Supporting information

One-pot Chemoselective Aerobic Synthesis of Allyl-Aryl Sulfinyls by Photoinduced Na_2 - Eosin Y

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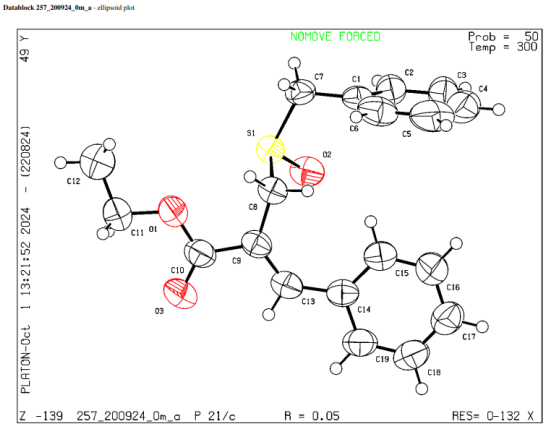
1. Single crystal X-ray diffraction

A colourless, block-like specimen of $C_{19}H_{20}O_3S$, approximate dimensions 0.103 mm x 0.143 mm x 0.330 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). The total exposure time was 1.36 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40667 reflections to a maximum θ angle of 28.35° (0.75 Å resolution), of which 4259 were independent (average redundancy 9.548, completeness = 99.4%, R_{int} = 4.91%, R_{sig} = 3.20%) and 2778 (65.23%) were greater than 2σ(F2). The final cell constants of a = 5.2763(4) Å, b = 22.1253(17) Å, c = 14.7638(12) Å, β = 95.053(2)°, volume = 1716.8(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9963 reflections above 20 σ(I) with 4.607° < 2θ < 48.49°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.898.

Table S1. Crystal data and structure refinement for BT-III-257(4s).

Identification code	257_200924
Empirical formula	$C_{19}H_{20}O_3S$
Formula weight	328.41 g/mol
Crystal system	monoclinic
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system, space group	Block, P 1 21/c 1
Unit cell dimensions	a = 5.2763(4) Å alpha = 90 deg. b = 22.1253(17) Å beta = 95 deg. c =14.7638(12) Å gamma = 90deg.
Volume	1716.8(2) $Å^3$
Z, Calculated density	4
Absorption coefficient	0.200 mm^{-1}
F (000)	696
Crystal size	0.103 x 0.143 x 0.330 mm
Theta range for data collection	2.30 to 28.35°
Limiting indices	-7<=h<=7, -29<=k<=29, -19<=l<=19
Reflections collected / unique	40667
Absorption correction	Multi-Scan
Independent reflections	4259 [R(int) = 0.0491]
Max. and min. transmission	0.9800 and 0.9370
Coverage of independent reflections	99.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4259 / 0 / 209
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1182
R indices (all data)	R1 = 0.0919, wR2 = 0.1484
Largest diff. peak and hole	0.303 and -0.256 $eÅ^{-3}$

Figure S1. Single - crystal X-ray structure of 4s (Ellipsoids contour of probability level is 50 %).



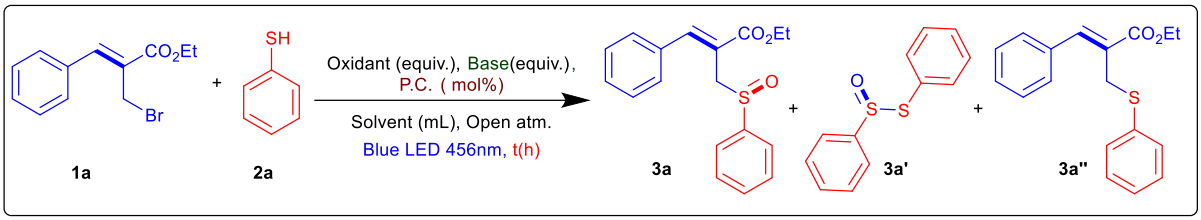
The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9370 and 0.9800. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{19}H_{20}O_3S$. The final anisotropic full-matrix least-squares refinement on F^2 with 209 variables converged at R1 = 5.10%, for the observed data and wR2 = 14.84% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.303 $e^-/Å^3$ and the largest hole was -0.256 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.271 g/cm^3 and F(000), 696 e^-.

2. General information

All reactions were carried out in oven dried glasswares. All the commercially available chemicals (Sigma Aldrich, TCI, Alfa acer, Avra and SRL) were used directly and freshly distilled dry solvents for anhydrous conditions. Column chromatography was performed with silica gel (200 - 300 mesh) using gradient elution with hexane and ethyl acetate mixture as eluent. All the reactions were monitored by thin layer chromatography (TLC) on precoated silica gel plates and visualized under UV chamber. ESI-HRMS spectra were recorded on Agilent advance bio 6545XT LC/Q-TOF mass spectrometer. NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker 500MHz NMR spectrometer. The solvent signal of $CDCl_3$ was referenced at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. Chemical shift values (δ) are quoted in ppm and coupling constants (*J*) are recorded in hertz (Hz). The following abbreviations classify the multiplicity- s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet etc. The UV-visible absorption spectra were recorded with a Jasco V-670 spectrophotometer. The fluorescence emission spectra were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. A 40 W Kessil PR160L – 456 nm LED photoreaction lighting (max frequency, max intensity) was employed as a visible light source without the use of filters.

Figure S2. The photo reaction setup with a 40 W Kessil PR160L - 456 nm LED photoreaction lighting and a fan

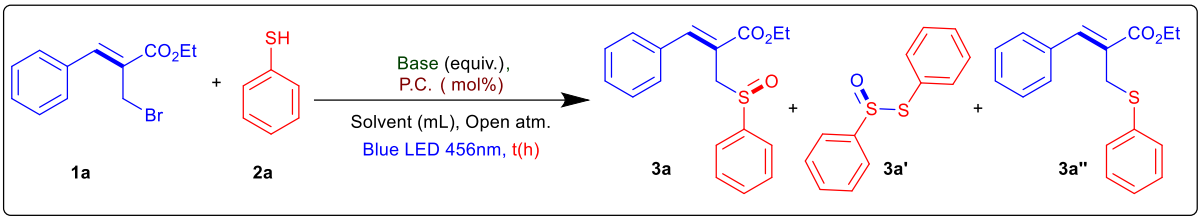
3. Full Optimization table



S.no	Oxidant (equiv.)	Photocatalyst (mol%)	Base (equiv.)	Solvent (ml)	t (h)	Yield (%) [a]		
						3a	3a'	3a''
1[b]	**TEMPO (0.03)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	40	5	trace
2	**TEMPO (0.1)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	55	trace	trace
3	**TEMPO (0.25)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	62	trace	trace
4	**TEMPO (0.5)**	**Na_2 - Eosin Y (3)**	**Et_3N (1)**	**CH_3CN (4)**	**20**	**91**	**trace**	**0**
5	**TEMPO (0.75)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	86	trace	0
6	**TEMPO (1)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	83	trace	0
7	**TEMPO (1.5)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	0	trace	31
8	**TEMPO (2)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	0	trace	64
9	**TEMPO (4)**	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	0	trace	90
10	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	**1**	0	0	95
11	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	**12**	64	trace	31
12	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	**18**	89	trace	0
13	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	**24**	83	trace	0
14[c]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	trace	2	40
15[d]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	68	13	trace
16	TEMPO (0.5)	Na_2 - Eosin Y (3)	**Nil**	CH_3CN (4)	20	0	0	0
17	TEMPO (0.5)	Na_2 - Eosin Y (3)	**Et_3N (0.5)**	CH_3CN (4)	20	43	trace	trace
18	TEMPO (0.5)	Na_2 - Eosin Y (3)	**Et_3N (2)**	CH_3CN (4)	20	71	trace	0
19	TEMPO (0.5)	Na_2 - Eosin Y (3)	**DABCO (1)**	CH_3CN (4)	20	51	trace	trace
20	**TEMPO (1)**	Na_2 - Eosin Y (3)	DABCO (1)	CH_3CN (4)	20	36	trace	trace
21	TEMPO (0.5)	Na_2 - Eosin Y (3)	**2,6-lutidine (1)**	CH_3CN (4)	20	31	trace	20
22	TEMPO (0.5)	Na_2 - Eosin Y (3)	**DBU (1)**	CH_3CN (4)	20	63	trace	0
23	TEMPO (0.5)	Na_2 - Eosin Y (3)	**TEOA (1)**	CH_3CN (4)	20	0	0	90
24	TEMPO (0.5)	Na_2 - Eosin Y (3)	**TMEDA (1)**	CH_3CN (4)	20	80	trace	trace
25[e]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	43	trace	trace
26	TEMPO (0.5)	**Eosin Y (3)**	Et_3N (1)	CH_3CN (4)	20	75	trace	17
27	TEMPO (0.5)	**Rhodamine 6G (3)**	Et_3N (1)	CH_3CN (4)	20	35	trace	trace
28	TEMPO (0.5)	**Rose Bengal(3)**	Et_3N (1)	CH_3CN (4)	20	trace	trace	trace
29	TEMPO (0.5)	**Fluorescein (3)**	Et_3N (1)	CH_3CN (4)	20	50	trace	trace
30	TEMPO (0.5)	**[Mes-Acr]$^+$ClO4$^-$ (3)**	Et_3N (1)	CH_3CN (4)	20	trace	trace	77
31	TEMPO (0.5)	**Nil**	Et_3N (1)	CH_3CN (4)	20	4	trace	80
32	TEMPO (0.5)	**Na_2 - Eosin Y (0.1)**	Et_3N (1)	CH_3CN (4)	20	63	trace	trace
33	TEMPO (0.5)	**Na_2 - Eosin Y (0.5)**	Et_3N (1)	CH_3CN (4)	20	52	trace	trace
34	TEMPO (0.5)	**Na_2 - Eosin Y (1)**	Et_3N (1)	CH_3CN (4)	20	41	trace	trace
35	TEMPO (0.5)	Nil	Et_3N (1)	CH_3CN (4)	20	0	0	85
36[f]	**$K_2S_2O_8$ (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	62	trace	0
37	**$(NH_4)_2S_2O_8$ (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	37	trace	trace
38	**$Na_2S_2O_8$ (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	trace	trace	trace
39	**H_2O_2 (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	31	trace	trace
40	**Oxone (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	35	trace	trace
41	***m*-CPBA (0.5)**	Na_2 - Eosin Y (0.03)	Et_3N (1)	CH_3CN (4)	20	trace	trace	trace
42[g]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	80	trace	trace
43[h]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	20	trace	trace	90
44[i]	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	7	49	trace	21
45	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**H_2O (4)**	20	22	0	39
46	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**DMSO (4)**	20	0	0	78
47	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**DMF (4)**	20	0	0	43
48	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**THF (4)**	20	13	0	34
49	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**EtOH (4)**	20	62	0	trace
50	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**MeOH (4)**	20	21	trace	46
51	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**DCM (4)**	20	0	0	91

52	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**CH_3CN: H_2O (3:1)**	20	78	trace	trace
53	TEMPO (0.5)	Na_2 - Eosin Y (3)	Et_3N (1)	**CH_3CN (2)**	20	40	trace	trace
54[j]	TEMPO (0.5)	Nil	Et_3N (1)	CH_3CN (4)	20	0	0	93
55[k]	TEMPO (0.5)	Nil	Et_3N (1)	CH_3CN (4)	20	0	0	90
	[a] Yield after purification; [b] 3 equiv. of thiol and unless we mentioned particularly it will be same for all; [c] O_2 atmosphere; [d] Ar atmosphere; [e] Presence of TBAHS; [f] Thermal condition; [g] Under Green LED 525 nm; [h] Under white LED strip 16w; [i] Under Sunlight; [j] 45°C; [k] 60°C.							

4. Optimization table for without TEMPO



S.no	Photocatalyst (mol%)	Base (equiv.)	Solvent (ml)	t (h)	Yield (%) [a]		
					3a	3a′	3a″
1[b]	**Na_2 - Eosin Y (3)**	**Et_3N (1)**	**CH_3CN (4)**	**24**	**69**	**11**	**trace**
2[c]	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	24	67	22	trace
3[d]	NIL	Et_3N (1)	CH_3CN (4)	24	0	0	89
4	Na_2 - Eosin Y (3)	**Nil**	CH_3CN (4)	24	0	0	0
5	**Rhodamine 6G (3)**	Et_3N (1)	CH_3CN (4)	24	57	22	8
6	**Rose Bengal(3)**	Et_3N (1)	CH_3CN (4)	24	trace	trace	trace
7	**Fluorescein (3)**	Et_3N (1)	CH_3CN (4)	24	64	10	trace
8	**$[Mes\text{-}Acr]^+ClO4^-$ (3)**	Et_3N (1)	CH_3CN (4)	24	0	0	10
9	Na_2 - Eosin Y (3)	Et_3N (1)	**DMSO (4)**	24	0	0	70
10	Na_2 - Eosin Y (3)	Et_3N (1)	**DCM (4)**	24	0	0	90
11	Nil	Et_3N (1)	CH_3CN (4)	24	0	0	65
12[e]	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	24	60	5	10
13[f]	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	24	57	trace	22
14[g]	Na_2 - Eosin Y (3)	Et_3N (1)	CH_3CN (4)	7	57	trace	trace
	[a] Yield after purification; [b] 3 equiv. of thiol and unless we mentioned particularly it will be same for all; [c] O_2 atmosphere; [d] 80°C ; [e] Under Green LED 525 nm; [f] Under white LED strip 16w; [g] Under Sunlight.						

5. Preparation of starting materials

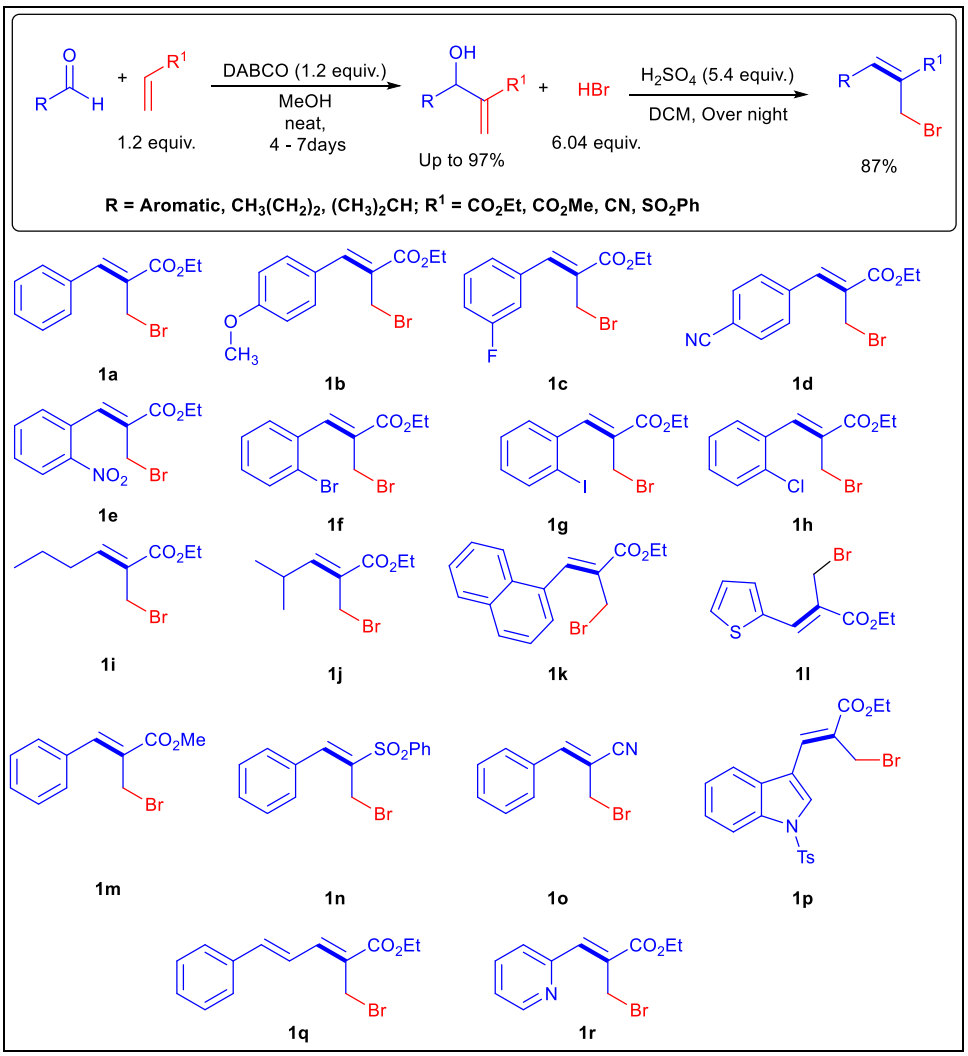
5.1. General procedure for preparation of MBH Alcohols and Bromides:[1]

Step-1:

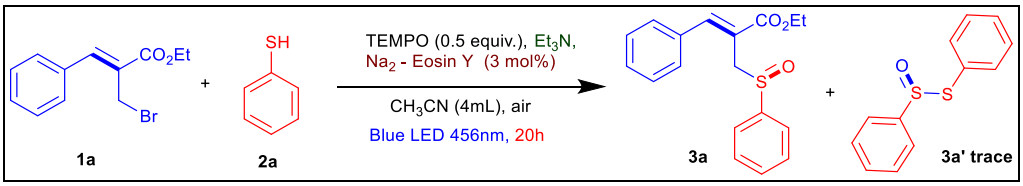
According to the known procedure, a variety of Morita-Baylis-Hillman alcohols have been prepared. In a 10 mL round-bottom flask, a mixture of a given activated olefin (1.2 equiv.), aldehyde (4.71 mmol, 1.0 equiv.), DABCO (1.2 equiv.), and MeOH (2 drops) was stirred at room temperature. The stirring was continued until full conversion of limiting starting material. Then, the reaction mixture was quenched with 0.1N HCl, extracted with H_2O and EtOAc. The organic layer was washed with $NaHCO_3$ and followed by brine solution. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (5%) as eluent to furnish the corresponding MBH alcohol.

Step-2:

According to known procedure, Morita-Baylis-Hillman alcohols (2.38 mmol, 1.0 equiv), were treated with HBr (6.04 equiv) dropwise in dichloromethane (50mL), then kept at 0 °C and allowed to stir for 10min. Then, Conc. H_2SO_4 was added slowly to a stirred solution and allowed to stir at room temperature for overnight. The reaction mixture was treated with water and extracted with dichloromethane. The organic layer was washed with $NaHCO_3$ and followed by brine solution. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (2%) as eluent to afford MBH allyl bromides (**1a** – **1r**).

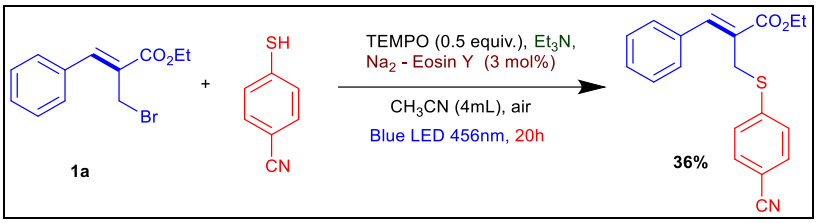


6. General procedure for the ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3a) synthesis

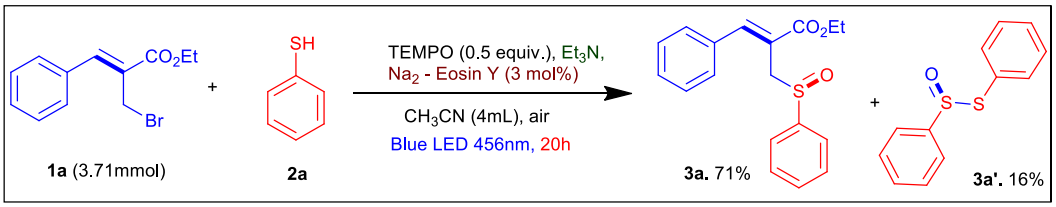


In a 5mL reaction vial, mixture of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate **1a** (0.111 mmol, 1 equiv) in 4mL of acetonitrile, Triethylamine (1 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (0.5 equiv.) were added. To the above solution mixture, thiophenol **2a** (3 equiv.) and three mole percent of disodium Eosin-Y as a photocatalyst were added and irradiated with Blue LED 456nm. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous sodium sulfate or directly without workup, the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (10%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 91% yield and trace amount of S-phenyl benzenesulfinothioate (**3a**′) as by-product. The same procedure is followed for all other substrate scope compounds.

4-Mercaptobenzonitrile gave only ethyl (Z)-2-(((4-cyanophenyl)thio)methyl)-3-phenylacrylate in 36% yield and desired product ethyl (Z)-2-(((4-cyanophenyl)sulfinyl)methyl)-3-phenylacrylate was did not observed. Product was confirmed by NMR and Mass analysis.



7. Gram-Scale Synthesis



In a 100mL RB, mixture of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate **1a** (3.71 mmol, 1 equiv) in 80mL of acetonitrile, Et_3N (1 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (0.5 equiv.) were added. To the above solution mixture, thiophenol **2a** (3 equiv.) and three mole percent of disodium Eosin-Y as a photocatalyst added and was irradiated with 456nm Blue LED. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (10%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 71% yield and 16% of S-phenyl benzenesulfinothioate (**3a**′) as by-product.

8. General procedure for table 4a experiments

8.1. Quenching with TEMPO

In a 5mL reaction vial, mixture of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate **1a** (0.111 mmol, 1 equiv) in 4mL of acetonitrile, Triethylamine (1 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (1.5 equiv.) were added. To the above solution mixture, thiophenol **2a** (3 equiv.) and three mole percent of disodium Eosin-Y as a photocatalyst were added and irradiated with Blue LED 456nm. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous sodium sulfate or directly without workup, the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (2%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 0% yield, trace amount of S-phenyl benzenesulfinothioate (**3a**′) and ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (**3a''**) in 31% as by-products.

8.2. Quenching with DABCO

In a 5mL reaction vial, mixture of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate **1a** (0.111 mmol, 1 equiv) in 4mL of acetonitrile, Triethylamine (1 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (0.5 equiv.) were added. To the above solution mixture, DABCO (2 equiv.), thiophenol **2a** (3 equiv.) and three mole percent of disodium Eosin-Y as a photocatalyst were added and irradiated with Blue LED 456nm. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous

sodium sulfate or directly without workup, the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (2%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 27% yield with 67% of ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (**3a''**) and 0% of S-phenyl benzenesulfinothioate (**3a**').

8.3. Quenching with BHT

In a 5mL reaction vial, mixture of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate **1a** (0.111 mmol, 1 equiv) in 4mL of acetonitrile, Triethylamine (1 equiv.) and butylated hydroxytoluene (2 equiv.) were added. To the above solution mixture, thiophenol **2a** (3 equiv.) and three mole percent of disodium Eosin-Y as a photocatalyst were added and irradiated with Blue LED 456nm. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous sodium sulfate or directly without workup, the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (2%) as eluent to afford the desired the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 71% yield, trace amounts of S-phenyl benzenesulfinothioate (**3a**') and ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (**3a''**) as by-products.

9. General procedure for table 4b experiments

In a 5mL reaction vial, mixture of ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (**3a''**) (1 equiv) in 4mL of acetonitrile, Triethylamine (1 equiv.) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (0.5 equiv.) were added. To the above solution mixture, three mole percent of disodium Eosin-Y as a photocatalyst were added and irradiated with Blue LED 456nm. The solution was allowed to stir for 20 h. After completion, the reaction mixture was treated with $NaHCO_3$ and extracted with ethylacetate. The organic layer was washed with brine solution. The combined organic layers were dried over anhydrous sodium sulfate or directly without workup, the solvent was evaporated in vacuo. The resulting crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (20%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** in 59% yield (table 4b. entry 1). The same procedure is followed for all other entries too. Without adding photocatalyst, the desired ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **(3a)** obtained in 1% only (table 4b. entry 2). When we were added 1 equiv. of KBr or TBAB salts to the standard condition procedure, found that yield of 3a was increased to 73% and 63% (table 4b. entry 3 and 4). Whereas by using above standard condition procedure with TBA – Eosin Y as photocatalyst, failed to give expected product (table 4b. entry 5).

10. Synthesis of Eosin Y bis(tetrabutylammonium salt)

In a 100mL round bottom flask, 0.1g of Na_2- Eosin Y (dark red) added in 30mL of CH_3CN solvent, stir the solution until its dissolved completely. Then, 2 equivalent of TBAB was added to the solution. The solution was allowed to stir for 5h. After the precipitation of NaBr formed, the reaction mixture was filtered. The solvent was evaporated in vacuo, desired product Eosin Y bis(tetrabutylammonium salt) obtained in orange semi solid and kept for recrystallization in DCM and hexane mixture (1:9). This product was partially confirmed with HRMS analysis.

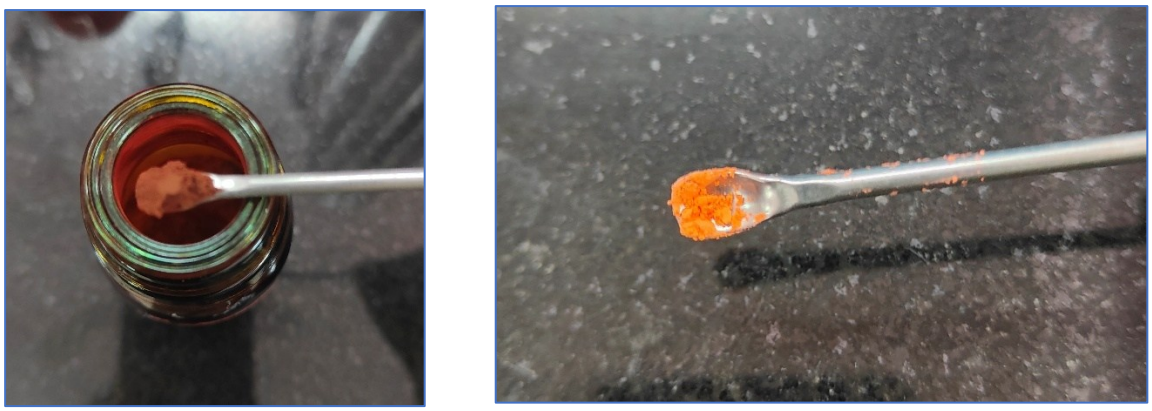
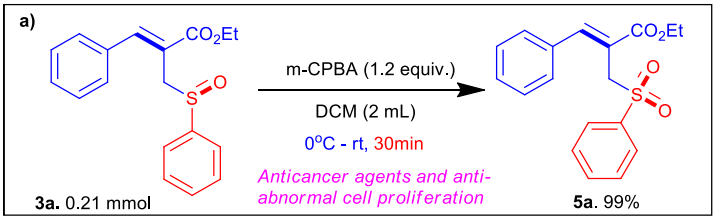


Figure S3. 1) Na_2 – Eosin Y and 2) TBA_2 - Eosin Y

11. Application of the developed strategy towards biologically relevant molecules[2]

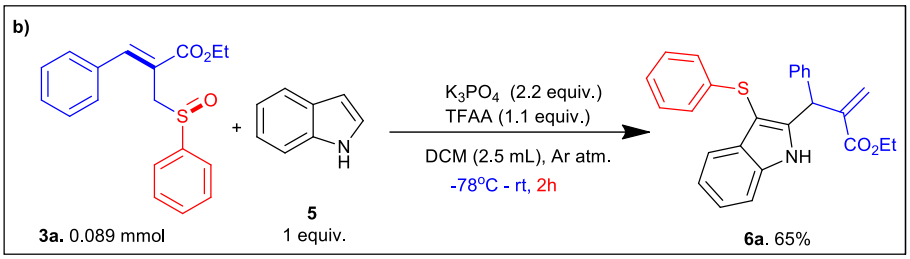
11.a. Synthesis of ethyl (Z)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (5a)[2a]

a) To an oven dried 5 mL round bottom flask with a magnetic stir bar and rubber septum was added ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **3a** (1 equiv.) in 2 mL of dichloroethane and followed by *m*-CPBA (1.2 equiv.) was added at 0°C. Then, purged the reaction mixture in argon atmosphere and stirred the solution for 30 min at room temperature. After the complete consumption of starting material, the reaction mixture was quenched with $NaHCO_3$, extracted with ethyl acetate followed by washed with brine solution, and combined organic layers were dried over Na_2SO_4. Then, the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (15%) as eluent to afford the desired ethyl (Z)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate **(5a)** in 99% yield.



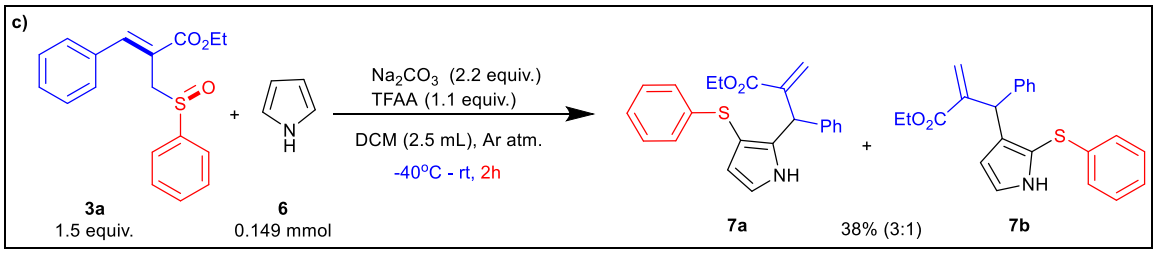
11.b. Interrupted Pummerer Reaction of 3a with Indole[2b]

b) A solution of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **3a** (0.089 mmol) and 1H-indole **5** (1 equiv.) in CH_2Cl_2 (2.5 mL) containing potassium phosphate (2.2 equiv.) under Ar atm. was cooled to -78 °C and TFAA (1.1 equiv.) was added dropwise. Reaction mixture was stirred at -78 °C for 15 min, then allowed to warm up to room temperature and stirred for 1 h. Crude reaction mixture was filtered through a plug of silica, eluted with CH_2Cl_2, and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (5%) as eluent to afford the desired ethyl 2-(phenyl(3-(phenylthio)-1H-indol-2-yl)methyl)acrylate **(6a)** in 65% yield.



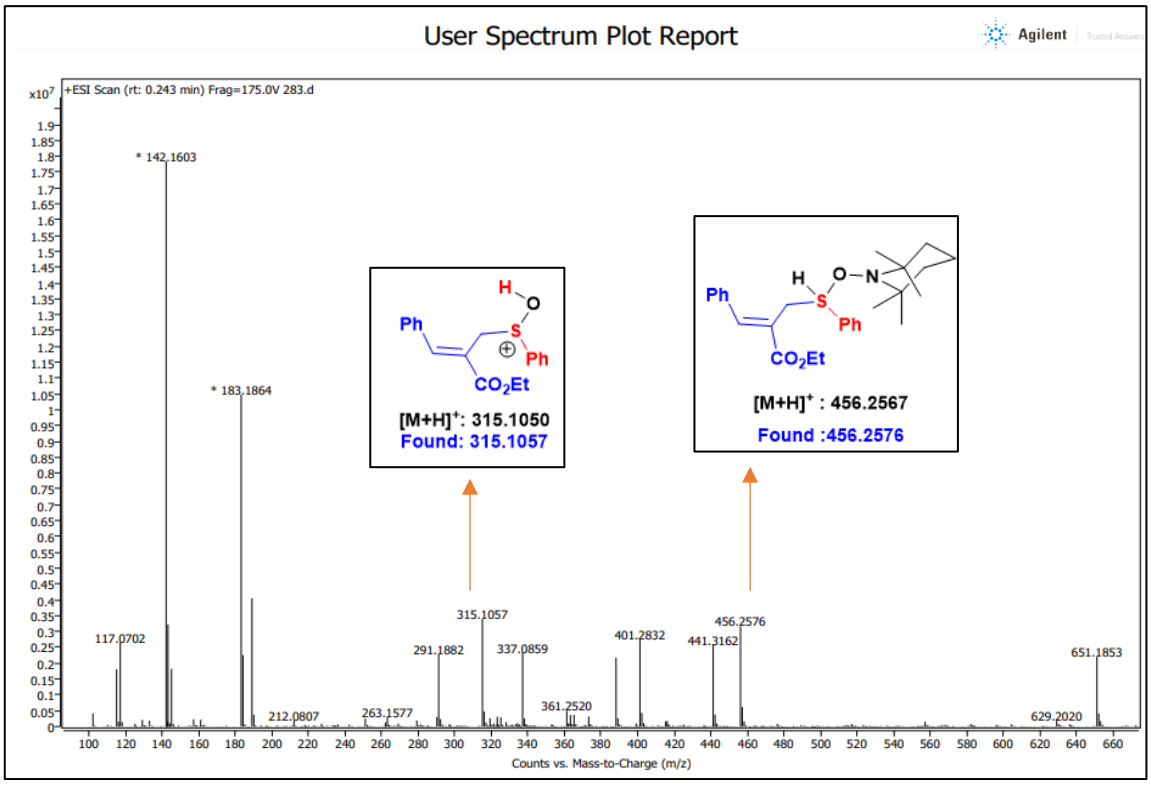
11.c. Interrupted Pummerer Reaction of 3a with Pyrrole[2b]

c) A solution of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate **3a** (1.5 equiv.) and 1H-pyrrole **6** (0.149 mmol) in CH_2Cl_2 (2.5 mL) containing sodium carbonate (2.2 equiv.) under Ar atm. was cooled to -40 °C and TFAA (1.6 equiv.) was added dropwise. Reaction mixture was stirred at -40 °C for 15 min, then allowed to warm up to room temperature and stirred for 1 h. Crude reaction mixture was filtered through a plug of silica, eluted with CH_2Cl_2, and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate (5%) as eluent to afford the desired ethyl 2-(phenyl(3-(phenylthio)-1H-pyrrol-2-yl)methyl)acrylate **(7a)** major and ethyl 2-(phenyl(2-(phenylthio)-1H-pyrrol-3-yl)methyl)acrylate **(7b)** minor in 38% yield as a mixture of regioisomers (7a : 7b = 3 : 1).

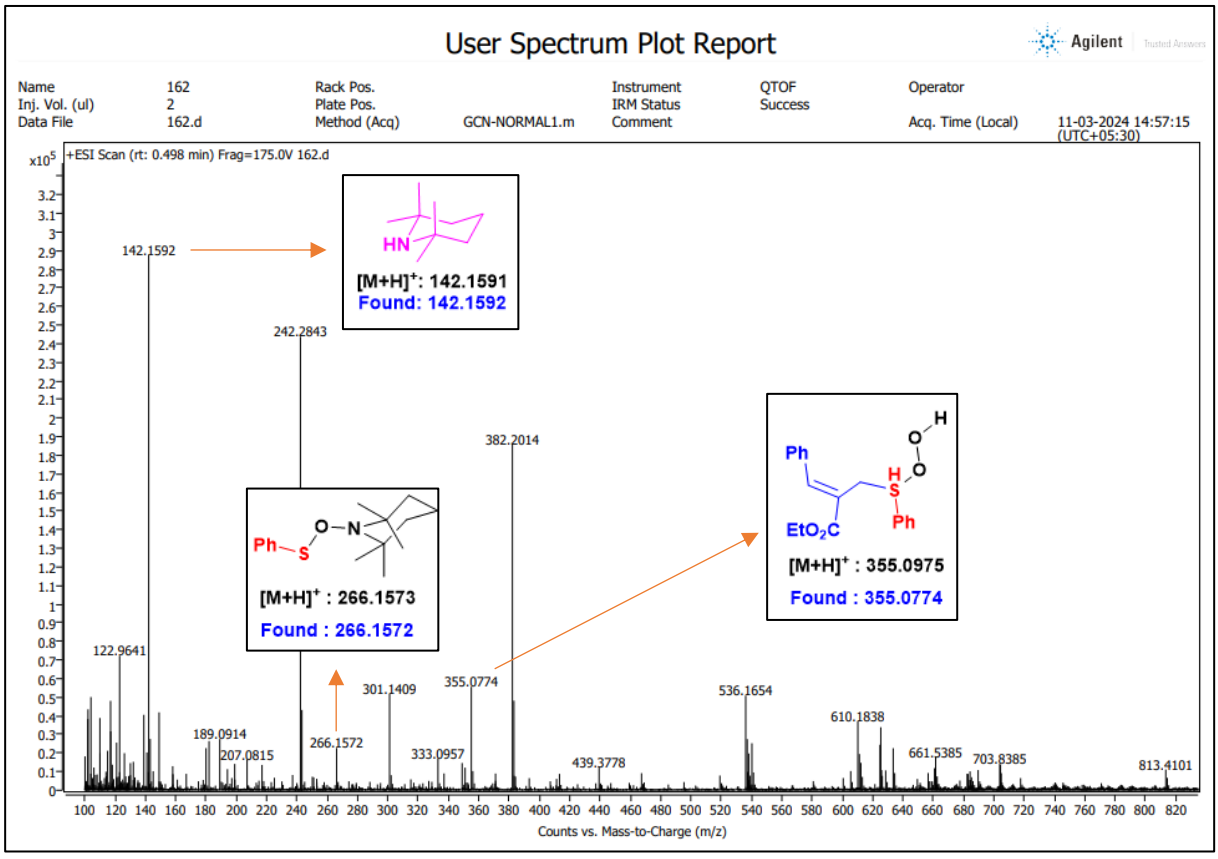


12. Identified structures from crude HRMS

12a. Crude HRMS of the reaction of 1a and 2a under Opt. Condition



12b. Crude HRMS of the reaction of 1a and 2a with 4 equiv. TEMPO under Opt. Condition



13. Fluorescence quenching studies

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing ethyl (Z)-2-(bromomethyl)-3-phenylacrylate (**1a**) in acetonitrile solvent (M = 0.37 × 10^{-8}mol/L). The absorption was recorded, and the obtained result was reported.

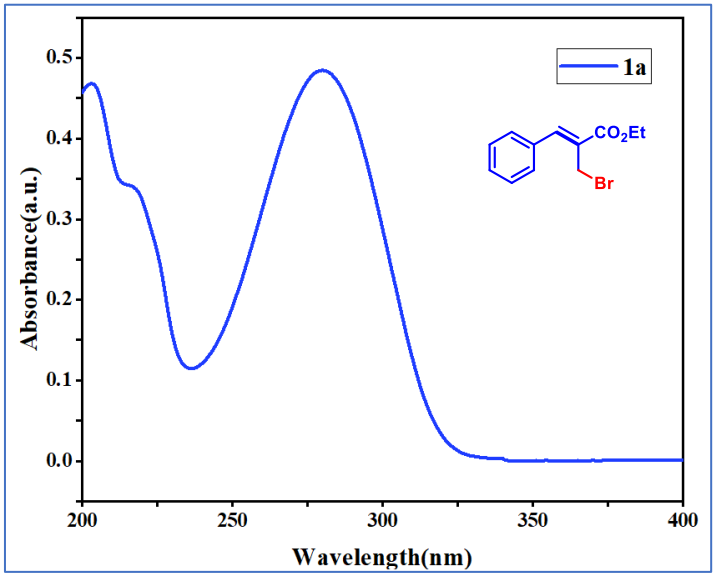


Figure S4. UV-visible spectra of **1a.**

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing thiophenol **(2a)** in acetonitrile solvent (M = 1.08 × 10^{-8} mol/L). The absorption was recorded, and the obtained result was reported.

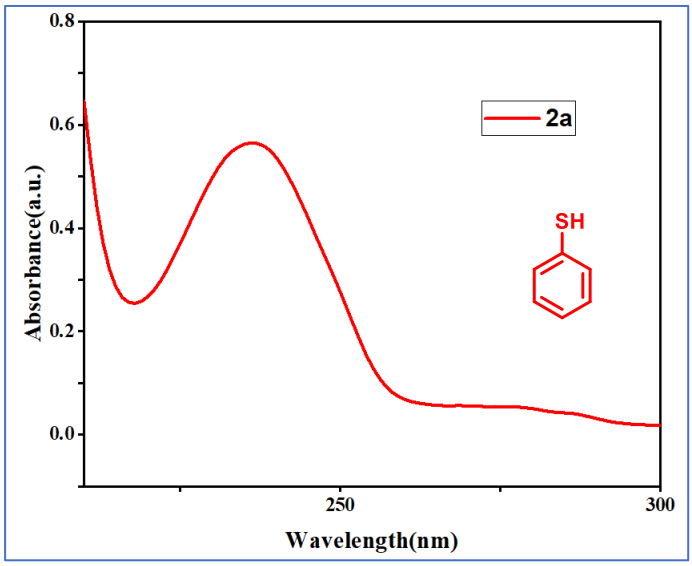


Figure S5. UV-visible spectra of **2a.**

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing **Et_3N** in acetonitrile solvent (M = 0.37 × 10^{-8} mol/L). The absorption was recorded, and the obtained result was reported.

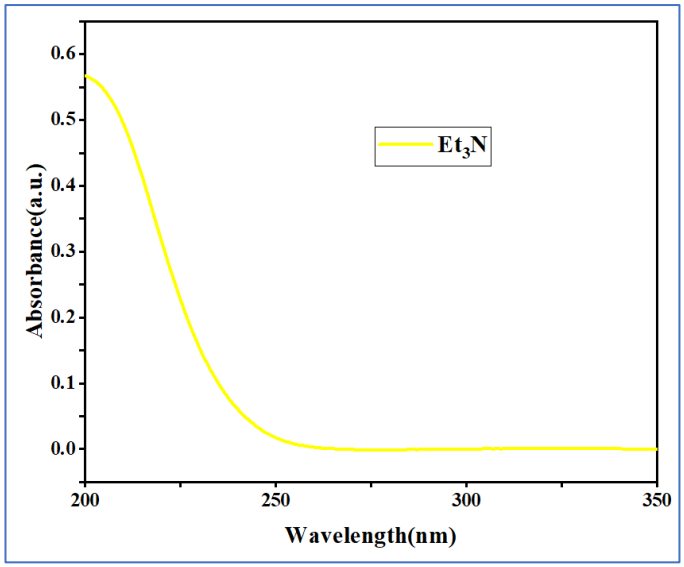


Figure S6. UV-visible spectra of **Et_3N**.

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing **TEMPO** in acetonitrile solvent (M = 0.19 × 10^{-8} mol/L). The absorption was recorded, and the obtained result was reported.

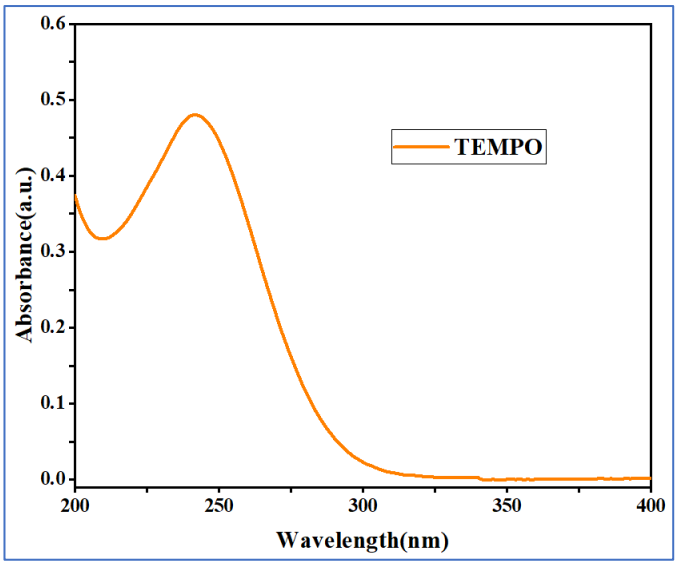


Figure S7. UV-visible spectra of **TEMPO**.

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a″**) in acetonitrile solvent (M = 0.31 × 10^{-8} mol/L). The absorption was recorded, and the obtained result was reported.

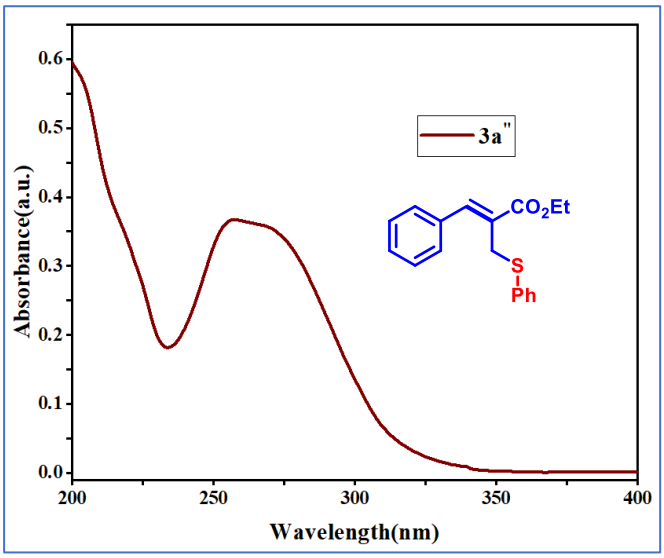


Figure S8. UV-visible spectra of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a″**).

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing Na_2 – Eosin Y **(P.C.)** in acetonitrile solvent (M = 0.011 × 10^{-8} mol/L). The absorption was recorded, and the obtained result was reported. For the same above solution mixture, the fluorescence emission spectra were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 500nm, and the emission wavelength was measured at 565nm (emission maximum).

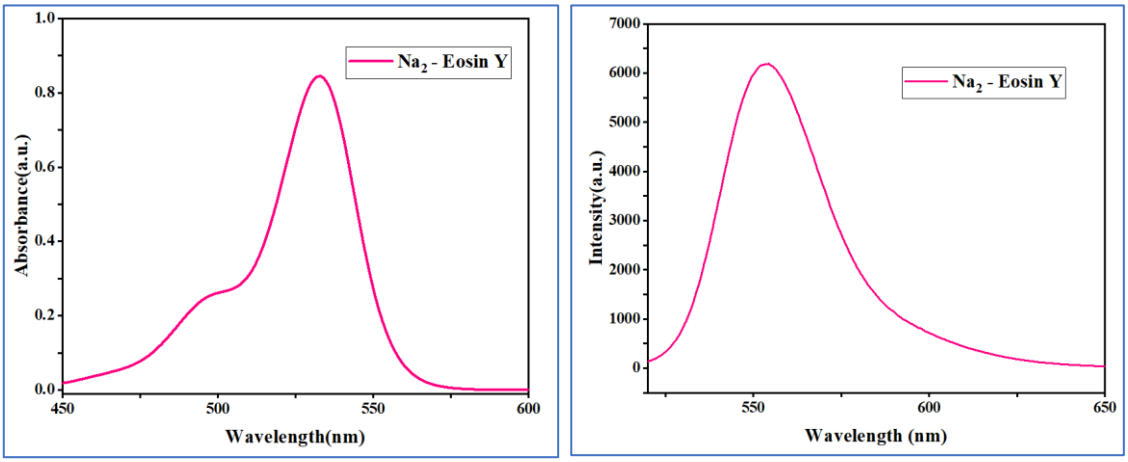


Figure S9. UV-visible spectra and fluorescence emission spectra of **Photo catalyst.**

The fluorescence emission intensities were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 510nm, and the emission wavelength was measured at 560nm (emission maximum). The samples were prepared by mixing by Na_2-EosinY (0.011 × 10^{-8} mol/L) and different amount of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate (**1a**) in acetonitrile solvent (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate (**1a**) stock solution is 0.37 × 10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate (**1a**) was titrated to a mixed solution of Na_2-EosinY (0.1mL, in a total volume = 1.0mL). Then the emission intensity was recorded.

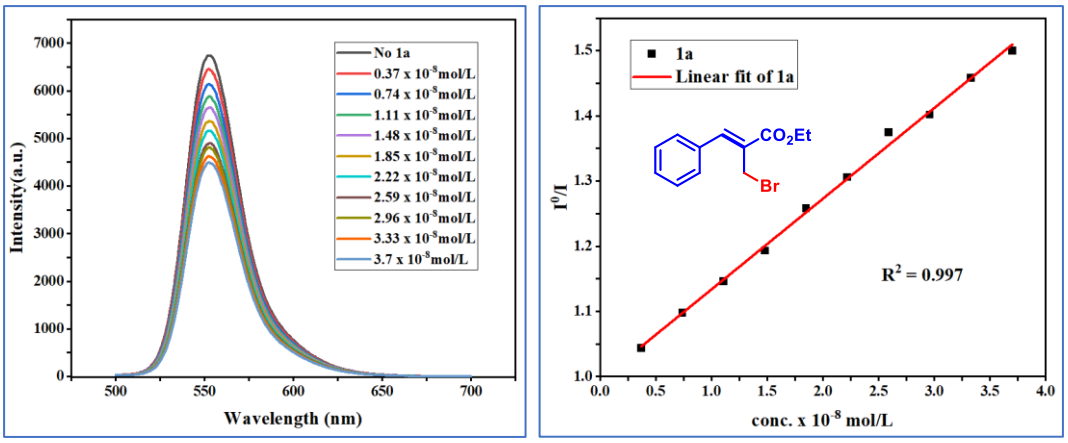


Figure S10. – Quenching of Na2-Eosin Y fluorescence emission in the presence of ethyl (Z)-2-(bromomethyl)-3-phenylacrylate (**1a**) and Stern-Volmer Plot.

The fluorescence emission intensities were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 510nm, and the emission wavelength was measured at 560nm (emission maximum). The samples were prepared by mixing by Na_2-EosinY (0.011 × 10^{-8} mol/L) and different amount of thiophenol (**2a**) in acetonitrile solvent (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of thiophenol (**2a**) stock solution is 1.08 × 10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of thiophenol (**2a**) was titrated to a mixed solution of Na_2-EosinY (0.1mL, in a total volume = 1.0mL). Then the emission intensity was recorded.

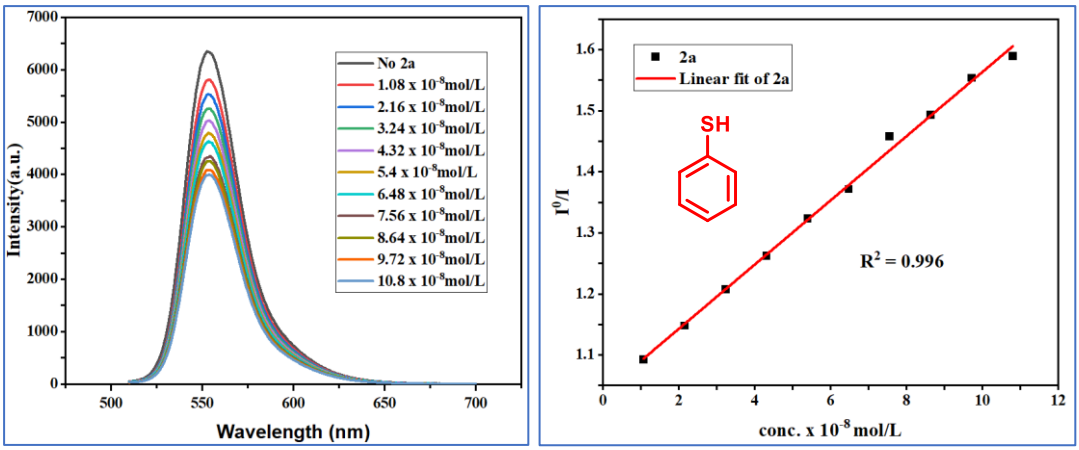


Figure S11. – Quenching of Na2-Eosin Y fluorescence emission in the presence of thiophenol (**2a**) and Stern-Volmer Plot

The fluorescence emission intensities were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 510nm, and the emission wavelength was measured at 560nm (emission maximum). The samples were prepared by mixing by Na_2-EosinY (0.011×10^{-8} mol/L) and different amount of **Et_3N** in acetonitrile solvent (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of **Et_3N** stock solution is 0.37×10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of **Et_3N** was titrated to a mixed solution of Na_2-EosinY (0.1mL, in a total volume = 1.0mL). Then the emission intensity was recorded.

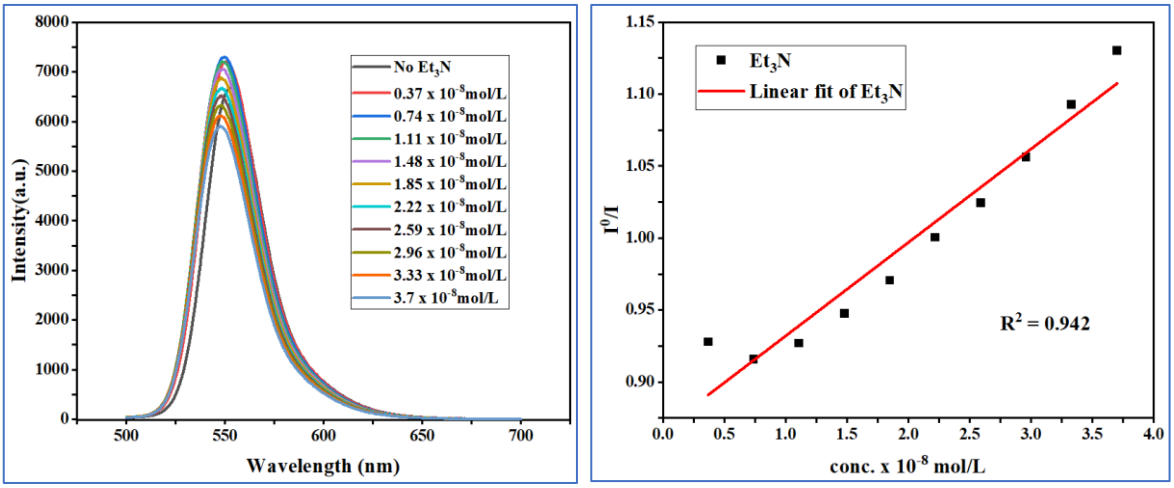


Figure S12. – Quenching of Na_2-Eosin Y fluorescence emission in the presence of **Et_3N** and Stern-Volmer Plot.

The fluorescence emission intensities were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 510nm, and the emission wavelength was measured at 560nm (emission maximum). The samples were prepared by mixing by Na_2-EosinY (0.011×10^{-8} mol/L) and different amount of **TEMPO** in acetonitrile solvent (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of **TEMPO** stock solution is 0.19×10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of **TEMPO** was titrated to a mixed solution of Na_2-EosinY (0.1mL, in a total volume = 1.0mL). Then the emission intensity was recorded.

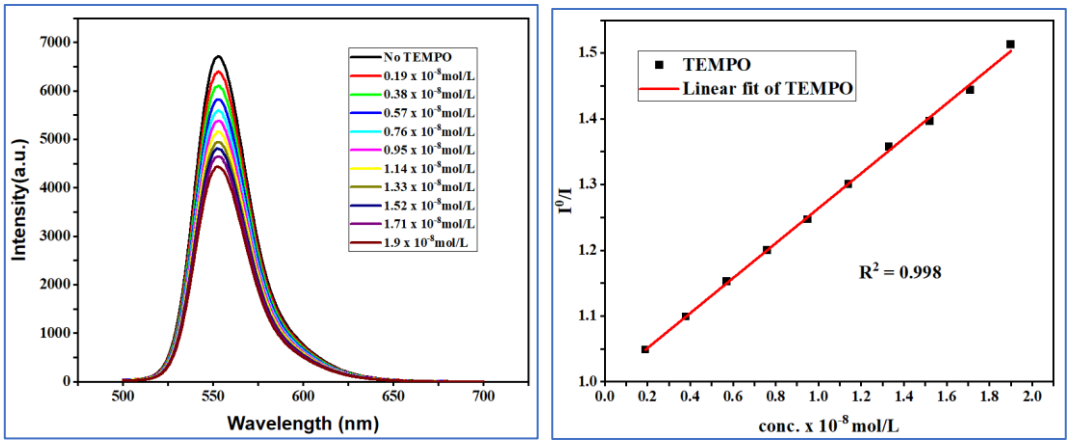


Figure S13. – Quenching of Na_2-Eosin Y fluorescence emission in the presence of **TEMPO** and Stern-Volmer Plot.

