-1.68938600	-1.37705800
C	3.63226600	-2.31380100	1.31792300
H	1.50199400	-2.66356600	1.42651400
C	4.47947800	-1.63957200	-0.85257300
H	2.99936900	-1.45549400	-2.42060700
C	4.70681400	-1.95034800	0.49542400
H	3.80526600	-2.56166000	2.36047000
H	5.31004700	-1.36913000	-1.49735700
H	5.71338700	-1.91452000	0.89925600

TS-epoxide





Electronic Energy: -1577.476318 Hartree

RMS Gradient Norm: 0.000307 Hartree/Bohr

Cartesian coordinates of the optimized structure

0 1

Atom	X	Y	Z
C	0.35817400	1.13385300	0.84954200
C	-0.65062900	1.85708900	1.78533300
H	-0.23094100	2.04125800	2.77555600
H	-1.14317800	2.74644400	1.39287700
C	0.08674000	1.44726800	-0.62348400
O	-0.16465000	0.65342500	-1.50437400
O	0.16120300	2.79327100	-0.82378300
C	-0.04633000	3.23665600	-2.19835000
H	-1.01408000	2.89041100	-2.56763400
H	-0.00829400	4.32400300	-2.15442100
H	0.74659800	2.84662800	-2.84044000
C	1.71538800	1.11592900	1.28834200
H	1.82485700	1.10699000	2.37085700
C	2.95573300	1.11192900	0.55317600
C	4.14889600	1.37471700	1.28284900
C	3.08856800	0.84765600	-0.83751100
C	5.39276800	1.40630800	0.65918000
H	4.07663200	1.56275500	2.35035800
C	4.33865000	0.88009800	-1.45393500
H	2.22473200	0.56545900	-1.42488000
C	5.49691600	1.16560000	-0.71796300

H	6.28319200	1.61474600	1.24411500
H	4.41259100	0.66138500	-2.51472400
H	6.46574200	1.18449200	-1.20622500
O	-0.28978400	-0.28783600	1.19477400
H	-0.01310000	-1.82863700	0.49790500
I	0.26069200	-3.35333700	-0.19168200
S	-1.84174900	0.36949500	1.98723200
C	-3.04146900	0.63977600	0.66846500
C	-3.09685800	-0.24304000	-0.41886500
C	-3.96919200	1.68765800	0.79428900
C	-4.09115300	-0.06901500	-1.38857100
H	-2.36270200	-1.03343400	-0.51798300
C	-4.95732700	1.85021000	-0.18210500
H	-3.92654200	2.36101000	1.64449400
C	-5.01907700	0.97218700	-1.27190800
H	-4.13267500	-0.74638000	-2.23452600
H	-5.67636300	2.65747000	-0.08913700
H	-5.78812300	1.10021500	-2.02662000

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These two papers (4 and 5) are the canonical references for the aug-cc-pVnZ-PP (including aug-cc-pVQZ-PP) basis sets for iodine.

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