The fluorescence emission intensities were recorded using a Horiba FluoroMax^{-4} spectrofluorometer. The excitation wavelength was fixed at 510nm, and the emission wavelength was measured at 560nm (emission maximum). The samples were prepared by mixing by Na_2-EosinY (0.011 × 10^{-8} mol/L) and different amount of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a''**) in acetonitrile solvent (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a''**) stock solution is 0.31 × 10^{-8}mol/L in CH_3CN. For each quenching experiment, 0.1mL of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a''**) was titrated to a mixed solution of Na_2-EosinY (0.1mL, in a total volume = 1.0mL). Then the emission intensity was recorded.

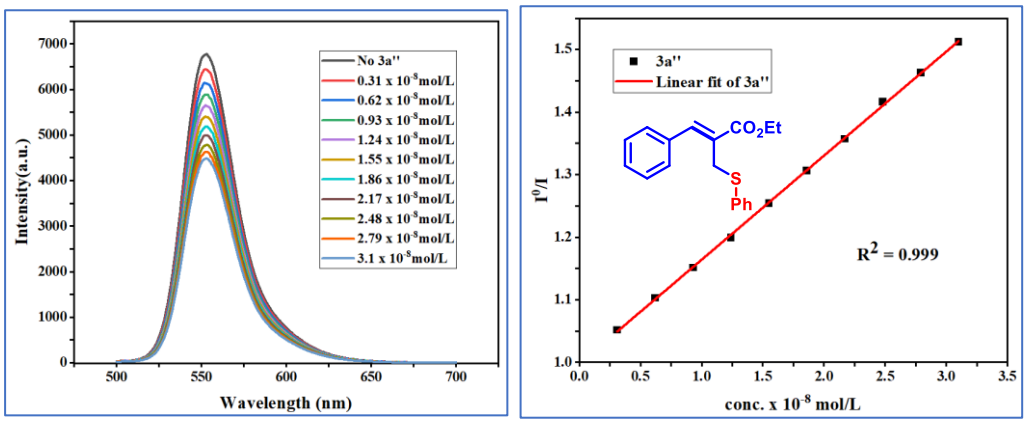
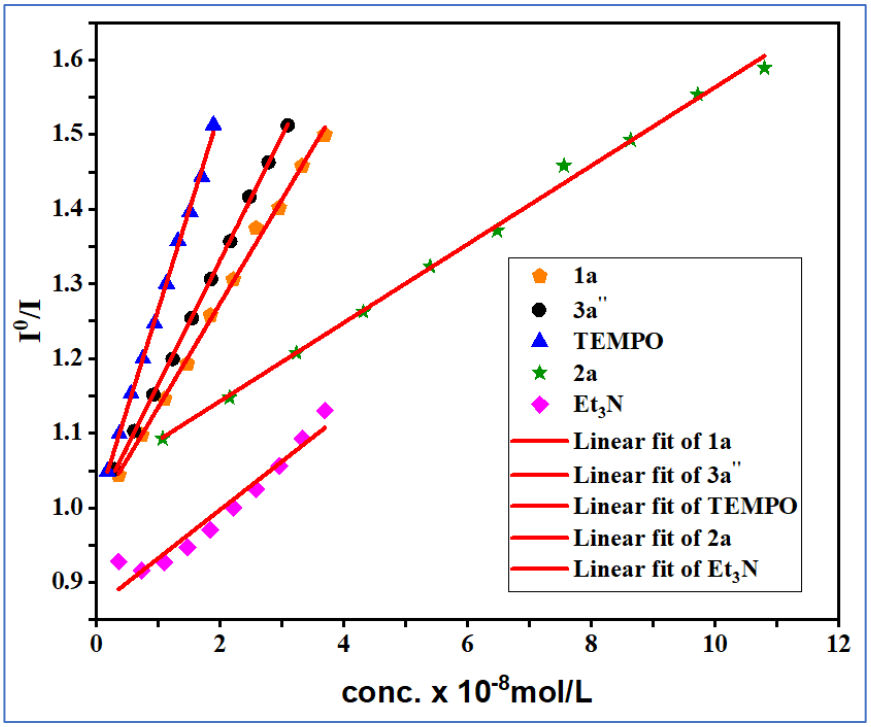
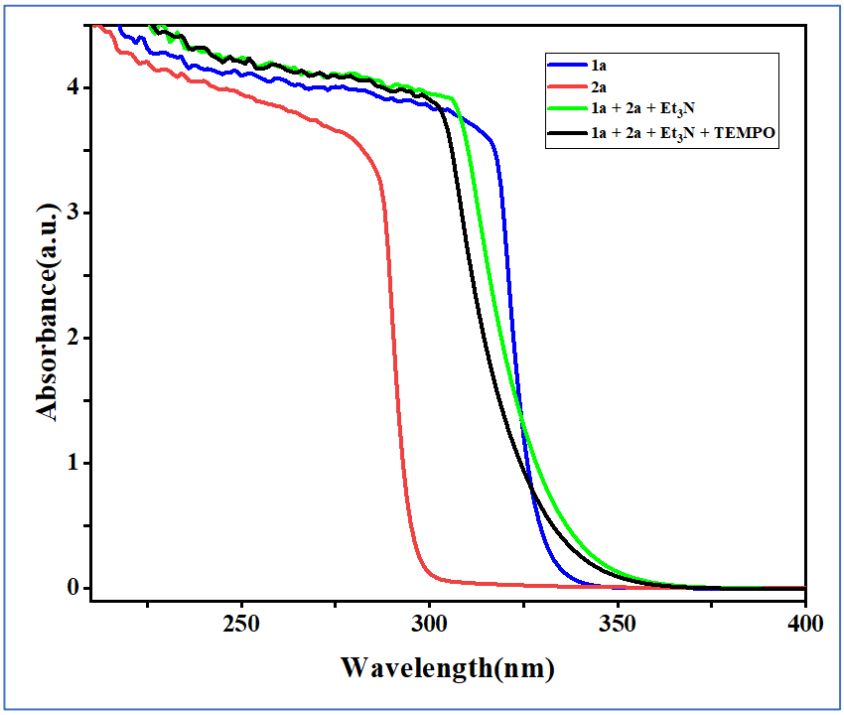


Figure S14. – Quenching of Na2-Eosin Y fluorescence emission in the presence of ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (**3a''**) and Stern-Volmer Plot.

Stern-Volmer Plot:



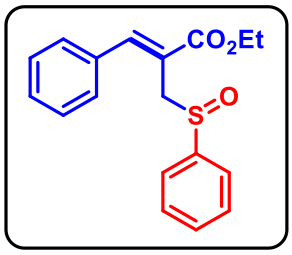
14. EDA complex studies



To verify the formation of an EDA complex, UV– Visible absorption spectra of all components in the reaction system were recorded individually, as shown in above figure. Upon mixing three components, **1a,** thiophenol (**2a**), and Et_3N, we were didn't observed bathochromic shift, even with the addition of TEMPO. Therefore, these results may conclude the nonexistence of EDA complex during the course of the reaction.

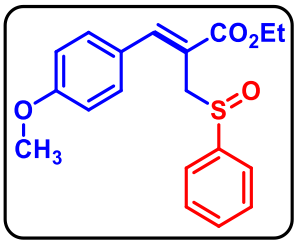
15. Spectral data of compounds

Ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3a)



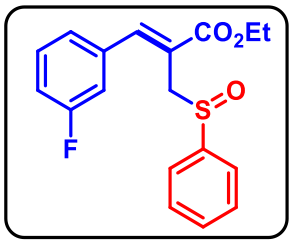
Yellow semisolid, 0.11mmol, 34 mg, 91%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.03 (s, 1H), 7.69 – 7.63 (m, 2H), 7.57 – 7.53 (m, 2H), 7.48 – 7.43 (m, 3H), 7.39 – 7.33 (m, 3H), 4.25 – 4.16 (m, 3H), 3.98 (d, *J* = 12.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.7, 145.9, 143.9, 134.0, 131.2, 129.5, 129.3, 129.1, 128.6, 124.2, 122.5, 61.5, 56.8, 14.2; HRMS (ESI): calcd. for $C_{18}H_{18}O_3S$ [M + Na^+] 337.0869; found 337.0869.

Ethyl (Z)-3-(4-methoxyphenyl)-2-((phenylsulfinyl)methyl)acrylate (3b)



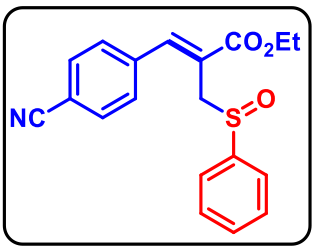
Yellow semisolid, 0.11mmol, 20mg, 55%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.98 (s, 1H), 7.70 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.47 (m, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.25 – 4.12 (m, 3H), 4.03 (d, *J* = 12.6 Hz, 1H), 3.84 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 167.0, 160.9, 145.6, 143.9, 131.5, 131.2, 129.0, 126.6, 124.2, 119.9, 114.1, 61.3, 57.0, 55.3, 14.2; HRMS (ESI): calcd. for $C_{19}H_{20}O_4S$ [M + Na^+] 367.0975; found 367.0981.

Ethyl (Z)-3-(3-fluorophenyl)-2-((phenylsulfinyl)methyl)acrylate (3c)



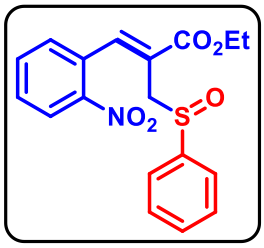
Yellow semisolid, 0.11mmol, 23mg, 67%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.99 (s, 1H), 7.69 – 7.64 (m, 2H), 7.51 – 7.47 (m, 3H), 7.36 – 7.31 (m, 2H), 7.31 – 7.28 (m, 1H), 7.05 (ddd, *J* = 8.7, 5.3, 2.3 Hz, 1H), 4.26 (qd, *J* = 7.1, 3.6 Hz, 2H), 4.15 – 4.11 (m, 1H), 3.95 (dd, *J* = 12.5, 0.5 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.3, 162.5, 160.6, 143.57 (d, *J* = 2.2 Hz), 142.8, 135.10 (d, *J* = 8.0 Hz), 130.2, 129.15 (d, *J* = 8.3 Hz), 128.1, 124.04 (d, *J* = 3.0 Hz), 123.1, 122.8, 115.3, 115.20 (d, *J* = 2.8 Hz), 115.0, 60.6, 55.6, 13.21; HRMS (ESI): calcd. for $C_{18}H_{17}FO_3S$ [M + Na^+] 355.0775; found 355.0775.

Ethyl (Z)-3-(4-cyanophenyl)-2-((phenylsulfinyl)methyl)acrylate (3d)



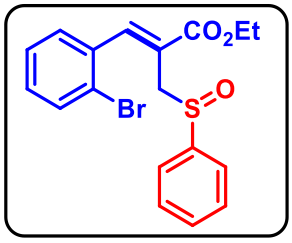
White semisolid, 0.16mmol, 37mg, 65%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.97 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 6.8, 4.1 Hz, 4H), 7.44 (dd, *J* = 5.1, 1.9 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 12.7 Hz, 1H), 3.84 (d, *J* = 12.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.0, 142.7, 137.4, 131.2, 130.3, 128.8, 128.3, 124.4, 122.9, 117.3, 111.8, 60.9, 55.7, 13.2; HRMS (ESI): calcd. for $C_{19}H_{17}NO_3S$ [M + Na^+] 362.0821; found 362.0816.

Ethyl (Z)-3-(2-nitrophenyl)-2-((phenylsulfinyl)methyl)acrylate (3e)



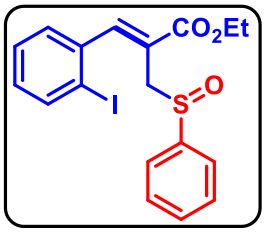
Yellow semisolid, 0.13mmol, 10mg, 21%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.04 (s, 1H), 7.70 – 7.63 (m, 2H), 7.55 (ddd, *J* = 3.7, 1.9, 0.5 Hz, 2H), 7.48 – 7.46 (m, 2H), 7.38 (dt, *J* = 3.7, 1.1 Hz, 3H), 4.28 – 4.16 (m, 3H), 4.01 – 3.97 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.1, 144.1 142.9, 133.3, 131.7, 130.2, 130.0, 129.5, 128.1, 126.4, 123.1, 123.0, 60.6, 55.9, 13.2; HRMS (ESI): calcd. for $C_{18}H_{17}NO_5S$ [M + H^+] 360.0900; found 360.0900.

Ethyl (Z)-3-(2-bromophenyl)-2-((phenylsulfinyl)methyl)acrylate (3f)



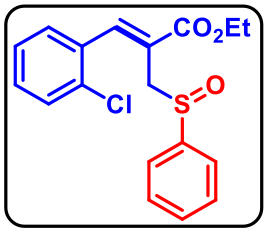
Yellow semisolid, 0.11mmol, 31mg, 70%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.99 (s, 1H), 7.72 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.31 – 7.28 (m, 1H), 7.15 (ddd, *J* = 7.5, 1.6, 0.8 Hz, 1H), 4.23 – 4.14 (m, 2H), 3.96 – 3.89 (m, 1H), 3.80 (dd, *J* = 12.5, 0.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.1, 144.1, 142.8, 133.3, 131.7, 130.2, 130.0, 129.5, 128.1, 126.4, 123.2 – 122.9 (m), 60.6, 55.8, 13.2; HRMS (ESI): calcd. for $C_{18}H_{17}BrO_3S$ [M + Na^+] 414.9974; found 414.9979.

Ethyl (Z)-3-(2-iodophenyl)-2-((phenylsulfinyl)methyl)acrylate (3g)



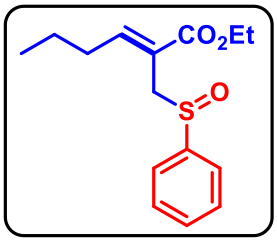
Yellow semisolid, 0.12mmol, 13mg, 25%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.00 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.12 (m, 1H), 4.24 – 4.13 (m, 2H), 3.92 (d, *J* = 12.5 Hz, 1H), 3.80 (d, *J* = 12.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.1, 144.1, 142.9, 133.3, 131.7, 130.1 (d, *J* = 17.6 Hz), 129.5, 128.1, 126.4, 123.29 – 122.98 (m), 60.6, 55.9, 13.2; HRMS (ESI): calcd. for $C_{18}H_{17}IO_3S$ [M + Na^+] 462.9835; found 462.9835.

Ethyl (Z)-3-(2-chlorophenyl)-2-((phenylsulfinyl)methyl)acrylate (3h)



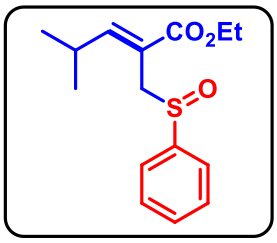
Yellow semisolid, 0.13mmol, 16 mg, 34%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.00 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.15 (td, *J* = 7.9, 1.5 Hz, 1H), 4.25 – 4.14 (m, 2H), 3.92 (d, *J* = 12.8 Hz, 1H), 3.80 (dd, *J* = 12.5, 0.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.1, 144.1, 142.9, 133.3, 131.7, 130.1 (d, *J* = 16.4 Hz), 129.5, 128.1, 126.4, 123.2 – 122.96 (m), 60.6, 55.9, 13.2; HRMS (ESI): calcd. for $C_{18}H_{17}ClO_3S$ [M + H^+] 349.0660; found 349.0661.

Ethyl (Z)-2-((phenylsulfinyl)methyl)hex-2-enoate (3i)



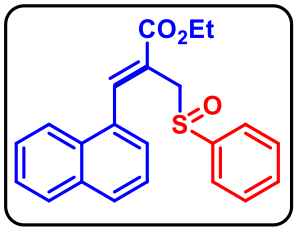
Yellow semisolid, 0.23mmol, 53mg, 82%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.56 (dd, *J* = 3.0, 2.3 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.06 – 3.96 (m, 2H), 3.87 (d, *J* = 12.5 Hz, 1H), 3.78 (d, *J* = 12.6 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.98 – 1.89 (m, 1H), 1.39 – 1.28 (m, 2H), 1.17 (td, *J* = 7.1, 0.9 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.1, 149.45, 142.5, 130.1, 127.9, 123.3, 120.8, 60.0, 54.8, 30.2, 20.8, 13.1, 12.8; HRMS (ESI): calcd. for $C_{15}H_{20}O_3S$ [M + Na^+] 303.1025; found 303.1026.

Ethyl (Z)-4-methyl-2-((phenylsulfinyl)methyl)pent-2-enoate (3j)



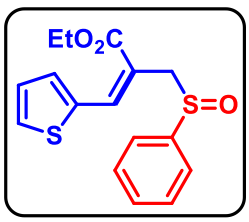
Yellow semisolid, 0.18mmol, 46mg, 89%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.59 – 7.54 (m, 2H), 7.44 – 7.39 (m, 3H), 6.83 (d, *J* = 10.7 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.85 (d, *J* = 12.6 Hz, 1H), 3.78 (d, *J* = 12.6 Hz, 1H), 2.62 – 2.45 (m, 1H), 1.17 (td, *J* = 7.1, 0.8 Hz, 3H), 1.00 (dd, *J* = 6.6, 0.7 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.3, 155.3, 142.6, 130.1, 128.0, 123.3, 118.5, 60.0, 54.9, 27.8, 21.2, 20.7, 13.1; HRMS (ESI): calcd. for $C_{15}H_{20}O_3S$ [M + Na^+] 303.1025; found 303.1026.

Ethyl(Z)-3-(naphthalen-1-yl)-2-((phenylsulfinyl)methyl)acrylate (3k)



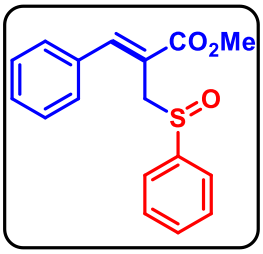
Yellow semisolid, 0.25mmol, 41mg, 44%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.55 (s, 1H), 7.85 (dd, *J* = 6.8, 2.1 Hz, 2H), 7.75 (ddd, *J* = 12.6, 6.2, 3.9 Hz, 2H), 7.56 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.37 – 7.30 (m, 3H), 4.38 – 4.27 (m, 2H), 4.09 (dd, *J* = 12.4, 0.4 Hz, 1H), 3.96 (dd, *J* = 12.4, 0.6 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.3, 143.4, 142.8, 132.2, 130.1, 130.0, 129.9, 128.6, 127.9, 127.5, 126.3, 125.5, 125.2, 124.3, 123.6, 123.3, 123.1, 60.6, 56.1, 13.2; HRMS (ESI): calcd. for $C_{22}H_{20}O_3S$ [M + Na^+] 387.1025; found 387.1026.

Ethyl (E)-2-((phenylsulfinyl)methyl)-3-(thiophen-2-yl)acrylate (3l)



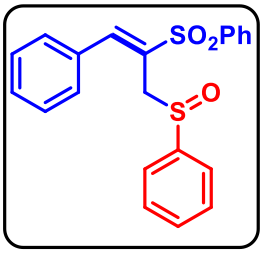
Yellow semisolid, 0.17mmol, 9mg, 16%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.01 (s, 1H), 7.69 – 7.57 (m, 2H), 7.47 (d, *J* = 5.1 Hz, 1H), 7.41 (dd, *J* = 5.0, 2.0 Hz, 4H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.36 (d, *J* = 12.7 Hz, 1H), 4.16 (d, *J* = 12.7 Hz, 1H), 4.06 – 3.91 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.6, 143.7, 137.2 (d, *J* = 15.6 Hz), 134.0, 131.3, 130.6, 129.7, 129.0, 127.7, 124.4, 117.8, 61.4, 57.1, 14.1; HRMS (ESI): calcd. for $C_{16}H_{16}O_3S_2$ [M + Na^+] 343.0433; found 343.0427.

Methyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3m)



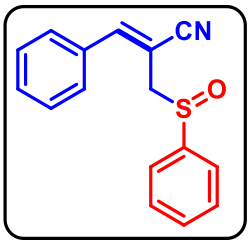
Yellow semisolid, 0.17mmol, 41mg, 74%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.96 (s, 1H), 7.61 – 7.56 (m, 2H), 7.46 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.33 – 7.27 (m, 3H), 4.11 (d, *J* = 12.5 Hz, 1H), 3.93 (d, *J* = 12.5 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 167.2, 146.2, 143.7, 133.9, 131.2, 129.5, 129.3, 129.1, 128.6, 124.2, 122.1, 56.7, 52.4; HRMS (ESI): calcd. for $C_{17}H_{16}O_3S$ [M + Na^+] 323.0712; found 323.0720.

(E)-((3-phenyl-2-(phenylsulfonyl)allyl)sulfinyl)benzene (3n)



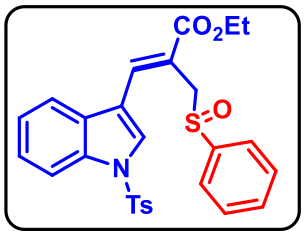
Yellow semisolid, 0.10mmol, 22mg, 57%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.03 (s, 1H), 7.95 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.56 – 7.50 (m, 4H), 7.42 (dd, *J* = 6.9, 1.1 Hz, 2H), 7.36 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.31 – 7.27 (m, 3H), 4.03 (d, *J* = 2.5 Hz, 1H), 3.84 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 144.2, 142.3, 138.1, 133.0, 132.0, 131.1, 130.5, 129.3, 128.5,128.4, 128.2, 127.7, 127.4, 123.0, 55.3; HRMS (ESI): calcd. for $C_{21}H_{18}O_3S_2$ [M + Na^+] 405.0590; found 405.0589.

(Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylonitrile (3o)



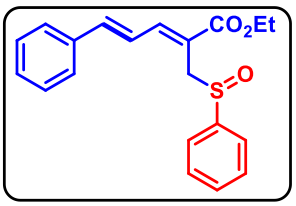
Yellow semisolid, 0.15mmol, 16mg, 40%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.62 (dd, *J* = 5.4, 1.9 Hz, 2H), 7.56 (dt, *J* = 7.6, 2.1 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.36 (s, 3H), 6.90 (s, 1H), 3.73 (dd, *J* = 13.2, 1.4 Hz, 1H), 3.64 (dd, *J* = 13.2, 1.7 Hz, 1H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 150.3, 141.2, 132.8, 131.9, 131.1, 129.4, 129.2, 128.9, 124.3, 117.5, 98.0, 61.9; HRMS (ESI): calcd. for $C_{16}H_{13}NOS$ [M + Na^+] 290.0610; found 290.0613.

Ethyl (Z)-2-((phenylsulfinyl)methyl)-3-(1-tosyl-1H-indol-3-yl)acrylate (3p)



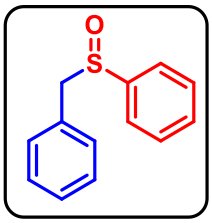
Yellow semisolid, 0.10mmol, trace, Eluent (10% ethyl acetate in hexane); HRMS (ESI): calcd. for $C_{27}H_{25}NO_5S_2$ [M + Na^+] 530.1066; found 530.1068.

Ethyl (2Z,4E)-5-phenyl-2-((phenylsulfinyl)methyl)penta-2,4-dienoate (3q)



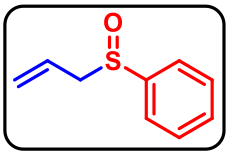
Yellow semisolid, 0.13mmol, trace, Eluent (10% ethyl acetate in hexane); HRMS (ESI): calcd. for $C_{20}H_{20}O_3S$ [M + H^+] 341.1206; found 341.1208.

(Benzylsulfinyl)benzene (3s)



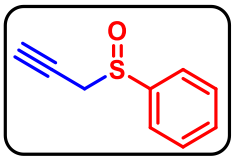
Pale Yellow solid, 0.17mmol, 27mg, 71%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.48 – 7.35 (m, 5H), 7.28 (ddd, *J* = 6.0, 3.5, 1.4 Hz, 2H), 7.24 (dd, *J* = 6.8, 1.7 Hz, 1H), 6.98 (d, *J* = 6.7 Hz, 2H), 4.05 (dd, *J* = 49.3, 12.6 Hz, 2H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 142.7, 131.1, 130.3, 129.1, 128.8, 128.4, 128.2, 124.4, 63.6; HRMS (ESI): calcd. for $C_{13}H_{12}OS$ [M + Na^+] 239.0501; found 239.0501.

(allylsulfinyl)benzene (3t)



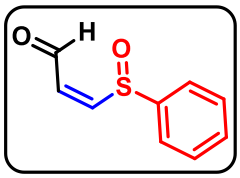
Pale Yellow solid, 0.41mmol, 27mg, 40%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.56 – 7.51 (m, 2H), 7.48 – 7.42 (m, 3H), 5.58 (ddt, *J* = 17.6, 10.2, 7.5 Hz, 1H), 5.29 – 5.24 (m, 1H), 5.13 (ddd, *J* = 17.1, 2.4, 1.2 Hz, 1H), 3.53 – 3.42 (m, 2H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 142.9, 131.1, 129.0, 125.2, 124.3, 123.9, 60.8; HRMS (ESI): calcd. for $C_9H_{10}OS$ [M + H^+] 167.0525; found 167.0524.

(prop-2-yn-1-ylsulfinyl)benzene (3u)



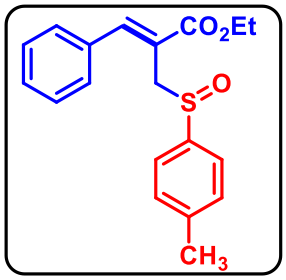
Yellow semisolid, 0.45mmol, 16mg, 21%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.68 – 7.63 (m, 2H), 7.50 – 7.46 (m, 3H), 3.59 (qd, J = 15.7, 2.7 Hz, 2H), 2.28 (t, J = 2.7 Hz, 1H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 142.7, 131.8, 129.1, 124.5, 76.4, 72.6, 47.7; HRMS (ESI): calcd. for C_9H_8OS [M + H^+] 165.0369; found 165.0364.

(Z)-3-(phenylsulfinyl)acrylaldehyde (3v)



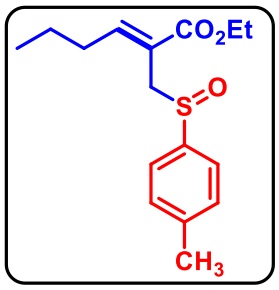
Yellow semisolid, 0.45mmol, 8 mg, 11%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 9.66 (d, *J* = 7.0 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.52 – 7.48 (m, 3H), 7.37 (d, *J* = 15.1 Hz, 1H), 6.90 (dd, *J* = 15.1, 7.0 Hz, 1H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 188.9, 157.3, 140.9, 132.2, 131.6, 130.0, 124.8; HRMS (ESI): calcd. for $C_9H_8O_2S$ [M + H^+] 181.0318; found 181.0326.

Ethyl (Z)-3-phenyl-2-((p-tolylsulfinyl)methyl)acrylate (4a)



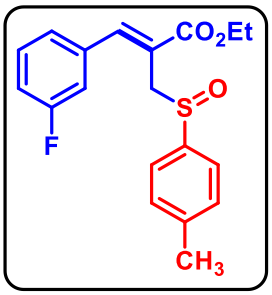
Yellow semisolid, 0.18mmol, 38mg, 63%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.93 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 4H), 7.33 – 7.26 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.18 – 4.07 (m, 3H), 3.90 (d, *J* = 12.8 Hz, 1H), 2.30 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.7, 144.7, 140.6, 139.5, 133.0, 128.7, 128.3 (d, *J* = 4.8 Hz), 127.5, 123.2, 121.5, 60.4, 55.8, 20.3, 13.2; HRMS (ESI): calcd. for $C_{19}H_{20}O_3S$ [M + Na^+] 351.1025; found 351.1032.

Ethyl (Z)-2-((p-tolylsulfinyl)methyl)hex-2-enoate (4b)



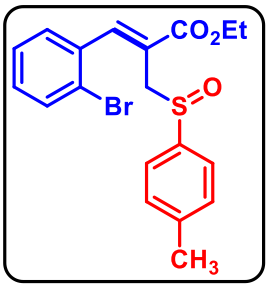
Yellow semisolid, 0.20mmol, 30mg, 51%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.88 (dd, *J* = 51.3, 12.5 Hz, 2H), 2.41 (s, 3H), 2.20 – 1.96 (m, 2H), 1.46 – 1.34 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.1, 150.3, 141.6, 140.3, 129.6, 124.4, 121.9, 61.0, 55.9, 31.2, 21.8, 21.4, 14.1, 13.8; HRMS (ESI): calcd. for $C_{16}H_{22}O_3S$ [M + Na^+] 317.1182; found 317.1189.

Ethyl (Z)-3-(3-fluorophenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4c)



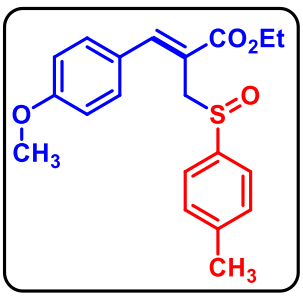
White semisolid, 0.11mmol, 18mg, 45%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.96 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.23 (d, *J* = 10.4 Hz, 2H), 7.08 – 7.02 (m, 1H), 4.31 – 4.21 (m, 2H), 4.12 (d, *J* = 12.5 Hz, 1H), 3.94 (d, *J* = 12.4 Hz, 1H), 2.39 (s, 3H), 1.35 (td, *J* = 7.1, 1.2 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.4, 163.6, 161.6, 144.4 (d, *J* = 2.1 Hz), 141.8, 140.5, 136.1 (d, *J* = 7.9 Hz), 130.1 (d, *J* = 8.3 Hz), 129.8, 125.0 (d, *J* = 2.9 Hz), 124.1, 123.8, 116.1 (dd, *J* = 21.9, 15.2 Hz), 61.6, 56.6, 21.3, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}FO_3S$ [M + Na^+] 369.0931; found 369.0942.

Ethyl (Z)-3-(2-bromophenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4d)



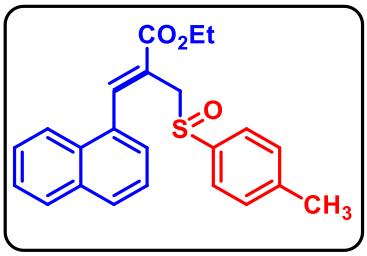
Yellow semisolid, 0.12mmol, 28mg, 56%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.97 (s, 1H), 7.71 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (td, *J* = 7.6, 0.7 Hz, 1H), 7.19 – 7.12 (m, 3H), 4.26 – 4.12 (m, 2H), 3.86 (dd, *J* = 63.0, 12.5 Hz, 2H), 2.31 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.2, 144.9, 141.7, 140.6, 134.4, 132.7, 131.1, 130.5, 129.8, 127.4, 124.2, 124.1, 61.6, 56.9, 21.4, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}BrO_3S$ [M + Na^+] 429.0130; found 429.0136.

Ethyl (Z)-3-(4-methoxyphenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4e)



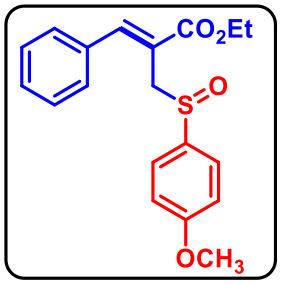
White semisolid, 0.14mmol, 22mg, 44%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.89 (s, 1H), 7.55 – 7.46 (m, 4H), 7.21 (s, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.16 – 4.05 (m, 3H), 3.94 (d, *J* = 12.6 Hz, 1H), 3.77 (s, 3H), 2.32 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.0, 159.8, 144.4, 140.6, 139.6, 130.4, 128.7, 125.6, 123.2, 119.0, 113.0, 60.3, 56.0, 54.3, 20.3, 13.2; HRMS (ESI): calcd. for $C_{20}H_{22}O_4S$ [M + Na^+] 381.1131; found 381.1138.

Ethyl (Z)-3-(naphthalen-1-yl)-2-((p-tolylsulfinyl)methyl)acrylate (4f)



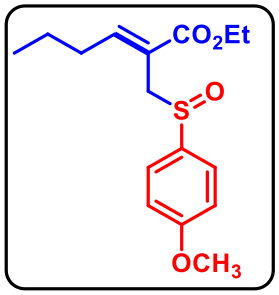
Yellow semisolid, 0.13mmol, 16mg, 30%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.51 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.71 (dd, *J* = 8.6, 0.9 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.49 (dddd, *J* = 16.7, 8.3, 6.9, 1.5 Hz, 3H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.12 – 7.04 (m, 2H), 4.32 (dd, *J* = 10.2, 7.2 Hz, 2H), 4.05 (ddd, *J* = 59.8, 12.3, 0.6 Hz, 2H), 2.26 (s, 3H), 1.40 (s, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.4, 144.2, 141.6, 140.4, 133.3, 131.2, 131.0, 129.7, 129.6, 128.5, 127.3, 126.4, 126.2, 125.3, 124.6, 124.3,124.2, 61.6, 57.0, 21.3, 14.3; HRMS (ESI): calcd. for $C_{23}H_{22}O_3S$ [M + Na^+] 401.1182; found 401.1189.

Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-phenylacrylate (4g)



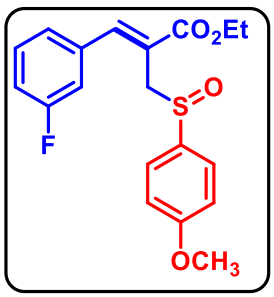
Yellow semisolid, 0.18mmol, 40mg, 58%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.99 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.40 – 7.33 (m, 3H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.30 – 4.13 (m, 3H), 3.99 (d, *J* = 12.5 Hz, 1H), 3.83 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.7, 162.1, 145.6, 134.5, 134.1, 129.3 (d, *J* = 6.6 Hz), 128.5, 126.1, 122.5, 114.5, 61.5, 56.7, 55.5, 14.2; HRMS (ESI): calcd. for $C_{19}H_{20}O_4S$ [M + Na^+] 367.0975; found 367.0976.

Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)hex-2-enoate (4h)



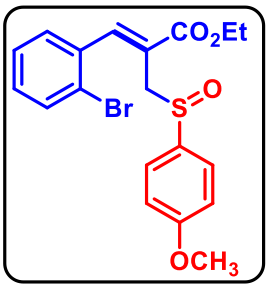
Yellow semisolid, 0.19mmol, 35mg, 60%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.56 (d, *J* = 8.9 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.15 – 4.03 (m, 2H), 3.94 (d, *J* = 12.5 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 1H), 2.20 – 1.98 (m, 2H), 1.48 – 1.34 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.16, 162.1, 150.1, 134.3, 126.2, 121.9, 114.5, 61.0, 55.8, 55.5, 31.2, 21.8, 14.1, 13.8; HRMS (ESI): calcd. for $C_{16}H_{22}O_4S$ [M + Na^+] 333.1131; found 333.1139.

Ethyl (Z)-3-(3-fluorophenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4i)



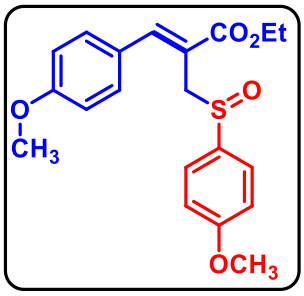
Yellow semisolid, 0.12mmol, 21mg, 46%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.94 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.33 (ddd, *J* = 22.8, 12.5, 6.8 Hz, 2H), 7.23 (dd, *J* = 9.7, 1.8 Hz, 1H), 7.05 (tdd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.30 – 4.20 (m, 2H), 4.13 (dd, *J* = 12.4, 0.4 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.84 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.4, 163.5, 162.2, 161.6, 144.2 (d, *J* = 2.2 Hz), 136.2 (d, *J* = 7.9 Hz), 134.4, 130.1 (d, *J* = 8.3 Hz), 126.0, 125.0 (d, *J* = 2.9 Hz), 123.8 (s), 116.2 (d, *J* = 19.8 Hz), 115.9, 114.6, 61.6, 56.6, 55.5, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}FO_4S$ [M + Na^+] 385.0880; found 385.0893.

Ethyl (Z)-3-(2-bromophenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4j)



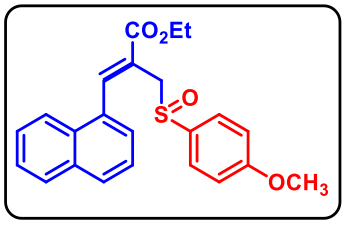
Yellow semisolid, 0.12mmol, 30mg, 61%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.02 (s, 1H), 7.75 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.37 (td, *J* = 7.5, 0.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.31 – 4.20 (m, 2H), 3.97 (ddd, *J* = 9.8, 8.1, 0.5 Hz, 2H), 3.84 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.1, 162.1, 144.8, 134.4 (d, *J* = 9.7 Hz), 132.7, 131.0, 130.5, 128.5, 127.4, 126.1, 124.1 (d, *J* = 13.8 Hz), 114.7, 61.6, 56.7, 55.5, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}BrO_4S$ [M + Na^+] 445.0080; found 445.0085.

Ethyl (Z)-3-(4-methoxyphenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4k)



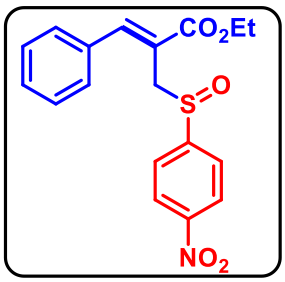
Yellow semisolid, 0.14mmol, 17mg, 35%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.86 (s, 1H), 7.51 (dd, *J* = 11.5, 8.7 Hz, 4H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.12 (ddd, *J* = 23.1, 14.2, 7.7 Hz, 3H), 3.95 (d, *J* = 12.5 Hz, 1H), 3.77 (d, *J* = 5.0 Hz, 6H), 1.23 (s, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 167.0, 162.1, 160.8, 145.3, 134.6, 131.4, 126.7, 126.1, 120.0, 114.5, 114.1, 61.3, 56.9, 55.4 (d, *J* = 17.4 Hz), 14.2; HRMS (ESI): calcd. for $C_{20}H_{22}O_5S$ [M + Na^+] 397.1080; found 397.1083.

Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4l)



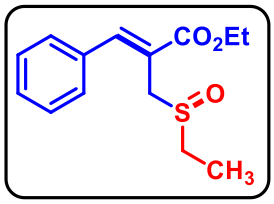
Yellow semisolid, 0.14mmol, 25mg, 45%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.48 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.68 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.41 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 4.33 (dddd, *J* = 17.9, 10.8, 7.1, 3.6 Hz, 2H), 4.07 (ddd, *J* = 60.0, 12.3, 0.5 Hz, 2H), 3.72 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.4, 161.9, 144.1, 134.3, 133.3, 131.2, 132.1, 129.6, 128.5, 127.2, 126.5, 126.2, 125.3, 124.6, 124.3, 61.6, 56.8, 55.3, 14.3; HRMS (ESI): calcd. for $C_{23}H_{22}O_4S$ [M + Na^+] 417.1131; found 417.1138.

ethyl (Z)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-phenylacrylate (4m)



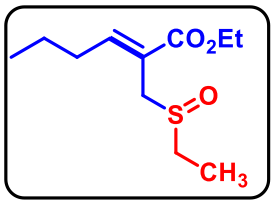
Yellow semisolid, 0.14mmol, 12mg, 23%; Eluent (2% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.03 – 7.90 (m, 2H), 7.79 (s, 1H), 7.35 (m, 5H), 7.24 – 7.21 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.7, 146.9, 142.4, 134.5, 129.4, 129.3, 128.8, 128.3, 127.3, 127.1, 123.8, 61.5, 30.4, 14.2; HRMS (ESI): calcd. for $C_{18}H_{17}NO_5S$ [M + Na^+] 382.0720; found 382.0723.

Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-phenylacrylate (4n)



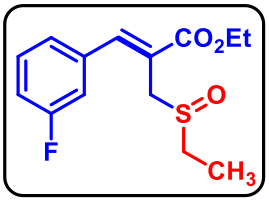
White semisolid, 0.18mmol, 27mg, 57%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.02 (s, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.34 (ddd, *J* = 13.3, 8.5, 4.4 Hz, 3H), 4.25 (d, *J* = 7.1 Hz, 2H), 3.88 (dd, *J* = 39.5, 12.6 Hz, 2H), 2.71 (ddd, *J* = 43.1, 13.2, 7.5 Hz, 2H), 1.28 (dt, *J* = 13.5, 7.3 Hz, 6H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.9, 145.6, 134.1, 129.5 (d, *J* = 7.9 Hz), 128.7, 122.8, 61.6, 50.7, 46.2, 14.2, 6.6; HRMS (ESI): calcd. for $C_{14}H_{18}O_3S$ [M + Na^+] 289.0869; found 289.0866.

Ethyl (Z)-2-((ethylsulfinyl)methyl)hex-2-enoate (4o)



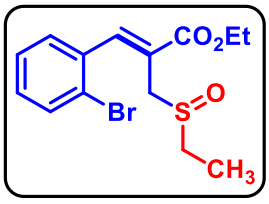
White semisolid, 0.19mmol, 17mg, 38%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.19 (t, *J* = 7.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 12.8 Hz, 1H), 3.72 (d, *J* = 12.8 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.35 (dt, *J* = 13.6, 7.6 Hz, 2H), 1.53 (ddd, *J* = 15.1, 7.3, 5.0 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.4, 150.30, 122.1, 61.2, 49.9, 45.6, 31.6, 21.9, 14.2, 13.9, 6.9; HRMS (ESI): calcd. for $C_{11}H_{20}O_3S$ [M + Na^+] 255.1025; found 255.1033.

Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-(3-fluorophenyl)acrylate (4p)



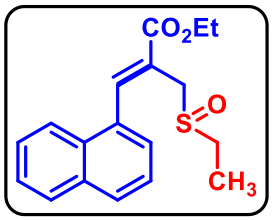
White semisolid, 0.12mmol, 17mg, 51%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.05 (s, 1H), 7.47 – 7.45 (m, 1H), 7.42 – 7.37 (m, 2H), 7.14 – 7.04 (m, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.97 – 3.84 (m, 2H), 2.89 – 2.74 (m, 2H), 1.37 (td, *J* = 7.3, 2.4 Hz, 6H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.6, 163.6, 161.7, 144.3 (d, *J* = 2.2 Hz), 136.2 (d, *J* = 7.9 Hz), 130.3 (d, *J* = 8.2 Hz), 125.2 (d, *J* = 3.0 Hz), 124.1, 116.3 (dd, *J* = 21.8, 18.8 Hz), 61.7, 50.5, 46.4, 14.2, 6.7; HRMS (ESI): calcd. for $C_{14}H_{17}FO_3S$ [M + Na^+] 307.0775; found 307.0778.

Ethyl (Z)-3-(2-bromophenyl)-2-((ethylsulfinyl)methyl)acrylate (4q)



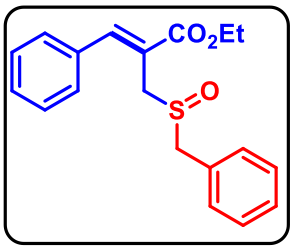
White semisolid, 0.10mmol, 20mg, 58%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.02 (d, *J* = 3.8 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 – 7.27 (m, 1H), 7.20 – 7.16 (m, 1H), 4.27 (d, *J* = 7.1 Hz, 2H), 3.77 – 3.70 (m, 2H), 2.76 – 2.54 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.2, 144.8, 134.5, 132.7, 131.2, 130.7, 127.7, 124.6, 123.9, 61.7, 50.8, 46.0, 14.2, 6.5; HRMS (ESI): calcd. for $C_{14}H_{17}BrO_3S$ [M + Na^+] 366.9974; found 366.9978.

Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4r)



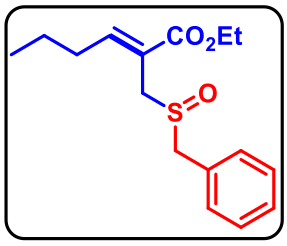
Yellow semisolid, 0.14mmol, trace, Eluent (10% ethyl acetate in hexane); HRMS (ESI): calcd. for $C_{18}H_{20}O_3S$ [M + K^+] 355.0765; found 355.0976.

Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-phenylacrylate (4s)



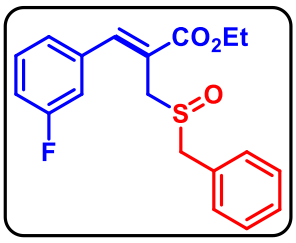
Yellow semisolid, 0.19mmol, 32mg, 52%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.08 (s, 1H), 7.60 – 7.50 (m, 2H), 7.39 – 7.28 (m, 8H), 4.28 (qd, *J* = 7.1, 1.6 Hz, 2H), 4.08 (q, *J* = 13.0 Hz, 2H), 3.94 (d, *J* = 12.8 Hz, 1H), 3.82 (dd, *J* = 12.6, 0.8 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.8, 145.9, 134.0, 130.3, 129.9, 129.5 (d, *J* = 5.6 Hz), 128.8, 128.6, 128.3, 122.7, 61.5, 58.9, 50.2, 14.2; HRMS (ESI): calcd. for $C_{19}H_{20}O_3S$ [M + Na^+] 351.1025; found 351.1037.

Ethyl (Z)-2-((benzylsulfinyl)methyl)hex-2-enoate (4t)



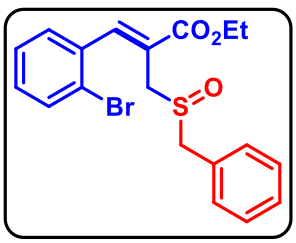
Yellow semisolid, 0.22mmol, 24mg, 36%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.43 – 7.28 (m, 5H), 7.20 (t, *J* = 7.7 Hz, 1H), 4.20 (qd, *J* = 7.1, 0.9 Hz, 2H), 4.01 (s, 2H), 3.73 (dd, *J* = 59.8, 12.8 Hz, 2H), 2.26 (ddd, *J* = 15.1, 9.6, 7.7 Hz, 2H), 1.48 (dt, *J* = 8.2, 7.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ166.4, 150.6, 130.4, 130.1, 128.9, 128.3, 122.2, 61.1, 58.8, 50.0, 31.5, 21.9, 14.1, 13.8; HRMS (ESI): calcd. for $C_{16}H_{22}O_3S$ [M + Na^+] 317.1182; found 317.1188.

Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(3-fluorophenyl)acrylate (4u)



White semisolid, 0.12mmol, 17mg, 42%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.96 (s, 1H), 7.32 – 7.21 (m, 8H), 7.01 – 6.92 (m, 1H), 4.20 (qd, *J* = 7.1, 1.8 Hz, 2H), 4.02 (q, *J* = 13.0 Hz, 2H), 3.72 (dd, *J* = 63.8, 12.6 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.5, 163.5, 161.6, 144.6, 136.1 (d, *J* = 7.9 Hz), 130.2 (d, *J* = 6.8 Hz), 129.7, 128.9, 128.4, 125.2 (d, *J* = 2.9 Hz), 124.0, 116.3 (dd, *J* = 21.8, 11.8 Hz), 61.6, 59.0, 49.9, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}FO_3S$ [M + Na^+] 369.0931; found 369.0929.

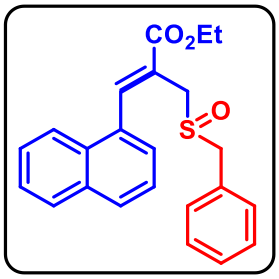
Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(2-bromophenyl)acrylate (4v)



White semisolid, 0.13mmol, 22mg, 41%; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.03 (s, 1H), 7.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.23 – 7.19 (m, 3H), 7.14 (td, *J* = 7.6, 1.4 Hz, 1H), 4.23 (qd, *J* = 7.1, 0.7 Hz, 2H), 3.94 (dd, *J* = 37.1, 13.0 Hz, 2H), 3.70 – 3.64 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H}

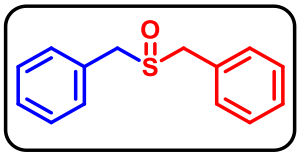
(125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.2, 145.1, 134.4, 132.7, 131.3, 130.6, 130.2, 129.8, 128.8, 128.3, 127.6, 124.5, 124.0, 61.7, 58.8, 50.4, 14.2; HRMS (ESI): calcd. for $C_{19}H_{19}BrO_3S$ [M + Na^+] 429.0130; found 429.0135.

Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4w)



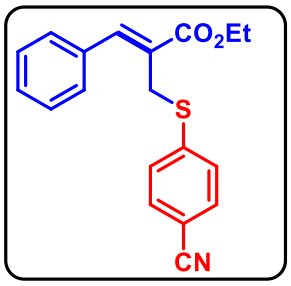
Yellow semisolid, 0.18mmol, 15mg, 22%; Eluent (10% ethyl acetate in hexane); ^1H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.63 (s, 1H), 7.90 – 7.85 (m, 3H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.47 – 7.44 (m, 1H), 7.29 – 7.27 (m, 3H), 7.22 – 7.14 (m, 2H), 4.34 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.94 (q, *J* = 13.0 Hz, 2H), 3.81 (dd, *J* = 26.7, 13.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^1H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.5, 144.4, 133.3, 131.2, 131.0, 130.1, 129.1, 129.7, 128.8, 128.7, 128.2, 127.7, 126.7, 126.3, 125.5, 125.1, 124.2, 61.6, 58.9, 50.8, 14.2; HRMS (ESI): calcd. for $C_{23}H_{22}O_3S$ [M + Na^+] 401.1182; found 401.1189.

(sulfinylbis(methylene))dibenzene (4x)



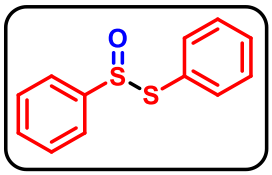
White solid, 0.29mmol, 34mg, 53%; Eluent (20% ethyl acetate in hexane); ^1H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.32 – 7.26 (m, 6H), 7.25 – 7.18 (m, 4H), 3.82 (q, *J* = 13.0 Hz, 4H); ^{13}C NMR{^1H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 130.8, 130.1, 128.9, 128.3, 57.2; HRMS (ESI): calcd. for $C_{14}H_{14}OS$ [M + H^+] 231.0838; found 231.0835.

ethyl (Z)-2-(((4-cyanophenyl)thio)methyl)-3-phenylacrylate



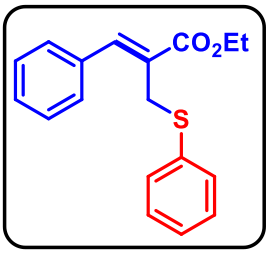
White semisolid, 0.13mmol, 15mg, 36%; Eluent (10% ethyl acetate in hexane); ^1H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.77 (s, 1H), 7.40 – 7.36 (m, 2H), 7.37 – 7.29 (m, 5H), 7.22 – 7.19 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^1H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.7, 144.1, 142.2, 134.5, 132.1, 129.3, 128.8, 128.1, 127.2, 118.8, 108.8, 61.4, 30.4, 14.2; HRMS (ESI): calcd. for $C_{19}H_{17}NO_2S$ [M + H^+] 324.1053; found 324.1027.

S-phenyl benzenesulfinothioate (3a′)



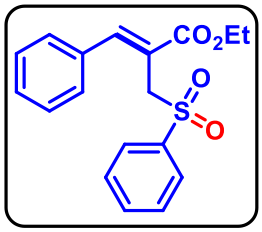
Yellow semisolid, 3.71mmol, 20mg, 16%; Eluent (10% ethyl acetate in hexane); ^1H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.57 (dddd, *J* = 6.8, 4.7, 2.8, 1.1 Hz, 3H), 7.49 – 7.45 (m, 1H), 7.42 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.37 – 7.31 (m, 4H); ^{13}C NMR{^1H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 142.9, 136.6, 133.6, 131.4, 129.4, 128.8, 127.8, 127.5; HRMS (ESI): calcd. for $C_{12}H_{10}OS_2$ [M + H^+] 235.0246; found 235.0246.

Ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (3a")



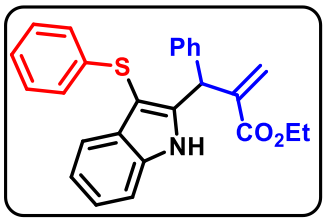
Yellow semisolid, 0.12mmol, 34mg, 95%; Eluent (5% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.76 (s, 1H), 7.41 – 7.29 (m, 7H), 7.23 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.20 – 7.16 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 299.1104. 167.2, 141.1, 136.0, 134.8, 130.8, 129.4, 128.9, 128.8, 128.6 (d, *J* = 3.2 Hz), 126.7, 61.2, 32.2, 14.2; HRMS (ESI): calcd. for $C_{18}H_{18}O_2S$ [M + H^+] 299.1100; found 299.1104.

Ethyl (Z)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (5a)



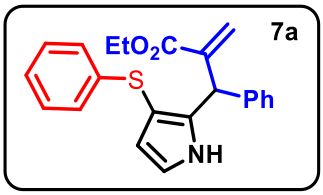
Yellow semisolid, 0.21mmol, 75mg, 99%; Eluent (15% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 7.85 (s, 1H), 7.76 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.42 – 7.37 (m, 4H), 7.27 (dd, *J* = 5.0, 1.8 Hz, 3H), 4.42 (s, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 165.4, 145.0, 138.3, 132.7, 132.6, 128.6, 128.1. 128.0, 127.7, 127.4, 120.1, 60.5, 54.0, 13.0; HRMS (ESI): calcd. for $C_{18}H_{18}O_4S$ [M + Na^+] 353.0818; found 353.0825.

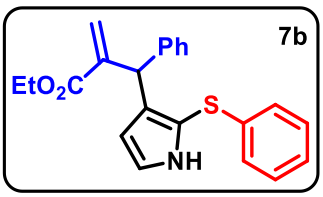
Ethyl 2-(phenyl(3-(phenylthio)-1H-indol-2-yl)methyl)acrylate (6a)



Yellow semisolid, 0.10mmol, 22mg, 65%; Eluent (5% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 9.04 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.13 (dd, *J* = 10.9, 4.1 Hz, 2H), 7.08 – 7.01 (m, 5H), 6.99 – 6.92 (m, 3H), 6.26 (s, 1H), 5.81 (s, 1H), 5.48 (s, 1H), 4.11 – 4.02 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.8, 143.2, 140.8, 139.8, 138.9, 135.6, 129.9, 129.1, 128.7, 128.6, 127.4, 126.9, 125.9, 124.7, 122.7, 120.8, 119.5, 111.4, 100.6, 61.3, 45.7, 14.0; HRMS (ESI): calcd. for $C_{26}H_{23}NO_2S$ [M + H^+] 414.1522; found 414.1533.

Ethyl 2-(phenyl(3-(phenylthio)-1H-pyrrol-2-yl)methyl)acrylate (7a) and Ethyl 2-(phenyl(2-(phenylthio)-1H-pyrrol-3-yl)methyl)acrylate (7b)

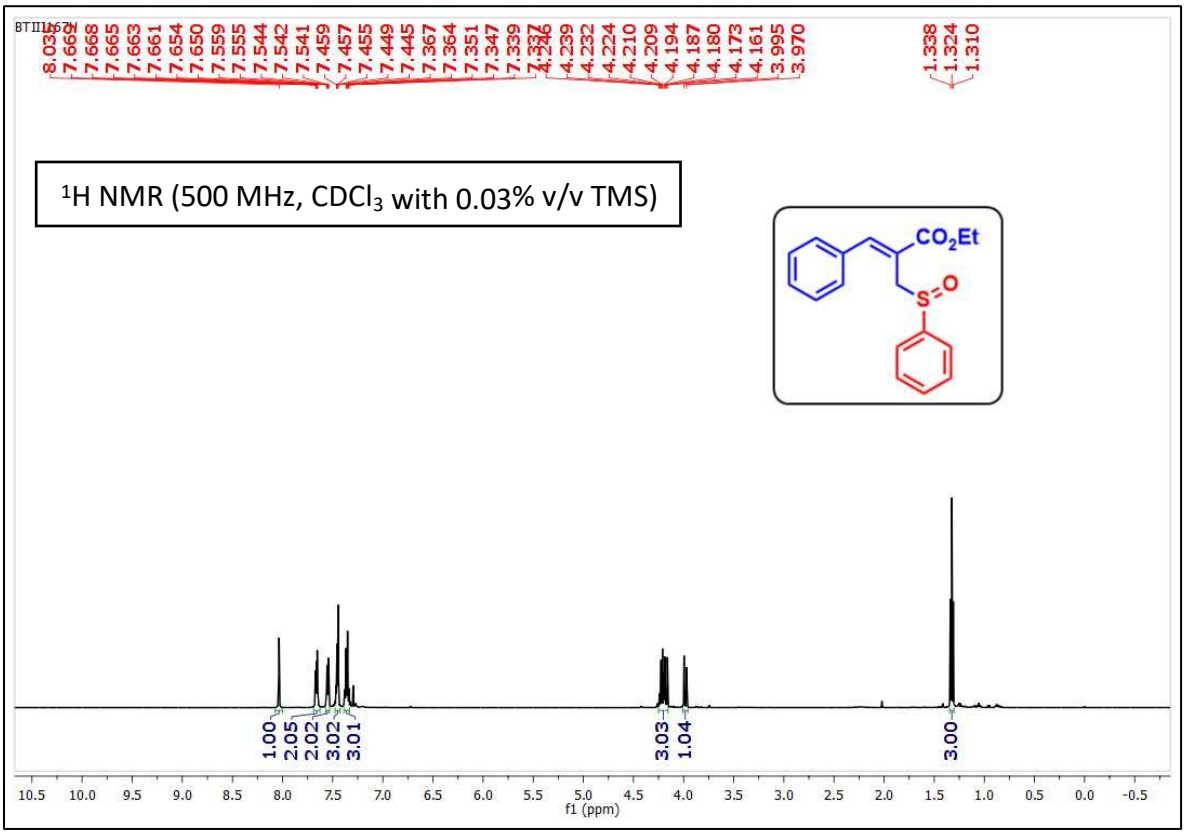


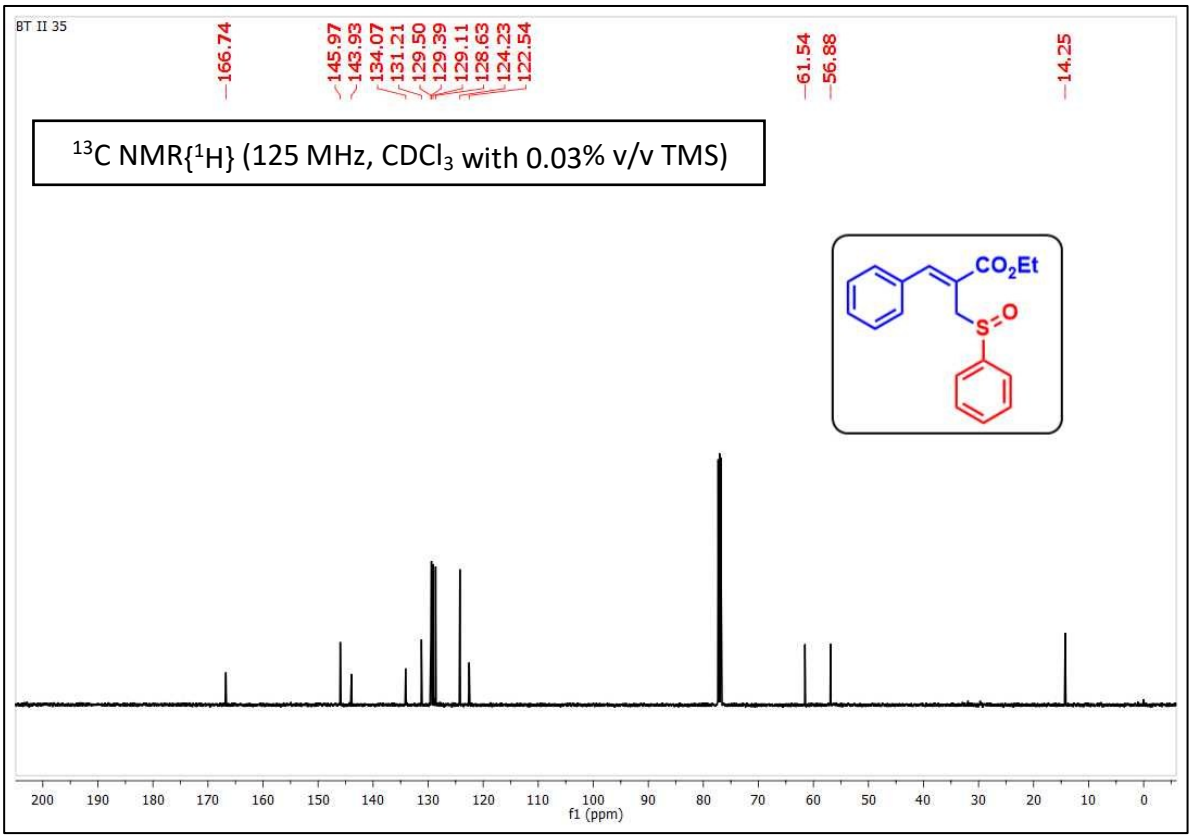


Yellow semisolid, 0.15mmol, 22mg, 38%, as a mixture of regioisomers (7a : 7b = 3 : 1); Eluent (5% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 8.92 (s, 0.28H), 8.20 (s, 1H), 7.15 – 7.12 (m, 2.60H), 7.08 – 7.05 (m, 5.43H), 7.00 – 6.95 (m, 2.56H), 6.85 (d, J = 7.6 Hz, 2H), 6.79 (s, 1H), 6.73 (s, 0.29H), 6.26 (s, 0.30H), 6.24 (s, 1H), 6.18 (s, 0.26H), 6.04 (s, 1H), 5.49 (s, 0.30H), 5.36 (s, 1.27H), 5.32 (s, 1H), 4.05 – 3.91 (m, 2.66H), 1.09 (t, J = 6.7 Hz, 1H), 1.02 (t, J = 7.1 Hz, 3H) ; ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$ with 0.03% v/v TMS) δ 166.9, 143.9, 142.8, 141.3, 140.7, 140.2, 138.5, 135.7, 131.9, 128.8, 128.7 – 128.3 (m), 128.2, 127.3, 126.6, 126.2, 126.1, 125.8, 125.3, 124.5, 120.9, 117.9, 114.8, 113.3, 110.6, 61.0, 60.5, 45.2, 44.6, 13.9; HRMS (ESI): calcd. for $C_{22}H_{21}NO_2S$ [M + H^+] 364.1366; found 364.1375.

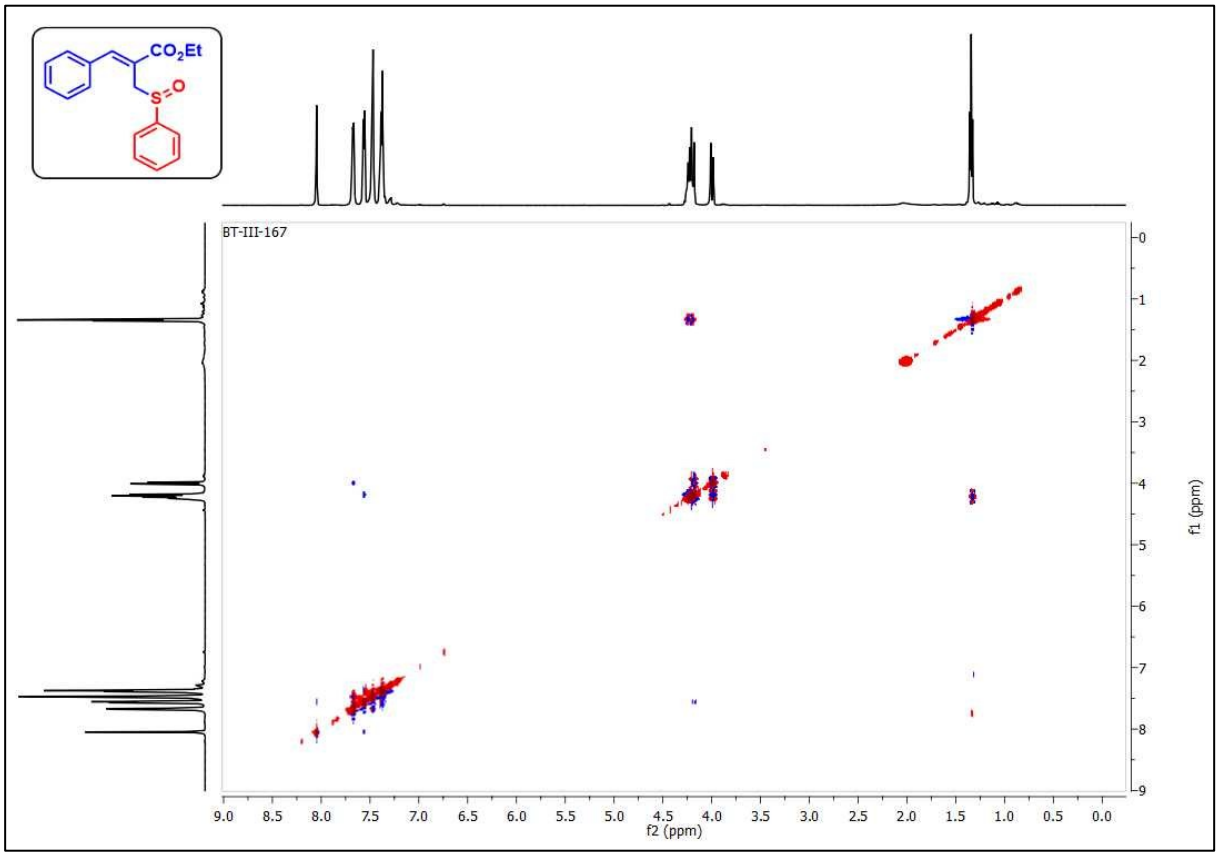
16. ^{1}H and ^{13}C NMR spectra of compounds

ethyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3a)

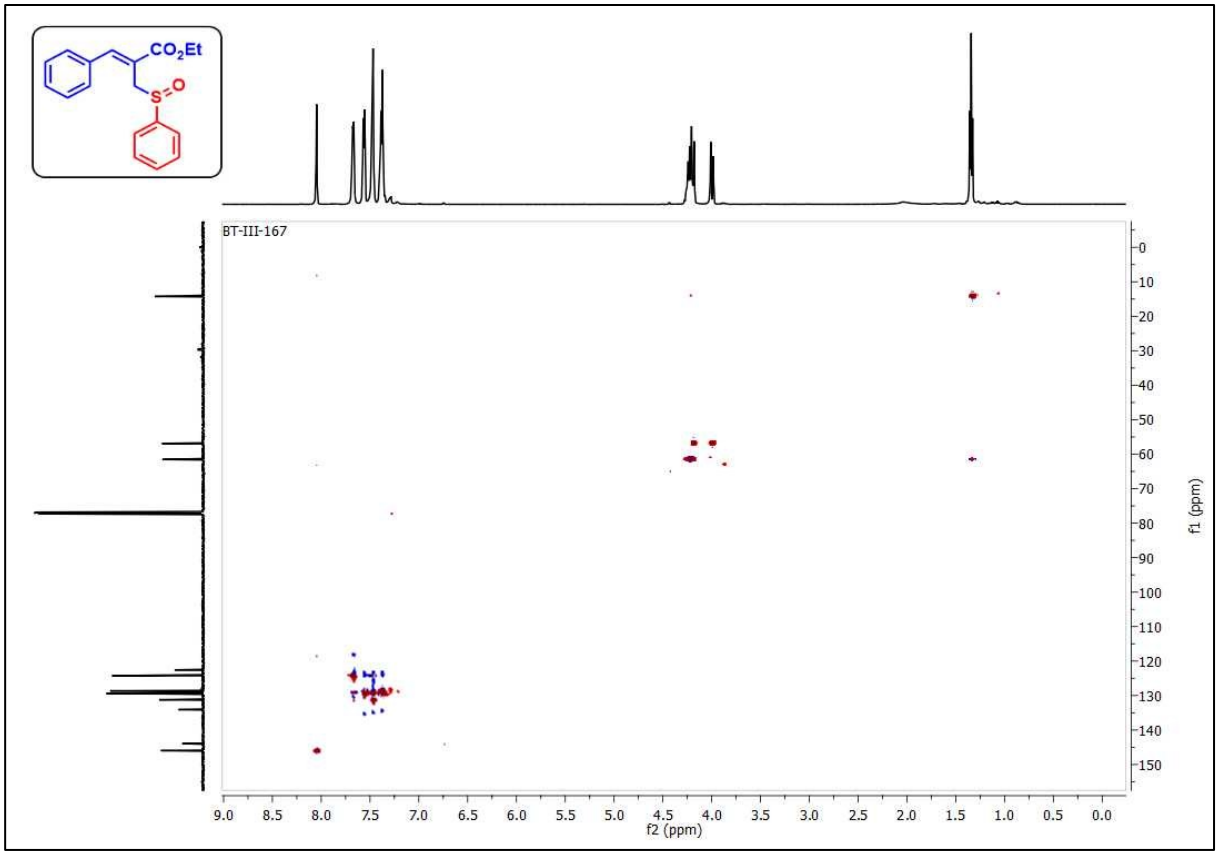




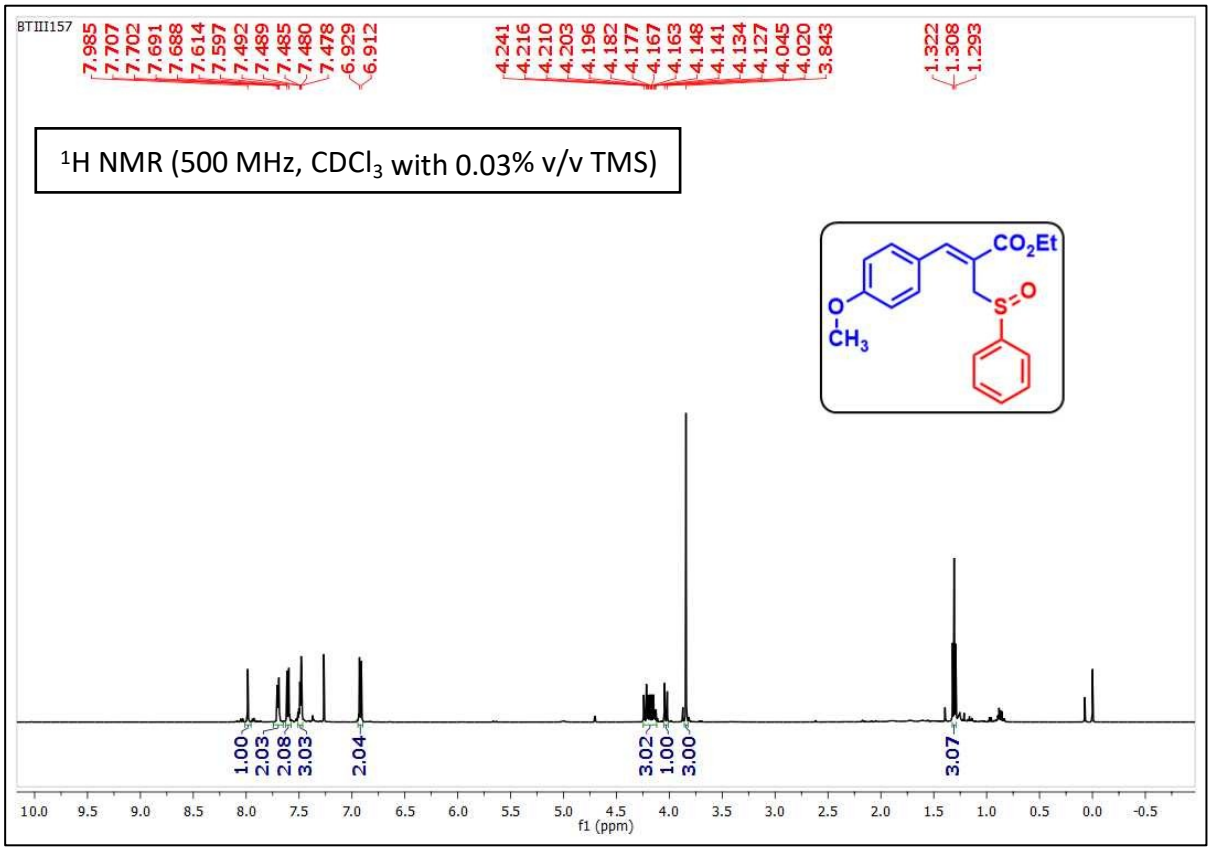
Phase sensitive NOESY spectra (3a)

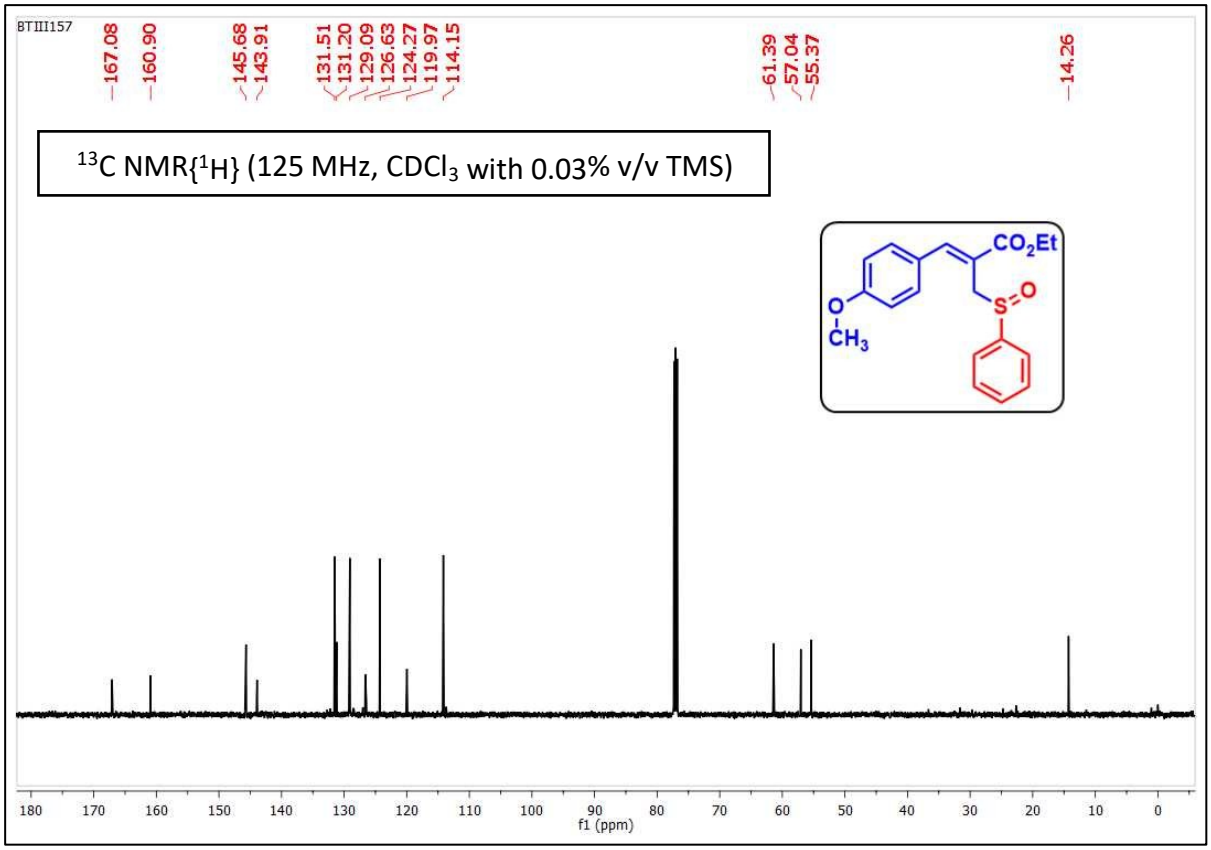


HSQC spectra (3a)

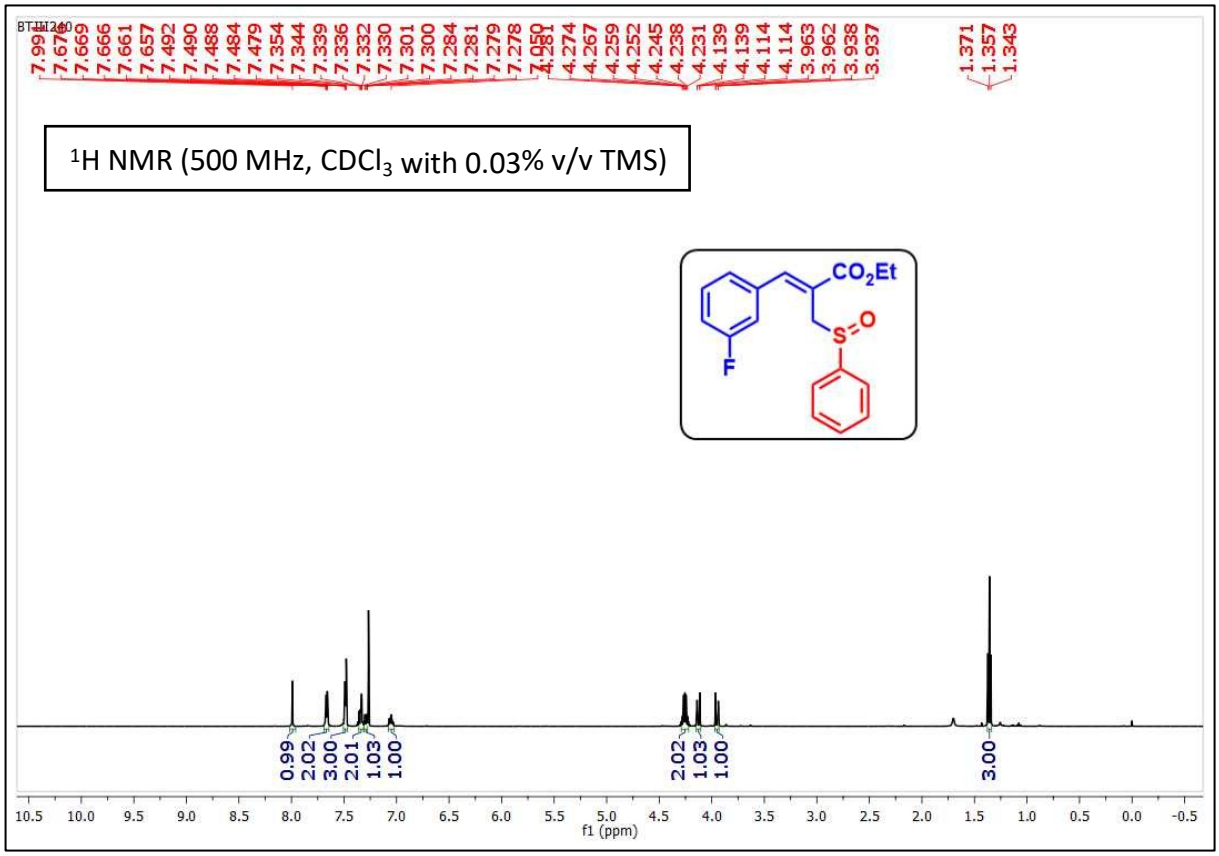


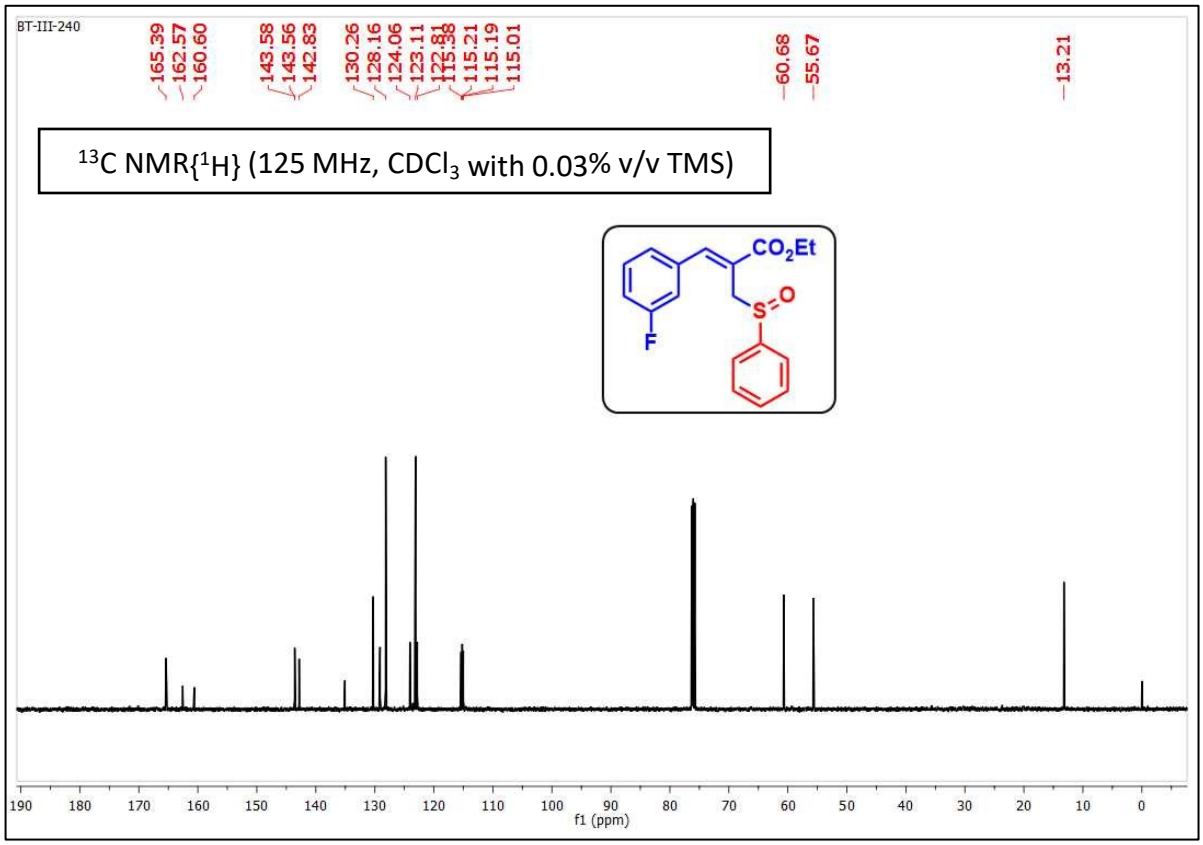
Ethyl (Z)-3-(4-methoxyphenyl)-2-((phenylsulfinyl)methyl)acrylate (3b)



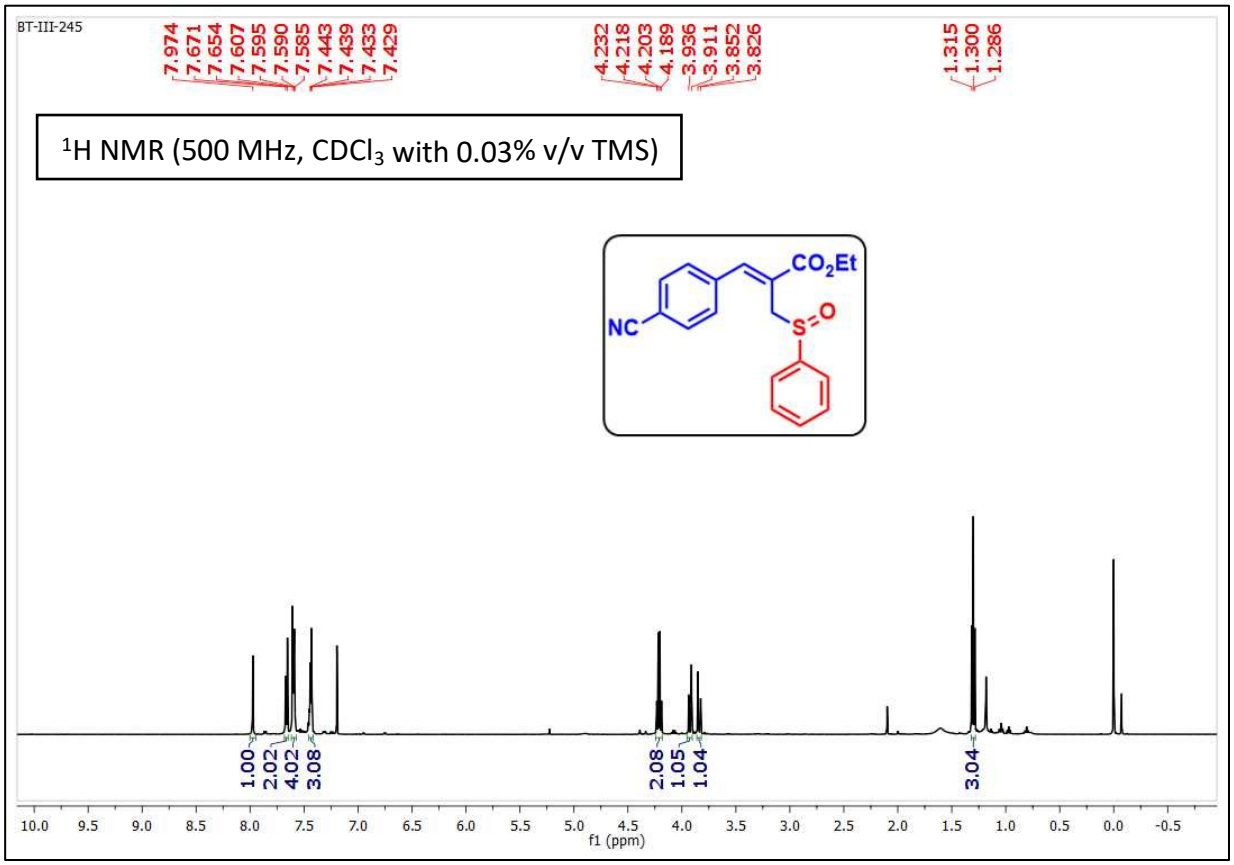


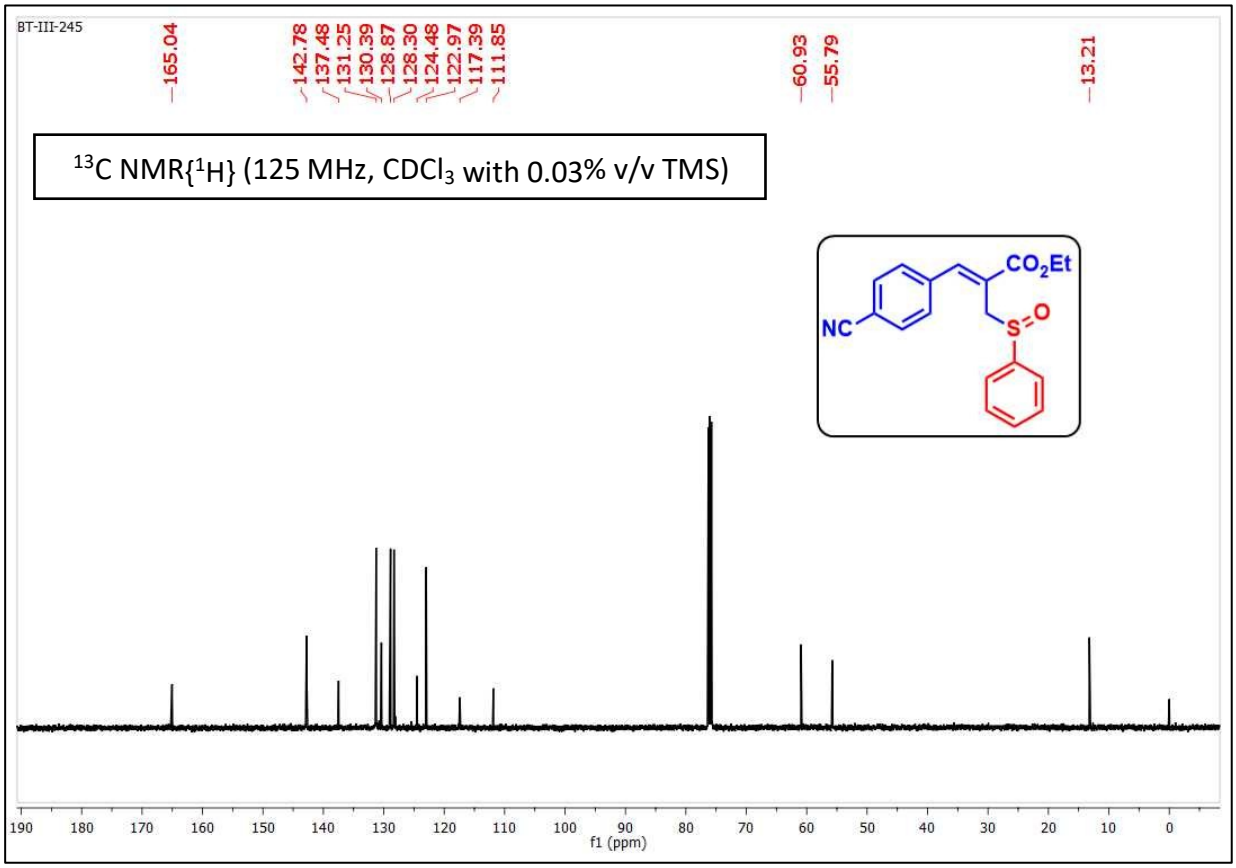
Ethyl (Z)-3-(3-fluorophenyl)-2-((phenylsulfinyl)methyl)acrylate (3c)



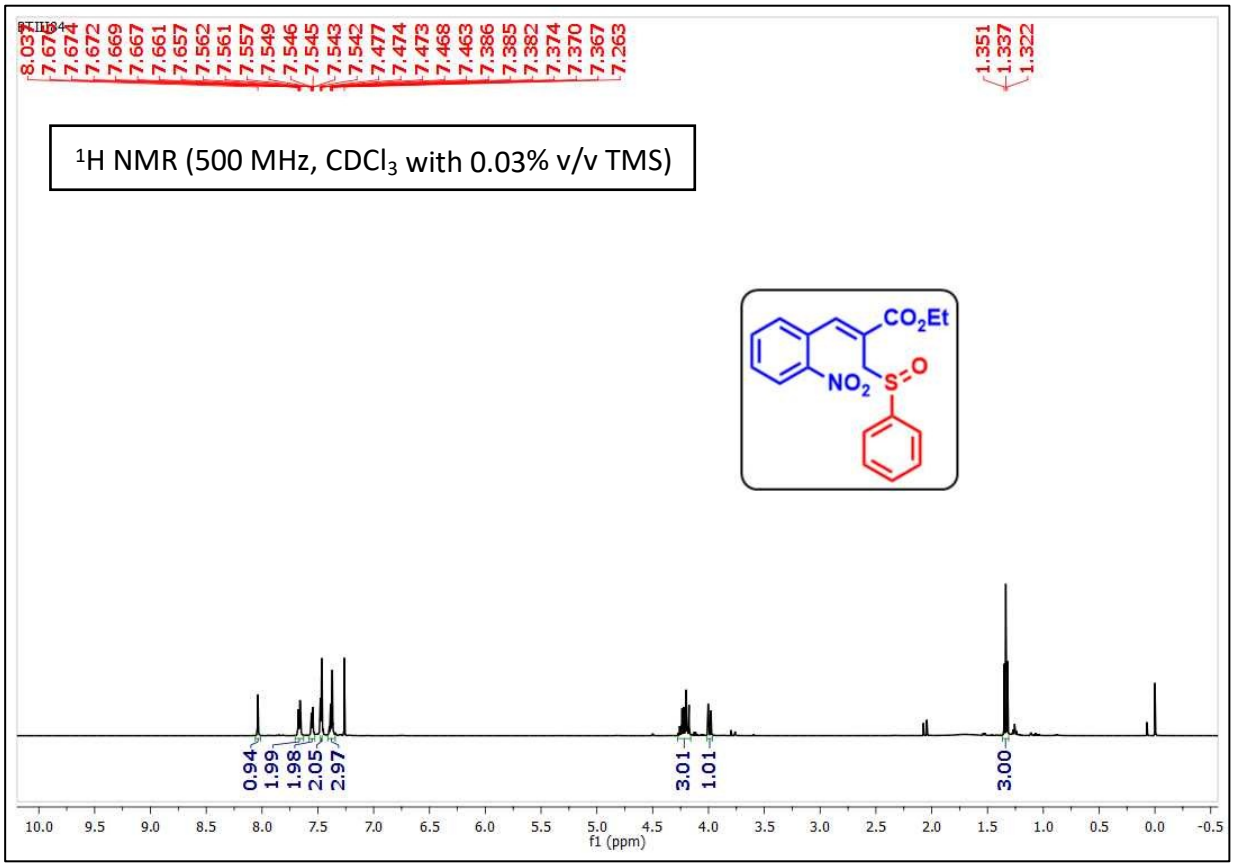


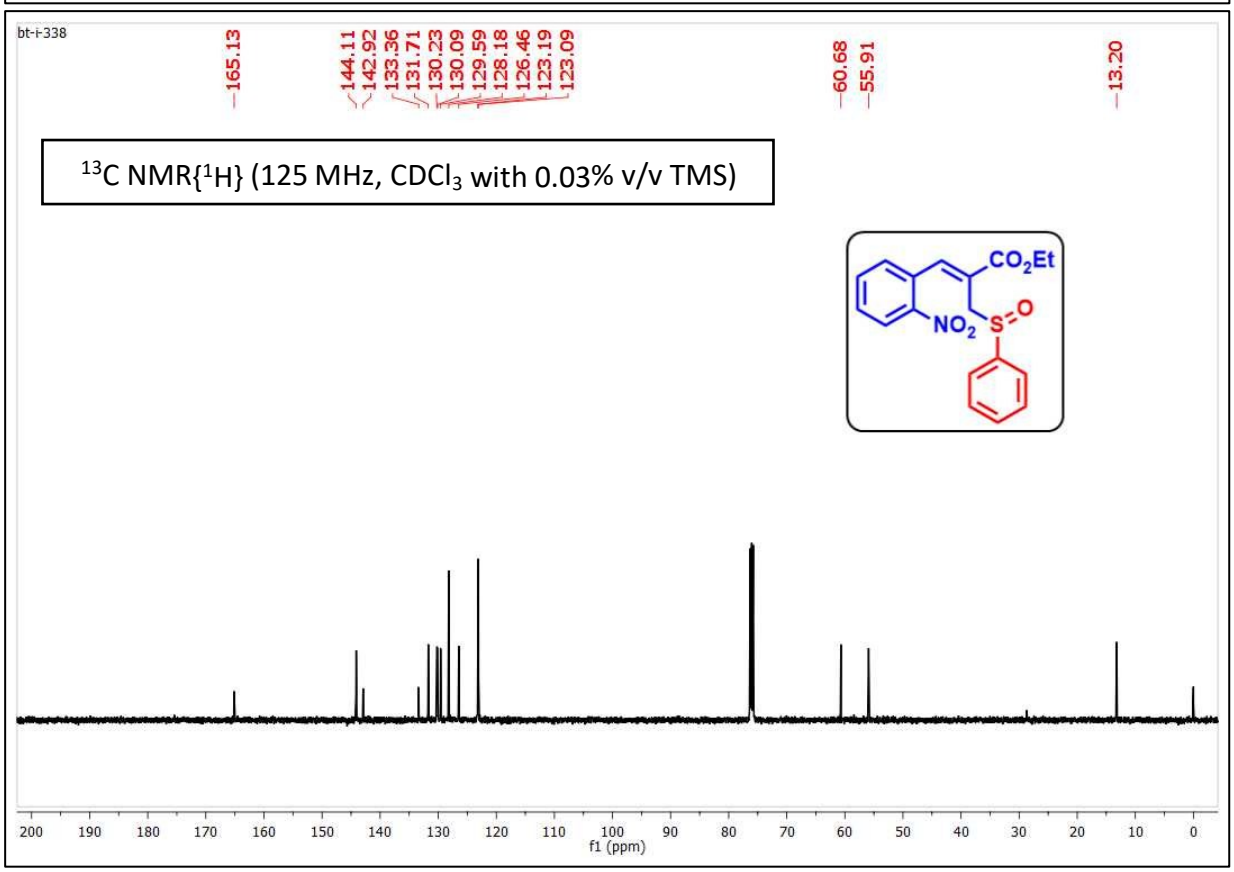
Ethyl (Z)-3-(4-cyanophenyl)-2-((phenylsulfinyl)methyl)acrylate (3d)



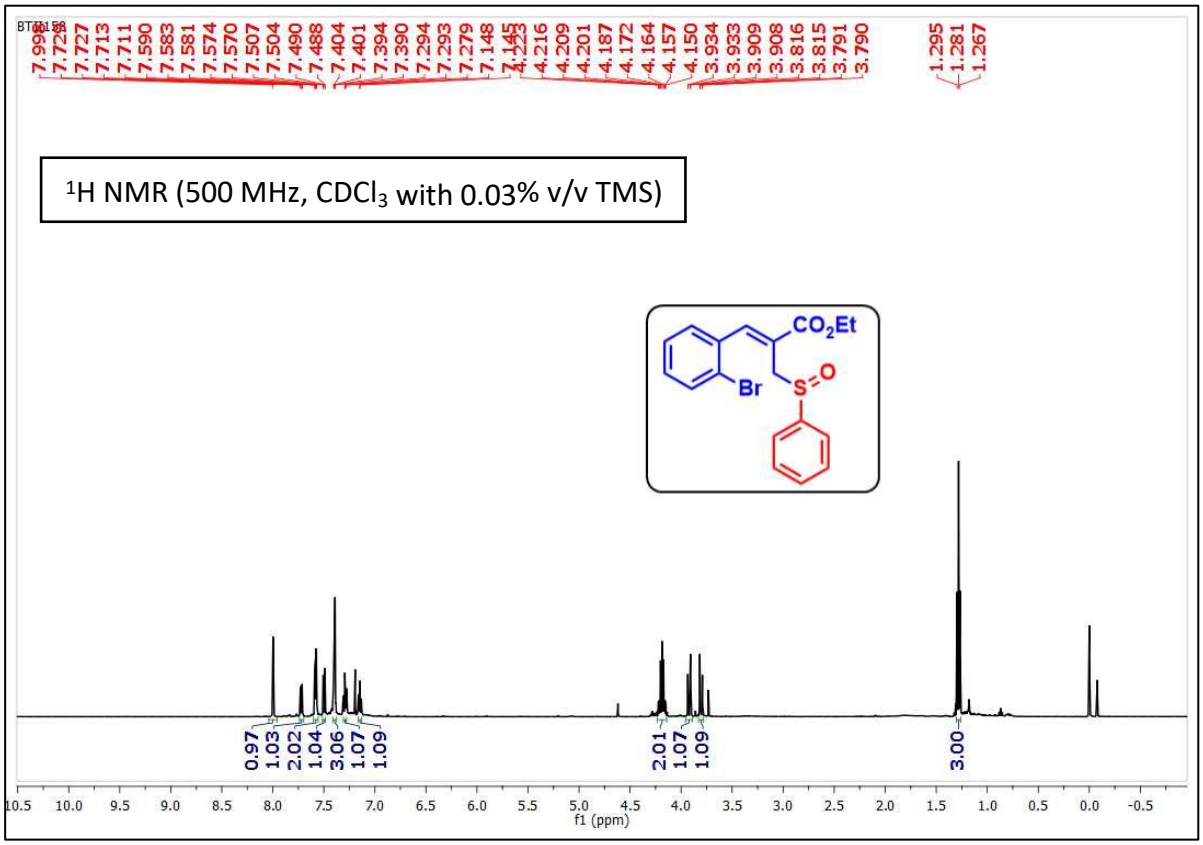


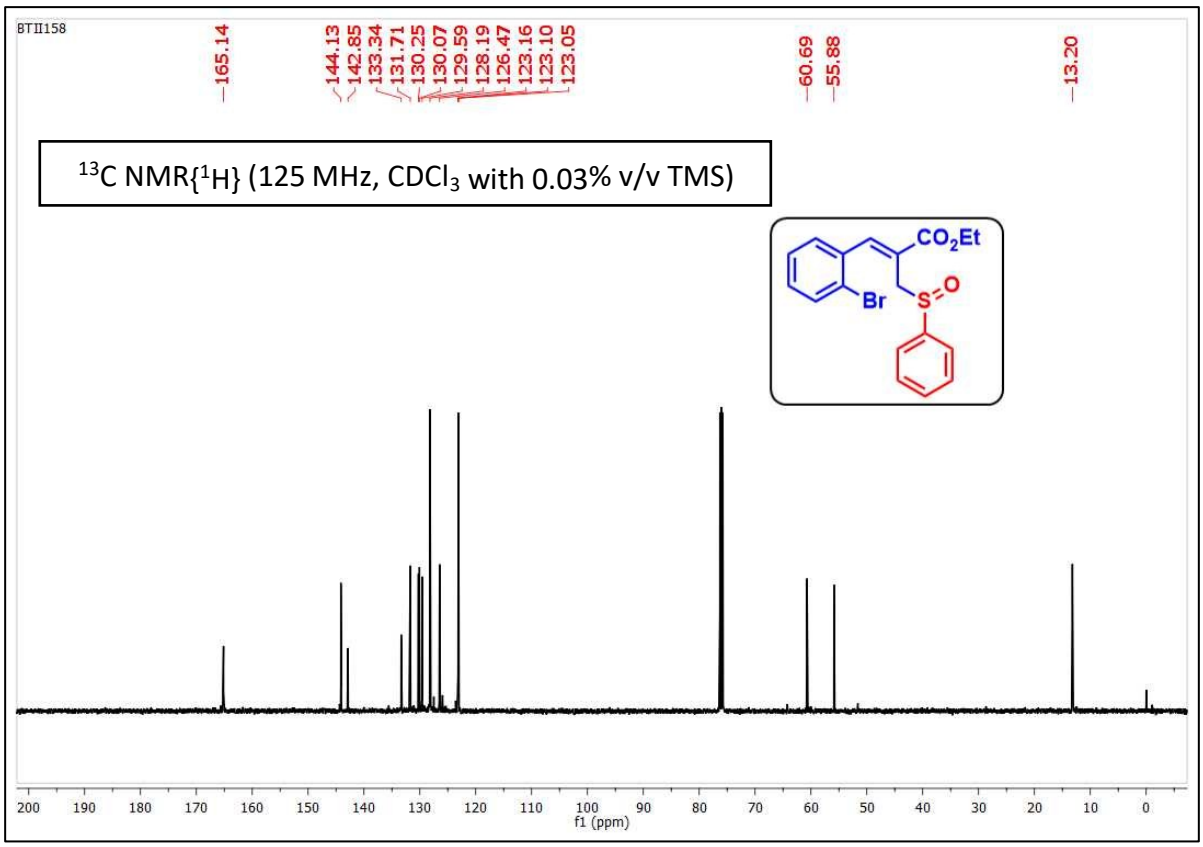
Ethyl (Z)-3-(2-nitrophenyl)-2-((phenylsulfinyl)methyl)acrylate (3e)



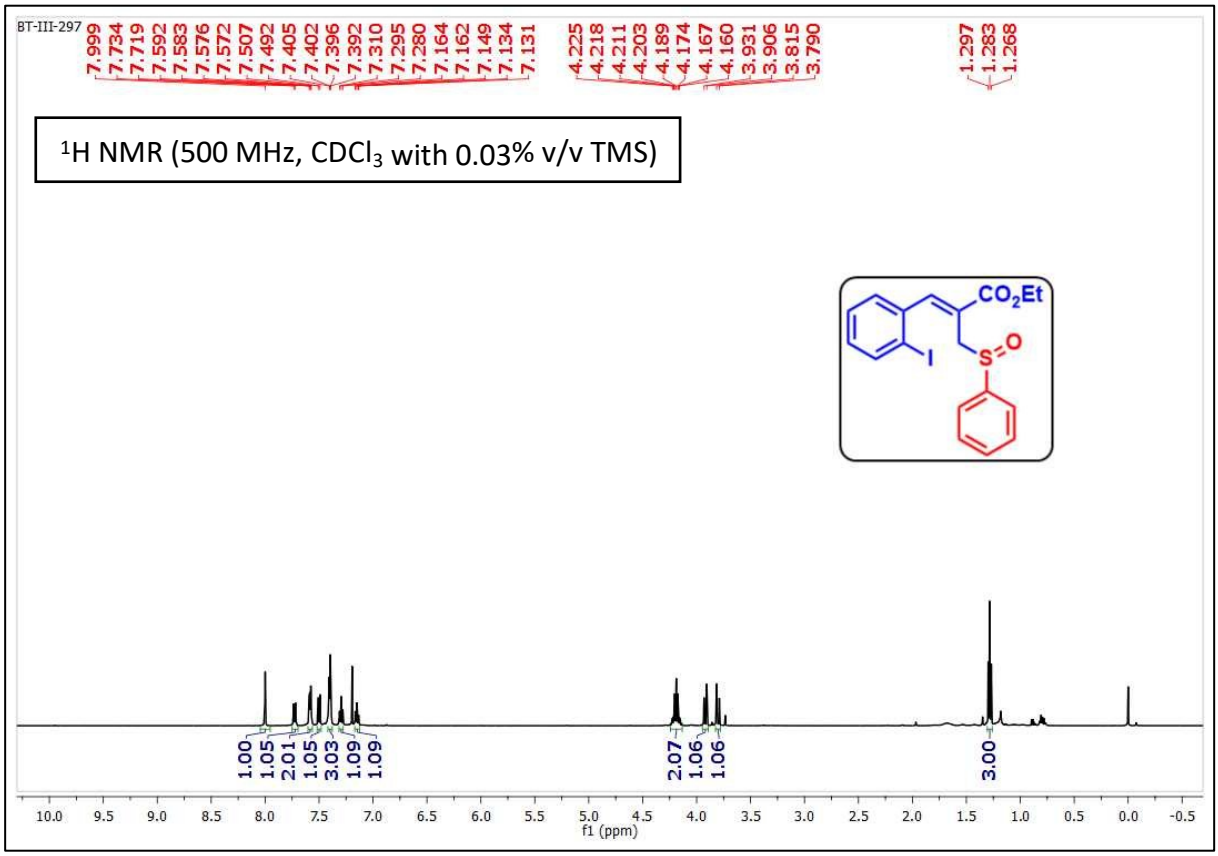


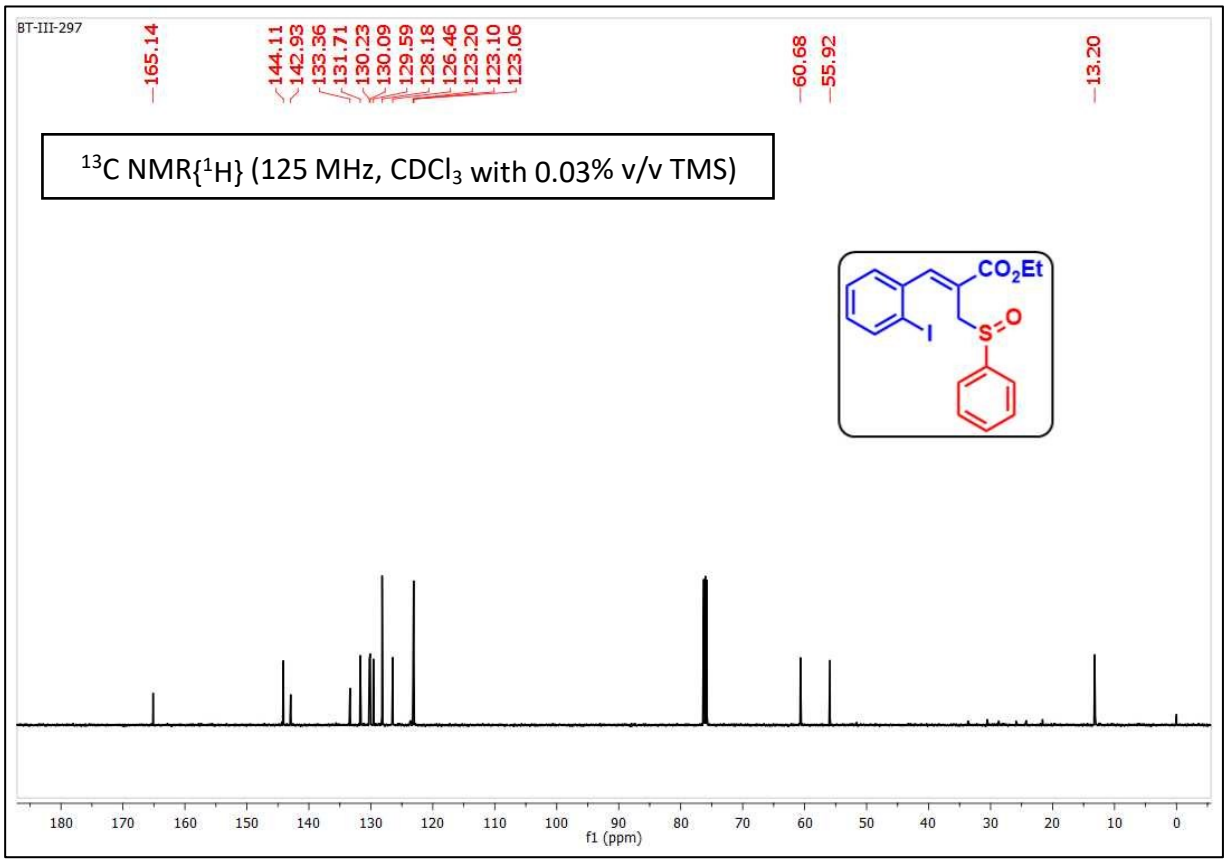
Ethyl (Z)-3-(2-bromophenyl)-2-((phenylsulfinyl)methyl)acrylate (3f)



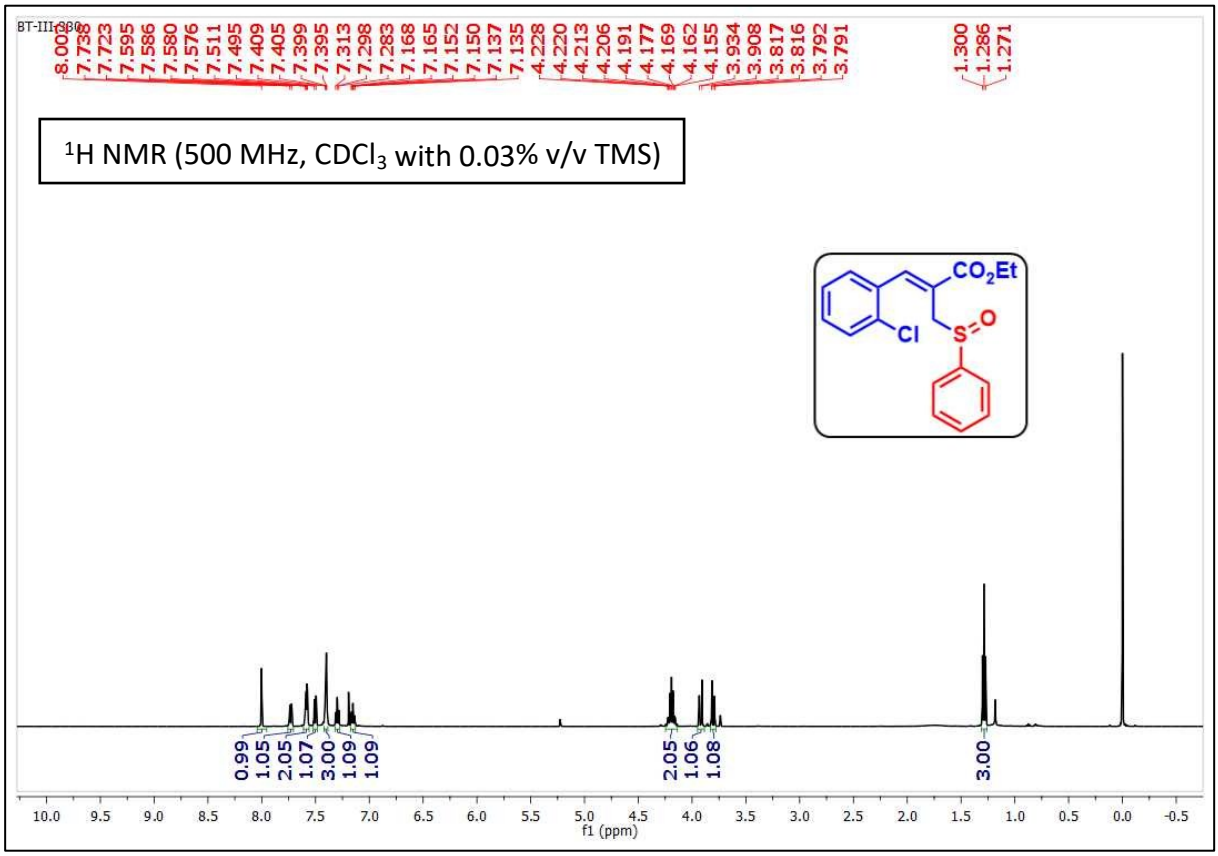


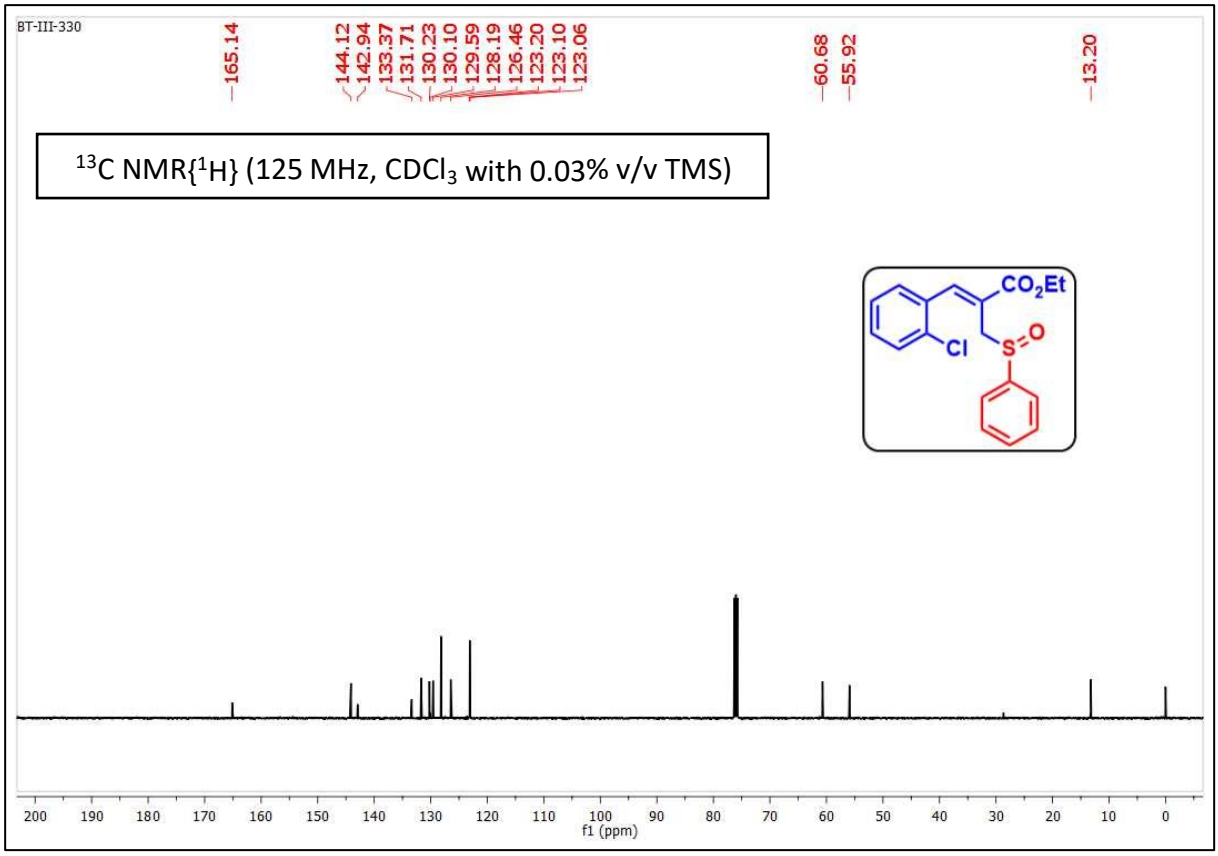
Ethyl (Z)-3-(2-iodophenyl)-2-((phenylsulfinyl)methyl)acrylate (3g)



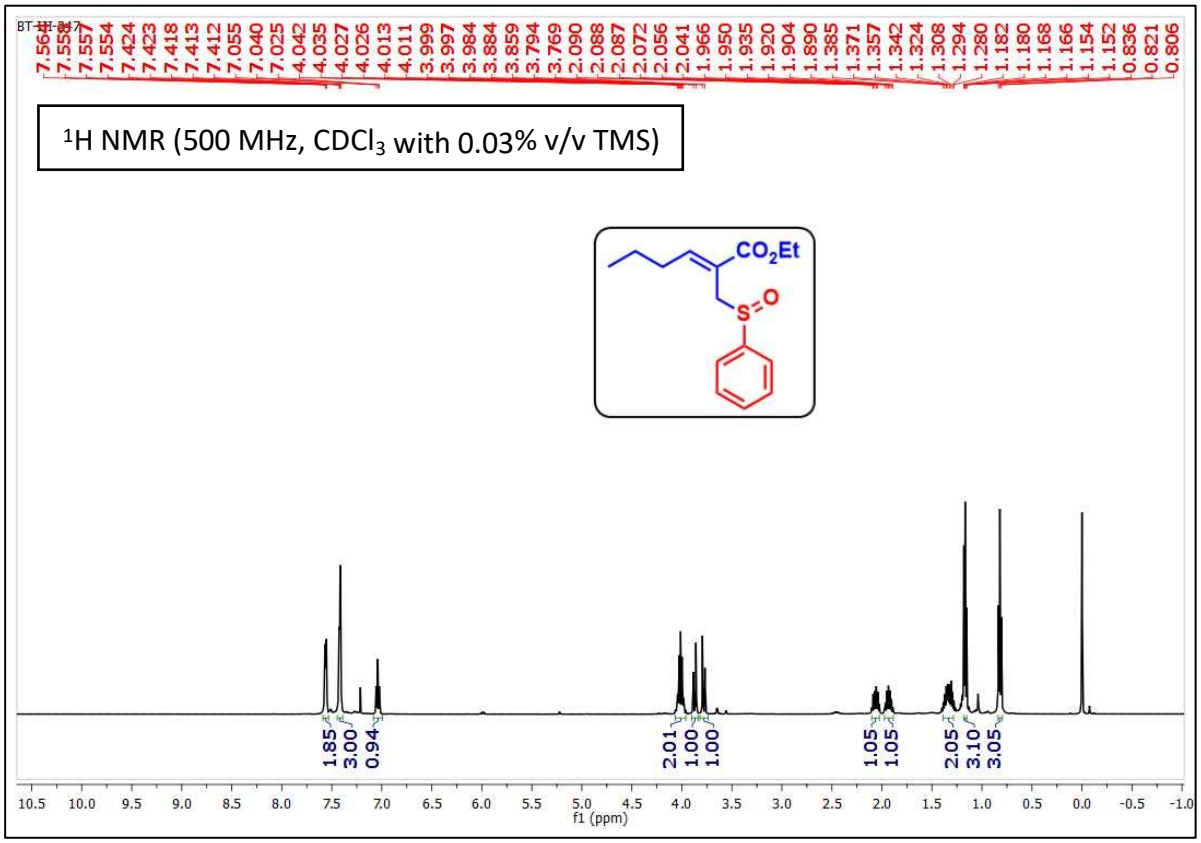


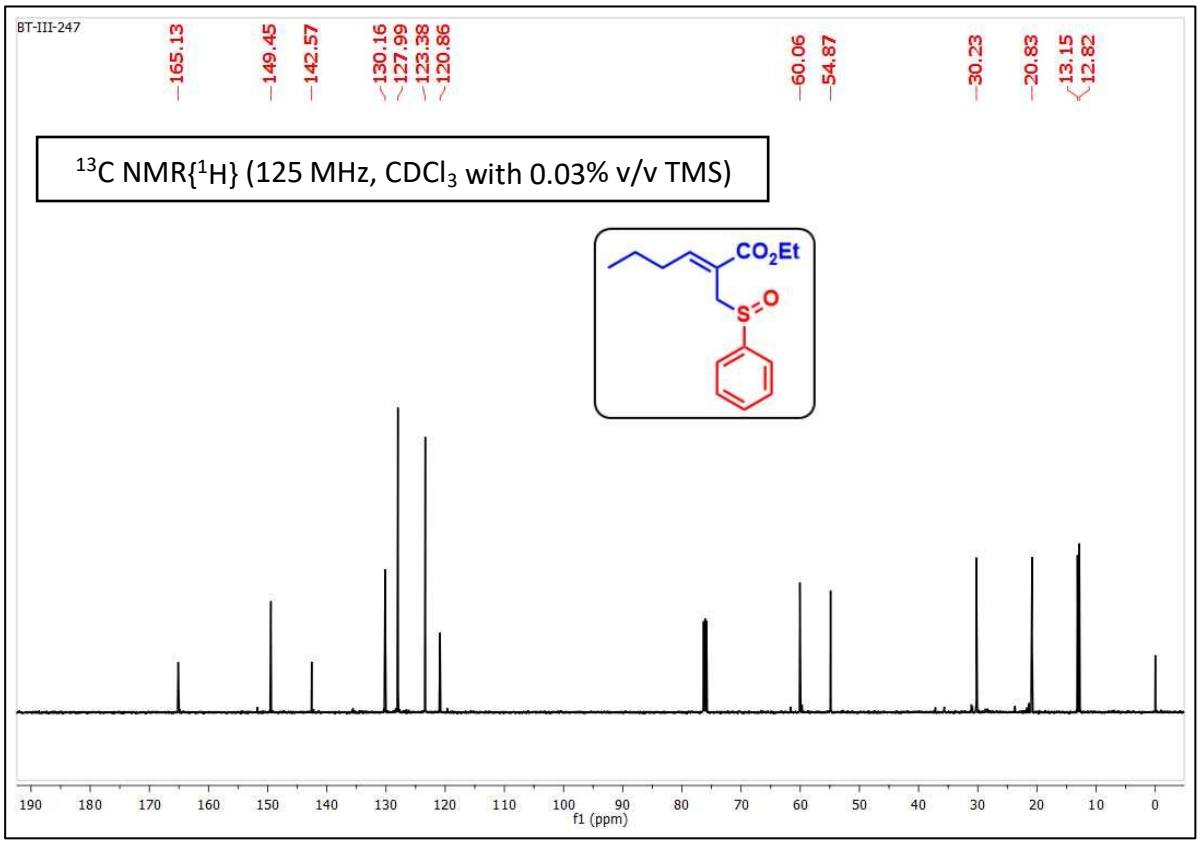
Ethyl (Z)-3-(2-chlorophenyl)-2-((phenylsulfinyl)methyl)acrylate (3h)



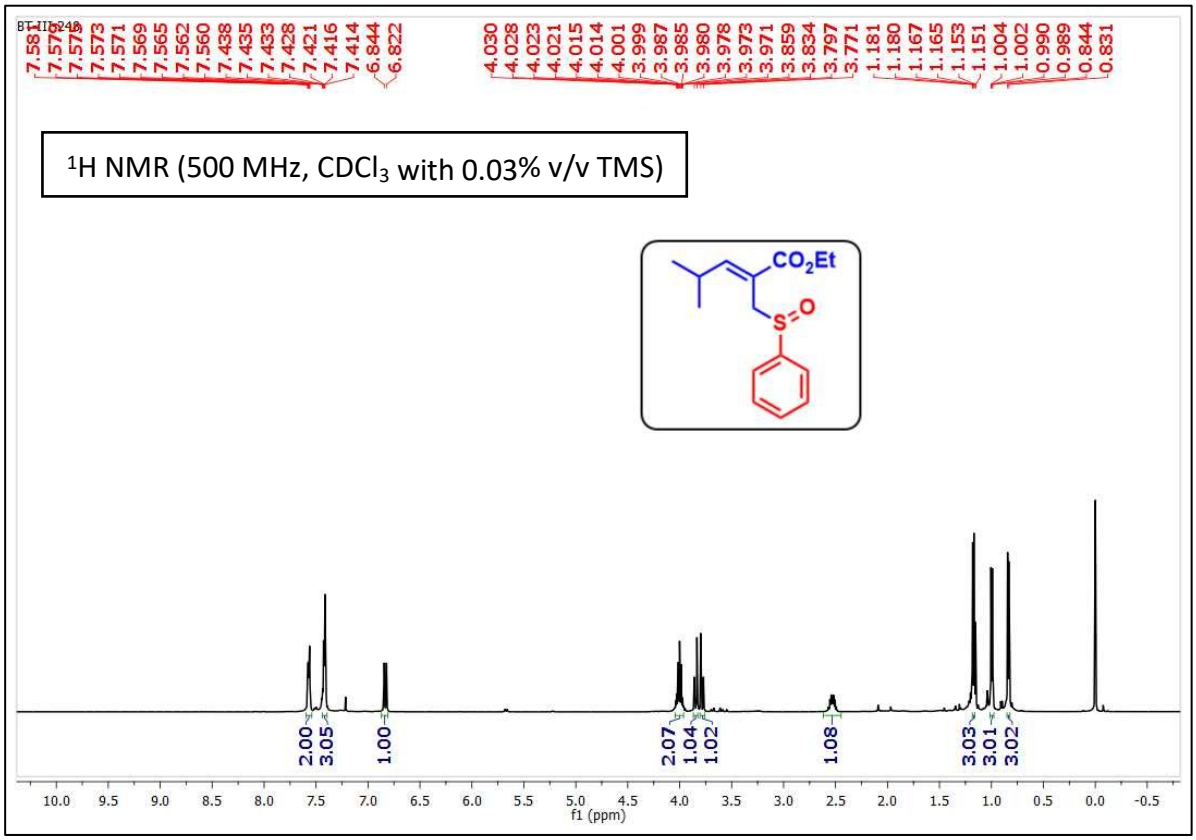


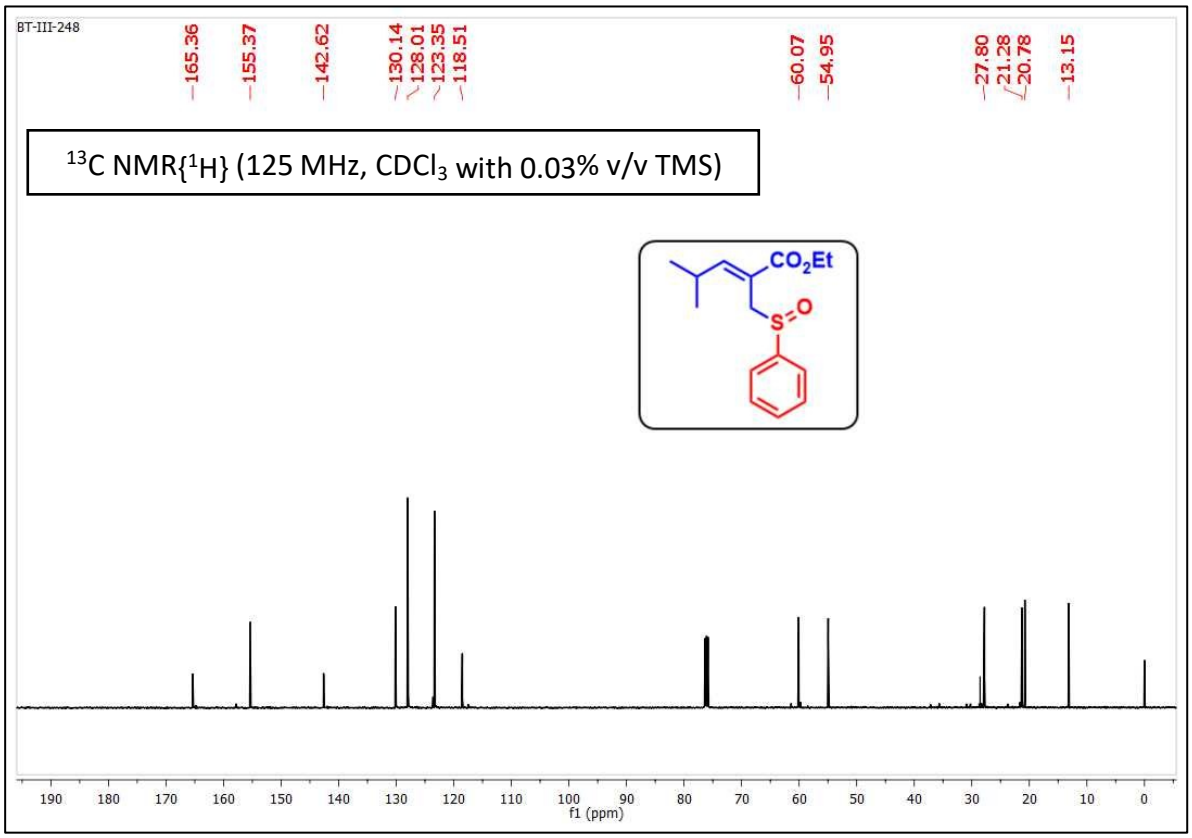
Ethyl (Z)-2-((phenylsulfinyl)methyl)hex-2-enoate (3i)



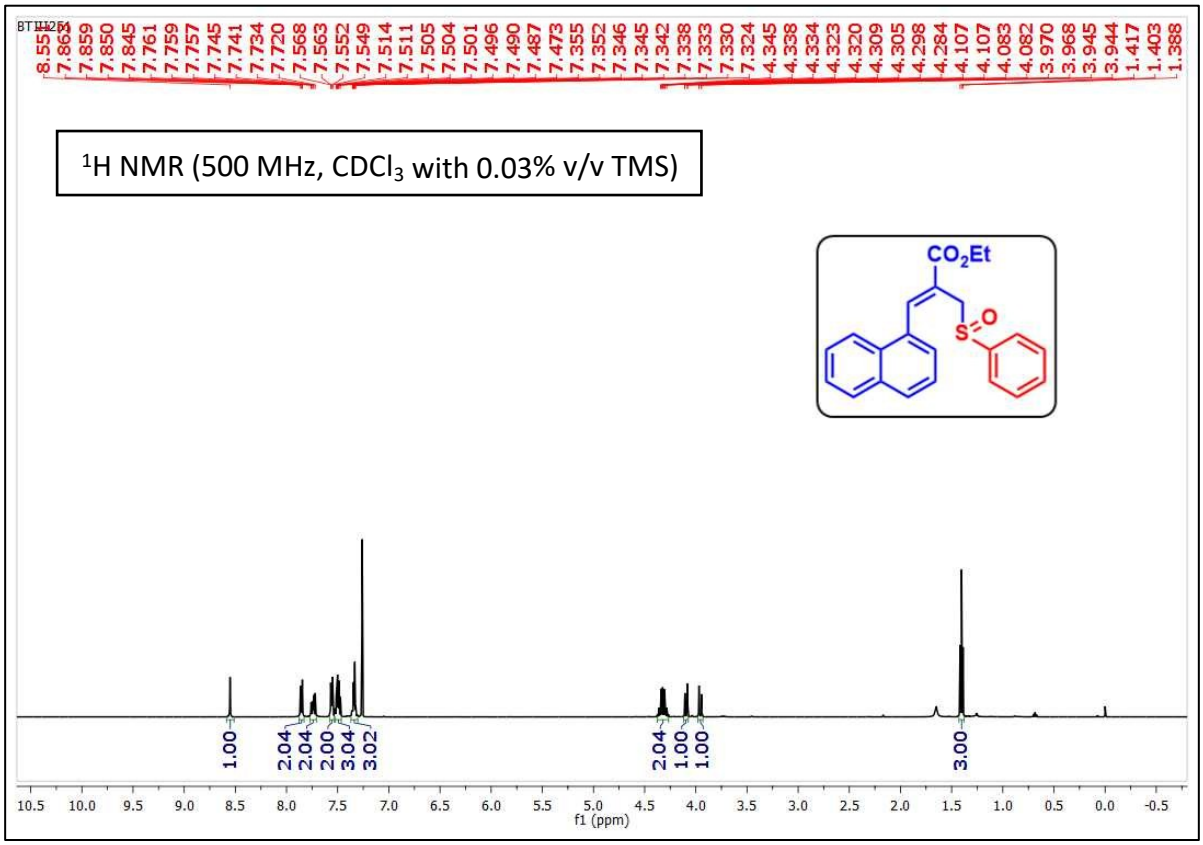


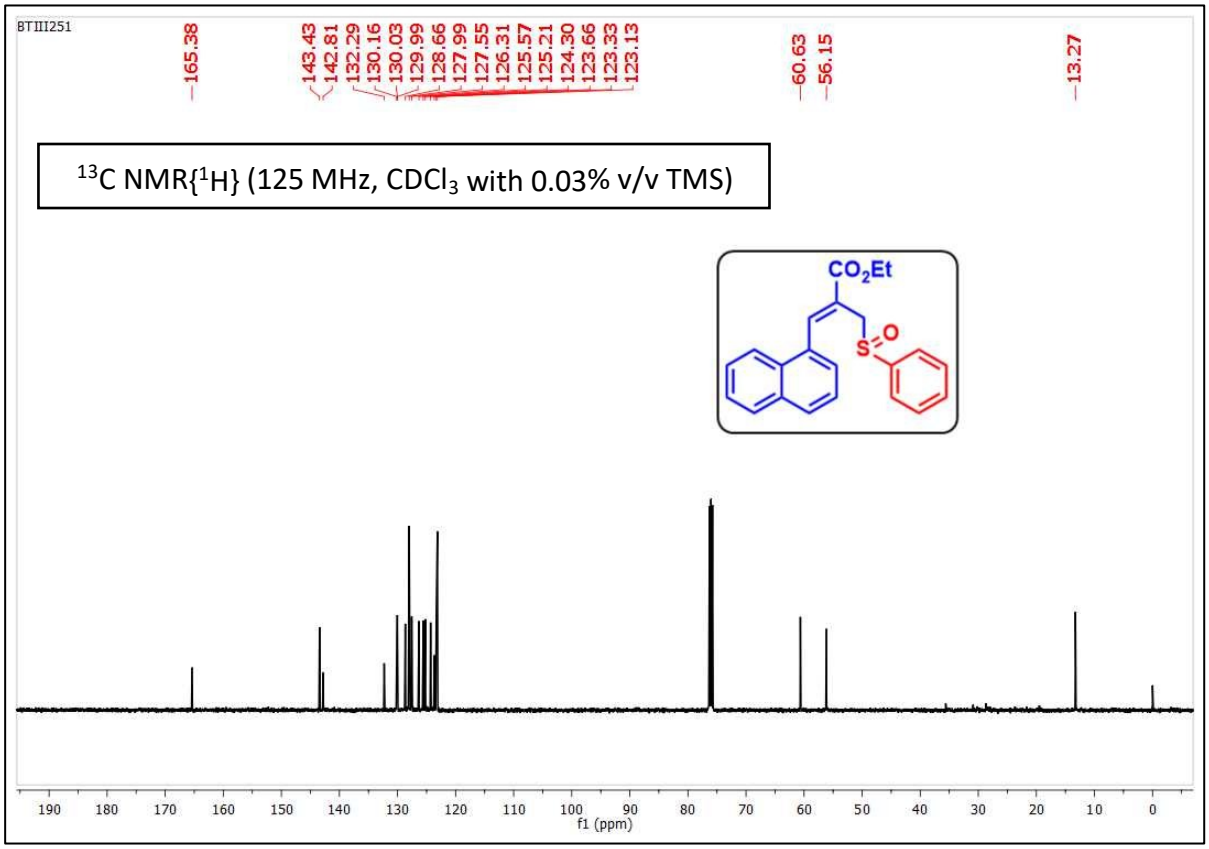
Ethyl (Z)-4-methyl-2-((phenylsulfinyl)methyl)pent-2-enoate (3j)



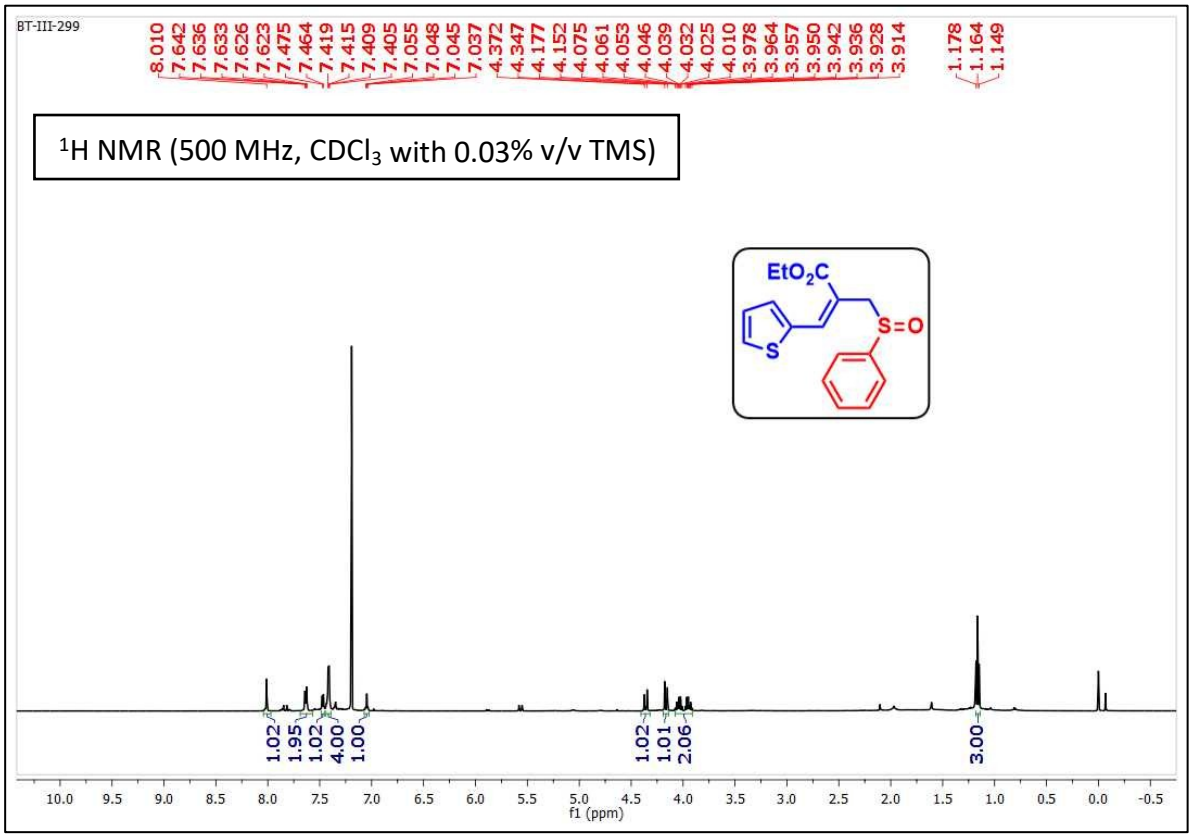


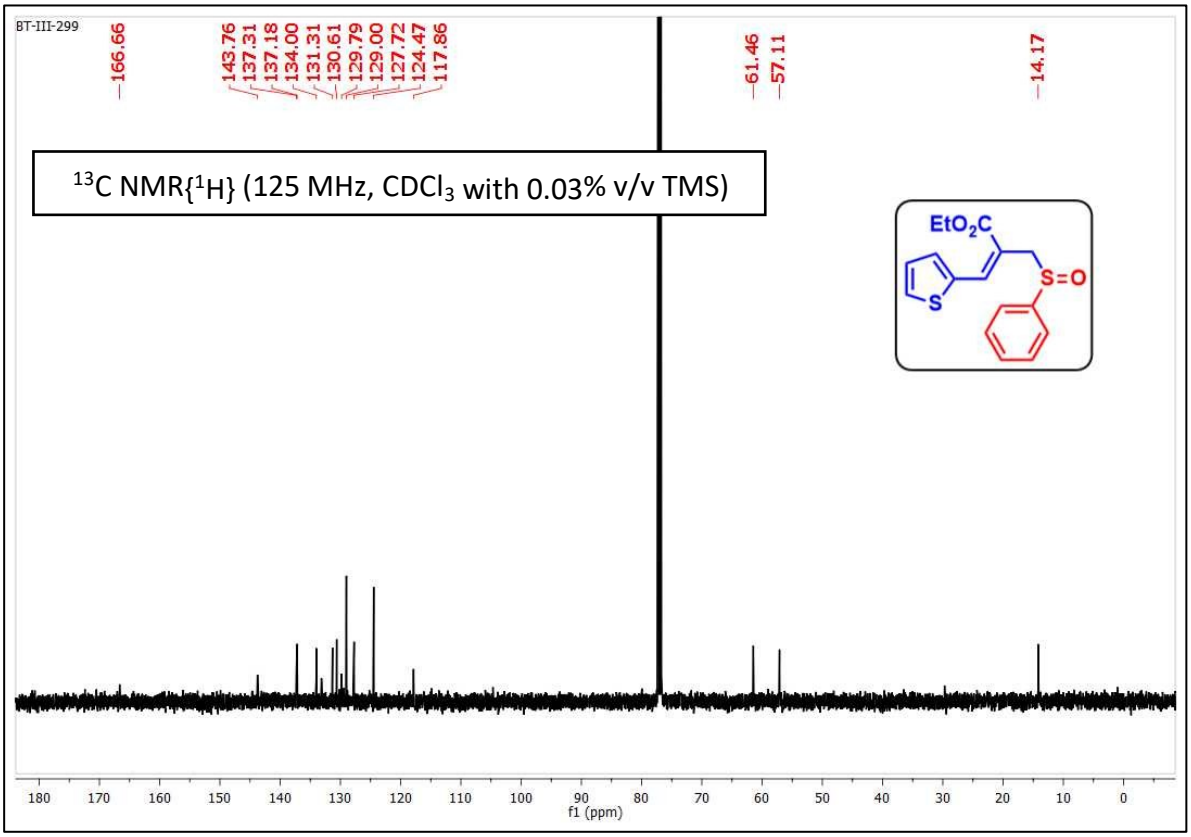
Ethyl(Z)-3-(naphthalen-1-yl)-2-((phenylsulfinyl)methyl)acrylate (3k)



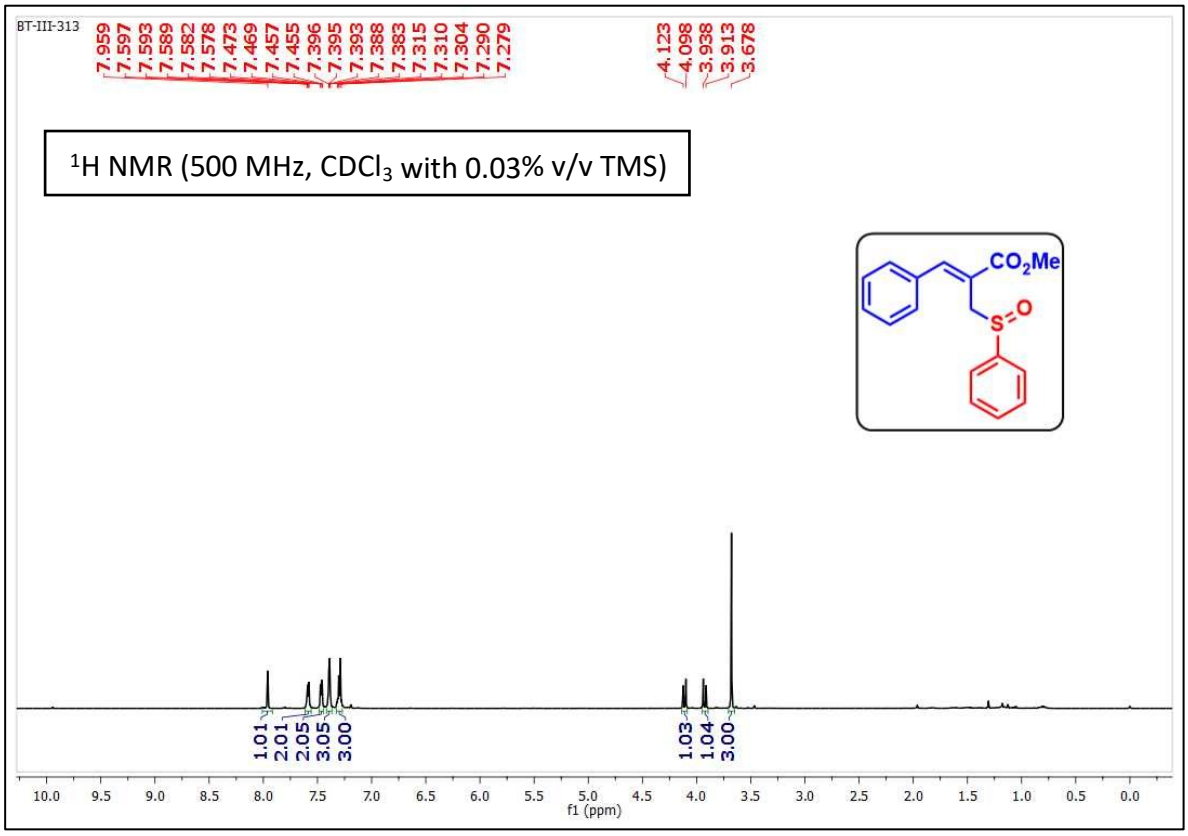


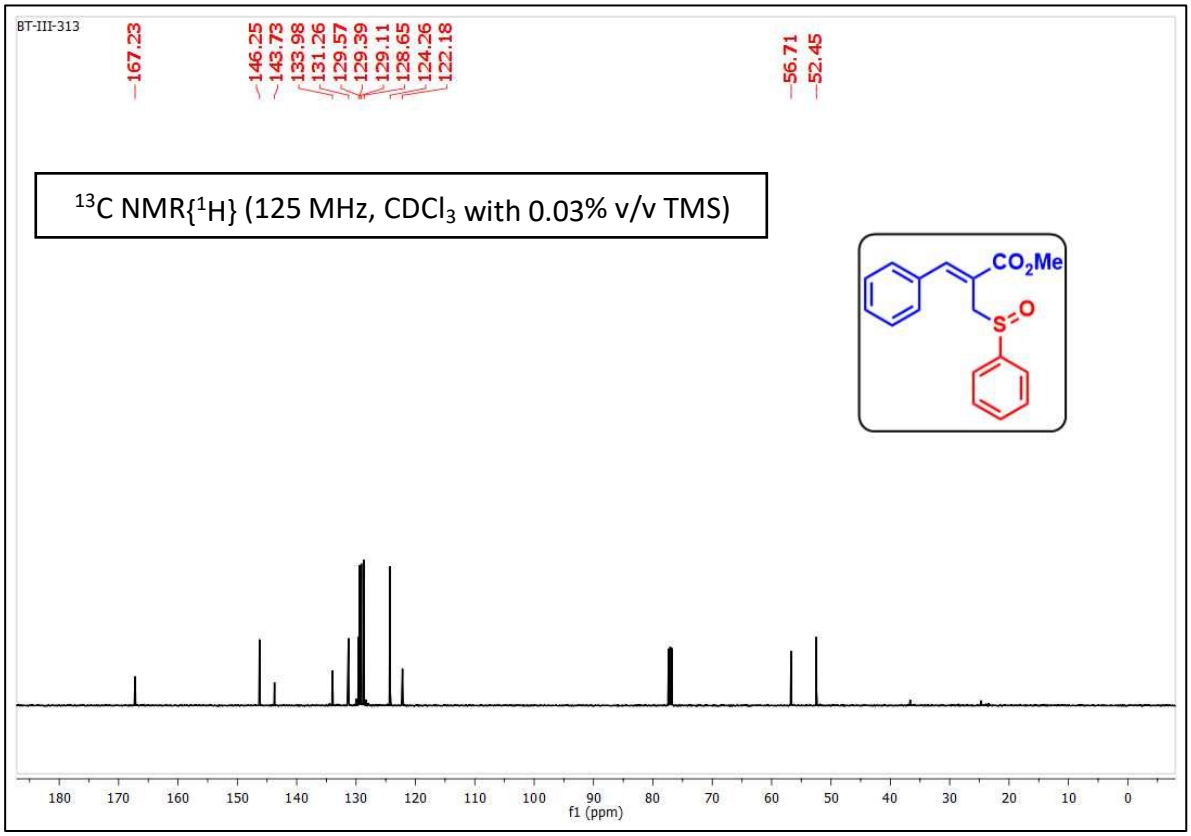
Ethyl (E)-2-((phenylsulfinyl)methyl)-3-(thiophen-2-yl)acrylate (3l)



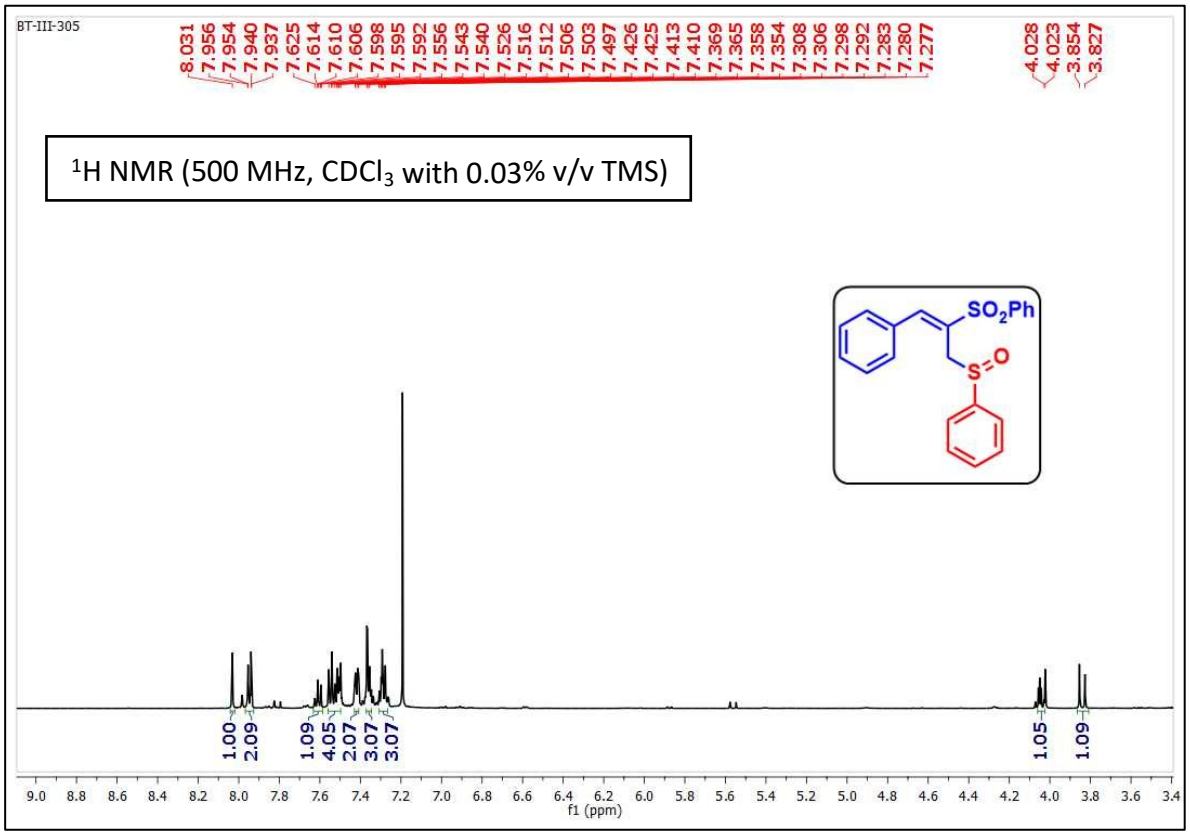


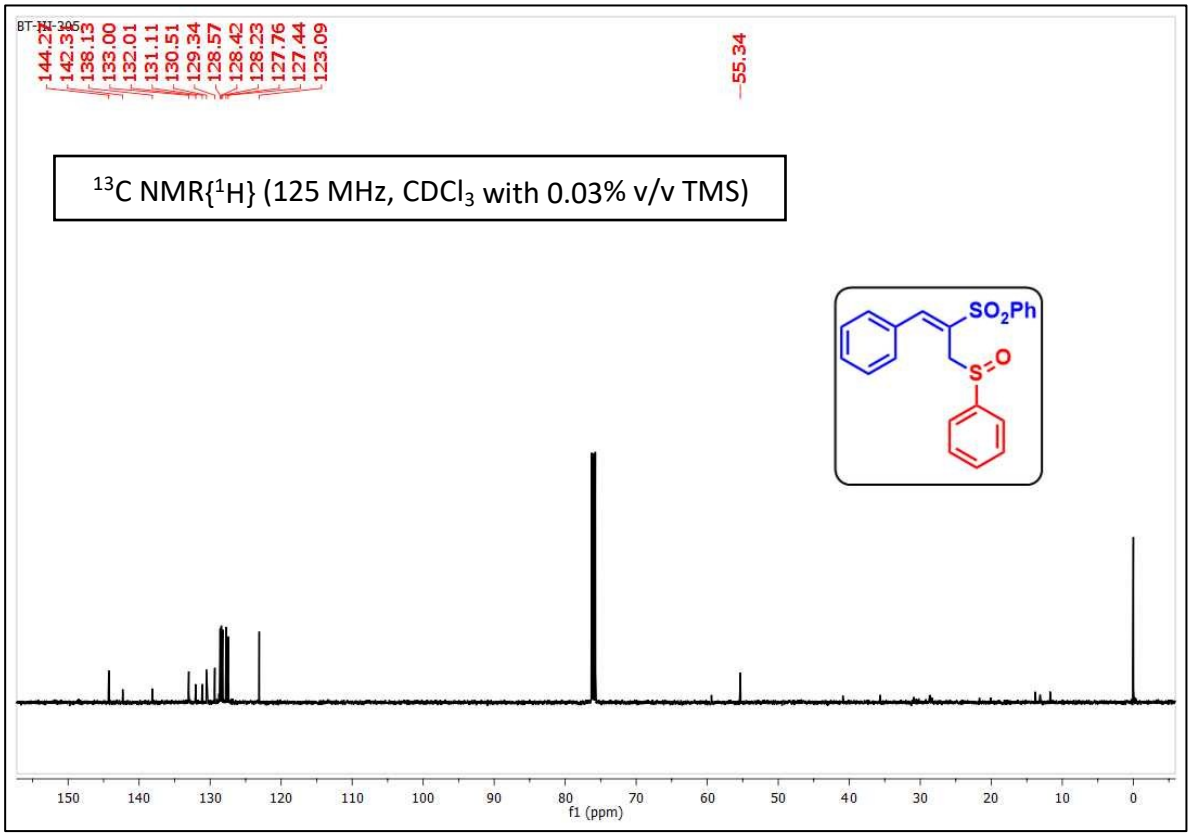
Methyl (Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylate (3m)



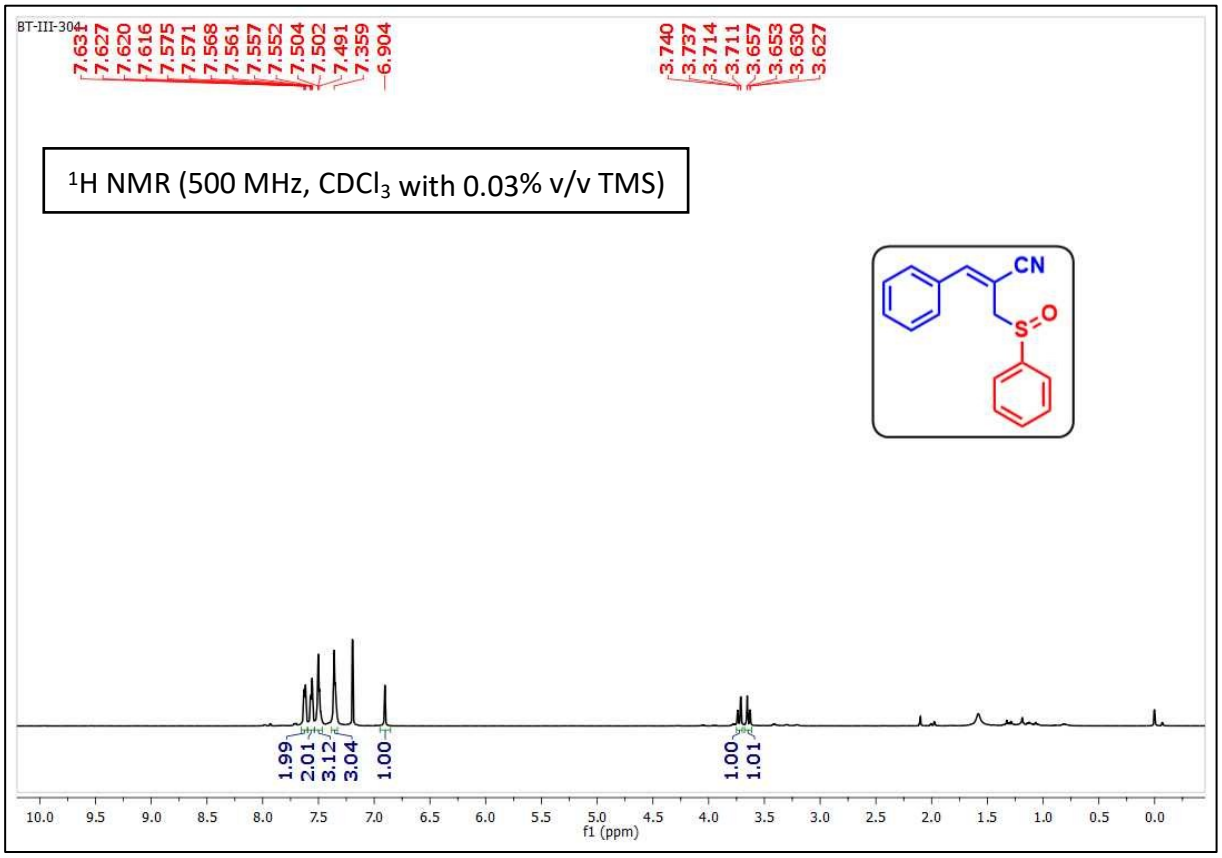


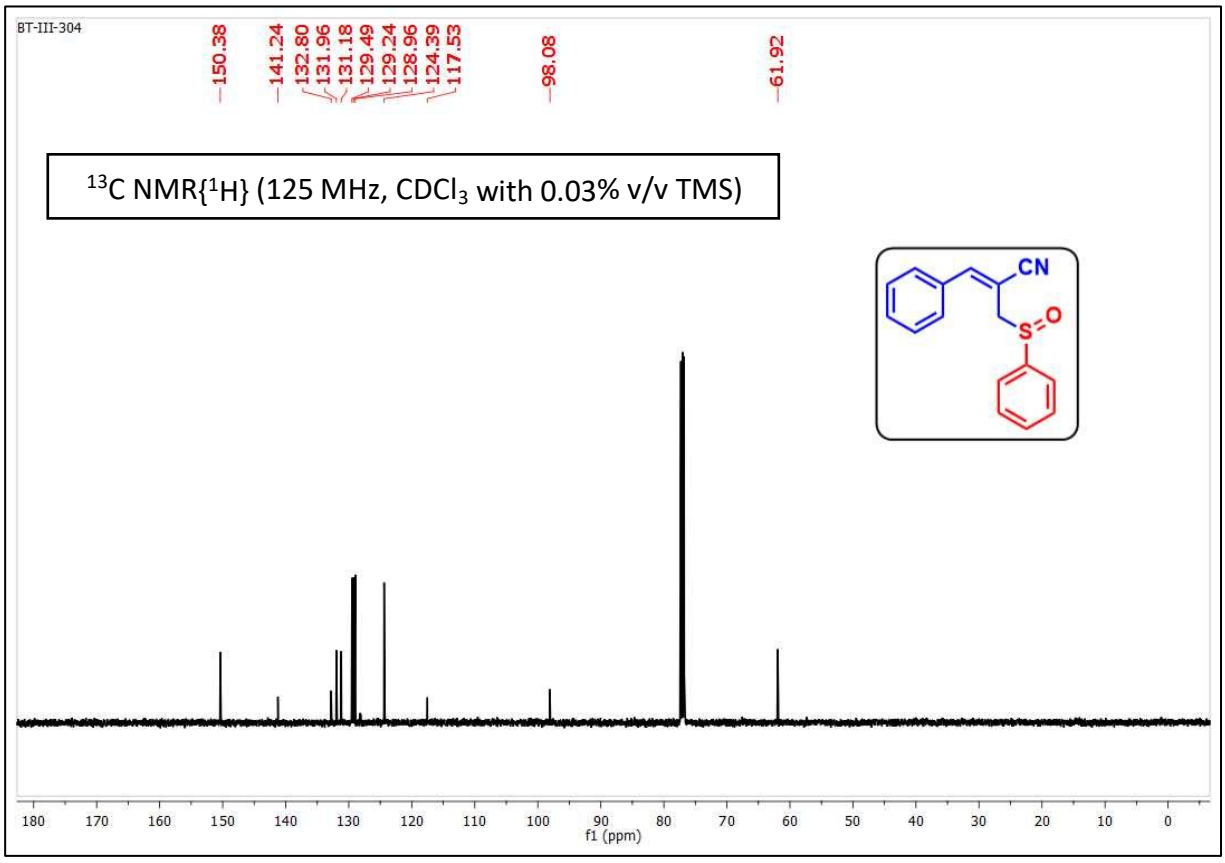
(E)-((3-phenyl-2-(phenylsulfonyl)allyl)sulfinyl)benzene (3n)



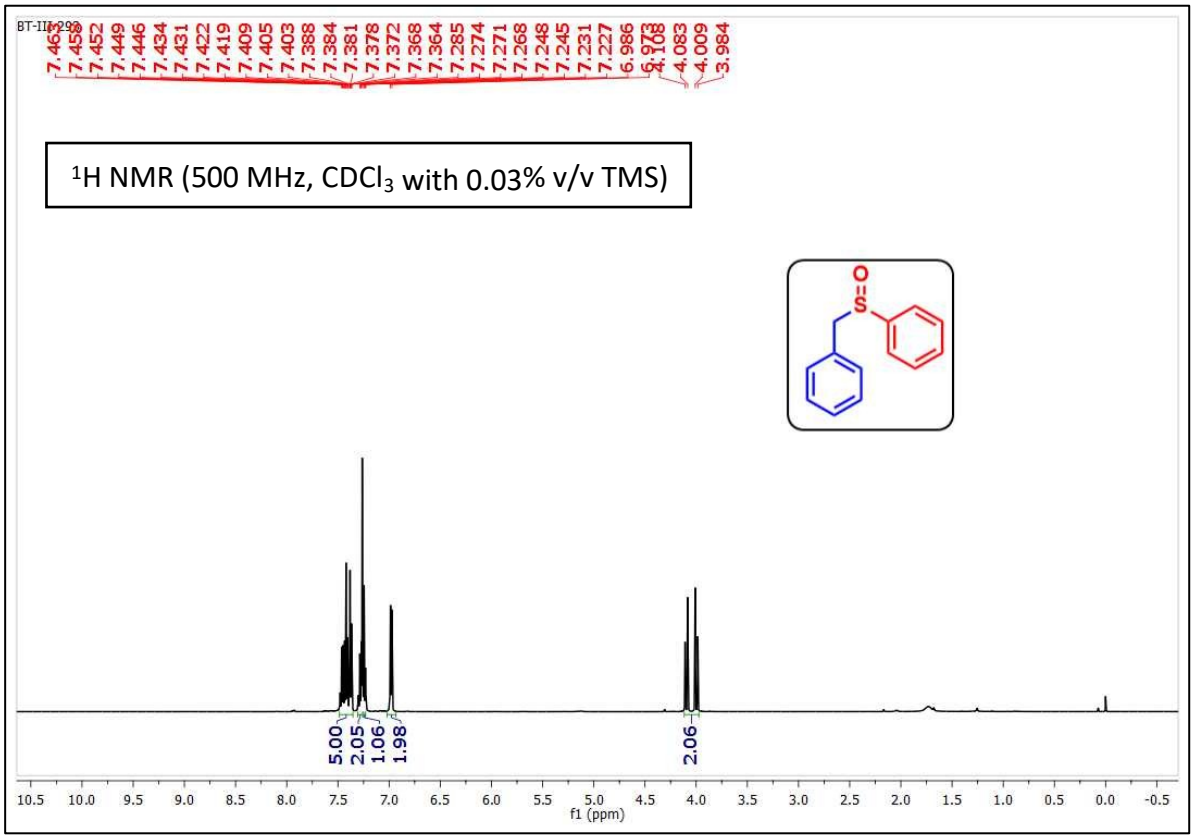


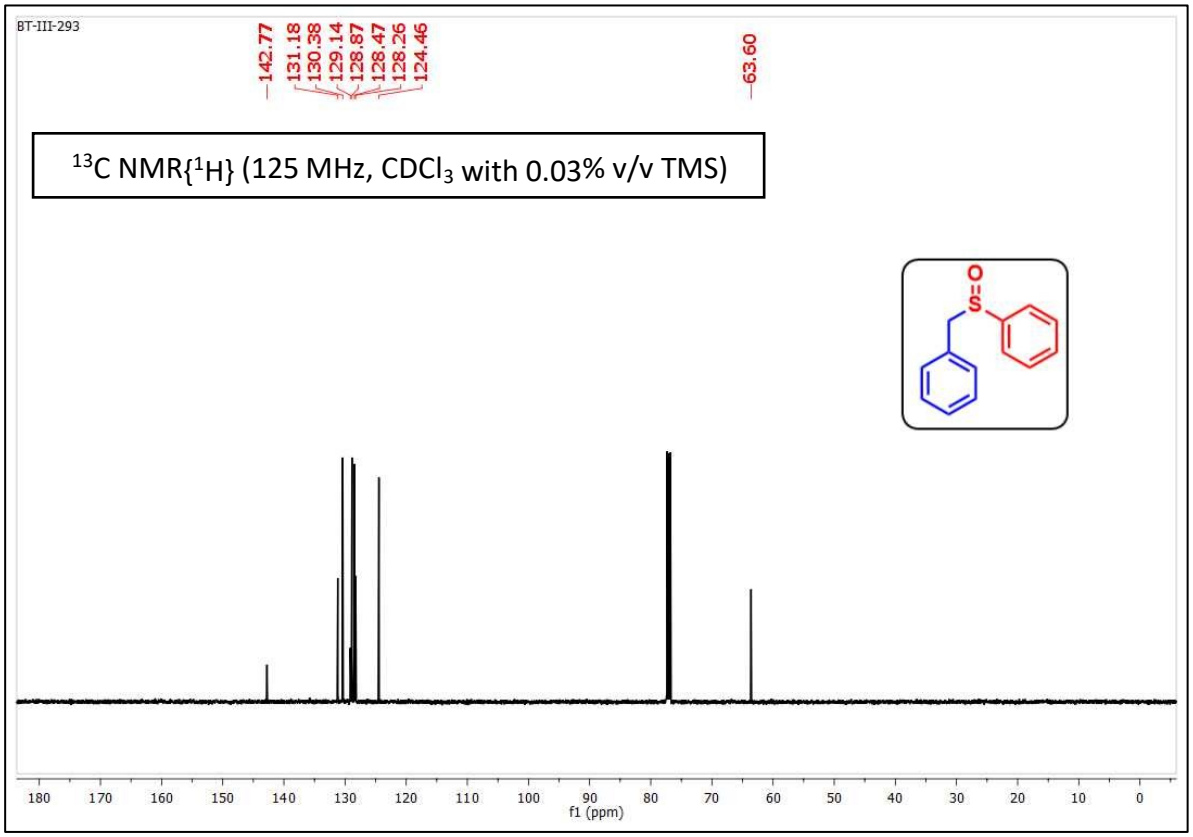
(Z)-3-phenyl-2-((phenylsulfinyl)methyl)acrylonitrile (3o)



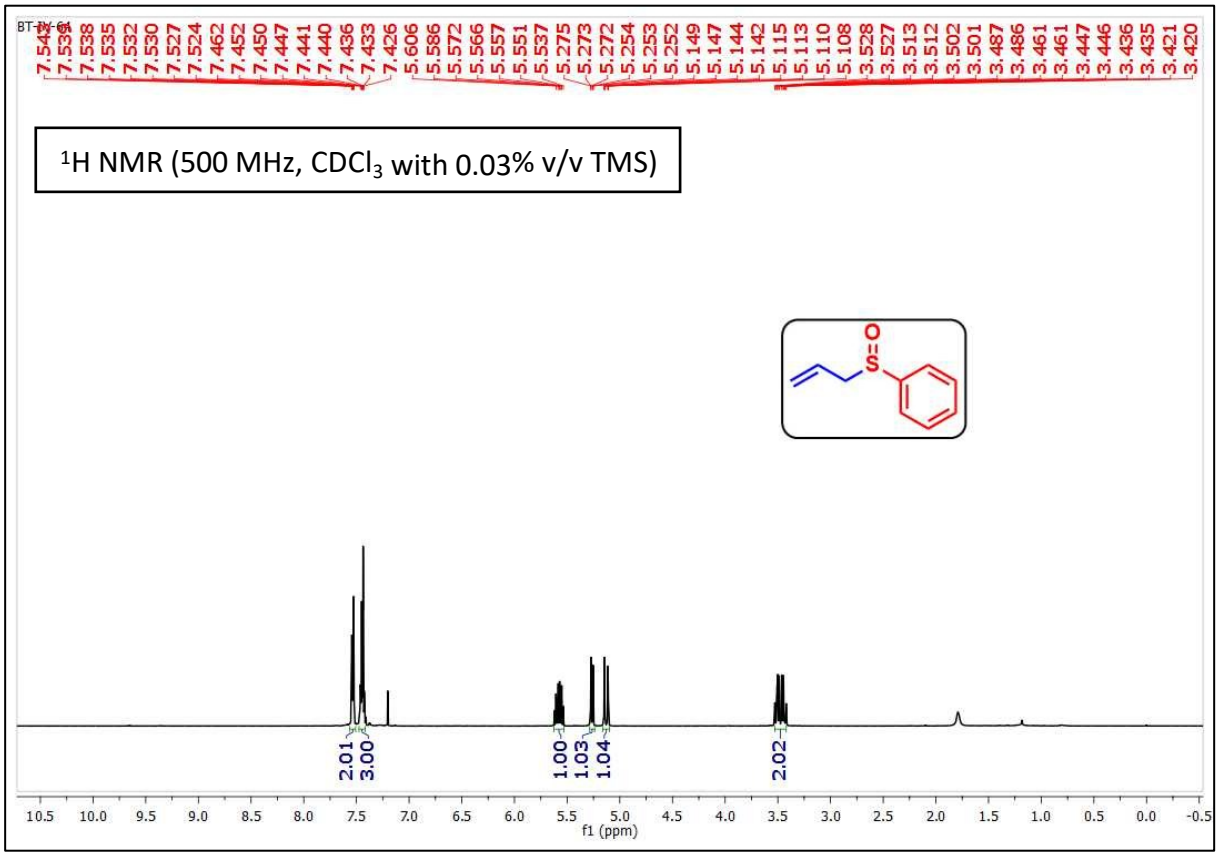


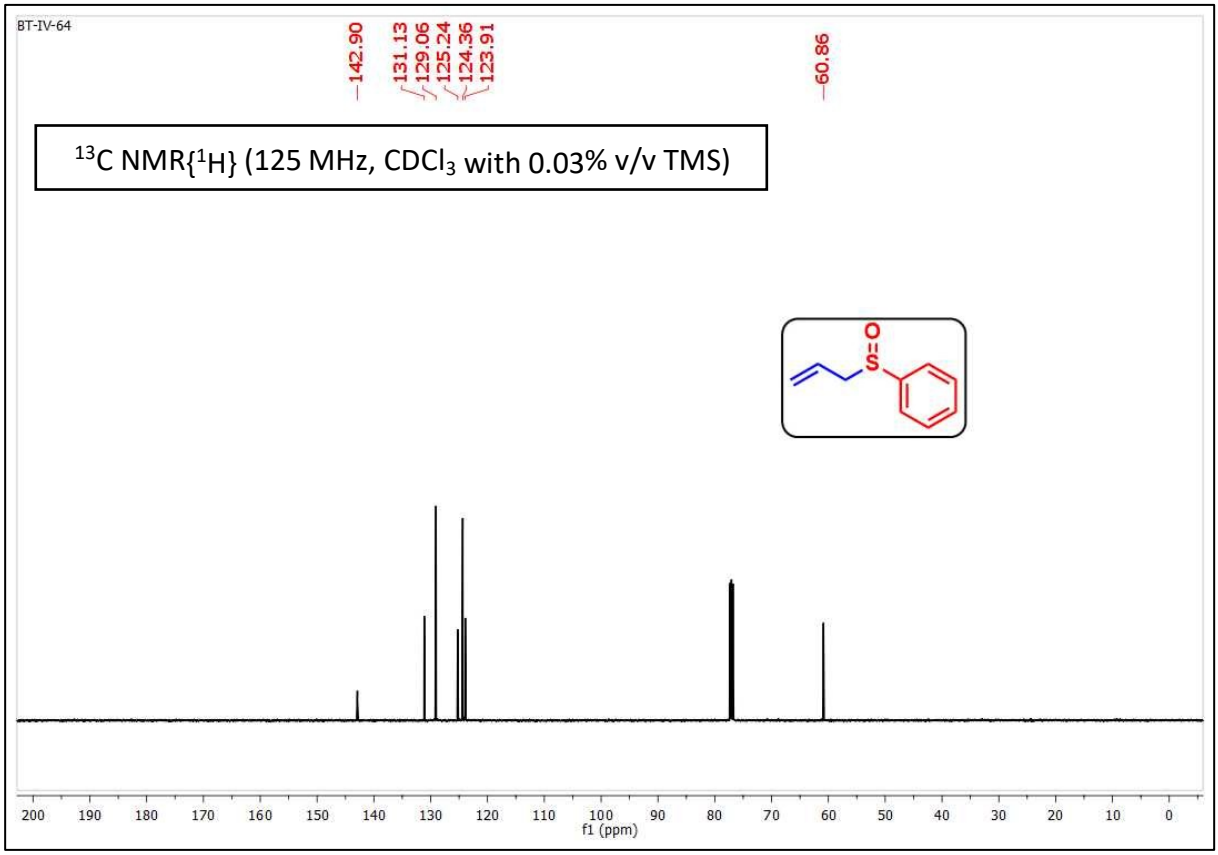
(Benzylsulfinyl)benzene (3s)



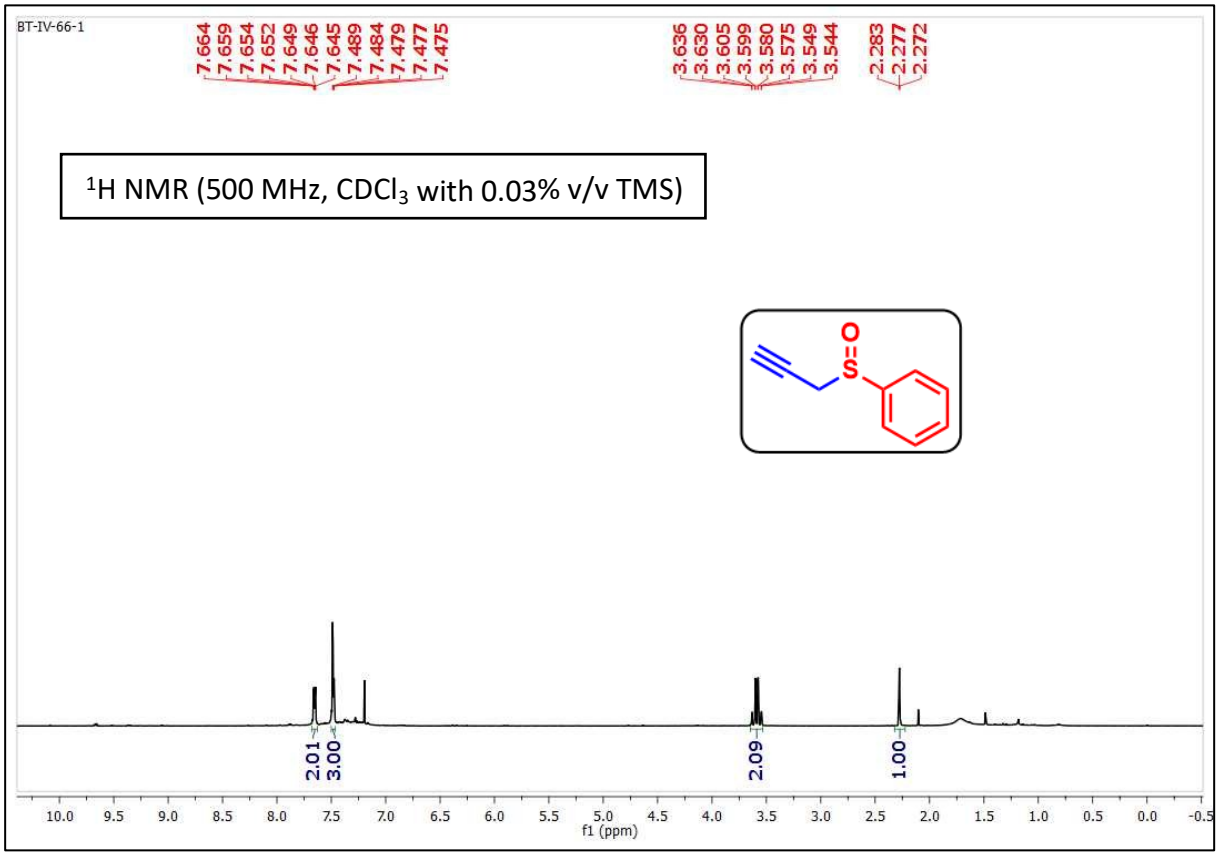


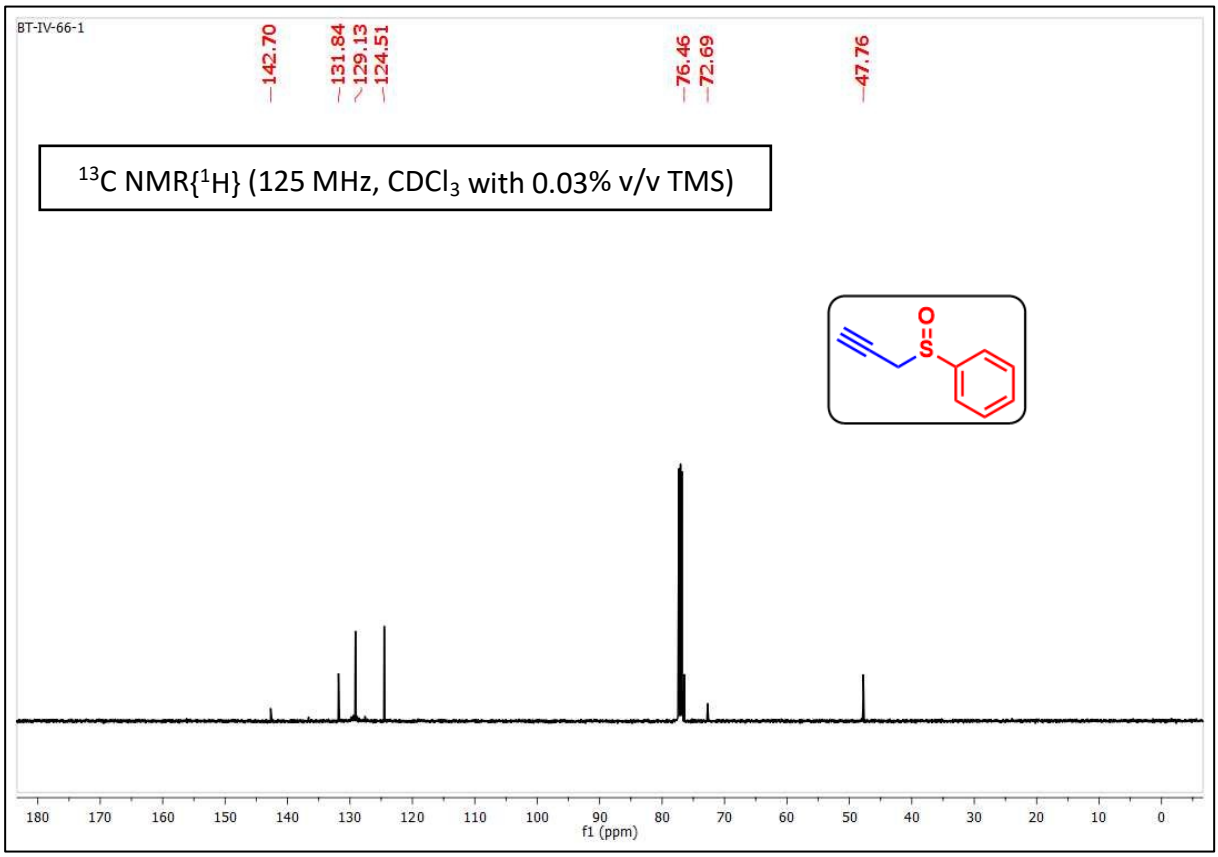
(allylsulfinyl)benzene (3t)



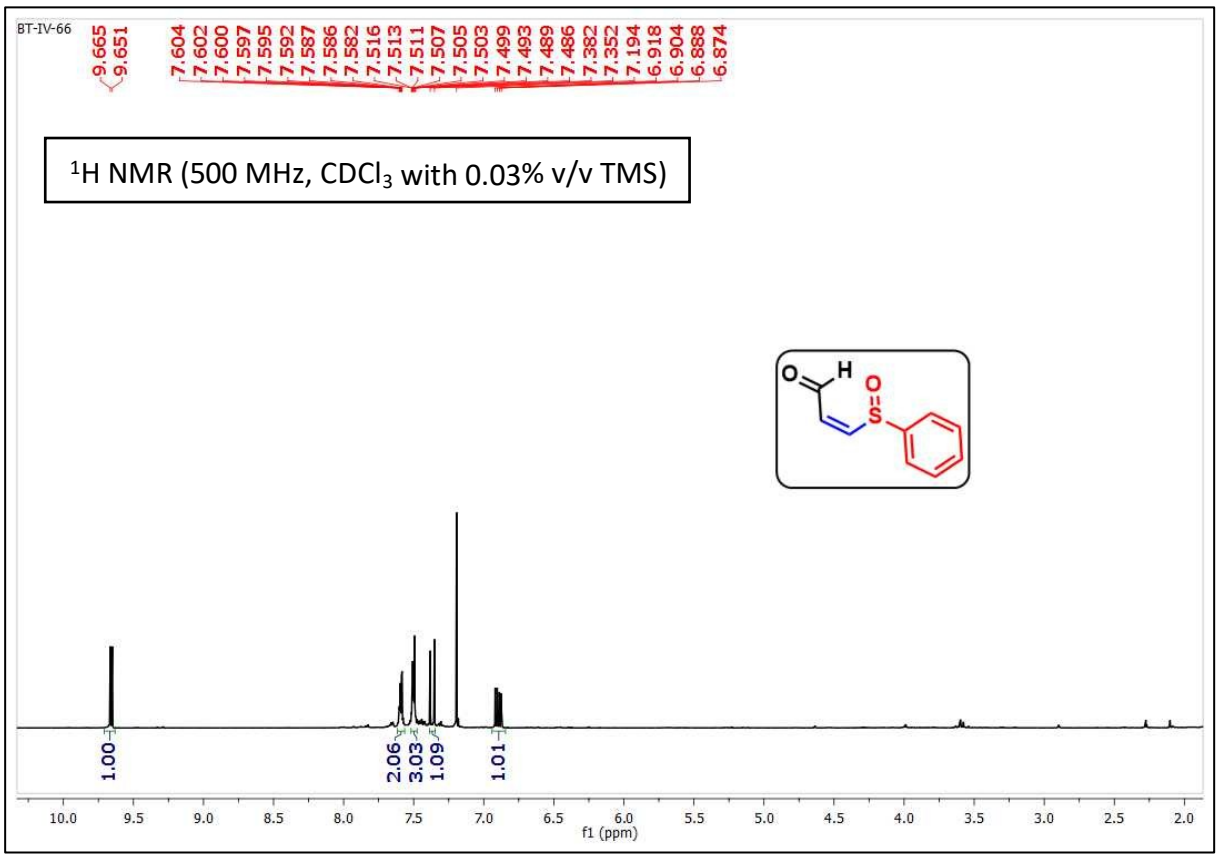


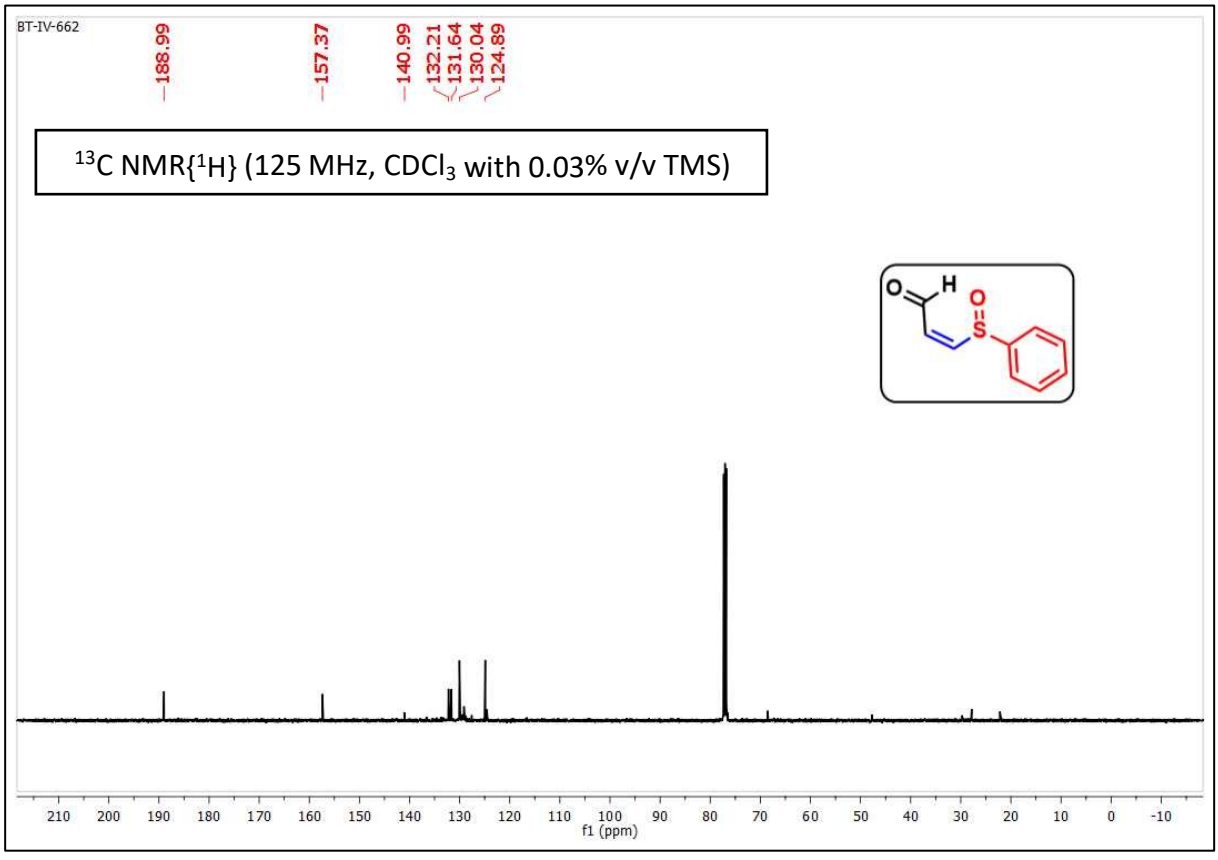
(prop-2-yn-1-ylsulfinyl)benzene (3u)



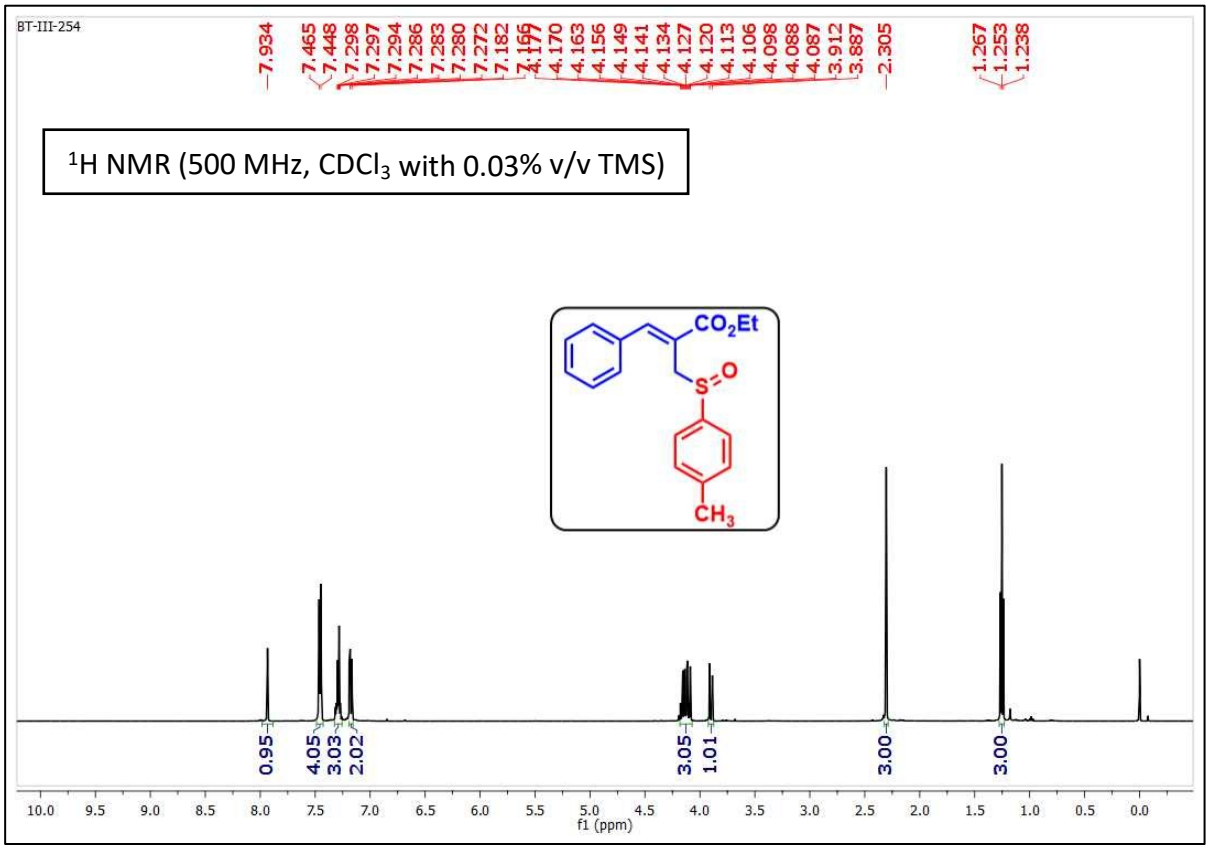


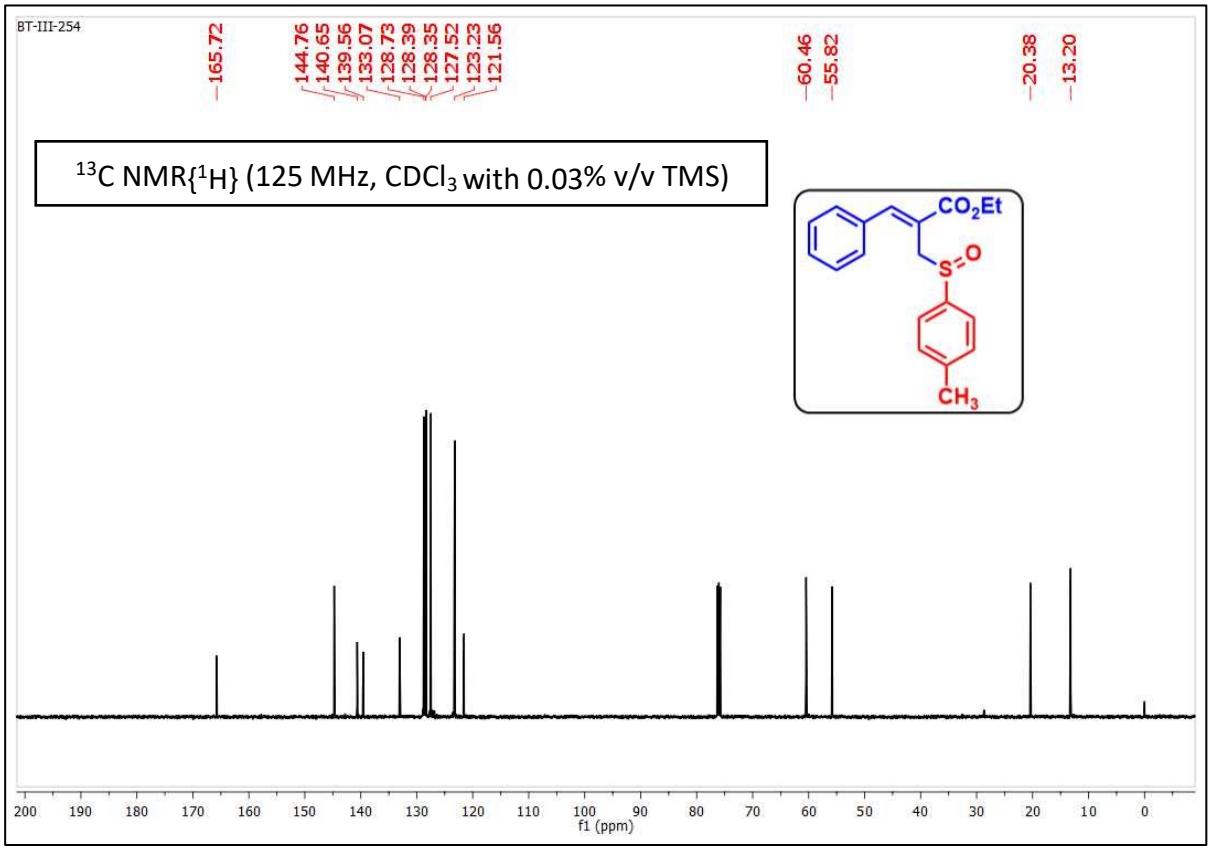
(Z)-3-(phenylsulfinyl)acrylaldehyde (3u)



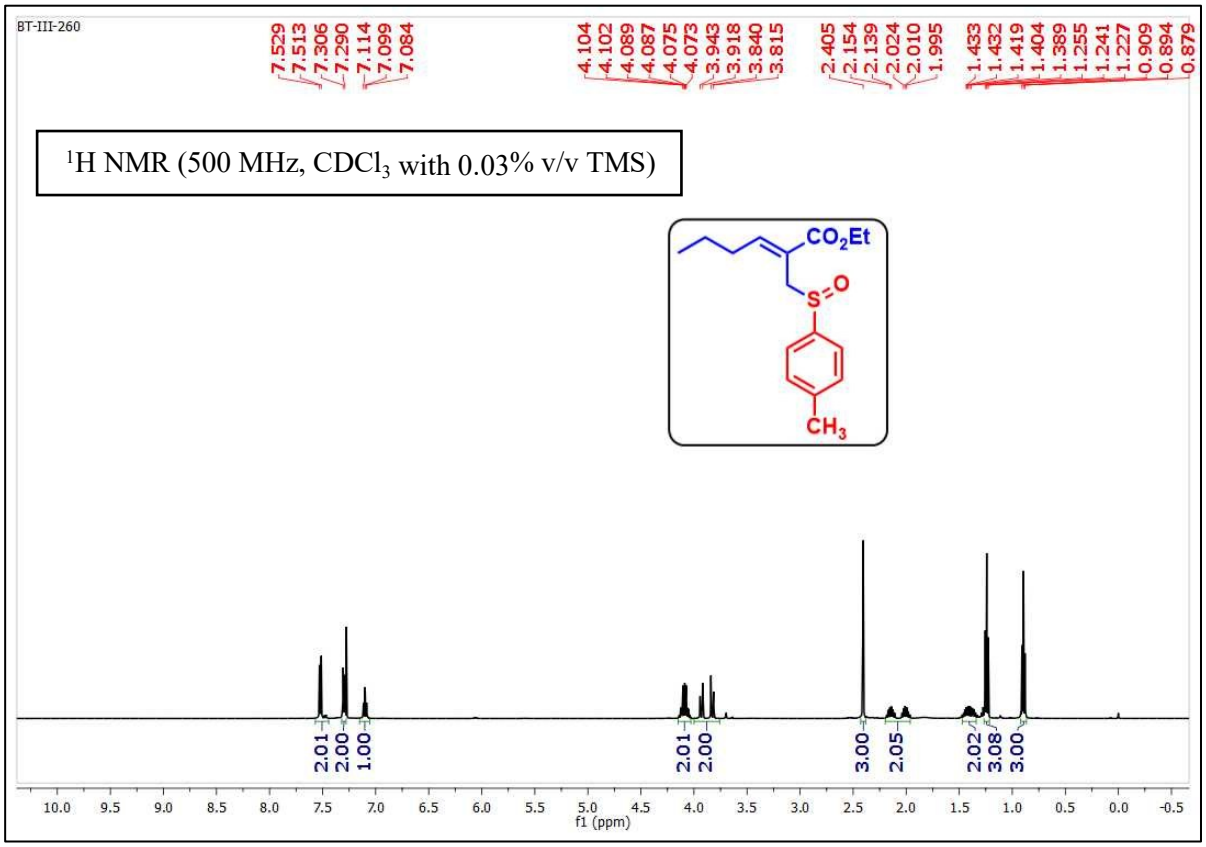


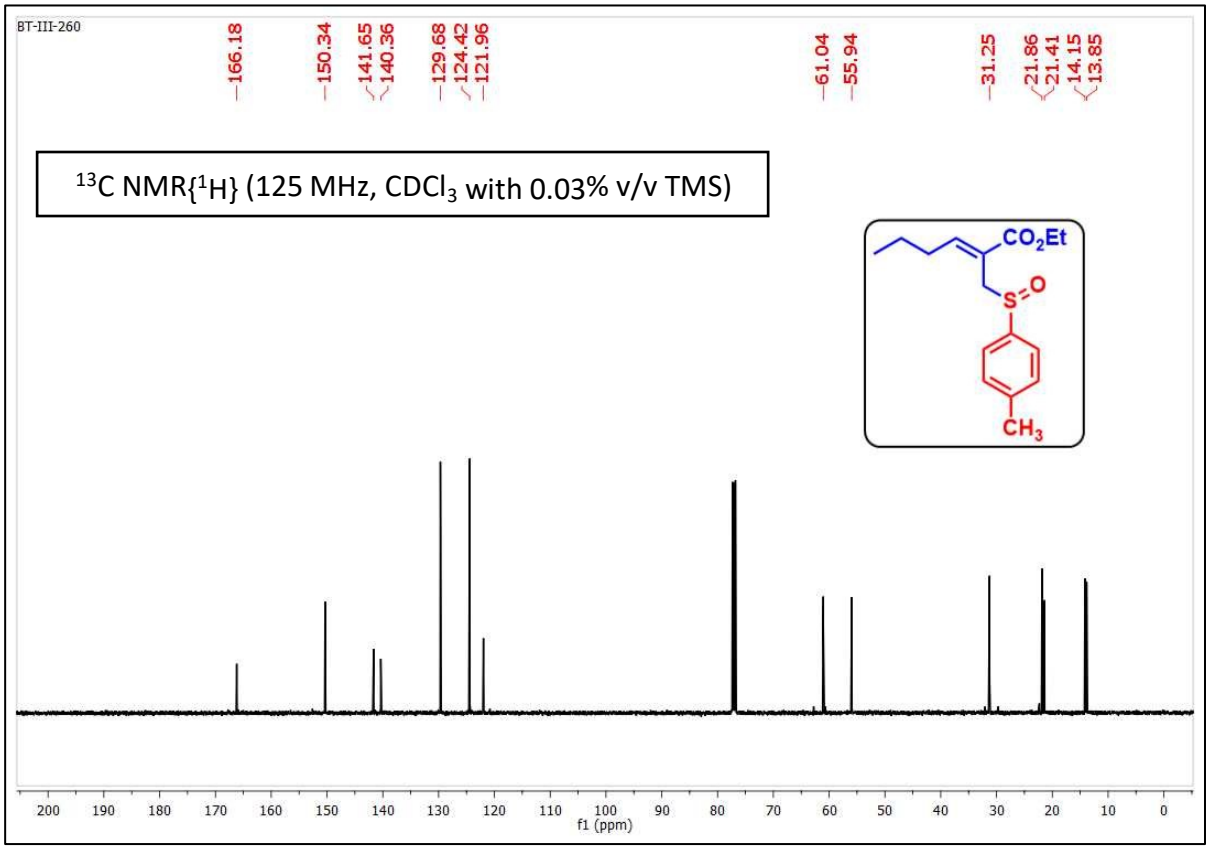
Ethyl (Z)-3-phenyl-2-((p-tolylsulfinyl)methyl)acrylate (4a)



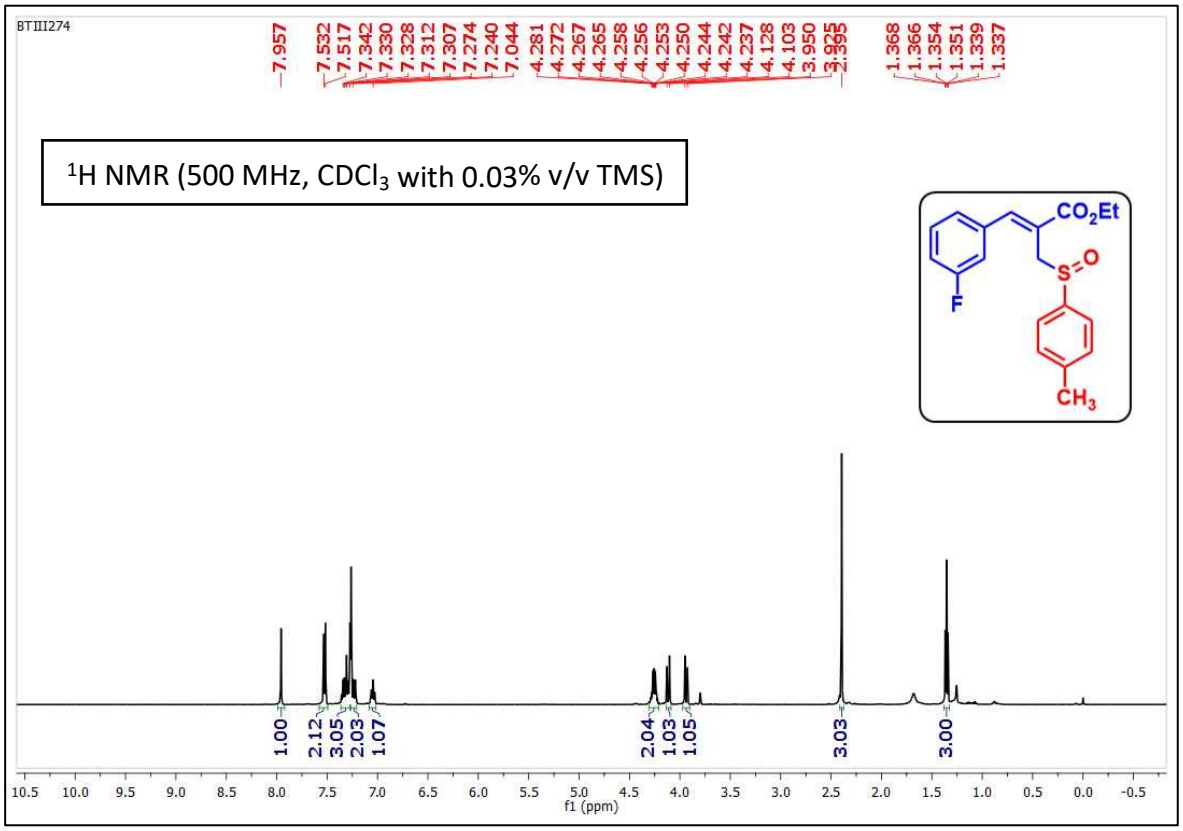


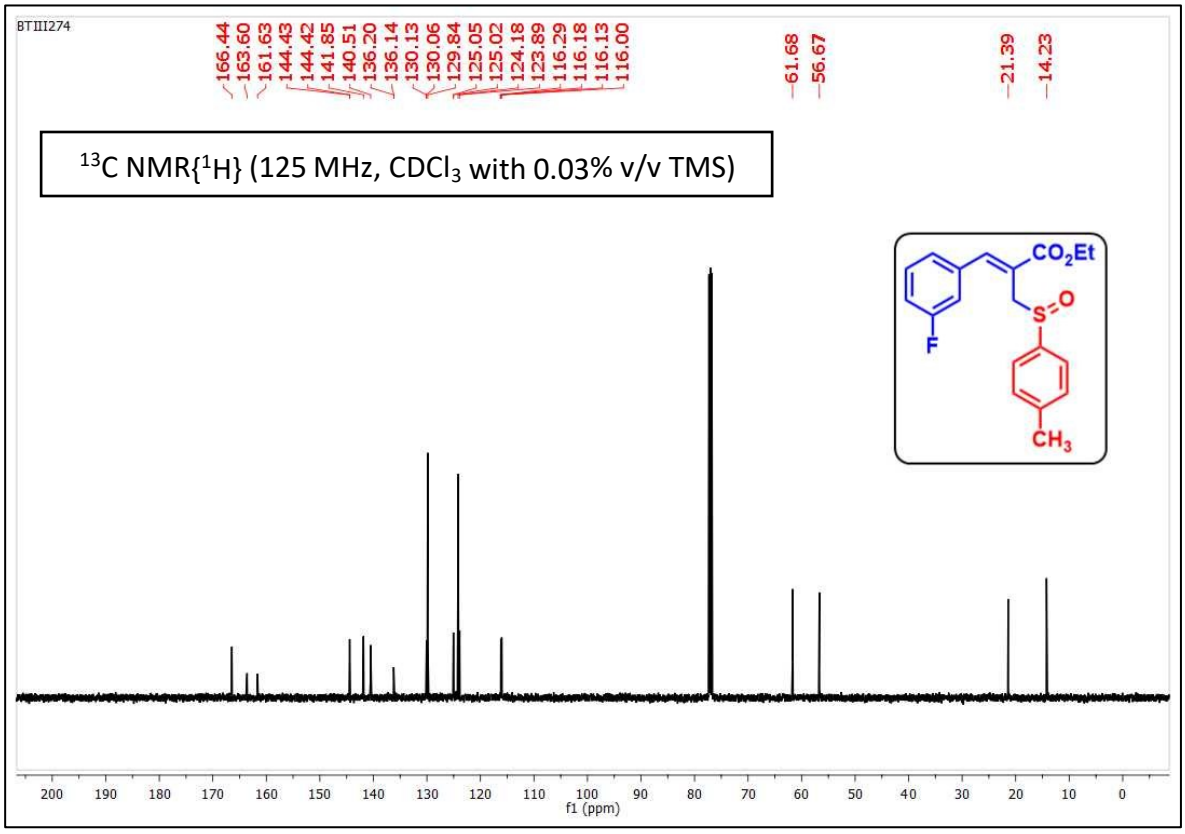
Ethyl (Z)-2-((p-tolylsulfinyl)methyl)hex-2-enoate (4b)



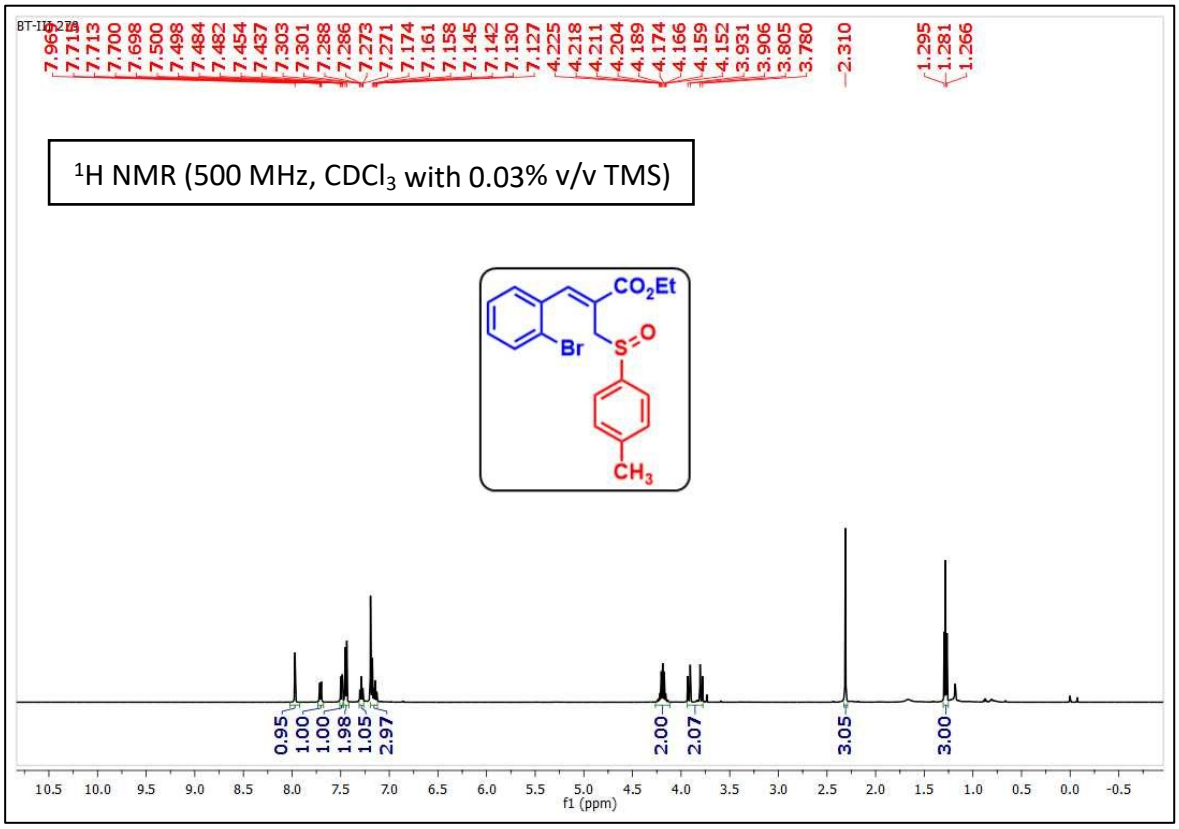


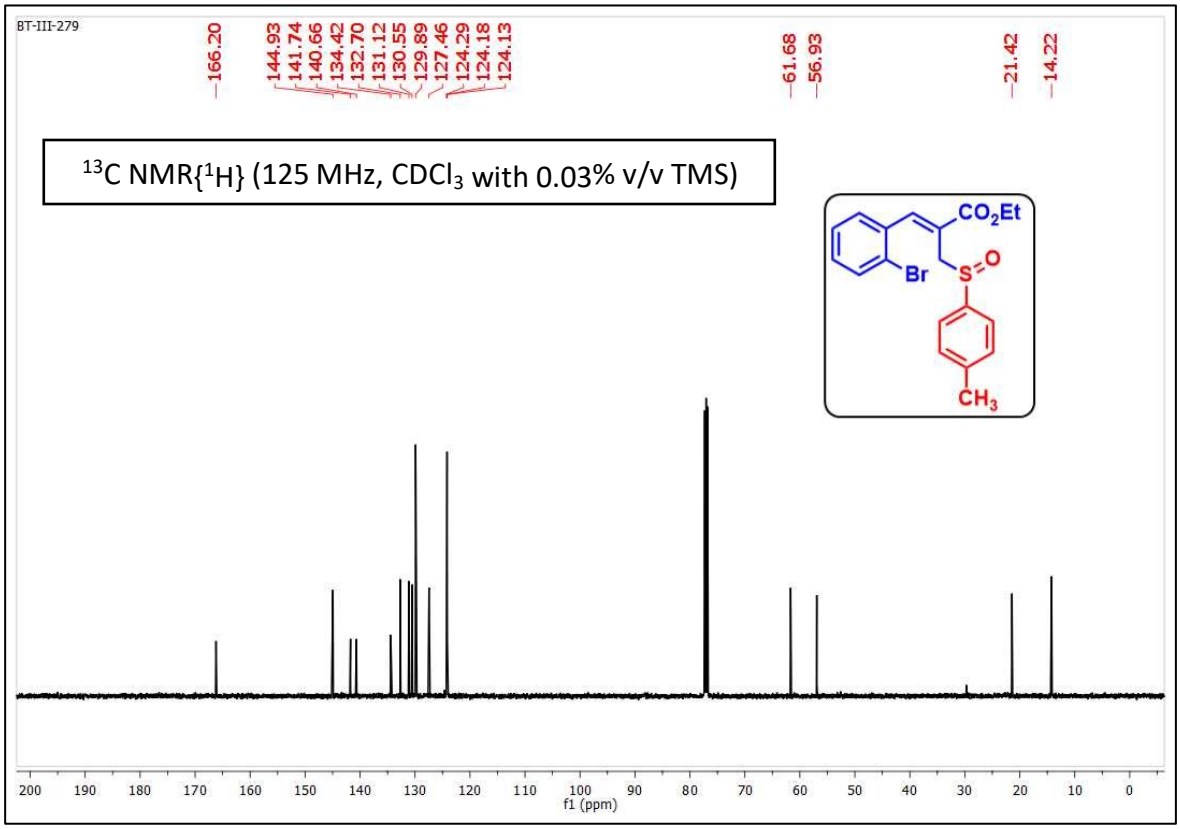
Ethyl (Z)-3-(3-fluorophenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4c)



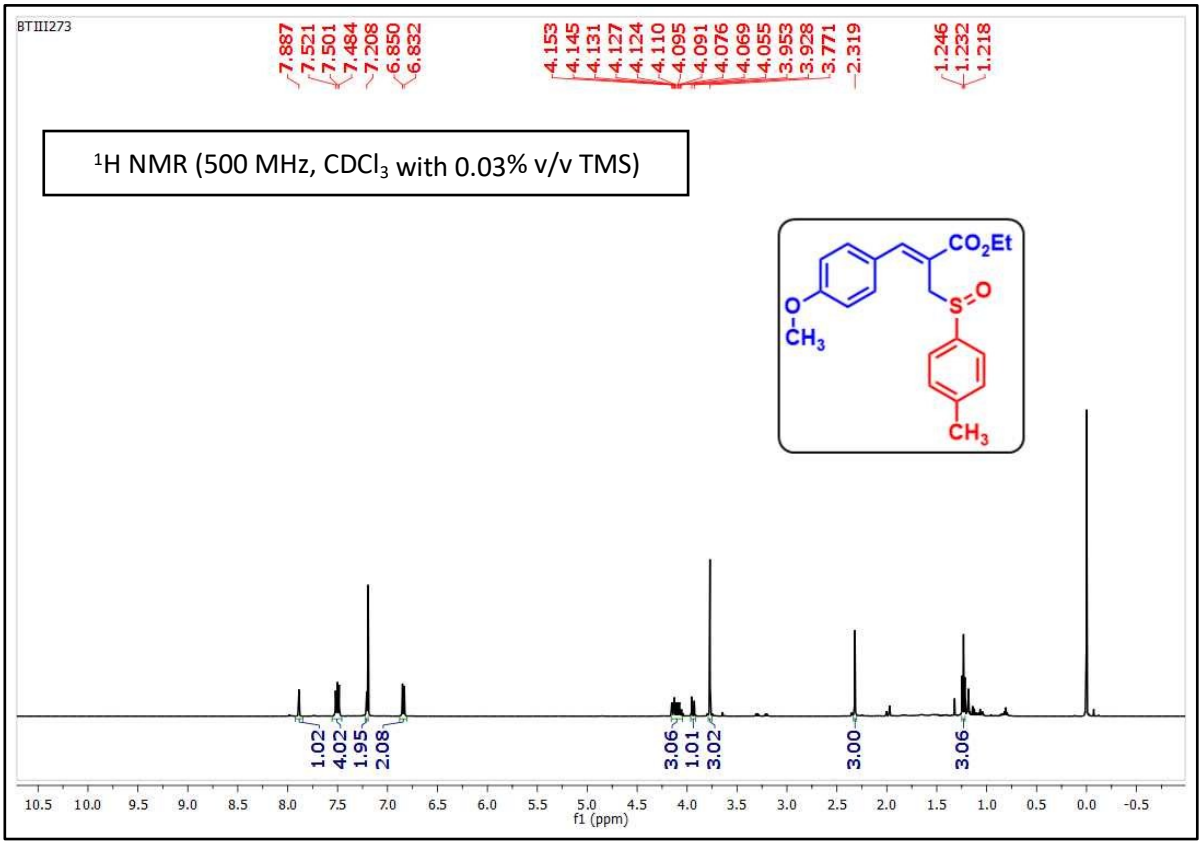


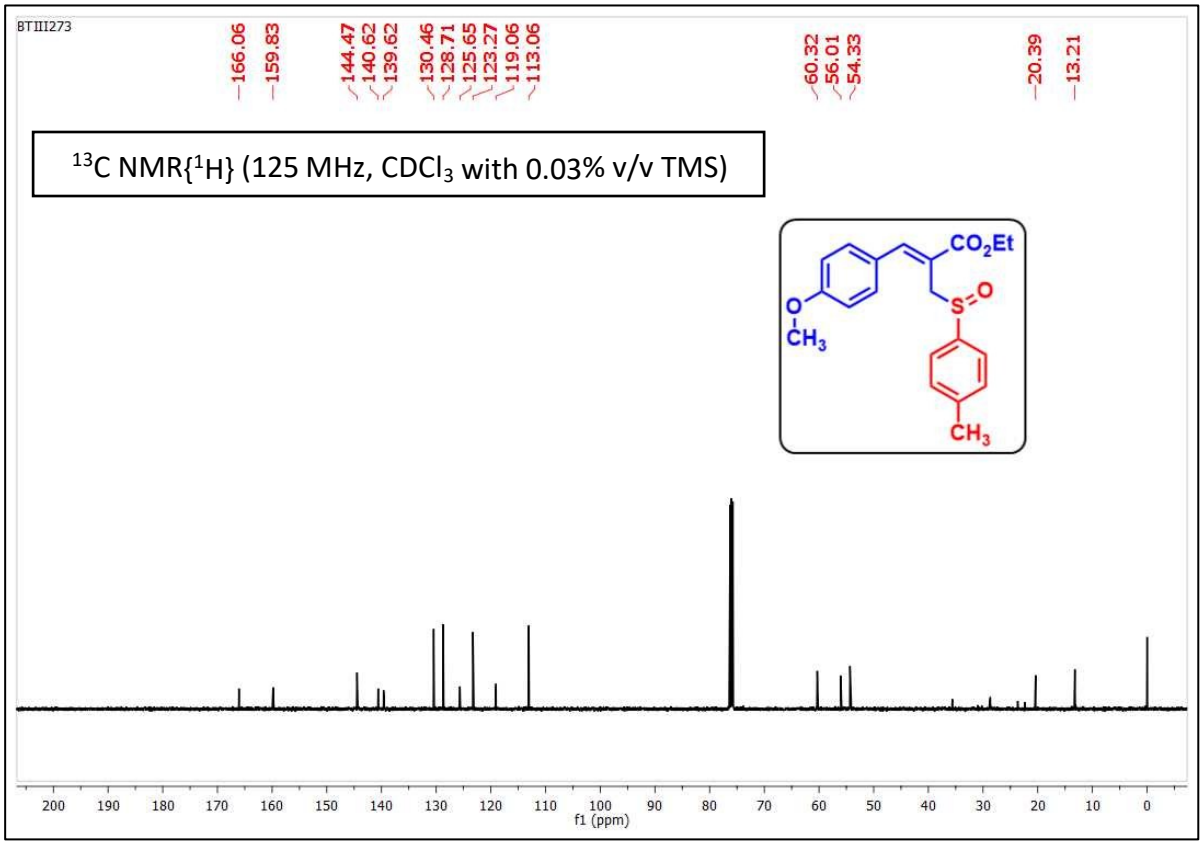
Ethyl (Z)-3-(2-bromophenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4d)



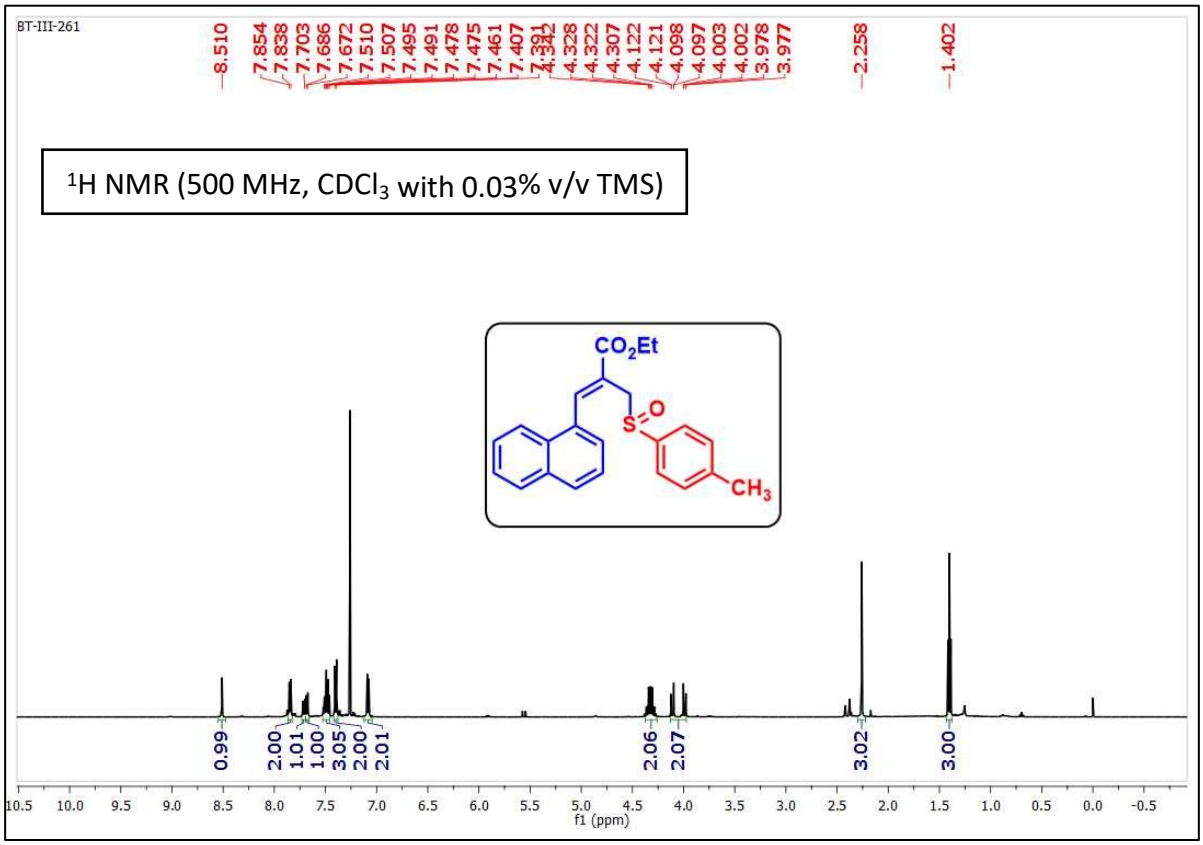


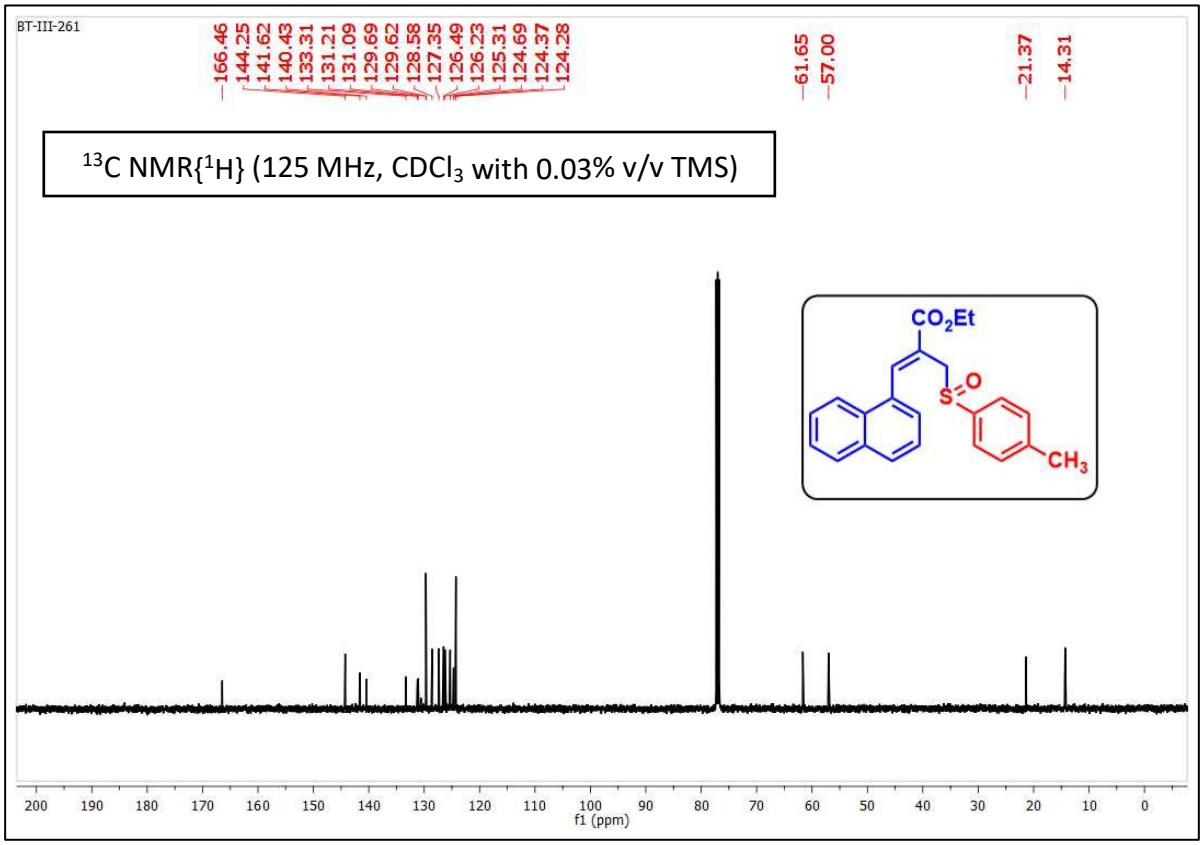
Ethyl (Z)-3-(4-methoxyphenyl)-2-((p-tolylsulfinyl)methyl)acrylate (4e)



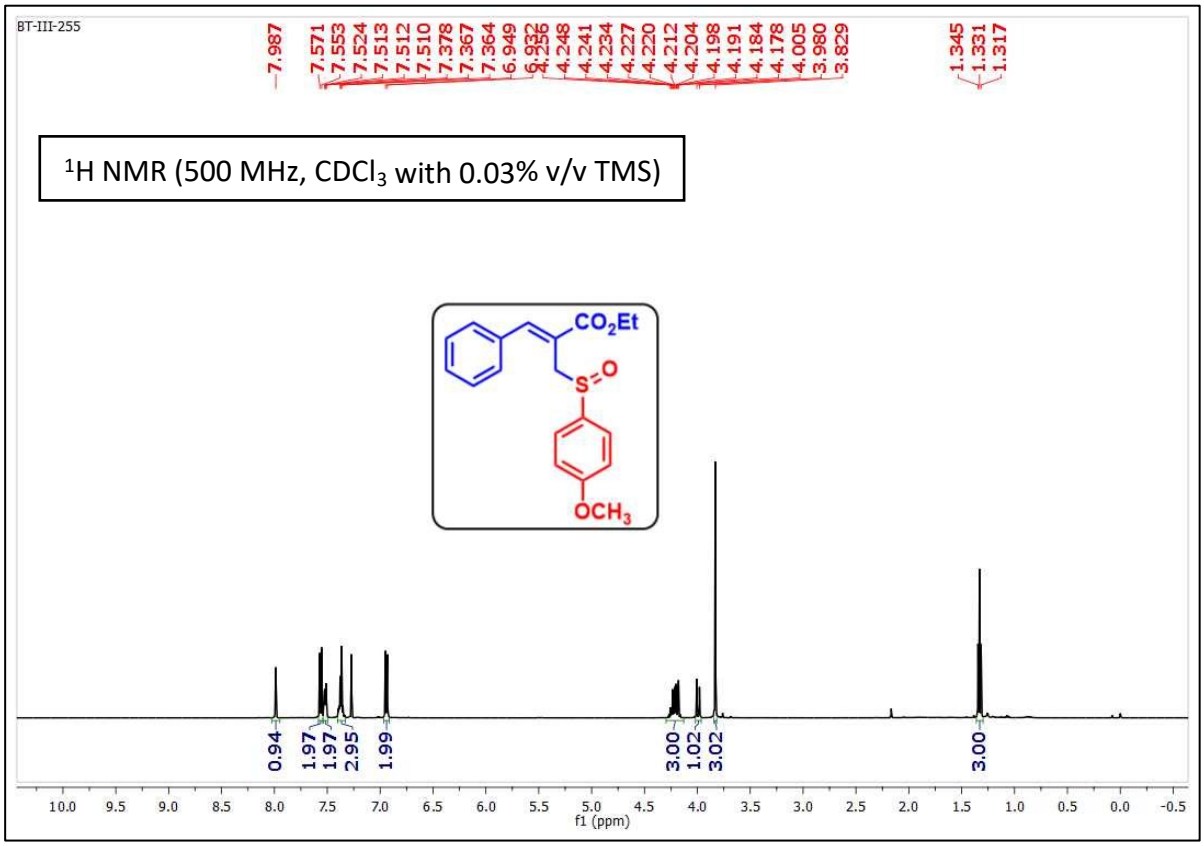


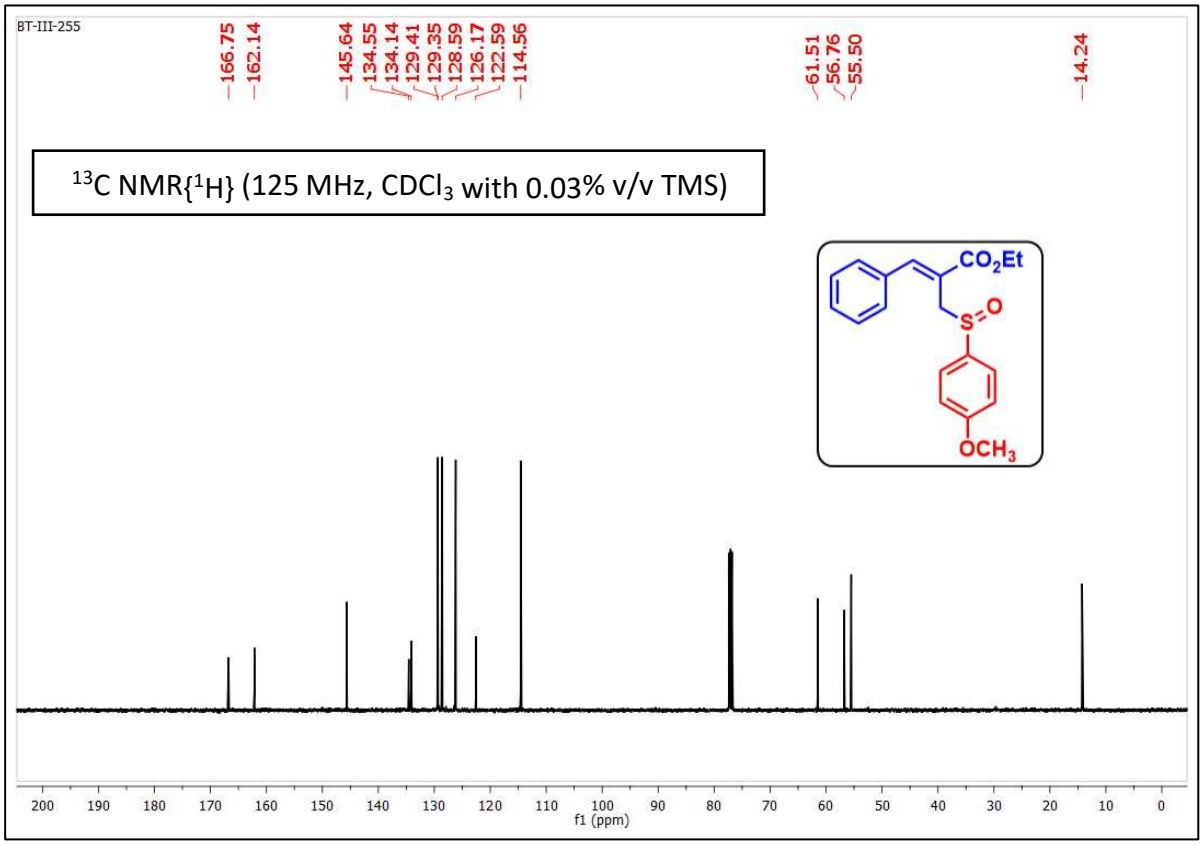
Ethyl (Z)-3-(naphthalen-1-yl)-2-((p-tolylsulfinyl)methyl)acrylate (4f)



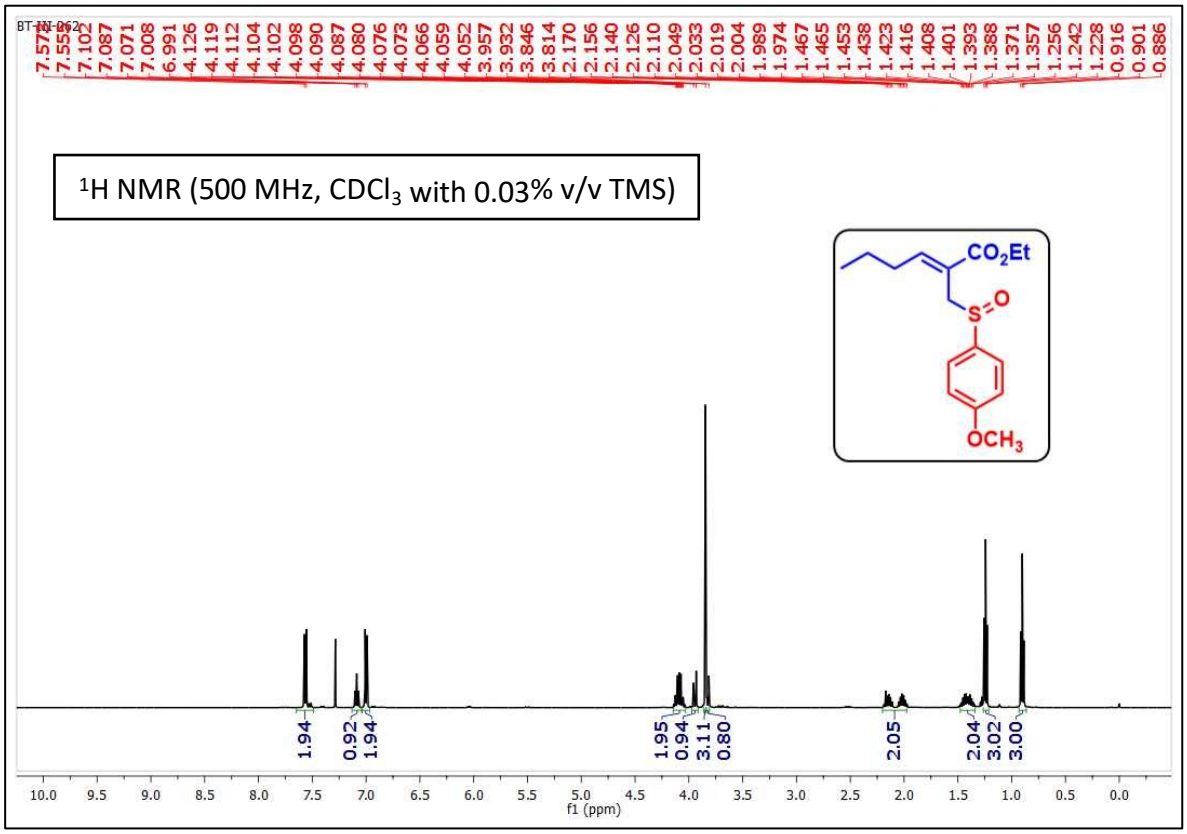


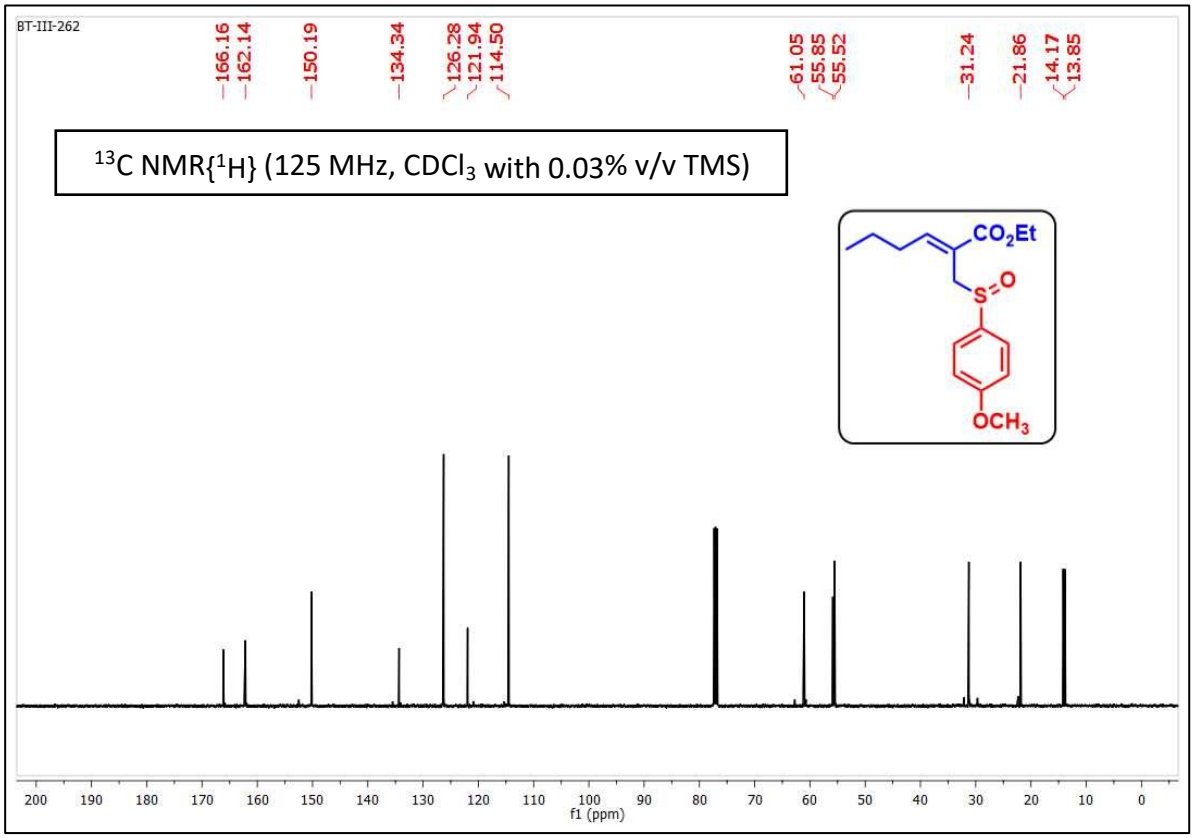
Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-phenylacrylate (4g)



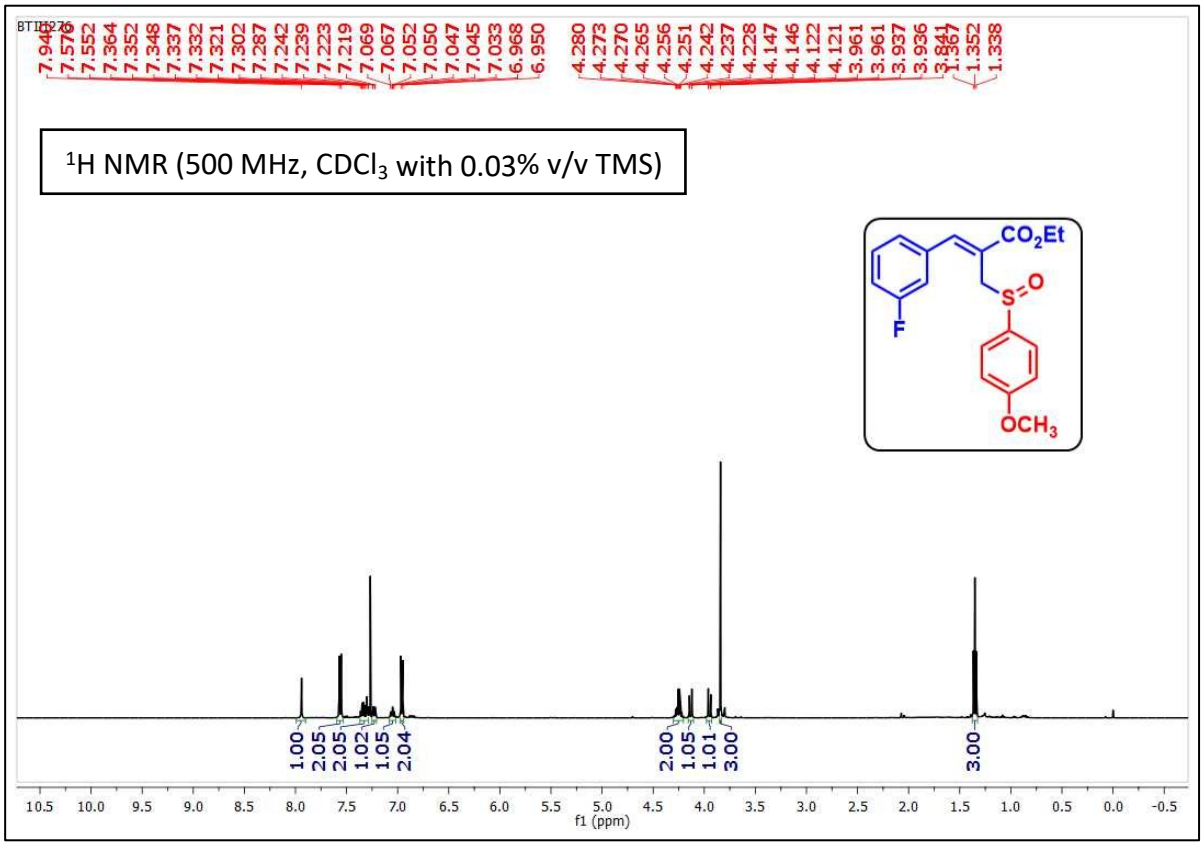


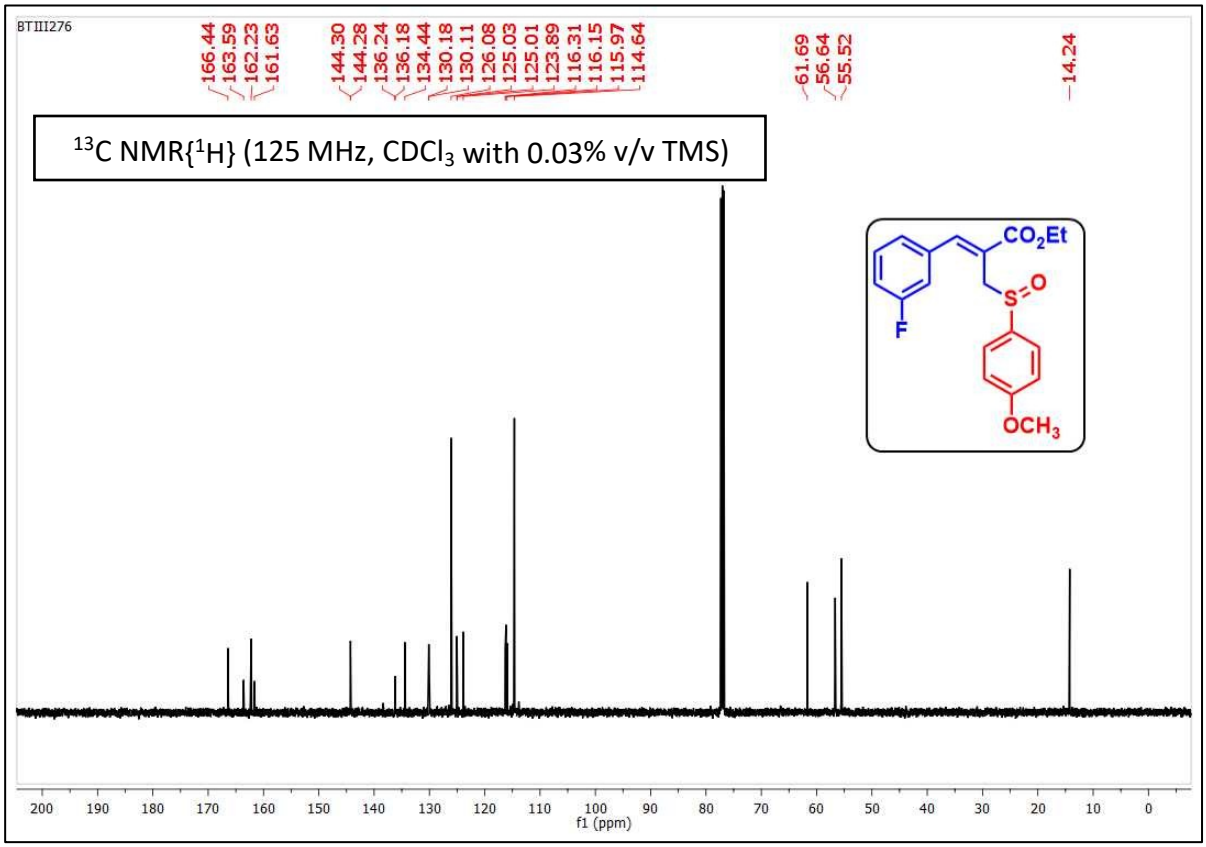
Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)hex-2-enoate (4h)



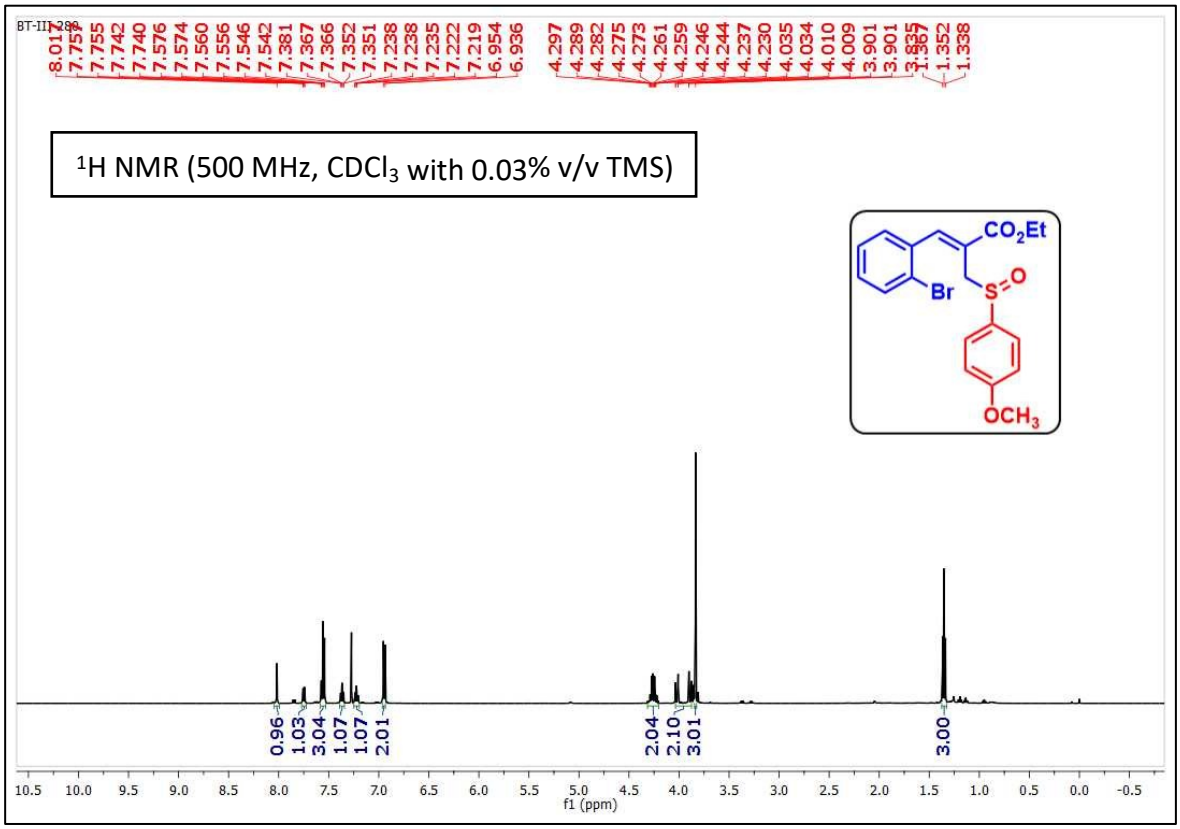


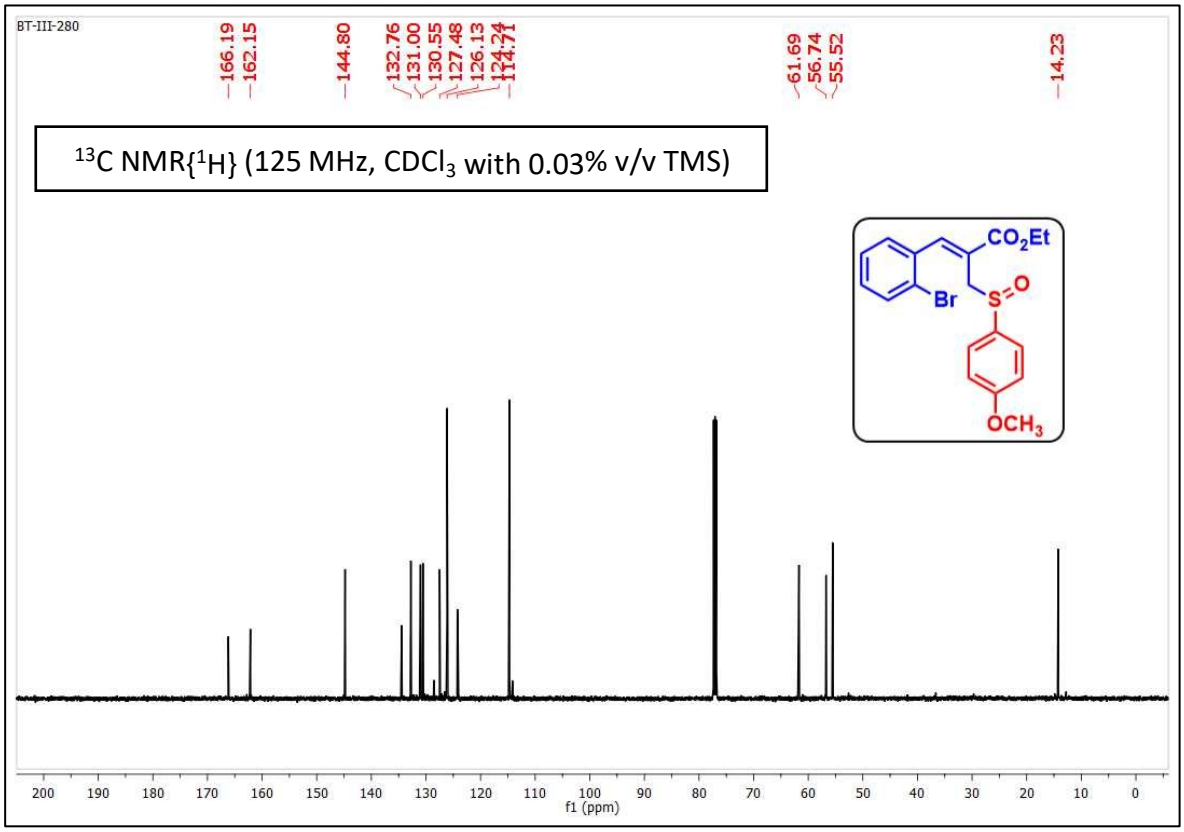
Ethyl (Z)-3-(3-fluorophenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4i)



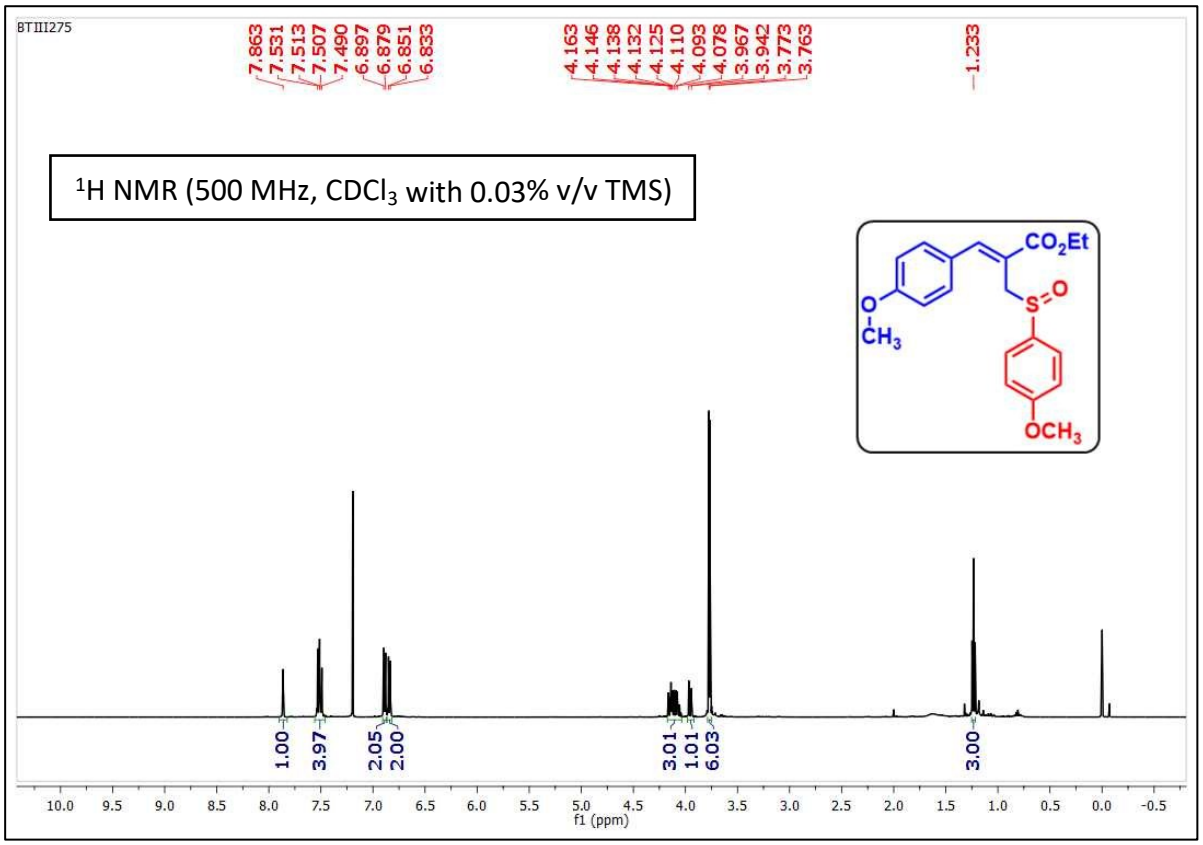


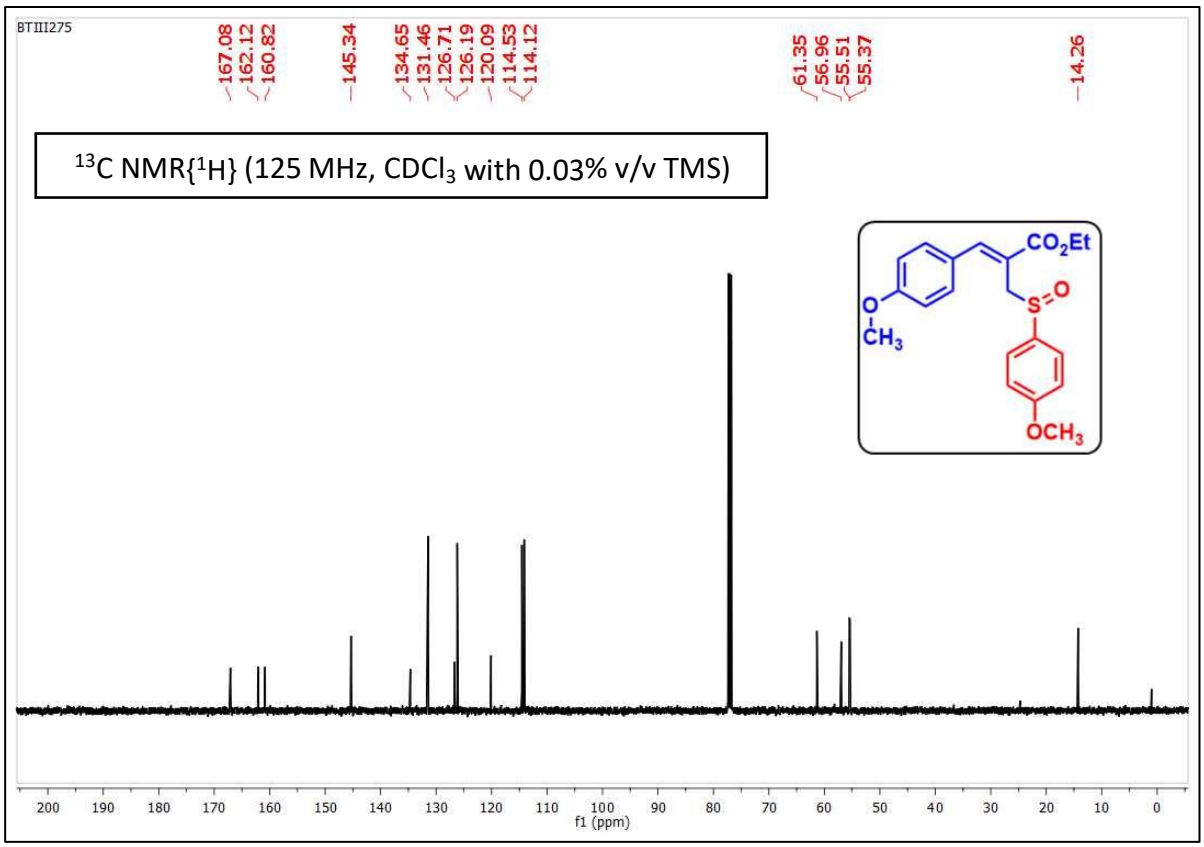
Ethyl (Z)-3-(2-bromophenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4j)



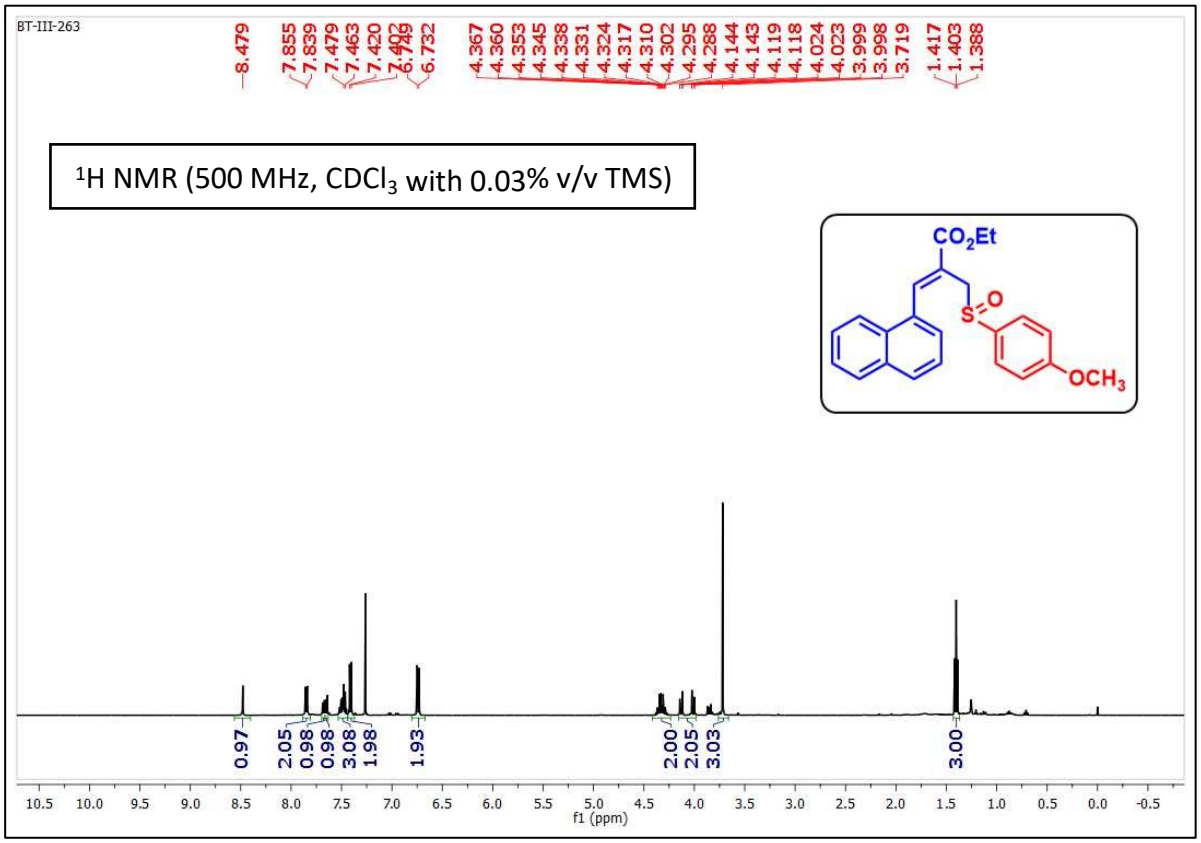


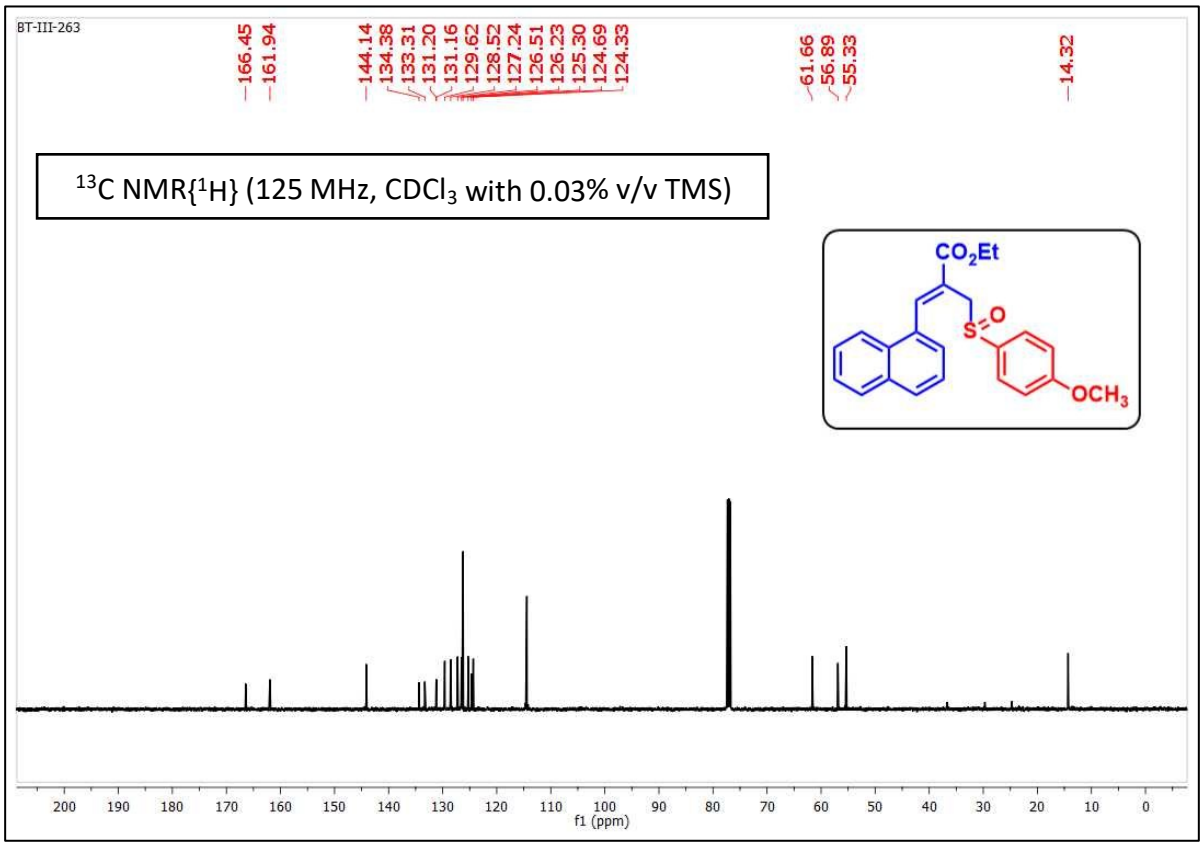
Ethyl (Z)-3-(4-methoxyphenyl)-2-(((4-methoxyphenyl)sulfinyl)methyl)acrylate (4k)



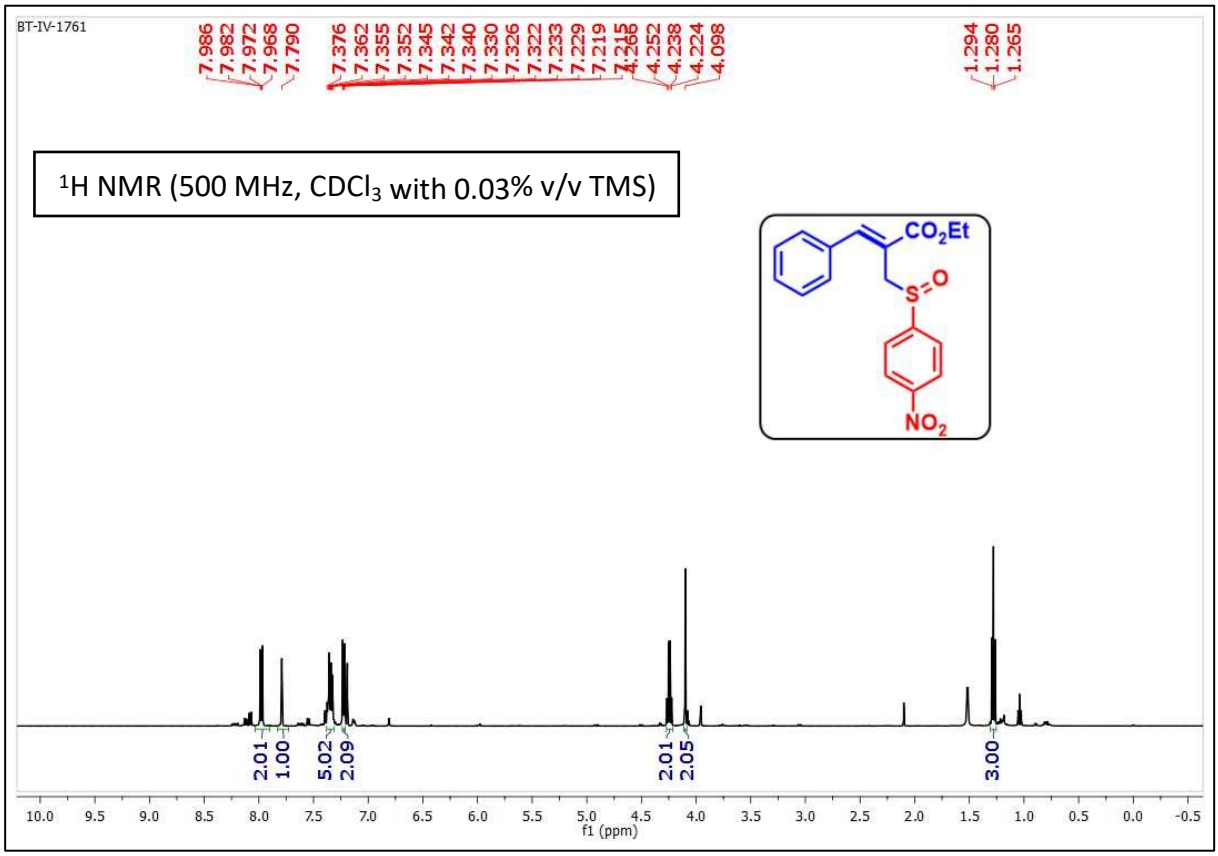


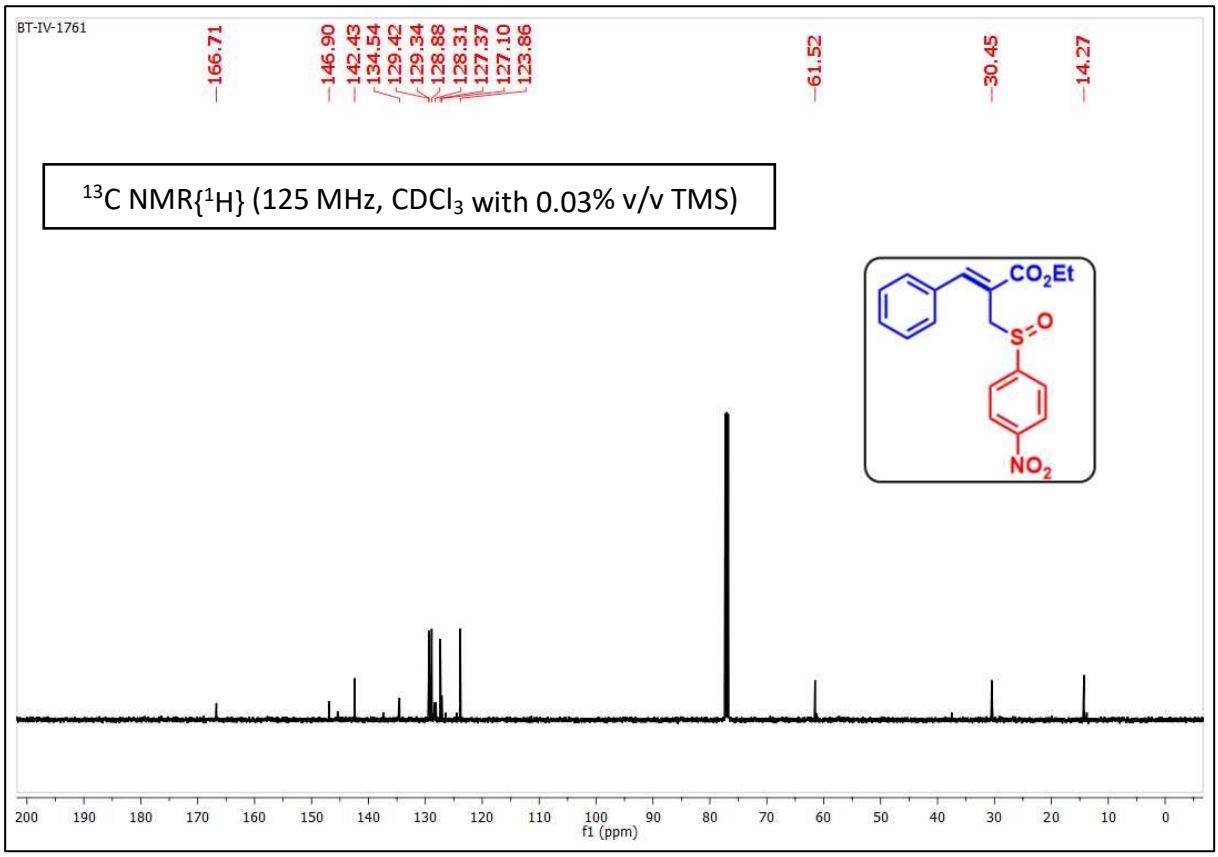
Ethyl (Z)-2-(((4-methoxyphenyl)sulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4l)



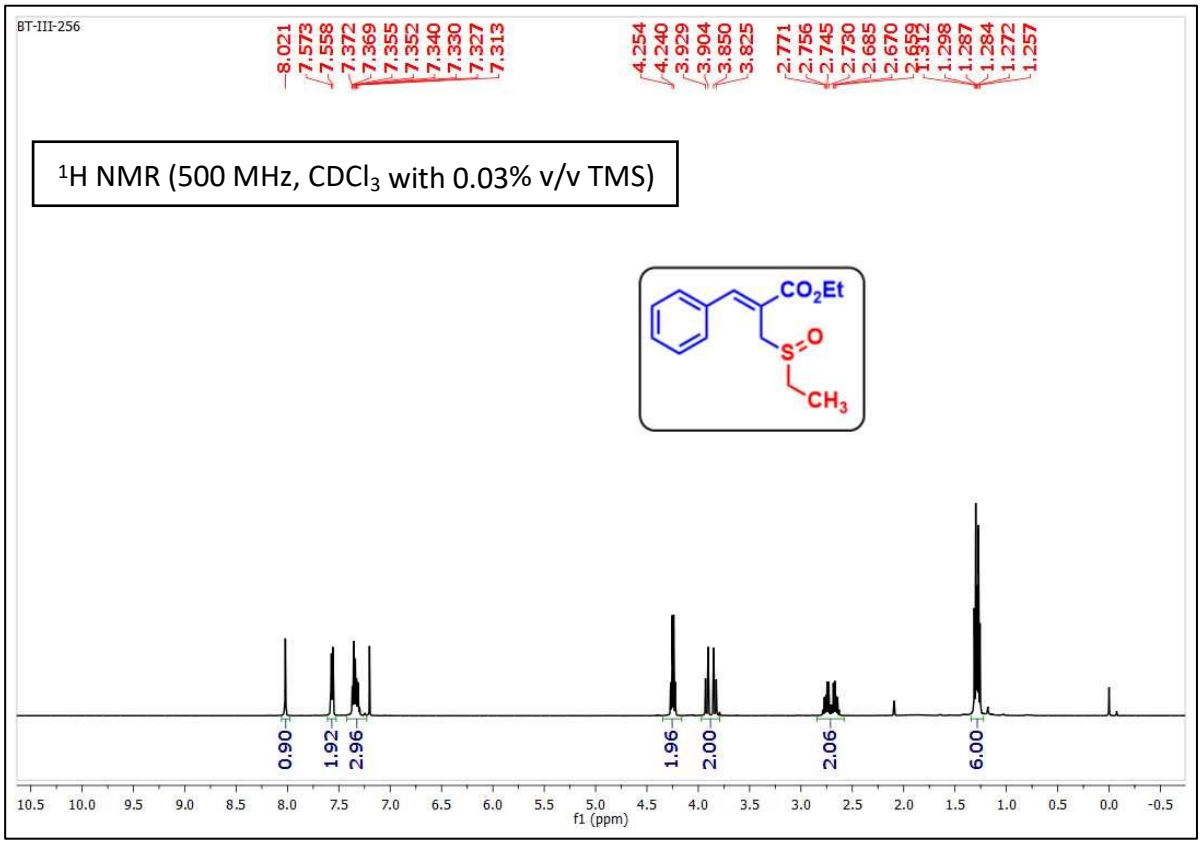


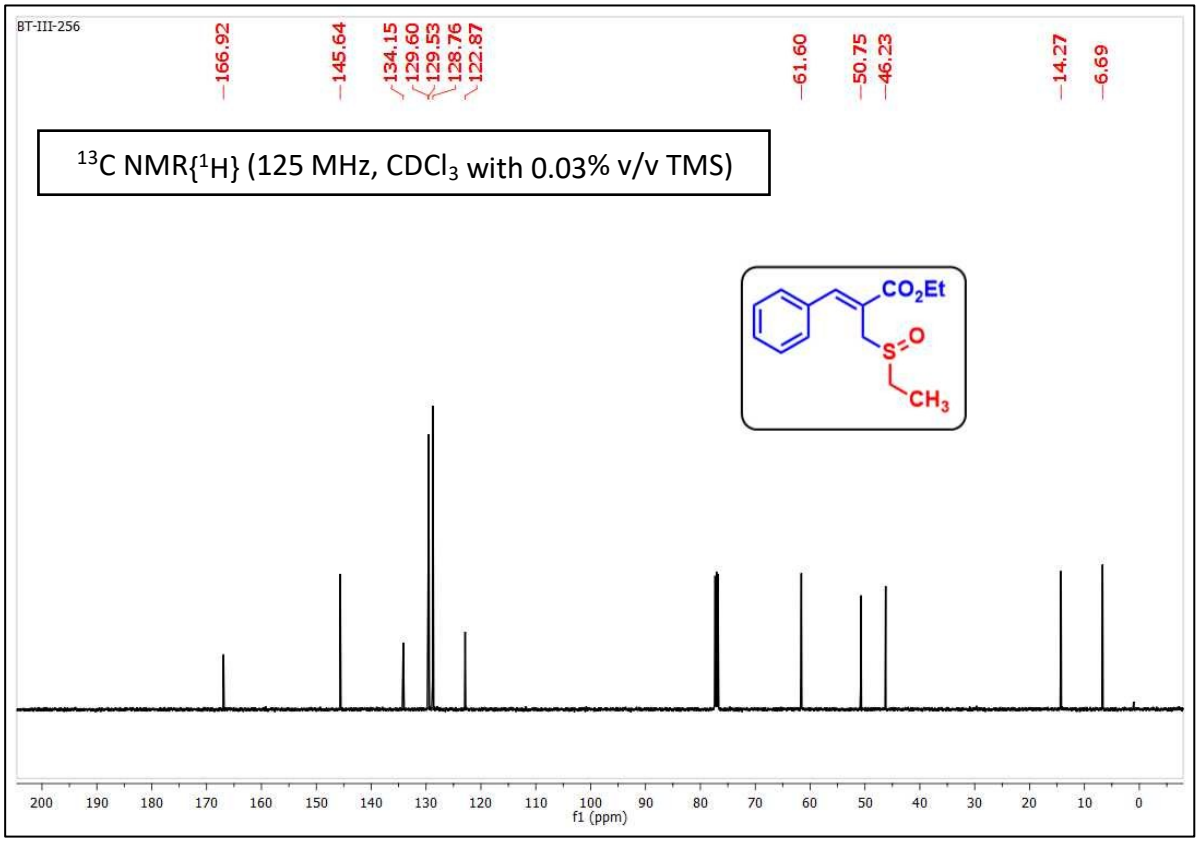
ethyl (Z)-2-(((4-nitrophenyl)sulfinyl)methyl)-3-phenylacrylate (4m)



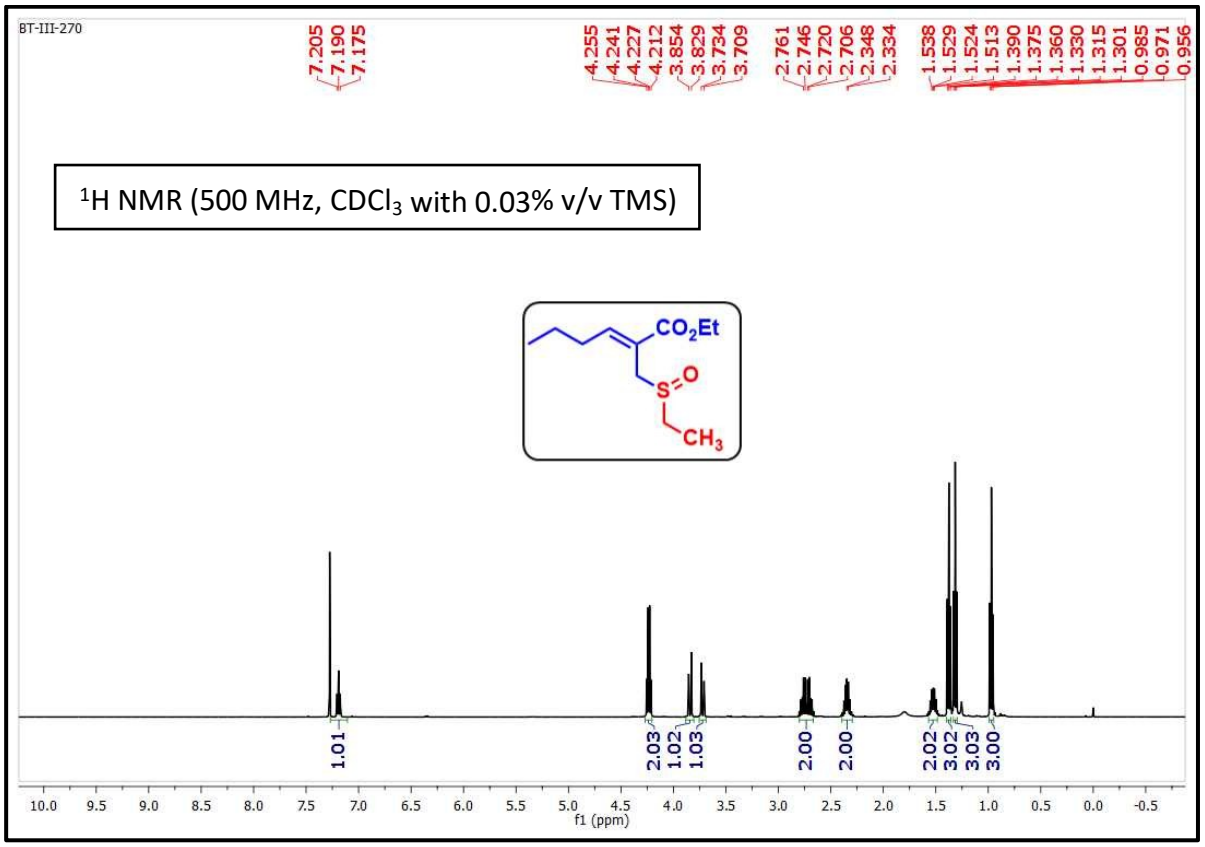


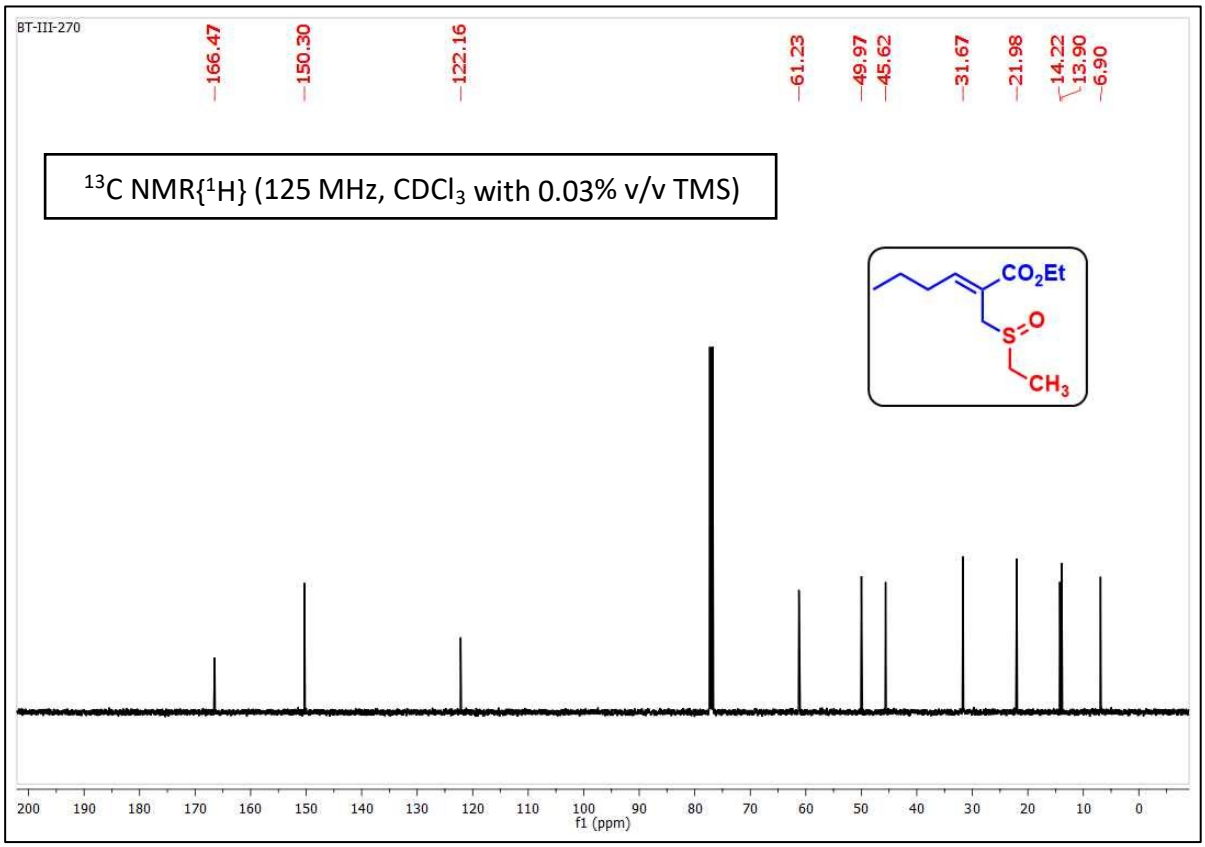
Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-phenylacrylate (4n)



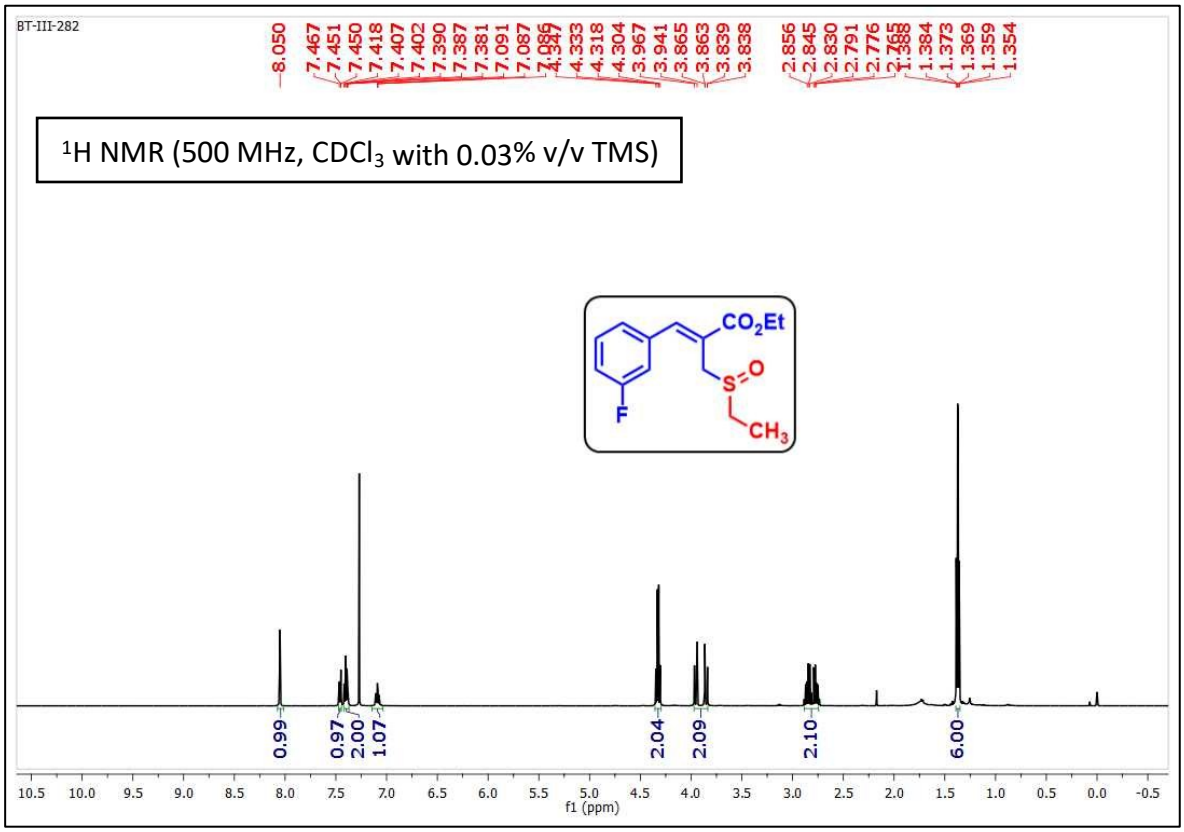


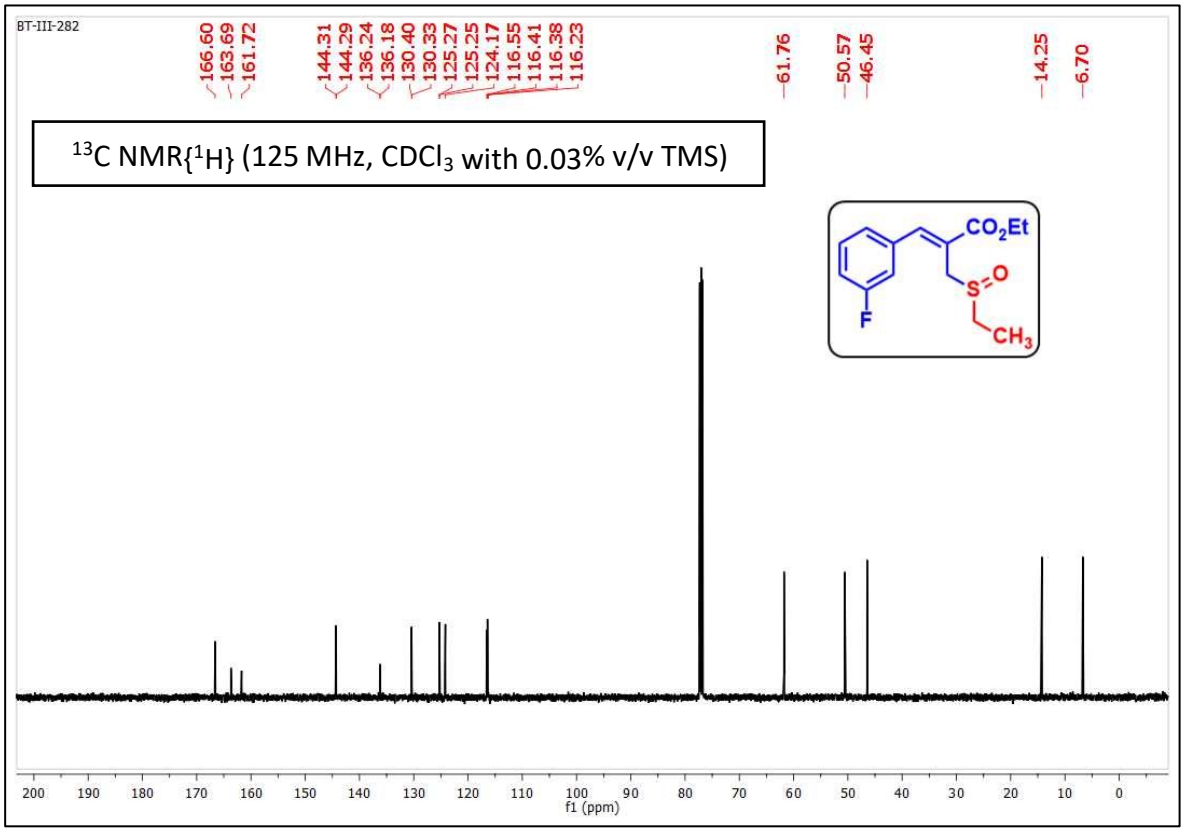
Ethyl (Z)-2-((ethylsulfinyl)methyl)hex-2-enoate (4o)



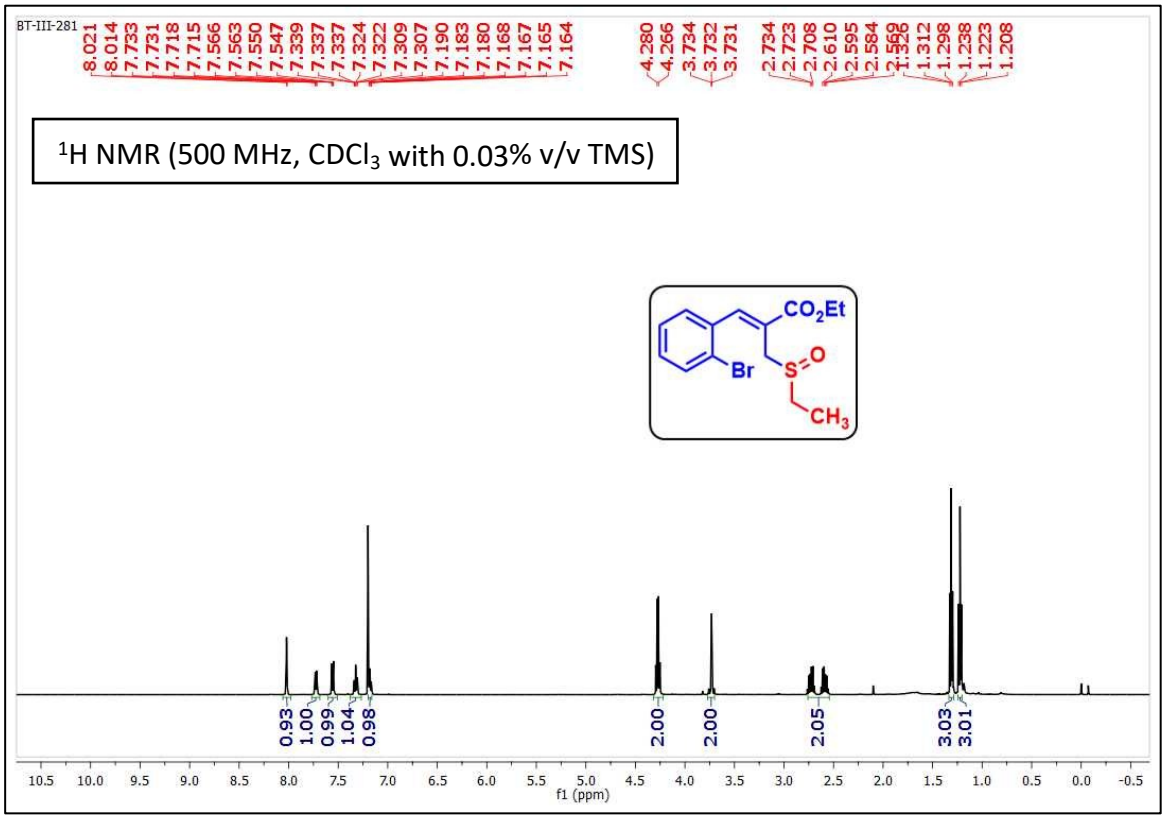


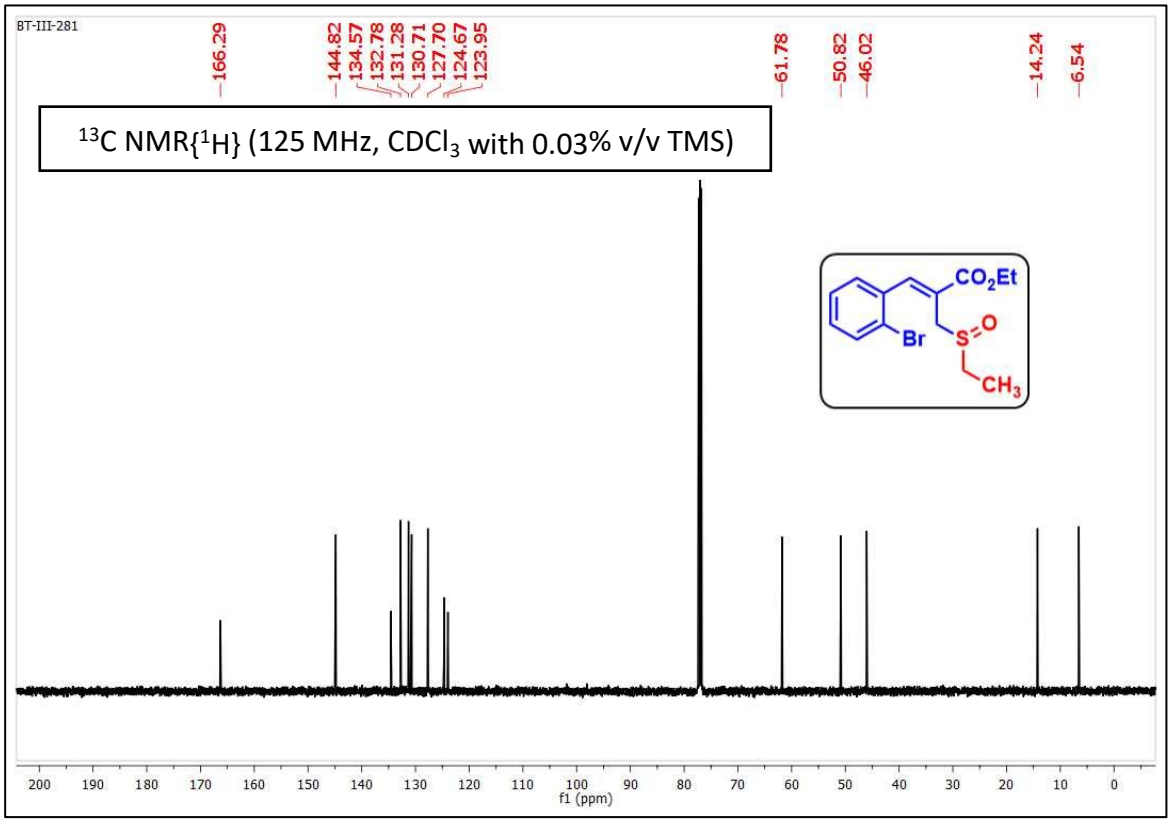
Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-(3-fluorophenyl)acrylate (4p)



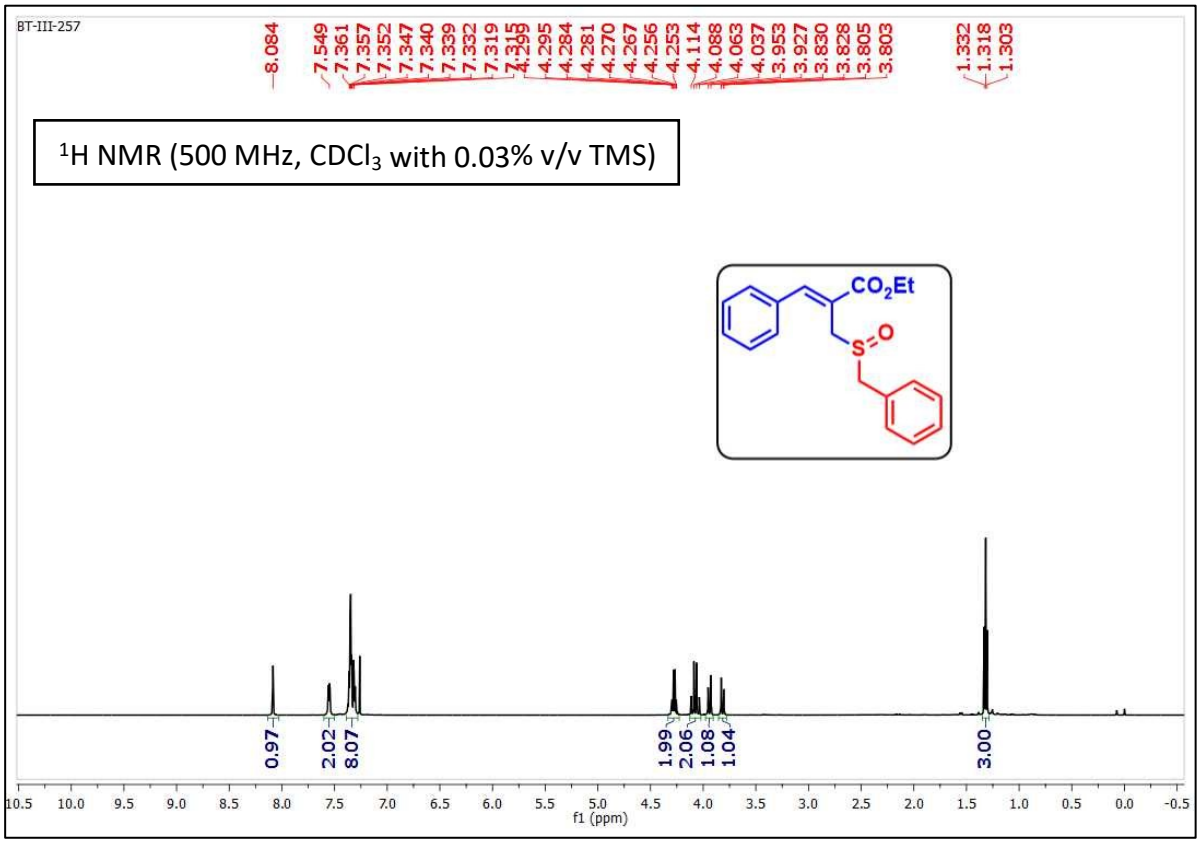


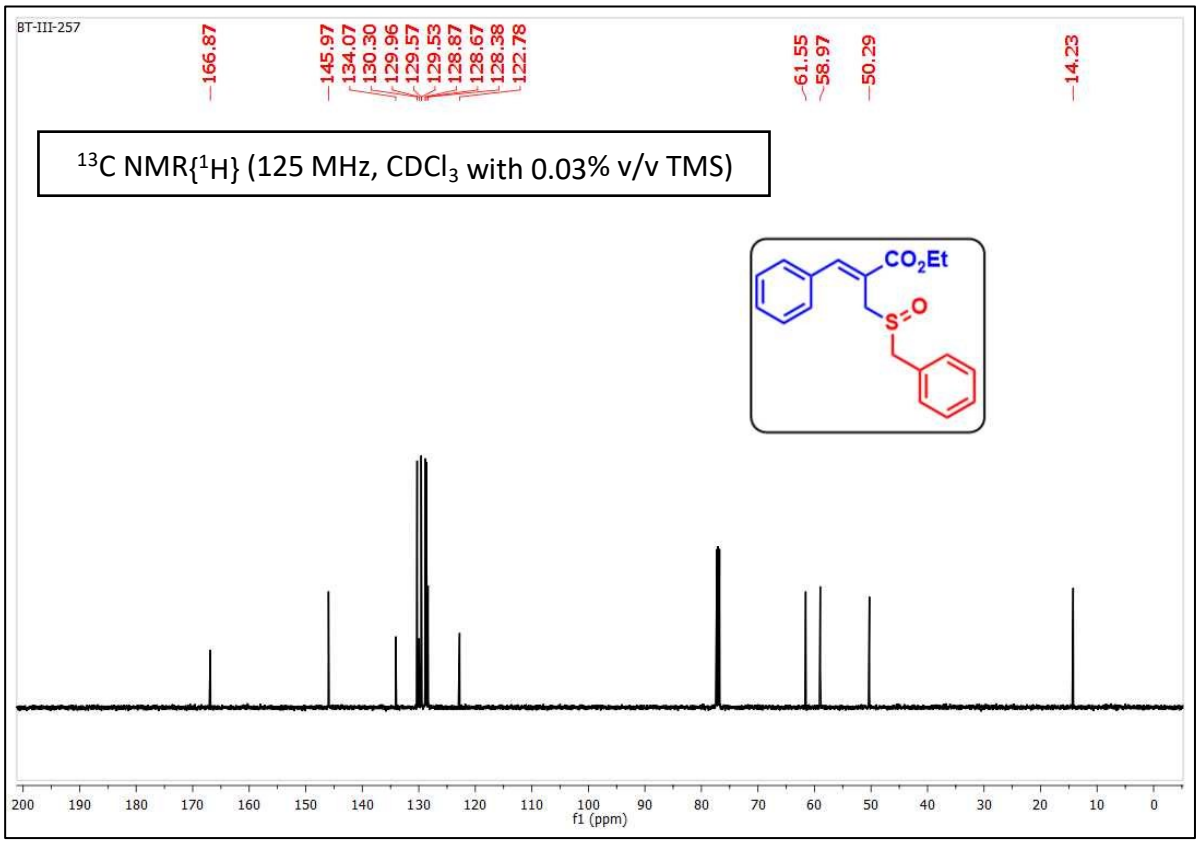
Ethyl (Z)-3-(2-bromophenyl)-2-((ethylsulfinyl)methyl)acrylate (4q)



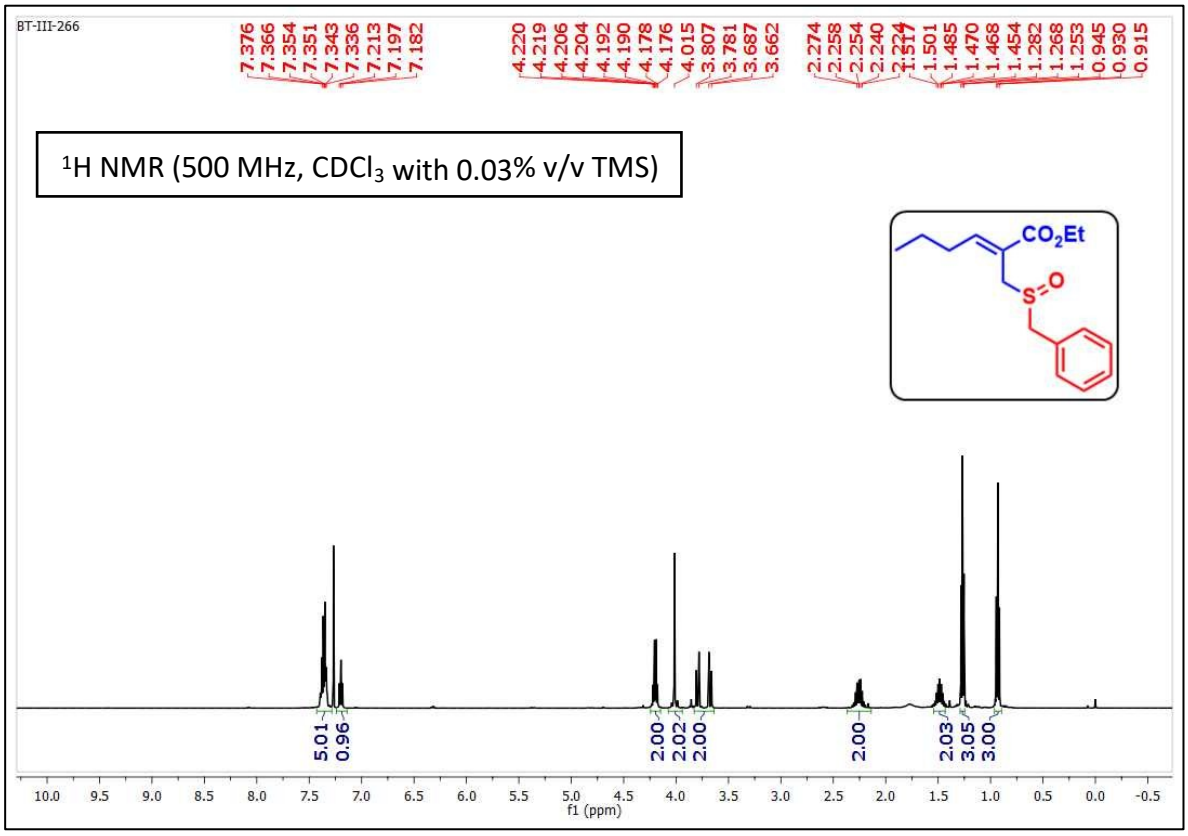


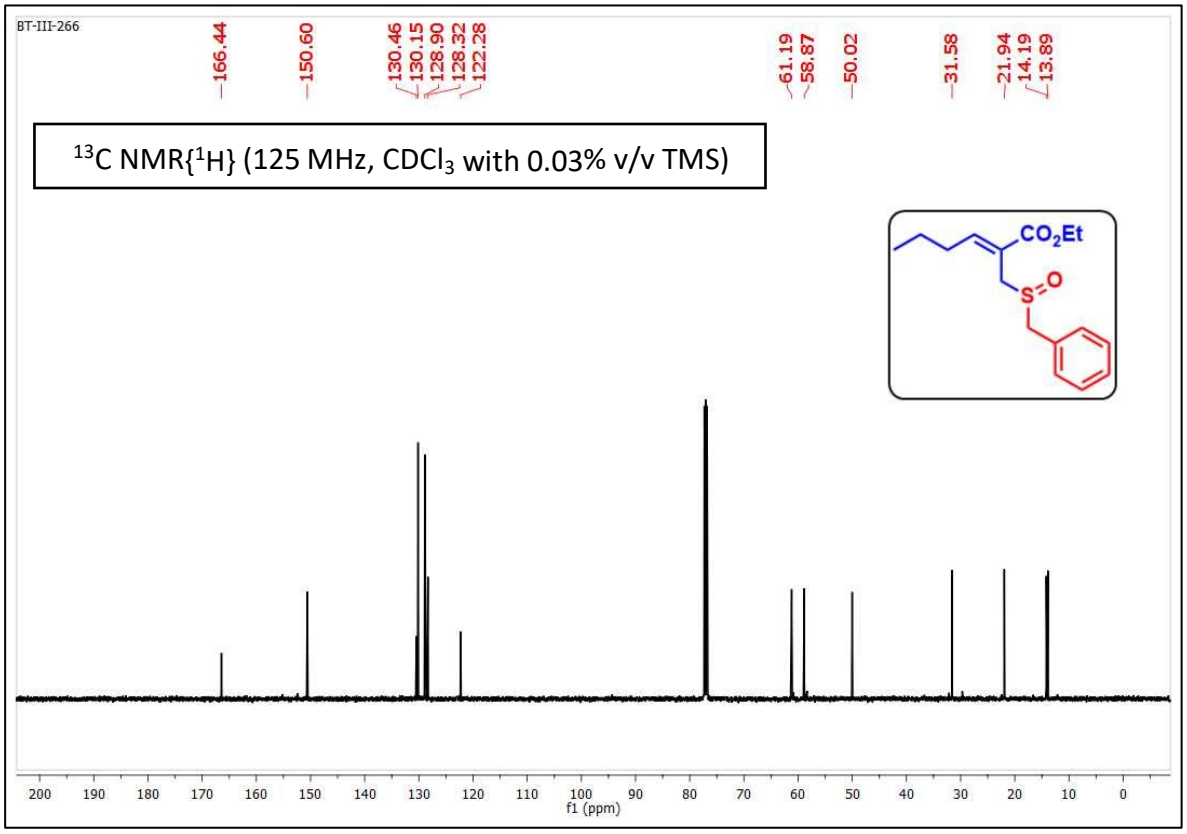
Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-phenylacrylate (4s)



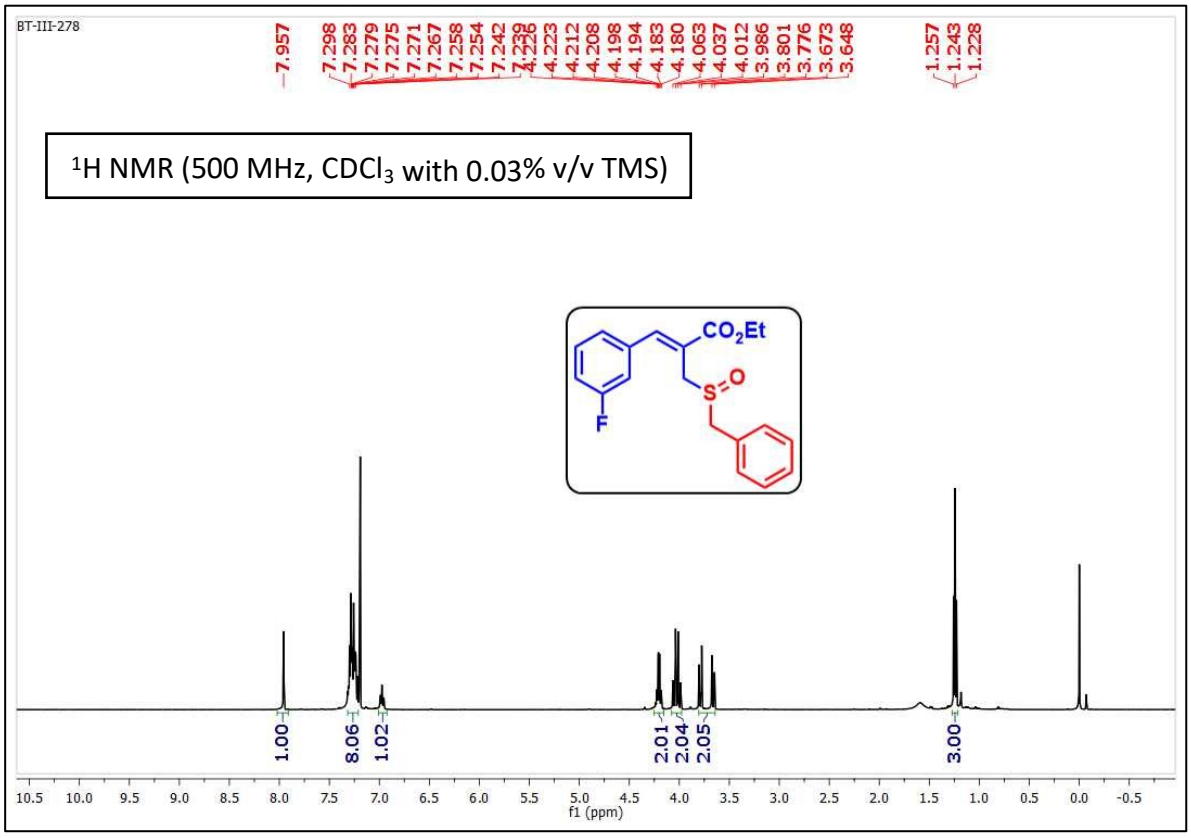


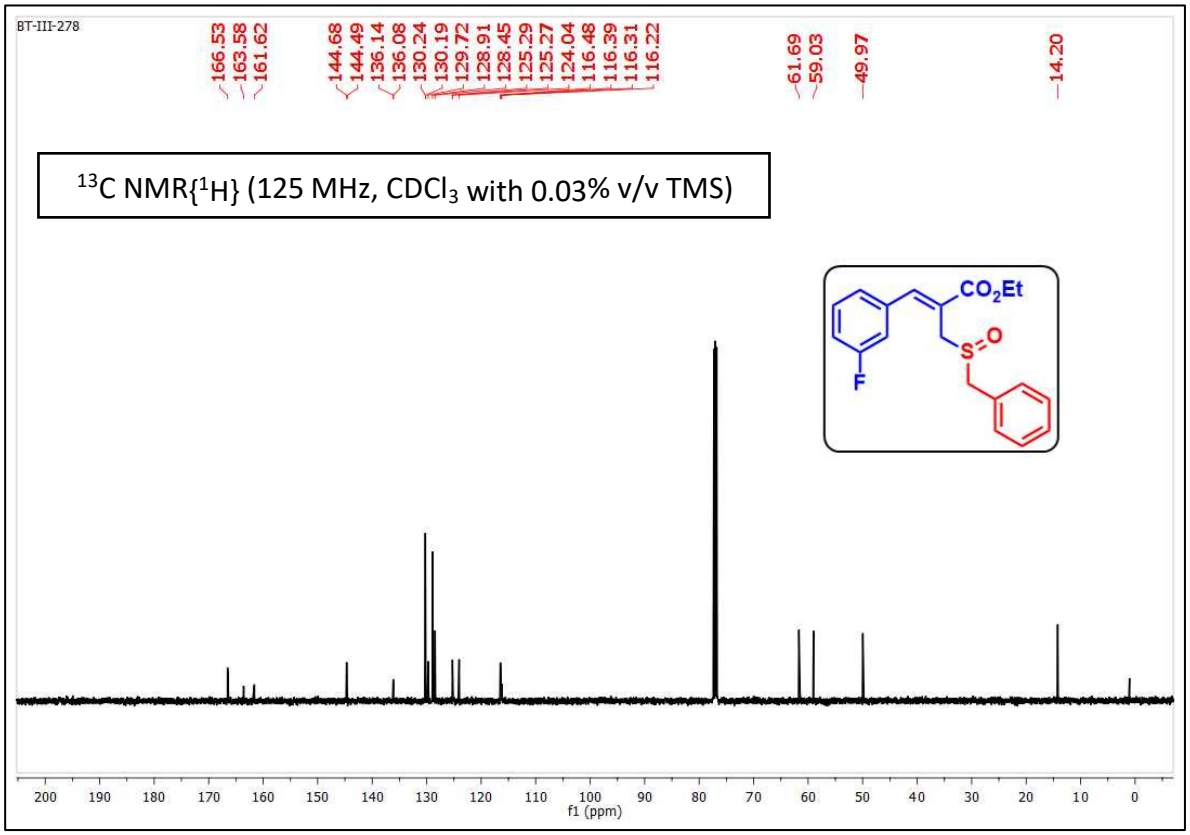
Ethyl (Z)-2-((benzylsulfinyl)methyl)hex-2-enoate (4t)



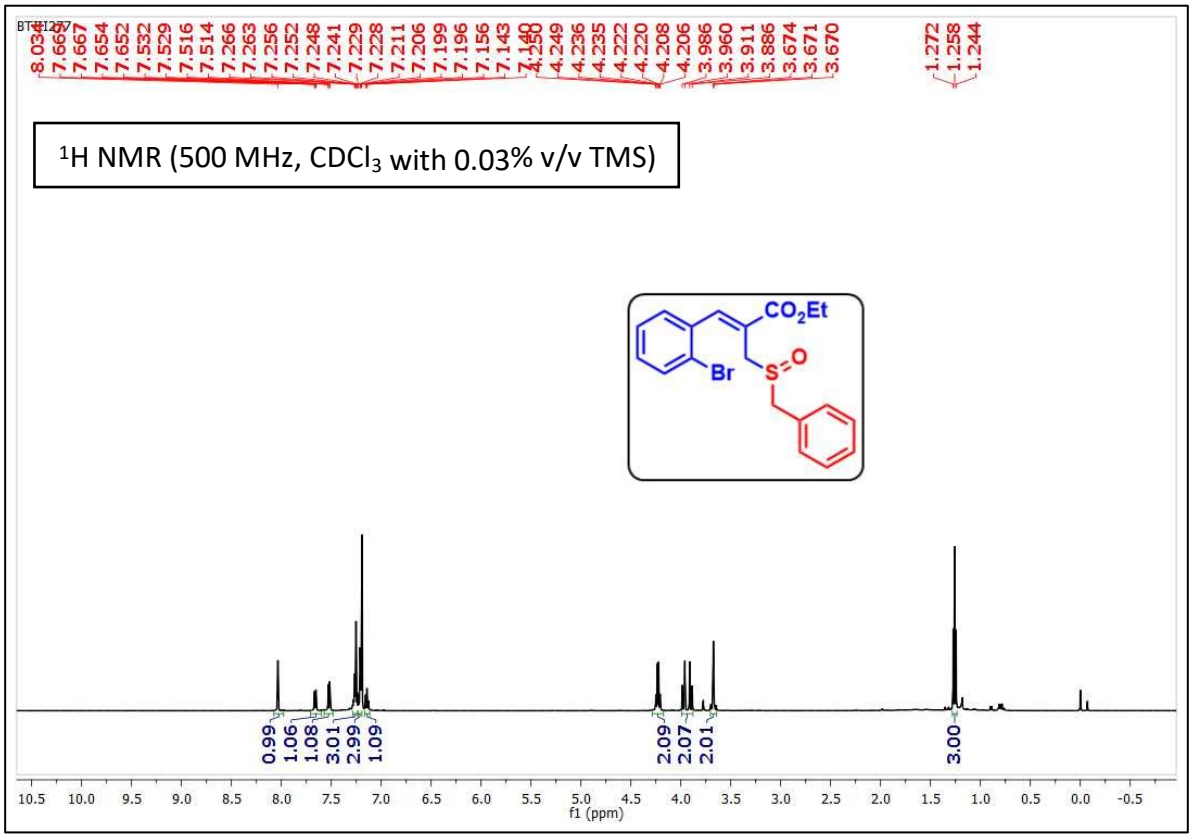


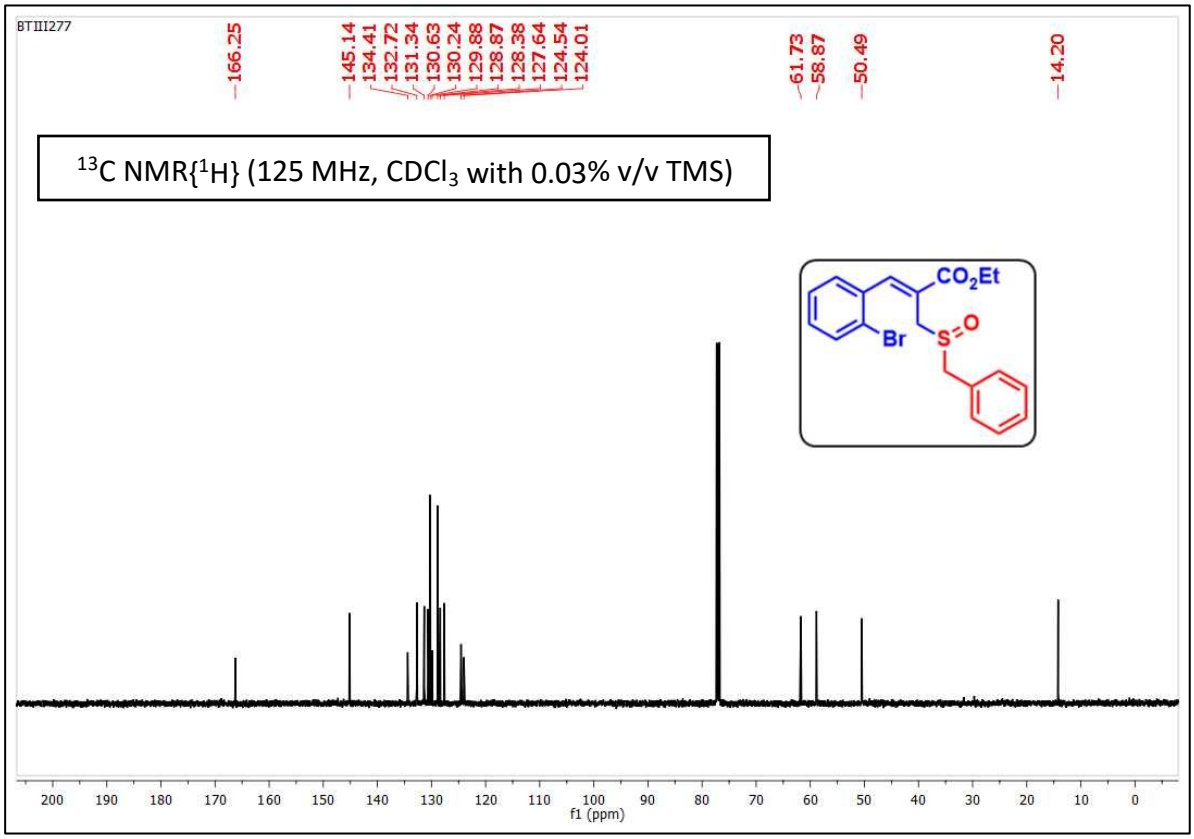
Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(3-fluorophenyl)acrylate (4u)



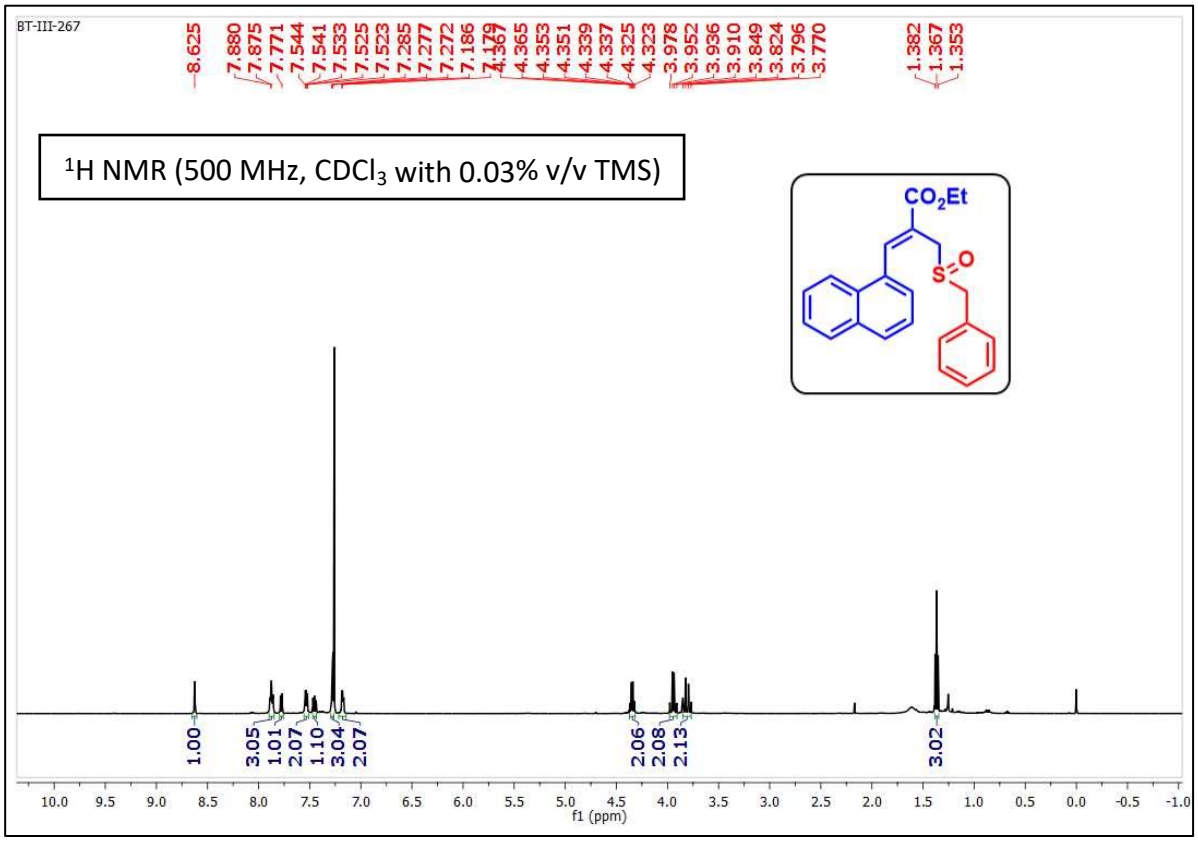


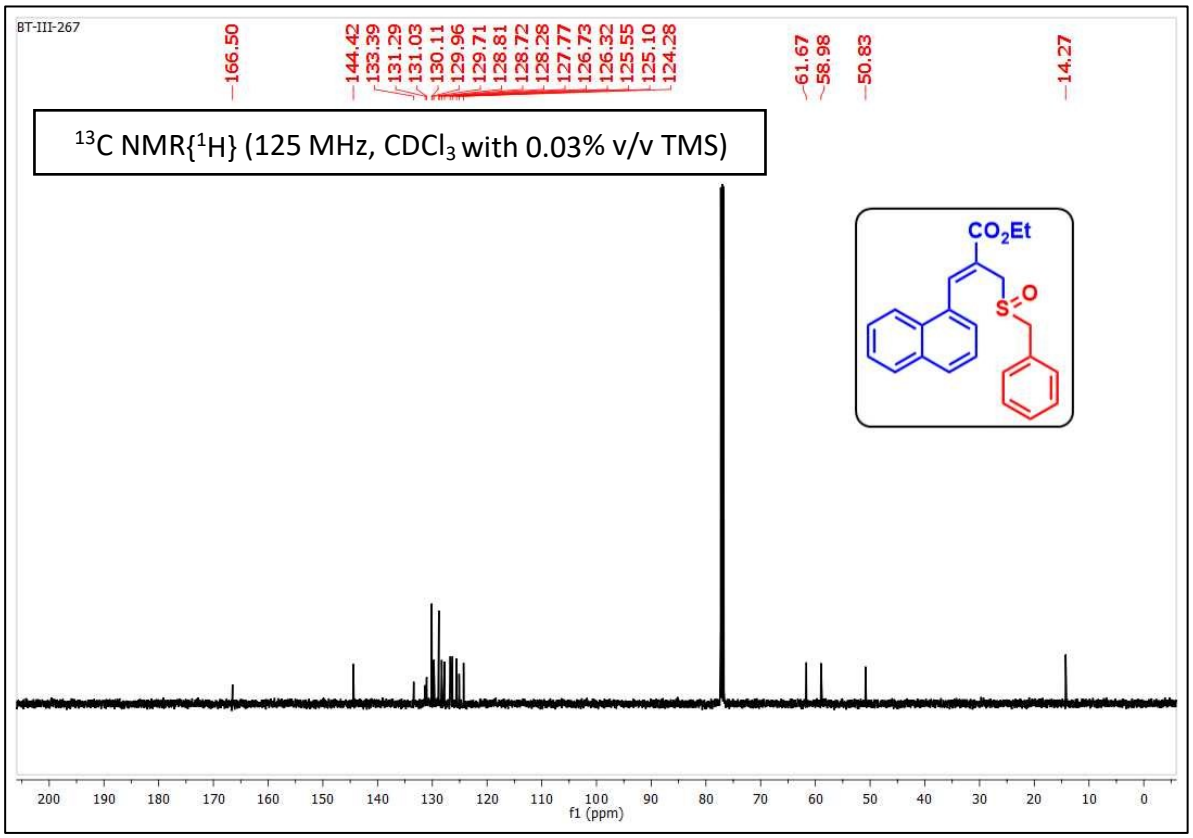
Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(2-bromophenyl)acrylate (4v)



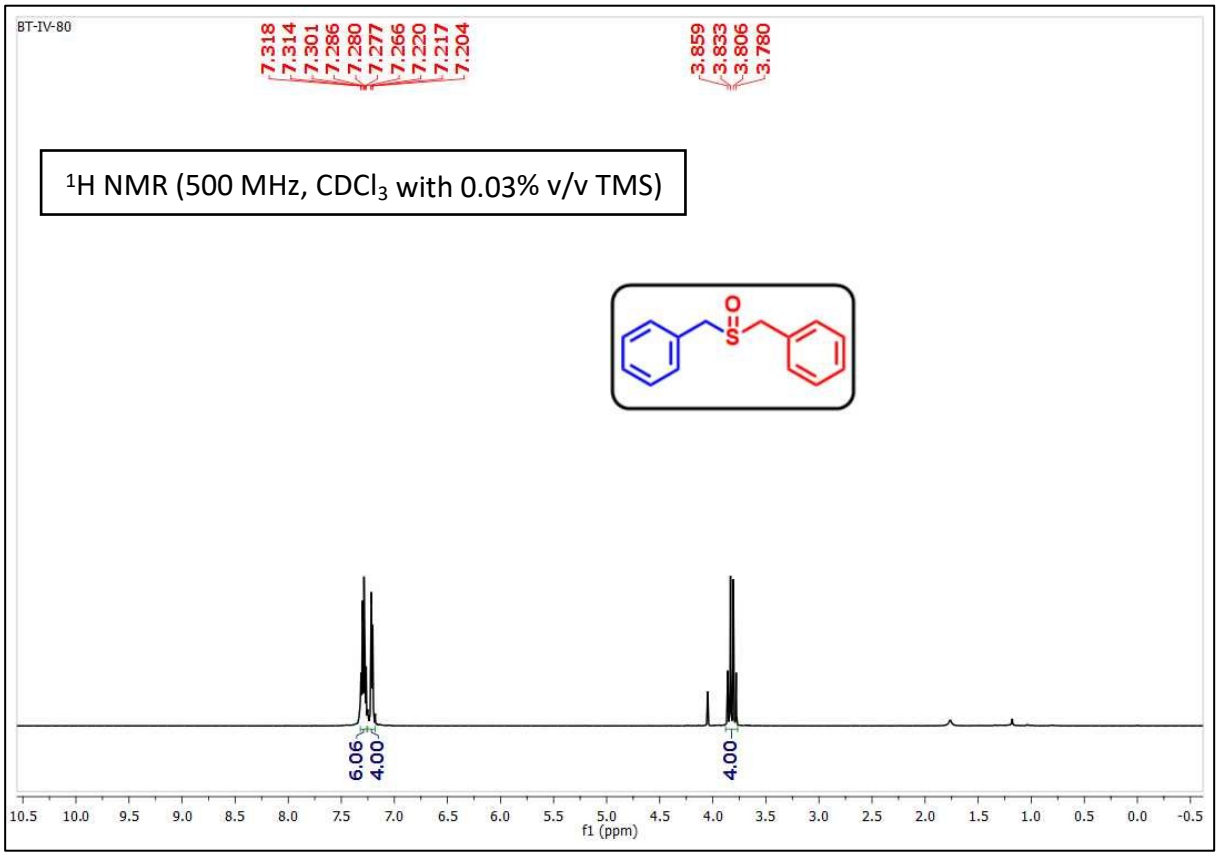


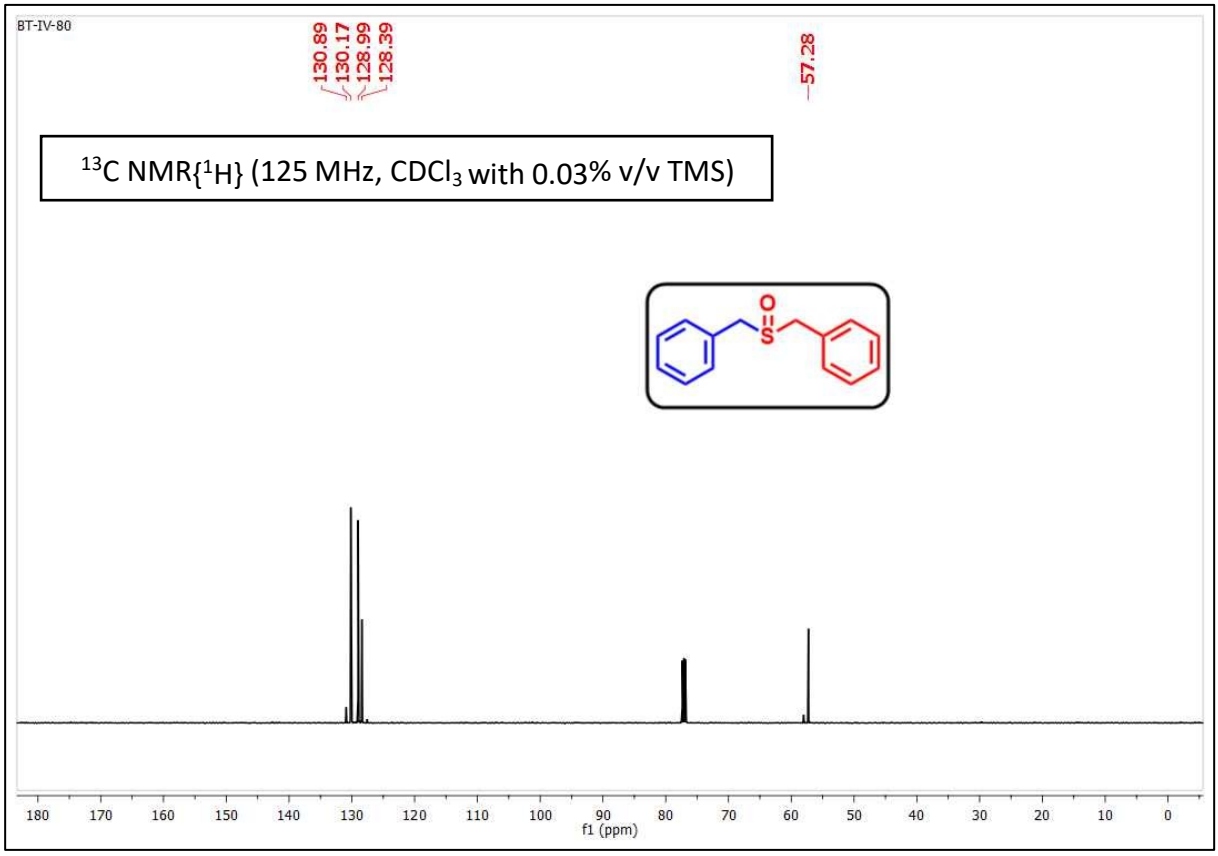
Ethyl (Z)-2-((benzylsulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4w)



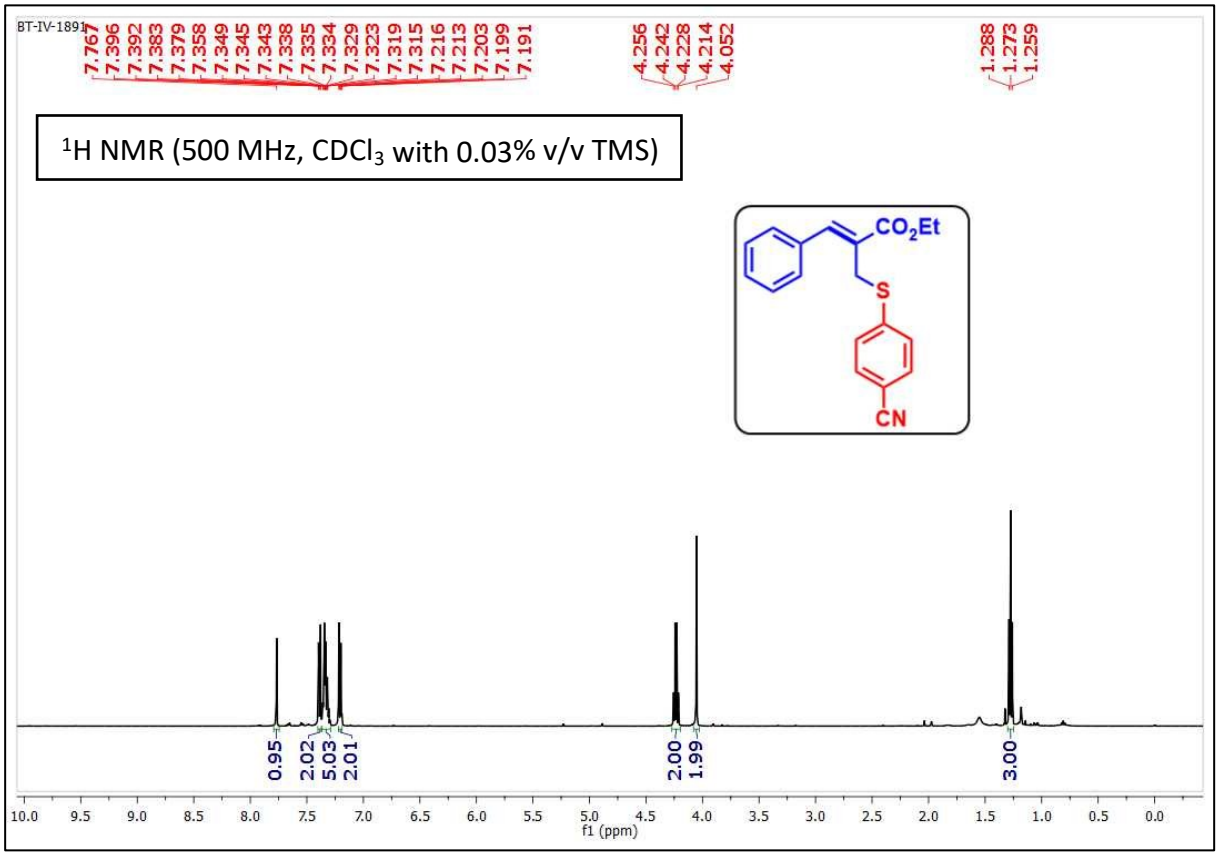


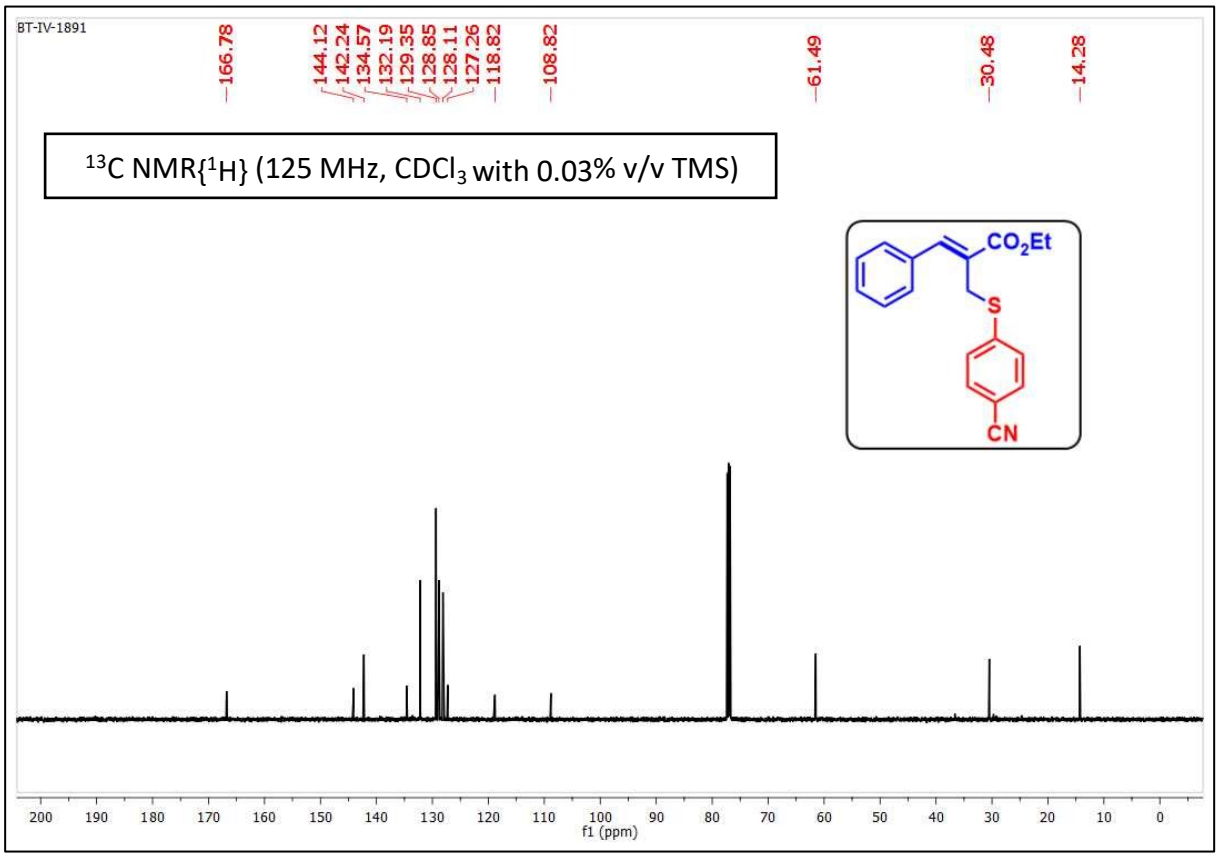
(sulfinylbis(methylene))dibenzene (4x)



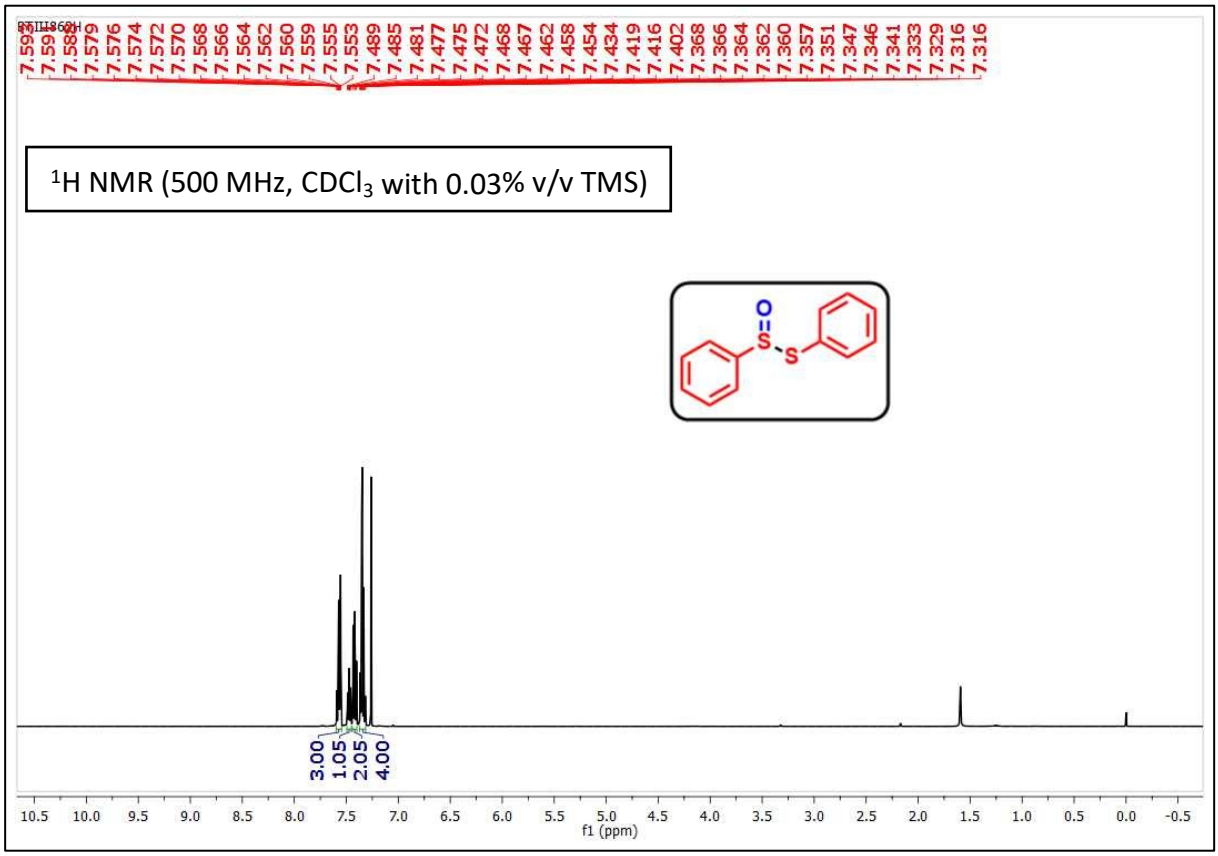


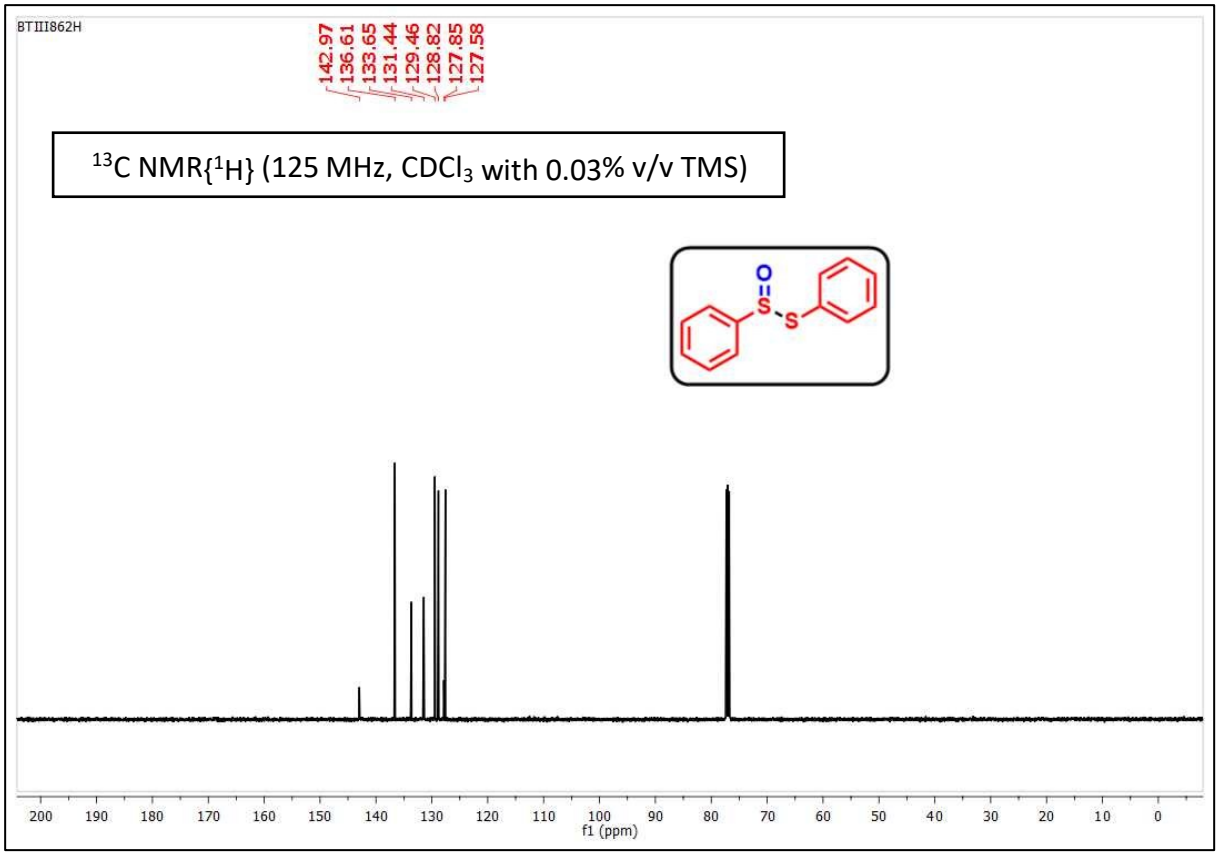
ethyl (Z)-2-(((4-cyanophenyl)thio)methyl)-3-phenylacrylate



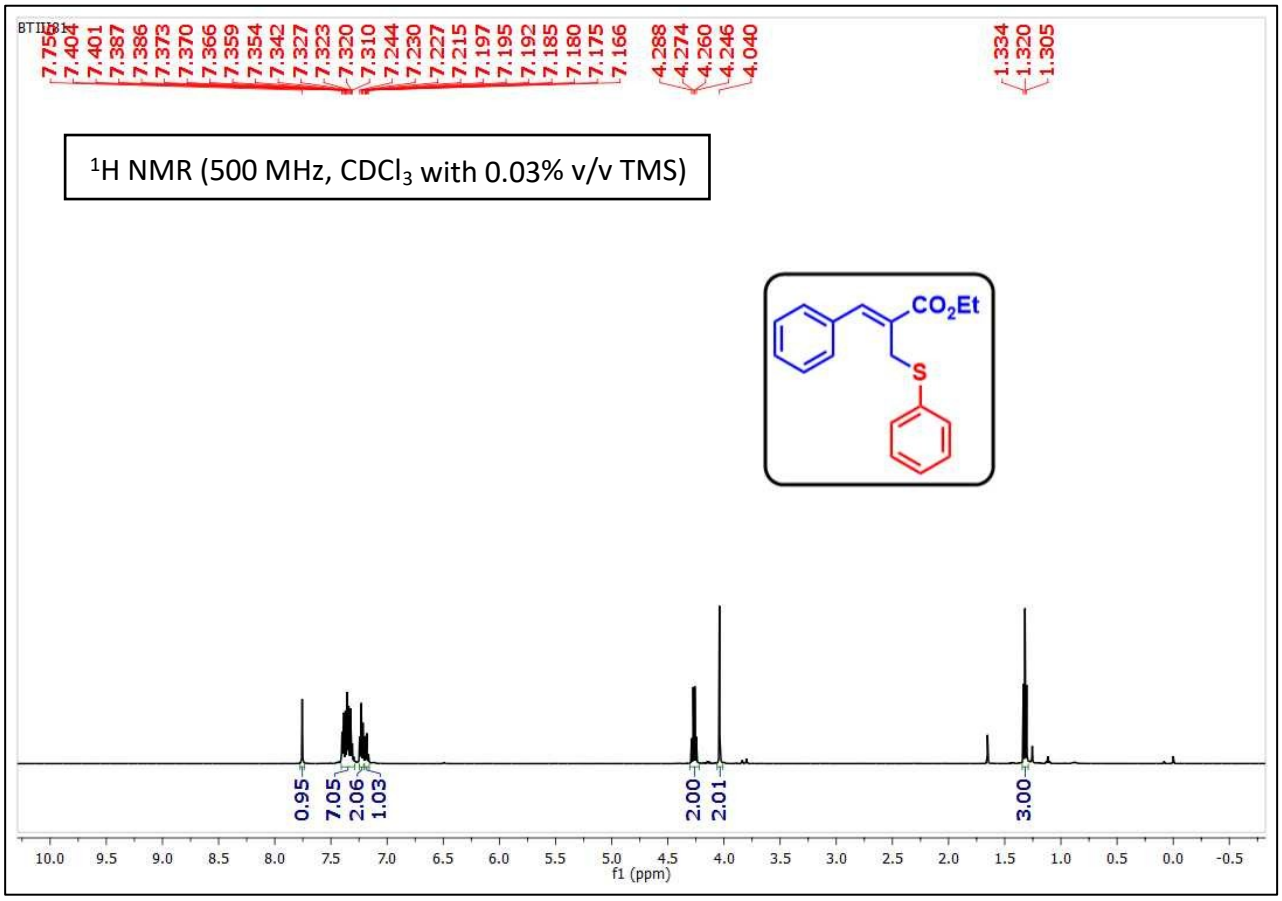


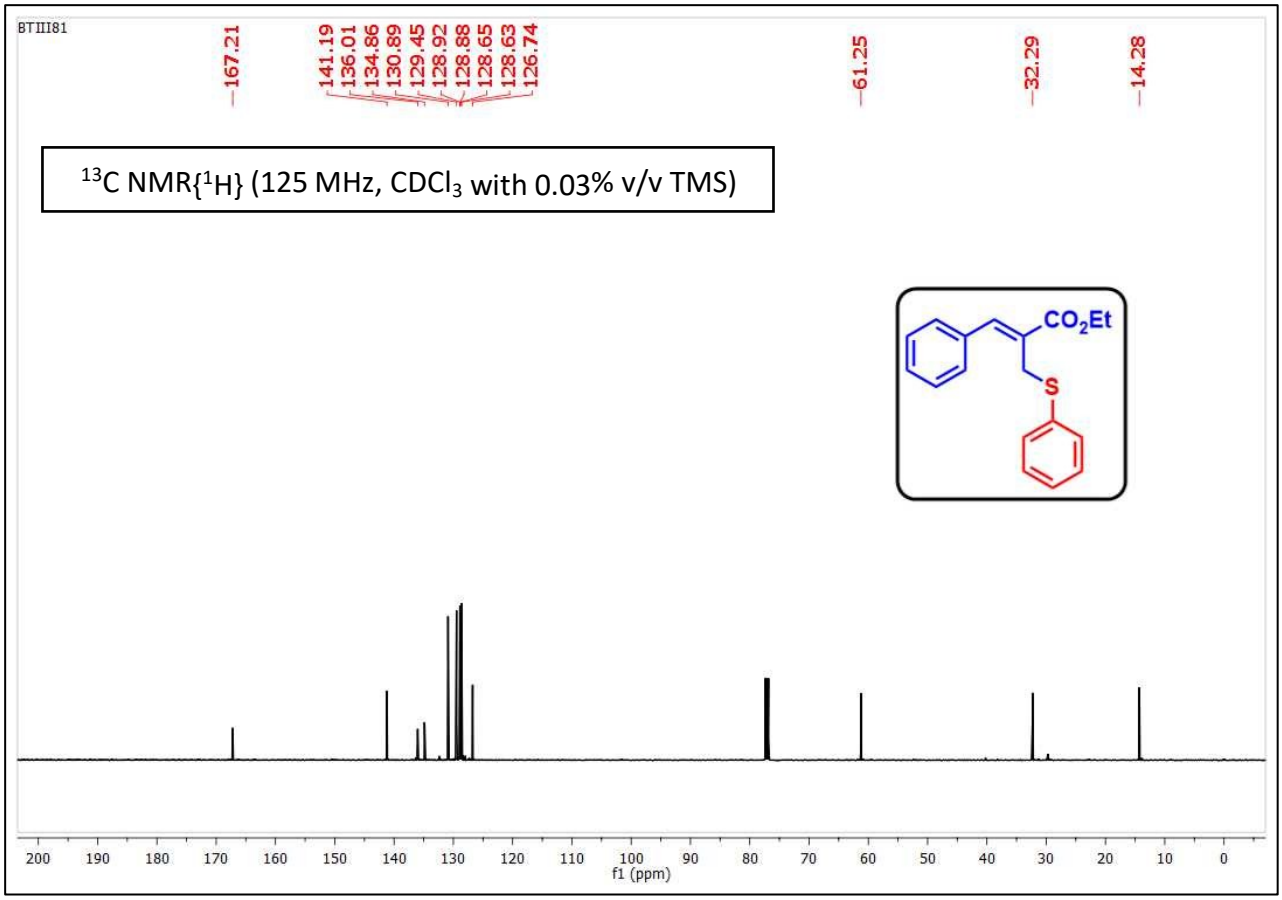
S-phenyl benzenesulfinothioate (3a′)



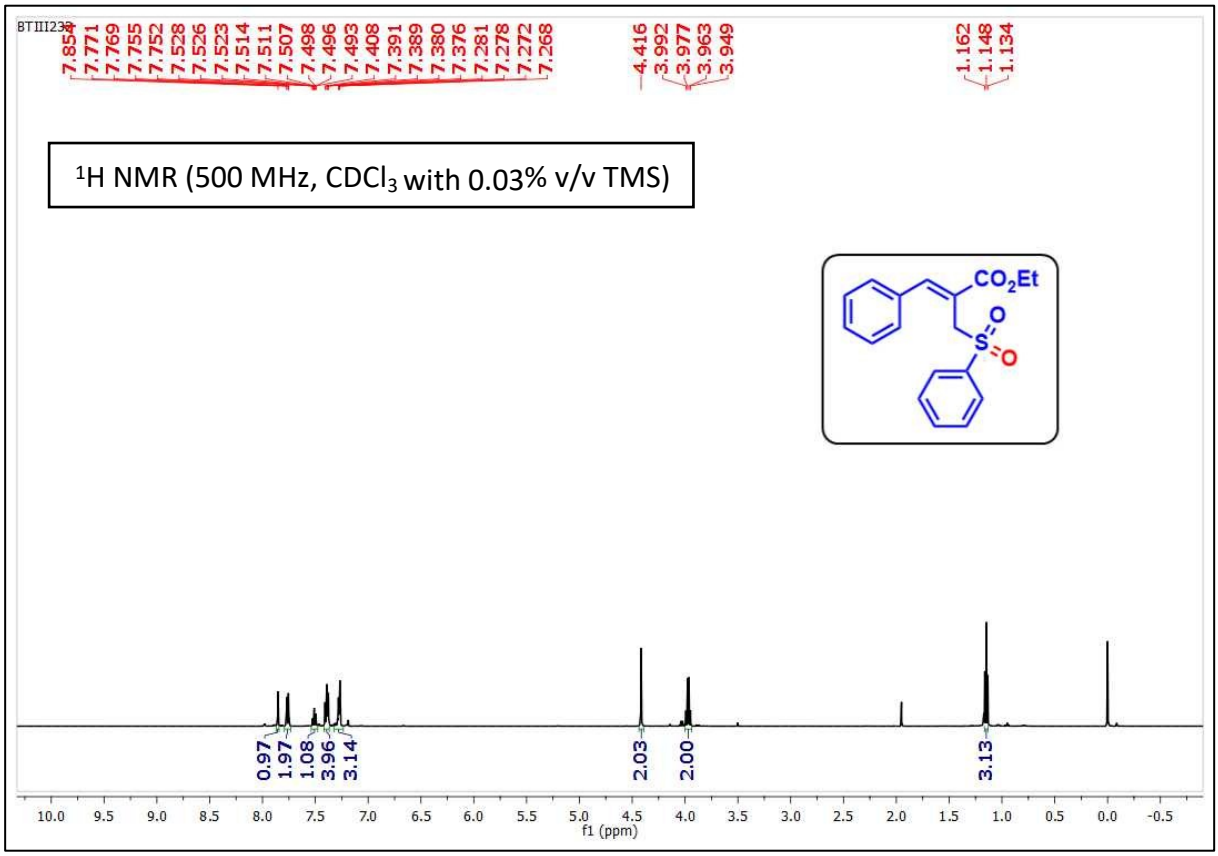


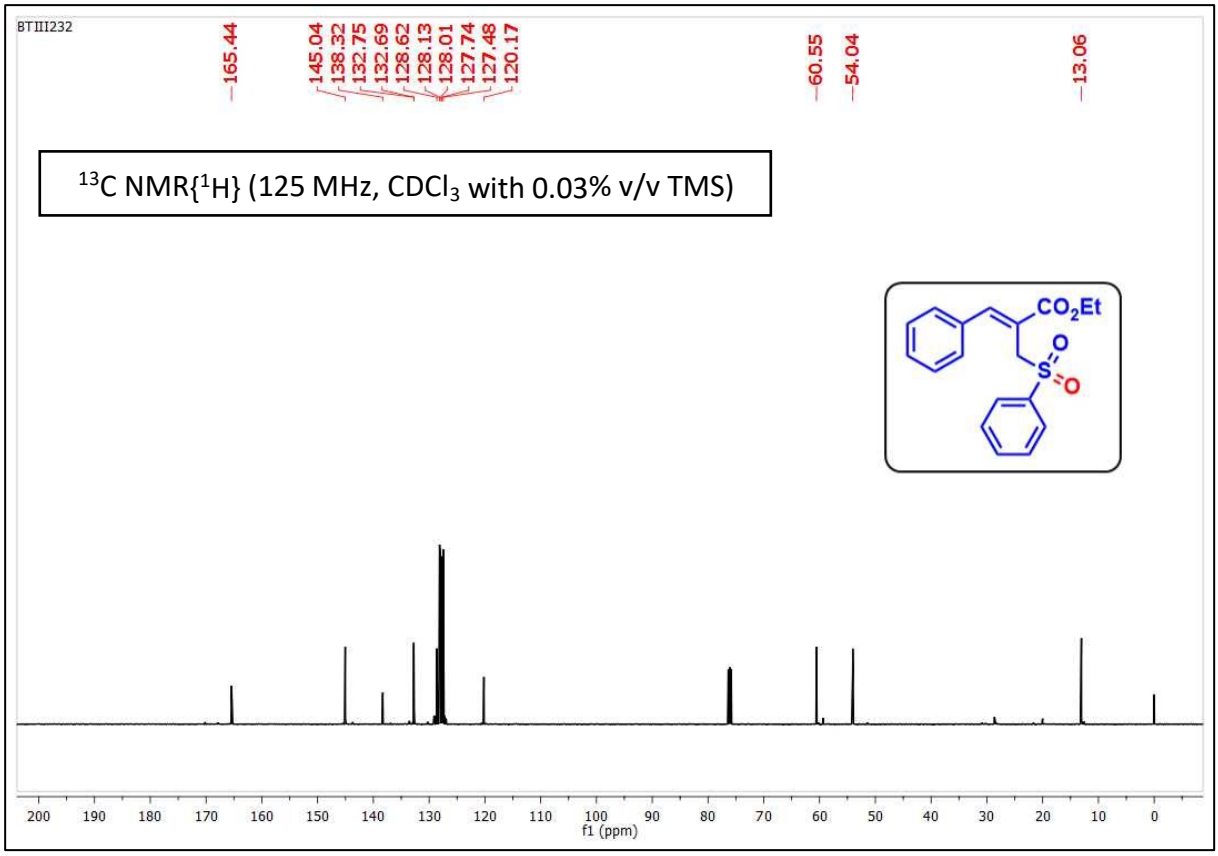
Ethyl (Z)-3-phenyl-2-((phenylthio)methyl)acrylate (3a″)



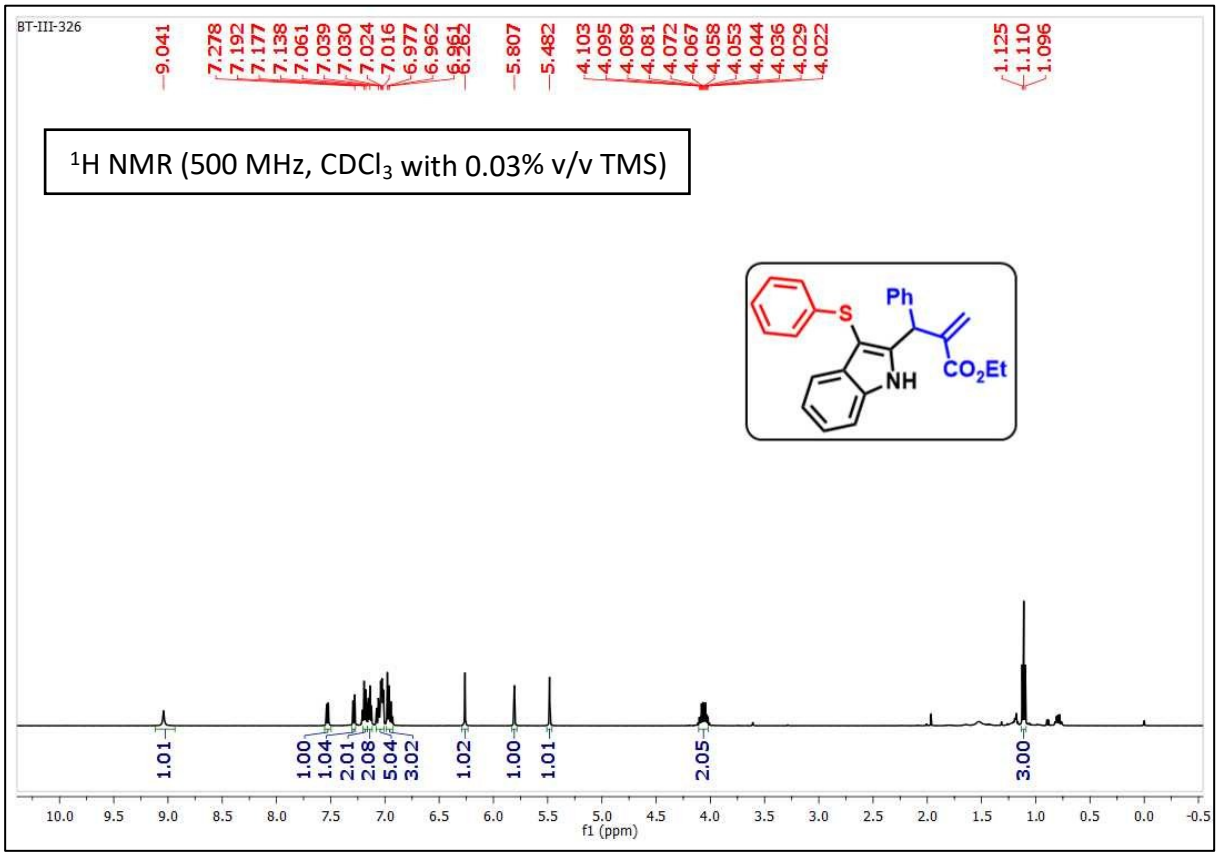


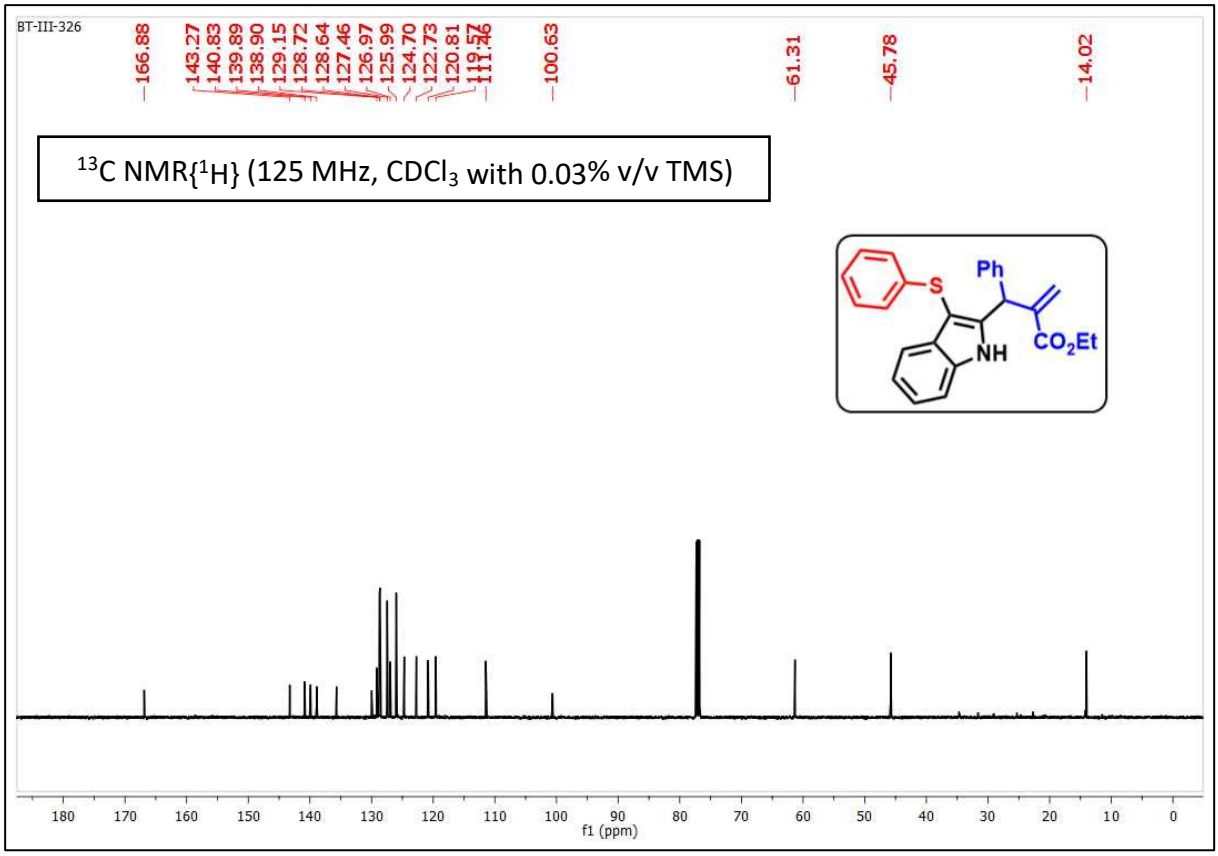
Ethyl (Z)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (5a)



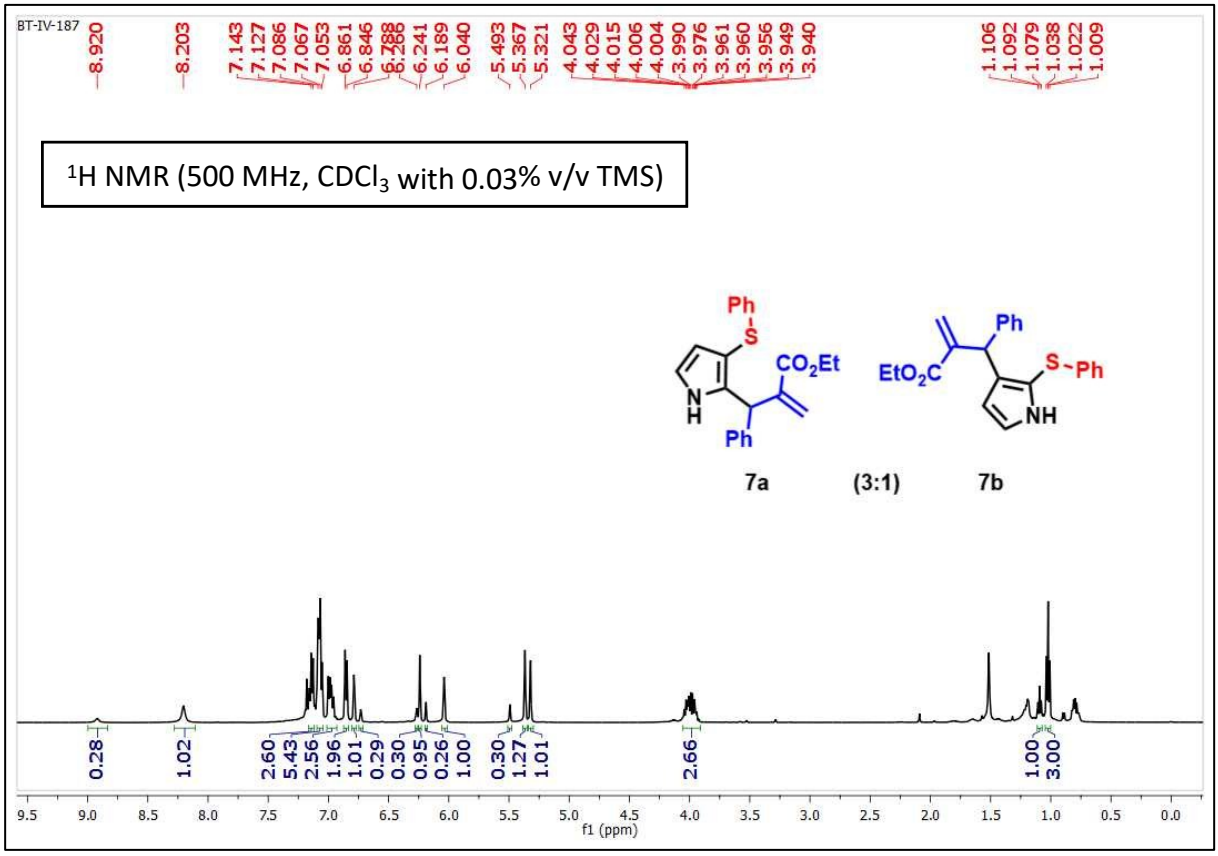


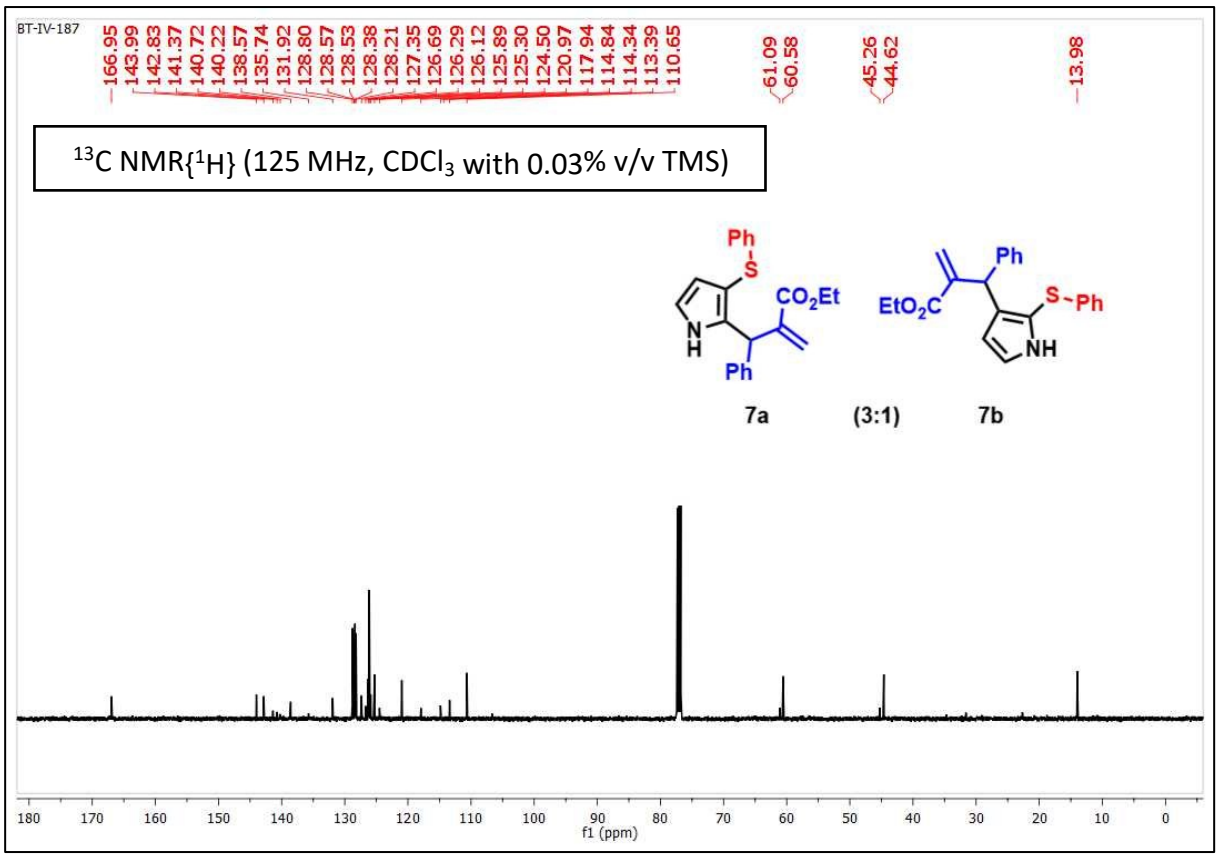
Ethyl 2-(phenyl(3-(phenylthio)-1H-indol-2-yl)methyl)acrylate (6a)





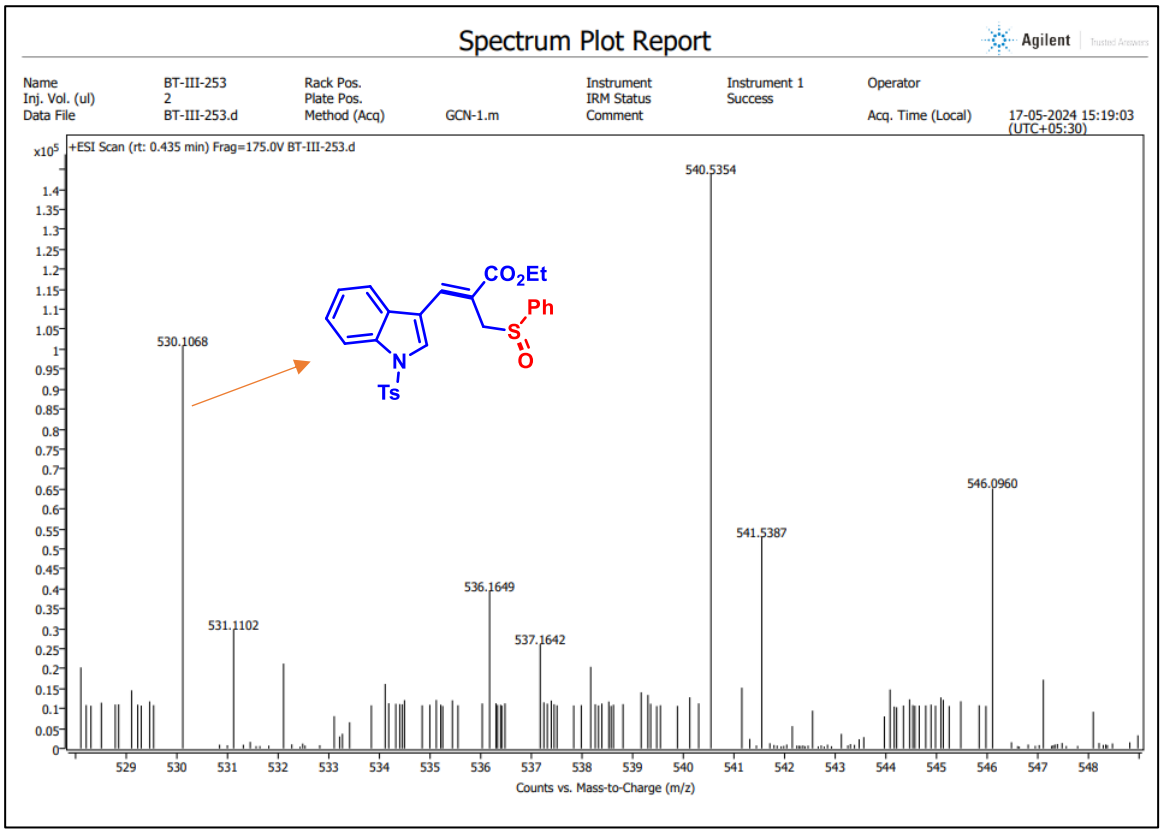
Ethyl 2-(phenyl(3-(phenylthio)-1H-pyrrol-2-yl)methyl)acrylate (7a) and Ethyl 2-(phenyl(2-(phenylthio)-1H-pyrrol-3-yl)methyl)acrylate (7b)



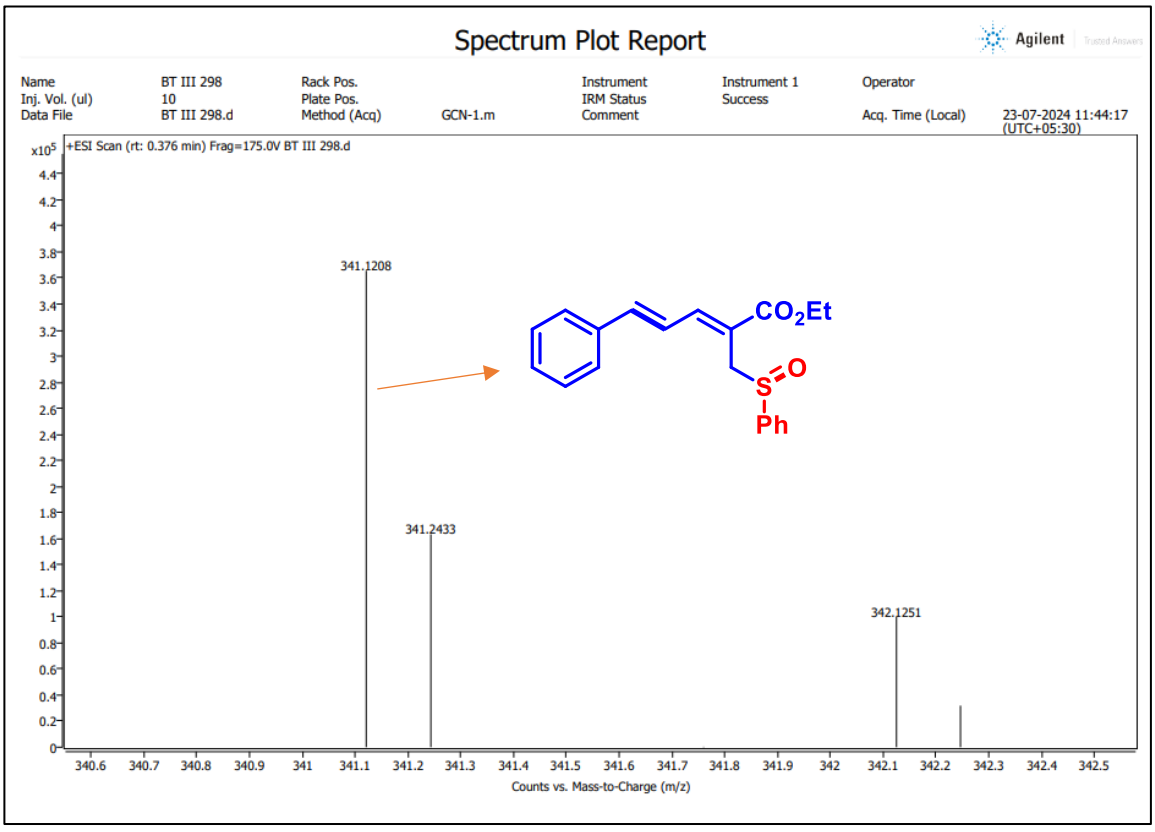


16. Mass spectral data of trace compounds

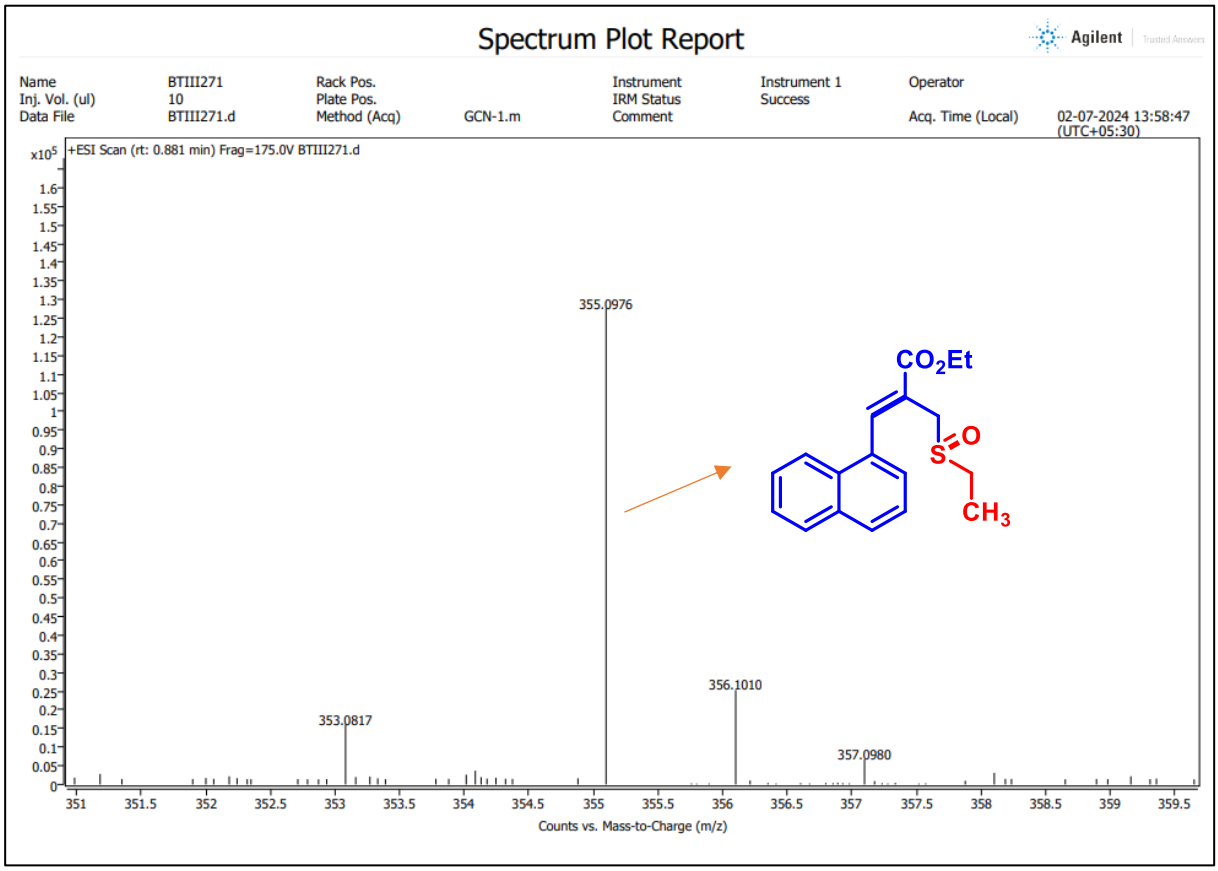
Ethyl (Z)-2-((phenylsulfinyl)methyl)-3-(1-tosyl-1H-indol-3-yl)acrylate (3p)



Ethyl (2Z,4E)-5-phenyl-2-((phenylsulfinyl)methyl)penta-2,4-dienoate (3q)



Ethyl (Z)-2-((ethylsulfinyl)methyl)-3-(naphthalen-1-yl)acrylate (4q)



17. References

1 (a) D. Basavaiah, A. Jaganmohan Rao and T. Satyanarayana, Recent Advances in the Baylis–Hillman Reaction and Applications, *Chem. Rev*., 2003, **103**, 811–892; (b) R. E. Plata and D. A. Singleton, A Case Study of the Mechanism of Alcohol-Mediated Morita Baylis–Hillman Reactions. The Importance of Experimental Observations, *J. Am. Chem. Soc*., 2015, **137**, 3811−3826; (c) D. Basavaiah, K. Ramesh Reddy and K. Nagaswamy, An expedient, facile and simple one-pot synthesis of 2-methylenealkanoates and alkanenitriles from the Baylis–Hillman bromides in aqueous media, *Nature Protocols*., 2007, **11**, 2665–2676; (d) A. Shankar, M. Waheed and R. J. Reddy, Simple and Efficient Synthesis of Allyl Sulfones through Cs_2CO_3-Mediated Radical Sulfonylation of Morita-Baylis-Hillman Adducts with Thiosulfonates, *Syn. Open*., 2021, **5**, 91–99.

2 (a) B. Trinadh, B. Kadamannil and B. Viswambharan, Na_2 – Eosin Y – Photocatalyzed Cross Dehydrogenative C−S Coupling of Arylthiols with Indole Derivatives, *ChemistrySelect*., 2024, **9**, 1; (b) M. Siauciulis, S. Sapmaz, A. P. Pulis and D. J. Procter, Dual Vicinal Functionalisation of Heterocycles: Via an Interrupted Pummerer Coupling/[3,3]-Sigmatropic Rearrangement Cascade, *Chem. Sci*., 2018, **9**, 754–759.